Efficient and Highly Aldehyde Selective Wacker Oxidation

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Supporting Information

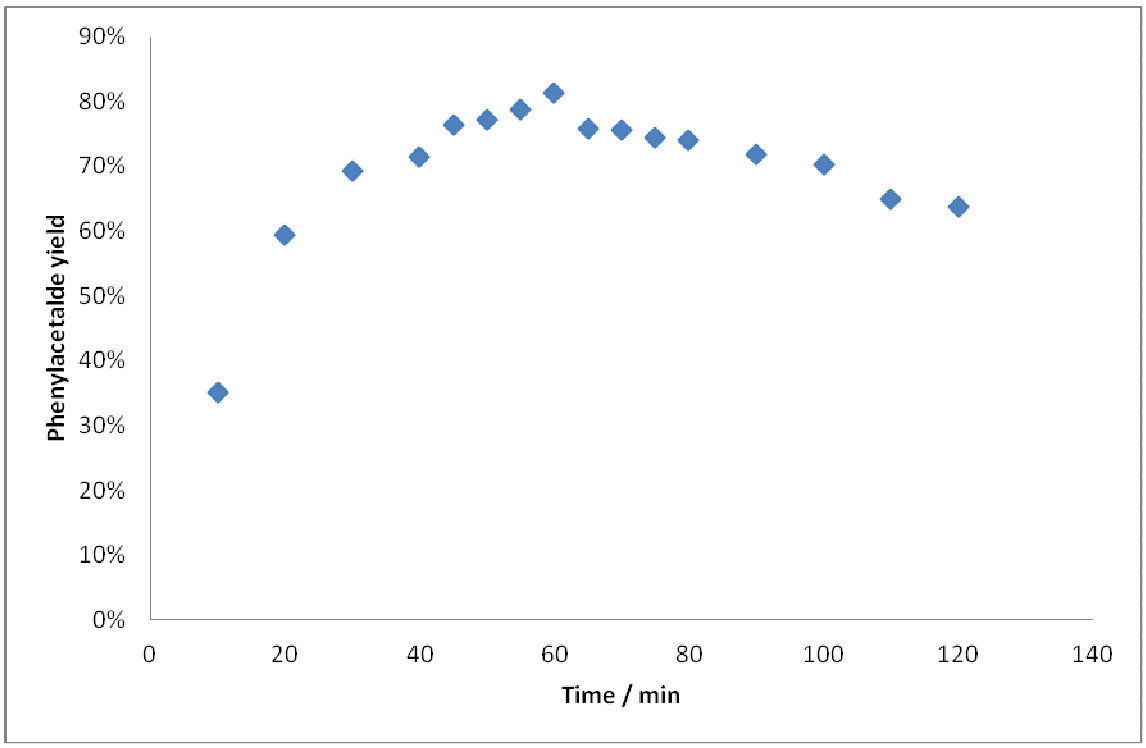


Fig. 1 Phenylacetaldehyde yield as a function of reaction time for styrene Wacker on 0.6 mmol scale.

General procedure:

All olefin oxidation reactions were carried out under aerobic conditions. $PdCl_2(MeCN)_2$, **1**, was prepared following literature procedures.[1] Commercial *p*-benzoquinone from Aldrich was recrystallized from *i*-PrOH prior to usage. All liquid olefins were filtered through a plug of basic alumina prior to usage. Methyl-4-vinylbenzoate was filtered through a plug of neutral alumina. 2, 4-dinitrophenylhydrazine solution was prepared following literature procedures.[2]

^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer and High resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer.

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatography system equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). Instrument conditions-inlet temperature: 250 ^{o}C; detector temperature: 250 ^{o}C; hydrogen flow: 30 ml/min; air flow: 400 ml/min.; constant col + makeup flow: 25 ml/min. Method: 50^{o}C for 2 min., followed by a temperature increase of 10 ^{o}C/min. to 115^{o}C, hold for 0.5 min., another temperature increase of 1^{o}C/min. to 125 ^{o}C, hold for 0.5 min., then a temperature increase of 5 ^{o}C/min. to 140 ^{o}C, hold 0.5 min. and a final temperature increase of 60 ^{o}C/min. to 300 ^{o}C and hold at 300 ^{o}C for 5 min. (total run time = 30.67 min.). Response factors were collected for styrene (**1**), 2-phenylacetaldehyde (**1a**) and acetophenone (**1b**) following literature procedures.[3]

GC sample preparation: Tridecane (0.00123 mmol, 3 μl) was added to the reaction mixture as an internal standard. The mixture was then diluted with diethyl ether (2 ml) and *ca.* 0.5 ml of the resultant mixture was filtered through a plug of silica gel followed by flushing with ethyl acetate

(*ca.* 1 ml). GC retention times (min) were as follows: styrene **1** (5.80), phenylacetaldehyde **1a** (8.37), acetophenone **1b** (8.75), 1-octene **12** (4.12) and tridecane (14.35).

Typical procedure for substrates 1-11

t-BuOH is preheated to 85^{o}C before being added (4.8 ml) to **1** (3.9 mg, 15 μmol) and *p*-benzoquinone (74.7 mg, 0.69 mmol) in a 20 ml glass vial. H_2O (12.2 μL, 0.6 mmol) and olefin (0.6 mmol) are then added and the mixture stirred for 60 min at 85^{o}C.

Typical procedure for isolation of aldehydes 1a-11a and ketones 1b-11b

All reaction mixtures were removed from heating and flash frozen at -78^{o}C (dry ice/EtOH bath) immediately after reaction and warmed to 30^{o}C after the mixture was completely frozen. A solution of 2, 4-dinitrophenylhydrazine (1.2 eq.) was added to the mixture at 30^{o}C and the mixture stirred for 1 h at room temperature. H_2O (*ca.* 10 ml) is added to the mixture, stirred for 1 min. and filtered. The residue is washed with cold H_2O (*ca.* 20 ml). The filtrate and aqueous washing is then combined and extracted with methylene chloride five times. The residue is re-dissolved in the organic extract and the solution dried over Na_2SO_4, followed by removal of solvent under reduced pressure. A crude ^{1}H NMR is taken with the solid product to determine the ratio of aldehyde to ketone. The material is purified using silica gel chromatography with 3% ethyl acetate in hexanes to obtain the aldehyde hydrazone (**c**) and ketone hydrazone (**d**) respectively. Aldehydes **1c**-**11c** exists as a mixture of *E* and *Z* isomers and the isolated yield reported is for the combined yield of both isomers. The *E* and *Z* isomers of **9c** have been isolated separately and the ^{1}H NMR of each isomer has been taken (*vide infra*) to prove the presence of

both isomers in the pure isolated **c** in each of **1c** to **11c**. Only NMR data for the major isomer is provided.

NMR data for aldehyde hydrazones **1c**, **2c**, **4c**, **9c** and ketone hydrazone **1d** matched that reported in literature[4-15].

2-methylphenylacetaldehyde-2, 4-dinitrophenylhydrazone, **3c**, orange solid, yield: 90%. ^{1}H NMR: δ 11.04 (s, 1H, NH), 9.12 (d, 1H, J 2.5 Hz), 8.32 (ddd, 1H, J 0.5, 2.5, 9.6 Hz), 7.94 (d, 1H, J 9.5 Hz), 7.55 (td, 1H, J 0.5, 5.5 Hz, HC=N), 7.23-2-7.19 (m, 4H), 3.76 (d, 2H, J 5.5 Hz, CH_2), 2.38 (s, 3H, CH_3). ^{13}C NMR: δ 150.0, 145.3, 138.2, 136.9, 133.9, 131.0, 130.3, 129.8, 129.2, 127.8, 126.7, 123.7, 116.7, 37.0, 19.8. HR-MS (FAB): calc: 315.1093, found: 315.1108.

4-nitrophenylacetaldehyde-2, 4-dinitrophenylhydrazone, **5c**, orange solid, yield: 96%. ^{1}H NMR: δ 11.13 (s, 1H), 9.13 (d, 1H, J 2.6 Hz), 8.34 (ddd, 1H, J 0.74, 2.6, 9.5 Hz), 8.24 (d, 2H, J 8.7 Hz), 7.91 (d, 1H, J 9.5 Hz), 7.62 (td, 1H, J 0.8, 5.6 Hz), 7.45 (m, 2H), 3.88 (d, 2H, J 5.5 Hz). ^{13}C NMR: δ 146.0, 143.9, 142.0, 129.1, 128.9, 126.9, 123.1, 122.4, 115.4, 115.1, 113.6, 37.7. HR-MS (FAB): calc: 346.0788, found: 346.0781.

3-nitrophenylacetaldehyde-2, 4-dinitrophenylhydrazone, **6c**, yellow solid, yield: 96%. ^{1}H NMR: δ 11.13 (s, 1H, NH), 9.13 (d, 1H, J 2.5 Hz), 8.34 (ddd, 1H, J 0.5, 2.5, 9.6 Hz), 8.19-8.15 (m, 2H), 7.92 (d, 1H, J 9.5 Hz), 7.64-7.61 (m, 2H), 7.57 (td, 1H, J 0.5, 7.0 Hz, HC=N), 3.89 (d, 2H, J 5.5 Hz, CH_2). ^{13}C NMR: δ 148.8, 148.0, 145.1, 138.6, 137.8, 135.4, 130.4, 130.1, 129.5, 124.2, 123.6, 122.7, 116.7, 38.7. HR-MS (FAB): calc: 346.0788, found: 346.0793.

4-fluorophenylacetaldehyde-2, 4-dinitrophenylhydrazone, **7c**, light orange solid, yield: 74%. ^{1}H NMR: δ 11.06 (s, 1H, NH), 9.13 (d, 1H, J 2.5 Hz), 8.33 (ddd, 1H, J 1.0, 2.5, 9.6 Hz), 7.65 (d, 1H, J 9.5 Hz), 7.57 (td, 1H, J 0.5, 6.0 Hz, HC=N), 7.25-7.21 (m, 2H), 7.08-7.03 (m, 2H), 3.74 (d, 2H, J 6.0 Hz, CH_2). ^{13}C NMR: δ 163.3, 150.0, 145.3, 138.3, 131.2, 130.8, 130.3, 123.7, 116.7, 116.2, 116.0, 38.4. HR-MS (FAB): calc: 319.0842, found: 319.0851.

4-chlorophenylacetaldehyde-2, 4-dinitrophenylhydrazone, **8c**, light orange solid, yield: 92%. ^{1}H NMR: δ 11.07 (s, 1H, NH), 9.13 (d, 1H, J 2.5 Hz), 8.33 (dd, 1H, J 2.5, 9.5 Hz), 7.95 (d, 1H, J 9.5 Hz), 7.57 (td, 1H, J 0.5, 6.0 Hz, HC=N), 7.35-2-7.32 (m, 2H), 7.21-7.19 (m, 2H), 3.74 (d, 2H, J 6.0 Hz, CH_2). ^{13}C NMR: δ 149.6, 145.2, 134.0, 133.5, 130.5, 130.3, 129.6, 129.3, 128.9, 123.7, 116.7, 38.6. HR-MS (FAB): calc: 335.0547, found: 335.0541.

4-bromophenylacetaldehyde-2, 4-dinitrophenylhydrazone, **9c**, light orange solid, yield: 90%. ^{1}H NMR: major isomer: δ 11.07 (s, 1H), 9.12 (d, 1H, J 3 Hz), 8.33 (ddd, 1H, J 0.5, 2.5, 9.5 Hz), 7.94 (d, 1H, J 9.5 Hz), 7.57 (td, 1H, J 0.5, 5.8 Hz), 7.50-7.48 (m, 2H), 7.15-7.13 (m, 2H), 3.72 (d, 2H, J 6 Hz), 2.38 (s, 3H); minor isomer: δ 11.34 (s), 9.16 (d, J 2.5 Hz), 8.38 (ddd, J 0.5, 2.5, 8.4 Hz), 8.09 (d, J 9.5 Hz), 7.62 (dt, J 1.5, 12.5 Hz), 7.44-2-7.41 (m), 7.14-7.08 (m), 3.67 (d, J 2 Hz).

Methyl 4-(2-oxoethyl)benzoate-2, 4-dinitrophenylhydrazone, **10c**, orange solid, yield: 59%. ^{1}H NMR: δ 11.09 (s, 1H, NH), 9.12 (d, 1H, J 2.5 Hz), 8.33 (ddd, 1H, J 0.5, 2.5, 9.6 Hz), 8.05-8.02 (m, 2H), 7.94 (d, 1H, J 9.5 Hz), 7.61 (td, 1H, J 0.5, 5.5 Hz, HC=N), 7.36-7.33 (m, 2H), 3.92 (s, 3H, CH_3), 3.82 (d, 2H, J 5.5 Hz, CH_2). ^{13}C NMR: δ 166.9, 149.2, 145.2, 140.9, 138.4, 130.7,

130.4, 130.3, 129.5, 129.3, 123.6, 116.8, 52.4, 39.2. HR-MS (FAB): calc: 359.0992, found: 359.0980.

2-(3, 5-bis(trifluoromethyl)phenyl)acetaldehyde-2, 4-dinitrophenylhydrazone, **11c**, yellow solid, 72%. %. ^{1}H NMR: δ 11.15 (s, 1H, NH), 9.13 (d, 1H, J 2.5 Hz), 8.34 (dd, 1H, J 2.5, 9.5 Hz), 7.89 (d, 1H, J 9.5 Hz), 7.84 (s, 1H), 7.75 (s, 2H), 7.64 (t, 1H, J 5.5 Hz, HC=N), 3.92 (d, J 5.5 Hz, CH_2). ^{13}C NMR: δ 147.3, 145.1, 138.2, 132.6, 132.3, 130.4, 129.6, 124.4, 123.6, 122.3, 121.6, 116.7, 38.7. HR-MS (FAB): calc: 437.0684, found: 437.0706.

4-methylacetophenone-2, 4-dinitrophenylhydrazone, **2d**, red solid. ^{1}H NMR: δ 11.36 (s, 1H, NH), 9.17 (d, 1H, J 2.5 Hz), 8.36 (ddd, 1H, J 0.5, 2.5, 9.75 Hz), 8.13 (d, 1H, J 9.5 Hz), 7.77-7.75 (m, 2H), 7.27-7.26 (m, 2H), 2.45 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR: δ 152.7, 145.2, 140.7, 138.3, 134.7, 130.3, 129.8, 129.6, 126.7, 123.8, 117.0, 21.6, 13.9. HR-MS (FAB): calc: 315.1093, found: 315.1087.

2-methylacetophenone-2, 4-dinitrophenylhydrazone, **3d**, light orange solid. ^{1}H NMR: δ 11.29 (s, 1H, NH), 9.17 (d, 1H, J 3.0 Hz), 8.32 (ddd, 1H, J 0.5, 2.5, 9.5 Hz), 8.01 (d, 1H, J 9.5 Hz), 7.37-7.28 (m, 4H), 2.48 (s, 3H, CH_3), 2.46 (s, 3H, CH_3). ^{13}C NMR: δ 157.7, 155.2, 148.6, 145.3, 144.9, 138.7, 138.4, 137.8, 135.9, 134.2, 131.6, 131.5, 130.38, 130.35, 130.2, 130.1, 129.8, 129.4, 129.1, 128.5, 127.5, 126.3, 126.2, 123.7, 116.9, 116.7, 116.5, 24.9, 21.2, 19.2, 17.8. HR-MS (FAB): calc: 315.1093, found: 315.1104. *cis* and *trans* isomers for **3d** exists in 3:1 mixture resulting in complicated ^{13}C NMR.

4-*tert*-butylacetophenone-2, 4-dinitrophenylhydrazone, **4d**, light orange solid. ^{1}H NMR: δ 11.36 (s, 1H, NH), 9.17 (d, 1H, J 2.5 Hz), 8.36 (ddd, 1H, J 0.5, 2.5, 9.5 Hz), 8.13 (d, 1H, 9.5 Hz), 7.82-7.79 (m, 2H), 7.50-7.47 (m, 2H), 2.46 (s, 3H, CH_3), 1.36 (s, 9H, $C(CH_3)_3$). ^{13}C NMR: δ 153.9, 152.7, 145.2, 138.3, 134.7, 130.3, 129.8, 126.5, 125.9, 123.8, 117.0, 35.1, 31.4, 13.9. HR-MS (FAB): calc: 357.1563, found: 357.1565.

4-nitroacetophenone-2, 4-dinitrophenylhydrazone, **5d**, intense orange solid. ^{1}H NMR: δ 11.45 (s, 1H, NH), 9.20 (d, 1H, J 2.5 Hz), 8.43 (dd, 1H, J 2.5, 9.5 Hz), 8.33-8.30 (m, 2H), 8.14 (d, 1H, J 9.5 Hz), 8.04-8.01 (m, 2H), 2.52 (s, 3H, CH_3). ^{13}C NMR: δ 149.5, 148.6, 144.8, 143.3, 139.3, 130.6, 130.5, 127.4, 124.2, 123.6, 117.0, 13.9. HR-MS (FAB): calc: 346.0788, found: 346.0793.

3-nitroacetophenone-2, 4-dinitrophenylhydrazone, **6d**, intense orange solid. ^{1}H NMR: δ 11.45 (s, 1H, NH), 9.20 (d, 1H, J 2.5 Hz), 8.43 (dd, 1H, J 2.5, 9.5 Hz), 8.33-8.30 (m, 2H), 8.14 (d, 1H, J 9.5 Hz), 8.04-8.01 (m, 2H), 2.52 (s, 3H, CH_3). ^{13}C NMR: δ 149.5, 148.9, 144.9, 139.2, 139.1, 132.2, 130.6, 130.4, 130.0, 124.6, 123.7, 121.6, 117.0, 13.9. HR-MS (FAB): calc: 346.0788, found: 346.0777.

4-fluoroacetophenone-2, 4-dinitrophenylhydrazone, **7d**, intense orange solid. ^{1}H NMR: δ 11.43 (s, 1H, NH), 9.19 (d, 1H, J 2.5 Hz), 8.70 (t, J 2 Hz), 8.44 (ddd, 1H, J 0.5, 2.5, 9.25 Hz), 8.31 (ddd, 1H, J 1.0, 2.5, 8.25 Hz), 8.21 (ddd, 1H, J 1.0, 2.0, 7.75), 8.15 (d, 1H, J 9.5 Hz), 7.66 (t, 1H, J 8.0 Hz), 2.53 (s, 3H, CH_3). ^{13}C NMR: δ165.2, 151.4, 145.2, 138.5, 133.6, 130.4, 128.7, 123.8, 116.9, 116.1, 115.9, 14.0. HR-MS (FAB): calc: 319.0842, found: 319.0843.

4-chloroacetophenone-2, 4-dinitrophenylhydrazone, **8d**, intense orange solid. ^{1}H NMR: δ 11.37 (s, 1H, NH), 9.18 (d, 1H, J 2.5 Hz), 8.38 (dd, 1H, J 2.0, 9.5 Hz), 8.11 (d, 1H, J 9.5 Hz), 7.88-7.85 (m, 2H), 7.17-7.13 (m, 2H), 2.46 (s, 3H, CH_3). ^{13}C NMR: δ 151.2, 145.1, 138.6, 136.5, 135.9, 130.4, 130.0, 129.2, 128.0, 123.7, 116.9, 13.8. HR-MS (FAB): calc: 335.0547, found: 335.0560.

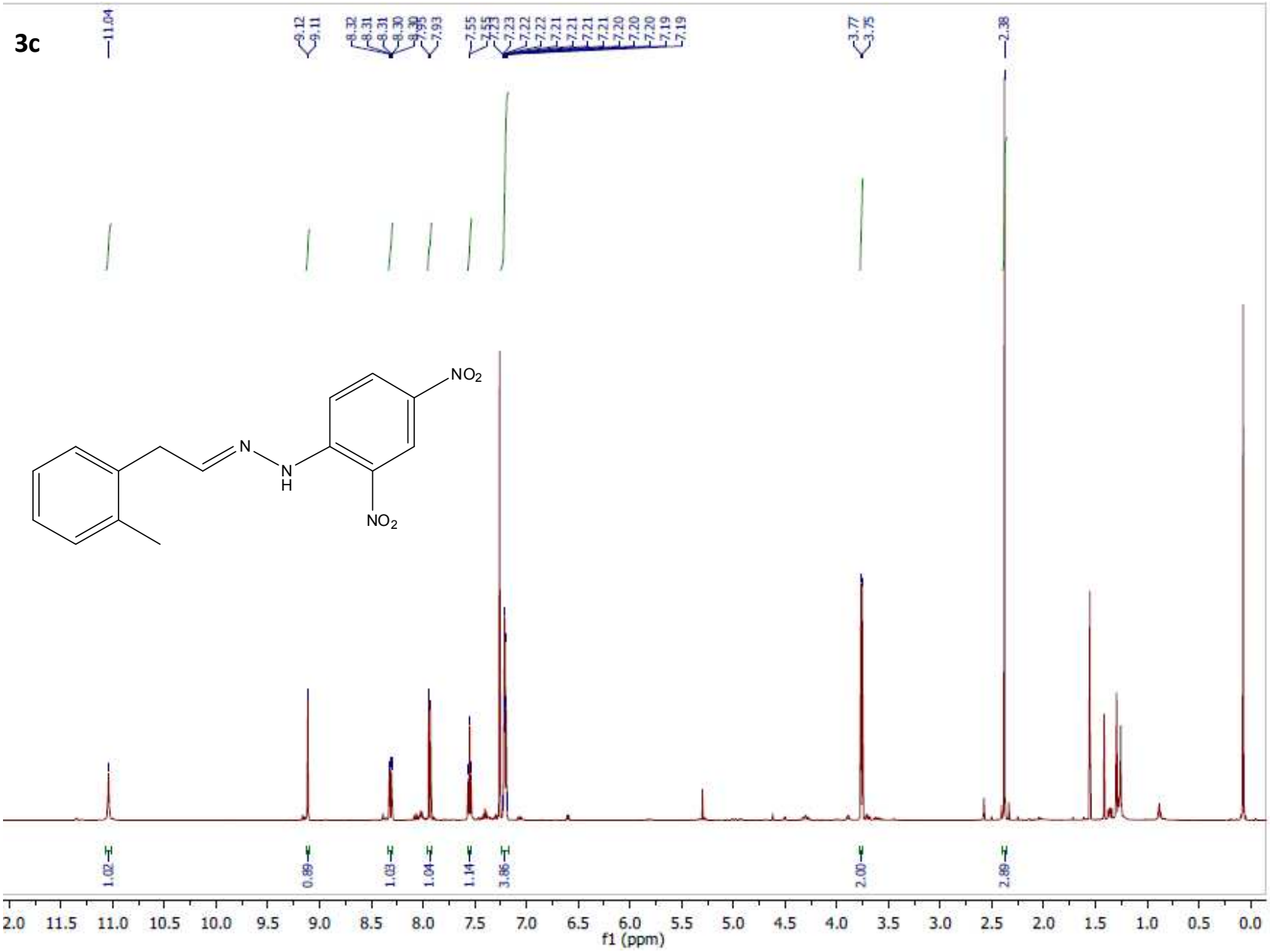
4-bromoacetophenone-2, 4-dinitrophenylhydrazone, **9d**, intense orange solid. ^{1}H NMR: δ 11.36 (s, 1H, NH), 9.18 (d, 1H, J 2.5 Hz), 8.38 (dd, 1H, J 2.5, 9.5 Hz), 8.11 (d, 1H, J 9.5 Hz), 7.75-7.72 (m, 2H), 7.61-7.57 (m, 2H), 2.45 (s, 3H, CH_3). ^{13}C NMR: δ 151.2, 145.1, 138.6, 136.4, 132.1, 130.4, 130.1, 128.2, 124.8, 123.7, 116.9, 13.8. HR-MS (FAB): calc: 379.0042, found: 379.0056.

Methyl 4-acetylbenzoate-2, 4-dinitrophenylhydrazone, **10d**, orange solid. ^{1}H NMR: δ 11.40 (s, 1H, NH), 9.18 (d, 1H, J 2.5 Hz), 8.40 (dd, 1H, J 2.0, 9.5 Hz), 8.16-8.10 (m, 3H), 7.94-7.92 (m, 2H), 3.96 (s, 3H, CH_3), 2.49 (s, 3H, CH_3). ^{13}C NMR: δ 166.7, 151.1, 145.0, 141.5, 138.8, 131.4, 130.4, 130.1, 126.6, 123.7, 117.0, 115.5, 52.6, 13.9. HR-MS (FAB): calc: 359.0992, found: 359.1005.

3, 5-bis(trifluoromethyl)acetophenone-2, 4-dinitrophenylhydrazone, **11d**, light orange solid. ^{1}H NMR: δ 11.44 (s, 1H, NH), 9.20 (d, 1H, J 2.5 Hz), 8.46 (ddd, 1H, J 0.5, 2.5, 9.6 Hz), 8.27 (s, 2H), 8.12 (d, J 9.5 Hz), 7.95(s, 1H), 2.53 (s, 3H, CH_3). ^{13}C NMR: δ 148.7, 144.8, 139.6, 139.3, 132.6, 132.4, 130.7, 126.5, 124.4, 123.6, 122.2, 117.0, 13.9. HR-MS (FAB): calc: 437.0684, found: 437.0684.

(1) Heck, R. F. *Palladium Reagents in Organic Synthesis: Best Synthetic Methods*; Academic Press: New York, 1985.
(2) McMurry, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 6821.
(3) Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740.
(4) Agrawal, M. K.; Ghosh, P. K. *J. Org. Chem.* **2009**, *74*, 7947.
(5) Yoshimura, A.; Banek, C. T.; Yusubov, M. S.; Nemykin, V. N.; Zhdankin, V. V. *J. Org. Chem.* **2011**, *76*, 3812.
(6) Matsuo, J.-i.; Iida, D.; Tatani, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 223.
(7) Fox, R. J.; Lalic, G.; Bergman, R. G. *J. Am. Chem. Soc.* **2007**, *129*, 14144.
(8) Miiller, S.; Schmidt, R. R. *Helv. Chim. Acta* **1993**, *76*, 616.
(9) Clyne, D. S.; Weiler, L. *Tetrahedron* **1999**, *55*, 13659.
(10) MacMillan, J. B.; Molinski, T. F. *J. Am. Chem. Soc.* **2004**, *126*, 9944.
(11) Jacob, P. *J. Organomet. Chem.* **1978**, *156*, 101.
(12) Critch, S. C.; Fallis, A. G. *Can. J. Chem.* **1977**, *55*, 2845.
(13) Chauvet, F.; Heumann, A.; Waegell, B. *J. Org. Chem.* **1987**, *52*, 1916.
(14) Mascal, M.; Nikitin, E. B. *Angew. Chem. Intl. Ed.* **2008**, *47*, 7924.
(15) Dydio, P.; Dzik, W. I.; De-Bruin, B.; Reek, J. N. H.; Lutz, M. *Angew. Chem. Intl. Ed.* **2011**, *50*, 396.

3c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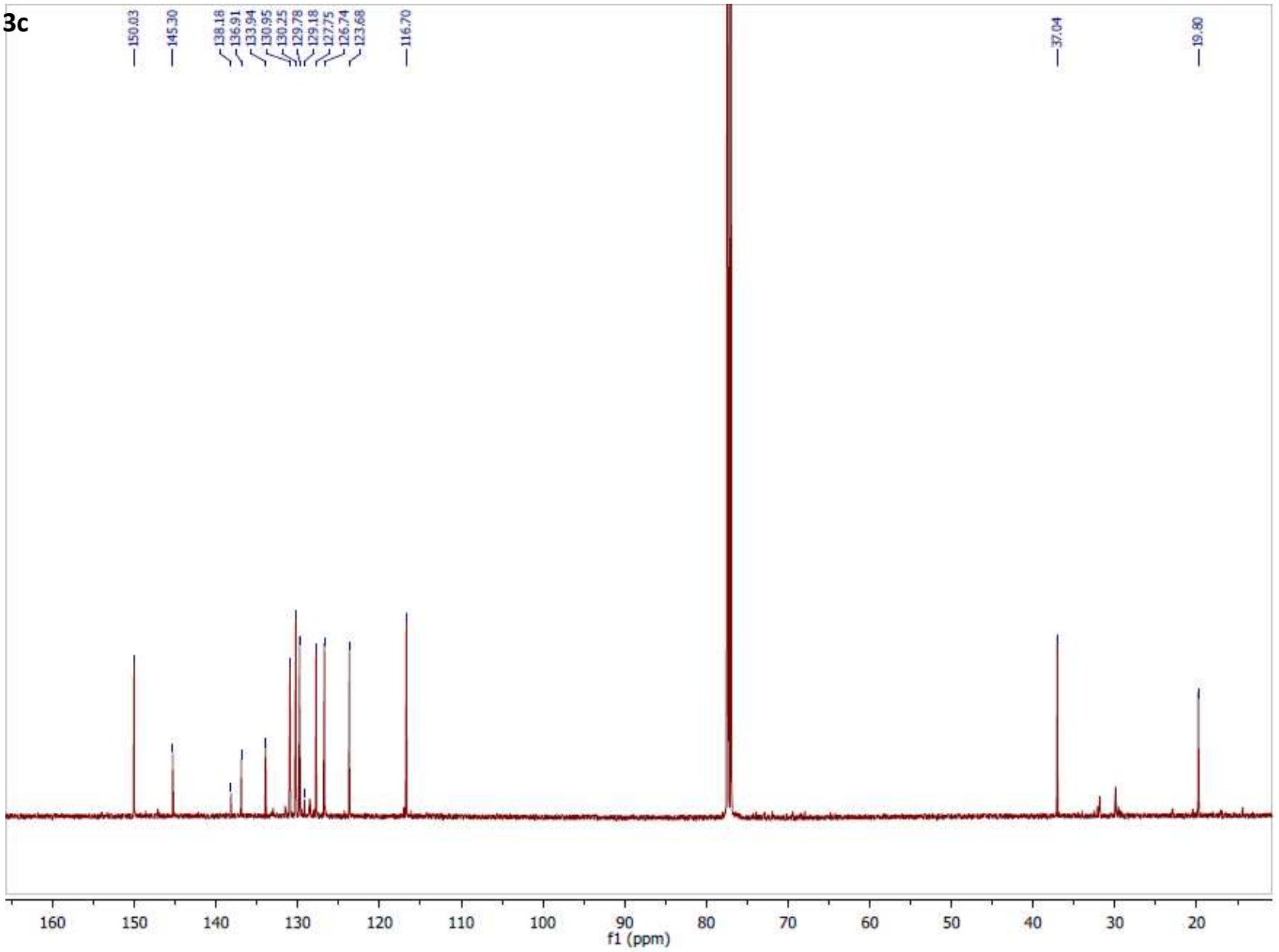
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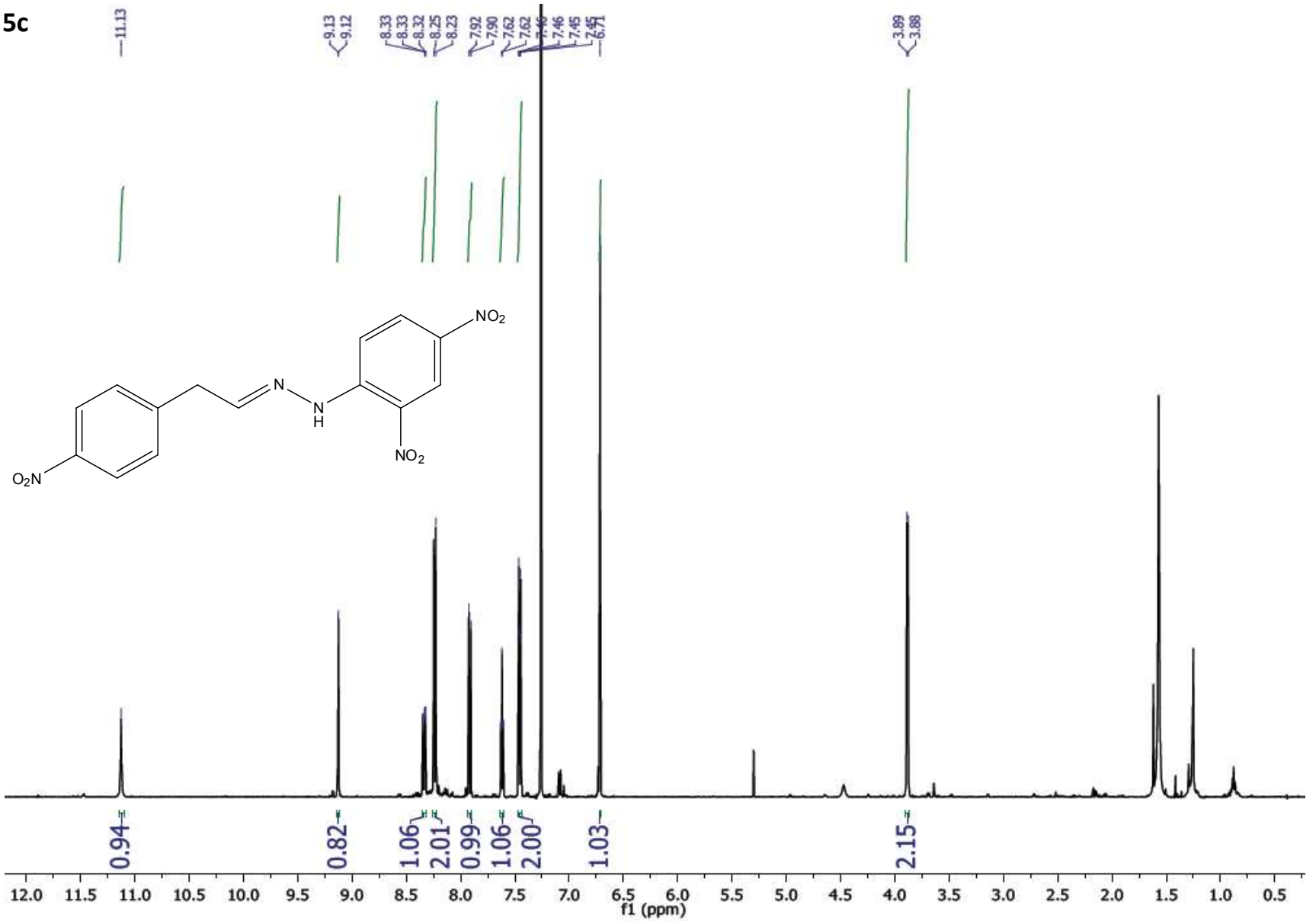
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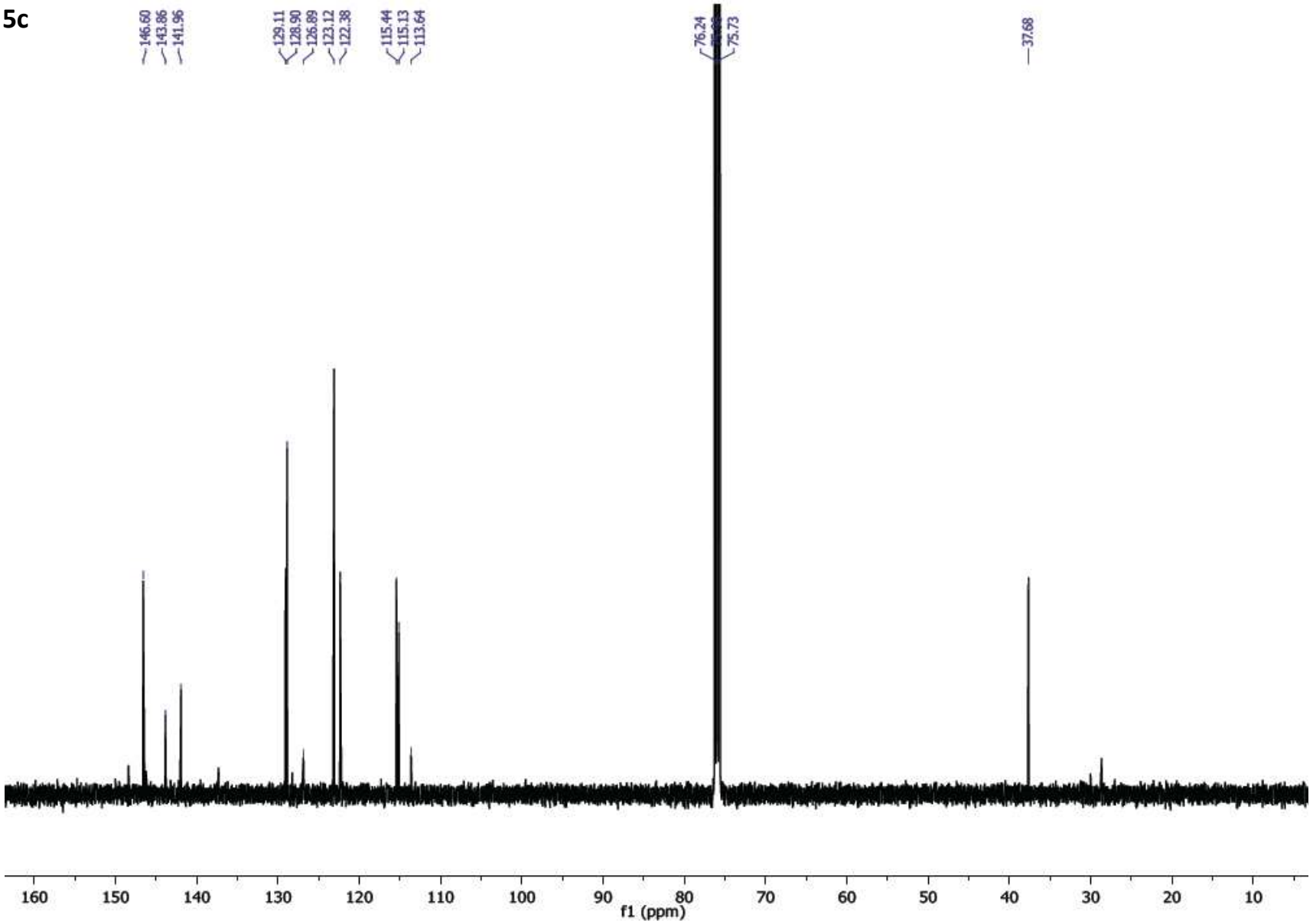
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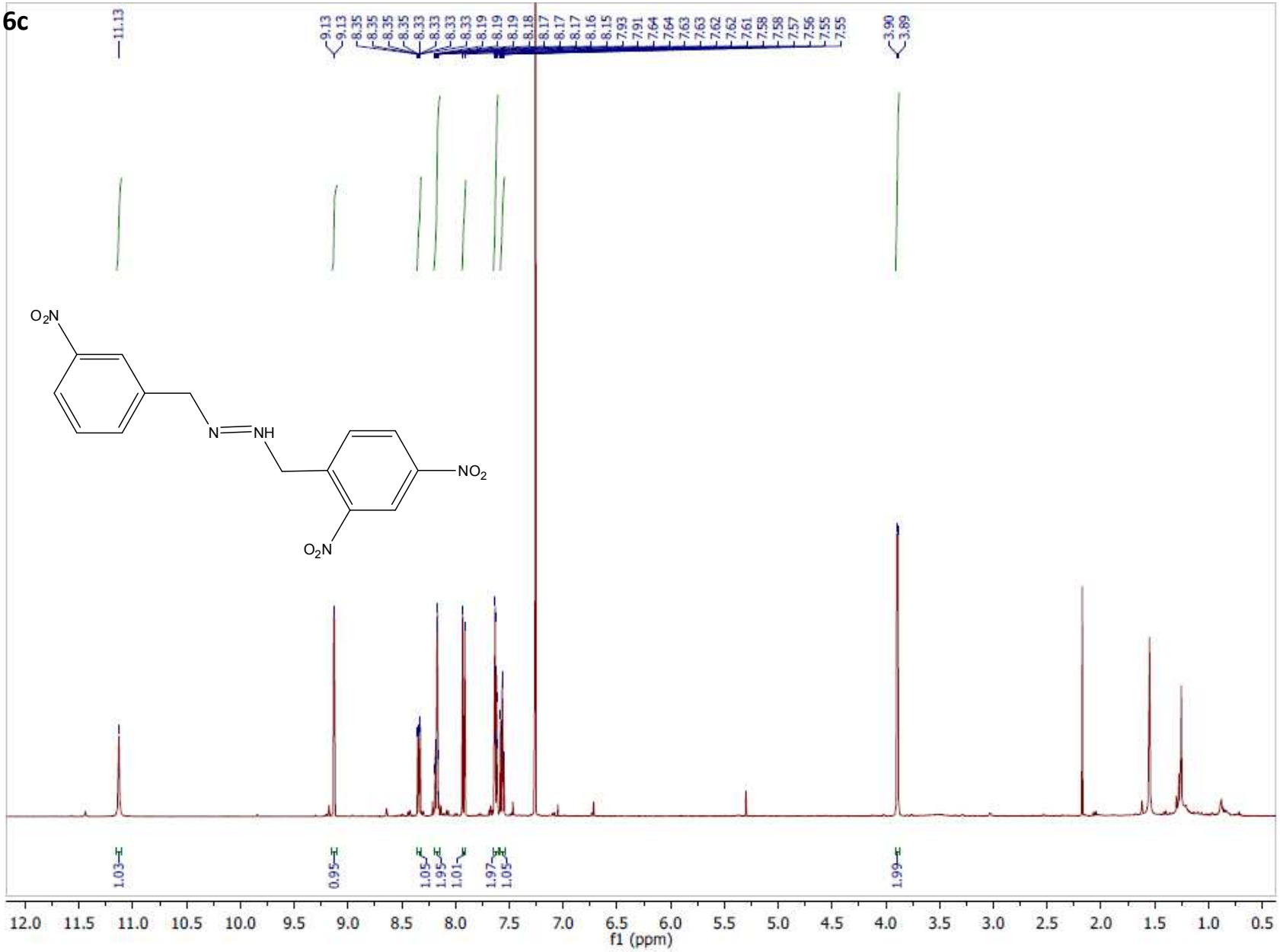
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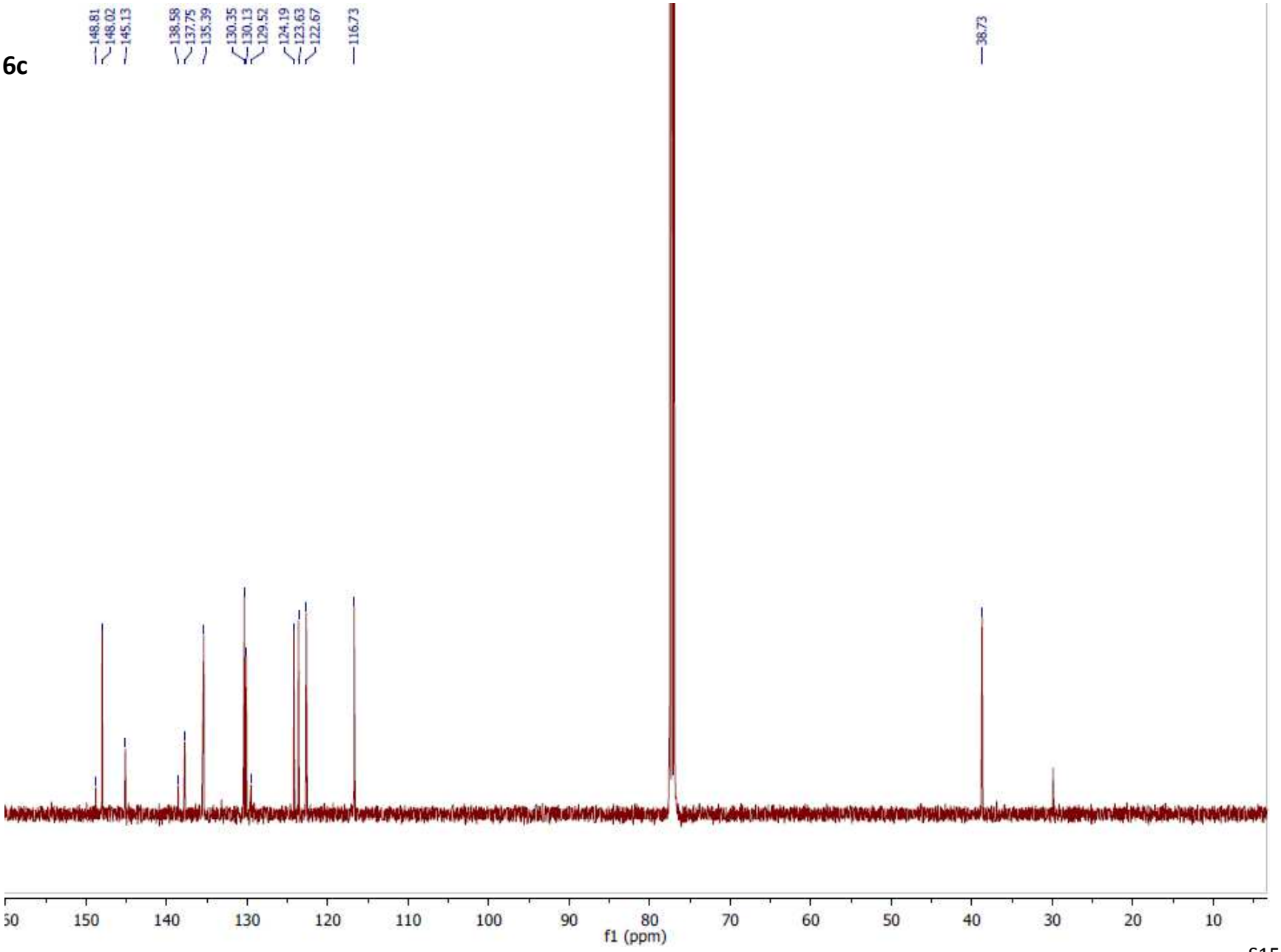
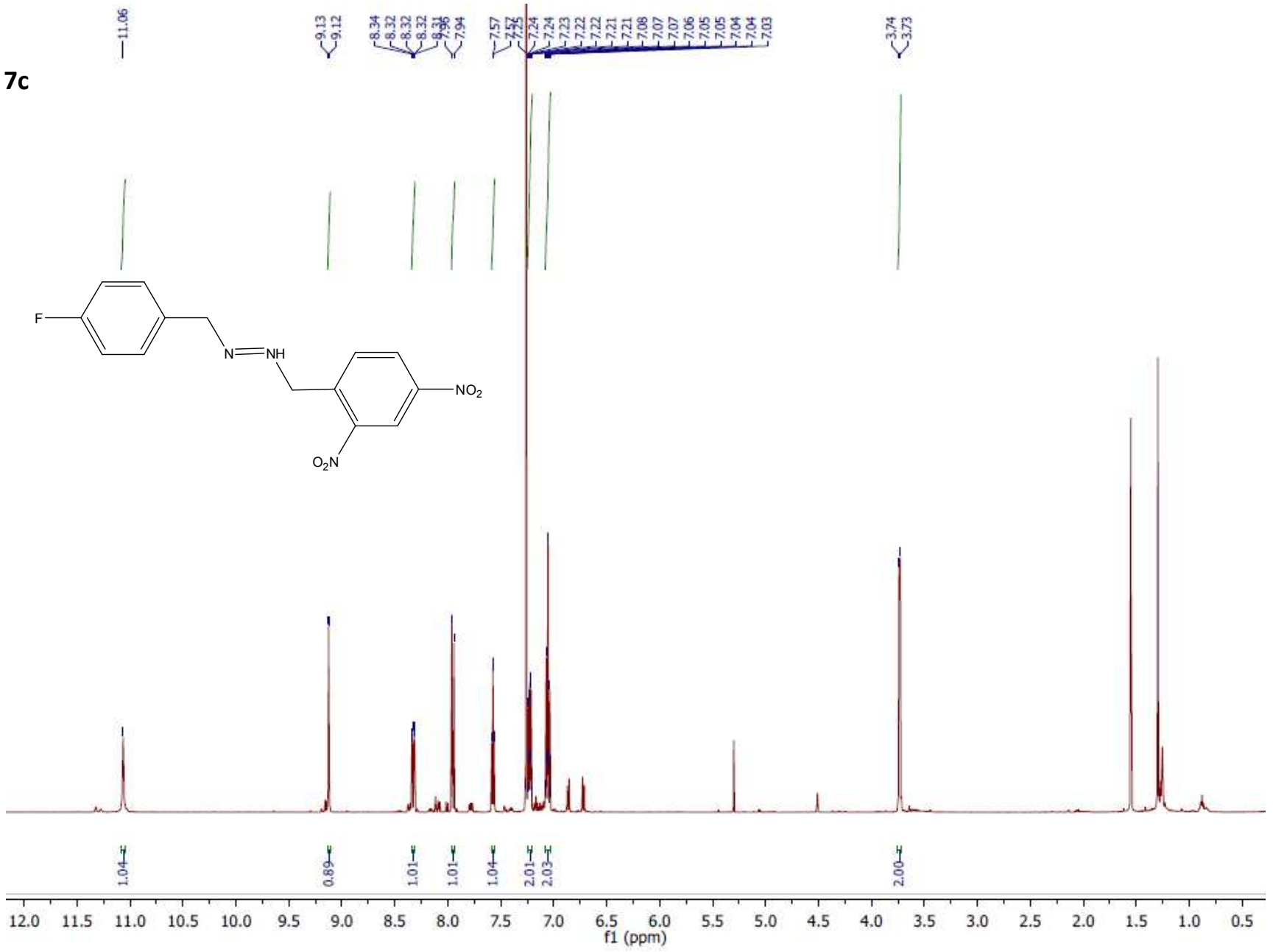
O2N
N=NH
NO2
O2N
1.03
0.95
1.05
1.95
1.01
1.97
1.05
1.99
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

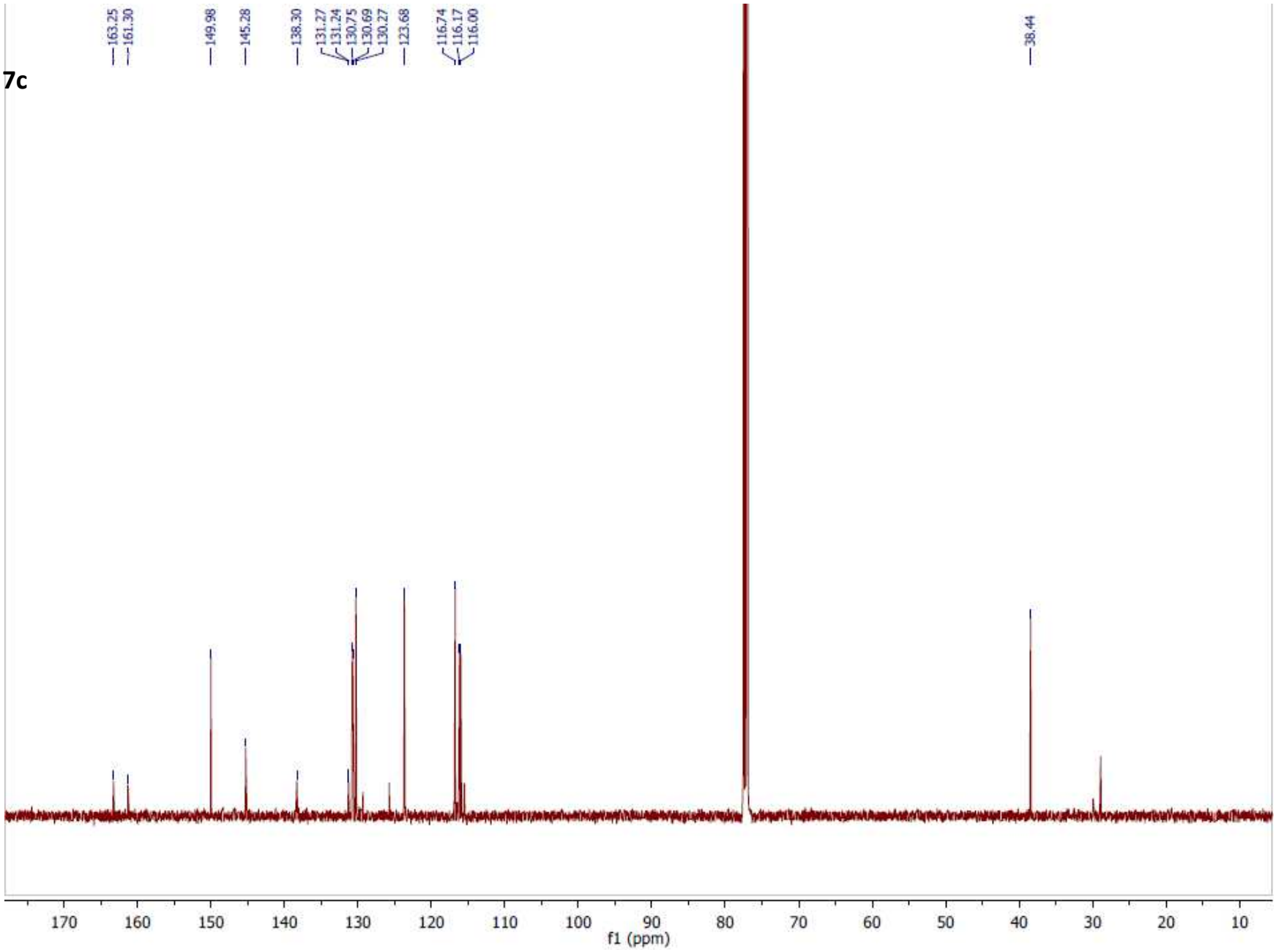
6c


148.81
148.02
145.13
138.58
137.75
135.39
130.35
130.13
129.52
124.19
123.63
122.67
116.73
38.73
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

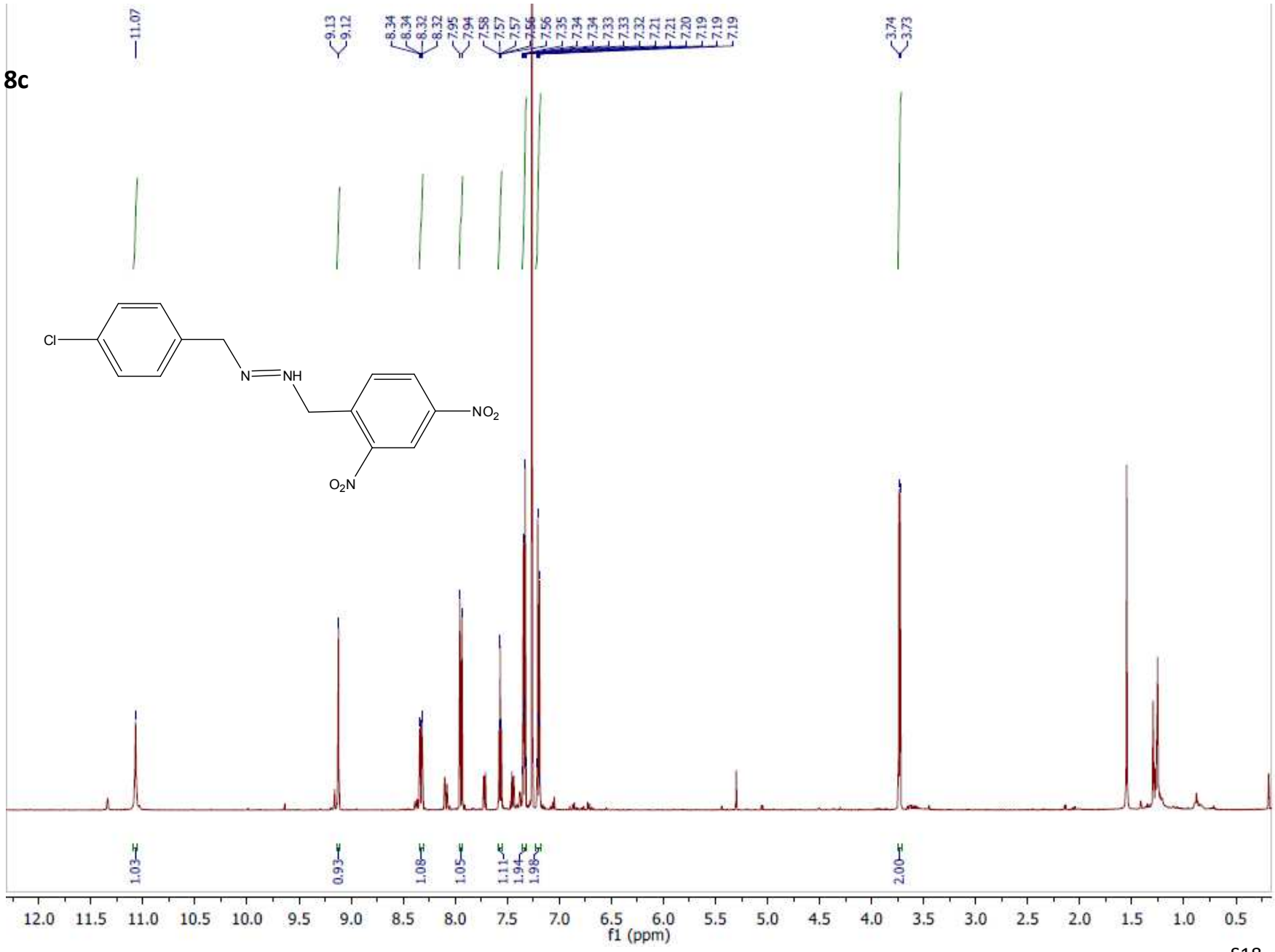
7c


11.06
9.13
9.12
8.34
8.32
8.32
8.32
8.31
7.96
7.94
7.57
7.57
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.08
7.07
7.07
7.06
7.05
7.05
7.04
7.04
7.03
3.74
3.73
F
N
NH
NO2
O2N
1.04
0.89
1.01
1.01
1.04
2.01
2.03
2.00
12.0
11.5
11.0
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)

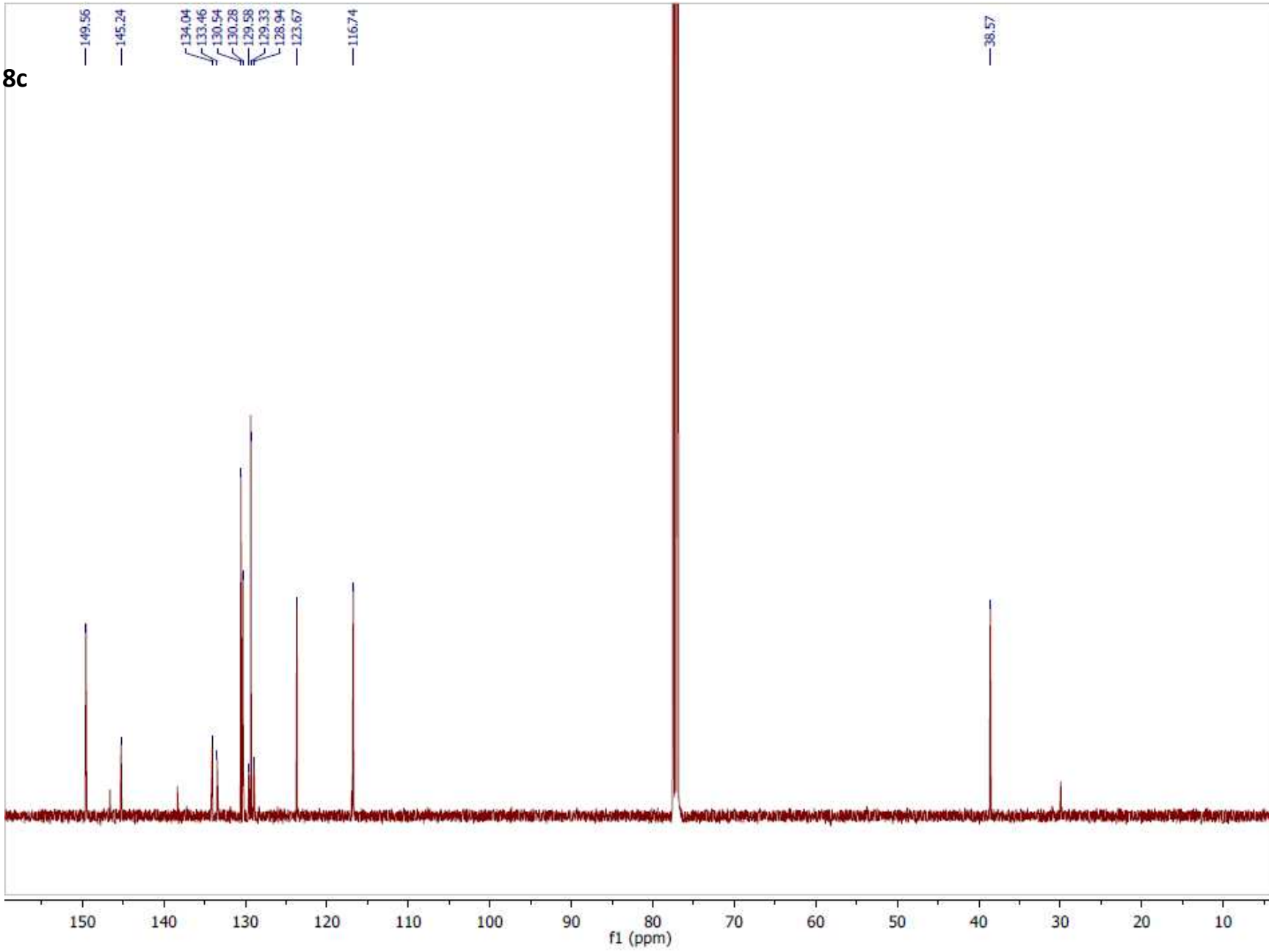
7c


163.25
161.30
149.98
145.28
138.30
131.27
131.24
130.75
130.69
130.27
123.68
116.74
116.17
116.00
38.44
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

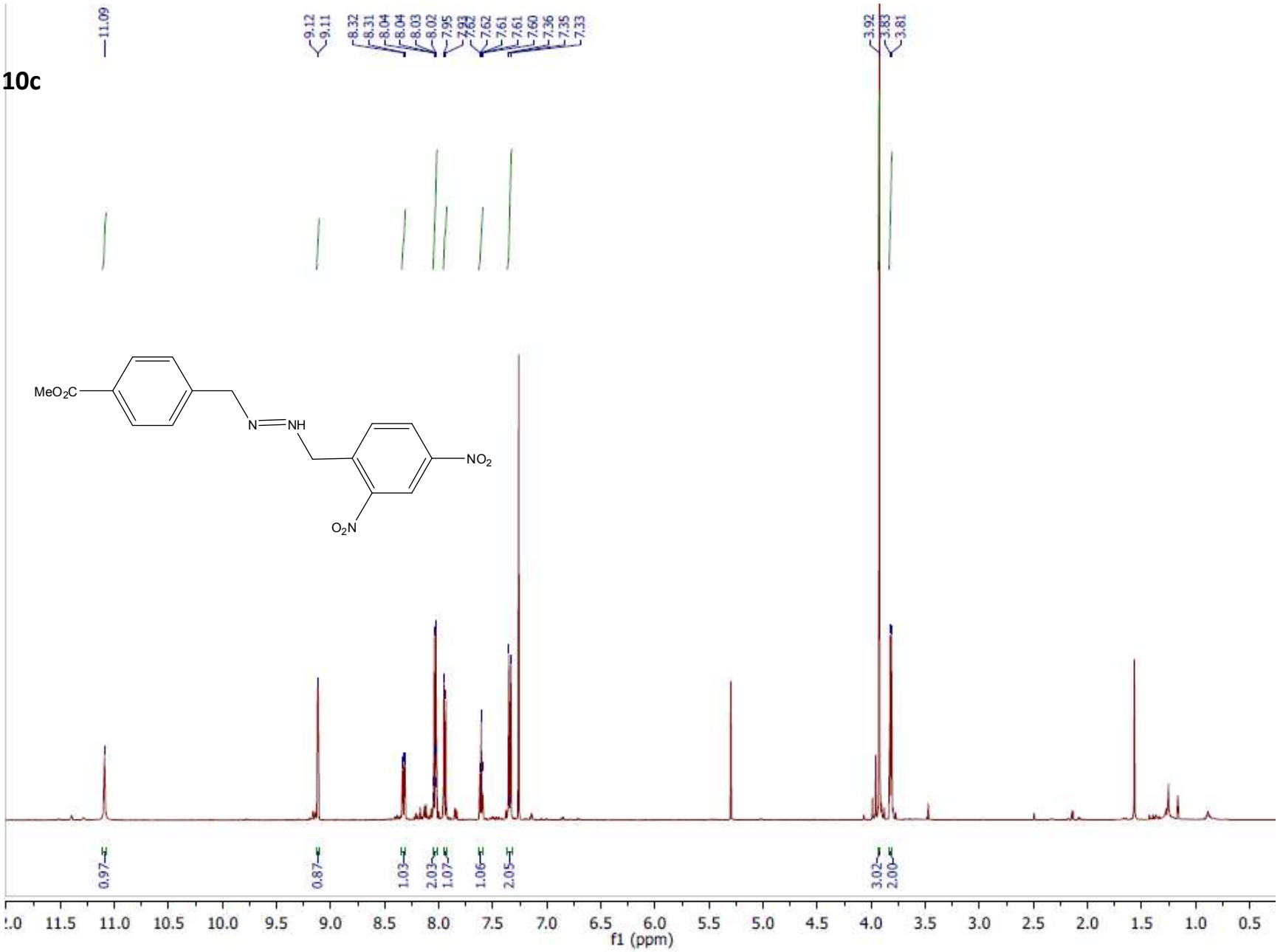
8c


11.07
9.13
9.12
8.34
8.34
8.32
8.32
7.95
7.94
7.58
7.57
7.57
7.56
7.56
7.35
7.34
7.34
7.33
7.33
7.32
7.21
7.21
7.20
7.19
7.19
7.19
3.74
3.73
Cl
N
NH
NO2
O2N
1.03
0.93
1.08
1.05
1.11
1.94
1.98
2.00
12.0
11.5
11.0
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)

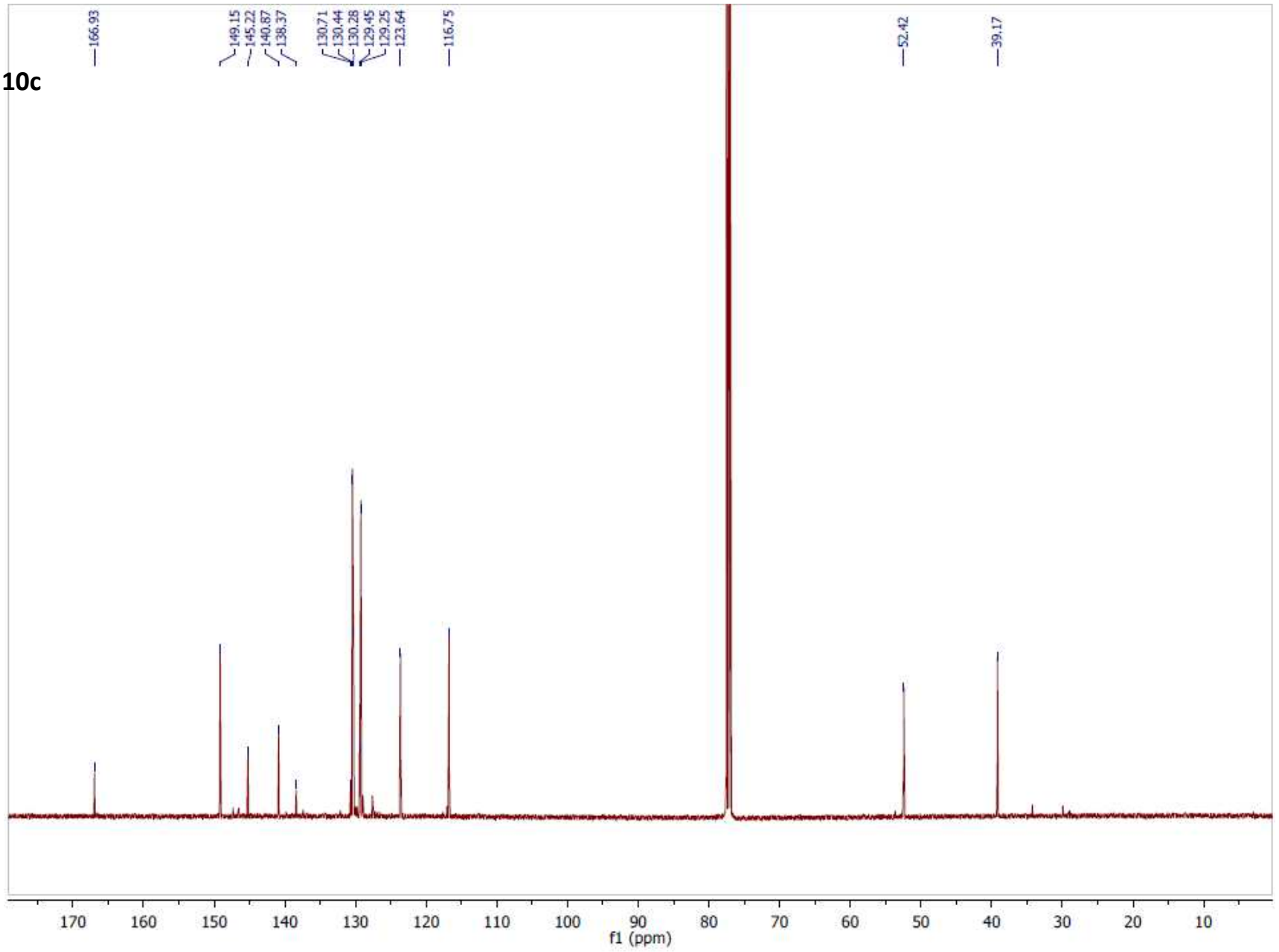
8c


149.56
145.24
134.04
133.46
130.54
130.28
129.58
129.33
128.94
123.67
116.74
38.57
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

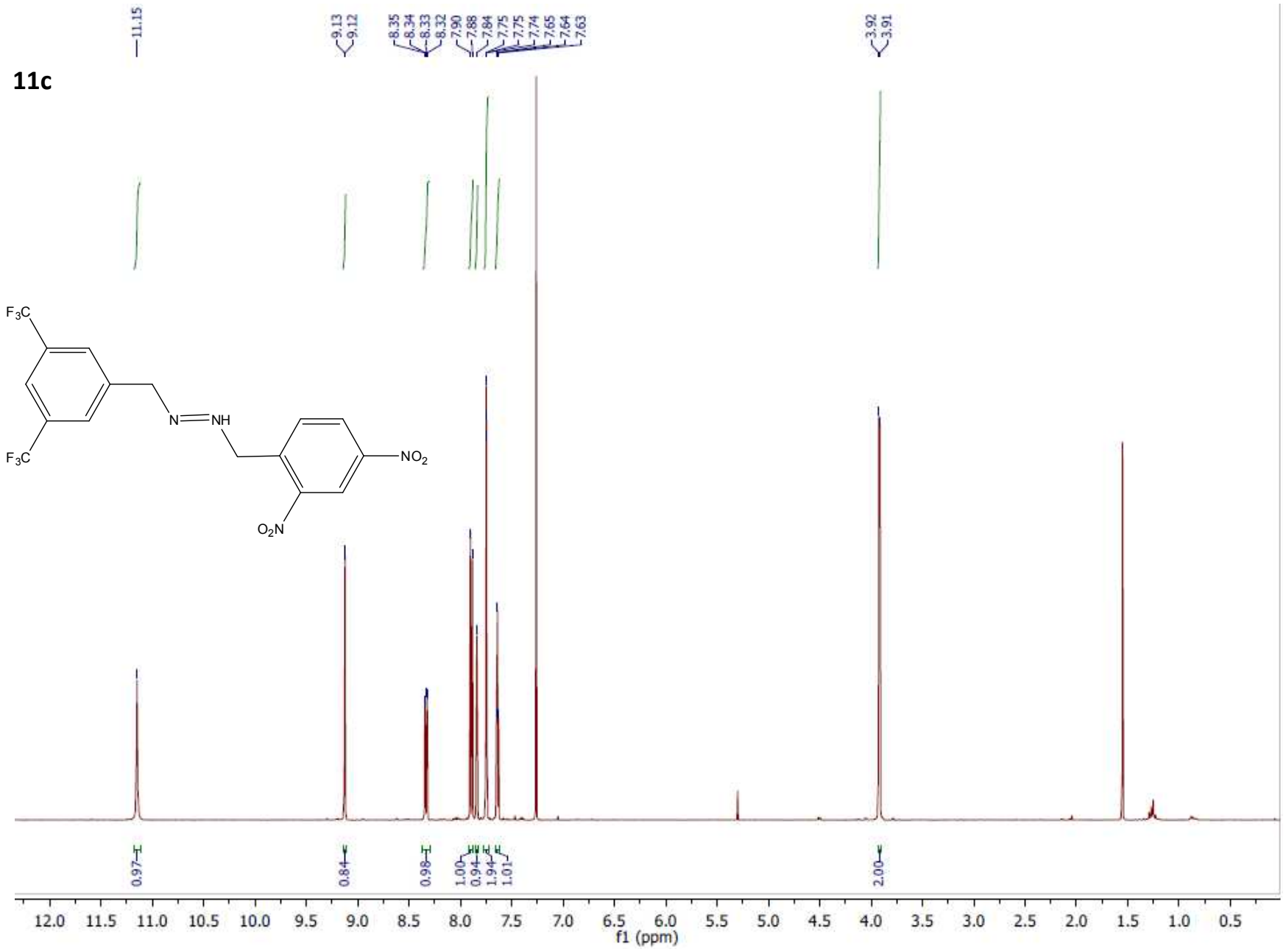
10c


11.09
9.12
9.11
8.32
8.31
8.04
8.04
8.03
8.02
7.95
7.62
7.61
7.61
7.60
7.36
7.35
7.33
3.92
3.83
3.81
MeO2C
N
NH
NO2
O2N
0.97
0.87
1.03
2.03
1.07
1.06
2.05
3.02
2.00
f1 (ppm)

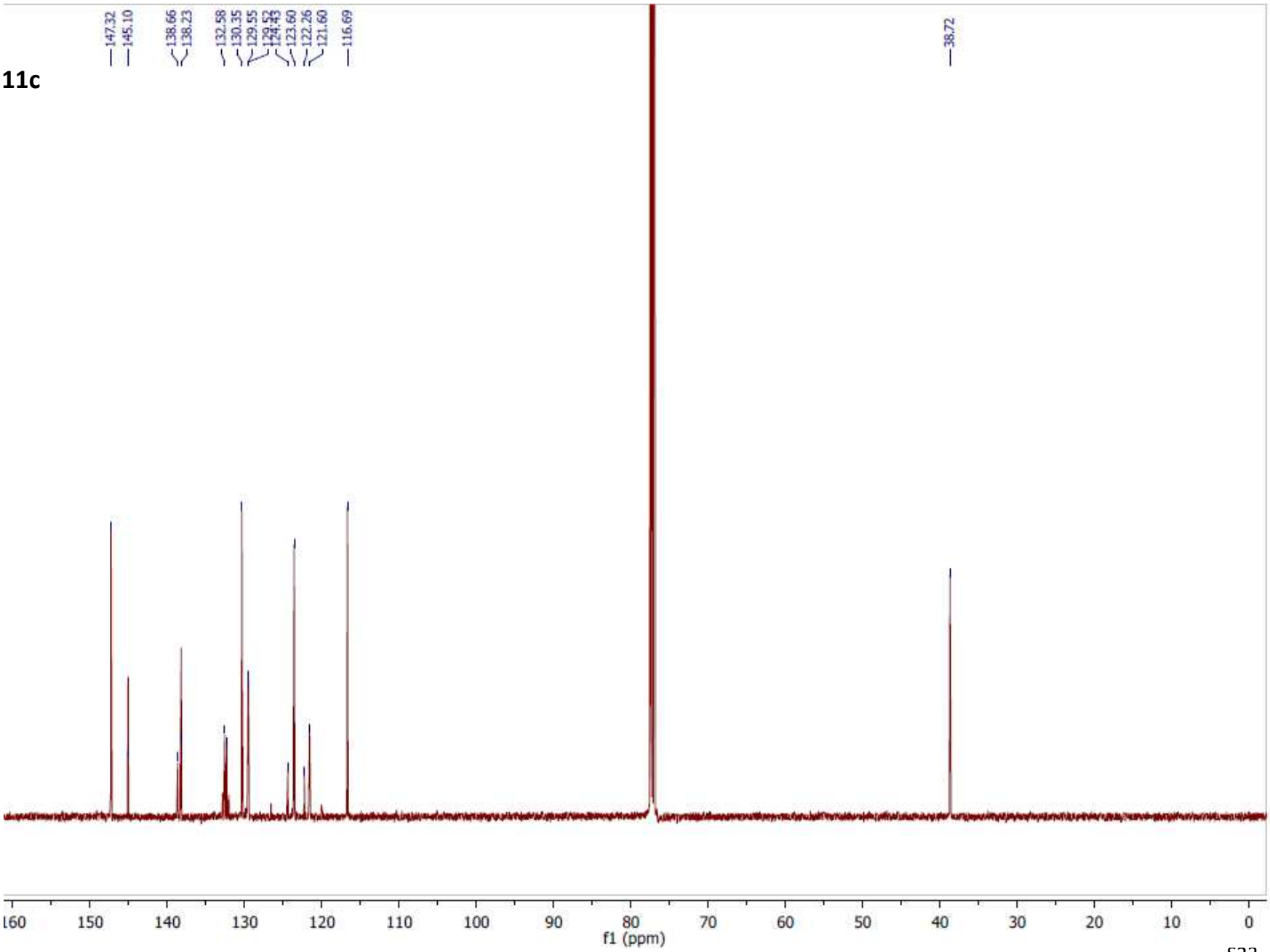
10c


166.93
149.15
145.22
140.87
138.37
130.71
130.44
130.28
129.45
129.25
123.64
116.75
52.42
39.17
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

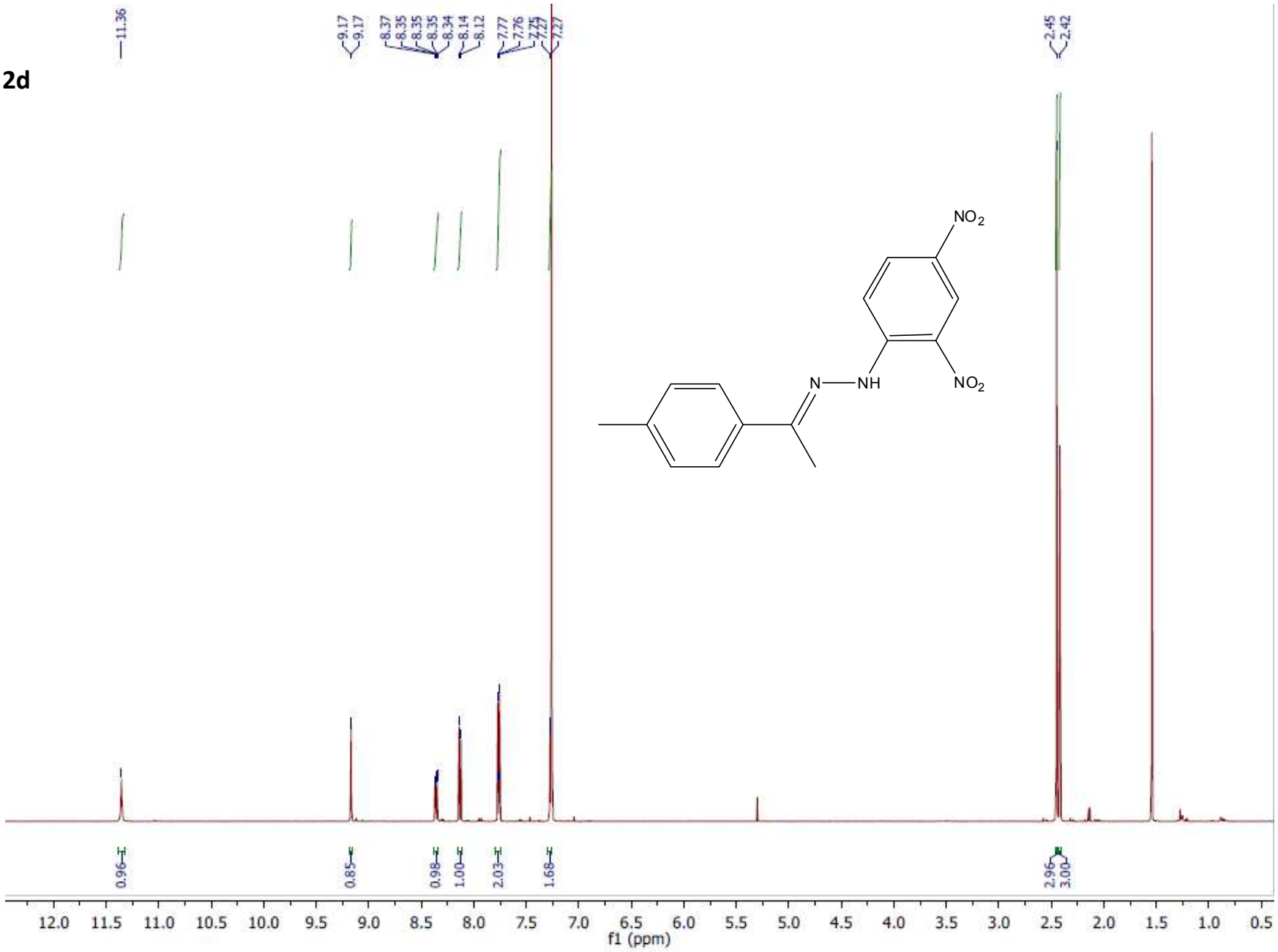
11c


11.15
9.13
9.12
8.35
8.34
8.33
8.32
7.90
7.88
7.84
7.75
7.75
7.74
7.65
7.64
7.63
3.92
3.91
F3C
F3C
N=NH
NO2
O2N
0.97
0.84
0.98
1.00
0.94
1.94
1.01
2.00
12.0 11.5 11.0 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)

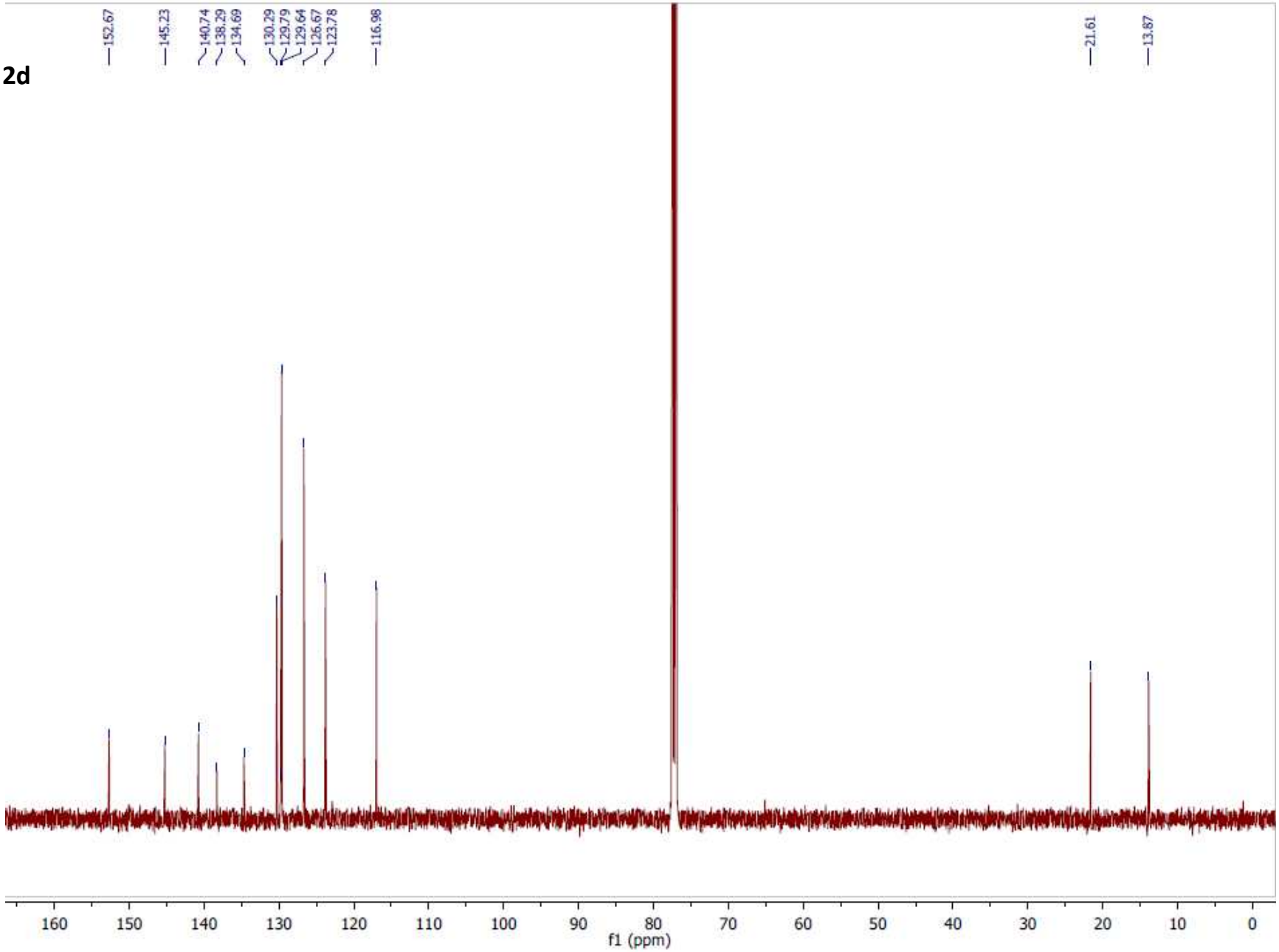
11c


147.32
145.10
138.66
138.23
132.58
130.35
129.55
129.52
124.43
123.60
122.26
121.60
116.69
38.72
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

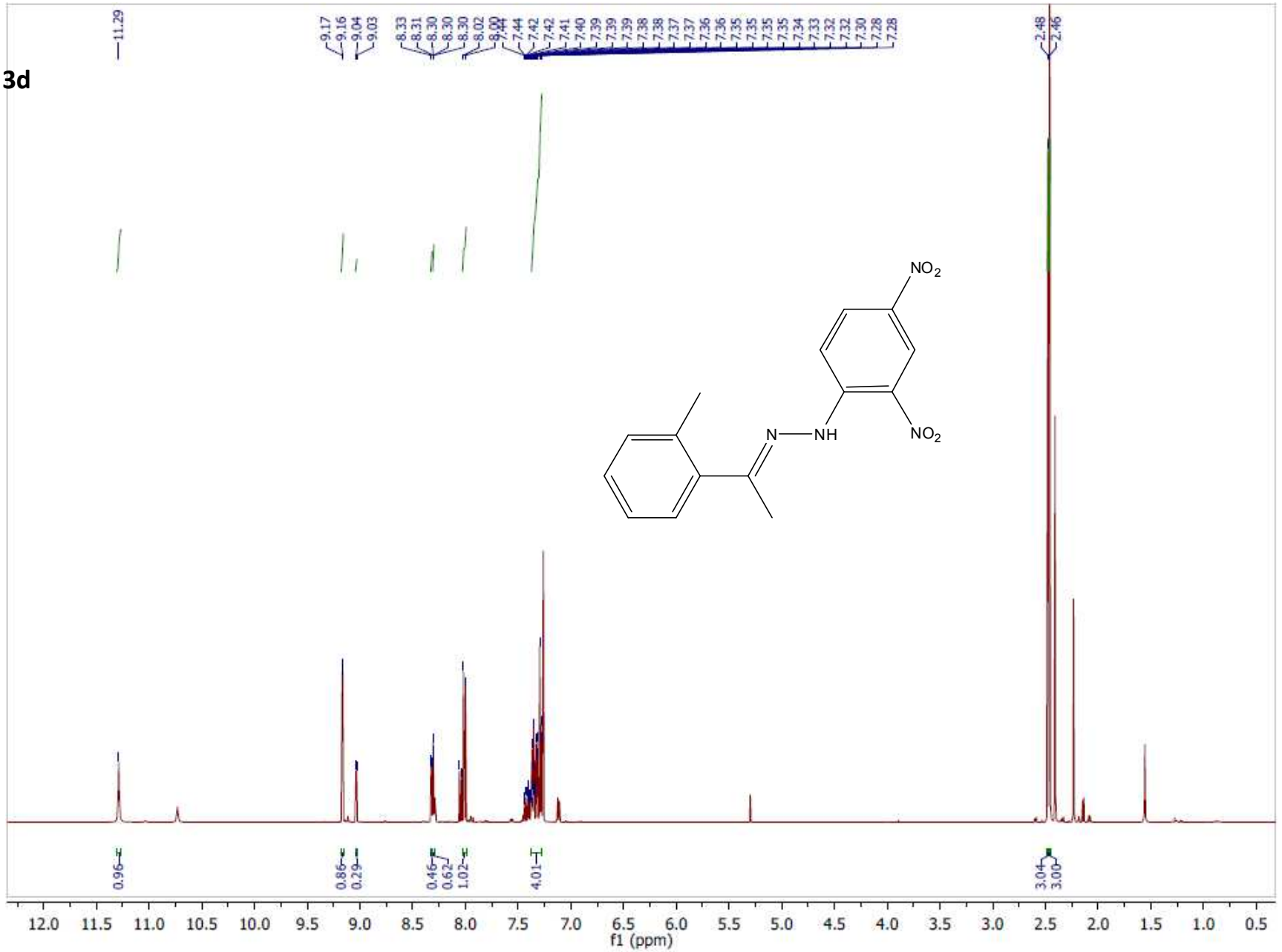
2d


11.36
9.17
9.17
8.37
8.35
8.35
8.35
8.34
8.14
8.12
7.77
7.76
7.27
7.27
2.45
2.42
NO2
NO2
N
NH
0.96
0.85
0.98
1.00
2.03
1.68
2.96
3.00
12.0
11.5
11.0
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)

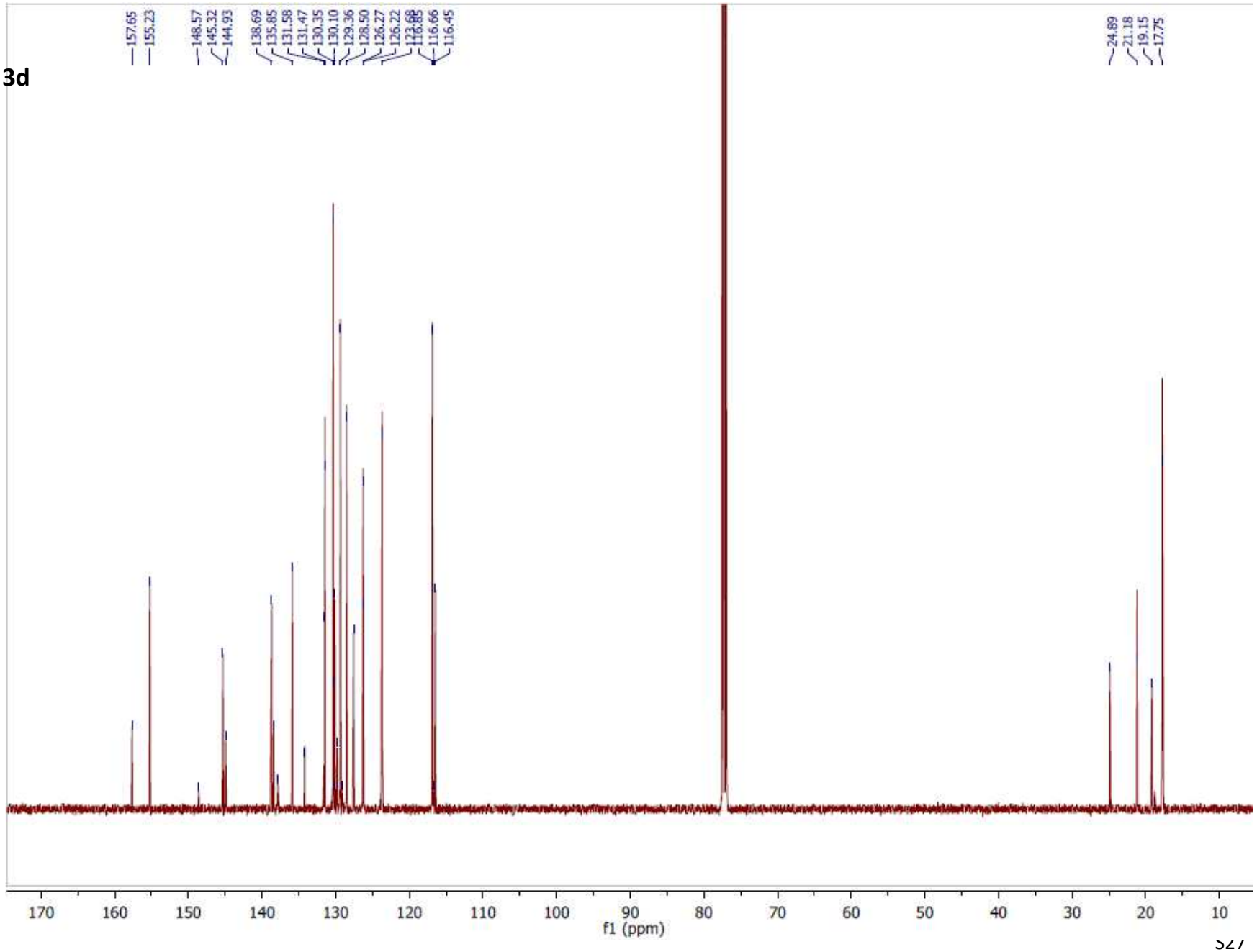
2d


152.67
145.23
140.74
138.29
134.69
130.29
129.79
129.64
126.67
123.78
116.98
21.61
13.87
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

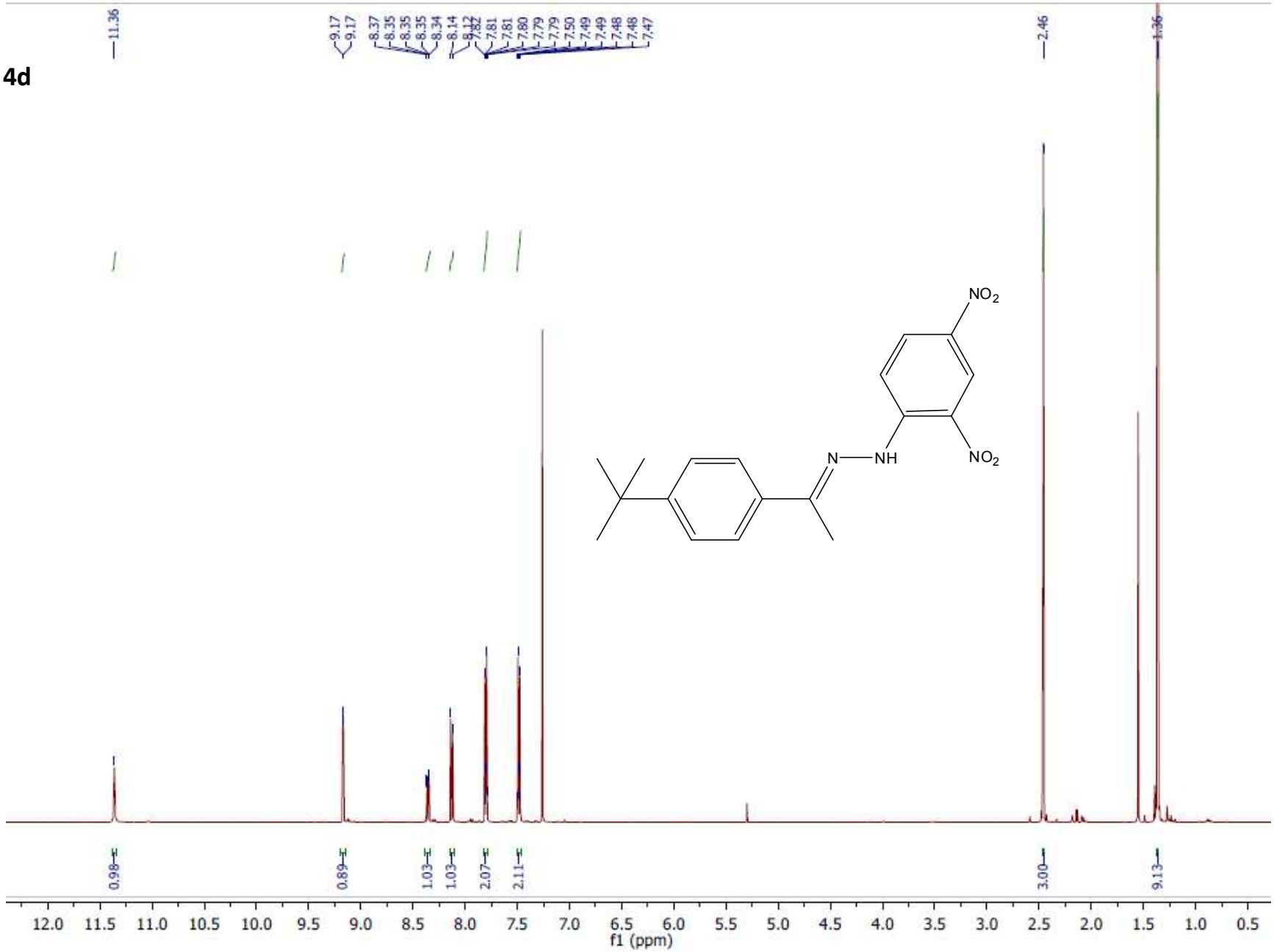
3d


11.29
9.17
9.16
9.04
9.03
8.33
8.31
8.30
8.30
8.30
8.02
8.00
7.44
7.42
7.42
7.41
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.33
7.32
7.32
7.30
7.28
7.28
2.48
2.46
NO2
NO2
N
NH
0.96
0.86
0.29
0.46
0.62
1.02
4.01
3.04
3.00
12.0 11.5 11.0 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)

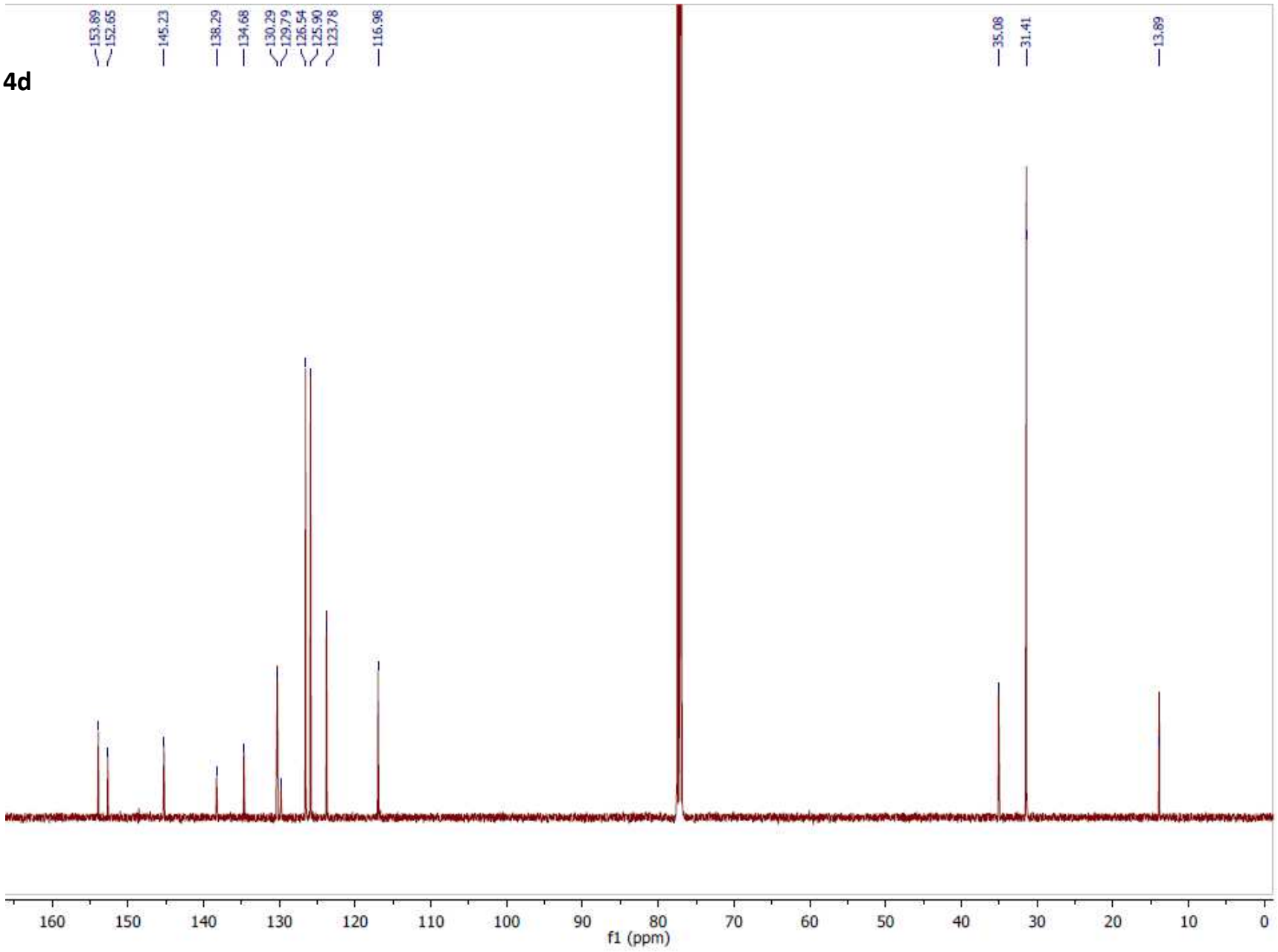
3d


157.65
155.23
148.57
145.32
144.93
138.69
135.85
131.58
131.47
130.35
130.10
129.36
128.50
126.27
126.22
116.66
116.45
24.89
21.18
19.15
17.75
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

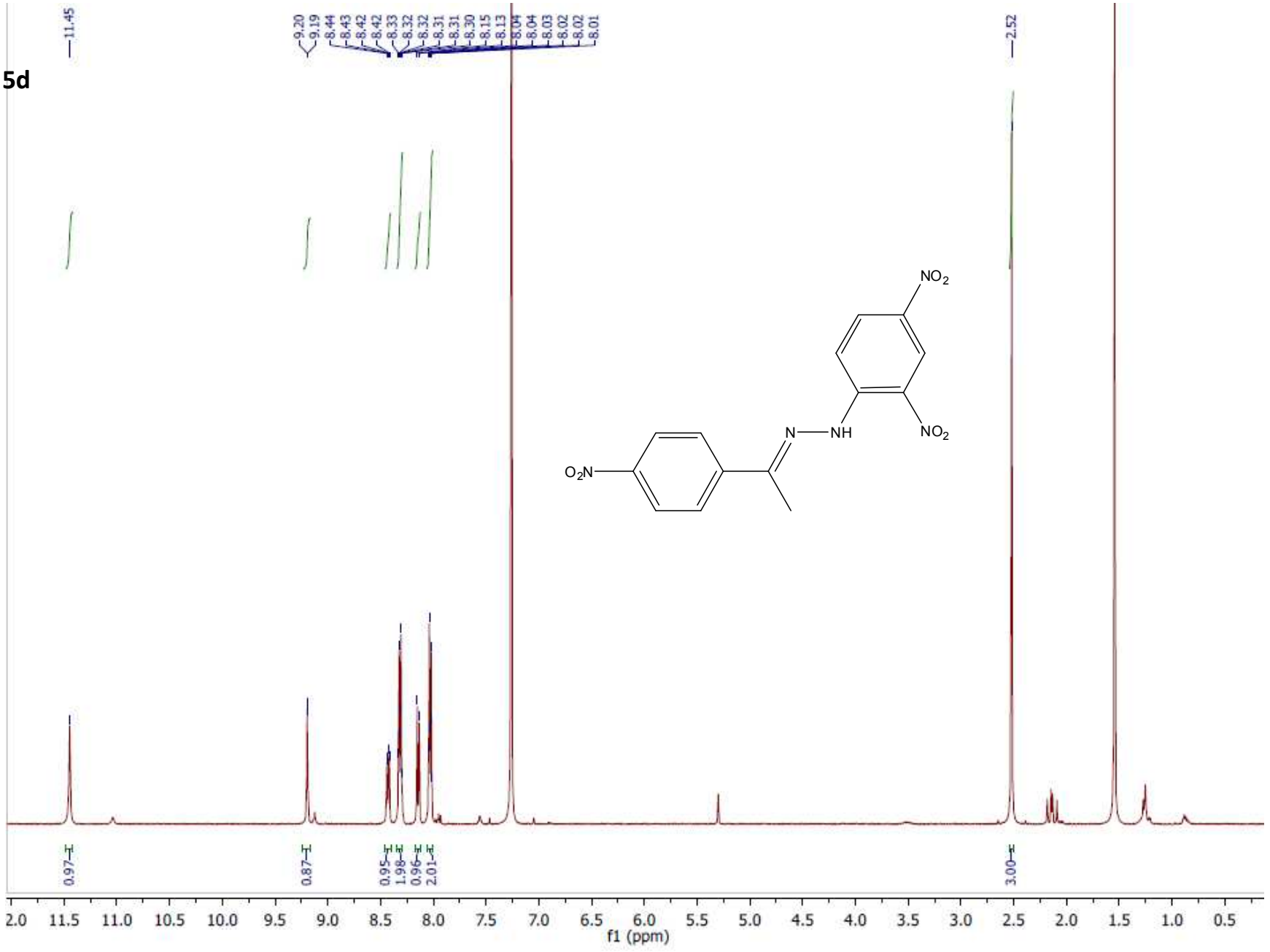
4d


11.36
9.17
9.17
8.37
8.35
8.35
8.35
8.34
8.14
8.12
7.82
7.81
7.81
7.80
7.79
7.79
7.50
7.49
7.49
7.48
7.48
7.47
2.46
1.36
NO2
NO2
N
NH
0.98
0.89
1.03
1.03
2.07
2.11
3.00
9.13
12.0 11.5 11.0 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)

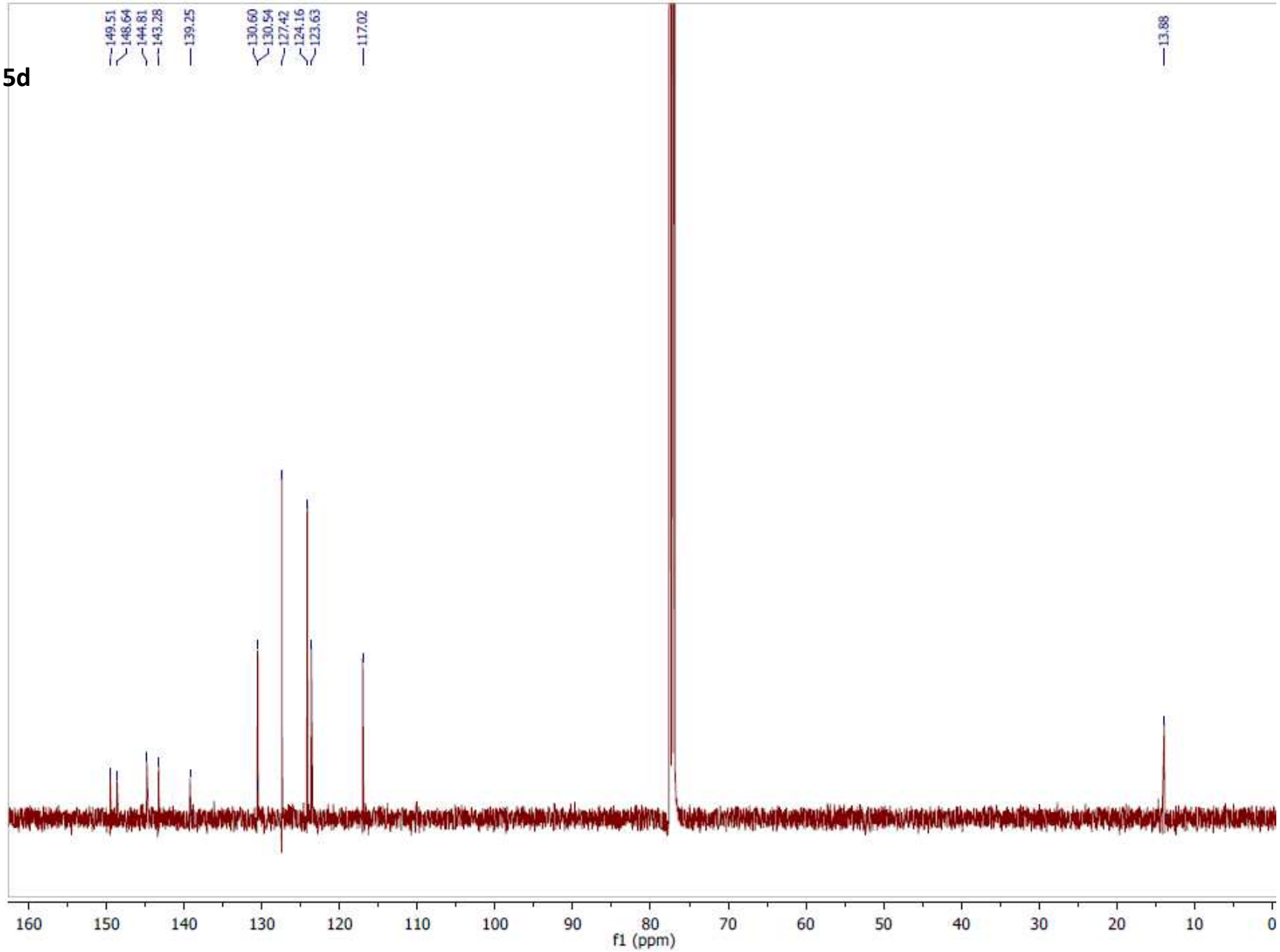
4d


153.89
152.65
145.23
138.29
134.68
130.29
129.79
126.54
125.90
123.78
116.98
35.08
31.41
13.89
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

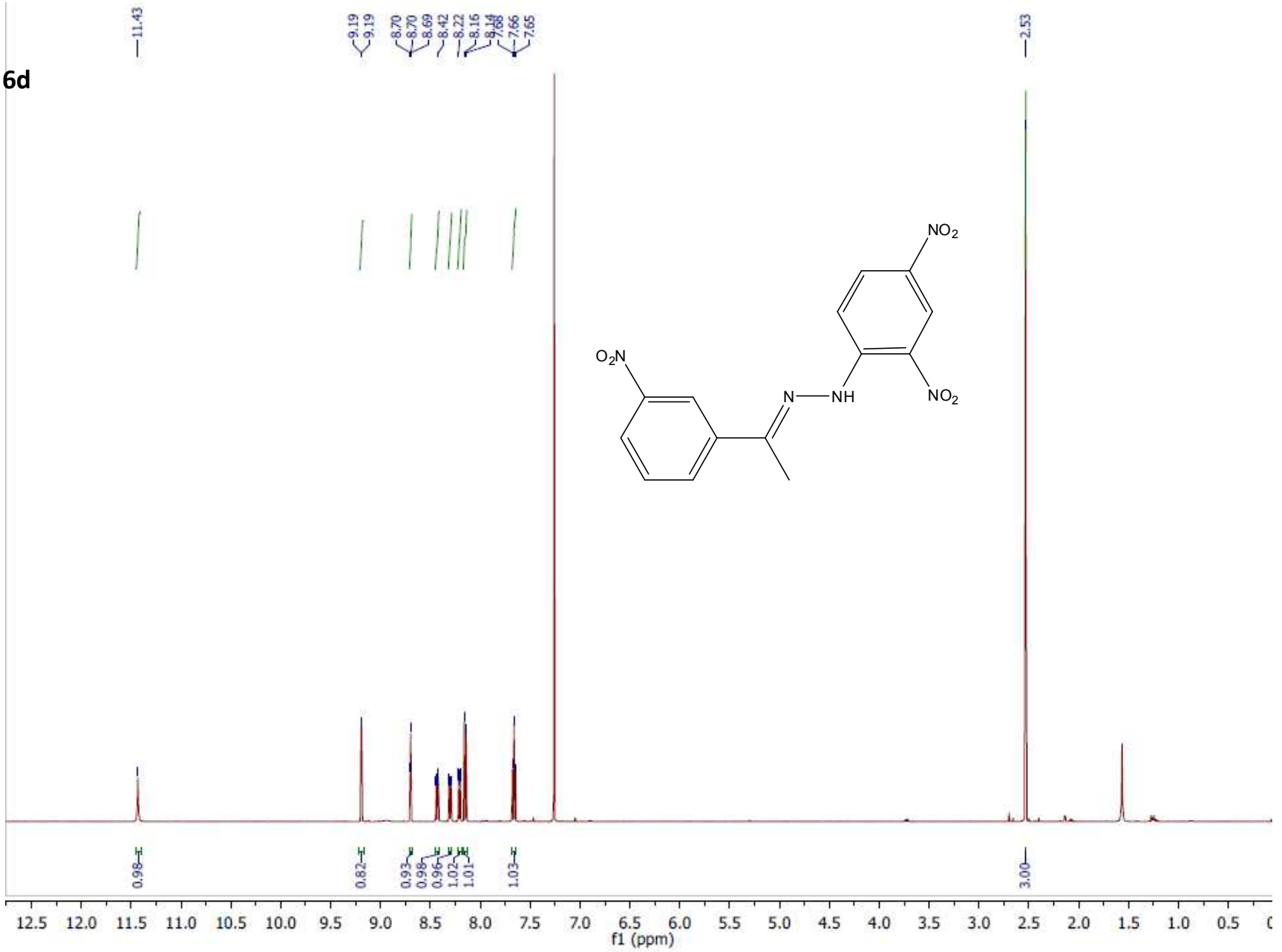
5d


11.45
9.20
9.19
8.44
8.43
8.42
8.42
8.33
8.32
8.32
8.31
8.31
8.30
8.15
8.13
8.04
8.04
8.03
8.02
8.02
8.01
2.52
NO2
NO2
N
NH
O2N
0.97
0.87
0.95
1.98
0.96
2.01
3.00
2.0
11.5
11.0
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)

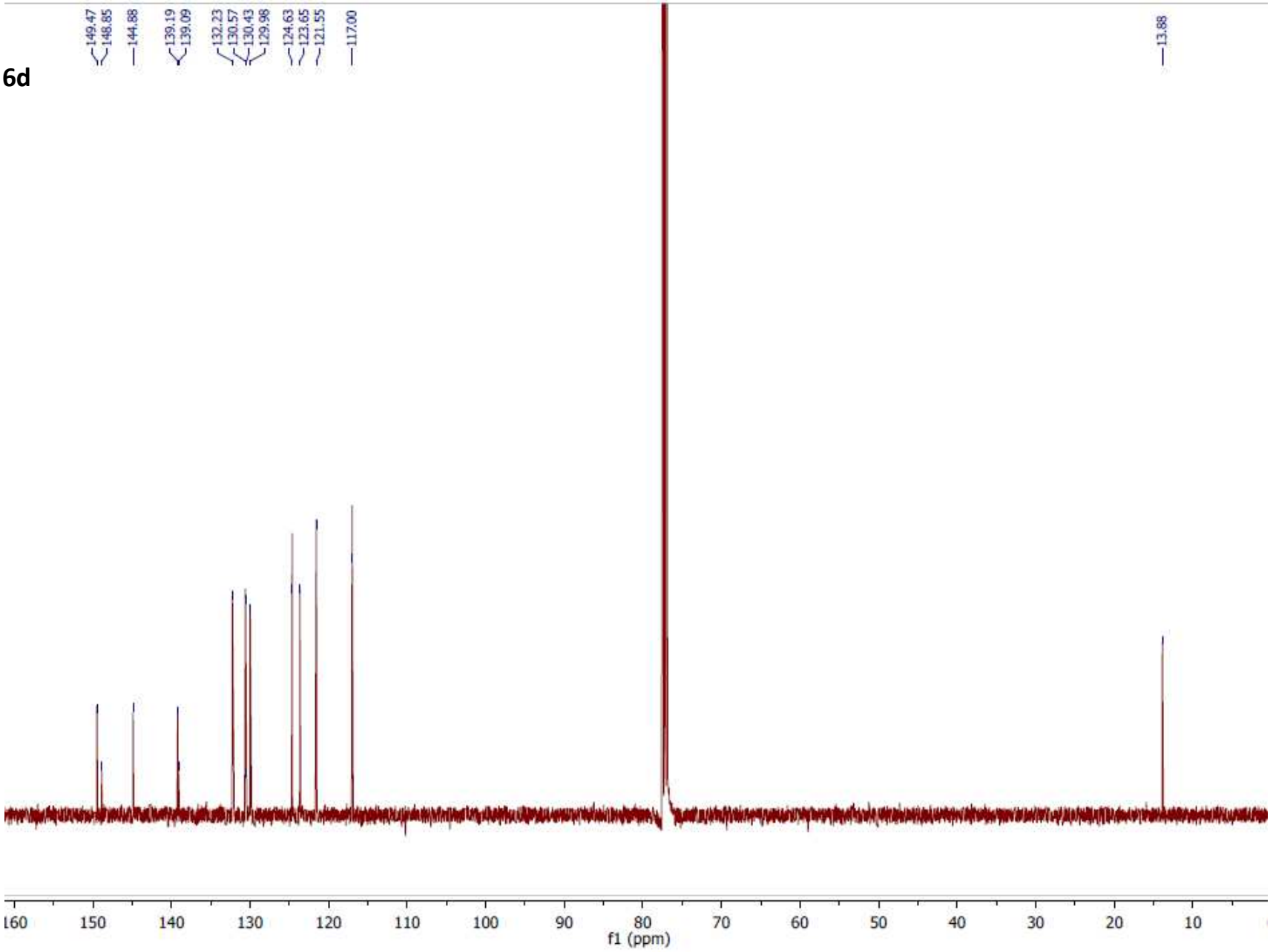
5d


149.51
148.64
144.81
143.28
139.25
130.60
130.54
127.42
124.16
123.63
117.02
13.88
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

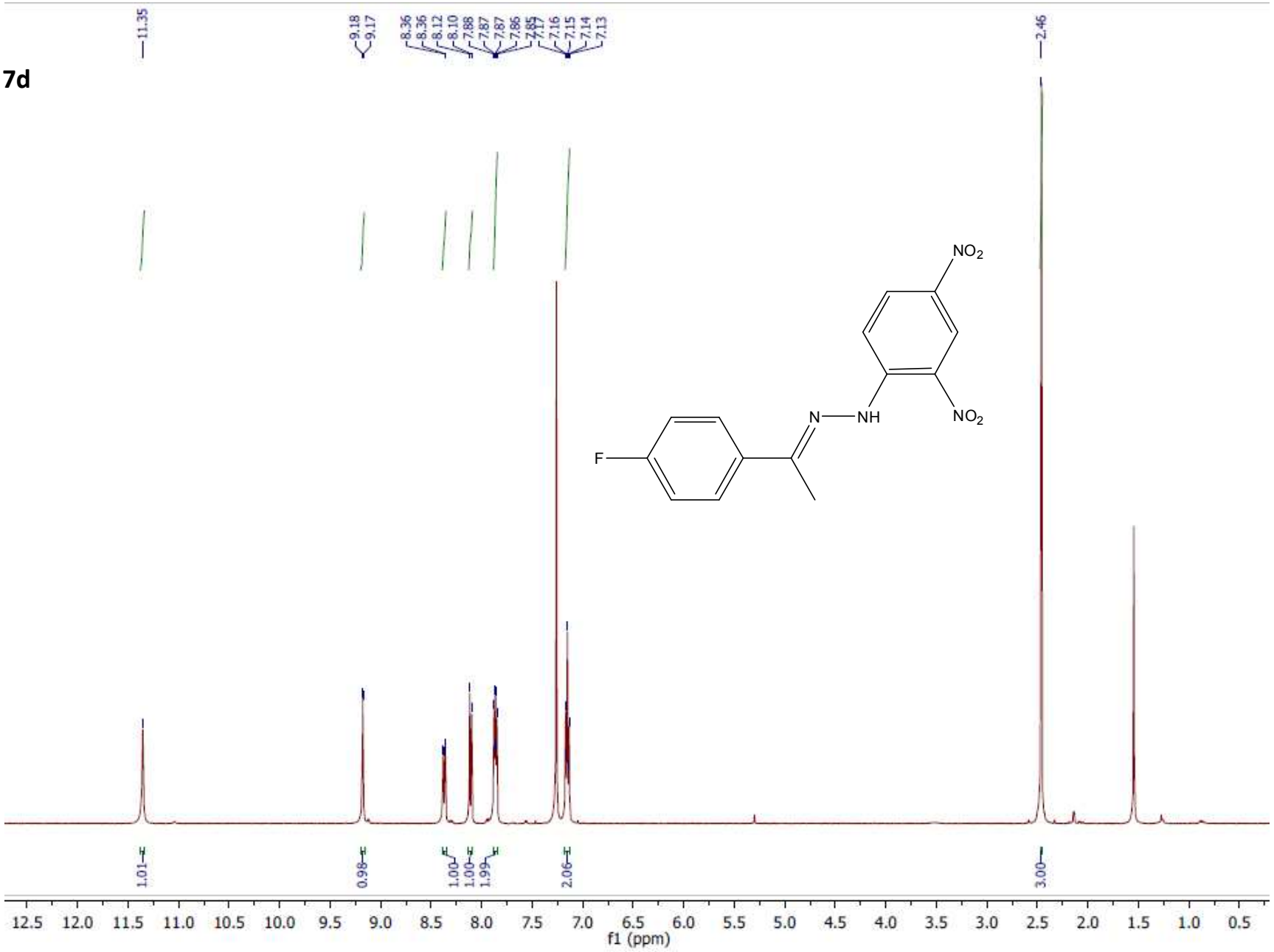
6d


11.43
9.19
9.19
8.70
8.70
8.69
8.42
8.22
8.16
8.14
7.68
7.66
7.65
2.53
NO_2
O_2N
N
NH
NO_2
0.98
0.82
0.93
0.98
0.96
1.02
1.01
1.03
3.00
12.5 12.0 11.5 11.0 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)

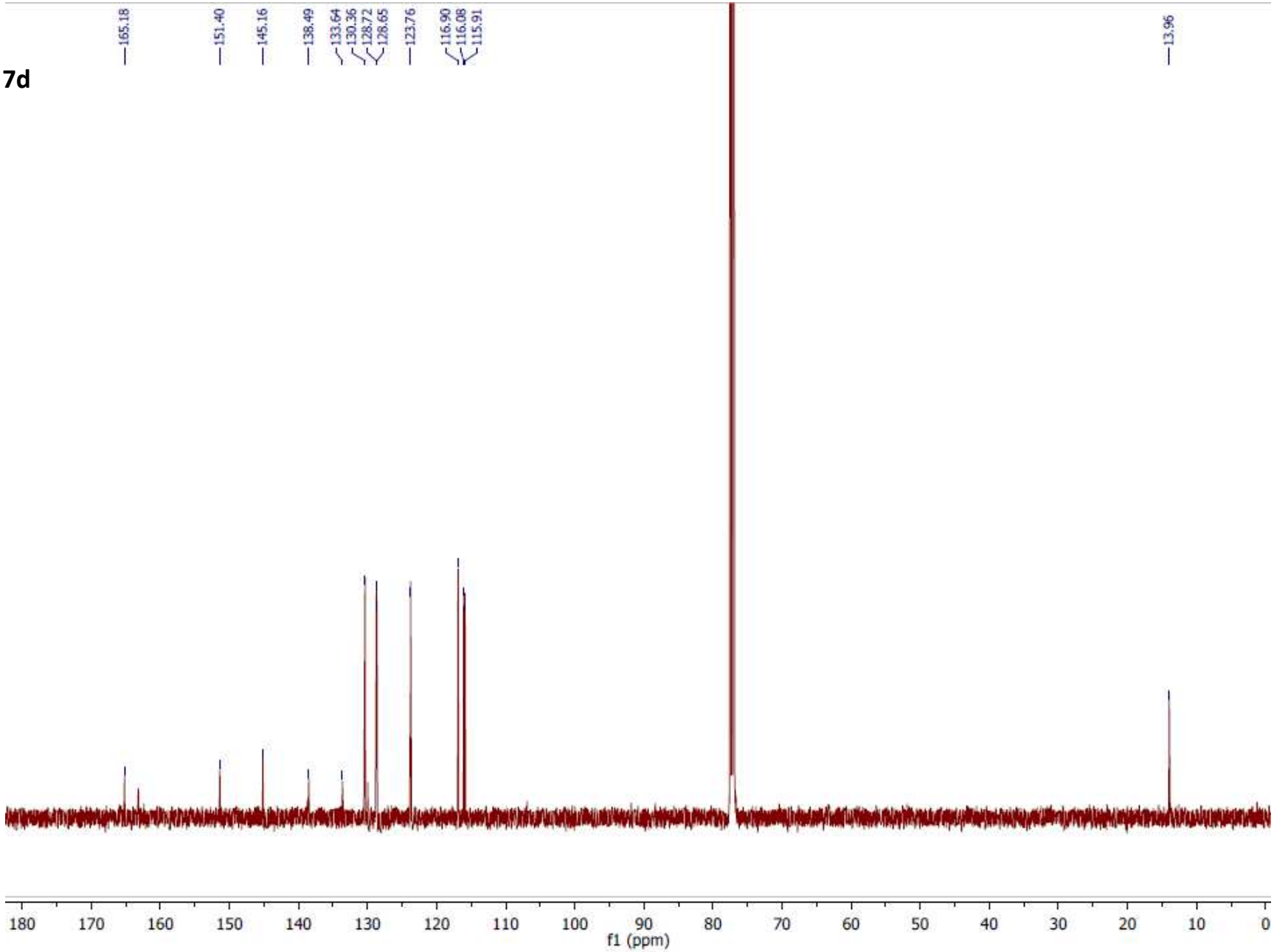
6d


149.47
148.85
144.88
139.19
139.09
132.23
130.57
130.43
129.98
124.63
123.65
121.55
117.00
13.88
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

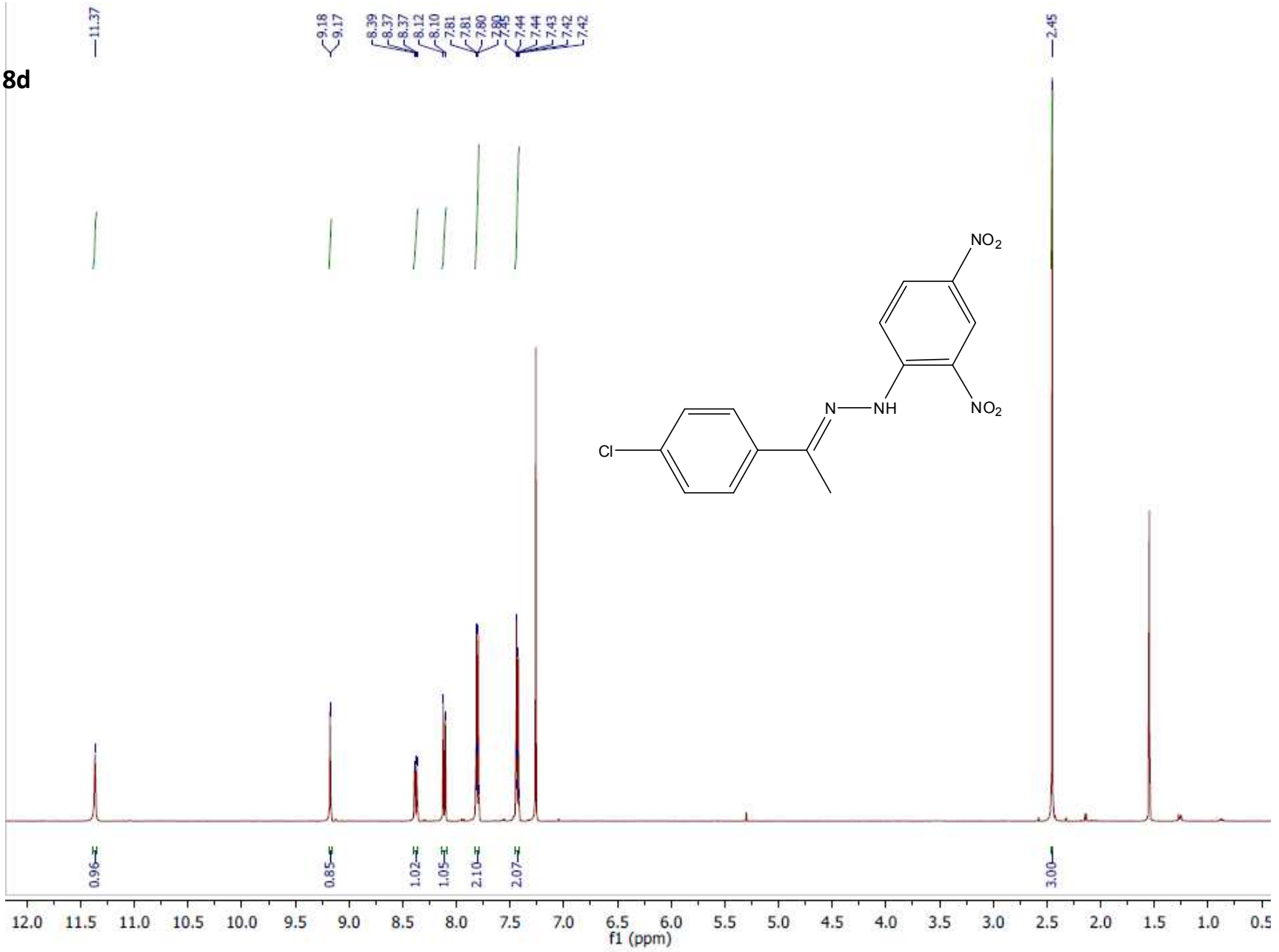
7d


11.35
9.18
9.17
8.36
8.36
8.12
8.10
7.88
7.87
7.87
7.86
7.85
7.17
7.16
7.15
7.14
7.13
2.46
NO2
NO2
N
NH
F
1.01
0.98
1.00
1.00
1.99
2.06
3.00
12.5 12.0 11.5 11.0 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)

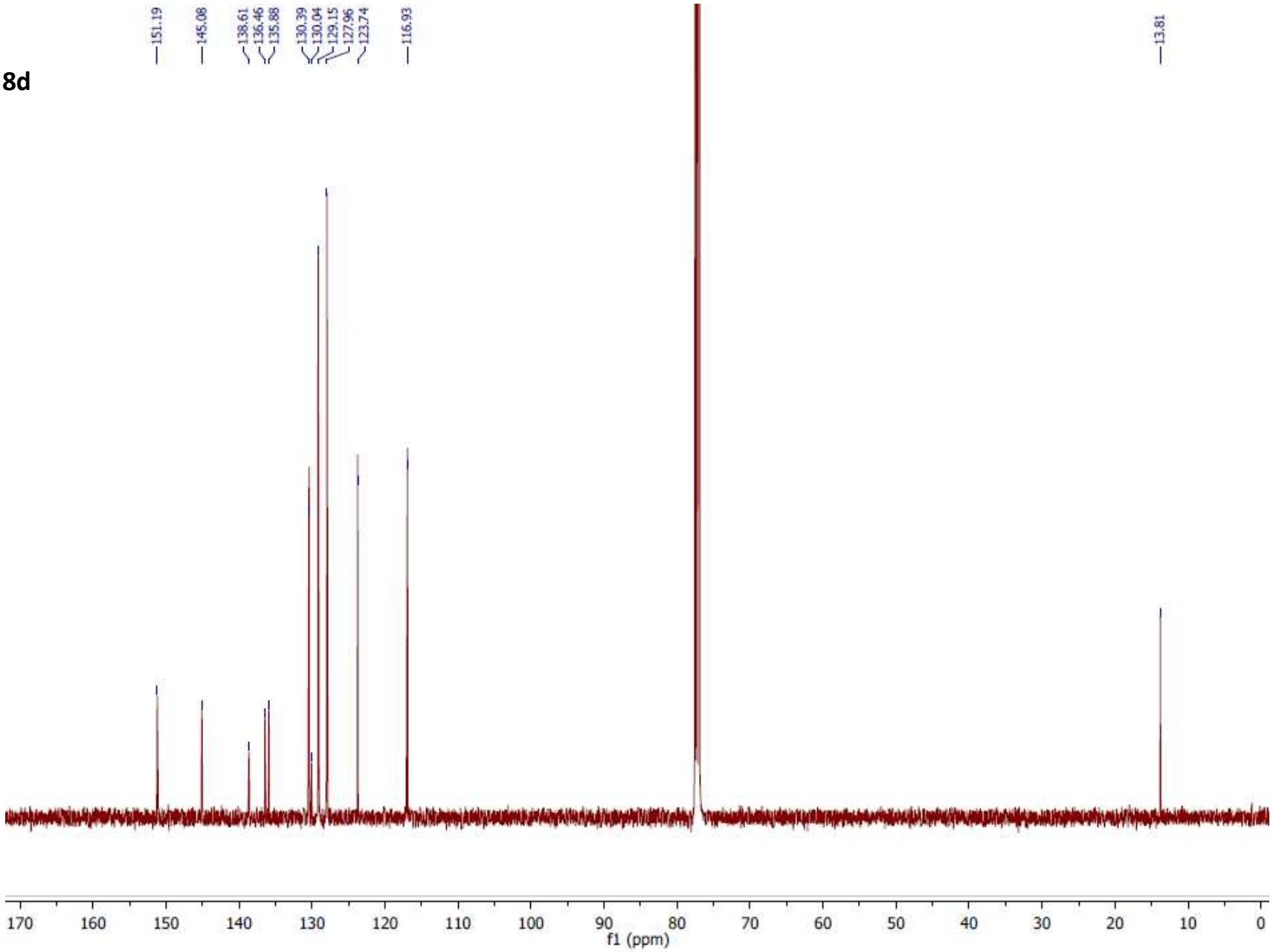
7d


165.18
151.40
145.16
138.49
133.64
130.36
128.72
128.65
123.76
116.90
116.08
115.91
13.96
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

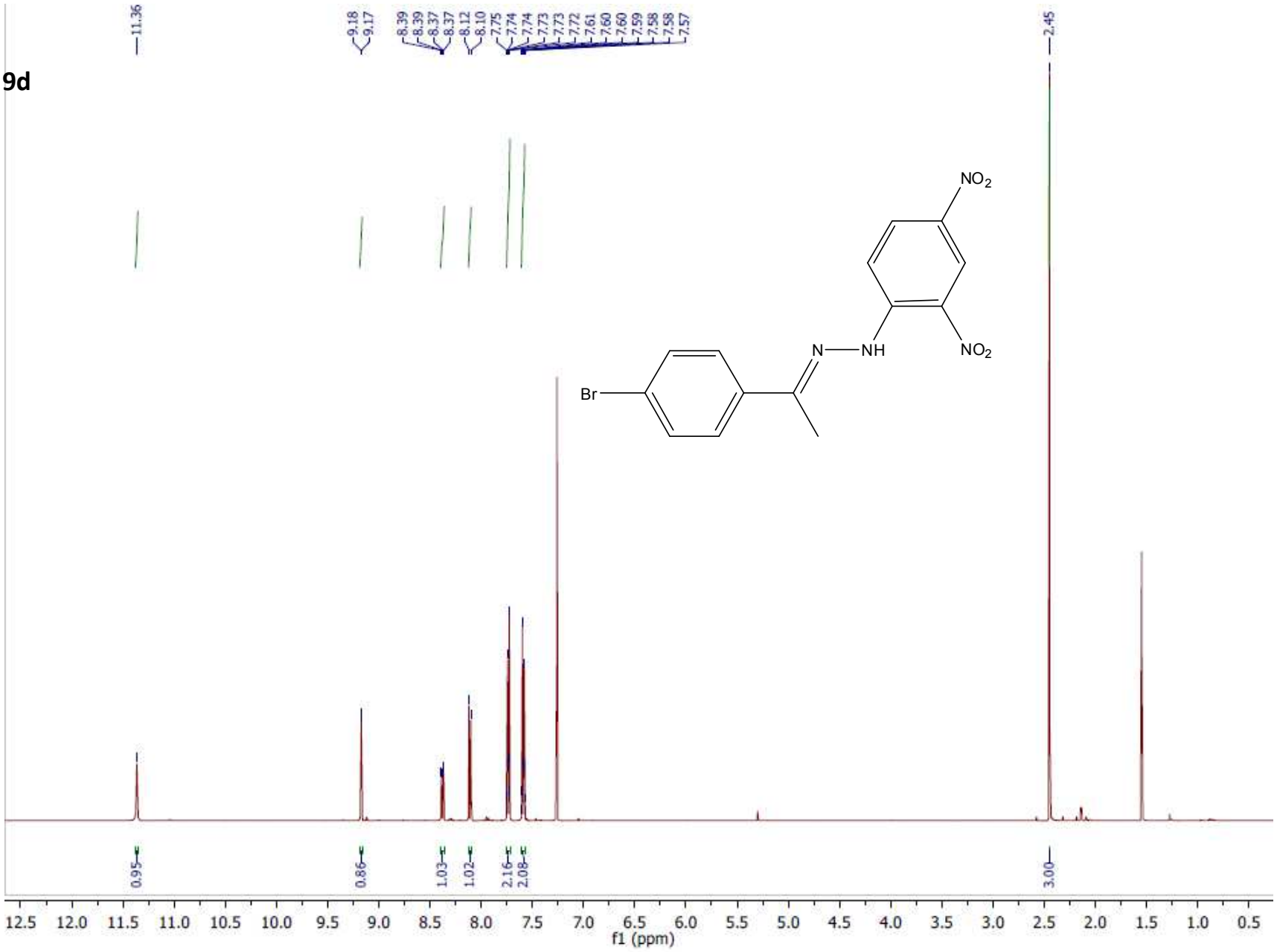
8d


11.37
9.18
9.17
8.39
8.37
8.37
8.12
8.10
7.81
7.81
7.80
7.80
7.45
7.44
7.44
7.43
7.42
7.42
2.45
NO2
NO2
N
NH
Cl
0.96
0.85
1.02
1.05
2.10
2.07
3.00
12.0
11.5
11.0
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)

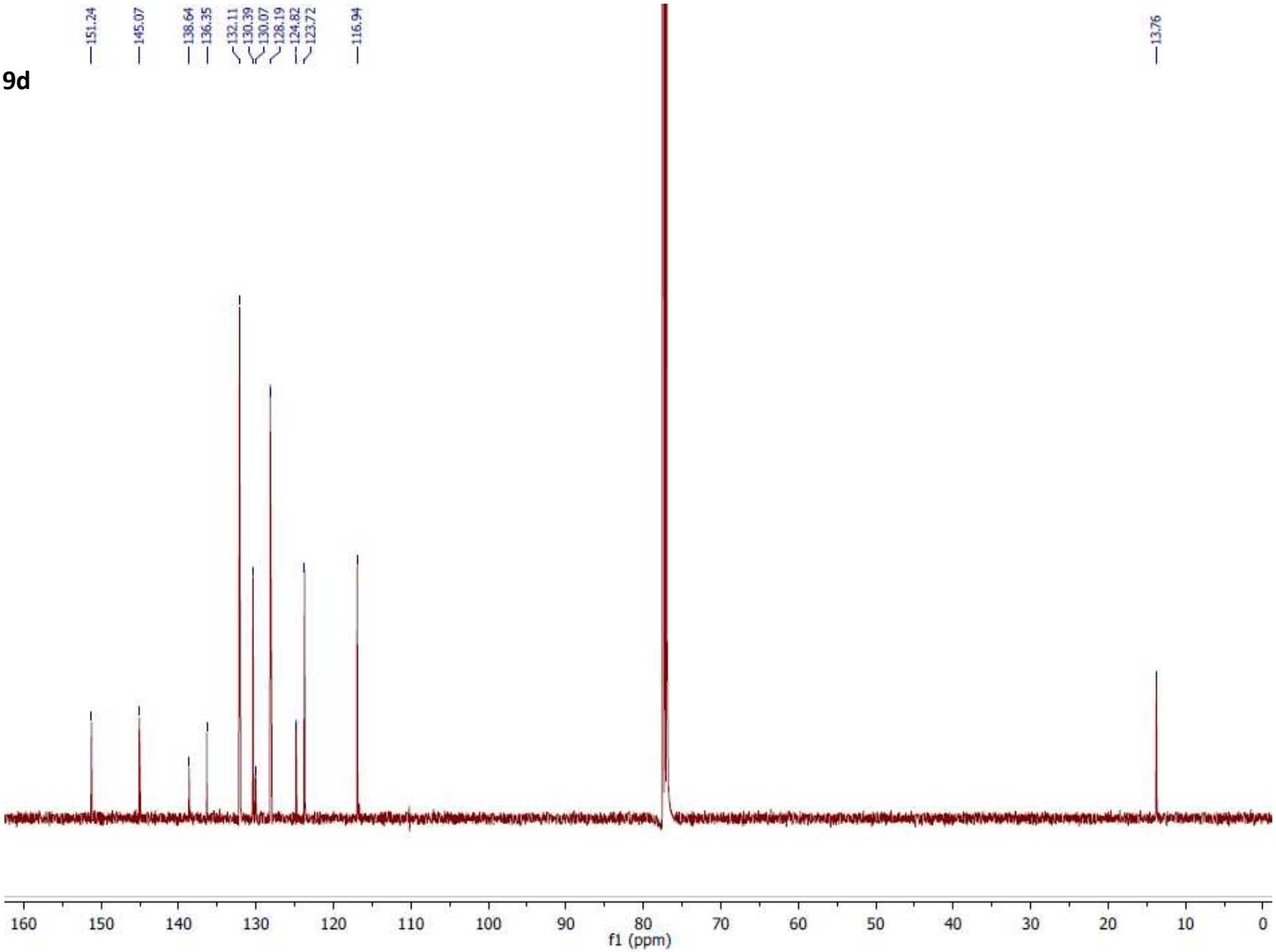
8d


151.19
145.08
138.61
136.46
135.88
130.39
130.04
129.15
127.96
123.74
116.93
13.81
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

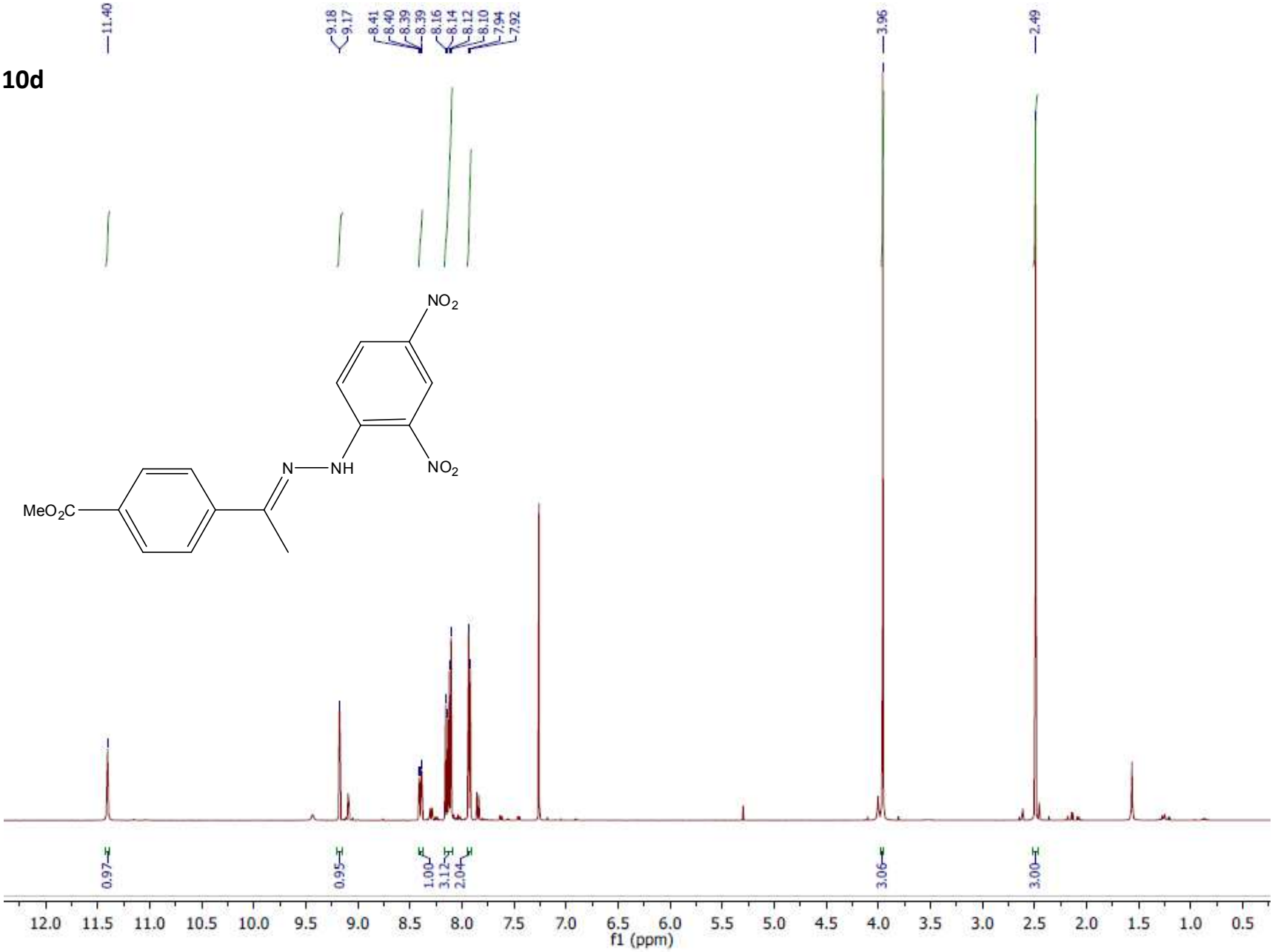
9d


11.36
9.18
9.17
8.39
8.39
8.37
8.37
8.12
8.10
7.75
7.74
7.74
7.73
7.73
7.72
7.61
7.60
7.60
7.59
7.58
7.58
7.57
2.45
NO2
NO2
N
NH
Br
0.95
0.86
1.03
1.02
2.16
2.08
3.00
12.5 12.0 11.5 11.0 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)

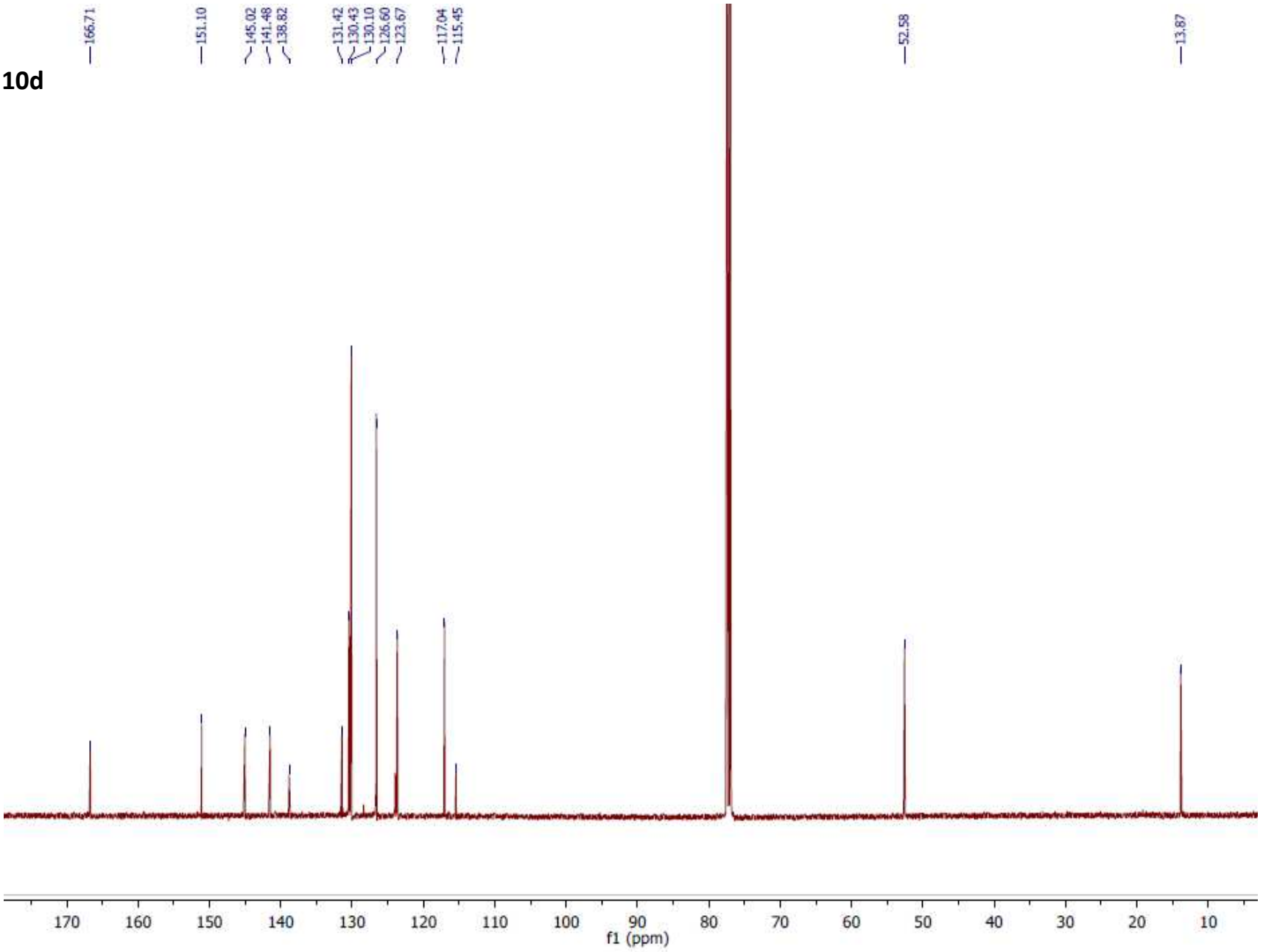
9d


151.24
145.07
138.64
136.35
132.11
130.39
130.07
128.19
124.82
123.72
116.94
13.76
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

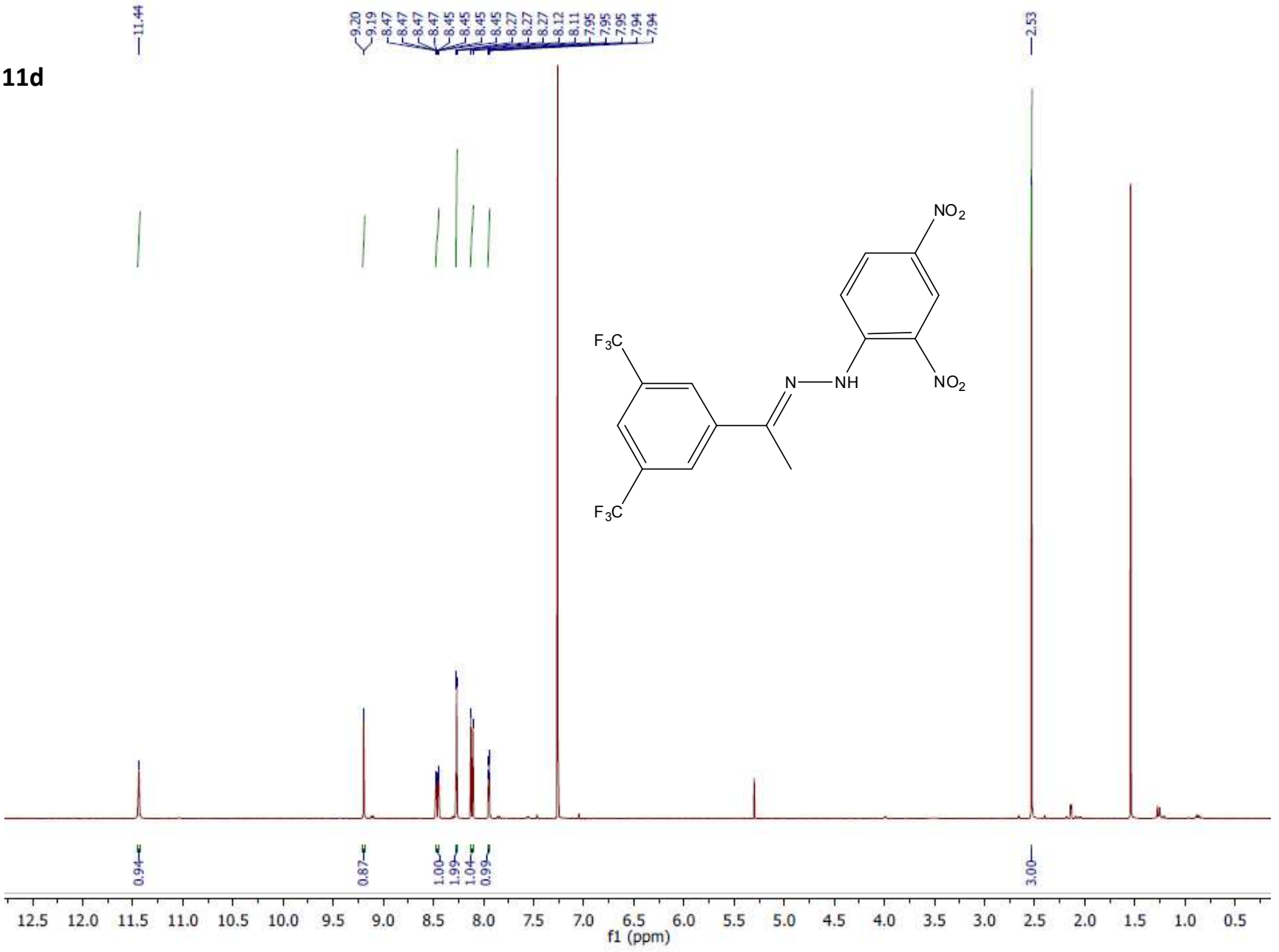
10d


11.40
9.18
9.17
8.41
8.40
8.39
8.39
8.16
8.14
8.12
8.10
7.94
7.92
3.96
2.49
NO2
NO2
N
NH
MeO2C
0.97
0.95
1.00
3.12
2.04
3.06
3.00
12.0 11.5 11.0 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)

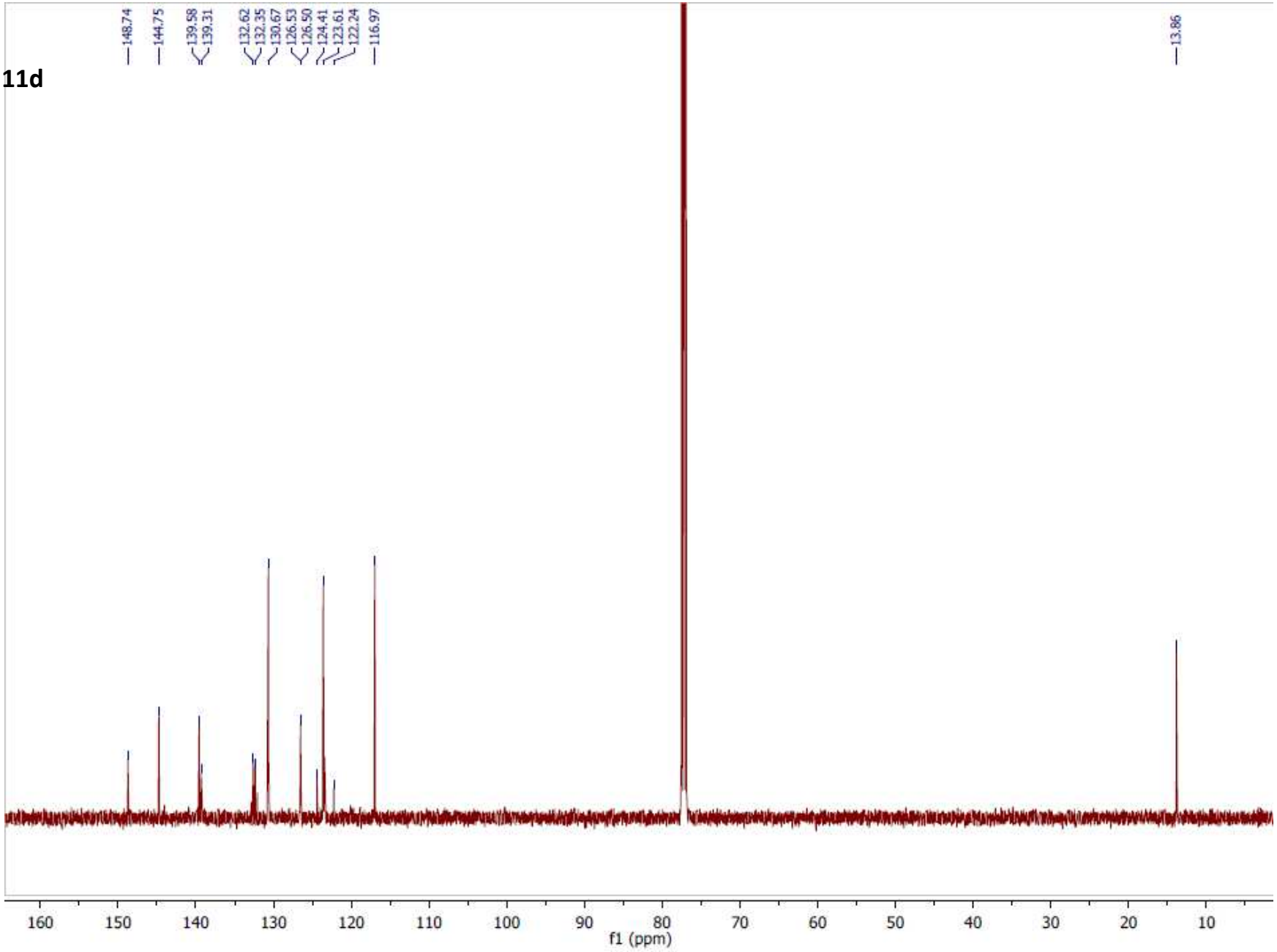
10d


166.71
151.10
145.02
141.48
138.82
131.42
130.43
130.10
126.60
123.67
117.04
115.45
52.58
13.87
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

11d


11.44
9.20
9.19
8.47
8.47
8.47
8.47
8.45
8.45
8.45
8.45
8.27
8.27
8.27
8.12
8.11
7.95
7.95
7.95
7.94
7.94
2.53
NO2
NO2
F3C
F3C
N
NH
0.94
0.87
1.00
1.99
1.04
0.99
3.00
12.5 12.0 11.5 11.0 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)

11d


148.74
144.75
139.58
139.31
132.62
132.35
130.67
126.53
126.50
124.41
123.61
122.24
116.97
13.86
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)