Supporting Information for

New mechanism, new chromophore: investigating the electrophilic behaviour of styrylindolium dyes

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Contents:

1. General Considerations

Solvents and reagents were purchased from Sigma-Aldrich and used as supplied. Water refers to deionised water. Infrared spectra were recorded as thin films using attenuated total reflectance with a Nicolet iS5 FTIR spectrometer. Mass spectra were recorded on a QToF 6520 mass spectrometer (Agilent Technologies, Palo Alto, USA). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively, using a Bruker Avance III HD400 spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane, the residual solvent peak being used for referencing purposes. Coupling constants are quoted to the nearest 0.1 Hz with peak multiplicities for single resonances being labelled as: s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet. UV-visible absorbance spectra were recorded using a Jenway 7315 spectrophotometer, scanning from 200–700 nm. Spectra were recorded in 3 mL quartz cuvettes of 1 cm path length. Fluorescence spectra were recorded using a BMG CLARIOstar plate reader in fluorescence intensity mode, using Greiner 96 well UV-transparent plates. Spectroscopic data for novel compounds are provided here; all other data are available in the supplementary information.

2. Synthesis of styrylindolium iodides 7a-g

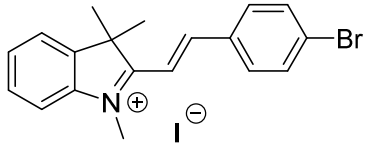
Styrylindolium iodides **7a**-**g** were prepared according to the methods of Metsov, Dudev and Koleva.[1] Iodides **7a**, **b** and **f** have previously been reported [34], whilst iodide **7e** has been reported[2] but lacks modern characterisation data hence such data are provided here.

General procedure:

A stirred solution of 1,2,3,3-tetramethylindolium iodide (**6**) (100 mg, 0.332 mmol) and the appropriate benzaldehyde derivative (0.398 mmol) in acetic acid (2 mL) was heated to reflux for 18 h. Upon cooling, the reaction mixture was poured into diethyl ether (10 mL) and the resulting precipitate was collected by vacuum filtration, washing with diethyl ether, to give the respective styrylindolium iodide.

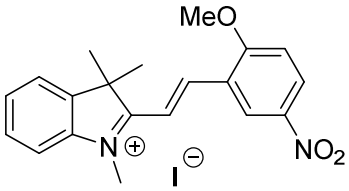
Yields: **7a**, 37%; **7b**, 80%; **7c**, 55%; **7d**, 30%; **7e**, 51%; **7f**, 83%; **7g**, 43%.

*Data for novel styrylindolium iodides **7c-e** and **g***

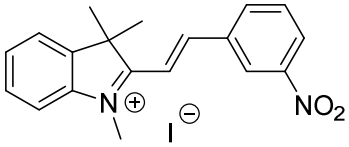


(*E*)-1,3,3-trimethyl-2-(4-bromostyryl)-3*H*-indol-1-ium iodide 7c

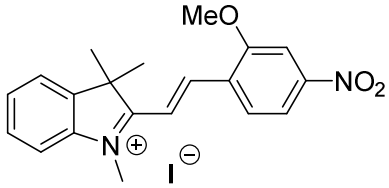
ν_{max} = 2998, 1600, 1528, 1469, 1401, 1319, 1068, 1005, 956, 803, 757 and 463 cm^{-1}; δH (400 MHz; DMSO-d$_6$) 8.40 (1 H, d, *J* 16.5, β-H), 8.19 (2 H, d, *J* 8.4, 2'- and 6'-H), 7.96-7.88 (2 H, m, 5- and 6-H), 7.83 (2 H, d, *J* 8.4, 3'- and 5'-H), 7.75 (1 H, d, *J* 16.5, α-H), 7.68-7.63 (2 H, m, 4- and 7-H), 4.10 (3 H, s, NMe) and 1.76 (6 H, s, CMe$_2$); δC (100 MHz; DMSO-d$_6$) 182.3 (C=N), 151.8, 144.2, 142.3, 134.2, 132.8, 132.5, 130.1, 129.5, 127.5, 123.4, 115.9, 114.4, 52.8 (*C*Me$_2$), 35.2 (NMe) and 25.6 (C*Me$_2$*); HRMS-ES (*m/z*): Found: 340.0491 (M$^+$, $C_{19}H_{19}BrN$ requires: 340.0695).



(*E*)-1,3,3-trimethyl-2-(2-methoxy-5-nitrostyryl)-3*H*-indol-1-ium iodide 7d
ν_{max} = 3010, 1739, 1602, 1510, 1455, 1367, 1337, 1256, 1216, 1065, 1009, 853, 746 and 540 cm^{-1}; δH (400 MHz; DMSO-d_6) 9.11 (1 H, s, 6'-H), 8.48 (1 H, d, *J* 9.0, 4'-H), 8.42 (1 H, d, *J* 16.9, β-H), 8.05-7.87 (3 H, m, α-, 5- and 6-H), 7.74-7.63 (2 H, m, 4- and 7-H), 7.48 (1 H, d, *J* 9.0, 3'-H), 4.20 (3 H, s, OMe), 4.12 (3 H, s, NMe) and 1.76 (6 H, s, CMe_2); δC (100 MHz; DMSO-d_6) 182.5 (C=N), 164.1, 145.7, 144.1, 142.3, 141.7, 130.3, 129.9, 129.6, 126.8, 123.5, 123.4, 116.6, 116.1, 113.6, 58.1 (OMe), 52.8 (CMe_2), 35.4 (NMe) and 25.8 (CMe_2); HRMS-ES (*m/z*): Found: 337.1479 (M^+, $C_{20}H_{21}N_2O_3$ requires: 337.1547).



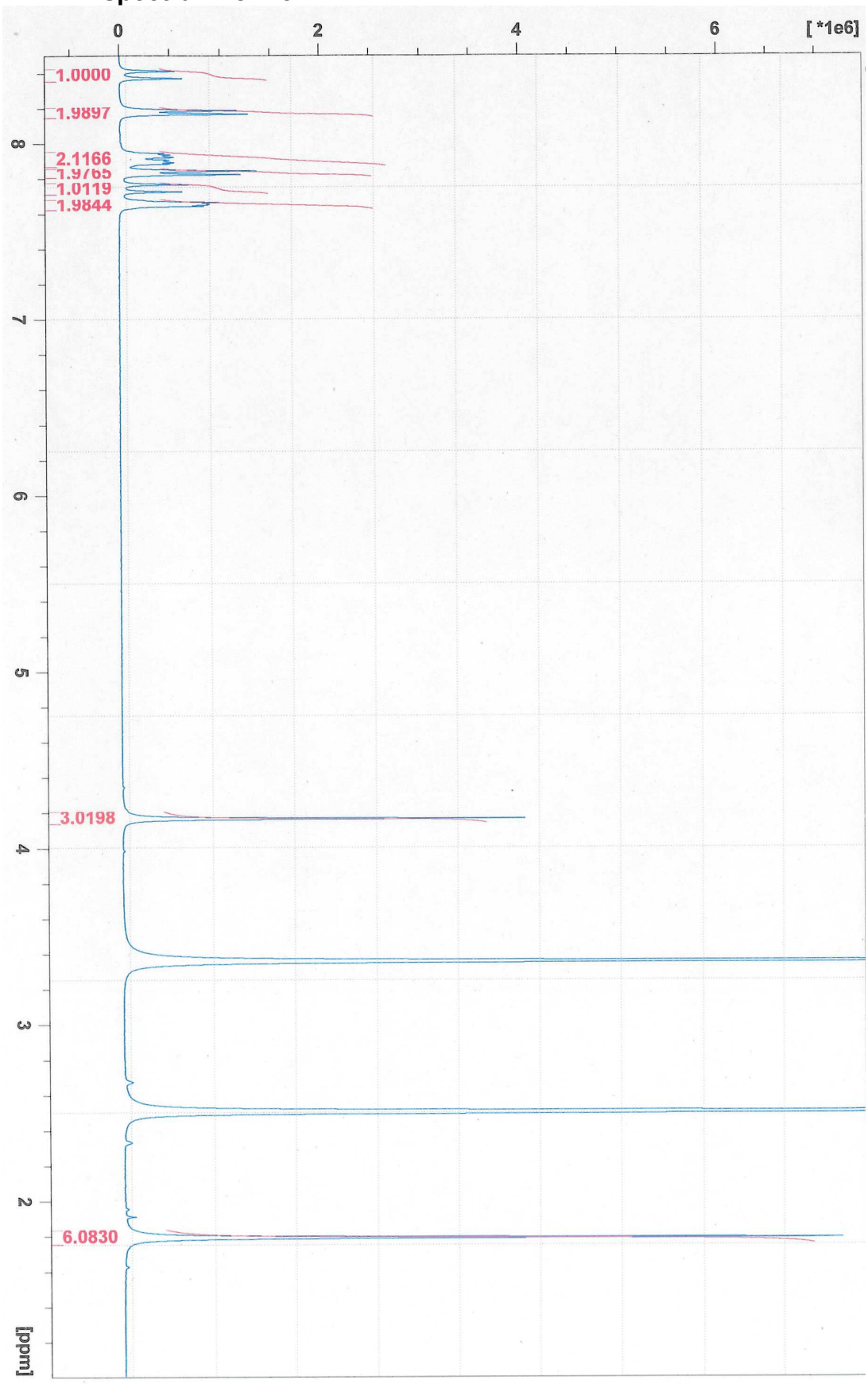
(*E*)-1,3,3-trimethyl-2-(3-nitrostyryl)-3*H*-indol-1-ium iodide 7e
ν_{max} = 3015, 1739, 1606, 1524, 1458, 1350, 1215, 1097, 972, 755 and 507 cm^{-1}; δH (400 MHz; DMSO-d_6) 9.12 (1 H, s, 2'-H), 8.75 (1 H, d, *J* 7.7, 4'-H), 8.55 (1 H, d, *J* 16.5, β-H), 8.39 (1 H, d, *J* 7.7, 6'-H), 8.05-7.80 (4 H, m, α-, 5'-, 5- and 6-H), 7.74-7.63 (2 H, m, 4- and 7-H), 4.23 (3 H, s, NMe) and 1.81 (6 H, s, CMe_2); δC (100 MHz; DMSO-d_6) 182.4 (C=N), 150.2, 149.0, 144.4, 142.2, 136.5, 135.7, 131.1, 130.4, 129.6, 127.2, 125.7, 123.4, 116.3, 116.1, 53.0 (CMe_2), 35.5 (NMe) and 25.4 (CMe_2); Found: 307.1414 (M^+, $C_{19}H_{19}N_2O_2$ requires: 307.1441).



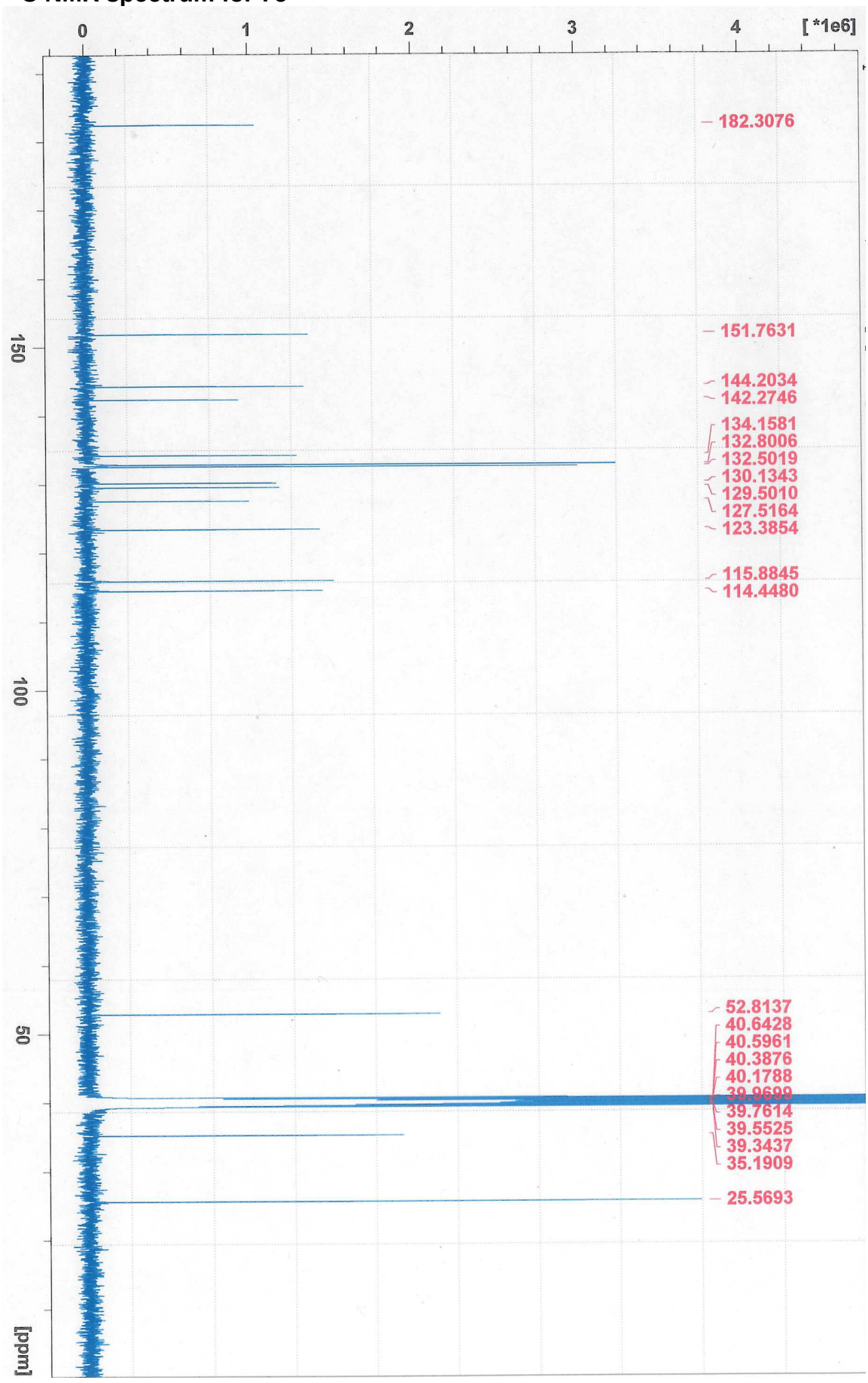
(*E*)-1,3,3-trimethyl-2-(2-methoxy-4-nitrostyryl)-3*H*-indol-1-ium iodide 7g
ν_{max} = 3001, 1739, 1600, 1519, 1457, 1344, 1250, 1089, 1022, 862, 750 and 525 cm^{-1}; δH (400 MHz; DMSO-d_6) 8.46 (1 H, d, *J* 8.5, 5'-H), 8.41 (1 H, d, *J* 16.8, β-H), 8.07-7.95 (3 H, m, 3'-, 5- and 6-H), 7.95-7.85 (2 H, m, a- and 6'-H), 7.74-7.65 (2 H, m, 4- and 7-H), 4.20 (3 H, s, OMe), 4.12 (3 H, s, NMe) and 1.77 (6 H, s, CMe_2); δC (100 MHz; DMSO-d_6) 182.2 (C=N), 159.6, 151.1, 144.5, 144.1, 142.3, 131.4, 130.5, 130.3, 129.6, 129.0, 123.4, 117.5, 116.2, 107.6, 57.7 (OMe), 52.9 (CMe_2), 35.5 (NMe) and 25.8 (CMe_2); Found: 337.1600 (M^+, $C_{20}H_{21}N_2O_3$ requires: 337.1547).

*NMR spectra for novel styrylindolium iodides **7c**-**e** and **g**:*

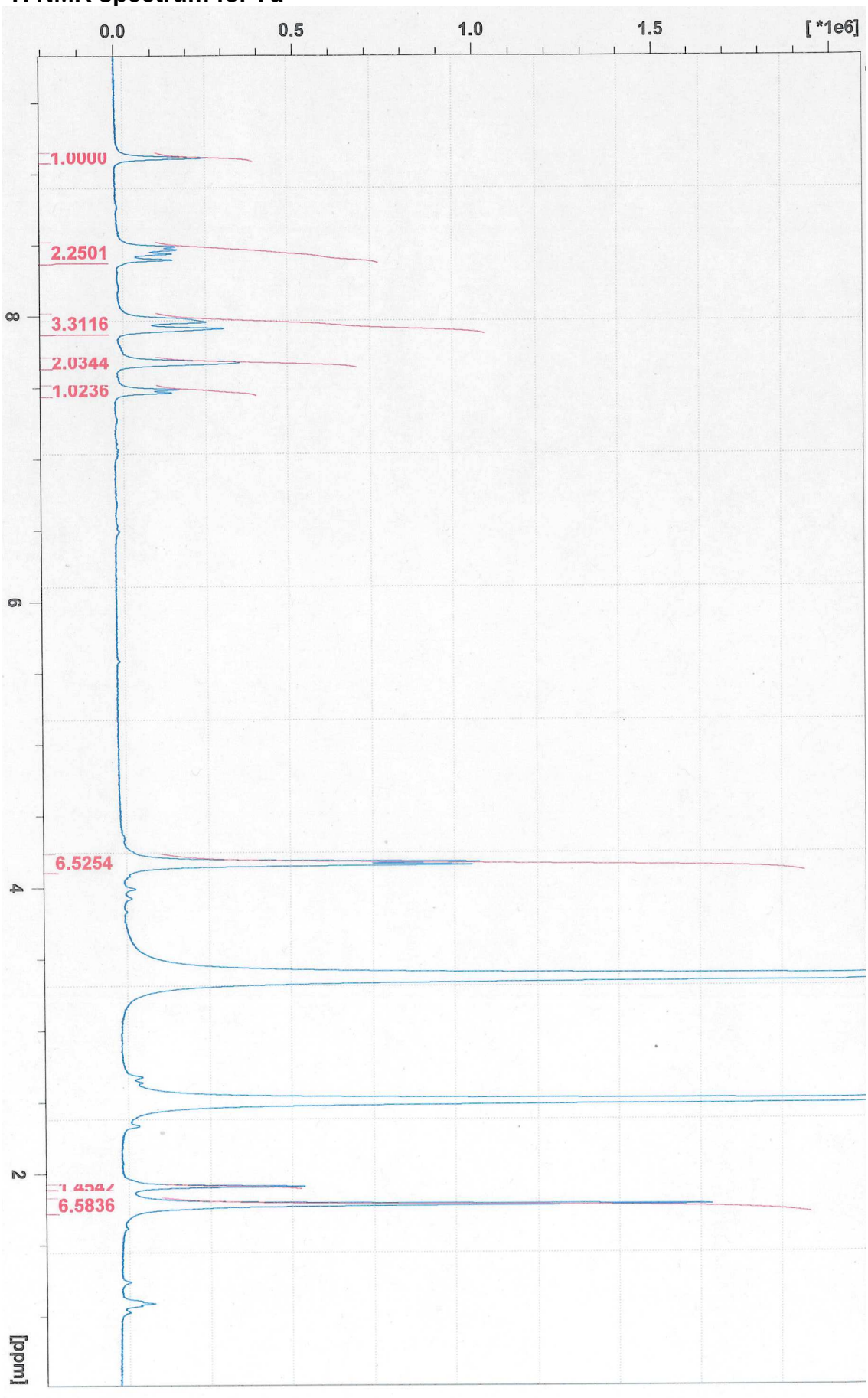
^{1}H NMR spectrum for 7c



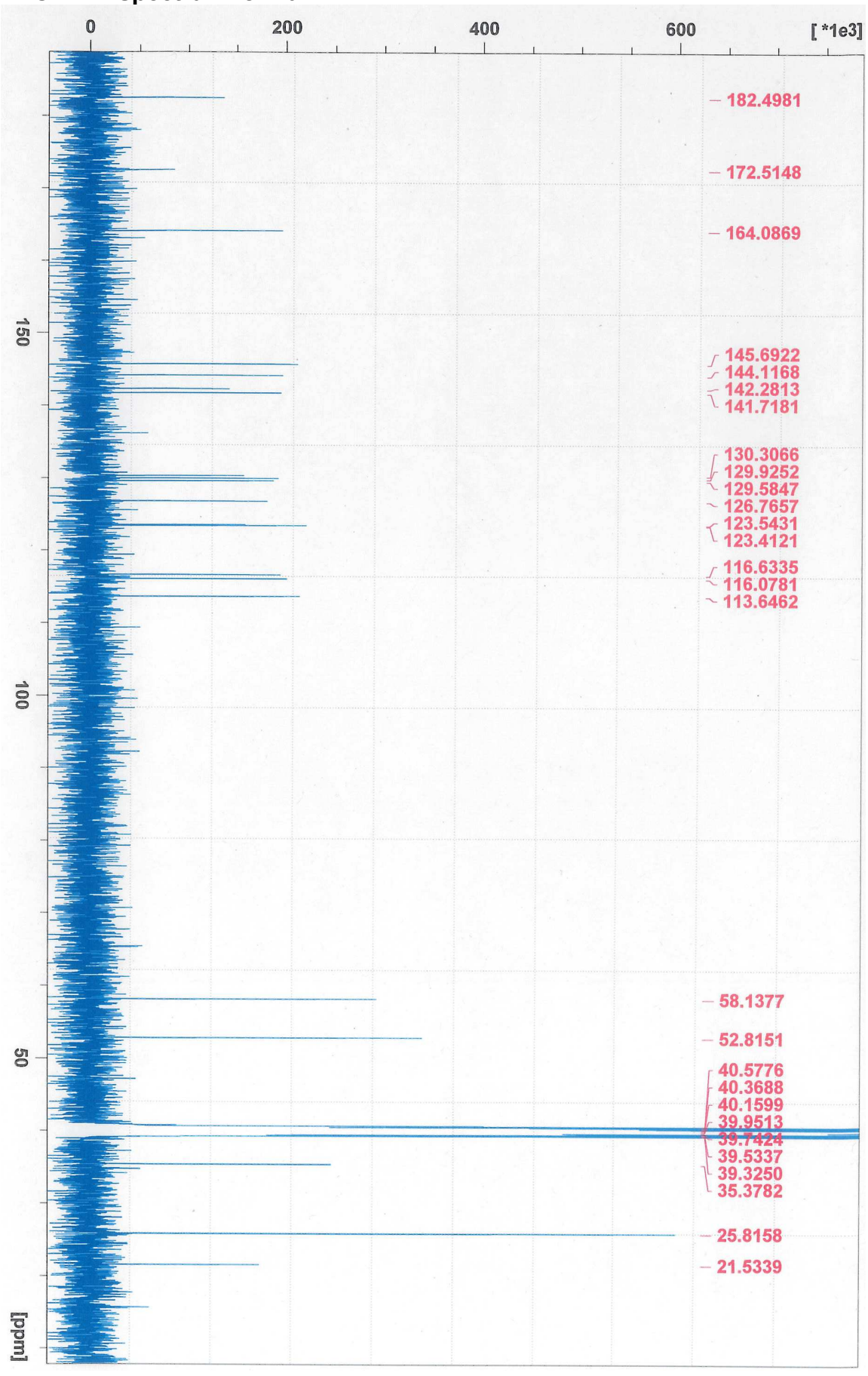
^{13}C NMR spectrum for 7c



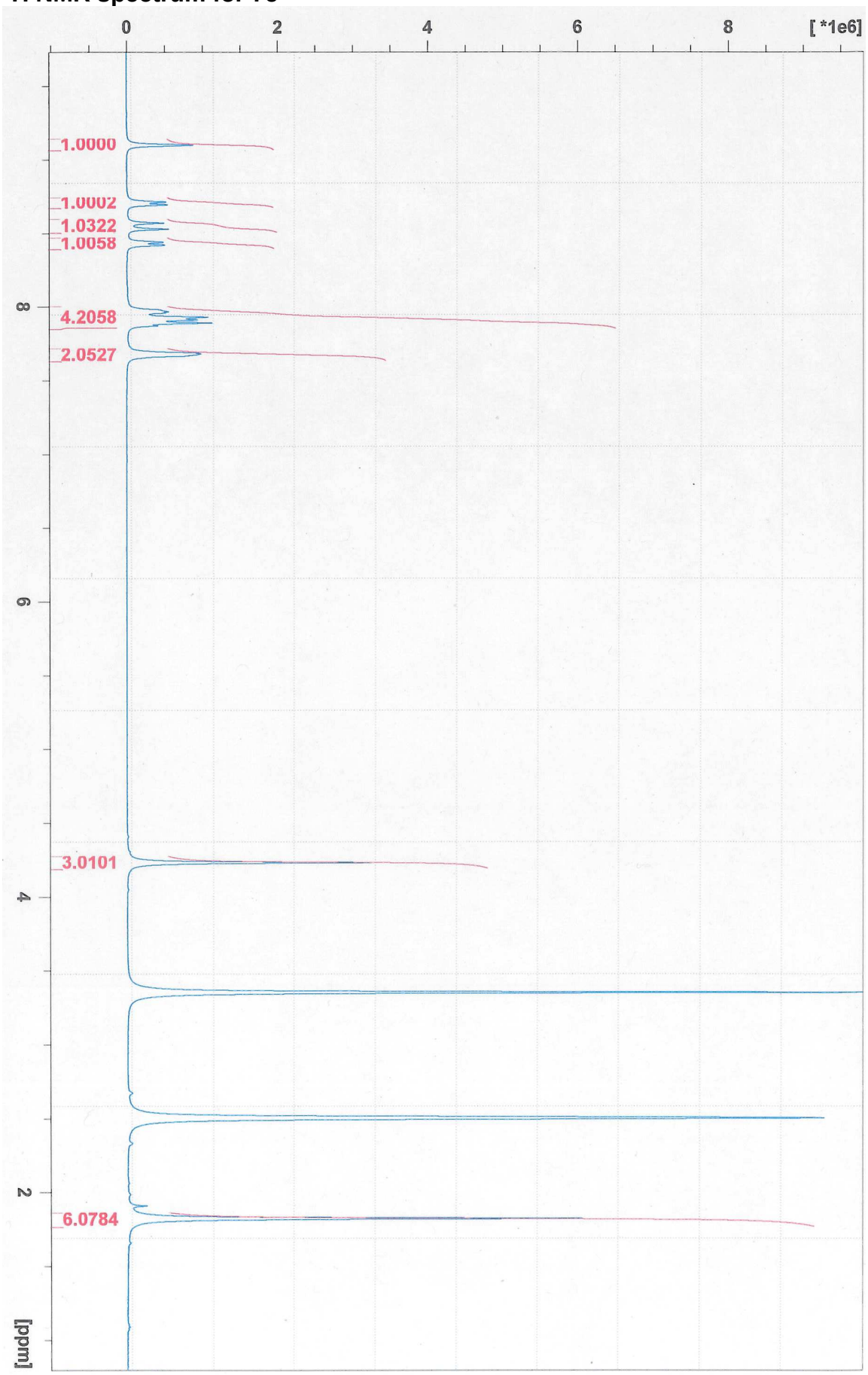
^{1}H NMR spectrum for 7d



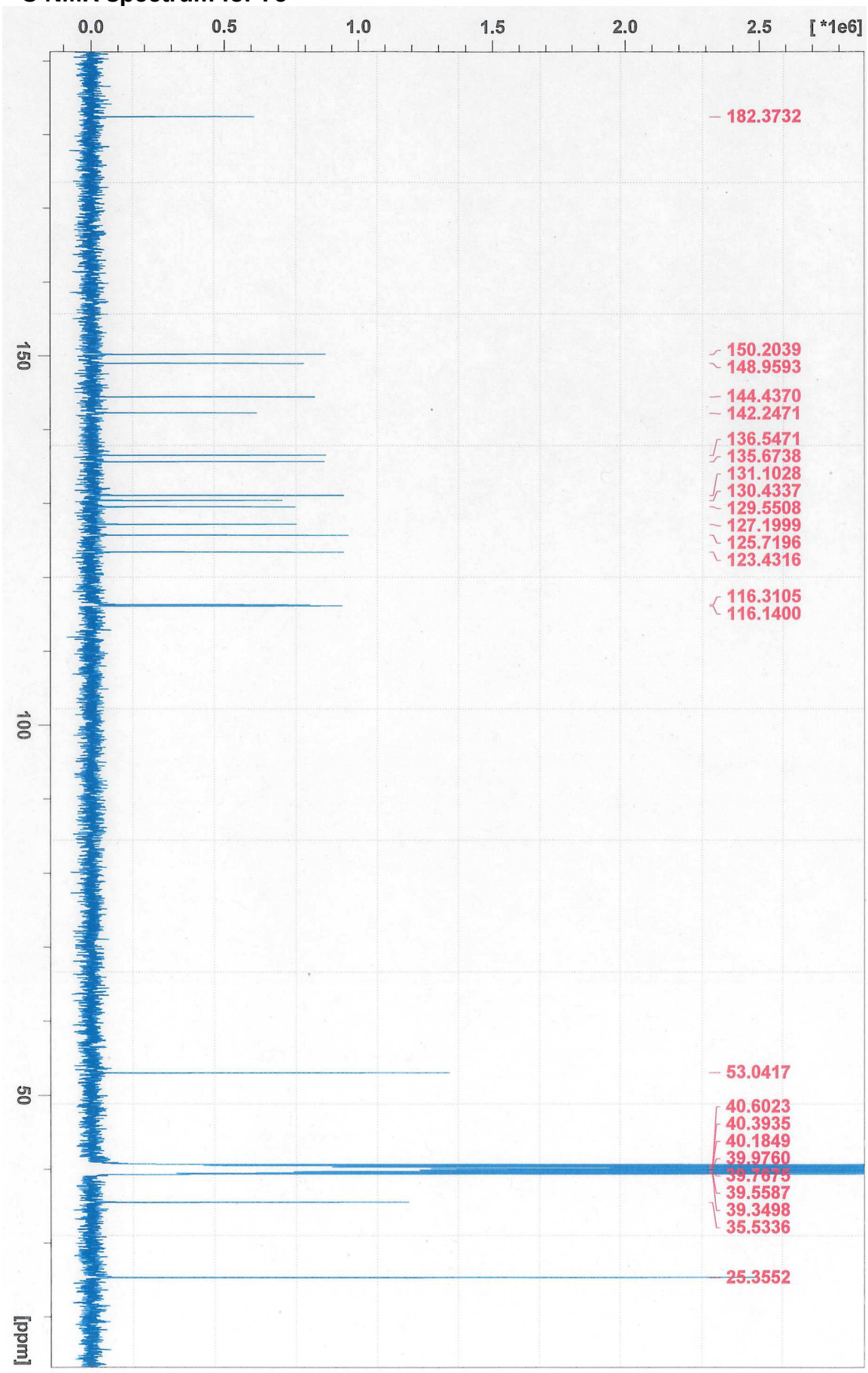
^{13}C NMR spectrum for 7d



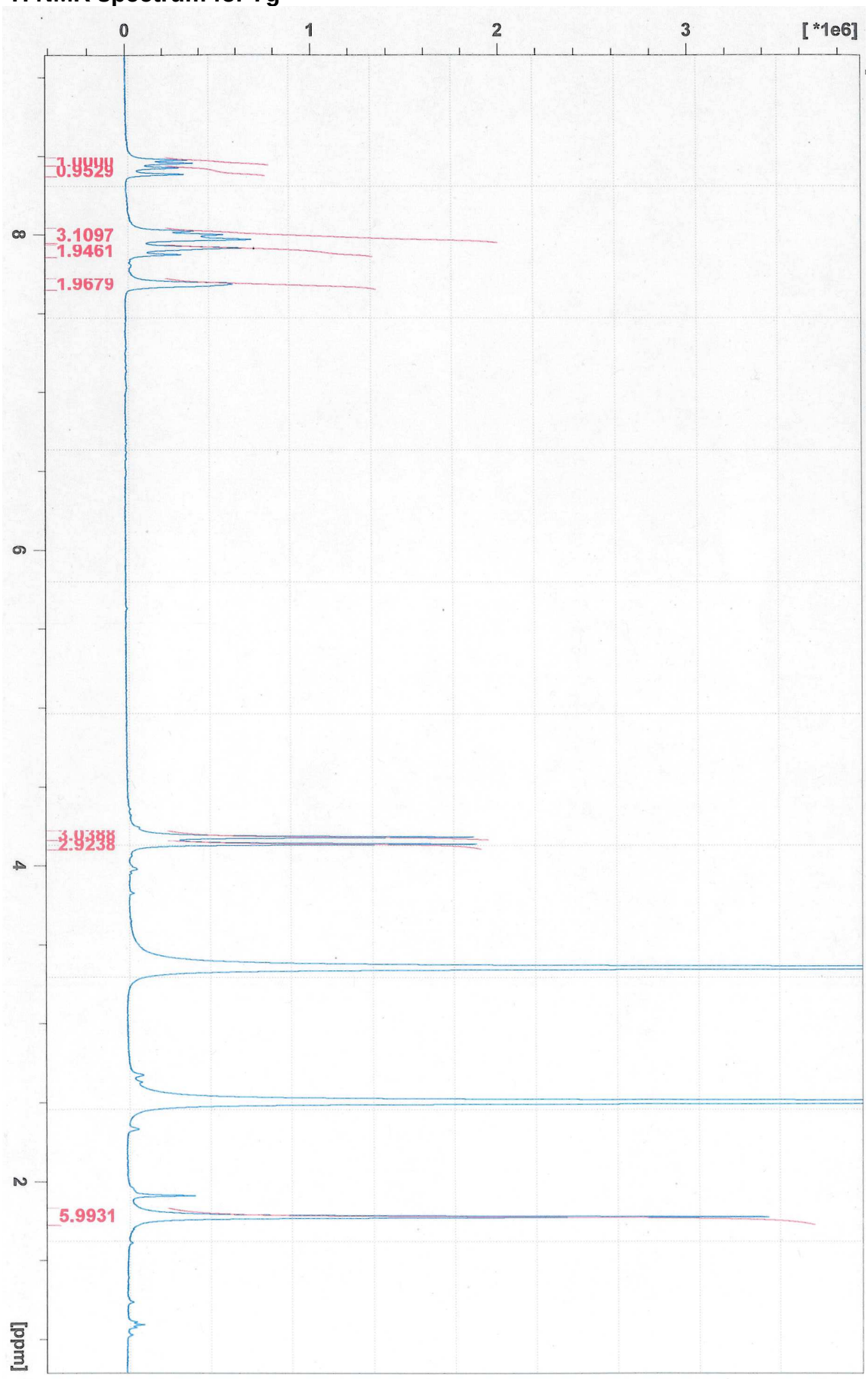
^{1}H NMR spectrum for 7e



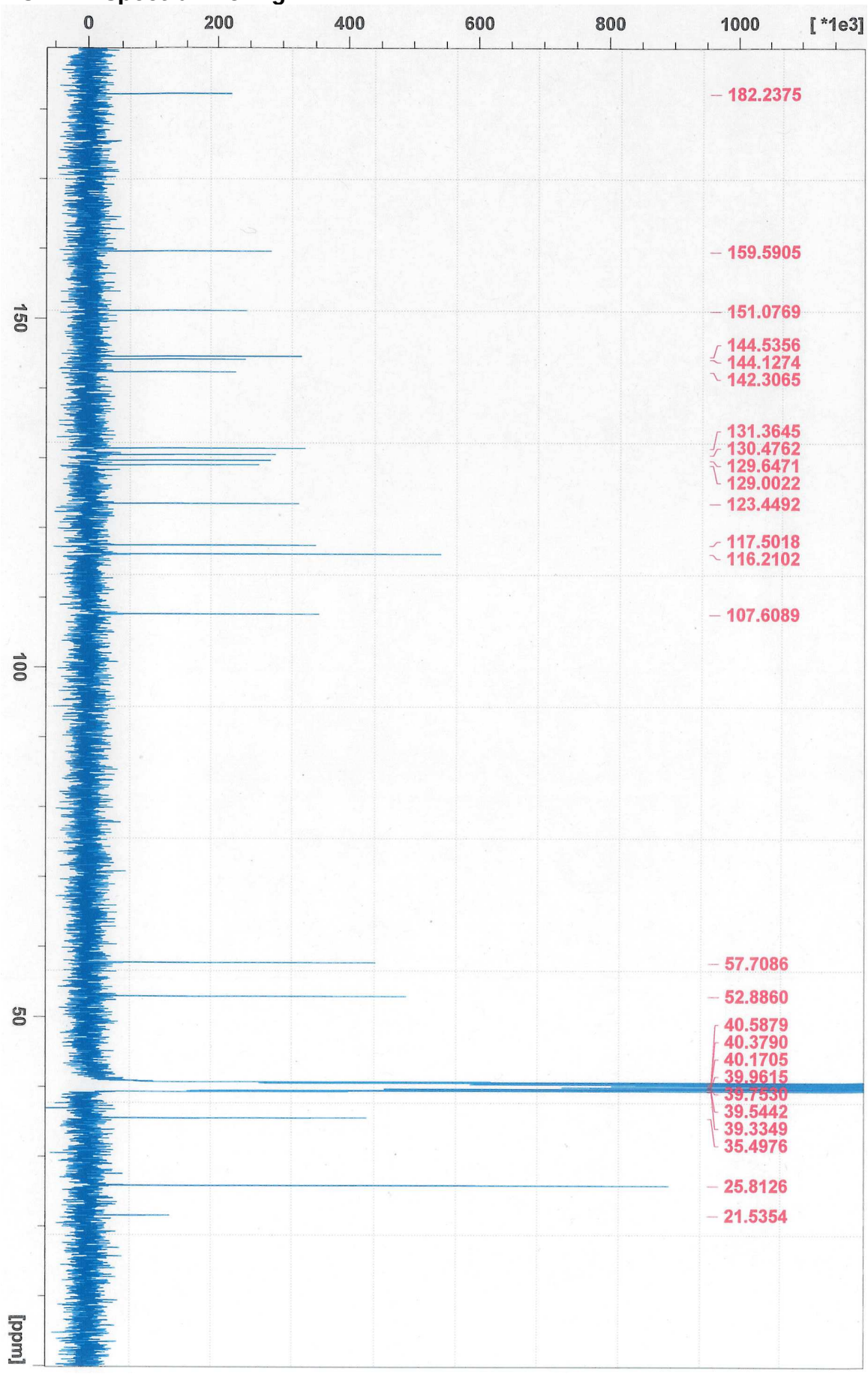
^{13}C NMR spectrum for 7e



^{1}H NMR spectrum for 7g



^{13}C NMR spectrum for 7g



3. NMR analysis of nucleophilic addition to styrylindolium iodides 7a-g: protocol, data and spectra

The NMR spectra which form the backbone of this study were collected under the following conditions:

To solutions of styrylindolium salts (0.03 mmol) in DMSO-d_6 (500 µL) in NMR tubes were added solutions of tetrabutylammonium cyanide, sodium methanethiolate or sodium sulfide nonahydrate (all 0.6 M in DMSO-d_6). Additions were made in 0.5 eq. increments (i.e. 25 µL of 0.6 M solution, 0.015 mmol) up to 5 eq. total, allowing 2 h between additions. ^{1}H NMR spectra were recorded as soon as possible following each addition, and again preceding the subsequent addition. ^{1}H NMR spectra were also recorded 24 h after the final addition.

The aim of this research was to investigate the response of styrylindolium dyes as sensors for nucleophilic analytes; as such, no attempt has been made to isolate the products of these reactions, and our focus has been on analysing product mixtures that would be produced in a sensing setting in solution. Consequently, the data presented herein does not refer to isolated novel compounds (as it would in a synthesis publication) and full characterisation data is therefore not relevant. On the other hand, assigned NMR data is powerful evidence to support this research and we have assigned such NMR spectra as fully as possible. In certain cases (particularly those involving sulfide addition), NMR spectra were too complex and/or broadened to assign peaks with confidence and these have been left unassigned.
For reactions that proceeded through competing pathways and gave multiple products, sequential spectra that document incremental addition of nucleophiles offer valuable insight and relevant spectra are included. For reactions that cleanly progressed from starting material to product, such detail is superfluous and hence, in these cases, we have solely included spectra that represent their end point.
All NMR spectra are assigned in accordance with the generic skeleton depicted in figure S1.

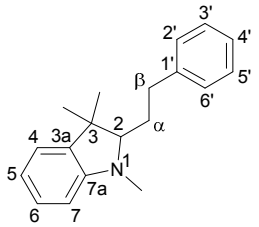
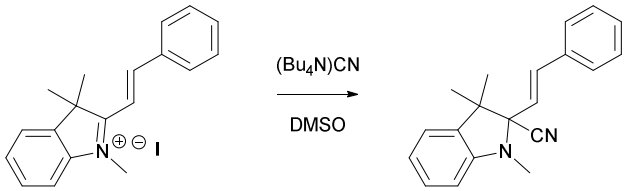


Figure S1: atom labelling for NMR assignment

3.1 Reactions of 7a

Reaction with tetrabutylammonium cyanide



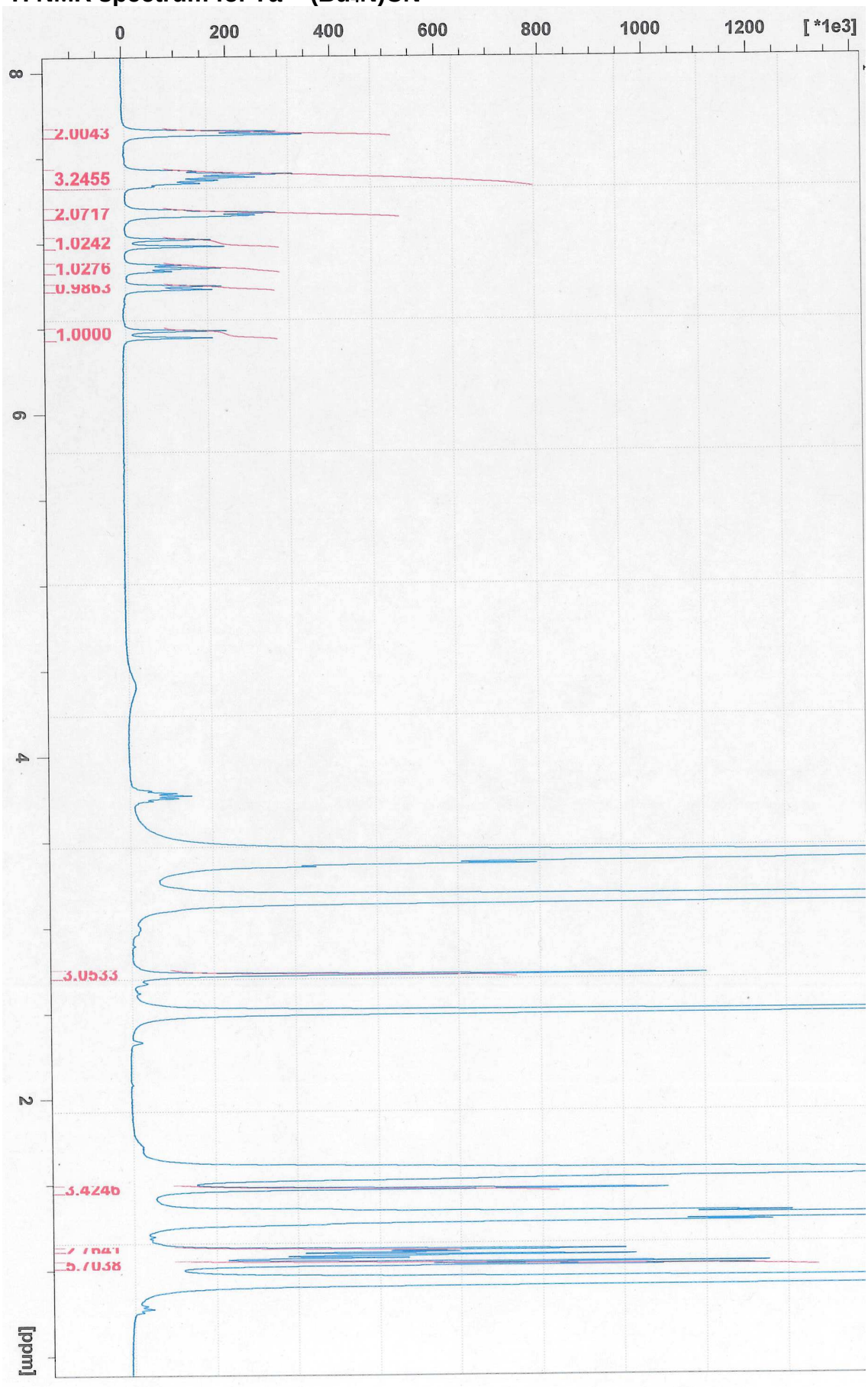
7a **8a**

Data for (*E*)-1,3,3-trimethyl-2-styrylindoline-2-carbonitrile 8a

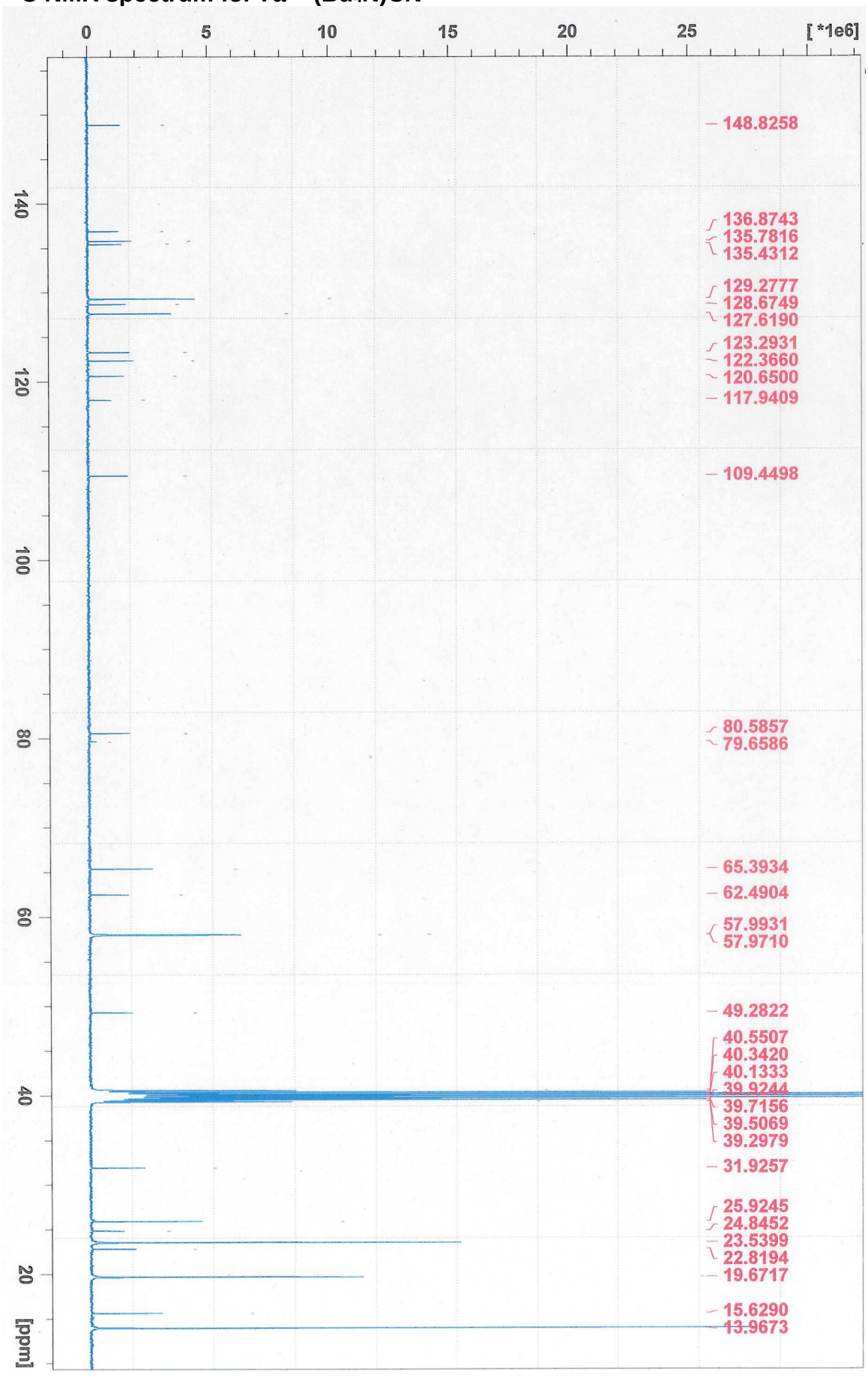
δH (400 MHz; DMSO-d_6) 7.65 (2 H, d, *J* 7.3, 2'- and 6'-H), 7.45-7.33 (3 H, m, 3'-, 4'- and 5'-H), 7.23-7.13 (2 H, m, 4- and 6-H), 7.00 (1 H, d, *J* 16.3, β-H), 6.86 (1 H, t, *J* 7.5, 5-H), 6.74 (1 H, d, *J* 7.5, 7-H), 6.47 (1 H, d, *J* 16.2, α-H), 2.73 (3 H, s, NMe), 1.48 (3 H, s, CMe) and 1.19 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 148.8 (7a-C),136.9 (3a-C), 135.8 (β-C), 135.4 (1'-C), 129.3 (3'- and 5'-C), 129.2 (4'-C), 128.7 (6-C), 127.6 (2'- and 6'-C), 123.3 (α-C), 122.4 (4-C), 120.7 (5-C), 117.9 (CN), 109.4 (7-C), 80.6 (*C*CN), 49.3 (*C*Me_2), 31.8 (NMe), 24.8 (C*Me*) and 22.8 (C*Me*).

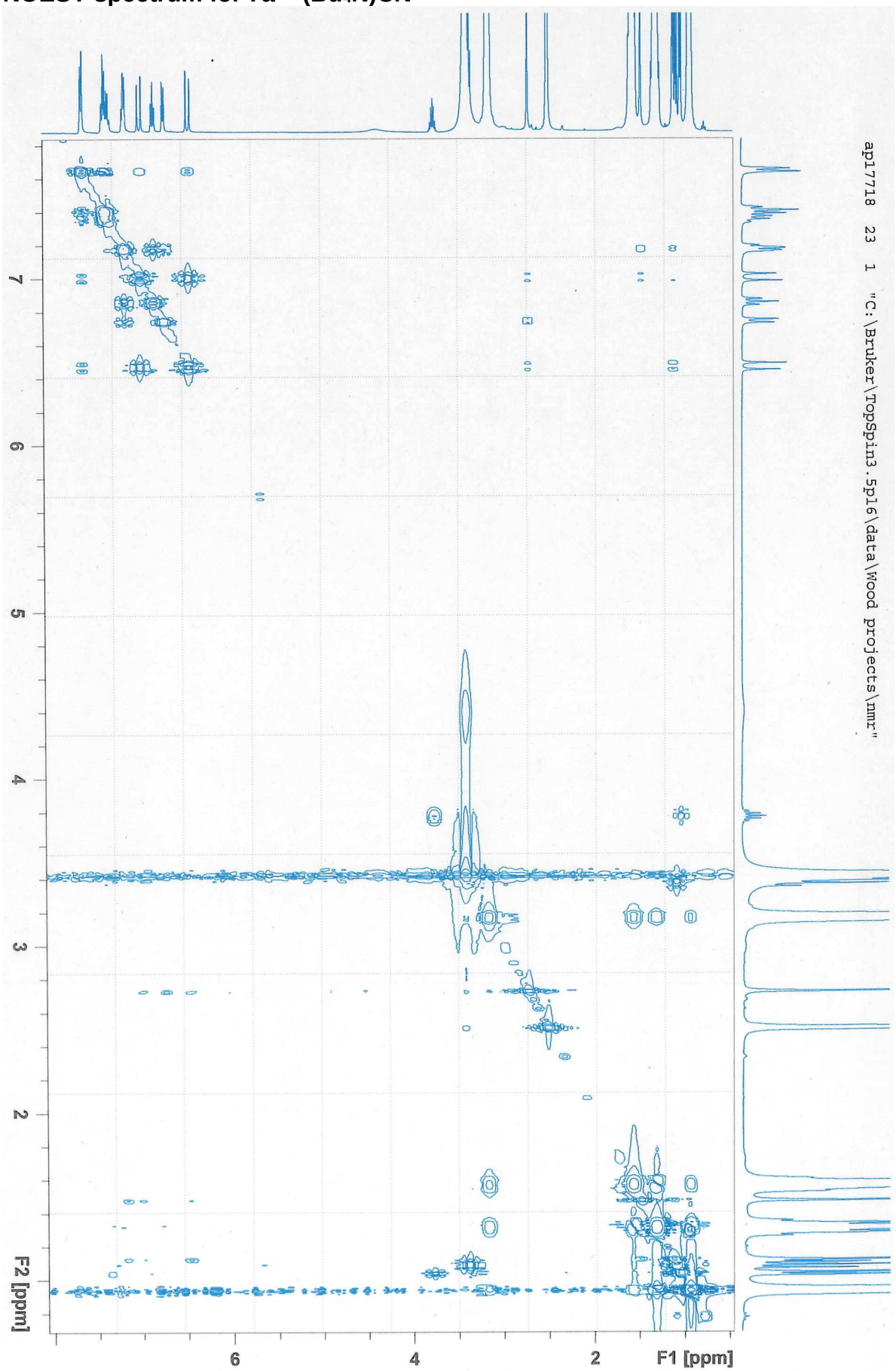
^{1}H NMR spectrum for 7a + (Bu_4N)CN



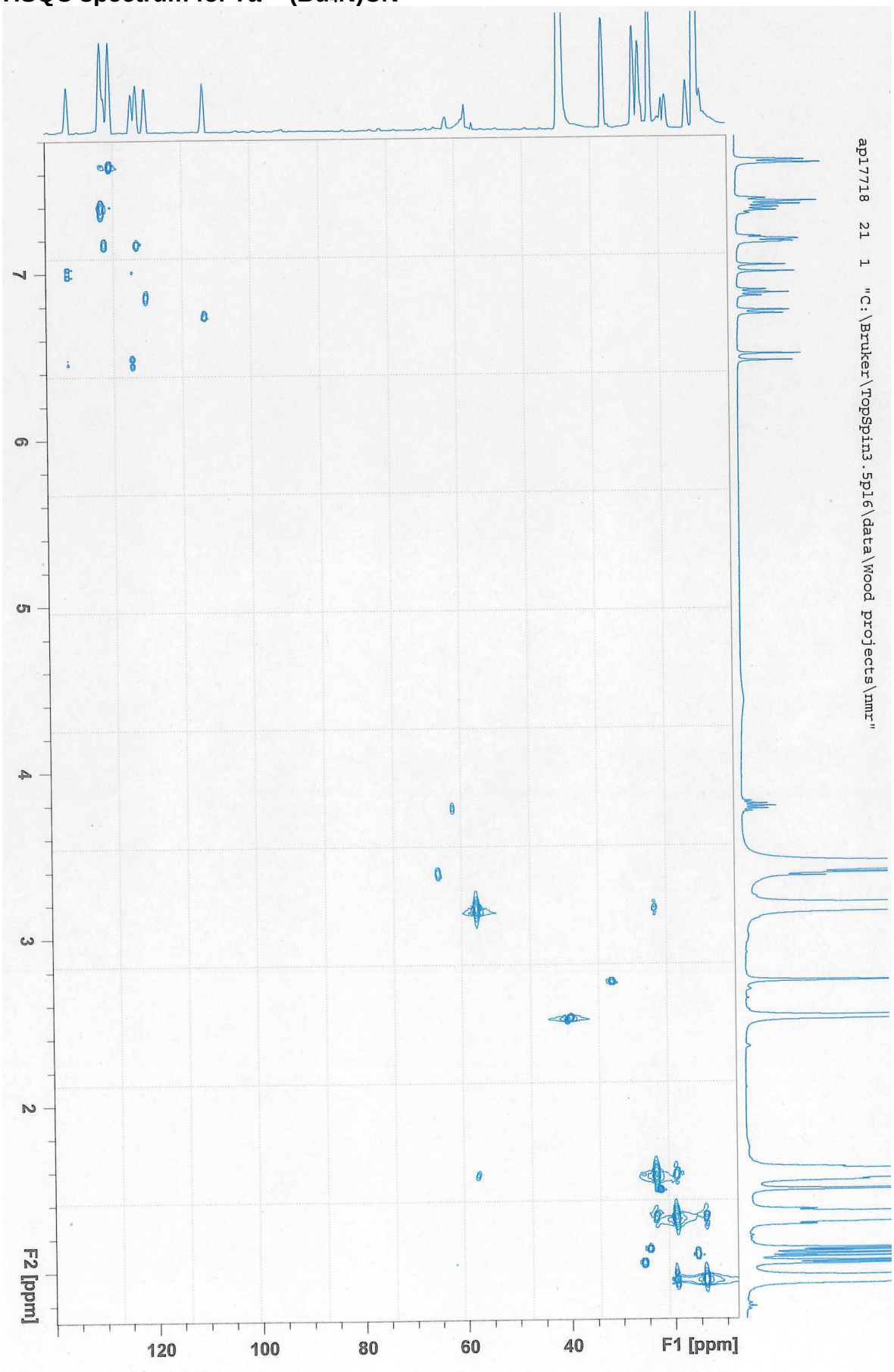
^{13}C NMR spectrum for 7a + (Bu_4N)CN



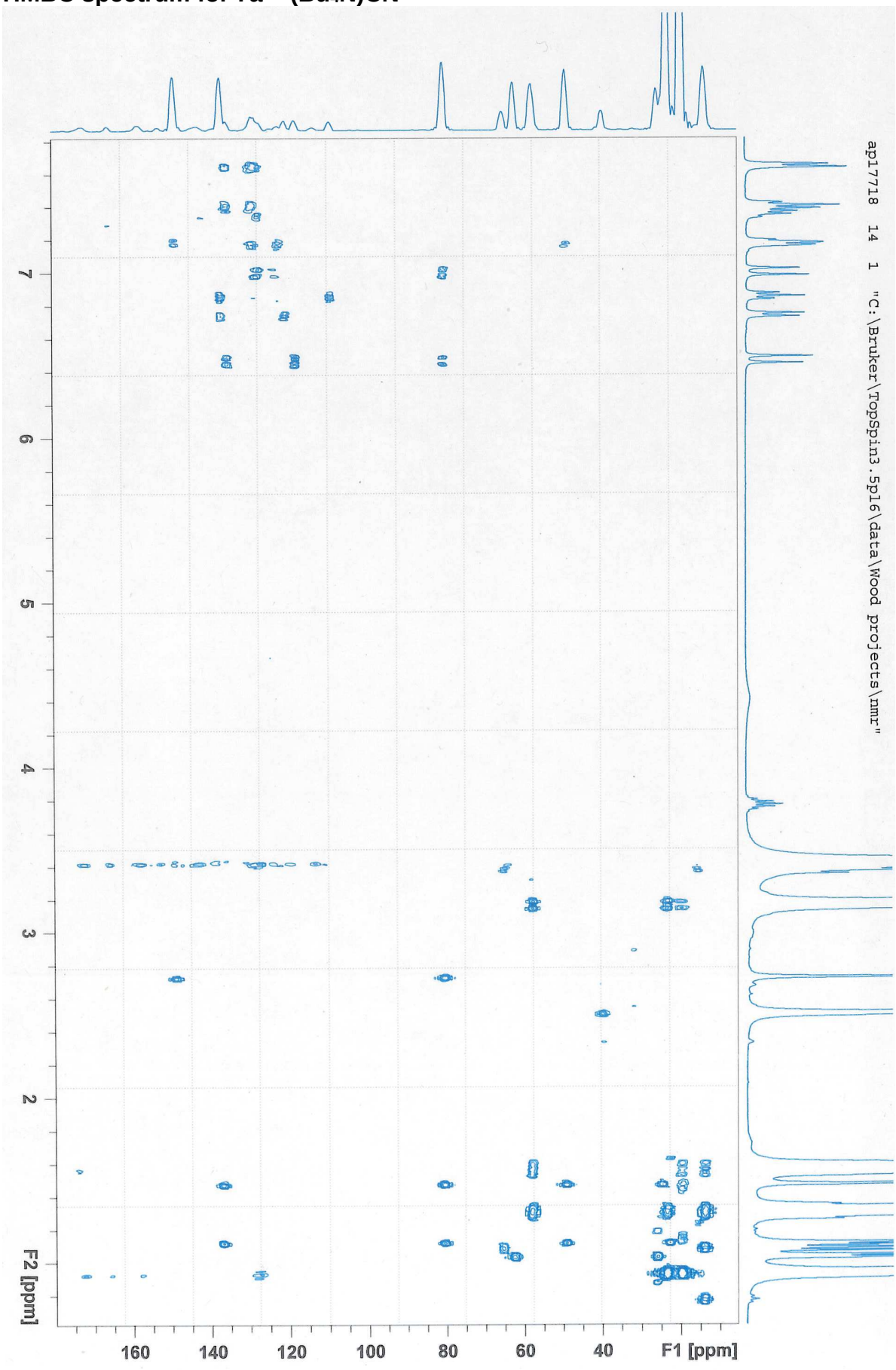
NOESY spectrum for 7a + (Bu_4N)CN



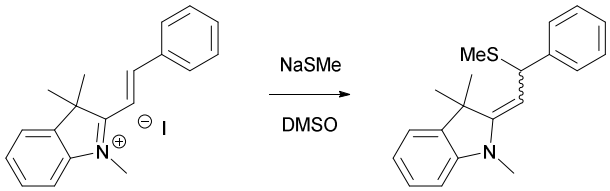
HSQC spectrum for 7a + (Bu_4N)CN



HMBC spectrum for 7a + (Bu_4N)CN



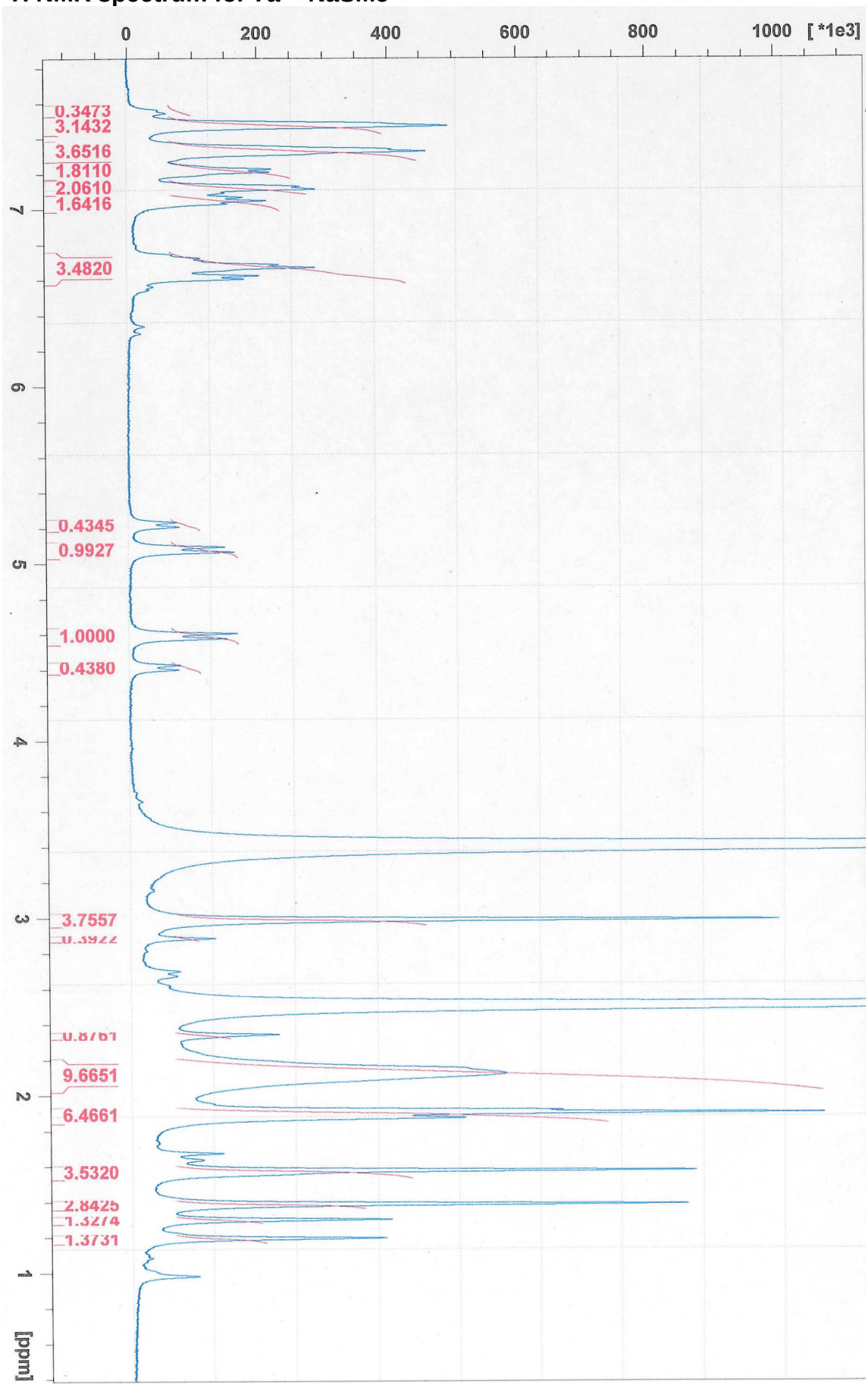
Reaction with sodium methanethiolate



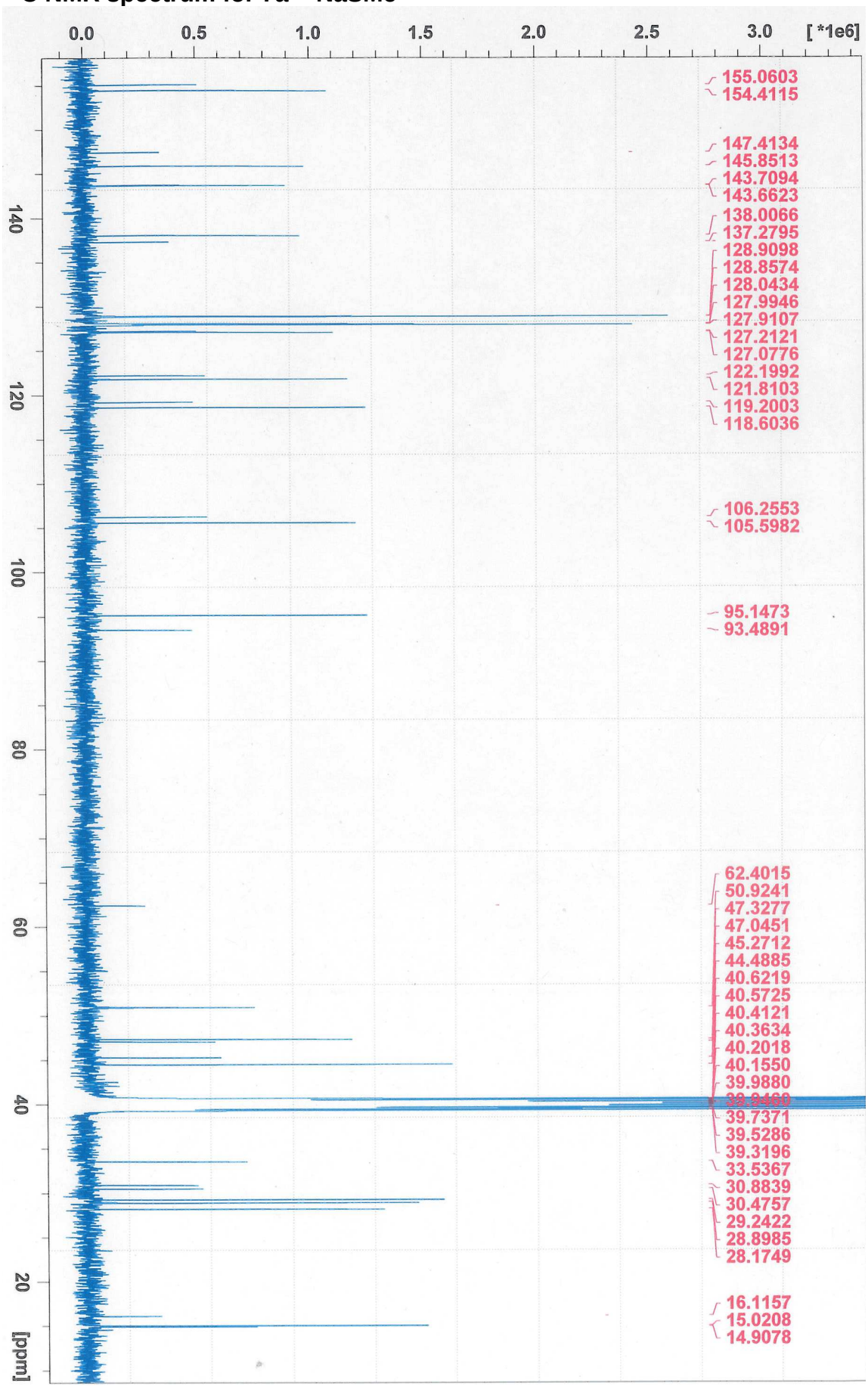
7a **9a**

Data for 1,3,3-trimethyl-2-(2-(methylthio)-2-phenylethylidene)indoline 9a
δH (400 MHz; DMSO-d_6; 29:71 *Z*:*E*) 7.57-7.54 (2 H, m, 2'- and 6'-H(*Z*)), 7.54-7.43 (2 H, m, 2'- and 6'-H(*E*)), 7.41-7.21 (4 H, m, 3'- and 5'-H(*E* and *Z*)), 7.27-7.18 (2 H, m, 4'-H(*E* and *Z*)), 7.16-7.08 (2 H, m, 4-H(*E* and *Z*)), 7.05 (2 H, t, *J* 7.5, 6-H(*E* and *Z*)), 6.78-6.54 (4 H, m, 5- and 7-H(*E* and *Z*)), 5.22 (1 H, d, *J* 10.3, β-H(*Z*)), 5.08 (1 H, d, *J* 11.1, β-H(*E*)), 4.59 (1 H, d, *J* 11.1, α-H(*E*)), 4.41 (1 H, d, *J* 10.3, α-H(*Z*)), 3.41 (3 H, s, NMe(*Z*)), 2.98 (3 H, s, NMe(*E*)), 1.89 (3 H, s, SMe(*E*)), 1.88 (3 H, s, SMe(*Z*)), 1.57 (3 H, s, CMe(*E*)), 1.40 (3 H, s, CMe(*E*)), 1.26 (3 H, s, CMe(*Z*)) and 1.20 (3 H, s, CMe(*Z*)).
δC (100 MHz; DMSO-d_6); (*E*)-isomer: 154.4 (2-C), 145.9 (7a-C), 143.7 (1'-C), 138.0 (3a-C), 128.9 (3'- and 5'-C), 128.0 (2'- and 6'-C), 127.9 (6-C), 127.1 (4'-C), 121.8 (4-C), 118.6 (5-C), 105.6 (7-C), 95.1 (α-C), 50.9 (SMe), 47.3 (β-C), 44.5 (*C*Me_2), 29.2 (NMe), 28.9 (C*Me*) and 28.2 (C*Me*); (*Z*)-isomer: 155.1 (2-C), 147.4 (7a-C), 143.7 (1'-C), 137.3 (3a-C), 128.9 (3'- and 5'-C), 128.0 (2'- and 6'-C), 127.9 (6-C), 127.2 (4'-C), 122.2 (4-C), 119.2 (5-C), 106.3 (7-C), 93.5 (α-C), 50.9 (SMe), 47.0 (β-C), 45.3 (*C*Me_2), 33.5 (NMe), 30.9 (C*Me*) and 30.5 (C*Me*).
LRMS-ES+ (*m/z*): 262 (100%, M^+-SCH_3).

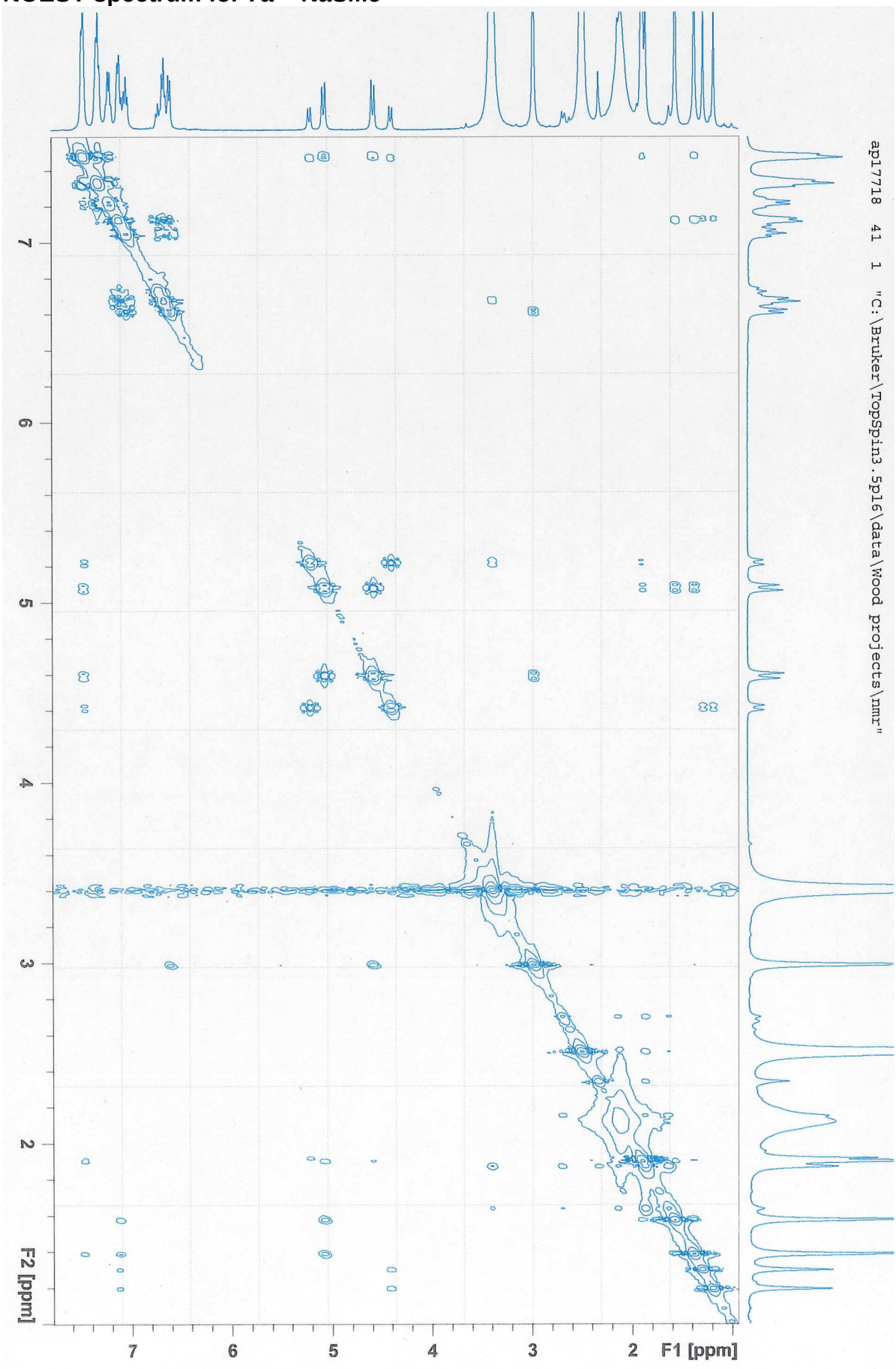
^{1}H NMR spectrum for 7a + NaSMe



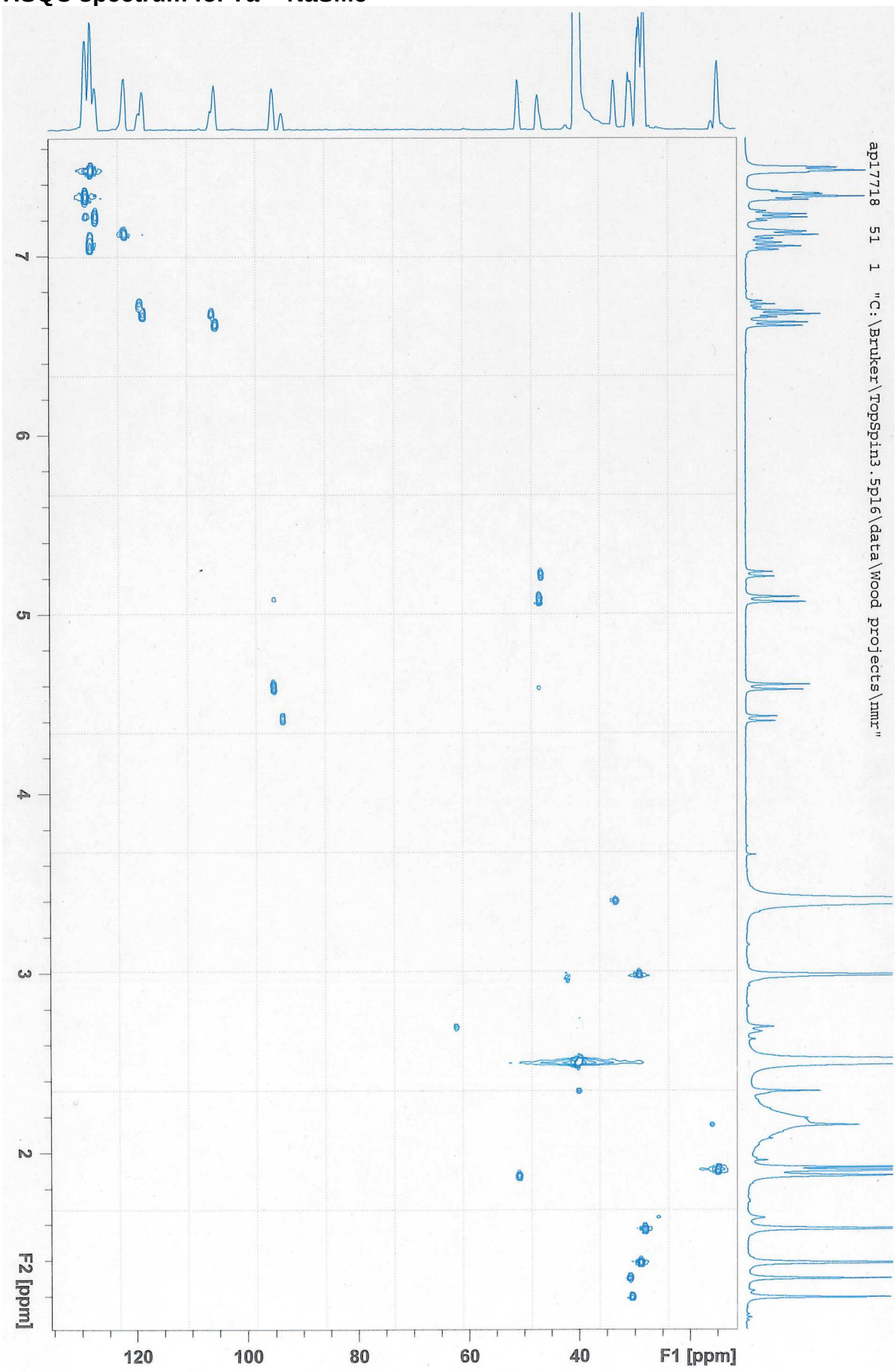
^{13}C NMR spectrum for 7a + NaSMe



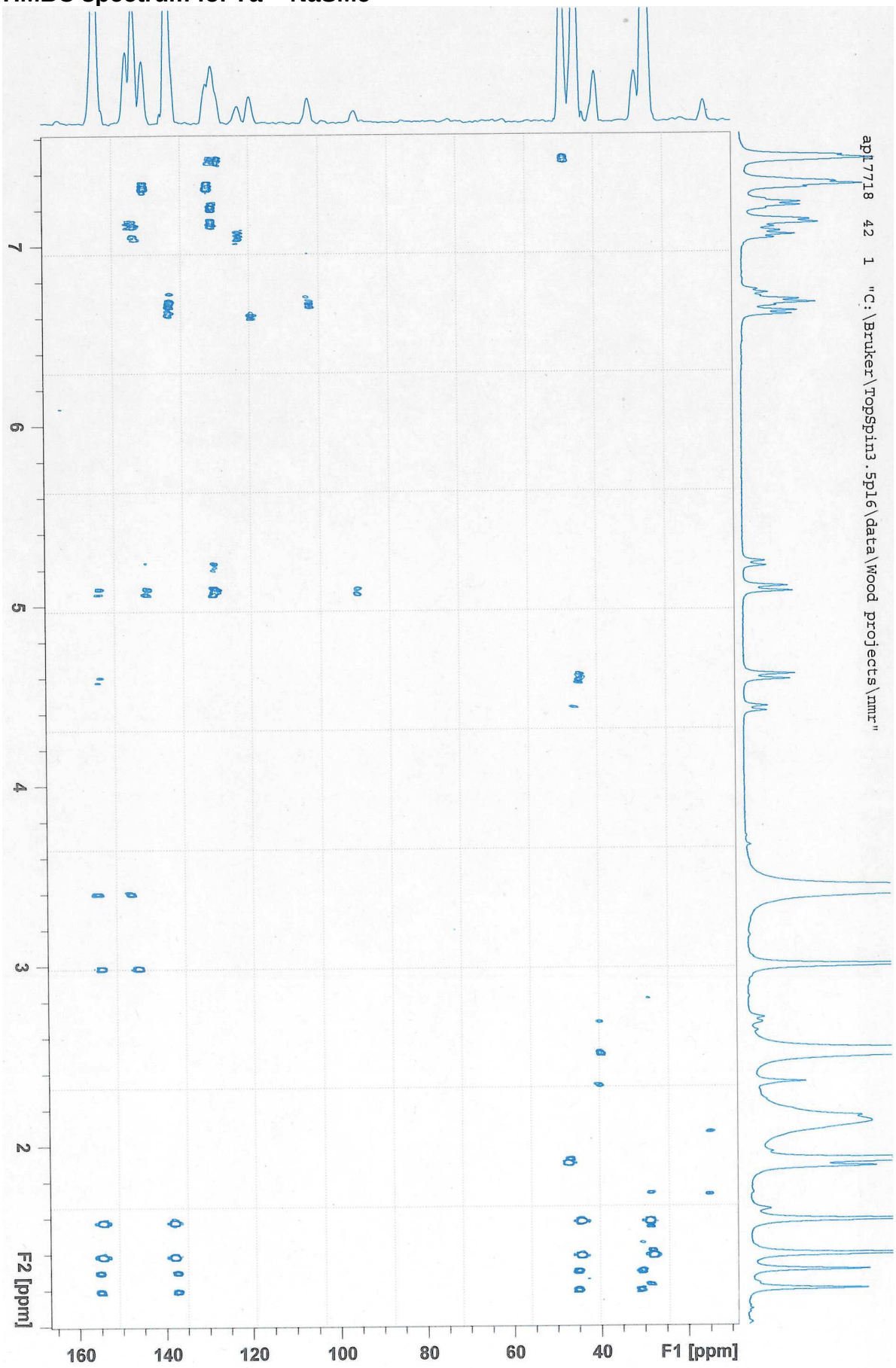
NOESY spectrum for 7a + NaSMe



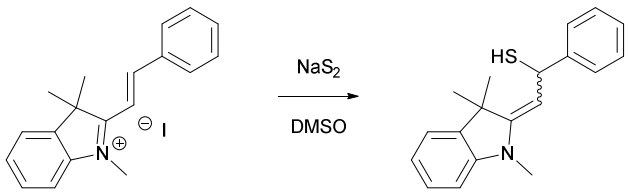
HSQC spectrum for 7a + NaSMe



HMBC spectrum for 7a + NaSMe



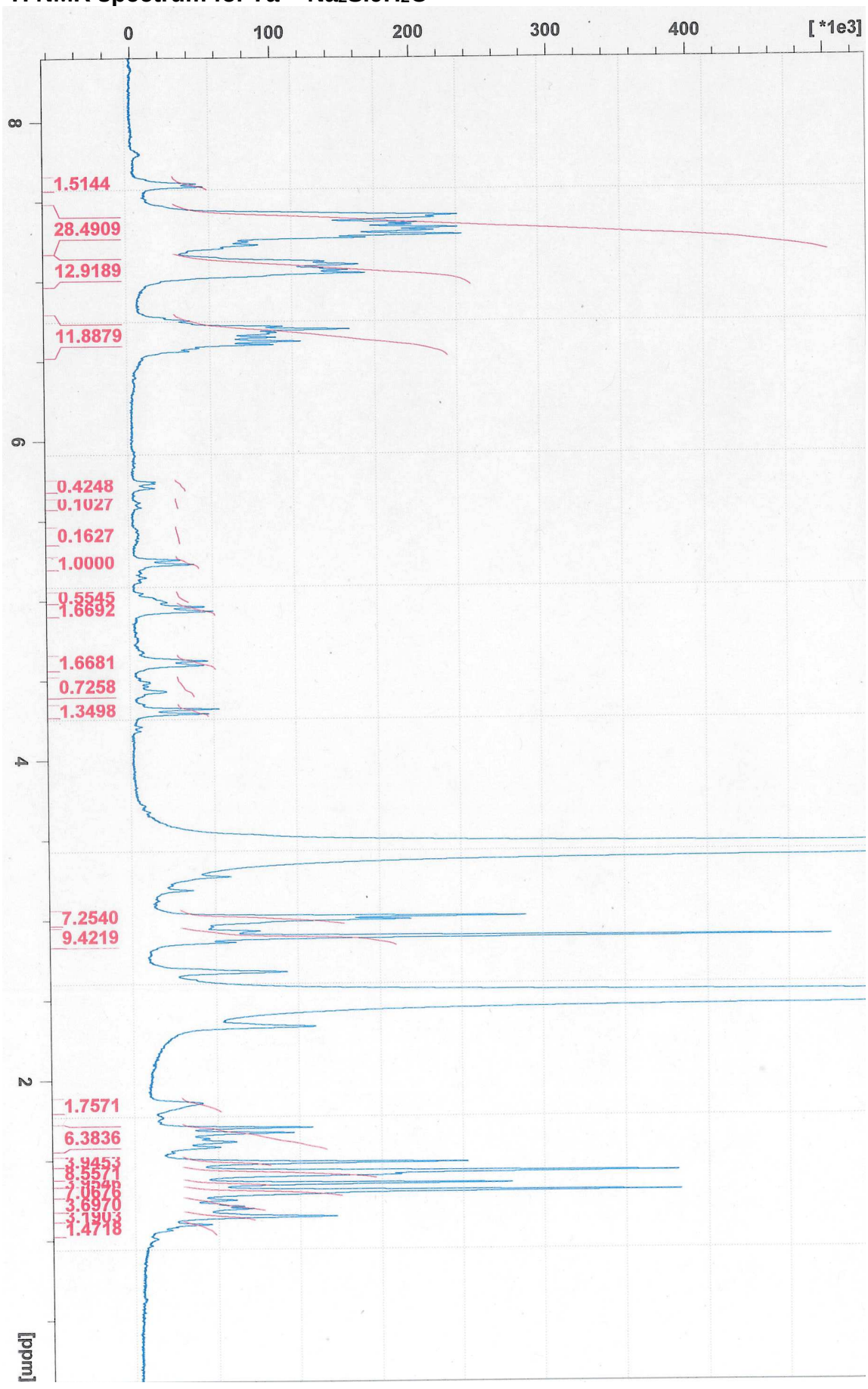
Reaction with sodium sulfide



7a **10a**

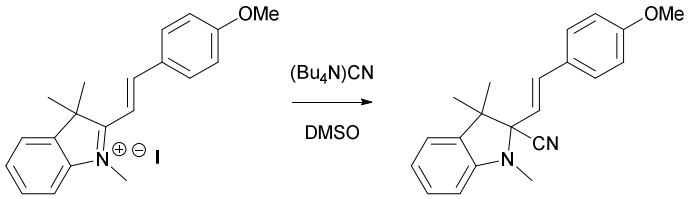
LRMS-ES+ (*m/z*): 262 (100%, M^+-SH).

^{1}H NMR spectrum for 7a + $Na_2S.9H_2O$



3.2 Reactions of 7b

Reaction with tetrabutylammonium cyanide



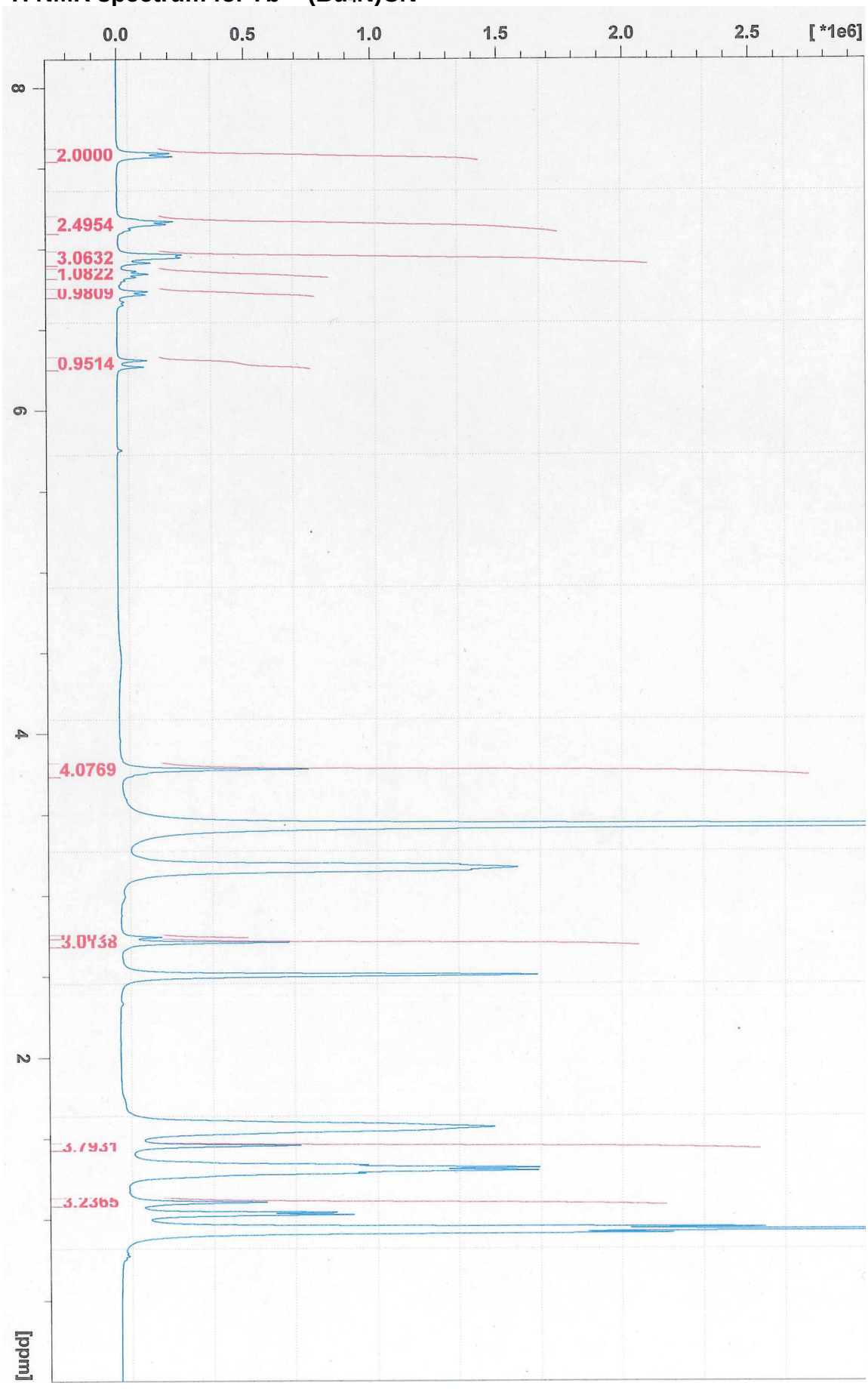
7b **8b**

Data for (*E*)-2-(4-methoxystyryl)-1,3,3-trimethylindoline-2-carbonitrile 8b

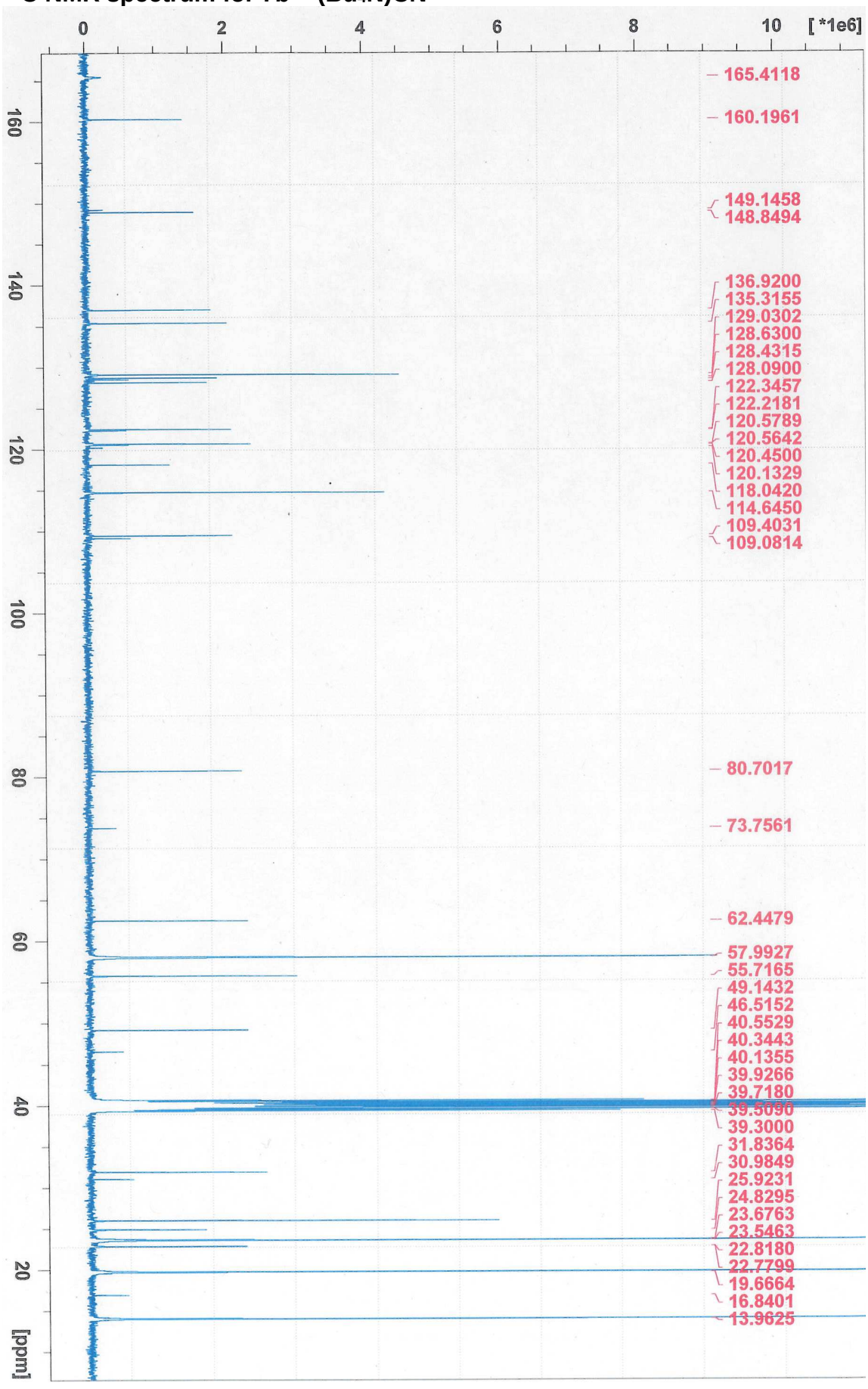
δH (400 MHz; DMSO-d_6) 7.60 (2 H, d, *J* 8.3, 2'- and 6'-H), 7.20-7.10 (2 H, m, 4- and 6-H), 7.00-6.87 (3 H, m, β-, 3'- and 5'-H), 6.85 (1 H, t, *J* 7.5, 5-H), 6.72 (1 H, d, *J* 7.5, 7-H), 6.30 (1 H, d, *J* 16.2, α-H), 3.76 (3 H, s, OMe), 2.72 (3 H, s, NMe), 1.42 (3 H, s, CMe) and 1.13 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 160.2 (4'-C), 148.8 (7a),136.9 (3a-C), 135.3 (β-C), 129.0 (2'- and 6'-C), 128.6 (6-C), 128.1 (1'-C), 122.3 (4-C), 120.6 (5-C), 120.5 (α-C), 118.0 (CN), 114.6 (3'- and 5'-C), 109.4 (7-C), 80.7 (*C*CN), 55.7 (OMe), 49.1 (*C*Me_2), 31.9 (NMe), 24.8 (C*Me*) and 22.8 (C*Me*).

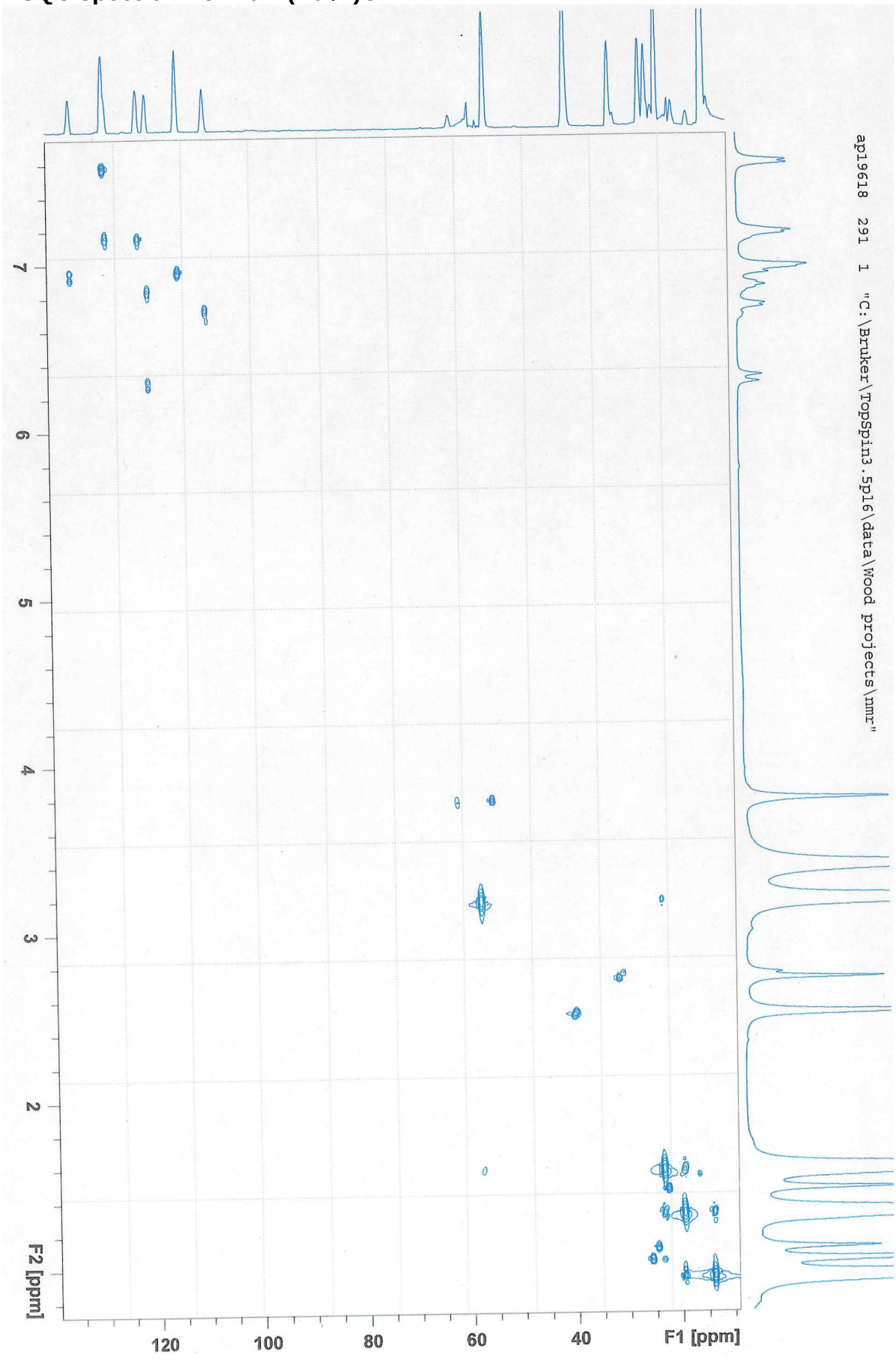
^{1}H NMR spectrum for 7b + (Bu_4N)CN



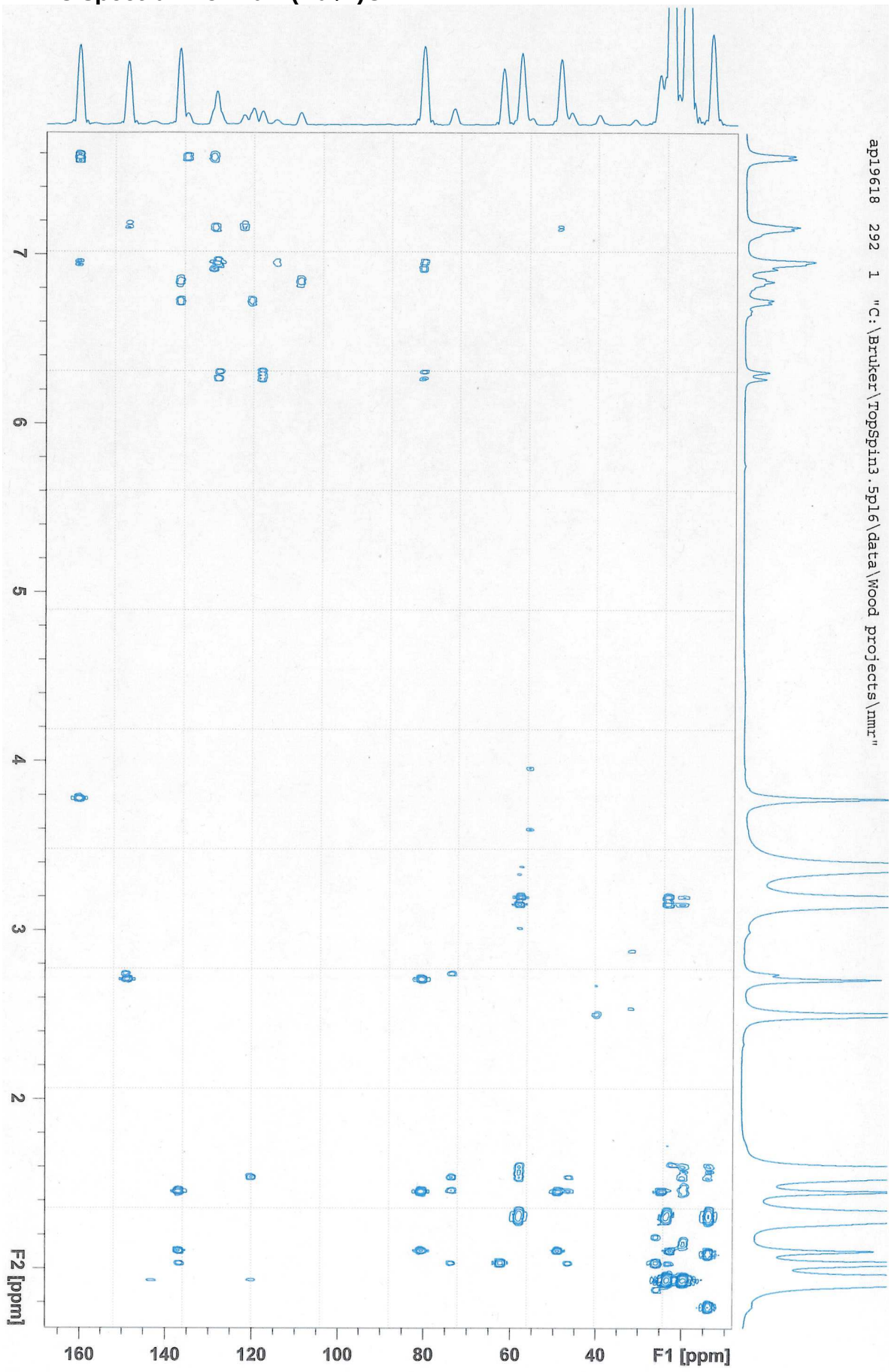
^{13}C NMR spectrum for 7b + (Bu_4N)CN



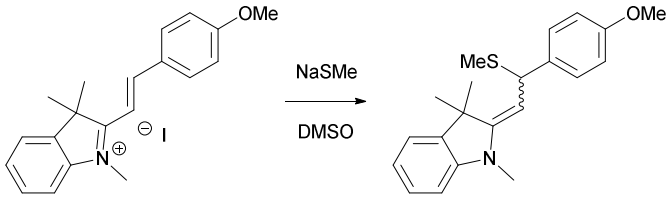
HSQC spectrum for 7b + (Bu_4N)CN



HMBC spectrum for 7b + (Bu_4N)CN



Reaction with sodium methanethiolate



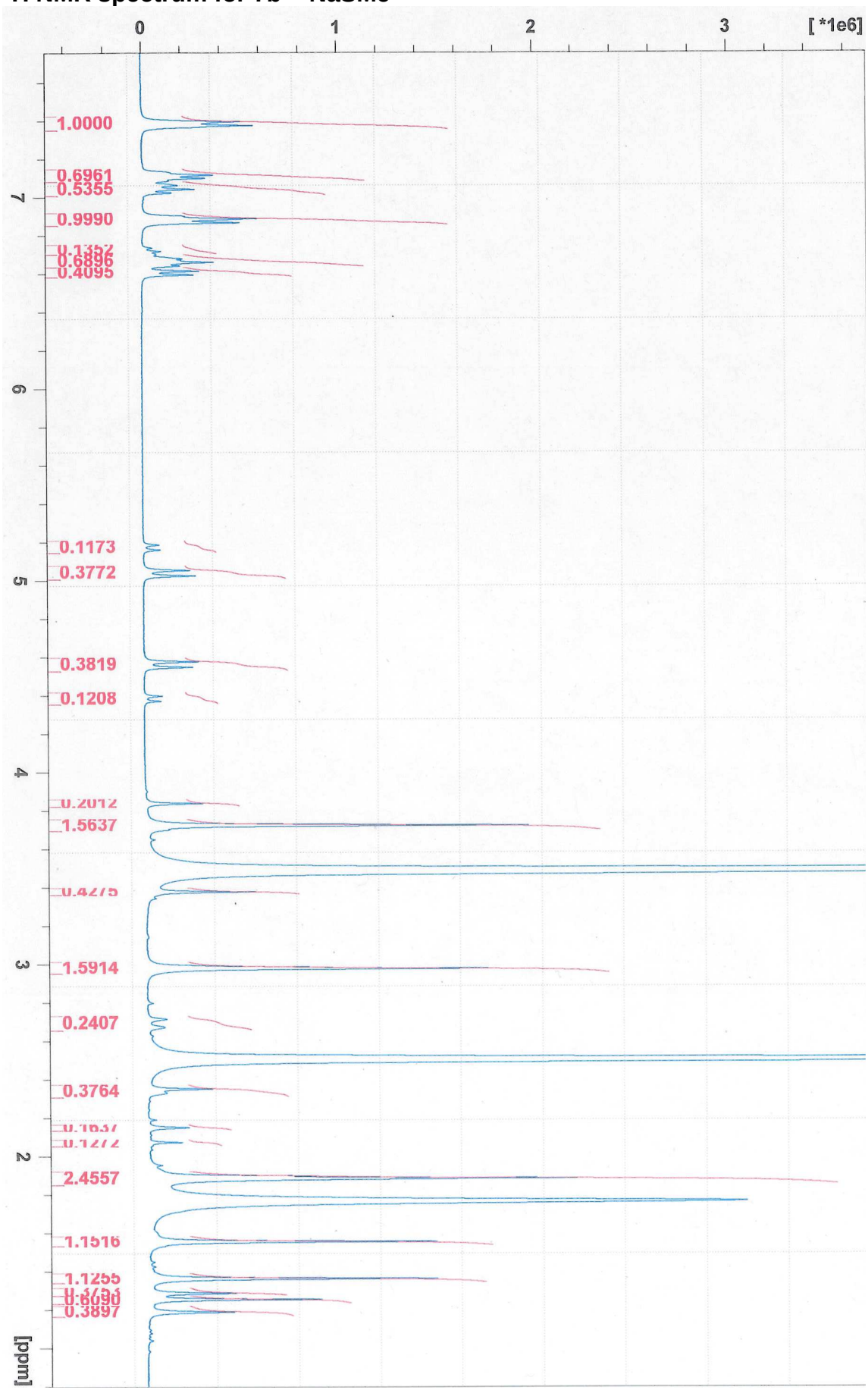
7b **9b**

Data for 2-(2-(4-methoxyphenyl)-2-(methylthio)ethylidene)-1,3,3-trimethylindoline 9b

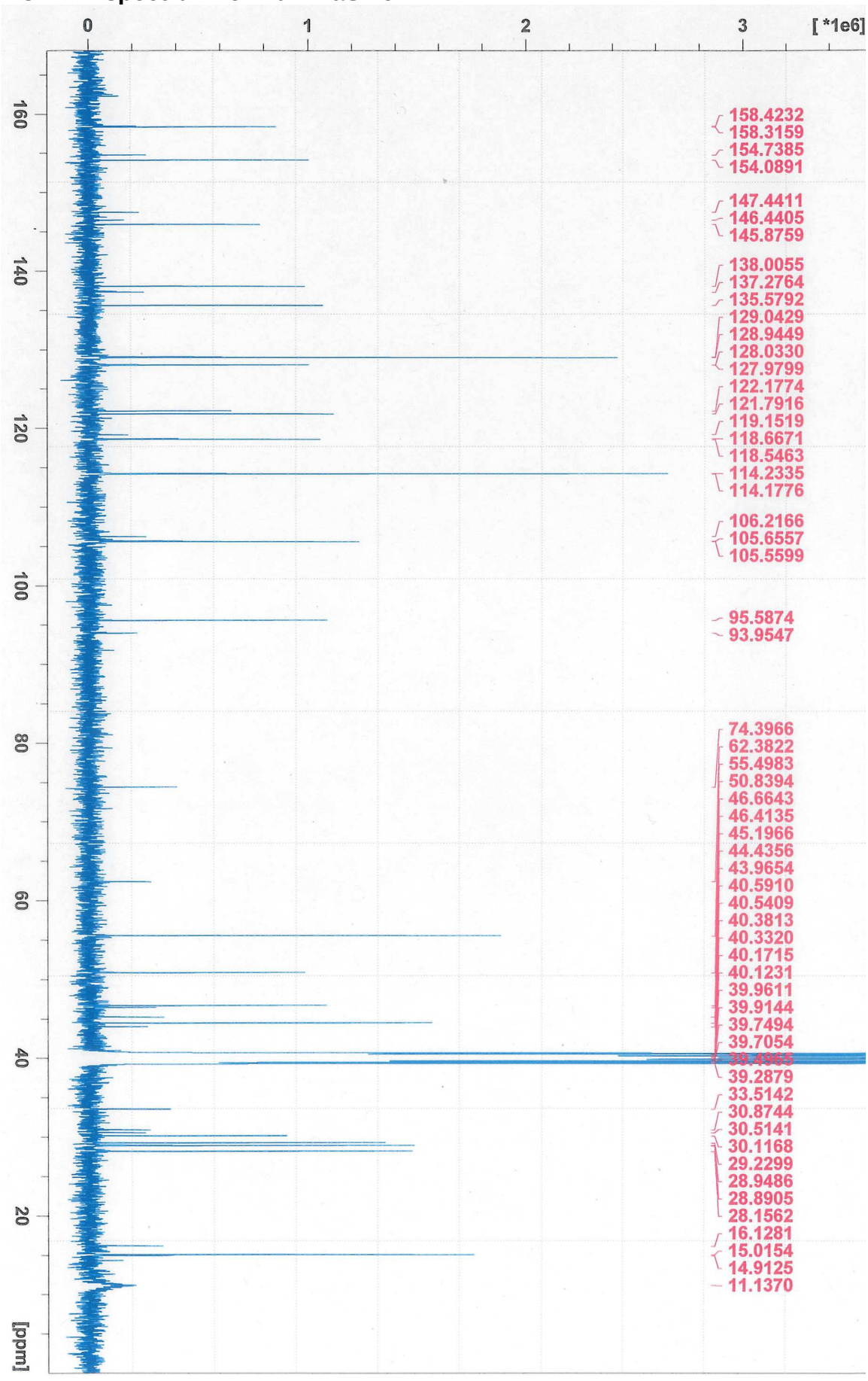
δH (400 MHz; DMSO-d_6; 24:76 *Z*:*E*) 7.39 (2 H, d, *J* 8.4, 2'- and 6'-H(*E*)), 7.11 (1 H, d, *J* 7.5, 4-H(*E*)), 7.04 (1 H, t, *J* 7.5, 6-H(*E*)), 6.89 (2 H, d, *J* 8.4, 3'- and 5'-H(*E*)), 6.71 (1 H, t, *J* 7.4, 5-H(*Z*)), 6.66 (1 H, t, *J* 7.5, 5-H(*E*)), 6.61 (1 H, d, *J* 7.5, 7-H(*E*)), 5.17 (1 H, d, *J* 10.6, β-H(*Z*)), 5.04 (1 H, d, *J* 11.4, β-H(*E*)), 4.56 (1 H, d, *J* 11.4, α-H(*E*)), 4.39 (1 H, d, *J* 10.6, α-H(*Z*)), 3.75 (3 H, s, OMe(*E*)), 3.45 (3 H, s, NMe(*Z*)), 2.97 (3 H, s, NMe(*E*)), 1.90 (3 H, s, SMe(*E*)), 1.54 (3 H, s, CMe(*E*)), 1.38 (3 H, s, CMe(*E*)), 1.27 (3 H, s, CMe(*Z*)) and 1.20 (3 H, s, CMe(*Z*)).

δC (100 MHz; DMSO-d_6); (*E*)-isomer: 158.3 (4'-C), 154.1 (2-C), 145.9 (7a-C), 138.0 (3a-C), 135.6 (1'-C), 128.9 (2'- and 6'-C), 128.0 (6-C), 121.8 (4-C), 118.5 (5-C), 114.2 (3'- and 5'-C), 105.6 (7-C), 95.6 (α-C), 55.5 (OMe), 50.8 (SMe), 46.7 (β-C), 44.4 (*C*Me$_2$), 30.1 (NMe), 28.9 (C*Me*) and 28.2 (C*Me*); (*Z*)-isomer: 158.4 (4'-C), 154.7 (2-C), 147.4 (7a-C), 137.3, 129.0 (2'- and 6'-C), 128.0 (6-C), 122.2 (4-C), 119.2, 118.7 (5-C), 114.2 (3'- and 5'-C), 105.7 (7-C), 94.0 (α-C), 62.4 (OMe), 46.4 (SMe), 45.2 (β-C), 44.0 (*C*Me$_2$), 33.5 (NMe), 30.9 (C*Me*) and 30.5 (C*Me*);

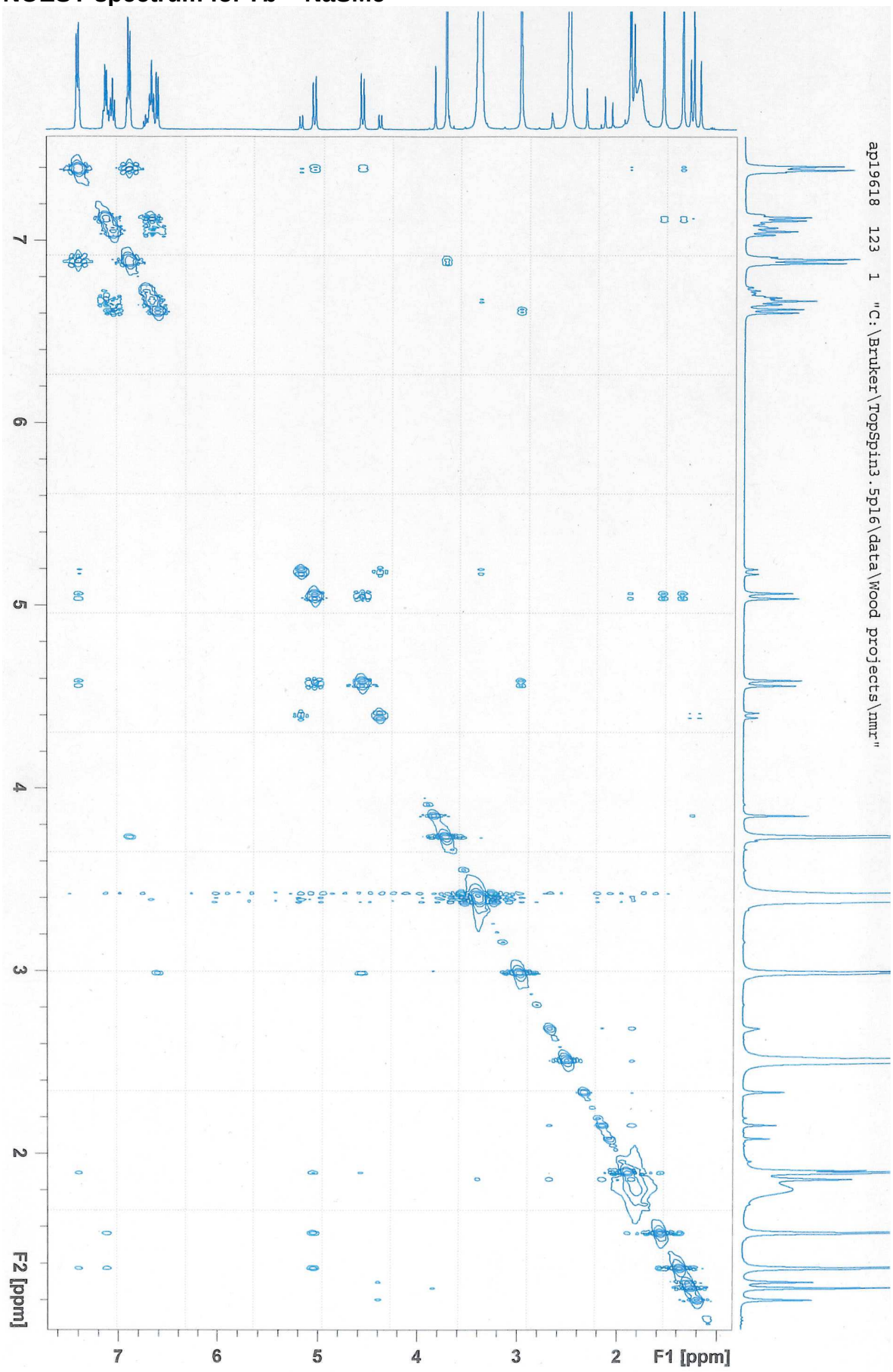
^{1}H NMR spectrum for 7b + NaSMe



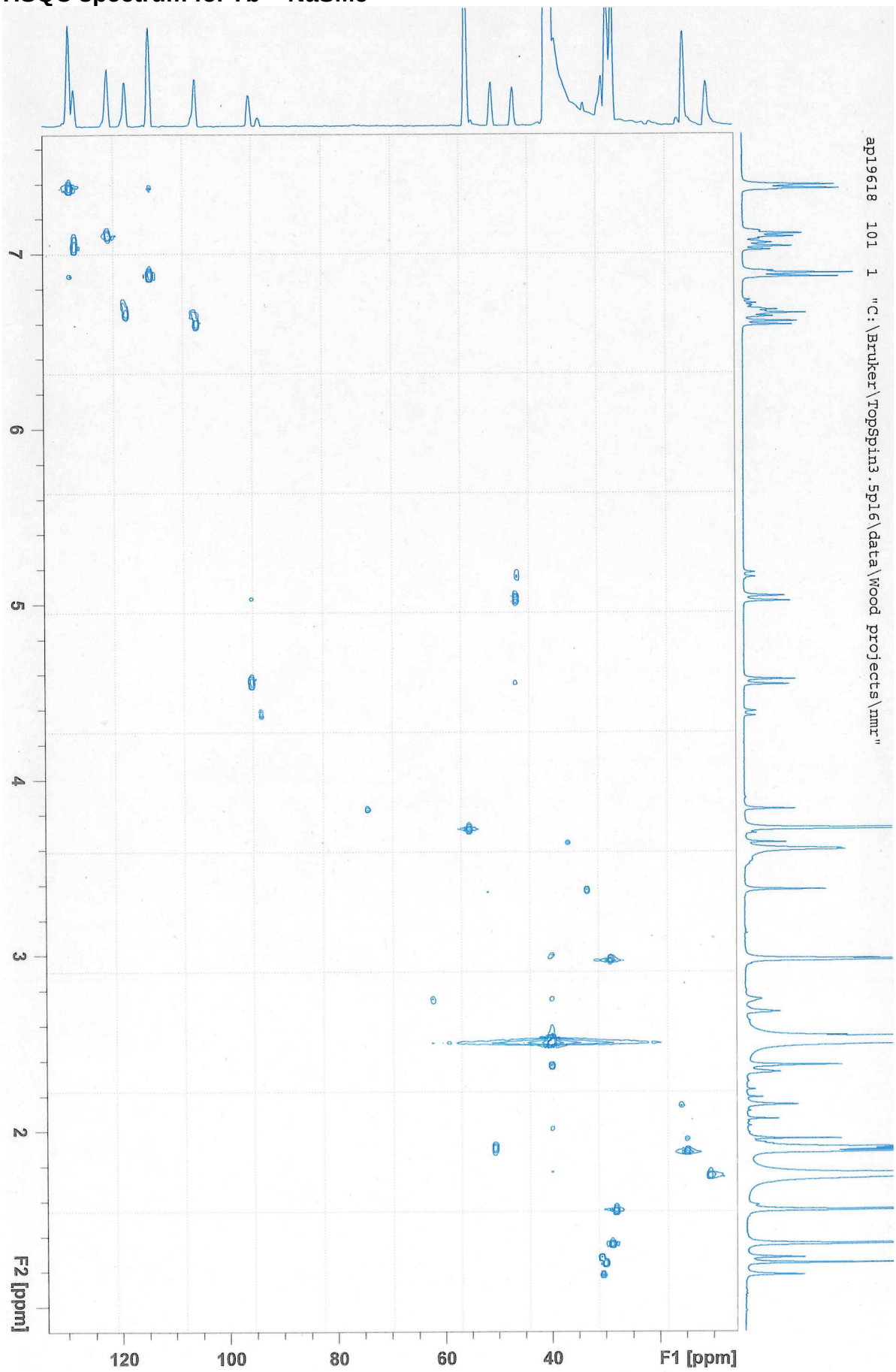
^{13}C NMR spectrum for 7b + NaSMe



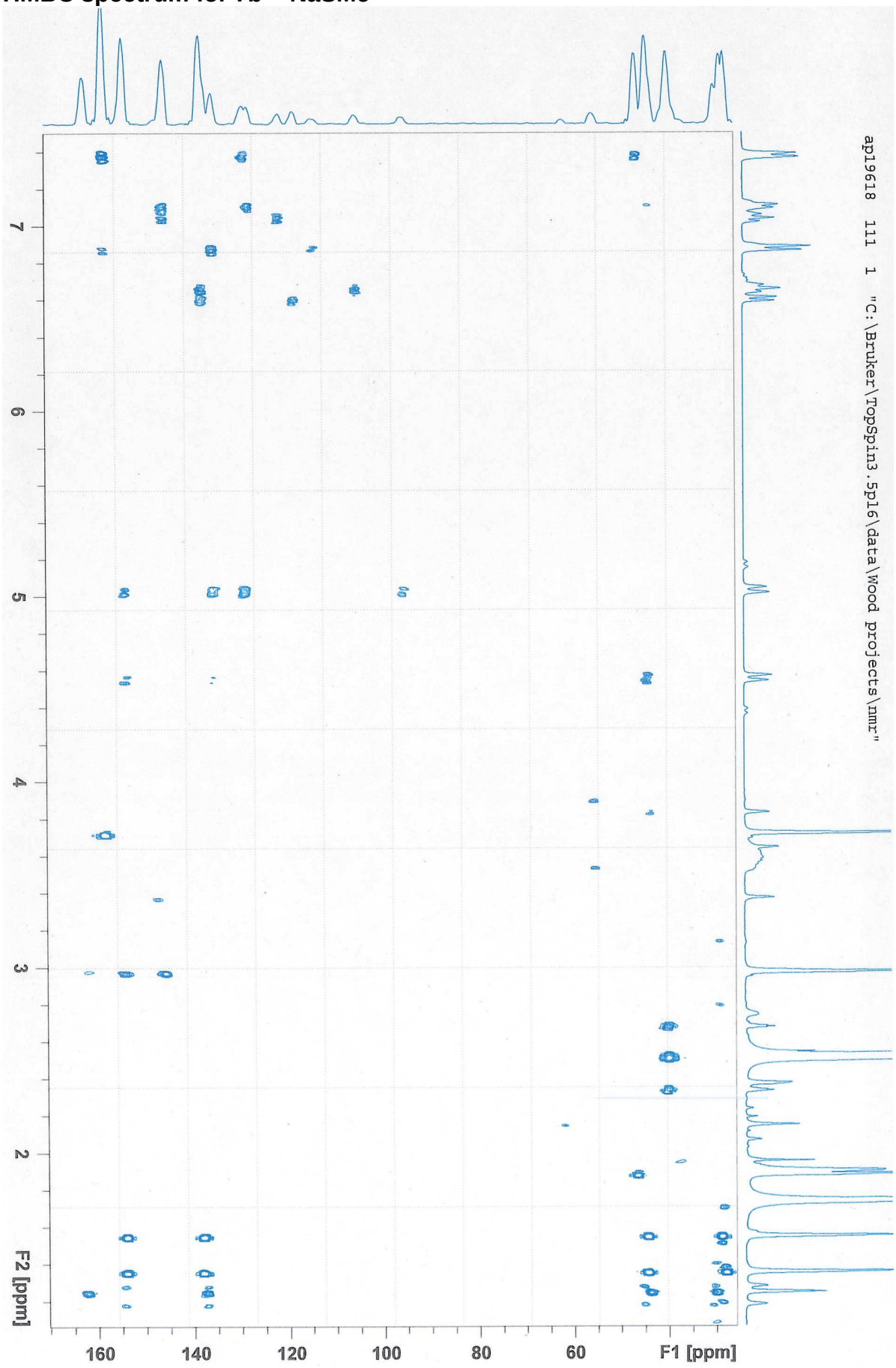
NOESY spectrum for 7b + NaSMe



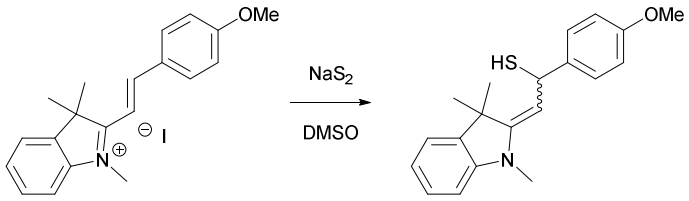
HSQC spectrum for 7b + NaSMe



HMBC spectrum for 7b + NaSMe



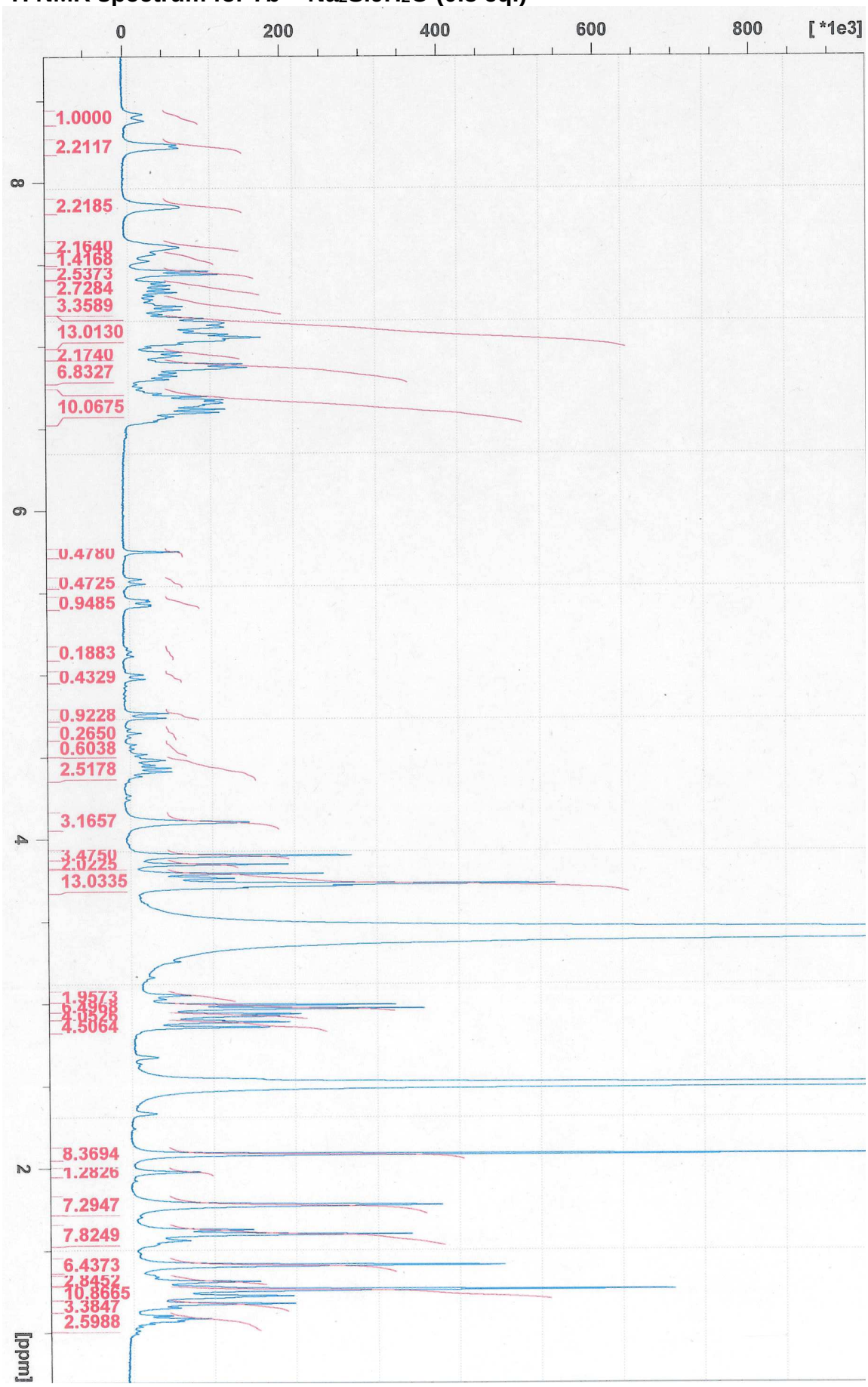
Reaction with sodium sulfide



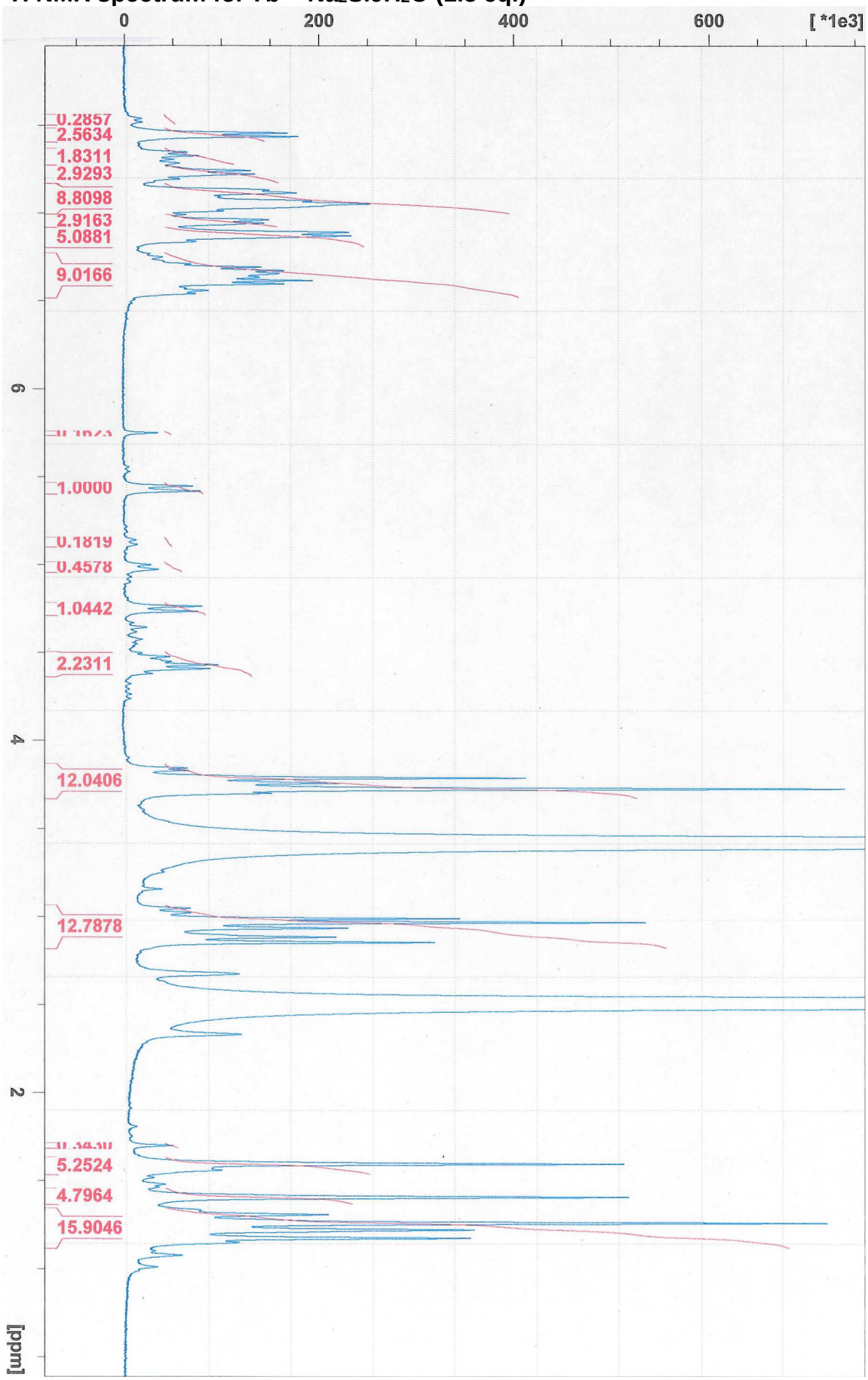
7b **10b**

LRMS-ES+ (*m/z*): 292 (30%, M^+-SH).

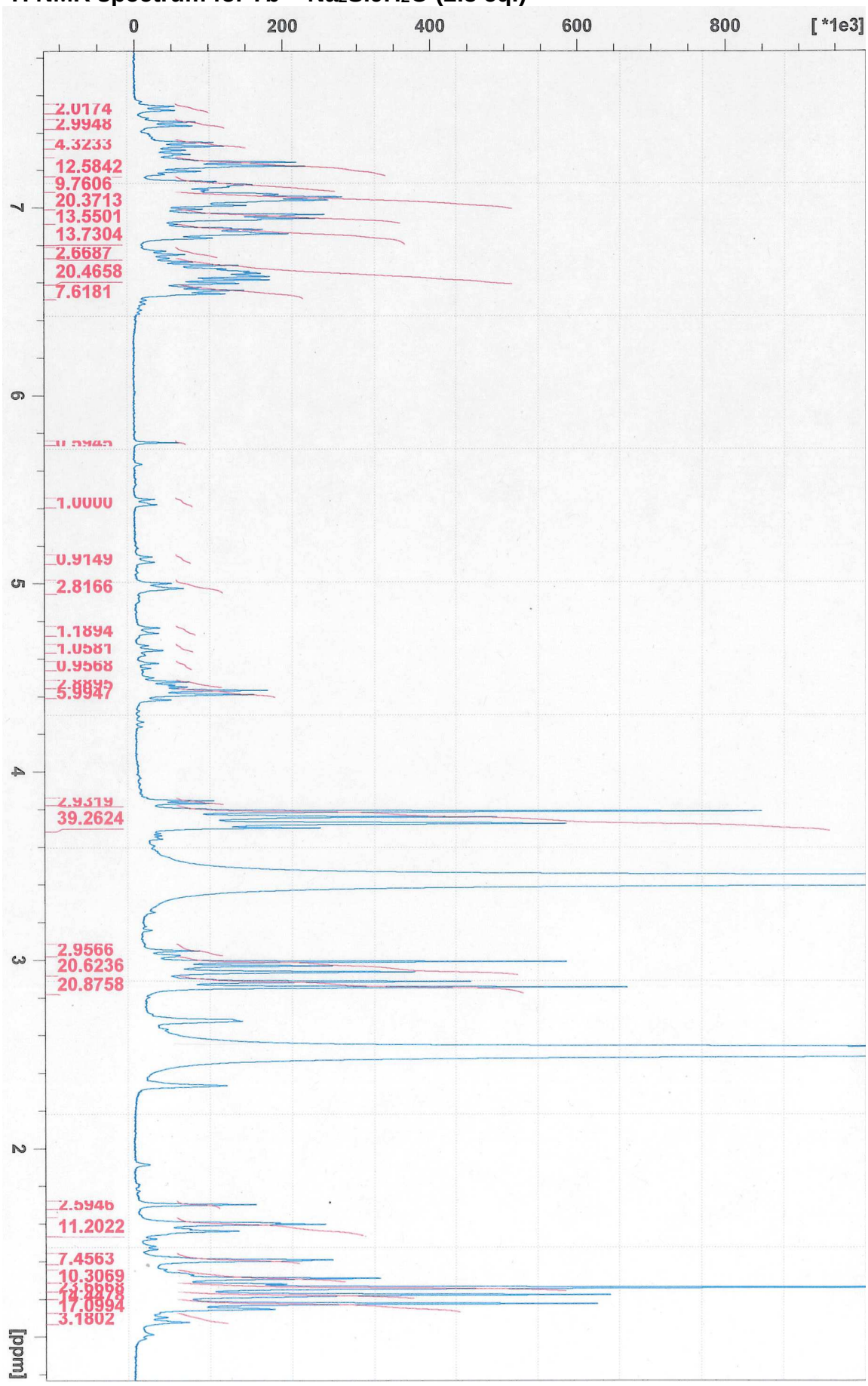
^{1}H NMR spectrum for 7b + $Na_2S.9H_2O$ (0.5 eq.)



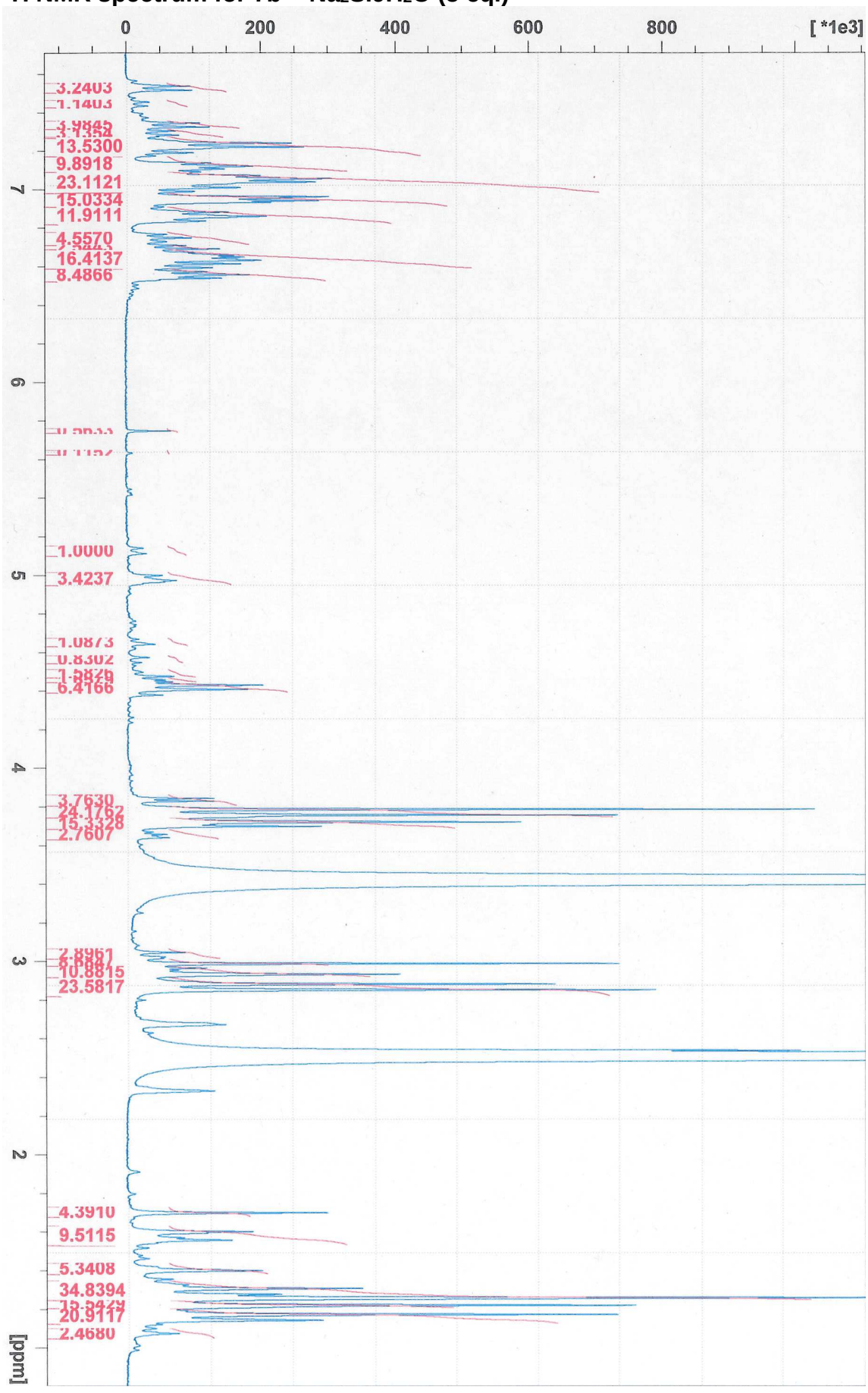
^{1}H NMR spectrum for 7b + $Na_2S.9H_2O$ (1.5 eq.)



^{1}H NMR spectrum for 7b + $Na_2S.9H_2O$ (2.5 eq.)

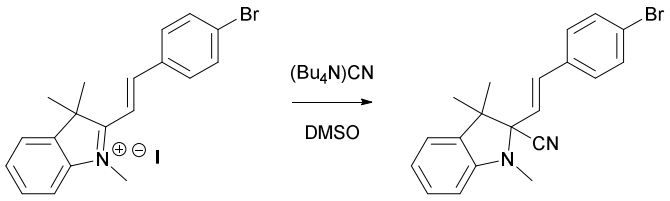


^{1}H NMR spectrum for 7b + $Na_2S.9H_2O$ (5 eq.)



3.3 Reactions of 7c

Reaction with tetrabutylammonium cyanide



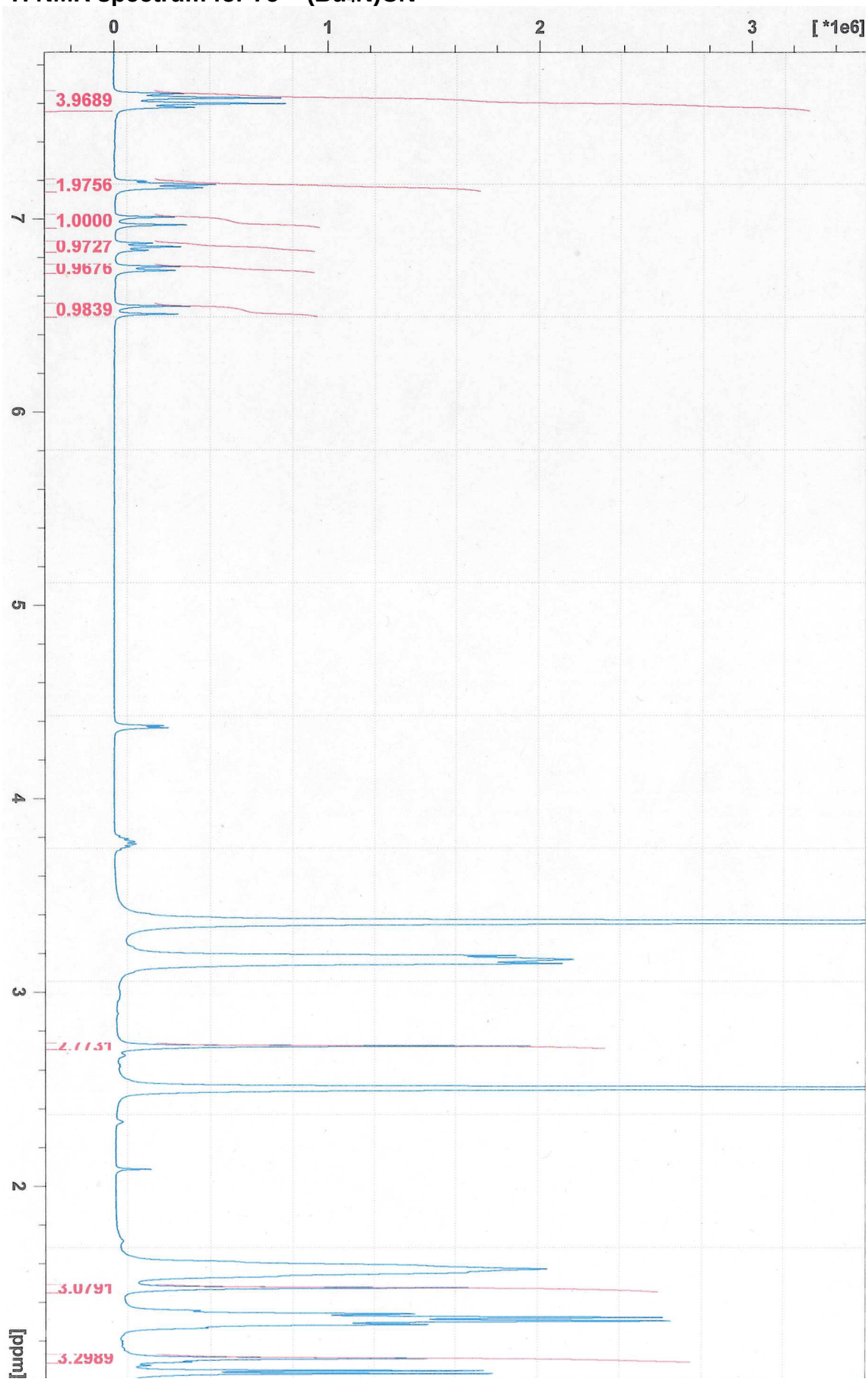
7c **8c**

Data for (*E*)-2-(4-bromostyryl)-1,3,3-trimethylindoline-2-carbonitrile 8c

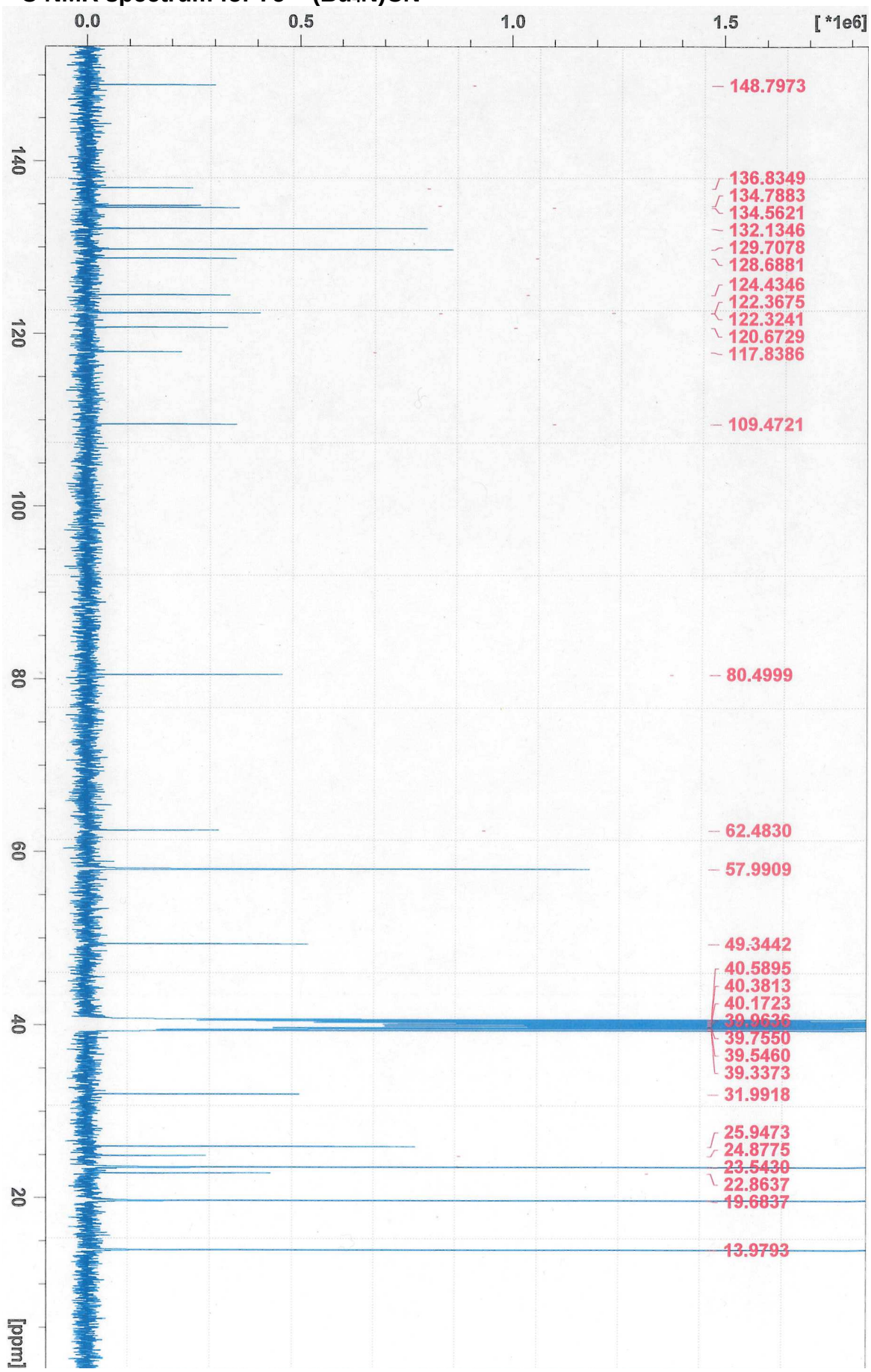
δH (400 MHz; DMSO-d_6) 7.64 (2 H, d, *J* 8.5, 2'- and 6'-H), 7.59 (2 H, d, *J* 8.5, 3'- and 5'-H), 7.20-7.15 (2 H, m, 4- and 6-H), 6.99 (1 H, d, *J* 16.2, β-H), 6.86 (1 H, t, *J* 7.5, 5-H), 6.74 (1 H, d, *J* 7.5, 7-H), 6.53 (1 H, d, *J* 16.2, α-H), 2.74 (3 H, s, NMe), 1.47 (3 H, s, CMe) and 1.10 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 148.8 (7a-C),136.8 (3a-C), 134.8 (β-C), 134.6, 132.1 (3'- and 5'-C), 129.7 (2'- and 6'-C), 128.7 (6-C), 124.4 (α-C), 122.4, 122.3 (4-C), 120.7 (5-C), 117.8 (CN), 109.4 (7-C), 80.5 (*C*CN), 49.3 (*C*Me_2), 32.0 (NMe), 24.9 (C*Me*) and 22.9 (C*Me*).

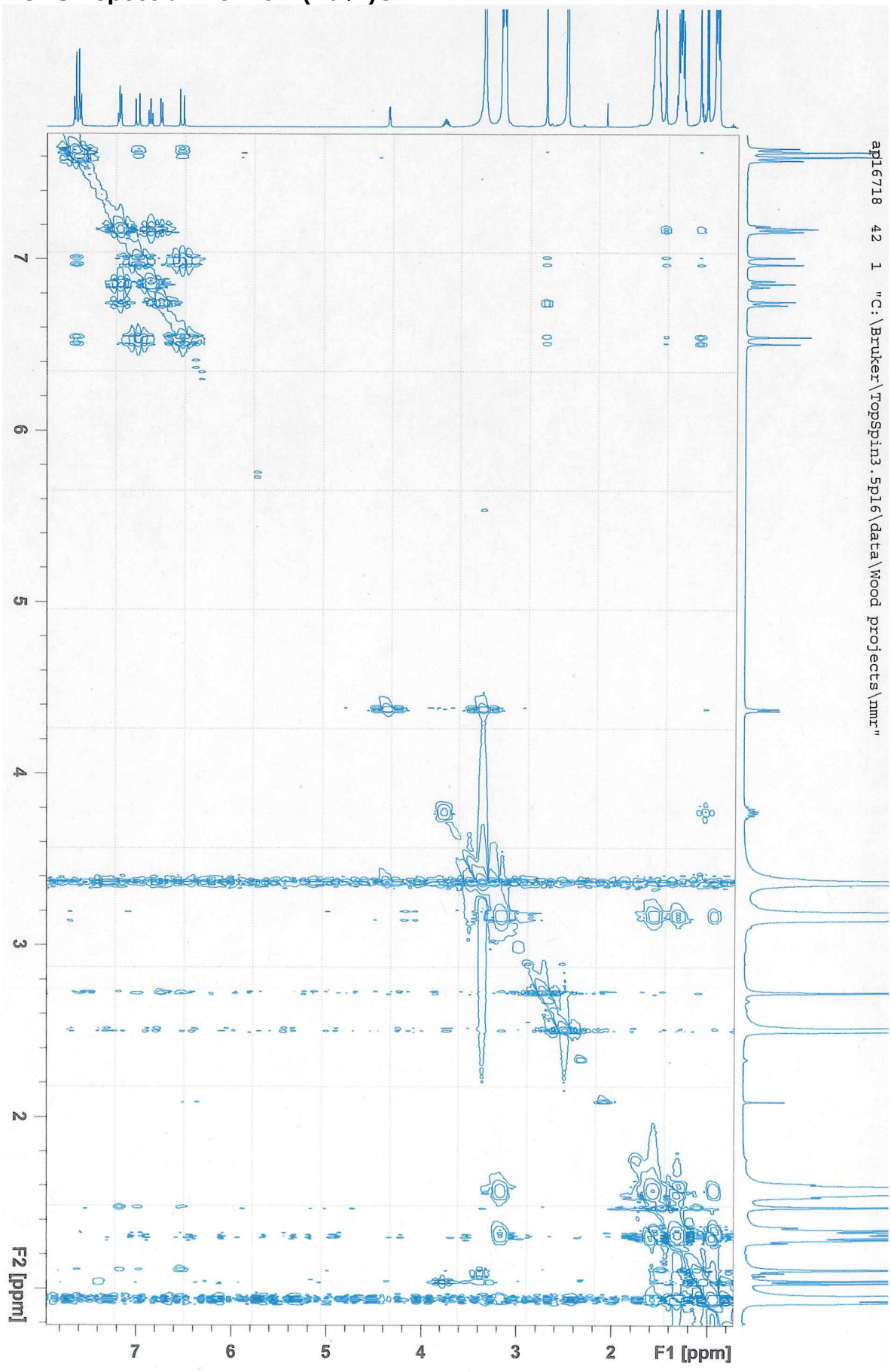
^{1}H NMR spectrum for 7c + (Bu_4N)CN



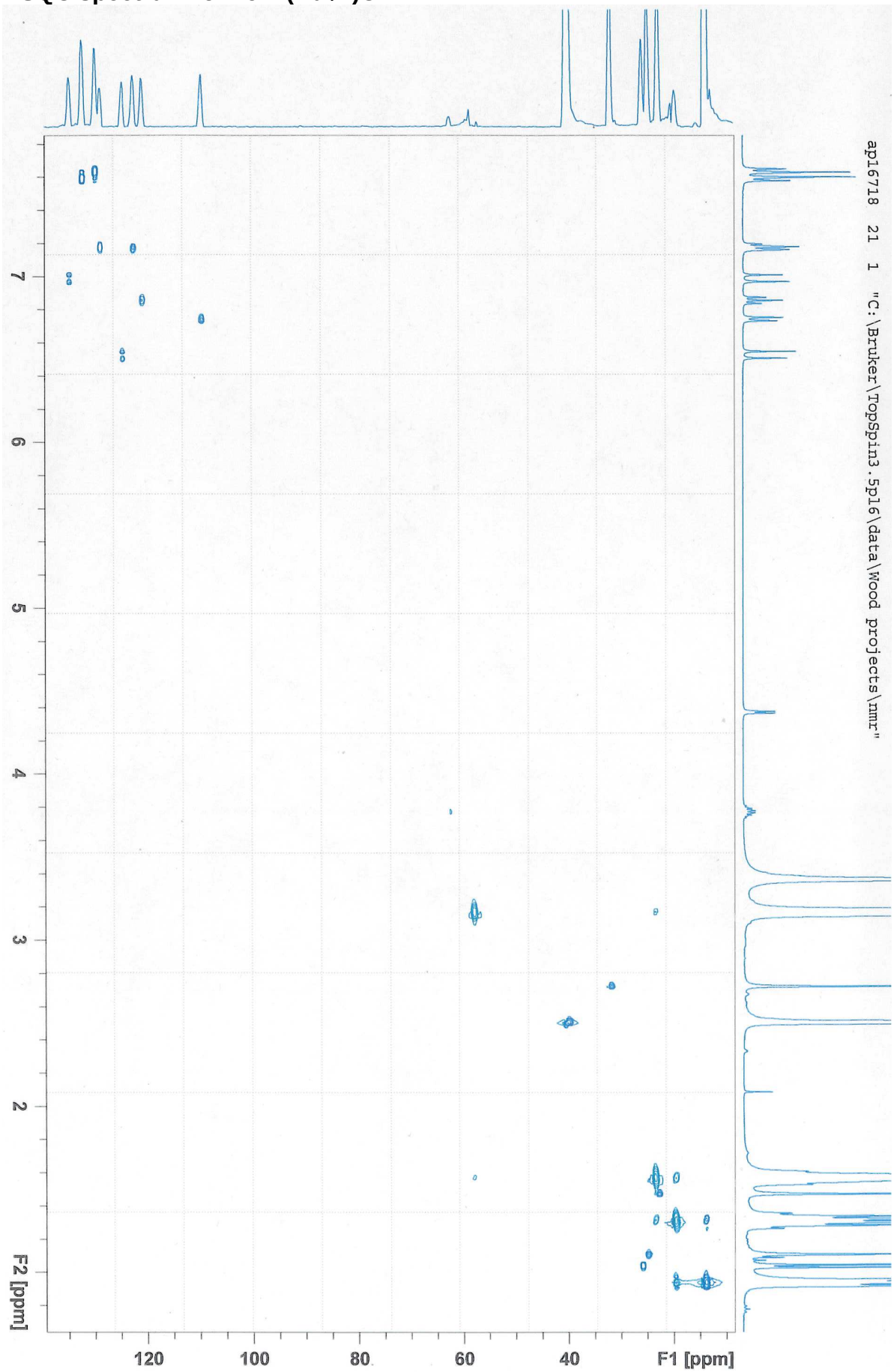
^{13}C NMR spectrum for 7c + (Bu_4N)CN



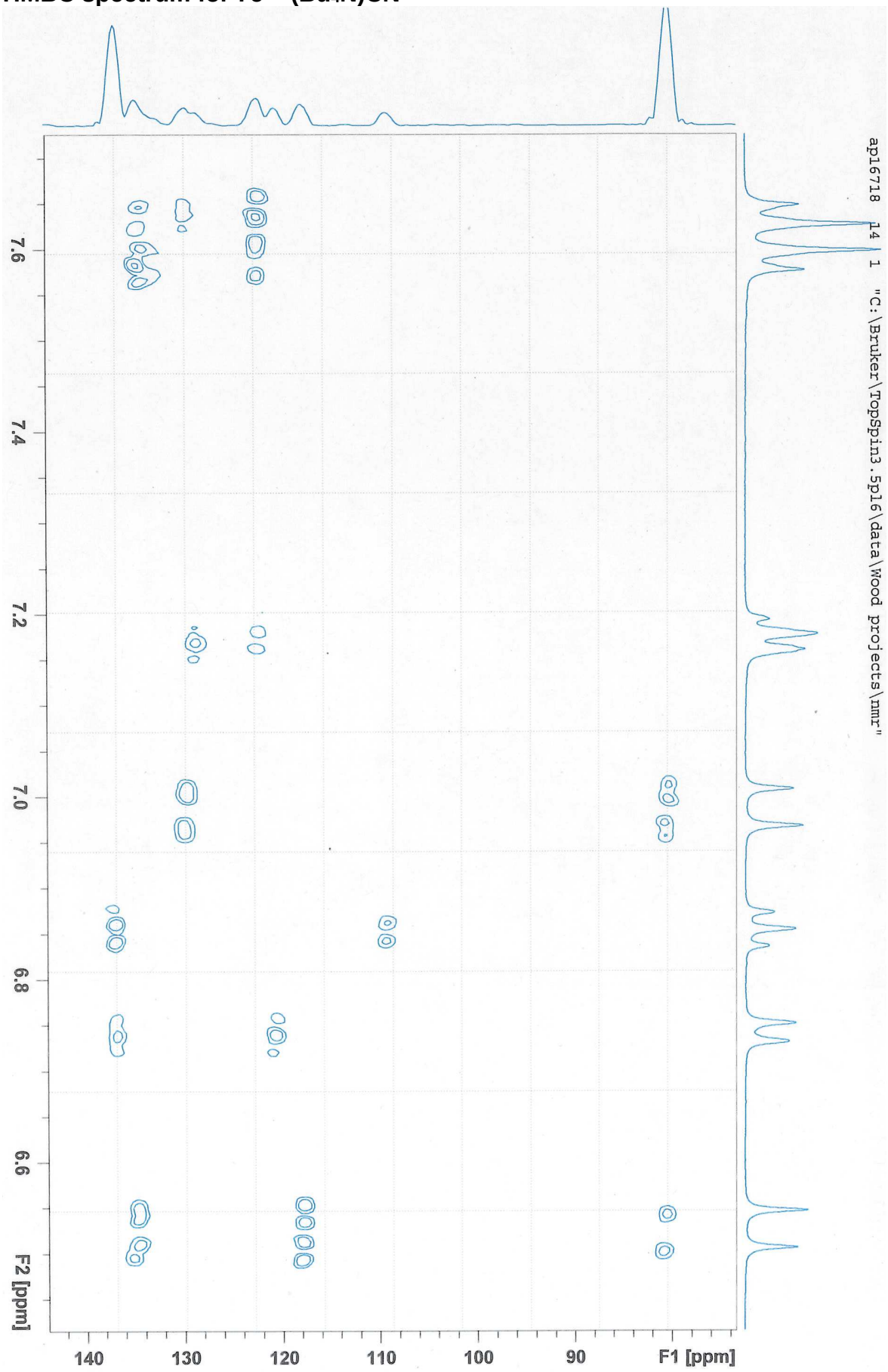
NOESY spectrum for 7c + (Bu_4N)CN



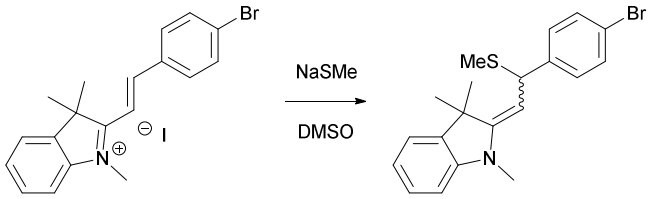
HSQC spectrum for 7c + (Bu_4N)CN



HMBC spectrum for 7c + (Bu_4N)CN



Reaction with sodium methanethiolate



7c **9c**

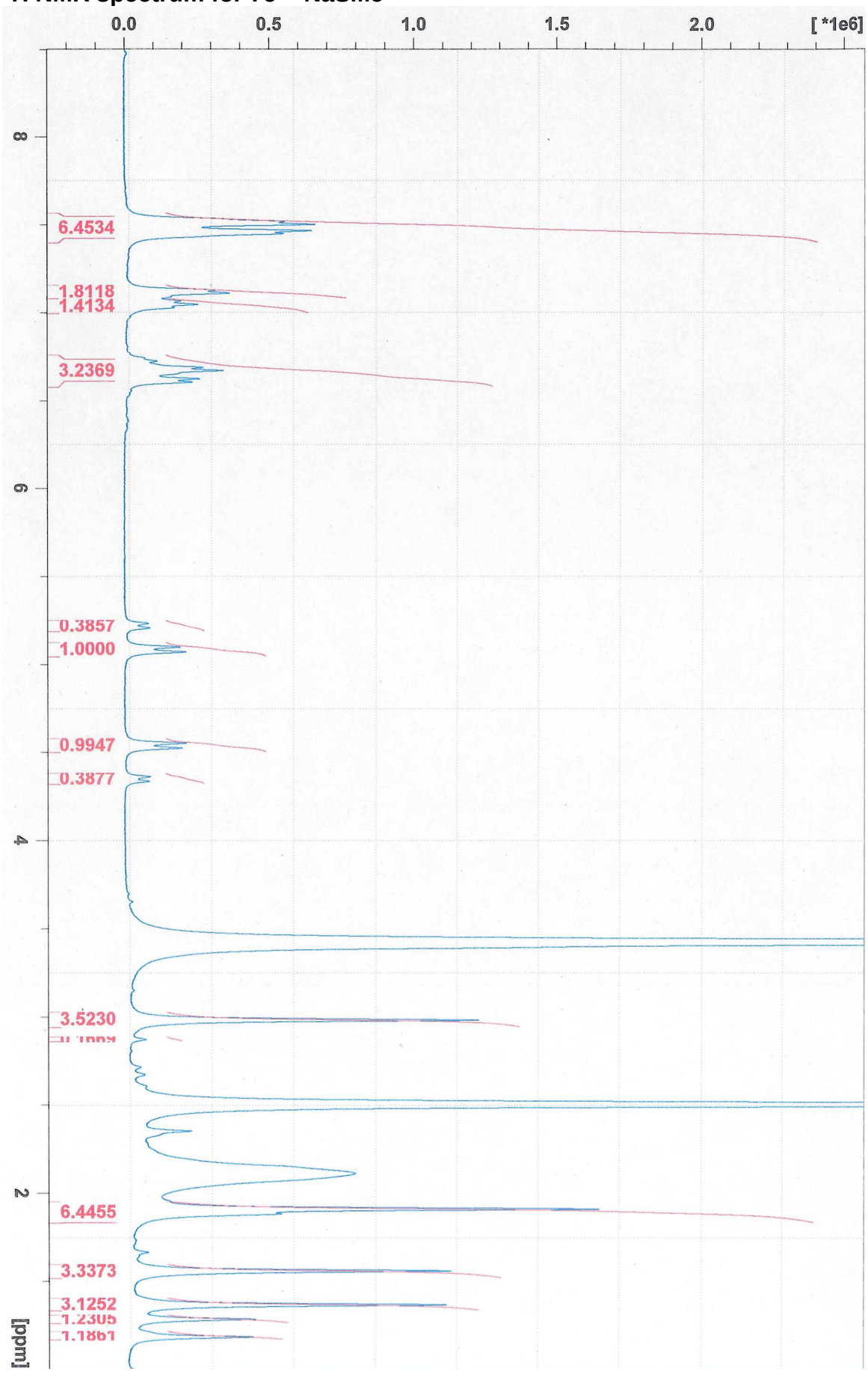
Data for 2-(2-(4-bromophenyl)-2-(methylthio)ethylidene)-1,3,3-trimethylindoline 9c

δH (400 MHz; DMSO-d_6; 29:71 *Z*:*E*) 7.51 (4 H, d, *J* 6.4, 2'- and 6'-H (*E* and *Z*)), 7.46 (4 H, d, *J* 6.4, 3'- and 5'-H (*E* and *Z*)), 7.12 (1 H, d, *J* 7.0, 4-H(*E*)), 7.05 (1 H, t, *J* 7.0, 6-H(*E*)), 6.73 (1 H, t, *J* 7.1, 5-H(*Z*)), 6.67 (2 H, t, *J* 7.0, 5-H(*E*) and 7-H(*Z*)), 6.62 (1 H, d, *J* 7.0, 7-H(*E*)), 5.22 (1 H, d, *J* 10.3, β-H(*Z*)), 5.09 (1 H, d, *J* 11.2, β-H(*E*)), 4.54 (1 H, d, *J* 11.2, α-H(*E*)), 4.35 (1 H, d, *J* 10.3, α-H(*Z*)), 3.42 (3 H, s, NMe(*Z*)), 2.98 (3 H, s, NMe(*E*)), 1.82 (3 H, s, SMe(*Z*)), 1.81 (3 H, s, SMe(*E*)), 1.55 (3 H, s, CMe(*E*)), 1.38 (3 H, s, CMe(*E*)), 1.30 (3 H, s, CMe(*Z*)) and 1.21 (3 H, s, CMe(*Z*)).

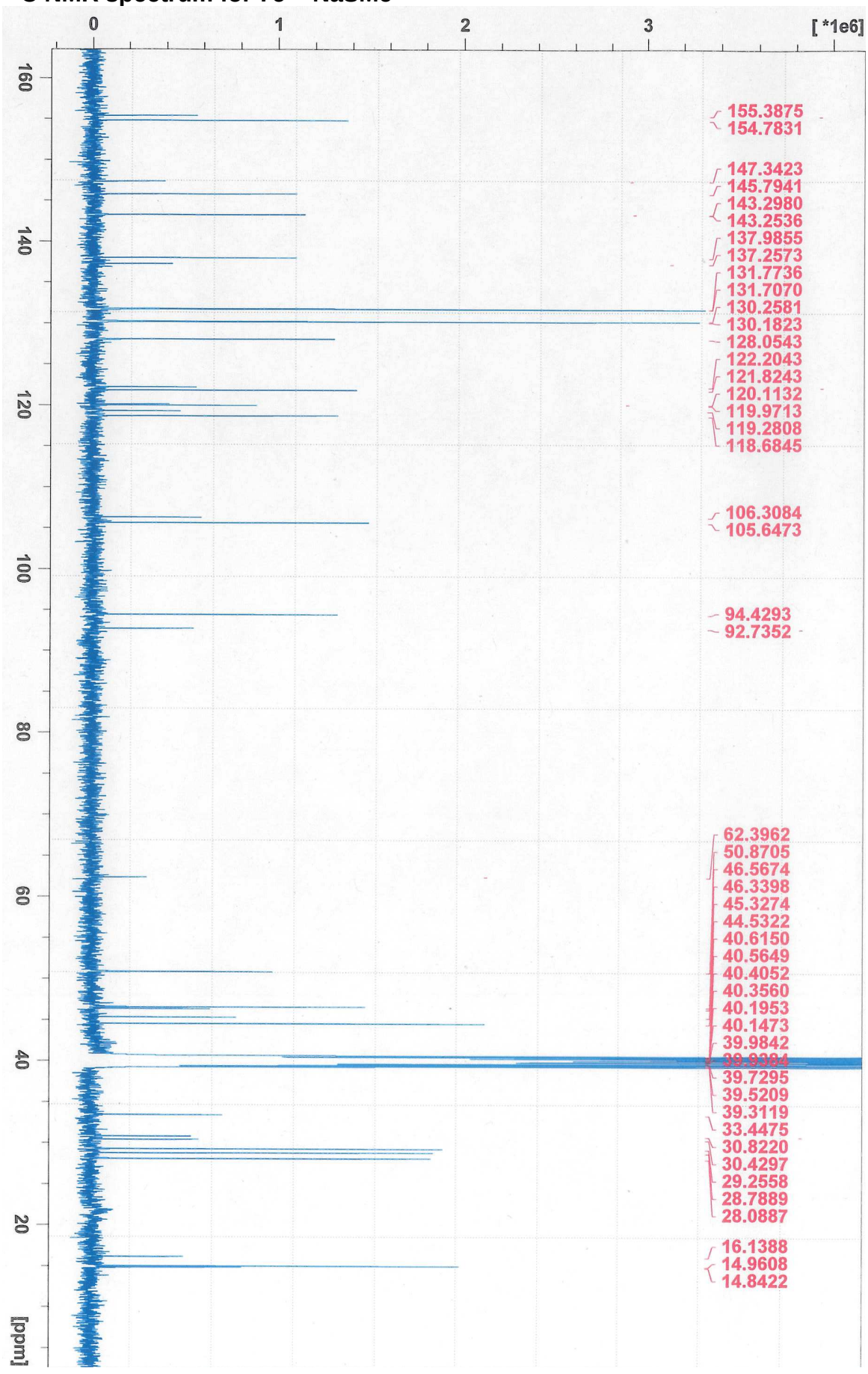
δC (100 MHz; DMSO-d_6); (*E*)-isomer: 154.8 (2-C), 145.8 (7a-C), 143.3 (1'-C), 138.0 (3a-C), 131.7 (2'- and 6'-C), 130.2 (3'- and 5'-C), 128.1 (6-C), 121.8 (4-C), 120.0 (4'-C), 118.7 (5-C), 105.6 (7-C), 94.4 (α-C), 50.9 (SMe), 46.6 (β-C), 44.5 (*C*Me_2), 29.3 (NMe), 28.8 (C*Me*) and 28.1 (C*Me*);
(*Z*)-isomer: 155.4 (2-C), 147.3 (7a-C), 143.3 (1'-C), 137.3 (3a-C), 131.8 (2'- and 6'-C), 130.3 (3'- and 5'-C), 128.1 (6-C), 122.2 (4-C), 120.1 (4'-C), 119.3 (5-C), 106.3 (7-C), 92.7 (α-C), 50.9 (SMe), 46.3 (β-C), 45.3 (*C*Me_2), 33.4 (NMe), 30.8 (C*Me*) and 30.4 (C*Me*).

LRMS-ES+ (*m/z*): 389 (5%, M{^{81}Br}$^+$), 387 (5%, M{^{79}Br}$^+$), 342 (80%, M{^{81}Br}$^+$−SCH_3), 340 (78%, M{^{79}Br}$^+$−SCH_3).

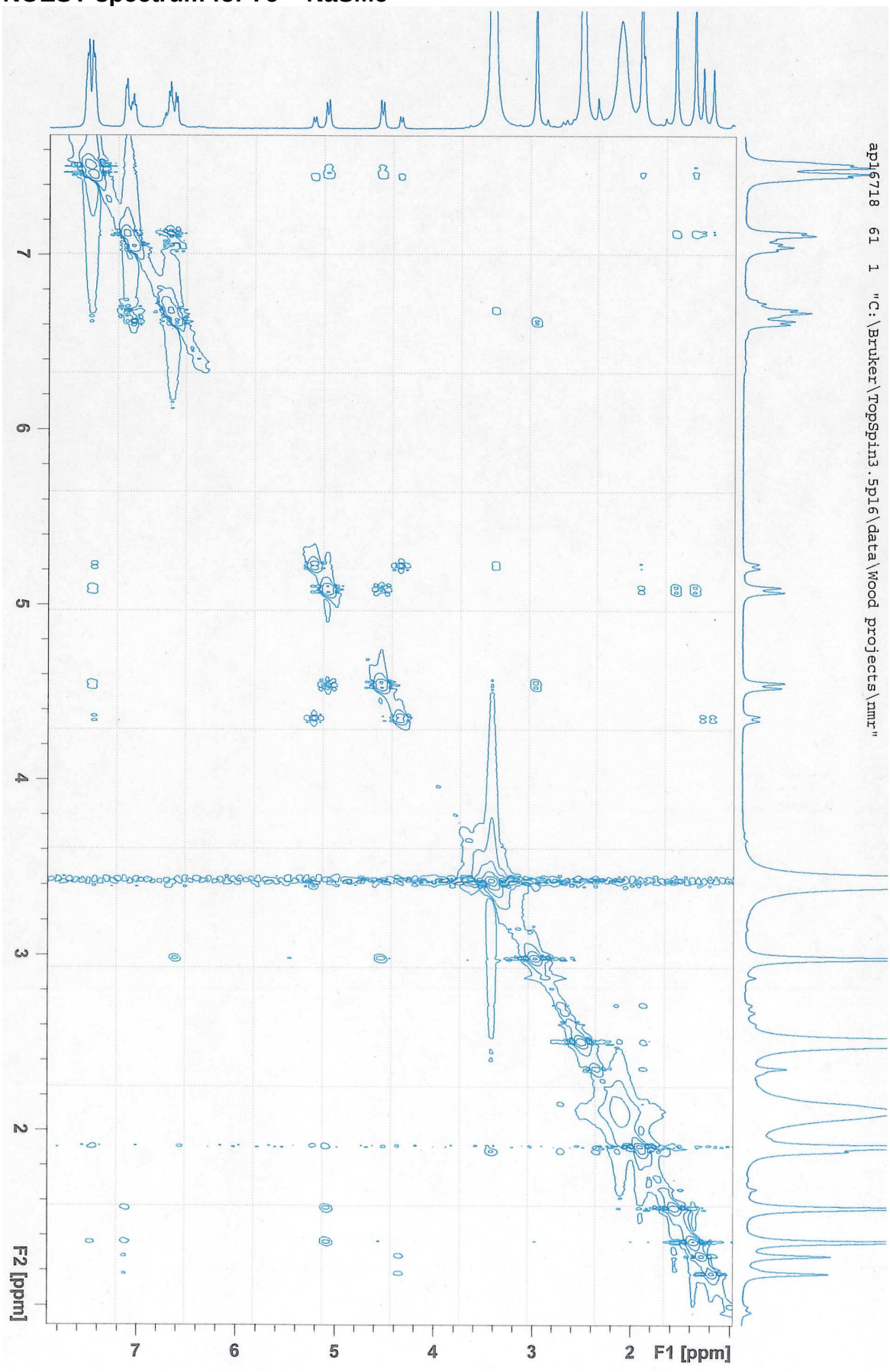
^{1}H NMR spectrum for 7c + NaSMe



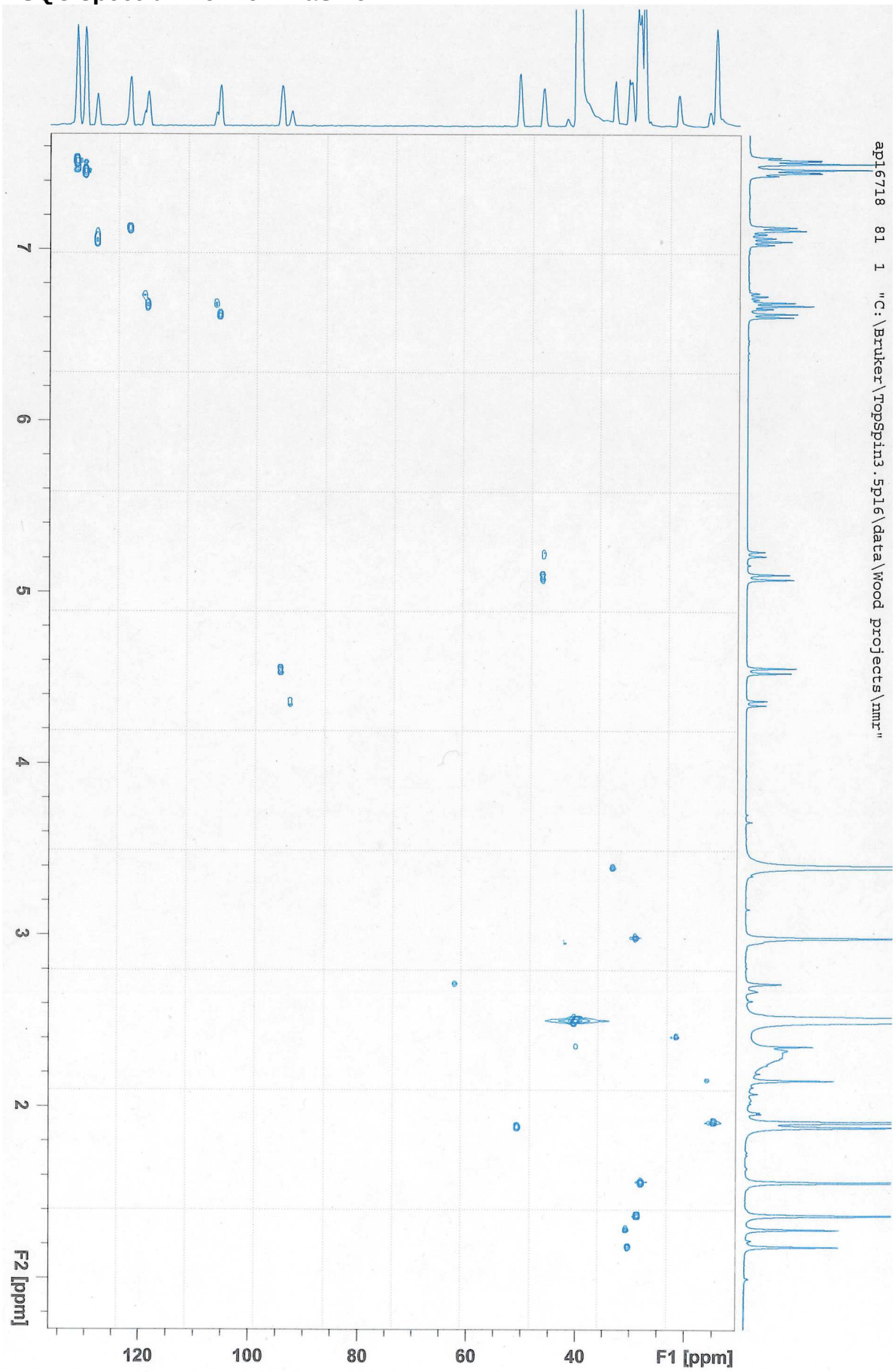
^{13}C NMR spectrum for 7c + NaSMe



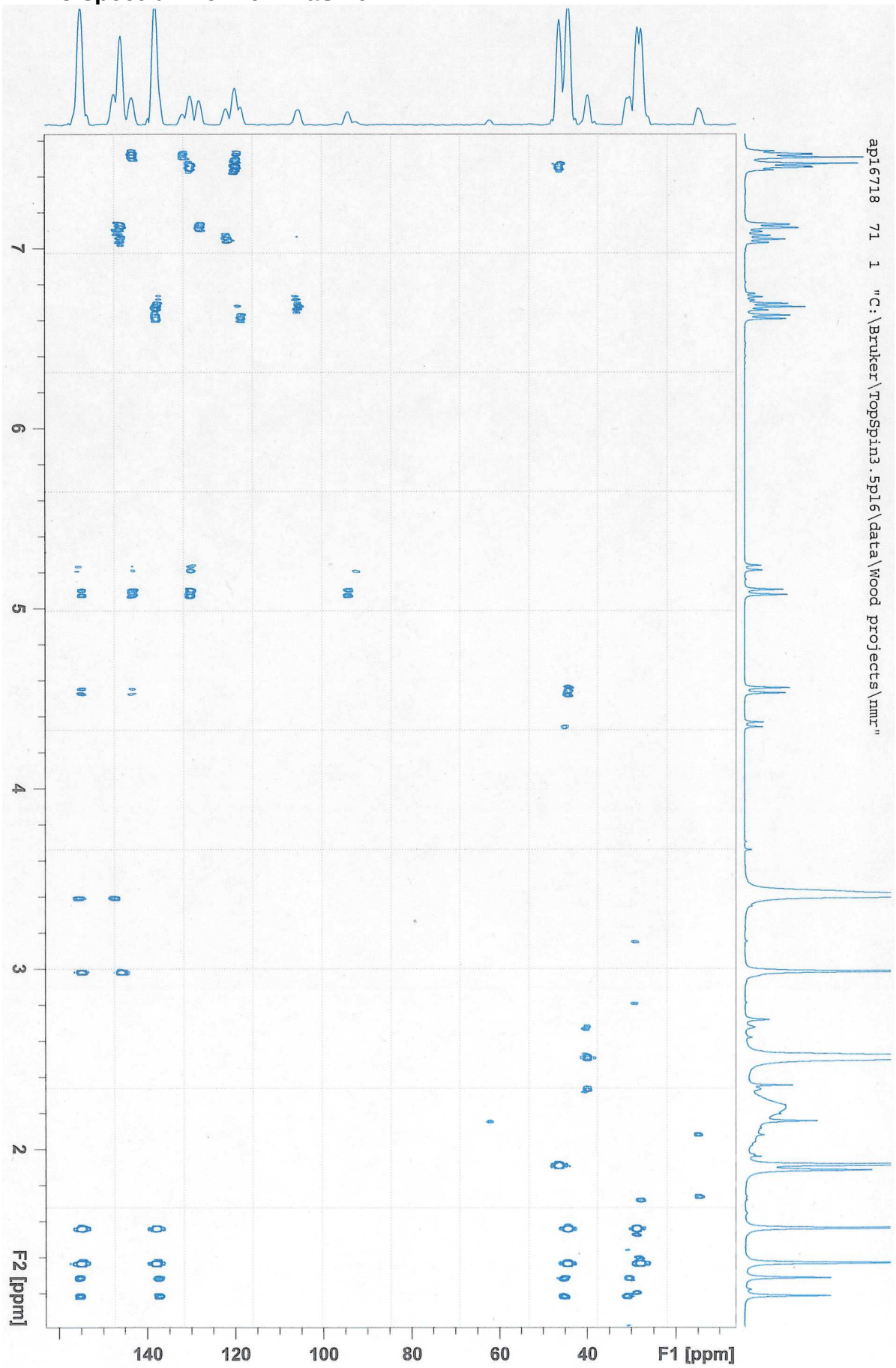
NOESY spectrum for 7c + NaSMe



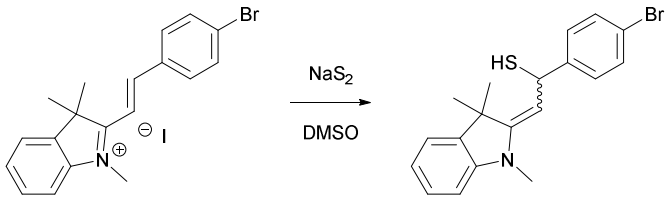
HSQC spectrum for 7c + NaSMe



HMBC spectrum for 7c + NaSMe



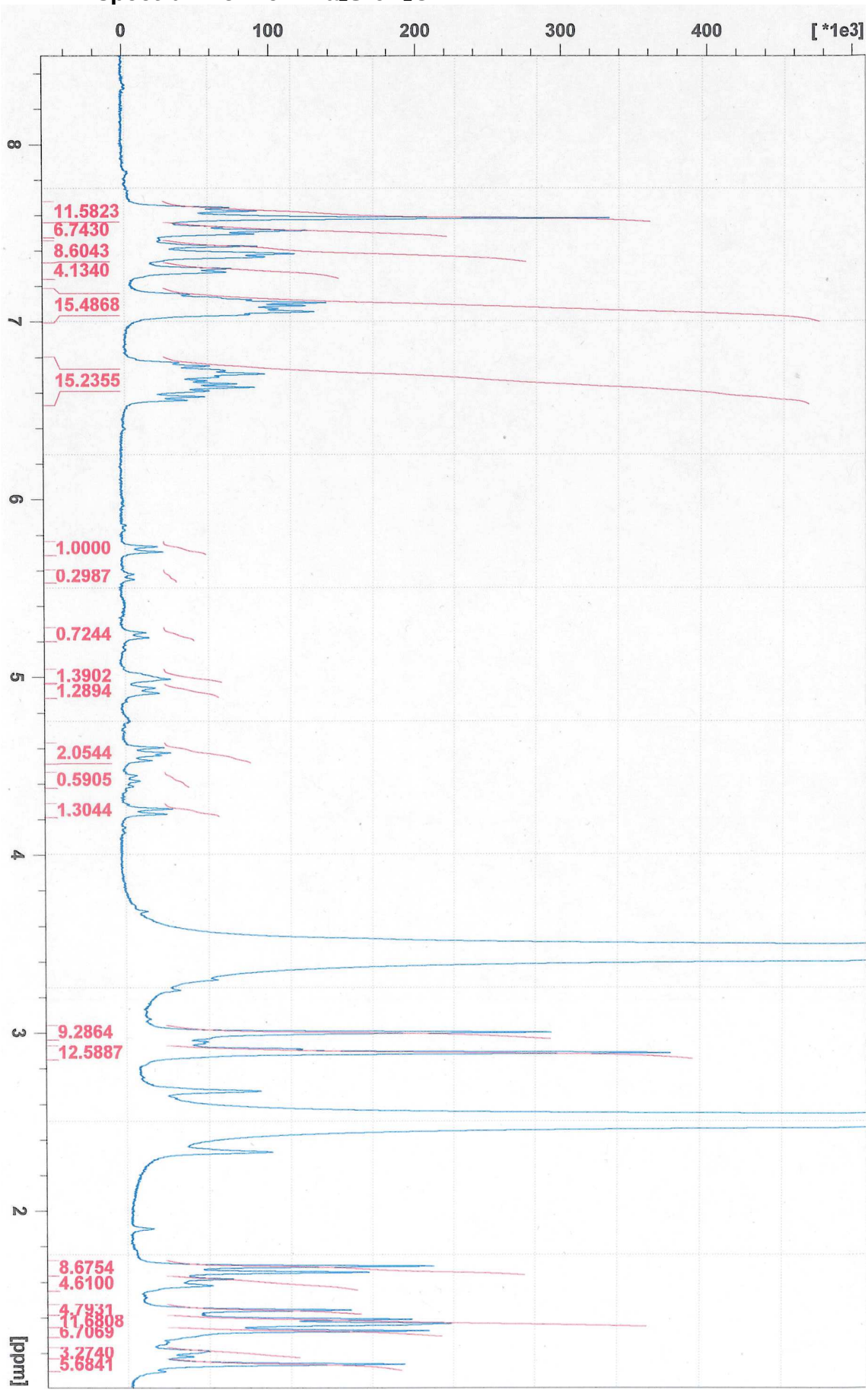
Reaction with sodium sulfide



7c **10c**

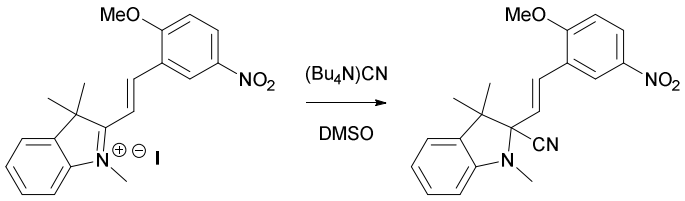
LRMS-ES+ (*m/z*): 342 (8%, M{^{81}Br}$^{+}$−SH), 340 (7%, M{^{79}Br}$^{+}$−SH), 262 (100%, M^{+}−SHBr).

^{1}H NMR spectrum for 7c + $Na_2S \cdot 9H_2O$



3.4 Reactions of 7d

Reaction with tetrabutylammonium cyanide



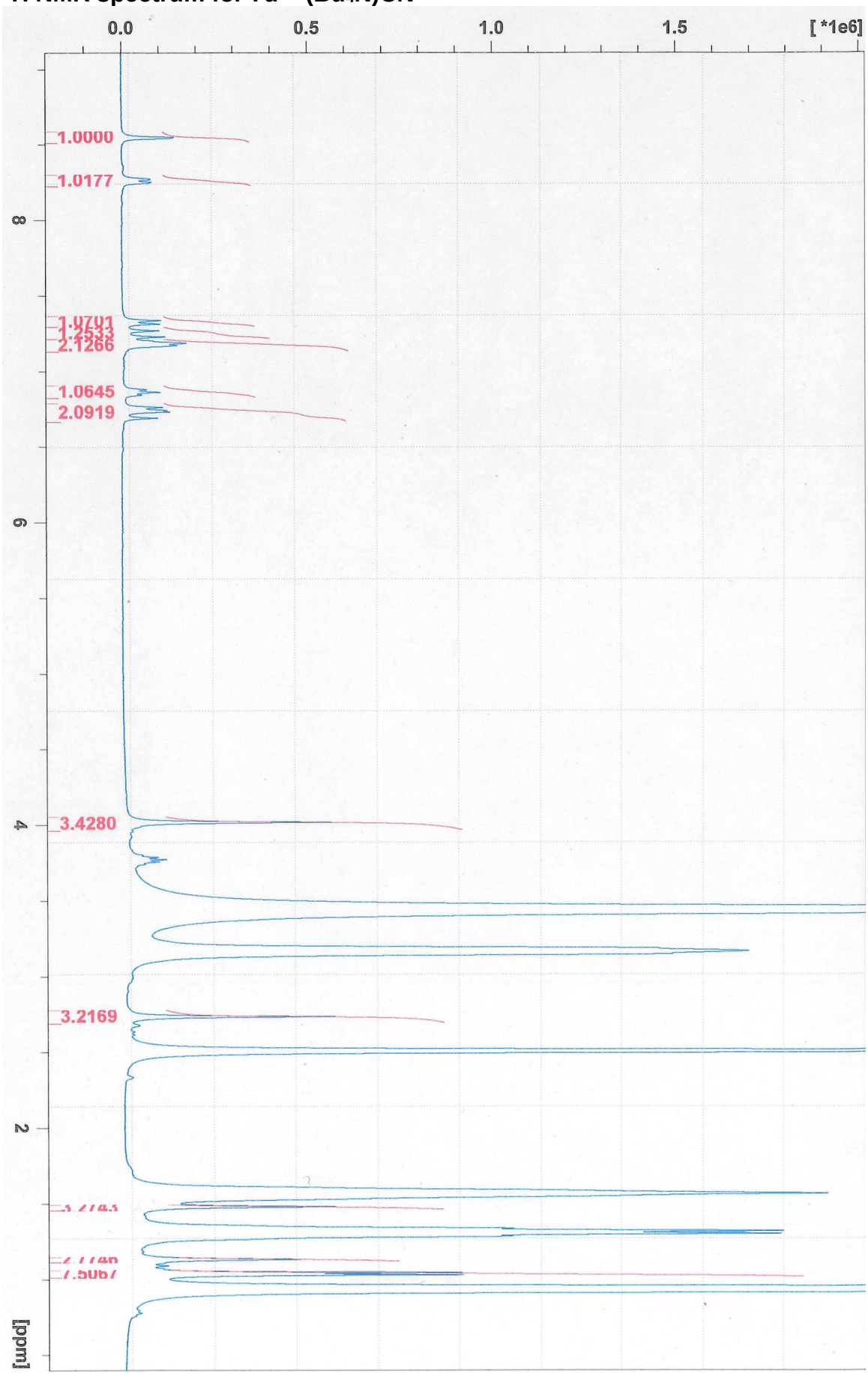
7d **8d**

Data for (*E*)-1,3,3-trimethyl-2-(2-methoxy-5-nitrostyryl)indoline-2-carbonitrile 8d

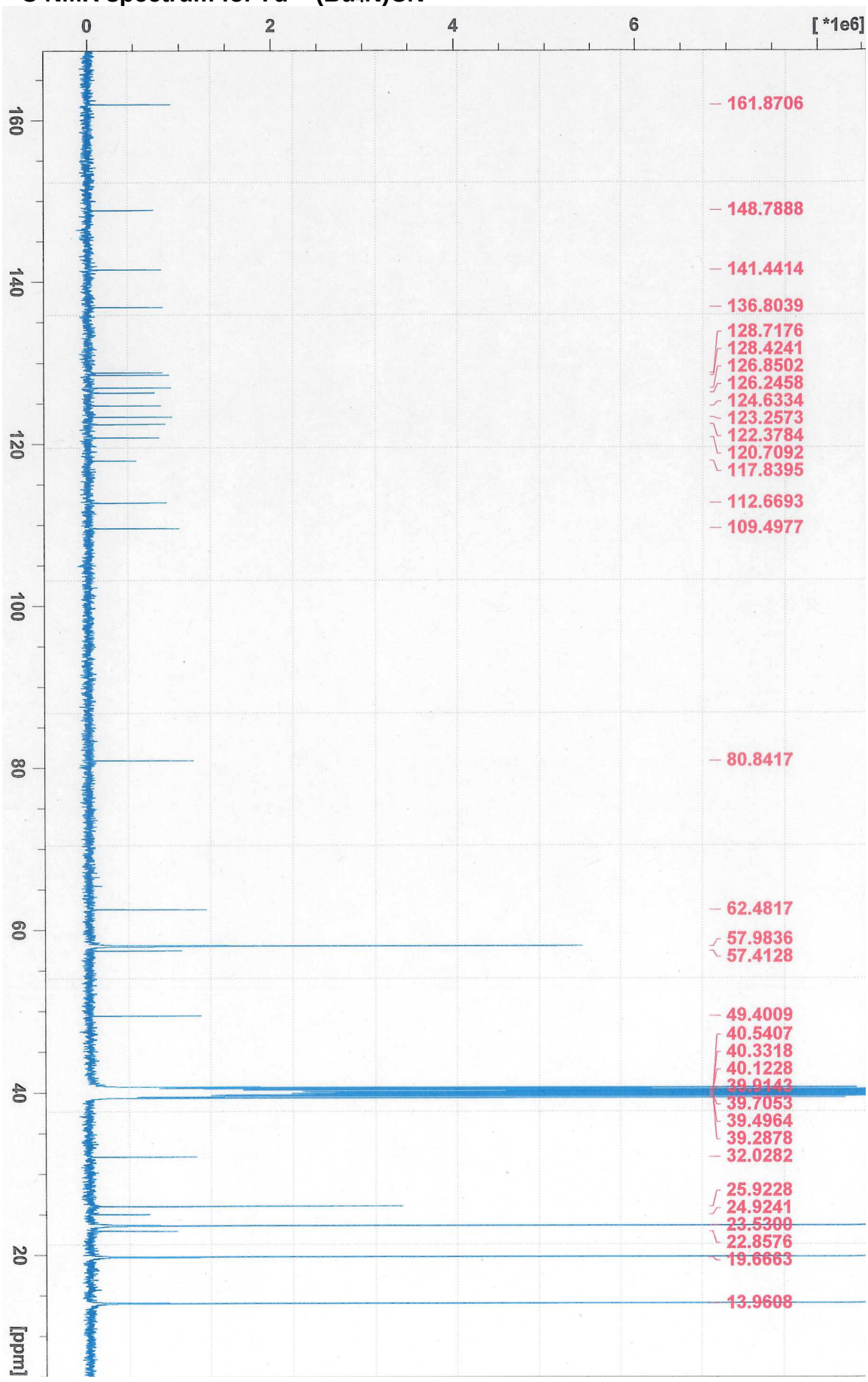
δH (400 MHz; DMSO-d_6) 8.55 (1 H, s, 6'-H), 8.26 (1 H, d, *J* 9.0, 4'-H), 7.38 (1 H, d, *J* 9.0, 3'-H), 7.25 (1 H, d, *J* 16.4, β-H), 7.23-7.13 (2 H, m, 4- and 6-H), 6.86 (1 H, t, *J* 7.5, 5-H), 6.75 (1 H, d, *J* 7.5, 7-H), 6.71 (1 H, d, *J* 16.4, α-H), 4.01 (3 H, s, OMe), 2.75 (3 H, s, NMe), 1.48 (3 H, s, CMe) and 1.16 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 161.9 (2'-C), 148.8 (7a-C), 141.4 (5'-C), 136.8 (3a-C), 128.7 (6-C), 128.4 (β-C), 126.9 (α-C), 126.2 (4'-C), 124.6 (1'-C), 123.3 (6'-C), 122.4 (4-C), 120.7 (5-C), 117.8 (CN), 112.7 (3'-C), 109.5 (7-C), 80.8 (*C*CN), 57.4 (OMe), 49.4 (*C*Me_2), 32.0 (NMe), 24.9 (C*Me*) and 22.9 (C*Me*).

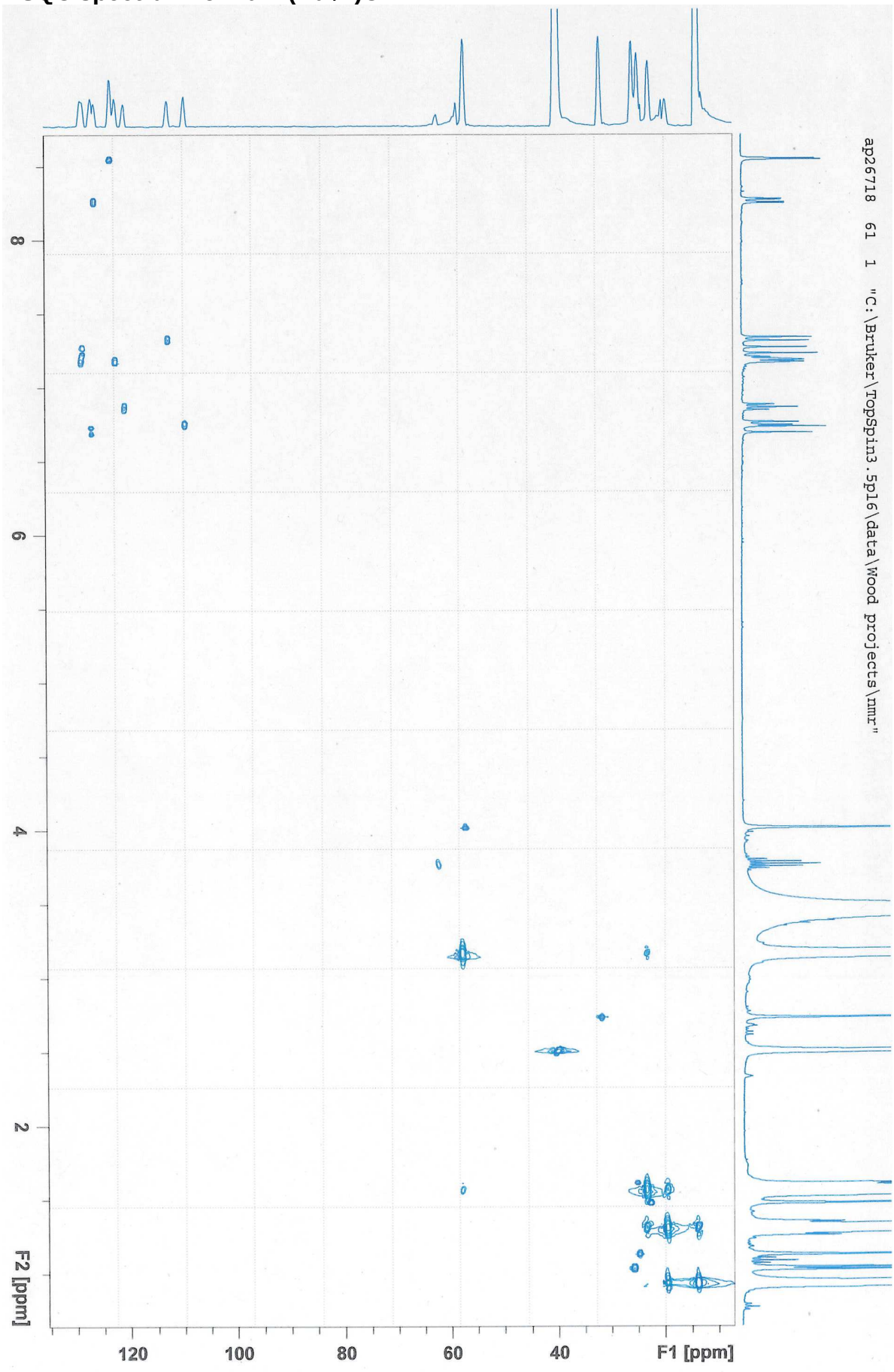
^{1}H NMR spectrum for 7d + (Bu_4N)CN



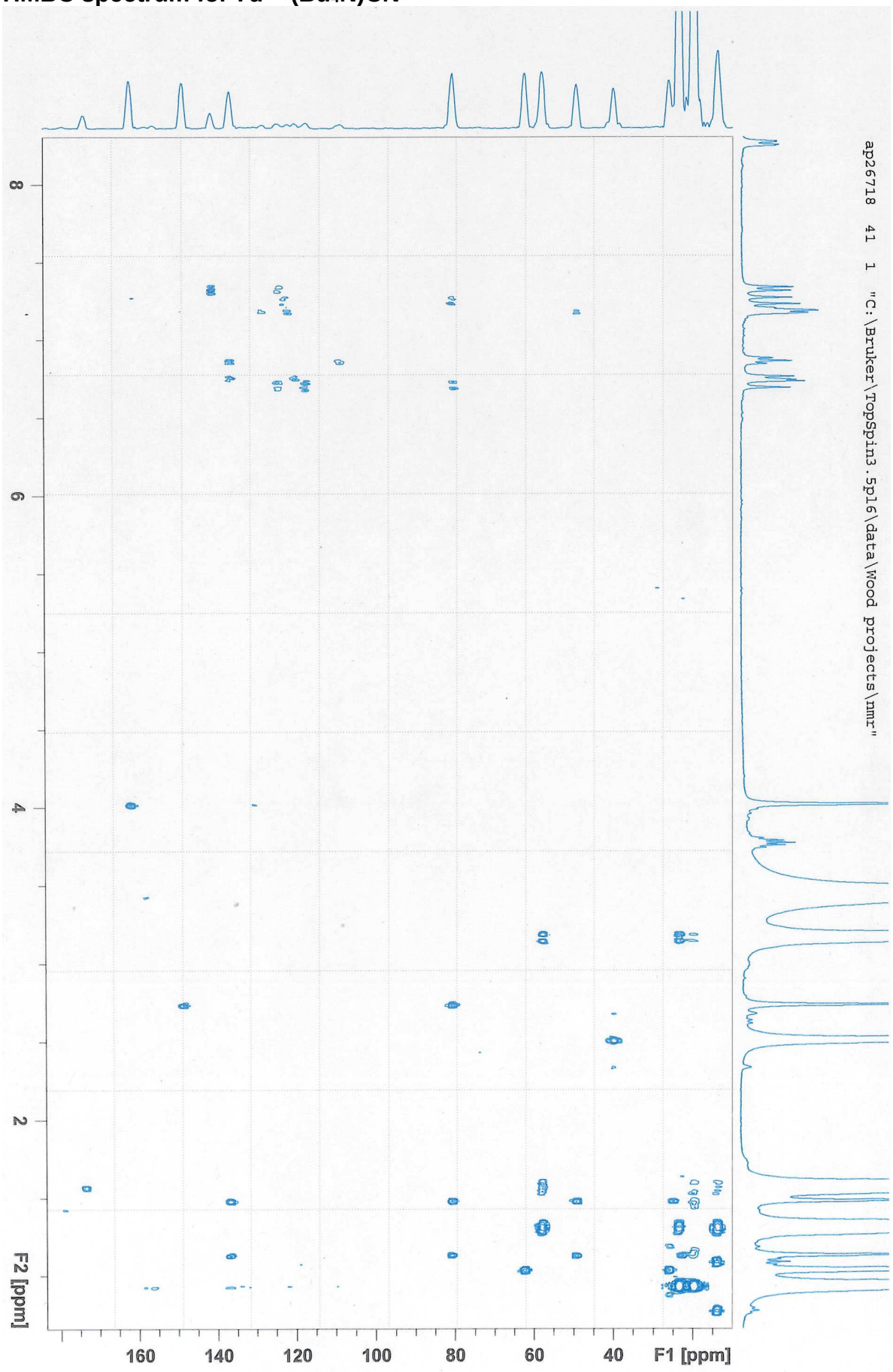
^{13}C NMR spectrum for 7d + (Bu_4N)CN



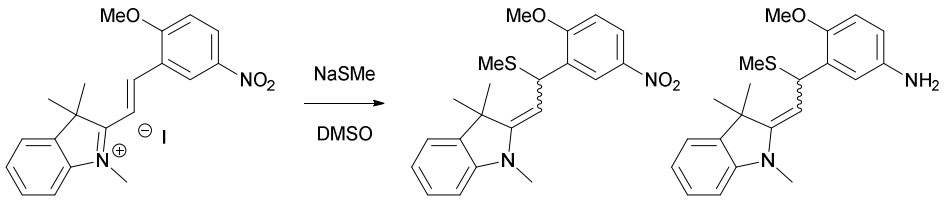
HSQC spectrum for 7d + (Bu_4N)CN



HMBC spectrum for 7d + (Bu_4N)CN



Reaction with sodium methanethiolate



7d **9d** **9i**

Data for initial product: 2-(2-(2-methoxy-5-nitrophenyl)-2-(methylthio)ethylidene)-1,3,3-trimethylindoline 9d

δH (400 MHz; DMSO-d_6; *Z*:*E* ratio unclear) 8.40 (1 H, br s, 6'-H), 8.15 (1 H, br s, 4'-H), 7.22 (1 H, br s, 3'-H), 7.10-6.90 (2 H, m, 4- and 6-H), 6.75-6.50 (2 H, m, 5- and 7-H), 5.50 (1 H, br s, β-H), 5.59 (1 H, d, *J* 11.6, β-H(*E*)), 4.57 (1 H, br s, α-H), 3.98 (3 H, br s, OMe), 2.97 (3 H, br s, NMe), 1.85 (3 H, br s, SMe), 1.54 (3 H, br s, CMe) and 1.30 (3 H, s, CMe).

LRMS-ES+ (*m/z*): 385 (4%, MH^+), 340 (73%, M^+-SMe).

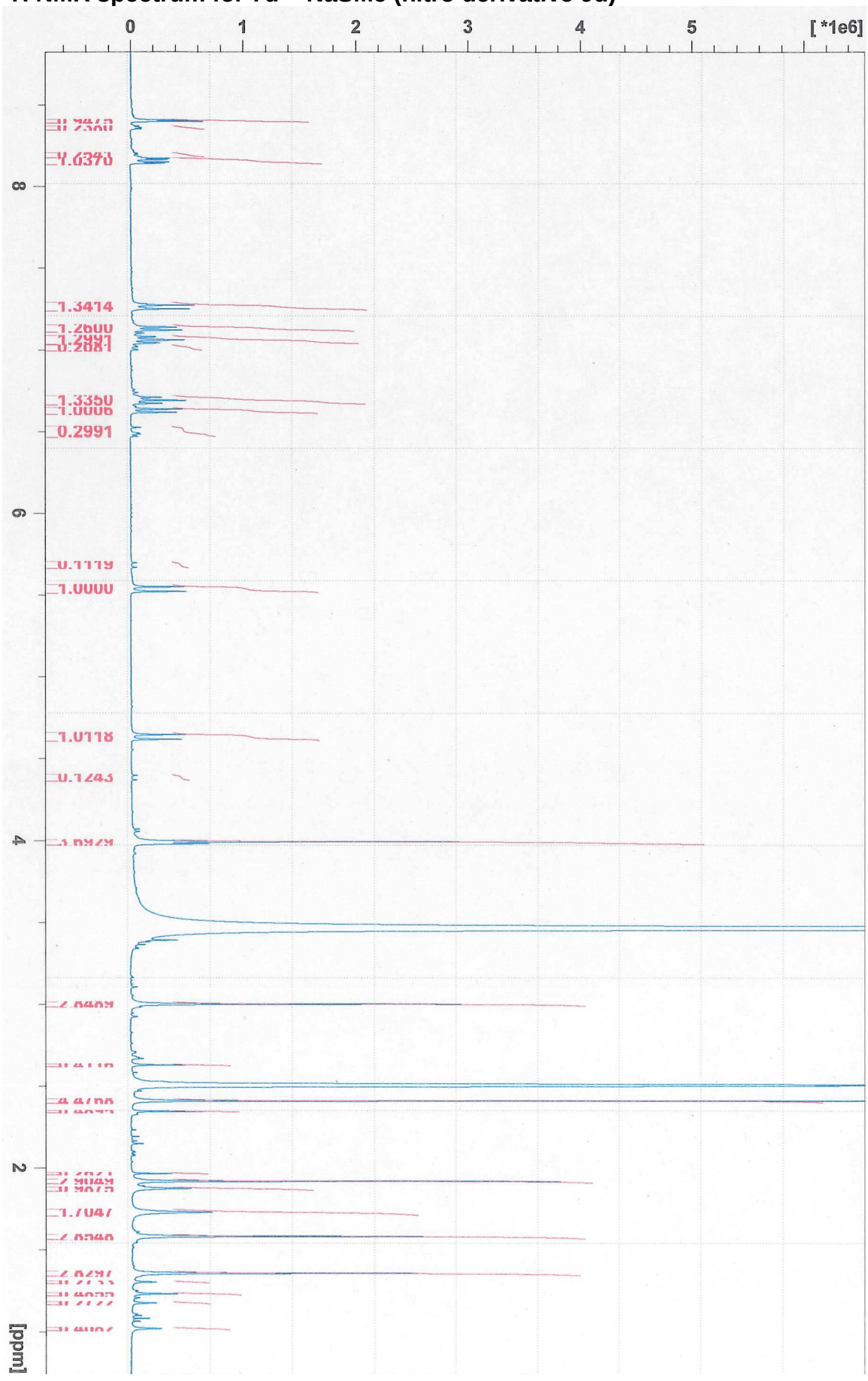
Data for reduced product: 4-methoxy-3-(1-(methylthio)-2-(1,3,3-trimethylindolin-2-ylidene)ethyl)aniline 9i

δH (400 MHz; DMSO-d_6; 9:91 *Z*:*E*) 7.96 (1 H, d, *J* 3.1, 6'-H(*E*)), 7.65 (1 H, dd, *J* 9.4 and 3.1, 4'-H(*E*)), 7.18-6.90 (2 H, m, 4- and 6-H(*E*)), 6.69 (1 H, t, *J* 7.1, 5-H(*Z*)), 6.64 (1 H, t, *J* 7.2, 5-H(*E*)), 6.58 (1 H, d, *J* 7.2, 7-H(*E*)), 6.00 (1 H, d, *J* 9.4, 3'-H(*Z*)), 5.99 (1 H, d, *J* 9.4, 3'-H(*E*)), 5.70 (1 H, d, *J* 11.0, β-H(*Z*)), 5.59 (1 H, d, *J* 11.6, β-H(*E*)), 4.56 (1 H, d, *J* 11.6, α-H(*E*)), 4.29 (1 H, d, *J* 11.0, α-H(*Z*)), 3.68 (3 H, s, OMe(*Z*)), 3.49 (3 H, s, OMe(*E*)), 3.15 (3 H, s, NMe(*Z*)), 2.99 (3 H, s, NMe(*E*)), 1.87 (6 H, s, SMe(*E* and *Z*)), 1.51 (3 H, s, CMe(*E*)), 1.33 (3 H, s, CMe(*E*)), 1.27 (3 H, s, CMe(*Z*)) and 1.21 (3 H, s, CMe(*Z*)).

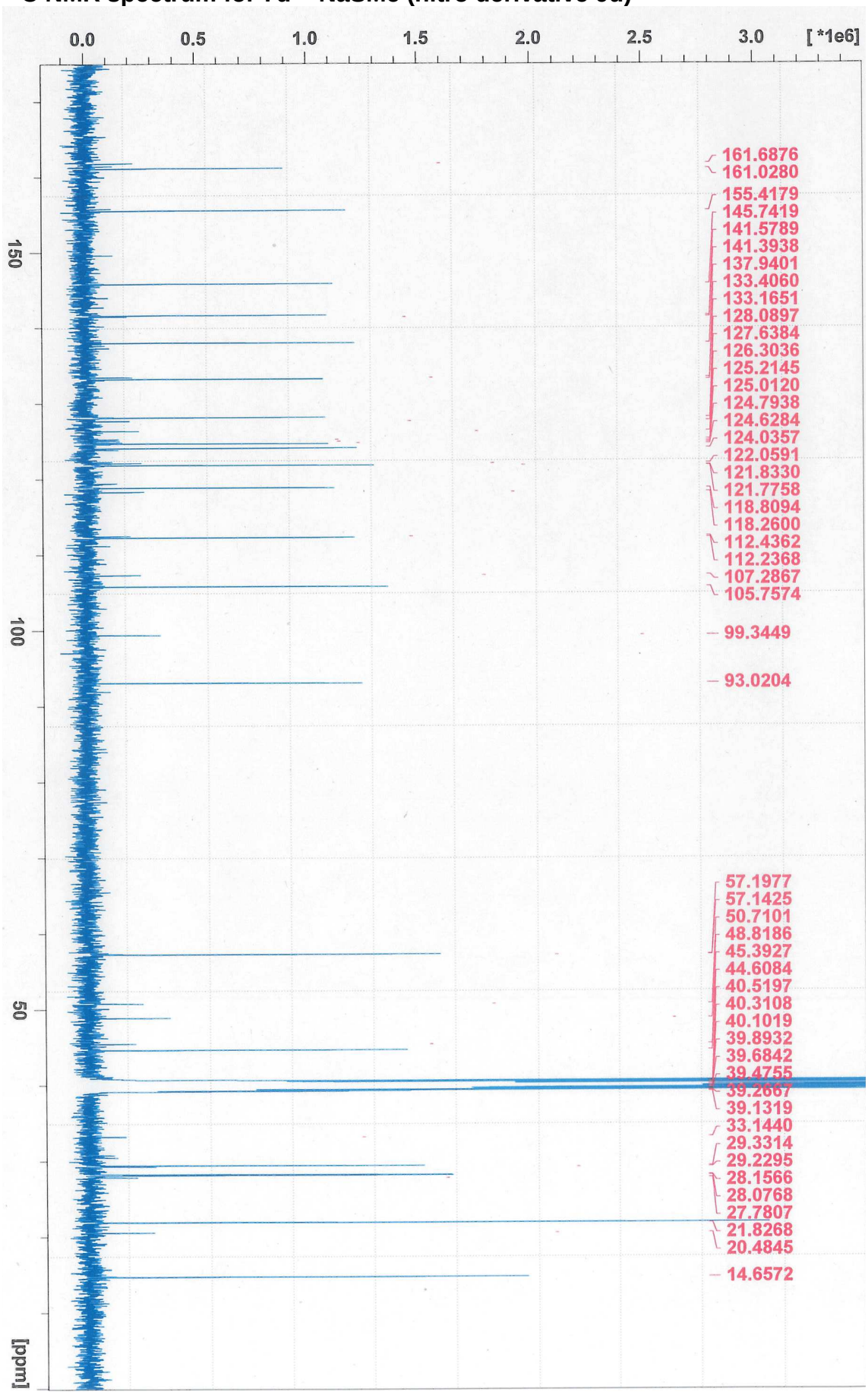
δC (100 MHz; DMSO-d_6; (*E*)-isomer only); 153.5 (2-C), 146.0 (7a-C), 138.4 (3a-C), 132.0 (2'-C), 128.1 (3'-C), 127.9 (6-C), 126.3 (4'-C), 125.4 (6'-C), 121.7 (4-C), 119.5, 118.8 (3'-C), 118.3 (5-C), 105.4 (7-C), 96.0 (α-C), 50.8 (SMe), 44.4 (*C*Me_2), 39.3 (β-C), 29.3 (NMe), 28.7 (C*Me*) and 28.0 (C*Me*).

LRMS-ES+ (*m/z*): 355 (36%, MH^+), 307 (73%, M^+-SMe).

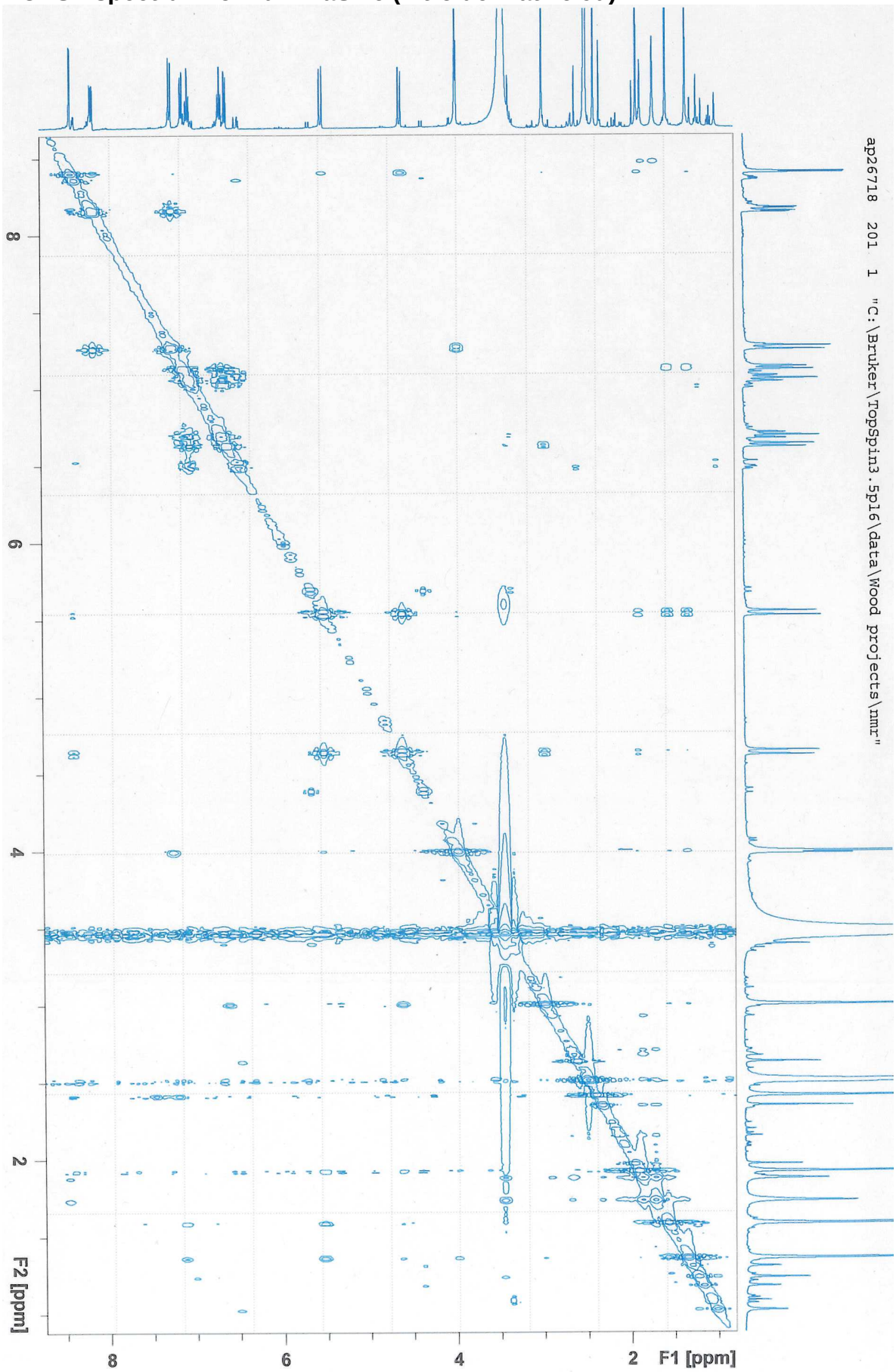
^{1}H NMR spectrum for 7d + NaSMe (nitro derivative 9d)



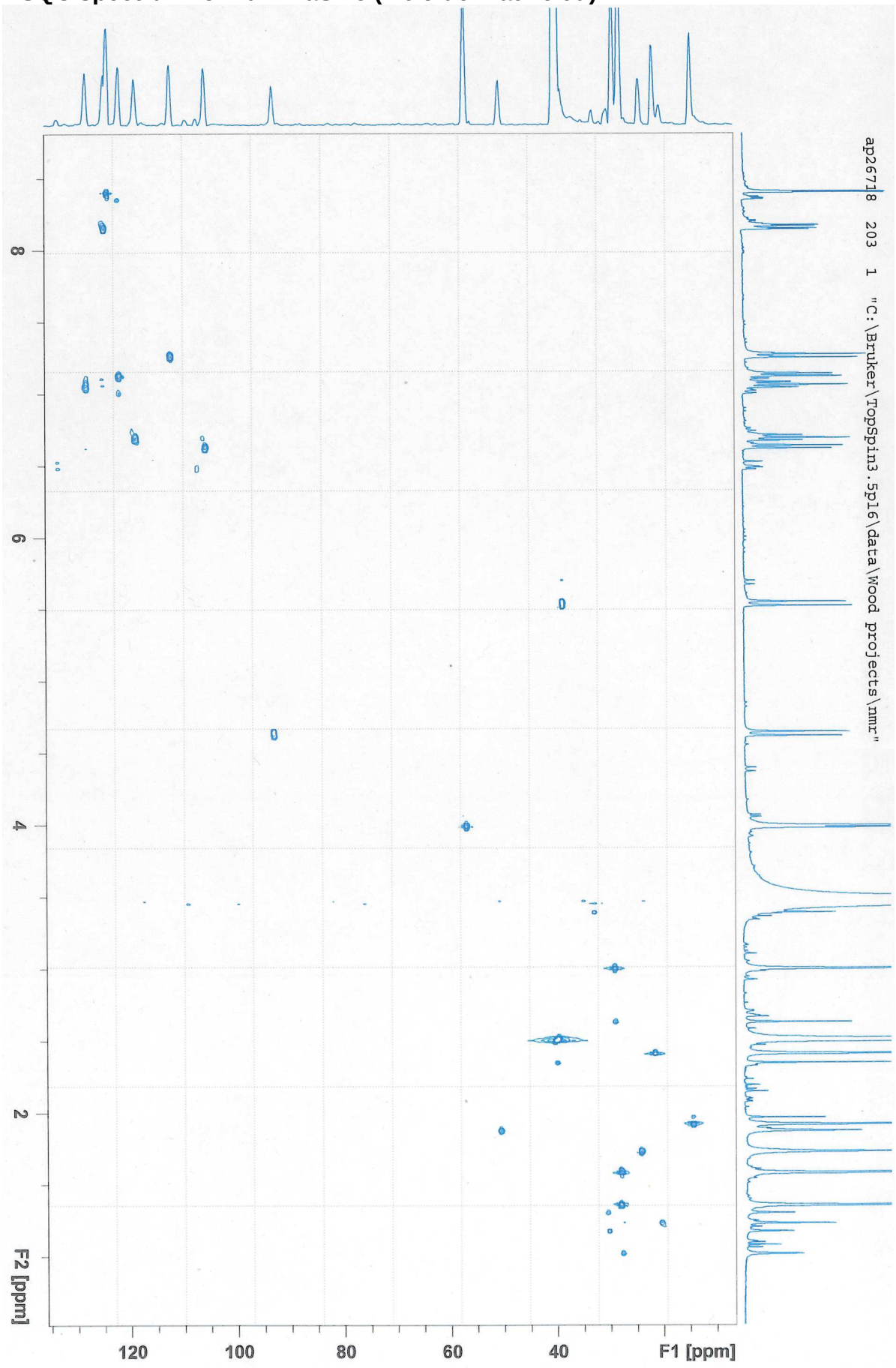
^{13}C NMR spectrum for 7d + NaSMe (nitro derivative 9d)



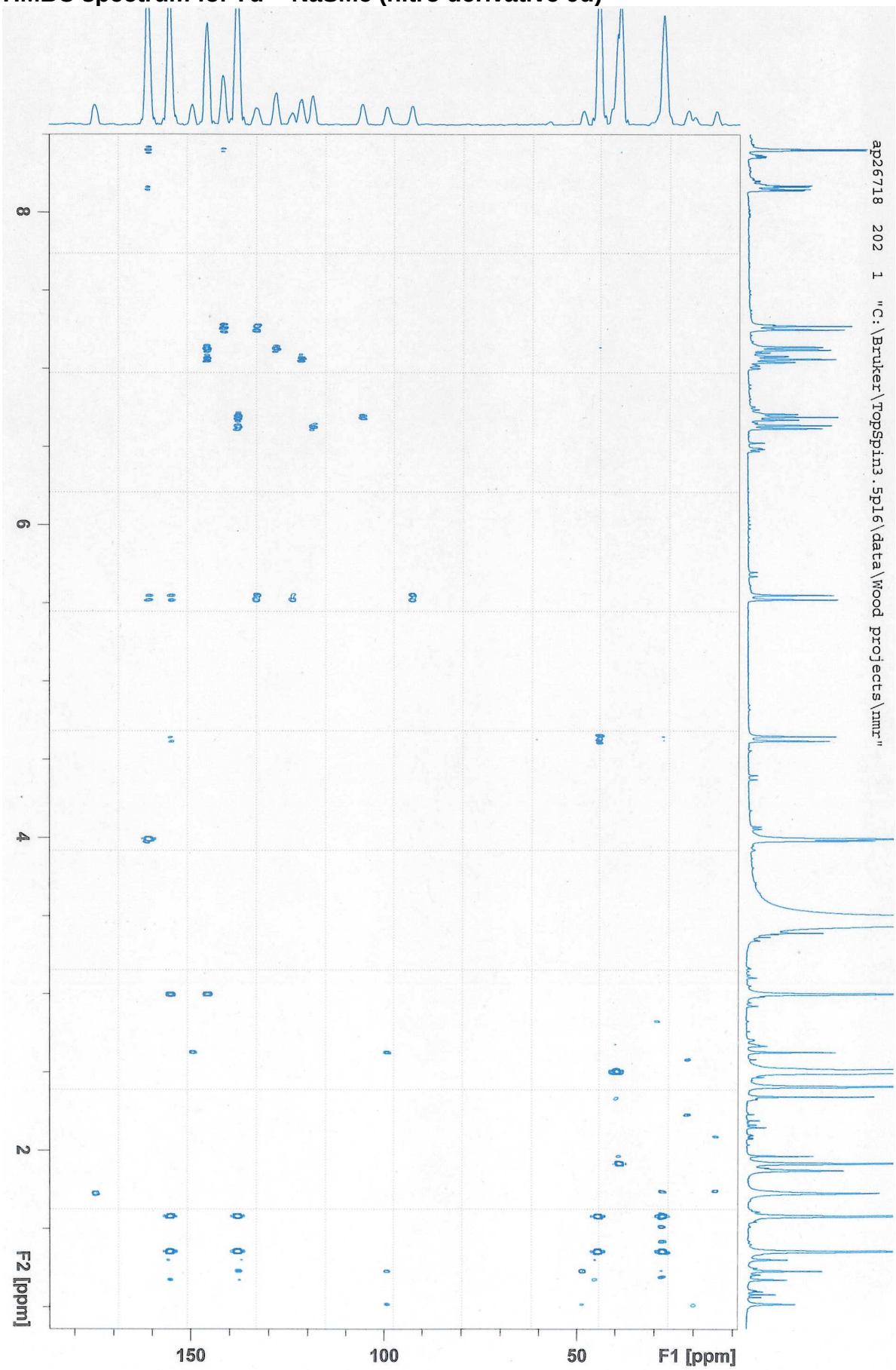
NOESY spectrum for 7d + NaSMe (nitro derivative 9d)



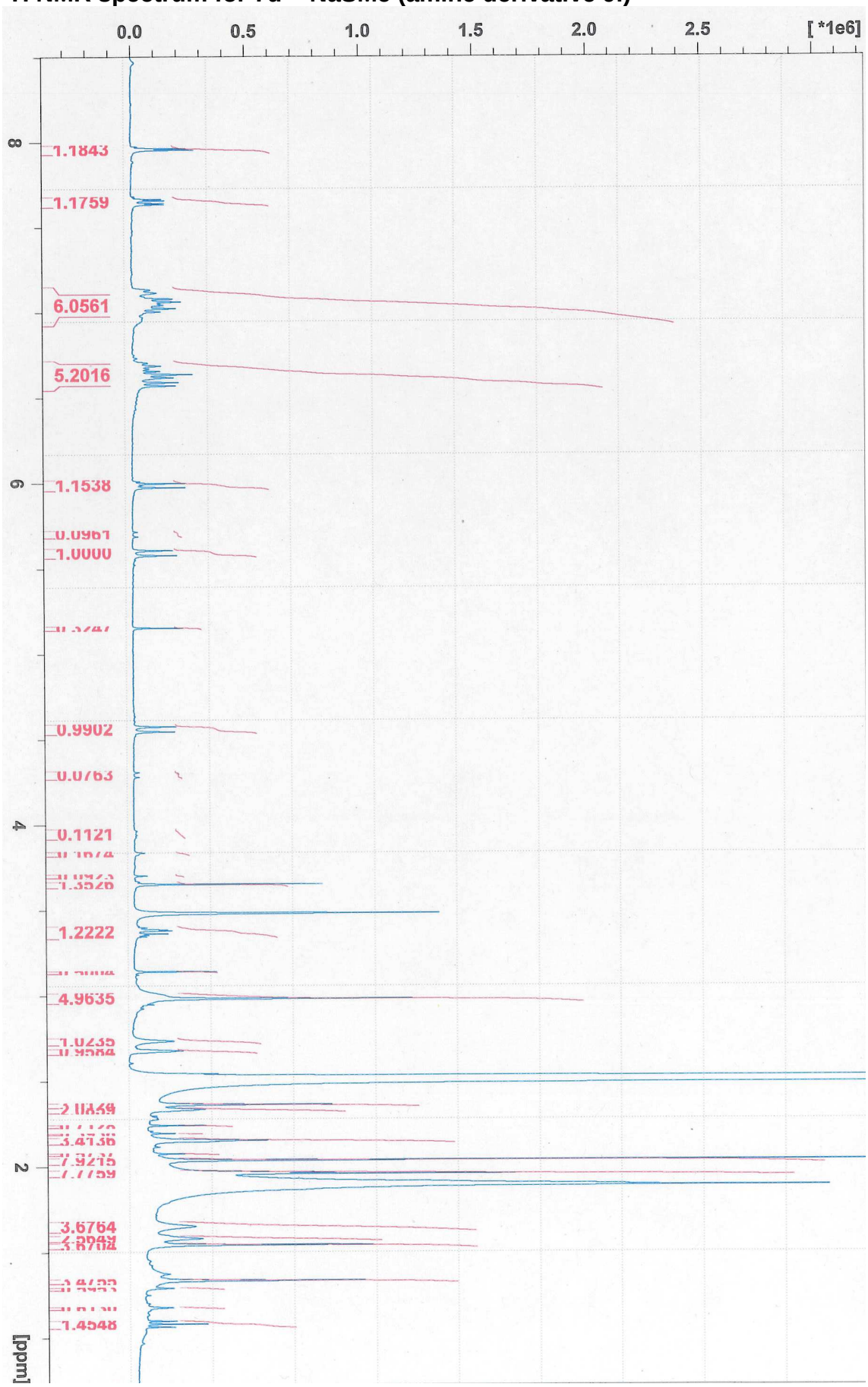
HSQC spectrum for 7d + NaSMe (nitro derivative 9d)



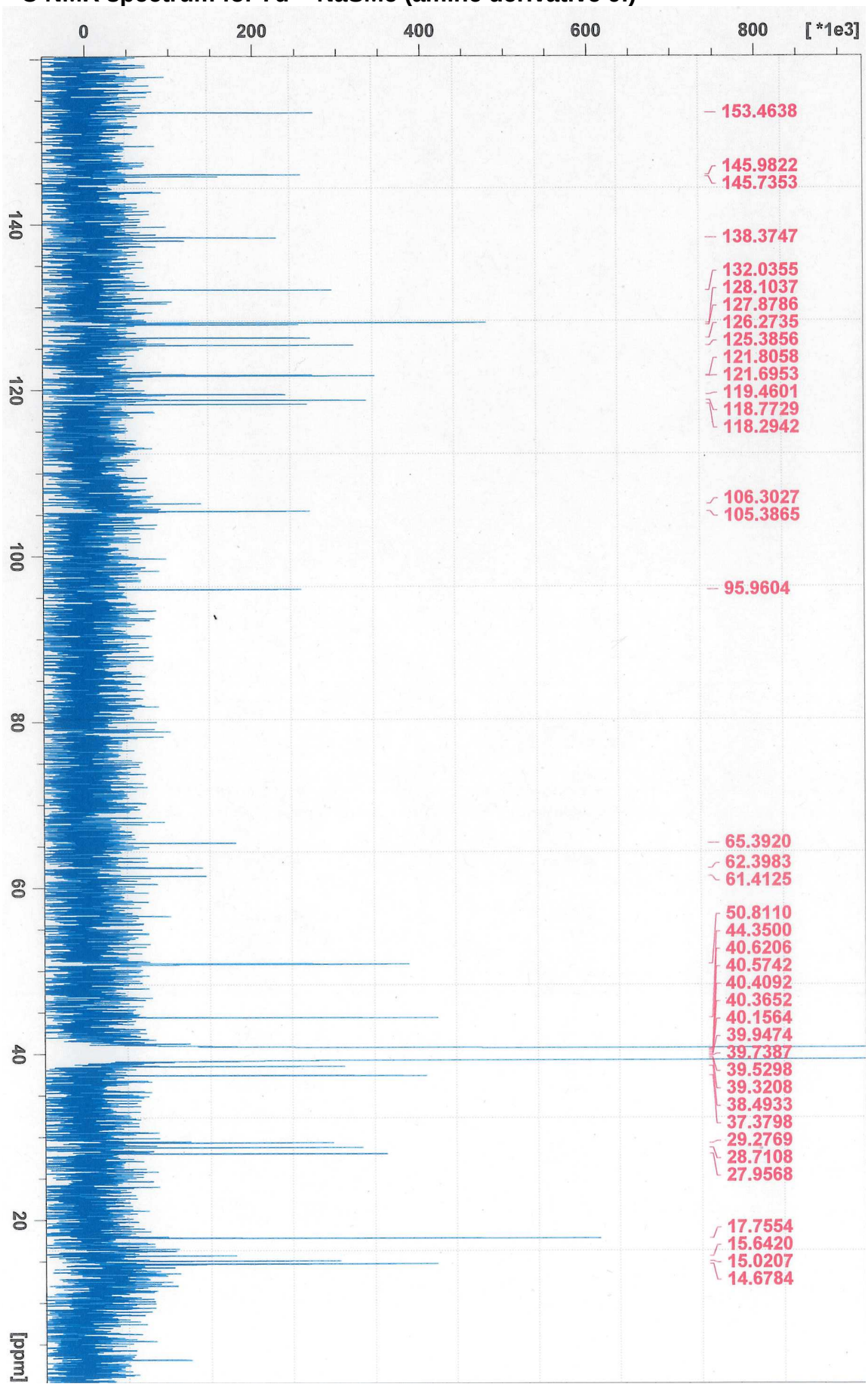
HMBC spectrum for 7d + NaSMe (nitro derivative 9d)



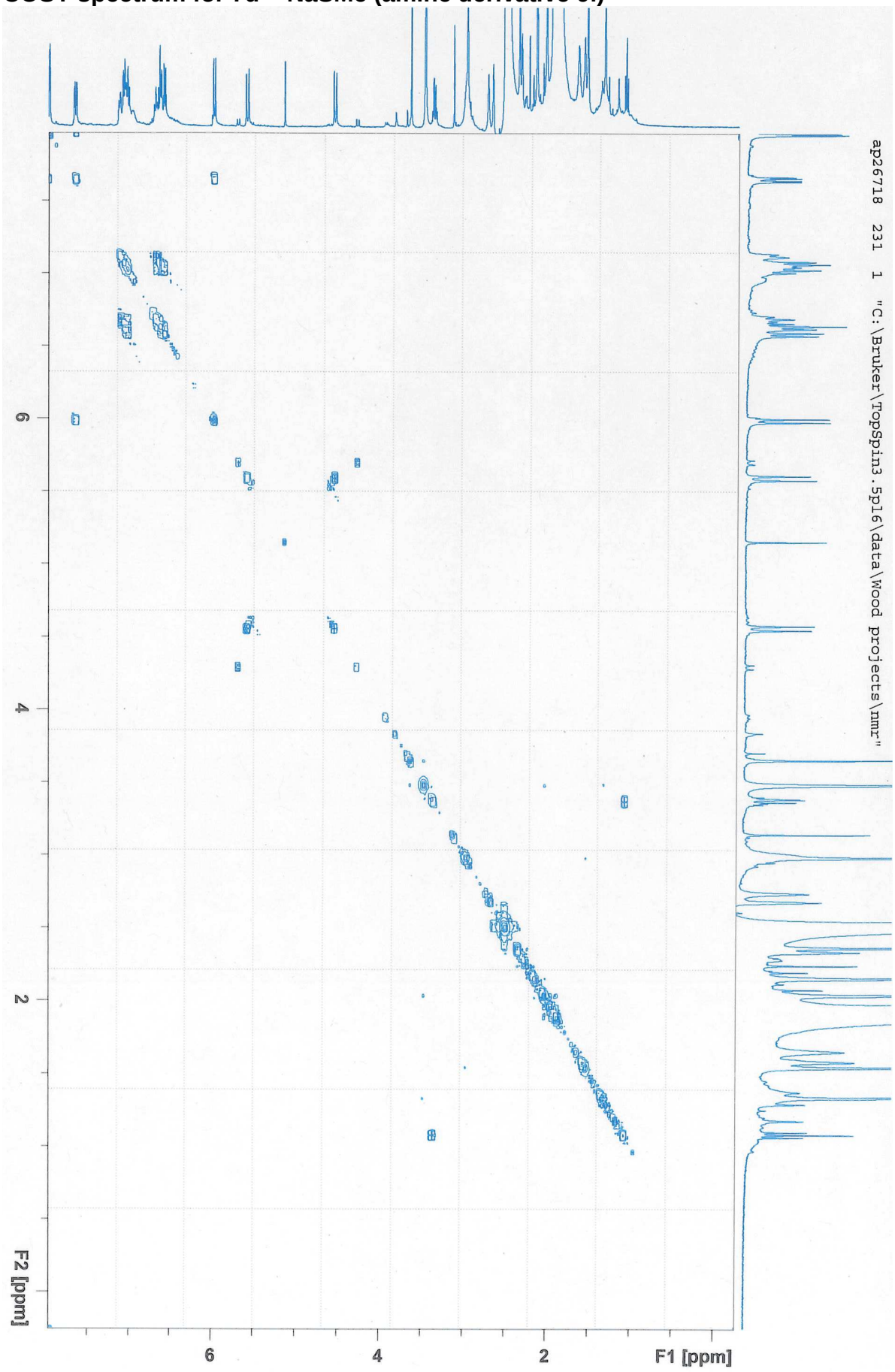
^{1}H NMR spectrum for 7d + NaSMe (amine derivative 9i)



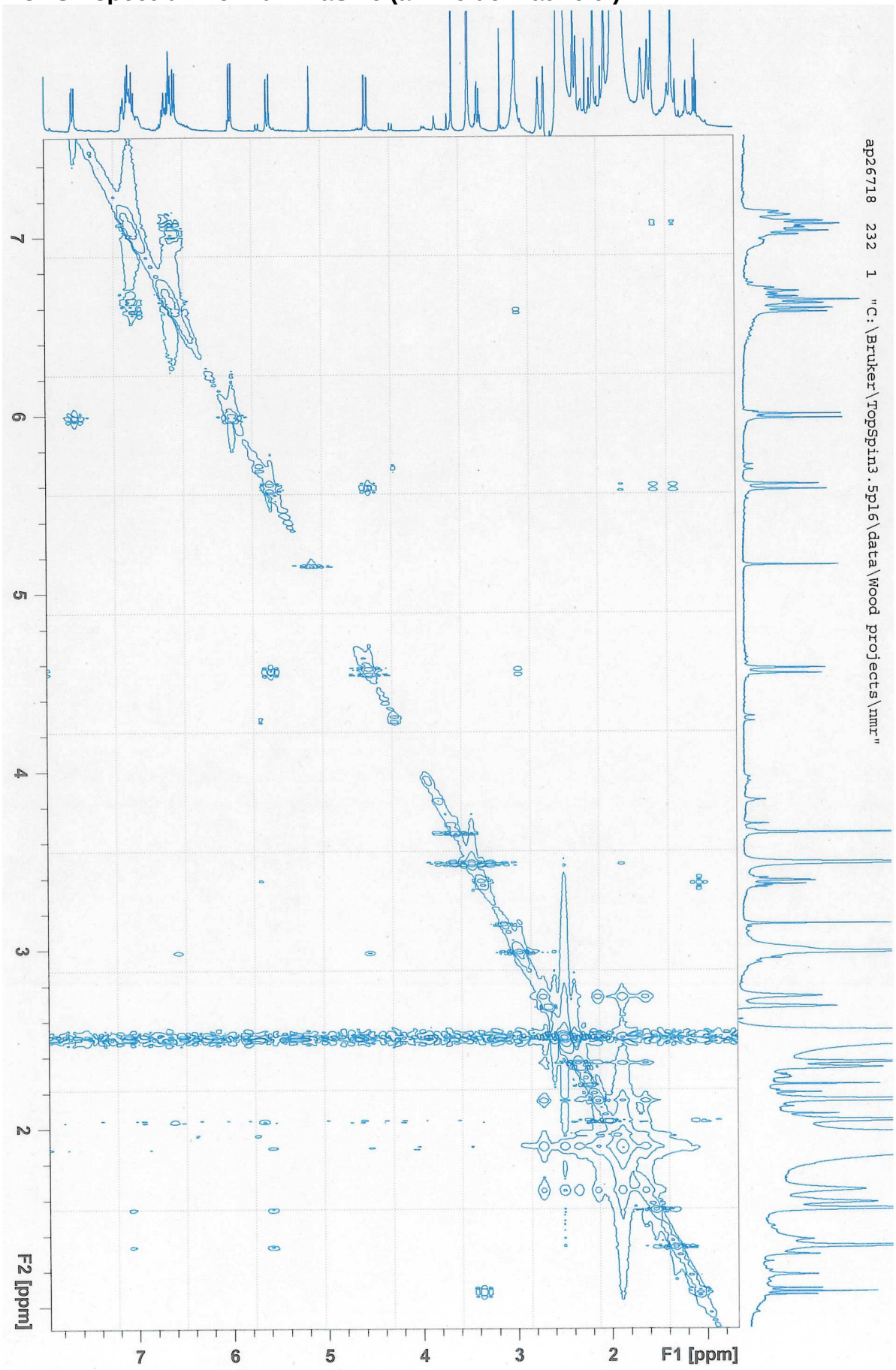
^{13}C NMR spectrum for 7d + NaSMe (amine derivative 9i)



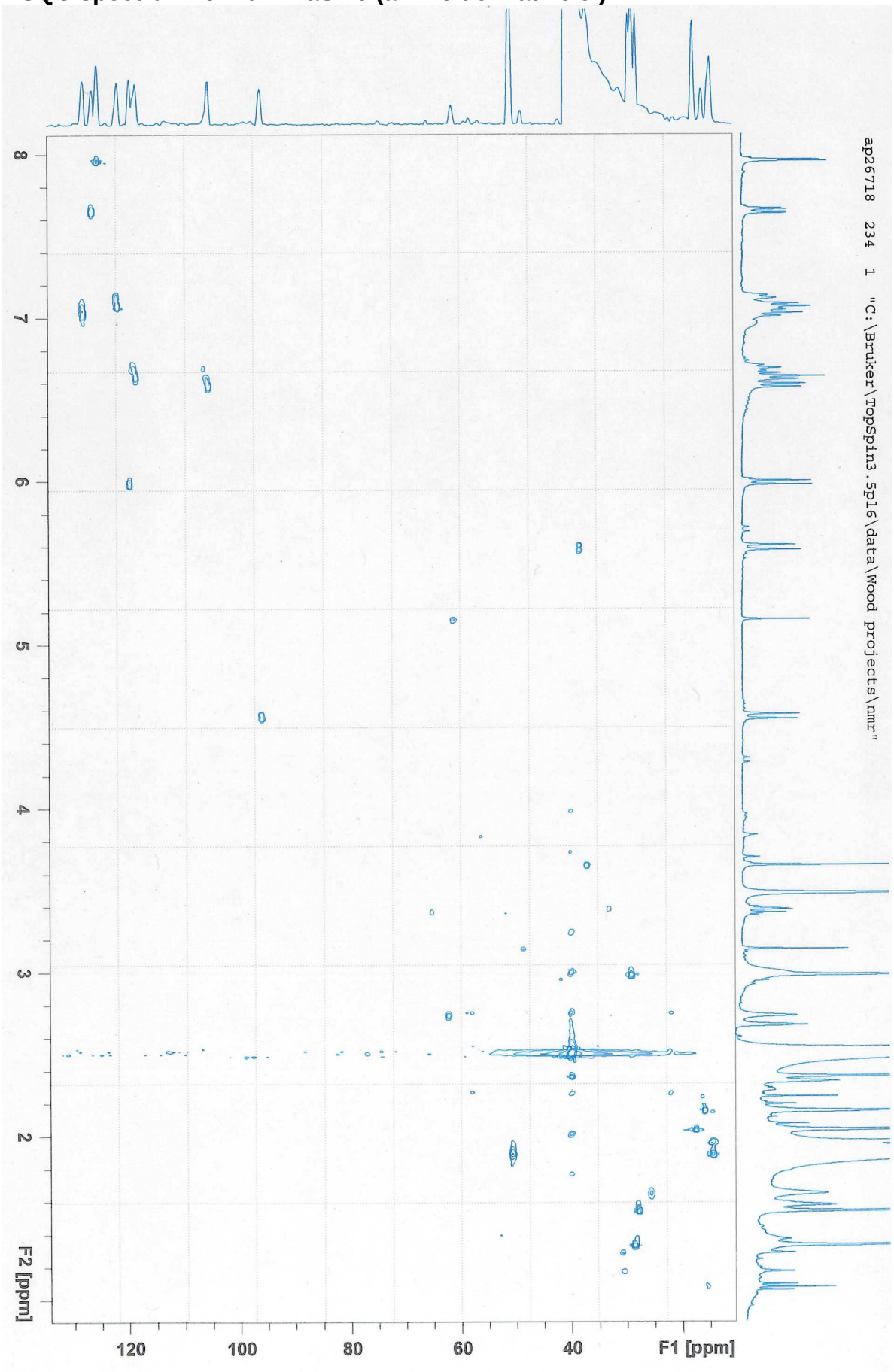
COSY spectrum for 7d + NaSMe (amine derivative 9i)



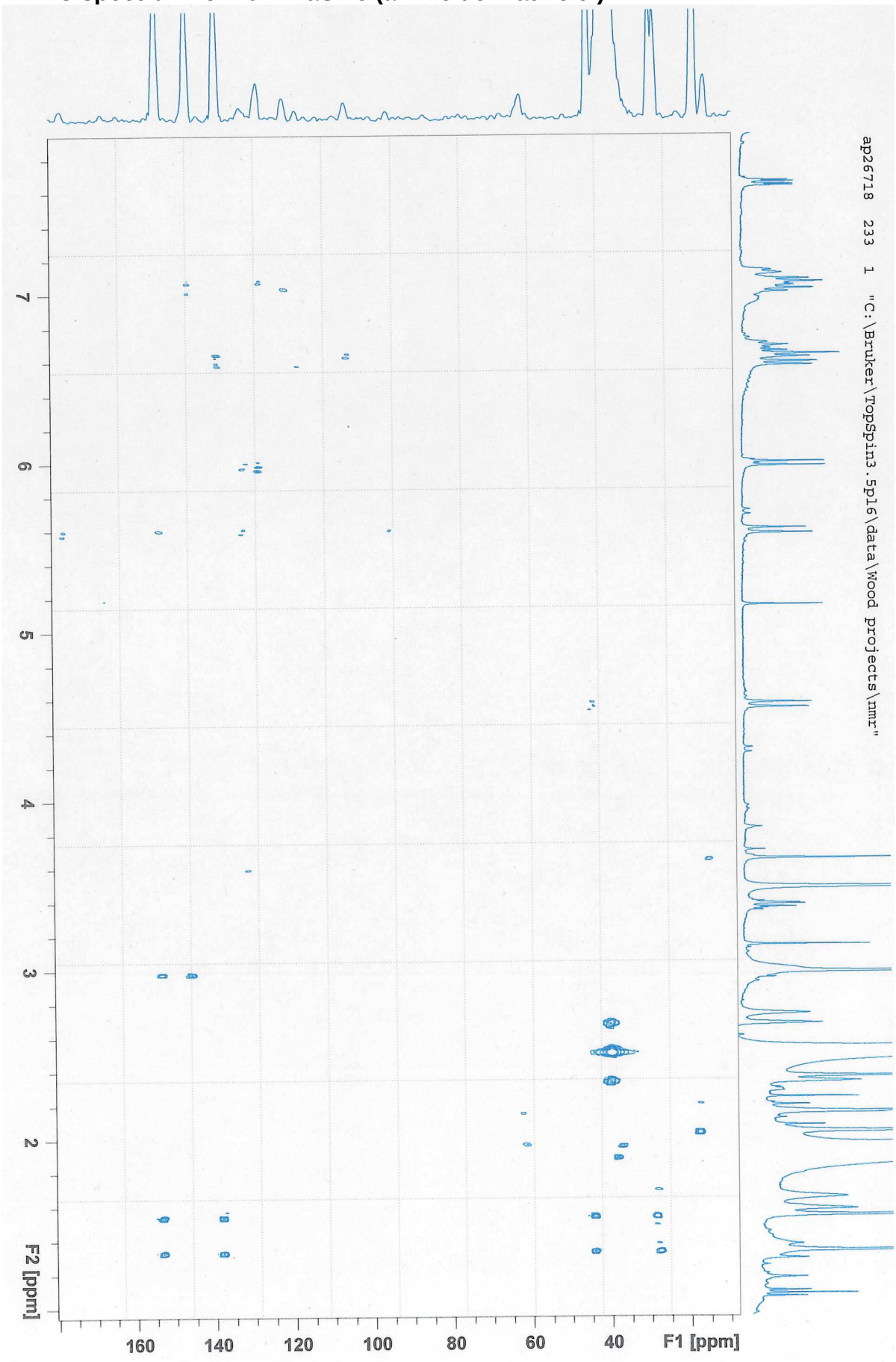
NOESY spectrum for 7d + NaSMe (amine derivative 9i)



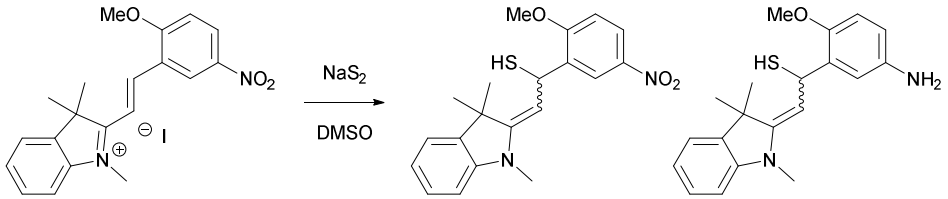
HSQC spectrum for 7d + NaSMe (amine derivative 9i)



HMBC spectrum for 7d + NaSMe (amine derivative 9i)



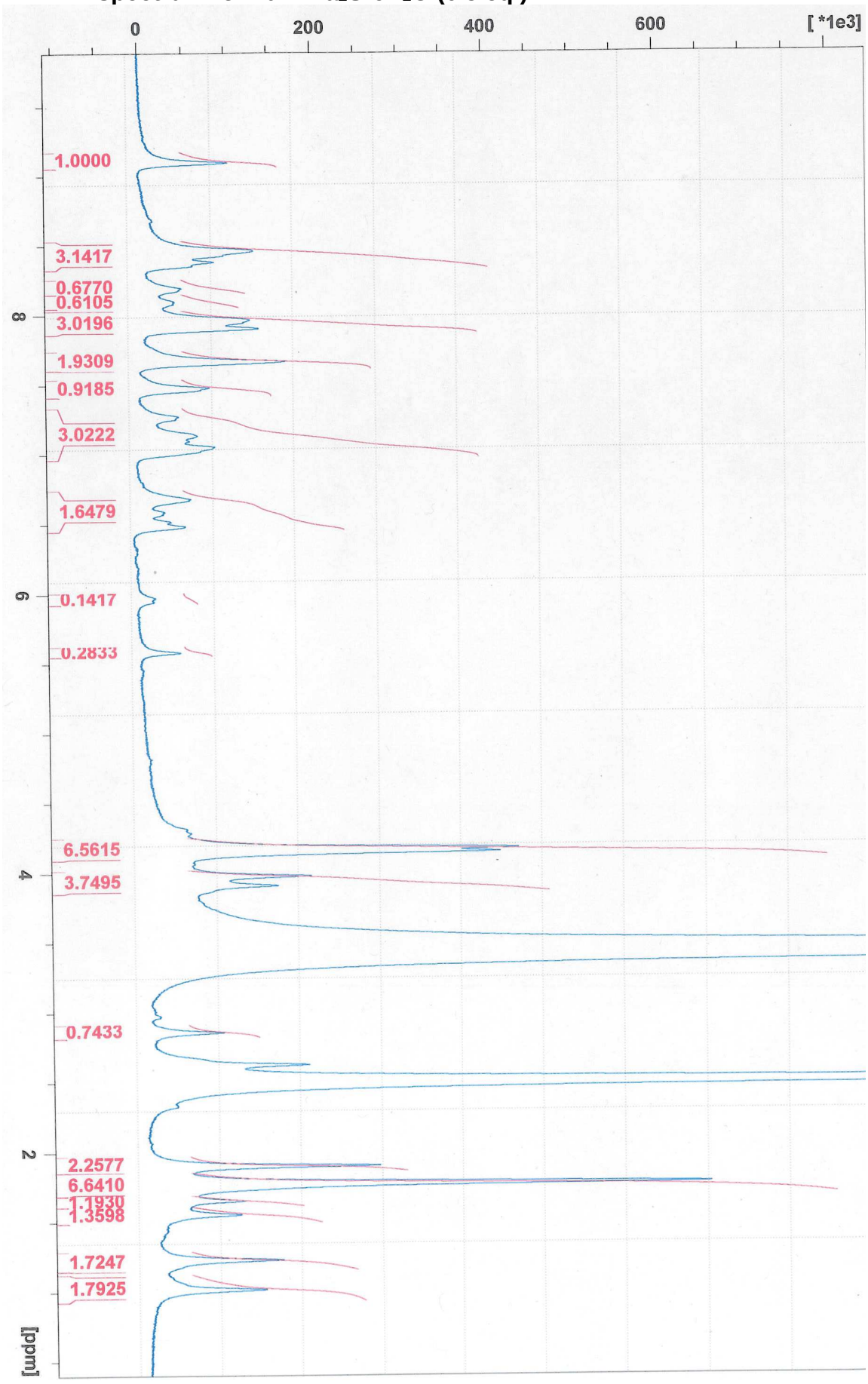
Reaction with sodium sulfide



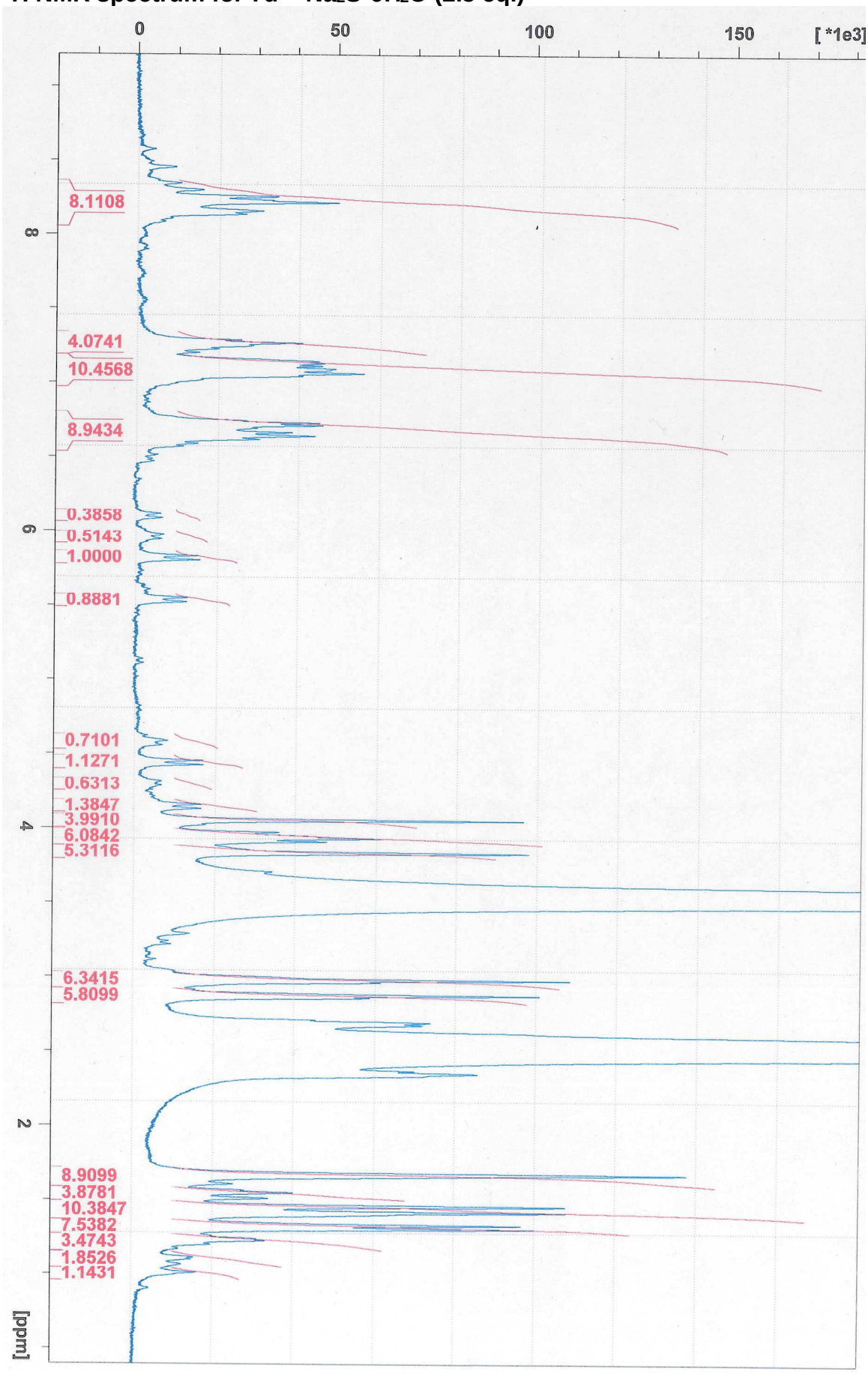
7d **10d** **10i**

LRMS-ES+ (*m/z*): *Initial* 337 (52%, **10d**$^{+}$−SH); *After 18 h* 337 (5%, **10d**$^{+}$−SH), 307 (10%, **10i**$^{+}$−SH).

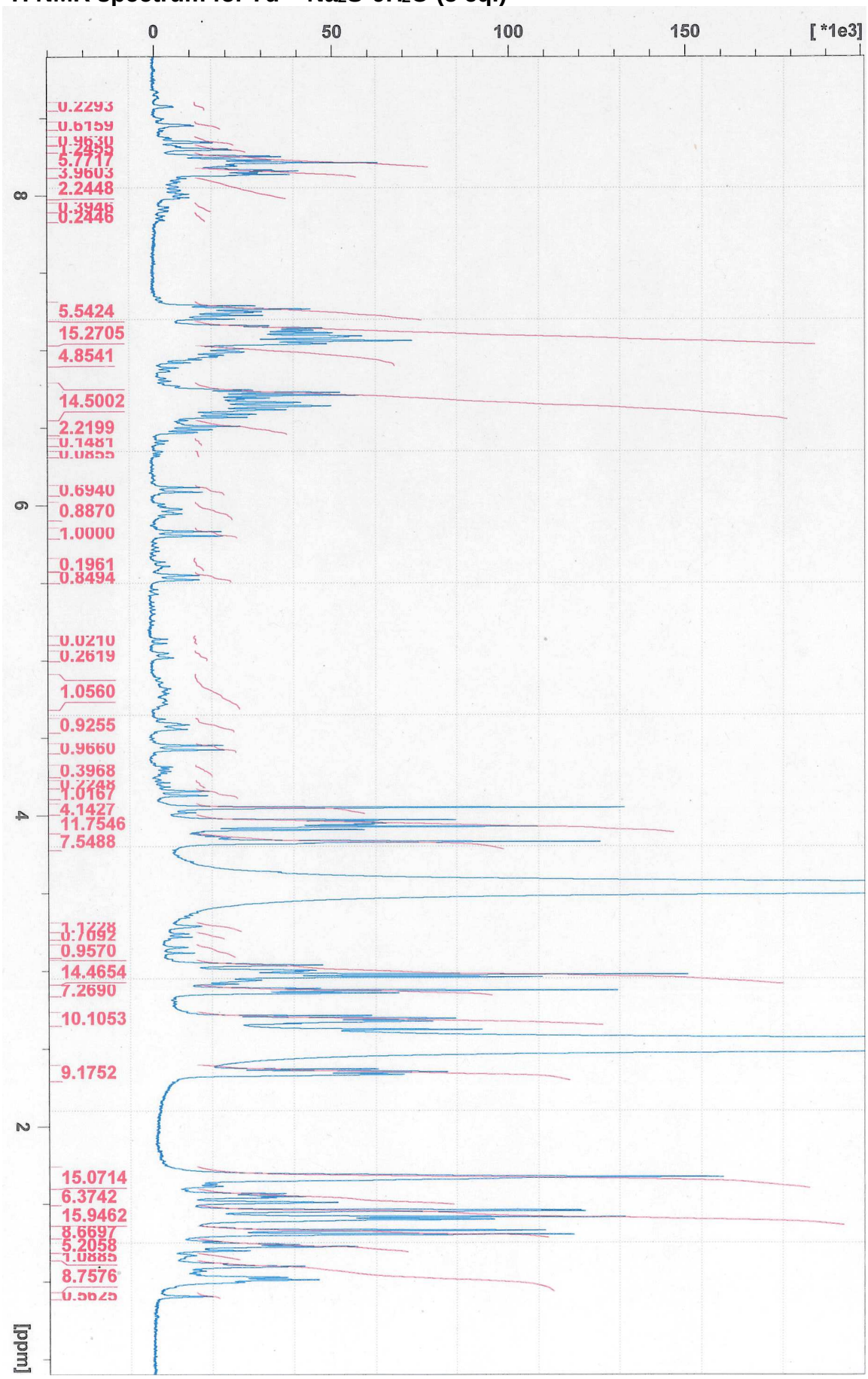
^{1}H NMR spectrum for 7d + $Na_2S \cdot 9H_2O$ (0.5 eq.)



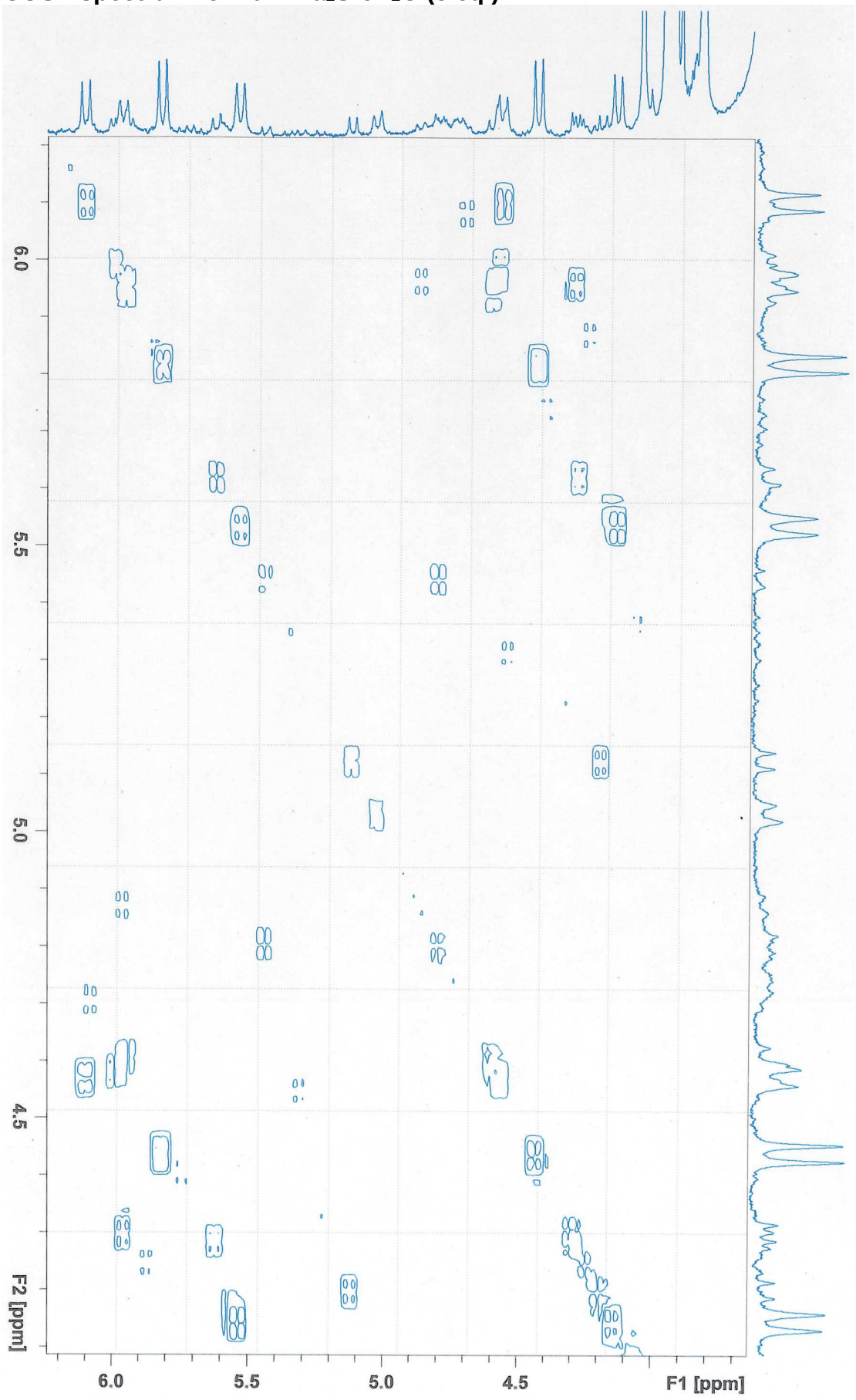
^{1}H NMR spectrum for 7d + $Na_2S \cdot 9H_2O$ (2.5 eq.)



^{1}H NMR spectrum for 7d + $Na_2S \cdot 9H_2O$ (5 eq.)

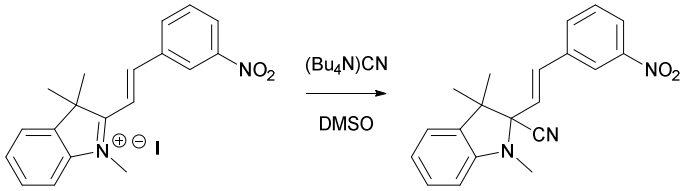


COSY spectrum for 7d + $Na_2S \cdot 9H_2O$ (5 eq.)



3.5 Reactions of 7e

Reaction with tetrabutylammonium cyanide



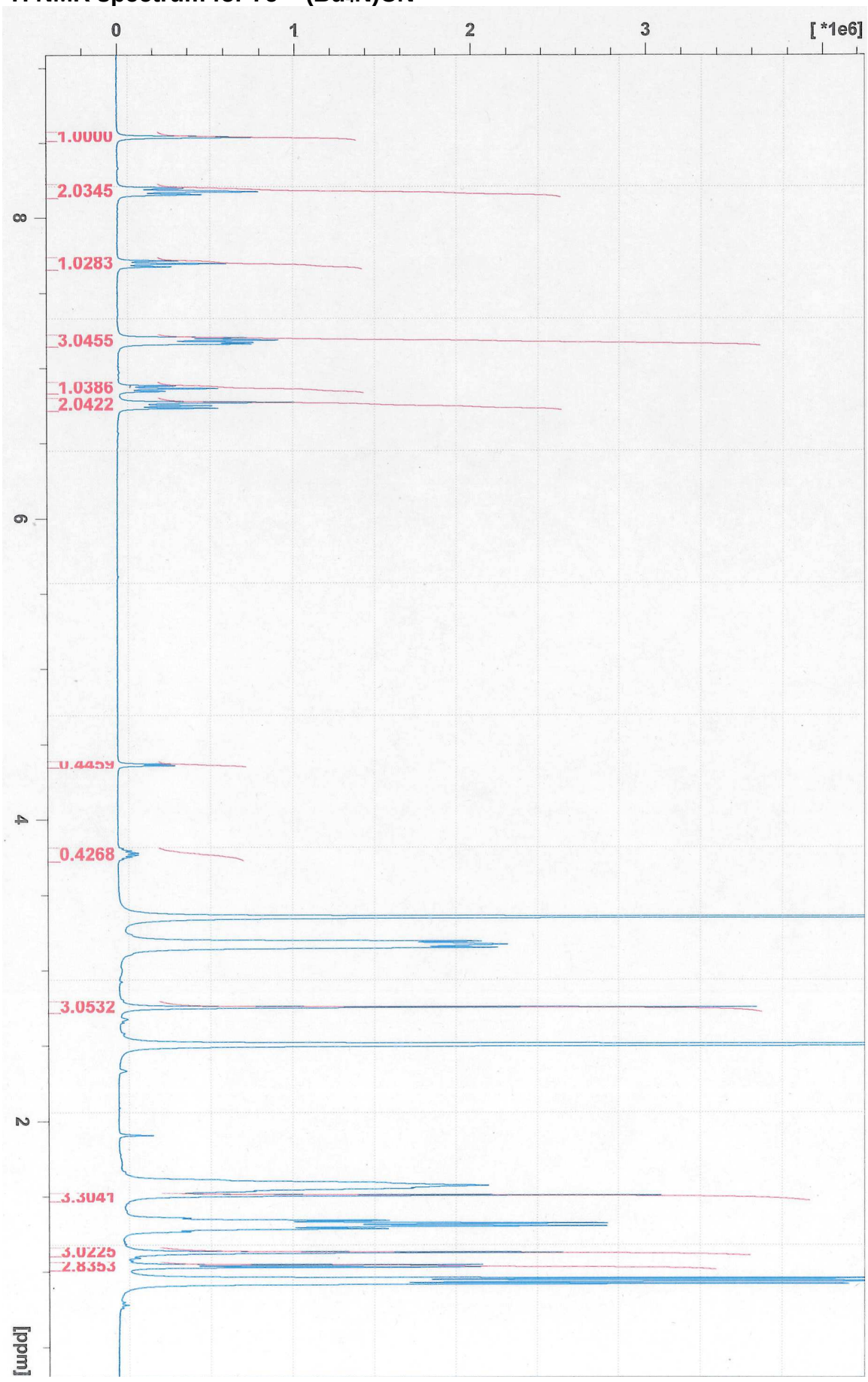
7e **8e**

Data for (*E*)-1,3,3-trimethyl-2-(3-nitrostyryl)indoline-2-carbonitrile 8e

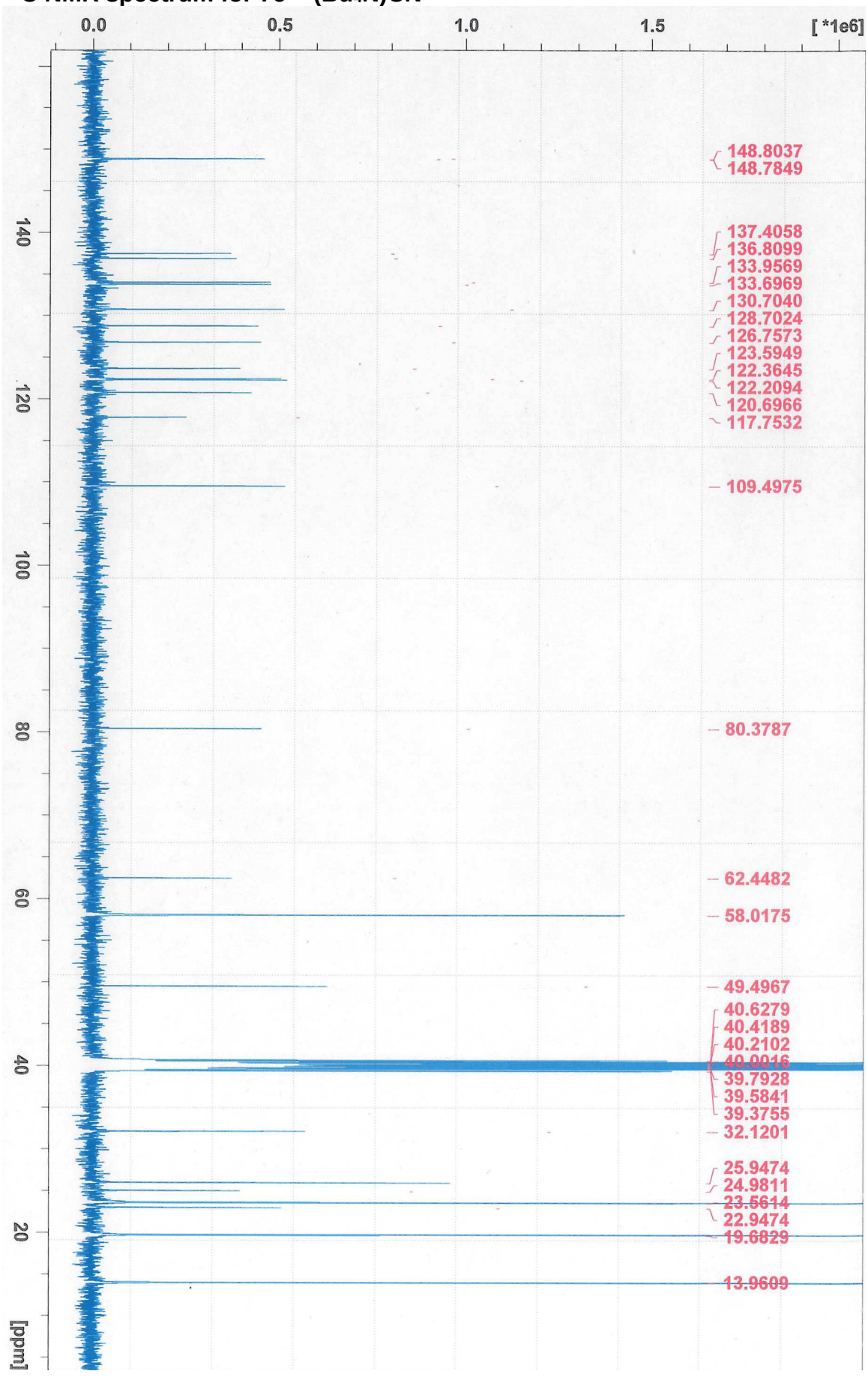
δH (400 MHz; DMSO-d_6) 8.54 (1 H, s, 2'-H), 8.19 (1 H, d, *J* 8.0, 4'-H), 8.17 (1 H, d, *J* 8.0, 6'-H), 7.70 (1 H, t, *J* 8.0, 5'-H), 7.21-7.15 (3 H, m, β-, 4- and 6-H), 6.87 (1 H, t, *J* 7.3, 5-H), 6.76 (1 H, d, *J* 16.2, α-H), 6.75 (1 H, d, *J* 7.3, 7-H), 2.74 (3 H, s, NMe), 1.50 (3 H, s, CMe) and 1.20 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 148.8 (7a-C), 148.7 (3'-C), 137.4 (1'-C), 136.8 (3a-C), 134.0 (6'-C), 133.7 (β-C), 130.7 (5'-C), 128.7 (6-C), 126.8 (α-C), 123.6 (4'-C), 122.4 (4-C), 122.2 (2'-C), 120.7 (5-C), 117.8 (CN), 109.5 (7-C), 80.4 (*C*CN), 49.5 (*C*Me_2), 32.1 (NMe), 25.0 (C*Me*) and 22.9 (C*Me*).

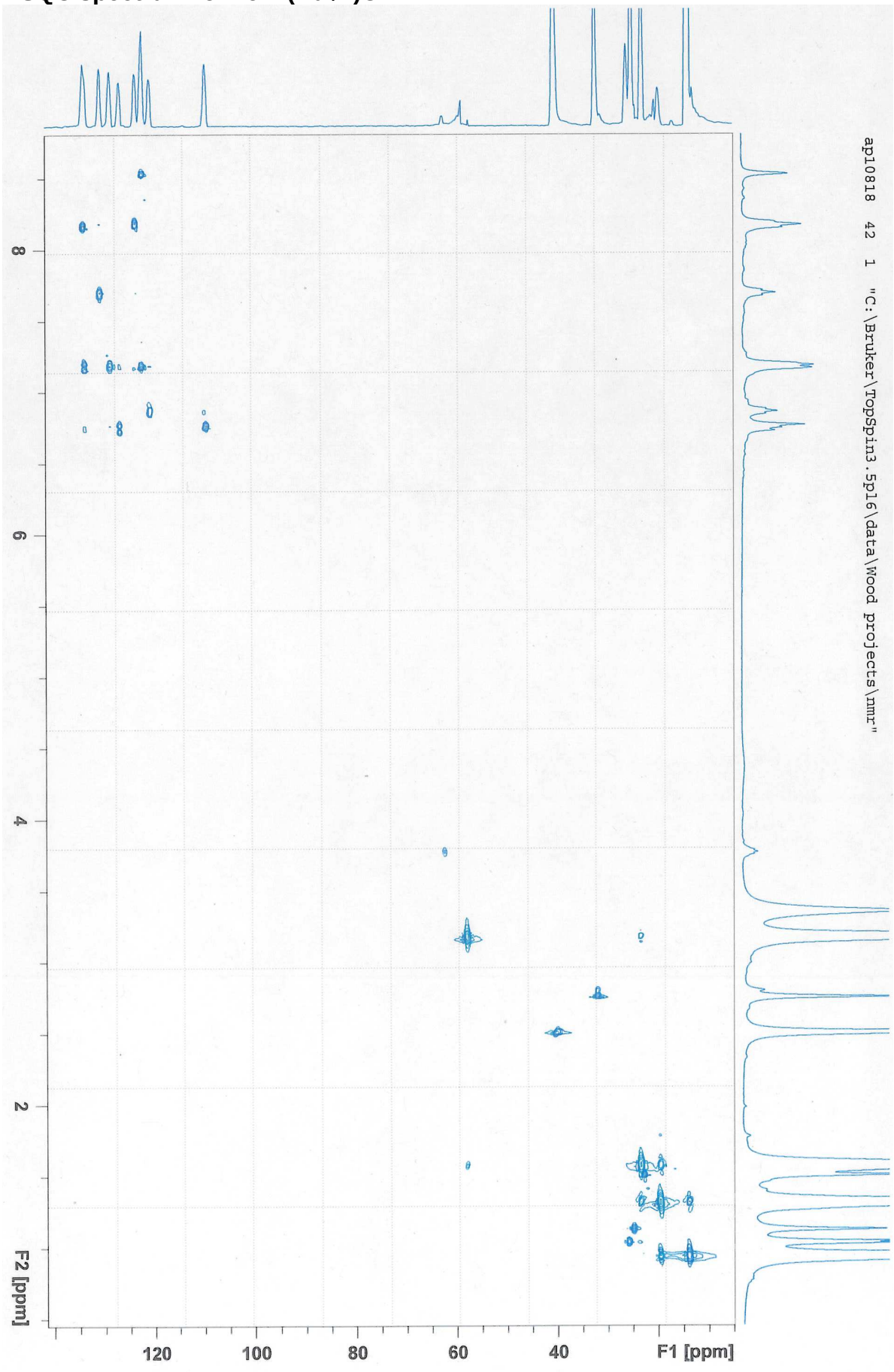
^{1}H NMR spectrum for 7e + (Bu_4N)CN



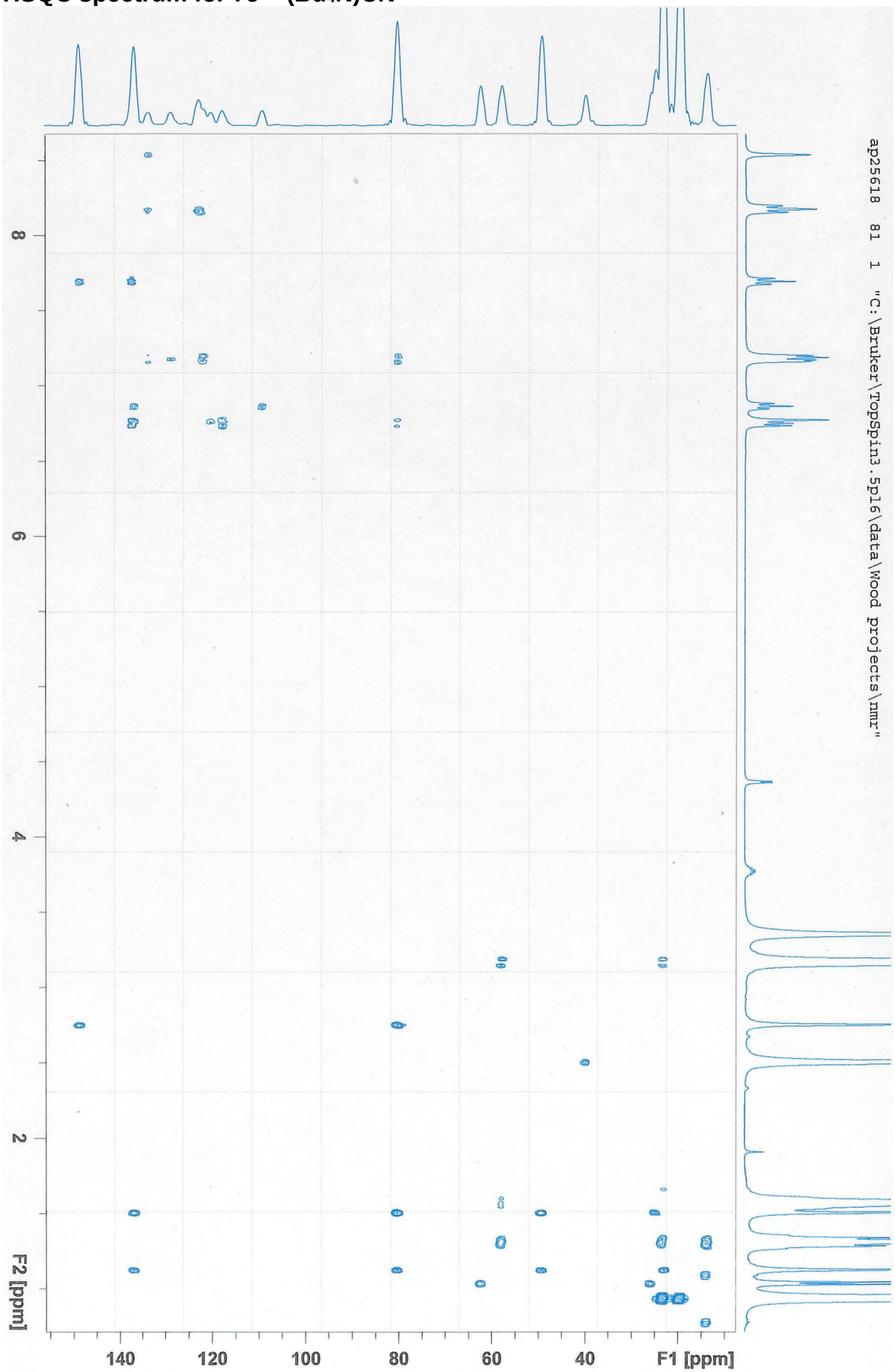
^{13}C NMR spectrum for 7e + (Bu_4N)CN



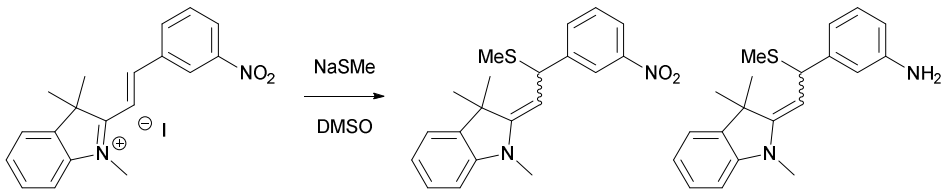
HSQC spectrum for 7e + (Bu_4N)CN



HSQC spectrum for 7e + (Bu_4N)CN



Reaction with sodium methanethiolate



7e **9e** **9h**

Data for initial product: 1,3,3-trimethyl-2-(2-(methylthio)-2-(3-nitrophenyl)ethylidene)indoline 9e

δH (400 MHz; DMSO-d_6; 15:85 *Z*:*E*) 8.38 (1 H, s, 2'-H(*E*)), 8.09 (1 H, d, *J* 8.0, 4'-H(*E*)), 8.00 (1 H, d, *J* 8.0, 6'-H(*E*)), 7.65 (1 H, t, *J* 8.0, 5'-H(*E*)), 7.14 (1 H, d, *J* 7.3, 4-H(*E*)), 7.06 (1 H, t, *J* 7.3, 6-H(*E*)), 6.69 (1 H, t, *J* 7.3, 5-H(*E*)), 6.63 (1 H, d, *J* 7.3, 7-H(*E*)), 5.42 (1 H, d, *J* 10.5, β-H(*Z*)), 5.32 (1 H, d, *J* 11.4, β-H(*E*)), 4.62 (1 H, d, *J* 11.4, α-H(*E*)), 4.41 (1 H, d, *J* 10.5, α-H(*Z*)), 3.01 (3 H, s, NMe(*E*)), 1.95 (3 H, s, SMe(*E*)), 1.59 (3 H, s, CMe(*E*)) and 1.40 (3 H, s, CMe(*E*)).

LRMS-ES+ (*m/z*): 355 (50%, M^+), 307 (100%, M^+-SCH_3).

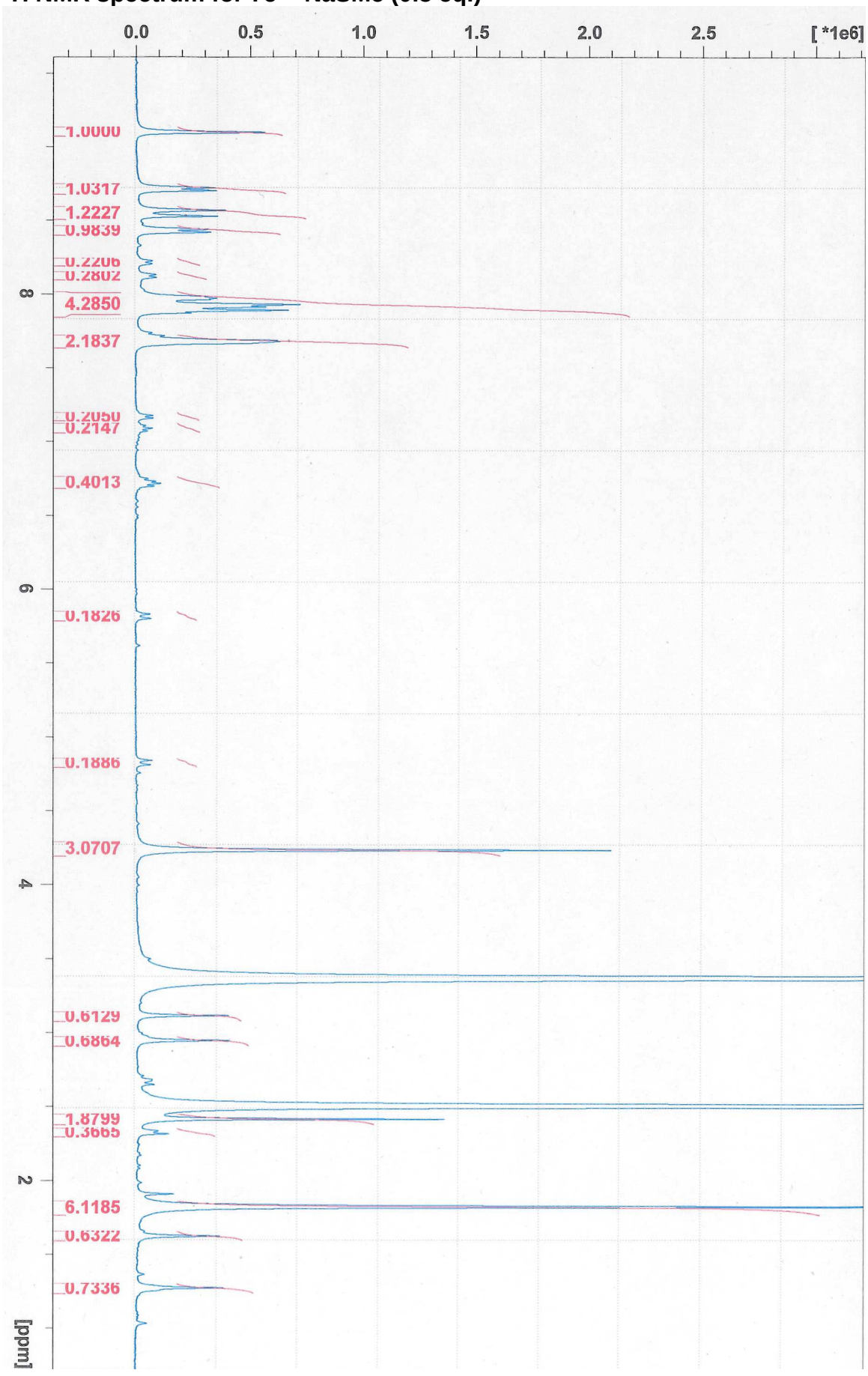
Data for reduced product: 3-(1-(methylthio)-2-(1,3,3-trimethylindolin-2-ylidene)ethyl)aniline 9h

δH (400 MHz; DMSO-d_6; *Z*:*E* ratio unclear) 8.50-7.50 (4 H, br, 2'-, 4'-, 5'- and 6'-H), 7.13 (1 H, d, *J* 7.5, 4-H), 7.06 (1 H, td, *J* 7.5, 1.0, 6-H), 6.69 (1 H, t, *J* 7.5, 5-H), 6.62 (1 H, d, *J* 7.5, 7-H), 5.70-4.40 (2 H, br, α- and β-H), 2.99 (3 H, s, NMe), 1.85 (3 H, s, SMe), 1.55 (3 H, s, CMe) and 1.38 (3 H, s, CMe).

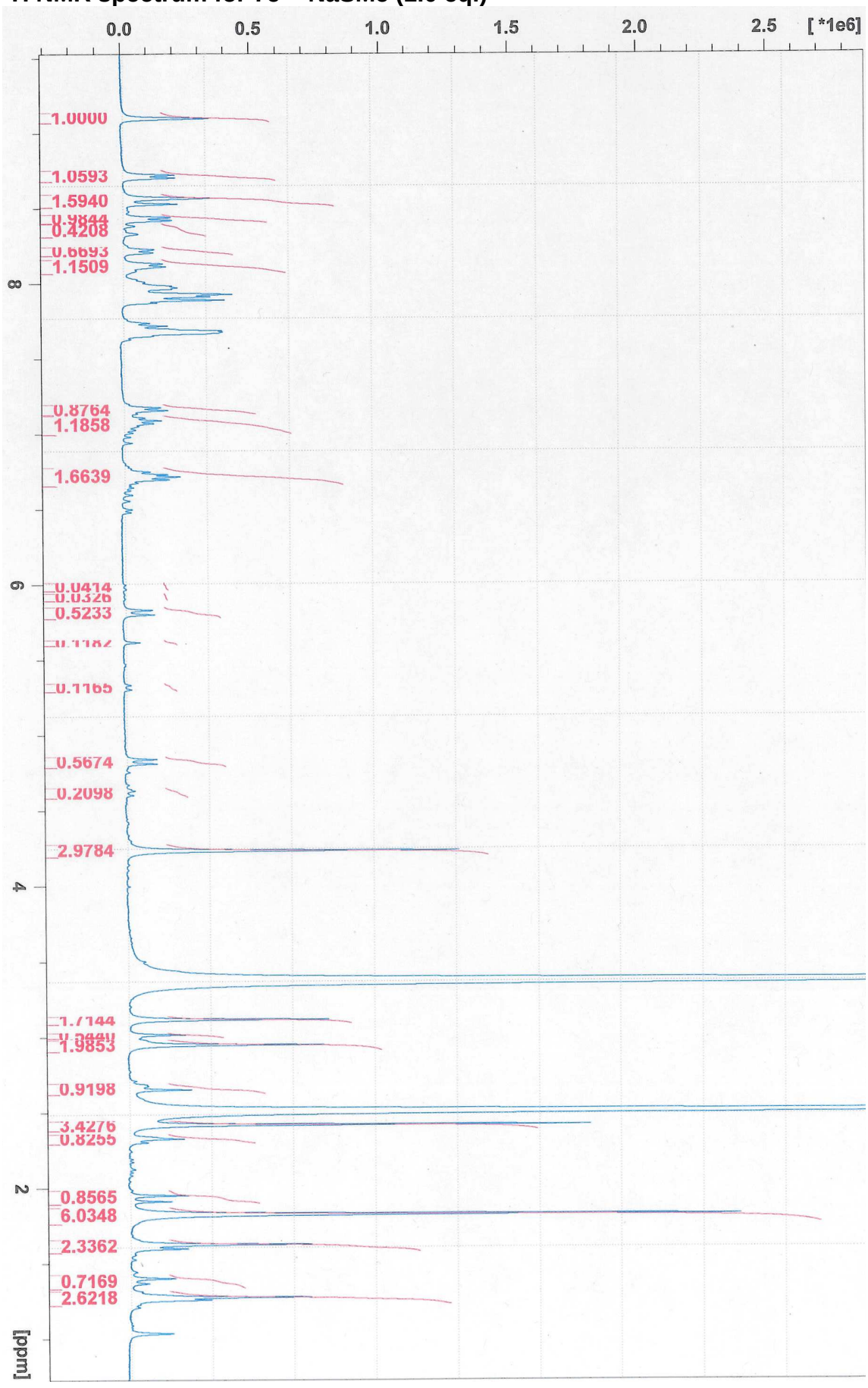
δC (100 MHz; DMSO-d_6; (*E*)-isomer only); 155.4, 148.3, 146.3, 145.8, 138.0, 134.6, 130.4, 128.1, 122.5, 122.1, 121.8, 118.8, 105.7 (7-C), 93.5 (α-C), 50.7 (SMe), 46.4 (β-C), 44.6 (*C*Me_2), 29.3 (NMe), 28.7 (C*Me*) and 28.0 (C*Me*).

LRMS-ES+ (*m/z*): 277 (5%, M^+-SCH_3).

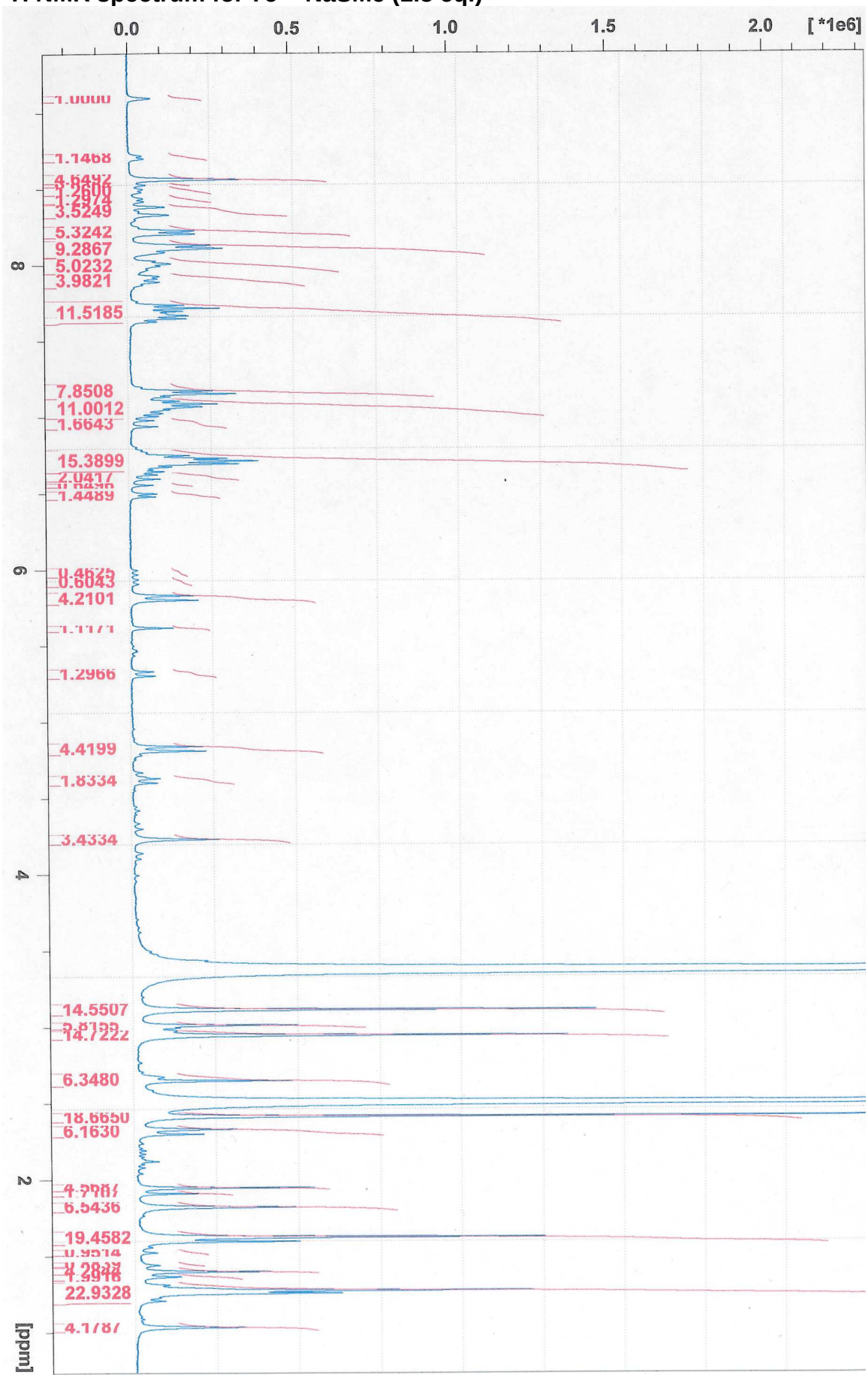
^{1}H NMR spectrum for 7e + NaSMe (0.5 eq.)



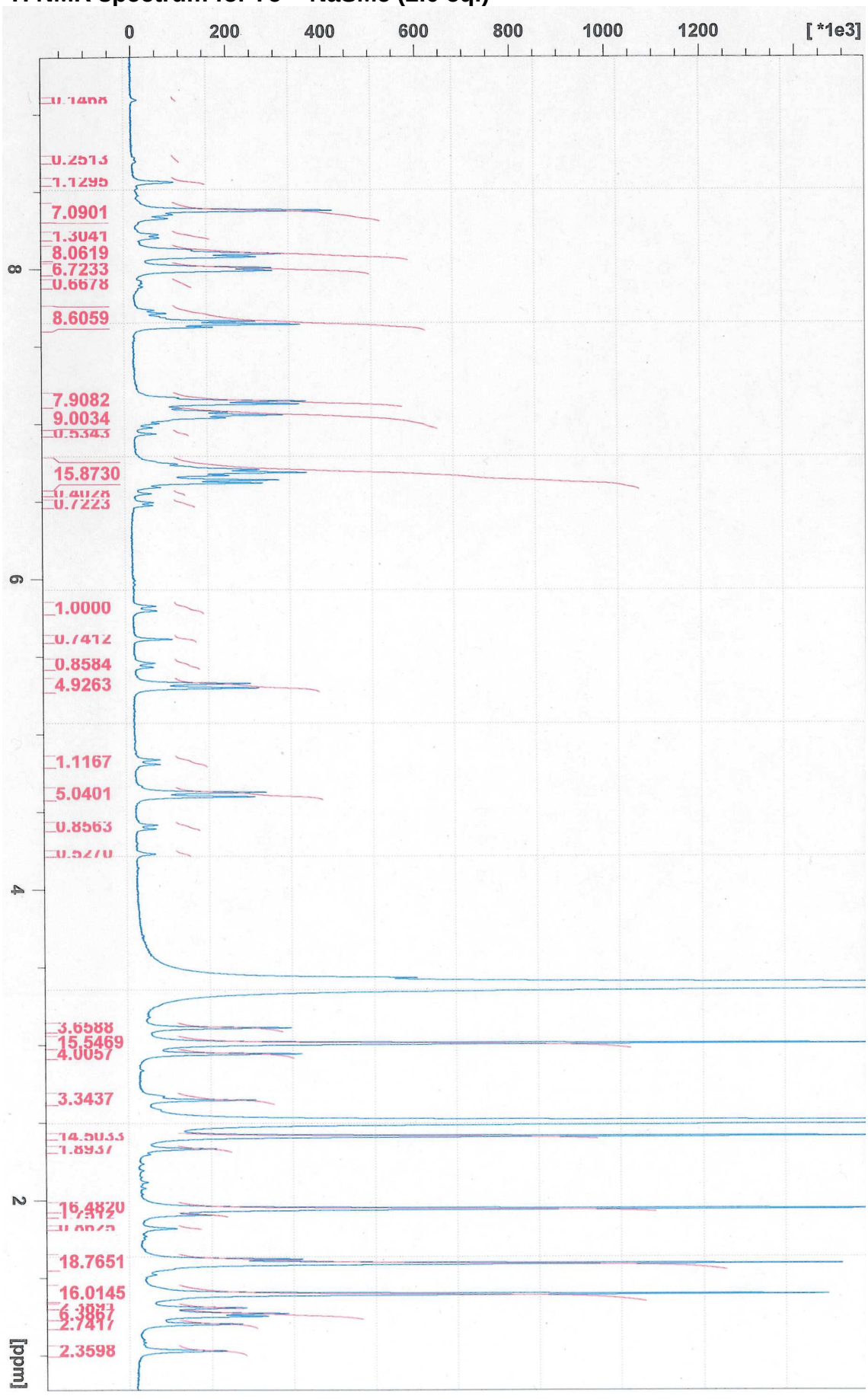
^{1}H NMR spectrum for 7e + NaSMe (1.0 eq.)



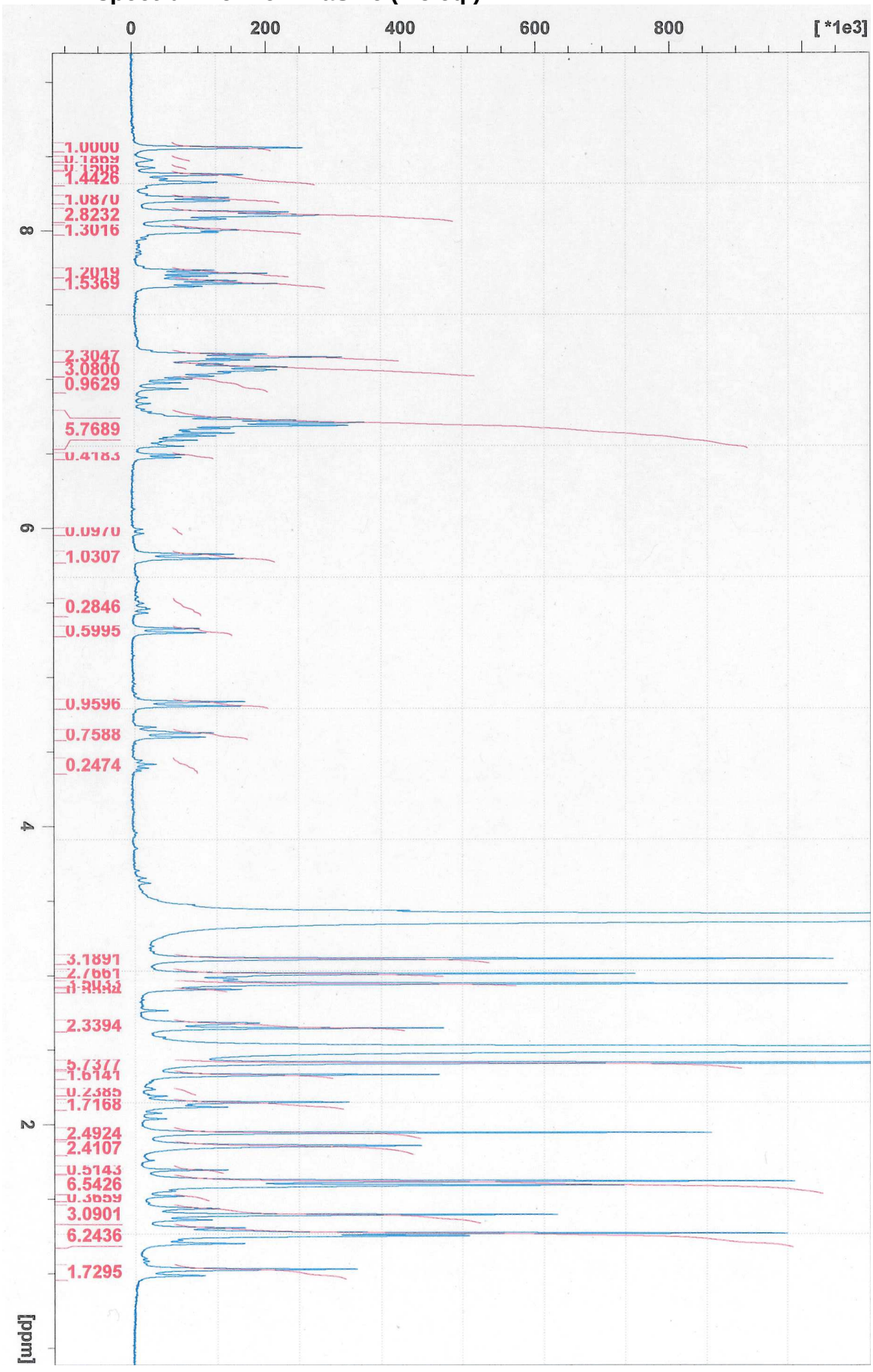
^{1}H NMR spectrum for 7e + NaSMe (1.5 eq.)



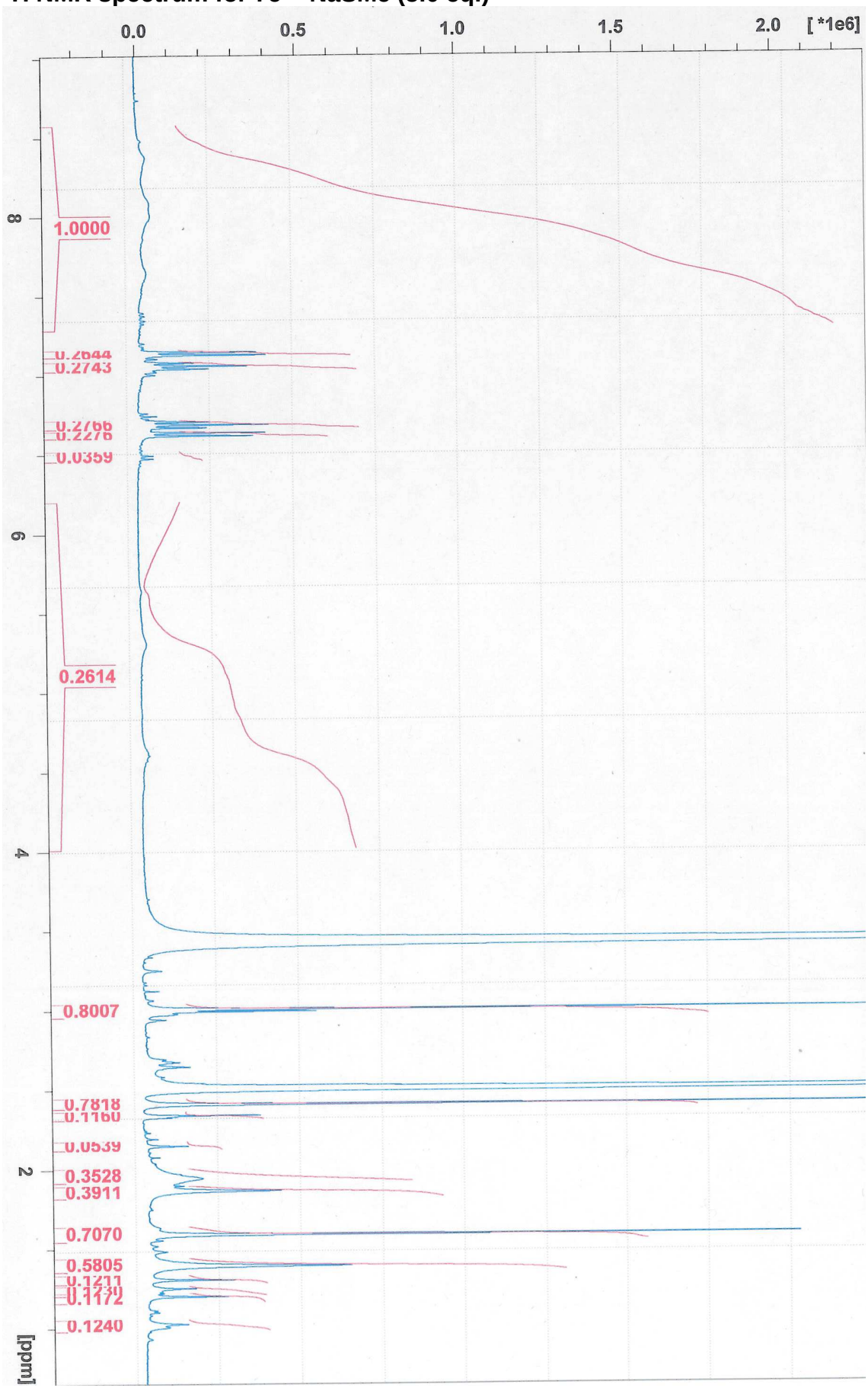
^{1}H NMR spectrum for 7e + NaSMe (2.0 eq.)



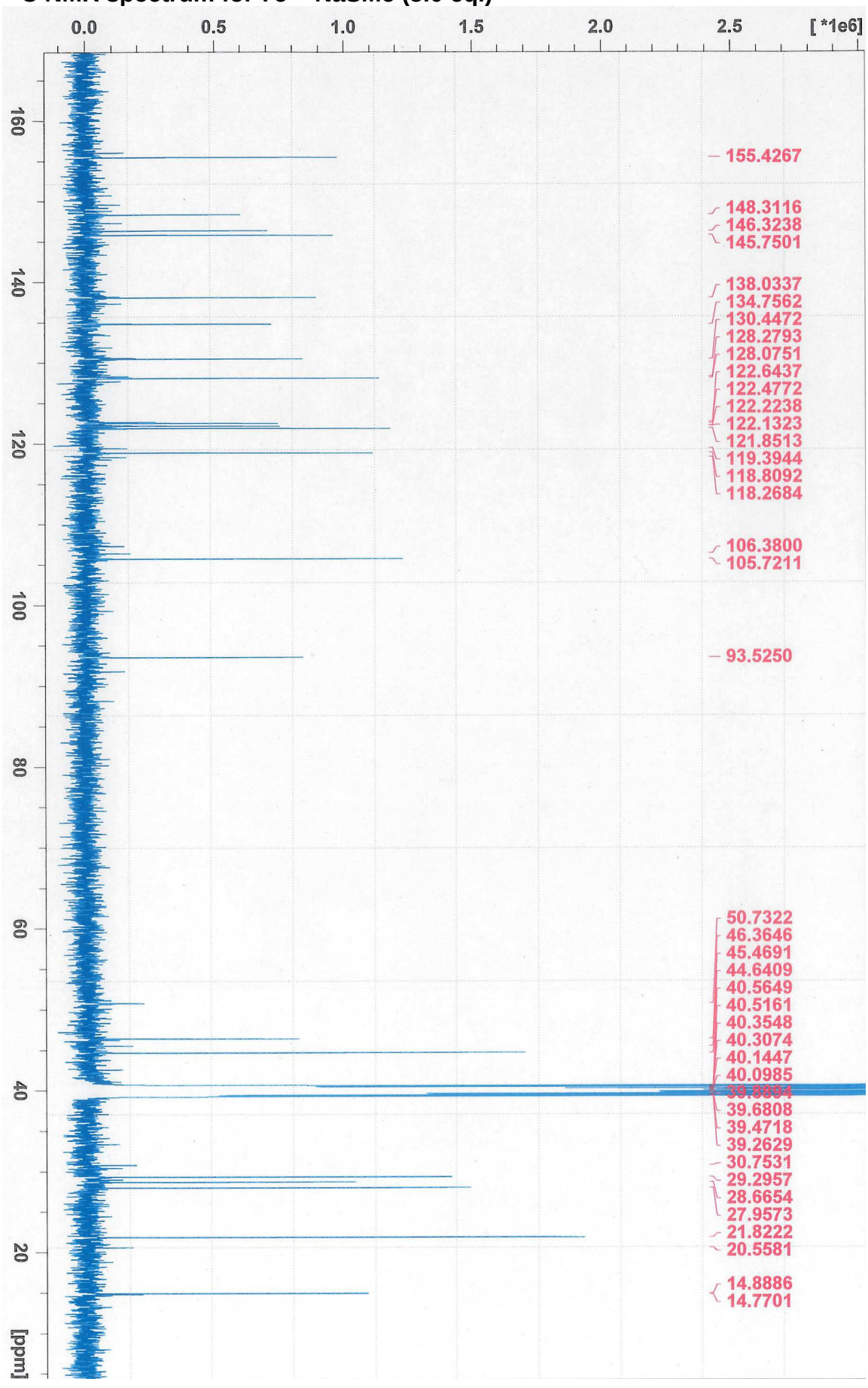
^{1}H NMR spectrum for 7e + NaSMe (2.5 eq.)



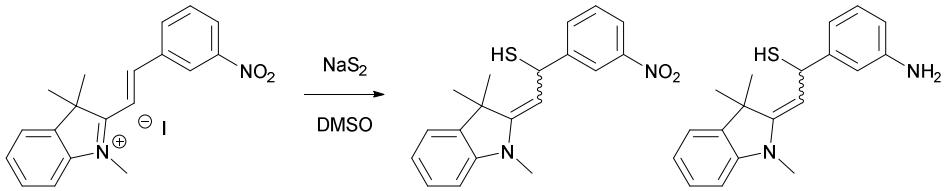
^{1}H NMR spectrum for 7e + NaSMe (5.0 eq.)



^{13}C NMR spectrum for 7e + NaSMe (5.0 eq.)



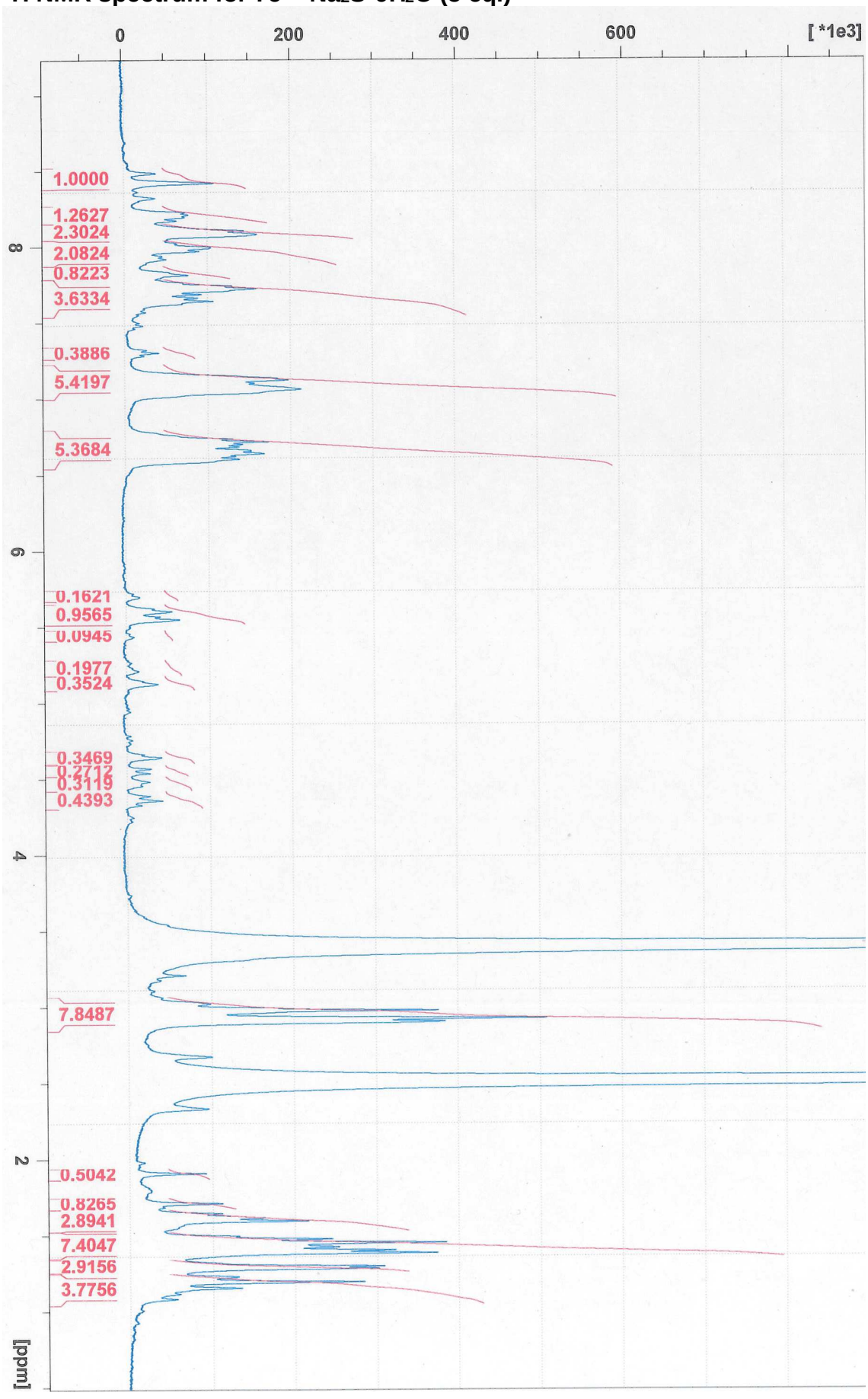
Reaction with sodium sulfide



7e **10e** **10h**

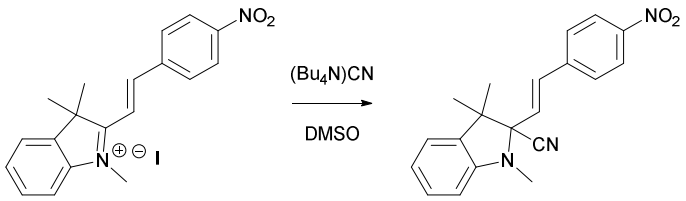
LRMS-ES+ (*m/z*): 307 (5%, **10e**$^{+}$−SH), 277 (5%, **10h**$^{+}$−SH).

^{1}H NMR spectrum for 7e + $Na_2S \cdot 9H_2O$ (5 eq.)



3.6 Reactions of 7f

Reaction with tetrabutylammonium cyanide



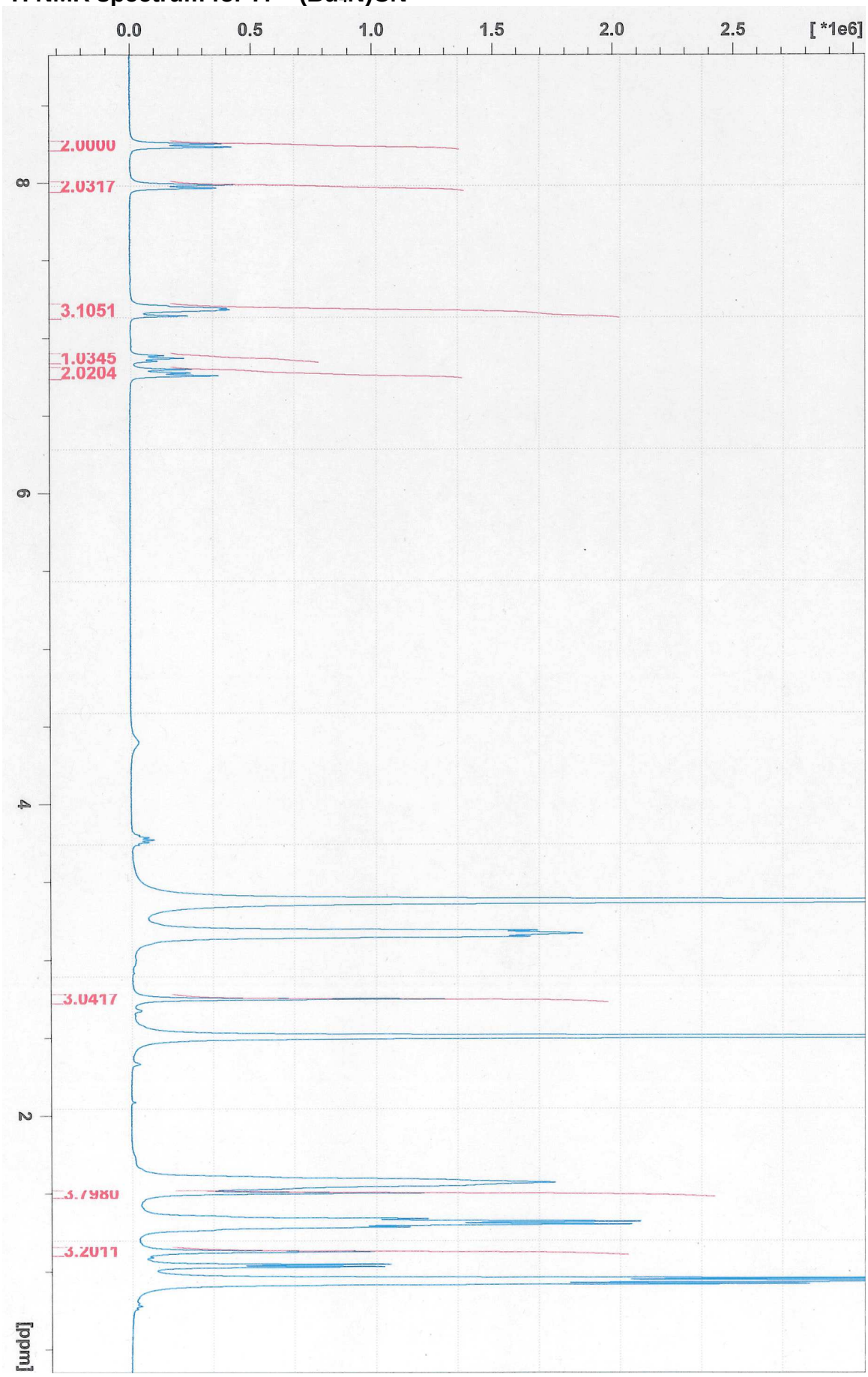
7f **8f**

Data for (*E*)-1,3,3-trimethyl-2-(4-nitrostyryl)indoline-2-carbonitrile 8f

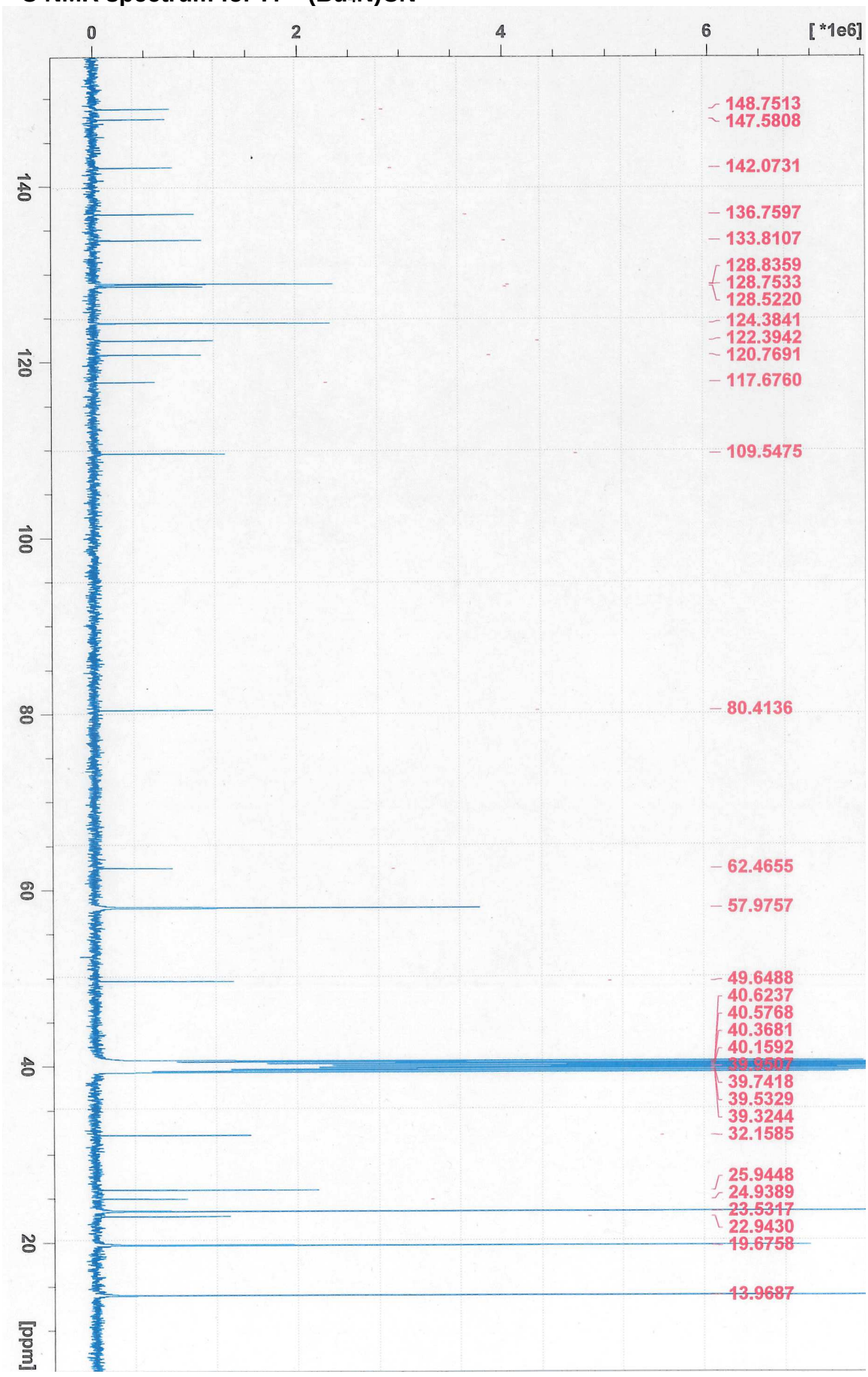
δH (400 MHz; DMSO-d_6) 8.24 (2 H, d, *J* 8.4, 3'- and 5'-H), 7.98 (2 H, d, *J* 8.4, 2'- and 6'-H), 7.23-7.13 (3 H, m, β-, 4- and 6-H), 6.87 (1 H, t, *J* 7.5, 5-H), 6.78 (1 H, d, *J* 7.5, 7-H), 6.76 (1 H, d, *J* 16.2, α-H), 2.71 (3 H, s, NMe), 1.45 (3 H, s, CMe) and 1.18 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 148.8 (7a-C), 147.6 (4'-C), 142.1 (1'-C), 136.8 (3a-C), 133.8 (β-C), 128.8 (2'- and 6'-C), 128.7 (6-C), 128.5 (α-C), 124.4 (3'- and 5'-C), 122.4 (4-C), 120.8 (5-C), 117.7 (CN), 109.5 (7-C), 80.4 (*C*CN), 49.6 (*C*Me_2), 32.2 (NMe), 24.9 (C*Me*) and 22.9 (C*Me*).

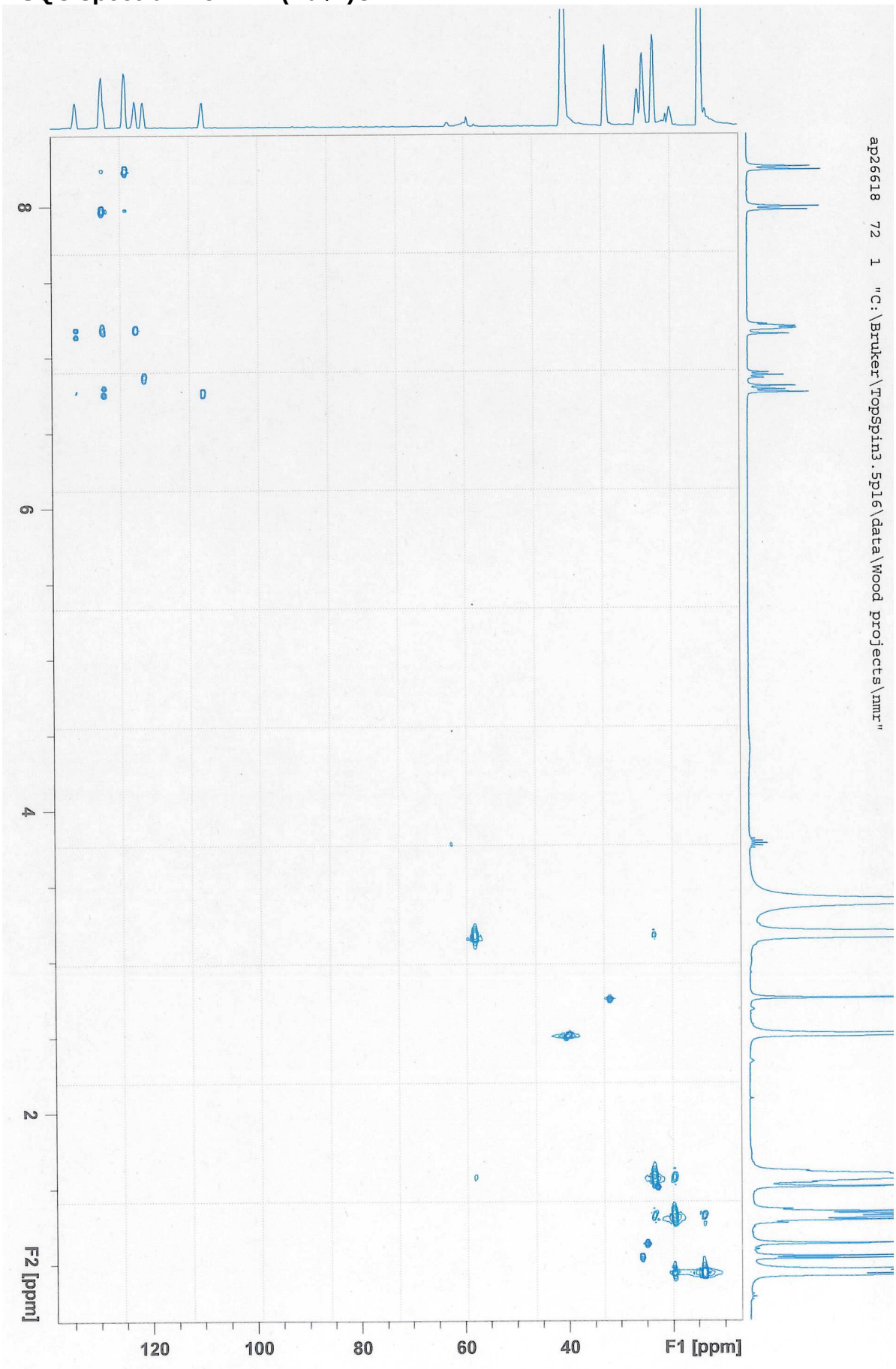
^{1}H NMR spectrum for 7f + (Bu_4N)CN



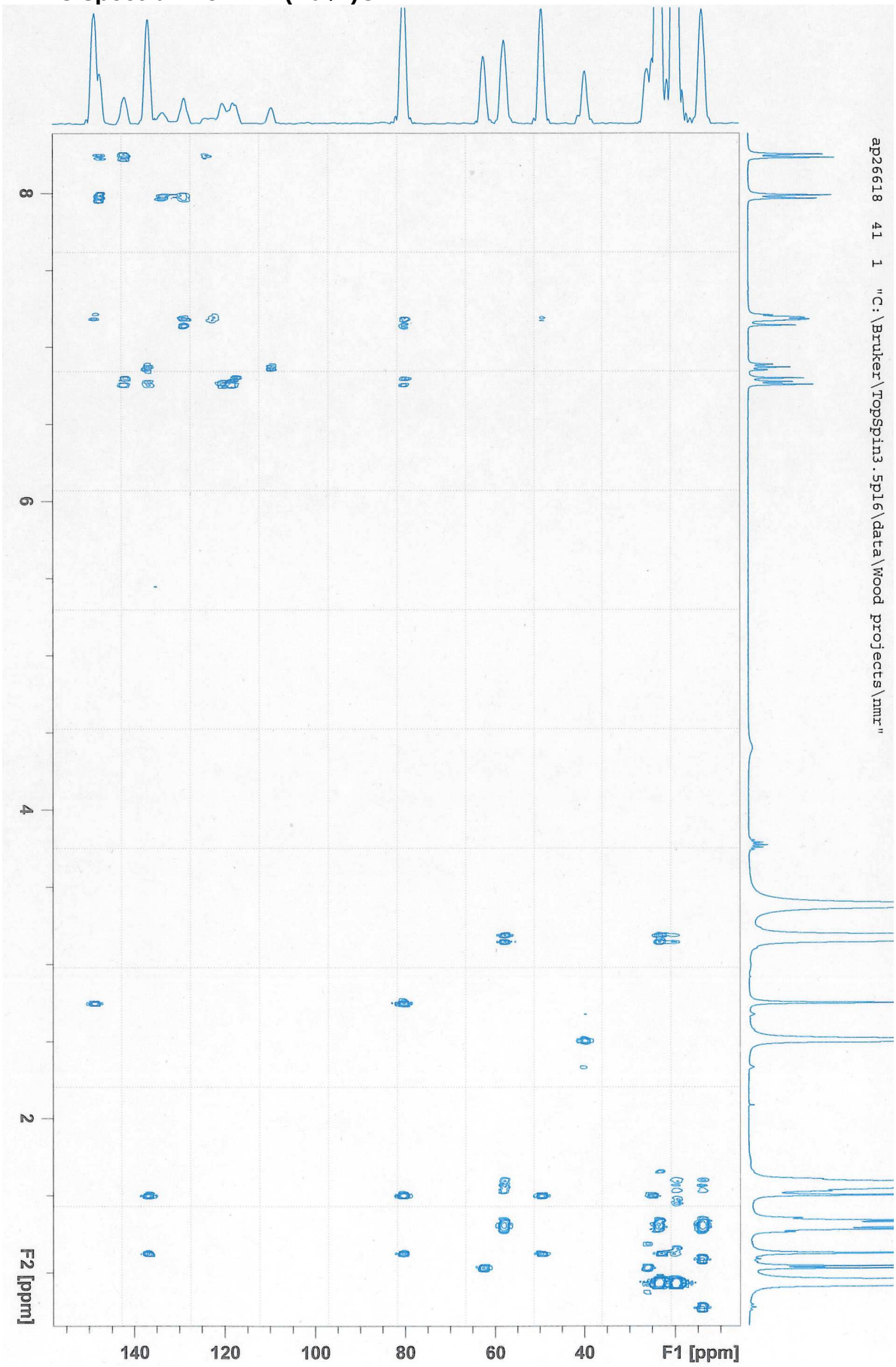
^{13}C NMR spectrum for 7f + (Bu_4N)CN



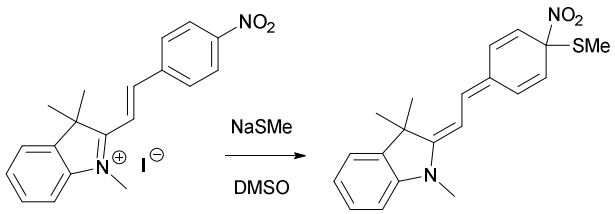
HSQC spectrum for 7f + (Bu_4N)CN



HMBC spectrum for 7f + (Bu_4N)CN



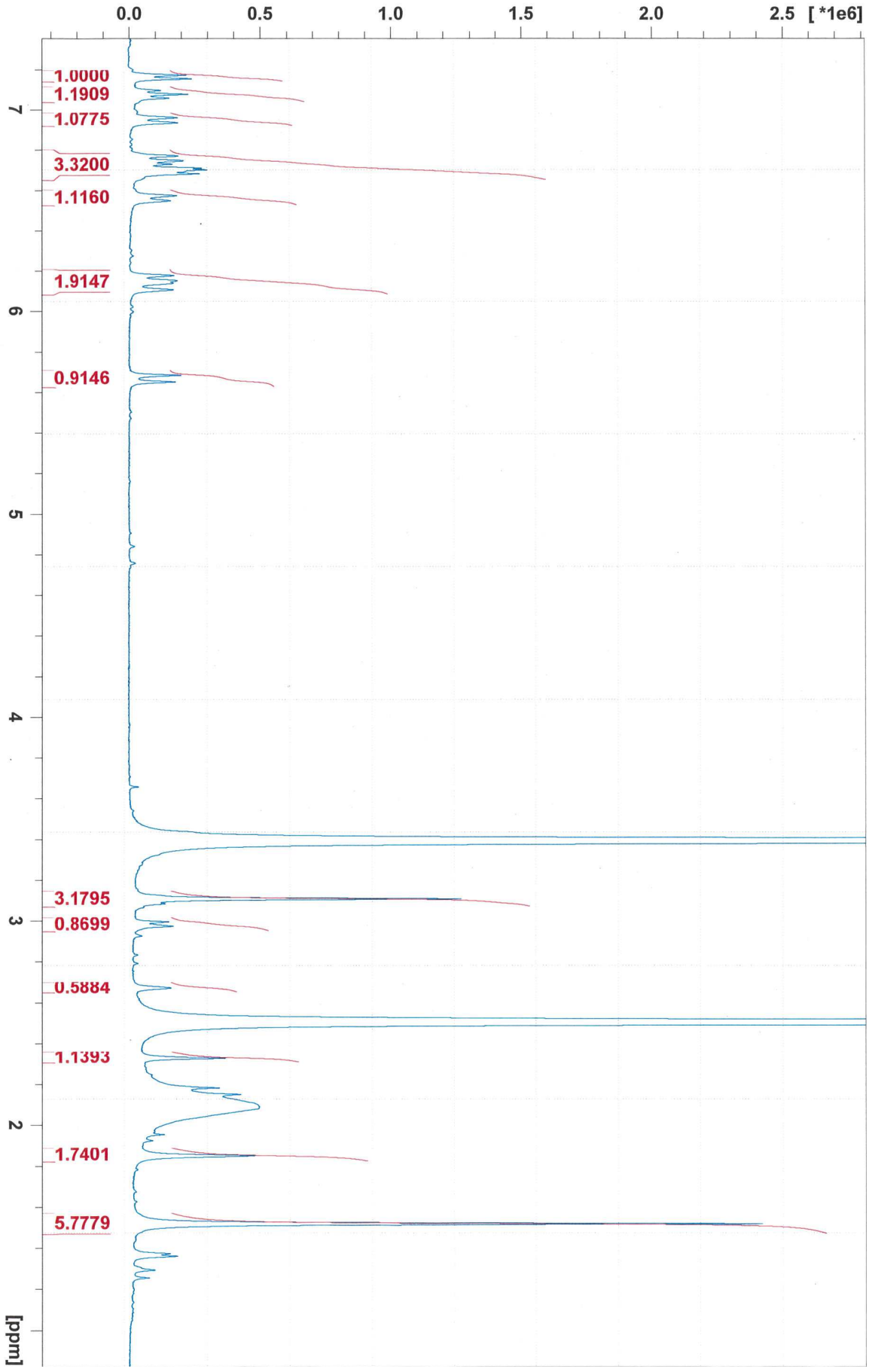
Reaction with sodium methanethiolate



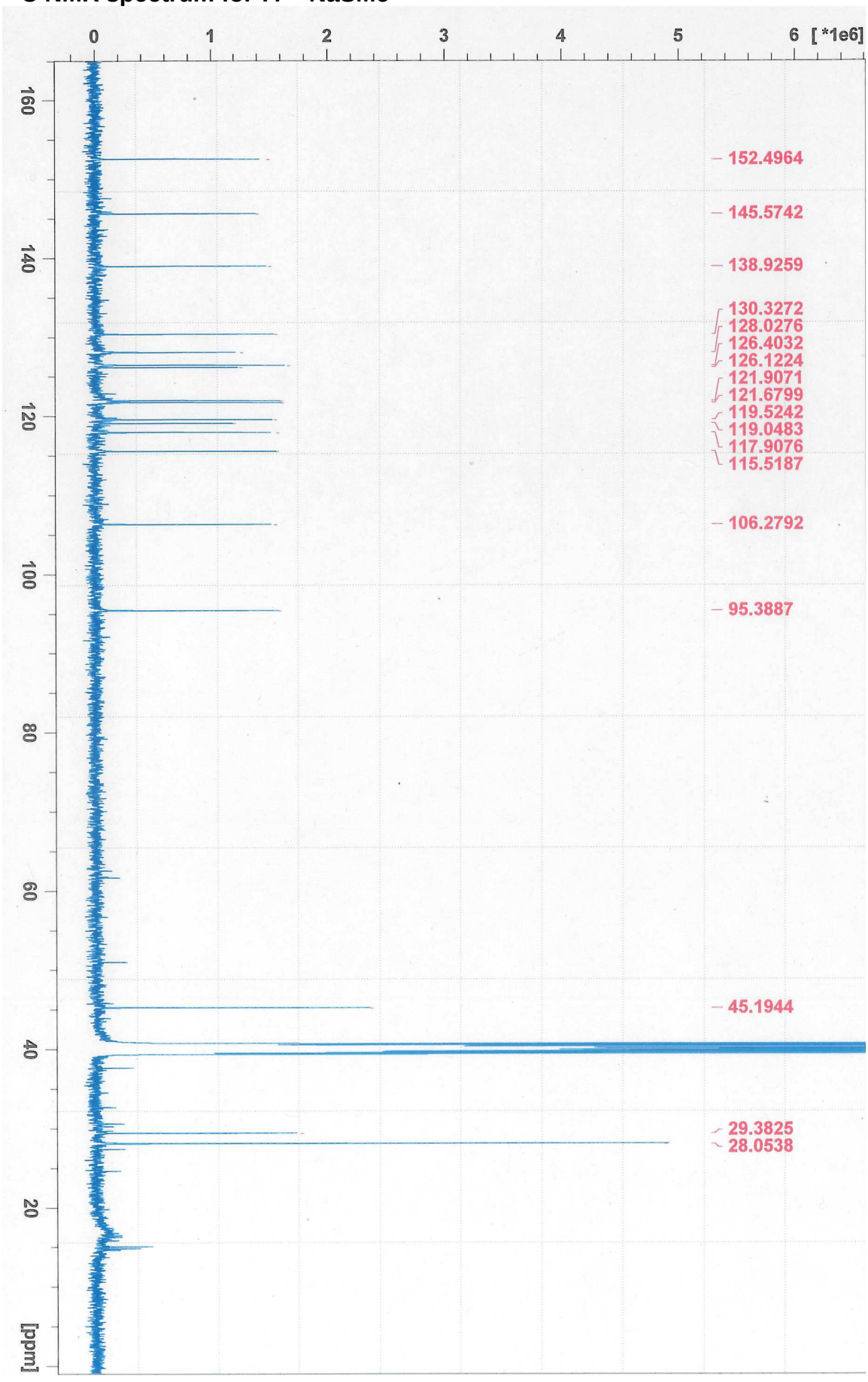
7f **11a**

Data for (*E*)-1-nitro-4-(2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexa-2,5-diene-1-methylthioether 11a
δH (400 MHz; DMSO-d_6) 7.16 (1 H, d, *J* 7.5, 4-H), 7.08 (1 H, t, *J* 7.5, 6-H), 6.95 (1 H, d, *J* 9.9, 6'-H), 6.80-6.64 (3 H, m, 2'-, 5- and 7-H), 6.56 (1 H, d, *J* 9.9, 5'-H), 6.17 (1 H, d, *J* 10.1, 3'-H), 6.13 (1 H, d, *J* 13.2, β-H), 5.67 (1 H, d, *J* 13.2, α-H), 3.12 (3 H, s, NMe), 1.86 (3 H, s, SMe) and 1.51 (6 H, s, CMe_2).
δC (100 MHz; DMSO-d_6); 152.4 (2-C), 145.6 (7a-C), 138.9 (3a-C), 130.3 (4'-C), 128.0 (6-C), 126.4 (3'-C), 126.1(1'-C), 121.9 (4-C), 121.8 (6'-C), 119.5 (2'-C), 119.0 (5-C), 117.9 (5'-C), 115.5 (β-C), 106.3 (7-C), 95.4 (α-C), 51.0 (SMe), 45.2 (CMe_2), 29.4 (NMe) and 28.1 (CMe_2).
LRMS-ES+ (*m/z*): 354 (60%, M^+), 307 (20%, M^+−SMe).

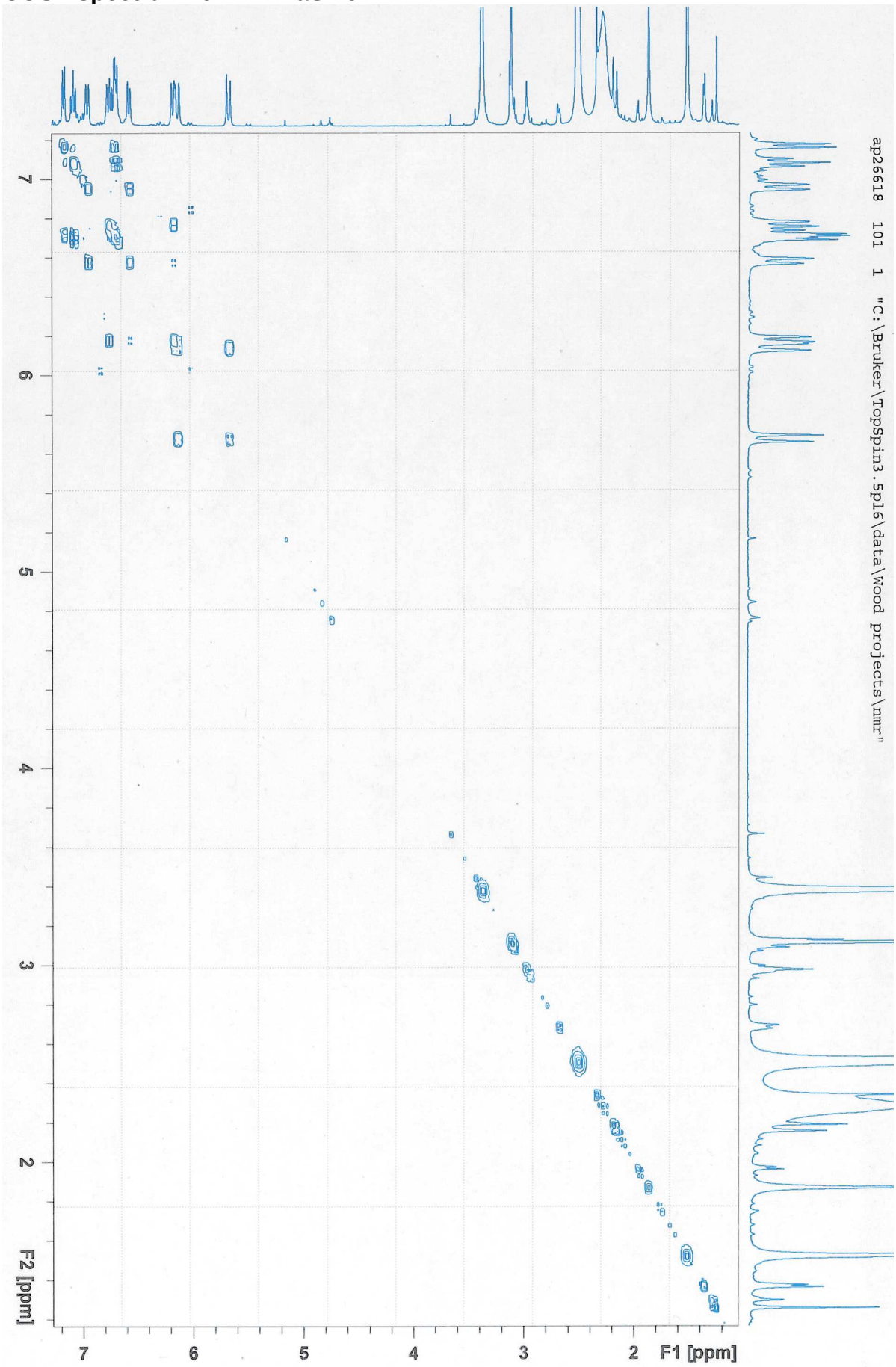
^{1}H NMR spectrum for 7f + NaSMe



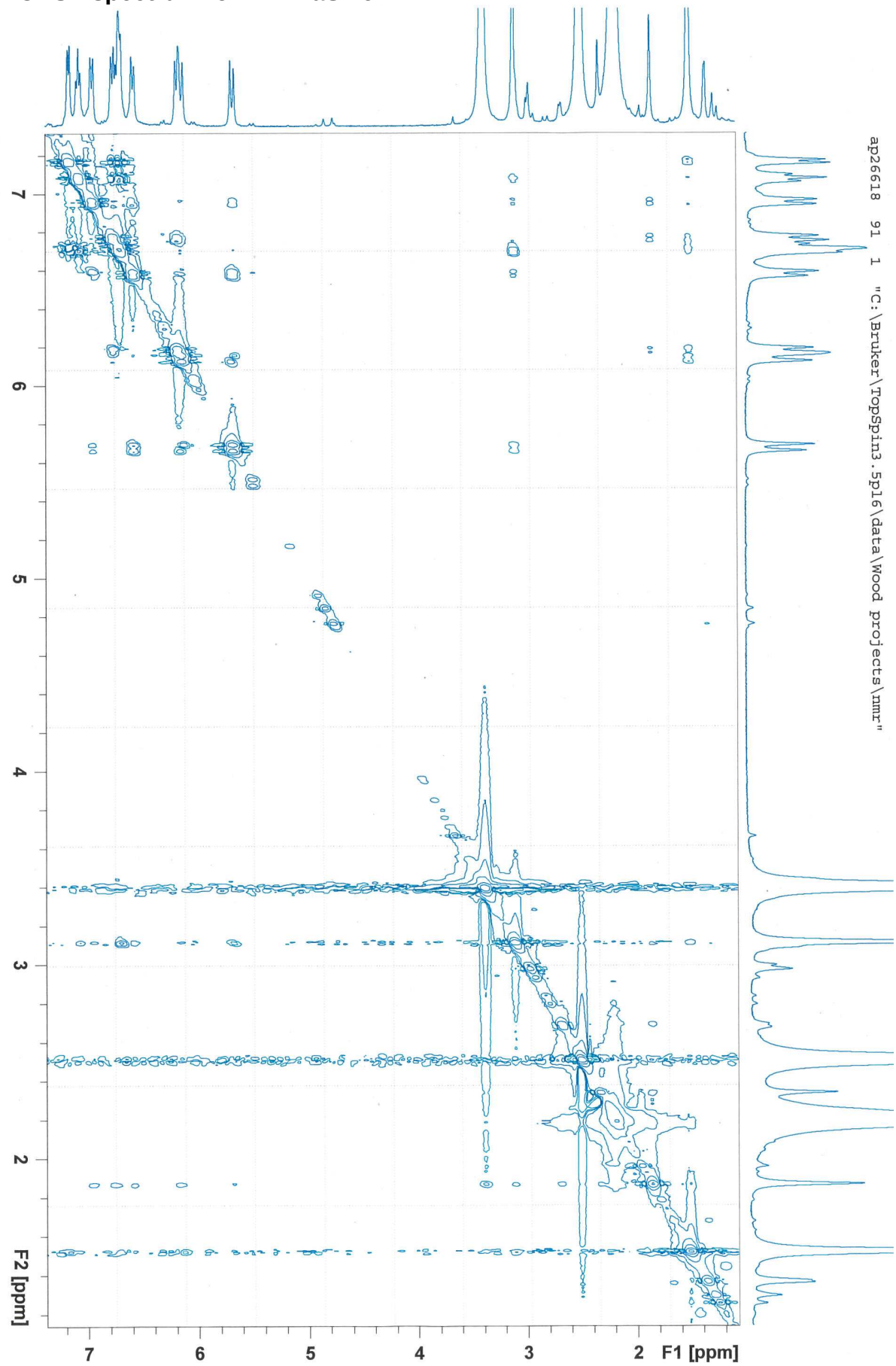
^{13}C NMR spectrum for 7f + NaSMe



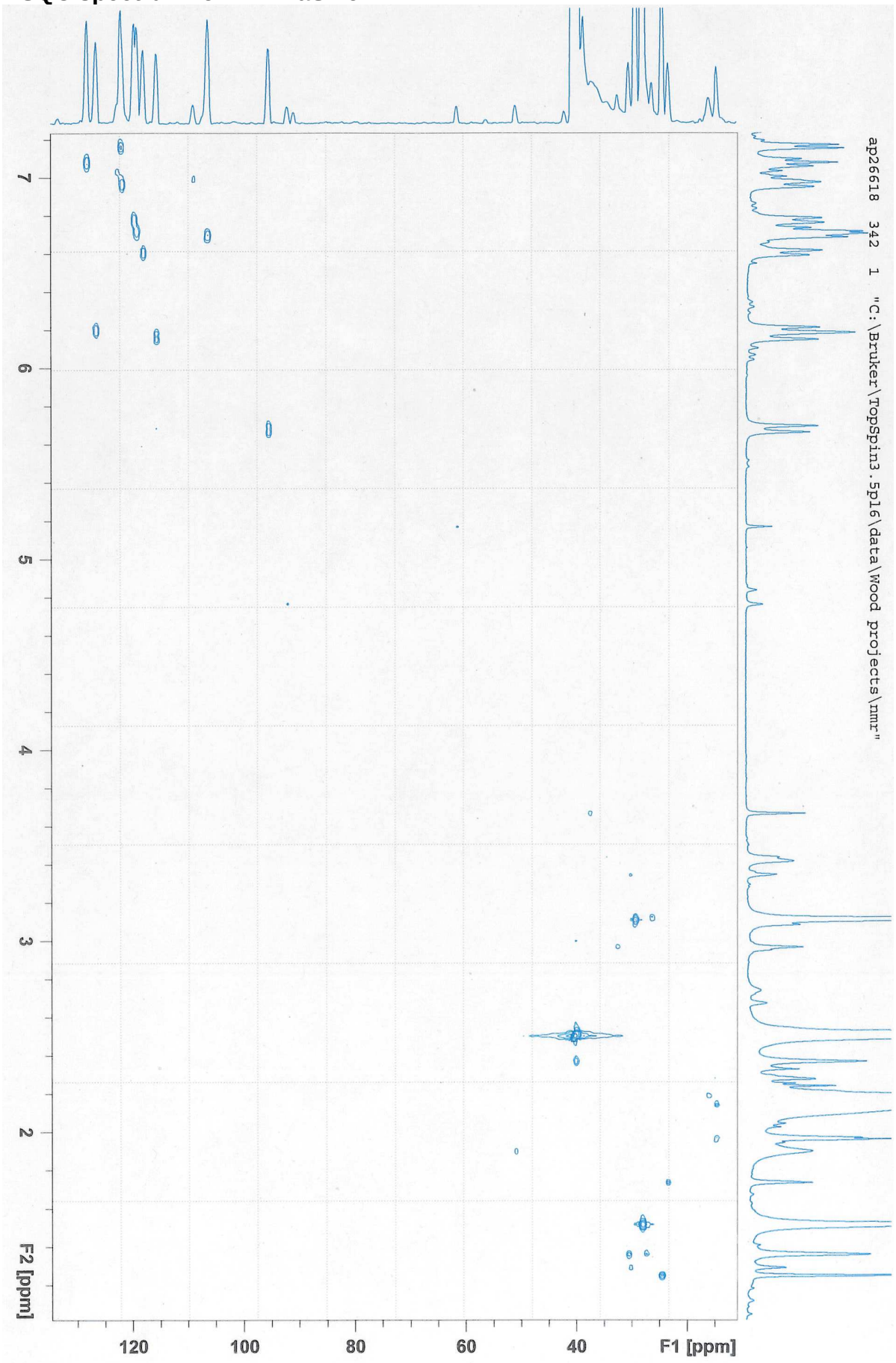
COSY spectrum for 7f + NaSMe



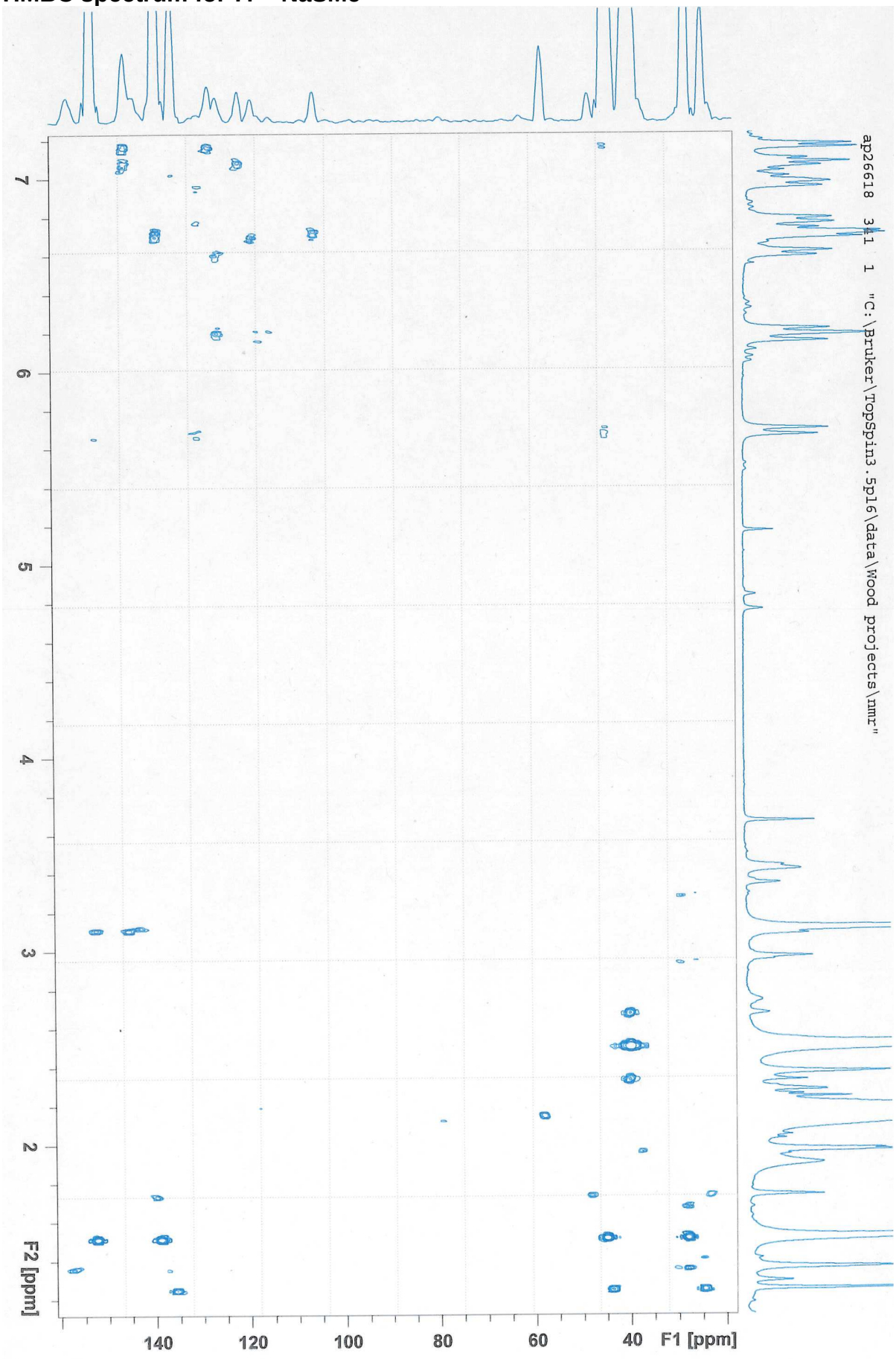
NOESY spectrum for 7f + NaSMe



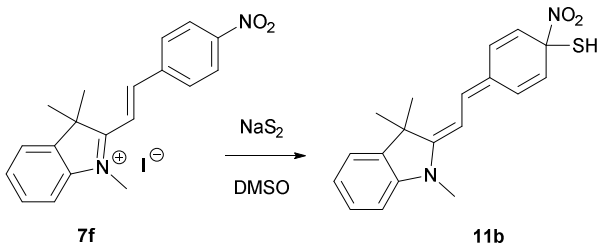
HSQC spectrum for 7f + NaSMe



HMBC spectrum for 7f + NaSMe



Reaction with sodium sulfide



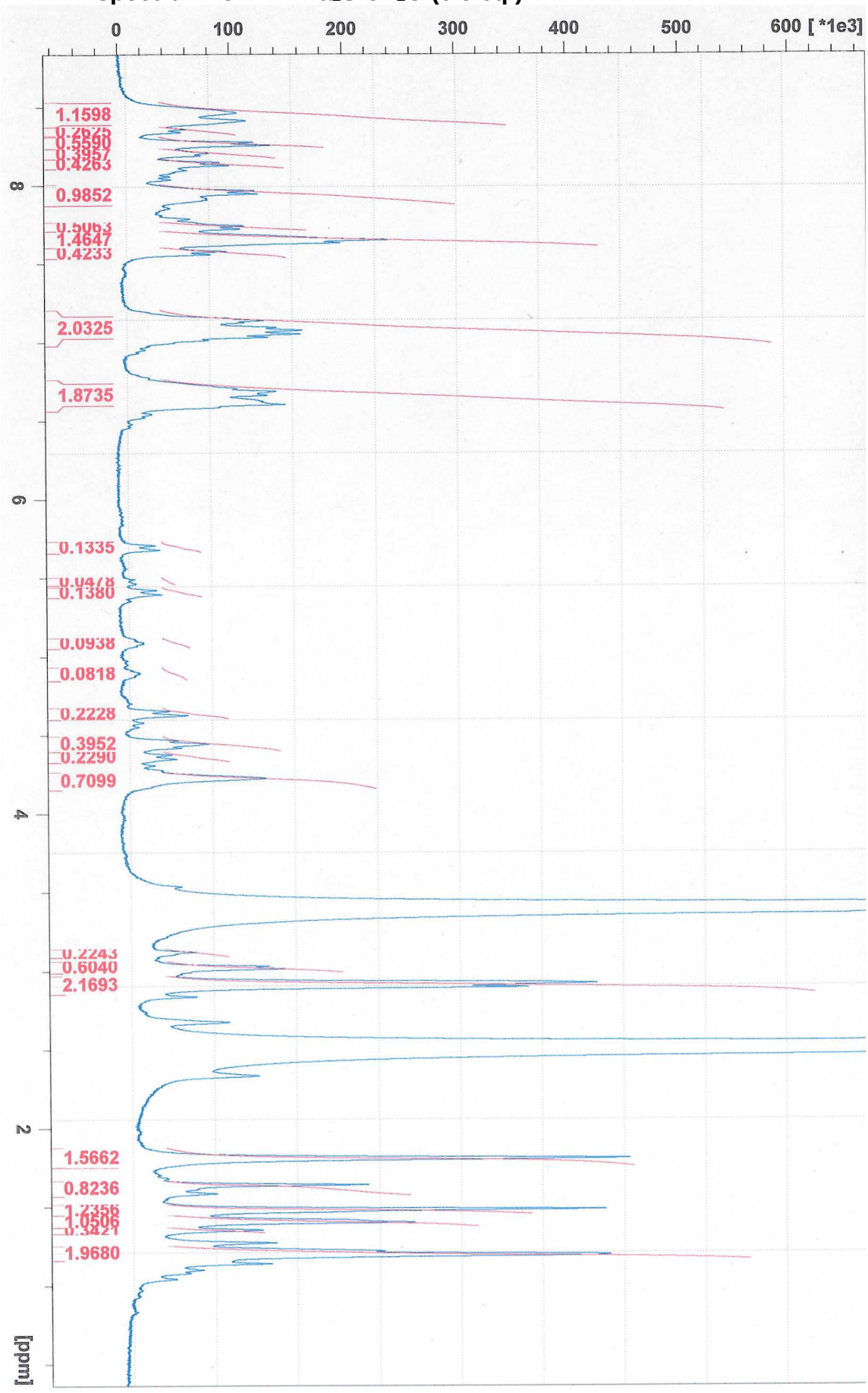
7f **11b**

Data for (*E*)-1-nitro-4-(2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexa-2,5-diene-1-thiol 11b

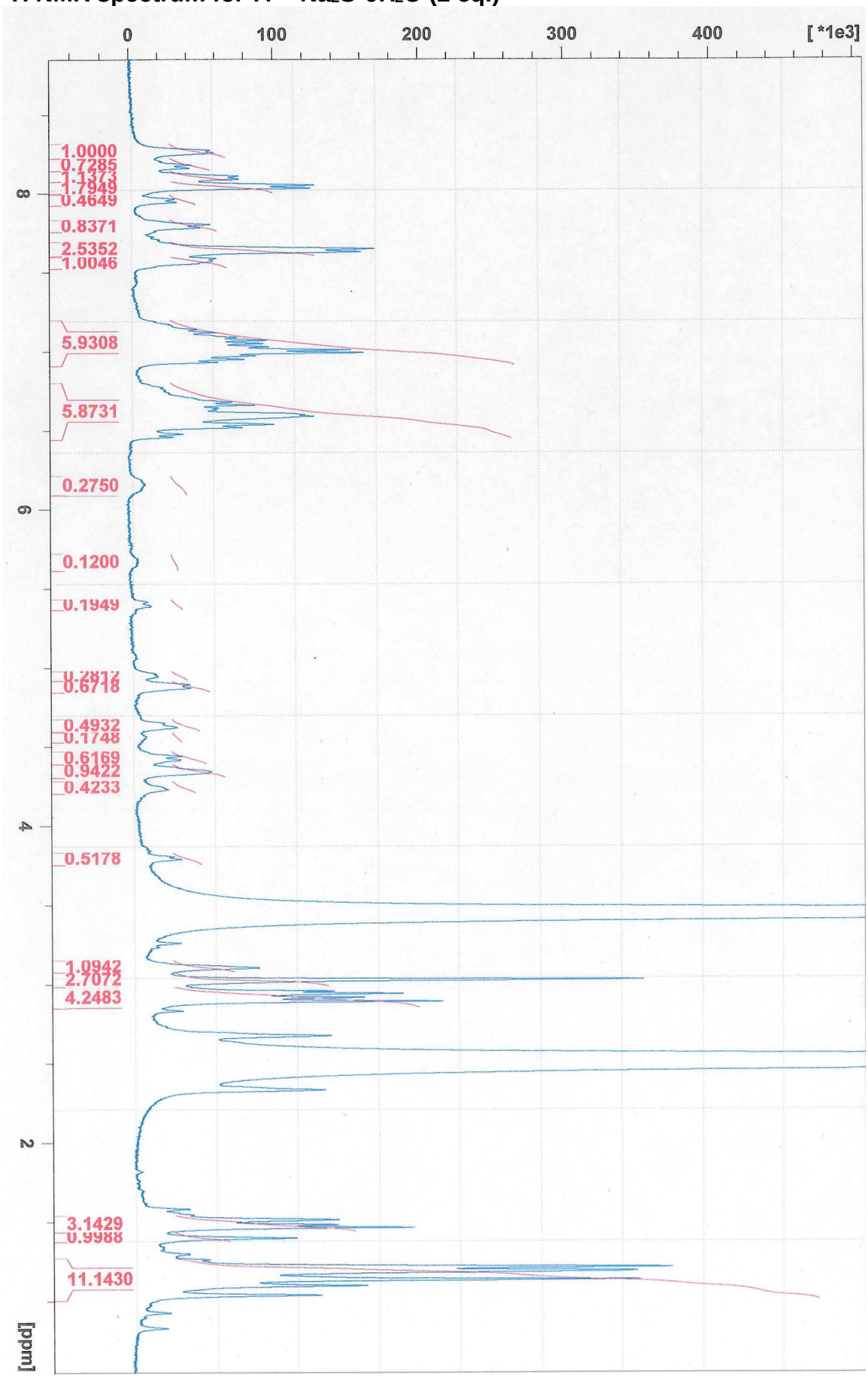
δH (400 MHz; DMSO-d_6) 7.16 (1 H, d, *J* 7.3, 4-H), 7.08 (1 H, t, *J* 7.3, 6-H), 6.95 (1 H, d, *J* 9.9, 6'-H), 6.76 (1 H, d, *J* 10.2, 2'-H), 6.75 (1 H, t, *J* 7.3, 5-H), 6.70 (1 H, d, *J* 7.3, 7-H), 6.59 (1 H, d, *J* 9.9, 5'-H), 6.19 (1 H, d, *J* 10.2, 3'-H), 6.15 (1 H, d, *J* 13.0, β-H), 5.68 (1 H, d, *J* 13.0, α-H), 3.11 (3 H, s, NMe) and 1.50 (6 H, s, CMe_2).

δC (100 MHz; DMSO-d_6); 152.4 (2-C), 145.6 (7a-C), 138.9 (3a-C), 130.4 (4'-C), 128.1 (6-C), 126.3 (3'-C), 121.9 (4-C), 121.8 (6'-C), 119.6 (2'-C), 119.1 (5-C), 118.3 (1'-C), 117.8 (5'-C), 115.3 (β-C), 106.3 (7-C), 95.3 (α-C), 45.2 (CMe_2), 29.4 (NMe) and 28.0 (CMe_2).

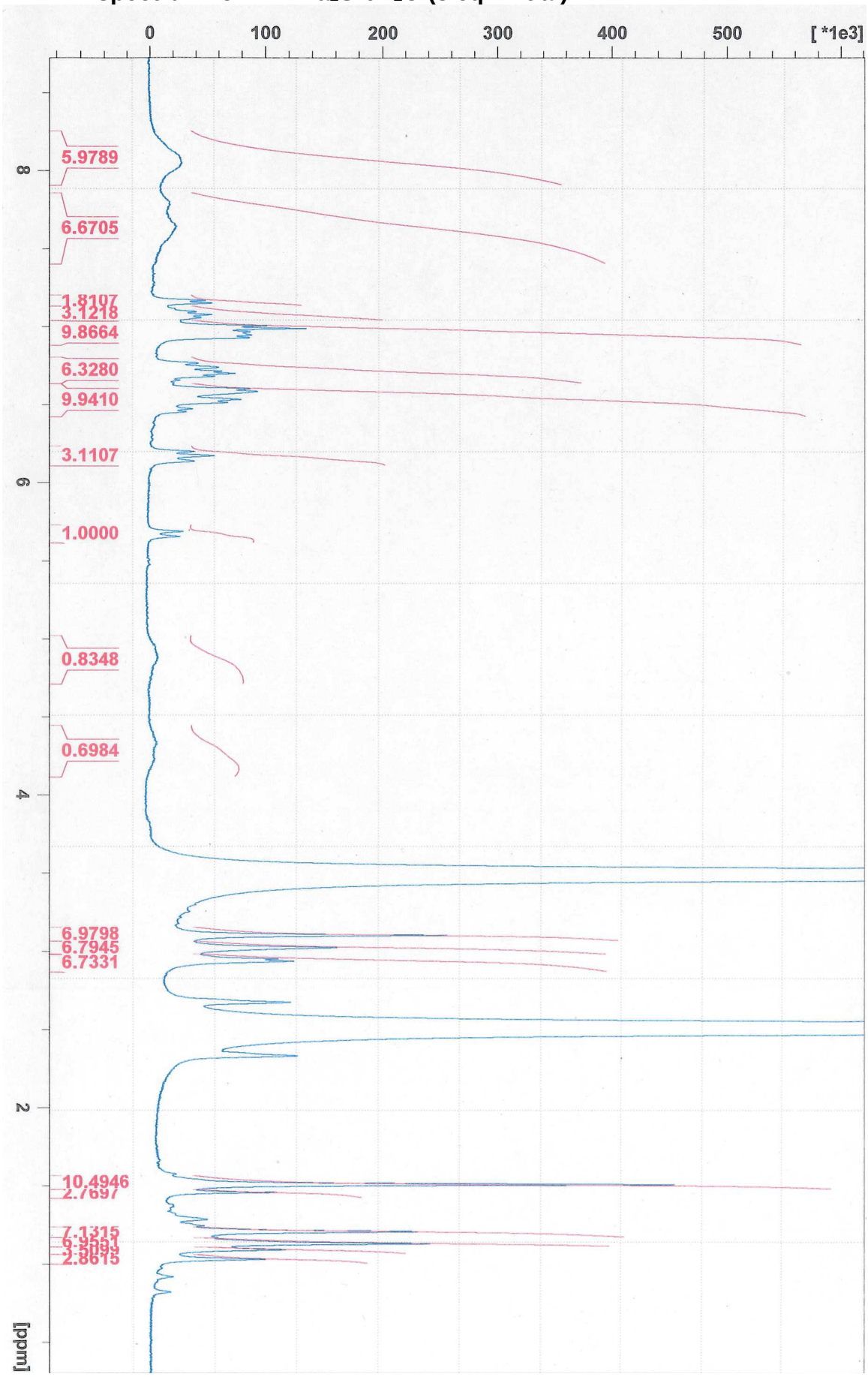
^{1}H NMR spectrum for 7f + $Na_2S \cdot 9H_2O$ (0.5 eq.)



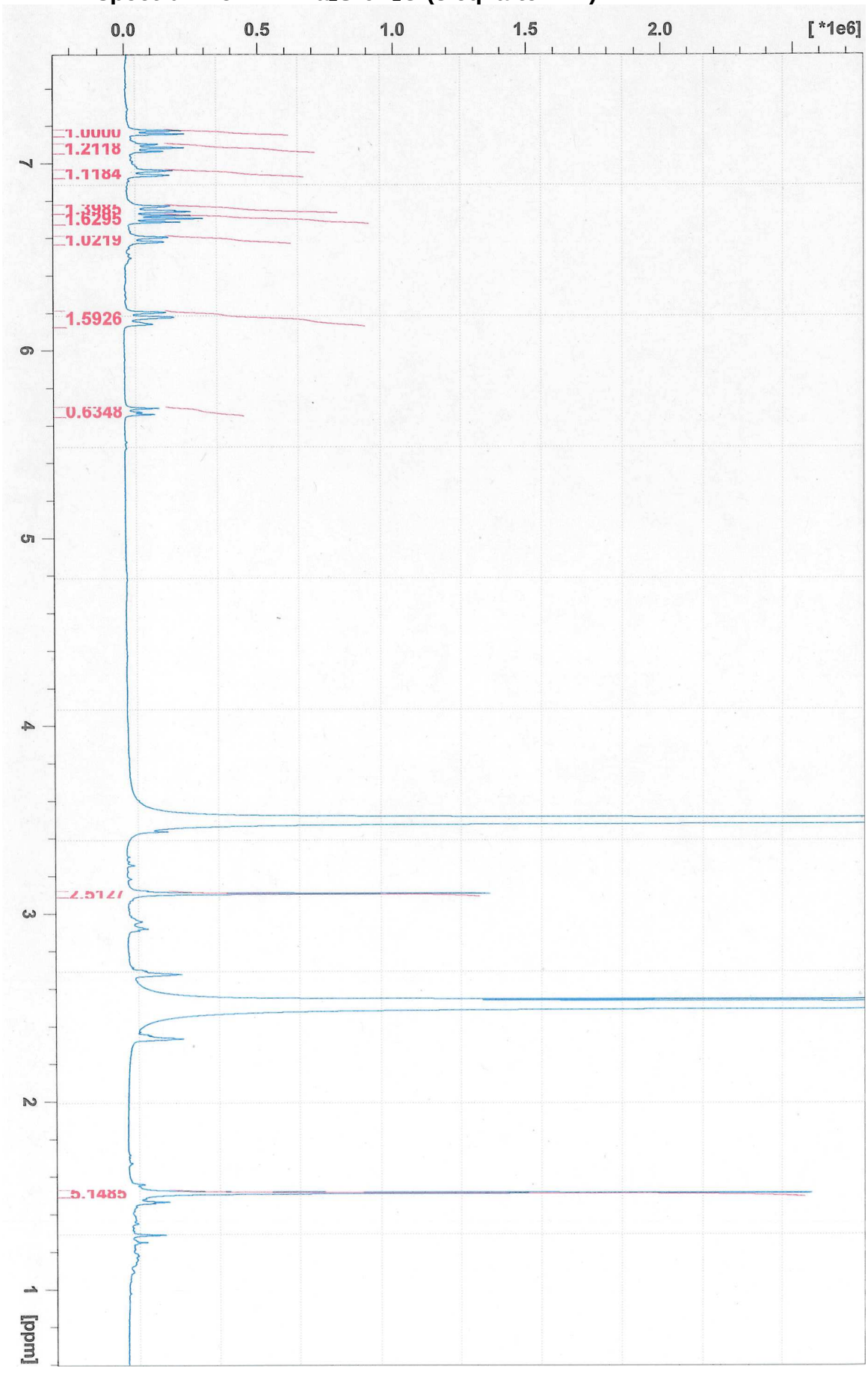
^{1}H NMR spectrum for 7f + $Na_2S \cdot 9H_2O$ (2 eq.)



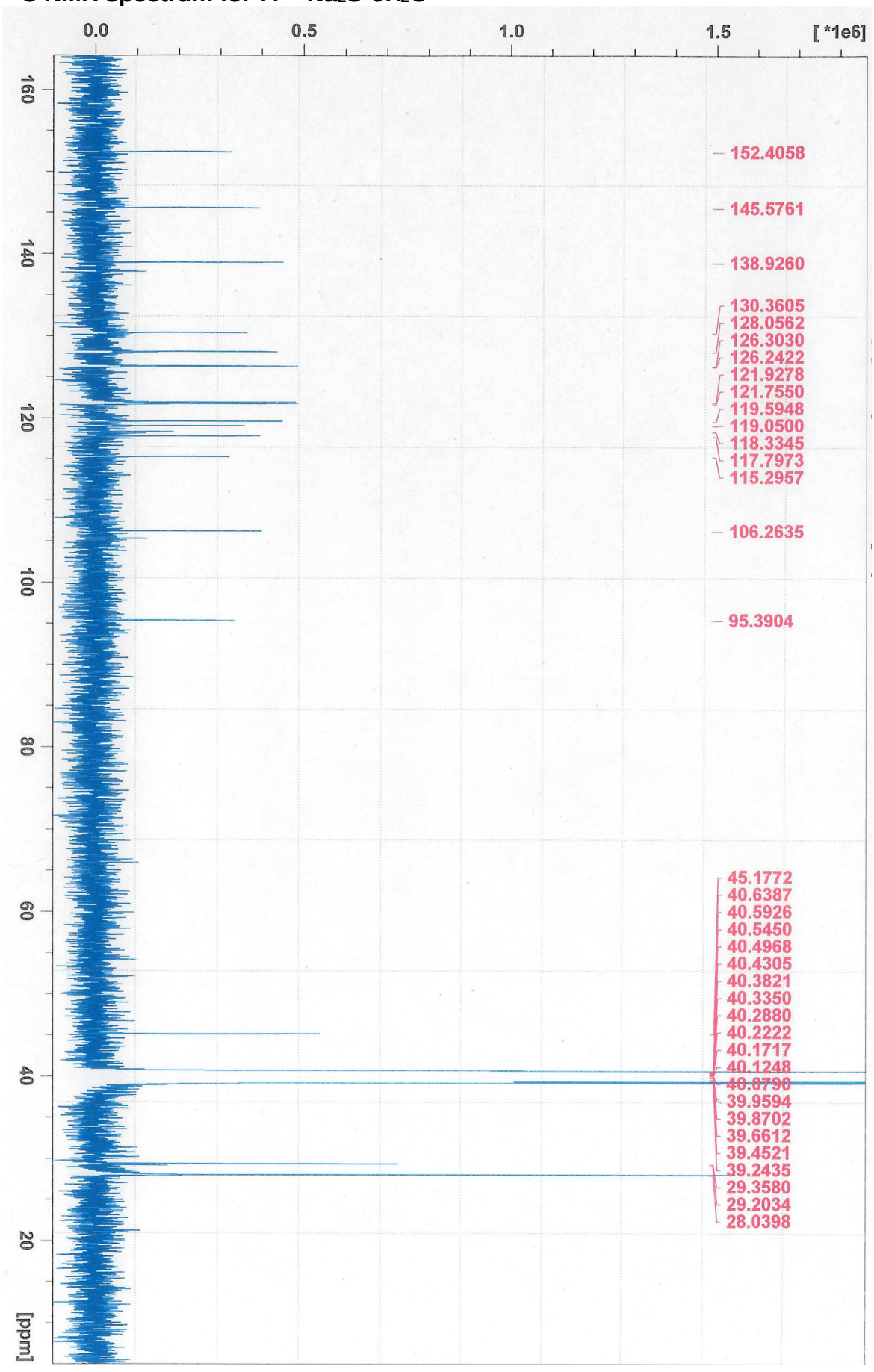
^{1}H NMR spectrum for 7f + $Na_2S \cdot 9H_2O$ (3 eq. initial)



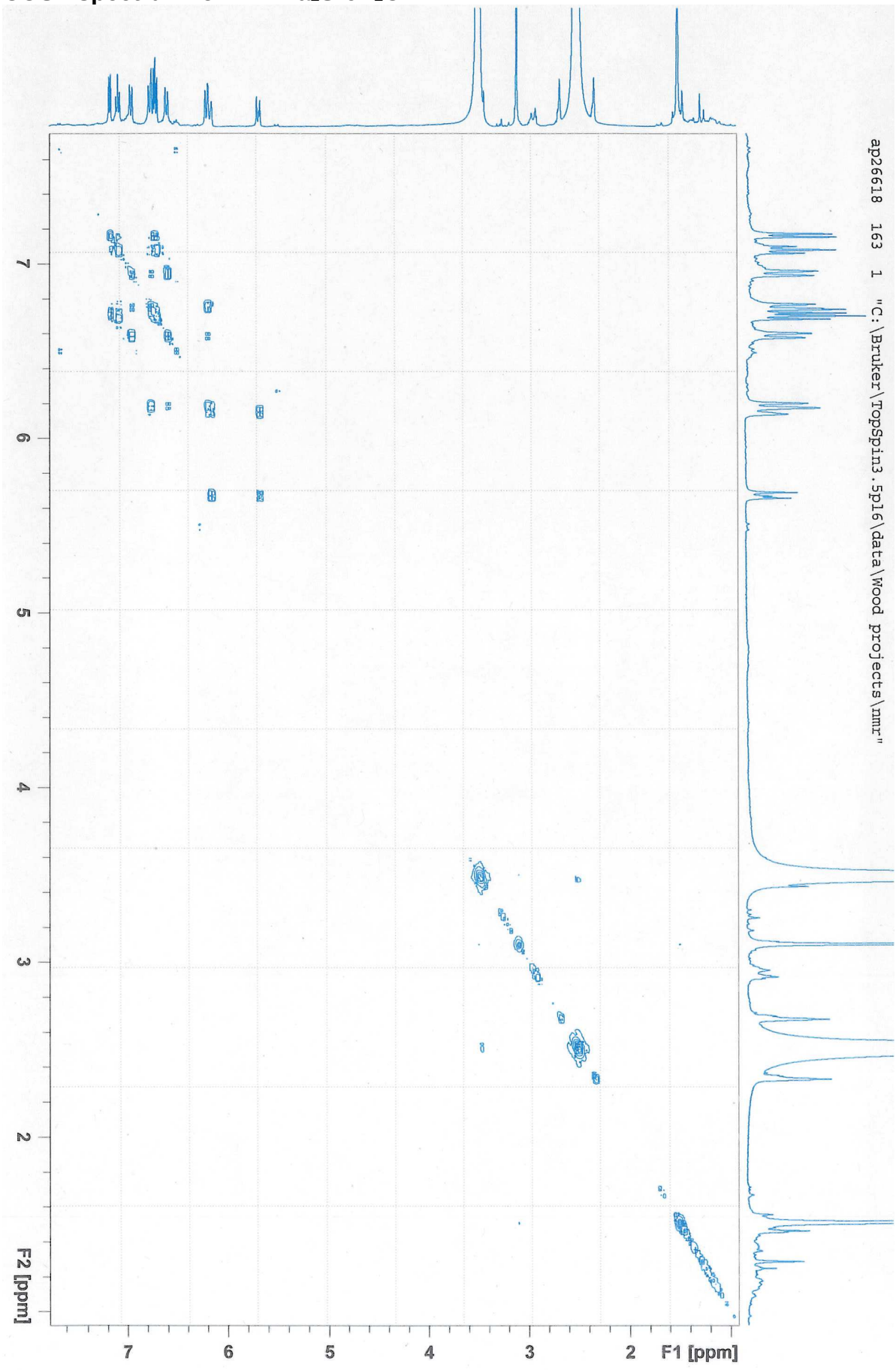
^{1}H NMR spectrum for 7f + $Na_2S \cdot 9H_2O$ (3 eq. after 2 h)



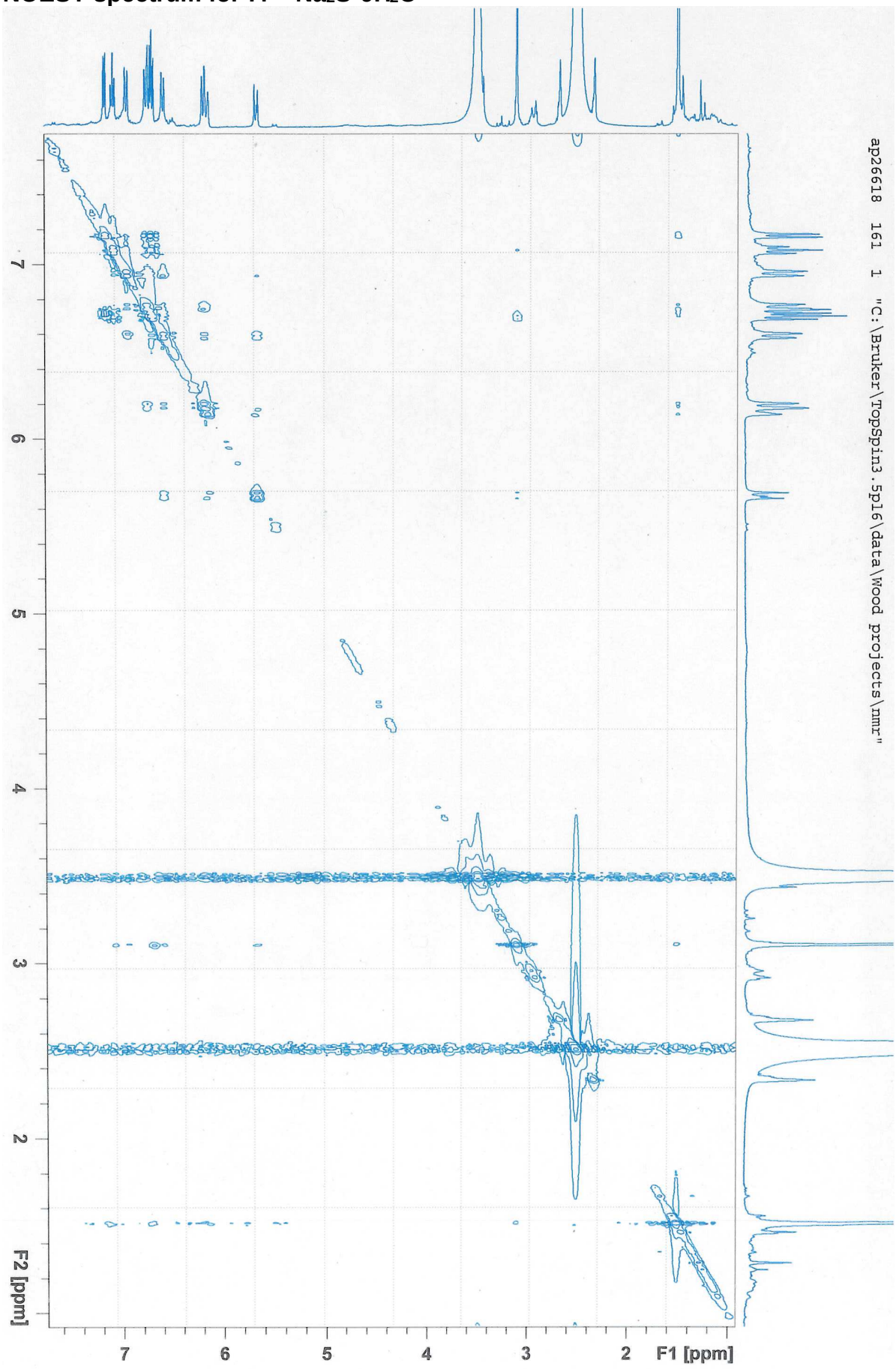
^{13}C NMR spectrum for 7f + $Na_2S \cdot 9H_2O$



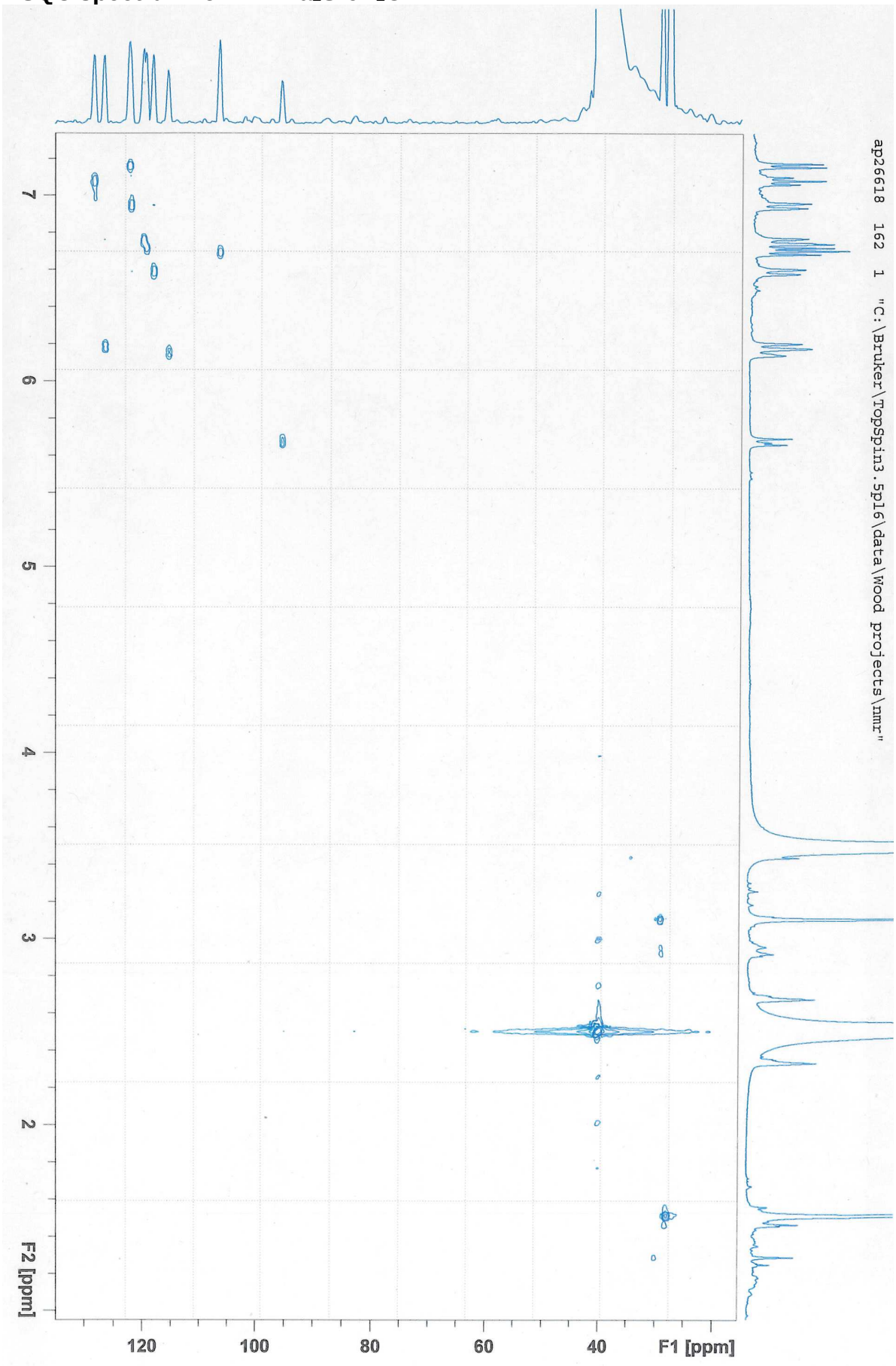
COSY spectrum for 7f + $Na_2S \cdot 9H_2O$



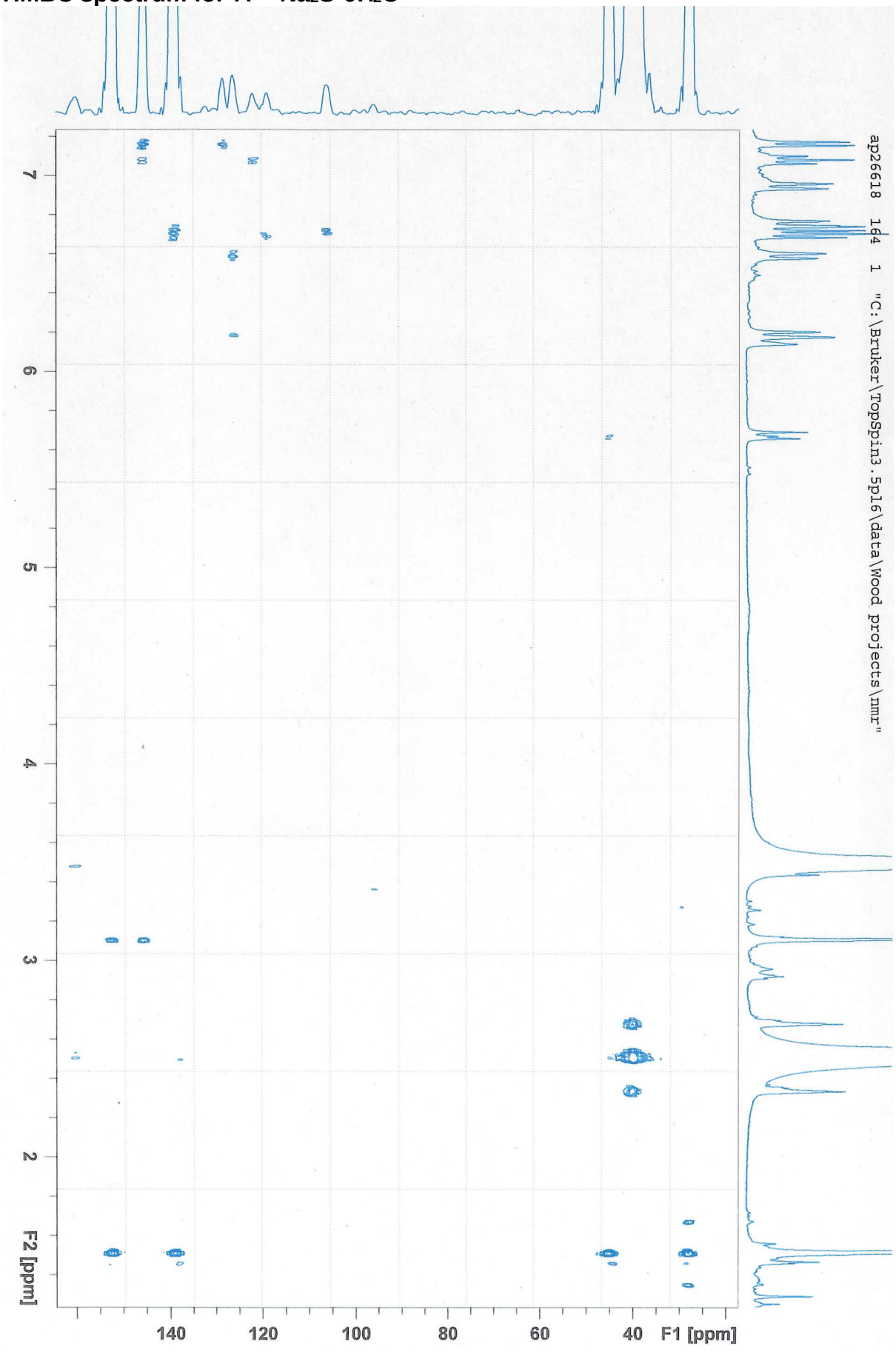
NOESY spectrum for 7f + $Na_2S \cdot 9H_2O$



HSQC spectrum for 7f + $Na_2S \cdot 9H_2O$

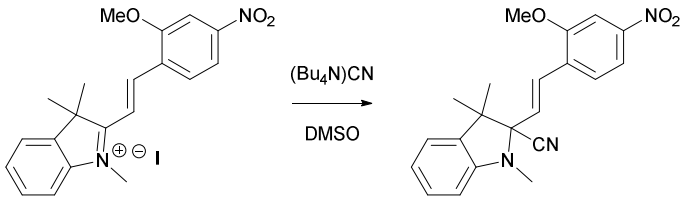


HMBC spectrum for 7f + $Na_2S \cdot 9H_2O$



3.7 Reactions of 7g

Reaction with tetrabutylammonium cyanide



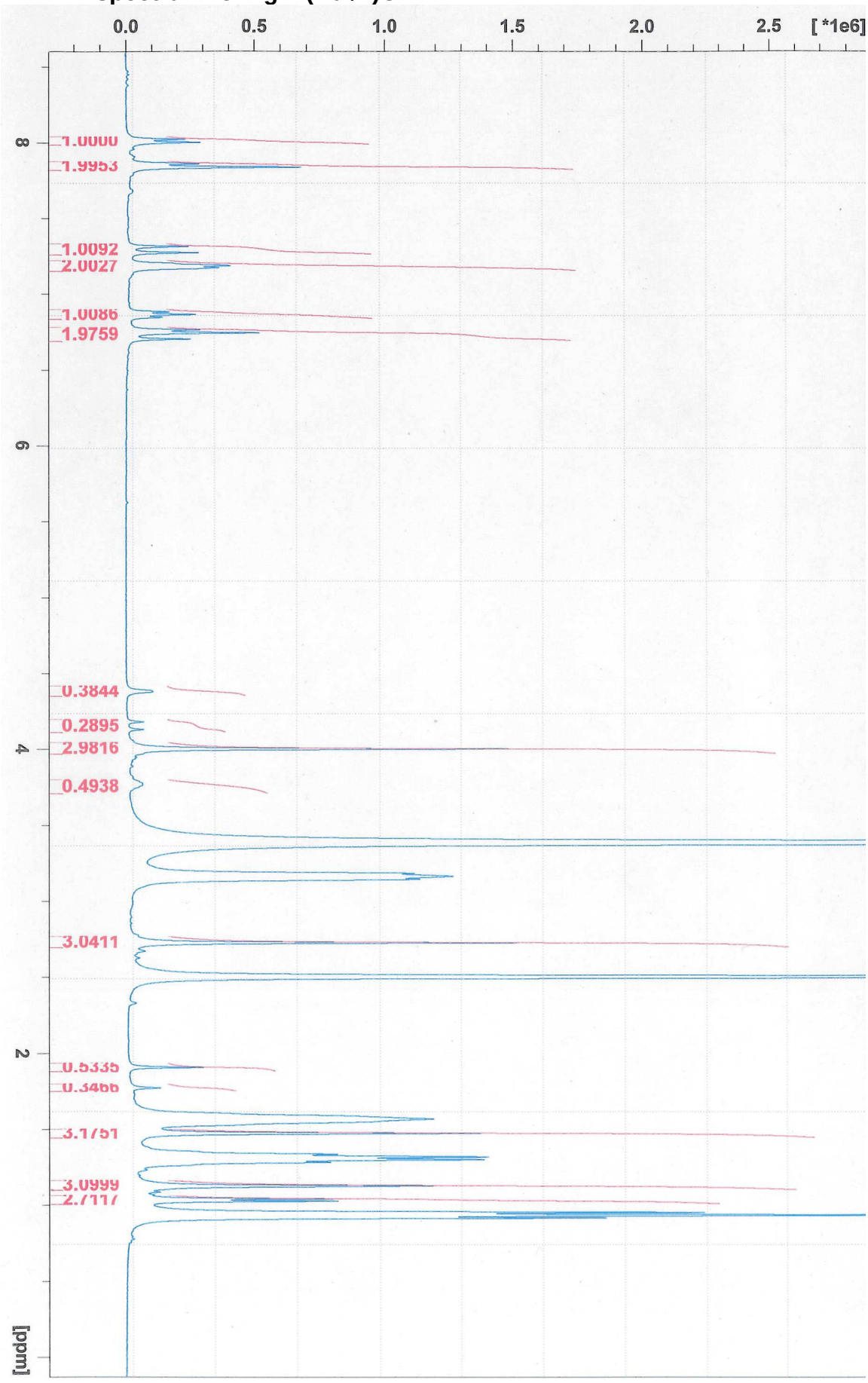
7g **8g**

Data for (*E*)-1,3,3-trimethyl-2-(2-methoxy-4-nitrostyryl)indoline-2-carbonitrile 8g

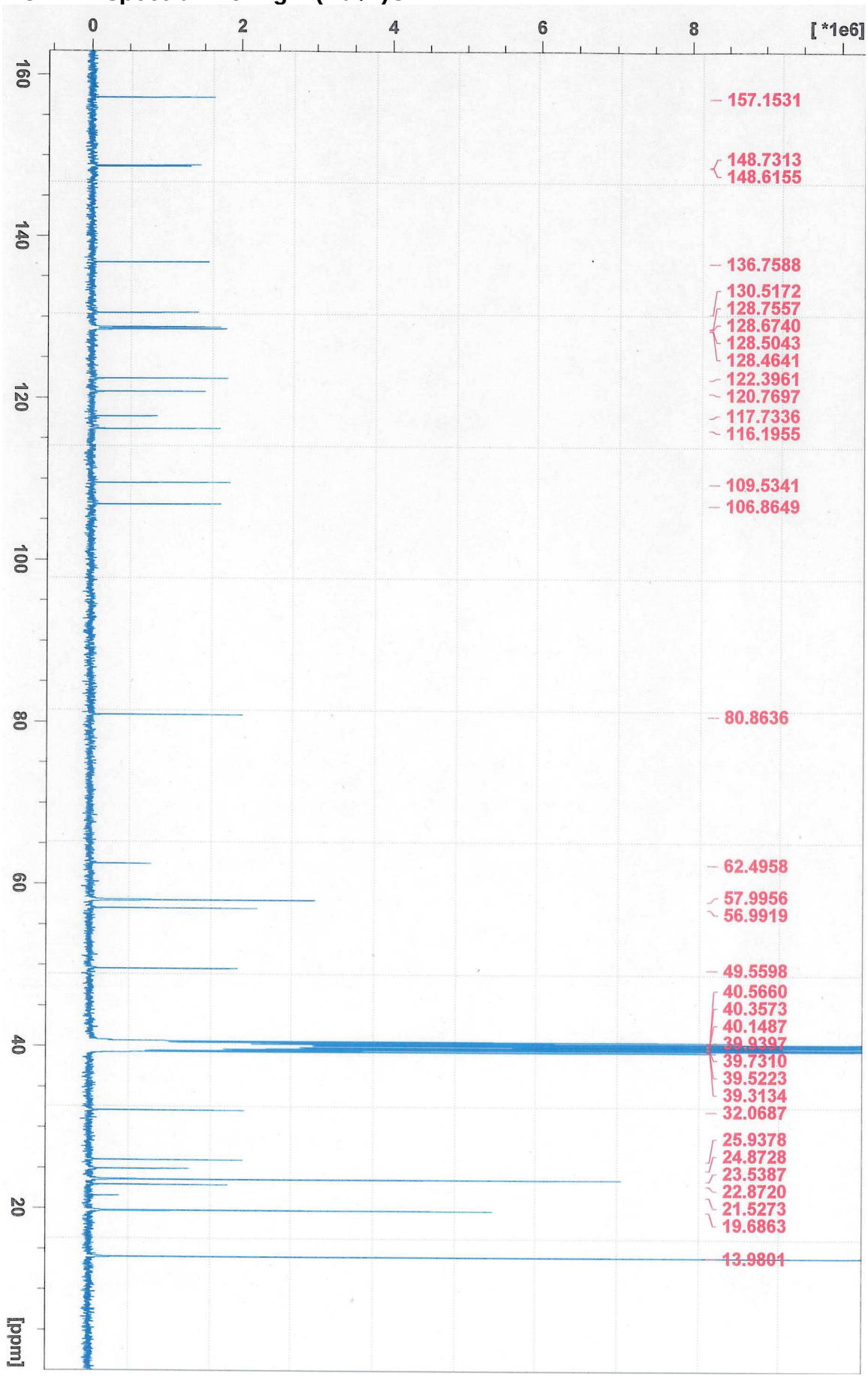
δH (400 MHz; DMSO-d_6) 8.01 (1 H, d, *J* 8.3, 5'-H), 7.85 (1 H, d, *J* 8.3, 6'-H), 7.84 (1 H, s, 3'-H), 7.29 (1 H, d, *J* 16.3, β-H), 7.25-7.15 (2 H, m, 4- and 6-H), 6.87 (1 H, t, *J* 7.5, 5-H), 6.76 (1 H, d, *J* 7.5, 7-H), 6.72 (1 H, d, *J* 16.3, α-H), 4.00 (3 H, s, OMe), 2.74 (3 H, s, NMe), 1.48 (3 H, s, CMe) and 1.16 (3 H, s, CMe).

δC (100 MHz; DMSO-d_6) 157.2 (2'-C), 148.7 (7a-C), 148.6 (4'-C), 136.8 (3a-C), 130.5 (1'-C), 128.8 (6-C), 128.7 (5'-C), 128.5 (α -C), 128.4 (β-C), 122.4 (4-C), 120.8 (5-C), 117.7 (CN), 116.2 (6'-C), 109.5 (7-C), 106.9 (3'-C), 80.8 (*C*CN), 57.0 (OMe), 49.6 (*C*Me_2), 32.1 (NMe), 24.9 (C*Me*) and 22.9 (C*Me*).

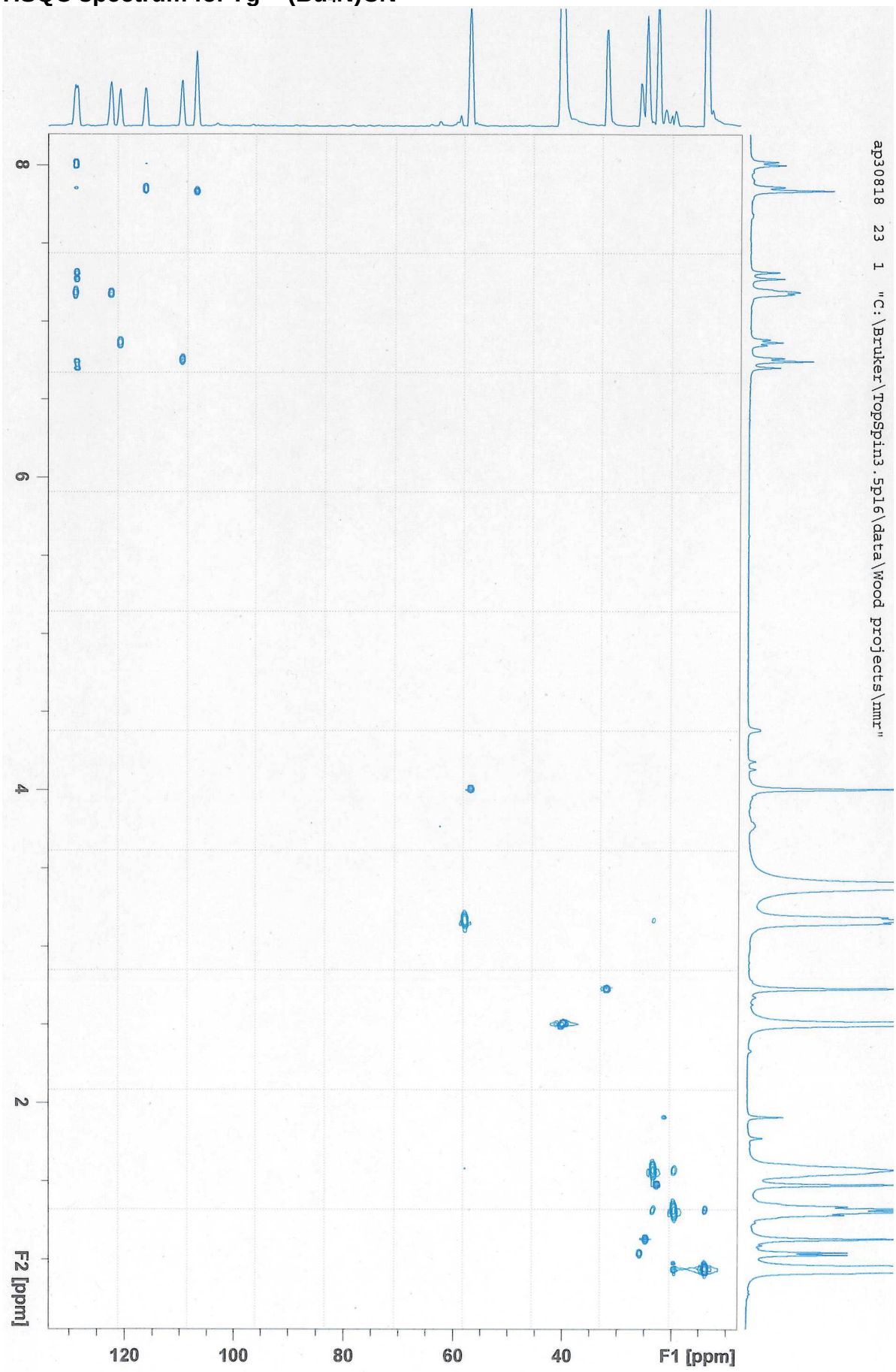
^{1}H NMR spectrum for 7g + (Bu_4N)CN



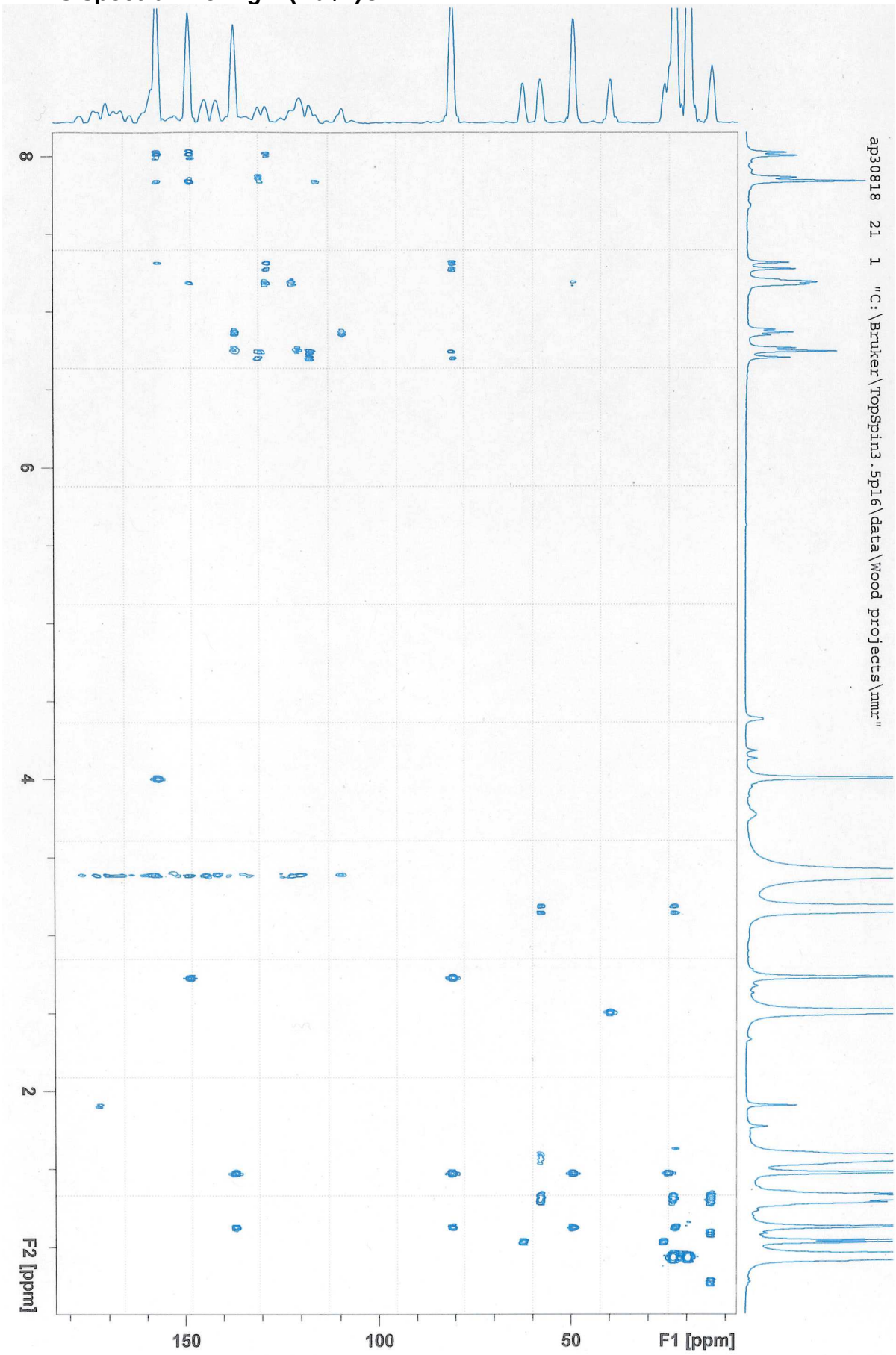
^{13}C NMR spectrum for 7g + (Bu_4N)CN



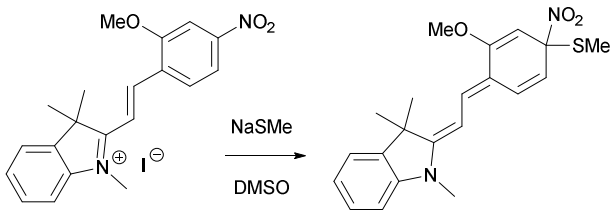
HSQC spectrum for 7g + (Bu_4N)CN



HMBC spectrum for 7g + (Bu_4N)CN



Reaction with sodium methanethiolate



7g **11c**

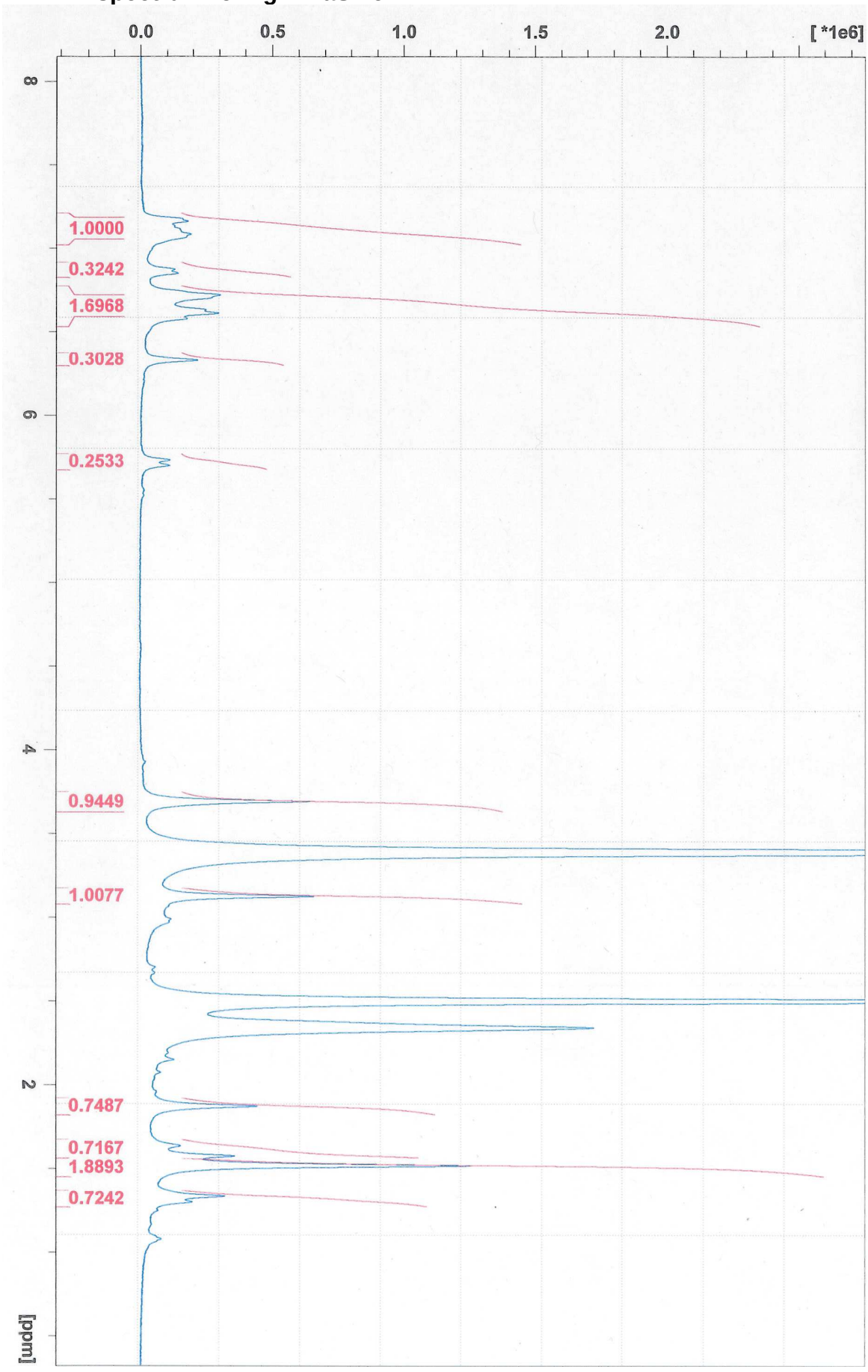
Data for (*E*)-1-nitro-3-methoxy-4-(2-(1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexa-2,5-diene-1-methylthioether 11c

δH (400 MHz; DMSO-d_6) 7.18 (1 H, d, *J* 7.3, 4-H), 7.09 (1 H, t, *J* 7.3, 6-H), 6.87 (1 H, d, *J* 9.9, 6'-H), 6.78-6.68 (2 H, m, 5- and 7-H), 6.63 (1 H, d, *J* 9.9, 5'-H), 6.60 (1 H, d, *J* 13.1, β-H), 6.34 (1 H, s, 2'-H), 5.72 (1 H, d, *J* 13.1, α-H), 3.70 (3 H, s, OMe), 3.19 (3 H, s, NMe) 1.89 (3 H, s, SMe) and 1.51 (6 H, s, CMe_2).

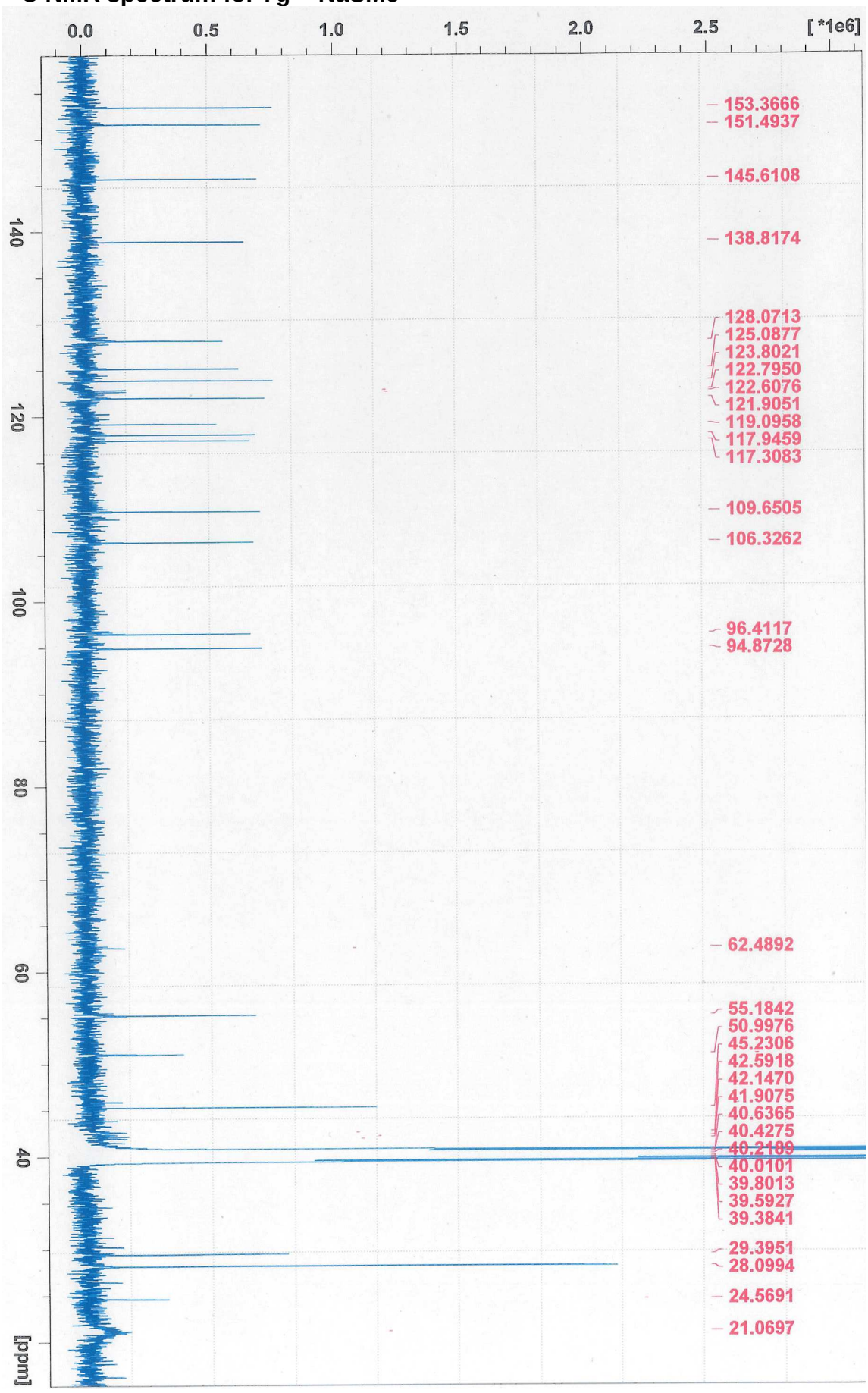
δC (100 MHz; DMSO-d_6) 153.4 (2-C), 151.5 (3'-C), 145.6 (7a-C), 138.8 (3a-C), 128.1 (6-C), 125.1 (4'-C), 123.8 (1'-C), 121.9 (4-C), 119.1 (5-C), 117.9 (6'-C), 117.3 (5'-C), 109.7 (β-C), 106.3 (7-C), 96.4 (2'-C), 94.9 (α-C), 55.2 (OMe), 51.0 (SMe), 45.2 (CMe_2), 29.4 (NMe) and 28.1 (CMe_2).

LRMS-ES+ (*m/z*): 337 (10%, M^+-SCH_3).

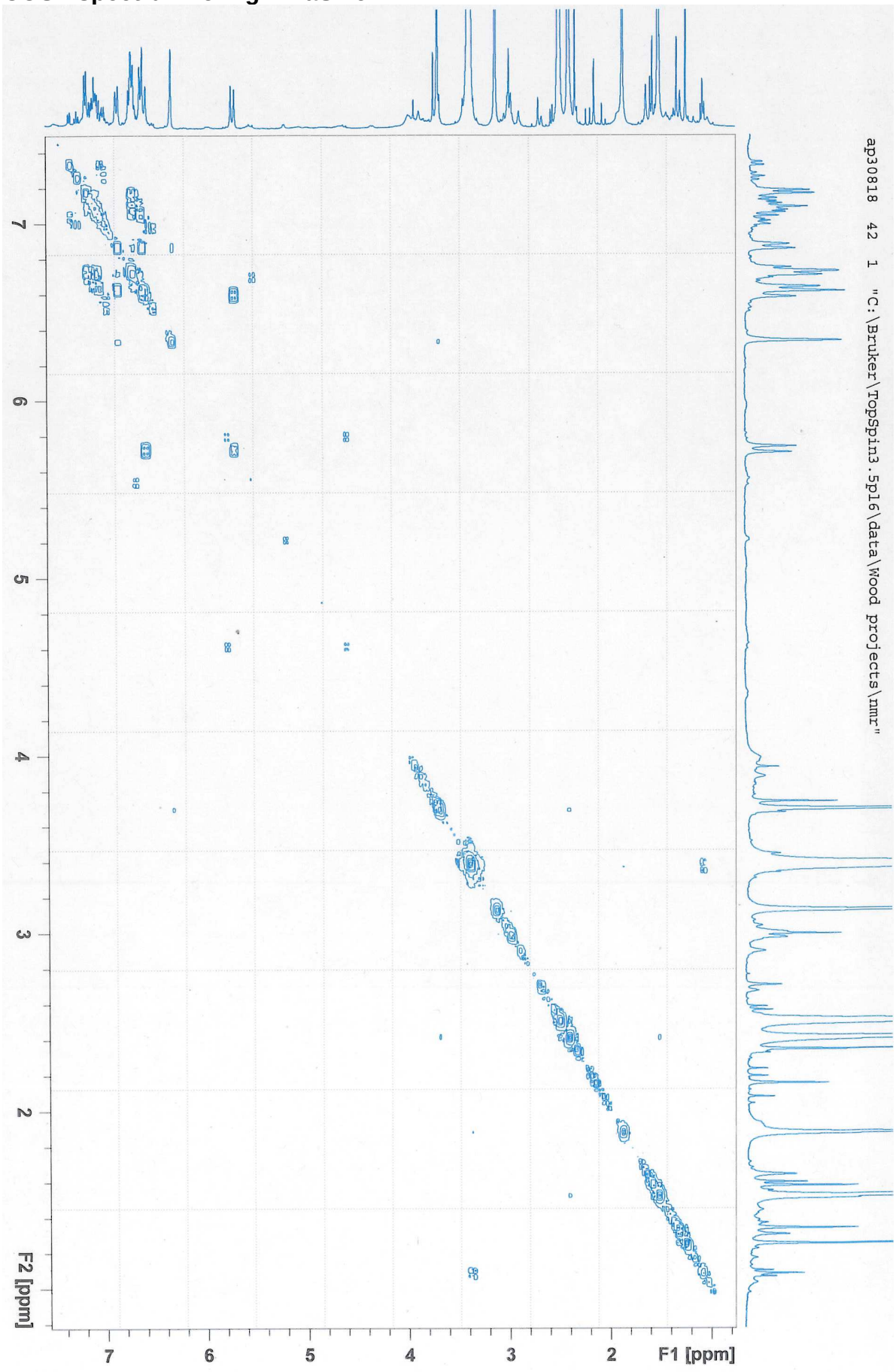
^{1}H NMR spectrum for 7g + NaSMe



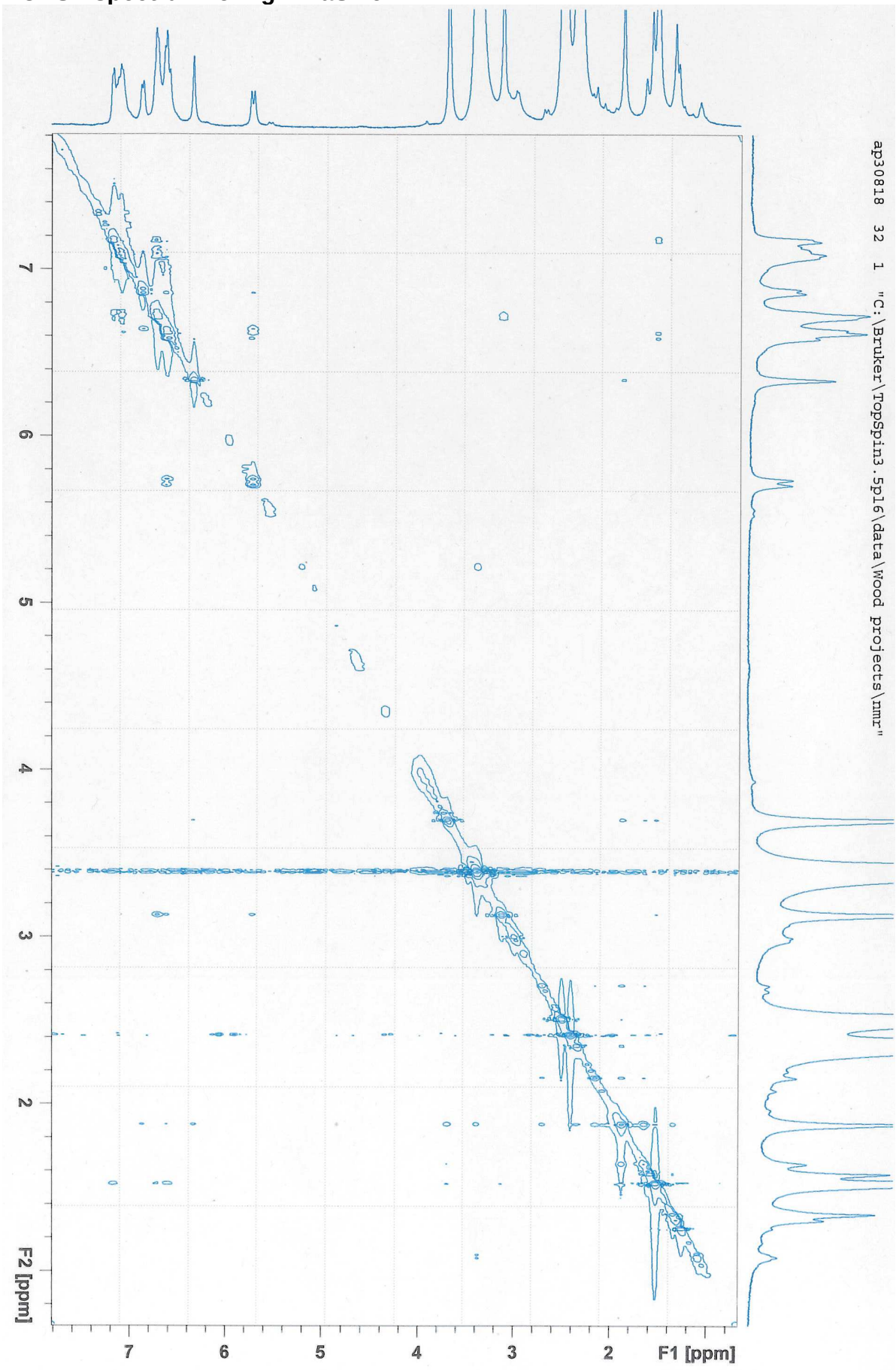
^{13}C NMR spectrum for 7g + NaSMe



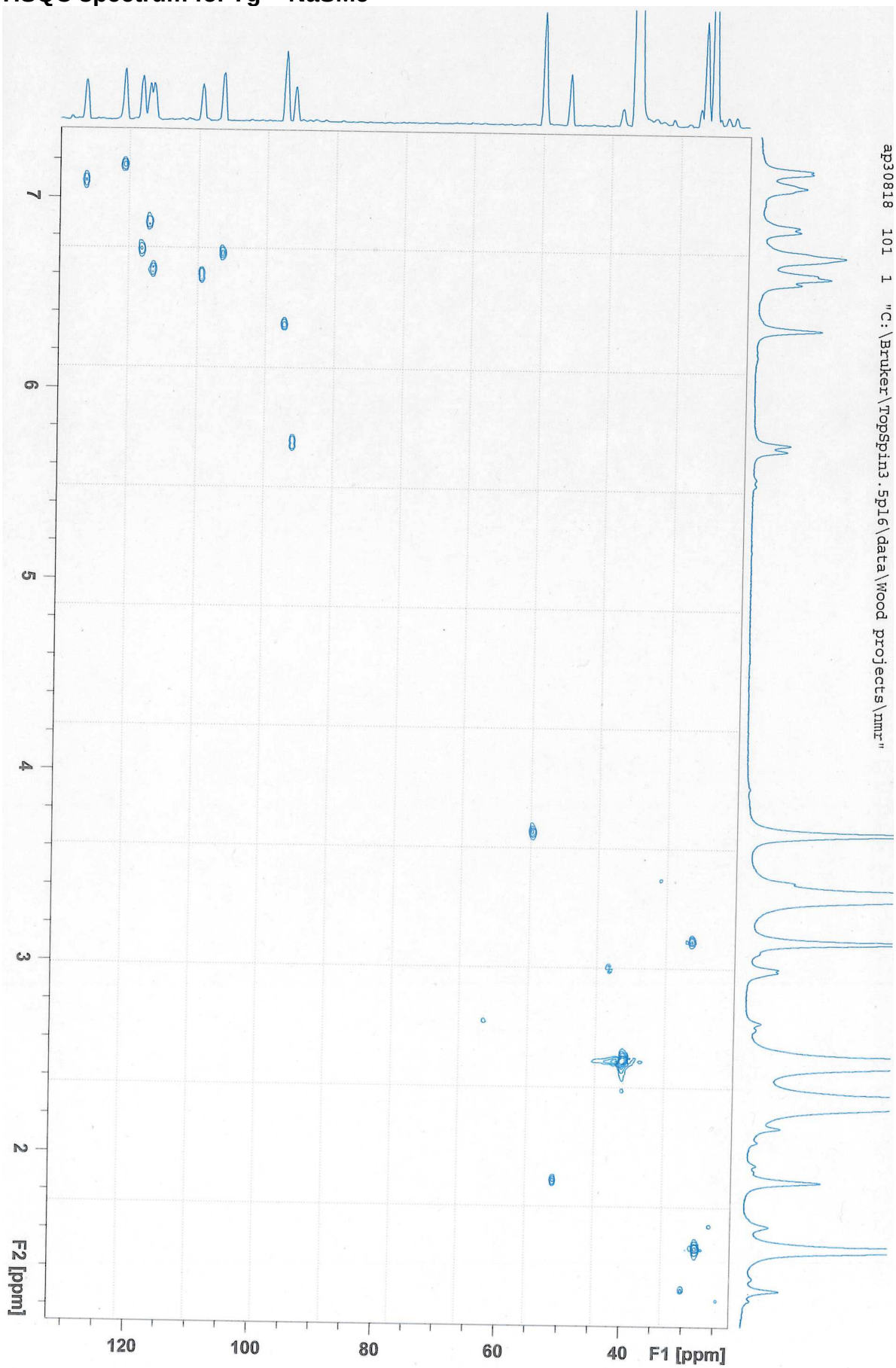
COSY spectrum for 7g + NaSMe



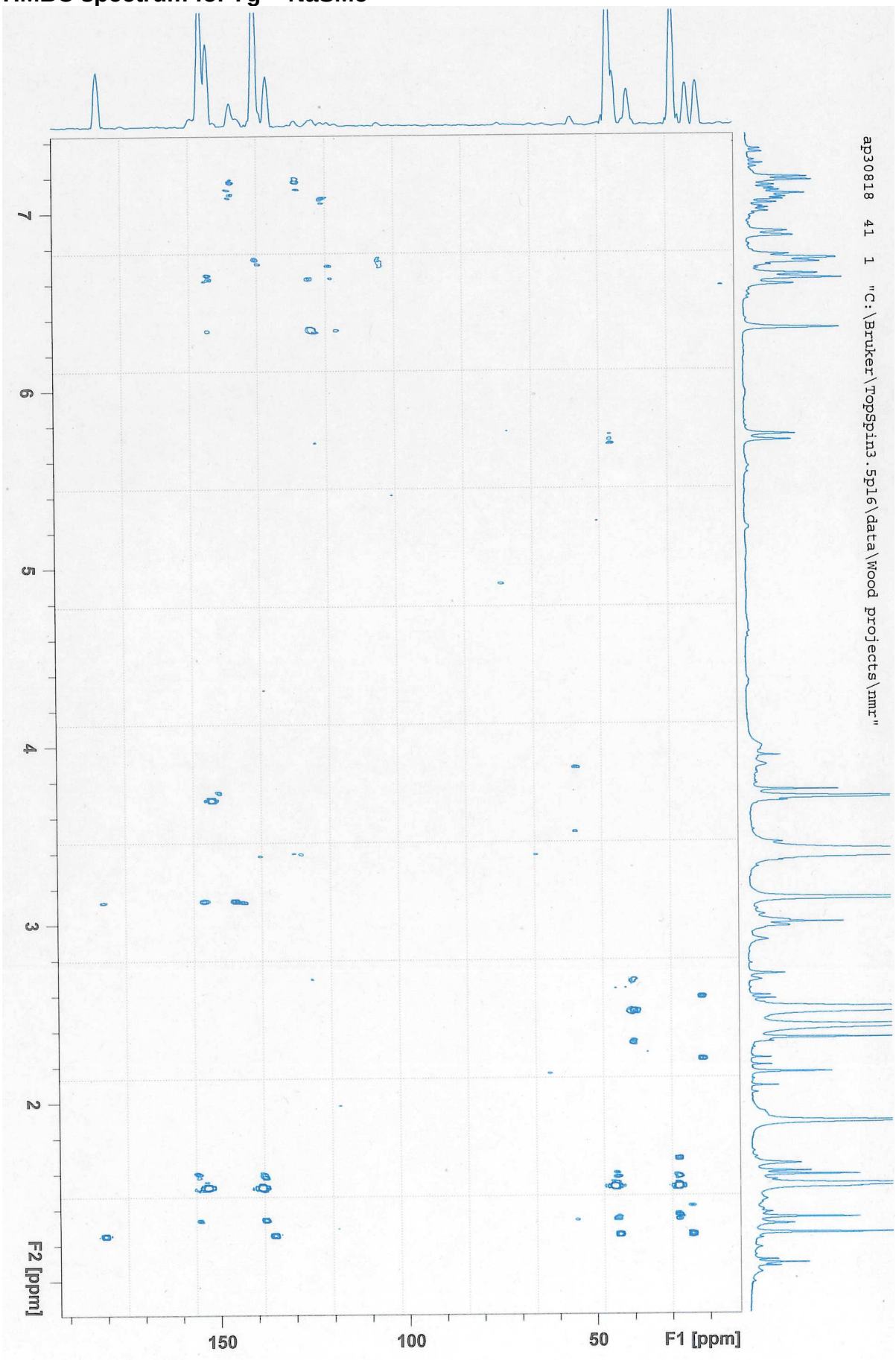
NOESY spectrum for 7g + NaSMe



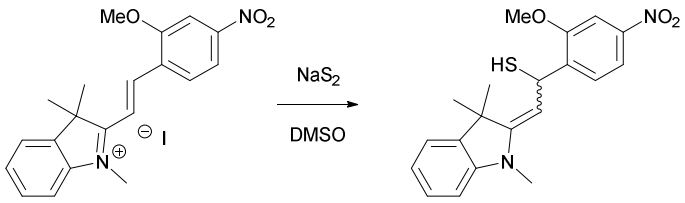
HSQC spectrum for 7g + NaSMe



HMBC spectrum for 7g + NaSMe



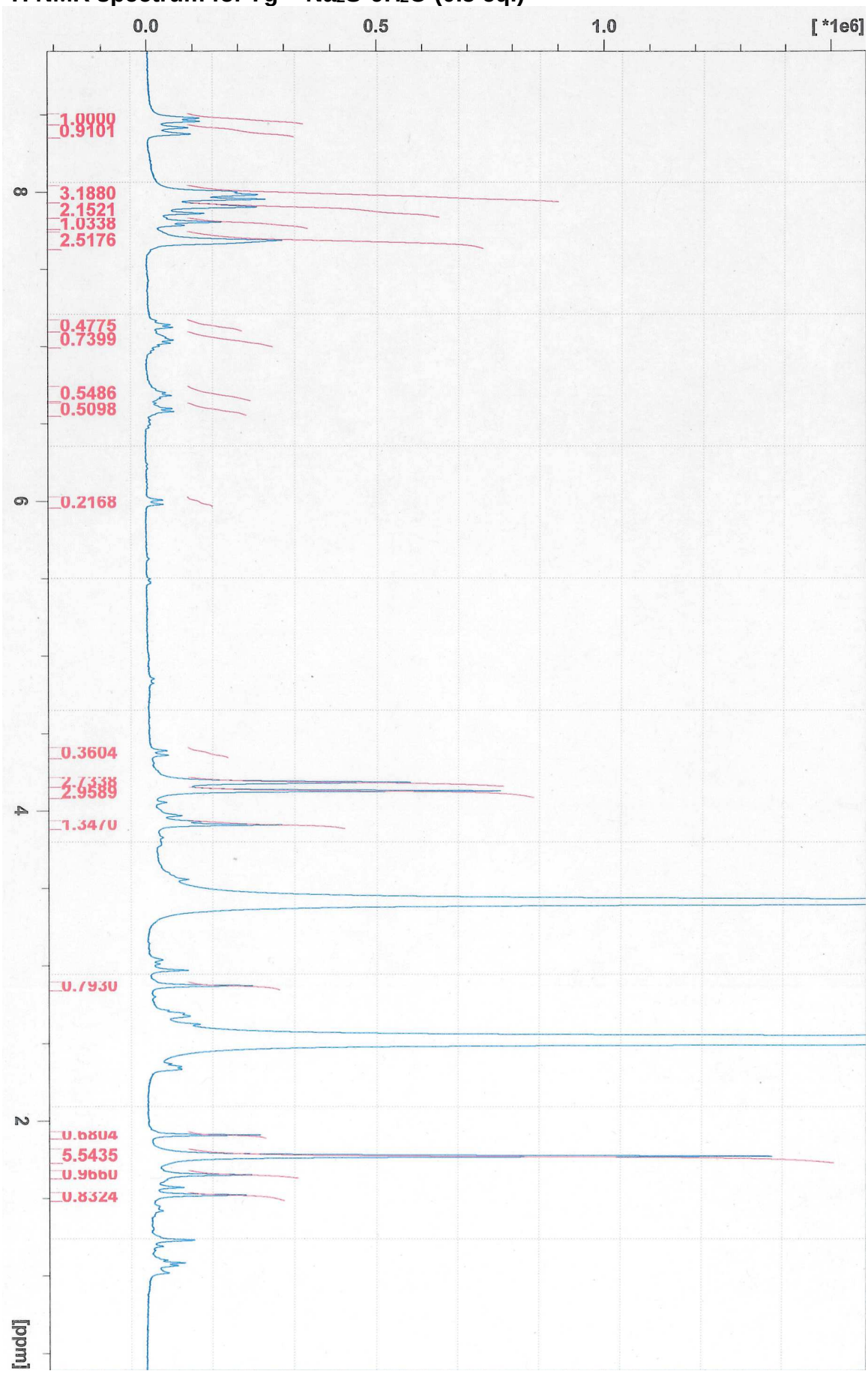
Reaction with sodium sulfide



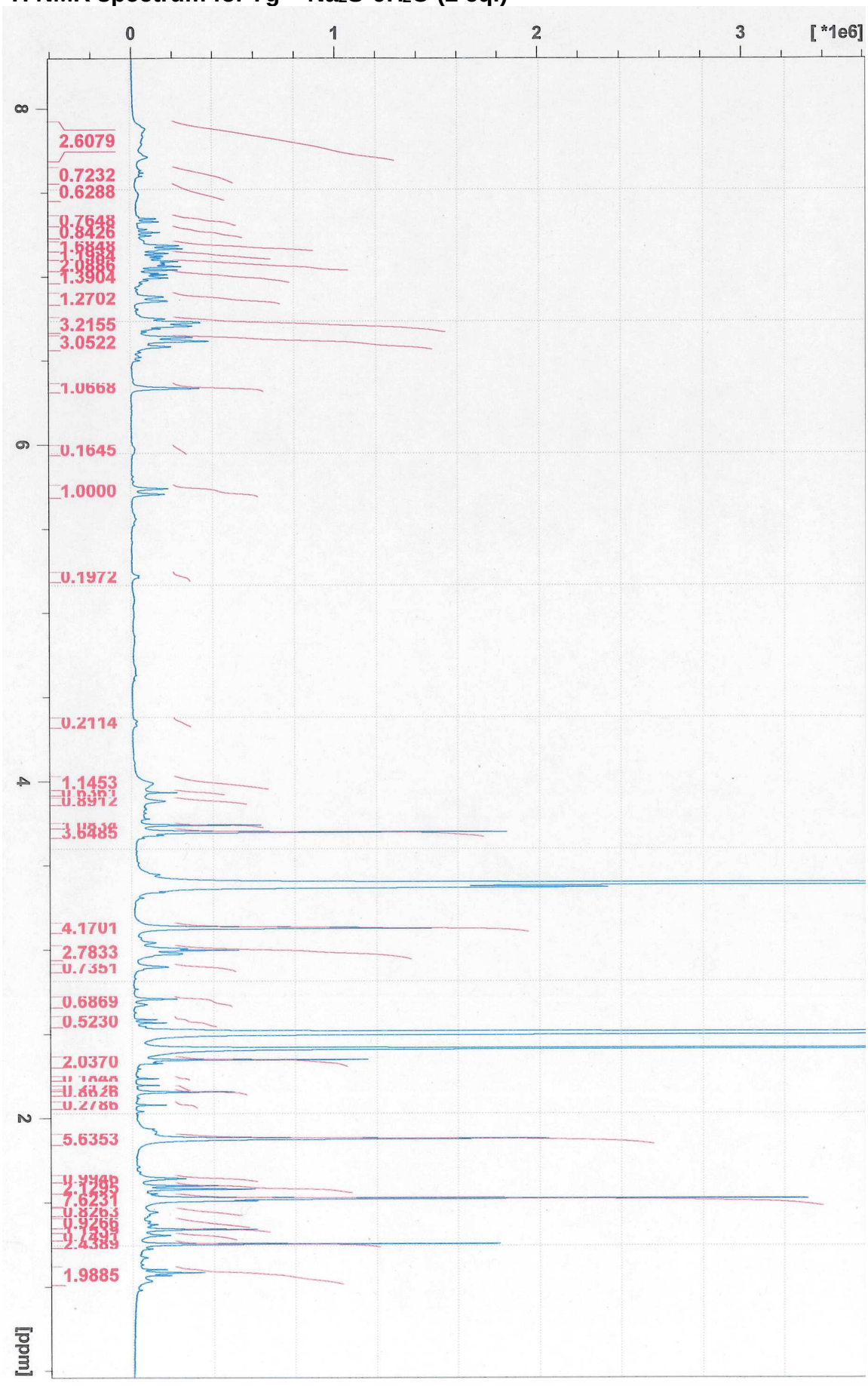
7g

LRMS-ES+ (*m/z*): 337 (10%, M^+-SH).

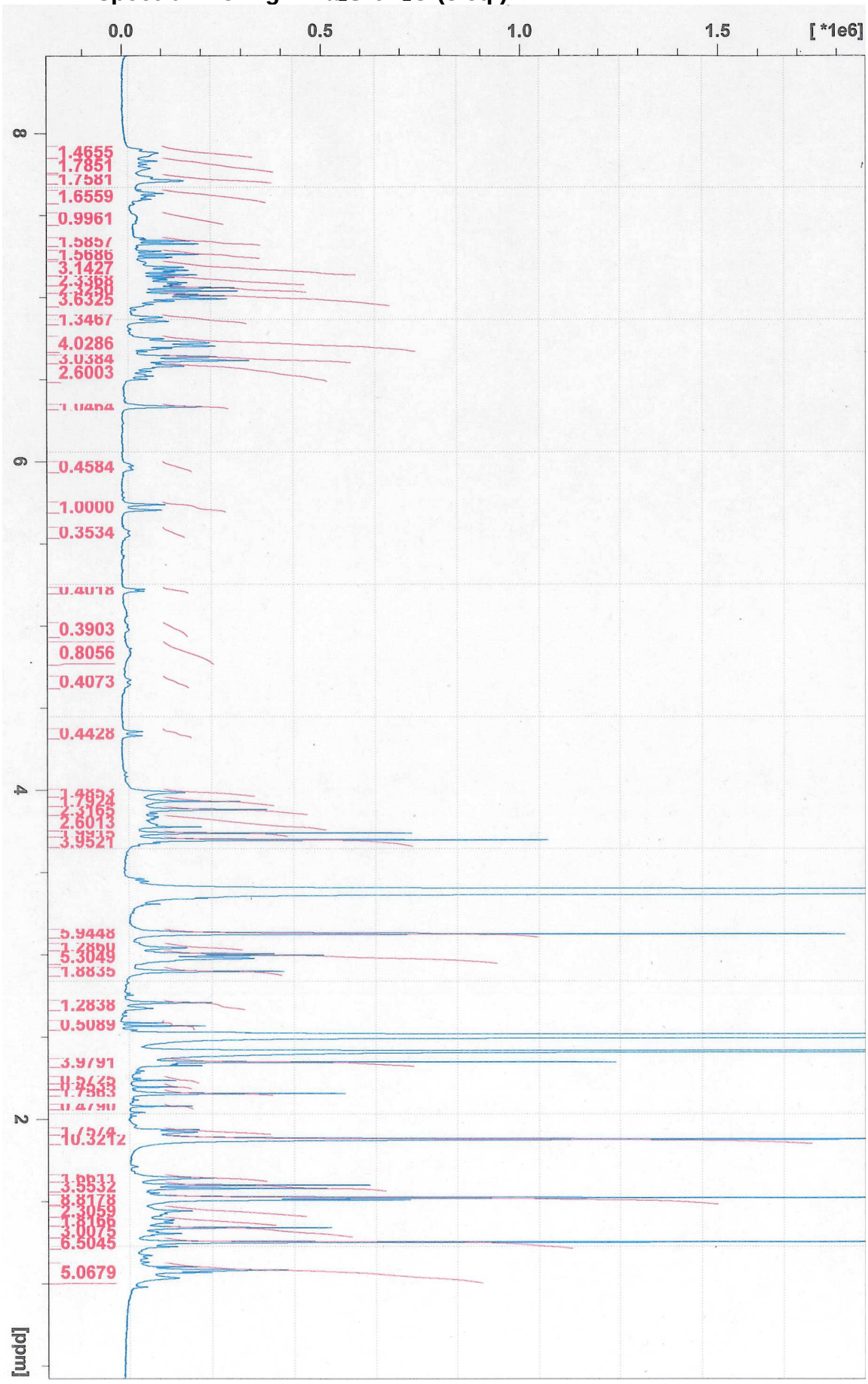
^{1}H NMR spectrum for 7g + $Na_2S \cdot 9H_2O$ (0.5 eq.)



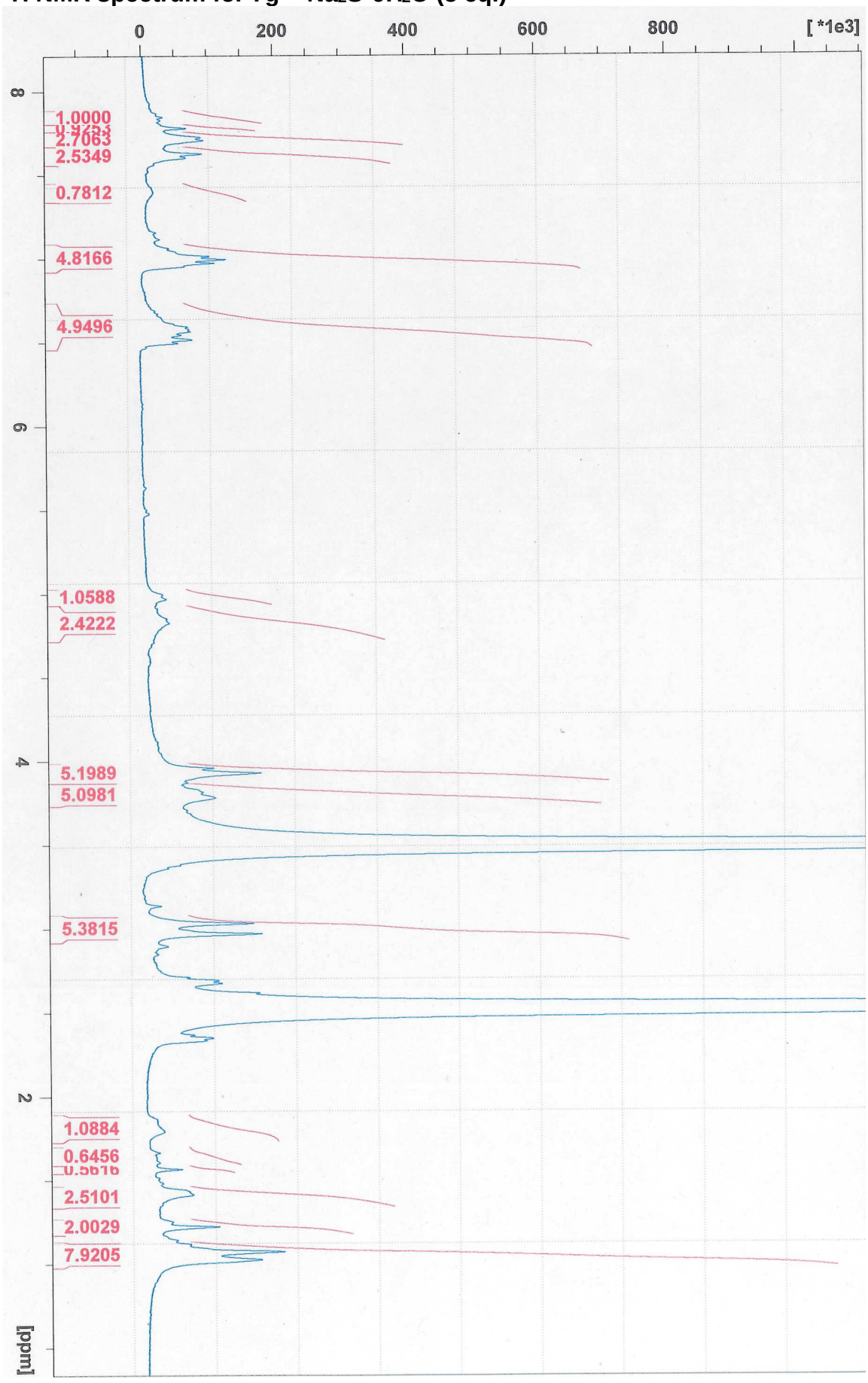
^{1}H NMR spectrum for 7g + $Na_2S \cdot 9H_2O$ (2 eq.)



^{1}H NMR spectrum for 7g + $Na_2S \cdot 9H_2O$ (3 eq.)



^{1}H NMR spectrum for 7g + $Na_2S \cdot 9H_2O$ (5 eq.)



4. Preparation of samples for analysis by UV-visible and fluorescence spectroscopy

Samples for the analysis, by UV-visible spectroscopy, of **7b**, **7f** and their reaction products with cyanide, methanethiolate and sulfide, were prepared as follows: to solutions of **7b** or **7f** (2 mL of 0.05 mM in DMSO, 0.1 µmol) were added solutions of tetrabutylammonium cyanide, sodium methanethiolate or sodium sulfide nonahydrate (10 µL of 0.1 mM in DMSO, 1 µmol), or DMSO (10 µL) (i.e. each sample contained a total volume of 2.01 mL; **7b/f** at 0.0498 mM and nucleophile at 0.498 mM). Samples were stirred for 5 minutes then analysed.

For analysis of **7f** + NaSMe by fluorescence spectroscopy, a 2.01 mL sample was prepared in an identical manner to that described above, with analysis performed upon a 200 µL aliquot withdrawn from the bulk sample.

5. References for supporting information

1. S. Metsov, T. Dudev and V. Koleva, Infrared and NMR study of some 2-styrylindolium dyes, *J. Mol Struct.*, 1995, **350**, 241–246.

2. M. Ogata, *Rikagaku Kenkyusho Iho*, 1937, **16**, 619–621.