Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Supporting Information

Symbiotic Transition-Metal and Organocatalysis for Catalytic Ambient Amine Oxidation and Alkene Reduction Reactions

Alexander T. Murray,[a] Rose King,[a] Joseph V. G. Donnelly,[a] Myles J. H. Dowley,[a] Floriana Tuna,[b] Daniel Sells,[b] Matthew P. John,[c] and David R. Carbery*[a]

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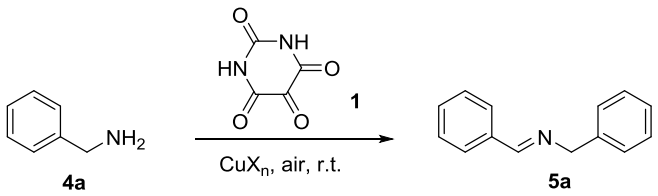
I GENERAL INFORMATION

All reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar or Sigma Aldrich and used without further purification. Flash chromatography was performed on chromatography grade, silica, 60 Å particle size 35-70 micron from Sigma Aldrich using the solvent system as stated. ^{1}H and ^{13}C NMR was performed on Brüker Avance 250 (^{1}H 250 MHz) Brüker Avance 300 (^{1}H 300 MHz and ^{13}C 75 MHz), Brüker Avance 400 (^{1}H 400 MHz and ^{13}C 100 MHz), Brüker Avance 500 (^{1}H 500 MHz and ^{13}C 125 MHz) or Agilent ProPulse 500 (^{1}H 500 MHz and ^{13}C 125 MHz) as stated. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) (δ = 0.00). Coupling constants are reported in Hertz (Hz) and signal multiplicity is denoted as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), sextet (sex.), septet (sept.), multiplet (m), and broad (br). High resolution mass spectrometry electrospray (ESI) was performed on a Brüker μTOF using electrospray ionisation (ESI) in either positive or negative ionisation. Infra-red spectroscopy was carried out using a Perkin Elmer Spectrum RX FT-IR system. HPLC data was recorded on an Agilent 1260 Infinity system using an Agilent Eclipse XDB-CN 5 μm, 4.6 x 150 mm cyano column. EPR spectroscopy was performed on a Brüker EMX Micro X-band with 1.0 T electromagnet.

II REACTION OPTIMISATION

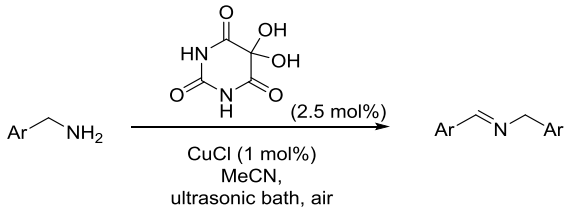


Entry	CuX_n [mol%]	**3** [mol%]	Solvent	t [h]	Conv[a] [%]
1	CuI (1)	5	MeCN	2	58
2	CuCl (1)	5	MeCN	2.5	100
3	$CuCl_2$ (1)	5	MeCN	2	16
4	CuCl (1)	5	MeOH	2	12
5	CuCl (1)	5	CH_2Cl_2	2	6
6	CuCl (1)	5	THF	2	<5
7	CuCl (1)	2.5	H_2O	0.5	<5
8	CuCl (1)	2.5	MeCN[b]	2	15
9	CuCl (1)	2.5	MeCN[c]	4	21
10	CuCl (1)	2.5	MeCN[d]	3	100 (76)[e]

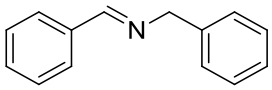
[a]Assayed against relevant ^{1}H NMR signals [b]Conducted under $CaCl_2$ drying tube, with 4 Å molecular sieves present [c]Containing 1000 ppm water [d]With sonication [e]Isolated yield.

III EXPERIMENTAL DATA

General Procedure for copper/alloxan-catalysed oxidative dimerisation of aromatic amines (General Procedure A)



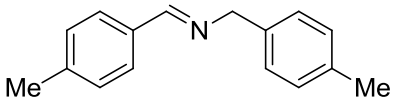
Copper (I) chloride (0.5 mg, 5 µmol, 1 mol%) and alloxan monohydrate **1** (2 mg, 12.5 µmol, 2.5 mol%) were added to a test tube containing MeCN in an ultrasonic bath. After 5 minutes, amine (0.5 mmol) was added by syringe and the mixture was sonicated under air for 3 h. After reaction was complete, the solvent was removed *in vacuo*, and the crude imine was purified by washing through a small pad of base-washed silica (1:2 petrol:EtOAc + 2% Et_3N).



N-benzylidene-1-phenylmethanamine (5a)

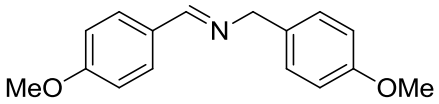
Following General Procedure A using benzylamine **4a** (55 µL) gave N-benzylidene-1-phenylmethanamine **5a** as an oil (37 mg, 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.41 (s, 1H), 7.84 – 7.76 (m, 2H), 7.49 – 7.21 (m, 8H), 4.84 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 162.1, 139.4, 136.3, 130.9, 128.7, 128.6, 128.4, 128.1, 127.1, 65.2. Data in accordance with literature.[1]



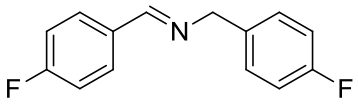
N-(4-methylbenzylidene)-1-(p-tolyl)methanamine (5b)

Following General Procedure A using 4-methylbenzylamine **4b** (64 µL) gave N-(4-methylbenzylidene)-1-(p-tolyl)methanamine **5b** as a white solid (51 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.24 (s, 1H), 7.57 (d, 2H, J=8.1), 7.16-7.01 (m, 6H), 4.67 (s, 2H), 2.28 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.8, 141.1, 136.6, 136.4, 133.7, 129.4, 129.2, 128.3, 128.0, 64.9, 21.6, 21.2. Data in accordance with literature.[1]



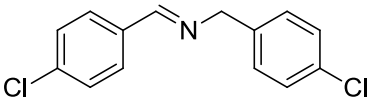
N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine (5c)

Following General Procedure A using 4-methoxybenzylamine **4c** (65 µL) gave N-(4-methoxybenzylidene)-1-(4-methoxyphenyl)methanamine **5c** as an oil (63 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.20 (s, 1H), 7.62 (d, 2H, J=8.6), 7.16 (d, 2H, J=8.7), 6.86-6.75 (m, 4H), 4.64 (s, 2H), 3.74 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.7, 161.0, 158.7, 131.7, 129.9, 129.2, 129.2, 114.0, 113.9, 64.5, 55.4, 55.3. Data in accordance with literature.[1]



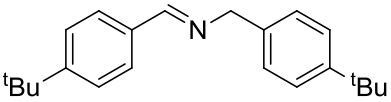
N-(4-fluorobenzylidene)-1-(4-fluorophenyl)methanamine (5d)

Following General Procedure A using 4-fluorobenzylamine **5d** (57 µL) gave N-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanamine **4d** as an oil (56 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.26 (s, 1H), 7.73 - 7.64 (m, 2H), 7.26 - 7.15 (m, 2H), 7.07 - 6.88 (m, 4H), 4.68 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 166.2, 163.7, 162.8, 160.7, 160.5, 135.0 (d, $J_{C,F}$ = 3.2 Hz), 132.4 (d, $J_{C,F}$ = 3.2 Hz), 130.3 (d, $J_{C,F}$ = 8.8 Hz), 129.6 (d, $J_{C,F}$ = 8.8 Hz), 115.8 (d, $J_{C,F}$ = 22.2 Hz), 115.4 (d, $J_{C,F}$ = 22.2 Hz), 64.3. Data in accordance with literature.[1]



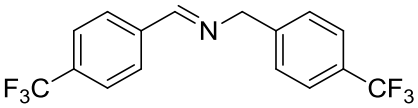
N-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanamine (5e)

Following General Procedure A using 4-chlorobenzylamine **4e** (61 µL) with reaction performed over 16 h gave N-(4-chlorobenzylidene)-1-(4-chlorophenyl)methanamine **5e** as a white powder (46 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.27 (s, 1H), 7.64 (d, 2H, J=8.6), 7.31 (d, 2H, J=8.5), 7.27 - 7.16 (m, 4H), 4.69 (s, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.0, 137.7, 137.0, 134.5, 132.9, 129.6, 129.4, 129.1, 128.8, 64.3. Data in accordance with literature.[1]



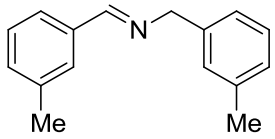
N-(4-(tert-butyl)benzylidene)-1-(4-(tert-butyl)phenyl)methanamine (5f)

Following General Procedure A using (4-(tert-butyl)phenyl)methanamine **4f** (88 µL) gave N-(4-(tert-butyl)benzylidene)-1-(4-(tert-butyl)phenyl)methanamine **5f** as an oil (71 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.29(s, 1H), 7.64 (d, 2H, J=8.7), 7.38 – 7.15 (m, 6H), 4.70 (s, 2H), 1.25 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.8, 154.2, 149.9, 136.6, 133.7, 128.2, 127.8, 125.7, 125.5, 65.0, 35.0, 34.6, 31.5, 31.4. Data in accordance with literature.[1]



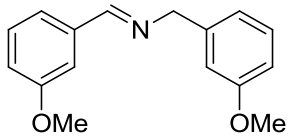
N-(4-(trifluoromethyl)benzylidene)-1-(4-(trifluoromethyl)phenyl)methanamine (5g)

Following General Procedure A using 4-(trifluoromethyl)benzylamine **4g** (71 µL) with 4% with reaction performed over 5 h gave N-(4-(trifluoromethyl)benzylidene)-1-(4-(trifluoromethyl)phenyl)methanamine **5g** as an oil (68 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.47 (s, 1H), 7.91 (d, 2H, J=8.1 Hz), 7.74 – 7.55 (m, 4h), 7.47 (d, 2H, J=8.1 Hz) 4.90 (s, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.3, 143.0, 139.0, 132.9, 132.5, 128.7, 128.6, 125.8 (q, JC,F = 3.9 Hz), 125.6 (q, JC,F = 3.9 Hz), 122.5, 64.6. Data in accordance with literature.[1]



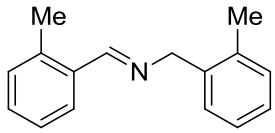
N-(3-methylbenzylidene)-1-(m-tolyl)methanamine (5h)

Following General Procedure A using 3-methylbenzylamine **4h** (63 µL) gave N-(3-methylbenzylidene)-1-(m-tolyl)methanamine **5h** as an oil (51 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.26 (s, 1H), 7.56 (s, 1H), 7.50 – 7.40 (m, 1H), 7.26 – 7.08 (m, 3H), 7.08 – 6.94 (m, 3H), 4.69 (s, 2H), 2.28 (s, 3H), 2.25 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 162.2, 139.2, 138.4, 138.2, 136.2, 131.7, 128.8, 128.5, 128.5, 127.8, 126.0, 125.2, 65.2. Data in accordance with literature.[2]



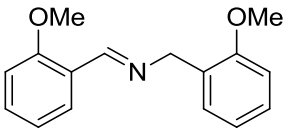
N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine (5i)

Following General Procedure A using 3-methoxybenzylamine **4i** (64 µL) gave N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine **5i** as an oil (53 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.36 (s, 1H), 7.40 (s, 1H), 7.36 – 7.24 (m, 3H), 7.02 – 6.97 (m, 1H), 6.95 – 6.88 (m, 2H), 6.85 – 6.78 (m, 1H), 4.81 (s, 2H), 3.85 (s, 3H), 3.82 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 162.1, 160.0, 159.9, 141.0, 137.7, 129.7, 129.6, 121.8, 120.5, 117.7, 113.8, 112.6, 111.8, 65.0, 55.5, 55.3. Data in accordance with literature.[2]



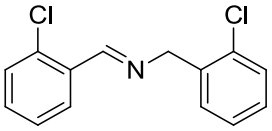
N-(2-methylbenzylidene)-1-(o-tolyl)methanamine (5j)

Following General Procedure A using 2-methylbenzylamine **4j** (62 µL) gave N-(3-methoxybenzylidene)-1-(3-methoxyphenyl)methanamine **5j** as an oil (44 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.58 (s, 1H), 7.88 – 7.81 (m, 1H), 7.26 – 7.06 (m, 7H), 4.74 (s, 2H), 2.42 (s, 3H), 2.31 (s, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 160.7, 137.8, 137.7, 136.2, 134.3, 130.9, 130.4, 130.2, 128.4, 127.8, 127.1, 126.3, 126.2, 63.4, 19.5, 19.4. Data in accordance with literature.[1]



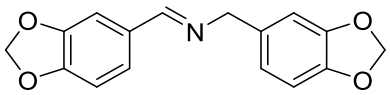
N-(2-methoxybenzylidene)-1-(2-methoxyphenyl)methanamine (5k)

Following General Procedure A using 2-methoxybenzylamine **4k** (65 µL) with reaction performed over 16 h gave N-(2-methoxybenzylidene)-1-(2-methoxyphenyl)methanamine **5k** as an oil (53 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.76 (s, 1H), 7.95 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.36 – 7.07 (m, 3H), 6.99 – 6.72 (m, 4H), 4.75 (s, 2H), 3.77 (s, 3H), 3.75 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 158.9, 158.4, 157.1, 131.9, 129.2, 128.2, 128.0, 127.6, 124.9, 120.8, 120.6, 111.1, 110.2, 59.8, 55.6, 55.4. Data in accordance with literature.[1]



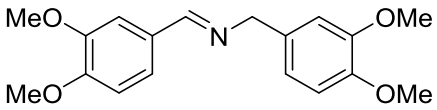
N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine (5l)

Following General Procedure A using 2-chlorobenzylamine **4l** (60 µL) gave N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine **5l** as a white powder (65 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.88 (s, 1H), 8.15 – 8.10 (m, 2H) 7.50 – 7.13 (m, 7H), 4.96 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_c 159.9, 137.0, 135.5, 133.6, 133.3, 131.9, 130.0, 129.8, 129.5, 128.6, 128.5, 127.2, 127.1. Data in accordance with literature.[2]



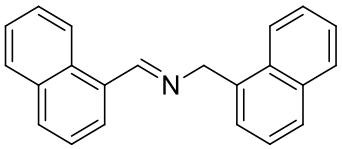
[(2H-1,3-benzodioxol-5-yl)methyl][(2H-1,3-benzodioxol-5-yl)methylidene] (5m)

Following General Procedure A using piperonylamine **4m** (62 µL) with reaction performed over 8 h gave **5m** as a white powder (63 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) 8.23 (s, 1H), 7.39 (d, *J* = 1.5 Hz, 1H), 7.14 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.87 – 6.68 (m, 4H), 5.99 (s, 2H), 5.93 (s, 2H), 4.68 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.0, 150.1, 128.4, 127.9, 146.7, 133.5, 131.1, 124.7, 121.2, 108.7, 108.3, 108.2, 106.9, 101.6, 101.0, 64.6. Data in accordance with literature.[1]



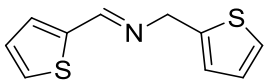
[(3,4-dimethoxyphenyl)methyl][(3,4-dimethoxyphenyl)methylidene]amine (5n)

Following General Procedure A using 3,4-dimethoxybenzylamine **4n** (75 µL) gave **5n** as a white powder (57 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.28 (s, 1H), 7.47 (s, 1H), 7.24 – 7.14 (m, 1H), 6.94 – 6.77 (m, 4H), 4.74 (s, 2H), 4.02 – 3.81 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 161.4, 151.6, 149.5, 149.1, 148.2, 132.1, 128.5, 123.4, 120.3, 222.6, 111.3, 110.5, 109.0, 64.8, 56.1, 56.1, 56.1, 56.0. Data in accordance with literature.[3]



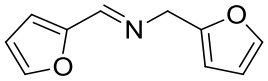
1-(naphthalen-1-yl)-N-(naphthalen-1-ylmethylene)methanamine (5o)

Following General Procedure A using 1-napthylmethylamine **4o** (73 µL) gave 1-(naphthalen-1-yl)-N-(naphthalen-1-ylmethylene)methanamine **5o** as an oil (48 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.09 (s, 1H), 8.96 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.77 (m, 5H), 7.63 – 7.44 (m, 7H), 5.42 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 162.1, 135.6, 134.0, 133.9, 131.8, 1331.7, 131.4, 131.3, 129.3, 128.8, 128.7, 127.9, 127., 126.3, 126.2, 126.0, 125.8, 125.8, 125.4, 124.5, 124.1, 63.4. Data in accordance with literature.[1]



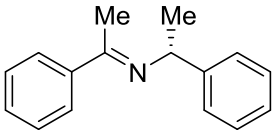
1-(thiophen-2-yl)-N-(thiophen-2-ylmethylene)methanamine (5p)

Following General Procedure A using 2-thiophenemethylamine **4p** (51 µL) for 5 h gave 1-(thiophen-2-yl)-N-(thiophen-2-ylmethylene)methanamine **5p** as an oil (50 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.42 (s, 1H), 7.42 (dt, *J* = 4.8, 1.0 Hz, 1H), 7.33 (dd, *J* = 3.6, 1.0 Hz, 1H), 4.8, 1.6 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 7.03 – 6.95 (m, 2H), 4.95 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 155.5, 142.2, 141.6, 131.1, 129.5, 127.5, 127.7, 125.4, 125.0, 58.6. Data in accordance with literature.[4]



1-(furan-2-yl)-N-(furan-2-ylmethylene)methanamine (5q)

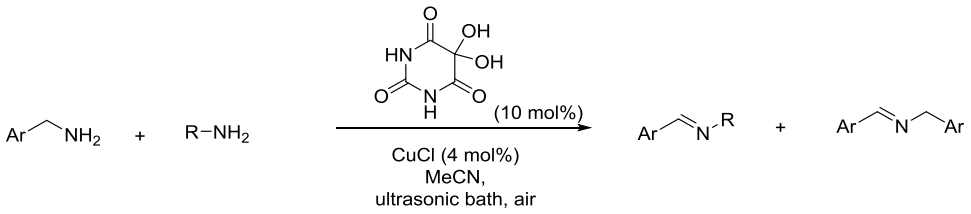
Following General Procedure A using furfurylamine **4q** (44 µL) and copper (I) methylsalicylate (2.1 mg, 5 µmol, 1%) as Cu source gave N-(2-chlorobenzylidene)-1-(2-chlorophenyl)methanamine **5q** as an oil (18 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.11 (t, *J* = 1.4 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.38 (dd, *J* = 1.9, 0.9 Hz, 1H,), 6.78 (d, *J* = 3.3 Hz, 1H), 6.47 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.28 (m, 1H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 152.0, 151.6, 151.4, 145.1, 142.2, 114.6, 142.4, 114.6, 111.8, 110.5, 109.1, 57.0. Data in accordance with literature.[1]



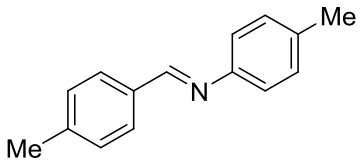
[(1R)-1-phenethyl](1-phenethylidene)amine (predominantly *E*) (5r)

Following General Procedure A using *(R)*-α-methylbenzylamine **4r** (61 µL) for 16 h gave (R)-**5r** as an oil (28 mg, 50%), in a 9.5:1 mixture of geometrical isomers ^{1}H NMR (400 MHz, $CDCl_3$) δ_{Hmajor} 7.97 – 7.90 (m, 2H), 7.63 – 7.24 (m, 10H), 4.92 (q, *J* = 6.6 Hz, 1H), 4.92 (s, 3H), 1.63 (d, *J* = 6.6 Hz, 3H); $\delta_{Hminor,visible}$ 4.51 (q, *J* = 6.6 Hz), 2.40 (s, 3H), 1.49 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ_{Cmajor} 136.6, 146.3, 141.6, 129.5, 128.5, 128.3, 126.9, 126.8, 126.6, 59.9, 25.2, 15.7; $\delta_{Cminor,visible}$ 167.5, 145.8, 139.5, 128.6, 125.9, 60.9, 29.5, 24.7. IR ν_{max} (neat) 2969, 1633, 1446, 1266 cm^{-1}; HRMS (ESI, +ve) *m/z* calcd. for $C_{16}H_{18}N$ 224.1438 found: 224.1448; $[\alpha]^{20}_D$ -70˚ (c 0.1, $CHCl_3$) (lit = -73.3˚, c 2.14, $CHCl_3$[5]). Major isomer data in accordance with literature (minor isomer may be visible on literature spectra but is not explicitly reported)[6]

General Procedure for copper/alloxan-catalysed oxidative dimerisation of aromatic amines (General Procedure B)

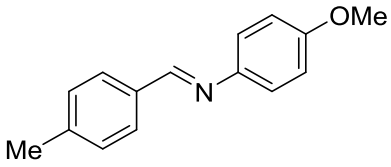


Copper (I) chloride (0.5 mg, 5 µmol, 2 mol%) and alloxan monohydrate **1** (2 mg, 12.5 µmol, 5 mol%) were added to a test tube containing MeCN in an ultrasonic bath. After 5 minutes, 'alkylating' amine (0.375 mmol) followed by benzylic amine (0.25 mmol) were added by syringe and the mixture was sonicated under air. After 2 h a further 2 mol% CuCl and 5 mol% alloxan monohydrate were added, and the mixture was sonicated for a further 22 h. Solvent was removed *in vacuo*, and the crude imine(s) were purified by washing through a small pad of base-washed silica (1:2 petrol:EtOAc + 2% Et_3N). In the case of mixed imines, identity of the cross product was achieved by comparison to literature reference and independently synthesised imines (by condensation of the relevant aldehyde and imine).



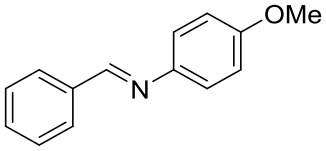
4-methyl-N-(4-methylbenzylidene)aniline (7a)

Following General Procedure B using 4-methylbenzylamine **4b** (32 µL) and *p*-toluidine **6a** (40 mg) gave 4-methyl-N-(4-methylbenzylidene)aniline **s** as a white solid (50 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.35 (s, 1H), 7.70 (d, 2H, J = 8.2 Hz), 7.23 – 7.00 (m, 8H), 2.33 (s, 3H), 2.29 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 159.7, 149.7, 141.8, 135.7, 133.9, 129.8, 129.6, 128.8, 120.9, 21.7, 21.1. Data in accordance with the literature.[7]



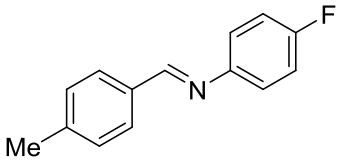
4-methoxy-N-(4-methylbenzylidene)aniline (7b)

Following General Procedure B using 4-methylbenzylamine **4b** (32 µL) and *p*-anisidine **6b** (46 mg) gave 4-methoxy-N-(4-methylbenzylidene) **7b** as a white solid (51 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.35 (s, 1H), 7.69 (d, 2H, J = 7.3 Hz), 7.28 – 7.03 (m, 4H), 6.84 (d, 2H, J = 8.8 Hz), 3.73 (s, 3H), 2.32 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 158.6, 158.2, 145.2, 141.6, 134.0, 129.6, 128.7, 122.3, 114.4, 55.6, 21.7. . Data in accordance with the literature.[7]



4-methoxy-N-(benzylidene)aniline (7c)

Following General Procedure B using benzylamine **4a** (28 µL) and *p*-anisidine **6b** (46 mg) gave 4-methoxy-N-(benzylidene)aniline **7c** as a white solid (34 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.40 (s, 1H), 7.88 – 7.77 (m, 2H), 7.45 – 7.33 (m, 3H), 7.17 (d, J = 8.9 Hz, 2H), 6.86 (d, J = 8.9 Hz, 2H), 3.75 (s, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 158.6, 158.4, 145.0, 136.5, 131.2, 128.9, 128.7, 122.3, 114.4, 55.6. IR ν_{max} 2916, 1622, 1245 cm^{-1}. . Data in accordance with the literature.[7]

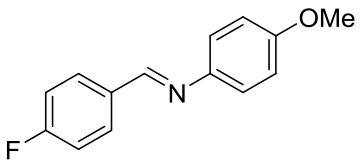


4-fluoro-N-(4-methylbenzylidene)aniline (7d)

Following general procedure B using 4-methylbenzylamine **4b** (32 µL) and 4-fluoroaniline **6c** (36 µL) gave 4-fluoro-N-(4-methylbenzylidene)aniline **7d** as a white solid (45 mg, 84%) ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.33 (s, 1H), 7.71 (d, 7.74 – 7.66 (m, 2H), 7.28 – 6.94 (m, 6H), 2.35 (s, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 162.2, 160.3, 160.2 (d, $J_{C,F}$ = 2 Hz), 148.4 (d, $J_{C,F}$ = 3 Hz), 142.1, 133.7, 129.3 (d, $J_{C,F}$ = 97 Hz), 122.4 (d, $J_{C,F}$ = 8 Hz), 116.0 (d, $J_{C,F}$ = 22 Hz), 21.8.

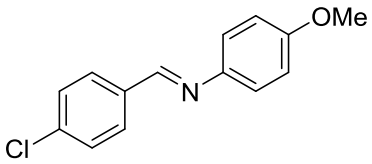
As this imine is a previously unreported compound we obtained full data on the pure compound obtained by condensation of 4-methylbenzaldehyde and 4-fluoroaniline. The slight difference in shift for one carbon could be related to concentration and/or spectrometer frequency.

4-methylbenzyaldehyde (117 µL, 1 mmol) and 4-fluoroaniline (94 µL, 1 mmol) were added to a suspension of $MgSO_4$ (240 mg, 2 mmol) in toluene (2 mL) for 18 h. Upon cooling, filtration and removal of solvent *in vacuo* gave **7d** as an oil (202 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.23 (s, 1H), 7.73 – 7.62 (m, 2H), 7.20 – 6.84 (m, 6H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 162.8, 160.1 (d, $J_{C,F}$ = 2 Hz), 159.6, 148.2 (d, $J_{C,F}$ = 3 Hz), 142.0, 133.6, 129.2 (d, $J_{C,F}$ = 55 Hz), 122.4 (d, $J_{C,F}$ = 5 Hz), 115.9 (d, $J_{C,F}$ = 12 Hz), 21.6; ^{19}F NMR (?? MHz, $CDCl_3$) δ_F -117.68 (apparent hep, $J_{F,H}$ = 4.4 Hz) FTIR (neat/cm^{-1}) 1683, 1623, 1607, 1498 cm^{-1}; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{13}NF$ 214.1032, found: 214.1036 $(M+H)^+$ MP : 64 – 66 ˚C



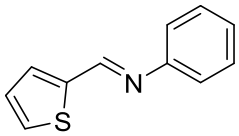
4-methoxy-N-(4-fluorobenzylidene)aniline (7e)

Following general procedure B using 4-fluorobenzylamine **4d** (29 µL) and *p*-anisidine **6b** (46 mg) gave 4-methoxy-N-(4-fluorobenzylidene)aniline **x** as a white solid (41 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.36 (s, 1H), 7.84 – 7.76 (m, 2H), 7.20 – 7.00 (m, 4H), 6.90 – 6.79 (m, 2H), 3.75 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 164.6 (d $J_{C,F}$ = 252 Hz), 158.4, 157.0, 144.7, 132.9 (d, $J_{C,F}$ = 3 Hz), 130.6 (d, $J_{C,F}$ = 9 Hz), 122.3, 116.0 (d, $J_{C,F}$ = 22 Hz), 114.5, 55.6. IR ν_{max} (neat) 2843, 1621, 1596, 1502 cm^{-1}; HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{13}NOF$ 229.0981, found: 246.1013 $(M+H)^+$. Data in accordance with the literature.[8]



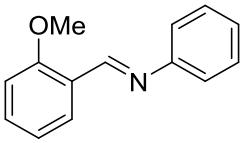
4-methoxy-N-(4-chlorobenzylidene)aniline (7f)

Following general procedure B using 4-chlorobenzylamine **4f** (30 µL) and *p*-anisidine **6b** (46 mg) gave 4-methoxy-N-(4-chlorobenzylidene)aniline **7f** as a white solid (34 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.37 (s, 1H), 8.49 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7,17 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 158.6, 156.9, 144.6, 139.1, 135.1, 129.9, 129.2, 122.4, 114.6, 55.7. IR ν_{max} 3013, 1620, 1595 cm^{-1} HRMS (ESI, +ve) *m/z* calcd. for $C_{14}H_{13}NOCl$ 246.0680, found: 246.0706 $(M+H)^+$. Data in accordance with the literature.[8]



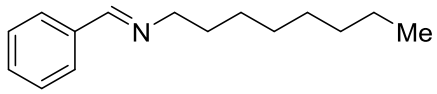
N-phenyl-1-(thiophen-2-yl)methanamine (7g)

Following general procedure B using 2-thiophenemethylamine **14a** (26 µL) and aniline **6d** (36 µL) gave a 1:1.6 mixture (26 mg) of cross-coupled product **7g** and benzylidene benzylamine **y**. Data for **x** overlays in ^{1}H and ^{13}C NMR with that obtained from an authentic sample of **x** synthesised by condensation.



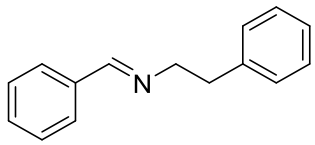
N-(2-methoxybenzylidene)aniline (7h)

Following general procedure B using 2-methoxybenzylamine **4k** (33 µL) and aniline **6d** (36 µL) gave N-(2-methoxybenzylidene)aniline **7h** as an oil (41 mg, 87%) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 8.93 (s, 1H), 8.17 – 8.14 (m, 2H), 7.48 – 7.38 (m, 3H), 7.27 – 7.20 (m, 3h), 7.08 – 7.03 (m, 1H), 6.99 – 6.95 (m, 1H), 3.91 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 159.6, 156.6, 152.9, 132.8, 129.1, 137.6, 125.7, 121.2, 121.0, 111.2, 55.7. IR ν_{max} 3062, 2838, 1619, 1588, 1249 cm^{-1} (ESI, +ve) *m/z* calcd. for $C_{14}H_{14}NO$ 212.1075, found: 212.1079 $(M+H)^+$. Data in accordance with literature.[2]



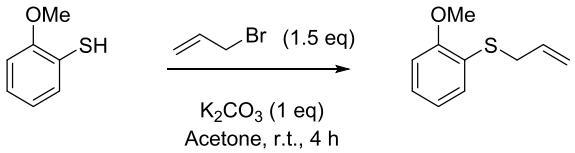
(N-benzlidene)octylamine (7i)

Following general procedure B using benzylamine **4a** (28 µL) and octylamine **6e** (62 µL) gave a mixture of products. Amounts of imines were gauged by addition of an internal standard of 1,3,5-trimethoxybenzene after SiO_2 filtration, and analysis by ^1H NMR spectroscopy. Imines were compared with authentic samples prepared by condensation.



(N-benzlidene)2-phenethylamine (7j)

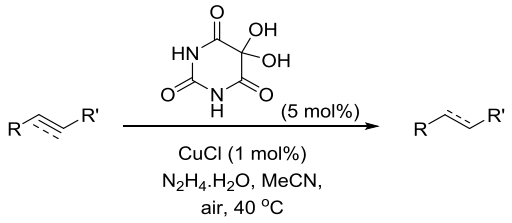
Following general procedure B using benzylamine **4a** (28 µL) and octylamine **6f** (47 µL) gave a mixture of products. Amounts of imines were gauged by addition of an internal standard of 1,3,5-trimethoxybenzene after SiO_2 filtration, and analysis by ^1H NMR spectroscopy. Imines were compared with authentic samples prepared by condensation.



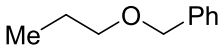
(2-methoxyphenyl)allyl sulfide (8d)

To a refluxing mixture of 2-methoxythiophenol (243 µL, 2 mmol) and K_2CO_3 (260 mg, 2 mmol) in acetone (5 mL), under an atmosphere of N_2, was added allyl bromide (173 µL, 2 mmol) dropwise. After 90 minutes, a further portion of allyl bromide (85 µL, 1 mmol) was added. After a total reaction time of 4 h the reaction was cooled and filtered. Acetone was removed *in vacuo* and the mixture was partitioned between Et_2O (20 mL) and water (5 mL). The aqueous layer was washed with Et_2O (2 x 10 mL), the combined organic layers were dried with $MgSO_4$ and solvent was removed *in vacuo*. The product was purified by column chromatography (0 – 2% EtOAc / pet. ether) to give (2-methoxyphenyl)allyl sulfide **8d** as an oil (204 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.30 (d, J = 7.6 Hz, 1H), 7.20 (t, J = 7.9 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.86 (t, J = 7.9 Hz, 1H), 5.89 (apparent sex., J = 8.1 Hz, 1H), 5.14 (d, J = 17.0 Hz, 1H), 5.10 (d, J = 10.0 Hz, 1H), 3.90 (s, 3H), 3.55 (d, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 158.0, 133.8, 130.7, 127.7, 121.5, 117.7, 110.6, 55.9, 35.6.; IR ν_{max} 2835, 1578, 1475, 1241 cm^{-1} HRMS (ESI, +ve) *m/z* calcd. for $C_{10}H_{12}SONa$ 203.0507, found: 203.0516 $(M+Na)^+$

General procedure for the reduction of alkenes or alkynes (General Procedure C)

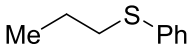


To a stirring solution of alloxan monohydrate (8 mg, 0.05 mmol) and copper(I) chloride (1 mg, 0.01 mg) in acetonitrile (2 mL) was added alkene or alkyne (1 mmol) followed by hydrazine monohydrate, the latter of which caused the mixture to become instantaneously cloudy. The reaction was heated to 40 °C. The crude reaction mixture was diluted with Et_2O and passed through a plug of silica, then analysed.



Propyl benzyl ether (9a)

Following general procedure C using allyl benzyl ether **8a** (154 µL) and hydrazine monohydrate (120 µL, 2.5 eq) gave propyl benzyl ether **9a** as an oil (139 mg, 93%) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.43 – 7.27 (m, 5H), 4.55 (s, 2H), 3.48 (2H, t, *J* = 6.7 Hz), 1.69 (2H, apparent sex., *J* = 7.1 Hz), 1.00 (3H, t, *J* = 7.4 Hz) ^{13}C NMR 138.8, 128.4, 127.7, 127.5, 72.9, 72.2, 23.0, 10.7. Data in accordance with literature.[9]



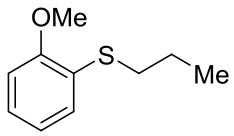
Propyl phenyl sulfide (9b)

Following general procedure C using allyl phenyl sulfide **8b** (148 µL) and hydrazine monohydrate (240 µL, 5 eq) gave propyl phenyl sulfide **9b** as an oil (138 mg, 82%) ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.42 – 7.12 (m, 5H), 2.93 (t, 2H, *J* = 7.4 Hz), 1.71 (apparent p, 2H, *J* = 7.4 Hz) 1.06 (t, 3H, *J* = 7.4 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 137.0, 128.9, 128.9, 125.7, 35.6, 22.6, 13.5. Data in accordance with literature.[9]

$C_{14}H_{30}$

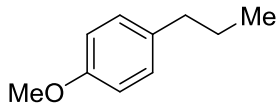
Tetradecane (9c)

Following general procedure C using 1-tetradecene **8c** (253 µL) and hydrazine monohydrate (120 µL, 2.5 eq) gave a mixture of tetradecane **9c** and a small amount of starting material, analysed by ^{1}H NMR spectroscopy.



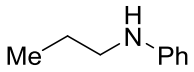
(2-methoxyphenyl)propyl sulfide (9d)

Following general procedure C using (2-methoxyphenyl)allyl sulfide **8d** (90 mg, 0.5 mmol), alloxan (4 mg, 5 mol%), CuCl (0.5 mg, 1 mol%), hydrazine monohydrate (120 µL, 6 mmol) and acetonitrile (1 mL) gave (2-methoxyphenyl)propyl sulfide **9d** as an oil (86 mg, 95%). ^{1}H NMR (500 Mhz, $CDCl_3$) δ_H 7.26 (d, *J* = 7.9 Hz, 1H), 7.16 (td, *J* = 11.5, 1.4 Hz, 1H), 6.92 (td, *J* = 11.5, 1.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 3.89 (s, 3H), 2.87 (t, *J* = 7.3 Hz, 2H) 1.69 (apparent p., *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 157.3, 129.0, 126.8, 125.3, 121.1, 110.5, 55.9, 34.1, 22.5, 13.7 IR ν_{max} 2960, 1577, 1474, 1240 cm^{-1} HRMS (ESI, +ve) *m/z* calcd. for $C_{10}H_{15}SO$ 183.0838, found: 183.0840 $(M+H)^+$



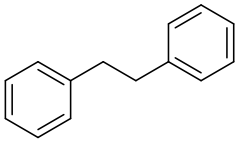
4-propylanisole (9e)

Following general procedure C using 4-allylanisole **8e** (154 µL) and hydrazine monohydrate (120 µL, 2.5 eq) gave 4-propylanisole **9e** as an oil (147 mg, 98%) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.62 (apparent sex., *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 157.8, 135.0, 129.5, 113.8, 55.4, 37.3, 24.9, 13.9. Data in accordance with literature.[10]



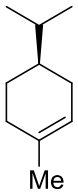
N-propylaniline (9f)

Following general procedure C using n-allylaniline **8f** (136 µL) and hydrazine monohydrate (120 µL, 2.5 eq) gave N-propylaniline **9f** as an oil (121 mg, 90%) ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.18 (apparent t, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 7.9 Hz, 1H), 6.62 (apparent t, *J* = 7.9 Hz, 2H), 3.09 (t, *J* = 7.1 Hz, 2H), 1.65 (apparent sex., *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C 148.6, 129.3, 117.2, 112.8, 45.9, 22.8, 11.8. Data in accordance with literature.[11]



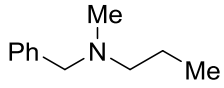
Bibenzyl (9g)

Following general procedure C using stilbene **8g** (180 mg) and and hydrazine monohydrate (240µL, 2.5 eq) gave a mixture of stilbene **8g** and bibenzyl **9g** which was analysed by ^{1}H NMR spectroscopy.



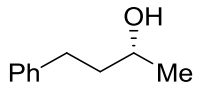
Dihydrolimonene (9h)

Following general procedure C using (S)-limonene **8h** (80 µL, 0.5 mmol), alloxan (4 mg, 5 mol%), CuCl (0.5 mg, 1 mol%), hydrazine monohydrate (60 µL, 2.5 mmol), naphthalene (3.2 mg, 5 mol%) as an internal standard and acetonitrile (1 mL) for 3 h gave dihydrolimonene **9h** as an oil. Yield was quantified by GC, comparing to an authentic sample of hydrolimonene produced by PtO_2 – catalysed hydrogenation.[14]



(N,N,N)methyl benzyl propyl amine (9i)

Following general procedure C using pargyline **8i** (169 µL) and hydrazine monohydrate (240 µL, 5 eq) gave **(**N,N,N)methyl benzyl propyl amine **9i** as an oil (112 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) 7.26 – 7.04 (m, 5H), 3.36 (s, 2H), 2.22 (t, 2H, *J* = 7.5 Hz), 2.07 (s, 3H), 1.42 (apparent sex., 2H, *J* = 7.4 Hz), 0.79 (t, 3H, *J* = 7.3 Hz) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 139.2, 129.1, 128.2, 126.9, 62.3, 59.5, 42.2, 20.5, 11.9. Data in accordance with literature.[12]



(2R)-4-phenylbutan-2-ol (9j)

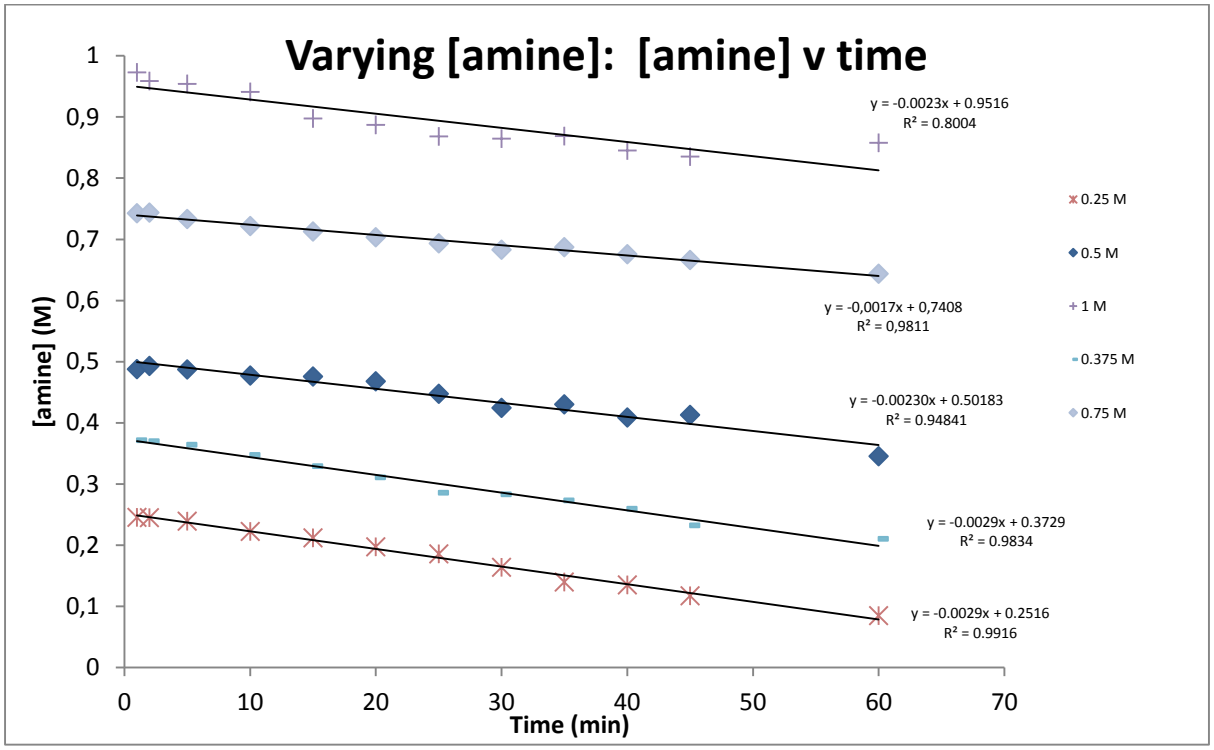
Following general procedure C using (2R)-4-phenylbut-3-yn-2-ol **8j** (73 mg, 0.5 mmol), alloxan (4 mg, 5 mol%), CuCl (0.5 mg, 1 mol%), hydrazine monohydrate (120 µL, 6 mmol) and acetonitrile (1 mL) for 72 h gave **9j** as an oil (65 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.34 – 7.15 (m, 5H), 3.83 (apparent sex, 1H, *J* = 6.2 Hz), 2.83 – 2.60 (m, 2H), 1.83 – 1.72 (m, 2H), 1.56 (bs, 1H), 3.83 (d, 3H, *J* = 6.2 Hz) ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 142.2, 128.5, 128.5, 126.0, 67.7, 41.0, 32.2, 23.8. $[\alpha]^{20}_D$ -11.8˚ (c 0.925, $CHCl_3$) (lit = -12.9˚, c 0.55, $CHCl_3$). Data in accordance with literature.[13]

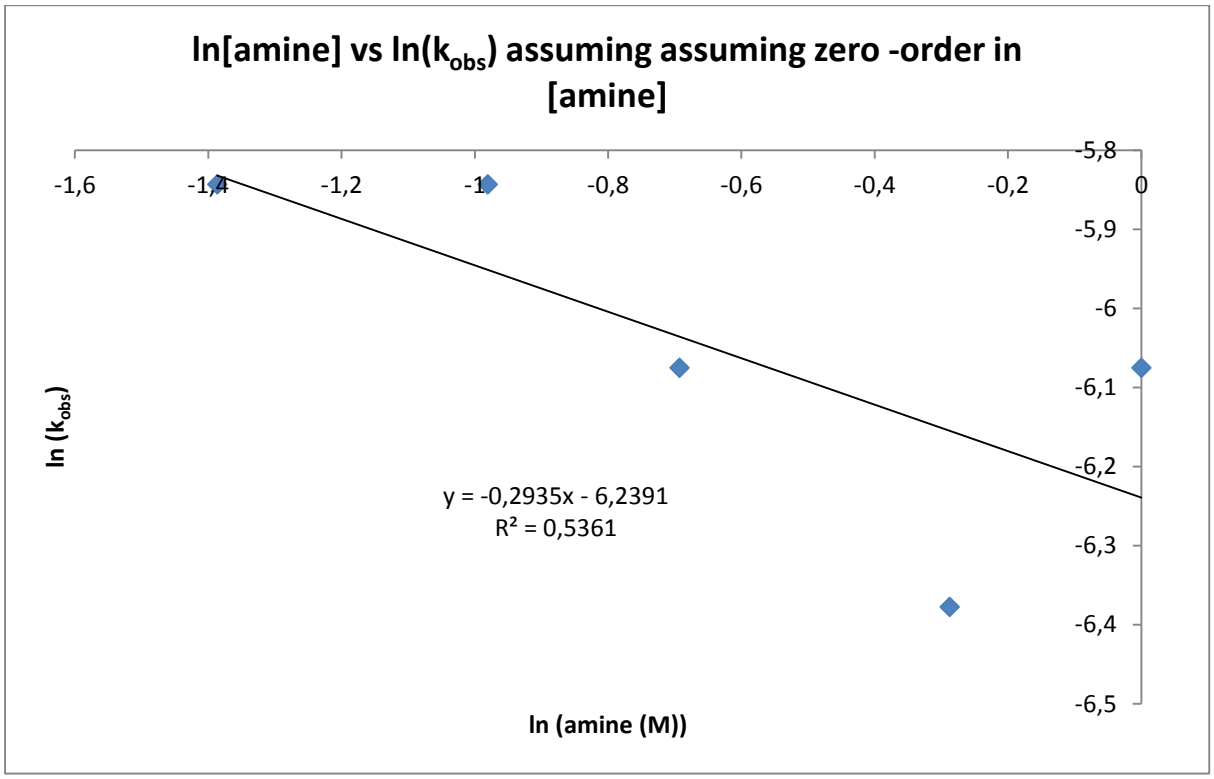
IV KINETIC EXPERIMENTS

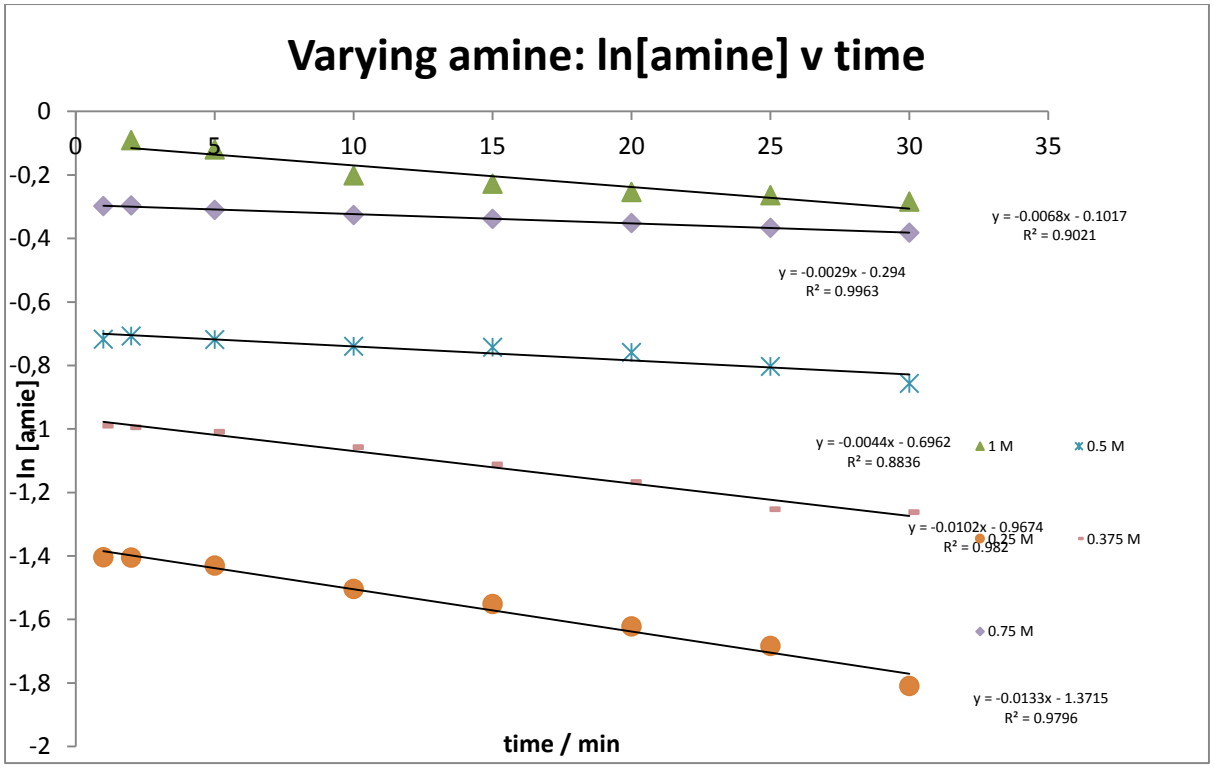
General Procedure for kinetic monitoring of imine production (General Procedure D)

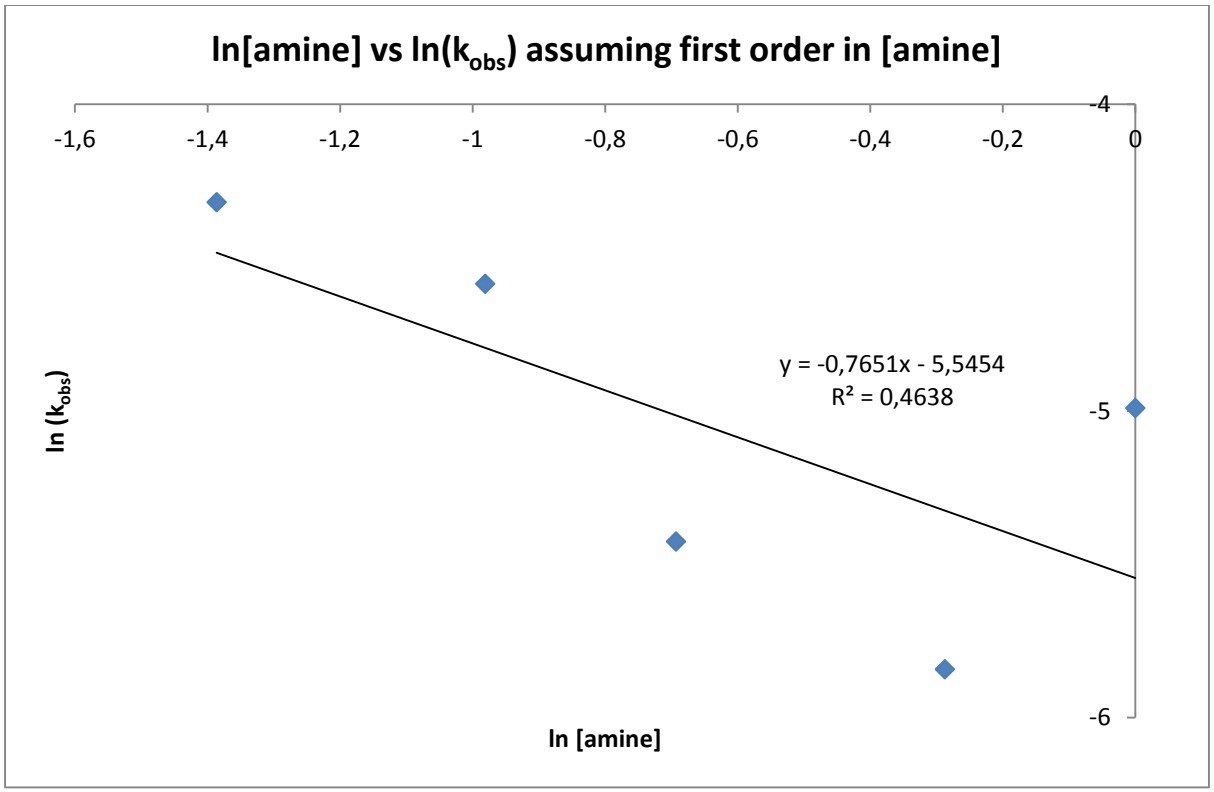
A mixture of alloxan monohydrate **1**, copper (I) chloride and naphthalene (5.1 mg, 40 µmol) in MeCN (1 mL) was sonicated for 5 mins and benzylamine **4a** was added. The reaction was sonicated further under air, with ice added if necessary to maintain the temperature at 30 ˚C, with aliquot samples of ca. 5 µL taken at specified intervals, diluted into ca. 20 µL MeOH in an HPLC vial which was then filled to 1.5 mL with MeCN and analysed by HPLC (UV detection) with naphthalene acting as an internal standard. Standard conditions unless stated to be deviated from were 0.5 M **4a**, 0.0125 M **1** and 0.005M CuCl.

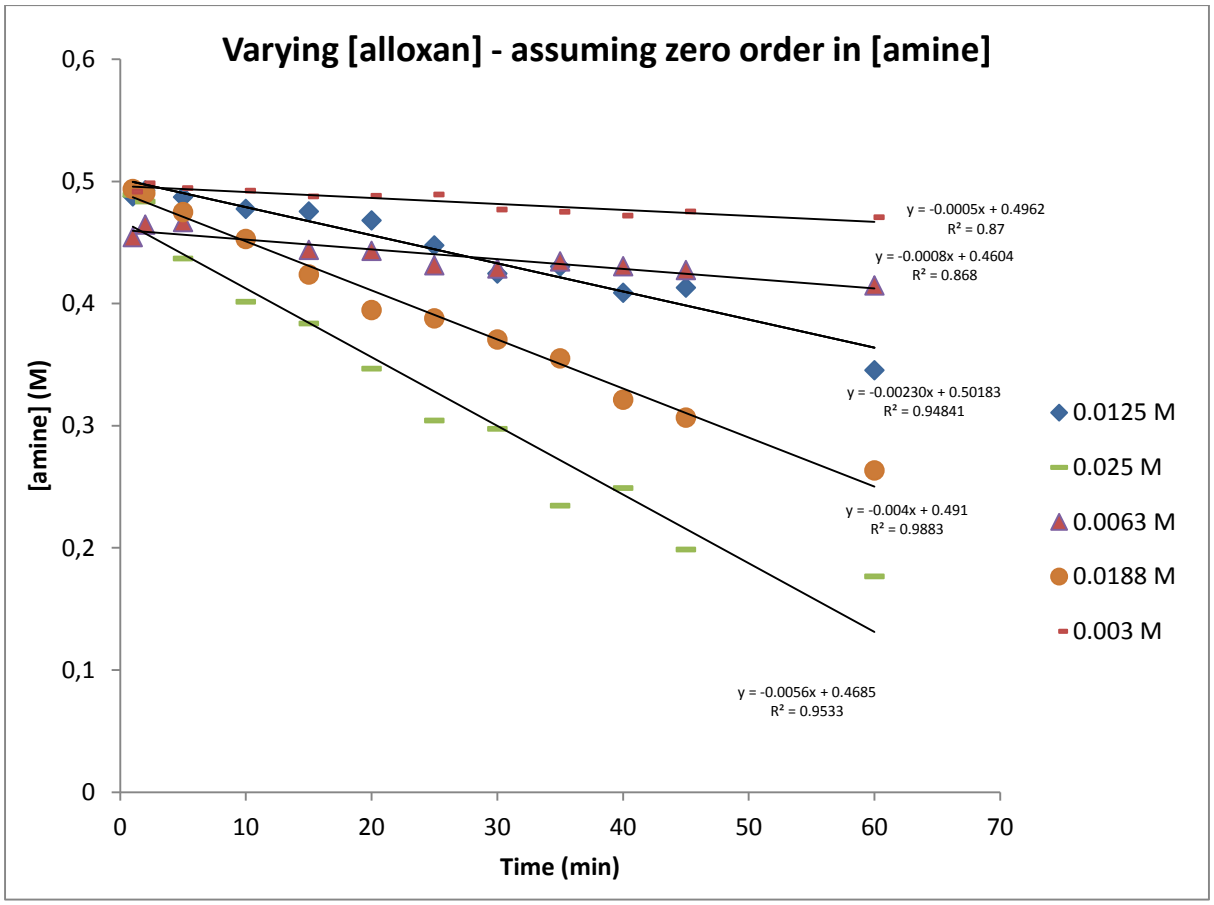
Kinetics results

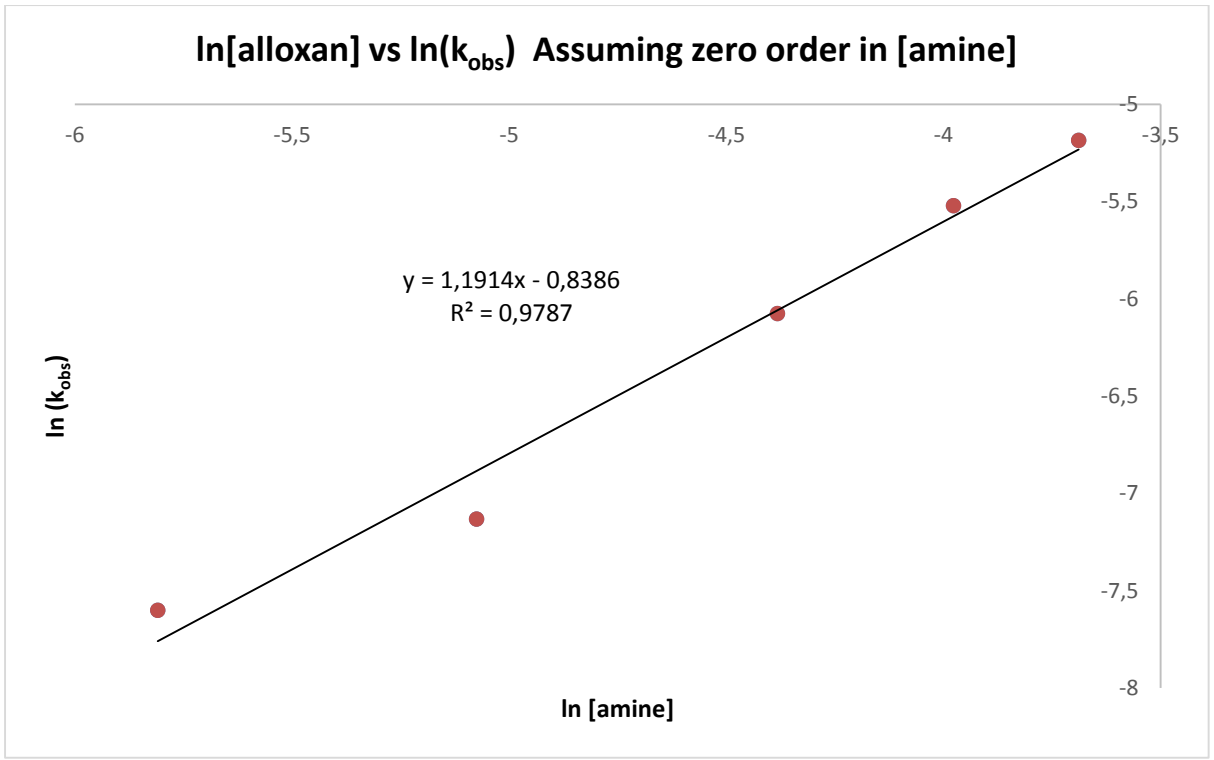


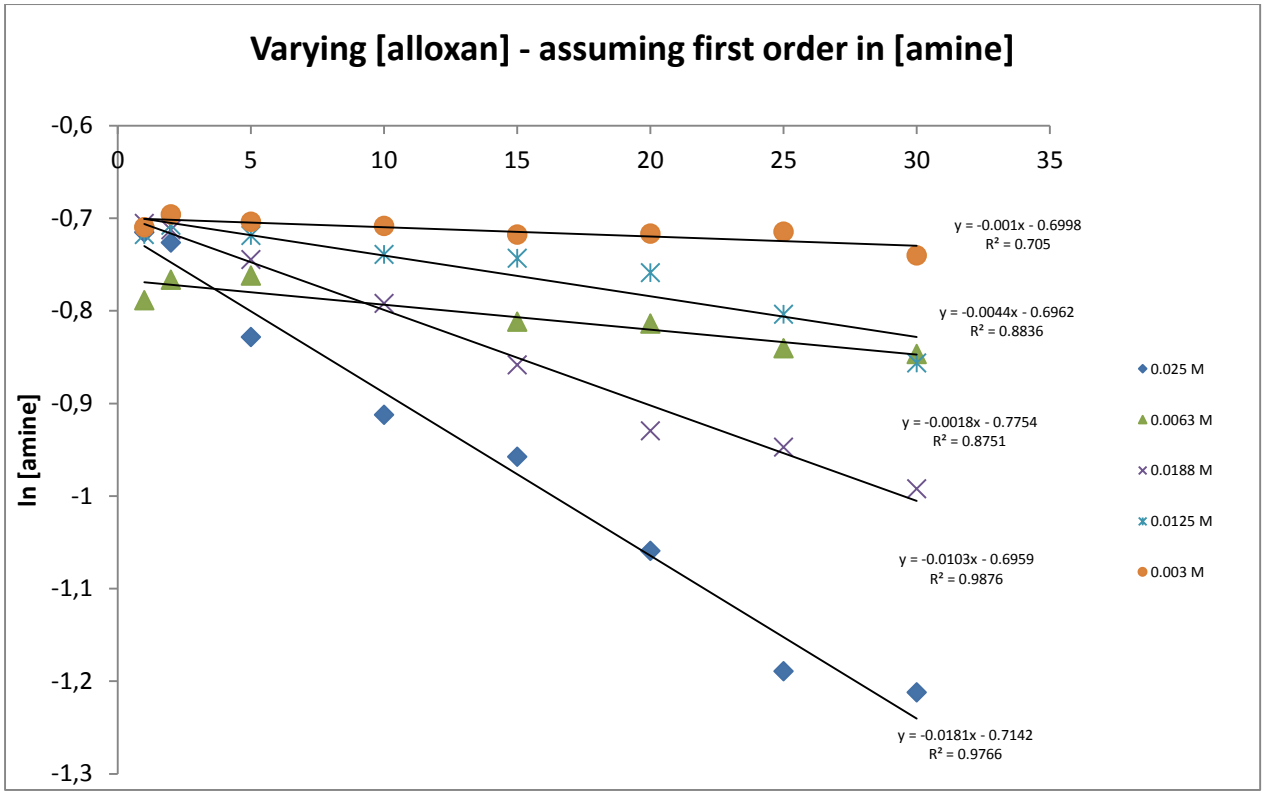


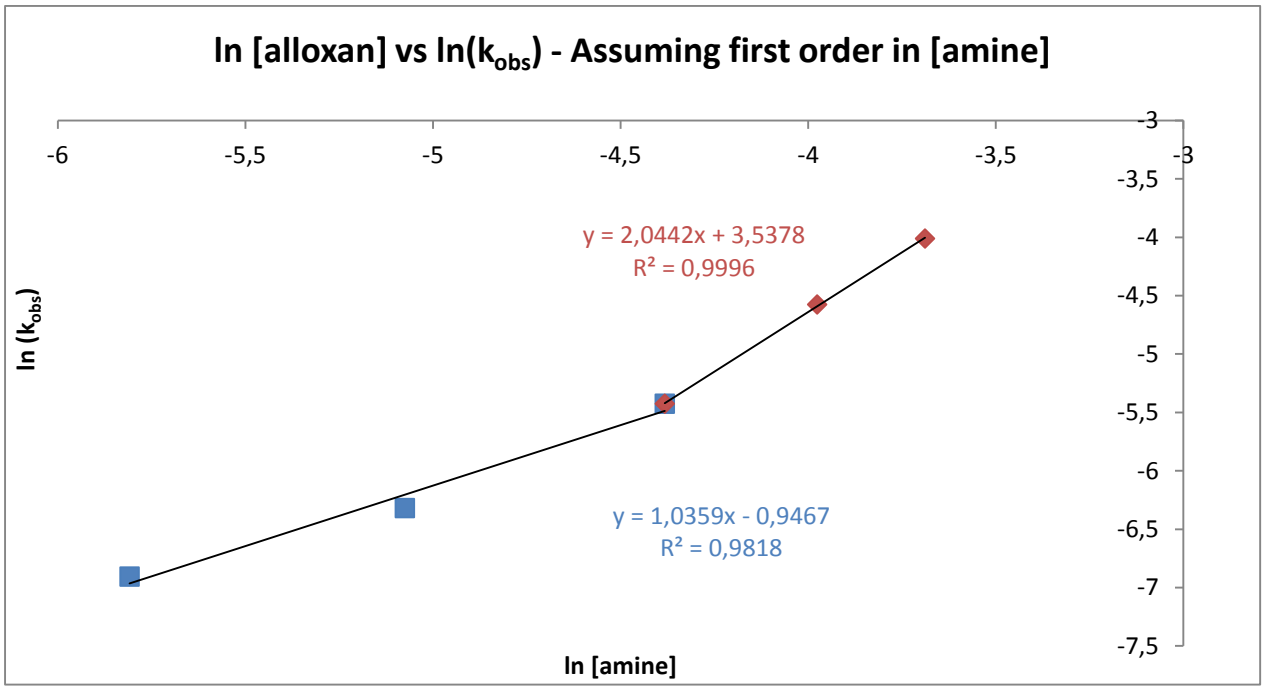

Varying amine: ln[amine] v time
0
-0,2
-0,4
-0,6
-0,8
-1
-1,2
-1,4
-1,6
-1,8
-2
0
5
10
15
20
25
30
35
ln [amie]
time / min
y = -0.0068x - 0.1017
R² = 0.9021
y = -0.0029x - 0.294
R² = 0.9963
y = -0.0044x - 0.6962
R² = 0.8836
y = -0.0102x - 0.9674
R² = 0.982
y = -0.0133x - 1.3715
R² = 0.9796
1 M
0.5 M
0.25 M
0.375 M
0.75 M

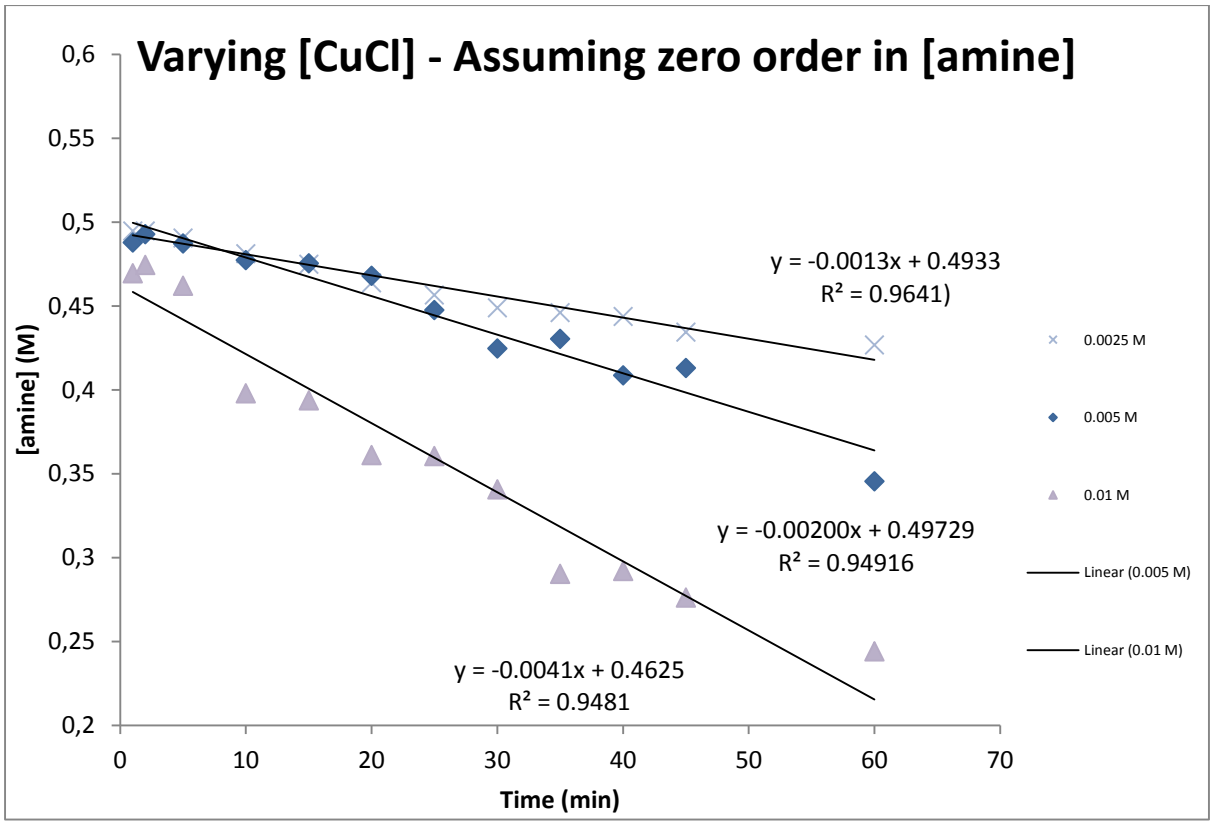

ln[amine] vs ln(kobs) assuming first order in [amine]
-1,6
-1,4
-1,2
-1
-0,8
-0,6
-0,4
-0,2
0
-4
-5
-6
ln (kobs)
ln [amine]
y = -0,7651x - 5,5454
R² = 0,4638

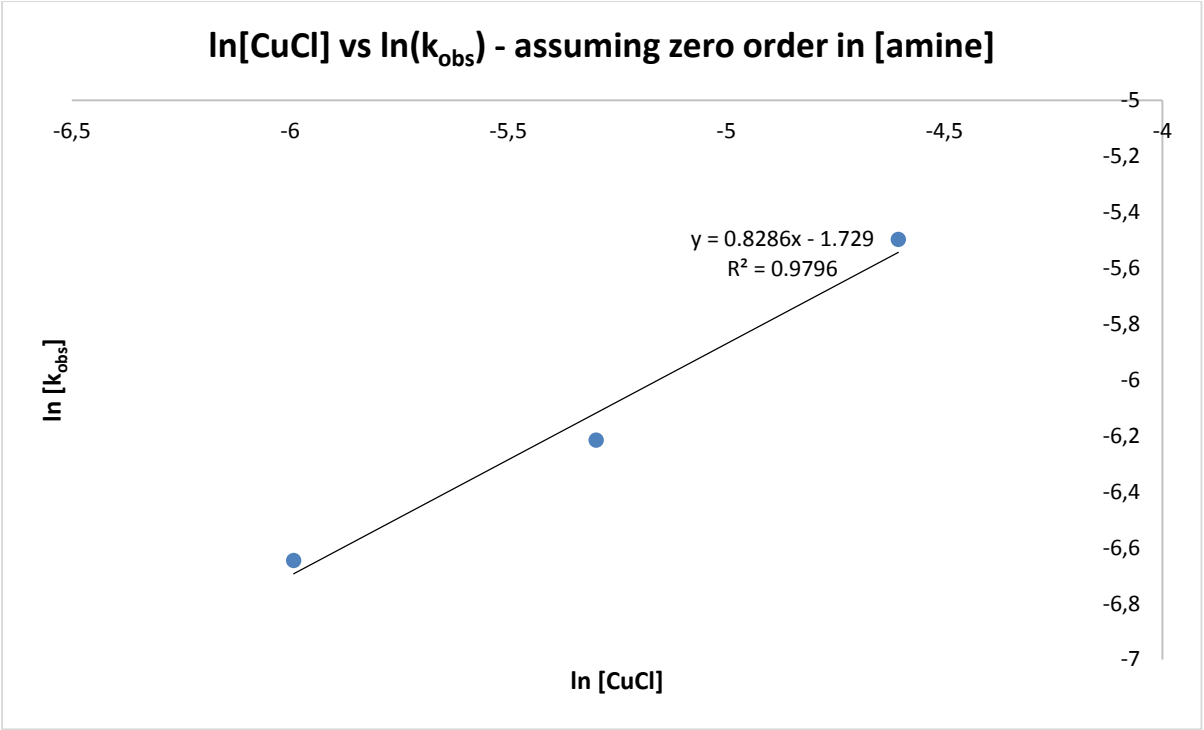

Varying [alloxan] - assuming zero order in [amine]
[amine] (M)
Time (min)
y = -0.0005x + 0.4962
R² = 0.87
y = -0.0008x + 0.4604
R² = 0.868
y = -0.00230x + 0.50183
R² = 0.94841
y = -0.004x + 0.491
R² = 0.9883
y = -0.0056x + 0.4685
R² = 0.9533
0.0125 M
0.025 M
0.0063 M
0.0188 M
0.003 M

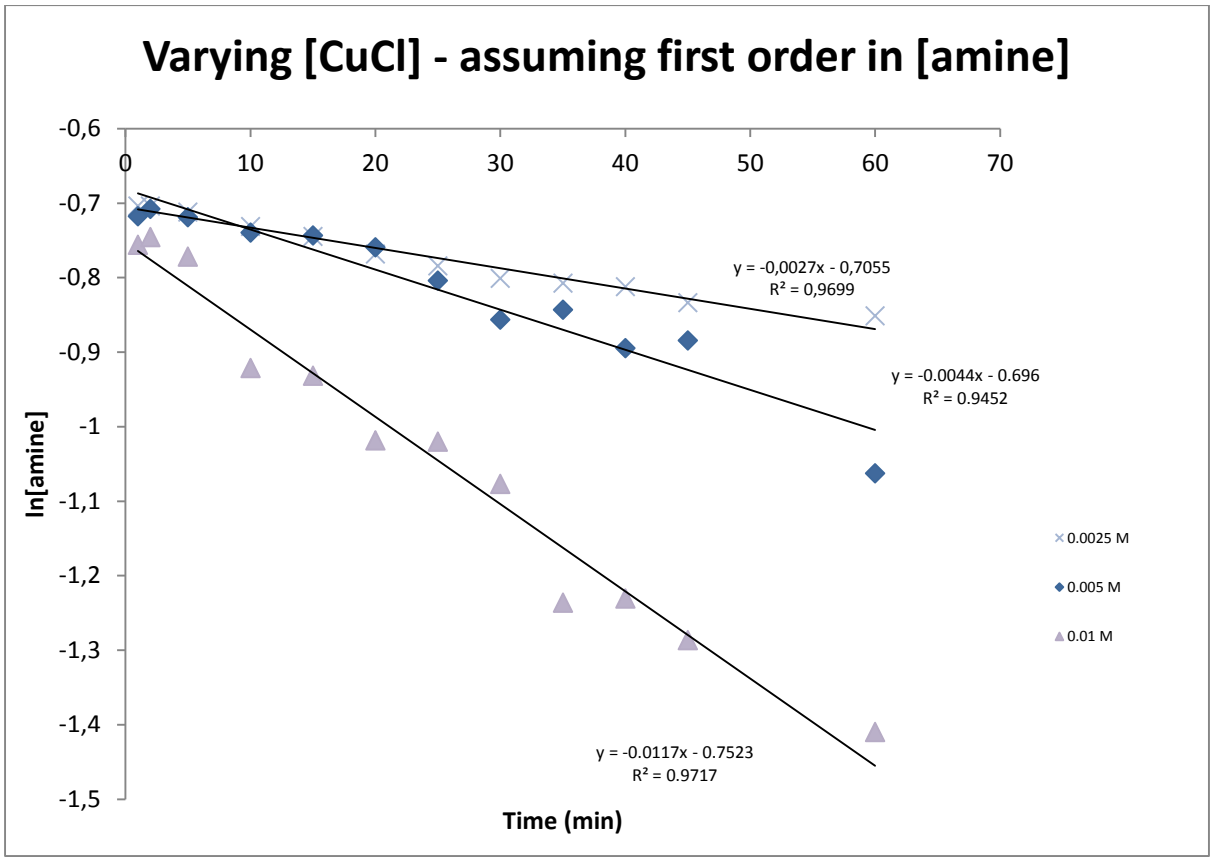

ln[alloxan] vs ln(kobs) Assuming zero order in [amine]
y = 1,1914x - 0,8386
R² = 0,9787
ln (kobs)
ln [amine]

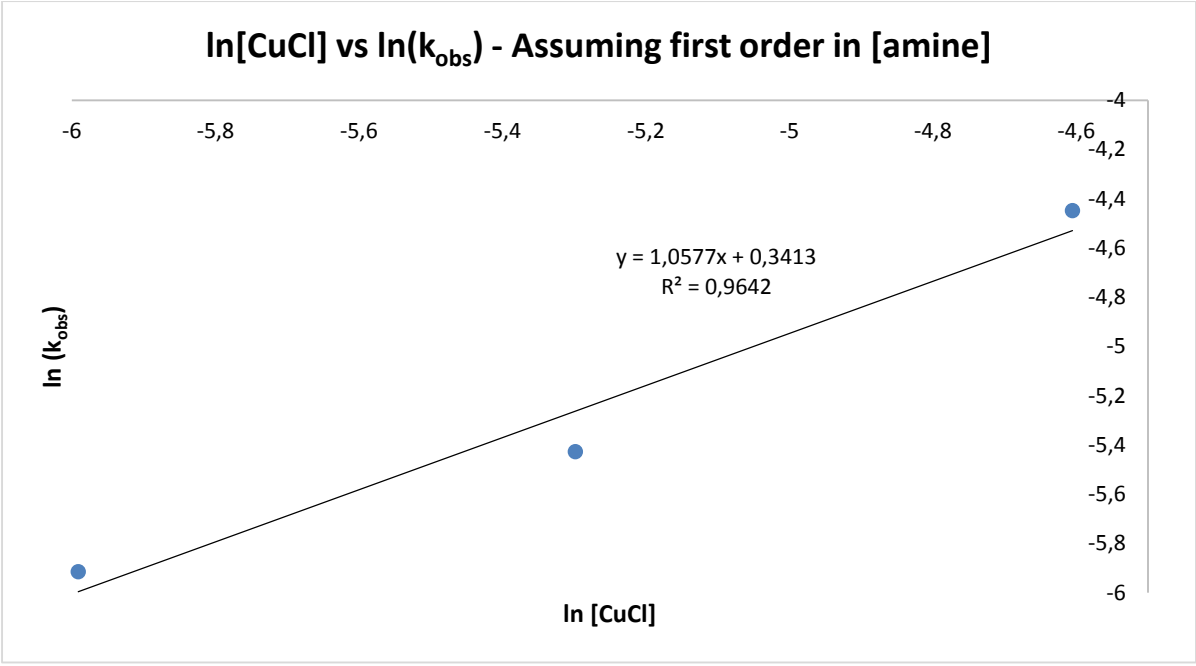

Varying [alloxan] - assuming first order in [amine]
ln [amine]
-0,6
-0,7
-0,8
-0,9
-1
-1,1
-1,2
-1,3
0
5
10
15
20
25
30
35
y = -0.001x - 0.6998
R² = 0.705
y = -0.0044x - 0.6962
R² = 0.8836
y = -0.0018x - 0.7754
R² = 0.8751
y = -0.0103x - 0.6959
R² = 0.9876
y = -0.0181x - 0.7142
R² = 0.9766
0.025 M
0.0063 M
0.0188 M
0.0125 M
0.003 M

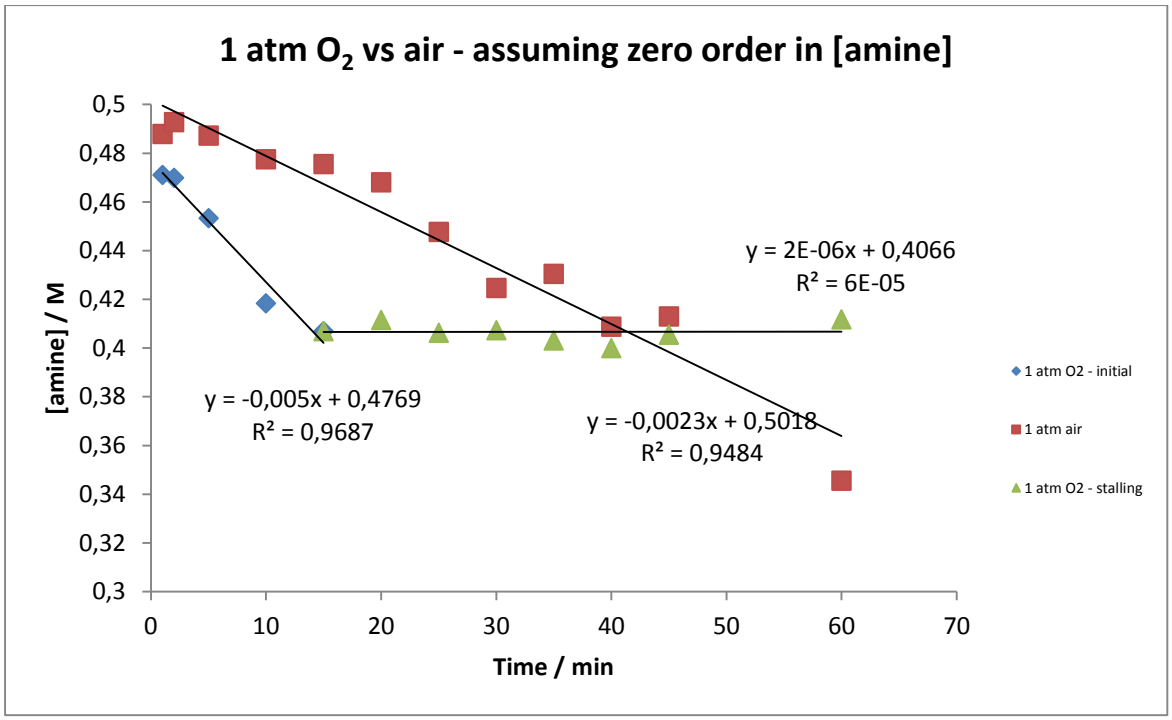

ln [alloxan] vs ln(kobs) - Assuming first order in [amine]
ln (kobs)
ln [amine]
-6
-5,5
-5
-4,5
-4
-3,5
-3
-3
-3,5
-4
-4,5
-5
-5,5
-6
-6,5
-7
-7,5
y = 2,0442x + 3,5378
R² = 0,9996
y = 1,0359x - 0,9467
R² = 0,9818

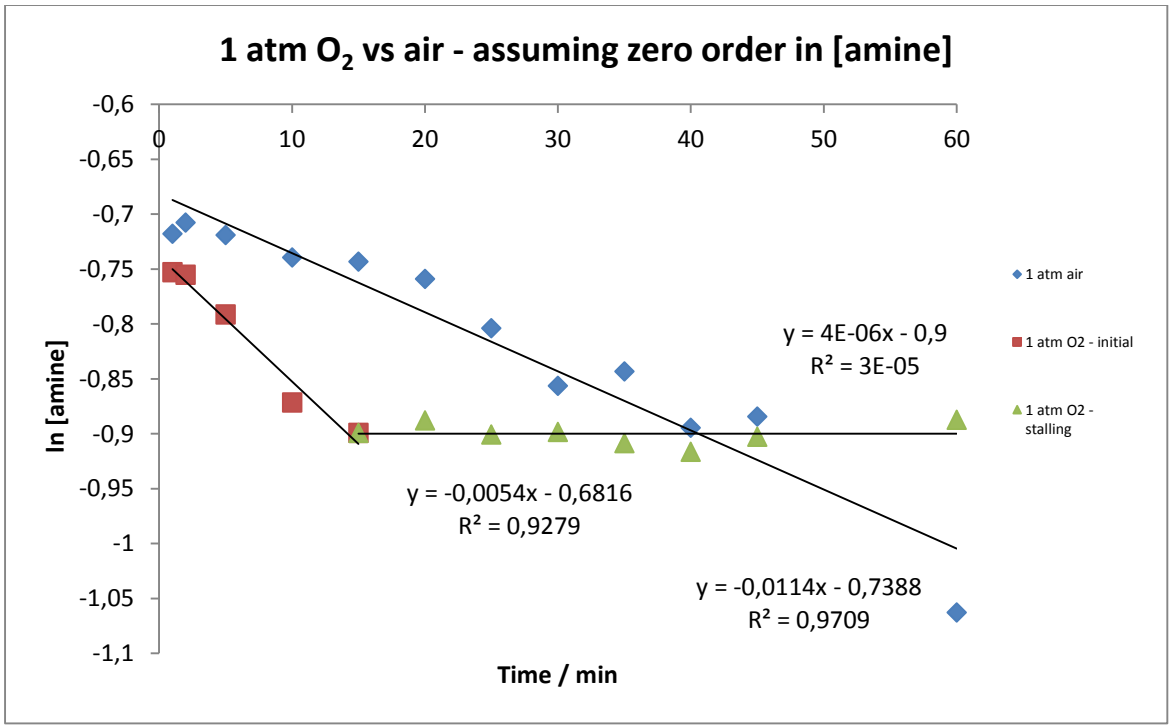

Varying [CuCl] - Assuming zero order in [amine]
[amine] (M)
Time (min)
y = -0.0013x + 0.4933
R² = 0.9641)
y = -0.00200x + 0.49729
R² = 0.94916
y = -0.0041x + 0.4625
R² = 0.9481
0.0025 M
0.005 M
0.01 M
Linear (0.005 M)
Linear (0.01 M)


ln[CuCl] vs ln(k_obs) - assuming zero order in [amine]
ln [k_obs]
ln [CuCl]
y = 0.8286x - 1.729
R² = 0.9796


Varying [CuCl] - assuming first order in [amine]
-0,6
-0,7
-0,8
-0,9
-1
-1,1
-1,2
-1,3
-1,4
-1,5
0
10
20
30
40
50
60
70
ln[amine]
Time (min)
y = -0,0027x - 0,7055
R² = 0,9699
y = -0.0044x - 0.696
R² = 0.9452
y = -0.0117x - 0.7523
R² = 0.9717
0.0025 M
0.005 M
0.01 M


ln[CuCl] vs ln(k_obs) - Assuming first order in [amine]
-6
-5,8
-5,6
-5,4
-5,2
-5
-4,8
-4,6
-4
-4,2
-4,4
-4,6
-4,8
-5
-5,2
-5,4
-5,6
-5,8
-6
ln (k_obs)
ln [CuCl]
y = 1,0577x + 0,3413
R² = 0,9642


1 atm O2 vs air - assuming zero order in [amine]
[amine] / M
Time / min
y = 2E-06x + 0,4066
R² = 6E-05
y = -0,005x + 0,4769
R² = 0,9687
y = -0,0023x + 0,5018
R² = 0,9484
1 atm O2 - initial
1 atm air
1 atm O2 - stalling


1 atm O2 vs air - assuming zero order in [amine]
ln [amine]
Time / min
y = 4E-06x - 0,9
R² = 3E-05
y = -0,0054x - 0,6816
R² = 0,9279
y = -0,0114x - 0,7388
R² = 0,9709
1 atm air
1 atm O2 - initial
1 atm O2 - stalling

V EPR EXPERIMENTS AND SPECTRA

Samples for EPR were produced by use of General Procedure A, with benzylamine, and EPR spectra taken directly, under air atmosphere, before addition of amine (**A**), directly (<5 mins) after (**B**) after 2.5 hours (**C**).

EPR Measurements: The X-band (~9.6 GHz) continous-wave EPR spectra of solutions and frozen glass samples (MeCN) at 120 K were recorded on an Bruker EMX Micro EPR Spectrometer. The field modulation frequency was 100 kHz, and diphenylpicrylhydrazyl (DPPH) was used as a reference.

Results:

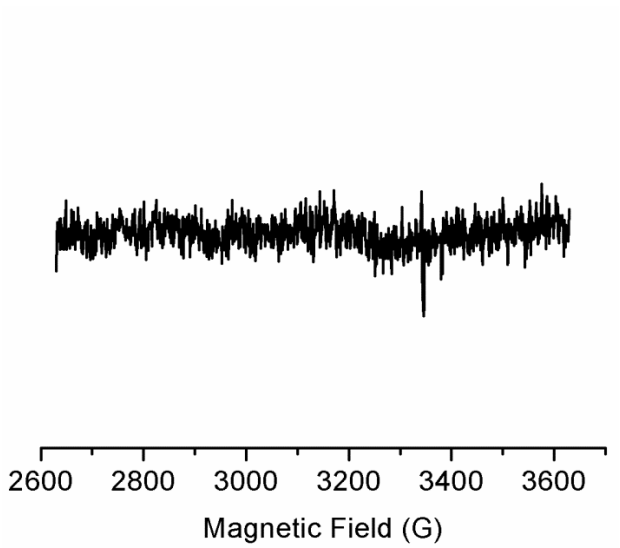


Fig. S1: EPR Spectrum of **A**; It shows no signal diamagnetic Cu(I) d^{10})

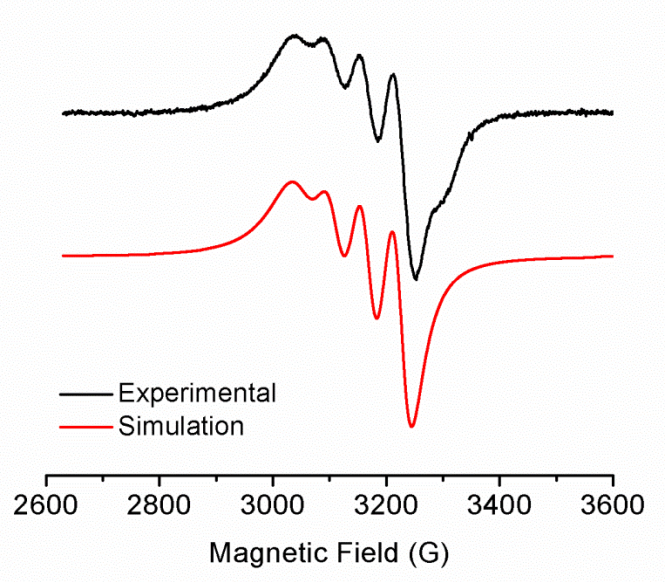


Fig. S2: Room-temperature solution X-band (9.6 GHz) EPR Spectrum of **B** Simulation parameters: g_{iso} = 2.134; A_{iso} = -55 G; Tumbling effect modeled with : - a = 41, b = 7.5 c =3, d = 0.5

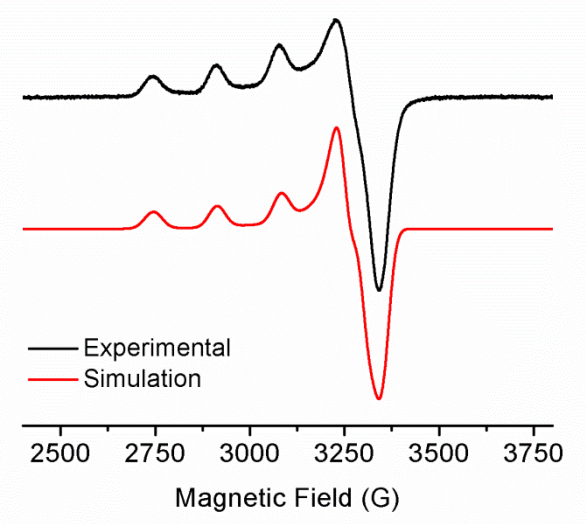


Fig. S3. Frozen solution (120K) X-band EPR Spectrum of **B; Simulation:** g_1 = 2.04, g_2 = 2.075, g_3 = 2.242; A_1 = 10 G, A_2 = 10 G, A_3 = 165 G; Linewidth (W) : Gaussian (W_1= 20 G, W_2 = 20 G, W_3 = 25 G)

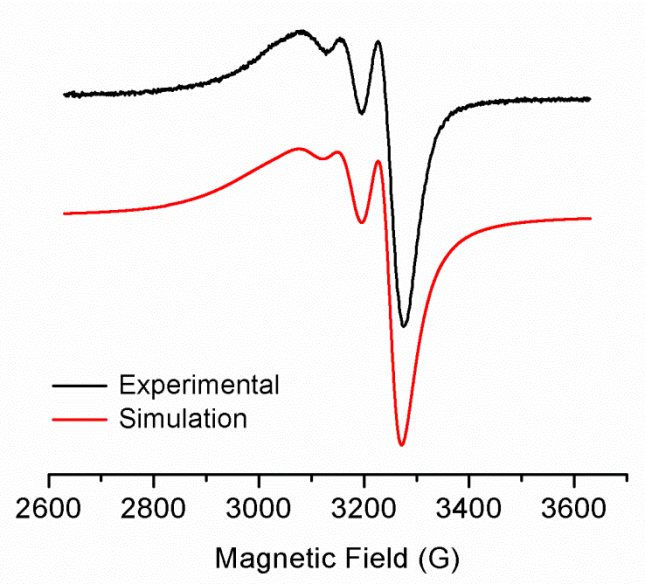


Fig. S4: Room-temperature solution EPR Spectrum of **C:** g(iso) = 2.129; A(iso) = -65 G; Tumbling - a = 70, b = 26, c = 8, d = 2

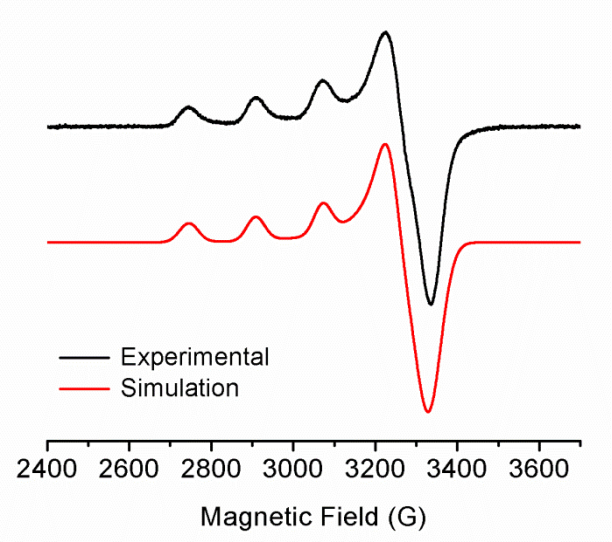


Fig. S5: Frozen Solution (120 K) X-band EPR Spectrum of **C:** g_1 = 2.055, g_2 = 2.055, g_3 = 2.242; A_1 = 10 G, A_2 = 10 G, A_3 = 160 G; Linewidth = Gaussian, 1 = 20 G, 2 = 20 G, 3 = 25 G

EPR spectral studies.

A refers to a mixture prepared according to General Procedure A, prior to addition of benzylamine. **B** refers to the same mixture immediately after $BnNH_2$ addition, and **C** upon standing for 2.5 h.

The X-band EPR spectra of the Cu(II) Complexes **A**, **B** and **C** were investigated as solution in MeCN at room temperature and as glassy (frozen) solutions at 120 K.

The EPR spectrum of **A** shows no signal, confirming a diamagnetic species. This should indicate that Cu is in oxidation state 1 (d^{10} configuration). As Cu(I) normally prefers a tetrahedral environment, we can assume that the coordination number is 4.

The solution EPR spectra of **B** and **C** at room temperature show a 4-line hyperfine structure due to the interaction of the electron (Cu^{2+}; $3d^9$ configuration; one unpaired electron) with the nuclear spin of copper (I=3/2 for both isotopes; natural abundance 69.1% of ^{63}Cu and 30.9% of ^{65}Cu) .

They were analyzed using the spin Hamiltonian eq. 1.

$$\hat{H} = \beta B g \hat{S} + \hat{I} A \hat{S}$$

where the symbols have their usual meaning ; S = ½ and I = 3/2 for Cu^{2+}.[15]

The RT solution spectra were modeled with isotropic g and isotropic A as molecules tumble in solution; the hyperfine constant of **C** is slightly larger than that of **B**, but the g tensors are comparable.

At 120 K, molecules are frozen in particular orientations with respect to the magnetic field and it is possible to determine the g tensors values along various axes. Simulation of the frozen solution EPR spectra of **B** and **C** gives g_{zz} values much larger than g_{xx}, and g_{yy}, suggesting an symmetry close to axial (e.g. square-planar or axially –elongated), and with the unpaired electron placed in the d_{x2-y2} orbital.

The signal of **C** appears resolved in g_{II} (or g_{zz}) = 2.42 > $g_{\perp}$ (or g_{xx}=g_{yy}) = 2.055 > 2.0, A_{II} = 160 G and $A_{\perp}$ = 32 G. The EPR spectral features are a characteristic of typical axial symmetry with the unpaired electron in the d_{x2-y2} orbital.

In general, for elongated tetragonal symmetry, the dz^2 orbital is stabilized and the unpaired electron will be in an orbital of b_{1g} symmetry (mainly $d_{x2—y2}$).

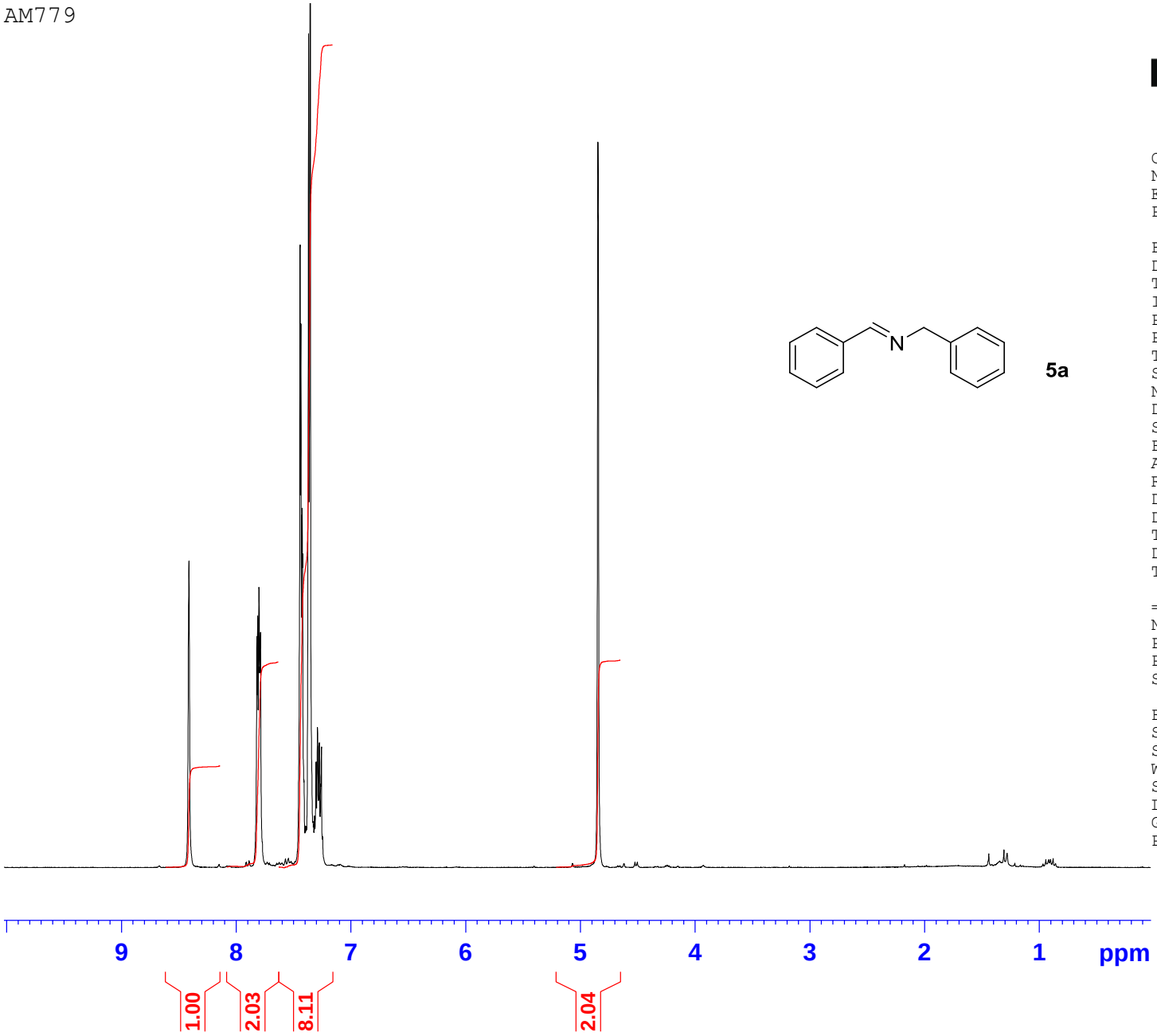
The *g*-values are given by $g_{\perp} = g_e - 2\lambda/\Delta E(b_{1g} - e_g)$;

$$g_{\parallel} = g_e - 8\lambda/\Delta E(b_{1g} - b_{2g})$$

where λ is spin-orbit coupling and $g_{\parallel} > g_{\perp} > g_e$.

The spectrum of **B** shows three components (at fields $B_{x(1)}$, $B_{y(2)}$ and $B_{z(3)}$) revealing a distortion toward rhombic of the coordination sphere. These signals correspond to the three different coordination axes x, y and z, of the magnetic tensor. This might be explained by diffrences in M-lig binds along x, y , z or differences in the nature of the ligands coordinated along these axes. When two of these three signals are close to each other, the spectrum is similar to the axial elongated type of signal.

AM779



5a

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PROCNO                 1

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TD                 32768
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NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
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P1                 7.10 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

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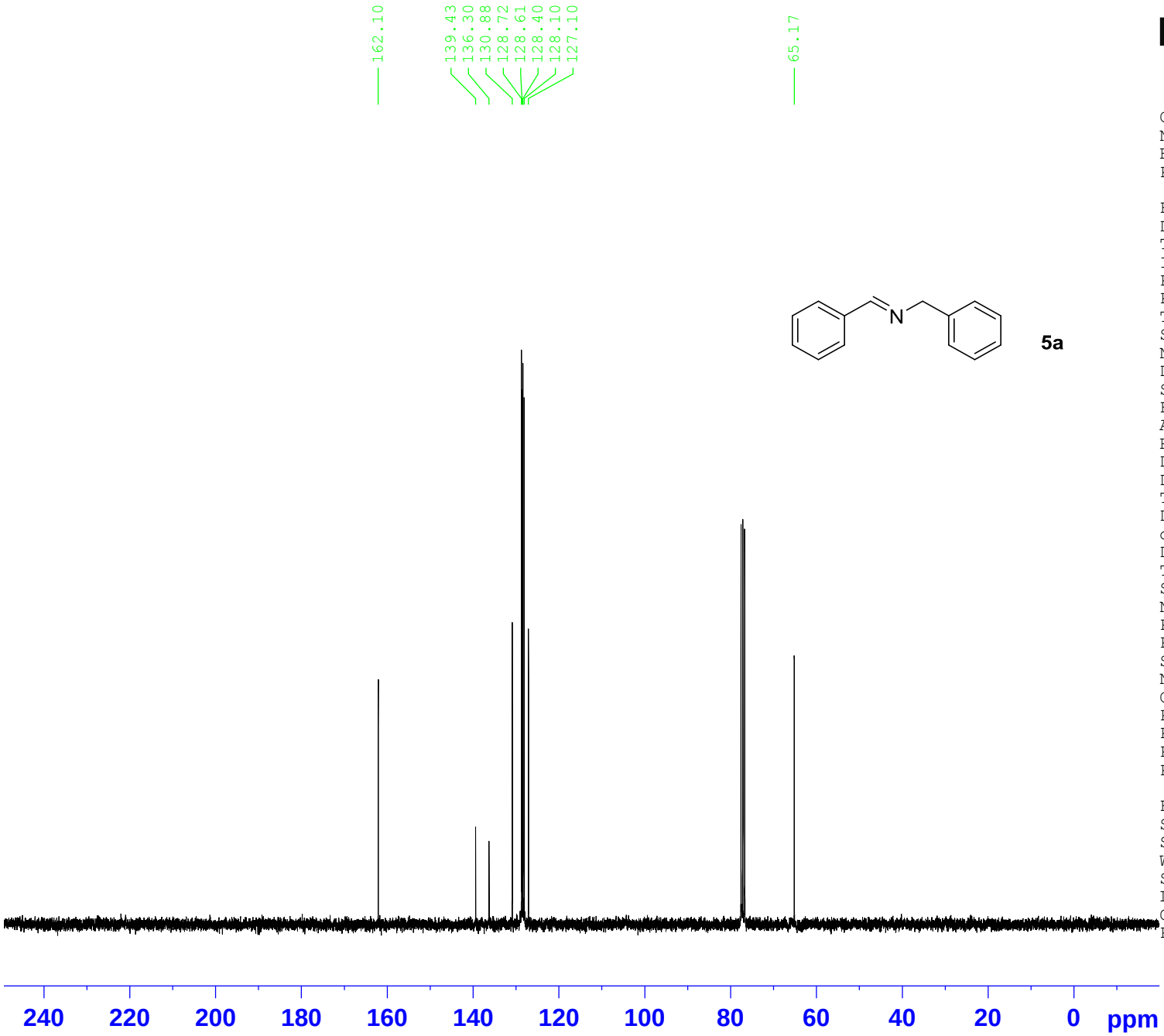
AM779



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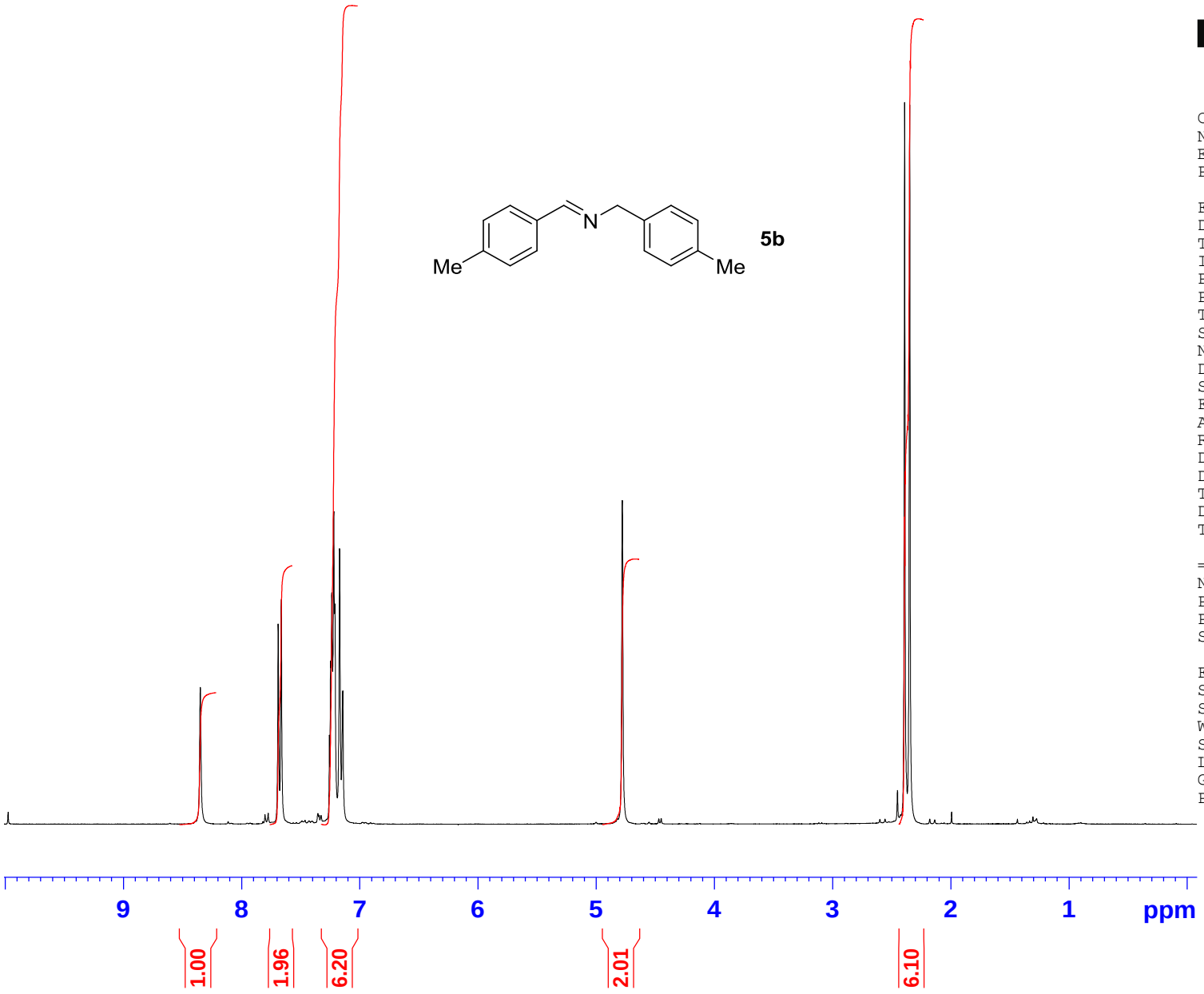
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 14596.5
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

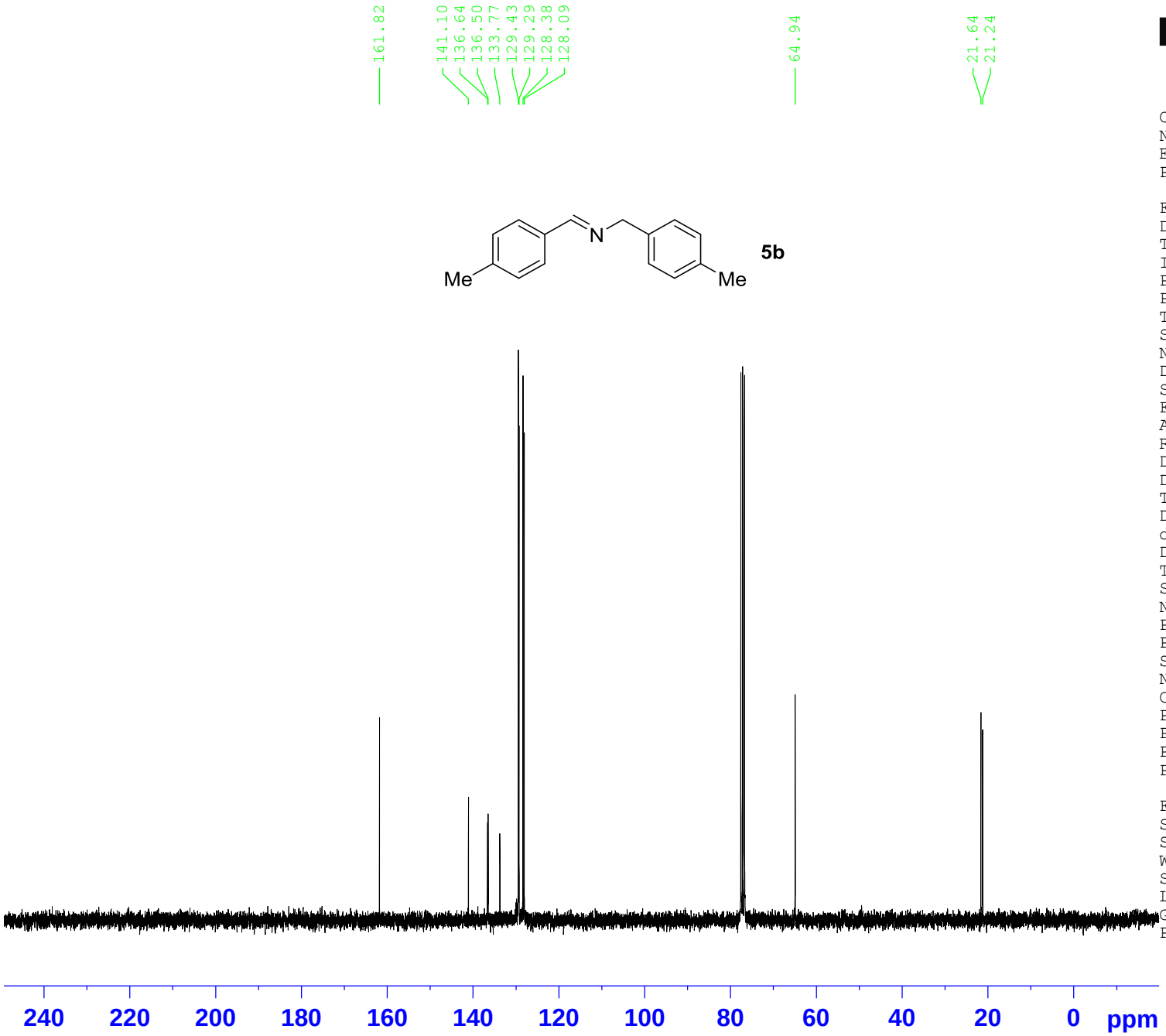
F2 - Processing parameters
SI 65536
SF 75.4903709 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

AM782




```
Current Data Parameters
NAME          Apr29-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130429
Time              18.06
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542079 sec
RG                  181
DW               81.000 usec
DE                6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200023 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

AM782

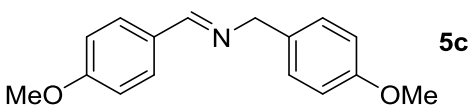


Current Data Parameters
NAME Apr29-2013
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130429
Time 18.23
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

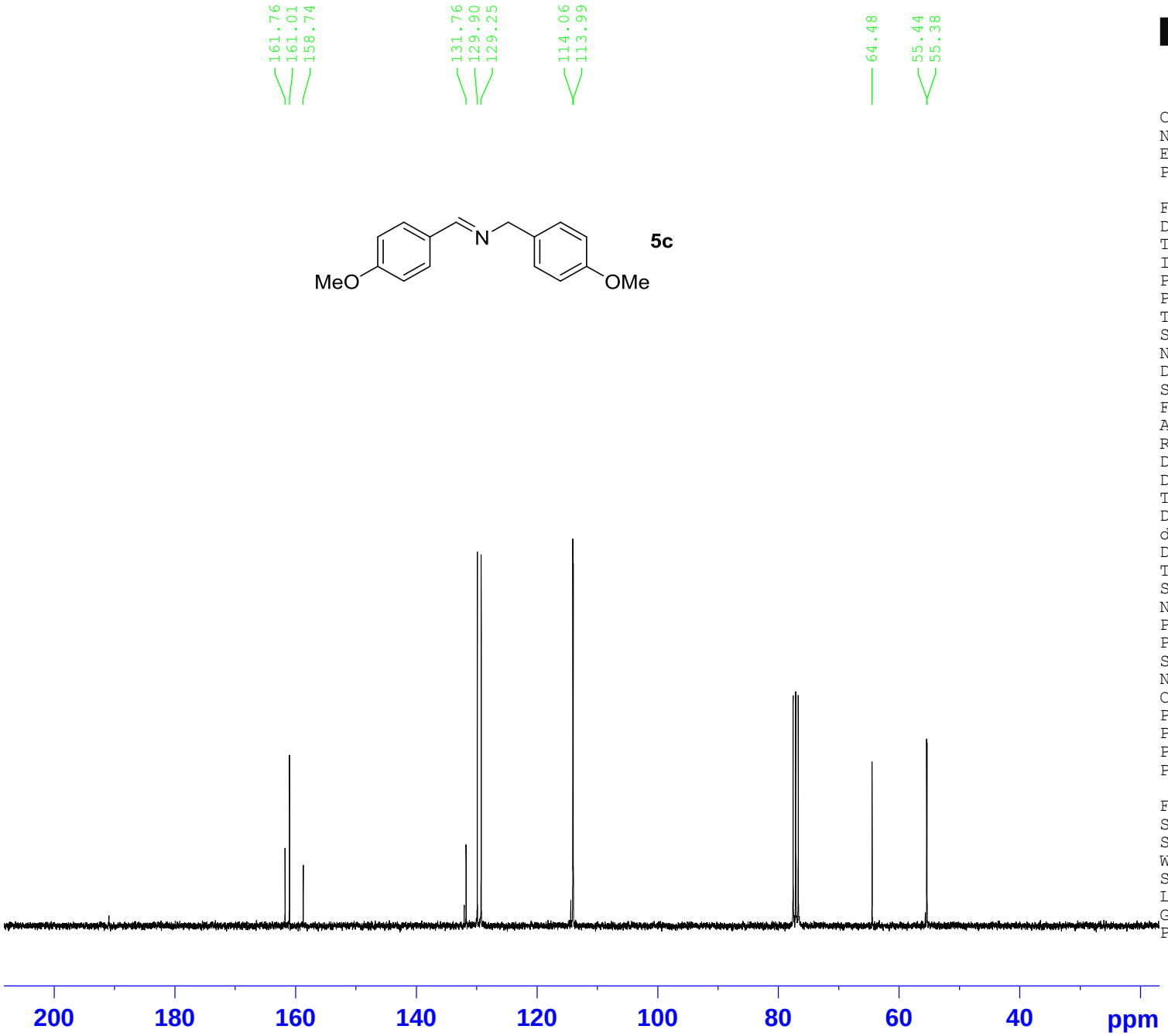
AM783



5c


```
Current Data Parameters
NAME          Apr29-2013
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130429
Time               18.29
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542079 sec
RG                  181
DW               81.000 usec
DE                6.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200023 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

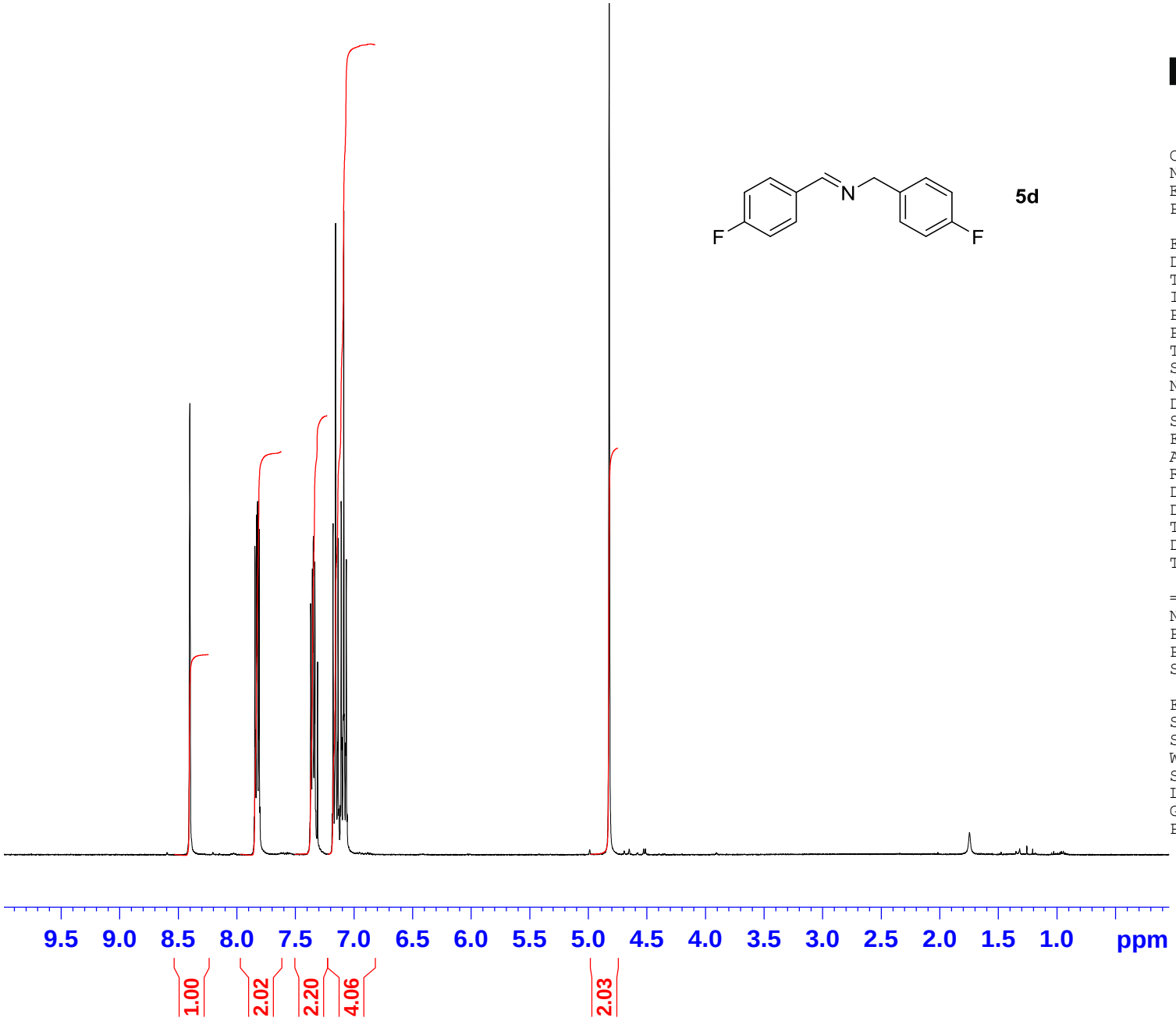
AM783



Current Data Parameters
NAME Apr29-2013
EXPNO 21
PROCNO 1

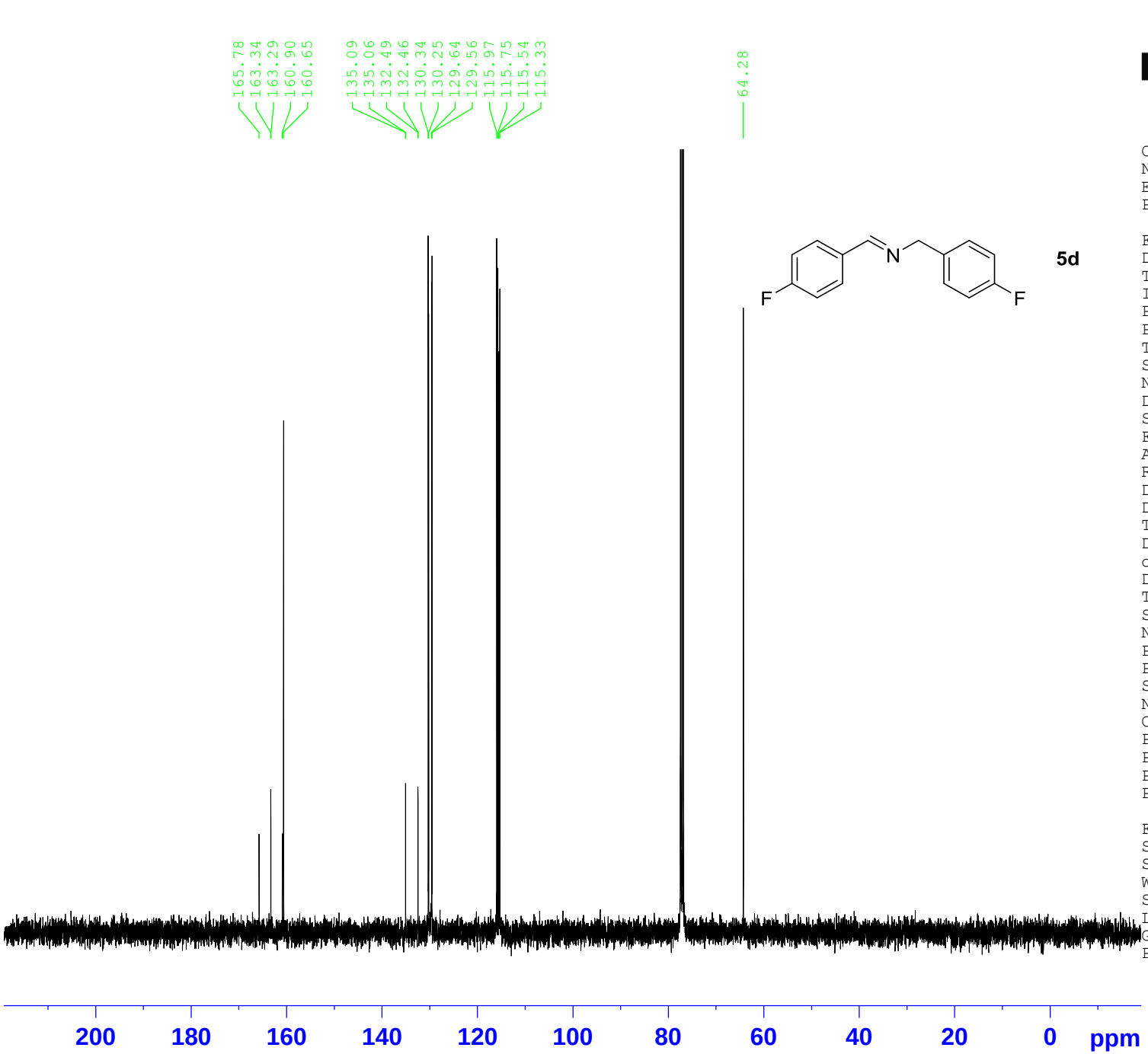
F2 - Acquisition Parameters
Date_ 20130429
Time 18.46
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903726 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



5d

```
Current Data Parameters
NAME                  AM793
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130506
Time                  15.52
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9583745 sec
RG                    228.1
DW                   60.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.50 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300000 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                   10.00
```



Current Data Parameters

NAME	AM793
EXPNO	2
PROCNO	1

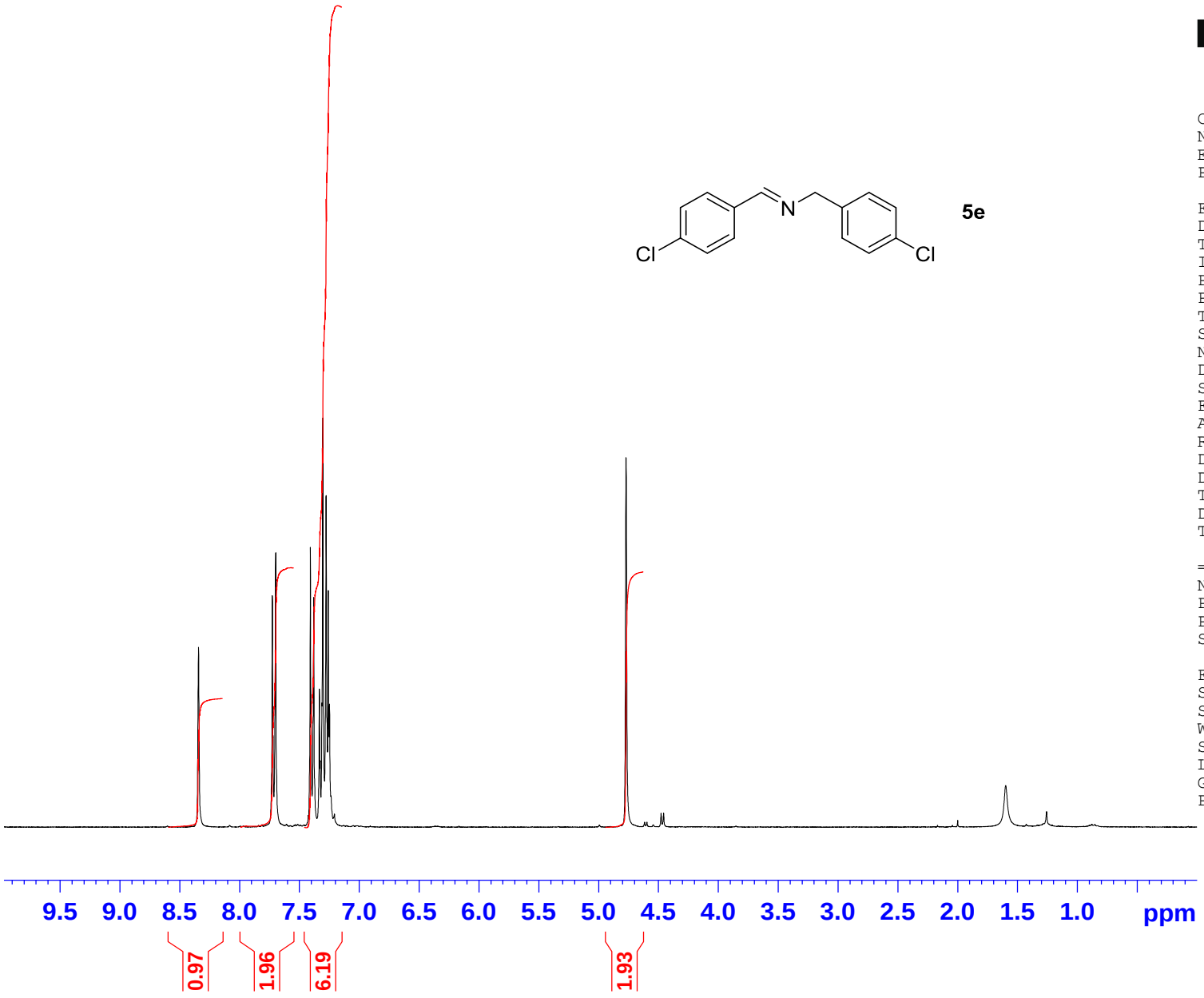
F2 - Acquisition Parameters

Date_	20130506
Time	16.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	283
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664256 sec
RG	7298.2
DW	20.850 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
SFO1	100.6228298 MHz
NUC1	13C
P1	7.30 usec
PLW1	-1.00000000 W
SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	-1.00000000 W
PLW12	-1.00000000 W
PLW13	-1.00000000 W

F2 - Processing parameters

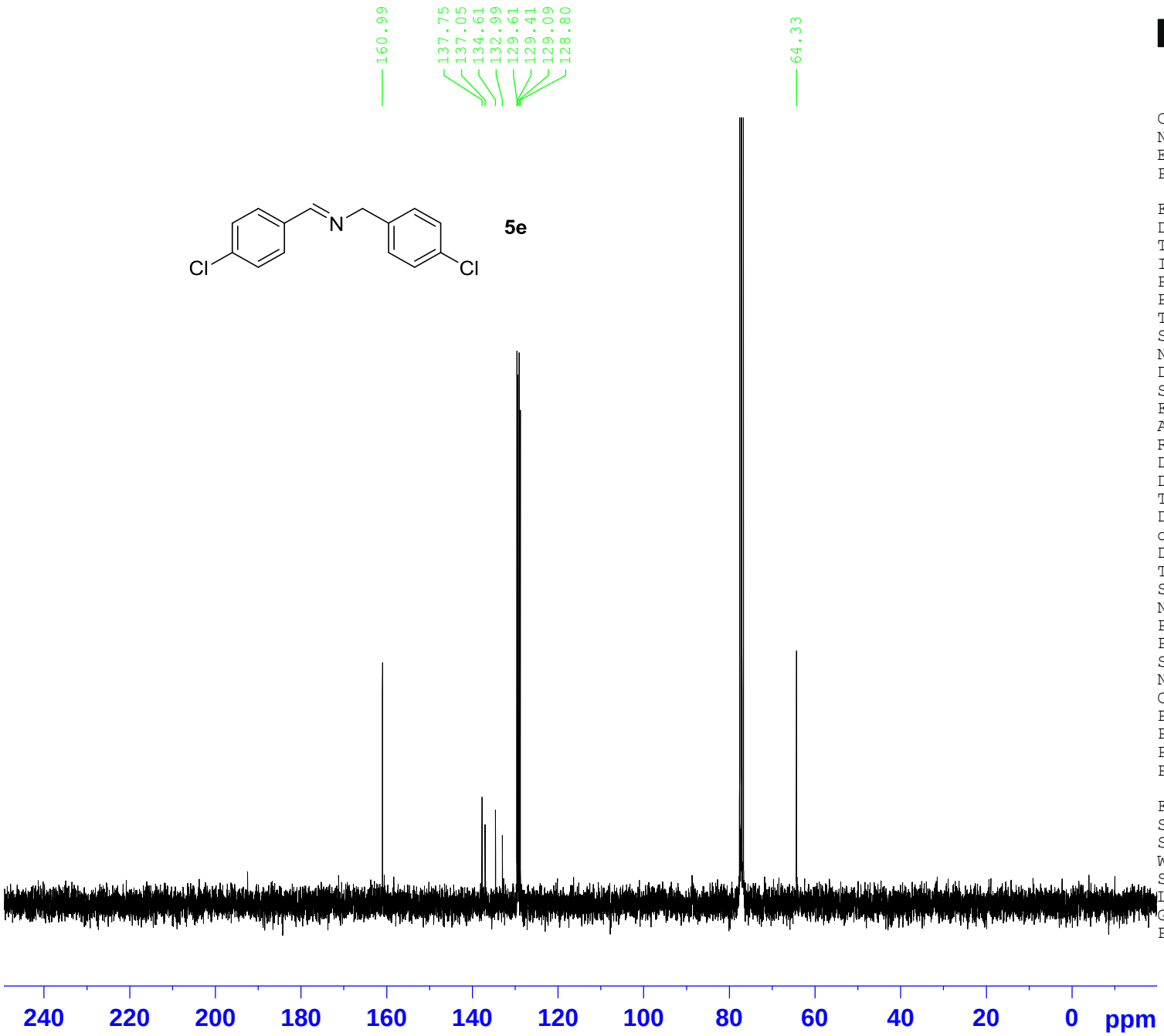
SI	32768
SF	100.6127598 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

AM799



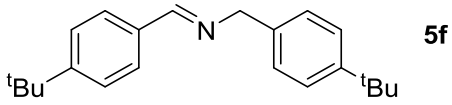

```
Current Data Parameters
NAME          May09-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130509
Time               22.23
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                 456.1
DW                81.000 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200023 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM799




```
Current Data Parameters
NAME          May09-2013
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130509
Time              22.40
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG              18390.4
DW               24.600 usec
DE                6.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                 7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903673 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

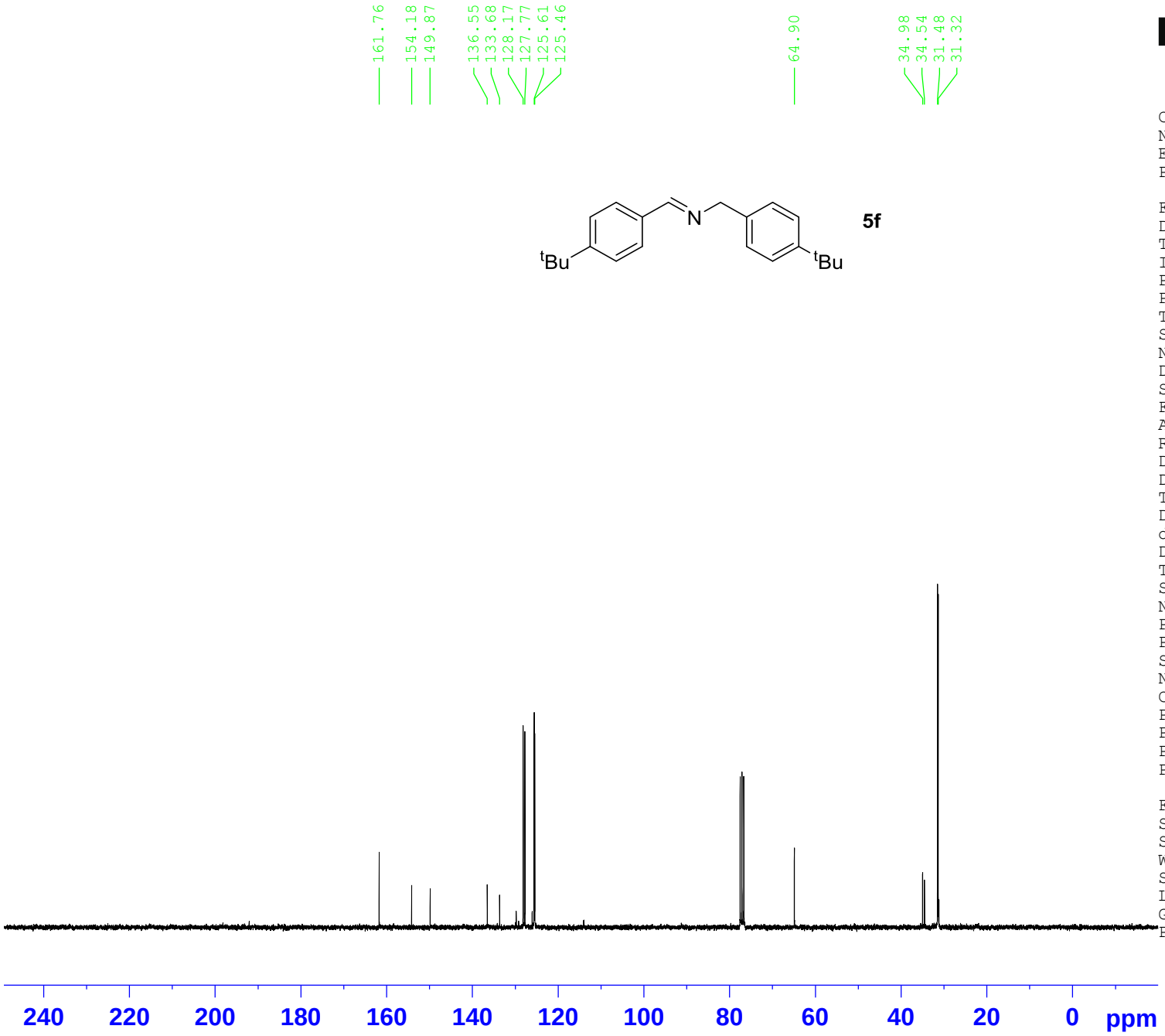
AM784



5f


```
Current Data Parameters
NAME          Apr29-2013
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130429
Time              18.53
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542079 sec
RG                 90.5
DW               81.000 usec
DE                6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200359 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

AM784

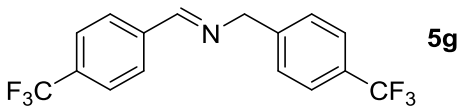


Current Data Parameters
NAME Apr29-2013
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130429
Time 19.10
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903738 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

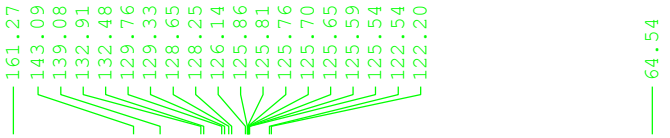
AM796

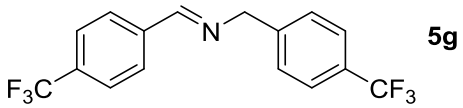


5g

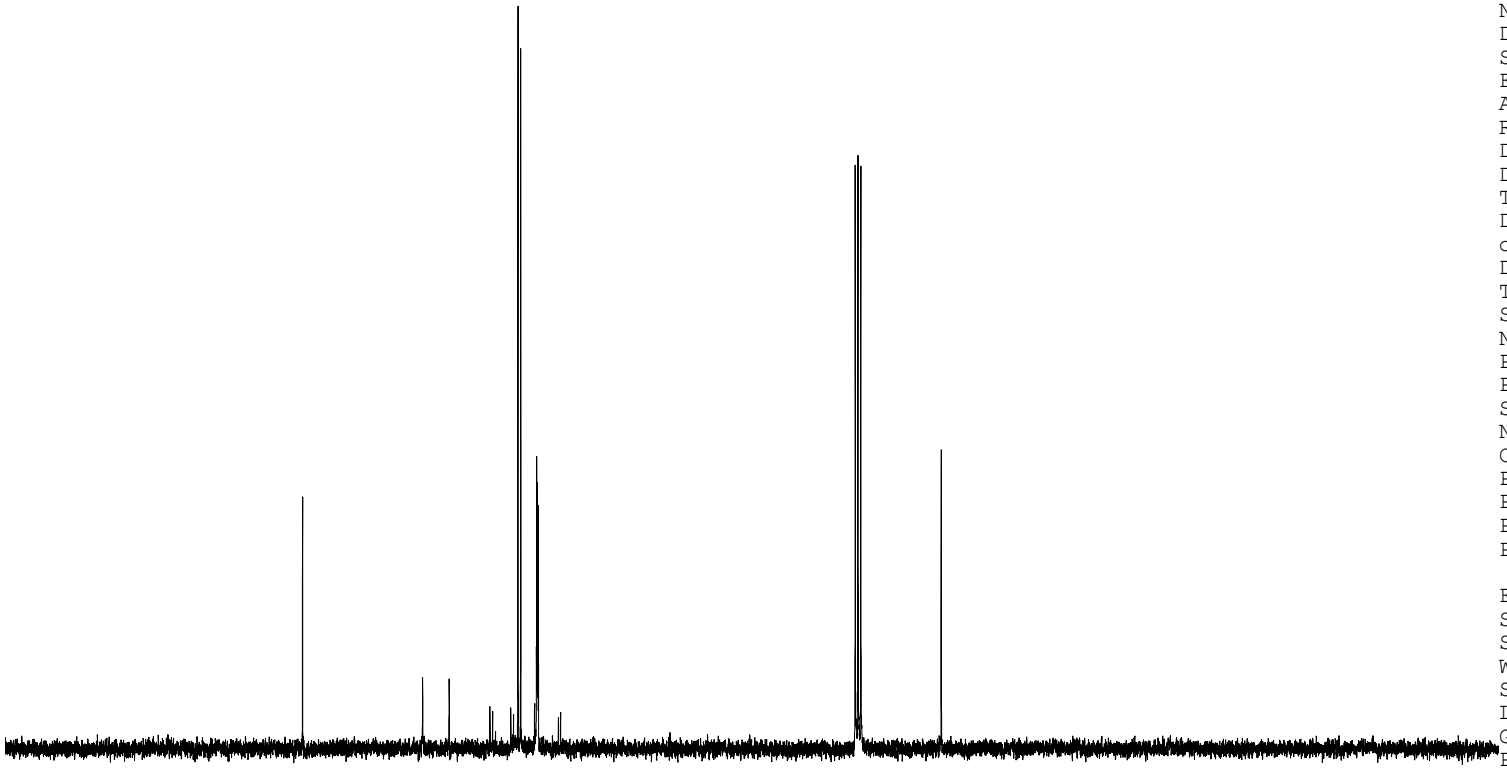

```
Current Data Parameters
NAME          May08-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130508
Time               20.56
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542079 sec
RG                  256
DW               81.000 usec
DE                6.00 usec
TE                293.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200023 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

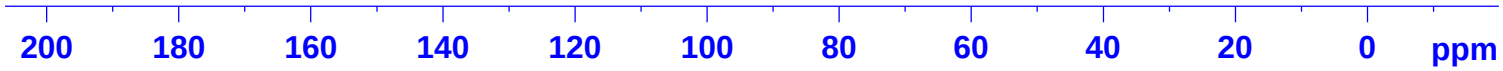
AM796



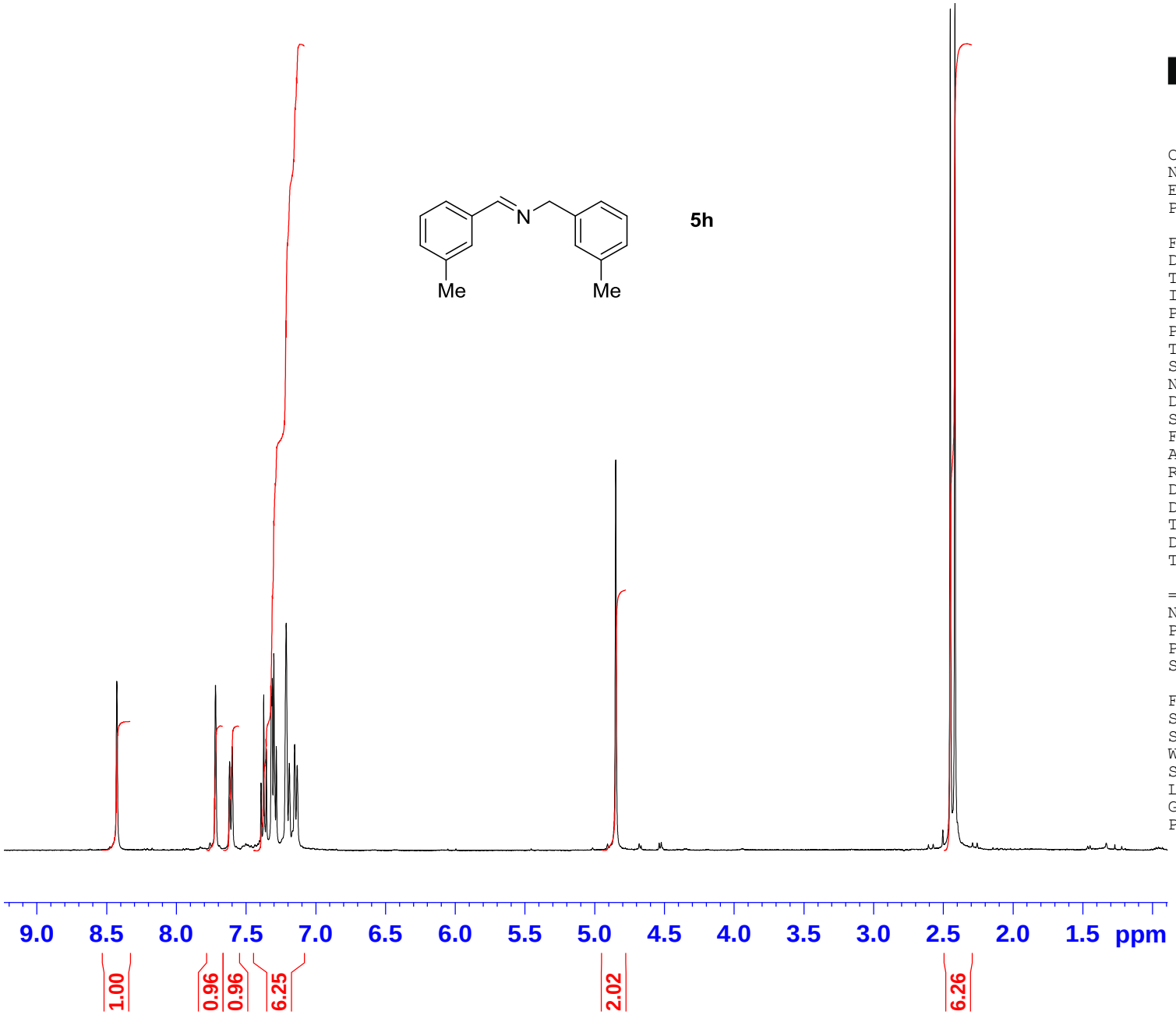


5g

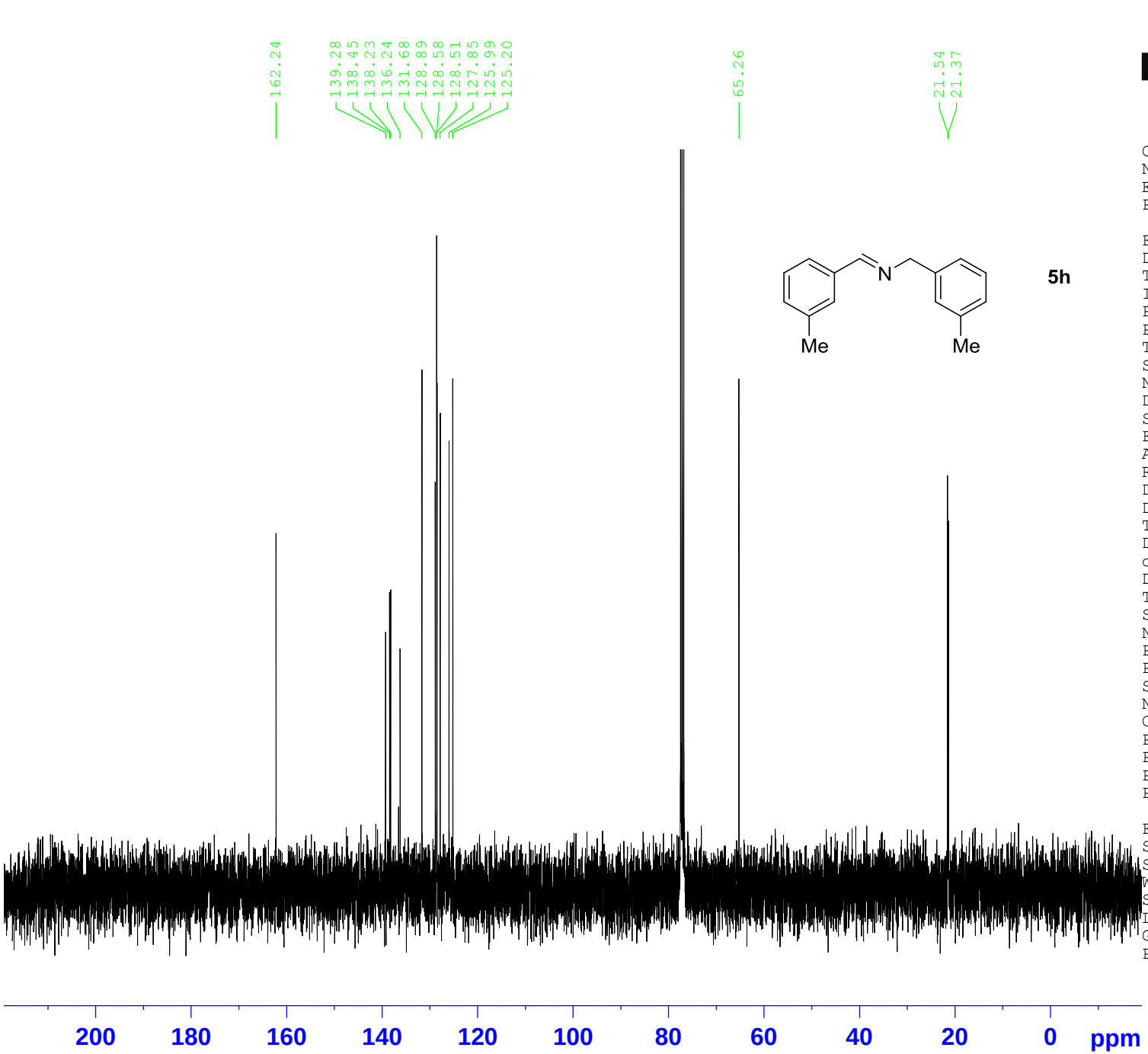





```
Current Data Parameters
NAME          May08-2013
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130508
Time              21.14
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG                16384
DW               24.600 usec
DE                6.00 usec
TE               293.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903691 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



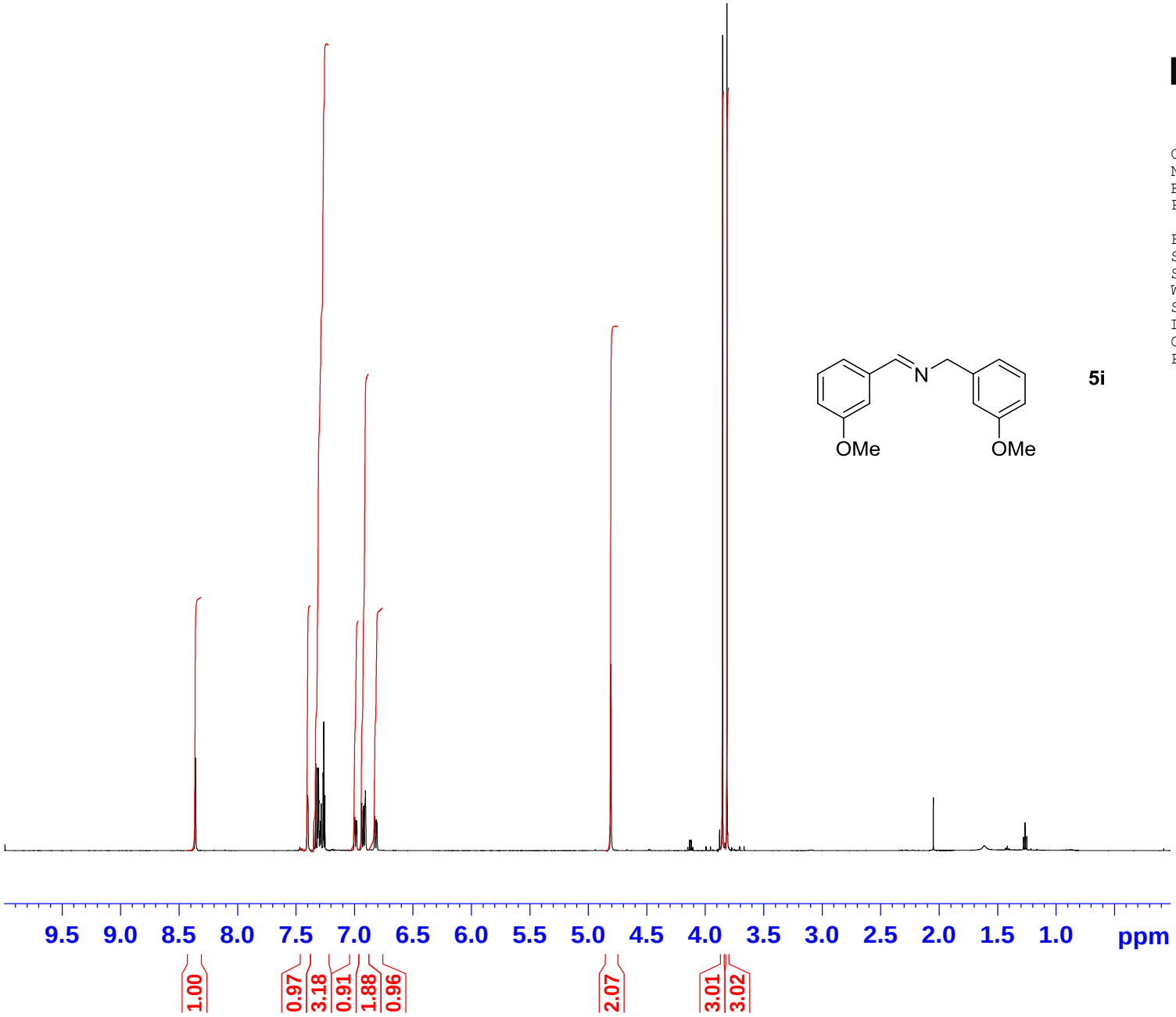

```
Current Data Parameters
NAME                  AM802
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130513
Time                 10.39
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                      128
DW                  60.400 usec
DE                   6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.50 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300000 MHz
WDW                     no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



Current Data Parameters
NAME AM802
EXPNO 2
PROCNO 1

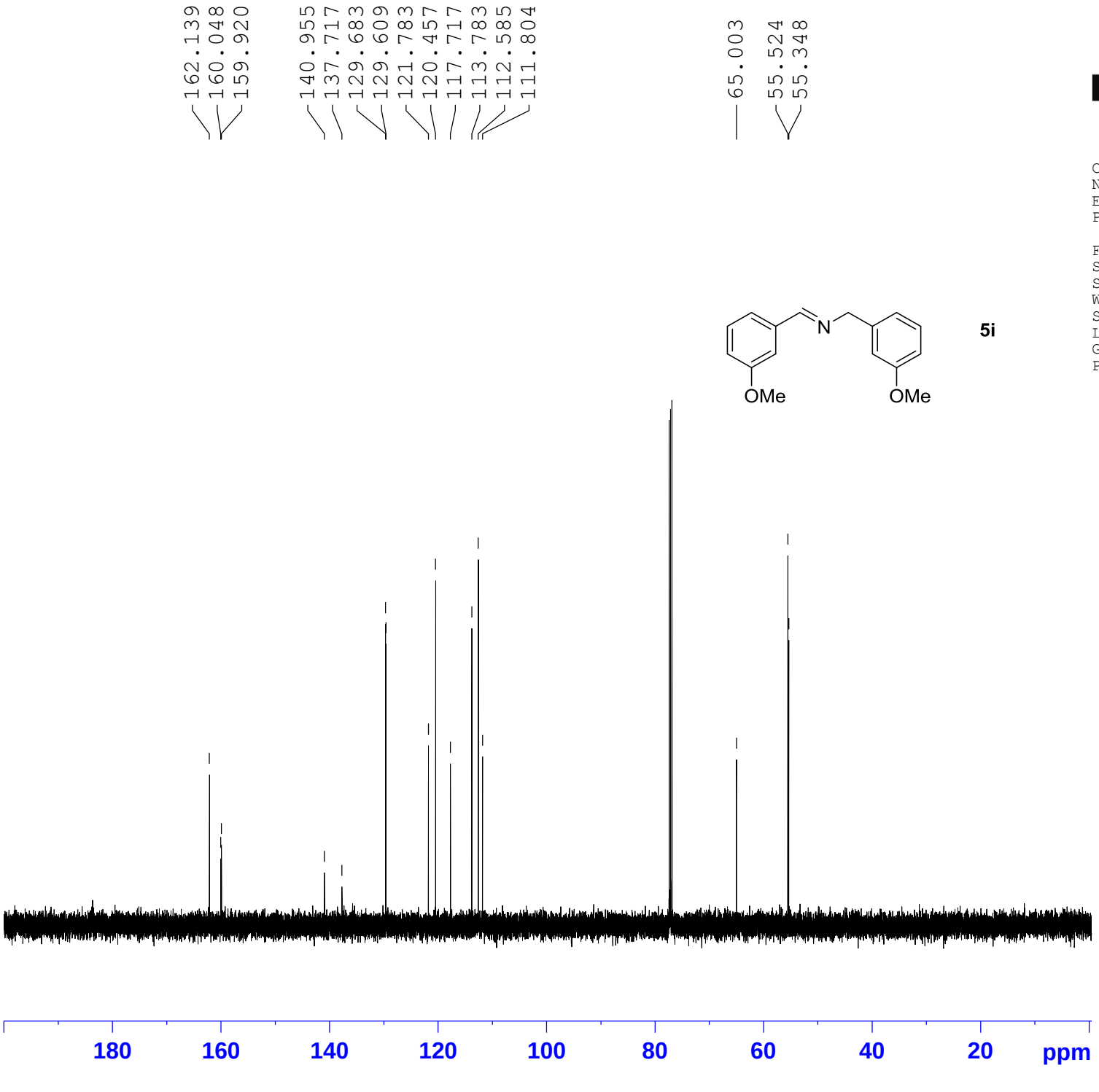
F2 - Acquisition Parameters
Date_ 20130513
Time 10.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 322
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 7298.2
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 7.30 usec
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 100.6127624 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

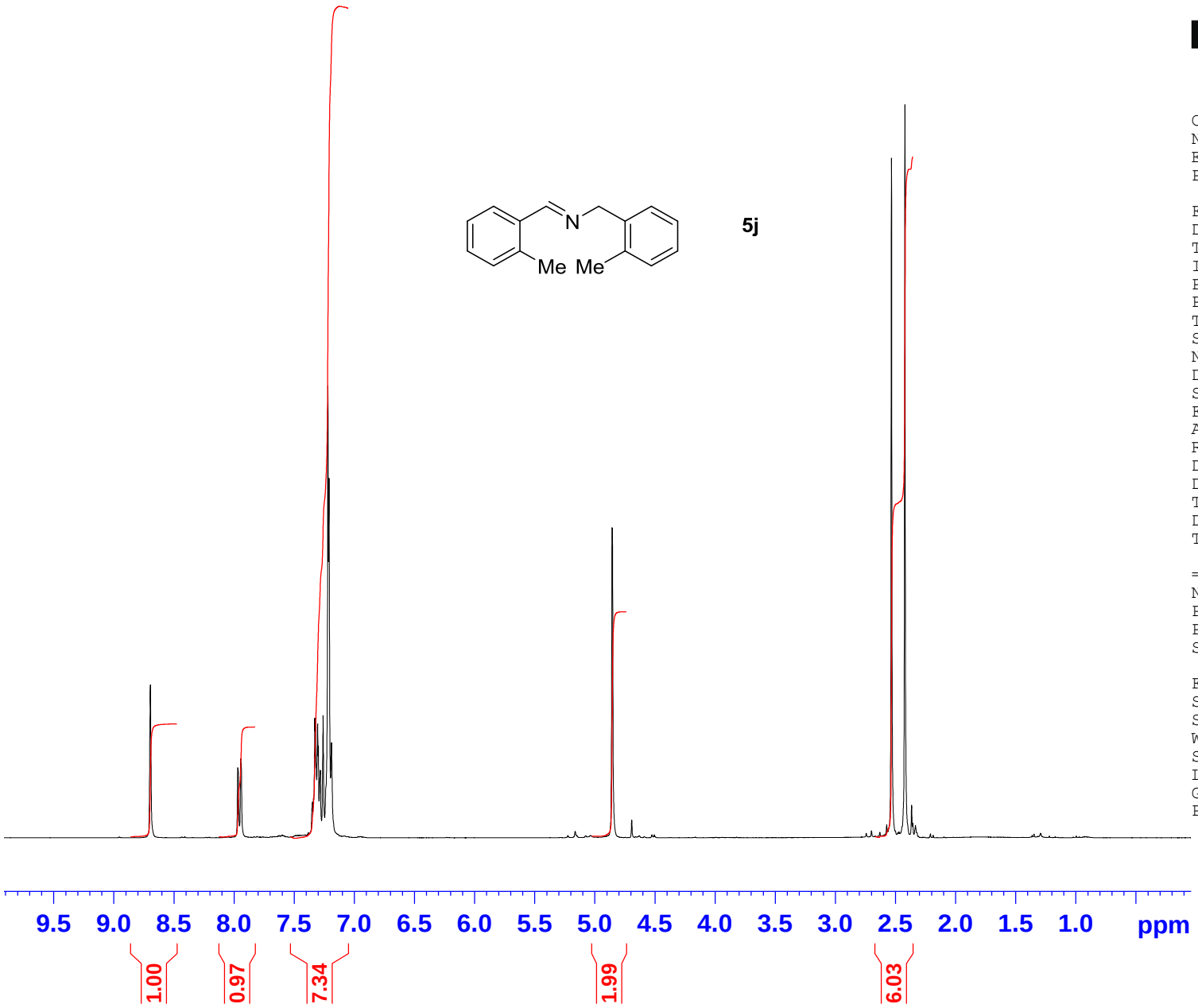


5i

```
Current Data Parameters
NAME      AM1364 PROTON_01.fid
EXPNO                       1
PROCNO                      1

F2 - Processing parameters
SI                      32768
SF           500.0586918 MHz
WDW                        no
SSB       0
LB        0 Hz
GB        0
PC                      1.00
```

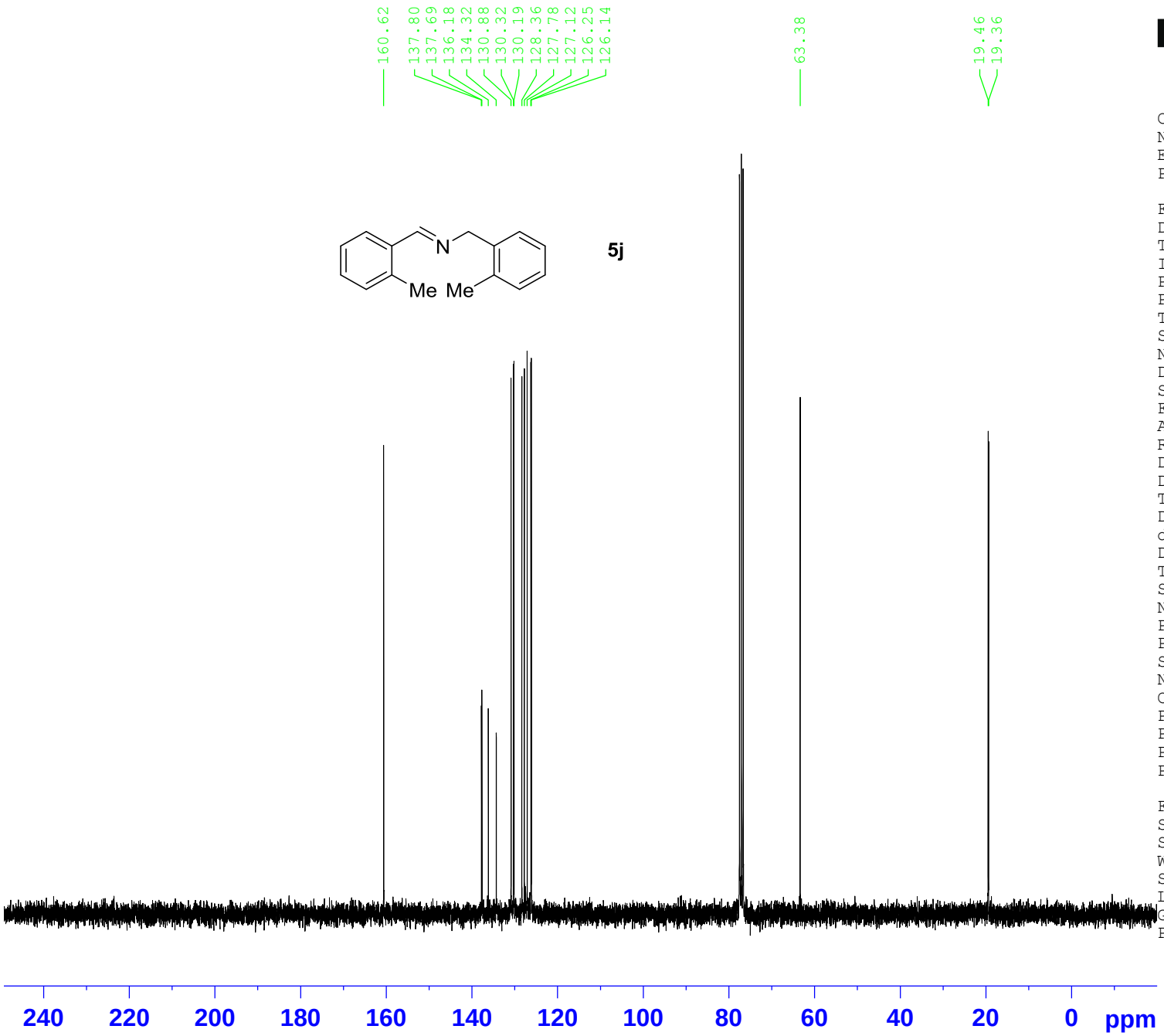

162.139
160.048
159.920
140.955
137.717
129.683
129.609
121.783
120.457
117.717
113.783
112.585
111.804
65.003
55.524
55.348
BRUKER
Current Data Parameters
NAME AM1364 CARBON_01.fid
EXPNO 1
PROCNO 1
F2 - Processing parameters
SI 65536
SF 125.7416295 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
N
OMe
OMe
5i
180
160
140
120
100
80
60
40
20
ppm

AM786




```
Current Data Parameters
NAME          Apr30-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130501
Time                6.36
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ            2.6542079 sec
RG                  181
DW               81.000 usec
DE                6.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200023 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

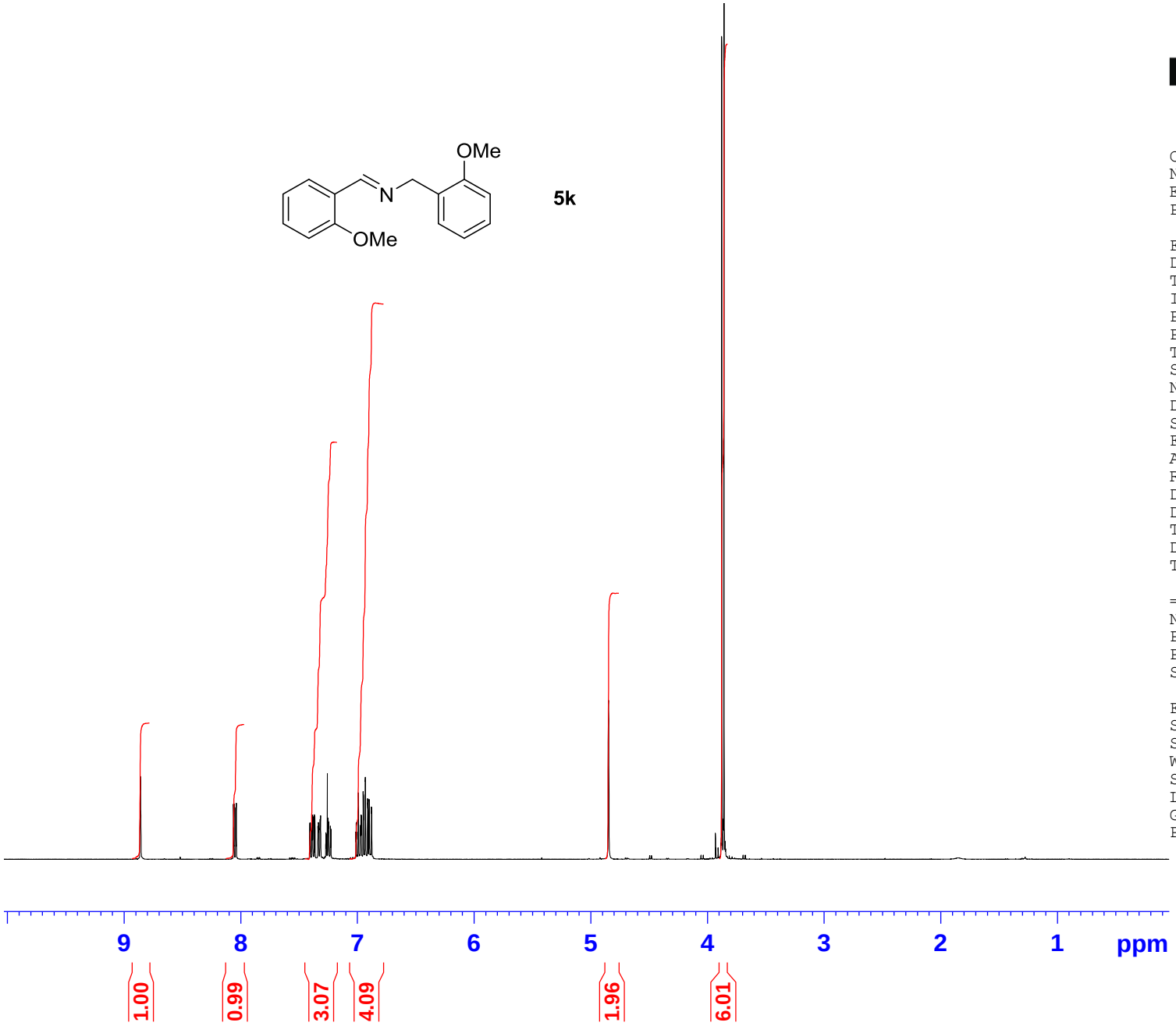
AM786



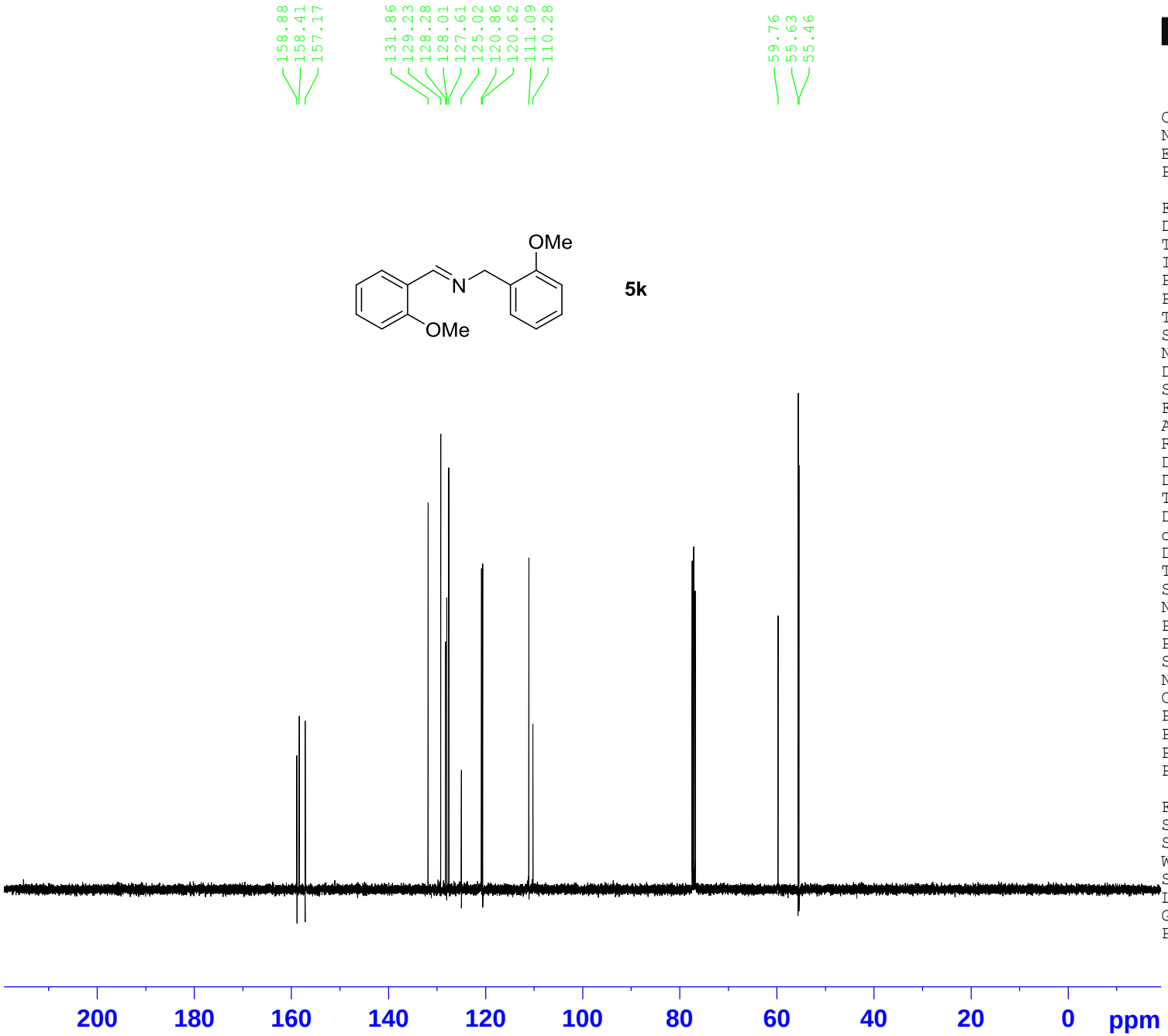
Current Data Parameters
NAME Apr30-2013
EXPNO 13
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130501
Time 6.54
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 16384
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903749 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



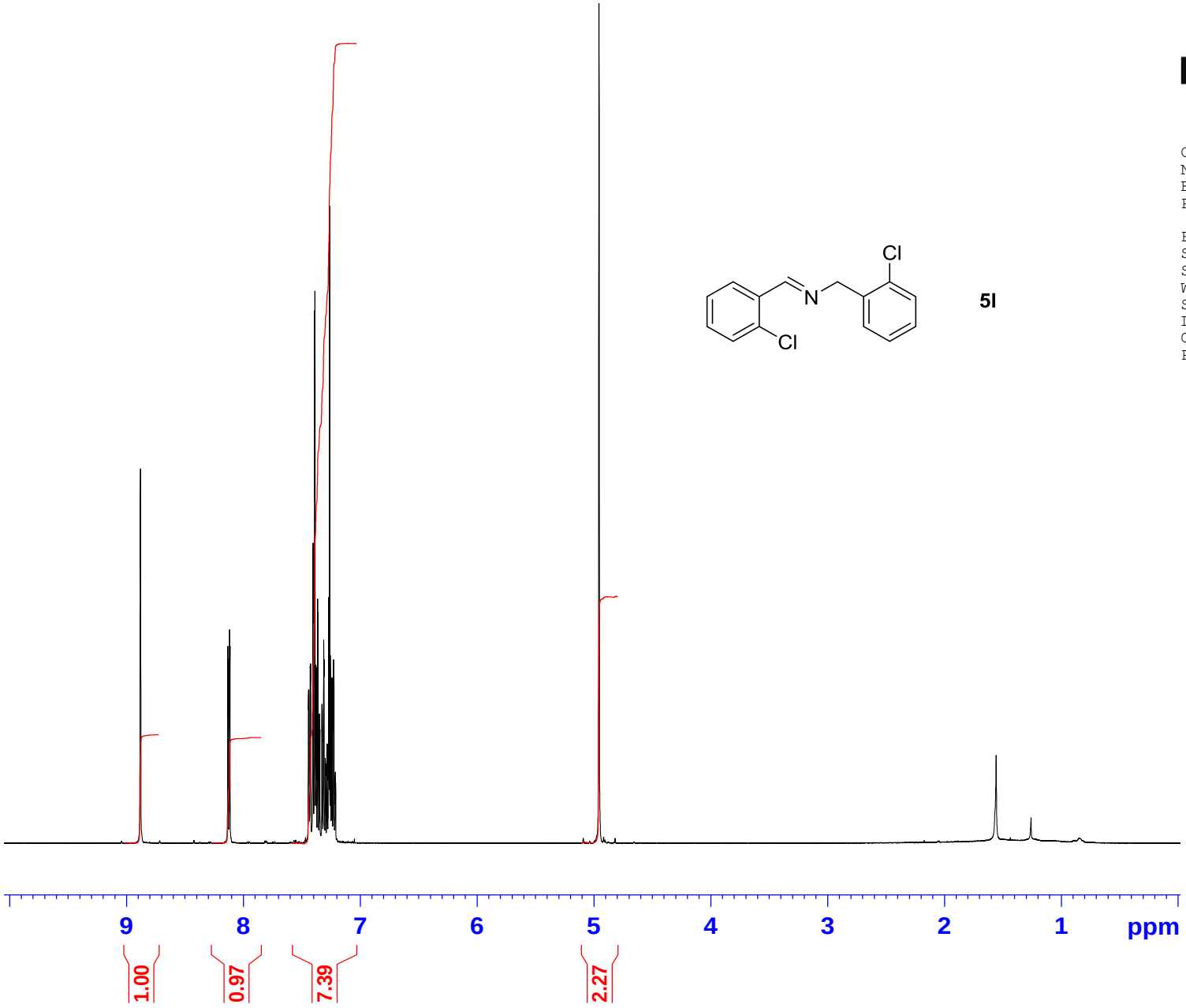

```
Current Data Parameters
NAME                  AM789
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130501
Time                  17.03
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                      128
DW                   60.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.50 usec
PL1        0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300211 MHz
WDW                      no
SSB        0
LB         0 Hz
GB         0
PC                     1.00
```



Current Data Parameters
NAME AM789
EXPNO 2
PROCNO 1

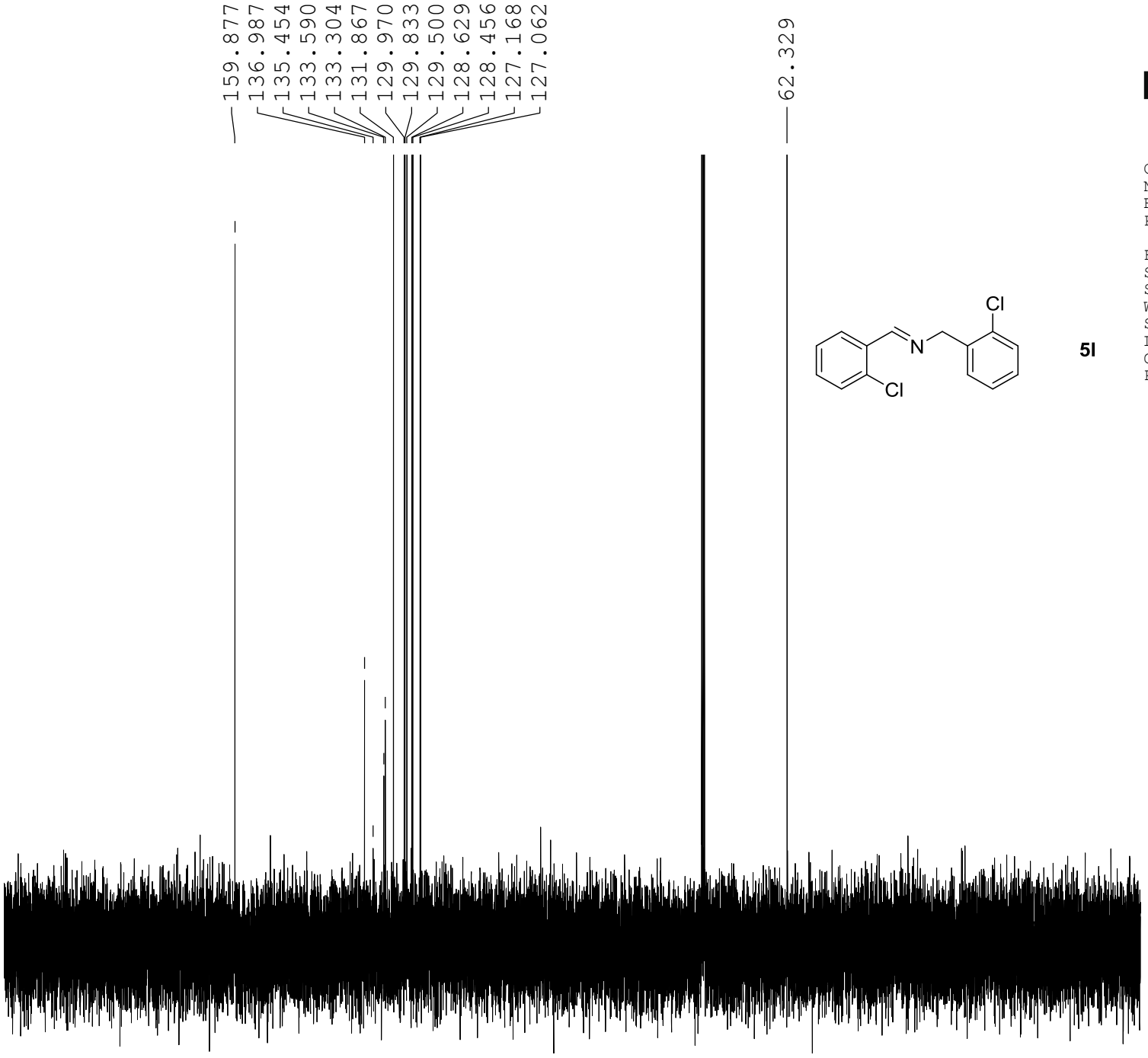
F2 - Acquisition Parameters
Date_ 20130501
Time 17.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664256 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 7.30 usec
PLW1 -1.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 32768
SF 100.6127636 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40



5l

```
Current Data Parameters
NAME      AM1367 PROTON_01.fid
EXPNO                      1
PROCNO                     1

F2 - Processing parameters
SI                     32768
SF           500.0586918 MHz
WDW                       no
SSB       0
LB        0 Hz
GB        0
PC                     1.00
```

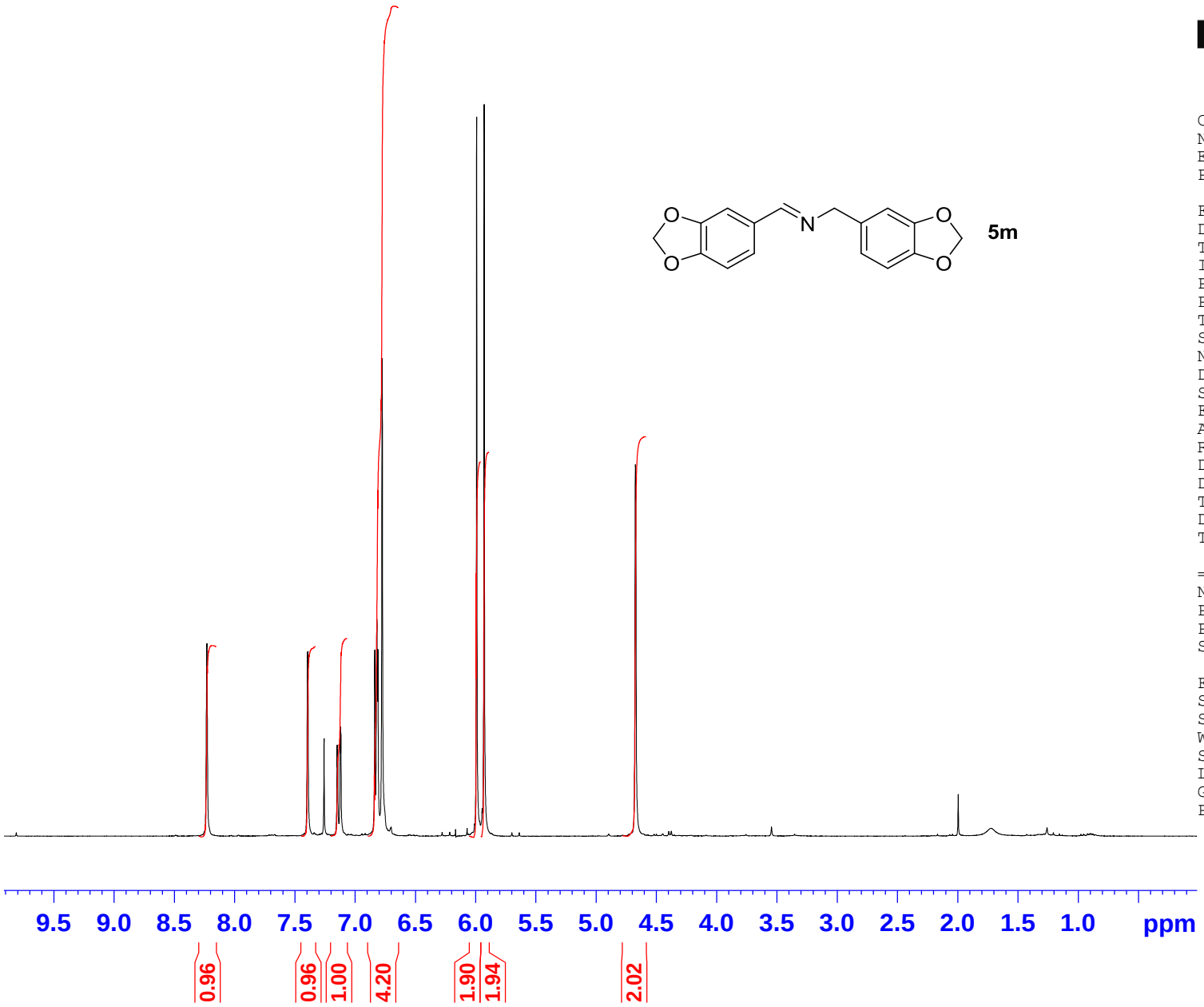


5l

Current Data Parameters
NAME AM1367 CARBON_01.fid
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 125.7416263 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

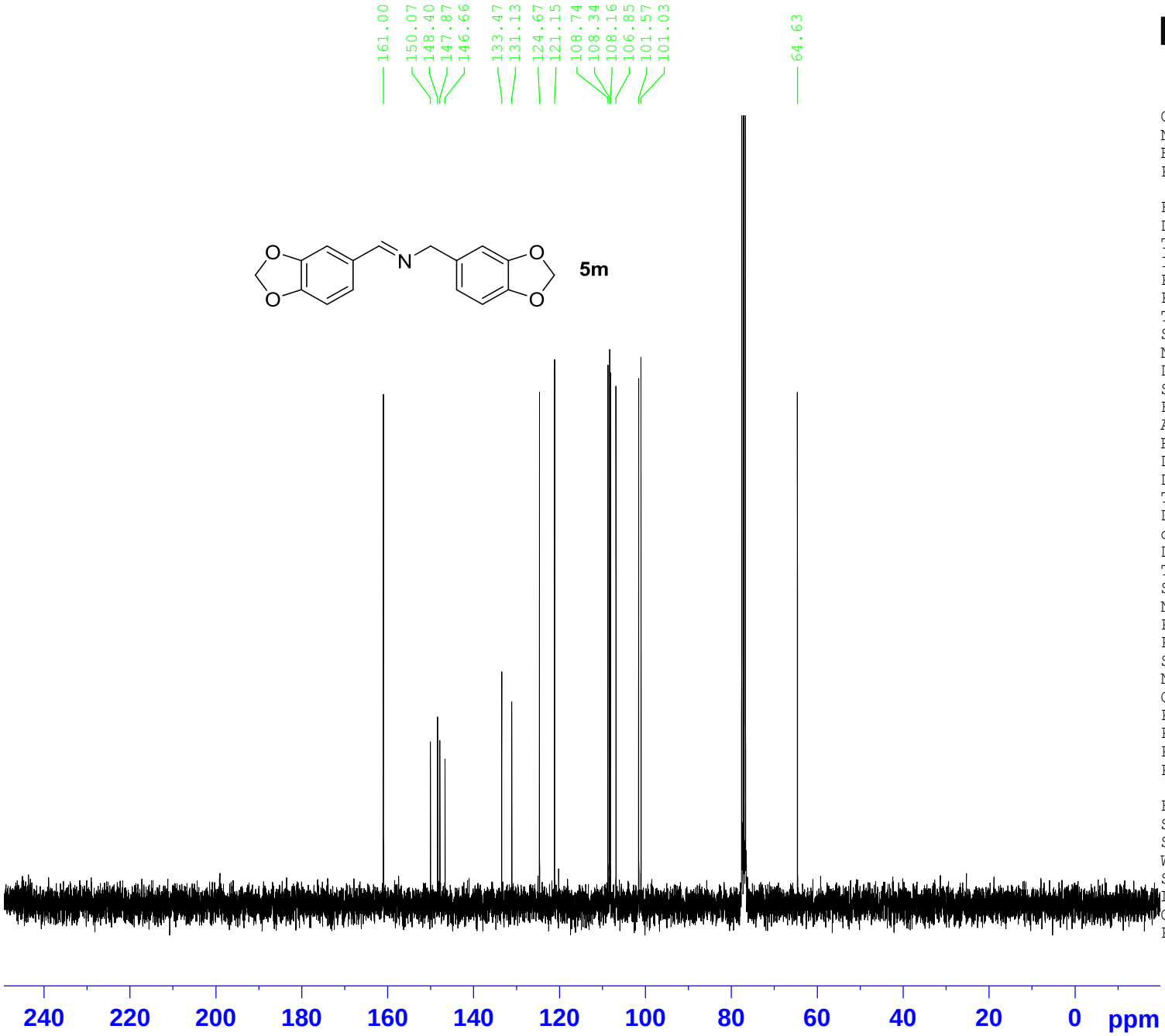
AM800



5m

```
Current Data Parameters
NAME          May09-2013
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130509
Time               22.46
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542079 sec
RG                322.5
DW               81.000 usec
DE                6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200023 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM800

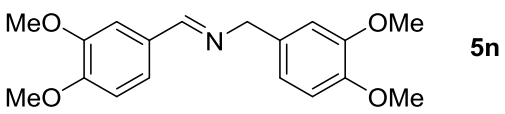


Current Data Parameters
NAME May09-2013
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130509
Time 23.03
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903691 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

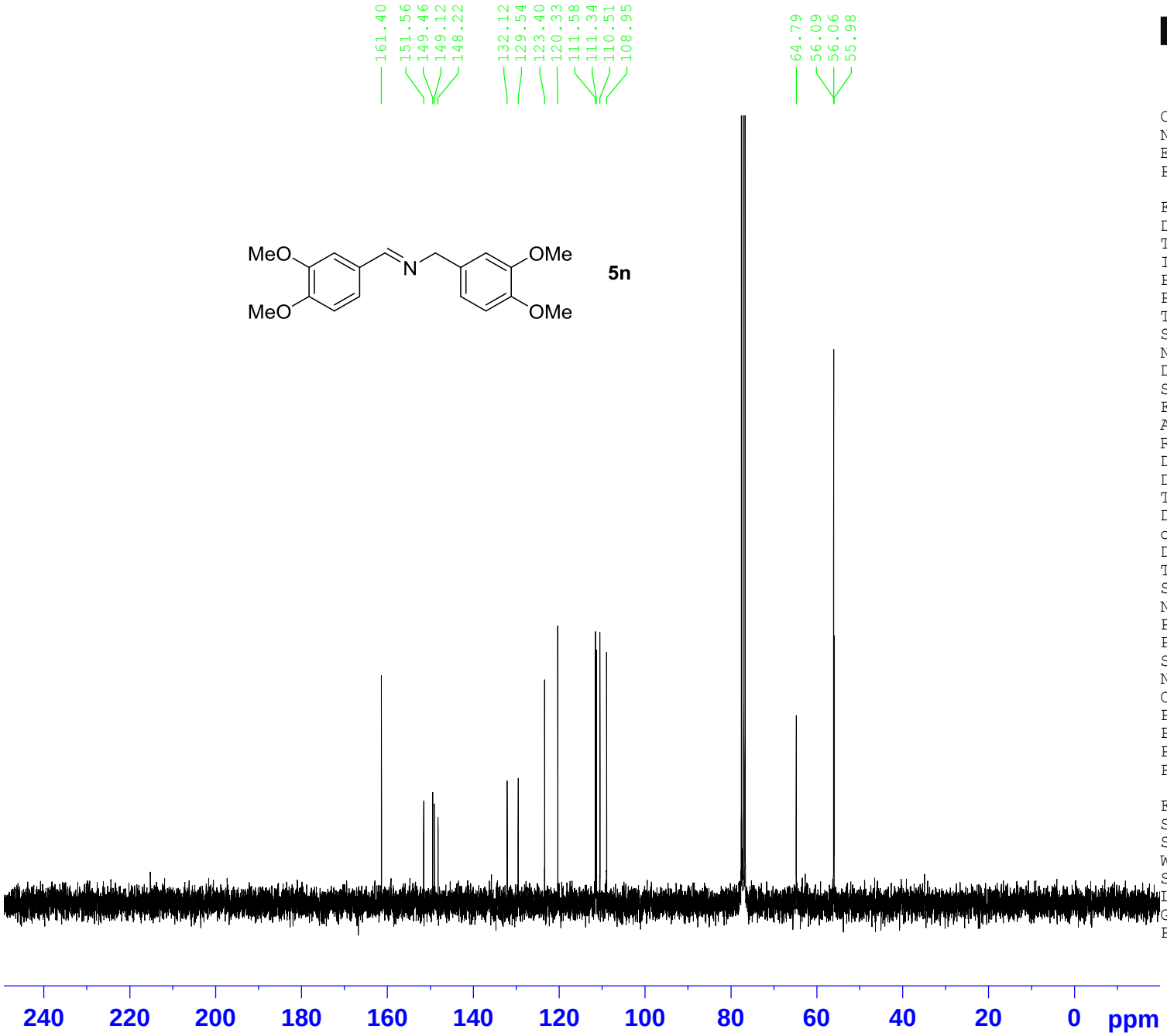
AM803



5n


```
Current Data Parameters
NAME          May13-2013
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130513
Time              18.03
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542079 sec
RG                322.5
DW               81.000 usec
DE                6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200177 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

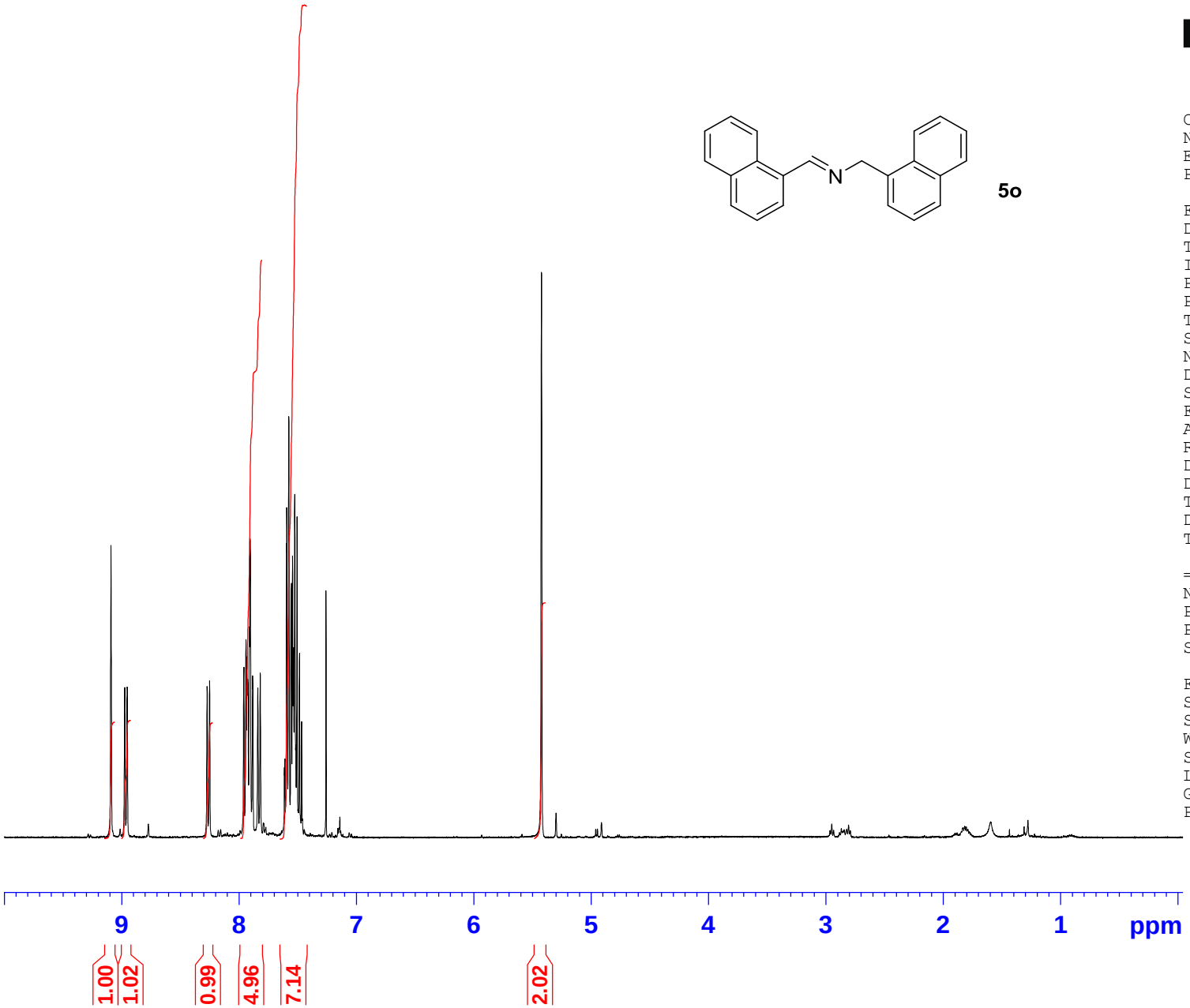
AM803



Current Data Parameters
NAME May13-2013
EXPNO 11
PROCNO 1

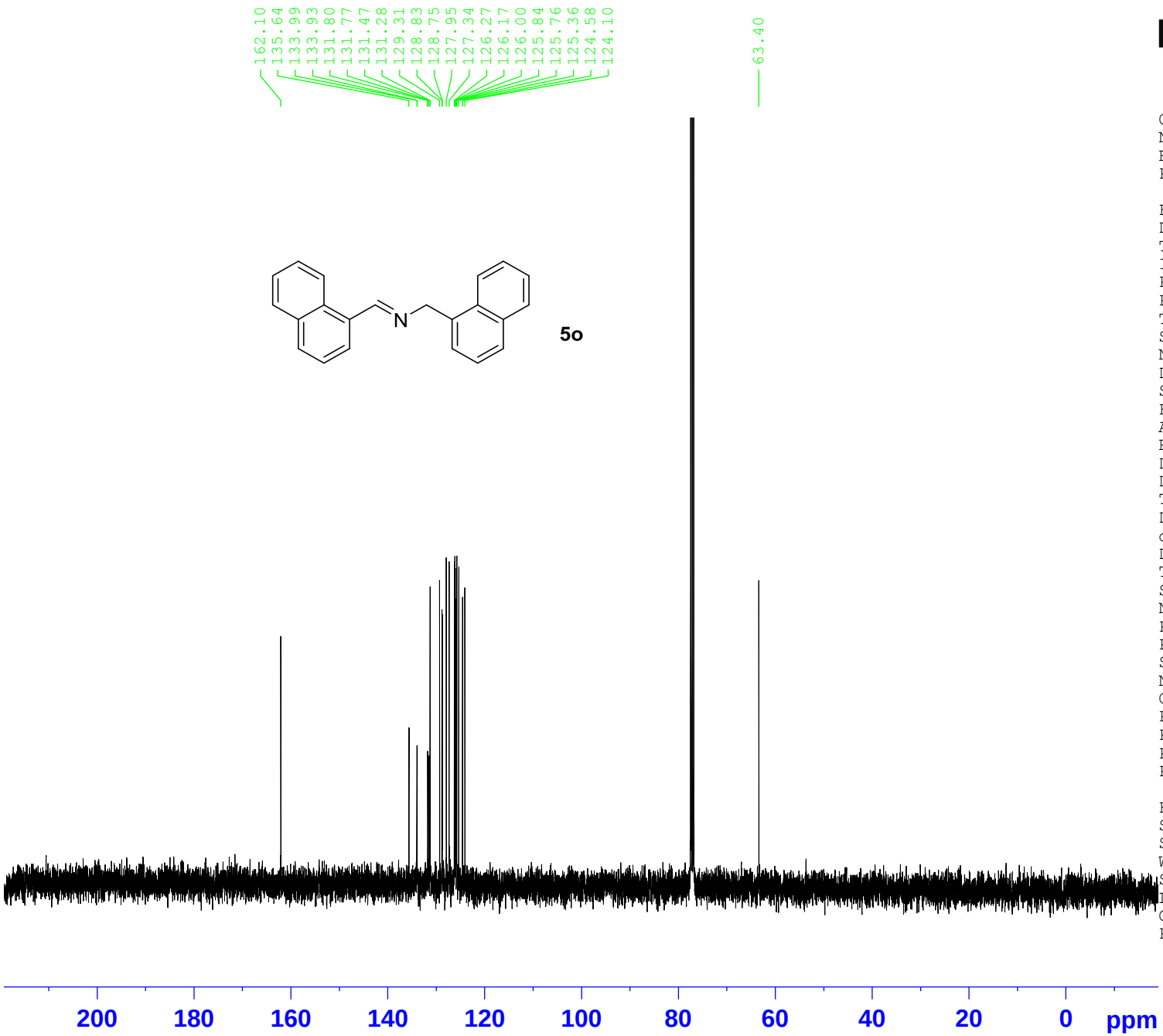
F2 - Acquisition Parameters
Date_ 20130513
Time 18.21
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 14596.5
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903724 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



5o

```
Current Data Parameters
NAME                  AM794
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130506
Time                  15.18
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9583745 sec
RG                      256
DW                   60.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.50 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300210 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



Current Data Parameters

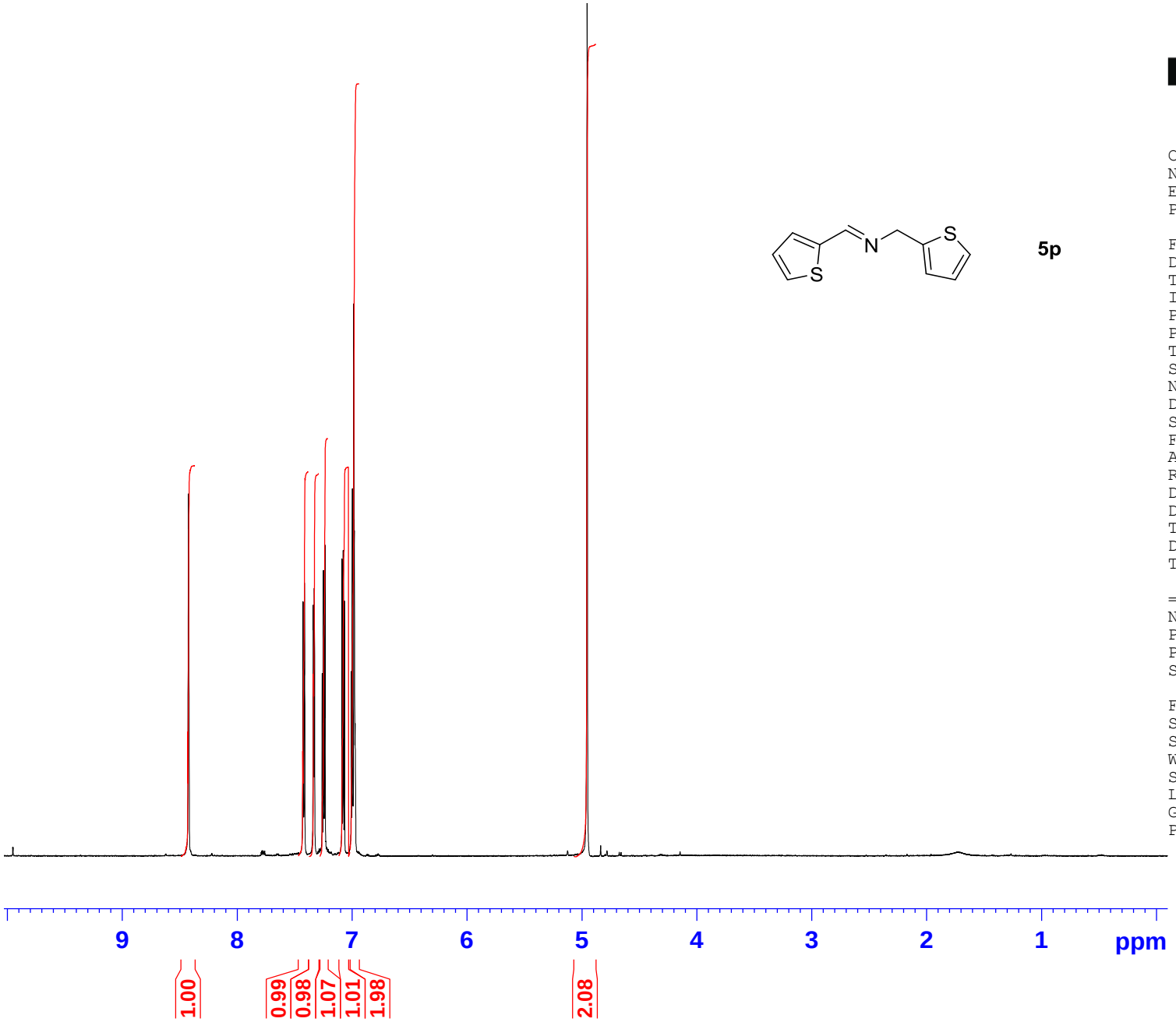
NAME	AM794
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20130506
Time	15.33
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	218
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664256 sec
RG	4597.6
DW	20.850 usec
DE	6.00 usec
TE	298.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
SFO1	100.6228298 MHz
NUC1	13C
P1	7.30 usec
PLW1	-1.00000000 W
SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	-1.00000000 W
PLW12	-1.00000000 W
PLW13	-1.00000000 W

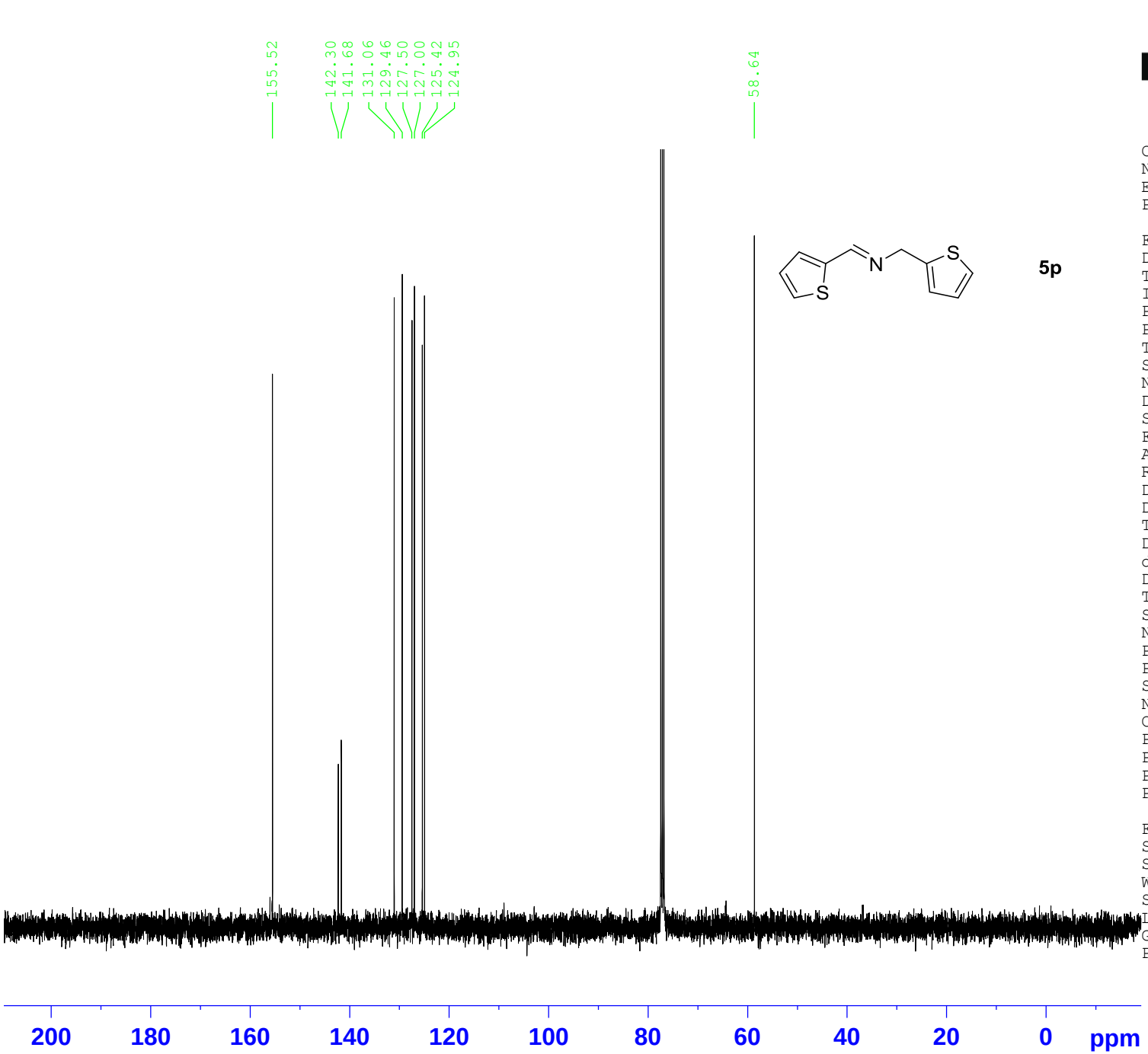
F2 - Processing parameters

SI	32768
SF	100.6127601 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



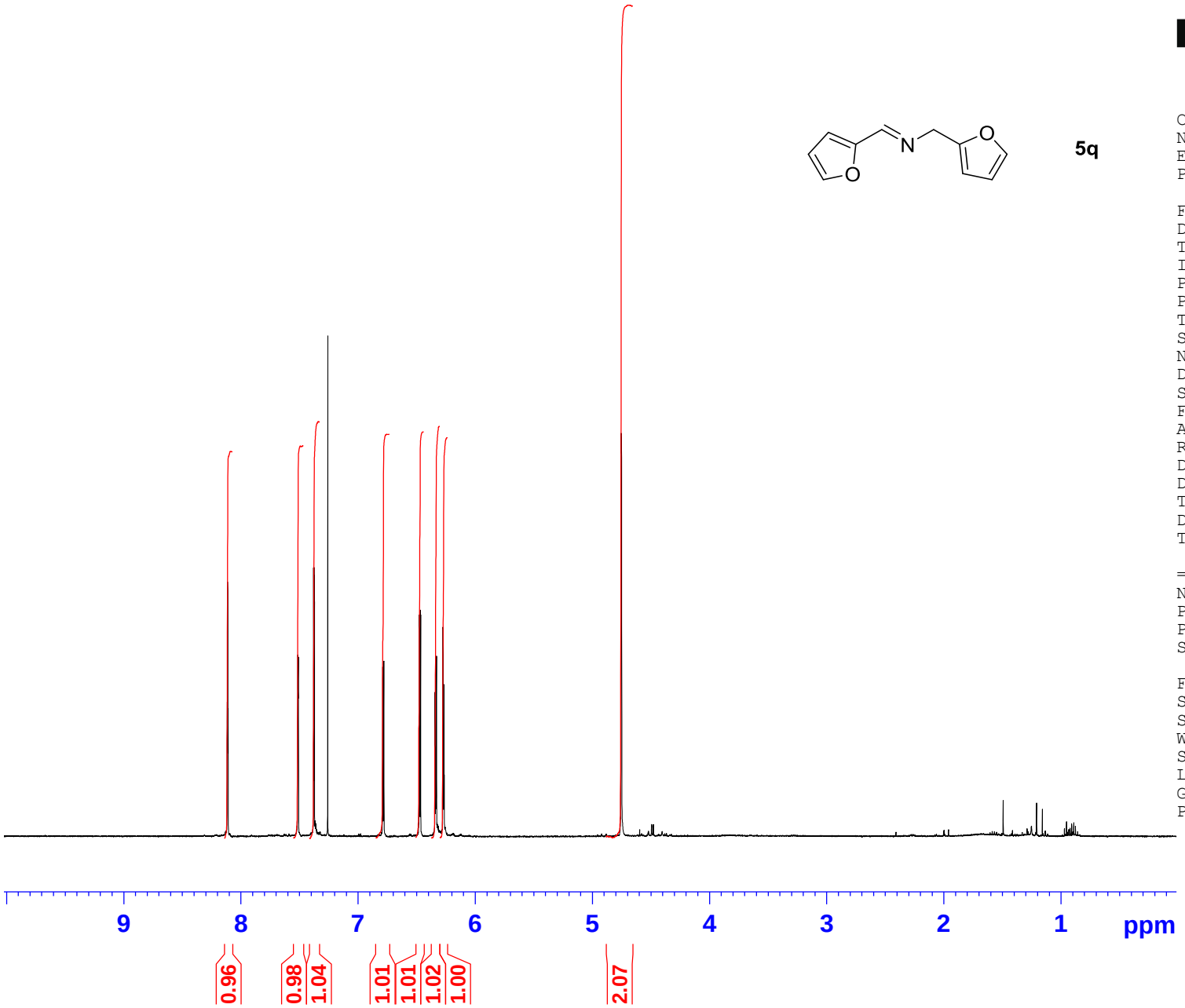
5p

```
Current Data Parameters
NAME                  AM787
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130501
Time                   9.31
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9583745 sec
RG                      256
DW                   60.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.50 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300211 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



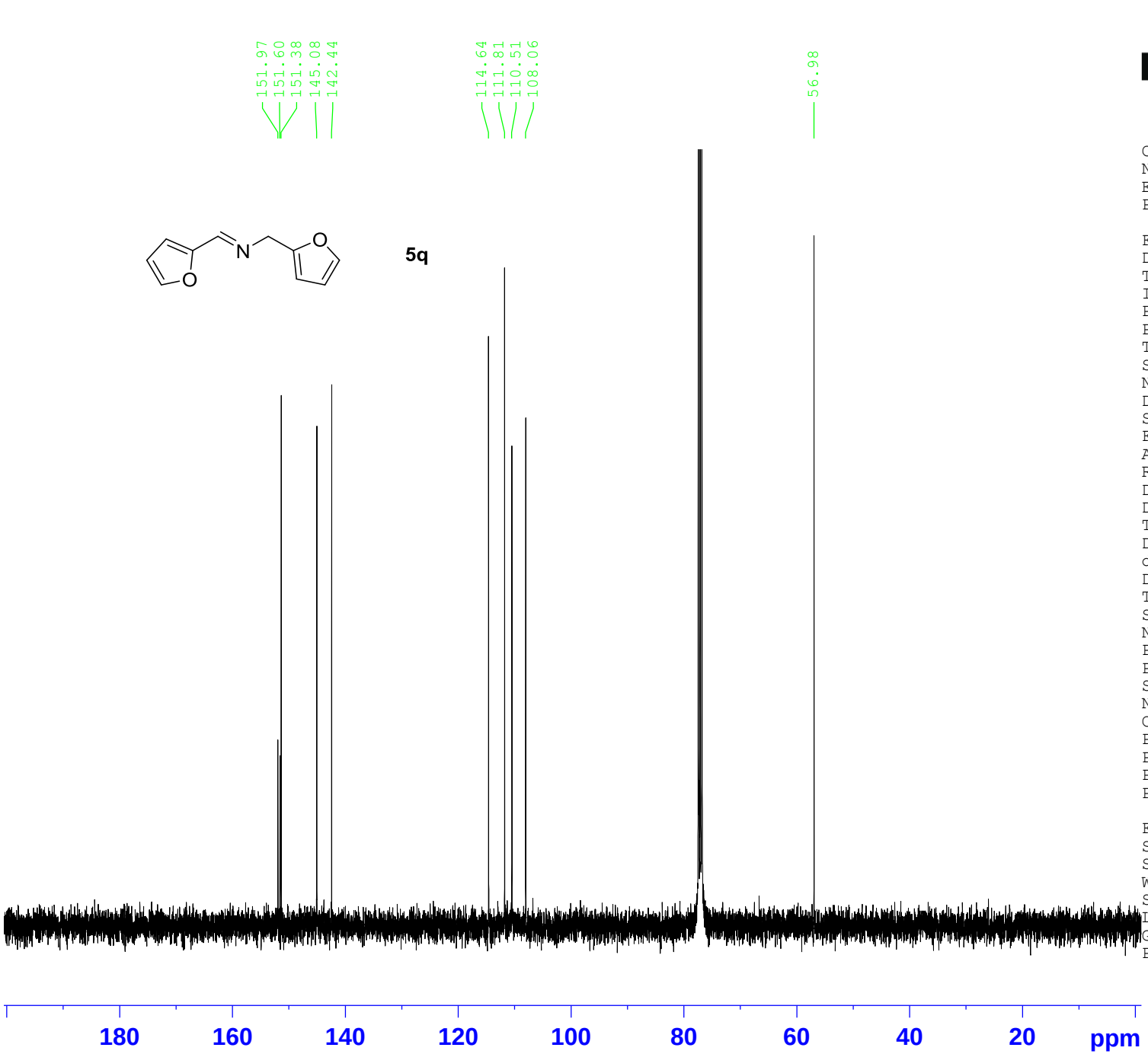
BRUKER

```
Current Data Parameters
NAME                  AM787
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130501
Time                   9.46
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      227
DS                        4
SWH              23980.814 Hz
FIDRES           0.365918 Hz
AQ               1.3664256 sec
RG                    16384
DW                  20.850 usec
DE                   6.00 usec
TE                  298.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1
SFO1           100.6228298 MHz
NUC1                    13C
P1                   7.30 usec
PLW1            -1.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W
PLW13           -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             100.6127627 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

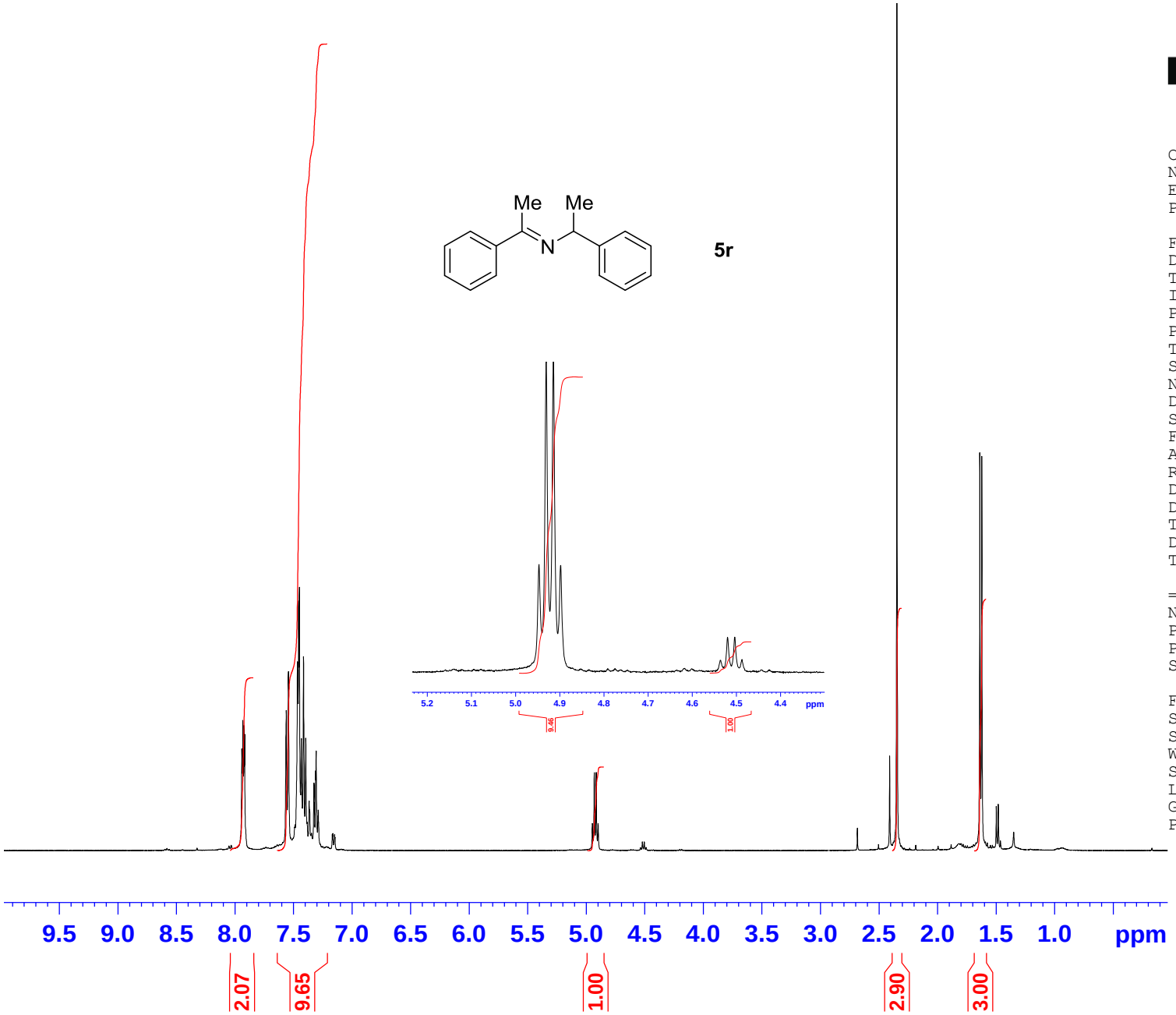


5q

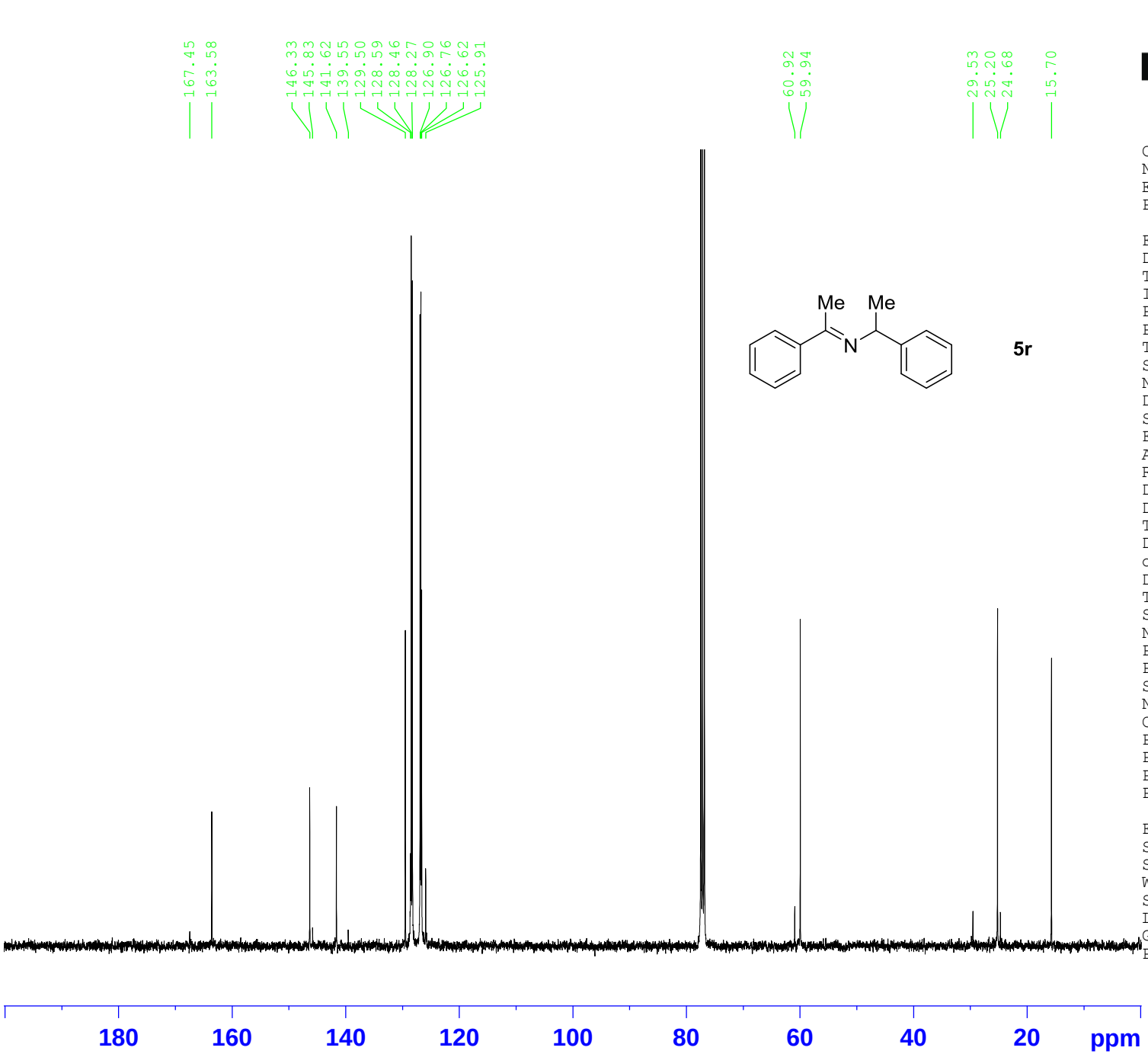
```
Current Data Parameters
NAME                  AM788
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130501
Time                 17.51
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9583745 sec
RG                     512
DW                60.400 usec
DE                 6.00 usec
TE                 298.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.50 usec
PL1        0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300212 MHz
WDW                    no
SSB        0
LB         0 Hz
GB         0
PC                   1.00
```




```
Current Data Parameters
NAME                  AM788
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130501
Time                  18.52
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1024
DS                        4
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ                1.3664256 sec
RG                    16384
DW                   20.850 usec
DE                    6.00 usec
TE                   298.0 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1
SFO1           100.6228298 MHz
NUC1                    13C
P1                    7.30 usec
PLW1            -1.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W
PLW13           -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             100.6127586 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```




```
Current Data Parameters
NAME                  AM1387
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150211
Time                  10.19
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                       64
DW                   60.400 usec
DE                    6.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   10.75 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            400.1300000 MHz
WDW                      no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```



Current Data Parameters

NAME	AM1387
EXPNO	2
PROCNO	1

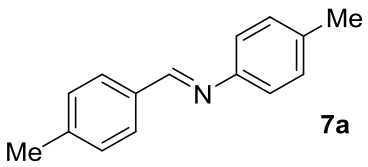
F2 - Acquisition Parameters

Date_	20150211
Time	10.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664256 sec
RG	14596.5
DW	20.850 usec
DE	6.00 usec
TE	298.0 K
D1	5.00000000 sec
d11	0.03000000 sec
DELTA	4.90000010 sec
TD0	1
SFO1	100.6228298 MHz
NUC1	13C
P1	7.30 usec
PLW1	-1.00000000 W
SFO2	400.1316005 MHz
NUC2	1H
CPDPRG[2	waltz16
PCPD2	80.00 usec
PLW2	-1.00000000 W
PLW12	-1.00000000 W
PLW13	-1.00000000 W

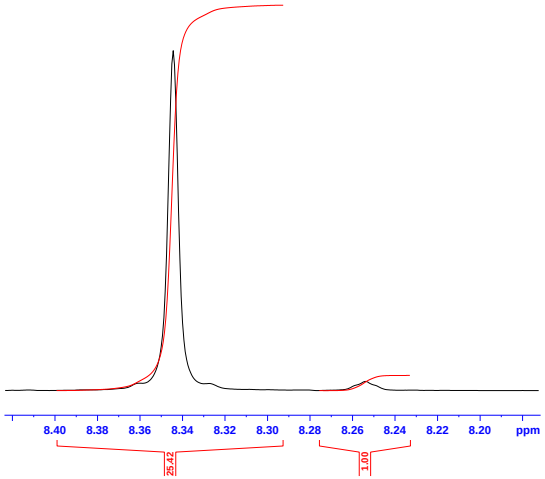
F2 - Processing parameters

SI	32768
SF	100.6127667 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

AM1062

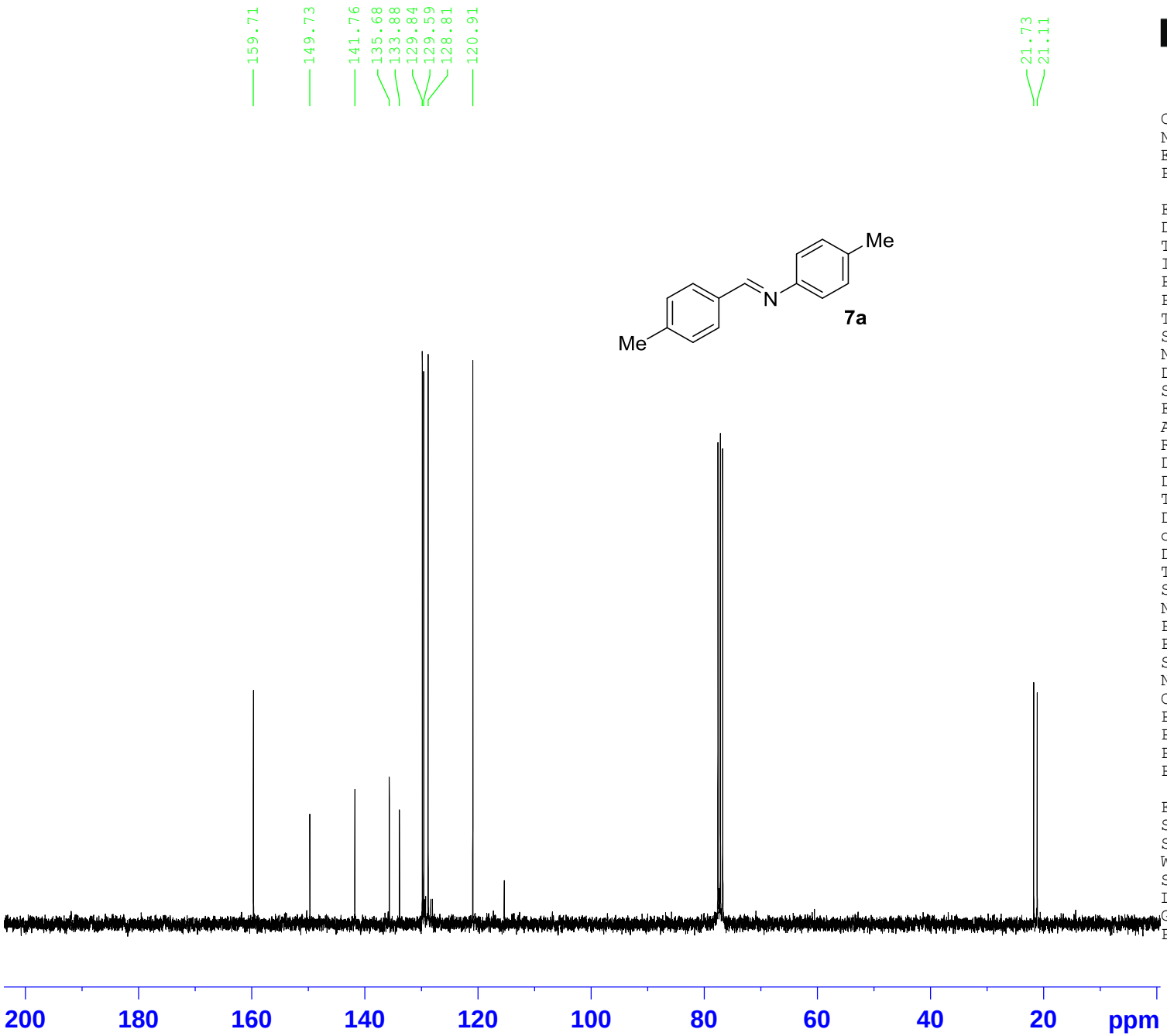


7a



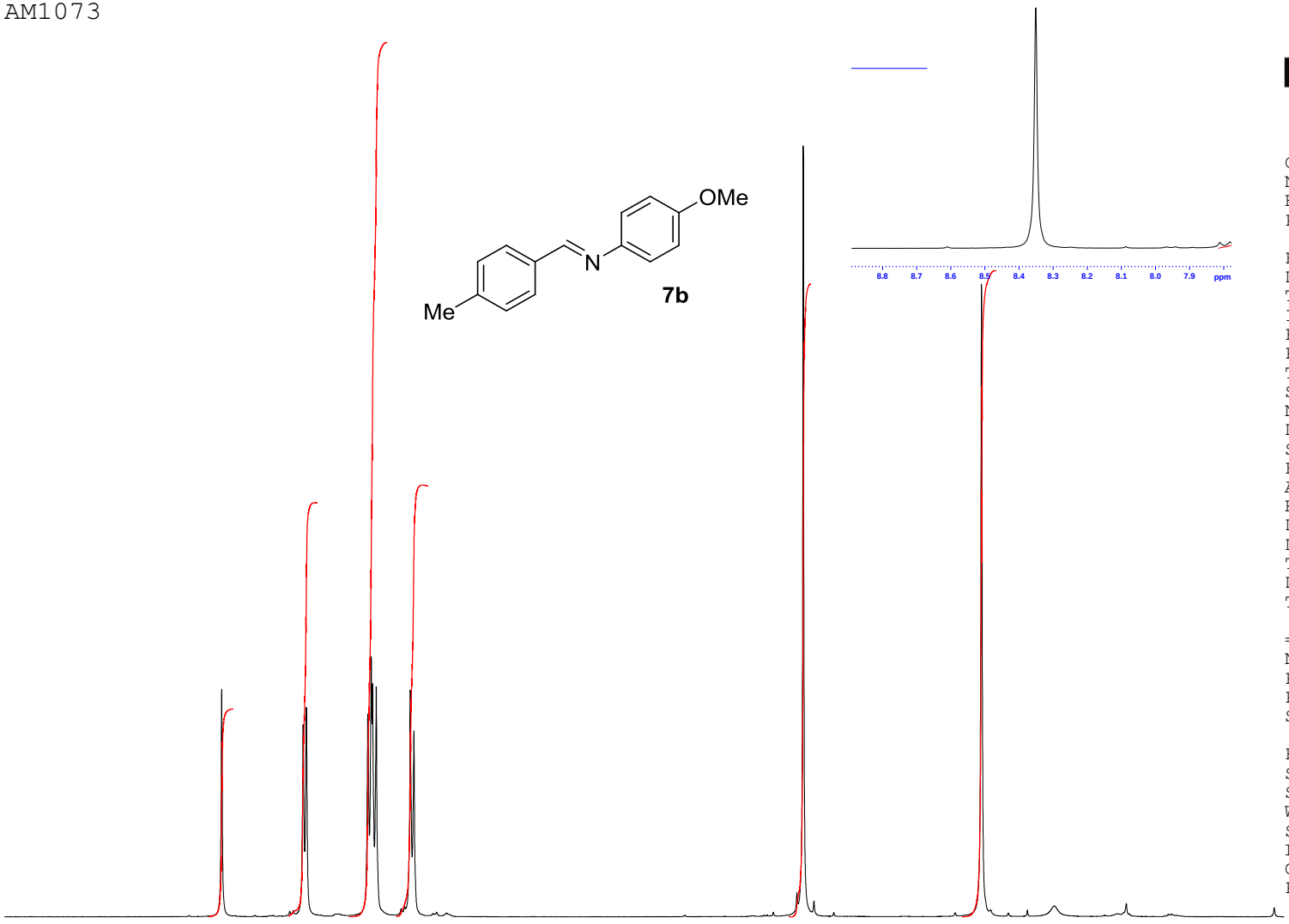

```
Current Data Parameters
NAME          Jan16-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140116
Time                21.20
INSTRUM             av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                293.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.40 usec
PL1                -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF          300.2200310 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1062



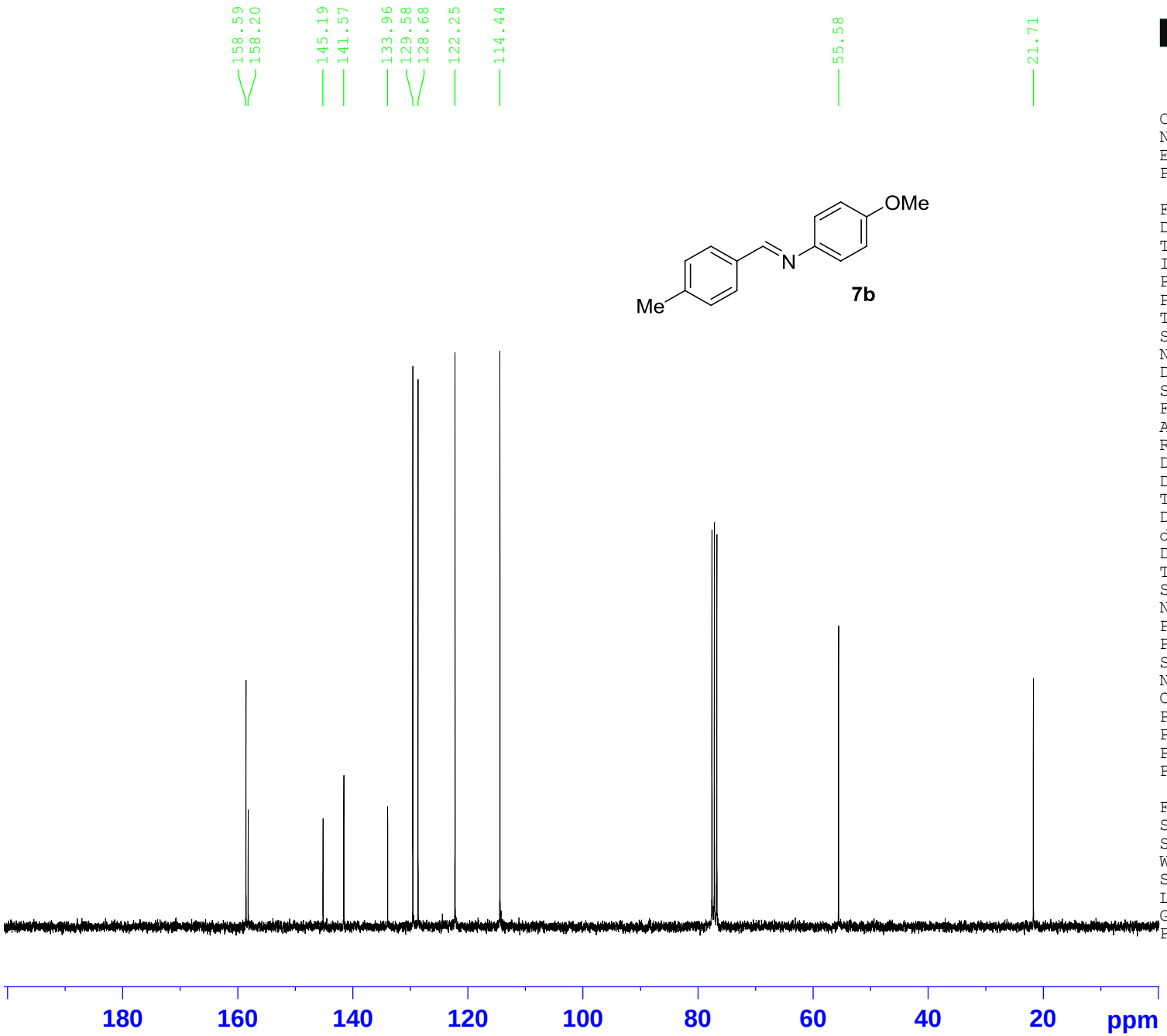

```
Current Data Parameters
NAME          Jan16-2014
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140116
Time              21.37
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG              18390.4
DW               24.600 usec
DE                6.00 usec
TE               294.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903722 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

AM1073




```
Current Data Parameters
NAME          Jan24-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140124
Time              16.09
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            6172.839 Hz
FIDRES         0.188380 Hz
AQ             2.6542079 sec
RG                  181
DW               81.000 usec
DE                6.00 usec
TE                293.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                32768
SF          300.2200309 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

AM1073

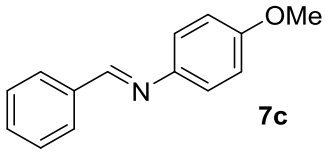


Current Data Parameters
NAME Jan24-2014
EXPNO 11
PROCNO 1

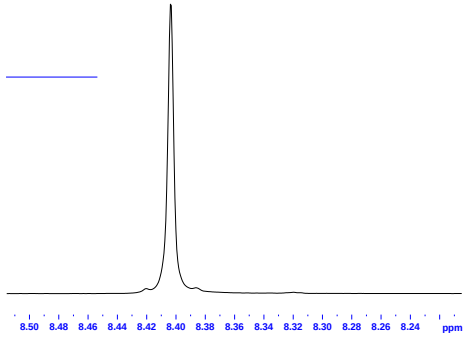
F2 - Acquisition Parameters
Date_ 20140124
Time 16.26
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 294.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903726 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

AM1265

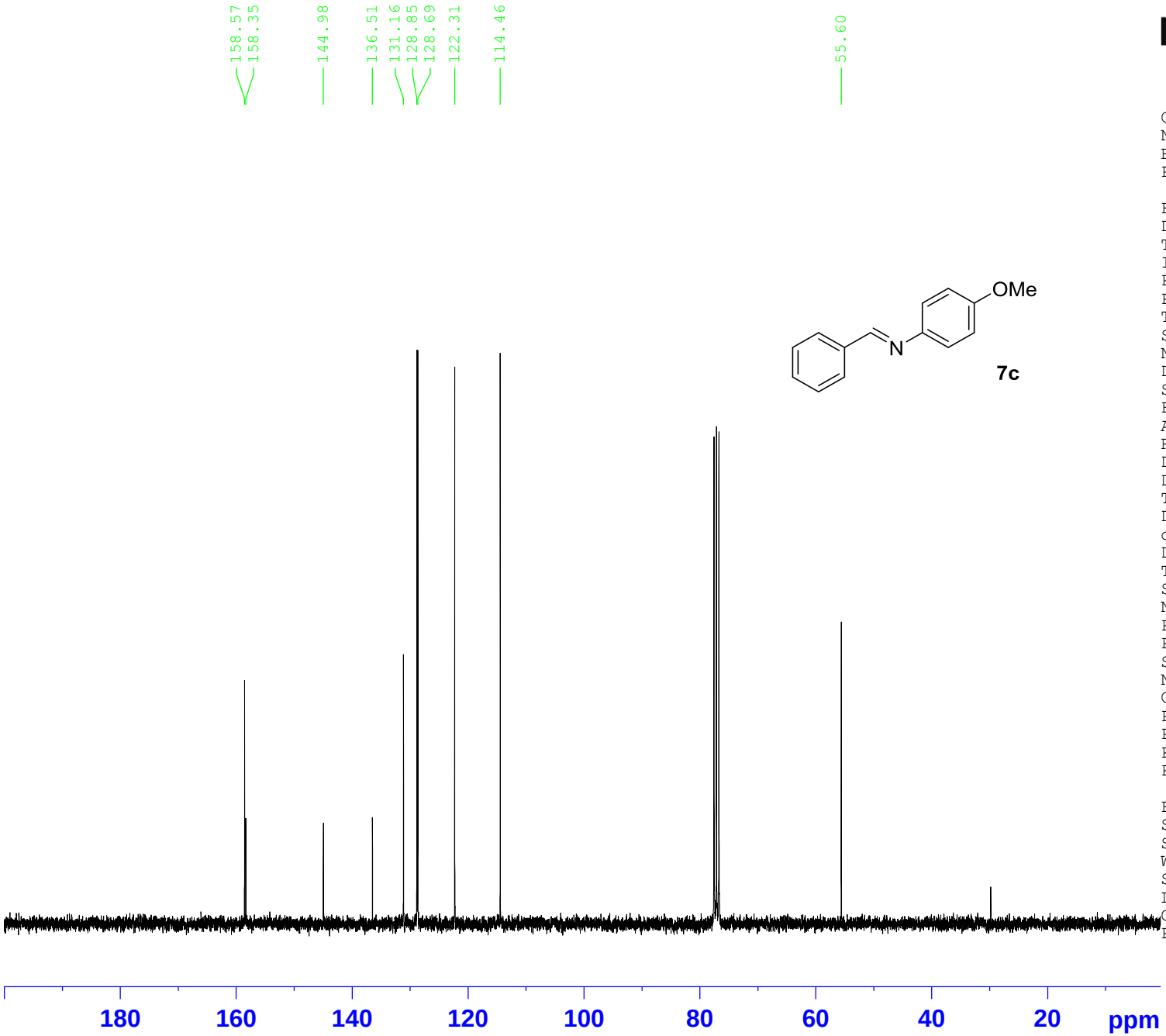


7c




```
Current Data Parameters
NAME          Sep16-2014
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140916
Time               16.06
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                291.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.40 usec
PL1                -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200277 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1265

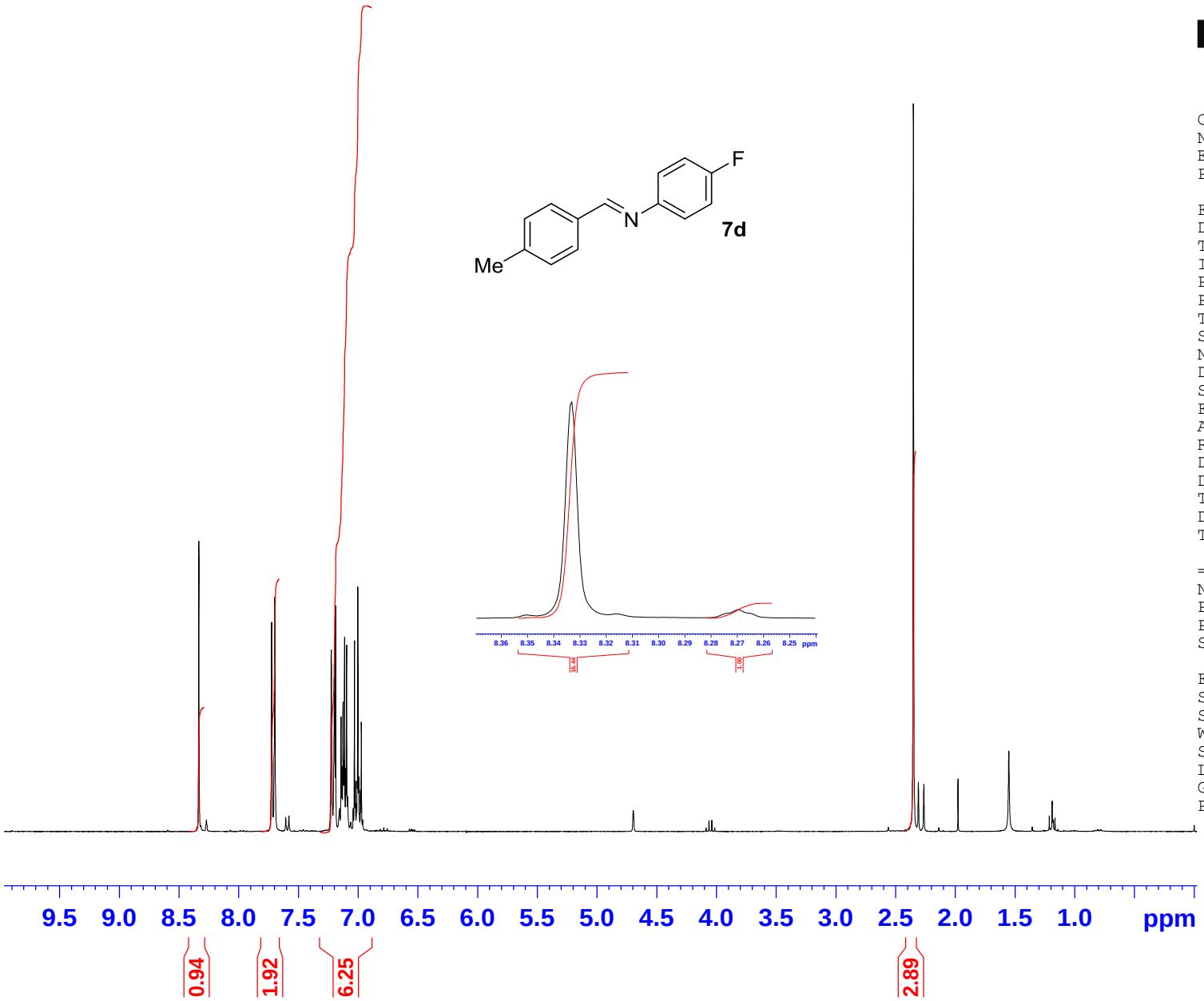


Current Data Parameters
NAME Sep16-2014
EXPNO 21
PROCNO 1

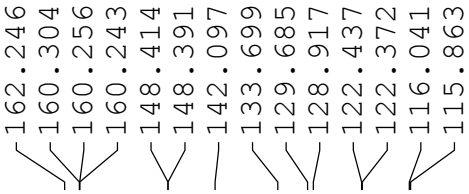
F2 - Acquisition Parameters
Date_ 20140916
Time 16.23
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 291.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

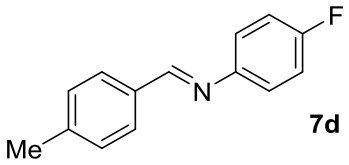
F2 - Processing parameters
SI 65536
SF 75.4903722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

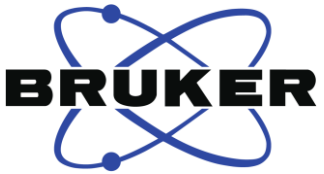
AM1292



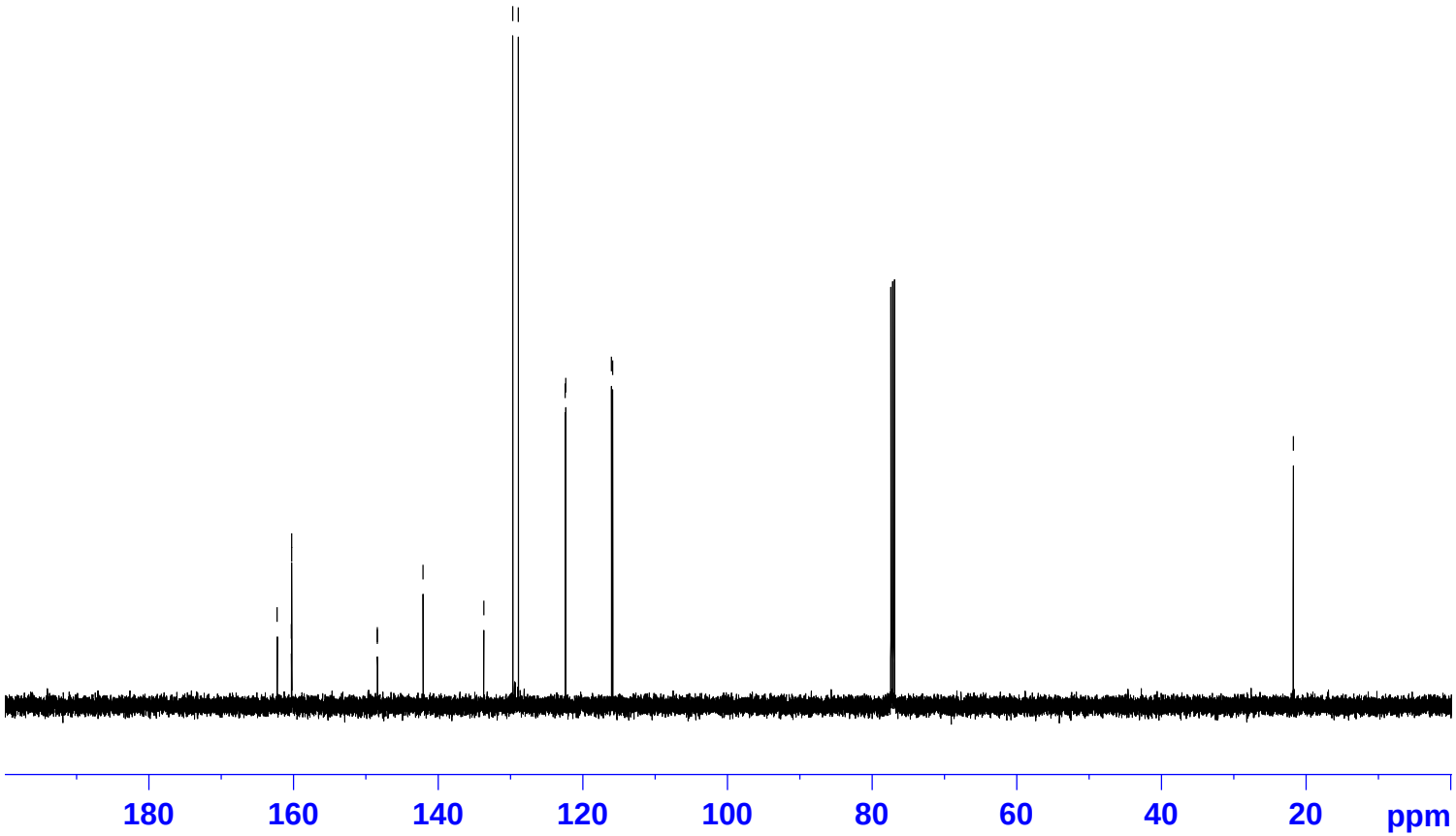

```
Current Data Parameters
NAME          Oct23-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141023
Time               18.44
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   362
DW                81.000 usec
DE                 6.00 usec
TE                673.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200241 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



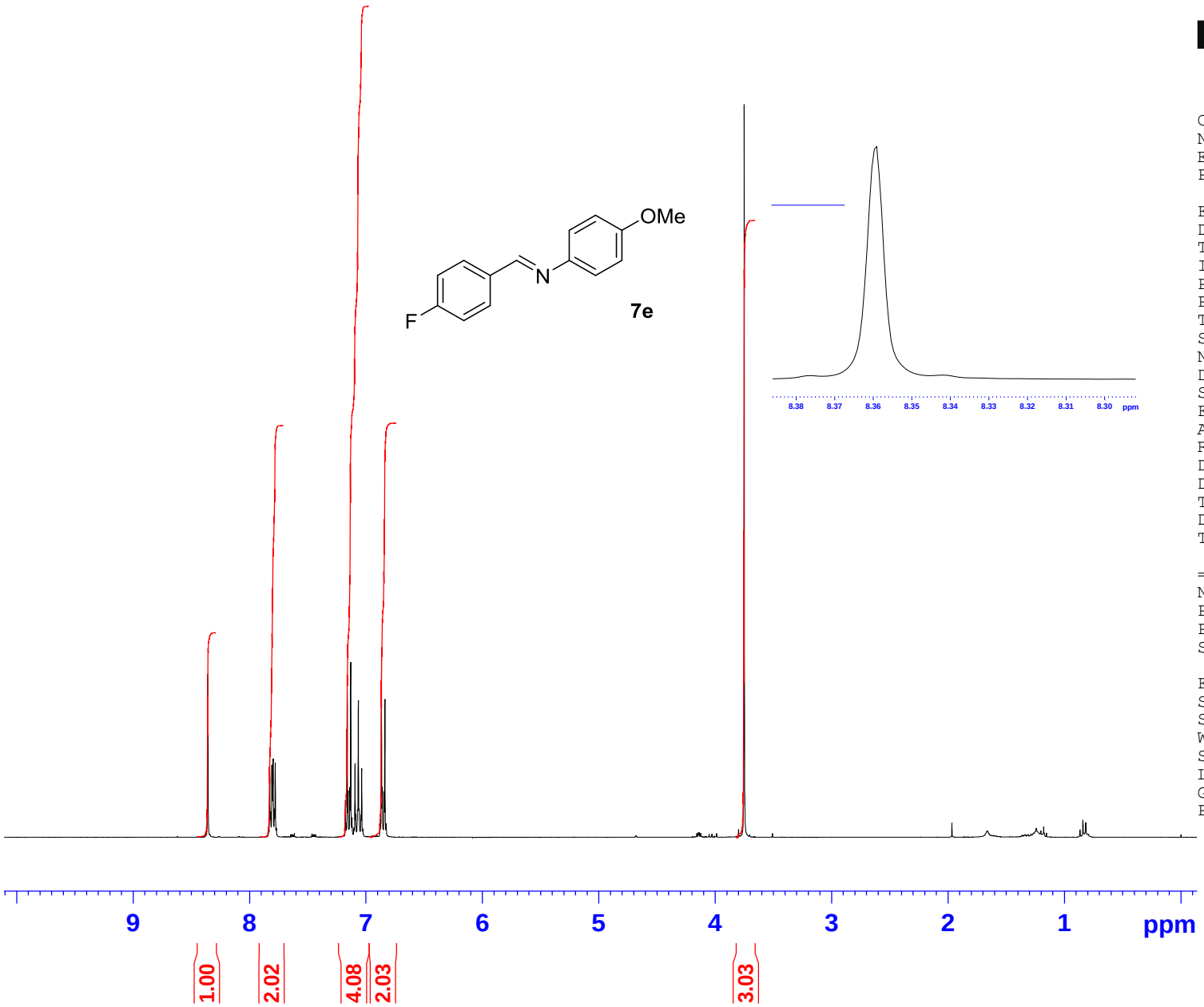





```
Current Data Parameters
NAME      AM1292 CARBON_01.fid
EXPNO                 1
PROCNO                1

F2 - Processing parameters
SI                65536
SF          125.7415788 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

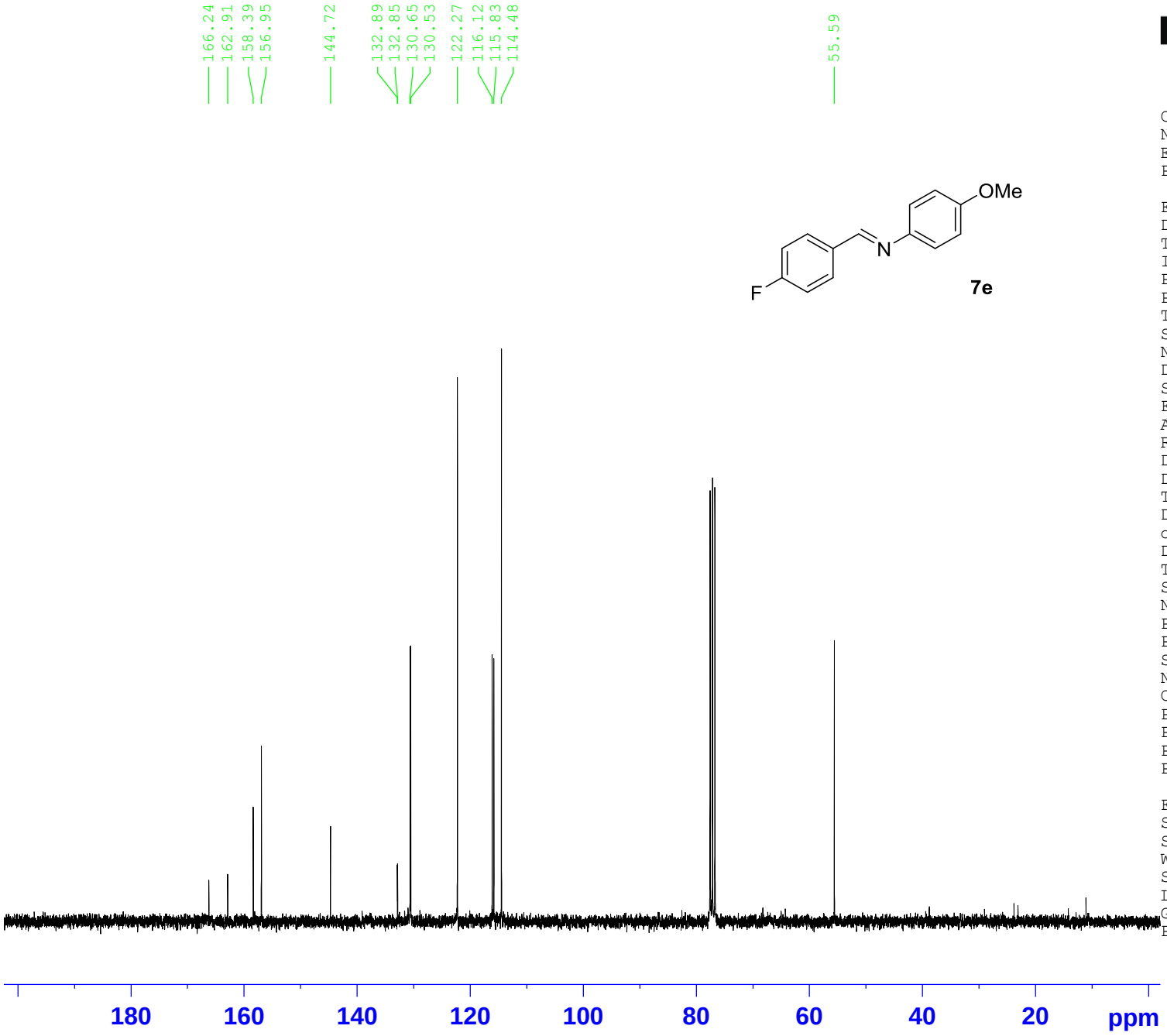


AM1294



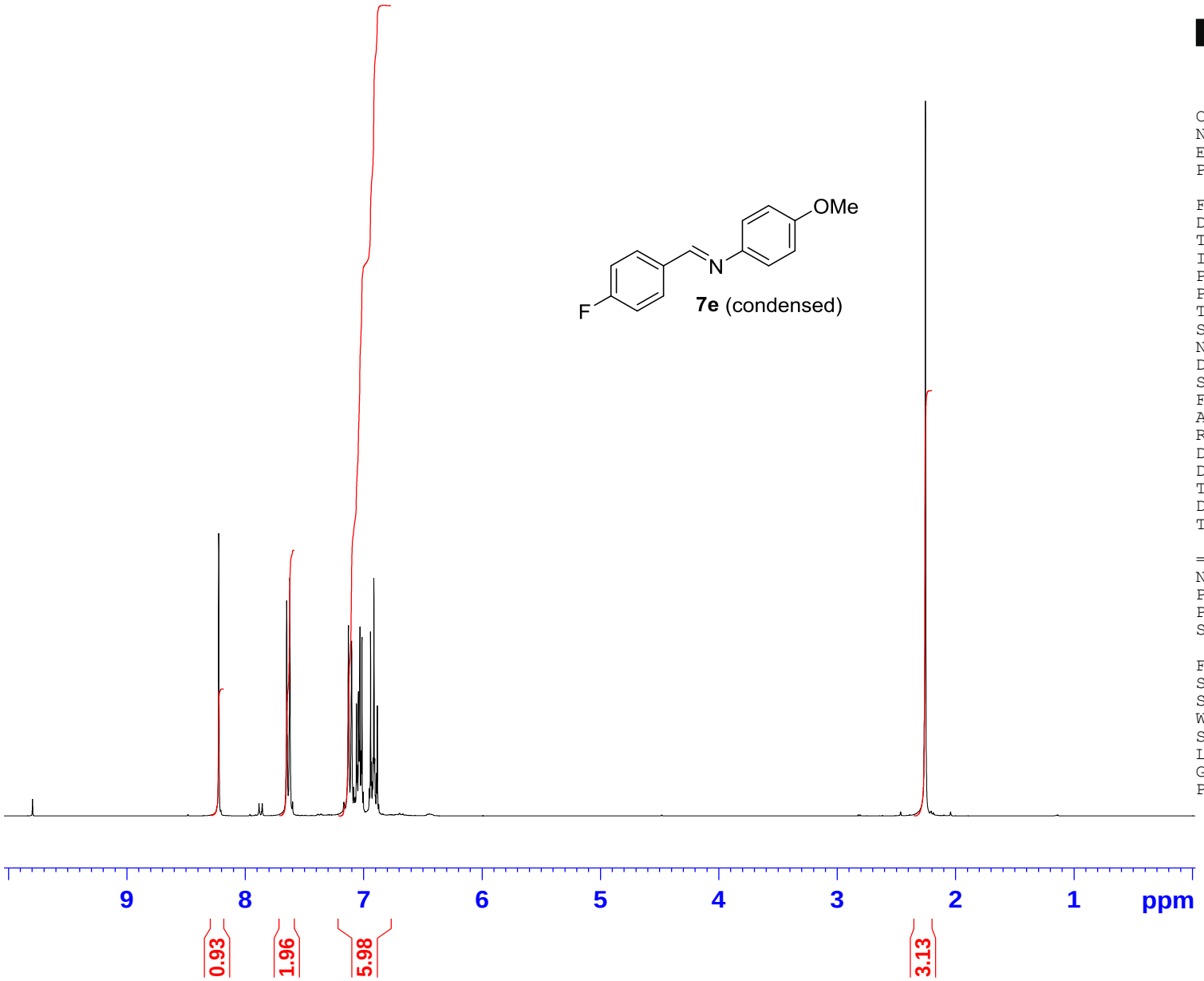

```
Current Data Parameters
NAME          Oct27-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141027
Time_              19.01
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                291.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF          300.2200268 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1294



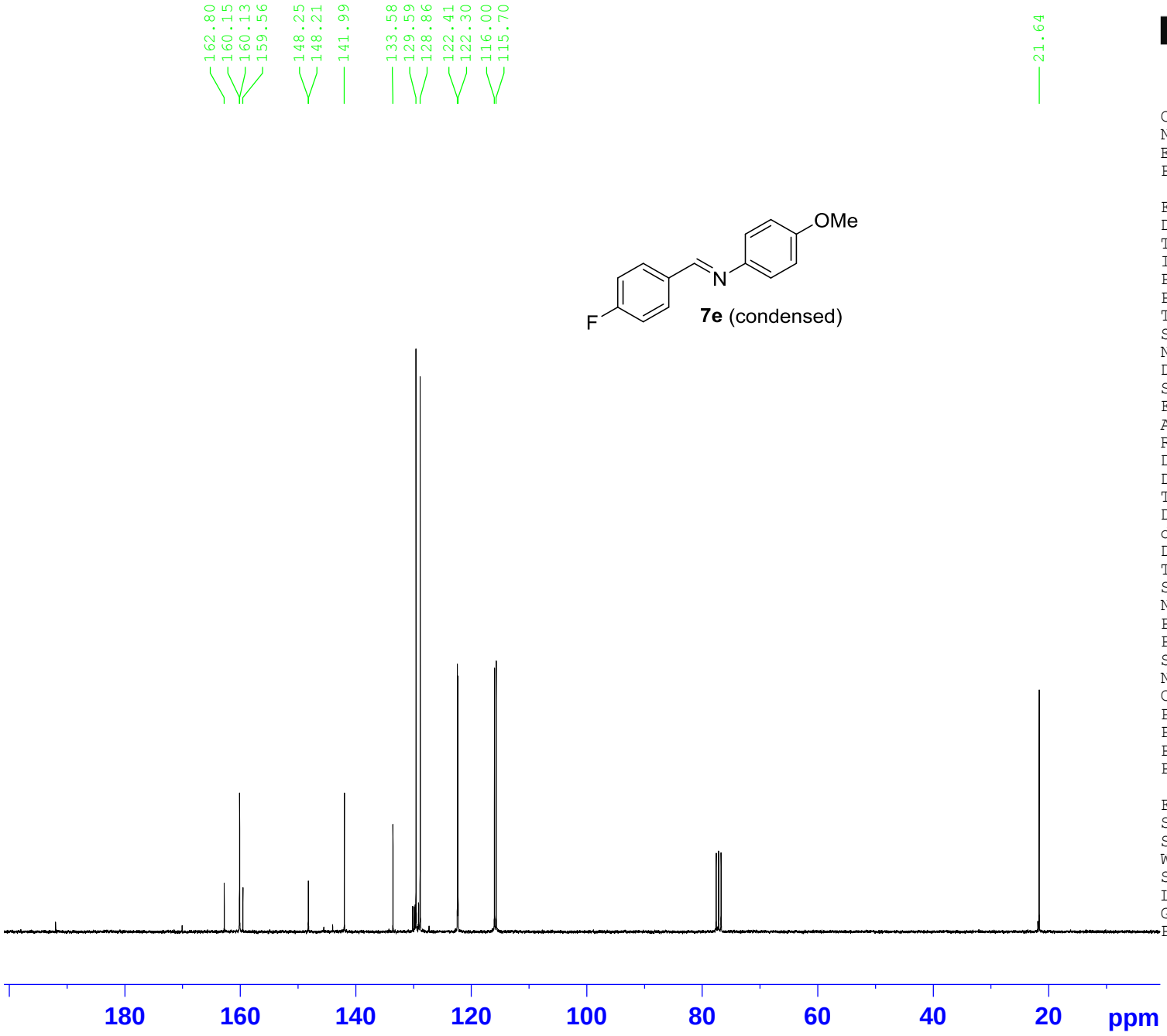

```
Current Data Parameters
NAME          Oct27-2014
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141027
Time              19.19
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG              18390.4
DW               24.600 usec
DE                6.00 usec
TE               291.5 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                 7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903724 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

AM1183




```
Current Data Parameters
NAME          Jun05-2014
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140605
Time               22.11
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                  40.3
DW                81.000 usec
DE                 6.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200545 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1183

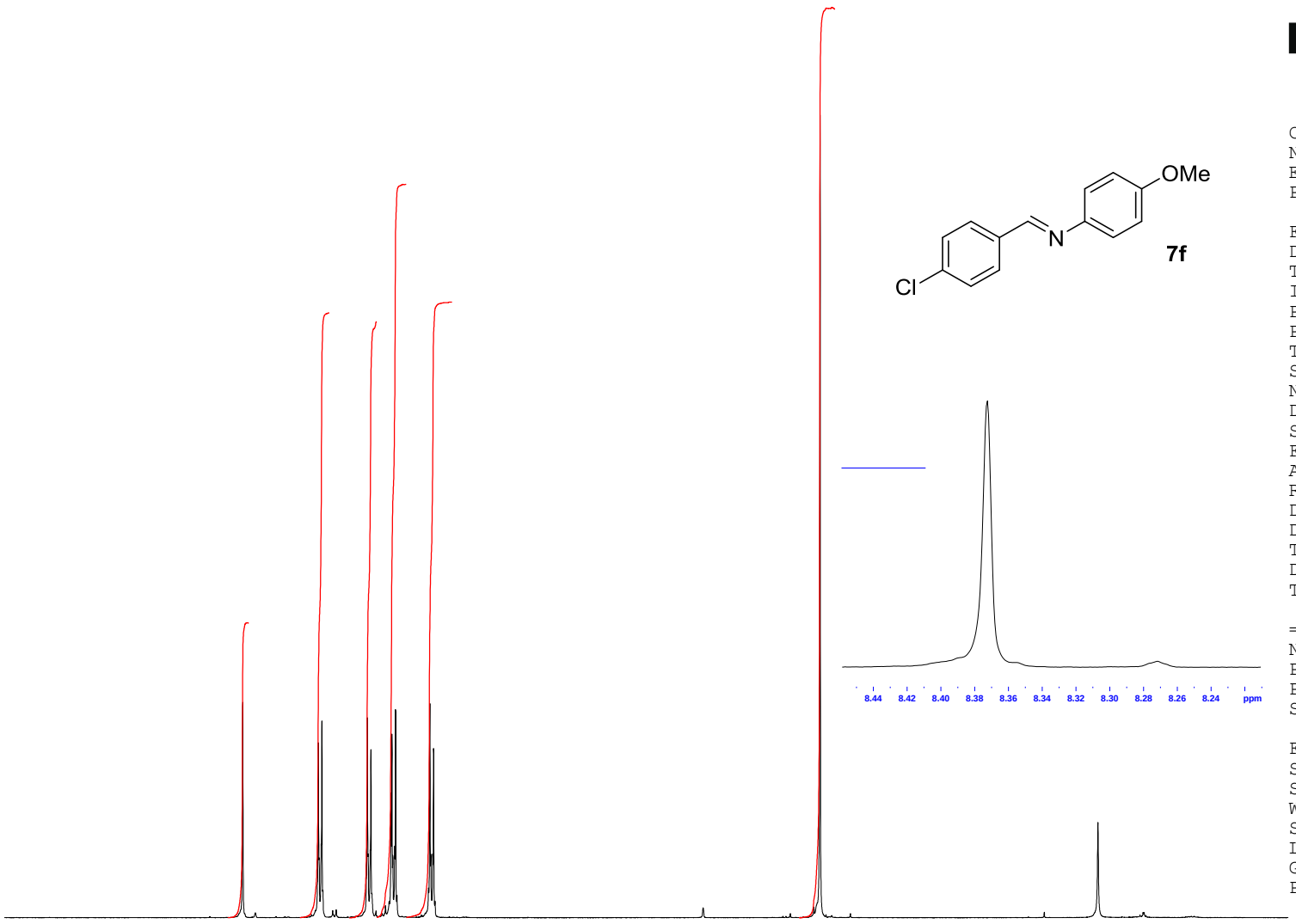


Current Data Parameters
NAME Jun05-2014
EXPNO 41
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140605
Time 22.28
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903786 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

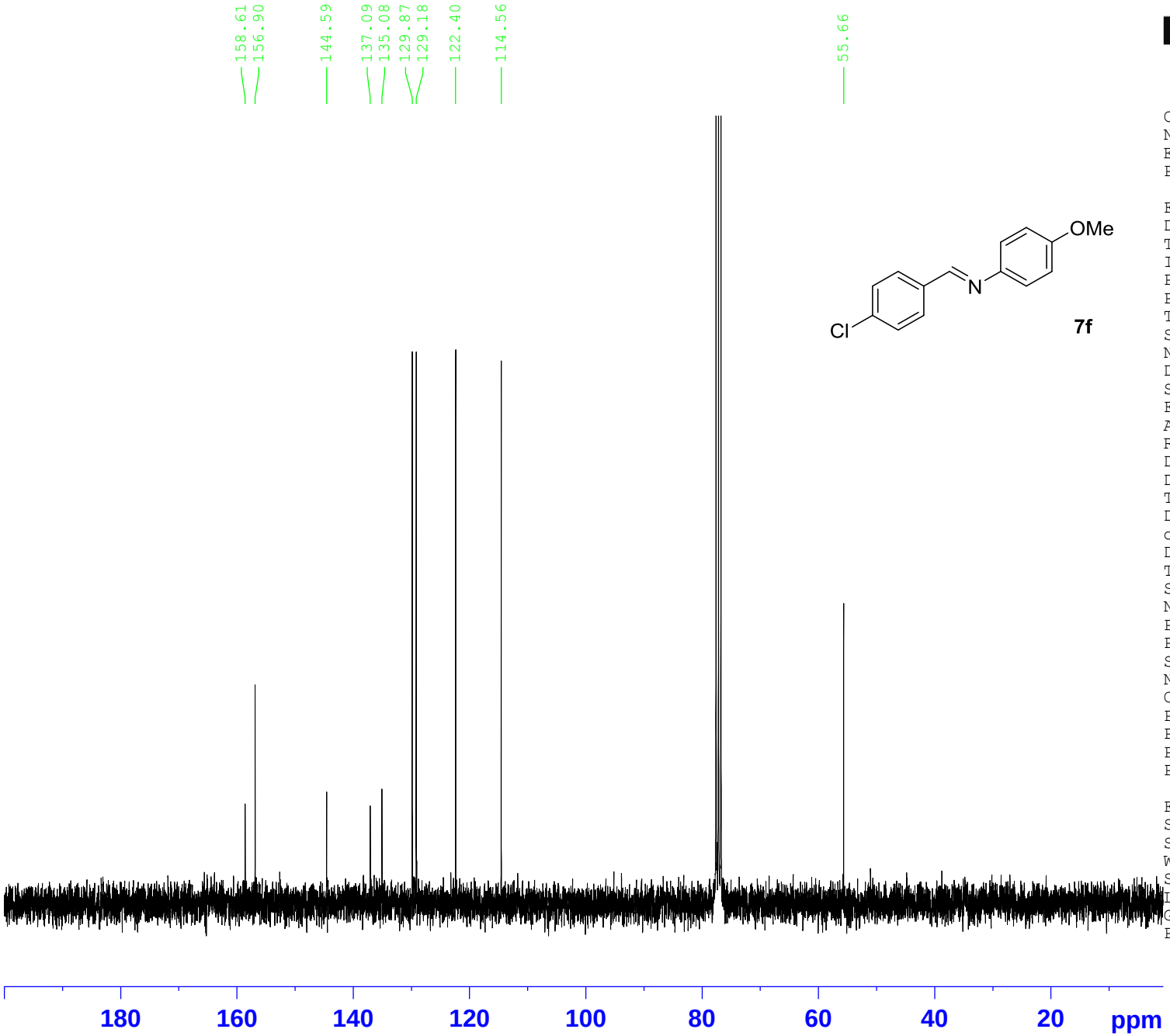
AM1310



7f


```
Current Data Parameters
NAME          Nov14-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141114
Time               11.34
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                   362
DW                81.000 usec
DE                 6.00 usec
TE                291.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200236 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

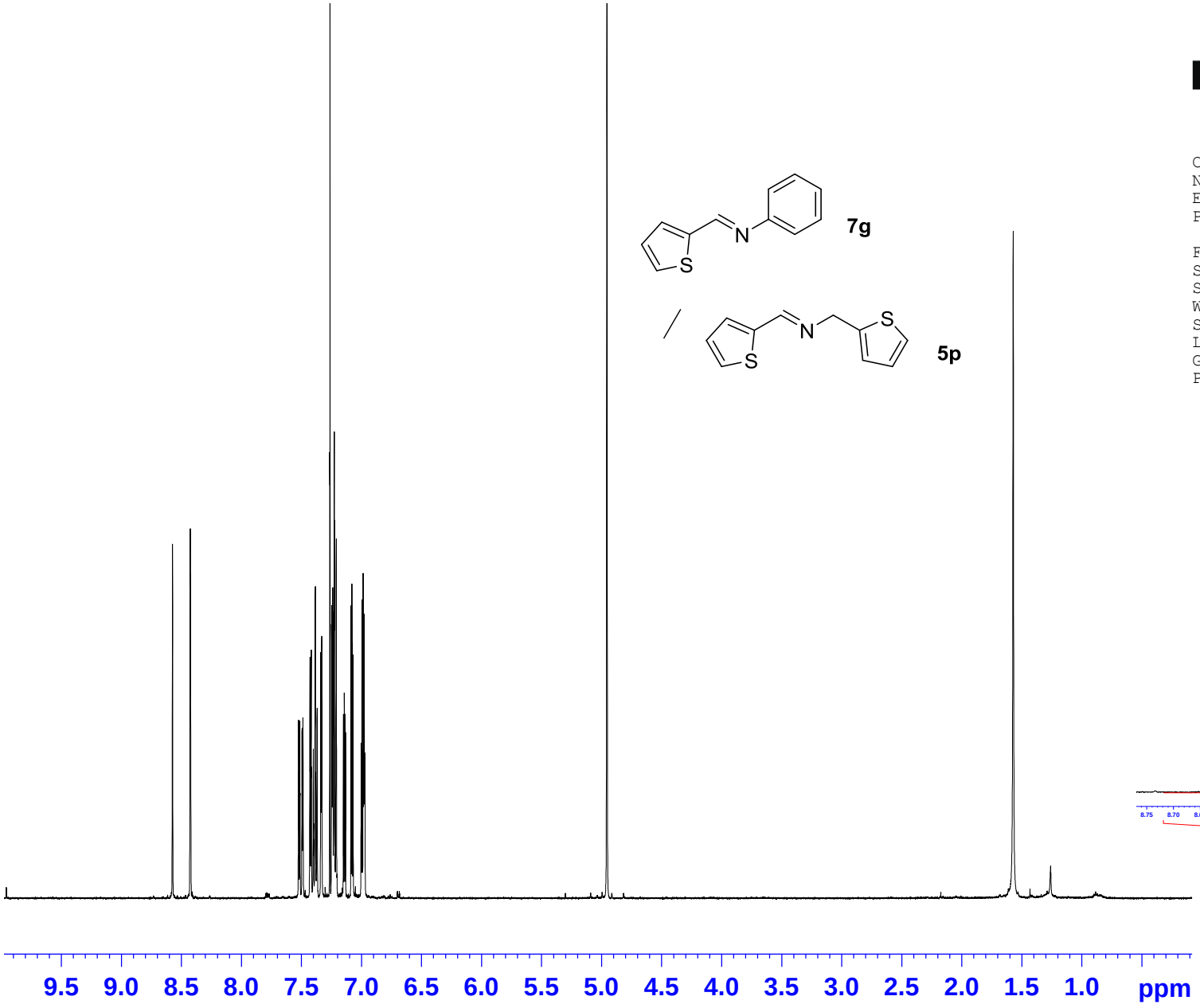
AM1310

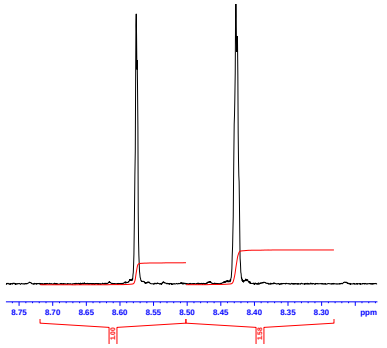


Current Data Parameters
NAME Nov14-2014
EXPNO 11
PROCNO 1

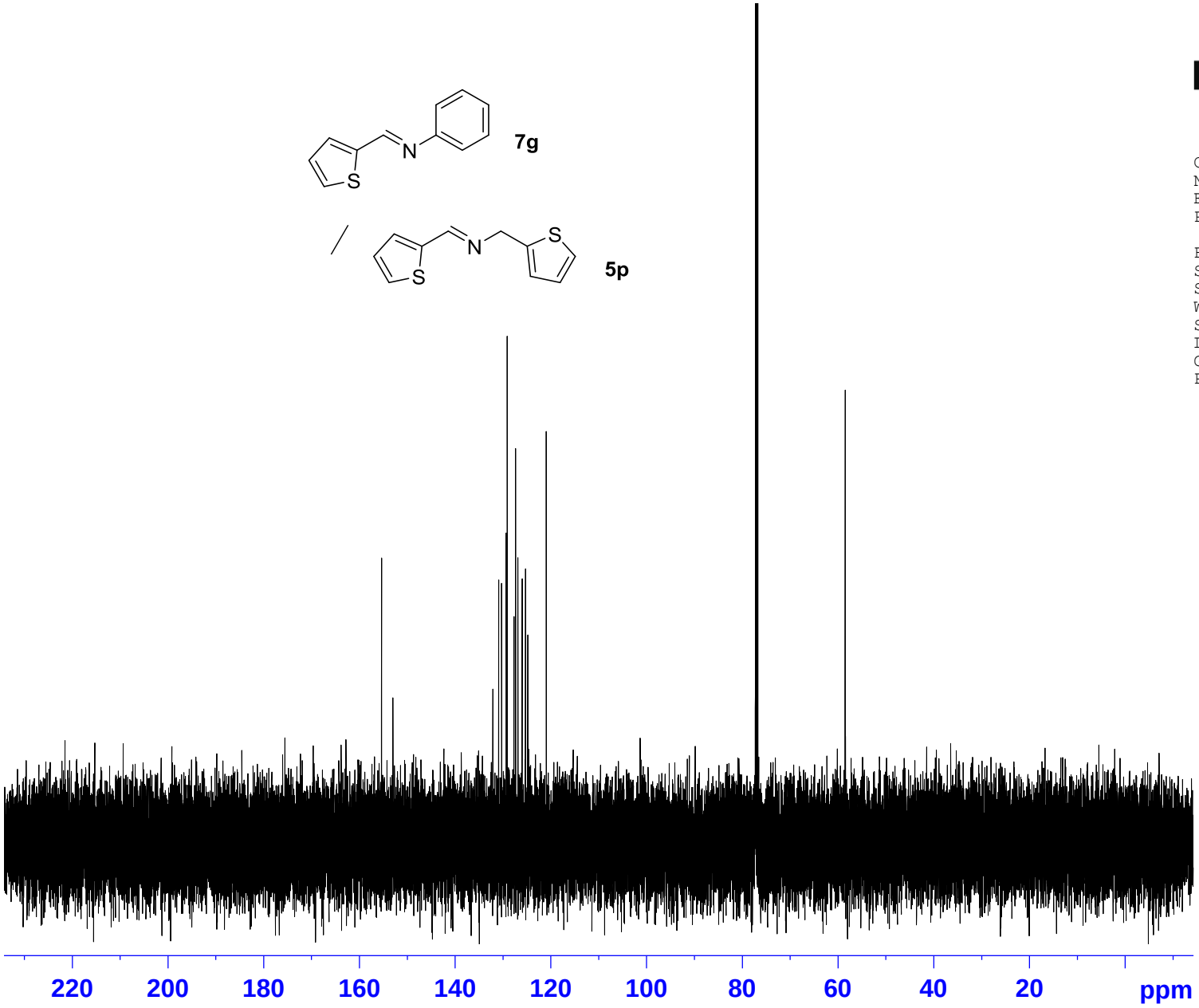
F2 - Acquisition Parameters
Date_ 20141114
Time 11.52
INSTRUM av300
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 20325.203 Hz
FIDRES 0.310138 Hz
AQ 1.6121856 sec
RG 18390.4
DW 24.600 usec
DE 6.00 usec
TE 291.9 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 75.4990304 MHz
NUC1 13C
P1 7.50 usec
PLW1 -1.00000000 W
SFO2 300.2212009 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 -1.00000000 W
PLW12 -1.00000000 W
PLW13 -1.00000000 W

F2 - Processing parameters
SI 65536
SF 75.4903678 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

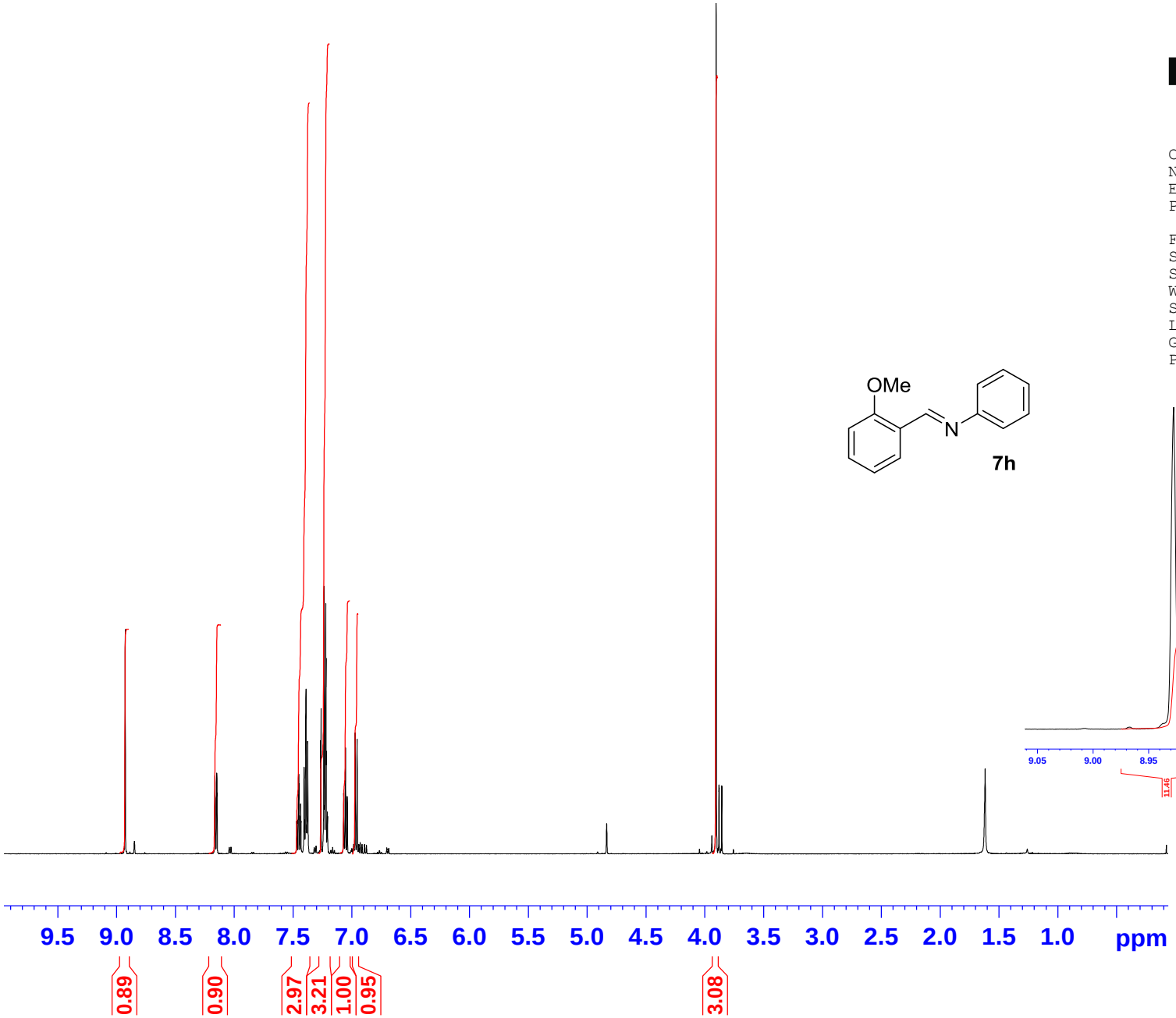




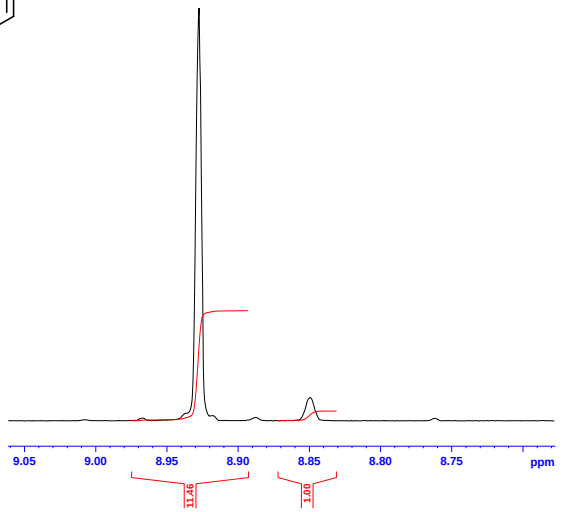

```
Current Data Parameters
NAME      AM1319 PROTON_01.fid
EXPNO                      1
PROCNO                     1

F2 - Processing parameters
SI                     32768
SF           500.0586918 MHz
WDW                       no
SSB       0
LB        0 Hz
GB        0
PC                      1.00
```



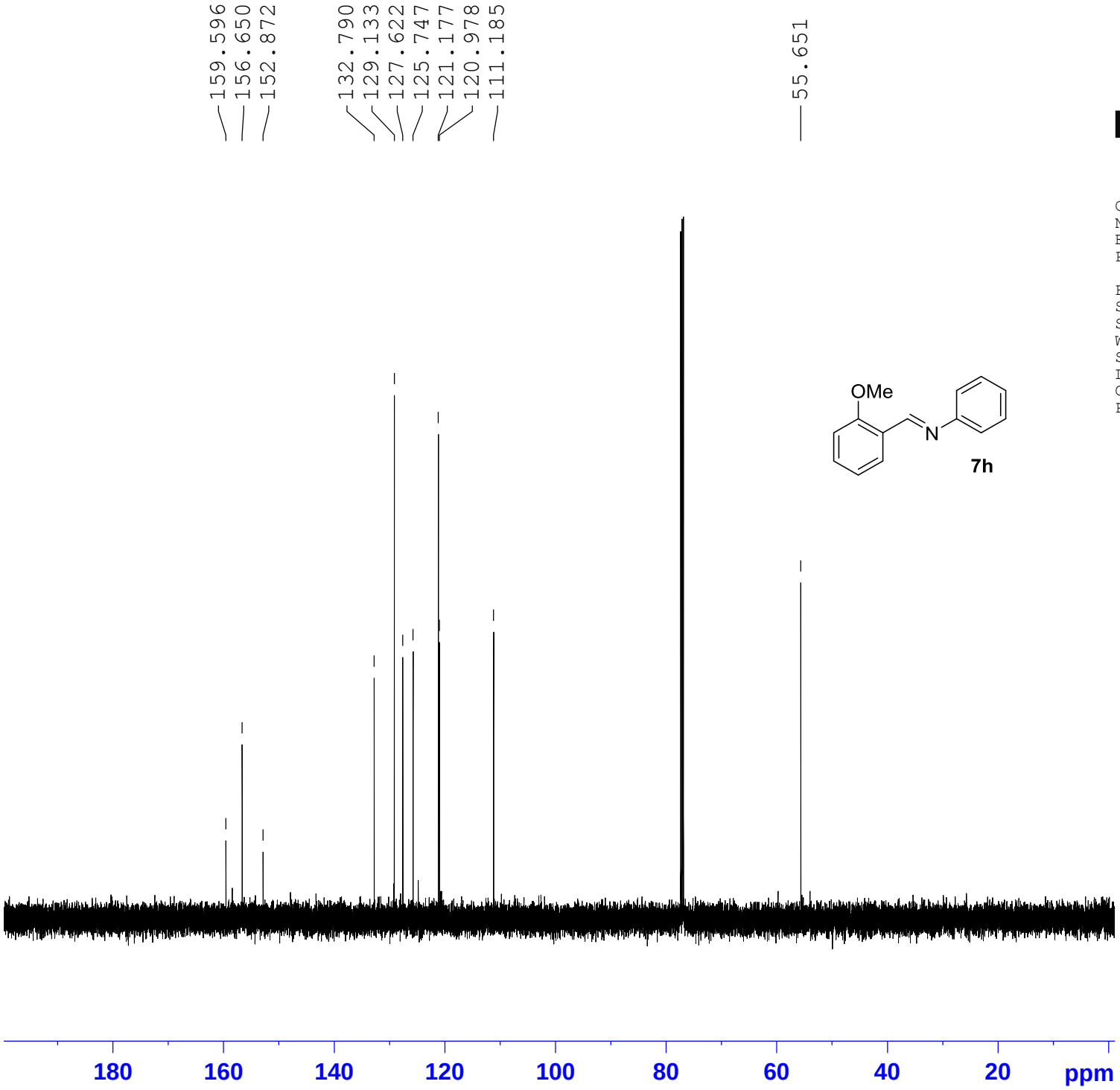

```
Current Data Parameters
NAME      AM1319 CARBON_01.fid
EXPNO                      1
PROCNO                     1

F2 - Processing parameters
SI                     65536
SF           125.7416469 MHz
WDW                       EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```



7h

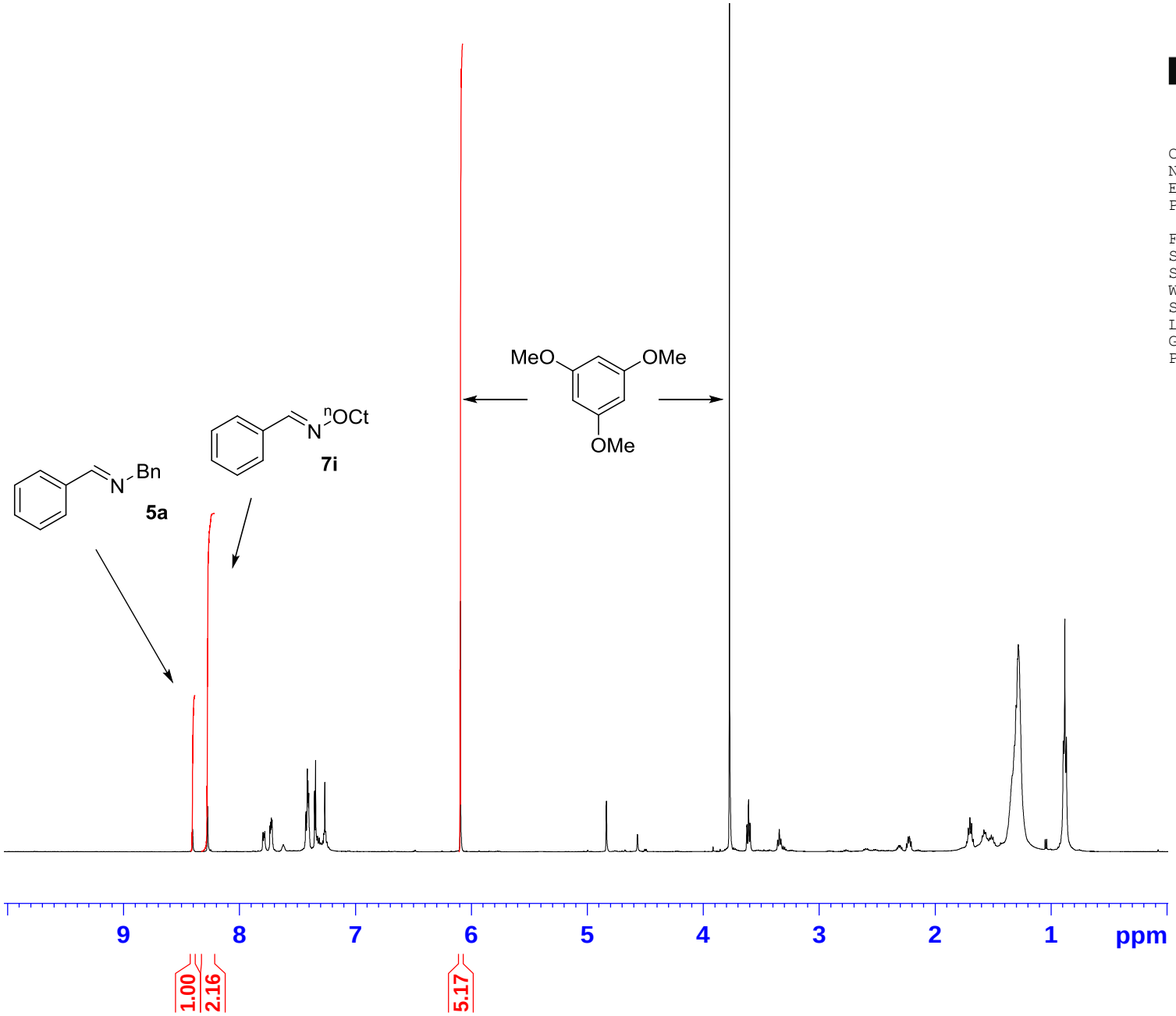



```
Current Data Parameters
NAME      AM1322 PROTON_01.fid
EXPNO                       1
PROCNO                      1

F2 - Processing parameters
SI                      32768
SF           500.0586918 MHz
WDW                        no
SSB       0
LB        0 Hz
GB        0
PC                      1.00
```



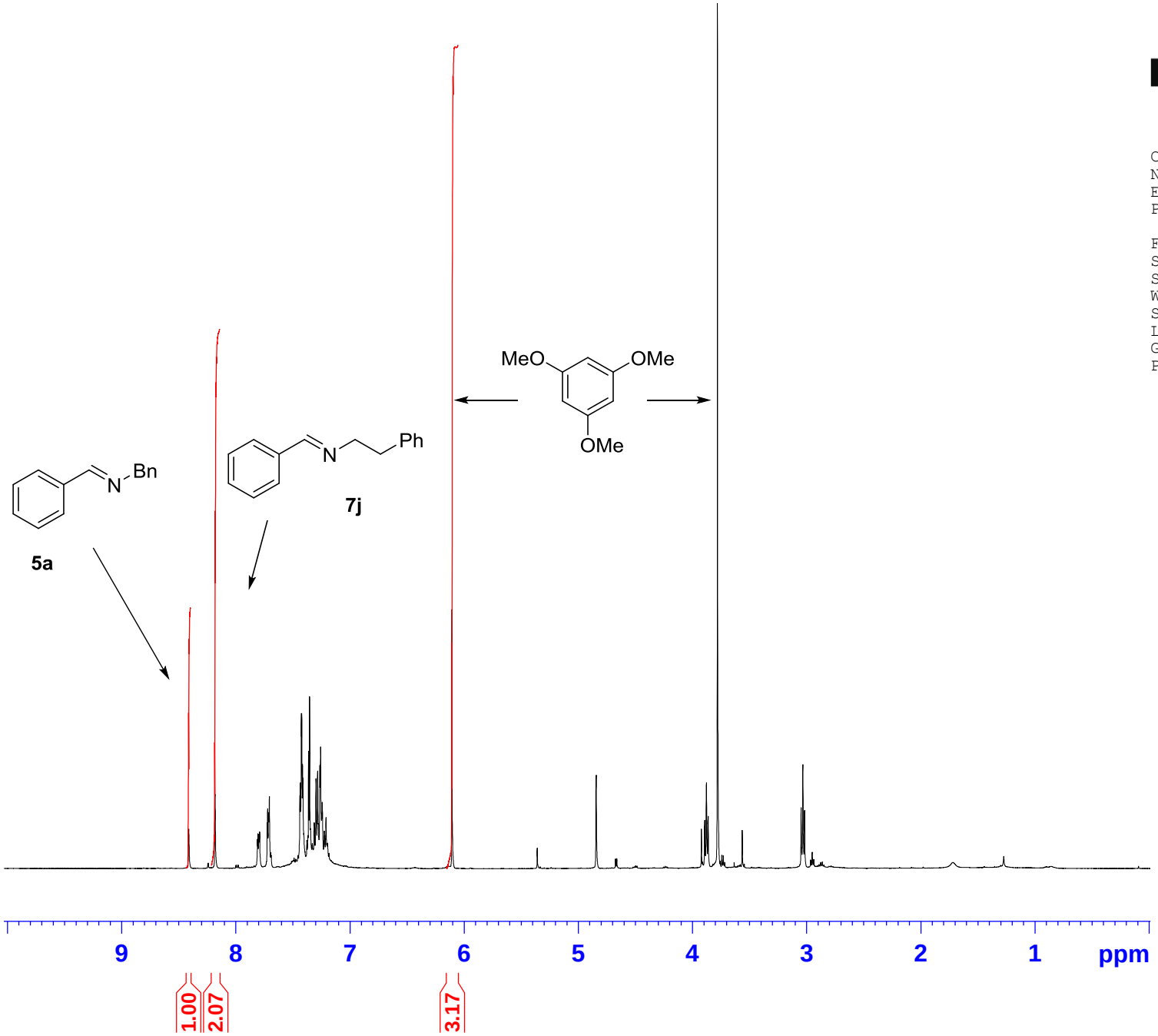
Current Data Parameters
NAME AM1322 CARBON_01.fid
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 125.7416353 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



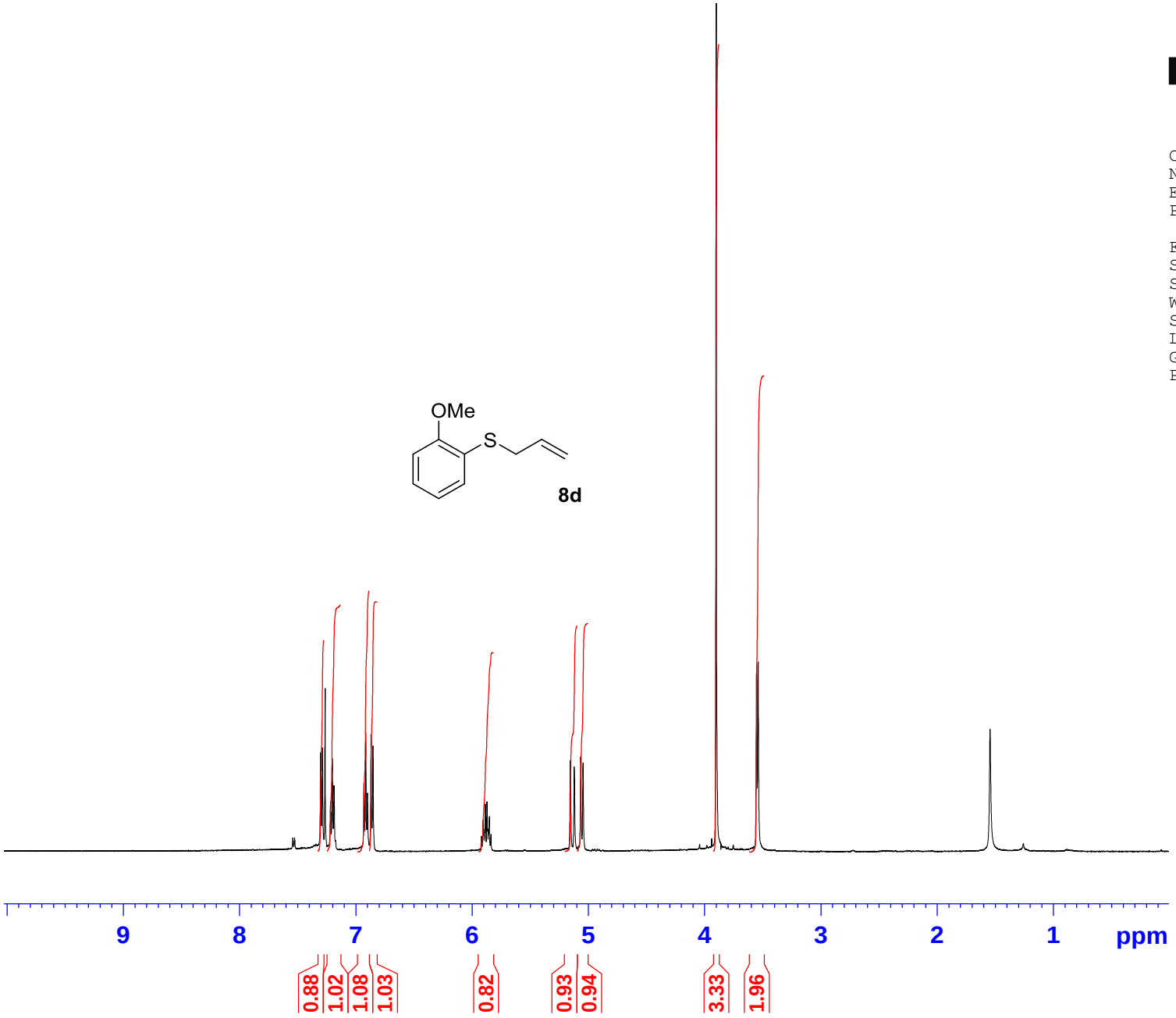
Current Data Parameters
NAME AM1365 PROTON_01.fid
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 32768
SF 500.0586918 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AM1366 PROTON_01.fid
EXPNO 1
PROCNO 1

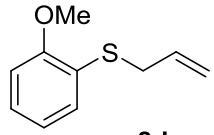
F2 - Processing parameters
SI 32768
SF 500.0586918 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



Current Data Parameters
NAME RK7 PROTON_01.fid
EXPNO 1
PROCNO 1

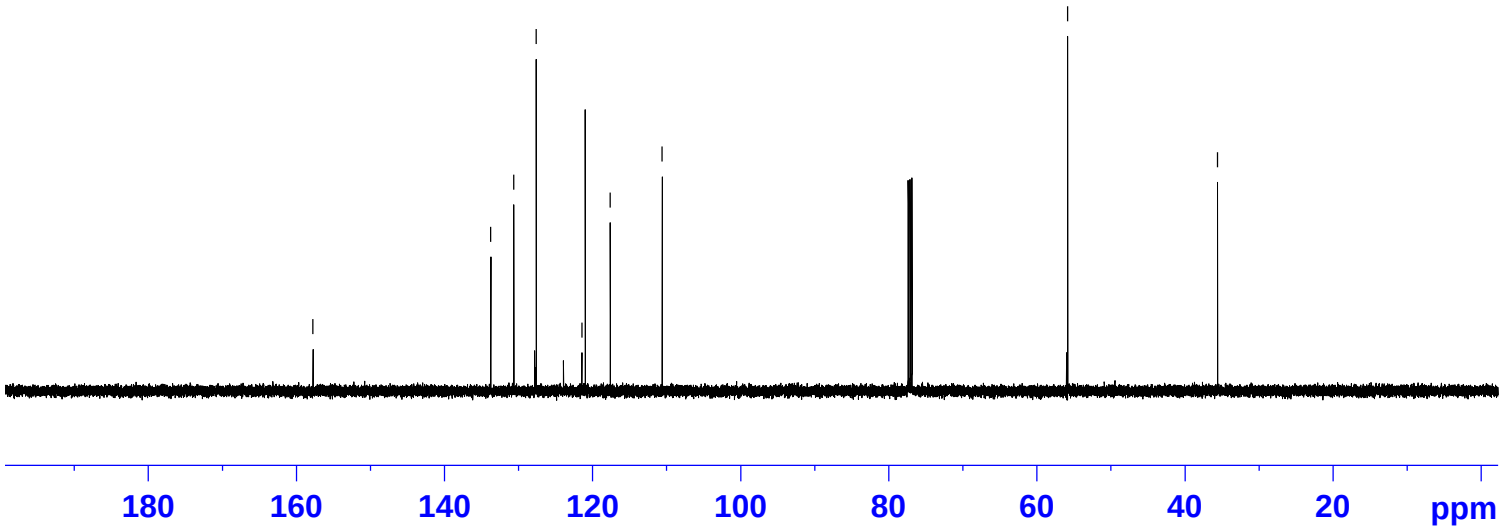
F2 - Processing parameters
SI 32768
SF 500.0586918 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

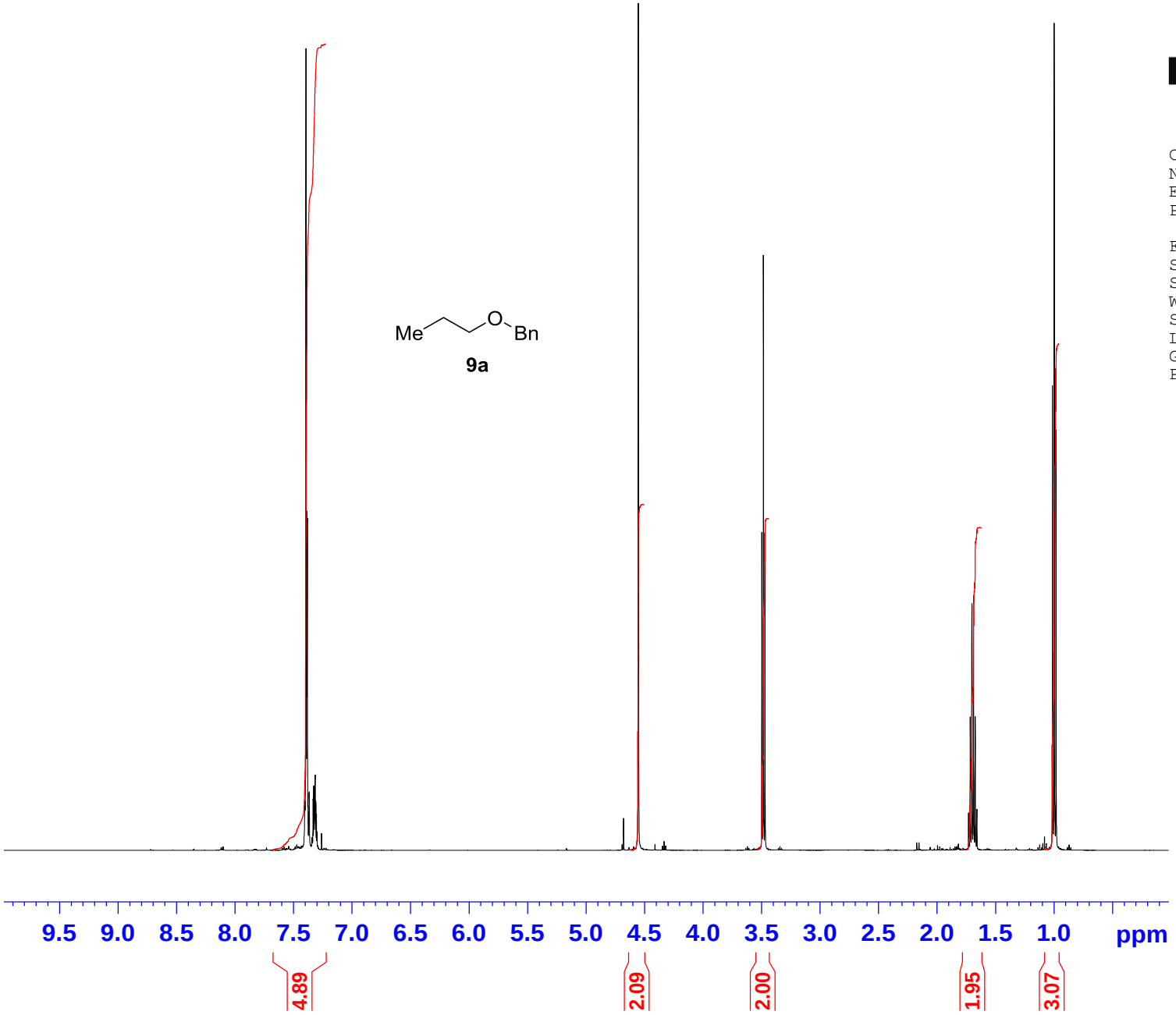
157.797
133.784
130.700
127.659
121.474
117.653
110.631
55.876
35.639



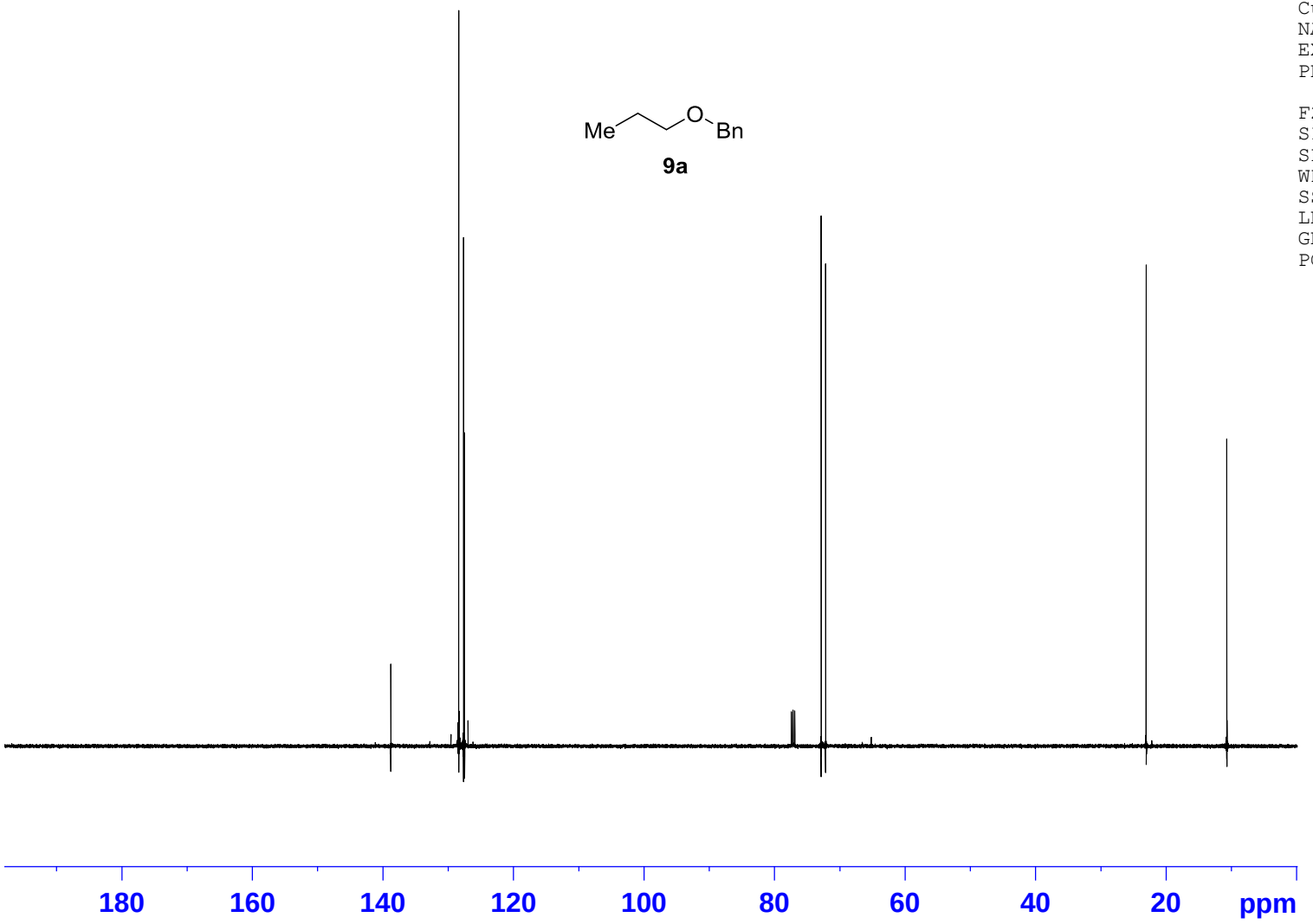
8d

```
Current Data Parameters
NAME      rk7 conc CARBON_01.fid
EXPNO                  1
PROCNO                 1

F2 - Processing parameters
SI                 65536
SF          125.7416299 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



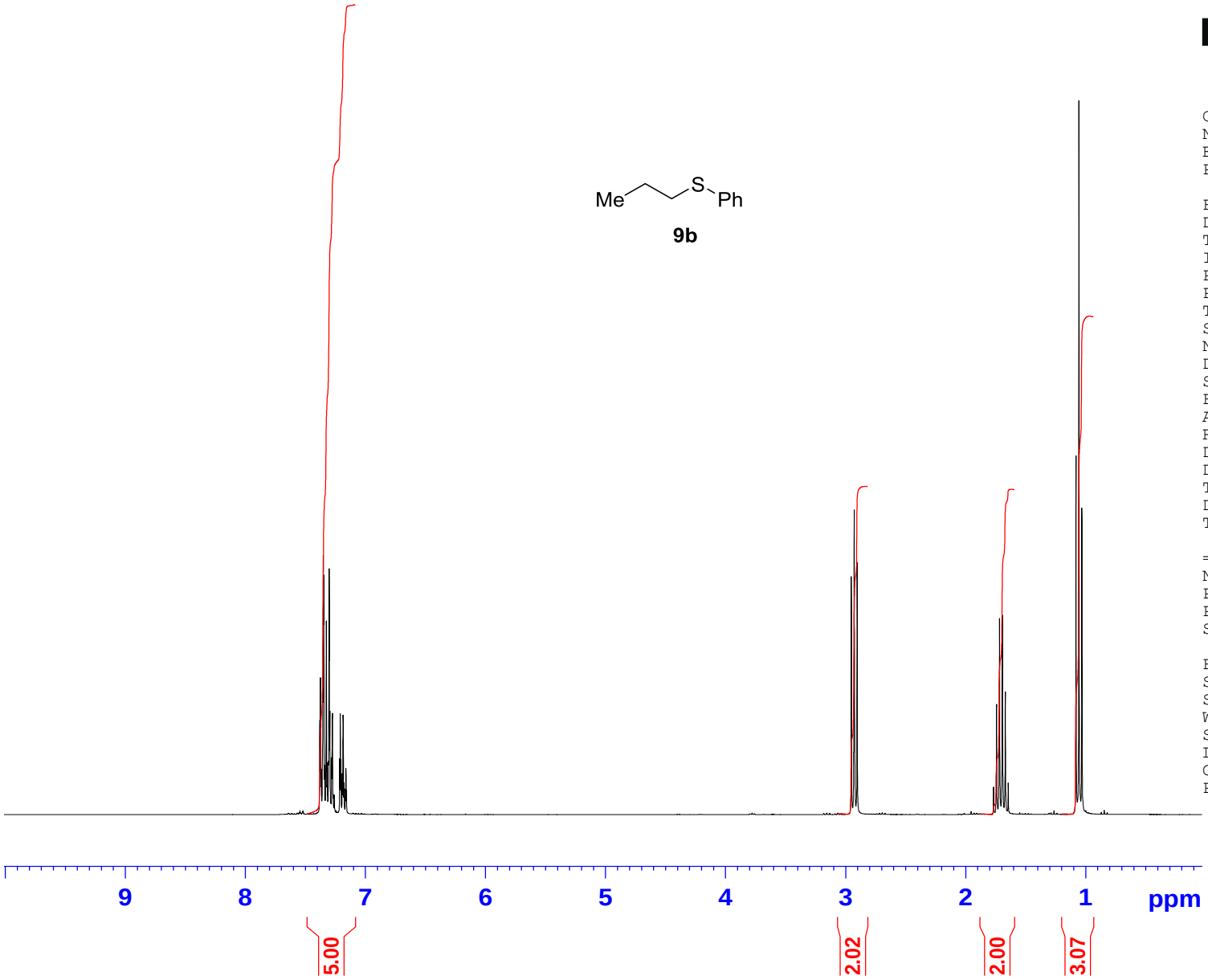



```
Current Data Parameters
NAME       PROTON_01.fid
EXPNO                  1
PROCNO                 1

F2 - Processing parameters
SI                 32768
SF          500.0586931 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```



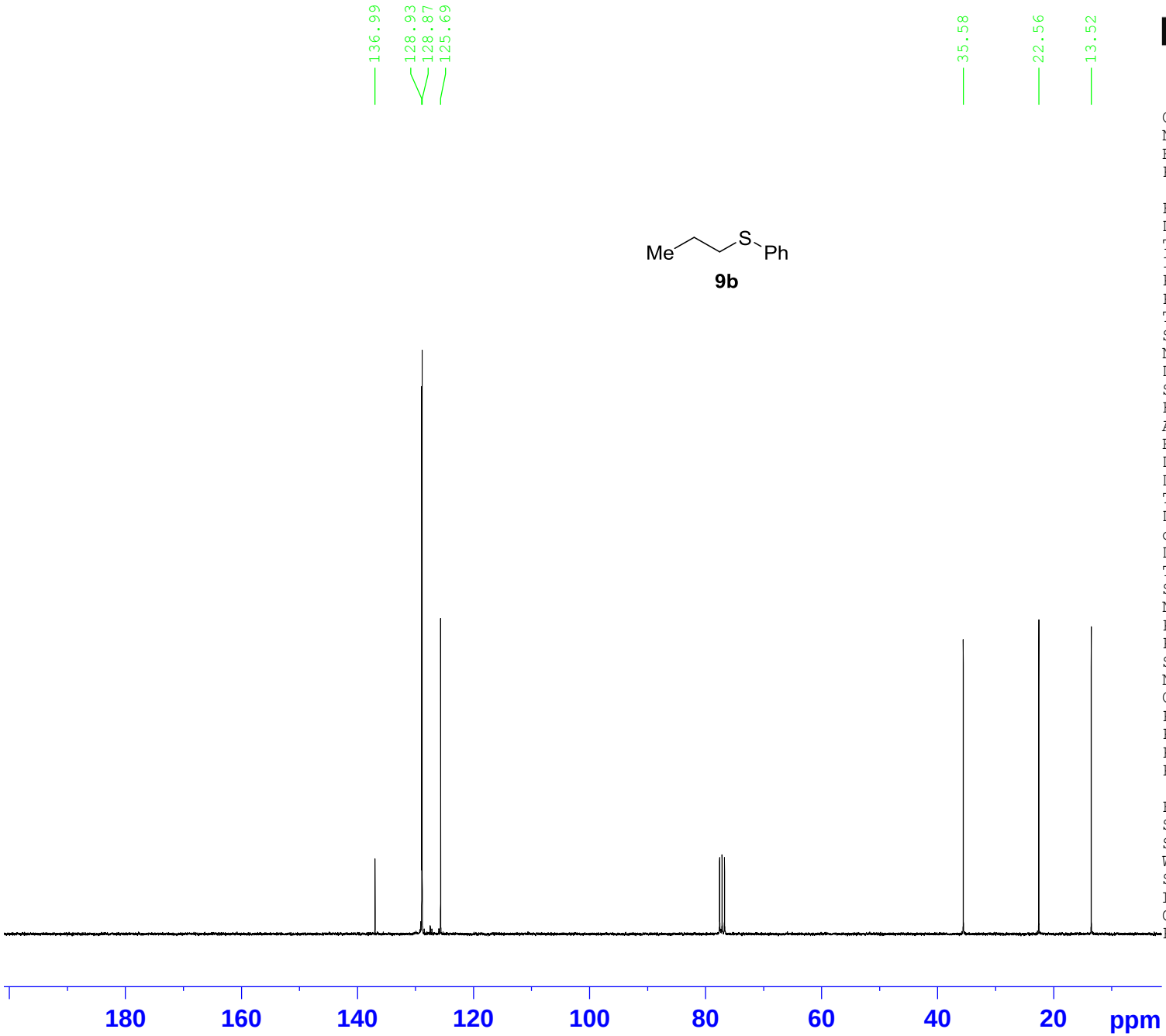

```
Current Data Parameters
NAME      AM1268 carbon.fid
EXPNO                    1
PROCNO                   1

F2 - Processing parameters
SI                   65536
SF           125.7416432 MHz
WDW                     no
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```

AM1266



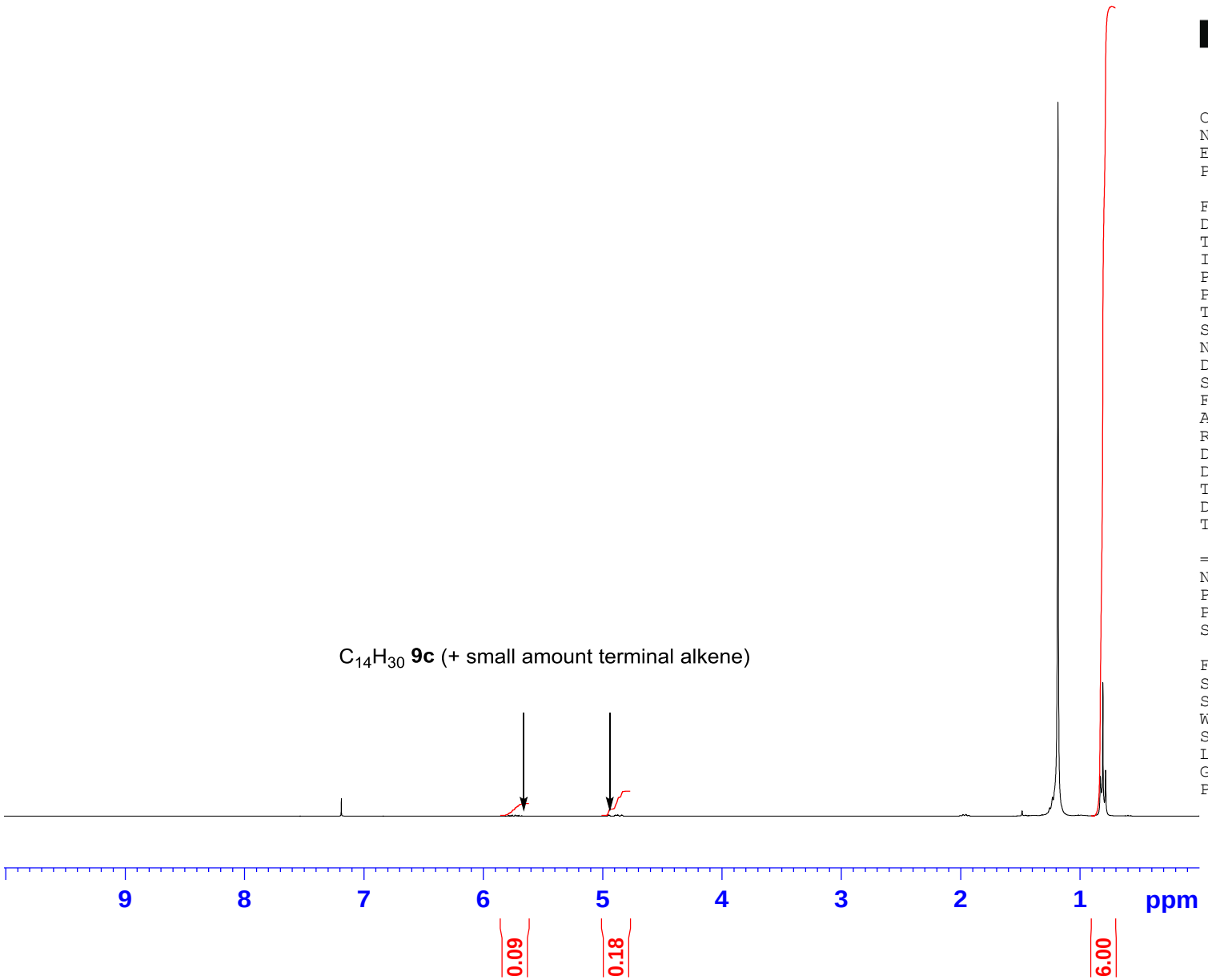

```
Current Data Parameters
NAME          Sep16-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140916
Time               13.31
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                    57
DW                81.000 usec
DE                 6.00 usec
TE                291.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200023 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1266

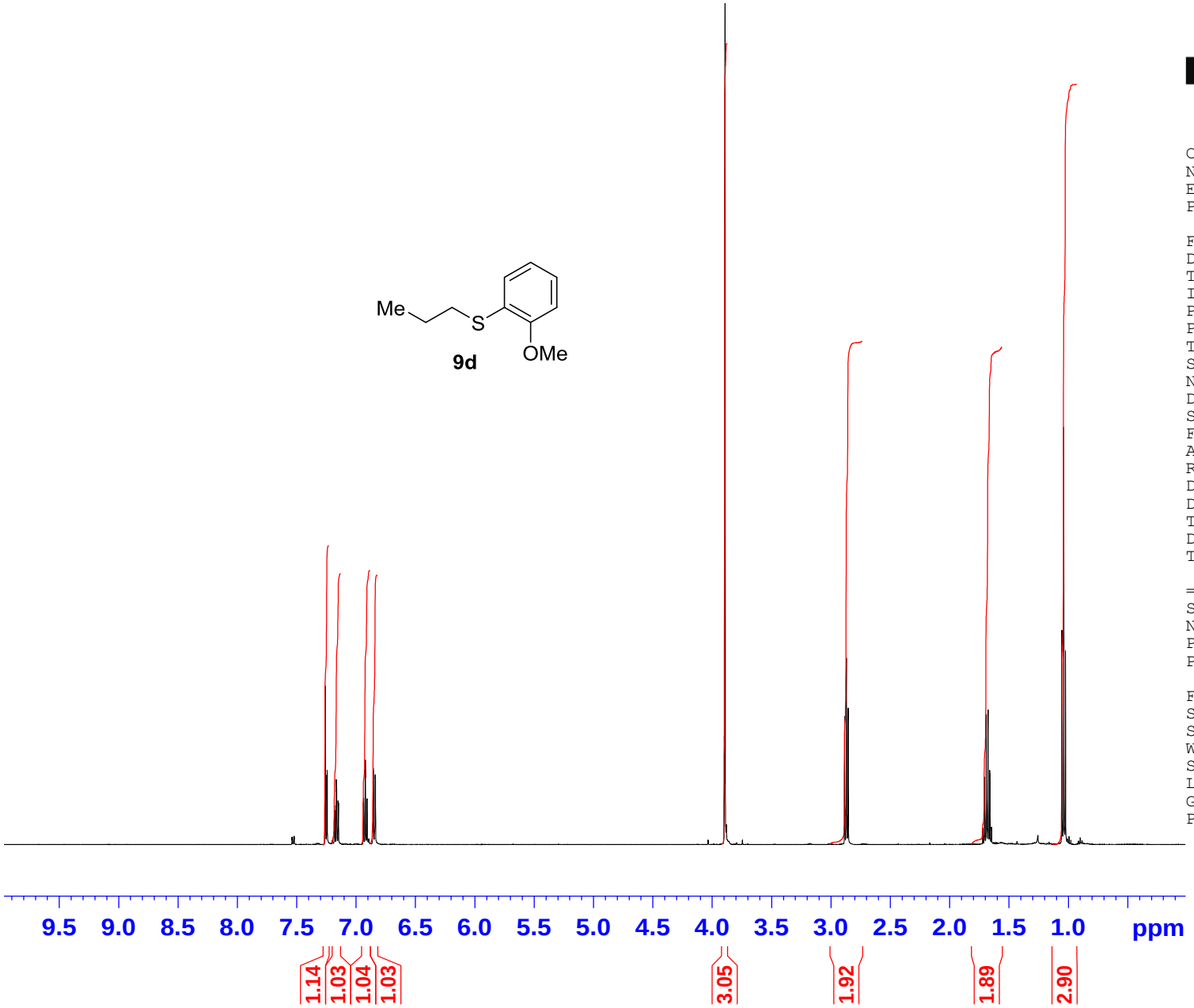



```
Current Data Parameters
NAME          Sep16-2014
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140916
Time              13.49
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG                16384
DW               24.600 usec
DE                6.00 usec
TE               291.6 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903787 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

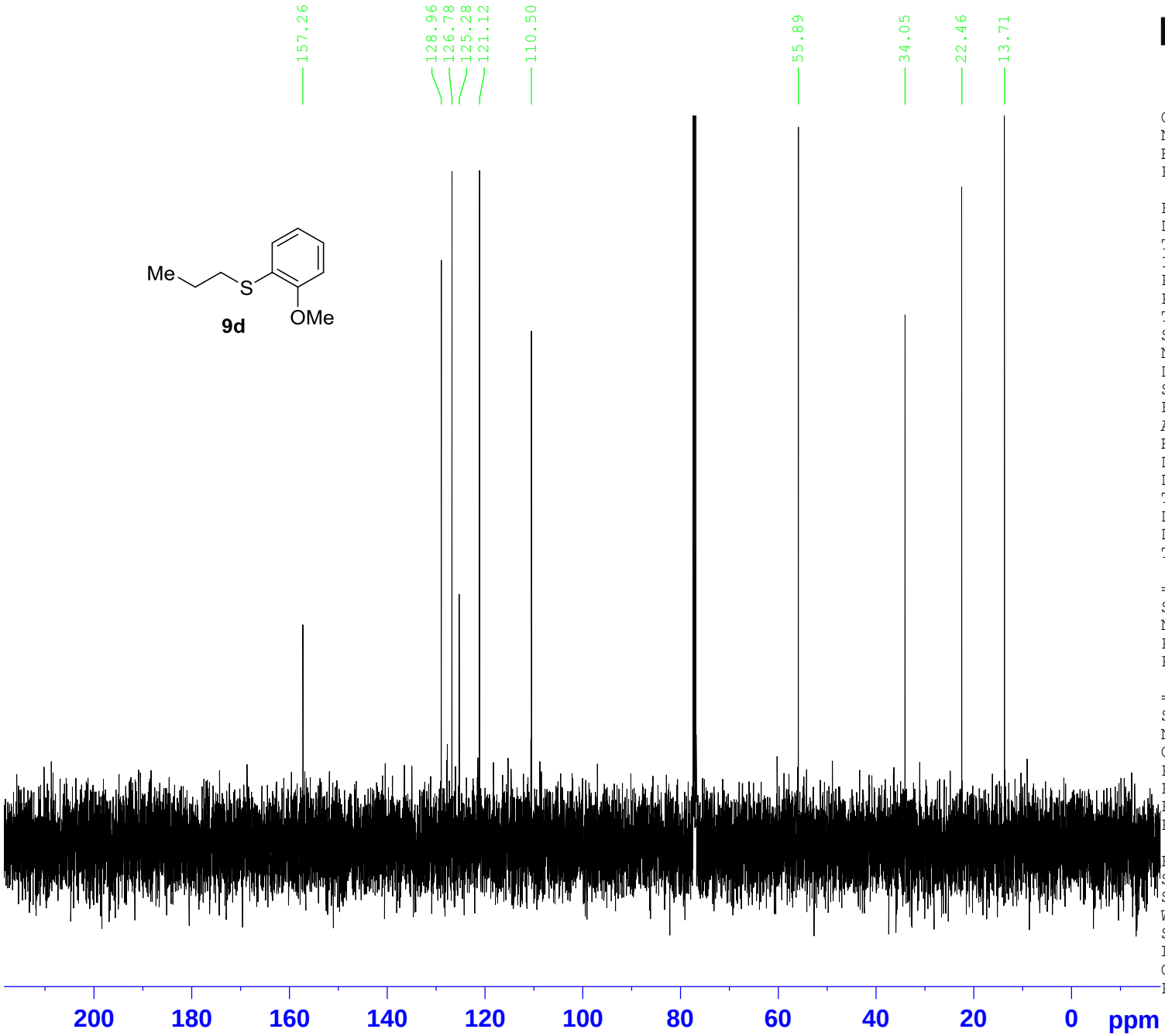
AM1269



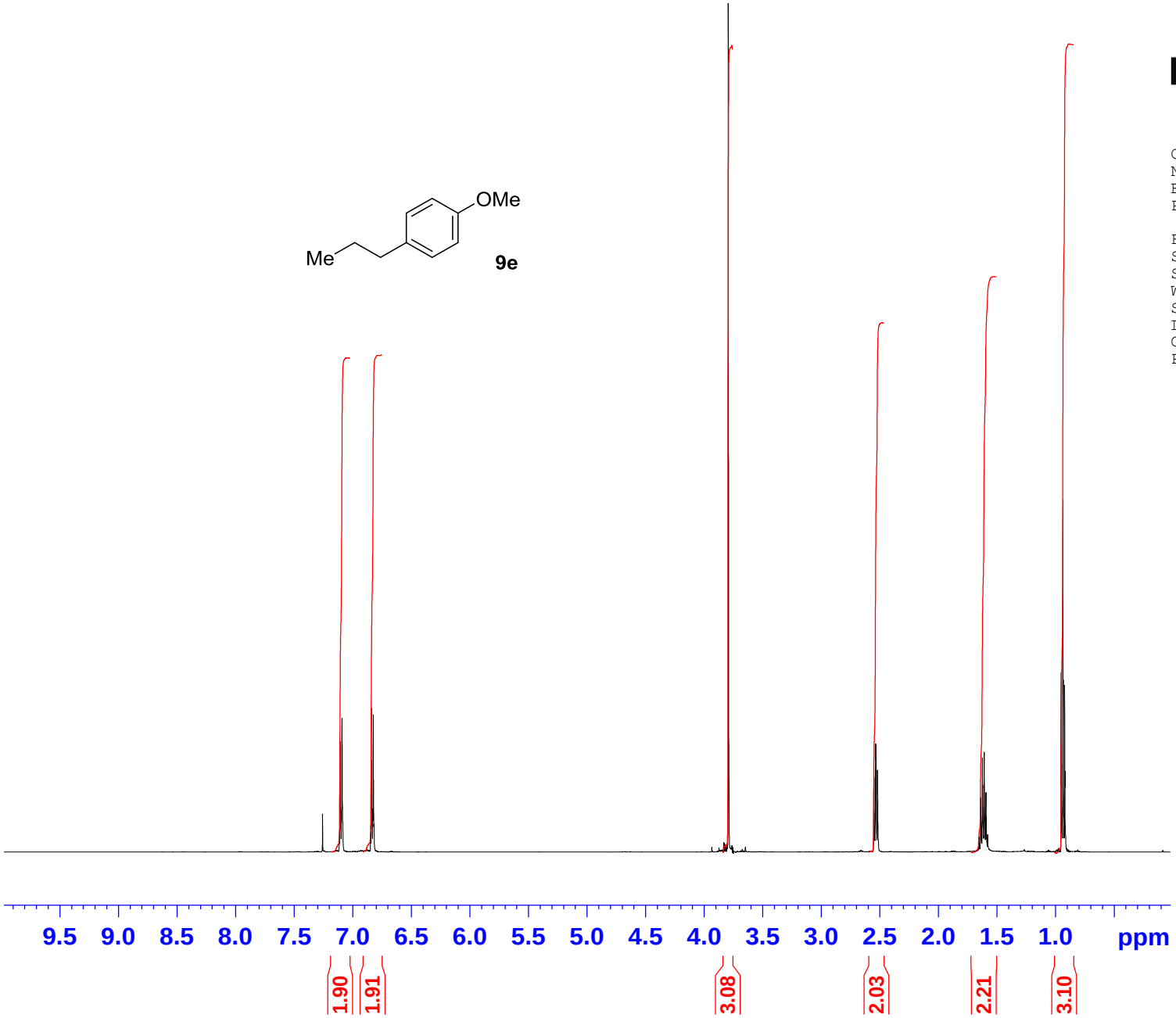

```
Current Data Parameters
NAME          Sep18-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140918
Time               18.42
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                  90.5
DW                81.000 usec
DE                 6.00 usec
TE                291.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1        300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF          300.2200233 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



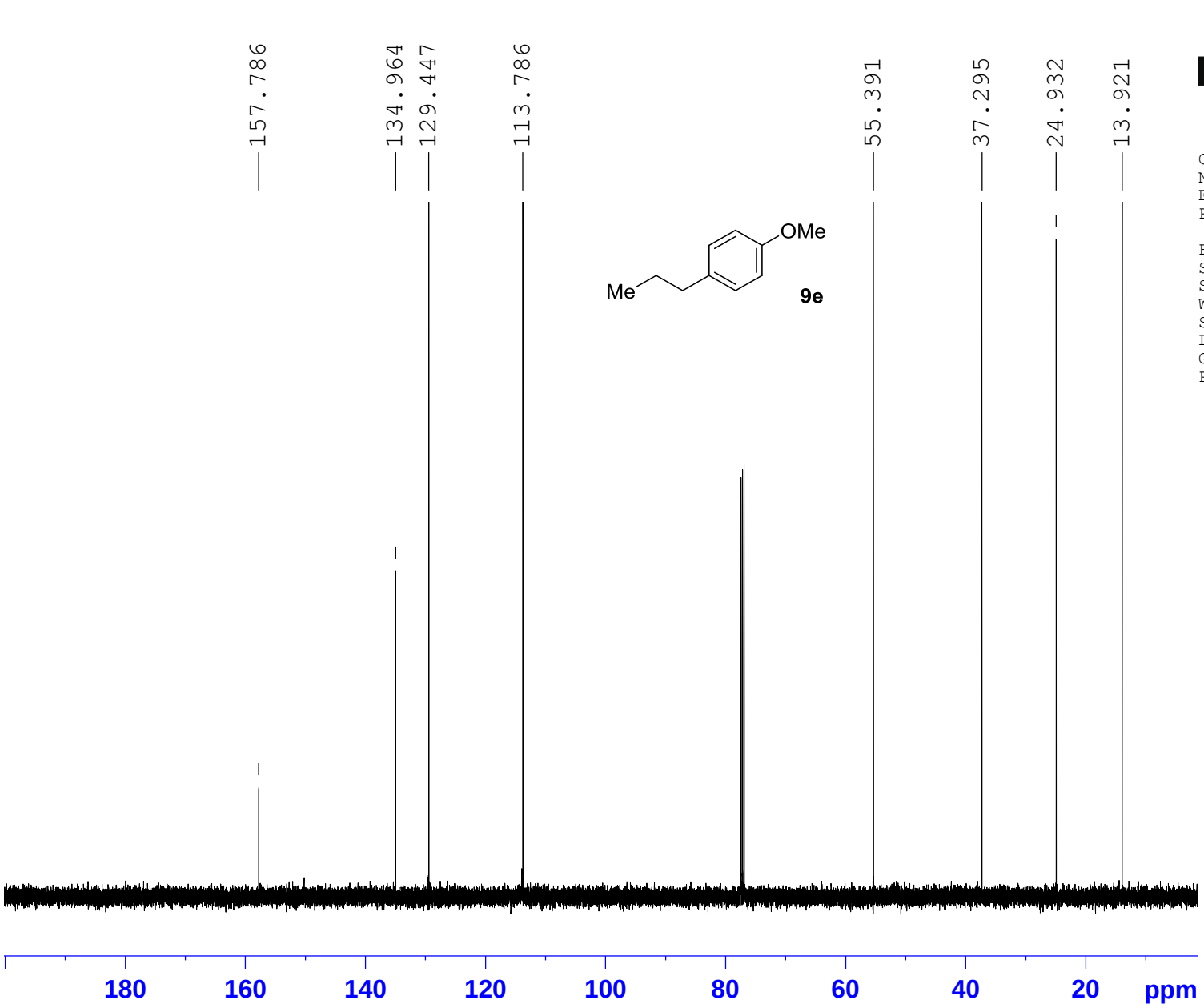

```
Current Data Parameters
NAME                  rk9 f
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150211
Time                 16.27
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719425 sec
RG                     228
DW                  48.400 usec
DE                   6.50 usec
TE                  298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                    1H
P1                   9.50 usec
PLW1         27.19599915 W

F2 - Processing parameters
SI                   32768
SF            500.1300122 MHz
WDW                    no
SSB       0
LB        0 Hz
GB        0
PC                   1.00
```




```
Current Data Parameters
NAME                  rk9 f
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20150211
Time                 16.30
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      25
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                    1150
DW                  16.800 usec
DE                   6.50 usec
TE                  298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7703643 MHz
NUC1                   13C
P1                    7.50 usec
PLW1           63.66600037 W

======== CHANNEL f2 ========
SFO2           500.1320005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           27.19599915 W
PLW12           0.34419000 W
PLW13           0.22028001 W

F2 - Processing parameters
SI                    32768
SF           125.7577747 MHz
WDW                      EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

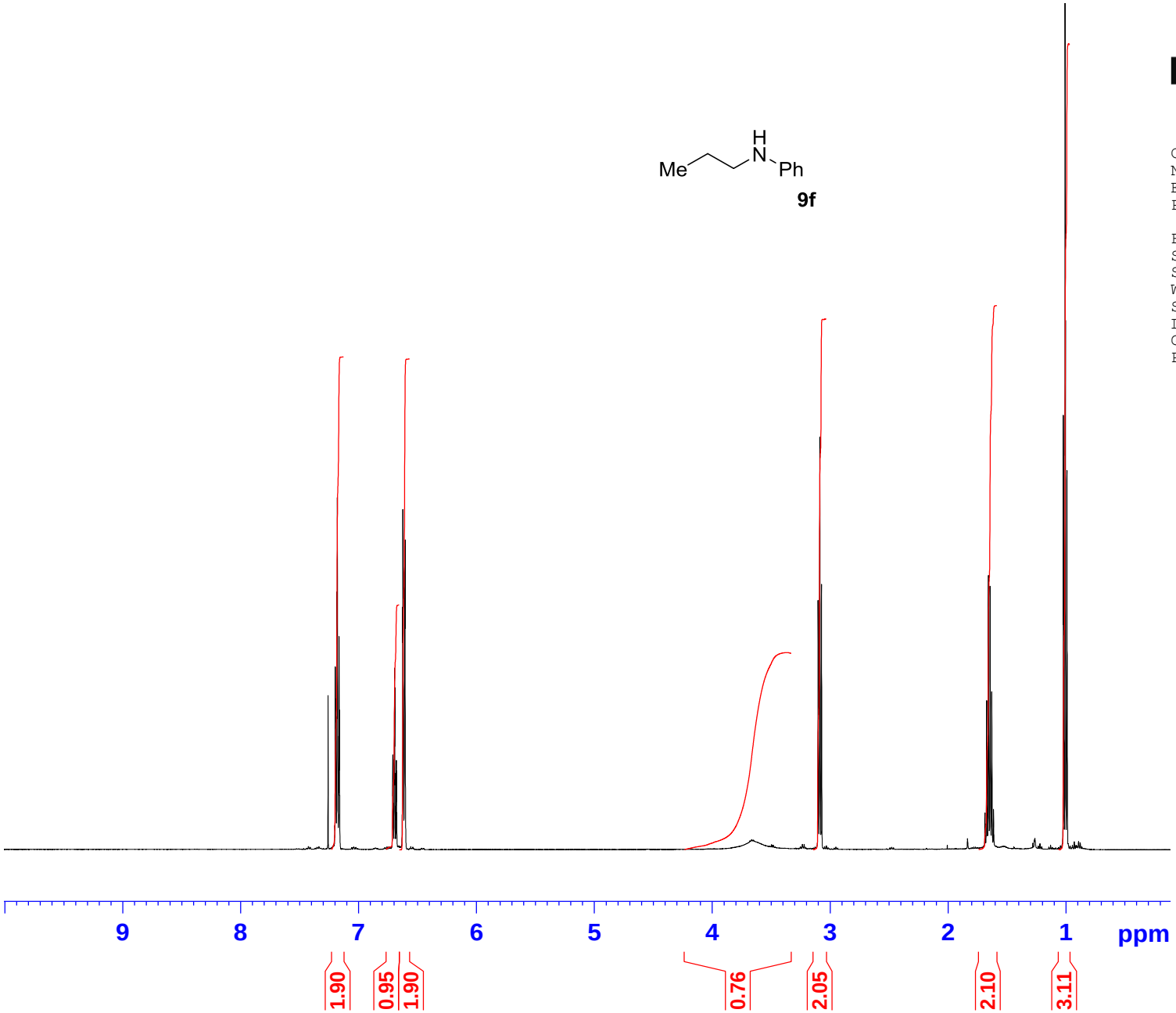



```
Current Data Parameters
NAME      AM1328 PROTON_01.fid
EXPNO                       1
PROCNO                      1

F2 - Processing parameters
SI                      32768
SF           500.0586944 MHz
WDW                        no
SSB       0
LB        0 Hz
GB        0
PC                      1.00
```



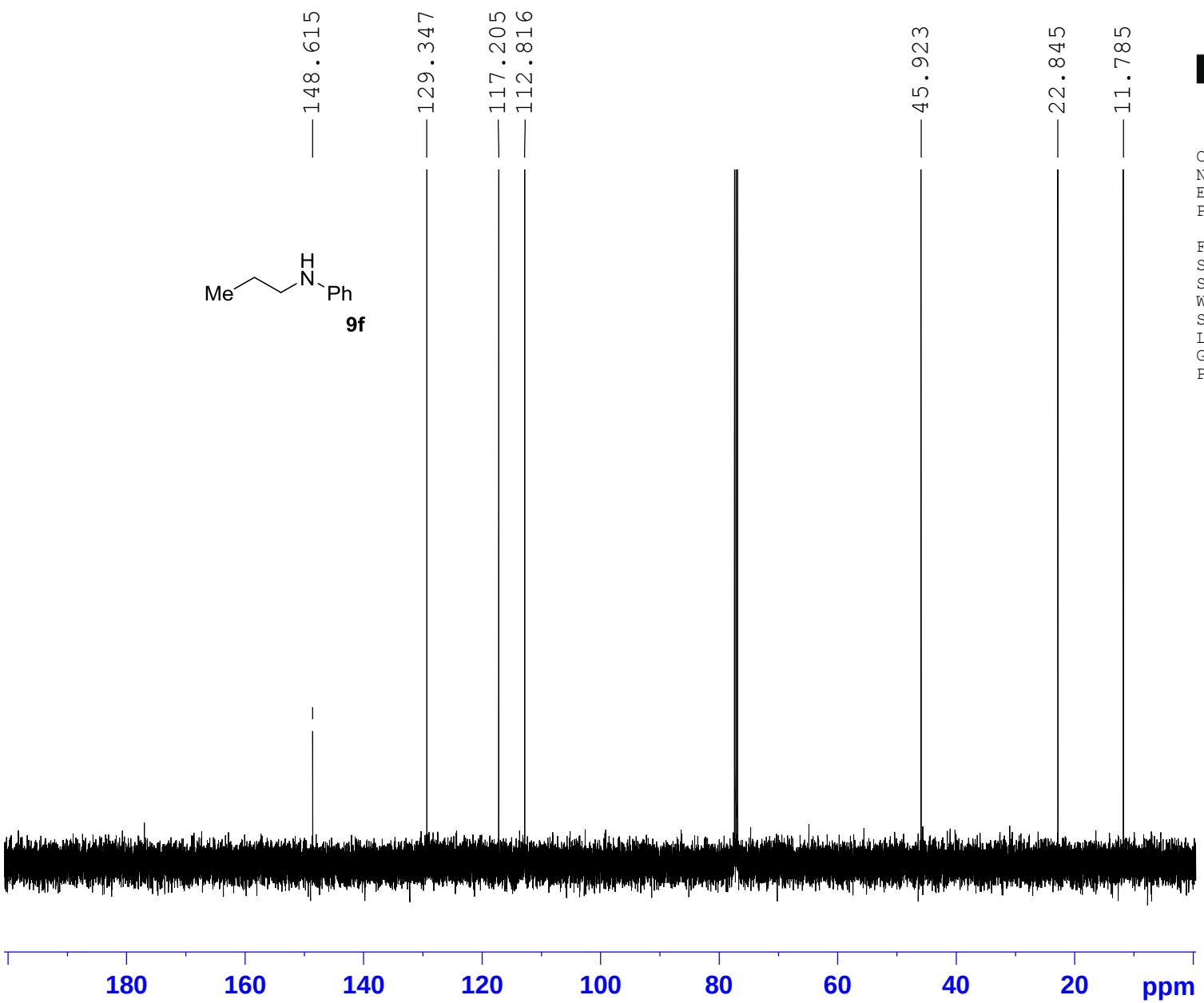
Current Data Parameters
NAME AM1328 CARBON_01.fid
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 125.7416275 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AM1321 PROTON_01.fid
EXPNO 1
PROCNO 1

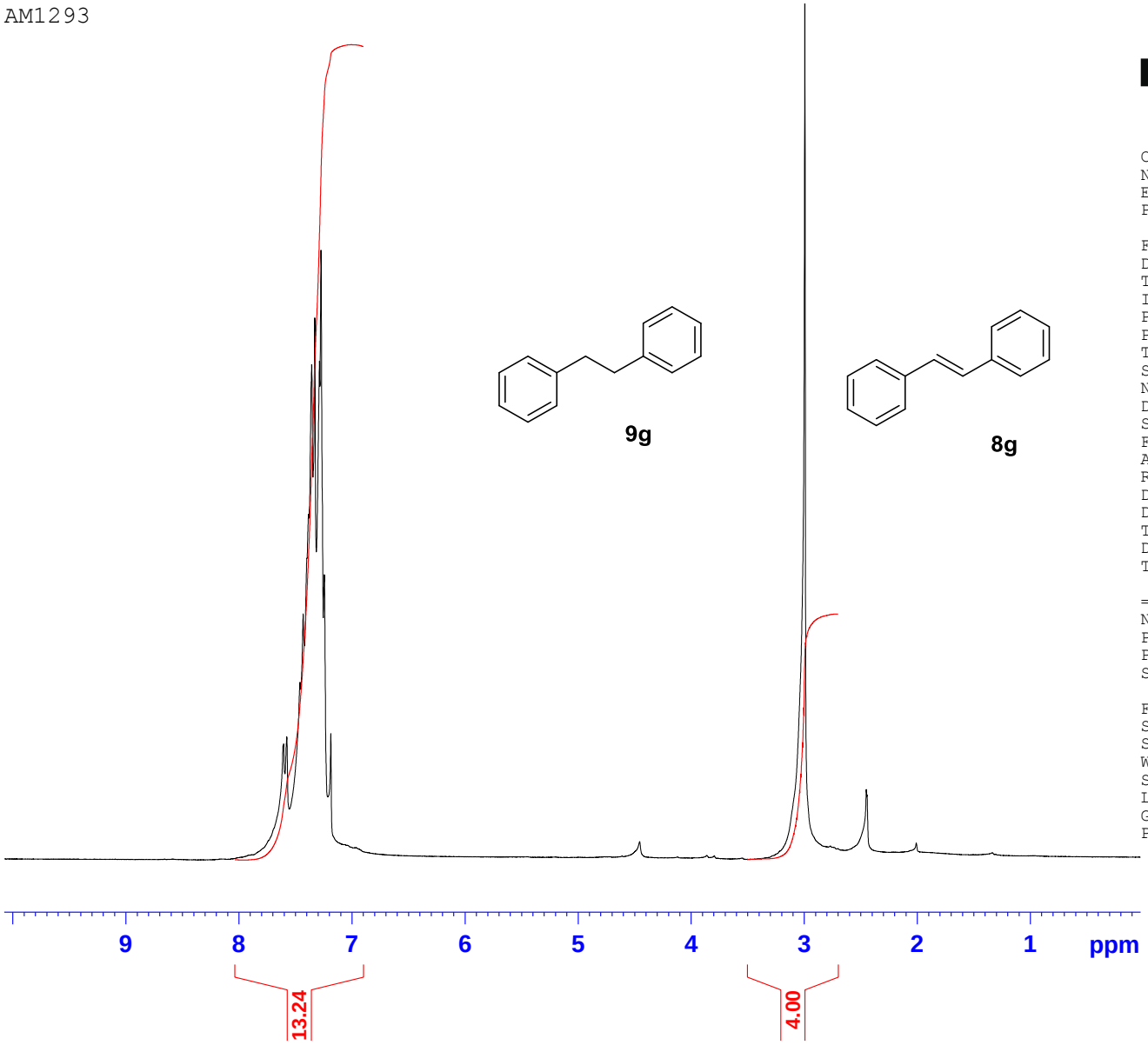
F2 - Processing parameters
SI 32768
SF 500.0586939 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00



Current Data Parameters
NAME AM1321 CARBON_01.fid
EXPNO 1
PROCNO 1

F2 - Processing parameters
SI 65536
SF 125.7416317 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

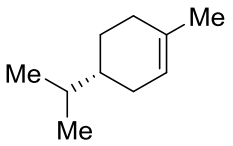
AM1293




```
Current Data Parameters
NAME            10272014
EXPNO                 40
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141027
Time              17.04
INSTRUM           spect
PROBHD   5 mm DUL 1H-13
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            5175.983 Hz
FIDRES         0.157958 Hz
AQ             3.1653888 sec
RG                  128
DW                96.600 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                11.00 usec
PL1       0 dB
SFO1        250.1315450 MHz

F2 - Processing parameters
SI                32768
SF          250.1300000 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

Data Filename	AM1397 3h.D	**Sample Name**	
Sample Type		**Position**	134
Instrument Name	5977MSD	**User Name**	mh
Acq Method	Liquid DB-FFAP (MeCN).M	**Acquired Time**	18/02/15 1:38:12 AM
IRM Calibration Status	Not Applicable	**DA Method**	default.m
Comment			

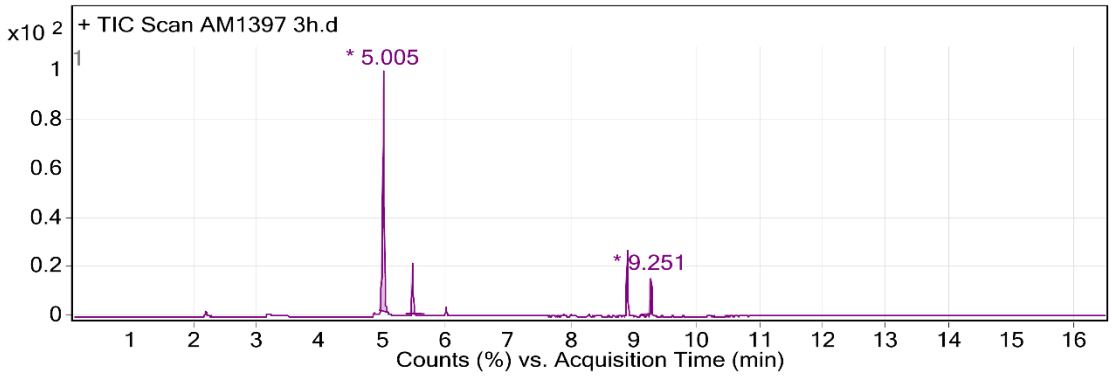
Expected Barcode		**Sample Amount**	
Dual Inj Vol	1	**TuneName**	ATUNE.U
TunePath	D:\MassHunter\GCMS\1\5977\	**MSFirmwareVersion**	6.00.19
OperatorName	mh	**RunCompletedFlag**	True
Acquisition SW Version	MassHunter GC/MS Acquisition B.07.00 SP2.1654 29-Aug-2013 Copyright © 1989-2013 Agilent Technologies, Inc.		



9h

User Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified



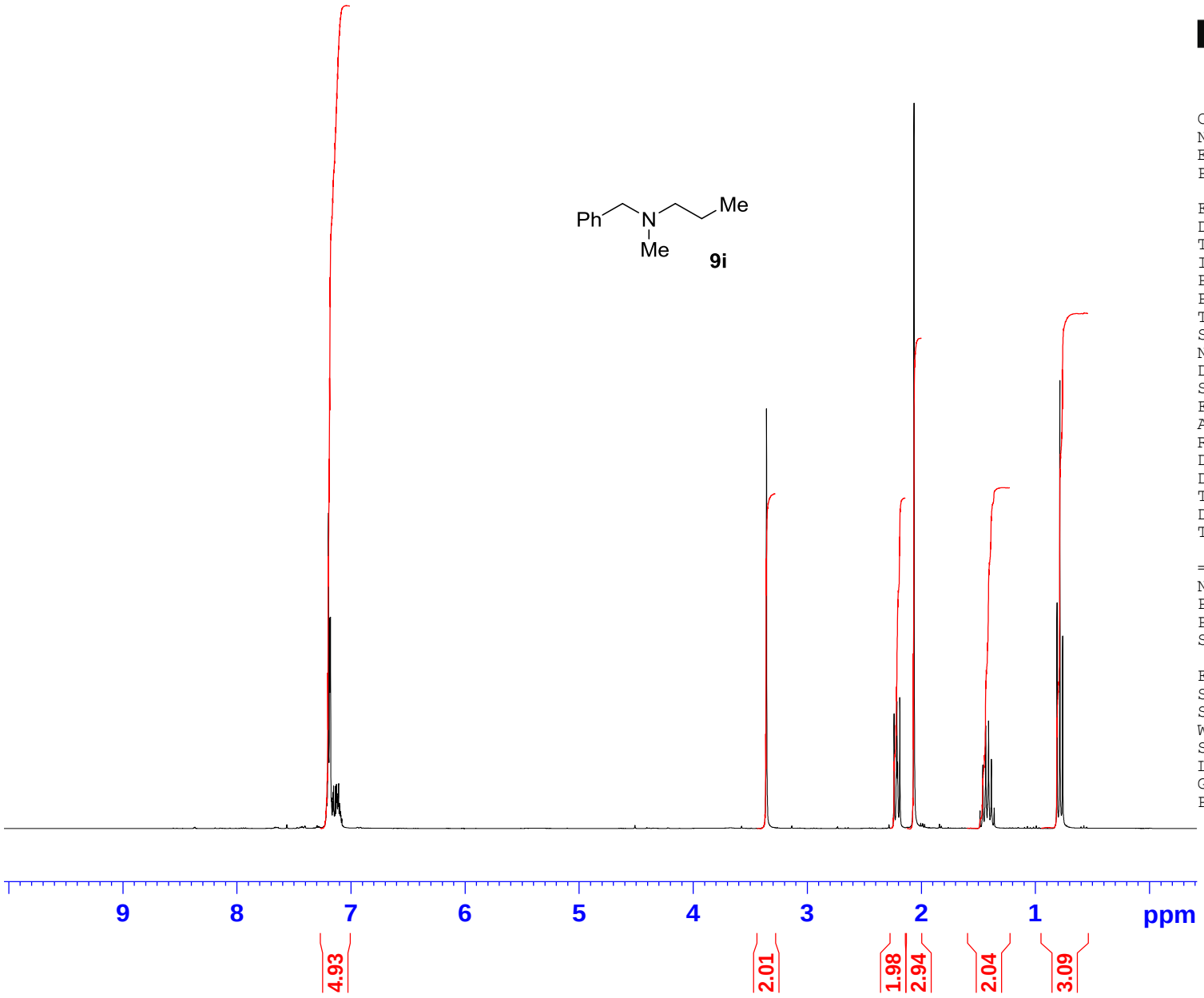
Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	4.952	5.005	5.112	12823742.67	21750142.66	100
2	5.374	5.463	5.677	2802796.79	3828479.4	17.6
3	9.12	9.251	9.263	1973335.38	2173125.79	9.99

User Spectra

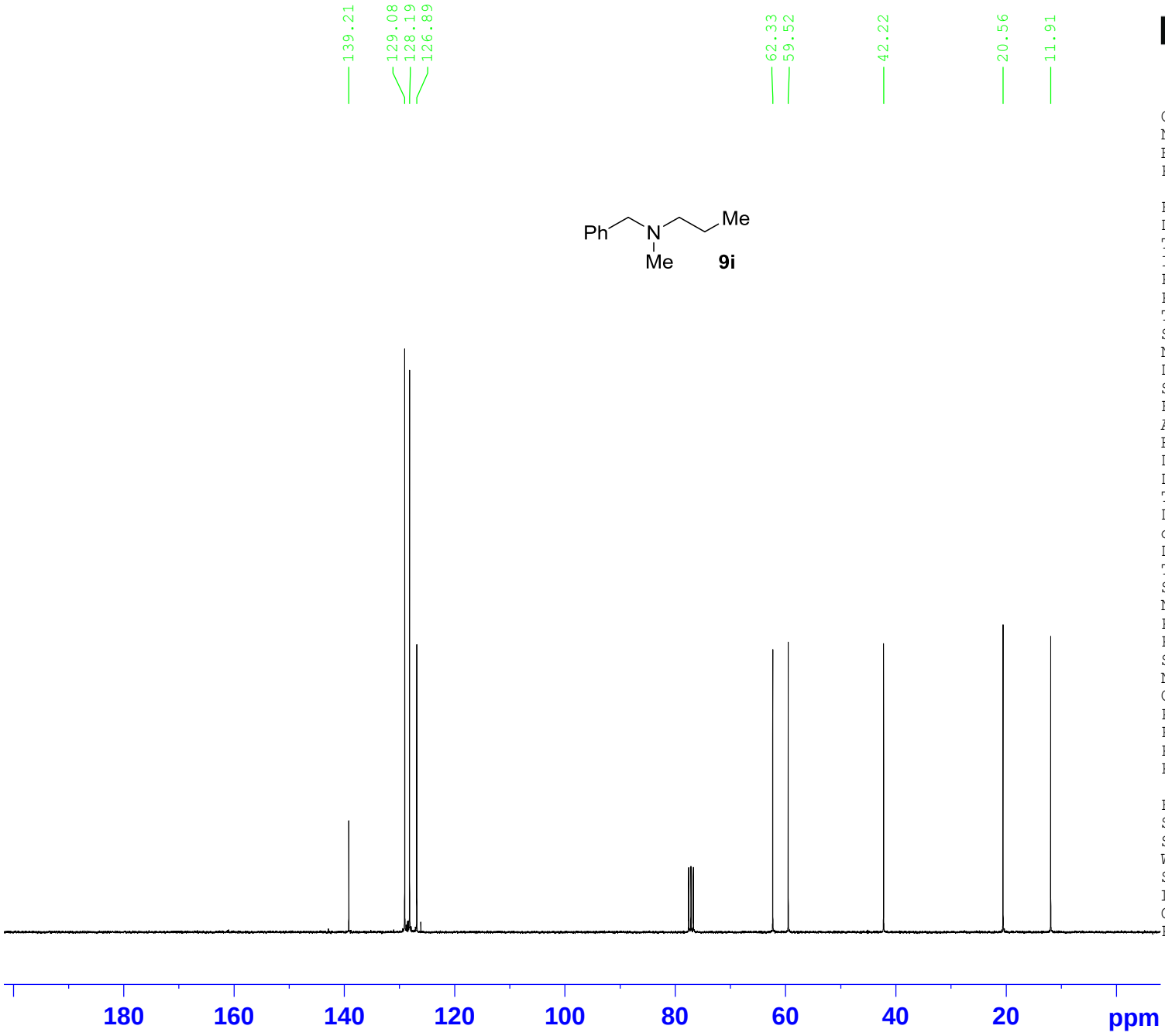
Collision Energy 0 **Ionization Mode** Unspecified

AM1285



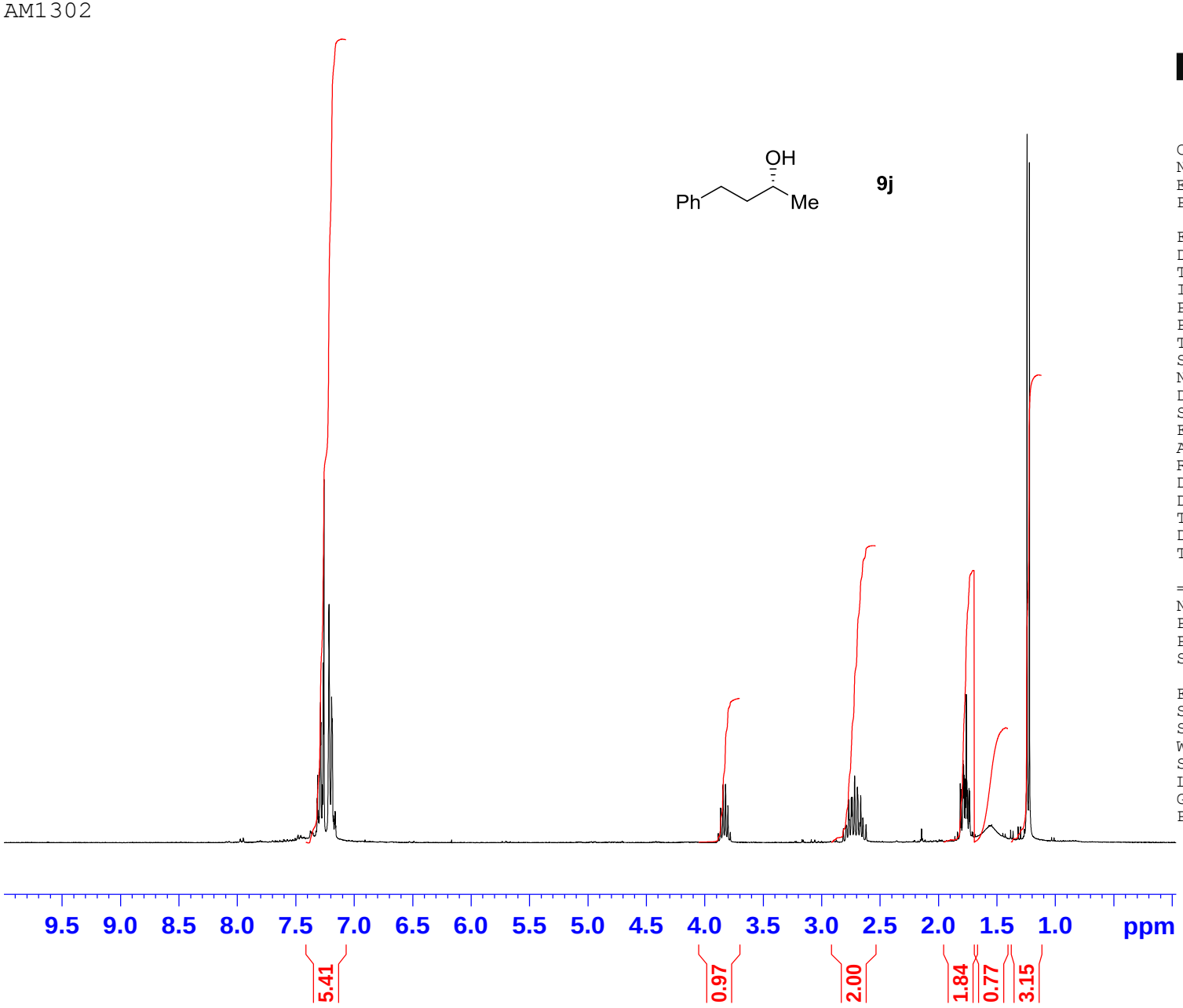

```
Current Data Parameters
NAME          Oct15-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141015
Time               19.21
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ             2.6542079 sec
RG                    32
DW                81.000 usec
DE                 6.00 usec
TE                291.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200494 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1285



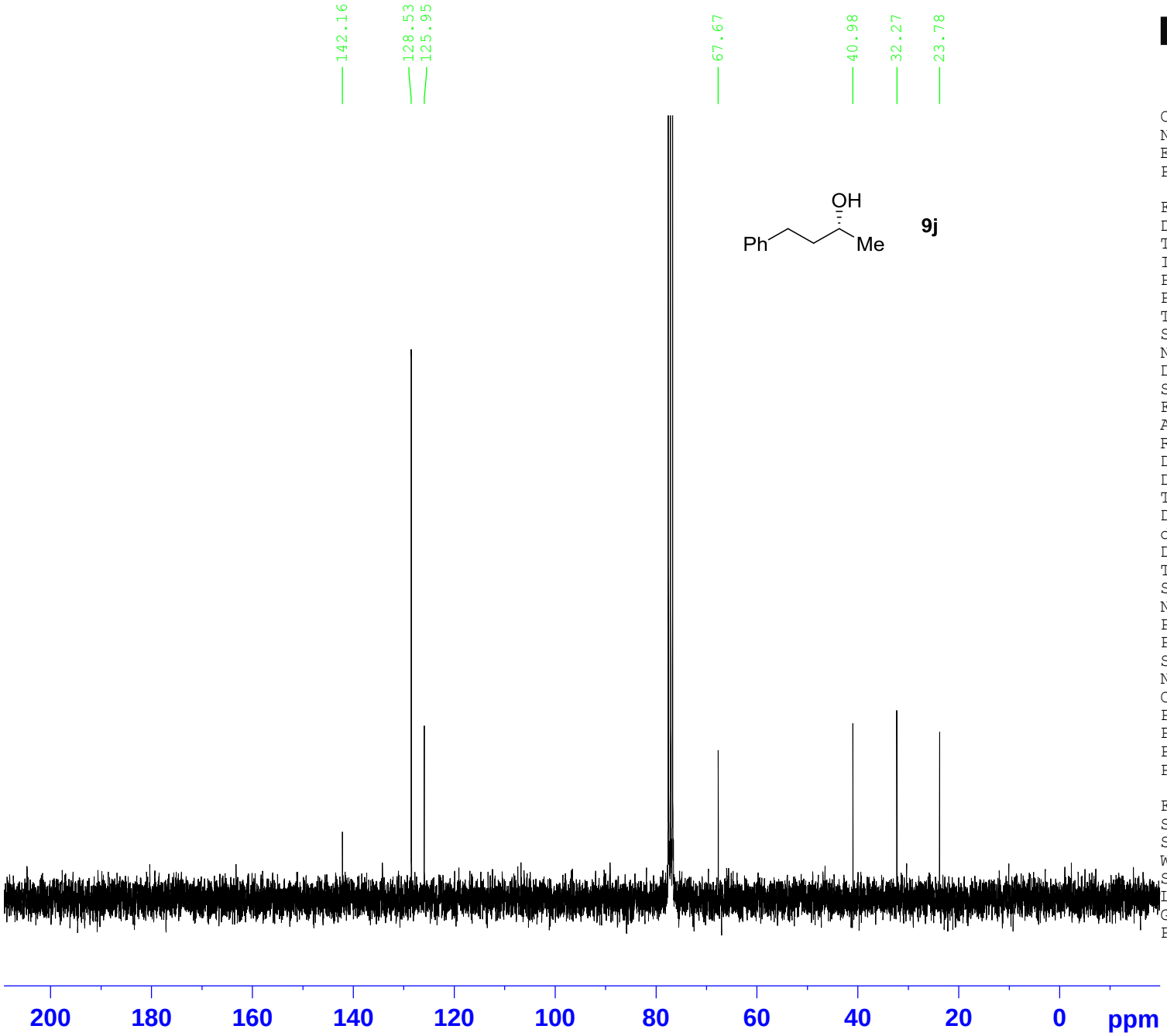

```
Current Data Parameters
NAME          Oct15-2014
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141015
Time              19.39
INSTRUM           av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           20325.203 Hz
FIDRES         0.310138 Hz
AQ            1.6121856 sec
RG                16384
DW               24.600 usec
DE                6.00 usec
TE                291.4 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1
SFO1          75.4990304 MHz
NUC1                 13C
P1                7.50 usec
PLW1         -1.00000000 W
SFO2         300.2212009 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                65536
SF           75.4903809 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

AM1302




```
Current Data Parameters
NAME          Nov03-2014
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141103
Time               15.07
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             6172.839 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                 456.1
DW                81.000 usec
DE                 6.00 usec
TE                291.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.40 usec
PL1               -1.50 dB
SFO1         300.2218540 MHz

F2 - Processing parameters
SI                 32768
SF           300.2200023 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

AM1302




```
Current Data Parameters
NAME          Nov03-2014
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141103
Time               15.24
INSTRUM            av300
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     2
SWH            20325.203 Hz
FIDRES          0.310138 Hz
AQ             1.6121856 sec
RG                18390.4
DW                24.600 usec
DE                 6.00 usec
TE                291.8 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                    1
SFO1           75.4990304 MHz
NUC1                  13C
P1                 7.50 usec
PLW1          -1.00000000 W
SFO2          300.2212009 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             80.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                 65536
SF            75.4903699 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

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