Supplementary information for

Amidine Dications: Isolation and [Fe]-Hydrogenase-Related Hydrogenation

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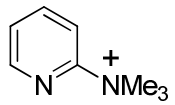
General experimental details:

All reagents were purchased from Alfa Aesar, Aldrich of Fluorochem Ltd., with the exception of d_3-acetonitrile, which was purchased from Goss Scientific Instruments Ltd. d_3-Acetonitrile and acetonitrile were distilled from P_2O_5 (0.5-1.0 mol%) under argon. Dry ether and toluene were obtained from an Innovative Technology Inc., Pure Solv dry solvent system. All glassware was oven or flame-dried prior to use. Hydrogenation reactions were carried out on a Cook hydrogenation apparatus (Chas W. Cook and Sons, Ltd., Scientific apparatus makers, model 583-11-71-6) with a 700 ml glass reaction vessel using either hydrogen or deuterium (Boc gases). Infra-red spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. NMR spectra were recorded in a Bruker DPX400 spectrometer, Bruker AV400 spectrometer or Bruker DPX500 spectrometer. High and low resolution mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre, Swansea on a JLZX 102, VGZAB-E or at the University of Strathclyde on a JEOL JMS-AX505HA instrument. Melting points (mp) were carried out on Griffin melting point apparatus and are uncorrected. Flash chromatography was performed using aluminium sheets of silica gel 60 F_{254}. Glovebox experiments were carried out in an Innovative Technology Inc., System One glovebox under oxygen-free, moisture-free conditions.

Trimethylpyridin-2-ylammonium Trifluoromethanesulfonate 16 [1]



16 $\overline{\text{OTf}}$

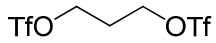
Methyl trifluoromethanesulfonate (0.47 ml, 5.0 mmol, 1.0 eq) was added dropwise to a solution of 2-DMAP (0.62 ml, 0.5 mmol, 1.0 eq) in dry DCM (1 ml) under argon at –78 °C. The reaction mixture was warmed to rt. and stirred for 18 h. Dry toluene (2 ml) was added to the reaction mixture and stirred for 30 min. The toluene was decanted and the white solid was washed with toluene (2 ml).

The white solid was collected and dried *in vacuo*. The reaction mixture was recrystallised from ethanol/ether to give trimethylpyridin-2-ylammonium trifluoromethanesulfonate **16** (0.906 g, 63 %) as white needles; mp 109-110 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ= 3.54 (s, 9H; CH_3), 7.64 (ddd, *J*(H,H)= 7.3, 4.7, 1.0 Hz, 1H; ArH), 7.85 (dd, *J*(H,H)= 8.5, 0.7 Hz, 1H; ArH), 8.13 (ddd, *J*(H,H) 8.5, 7.3, 1.8 Hz, 1H, ArH), 8.61 (ddd, *J*(H,H)= 4.7, 1.8, 0.7, 1H; ArH); ^{13}C NMR (100 MHz, d_6-DMSO) 54.5 (CH_3), 115.2 (CH), 120.7 (q, *J*(H,F)= 319 Hz; CF_3) 126.2 (CH), 141.1 (CH), 148.6 (CH), 156.7 (C); IR (KBr disc) $\tilde{\nu}$= 3128, 3076, 3042, 2973, 1600, 1576, 1497, 1474, 1439, 1265, 1165, 1029, 997, 847, 790, 745, 638, 574, 519; MS (ESI) 137 (100) $[M\text{-}OTf]^+$; HRMS: *m*/*z* calcd for $C_8H_{13}N_2$ $[M\text{-}OTf]^+$: 137.1073; found: 137.1075.

Attempted Hydrogenation of Trimethylpyridin-2-ylammonium Trifluoromethanesulfonate 16

A solution of trimethylpyridin-2-ylammonium trifluoromethanesulfonate **16** (0.284 g, 1.0 mmol, 1.0 eq) and palladium on activated carbon (10 wt%, 0.011 g, 0.01 mmol, 1 mol%) in dry acetonitrile (20 ml) was transferred to the Cook hydrogenation vessel. The vessel was evacuated using a vacuum pump and filled with hydrogen gas (54 psi). The reaction mixture was shaken for 3 h, and then returned to atmospheric pressure. Methyl trifluoromethanesulfonate (0.12 ml, 1.1 mmol, 1.1 eq) was added to the reaction mixture to methylate any pyridine that may have been formed during the reaction (and hence to facilitate its detection). The reaction mixture was filtered through celite and the celite was rinsed with acetonitrile (20 ml). The acetonitrile layers were combined and the solvent was removed *in vacuo*. The residue was washed with dry ether (2 x 10 ml) to remove any excess methyl trifluoromethanesulfonate and the residue was evaporated *in vacuo* to give recovered trimethylpyridin-2-ylammonium trifluoromethanesulfonate **16** (0.280 g, 99 %) as a white solid.

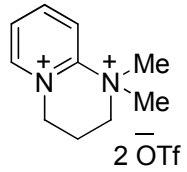
1,3-*Bis*(trifluoromethanesulfonyloxy)propane 17[2]



17

1,3-Propanediol (2.9 ml, 40.0 mmol, 1.0 eq) and pyridine (6.5 ml, 80 mmol, 2.0 eq) in dry DCM (20 ml) were added dropwise to a solution of trifluoromethanesulfonic anhydride (13.5 ml, 80.0 mmol, 2.0 eq) in dry DCM (100 ml) at –78 °C under argon. The reaction mixture was warmed to r.t. and stirred for 1 h to give a pink solution with a white precipitate. The reaction mixture was washed with distilled water (3 x 20 ml), dried over anhydrous Na_2SO_4 and filtered through silica gel (40 g). The silica gel was washed with DCM (50 ml) and combined with the first washing. The solvent was removed *in vacuo* to give 1,3-*bis*(trifluoromethanesulfonyloxy)propane **17** (12.510 g, 92 %) as a red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 2.38 (quintet, J(H,H)= 5.8 Hz, 2H; CH_2-CH_2-CH_2), 4.69 (t, J(H,H)= 5.8 Hz, 4H; CH_2-OTf); ^{13}C NMR (125 MHz, $CDCl_3$) 29.6 (CH_2), 71.6 (CH_2), 118.9 (q, J(H,F)= 322 Hz; CF_3); IR (thin film) $\tilde{\nu}$= 2991, 1417, 1248, 1207, 929, 854, 812, 735, 614, 581.

2-DMAP Disalt 18

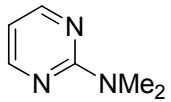


18

2-DMAP (2.48 ml, 20.0 mmol, 1.0 eq) was added using a syringe pump (1.27 ml.h^{-1}) to a flask containing 1,3-*bis*(trifluoromethanesulfonyloxy)propane **17** (8.165 g, 24.0 mmol, 1.2 eq) at 0 ºC under argon. A white solid began to precipitate out of the reaction mixture. After addition of half of the 2-DMAP **15**, dry ether (4 ml) was added to the reaction mixture to allow stirring

to continue. After the addition of all the 2-DMAP, the reaction mixture was stirred at 0 ºC for 1 h, then warmed to rt. The resulting white powder was stirred with dry ether (30 ml) for 30 min, and then filtered and the residual solvent removed *in vacuo*. The powder was recrystallised from dry acetonitrile/ether to give *2-DMAP disalt* **18** (9.089 g, 98 %) as a white solid; mp 113-116 ºC; ^{1}H NMR (400 MHz, CD_3CN) δ= 2.67 (tt, *J*(H,H)= 6.2, 5.7 Hz, 2H; CH_2-CH_2-CH_2), 3.82 (s, 6H; N-CH_3), 4.15 (t, *J*(H,H)= 5.7 Hz, 2H; N-CH_2), 4.90 (t, *J*(H,H)= 6.2 Hz, 2H; N-CH_2), 8.22 (ddd *J*(H,H)= 7.5, 6.3, 1.1 Hz, 1H; ArH), 8.57 (dd, *J*(H,H)= 8.2, 1.6 Hz, 1H; ArH), 8.79-8.84 (m, 2H; ArH); ^{13}C NMR (125 MHz, CD_3CN) 17.6 (CH_2), 56.9 (CH_2), 60.4 (CH_3), 63.4 (CH_2), 122.0 (q, *J*(C,F)= 324 Hz; CF_3), 124.5 (CH), 130.7 (CH), 148.9 (CH), 151.3 (C), 151.5 (CH); IR (KBr disc) $\tilde{\nu}$= 3136, 3102, 3080, 3050, 1638, 1591, 1519, 1488, 1452, 1256, 1228, 1155, 1033, 992, 962, 780, 636, 575, 519; MS (ESI) 313 (20) $[M\text{-}OTf]^+$, 181 (10), 163 (15), 149 (8), 123 (7), 82 (100) $[M\text{-}2OTf]^{2+}$; HRMS: *m*/*z* calcd for $C_{11}H_{16}O_3N_2F_3S$ $[M\text{-}OTf]^+$: 313.0828; found: 313.0826. The structure was supported by X-ray crystallography. See section B, page S13-S14.

2-Dimethylaminopyrimidine 19

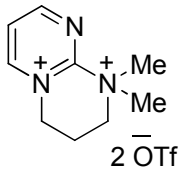


19

Dimethylamine solution (40% in water, 10.5 ml, 60 mmol, 3.0 eq) was added to a solution of 2-bromopyrimidine (3.180 g, 20 mmol, 1.0 eq) in acetonitrile (60 ml) under argon and stirred for 18 h. The reaction mixture was filtered through a plug of potassium carbonate, which was then washed with acetonitrile (50 ml). The solvent was removed *in vacuo* to give 2-dimethylaminopyrimidine **19** (2.3217 g, 94%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 3.19 (s, 3H; NCH_3) 6.45 (t, *J*(H,H)= 4.5 Hz, 1H; ArH), 8.31 (d, *J*(H,H) 4.5 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) 37.2 (CH_3), 109.0 (CH), 157.7 (CH), 162.4 (C); IR (thin film) $\tilde{\nu}$= 2936,

2863, 2793, 1754, 1591, 1549, 1404, 1379, 1312, 1206, 1085, 988, 799, 638, 515; MS (CI) 124 (100) $[M+H]^+$, 114 (5), 110 (7), 58 (5), 52 (36), 46 (5) 44 (10); HRMS: *m/z* calcd for $C_6H_{10}N_3$ $[M+H]^+$: 124.0869; found: 124.0868.

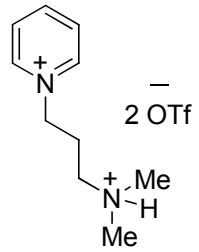
2-Dimethylaminopyrimidine Disalt 20:



20

2-Dimethylaminopyrimidine **19** (0.616 g, 5.0 mmol, 1.0 eq) was added dropwise to a tube containing 1,3-*bis*(trifluoromethanesulfonyloxy)propane **17** (2.041 g, 6.0 mmol, 1.2 eq) in a glovebox. The reaction mixture was stirred for 1.5 h, then dry ether (1 ml) was added to the reaction mixture and stirred for a further 30 min causing an orange solid to precipitate. The solid was filtered and the residual solvent was removed *in vacuo*. Recrystallisation from dry acetonitrile/ether in a glovebox gave *2-dimethylaminopyrimidine disalt* **20** (1.508 g, 65%) as an off-white solid; mp 160-163 ºC; ^{1}H NMR (500 MHz, CD_3CN) δ= 2.73 (tt, *J*(H,H)= 6.3, 5.7 Hz, 2H; CH_2-CH_2-CH_2), 3.85 (s, 6H; N-CH_3), 4.27 (t, *J*(H,H)= 5.7 Hz, 2H; N-CH_2), 4.99 (t, *J*(H,H)= 6.3 Hz, 2H; N-CH_2), 8.37 (dd *J*(H,H)= 6.2, 4.8 Hz, 1H; ArH), 9.21 (dd, *J*(H,H)= 6.2, 1.9 Hz, 1H; ArH), 9.50 (dd *J*(H,H)= 4.8, 1.9 Hz, 1H; ArH); ^{13}C NMR (125 MHz, CD_3CN) 17.4 (CH_2), 57.6 (CH_2), 59.3 (CH_3), 62.3 (CH_2), 122.0 (q, *J*(C,F)= 320 Hz; CF_3), 127.3 (CH), 154.3 (C), 157.9 (CH), 168.4 (CH); IR (KBr disc) $\tilde{\nu}$= 3167, 3114, 3083, 2985, 2935, 2879, 1749, 1634, 1599, 1565, 1495, 1479, 1443, 1376, 1259, 1155, 1031, 988, 902, 877, 837, 828, 771, 639, 575, 517; MS (ESI) 432 (38), 314 (100) $[M\text{-}OTf]^+$, 196 (38), 182 (13), 164 (46), 150 (26), 124 (17), 103 (31), 83 (54) $[M\text{-}2OTf]^{2+}$; HRMS: *m/z* calcd for $C_{10}H_{15}O_3N_3F_3S$ $[M\text{-}OTf]^+$: 314.0781; found 314.0782.
The structure was supported by X-ray crystallography. See section B, page S15-S16.

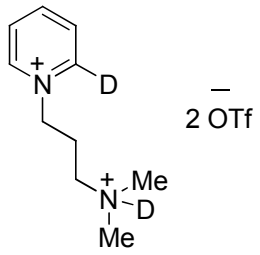
Hydrogenation of 2-DMAP Disalt 14 to afford pyridinium salt 23



23

A solution of 2-DMAP disalt **18** (0.462 g, 1.0 mmol, 1.0 eq) and palladium on activated carbon (10 wt%, 0.011 g, 0.01 mmol, 1 mol%) in dry acetonitrile (20 ml) was transferred to the Cook hydrogenation vessel. The vessel was evacuated using a vacuum pump and filled with hydrogen gas (52 psi). The reaction mixture was shaken for 3 h, and then returned to atmospheric pressure. The reaction mixture was filtered through celite and the celite was rinsed with acetonitrile (20 ml). The acetonitrile layers were combined and the solvent was removed *in vacuo* to give *1-(3-dimethylammoniopropyl)pyridinium trifluoromethanesulfonate* **23** (0.458 g, 99 %) as a viscous brown oil; ^{1}H NMR (400 MHz, CD_3CN) δ= 2.36-2.44 (m, 2H; CH_2), 2.85 (d, J(H,H) = 5.2 Hz, 6H; NCH_3), 3.17-3.22 (m, 2H; CH_2), 4.59 (t, J(H,H) = 7.6 Hz, 2H; CH_2), 7.64 (bs, 1H; NH), 8.08 (t, J(H,H) = 7.1 Hz, 2H; ArH), 8.55 (t, J(H,H) = 7.9 Hz, 1H; ArH), 8.74 (d, J(H,H) = 5.8 Hz, 2H; ArH); ^{13}C NMR (100 MHz, CD_3CN) 27.0 (CH_2), 44.3 (CH_3), 55.2 (CH_2), 59.3 (CH_2), 122.0 (q, J(C,F)= 322 Hz; CF_3), 129.6 (CH), 145.8 (CH), 147.4 (CH); IR (thin film) $\tilde{\nu}$= 3511, 3140, 3072, 2792, 1638, 1492, 1258, 1227, 1163, 1030, 969, 776, 758, 686, 639, 575, 518; MS (ESI) 315 (52) $[M\text{-}OTf]^+$, 225 (4), 200 (7), 182 (3), 165 (100) $[M\text{-}H\text{-}2OTf]^+$; HRMS: m/z calcd for $C_{11}H_{18}O_3N_2F_3S$ $[M\text{-}OTf]^+$: 315.0985; found: 315.0985.

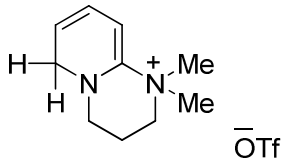
Deuteration of 2-DMAP Disalt 18 to afford pyridinium salt 24



24

A solution of 2-DMAP disalt (0.462 g, 1.0 mmol, 1.0 eq) and palladium on activated carbon (10 wt%, 0.011 g, 0.01 mmol, 1 mol%) in dry acetonitrile (20 ml) was transferred to the Cook hydrogenation vessel. The vessel was evacuated using a vacuum pump and filled with deuterium gas (54 psi). The reaction mixture was shaken for 3 h, then returned to atmospheric pressure. The reaction mixture was filtered through celite and the celite was rinsed with acetonitrile (20 ml). The acetonitrile layers were combined and the solvent was removed *in vacuo* to give *deuterated pyridinium salt* **24** (0.458 g, 99 %) as a viscous brown oil; ^{1}H NMR (500 MHz, CD_3CN) δ= 2.38-2.44 (m, 2H; CH_2), 2.84 (s, 6H; NCH_3), 3.20 (t, *J*(H,H) = 8.0 Hz, 2H; CH_2), 4.61 (t, *J*(H,H) = 7.5 Hz, 2H; CH_2), 8.06-8.08 (m, 2H; ArH), 8.55 (ddd, *J*(H,H) = 7.9, 7.8, 0.9, 1H; ArH), 8.78 (d, J(H,H) = 5.8 Hz, 1H; ArH); ^{13}C NMR (125 MHz, CD_3CN) 27.0 (CH_2), 44.3 (CH_3), 55.2 (CH_2), 59.3 (CH_2), 122.0 (q, *J*(C,F) = 320 Hz, CF_3), 129.6 (CH/CD), 129.7 (CH/CD), 145.8 (CH), 147.4 (CH); IR (thin film) $\tilde{\nu}$= 3501, 3060, 2787, 2303, 1627, 1471, 1255, 1160, 1030, 803, 758, 638, 574, 517; MS (ESI) 488 (13) 316 (48) [M-^{2}H-OTf+H]$^{+}$, 185 (36), 166 (100) [M-H-2OTf]$^{+}$, 130 (16); HRMS: *m*/*z* calcd for $C_{11}H_{17}{}^{2}H_1O_3N_2F_3S$ [M-^{2}H-OTf+H]$^{+}$: 316.1048; found: 316.1050; *m*/*z* calcd for $C_{10}H_{16}{}^{2}H_1N_2$ [M-^{2}H-2OTf]$^{+}$: 166.1449; found: 166.1447. (We note that exchange of one D atom is retained in the mass spectrum sample).

1,1-Dimethyl-1,3,4,6-tetrahydro-2*H*-pyrido[1,2-α]pyrimidin-1-ium Trifluoromethanesulfonate 25



25

Lithium aluminium hydride (0.076 g, 2.0 mmol, 2.0 eq) was added to a solution of 2-DMAP dication **18** (0.462 g, 1.0 mmol, 1.0 eq) in dry acetonitrile (10 ml) and stirred at r.t. under argon for 3 h. The reaction mixture was filtered through celite and the solvent was removed *in vacuo*. Purification by column chromatography using silica gel (CH_3CN/DCM 1:1) gave *1,1-dimethyl-1,3,4,6-tetrahydro-2H-pyrido[1,2-α]pyrimidin-1-ium trifluoromethanesulfonate* **25** (0.200 g, 64 %) as a pale orange solid; mp 110 ºC (dec.); ^{1}H NMR (400 MHz, d_6-DMSO) δ= 2.14 (tt, J(H,H) = 5.9, 5.9 Hz, 2H; CH_2), 3.00 (t, J(H,H) = 5.9 Hz, 2H; CH_2), 3.36 (s, 6H; NCH_3), 3.63 (t, J(H,H) = 5.9 Hz, 2H; CH_2), 3.85 (dd, J(H,H) = 4.2, 1.6, 2H; CH_2), 5.38 (dt, J(H,H) = 8.9, 4.2 Hz, 1H; CH), 5.86 (d, J(H,H) = 5.8 Hz, 1H; CH), 5.96-6.00 (m, 1H; CH); ^{13}C NMR (100 MHz, d_6-DMSO) 19.4 (CH_2), 48.8 (CH_2), 51.0 (CH_2), 52.3 (CH_3), 64.0 (CH_2), 99.1 (CH), 116.8 (CH), 120.7 (q, J(C,F)= 322 Hz; CF_3), 121.7 (CH), 147.1 (C); IR (KBr disc) $\tilde{\nu}$= 3060, 2926, 2857, 1654, 1590, 1488, 1471, 1413, 1293, 1252, 1174, 1049, 765, 733, 640, 515; MS (ESI) 479 (20), 165 (100) $[M\text{-}OTf]^+$; HRMS: m/z calcd for $C_{10}H_{17}N_2$ $[M\text{-}OTf]^+$: 165.1386; found: 165.1388.

References.

1. J. J. Folmer, C. Acero, D. L. Thai, H. Rapoport, *J. Org. Chem.*, **1998**, *63*, 8170-8182.
2. R. W. Alder, D. D. Ellis, R. Gleiter, C. J. Harris, H. Large, A. G. Orpen, D. Read and P. N. Taylor, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1657-1668.

Part B - **Crystallographic Data**.

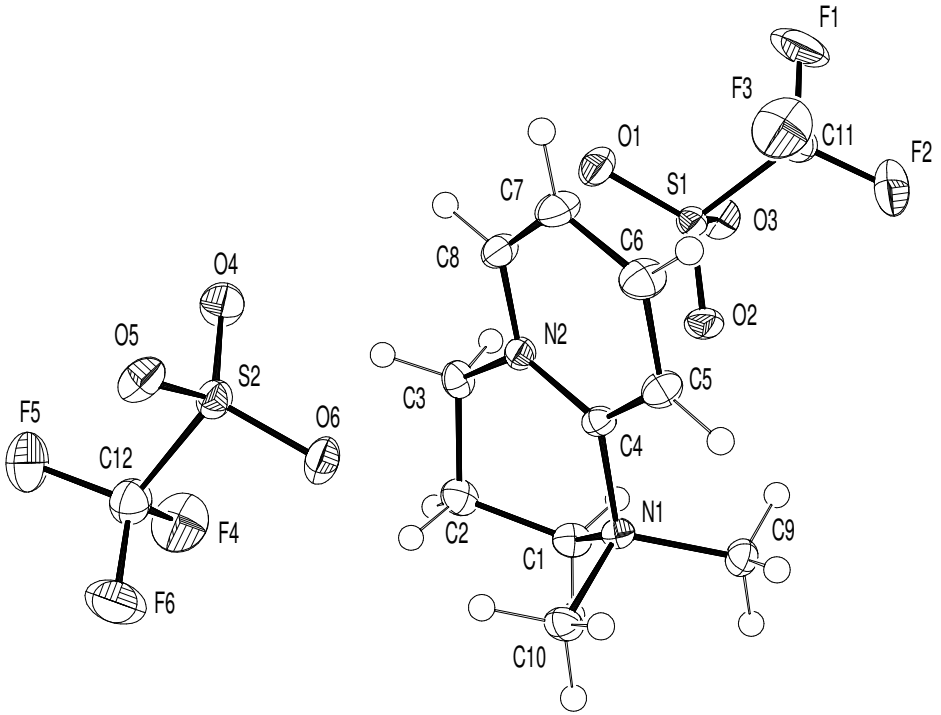
All measurements were made with an Oxford Diffraction Xcalibur S instrument.

Crystallographic data (excluding structure factors) for the compounds reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 708479 & 708480. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

CCDC 708479

Crystal Data for **18**: [CCDC 708479]

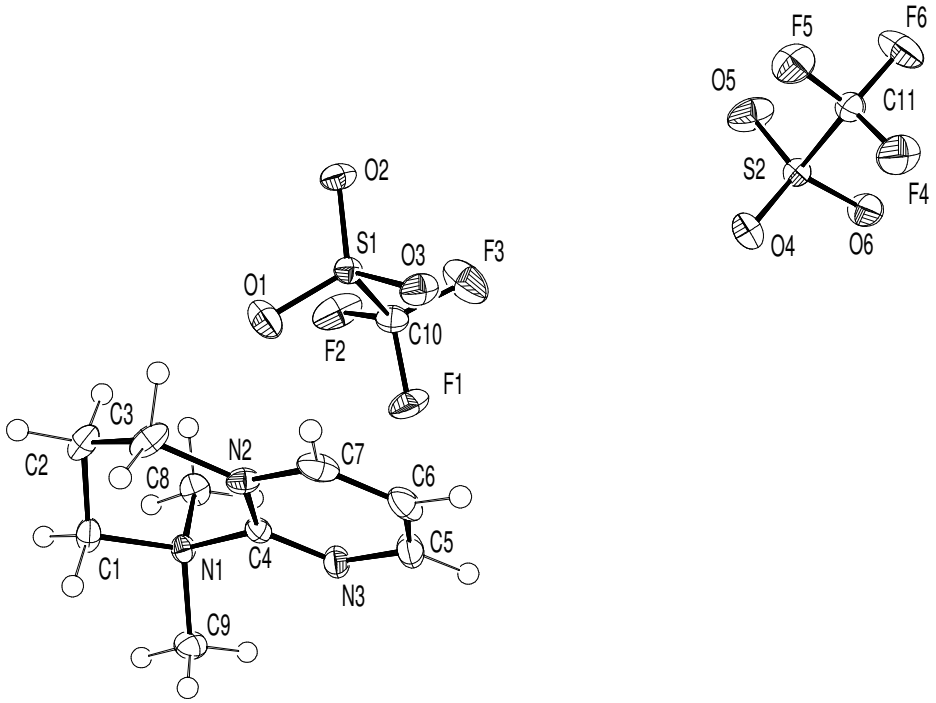
$C_{12}H_{16}F_6N_2O_6S_2$ Monoclinic space group $P2_1/n$, a = 8.2712(3) b = 22.5001(7) c = 10.3639(5) Å, β = 112.117(5) ° V = 1786.83(12) Å^3, T = 123 K, Z = 4, $2\theta_{max}$ = 60.0 °, MoK$_\alpha$ λ = 0.71073Å. Collected 15663 reflections, R_{int} = 0.0281. The structure was solved and refined on F^2 (SHELXS and SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany) to convergence at $R1$ = 0.0320 (for 3454 reflections with $I>2\sigma(I)$) $wR2$ = 0.0736 and S = 0.952 for 255 parameters and 4934 unique reflections. Minimum/maximum residual electron density –0.346/0.400 eÅ^{-3}.



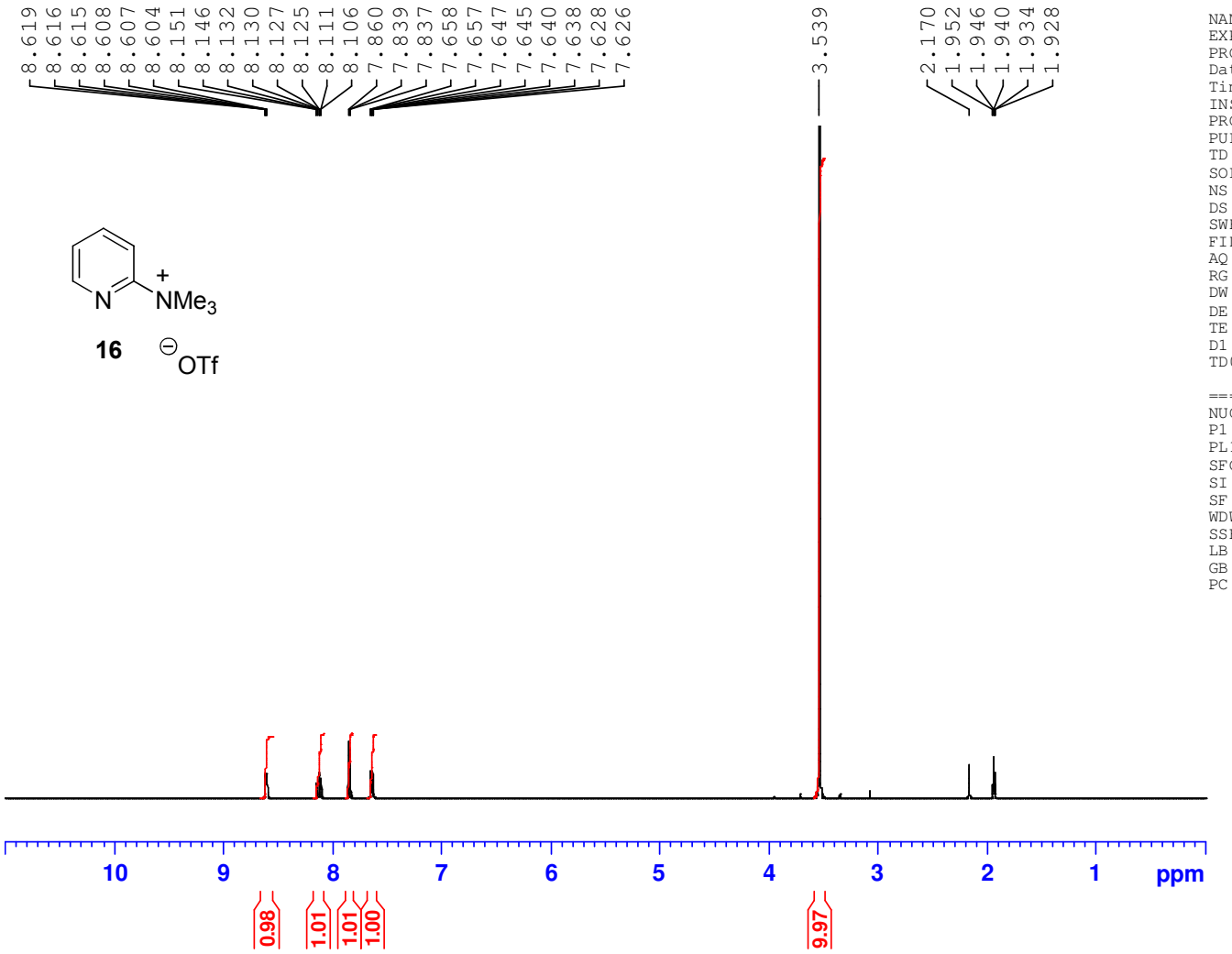
Above – ORTEP drawing of Compound **18** with all non-H atoms drawn as 50% probability ellipsoids.

Crystal Data for **20**: [CCDC 708480]

$C_{11}H_{15}F_6N_3O_6S_2$ Monoclinic space group $P2_1/c$, a = 9.3365(8) b = 14.1848(12) c = 13.2684(10) Å, β = 95.355(8) ° V = 1749.5(2) Å^3, T = 123 K, Z = 4, $2\theta_{max}$ = 61.44 °, MoK_α λ = 0.71073Å. Collected 16200 reflections, R_{int} = 0.0249. The structure was solved and refined on F^2 (SHELXS and SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany) to convergence at $R1$ = 0.0389 (for 4112 reflections with $I>2\sigma(I)$) $wR2$ = 0.1110 and S = 1.113 for 255 parameters and 4957 unique reflections. Minimum/maximum residual electron density –0.515/0.648 eÅ^{-3}.



Above – ORTEP drawing of Compound **20** with all non-H atoms drawn as 50% probability ellipsoids.



BRUKER

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PROCNO	1
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SOLVENT	CD3CN
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.252629 Hz
AQ	1.9792372 sec
RG	181
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
TD0	1

======== CHANNEL f1 ========

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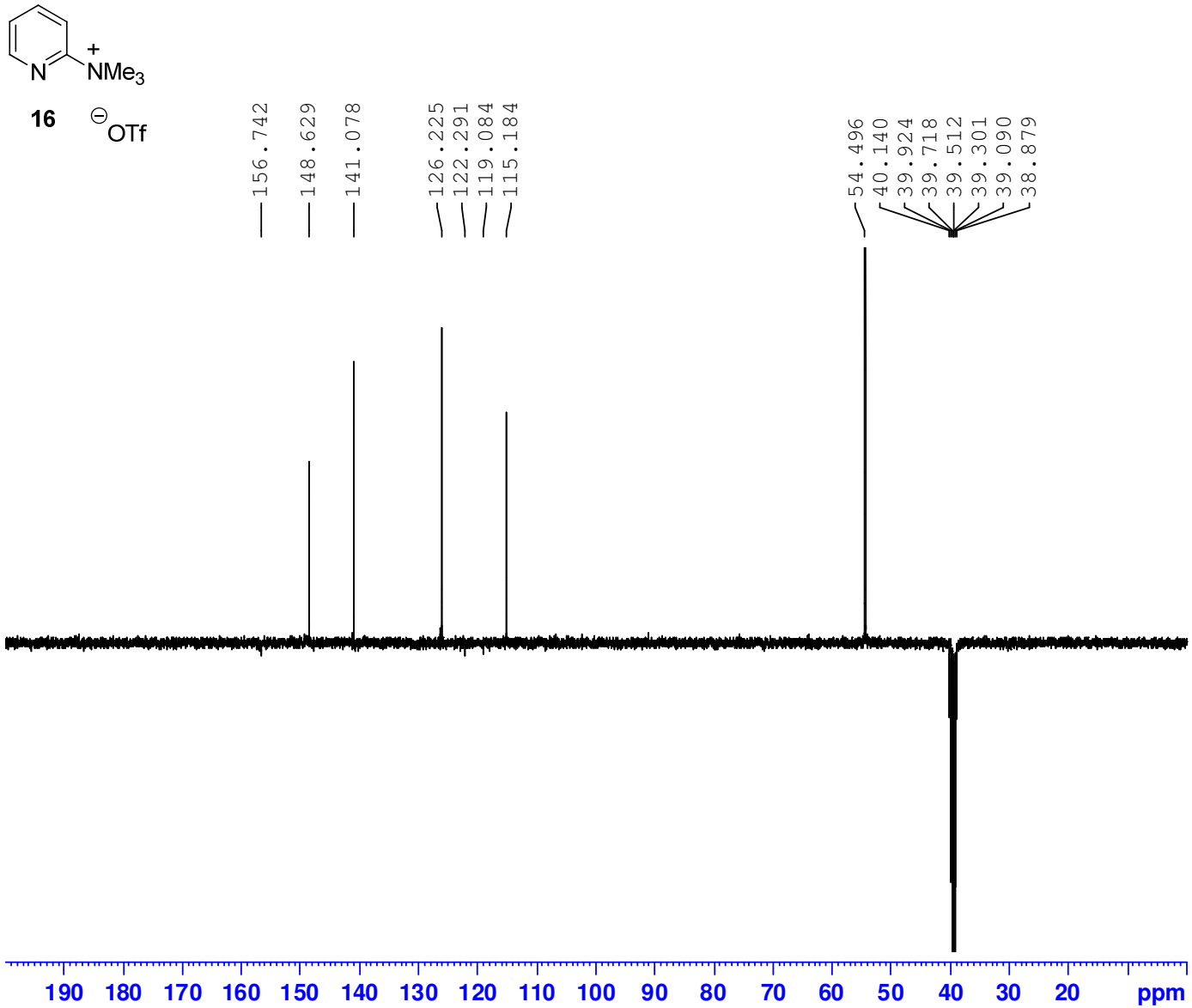
P1	12.00 usec
PL1	-2.50 dB
SFO1	400.0324703 MHz
SI	32768
SF	400.0300084 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

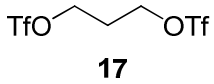


BRUKER

```
NAME                 D110559
EXPNO                      2
PROCNO                     1
Date_               20080501
Time                   1.04
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                 jmod
TD                     16384
SOLVENT                DMSO
NS                      512
DS                        4
SWH              23980.814 Hz
FIDRES            1.463673 Hz
AQ               0.3416564 sec
RG                     4096
DW                   20.850 usec
DE                    6.00 usec
TE                   296.2 K
CNST2           145.0000000
CNST11            1.0000000
D1               4.00000000 sec
d20              0.00689655 sec
DELTA            0.00001019 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    8.00 usec
p2                   16.00 usec
PL1                  -2.60 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.00 dB
SFO2           400.1316005 MHz
SI                    32768
SF             100.6128147 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```



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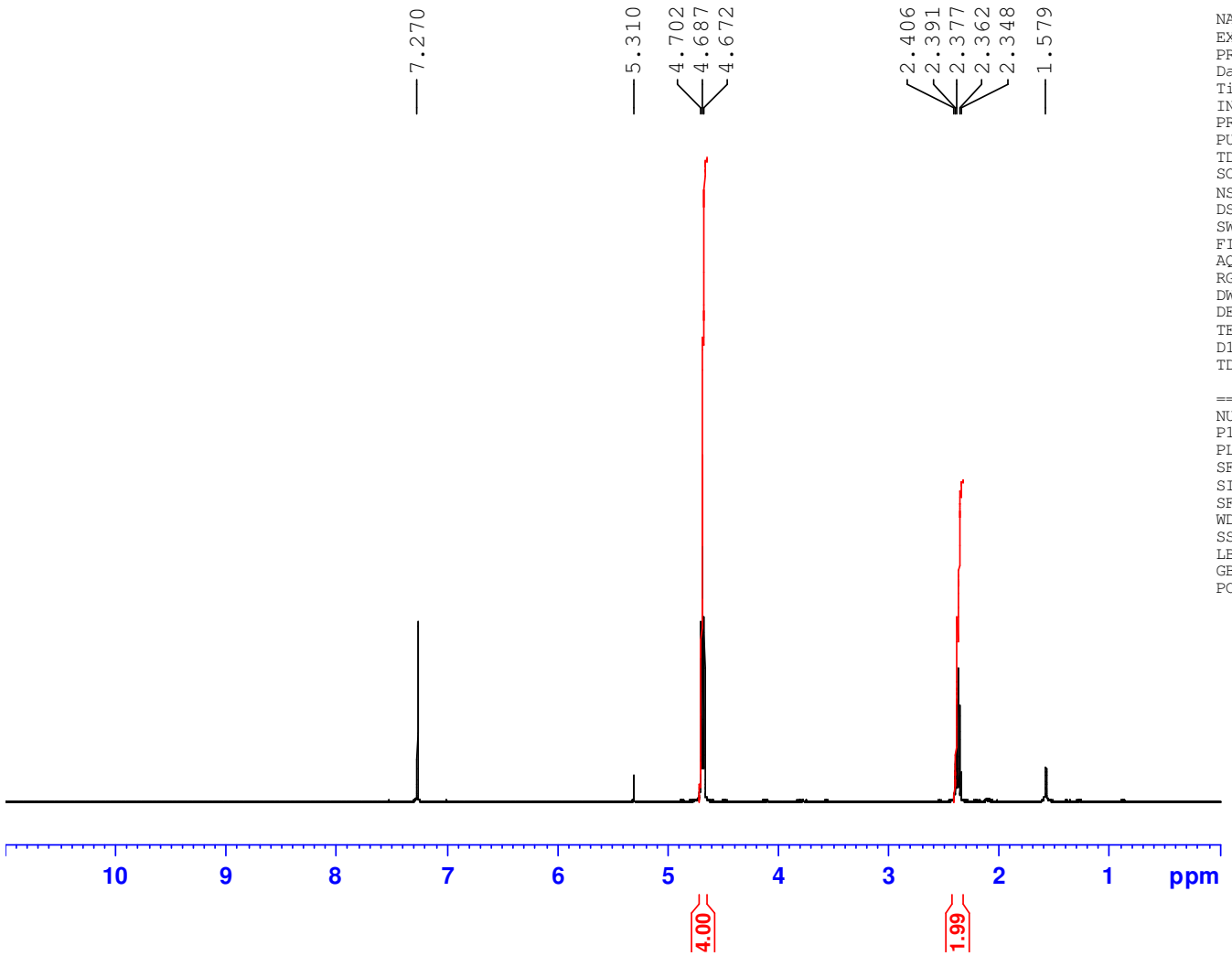
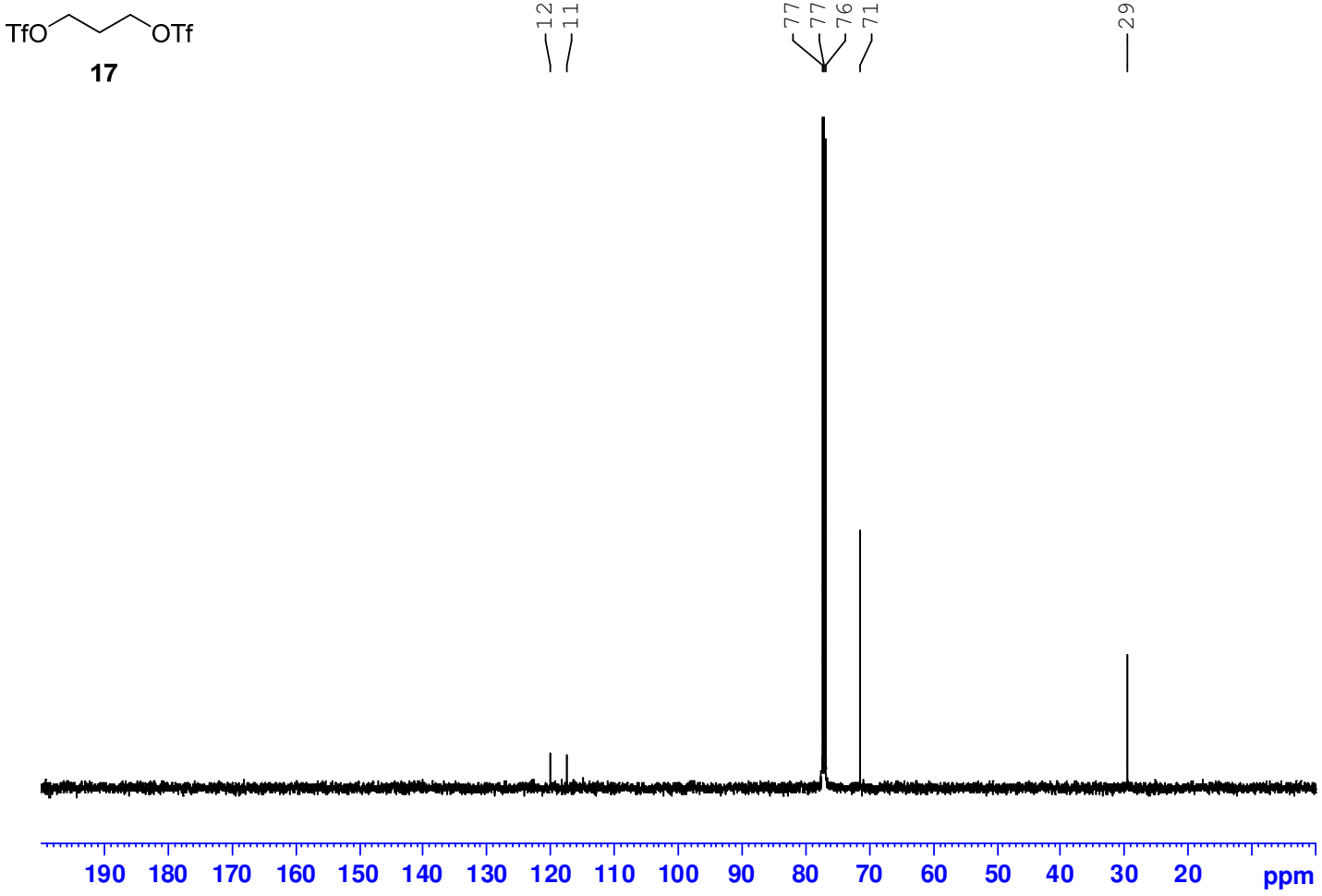
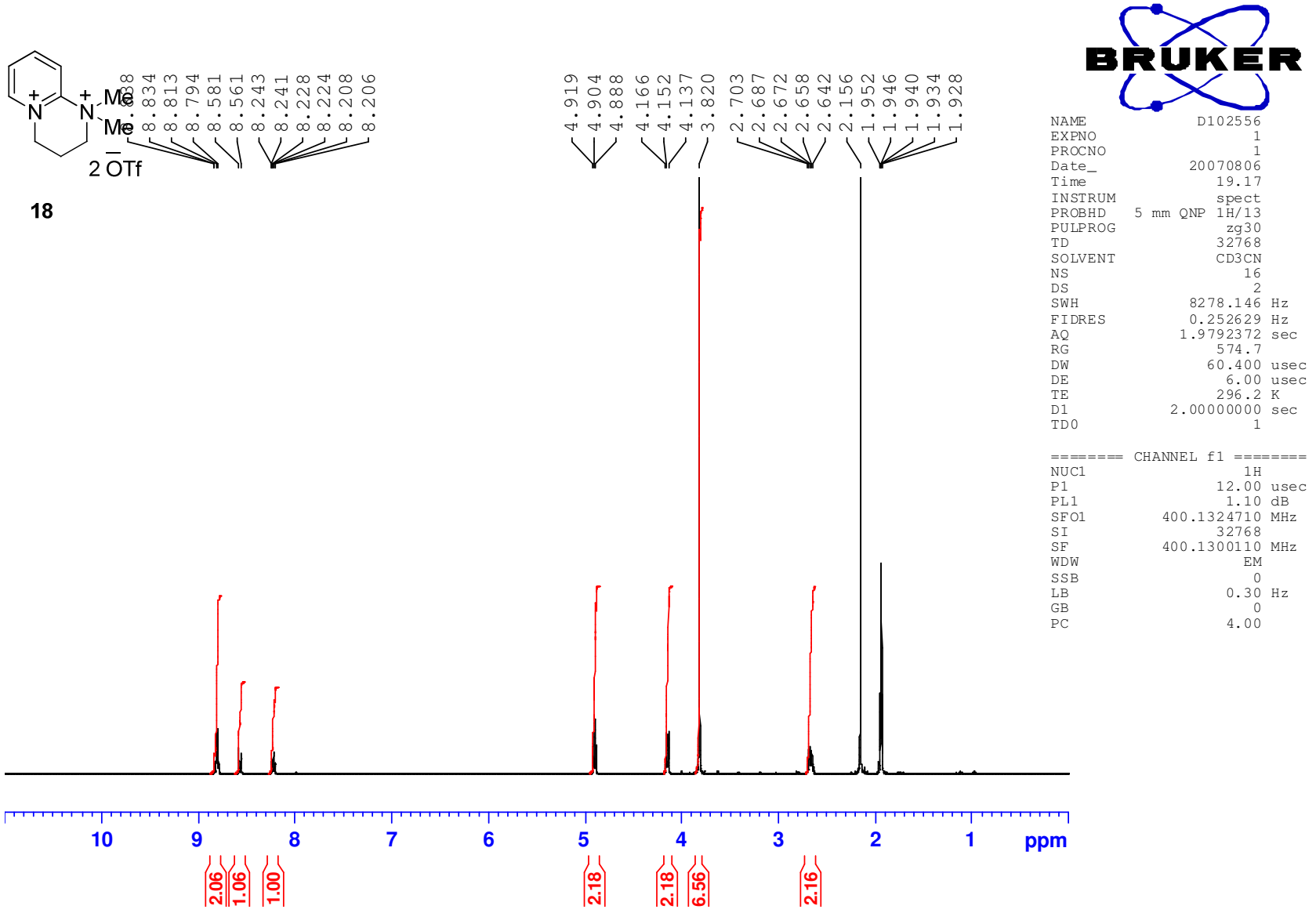



```
NAME                 D98391
EXPNO                     1
PROCNO                    1
Date_              20070418
Time                  1.51
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES             0.252629 Hz
AQ                 1.9792372 sec
RG                     645.1
DW                    60.400 usec
DE                     6.00 usec
TE                    296.2 K
D1              2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                     1.10 dB
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300053 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     4.00
```




```
NAME                A05717
EXPNO                    1
PROCNO                   1
Date_             20080806
Time                 17.10
INSTRUM              DRX500
PROBHD   5 mm DUL 13C-1
PULPROG             zgpg30
TD                   16384
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              30120.482 Hz
FIDRES            1.838408 Hz
AQ               0.2720244 sec
RG                  9195.2
DW                  16.600 usec
DE                   6.00 usec
TE                  300.0 K
D1              0.69999999 sec
d11             0.03000000 sec
DELTA           0.59999996 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.00 usec
PL1                  -2.30 dB
SFO1           125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -2.30 dB
PL12                 15.00 dB
PL13                120.00 dB
SFO2           500.1320005 MHz
SI                   32768
SF             125.7577602 MHz
WDW                    EM
SSB                     0
LB                   2.00 Hz
GB                      0
PC                   1.40
```

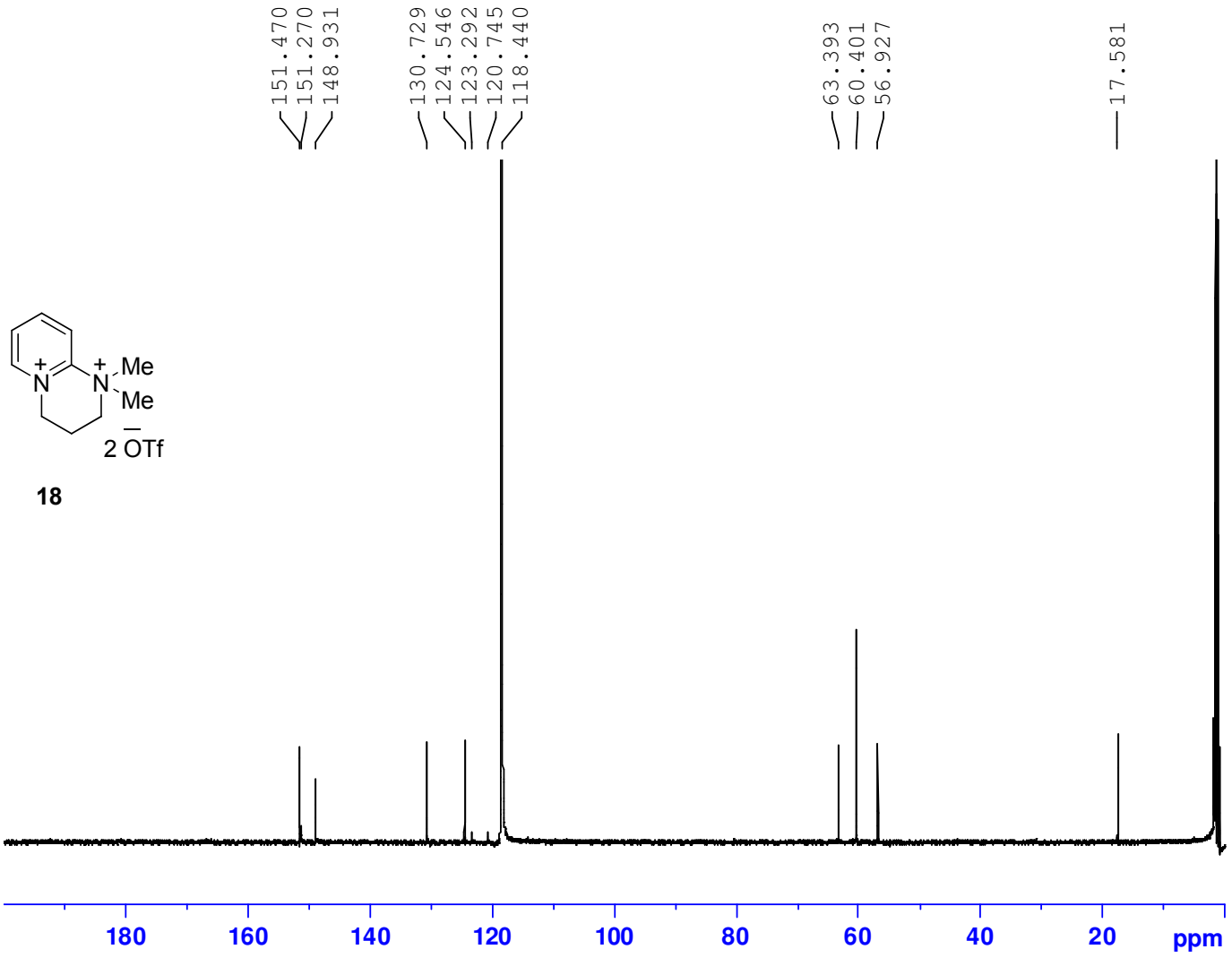


BRUKER

NAME	D102556
EXPNO	1
PROCNO	1
Date_	20070806
Time	19.17
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CD3CN
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.252629 Hz
AQ	1.9792372 sec
RG	574.7
DW	60.400 usec
DE	6.00 usec
TE	296.2 K
D1	2.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
P1	12.00 usec
PL1	1.10 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300110 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	4.00



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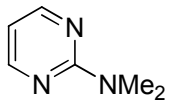
```
NAME                A00761
EXPNO                    1
PROCNO                   1
Date_             20070904
Time                 13.37
INSTRUM              DRX500
PROBHD   5 mm DUL 13C-1
PULPROG            zgpg30
TD                   16384
SOLVENT              CD3CN
NS                    1024
DS                       4
SWH           30120.482 Hz
FIDRES         1.838408 Hz
AQ            0.2720244 sec
RG                    8192
DW                16.600 usec
DE                 6.00 usec
TE                 300.0 K
D1            0.69999999 sec
d11           0.03000000 sec
DELTA         0.59999996 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1                -2.30 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                -2.30 dB
PL12               15.00 dB
PL13              120.00 dB
SFO2        500.1320005 MHz
SI                 32768
SF          125.7576543 MHz
WDW                   EM
SSB                    0
LB                2.00 Hz
GB                     0
PC                 1.40
```



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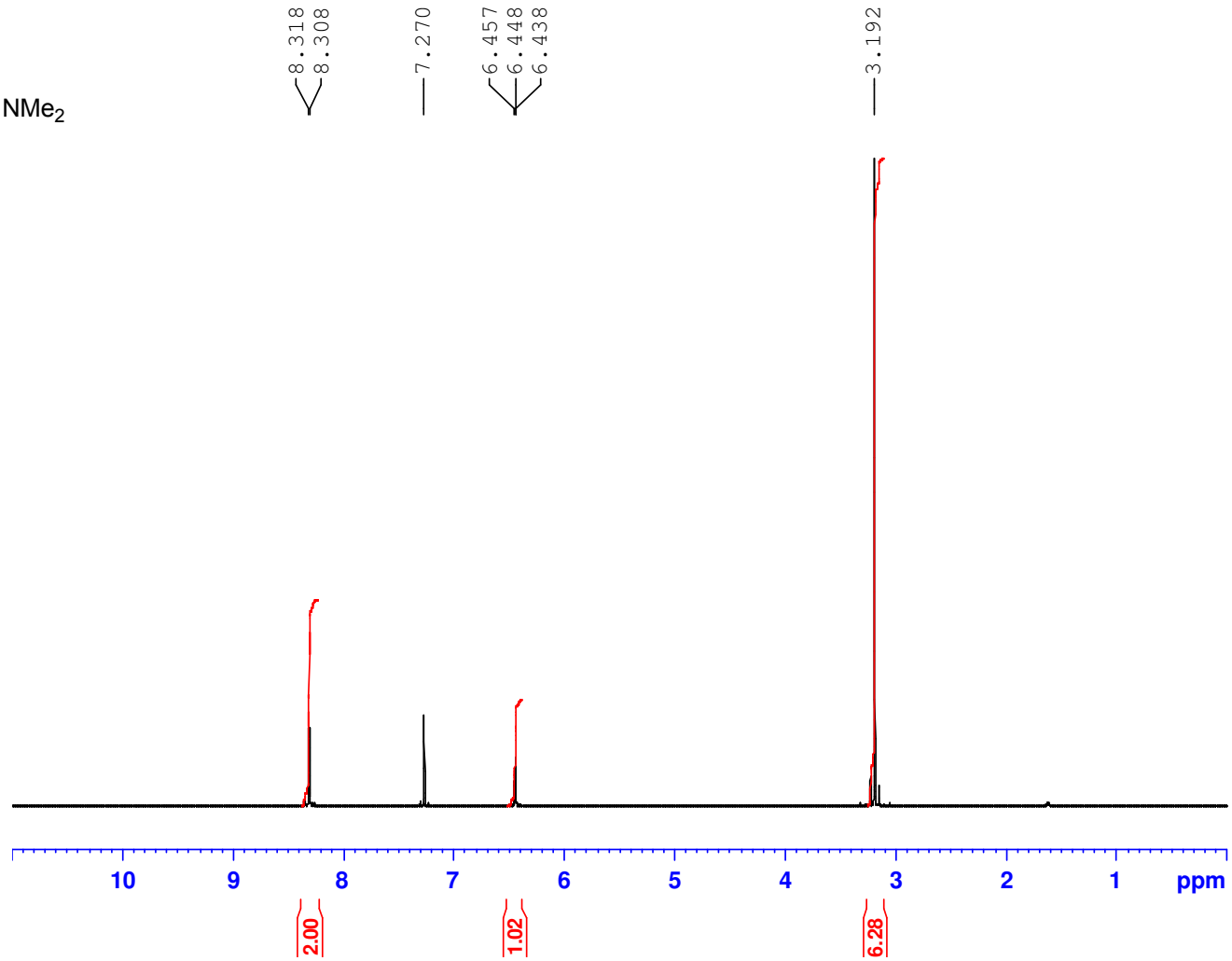
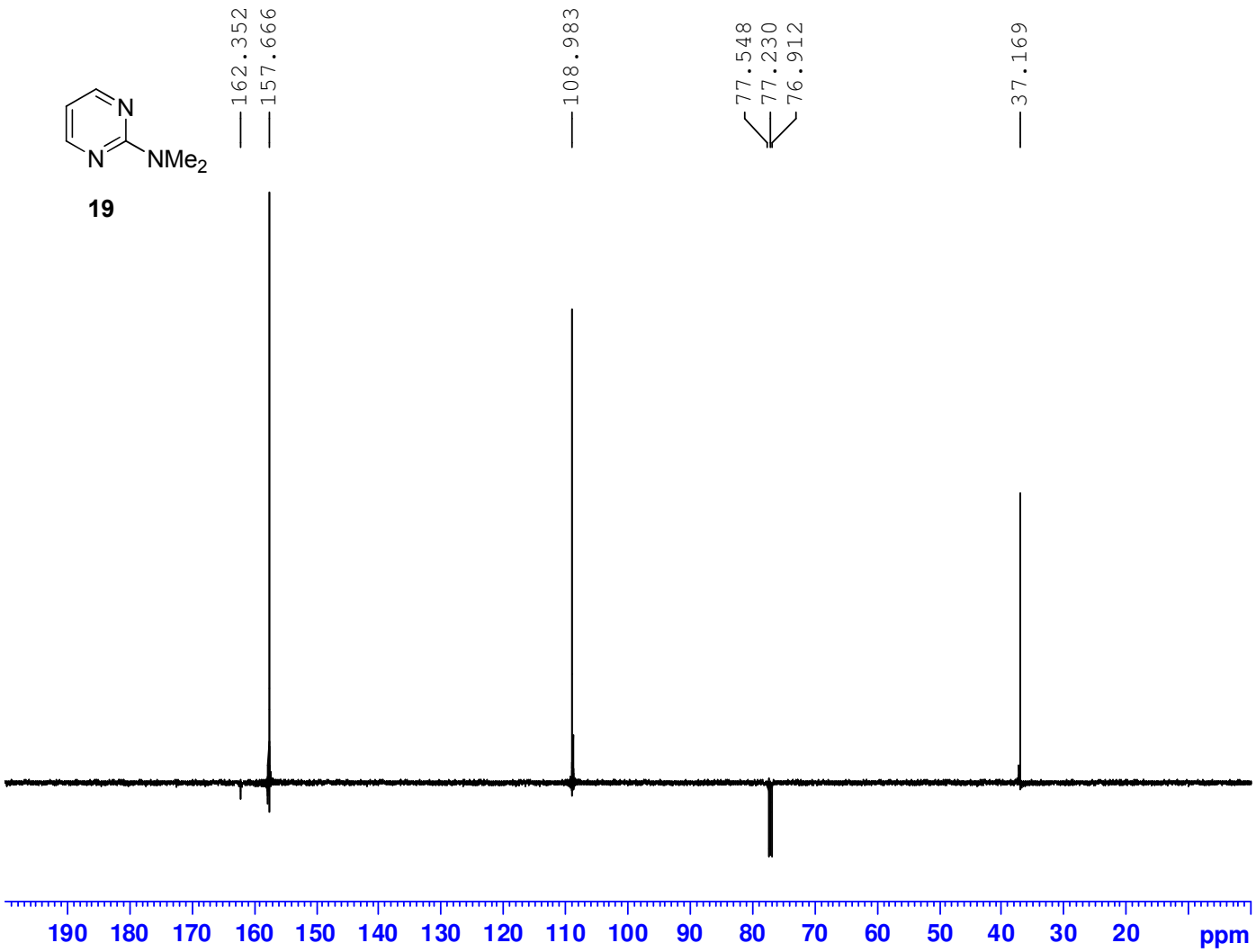
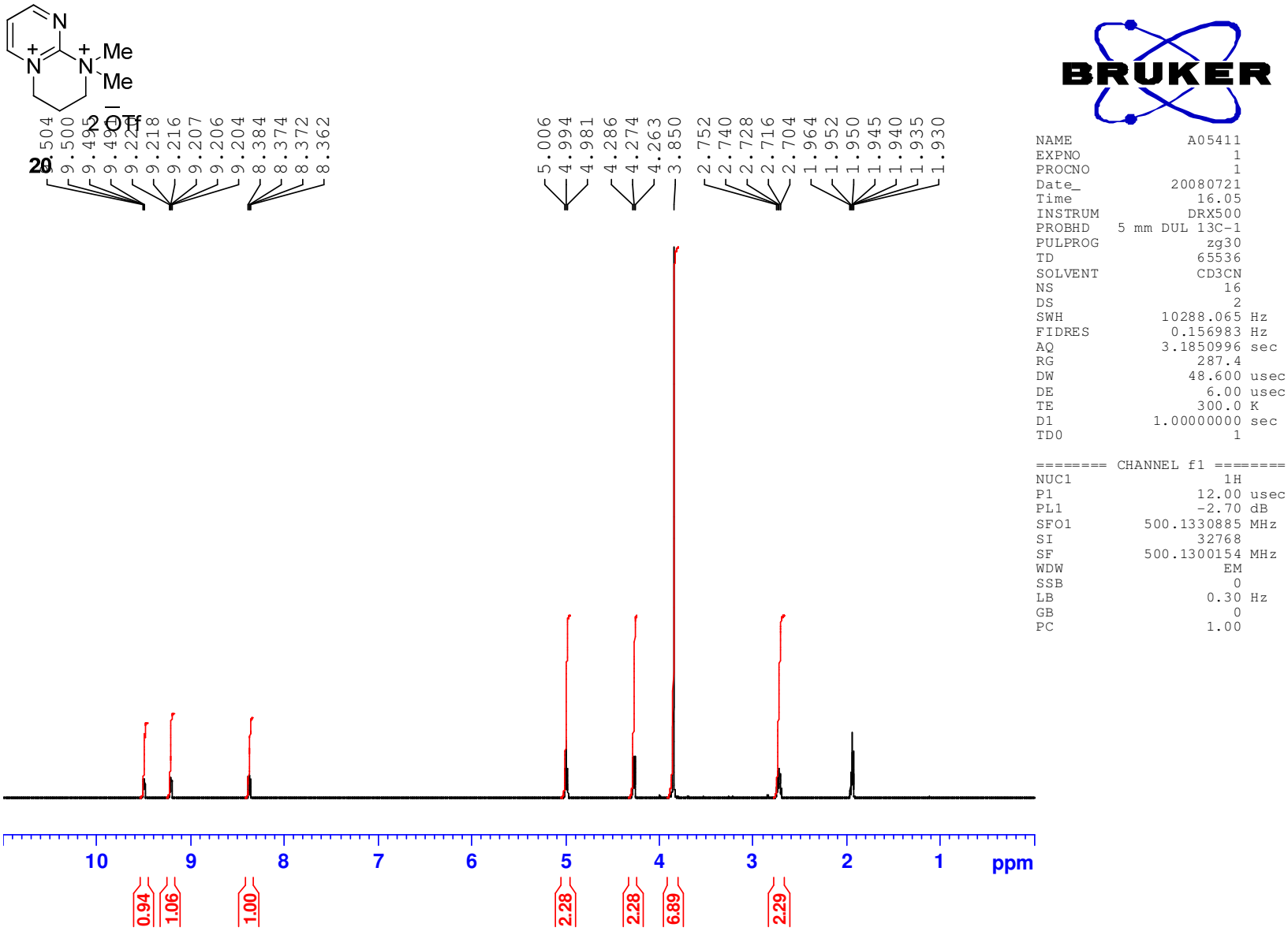



```
NAME                 A03587
EXPNO                     1
PROCNO                    1
Date_              20080305
Time                  10.45
INSTRUM              DRX500
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CDC13
NS                       16
DS                        2
SWH              10288.065 Hz
FIDRES           0.156983 Hz
AQ               3.1850996 sec
RG                      512
DW                   48.600 usec
DE                    6.00 usec
TE                   300.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.00 usec
PL1                  -2.70 dB
SFO1          500.1330885 MHz
SI                    32768
SF            500.1300081 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```




```
NAME                D112319
EXPNO                     2
PROCNO                    1
Date_              20080711
Time                   5.24
INSTRUM                spect
PROBHD    5 mm QNP 1H/13
PULPROG                jmod
TD                    16384
SOLVENT               CDCl3
NS                      512
DS                        4
SWH               23980.814 Hz
FIDRES             1.463673 Hz
AQ                0.3416564 sec
RG                     3251
DW                   20.850 usec
DE                    6.00 usec
TE                   300.2 K
CNST2            145.0000000
CNST11             1.0000000
D1                 4.00000000 sec
d20                0.00689655 sec
DELTA              0.00001019 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    8.00 usec
p2                   16.00 usec
PL1                  -2.60 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.00 dB
SFO2            400.1316005 MHz
SI                    32768
SF              100.6127513 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

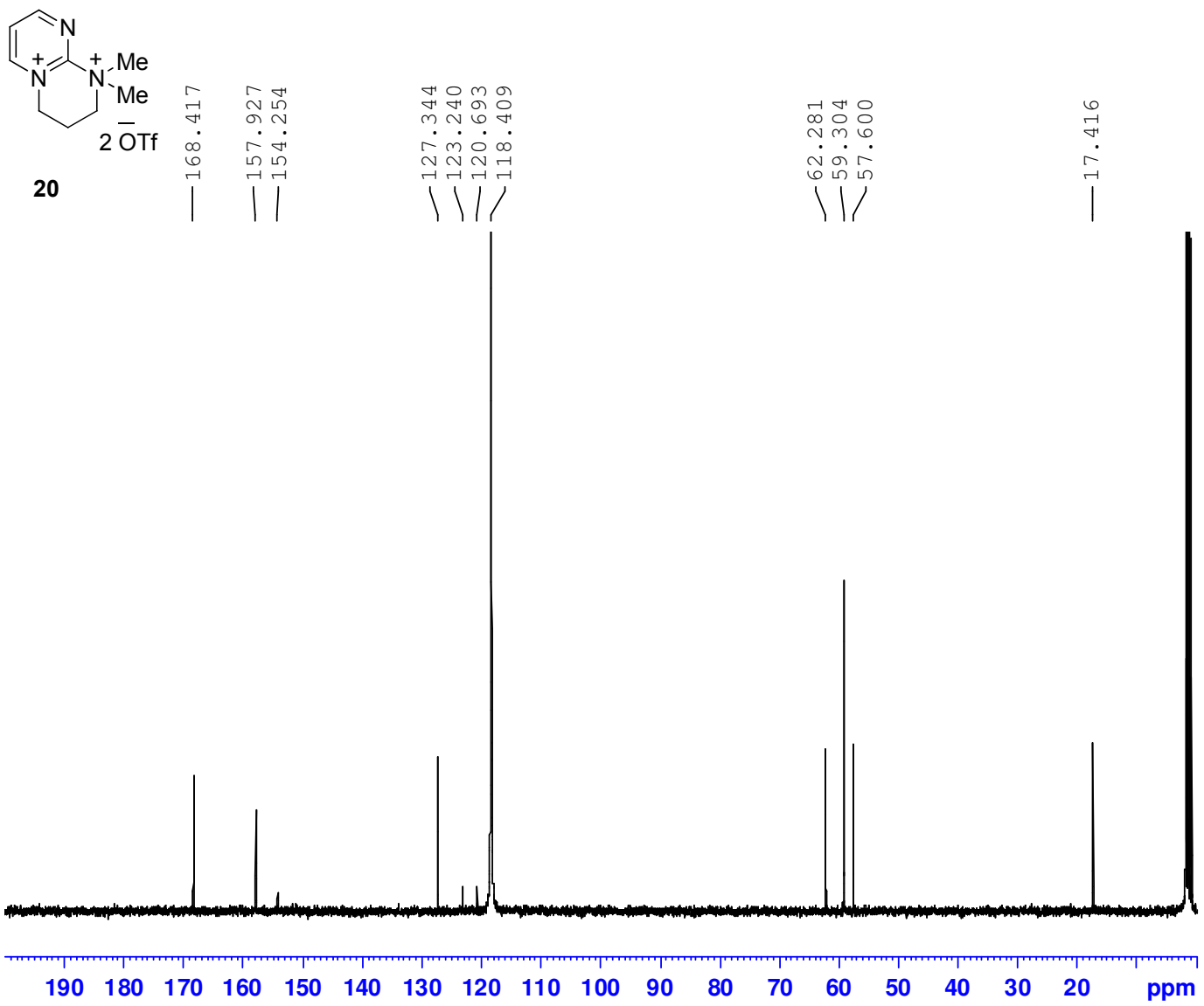


BRUKER

NAME	A05411
EXPNO	1
PROCNO	1
Date_	20080721
Time	16.05
INSTRUM	DRX500
PROBHD	5 mm DUL 13C-1
PULPROG	zg30
TD	65536
SOLVENT	CD3CN
NS	16
DS	2
SWH	10288.065 Hz
FIDRES	0.156983 Hz
AQ	3.1850996 sec
RG	287.4
DW	48.600 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
TD0	1

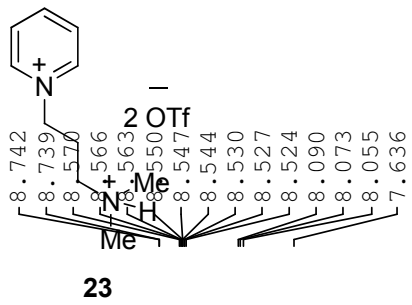
======== CHANNEL f1 ========

NUC1	1H
P1	12.00 usec
PL1	-2.70 dB
SFO1	500.1330885 MHz
SI	32768
SF	500.1300154 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

NAME	A05411
EXPNO	2
PROCNO	1
Date_	20080721
Time	16.46
INSTRUM	DRX500
PROBHD	5 mm DUL 13C-1
PULPROG	zgpg30
TD	16384
SOLVENT	CD3CN
NS	2048
DS	4
SWH	30120.482 Hz
FIDRES	1.838408 Hz
AQ	0.2720244 sec
RG	10321.3
DW	16.600 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-2.30 dB
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.30 dB
PL12	15.00 dB
PL13	120.00 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7576527 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40



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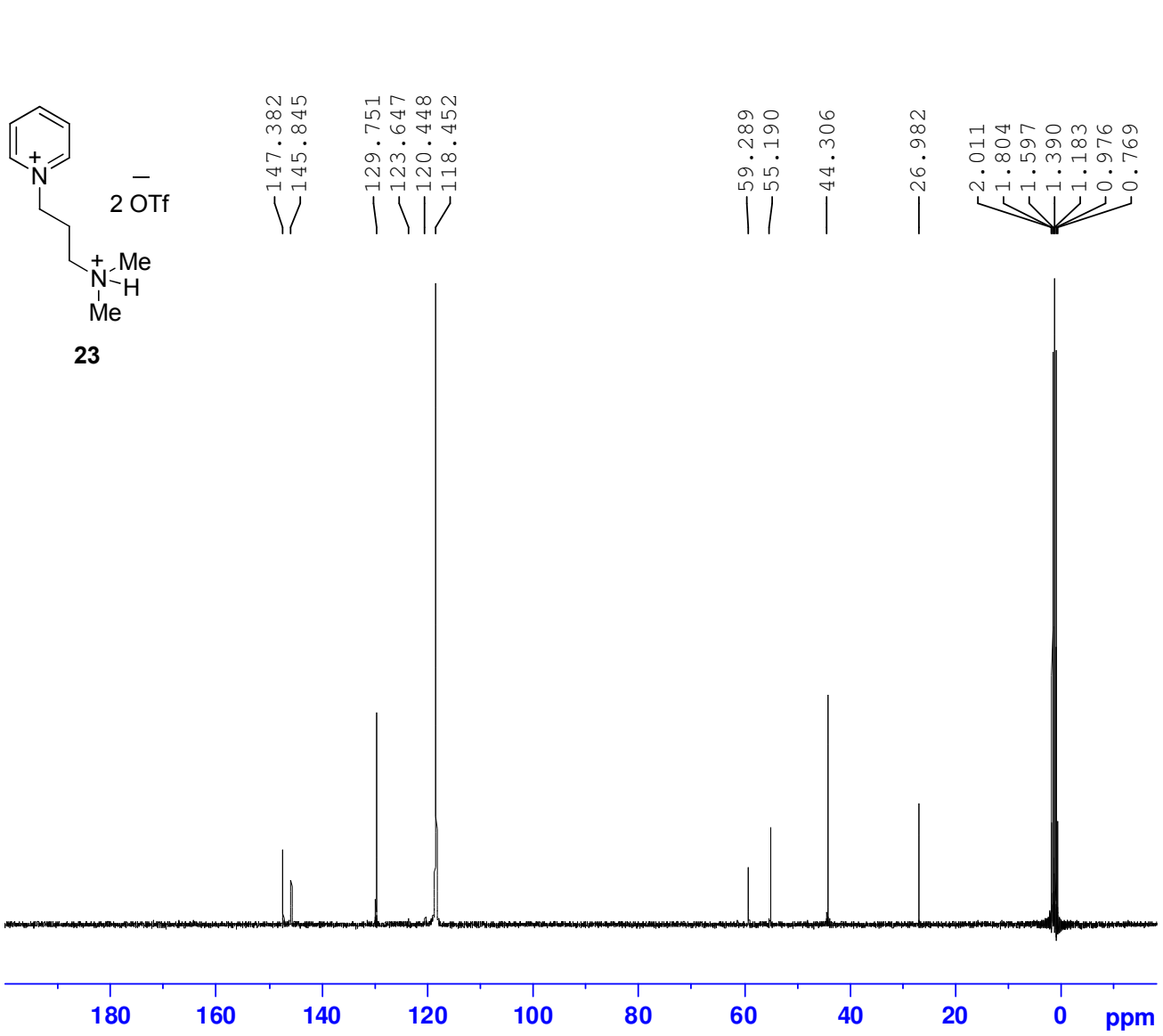
BRUKER

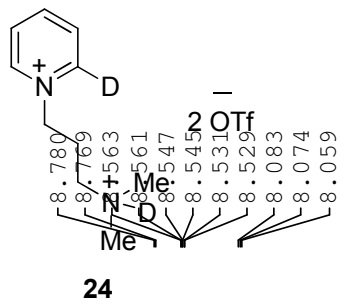
NAME	D116278
EXPNO	1
PROCNO	1
Date_	20081218
Time	19.47
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	32768
SOLVENT	CD3CN
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.252629 Hz
AQ	1.9792372 sec
RG	203.2
DW	60.400 usec
DE	6.00 usec
TE	300.2 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.00 usec
PL1	1.10 dB
SFO1	400.1324710 MHz
SI	32768
SF	400.1300108 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	4.00




```
NAME                 B11321
EXPNO                     1
PROCNO                    1
Date_              20090302
Time                 10.48
INSTRUM              AV400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    16384
SOLVENT               CD3CN
NS                     1024
DS                        2
SWH              23980.814 Hz
FIDRES            1.463673 Hz
AQ               0.3416564 sec
RG                 18390.4
DW                   20.850 usec
DE                   20.00 usec
TE                   300.0 K
D1             0.69999999 sec
d11            0.03000000 sec
DELTA          0.59999996 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.00 usec
PL1                   -2.80 dB
SFO1          100.5976818 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                    1H
PCPD2                90.00 usec
PL12                 14.30 dB
PL13                 15.30 dB
PL2                  -3.20 dB
SFO2          400.0316001 MHz
SI                   32768
SF            100.5875150 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



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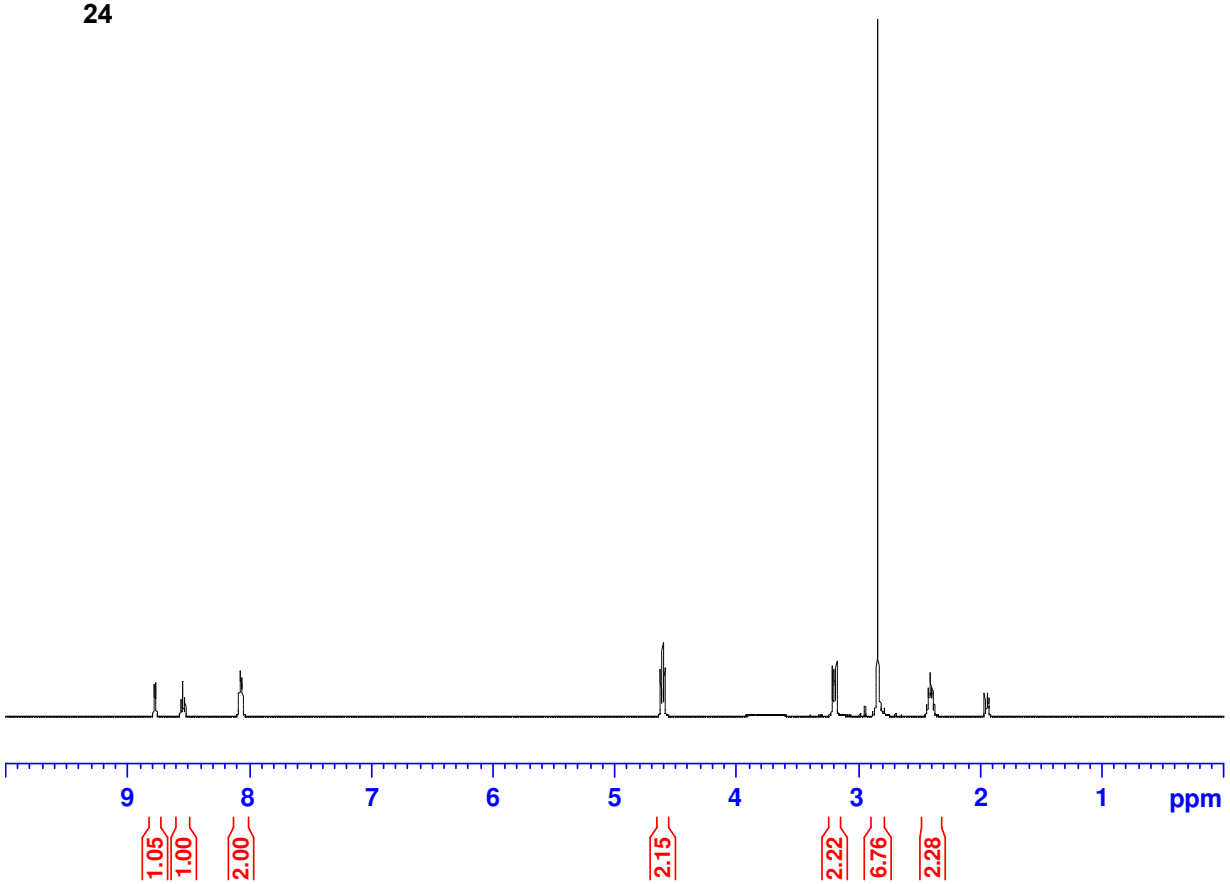
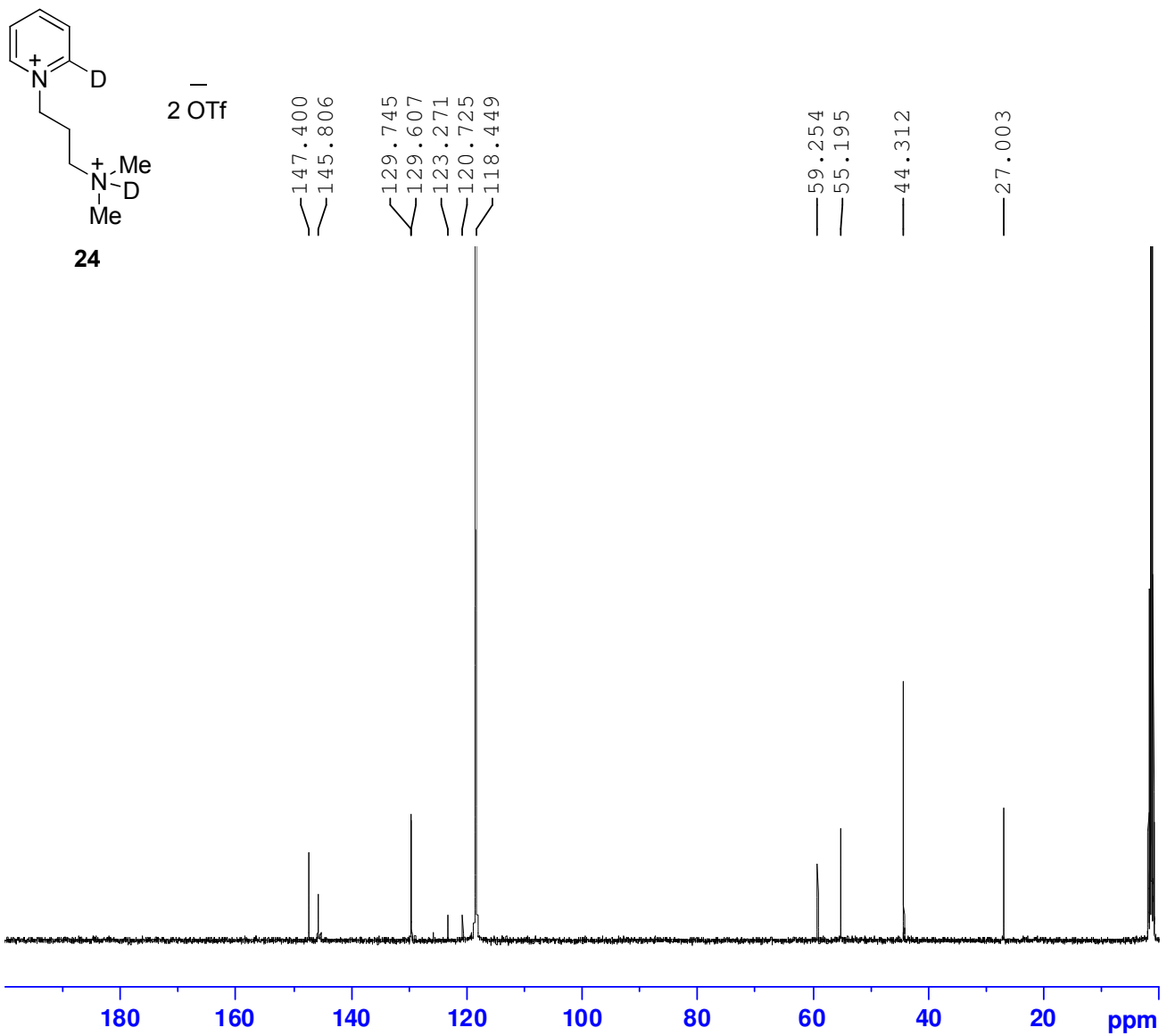
8.780 8.769 8.563 8.561 8.547 8.545 8.531 8.529 8.083 8.074 8.059

4.623 4.608 4.592 3.213 3.197 3.181 2.844 2.442 2.426 2.418 2.410 2.404 2.395 2.379 2.005 1.980 1.964 1.957 1.950 1.945 1.940 1.935 1.930




```
NAME                 A09911
EXPNO                     1
PROCNO                    1
Date_              20090424
Time                  12.37
INSTRUM              DRX500
PROBHD    5 mm DUL 13C-1
PULPROG                zg30
TD                    65536
SOLVENT               CD3CN
NS                       16
DS                        2
SWH              10288.065 Hz
FIDRES            0.156983 Hz
AQ               3.1850996 sec
RG                   143.7
DW                  48.600 usec
DE                   6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.00 usec
PL1                  -2.70 dB
SFO1          500.1330885 MHz
SI                    32768
SF            500.1300151 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```



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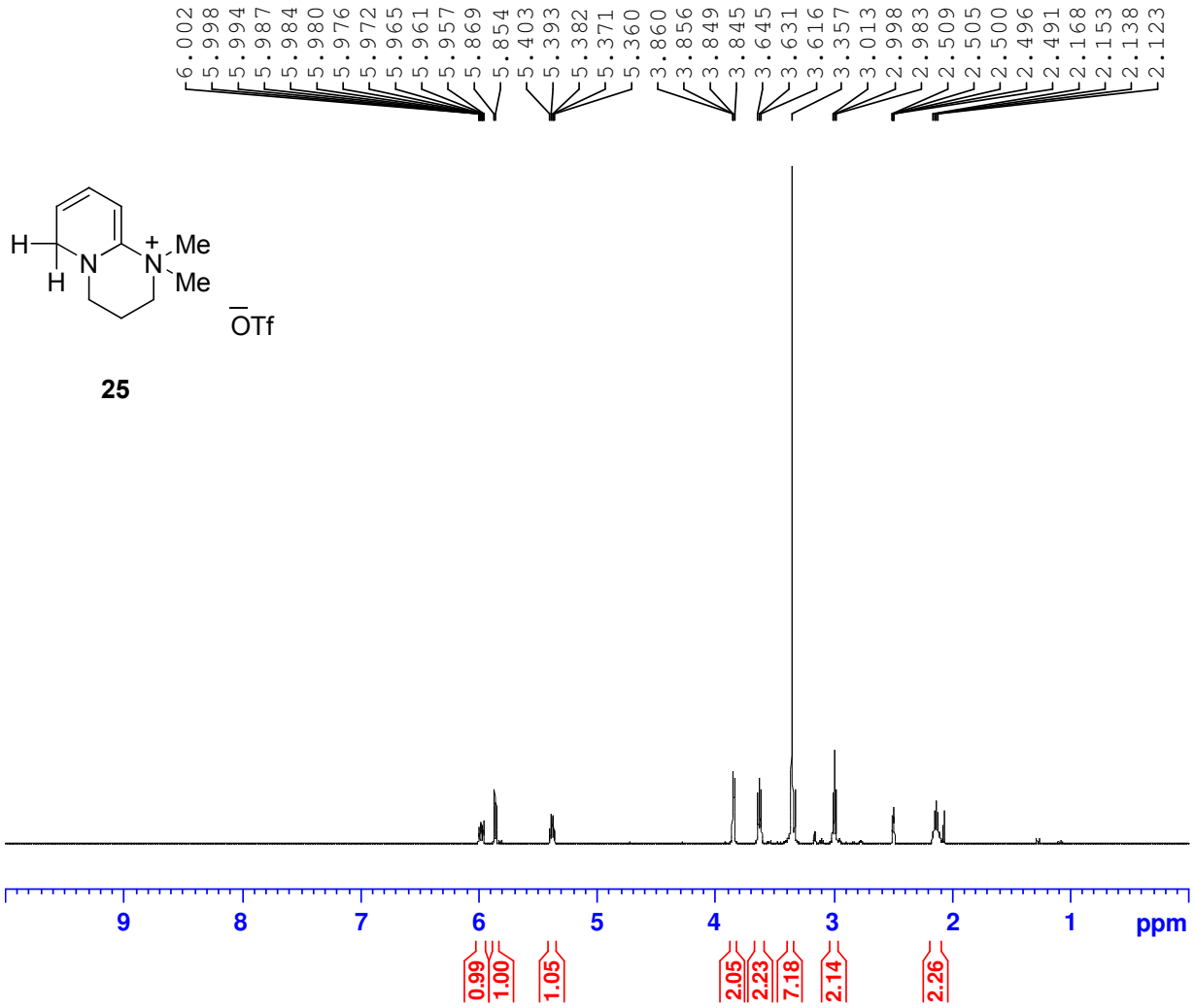
BRUKER

NAME	A09911
EXPNO	2
PROCNO	1
Date_	20090424
Time	12.55
INSTRUM	DRX500
PROBHD	5 mm DUL 13C-1
PULPROG	zgpg30
TD	16384
SOLVENT	CD3CN
NS	1024
DS	4
SWH	30120.482 Hz
FIDRES	1.838408 Hz
AQ	0.2720244 sec
RG	9195.2
DW	16.600 usec
DE	6.00 usec
TE	300.0 K
D1	0.69999999 sec
d11	0.03000000 sec
DELTA	0.59999996 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	-2.30 dB
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.30 dB
PL12	15.00 dB
PL13	120.00 dB
SFO2	500.1320005 MHz
SI	32768
SF	125.7576534 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40



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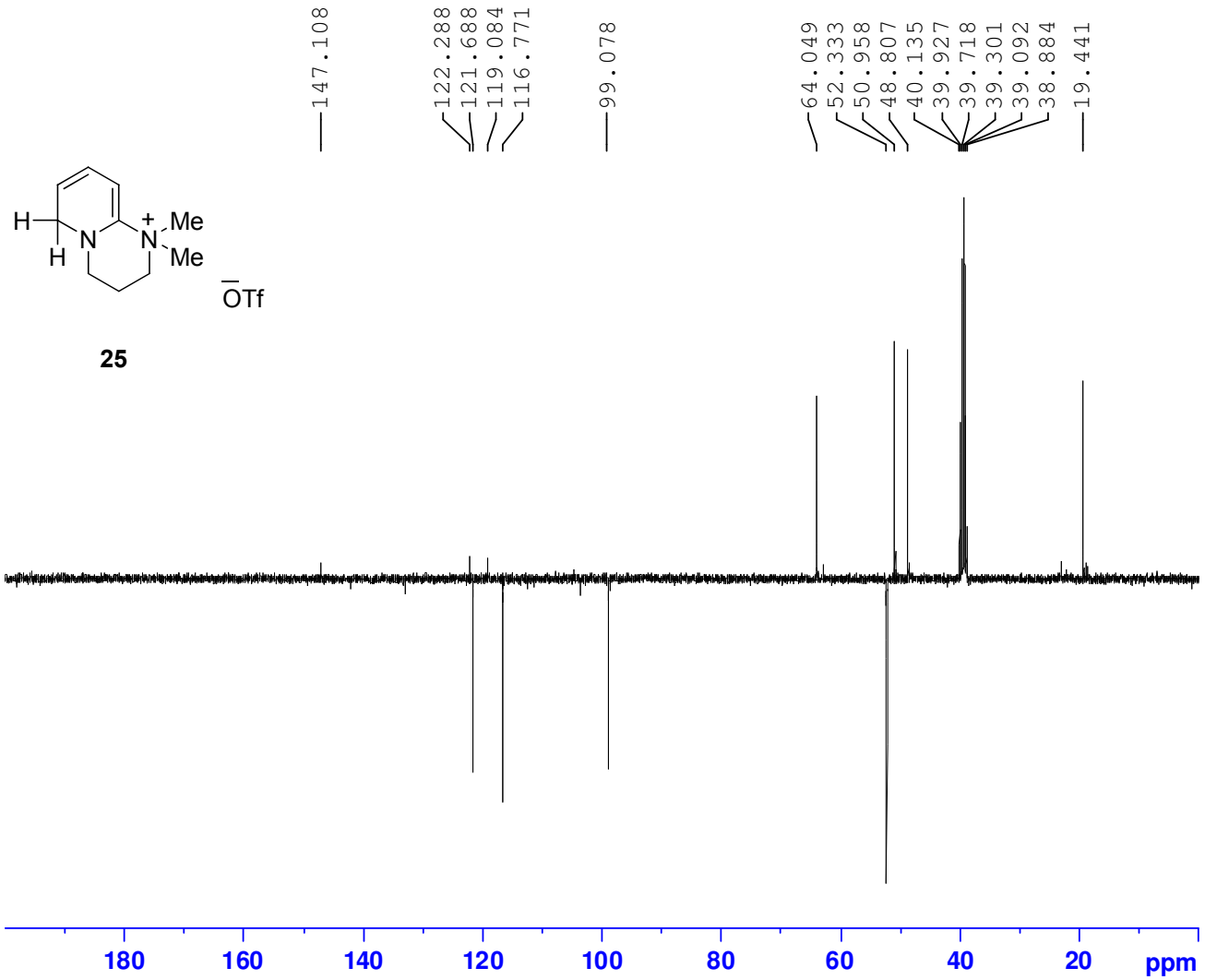
BRUKER

```
NAME                 D119524
EXPNO                      1
PROCNO                     1
Date_               20090327
Time                   17.58
INSTRUM                spect
PROBHD    5 mm QNP 1H/13
PULPROG                 zg30
TD                     32768
SOLVENT                 DMSO
NS                         16
DS                          2
SWH                 8278.146 Hz
FIDRES              0.252629 Hz
AQ                1.9792372 sec
RG                     161.3
DW                    60.400 usec
DE                     6.00 usec
TE                     300.2 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                     1.10 dB
SFO1           400.1324710 MHz
SI                     32768
SF             400.1300024 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      4.00
```



BRUKER

NAME	D119524	
EXPNO	3	
PROCNO	1	
Date_	20090327	
Time	21.24	
INSTRUM	spect	
PROBHD	5 mm QNP 1H/13	
PULPROG	jmod	
TD	16384	
SOLVENT	DMSO	
NS	512	
DS	4	
SWH	23980.814	Hz
FIDRES	1.463673	Hz
AQ	0.3416564	sec
RG	16384	
DW	20.850	usec
DE	6.00	usec
TE	300.2	K
CNST2	145.0000000	
CNST11	1.0000000	
D1	4.00000000	sec
d20	0.00689655	sec
DELTA	0.00001019	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	8.00	usec
p2	16.00	usec
PL1	-2.60	dB
SFO1	100.6228298	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	17.00	dB
SFO2	400.1316005	MHz
SI	32768	
SF	100.6128153	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	