Supporting Information

for

Synthesis of novel derivatives of 5-hydroxymethylcytosine and 5-formylcytosine as tools for epigenetics

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Experimental details and analytical data of all synthesized compounds

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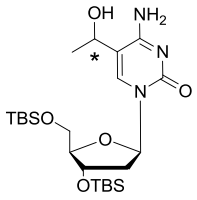
General experimental methods:

All reactions were run under an atmosphere of argon unless otherwise indicated. Room temperature refers to 22 °C, ambient pressure to 1013 hPa. Reagents and anhydrous solvents were transferred via oven-dried syringe or cannula. Flasks were flame dried under vacuum and cooled under a constant stream of argon. Tetrahydrofuran (THF) was distilled under argon from potassium, dichloromethane from SICAPENT (phosphorus pentoxide on solid support with indicator). Pyridine was purchased from Acros (anhydrous over molecular sieves). All other chemicals were purchased from ABCR, Acros, Aldrich, Alfa Aesar, TCI Europe and VWR at the highest commercially available purity and used as such. Reactions were monitored by thin layer chromatography using Merck silica gel 60 F_{254} TLC aluminium sheets and visualized under a UV lamp and/or with anisaldehyde staining solution. Chromatographic purification was performed as flash chromatography on Acros silica gel 35–70, 60 Å, using a forced flow of eluent (method of Still) or MACHEREY-NAGEL silica gel 60 M C18-Reversed phase. Concentration under reduced pressure was performed by rotary evaporation at 40 °C at the appropriate pressure. NMR spectra were recorded on a Varian Mercury plus 300 (operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C acquisitions), a Varian Mercury plus 400 (operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C). Chemical shifts δ are reported in ppm with the solvent resonance as internal standard (chloroform-d_1: 7.26 (^{1}H NMR), 77.16 (^{13}C NMR); methanol-d_4: 3.31 (^{1}H NMR), 49.00 (^{13}C NMR); dimethyl sulfoxide-d_6: 2.50 (^{1}H NMR), 39.52 (^{13}C NMR). Coupling constants *J* are given in Hertz (Hz). Multiplicities are classified by the following abbreviations: s = singlet, d = doublet, t = triplet and combinations thereof, or m = multiplet or bs = broad signal. High resolution mass spectra were obtained on a Bruker Daltonics ESI-FT-ICR-MS APEX II [7 T]. IR spectra were obtained on an ATI/MATTSON Genesis FT-IR as thin film or KBr disk. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Melting points were measured with a Büchi "Melting Point B-540" and are uncorrected. Optical rotation data was obtained with a Schmidt+Haensch Polartronic MHZ-8 at the sodium-D line (589 nm) using a 50 mm path-length cell in the solvent and concentration indicated.

In ^{13}C NMR reports of diastereomeric mixtures one value is given in the case of overlapped signals, otherwise the corresponding signal is given in parentheses.

In ^{1}H NMR reports of diastereomeric mixtures protons marked with asterisk indicate the signals of corresponding minor diastereomer. The ratio of the diastereomers was determined by ^{1}H NMR.

3',5'-Di(*tert*-butyldimethylsilyl)-5-(1-hydroxyethyl)-2'-deoxycytidine (2a)



2a

To an ice-cooled solution of aldehyde **1** (100 mg, 207 µmol, 1.0 equiv) in THF (2.00 mL) methylmagnesium bromide (3.0 M in Et_2O; 138 µL, 413 µmol, 2.0 equiv) was added dropwise and the solution stirred at 0 °C. After one hour the reaction mixture was allowed to warm to room temperature and stirred at this temperature for four hours. Subsequently additional amount of methylmagnesium bromide (3.0 M in Et_2O; 69.0 µL, 207 µmol, 1.0 equiv) was added and the reaction mixture was stirred overnight at room temperature. Additional portion of methylmagnesium bromide (3.0 M in Et_2O; 69.0 µL, 207 µmol, 1.0 equiv) was then added and the reaction mixture was stirred for another three hours at room temperature before it was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with DCM (10 mL). The phases were separated and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) to yield a mixture of diastereomeric alcohols **2a** with a ratio of 1.1:1 (99.0 mg, 198 µmol, 96%) as a colourless oil.

R_f: 0.37 (DCM/MeOH = 15:1 *v/v*).

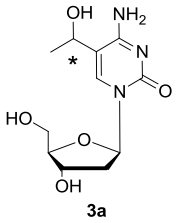
IR: (KBr) ν_{max} = 2858, 2954, 2857, 1656, 1435, 1095, 838, 780, 554 cm^{-1}.

^{1}H-NMR: (400 MHz, CD_3OD) δ (ppm) 7.76 (s, 1H, **H-6**), 7.73 (s, 1H, **H-6***), 6.30-6.26 (m, 2H, **H-1'**, **H-1'***), 4.74-4.44 (m, 2H, C**H**-CH_3, C**H***-CH_3), 4.47-4.42 (m, 2H, **H-3'**, **H-3'***), 3.96-3.95 (m, 2H, **H-4'**, **H-4'***), 3.82-3.81 (m, 4H, **H-5'**, **H-5'***), 2.36-2.30 (m, 2H, **H-2'**, **H-2'***), 2.11-2.03 (m, 2H, **H-2'**, **H-2'***), 1.43-1.42 (m, 6H, CH-C**H**$_3$, CH-C**H**$_3$*****), 0.93-0.91 (m, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.91 (s, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.12 (s, 12H, Si-(C**H**$_3$)$_2$, Si-(C**H**$_3$)$_2$*****), 0.11 (s, 12H, Si-(C**H**$_3$)$_2$, Si-(C**H**$_3$)$_2$*****).

^{13}C-NMR: (100 MHz, CD_3OD) δ (ppm) 165.0 (**C-4**), 157.9 (**C-2**), 138.3 (**C-6**), 89.5 (89.4) (**C-4'**), 87.4 (87.3) (**C-1'**), 73.9 (73.8) (**C-3'**), 65.7 (**C**H-CH_3), 64.3 (**C-5'**), 42.3 (42.1) (**C-2'**), 26.5 (Si-C(**C**H_3)$_3$), 26.2 (Si-C(**C**H_3)$_3$), 22.9 (22.8) (CH-**C**H_3), 19.2 (Si-**C**(CH_3)$_3$), 18.8 (Si-**C**(CH_3)$_3$), -4.6 (Si-**C**H_3), -4.7 (Si-**C**H_3), -5.2 (Si-**C**H_3). **C-5** is not observed.

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{23}H_{46}N_3O_5Si_2$: 500.29705, found: 500.29727, $[2M+H]^+$ calcd for $C_{46}H_{91}N_6O_{10}Si_4$: 999.58683, found: 999.58716.

5-(1-Hydroxyethyl)-2'-deoxycytidine (3a)



3a

In a polypropylene tube the mixture of epimeric alcohols **2a** (98.0 mg, 196 µmol, 1.0 equiv) was dissolved in DCM (10.0 mL) and cooled to 0 °C. Subsequently $HF \cdot Et_3N$ (64.0 µL, 392 µmol, 2.0 equiv) was added in one portion. The solution was allowed to warm to room temperature and stirred overnight. After addition of TMSOMe (0.700 mL, 5.08 mmol, 26 equiv) the reaction mixture was stirred for another 30 min. The suspension was centrifuged for 10 min at 5000 rpm, the supernatant was collected and the residue was resuspended in DCM and centrifuged for 10 min at 5000 rpm. The procedure was repeated one more time and the crude product was purified by reversed phase column chromatography (H_2O/MeCN 4:1 *v/v*) to yield a mixture of diastereomeric alcohols **3a** (40.0 mg, 147 µmol, 75%) as a colourless oil. A ratio could not be calculated.

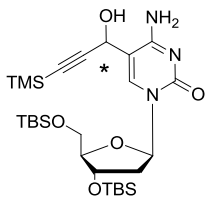
IR: (CCl_4) ν_{max} = 3441, 2924, 2360, 1736, 1652, 1383, 1247, 1026, 795, 602, 456 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 8.06 -8.05 (m, 2H, **H-6, H-6***), 6.31-6.26 (m, 2H, **H-1'**, **H-1'***), 4.75-4.68 (m, 2H, C**H**-CH_3, C**H**-CH_3*****), 4.42-4.37 (m, 2H, **H-3'**, **H-3'***), 3.98-3.94 (m, 2H, **H-4'**, **H-4'***), 3.87-3.81 (m, 2H, **H-5'**, **H-5'***), 3.78-3.73 (m, 2H, **H-5'**, **H-5'***), 2.42-2.34 (m, 2H, **H-2'**, **H-2'***), 2.21-2.12 (m, 2H, **H-2'**, **H-2'***), 1.48-1.46 (m, 6H, CH-C**H_3,** CH-C**H_3***).

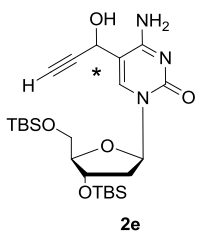
^{13}C-NMR: (100 MHz, CD_3OD) δ (ppm) 166.1 (**C-4**), 157.9 (**C-2**), 139.3 (**C-6**), 111.8 (111.7) (**C-5**), 88.90 (88.88) (**C-4'**), 87.7 (87.6) (**C-1'**), 71.92 (71.90) (**C-3'**), 65.8 (65.7) (**C**H-CH_3), 62.6 (**C-5'**), 42.21 (42.18) (**C-2'**), 22.42 (22.40) (CH-**C**H_3).

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{11}H_{17}N_3O_5Na$: 294.10604, found: 294.10617, $[2M+Na]^+$ calcd for $C_{22}H_{34}N_6O_{10}Na$: 565.22286, found: 565.22330.

3',5'-Di(*tert*-butyldimethylsilyl)-5-(1-hydroxy-3-(trimethylsilyl)prop-2-ynyl)-2'-deoxycytidine (2b) and 3',5'-di(*tert*-butyldimethylsilyl)-5-(1-hydroxyprop-2-ynyl)-2'-deoxycytidine (2e)



2b



2e

To a stirred solution of trimethylsilylacetylene (671 µL, 4.71 mmol, 4.0 equiv) in THF (9.00 mL) *n*-BuLi (2.5 M in *n*-hexane; 1.89 mL, 4.71 mmol, 4.0 equiv) was added dropwise at −40 °C. The reaction mixture was warmed to −20 °C. After stirring at this temperature for one hour reaction mixture was cooled down to −40 °C and a solution of aldehyde **1** (570 mg, 1.18 mmol, 1.0 equiv) in THF (11.0 mL) was added dropwise. The reaction was stirred at −40 °C for three hours, thereafter at −20 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (20 mL), diluted with Et_2O (30 mL) and the aqueous layer extracted with Et_2O (3 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by silica gel chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) yielded mixture of diastereomeric alcohols **2b** with a ratio of 1.9:1 (296 mg, 509 µmol, 43 %) as yellow solid and a mixture of diastereomeric alcohols **2e** with a ratio of 1.2:1 (154 mg, 302 µmol, 26%) as a slight yellow oil.

2b:

R_f: 0.21 (DCM/MeOH = 30:1 *v/v*).

IR: (KBr) ν_{max} = 3427, 2955, 2858, 1658, 1604, 1385, 1253, 1094, 840, 779, 555 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 7.96 (s, 1H, **H-6**), 7.95 (s, 1H, **H-6***), 6.24-6.17 (m, 2H, **H-1'**, **H-1'***), 5.30 (s, 2H, C**H**-OH, C**H***-OH), 4.45-4.41 (m, 2H, **H-3'**, **H-3'***), 4.03-3.98 (m, 2H, **H-4'**, **H-4'***), 3.83-3.81 (m, 4H, **H-5'**, **H-5'***), 2.48-2.40 (m, 2H, **H-2'**, **H-2'***), 2.14-2.01 (m, 2H, **H-2'**, **H-2'***), 0.92-0.91 (m, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*****), 0.19-0.18 (m, 18H, Si-(C**H$_3$**)$_3$, Si-(C**H$_3$**)$_3$*****), 0.12-0.11 (m, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 162.8 (162.6) (**C-4**), 154.9 (**C-2**), 140.2 (139.9) (**C-6**), 106.6 (**C-5**), 102.3 (102.1) (**C**≡C-TMS), 92.8 (92.5) (C≡**C**-TMS), 88.7 (88.5) (**C-4'**), 87.3 (87.1) (**C-1'**), 72.8 (72.5) (**C-3'**), 63.5 (63.4) (**C-5'**), 60.3 (60.2) (**C**H-OH), 42.1 (41.8) (**C-2'**), 26.19 (26.16) (Si-C(**C**H$_3$)$_3$), 26.0 (Si-C(**C**H$_3$)$_3$), 18.59 (18.57) (Si-**C**(CH$_3$)$_3$), 18.2 (Si-**C**(CH$_3$)$_3$), 0.05 (Si-(**C**H$_3$)$_3$), -4.31 (-4.34) (Si-**C**H$_3$), -4.63 (-4.65) (Si-**C**H$_3$), -5.06 (Si-**C**H$_3$), -5.11 (Si-**C**H$_3$).

HR-MS: (ESI positive, EtOAc), $[M+Na]^+$ calcd for $C_{27}H_{51}N_3O_5Si_3Na$: 604.30287, found: 604.30327, $[2M+H]^+$ calcd for $C_{54}H_{103}N_6O_{10}Si_6$: 1163.63458, found: 1163.63592, $[2M+Na]^+$ calcd for $C_{54}H_{102}N_6O_{10}Si_6Na$: 1185.61652, found: 1185.61555.

2e:

R_f: 0.15 (DCM/MeOH = 30:1 *v/v*).

IR: (CCl_4) ν_{max} = 3444, 2929, 1660, 1361, 1256, 1093, 837, 780 cm^{-1}.

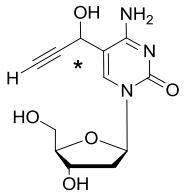
^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 8.01 (s, 1H, **H-6***), 7.99 (s, 1H, **H-6**), 6.26-6.20 (m, 2H, **H-1'**, **H-1'***), 5.34-5.32 (m, 2H, C**H**-OH, C**H***-OH), 4.47-4.44 (m, 2H, **H-3'**, **H-3'***), 4.01-3.98 (m, 2H, **H-4'**, **H-4'***), 3.82-3.79 (m, 4H, **H-5'**, **H-5'***), 3.15-3.13 (m, 2H, C≡C-**H,** C≡C-**H***), 2.47-2.38 (m, 2H, **H-2'**, **H-2'***), 2.13-2.03 (m, 2H, **H-2'**, **H-2'***), 0.91-0.90 (m, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*****), 0.11 (s, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, CD_3OD) δ (ppm) 164.5 (**C-4**), 157.7 (**C-2**), 140.3 (**C-6**), 108.4 (**C-5**), 89.8 (89.7) (**C-4'**), 88.1 (88.0) (**C-1'**), 82.4 (82.3) (**C**≡C-H), 76.72 (76.69) (C≡**C**-H), 74.2

(74.1) (**C-3'**), 64.38 (64.35) (**C-5'**), 59.81 (59.77) (**C**H-OH), 42.4 (42.3) (**C-2'**), 26.43 (26.41) (Si-C($\mathbf{C}H_3)_3$), 26.21 (26.18) (Si-C($\mathbf{C}H_3)_3$), 19.2 (19.1) (Si-**C**$(CH_3)_3$), 18.8 (Si-**C**$(CH_3)_3$), -4.56 (-4.55) (Si-**C**H_3), -4.7 (Si-**C**H_3), -5.2 (Si-**C**H_3), -5.30 (-5.32) (Si-**C**H_3).

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{24}H_{44}N_3O_5Si_2$: 510.2814, found: 510.28181, $[2M+H]^+$ calcd for $C_{48}H_{87}N_6O_{10}Si_4$: 1019.55553, found: 1019.55476.

5-(1-Hydroxyprop-2-ynyl)-2'-deoxycytidine (3b)



3b

To a solution of epimeric alcohols **2b** (68.6 mg, 118 µmol, 1.0 equiv) in EtOAc (2.80 mL) in a polypropylene tube pyridine (44.0 µL, 542 µmol, 4.6 equiv) and HF·pyridine (70% HF, 13.5 µL, 514 µmol, 4.4 equiv) were added subsequently. After stirring for six hours another portion of pyridine (44.0 µL, 542 µmol, 4.6 equiv) and HF·pyridine (70% HF, 13.5 µL, 514 µmol, 4.4 equiv) was added to the reaction mixture. After stirring for 23 hours an additional portion of pyridine (44.0 µL, 542 µmol, 4.6 equiv) and HF·pyridine (70% HF, 13.5 µL, 514 µmol, 4.4 equiv) was added and the stirring was continuing overnight. After addition of TMSOMe (0.50 mL, 3.63 mmol, 31 equiv) and stirring for one hour, a suspension was formed and centrifuged for 10 min at 3000 rpm. The supernatant was collected, the residue resuspended in EtOAc and centrifuged for 10 min at 3000 rpm. The crude product was purified by reversed phase column chromatography (H_2O/MeCN 4:1 *v/v*) to yield a mixture of diastereomeric alcohols **3b** (20.0 mg, 71.1 µmol, 60%) as a white solid. A ratio could not be calculated.

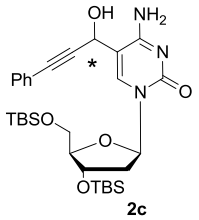
IR: (CCl_4) ν_{max} = 3444, 2921, 2239, 1733, 1625, 1384, 711, 602, 454 cm^{-1}.

^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 8.22-8.20 (m, 2H, **H-6**, **H-6***), 6.27-6.24 (m, 2H, **H-1'**, **H-1'***), 5.31-5.30 (m, 2H, C**H**-OH, C**H***-OH), 4.37-4.33 (m, 2H, **H-3'**, **H-3'***), 3.96-3.94 (m, 2H, **H-4'**, **H-4'***), 3.81-3.71 (m, 4H, **H-5'**, **H-5'***), 3.13-3.12 (m, 2H, C≡C-**H,** C≡C-**H***), 2.42-2.36 (m, 2H, **H-2'**, **H-2'***), 2.17-2.09 (m, 2H, **H-2'**, **H-2'***).

^{13}C-NMR: (75 MHz, CD_3OD) δ (ppm): 165.5 (**C-4**), 157.8 (**C-2**), 141.1 (**C-6**), 108.0 (**C-5**), 89.0 (**C-4'**), 87.82 (87.79) (**C-1'**), 82.4 (**C**≡C-H), 76.73 (76.66) (C≡**C**-H), 72.20 (72.17) (**C-3'**), 63.00 (62.95) (**C-5'**), 60.0 (**C**H-OH), 42.1 (**C-2'**).

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{12}H_{16}N_3O_5$: 282.10845, found: 282.10885, $[M+Na]^+$ calcd for $C_{12}H_{15}N_3O_5Na$: 304.09039, found: 304.09060, $[2M+H]^+$ calcd for $C_{24}H_{31}N_6O_{10}$: 563.20962, found: 563.20940.

3',5'-Di(*tert*-butyldimethylsilyl)-5-(1-hydroxy-3-phenylprop-2-ynyl)-2'-deoxycytidine (2c)



2c

To a stirred solution of phenylacetylene (91.0 µL, 827 µmol, 4.0 equiv) in THF (1.50 mL) at −78 °C *n*-BuLi (2.5 M in *n*-hexane; 331 µL, 827 µmol, 4.0 equiv) was added dropwise. After stirring the reaction mixture at this temperature for 90 min a solution of aldehyde **1** (100 mg, 207 µmol, 1.0 equiv) in THF (2.00 mL) was added dropwise. The reaction was stirred at −78 °C for three hours thereafter at −50 °C till no starting material was detected by TLC. The reaction was quenched with saturated aqueous NH_4Cl (5 mL), diluted with DCM (10 mL). The aqueous layer was extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by silica gel chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) yielded a mixture of diastereomeric alcohols **2c** with a ratio of 1.2:1 (82.0 mg, 140 µmol, 68%) as a slight yellow oil.

R_f: 0.24 (DCM/MeOH = 30:1 *v/v*).

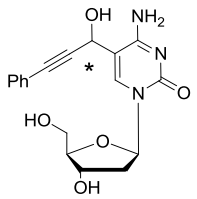
IR: (KBr) ν_{max} = 3420, 2929, 1655, 1470, 1384, 1095, 838, 780, 558 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 8.08 (d, *J* = 0.8 Hz, 1H, **H-6***), 8.06 (d, *J* = 0.7 Hz, 1H, **H-6**), 7.49-7.45 (m, 4H, C**H** aromat., C**H*** aromat.), 7.40-7.36 (m, 6H, C**H** aromat., C**H*** aromat.), 6.29-6.23 (m, 2H, **H-1'**, **H-1'***), 5.58 (5.57) (m, 2H, C**H**-OH, C**H***-OH), 4.47-4.42 (m, 2H, **H-3'**, **H-3'***), 4.02-3.99 (m, 2H, **H-4'**, **H-4'***), 3.78-3.74 (m, 4H, **H-5'**, **H-5'***), 2.51-2.42 (m, 2H, **H-2'**, **H-2'***), 2.15-2.05 (m, 2H, **H-2'**, **H-2'***), 0.93 (s, 18H, Si-C(C**H$_3$**)$_3$, Si-C(C**H$_3$**)$_3$*****), 0.88 (s, 9H, Si-C(C**H$_3$**)$_3$), 0.87 (s, 9H, Si-C(C**H$_3$**)$_3$*****), 0.11 (m, 12H, Si-(C**H$_3$**)$_2$, Si-(C**H$_3$**)$_2$*****), 0.04 (m, 6H), 0.03 (s, 3H**)**, 0.02 (s, 3H).

^{13}C-NMR: (75 MHz, CD_3OD) δ (ppm) 164.9 (**C-4**), 158.1 (**C-2**), 140.2 (**C-6**), 132.7 (132.6) (**C** aromat.), 130.03 (130.00) (**C** aromat.), 129.62 (129.61) (**C** aromat.), 123.3 (**C** aromat.), 89.75 (89.72), 88.1 (88.0), 87.6 (87.5), 74.3 (74.2) (**C-3'**), 64.6 (**C-5'**), 60.6 (60.5) (**C**H-OH), 42.46 (42.40) (**C-2'**), 26.39 (26.36) (Si-C(**C**H$_3$)$_3$), 26.2 (Si-C(**C**H$_3$)$_3$), 19.11 (19.08) (Si-**C**(CH$_3$)$_3$), 18.8 (Si-**C**(CH$_3$)$_3$), -4.6 (Si-**C**H$_3$), -4.7 (Si-**C**H$_3$), -5.2 (-5.3) (Si-**C**H$_3$), -5.3 (-5.4) (Si-**C**H$_3$).

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{30}H_{48}N_3O_5Si_2$: 586.31270, found: 586.31259, $[2M+H]^+$ calcd for $C_{60}H_{95}N_6O_{10}Si_4$: 1171.61813, found: 1171.61902.

5-(1-Hydroxy-3-phenylprop-2-ynyl)-2'-deoxycytidine (3c)



3c

In a polypropylene tube the mixture of epimeric alcohols **2c** (75.0 mg, 128 µmol, 1.0 equiv) was dissolved in EtOAc (3.70 mL), subsequently pyridine (52.0 µL, 640 µmol, 5.0 equiv) and HF·pyridine (70% HF, 48.0 µL, 1.92 mmol, 15 equiv) were added and the reaction mixture was stirred overnight at room temperature. After addition of TMSOMe (0.50 mL, 3.84 mmol, 30 equiv) and stirring for one hour the suspension was centrifuged for 10 min at 3000 rpm and the crude product was purified by reversed phase column chromatography (H_2O/MeCN 4:1 → 2:1 *v/v*) to yield a mixture of diastereomeric alcohols **3c** with a ratio of 1.1:1 (33.0 mg, 92.3 µmol, 72%) as a colourless oil.

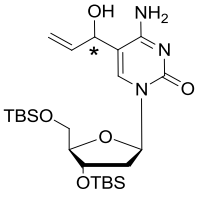
IR: (CCl_4) ν_{max} = 3355, 2922, 1660, 1488, 1299, 1093, 1029, 758, 607, 454 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 8.21 (s, 1H, **H-6'**), 8.19 (s, 1H, **H-6'***) 7.49-7.46 (m, 4H, C**H** aromat., C**H*** aromat.), 7.36-7.34 (m, 6H, C**H** aromat., C**H*** aromat.), 6.25 (m, 2H, **H-1'**, **H-1'***), 5.54 (s, 2H, C**H**-OH**,** C**H***-OH), 4.36-4.32 (m, 2H, **H-3'**, **H-3'***), 3.97-3.92 (m, 2H, **H-4'**, **H-4'***), 3.72-3.68 (m, 4H, **H-5'**, **H-5'***), 2.45-2.36 (m, 2H, **H-2'**, **H-2'***), 2.18-2.09 (m, 2H, **H-2'**, **H-2'***).

^{13}C-NMR: (100 MHz, CD_3OD) δ (ppm) 165.5 (**C-4**), 157.8 (**C-2**), 141.0 (140.9) (**C-6**), 132.7 (**C** aromat.), 129.9 (**C** aromat.), 129.6 (**C** aromat.), 123.5 (**C** aromat.), 108.2 (**C**-5), 89.03 (88.97) (**C**-4'), 87.9 (87.8), 87.70 (87.68), 87.5 (87.4), 72.3 (72.2) (**C**-3'), 63.04 (62.98), 60.8 (60.7), 42.08 (42.06) (**C**-2').

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{18}H_{20}N_3O_5$: 358.13975, found: 358.13957, $[M+Na]^+$ calcd for $C_{18}H_{19}N_3O_5Na$: 380.12169, found: 380.12140, $[2M+H]^+$ calcd for $C_{36}H_{39}N_6O_{10}$: 715.27222, found: 715.27221

3',5'-Di(*tert*-butyldimethylsilyl)-5-(1-hydroxyprop-2-enyl)-2'-deoxycytidine (2d)



2d

To an ice-cooled solution of aldehyde **1** (50.0 mg, 103 µmol, 1.0 equiv) in THF (1.00 mL) vinylmagnesium bromide (1.0 M in THF; 155 µL, 155 µmol, 1.5 equiv) was added dropwise. After stirring for 20 min the reaction mixture was allowed to warm to room temperature and

was stirred for additional two hours. Subsequently an additional amount of vinylmagnesium bromide (1.0 M in THF; 258 µL, 258 µmol, 2.5 equiv) was added at 0 °C and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with Et_2O (10 mL). The phases were separated and the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) to yield a mixture of diastereomeric alcohols **2d** with a ratio of 1.1:1 (41.0 mg, 0.19 mmol, 77%) as a slight yellow solid.

R_f: 0.36 (DCM/MeOH = 15:1 *v/v*).

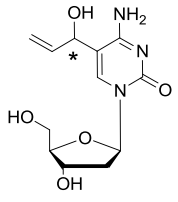
IR: (KBr) ν_{max} = 3420, 1638, 1428, 1385, 1093, 838, 780, 550 cm^{-1}.

^{1}H-NMR: (300 MHz, CD_3OD) δ (ppm) 7.75 (s, 1H, **H-6***), 7.73 (s, 1H, **H-6**), 6.29-6.24 (m, 2H, **H-1'**, **H-1'***), 6.01-5.95 (m, 2H, C**H**═CH_2, C**H***═CH_2), 5.43-5.35 (m, 2H, CH═C**H_2**, CH═C**H_2***), 5.28-5.23 (m, 2H, CH═C**H_2**, CH═C**H_2***), 5.06-5.04 (m, 2H, C**H**-OH, C**H***-OH), 4.46-4.43 (m, 2H, **H-3'**, **H-3'***), 3.99-3.92 (m, 2H, **H-4'**, **H-4'***), 3.81-3.80 (m, 4H, **H-5'**, **H-5'***), 2.39-2.31 (m, 2H, **H-2'**, **H-2'***), 2.14-1.98 (m, 2H, **H-2'**, **H-2'***), 0.93 (s, 18H, Si-C(C**H_3**)$_3$, Si-C(C**H_3**)$_3$*****), 0.91 (s, 18H, Si-C(C**H_3**)$_3$, Si-C(C**H_3**)$_3$*****), 0.12 (s, 12H, Si-(C**H_3**)$_2$ Si-(C**H_3**)$_2$*****), 0.11 (s, 12H, Si-(C**H_3**)$_2$, Si-(C**H_3**)$_2$*****).

^{13}C-NMR: (75 MHz, CD_3OD) δ (ppm) 165.1 (**C-4**), 157.8 (**C-2**), 139.7 (**C-6**), 139.04 (138.97) (**C**H═CH_2), 116.7 (116.6) (CH═**C**H_2), 89.52 (89.47) (**C-4'**), 87.5 (**C-1'**), 73.96 (73.94), 70.7 (70.5), 64.4 (**C-5'**), 42.34 (42.26) (**C-2'**), 26.5 (Si-C(**C**H_3)$_3$), 26.4 (Si-C(**C**H_3)$_3$), 19.2 (Si-**C**(CH_3)$_3$), 18.8 (Si-**C**(CH_3)$_3$), -4.5 (Si-**C**H_3), -4.7 (Si-**C**H_3), -5.18 (Si-**C**H_3), -5.23 (Si-**C**H_3). **C-5** is not observed.

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{24}H_{46}N_3O_5Si_2$: 512.29705, found: 512.29713.

5-(1-Hydroxyprop-2-enyl)-2'-deoxycytidine (3d)



3d

In a polypropylene tube mixture of epimeric alcohols **2d** (134 mg, 262 µmol, 1.0 equiv) was dissolved in EtOAc (6.00 mL). Subsequently pyridine (97.0 µL, 1.20 mmol, 4.6 equiv) and HF·pyridine (70% HF, 30.0 µL, 1.15 mmol, 4.4 equiv) were added and the solution was stirred for six hours. An additional portion of pyridine (97.0 µL, 1.20 mmol, 4.6 equiv) and HF·pyridine (70% HF, 30.0 µL, 1.15 mmol, 4.4 equiv) was added to the reaction mixture which was stirred for 46 hours. After the addition of TMSOMe (1.00 mL, 7.24 mmol, 28 equiv) a suspension was formed, which was stirred for two hours and centrifuged for 10 min at 3000 rpm. The supernatant was then collected and the residue resuspended in EtOAc and centrifuged for 10 min at 3000 rpm. The procedure was repeated one more time. The

reaction yielded a mixture of diastereomeric alcohols **3d** (54.0 mg, 191 µmol, 73%) as a slight yellow oil. A ratio could not be calculated.

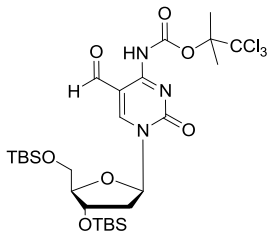
IR: (KBr) ν_{max} = 3419, 1656, 1603, 1516, 1480, 1300, 1257, 1094, 1054, 931, 789, 765, 545 cm^{-1}.

^{1}H-NMR: (400 MHz, CD_3OD) δ (ppm) 8.02-8.01 (m, 2H, **H-6**, **H-6***), 6.26-6.23 (m, 2H, **H-1'**, **H-1'***), 6.12-5.93 (m, 2H, C**H**═CH_2, C**H**═CH_2*****), 5.42-5.36 (m, 2H, CH═C**H$_2$**, CH═C**H$_2$***), 5.27-5.24 (m, 2H, CH═C**H$_2$**, CH═C**H$_2$***), 5.04-5.02 (m, 2H, C**H**-OH, C**H***-OH), 4.38-4.34 (m, 2H, **H-3'**, **H-3'***), 3.95-3.92 (m, 2H, **H-4'**, **H-4'***), 3.83-3.66 (m, 4H, **H-5'**, **H-5'***), 2.39-2.33 (m, 2H, **H-2'**, **H-2'***), 2.16-2.10 (m, 2H, **H-2'**, **H-2'***).

^{13}C-NMR: (75 MHz, CD_3OD) δ (ppm) 165.7 (**C-4**), 157.7 (**C-2**), 140.6 (**C-6**), 139.1 (139.0) (**C**H═CH_2), 116.51 (116.45) (CH═**C**H_2), 109.5 (**C-5**), 88.9 (**C-4'**), 87.6 (**C-1'**), 71.87 (71.85) (**C-3'**), 70.8 (70.70) (**C**H-OH), 62.6 (**C-5'**), 42.13 (42.09) (**C-2'**).

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{12}H_{18}N_3O_5$: 284.12410, found: 284.12412, $[M+Na]^+$ calcd for $C_{12}H_{17}N_3O_5Na$: 306.10604, found: 306.10606.

3',5'-Di(*tert*-butyldimethylsilyl)-*N*^{4}-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-5-formyl-2'-deoxycytidine (4)



4

To a solution of aldehyde **1** (0.500 g, 1.03 mmol, 1.0 equiv) in DCM (4.00 mL) pyridine (100 µL, 1.24 mmol, 1.2 equiv) was added. The reaction mixture was cooled to 0 °C whereby the solution of TCBocCl (0.300 g, 1.25 mmol, 1.2 equiv) in DCM (2.00 mL) was added dropwise. The resulting clear solution was warmed to room temperature and stirred overnight. Subsequently it was poured into ice. After the phases were separated and the aqueous layer was extracted with DCM (3 × 5 mL), the combined organic phases were washed several times with saturated aqueous $CuSO_4$ solution and dried over $MgSO_4$. The solvents were removed under reduced pressure. The crude product was purified by column chromatography (Hex/EtOAc, 6:1 → 1:1 *v/v*) to yield **4** (395 mg, 5.75 µmol, 56%) as a yellow solid.

R_f: 0.48 (Hex/EtOAc = 2:1 *v/v*).

IR: (CCl_4) ν_{max} = 2954, 2857, 1778, 1663, 1564, 1489, 1386, 1254, 1142, 1029, 837, 782 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 10.63 (s, 1H, N**H**), 9.46 (s, 1H, C**H**O), 8.71 (s, 1H, **H-6**), 6.19 (dd, *J* = 6.0, 6.0 Hz, 1H, **H-1'**), 4.35-4.32 (m, 1H, **H-3'**), 4.10-4.07 (m, 1H, **H-4'**), 3.98 (dd, *J* = 11.7, 2.5 Hz, 1H, **H-5'**), 3.78 (dd, *J* = 11.7, 2.5 Hz, 1H**, H-5'**), 2.71-2.65 (m, 1H,

H-2'), 2.13-2.06 (m, 1H, **H-2'**), 2.00-1.99 (m, 6H, C(C**H**$_3$)$_2$), 0.89 (s, 18H, 2xSi-C(C**H$_3$**)$_3$), 0.10 (s, 3H, Si-C**H$_3$**), 0.07 (s, 6H, 2xSi-C**H$_3$**), 0.06 (s, 3H, Si-C**H$_3$**).

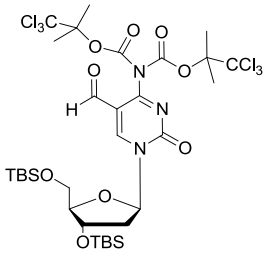
^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) 187.3 (**C**HO), 159.8 (**C-2**), 154.0 (NH**C**OO), 152.5 (**C-6**), 147.2 (**C-4**), 105.2 (**C**Cl$_3$), 90.3 (**C-5**), 89.2 (**C-4'**), 88.7 (**C-1'**), 71.6 (**C-3'**), 62.7 (**C-5'**), 42.9 (**C-2'**), 26.1 (Si-C(**C**H$_3$)$_3$), 25.9 (Si-C(**C**H$_3$)$_3$), 21.6 (C(**C**H$_3$)), 21.5 (C(**C**H$_3$)) 18.6 (Si-**C**(CH$_3$)$_3$), 18.1 (Si-**C**(CH$_3$)$_3$), -4.4 (Si-**C**H$_3$), -4.8 (Si-**C**H$_3$), -5.1 (Si-**C**H$_3$), -5.2 (Si-**C**H$_3$). **C**(CH$_3$)$_2$ is not observed.

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{27}H_{47}Cl_3N_3O_7Si_2$: 686.20126, found: 686.20085.

Melting range: 46 °C - 48 °C.

Optical rotation: $[\alpha]_D^{24}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +26.8$ (c = 1.0, $CHCl_3$).

3',5'-(*tert*-Butyldimethylsilyl)-N^4, N^4-bis(2,2,2-trichloro-*tert*-butyloxycarbonyl)-5-formyl-2'-deoxycytidine (5)



5

To a solution of aldehyde **1** (1.50 g, 3.10 mmol, 1.0 equiv) in DCM (44.0 mL) and pyridine (30.0 mL) a solution of TCBocCl (5.22 g, 21.7 mmol, 7.0 equiv) in DCM (12.0 mL) was added dropwise at room temperature. After stirring at this temperature overnight the reaction mixture was poured into ice. After phase separation, the aqueous layer was extracted with DCM (3 × 30 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvents were removed under reduced pressure. The crude product was purified by column chromatography (Hex/EtOAc, 20:1 → 1:1 *v/v*) to yield **5** (1.39 g, 1.56 mmol, 50%) as a yellow solid.

R_f: 0.61 (Hex/EtOAc = 2:1 *v/v*).

IR: (KBr) ν_{max} = 3441, 2954, 1819, 1686, 1520, 1389, 1289, 1110, 838, 792 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 9.62 (s, 1H, C**H**O), 8.90 (s, 1H, **H-6**), 6.19 (dd, *J* = 5.8, 5.8 Hz, 1H, **H-1'**), 4.37-4.41 (m, 1H, **H-3'**), 4.06-4.08 (m, 1H, **H-4'**), 3.99 (dd, *J* = 11.6, 2.9 Hz, 1H, **H-5'**), 3.81 (dd, *J* = 11.6, 2.9 Hz, 1H, **H-5'**), 2.62-2.68 (m, 1H, **H-2'**), 2.03-2.09 (m, 1H, **H-2'**), 1.92-1.91 (m, 12H, 2xC(C**H**$_3$)$_2$, 0.92 (s, 9H, Si-C(C**H$_3$**)$_3$, 0.90 (s, 9H, Si-C(C**H$_3$**)$_3$, 0.12 (s, 3H, Si-C**H$_3$**),0.11 (s, 9H, 3xSi-C**H$_3$**);

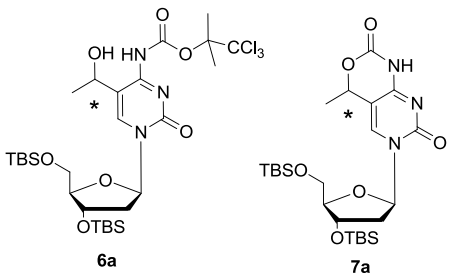
^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 183.3 (**C**HO), 160.9 (**C-2**), 153.6 (N**C**OO), 152.0 (**C-6**), 146.1 (**C-4**), 113.5, 105.4 (**C**Cl_3), 91.7, 88.8 (**C-4'**), 88.3 (**C-1'**), 70.3 (**C-3'**), 62.1 (**C-5'**), 42.4 (**C-2'**), 26.2 (Si-C(**C**H_3)$_3$), 25.8 (Si-C(**C**H_3)$_3$), 21.39 (C(**C**H_3)$_2$), 21.36 (C(**C**H_3)$_2$), 18.7 (Si-**C**$(CH_3)_3$), 18.1 (Si-**C**$(CH_3)_3$), -4.4 (Si-**C**H_3), -4.7 (Si-**C**H_3), -4.9 (Si-**C**H_3), -5.2 (Si-**C**H_3).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+Na]^+$ calcd for $C_{32}H_{51}Cl_6N_3O_9Si_2Na$: 910.11872, found: 910.11808.

Melting range: 64 °C-66 °C.

Optical rotation: $[\alpha]_D^{24}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +31.6$ (c = 1.0, $CHCl_3$).

3',5'-Di(*tert*-butyldimethylsilyl)-*N*^{4}-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-5-(1-hydroxyethyl)-2'-deoxycytidine (6a) and 6-((2*R*,4*S*,5*R*)-4-(*tert*-butyldimethylsilyloxy)-5-((*tert*-butyldimethylsilyloxy)methyl)tetrahydrofuran-2-yl)-4-methyl-1*H*-pyrimido[4,5-*d*][1,3]oxazine-2,7(4*H*,6*H*)-dione (7a)



To an ice-cooled solution of aldehyde **4** (81.0 mg, 118 µmol, 1.0 equiv) in THF (3.00 mL) methylmagnesium bromide (3.0 M in Et_2O; 78.0 µL, 236 µmol, 2.0 equiv) was added dropwise and the solution was allowed to warm to room temperature. After one hour the reaction mixture was cooled down to 0 °C and an additional amount of methylmagnesium bromide (3.0 M in Et_2O; 78.0 µL, 236 µmol, 2.0 equiv) was added dropwise. The reaction mixture was stirred overnight at room temperature. Afterwards the reaction was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with DCM (5 mL). The phases were separated and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (Hex/EtOAc, 20:1 → 2:1 *v/v* and than DCM/MeOH, 30:1 → 15:1 *v/v*) to yield a mixture of diastereomeric alcohols **6a** (23 mg, 32.7 µmol, 28%) as yellow oil (a ratio could not be calculated) and a mixture of diastereomers **7a** with a ratio of 1.9:1 (22 mg, 41.8 µmol, 35%) as a slight yellow oil.

6a:

R_f: 0.57 (Hex/EtOAc = 3:1 *v/v*).

Due to spontaneous cyclisation of **6a** to **7a** ^{1}H-NMR spectrum of **6a** contains compound **7a**.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 12.05 (s, 2H), 7.60 (s, 1H, **H-6**), 7.59 (s, 1H, **H-6***), 6.28-6.21 (m, 2H, **H-1'**, **H-1'***), 4.72-4.67 (m, 2H, C**H**-CH_3, C**H***-CH_3), 4.40-4.36 (m, 2H,

H-3', **H-3'***), 4.00-3.97 (m, 2H, **H-4'**, **H-4'***), 3.81-3.77 (m, 4H, **H-5'**, **H-5'***), 2.39-2.30 (m, 2H, **H-2'**, **H-2'***), 2.07-1.95 (m, 14H, **H-2'**, **H-2'***, $C(C\mathbf{H}_3)_2$, $C(C\mathbf{H}_3)_2$*****), 1.50-1.46 (m, 3H, CH-C**H$_3$,** CH-C**H$_3$***), 0.91 (s, 18H, Si-$C(C\mathbf{H}_3)_3$, Si-$C(C\mathbf{H}_3)_3$*****), 0.89 (s, 18H, Si-$C(C\mathbf{H}_3)_3$, Si-$C(C\mathbf{H}_3)_3$*****), 0.10 (s, 12H, Si-$(C\mathbf{H}_3)_2$, Si-$(C\mathbf{H}_3)_2$*****), 0.08-0.07 (m, 12H, Si-$(C\mathbf{H}_3)_2$, Si-$(C\mathbf{H}_3)_2$*****).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{28}H_{51}Cl_3N_3O_7Si_2$: 702.23256, found: 702.23273.

7a:

R$_f$: 0.24 (DCM/MeOH = 30:1 *v/v*).

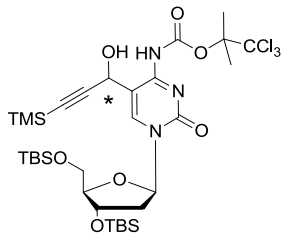
IR: (CCl_4) ν_{max} = 2929, 2857, 1758, 1669, 1561, 1489, 1362, 1254, 1077, 837, 780, 668 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 8.38 (bs, 2H, N**H,** N**H***), 8.00 (d, *J* = 1.1 Hz, 1H, **H-6**), 7.94 (d, *J* = 1.2 Hz, 1H, **H-6***), 6.24-6.17 (m, 2H, **H-1'**, **H-1'***), 5.36-5.28 (m, 2H, C**H**-CH_3, C**H***-CH_3), 4.37-4.30 (m, 2H, **C-3'**, **C-3'***), 4.08-3.99 (m, 2H, **C-4'**, **C-4'***), 3.93-3.84 (m, 2H, **C-5'**, **C-5'***), 3.78-3.73 (m, 2H, **C-5'**, **C-5'***), 2.64-2.56 (m, 2H, **C-2'**, **C-2'***), 2.03-1.89 (m, 2H, **C-2'**, **C-2'***), 1.65 (d, *J* = 1.0 Hz, 3H, CH-C**H**$_3$), 1.62 (d, *J* = 0.8 Hz, 3H, CH-C**H**$_3$*****), 0.90-0.88 (m, 36H, 2xSi-$C(C\mathbf{H}_3)_3$, 2xSi-$C(C\mathbf{H}_3)_3$*****), 0.09-0.06 (m, 24H, 2xSi-$(C\mathbf{H}_3)_2$, 2xSi-$(C\mathbf{H}_3)_2$*****).

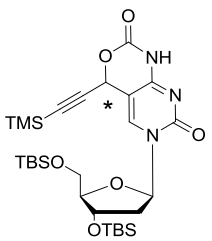
^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) 159.1 (158.9) (**C-4**), 154.6 (**C-2**), 149.8 (149.6) (NH**C**OO), 138.4 (138.1) (**C-6**), 101.6 (101.3) (**C-5**), 88.8 (88.7) (**C-4'**), 88.0 (87.7) (**C-1'**), 72.9 (72.7), 72.1 (72.0), 63.0 (62.9) (**C-5'**), 42.8 (42.7) (**C-2'**), 26.1 (26.0) (Si-$C(\mathbf{C}H_3)_3$), 25.9 (Si-$C(\mathbf{C}H_3)_3$), 20.9 (20.3) (CH-$\mathbf{C}H_3$), 18.6 (18.50) (Si-$\mathbf{C}(CH_3)_3$), 18.14 (18.12) (Si-$\mathbf{C}(CH_3)_3$), -4.4 (-4.5) (Si-$\mathbf{C}H_3$), -4.8 (Si-$\mathbf{C}H_3$), -5.1 (-5.2) (Si-$\mathbf{C}H_3$), -5.3 (Si-$\mathbf{C}H_3$).

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{24}H_{43}N_3O_6Si_2Na$: 548.25826, found: 548.25858, $[2M+Na]^+$ calcd for $C_{48}H_{86}N_6O_{12}Si_4Na$: 1073.52730, found: 1073.52735.

3',5'-Di(*tert*-butyldimethylsilyl)-*N*^{4}-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-5-(1-hydroxy-3-(trimethylsilyl)prop-2-ynyl)-2'-deoxycytidine (6b) and 6-((2*R*,4*S*,5*R*)-4-(*tert*-butyldimethylsilyloxy)-5-((*tert*-butyldimethylsilyloxy)methyl)tetrahydrofuran-2-yl)-4-((trimethylsilyl)ethynyl)-1*H*-pyrimido[4,5-*d*][1,3]oxazine-2,7(4*H*,6*H*)-dione (7b)



6b



7b

To a stirred solution of trimethylsilylacetylene (124 µL, 873 µmol, 4.0 equiv) in THF (1.50 mL) *n*-BuLi (2.5 M in *n*-hexane; 349 µL, 873 µmol, 4.0 equiv) was added dropwise at −40 °C. The reaction mixture was stirred at this temperature for one hour. After the reaction mixture was cooled down to −60 °C a solution of aldehyde **4** (150 mg, 218 µmol, 1.0 equiv) in THF

(1.50 mL) was added dropwise. The reaction mixture was stirred at −60 °C for two and a half hours and thereafter at −50 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (5 mL), diluted with DCM (5 mL) and the aqueous layer was extracted with DCM (3 × 5 mL). The combined organic phases were washed with brine, dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by silica gel chromatography (Hex/EtOAc, 20:1 → 1:1 *v/v* and than DCM/MeOH, 30:1 → 15:1 *v/v*) yielded a mixture of diastereomeric alcohols **6b** with a ratio of 2:1 (72.0 mg, 91.7 µmol, 42%) as a yellow oil and a mixture of diastereomers **7b** with a ratio of 1.1:1 (40.0 mg, 65.8 µmol, 30%) as a yellow oil.

6b:

R_f: 0.55 (Hex/EtOAc = 3:1 *v/v*).

IR: (CCl_4) ν_{max} = 3337, 2955, 2858, 1769, 1666, 1564, 1472, 1371, 1253, 1030, 840, 786 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 12.02 (bs, 2H), 7.94 (s, 1H, **H-6**), 7.90 (s, 1H, **H-6***), 6.19-6.12 (m, 2H, **H-1'**, **H-1'***), 5.38 (s, 1H, C**H**-OH), 5.31(s, 1H, C**H***-OH), 4.37-4.35 (m, 2H, **H-3'**, **H-3'***), 4.05-4.01 (m, 2H, **H-4'**, **H-4'***), 3.80-3.71 (m, 4H, **H-5'**, **H-5'***), 2.46-2.43 (m, 2H, **H-2'**, **H-2'***), 2.09-2.01 (m, 2H, **H-2'**, **H-2'***), 1.95 (s, 12H, C(C**H$_3$**)$_2$, C(C**H$_3$**)$_2$*****), 0.90 (s, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*****), 0.19 (s, 18H, Si-(C**H$_3$**)$_3$, Si-(C**H$_3$**)$_3$*****), 0.09-0.08 (m, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*****).

In ^{13}C-NMR spectrum of **6b** signals of **7b** could be observed due to spontaneous cyclisation of diastereomeric alcohols **6b**.

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 159.6, 147.2, 138.3, 112.7, 106.3, 102.5, 97.7, 96.9, 92.1, 88.8, 87.4, 73.12 (72.8), 63.5, 60.5, 41.7, 26.0, 25.9, 21.43, 21.40, 18.5, 18.1, 0.01, -4.50, -4.69, -5.14, -5.18.

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{32}H_{57}Cl_3N_3O_7Si_3$: 784.25644, found: 784.25647, $[M+Na]^+$ calcd for $C_{32}H_{56}Cl_3N_3O_7Si_3Na$: 806.23838, found: 806.23818.

7b:

R_f: 0.27 (DCM/MeOH = 30:1 *v/v*).

IR: (CCl_4) ν_{max} =3186, 2929, 2857, 1766, 1673, 1564, 1491, 1362, 1316, 1252, 1058, 840, 780, 669 cm^{-1}.

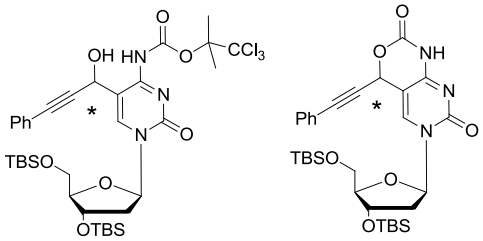
^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H, **H-6**), 8.19 (s, 1H, **H-6***), 6.21-6.14 (m, 2H, **H-1'**, **H-1'***), 5.81 (d, *J* = 1.0 Hz, 1H, C**H***-C≡C-TMS), 5.80 (d, *J* = 0.9 Hz, 1H, C**H***-C≡C-TMS), 4.57 (bs, 2H), 4.35-4.32 (m, 2H, **H-3'**, **H-3'***), 4.10-4.07 (m, 1H, **H-4'**), 4.10-4.03 (m, 1H, **H-4'***), 3.89-3.84 (m, 2H, **H-5'**, **H-5'***), 3.80-3.74 (m, 2H, **H-5'**, **H-5'***), 2.73-2.56 (m, 2H, **H-2'**, **H-2'***), 2.08-1.98 (m, 2H, **H-2'**, **H-2'***), 0.91-0.88 (m, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*****), 0.20 (s, 9H, Si-(C**H$_3$**)$_3$), 0.19 (s, 9H, Si-(C**H$_3$**)$_3$*), 0.09-0.07 (m, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) 158.7 (**C-4**), 154.6 (**C-2**), 148.7 (NH**C**OO), 140.1 (**C-6**), 97.9 (**C-5**), 97.0 (**C**≡C-TMS), 96.5 (C≡**C**-TMS), 89.1 (**C-4'**), 88.6 (**C-1'**), 72.3 (72.0) (**C-3'**), 66.2 (65.9) (**C**H-C≡C-TMS), 63.0 (**C-5'**), 42.8 (C-2'), 26.2 (26.1) (Si-C(**C**H$_3$)$_3$), 26.0

(25.9) (Si-C($\mathbf{C}H_3)_3$), 18.4 (18.1) (Si-$\mathbf{C}(CH_3)_3$), - 0.029 (-0.351) (Si-($\mathbf{C}H_3)_3$), -4.4 (Si-$\mathbf{C}H_3$), -4.8 (Si-$\mathbf{C}H_3$), -5.2 (Si-$\mathbf{C}H_3$), -5.3 (Si-$\mathbf{C}H_3$).

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{28}H_{49}N_3O_6Si_3Na$: 630,28269, found: 630.28187.

3',5'-Di(*tert*-butyldimethylsilyl)-N^4-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-5-(1-hydroxy-3-phenylprop-2-ynyl)-2'-deoxycytidine (6c) and 6-((2*R*,4*S*,5*R*)-4-(*tert*-butyldimethylsilyloxy)-5-((*tert*-butyldimethylsilyloxy)methyl)tetrahydrofuran-2-yl)-4-(phenylethynyl)-1*H*-pyrimido[4,5-*d*][1,3]oxazine-2,7(4*H*,6*H*)-dione (7c)



To a stirred solution of phenylacetylene (77.0 µL, 698 µmol, 4.0 equiv) in THF (1.50 mL) at −85 °C 1.89 ml of *n*-BuLi (2.5 M in *n*-hexane; 279 µL, 698 µmol, 4.0 equiv) was added dropwise. Subsequently the temperature was increased to −40 °C in the course of 1 hour and lowered to -78 °C. A solution of aldehyde **4** (120 mg, 175 µmol, 1.0 equiv) in THF (3.00 mL) was added dropwise and this mixture stirred for one hour. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL), diluted with DCM (5 mL) and the aqueous layer was extracted with DCM (3 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were rotary evaporated. Purification by silica gel chromatography (Hex/EtOAc, 20:1 → 2:1 *v/v* and than DCM/MeOH, 30:1 → 15:1 *v/v*) yielded a mixture of diastereomeric alcohols **6c** with a ratio of 1.6:1 (58.0 mg, 73.5 µmol, 47% brsm) as a yellow oil and a mixture of diastereomers **7c** with a ratio of 1.4:1 (32.0 mg, 52.3 µmol, 34% brsm) as an orange solid. And 14.0 mg (2.04 µmol, 12%) of recovered starting material.

6c:

R_f: 0.18 (Hex/EtOAc = 4:1 *v/v*)

IR: (CCl_4) ν_{max} = 3390, 2929, 1770, 1664, 1562, 1255, 1148, 1028, 837, 781 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 12.04 (bs, 2H), 8.01 (s, 2H, **H-6**, **H-6***), 7.49-7.42 (m, 4H, C**H** aromat., C**H*** aromat.), 7.37-7.28 (m, 6H, C**H** aromat., C**H*** aromat.), 6.23-6.15 (m, 2H, **H-1', H-1'***), 5.61 (s, 1H, C**H**-C≡C-Ph), 5.57 (s, 1H, C**H***-C≡C-Ph) 4.37-4.33 (m, 2H, **H-3', H-3'***), 4.03-3.99 (m, 2H, **H-4', H-4'***), 3.73-3.58 (m, 4H, **H-5', H-5'***), 2.50-2.40 (m, 2H, **H-2'**, **H-2'***), 2.06-1.99 (m, 2H, **H-2'**, **H-2'***), 1.96 (s, 12H, C($C\mathbf{H}_3)_2$, C($C\mathbf{H}_3)_2$*****), 0.89 (s, 18H, Si-C($C\mathbf{H_3})_3$, Si-C($C\mathbf{H_3})_3$*****), 0.85-0.84 (m, 18H, Si-C($C\mathbf{H_3})_3$, Si-C($C\mathbf{H_3})_3$*****), 0.07-0.06 (m, 12H, Si-($C\mathbf{H_3})_2$, Si-($C\mathbf{H_3})_2$*****), 0.00-(-0.04) (m, 12H, Si-($C\mathbf{H_3})_2$, Si-($C\mathbf{H_3})_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 159.7, 147.2, 137.9, 131.9 131.8, 128.92, 128.88, 128.50, 128.47, 122.3, 113.1, 106.3, 89.1, 88.84, 88.75, 87.3, 87.2, 86.9, 86.2, 73.0 (72.9),

63.4 (63.3), 60.6 (60.4), 41.8 (41.6), 26.02 (26.0), 25.91, 25.85, 21.44 (21.42), 18.43 (18.42), 18.10 (18.09), -4.55, -4.73, -5.30, -5.42.

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{35}H_{52}Cl_3N_3O_7Si_2Na$: 810.23071, found: 810.22997.

7c:

R_f: 0.24 (DCM/MeOH = 30:1 *v/v*).

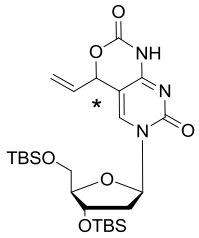
IR: (CCl_4) ν_{max} = 2928, 2857, 1765, 1669, 1564, 1491, 1254, 1093, 1031, 837, 782, 603 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 8.31 (s, 1H, **H-6**), 8.26 (s, 1H, **H-6***), 7.45 (m, 4H, C**H** aromat., C**H*** aromat.), 7.41-7.30 (m, 6H, C**H** aromat., C**H*** aromat.), 6.23-6.18 (m, 2H, **H-1'**, **H-1'***), 6.09 -6.07 (m, 2H**,** C**H**-C≡C-Ph, C**H***-C≡C-Ph), 4.35-4.32 (m, 2H, **H-3'**, **H-3'***), 4.07-4.04 (m, 2H, **H-4'**, **H-4'***), 3.88-3.80 (m, 2H, **H-5'**, **H-5'***), 3.76-3.71 (m, 2H, **H-5'**, **H-5'***), 2.69-2.59 (m, 2H, **H-2'**, **H-2'***), 2.08-1.99 (m, 2H, **H-2'**, **H-2'***), 0.88-0.87 (m, 18H, Si-C(C**H$_3$**)$_3$, Si-C(C**H$_3$**)$_3$*****), 0.86-0.85 (m, 18H, Si-C(C**H$_3$**)$_3$, Si-C(C**H$_3$**)$_3$*****), 0.08-0.05 (m, 12H, Si-(C**H$_3$**)$_2$, Si-(C**H$_3$**)$_2$*****), 0.03-0.01 (m, 12H, Si-(C**H$_3$**)$_2$, Si-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 158.8 (**C-4**), 155.0 (**C-2**), 148.8 (NH**C**OO), 140.1 (139.7) (**C-6**), 132.3 (132.1) (**C** aromat.), 130.0 (129.9) (**C** aromat.), 128.7 (**C** aromat.), 120.7 (**C** aromat.), 98.2 (**C-5**), 90.2 (90.0), 89.1 (88.8), 88.5 (88.2), 81.7 (81.5), 72.2 (**C-3'**), 66.5 (66.3) (**C**H-C≡C-Ph), 63.0 (62.9) (**C-5'**), 42.8 (42.6) (**C-2'**), 26.1 (26.0) Si-C(**C**H$_3$)$_3$, 26.0 (25.9) (Si-C(**C**H$_3$)$_3$), 18.5 (18.4) (Si-**C**(CH$_3$)$_3$), 18.1 (Si-**C**(CH$_3$)$_3$), -4.4 (-4. 5) (Si-**C**H$_3$), -4.76 (-4.78) (Si-**C**H$_3$), -5.3 (Si-**C**H$_3$), -5.35 (-5.37) (Si-**C**H$_3$).

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{31}H_{45}N_3O_6Si_2Na$: 634.27391, found: 634.27421, $[2M+Na]^+$ calcd for $C_{62}H_{90}N_6O_{12}Si_4Na$: 1245.55860, found: 1245.55822.

6-((2*R*,4*S*,5*R*)-4-(*tert*-Butyldimethylsilyloxy)-5-((*tert*-butyldimethylsilyloxy)methyl)tetrahydrofuran-2-yl)-4-vinyl-1*H*-pyrimido[4,5-*d*][1,3]oxazine-2,7(4*H*,6*H*)-dione (7d)



7d

To an ice-cooled solution of aldehyde **4** (182 mg, 265 µmol, 1.0 equiv) in THF (3.00 mL) vinylmagnesium bromide (0.7 M in THF; 757 µl, 530 µmol, 2.0 equiv) was added dropwise and the solution was stirred at 0 °C for 30 min. The reaction mixture was allowed to warm to room temperature whereby it was stirred for three hours. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with Et_2O (5 mL). After phase separation the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced

pressure. The crude product was purified by column chromatography (DCM/MeOH, 30:1 → 15:1 *v/v*) to yield a mixture of diastereomers **7d** with a ratio of 2.3:1 (98.0 mg, 182 µmol, 69%) as a slight yellow oil.

7d:

R_f: 0.27 (DCM/MeOH = 30:1 *v/v*).

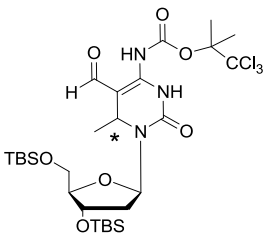
IR: (KBr) ν_{max} = 3428, 2954, 2858, 1759, 1663, 1567, 1384, 1254, 1093, 838, 780 cm^{-1}.

^{1}H-NMR: (400 MHz, DMSO) δ (ppm) 11.31 (bs, 2H, N**H,** N**H***), 7.84 (s, 1H, **H-6**), 7.80 (s, 1H, **H-6***), 6.09-5.94 (m, 4H, **H-1'**, **H-1'***, C**H**═CH_2, C**H***═CH_2), 5.84 (d, *J* = 6.0 Hz, 1H, C**H***-CH═CH_2), 5.80 (d, *J* = 6.1 Hz, 1H, C**H**-CH═CH_2), 5.41-5.34 (m, 4H, CH═C**H**$_2$, CH═C**H**$_2$*****), 4.34-4.30 (m, 2H, **H-3'**, **H-3'***), 3.93-3.89 (m, 2H, **H-4'**, **H-4'***), 3.77-3.65 (m, 4H, **H-5'**, **H-5'***), 2.34-2.27 (m, 2H, **H-2'**, **H-2'***), 2.16-2.08 (m, 2H, **H-2'**, **H-2'***), 0.87 (s, 18H, Si-C(C**H$_3$**)$_3$, Si-C(C**H$_3$**)$_3$*****), 0.85 0.84 (m, 18H, Si-C(C**H$_3$**)$_3$, Si-C(C**H$_3$**)$_3$*****), 0.07 (s, 12H, Si-(C**H$_3$**)$_2$**,** Si-(C**H$_3$**)$_2$*****), 0.04 (s, 12H, Si-(C**H$_3$**)$_2$**,** Si-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, DMSO) δ (ppm) 159.4 (159.3) (**C-4**), 154.0 (**C-2**), 149.9 (149.8) (NH-**C**OO), 139.4 (139.0) (**C**H═CH_2), 134.1 (133.9) (**C-6**), 119.6 (119.4) (CH═**C**H_2), 98.8 (98.5) (**C-5**), 87.8 (87.7) (**C-4'**), 86.9 (86.7) (**C-1'**), 75.4, 75.3 (**C**H-CH═CH_2), 72.34 (72.30) (**C-3'**), 62.8, 62.7 (**C-5'**), 40.7 (40.5) (**C-2'**), 25.8 (25.7) (Si-C(**C**H_3)$_3$), 25.7 (Si-C(**C**H_3)$_3$), 18.0 (17.9) (Si-**C**(CH_3)$_3$), 17.7 (Si-**C**(CH_3)$_3$), -4.8 (Si-**C**H_3), -5.0 (Si-**C**H_3), -5.5 (Si-**C**H_3), -5.5 (Si-**C**H_3).

HR-MS: (ESI positive, DCM/MeOH), $[M+Na]^+$ calcd for $C_{25}H_{43}N_3O_6Si_2Na$: 560.25881, found: 560.25898, $[2M+Na]^+$ calcd for $C_{50}H_{86}N_6O_{12}Si_4Na$: 1097.52785 found: 1097.52679.

3',5'-Di(*tert*-butyldimethylsilyl)-*N*^{4}-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-3,6-dihydro-5-formyl-6-methyl-2'-deoxycytidine (8a)



8a

To an ice-cooled solution of aldehyde **5** (80.0 mg, 89.8 µmol, 1.0 equiv) in THF (2.00 mL) methylmagnesium bromide (3.0 M in Et_2O; 60.0 µL, 180 µmol, 2.0 equiv) was added dropwise and the solution was stirred for three hours. The reaction mixture was then allowed to warm to room temperature whereby it was stirred for three hours. Subsequently it was cooled to 0 °C and an additional amount of methylmagnesium bromide (3.0 M in Et_2O; 30.0 µL, 90.0 µmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred overnight at room temperature, then quenched with saturated aqueous NH_4Cl (5 mL) and diluted with DCM (5 mL). The phases were separated and the aqueous layer extracted with DCM (2 × 5 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was

purified by column chromatography (Hex/EtOAc, 20:1 → 2:1 *v/v*) to yield a mixture of diastereomers **8a** (24.0 mg, 34.1 mmol, 38%) with a ratio of 2.4:1 as a yellow oil.

R_f: 0.23 (Hex/EtOAc = 10:1 *v/v*).

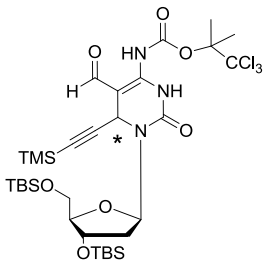
IR: (CCl_4) ν_{max} = 2929, 1705, 1598, 1387, 1254, 1146, 836, 785 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 11.87 (bs, 2H, N**H**COO, N**H***COO), 9.59 (s, 1H, N**H**), 9.56 (s, 1H, N**H***), 9.07 (s, 1H, C**H**O), 9.06 (s, 1H, C**H**O*****), 6.18 (dd, *J* = 8.6, 5.7 Hz, 1H, **H-1'**), 6.10-6.02 (m, 1H, **H-1'***), 4.62 (q, *J* = 6.6 Hz, 1H, **H-6***), 4.46 (q, *J* = 6.4 Hz, 1H, **H-6**), 4.40-4.34 (m, 2H, **H-3'**, **H-3'***), 3.86-3.82 (m, 1H, **H-4'**), 3.82-3.79 (m, 1H, **H-4'***), 3.74-3.70 (m, 4H, **H-5'**, **H-5'***), 2.22-2.15 (m, 1H, **H-2'***), 2.13-2.01 (m, 2H, **H-2'**, **H-2'***), 1.98-1.97 (m, 7H, **H-2',** C(C**H**$_3$)$_3$, C(C**H**$_3$)*****), 1.96 (s, 6H, C(C**H**$_3$)$_3$, C(C**H**$_3$)*****), 1.38 (d, *J* = 6.4 Hz, 3H, CH-C**H**$_3$), 1.33-1.28 (m, 3H, CH-C**H**$_3$*****), 0.91 (s, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.89-0.88 (m, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.09-0.06 (m, 24H, 2xSi-(C**H**$_3$)$_2$, 2xSi-(C**H**$_3$)$_2$*****).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) 186.5 (186.4) (**C**HO), 151.7 (NH**C**OO), 150.3 (**C-2**), 147.5 (**C-4**), 105.1 (**C**Cl$_3$), 96.3 (96.2) (**C-5**), 91.2 (**C**(CH$_3$)$_2$), 87.0 (86.4) (**C-4'**), 85.4 (85.41) (**C-1'**), 72.7 (72.3) (**C-3'**), 63.6 (63.3) (**C-5'**), 46.7 (46.3) (**C-6**), 38.9 (**C-2'**), 26.11 (26.09) (Si-C(**C**H$_3$)$_3$), 26.0 (25.9) (Si-C(**C**H$_3$)$_3$), 24.7 (CH-**C**H$_3$), 21.68 (21.66) (C(**C**H$_3$)$_2$), 21.64 (21.63) (C(**C**H$_3$)$_2$), 18.6 (Si-**C**(CH$_3$)$_3$), 18.2 (Si-**C**(CH$_3$)$_3$), -4.5 (Si-**C**H$_3$), -4.60 (-4.62) (Si-**C**H$_3$), -5.2 (Si-**C**H$_3$), -5.27 (-5.29) (Si-**C**H$_3$).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{28}H_{51}Cl_3N_3O_7Si_2$: 702.23256, found: 702.23296, $[M+Na]^+$ calcd for $C_{28}H_{50}Cl_3N_3O_7Si_2Na$: 724.21451, found: 724.21520.

3',5'-Di(*tert*-butyldimethylsilyl)-*N*^{4}-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-3,6-dihydro-5-formyl-6-(trimethylsilylethynyl)-2'-deoxycytidine (8b)



8b

To a stirred solution of trimethylsilylacetylene (51.1 µL, 359 µmol, 4.0 equiv) in THF (0.60 mL) at −40 °C, *n*-BuLi (2.5 M in *n*-hexane; 144 µL, 359 µmol, 4.0 equiv) was added dropwise. The temperature was increased to −20 °C whereby the reaction mixture was stirred for one hour. Afterwards the temperature was lowered again to −40 °C. A solution of aldehyde **5** (80.0 mg, 89.8 µmol, 1.0 equiv) in THF (1.50 mL) was added dropwise and the reaction mixture was stirred at −50 °C for three hours. The reaction mixture was quenched with saturated aqueous NH_4Cl (3 mL), diluted with DCM (5 mL) and the aqueous layer extracted with DCM (3 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by chromatography (Hex/EtOAc 30:1 → 15:1 *v/v*) afforded diastereomer **8b**

(42.9 mg, 54.6 µmol, 61%) as a yellow oil and diastereomer **8b*** (13.6 mg, 17.3 µmol, 19%) as a yellow oil. The total yield of the reaction is 80 % (56.5 mg, 91.7 µmol).

diastereomer **8b**

R_f: 0.68 (Hex/EtOAc = 5:1 *v/v*).

IR: (CCl_4) ν_{max} = 2926, 1715, 1666, 1603, 1463, 1252, 1140, 1030, 839, 777, 597 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 11.86 (s, 1H, N**H**COO), 9.65 (s, 1H, N**H**), 9.13 (s, 1H, C**H**O), 5.87 (dd, *J* = 7.8, 5.7 Hz, 1H, **H-1'**), 5.21 (s, 1H, **H-6**), 4.38– 4.35 (m, 1H, **H-3'**), 3.92– 3.89 (m, 1H, **H-4'**), 3.74-3.63 (m, 2H, **H-5'**), 2.28-2.21 (m, 1H, **H-2'**), 2.14-2.09 (m, 1H, **H-2'**), 1.98 (s, 3H, C(C**H**$_3$)$_2$), 1.96 (s, 3H, C(C**H**$_3$)$_2$), 0.91 (s, 9H, Si-C(C**H$_3$**)$_3$), 0.89 (s, 9H, Si-C(C**H$_3$**)$_3$), 0.13 (s, 9H, Si-(C**H**$_3$)$_3$), 0.07 (m, 12H, 2 x Si-(C**H**$_3$)$_2$).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 186.4 (**C**HO), 151.6 (NH**C**OO), 149.7 (**C-2**), 147.9 (**C-4**), 105.1 (**C**Cl_3), 103.2 (**C**≡C-TMS), 92.4 (**C-5**), 91.4 (**C**$(CH_3)_2$), 88.6 (C≡**C**-TMS), 87.7 (**C-4'**), 87.0 (**C-1'**), 73.0 (**C-3'**), 63.8 (**C-5'**), 43.5 (**C-6**), 39.5 (**C-2'**), 26.1 (Si-C(**C**H_3)$_3$), 25.9 (Si-C(**C**H_3)$_3$), 21.6 (C(**C**H_3)$_2$), 18.6 (Si-**C**$(CH_3)_3$), 18.1 (Si-**C**$(CH_3)_3$), -0.01 (Si-(**C**H_3)$_3$), -4.5 (Si-**C**H_3), -4.6 (Si-**C**H_3), -5.1 (Si-**C**H_3), -5.1 (Si-**C**H_3).

HR-MS: (ESI positive, DCM/MeOH), $[M+Na]^+$ calcd for $C_{32}H_{56}Cl_3N_3O_7Si_3Na$: 806.23838, found: 806.23863.

Optical rotation: $[\alpha]_D^{25}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +6.0$ (c = 1.0, $CHCl_3$).

diastereomer **8b*:**

R_f: 0.60 (Hex/EtOAc = 5:1 *v/v*).

IR: (CCl_4) ν_{max} =3326, 2928, 1712, 1667, 1602, 1463, 1386, 1252, 1141, 1027, 839, 778 cm^{-1}.

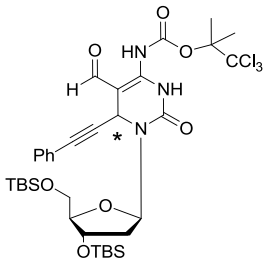
^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 11.84 (s, 1H, N**H*****COO), 9.66 (s, 1H, N**H***), 9.10 (s, 1H, C**H**O*), 6.23 (dd, *J* = 8.3, 5.9 Hz, 1H, **H-1'***), 5.38 (s, 1H, **H-6***), 4.41-4.38 (m, 1H, **H-4'***), 3.85-3.67 (m, 3H, **H-3'***, **H-5'***), 2.58-2.51 (m, 1H, **H-2'***), 2.06-2.01 (m, 1H, **H-2'***), 1.99 (s, 3H, C(C**H**$_3$)$_2$*), 1.97 (s, 3H, C(C**H**$_3$)$_2$*), 0.93 (s, 9H, Si-C(C**H$_3$**)$_3$*), 0.90 (s, 9H, Si-C(C**H$_3$**)$_3$*), 0.13 (s, 9H, Si-(C**H**$_3$)$_3$*), 0.11 (s, 3H, Si-C**H$_3$***), 0.10 (s, 3H, Si-C**H$_3$***), 0.08 (m, 6H, Si-(C**H$_3$**)$_2$*).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 186.5 (**C**HO), 151.7 (NH**C**OO), 149.5 (**C-2**), 148.0 (**C-4**), 105.1 (**C**Cl_3), 104.4 (**C**≡C-TMS), 92.5 (**C-5**), 91.4 (**C**$(CH_3)_2$), 89.1 (C≡**C**-TMS), 86.4 (**C-4'**), 84.4 (**C-1'**), 72.3 (**C-3'**), 63.3 (**C-5'**), 40.3 (**C-6**), 38.2 (**C-2'**), 26.2 (Si-C(**C**H_3)$_3$), 25.9 (Si-C(**C**H_3)$_3$), 21.7 (C(**C**H_3)$_2$), 18.7 (Si-**C**$(CH_3)_3$), 18.2 (Si-**C**$(CH_3)_3$), -0.1 (Si-(**C**H_3)$_3$), -4.4 (Si-**C**H_3), -4.6 (Si-**C**H_3), -5.1 (Si-**C**H_3), -5.2 (Si-**C**H_3).

HR-MS: (ESI positive, DCM/MeOH), $[M+Na]^+$ calcd for $C_{32}H_{56}Cl_3N_3O_7Si_3Na$: 806.23838, found: 806.23854.

Optical rotation: $[\alpha]_D^{22}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +10.14$ (c = 0.46, $CHCl_3$).

3',5'-Di(*tert*-butyldimethylsilyl)-N^4-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-3,6-dihydro-5-formyl-6-(2-phenylethynyl)-2'-deoxycytidine (8c)



8c

To a stirred solution of phenylacetylene (49.3 µL, 449 µmol, 4.0 equiv) in THF (1.50 mL) at −78 °C n-BuLi (2.5 M in *n*-hexane; 180 µL, 449 µmol, 4.0 equiv) was added dropwise, whereby the reaction mixture was stirred for 80 min. Subsequently a solution of aldehyde **5** (100 mg, 112 µmol, 1.0 equiv) in THF (2.10 mL) was added dropwise. The temperature was increased to −50 °C, whereby the mixture was stirred for 140 min. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL), diluted with DCM (5 mL) and the aqueous layer extracted with DCM (3 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by silica gel chromatography (Hex/EtOAc, 20:1 → 1:1 *v/v*) yielded a mixture of diastereomers **8c** with a ratio of 1.1:1 (63.0 mg, 79.8 µmol, 71%) as a yellow oil.

R_f: 0.26 (Hex/EtOAc = 10:1 *v/v*).

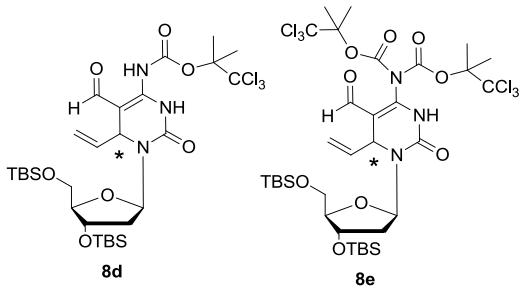
IR: (CCl_4) ν_{max} = 3323, 2929, 1710, 1601, 1470, 1389, 1256, 1208, 1141, 1028, 837, 784, 690 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 11.88-11.87 (m, 2H, N**H**COO**,** N**H***COO), 9.75-9.74 (m, 2H, N**H**, N**H ***), 9.21 (s, 1H, C**H**O), 9.19 (s, 1H, C**H**O*****), 7.38-7.34 (m, 4H, C**H** aromat., C**H*** aromat.), 7.32-7.27 (m, 6H, C**H** aromat., C**H*** aromat.), 6.26 (dd, *J* = 7.8, 6.0 Hz, 1H, **H-1'***), 6.03 (dd, *J* = 7.9, 5.7 Hz, 1H, **H-1'**), 5.65 (s, 1H, **H-6***), 5.46 (s, 1H, **H-6**), 4.46-4.43 (m, 1H, **H-4'***), 4.39-4.38 (m, 1H, **H-3'**), 3.95-3.92 (m, 1H, **H-4'**), 3.86-3.82 (m, 2H, **H-5'**), 3.71-3.69 (m, 3H, **H-3'***, **H-5'***), 2.62-2.55 (m, 1H, **H-2'***), 2.27-2.20 (m, 1H, **H-2'**), 2.18-2.09 (m, 2H, **H-2'**, **H-2'***), 1.96-1.95 (m, 12H, C(C**H$_3$**)$_2$, C(C**H$_3$**)$_2$*****), 0.92 (s, 6H, Si-C(C**H$_3$**), Si-C(C**H$_3$**)*****), 0.89-0.88 (m, 24H, 2xSi-C(C**H$_3$**), 2xSi-C(C**H$_3$**)*****), 0.86 (s, 6H, Si-C(C**H$_3$**), Si-C(C**H$_3$**)*****), 0.12-0.11 (m, 6H, Si-C**H$_3$**, Si-C**H$_3$***), 0.09-0.07 (m, 6H, Si-C**H$_3$**, Si-C**H$_3$***), 0.05-0.04 (m, 6H, Si-C**H$_3$**, Si-C**H$_3$***), 0.02 (s, 6H, Si-C**H$_3$**, Si-C**H$_3$***).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 186.4 (186.3) (**C**HO), 151.61 (151.58) (NH**C**OO), 150.0 (149.5) (**C-2**), 148.2 (148.0) (**C-4**), 131.9 (131.7) (**C** aromat.), 128.9 (128.7) (**C** aromat.), 128.5 (128.3) (**C** aromat.), 122.3 (122.0) (**C** aromat.), 105.0 (**C**Cl_3), 92.65 (92.62) (**C-5**), 91.4 (**C**$(CH_3)_2$), 88.2, 87.7, 87.4, 86.5, 86.4 , 84.4, 84.0, 83.6, 81.3, 72.8 (72.0) (**C-3'**), 63.7 (63.2) (**C-5'**), 42.9 (40.2) (**C-6**), 39.6 (38.6) (**C-2'**), 26.2 (26.1) (Si-C(**C**$H_3)_3$), 25.91 (25.88) (Si-C(**C**$H_3)_3$), 21.7 (21.6) (C(**C**$H_3)_2$), 21.64 (21.59) (C(**C**$H_3)_2$), 18.7 (18.1) (Si-**C**$(CH_3)_3$), 18.6 (18.1) (Si-**C**$(CH_3)_3$), -4.49 (-4.54) (Si-**C**H_3), -4.63 (-4.71) (Si-**C**H_3), -5.1 (-5.2) (Si-**C**H_3), -5.2 (-5.3) (Si-**C**H_3).

HR-MS: (ESI positive, DCM/MeOH), $[M+Na]^+$ calcd for $C_{35}H_{52}Cl_3N_3O_7Si_2Na$: 810.23016, found: 810.22984.

3',5'-Di(*tert*-butyldimethylsilyl)-N^4-(2,2,2-trichloro-*tert*-butyloxycarbonyl)-3,6-dihydro-5-formyl-6-vinyl-2'-deoxycytidine (8d) and 3',5'-Di(*tert*-butyldimethylsilyl)-N^4, N^4-bis(2,2,2-trichloro-*tert*-butyloxycarbonyl)-3,6-dihydro-5-formyl-6-vinyl-2'-deoxycytidine (8e)



To an ice-cooled solution of aldehyde **5** (100 mg, 112 µmol, 1.0 equiv) in THF (2.30 mL) vinylmagnesium bromide (0.7 M in THF; 320 µL, 225 µmol, 2.0 equiv) was added dropwise and the solution was stirred at 0 °C. After 135 min the reaction was quenched with saturated aqueous NH_4Cl (5 mL) and diluted with Et_2O (5 mL). The phases were separated and the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (Hex/EtOAc, 20:1 → 1:1 *v/v*) to yield a mixture of diastereomers **8d** with a ratio of 2.6:1 (32.0 mg, 44.7 µmol, 37%) as a yellow oil and a mixture of diastereomers **8e** with a ratio of 5.7:1 (18.0 mg, 19.6 µmol, 17%) as a yellow oil.

8d:

R_f: 0.44 (Hex/EtOAc = 4:1 *v/v*).

IR: (CCl_4) ν_{max} = 3328, 2929, 2857, 1707, 1665, 1599, 1515, 1389, 1254, 1209, 1140, 1026, 836, 778 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 11.94 (s, 1H, N**H**COO), 11.86 (s, 1H, N**H***COO), 9.58 (s, 2H, N**H**, N**H***), 9.07 (s, 1H, C**H**O*****), 9.03 (s, 1H, C**H**O), 6.23 (dd, *J* = 8.5, 5.8 Hz, 1H, **H-1'***), 6.09 (dd, *J* = 8.3, 5.6 Hz, 1H, **H-1'**), 6.04-5.91 (m, 1H, CH-C**H**=CH_2), 5.85-5.76 (m, 1H, CH-C**H***=CH_2), 5.16-5.12 (m, 2H, CH-CH=C**H**$_2$, CH-CH=C**H**$_2$*****), 5.12-5.05 (m, 2H, CH-CH=C**H**$_2$, CH-CH=C**H**$_2$*****), 5.04-5.02 (m, 1H, **H-6***), 4.90-4.89 (m, 1H, **H-6**), 4.37-4.30 (m, 2H, **H-3'**, **H-3'***), 3.86-3.84 (m, 1H, **H-4'**), 3.78-3.75 (m, 1H, **H-4'***), 3.73-3.72 (m, 2H, **H-5'***), 3.70-3.68 (m, 2H, **H-5'**), 2.19-2.10 (m, 2H, **H-2'**, **H-2'***), 2.03-1.99 (m, 1H, **H-2'**) 1.99-1.87 (m, 13H, **H-2'***, C(C**H**$_3$)$_2$, C(C**H**$_3$)$_2$*****), 0.91-0.90 (m, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.88 (s, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.08 (s, 6H, Si-(C**H**$_3$)$_2$*****), 0.07-0.05 (m, 18H, Si-(C**H**$_3$)$_2$*****, 2xSi-(C**H**$_3$)$_2$).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 186.9 (186.8) (**C**HO), 151.7 (NH**C**OO), 150.3 (**C-2**), 148.0 (147.8) (**C-4**), 138.2 (137.8) (**C**H=CH_2), 115.3 (114.3) (CH=**C**H$_2$), 105.1 (**C**Cl_3), 93.2 (**C-5**), 91.3 (**C**(CH_3)$_2$), 86.2 (**C-4'**), 84.6 (**C-1'**), 72.5 (72.1) (**C-3'**), 63.4 (**C-5'**), 52.3 (51.1) (**C-6**), 39.1 (38.7) (**C-2'**), 26.14 (26.10) (Si-C(**C**H$_3$)$_3$), 21.7 (21.6) (C(**C**H$_3$)$_2$), 18.6

(Si-**C**$(CH_3)_3$), 18.2 (18.1) (Si-**C**$(CH_3)_3$), -4.5 (Si-**C**H_3), -4.6 (Si-**C**H_3), -5.1 (Si-**C**H_3), -5.2 (Si-**C**H_3).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+Na]^+$ calcd for $C_{29}H_{50}Cl_3N_3O_7Si_2Na$: 736.21451, found: 736.21428.

8e:

R_f: 0.34 (Hex/EtOAc = 3:1 *v/v*).

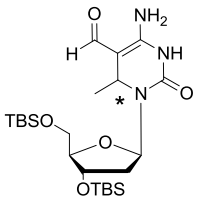
IR: (CCl_4) ν_{max} = 2929, 2857, 1816, 1654, 1463, 1389, 1257, 1138, 837, 789 cm^{-1}.

^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 9.61 (s, 1H, C**H**O), 9.59 (s, 1H, C**H**O*****), 6.08-5.96 (m, 2H, **H-1'** , **H-1'***), 5.87-5.74 (m, 2H, C**H**═CH_2, C**H***═CH_2), 5.26-5.15 (m, 2H, CH═C**H**$_2$, CH═C**H**$_2$*****), 5.13-5.02 (m, 4H, CH═C**H**$_2$, C**H**-CH═CH_2, CH═C**H**$_2$***,** C**H***-CH═CH_2), 4.42-4.23 (m, 2H, **H-3', H-3'***), 3.86-3.74 (m, 2H, **H-4'**, **H-4'***), 3.74-3.60 (m, 2H, **H-5', H-5'***), 3.54-3.50 (m, 2H, **H-5', H-5'***), 2.15-2.08 (m, 2H, **H-2', H-2'***), 2.03-1.85 (m, 26H, **H-2', H-2'*,** 2xC(C**H**$_3$)$_2$, 2xC(C**H**$_3$)$_2$*****), 0.91-0.89 (m, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*****), 0.11-0.06 (m, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 183.9 (**C**HO), 153.5 (C-2), 149.7 (N**C**OO) 142.8 (C-4), 135.6 (**C**H═CH_2), 116.4 (CH═**C**H_2), 111.9 (**C-5**), 104.9 (CCl_3), 92.5 (**C**$(CH_3)_2$), 86.9 (**C-4'**), 85.4 (**C-1'**), 72.5 (72.3)(**C-3'**), 63.5 (**C-5'**), 50.9 (C-6), 38.0 (**C-2'**), 26.2 (26.1) (Si-C(**C**H_3)$_3$), 25.97 (25.90) (Si-C(**C**H_3)$_3$), 21.5 (21.4) (C(**C**H_3)$_2$), 18.6 (18.2), -4.5 (-4.6), -5.2.

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+Na]^+$ calcd for $C_{34}H_{55}Cl_6N_3O_9Si_2Na$: 938,15002, found: 938,15004.

3',5'-Di(*tert*-butyldimethylsilyl)-3,6-dihydro-5-formyl-6-methyl-2'-deoxycytidine (9a)



9a

10% Cd–Pb couple (80.0 mg, 711 µmol cadmium, 5.0 equiv) was added in one portion to a vigorously stirred mixture of diastereomers **8a** (100 mg, 142 µmol, 1.0 equiv) in THF (2.20 mL) and aqueous NH_4OAc (1.0 M, 2.20 mL). After stirring for three and a half hours another portion of 10% Cd–Pb (80.0 mg, 712 µmol, 5.0 equiv) was added. The reaction mixture was stirred at room temperature overnight, and then the solids were filtered and rinsed with H_2O and DCM. The phases were separated and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) to yield a mixture of diastereomers **9a** with a ratio of 2.4:1 (28.5 mg, 56.0 µmol, 40%) as a pale yellow waxy solid.

R_f: 0.32 (DCM/MeOH = 15:1 *v/v*).

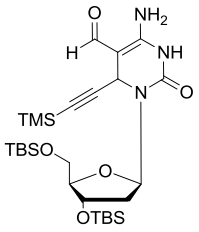
IR: (CCl_4) ν_{max} = 2929, 2857, 1698, 1655, 1541, 1382, 1338, 1255, 1081, 835, 777, 667 cm^{-1}.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 9.64 (s, 1H, N**H**), 9.55 (s, 1H, N**H***), 8.91 (s, 2H, C**H**O, C**H**O*****), 6.20-6.13 (m, 1H, **H-1'**), 6.13-6.07 (m, 1H, **H-1'***), 4.55 (q, *J* = 6.4 Hz, 1H, **H-6***), 4.40-4.33 (m, 3H, **H-6, H-3'**, **H-3'***), 3.83-3.79 (m, 2H, **H-4'**, **H-4'***), 3.73-3.65 (m, 4H, **H-5'**, **H-5'***), 2.22-2.02 (m, 2H, **H-2'**, **H-2'***), 1.97-1.84 (m, 2H, **H-2'**, **H-2'***), 1.34 (d, *J* = 6.4 Hz, 3H, CH-C**H**$_3$), 1.29-1.23 (m, 3H, CH-C**H**$_3$*****), 0.91 (s, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.89-0.88 (m, 18H, Si-C(C**H**$_3$)$_3$, Si-C(C**H**$_3$)$_3$*****), 0.08 (s, 12H, Si-(C**H**$_3$)$_2$, Si-(C**H**$_3$)$_2$*), 0.07 (s, 12H, Si-(C**H**$_3$)$_2$, Si-(C**H**$_3$)$_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 182.9 (182.7) (**C**HO), 153.6 (153.5), 153.3, 92.8 (**C-5**), 86.8 (86.3) (**C-4'**), 84.9 (84.7) (**C-1'**), 72.8 (72.3) (**C-3'**), 63.6 (63.3) (**C-5'**), 47.2 (46.5) (**C-6**), 38.5 (38.1) (**C-2'**), 26.1 (Si-C(**C**H$_3$)$_3$), 25.93 (25.90) (Si-C(**C**H$_3$)$_3$), 25.7 (25.3) (CH-**C**H$_3$,), 18.5 (Si-**C**(CH$_3$)$_3$), 18.2 (18.1) (Si-**C**(CH$_3$)$_3$), -4.5 (Si-**C**H$_3$), -4.59 (-4.62) (Si-**C**H$_3$), -5.2 (Si-**C**H$_3$), -5.3 (-5.4) (Si-**C**H$_3$).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{23}H_{46}N_3O_5Si_2$: 500.29705, found: 500.29709, $[M+Na]^+$ calcd for $C_{23}H_{45}N_3O_5Si_2Na$: 522.27900, found: 522.27887.

3',5'-Di(*tert*-butyldimethylsilyl)-3,6-dihydro-5-formyl-6-(trimethylsilylethynyl)-2'-deoxycytidine (9b)



9b

10% Cd–Pb couple (44.0 mg, 391 µmol cadmium, 2.9 equiv) was added in one portion to a vigorously stirred solution of diastereomer **8b** (106 mg, 134 µmol, 1.0 equiv) in THF (2.00 mL) and aqueous NH_4OAc (1.0 M, 2.00 mL). After stirring for three and a half hours the solids were filtered and rinsed with H_2O and DCM. The phases were separated and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) to yield diastereomer **9b** (60.6 mg, 104 µmol, 77%) as a yellow waxy solid.

R_f: 0.36 (DCM/MeOH = 15:1 *v/v*).

IR: (KBr) ν_{max} = 2929, 2858, 2166, 1706, 1543, 1463, 1362, 1252, 1081, 778, 667, 569 cm^{-1}.

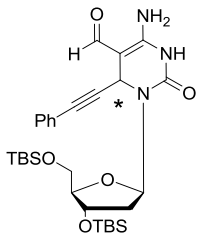
^{1}H-NMR: (400 MHz, $CDCl_3$) δ (ppm) 9.40 (s, 1H, NH), 8.96 (s, 1H, C**H**O), 5.95 (dd, *J* = 8.4, 5.6 Hz, 1H, **H-1'**), 5.04 (s, 1H, **H-6**), 4.39-4.37 (m, 1H, **H-4'**), 3.90-3.87 (m, 1H, **H-3'**), 3.75 (dd, *J* = 10.8, 4.4 Hz, 1H, **H-5'**), 3.64 (dd, *J* = 10.8, 5.7 Hz, 1H, **H-5'**), 2.27-2.21 (m, 1H, **H-2'**), 1.99 (ddd, *J* = 12.9, 5.7, 2.2 Hz, 1H, **H-2'**), 0.91 (s, 9H, Si-C(C**H**$_3$)$_3$), 0.88 (s, 9H, Si-C(C**H**$_3$)$_3$), 0.11 (s, 9H, Si-(**C**H$_3$)$_3$), 0.09-0.08 (m, 6H, Si-(C**H**$_3$)$_2$), 0.07 (s, 6H, Si-(C**H**$_3$)$_2$).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 182.9 (**C**HO), 153.4, 152.8, 104.7 (**C**≡C-TMS), 89.3 (C≡**C**-TMS), 87.4 (**C-4'**), 86.2 (**C-1'**), 73.0 (**C-3'**), 64.0 (**C-5'**), 43.7 (**C-6**), 38.2 (**C-2'**), 26.1 (Si-C(**C**H_3)$_3$), 25.9 (Si-C(**C**H_3)$_3$), 18.6 (Si-**C**(CH_3)$_3$), 18.1 (Si-**C**(CH_3)$_3$), 0.1 (Si-(**C**H_3)$_3$), -4.6 (Si-**C**H_3), -4.6 (Si-**C**H_3), -5.1 (Si-**C**H_3). **C-5** is not observed.

HR-MS: (ESI positive, MeOH), $[M+Na]^+$ calcd for $C_{27}H_{51}N_3O_5Si_3Na$: 604.30287, found: 604.30347.

Optical rotation: $[\alpha]_D^{25}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +18.8$ (c = 1, $CHCl_3$).

3',5'-Di(*tert*-butyldimethylsilyl)-3,6-dihydro-5-formyl-6-(2-phenylethynyl)-2'-deoxycytidine (9c)



9c

10% Cd–Pb couple (121 mg, 1.08 mmol cadmium, 5.0 equiv) was added in one portion to a vigorously stirred mixture of diastereomers **8c** (170 mg, 215 µmol, 1.0 equiv) in THF (3.00 mL) and aqueous NH_4OAc (1.0 M, 3.00 mL). After stirring for three hours the solids were filtered and rinsed with H_2O and DCM. The phases were separated and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 60:1 → 15:1 *v/v*) to yield a mixture of diastereomers **9c** with a ratio of 1:1 (55.0 mg, 93.9 µmol, 44%) as a yellow oil.

R_f: 0.32 (DCM/MeOH = 15:1 *v/v*).

IR: (CCl_4) ν_{max} = 3308, 2928, 2857, 1700, 1659, 1541, 1362, 1254, 1097, 834, 779, 690 cm^{-1}.

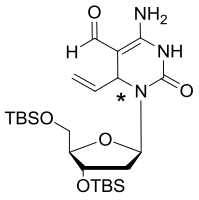
^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 9.64-9.59 (m, 2H, N**H**, N**H***), 9.04 (bs, 2H, C**H**O, C**H**O*****), 7.37-7.35 (m, 4H, C**H** aromat., C**H*** aromat.), 7.30-7.21 (m, 6H, C**H** aromat., C**H*** aromat.), 6.23 (dd, *J* = 6.9, 6.9 Hz, 1H, **H-1'**), 6.17-6.04 (m, 1H, **H-1'***), 5.54 (s, 1H, **H-6**), 5.30 (s, 1H, **H-6***), 4.45-4.40 (m, 2H), 3.93-3.89 (m, 1H), 3.85-3.77 (m, 3H), 3.75-3.72 (m, 1H), 3.70-3.60 (m, 2H), 2.67-2.58 (m, 1H), 2.31-2.22 (m, 1H), 2.14-1.96 (m, 2H, m, 2H, **H-2'**, **H-2'***), 0.93 (s, 9H, Si-C(C**H$_3$**)$_3$,), 0.88 (s, 9H, Si-C(C**H$_3$**)$_3$*****), 0.87-0.86 (m, 18H, Si-C(C**H$_3$**)$_3$), Si-C(C**H$_3$**)$_3$*****), 0.12 (s, 6H, Si-(C**H$_3$**)$_2$), 0.08 (s, 6H, Si-(C**H$_3$**)$_2$*), 0.04 (s, 6H, Si-(C**H$_3$**)$_2$), 0.00 (s, 6H, Si-(C**H$_3$**)$_2$*****).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ (ppm) 183.0 (182.7) (**C**HO), 153.8 (153.6) , 153.3 (152.5), 131.9 (131.8) (**C** aromat.), 128.5 (**C** aromat.), 128.4 (128.3) (**C** aromat.), 128.3 (**C** aromat.), 122.7 (122.6) (**C** aromat.), 89.4 (89.3), 88.8, 87.3, 86.4, 85.7, 84.2, 83.2, 83.0, 72.9 (72.2) (**C-3'**), 63.9 (63.3) (**C-5'**), 43.1 (41.0) (**C-6'**), 38.4 (38.0) (**C-2'**), 26.2 (26.1) (Si-C(**C**H_3)$_3$),

25.9 (Si-C(**C**H_3)$_3$), 18.6 (18.5) (Si-**C**(CH_3)$_3$), 18.13 (18.10) (Si-**C**(CH_3)$_3$), -4.5 (-4.56) (Si-**C**H_3), -4.57 (-4.67) (Si-**C**H_3), -5.12 (-5.23) (Si-**C**H_3), -5.31 (-5.32) (Si-**C**H_3).

HR-MS: (ESI positive, $CHCl_3$/MeOH), $[M+H]^+$ calcd for $C_{30}H_{48}N_3O_5Si_2$: 586.31270, found: 586.31308, $[M+Na]^+$ calcd for $C_{30}H_{47}N_3O_5Si_2Na$: 608.29465, found: 608.29493.

3',5'-Di(*tert*-butyldimethylsilyl)-3,6-dihydro-5-formyl-6-vinyl-2'-deoxycytidine (9d)



9d

10% Cd–Pb couple (19.7 mg, 175 µmol cadmium, 5.0 equiv) was added in one portion to a vigorously stirred mixture of diastereomers **8d** (25.0 mg, 34.9 µmol, 1.0 equiv) in THF (1.10 mL) and aqueous NH_4OAc (1.0 M, 1.10 mL). The reaction mixture was stirred at room temperature overnight, and then the solids were filtered and rinsed with H_2O and DCM. The phases were separated and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography (DCM/MeOH, 30:1 *v/v*) to yield a mixture of the diastereomers **9d** with a ratio of 2.6:1 (11.0 mg, 21.5 µmol, 61%) as a yellow waxy solid.

R_f: 0.47 (DCM/MeOH = 15:1 *v/v*).

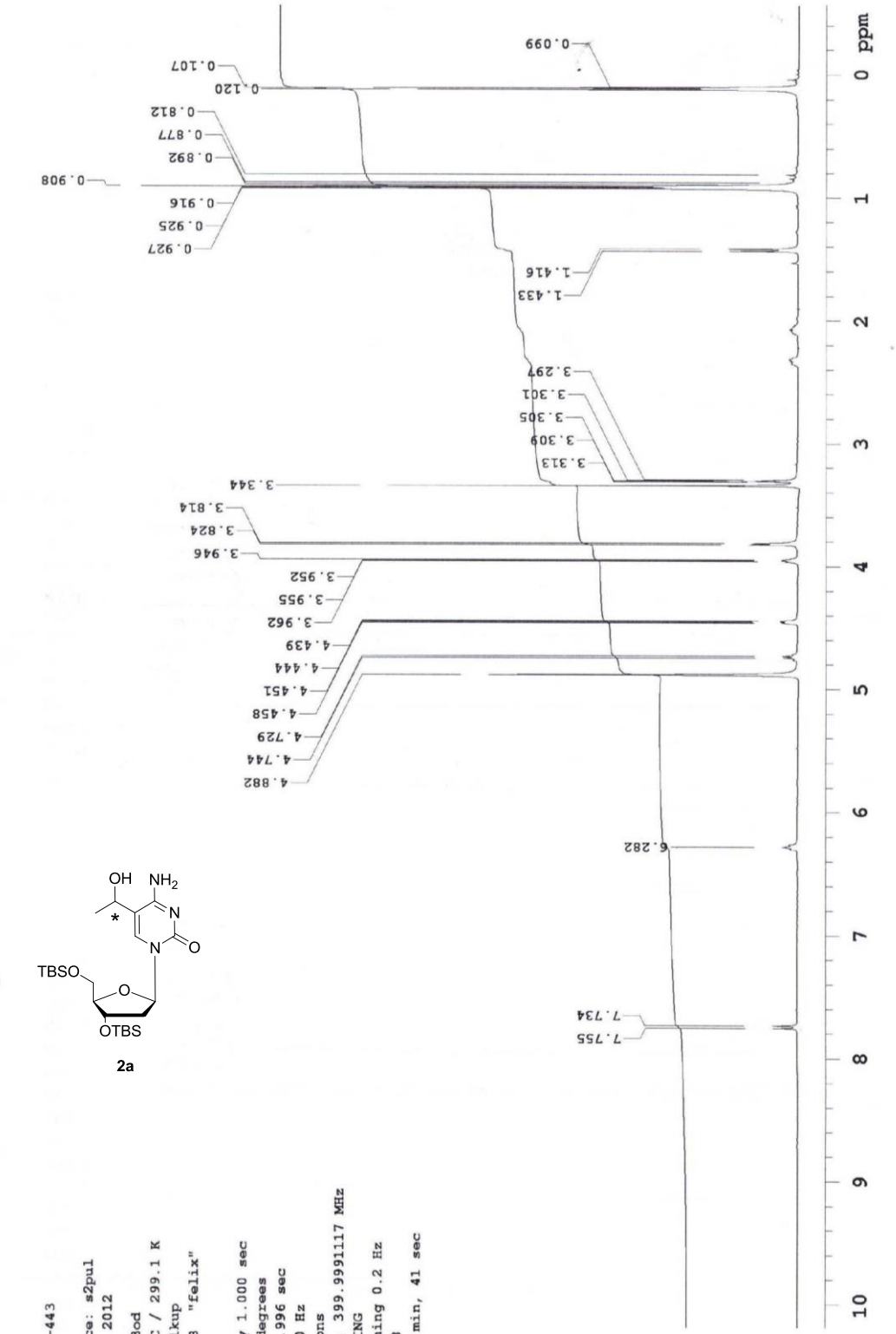
IR: (CCl_4) ν_{max} = 3343, 2928, 2857, 1698, 1655, 1541, 1362, 1255, 1096, 836, 778 cm^{-1}.

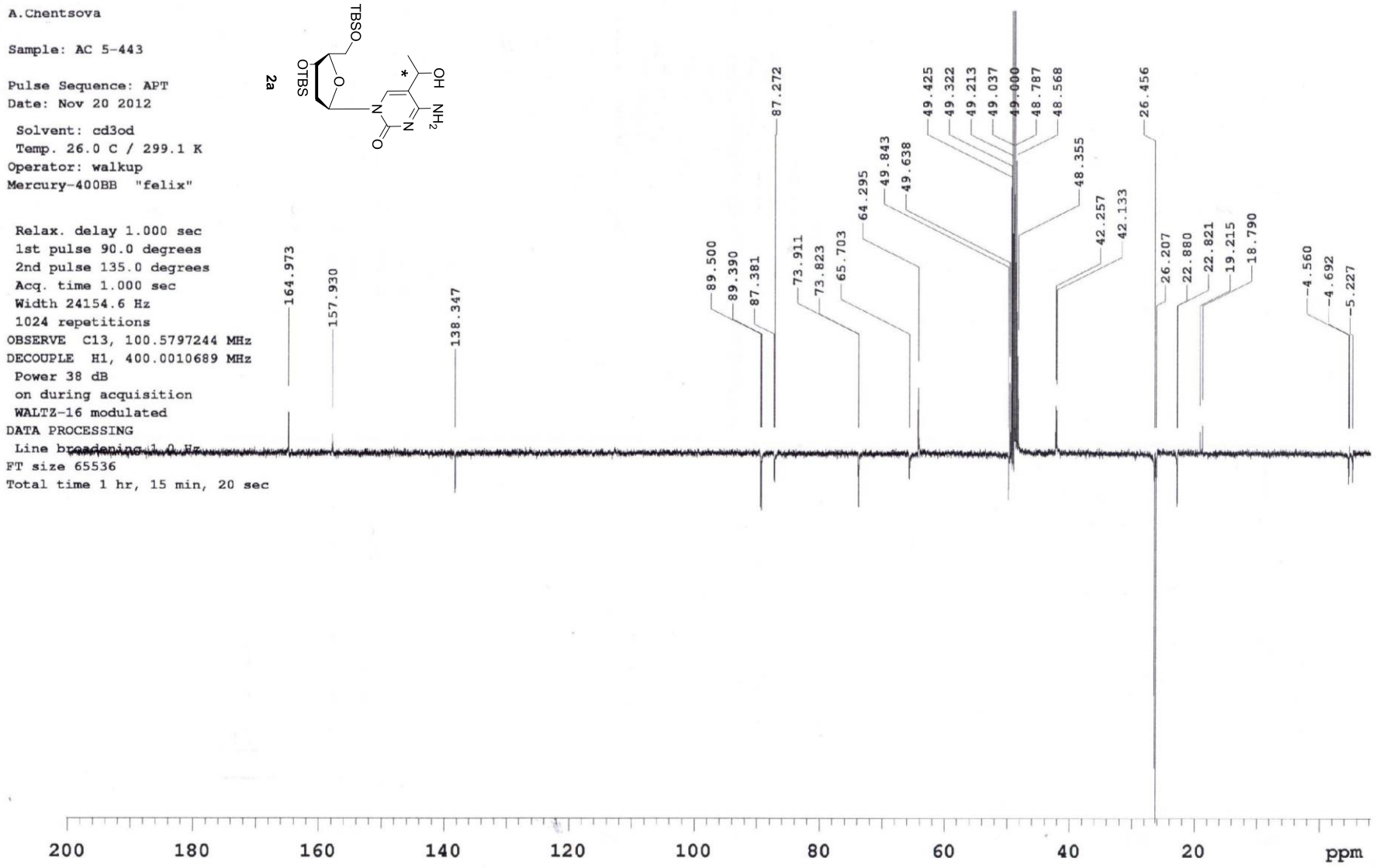
^{1}H-NMR: (300 MHz, $CDCl_3$) δ (ppm) 9.42 (s, 2H, N**H**, N**H** *), 8.91 (s, 1H, C**H**O*), 8.86 (s, 1H, C**H**O), 6.22 (dd, *J* = 8.7, 5.6 Hz, 1H, **H-1'***), 6.12 (dd, *J* = 8.7, 5.6 Hz, 1H, **H-1'**), 5.98 (ddd, *J* = 17.1, 10.1, 4.7 Hz, 1H, CH-C**H**=CH_2), 5.78 (ddd, *J* = 17.0, 10.1, 5.5 Hz, 1H, CH-C**H***=CH_2), 5.11-4.97 (m, 4H, CH-CH=C**H**$_2$, CH-CH=C**H**$_2$*), 4.93 (d, *J* = 5.4 Hz, 1H, **H-6***), 4.76 (d, *J* = 4.7 Hz, 1H, **H-6**), 4.36-4.33 (m, 2H, **H-3'**, **H-3'***), 3.85-3.81 (m, 1H, **H-4'**), 3.78-3.76 (m, 1H, **H-4'***), 3.72- 3.67 (m, 4H, **H-5'**, **H-5'***), 2.23-2.09 (m, 2H, **H-2'**, **H-2'***), 1.97-1.84 (m, 2H, **H-2'**, **H-2'***), 0.91-0.88 (m, 36H, 2xSi-C(C**H$_3$**)$_3$, 2xSi-C(C**H$_3$**)$_3$*), 0.08-0.06 (m, 24H, 2xSi-(C**H$_3$**)$_2$, 2xSi-(C**H$_3$**)$_2$*).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ (ppm) 183.4 (**C**HO), 153.8, 153.2, 139.5 (**C**H=CH_2), 114.7 (CH=**C**H_2), 87.0 (**C-4'**), 85.3 (**C-1'**), 72.4 (**C-3'**), 63.5 (**C-5'**), 52.8 (**C-6**), 38.2 (**C-2'**), 26.14 (26.11) (Si-C(**C**H_3)$_3$), 25.92 (25.90) (Si-C(**C**H_3)$_3$), 18.60 (18.55) (Si-**C**(CH_3)$_3$), 18.15 (18.13) (Si-**C**(CH_3)$_3$), -4.5 (Si-**C**H_3), -4.6 (Si-**C**H_3), -5.2 (Si-**C**H_3), -5.3 (Si-**C**H_3). **C-5** is not observed.

HR-MS: (ESI positive, MeOH), $[M+H]^+$ calcd for $C_{24}H_{46}N_3O_5Si_2$: 512.29705, found: 512.29711, $[M+Na]^+$ calcd for $C_{24}H_{45}N_3O_5Si_2Na$: 534.27900, found: 534.27848.

NMR Spectra:


A.Chantsova
Sample: AC 5-443
Pulse Sequence: s2pul
Date: Nov 20 2012
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9991117 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 41 sec
0.099
0.107
0.120
0.812
0.877
0.892
0.908
0.916
0.925
0.927
1.416
1.433
3.297
3.301
3.305
3.309
3.313
3.344
3.814
3.824
3.946
3.952
3.955
3.962
4.439
4.444
4.451
4.458
4.729
4.744
4.882
6.282
7.734
7.755
0 ppm
1
2
3
4
5
6
7
8
9
10
OH
NH2
N
O
TBSO
O
OTBS
*
2a


A.Chentsova
Sample: AC 5-443
Pulse Sequence: APT
Date: Nov 20 2012
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.5797244 MHz
DECOUPLE H1, 400.0010689 MHz
Power 38 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 15 min, 20 sec
TBSO
OTBS
OH
NH2
2a
164.973
157.930
138.347
89.500
89.390
87.381
87.272
73.911
73.823
65.703
64.295
49.843
49.638
49.425
49.322
49.213
49.037
49.000
48.787
48.568
48.355
42.257
42.133
26.456
26.207
22.880
22.821
19.215
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4.692
5.227
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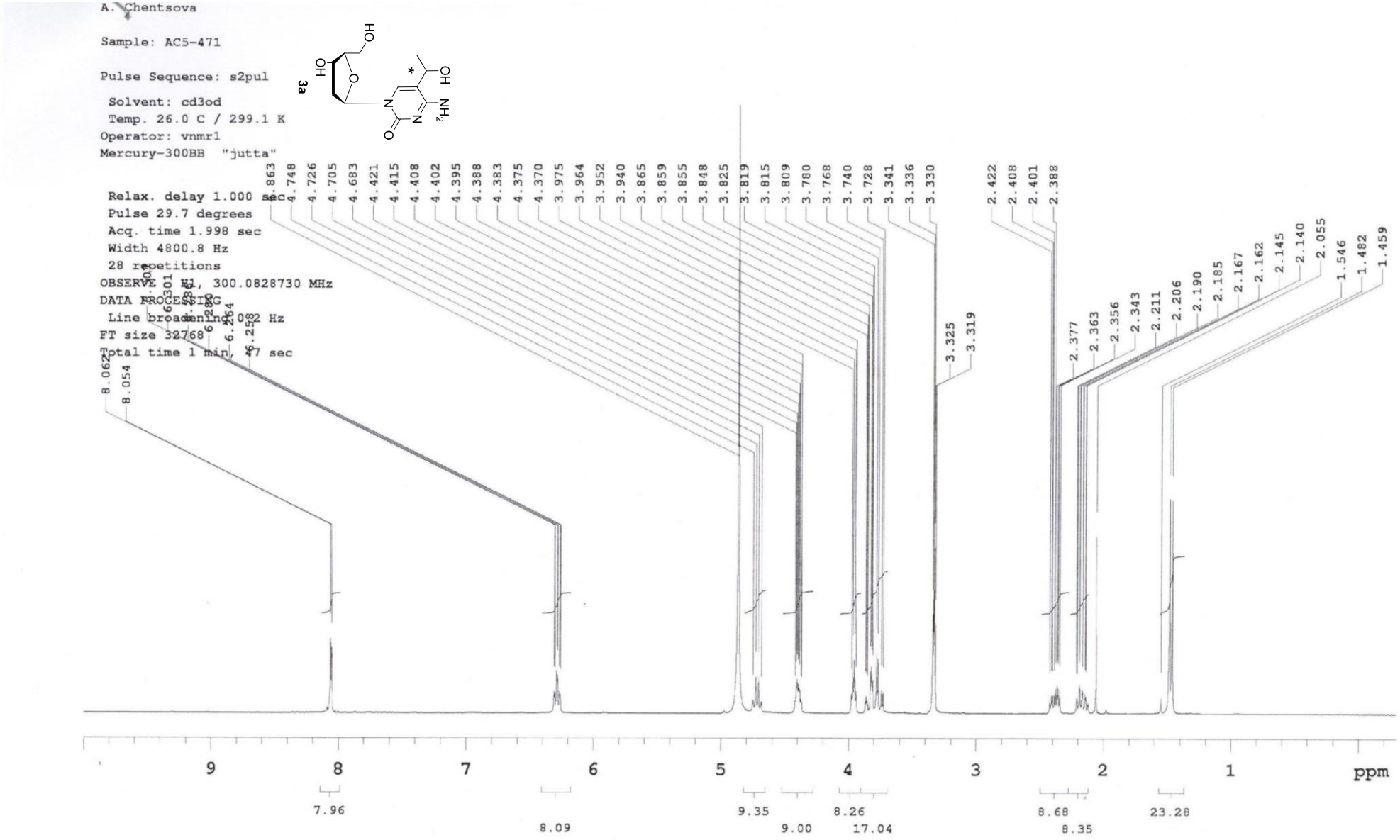
160
140
120
100
80
60
40
20
ppm


A. Chentsova
Sample: AC5-471
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
28 repetitions
OBSERVE H1, 300.0828730 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
3a
8.062
8.054
6.301
6.264
6.258
4.863
4.748
4.726
4.705
4.683
4.421
4.415
4.408
4.402
4.395
4.388
4.383
4.375
4.370
3.975
3.964
3.952
3.940
3.865
3.859
3.855
3.848
3.825
3.819
3.815
3.809
3.780
3.768
3.740
3.728
3.341
3.336
3.330
3.325
3.319
2.422
2.408
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2.377
2.363
2.356
2.343
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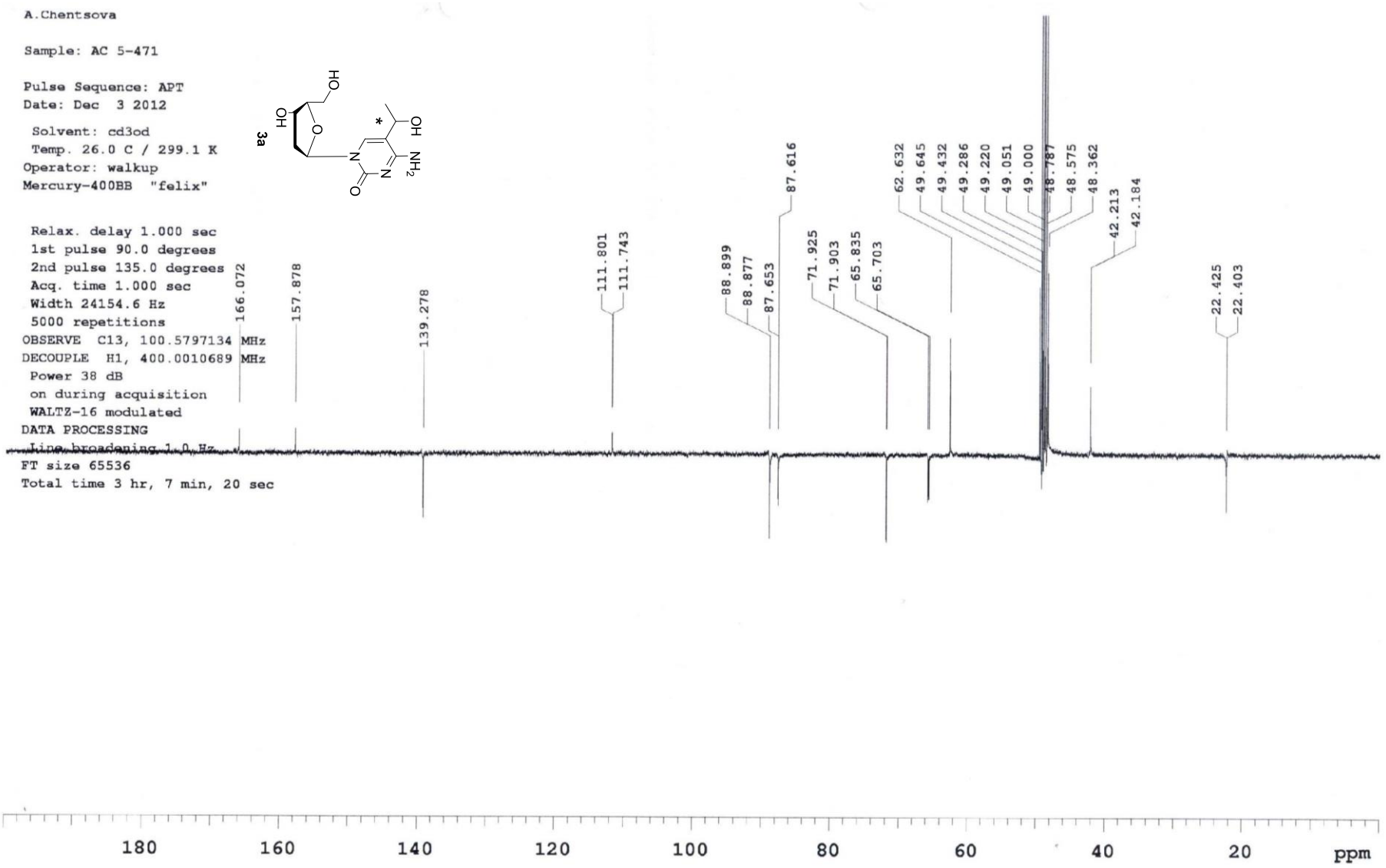
2.190
2.185
2.167
2.162
2.145
2.140
2.055
1.546
1.482
1.459
9
8
7
6
5
4
3
2
1
ppm
7.96
8.09
9.35
9.00
8.26
17.04
8.68
8.35
23.28


A.Chentsova
Sample: AC 5-471
Pulse Sequence: APT
Date: Dec 3 2012
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
3a
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 24154.6 Hz
5000 repetitions
OBSERVE C13, 100.5797134 MHz
DECOUPLE H1, 400.0010689 MHz
Power 38 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 7 min, 20 sec
166.072
157.878
139.278
111.801
111.743
88.899
88.877
87.653
87.616
71.925
71.903
65.835
65.703
62.632
49.645
49.432
49.286
49.220
49.051
49.000
48.787
48.575
48.362
42.213
42.184
22.425
22.403
180
160
140
120
100
80
60
40
20
ppm

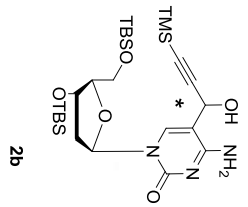
A.Chentsova

Sample: AC5-28AM

Pulse Sequence: s2pul

Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
28 repetitions
OBSERVE H1, 300.0828807 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec



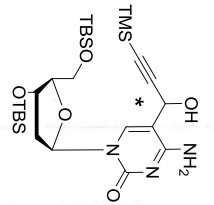
2b

E. Kapourani

Sample: EK-24C

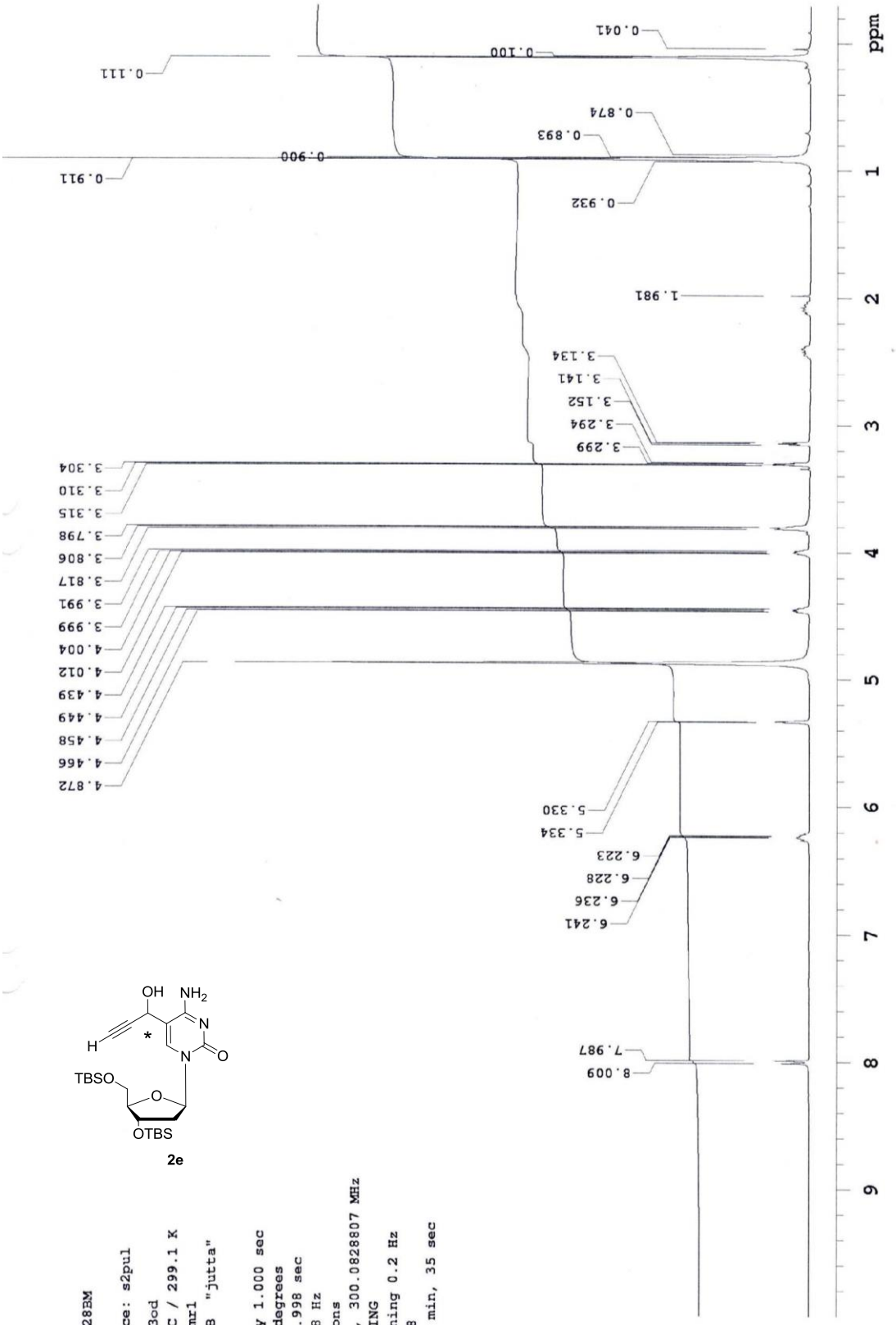
Pulse Sequence: s2pul
Date: Aug 28 2012

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"



2b

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
2000 repetitions
OBSERVE C13, 100.5794365 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 21 min, 50 sec



2e

A.Chentsova

Sample: AC5-28BM

Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
64 repetitions
OBSERVE H1, 300.0828807 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec

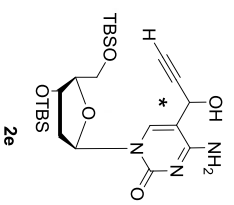
A. Chentsova

Sample: AC5-28BM

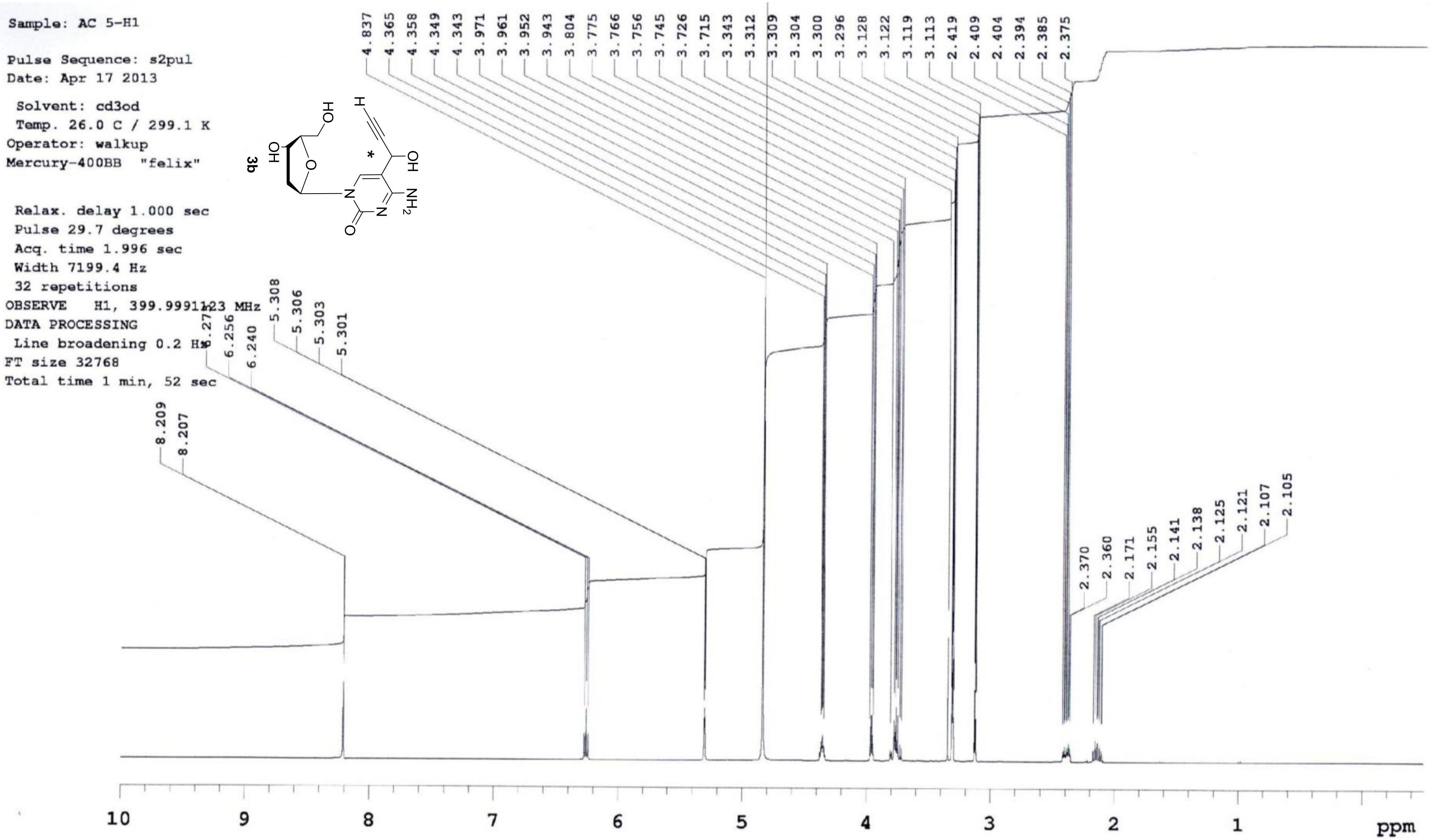
Pulse Sequence: APT
Date: Oct 26 2012

Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 24154.6 Hz
848 repetitions
OBSERVE C13, 100.5797274 MHz
DECOUPLE H1, 400.0010689 MHz
Power 38 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 15 min, 20 sec



2e


Sample: AC 5-H1
Pulse Sequence: s2pul
Date: Apr 17 2013
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 7199.4 Hz
32 repetitions
OBSERVE H1, 399.9991123 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 52 sec
3b
8.209
8.207
6.27
6.256
6.240
5.308
5.306
5.303
5.301
4.837
4.365
4.358
4.349
4.343
3.971
3.961
3.952
3.943
3.804
3.775
3.766
3.756
3.745
3.726
3.715
3.343
3.312
3.309
3.304
3.300
3.296
3.128
3.122
3.119
3.113
2.419
2.409
2.404
2.394
2.385
2.375
2.370
2.360
2.171
2.155
2.141
2.138
2.125
2.121
2.107
2.105
10
9
8
7
6
5
4
3
2
1
ppm

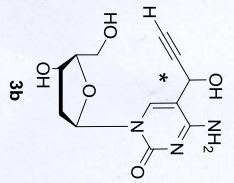
A. Chentsova

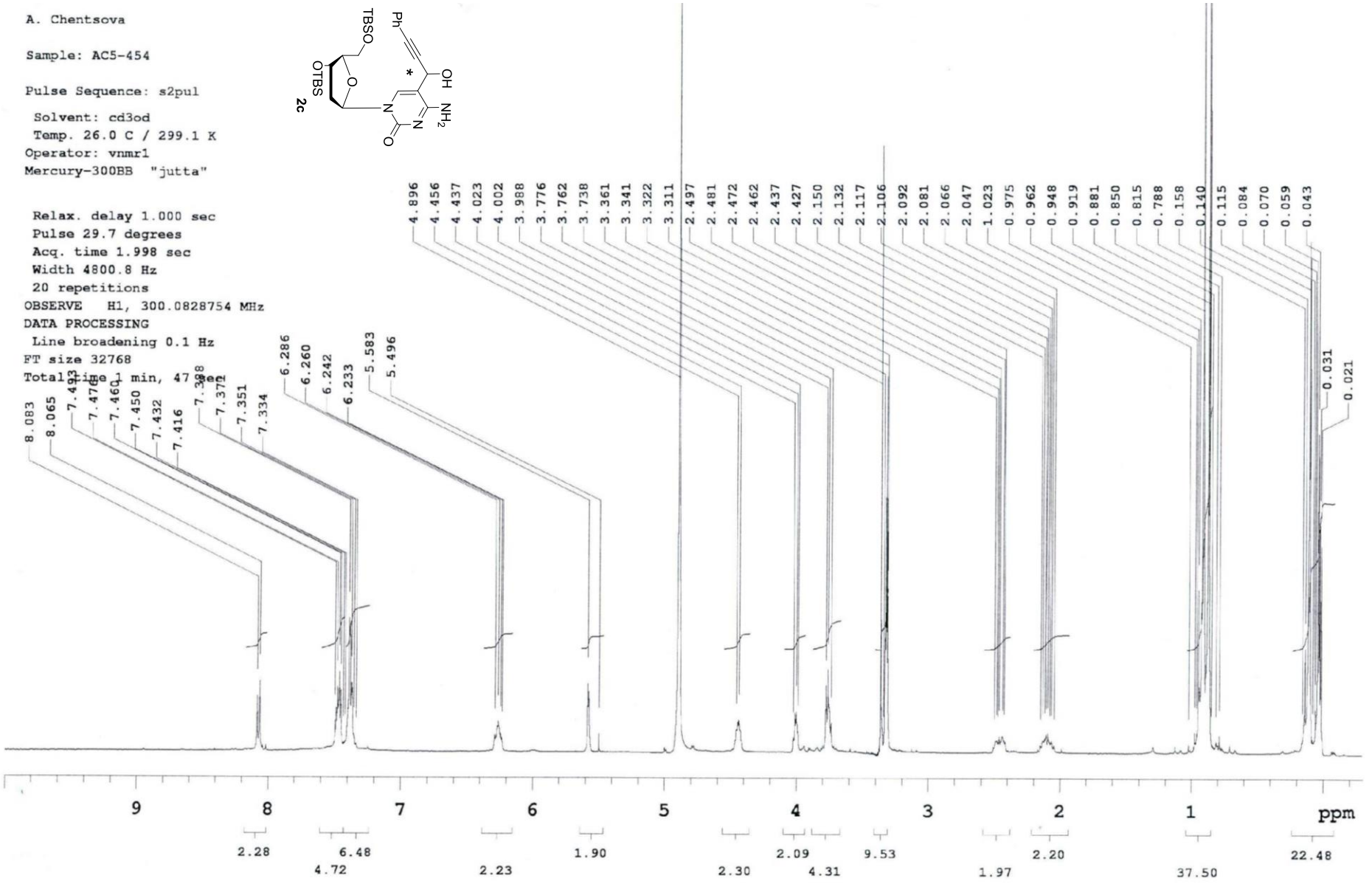
Sample: AC5-H1

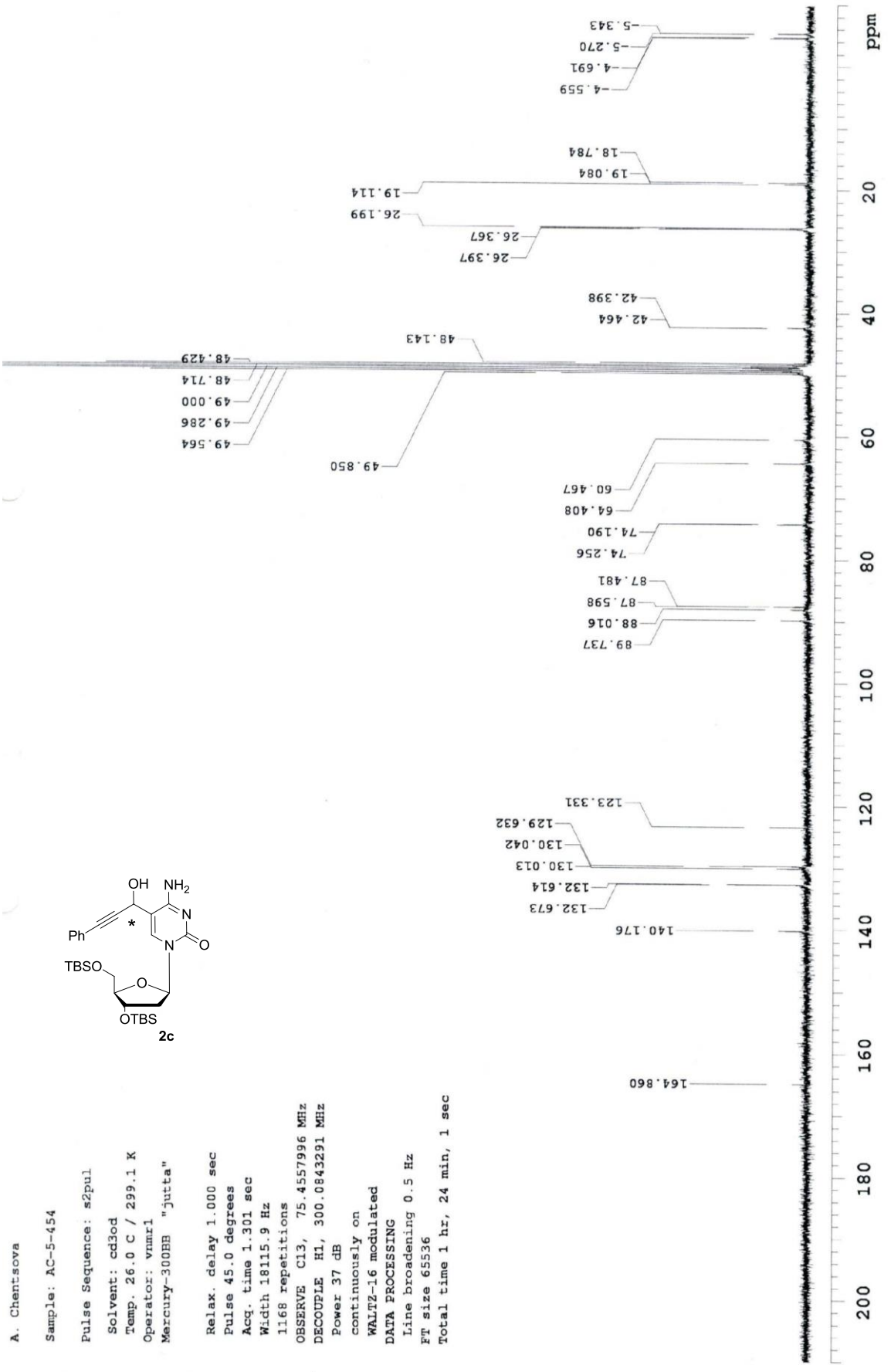
Pulse Sequence: s2pul

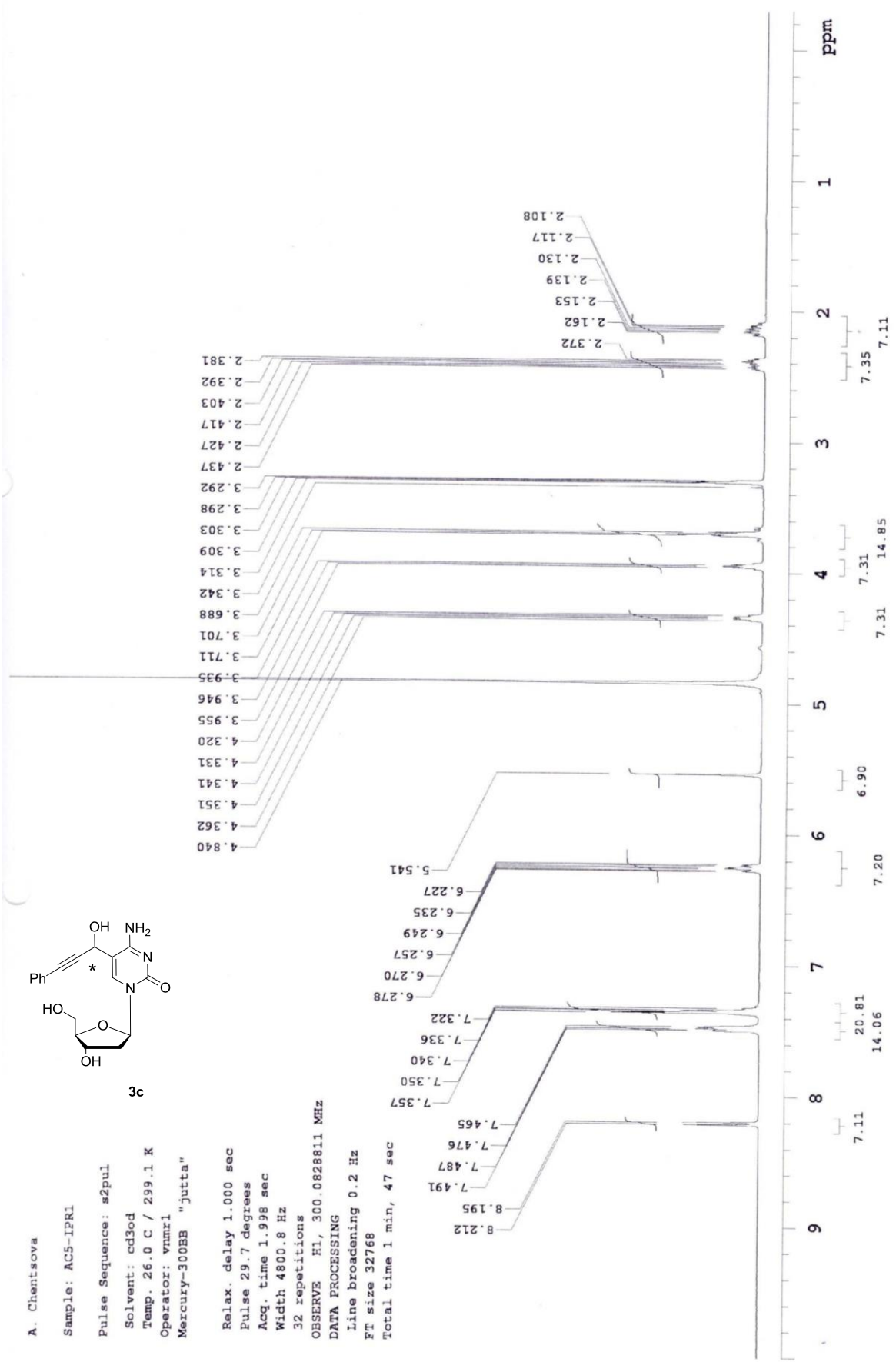
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
736 repetitions
OBSERVE C13, 75.4557935 MHz
DECOUPLE H1, 300.0843291 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec




A. Chentsova
Sample: AC5-454
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
20 repetitions
OBSERVE H1, 300.0828754 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 47 sec
2c
TBSO
OTBS
Ph
OH
NH2
8.083
8.065
7.493
7.476
7.460
7.450
7.432
7.416
7.398
7.371
7.351
7.334
6.286
6.260
6.242
6.233
5.583
5.496
4.896
4.456
4.437
4.023
4.002
3.988
3.776
3.762
3.738
3.361
3.341
3.322
3.311
2.497
2.481
2.472
2.462
2.437
2.427
2.150
2.132
2.117
2.106
2.092
2.081
2.066
2.047
1.023
0.975
0.962
0.948
0.919
0.881
0.850
0.815
0.788
0.158
0.140
0.115
0.084
0.070
0.059
0.043
0.031
0.021
9
8
7
6
5
4
3
2
1
ppm
2.28
6.48
4.72
2.23
1.90
2.30
2.09
4.31
9.53
1.97
2.20
37.50
22.48


A. Chentsova
Sample: AC-5-454
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
1168 repetitions
OBSERVE C13, 75.4557996 MHz
DECOUPLE H1, 300.0843291 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec
OH
NH2
Ph
TBSO
OTBS
2c
ppm
200
180
160
140
120
100
80
60
40
20
164.860
140.176
132.673
132.614
130.013
130.042
129.632
123.331
89.737
88.016
87.598
87.481
74.256
74.190
64.408
60.467
49.850
49.564
49.286
49.000
48.714
48.429
48.143
42.464
42.398
26.397
26.367
26.199
19.114
19.084
18.784
-4.559
-4.691
-5.270
-5.343

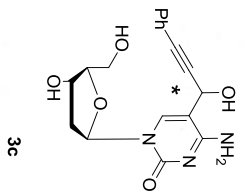

A. Chentsova
Sample: AC5-IPR1
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Opeazor: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0828811 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
OH
NH2
Ph
HO
O
N
OH
3c
ppm

Chentsova

Sample: AC 5-IPR1

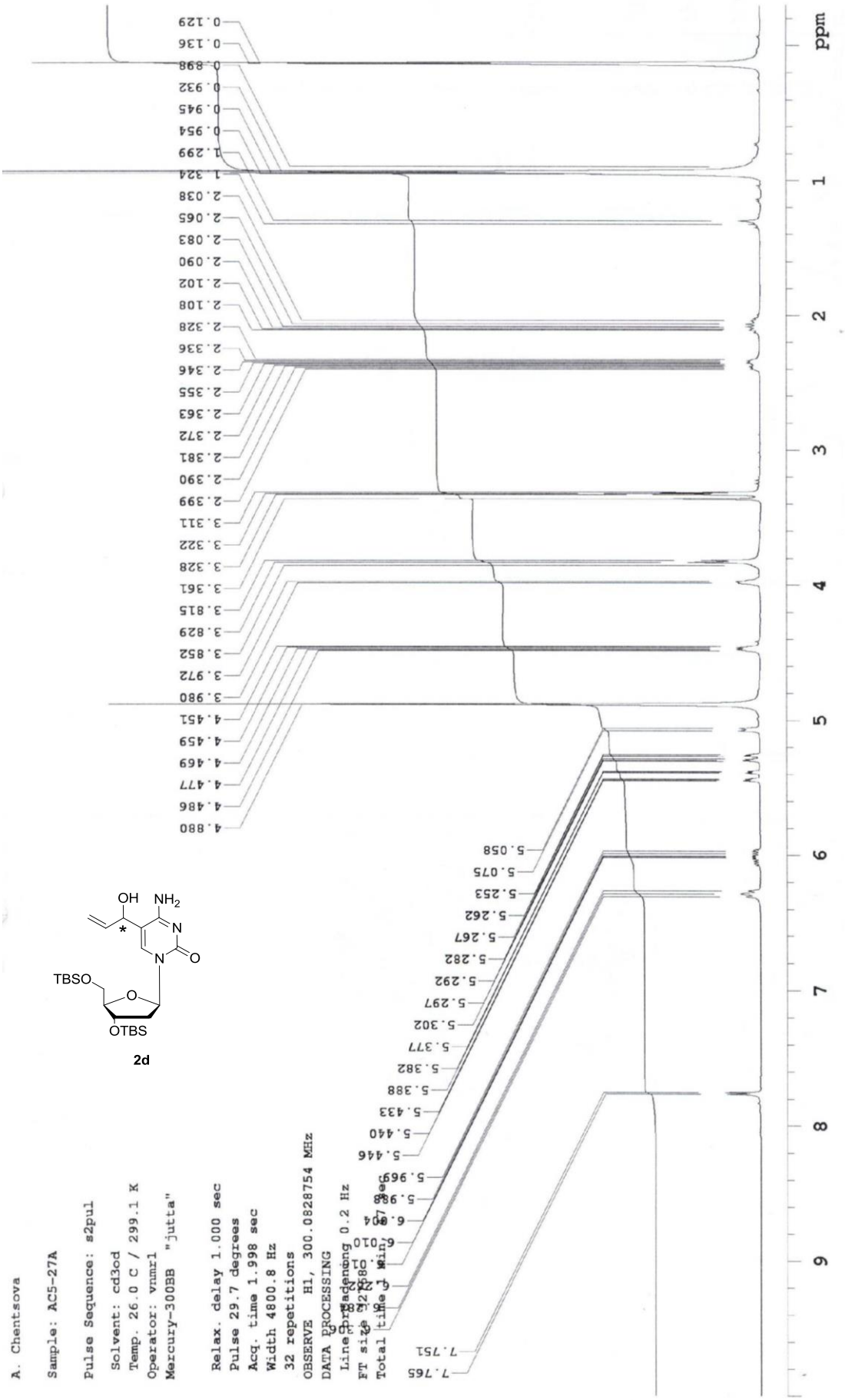
Pulse Sequence: s2pul
Date: Apr 16 2013

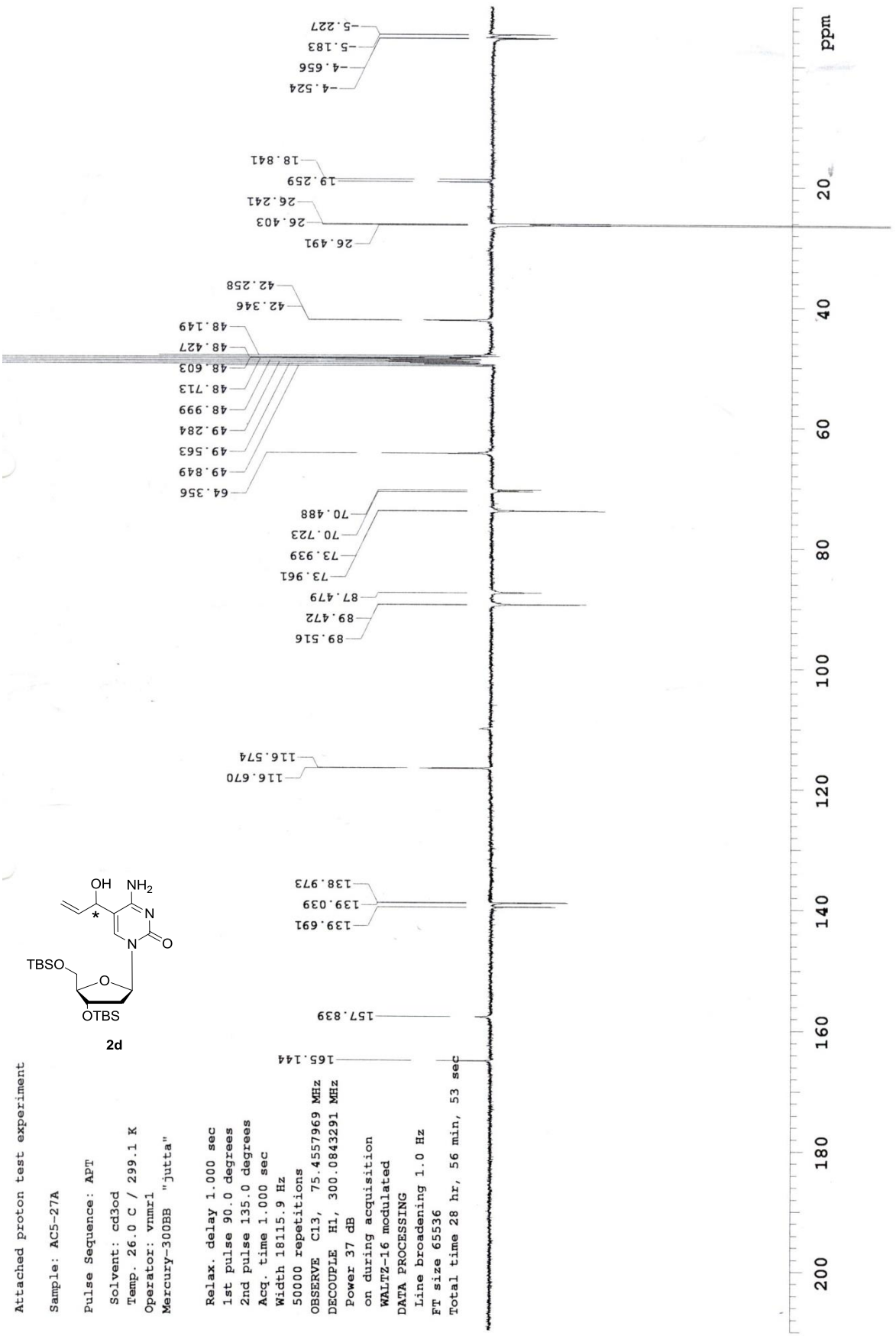
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

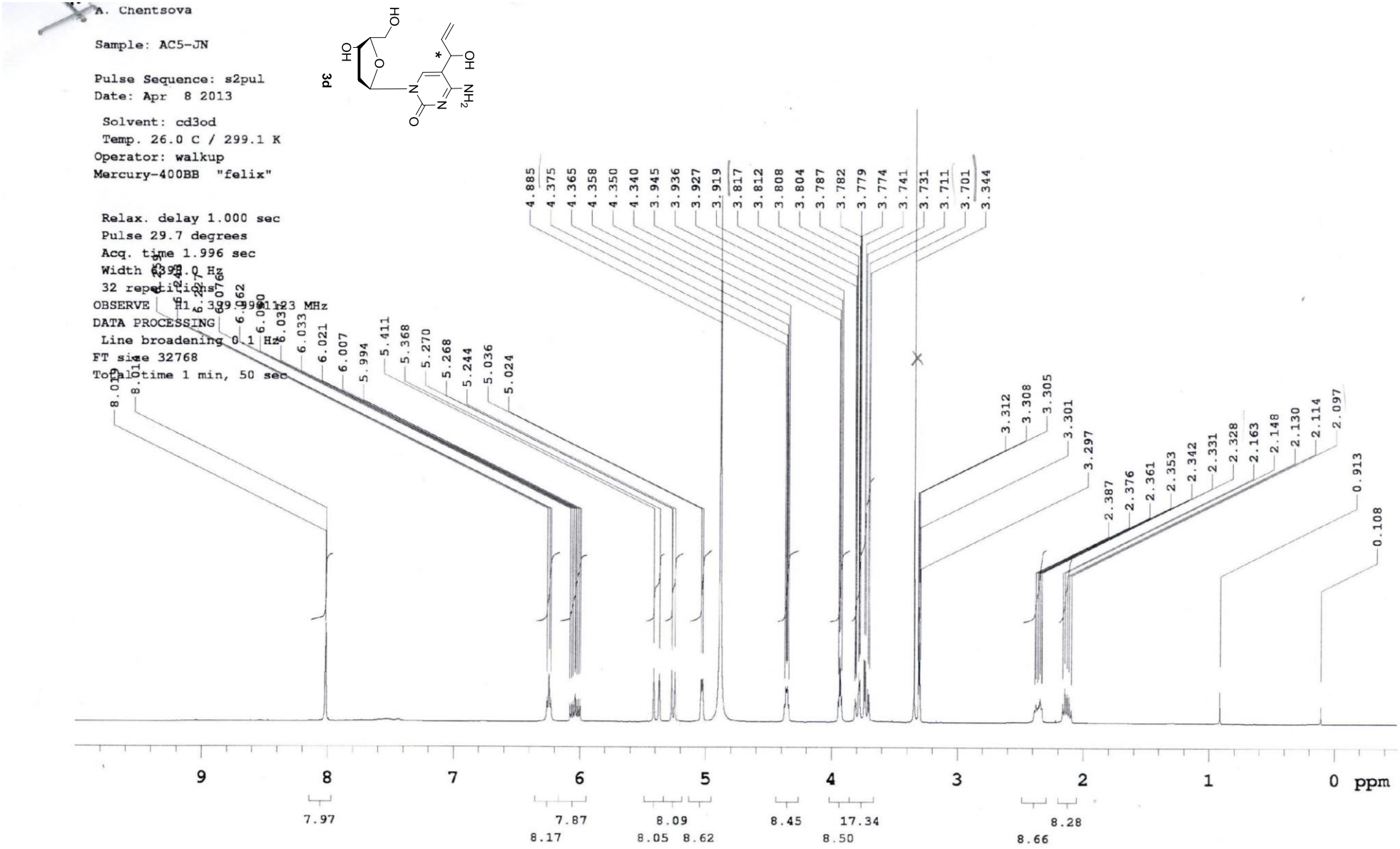


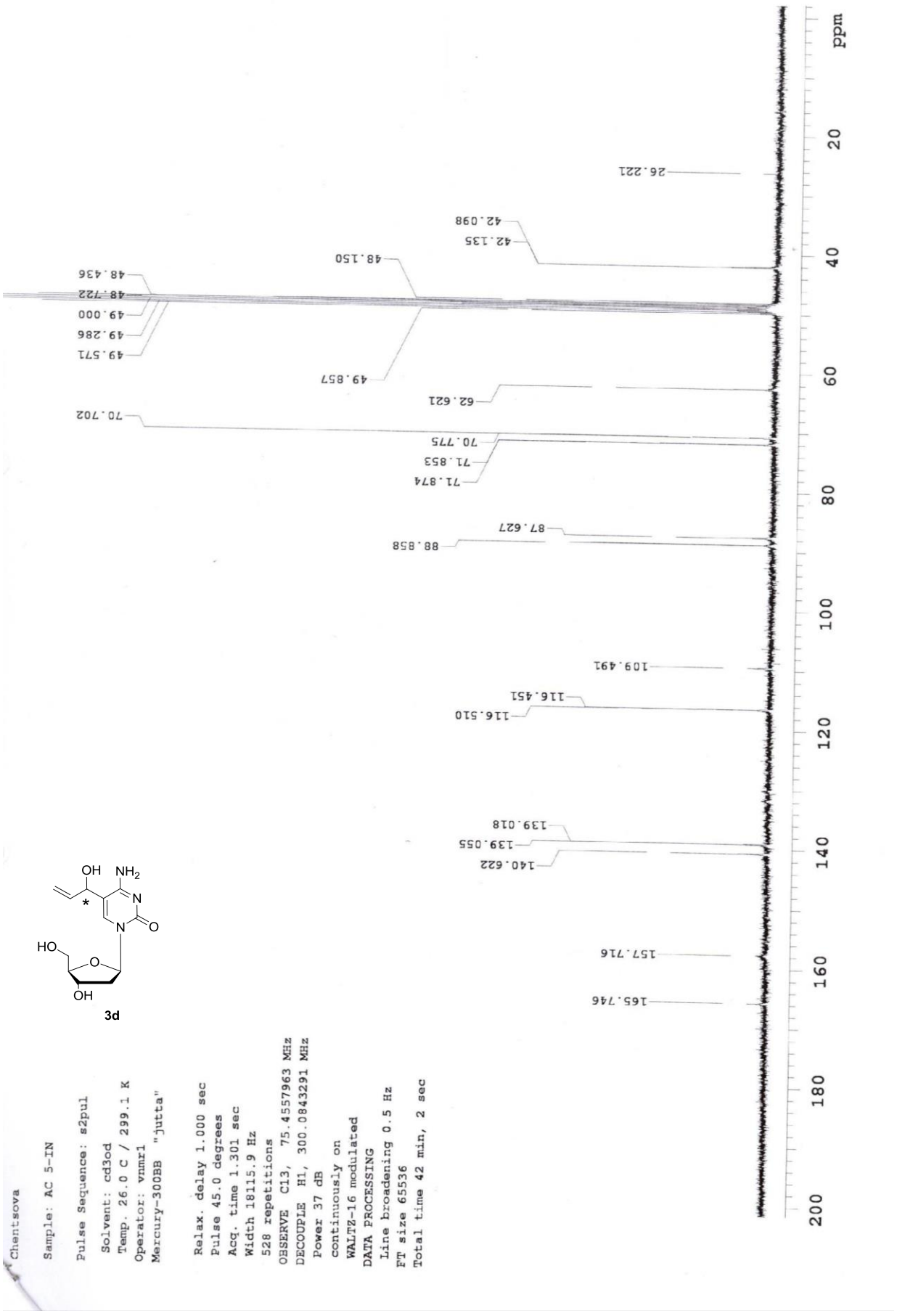
3c

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
512 repetitions
OBSERVE C13, 100.5797156 MHz
DECOUPLE H1, 400.0010689 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 25 min, 53 sec

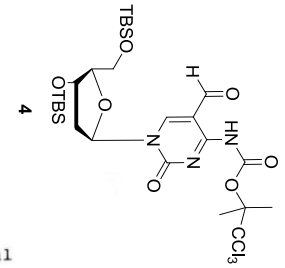

A. Chentsova
Sample: AC5-27A
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0828754 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 9 sec
ppm
OH
NH2
N
O
TBSO
O
OTBS
2d


-5.227
-5.183
-4.656
-4.524
18.841
19.259
26.241
26.403
26.491
42.258
42.346
48.149
48.427
48.603
48.713
48.999
49.284
49.563
49.849
64.356
70.488
70.723
73.939
73.961
87.479
89.472
89.516
116.574
116.670
138.973
139.039
139.691
157.839
165.144
ppm
20
40
60
80
100
120
140
160
180
200
OH
NH2
N
O
TBSO
O
OTBS
2d
Attached proton test experiment
Sample: AC5-27A
Pulse Sequence: APT
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Marcury-300BB "jutta"
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 18115.9 Hz
50000 repetitions
OBSERVE C13, 75.4557969 MHz
DECOUPLE H1, 300.0843291 MHz
Power 37 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 28 hr, 56 min, 53 sec


A. Chentsova
Sample: AC5-JN
Pulse Sequence: s2pul
Date: Apr 8 2013
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9911123 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 50 sec
3d
4.885
4.375
4.365
4.358
4.350
4.340
3.945
3.936
3.927
3.919
3.817
3.812
3.808
3.804
3.787
3.782
3.779
3.774
3.741
3.731
3.711
3.701
3.344
8.017
8.011
6.076
6.062
6.033
6.021
6.007
5.994
5.411
5.368
5.270
5.268
5.244
5.036
5.024
3.312
3.308
3.305
3.301
3.297
2.387
2.376
2.361
2.353
2.342
2.331
2.328
2.163
2.148
2.130
2.114
2.097
0.913
0.108
9
8
7
6
5
4
3
2
1
0 ppm
7.97
8.17
7.87
8.09
8.05
8.62
8.45
17.34
8.50
8.28
8.66


Chentsova
Sample: AC 5-IN
Pulse Sequence: s2pul
Solvent: cd3od
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
528 repetitions
OBSERVE C13, 75.4557963 MHz
DECOUPLE H1, 300.0843291 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 min, 2 sec
OH
NH2
N
O
HO
O
OH
3d
ppm
200
180
160
140
120
100
80
60
40
20
165.746
157.716
140.622
139.055
139.018
116.510
116.451
109.491
88.858
87.627
71.874
71.853
70.775
70.702
62.621
49.857
48.150
49.571
49.286
49.000
48.722
48.436
42.135
42.098
26.221

A. Chentsova



Sample: AC5-13B

Pulse Sequence: s2pul
Date: Aug 8 2012

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9975361 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec

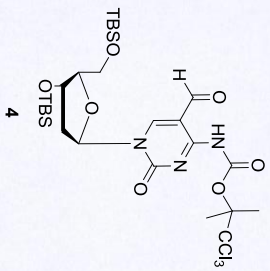
A. Chentsova

Sample: AC6-MP9

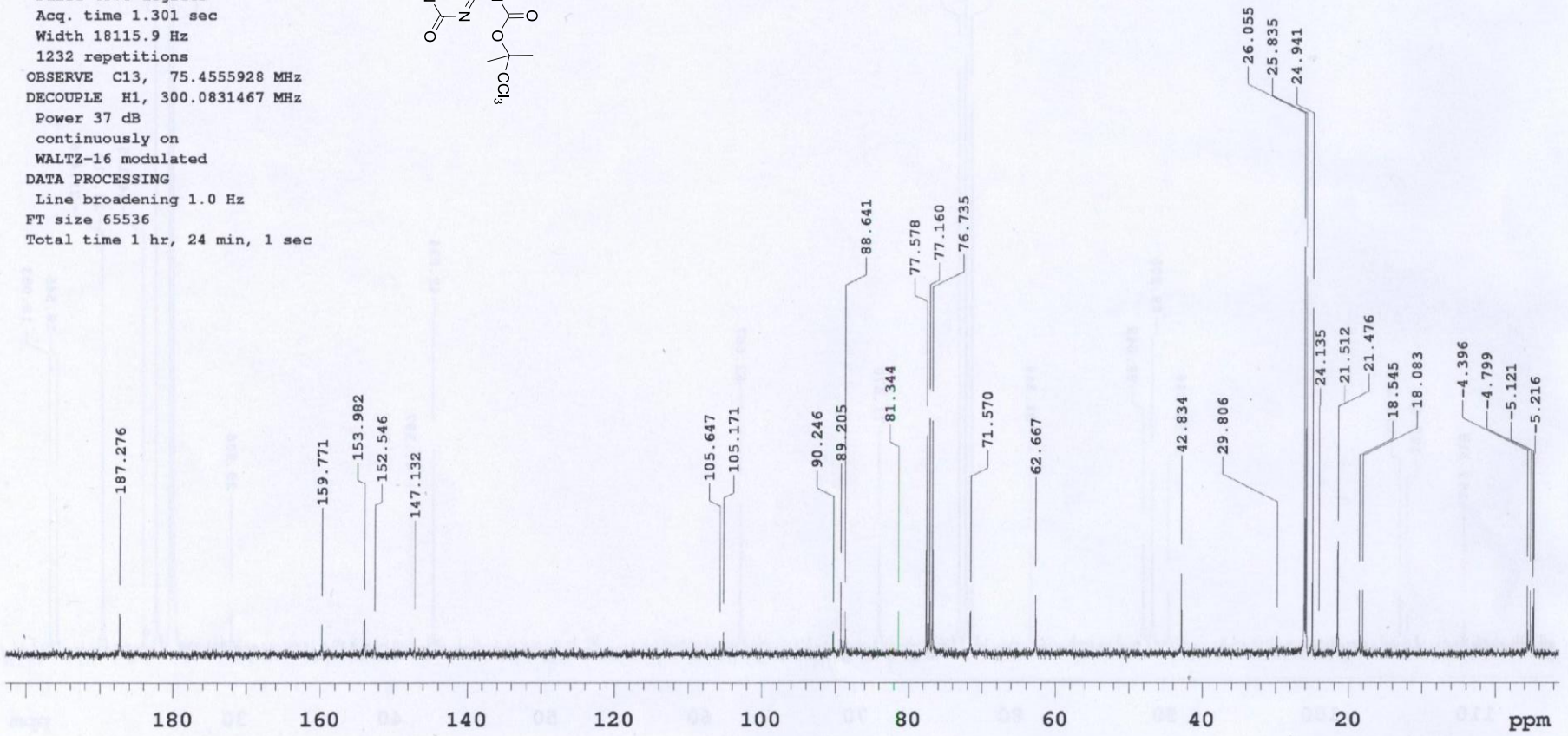
Pulse Sequence: s2pul

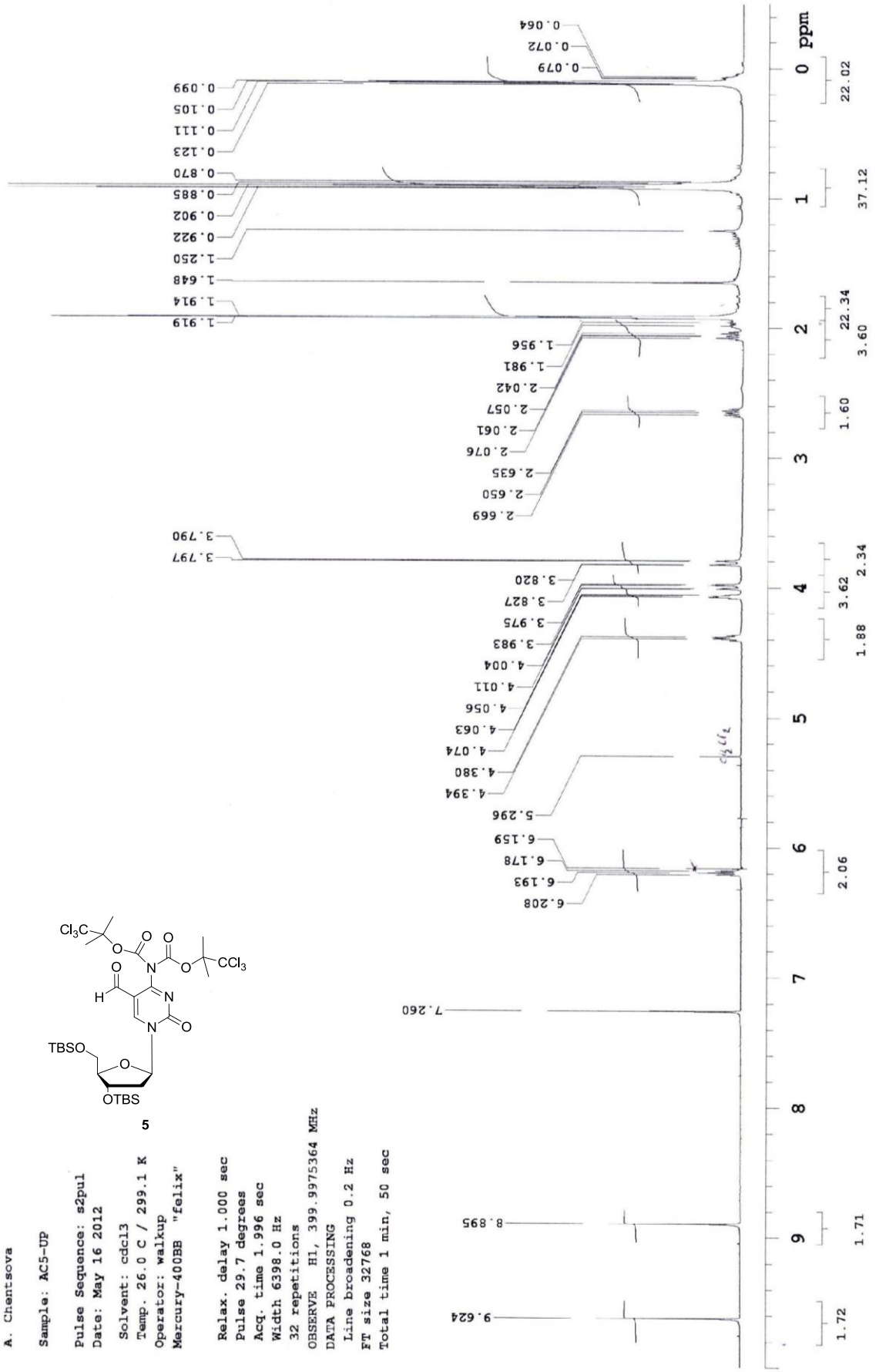
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

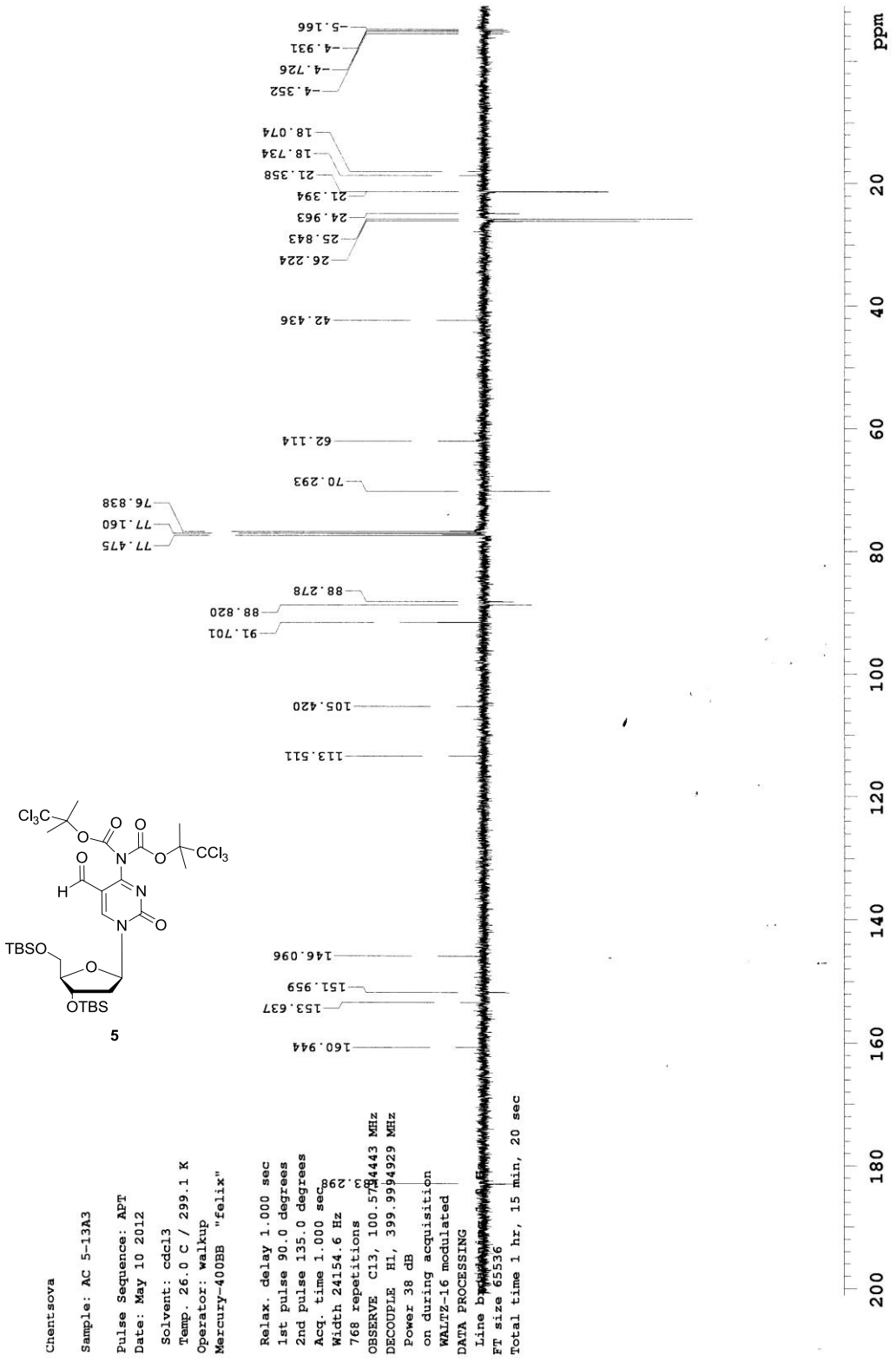
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
1232 repetitions
OBSERVE C13, 75.4555928 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec

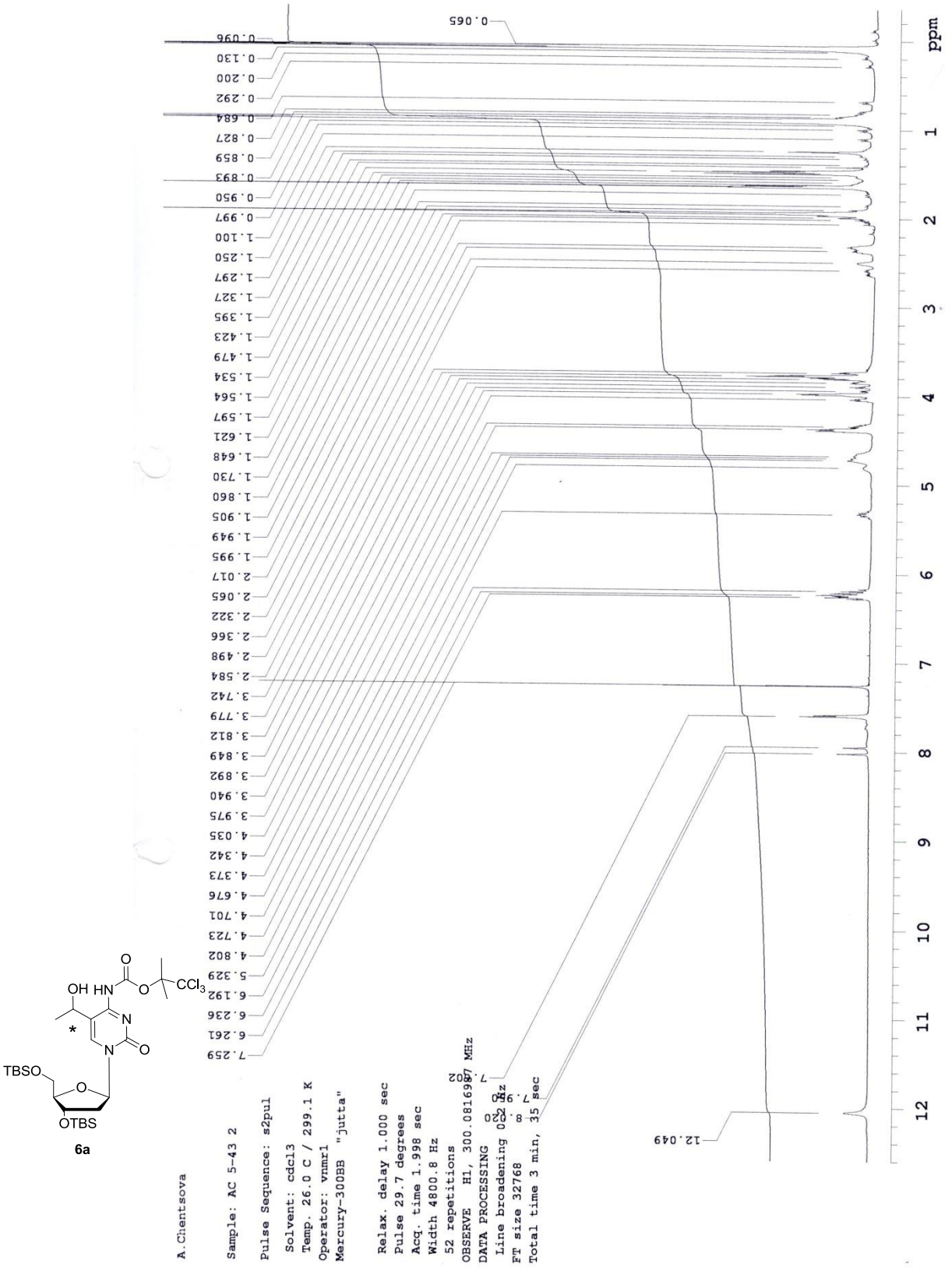


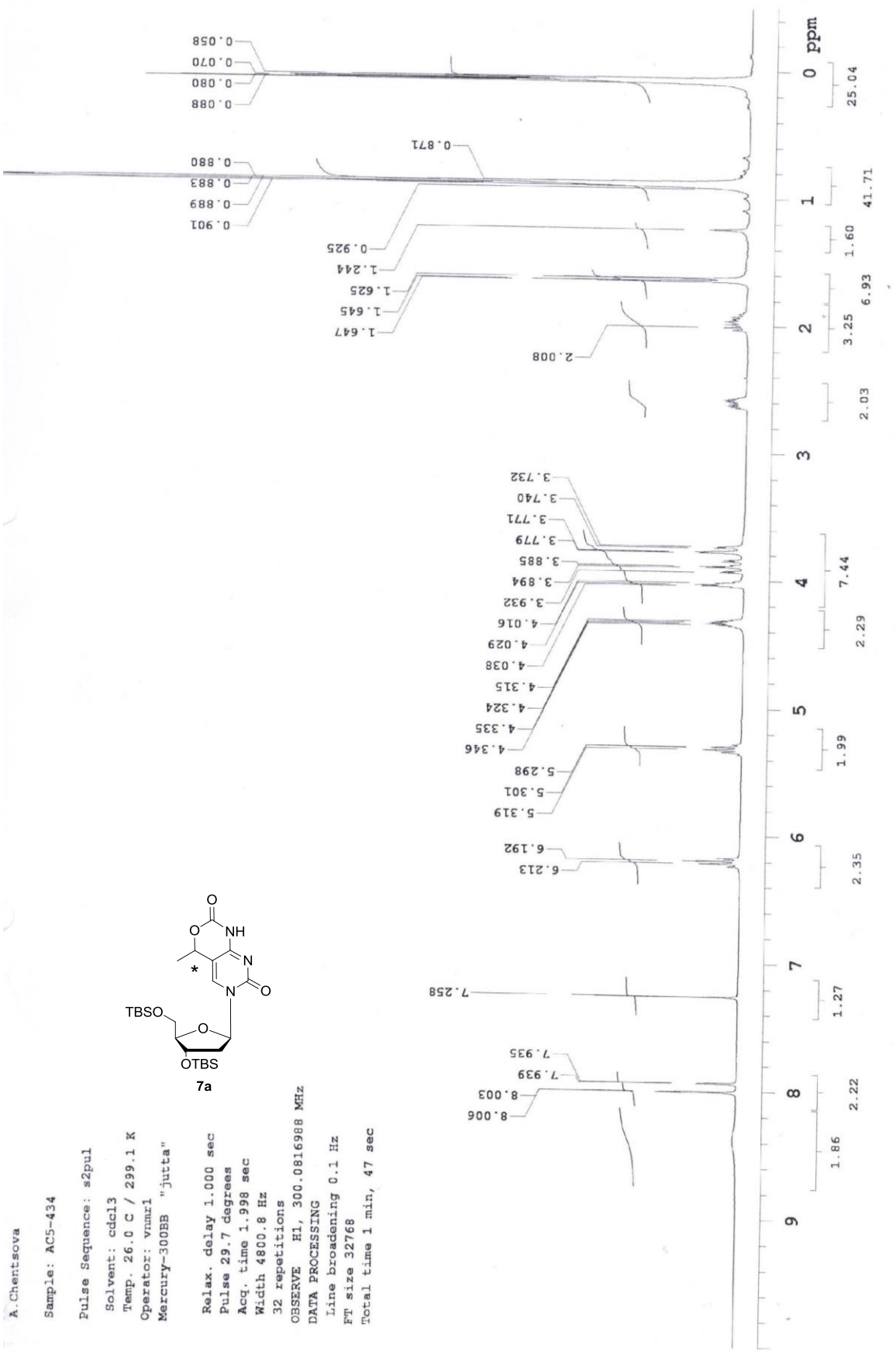
4




A. Chantsova
Sample: AC5-UP
Pulse Sequence: s2pul
Date: May 16 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9975364 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec
5
TBSO
OTBS
Cl_3C
CCl_3
9.624
8.895
7.260
6.208
6.193
6.178
6.159
5.296
4.394
4.380
4.074
4.063
4.056
4.011
4.004
3.983
3.975
3.827
3.820
3.797
3.790
2.669
2.650
2.635
2.076
2.061
2.057
2.042
1.981
1.956
1.919
1.914
1.648
1.250
0.922
0.902
0.885
0.870
0.123
0.111
0.105
0.099
0.079
0.072
0.064
0 ppm
1.72
1.71
2.06
1.88
3.62
2.34
1.60
22.34
3.60
22.02
37.12


Chentsova
Sample: AC 5-13A3
Pulse Sequence: APT
Date: May 10 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Marcury-400BB "felix"
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 24154.6 Hz
768 repetitions
OBSERVE C13, 100.5744443 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 1 hr, 15 min, 20 sec
-5.166
-4.931
-4.726
-4.352
18.074
18.734
21.358
21.394
24.963
25.843
26.224
42.436
62.114
70.293
76.838
77.160
77.475
88.278
88.820
91.701
105.420
113.511
146.096
151.959
153.637
160.944
ppm
200
180
160
140
120
100
80
60
40
20
TBSO
OTBS
5


A.Chentsova
Sample: AC 5-43 2
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
52 repetitions
OBSERVE H1, 300.0816907 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec
ppm
OH HN
CCl3
TBSO
OTBS
*
6a

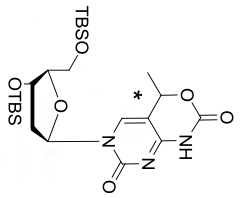

A.Chentsova
Sample: AC5-434
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0816988 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 1 min, 47 sec
TBSO
OTBS
7a
0.058
0.070
0.080
0.088
0.871
0.880
0.883
0.889
0.901
0.925
1.244
1.625
1.645
1.647
2.008
3.732
3.740
3.771
3.779
3.885
3.894
3.932
4.016
4.029
4.038
4.315
4.324
4.335
4.346
5.298
5.301
5.319
6.192
6.213
7.258
7.935
7.939
8.003
8.006
0 ppm
25.04
41.71
1.60
6.93
3.25
2.03
7.44
2.29
1.99
2.35
1.27
2.22
1.86

Std Carbon experiment
A.Chentsova

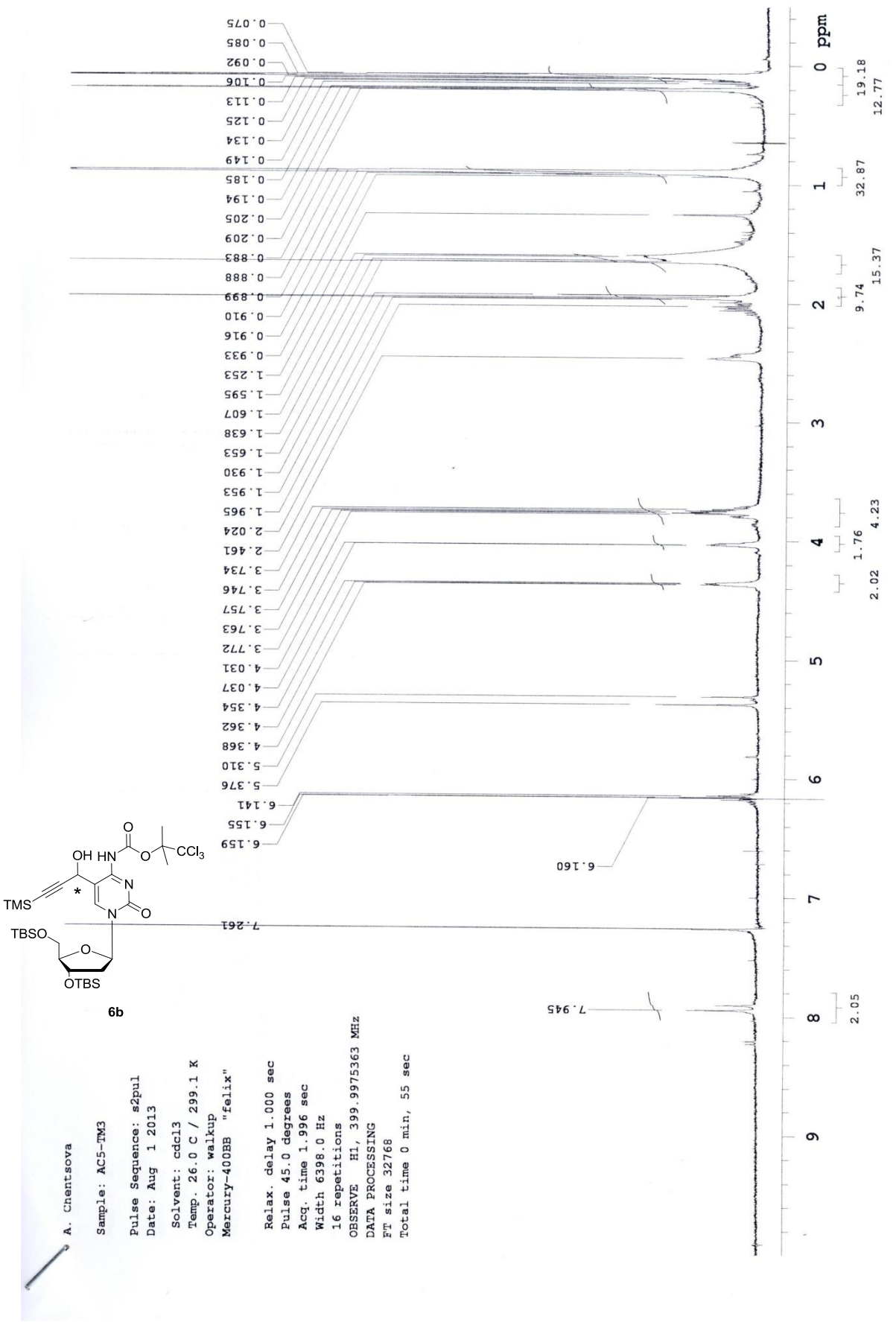
Sample: AC5-434

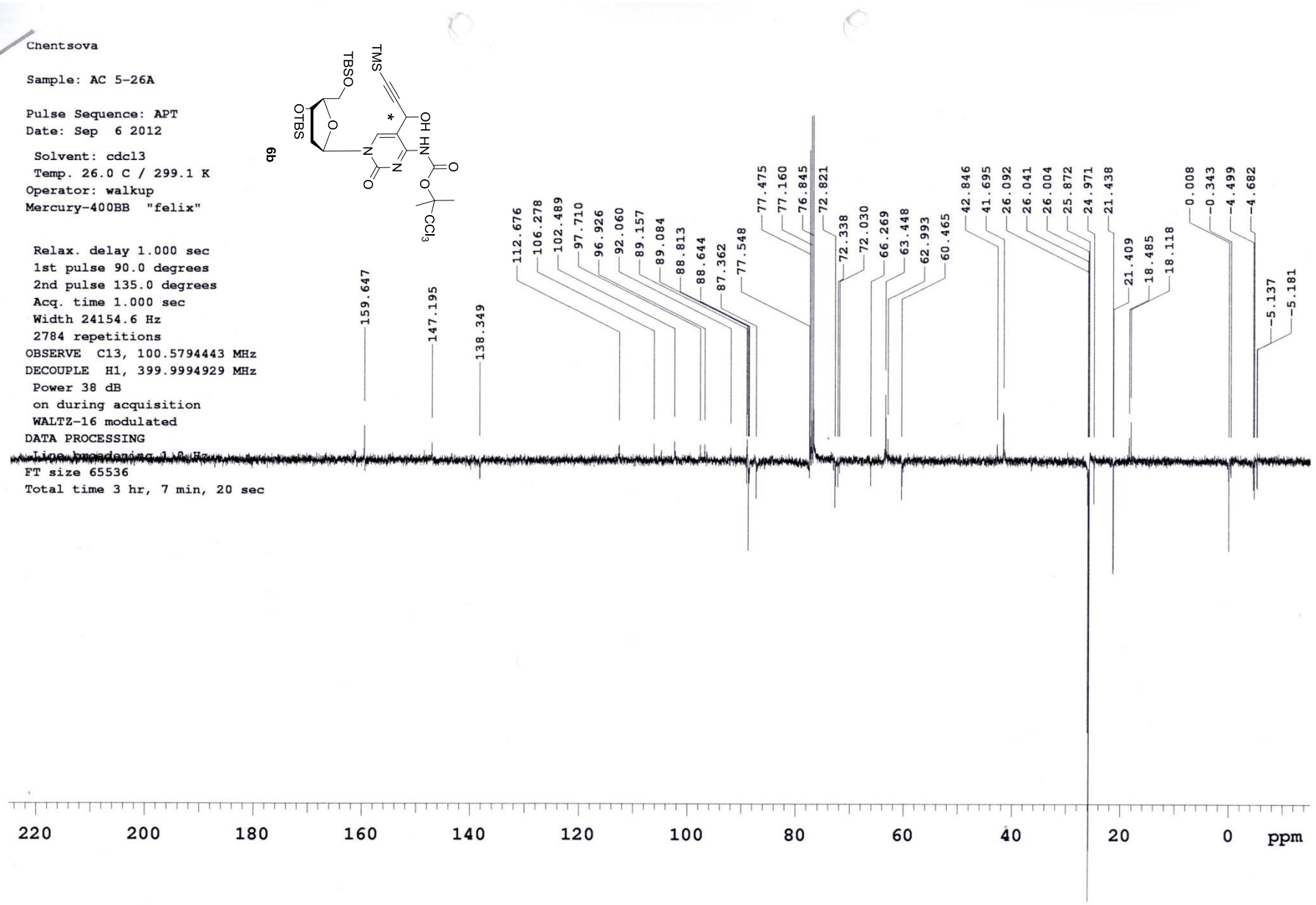
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
2000 repetitions
OBSERVE C13, 75.4555916 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec



7a


A. Chentsova
Sample: AC5-TM3
Pulse Sequence: s2pul
Date: Aug 1 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
16 repetitions
OBSERVE H1, 399.9975363 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 55 sec
OH HN
O
O
CCl3
TMS
*
N
N
O
TBSO
O
OTBS
6b
0.075
0.085
0.092
0.106
0.113
0.125
0.134
0.149
0.185
0.194
0.205
0.209
0.883
0.888
0.899
0.910
0.916
0.933
1.253
1.595
1.607
1.638
1.653
1.930
1.953
1.965
2.024
2.461
3.734
3.746
3.757
3.763
3.772
4.031
4.037
4.354
4.362
4.368
5.310
5.376
6.141
6.155
6.159
6.160
7.261
7.945
ppm
0
1
2
3
4
5
6
7
8
9
19.18
12.77
32.87
9.74
15.37
1.76
2.02
4.23
2.05


Chentsova
Sample: AC 5-26A
Pulse Sequence: APT
Date: Sep 6 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 24154.6 Hz
2784 repetitions
OBSERVE C13, 100.5794443 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
FT size 65536
Total time 3 hr, 7 min, 20 sec
TBSO
OTBS
TMS
OH
HN
CCl3
9b
159.647
147.195
138.349
112.676
106.278
102.489
97.710
96.926
92.060
89.157
89.084
88.813
88.644
87.362
77.548
77.475
77.160
76.845
72.821
72.338
72.030
66.269
63.448
62.993
60.465
42.846
41.695
26.092
26.041
26.004
25.872
24.971
21.438
21.409
18.485
18.118
0.008
-0.343
-4.499
-4.682
-5.137
-5.181
220
200
180
160
140
120
100
80
60
40
20
0
ppm

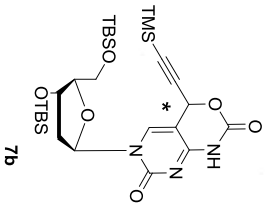
hentsova

Sample: AC5-Li3

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
24 repetitions
OBSERVE H1, 300.0816984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec



7b

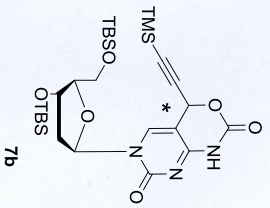
Std Carbon experiment

Sample: AC5-L3

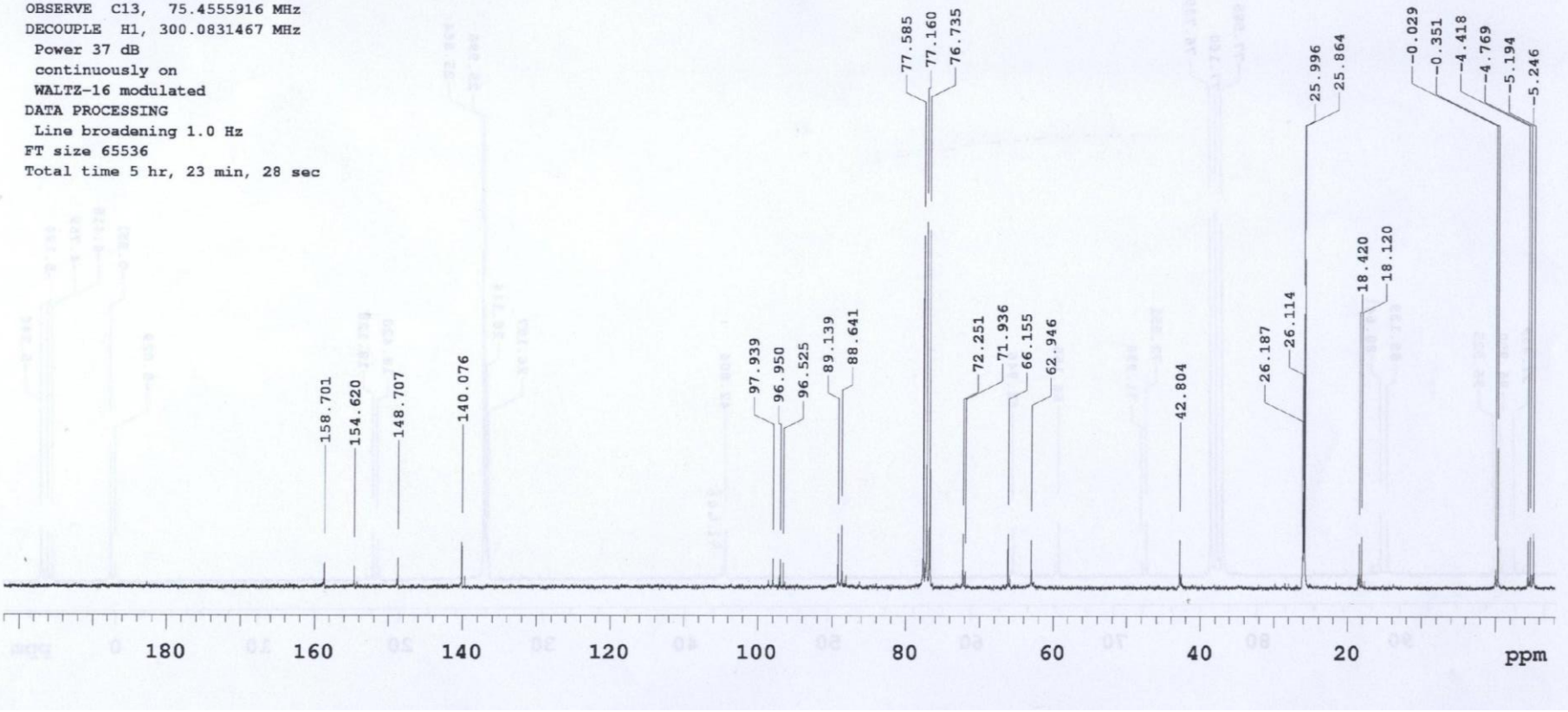
Pulse Sequence: s2pul

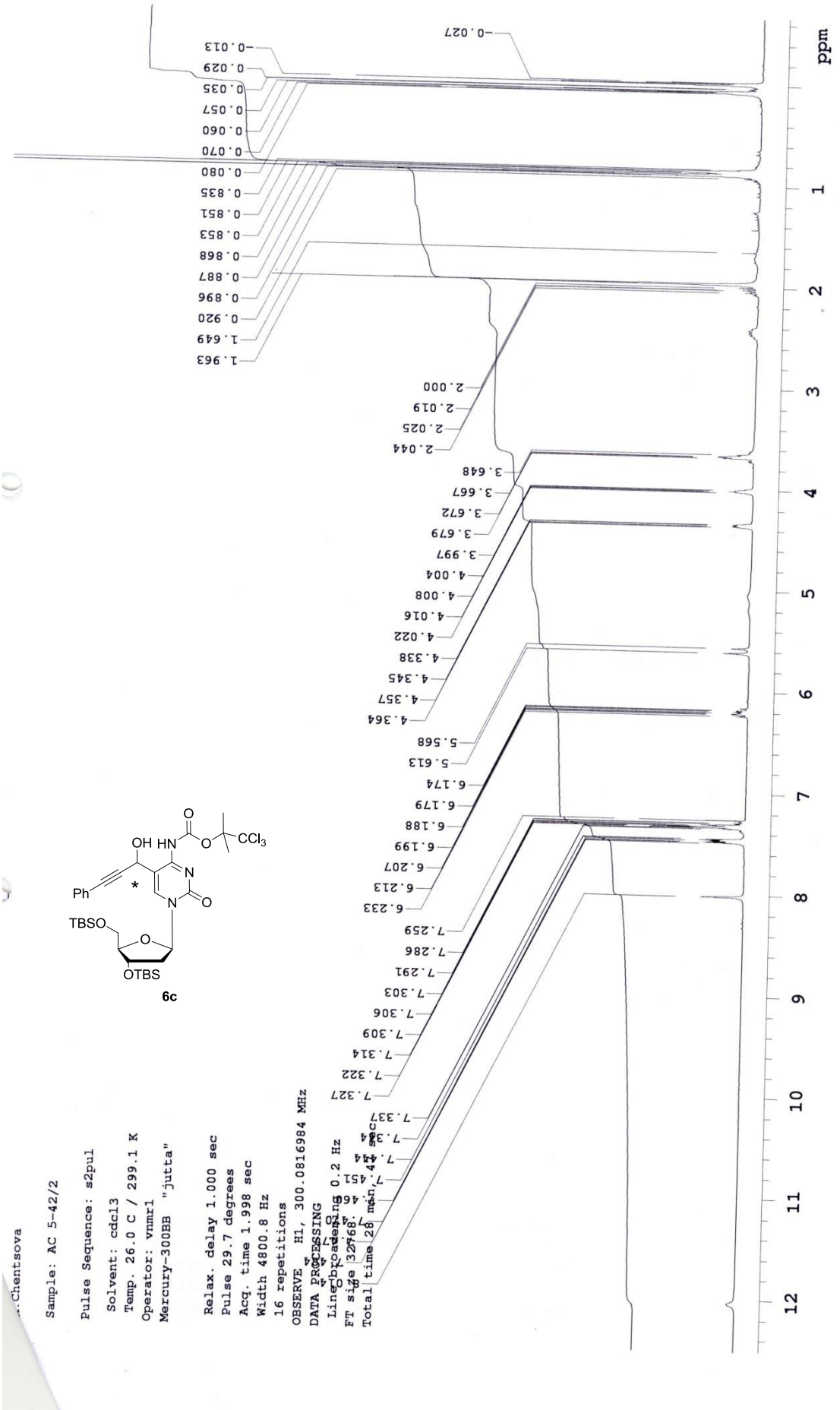
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

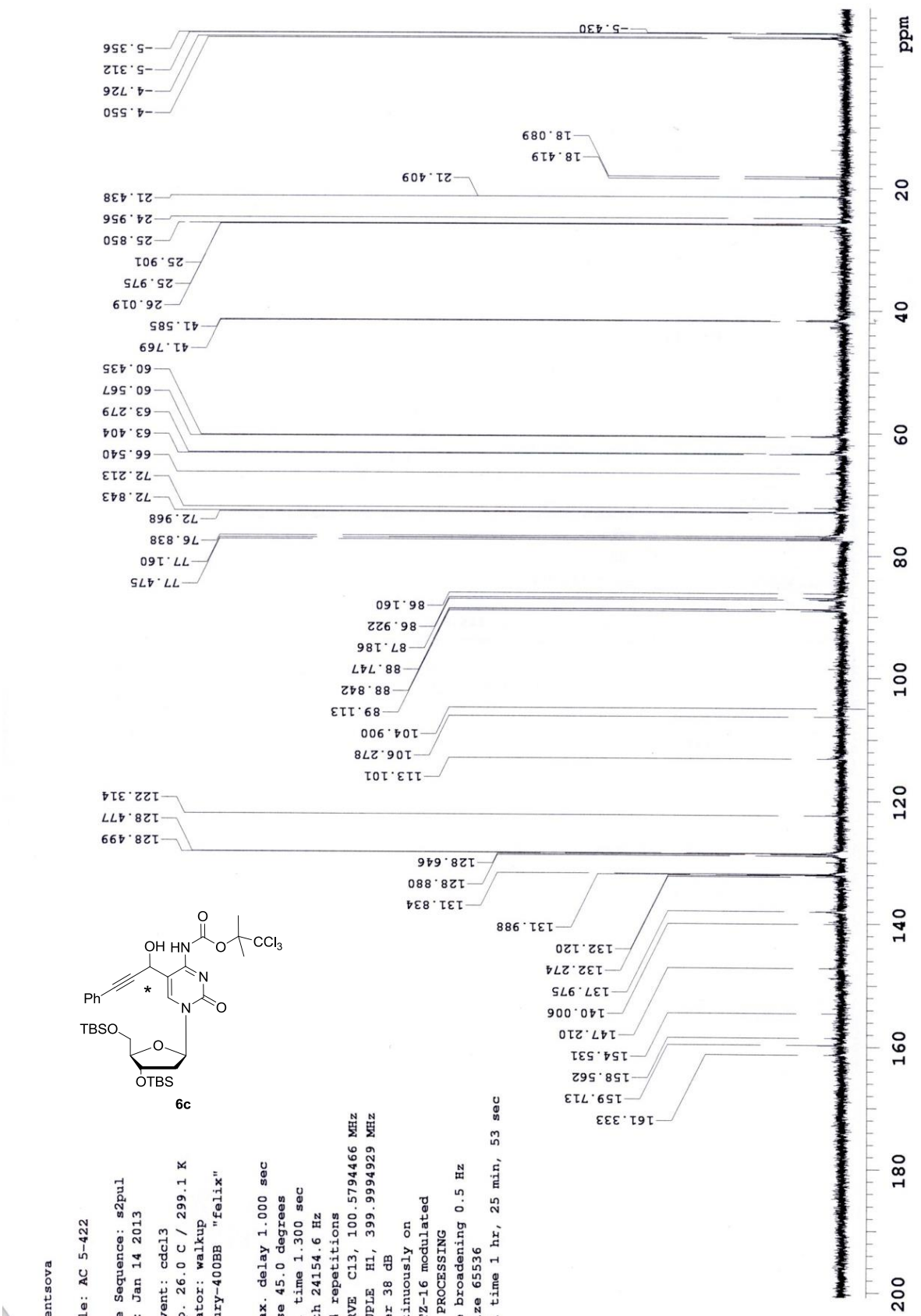
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
8000 repetitions
OBSERVE C13, 75.4555916 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 5 hr, 23 min, 28 sec



7b




Sample: AC 5-42/2
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
16 repetitions
OBSERVE H1, 300.0816984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 28 min, 44 sec
OH HN
O
O
CCl3
N
N
O
Ph
*
TBSO
O
OTBS
6c
ppm


A.Chentsova
Sample: AC 5-422
Pulse Sequence: s2pul
Date: Jan 14 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1024 repetitions
OBSERVE C13, 100.5794466 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 25 min, 53 sec
OH HN
O
O
CCl3
N
Ph
*
N
O
TBSO
O
OTBS
6c
ppm

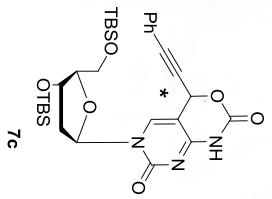
Chentsova

Sample: AC5-424A

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
16 repetitions
OBSERVE H1, 300.0816981 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec



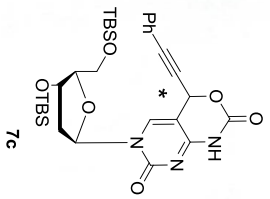
A. Chentsova

Sample: AC5-424A

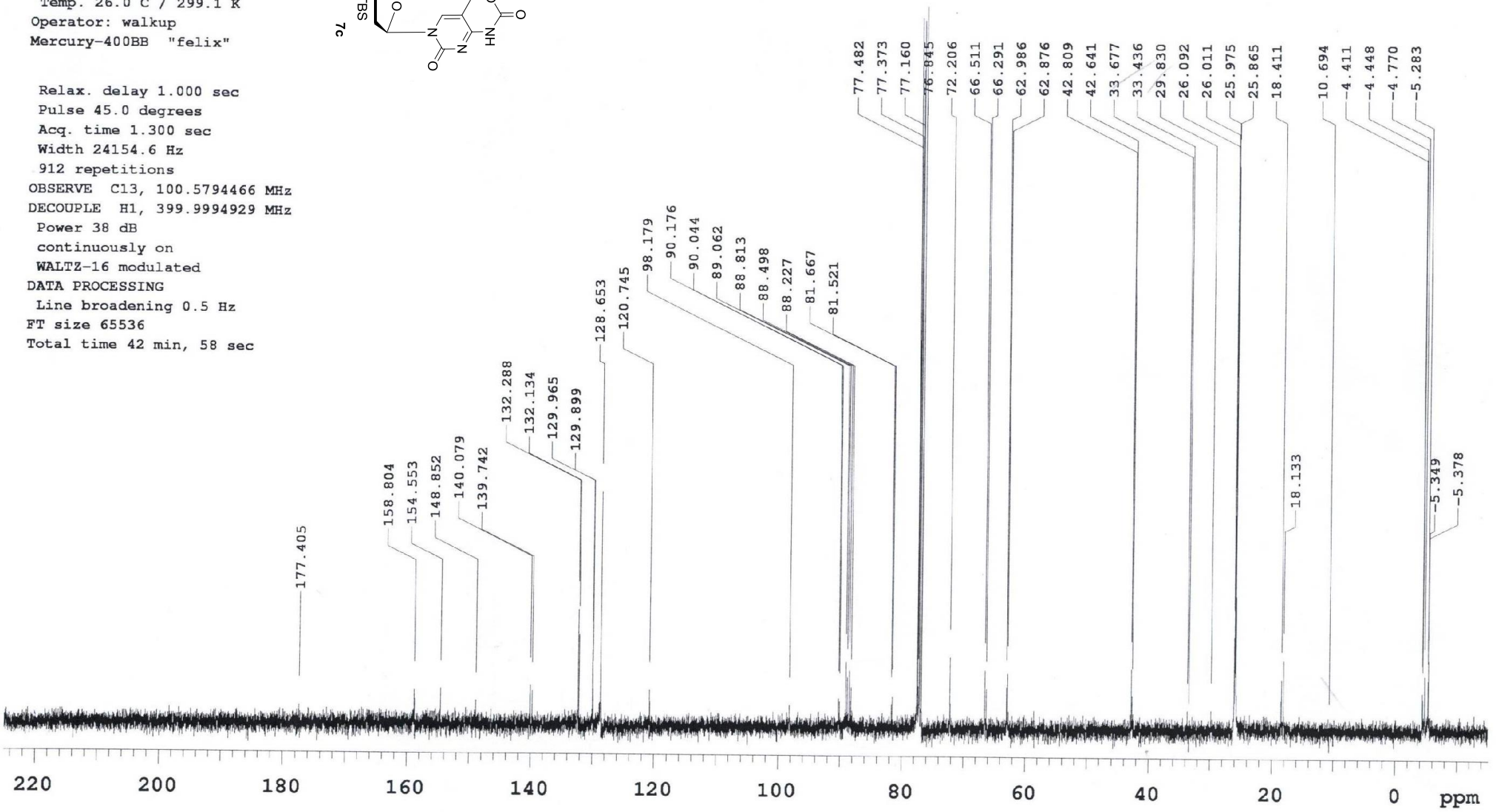
Pulse Sequence: s2pul
Date: Apr 9 2013

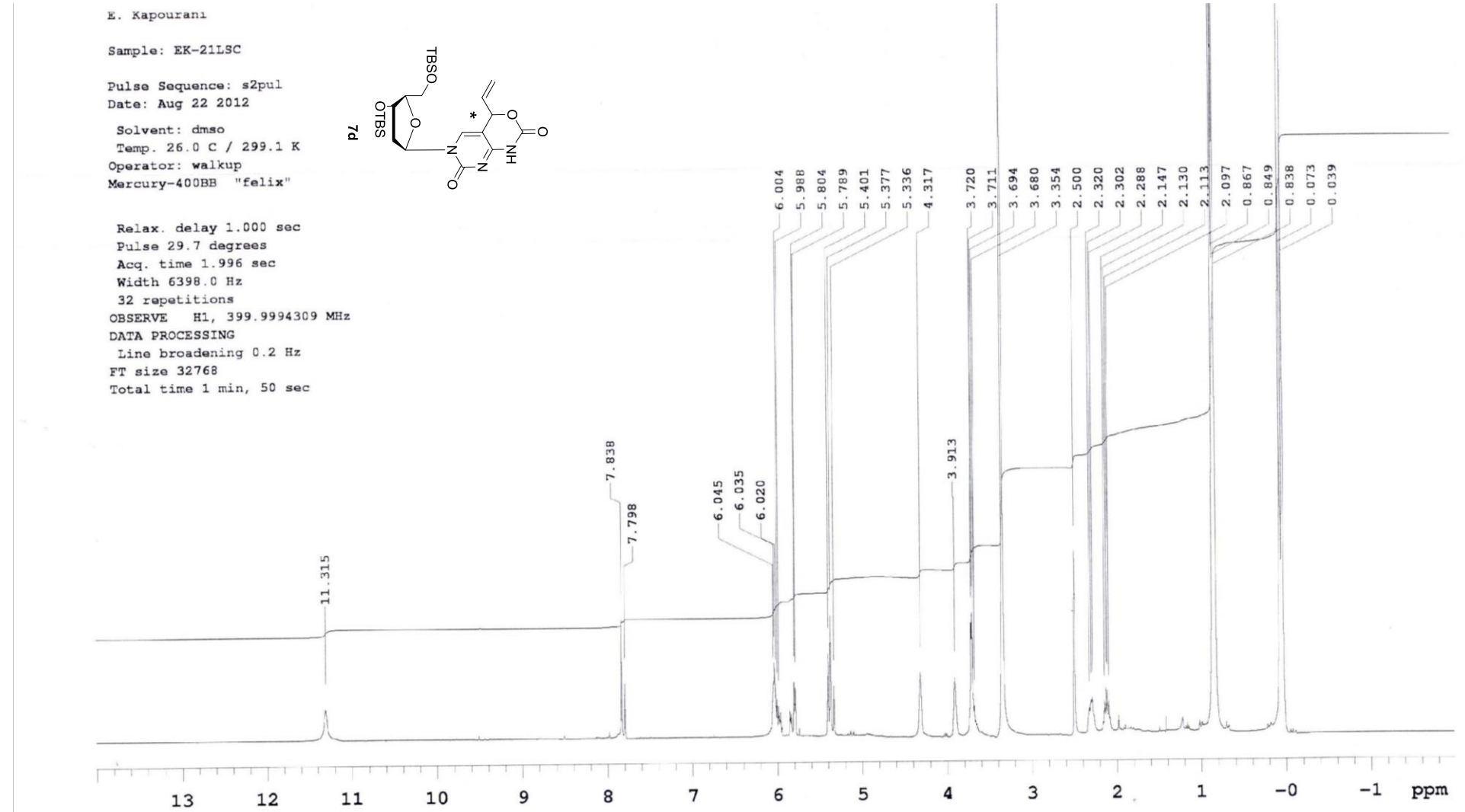
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
912 repetitions
OBSERVE C13, 100.5794466 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 min, 58 sec



7c



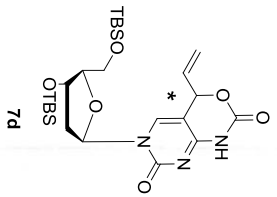

E. Kapourani
Sample: EK-21LSC
Pulse Sequence: s2pul
Date: Aug 22 2012
Solvent: dmso
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9994309 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec
7d
TBSO
OTBS
11.315
7.838
7.798
6.045
6.035
6.020
6.004
5.988
5.804
5.789
5.401
5.377
5.336
4.317
3.913
3.720
3.711
3.694
3.680
3.354
2.500
2.320
2.302
2.288
2.147
2.130
2.113
2.097
0.867
0.849
0.838
0.073
0.039
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

E. Kapourani

Sample: EK-21LSC

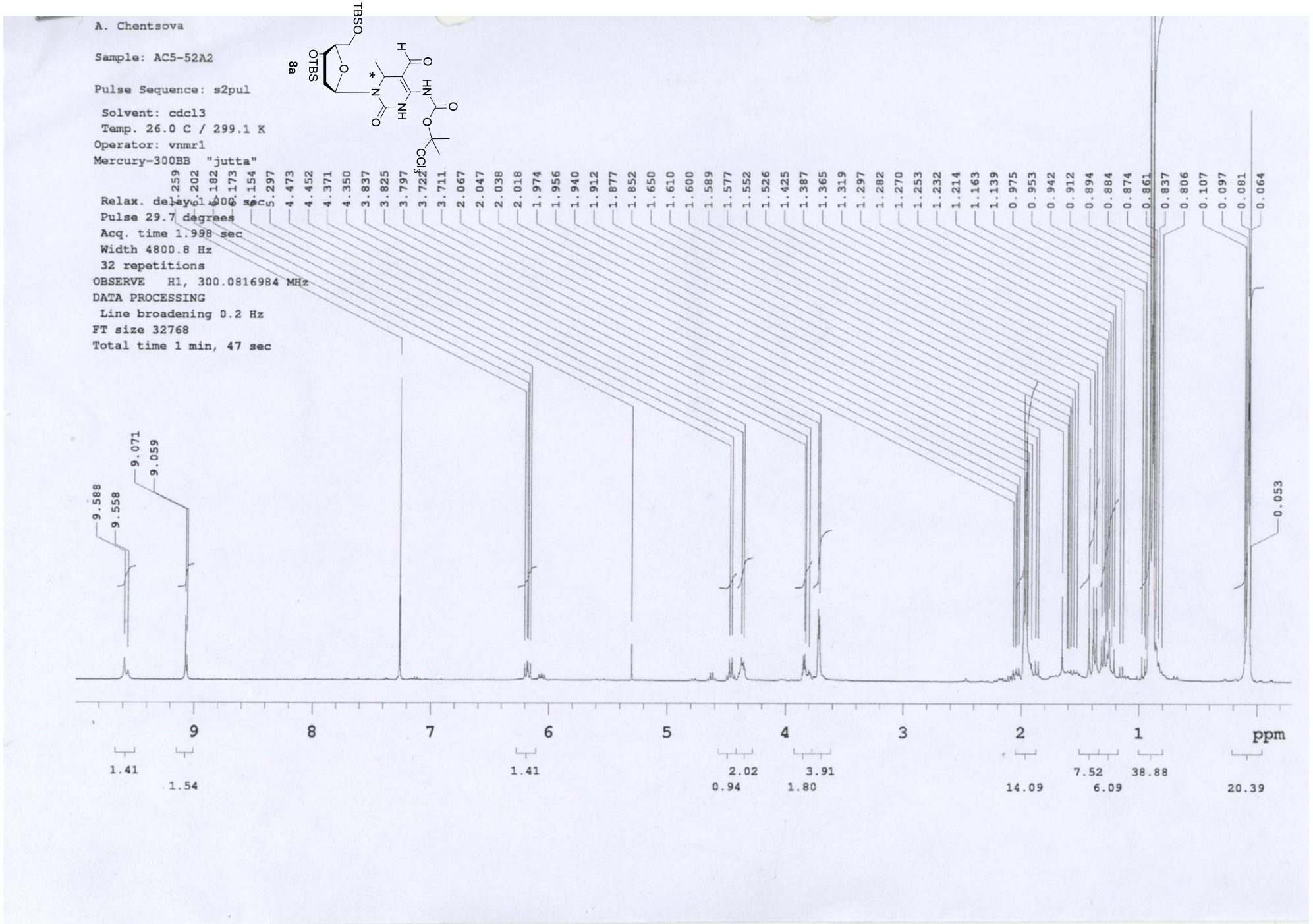
Pulse Sequence: s2pul
Date: Aug 22 2012

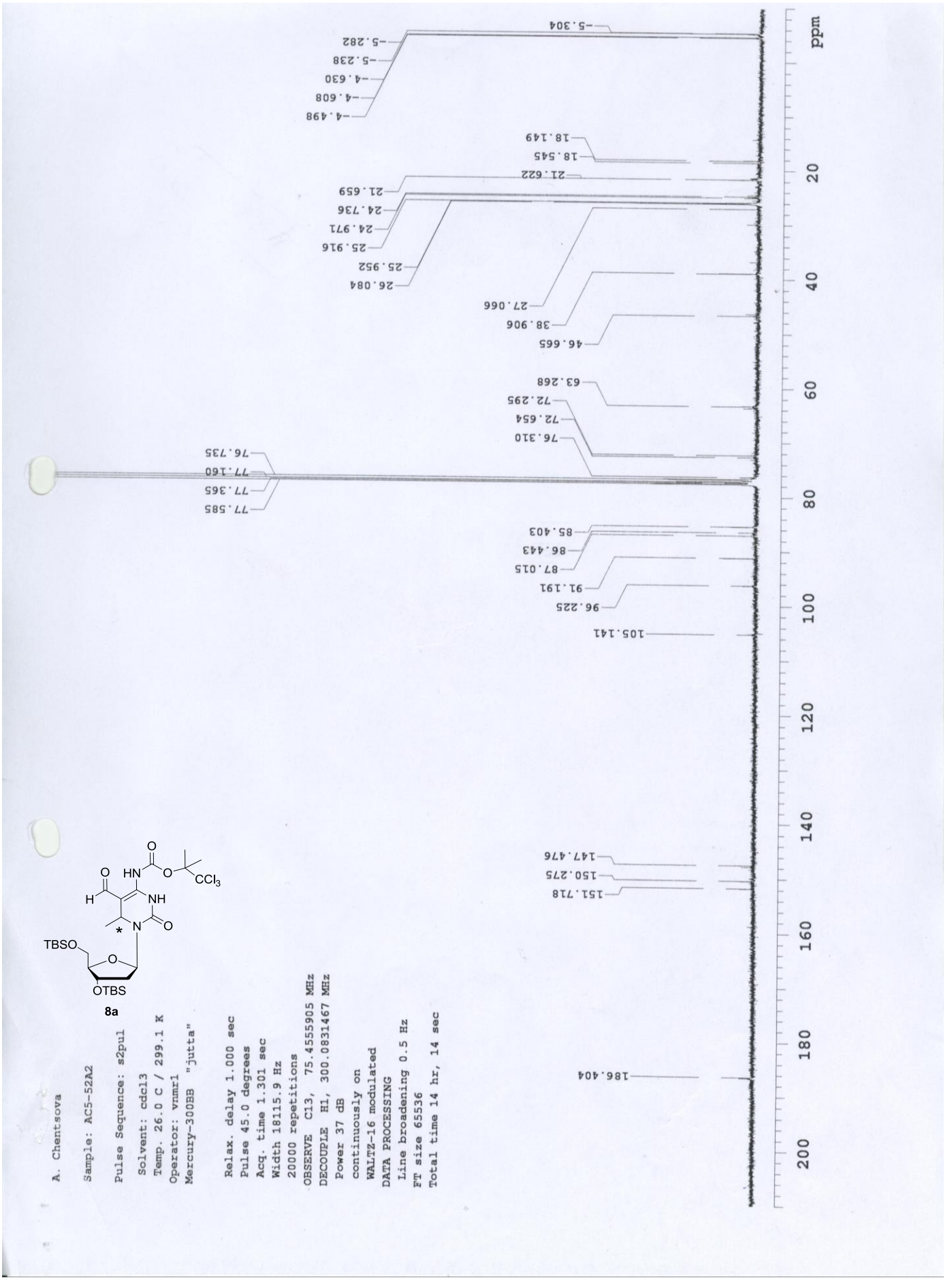
Solvent: dmso
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"



7d

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
10000 repetitions
OBSERVE C13, 100.5799830 MHz
DECOUPLE H1, 400.0013929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 49 min, 3 sec


A. Chentsova
Sample: AC5-52A2
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0816984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
8a
TBSO
OTBS
CCl3
9.588
9.558
9.071
9.059
0.053
ppm
1.41
1.54
1.41
2.02
0.94
3.91
1.80
14.09
7.52
6.09
38.88
20.39


A. Chentsova
Sample: AC5-52A2
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
20000 repetitions
OBSERVE C13, 75.4555905 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 14 hr, 14 sec
8a
ppm
-5.304
-5.282
-5.238
-4.630
-4.608
-4.498
18.149
18.545
21.622
21.659
24.736
24.971
25.916
25.952
26.084
27.066
38.906
46.665
63.268
72.295
72.654
76.310
76.735
77.160
77.365
77.585
85.403
86.443
87.015
91.191
96.225
105.141
147.476
150.275
151.718
186.404

A. Chentsova

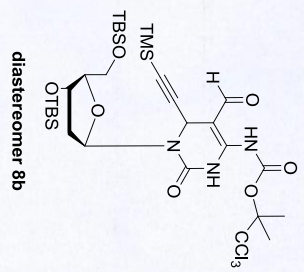
Sample: AC5-501

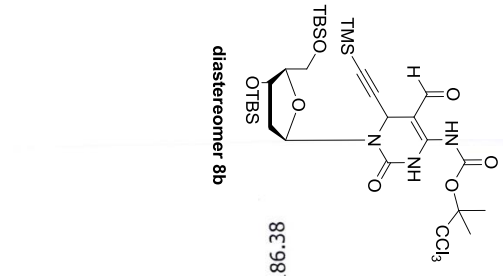
Pulse Sequence: s2pul
Date: Dec 19 2012

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9975363 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec

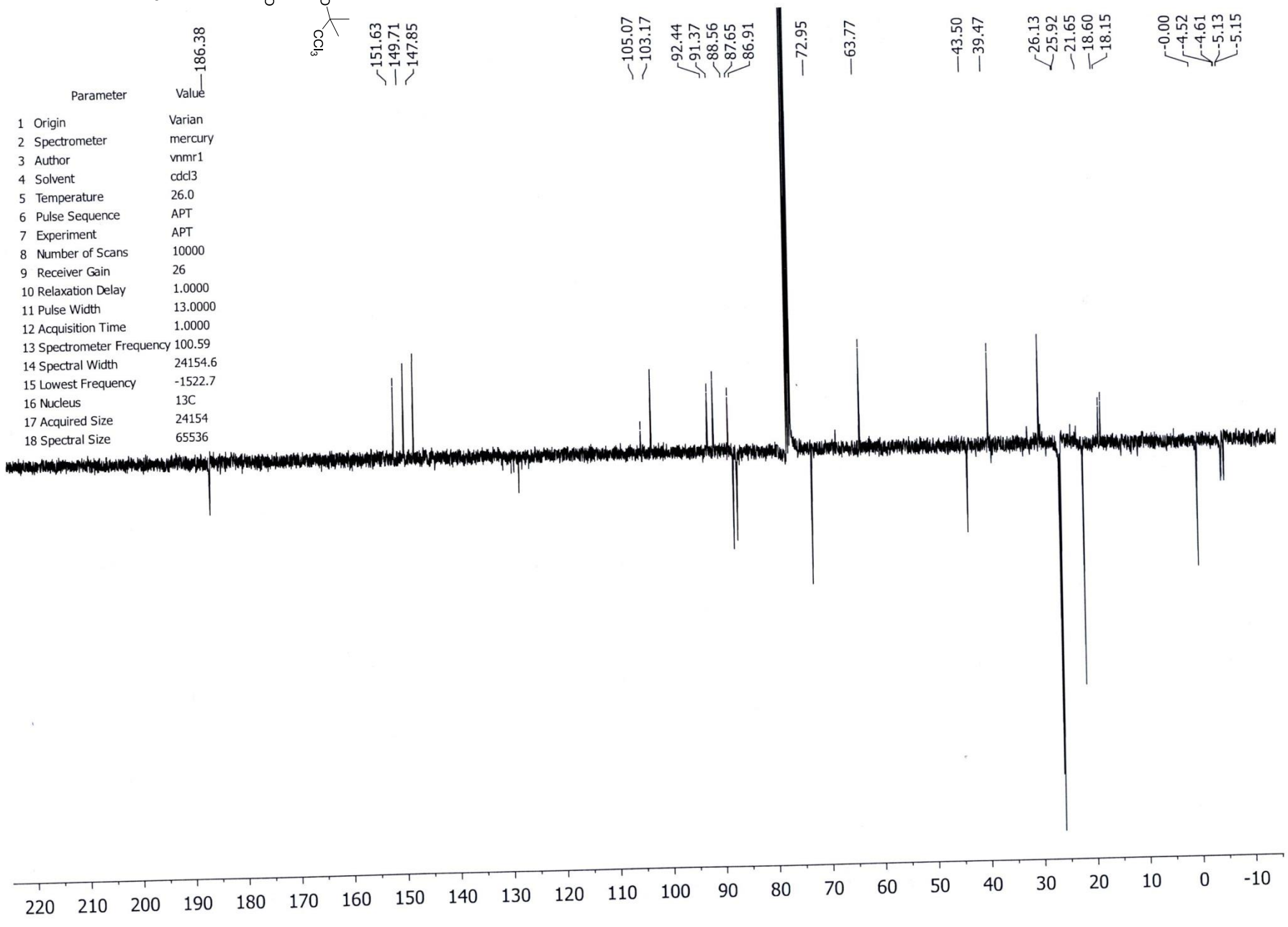
diastereomer 8b

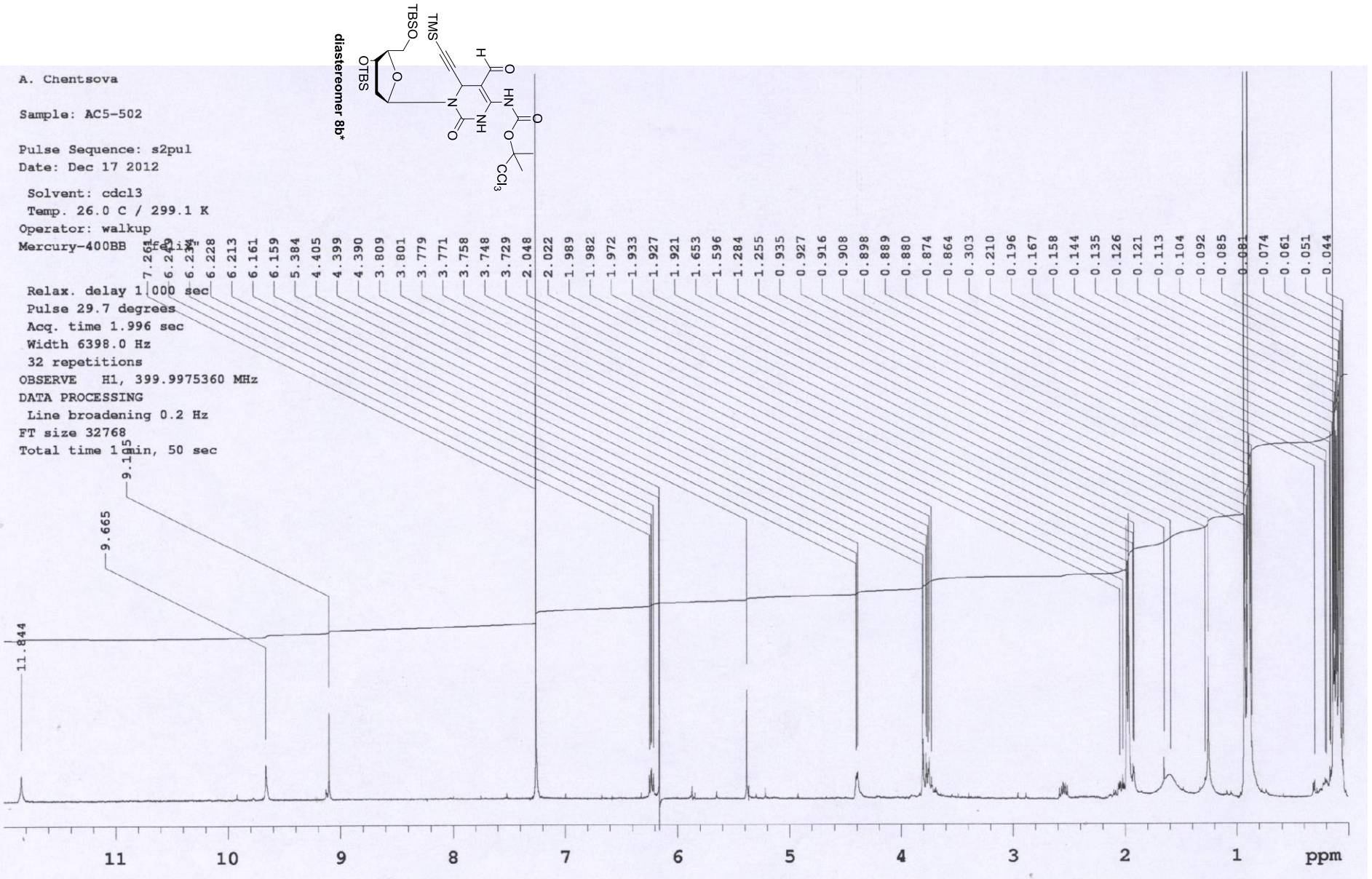




diastereomer 8b

Parameter	Value
1 Origin	Varian
2 Spectrometer	mercury
3 Author	vnmr1
4 Solvent	cdcl3
5 Temperature	26.0
6 Pulse Sequence	APT
7 Experiment	APT
8 Number of Scans	10000
9 Receiver Gain	26
10 Relaxation Delay	1.0000
11 Pulse Width	13.0000
12 Acquisition Time	1.0000
13 Spectrometer Frequency	100.59
14 Spectral Width	24154.6
15 Lowest Frequency	-1522.7
16 Nucleus	13C
17 Acquired Size	24154
18 Spectral Size	65536

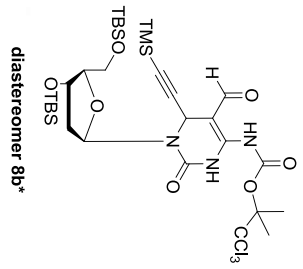



diastereomer 8b*
TBSO
OTBS
TMS
H
O
HN
NH
N
O
O
O
CCl3
A. Chentsova
Sample: AC5-502
Pulse Sequence: s2pul
Date: Dec 17 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9975360 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec
11.844
9.665
9.185
7.261
6.243
6.234
6.228
6.213
6.161
6.159
5.384
4.405
4.399
4.390
3.809
3.801
3.779
3.771
3.758
3.748
3.729
2.048
2.022
1.989
1.982
1.972
1.933
1.927
1.921
1.653
1.596
1.284
1.255
0.935
0.927
0.916
0.908
0.898
0.889
0.880
0.874
0.864
0.303
0.210
0.196
0.167
0.158
0.144
0.135
0.126
0.121
0.113
0.104
0.092
0.085
0.081
0.074
0.061
0.051
0.044
11
10
9
8
7
6
5
4
3
2
1
ppm

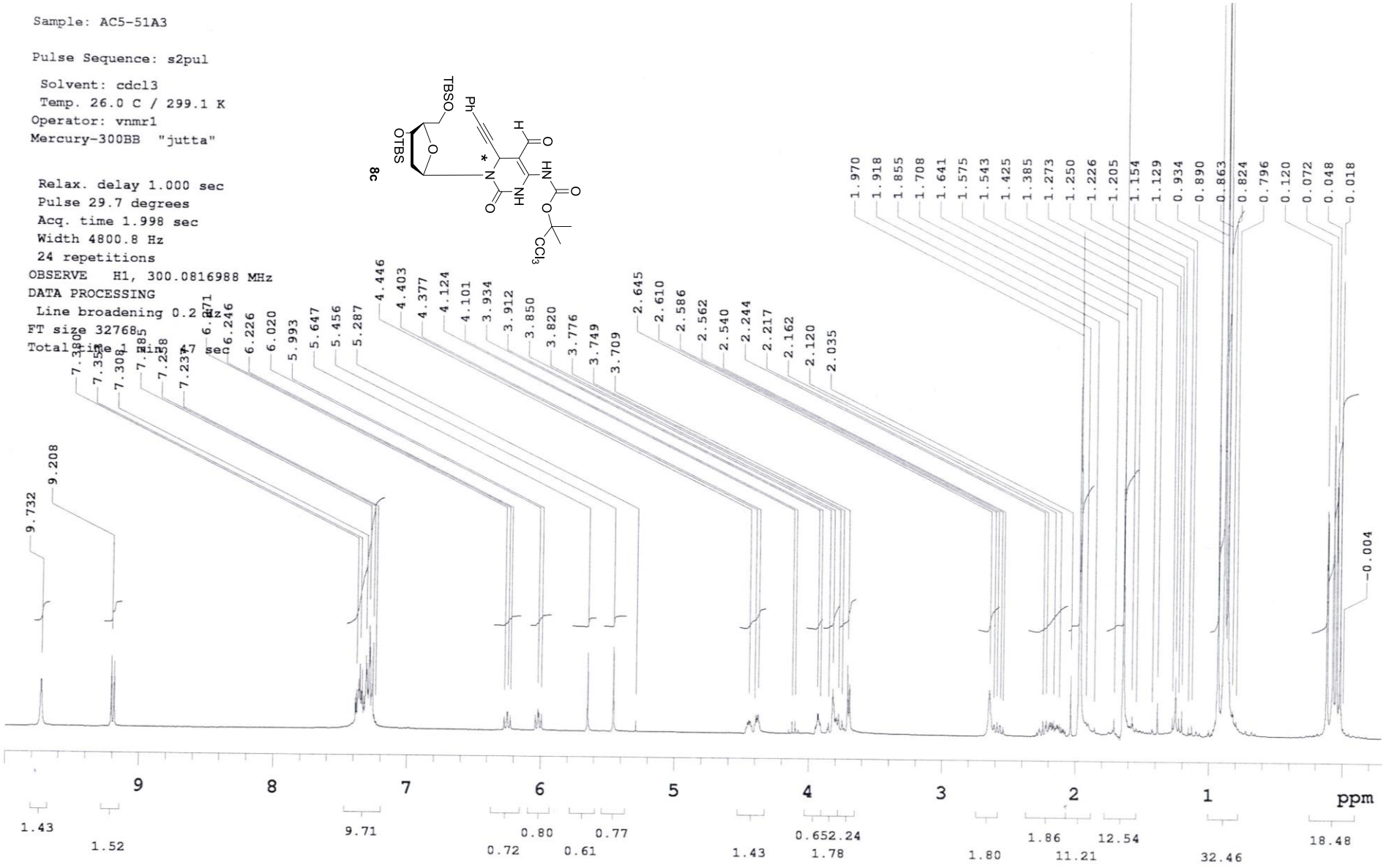
A. Chentsova

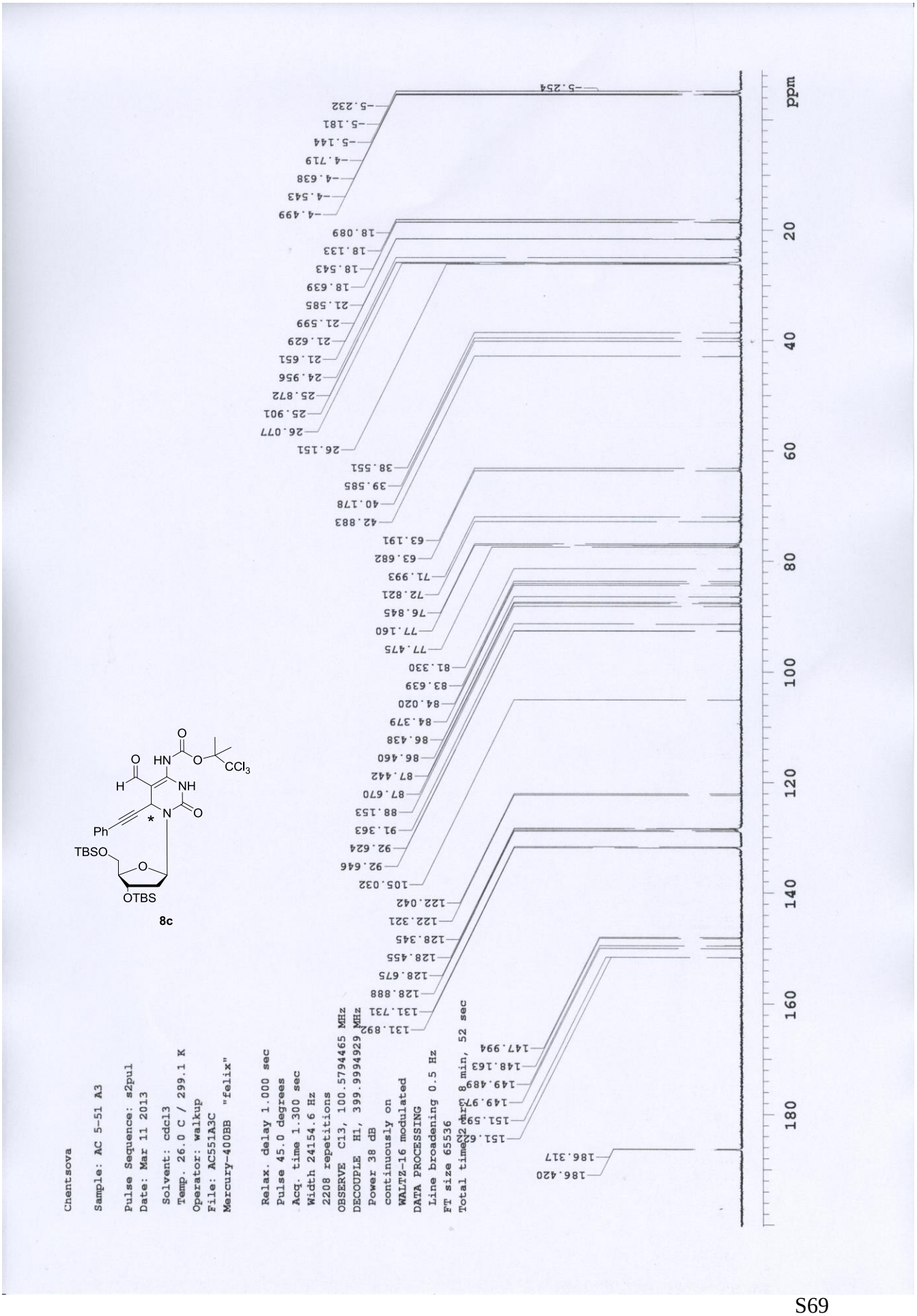
exp3 Carbon

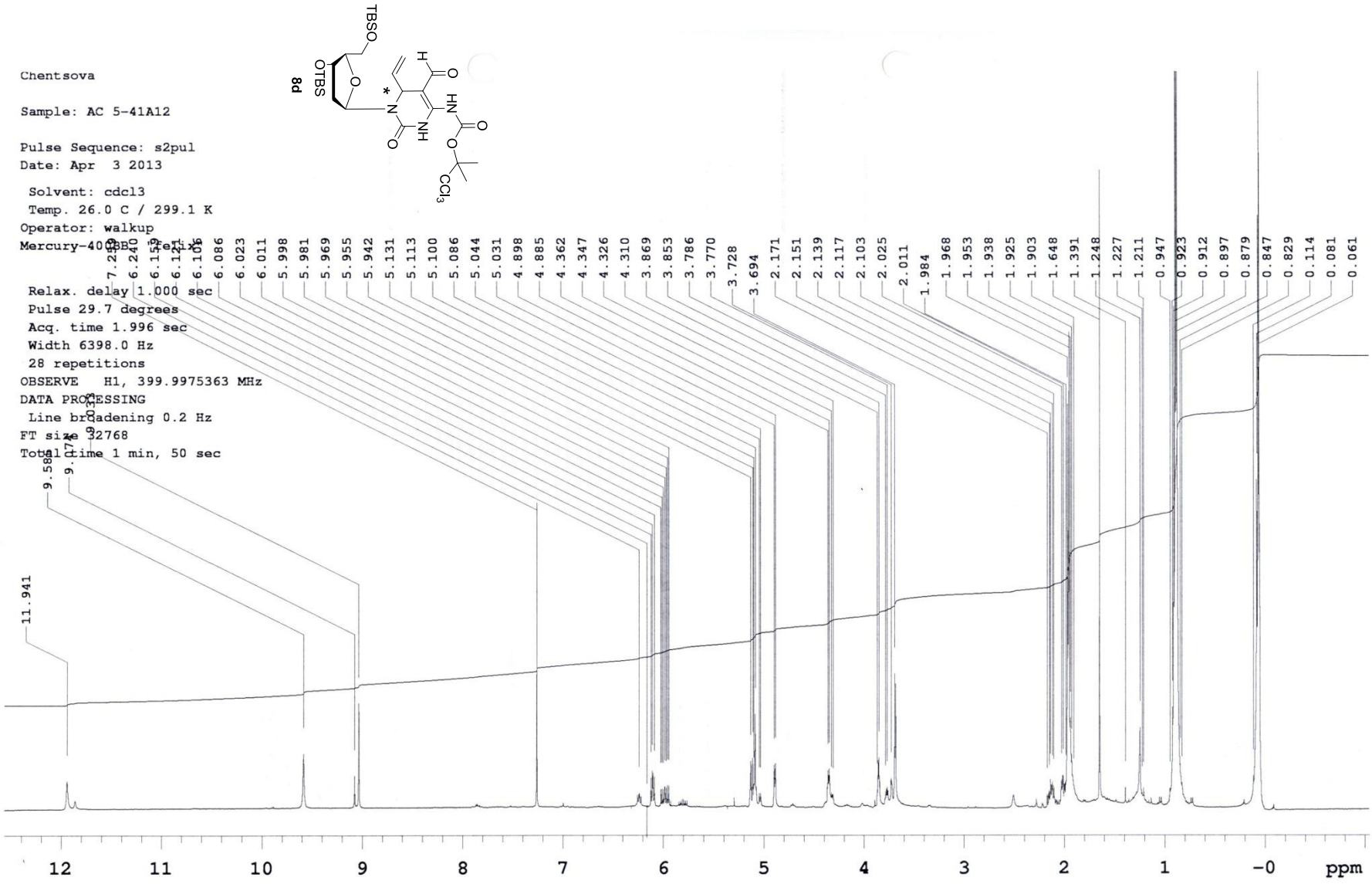
SAMPLE		SPECIAL	
date	Dec 17 2012	temp	26.0
solvent	cdcl3	gain	20
file	exp	spin	20
ACQUISITION		hst	0.008
sw	24154.6	pw90	13.000
at	1.300	alfa	10.000
np	62826	FLAGS	
fb	13400	il	n
bs	32	in	n
d1	1.000	dp	y
nt	20000	hs	nn
ct	20000	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.590	DISPLAY	
tof	1054.2	sp	-1522.8
tpwr	59	wp	24153.9
pw	6.500	rfl	9284.3
DECOUPLER		rfp	7760.7
dn	H1	rp	85.6
dof	0	lp	-149.0
dm	yyy	PLOT	
dmm	w	wc	250
dpwr	38	sc	0
dmf	9100	vs	5522
		th	3
		ai cdc ph	

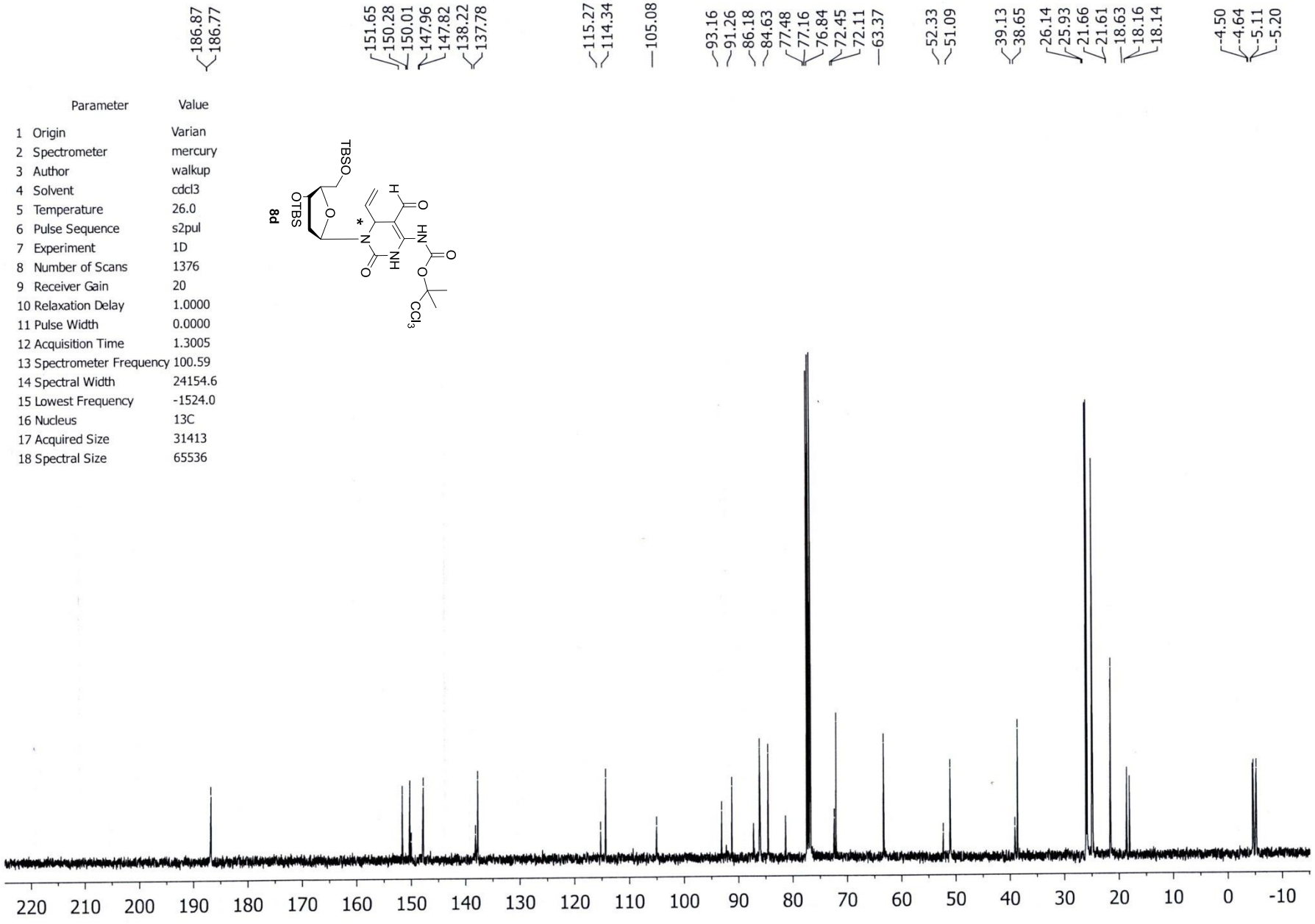


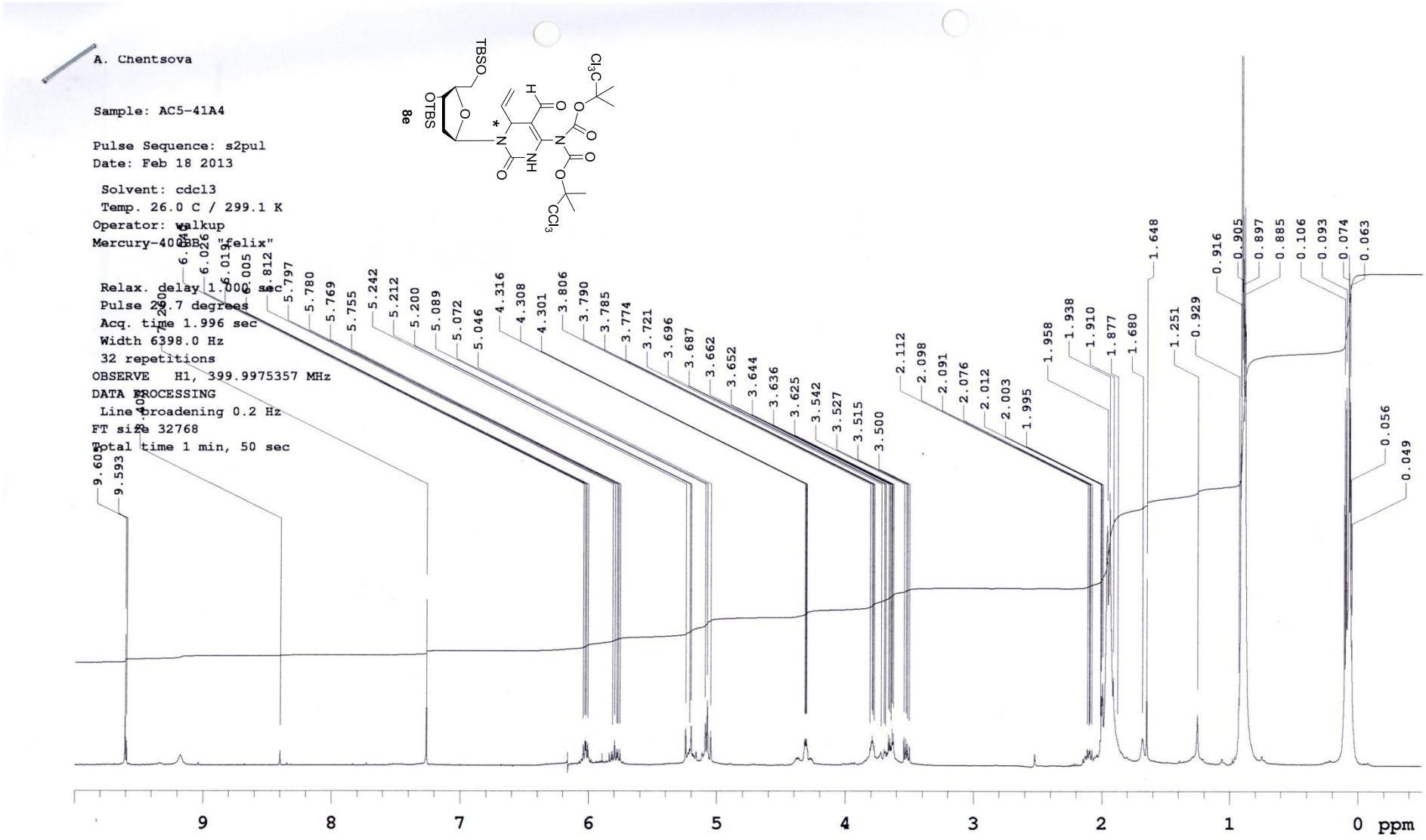
diastereomer 8b*

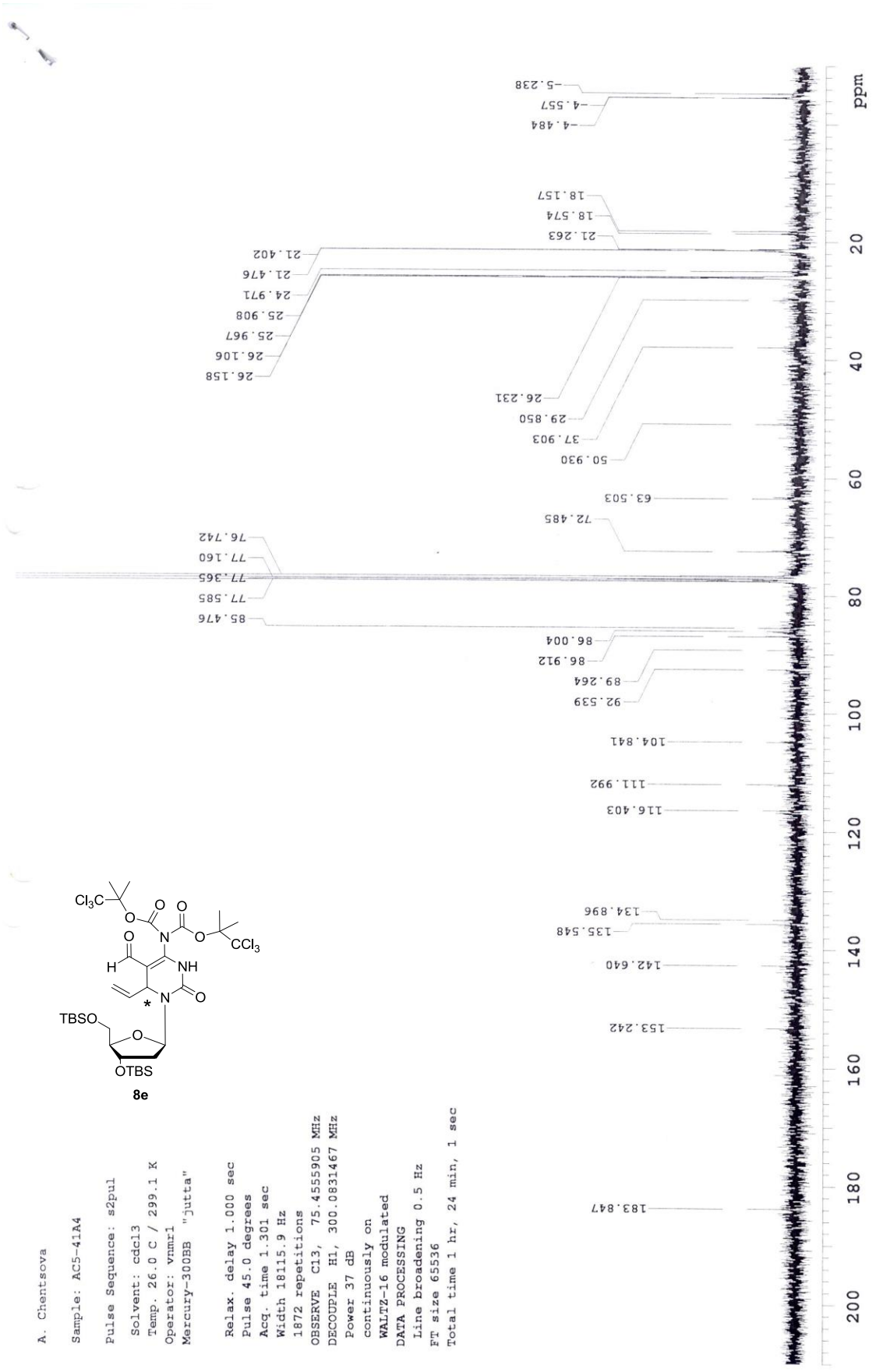

Sample: AC5-51A3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
24 repetitions
OBSERVE H1, 300.0816988 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
8c
TBSO
OTBS
Ph
H
O
NH
HN
O
O
O
CCl3
9.732
9.208
7.380
7.355
7.308
7.285
7.258
7.237
6.871
6.246
6.226
6.020
5.993
5.647
5.456
5.287
4.446
4.403
4.377
4.124
4.101
3.934
3.912
3.850
3.820
3.776
3.749
3.709
2.645
2.610
2.586
2.562
2.540
2.244
2.217
2.162
2.120
2.035
1.970
1.918
1.855
1.708
1.641
1.575
1.543
1.425
1.385
1.273
1.250
1.226
1.205
1.154
1.129
0.934
0.890
0.863
0.824
0.796
0.120
0.072
0.048
0.018
-0.004
9
8
7
6
5
4
3
2
1
ppm
1.43
1.52
9.71
0.72
0.80
0.61
0.77
1.43
0.652.24
1.78
1.80
1.86
11.21
12.54
32.46
18.48

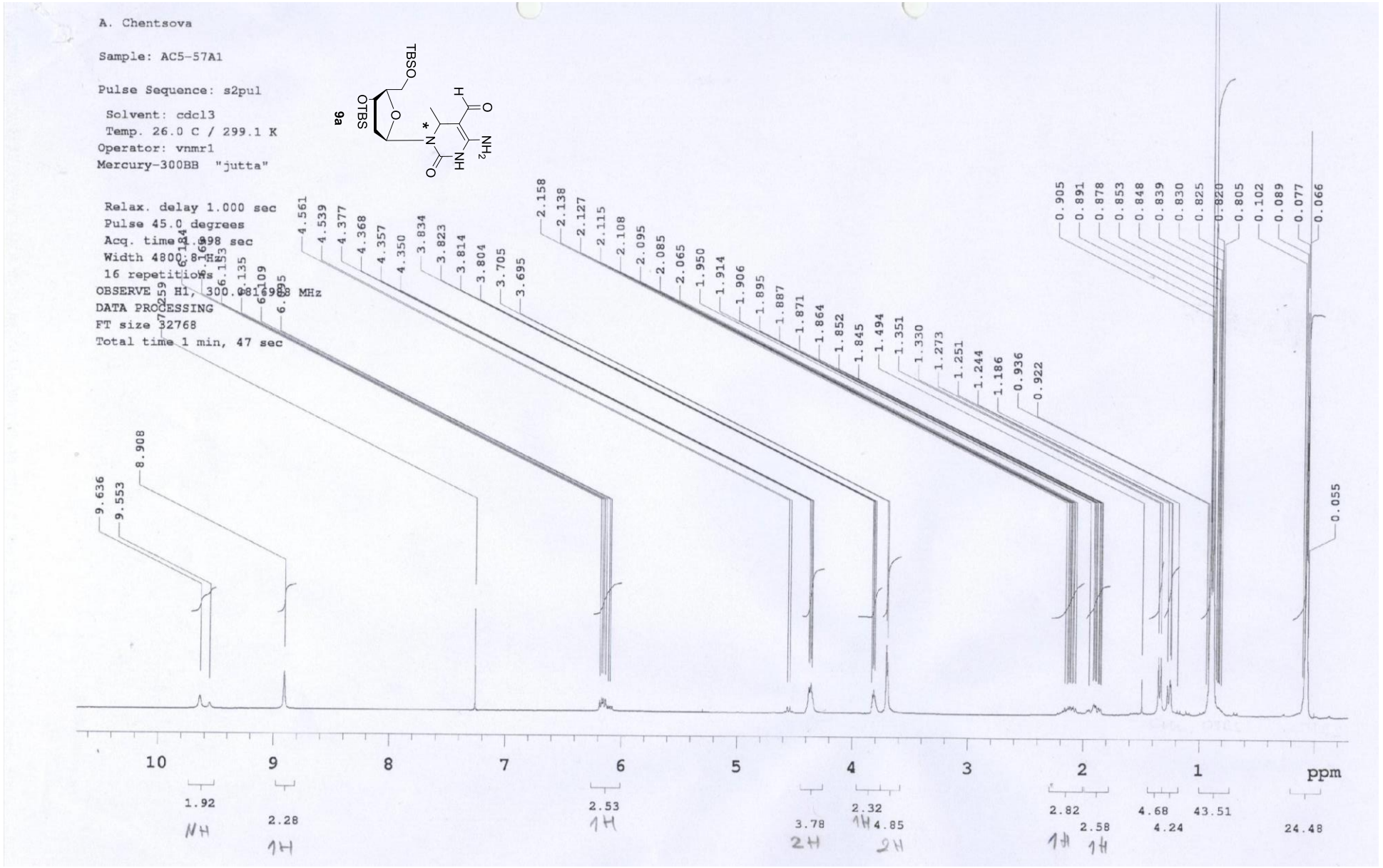

Chentsova
Sample: AC 5-51 A3
Pulse Sequence: s2pul
Date: Mar 11 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
File: AC551A3C
Marcury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
2208 repetitions
OBSERVE C13, 100.5794465 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 2 hr, 8 min, 52 sec
-5.254
-5.232
-5.181
-5.144
-4.719
-4.638
-4.543
-4.499
18.089
18.133
18.543
18.639
21.585
21.599
21.629
21.651
24.956
25.872
25.901
26.077
26.151
38.551
39.585
40.178
42.883
63.191
63.682
71.993
72.821
76.845
77.160
77.475
81.330
83.639
84.020
84.379
86.438
86.460
87.442
87.670
88.153
91.363
92.624
92.646
105.032
122.042
122.321
128.345
128.455
128.675
128.888
131.731
131.892
147.994
148.163
149.489
149.972
151.598
151.624
186.317
186.420
ppm
20
40
60
80
100
120
140
160
180
O
HN
O
CCl3
O
H
NH
N
O
Ph
*
TBSO
O
OTBS
8c


TBSO
OTBS
8d
Chentsova
Sample: AC 5-41A12
Pulse Sequence: s2pul
Date: Apr 3 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB 3ehzi
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
28 repetitions
OBSERVE H1, 399.9975363 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec
11.941
9.581
9.077
7.240
6.240
6.154
6.121
6.106
6.086
6.023
6.011
5.998
5.981
5.969
5.955
5.942
5.131
5.113
5.100
5.086
5.044
5.031
4.898
4.885
4.362
4.347
4.326
4.310
3.869
3.853
3.786
3.770
3.728
3.694
2.171
2.151
2.139
2.117
2.103
2.025
2.011
1.984
1.968
1.953
1.938
1.925
1.903
1.648
1.391
1.248
1.227
1.211
0.947
0.923
0.912
0.897
0.879
0.847
0.829
0.114
0.081
0.061
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


186.87
186.77
151.65
150.28
150.01
147.96
147.82
138.22
137.78
115.27
114.34
105.08
93.16
91.26
86.18
84.63
77.48
77.16
76.84
72.45
72.11
63.37
52.33
51.09
39.13
38.65
26.14
25.93
21.66
21.61
18.63
18.16
18.14
-4.50
-4.64
-5.11
-5.20
Parameter Value
1 Origin Varian
2 Spectrometer mercury
3 Author walkup
4 Solvent cdcl3
5 Temperature 26.0
6 Pulse Sequence s2pul
7 Experiment 1D
8 Number of Scans 1376
9 Receiver Gain 20
10 Relaxation Delay 1.0000
11 Pulse Width 0.0000
12 Acquisition Time 1.3005
13 Spectrometer Frequency 100.59
14 Spectral Width 24154.6
15 Lowest Frequency -1524.0
16 Nucleus 13C
17 Acquired Size 31413
18 Spectral Size 65536
8d
TBSO
OTBS
O
N
HN
O
H
O
O
CCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


A. Chentsova
Sample: AC5-41A4
Pulse Sequence: s2pul
Date: Feb 18 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 26.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
32 repetitions
OBSERVE H1, 399.9975357 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec
8e
TBSO
OTBS
9.601
9.593
6.044
6.026
6.015
6.005
5.812
5.797
5.780
5.769
5.755
5.242
5.212
5.200
5.089
5.072
5.046
4.316
4.308
4.301
3.806
3.790
3.785
3.774
3.721
3.696
3.687
3.662
3.652
3.644
3.636
3.625
3.542
3.527
3.515
3.500
2.112
2.098
2.091
2.076
2.012
2.003
1.995
1.958
1.938
1.910
1.877
1.680
1.648
1.251
0.929
0.916
0.905
0.897
0.885
0.106
0.093
0.074
0.063
0.056
0.049
9
8
7
6
5
4
3
2
1
0 ppm


A. Chentsova
Sample: AC5-41A4
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
1872 repetitions
OBSERVE C13, 75.4555905 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec
8e
ppm
-5.238
-4.557
-4.484
18.157
18.574
21.263
21.402
21.476
24.971
25.908
25.967
26.106
26.158
26.231
29.850
37.903
50.930
63.503
72.485
76.742
77.160
77.365
77.585
85.476
86.004
86.912
89.264
92.539
104.841
111.992
116.403
134.896
135.548
142.640
153.242
183.847


A. Chentsova
Sample: AC5-57A1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
16 repetitions
OBSERVE H1, 300.0816988 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 47 sec
TBSO
OTBS
9a
ppm
1.92
2.28
2.53
3.78
2.32
4.85
2.82
2.58
4.68
4.24
43.51
24.48

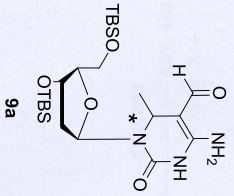
Chentsova

Sample: AC 5-57A1

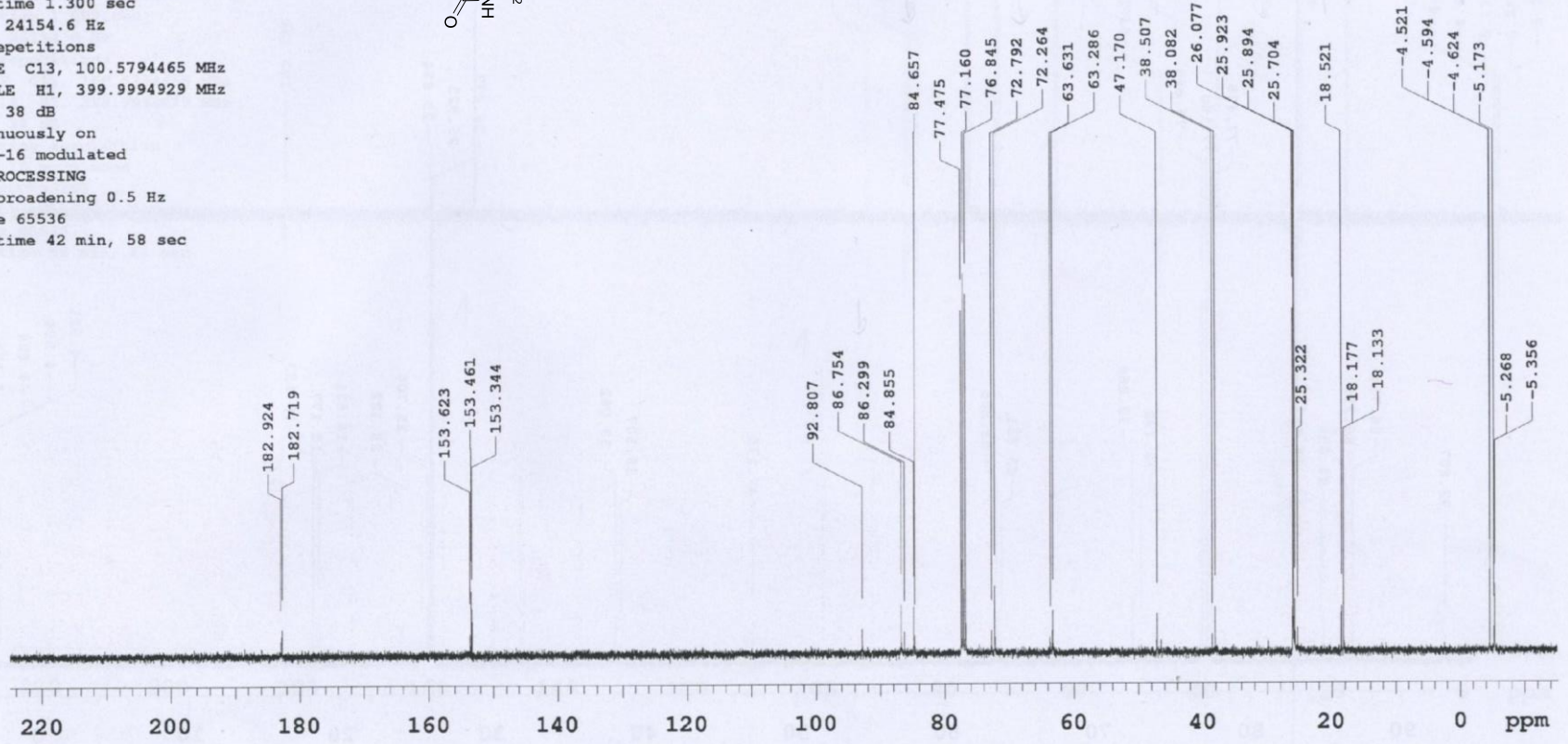
Pulse Sequence: s2pul
Date: Apr 4 2013

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
736 repetitions
OBSERVE C13, 100.5794465 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 min, 58 sec



9a



S73

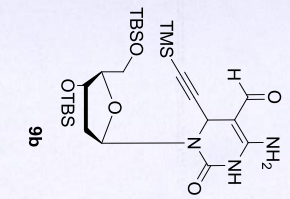
A. Chentsova

Sample: AC5-58

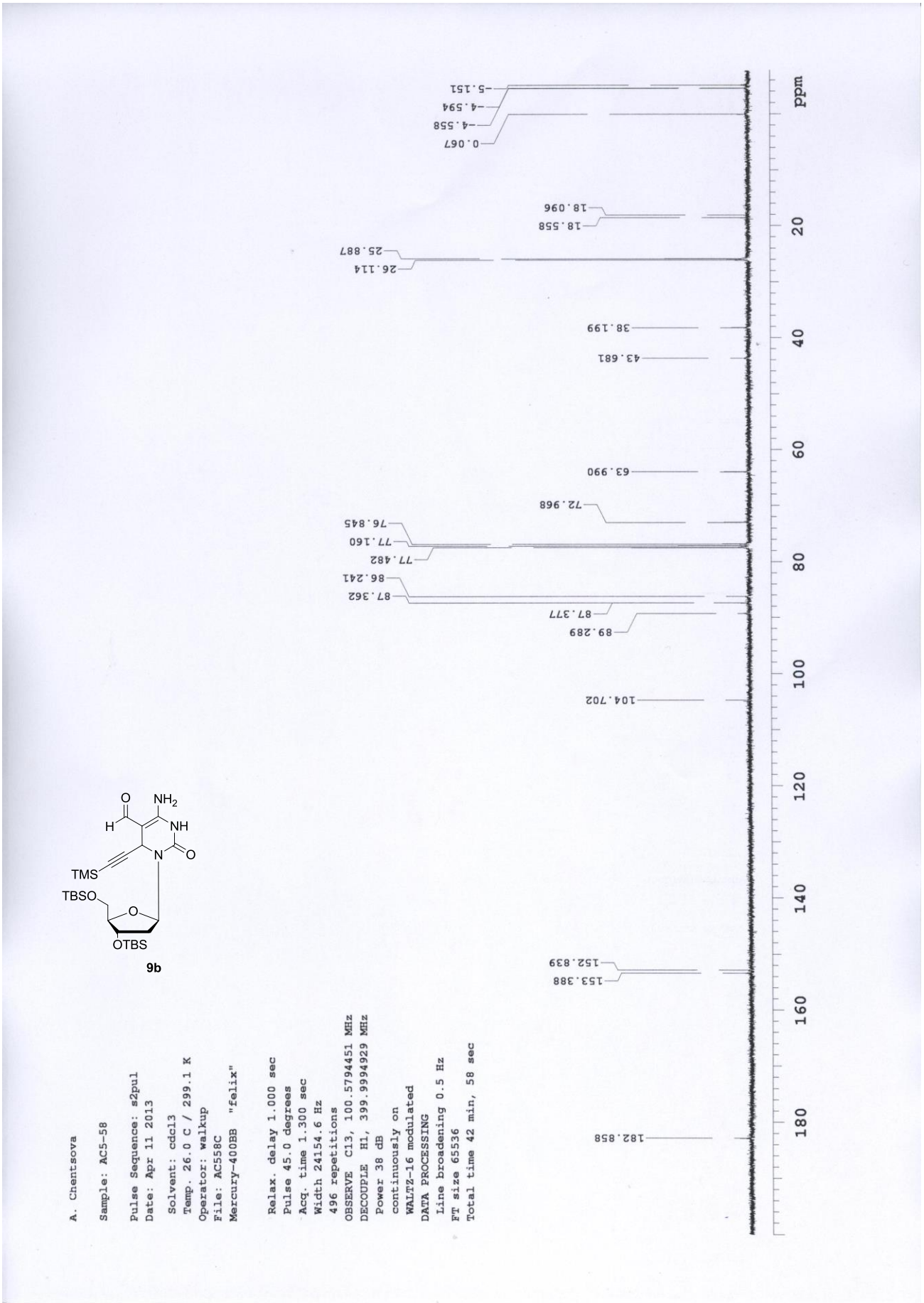
Pulse Sequence: s2pul
Date: Apr 11 2013

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 7199.4 Hz
16 repetitions
OBSERVE H1, 399.9975363 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 52 sec



9b


A. Chentsova
Sample: AC5-58
Pulse Sequence: s2pul
Date: Apr 11 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
File: AC558C
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
496 repetitions
OBSERVE C13, 100.5794451 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 min, 58 sec
O
NH2
H
NH
N
O
TMS
TBSO
O
OTBS
9b
182.858
153.388
152.839
104.702
89.289
87.377
87.362
86.241
77.482
77.160
76.845
72.968
63.990
43.681
38.199
26.114
25.887
18.558
18.096
0.067
-4.558
-4.594
-5.151
ppm
180
160
140
120
100
80
60
40
20

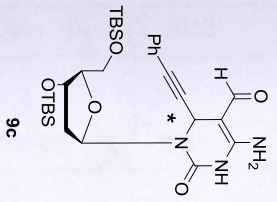
Std Proton parameters
A. Chentsova

Sample: AC5-56

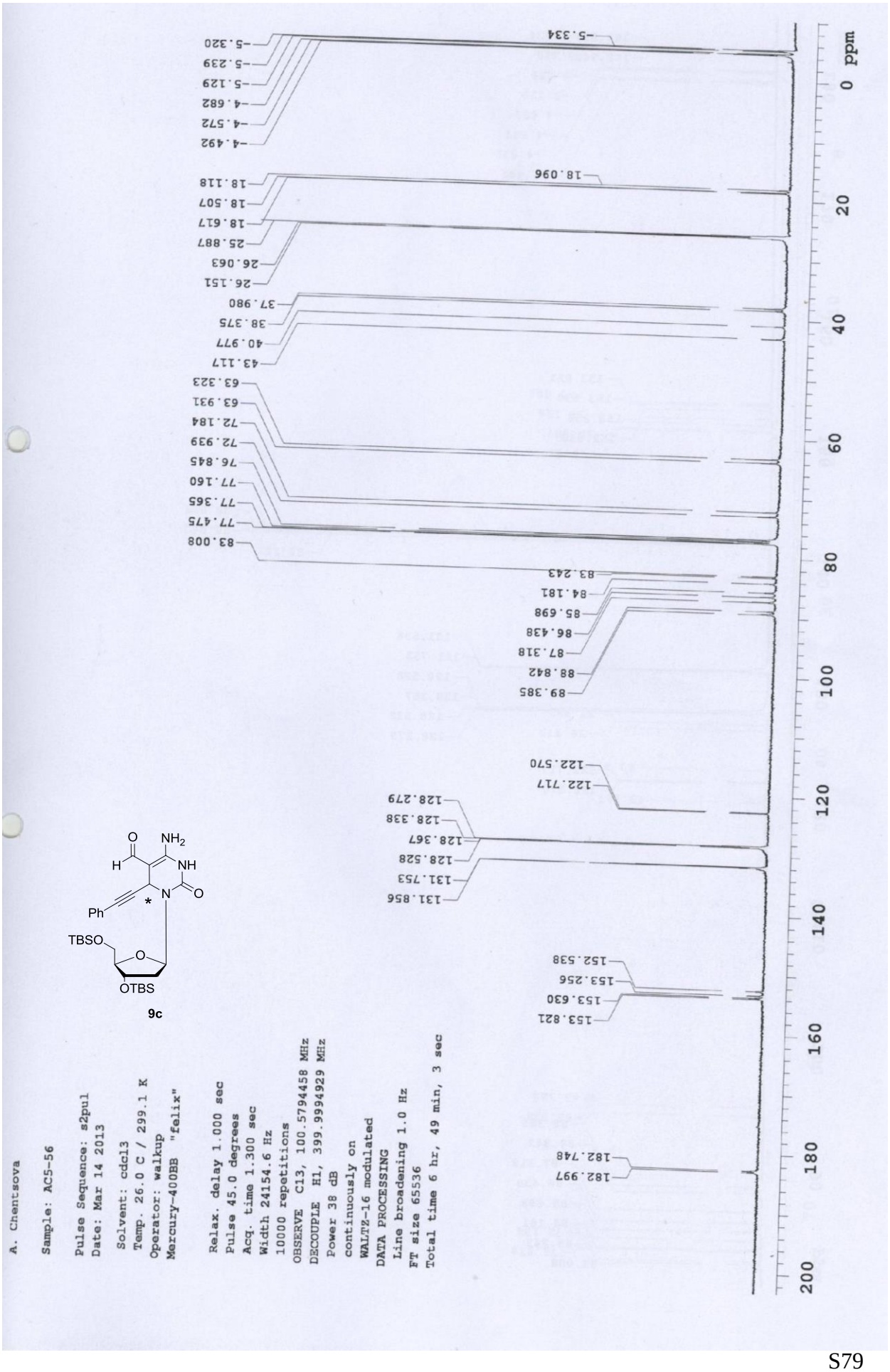
Pulse Sequence: s2pul

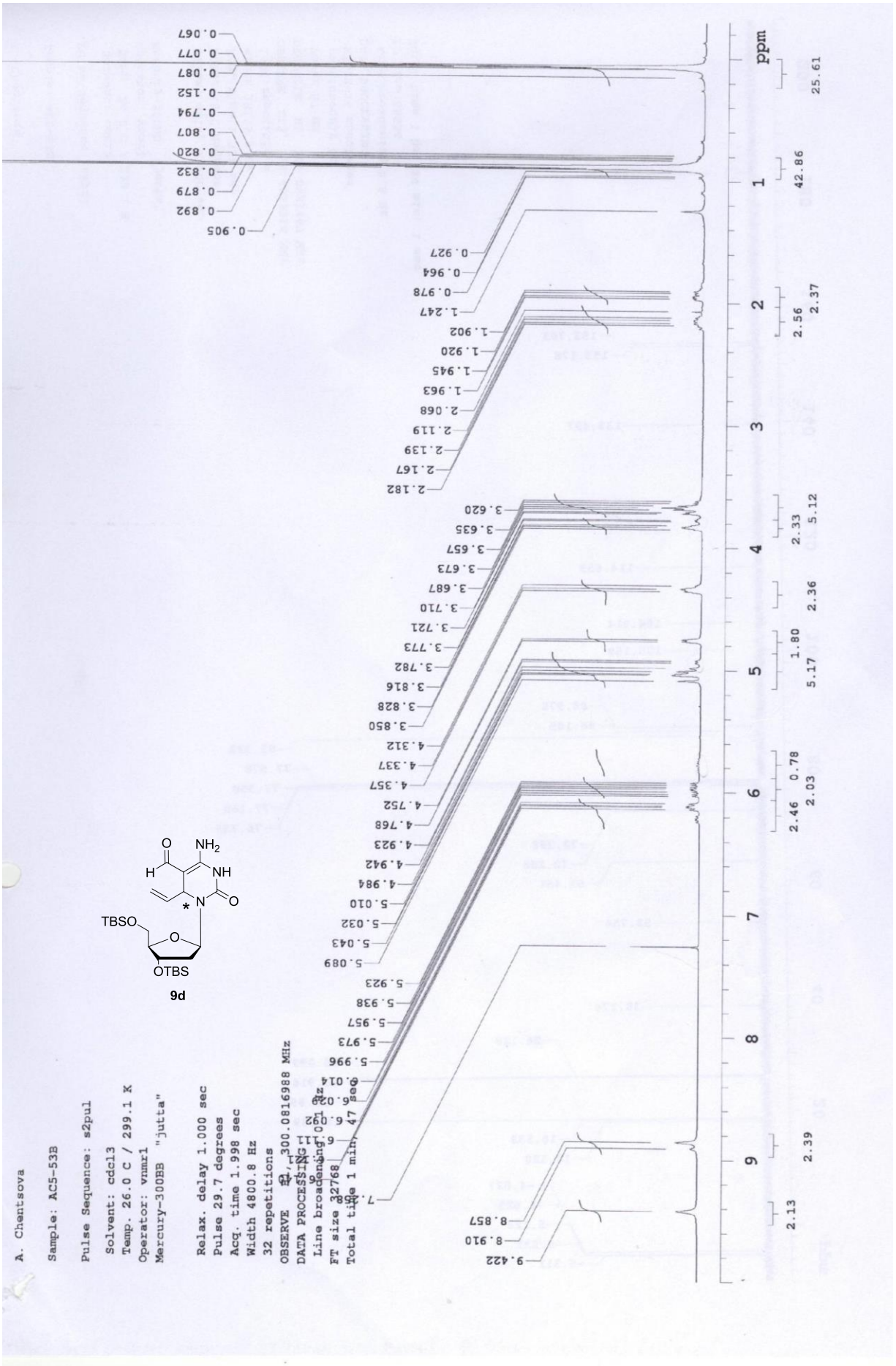
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"

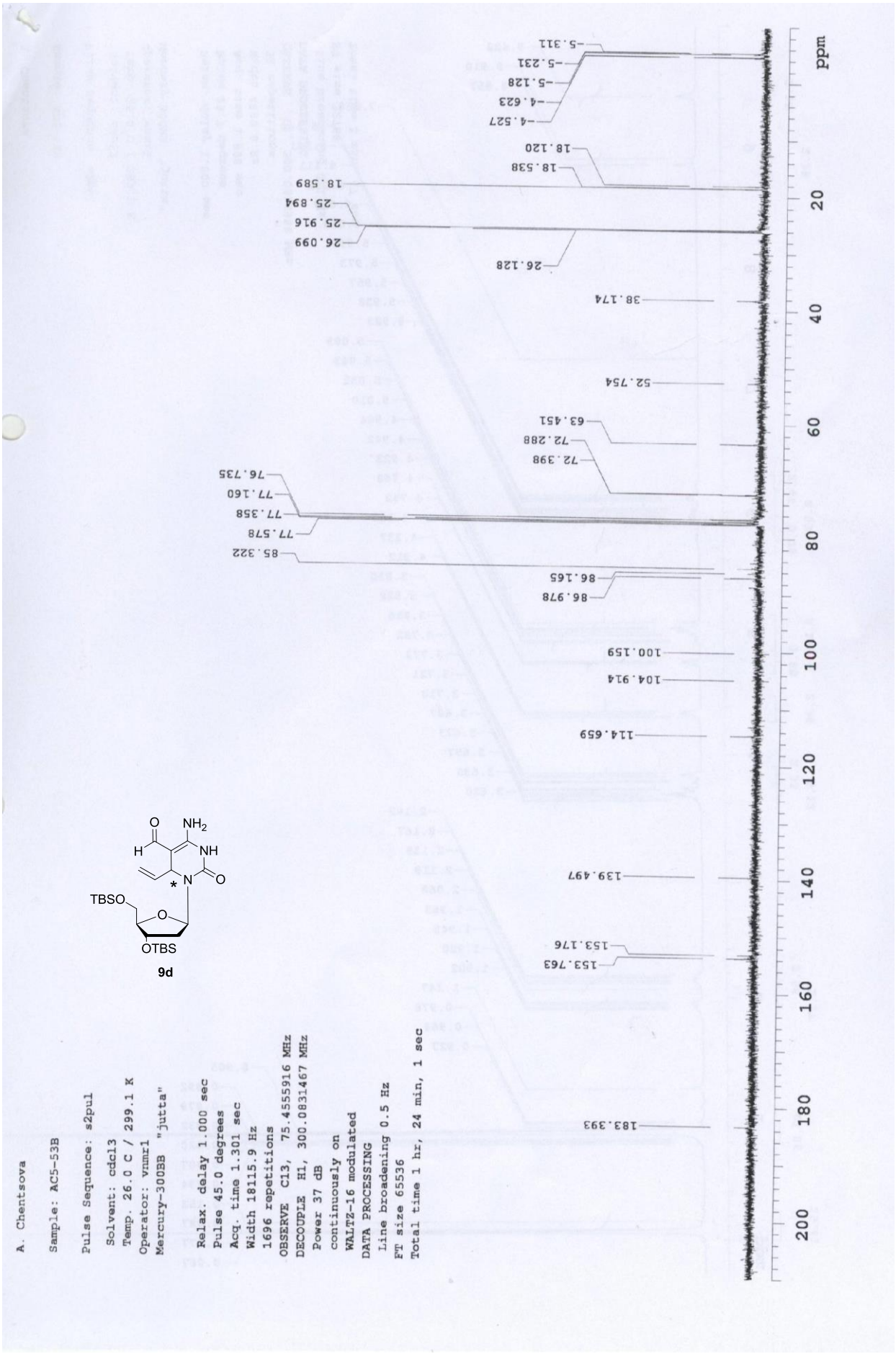
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 4800.8 Hz
16 repetitions
OBSERVE H1, 300.0816981 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 11 sec



9c


A. Chentsova
Sample: AC5-56
Pulse Sequence: s2pul
Date: Mar 14 2013
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
10000 repetitions
OBSERVE C13, 100.5794458 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 6 hr, 49 min, 3 sec
9c
-5.334
-5.320
-5.239
-5.129
-4.682
-4.572
-4.492
18.096
18.118
18.507
18.617
25.887
26.063
26.151
37.980
38.375
40.977
43.117
63.323
63.931
72.184
72.939
76.845
77.160
77.365
77.475
83.008
83.243
84.181
85.698
86.438
87.318
88.842
89.385
122.570
122.717
128.279
128.338
128.367
128.528
131.753
131.856
152.538
153.256
153.630
153.821
182.748
182.997
0 ppm
20
40
60
80
100
120
140
160
180
200


A. Chantsova
Sample: AC5-53B
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0816988 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
ppm
TBSO
OTBS
9d


A. Chentsova
Sample: AC5-53B
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
1696 repetitions
OBSERVE C13, 75.4555916 MHz
DECOUPLE H1, 300.0831467 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 24 min, 1 sec
-5.311
-5.231
-5.128
-4.623
-4.527
18.120
18.538
18.589
25.894
25.916
26.099
26.128
38.174
52.754
63.451
72.288
72.398
76.735
77.160
77.358
77.578
85.322
86.165
86.978
100.159
104.914
114.659
139.497
153.176
153.763
183.393
ppm
200
180
160
140
120
100
80
60
40
20
O
NH2
H
NH
N
O
*
TBSO
O
OTBS
9d