Supporting Information

The Hünlich Base – (Re)Discovery, Synthesis and Structure Elucidation after a Century

Stephan Rigol,[†] Lothar Beyer,[‡] Lothar Hennig,[†] Joachim Sieler,[‡] and Athanassios Giannis[*,†]

† Institut für Organische Chemie, Fakultät für Chemie und Mineralogie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany
‡ Institut für Anorganische Chemie, Fakultät für Chemie und Mineralogie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany
*e-mail: giannis@uni-leipzig.de (A.Giannis)

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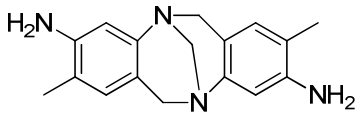
Experimental Section

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). Acetone, acetonitrile and pyridine were purchased from Acros or Aldrich (anhydrous over molecular sieves). All other chemicals were purchased from ABCR, Acros, Aldrich, Alfa Aesar, Fluorochem, TCI Europe and VWR at 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 an UV lamp and/or with ceric ammonium molybdate, potassium permanganate or vanillin 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 as preparative TLC on Merck silica gel 60 F_{254} glass plates with concentration zone. 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), and a Bruker Avance-700 (operating at 700 MHz for ^{1}H, 175 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). 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 br = 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.

2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine-3,9-diamine (Hünlich's base)



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Formaldehyde (37 % in H_2O, 10.9 ml, 11.9 g, 146 mmol, 1.00 eq.) was added dropwise to a solution of 2,4-diaminotoluene (36.6 g, 300 mmol, 2.05 eq.) in aqueous sulfuric acid (5 %, 1000 ml). After the reaction was stirred for 36 h ammonia (25 %, 300 ml) was added and the precipitated crude product was separated by filtration. Purification was achieved by dissolving the raw material in hot methanol (150 ml) and slow addition of hot water (30-45 ml). Filtration yielded Hünlich's base (13.5 g, 48.3 mmol, 33 %) as light brown solid.

R_f: 0.43 (dichloromethane/methanol = 10:1 *v/v*)

^{1}H-NMR: (400 MHz, $CDCl_3$) δ [ppm] 2.04 (s, 6H, 2 × -C**H_3**), 3.48 (br, 4H, 2 × -N**H_2**), 4.02 (d, $^2J_{H,H}$ = 16.0 Hz, 2H, **H-6a**, **H-12a**), 4.25 (s, 2H, -N-C**H_2**-N-), 4.55 (d, $^2J_{H,H}$ = 16.0 Hz, 2H, **H-6b**, **H-12b**), 6.43 (s, 2H, **H-4**, **H-10**), 6.55 (s, 2H, **H-1**, **H-7**).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ [ppm] 17.1 (2 × -**C**H_3), 58.5 (**C-6**, **C-12**), 67.4 (**C-13**), 110.8 (**C-4**, **C-10**), 118.0 (**C-6a**, **C-12a**), 119.4 (**C-2**, **C-8**), 128.6 (**C-1**, **C-7**), 143.9 (**C-3**, **C-9**), 147.4 (**C-4a**, **C-10a**).

HR-MS: (ESI positive, CH_3OH) calc. for $[C_{17}H_{21}N_4]^+$: $[M+H]^+$ 281.17607, found 281.17590.

UV: (CH_3OH) λ (lgε) = 221 nm (4.581), 301 (3.904).

IR: (KBr) ν_{max} = 3409 cm^{-1}, 3347, 1630, 1574, 1500, 1180, 1087, 916, 875.

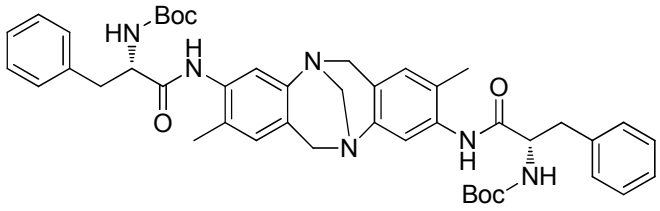
Optical rotation: enantiomer 1: $[\alpha]_D^{22}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +58.0$ (c = 1.0, CH_3OH)
enantiomer 2: $[\alpha]_D^{22}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = -63.0$ (c = 0.33, CH_3OH)

Melting point: 225-230 °C

Resolution of both enantiomers was achieved via the amino acid derivatives (**7a**, **7a'** or **8a**, **8a'** respectively) by basic hydrolysis. Example for hydrolysis of **8a** to form enantiomer 1 of Hünlich's base (**3a**):

To a solution of compound **8a** (100 mg, 0.147 mmol) in THF (3.0 ml) was added saturated aqueous KOH (3.0 ml) solution. The reaction mixture was stirred at 120 °C in a sealed Pyrex tube for 48 h. After cooling to rt and solvent removal the crude product was purified by column chromatography to furnish enantiomer 1 of Hünlich's base (39.2 mg, 0.140 mmol, 95 %).

di-*tert*-butyl [(5,13-dimethyl-1,9-diazatetracyclo[7.7.1.0^{2,7}.0^{10,15}]heptadeca-2,4,6,10,12,14-hexaene-4,12-diyl)bis{imino[(2*S*)-1-oxo-3-phenylpropane-1,2-diyl]}]biscarbamate



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Hünlich's base (841 mg, 3.00 mmol, 1 eq.), *N*-[(1,1-dimethylethoxy)carbonyl]-L-phenylalanine (1.59 g, 6.00 mmol, 2 eq.) and 2-ethoxy-2*H*-quinoline-1-carboxylic acid ethyl ester (1.85 g, 7.50 mmol, 2.5 eq.) were dissolved in chloroform (150 ml) before triethylamine (1.05 ml, 759 mg, 7.50 mmol, 2.5 eq.) was added and the mixture was heated to reflux for twelve hours. Then, the solvent was removed under reduced pressure und the residue was taken up in ethyl acetate (60 ml), washed twice with water (60 ml) and dried over Na_2SO_4 before all volatiles were removed under reduced pressure. Purification was achieved by column chromatography to yield the titled compound (1.58 g, 2.04 mmol, 68 %) as white solid. Separation of diastereomers was accomplished by HPLC (Nucleosil 50-7, chloroform/methanol 99:1 → 9:1).

diastereomer 1:

R_f: 0.37 (dichloromethane/methanol = 10:1 *v/v*)

^{1}H-NMR: (300 MHz, $CDCl_3$) δ [ppm] 1.42 (s, 18H, 2 × -C(C**H$_3$**)$_3$), 1.89 (s, 6H, 2 × C**H$_3$**), 3.14-3.17 (m, 4H, 2 × Ph-C**H$_2$**-), 4.11 (d, $^2J_{H,H}$ = 16.2 Hz, 2H, **H-8a**, **H-16a**), 4.25 (s, 2H, -N-C**H$_2$**-N-), 4.44 (dd, $^3J_{H,H}$ = 14.7, 7.2 Hz, 2H, 2 × -C**H**-NH-), 4.57 (d, $^2J_{H,H}$ = 16.5 Hz, 2H, **H-8b**, **H-16b**), 5.07 (br, 2H, 2 × -O-CO-N**H**), 6.64 (s, 2H, **H-6**, **H-14**), 7.22-7.34 (m, 10H, 10 × **H$_{Ph}$**), 7.44 (br, 2H, 2 × CO-N**H**), 7.65 (s, 2H, **H-3**, **H-11**).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ [ppm] 17.0 (2 × -**C**H$_3$), 28.4 (2 × -C(**C**H$_3$)$_3$), 38.1 (2 × Ph-**C**H$_2$-), 57.0 (2 × -**C**H-NH-), 58.4 (**C-8**, **C-16**), 67.1 (-N-**C**H$_2$-N-), 80.7 (2 × -**C**(CH$_3$)$_3$), 118.5 (**C-3**, **C-11**), 124.5 (**C-5**, **C-7**, **C-13, C-15**), 127.3 (**C$_{Ph}$-4**, **C$_{Ph}$-4'**), 128.6 (**C-6**, **C-14**), 129.0 (**C$_{Ph}$-3**, **C$_{Ph}$-3'**, **C$_{Ph}$-3''**, **C$_{Ph}$-3'''**), 129.4 (**C$_{Ph}$-2**, **C$_{Ph}$-2'**, **C$_{Ph}$-2''**, **C$_{Ph}$-2'''**), 134.5 (**C-4**, **C-12**), 136.8 (**C$_{Ph}$-1**, **C$_{Ph}$-1'**), 146.6 (**C-2**, **C-10**), 155.8 (2 × NH-**C**O-O), 169.4 (2 × NH-**C**O).

HR-MS: (ESI positive, CH_3OH) calc. for $[C_{45}H_{55}N_6O_6]^+$: $[M+H]^+$ 775.41780, found 775.41840, calc. for $[C_{45}H_{54}N_6O_6Na]^+$: $[M+Na]^+$ 797.39970, found 797.39998, calc. for $[C_{45}H_{54}N_6O_6K]^+$: $[M+K]^+$ 813.37400, found 813.37460.

UV: (CH_2Cl_2) λ (lgε) = 231 nm (4.458), 243 (4.439), 298 (3.735).

IR: (KBr) ν_{max} = 3422 cm^{-1}, 2976, 2928, 1692, 1522, 1497, 1454, 1367, 1168, 921, 701.

Optical rotation: $[\alpha]_D^{22}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = +79.9$ (c = 1.0, $CHCl_3$)

Melting point: 205-206 °C

diastereomer 2:

R_f: 0.36 (dichloromethane/methanol = 10:1 *v/v*)

^{1}H-NMR: (400 MHz, $CDCl_3$) δ [ppm] 1.43 (s, 18H, 2 × -C(C**H$_3$**)$_3$), 1.88 (s, 6H, 2 × C**H$_3$**), 3.09-3.23 (m, 4H, 2 × Ph-C**H$_2$**-), 4.11 (d, $^2J_{H,H}$ = 16.8 Hz, 2H, **H-8a**, **H-16a**), 4.25 (s, 2H, -N-C**H$_2$**-N-), 4.45 (dd, $^3J_{H,H}$ = 13.8, 7.0 Hz, 2H, 2 × -C**H**-NH-), 4.57 (d, $^2J_{H,H}$ = 16.4 Hz, 2H, **H-8b**, **H-16b**), 5.08 (br, 2H, 2 × -O-CO-N**H**), 6.64 (s, 2H, **H-6**, **H-14**), 7.25-7.34 (m, 10H, 10 × **H$_{Ph}$**), 7.47 (br, 2H, 2 × CO-N**H**), 7.65 (s, 2H, **H-3**, **H-11**).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ [ppm] 16.9 (2 × -**C**H$_3$), 28.4 (2 × -C(**C**H$_3$)$_3$), 38.1 (2 × Ph-**C**H$_2$-), 56.8 (2 × -**C**H-NH-), 58.4 (**C-8**, **C-16**), 67.1 (-N-**C**H$_2$-N-), 80.8 (2 × -**C**(CH$_3$)$_3$), 118.7 (**C-3**, **C-11**), 124.6 (**C-5**, **C-7**, **C-13, C-15**), 127.3 (**C$_{Ph}$-4**, **C$_{Ph}$-4'**), 128.6 (**C-6**, **C-14**), 129.1 (**C$_{Ph}$-3**, **C$_{Ph}$-3'**, **C$_{Ph}$-3''**, **C$_{Ph}$-3'''**), 129.5 (**C$_{Ph}$-2**, **C$_{Ph}$-2'**, **C$_{Ph}$-2''**, **C$_{Ph}$-2'''**), 134.4 (**C-4**, **C-12**), 136.7 (**C$_{Ph}$-1**, **C$_{Ph}$-1'**), 146.4 (**C-2**, **C-10**), 155.8 (2 × NH-**C**O-O), 169.4 (2 × NH-**C**O).

HR-MS: (ESI positive, CH_3OH) calc. for $[C_{45}H_{55}N_6O_6]^+$: $[M+H]^+$ 775.41780, found 775.41840, calc. for $[C_{45}H_{54}N_6O_6Na]^+$: $[M+Na]^+$ 797.39970, found 797.39998, calc. for $[C_{45}H_{54}N_6O_6K]^+$: $[M+K]^+$ 813.37400, found 813.37460.

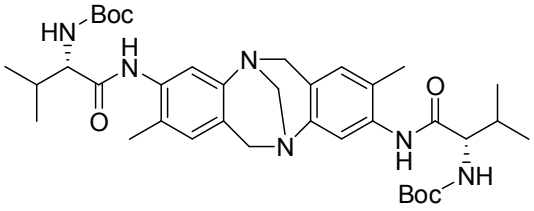
UV: (CH_2Cl_2) λ (lgε) = 231 nm (4.565), 245 (4.542), 301 (3.746).

IR: (KBr) ν_{max} = 3419 cm^{-1}, 2977, 2930, 1691, 1519, 1496, 1454, 1367, 1168, 921, 700.

Optical rotation: $[\alpha]_D^{22}\left(\deg cm^3\ g^{-1}\ dm^{-1}\right) = -50.1$ (c = 0.50, $CHCl_3$)

Melting point: 152-153 °C

di-*tert*-butyl [(5,13-dimethyl-1,9-diazatetracyclo[7.7.1.0^{2,7}.0^{10,15}]heptadeca-2,4,6,10,12,14-hexaene-4,12-diyl)bis{imino[(2*S*)-3-methyl-1-oxobutane-1,2-diyl]}]biscarbamate



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Hünlich's base (841 mg, 3.00 mmol, 1 eq.), *N*-[(1,1-dimethylethoxy)carbonyl]-L-valine (1.39 g, 6.00 mmol, 2 eq.) and 2-ethoxy-2*H*-quinoline-1-carboxylic acid ethyl ester (1.85 g, 7.50 mmol, 2.5 eq.) were dissolved in chloroform (150 ml) before triethylamine (1.05 ml, 759 mg, 7.50 mmol, 2.5 eq.) was added and the mixture was heated to reflux for twelve hours. Then, the solvent was removed under reduced pressure und the residue was taken up in ethyl acetate (60 ml), washed twice with water (60 ml) and dried over Na_2SO_4 before all volatiles were removed under reduced pressure. Purification was achieved by column chromatography to yield the titled compound (1.51 g, 2.22 mmol, 74 %) as white solid. Separation of diastereomers was accomplished by HPLC (Nucleosil 50-7, chloroform/methanol 99:1 → 9:1).

diastereomer 1:

R_f: 0.33 (chloroform/methanol = 50:1 *v/v*)

^{1}H-NMR: (300 MHz, $CDCl_3$) δ [ppm] 0.98 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, 2 × -CH-C**H$_3$**), 1.03 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, 2 × -CH-C**H$_3$**), 1.43 (s, 18H, 2 × -C(C**H$_3$**)$_3$), 2.09 (s, 6H, 2 × C**H$_3$**), 2.21-2.31 (m, 2H, 2 × -C**H**$(CH_3)_2$), 4.00 (dd, $^3J_{H,H}$ = 8.7, 6.6 Hz, 2H, 2 × -C**H**-NH-), 4.11 (d, $^2J_{H,H}$ = 16.2 Hz, 2H, **H-8a**, **H-16a**), 4.23 (s, 2H, -N-C**H$_2$**-N-), 4.54 (d, $^2J_{H,H}$ = 16.5 Hz, 2H, **H-8b**, **H-16b**), 5.12 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, 2 × -O-CO-N**H**), 6.65 (s, 2H, **H-6**, **H-14**), 7.66 (s, 2H, **H-3**, **H-11**), 7.72 (s, 2H, 2 × CO-N**H**).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ [ppm] 17.3 (2 × -**C**H_3), 18.1 (2 × -CH-**C**H_3), 19.6 (2 × -CH-**C**H_3), 28.5 (2 × -C(**C**H_3)$_3$), 30.3 (2 × -**C**H$(CH_3)_2$), 58.4 (**C-8**, **C-16**), 61.1 (2 × -**C**H-NH-), 67.1 (-N-**C**H_2-N-), 80.5 (2 × -**C**$(CH_3)_3$), 119.0 (**C-3**, **C-11**), 124.6 (**C-7**, **C-15**), 124.9 (**C-5**, **C-13**), 128.7 (**C-6**, **C-14**), 134.6 (**C-4**, **C-12**), 146.3 (**C-2**, **C-10**), 156.3 (2 × NH-**C**O-O), 170.1 (2 × NH-**C**O).

HR-MS: (ESI positive, CH_3OH) calc. for $[C_{37}H_{55}N_6O_6]^+$: $[M+H]^+$ 679.41776, found 679.41805, calc. for $[C_{37}H_{54}N_6O_6Na]^+$: $[M+Na]^+$ 701.39970, found 701.40023.

UV: (CH_2Cl_2) λ (lgε) = 229 nm (4.330), 299 (3.480).

IR: (KBr) ν_{max} = 3435 cm^{-1}, 2969, 2931, 1688, 1623, 1518, 1498, 1367, 1170, 920.

Optical rotation: $[\alpha]_D^{21}\left(\deg cm^3\, g^{-1}\, dm^{-1}\right) = +83.6$ (c = 1.0, $CHCl_3$)

Melting point: 255-256 °C

diastereomer 2:

R_f: 0.30 (chloroform/methanol = 50:1 *v/v*)

^{1}H-NMR: (400 MHz, $CDCl_3$) δ [ppm] 0.98 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, 2 × -CH-C**H$_3$**), 1.03 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, 2 × -CH-C**H$_3$**), 1.45 (s, 18H, 2 × -C(C**H$_3$**)$_3$), 2.10 (s, 6H, 2 × C**H$_3$**), 2.27-2.32 (m, 2H, 2 × -C**H**$(CH_3)_2$), 3.98 (dd, $^3J_{H,H}$ = 8.0, 6.6 Hz, 2H, 2 × -C**H**-NH-), 4.13 (d, $^2J_{H,H}$ = 16.4 Hz, 2H, **H-8a**, **H-16a**), 4.24 (s, 2H, -N-C**H$_2$**-N-), 4.55 (d, $^2J_{H,H}$ = 16.8 Hz, 2H, **H-8b**, **H-16b**), 5.09 (br, 2H, 2 × -O-CO-N**H**), 6.68 (s, 2H, **H-6**, **H-14**), 7.66 (s, 2H, **H-3**, **H-11**), 7.67 (s, 2H, 2 × CO-N**H**).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ [ppm] 17.3 (2 × -**C**H_3), 18.0 (2 × -CH-**C**H_3), 19.7 (2 × -CH-**C**H_3), 28.4 (2 × -C(**C**H_3)$_3$), 30.2 (-**C**H$(CH_3)_2$), 58.4 (**C-8**, **C-16**), 61.1 (2 × -**C**H-NH-), 67.1 (-N-**C**H_2-N-), 80.5 (2 × -**C**$(CH_3)_3$), 119.0 (**C-3**, **C-11**), 124.5 (**C-7**, **C-15**), 125.0 (**C-5**, **C-13**), 128.7 (**C-6**, **C-14**), 134.5 (**C-4**, **C-12**), 146.3 (**C-2**, **C-10**), 156.3 (2 × NH-**C**O-O), 169.9 (2 × NH-**C**O).

HR-MS: (ESI positive, CH_3OH) calc. for $[C_{37}H_{55}N_6O_6]^+$: $[M+H]^+$ 679.41776, found 679.41805, calc. for $[C_{37}H_{54}N_6O_6Na]^+$: $[M+Na]^+$ 701.39970, found 701.40023.

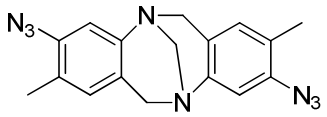
UV: (CH_2Cl_2) λ (lgε) = 231 nm (4.998), 298 (4.191).

IR: (KBr) ν_{max} = 3429 cm^{-1}, 2969, 2931, 1689, 1497, 1367, 1170, 921.

Optical rotation: $[\alpha]_D^{22}\left(\text{deg cm}^3\ \text{g}^{-1}\ \text{dm}^{-1}\right) = -151.7$ (c = 1.0, $CHCl_3$)

Melting point: 182-184 °C

3,9-diazido-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine



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Method A:

To an ice-cooled suspension of Hünlich's base (6.00 g, 21.4 mmol, 1 eq.) in water (15.0 ml) was subsequently added concentrated sulfuric acid (4.20 ml, 7.68 g, 78.6 mmol, 3.67 eq.), $NaNO_3$ (1.62 g, 19.1 mmol, 0.9 eq.) in water (9.60 ml), NaN_3 (1.42 g, 21.8 mmol, 1.02 eq.) in water (15.0 ml) and dichloromethane (36 ml). Then, the mixture was stirred one hour at 0 °C and one hour at rt. After separation of the phases, the aqueous one was extracted twice with dichloromethane (120 ml). The combined organic layers were dried over Na_2SO_4 and after solvent removal the product was purified by recrystallization from dichloromethane to furnish the desired compound (2.40 g, 7.20 mmol, 34 %) as yellow solid.

Method B:

To a solution of Hünlich's base (50.0 mg, 0.178 mmol, 1.0 eq.), potassium carbonate (83.8 mg, 0.606 mmol, 3.4 eq.) and copper sulfate (0.28 µg, 1.78 µmol, 0.01 eq.) in methanol (900 µl) was added freshly prepared 1*H*-imidazole-1-sulfonyl azide hydrochloride (89.7 mg, 0.428 mmol, 2.4 eq.) and the resulting mixture was stirred at rt for 18 h. After addition of water (1.0 ml) and slight acidification with hydrochloric acid the mixture was extracted with ethyl acetate (3 × 3 ml). The combined organic layers were dried over $MgSO_4$ and after solvent removal the product was purified by column chromatography to furnish the desired compound (33.2 mg, 0.100 mmol, 56 %) as faintly yellow solid.

R_f: 0.24 (*n*-hexane/ethyl acetate = 5:1 *v/v*)

^{1}H-NMR: (300 MHz, $CDCl_3$) δ [ppm] 2.07 (s, 6H, 2 × -C**H$_3$**), 4.11 (d, $^2J_{H,H}$ = 16.5 Hz, 2H, **H-6a**, **H-12a**), 4.28 (s, 2H, -N-C**H$_2$**-N-), 4.63 (d, $^2J_{H,H}$ = 16.5 Hz, 2H, **H-6b**, **H-12b**), 6.70 (s, 2H, **H-1**, **H-7**), 6.87 (s, 2H, **H-4**, **H-10**).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ [ppm] 16.8 (2 × -**C**H$_3$), 58.5 (**C-6**, **C-12**), 67.0 (**C-13**), 114.2 (**C-4**, **C-10**), 124.0 (**C-6a**, **C-12a**), 125.9 (**C-2**, **C-8**), 129.4 (**C-1**, **C-7**), 137.7 (**C-3**, **C-9**), 146.8 (**C-4a**, **C-10a**).

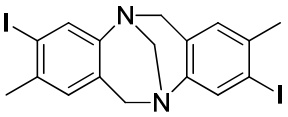
HR-MS: (ESI positive, CH_3OH) calc. for $[C_{17}H_{17}N_8]^+$: $[M+H]^+$ 333.15707, found 333.15677.

UV: ($CHCl_3$) λ (lgε) = 249 nm (4.487), 309 (3.984).

IR: (KBr) ν_{max} = 2951 cm^{-1}, 2902, 2108, 1616, 1572, 1490, 1306, 1290, 1080, 1030, 920.

Melting point: 182-185 °C

3,9-diiodo-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine



10

To an ice-cooled suspension of Hünlich's base (6.00 g, 21.4 mmol, 1 eq.) in water (15.0 ml) was subsequently added concentrated sulfuric acid (4.20 ml, 7.68 g, 78.6 mmol, 3.67 eq.), $NaNO_3$ (1.62 g, 19.1 mmol, 0.9 eq.) in water (9.60 ml), NaI (3.27 g, 21.8 mmol, 1.02 eq.) in water (15.0 ml) and dichloromethane (36.0 ml). Then, the mixture was stirred one hour at 0 °C and one hour at rt. After separation of the phases, the aqueous one was extracted twice with dichloromethane (120 ml). The combined organic layers were dried over Na_2SO_4 and after solvent removal the product was purified by column chromatography on silica to furnish the desired compound (5.16 g, 10.3 mmol, 48 %) as brownish solid.

R_f: 0.32 (*n*-hexane/ethyl acetate = 5:1 *v/v*)

^{1}H-NMR: (400 MHz, $CDCl_3$) δ [ppm] 2.29 (s, 6H, 2 × -C**H$_3$**), 4.05 (d, $^2J_{H,H}$ = 17.0 Hz, 2H, **H-6a**, **H-12a**), 4.21 (s, 2H, -N-C**H$_2$**-N-), 4.55 (d, $^2J_{H,H}$ = 17.0 Hz, 2H, **H-6b**, **H-12b**), 6.77 (s, 2H, **H-1**, **H-7**), 7.58 (s, 2H, **H-4**, **H-10**).

^{13}C-NMR: (100 MHz, $CDCl_3$) δ [ppm] 27.4 (2 × -**C**H$_3$), 58.6 (**C-6**, **C-12**), 66.9 (**C-13**), 98.7 (**C-3**, **C-9**), 127.74 (**C-4**, **C-10**), 127.77 (**C-6a**, **C-12a**), 135.2 (**C-1**, **C-7**), 137.1 (**C-2**, **C-8**), 146.9 (**C-4a**, **C-10a**).

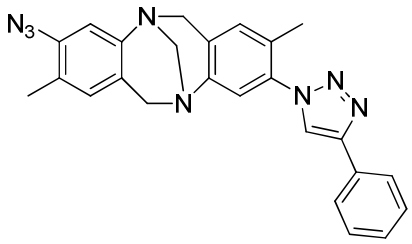
HR-MS: (ESI positive, CH_3OH) calc. for $[C_{17}H_{17}I_2N_2]^+$: $[M+H]^+$ 502.94756, found 502.94722.

UV: ($CHCl_3$) λ (lgε) = 241 nm (4.319), 298 (3.665).

IR: (KBr) ν_{max} = 3436 cm^{-1}, 2941, 2911, 1599, 1471, 1434, 1200, 1066, 955, 875.

Melting point: 205-210 °C

3-azido-2,8-dimethyl-9-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine



11

Triethylamine (51.5 µl, 38.9 mg, 0.301 mmol, 2.0 eq.) and phenylacetylene (33.0 µl, 30.7 mg, 0.301 mmol, 2.0 eq.) was subsequently added to a suspension of 3,9-diazido-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (50.0 mg, 0.150 mmol, 1.0 eq.) and cuprous iodide (28.6 mg, 0.150 mmol, 1.0 eq.) in dichloromethane (2.5 ml). After stirring at rt for 24 h water (12.5 ml) was added. Then, the reaction mixture was extracted with 2-methoxy-2-methylpropane (3 × 10 ml) before the combined organic layers were dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Colum chromatography furnished the titled compound (26.1 mg, 0.0600 mmol, 40 %) as brown solid.

R_f: 0.24 (*n*-hexane/ethyl acetate = 2:1 *v/v*)

^{1}H-NMR: (300 MHz, $CDCl_3$) δ [ppm] 2.09 (s, 3H, C-2-C**H_3**), 2.14 (s, 3H, C-8-C**H_3**), 4.12 (d, $^2J_{H,H}$ = 16.8 Hz, 1H, **H-12a**), 4.23 (d, $^2J_{H,H}$ = 16.8 Hz, 1H, **H-6a**), 4.31 (s, 2H, -N-C**H_2**-N-), 4.63 (d, $^2J_{H,H}$ = 17.1 Hz, 1H, **H-12b**), 4.71 (d, $^2J_{H,H}$ = 16.8 Hz, 1H, **H-6b**), 6.71 (s, 1H, **H-1**), 6.89 (s, 1H, **H-4**), 6.94 (s, 1H, **H-7**), 7.18 (s, 1H, **H-10**), 7.33-7.39 (m, 1H, **H_{Ph}-4**), 7.44-7.48 (m, 2H, **H_{Ph}-3, H_{Ph}-3'**), 7.88-7.91 (m, 3H, **$H_{triazole}$-5**, **H_{Ph}-2, H_{Ph}-2'**).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ [ppm] 16.8 (C-2-**C**H_3), 17.5 (C-8-**C**H_3), 58.6 (**C-12**), 58.7 (**C-6**), 67.0 (-N-**C**H_2-N-), 114.2 (**C-4**), 121.2 (**$C_{triazole}$-5**), 122.5 (**C-10**), 123.8 (**C-12a**), 126.0 (**C_{Ph}-2**, **C_{Ph}-2'**), 126.1 (**C-2**), 128.5 (**C_{Ph}-4**), 129.1 (**C_{Ph}-3**, **C_{Ph}-3'**), 129.2 (**C-6a**), 129.5 (**C-1**), 129.8 (**C-8**), 130.5 (**C-7**), 135.7 (**C-9**), 137.9 (**C-3**), 146.8 (**C-4a**), 147.0 (**C-10a**), 147.8 (**$C_{triazole}$-4**).

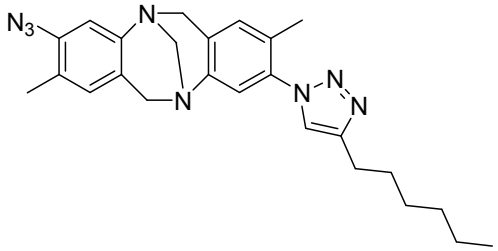
HR-MS: (ESI positive, $CDCl_3$/CH_3OH) calc. for $[C_{25}H_{22}N_8Na]^+$: $[M+Na]^+$ 457.18596, found 457.18616.

UV: ($CHCl_3$) λ (lgε) = 253 nm (4.545), 256 (4.541).

IR: (KBr) ν_{max} = 2924 cm^{-1}, 2852, 2116, 1617, 1575, 1491, 1385, 1304, 1294, 1081, 1034, 766.

Melting point: 197-202 °C

3-azido-9-(4-hexyl-1*H*-1,2,3-triazol-1-yl)-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine



12

Hünig's base (22.5 µl, 17.0 mg, 0.131 mmol, 2.0 eq.), acetic acid (7.50 µl, 7.88 mg, 0.131 mmol, 2.0 eq.), and 1-octyne (58.1 µl, 43.4 mg, 0.394 mmol, 6.0 eq.) was subsequently added to a suspension of 3,9-diazido-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b*,*f*][1,5]diazocine (21.8 mg, 0.0656 mmol, 1.0 eq.) and cuprous iodide (12.5 mg, 0.0656 mmol, 1.0 eq.) in dichloromethane (1.25 ml). After stirring at rt for 24 h water (6.0 ml) was added. Then, the reaction mixture was extracted with ethyl acetate (3 × 5 ml) before the combined organic layers were dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Colum chromatography furnished the titled compound (11.6 mg, 0.0262 mmol, 40 %) as brown solid.

R_f: 0.20 (*n*-hexane/ethyl acetate = 1:1 *v/v*)

^{1}H-NMR: (300 MHz, $CDCl_3$) δ [ppm] 0.87-0.91 (m, 3H, -C**H_3**), 1.31-1.43 (m, 6H, **H_{Hex}-3**, **H_{Hex}-3'**, **H_{Hex}-4**, **H_{Hex}-4'**, **H_{Hex}-5**, **H_{Hex}-5'**), 1.67-1.75 (m, 2H, **H_{Hex}-2**, **H_{Hex}-2'**), 2.07 (s, 3H, C-8-C**H_3**), 2.08 (s, 3H, C-2-C**H_3**), 2.79 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, **H_{Hex}-1**, **H_{Hex}-1'**), 4.11 (d, $^2J_{H,H}$ = 16.8 Hz, 1H, **H-12a**), 4.21 (d, $^2J_{H,H}$ = 17.1 Hz, 1H, **H-6a**), 4.30 (s, 2H, -N-C**H_2**-N-), 4.61 (d, $^2J_{H,H}$ = 16.5 Hz, 1H, **H-12b**), 4.70 (d, $^2J_{H,H}$ = 17.4 Hz, 1H, **H-6b**), 6.69 (s, 1H, **H-1**), 6.89 (s, 1H, **H-4**), 6.90 (s, 1H, **H-7**), 7.12 (s, 1H, **H-10**), 7.41 (s, 1H, **$H_{triazole}$-5**).

^{13}C-NMR: (75 MHz, $CDCl_3$) δ [ppm] 14.2 (-**C**H_3), 16.8 (C-2-**C**H_3), 17.4 (C-8-**C**H_3), 22.7 (**C_{Hex}-5**), 25.7 (**C_{Hex}-1**), 29.1 (**C_{Hex}-3**), 29.5 (**C_{Hex}-2**), 31.7 (**C_{Hex}-4**), 58.5 (**C-12**), 58.6 (**C-6**), 67.0 (-N-**C**H_2-N-), 114.1 (**C-4**), 122.3 (**$C_{triazole}$-5**), 122.5 (**C-10**), 123.8 (**C-12a**), 126.1 (**C-2**), 129.2 (**C-8**), 129.3 (**C-6a**), 129.5 (**C-1**), 129.7 (**C-7**), 136.0 (**C-9**), 137.8 (**C-3**), 146.6 (**C-4a**), 146.7 (**C-10a**), 148.4 (**$C_{triazole}$-4**).

HR-MS: (ESI positive, $CHCl_3/CH_3OH$) calc. for $[C_{25}H_{31}N_8]^+$: $[M+H]^+$ 443.26662, found 443.26640, calc. for $[C_{25}H_{30}N_8Na]^+$: $[M+Na]^+$ 465.24856, found 465.24833.

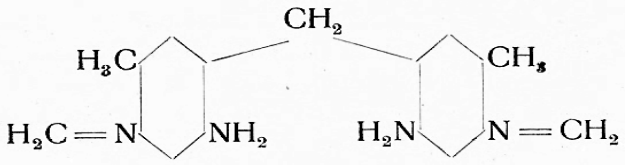
UV: (CH_2Cl_2) λ (lgε) = 231 nm (4.238), 302 (3.543).

IR: (KBr) ν_{max} = 2952 cm^{-1}, 2854, 2115, 1711, 1619, 1572, 1503, 1492, 1455, 1302, 1039, 916.

Melting point: 88-90 °C

Proposed structures for the synthesized base by Walter Hünlich:

I.



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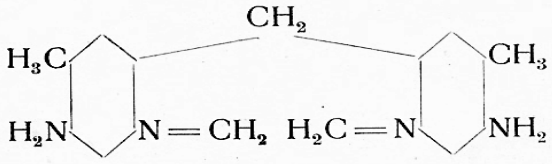

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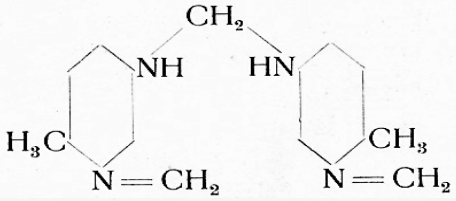
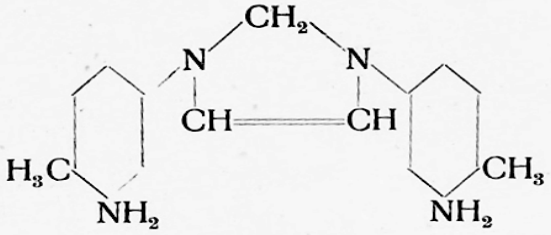
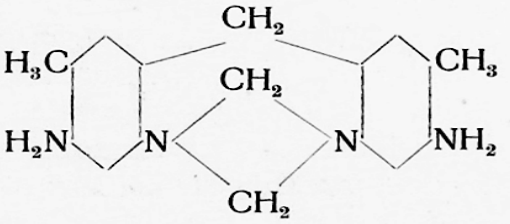


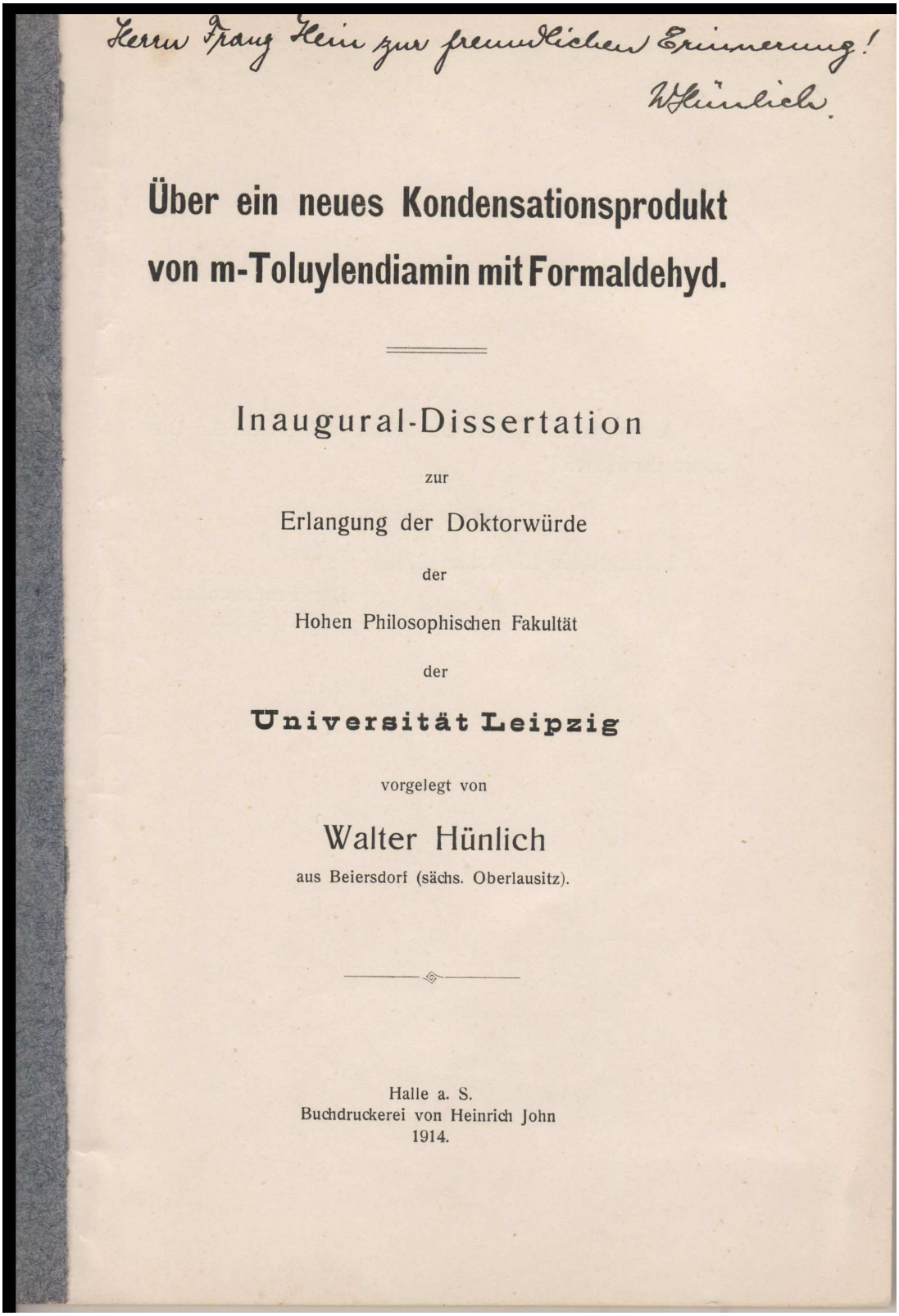
IV.



V.



Cover of W. Hünlichs Ph.D. work.



Herrn Franz Hein zur freundlichen Erinnerung!
WHünlich.

Über ein neues Kondensationsprodukt von m-Toluylendiamin mit Formaldehyd.

Inaugural-Dissertation

zur

Erlangung der Doktorwürde

der

Hohen Philosophischen Fakultät

der

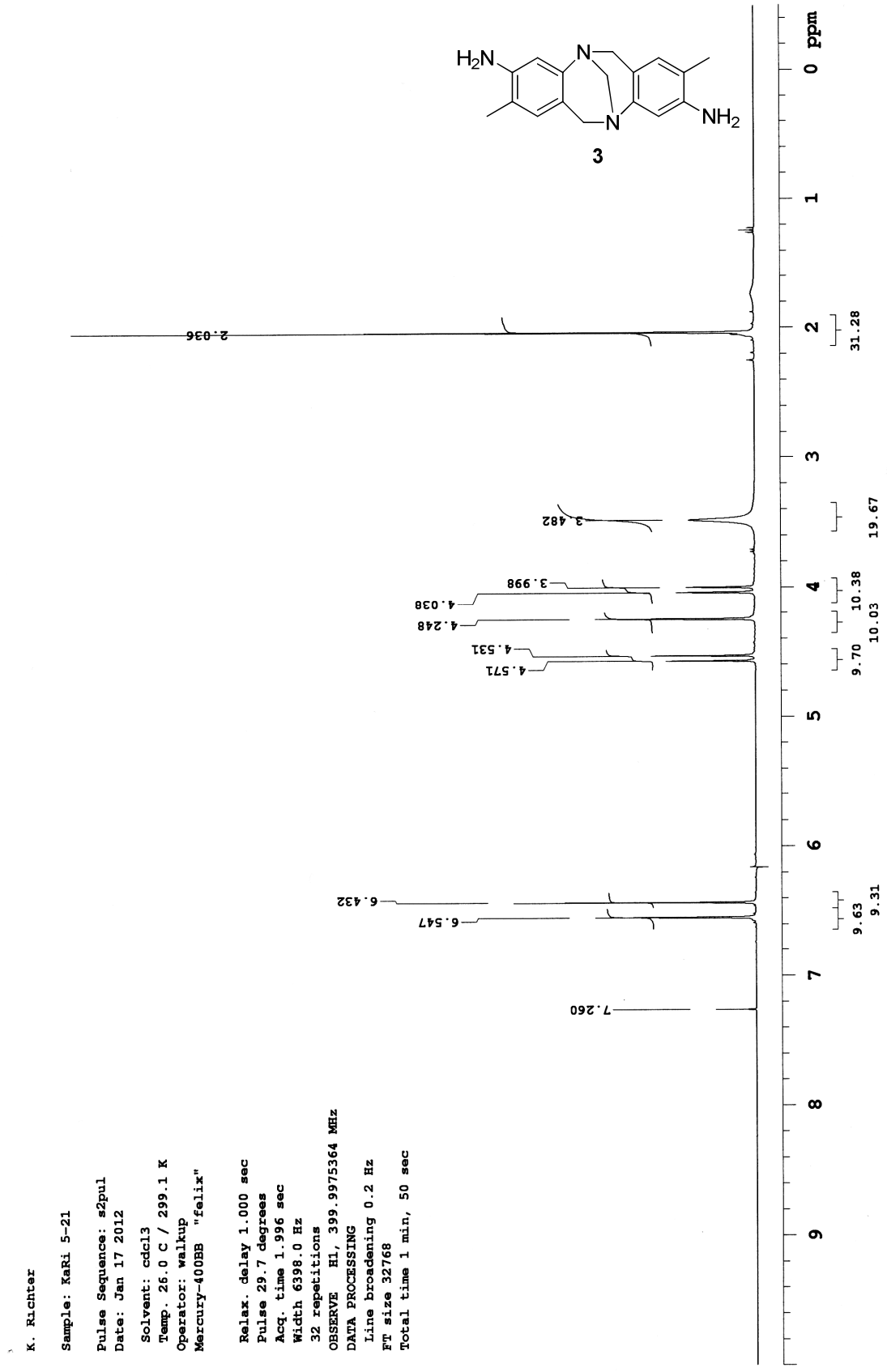
Universität Leipzig

vorgelegt von

Walter Hünlich
aus Beiersdorf (sächs. Oberlausitz).

Halle a. S.
Buchdruckerei von Heinrich John
1914.

German handwritten text at the top: „Herrn Franz Hein zur freundlichen Erinnerung! WHünlich.“


K. Richter
Sample: KaRi 5-21
Pulse Sequence: s2pul
Data: Jan 17 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
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3.482
3.998
4.038
4.248
4.531
4.571
6.432
6.547
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31.28
19.67
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10.03
9.70
9.63
9.31
0 ppm
1
2
3
4
5
6
7
8
9
H2N
NH2
N
N
3

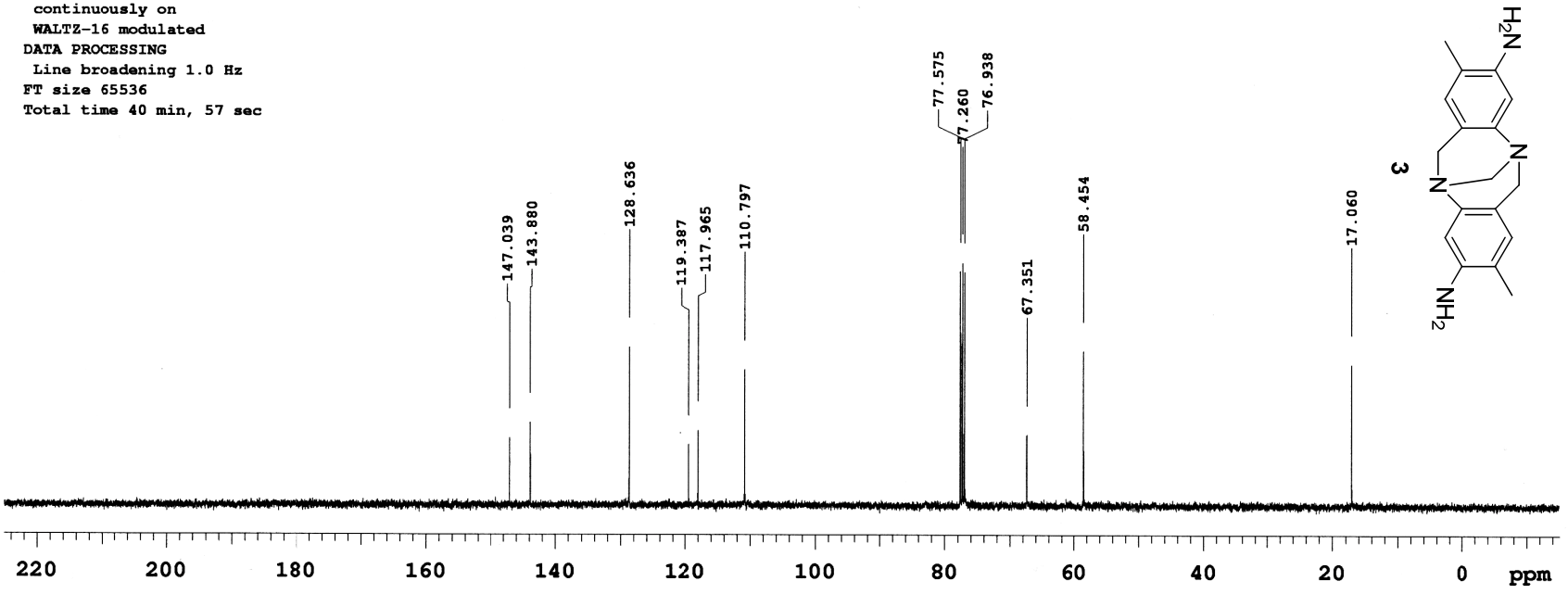
K. Richter

Sample: KaRi 5-21

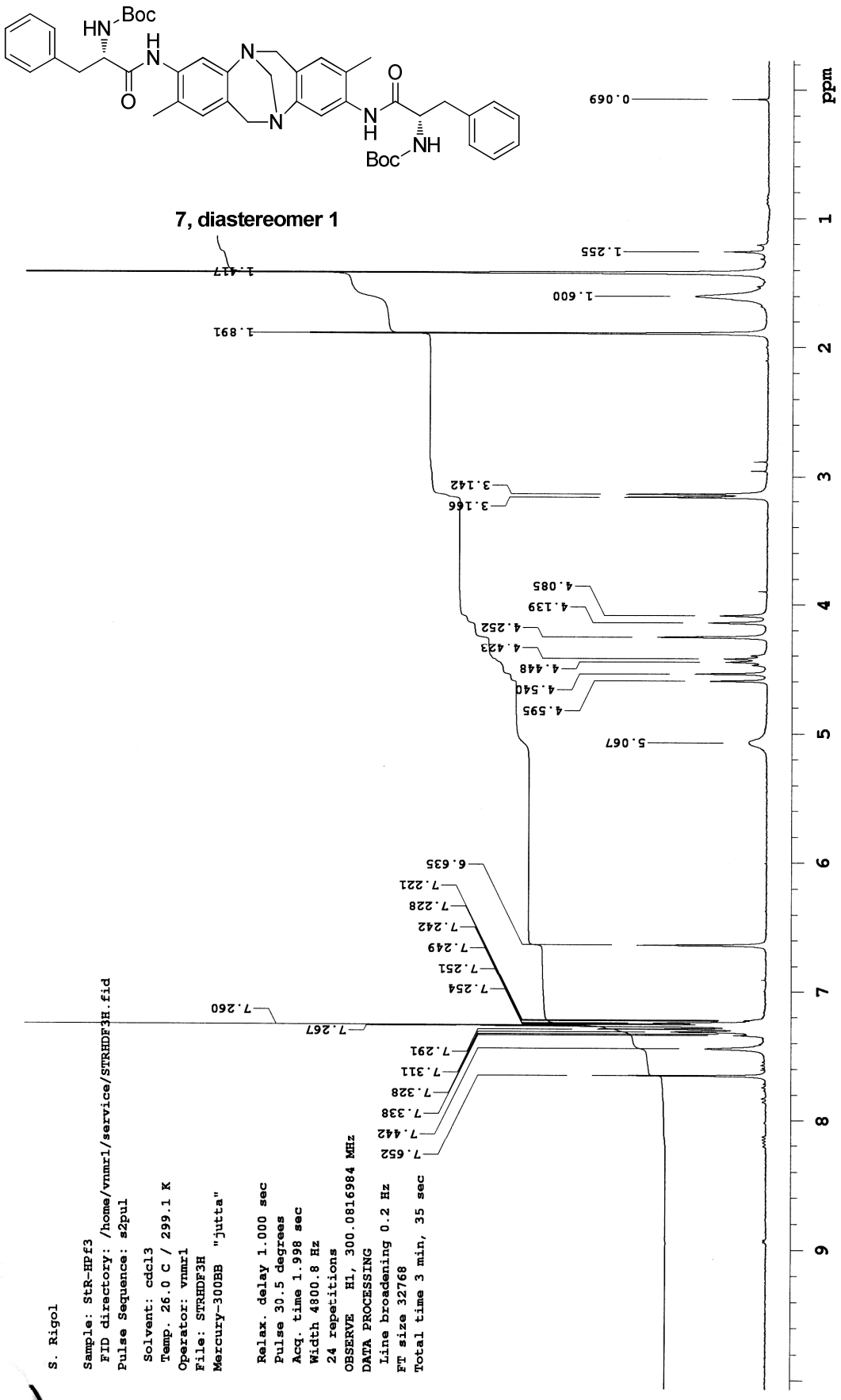
Pulse Sequence: s2pul
Date: Jan 17 2012

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 1.300 sec
Width 24154.6 Hz
128 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 40 min, 57 sec



3


7, diastereomer 1
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1.600
1.891
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4.085
4.139
4.252
4.423
4.448
4.540
4.595
5.067
6.635
7.221
7.228
7.242
7.249
7.251
7.254
7.260
7.267
7.291
7.311
7.328
7.338
7.442
7.652
ppm
S. Rigol
Sample: StR-HPf3
FID directory: /home/vnmr1/service/STRHDF3H.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
File: STRHDF3H
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 30.5 degrees
Acq. time 1.998 sec
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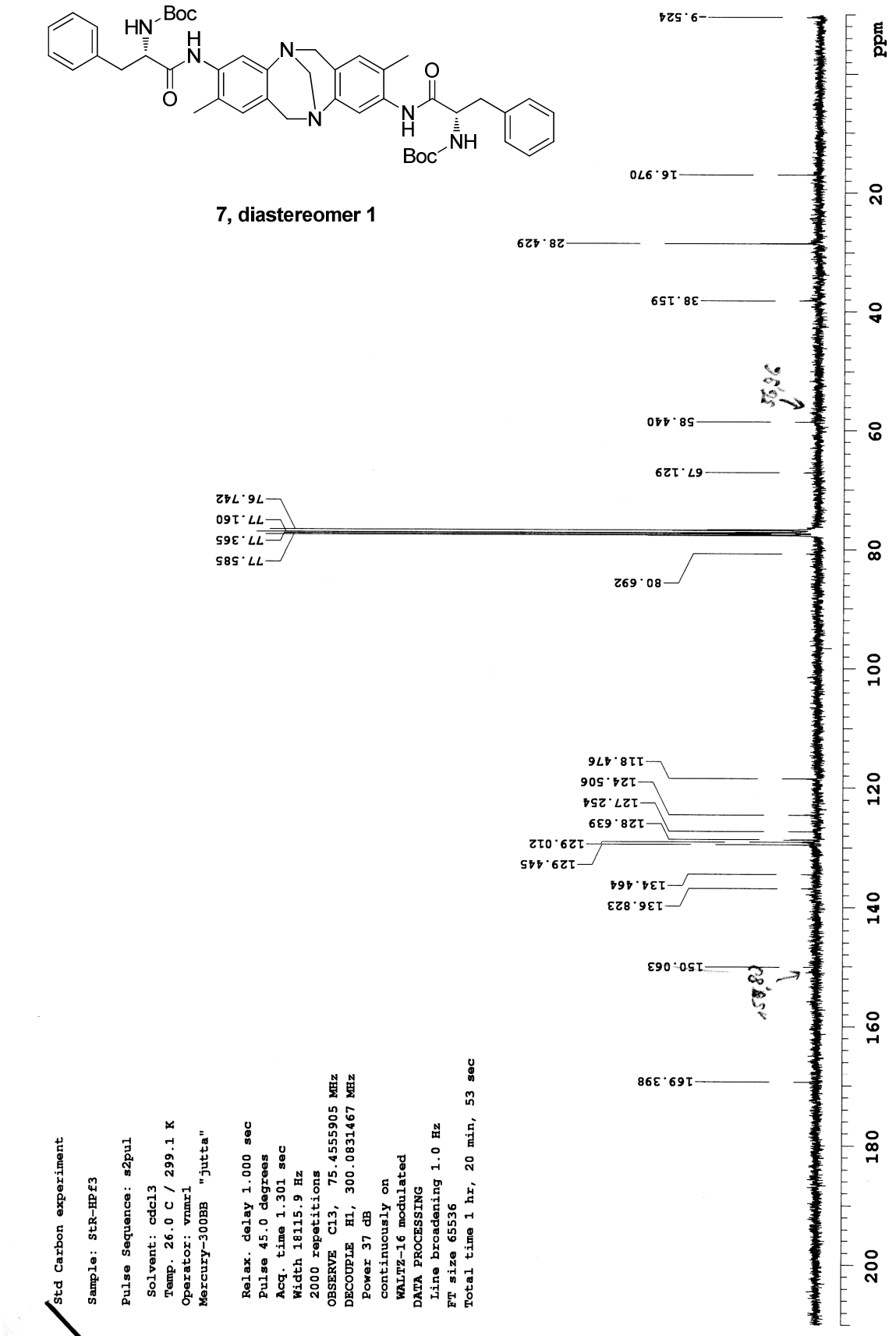
24 repetitions
OBSERVE H1, 300.0816984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec


Boc
HN
H
N
O
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N
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N
H
NH
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38.159
58.440
67.129
76.742
77.160
77.365
77.585
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118.476
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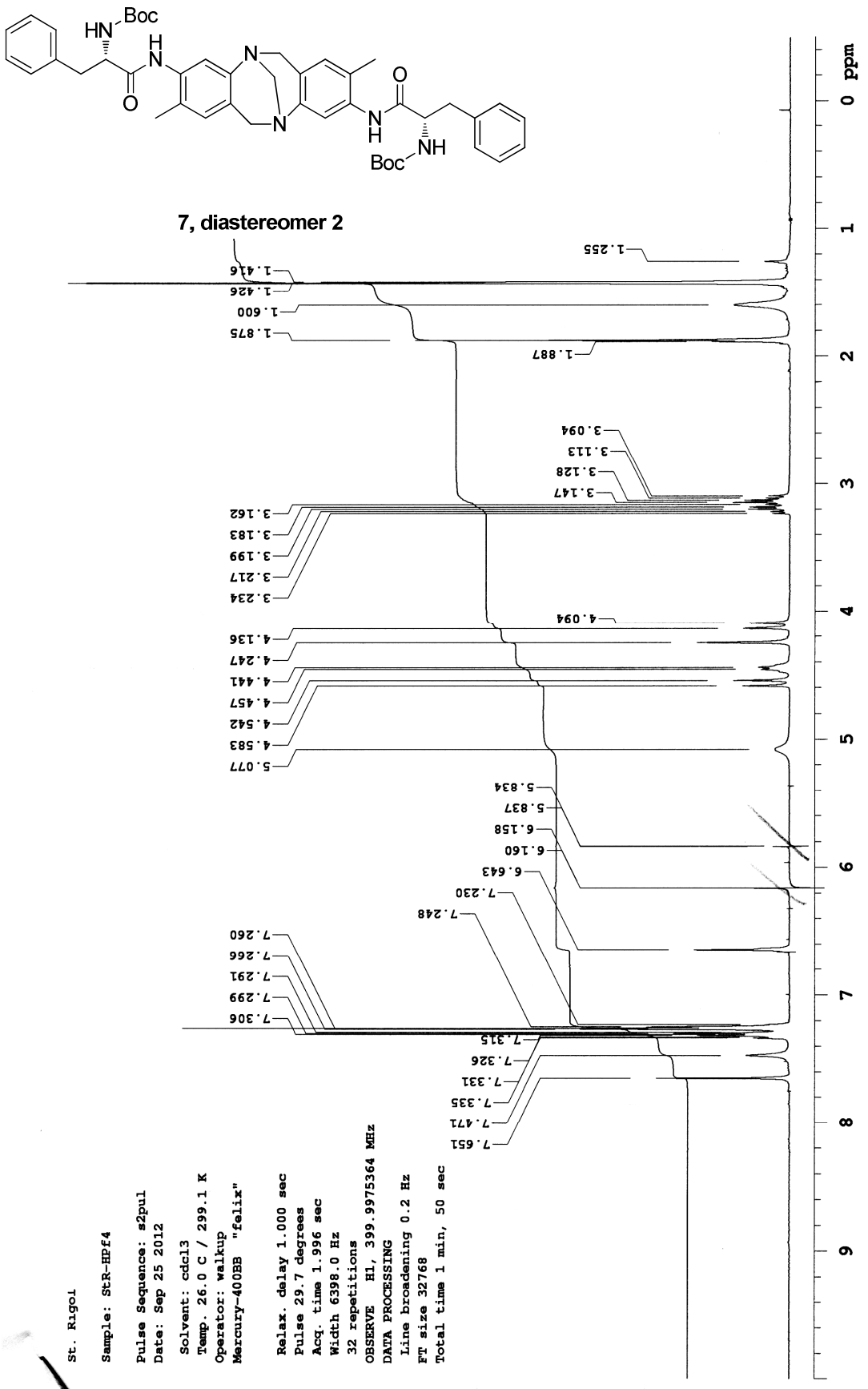
129.445
134.464
136.823
150.063
169.398
ppm
20
40
60
80
100
120
140
160
180
200
Std Carbon experiment
Sample: StR-HPf3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Mercury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
2000 repetitions
OBSERVE C13, 75.4555905 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, 20 min, 53 sec


7, diastereomer 2
St. Rigol
Sample: StR-HPf4
Pulse Sequence: s2pul
Date: Sep 25 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
1.255
1.416
1.426
1.600
1.875
1.887
3.094
3.113
3.128
3.147
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5.834
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6.158
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7.299
7.306
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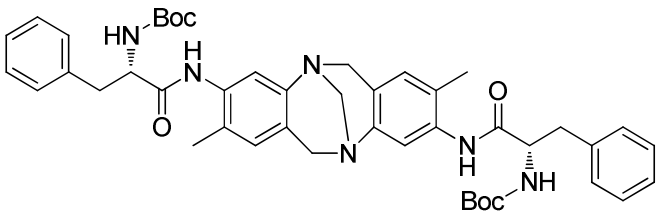
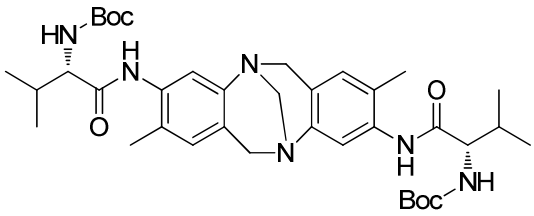
2
3
4
5
6
7
8
9



7, diastereomer 2



8, diastereomer 1

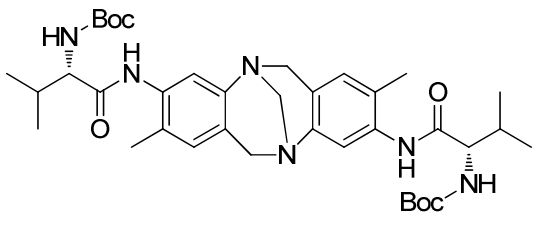
S. Rigol

Sample: StR-HVDS1

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
20 repetitions
OBSERVE H1, 300.0816988 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec



8, diastereomer 1

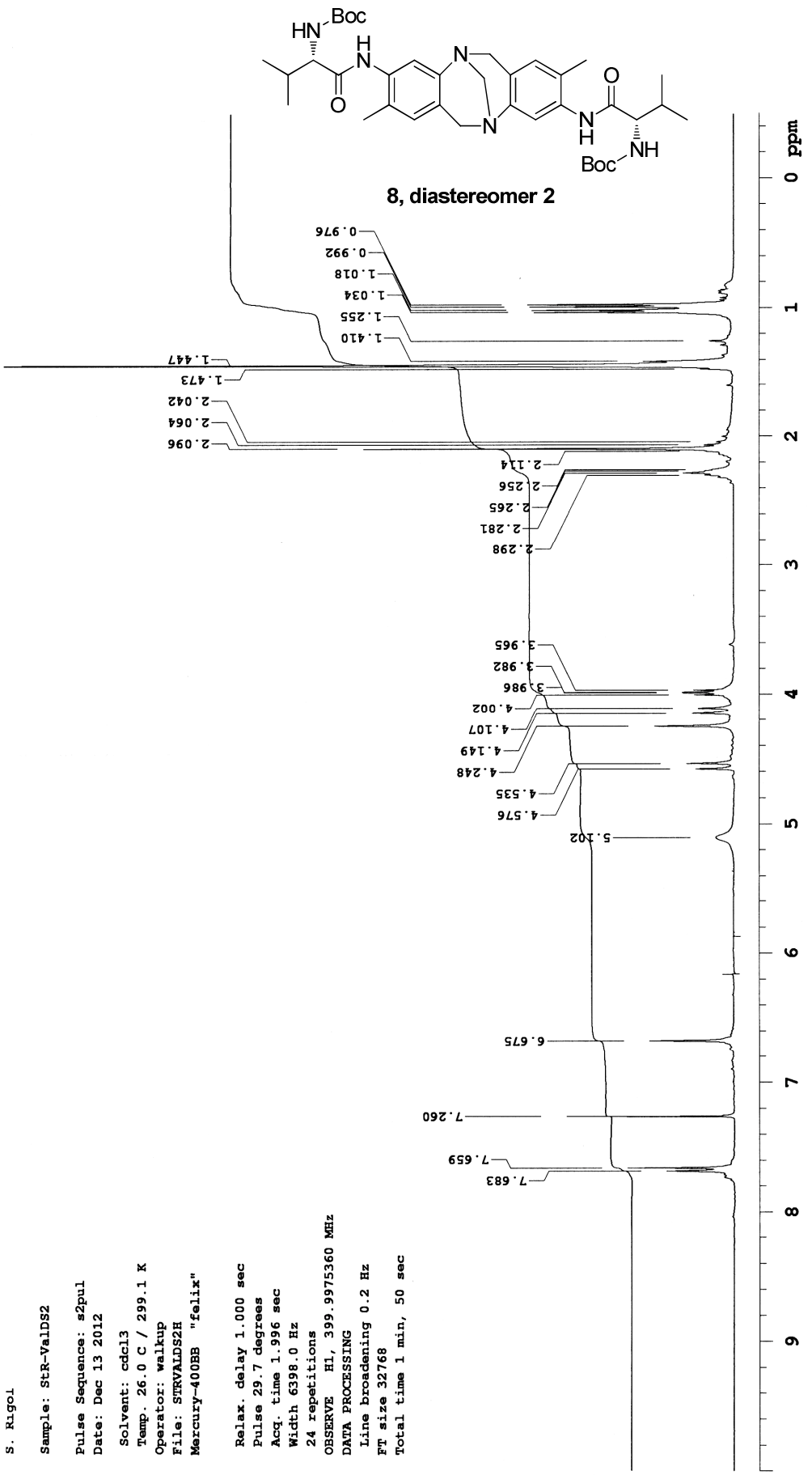
St. Rigol

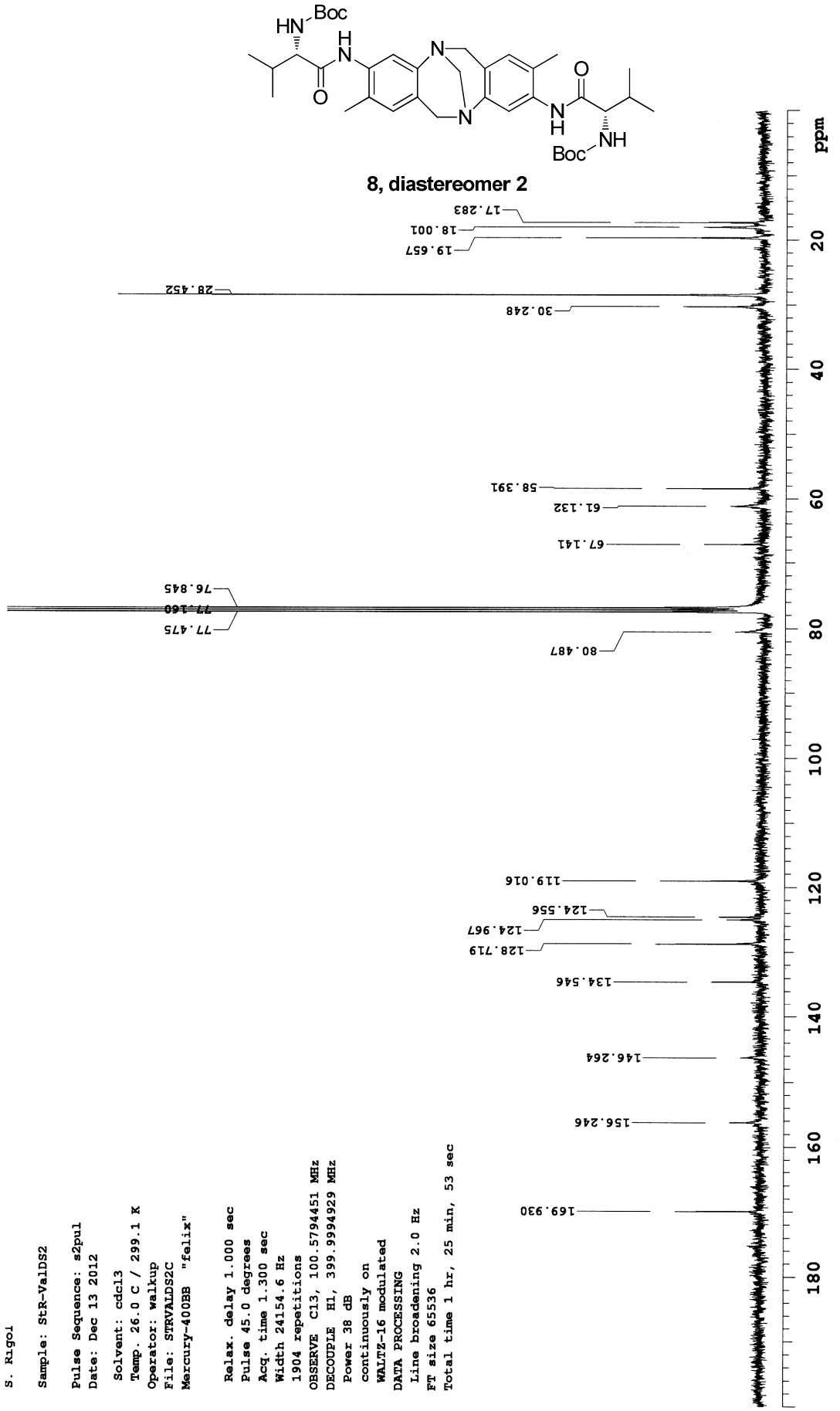
Sample: StR-HVDS1

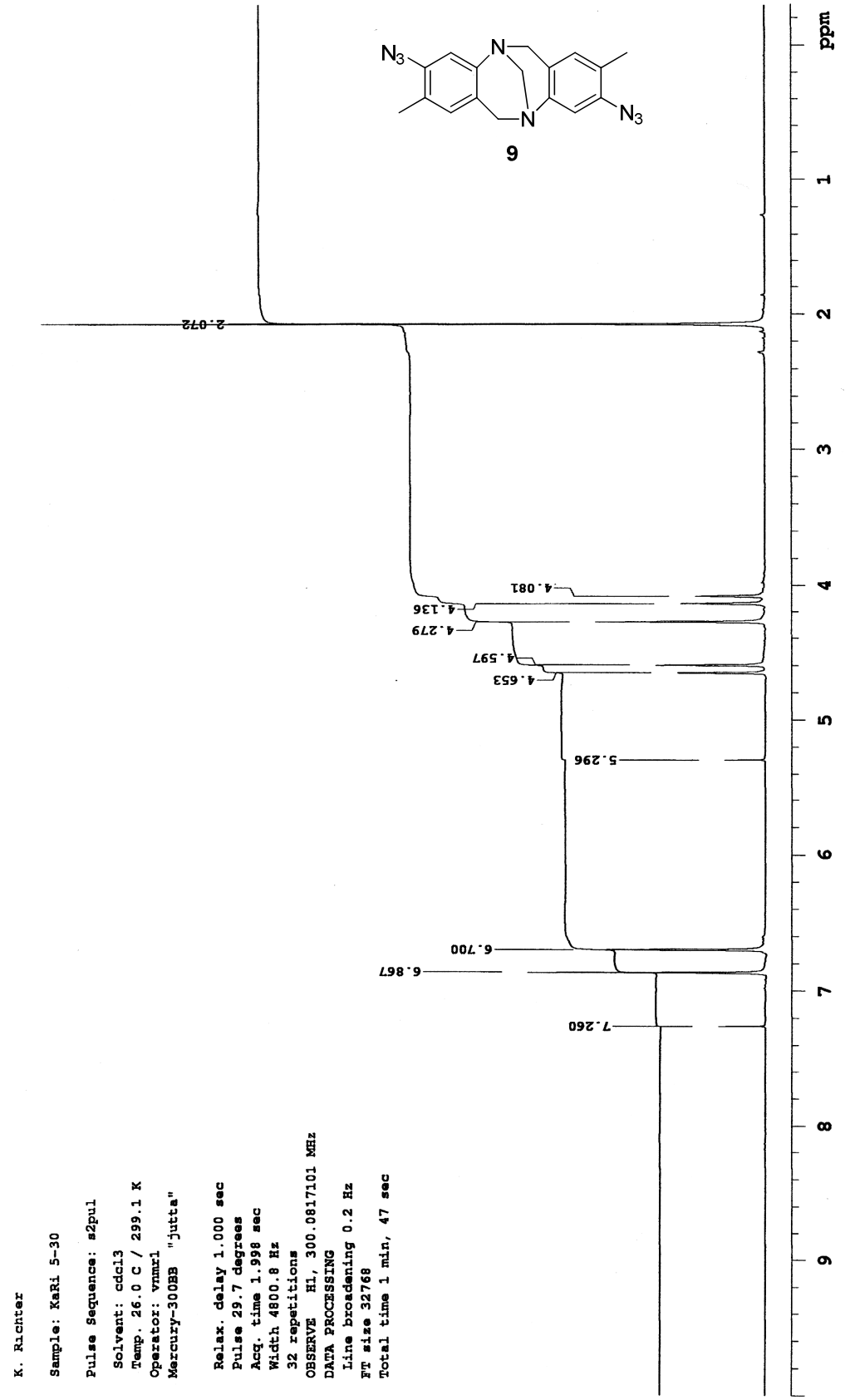
Pulse Sequence: s2pul

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
848 repetitions
OBSERVE C13, 75.4555922 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


8, diastereomer 2
0.976
0.992
1.018
1.034
1.255
1.410
1.447
1.473
2.042
2.064
2.096
2.114
2.256
2.265
2.281
2.298
3.965
3.982
3.986
4.002
4.107
4.149
4.248
4.535
4.576
5.102
6.675
7.260
7.659
7.683
0 ppm
S. Rigol
Sample: StR-ValDS2
Pulse Sequence: s2pul
Date: Dec 13 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
File: STRVALDS2H
Mercury-400BB "felix"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.996 sec
Width 6398.0 Hz
24 repetitions
OBSERVE H1, 399.9975360 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 50 sec


HN
Boc
H
N
O
N
N
O
N
H
Boc
NH
8, diastereomer 2
17.283
18.001
19.657
28.452
30.248
58.391
61.132
67.141
76.845
77.160
77.475
80.487
119.016
124.556
124.967
128.719
134.546
146.264
156.246
169.930
ppm
20
40
60
80
100
120
140
160
180
S. Rigol
Sample: StR-ValDS2
Pulse Sequence: s2pul
Date: Dec 13 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
File: STRVALDS2C
Marcury-400BB "felix"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1904 repetitions
OBSERVE C13, 100.5794451 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 1 hr, 25 min, 53 sec


K. Richter
Sample: KaRi 5-30
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, 300.0817101 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec
2.072
4.081
4.136
4.279
4.597
4.653
5.296
6.700
6.867
7.260
ppm
1
2
3
4
5
6
7
8
9
N3
N
N
N3
9

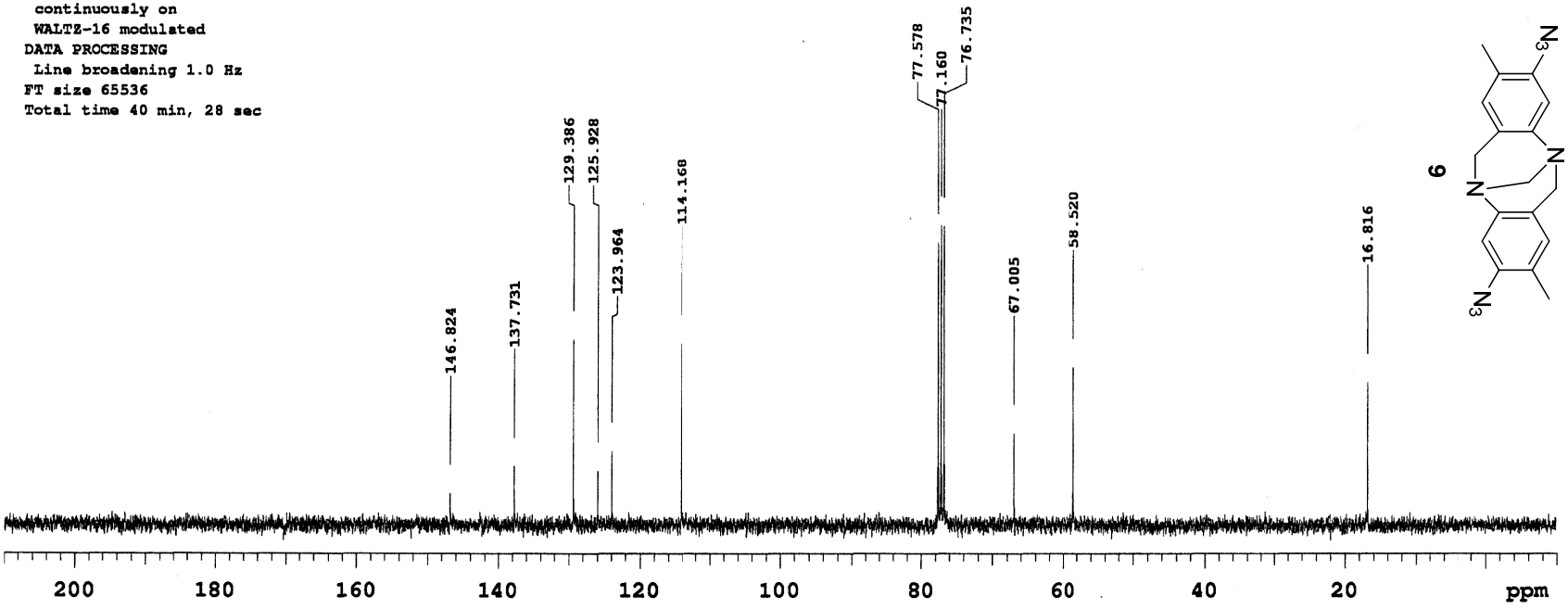
Std Carbon experiment

Sample: KaRi 5-30

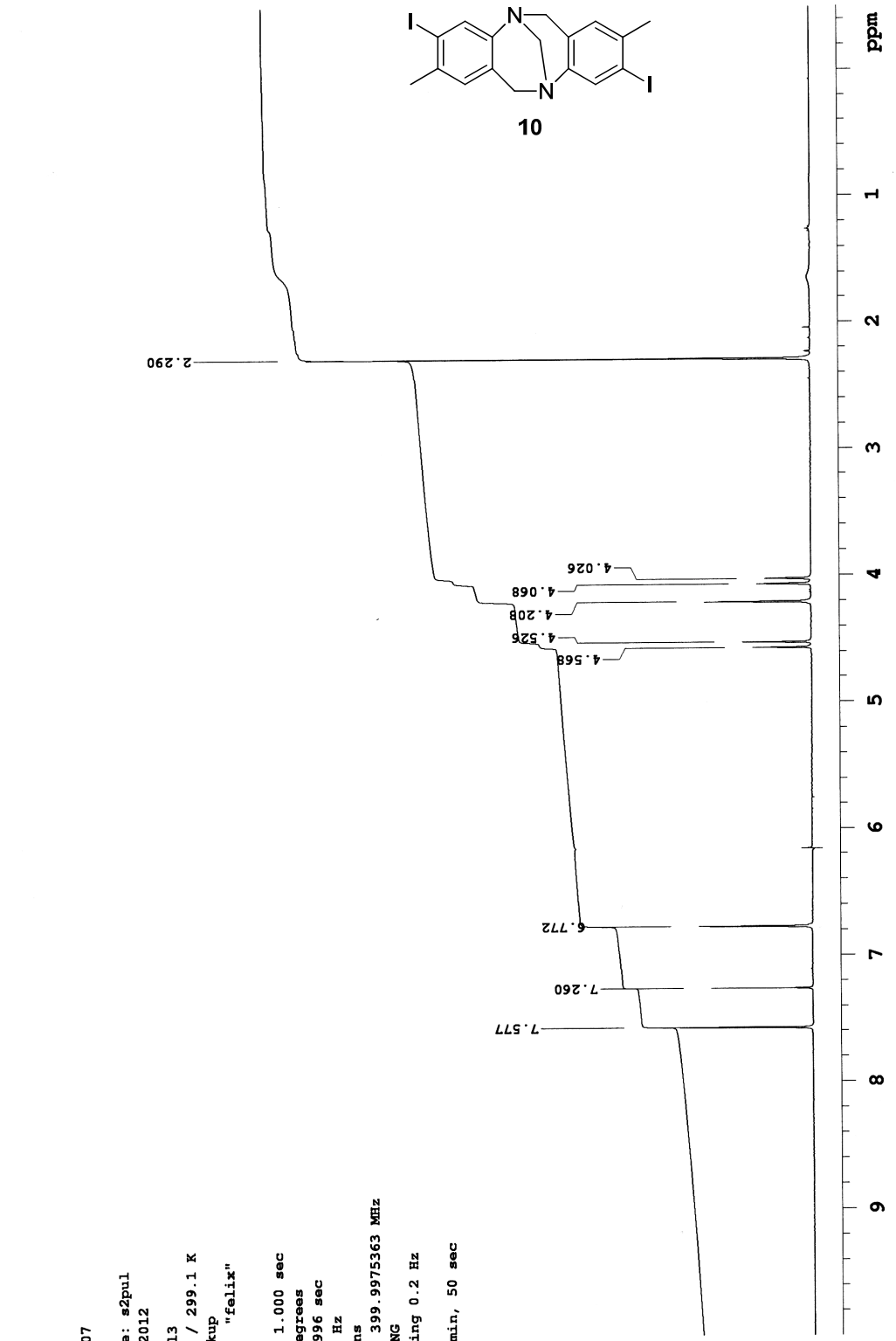
Pulse Sequence: s2pul

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
224 repetitions
OBSERVE C13, 75.4555946 MHz
DECOUPLE H1, 300.0832710 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 40 min, 28 sec



6


S.Rigol
Sample: StR-307
Pulse Sequence: s2pul
Date: Apr 13 2012
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Marcury-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
2.290
4.026
4.068
4.208
4.525
4.568
6.772
7.260
7.577
ppm
I
N
N
I
10

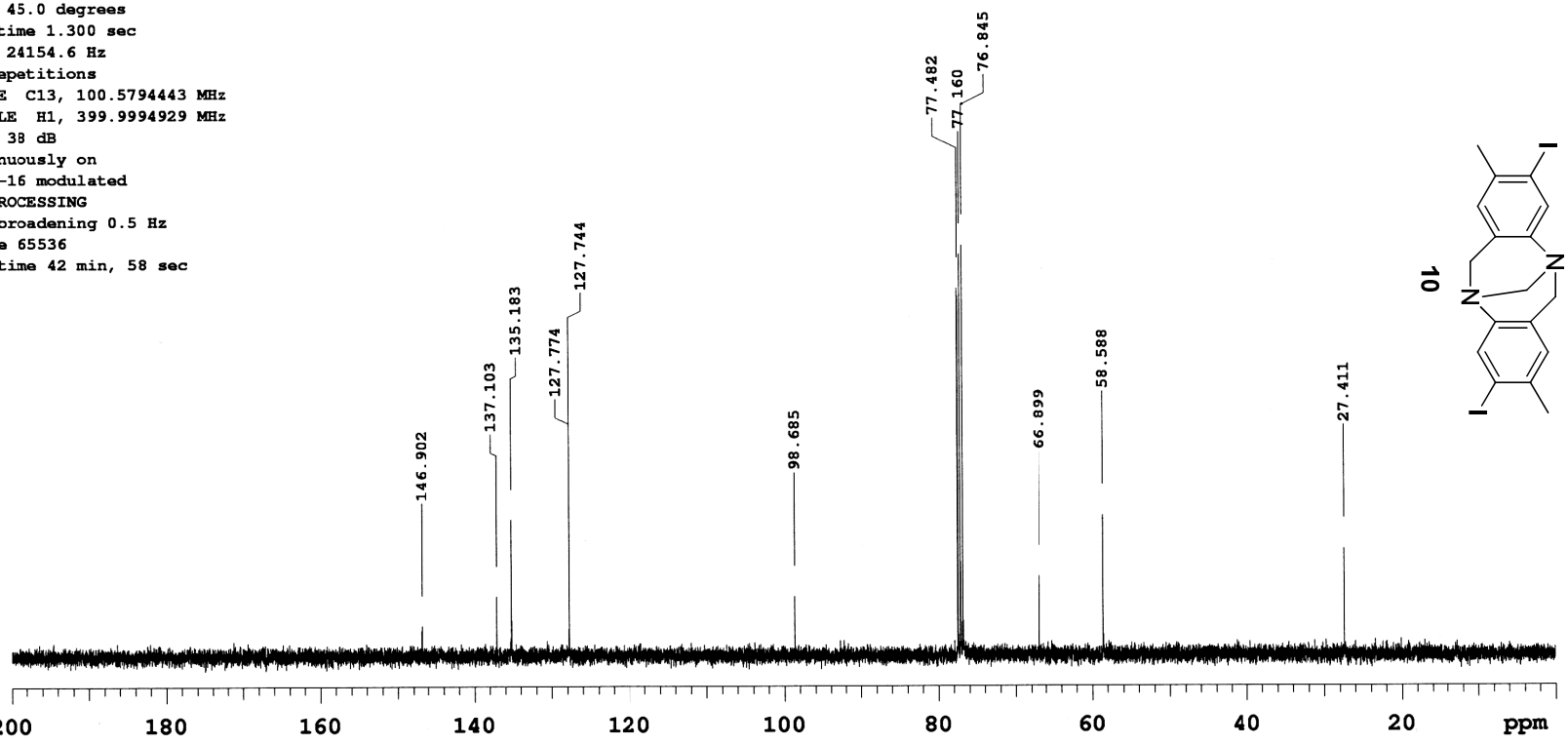
S.Rigol

Sample: StR-307

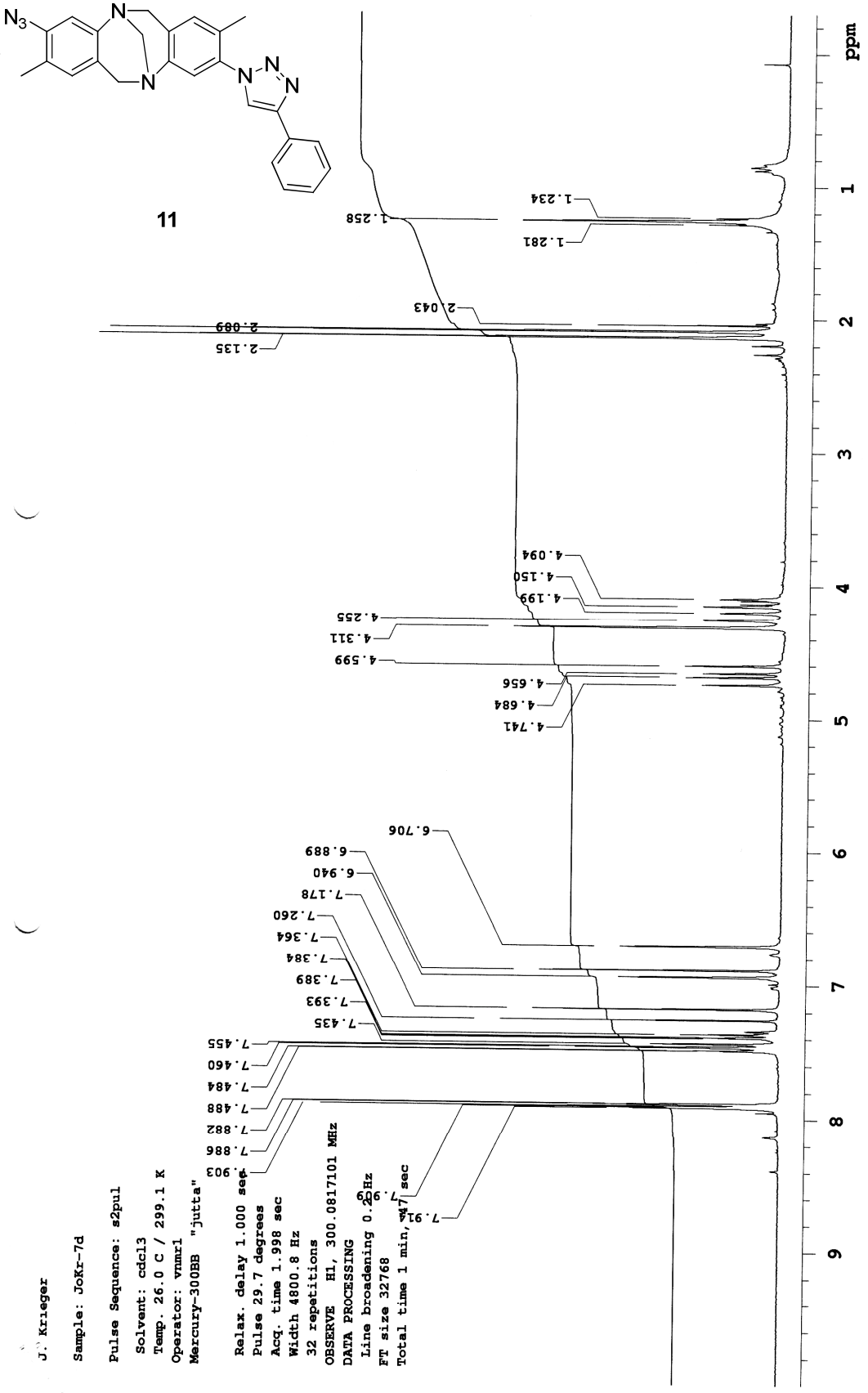
Pulse Sequence: s2pul
Date: Apr 13 2012

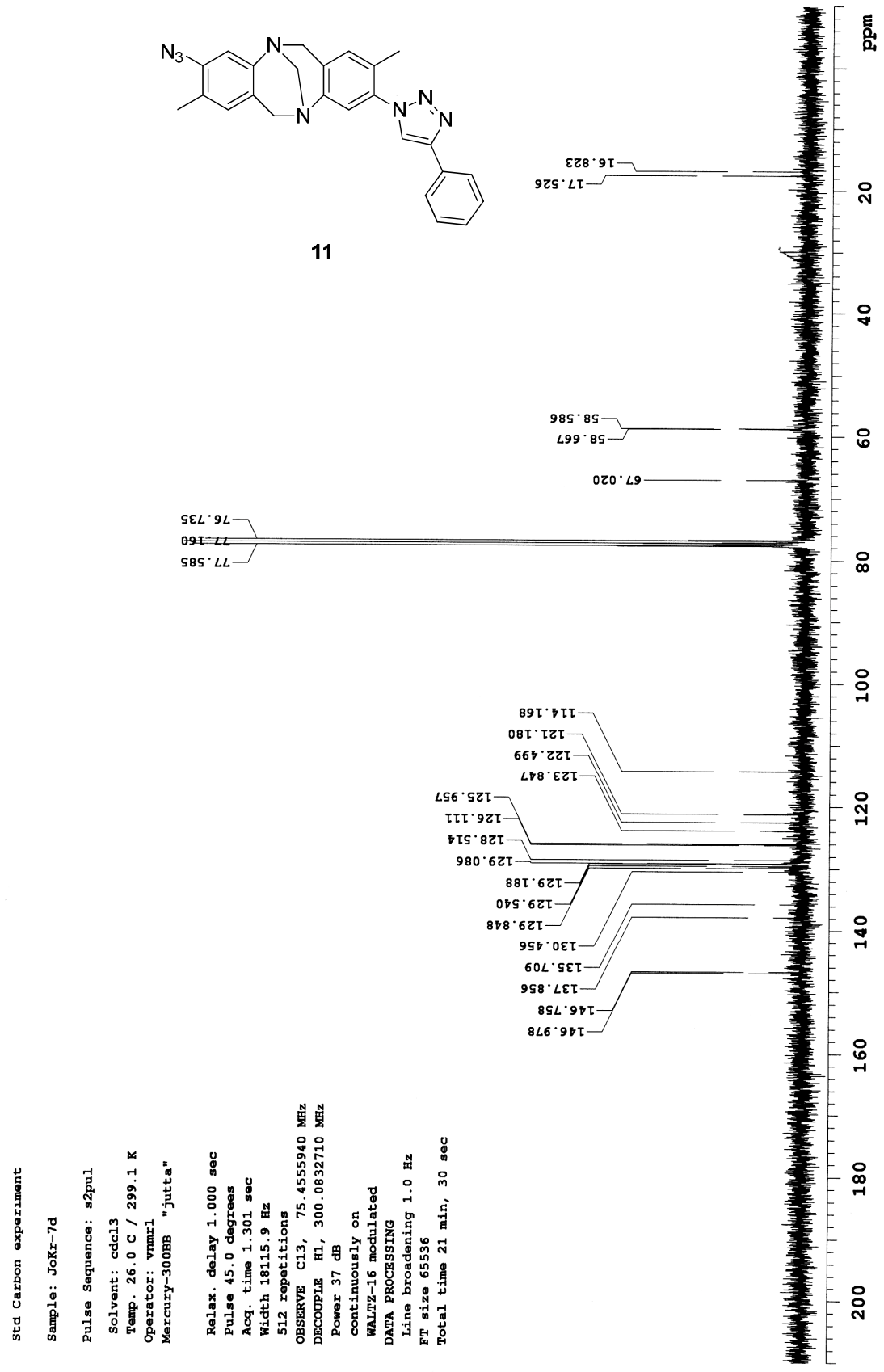
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
Mercury-400BB "felix"

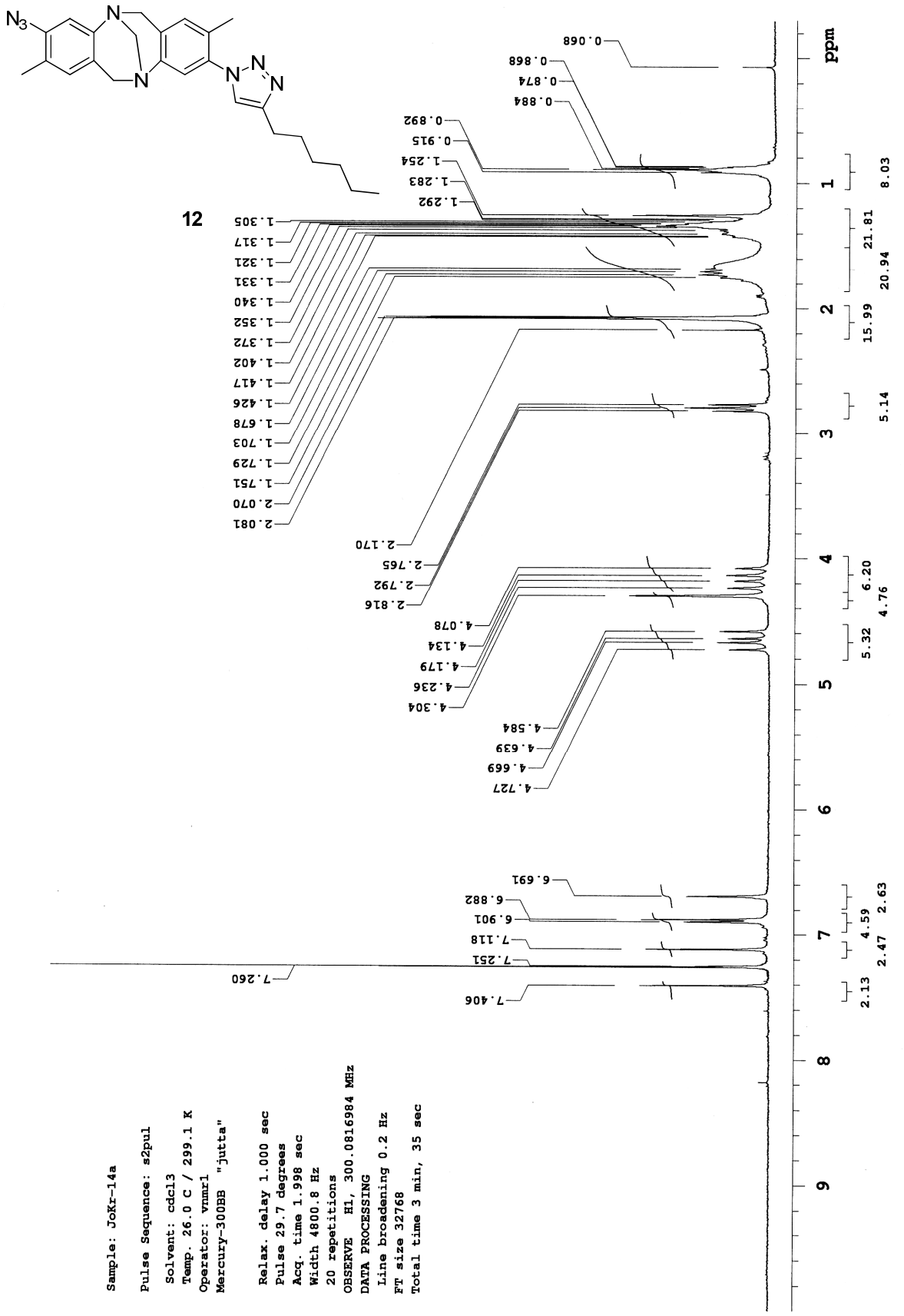
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
304 repetitions
OBSERVE C13, 100.5794443 MHz
DECOUPLE H1, 399.9994929 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 42 min, 58 sec

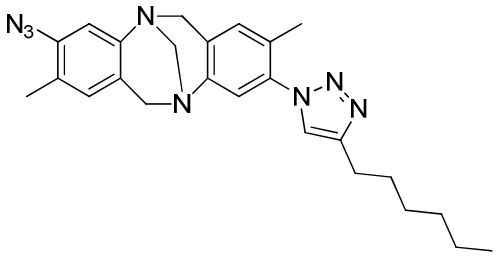


10


11
1.234
1.258
1.281
2.043
2.089
2.135
4.094
4.150
4.199
4.255
4.311
4.599
4.656
4.684
4.741
6.706
6.889
6.940
7.178
7.260
7.364
7.384
7.389
7.393
7.435
7.455
7.460
7.484
7.488
7.882
7.886
7.903
7.917
7.969
ppm
1
2
3
4
5
6
7
8
9
J. Krieger
Sample: JoKr-7d
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: vnmr1
Marcury-300BB "jutta"
Relax. delay 1.000 sec
Pulse 29.7 degrees
Acq. time 1.998 sec
Width 4800.8 Hz
32 repetitions
OBSERVE H1, 300.0817101 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min, 47 sec


Std Carbon experiment
Sample: JoKr-7d
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
512 repetitions
OBSERVE C13, 75.4555940 MHz
DECOUPLE H1, 300.0832710 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 21 min, 30 sec
N3
N
N
N
N
N
11
16.823
17.526
58.586
58.667
67.020
76.735
77.160
77.585
114.168
121.180
122.499
123.847
125.957
126.111
128.514
129.086
129.188
129.540
129.848
130.456
135.709
137.856
146.758
146.978
ppm
200
180
160
140
120
100
80
60
40
20


12
Sample: JoKr-14a
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
20 repetitions
OBSERVE H1, 300.0816984 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 3 min, 35 sec
ppm



12

J. Krieger

Sample: JoKr-14a

Pulse Sequence: s2pul
Date: Sep 27 2012

Solvent: cdcl3
Temp. 26.0 C / 299.1 K
Operator: walkup
File: JOKR14AC
Mercury-400BB "felix"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
2000 repetitions
OBSERVE C13, 100.5794465 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