Supporting Information

Potent CXCR4 Antagonists Containing Amidine-type Peptide Bond Isosteres

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Experimental Section

General Methods. All moisture-sensitive reaction were performed using syringe-septum cap techniques under an argon atmosphere and all glassware was dried in an oven at 80 °C for 2 h prior to use. Optical retations were measured with a JASCO P-1020 polarimeter. For flash chromatography, Wakogel C-300E or Chromatorex was employed. For analytical HPLC, a Cosmosil 5C18-ARII column (4.6 x 250 mm, Nacalai Tesque Inc., Kyoto, Japan) was employed with a linear gradient of CH_3CN containing 0.1 % (v/v) TFA at a flow rate of 1 mL/min on Shimadzu LC-20ADvp (Shimadzu corporation, Ltd, Kyoto, Japan). Preparative HPLC was performed using a Cosmosil 5C18-ARII column (20 x 250 mm, Nacalai Tesque Inc.) with a linear gradient of CH_3CN containing 0.1 % (v/v) TFA at a flow rate of 8 mL/min on Shimadzu LC-6AD (Shimadzu corporation, Ltd). ^{1}H NMR spectra were recorded using a JEOL ECA-500 spectrometer, and chemical shifts are reported in δ (ppm) relative to TMS (in DMSO-d_6) as internal standard. ^{13}C NMR spectra were recorded using a JEOL ECA-500 spectrometer and referenced to the residual DMSO signal. Chemical shifts were reported in parts per million with the residual solvent peak used as an internal standard. ^{1}H NMR spectra are tabulated as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), number of protons, and coupling constant(s). Exact mass (HRMS) spectra were recorded on a JMS-HX/HX 110A mass spectrometer. The purity of the peptides for bioassay was calculated as >95% by HPLC on a Cosmosil 5C18-ARII analytical column at 220 nm absorbance (Figure S3).Resin and Fmoc-protected amino acids were purchased from Watanabe Chemical Industries, Ltd (Hiroshima, Japan) or Kokusan Chemical Co. Ltd. (Kanagawa, Japan). All the other chemicals were purchased from either Nacalai Tesque Inc. (Kyoto, Japan) or Sigma-Aldrich JAPAN (Tokyo, Japan).

H_2N-O-(2-Cl)Trt resin (8). 2-Chlorotrityl resin chloride (loading: 1.31 mmol/g, 76.3 mg) was reacted with Fmoc-NHOH (128 mg, 0.500 mmol) and pyridine (810 μL, 1.00 mmol) in THF (800 μL) at 60 °C for 6 h. The solution was removed by filtration and the resulting resin was washed with the solution of DMF–(i-Pr)$_2$NEt–MeOH (17:2:1). The Fmoc-protecting group was removed by treating the resin with a DMF–piperidine solution (80:20, v/v). The loading was determined by measuring at 290 nm UV absorption of the piperidine-treated sample: 0.900 mmol/g, 89%.

Fmoc-3-(2-naphthyl)alaninal (9b). Aldehyde **9b** was prepared from Fmoc-Nal-NMe(OMe) by the literature procedure.[1] The crude product was used for the next step without further purification.

General procedure for the preparation of peptide aldoxime 12: H-Gly-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-aldoxime (12b). The solid supported hydroxyamine **8** (loading: 0.900 mmol/g, 91.6 mg, 0.0820 mmol) was reacted with Fmoc-3-(2-naphthyl)alaninal **9b** (0.500 mmol) in dichloroethane (700 μL), $HC(OMe)_3$ (500 μL) and AcOH (1 μL) at 60 °C for 2 h. The solution was removed by filtration and the resulting resin was washed with DMF to afford resin **10b**. The peptide-resin **11b** was manually constructed using Fmoc-based solid-phase synthesis on resin **10b**. The Fmoc-protecting group was removed by treating the resin with a DMF–piperidine solution (80:20, v/v). Fmoc-protected amino acid (0.500 mmol, 6.1 equiv) was successively coupled using DIC (77 μL, 0.500 mmol, 6.1 equiv) in the presence of HOBt (77 mg, 0.500 mmol, 6.1 equiv) to give resin **11b**. *t*-Bu ether for Tyr and 2,2,4,6,7-pentamethyldihydrobenzofuran-5-sulfonyl (Pbf) for Arg were employed for side-chain protection. Resin **11b** was treated with TFA–TIS–CH_2Cl_2 (20 mL, 0.5:0.1:99.4) at room temperature for 1.5 h. After removal of the resin by filtration, the filtrate was concentrated under reduced pressure to give off a crude peptide aldoxime **12b** as a yellow oil. The crude product was used for the next step without further purification.

H-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-Gly-aldoxime (12a). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of Fmoc-glycinal **9a** gave the title compound **12a**.

H-Gly-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-D-Nal-aldoxime (12c). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of Fmoc-D-3-(2-naphthyl)alaninal **9c** gave the title compound **12c**.

H-Nal-Gly-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Boc)$_2$-aldoxime (12d). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of di-Boc-protected Fmoc-arginal **9d** gave the title compound **12d**.

H-Arg(Pbf)-Nal-Gly-D-Tyr(*t*-Bu)-Arg(Boc)$_2$-aldoxime (12e). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of di-Boc-protected Fmoc-arginal **9d** gave the title compound **12e**.

H-Arg(Pbf)-Arg(Pbf)-Nal-Gly-D-Tyr(*t*-Bu)-aldoxime (12f). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of *t*-Bu-protected Fmoc-D-tyrosinal **9f** gave the title compound **12f**.

H-Arg(Pbf)-Arg(Pbf)-Nal-Gly-Tyr(*t*-Bu)-aldoxime (12g). By use of a procedure identical with that described for the preparation of **12b** from **9b**, the reaction of *t*-Bu-protected Fmoc-tyrosinal **9g** gave the title compound **12g**.

General Procedure for nitrile oxide-mediated cyclization: *Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-ψ[C(=NOH)-NH]-Gly-] (13b). To a solution of peptide aldoxime **12b** in DMF (1 mL) was added *N*-chlorosuccinimide (14.7 mg, 0.100 mmol). The solution was stirred at room temperature overnight, and then DMF (40 mL) and Et_3N (400 μL) were added. The mixture was stirred at room temperature overnight, and was then concentrated under reduced pressure. The residue was extracted with EtOAc and the extract was washed with brine. The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure to give a yellow oil, which was purified by column chromatography over silica gel with CH_2Cl_2–MeOH (95:5) to give **13b** (41.7 mg, 33% yield from resin **8**) as a yellow oil: $[\alpha]^{26}_D$ –28.1 (*c* 0.105, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21 (s, 9H), 1.36 (s, 3H), 1.37 (s, 3H), 1.39 (s, 3H), 1.40 (s, 3H), 1.45–1.90 (m, 8H), 1.99 (s, 3H), 2.00 (s, 3H), 2.42 (s, 6H), 2.48 (s, 6H), 2.50 (s, 2H), 2.56 (s, 2H), 2.80–2.96 (m, 8H), 3.16–3.20 (m, 1H), 3.61–3.68 (m, 1H), 3.91–3.98 (m, 1H), 4.13–4.21 (m, 2H), 4.36–4.42 (m, 1H), 5.73–5.79 (m, 1H), 6.38 (br s, 2H), 6.82 (d, J = 7.4 Hz, 2H), 7.09 (d, J = 7.4 Hz, 2H), 7.36 (d, J = 8.3 Hz, 1H), 7.41–7.46 (m, 2H), 7.54 (d, J = 9.5 Hz, 1H), 7.65 (s, 1H), 7.74–7.85 (m, 4H), 8.45 (d, J = 8.5 Hz, 1H), 8.55–8.60 (m, 1H), 8.86–8.90 (m, 1H), 9.46 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3 (2C), 17.3 (2C), 17.6 (2C), 18.9 (2C), 24.0, 28.2 (2C), 28.3 (2C), 28.4 (2C), 29.5 (4C), 30.8 (3C), 35.8, 42.5, 45.7 (2C), 52.8, 56.6, 77.6, 86.2, 86.3, 116.0, 116.3, 118.5, 123.4, 124.3 (2C), 124.4 (2C), 125.3, 125.9, 127.2, 127.3, 127.4, 127.5, 127.5, 127.8, 129.7, 130.3, 131.4, 131.8, 132.9, 135.7, 136.6, 137.2, 153.7, 156.1, 157.5, 157.9, 158.4, 160.7, 161.5, 162.3, 170.9, 171.5, 179.4; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{12}S_2$ (MH^+) 1305.6164; found 1305.6160.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-Gly-ψ[C(=NOH)-NH]-] (13a).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12a** was converted into the title compound **13a** (32% yield from **8**). Yellow oil; $[\alpha]^{27}_D$ +4.02 (*c* 0.141, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.25 (s, 9H), 1.32–1.40 (m, 4H), 1.39 (s, 12H), 1.42–1.60 (m, 4H),

1.97–1.99 (m, 6H), 2.43 (s, 6H), 2.48 (s, 6H), 2.93 (d, J = 14.3 Hz, 2H), 2.85–3.00 (m, 6H), 3.82–4.00 (m, 1H), 4.10–4.23 (m, 2H), 4.47–4.60 (m, 1H), 5.30 (d, J = 10.5 Hz, 1H), 6.25–6.45 (br s, 2H), 6.87 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 9.0 Hz, 1H), 7.36–7.47 (m, 2H), 7.58 (s, 1H), 7.63–7.70 (m, 1H), 7.74–7.82 (m, 5H), 8.43–8.49 (m, 1H), 9.51 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3 (2C), 17.0, 17.2, 17.2 (2C), 17.7, 21.7, 22.3, 22.6, 22.7, 22.8 (3C), 22.9, 23.0, 24.1, 33.3 (3C), 33.4, 33.6, 33.7, 34.7, 35.9, 40.9 (2C), 47.4, 47.6, 82.9, 91.2, 91.4, 121.3 (2C), 121.4 (2C), 128.7 (3C), 128.7, 129.4 (2C), 129.5 (2C), 132.6, 132.6, 132.9, 134.1 (2C), 134.7, 135.2, 136.6 (2C), 136.9, 138.0, 138.3, 139.3, 139.3, 142.4, 160.2 (2C), 162.6, 167.4 (2C), 167.5, 176.1; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{12}S_2$ (MH^+) 1305.6164; found 1305.6160.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-D-Nal-ψ[C(=NOH)-NH]-Gly-] (13c).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12c** was converted into the title compound **13c** (58% yield from **8**). Yellow oil; $[\alpha]^{27}_D$ +44.5 (c 0.213, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21 (s, 9H), 1.21–1.40 (m, 8H), 1.38 (s, 12H), 2.00 (s, 6H), 2.41 (s, 3H), 2.42 (s, 3H), 2.45 (s, 3H), 2.48 (s, 3H), 2.58–2.70 (m, 6H), 2.94 (s, 4H), 3.21 (dd, J = 13.5, 6.2 Hz, 1H), 3.68–3.77 (m, 2H), 3.78–3.85 (m, 2H), 4.04 (dd, J = 12.8, 5.9 Hz, 1H), 4.32–4.38 (m, 1H), 4.78 (dd, J = 14.8, 8.5 Hz, 1H), 6.00–6.08 (m, 1H), 6.27–6.49 (br s, 4H), 6.82 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.29–7.42 (m, 3H), 7.66 (s, 1H), 7.68–7.85 (m, 3H), 7.88–7.98 (m, 2H), 8.00–8.09 (m, 1H), 8.63 (d, J = 6.7 Hz, 1H), 9.84 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3 (2C), 17.6 (2C), 19.0 (2C), 25.0, 27.7, 28.3 (2C), 28.5 (2C), 28.6 (2C), 28.7, 29.0, 29.5 (4C), 30.8 (2C), 35.8, 42.5, 48.6 (2C), 54.6, 55.2, 77.7, 79.2, 86.3, 116.3 (2C), 123.6, 124.3 (2C), 124.4 (2C), 125.2, 125.8, 127.3, 127.4, 127.5, 127.5, 127.6, 128.0, 129.5, 131.3, 131.4, 131.5, 131.7, 132.9, 134.2, 136.3, 137.3, 151.1, 153.7, 155.9, 157.5 (2C), 162.3, 169.9, 171.5, 171.9, 172.5, 179.4; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{12}S_2$ (MH^+) 1305.6164; found 1305.6150.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Boc)$_2$-ψ[C(=NOH)-NH]-Nal-Gly-] (13d).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12d** was converted into the title compound **13d** (34% yield from **8**). Yellow oil; $[\alpha]^{25}_D$ –7.04 (c 0.412, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.22 (s, 9H), 1.28–1.49 (m, 4H), 1.35 (s, 6H), 1.37 (s, 9H), 1.38 (s, 9H), 1.99 (s, 3H), 2.40 (s, 3H), 2.46 (s, 3H), 2.70–2.72 (m, 2H), 2.90–2.98 (m, 6H), 3.38 (s, 2H), 4.16–4.25 (m, 1H), 4.26–4.38 (m, 2H), 4.39–4.60 (m, 3H), 6.76–6.83 (m, 4H), 7.10 (d, J = 6.9 Hz, 1H), 7.40–7.50 (m, 5H), 7.75–7.86 (m, 4H), 8.17–8.25 (m, 4H), 9.58 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.2, 15.7, 18.9, 27.4 (2C), 27.6 (2C), 27.7 (2C), 28.0 (2C), 28.0 (2C), 28.3 (2C), 28.5,

28.7 (3C), 29.5 (6C), 40.1, 42.5, 77.6, 78.1, 82.9, 86.3 (2C), 116.2, 123.3, 123.4, 124.3, 125.3 (2C), 125.9 (2C), 126.0, 127.3, 127.4, 127.6, 127.8, 129.6, 129.7, 131.4, 131.9, 133.0, 134.1, 134.2, 136.3, 137.3, 149.4, 152.1, 153.5, 155.2, 156.0, 157.4, 163.1, 179.4 (2C); HRMS (FAB) calcd for $C_{63}H_{89}N_{12}O_{13}S$ (MH^+) 1253.6393; found 1253.6390.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Boc)$_2$-*ψ*[C(=NOH)-NH]-Arg(Pbf)-Nal-Gly-] (13e).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12e** was converted into the title compound **13e** (40% yield from **8**). Yellow oil; $[\alpha]^{25}_D$ +7.60 (*c* 0.401, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21 (s, 9H), 1.21–1.25 (m, 4H), 1.34–1.40 (m, 4H), 1.37 (s, 9H), 1.38 (s, 6H), 1.46 (s, 9H), 1.99 (s, 3H), 2.41 (s, 3H), 2.47 (s, 3H), 2.54–2.56 (m, 2H), 2.90–2.97 (m, 4H), 3.05–3.12 (m, 2H), 3.35 (s, 2H), 3.56 (dd, *J* = 16.5, 6.2 Hz, 1H), 3.64–3.72 (m, 1H), 4.38 (dd, *J* = 15.6, 7.7 Hz, 1H), 4.43 (dd, *J* = 14.2, 7.7 Hz, 1H), 4.51 (dd, *J* = 14.9, 8.0 Hz, 1H), 6.12 (d, *J* = 11.3 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.80–6.86 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.43–7.46 (m, 2H), 7.73 (s, 1H), 7.79–7.85 (m, 4H), 8.14 (t, *J* = 5.5 Hz, 1H), 8.25 (t, *J* = 5.9 Hz, 1H), 8.63 (t, *J* = 5.7 Hz, 1H), 9.90 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.1, 17.6, 18.9 (2C), 25.2, 27.6 (4C), 28.0 (4C), 28.3 (3C), 28.5 (5C), 29.5 (5C), 42.5, 78.0, 79.2, 82.9 (2C), 86.2, 116.3, 123.3 (2C), 124.3, 125.6, 126.1, 127.3, 127.3, 127.4, 127.5, 127.5, 127.7, 129.6 (2C), 131.4, 131.9, 132.6, 133.0, 134.7, 152.2, 153.3, 155.2, 156.1, 157.5, 162.3, 163.1, 168.2, 169.2, 171.8, 174.7, 179.4; HRMS (FAB) calcd for $C_{63}H_{89}N_{12}O_{13}S$ (MH^+) 1253.6393; found 1253.6398.

***Cyclo*[-D-Tyr(*t*-Bu)-*ψ*[C(=NOH)-NH]-Arg(Pbf)-Arg(Pbf)-Nal-Gly-] (13f).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12f** was converted into the title compound **13f** (27% yield from **8**). Yellow oil; $[\alpha]^{26}_D$ –150.9 (*c* 0.103, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.25 (s, 9H), 1.25–1.30 (m, 4H), 1.39 (s, 6H), 1.40 (s, 6H), 1.40–1.80 (m, 4H), 1.98 (s, 6H), 2.40–2.43 (m, 6H), 2.45–2.47 (m, 6H), 2.89–2.95 (m, 8H), 2.50 (s, 2H), 2.57 (s, 2H), 3.13–3.20 (m, 1H), 3.52–3.69 (m, 2H), 4.23–4.25 (m, 1H), 4.50–4.55 (m, 2H), 5.50 (s, 1H), 6.25–6.50 (br s, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 7.08–7.15 (m, 1H), 7.35–7.49 (m, 4H), 7.70–7.80 (m, 4H), 8.23–8.27 (m, 1H), 8.27–8.29 (m, 1H), 9.31 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.2, 12.3, 12.4, 17.6 (2C), 18.9, 22.1 (2C), 24.0, 28.3, 28.5 (4C), 28.6, 29.0, 29.5 (4C), 30.8, 31.3, 35.8 (3C), 42.4, 45.7 (2C), 77.6, 86.2, 86.3, 116.3, 123.3 (2C), 123.4 (2C), 124.3, 125.9 (2C), 127.3 (2C), 127.4, 127.7 (2C), 129.5 (2C), 129.7 (2C), 131.4, 131.7, 132.9, 133.2, 134.2, 136.4, 137.3, 153.3, 157.1, 157.5, 158.2, 161.5 (2C), 162.3, 168.6, 170.4, 171.7, 179.3; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{12}S_2$ (MH^+) 1305.6164; found 1305.6160.

***Cyclo*[-Tyr(*t*-Bu)-*ψ*[C(=NOH)-NH]-Arg(Pbf)-Arg(Pbf)-Nal-Gly-] (13g).** By use of a procedure identical with that described for the preparation of **13b** from **12b**, the peptide aldoxime **12g** was converted into the title compound **13g** (50% yield from **8**). Yellow oil; $[\alpha]^{27}_{D}$ –64.9 (*c* 0.436, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.26 (s, 9H), 1.26–1.40 (m, 4H), 1.40 (s, 12H), 1.51–1.60 (m, 4H), 1.99 (s, 3H), 2.00 (s, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 2.46 (s, 3H), 2.50 (s, 3H), 2.60–2.67 (m, 1H), 2.71–2.76 (m, 1H), 2.87–2.99 (m, 6H), 3.07–3.14 (m, 1H), 3.16 (s, 2H), 3.17 (s, 2H), 3.19–3.25 (m, 1H), 3.40–3.48 (m, 1H), 3.52–3.58 (m, 1H), 3.65–3.71 (m, 1H), 4.24–4.36 (m, 3H), 4.63–4.68 (m, 1H), 6.22 (d, *J* = 11.6 Hz, 2H), 6.23–6.30 (br s, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 10.3 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.36–7.41 (m, 2H), 7.50–7.55 (m, 1H), 7.60 (s, 1H), 7.72–7.81 (m, 3H), 7.91 (s, 1H), 8.52–8.58 (m, 1H), 10.06 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.2, 12.3, 17.6, 17.7, 18.9, 19.0, 28.2, 28.3, 28.4 (2C), 28.5 (3C), 29.0, 29.5 (4C), 29.6, 30.1, 30.8, 35.8 (2C), 42.4 (2C), 49.1 (2C), 54.5, 77.6, 86.3, 86.4, 116.3, 123.2, 123.4, 124.3, 124.4, 125.2, 125.9, 127.1, 127.3, 127.4, 127.6, 127.7, 129.7, 129.8, 131.4, 131.7, 132.9, 133.5, 136.6, 137.3, 137.4, 148.9, 153.1, 156.0, 157.5, 157.5, 161.6, 162.4 (2C), 168.5, 169.7, 172.8, 176.2, 179.4, 179.6; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{12}S_2$ (MH^+) 1305.6164; found 1305.6160.

General procedure for the conversion of the amidoxime 13 to the amidine 14: *Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-*ψ*[C(=NH)-NH]-Gly-] (14b). To a solution of amidoxime **13b** (41.7 mg, 0.0330 mmol) in MeOH (600 μL) and AcOH (6 μL) was added Raney Ni (440 μL, slurry in H_2O) and the mixture was stirred under H_2 atmospheres at room temperature for 2 h. The mixture was filtered through celite. Concentration under reduced pressure followed by flash chromatography over Chromatorex with CH_2Cl_2–MeOH (95:5) gave the title compound **14b** (19.5 mg, 46% yield) as a yellow oil: $[\alpha]^{26}_{D}$ –2.79 (*c* 0.274, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21 (s, 9H), 1.21–1.24 (m, 4H), 1.32–1.40 (m, 4H), 1.38 (s, 6H), 1.39 (s, 6H), 1.98 (s, 6H), 2.40 (s, 6H), 2.44 (s, 6H), 2.45–2.50 (m, 4H), 2.86–2.92 (m, 4H), 2.93 (s, 4H), 3.01–3.04 (m, 1H), 3.61–3.69 (m, 1H), 4.00–4.10 (m, 2H), 4.30 (dd, *J* = 10.5, 7.4 Hz, 1H), 4.44–4.48 (m, 1H), 6.30–6.50 (br s, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.78–7.00 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.05–7.10 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.34–7.38 (m, 2H), 7.40–7.44 (m, 1H), 7.64–7.72 (m, 1H), 7.74–7.84 (m, 2H), 8.15–8.20 (br s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3 (2C), 17.6 (2C), 17.7 (2C), 18.9 (2C), 19.0 (2C), 25.6, 28.3 (5C), 28.5 (6C), 29.1, 29.5, 40.4, 42.5 (2C), 54.2, 77.5, 79.2, 86.3, 116.3, 123.3 (2C), 124.3, 124.4 (2C), 125.3, 125.9, 127.1, 127.2, 127.3 (2C), 127.5, 128.1, 129.6 (2C), 129.7, 131.4 (2C), 131.5, 131.9, 132.7,

133.0, 134.2, 134.6, 137.2, 137.3, 153.2, 156.0, 156.1, 156.2, 157.5 (2C), 170.1, 171.0; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{11}S_2$ (MH^+) 1289.6215; found 1289.6222.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-Nal-Gly-*ψ*[C(=NH)-NH]-] (14a)**. By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13a** was converted into the title compound **14a** (37% yield). Yellow oil; $[\alpha]^{27}_D$ –4.12 (*c* 0.100, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.96 (s, 9H), 0.98 (s, 3H), 1.20 (s, 3H), 1.23 (s, 3H), 1.24 (s, 3H), 1.32–1.40 (m, 8H), 1.92–2.00 (m, 6H), 2.37–2.44 (br s, 6H), 2.55 (s, 6H), 2.85–2.97 (m, 8H), 3.85–3.92 (m, 1H), 4.03–4.25 (m, 2H), 4.40–4.58 (m, 1H), 5.11 (s, 1H), 5.29 (d, *J* = 12.1 Hz, 1H), 6.29–6.46 (br s, 2H), 6.75–6.89 (br s, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 7.32–7.44 (m, 5H), 7.68–8.85 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.1, 12.3, 17.6 (2C), 17.8 (4C), 18.9 (2C), 28.1 (2C), 28.3 (2C), 28.5, 28.5, 29.0 (4C), 29.5 (4C), 42.2 (2C), 42.5 (2C), 86.1, 86.3, 86.3, 116.3, 123.6 (2C), 123.7, 124.4 (2C), 125.8, 125.9, 127.4, 127.7 (2C), 127.8 (2C), 130.1 (2C), 131.4, 131.5 (2C), 131.8, 133.2 (2C) 134.2 (2C), 137.3 (2C), 155.0, 156.1, 157.5, 157.6, 162.3 (2C), 163.2, 170.0, 171.1, 179.4; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{11}S_2$ (MH^+) 1289.6215; found 1289.6216.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Pbf)-D-Nal-*ψ*[C(=NH)-NH]-Gly-] (14c).** By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13c** was converted into the title compound **14c** (35% yield). Yellow oil; $[\alpha]^{27}_D$ –9.02 (*c* 0.106, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.20–1.30 (m, 6H), 1.22 (s, 9H), 1.23 (s, 6H), 1.34 (s, 3H), 1.36 (s, 3H), 1.39 (s, 3H), 1.40 (s, 3H), 1.50–1.52 (m, 1H), 1.62–1.67 (m, 1H), 1.99 (s, 6H), 2.40 (s, 3H), 2.43 (s, 3H), 2.84–3.00 (m, 6H), 2.94 (s, 4H), 3.00–3.07 (m, 1H), 3.11–3.17 (m, 1H), 3.62–3.74 (m, 1H), 4.02–4.17 (m, 2H), 4.27–4.35 (m, 1H), 4.45–4.51 (m, 1H), 4.52–4.61 (m, 2H), 6.29–6.51 (br s, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.34–7.40 (m, 2H), 7.42–7.46 (m, 2H) 7.65–7.74 (m, 2H), 7.56–7.83 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3, 12.4, 17.6 (2C), 18.8 (2C), 25.0, 27.7, 28.2, 28.3 (2C), 28.5, 28.6, 28.7 (2C), 29.0, 29.3, 29.5 (2C), 30.8, 35.8, 37.0, 42.5, 45.9, 48.6 (2C), 54.6, 55.2, 77.7, 79.2, 86.3, 116.3 (2C), 123.6, 124.3 (2C), 124.4, 125.2, 125.8, 127.3, 127.4 (2C), 127.5 (2C), 128.0, 129.5, 131.4, 131.4, 131.5, 131.7, 132.9, 134.2, 136.3, 137.3, 151.1, 153.7, 155.9 (2C), 157.5 (2C), 162.4, 169.9, 171.5, 171.9, 172.5, 177.4; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{11}S_2$ (MH^+) 1289.6215; found 1289.6223.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Pbf)-Arg(Boc)$_2$-*ψ*[C(=NH)-NH]-Nal-Gly-] (14d).** By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13d** was converted

into the title compound **14d** (56% yield). Yellow oil; $[\alpha]^{26}_{D}$ +3.50 (*c* 0.114, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.13–1.22 (m, 4H), 1.23 (s, 9H), 1.37 (s, 6H), 1.39 (s, 9H), 1.47 (s, 9H), 1.50–1.62 (m, 4H), 1.99 (s, 3H), 2.42 (s, 3H), 2.49 (s, 3H), 2.81–2.90 (m, 4H), 2.90 (s, 2H), 3.00–3.18 (m, 4H) 3.24–3.31 (m, 2H), 3.46–3.63 (m, 1H), 4.11–4.16 (m, 1H), 4.37–4.49 (m, 1H), 4.49–4.60 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.29–7.36 (m, 1H), 7.36–7.49 (m, 2H), 7.62 (s, 1H), 7.72–7.86 (m, 3H), 8.10–8.28 (m, 2H) ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.1 (2C), 17.6, 19.0 (2C), 25.1 (2C), 27.5, 27.6, 27.7, 28.0 (2C), 28.2 (3C), 28.5 (3C), 30.7 (4C), 35.7, 42.5 (3C), 78.1, 79.0, 82.9 (2C), 86.2, 114.4, 123.3 (2C), 124.2 (2C), 125.8 (3C), 127.4 (4C), 127.5 (2C), 127.8, 129.4 (3C), 129.6, 131.4 (2C), 131.7 (2C), 132.9, 153.2, 157.0 (2C), 157.2 (2C), 162.1 (2C), 163.1, 164.0; HRMS (FAB) calcd for $C_{63}H_{89}N_{12}O_{12}S$ (MH^+) 1237.6444; found 1237.6438.

***Cyclo*[-D-Tyr(*t*-Bu)-Arg(Boc)$_2$-ψ[C(=NH)-NH]-Arg(Pbf)-Nal-Gly-] (14e).** By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13e** was converted into the title compound **14e** (26% yield). Yellow oil; $[\alpha]^{27}_{D}$ –4.21 (*c* 0.491, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.21–1.23 (m, 4H), 1.23 (s, 9H), 1.36 (s, 6H), 1.39 (s, 9H), 1.46 (s, 9H), 1.46–1.52 (m, 4H), 1.99 (s, 3H), 2.42 (s, 3H), 2.48 (s, 3H), 2.72–2.90 (m, 4H), 2.91 (s, 2H), 3.00–3.12 (m, 2H), 3.15–3.30 (m, 2H), 3.50–3.55 (m, 1H), 3.58–3.64 (m, 1H), 4.12–4.23 (m, 1H), 4.37–4.47 (m, 2H), 4.49–4.60 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.37–7.46 (m, 2H), 7.63 (s, 1H), 7.73–7.83 (m, 2H), 8.12–8.27 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.2 (2C), 17.6, 18.9 (2C), 25.1 (2C), 27.6 (2C), 27.7, 28.0 (2C), 28.2 (3C), 28.5 (3C), 30.7 (5C), 35.7, 42.5 (2C), 78.1, 79.1, 82.9, 86.2 (2C), 114.4, 123.3 (2C), 124.2 (2C), 125.8 (2C), 127.4 (3C), 127.5 (3C), 127.8 (2C), 129.4 (3C), 129.6, 131.4 (2C), 131.7 (2C), 132.9, 153.2, 157.4 (2C), 157.5, 162.3 (2C), 163.1 (2C); HRMS (FAB) calcd for $C_{63}H_{89}N_{12}O_{12}S$ (MH^+) 1237.6444; found 1237.6445.

***Cyclo*[-D-Tyr(*t*-Bu)-ψ[C(=NH)-NH]-Arg(Pbf)-Arg(Pbf)-Nal-Gly-] (14f).** By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13f** was converted into the title compound **14f** (50% yield). Yellow oil; $[\alpha]^{26}_{D}$ –18.1 (*c* 0.338, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.18 (s, 9H), 1.23 (s, 3H), 1.25 (s, 3H), 1.34 (s, 3H), 1.35 (s, 3H), 1.36–1.40 (m, 8H), 1.98 (s, 3H), 1.99 (s, 3H), 2.40 (s, 3H), 2.42 (s, 3H), 2.45 (s, 3H), 2.49 (s, 3H), 2.81–2.89 (m, 2H), 2.91–2.95 (m, 4H), 2.94 (s, 4H), 2.97–3.05 (m, 2H), 3.51–3.60 (m, 2H), 3.75–3.95 (m, 2H), 4.26–4.31 (m, 1H), 4.55–4.65 (br s, 1H), 6.40–6.60 (br s, 2H), 6.68 (d, *J* = 7.6 Hz, 2H), 6.76–6.88 (br s, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.36–7.42 (m, 2H), 7.62 (s, 1H), 7.71–7.81 (m, 4H),

8.50–8.56 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.8 (2C), 18.1, 18.2, 19.5 (2C), 25.7, 25.8 (2C), 28.8 (3C), 28.9 (3C), 29.1 (5C), 29.2 (2C), 30.0, 30.1, 37.3, 43.0 (2C), 55.7, 78.0, 79.7, 86.8, 116.7, 116.8, 123.6 (2C), 124.9 (2C), 125.0, 125.9 (2C), 126.5, 127.8 (2C), 127.9, 128.1 (2C), 130.1, 131.9 (4C), 132.3 (4C), 133.4, 134.7, 135.5, 137.8, 153.8, 156.7 (2C), 158.0 (2C), 171.8, 173.2; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{11}S_2$ (MH^+) 1289.6215; found 1289.6215.

***Cyclo*[-Tyr(*t*-Bu)-*ψ*[C(=NH)-NH]-Arg(Pbf)-Arg(Pbf)-Nal-Gly-] (14g).** By use of a procedure identical with that described for the preparation of **14b** from **13b**, the amidoxime **13g** was converted into the title compound **14g** (36% yield). Yellow oil; $[\alpha]^{27}_D$ –11.2 (*c* 0.108, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.24 (s, 6H), 1.25 (s, 9H), 1.26–1.38 (m, 8H), 1.39 (s, 6H), 1.45–1.62 (m, 2H), 2.00 (s, 6H), 2.43 (s, 6H), 2.82–2.93 (m, 1H), 3.00–3.14 (m, 1H), 3.16–3.40 (m, 4H), 3.49–3.52 (m, 1H), 3.65–3.75 (m, 2H), 4.14 (t, *J* = 5.3 Hz, 2H), 4.48 (dd, *J* = 8.2, 5.3 Hz, 1H), 4.53 (dd, *J* = 7.8, 4.5 Hz, 2H), 6.29–6.52 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.83–6.84 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.12–7.19 (br s, 1H), 7.33–7.45 (m, 2H), 7.58–7.82 (m, 5H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 12.3, 12.4, 17.6, 17.7, 18.9, 19.1, 28.3, 28.3 (3C), 28.3 (4C), 28.6 (4C), 28.7, 29.6 (4C), 30.9, 35.9, 42.5 (2C), 49.2, 77.6, 86.4, 86.4, 116.4, 123.3, 123.5, 124.4 (2C), 124.6, 125.3, 125.9, 127.2, 127.4, 127.5, 127.6, 127.7, 129.8, 129.9, 131.5, 131.8, 132.9, 133.6, 136.7, 137.4, 149.1, 153.1, 156.1, 157.5, 157.6, 161.7 (2C), 162.4, 168.6, 169.8, 172.9, 176.3, 179.5, 179.6; HRMS (FAB) calcd for $C_{66}H_{89}N_{12}O_{11}S_2$ (MH^+) 1289.6215; found 1289.6223.

General procedure for final deprotection: *Cyclo*[-D-Tyr-Arg-Arg-Nal-*ψ*[C(=NH)-NH]-Gly-] (15b). The protected amidine **14b** (19.5 mg, 0.015 mmol) was treated with 1M TMSBr–thioanisole in TFA (1 mL) in the presence of *m*-cresol (10 μL) and 1,2-ethanedithiol (50 μL) at 4 °C for 15 min. The mixture was poured into ice-cold dry Et_2O (10 mL). The resulting powder was collected by centrifugation and the washed three times with ice-cold dry Et_2O. The crude product was purified by preparative HPLC to afford the expected peptide **15b** as a white powder (3.6 mg, 0.0050 mmol, 33% yield): $[\alpha]^{26}_D$ –67.7 (*c* 0.132, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.08–1.27 (m, 2H), 1.22–1.40 (m, 2H), 1.51–1.68 (m, 2H), 1.71–1.86 (m, 1H), 2.74 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.82 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.98 (br s, 1H), 3.35–3.52 (m, 4H), 3.94–4.07 (m, 3H), 4.12 (dd, *J* = 15.4, 7.7 Hz, 1H), 4.24 (dd, *J* = 14.2, 7.4 Hz, 1H), 4.71 (dd, *J* = 15.4, 7.2 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.80–7.40 (br s, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.44–7.54 (m, 2H), 7.55–7.63 (m, 2H), 7.74 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 7.6 Hz, 1H), 8.96 (d, *J* = 6.2 Hz, 1H), 9.03 (br s, 1H), 9.22 (s, 1H), 9.25 (s, 1H), 9.57 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 24.8 (2C),

27.9, 28.0, 34.9, 35.2, 44.4, 52.8, 52.9, 53.8 (2C), 56.3 (2C), 115.1 (2C), 125.9, 126.3, 127.0, 127.4, 127.5, 127.6, 128.1, 130.0 (2C), 130.1, 132.0, 132.9, 134.0, 156.0, 156.7, 156.8, 158.6, 167.1, 167.8, 170.8, 171.3; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3948.

***Cyclo*[-D-Tyr-Arg-Arg-Nal-Gly-*ψ*[C(=NH)-NH]-] (15a)**. By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14a** was converted into the title compound **15a** (18% yield). $[\alpha]^{26}_D$ –40.0 (*c* 0.140, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.18–1.40 (m, 4H), 1.42–1.62 (m, 4H), 2.79 (dd, *J* = 13.0, 8.9 Hz, 1H), 2.89 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.95–3.07 (m, 5H), 3.17 (dd, *J* = 13.2, 8.2 Hz, 1H), 3.74–3.82 (m, 2H), 4.05–4.17 (m, 2H), 4.31 (dd, *J* = 14.2, 8.0 Hz, 1H), 4.42 (dd, *J* = 14.4, 7.2 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 2H), 6.73–7.50 (br s, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.44–7.51 (m, 2H), 7.53–7.59 (m, 2H), 7.63 (br s, 1H), 7.78–7.89 (m, 4H), 8.33–8.39 (m, 1H), 8.44 (d, *J* = 7.2 Hz, 1H), 8.62 (d, *J* = 5.2 Hz, 1H), 8.85 (d, *J* = 7.0 Hz, 1H), 9.10 (s, 1H), 9.25 (s, 1H), 9.60 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 25.0 (2C), 29.1 (2C), 31.3 (2C), 52.9, 56.6, 58.9 (2C), 109.5 (2C), 112.4, 115.4, 125.1, 126.1, 127.3, 127.3, 127.5, 127.7, 127.7, 128.9, 130.1, 131.8, 132.9, 135.6, 156.5, 156.7, 156.9, 169.7, 171.5, 172.3, 174.3, 175.2, 176.4, 177.1; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3947.

***Cyclo*[-D-Tyr-Arg-Arg-D-Nal-*ψ*[C(=NH)-NH]-Gly-] (15c).** By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14c** was converted into the title compound **15c** (33% yield). $[\alpha]^{26}_D$ +18.4 (*c* 0.126, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.12–1.21 (m, 1H), 1.21–1.28 (m, 2H), 1.28–1.42 (m, 2H), 1.45–1.56 (m, 1H), 1.58–1.66 (m, 1H), 1.66–1.76 (m, 1H), 2.70–2.85 (m, 2H), 3.15–3.29 (m, 3H), 3.86 (dd, *J* = 15.7, 4.4 Hz, 1H), 3.97–4.04 (m, 1H), 4.04–4.14 (m, 2H), 4.21 (dd, *J* = 14.6, 7.3 Hz, 1H), 4.84 (dd, *J* = 14.6, 7.9 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 2H), 6.70–7.50 (br s, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 5.9 Hz, 1H), 7.39 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.46–7.53 (m, 3H), 7.56 (t, *J* = 5.9 Hz, 1H), 7.72 (s, 1H), 7.82–7.89 (m, 3H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 6.2 Hz, 1H), 8.72 (d, *J* = 6.4 Hz, 1H), 8.89 (s, 1H), 9.17 (s, 1H), 9.25 (s, 1H), 9.48 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 24.9, 25.0 (2C), 28.4 (2C), 28.5, 53.1 (2C), 53.5 (2C), 53.5, 54.1, 56.2, 115.0 (2C), 126.3, 127.1, 127.2, 127.5, 127.5 (2C), 128.0, 130.0 (2C), 132.9 (2C), 133.2 (2C), 156.0, 156.7, 156.8, 166.6, 168.6, 170.0, 171.3, 171.8; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3948.

***Cyclo*[-D-Tyr-Arg-Arg-*ψ*[C(=NH)-NH]-Nal-Gly-] (15d).** By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14d** was converted into the title

compound **15d** (18% yield). $[\alpha]^{26}_{D}$ –60.0 (*c* 0.101, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.15–1.26 (m, 1H), 1.28–1.49 (m, 4H), 1.52–1.74 (m, 3H), 2.68–2.81 (m, 2H), 2.98–3.16 (m, 3H), 3.43–3.53 (m, 1H), 3.65 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.79–3.87 (m, 1H), 4.23 (dd, *J* = 14.0, 6.5 Hz, 1H), 4.54 (dd, *J* = 14.5, 7.7 Hz, 1H), 4.76 (dd, *J* = 16.5, 7.7 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.88–7.40 (br s, 4H), 7.39–7.53 (m, 3H), 7.56–7.62 (m, 1H), 7.70–7.76 (m, 1H), 7.76 (s, 1H), 7.79–7.89 (m, 3H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.36 (d, *J* = 4.4 Hz, 1H), 8.68 (t, *J* = 5.7 Hz, 1H), 9.20 (s, 1H), 9.31 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 25.0 (2C), 26.1, 27.5, 29.6, 35.9, 37.2, 43.7, 50.2, 54.7, 54.9, 56.5 (2C), 115.0 (2C), 125.8, 126.2, 126.9, 127.4, 127.5, 127.6, 127.9, 128.1, 130.1 (2C), 132.0, 132.8, 133.0, 155.9, 156.8, 156.8, 158.3, 165.8, 168.7, 171.1, 171.5; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3948.

***Cyclo*[-D-Tyr-Arg-ψ[C(=NH)-NH]-Arg-Nal-Gly-] (15e).** By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14e** was converted into the title compound **15e** (53% yield). $[\alpha]^{26}_{D}$ –41.5 (*c* 0.133, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.23 (s, 1H), 1.26–1.37 (m, 2H), 1.38–1.47 (m, 1H), 1.52–1.68 (m, 2H), 1.73–1.83 (m, 1H), 2.71–2.82 (m, 2H), 3.01–3.13 (m, 4H), 3.17 (dd, *J* = 13.4, 8.2 Hz, 1H), 3.46 (dd, *J* = 15.7, 4.7 Hz, 1H), 3.76 (dd, *J* = 16.0, 7.3 Hz, 1H), 4.15–4.22 (m, 1H), 4.25–4.34 (m, 2H), 4.41 (dd, *J* = 14.6, 7.3 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.91–7.30 (br s, 4H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.44–7.55 (m, 3H), 7.61–7.74 (m, 3H), 7.81–7.90 (m, 3H), 8.27–8.34 (m, 1H), 8.52 (d, *J* = 7.0 Hz, 1H), 8.59 (d, *J* = 3.6 Hz, 1H), 8.84 (d, *J* = 9.0 Hz, 1H), 9.20 (s, 1H), 9.23 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 24.8 (2C), 28.1 (2C), 28.5 (2C), 52.2, 53.2, 54.4 (2C), 115.0 (2C), 126.1, 126.2, 126.9, 127.3, 127.4, 127.5 (2C), 127.8, 130.0 (2C), 131.8 (2C), 131.9, 132.9, 155.9 (2C), 156.7 (2C), 167.4, 168.0, 168.1, 168.9, 170.1, 171.4; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3944.

***Cyclo*[-D-Tyr-ψ[C(=NH)-NH]-Arg-Arg-Nal-Gly-] (15f).** By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14f** was converted into the title compound **15f** (40% yield). $[\alpha]^{26}_{D}$ –100.9 (*c* 0.114, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.68–0.79 (m, 1H), 0.81–0.93 (m, 1H), 1.24–1.41 (m, 2H), 1.54–1.66 (m, 1H), 1.74–1.85 (m, 1H), 1.89–1.99 (m, 1H), 2.80–2.98 (m, 3H), 2.98–3.13 (m, 3H), 3.20–3.26 (m, 1H), 3.80 (dd, *J* = 16.4, 6.1 Hz, 1H), 3.91 (dd, *J* = 16.4, 6.1 Hz, 1H), 3.93–4.02 (m, 1H), 4.17 (dd, *J* = 15.8, 7.9 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 2H), 6.50–7.50 (br s, 4H), 7.00 (d, *J* = 8.3 Hz, 2H), 7.38–7.50 (m, 3H), 7.51–7.57 (m, 1H), 7.62 (br s, 1H), 7.72 (s, 1H), 7.86 (m, 3H), 7.92 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 9.10 (s, 1H), 9.26 (s, 1H) , 9.38 (s, 1H), 9.45 (s, 1H), 9.76 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR

(125 MHz, DMSO-d_6) δ 25.0 (2C), 29.1 (2C), 31.3 (2C), 52.9, 56.6, 58.9 (2C), 109.5 (2C), 112.4, 115.4, 125.1, 126.1, 127.3, 127.3, 127.5, 127.7, 127.7, 128.9, 130.1, 131.8, 132.9, 135.6, 156.5, 156.7, 156.9, 169.7, 171.5, 172.3, 174.3, 175.2, 176.4, 177.1; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3939.

***Cyclo*[-Tyr-*ψ*[C(=NH)-NH]-Arg-Arg-Nal-Gly-] (15g).** By use of a procedure identical with that described for the preparation of **15b** from **14b**, the protected amidine **14g** was converted into the title compound **15g** (32% yield). $[\alpha]^{26}_D$ +61.6 (*c* 0.160, DMSO); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.12–1.22 (m, 1H), 1.23–1.32 (m, 1H), 1.37–1.50 (m, 2H), 1.53–1.64 (m, 2H), 1.70–1.80 (m, 1H), 1.85–1.96 (m, 1H), 2.87–2.96 (m, 2H), 2.99 (dd, *J* = 14.2, 9.0 Hz, 1H), 3.07 (dd, *J* = 13.6, 10.2 Hz, 1H), 3.11–3.18 (m, 1H), 3.85 (dd, *J* = 15.0, 7.5 Hz, 1H), 3.98 (dd, *J* = 15.0, 5.8 Hz, 1H), 4.30 (dd, *J* = 15.3, 9.2 Hz, 1H), 4.42 (td, *J* = 9.1, 5.0 Hz, 1H), 4.68 (dd, *J* = 15.1, 6.5 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 6.80–7.40 (br s, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.43–7.50 (m, 2H), 7.53 (t, *J* = 5.5 Hz, 1H), 7.67 (s, 1H), 7.74–7.88 (m, 3H), 8.02 (d, *J* = 4.9 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 8.40 (d, *J* = 6.9 Hz, 1H), 8.50 (d, *J* = 6.4 Hz, 1H), 8.91 (d, *J* = 9.5 Hz, 1H), 9.13 (s, 1H), 9.39 (s, 1H), 9.63 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 25.1 (2C), 27.8 (2C), 36.1, 36.3, 53.7, 54.4, 56.4, 57.7, 115.3 (2C), 125.5, 126.0, 127.4, 127.7 (2C), 130.1 (3C), 131.8 (2C), 132.9 (3C), 135.9, 156.4, 156.7, 156.9 (2C), 159.0, 167.4, 168.3, 169.5, 170.8, 171.0; HRMS (FAB) calcd for $C_{36}H_{49}N_{12}O_5$ (MH^+) 729.3949; found 729.3939.

[^{125}I]-SDF-1 binding and displacement. Membrane extracts were prepared from HEK293 cell lines expressing CXCR4. For ligand binding, 50 μL of the inhibitor, 25 μL of [^{125}I]-SDF-1α (0.3 nM, Perkin-Elmer Life Sciences) and 25 μL of the membrane/beads mixture [7.5 μg/well of membrane, 0.5 mg/well of PVT WGA beads (Amersham)] in assay buffer (25 mM HEPES pH 7.4, 1 mM $CaCl_2$, 5 mM $MgCl_2$, 140 mM NaCl, 250 mM sucrose, 0.5% BSA) were incubated in the wells of an Optiplate places (Perkin-Elmer Life Sciences) at room temperature for 1 h. The bound radioactivity was counted for 1 min/well in a TopCount (Packard). Inhibitory activity of the test compounds was determined based on the inhibition of [^{125}I]-SDF-1 binding to the receptors (IC_{50}, triplicate experiments, Figure S4 and Table 1) .

Determination of anti-HIV activity. The peptide sensitivity of three HIV-1 strains was determined by the MAGI assay. The target cells (HeLa-CD4/CCR5-LTR-β-gal; 104 cells/well) were plated in 96-well flat microtiter culture plates. On the following day, the cells were inoculated with the HIV-1

(60 MAGI U/well, giving 60 blue cells after 48 h of incubation) and cultured in the presence of various concentrations of the drugs in fresh medium. Forty-eight hours after viral exposure, all the blue cells strained with X-Gal (5-bromo-4-chloro-3-indolyl-β-D-galactopyranoside) were counted in each well. The activity of test compounds was determined as the concentration that blocked HIV-1 replication by 50% (50% effective concentration [EC_{50}]). EC_{50} was determined by using the following formula:

$$EC_{50} = 10^{\wedge}[\log(A/B) \times (50 - C)/(D - C) + \log(B)],$$

wherein

A: of the two points on the graph which bracket 50% inhibition, the higher concentration of the test compound,

B: of the two points on the graph which bracket 50% inhibition, the lower concentration of the test compound,

C: inhibitory activity (%) at the concentration B,

D: inhibitory activity (%) at the concentration A.

References

(1) Van Rompaey, K.; Van den Eynde, I.; De kimpe, N.; Tourwe, D. A versatile synthesis of 2-substituted 4-amino-1,2,4,5-tetrahydro-2-benzadepine-3-ones. *Tetrahedron* **2003**, *59*, 4421–4432.

Figure S1. HPLC analysis of (a) compound **14b**; (b) compound **14c**; (c) the mixture of compounds **14b** and **14c**. *HPLC conditions*: a linear gradient of MeCN (50-70% over 20 min), detection at 220 nm.

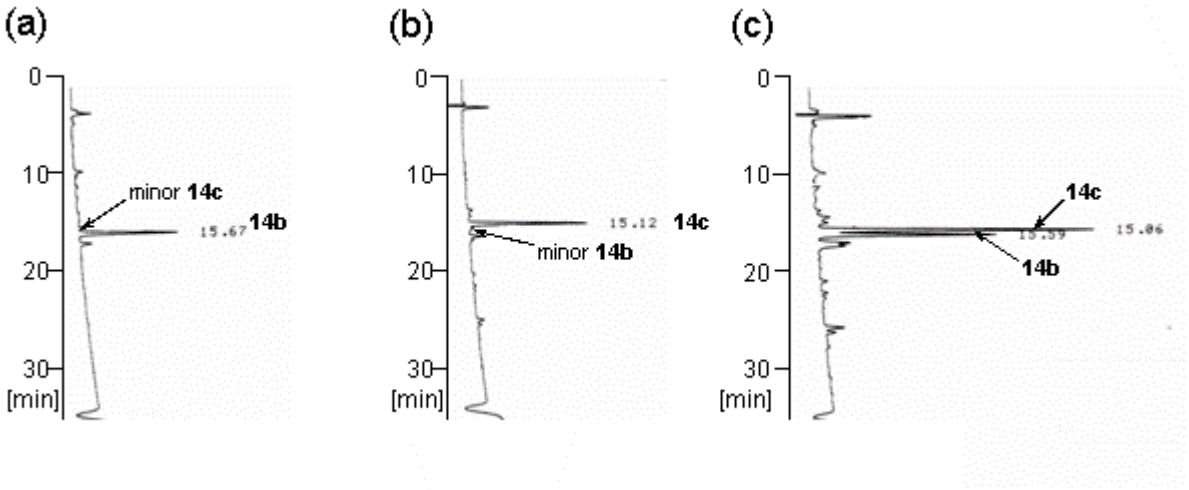


Figure S2. HPLC analysis of (d) compound **13f**; (e) compound **13g**; (f) the mixture of compounds **13f** and **13g**. *HPLC conditions*: a linear gradient of MeCN (50-70% over 20 min), detection at 220 nm.

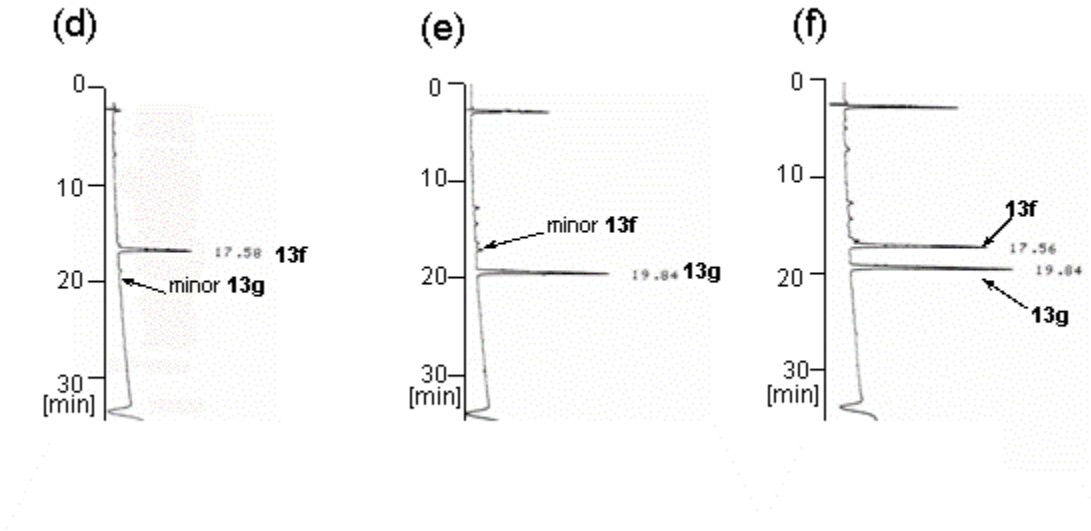


Figure S3. HPLC analysis of compounds **15a**–**g**. *HPLC conditions*: a linear gradient of MeCN (20-35% over 15 min), detection at 220 nm.

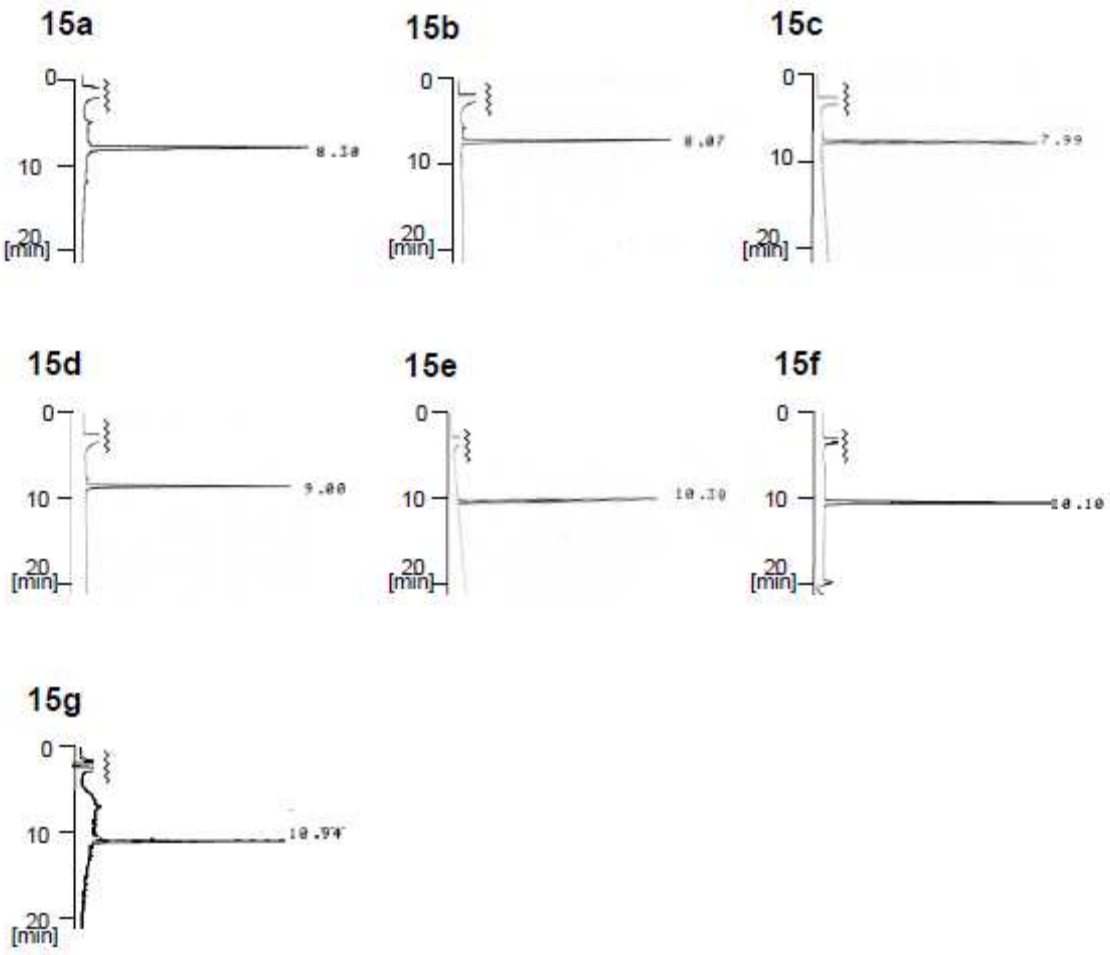
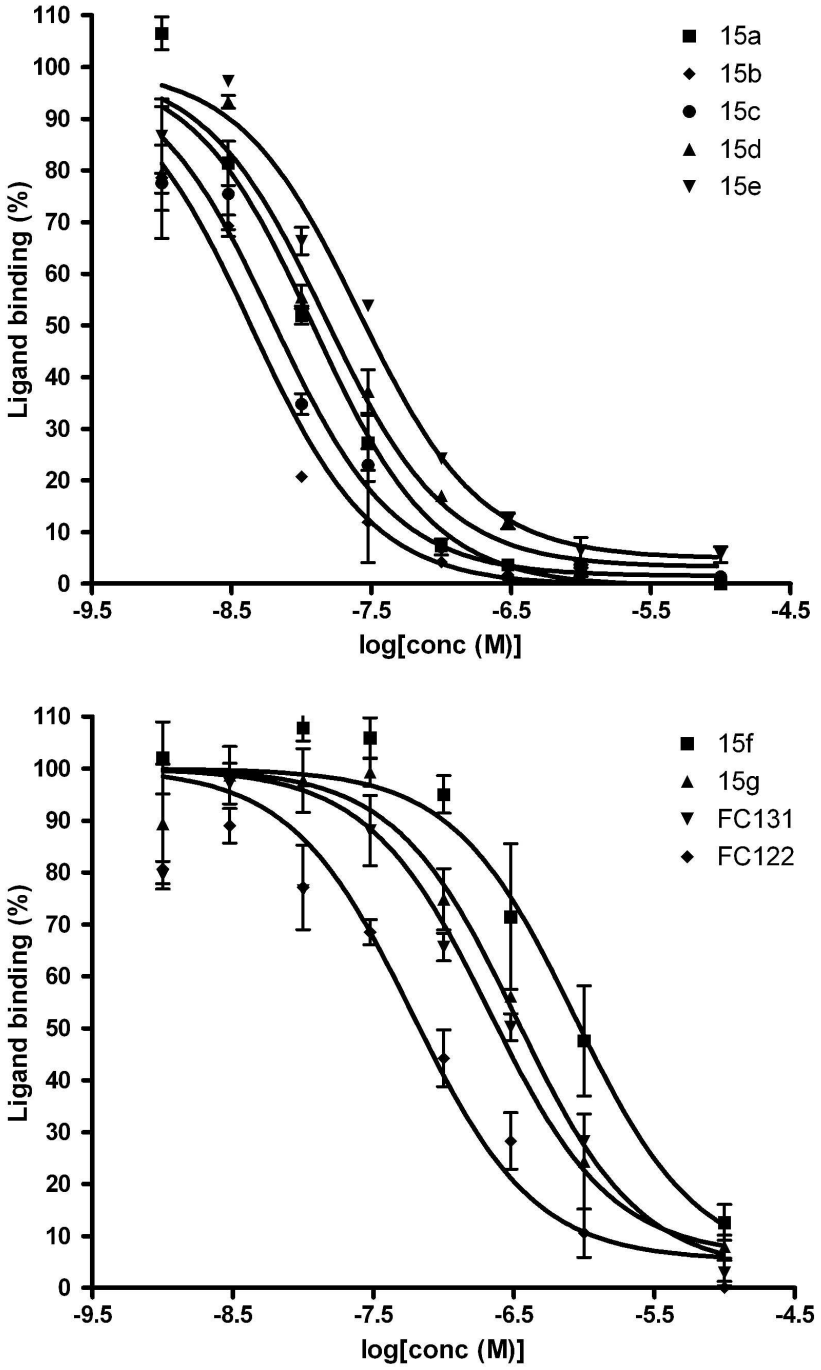


Figure S4. The representative dose-response curves of the [^{125}I]-SDF-1 binding inhibition by FC131 analogs **15a**–**g** (n = 2). The same experiments were performed in triplicate (for IC_{50}, see Table 1).



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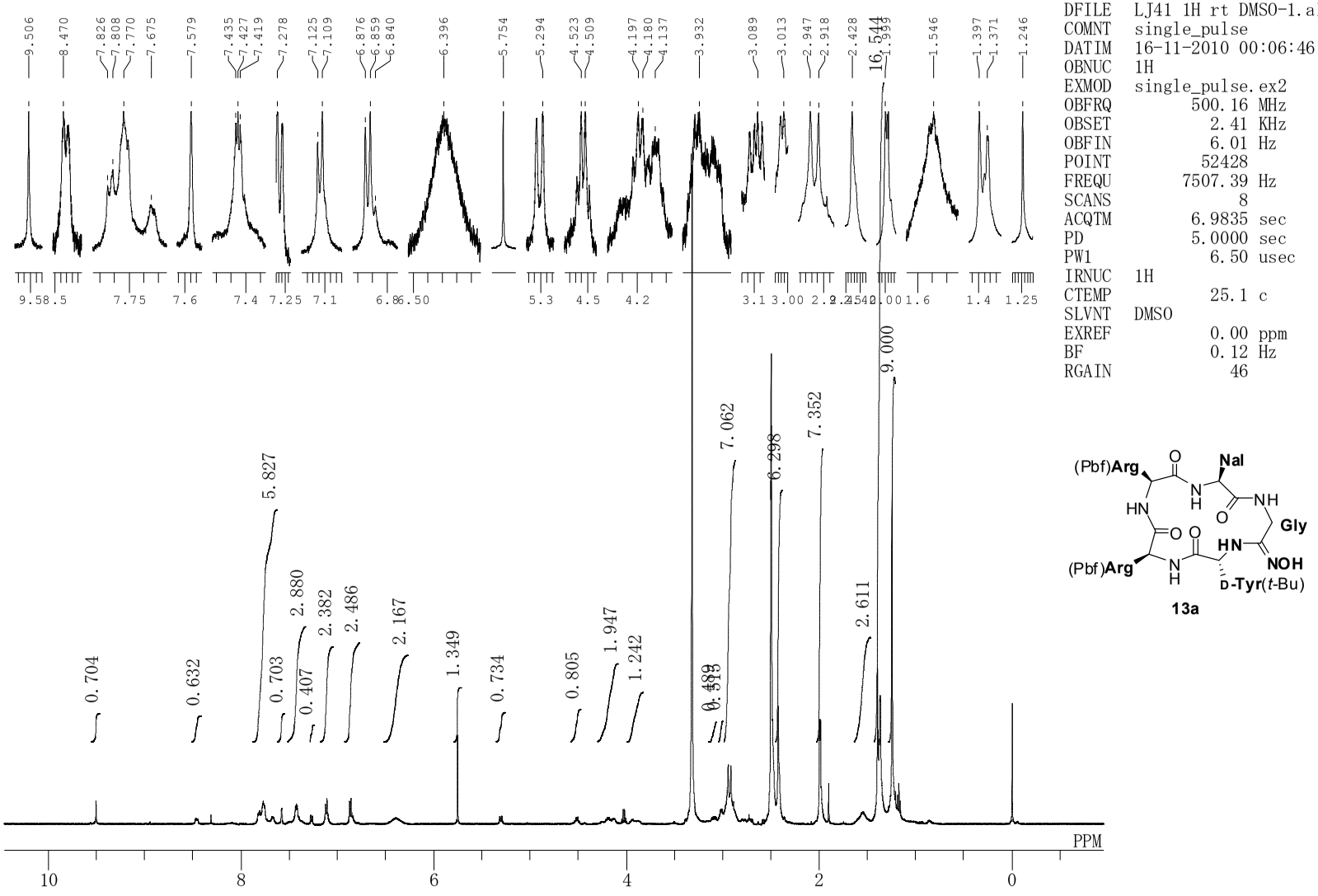
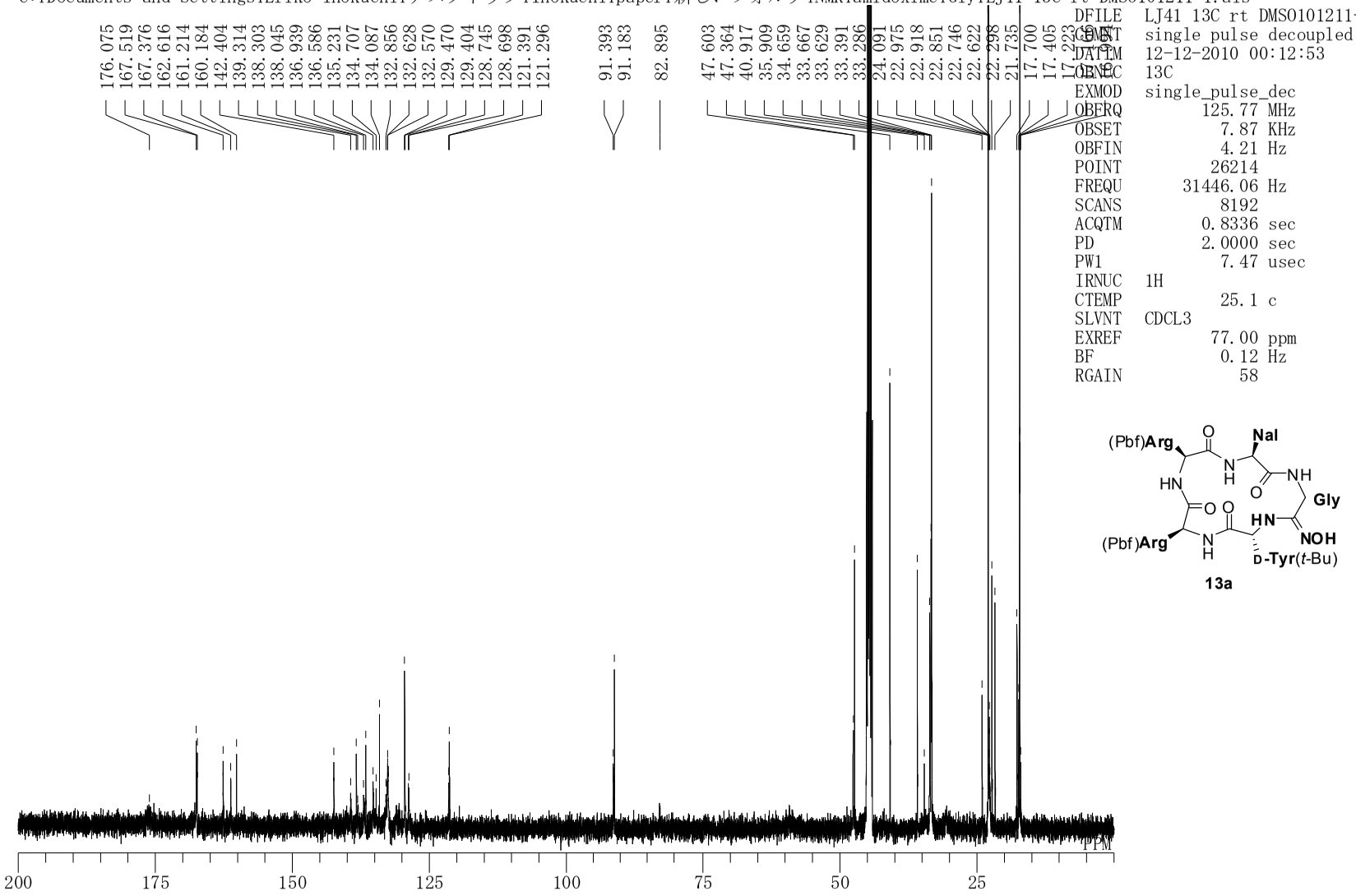


13a

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥Gly¥LJ41 13C rt DMSO101211-1.als



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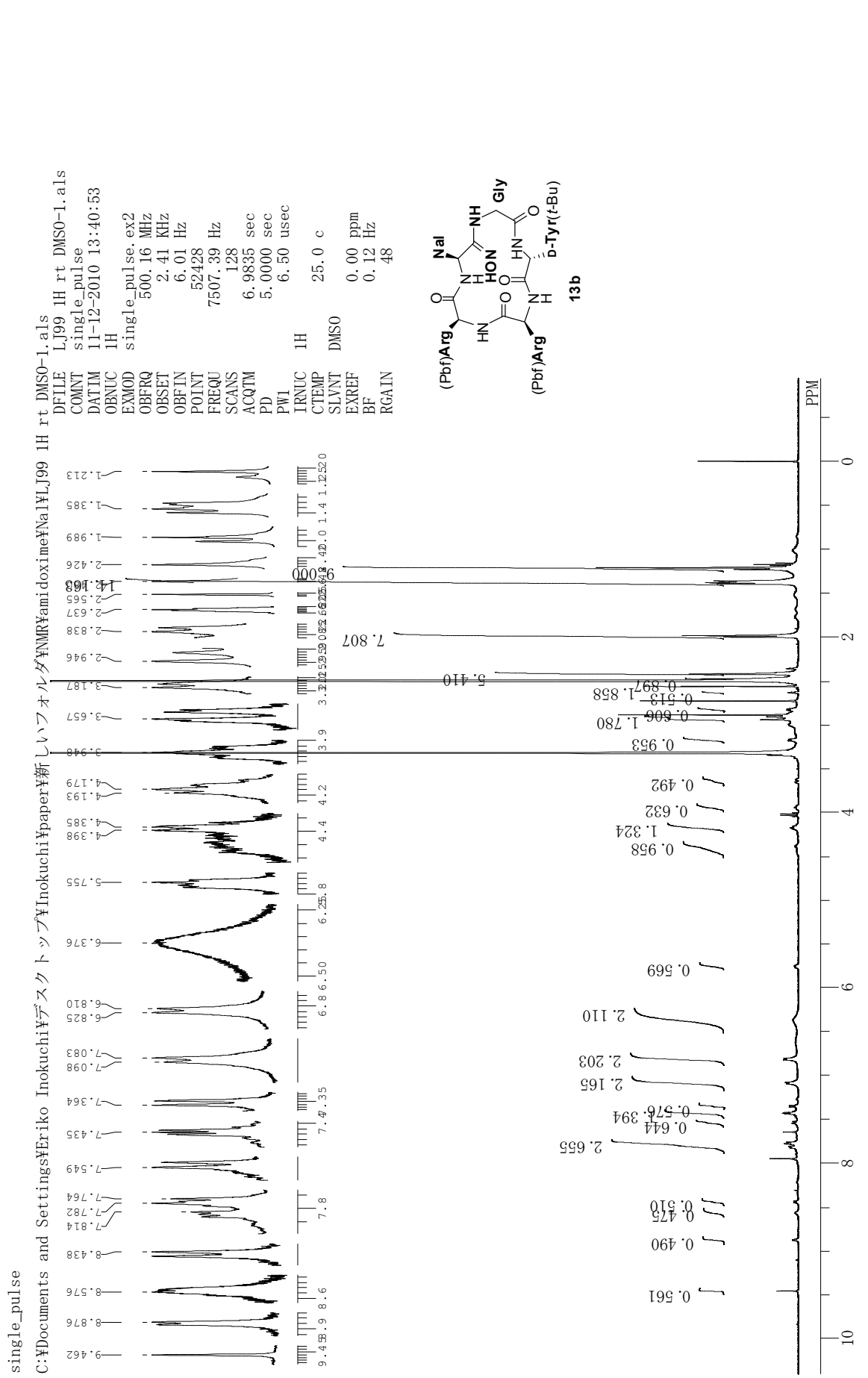
RGAIN	58

13a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CTEMP 25.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
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Nal
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Gly
D-Tyr(t-Bu)
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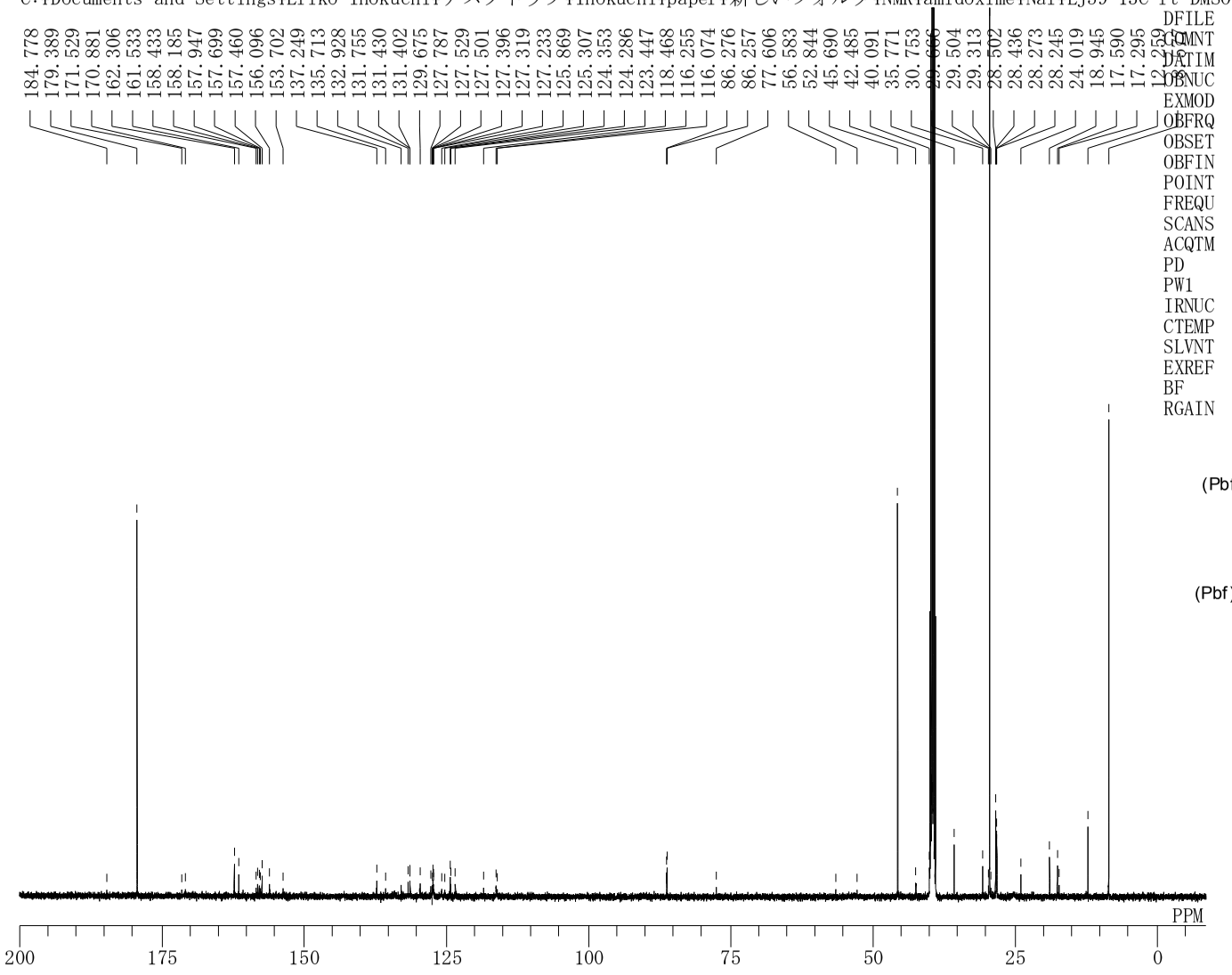
13b
PPM

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥Nal¥LJ59 13C rt DMSO101127-1.als



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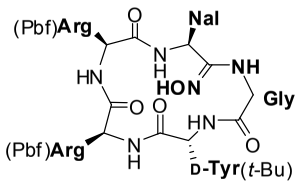
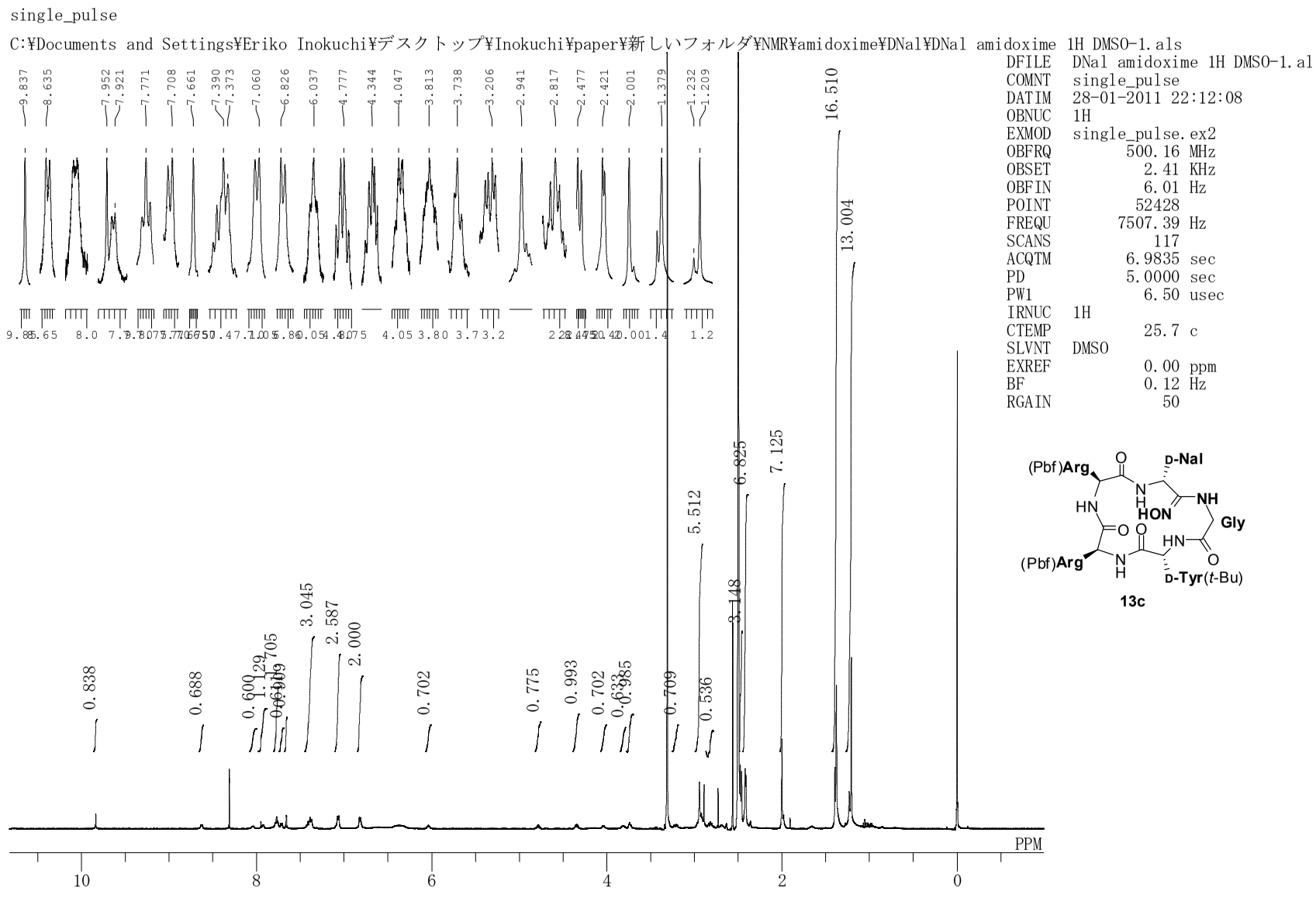
RGAIN	58



13b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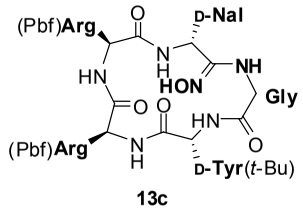
single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥DNal¥DNal amidoxime 13C DMSO 110201-2-1.als

179.427 172.464 171.921 171.539 169.870 162.354 157.499 155.982 153.664 151.127 137.287 136.323 134.196 132.899 131.697 131.478 131.430 131.364 129.513 128.025 127.529 127.472 127.405 127.357 127.291 125.831 125.240 124.353 124.315 123.571 116.293 86.295 79.170 77.663 55.162 54.590 48.619 42.485 35.799 30.792 29.523 29.008 28.712 28.512 28.464 28.283 27.701 25.049 18.964 17.610 12.287

DFILE	DNal amidoxime 13C DMSO 110
COMNT	single pulse decoupled gate
DATIM	02-02-2011 00:40:18
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	5273
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	54



13c

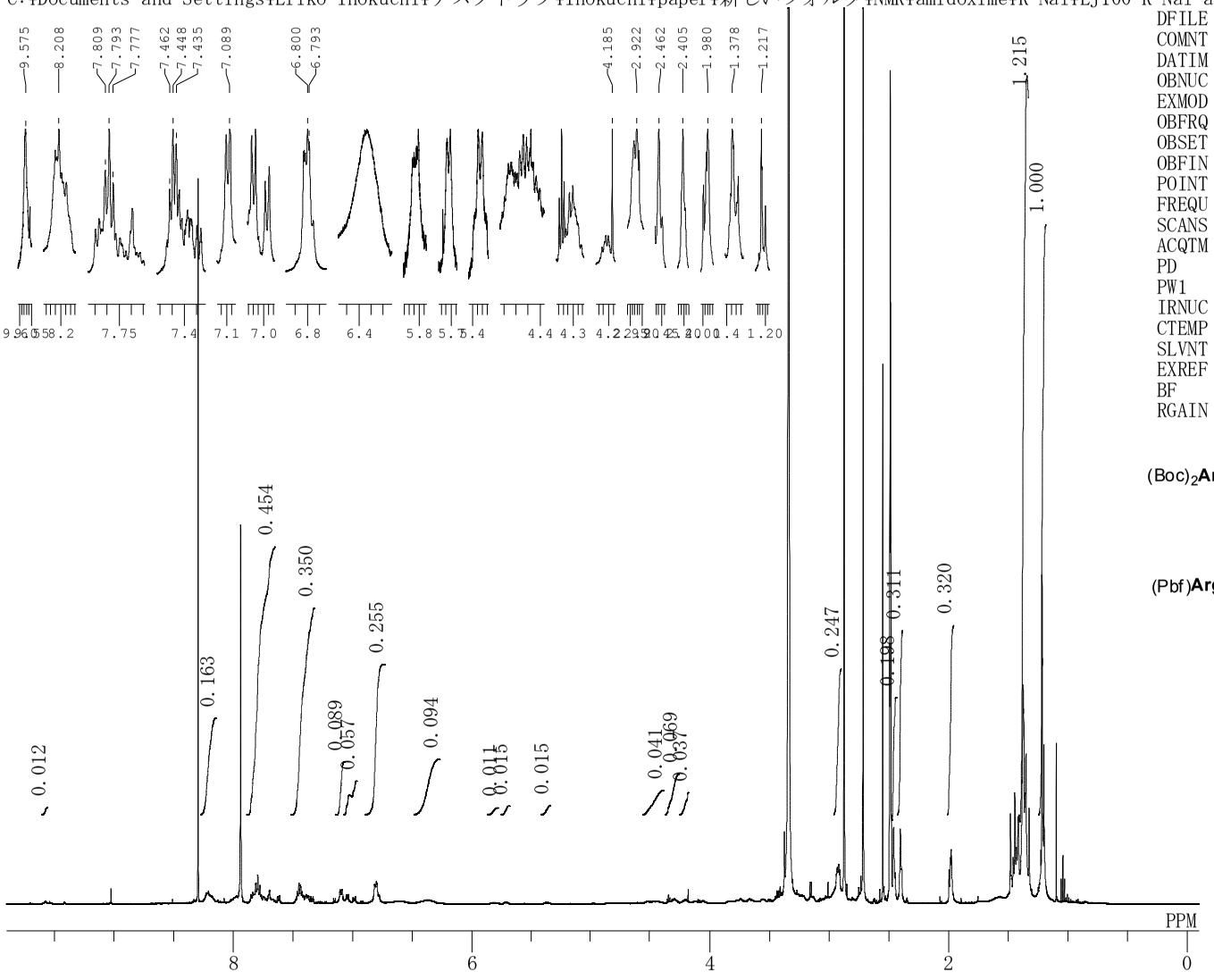
PPM

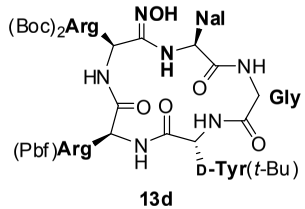
200 175 150 125 100 75 50 25 0

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥R-Nal¥LJ100 R-Nal amidoxime 1H rt DMSO-2.als

DFILE	LJ100 R-Nal amidoxime 1H rt
COMNT	single_pulse
DATIM	06-01-2011 15:17:13
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	52428
FREQU	7507.39 Hz
SCANS	200
ACQTM	6.9835 sec
PD	5.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	40

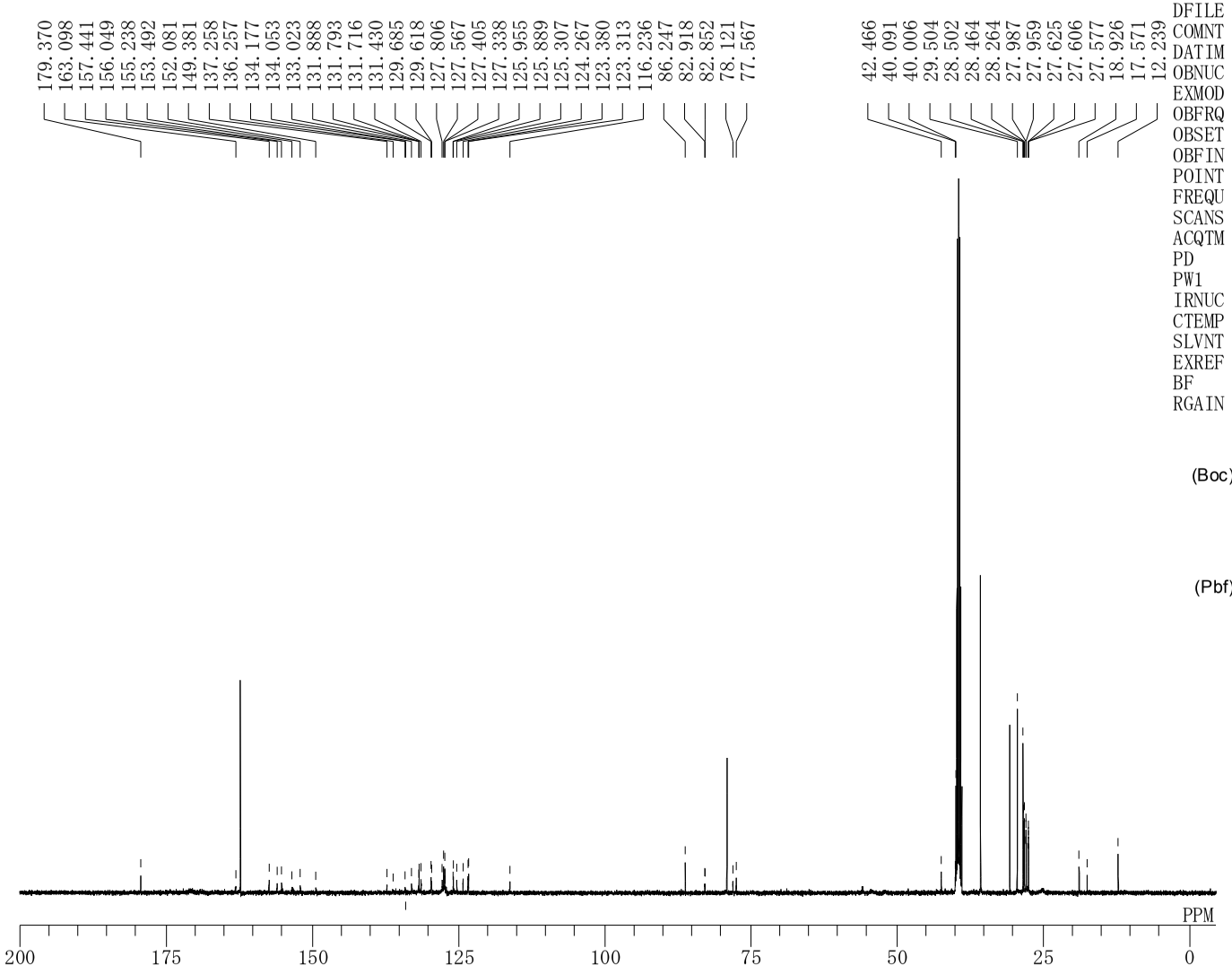




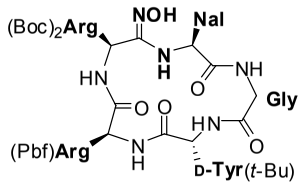
13d

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥R-Nal¥LJ100 R-Nal amidoxime 13C rt DMSO-1.als



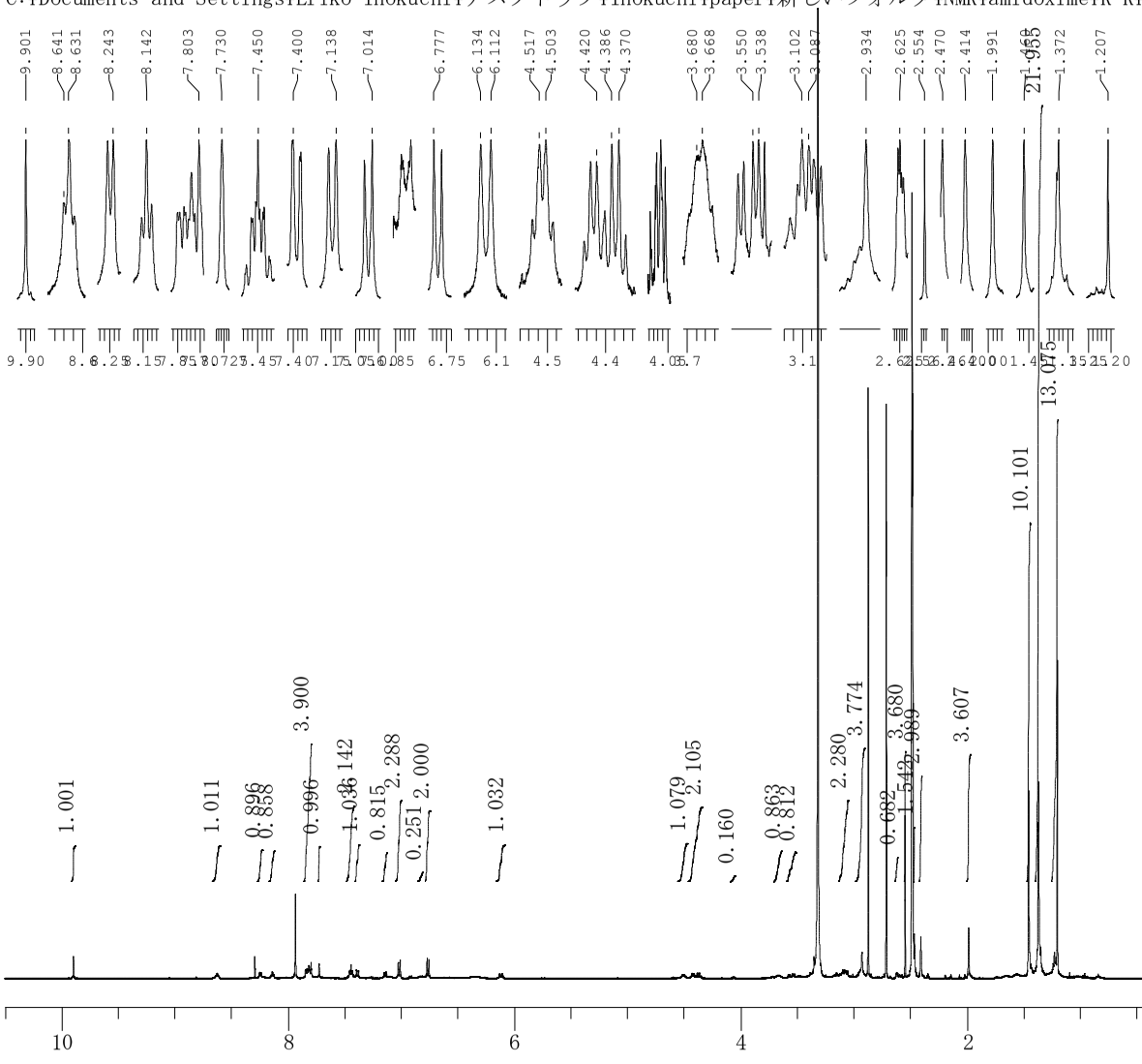
DFILE	LJ100 R-Nal amidoxime 13C r
COMNT	single pulse decoupled gate
DATIM	29-12-2010 09:49:19
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	14435
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	26.4 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	58



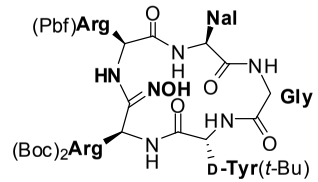
13d

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥R-R¥LJ101 R-R amidoxime 1H rt DMSO110104-1.als



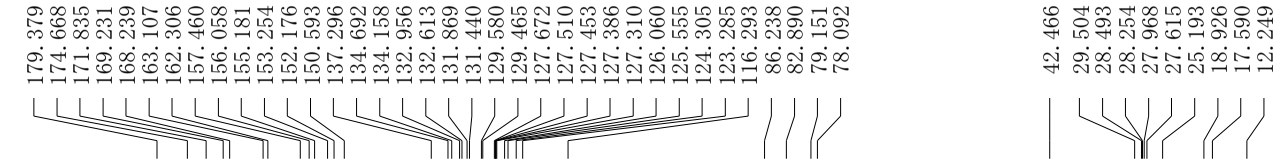
DFILE	LJ101 R-R amidoxime 1H rt D	
COMNT	single_pulse	
DATIM	04-01-2011 22:21:40	
OBNUC	1H	
EXMOD	single_pulse.ex2	
OBFRQ	500.16	MHz
OBSET	2.41	KHz
OBFIN	6.01	Hz
POINT	52428	
FREQU	7507.39	Hz
SCANS	256	
ACQTM	6.9835	sec
PD	5.0000	sec
PW1	6.50	usec
IRNUC	1H	
CTEMP	25.6	c
SLVNT	DMSO	
EXREF	2.49	ppm
BF	0.12	Hz
RGAIN	44	



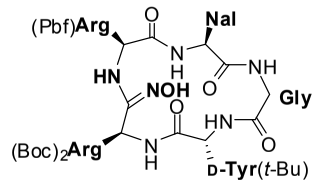
13e

single pulse decoupled gated NOE

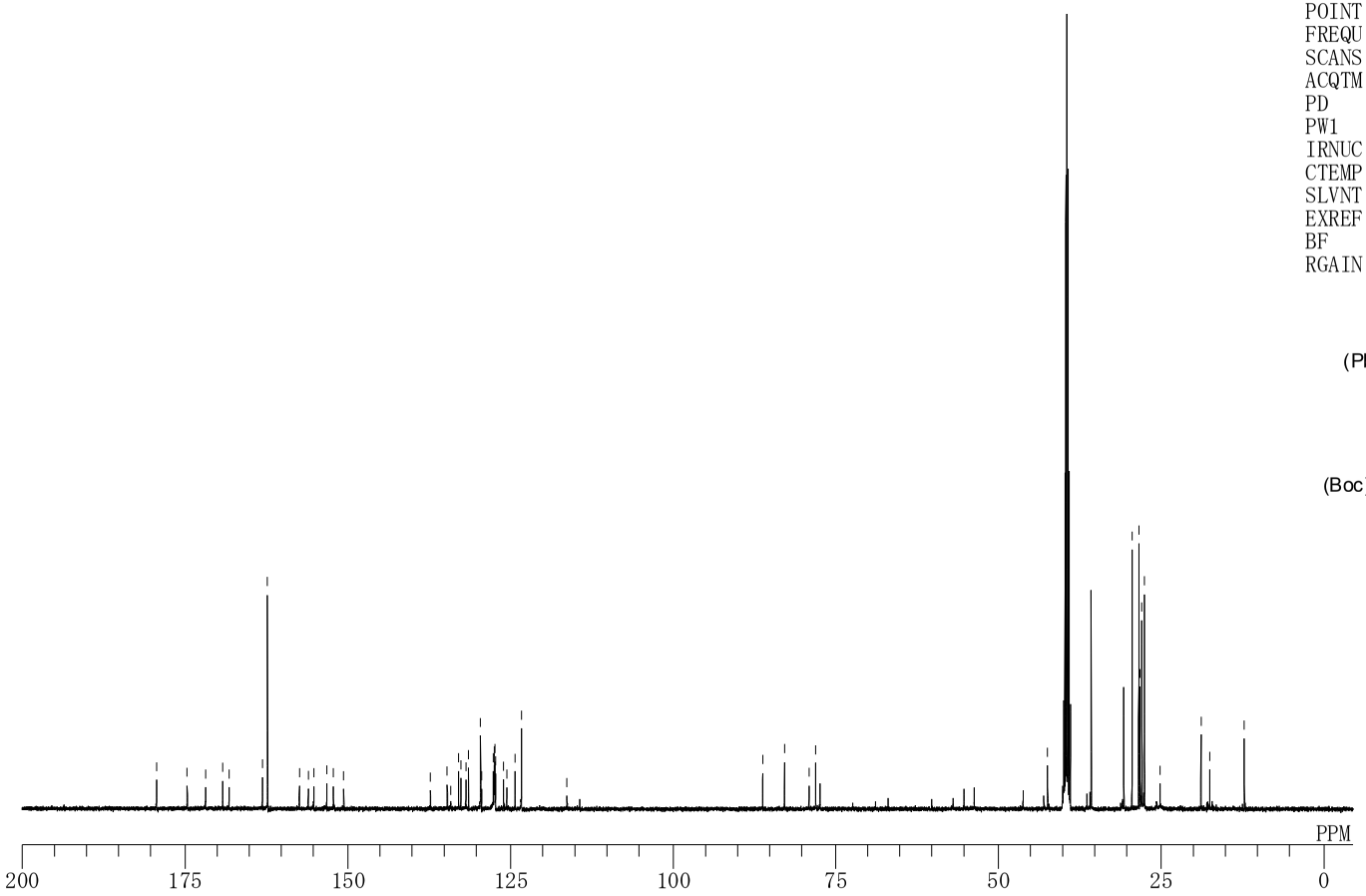
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥R-R¥LJ101 R-R amidoxime 13C rt DMSO-1.als

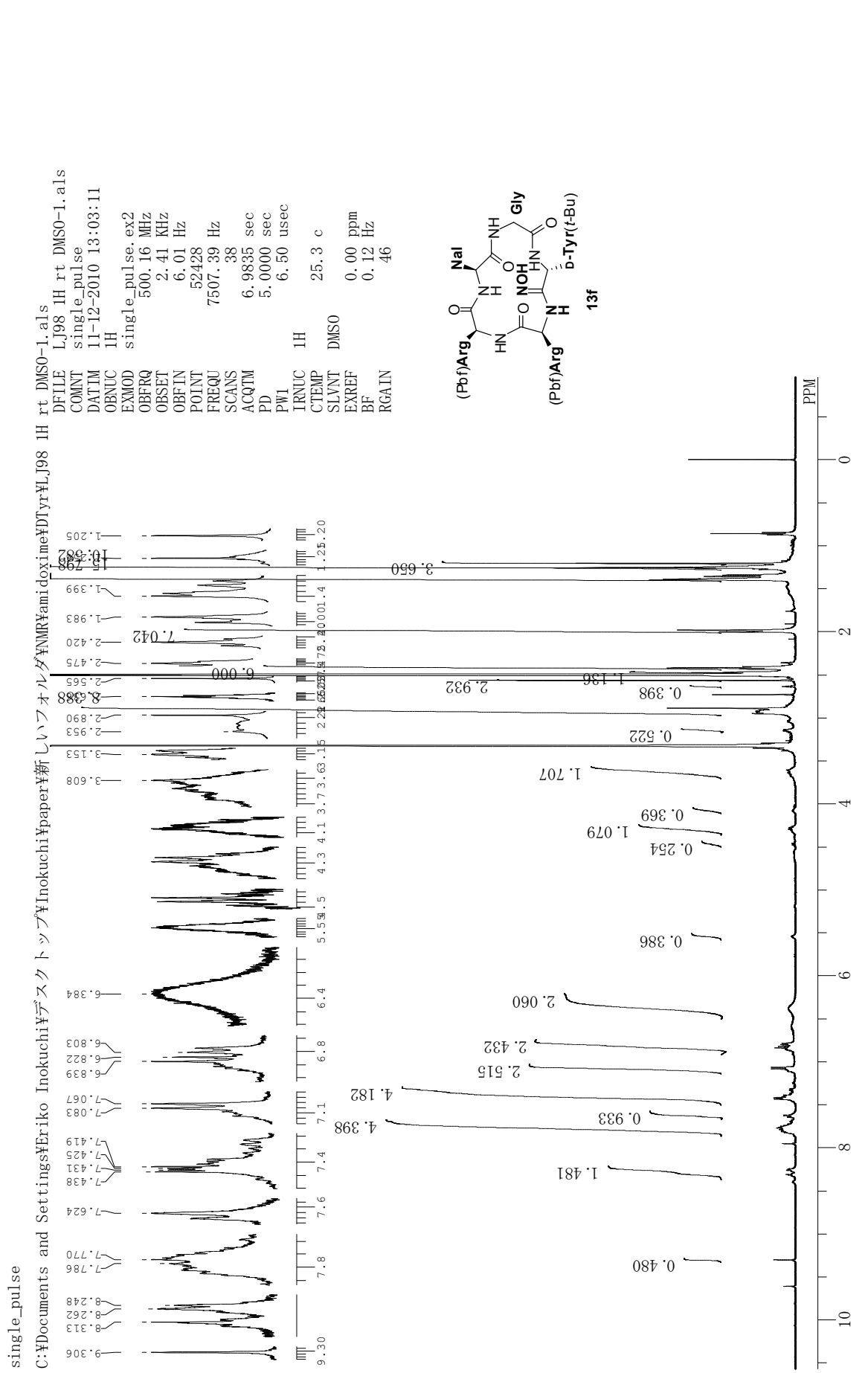


DFILE	LJ101 R-R amidoxime 13C rt	
COMNT	single pulse decoupled gate	
DATIM	30-12-2010 10:12:46	
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	125.77	MHz
OBSET	7.87	KHz
OBFIN	4.21	Hz
POINT	26214	
FREQU	31446.06	Hz
SCANS	14922	
ACQTM	0.8336	sec
PD	2.0000	sec
PW1	7.47	usec
IRNUC	1H	
CTEMP	26.2	c
SLVNT	DMSO	
EXREF	39.50	ppm
BF	0.12	Hz
RGAIN	58	



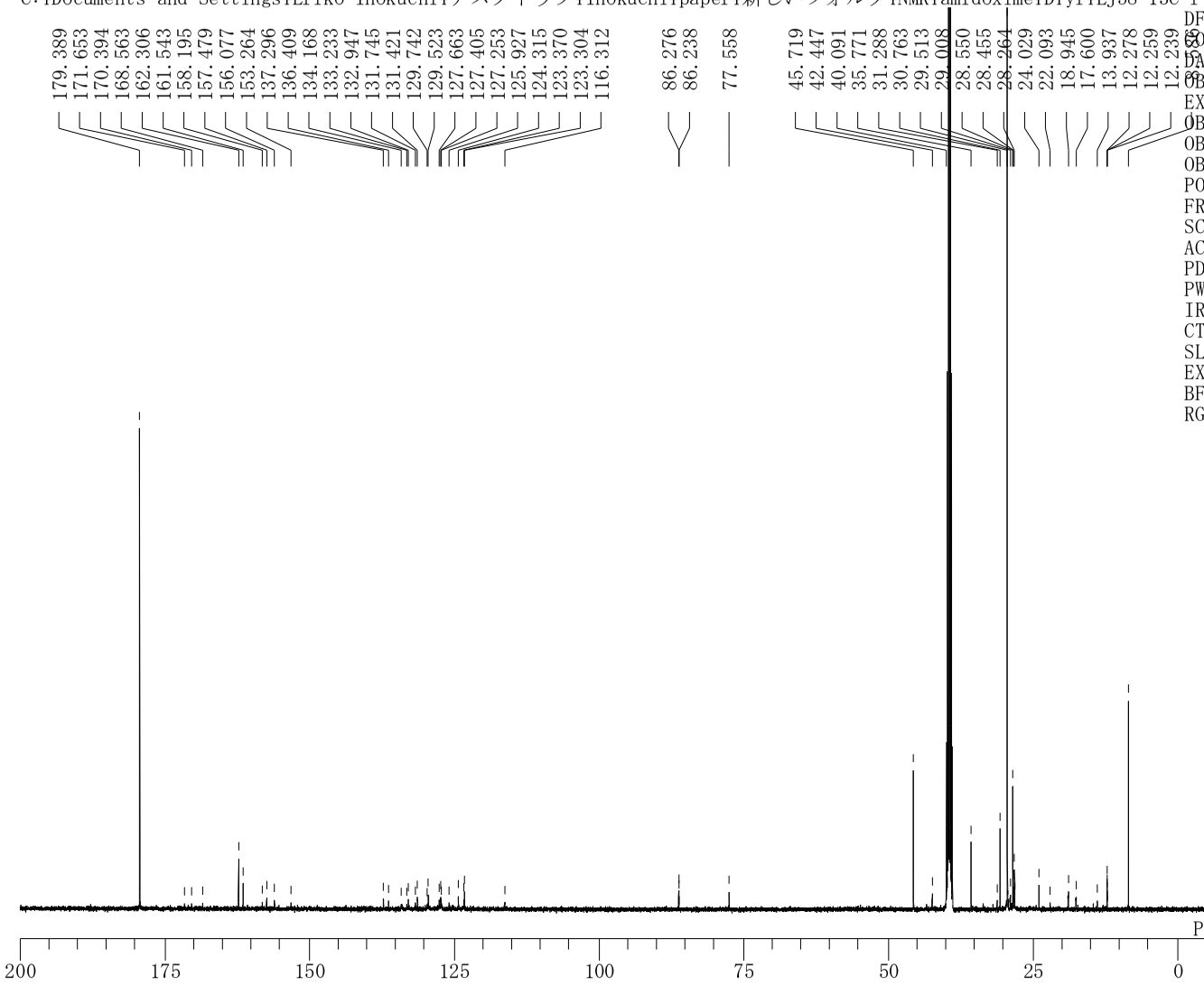
13e



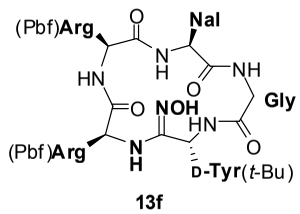

single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥DTyr¥LJ98 1H rt DMSO-1.als
DFILE LJ98 1H rt DMSO-1.als
COMNT single_pulse
DATIM 11-12-2010 13:03:11
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 38
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46
(Pbf)Arg
Nal
NOH
Gly
(Pbf)Arg
D-Tyr(t-Bu)
13f
PPM

single pulse decoupled gated NOE

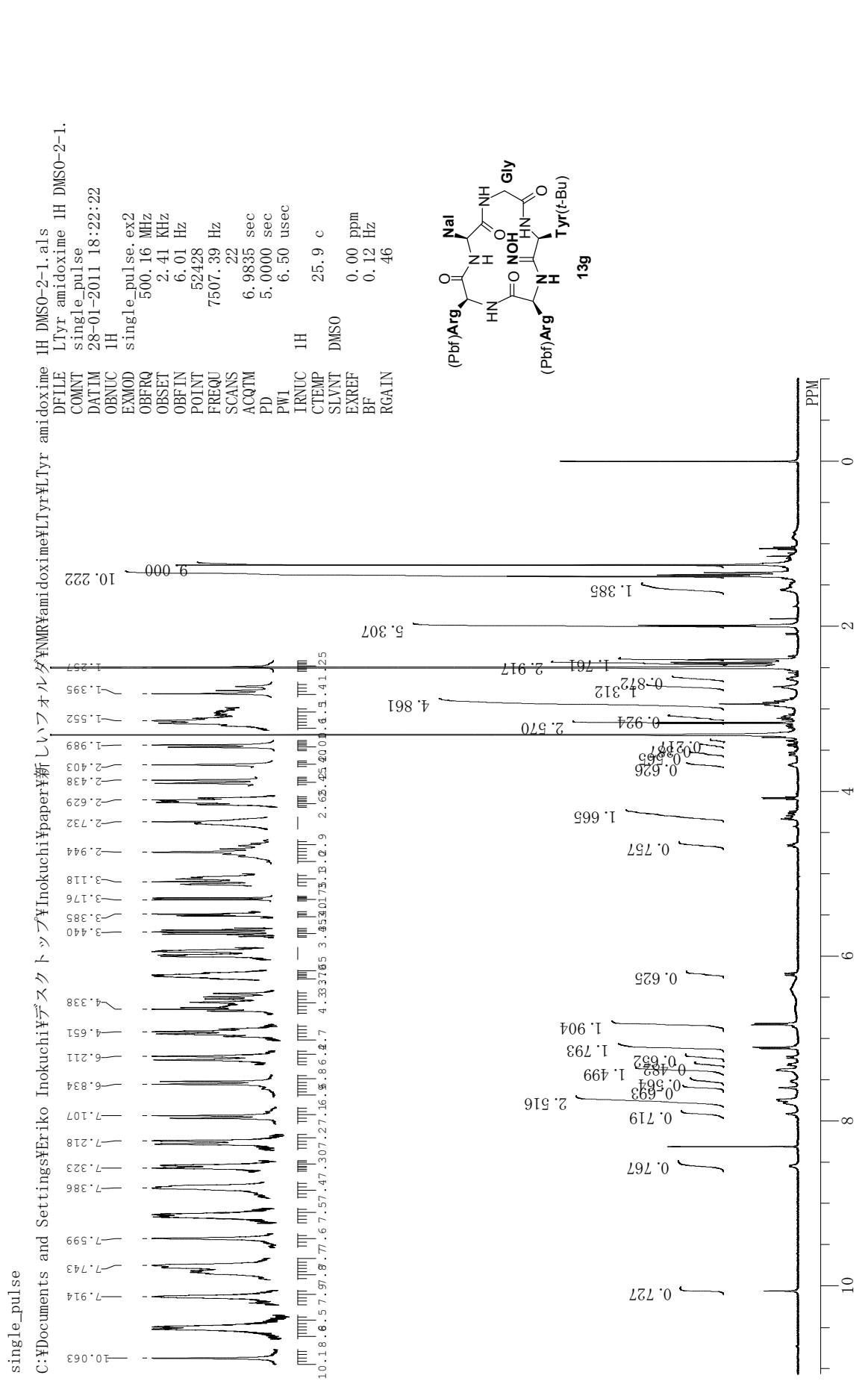
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥DTyr¥LJ58 13C rt DMSO101126-1.als



DFILE LJ58 13C rt DMSO101126-1.al
COMNT single pulse decoupled gate
DATIM 27-11-2010 08:27:36
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.06 Hz
SCANS 12288
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.73 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 56

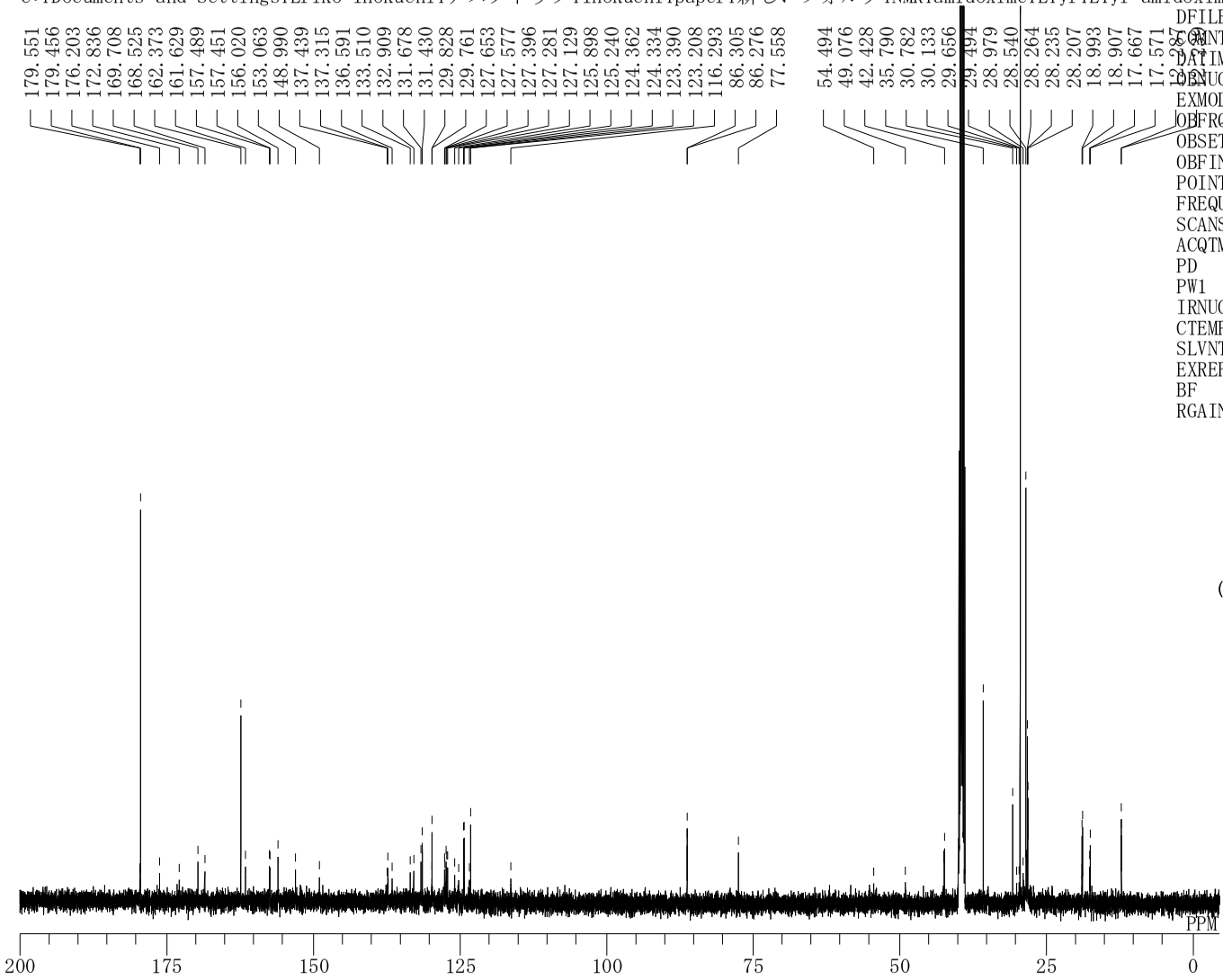


13f

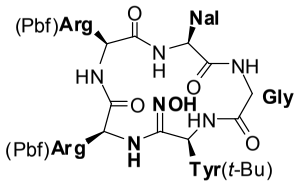

single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥LTyr¥LTyr amidoxime 1H DMSO-2-1.als
LTyr amidoxime 1H DMSO-2-1.
DFILE
COMNT single_pulse
DATIM 28-01-2011 18:22:22
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 22
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46
(Pbf)Arg
Nal
Gly
NOH
(Pbf)Arg
Tyr(t-Bu)
13g
PPM

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidoxime¥LTyr¥LTyr amidoxime protected 13C DMSO110201-1.a



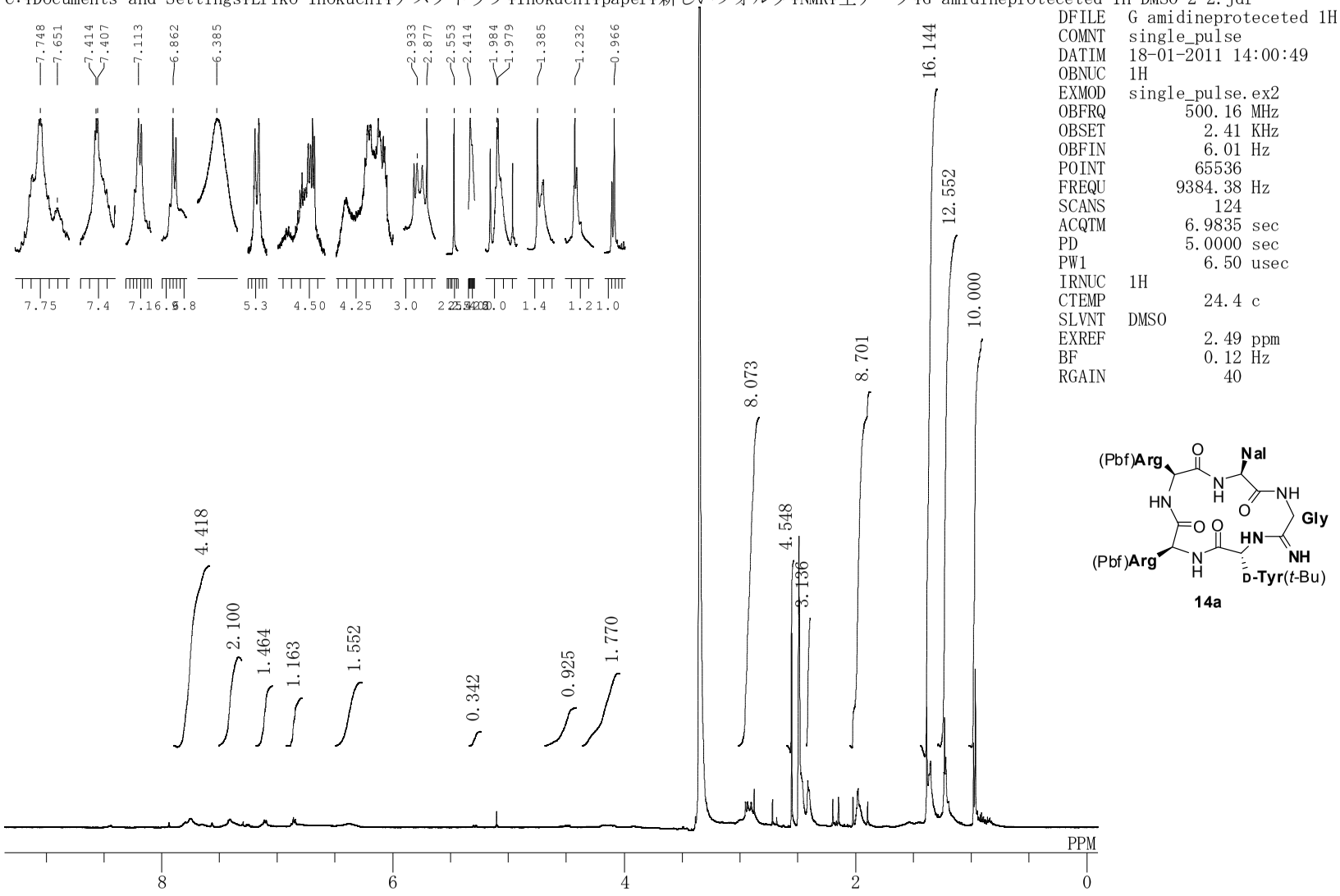
DFILE	LTyr amidoxime protected 13
COMNT	single pulse decoupled gate
DATIM	02-02-2011 08:41:29
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	10000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	58



13g

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥生データ¥G amidineproteceted 1H DMSO-2-2.jdf

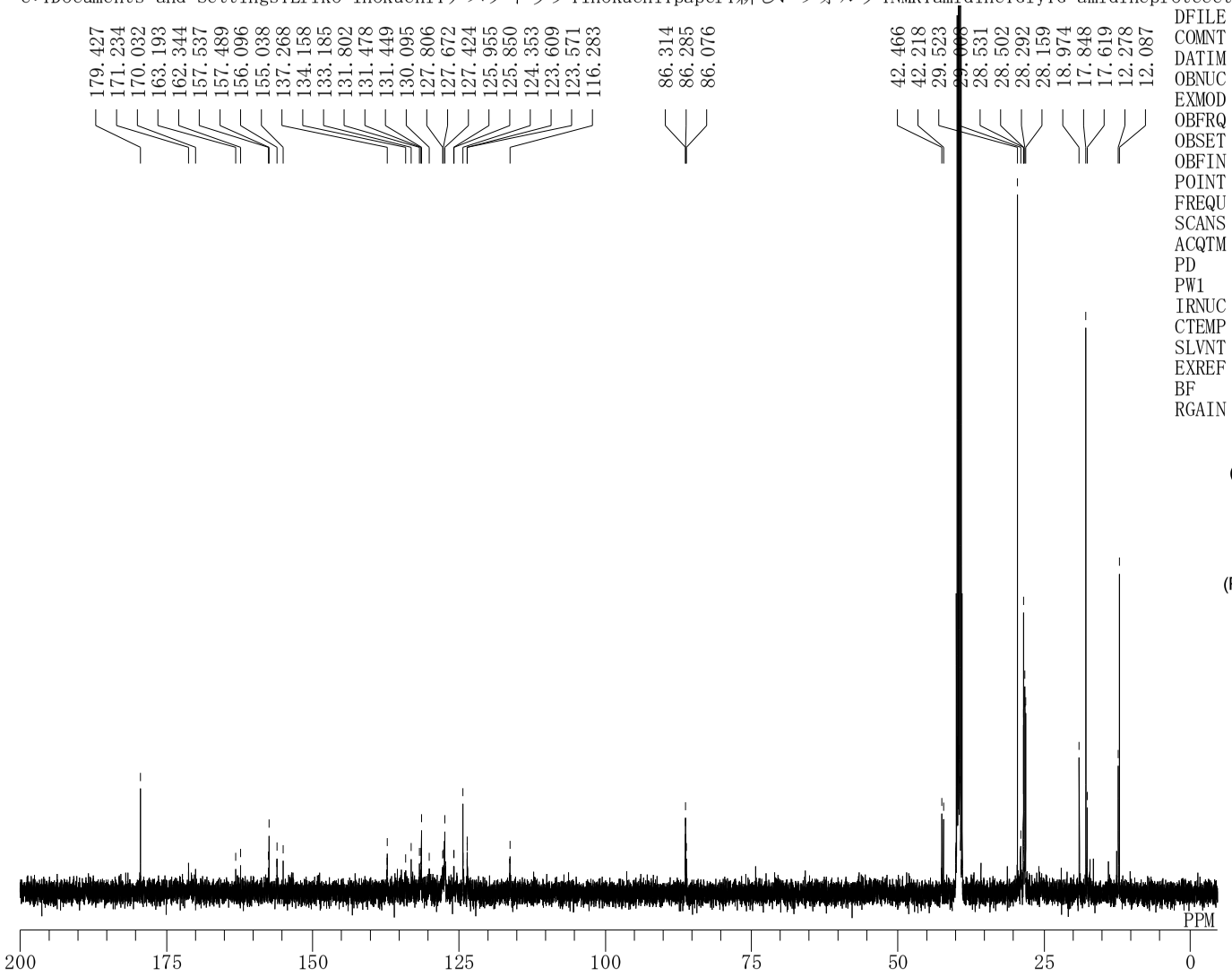


DFILE G amidineproteceted 1H DMSC
COMNT single_pulse
DATIM 18-01-2011 14:00:49
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 65536
FREQU 9384.38 Hz
SCANS 124
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 40

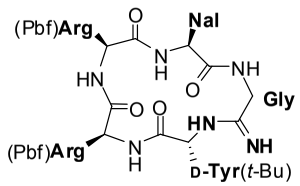
14a

single pulse decoupled gated NOE

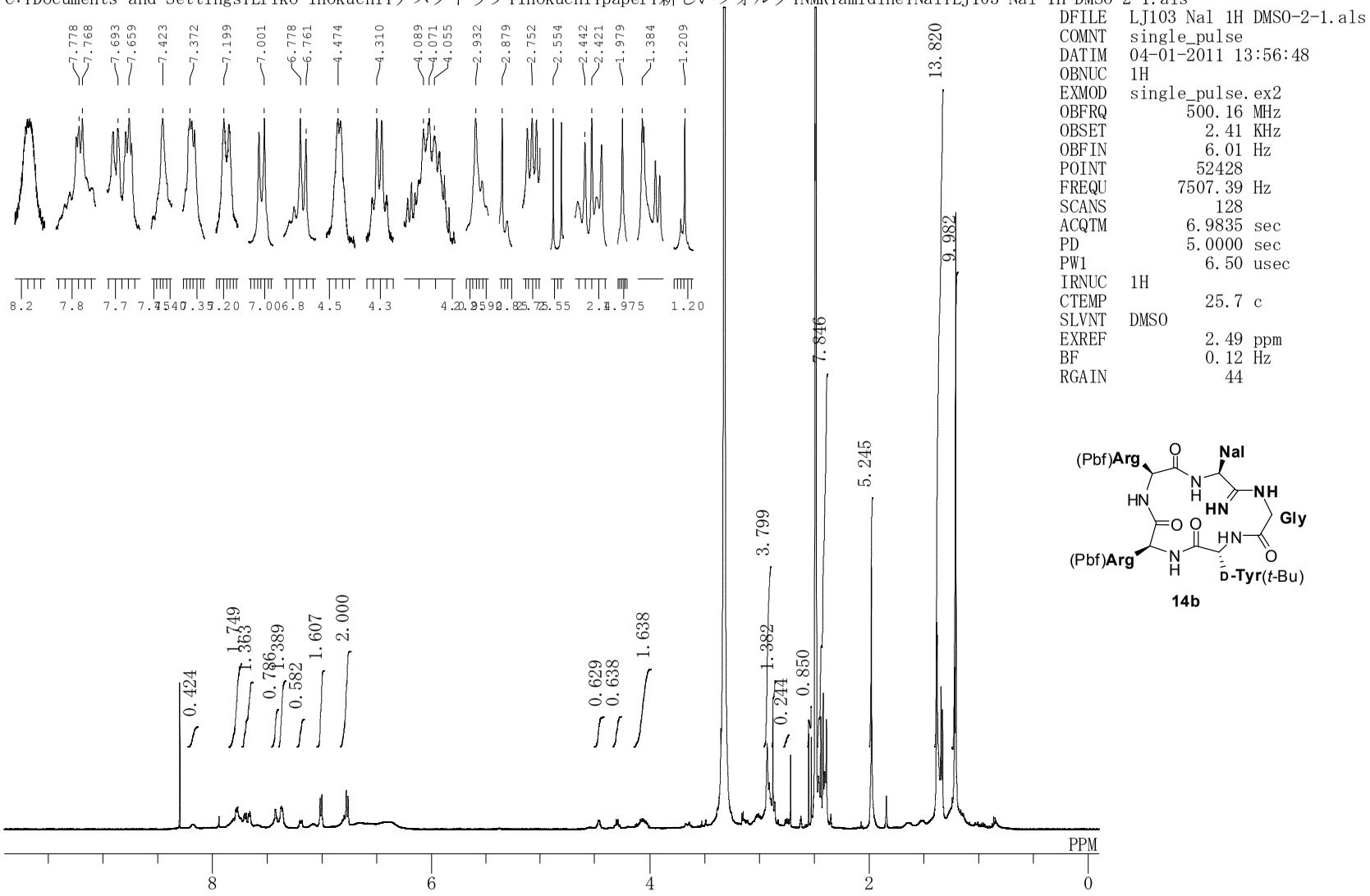
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥Gly¥G amidineproteceted 13C DMSO-2-1.als



DFILE	G amidineproteceted 13C DMS	
COMNT	single pulse decoupled gate	
DATIM	13-01-2011 21:05:06	
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	125.77	MHz
OBSET	7.87	KHz
OBFIN	4.21	Hz
POINT	26214	
FREQU	31446.06	Hz
SCANS	2048	
ACQTM	0.8336	sec
PD	2.0000	sec
PW1	7.47	usec
IRNUC	1H	
CTEMP	25.1	c
SLVNT	DMSO	
EXREF	39.50	ppm
BF	0.12	Hz
RGAIN	54	

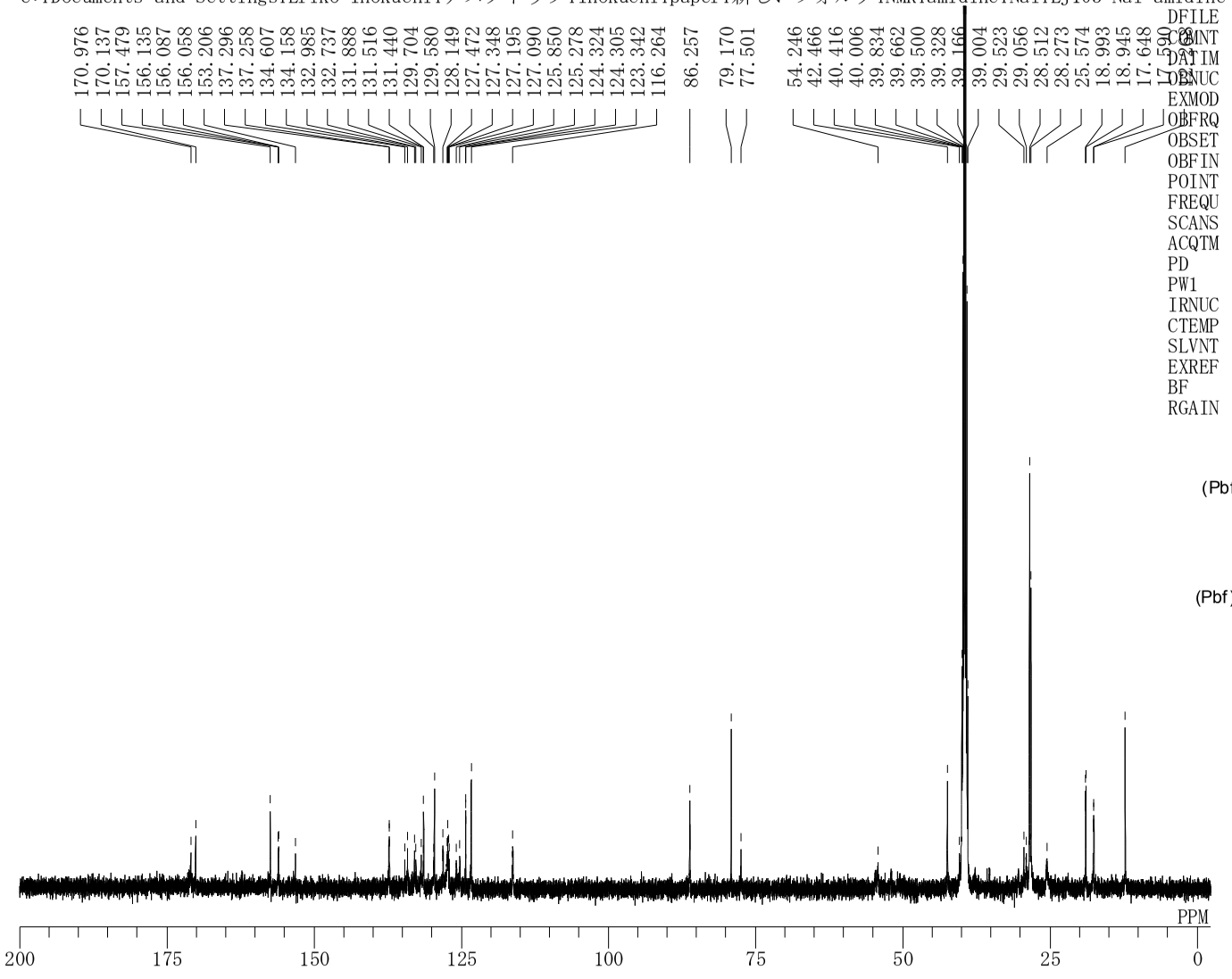


14a

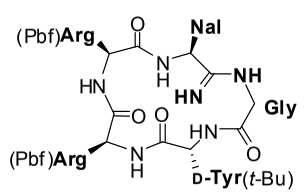

single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥Nal¥LJ103 Nal 1H DMSO-2-1.als
DFILE LJ103 Nal 1H DMSO-2-1.als
COMNT single_pulse
DATIM 04-01-2011 13:56:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 128
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 44
(Pbf)Arg
Nal
Gly
D-Tyr(t-Bu)
14b
PPM

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥Nal¥LJ103 Nal amidine 13C rt DMSO-1.als



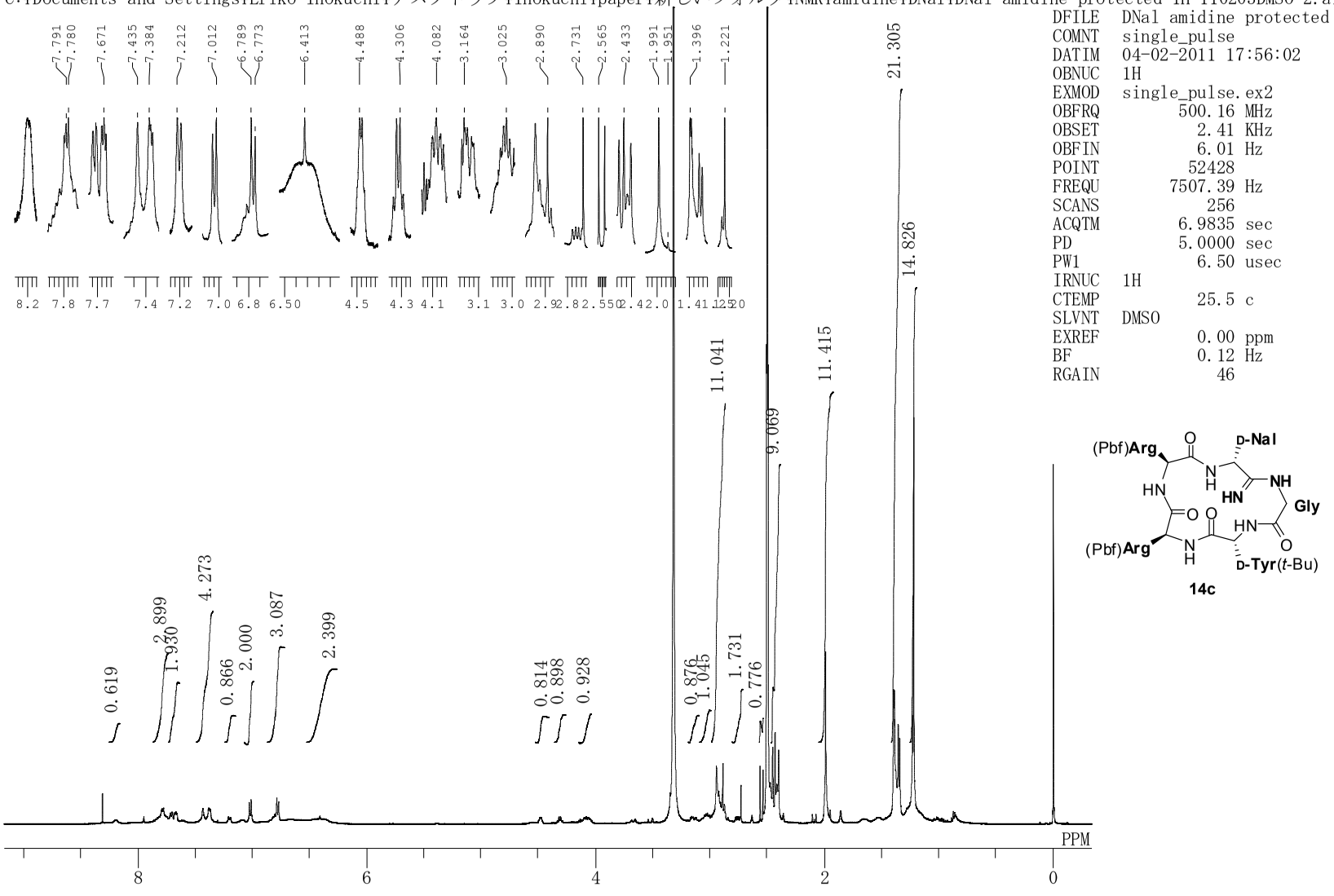
DFILE	LJ103 Nal amidine 13C rt DM
COMNT	single pulse decoupled gate
DATIM	06-01-2011 21:14:09
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	56



14b

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥DNal¥DNal amidine protected 1H 110203DMSO-2.als



DFILE	DNal amidine protected 1H 1	
COMNT	single_pulse	
DATIM	04-02-2011 17:56:02	
OBNUC	1H	
EXMOD	single_pulse.ex2	
OBFRQ	500.16	MHz
OBSET	2.41	KHz
OBFIN	6.01	Hz
POINT	52428	
FREQU	7507.39	Hz
SCANS	256	
ACQTM	6.9835	sec
PD	5.0000	sec
PW1	6.50	usec
IRNUC	1H	
CTEMP	25.5	c
SLVNT	DMSO	
EXREF	0.00	ppm
BF	0.12	Hz
RGAIN	46	

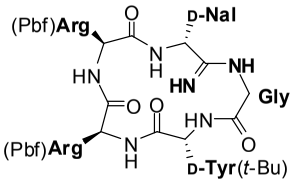
14c

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥DNal¥DNal amidine 13C DMSO.als

179.427 172.464 171.921 171.539 169.870 162.354 157.499 155.982 153.664 151.127 137.287 136.323 134.196 132.899 131.697 131.478 131.430 131.364 129.513 128.025 127.529 127.472 127.405 127.357 127.291 125.831 125.240 124.353 124.315 123.571 116.293 86.295 79.170 77.663 55.162 54.590 48.619 45.996 42.485 37.039 35.799 30.792 29.523 29.342 29.008 28.712 28.512 28.464 28.283 27.701 25.049 18.964 17.610 12.287

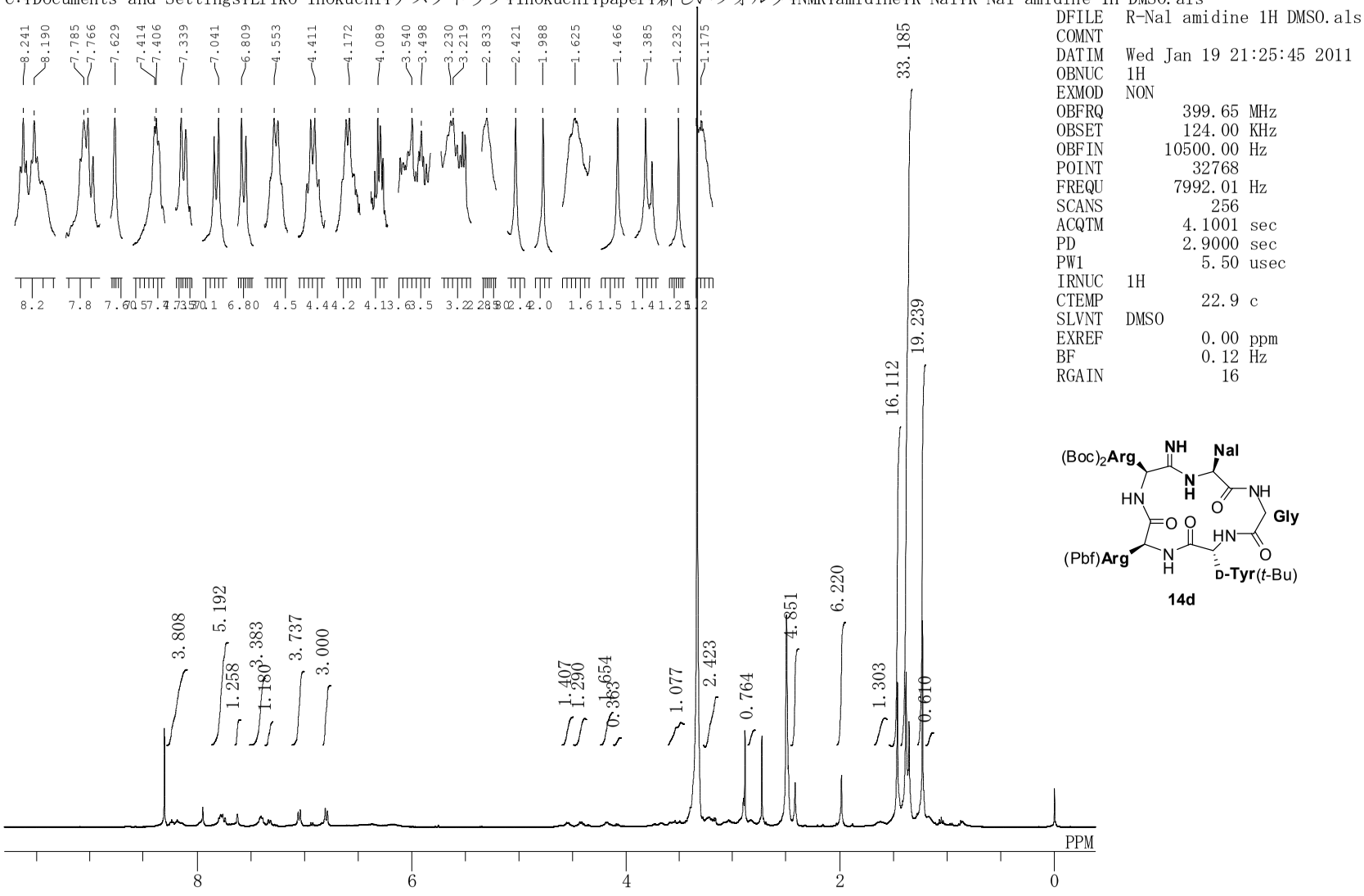
DFILE	DNal amidine 13C DMSO.als
COMNT	single pulse decoupled gate
DATIM	02-02-2011 00:40:18
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	5273
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	54



14c

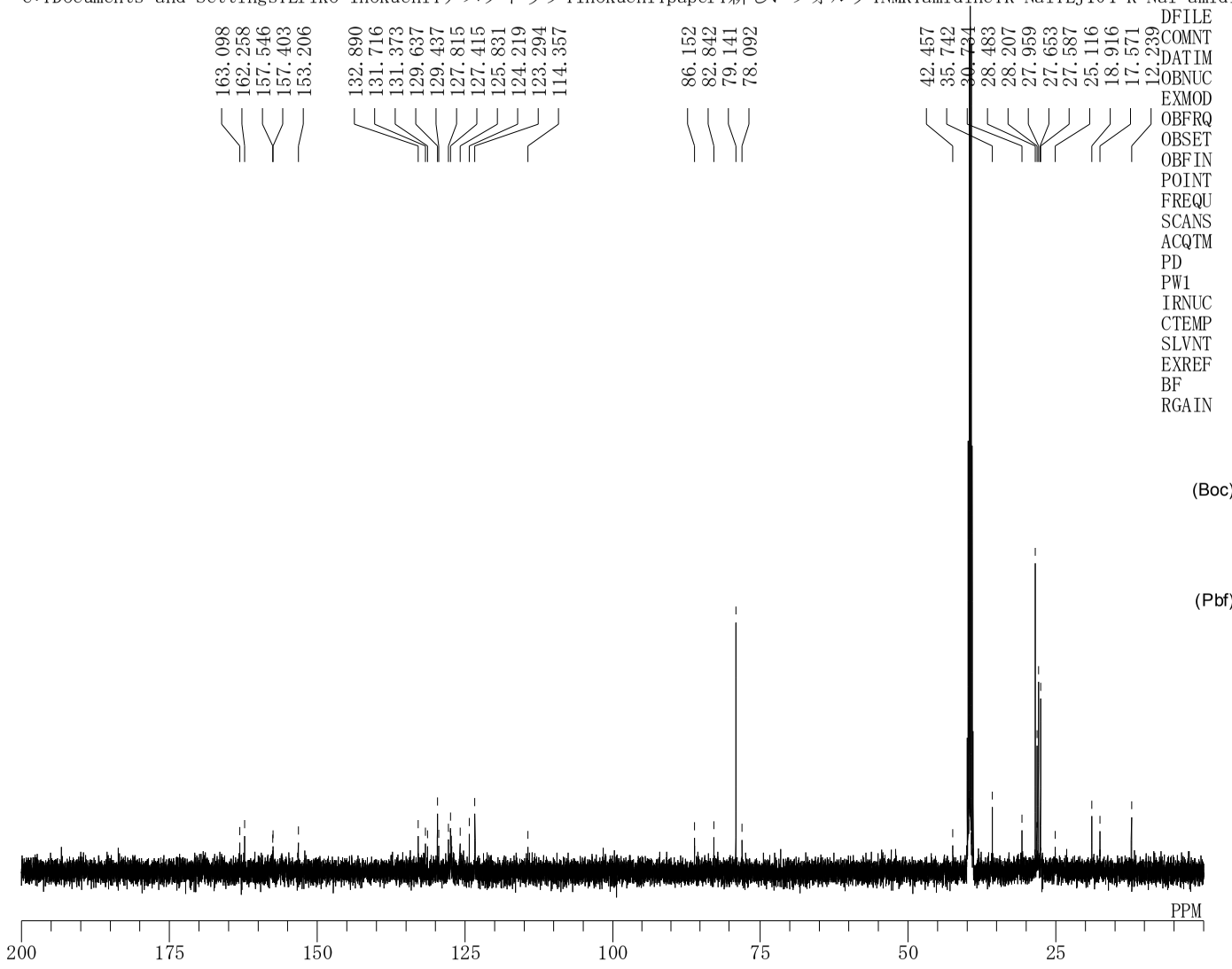
PPM

200 175 150 125 100 75 50 25 0

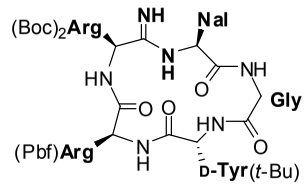

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥R-Nal¥R-Nal amidine 1H DMSO.als
DFILE R-Nal amidine 1H DMSO.als
COMNT
DATIM Wed Jan 19 21:25:45 2011
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 256
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
(Boc)2Arg
NH
Nal
HN
N
H
NH
O
Gly
HN
(Pbf)Arg
D-Tyr(t-Bu)
14d
PPM

single pulse decoupled gated NOE

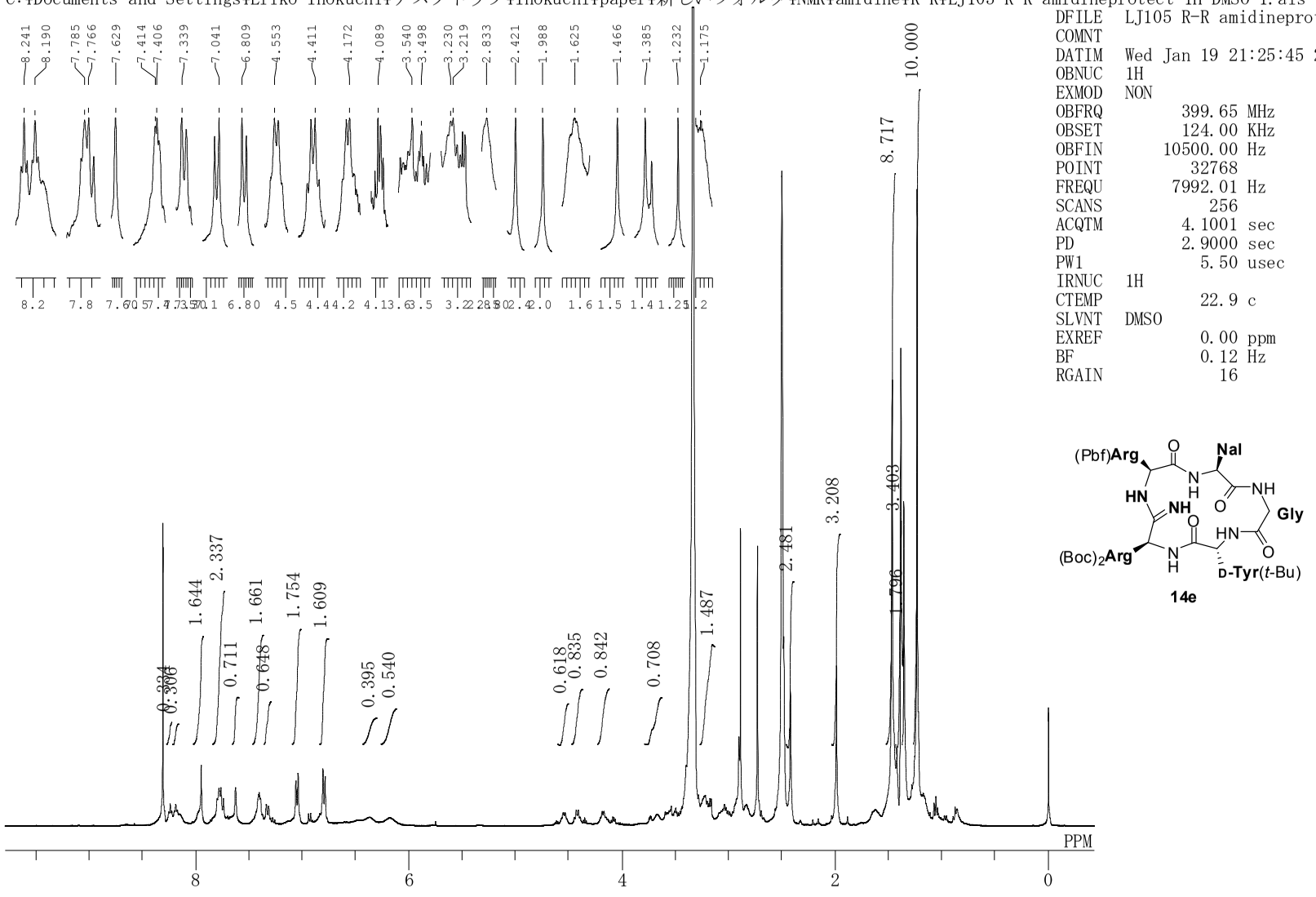
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥R-Nal¥LJ104 R-Nal amidineprotect 13C DMSO-1.als



DFILE	LJ104 R-Nal amidineprotect
COMNT	single pulse decoupled gate
DATIM	19-01-2011 10:42:52
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	54

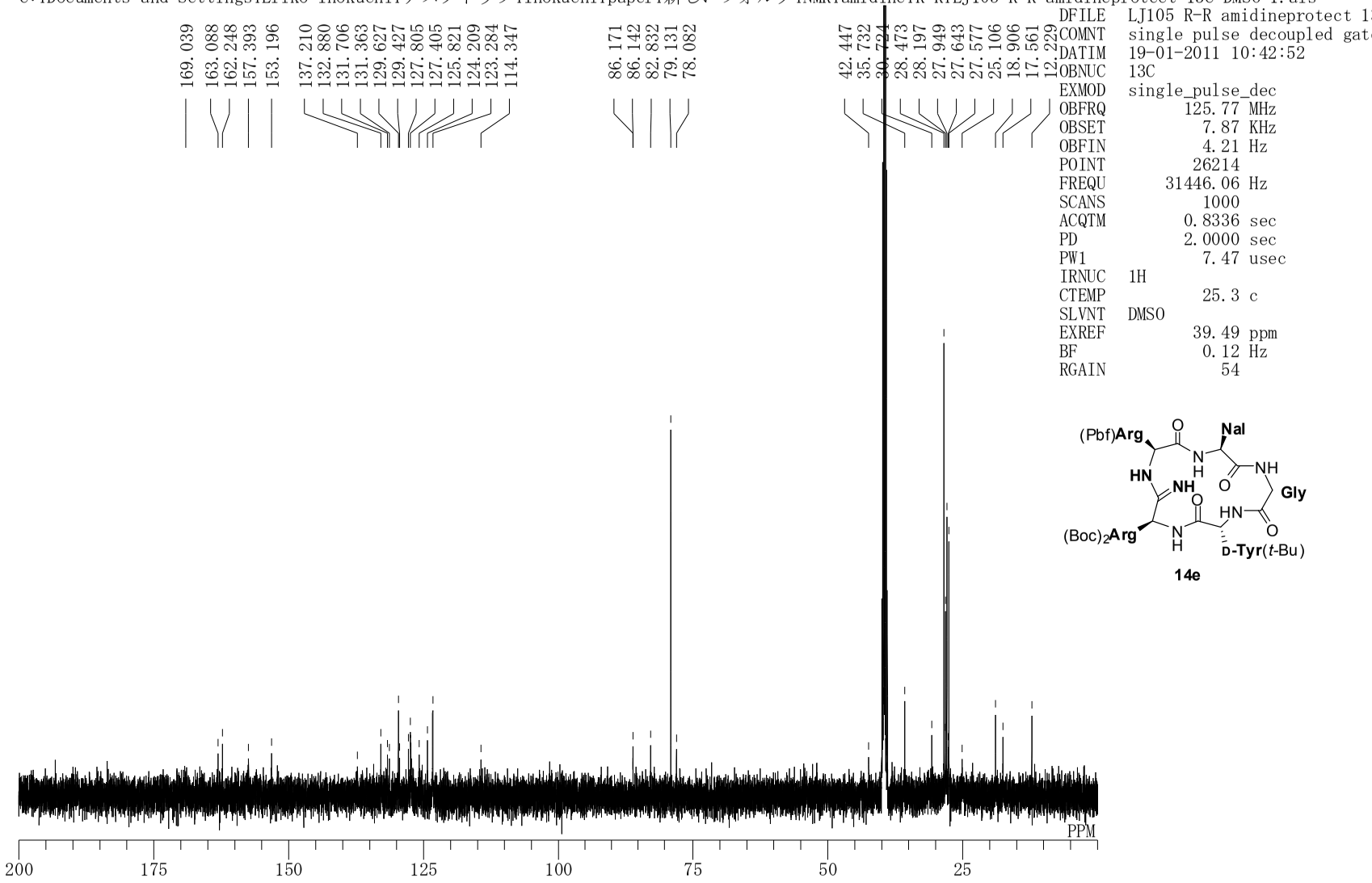


14d


C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥R-R¥LJ105 R-R amidineprotect 1H DMSO-1.als
DFILE LJ105 R-R amidineprotect 1H
COMNT
DATIM Wed Jan 19 21:25:45 2011
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7992.01 Hz
SCANS 256
ACQTM 4.1001 sec
PD 2.9000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
(Pbf)Arg
Nal
Gly
(Boc)2Arg
D-Tyr(t-Bu)
14e
PPM

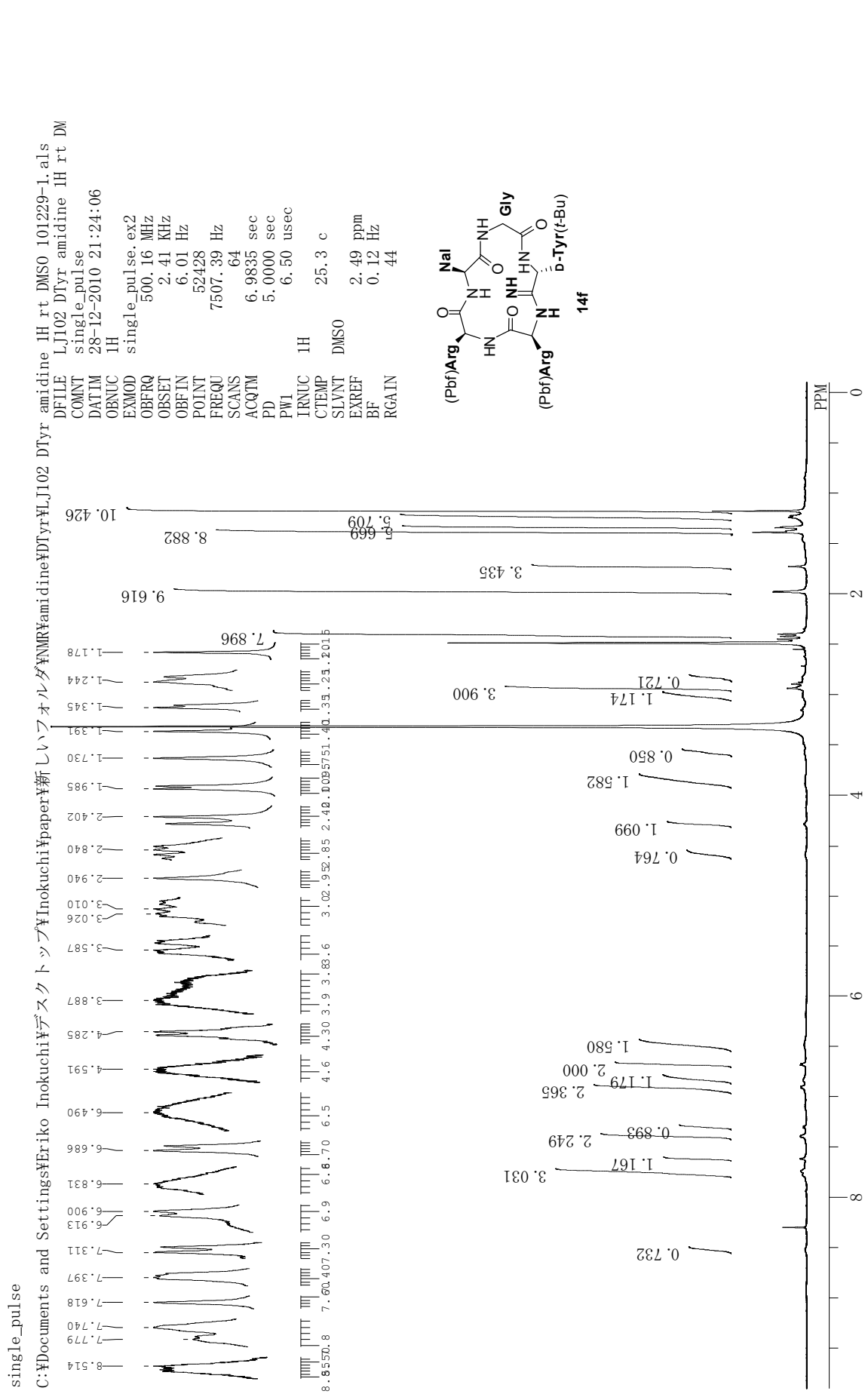
single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥R-R¥LJ105 R-R amidineprotect 13C DMSO-1.als



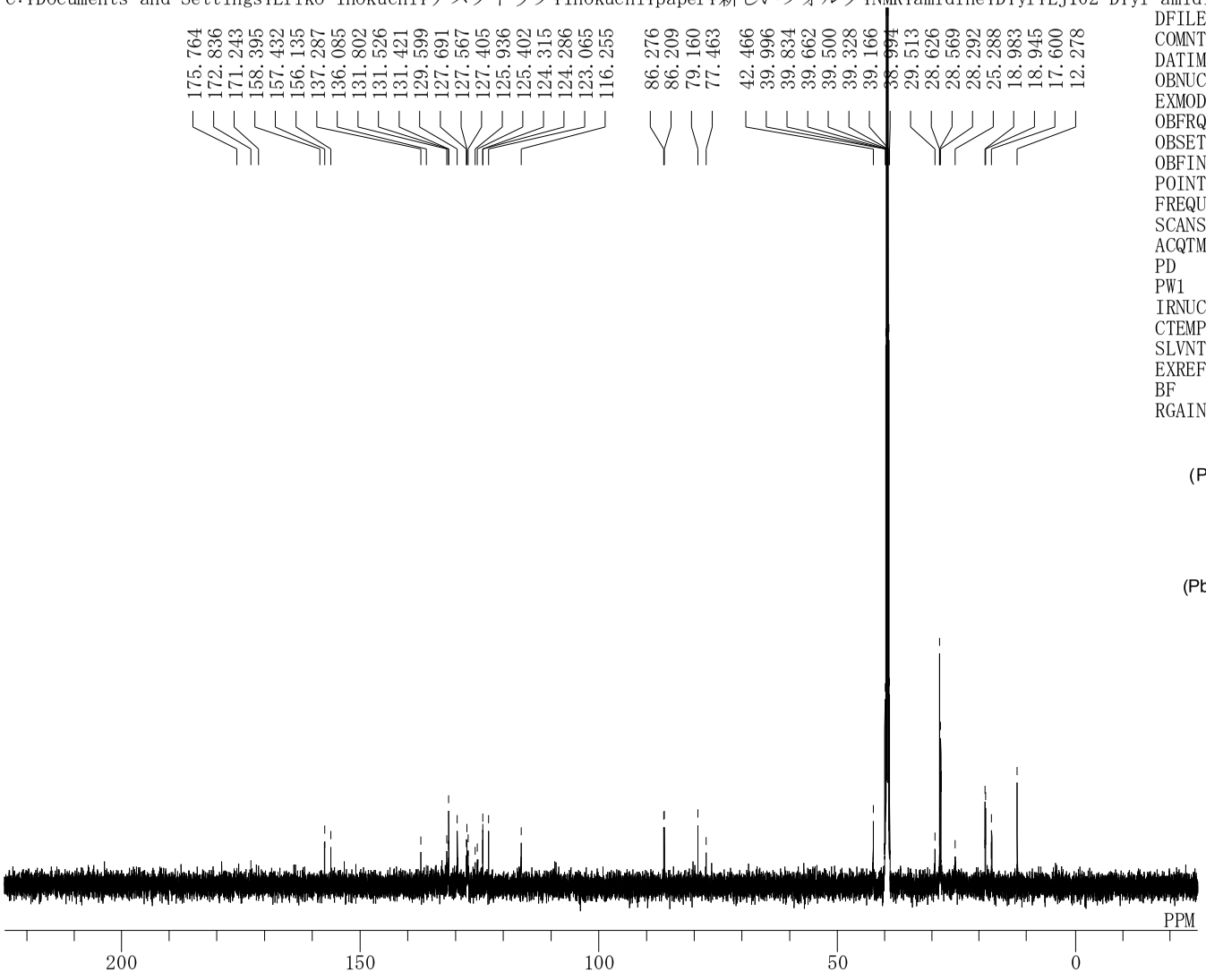
DFILE	LJ105 R-R amidineprotect 13
COMNT	single pulse decoupled gate
DATIM	19-01-2011 10:42:52
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	DMSO
EXREF	39.49 ppm
BF	0.12 Hz
RGAIN	54

14e

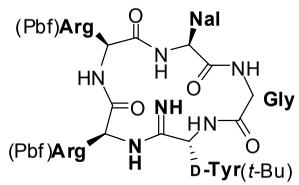

single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥DTyr¥LJ102 DTyr amidine 1H rt DMSO 101229-1.als
DFILE LJ102 DTyr amidine 1H rt DMSO 101229-1.als
COMNT single_pulse
DATIM 28-12-2010 21:24:06
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 64
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 44
(Pbf)Arg
Nal
Gly
D-Tyr(t-Bu)
(Pbf)Arg
14f
PPM

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥DTyr¥LJ102 DTyr amidine 13C rt DMSO-1.als



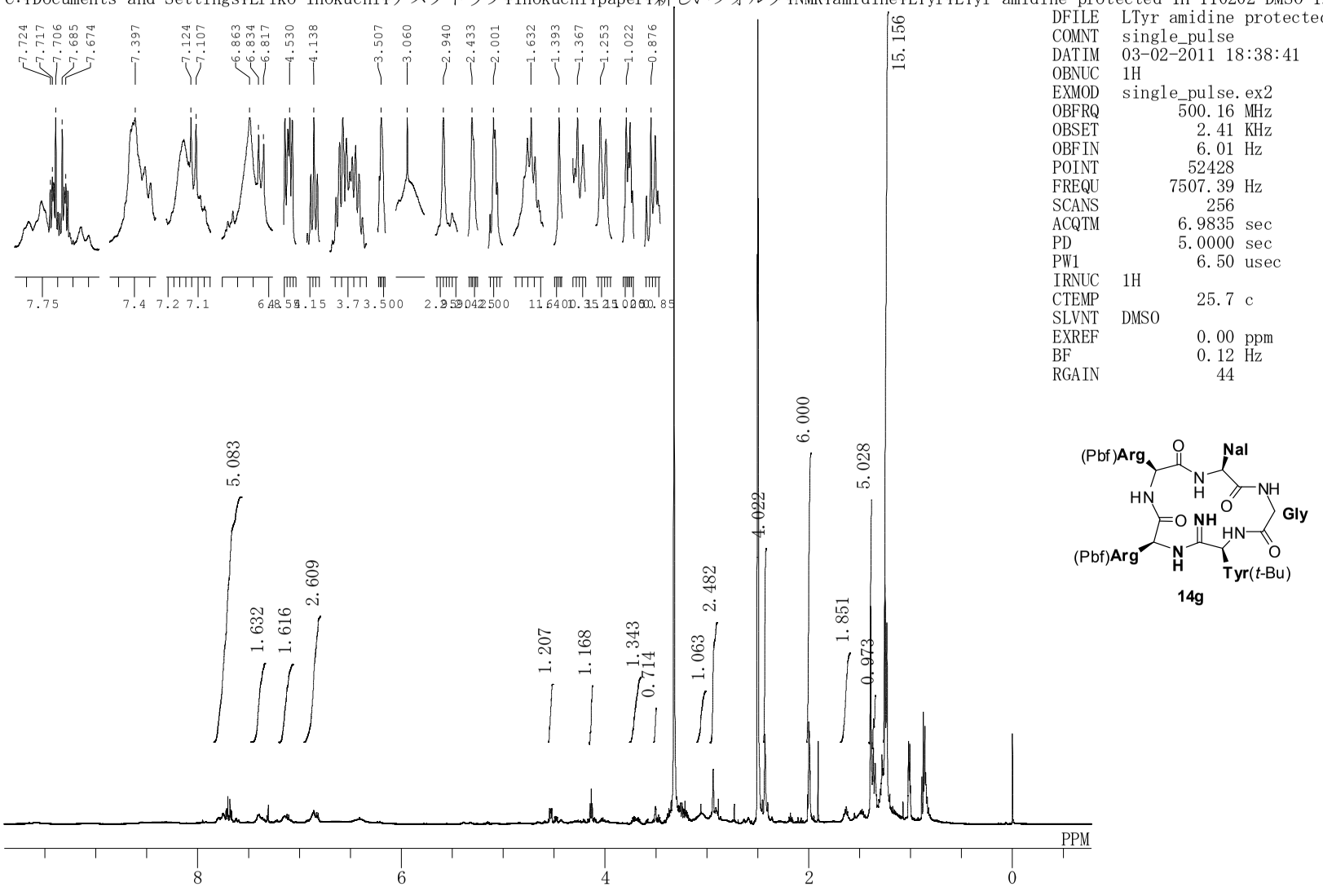
DFILE	LJ102 DTyr amidine 13C rt D
COMNT	single pulse decoupled gate
DATIM	06-01-2011 18:15:44
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1000
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	24.8 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	58



14f

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥LTyr¥LTyr amidine protected 1H 110202 DMSO-1.als

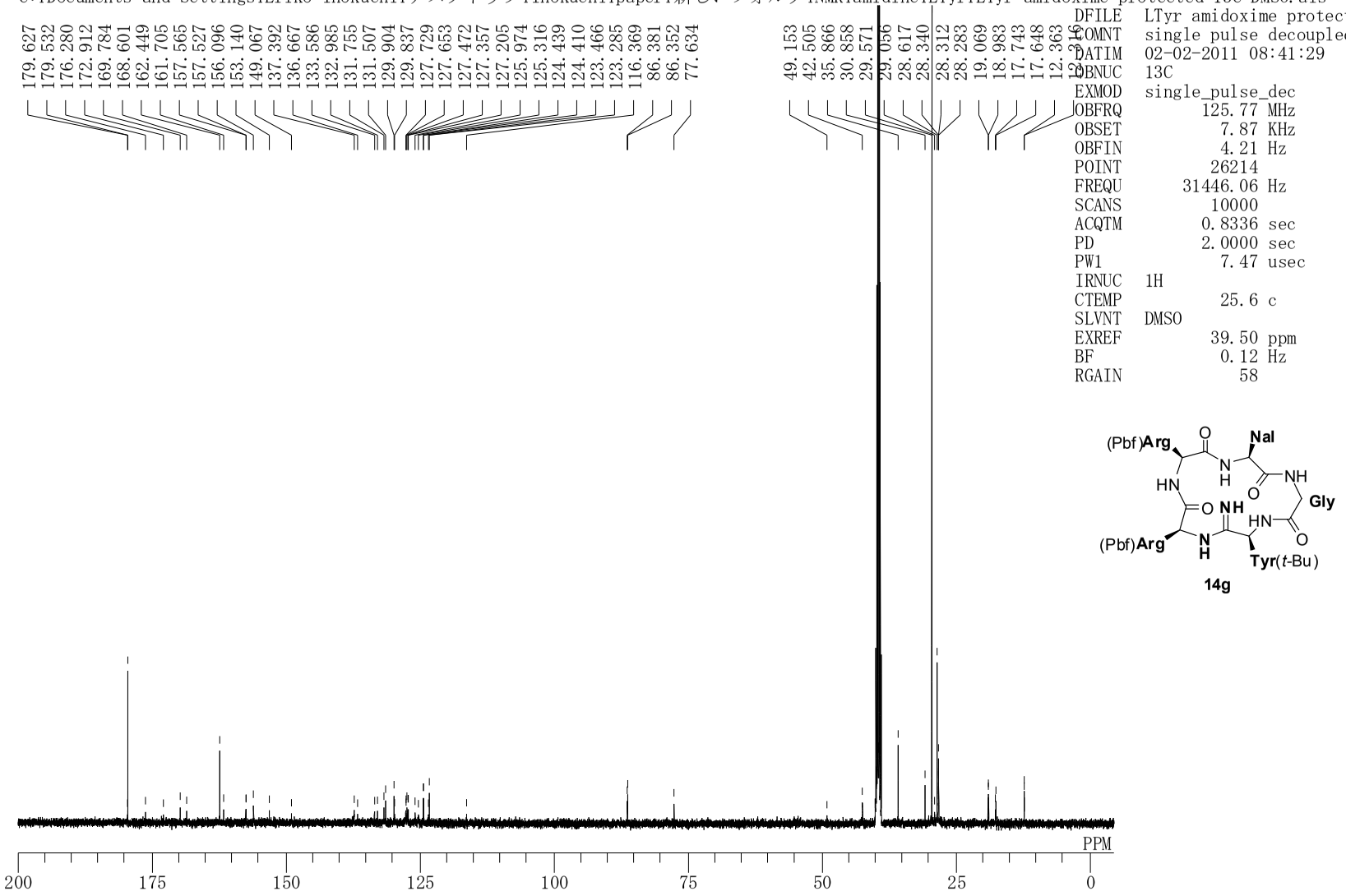


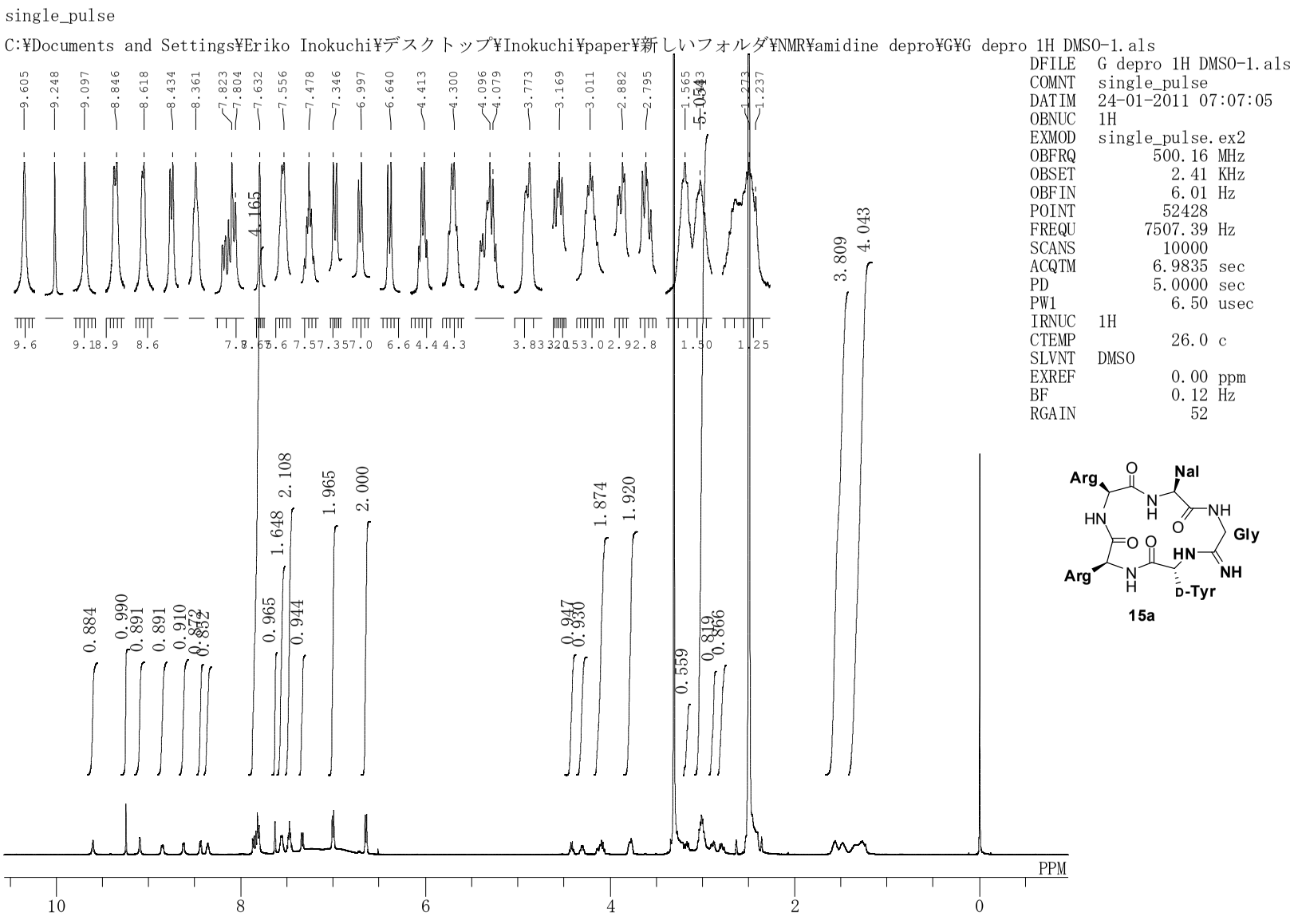
DFILE LTyr amidine protected 1H 1
COMNT single_pulse
DATIM 03-02-2011 18:38:41
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 256
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44

14g

single pulse decoupled gated NOE

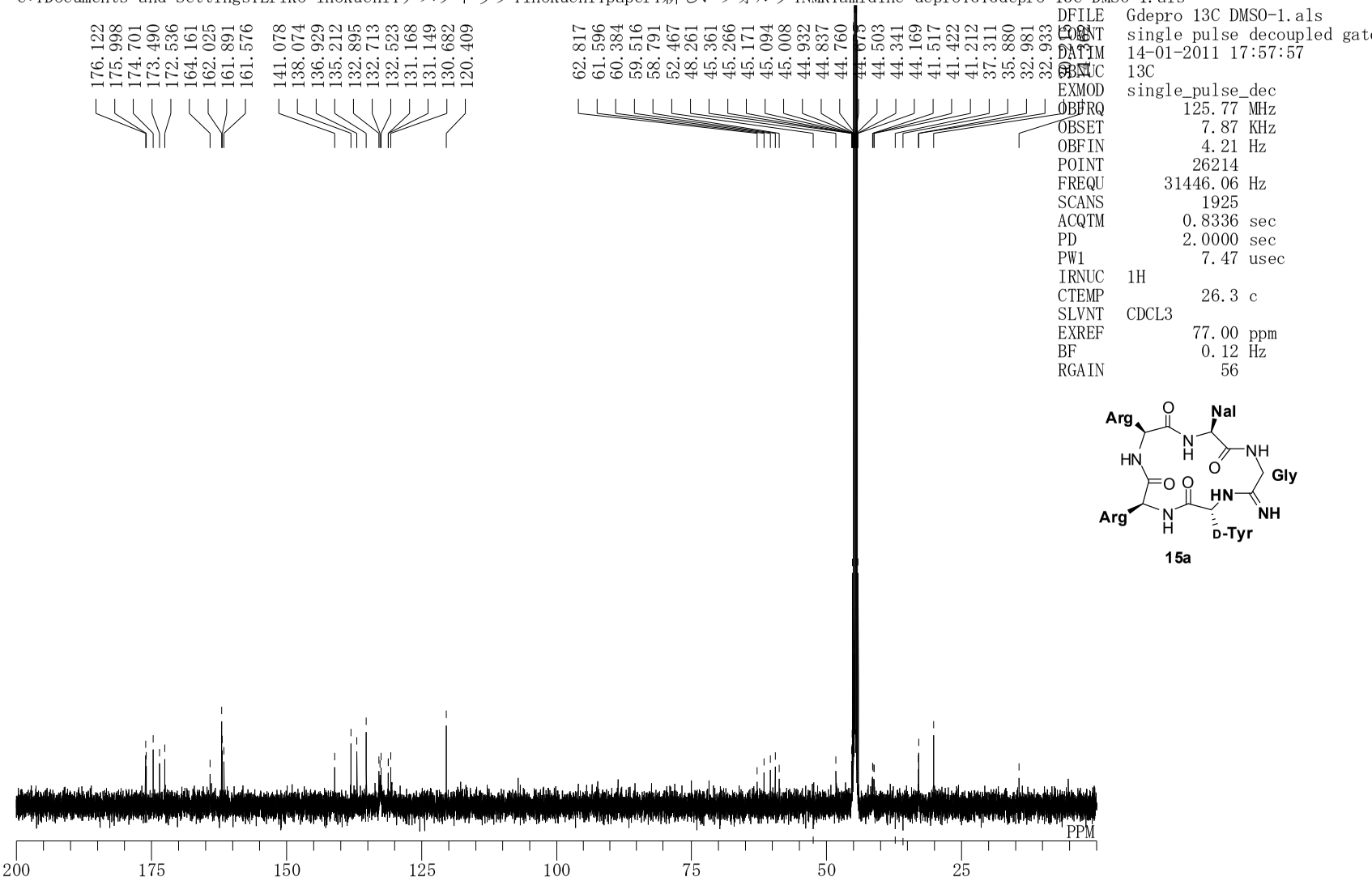
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine¥LTyr¥LTyr amidoxime protected 13C DMSO.als




single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥G¥G depro 1H DMSO-1.als
DFILE G depro 1H DMSO-1.als
COMNT single_pulse
DATIM 24-01-2011 07:07:05
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 10000
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 26.0 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 52
Arg
Nal
Gly
Arg
D-Tyr
15a
PPM

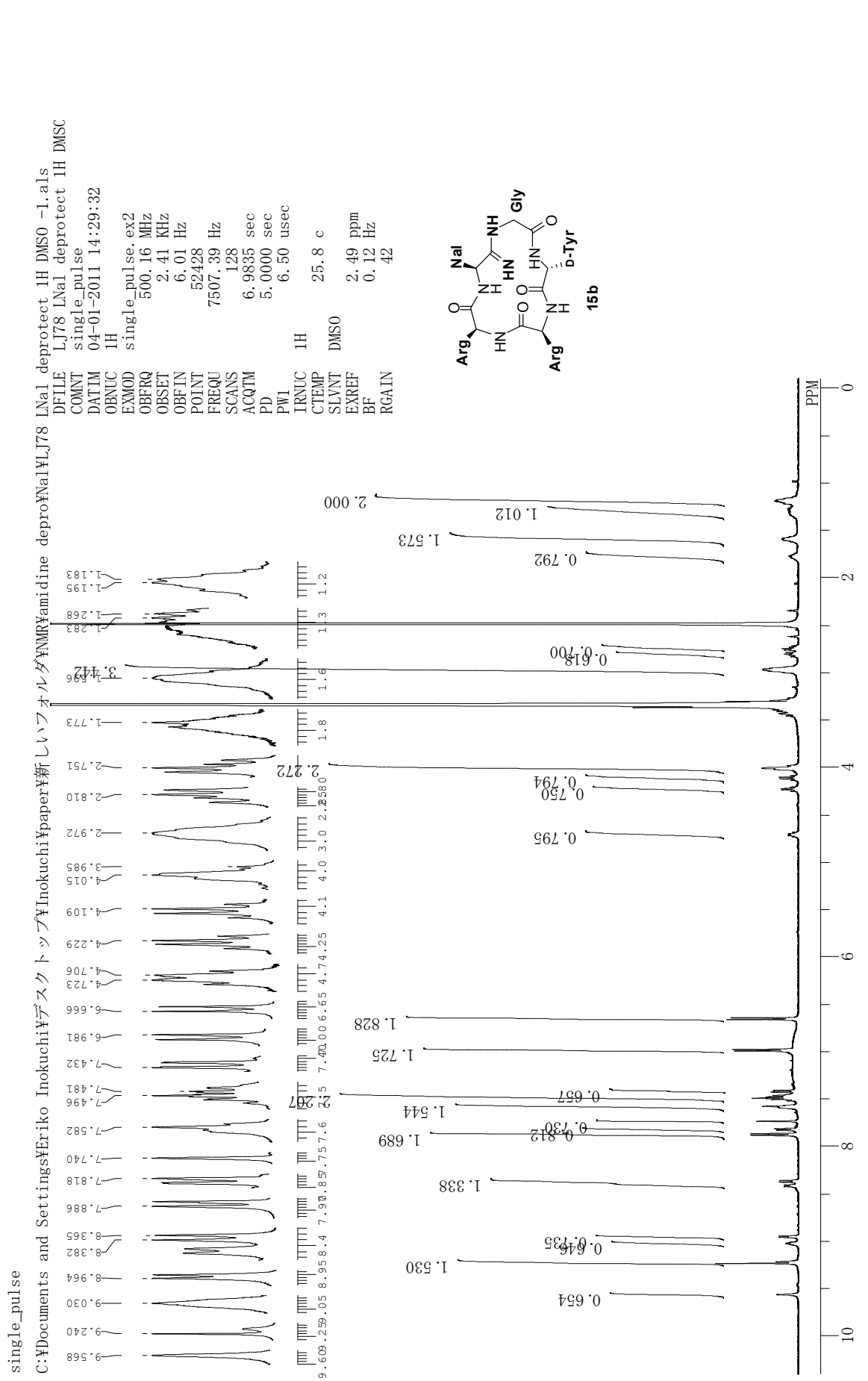
single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥G¥Gdepro 13C DMSO-1.als



DFILE	Gdepro 13C DMSO-1.als
COMNT	single pulse decoupled gate
DATIM	14-01-2011 17:57:57
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1925
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	56

15a


single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥Nal¥LJ78 LNal deprotect 1H DMSO -1.als
DFILE LJ78 LNal deprotect 1H DMSO -1.als
COMNT single_pulse
DATIM 04-01-2011 14:29:32
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 128
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 42
Arg
Nal
HN
NH
Gly
D-Tyr
Arg
15b
PPM

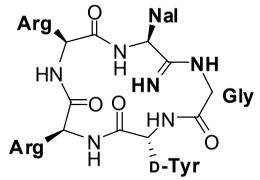
single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥Nal¥LJ78 LNal deprotect 13C DMSO -1.als

171.272
171.138
170.785
167.838
167.132
158.567
156.783
156.735
155.992
133.977
132.890
132.031
130.085
130.028
128.063
127.586
127.548
127.367
126.985
126.327
125.850
115.053

56.268
53.807
52.920
52.892
44.403
40.244
40.130
40.091
39.996
39.920
39.834
39.758
39.662
39.586
39.500
39.414
39.328
39.166
38.994
35.208
34.912
28.035

DFILE	LJ78 LNal deprotect 13C DMS
COMNT	single pulse decoupled gate
DATIM	03-01-2011 07:03:52
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	16384
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	58



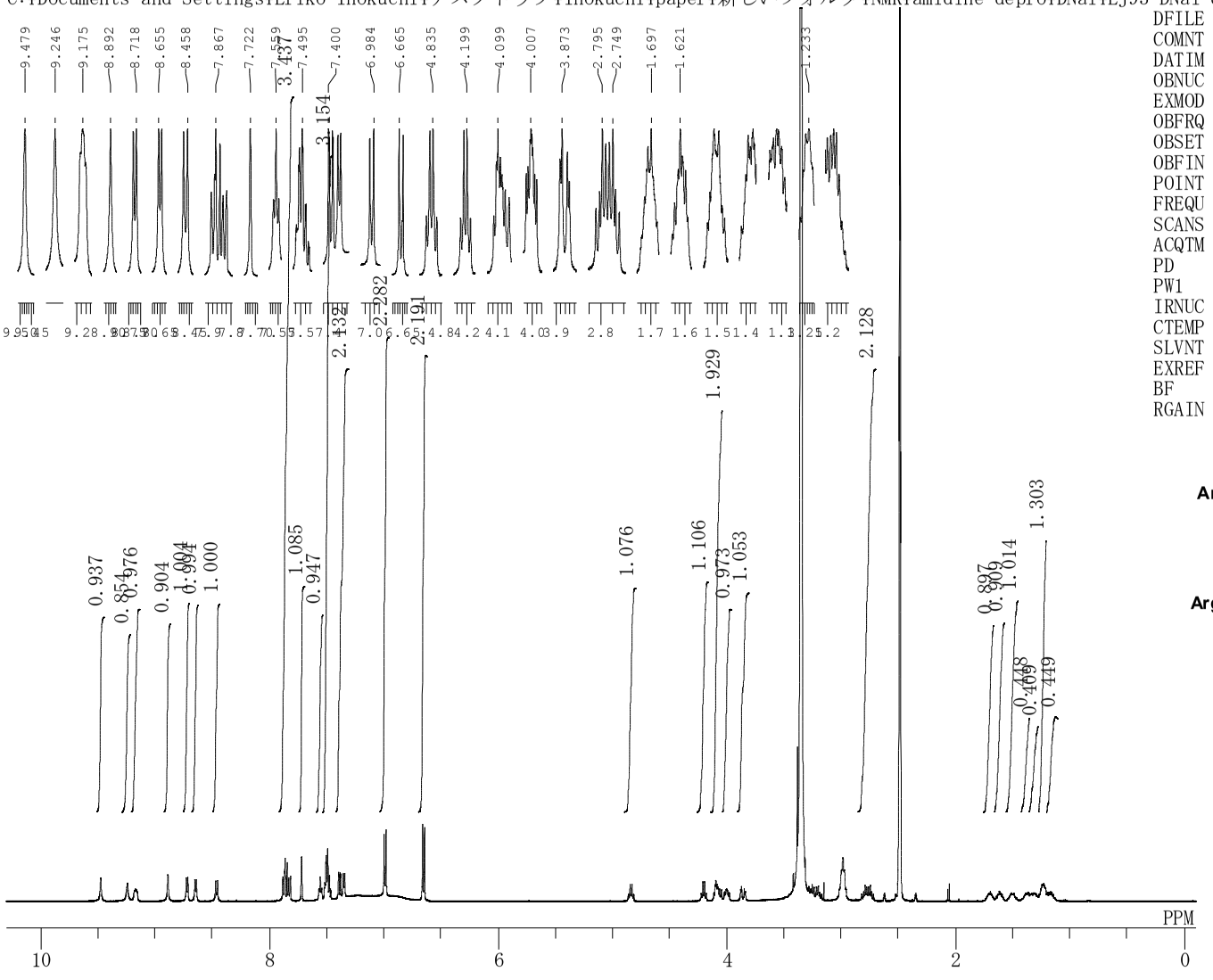
15b

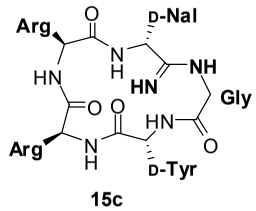
200 175 150 125 100 75 50 25 PPM

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥DNal¥LJ93 DNal depro 1H DMSO-1.als

DFILE	LJ93 DNal depro 1H DMSO-1.a
COMNT	single_pulse
DATIM	14-01-2011 18:46:54
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	52428
FREQU	7507.39 Hz
SCANS	204
ACQTM	6.9835 sec
PD	5.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	42





15c

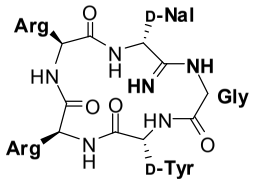
single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥DNal¥LJ93 DNal depro 13C DMSO-1.als

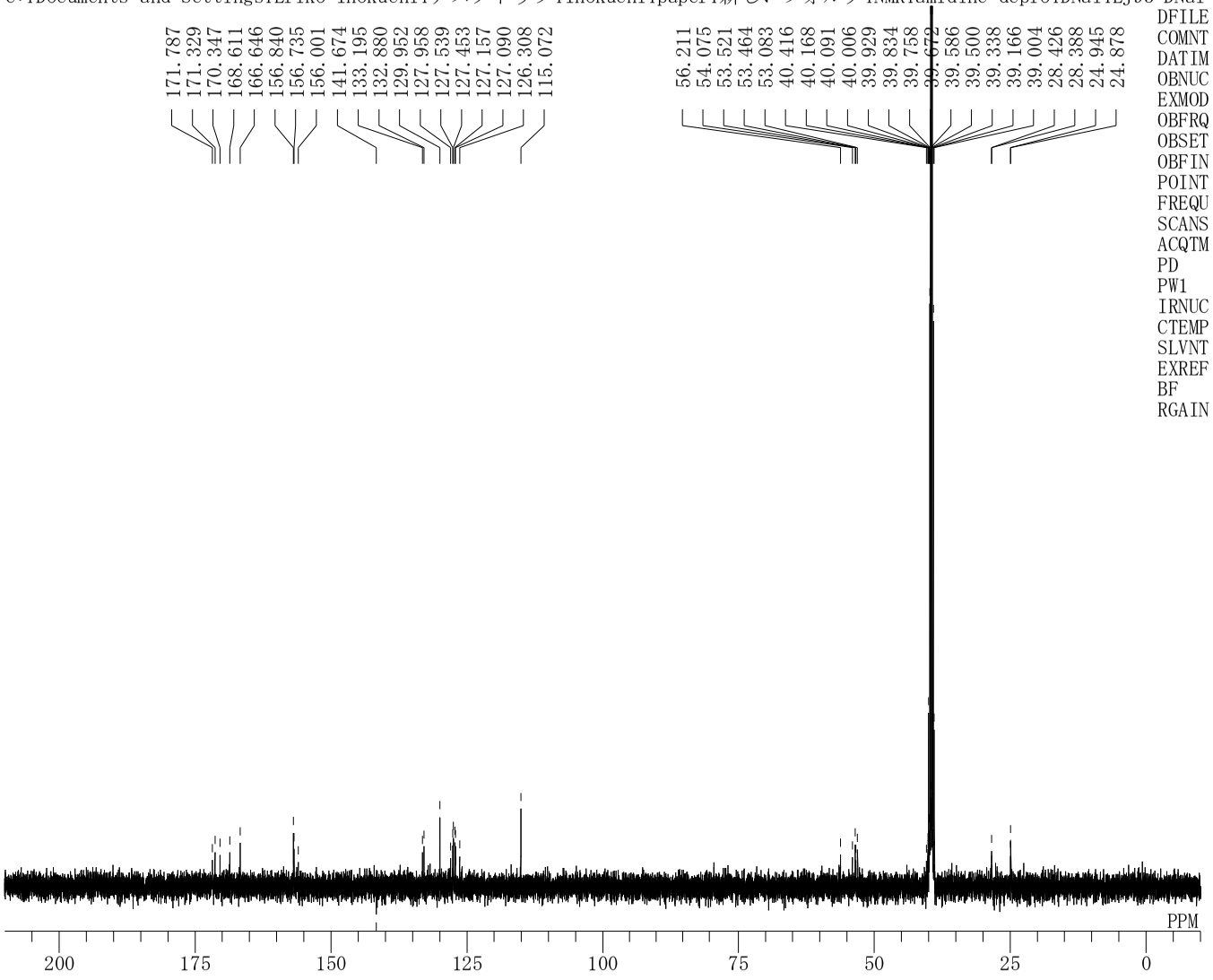
171.787
171.329
170.347
168.611
166.646
156.840
156.735
156.001
141.674
133.195
132.880
129.952
127.958
127.539
127.453
127.157
127.090
126.308
115.072

56.211
54.075
53.521
53.464
53.083
40.416
40.168
40.091
40.006
39.929
39.834
39.758
39.672
39.586
39.500
39.338
39.166
39.004
28.426
28.388
24.945
24.878

DFILE	LJ93 DNal depro 13C DMSO-1.
COMNT	single pulse decoupled gate
DATIM	14-01-2011 13:16:11
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1024
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	56

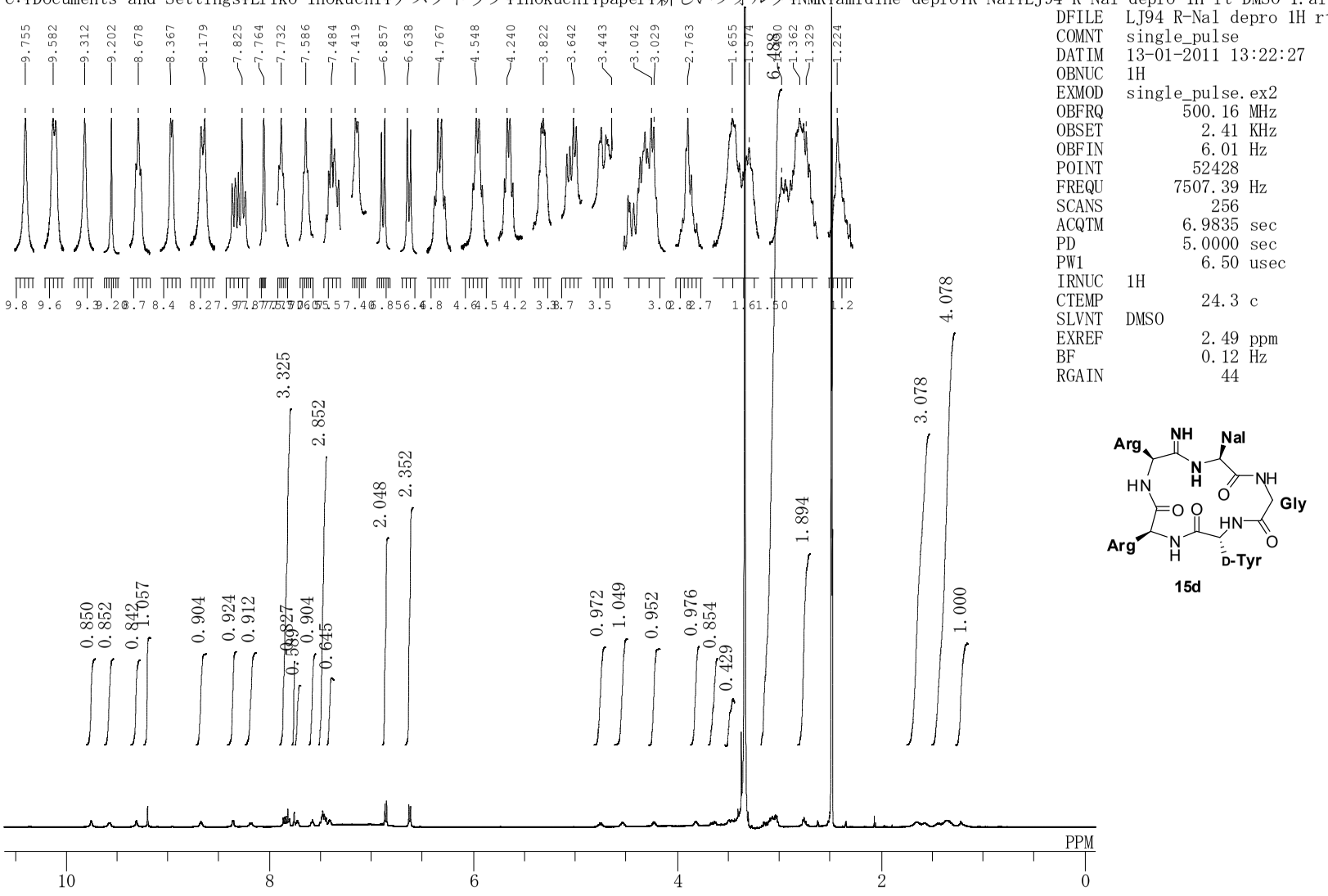


15c



single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥R-Nal¥LJ94 R-Nal depro 1H rt DMSO-1.als

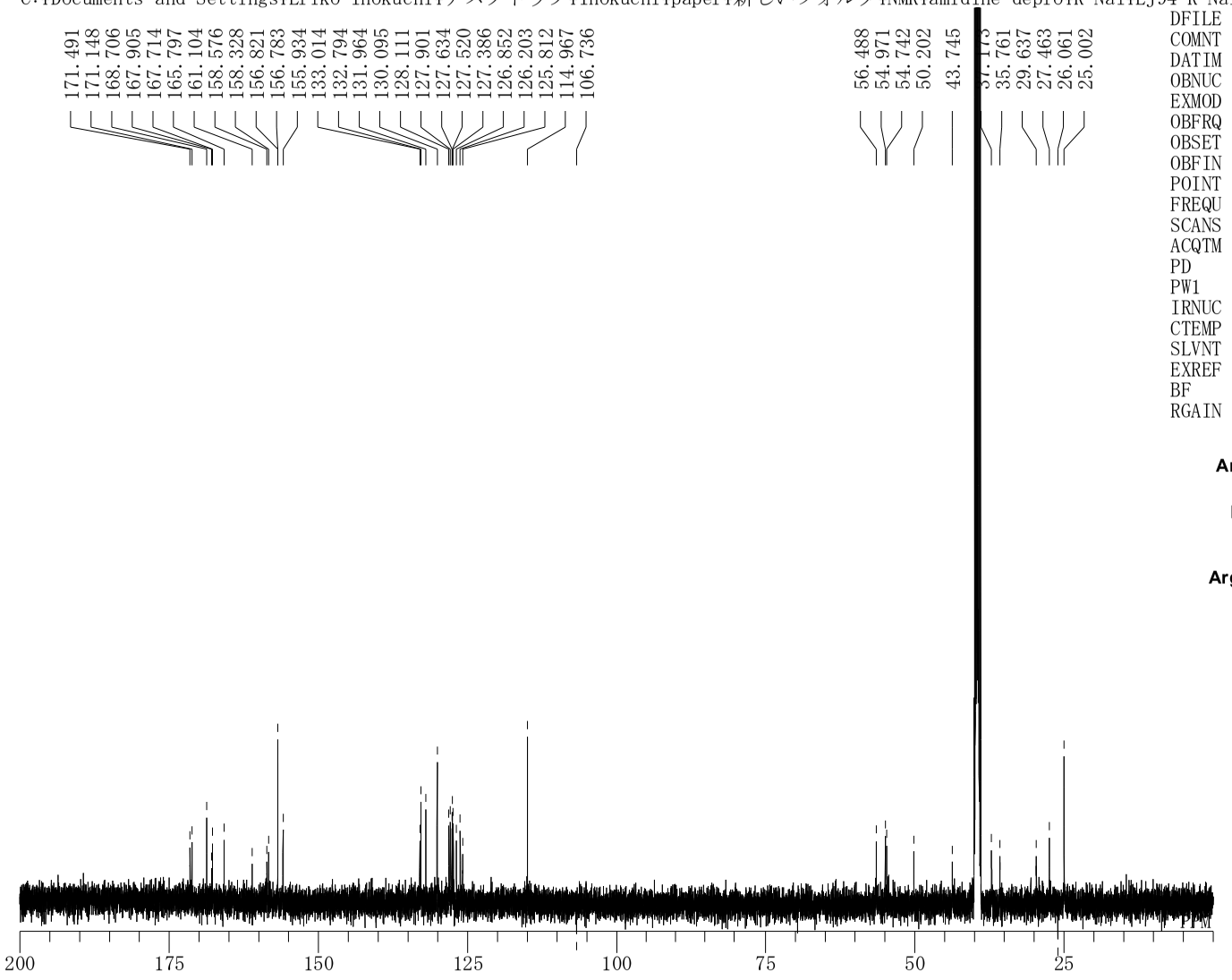


DFILE LJ94 R-Nal depro 1H rt DMSC
COMNT single_pulse
DATIM 13-01-2011 13:22:27
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 256
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.12 Hz
RGAIN 44

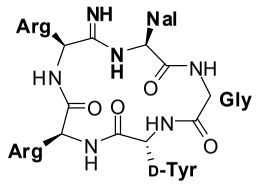
15d

single pulse decoupled gated NOE

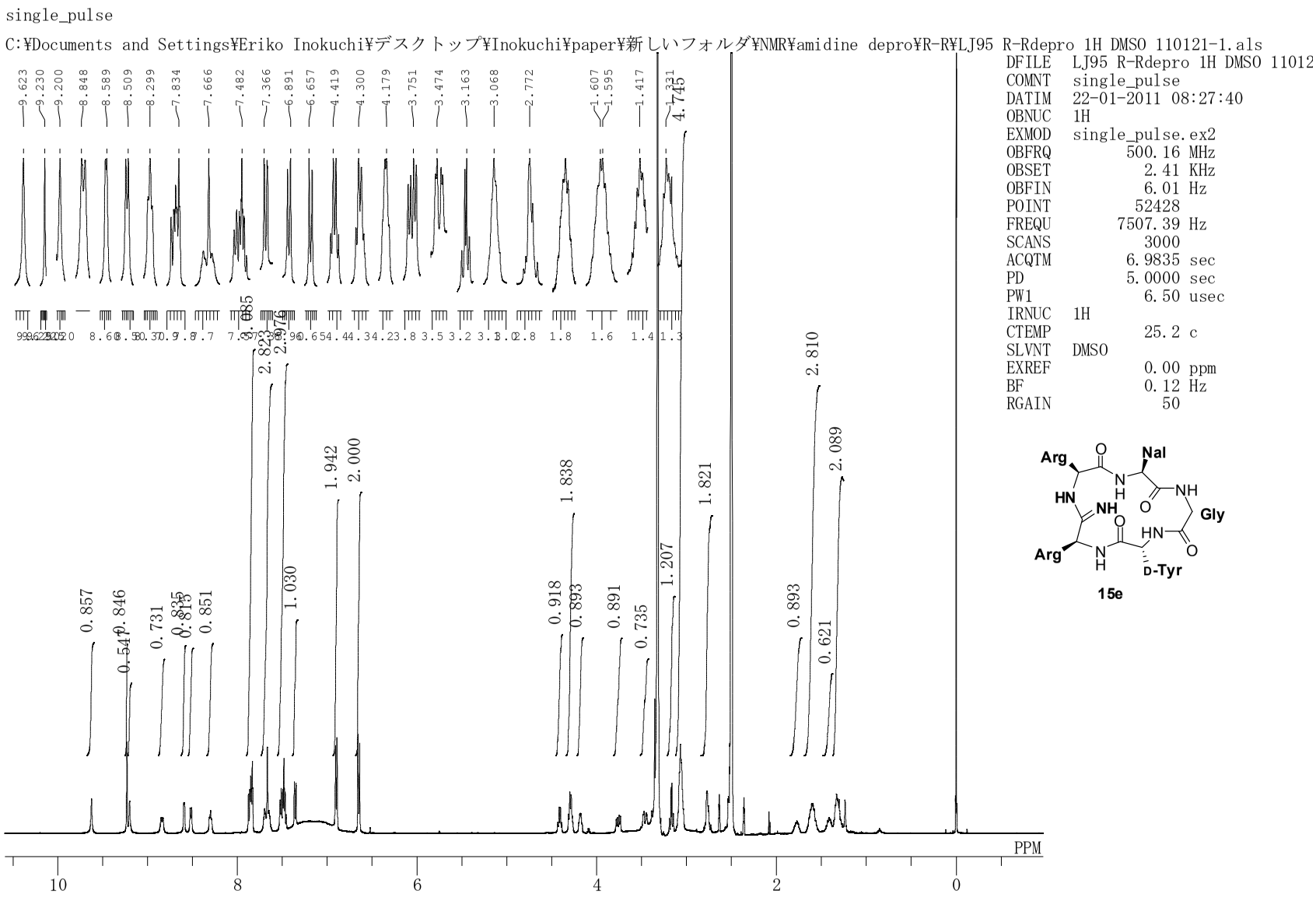
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥R-Nal¥LJ94 R-Nal depro 13C rt DMSO-1.als



DFILE	LJ94 R-Nal depro 13C rt DMS	
COMNT	single pulse decoupled gate	
DATIM	11-01-2011 08:36:34	
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	125.77	MHz
OBSET	7.87	KHz
OBFIN	4.21	Hz
POINT	26214	
FREQU	31446.06	Hz
SCANS	20000	
ACQTM	0.8336	sec
PD	2.0000	sec
PW1	7.47	usec
IRNUC	1H	
CTEMP	25.0	c
SLVNT	DMSO	
EXREF	39.50	ppm
BF	0.12	Hz
RGAIN	54	

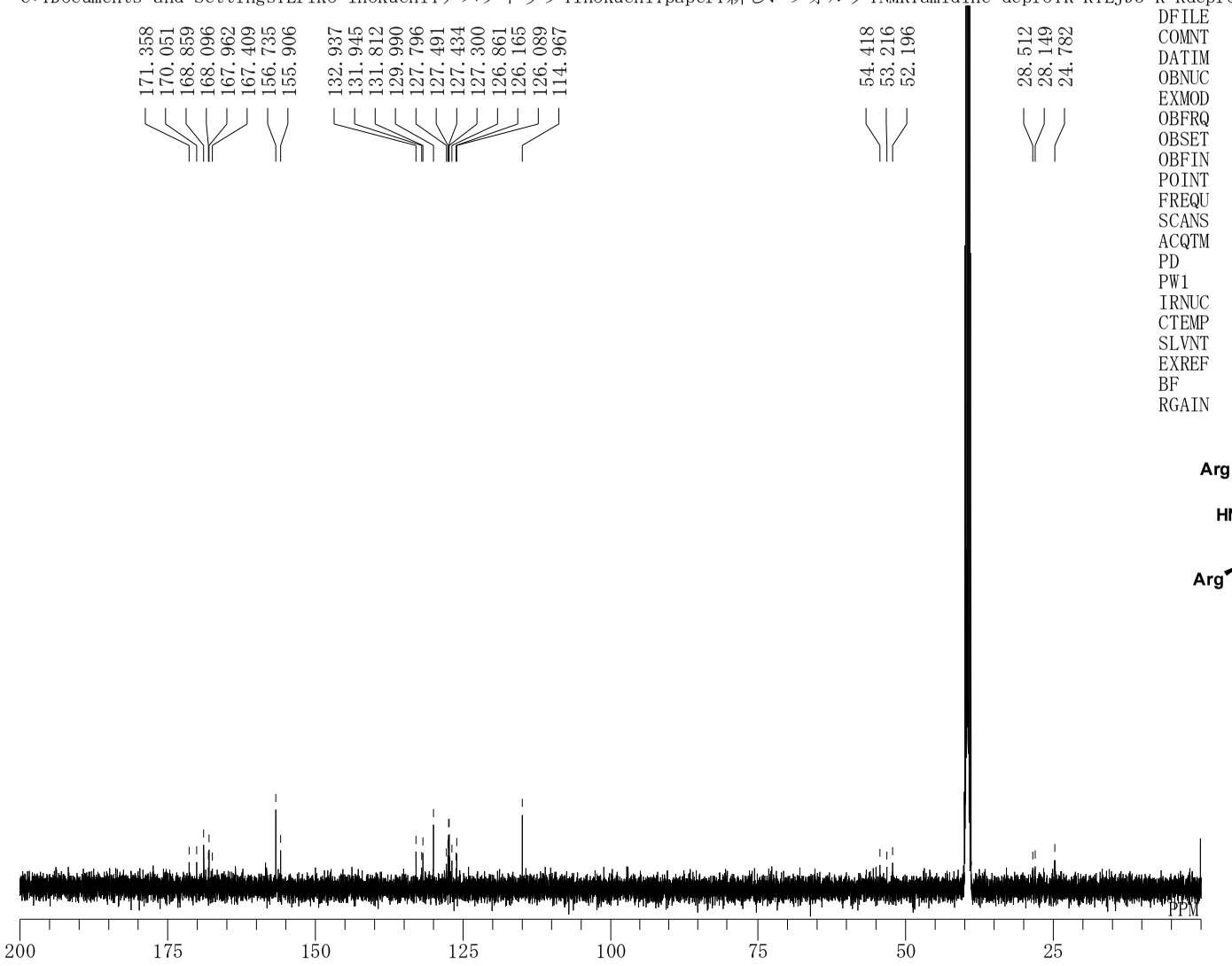


15d

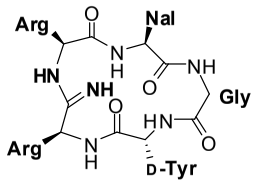

single_pulse
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥R-R¥LJ95 R-Rdepro 1H DMSO 110121-1.als
DFILE LJ95 R-Rdepro 1H DMSO 11012
COMNT single_pulse
DATIM 22-01-2011 08:27:40
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 52428
FREQU 7507.39 Hz
SCANS 3000
ACQTM 6.9835 sec
PD 5.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT DMSO
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 50
Arg
Nal
Gly
Arg
D-Tyr
15e
PPM

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥R-R¥LJ95 R-Rdepro 13C DMSO 110119-1.als



DFILE	LJ95 R-Rdepro 13C DMSO 1101	
COMNT	single pulse decoupled gate	
DATIM	20-01-2011 07:57:59	
OBNUC	13C	
EXMOD	single_pulse_dec	
OBFRQ	125.77	MHz
OBSET	7.87	KHz
OBFIN	4.21	Hz
POINT	26214	
FREQU	31446.06	Hz
SCANS	12000	
ACQTM	0.8336	sec
PD	2.0000	sec
PW1	7.47	usec
IRNUC	1H	
CTEMP	26.0	c
SLVNT	DMSO	
EXREF	39.50	ppm
BF	0.12	Hz
RGAIN	56	

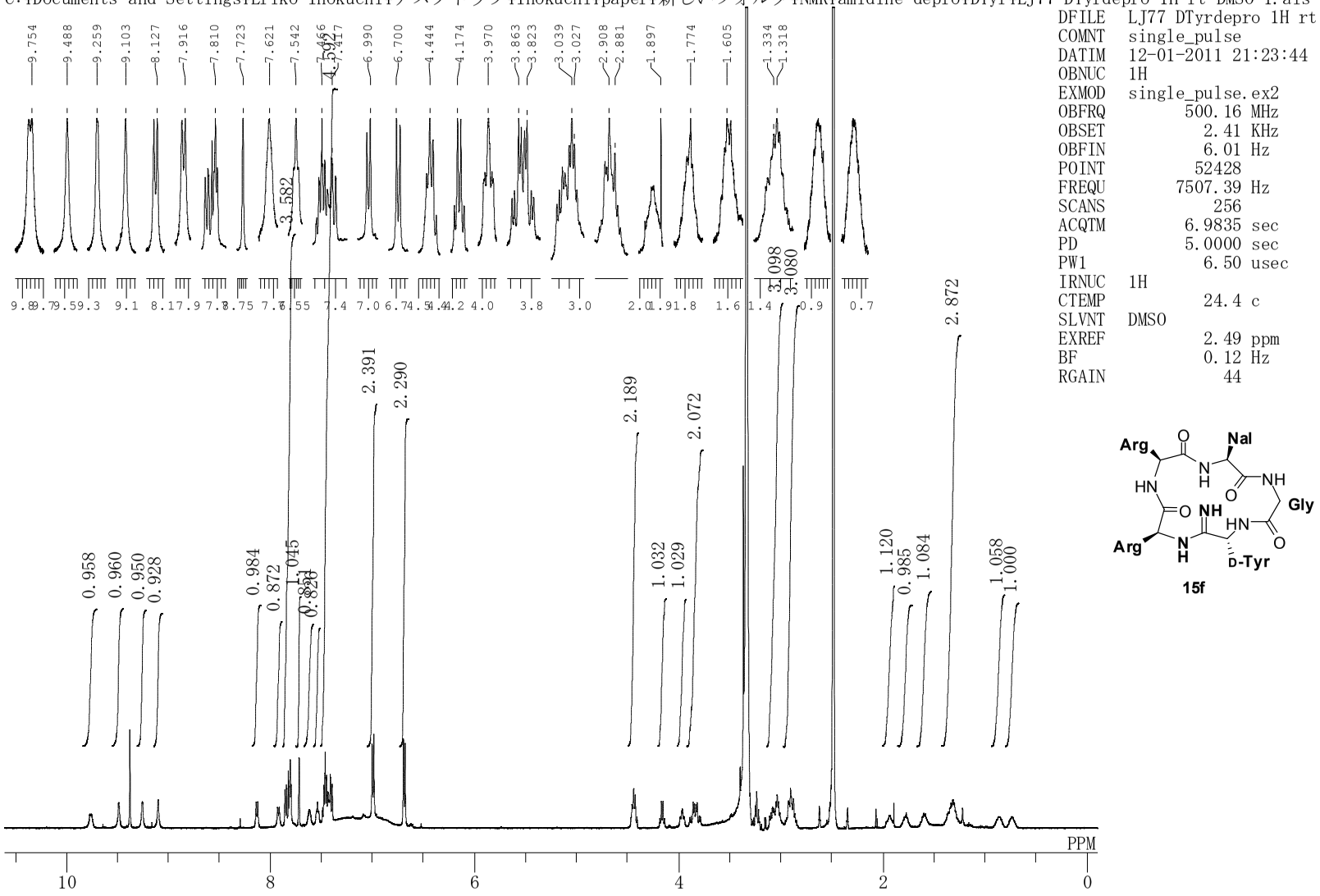


15e

single_pulse

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥DTyr¥LJ77 DTyrdepro 1H rt DMSO-1.als

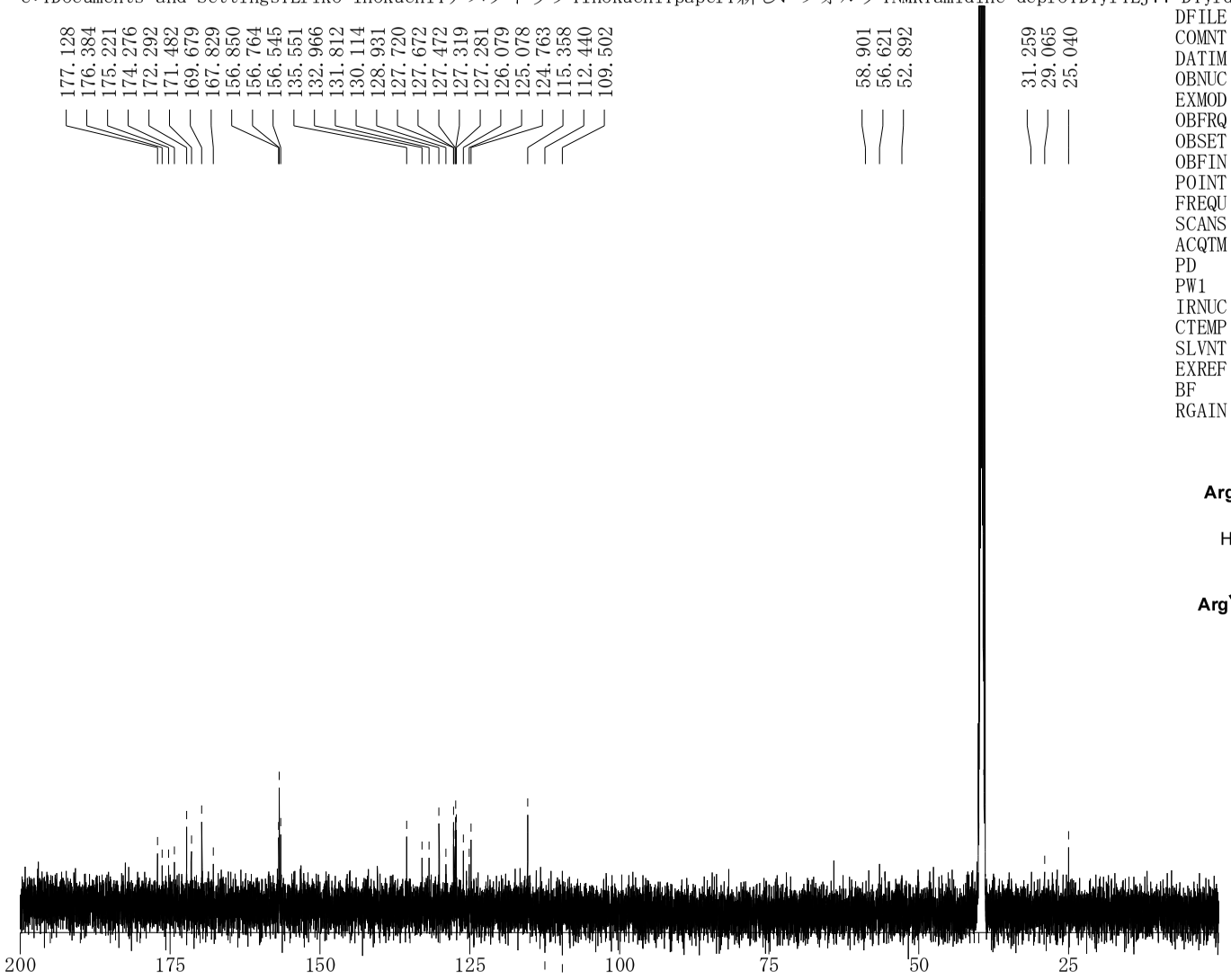
DFILE	LJ77 DTyrdepro 1H rt DMSO-1
COMNT	single_pulse
DATIM	12-01-2011 21:23:44
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	52428
FREQU	7507.39 Hz
SCANS	256
ACQTM	6.9835 sec
PD	5.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.4 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	44



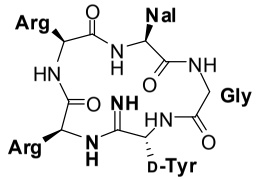
15f

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥DTyr¥LJ77 DTyrdepro 13C rt DMSO-1.als



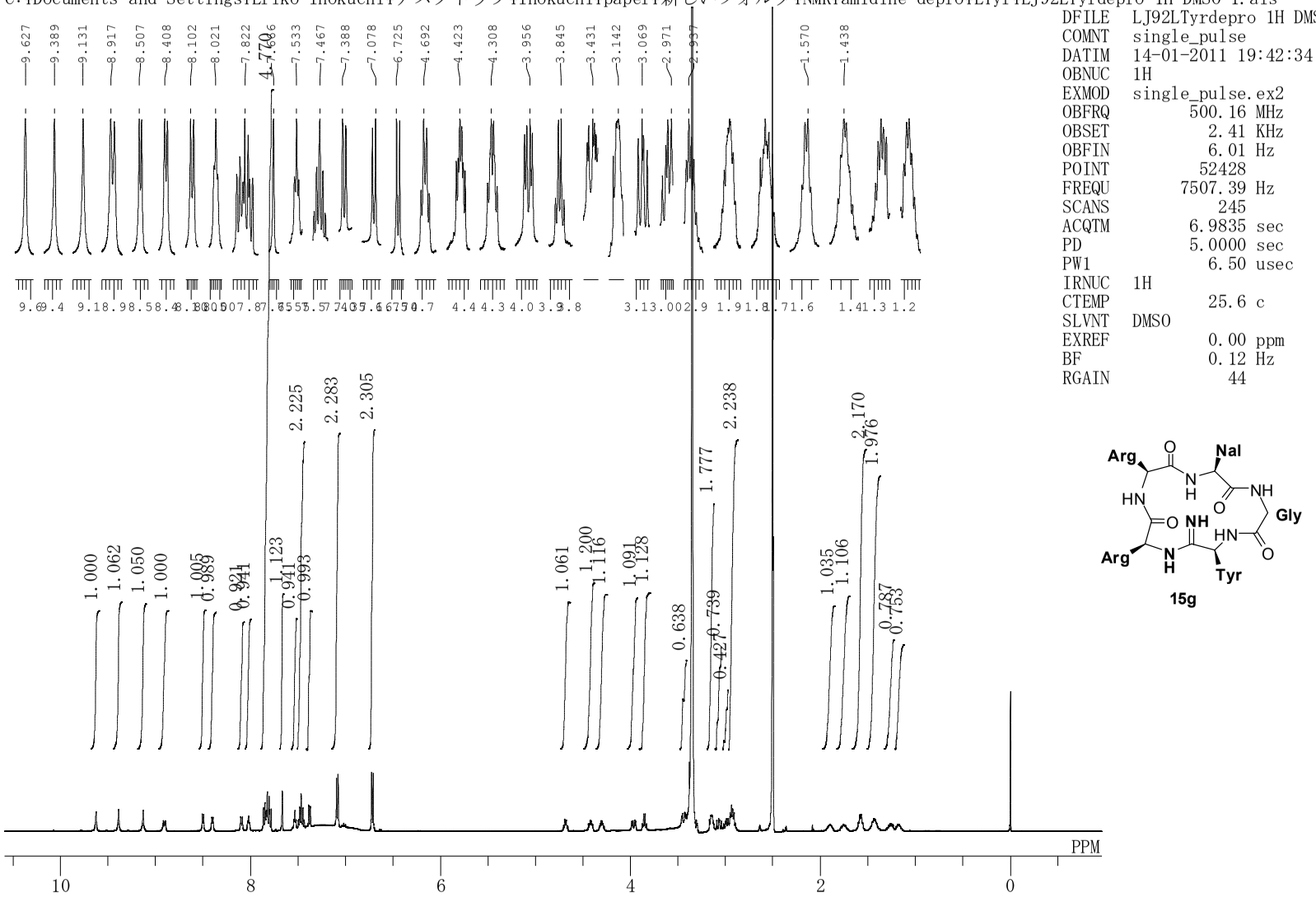
DFILE	LJ77 DTyrdepro 13C rt DMSO-
COMNT	single pulse decoupled gate
DATIM	07-01-2011 08:17:35
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	12288
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.73 usec
IRNUC	1H
CTEMP	27.0 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.12 Hz
RGAIN	58



15f

single_pulse

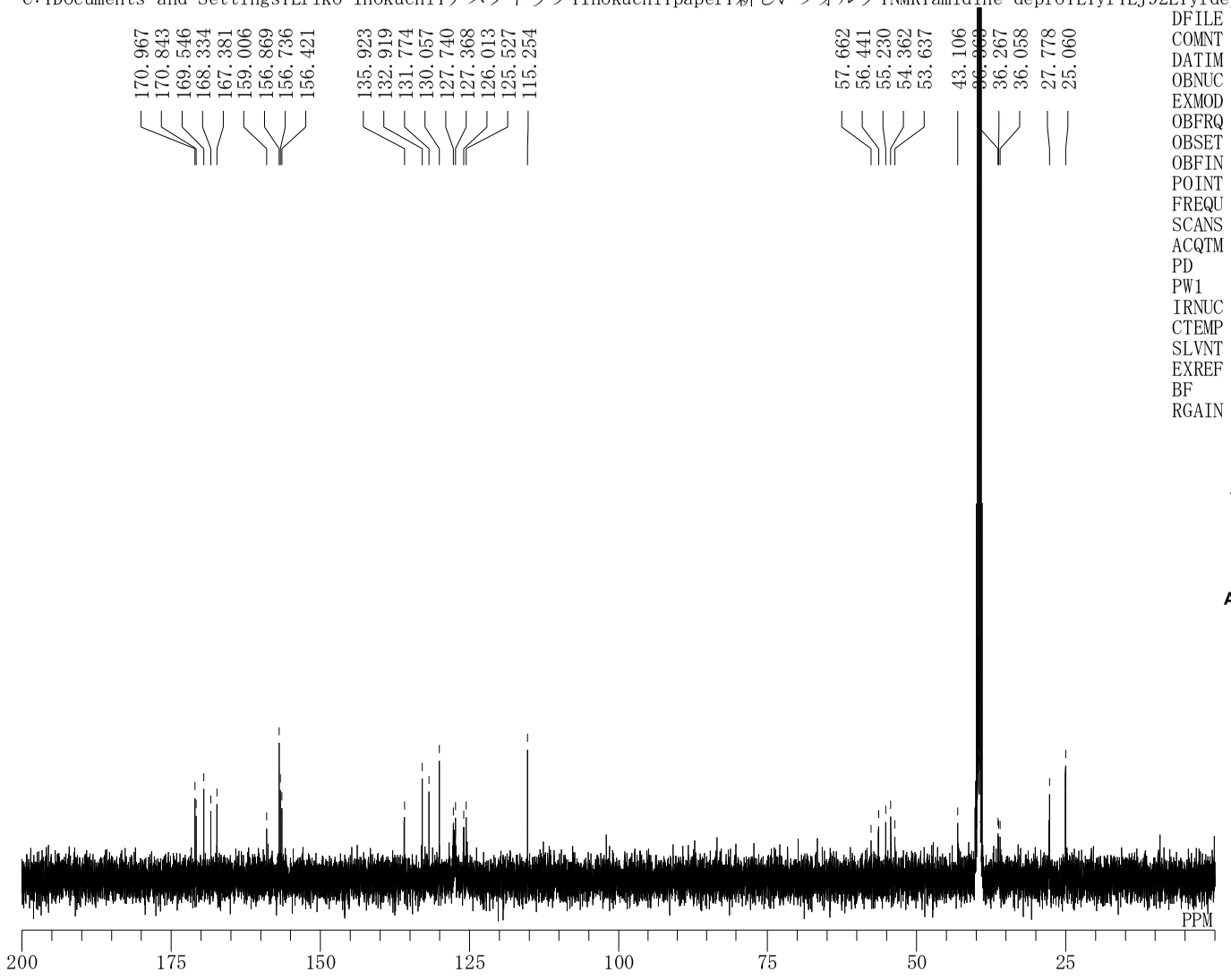
C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥LTyr¥LJ92LTyrdepro 1H DMSO-1.als



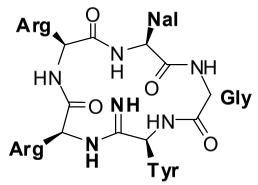
DFILE	LJ92LTyrdepro 1H DMSO-1.als
COMNT	single_pulse
DATIM	14-01-2011 19:42:34
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	52428
FREQU	7507.39 Hz
SCANS	245
ACQTM	6.9835 sec
PD	5.0000 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	DMSO
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	44

single pulse decoupled gated NOE

C:¥Documents and Settings¥Eriko Inokuchi¥デスクトップ¥Inokuchi¥paper¥新しいフォルダ¥NMR¥amidine depro¥LTyr¥LJ92LTyrdepro 13C DMSO-1.als



DFILE	LJ92LTyrdepro 13C DMSO-1.al
COMNT	single pulse decoupled gate
DATIM	14-01-2011 17:57:57
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.06 Hz
SCANS	1925
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	7.47 usec
IRNUC	1H
CTEMP	26.3 c
SLVNT	CDCL3
EXREF	39.52 ppm
BF	0.12 Hz
RGAIN	56



15g