Supporting Information

Direct Catalytic Asymmetric Mannich-type Reaction of α-Sulfanyl Lactones

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1. General

The direct catalytic asymmetric Mannich reaction was performed in a glass test tube with a Teflon-coated magnetic stirring bar unless otherwise noted. The flasks or test tubes were fitted with a 3-way glass stopcock and reactions were run under Ar atmosphere. Air- and moisture-sensitive liquids were transferred via a gas-tight syringe and a stainless-steel needle. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Flash chromatography was performed using silica gel 60 (230-400 mesh) purchased from Merck.

2. Instrumentation

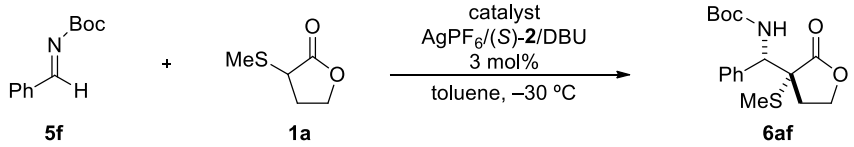
Infrared (IR) spectra were recorded on a HORIBA FT210 Fourier transform infrared spectrophotometer. NMR was recorded on JEOL ECS-400 and ECX-600 spectrometers. Chemical shifts for proton are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ppm, CD_3OD: δ 3.30 ppm). For ^{13}C NMR, chemical shifts were reported in the scale relative to NMR solvent ($CDCl_3$: δ 77.0 ppm, CD_3OD: δ 49.0 ppm) as an internal reference. For ^{19}F NMR, chemical shifts were reported in the scale relative to TFA (δ –76.5 ppm) as an external reference. For ^{31}P NMR, chemical shifts were reported in the scale relative to 85% H_3PO_4 in D_2O (δ 0.0 ppm) as an external reference. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, sep: septet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. Optical rotation was measured using a 2 mL cell with a 1.0 dm path length on a JASCO polarimeter P-1030. High-resolution mass spectra (ESI TOF (+)) were measured on ThermoFisher Scientific LTQ Orbitrap XL. HPLC analysis was conducted on a JASCO HPLC system equipped with Daicel chiral-stationary-phase columns (0.46 cm ϕ x 25 cm).

3. Materials

Unless otherwise noted, materials were purchased from commercial suppliers and were used without purification. Toluene, THF, diethyl ether, and CH_2Cl_2 were purified by passing through a solvent purification system (Glass Contour). Dry toluene were purchased from Kanto Chemical Co. Ltd. and used as received. $AgPF_6$ and other metal salts were purchased from Aldrich and used as received. (*R*)- and (*S*)-**2** were purchased from Aldrich or Strem Chemical Co. Ltd. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Sulfanyl lactones **1a-1c** were prepared by following procedure.[1]

4. General Procedure and Characterization of the Products

4-1. General procedure for the direct catalytic asymmetric Mannich reaction of α-sulfanyl lactones **1a** (For Table 2, entry 4).



*Preparation of $AgPF_6$/(S)-**2** in toluene*

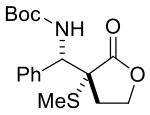
To a flame dried pear-shaped flask equipped with a stirring bar and 3-way glass stopcock were charged with $AgPF_6$ (10.1 mg, 0.04 mmol) and (*S*)-3,5-di-*tert*-butyl-4-methoxy-MeO-BIPHEP ((*S*)-**2**) (min 97%, 47.5 mg, 0.04 mmol) in a dry box under Ar atmosphere. Dry toluene (0.4 mL) was added to the flask via a gastight syringe and needle, and the resulting solution was stirred at room temperature for 30 min to give a 0.1 M $AgPF_6$/(*S*)-**2** in toluene.

To a flame dried test tube equipped with a stirring bar and 3-way glass stopcock were added dry toluene (322 μL), toluene solution of $AgPF_6$/(*S*)-**2** (60 μL, 0.006 mmol, 0.1 M), and 2-methylthio-γ-butyrolactone (**1a**) (21 μL, 0.2 mmol by well-dried syringe and needle at room temperature. The mixture was cooled to –30 °C and DBU (12 μL, 0.006 mmol) was added, then the resulting solution was stirred at the same temperature for 5 min. After 5 minutes, benzaldehyde

[1] Trost, B. M.; Arndt, H. C. *J. Org. Chem.* **1973**, *38*, 3140.

N-Boc imine **5f** (48 μL, 0.24 mmol) was added to the mixture and resulting solution was stirred at the same temperature for 48 h. The reaction was quenched with silica gel (Silica gel Merck 60, 230–400 mesh, ca. 0.9 cc) and the resulting mixture was passed through a short pad of silica gel with ethyl acetate as eluent. Volatiles were removed under reduced pressure and the resulting residue was purified by flash column chromatography (*n*-hexane/EtOAc = 5/1) to remove some impurities for determination of diastereomeric ratio by ^{1}H NMR analysis (*syn*/*anti* = 14/1). The partially purified product was repurified by flash column chromatography (CH_2Cl_2/*n*-hexane = 8/1 to 100/), then (*n*-hexane/ethyl acetate = 7/1) to afford **6af** (54.2 mg, 0.161 mmol, 80%) as a white solid. Enantiomeric excess was determined by HPLC analysis (*syn* = 96% ee, DAICEL CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.9 min (*syn* major-enantiomer), 10.1 min (*syn* minor-enantiomer). Absolute configuration of *ent*-**6af** (prepared from (*R*)-**2** catalyst) was determined unequivocally by X-ray crystallographic analysis.

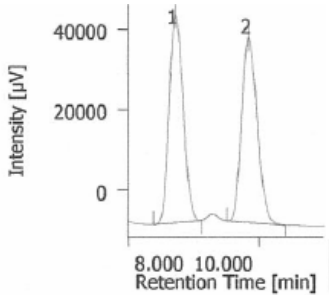
***tert*-Butyl ((*S*)-((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)(phenyl)methyl)carbamate (6af)**



6af

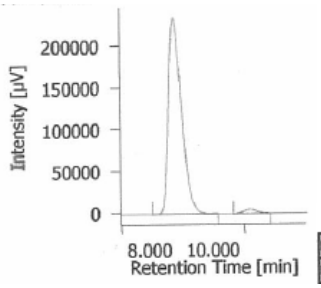
White solid; m.p. 178-180 °C; IR (KBr) *ν* 3417, 2969, 2365, 1744, 1711, 1509, 1368, 1245, 1168, 1027, 873, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40-7.25 (m, 5H), 5.33 (brd, *J* = 7.1 Hz, 1H), 5.16 (brs, 1H), 4.27 (ddd, *J* = 6.6, 8.9, 9.6 Hz, 1H), 3.96 (ddd, *J* = 1.8, 8.9, 8.9 Hz, 1H), 2.51 (ddd, *J* = 8.9, 9.6, 13.5 Hz, 1H), 2.14 (s, 3H), 1.88 (ddd, *J* = 1.8, 6.6, 13.5 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.4, 155.3, 137.4, 128.5, 128.2, 128.0, 80.2, 65.2, 54.6, 53.6, 30.7, 28.2, 12.1; $[\alpha]_D^{27}$ –1.4 (*c* 0.65, $CHCl_3$, 96% ee sample); HRMS (ESI) Anal. calcd. for $C_{17}H_{23}NO_4SNa$ *m*/*z* 360.1240 $[M+Na]^+$, found 360.1236; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.9 min (major), 10.1 min (minor).

racemic sample



	tR [min]	area%
Unknown	8.717	49.855
Unknown	9.833	50.145

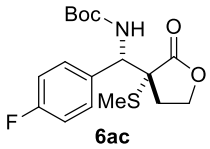
reaction sample



	tR [min]	area%
Unknown	8.858	97.833
Unknown	10.083	2.167

4-2. Characterization of Mannich Products

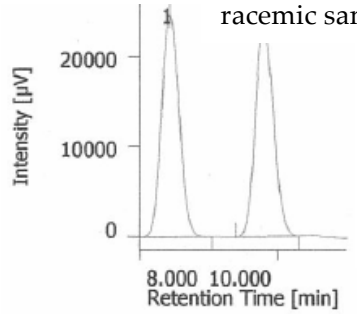
***tert*-Butyl ((*S*)-(4-fluorophenyl)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)carbamate (6ac)**



6ac

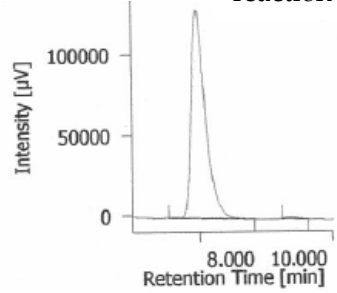
Colorless solid; m.p. 123-124 °C; IR (KBr) *ν* 3396, 2970, 2360, 2341, 1747, 1708, 1509, 1369, 1227, 1162, 1026, 843, 526 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.38-7.33 (m, 2H), 7.05-6.98 (m, 2H), 5.31 (brd, *J* = 6.4 Hz, 1H), 5.12 (brd, *J* = 5.5 Hz, 1H), 4.30 (ddd, *J* = 6.4, 9.2 9.8 Hz, 1H), 4.02 (ddd, *J* = 1.6, 9.2, 9.2 Hz, 1H), 2.48 (ddd, *J* = 9.2, 9.8, 13.5 Hz, 1H), 2.12 (s, 3H), 1.89 (ddd, *J* = 1.6, 6.4, 13.5 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.2, 162.4 (d, $J^1_{C\text{-}F}$ = 246 Hz), 155.3, 133.26, 129.9 (d, $J^3_{C\text{-}F}$ = 8.6 Hz), 115.4 (d, $J^2_{C\text{-}F}$ = 20 Hz), 80.4, 65.3, 54.2, 53.4, 30.7, 28.2, 12.0; ^{19}F NMR ($CDCl_3$) δ –114.0; $[\alpha]_D^{27}$ –0.27 (*c* 0.80, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{17}H_{22}FNO_4SNa$ *m*/*z* 378.1146 $[M+Na]^+$, found 378.1143; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.0 min (major), 9.4 min (minor).

racemic sample



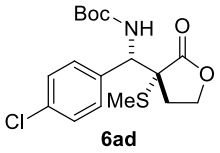
	tR [min]	area%
Unknown	8.433	50.223
Unknown	9.792	49.777

reaction sample



	tR [min]	area%
Unknown	7.975	99.424
Unknown	9.375	0.576

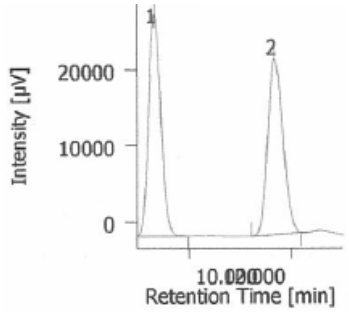
***tert*-Butyl ((*S*)-(4-chlorophenyl)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)carbamate (6ad)**



6ad

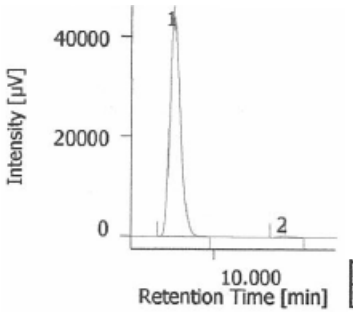
White solid; m.p. 162-164 °C; IR (KBr) ν 3369, 2979, 2927, 1758, 1699, 1492, 1367, 1249, 1169, 1029, 840, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35-7.27 (m, 4H), 5.33 (brd, J = 6.4 Hz, 1H), 5.11 (brd, J = 5.8Hz, 1H), 4.29 (ddd, J = 6.6, 9.0, 9.8 Hz, 1H), 4.03 (ddd, J = 1.6, 9.0, 9.2 Hz, 1H), 2.47 (ddd, J = 9.2, 9.8, 13.5 Hz, 1H), 2.13 (s, 3H), 1.88 (ddd, J = 1.6, 6.6, 13.5 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.1, 155.2, 136.1, 133.9, 129.6, 128.6, 80.5, 65.3, 54.2, 53.4, 30.1, 28.2, 12.1; $[\alpha]_D^{25}$ 3.2 (*c* 1.75, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{17}H_{22}ClNO_4SNa$ m/z 394.0851 $[M+Na]^+$, found 394.0847; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 9.0 min (major), 11.8 min (minor).

racemic sample



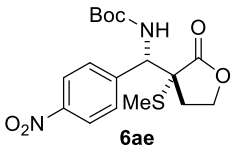
	tR [min]	area%
Unknown	9.333	50.083
Unknown	11.675	49.917

reaction sample



	tR [min]	area%
Unknown	9.033	99.261
Unknown	11.750	0.739

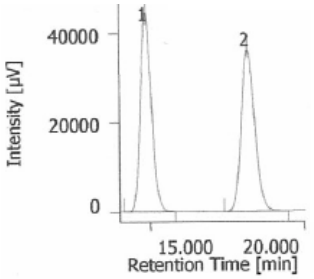
***tert*-Butyl ((*S*)-((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)(4-nitrophenyl)methyl)carbamate (6ae)**



6ae

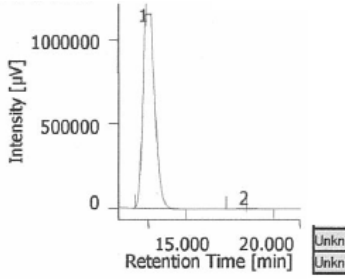
Colorless solid; m.p. 146-148 °C; IR (KBr) ν 3310, 2979, 2364, 1762, 1750, 1706, 1523, 1378, 1346, 1179, 1033, 865, 738, 709, 694, 541 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.22-8.16 (m, 2H), 7.59 (d, J = 8.9 Hz, 2H), 5.45 (brd, J = 6.0 Hz, 1H), 5.19 (brd, J = 4.6 Hz, 1H), 4.33 (ddd, J = 6.4, 9.0, 10.3 Hz, 1H), 4.08 (ddd, J = 1.2, 9.0, 9.0 Hz, 1H), 2.39 (ddd, J = 9.0, 10.3, 13.5 Hz, 1H), 2.14 (s, 3H), 1.94 (ddd, J = 1.2, 6.4, 1.5 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 172.7, 155.2, 147.6, 145.2, 129.3, 123.6, 80.9, 65.4, 54.6, 53.2, 30.7, 28.2, 12.1; $[\alpha]_D^{24}$ –9.7 (*c* 1.06, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{17}H_{22}N_2O_6SNa$ m/z 405.1091 $[M+Na]^+$, found 405.1079; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 14.9 min (major), 18.2 min (minor).

racemic sample



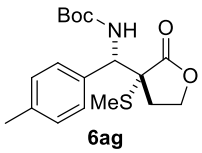
	tR [min]	area%
Unknown	14.850	49.977
Unknown	18.158	50.023

reaction sample



	tR [min]	area%
Unknown	14.908	99.671
Unknown	18.233	0.329

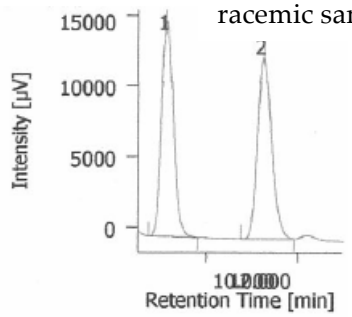
***tert*-Butyl ((*S*)-((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)(p-tolyl)methyl)carbamate (6ag)**



6ag

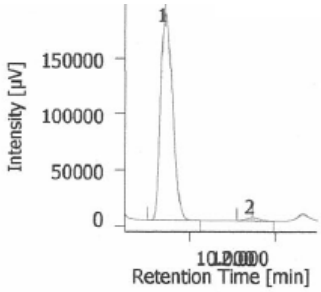
White solid; m.p. 143-144 °C; IR (KBr) ν 3403, 3389, 2972, 2923, 2360, 1748, 1707, 1507, 1368, 1246, 1161, 1026, 875, 779, 503 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 5.29 (brd, J = 7.1 Hz, 1H), 5.14 (brs, 1H), 4.26 (ddd, J = 6.6, 9.4, 9.4 Hz, 1H), 3.96 (ddd, J = 1.8, 9.4, 9.4 Hz, 1H), 2.52 (ddd, J = 9.4, 9.4, 13.5 Hz, 1H), 2.31 (s, 3H), 2.15 (s, 3H), 1.87 (ddd, J = 1.8, 6.6, 13.5 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.4, 155.3, 137.6, 134.3, 129.1, 128.1, 80.1, 65.2, 54.3, 53.6, 30.6, 28.2, 21.0, 12.1; $[\alpha]_D^{26}$ 3.5 (*c* 1.23, $CHCl_3$, 97% ee sample); HRMS (ESI) Anal. calcd. for $C_{18}H_{25}NO_4SNa$ m/z 374.1397 $[M+Na]^+$, found 374.1389; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 9.4 min (major), 11.5 min (minor).

racemic sample



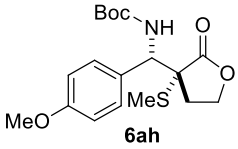
	tR [min]	area%
Unknown	9.125	50.082
Unknown	11.258	49.918

reaction sample



	tR [min]	area%
Unknown	9.433	98.356
Unknown	11.467	1.644

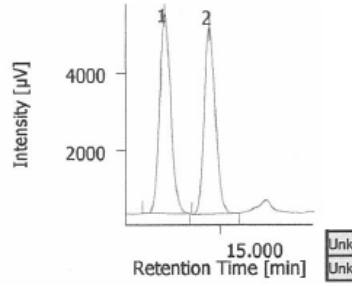
***tert*-Butyl ((*S*)-(4-methoxyphenyl)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)carbamate (6ah)**



6ah

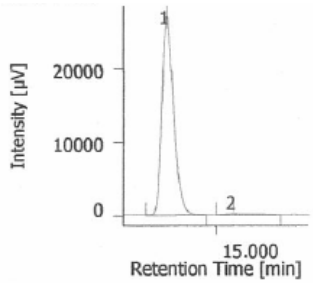
colorless solid; m.p. 154-156 °C; IR (KBr) ν 3390, 2976, 2929, 2361, 1750, 1708, 1507, 1247, 1186, 1162, 1032, 1024, 833, 546, 517 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 6.88-6.83 (m, 2H), 5.26 (brd, J = 7.1 Hz, 1H), 5.11 (brd, J = 4.8 Hz, 1H), 4.27 (ddd, J = 6.6, 9.2, 9.2, Hz, 1H), 3.98 (ddd, J = 2.0, 9.2, 9.2 Hz, 1H), 3.79 (s, 3H), 2.53 (ddd, J = 9.2, 9.2, 13.5 Hz, 1H), 2.14 (s, 3H), 1.87 (ddd, J = 2.0, 6.6, 13.5 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.5, 159.2, 155.3, 129.3, 129.3, 113.8, 80.2, 65.2, 55.2, 54.1, 53.6, 30.7, 28.2, 12.1; $[\alpha]_D^{26}$ 5.6 (c 0.47, $CHCl_3$, 97% ee sample); HRMS (ESI) Anal. calcd. for $C_{18}H_{25}NO_5SNa$ m/z 390.1346 $[M+Na]^+$, found 390.1336; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 13.4 min (major), 15.6 min (minor).

racemic sample



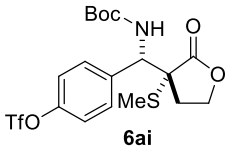
	tR [min]	area%
Unknown	13.242	51.655
Unknown	14.667	48.345

reaction sample



	tR [min]	area%
Unknown	13.383	98.358
Unknown	15.550	1.642

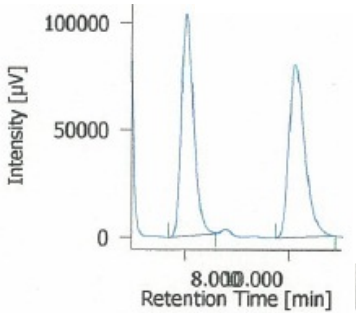
4-((*S*)-((*tert*-Butoxycarbonyl)amino)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)phenyl trifluoromethanesulfonate (6ai)



6ai

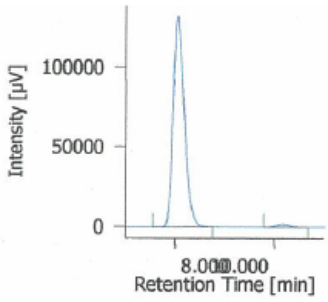
Colorless solid; m.p. 152-153 °C; IR (KBr) ν 3386, 3007, 2983, 2921, 1747, 1712, 1500, 1425, 1251, 1219, 1159, 1140, 1025, 897, 851, 786, 741, 651, 605, 524 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 5.34 (brd, J = 6.4 Hz, 1H), 5.14 (brs, 1H), 4.36-4.28 (m, 1H), 4.11-4.00 (m, 1H), 2.49-2.35 (m, 1H), 2.08 (s, 3H), 1.98-1.88 (m, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.0, 155.2, 149.1, 138.3, 130.3, 121.3, 118.7 (q, $J^1_{C\text{-}F}$ = 318.9 Hz), 80.7, 65.3, 54.4, 53.4, 30.9, 28.2, 12.1; ^{19}F NMR ($CDCl_3$) δ –72.6; $[\alpha]_D^{23}$ 2.3 (c 1.64, $CHCl_3$, 96% ee sample); HRMS (ESI) Anal. calcd. for $C_{18}H_{22}F_3NO_7S_2Na$ m/z 508.0682 $[M+Na]^+$, found 508.0671; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 8.1 min (major), 10.2 min (minor).

racemic sample



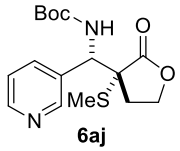
	tR [min]	area%
Unknown	8.033	49.276
Unknown	10.092	50.724

reaction sample



	tR [min]	area%
Unknown	8.050	98.234
Unknown	10.150	1.766

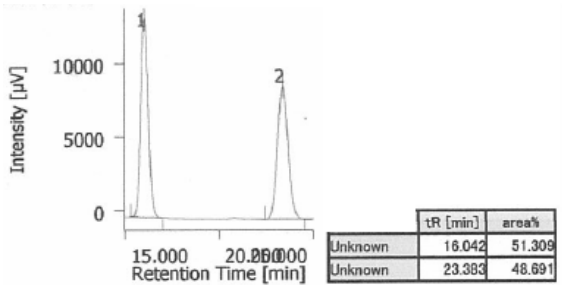
***tert*-Butyl ((*S*)-((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)(pyridin-3-yl)methyl)carbamate (6aj)**



6aj

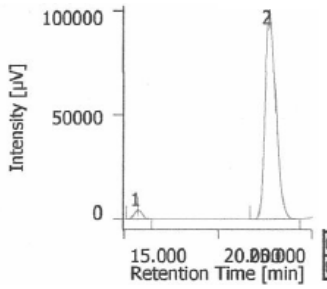
White solid; m.p. 178-180 °C; IR (KBr) ν 3422, 3168, 2970, 2360, 1765, 1742, 1712, 1509, 1367, 1245, 1167, 1027, 872, 716, 651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.65 (d, J = 2.1 Hz, 1H), 8.54 (dd, J = 1.4, 4.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.30-7.26 (m, 1H), 5.37 (brd, J = 6.9 Hz, 1H), 5.14 (brd, J = 5.7 Hz, 1H), 4.39-4.30 (ddd, J = 6.4, 9.2, 10.1 Hz, 1H), 4.14-4.05 (ddd, J = 1.0, 9.2, 9.2, 1H), 2.50 (ddd, J = 9.2, 10.1, 13.5 Hz, 1H), 2.08 (s, 3H), 2.00-1.93 (ddd, J = 1.0, 6.4, 13.5 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 172.8, 155.2, 149.6, 149.2, 136.5, 133.3, 123.3, 80.7, 65.4, 53.4, 53.4, 31.0, 28.2, 12.2; $[\alpha]_D^{25}$ 9.3 (c 0.64, $CHCl_3$, 94% ee sample); HRMS (ESI) Anal. calcd. for $C_{16}H_{22}N_2O_4SNa$ m/z 361.1193 $[M+Na]^+$, found 361.1186; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 15.8 min (minor), 22.7 min (major).

racemic sample



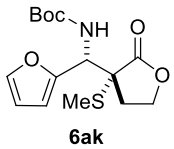
	tR [min]	area%
Unknown	16.042	51.309
Unknown	23.383	48.691

reaction sample



	tR [min]	area%
Unknown	15.775	2.937
Unknown	22.733	97.063

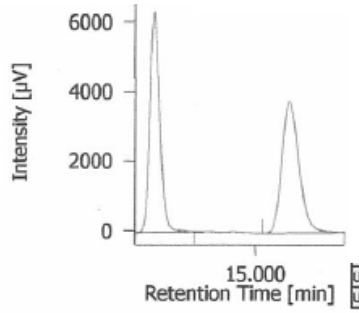
***tert*-Butyl ((*S*)-furan-2-yl((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)carbamate (6ak)**



6ak

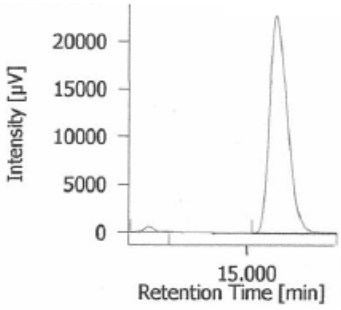
Colorless solid; m.p. 117-119 °C; IR (KBr) ν 3388, 3122, 2968, 2928, 1747, 1698, 1524, 1335, 1250, 1190, 1167, 1026, 872, 836, 741, 676, 580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38-7.35 (m, 1H), 6.34 (dd, J = 1.8, 3.2 Hz, 1H), 6.30 (d, J = 3.2 Hz, 1H), 5.41-5.25 (m, 1H), 5.06 (brd, J = 8.5 Hz, 1H), 4.33 (ddd, J = 6.6, 8.7, 10.3 Hz, 1H), 4.14 (ddd, J = 1.6, 8.7, 8.9 Hz, 1H), 2.48 (ddd, J = 8.9, 10.3, 13.5 Hz, 1H), 2.21 (s, 3H), 1.94 (ddd, J = 1.6, 6.6, 13.5 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.0, 155.2, 150.4, 142.4, 110.8, 109.2, 80.3, 65.1, 54.0, 49.4, 31.2, 28.2, 12.5; $[\alpha]_D^{24}$ 3.3 (c 1.47, $CHCl_3$, 97% ee sample); HRMS (ESI) Anal. calcd. for $C_{15}H_{21}NO_5SNa$ m/z 350.1033 $[M+Na]^+$, found 350.1027; CHIRALCEL OJ-H (ϕ 0.46 cm x 25 cm), ethanol/n-hexane = 1/9, flow rate 1.0 mL/min, detection at 254 nm, t_R = 11.7 min (minor), 16.0 min (major).

racemic sample



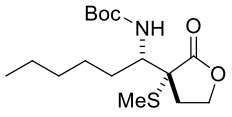
	tR [min]	area%
Unknown	11.633	49.761
Unknown	16.125	50.239

reaction sample



	tR [min]	area%
Unknown	11.650	1.539
Unknown	15.992	98.461

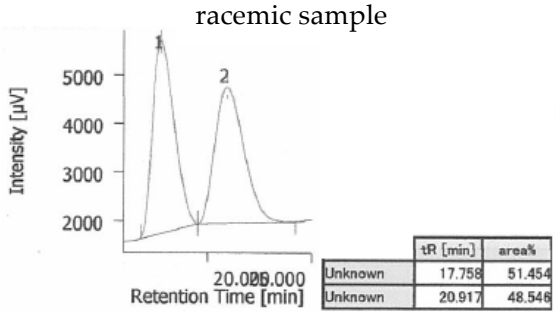
***tert*-Butyl ((*S*)-1-((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)hexyl)carbamate (6al)**



6al

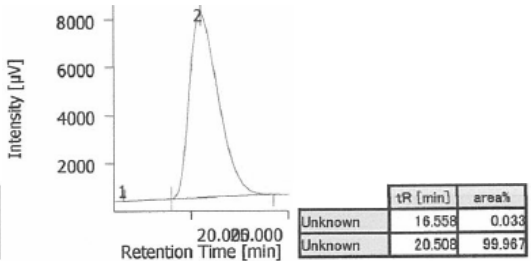
Colorless oil; IR (neat) ν 3361, 2959, 2929, 2361, 1758, 1701, 1523, 1366, 1171, 1030, 866, 771, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.40 (ddd, J = 6.4, 8.9, 10.3 Hz, 1H), 4.34-4.23 (m, 2H), 4.06-3.90 (m, 1H), 2.57-2.44 (m, 1H), 2.18 (s, 3H), 1.95-1.87 (m, 1H), 1.60-1.18 (m, 17H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 173.8, 156.0, 79.6, 65.2, 54.1, 51.6, 31.6, 31.3, 29.7, 28.3, 26.3, 22.5, 14.0, 12.7; $[\alpha]_D^{24}$ 22.2 (c 0.66, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{16}H_{29}NO_4SNa$ m/z 354.1710 $[M+Na]^+$, found 354.1701; CHIRALPAK IC (ϕ 0.46 cm x 25 cm), ^{i}PrOH/n-hexane = 1/99, flow rate 3.0 mL/min, detection at 254 nm, t_R = 16.6 min (minor), 20.5 min (major).

racemic sample



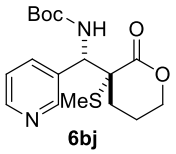
	tR [min]	area%
Unknown	17.758	51.454
Unknown	20.917	48.546

reaction sample



	tR [min]	area%
Unknown	16.558	0.033
Unknown	20.508	99.967

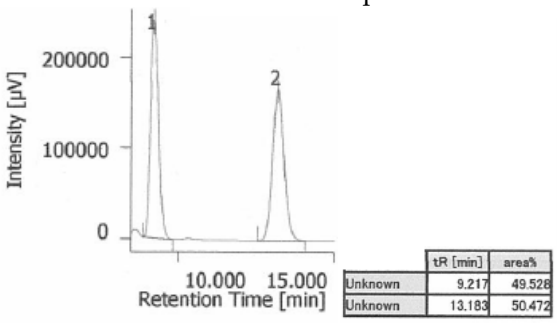
***tert*-Butyl ((*S*)-((*R*)-3-(methylthio)-2-oxotetrahydro-2*H*-pyran-3-yl)(pyridin-3-yl)methyl)carbamate (6bj)**



6bj

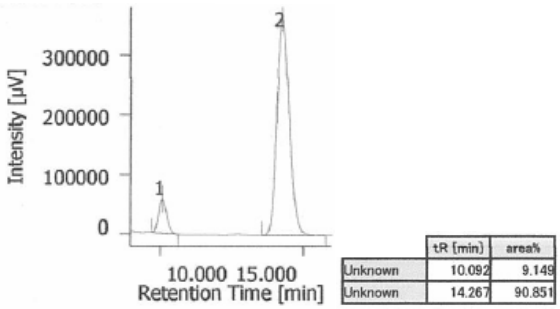
White solid; m.p. 145-147 °C; IR (KBr) ν 3276, 2973, 2925, 1717, 1537, 1480, 1447, 1425, 1403, 1315, 1261, 1165, 1083, 1017, 956, 881, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.67 (s, 1H), 8.51 (d, J = 3.9 Hz, 1H), 7.77 (d, J = 5.2 Hz, 1H), 7.27-7.22 (m, 1H), 5.43 (brd, J = 6.4 Hz, 1H), 5.24 (brd, J = 6.4 Hz, 1H), 4.48-4.38 (m, 1H), 4.05-3.97 (m, 1H), 2.25-2.18 (m, 1H), 2.10-1.89 (m, 4H), 1.85-1.79 (m, 1H), 1.62-1.05 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 167.6, 155.3, 149.9, 148.9, 136.9, 133.9, 123.1, 80.5, 69.0, 55.0, 53.6, 28.2, 28.1, 20.7, 13.3; $[\alpha]_D^{24}$ 5.3 (c 0.91, $CHCl_3$, 82% ee sample); HRMS (ESI) Anal. calcd. for $C_{17}H_{25}N_2O_4S$ m/z 353.1530 $[M+H]^+$, found 353.1528; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/n-hexane = 1/4, flow rate 1.0 mL/min, detection at 254 nm, t_R = 10.1 min (minor), 14.3 min (major).

racemic sample



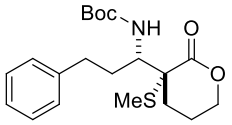
	tR [min]	area%
Unknown	9.217	49.528
Unknown	13.183	50.472

reaction sample



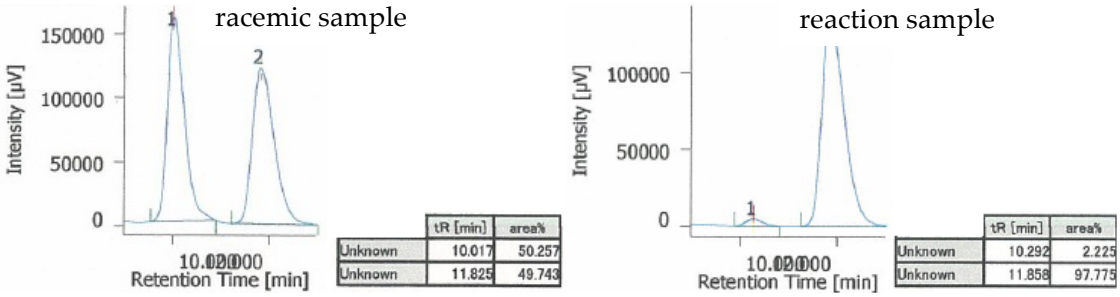
	tR [min]	area%
Unknown	10.092	9.149
Unknown	14.267	90.851

***tert*-Butyl ((*S*)-1-((*R*)-3-(methylthio)-2-oxotetrahydro-2*H*-pyran-3-yl)-3-phenylpropyl)carbamate (6bm)**



6bm

White amorphous; m.p. 46-48 °C; IR (KBr) ν 3361, 2977, 2927, 1717, 1522, 1454, 1392, 1366, 1253, 1164, 1083, 1045, 1025, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 4.58-4.52 (m, 1H), 4.46-4.35 (m, 1H), 4.26-4.15 (m, 2H), 2.81-2.69 (m, 2H), 2.25-2.03 (m, 5H), 1.94-1.84 (m, 1H), 1.78-1.65 (m, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 168.3, 156.0, 141.6, 128.4, 128.4, 125.9, 79.5, 68.8, 54.2, 53.3, 34.8, 33.4, 28.3, 27.2, 20.8, 13.7; $[\alpha]_D^{27}$ 19.4 (c 1.61, $CHCl_3$, 96% ee sample); HRMS (ESI) Anal. calcd. for $C_{20}H_{29}NO_4SNa$ m/z 402.1710 $[M+Na]^+$, found 402.1706; CHIRALCEL OZ-H (ϕ 0.46 cm x 25 cm), isopropanol/n-hexane = 1/19, flow rate 1.0 mL/min, detection at 254 nm, t_R = 10.3 min (minor), 11.9 min (major).



5. Determination of the absolute configuration of Mannich adducts (Table 1)

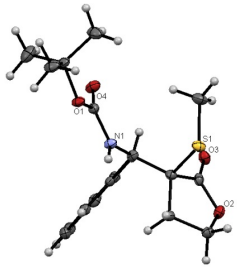
AcOEt solution of *ent*-**6af** prepared from (*R*)-catalyst was left stand at room temperature to grow a single crystal. Single-crystal X-ray data were collected on a Rigaku R-AXIS RAPID II imaging plate area detector with graphite-monochromated Cu-Kα radiation. Data collection was conducted at 93 K. All structures were solved by direct methods and refined by full matrix least-squares against F^2 with all reflections. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions, and were refined with an isotropically. Refined crystallographic parameters are summarized in Table S1. The absolute and relative configuration of the major diastereomer of *ent*-**6af** was determined to be as depicted in Figure S1 by Flack parameter.[2] The absolute configuration of other products was deduced by analogy.

Table S1. Selected crystallographic data of *ent*-**6af**

	ent-**6af**
molecular formula	$C_{17}H_{23}NO_4S$
formula weight	337.43
crystal color, habit	colorless, needle
crystal system	orthorhombic
space group	P21
cell constants	
a (Å)	6.42235(12)
b (Å)	10.7946(2)
c (Å)	24.6088(5)
α (deg)	90.0000
β (deg)	90.0000
γ (deg)	90.0000
V (Å^3)	1706.05(6)
Z	4
ρ_{calcd} (g cm^{-3})	1.314
R_1	0.0309
wR_2	0.0840
F(000)	720.00

Structure of *ent*-**6af** (prepared from (*R*)-**2** catalyst) was determined unequivocally by X-ray crystallographic analysis.

[2] Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876.



Therefore, absolute configuration of **6ac** was assigned as mentioned above.

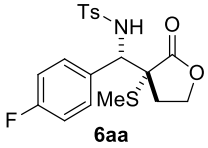
*Absolute configuration of **6aa**:*

6ac (prepared from (*S*)-catalyst) was treated with 4N HCl/dioxane to remove Boc group. The resulting amine hydrochloride was converted to **6aa** with TsCl and NEt_3 to afford **6aa**. Thus obtained **6aa** has identical absolute configuration to that of **6aa** obtained from the Mannich reaction using (*S*)-catalyst (in HPLC analysis). Therefore, **6aa** and **6ac** obtained from (*S*)-catalyst have identical absolute configuration.

*Absolute configuration of **6ab:***

Mannich adduct of benzaldehyde-derived diphenylphosphinoyl imine (prepared form (*S*)-catalyst) was treated with conc. HCl in THF (conc. HCl/THF = 1/6) and stirred overnight at room temperature. The resulting amine hydrochloride was converted to **6af** with Boc_2O and $^iPr_2NEt$. Thus obtained **6af** has identical absolute configuration to that of **6af** obtained from the Mannich reaction of **1a** and **5f** using (*S*)-catalyst (in HPLC analysis). By assuming that *para*-fluoro substituent had no influence on stereodifferentiation, **6ab** has identical absolute configuration to **6ac**.

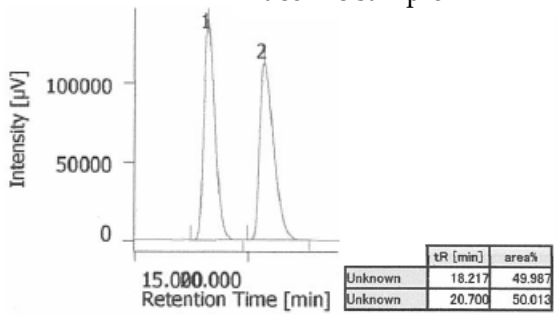
***N*-((*S*)-(4-Fluorophenyl)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)-4-methylbenzenesulfonamide (6aa)**



6aa

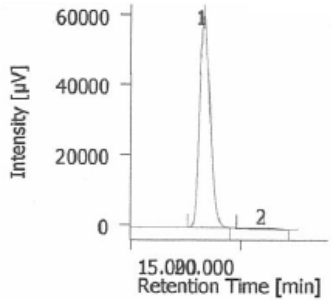
white solid; m.p. 155-157 °C; IR (KBr) ν 3358, 3305, 3261, 1731, 1604, 1511, 1457, 1337, 1223, 1190, 1161, 1089, 842, 813, 677, 655, 566, 542 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (d, J = 5.5 Hz, 2H), 7.25-7.20 (m, 2H), 7.17 (d, J = 5.5 Hz, 2H), 6.88-6.83 (m, 2H), 5.57 (d, J = 1.8 Hz, 1H), 4.62 (d, J = 1.8 Hz, 1H), 4.29-4.22 (m, 1H), 4.05-3.98 (m, 1H), 2.61-2.54 (m, 1H), 2.38 (s, 3H), 1.87-1.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 172.2, 162.6 (d, $J^1_{C\text{-}F}$ = 247.0 Hz), 144.0, 135.7, 131.2 (d, $J^3_{C\text{-}F}$ = 8.6 Hz), 130.1 (d, $J^4_{C\text{-}F}$ = 2.9 Hz), 129.5, 127.5, 115.1 (d, $J^2_{C\text{-}F}$ = 21.5 Hz), 65.5, 56.6, 53.7, 30.3, 21.5, 11.2; ^{19}F NMR ($CDCl_3$) δ –113.3; $[\alpha]_D^{25}$ 78.3 (*c* 0.30, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{19}H_{20}FNO_4S_2Na$ *m*/*z* 432.0710 $[M+Na]^+$, found 432.0702; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ethanol/*n*-hexane = 1/4, flow rate 1.0 mL/min, detection at 254 nm, t_R = 18.3 min (major), 21.1 min (major).

racemic sample



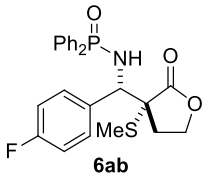
	tR [min]	area%
Unknown	18.217	49.987
Unknown	20.700	50.013

reaction sample



	tR [min]	area%
Unknown	18.317	99.601
Unknown	21.050	0.399

***N*-((*S*)-(4-Fluorophenyl)((*R*)-3-(methylthio)-2-oxotetrahydrofuran-3-yl)methyl)-*P*,*P*-diphenylphosphinic amide (6ab)**

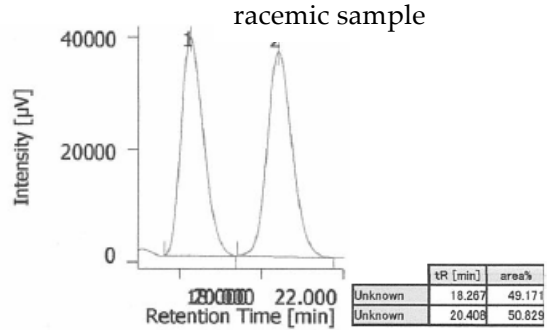


6ab

White solid; m.p. 215-217 °C; IR (KBr) ν 3422, 3193, 2923, 1754, 1605, 1510, 1438, 1226, 1177, 1124, 1107, 1029, 847, 751, 726, 696, 544, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82-7.74 (m, 2H), 7.63-7.35 (m, 6H), 7.32-7.20 (m, 4H), 6.91-6.84 (m, 2H), 4.61-4.54 (m, 1H), 4.39-4.30 (m, 1H), 4.17-4.10 (m, 1H), 4.05-3.98 (m, 1H), 3.06-2.95 (m, 1H), 2.00-1.90 (m, 4H); ^{13}C NMR ($CDCl_3$) ($J_{C\text{-}P}$ coupling was not identified due to extensive overlap of multiple peaks in aromatic region. Observed peaks are reported.) δ 173.1, 162.2 (d, $J^1_{C\text{-}F}$ = 246.0 Hz), 133.4, 132.6, 132.3, 132.2, 131.9, 131.8, 131.6, 131.6, 131.5, 131.4, 131.2, 131.1, 130.3, 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.1 (d, $J_{C\text{-}P}$ = 13.4 Hz), 114.7 (d, $J^2_{C\text{-}F}$ = 21.0 Hz), 65.7, 56.0, 54.6 (d, $J^2_{C\text{-}P}$ = 6.7 Hz), 31.9, 12.4; ^{19}F

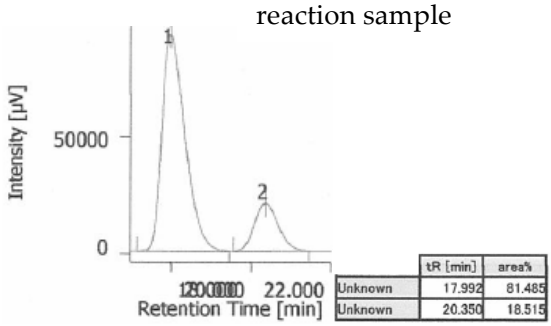
NMR ($CDCl_3$) δ –113.9; ^{31}P NMR ($CDCl_3$) δ 24.4; $[\alpha]_D^{22}$ 12.7 (*c* 0.13, $CHCl_3$, 63% ee sample); HRMS (ESI) Anal. calcd. for $C_{24}H_{24}FNO_3PS$ *m*/*z* 456.1194 $[M+H]^+$, found 456.1183; CHIRALPAK AD-H (ϕ 0.46 cm x 25 cm), ^{i}PrOH/*n*-hexane = 4/1, flow rate 1.0 mL/min, detection at 254 nm, t_R = 18.0 min (major), 20.4 min (minor).

racemic sample



	tR [min]	area%
Unknown	18.267	49.171
Unknown	20.408	50.829

reaction sample



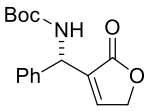
	tR [min]	area%
Unknown	17.992	81.485
Unknown	20.350	18.515

6. Transformation of the Mannich products.

6-1. Synthesis of aza-Morita-Baylis-Hillman adducts (β-elimination product, for **8af**)

To a stirred mixture of **6af** (33.7 mg, 0.10 mmol) and $NaHCO_3$ (10.1 mg, 0.12 mmol) in CH_2Cl_2 (1.0 mL) was added *m*CPBA (max 77% purity, 22.4 mg, 0.10 mmol) at 0 °C. After stirring the resulting solution at the same temeperature for 15 min, sat. $NaHCO_3$ aq was added. The resulting mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4. Volatiles were removed under reduced pressure and the resulting residue was engaged to the next step. The crude sulfoxide was dissolved in toluene (2.0 mL) and resulting mixture was stirred at 100 °C. After 1 h, the reaction mixture was cooled to the ambient temperature and AcOEt was added. The resulting biphasic mixture was washed with sat. $NaHCO_3$ aq., brine and dried over Na_2SO_4. Volatiles were removed under reduced pressure and the resulting residue was purified by flash silica gel column chromatography (*n*-hexane/ethyl acetate = 2/1) to give **8af** (26.0 mg, 90%) as a colorless solid. **8al** was synthesized in a similar procedure.

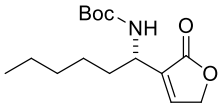
(*S*)-*tert*-Butyl ((2-oxo-2,5-dihydrofuran-3-yl)(phenyl)methyl)carbamate (8af)



8af

White solid; m.p. 125-126 °C; IR (KBr) ν 3441, 3083, 2976, 2930, 1741, 1710, 1509, 1365, 1346, 1312, 1233, 1175, 1098, 1041, 885, 837, 702, 615, 516 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ; 7.40-7.26 (m, 6H), 5.74 (brs, 2H), 4.84 (s, 2H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 172.3, 154.9, 146.1, 139.0, 133.8, 128.8, 128.0, 126.7, 80.2, 70.3, 51.6, 28.3; $[\alpha]_D^{27}$ 34.3 (*c* 0.37, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{16}H_{19}NO_4Na$ *m*/*z* 312.1207 $[M+Na]^+$, found 312.1198.

(*S*)-*tert*-Butyl (1-(2-oxo-2,5-dihydrofuran-3-yl)hexyl)carbamate (8al)

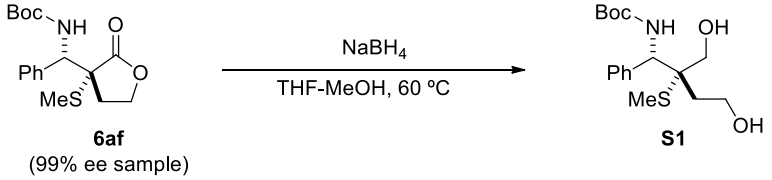


8al

Colorless oil; IR (neat) ν 3388, 2931, 1750, 1692, 1519, 1366, 1248, 1170, 1067, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28-7.20 (m, 1H), 5.21 (brd, *J* = 7.8 Hz, 1H), 4.81 (s, 2H), 4.56-4.42 (m, 1H), 1.78-1.67 (m, 2H), 1.43 (s, 9H), 1.36-1.21 (m, 6H), 0.93-0.79 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 172.7, 155.2, 145.5, 134.0, 79.6, 70.1, 48.0, 33.4, 31.3, 28.3, 25.7, 22.5, 13.9; $[\alpha]_D^{23}$ –22.8 (*c* 0.46, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{15}H_{25}NO_4Na$ *m*/*z* 306.1676 $[M+Na]^+$, found 306.1678.

6-2. Synthesis of trisubstituted aziridine

***tert*-Butyl ((1*S*,2*R*)-4-hydroxy-2-(hydroxymethyl)-2-(methylthio)-1-phenylbutyl)carbamate (S1)**



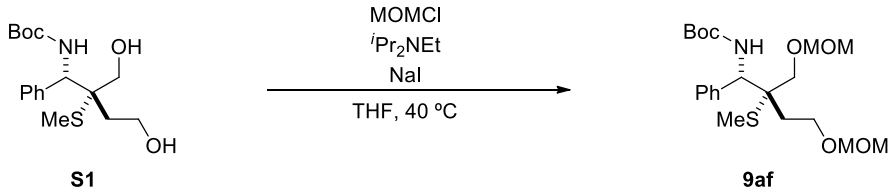
6af
(99% ee sample)

S1

To a stirred solution of **6af** (241 mg, 0.714 mmol) in dry THF (7.2 mL) was added $NaBH_4$ (54.0 mg, 1.43 mmol) at room temperature under Ar atmosphere. The resulting mixture was warmed to 60 °C and stirred for 15 min at the same temperature. MeOH (1.4 mL) was carefully added to the reaction mixture over 30 min. After stirring at the same temperature for 15 min, additional $NaBH_4$ (13.5 mg, 0.358 mmol) was carefully added and continued stirring at the same temperature. After 30 min, resulting mixture was cooled to ambient temperature and sat. NH_4Cl aq. was added. The resulting mixture was extracted with ethyl acetate, then dried over Na_2SO_4. Volatiles were removed under reduced pressure and the resulting residue was purified by flash silica gel column chromatography (*n*-hexane/ethyl acetate = 1/1) to give **S1** (235 mg, 96%) as a sticky colorless oil.

Sticky colorless oil; IR (neat) ν 3391, 2978, 2928, 1684, 1496, 1366, 1249, 1168, 1044, 910, 733, 704, cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.43-7.20 (m, 6H), 5.32-5.24 (m, 1H), 4.78 (d, J = 9.2 Hz, 1H), 4.73-4.68 (m, 1H), 3.63-3.56 (m, 2H), 3.42-3.37 (m, 1H), 3.25-3.19 (m, 1H), 1.87-1.74 (m, 4H), 1.66-1.58 (m, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 156.2, 138.1, 128.5, 127.9, 127.6, 80.1, 64.3, 58.2, 58.0, 54.3, 35.4, 28.2, 11.0; $[\alpha]_D^{26}$ 0.28 (*c* 0.69, $CHCl_3$); HRMS (ESI) Anal. calcd. for $C_{17}H_{27}NO_4SNa$ m/z 364.1553 $[M+Na]^+$, found 364.1550.

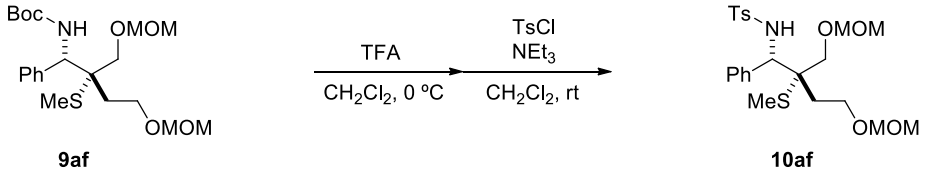
***tert*-Butyl(1*S*,2*R*)-4-(methoxymethoxy)-2-((methoxymethoxy)methyl)-2-(methylthio)-1-phenylbutyl)carbamate (9af)**



To a stirred solution of **S1** (247 mg, 0.723 mmol) in dry THF (7.2 mL) were added $^iPr_2NEt$ (0.67 mL, 3.76 mmol), NaI (54.2 mg, 0.362 mmol) and chloromethyl methyl ether (0.27 mL, 3.62 mmol) successively at room temperature. The resulting mixture was warmed to 40 °C. After stirring at the same temperature for 15 h, the resulting mixture was cooled to ambient temperature and sat. $NaHCO_3$ aq. was added and the resulting mixture was extracted with AcOEt. Combined organic layer was washed with brine, dried over Na_2SO_4. Volatiles were removed under reduced pressure and the resulting residue was purified by flash silica gel column chromatography (*n*-hexane/ethyl acetate = 3/1) to give **9af** (294 mg, 95%) as a colorless oil.

Colorless oil; IR (neat) ν 3431, 2930, 2885, 1714, 1495, 1366, 1166, 1106, 1041, 918, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42-7.25 (m, 5H), 6.19 (brd, J = 8.2 Hz, 1H), 4.93 (brd, J = 9.0 Hz, 1H), 4.69 (s, 2H), 4.64 (s, 2H), 3.84-3.72 (m, 2H), 3.61-3.33 (m, 8H), 2.11-1.90 (m, 2H), 1.83 (s, 3H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 154.8, 138.8, 128.5, 127.7, 127.4, 96.7, 96.4, 79.1, 70.3, 63.7, 58.2, 55.6, 55.2, 52.1, 31.6, 28.2, 11.1; $[\alpha]_D^{25}$ –5.6 (*c* 0.51, $CHCl_3$); HRMS (ESI) Anal. calcd. for $C_{21}H_{35}NO_6SNa$ m/z 452.2078 $[M+Na]^+$, found 452.2070.

***N*-((1*S*,2*R*)-4-(Methoxymethoxy)-2-((methoxymethoxy)methyl)-2-(methylthio)-1-phenylbutyl)-4-methylbenzenesulfonamide (10af)**



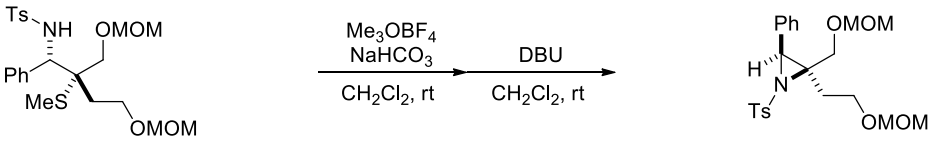
To a stirred solution of **9af** (335 mg, 0.78 mmol) in CH_2Cl_2 (3.9 mL) was added TFA (3.9 mL) dropwise at 0 °C and resulting mixture was stirred at the same temperature for 2 h. Volatiles were removed under reduced pressure and the crude amine TFA salt was engaged to the next step without purification.

The residue was dissolved in dry CH_2Cl_2 (7.8 mL) and cooled to 0 °C. To the stirred resulting solution, NEt_3 (0.43 mL, 3.12 mmol) and TsCl (149 mg, 0.78 mmol) were added successively and warmed to the ambient temperature. After stirring the resulting mixture for 2 h, sat. $NaHCO_3$ aq. was added and the resulting biphasic mixture was extracted with CH_2Cl_2 and combined organic phase was washed with brine, dried over Na_2SO_4. Volatiles were removed under

reduced pressure and the resulting residue was purified by flash silica gel column chromatography (*n*-hexane/ethyl acetate = 4/1) to give **10af** (242 mg, 64%, 2 steps) as a colorless solid.

Colorless solid; m.p. 82-84 °C; IR (KBr) ν 3330, 2925, 2894, 1723, 1598, 1422, 1321, 1156, 1102, 1025, 920, 708, 670, 574 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.12-6.99 (m, 5H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.12 (brd, *J* = 9.2 Hz, 1H), 4.72-4.59 (m, 5H), 3.83-3.3.72 (m, 2H), 3.56 (d, *J* = 10.1 Hz, 1H), 3.45 (d, *J* = Hz, 1H), 3.44 (s, 3H), 3.37 (s, 3H), 2.26 (s, 3H), 2.07-1.97 (m, 1H), 1.96-1.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 142.4, 137.6, 136.0, 128.8, 128.6, 127.5, 127.3, 126.7, 96.8, 96.4, 70.2, 63.5, 61.4, 55.9, 55.3, 52.3, 31.8, 21.2, 11.2; $[\alpha]_D^{26}$ –14.6 (*c* 0.59, $CHCl_3$); HRMS (ESI) Anal. calcd. for $C_{23}H_{33}NO_6S_2Na$ *m*/*z* 506.1642 $[M+Na]^+$, found 506.1630.

(2*S*,3*S*)-2-(2-(methoxymethoxy)ethyl)-2-((methoxymethoxy)methyl)-3-phenyl-1-tosylaziridine (11af)

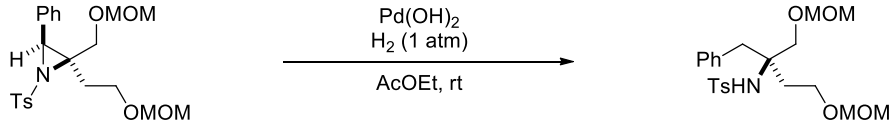


10af **11af**

To a stirred mixture of **10af** (69 mg, 0.143 mmol) and $NaHCO_3$ (12.0 mg, 0.143 mmol) in dry CH_2Cl_2 (2.8 mL) was added Me_3OBF_4 (95%, 23.3 mg, 0.150 mmol) at room temperature and resulting mixture was stirred at the same temperature for 1.5 h. After complete disappearance of **10af** in TLC analysis, DBU (85 μL, 0.571 mmol) was added. After stirring the resulting mixture for x min, sat. NH_4Cl aq. was added. Resulting biphasic mixture was extracted with CH_2Cl_2 and combined organic phase was dried over Na_2SO_4. Volatiles were removed under reduced pressure and the resulting residue was purified by flash silica gel column chromatography (*n*-hexane/ethyl acetate = 4/1) to give **11af** (56.1 mg, 90%) as a colorless oil.

Colorless oil; IR (neat) ν 2931, 2885, 2823, 1599, 1451, 1327, 1158, 1048, 918, 816, 746, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23-7.17 (m, 3H), 7.07-7.00 (m, 2H), 4.73 (d, *J* = 6.6 Hz, 1H), 4.71 (d, *J* = 6.6 Hz, 1H), 4.62 (d, *J* = 6.4 Hz, 1H), 4.45 (d, *J* = 6.4 Hz, 1H), 4.20 (s, 1H), 3.92-3.80 (m, 2H), 3.44 (d, *J* = 11.5 Hz, 1H), 3.40 (s, 3H), 3.21 (s, 3H), 3.05 (d, *J* = 11.5 Hz, 1H), 2.74 (dt, *J* = 3.9, 14.2 Hz, 1H), 2.61-2.52 (m, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 144.0, 137.8, 133.2, 129.6, 128.2, 127.7, 127.4, 126.8, 96.5, 95.9, 67.0, 64.5, 55.8, 55.4, 55.2, 51.6, 29.9, 21.6; $[\alpha]_D^{26}$ 50.9 (*c* 0.98, $CHCl_3$); HRMS (ESI) Anal. calcd. for $C_{22}H_{29}NO_6SNa$ *m*/*z* 458.1608 $[M+Na]^+$, found 458.1596.

(*R*)-*N*-(6-benzyl-2,4,9,11-tetraoxadodecan-6-yl)-4-methylbenzenesulfonamide (12af)



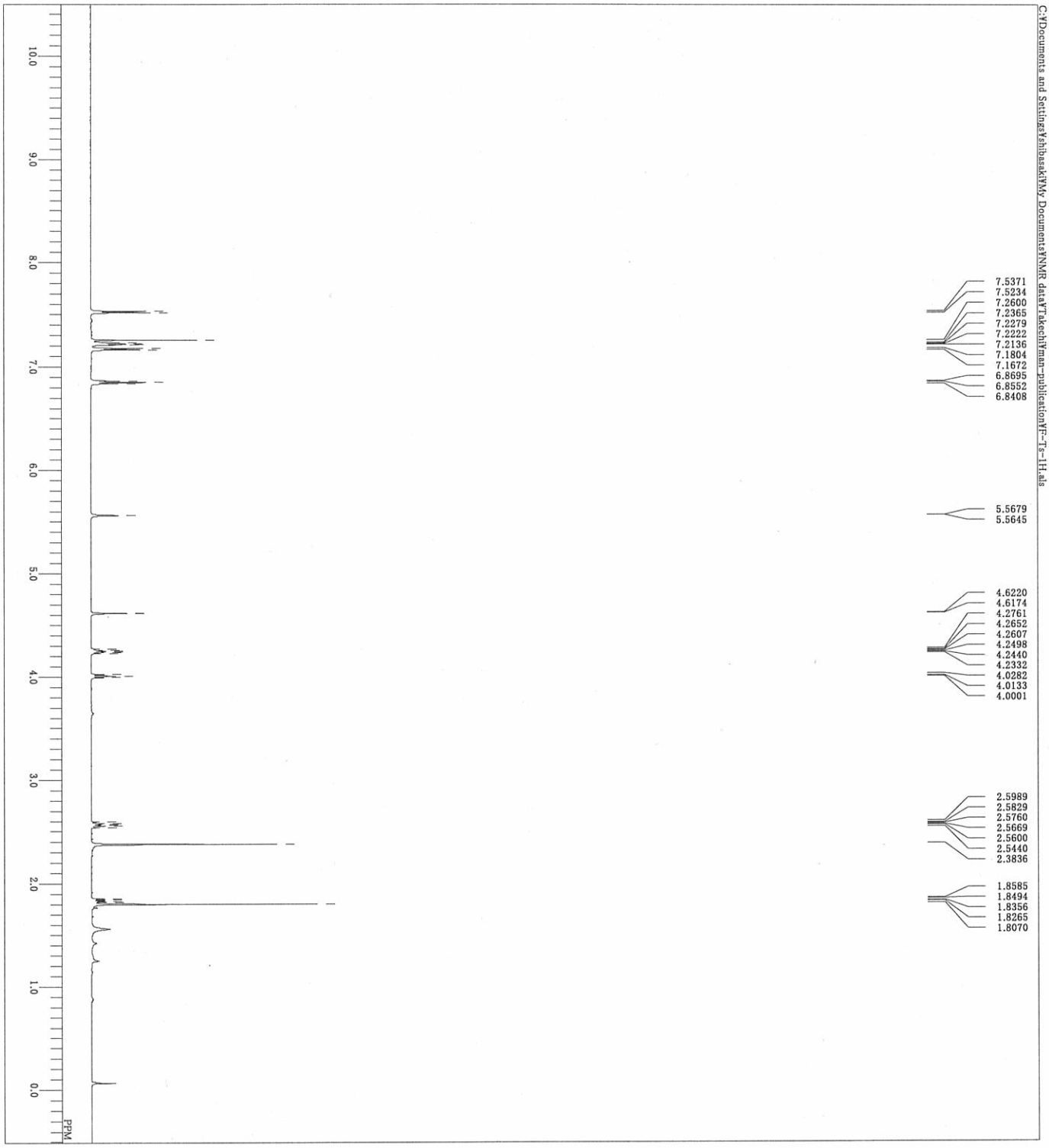
11af **12af**

To a stirred mixture of **11af** (12.9 mg, 0.030 mmol) in AcOEt (0.6 mL) was added wet $Pd(OH)_2$ on carbon (6.5 mg, 5% w/w based on Pd) and resulting mixture was stirred at room temperature under hydrogen atmosphere (1 atm) for 24 h. After 24 h, reaction mixture was filtrated thorough a plug of Celite and eluted with AcOEt. Volatiles were removed under reduced pressure to give **12af** (12.9 mg, 99%) as a colorless oil.

Colorless oil; IR (neat) ν 3278, 2884, 1454, 1321, 1153, 1108, 1041, 918, 815, 705, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.77 (d, *J* =8.3 Hz, 2H), 7.31-7.18 (m, 7H), 5.37 (s, 1H), 4.52 (s, 2H), 4.49 (s, 2H), 3.67-3.57 (m, 2H), 3.47 (d, *J* = 10.3 Hz, 1H), 3.44 (d, *J* = 10.3 Hz, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.06 (d, *J* = 13.5 Hz, 1H), 2.99 (d, *J* = 13.5 Hz, 1H), 2.41 (s, 3H), 1.98 (dt, *J* = 6.4, 14.6 Hz, 1H), 1.82 (dt, *J* = 6.2, 14.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 143.0, 140.6, 136.1, 130.9, 129.5, 128.2, 126.7, 96.9, 96.5, 70.9, 63.7, 62.0, 55.8, 55.4, 41.9, 33.8, 21.5; $[\alpha]_D^{25}$ –16.3 (*c* 0.57, $CHCl_3$, 99% ee sample); HRMS (ESI) Anal. calcd. for $C_{22}H_{31}NO_6SNa$ *m*/*z* 460.1765 $[M+Na]^+$, found 460.1753.

7. NMR Spectra of New Compounds

F-Ts



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9008.87 Hz
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1H
25.0 c
CDCl3
7.26 ppm
1.20 Hz
48

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
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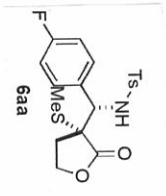
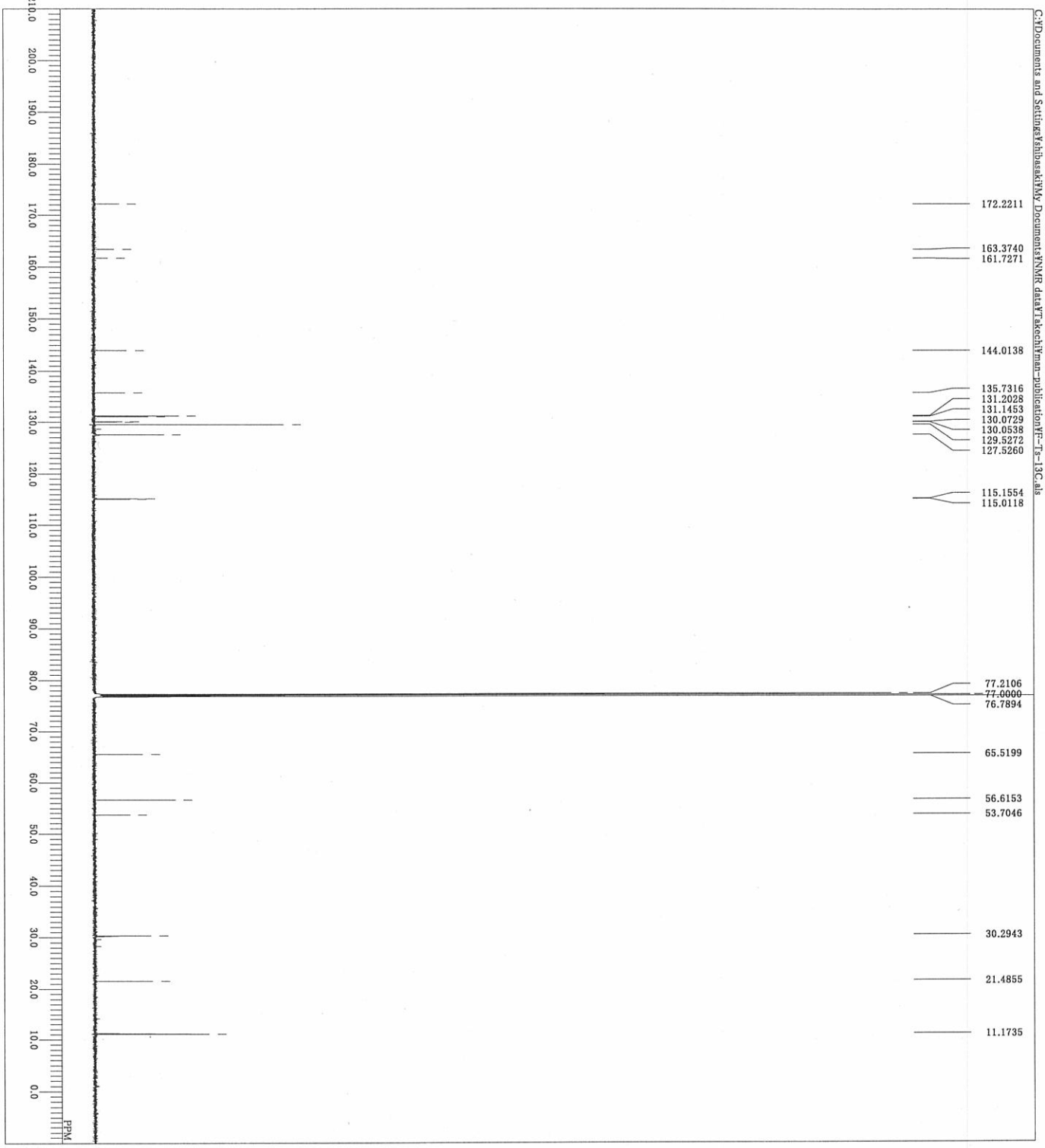


6aa

F-Ts-13C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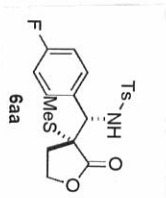
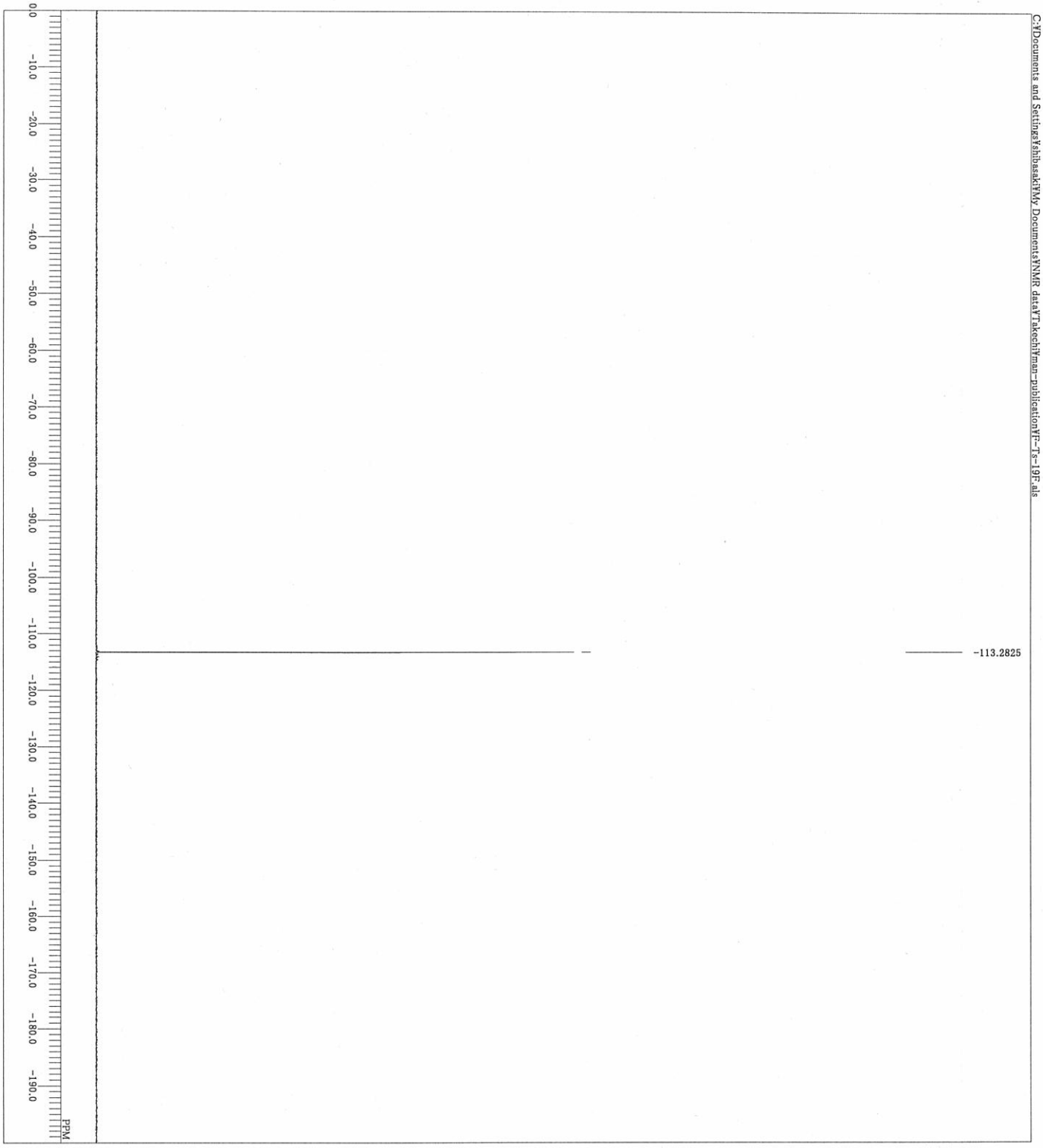

F
MeS
Ts
NH
O
O

6aa

F-Ts-19F



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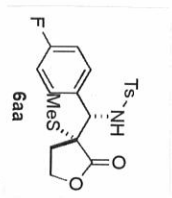
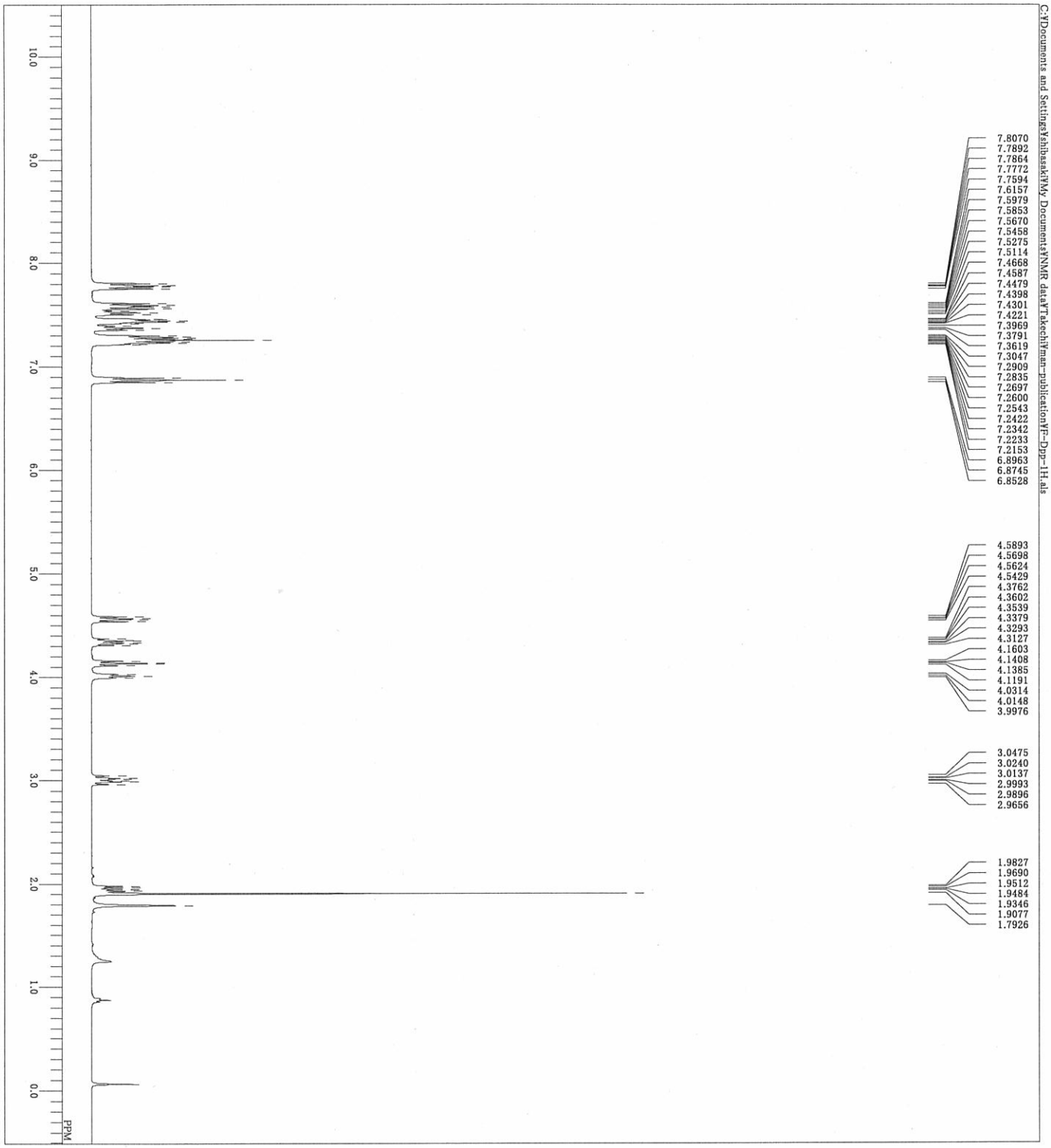


6aa

F-Dpp-1H



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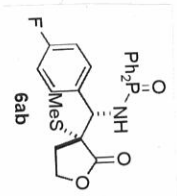
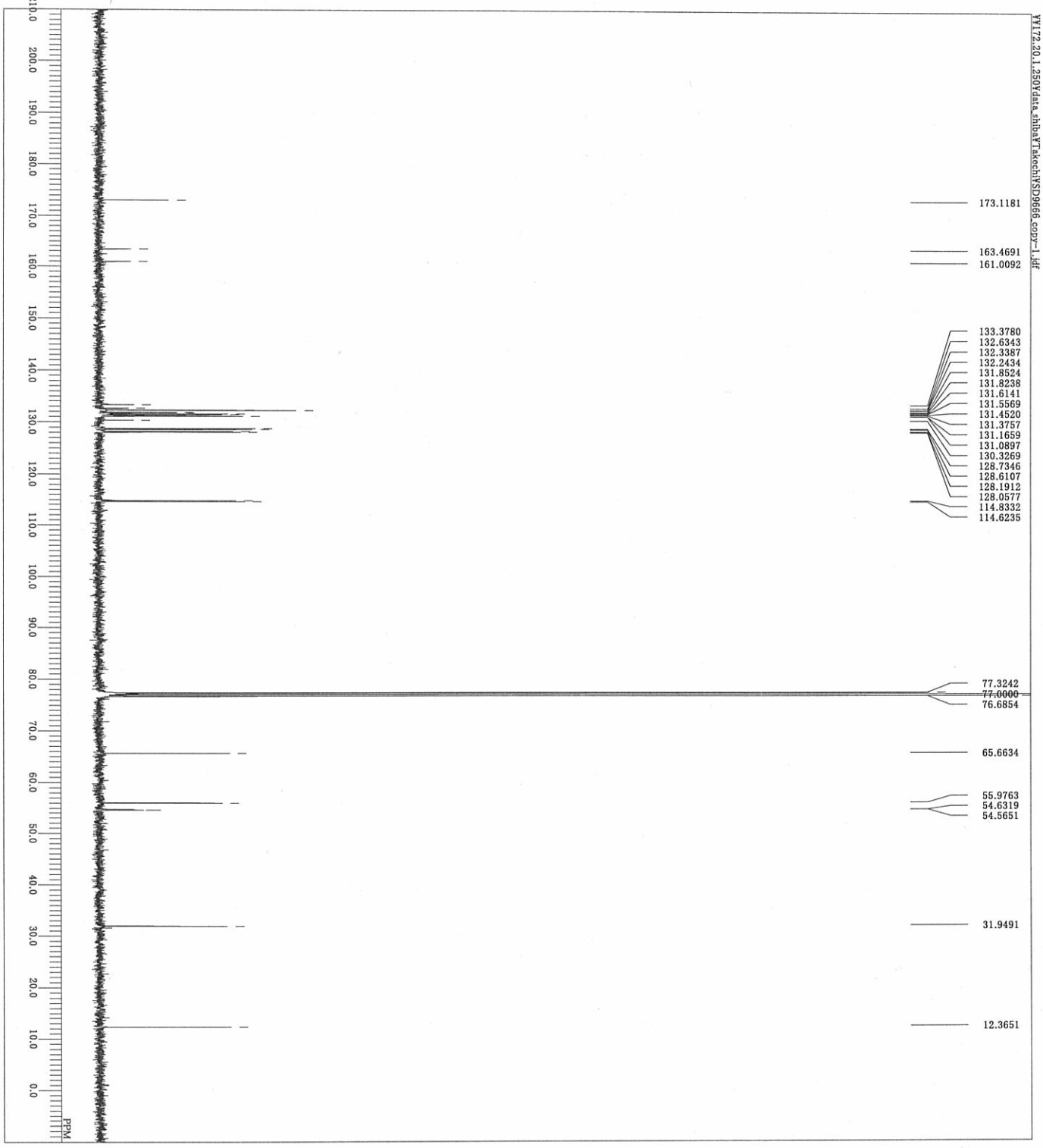
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	32768
FREQU	7503.00 Hz
SCANS	8
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	40



F-Dpp-13C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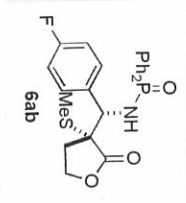
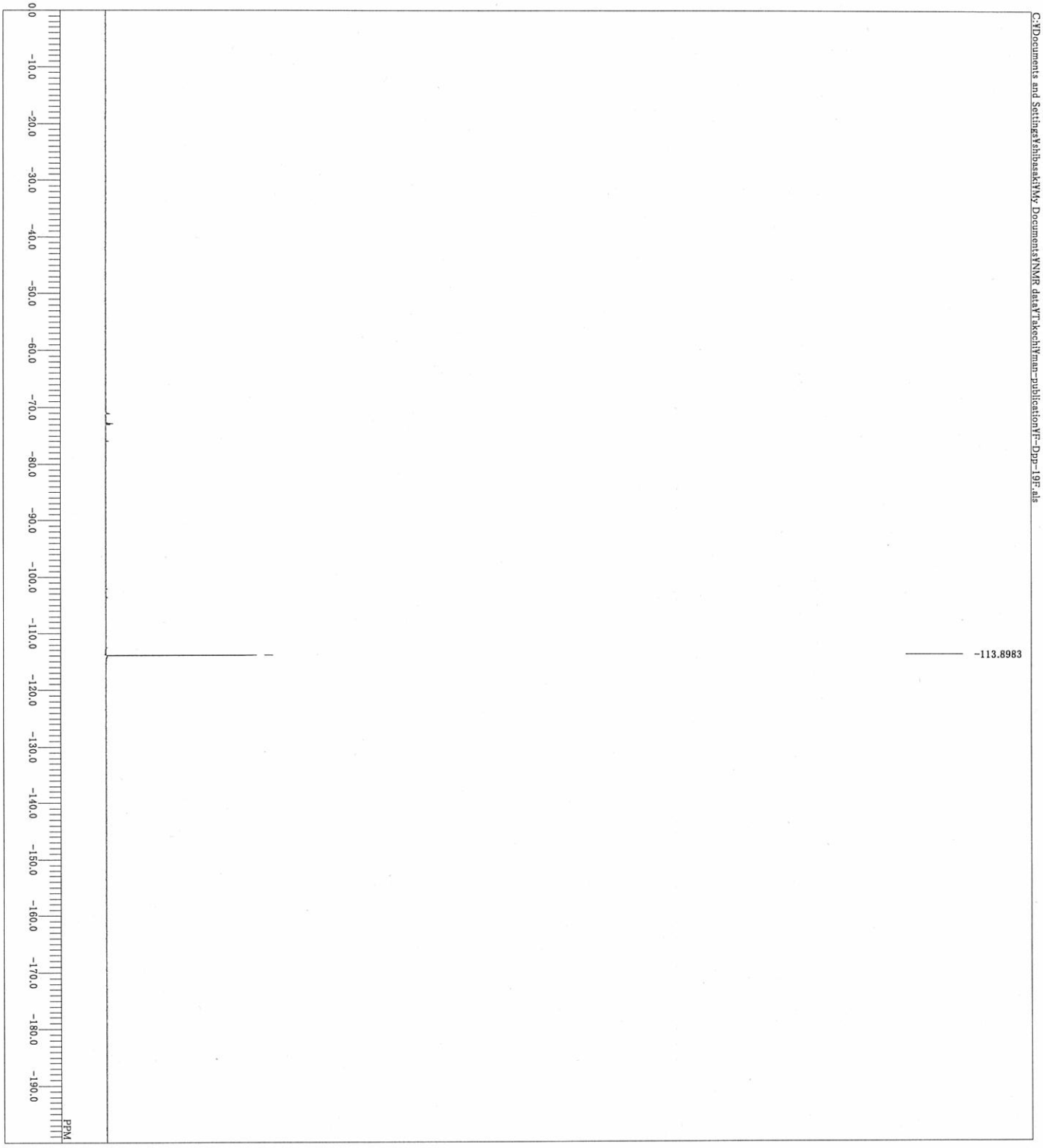
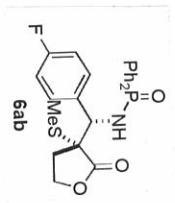
132.2434
131.8524
131.8238
131.6141
131.5569
131.4520
131.3757
131.1659
131.0897
130.3269
128.7346
128.6107
128.1912
128.0577
114.8332
114.6235
77.3242
77.0000
76.6854
65.6634
55.9763
54.6319
54.5651
31.9491
12.3651
PPM
DFILE SD9666.copy-1.idf
COMNT F-Dpp-13C
DATIM 2013-03-29 00:55:04
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.03 Hz
SCANS 466
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.83 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60


F
Ph2P=O
NH
Mes
O
O
6ab

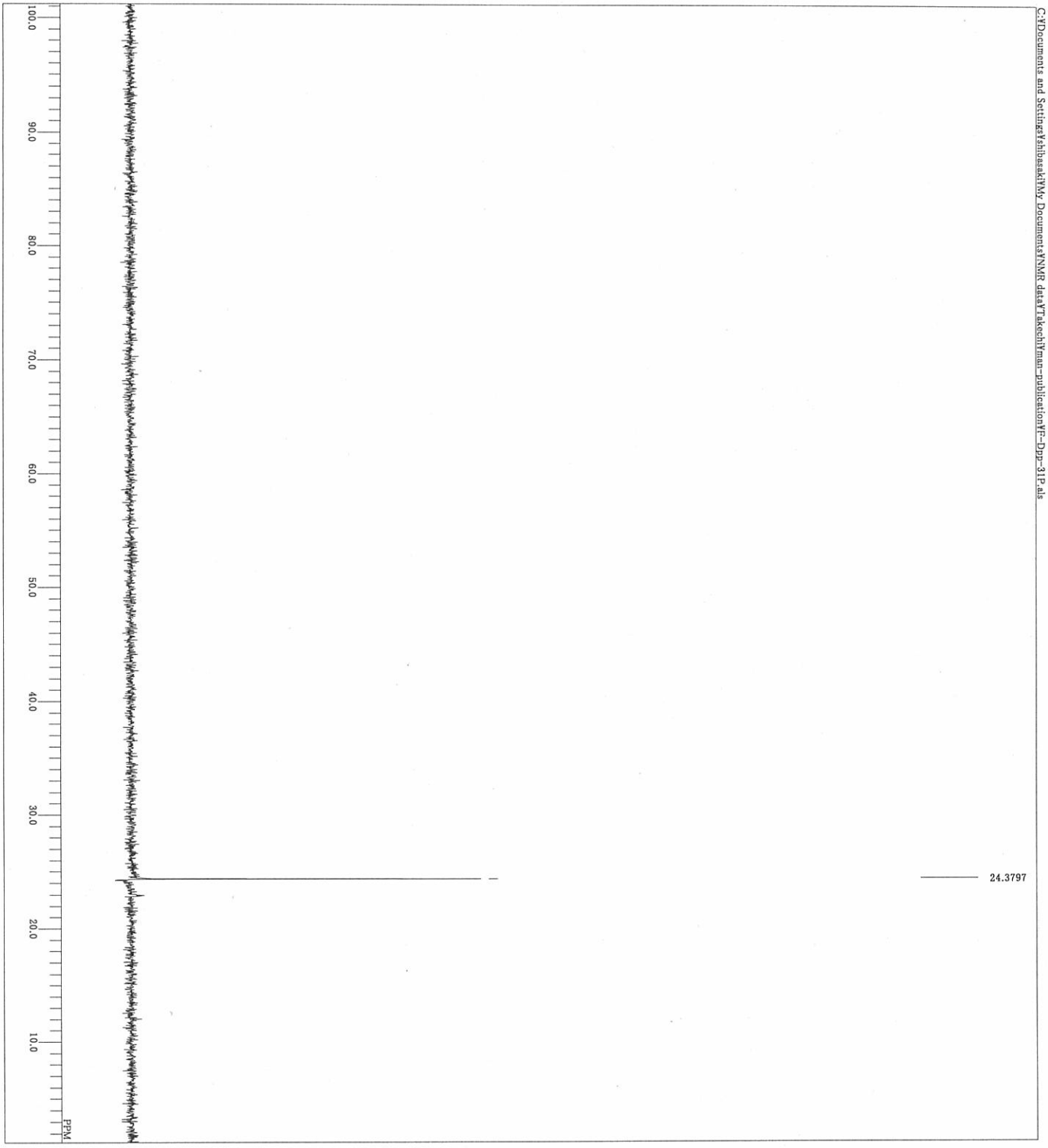
F-Dpp-19F



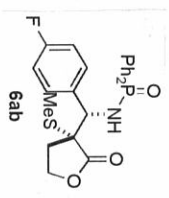
DFILE	F-Dpp-19F.als
COMNT	F-Dpp-19F
DATIM	2013-03-18 22:33:53
OBNUC	19F
EXMOD	single_pulse.ex2
OBFRQ	376.17 MHz
OBSET	1.05 KHz
OBFIN	3.93 Hz
POINT	26214
FREQU	151512.84 Hz
SCANS	102
ACQTM	0.1730 sec
PD	5.0000 sec
PW1	5.50 usec
IRNUC	19F
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	-76.50 ppm
BF	0.12 Hz
RGAIN	46



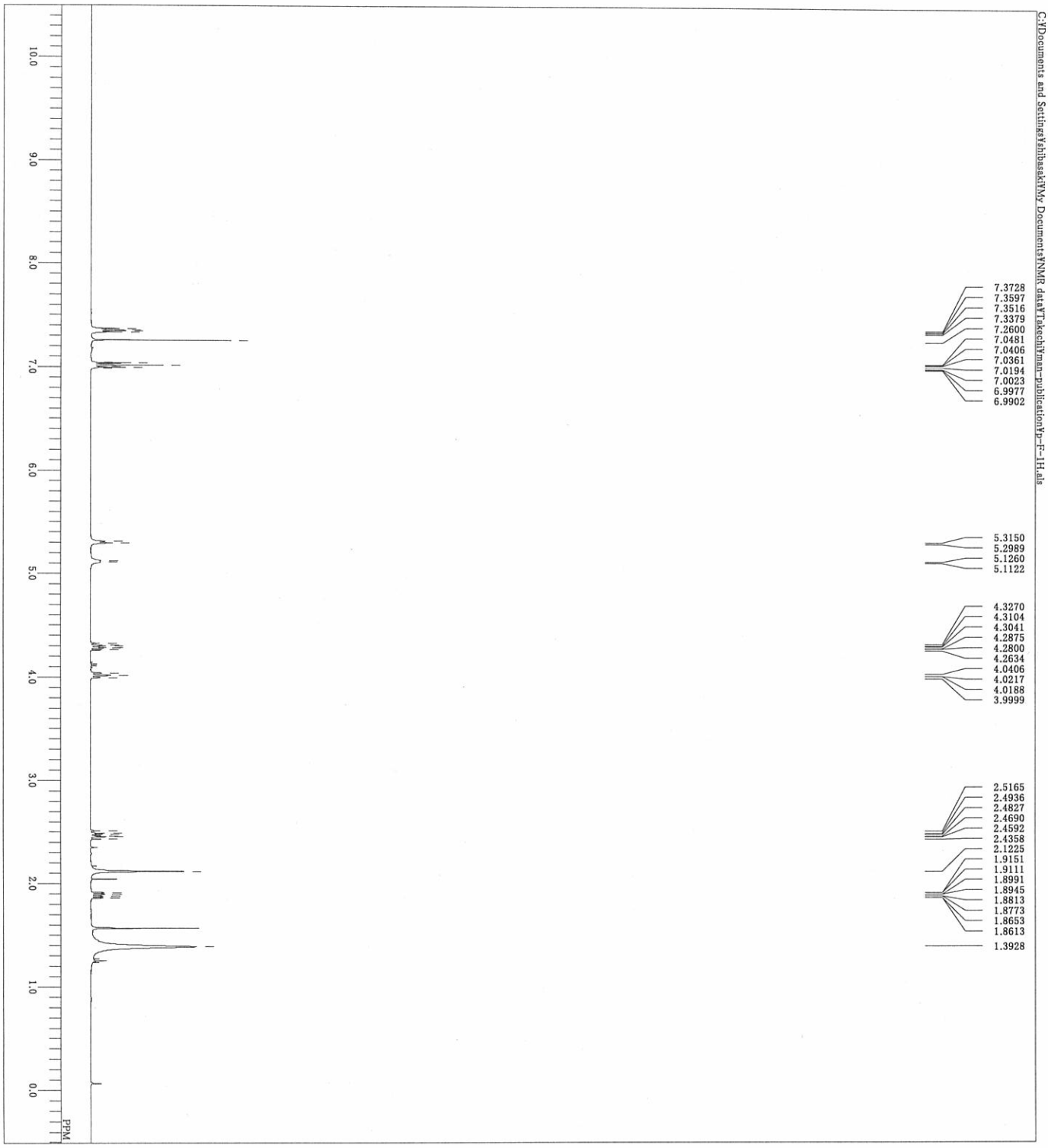
F-Dpp-31P



DFILE F-Dpp-31P.als
COMNT F-Dpp-31P
DATIM 2013-03-18 22:40:10
OBNUC 31P
EXMOD single pulse.dec
OBFRQ 161.83 MHz
OBSET 4.69 KHz
OBFIN 3.09 Hz
POINT 26214
FREQU 114283.97 Hz
SCANS 103
ACQTM 0.2294 sec
PD 2.0000 sec
PW1 4.00 usec
IRNUC 1H
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 56



2354-p-F-1H


C:¥Documents and Settings¥shibasaki¥My Documents¥NMR data¥Takeshi¥mar-publication¥p-F-1H.als
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7.0406
7.0361
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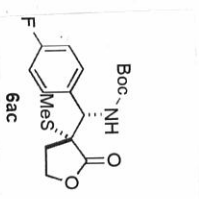
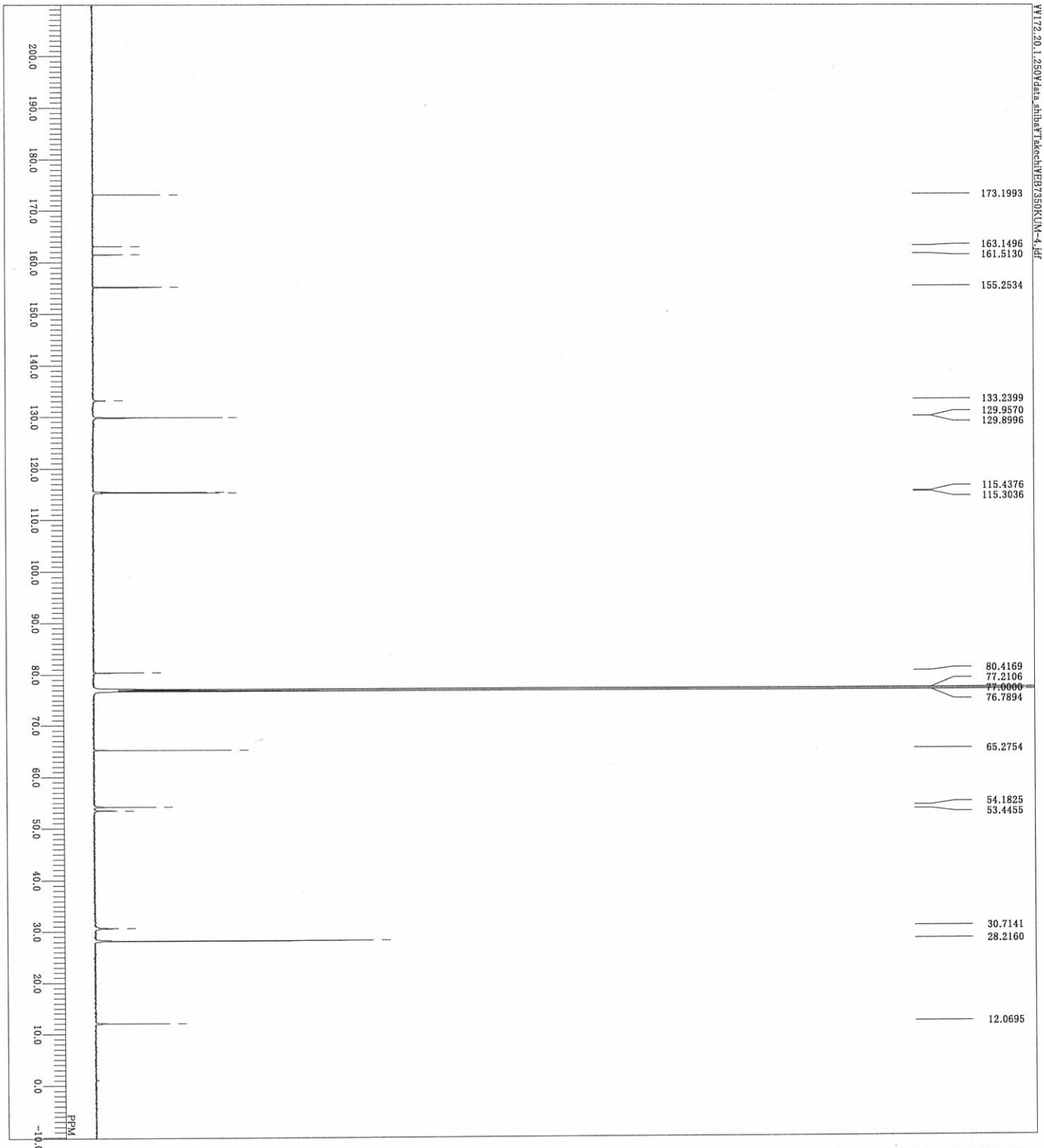
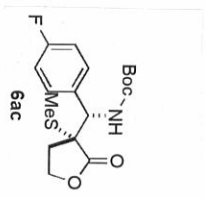
7.0023
6.9977
6.9902
5.3150
5.2989
5.1260
5.1122
4.3270
4.3104
4.3041
4.2875
4.2800
4.2634
4.0406
4.0217
4.0188
3.9999
2.5165
2.4936
2.4827
2.4690
2.4592
2.4358
2.1225
1.9151
1.9111
1.8991
1.8945
1.8813
1.8773
1.8653
1.8613
1.3928
PPM
DFILE p-F-1H.als
COMNT 2354-p-F-1H
DATIM 2013-01-08 11:07:26
OBNUC 1H
EXMOD single_pulse_ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.31 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 48

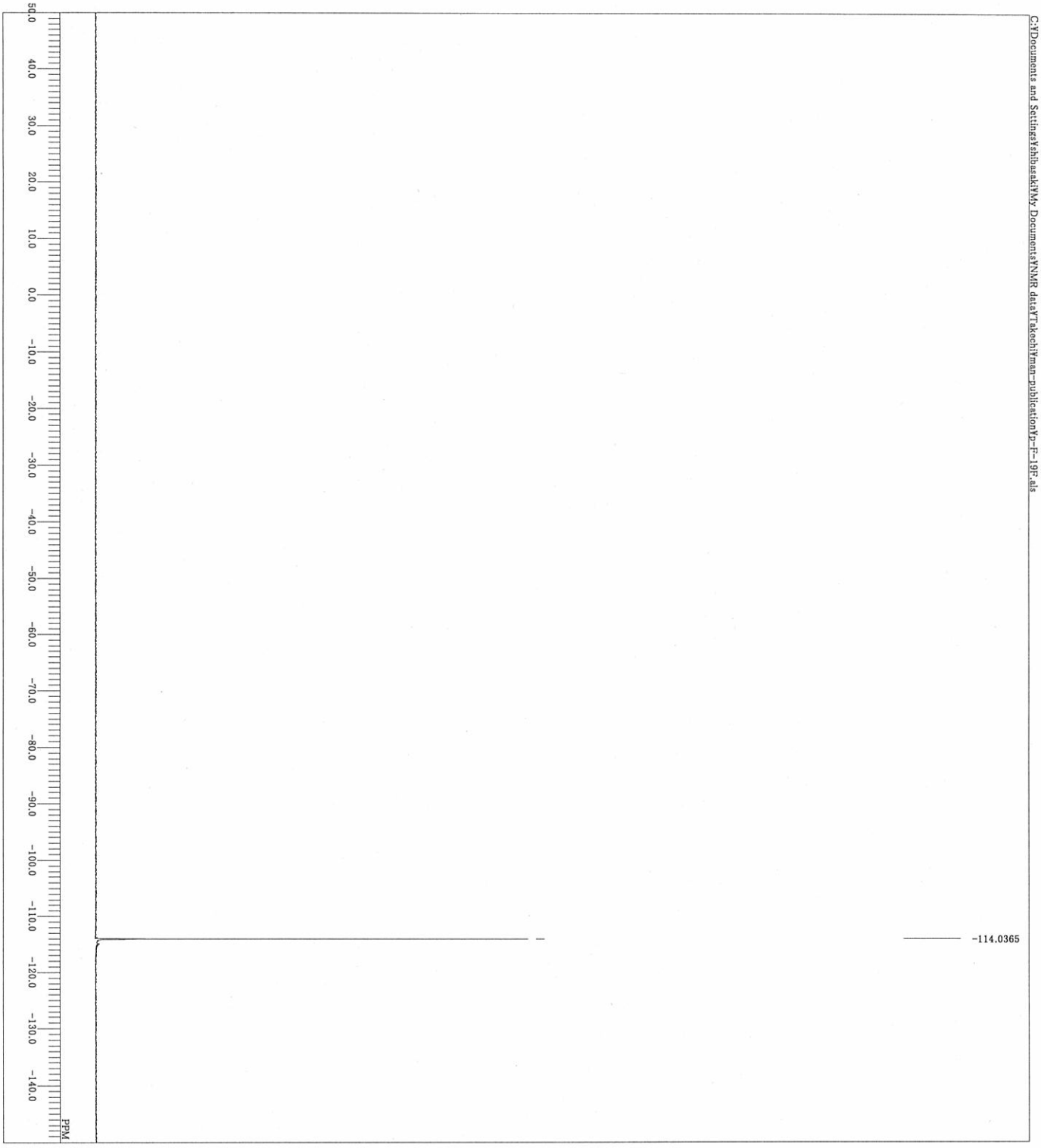

F
Boc
NH
O
MeS
O
6ac

P-F-13C 15mg 13C

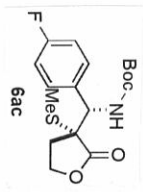




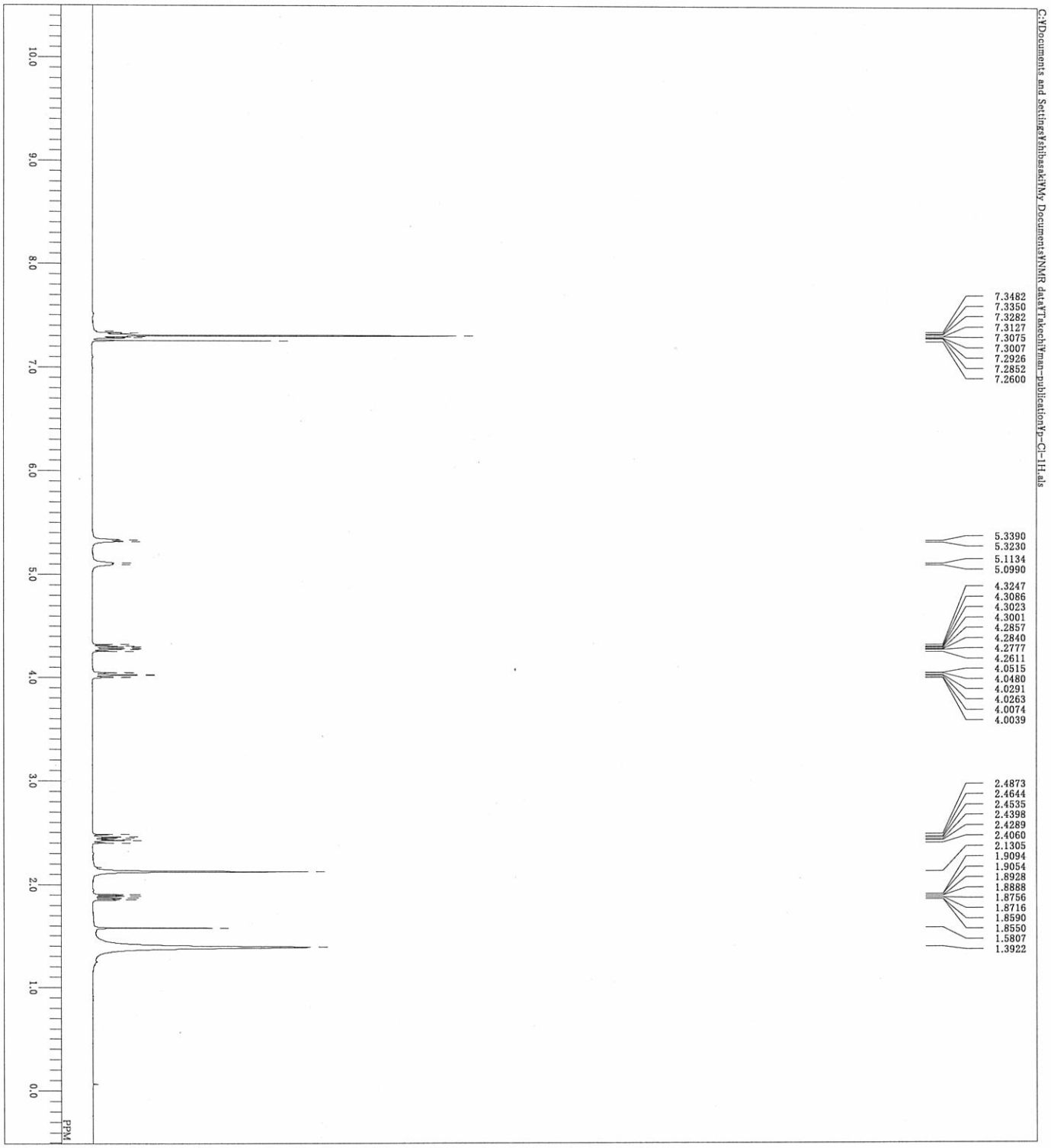
p-F-1H



DFILE	p-F-19F.als
COMNT	p-F-1H
DATIM	2013-03-14 00:03:39
OBNUC	19F
EXMOD	single_pulse.ex2
OBFREQ	376.051 MHz
OBSET	105.1 kHz
OBSFIN	3.99 Hz
POINT	262144
FREQU	151512.84 Hz
SCANS	32
ACQTM	0.1730 sec
PD	5.0000 sec
PW1	5.50 usec
IRNUC	
CTEMP	19F
SLVNT	21.3 c
EXREF	CDCL3
BF	-76.50 ppm
RGAIN	1.20 Hz
	46



2369-p-Cl-1H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4.0291
4.0263
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4.0039
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2.4644
2.4535
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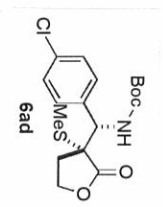
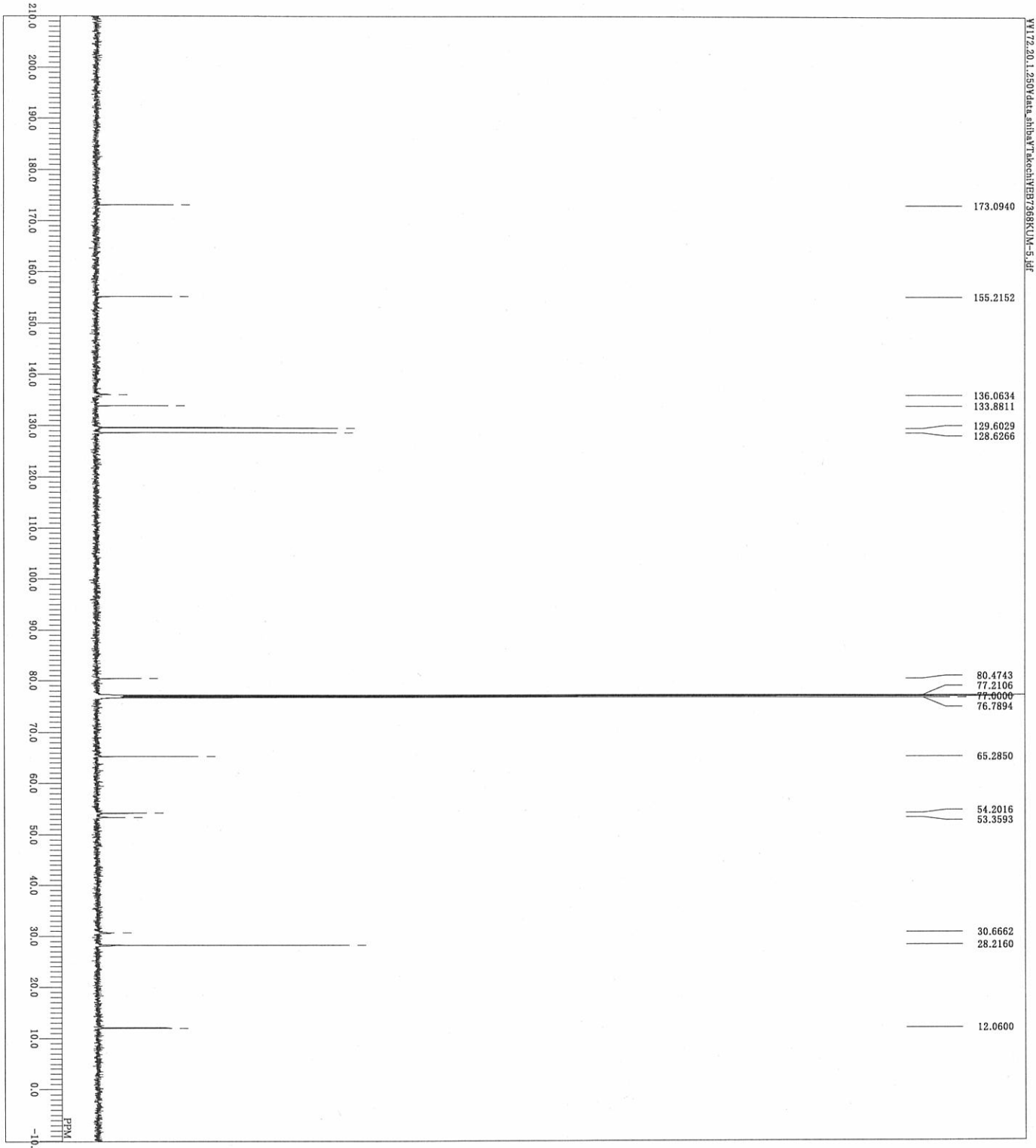
2.1305
1.9094
1.9054
1.8928
1.8888
1.8756
1.8716
1.8590
1.8550
1.5807
1.3922
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
DFILE p-Cl-1H.als
COMNT 2369-p-Cl-1H
DATIM 2013-01-07 16:38:54
OBNUC 1H
EXMOD single_pulse.exp
OBFRQ 399.78 MHz
OBSET 4.19 kHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.31 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 44


Cl
Boc
NH
O
MeS
O
6ad


P-Cl-13C 13C
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128.6266
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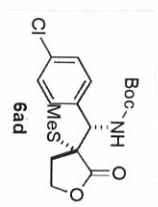
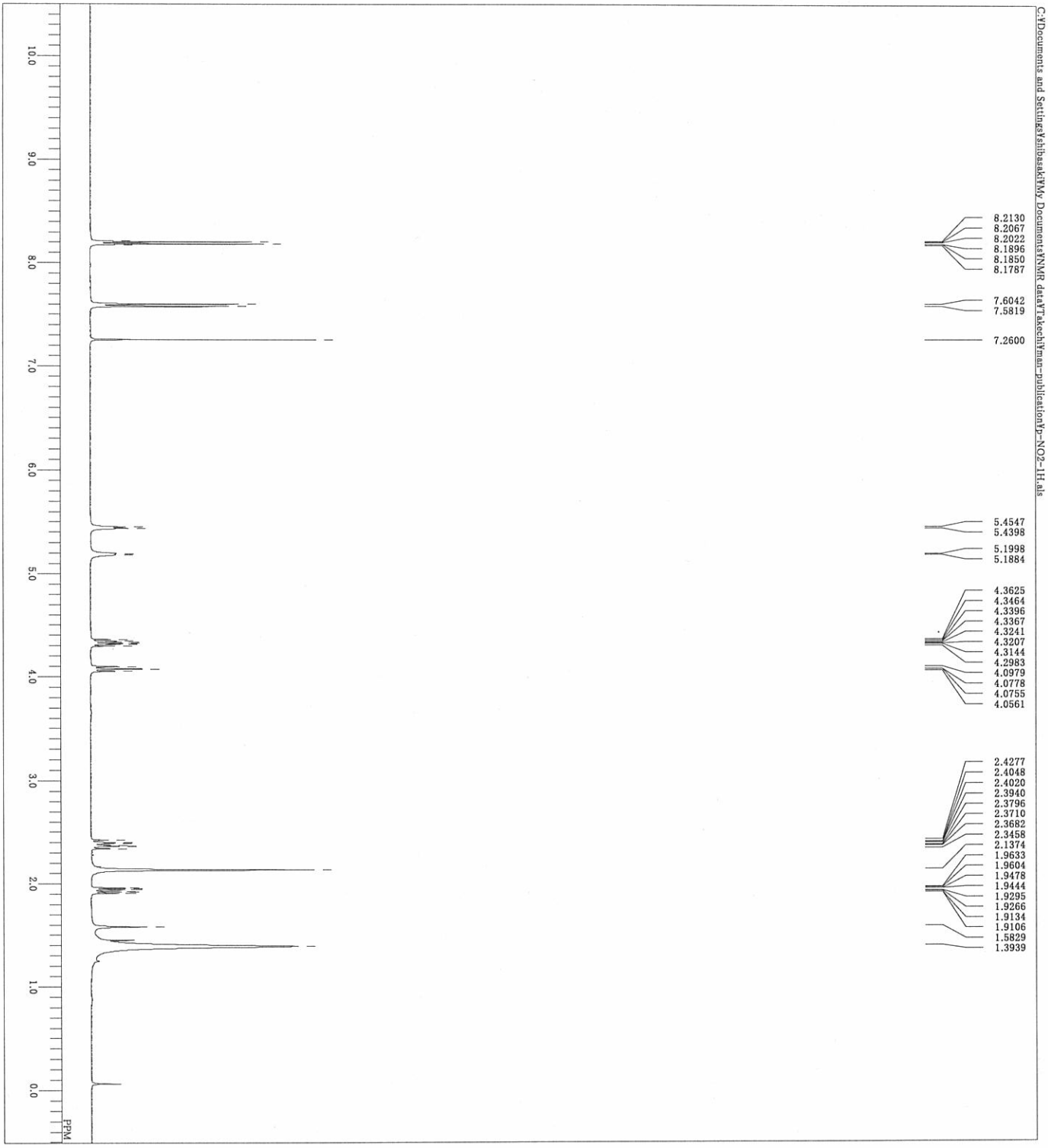
77.0000
76.7894
65.2850
54.2016
53.3593
30.6662
28.2160
12.0600
PPM
DFILE EB7368KUM-5.jdf
COMNT P-Cl-13C 13C
DATIM 2013-01-11 19:00:32
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32781
FREQU 47348.49 Hz
SCANS 1201
ACQTM 0.6921 sec
PD 1.5000 sec
PW1 3.92 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40

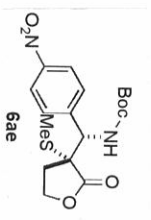

Cl
Boc
NH
O
MeS
O
O

6ad

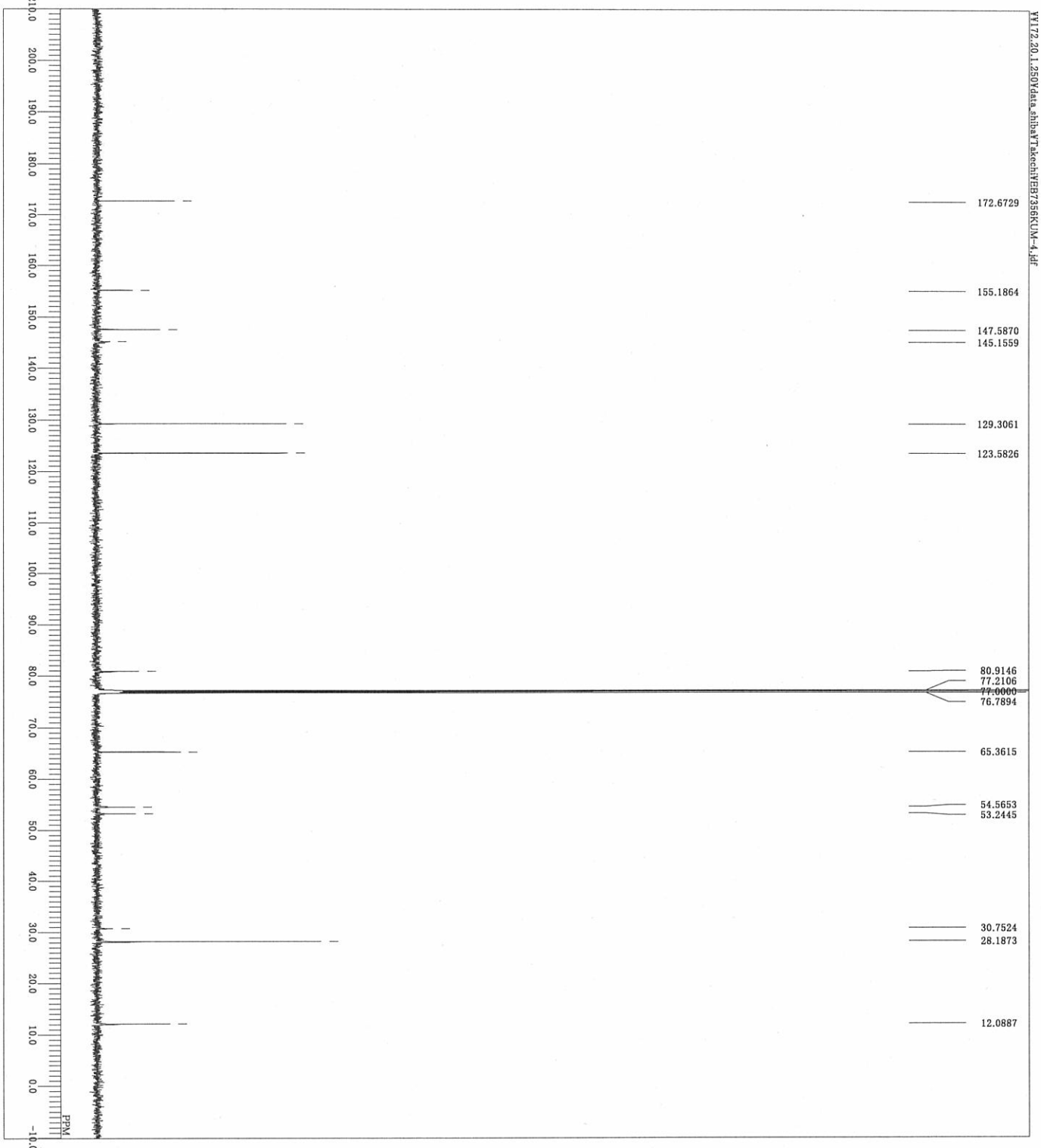
2351-p-NO2-1H



DFILE	p-NO2-1H.als
COMNT	2351-p-NO2-1H
DATIM	2013-01-07 16:22:41
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	7.29 kHz
OBFIN	7.29 Hz
POINT	26214
FREQU	6002.31 Hz
SCANS	16
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	44



P-NO2 13C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129.3061
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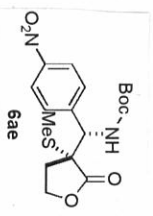
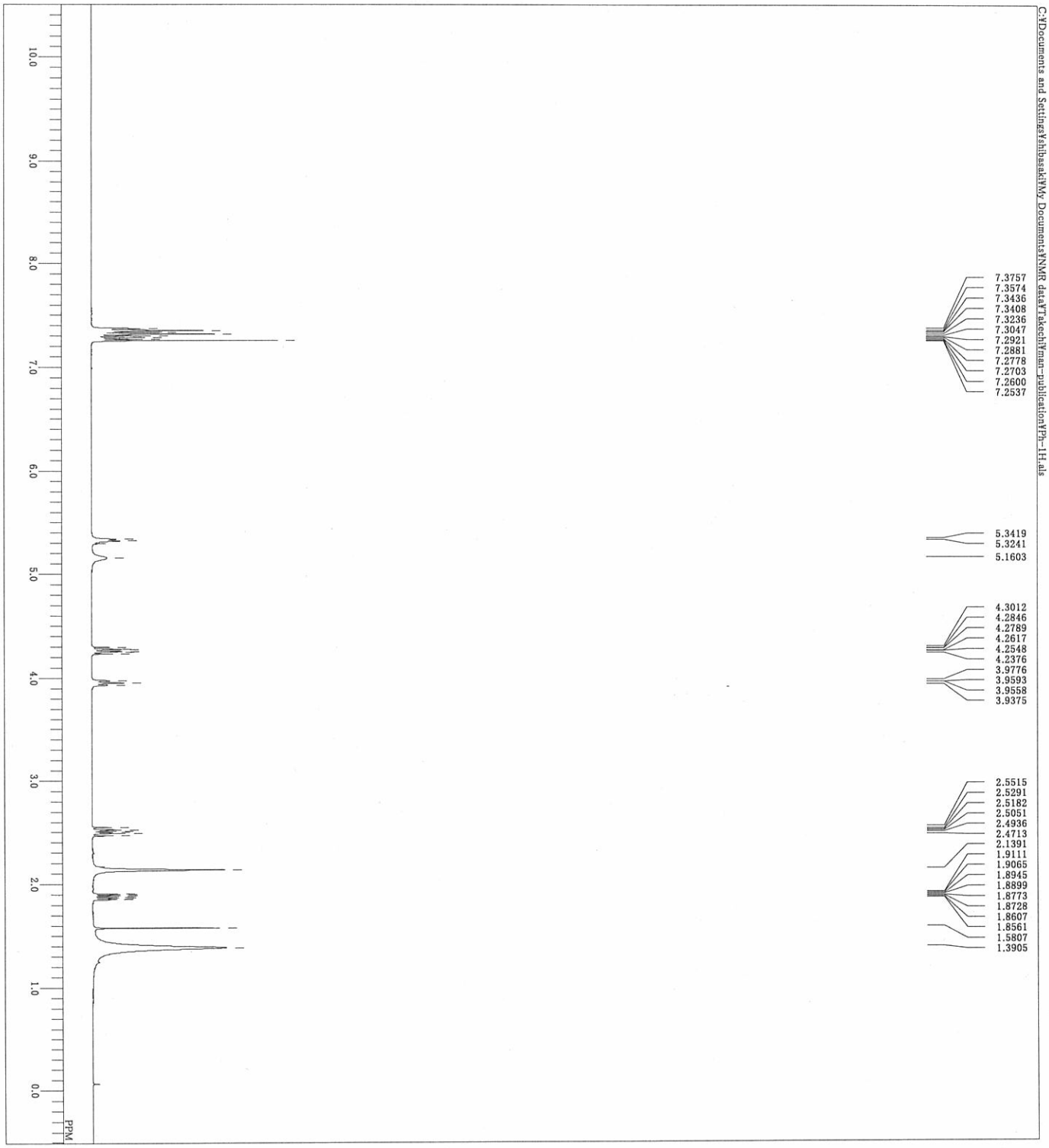
77.0000
76.7894
65.3615
54.5653
53.2445
30.7524
28.1873
12.0887
PPM
DFILE EB7356KUM-4.jdf
COMNT P-NO2 13C
DATIM 2013-01-10 14:20:55
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32781
FREQU 47348.49 Hz
SCANS 653
ACQTM 0.6921 sec
PD 1.5000 sec
PW1 3.92 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40


O2N
Boc
NH
MeS
O
O
6ae

Ph-syn-1H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7.2600
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5.3241
5.1603
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4.2617
4.2548
4.2376
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3.9593
3.9558
3.9375
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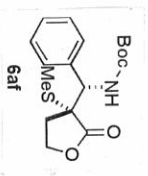
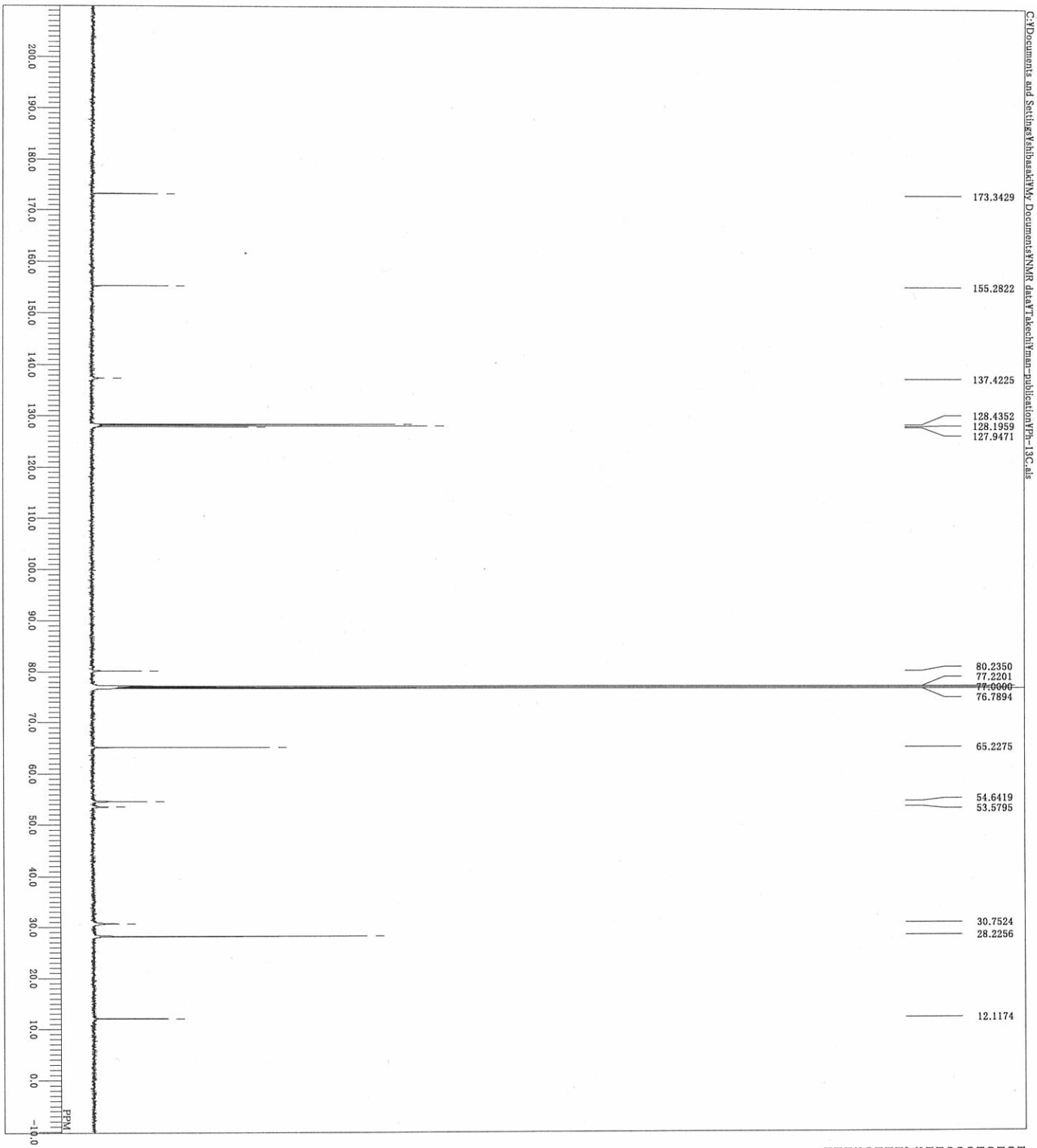
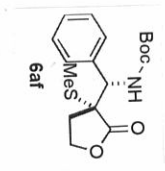
1.5807
1.3905
PPM
DFILE Ph-1H.als
COMNT Ph-syn-1H
DATIM 2013-01-08 00:52:02
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 kHz
OBFIN 2624.1 Hz
POINT 26214
FREQU 6002.31 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP * 20.6 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 42

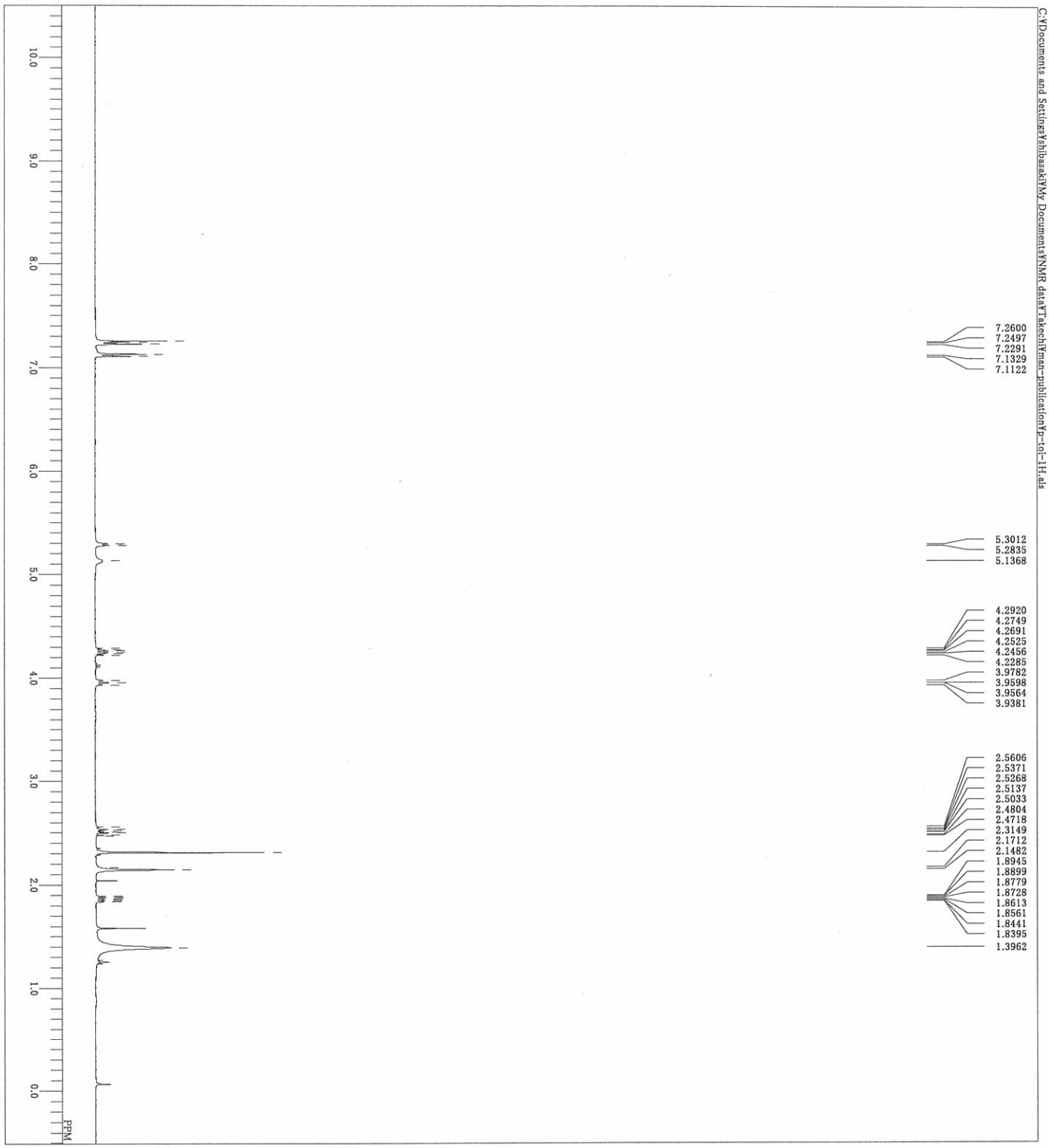

Boc
NH
O
MeS
O
6af

phenyl-13C 15mg 13C





6af


2385-p-tol
C:¥Documents and Settings¥shibasaki¥My Documents¥NMR data¥Takechi¥man-publication¥p-tol-1H.als
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5.1368
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4.2691
4.2525
4.2456
4.2285
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3.9564
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2.5268
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2.4804
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1.8899
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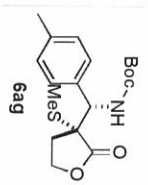
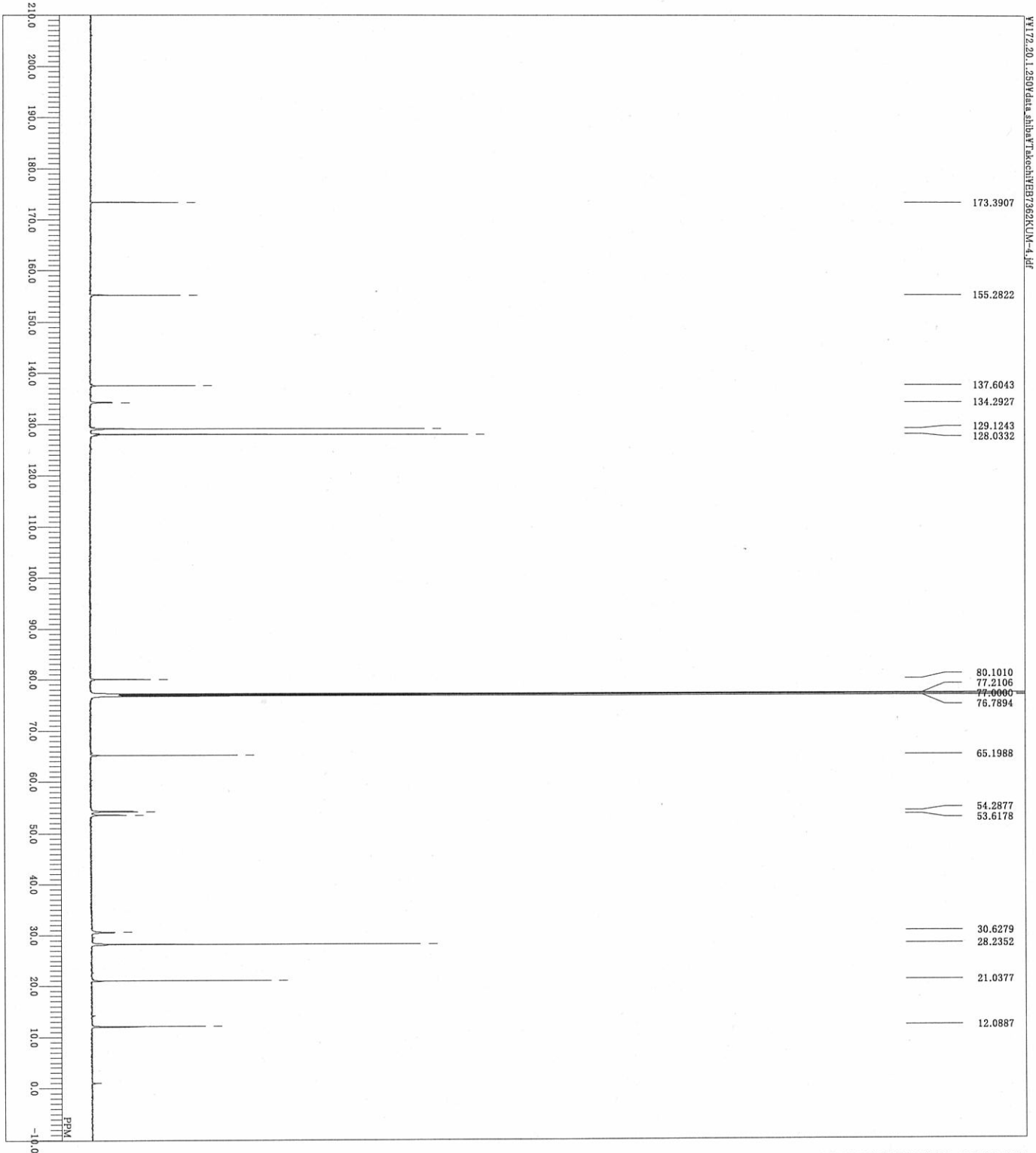
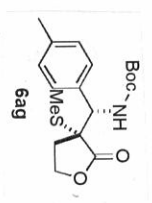
1.8728
1.8613
1.8561
1.8441
1.8395
1.3962
PPM
DFILE p-tol-1H.als
COMNT 2385-p-tol
DATIM 2013-01-08 11:31:48
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.31 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP 20.2 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 42


Boc
NH
O
MeS
O
6ag

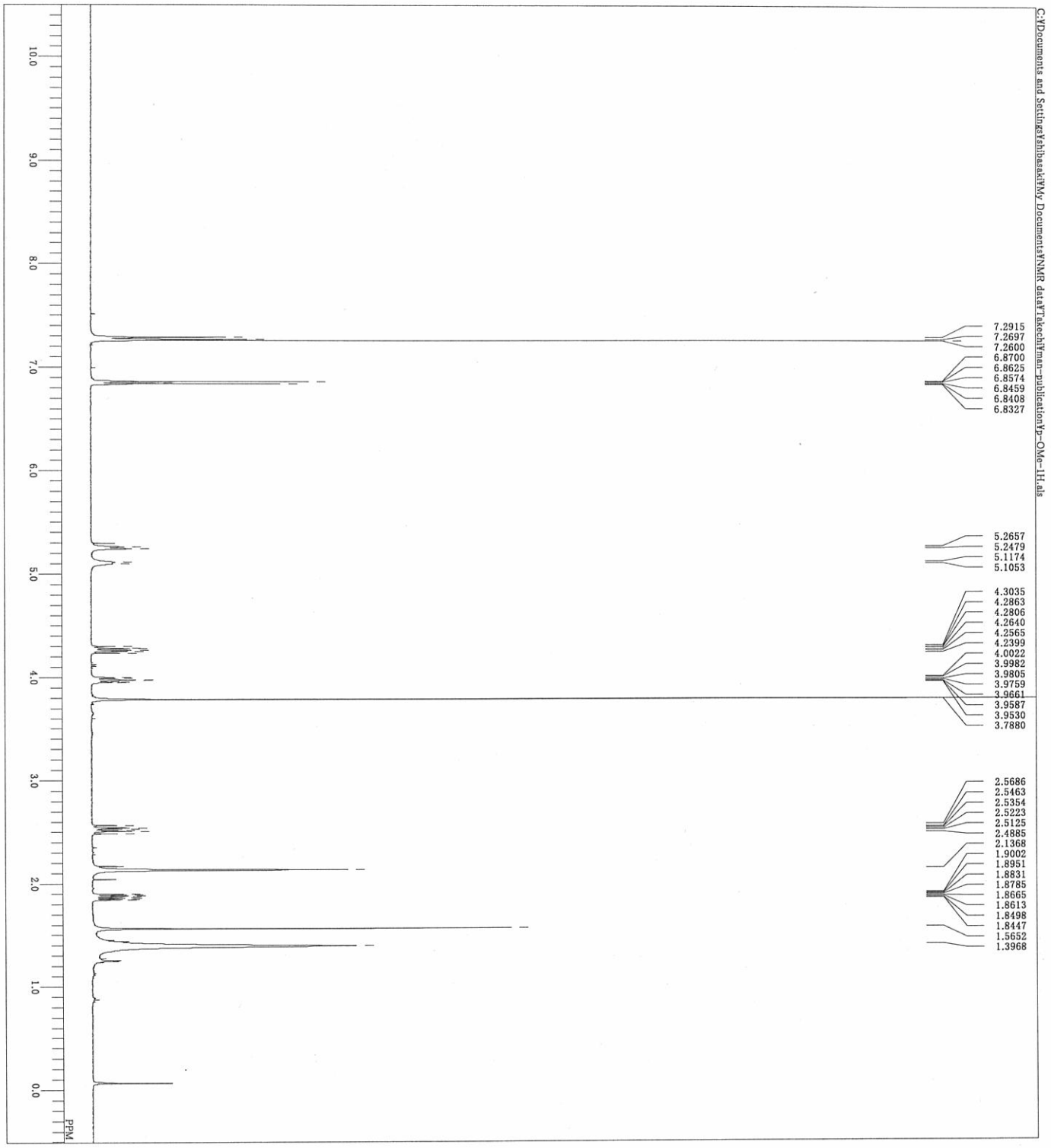
p-tol-13C 13C





6ag

2371-p-OMe-1H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4.2863
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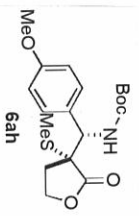
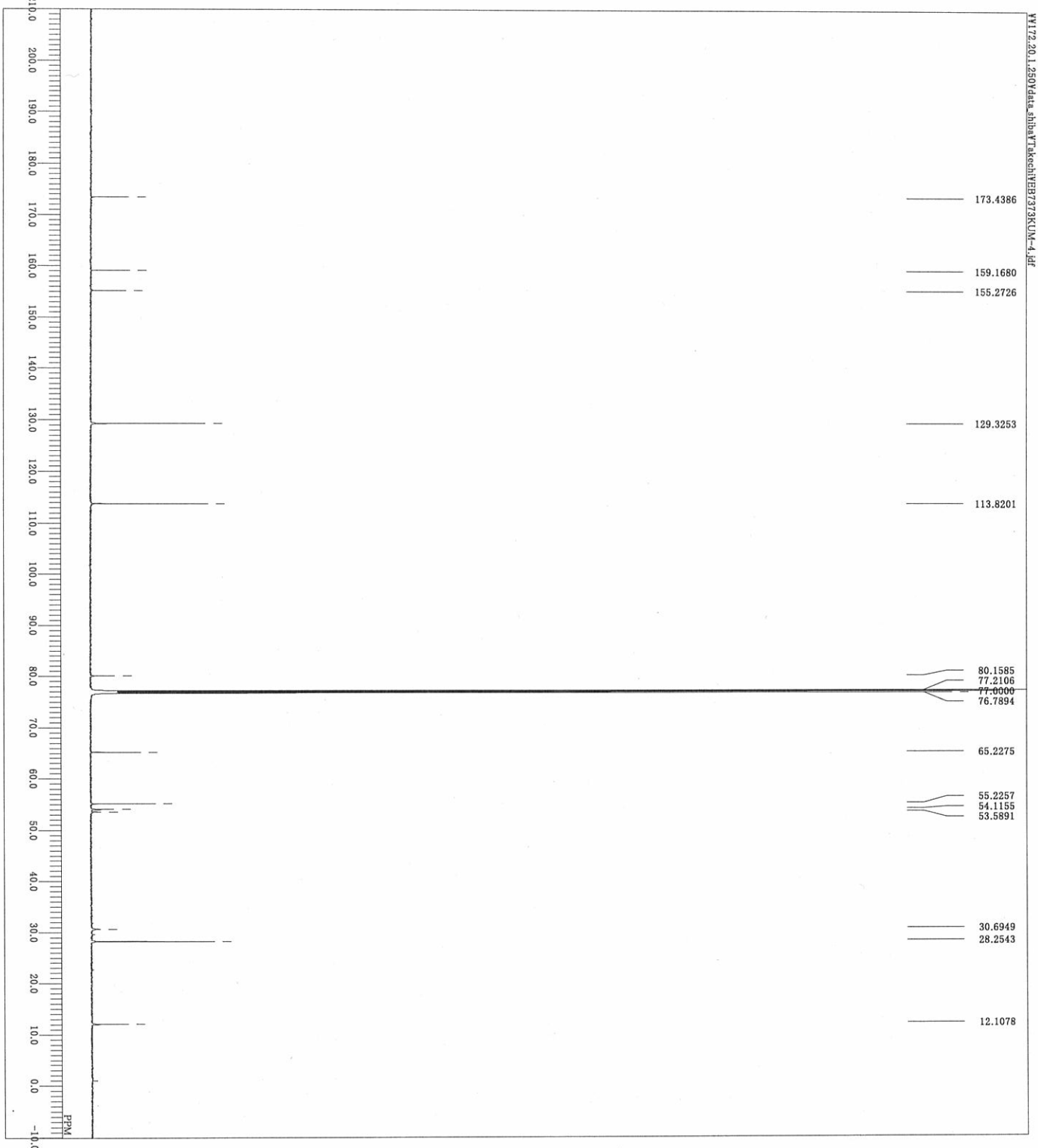
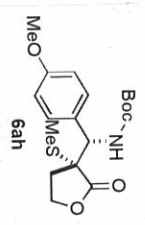
4.2640
4.2565
4.2399
4.0022
3.9982
3.9805
3.9759
3.9661
3.9587
3.9530
3.7880
2.5686
2.5463
2.5354
2.5223
2.5125
2.4885
2.1368
1.9002
1.8951
1.8831
1.8785
1.8665
1.8613
1.8498
1.8447
1.5652
1.3968
PPM
DFILE p-OMe-1H.als
COMNT 2371-p-OMe-1H
DATIM 2013-01-08 11:22:24
OBNUC 1H
EXMOD single pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 kHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6002.31 Hz
SCANS 16
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP 20.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 50

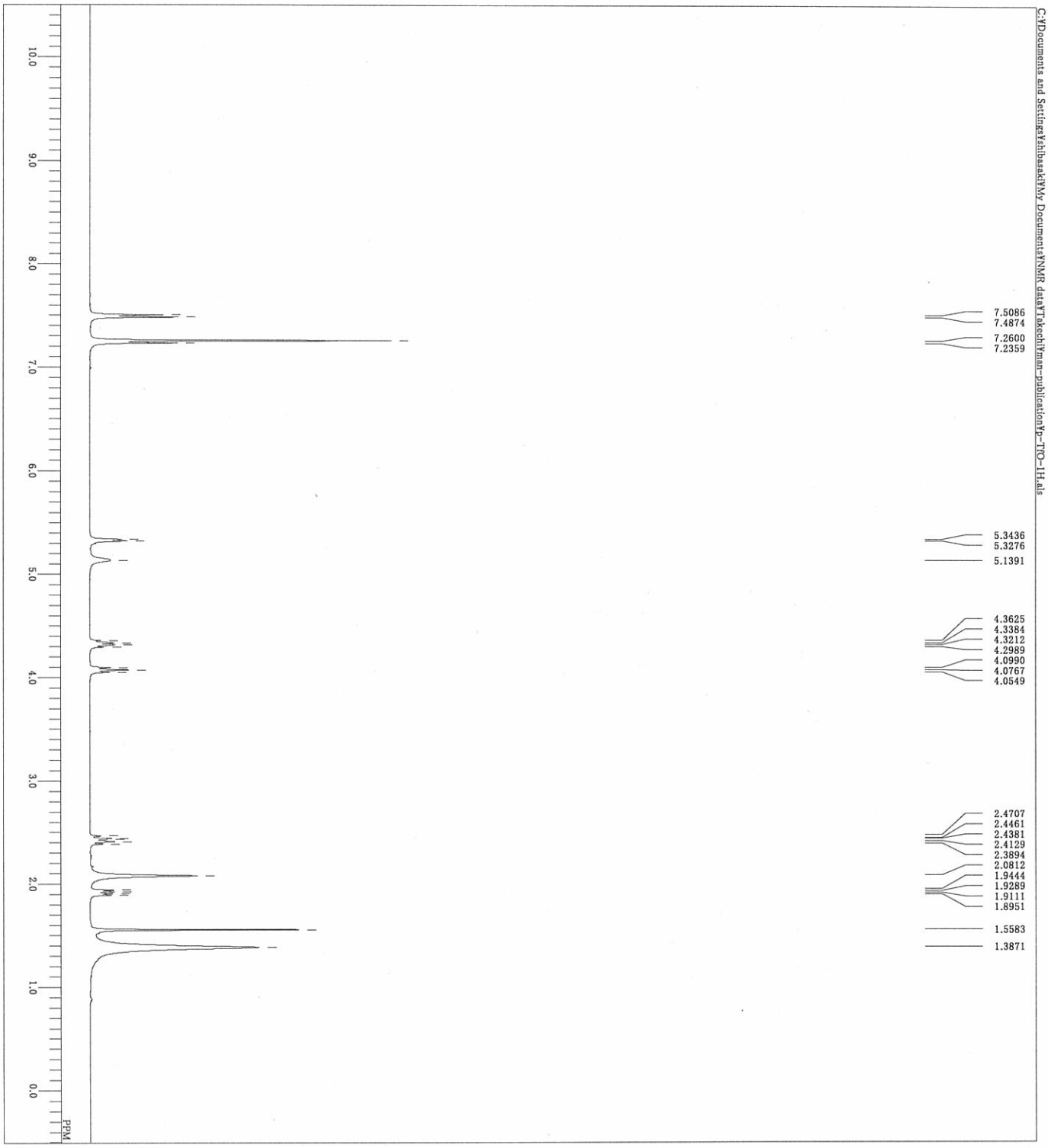

MeO
Mes
Boc
NH
O
O
6ah

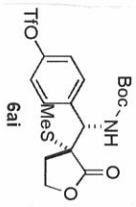
P-OMe-13C 13C


173.4386
159.1680
155.2726
129.3253
113.8201
80.1585
77.2106
77.0000
76.7894
65.2275
55.2257
54.1155
53.5891
30.6949
28.2543
12.1078
PPM

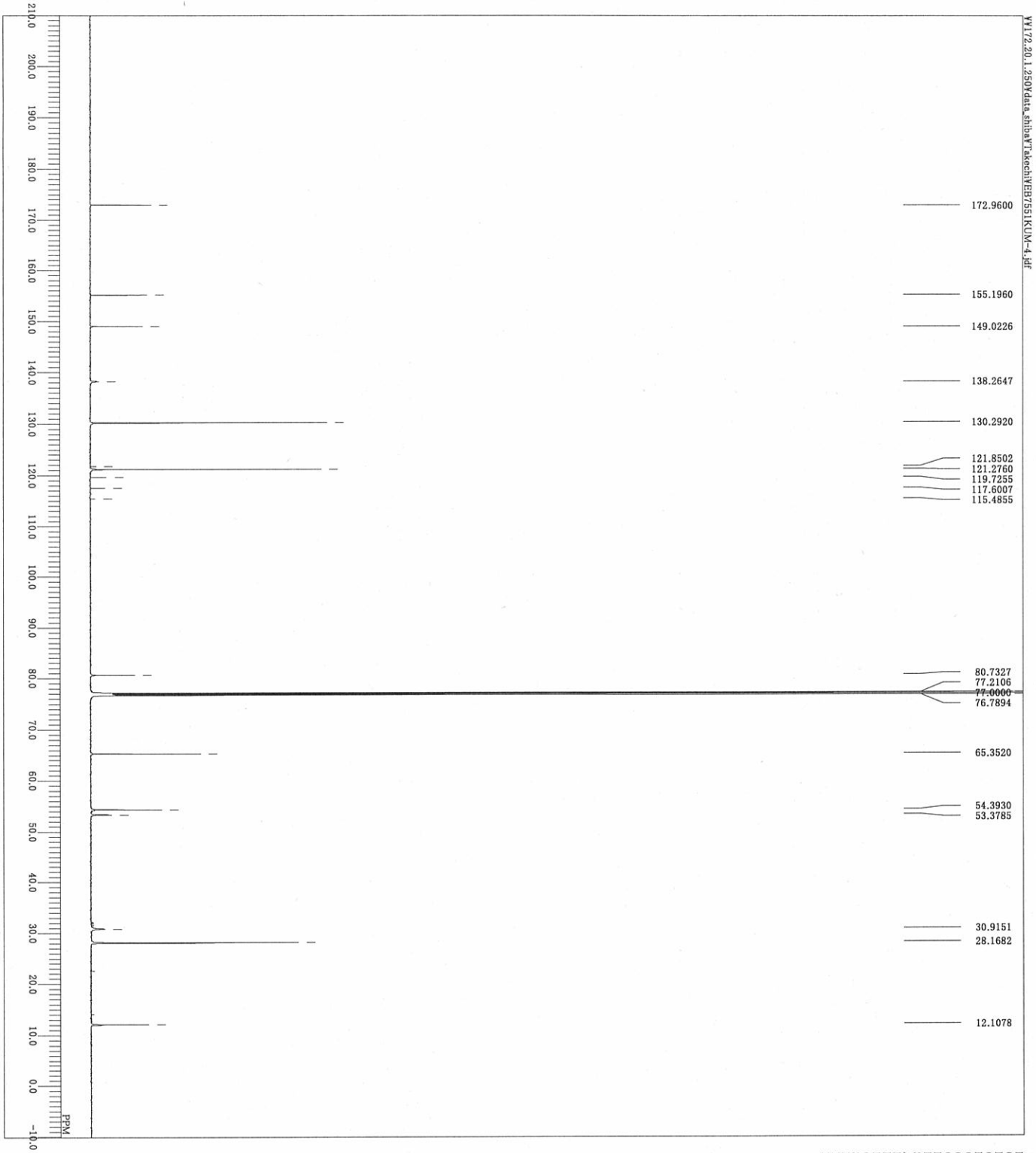

MeO
Boc
NH
MeS
O
O
6ah

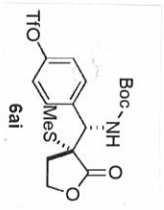
TfO-Mannich-pure



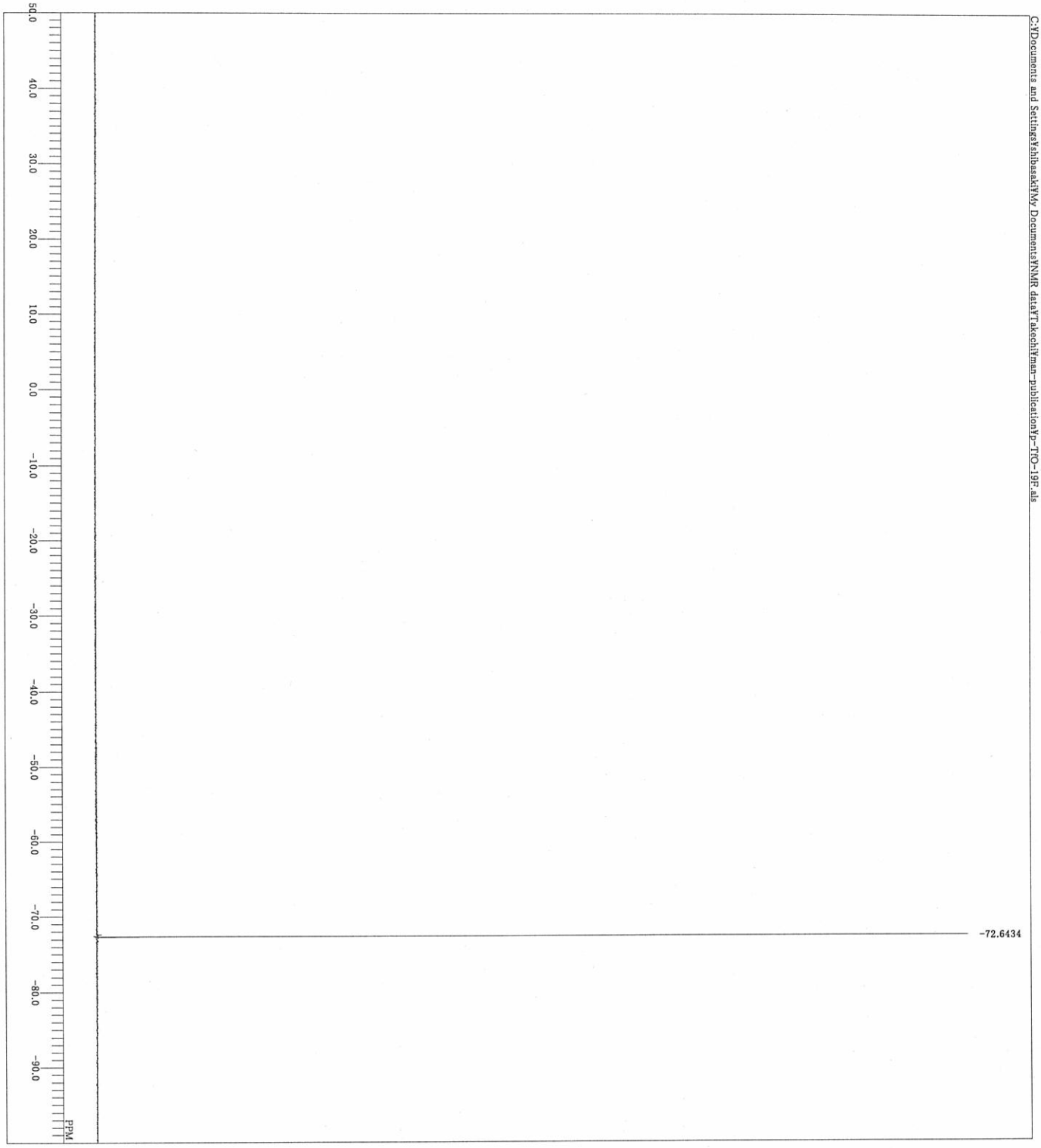


P-TfO ~20mg 13C

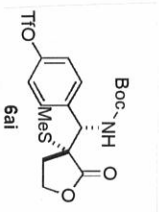




TfO-Boc-19F

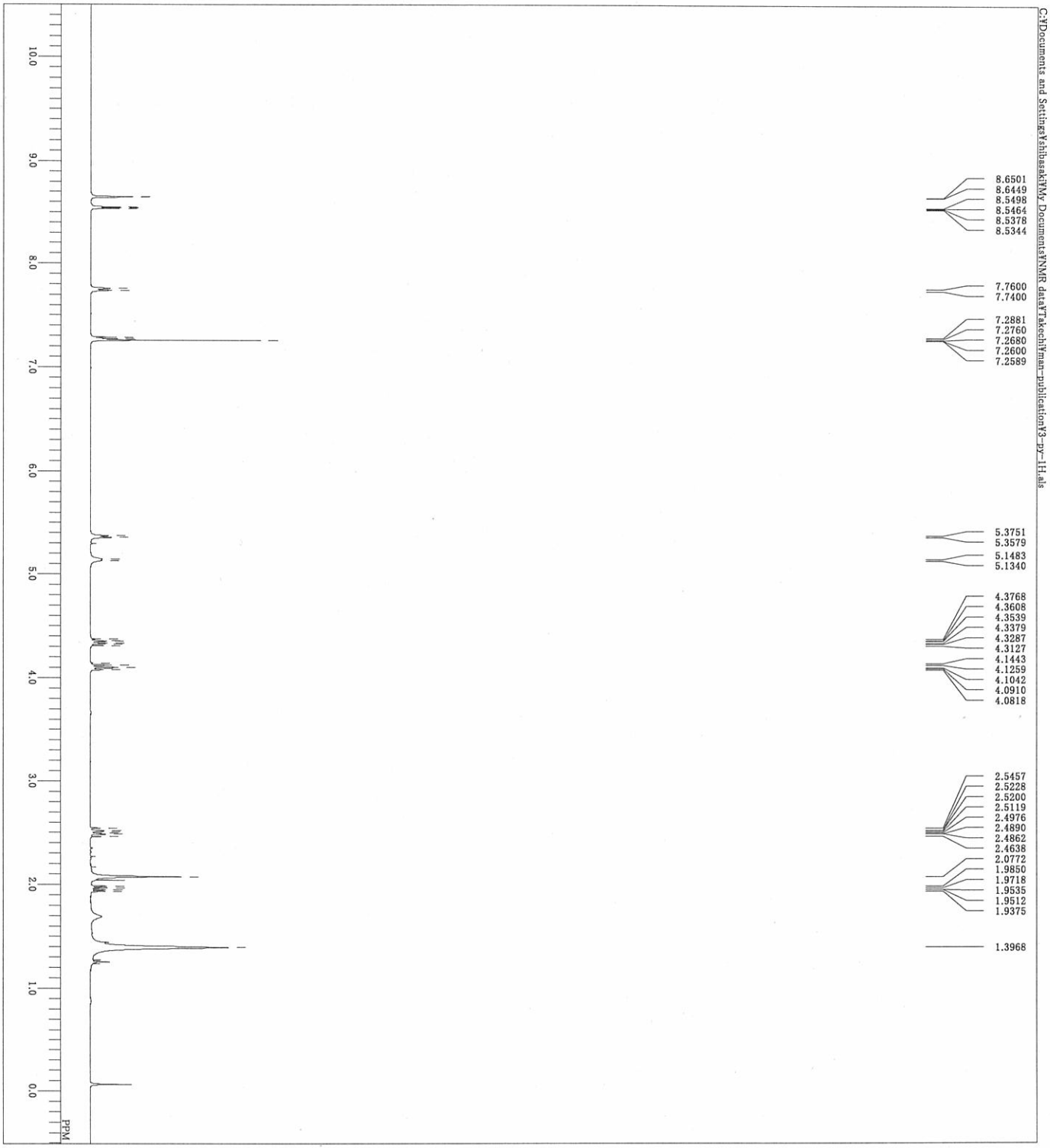


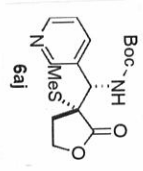
DFILE p-TfO-19F.als
COMNT TfO-Boc-19F
DATIM 2013-03-13 23:05:54
OBNUC 19F
EXMOD single_pulse.ex2
OBFRQ 376.17 MHz
OBSET 1.05 KHz
OBFIN 3.93 Hz
POINT1 262144
FREQU 15151.84 Hz
SCANS 52
ACQTM 0.1730 sec
PD 5.0000 sec
PW1 5.50 usec
IRNUC 19F
CTEMP 20.9 c
SLVNT CDCl3
EXREF -76.50 ppm
BF 0.12 Hz
RGAIN 46



6ai

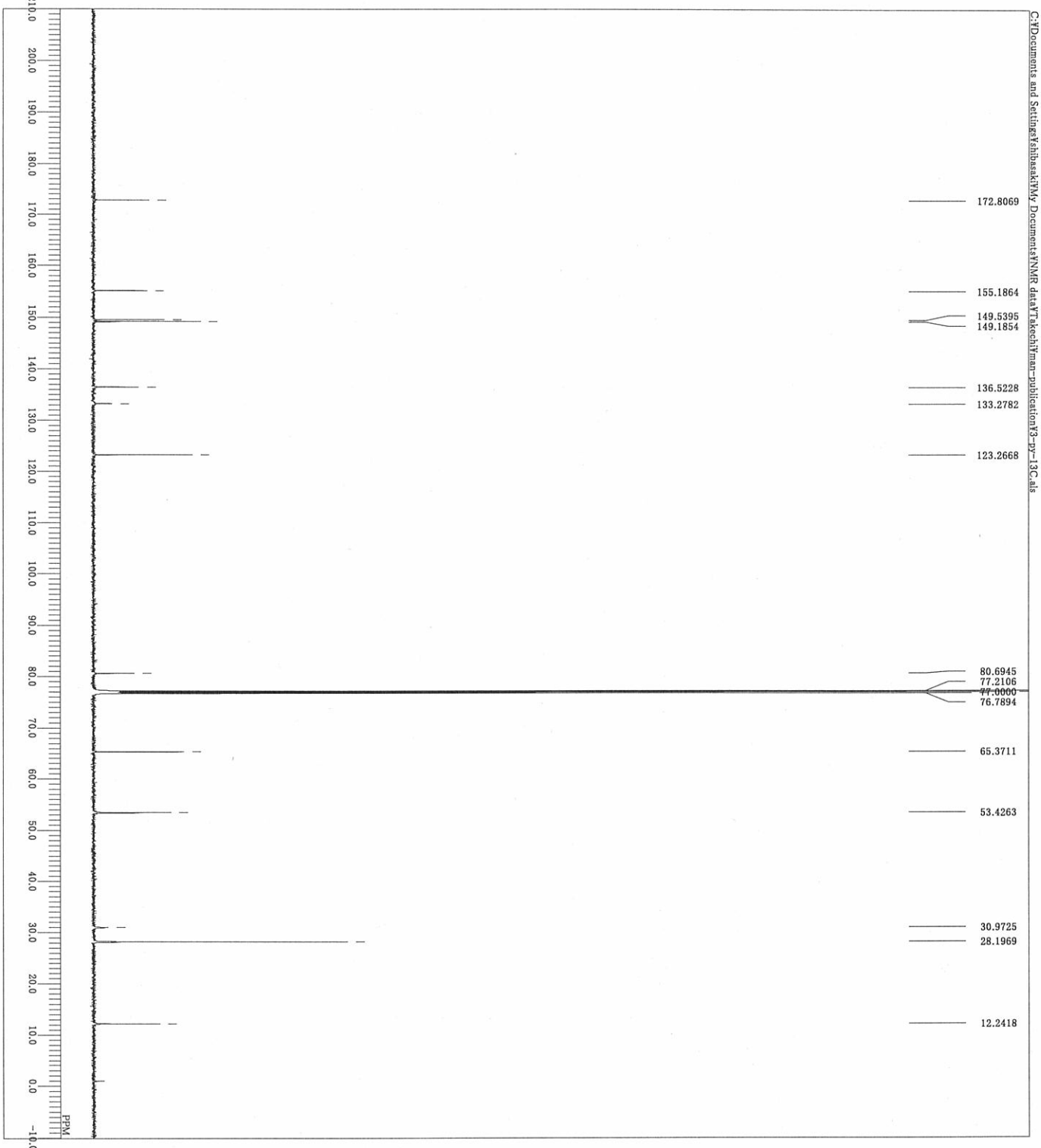
2370-3-py-1H

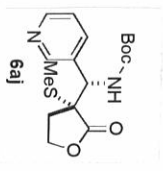




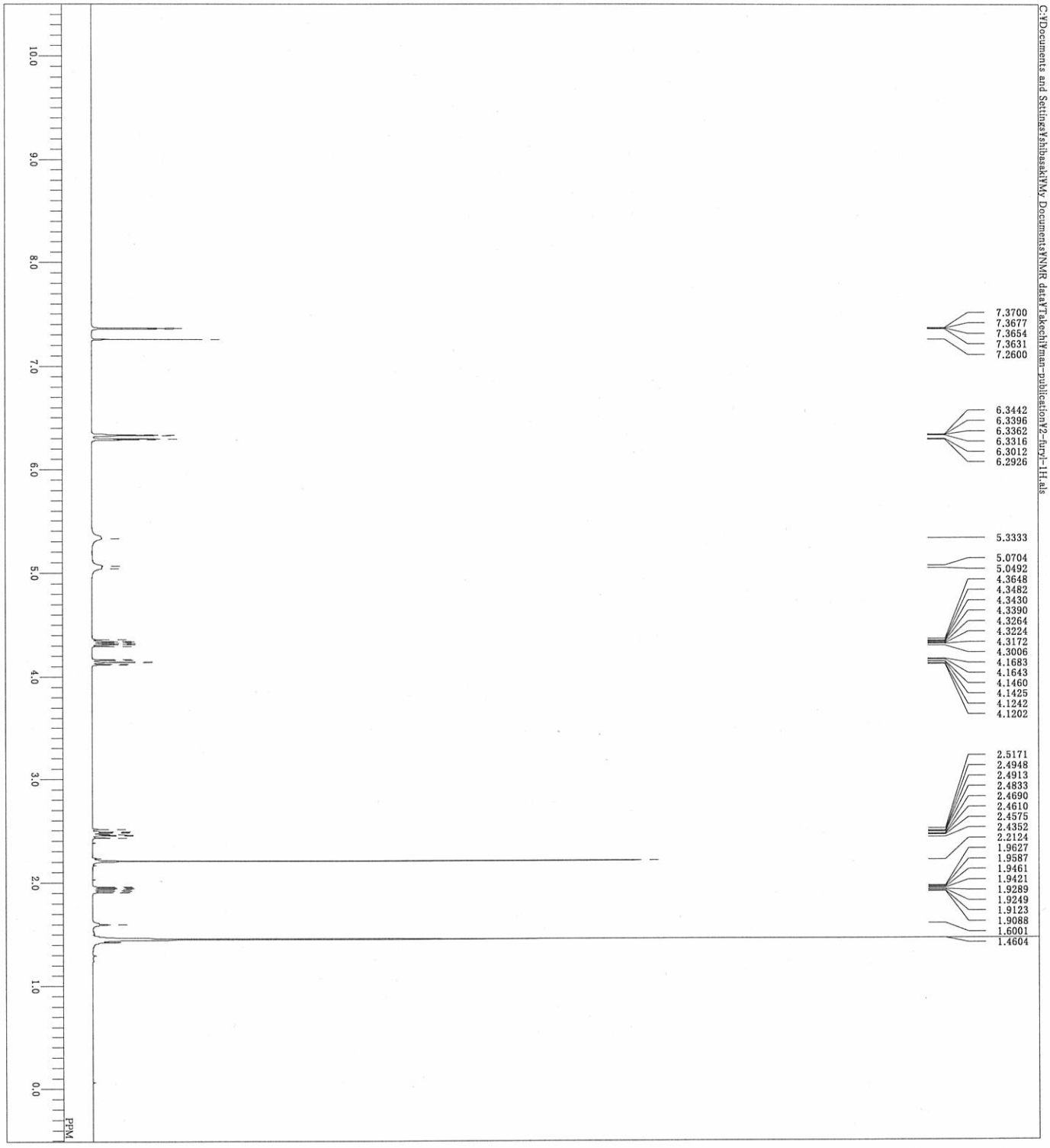
6aj

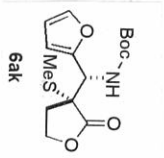
3-Py-13C 13C


C:¥Documents and Setting¥Ishibashi¥My Documents¥NMR data¥Takeuchi¥mar-publication¥3-py-13C.als
172.8069
155.1864
149.5395
149.1854
136.5228
133.2782
123.2668
80.6945
77.2106
77.0000
76.7894
65.3711
53.4263
30.9725
28.1969
12.2418
PPM
DFILE 3-py-13C.als
COMNT 3-Py-13C 13C
DATIM 2013-01-11 15:59:57
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 26224
FREQU 37878.21 Hz
SCANS 4153
ACQTM 0.6921 sec
PD 1.5000 sec
PW1 3.92 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40


Boc
NH
O
N
MeS
O
6aj

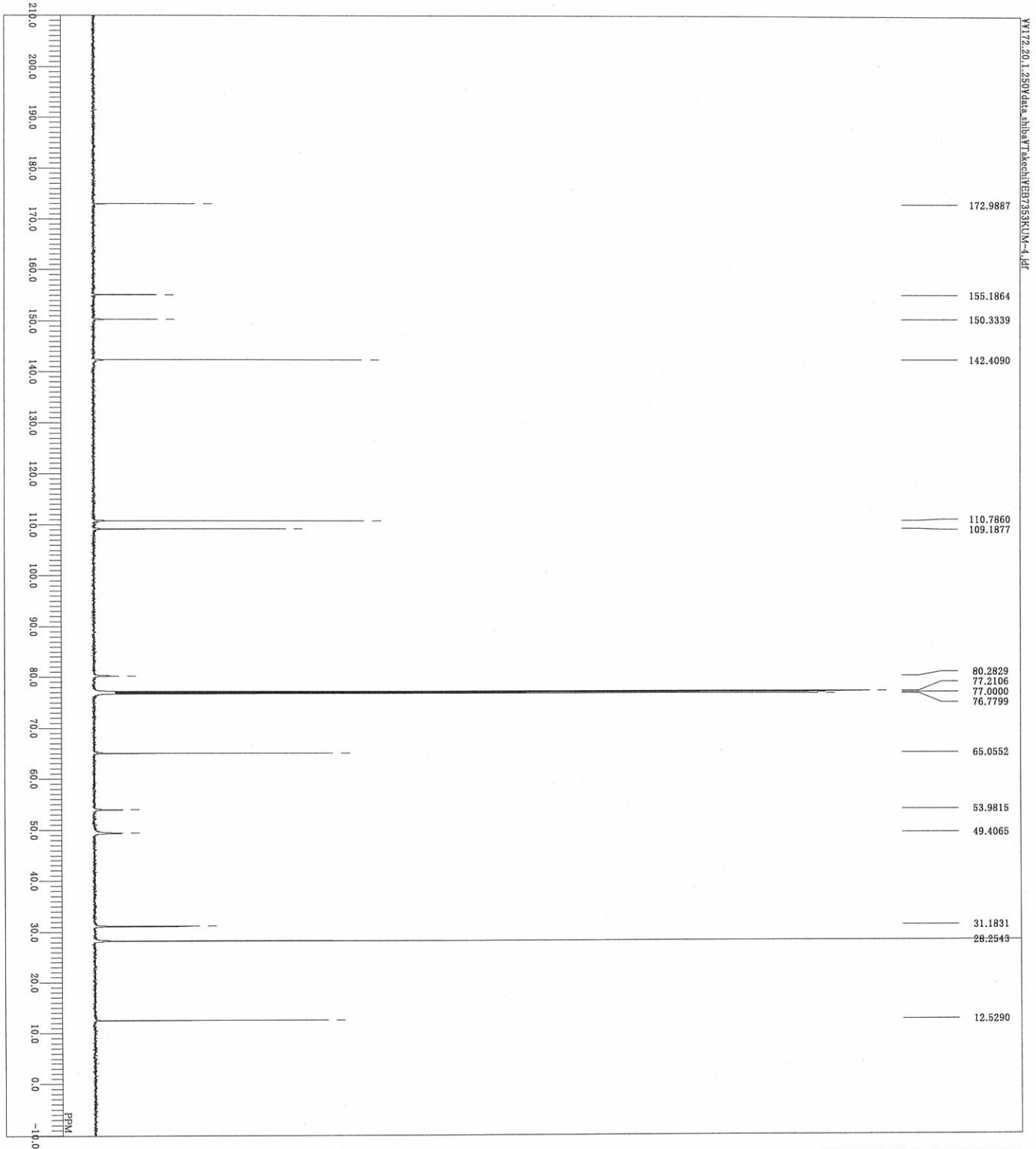
2353-furyl-1H

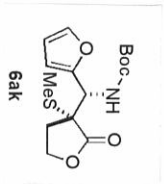




6ak

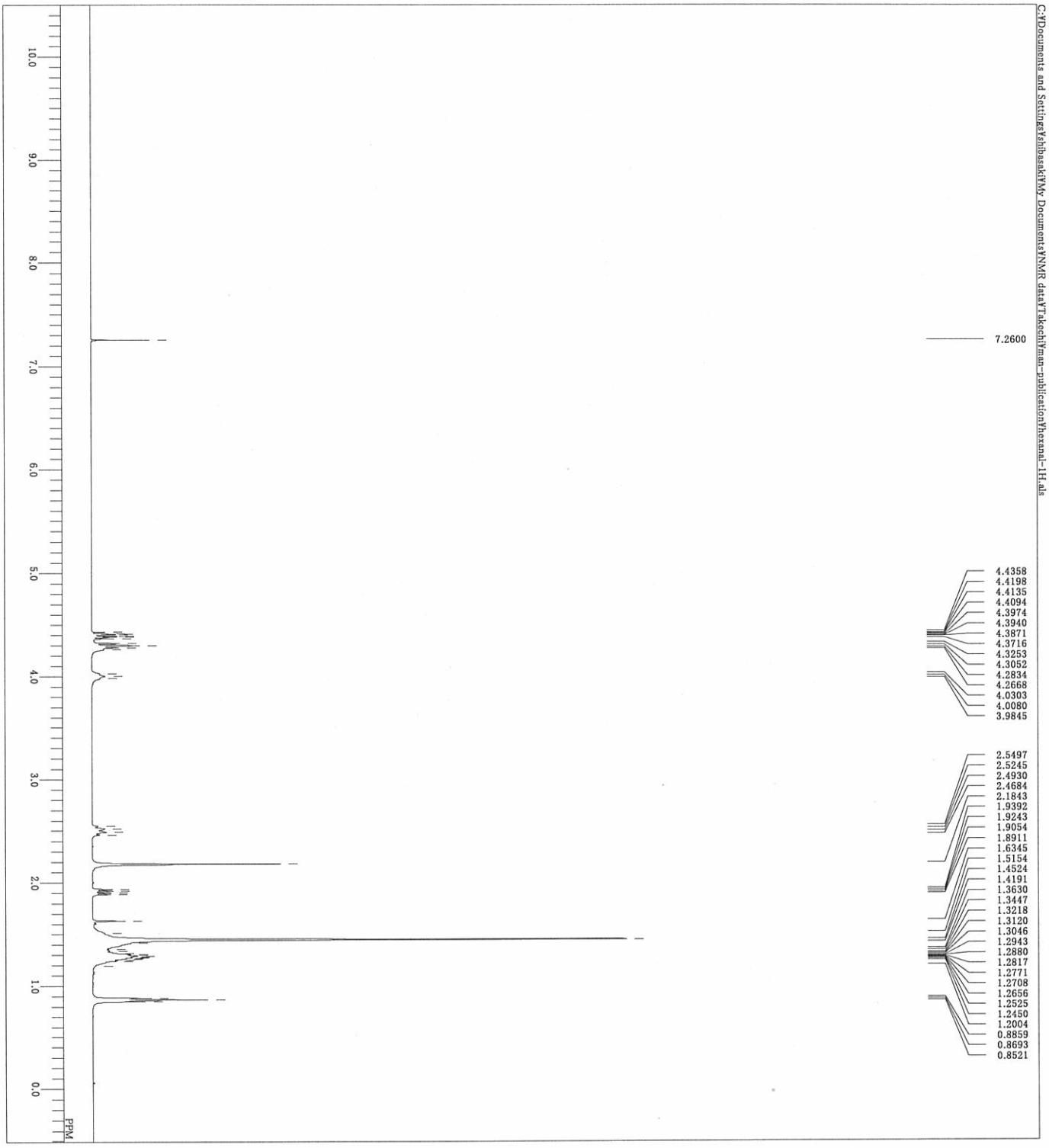
Furyl-13C 13C



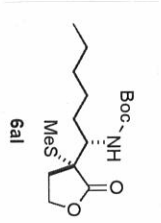


6ak

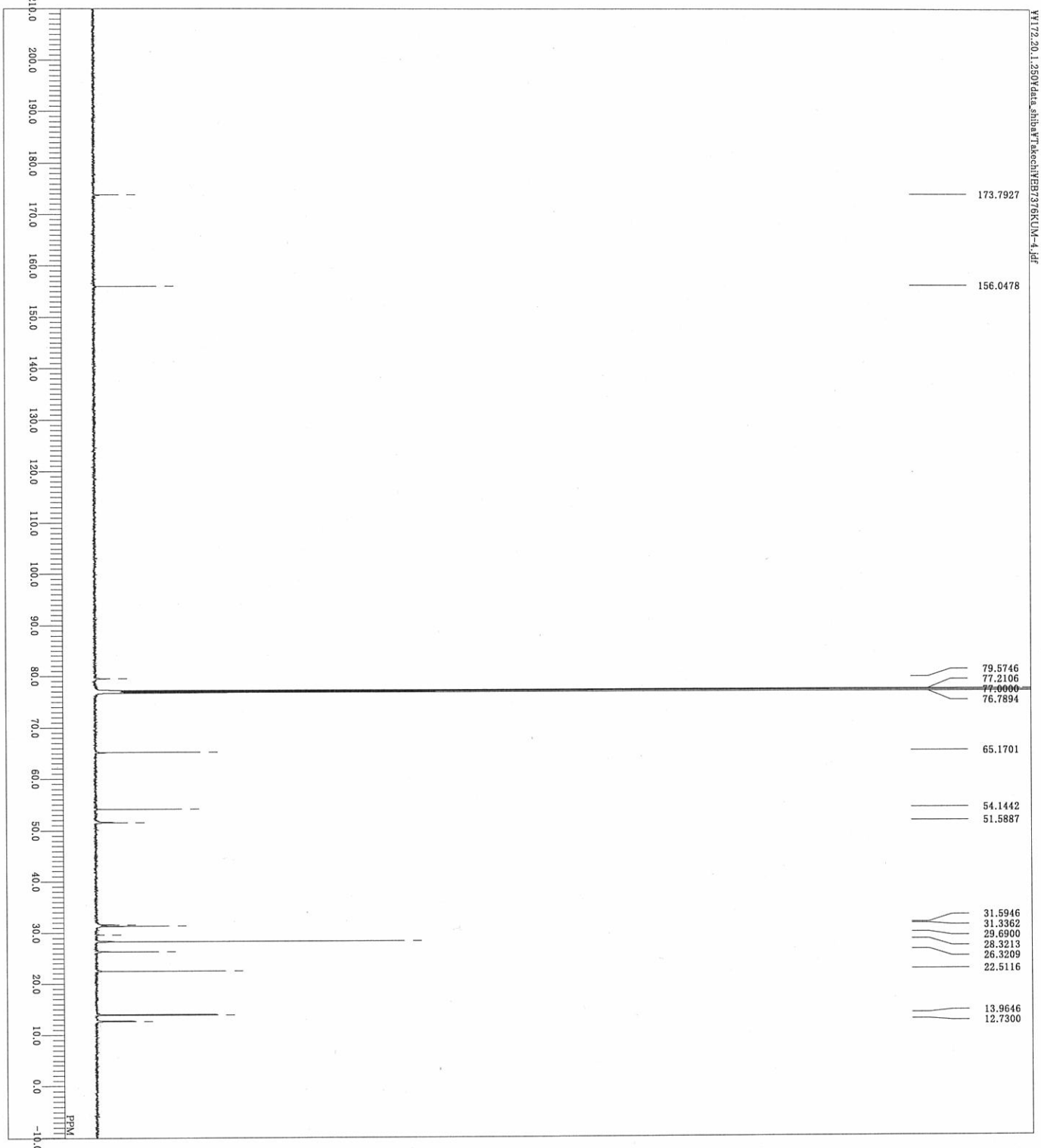
2367-hexanal-1H

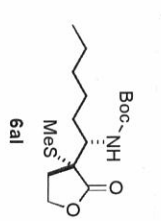


DFILE	hexanal-1H.als
COMNT	2367-hexanal-1H
DATIM	2013-01-07 16:30:39
OBNUC	1H
EXMOD	single_pulse_ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	26214
FREQU	6002.31 Hz
SCANS	16
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



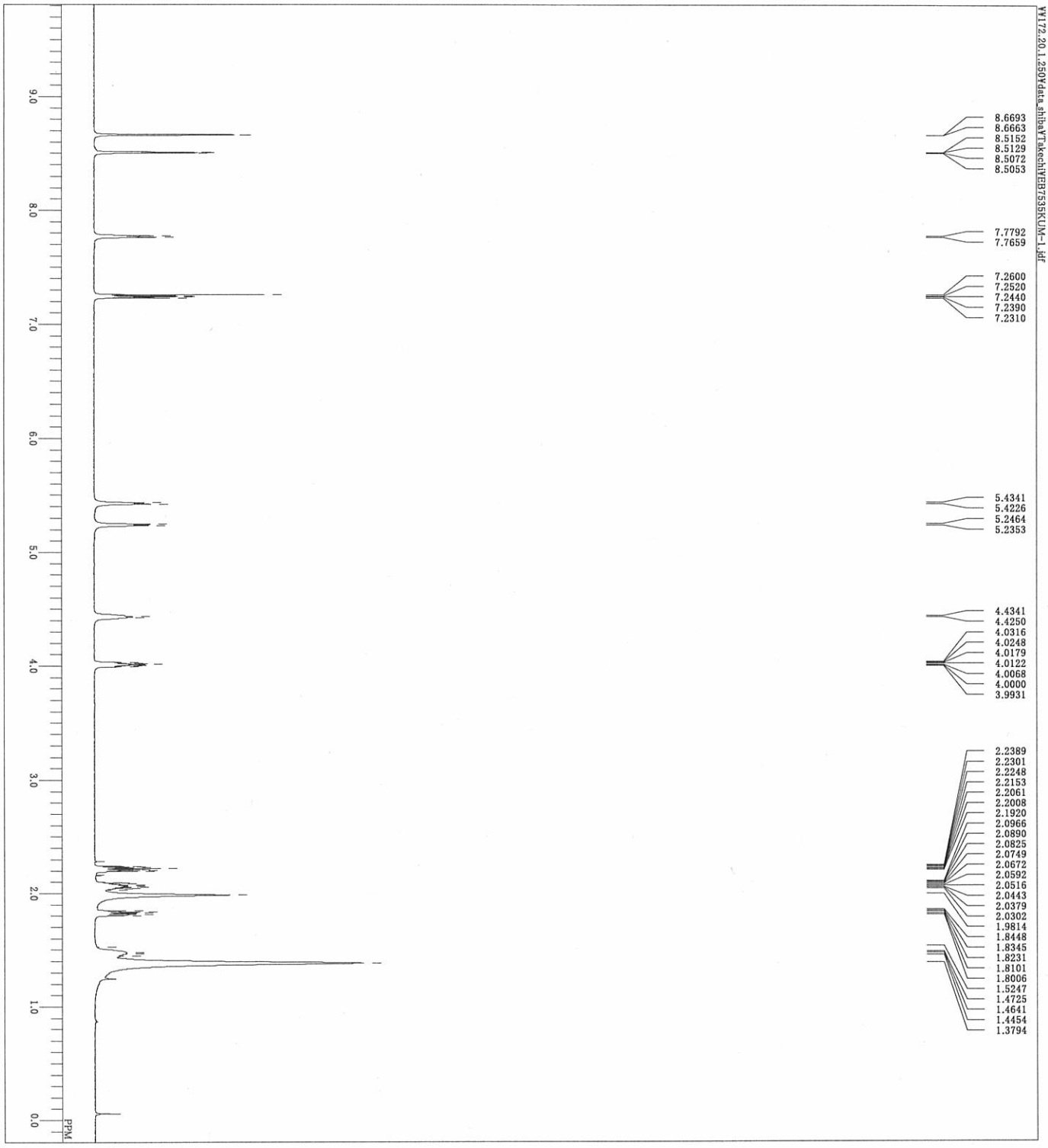
Hexanal-13C 13C



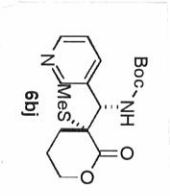


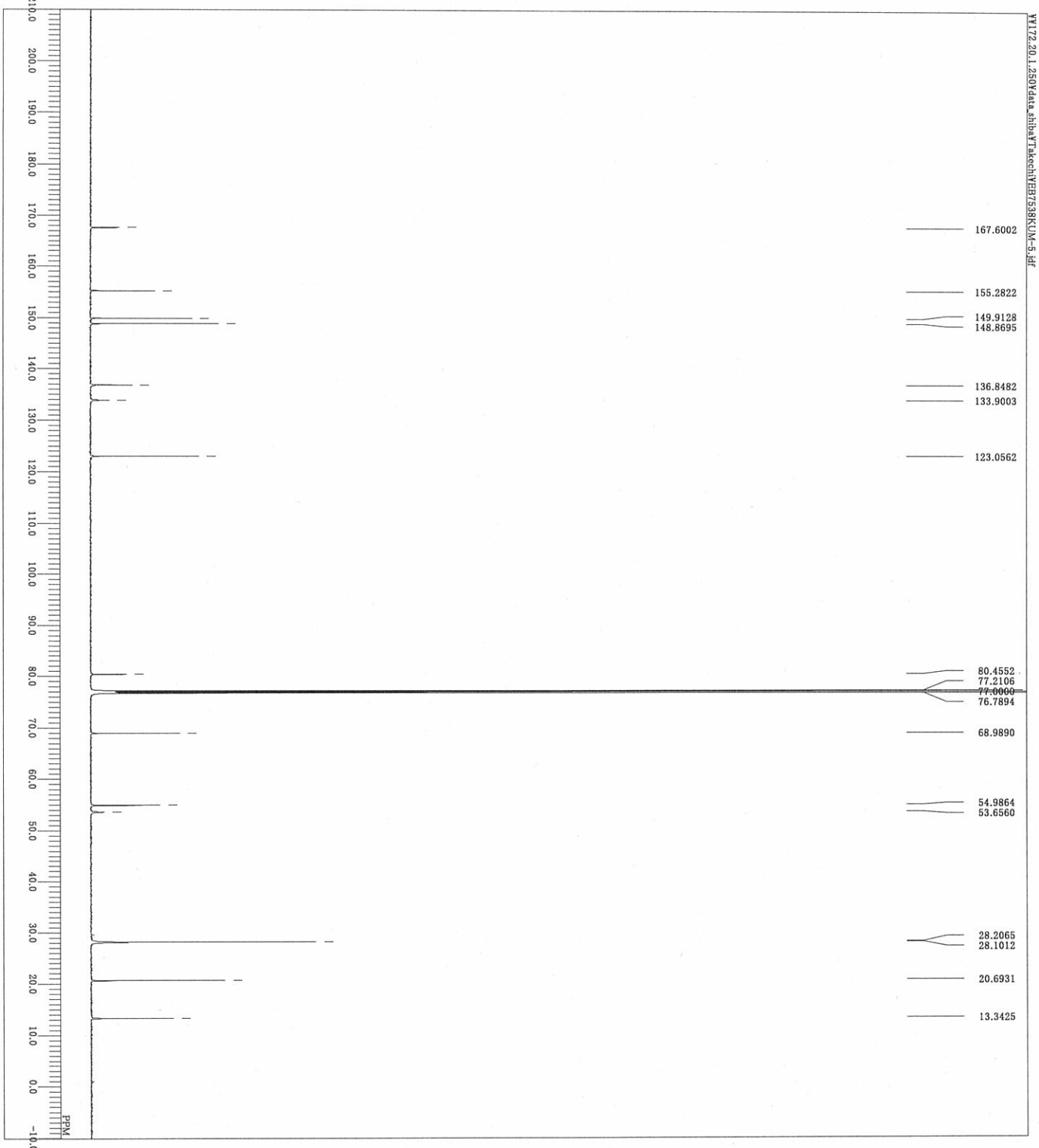
6al

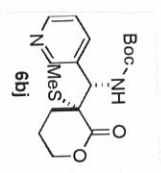
6-Py ~20mg 1H



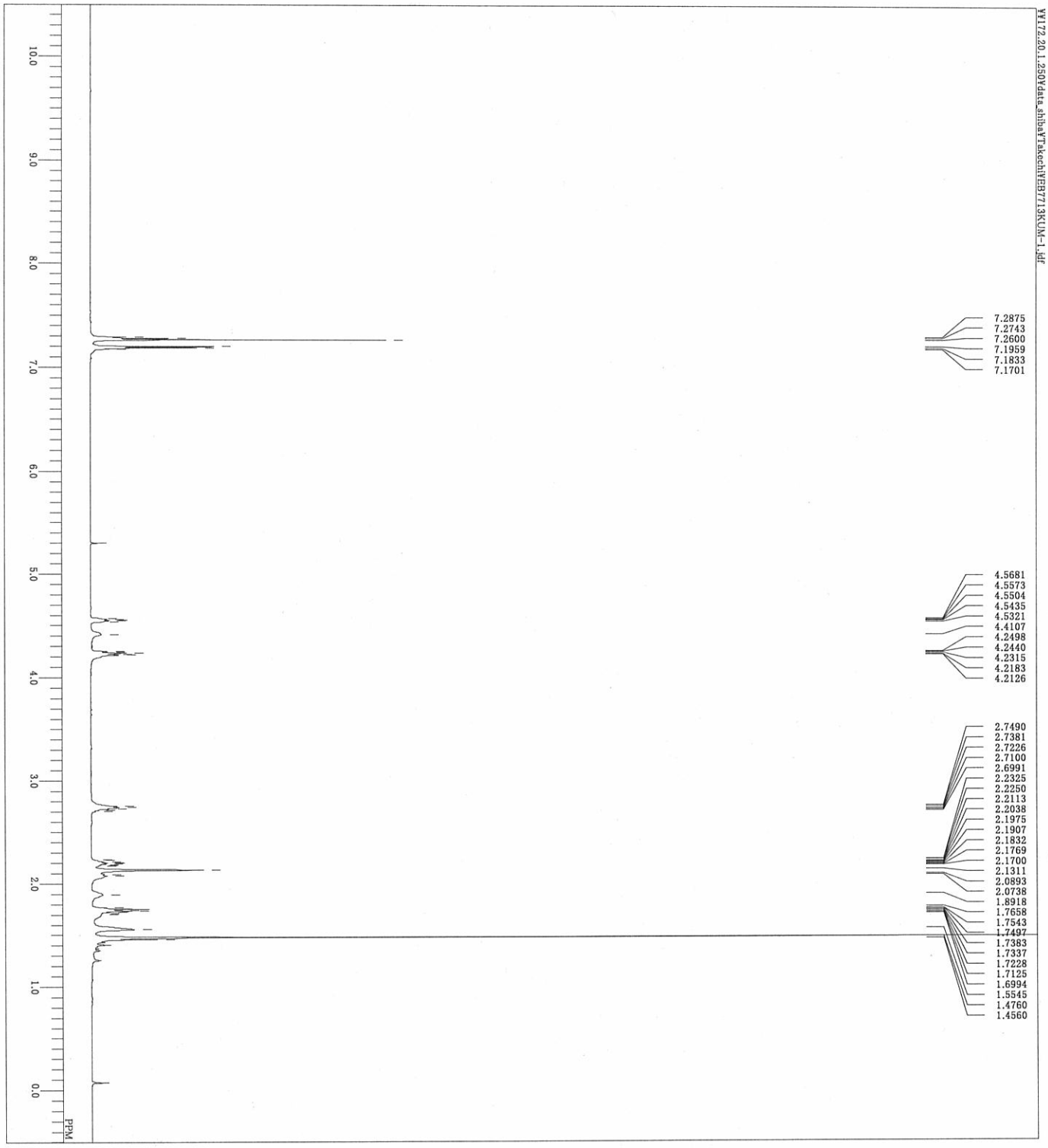
DFILE EB7535KUM-1.jdf
COMNT 6-Py ~20mg 1H
DATIM 2013-02-22 20:31:50
OBNUC 1H
EXMOD single_pulse_ex2
OBFRQ 600.17 MHz
OBSET 5.18 KHz
OBFIN 5.43 Hz
POINT 32768
FREQU 7503.00 Hz
SCANS 4
ACQTM 4.3673 sec
PD 3.5000 sec
PW1 6.65 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 40

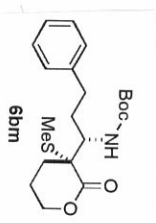


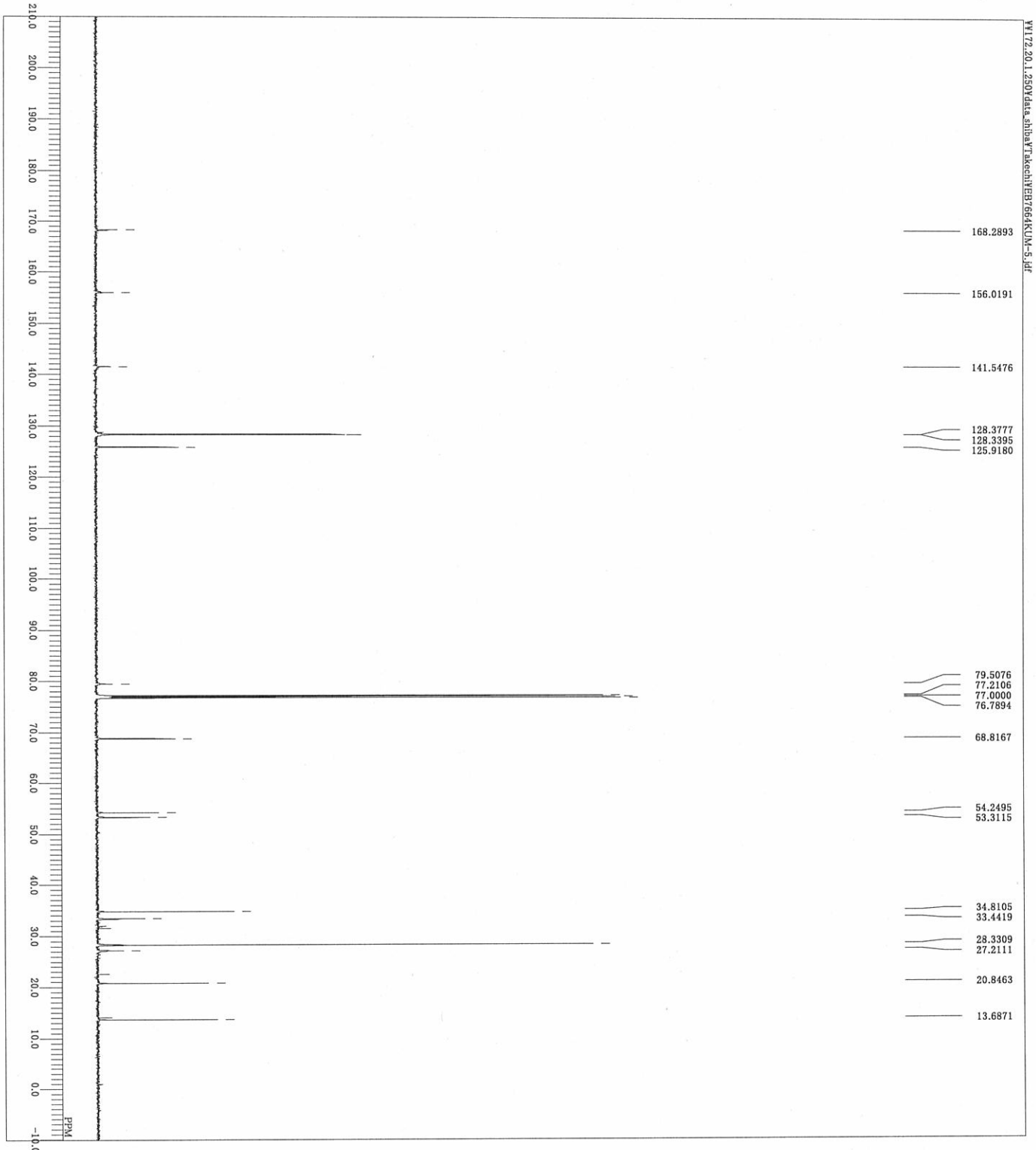

6-Py ~20mg 13C non noe
YY172.20.1.250Y data shiba YTakeuchi YEB7538KUM-5.jdf
167.6002
155.2822
149.9128
148.8695
136.8482
133.9003
123.0562
80.4552
77.2106
77.0000
76.7894
68.9890
54.9864
53.6560
28.2065
28.1012
20.6931
13.3425
PPM
DFILE EB7538KUM-5.jdf
COMNT 6-Py ~20mg 13C non noe
DATIM 2013-02-23 15:34:12
OBNUC 13C
EXMOD single pulse.dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32781
FREQU 47348.49 Hz
SCANS 30000
ACQTM 0.6921 sec
PD 1.5000 sec
PW1 3.92 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40

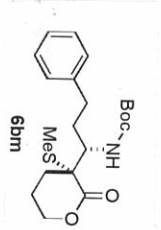

Boc
NH
O
O
N
MeS
6bj

6-hydrocinnam-1H

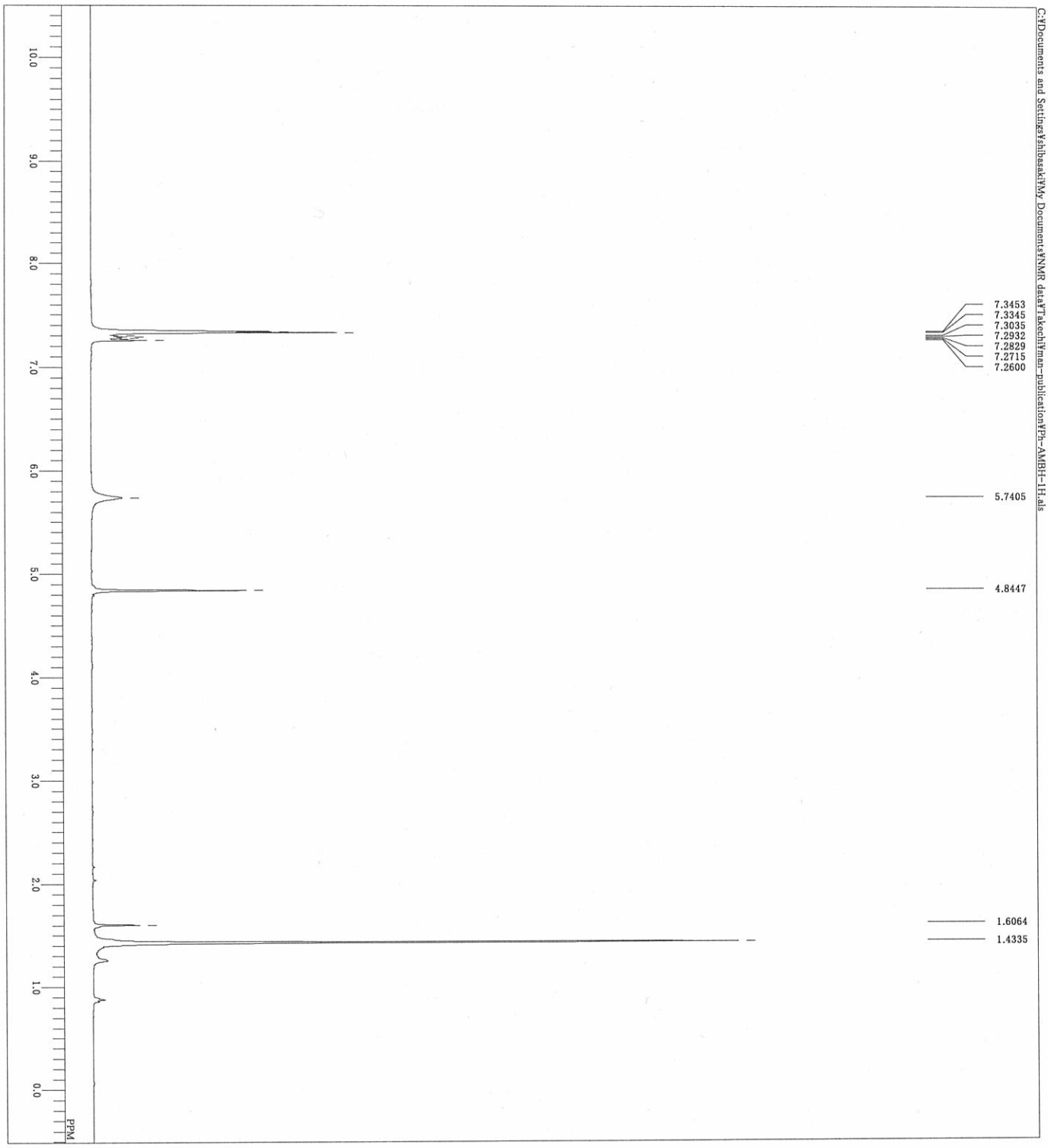


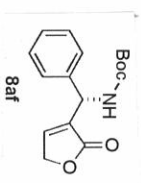



6-hydro cinnam ~20mg 13C
¥¥172.20.1.250¥data_shiba¥Takeuchi¥EB7664KUM-5.jdf
168.2893
156.0191
141.5476
128.3777
128.3395
125.9180
79.5076
77.2106
77.0000
76.7894
68.8167
54.2495
53.3115
34.8105
33.4419
28.3309
27.2111
20.8463
13.6871
PPM
DFILE EB7664KUM-5.jdf
COMNT 6-hydro cinnam ~20mg 13C
DATIM 2013-03-19 11:46:39
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 1.52 kHz
OBFIN 32781 Hz
POINT 47348.49 Hz
FREQU 1150
SCANS 0.6921 sec
ACQTM 2.0000 sec
PD 3.92 usec
PW1
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40

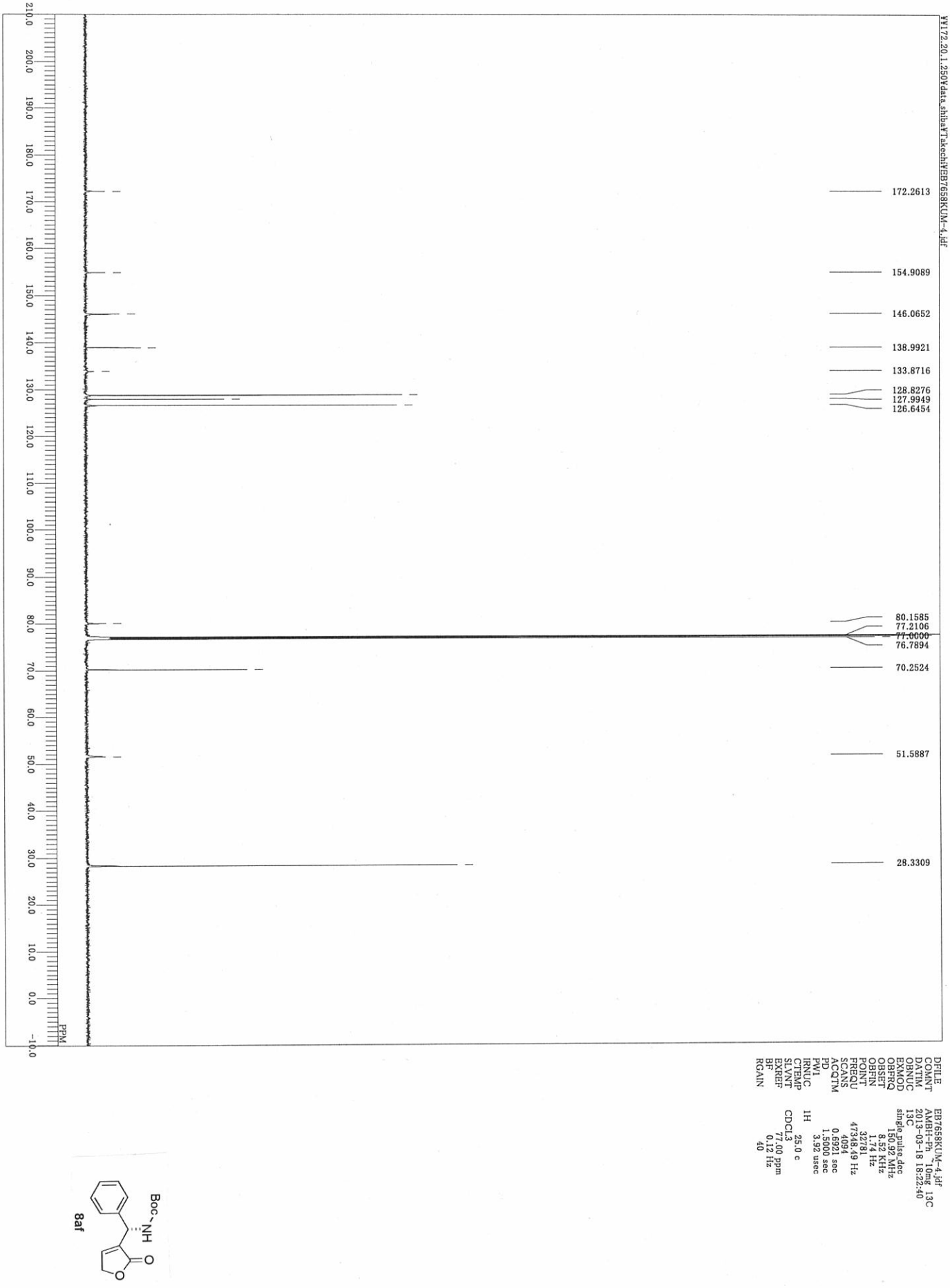

Boc
NH
MeS
O
O
6bm

AMBH-rac

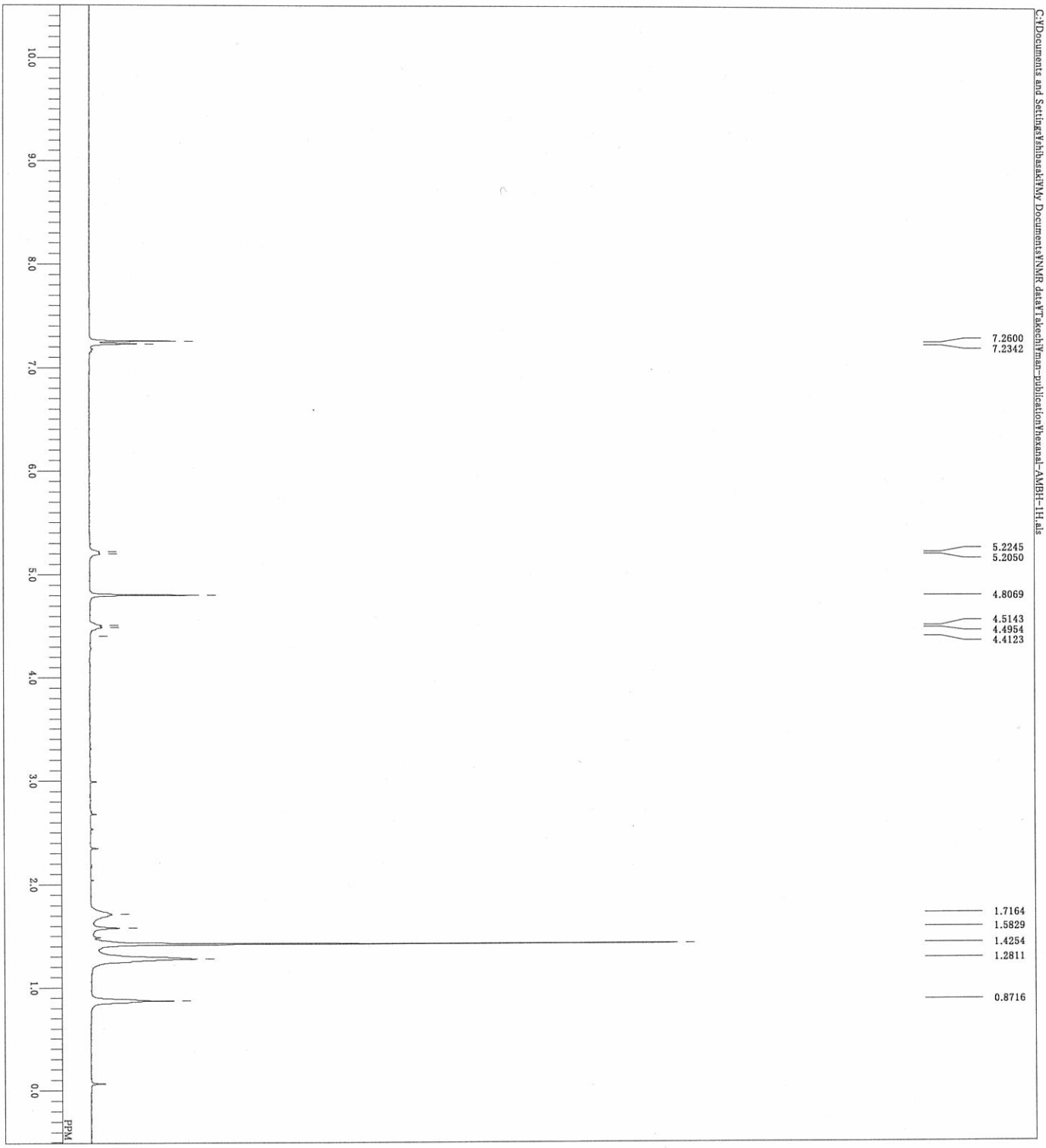

C:¥Documents and Settings¥shibasaki¥My Documents¥NMR data¥Takeochi¥man-publication¥Ph-AMBH-1H.als
7.3453
7.3345
7.3035
7.2932
7.2829
7.2715
7.2600
5.7405
4.8447
1.6064
1.4335
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
DFILE Ph-AMBH-1H.als
COMNT AMBH-rac
DATIM 2013-03-07 13:22:34
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 26214
FREQU 6009.31 Hz
SCANS 8
ACQTM 4.3673 sec
PD 5.0000 sec
PW1 5.38 usec
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCl3
EXREF 7.26 ppm
BF 1.20 Hz
RGAIN 40

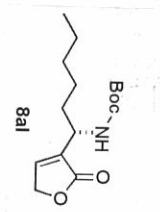

Boc
NH
O
O

8af

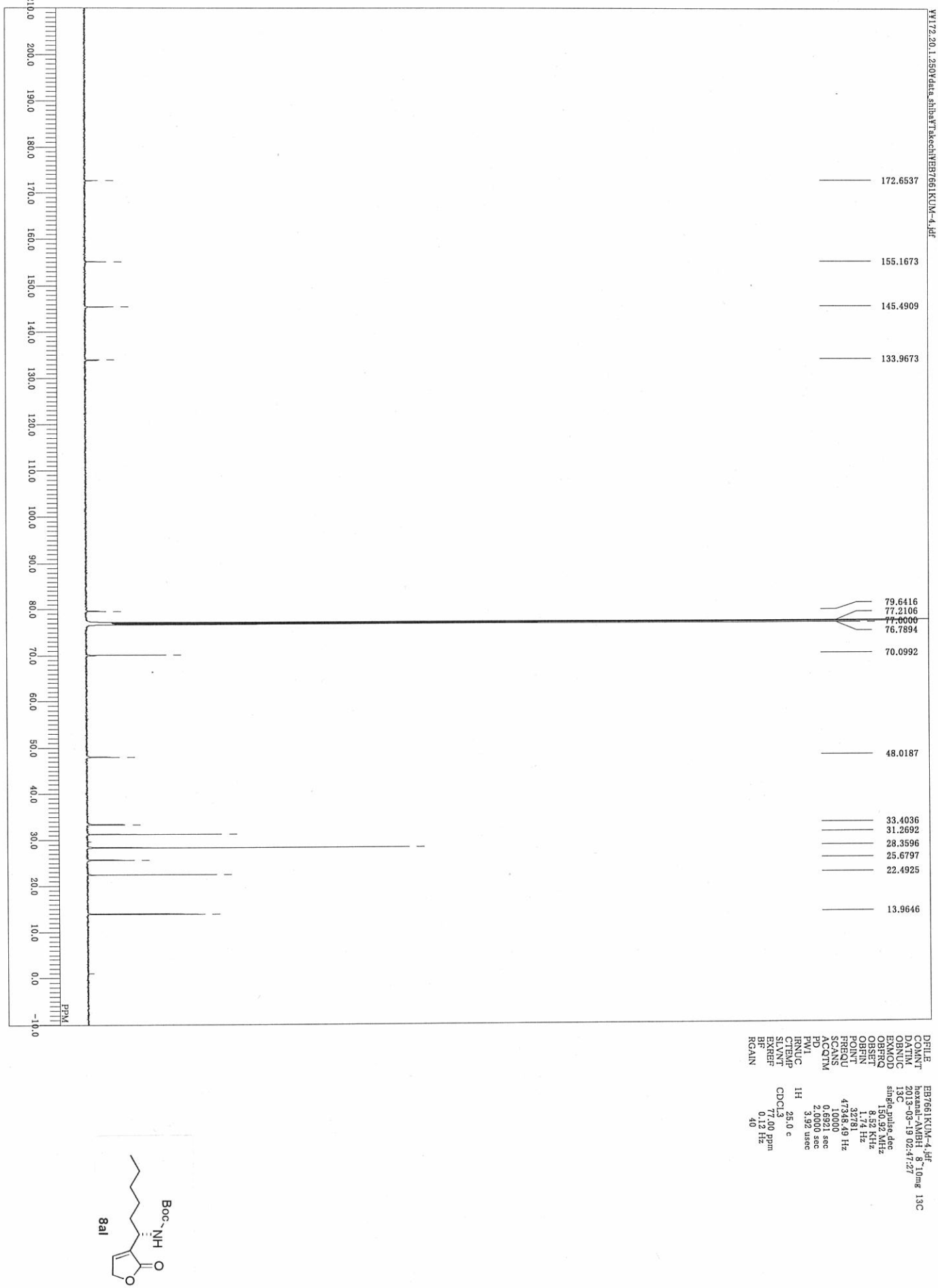

AMBH-Ph ~10mg 13C
YY172.20.1.250Ydata_shibaYTakechiYEB7658KUM-4.jdf
172.2613
154.9089
146.0652
138.9921
133.8716
128.8276
127.9949
126.6454
80.1585
77.2106
77.0000
76.7894
70.2524
51.5887
28.3309
PPM
DFILE EB7658KUM-4.jdf
COMNT AMBH-Ph 10mg 13C
DATIM 2013-03-18 18:22:40
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 1.74 kHz
OBFIN 32781
POINT 47348.49 Hz
FREQU 4094
SCANS 0.6921 sec
ACQTM 1.5000 sec
PD 3.92 usec
PW1
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40
Boc
NH
O
O
8af

hexanal-AMBH-cr

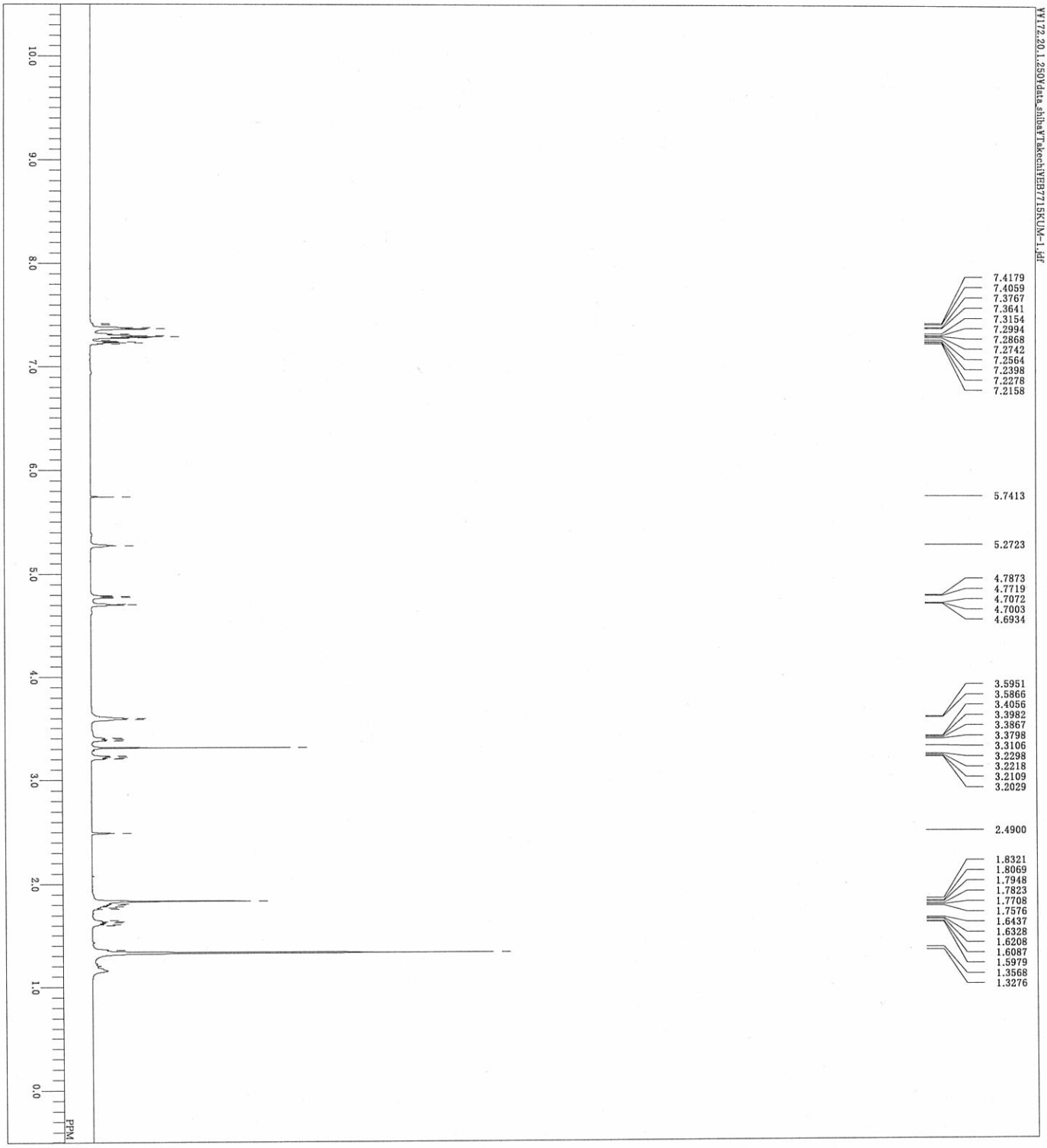




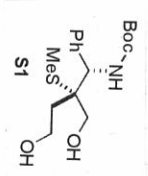
8al


hexanal-AMBH 8~10mg 13C
¥¥172.20.1.250¥data_shiba¥Takeshi¥EB7661KUM-4.jdf
172.6537
155.1673
145.4909
133.9673
79.6416
77.2106
77.0000
76.7894
70.0992
48.0187
33.4036
31.2692
28.3596
25.6797
22.4925
13.9646
PPM
DFILE EB7661KUM-4.jdf
COMNT hexanal-AMBH 8~10mg 13C
DATIM 2013-03-19 02:47:27
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32781
FREQU 47348.49 Hz
SCANS 10000
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 3.92 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 40
Boc
NH
O
O
8al

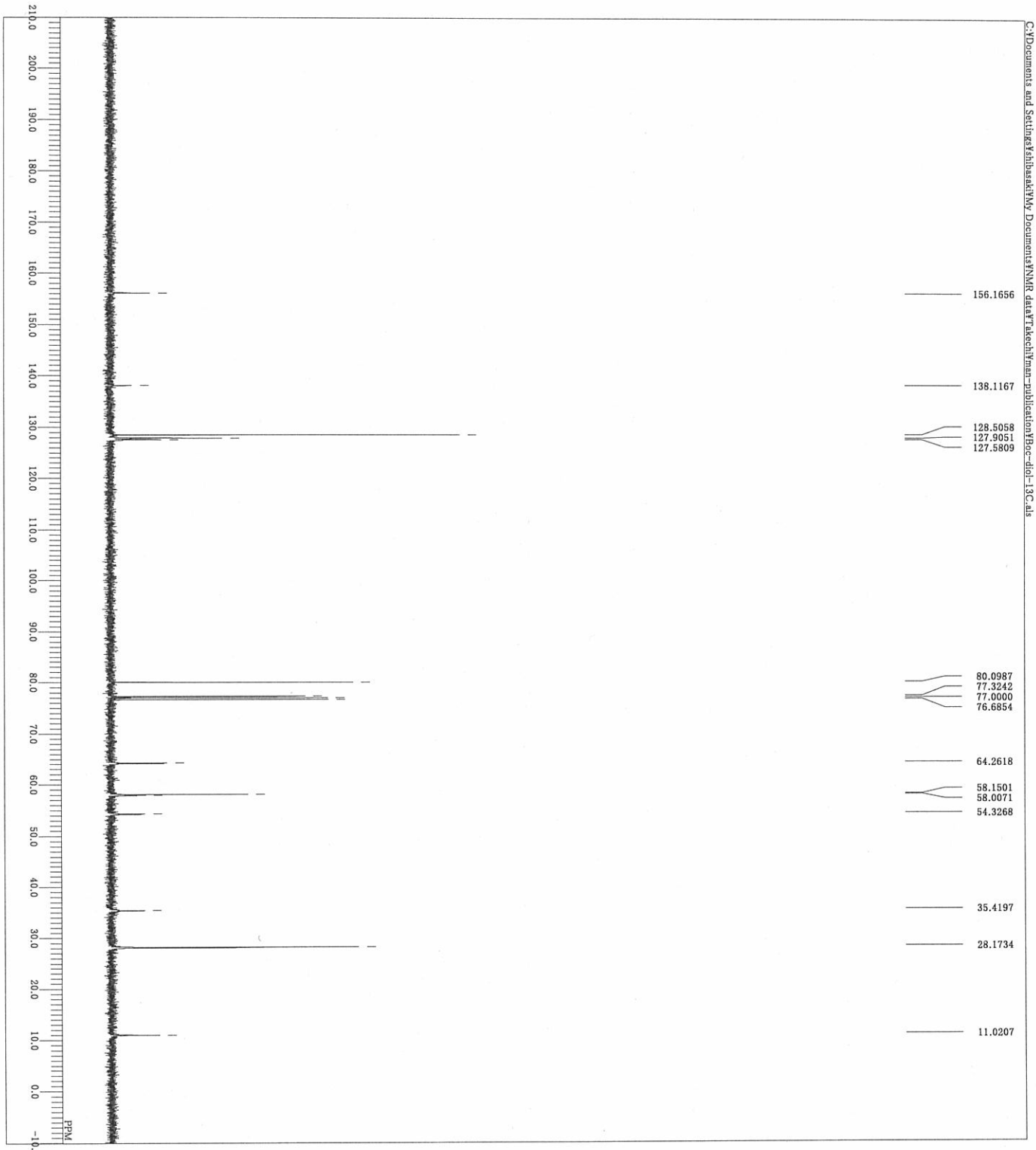
Boc-diol in DMSO



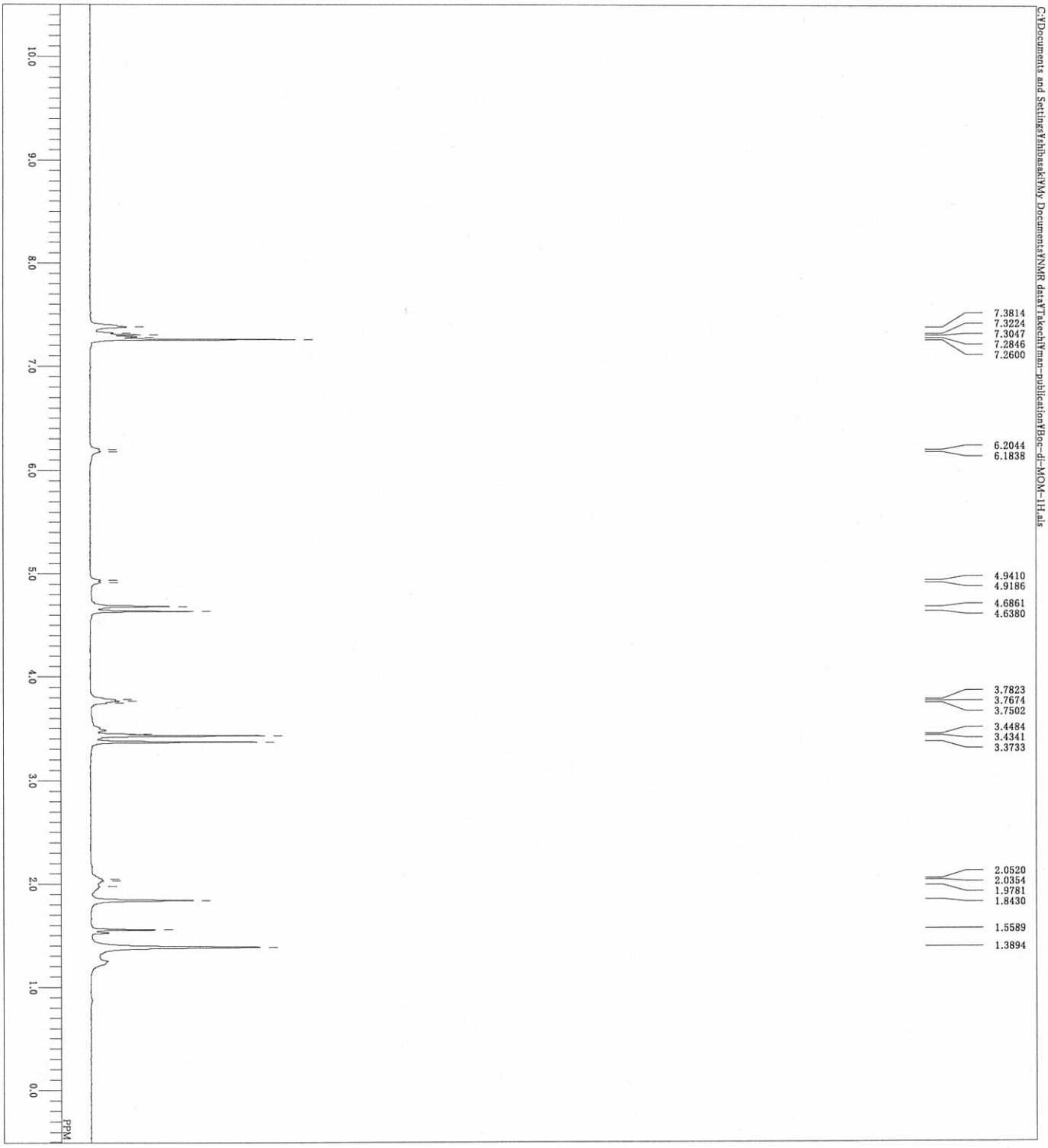
DFILE	EB7715KUM-1.jdf
COMNT	Boc-diol in DMSO
DATIM	2013-03-23 22:29:27
OBNUC	1H
EXMOD	single_pulse_ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	32768
FREQU	11261.26 Hz
SCANS	16
ACQTM	2.9098 sec
PD	3.5000 sec
PW1	6.65 usec
IRNUC	1H
CTEMP	25.0 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	1.20 Hz
RGAIN	40

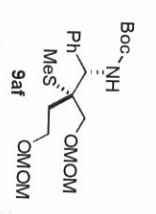


S1


Boc-diol-13C
C:¥Documents and Settings¥shibasaki¥My Documents¥NMR data¥Takechi¥man-publication¥Boc-diol-13C.als
156.1656
138.1167
128.5058
127.9051
127.5809
80.0987
77.3242
77.0000
76.6854
64.2618
58.1501
58.0071
54.3268
35.4197
28.1734
11.0207
PPM
DFILE Boc-diol-13C.als
COMNT Boc-diol-13C
DATIM 2013-03-20 00:13:58
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 26201 Hz
POINT 251252 Hz
FREQU 60
SCANS 1.0433 sec
ACQTM 2.0000 sec
PD 2.83 usec
PW1 1H
IRNUC 21.1 c
CTEMP CDCl3
SLVNT 77.00 ppm
EXREF 0.12 Hz
BF 60
RGAIN
Boc
NH
Ph
MeS
OH
OH
S1

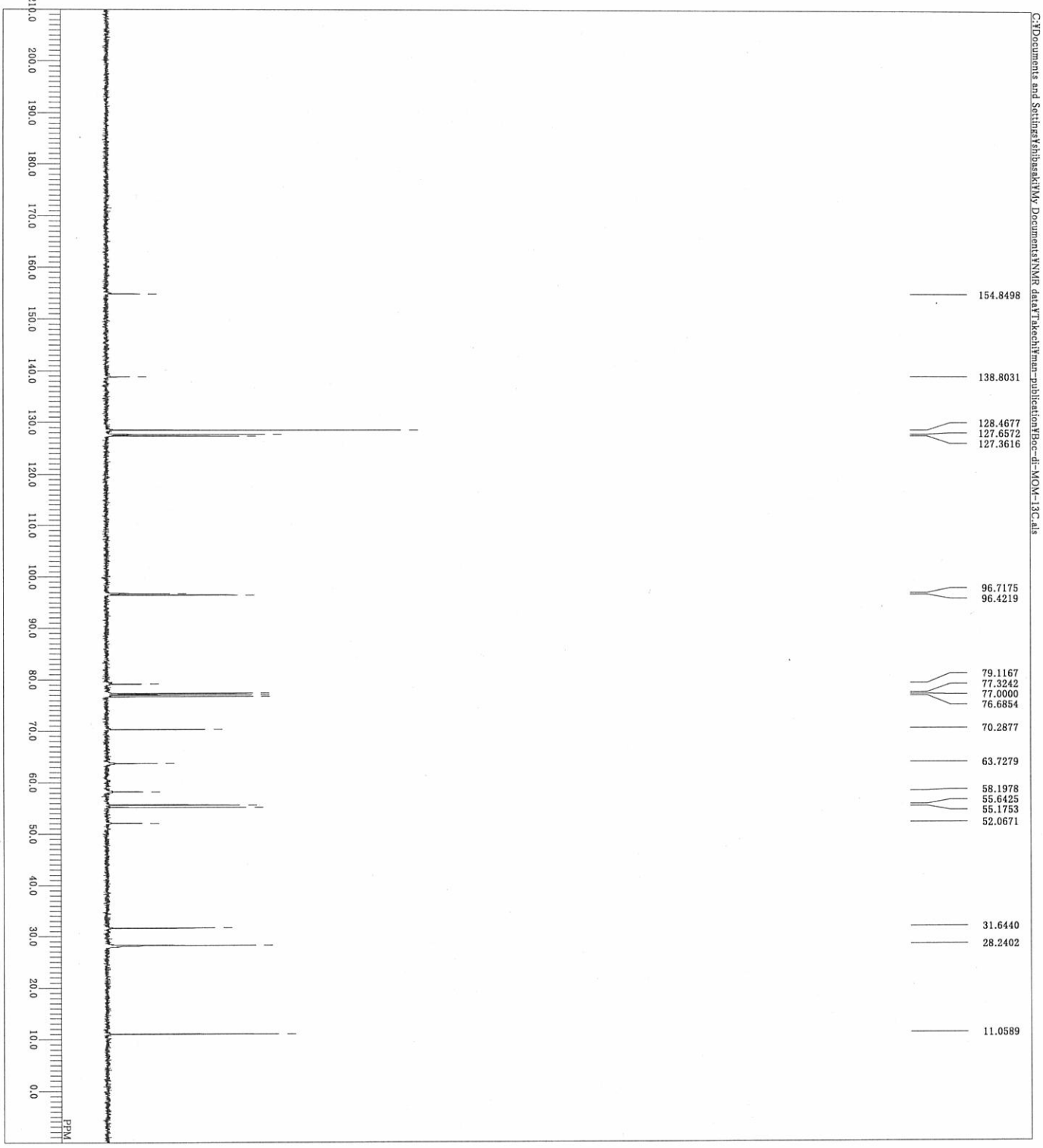
Boc-di-MOM-1H

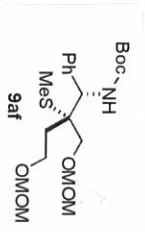




9af

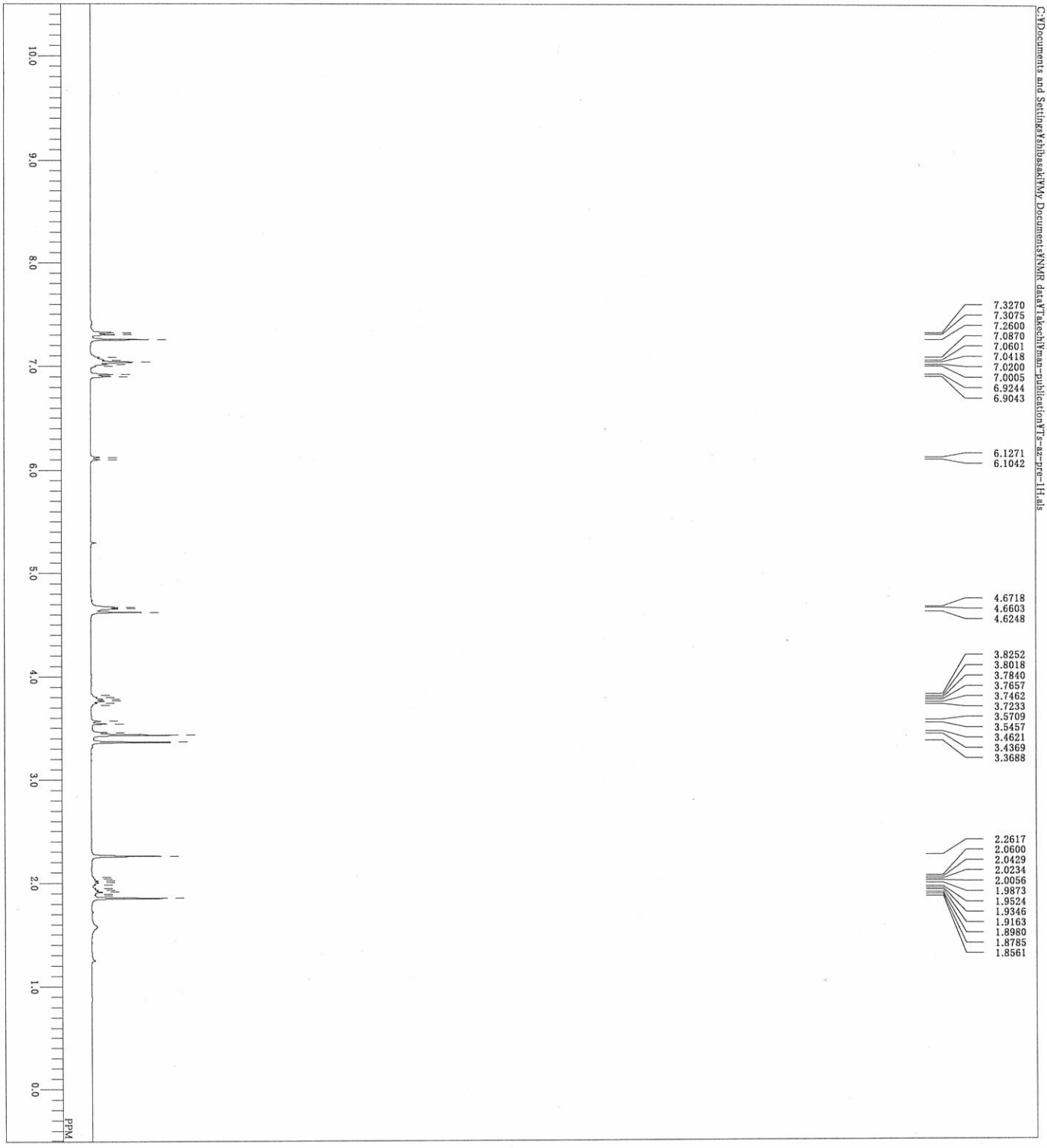
Boc-di-MOM-13C



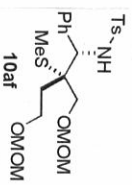


9af

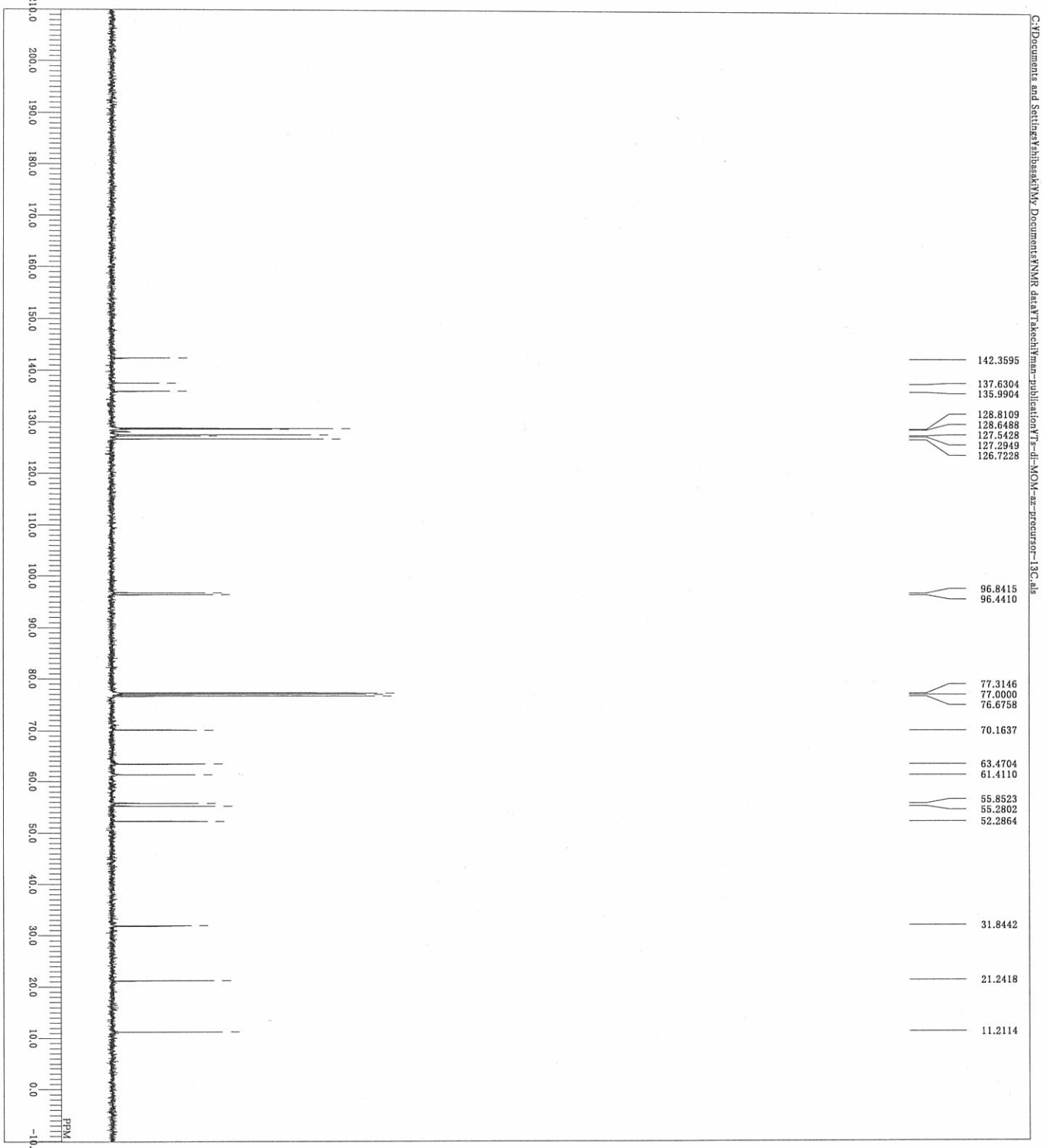
Ts-az-pre-1H

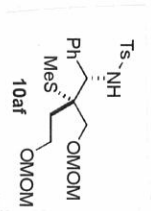


DFILE	Ts-az-pre-1H.als
COMNT	Ts-az-pre-1H
DATIM	2013-03-14 17:39:06
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	26214
FREQU	6002.31 Hz
SCANS	16
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	50

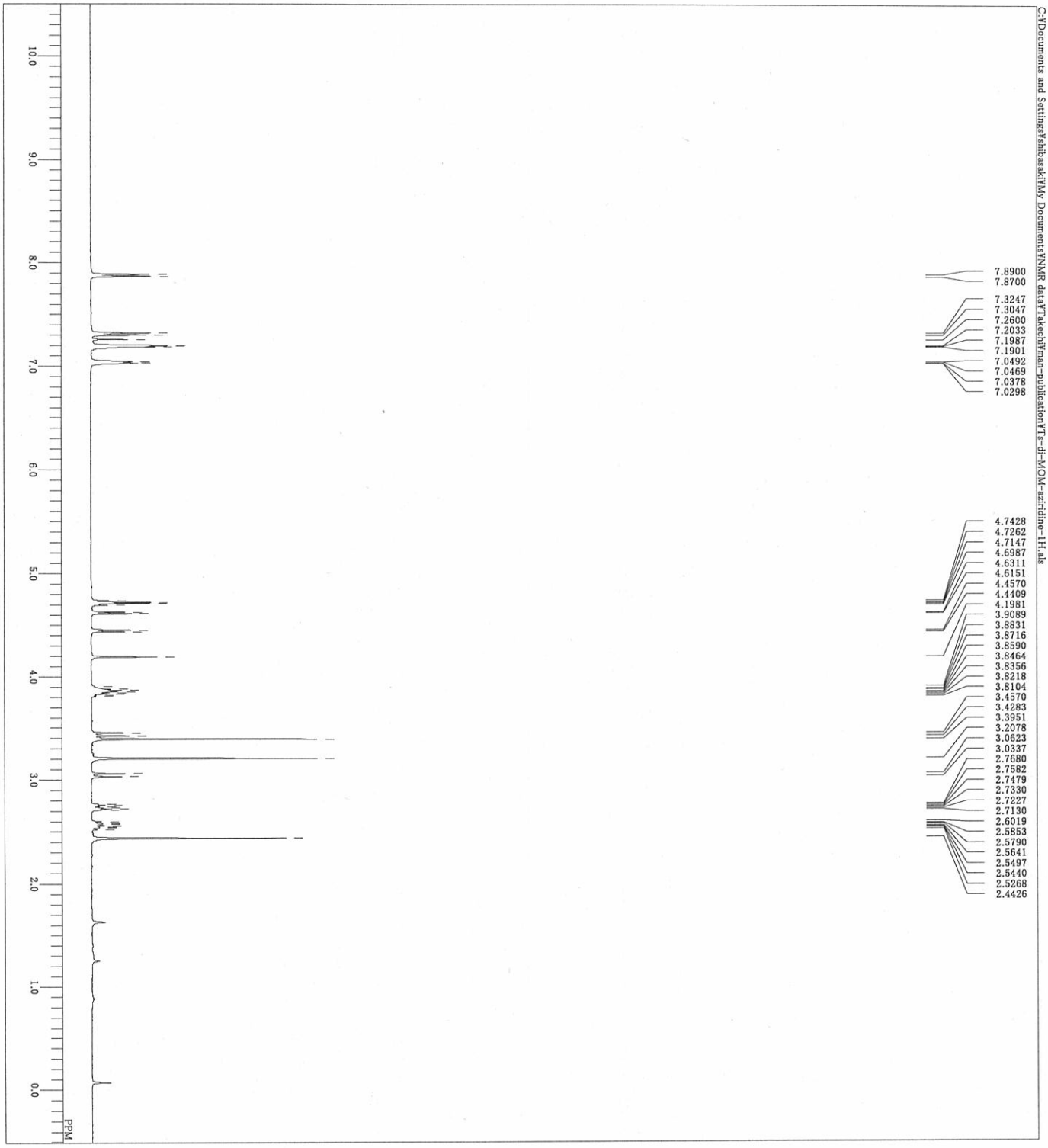


Ts-az-pre-13C

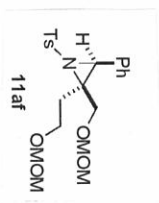

C:¥Documents and Settings¥shibasaki¥My Documents¥NMR data¥Takechi¥man-publication¥Ts-di-MOM-az-precursor-13C.als
142.3595
137.6304
135.9904
128.8109
128.6488
127.5428
127.2949
126.7228
96.8415
96.4410
77.3146
77.0000
76.6758
70.1637
63.4704
61.4110
55.8523
55.2802
52.2864
31.8442
21.2418
11.2114
PPM
DFILE Ts-di-MOM-az-precursor-13C.als
COMNT Ts-az-pre-13C
DATIM 2013-03-14 18:59:30
OBNUC 13C
EXMOD single pulse.doc
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 74
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.83 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 60


Ts
NH
Ph
MeS
OMOM
OMOM
10af

aziridine-1H

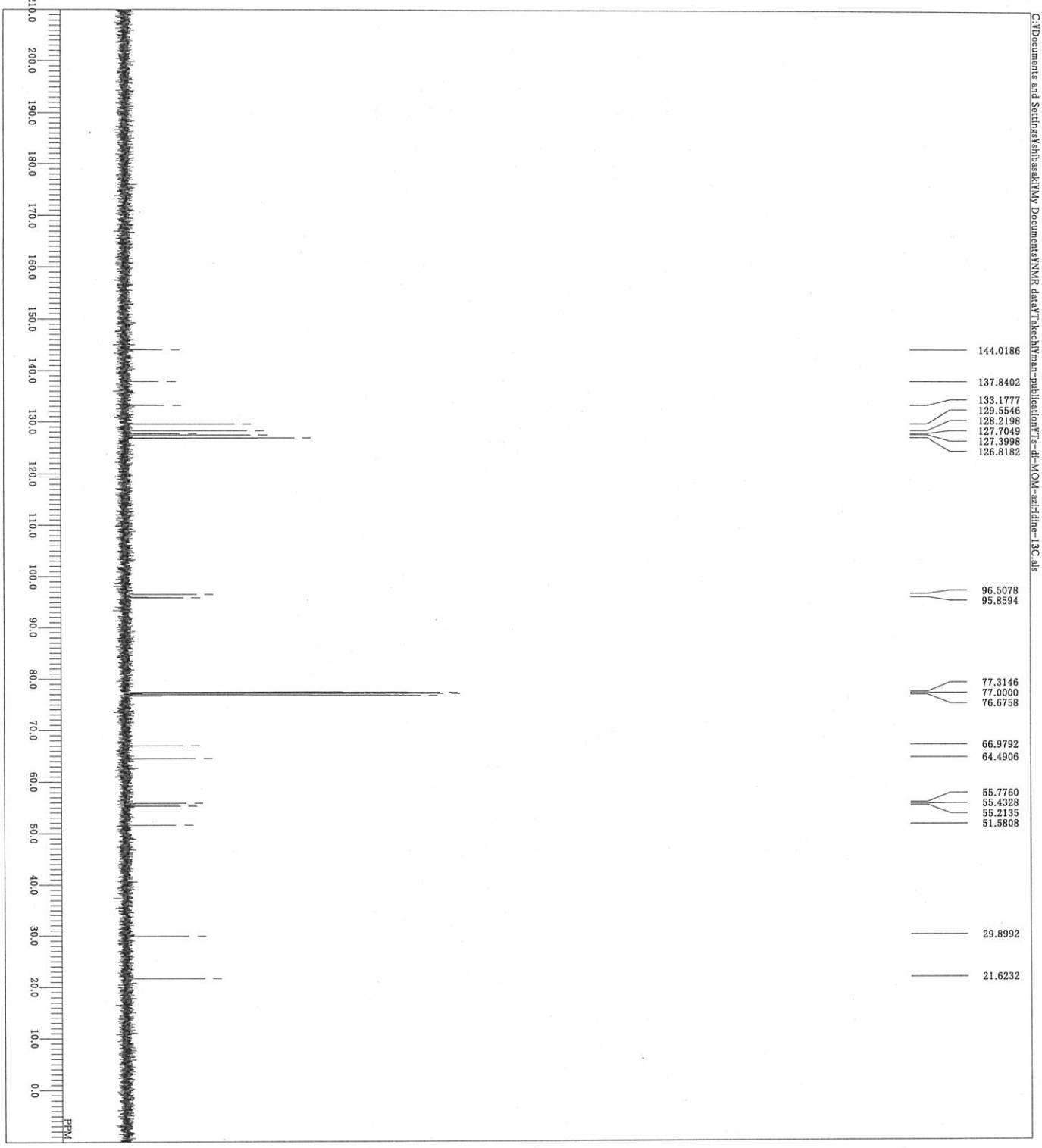


DFILE	Ts-di-MOM-aziridine-1H.als
COMNT	aziridine-1H
DATIM	2013-03-15 15:35:08
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	26214
FREQU	6002.31 Hz
SCANS	8
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	
CTEMP	1H 20.4 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	36

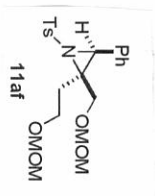


11af

az-13C

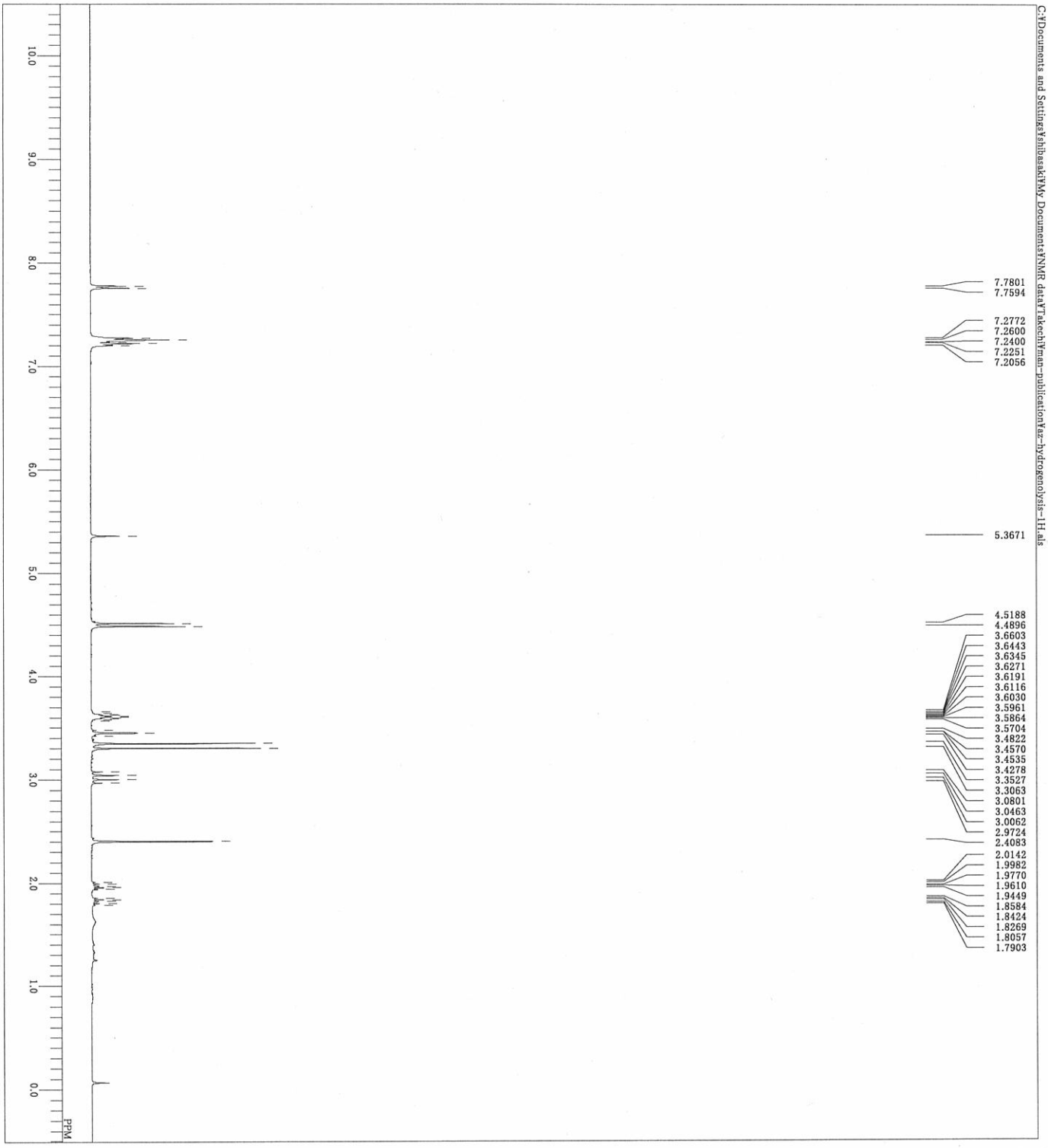


DFILE Ts-di-MOM-aziridine-13C.als
COMNT az-13C
DATIM 2013-03-15 15:42:32
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.24 Hz
SCANS 102
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 2.83 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

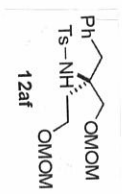


11af

az-hydrogenolysis

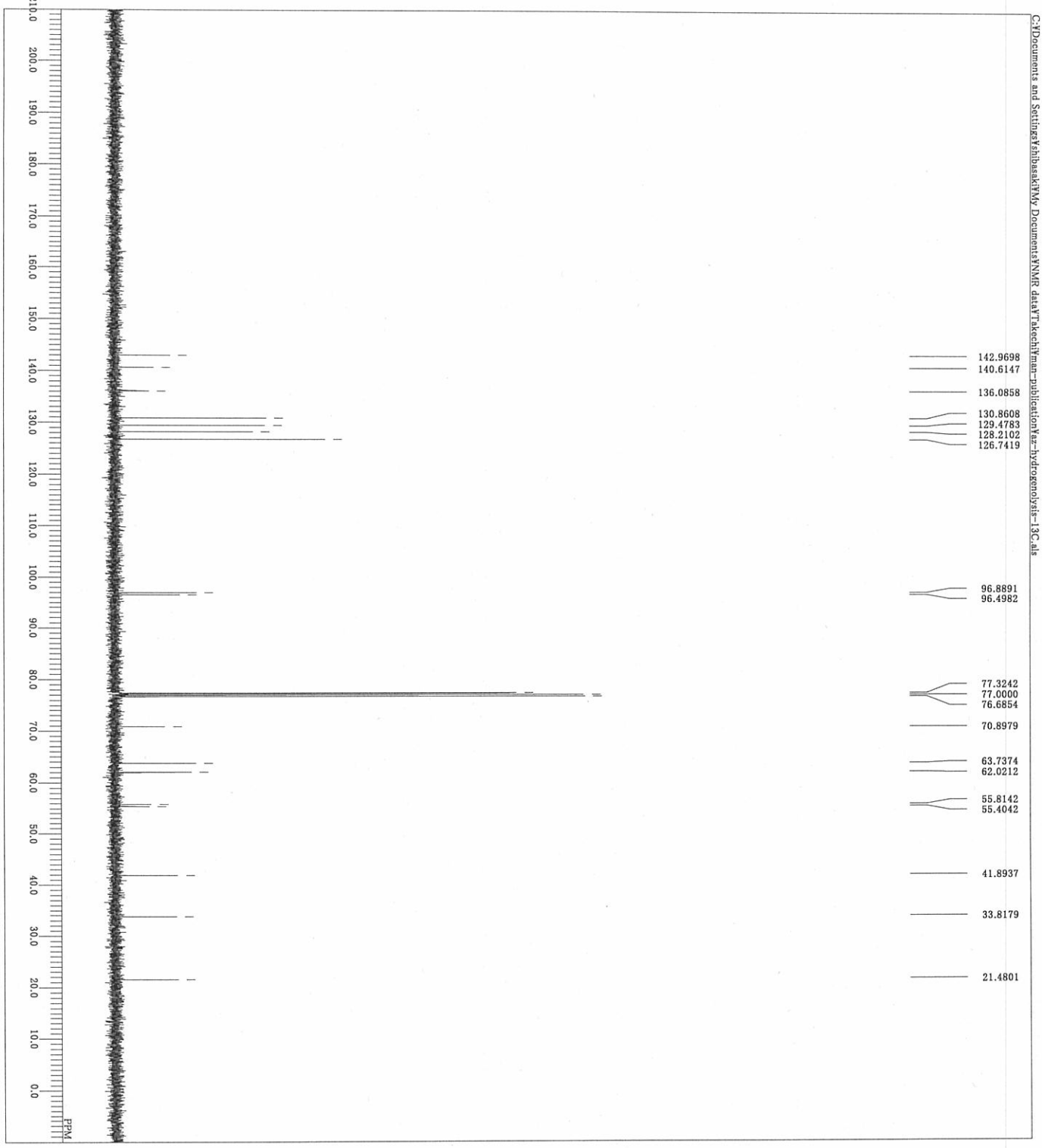


DFILE	az-hydrogenolysis-1H.als
COMNT	az-hydrogenolysis
DATIM	2013-03-19 15:15:41
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	26214
FREQU	6002.31 Hz
SCANS	8
ACQTM	4.3673 sec
PD	5.0000 sec
PW1	5.38 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCl3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



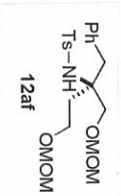
12af

az-hydrogenolysis-13C



az-hydrogenolysis-13C.als
az-hydrogenolysis-13C
2013-03-19 15:36:36
13C
single_pulse_dec
100.53 MHz
5.35 KHz
5.86 Hz
26214
25125.24 Hz
202
1.0433 sec
2.0000 sec
2.83 usec
1H
21.6 c
CDCL3
77.00 ppm
0.12 Hz
60

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN



12af