Supporting Information

Sulfonylcarbamate as a Versatile and Unique Hydroxy Protecting Group

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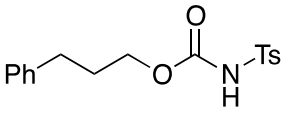
General Procedures. All commercial reagents were used without further purification. Analytical TLC was performed on silica gel 60 F_{254} plates and visualized by UV fluorescence quenching and 12 Molybdo(VI) phosphoric acid acid/phosphoric acid staining. Flash column chromatography was performed on silica gel 60N (spherical, neutral, 40–100 μm). Yields refer to chromatographically and spectroscopically pure compounds. ^{1}H- and ^{13}C-NMR spectra were recorded at ambient temperature (23–24 °C) in $CDCl_3$ using a 400 MHz spectrometer. Chemical shifts are reported in ppm relative to internal TMS (δ = 0.00 ppm) for ^{1}H- and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C-NMR spectra. HRMS was measured by Quadrupole-TOF mass spectrometry. CHIRALPAK AD and CHIRALCEL OD-H (DAICEL Co.) were used for enantiopurity check of deprotection products **5a** and **6a**.

General procedure for protection

(Method A) To a solution of alcohol (1.0 mmol) in THF (5 mL), *p*-toluenesulfonyl isocyanate (1.1 mmol) was added at room temperature. The mixture was stirred under N_2 atmosphere. After starting material was disappeared by TLC analysis, the solvent was evaporated. The residue was purified by silica gel column chromatography to afford the product.

(Method B) To a solution of alcohol (1.0 mmol) in THF (5 mL), *p*-toluenesulfonyl isocyanate (1.1 mmol) was added at room temperature. The mixture was stirred under N_2 atmosphere. After starting material was disappeared by TLC analysis, the mixture was diluted with brine and EtOAc. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine again. After drying the mixture over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography to afford the product.



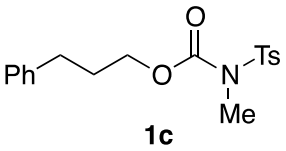
1b

^{1}H-NMR δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.14–7.26 (m, 3H), 7.08 (d, *J* = 6.8 Hz, 2H), 4.08 (t, *J* = 6.4 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 2.40 (s, 3H), 1.87 (quint, *J* = 6.4 Hz, 2H); ^{13}C-NMR δ 150.4, 145.3, 140.8, 135.6, 129.8, 128.6, 128.5,

128.5, 126.3, 66.5, 32.0, 30.1, 21.8; IR 3239, 1745, 1725, 1154, 1089 cm^{-1}; HRMS calcd for $[C_{17}H_{19}NO_4S+Na]^+$ 356.0927, found 356.0930.

General procedure for alkylation

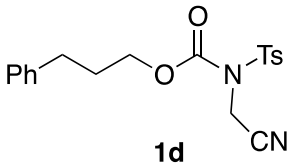
Methylation



1c

To a solution of sulfonyl carbamate (1.81 g, 5.22 mmol) in benzene/MeOH (52 mL/12 mL), $TMSCHN_2$ (2.0 M, hexane solution, 3.5 mL, 7.0 mmol) was added dropwise. After starting material was disappeared by TLC analysis, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:EtOAc 5:1) to give 1.71 g (90%) of *N*-methylsulfonyl carbamate.

^{1}H-NMR δ 7.90 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 4.17 (t, J = 7.6 Hz, 2H), 3.44 (s, 3H), 2.66 (t, J = 7.6 Hz, 2H), 2.48 (s, 3H), 1.96 (2H, quint, J = 7.6 Hz); ^{13}C-NMR δ 152.7, 144.8, 140.9, 136.6, 129.6, 128.6, 128.4, 128.1, 126.2, 66.9, 33.5, 31.9, 30.0, 21.7; IR 1729, 1355, 1282, 1162, 1089 cm^{-1}; calcd for $[C_{18}H_{21}NO_4S+Na]^+$ 370.1083, found 370.1084.

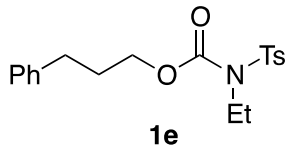


1d

To a solution of sulfonyl carbamate (1.0 g, 3.0 mmol) in MeCN (20 mL), iodoacetonitrile (0.3 mL, 4.5 mmol), and K_2CO_3 (621 mg, 4.5 mmol) was added at room temperature. The mixture was heated at reflux. After starting material was disappeared by TLC analysis, the reaction mixture was filtered off and the filtrate was evaporated. The residue was purified by silica gel column chromatography (hexane:EtOAc 4:1) to give 916 mg (82%) of *N*-cyanomethyl sulfonyl carbamate.

^{1}H-NMR δ 7.90 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.27 (dd, J = 6.8 Hz, 7.6

Hz, 2H), 7.19 (dd, J = 7.6 Hz, 7.6 Hz, 1H), 7.10 (d, J = 6.8 Hz, 2H), 4.68 (s, 2H), 4.16 (t, J = 6.8 Hz, 2H), 2.59 (t, J = 6.8 Hz, 2H), 2.42 (s, 3H), 1.91 (quint, J = 6.8 Hz, 2H); ^{13}C-NMR δ 151.0, 146.0, 140.6, 134.9, 129.9, 128.7, 128.5, 128.5, 128.4, 126.3, 1260, 115.0, 68.1, 62.3, 34.3, 33.7, 32.2, 31.9, 29.8, 21.8; IR 1741, 1363, 1170, 1089 cm^{-1}; HRMS calcd for $[C_{19}H_{20}N_2O_4S+Na]^+$ 395.1036, found 395.1036.



1e

To a solution of **1b** (125 mg 0.375 mmol), PPh_3 (148 mg, 0.563 mmol), and EtOH (18 μL, 0.563 mmol) in THF (1.0 mL), DEAD toluene solution (0.25 mL) was added at 4 °C. After 5 h, the mixture was concentrated, and the residue was purified by silica gel column chromatography (hexane:EtOAc 7:3-1:1) to give **1e** (124 mg, 94%).

^{1}H-NMR δ 7.82 (d, J = 8.0 Hz, 2H), 7.29-7.09 (m, 7H), 4.08 (t, J = 6.4 Hz, 2H), 3.92 (q, J = 7.2 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 2.40 (t, J = 7.6 Hz, 3H), 1.86 (m, 1H), 1.35 (t, J = 6.4 Hz, 3H); ^{13}C-NMR δ 152.4, 144.6, 140.9, 137.1, 129.8, 129.5, 128.6, 128.4, 128.2, 126.2, 66.7, 42.8, 32.0, 30.1, 21.7, 15.7; HRMS calcd for $[C_{19}H_{23}NO_4S+Na]^+$ 384.1348, found 384.1340.

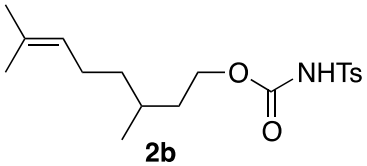
General procedure for removal of sulfonyl group

Removal by NaOH

To a solution of alkylated sulfonyl carbamate (100 mg, 0.29 mmol) in MeOH (1.5 mL), 1 M NaOH aq. (1.45 mL, 1.45 mmol) was dropped. After completion of the reaction, the reaction mixture was diluted with brine. The aqueous layer was extracted with EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:EtOAc 5:1) to afford the products.

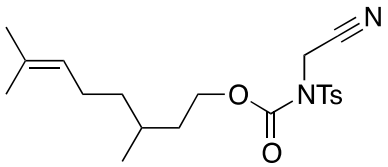
Removal by Pyridine:MeOH

A solution of sulfonyl carbamate (100 mg) in pyridine:MeOH (5 mL, 7:3) was stirred at 50 °C until the starting material was consumed. After evaporation, the residue was purified by silica gel column chromatography.

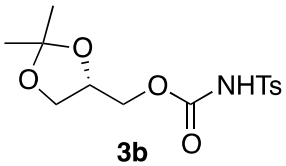


2b

^{1}H-NMR δ 7.90 (d, *J* = 8.4 Hz, 2H), 5.03 (t, *J* = 7.1 Hz, 1H), 4.15-4.03 (m, 2H), 2.43 (s, 3H), 2.00-1.90 (m, 2H), 1.66 (s, 3H), 1.57 (s, 3H), 1.57-1.22 (m, 3H), 1.16-1.20 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR δ 150.6, 145.2, 135.7, 131.7, 129.8, 128.5, 124.5, 65.8, 37.0, 35.4, 37.0, 35.4, 29.3, 25.8, 25.5, 21.8, 19.4, 17.8; HRMS calcd for $[C_{18}H_{27}NO_4S+Na]^+$ 376.1553, found 376.1553.

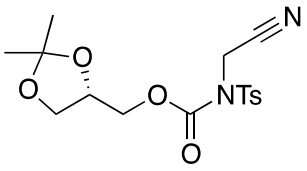


^{1}H-NMR δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.04 (t, *J* = 6.8 Hz, 1H), 4.75 (s, 2H), 4.22-4.11 (m, 2H), 2.44 (s, 3H), 2.02-1.90 (m, 2H), 1.66 (s, 3H), 1.58 (s, 6H), 1.41-1.35 (m, 2H), 1.35-1.30 (m, 1H), 1.20-1.15 (m, 1H), 0.84 (d, *J* = 6.3 Hz, 3H); ^{13}C-NMR δ 150.7, 145.6, 134.7, 131.4, 129.6, 128.5, 124.1, 115.7, 67.3, 36.9, 35.2, 33.7, 29.1, 25.8, 25.4, 21.8, 19.3, 17.8; HRMS calcd for $[C_{21}H_{29}NO_4S+Na]^+$ 414.1710, found 414. 1719.

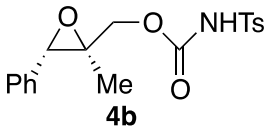


3b

^{1}H-NMR δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.24-4.08 (m, 2H), 4.03-3.98 (m, 2H), 3.64 (dd, *J* = 5.6 Hz, 8.4 Hz, 1H), 2.42 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H); ^{13}C-NMR δ 150.4, 145.3, 135.5, 129.8, 128.5, 126.6, 110.2, 73.2, 66.8, 66.0, 26.7, 25.3, 21.8; $[\alpha]^{24}_{D}$ 9.8 (*c* 0.66, $CHCl_3$); HRMS calcd for $[C_{20}H_{20}N_2O_5S+Na]^+$ 423.0985, found 423.0982.

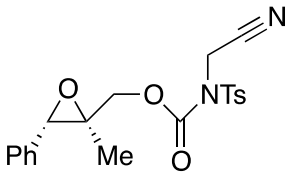


^{1}H-NMR δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 2H), 4.25-4.08 (m, 4H), 4.00 (t, *J* = 6.0 Hz, 1H), 3.66 (dd, *J* = 5.2 Hz, 8.4 Hz, 1H), 2.45 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H); ^{13}C-NMR δ 150.5, 145.8, 134.4, 129.7, 128.6, 126.3, 126.3, 114.5, 110.0, 72.8, 68.2, 66.0, 33.9, 26.8, 25.3, 21.9; $[\alpha]^{24}_{D}$ 2.2 (*c* 0.90, $CHCl_3$); calcd for $[C_{16}H_{20}N_2O_6S+Na]^+$ 391.0934, found 391.0932.

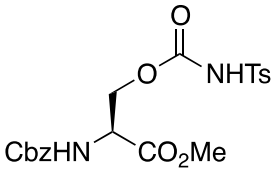


4b

^{1}H-NMR δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.57-7.19 (m, 7H), 4.31 (d, *J* = 18.0 Hz, 1H), 4.11 (d, *J* = 18.0 Hz, 1H), 3.90 (s, 1H), 2.41 (3H, s), 1.02 (s, 3H); ^{13}C-NMR δ 150.1, 144.9, 135.2, 134.3, 129.5, 128.8, 128.2, 128.1, 128.0, 128.0, 127.7, 126.2, 125.1, 69.6, 61.3, 60.8, 21.7, 13.5; $[\alpha]^{24}_{D}$ -22.1 (*c* 0.98, $CHCl_3$); HRMS calcd for $[C_{18}H_{19}NO_5S+Na]^+$ 384.0876, found 384.0870.

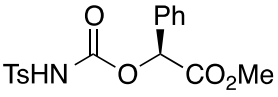


^{1}H-NMR δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.35-7.22 (m, 7H), 4.82 (d, *J* = 18.0 Hz, 1H), 4.77 (d, *J* = 18.0 Hz, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.17 (d, *J* = 11.6 Hz, 1H), 3.93 (s, 1H), 2.41 (s, 3H), 1.03 (s, 3H); ^{13}C-NMR δ 150.5, 145.8, 134.4, 134.2, 129.7, 128.5, 128.0, 127.7, 126.2, 114.6, 71.5, 61.3, 60.3, 34.0, 21.8, 13.5; $[\alpha]^{24}_{D}$-3.7 (*c* 1.70, $CHCl_3$); HRMS calcd for $[C_{20}H_{20}N_2O_5S+Na]^+$ 423.0985, found 423.0978.



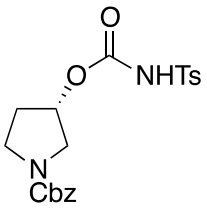
5b

^{1}H-NMR δ 7.87-7.85 (m, 2H), 7.33-7.15 (m, 7H), 5.49 (d, J = 8.4 Hz, 1H), 5.08 (s, 2H), 4.58 (m, 1H), 4.42-4.34 (m, 2H), 3.71 (s, 3H), 2.37 (s, 3H); ^{13}C-NMR δ 169.7, 155.9, 150.1, 145.3, 143.7, 139.2, 136.0, 135.5, 129.8, 129.8, 128.7, 128.4, 128.3, 126.6, 67.5, 66.4, 53.2, 21.8; [α] $^{24}_{D}$ 21.6 (*c* 2.17, $CHCl_3$); HRMS calcd for $[C_{20}H_{22}N_2O_8S+Na]^+$ 473.0989, found 473.1000.



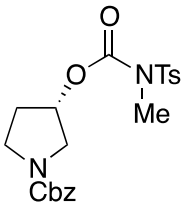
6b

^{1}H-NMR δ 7.89 (d, J = 8.4 Hz, 2H), 7.66 (s, 1H), 7.36-7.29 (m, 7H), 5.85 (s, 1H), 3.66 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR δ 168.7, 150.0, 145.2, 135.4, 132.9, 129.7, 129.0, 128.5, 127.7, 75.9, 52.9, 21.8; [α] 105.7 (*c* 0.80, $CHCl_3$); calcd for $[C_{17}H_{17}NO_6S+Na]^+$ 386.0663, found 386.0669.

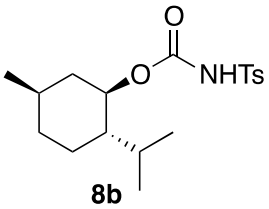


7b

^{1}H-NMR δ 7.85 (d, J = 8.4 Hz, 2H), 7.35-7.18 (m, 7H), 5.19 (bs, 1H), 5.12 (d, J = 6.8 Hz), 3.76-3.40 (m, 3H), 3.34-3.31 (m, 1H), 2.40 (s, 3H), 2.1-1.9 (m, 2H), 1.69 (bs, 1H), ^{13}C-NMR δ 155.0, 154.8, 150.2, 150.1, 145.3, 136.6, 145.6, 129.8, 129.8, 129.1, 128.6, 128.6, 128.4, 128.2, 128.1, 128.1, 128.0, 126.5, 125.4, 76.5, 75.7, 67.2, 51.8, 51.6, 44.1, 43.8, 31.6, 30.7, 21.8; [α] -9.4 (*c* 0.7, $CHCl_3$); HRMS calcd for $[C_{20}H_{22}N_2O_6S+Na]^+$ 441.1091, found 441.1088.

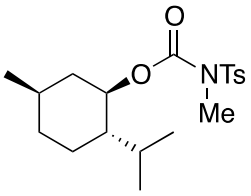


^{1}H-NMR δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.37-7.19 (m, 7H), 4.22-5.15 (m, 3H), 3.54-3.35 (m, 5H), 2.36 (s, 3H), 2.02 (m, 2H); ^{13}C-NMR δ 154.8, 154.6, 152.0, 150.0, 136.8, 136.5, 129.9, 129.7, 128.7, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4, 76.4, 67.1, 51.7, 51.5, 44.1, 43.8, 33.5, 31.8, 30.9, 21.7; [α] -10.6 (*c* 1.14, $CHCl_3$); HRMS calcd for $[C_{21}H_{24}N_2O_6S+Na]^+$ 455.1247, found 455.1241.

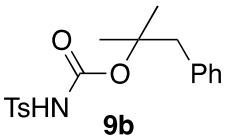


8b

^{1}H-NMR δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.35 (bs, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.53 (m, 1H), 2.43 (s, 3H), 1.90 (d, *J* = 11.6 Hz, 1H), 1.63-1.60 (m, 4H), 1.37 (m, 1H), 1.24 (m, 1H), 0.97-0.85 (m, 3H), 0.84 (d, *J* = 6.4 Hz, 3H), 0.76 (d, *J* = 6.8 Hz, 3H), 0.62 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR δ 150.2, 145.0, 135.9, 129.7, 128.5, 78.0, 47.1, 40.7, 34.1, 31.5, 26.0, 23.3, 22.0, 21.8, 20.9, 16.1; [α] -47.0 (*c* 0.97, $CHCl_3$); HRMS calcd for $[C_{18}H_{27}NO_4S+Na]^+$ 376.1553, found 376.1553.

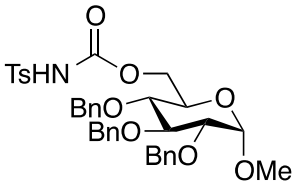


^{1}H-NMR δ □7.52 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.32 (m, 1H), 3.13 (s, 3H), 2.17 (s, 3H), 1.61 (d, *J* = 12.4 Hz, 1H), 1.38-1.33 (m, 4H), 1.20-1.11 (m, 2H), 1.00-0.93 (m, 1H), 0.73-0.67 (m, 1H), 0.58 (d, *J* = 6.4 Hz, 3H), 0.49 (d, *J* = 6.8 Hz, 3H), 0.36 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR δ 152.4, 144.8, 137.3, 129.5, 128.0, 78.3, 47.1, 40.6, 34.1, 33.4, 31.5, 25.7, 23.0, 22.0, 21.8, 21.0, 15.9; [α] -36.6 (*c* 1.18, $CHCl_3$); HRMS calcd for $[C_{19}H_{29}NO_4S+Na]^+$ 390.1710, found 390.1713.



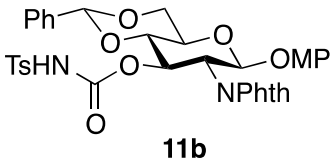
9b

^{1}H-NMR δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16-7.14 (m, 3H), 6.93 (d, *J* = 6.0 Hz, 2H), 2.99 (s, 2H), 2.44 (s, 3H), 1.37 (s, 6H); ^{13}C-NMR δ 149.2, 145.0, 136.5, 135.9, 130.5, 129.7, 128.5, 128.2, 126.7, 85.8, 45.6, 26.2, 21.8; HRMS calcd for $[C_{18}H_{21}NO_4S+Na]^+$ 370.1083, found 370.1081.



10b

^{1}H-NMR δ 7.86 (d, *J* = 6.8 Hz, 2H), 7.33-7.16 (m, 17H), 4.97 (d, *J* = 11.6 Hz, 1H), 4.79-4.74 (m, 3H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.49 (m, 1H), 4.38 (d, *J* = 9.2 Hz, 1H), 4.19 (s, 2H), 3.94 (t, *J* = 8.0 Hz, 1H), 3.71 (m, 1H), 3.44 (m, 1H), 3.32-3.28 (m, 1H), 3.28 (s, 3H); ^{13}C-NMR δ 150.1, 145.3, 138.7, 138.1, 137.7, 135.5, 129.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 98.2, 82.1, 79.8, 75.9, 75.0, 73.6, 68.4, 65.4, 55.5, 21.8; [α] 32.9 (*c* 0.79, $CHCl_3$); HRMS calcd for $[C_{36}H_{39}NO_9S+Na]^+$ 684.2238, found 684.2243.

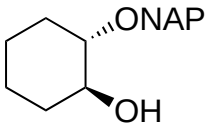


11b

To a solution of alcohol (200 mg, 0.397 mmol) in CH_2Cl_2 (2 mL), *p*-toluenesulfonyl isocyanate (235 μL, 1.19 mmol) was added. The mixture was stirred under Ar atmosphere 1 h at room temperature. After evaporation, the mixture was purified by silica gel column chromatography (hexane:EtOAc 2:1-1:1) to give 257 mg (95 %) of sulfonyl carbamate.

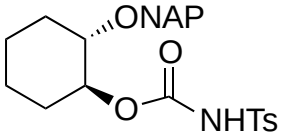
^{1}H-NMR δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.66 (m, 4H), 7.26-7.23 (m, 5H), 6.98 (d, *J* = 8.0

Hz, 2H), 6.76 (d, *J* = 9.2 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 5.85 (d, *J* = 8.5 Hz, 1H), 5.79 (t, *J* = 10.3 Hz, 1H), 5.10 (s, 1H), 4.54 (t, *J* = 10.2 Hz, 1H), 4.35 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.84-3.69 (m, 3H), 3.64 (s, 3H), 2.26 (s, 3H); ^{13}C-NMR δ□155.9, 150.4, 136.6, 135.3, 134.4, 131.4, 129.6, 129.3, 128.4, 128.2, 126.3, 124.0, 118.9, 101.7, 98.1, 79.1, 72.3, 68.6, 66.2, 55.7, 55.1, 21.8; $[\alpha]^{24}_{D}$ -7.4 (*c* 1.0, $CHCl_3$); HRMS calcd for $[C_{36}H_{32}N_2O_{11}S+Na]^+$ 723.1619, found 723.1611.



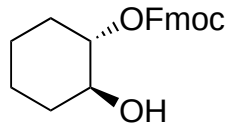
To a solution of 1,2-*trans* cyclohexanediol (116 g, 10 mmol) and NAPBr (2.21 g, 10 mmol) in DMF (10 mL), NaH (60%, 0.40 g, 10 mmol) was added at 4 °C. The mixture was stirred at room temperature under N_2 atmosphere overnight. After addition of sat. NH_4Cl, the aqueous layer was extracted with EtOAc. The aqueous layers were extracted with EtOAc and the combined layers were washed with brine. After drying the extracts over Na_2SO_4, the solvent was removed under reduces pressure. The residue was purified by silica gel column chromatography (hexane:EtOAc 7:1-1:1) to give mono-NAP ether (1.05 g, 42%).

^{1}H-NMR δ 7.85-7.79 (m, 4H), 7.50-7.47 (m, 3H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 3.52 (m, 1H), 3.25 (m, 1H), 2.17 (m, 1H), 2.02 (m, 1H), 1.75-1.70 (m, 4H), 1.290-1.24 (m, 4H); ^{13}C-NMR δ 136.0, 133.3, 133.0, 128.3, 127.9, 127.7, 126.4, 126.1, 125.9, 125.8, 83.5, 73.9, 70.9, 32.0, 29.3, 24.3, 23.9; HRMS calcd for $[C_{17}H_{20}O_2+Na]^+$ 279.1356, found 279.1357.



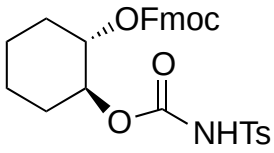
^{1}H-NMR δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.36-7.19 (m, 9H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.69 (s, 2H), 4.17 (t, *J* = 6.0 Hz, 2H), 3.79 (t, *J* = 6.4 Hz, 1H), 2.71 (t, *J* = 7.2 Hz, 1H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.95-1.87 (m, 3H); ^{13}C-NMR δ 150.3, 150.0, 136.1, 135.8, 133.3, 133.0, 129.7, 128.5, 128.4, 128.1, 128.0, 127.8, 126.3, 126.2, 125.9, 125.9, 76.5, 78.4, 71.5, 63.2, 29.9, 23.2, 21.8, 14.3; HRMS calcd for $[C_{25}H_{27}NO_5S+Na]^+$ 476.1502,

found 476.1500.

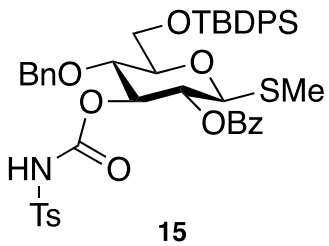


To a solution of 1,2-*trans* cyclohexanediol (1.16 g, 10 mmol) in pyridine (20 mL), FmocCl (2.58 g, 10 mmol) was added at 4°C. After 2 h, the solvent was removed under reduced pressure, and the residue was dissolved in $CHCl_3$. The organic layer was extracted with 1 M HCl, and brine. After concentration, the residue was purified by silica gel column chromatography (hexane:EtOAc 1:1) to give Fmoc product (1.85 g, 50%).

^{1}H-NMR δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.46-7.61 (m, 2H), 7.43-7.39 (m, 2H), 7.34-7.31 (m, 2H), 4.46-4.41 (m, 3H), 4.29-4.26 (m, 1H), 3.66-3.60 (m, 1H), 2.12-2.04 (m, 2H), 2.00 (bs 1H), 1.75-1.73 (m, 2H), 1.38-1.26 (m, 4H); ^{13}C-NMR δ 155.2, 143.6, 143.5, 141.5, 128.0, 127.3, 127.3, 125.3, 125.2, 120.2, 82.4, 72.7, 69.9, 47.0, 33.0, 30.0, 24.0, 23.9; HRMS calcd for $[C_{21}H_{22}O_4+Na]^+$ 361.1410, found 361.1412.



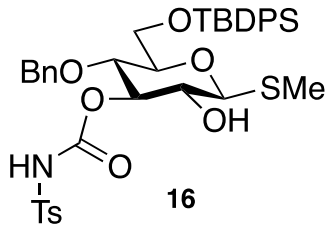
^{1}H-NMR δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.75 (bs, 1H), 7.59 (d, *J* = 4.8 Hz, 2H), 7.42-7.24 (m, 7H), 4.70 (m, 1H), 4.60 (m, 1H), 4.40-4.32 (m, 2H), 4.21 (t, J = 7.2 Hz, 1H), 2.34 (s, 3H), 2.06 (m, 2H), 1.71 (m, 4H), 1.31 (m, 4H); ^{13}C-NMR δ 155.7, 149.9, 145.1, 143.6, 143.4, 141.4, 141.4, 135.7, 129.7, 128.5, 128.1, 128.0, 127.4, 127.3, 125.4, 120.2, 77.3, 70.1, 46.8, 30.1, 30.1, 23.3, 21.7; HRMS calcd for $[C_{29}H_{29}NO_7S+Na]^+$ 558.1557, found 558.1558.



15

To a solution of alcohol **14** (500 mg, 0.779 mmol) in THF (7 mL), *p*-toluenesulfonyl isocyanate (0.15 mL, 0.982 mmol) was added. The mixture was stirred under N_2 atmosphere overnight at room temperature. After evaporation, the mixture was purified by silica gel column chromatography (hexane:EtOAc 7:3-1:1) to give 654 mg (quant.) of sulfonyl carbamate **15**.

^{1}H-NMR δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 6.4 Hz, 2H), 7.7-7.67 (m, 4H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.4-7.1 (m, 14H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.23 (t, *J* = 9.6 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 4.41 (d, *J* = 10.0 Hz, 1H), 4.1-3.9 (m, 3H), 3.44 (d, *J* = 9.6 Hz, 1H), 2.28 (s, 3H), 2.14 (s, 3H), 1.10 (s, 9H); ^{13}C-NMR δ 165.4, 149.6, 144.8, 137.6, 136.0, 135.7, 135.4, 133.5, 133.3, 132.9, 130.0, 130.0, 130.0, 129.6, 129.1, 128.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 82.7, 80.0, 78.7, 76.8, 75.1, 75.0, 70.0, 62.3, 31.1, 27.0, 21.8, 19.5, 11.4; $[\alpha]^{24}_{D}$ 28 (*c* 0.97, MeOH); calcd for $[C_{45}H_{49}NO_9S_2Si+Na]^+$ 862.2510, found 862.2511.

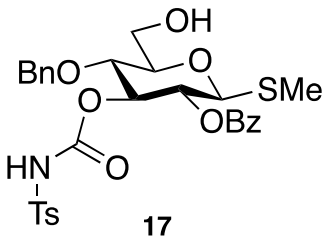


16

To a solution of benzoate **15** (34.5 mg, 0.0411 mmol) in anhydrous MeOH (0.5 mL), 28% NaOMe solution (55 μL, MeOH solution) was dropped in the presence of phenolphtalein. After stirring the mixture for 10 h under N_2 atmosphere at room temperature, the mixture was neutralized by addition of Amberlyst 15E until the color was disappeared. After filtration, the resins were washed with MeOH and chloroform. After evaporation, the crude was purified by preparative TLC to afford 27.0 mg (89 %) of the product **16.**

^{1}H-NMR δ 7.92 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 6.4 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 2H), 7.45-7.28 (m, 12H), 7.10-7.08 (m, 2H), 4.95 (t, *J* = 9.2 Hz, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 9.6 Hz, 1H), 3.92 (s, 2H), 3.78 (t, *J* = 9.6 Hz, 1H), 3.39 (t, *J* = 9.2 Hz, 1H), 3.37 (t, *J* = 8.8 Hz, 1H), 2.39 (s, 3H), 2.17 (s, 3H), 1.09 (s, 9H); ^{13}C-NMR δ 150.3, 145.3, 137.7, 136.0, 135.7, 135.7, 133.6, 133.0, 129.9, 129.8, 128.6, 128.6, 128.2, 128.1, 127.9, 127.8, 85.4, 81.5, 79.9, 75.0, 74.8, 70.8, 62.4, 27.0,

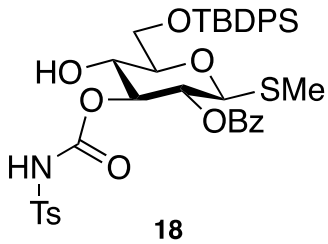
21.8, 19.5, 11.5; $[\alpha]^{24}_{D}$ - 6.3 (*c* 0.92, MeOH); calcd for $[C_{38}H_{45}NO_8S_2Si+Na]^+$ 758.2248, found 758.2249.



17

To a solution of TBDPS ether **15** (134.0 mg, 0.160 mmol) in CH_3CN (4 mL), aq. 48% HF (1 mL) was added. After overnight, the mixture was diluted with water. The aqueous layer was extracted with $CHCl_3$. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography ($CHCl_3$:EtOAc 4:1-1:1) to give 87.8 mg of white solid **17** (92 %).

^{1}H-NMR δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.24-7.70 (m, 3H), 7.57 (m, 1H), 7.43-7.29 (m, 2H), 7.15 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 5.24 (t, *J* = 9.6 Hz, 1H), 5.12 (t, *J* = 9.6 Hz, 1H), 5.24 (t, *J* = 9.6 Hz, 1H), 5.12 (t, *J* = 9.6 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 4.42 (d, *J* = 9.6 Hz, 1H), 3.98 (s, 2H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.71 (s, 1H), 3.45 (d, *J* = 10.0 Hz, 1H), 2.30 (s, 3H), 2.15 (s, 3H), 1.11 (s, 9H); ^{13}C-NMR δ 165.4, 149.5, 144.9, 137.6, 136.0, 135.7, 133.5, 133.3, 132.9, 130.0, 130.0, 129.9, 129.6, 129.2, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 82.8, 80.0, 78.8, 75.1, 75.0, 70.0, 67.2, 62.3, 27.0, 21.8, 19.5, 19.5, 11.4; $[\alpha]^{24}_{D}$ 11.5 (*c* 1.20, MeOH); HRMS calcd for $[C_{29}H_{31}NO_9S_2+Na]^+$ 624.1332, found 624.1334.

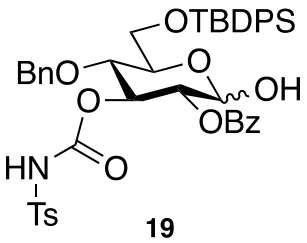


18

To a solution of benzyl ether **15** (145.4 mg, 0.173 mmol) in CH_2Cl_2 (2 mL) and H_2O (1 mL), DDQ (78.0 mg, 0.345 mmol) was added. The mixture was refluxed overnight. The reaction was quenched with acsorbate buffer, and the aqueous layer was extracted with

EtOAc. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by preparative TLC (hexane:EtOAc 1:1) to give 88.3 mg (68%) of product **18**.

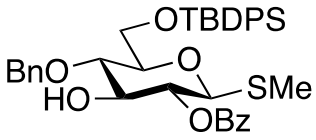
^{1}H-NMR δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 6.8 Hz, 2H), 7.85-7.66 (m, 5H), 7.55 (t, *J* = 8.0 Hz), 7.47-7.36 (m, 8H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.11 (t like dd, *J* = 9.2 Hz, 1H), 5.10 (t like dd, *J* = 9.2 Hz, 1H), 4.42 (d, *J* = 9.6 Hz, 1H), 3.95-3.45 (m, 3H), 2,32 (s, 3H), 2.11 (s, 3H), 1.10 (s, 9H); ^{13}C-NMR δ 166.7, 165.7, 149.6, 149.5, 145.0, 137.6, 137.4, 135.9, 135.8, 135.6, 135.6, 135.4, 135.3, 133.5, 133.4, 132.9, 129.9, 129.8, 129.7, 129.5, 128.5, 128.1, 127.9, 127.7, 127.6, 126.4, 90.0, 75.9, 75.2, 72.5, 71.3, 62.3, 26.9, 21.6, 19.4; HRMS calcd for $[C_{38}H_{43}NO_9S_2Si+Na]^+$ 772.2041, found 772.2039.



19

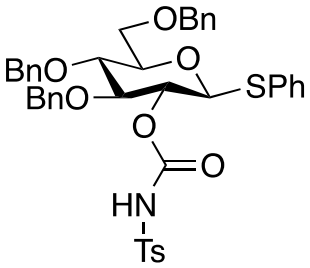
To a solution of thioglycoside **15** (68.1 mg, 0.0811 mmol) in acetone (2 mL) and H_2O (0.5 mL), NBS (100 mg, 0.56 mmol) was added. The reaction was quenched by 10% $Na_2S_2O_3$ aq. The aqueous layer was extracted with EtOAc three times. The combined layers were washed with brine. After drying the extract over Na_2SO_4, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane:EtOAc 3:2) to give the product (54.8 mg, 83%). From ^{1}HNMR analysis, main product was α isomer.

^{1}H-NMR δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.75-7.66 (m, 6H), 5.52 (m, 1H), 7.43-7.32 (m, 8H), 7.27-7.24 (m, 4H), 7.13-7.11 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.60 (t like dd, *J* = 9.6 Hz, 1H), 5.52 (bs, 1H), 4.70 (dd, *J* = 3.6 Hz, 8.0 Hz, 1H), 4.56 (s, H), 3.99-3.85 (m, 4H), 2.72 (bs, 1H), 2.30 (s, 3H), 1.22 (s, 9H); ^{13}C-NMR δ 165.3, 150.2, 144.9, 143.6, 135.6, 135.6, 135.1, 133.3, 132.8, 132.7, 129.9, 129.9, 129.7, 129.5, 129.5, 129.0, 128.4, 128.3, 127.9, 127.8, 127.8, 126.5, 82.6, 79.5, 79.1, 69.8, 69.3, 63.9, 26.8, 21.7, 21.5, 19.2, 11.2; $[\alpha]^{24}_D$ 52.5 (*c* 1.10, $CHCl_3$); calcd for $[C_{44}H_{47}NO_{10}SSi+Na]^+$ 832.2582, found 832.2582.



14

A solution of sulfonylcarbamate **15** (32.6 mg, 0.0396 mmol) in pyridine (0.7 mL) and MeOH (0.3 mL) was stirred at 50 °C for 10 h. After evaporation, the residue was purified by preparative TLC (hexane:EtOAc 4:1) to give 23.7 mg (93%) of product **14**. ^{1}H-NMR δ 8.08 (dd, *J* = 7.1 Hz, 1.5 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.72 (dd, *J* = 8.1 Hz, 1.5 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.4-7.2 (m, 13H), 5.20 (t, *J* = 9.2 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 10.0 Hz, 1H), 4.0-3.9 (m, 3H), 3.87 (t, *J* = 9.2 Hz, 1H), 3.46 (dt, *J* = 9.2 Hz, 0.9 Hz, 1H), 2.51 (bs, 1H), 2.21 (s, 3H), 1.10 (s, 9H); ^{13}C-NMR δ 165.8, 138.0, 137.6, 135.7, 135.4, 133.4, 133.1, 132.8, 129.88, 129.58, 129.5, 128.8, 128.4, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 125.1 82.3, 79.9, 77.8, 76.7, 75.1, 72.5, 62.6, 26.9, 21.6, 19.4, 11.1; $[\alpha]^{24}_{D}$ 6.9 (*c* 1.34, $CHCl_3$); Anal. Calcd for $C_{37}H_{40}O_6SSi$: C, 69.34; H, 6.29. Found: C, 69.39; H, 6.02.

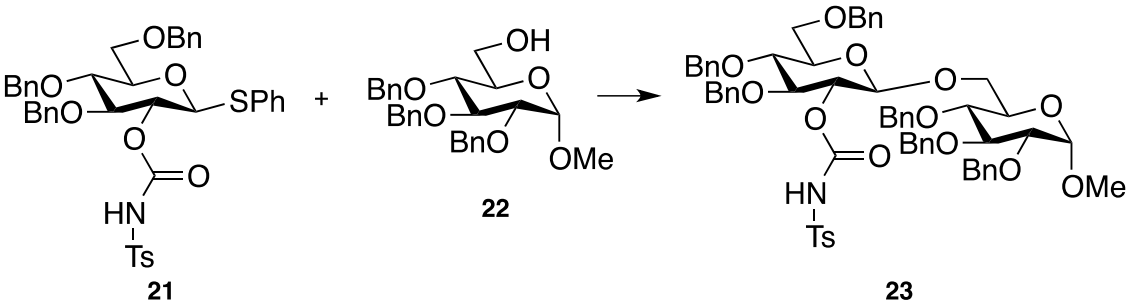


21

To a solution of alcohol **20** (191 mg, 0.397 mmol) in THF (4 mL), *p*-toluenesulfonyl isocyanate (235 μL, 1.19 mmol) was added. The mixture was stirred under Ar atmosphere 1.5 h at room temperature. After evaporation, the mixture was purified by silica gel column chromatography (hexane:EtOAc 4:1-7:3, then 1:1) to give 230 mg (97 %) of sulfonyl carbamate **21**.

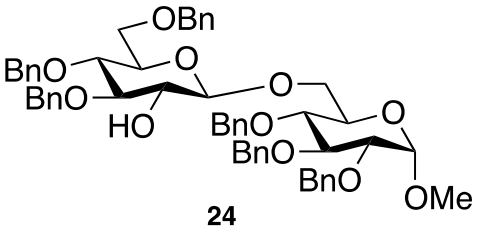
^{1}H-NMR δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.26-7.12 (m, 19H), 4.77 (t, *J* = 9.2 Hz, 1H), 4.73 (d, *J* = 10.7 Hz, 1H), 4.61-4.46 (m, 5H), 4.03 (d, *J* = 9.7 Hz, 1H), 3.69-3.57 (m, 4H), 3.44 (m, 1 H), 2.36 (s, 3H), 1.96 (s, 3H); ^{13}C-NMR δ□149.1, 145.3, 138.2, 137.8, 137.8, 135.7, 132.8, 132.1, 129.7, 128.9, 128.6, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 85.3, 83.4, 79.5, 77.7, 75.4, 75.3, 74.5, 73.6, 68.9, 21.8; $[\alpha]^{24}_{D}$ 13.4 (*c* 1.3,

$CHCl_3$); HRMS calcd for $[C_{36}H_{39}NO_8S_2+Na]^+$ 700.2009, found 700.2017.



To a solution of donor **21** (66 mg, 0.11 mmol) and acceptor **22** (74 mg, 0.13 mmol) in dry CH_2Cl_2 (3 mL) was added molecular sieves 4Å (200 mg), and the mixture was stirred under Ar atmosphere 3 h at room temperature, then cooled to -40 °C. *N*-iodosuccinimide (NIS; 50 mg, 0.22 mmol) and trifluoromethanesulfonic acid (TfOH, 2 □L, 22.6 □mol) were added to the mixture, and it was stirred under Ar atmosphere 15 min at -40 °C. After dilution with chloroform, the precipitate was filtered off, and washed with chloroform. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and sodium thiosulfate, dried (Na_2SO_4) and concentrated. Column chromatography ($CHCl_3$:EtOAc 2:1-1:1) of the residue on silica gel afforded disaccharide (115 mg, 94 %) as an amorphous mass **23**.

^{1}H-NMR δ 7.84 (d, 2H, *J* = 8.0 Hz), 7.32-7.07 (m, 32 H), 4.97 (d, *J* = 10.9 Hz, 1H), 4.83-4.62 (m, 6H), 4.56-4.45 (m, 6H), 4.39 (d, *J* = 10.9 Hz, 1H), 4.27 (d, *J* = 7.8 Hz, 1H), 4.01 (dd, *J* = 1.5, *J* = 11.7 Hz, 1H), 3.94 (t, *J* = 9.0 Hz, 1H), 3.72 (dd, *J* = 4.4, *J* = 9.8 Hz, 1H), 3.63-3.50 (m, 6H), 3.36-3.31 (m, 2H), 3.28 (s, 3H), 2.31 (s, 3H); ^{13}C-NMR δ□149.1, 145.2, 138.9, 138.5, 138.4, 138.1, 137.8, 137.7, 135.6, 129.7, 128.6, 128.5, 128.3, 128.1, 128.1, 128.1, 127.8, 100.7, 97.9, 82.2, 82.0, 80.0, 80.0, 77.5, 75.4, 75.2, 74.9, 74.8, 73.6, 73.5, 69.7, 68.7, 55.2, 21.8; $[\alpha]^{24}_D$ 19.0 (*c* 0.5, $CHCl_3$); calcd for $[C_{63}H_{67}NO_{14}S+Na]^+$ 1116.4174, found 1116.4189.

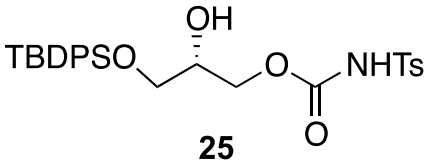


24

A solution of disaccharide (380 mg, 0.351 mmol) in pyridine-MeOH (7:3, 10 mL) was stirred at 50 °C overnight. After evaporation, the residue was purified by silica gel column chromatography (hexane:EtOAc 7:3-1:1) to give disaccharide **22** (279 mg, 90%).[1,2]

^{1}H–NMR δ 7.33-7.27 (m, 28H), 7.16-7.14 (m, 2H), 4.96 (d, *J* = 10.8 Hz, 1H), 4.91-4.75 (m, 6H), 4.65-4.48 (m, 6H), 4.21 (d, *J* = 6.4 Hz, 1H), 4.13 (d, *J* = 10.8 Hz, 1H), 3.98 (t, *J* = 8.8 Hz, 1H), 3.79 (m, 1H), 3.72-3.66 (m, 3H), 3.55-3.44 (m, 6H), 3.36 (s, 3H); ^{13}C-NMR δ 138.8, 138.8, 138.4, 138.2, 128.6, 128.5, 128.5, 128.3, 128.1, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 103.6, 98.2, 84.6, 82.1, 79.9, 78.2, 77.6, 77.5, 75.9, 75.5, 75.2, 74.6, 73.6, 73.5, 70.0, 69.1, 68.9, 55.4; [α] 15.5 (*c* 1.5, $CHCl_3$); HRMS calcd for $[C_{55}H_{60}O_{11}+Na]^+$ 684.2238, found 684.2243.

1. Schmid, U.; Waldman, H. *Chem. Eur. J.* **1998,** *4*, 494-501.
2. Honda, E.; Gin, D. Y. *J. Am. Chem. Soc*. **2002**, *124*, 7343-7352.

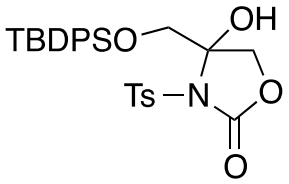


25

A solution of acetal **3b** (1.77 g, 5.38 mmol) in TFA-H_2O (4 mL, 1:1) was stirred at room temperature for 30 min. The mixture was concentrated *in vacuo* and toluene was added, and evaporated. After drying the crude under high vacuum, the residue was dissolved in pyridine (5 mL) and TBDPSCl (1.5 mL, 5.92 mmol) and DMAP (0.13 g, 1.08 mmol) were added at 4 °C. The mixture was stirred was allowed to warm at room temperature and stirred overnight. After concentration, the residue was dissolved in $CHCl_3$ and the organic layer was washed with 1 M HCl. The aqueous layer was extracted with $CHCl_3$ and the combined layers were washed with brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography ($CHCl_3$:EtOAc 9:1-7:3) to give mono-TBDPS ether **25** as an oil (2.34 g, 91%).

^{1}H-NMR δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.61-7.59 (m, 3H), 7.55-7.23 (m, 9H), 4.18-4.08 (m, 3H), 3.86-3.83 (m, 1H), 3.65-3.55 (m, 2H), 2.41 (s, 3H), 1.03 (s, 9H); ^{13}C-NMR δ 150.6, 145.3, 135.6, 135.5, 132.8, 130.1, 129.9, 129.8, 128.5, 128.0, 69.8, 67.5, 64.2, 26.9,

21.8, 19.3; HRMS calcd for $[C_{27}H_{33}NO_6SSi+Na]^+$ 550.1690, found 550.1694.

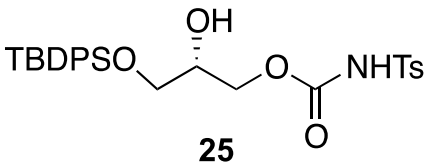


26

To a solution of alcohol **25** (0.58 g, 1.10 mmol) in CH_2Cl_2 (5 mL), Dess-Martin reagent (932 mg, 2.20 mmol) was added. After stirring the mixture for 2 h, 10% $Na_2S_2O_3$ was added to quench the reaction. The aqueous layer was extracted with $CHCl_3$ and the combined layers were washed with brine. The extract was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (hexane:EtOAc 7:3) to give ketone **26** (365 mg, 63%).

^{1}H-NMR δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.64-7.58 (m, 4H), 7.46-7.24 (m, 9H), 4.27 (dd, *J* = 10.8 Hz, 5.2 Hz), 4.05 (d, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 10.8 Hz, 1H), 2.40 (s, 3H), 1.02 (s, 9H); ^{13}C-NMR δ 151.5, 145.8, 135.8, 135.8, 134.9, 132.4, 132.2, 130.4, 130.3, 129.8, 129.0, 128.2, 128.1, 91.6, 72.3, 66.9, 26.8, 21.9, 19.3; HRMS calcd for $[C_{27}H_{31}NO_6SSi+Na]^+$ 548.1534, found 548.1536.

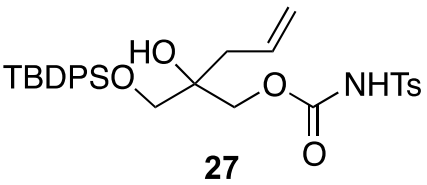
To a solution of alcohol **25** (247.1 mg, 0.469 mmol) in acetone (4 mL), 2.5 M Jones reagent was slowly added at 4 °C until alcohol was consumed on TLC analysis. Then, *i*-PrOH was added to destroy excess of Jones reagent and diluted with acetone. The precipitate was filtered through celite and washed with acetone. After evaporation, the residue was purified by silica gel column chromatography (hexane:EtOAc 7:3) to give ketone **26** (174.3 mg, 71%).



25

To a solution of ketone **26** (137 mg, 0.261 mmol) in MeOH (1 mL) and THF (0.5 mL), $NaBH_4$ (20 mg, 0.522 mmol) was added at 4 °C. After 30 min, 1M HCl was added, and

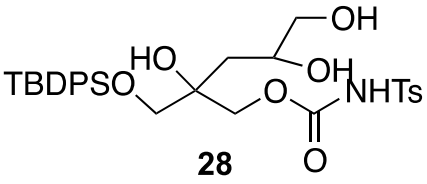
the aqueous layer was extracted with $CHCl_3$. The organic layers were washed with brine and dried over Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (hexane:EtOAc 1:1) to give alcohol **25** (138.9 mg, quant.).



27

To a solution of hemiketal **26** (291 mg, 0.554 mmol) in THF (5 mL), allyl magnesium bromide (1.5 mL, ca. 1.0 M in Et_2O) was added dropwise at 4 °C. After stirring the mixture for 3 h, sat. NH_4Cl was added to quench the reaction. The aqueous layer was extracted with $CHCl_3$ several times and the combined layers were washed with brine. The mixture was concentrated after drying the extract over Na_2SO_4. The residue was purified by silica gel column chromatography ($CHCl_3$:EtOAc 4:1-1:1) to give adduct **27** (290 mg, 92%).

^{1}H-NMR δ 7.89 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 4H), 7.45-7.35 (m, 6H), 7.28-7.24 (m, 2H), 5.68 (m, 1H), 5.02 (m, 2H), 4.09 (d, J = 11.2 Hz, 1H), 4.03 (d, J = 11.2 Hz, 1H), 3.45 (s, 2H), 2.39 (s, 3H), 2.23-2.19 (m, 2H), 1.02 (s, 9H); ^{13}C-NMR δ 150.2, 145.3, 135.7, 135.6, 132.7, 131.9, 130.2, 129.8, 128.4, 128.0, 119.6, 73.2, 68.6, 65.9, 38.7, 27.0, 21.8, 19.4; HRMS calcd for $[C_{30}H_{37}NO_6SSi+Na]^+$ 590.2003, found 590.2010.



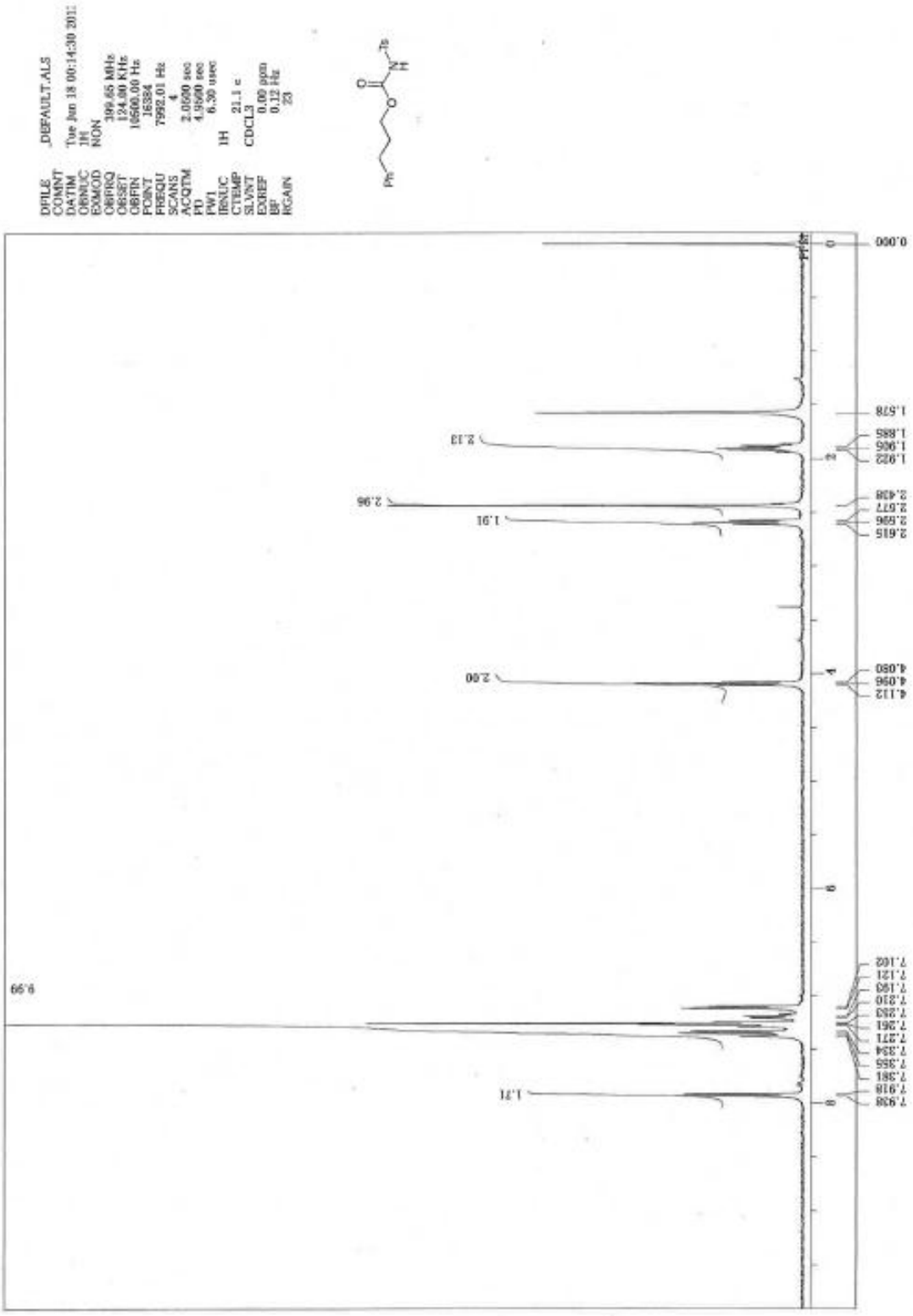
28

To a solution of substrate **27** (187.2 mg, 0.330 mmol) in acetone *N*-methylmorpholine *N*-oxide (29 mg, 0.495 mmol) in acetone (1 mL) and H_2O (2 mL), OsO_4 (2.5 % *tert*-butanol solution, 0.1 mL) was added. The mixture was stirred at room temperature overnight, and 10% $Na_2S_2O_3$ was added to quench the reaction. The aqueous layer was extracted with $CHCl_3$ and the combined layers were washed with 1 M HCl and brine. The combined layers were concentrated after drying over Na_2SO_4. The residue was

purified by silica gel column chromatography ($CHCl_3$:EtOAc 1:1-3:7) to give triol **28** (178 mg, 90%). The diastereomer ratio could not be determined.

^{1}H-NMR (as a mixture, CD_3OD) δ 7.89-7.85 (m, 2H), 7.59-7.55 (m, 4H), 7.44-7.35 (m, 6H), 7.28-7.25 (m, 2H), 4.21-4.03 (m, 3H), 3.61 (m, 0.44 H), 3.61-3.34 (m, 4H), 2.39 (s, 3H), 1.02 (s, 9H); ^{13}C-NMR (as a mixture, CD_3OD) δ 150.6, 145.2, 135.7, 132.9, 132.8, 132.6, 132.6, 130.2, 130.2, 129.8, 128.4, 128.4, 128.1, 74.6, 74.1, 73.9, 69.8, 69.0, 68.8, 68.5, 68.0, 67.4, 67.2, 67.1, 67.0, 66.9, 66.3, 65.7, 65.1, 36.4, 36.2, 36.1, 34.5, 27.1, 27.0, 21.8, 19.4; HRMS calcd for $[C_{30}H_{39}NO_8SSi+Na]^+$ 624.2058, found 624.2066.

^{1}H-NMR of **1b**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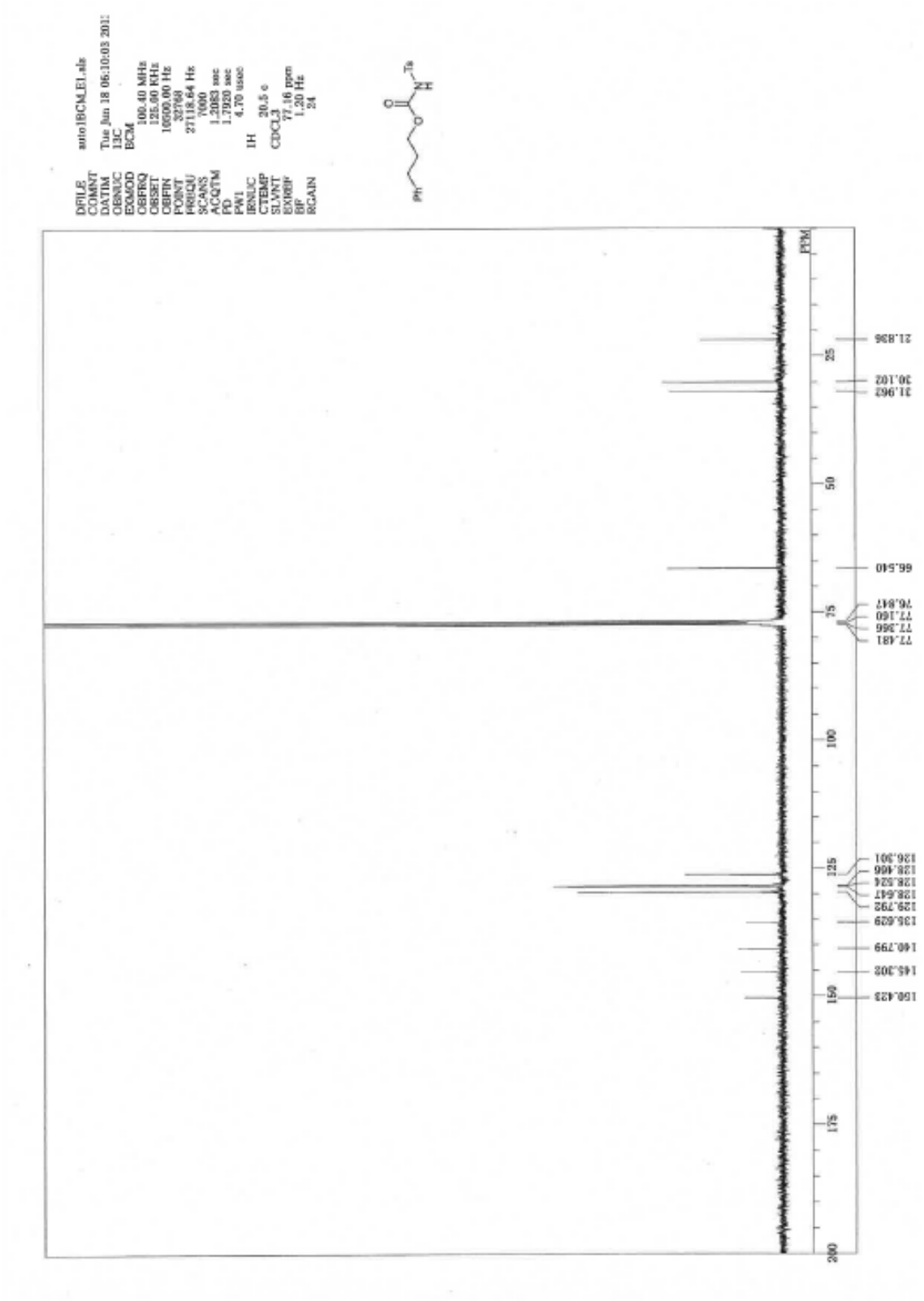
^{13}C-NMR of **1b**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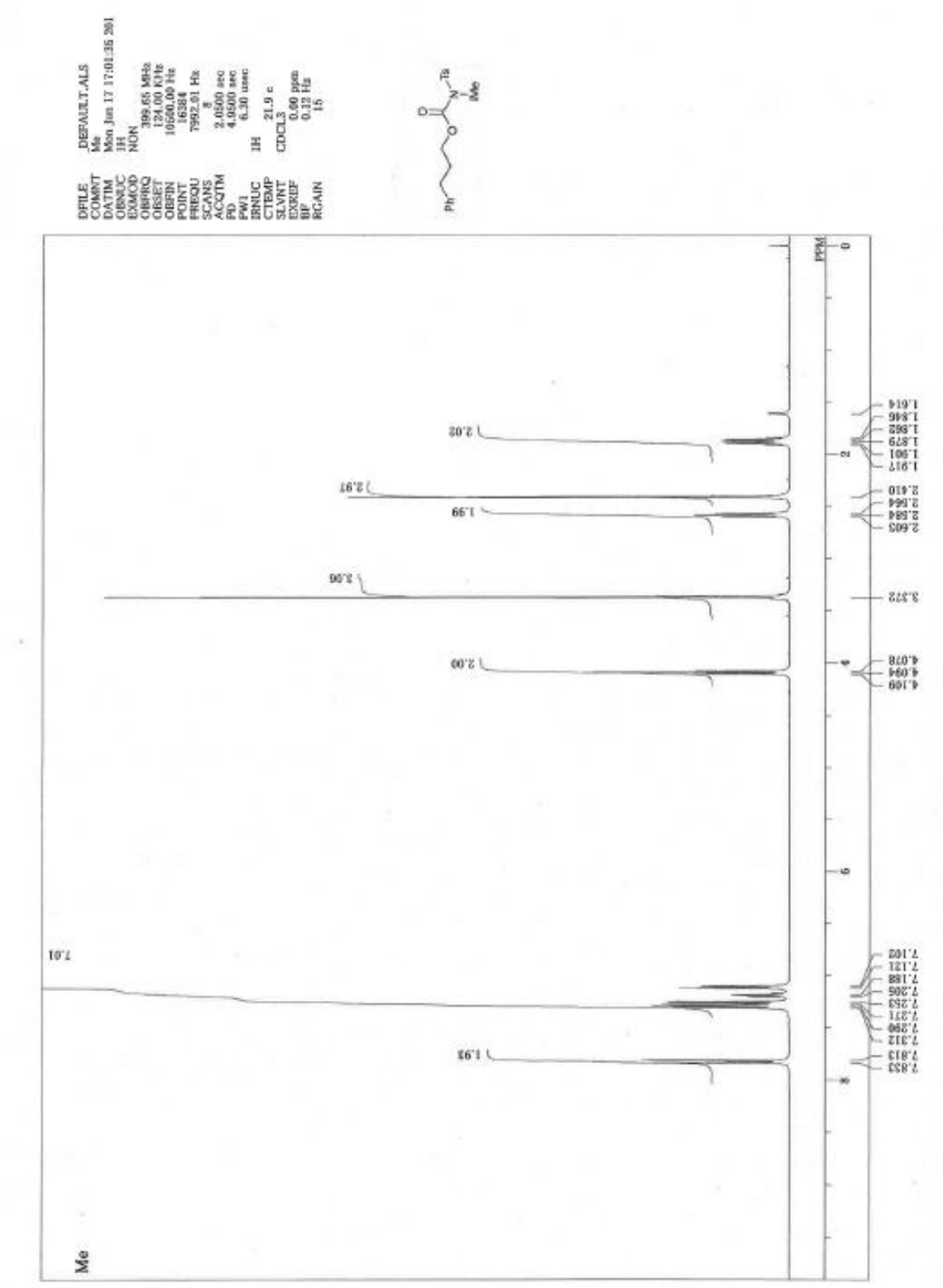
^{1}H-NMR of **1c**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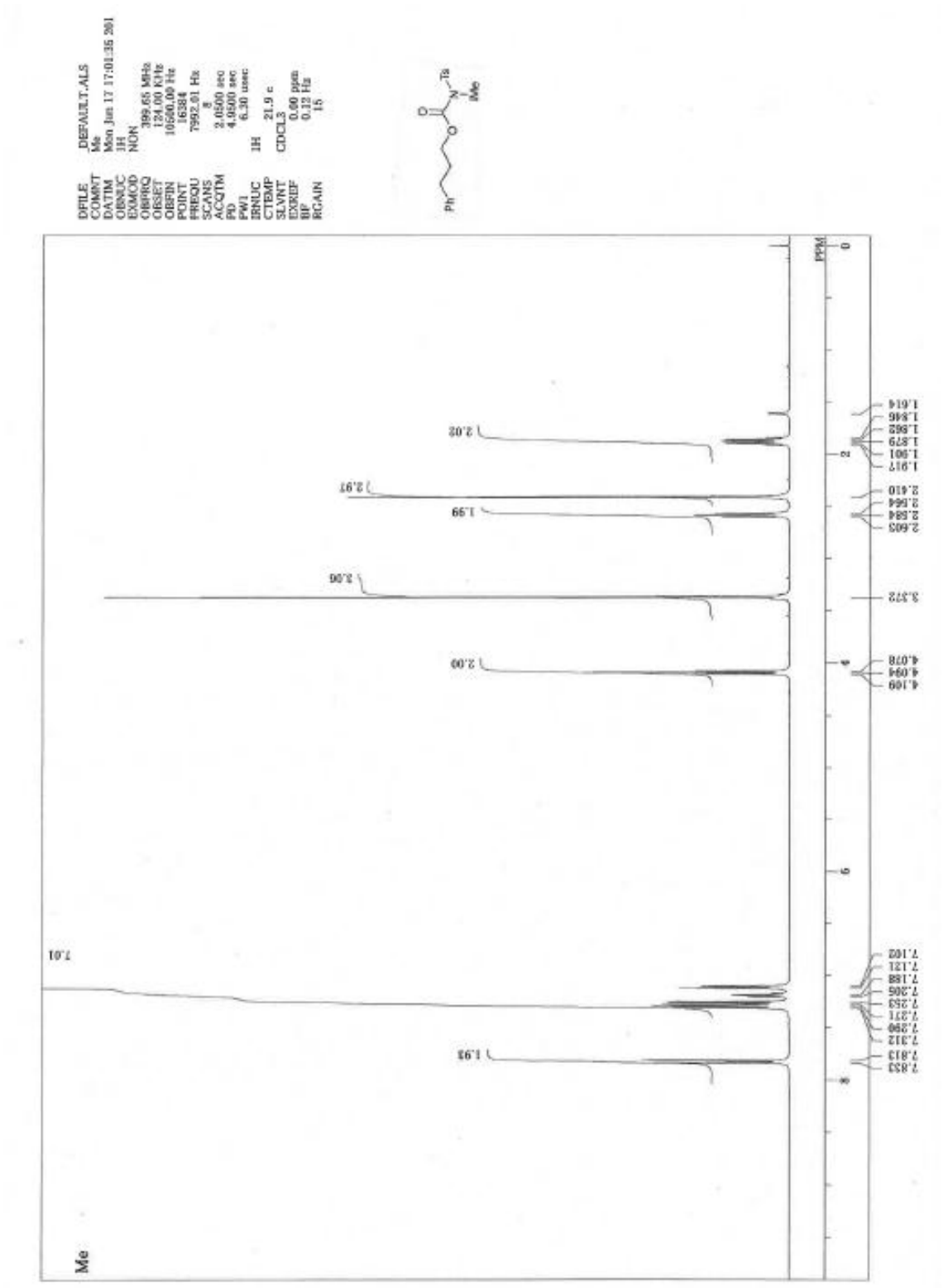
^{13}C-NMR of **1c**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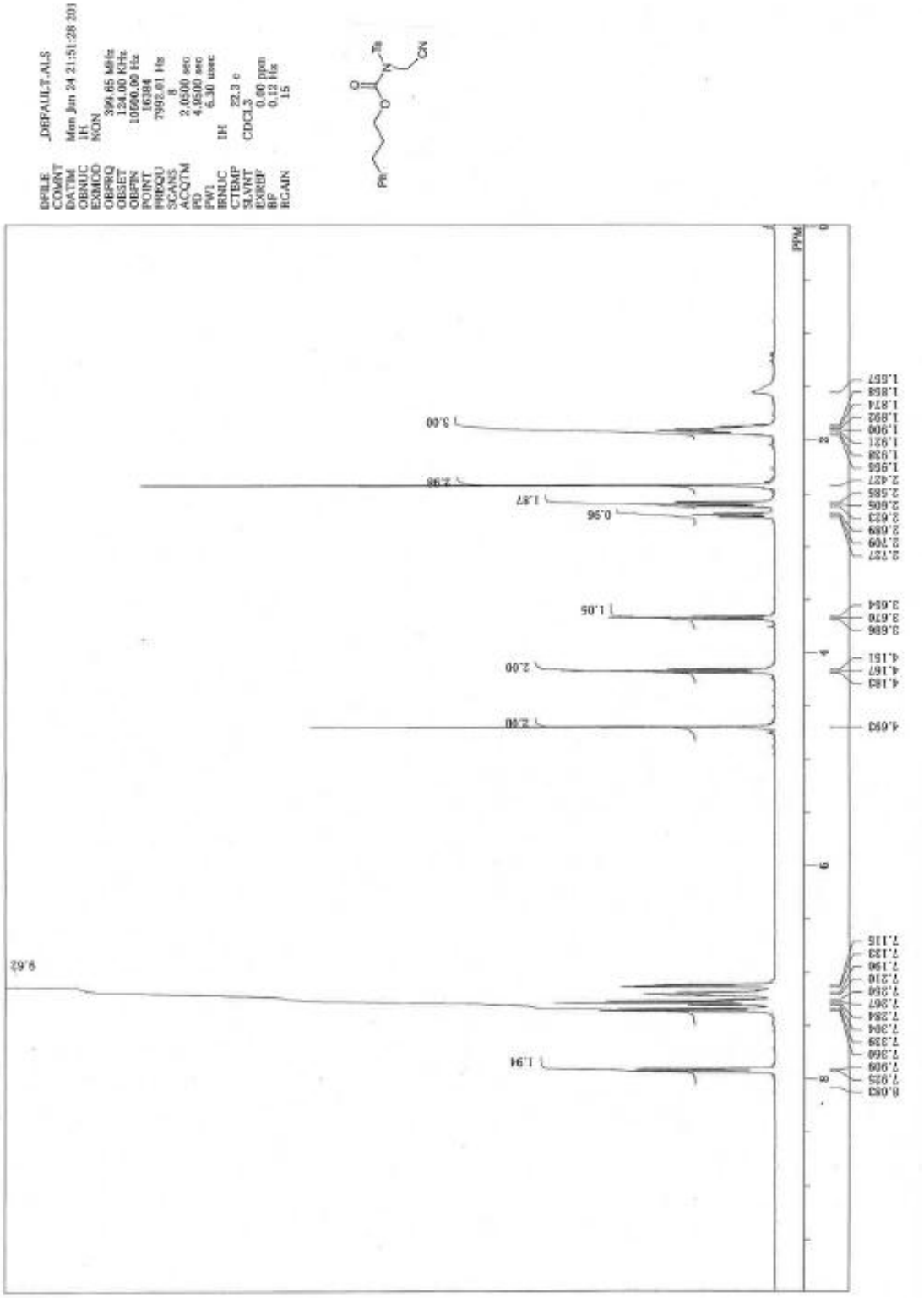
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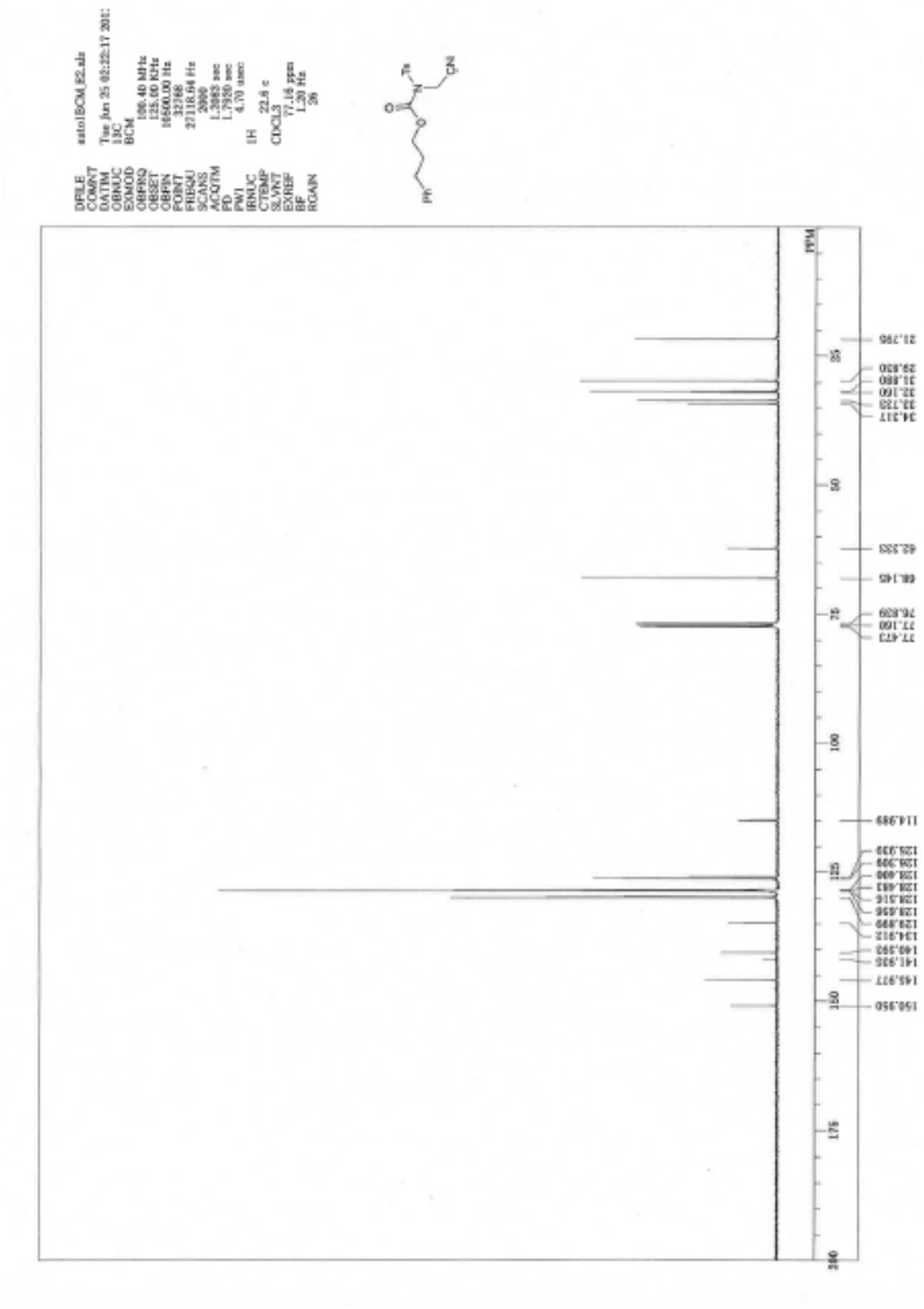
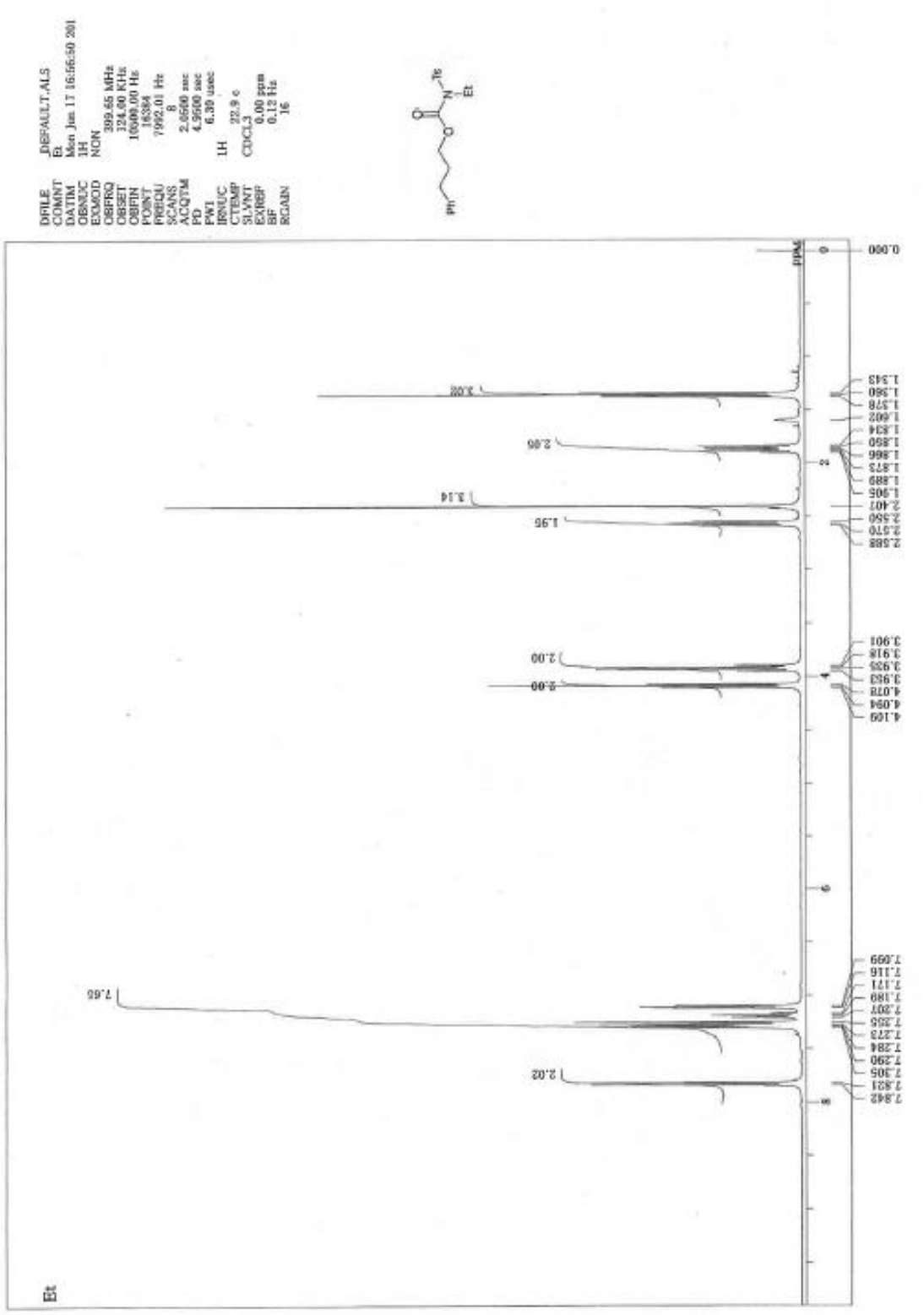
^{13}C-NMR of **1d**



^{1}H-NMR of **1e**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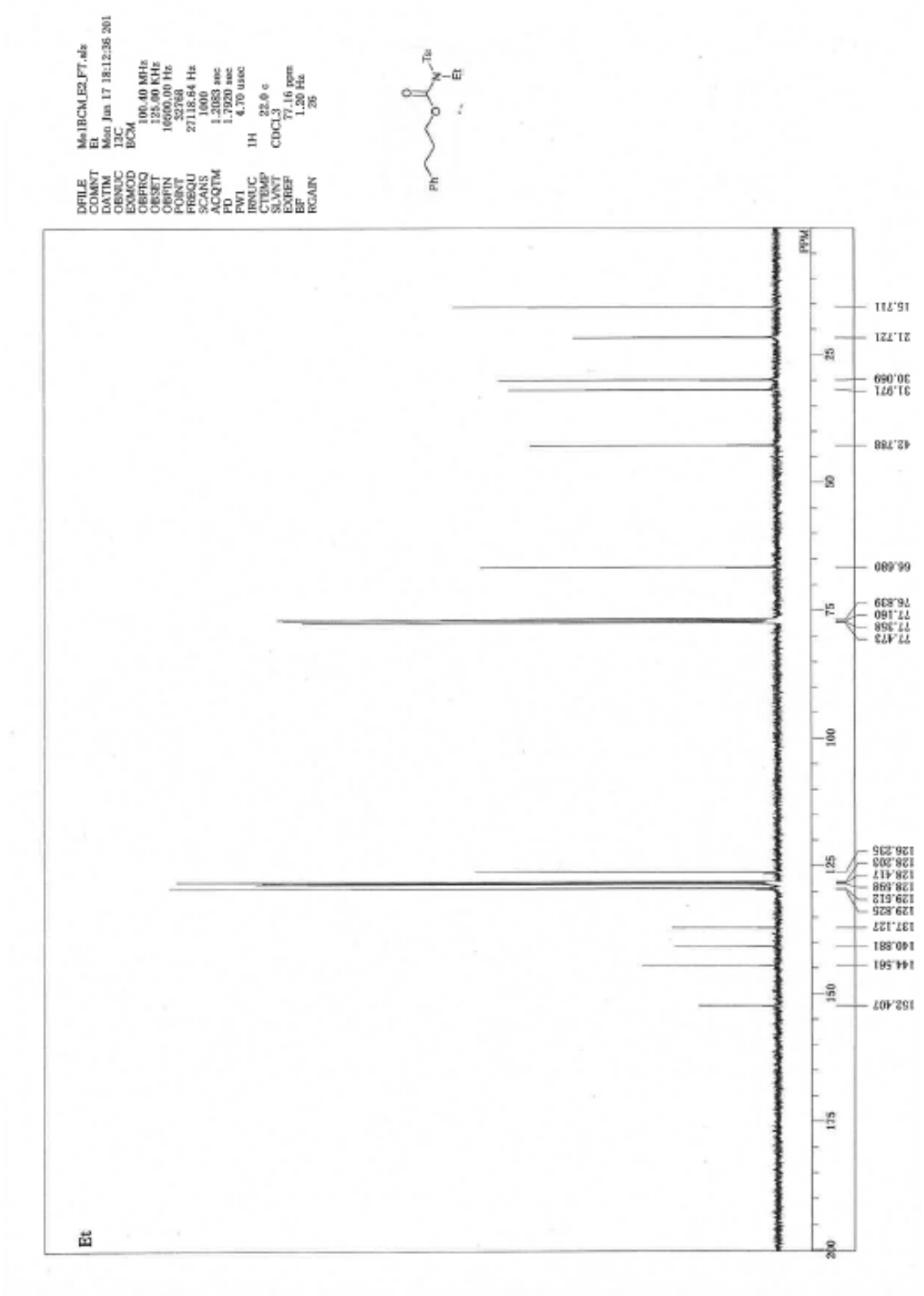
^{13}C-NMR of **1e**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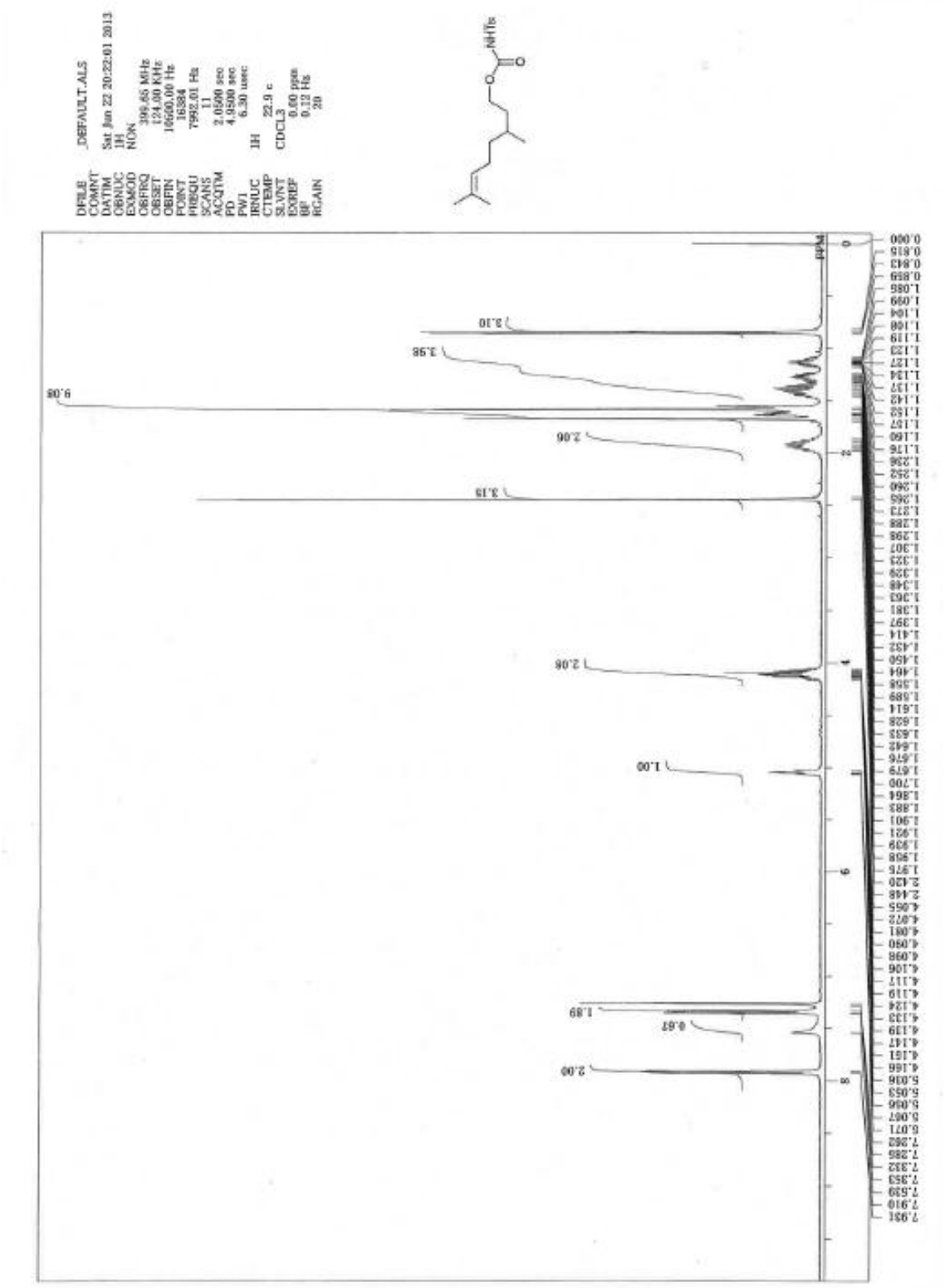
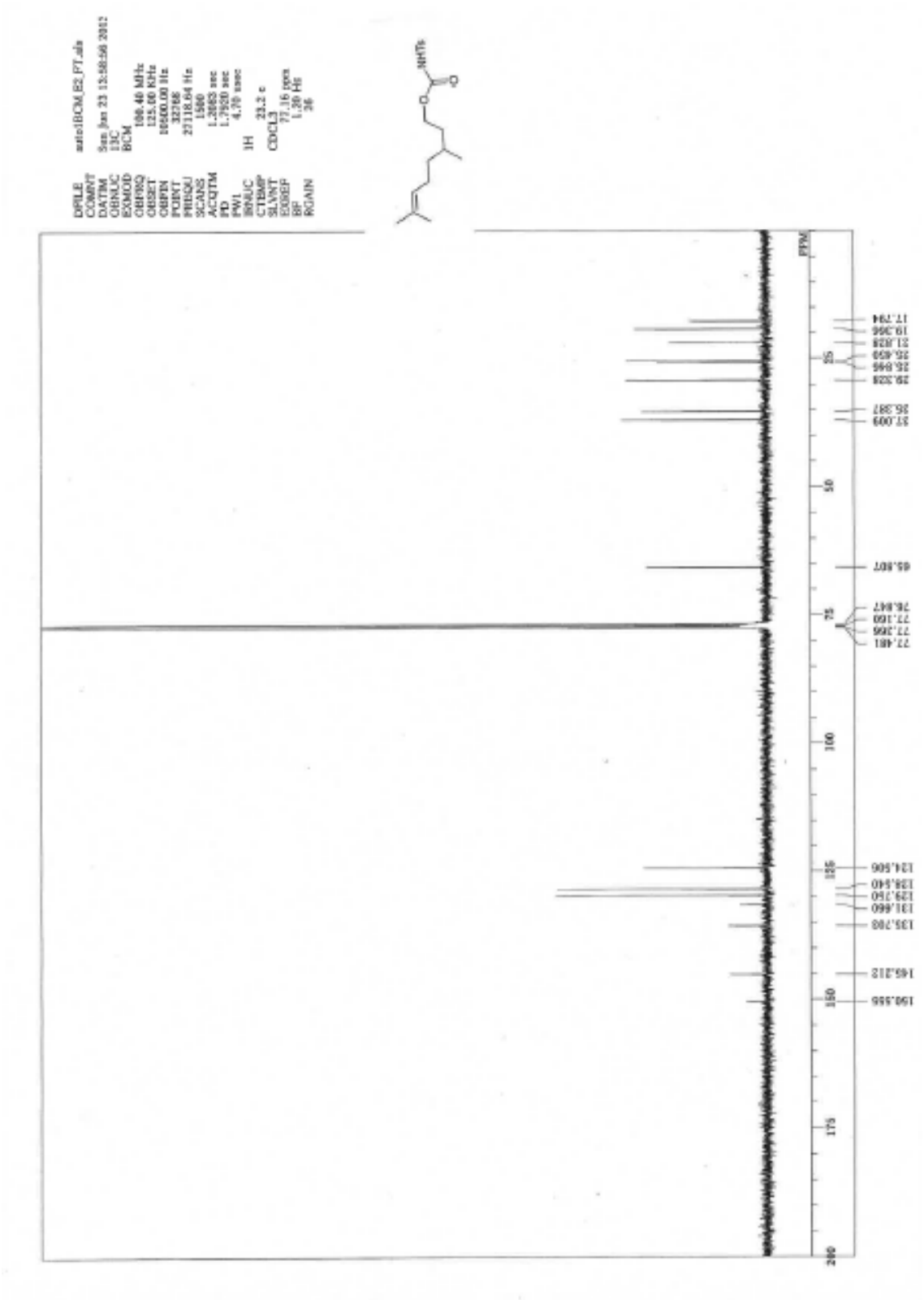
Et

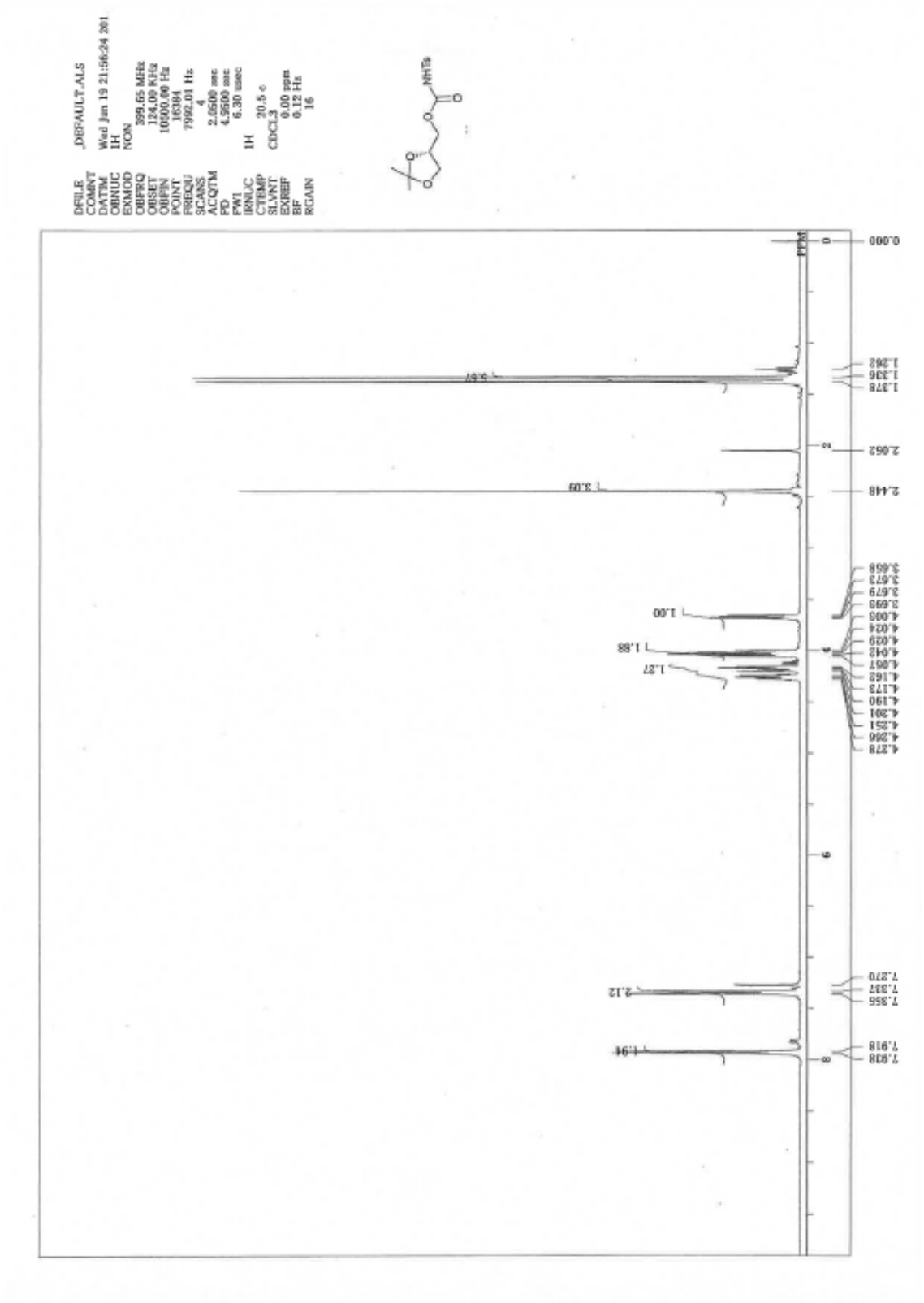
^{1}H-NMR of **2b**


DEFAULT.ALS
Sat Jun 22 20:22:01 2013
1H
NON
399.65 MHz
124.00 KHz
16660.00 Hz
16384
7992.01 Hz
11
2.0500 sec
4.9500 sec
6.30 usec
1H
22.9 c
CDCL3
0.00 ppm
0.12 Hz
20
NHTs
9.08
3.10
3.58
2.06
3.19
2.06
1.00
1.89
0.87
2.00

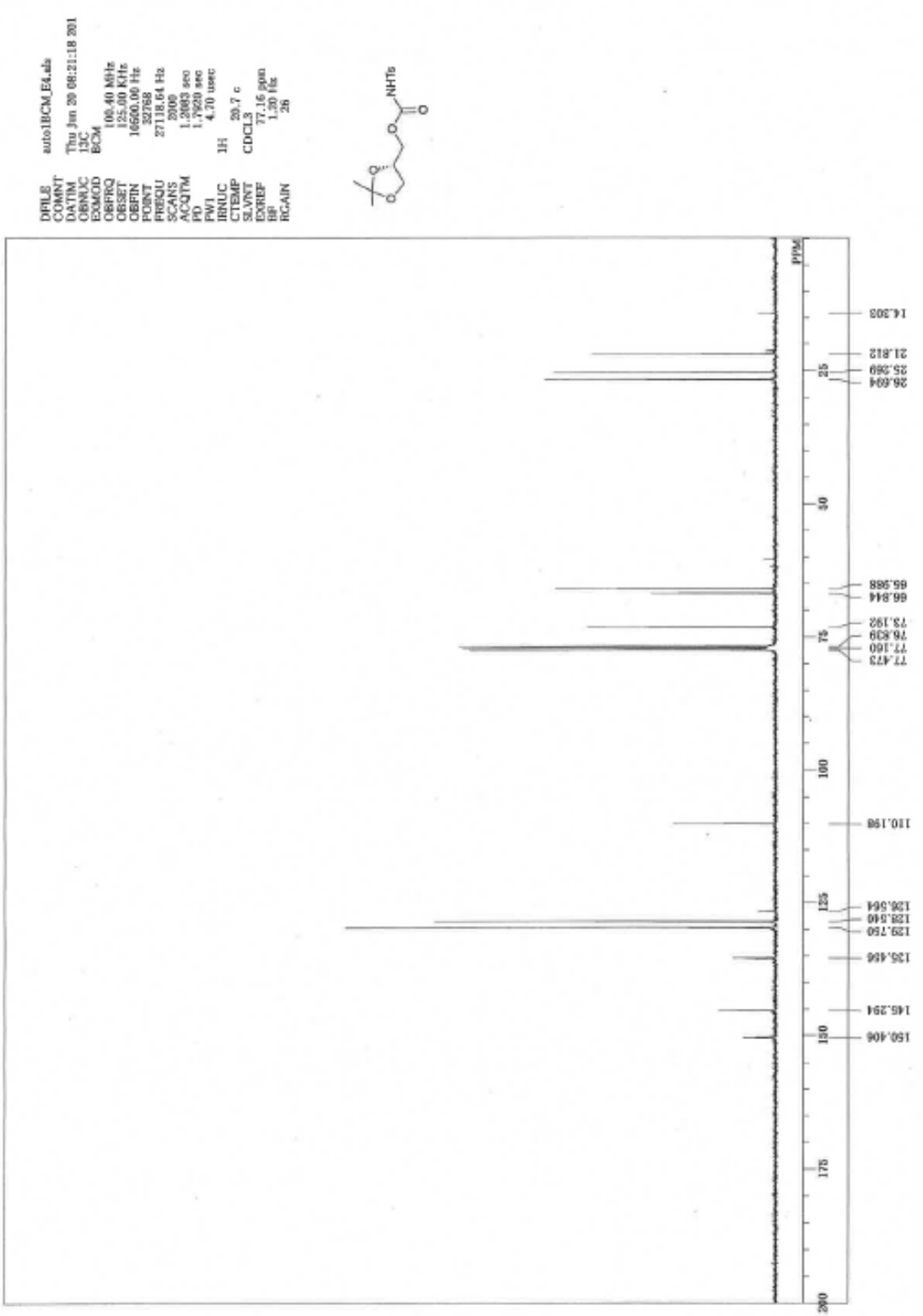
^{13}C-NMR of **2b**


NHTs
17.794
19.366
21.028
25.859
25.895
29.328
35.387
37.009
65.807
76.867
77.160
77.366
77.481
124.506
128.640
129.760
131.660
135.788
165.215
169.956
PPM

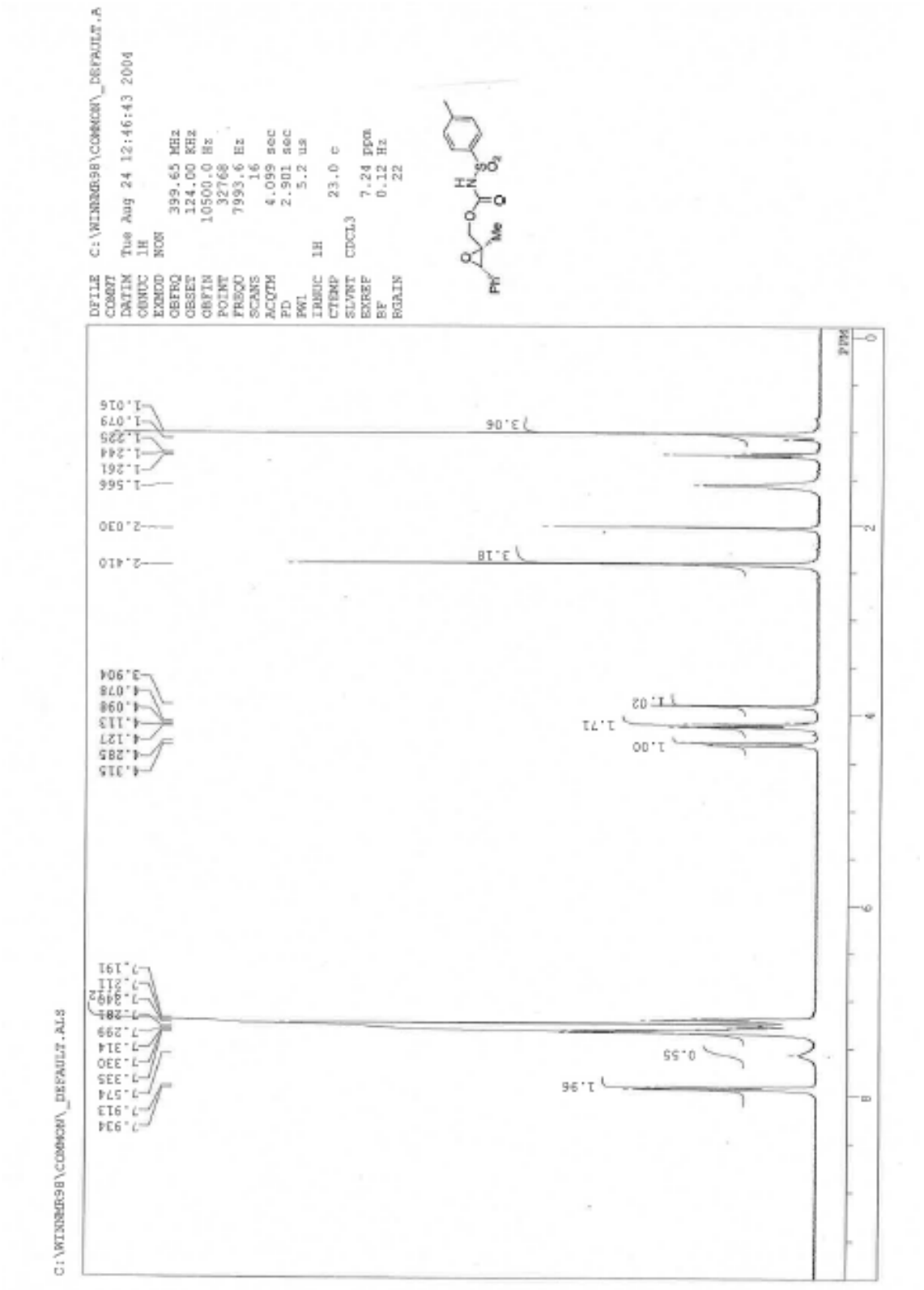
^{1}H-NMR of **3b**


DEFAULT.ALS
Wed Jan 19 21:56:24 201
1H
NON
399.65 MHz
124.00 KHz
16384
7992.01 Hz
4
2.0500 sec
4.5600 sec
6.30 usec
1H
20.5 c
CDCL3
0.00 ppm
0.12 Hz
16
NH2
5.97
3.09
1.00
1.88
1.27
2.12
1.94
2.052
2.448
1.378
1.336
1.282
7.270
7.337
7.356
7.918
7.928
4.278
4.286
4.251
4.201
4.190
4.173
4.162
4.057
4.042
4.029
4.024
4.003
3.693
3.679
3.673
3.658
0.000

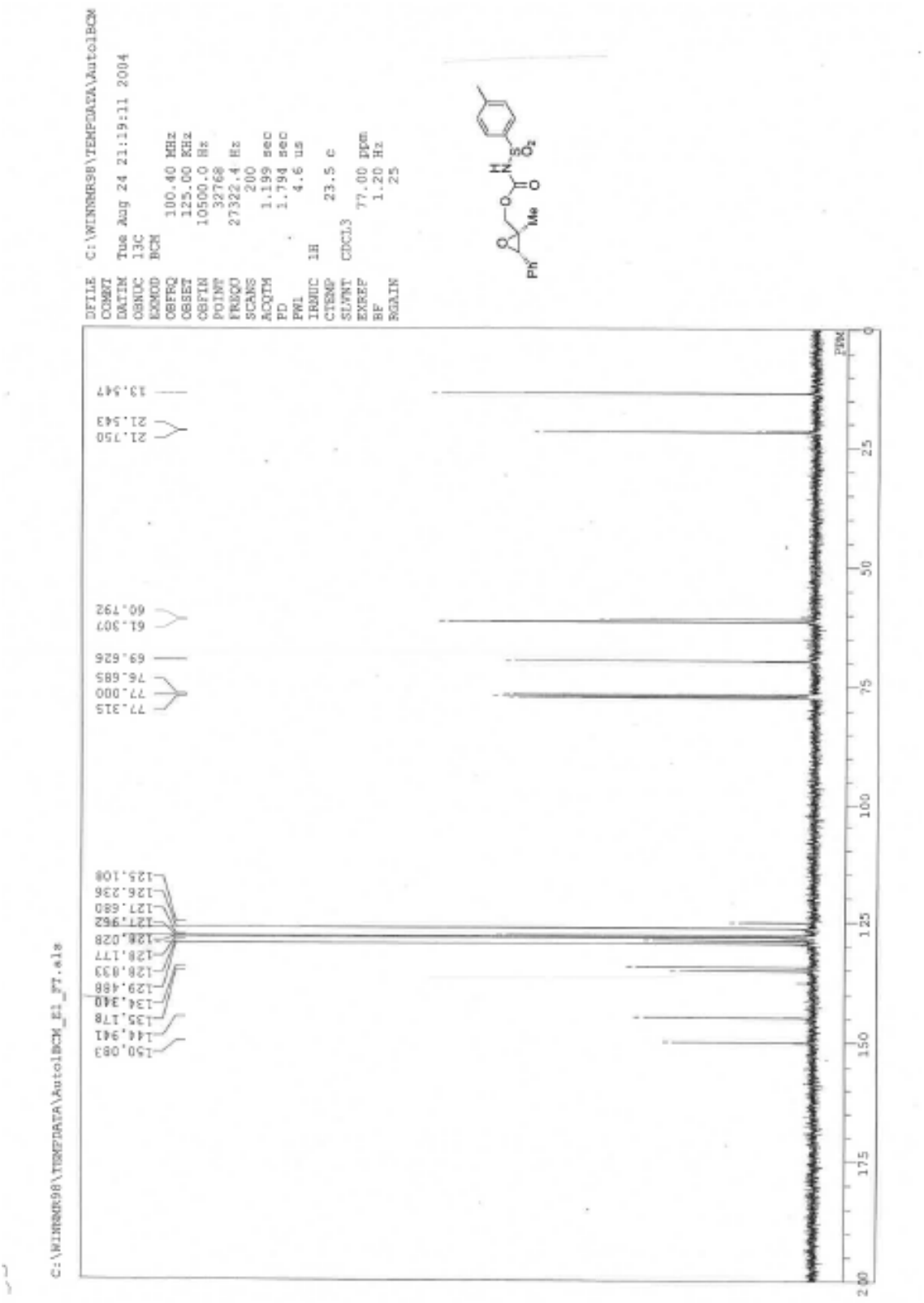
^{13}C-NMR of **3b**


DFILE auto1BCM_E4.als
COMNT
DATIM Thu Jun 20 08:21:18 201
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 16660.00 Hz
POINT 32768
PRSQU 27118.64 Hz
SCANS 2000
ACQTM 1.2683 sec
PD 1.7929 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 29.7 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.30 Hz
RGAIN 26
NHTs
PPM
14.303
21.812
25.360
26.694
66.988
66.844
73.192
76.839
77.160
77.473
110.198
126.564
128.540
129.760
135.466
145.294
150.406

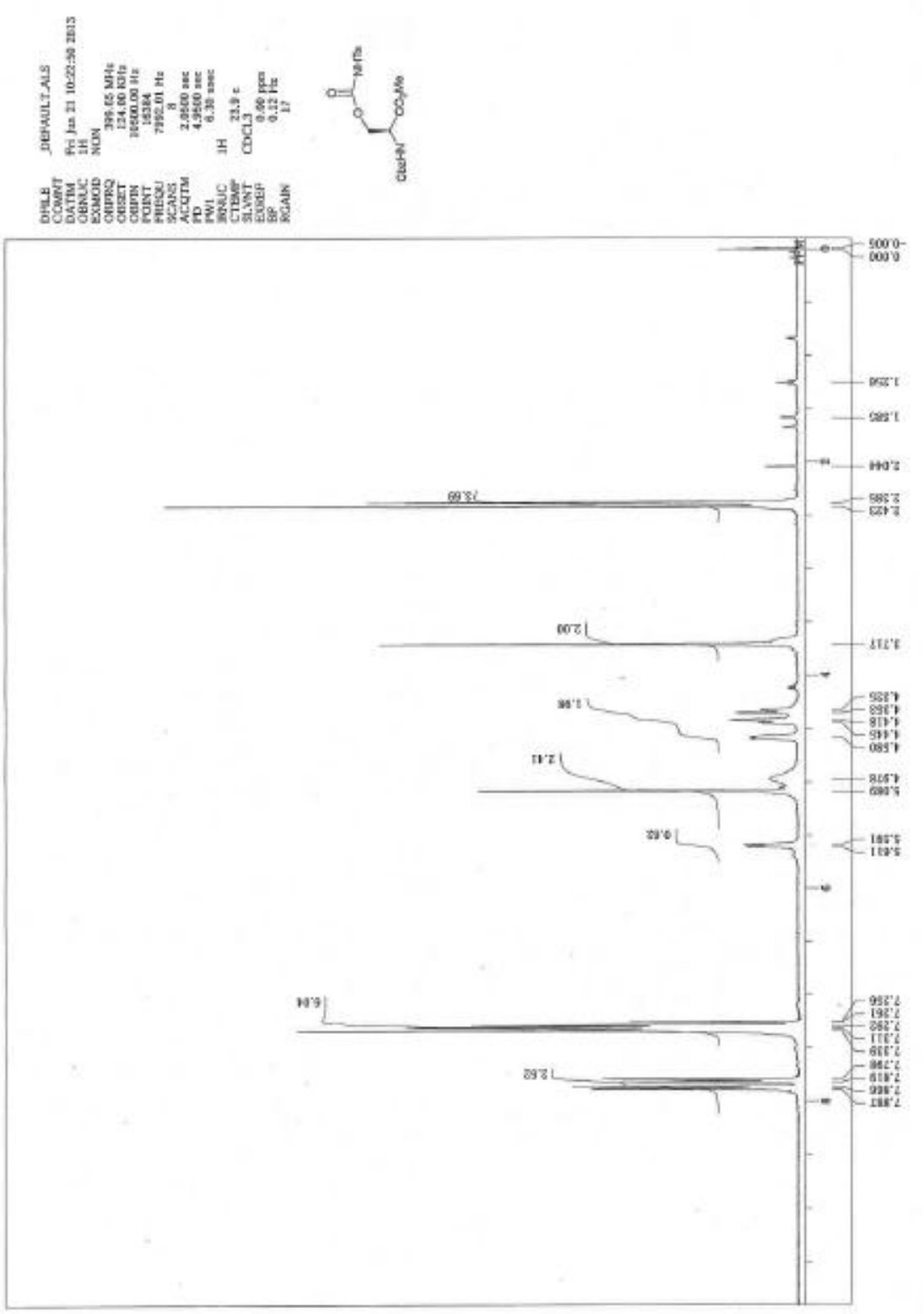
^{1}H-NMR of **4b**


C:\WINNMR98\COMMON_DEFAULT.AU
DFILE C:\WINNMR98\COMMON_DEFAULT.A
COMNT
DATIM Tue Aug 24 12:46:43 2004
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FRQUD 7993.6 Hz
SCANS 16
ACQTM 4.099 sec
PD 2.901 sec
PW1 5.2 us
IN1NUC 1H
CTEMP 23.0 c
SLVNT CDCL3 7.24 ppm
EXREF 0.12 Hz
BF 22
RGAIN
Ph
Me
PPM
1.016
1.079
1.225
1.244
1.261
1.566
2.030
2.410
3.904
4.078
4.098
4.113
4.127
4.285
4.315
7.191
7.211
7.249
7.281
7.299
7.314
7.330
7.335
7.574
7.913
7.934
3.06
3.18
1.02
1.71
1.00
0.55
1.96

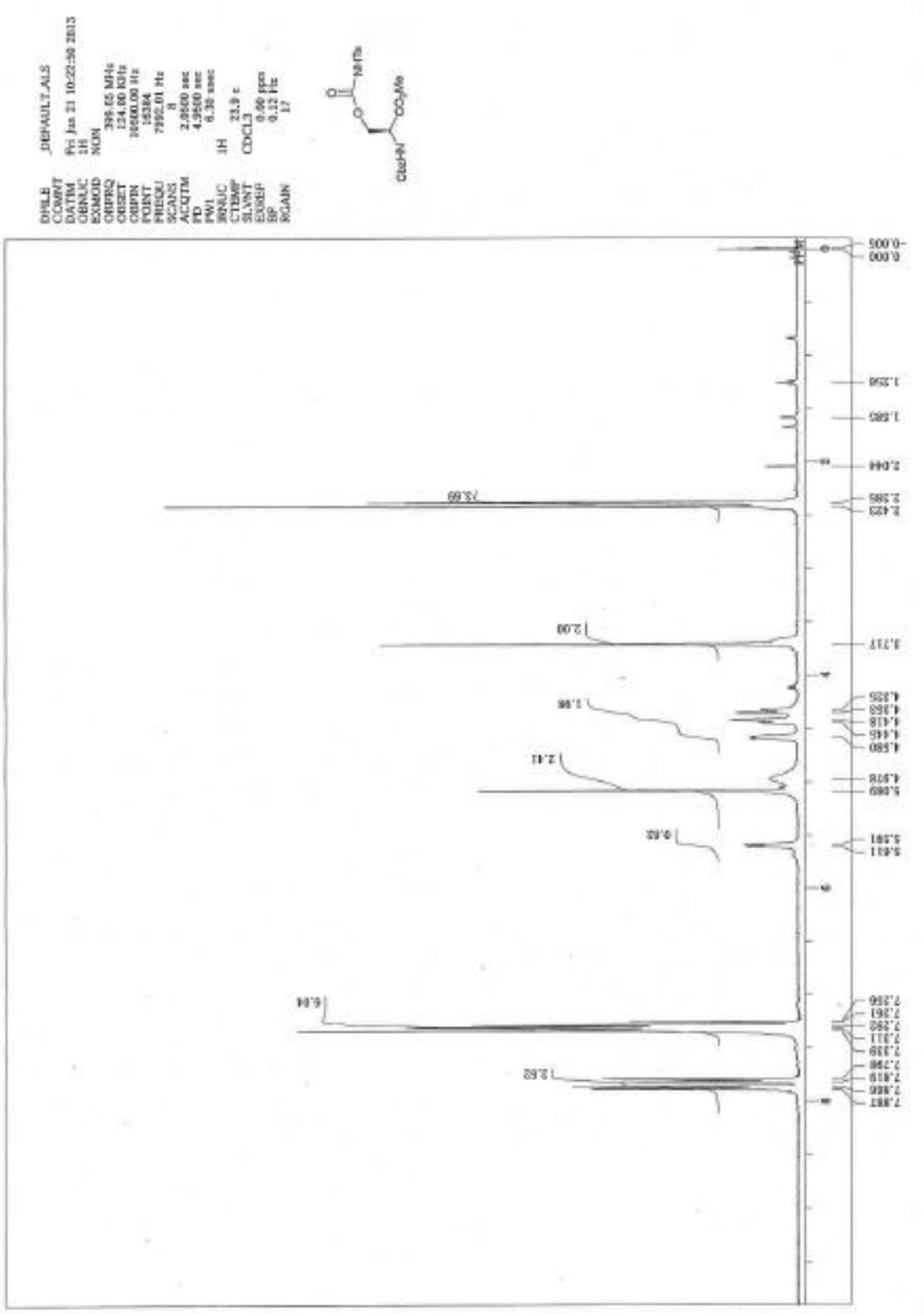
^{13}C-NMR of **4b**


DFILE C:\WINNMR98\TEMPDATA\AutolBCM
COMNT
DATIM Tue Aug 24 21:19:11 2004
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FRQQO 27322.4 Hz
SCANS 200
ACQTM 1.199 sec
PD 1.794 sec
PW1 4.6 us
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 25
Ph
Me
13.547
21.543
21.750
60.792
61.307
69.626
76.685
77.000
77.315
125.108
126.236
127.680
127.962
128.028
128.177
128.833
129.488
134.340
135.178
144.941
150.083
PPM
C:\WINNMR98\TEMPDATA\AutolBCM_E1_97.als

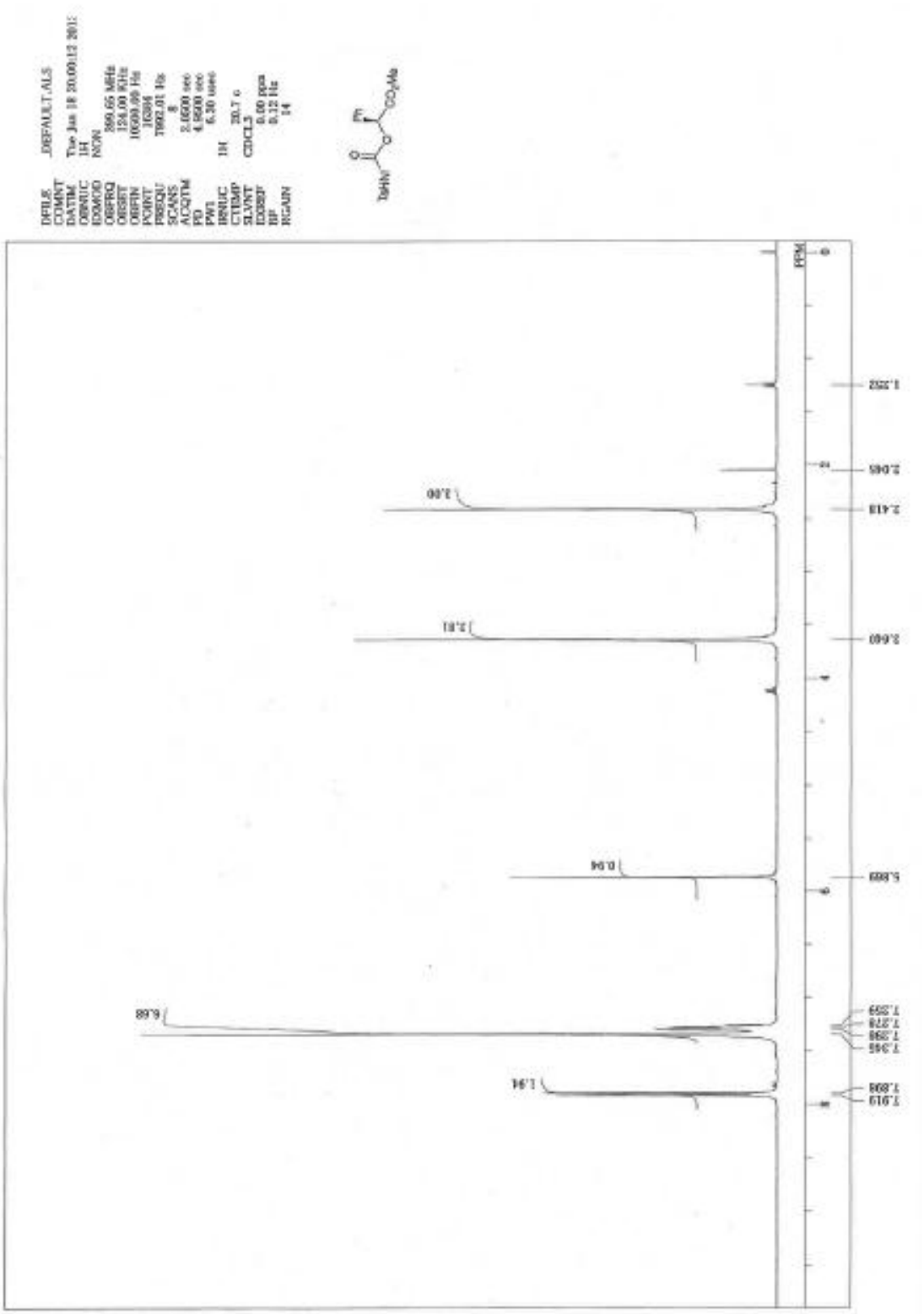
^{1}H-NMR of **5b**



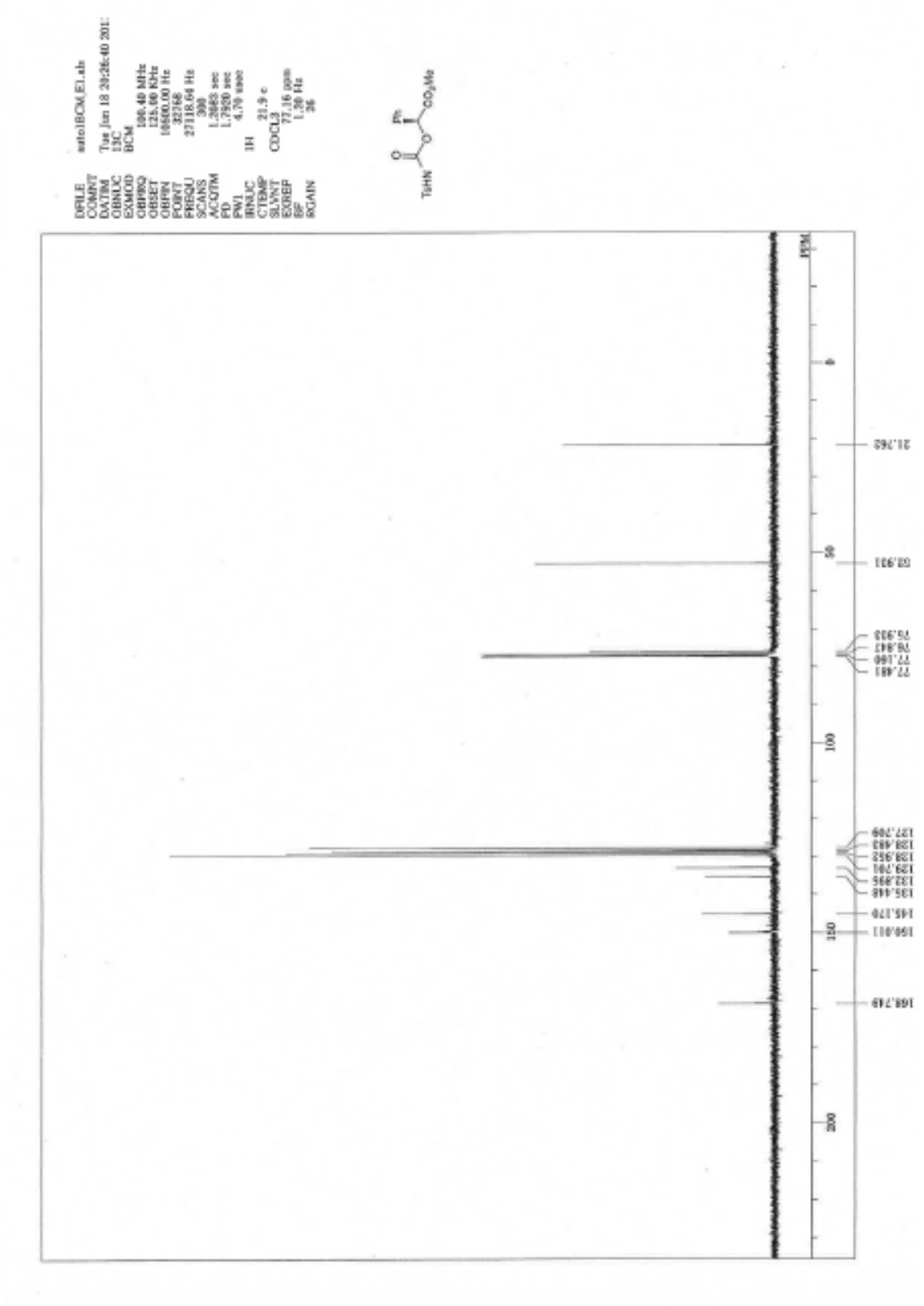
^{13}C-NMR of **5b**



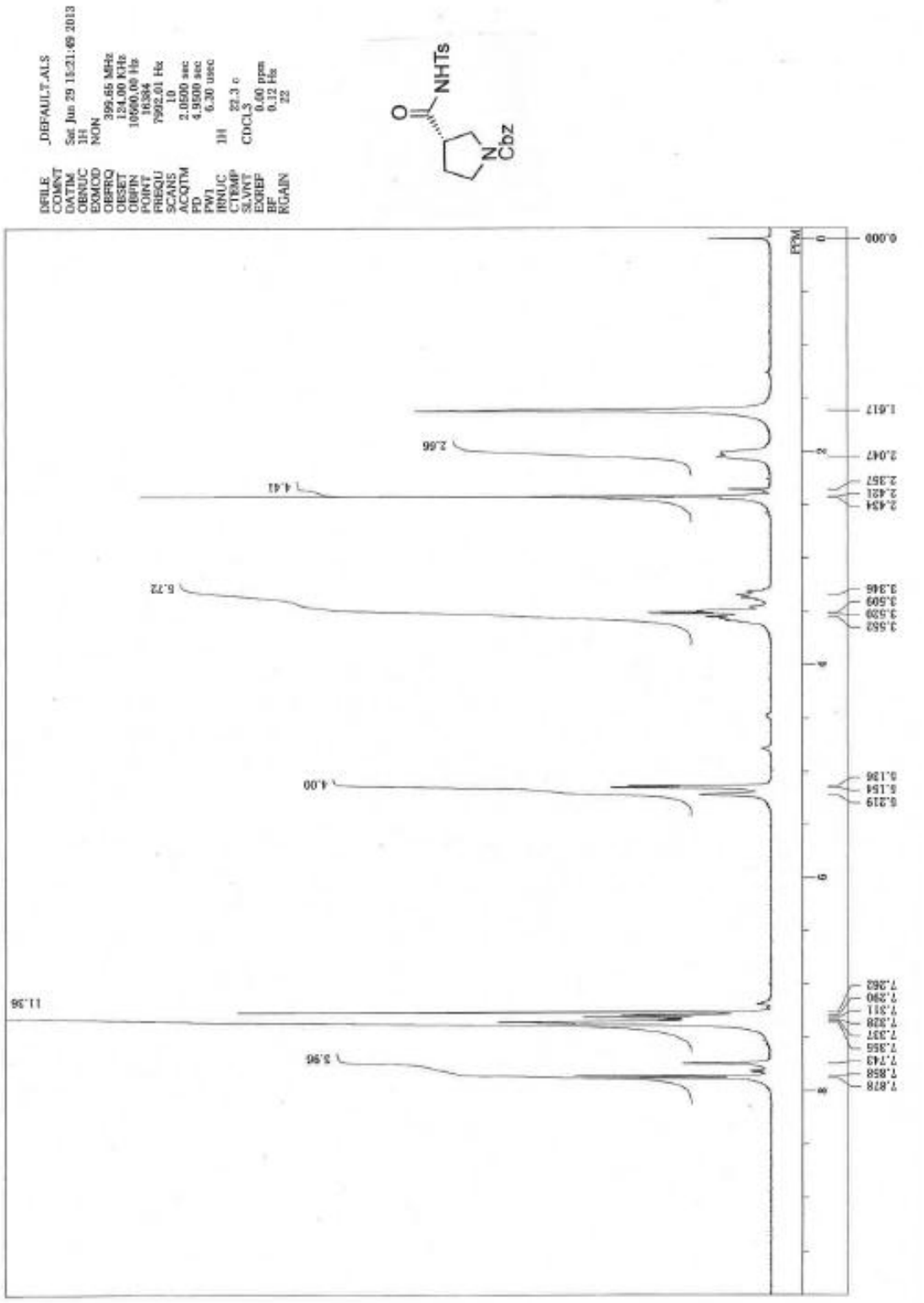
^{1}H-NMR of **6b**



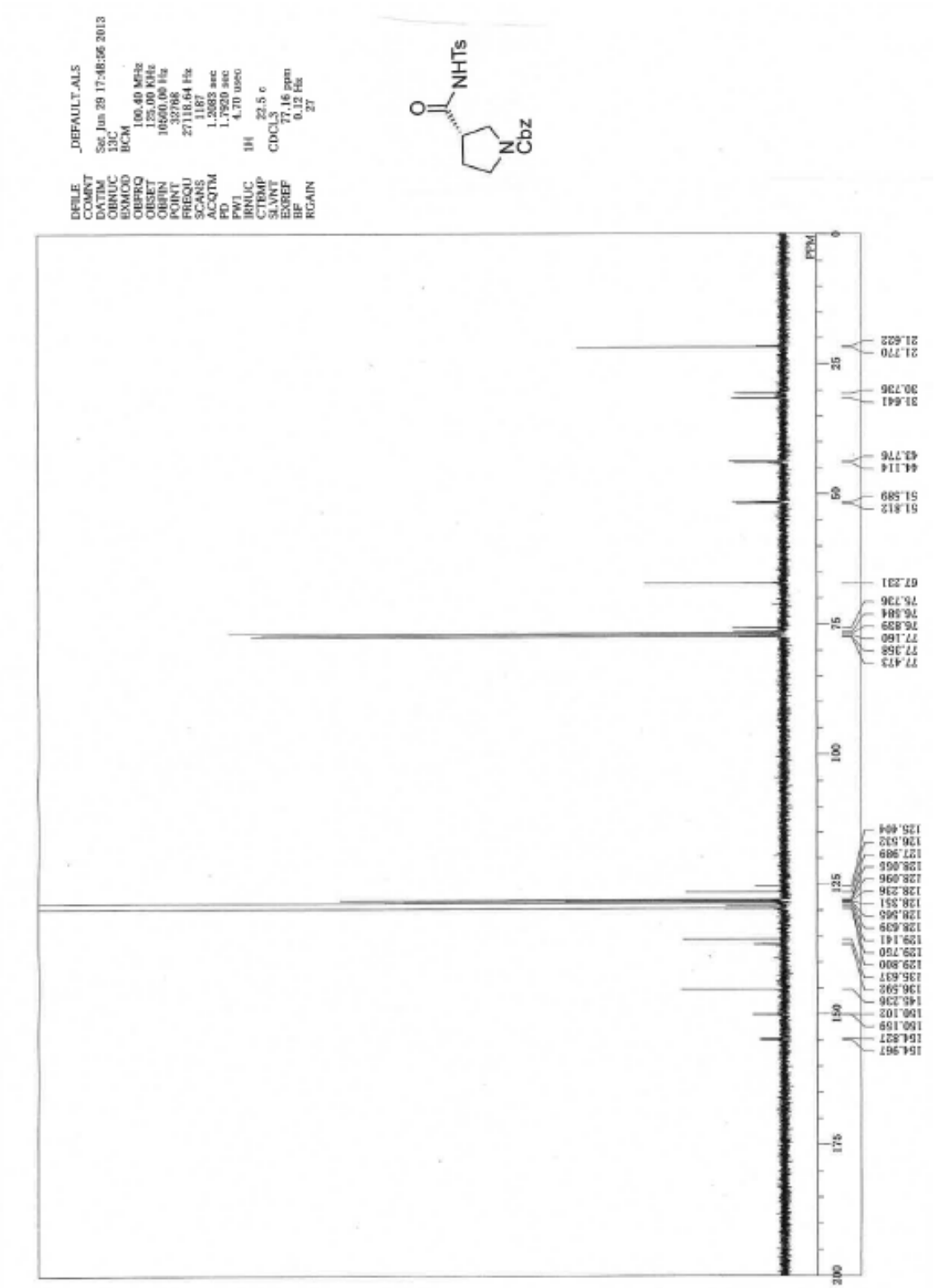
^{13}C-NMR of **6b**


DATA SET
antol8CM_E1.als
Tue Jun 18 20:26:40 201
13C
8CM
106.40 MHz
125.00 KHz
16500.00 Hz
32768
27118.64 Hz
300
1.2583 sec
1.7930 sec
4.79 usec
1H
21.9 c
CDCl3
77.16 ppm
1.26 Hz
26
Ph
CO2Me
TsHN
21.762
52.901
75.923
76.847
77.166
77.481
127.799
128.493
128.952
129.796
132.896
135.448
145.179
150.011
168.749

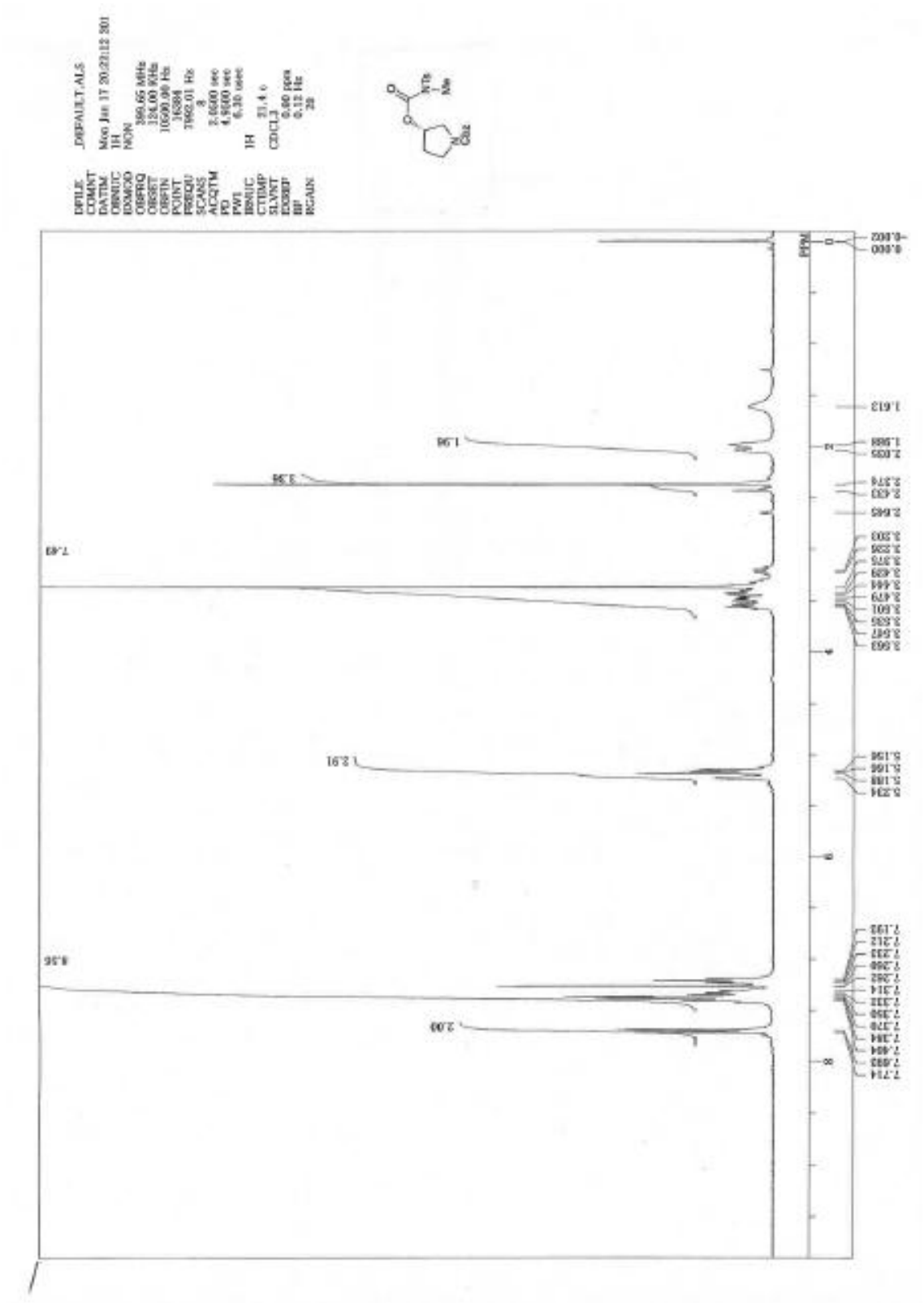
^{1}H-NMR of **7b**


NHTs
O
N
Cbz
11.36
5.96
4.00
5.72
4.41
2.66
1.617
2.047
2.357
2.431
2.454
3.396
3.509
3.529
3.552
5.136
5.154
5.219
7.262
7.290
7.311
7.328
7.337
7.355
7.749
7.858
7.878
PPM

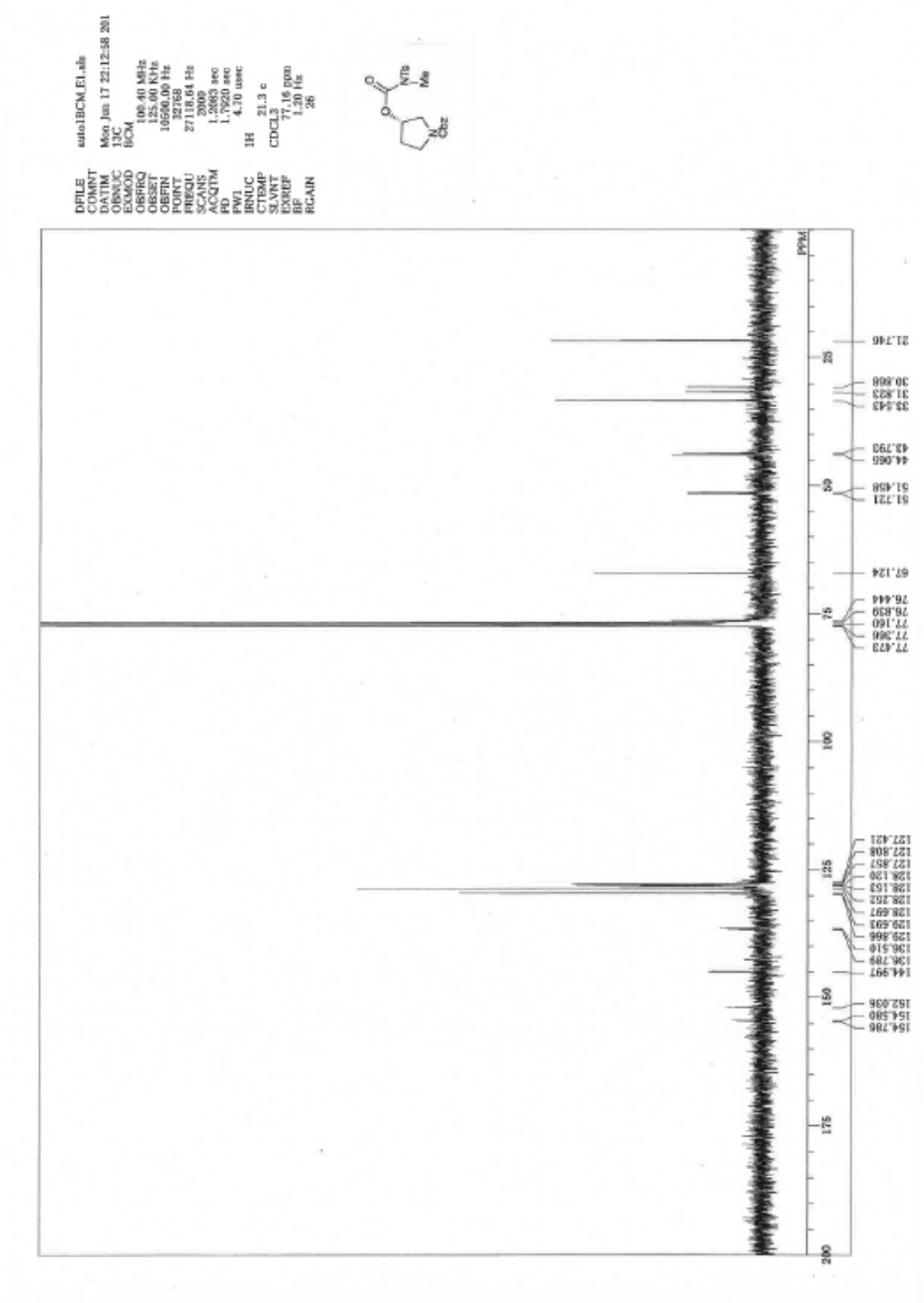
^{13}C-NMR of **7b**



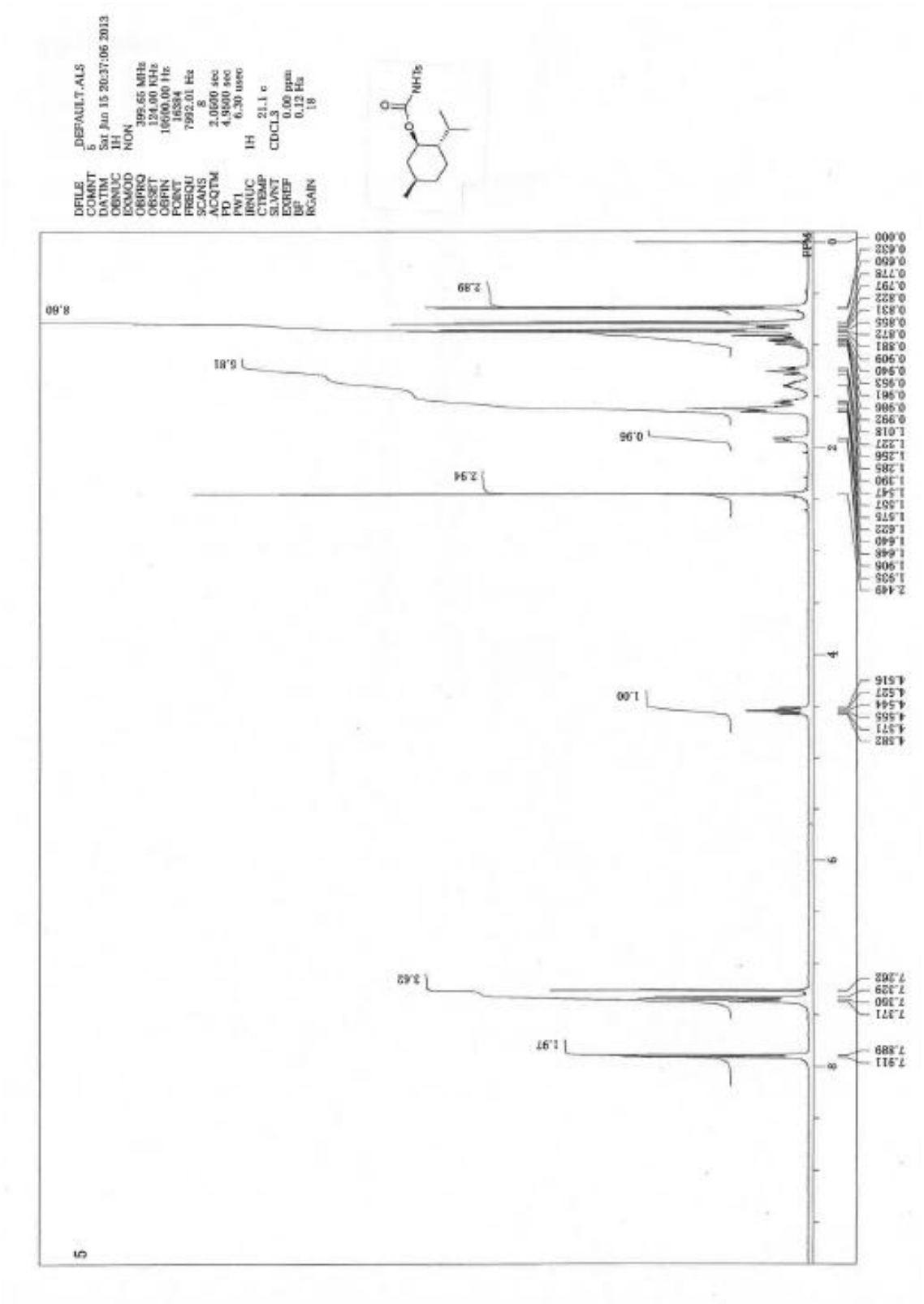
^{1}H-NMR of methylated **7b**



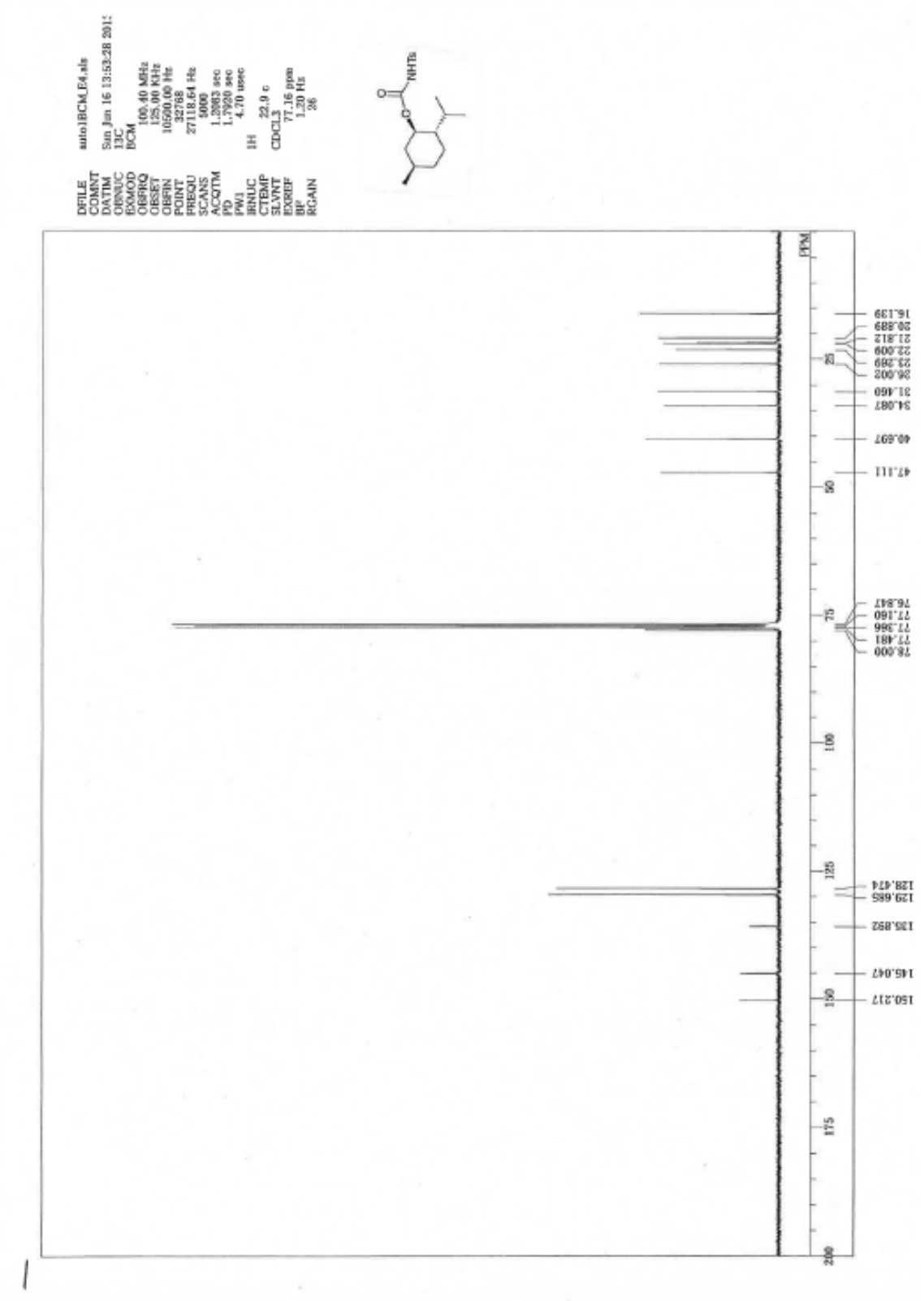
^{13}C-NMR of methylated **7b**



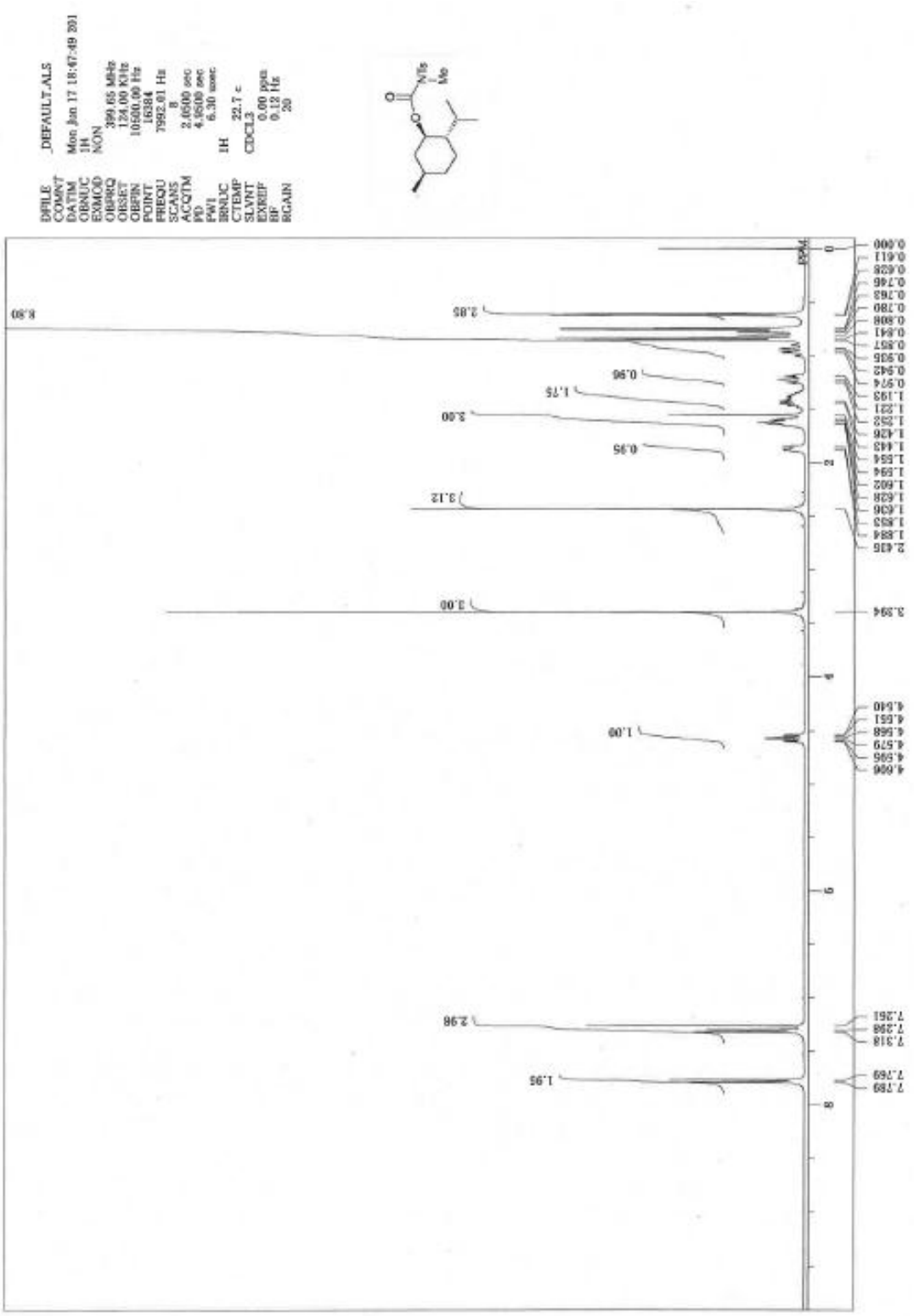
^{1}H-NMR of **8b**


DFILE DEFAULT.ALS
COMNT 5
DATIM Sat Jun 15 20:37:06 2013
OBNUC 1H
EXMOD NON
OBSFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 16000.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H 21.1 c
CTEMP CDCL3
SLVNT 0.00 ppm
EXREF 0.12 Hz
BF 18
RGAIN
NH2s
PPM
8.60
5.81
2.89
2.94
0.96
1.00
3.62
1.97

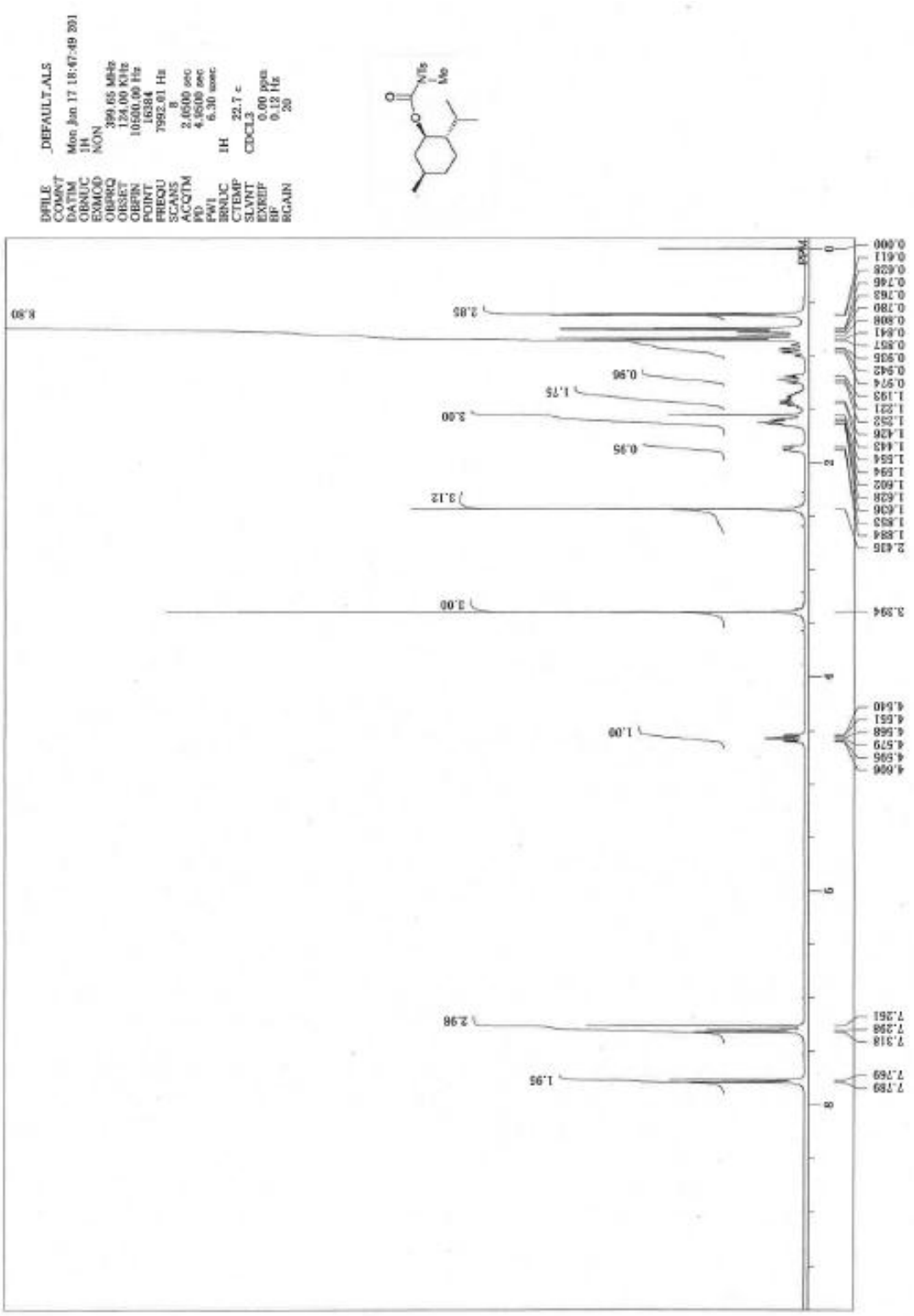
^{13}C-NMR of **8b**


auto18CM_F4.als
Sun Jan 16 13:53:28 2011
13C
BCM
100.40 MHz
125.00 KHz
10500.00 Hz
32768
27118.64 Hz
5000
1.2983 sec
1.7930 sec
4.70 usec
1H
22.9 c
CDCl3
77.16 ppm
1.20 Hz
36
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
PREGU
SCANS
ACQTM
PD
PW1
INUC
CTEMP
SLVNT
EXREF
BF
RGAIN
NHTs
PPM
16.139
20.889
21.812
22.009
25.289
26.002
31.460
34.087
40.697
47.111
76.847
77.160
77.386
77.481
78.000
128.474
129.685
136.892
146.047
150.317

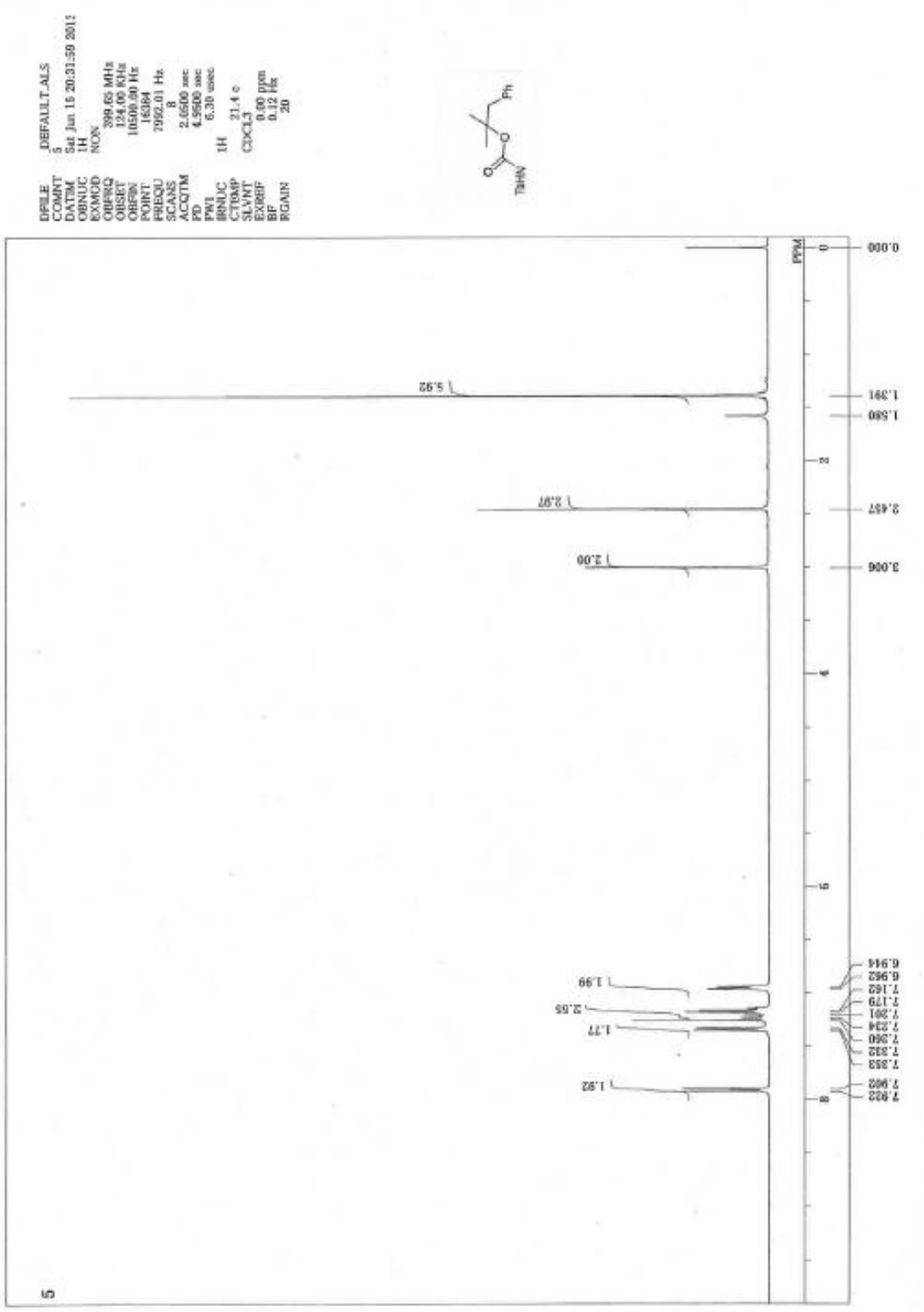
^{1}H-NMR of methylated **8b**



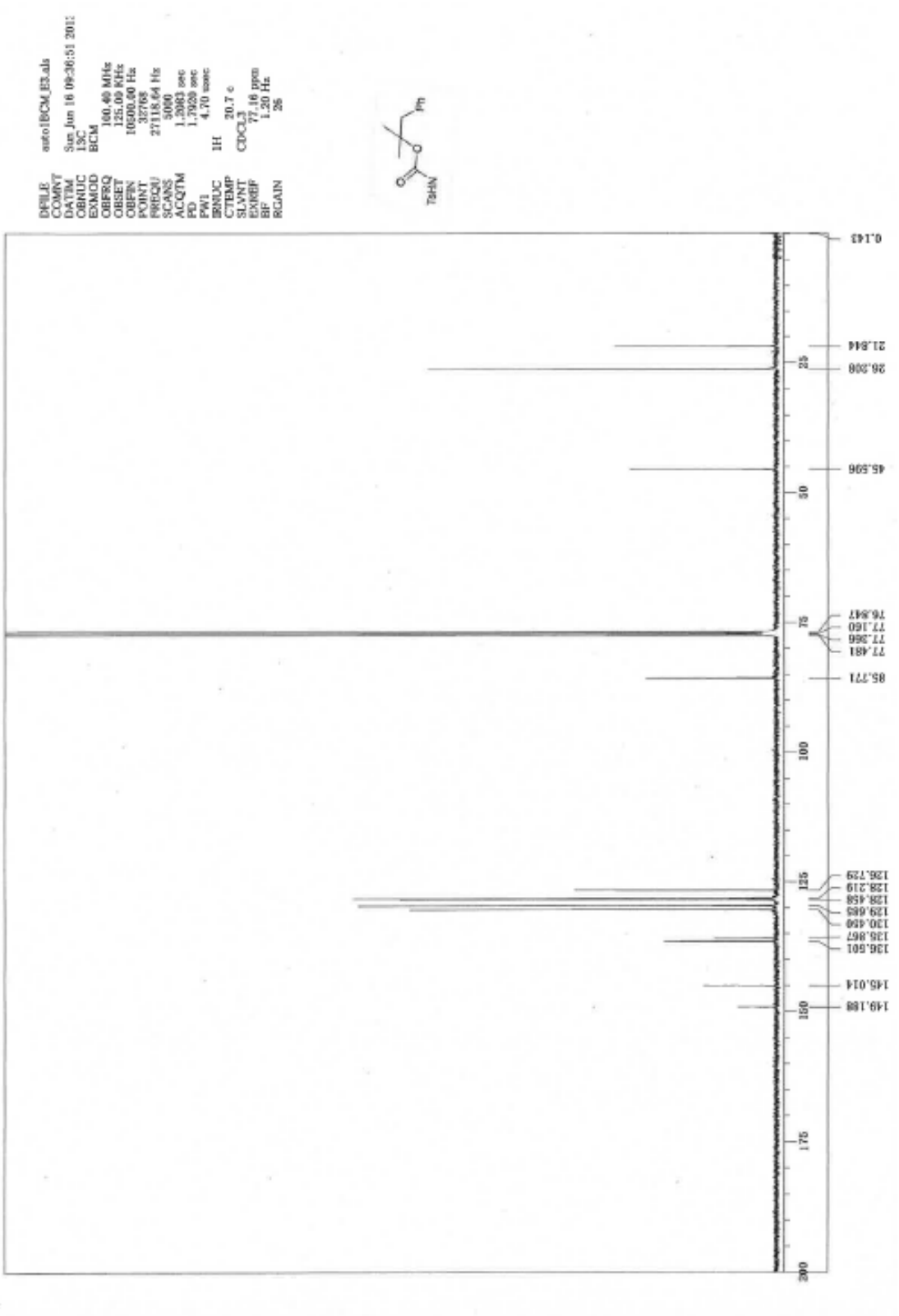
^{13}C-NMR of methylated **8b**



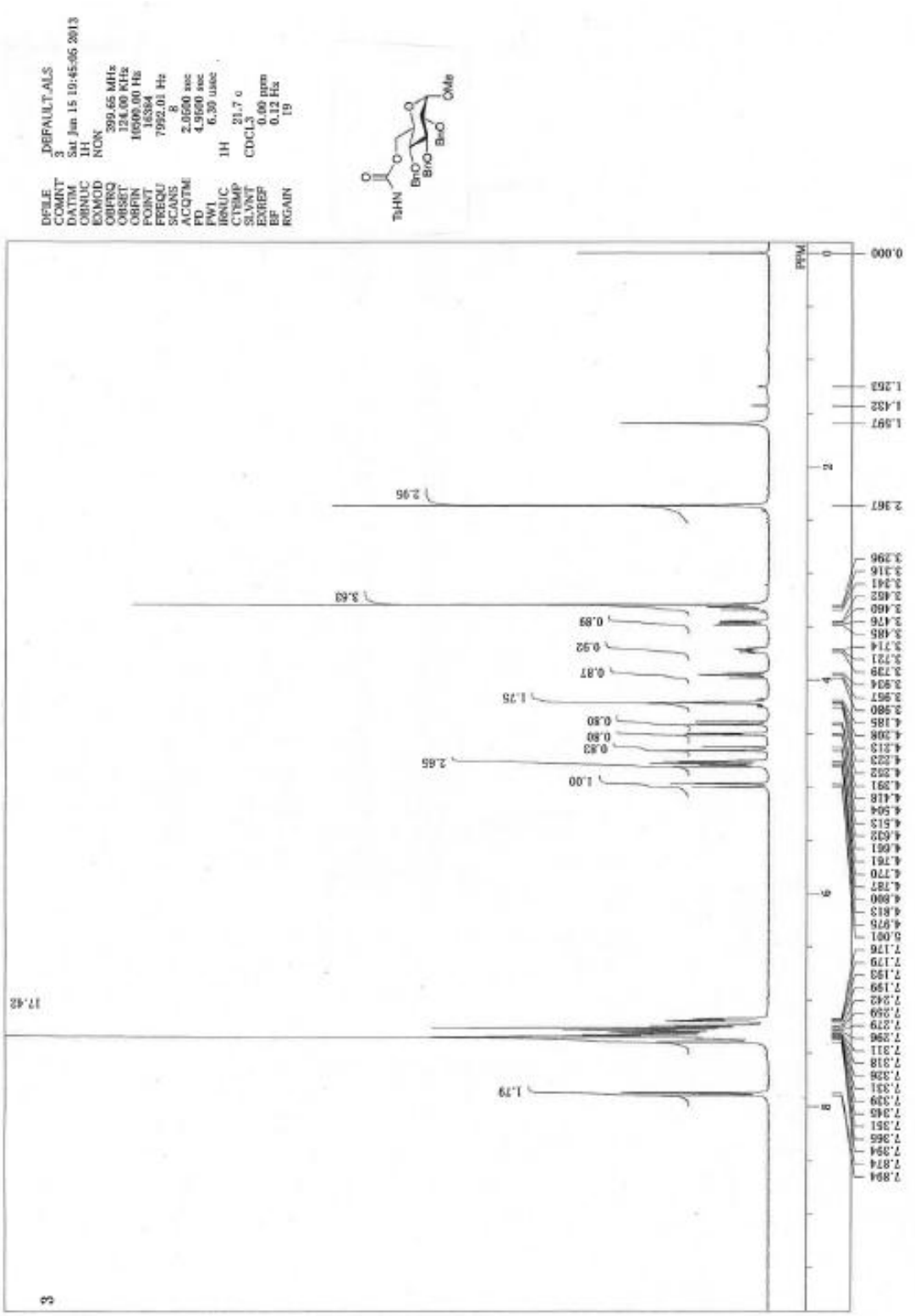
^{1}H-NMR of **9b**


DEFAULT.ALS
Sat Jun 15 20:31:59 2013
1H
399.65 MHz
124.00 KHz
10500.00 Hz
16384
7992.01 Hz
8
2.0500 sec
4.5500 sec
6.30 usec
1H
21.4 c
CDCl3
0.00 ppm
0.12 Hz
20
Ph
NHBz
PPM
0.000
1.391
1.580
2.457
3.006
6.914
6.962
7.162
7.179
7.201
7.234
7.260
7.332
7.353
7.902
7.922
5.92
2.97
2.00
1.99
2.55
1.77
1.92
5

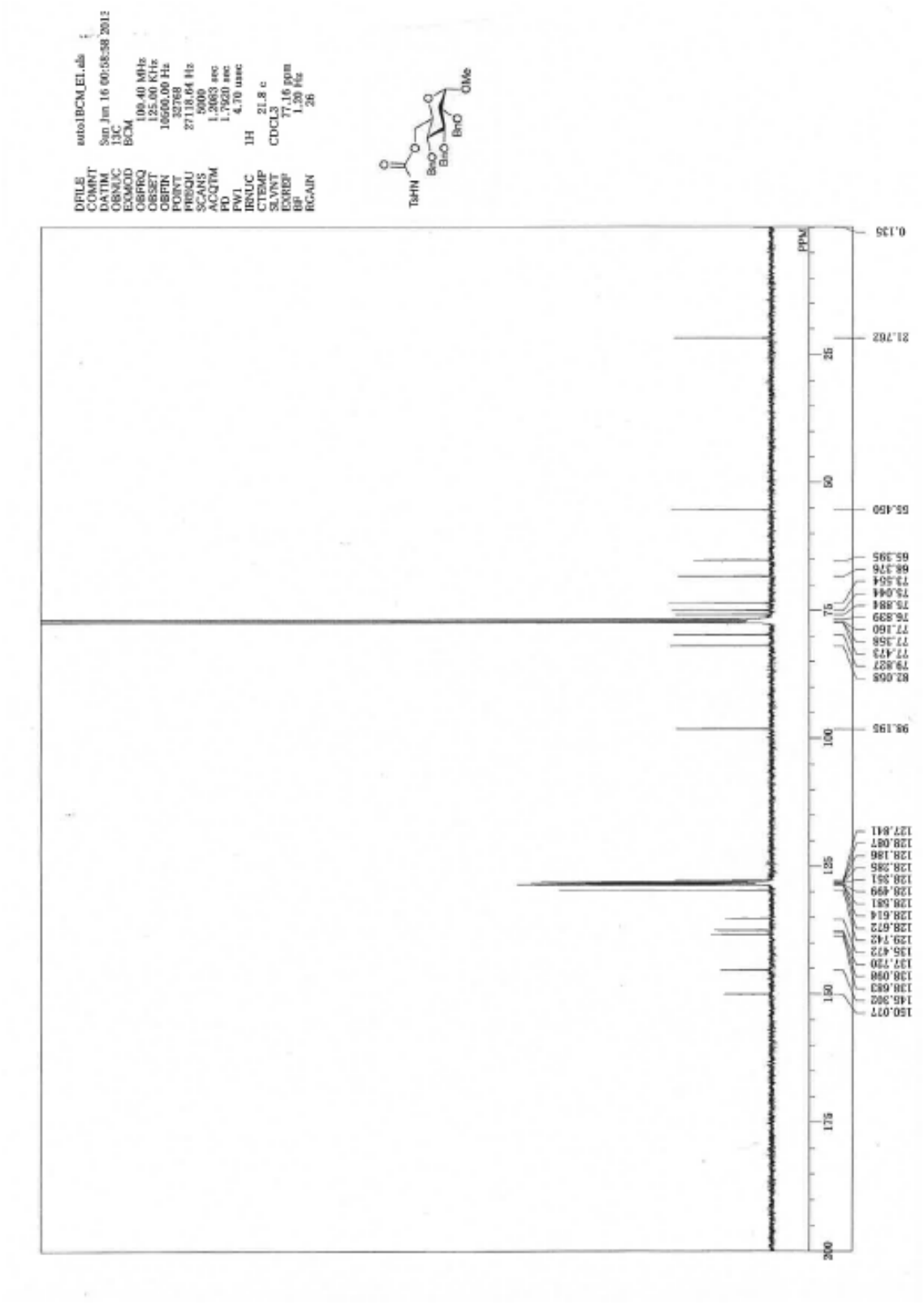
^{13}C-NMR of **9b**


DPRLE autoIBCM_03.als
COMNT
DATIM Sun Jun 16 09:36:51 2013
OBNUC 13C
EXMOD BCM
OBFRQ 160.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FRQU 27118.64 Hz
SCANS 3000
ACQTM 1.2083 sec
PD 1.7929 sec
PW1 4.70 usec
BNUC 1H
CTEMP 20.7 c
SLVNT CDCl3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 26
Ph
O
NHBn
0.143
21.844
26.208
45.506
76.847
77.160
77.366
77.481
85.771
126.729
128.219
128.458
129.685
130.490
136.867
136.501
146.014
149.188

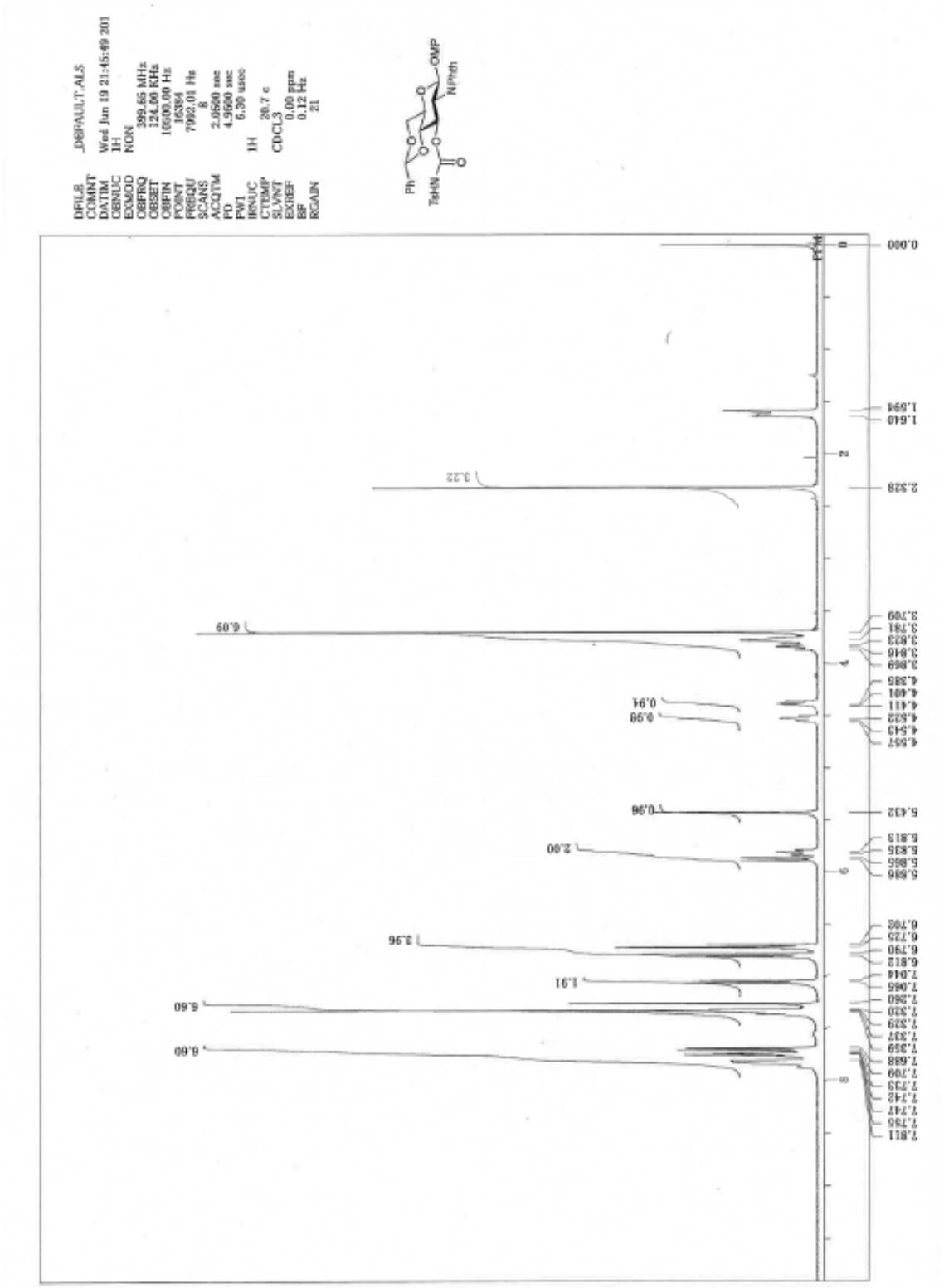
^{1}H-NMR of **10b**


DEFAULT.ALS
Sat Jan 15 19:45:05 2013
1H
399.65 MHz
124.00 KHz
16000.00 Hz
16384
7992.01 Hz
8
2.0500 sec
4.9560 sec
6.50 usec
1H
21.7 c
CDCl3
0.00 ppm
0.12 Hz
19
TsHN
BnO
BnO
BnO
BnO
OMe
2.96
3.63
0.89
0.92
0.87
1.75
0.80
0.80
0.83
2.65
1.00
17.42
1.79
PPM

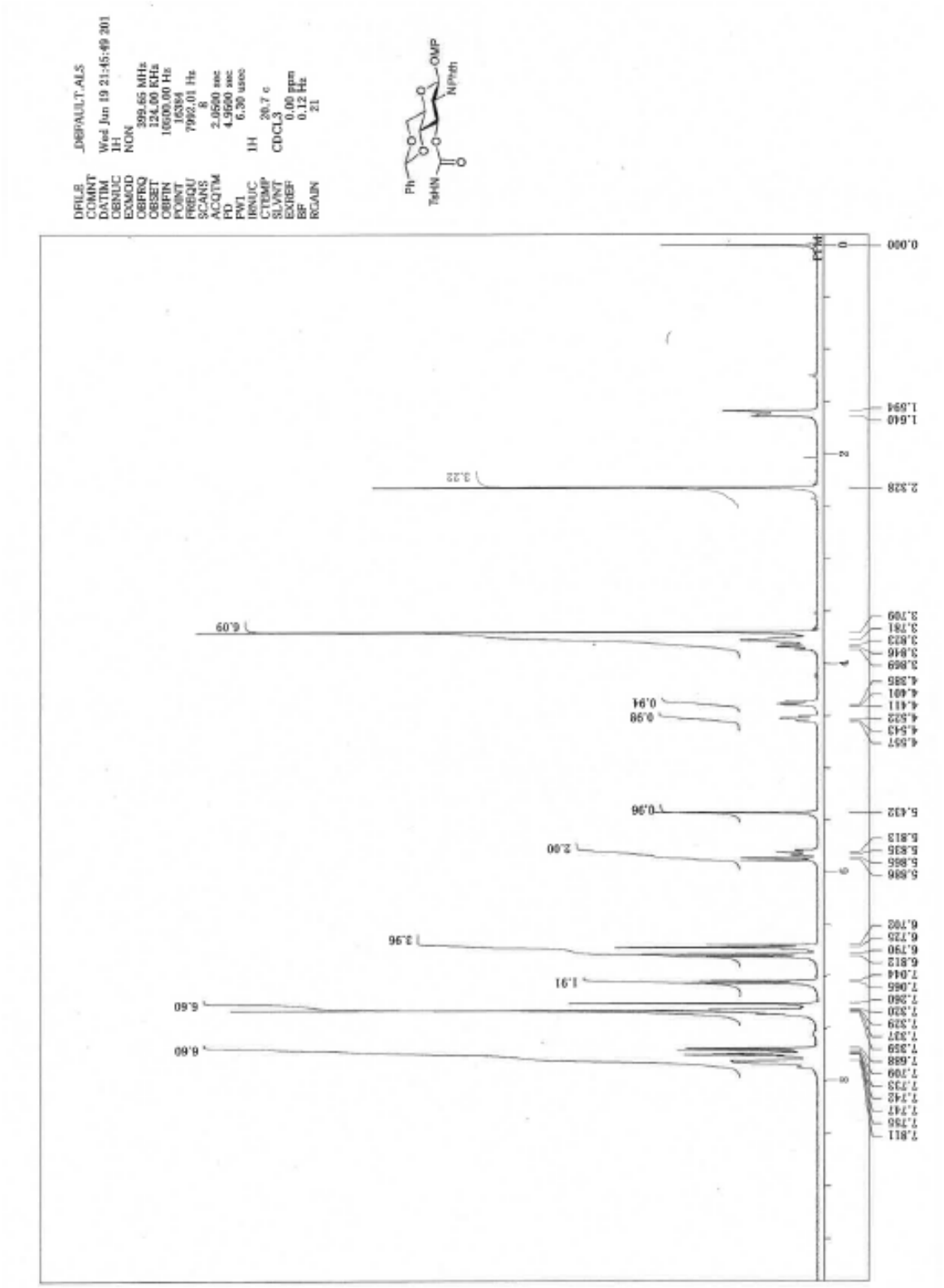
^{13}C-NMR of **10b**



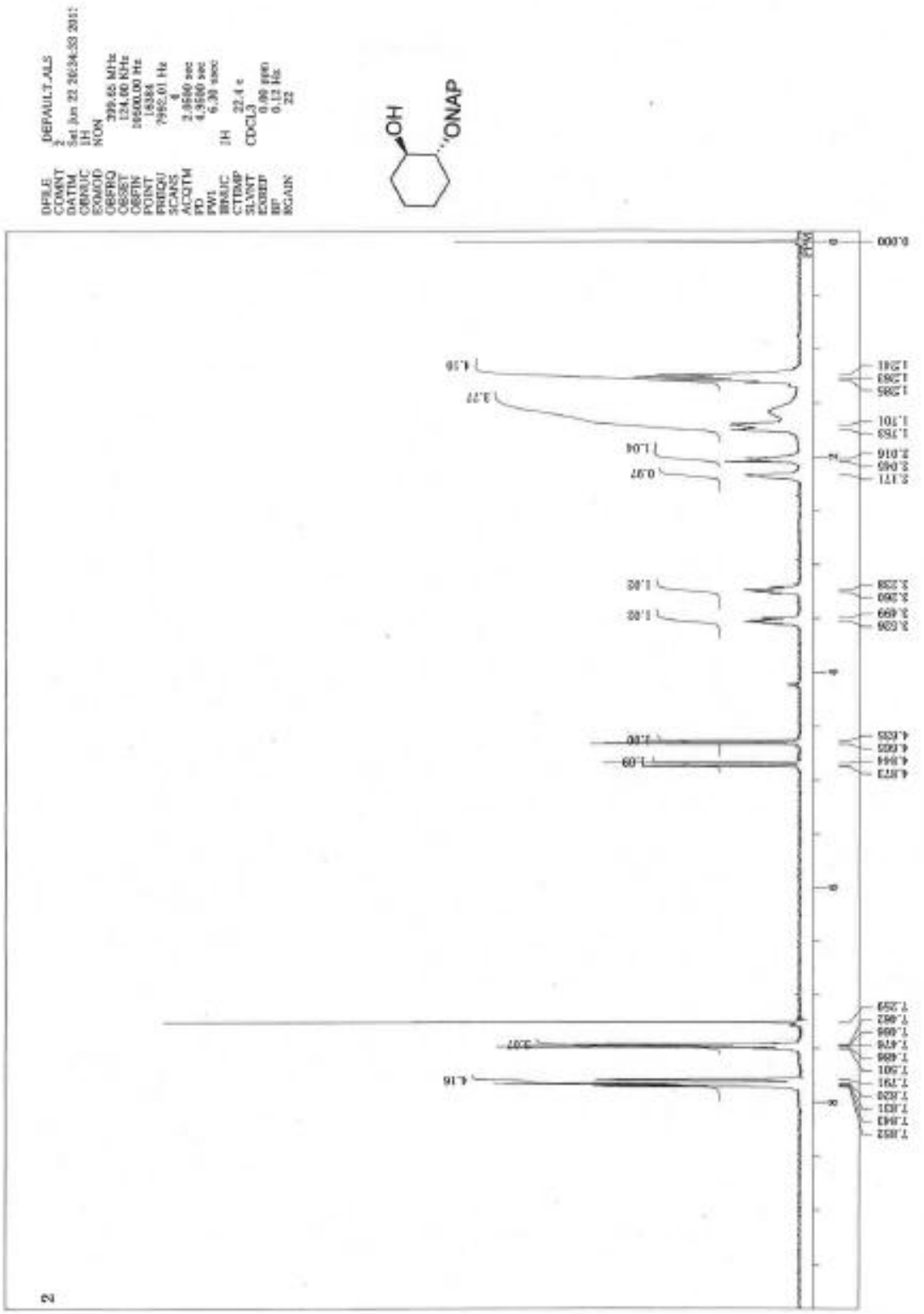
^{1}H-NMR of **11b**


DATA JDEFAULT.ALS
COMMENT
DATIM Wed Jun 19 21:45:49 201
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10000.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21
OMP
NPhth
Ph
TsHN
PPM
0.000
1.594
1.610
2.328
3.709
3.781
3.823
3.846
3.869
4.385
4.401
4.411
4.522
4.543
4.557
5.432
5.813
5.836
5.855
5.886
6.702
6.725
6.790
6.812
7.044
7.065
7.260
7.320
7.329
7.337
7.359
7.688
7.709
7.735
7.742
7.747
7.756
7.811
3.22
6.09
0.94
0.98
0.96
2.00
3.96
1.91
5.60
6.60

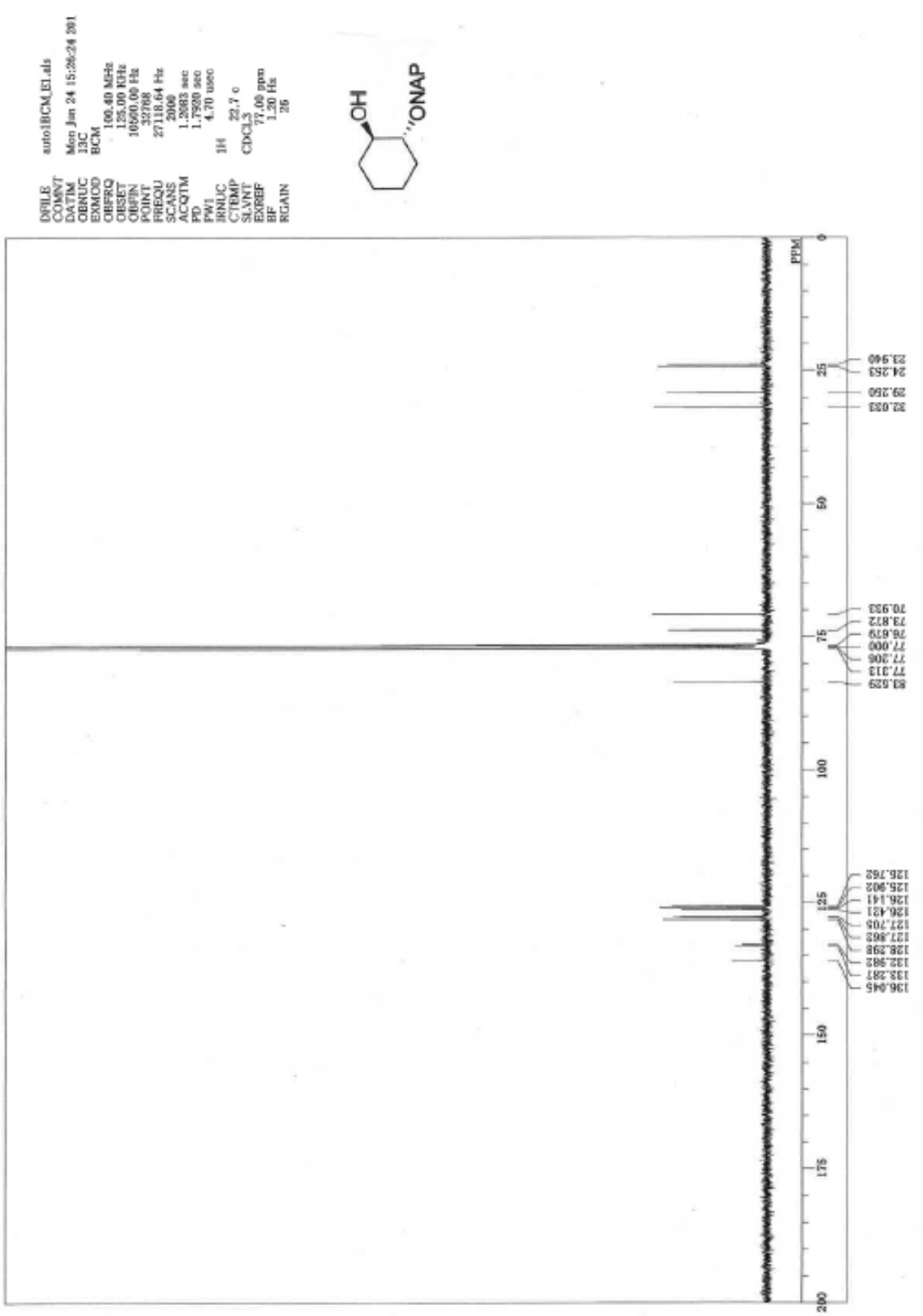
^{13}C-NMR of **11b**



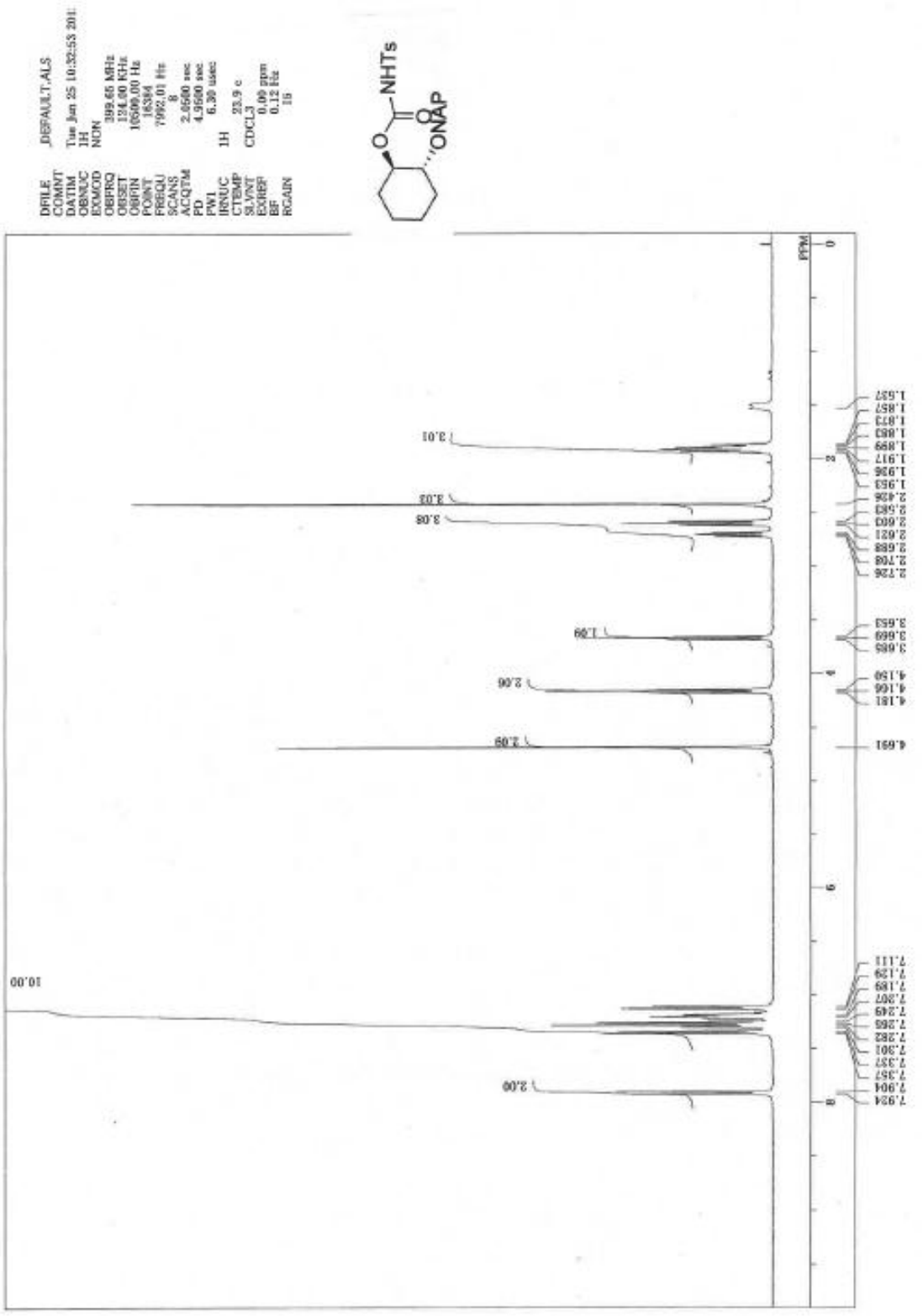
^{1}H-NMR of **12a**



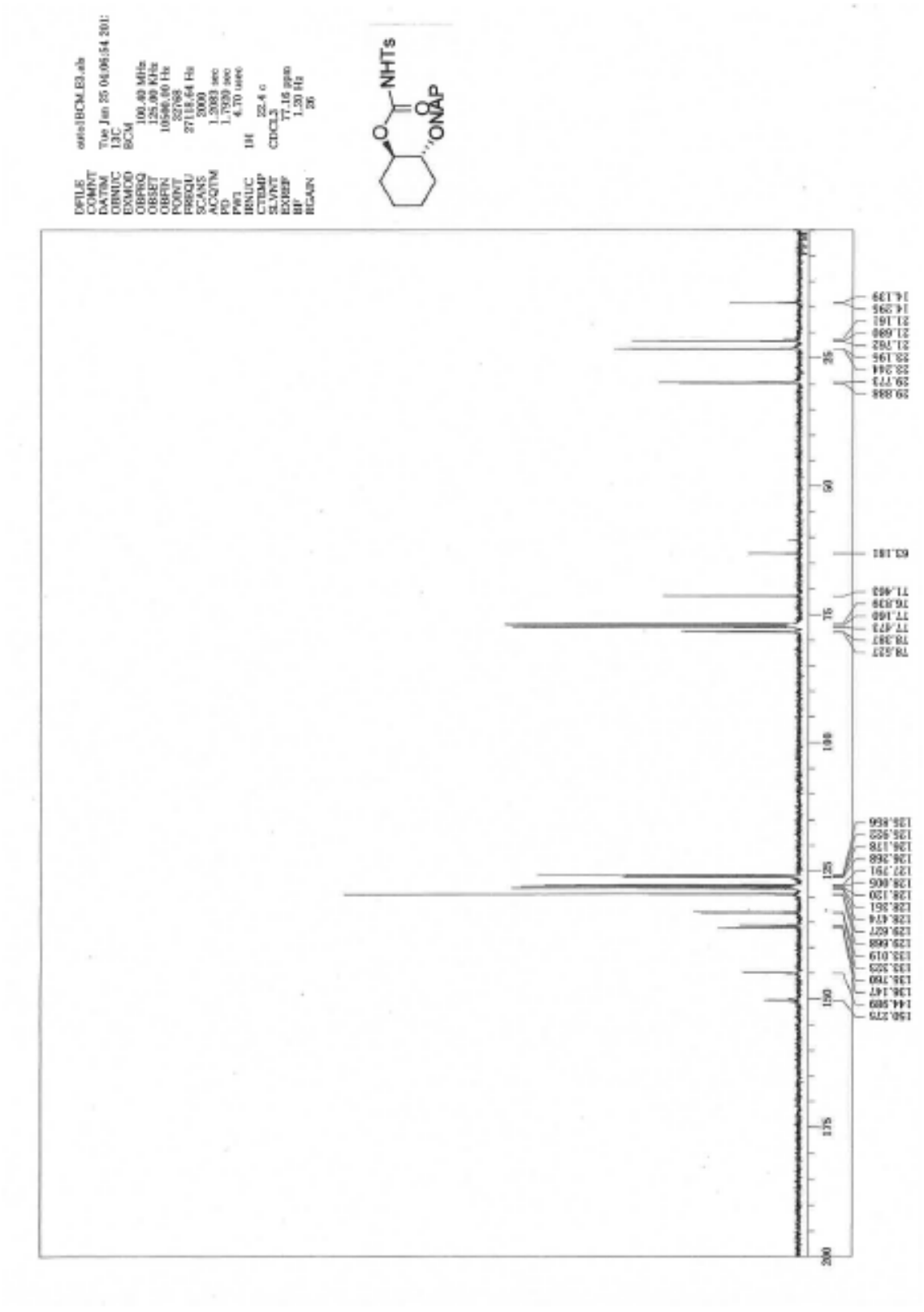
^{13}C-NMR of **12a**



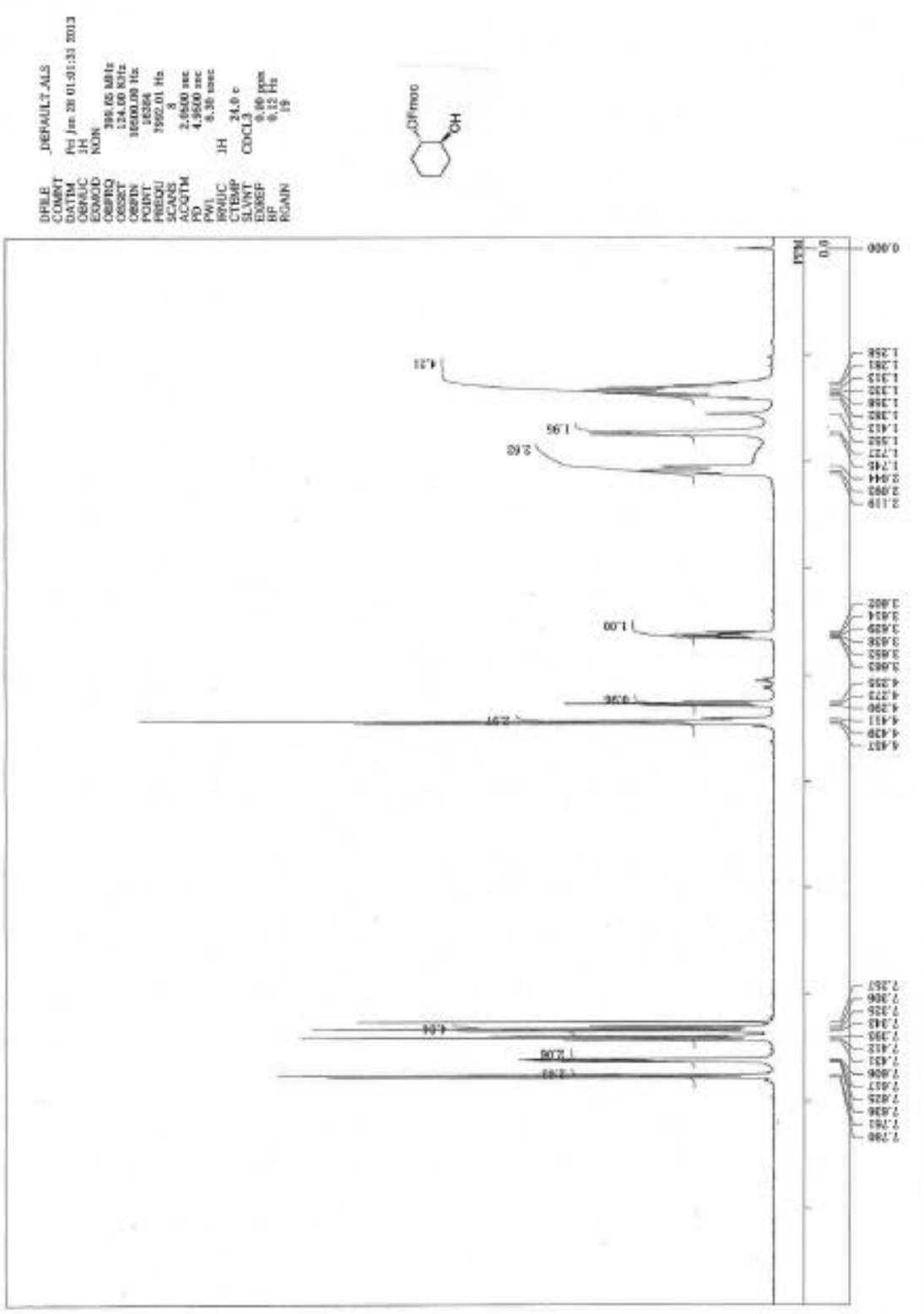
^{1}H-NMR of **12b**



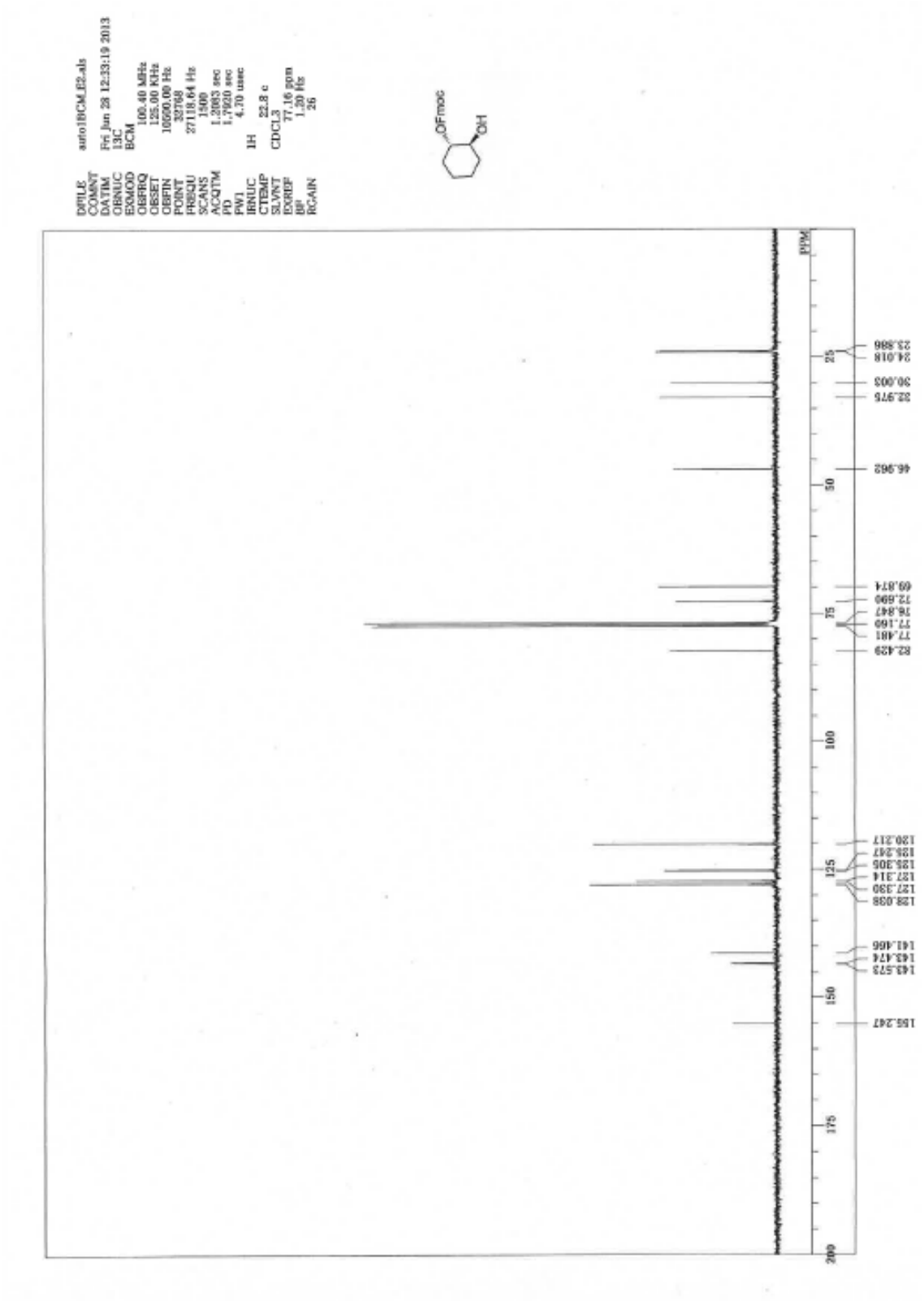
^{13}C-NMR of **12b**



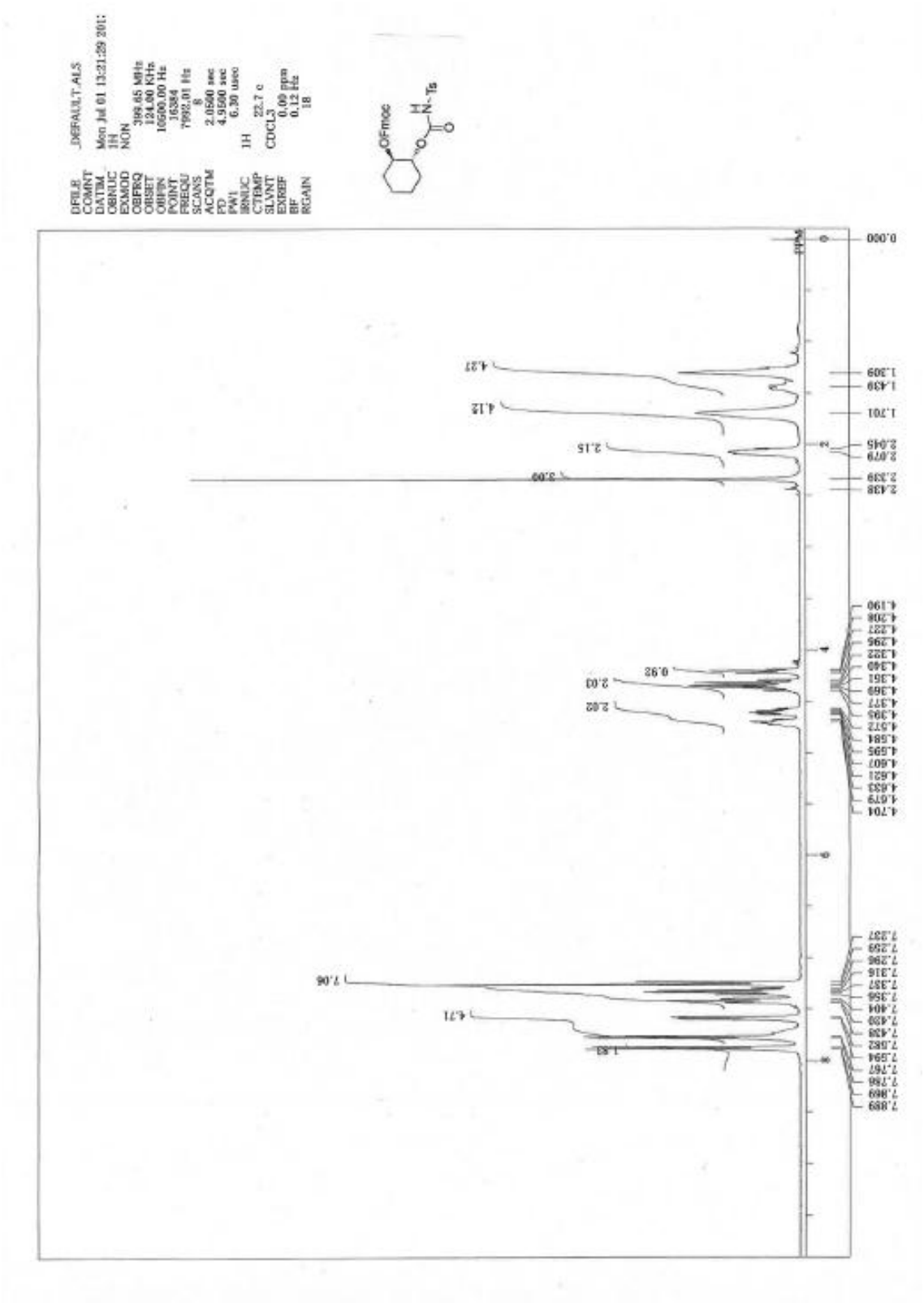
^{1}H-NMR of **13a**



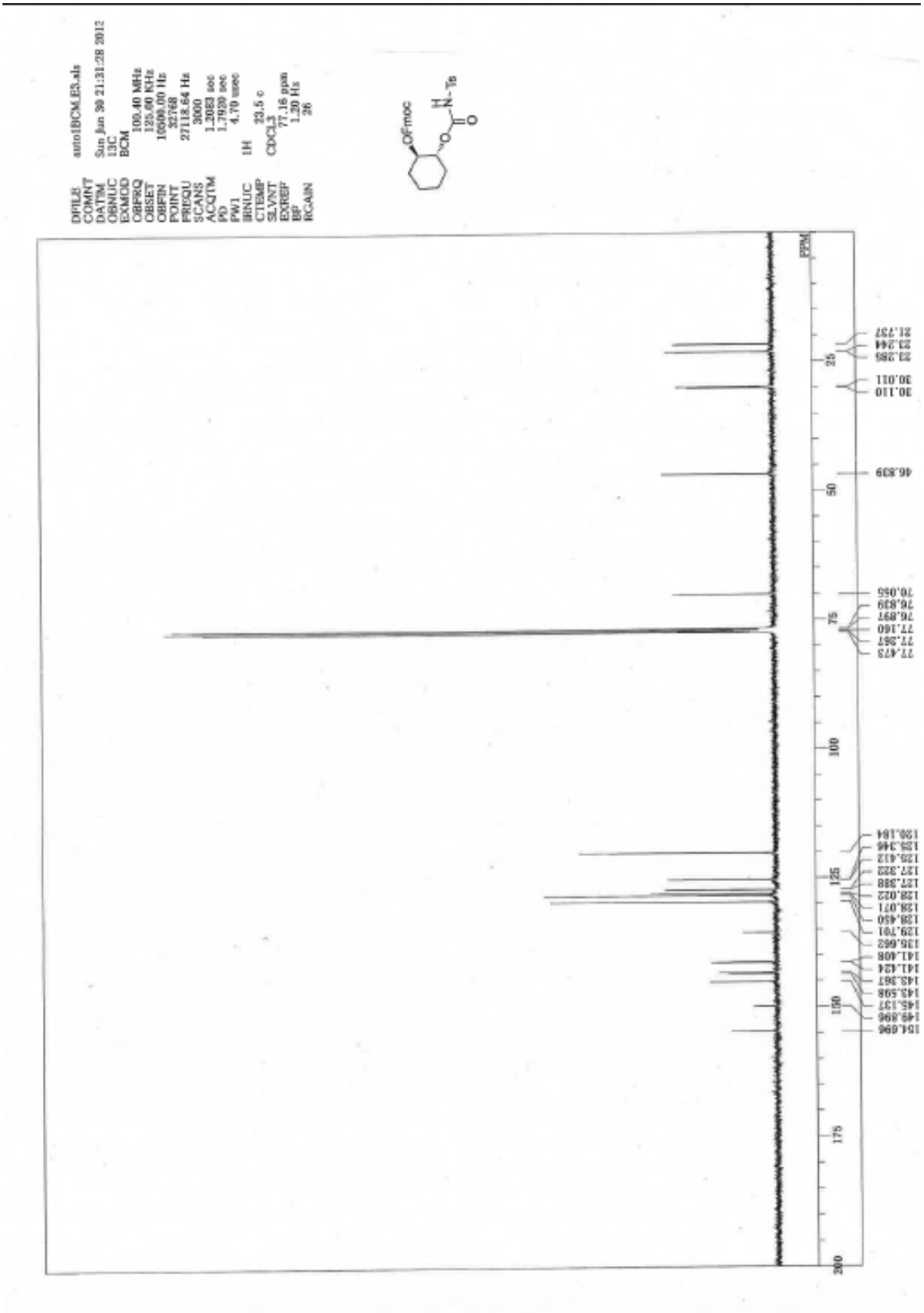
^{13}C-NMR of **13a**



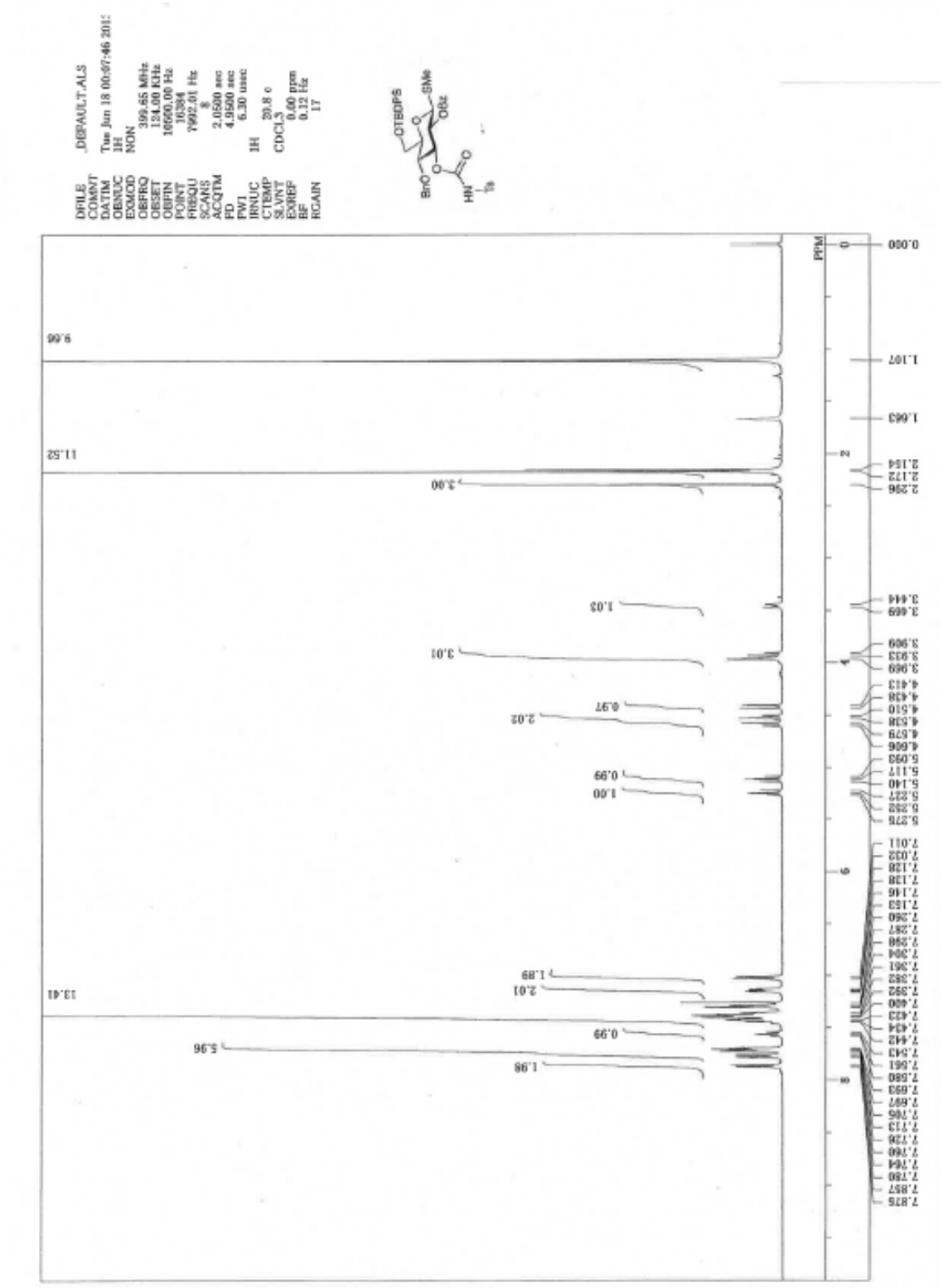
^{1}H-NMR of **13b**


DEFAULT.ALS
Mon Jul 01 13:21:29 201:
1H
NON
399.65 MHz
124.00 KHz
16000.00 Hz
16384
7992.01 Hz
8
2.0500 sec
4.9500 sec
6.30 usec
1H
22.7 c
CDCL3
0.09 ppm
0.12 Hz
18
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
OPmse
H
N-Ts
4.27
4.12
2.15
3.09
0.92
2.03
2.02
7.06
4.71
1.83

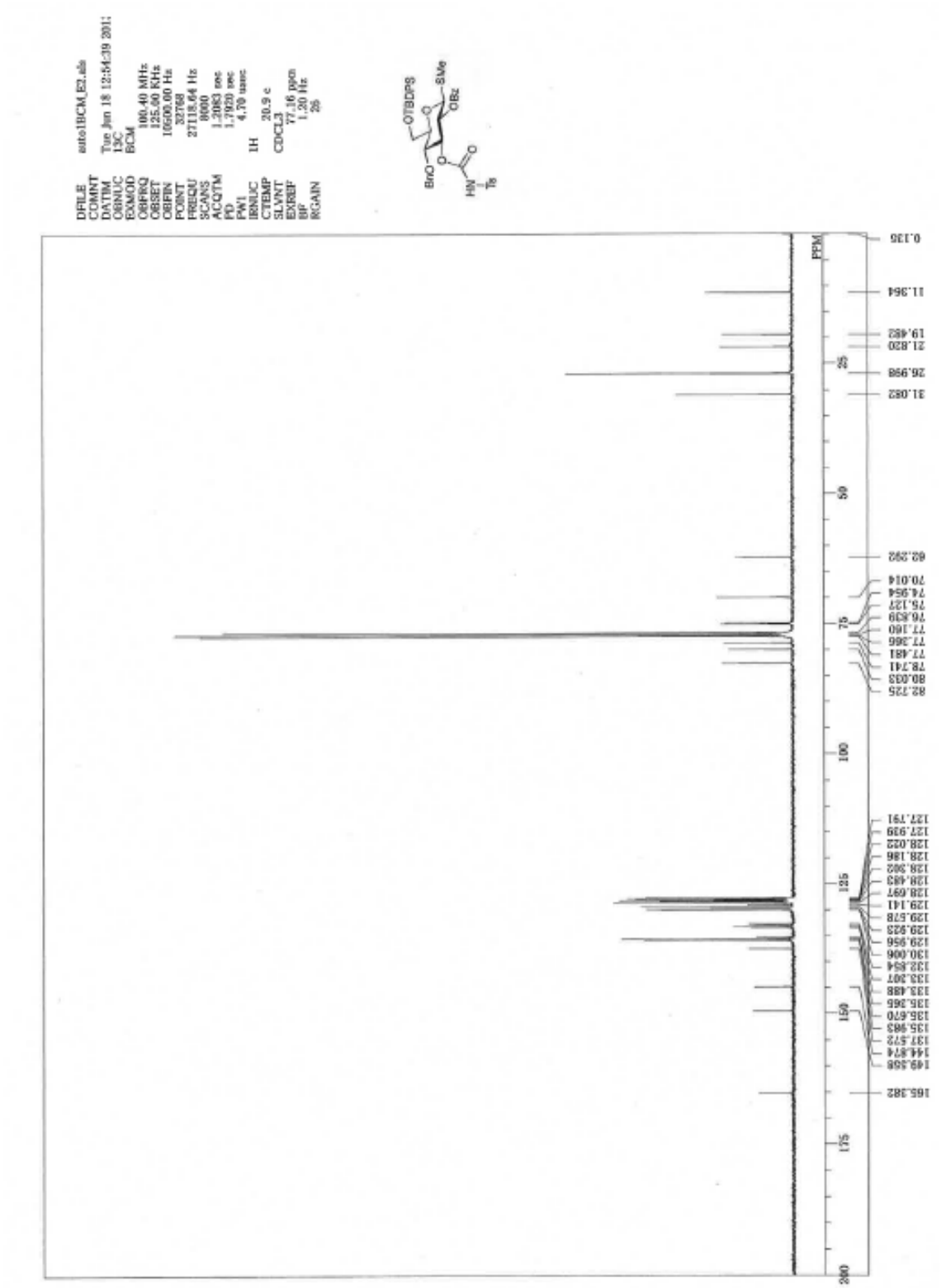
13C-NMR of 13b



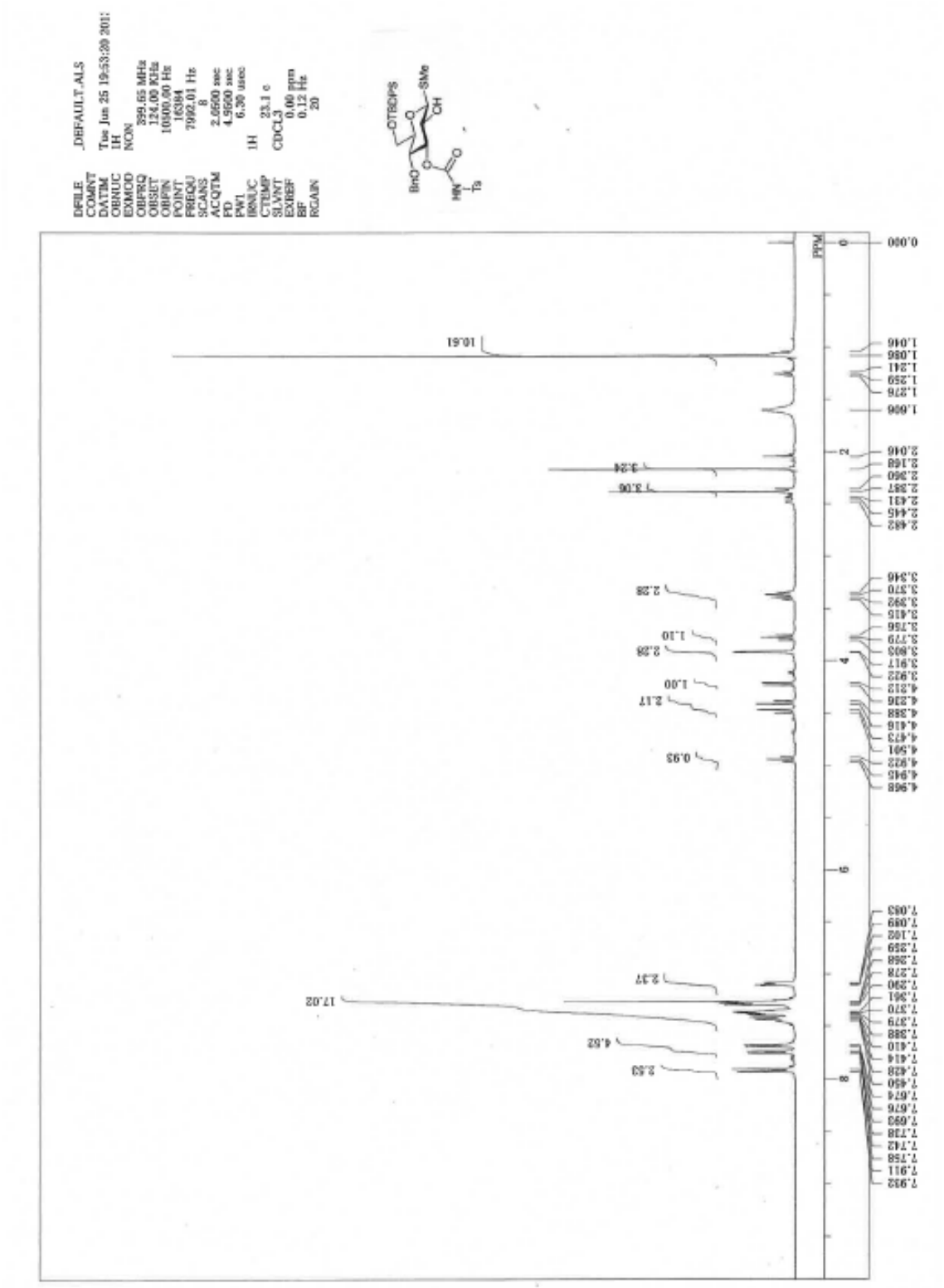
^{1}H-NMR of **15**


OTBDPS
SiMe
OBz
BnO
HN
Ph
PPM
9.66
11.52
3.00
1.03
3.01
0.97
2.02
0.99
1.00
1.89
2.01
13.41
0.99
5.96
1.98

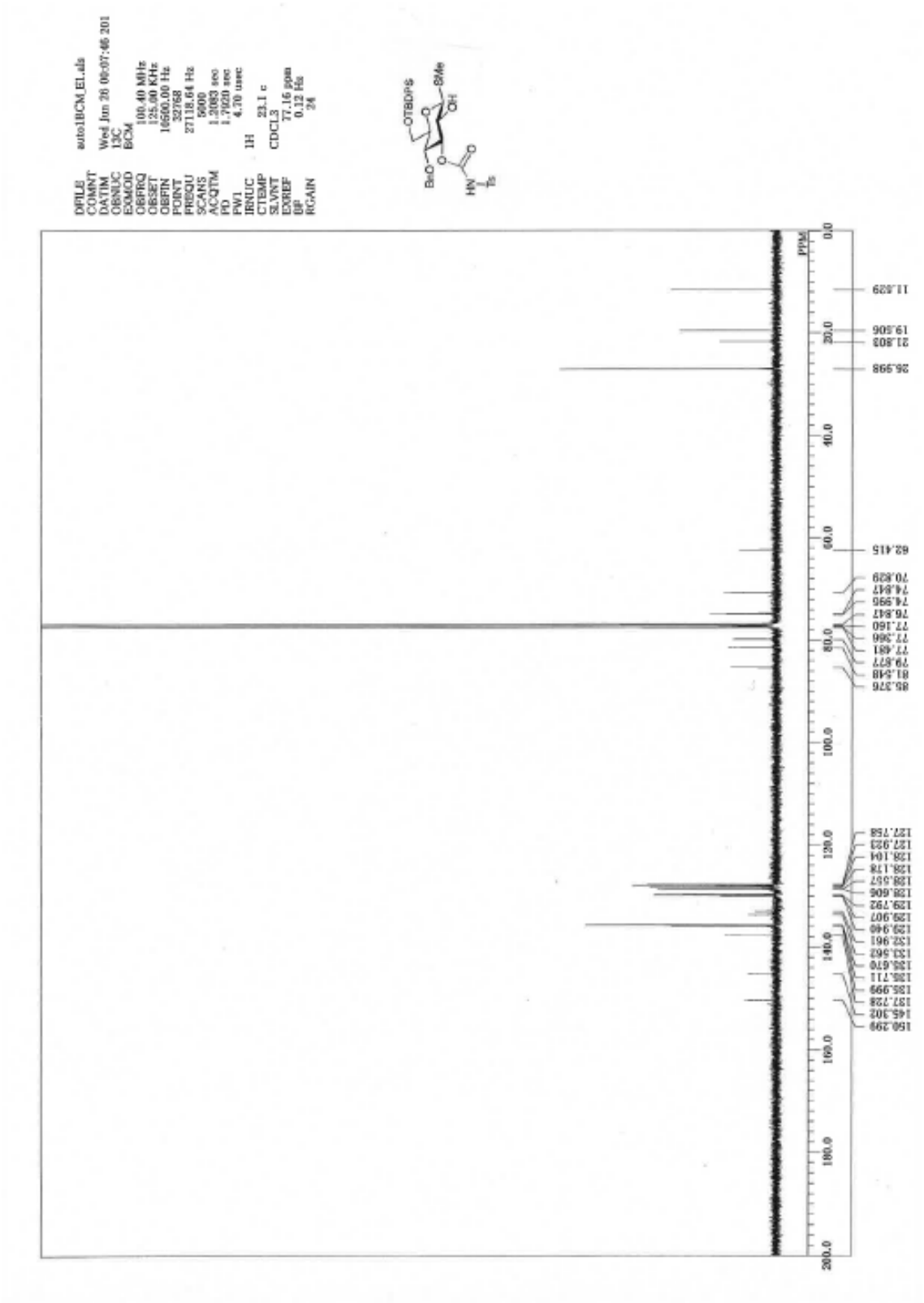
^{13}C-NMR of **15**


DATE auto18CM_E2..als
COMNT
DATIM Tue Jun 18 12:54:39 2013
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 8000
ACQTM 1.2083 sec
PD 1.7930 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 25
OTBDPS
SiMe
OBz
BnO
HN
Ts
PPM
0.136
11.364
19.482
21.820
26.958
31.082
60.292
70.014
74.954
75.127
76.839
77.160
77.366
77.481
78.741
80.033
82.725
127.791
127.939
128.022
128.186
128.302
128.483
128.697
129.141
129.578
129.925
129.956
130.006
132.854
133.307
133.488
135.365
135.670
135.983
137.572
144.874
149.358
165.382

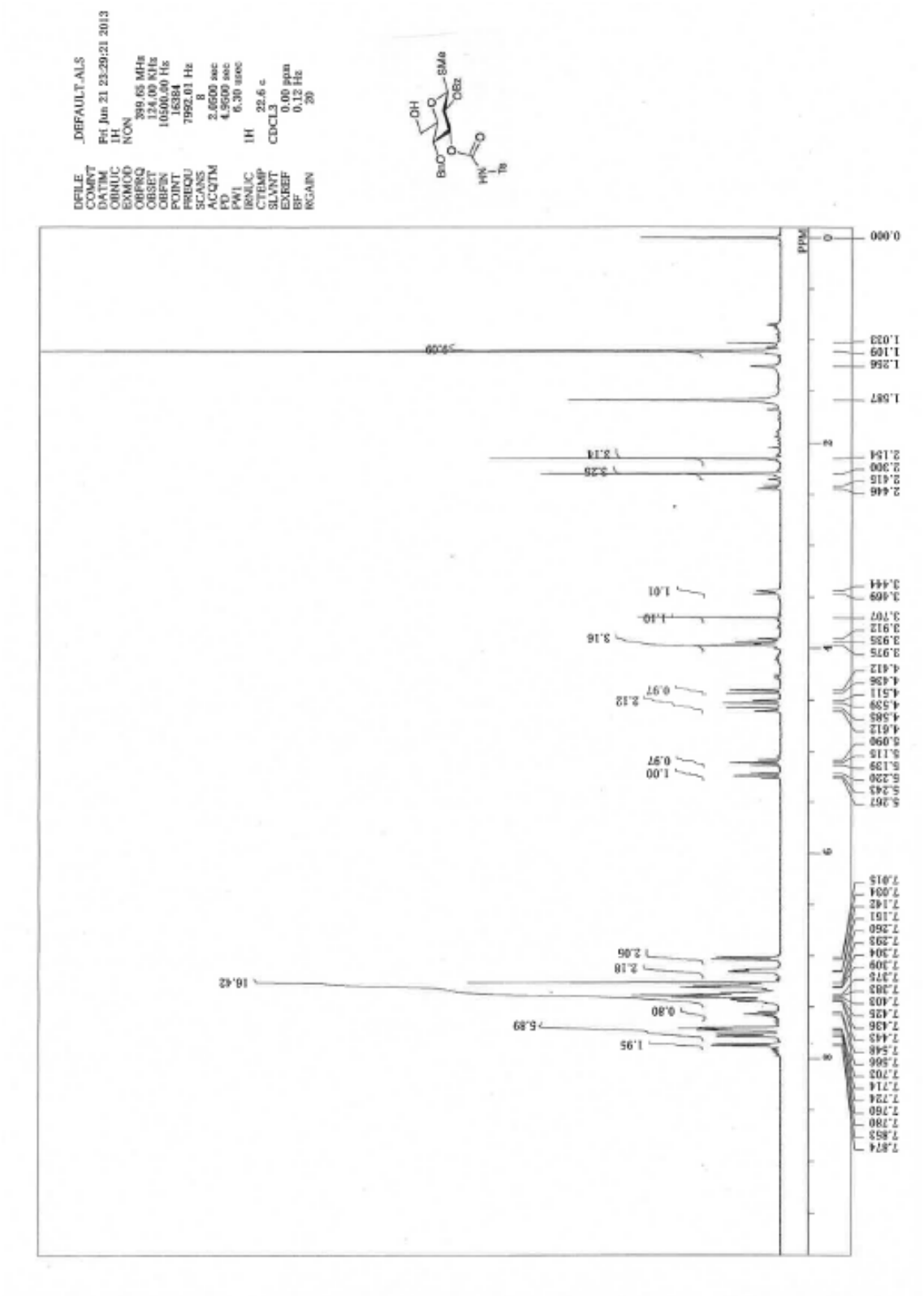
^{1}H-NMR of **16**


DFILE JDEFAULT.ALS
COMNT
DATIM Tue Jun 25 19:53:39 201
OBNUC 1H
EXMOD NON
OBSFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10900.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
OTBDPS
SMe
OH
BnO
HN
Ts
PPM
10.61
3.24
3.06
2.28
1.10
2.28
1.00
2.17
0.93
2.37
17.02
4.62
2.50

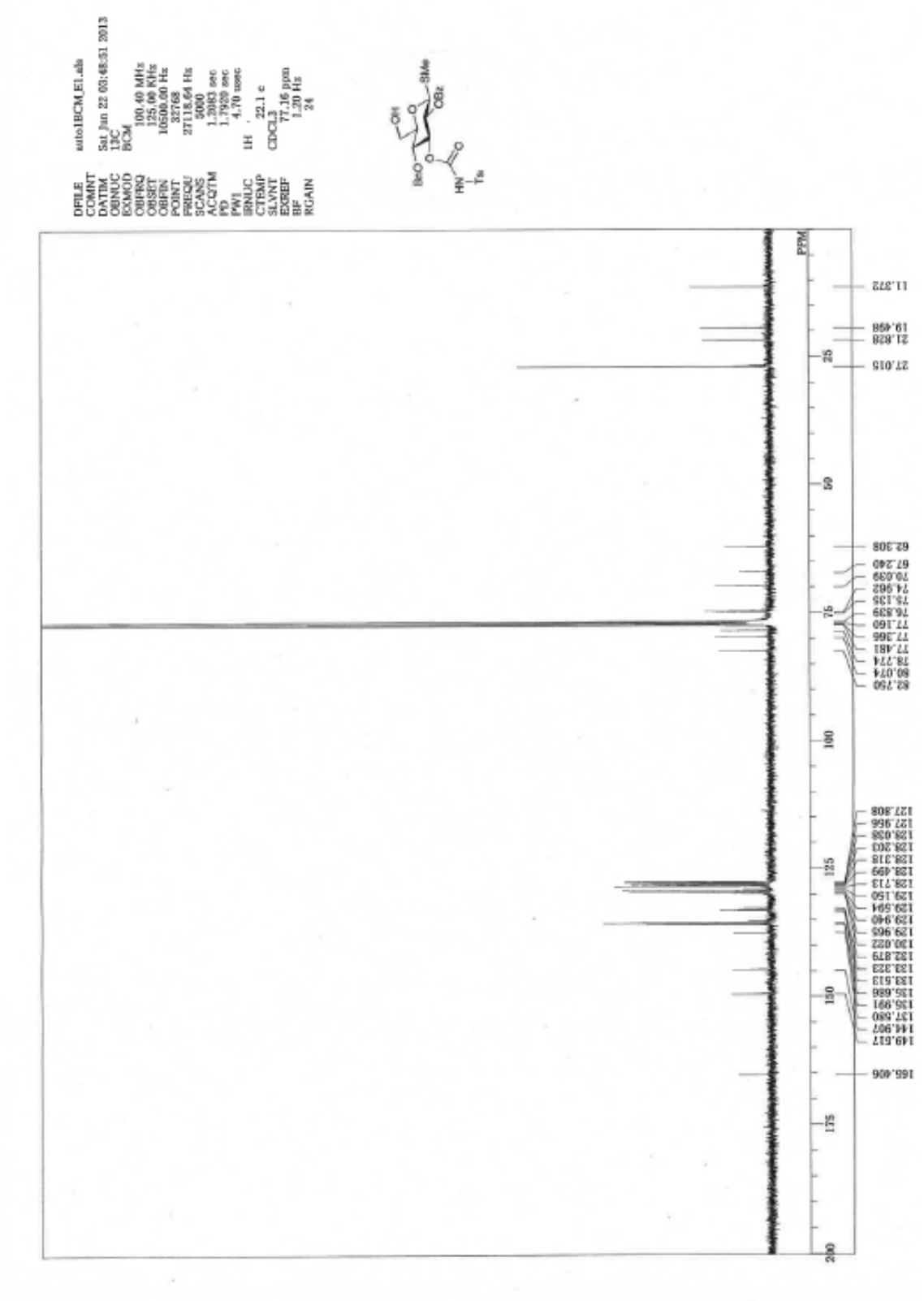
^{13}C-NMR of **16**


PPM
11.629
19.506
21.803
26.998
62.416
70.829
74.847
74.996
76.847
77.160
77.360
77.481
79.877
81.548
86.376
127.758
127.923
128.104
128.178
128.357
128.606
128.792
129.907
129.946
132.961
133.562
135.670
135.711
135.999
137.728
145.302
150.299

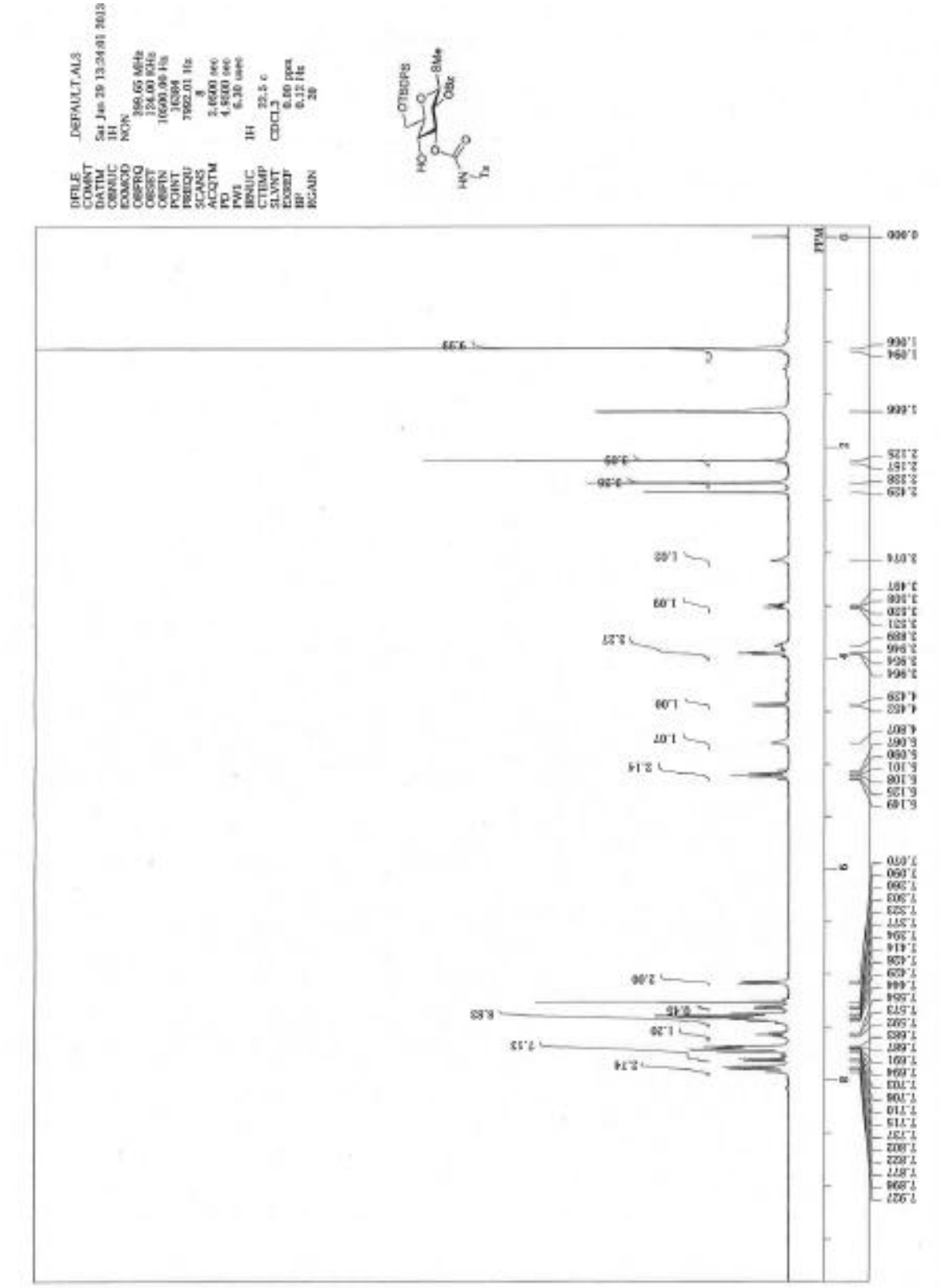
^{1}H-NMR of **17**


DEFAULT.ALS
Fri Jun 21 23:29:21 2013
1H
NON
399.65 MHz
124.00 KHz
10500.00 Hz
16384
7992.01 Hz
8
2.6500 sec
4.5600 sec
6.30 usec
1H
22.6 c
CDCL3
0.09 ppm
0.12 Hz
20
DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN
OH
BnO
OBz
HN
Tr
PPM
0.000
1.023
1.109
1.256
1.587
2.154
2.300
2.415
2.446
3.444
3.469
3.707
3.912
3.935
3.975
4.412
4.436
4.511
4.539
4.585
4.612
5.090
5.118
5.139
5.230
5.243
5.267
7.015
7.034
7.142
7.151
7.260
7.295
7.304
7.309
7.375
7.383
7.403
7.425
7.436
7.445
7.548
7.566
7.703
7.714
7.724
7.760
7.780
7.853
7.874
5.939
3.14
3.25
1.01
1.10
3.16
0.97
2.12
0.97
1.00
2.06
2.18
16.42
0.80
5.89
1.95

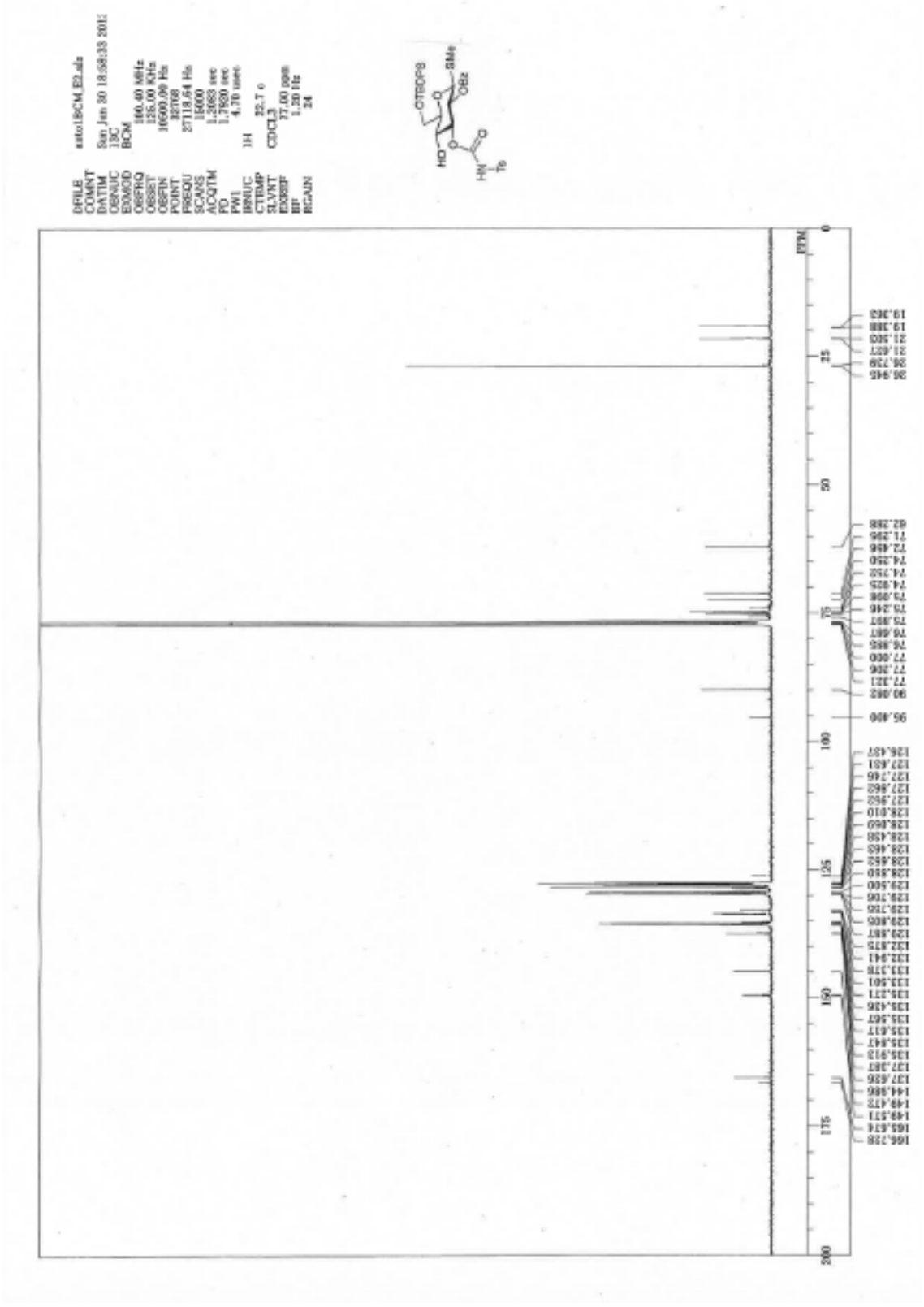
^{13}C-NMR of **17**


DPFILE auto18CM_E1.als
COMNT
DATIM Sat Jun 22 03:48:51 2013
OBNUC 13C
EXMOD 8CM
OBFRQ 100.49 MHz
OBSET 125.06 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 5000
ACQTM 1.3083 sec
PD 1.7939 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 22.1 c
SLVNT CDCl3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 24
OH
OBz
BnO
HN
Ts
PPM
11.372
19.498
21.828
27.015
62.308
67.240
70.099
74.962
75.135
76.839
77.160
77.366
77.481
78.774
80.074
82.790
127.808
127.966
128.038
128.303
128.318
128.499
128.713
129.150
129.594
129.940
129.965
130.022
132.879
133.323
133.513
135.688
135.991
137.690
144.907
149.617
166.406

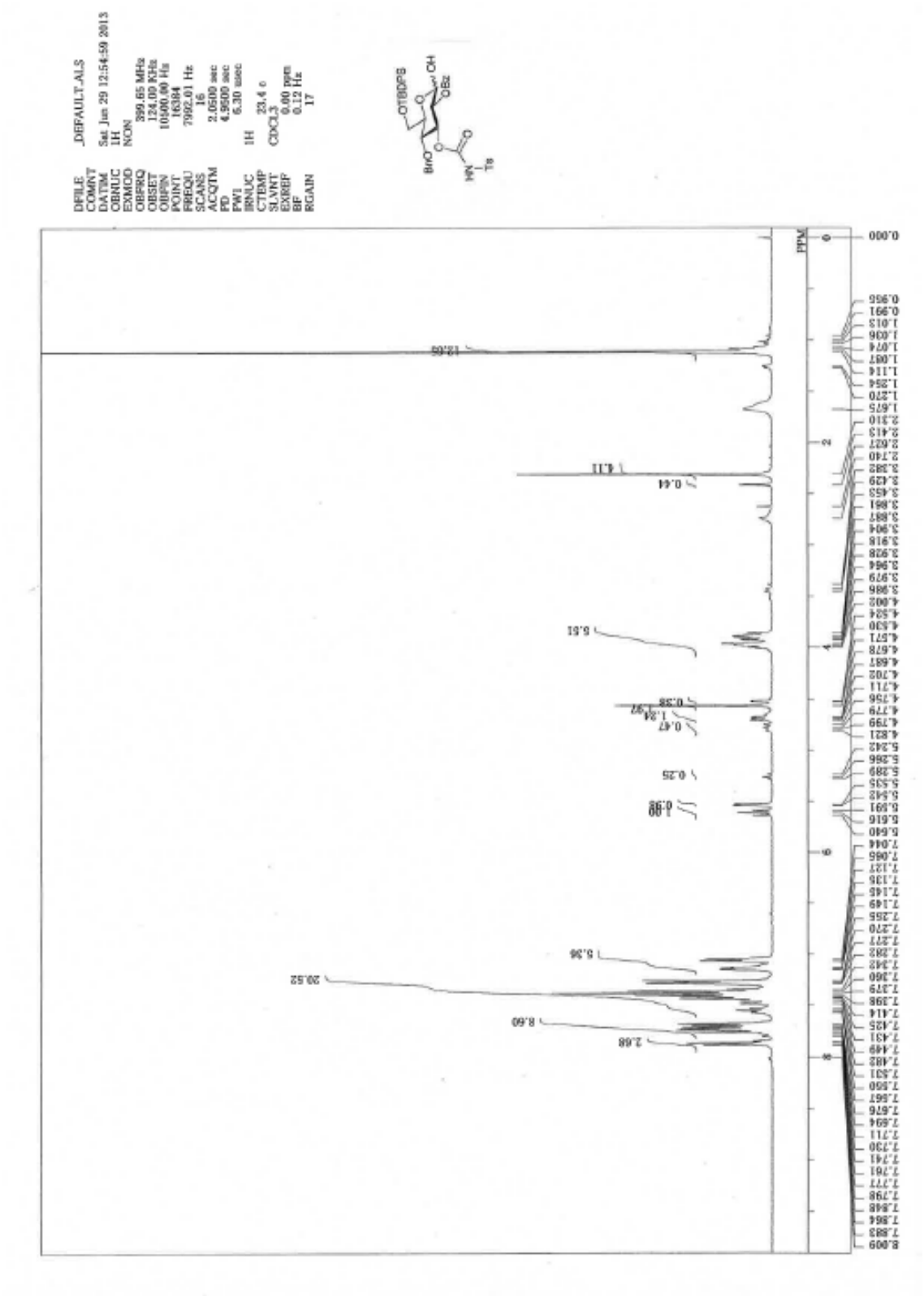
^{1}H-NMR of **18**



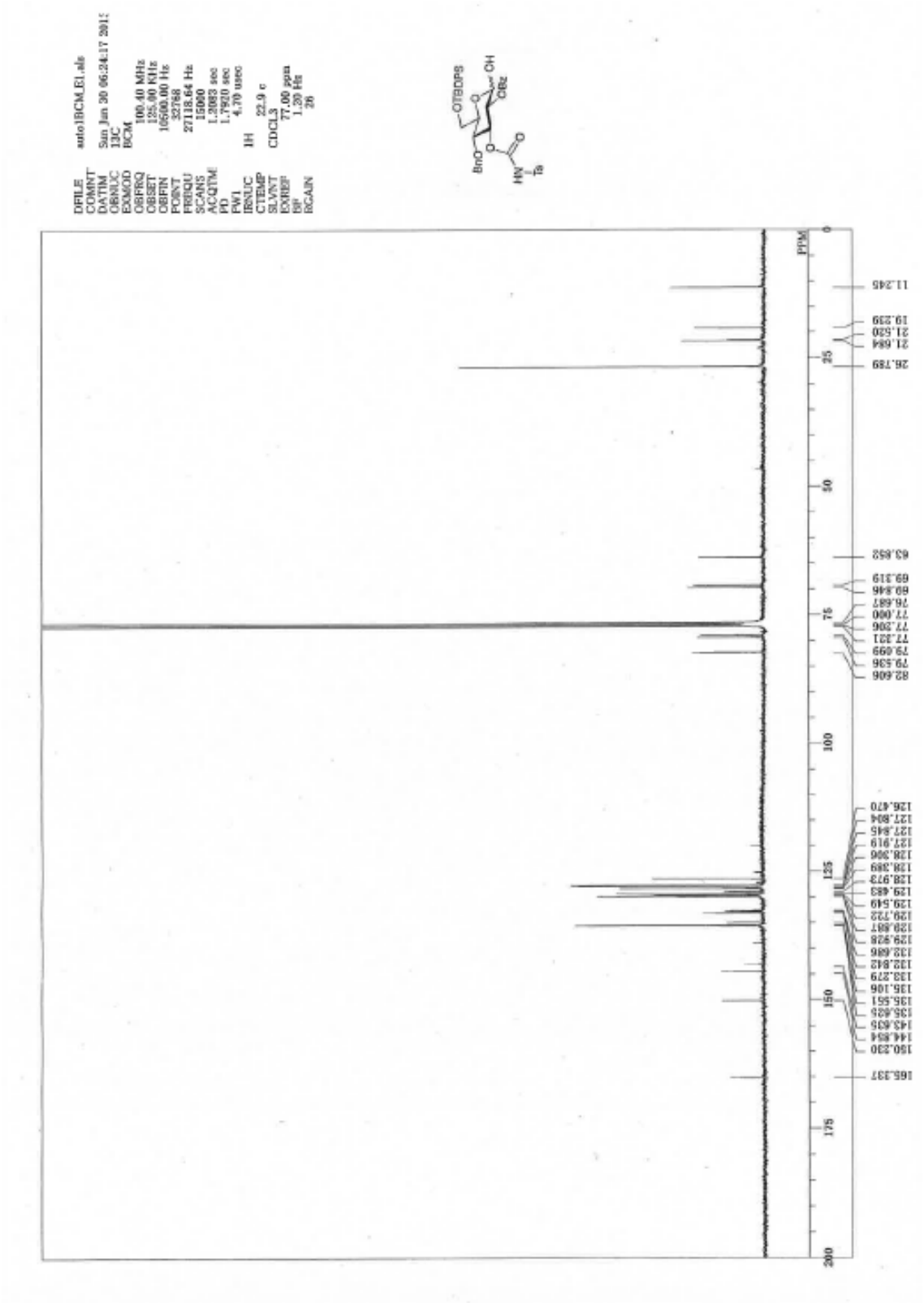
^{13}C-NMR of **18**



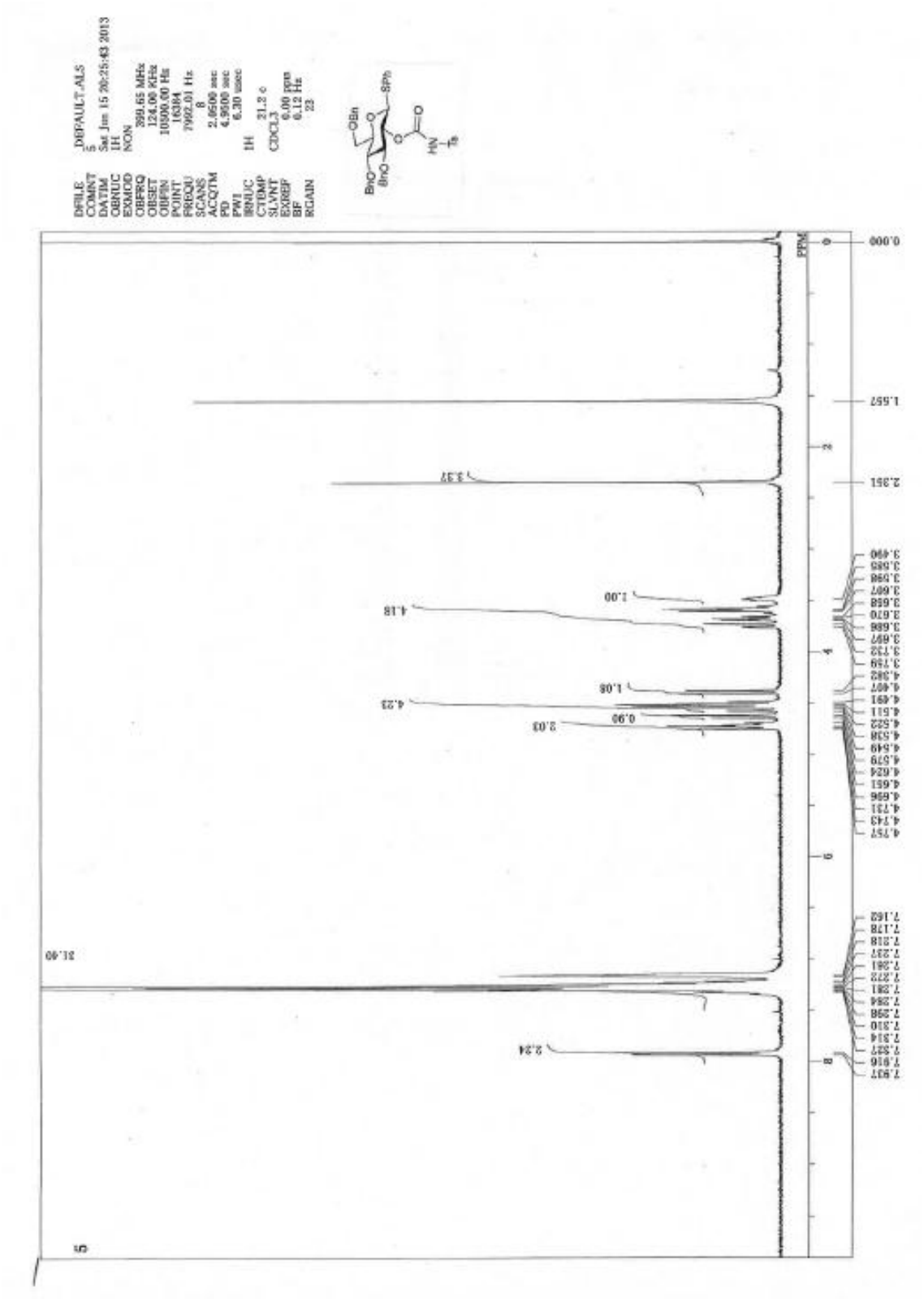
^{1}H-NMR of **19**


DEFAULT.ALS
Sat Jun 29 12:54:59 2013
1H
399.65 MHz
124.00 KHz
16384
7992.01 Hz
16
2.0509 sec
4.9500 sec
6.30 usec
23.4 c
CDCl3
0.00 ppm
0.12 Hz
17
OTBDPS
OH
OBz
BnO
NH
Ts
12.00
6.11
0.44
5.61
0.38
1.84
0.67
0.25
1.00
0.98
5.36
20.52
8.60
2.68
PPM

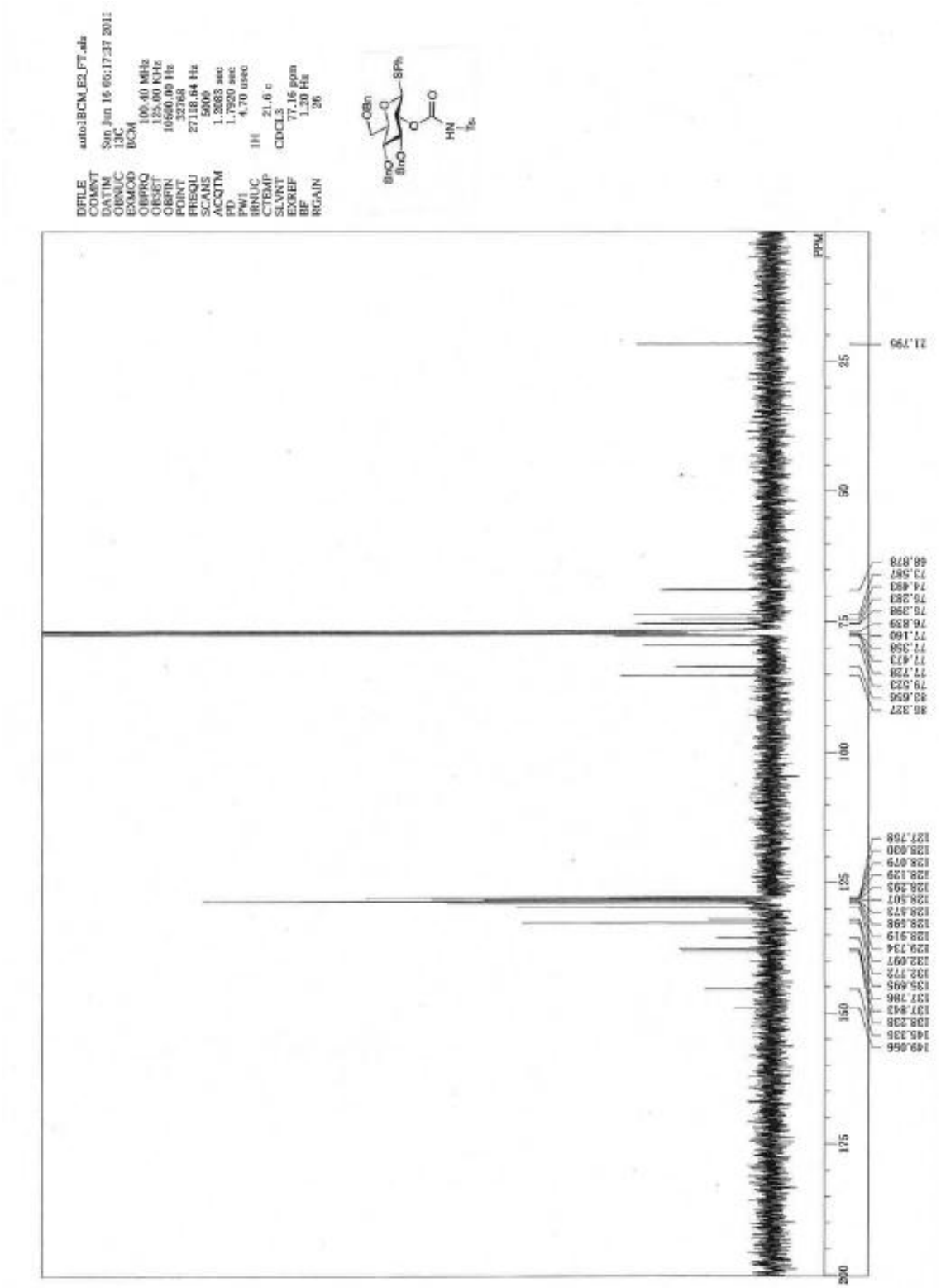
^{13}C-NMR of **19**


OTBDPS
OH
OBz
BnO
O
HN
Ts
PPM
11.246
19.239
21.520
21.684
26.789
63.652
69.319
69.846
76.687
77.000
77.206
77.321
79.099
79.536
82.606
126.470
127.804
127.845
127.919
128.306
128.389
128.979
129.483
129.549
129.722
129.887
129.928
132.686
132.842
133.279
135.106
135.551
135.625
143.635
144.854
150.230
166.337

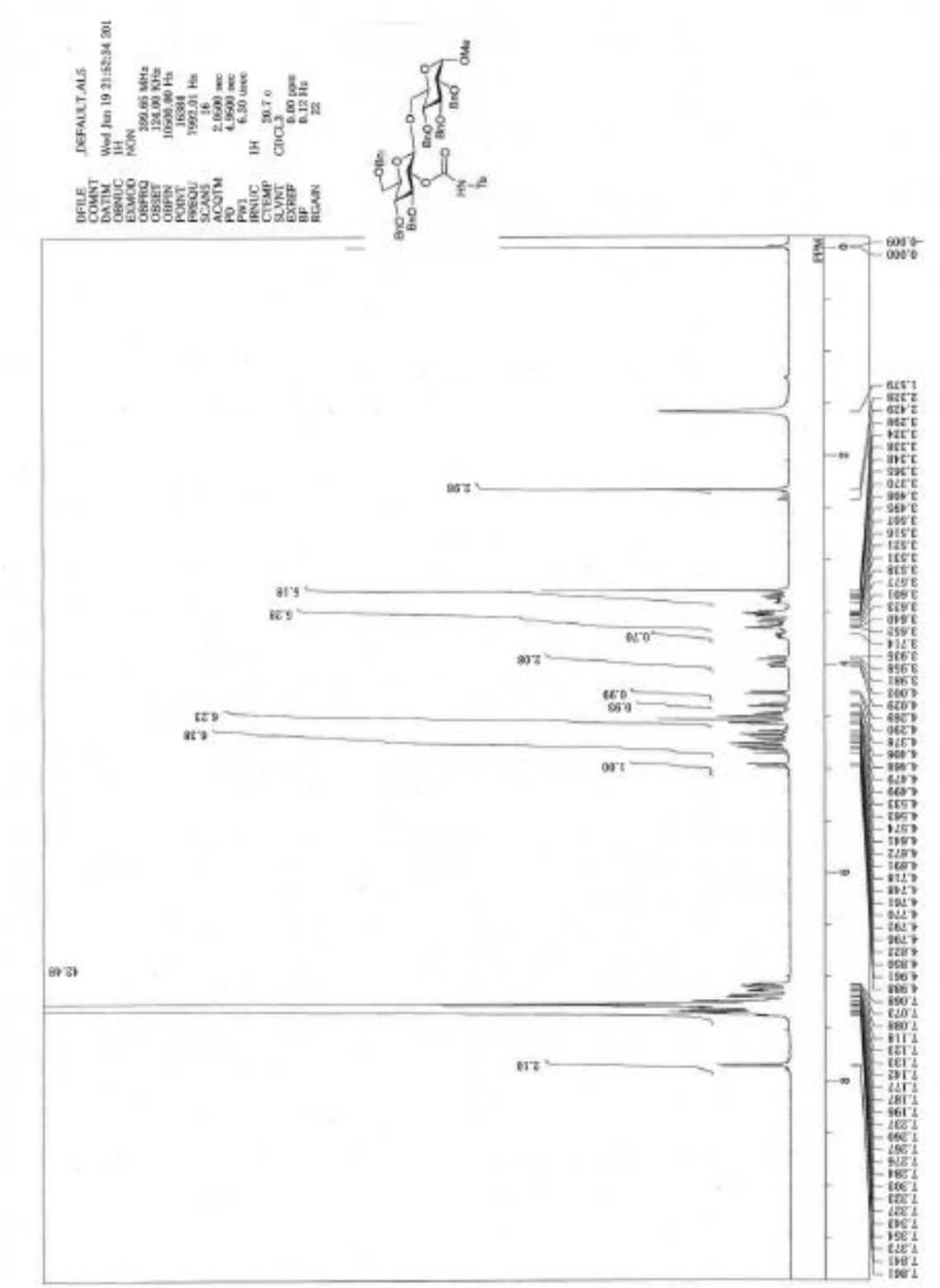
^{1}H-NMR of **20**


DEFAULT.AL5
5
Sat Jun 15 20:25:43 2013
1H
NON
399.65 MHz
124.00 KHz
10500.00 Hz
16384
7992.01 Hz
8
2.6600 sec
4.9500 sec
6.30 usec
1H
21.2 c
CDCl3
6.00 ppm
0.12 Hz
23
OBn
BnO
OBn
NH
Ts
PPM
0.000
1.557
2.351
3.990
3.969
3.958
3.697
3.658
3.670
3.686
3.697
3.732
3.759
4.382
4.697
4.691
4.511
4.522
4.538
4.549
4.579
4.624
4.651
4.696
4.731
4.743
4.757
7.162
7.178
7.218
7.237
7.261
7.272
7.281
7.284
7.298
7.310
7.314
7.327
7.916
7.937
3.37
1.00
4.18
1.08
4.23
0.90
2.03
31.49
2.24
5

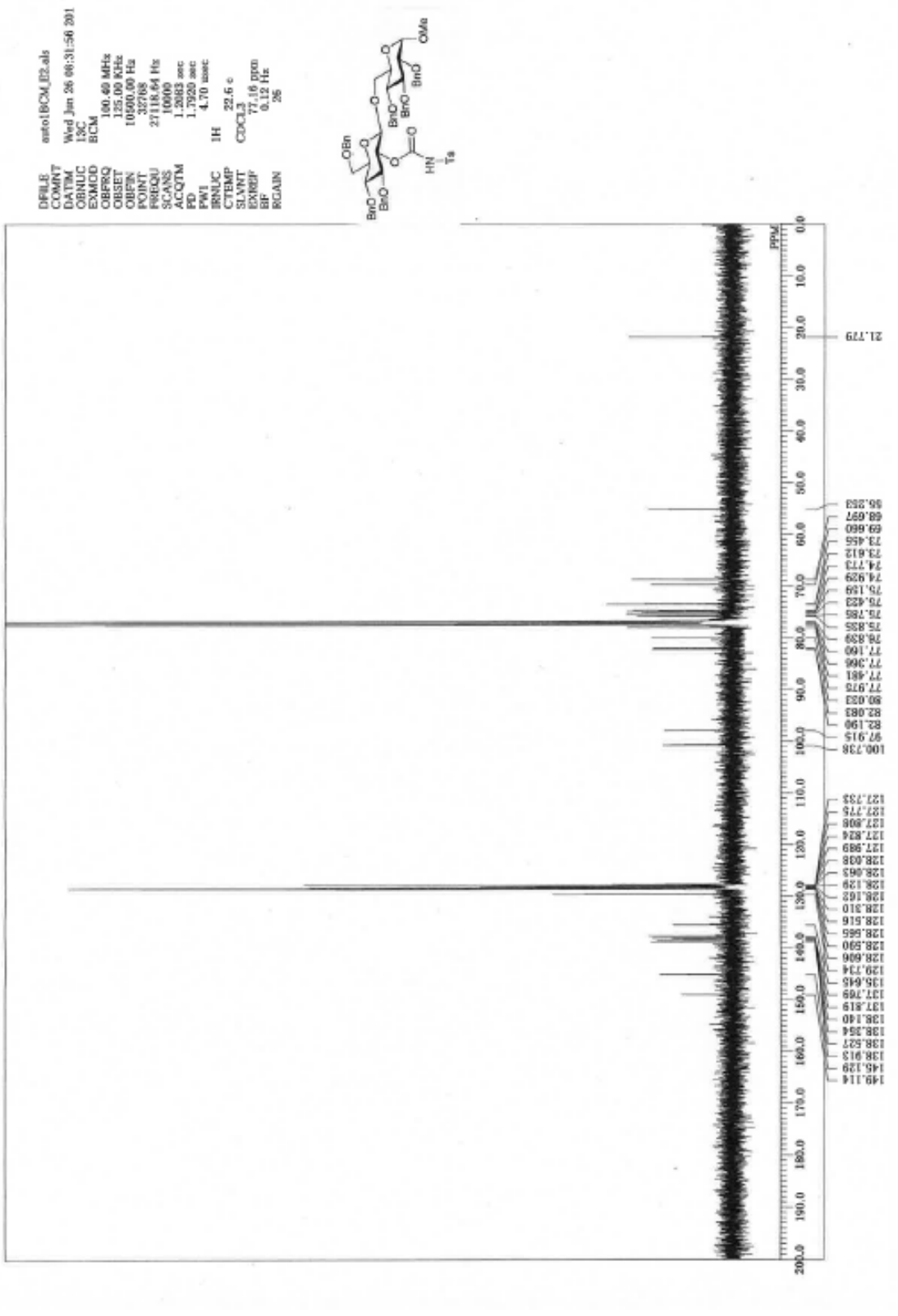
^{13}C-NMR of **20**


DFILE auto1BCM_E2_FT.alx
COMNT
DATIM Sun Jun 16 06:17:37 2013
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10560.09 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 5000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 26
OBn
OBn
OBn
SPh
HN
Ts
PPM
21.799
68.878
73.587
74.693
75.283
75.398
76.839
77.160
77.358
77.673
77.728
79.523
83.696
86.327
127.758
128.000
128.079
128.129
128.395
128.507
128.573
128.598
128.919
129.134
132.097
132.773
135.695
137.786
137.843
138.238
165.336
169.056

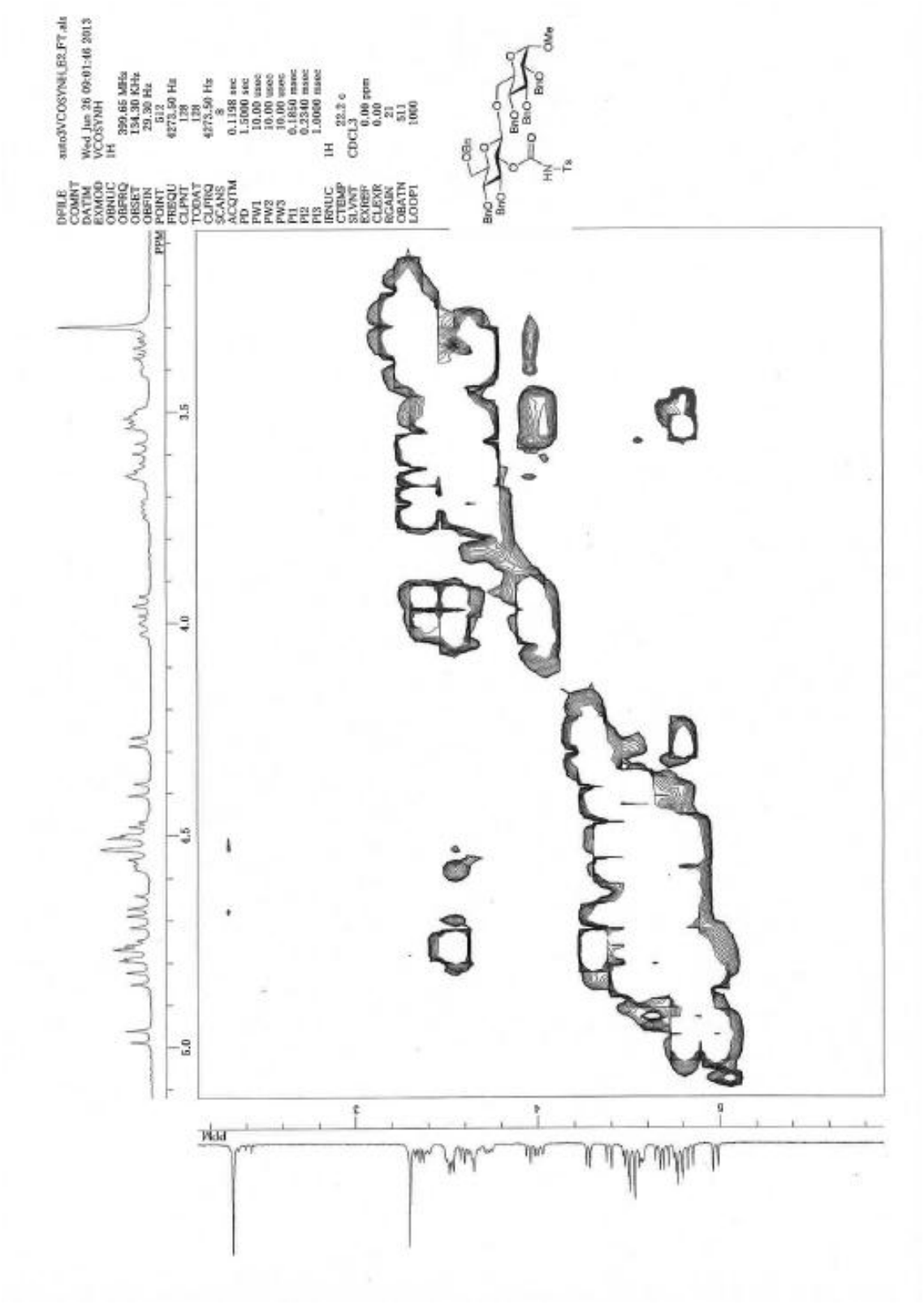
^{1}H-NMR of **23**



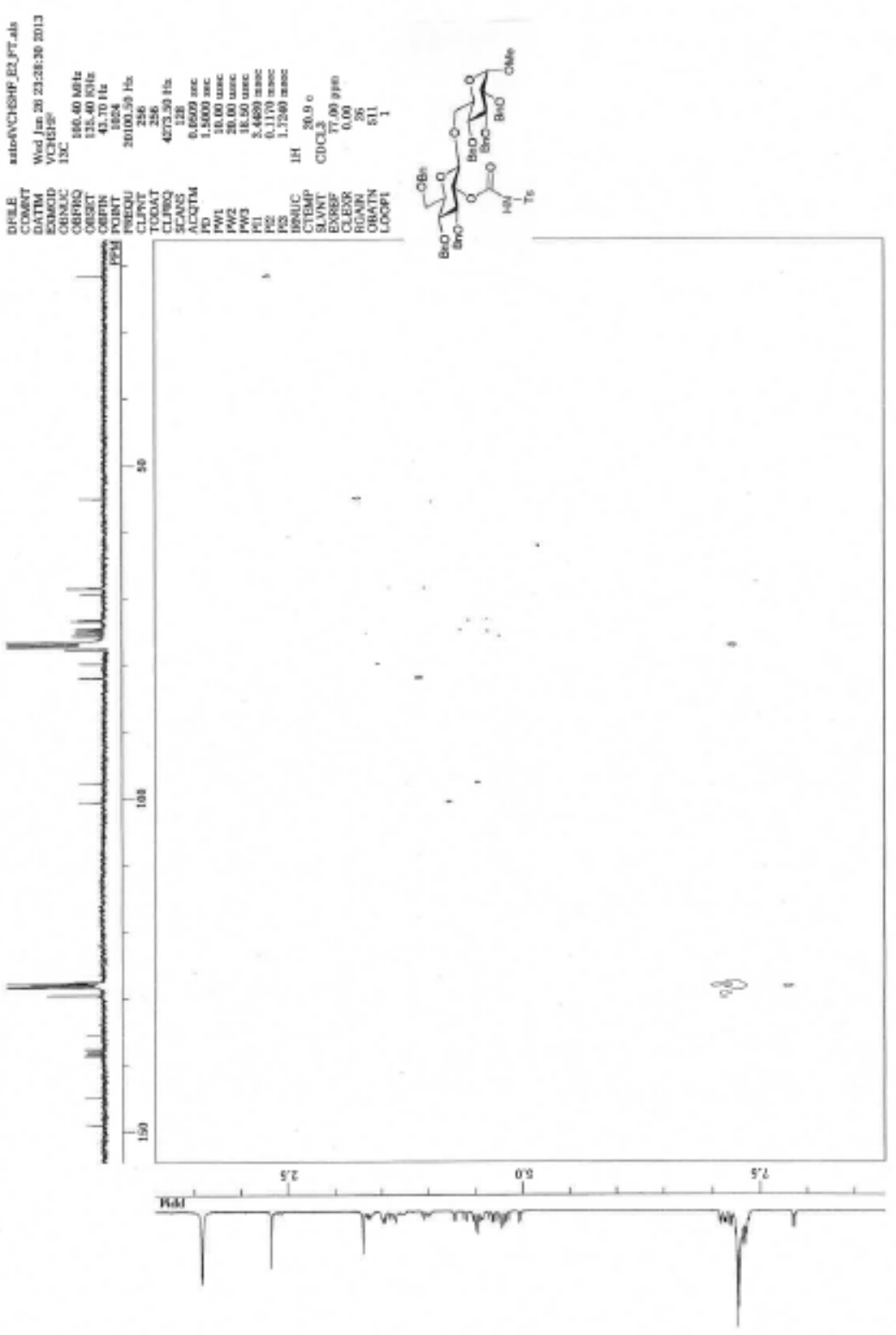
^{13}C-NMR of **23**


DFILE anto1BCM_f02.als
COMNT
DATIM Wed Jun 26 09:31:56 201
OBNUC 13C
EXMOD BCM
OBFRQ 100.49 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 10000
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.70 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCl3
EXREF 77.16 ppm
BF 0.12 Hz
RGAIN 26
OBn
BnO
BnO
BnO
BnO
BnO
OMe
HN
Ts
PPM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
21.779
55.253
68.697
69.660
73.456
73.612
74.773
74.929
75.139
75.423
75.785
75.835
76.839
77.160
77.366
77.481
77.975
80.023
82.083
82.190
97.915
100.738
127.733
127.775
127.808
127.824
127.989
128.008
128.043
128.129
128.162
128.310
128.516
128.565
128.590
128.606
129.134
135.646
137.769
137.819
138.140
138.354
138.527
138.915
146.129
149.114

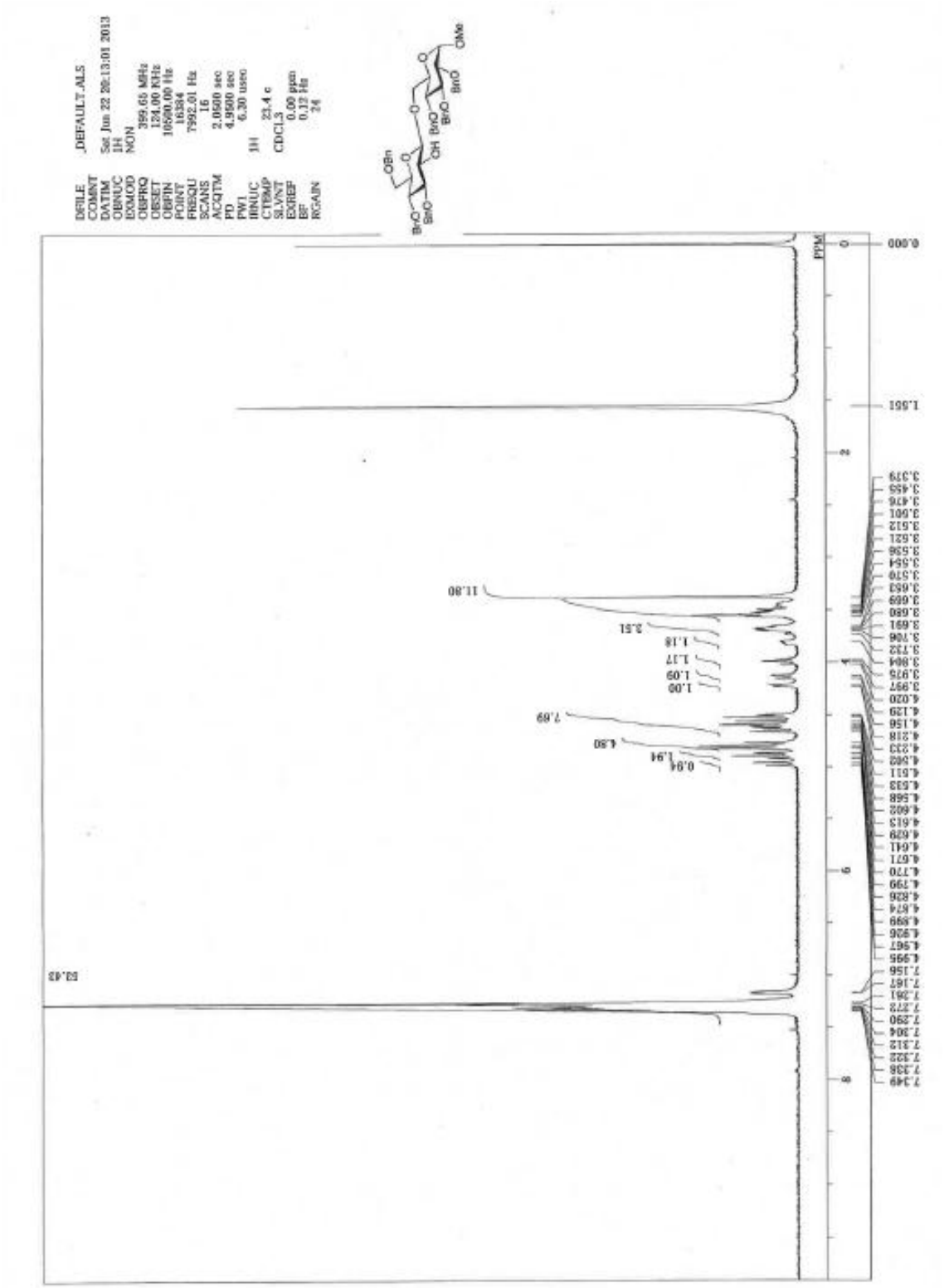
COSY of **23**


DFILE xato3VCOSYNH.i52.FT.als
COMNT
DATIM Wed Jun 26 09:01:46 2013
EXMOD VCOSYNH
OBNUC 1H
OBFRQ 399.65 MHz
OBSET 134.30 KHz
OBFIN 29.36 Hz
POINT 512
PRESQU 273.50 Hz
CLPNT 128
TODAT 128
CLFRQ 273.50 Hz
SCANS 8
ACQTM 0.1198 sec
PD 1.5000 sec
PW1 10.00 usec
PW2 10.00 usec
PW3 10.00 msec
P1 0.1850 msec
P2 0.2340 msec
P3 1.0000 msec
IRNUC 1H
CTEMP 22.2 c
SLVNT CDCL3
EXREF 6.00 ppm
CLEXR 6.00
RGAIN 21
OBATN 511
LOOP1 1000
PPM
5.0
4.5
4.0
3.5
F2
F1
OBn
BnO
BnO
BnO
BnO
BnO
OMe
HN
Ts

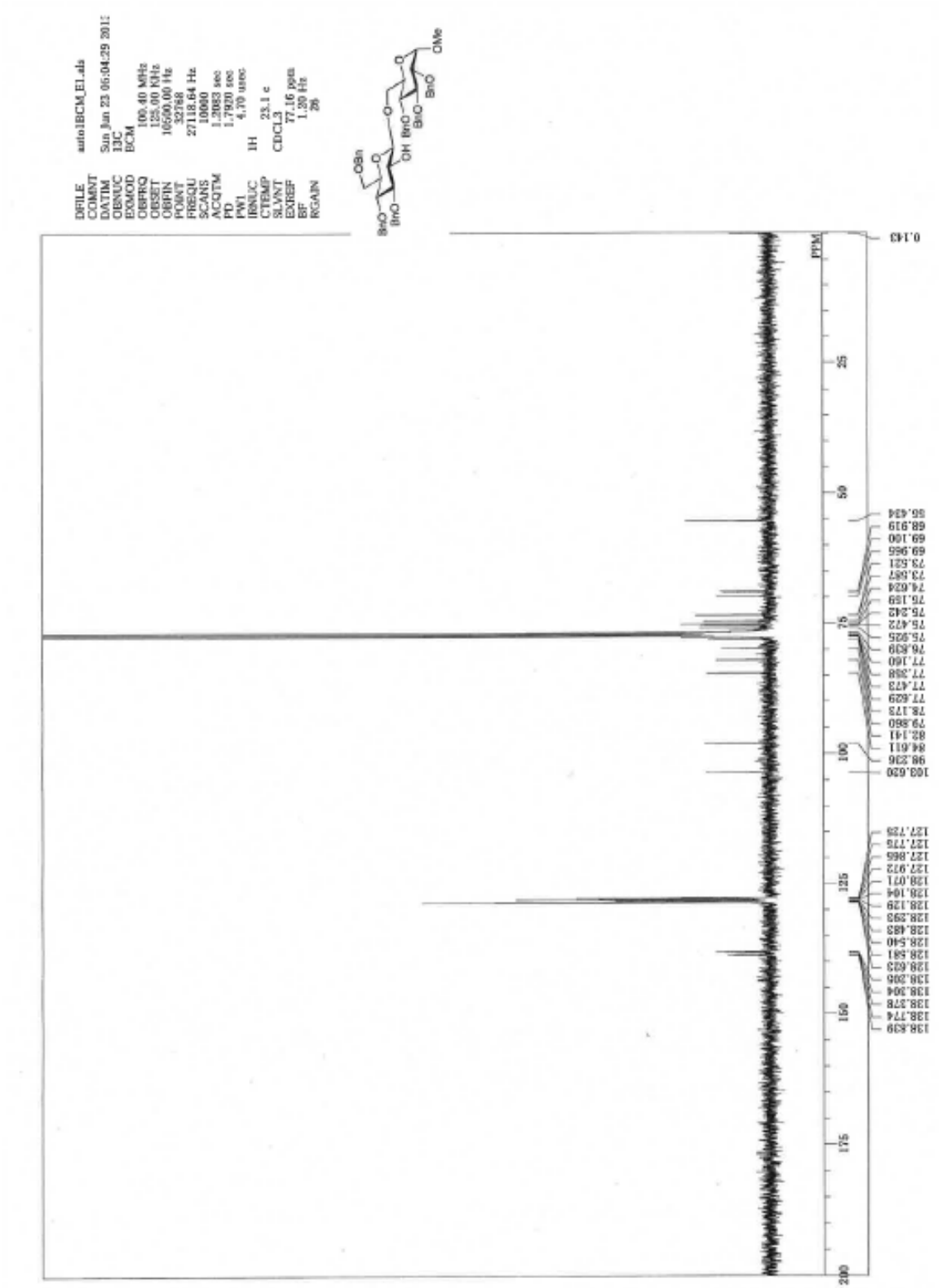
CH-COSY of **23**



^{1}H-NMR of **24**



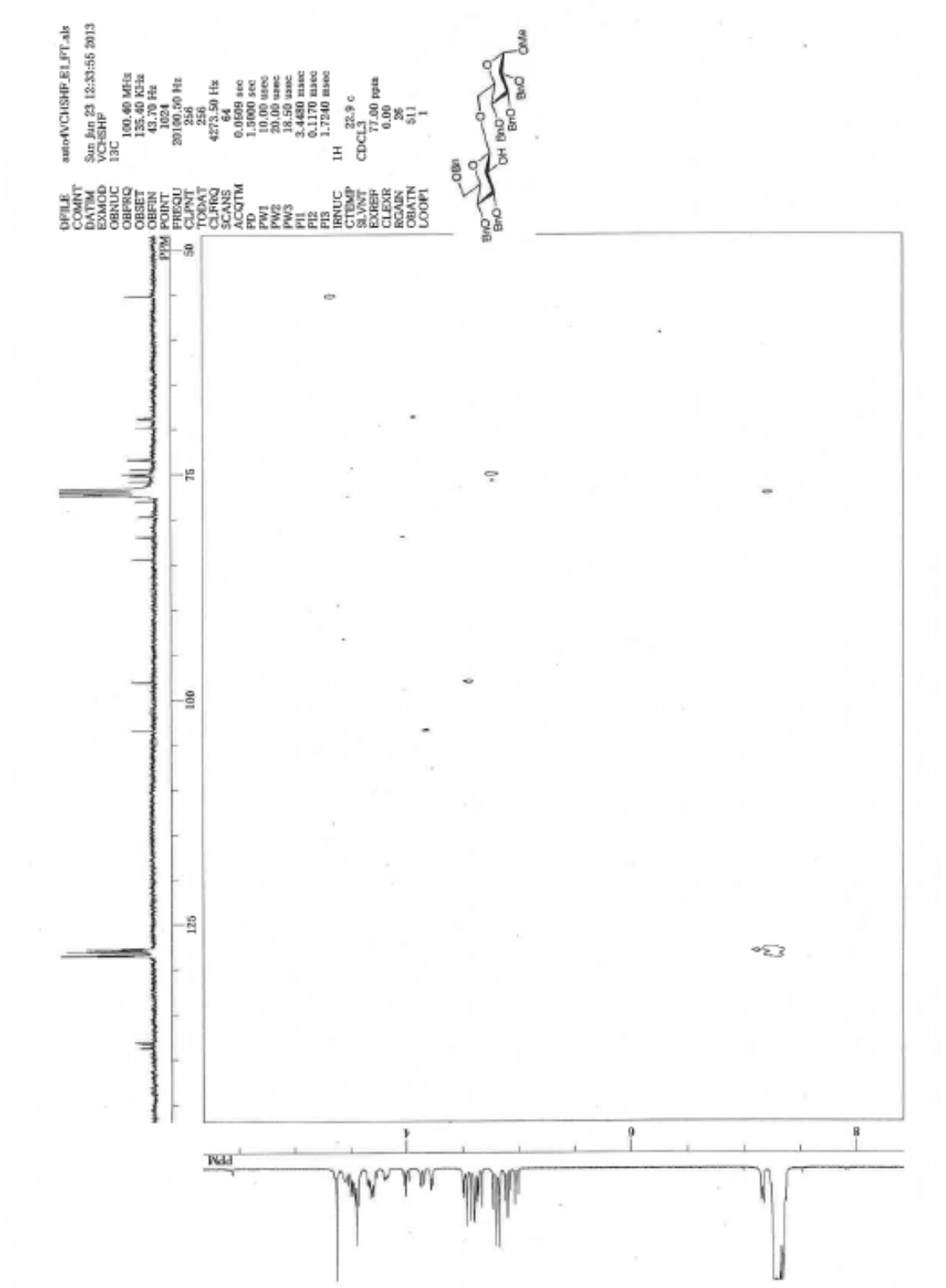
^{13}C-NMR of **24**


DFILE auto1BCM_E1.als
COMNT
DATIM Sun Jun 23 06:04:29 2013
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 16500.00 Hz
PONT 32768
FREQU 27118.64 Hz
SCANS 10000
ACQTM 1.2083 sec
PD 1.7930 sec
PW1 4.70 usec
IBNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 26
OBn
BnO
BnO
OH
BnO
BnO
BnO
OMe
PPM
0.143
50.634
68.919
69.160
69.966
73.521
73.697
74.624
75.159
75.343
75.472
75.926
76.839
77.160
77.358
77.473
77.629
78.175
79.860
82.141
84.611
98.236
103.620
127.729
127.776
127.866
127.972
128.071
128.164
128.129
128.293
128.485
128.540
128.581
128.623
138.206
138.304
138.378
138.774
138.839

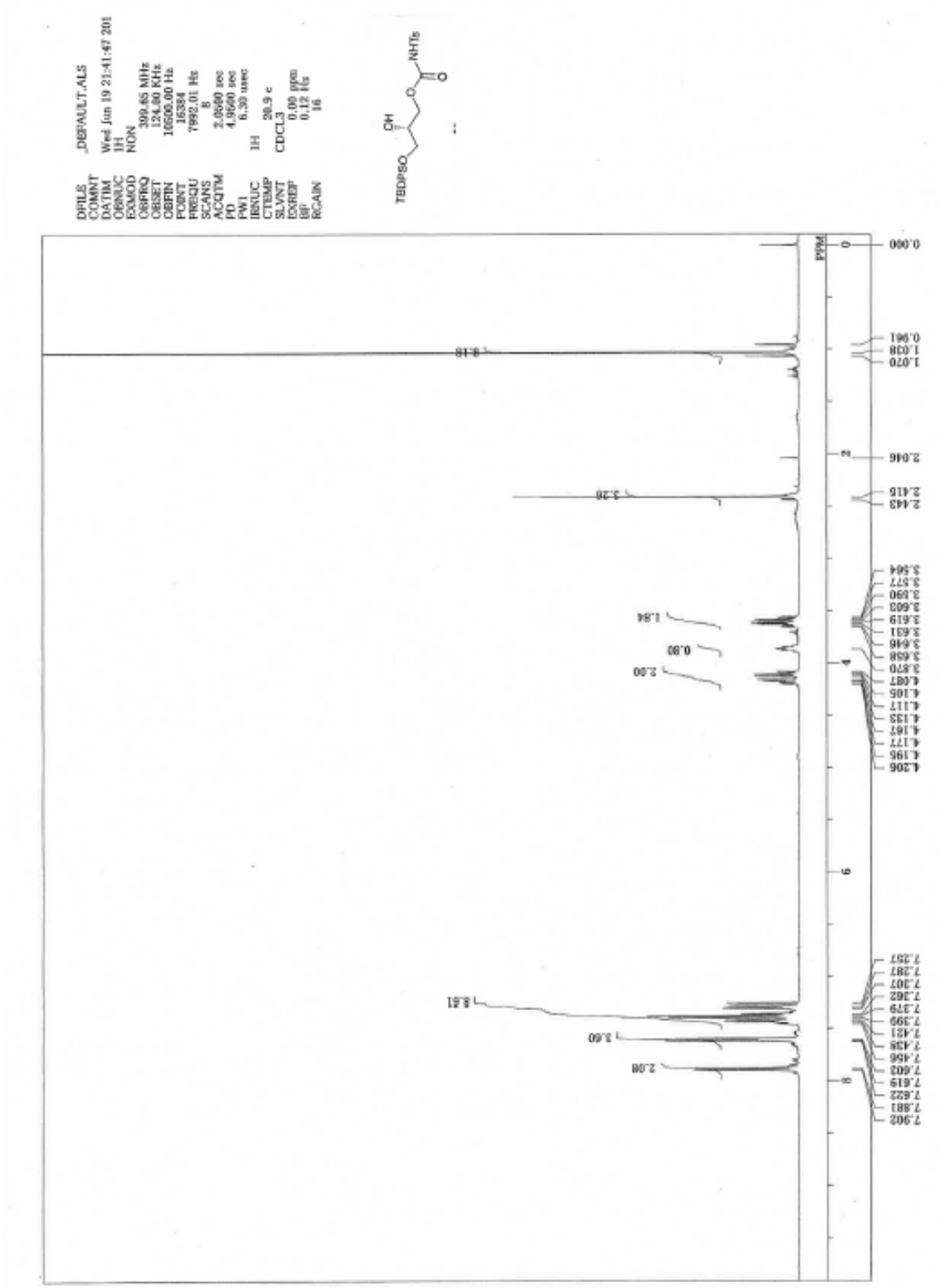
COSY of **24**


DFILE auto3VCOSYNHLE1_FT.ab
COMNT
DATIM Sun Jun 23 05:20:23 2013
EXMOD VCOSYNH
OBNUC 1H
OBFRQ 399.65 MHz
OBSET 134.39 KHz
OBFIN 35.10 Hz
POINT 512
FREQU 4259.85 Hz
CLPNT 128
TODAT 128
CLFRQ 4255.33 Hz
SCANS 4
ACQTM 0.1202 sec
PD 1.6000 sec
PW1 10.00 usec
PW2 10.00 usec
PW3 10.00 usec
F1 0.1850 msec
F2 0.2350 msec
F3 1.0000 msec
1H 22.5 c
BNUC
CTEMP CDCl3
SLVNT 0.00 ppm
EXREF 0.00
CLEXR 22
RGAIN 511
OBATN 1000
LOOP1
OBn
BnO
BnO
OH
BnO
BnO
BnO
OMe
PPM
3.5
4.0
4.5
5.0
8
9
Hold

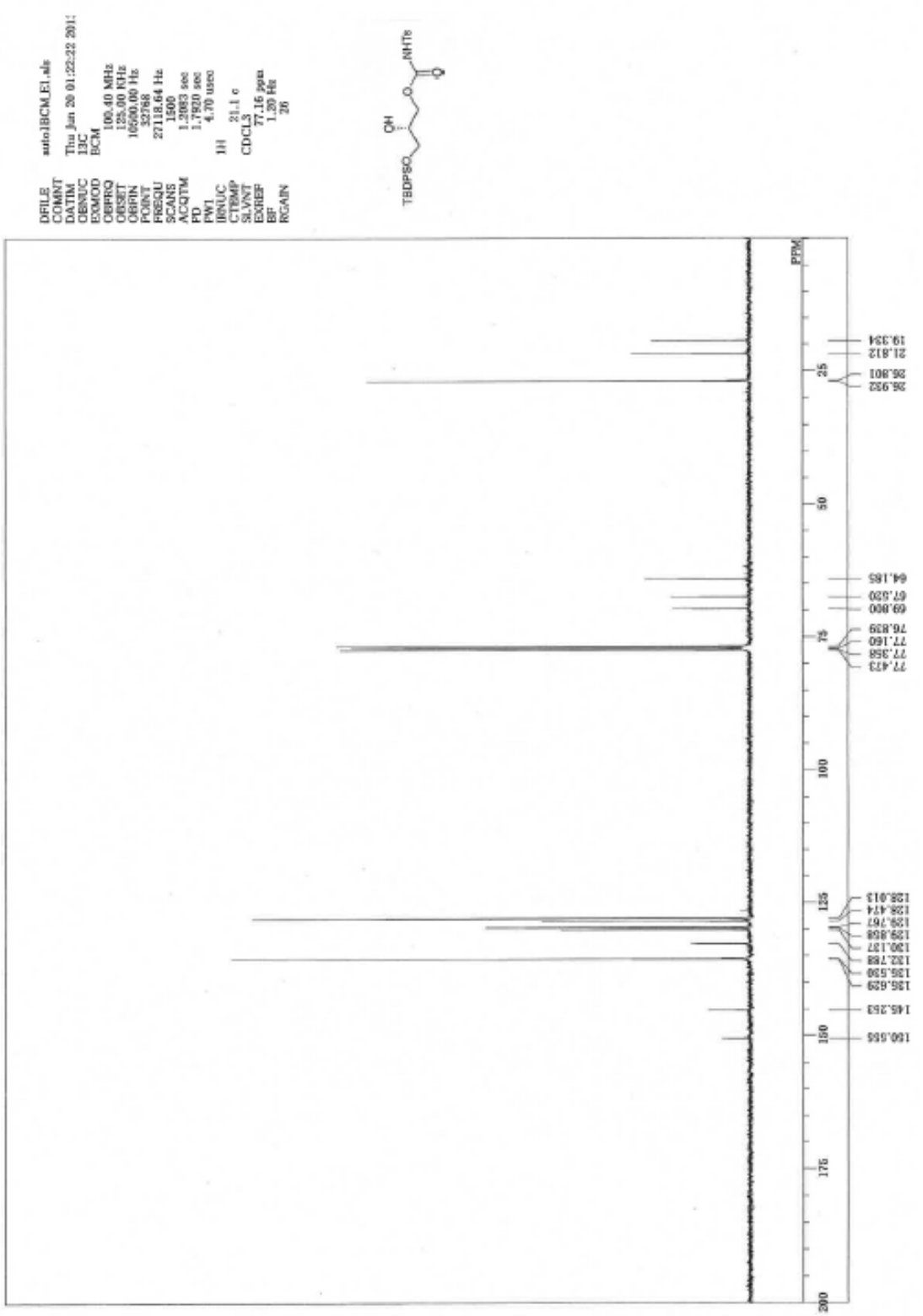
CH-COSY of **24**


DFILE auto4VCHSHF_E1_FT.als
COMNT
DATIM Sun Jun 23 12:33:55 2013
EXMOD VCHSHF
OBNUC 13C
OBFRQ 100.40 MHz
OBSET 155.40 KHz
OBFIN 43.70 Hz
POINT 1024
FREQU 29160.56 Hz
CLPNT 256
TODAT 256
CLFRQ 4273.50 Hz
SCANS 64
ACQTM 0.0509 sec
PD 1.5000 sec
PW1 10.00 usec
PW2 20.00 usec
PW3 18.50 usec
F1 3.4480 msec
F2 0.1170 msec
F3 1.7240 msec
1H
IRNUC
CTEMP 22.9 c
SLVNT CDCL3
EXREF 77.00 ppm
CLEXR 0.00
RGAIN 26
OBATN 511
LOOP1 1
OBn
BnO
BnO
OH
BnO
BnO
BnO
OMe
PPM
50
75
100
125
9
8
PPM

^{1}H-NMR of **25**


DPILE _DEFAULT.ALS
COMNT
DATIM Wed Jun 19 21:41:47 201
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
PRESAT 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IBNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
TBDPSO
OH
O
O
NHTs
PPM
0.000
0.961
1.028
1.070
2.046
2.416
2.443
3.564
3.577
3.590
3.603
3.619
3.631
3.646
3.658
3.670
4.087
4.105
4.117
4.135
4.167
4.177
4.196
4.206
7.257
7.287
7.307
7.362
7.379
7.399
7.421
7.439
7.456
7.603
7.619
7.622
7.881
7.902
8.18
3.20
1.84
0.80
2.00
8.61
3.60
2.08

^{13}C-NMR of **25**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COMNT
DATIM Thu Jun 20 01:22:22 2013
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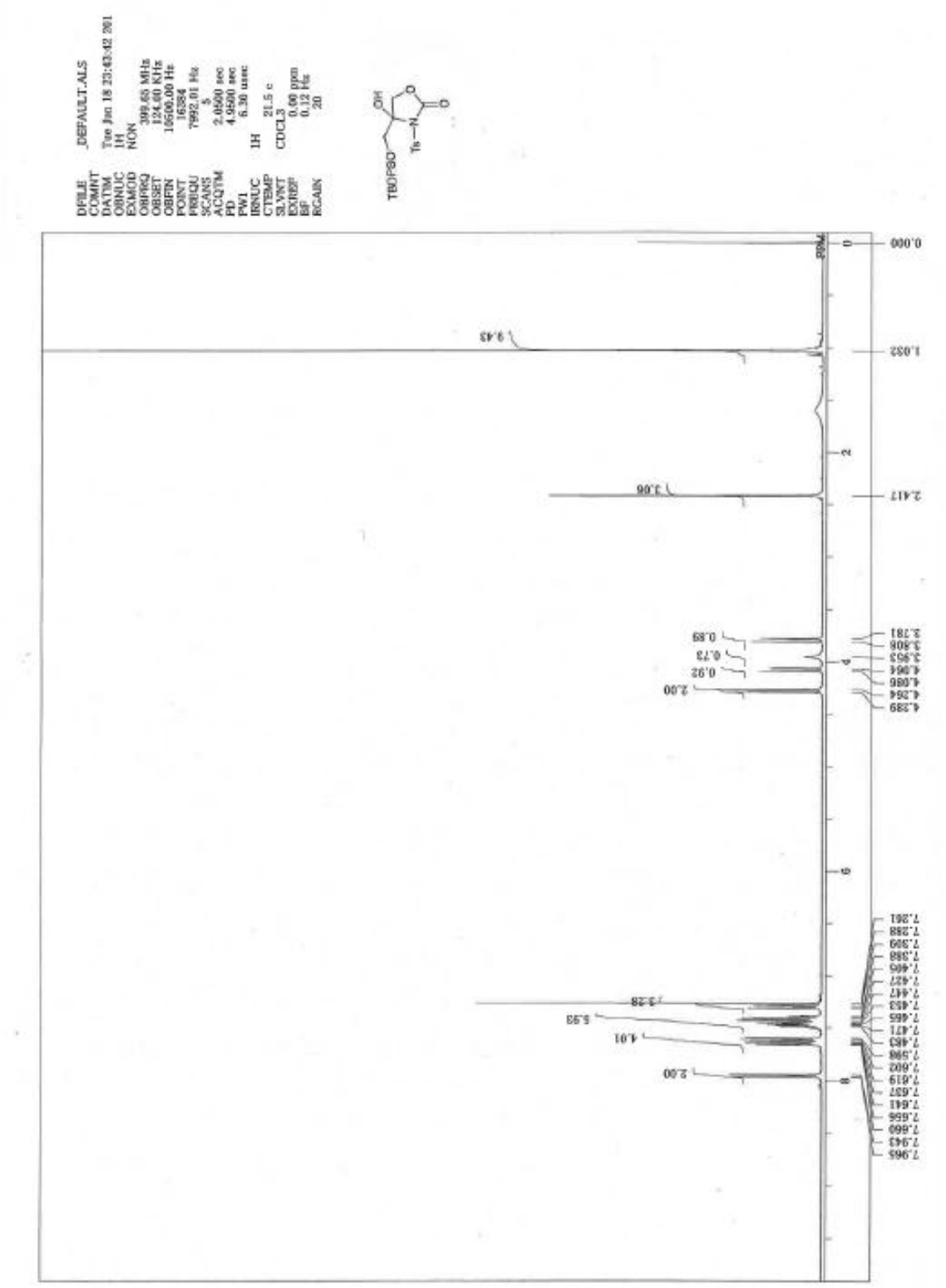
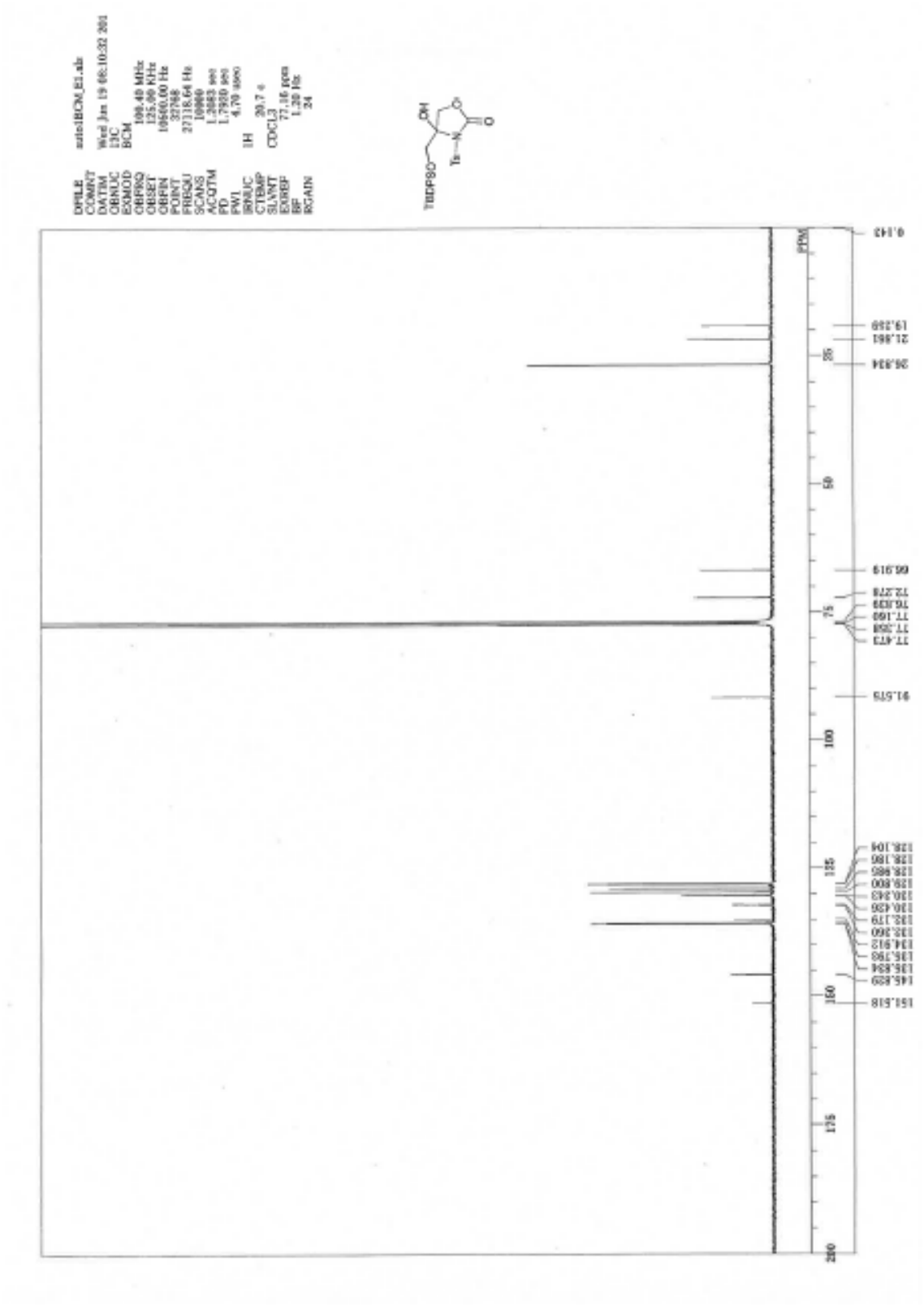
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBPIN 16500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 1500
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 4.70 used
IRNUC 1H
CTEMP 21.1 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 1.20 Hz
RGAIN 26
TBDPSO
OH
NHTs
PPM
19.334
21.812
26.801
26.952
64.185
67.020
69.800
76.839
77.160
77.358
77.473
128.013
128.474
129.767
129.858
130.137
132.788
135.530
135.659
145.263
160.656

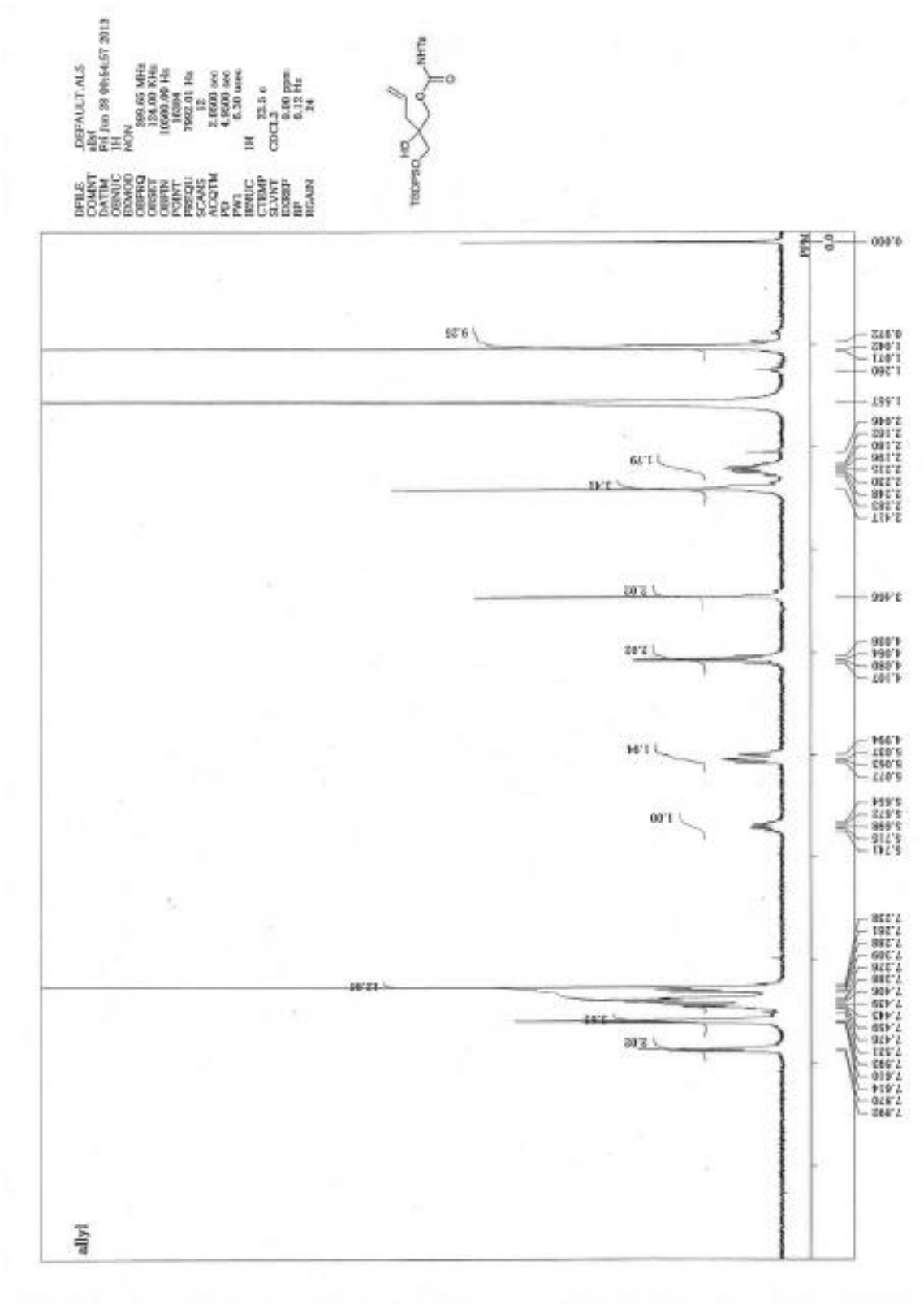
^{1}H-NMR of **26**


DFILE DEFAULT.ALS
COMNT
DATIM Tue Jan 18 23:43:42 201
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.60 KHz
OBFIN 16500.00 Hz
POINT 16384
PRBGU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
TBDPSO
OH
Ts
PPM
0.000
1.052
2.417
3.781
3.808
3.953
4.064
4.086
4.254
4.289
7.261
7.288
7.399
7.458
7.466
7.627
7.647
7.653
7.665
7.671
7.683
7.698
7.702
7.819
7.837
7.841
7.856
7.860
7.943
7.965
9.43
3.06
0.89
0.73
0.92
2.00
3.28
5.59
4.01
2.00

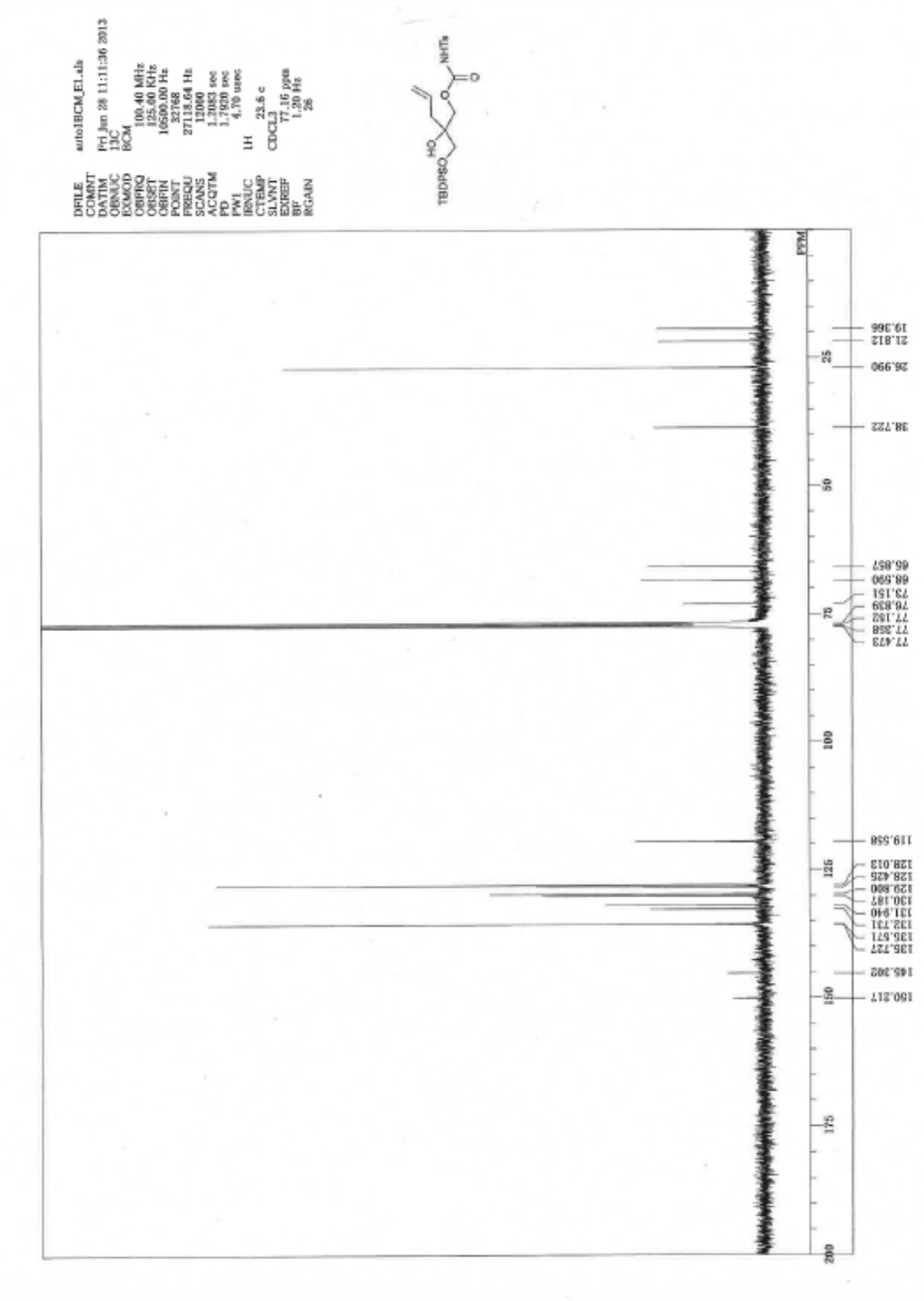
^{13}C-NMR of **26**



^{1}H-NMR of **27**



^{13}C-NMR of **27**


DATA
auto1BCM_E1.als
DATE
Fri Jan 28 11:11:36 2013
COMNT
DATIM
13C
OBNUC
BCM
EXMOD
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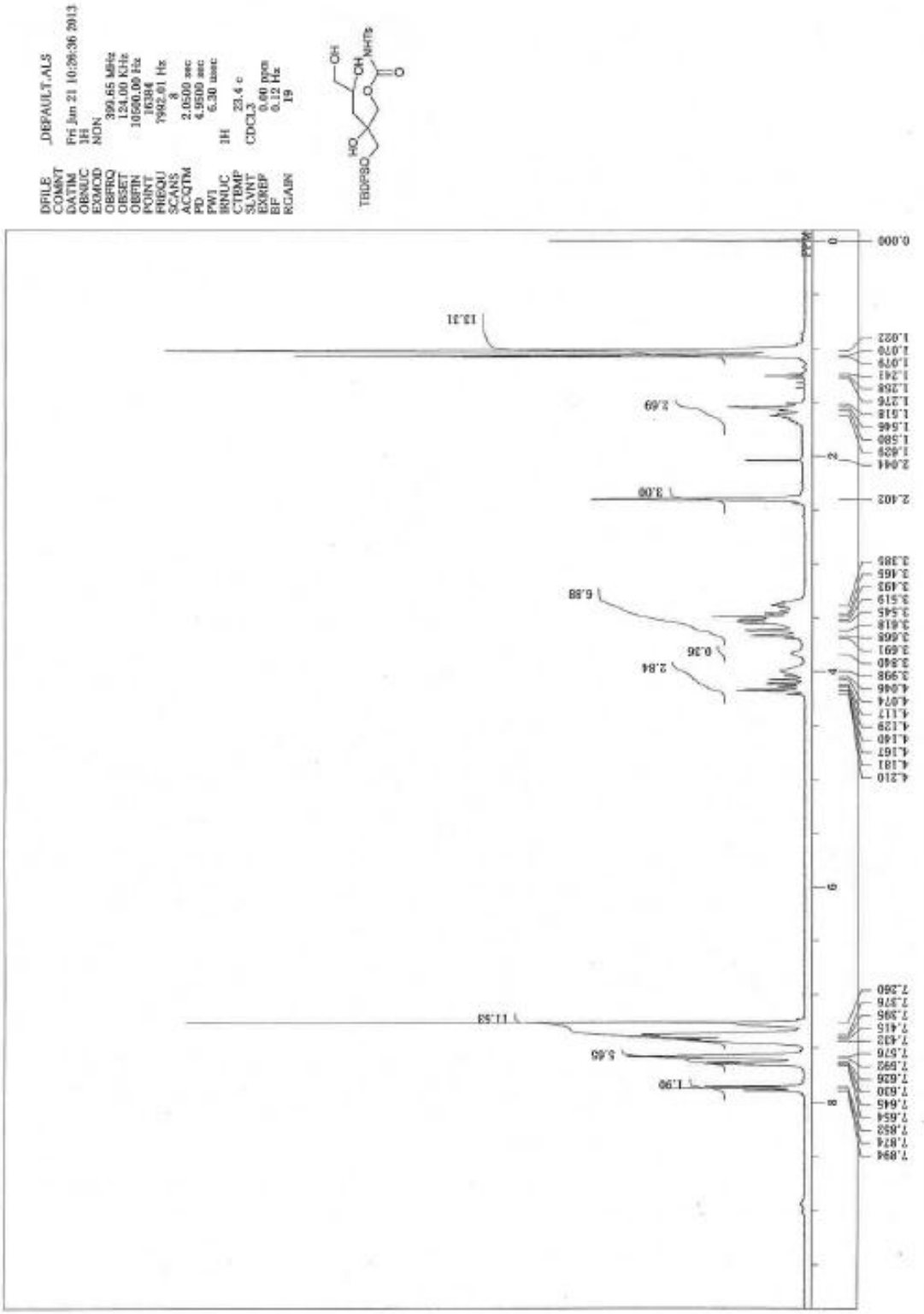
OBFRQ
125.60 KHz
OBSET
10500.00 Hz
OBFIN
32768
POINT
27118.64 Hz
FREQU
12000
SCANS
1.2083 sec
ACQTM
1.7929 sec
PD
4.70 usec
PW1
1H
IRNUC
23.6 c
CTEMP
CDCL3
SLVNT
77.16 ppm
EXREF
1.20 Hz
BF
26
RGAIN
TBDPSO
HO
NHTs
PPM
19.366
21.812
26.990
38.722
66.857
66.990
73.151
76.839
77.162
77.358
77.473
119.559
128.013
128.425
129.800
130.187
131.940
132.731
136.571
136.727
165.202
150.217

^{1}H-NMR of **28**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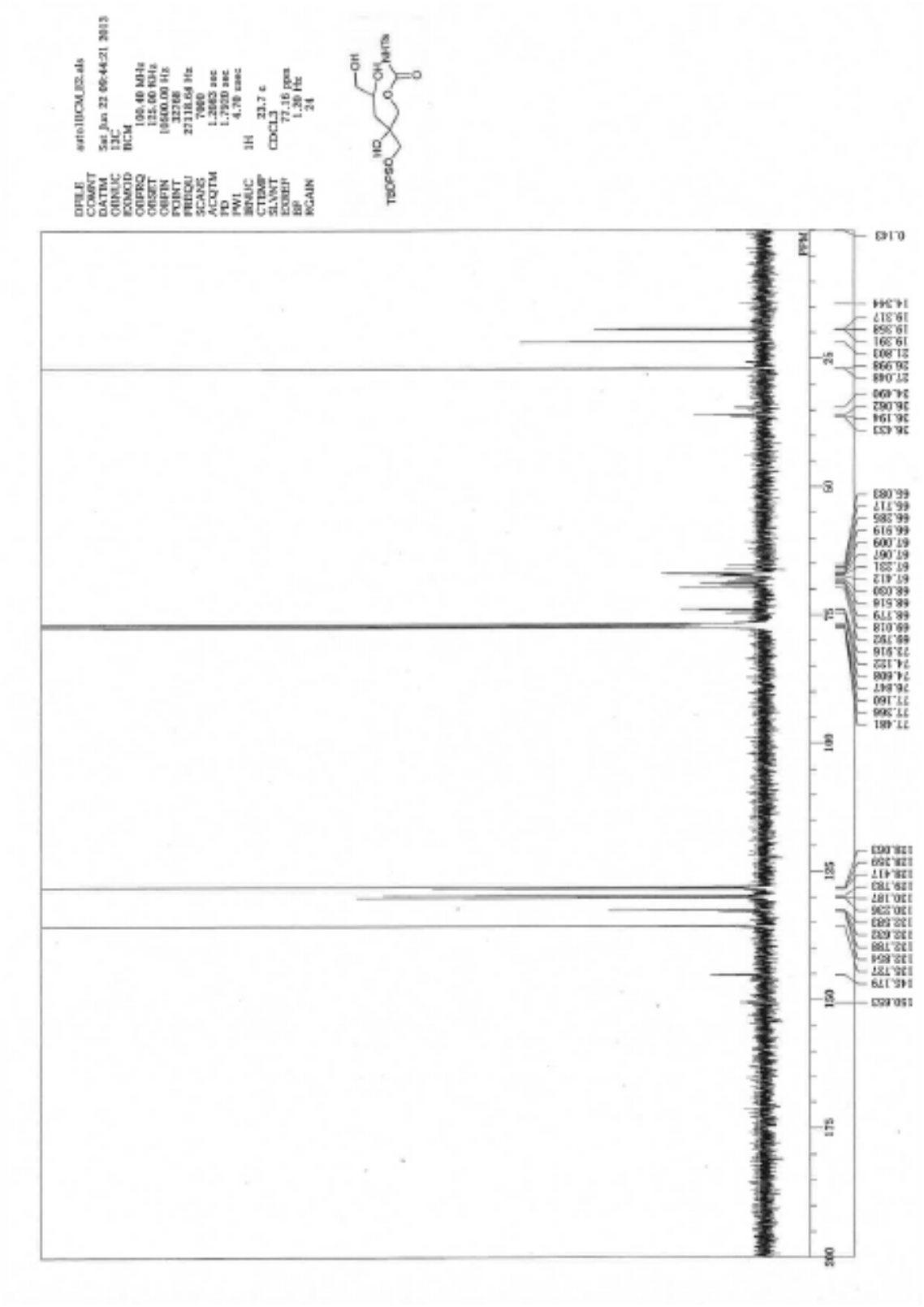
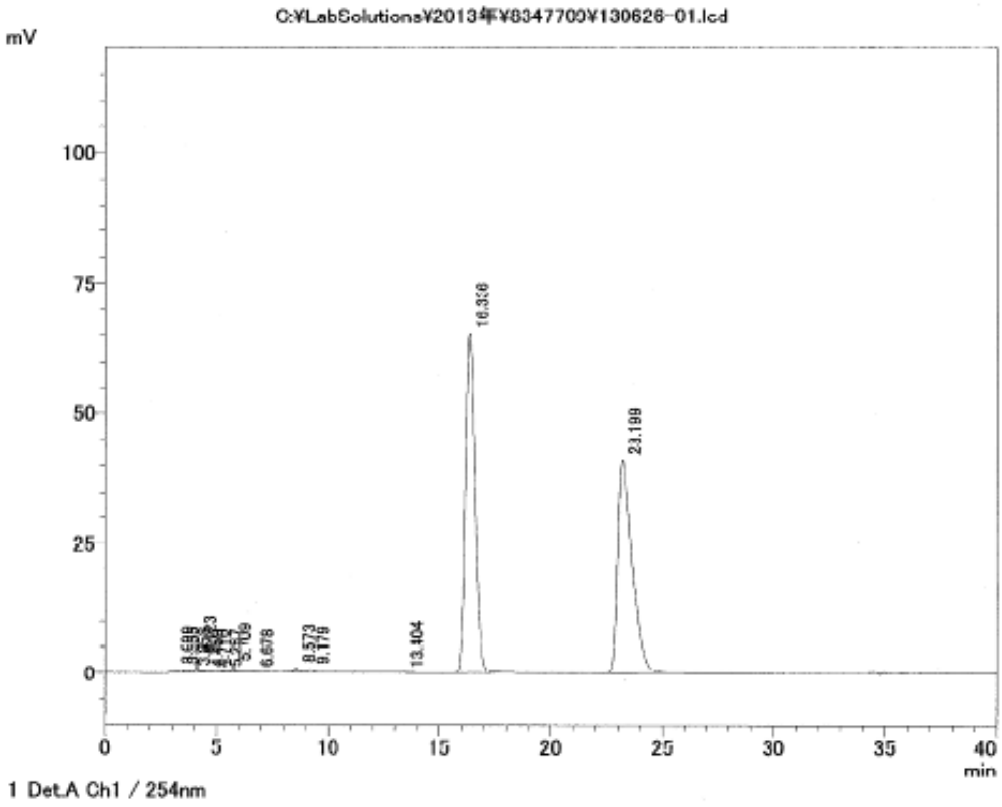
DATIM Fri Jun 21 10:26:36 2013
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10560.09 Hz
POINT 16384
FREQU 7992.61 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H 23.4 c
CTEMP
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 19
OH
OH
NHTs
O
HO
O
TBDPSO
PPM
0.000
13.31
2.69
3.09
6.88
0.36
2.84
11.58
5.65
1.99

^{13}C-NMR of **28**



Chiral HPLC spectrum of **5a** (racemic)

受注番号 : 8347709
分析者 : Ishihara
サンプル名 : dl Cbz-セリンメチルエステル 5mg/mL
バイアル番号 : 1
注入量 : 20 uL
データファイル : 130626-01.lcd
メソッドファイル : メソッド.lcm
分析日時 : 2013/06/26 15:51:45



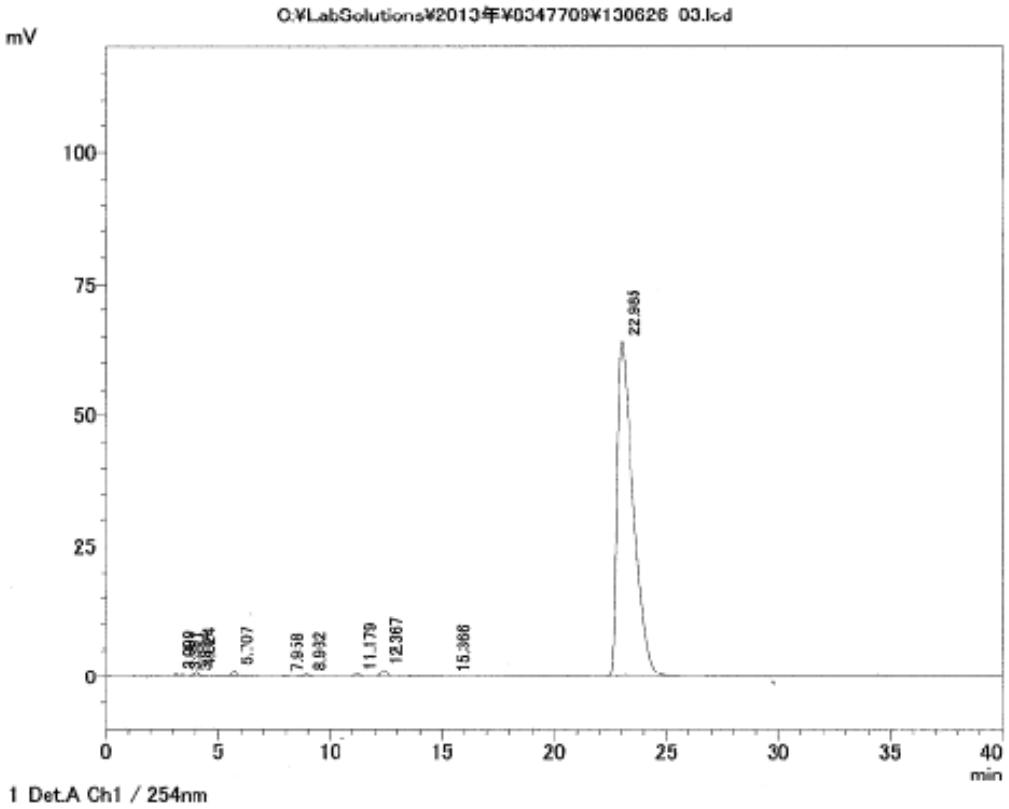
検出器A Ch1 254nm

ピーク#	保持時間	成分名	面積	高さ	面積%	高さ%
1	3.099		4201	783	0.107	0.684
2	3.355		6120	676	0.156	0.590
3	3.858		5416	471	0.138	0.411
4	4.123		17976	2659	0.459	2.323
5	4.450		1298	152	0.033	0.132
6	4.710		1689	115	0.043	0.100
7	5.267		1920	154	0.049	0.135
8	5.709		11974	1291	0.306	1.128
9	6.678		1027	108	0.026	0.094
10	8.573		12860	1010	0.328	0.882
11	9.179		10321	698	0.264	0.610
12	13.404		1780	85	0.045	0.075
13	16.336		1928346	65231	49.245	56.980
14	23.199		1910887	41047	48.799	35.855
合計			3915820	114480	100.000	100.000

CHIRALPAK AD (5μm, 4.6mm x 250mm) hexane:*i*-PrOH 9:1, 254nm, 1.0 mL/min

Chiral HPLC spectrum of **5a** after deprotection

受注番号 : 8347709
分析者 : Ishihara
サンプル名 : サンプル Cbz-セリンメチルエステル 5mg/mL
バイアル番号 : 3
注入量 : 20 uL
データファイル : 130626-03.lcd
メソッドファイル : メソッド.lcm
分析日時 : 2013/06/26 17:12:51



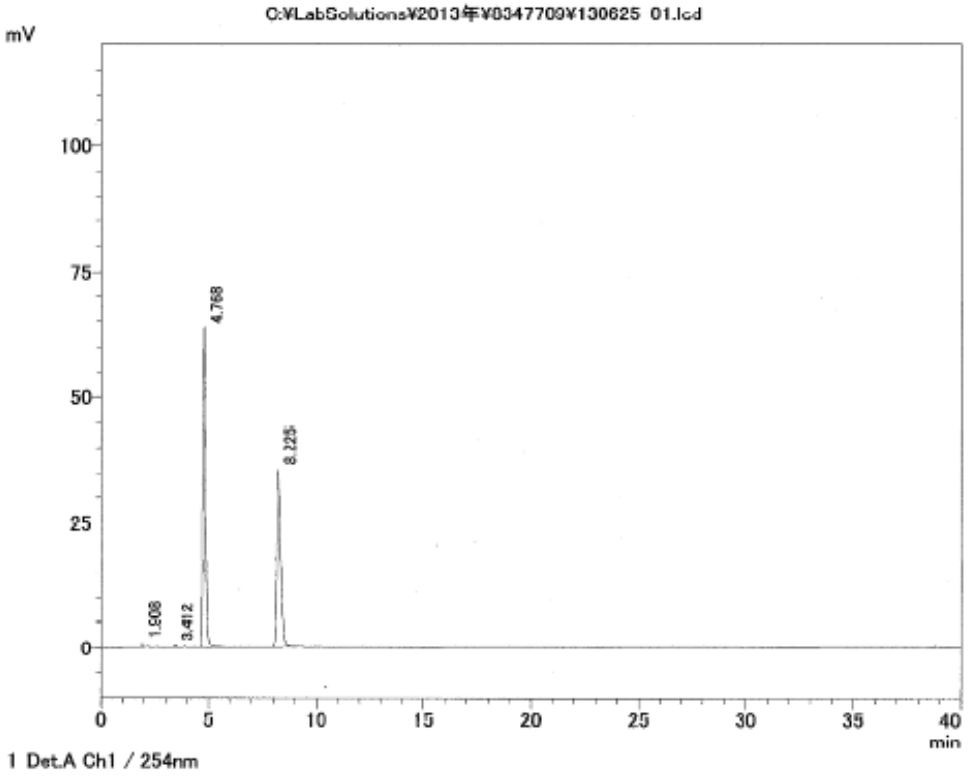
検出器A Ch1 254nm

ピーク#	保持時間	成分名	面積	高さ	面積%	高さ%
1	3.099		3251	573	0.098	0.820
2	3.391		2505	408	0.076	0.584
3	3.864		2624	317	0.079	0.453
4	4.024		8869	1106	0.268	1.581
5	5.707		13652	1344	0.413	1.922
6	7.958		1302	85	0.039	0.122
7	8.932		4397	278	0.133	0.398
8	11.179		7184	378	0.217	0.540
9	12.367		28593	1440	0.865	2.059
10	15.366		1299	59	0.039	0.085
11	22.985		3233620	63953	97.772	91.437
合計			3307296	69943	100.000	100.000

CHIRALPAK AD (5μm, 4.6mm x 250mm) hexane:*i*-PrOH 9:1, 254nm, 1.0 mL/min

HPLC spectrum of **6a**

受注番号 : 8347709
分析者 : Ishihara
サンプル名 : dl マンデル酸メチルエステル
バイアル番号 : 1
注入量 : 20 uL
データファイル : 130625-01.lcd
メソッドファイル : メソッド.lcm
分析日時 : 2013/06/25 17:20:48



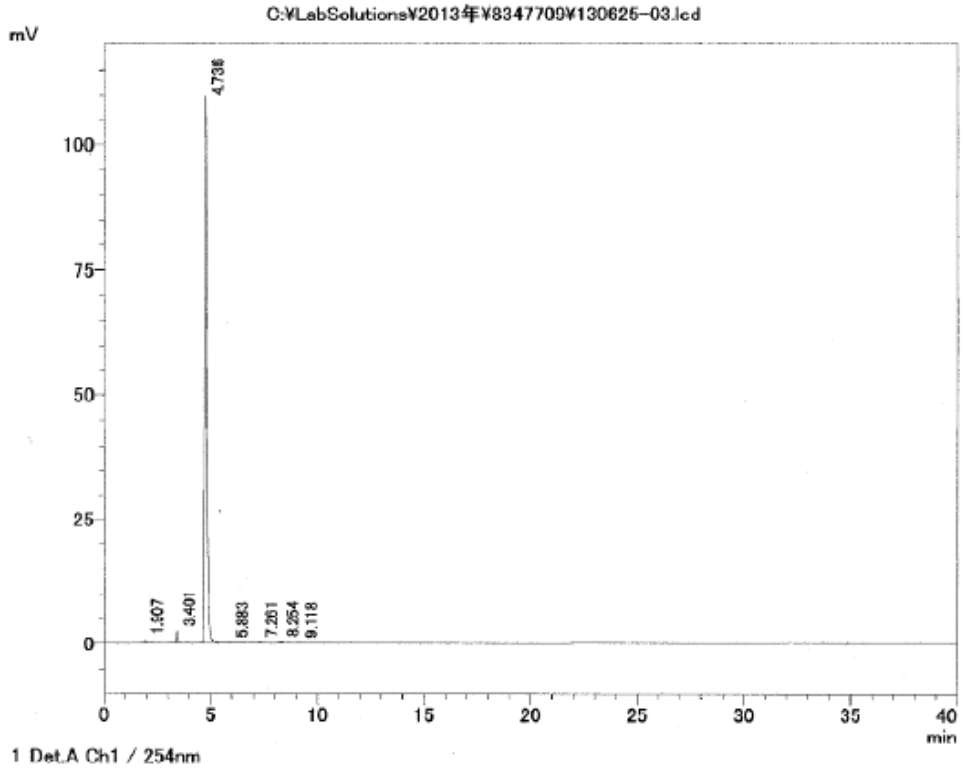
検出器A Ch1 254nm

ピーク#	保持時間	成分名	面積	高さ	面積%	高さ%
1	1.908		4643	1037	0.435	1.026
2	3.412		3058	534	0.287	0.528
3	4.768		533400	63890	50.023	63.185
4	8.225		525221	35655	49.255	35.261
合計			1066331	101116	100.000	100.000

CHIRALCEL OD-H, 5μm, 4.6mm x 150mm, hexane:*i*-PrOH 9:1, 1.0 mL/min, 254nm

HPLC spectrum of **6a** after deprotection

受注番号 : 8347709
分析者 : Ishihara
サンプル名 : サンプル　マンデル酸メチルエステル
バイアル番号 : 3
注入量 : 20 uL
データファイル : 130625-03.lcd
メソッドファイル : メソッド.lcm
分析日時 : 2013/06/25 18:41:51



検出器A Ch1 254nm

ピーク#	保持時間	成分名	面積	高さ	面積%	高さ%
1	1.907		3223	729	0.340	0.641
2	3.401		13119	2453	1.385	2.158
3	4.736		922364	109855	97.359	96.642
4	5.883		1335	118	0.141	0.103
5	7.261		2726	195	0.288	0.172
6	8.254		3514	266	0.371	0.234
7	9.118		1102	57	0.116	0.050
合計			947383	113672	100.000	100.000

CHIRALCEL OD-H, 5µm, 4.6mm x 150mm, hexane:*i*-PrOH 9:1, 1.0 mL/min, 254nm