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Asymmetric Total Synthesis of Martinelline and Martinellic acid

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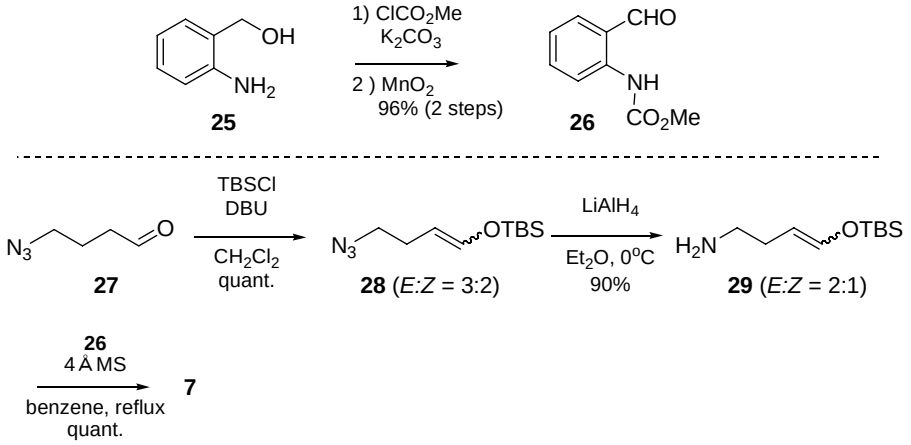
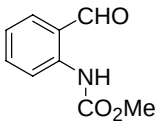
General procedure. All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated tetrahydrofuran (THF) and dichlorometane (CH_2Cl_2) were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard prorocols. Reagents were odtained from commercial suppliers and used without further purification, unless otherwise noted. $BF_3 \cdot OEt_2$ was distilled under an argon atmosphere. Reactions were monitored by thin-layer chromatography (TLC) carried out on silicagel plates (Merck Kieselgel 60 F_{254}) or NH-silicagel plates (FUJI SILYSIA CHEMICAL Co., Ltd.). Column chromatography was performed on Silicagel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm) and flash column chromatography was performed on Silicagel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm), then amine column chromatography was performed on Chromatorex® NHDM 1020 (FUJI SILYSIA CHEMICAL Co., Ltd., 100-200 mesh). All melting points were determined with Yazawa Micro Melting Point BY-2 and are uncorrected. Optical rotations were measured on a JASCO DIP-370 Digital Polarimeter at room temperature, using the sodium D line. IR spectra were recorded on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrophitimeter or Travel-*IR*™. ^{1}H-NMR (400, 500 and 600 MHz) and ^{13}C-NMR spectra (100, 125, 150 MHz) were recorded on JEOL JMN AL-400, JEOL ECA-500 and JEOL ECP-600 spectrometers, respectively. Chemical shifts (δ) are given from TMS (0 ppm) as internal standard for ^{1}H-NMR and $^{13}CDCl_3$ (77.0 ppm) for ^{13}C-NMR. The following abbreviations were used to explain the multiplicities : s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep = septet, br = broad. Mass spectra were recorded on JEOL JMS-DX303, JEOL JNM-AL500 and JEOL JMS-700. Elemental analyses were measured on Yanaco CHN CORDER MT-6. HPLC was performed by Gilson Model 305 or 307 as a pump and Gilson Model 112 or 119 as a detector at 254 or 330 nm.

1. Preparation of the model Imine 7[1,2]



Scheme S-1

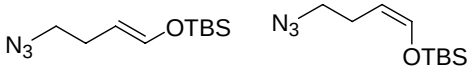
Methyl 2-formylphenylcarbamate (26)[1]



To a solution of 2-aminobenzylalcohol **25** (5 g, 40.6 mmol) in THF-H_2O (203 mL, 2:1 v/v) were successively added K_2CO_3 (56 g, 406 mmol) and methyl chloroformate (4.7 mL, 60.9 mmol). After the mixture was stirring for 1 h at room temperature, water was added and the resultant solution was extracted with AcOEt. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the crude alcohol which was used in the next step without further purification. To a solution of crude alcohol in CH_2Cl_2 (200 mL) was added MnO_2 (35 g, 403 mmol). After stirring for 2 h, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated *in vacuo*. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 1:2) to give the aldehyde **26** (6.9 g, 96% over 2 steps from **25**) as a white solid. **26** was recrystallized from acetone to give analytical sample.

26: M.p. = 88-89 ℃ [lit.[1] 90-92.5 ℃] ; IR (neat) : 3276, 1731, 1654, 1586, 1522, 1457, 1031, 1245, 1216, 1196, 1169, 1059, 1044, 876, 768 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 10.61 (1H, br s), 9.94 (1H, s), 8.45 (1H, d, *J* = 8.8 Hz), 7.64 (1H, dd, *J* = 7.8, 1.4 Hz), 7.58 (1H, ddd, *J* = 8.8, 7.2, 1.2 Hz), 7.16 (1H, td, *J* = 7.5, 1.0 Hz), 3.80 (3H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ:195.0, 154.0, 141.1, 135.9, 121.8, 121.2, 118.1, 52.3 ; MS m/z : 179 (M^+, 100%) ; HRMS calad. for $C_9H_9NO_3$: 179.0582, found : 179.0580.

(*E*),(*Z*)-4-Azidobut-1-enyloxy-(*tert*-butyldimethyl)silane (28-*E*),(28-*Z*)



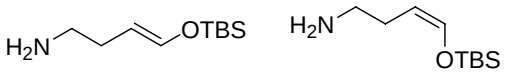
To a solution of aldehyde[2] **27** (100 mg, 0.88 mmol) in CH_2Cl_2 (1.2 mL) were successively

added DBU (0.16 mL, 1.06 mmol), TBSCl (140 mg, 0.97 mmol). After stirring for 10 min at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane: Et_2O, 50:1) to give the silyl enol ether **28-*E*** **(**120 mg, 0.53 mmol, 60%) and **28-*Z*** (180 mg, 0.35 mmol, 40%) as a colorless oil.

28 (*E*): IR (neat) : 2099, 1665, 1170 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 220.15 (6H, s), 0.90 (9H, s), 2.20 (2H, q, *J* = 7.1 Hz), 3.22 (2H, t, *J* = 7.1 Hz), 4.95 (1H, dt, *J* = 12.0, 7.1 Hz), 6.34 (1H, d, *J* = 12.0 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.4, 18.2, 25.5, 27.3, 51.7, 106.4, 142.4 ; MS m/z : 227 (M^+), 73 (100%) ; HRMS calad. for $C_{10}H_{21}N_3OSi$: 227.1454, found : 227.1459.

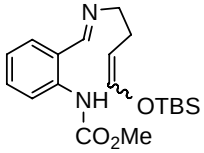
28 (*Z*): IR (neat) : 2098, 1656, 1122 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.15 (6H, s), 0.93 (9H, s), 2.42 (2H, q, *J* = 7.1 Hz), 3.26 (2H, t, *J* = 7.1 Hz), 4.47 (1H, q, *J* = 7.1 Hz), 6.28 (1H, d, *J* = 7.1 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.4, 18.2, 23.7, 25.6, 51.0, 105.1, 140.8 ; MS m/z : 170 (M^+-*t* -Bu), 73 (100%) ; HRMS calad. for $C_6H_{12}ON_3Si$: 170.0752, found : 170.0740.

(*E*),(*Z*)-4-(*tert*-Butyldimetylsilyloxy)but-3-enyla mine (29-*E*),(29-*Z*)



To a cooled (0 ℃) suspension of $LiAlH_4$ (0.30 g, 7.80 mol) in Et_2O (10 mL) was added azide **28-*E*** (2.36 g, 10.4 mmol) in Et_2O (32 mL). After stirring for 30 min at that temperature, the mixture was quenched with H_2O (0.90 mL) and 15% NaOH (0.30 mL) and stirred for 30 min. H_2O (0.90 mL) and $MgSO_4$ was added and the mixture was stirred for 1 h. The reaction mixture was filtered through a Celite pad eluting with Et_2O and the filtrate was concentrated *in vacuo* (volatile!) to give the crude amine **29-*E*** (2.42 g) as a clear oil which was used in the next step without further purification. Following this procedure, azide **28-*Z*** (5.60 g, 24.7 mmol) was also converted to the crude amine **29-*Z*** (4.65 g).

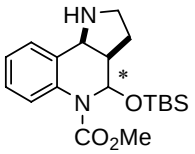
Methyl(2-{[4-(tert-butyldimethylsilyloxy)-but-3-enylimino]methyl}pheny l)carbamate (7)



General procedure

To the mixture of **29** (1.5 eq.) and **26** (1.0 eq.) in benzene (0.1 M) was added 4Å MS (100 wt%) and the mixture was heated to reflux for 14 h. After cooled to room temperature, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated *in vacuo* to give a crude imine **7** (quant.) which was used in the next step without further purification.

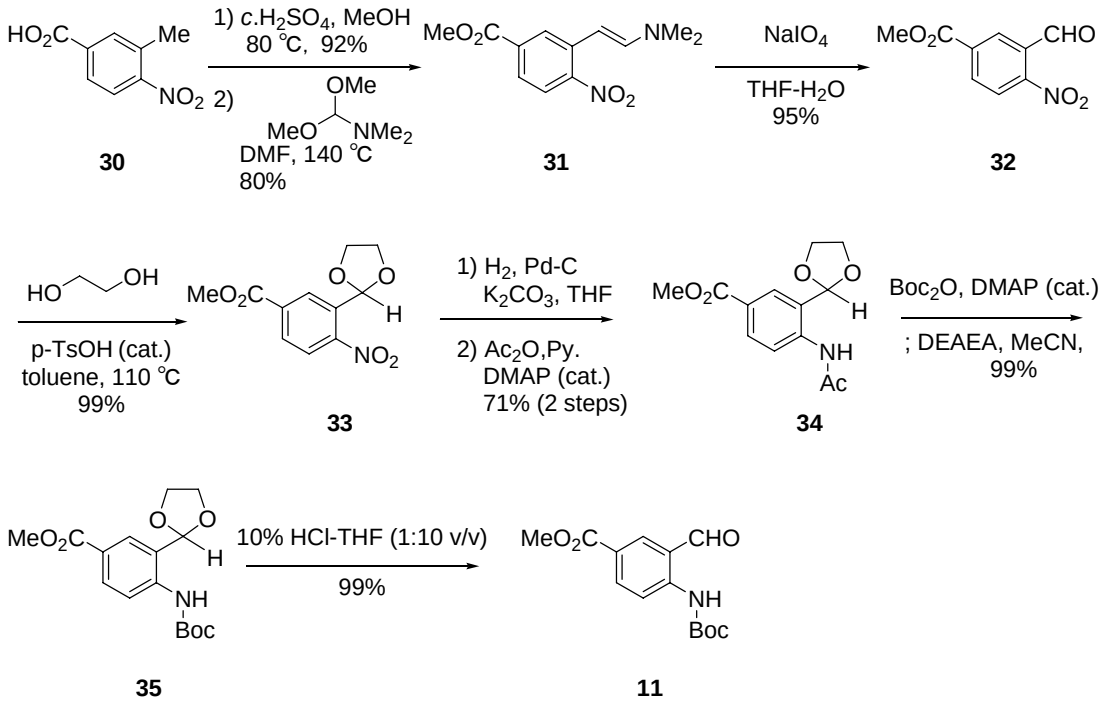
(3a*R,9b*S**)-5-Methoxycarbonyl-4-(*tert*-butyldimethylsilyloxy)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (9)**



To a solution of (*Z*)-imine **7** (288 mg, 0.80 mmol) in MeCN (4 mL) was added $LiBF_4$ (374 mg, 4.00 mmol) and stirred for 30 min at 60 ℃. After cooled to room temperature, the reaction mixture was quenched with sat. Na_2CO_3 and the resultant solution was extracted with $CHCl_3$. The extracts were washed with brine, dried over K_2CO_3 and concentrated under reduced pressure. The crude mixture was purified by amine silica gel column chromatography (hexane:AcOEt, 2:1) to give the aminal **9** (106 mg, 36%) as a colorless sticky oil. Following this procedure, (*E*)-imine **7** was also converted to the aminal **9** (24%).

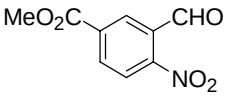
9: IR (neat) : 3374, 2952, 1514, 1442, 1337, 1234, 1035, 762 cm^{-1} ; ^{1}H-NMR (600 MHz, CD_3OD) δ : -0.04 (3H, s), 0.13 (3H, s), 0.68 (9H, s), 1.96 (1H, m), 2.24 (1H, m), 2.60 (1H, m), 2.88 (1H, dt, *J* = 15.0, 9.0 Hz), 3.14 (1H, dt, *J* = 15.0, 9.0 Hz), 3.97 (1H, d, *J* = 7.6 Hz), 6.07 (1H, d, *J* = 2.8 Hz), 7.15 (1H, t, *J* = 7.6 Hz), 7.27(1H, t, *J* = 7.6 Hz), 7.53 (2H, d, *J* = 7.6 Hz) ; ^{13}C-NMR (150 MHz, CD_3OD) δ: -5.28, -4.86, 18.5, 25.9, 29.8, 43.6, 46.8, 53.6, 59.1, 79.5, 125.7, 126.1, 128.5, 129.7, 130.2, 135.2, 154.8 ; MS m/z : 362 (M^+), 305 (100%) ; HRMS calad. for $C_{19}H_{30}N_2O_3Si$: 362.2026, found : 362.2044.

2. Synthesis of the aldehyde 11.[3a,b]



Scheme S-2

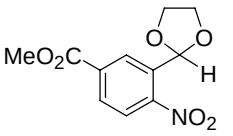
Methyl 3-formyl-4-nitrobenzoate (32)



Aldehyde **32** was prepared following the known procedure.[3a]

32 (light yellow solid): M.p. = 66-68 ℃ [lit.[3a] 67-68℃] ; IR (neat) : 1713, 1696, 1526, 1439, 1343, 1297, 1250, 1198, 1171, 845, 803, 776, 743, 706 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 10.4 (1H, s), 8.56 (1H, d, *J* = 2.0 Hz), 8.40 (1H, dd, *J* = 8.3, 2.0 Hz), 8.32 (1H, d, *J* = 8.3 Hz), 4.02 (3H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 186.8, 164.0, 151.5, 135.0, 134.5, 131.0, 130.8, 124.6, 53.1 ; MS m/z : 209 (M^+), 179 (100%) ; HRMS calad. for $C_9H_7NO_5$: 209.0324, found : 209.0297.

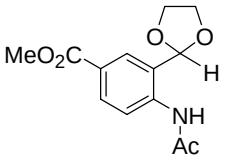
Methyl 3-(1,3-dioxolan-2-yl)-4-nitrobenzoate (33)



To the mixture of aldehyde **32** (20g, 95.68 mmol) and ethylene glycol (8 mL, 143.52 mmol) in toluene (150 mL) was added *p*-TsOH・H_2O (182 mg, 0.96 mmol) and the mixture was heated to reflux for 6 h with azetropic removal of water. After cooled to room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residual solid was recrystallized from MeOH (80 mL) to give the acetal **33** (23.9 g, 99%) as light yellow plate crystals.

33: M.p. = 79-80 ℃ ; IR (neat) : 2955, 2896, 1730, 1536, 1295, 1112 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 8.43 (1H, d, *J* = 1.9 Hz), 8.15 (1H, dd, *J* = 8.3, 2.0 Hz), 7.91 (1H, d, *J* = 8.6 Hz), 6.45 (1H, s), 4.06 (4H, m), 3.98 (3H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 165.0, 151.2, 133.7, 133.5, 130.8, 129.1, 124.4, 99.1, 65.4, 52.7 ; MS m/z : 253 (M^+), 206 (100%) ; HRMS calad. for $C_{11}H_{11}NO_6$: 253.0586, found : 253.0540 ; *Anal.* calad. for $C_{11}H_{11}NO_6$: C, 52.18 ; H, 4.38 ; N, 5.53, found : C, 52.02 ; H, 4.34 ; N, 5.49.

Methyl 4-acetamido-3-(1,3-dioxolan-2-yl)benzoate (34)

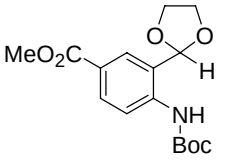


A solution of nitro **33** (19.8 g, 78.24 mmol) and K_2CO_3 (2.16 g, 15.65 mmol) in THF (150 mL) was hydrogenated in the presence of Pd-C (10 wt%, 2 g) under atomospheric pressure of H_2. After the mixture was stirring for 18 h at room temperature, pyridine (6.33 mL, 78.24 mmol) was added and the mixture was filtered through a Celite pad eluting with AcOEt, then the filtrate was concentrated *in vacuo*. To the residual solution were successively added CH_2Cl_2 (100 mL), pyridine (6.33 mL, 78.24 mmol), Ac_2O (8.12 mL, 86.06 mmol) and DMAP (478 mg, 3.91 mmol). After the mixture was stirred for 15 h, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over

$MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 2:3) to give the crude amide. The crude amide was recrystallized from Et_2O/AcOEt to give the pure amide **34** (14.8 g, 71% over 2 steps from **33**) as white needles.

34: M.p. = 149-150 ℃ ; IR (neat) : 3377, 1717, 1694, 1588, 1432, 1281, 1218, 1200, 1227, 1077, 996, 955, 907, 768 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 8.76 (1H, br s), 8.36 (1H, d, *J* = 8.6 Hz), 8.11 (1H, d, *J* = 1.7 Hz), 8.03 (1H, dd, *J* = 8.5, 2.2 Hz), 5.89 (1H, s), 4.12 (4H, m), 3.90 (3H, s), 2.20 (3H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 168.2, 166.3, 140.5, 131.4, 128.6, 125.1, 124.9, 121.1, 65.0, 52.1, 25.2 ; MS m/z : 265 (M^+), 195 (100%) ; HRMS calad. for $C_{13}H_{15}NO_5$: 265.0950, found : 265.0942 ; *Anal.* calad. for $C_{13}H_{15}NO_5$: C, 58.86 ; H, 5.70 ; N, 5.28, found : C, 58.73 ; H, 5.84 ; N, 5.29.

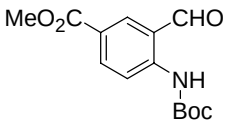
Methyl 4-(*tert*-butoxycarbonylamino)-3-(1,3-dioxolan-2-yl)benzoate (35)[3b]



To a solution of amide **34** (7.2 g, 27.16 mmol) in MeCN (70 mL) were successively added DMAP (332 mg, 2.72 mmol) and Boc_2O (8.2 mL, 34.34 mmol), then stirred for 2 h at room temperature. DEAEA (7.63 mL, 54.32 mmol) was added to the mixture and stirred further for 1.5 h. The reaction mixture was quenched with sat. NH_4Cl and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 4:1) to give the carbamate **35** (8.65 g, 99%) as a white solid.

35: M.p. = 101-104 ℃ ; IR (neat) : 3382, 1731, 1713, 1594, 1528, 1233, 1156, 1135, 1108, 1073, 1046, 1023, 965, 947, 764 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 8.19 (1H, d, *J* = 8.8 Hz), 8.08 (1H, d, *J* = 1.7 Hz), 8.00 (1H, dd, *J* = 8.6, 2.1 Hz), 7.96 (1H, s), 5.87 (1H, s), 4.11 (4H, m), 3.89 (3H, s), 1.53 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 166.4, 152.2, 141.3, 131.3, 128.7, 124.3, 123.6, 119.2, 102.3, 80.9, 65.0, 51.9, 28.3 ; MS m/z : 323 (M^+), 267 (100%) ; HRMS calad. for $C_{16}H_{21}NO_6$: 323.1369, found : 323.1364 ; *Anal.* calad. for $C_{16}H_{21}NO_6$: C, 59.43 ; H, 6.55 ; N, 4.33, found : C, 59.14 ; H, 6.59 ; N, 4.33.

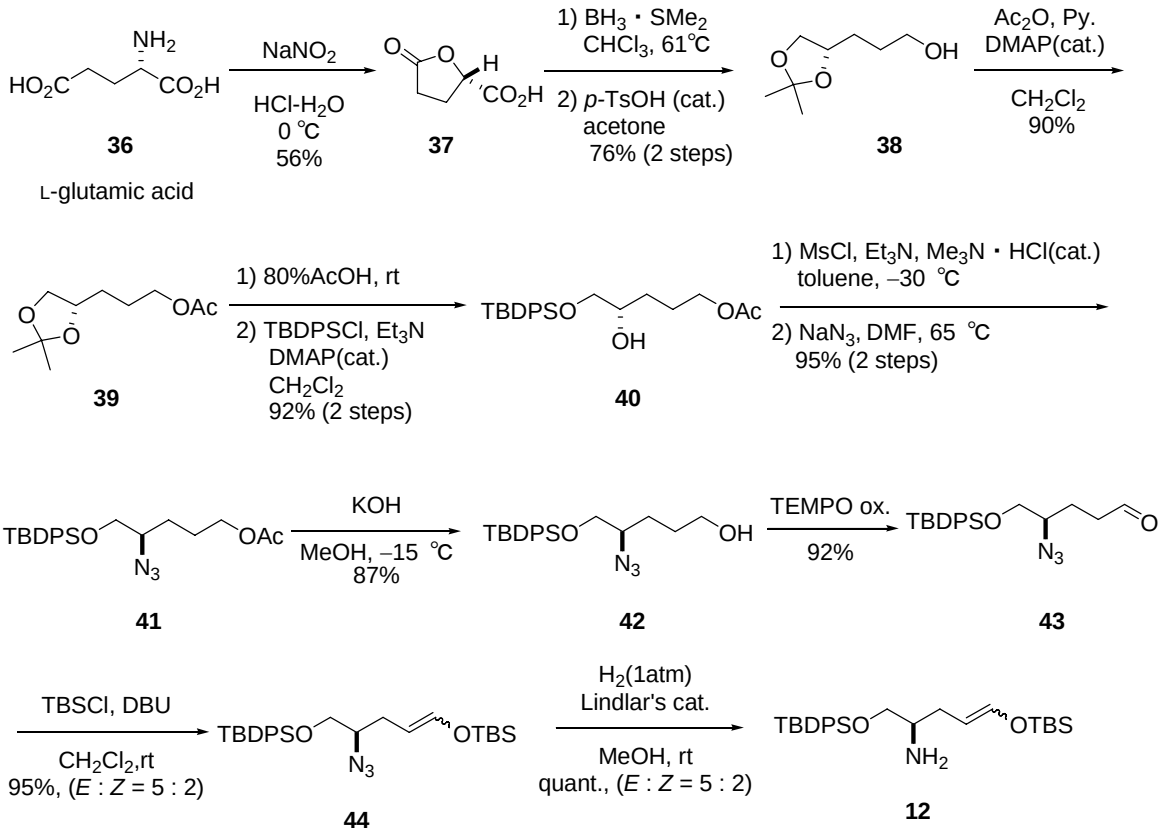
Methyl 4-(*tert*-butoxycarbonylamino)-3-formylbenzoate (11)



To a solution of carbamate **35** (8.1 g, 25.07 mmol) in THF (70 mL) was added 10% HCl (7 mL) and stirred for 2.5 h at room temperature. The reaction mixture was quenched with sat. $NaHCO_3$ and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residual solid was recrystallized from MeOH (250 mL) to give the aldehyde **11** (6.7 g, 99%) as a white powder.

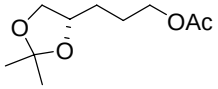
11: M.p. = 150-153 ℃ ; IR (neat) : 3272, 2360, 1731, 1679, 1533, 1447, 1251, 769, 706 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 10.6 (1H, s), 9.95 (1H, s), 8.54 (1H, d, *J* = 9.0 Hz), 8.34 (1H, d, *J* = 2.0 Hz), 8.00 (1H, dd, *J* = 9.0, 2.0 Hz), 3.94 (3H, s), 1.55 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 194.3, 165.4, 152.3, 145.3, 137.8, 136.6, 123.1, 120.5, 117.8, 81.7, 52.2, 28.2 ; MS m/z : 279 (M^+), 179 (100%) ; HRMS calad. for $C_{14}H_{17}NO_5$: 279.1107, found : 279.1104 ; *Anal.* calad. for $C_{14}H_{17}NO_5$: C, 60.21 ; H, 6.14 ; N, 5.02, found : C, 60.27 ; H, 6.14 ; N, 5.02.

3. Synthesis of the chiral amine 12 and key inine 10.[4a-d]



Scheme S-3

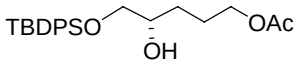
(4*S*)-3-(2,2-Dimethyl-1,3-dioxolan-4-yl)propylacetate (39)



To a cooled (0 ℃) solution of alcohol[4a,b] **38** (1.80 g, 11.24 mmol) in CH_2Cl_2 (28 mL) were successively added pyridine (1.36 mL, 16.86 mmol), Ac_2O (1.38 mL, 14.61 mmol) and DMAP (69 mg, 0.56 mmol). After stirring for 5 min at 0 ℃, the mixture was allowed to warm up to room temperature and stirred for 15min at that temperature. Water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and

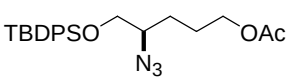
concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 8:1) to give the acetate **39** (2.05 g, 90%) as a colorless oil.
39: $[\alpha]_D^{28}$ +13.4° (c 1.17, $CHCl_3$) ; IR (neat) : 2986, 2359, 1742, 1456, 1369, 1243, 1160, 1052, 855, 792 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 1.35 (3H, s), 1.41 (3H, s), 1.56-1.80 (4H, m), 2.05 (3H, s), 3.53 (1H, dd, *J* = 7.6, 7.1 Hz), 4.06 (1H, dd, *J* = 7.6, 6.1 Hz), 4.12 (1H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 20.9, 24.9, 25.6, 26.9, 30.0, 64.0, 69.2, 75.4, 108.7, 170.8 ; MS m/z : 187 (M^+-Me, 100%) ; HRMS calad. for $C_9H_{15}O_4$ (M^+-Me) : 187.0970, found : 187.0970.

(4*S*)-5-(*tert*-Butyldiphenylsilyloxy)-4-hydroxypentylacetate (40)



Acetonide **39** (4.06 g, 20.10mmol) was dissolved in a mixture of AcOH (16 mL) and H_2O (4 mL). After stirring for 18 h at room temperature, the solvent was removed *in vacuo* to afford the crude diol as a colorless oil which was used in the next step without further purification. To a solution of crude diol in CH_2Cl_2 (20 mL) were successively added Et_3N (4.2 mL, 30 mmol), TBDPSCl (6.17 mL, 24 mmol) and DMAP (122 mg, 1 mmol). After stirring for 12 h at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 12:1) to give the alcohol **40** (7.40 g, 92% over 2 steps from **39**) as a colorless oil.
40: $[\alpha]_D^{27}$ –1.90° (c 1.02, $CHCl_3$) ; IR (neat) : 3463, 3071, 2931, 2858, 2360, 1739, 1472, 1428, 1390, 1364, 1245, 1113, 824, 741, 704 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 1.07 (9H, s), 1.45 (2H, m), 1.63 (1H, m), 1.79 (1H, m), 2.03 (3H, s), 2.51 (1H, d, *J* = 3.7 Hz), 3.49 (1H, dd, *J* = 10.1, 7.4 Hz), 3.66 (1H, dd, *J* = 10.1, 3.4 Hz), 3.72 (1H, m), 4.05 (1H, t, *J* = 6.5 Hz), 7.44 (6H, m), 7.65 (4H, d, *J* = 7.6 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 19.1, 20.8, 24.7, 26.8, 29.1, 64.2, 67.8, 71.3, 127.6, 129.6, 132.9, 135.3, 170.8 ; MS m/z : 343 (M^+-*t*-Bu), 199 (100%) ; HRMS calad. for $C_{19}H_{23}O_4Si$ (M^+- *t*-Bu) : 343.1366, found : 343.1373 ; *Anal.* calad. for $C_{23}H_{32}O_4Si$: C, 68.96 ; H, 8.05, found : C, 69.00 ; H, 8.05.

(4*R*)-4-Azido-5-(*tert*-butyldiphenylsilyloxy)pentylacetate (41)

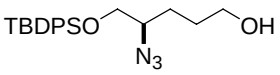


To a cooled (－30 ℃) solution of alcohol **40** (7.35 g, 18.37 mmol) in toluene (18 mL) were successively added Et_3N (5.14 mL, 36.74 mmol), Me_3N・HCl (176 mg, 1.84 mmol) and MsCl (2.13 mL, 27.56 mmol). After stirring for 5 min at that temperature, water was added and allowed to warm up to room temperature. The mixture was extracted with Et_2O, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the crude mesylate which was used in the next step without further purification. To a solution of crude mesylate

in DMF (46 mL) was added NaN_3 (7.16 g, 110.22 mmol) and stirred for 3.5 h at 65 ℃. Aftetr the mixture was cooled to room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 15:1) to give the azide **41** (7.42 g, 95% over 2 steps from **40**) as a colorless oil.

41: $[\alpha]_D^{29}$ +17.6° (c 1.04, $CHCl_3$) ; IR (neat) : 2932, 2106, 1740, 1242, 1113, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 1.08 (9H, s), 1.46 (2H, m), 1.65 (1H, m), 1.72 (1H, m), 2.03 (3H, s), 3.42 (1H, m), 3.64 (1H, dd, *J* = 10.7, 6.8 Hz), 3.72 (1H, dd, *J* = 10.5, 3.9 Hz), 4.04 (2H, dd, *J* = 6.3, 2.9 Hz), 7.44 (6H, m), 7.67 (4H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 19.1, 20.8, 25.2, 26.7, 26.9, 63.2, 63.8, 66.8, 127.6, 129.7, 132.7, 135.4, 170.7 ; MS m/z : 368 (M^+-*t*-Bu), 199 (100%) ; HRMS calad. for $C_{19}H_{22}N_3O_3Si$ (M^+- *t*-Bu) : 368.1431, found : 368.1475 ; *Anal.* calad. for $C_{23}H_{31}N_3O_3Si$: C, 64.91 ; H, 7.34 ; N, 9.87, found : C, 64.93 ; H, 7.40 ; N, 9.72.

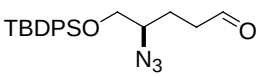
(4*R*)-4-Azido-5-(*tert*-butyldiphenylsilyloxy)pentan-1-ol (42)



To a cooled (−15 ℃) solution of acetate **41** (7.16 g, 16.84 mmol) in MeOH (42 mL) was added KOH (1.23 g, 21.89 mmol). After stirring for 2.5 h at that temperature, the mixture was neutralized with NH_4Cl (1.35 g, 25.26 mmol) and allowed to warm up to room temperature. After the solvent was evaporated, the residue was taken up in AcOEt and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 5:1) to give the alcohol **42** (5.60 g, 87%) as a colorless oil.

42: $[\alpha]_D^{28}$ +18.4° (c 1.24, $CHCl_3$) ; IR (neat) : 3350, 2932, 2859, 2105, 1428, 1113, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 1.08 (9H, s), 1.42-1.71 (4H, m), 3.43 (1H, m), 3.58-3.68 (3H, m), 3.73 (1H, dd, *J* = 10.7, 3.9 Hz), 7.42 (6H, m), 7.68 (4H, d, *J* = 6.0, 1.6 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 19.2, 26.75, 26.80, 29.2, 62.3, 63.7, 67.0, 127.7, 129.7, 132.87, 132.93, 135.5 ; MS m/z : 326 (M^+-*t*-Bu), 199 (100%) ; HRMS calad. for $C_{17}H_{20}N_3O_2Si$ (M^+- *t*-Bu) : 326.1325, found : 326.1314 ; *Anal.* calad. for $C_{21}H_{29}N_3O_2Si$: C, 65.76 ; H, 7.62 ; N, 10.96, found : C, 65.90 ; H, 7.65 ; N, 11.00.

(4*R*)-4-Azido-5-(*tert*-butyldiphenylsilyloxy)pentan-1-al (43)

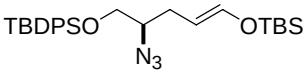


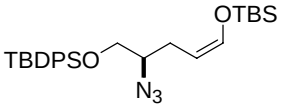
To a cooled (0℃) solution of alcohol **42** (950 mg, 2.48 mmol) in CH_2Cl_2 (12 mL) were successively added sat. $NaHCO_3$ (6 mL), KBr (30 mg, 0.248 mmol), TBAB (40 mg, 0.124 mmol) and TEMPO (8 mg, 0.050 mmol). To the mixture was added NaClO (1.5 M aqueous

solution, 1.65 mL) in sat. $NaHCO_3$ (6 mL) dropwise. After stirring for 5 min, the layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 50:1) to give the aldehyde **43** (871 mg, 92%) as a colorless oil.

43: $[\alpha]_D^{29}$ +30.0° (c 1.08, $CHCl_3$) ; IR (neat) : 2931, 2858, 2114, 1725, 1113, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 1.08 (9H, s), 1.65 (2H, m), 1.78 (1H, m), 2.54 (1H, dd, *J* = 7.1, 2.9 Hz), 3.47 (1H, m), 3.65 (1H, dd, *J* = 10.7, 6.8 Hz), 3.74 (1H, dd, *J* = 10.6, 4.0 Hz), 7.44 (6H, m), 7.67 (4H, m), 9.74 (1H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 19.2, 22.9, 26.7, 40.3, 62.8, 66.9, 127.7, 129.8, 132.72, 132.75, 135.5, 200.8 ; MS m/z : 324 (M^+-*t*-Bu), 199 (100%) ; HRMS calad. for $C_{17}H_{18}N_3O_2Si$ (M^+- *t*-Bu) : 324.1169, found : 324.1162 ; *Anal.* calad. for $C_{21}H_{27}N_3O_2Si$: C, 66.11 ; H, 7.13 ; N, 11.01, found : C, 66.40 ; H, 7.28 ; N, 11.00.

(8*R*,*E*),(8*R*,*Z*)-8-Azido-2,2,3,3,12,12-hexamethyl-11,11-diphenyl-4,10-dioxa-3,11-disilatridec-5-ene (44-*E*),(44-*Z*)[4c]





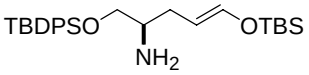
To a solution of aldehyde **43** (1.15 g, 3.02 mmol) in CH_2Cl_2 (3 mL) were successively added DBU (0.59 mL, 3.93 mmol), TBSCl (546 mg, 3.62 mmol). After stirring for 1 h at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 200:1) to give the enol ether **44-*E*** (1.01 g, 68%) and **44-*Z*** (0.41g, 27%) as a colorless oil.

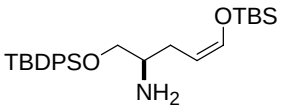
44 (*E*): $[\alpha]_D^{28}$ +3.7° (c 3.08, $CHCl_3$) ; IR (neat) : 3072, 3049, 2931, 2858, 2101, 1664, 1472, 1428, 1254, 1171, 1113, 839, 784, 740, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.15 (6H, s), 0.95 (9H, s), 1.12 (9H, s), 2.16 (2H, dd, *J* = 13.4, 6.6 Hz), 3.37 (1H, m), 3.68 (1H, dd, *J* = 10.6, 6.5 Hz), 3.76 (1H, dd, *J* = 10.6, 4.0 Hz), 4.94 (1H, dt, *J* = 12.0, 7.8 Hz), 6.31 (1H, d, *J* = 12.0 Hz), 7.43 (6H, m), 7.72 (4H, d, *J* = 6.1 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.17, -5.16, 18.3, 19.2, 25.7, 26.8, 28.7, 64.0, 66.1, 105.9, 127.7, 130.0, 132.94, 132.96, 135.47, 142.7 ; MS m/z : 438 (M^+-*t*-Bu), 171 (100%) ; HRMS calad. for $C_{23}H_{32}N_3O_2Si_2$ (M^+- *t*-Bu) : 438.2033, found : 438.2026.

44 (*Z*): $[\alpha]_D^{29}$ +16.8° (c 1.08, $CHCl_3$) ; IR (neat) : 3072, 3048, 2930, 2858, 2101, 1656, 1472, 1428, 1257, 1113, 838, 786, 741, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.076 (3H, s), 0.084 (3H, s), 0.87 (9H, s), 2.29 (2H, m), 3.44 (1H, m), 3.64 (1H, dd, *J* = 10.9, 6.8 Hz), 3.74 (1H, dd, *J* = 10.6, 3.8 Hz), 4.41 (1H, td, *J* = 7.2, 5.8 Hz), 6.22 (1H, d, *J* = 5.8 Hz), 7.40 (6H, m), 7.68 (4H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.3, 18.2, 19.2, 25.2, 25.6, 26.8, 63.9, 66.7,

104.6, 127.6, 129.6, 133.04, 133.11, 135.51, 135.52, 140.7 ; MS m/z : 438 (M^+-*t*-Bu), 171 (100%) ; HRMS calad. for $C_{23}H_{32}N_3O_2Si_2$ (M^+- *t*-Bu) : 438.2033, found : 438.2018.

(6*R*,*E*),(6*R*,*Z*)-2,2,11,11,12,12-Hexamethyl-3,3-diphenyl-4,10-dioxa-3,11-disilatridec-8-en-6-amine (12-*E*),(12-*Z*)[4d]



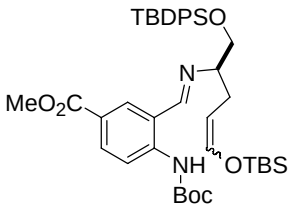


A solution of azide **44-*E*** (150 mg, 0.303 mmol) in MeOH (3 mL) was hydrogenated in the presence of Lindlar's catalyst (Aldrich, 25 mg) under atomospheric pressure of H_2. After stirring for 24 h at room temperature, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated *in vacuo*. The residue was purified by amine silica gel column chromatography (hexane:AcOEt, 20:1 to 4:1) to give the amine **12-*E*** (140 mg, quant.) as a colorless oil. Following this procedure, azide **44-*Z*** (50 mg, 0.101 mmol) was also converted to the amine **12-*Z*** (49 mg, quant.).

12 (*E*): $[\alpha]_D^{27}$ +3.0° (c 2.80, $CHCl_3$) ; IR (neat) : 3380, 3071, 3048, 2930, 2857, 1661, 1472, 1428, 1254, 1165, 1112, 1007, 927, 839, 783, 741, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.11 (6H, s), 0.90 (9H, s), 1.07 (9H, s), 1.44 (2H, br s), 1.88 (1H, m), 2.05 (1H, m), 2.86 (1H, m), 3.37 (1H, m), 3.46 (1H, dd, *J* = 10.0, 7.0 Hz), 3.62 (1H, dd, *J* = 9.8, 4.4 Hz), 4.94 (1H, m), 6.26 (1H, d, *J* = 12.0 Hz), 7.38 (6H, m), 7.67 (4H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.2, 18.3, 19.3, 25.7, 26.9, 31.8, 53.0, 68.4, 107.1, 127.5, 129.5, 133.4, 135.35, 135.37, 142.0 ; MS m/z : 412 (M^+-*t*-Bu), 298 (100%) ; HRMS calad. for $C_{23}H_{34}NO_2Si_2$ (M^+- *t*-Bu) : 412.2128, found : 412.2132.

12 (*Z*): $[\alpha]_D^{27}$ +4.8° (c 0.98, $CHCl_3$) ; IR (neat) : 3071, 2930, 2857, 1654, 1472, 1428, 1256, 1112, 837, 785, 741, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.082 (3H, s), 0.089 (3H, s), 0.88 (9H, s), 1.06 (9H, s), 1.46 (2H, br s), 2.17 (2H, m), 2.91 (1H, m), 3.46 (1H, dd, *J* = 10.0, 6.8 Hz), 3.65 (1H, dd, *J* = 10.0, 4.3 Hz), 4.42 (1H, td, *J* = 7.3, 5.9 Hz), 6.24 (1H, d, *J* = 5.9 Hz), 7.39 (6H, m), 7.66 (4H, d, *J* = 7.8 Hz) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.31, -5.30, 18.2, 19.3, 25.7, 26.9, 28.4, 53.3, 68.9, 106.3, 127.5, 129.5, 133.58, 135.46, 135.47, 140.1 ; MS m/z : 412 (M^+-*t*-Bu), 298 (100%) ; HRMS calad. for $C_{23}H_{34}NO_2Si_2$ (M^+- *t*-Bu) : 412.2128, found : 412.2145.

Methyl4-(*tert*-butoxycarbonylamino)-3-{(*E*)-[(6*R*,*E*),(6*R*,*Z*)-2,2,11,11,12,12-hexamethyl-3,3-diphenyl-4,10-dioxa-3,11-disilatridec-8-en-6-ylimino]methyl}benzoate (10-*E*),(10-*Z*)



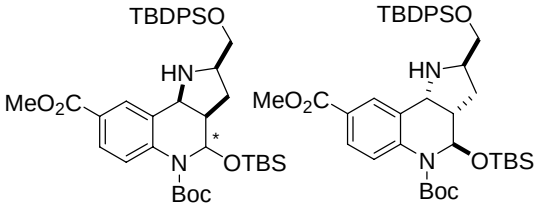
To the mixture of amine **12-*E*** (140 mg, 0.298 mmol) and aldehyde **11** (83 mg, 0.298 mmol) in benzene (1.5 mL) were successively added 4Å MS (140 mg), $LiBF_4$ (1 mg, 0.01 mmol) and the mixture was heated to reflux for 8 h. After cooled to room temperature, the reaction mixture was filtered through a Celite pad eluting with Et_2O and the filtrate was concentrated *in vacuo*. The residue was purified by amine silica gel column chromatography (hexane:AcOEt, 200:1) to give the imine **10-*E*** (140 mg, 89%) as a white foam. Following this procedure, amine **12-*Z*** (50 mg, 0.107 mmol) was also converted to the imine **10-*Z*** (64 mg, 82%); amine **12** (*E:Z* = 5:2, 6.17 g, 13.2 mmol) was also converted to the imine **10** (*E:Z* = 5:2, 8.44 g, 11.6 mmol, 88%).

10 (*E*): $[\alpha]_D^{27}$ –37.5° (c 3.80, $CHCl_3$) ; IR (neat) : 2931, 2858, 1722, 1661, 1637, 1589, 1530, 1472, 1429, 1391, 1367, 1286, 1243, 1162, 1112, 1050, 927, 839, 769, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.04 (3H, s), 0.05 (3H, s), 0.84 (9H, s), 1.01 (9H, s), 1.51 (9H, s), 2.20 (1H, m), 2.28 (1H, m), 3.32 (1H, m), 3.70 (1H, dd, *J* = 10.0, 8.1 Hz), 3.84 (1H, dd, *J* = 10.0, 4.3 Hz), 3.89 (3H, s), 4.97 (1H, m), 6.23 (1H, d, *J* = 12.0 Hz), 7.30 (6H, m), 7.56 (2H, d, *J* = 7.3 Hz), 7.62 (2H, d, *J* = 6.6 Hz), 7.56 (2H, d, *J* = 7.3 Hz), 8.00 (1H, s), 8.03 (1H, dd, *J* = 8.8, 1.7 Hz), 8.35 (1H, s), 8.50 (1H, d, *J* = 8.8 Hz), 12.4 (1H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.35, -5.29, 14.1, 18.3, 19.2, 22.6, 25.6, 26.8, 28.3, 30.6, 31.6, 51.8, 66.6, 72.6, 80.1, 106.6, 117.2, 119.4, 122.4, 127.44, 127.50, 129.48, 129.51, 132.3, 133.1, 133.4, 134.7, 135.3, 142.0, 144.7, 153.0, 163.5, 166.1 ; MS m/z : 730 (M^+), 617 (100%) ; HRMS calad. for $C_{41}H_{58}N_2O_6Si_2$ (M^+) : 730.3833, found : 730.3814.

10 (*Z*): $[\alpha]_D^{27}$ –44.4° (c 1.24, $CHCl_3$) ; IR (neat) : 2931, 2858, 1722, 1638, 1589, 1530, 1286, 1242, 1158, 1112, 838, 770, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 0.05 (3H, s), 0.06 (3H, s), 0.86 (9H, s), 0.99 (9H, s), 1.48 (9H, s), 2.35 (1H, m), 2.50 (1H, m), 3.40 (1H, m), 3.73 (1H, dd, *J* = 10.0, 8.3 Hz), 3.84 (1H, dd, *J* = 10.2, 4.2 Hz), 3.91 (3H, s), 4.48 (1H, m), 6.19 (1H, d, *J* = 5.9 Hz), 7.31 (6H, m), 7.56 (2H, d, *J* = 6.6 Hz), 7.61 (2H, d, *J* = 6.6 Hz), 8.00 (1H, s), 8.03 (1H, d, *J* = 8.8 Hz), 8.38 (1H, s), 8.48 (1H, d, *J* = 8.8 Hz), 12.5 (1H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.35, 14.2, 18.2, 19.3, 22.7, 25.6, 26.9, 28.3, 31.6, 52.0, 66.7, 72.3, 80.1, 105.4, 117.3, 119.6, 122.4, 127.46, 127.52, 129.45, 129.49, 132.3, 133.3, 134.8, 135.4, 140.0, 144.8, 153.1, 163.0, 166.3 ; MS m/z : 730 (M^+), 617 (100%) ; HRMS calad. for $C_{41}H_{58}N_2O_6Si_2$ (M^+) : 730.3833, found : 730.3846.

3. Completion of Asymmetric Total Synthesis of (–)-1 and 2 or (+)-1 and 2.

(2*R*,3a*R*,9b*S*),(2*R*,3a*S*,4*S*,9b*R*)-5-(*tert*-Butoxy carbonyl)-8-methoxycarbonyl-4-(*tert*-butyldi methylsilyloxy)-2-[(*tert*-butyldiphenylsilyloxy)methyl]-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2 -*c*]quinoline (13a),(13b)



major minor

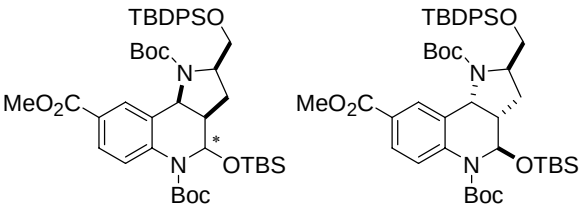
To a cooled (－40 ℃) solution of **10** (*E:Z* = 5:2, 340 mg, 0.465 mmol) and 4 Å MS (170 mg) in CH_2Cl_2 (9.3 mL) was added $BF_3 \cdot OEt_2$ (88 μL, 0.465 mmol) slowly and the mixture was stirred for 10 min at that temperature, then allowed to warm up to 0 ℃. After stirring for 3 h, the reaction mixture was quenched with 2N NaOH (0.45 mL) and allowed to warm up to room temperature. After stirring for 1 h, the reaction mixture was filtered through a Celite pad eluting with Et_2O. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over K_2CO_3 and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1 to 5:1) to give the amine [major isomer **13a** (128 mg, 38%), minor isomer **13b** (30 mg, 9%)] as a white amorphas

13a (major): $[\alpha]_D^{25}$ –4.8° (c 1.34, $CHCl_3$) ; IR (neat) : 2930, 2858, 1702, 1612, 1583, 1498, 1471, 1429, 1389, 1368, 1323, 1107, 1014, 940, 839, 763, 703, 666 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : -0.08 (3H, s), 0.00 (3H, s), 0.55 (9H, s), 1.07 (9H, s), 1.54 (9H, s), 1.65 (2H, m), 2.41 (1H, m), 2.56 (1H, m), 3.37 (1H, m), 3.52 (1H, m), 3.87 (3H, s), 4.00 (2H, m), 6.00 (1H, s), 7.38 (6H, m), 7.55 (1H, br s), 7.67 (4H, d, *J* = 7.3 Hz), 7.87 (1H, d, *J* = 8.5 Hz), 8.25 (1H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : -5.07, 17.6, 19.3, 25.5, 26.9, 28.4, 33.8, 43.8, 51.9, 57.8, 60.8, 67.1, 77.2, 82.0, 124.6, 125.4, 127.5, 127.9, 129.5, 130.2, 130.7, 133.4, 133.5, 135.4, 138.4, 151.3, 166.7 ; MS m/z : 730 (M^+), 229 (100%) ; HRMS calad. for $C_{41}H_{58}N_2O_6Si_2$ (M^+) : 730.3833, found : 730.3817 ; *Anal.* calad. for $C_{41}H_{58}N_2O_6Si_2$: C, 67.36 ; H, 8.00 ; N, 3.83, found : C, 67.14 ; H, 7.89 ; N, 3.83.

13b (minor): $[\alpha]_D^{33}$ +9.5° (c 2.10, $CHCl_3$) ; IR (neat) : 3336, 2930, 2857, 1720, 1612, 1498, 1471, 1437, 1389, 1368, 1326, 1277, 1164, 1108, 1020, 838, 766, 703 cm^{-1} ; ^{1}H-NMR (600 MHz, $CDCl_3$) δ : -0.06 (3H, s), 0.09 (3H, s), 0.64 (9H, s), 1.07 (9H, s), 1.53 (9H, s), 2.03 (1H, dd, *J* = 13.2, 2.4 Hz), 2.07 (1H, br s), 2.19 (1H, dd, *J* = 13.8, 4.8 Hz), 2.53 (1H, m), 2.53 (1H, m), 3.39 (1H, m), 3.64 (1H, dd, *J* = 10.2, 6.3 Hz), 3.72 (1H, dd, *J* = 10.2, 4.8 Hz), 3.88 (3H, s), 4.10 (1H, d, *J* = 7.2 Hz), 6.02 (1H, d, *J* = 3.0 Hz), 7.39 (6H, m), 7.57 (1H, br s), 7.71 (2H, m), 7.75 (2H, m), 7.86 (1H, dd, *J* = 9.0, 2.4 Hz), 8.24 (1H, s) ; ^{13}C-NMR (150 MHz, $CDCl_3$) δ : -5.5, -5.1, 17.6, 19.3, 25.4, 26.9, 28.3, 32.3, 44.2, 51.8, 56.8, 59.2, 67.8, 78.0, 82.0, 124.5, 125.4,

127.61, 127.64, 127.9, 129.56, 129.58, 130.8, 133.75, 133.79, 135.60, 135.62, 138.5, 151.5, 166.8 ; MS m/z : 730 (M^+), 229 (100%) ; HRMS calad. for $C_{41}H_{58}N_2O_6Si_2$ (M^+) : 730.3833, found : 730.3841.

(2*R*,3a*R*,9b*S*),(2*R*,3a*S*,4*R*,9b*R)*-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-(*tert*-butyldimethylsilyloxy)-2-[(*tert*-butyldiphenylsilyloxy)methyl]-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (45),(46)



To a cooled (0 ℃) solution of amine **13a** (275 mg, 0.377 mmol) and Boc_2O (0.27 mL, 1.131 mmol) in THF (2.5 mL) was added NaHMDS (1.9 M THF solution, 0.30 mL, 0.570 mmol) slowly and the mixture was stirred for 10 min at that temperature, then allowed to warm up to room temperature. After stirring for 1.5 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 20:1) to give the carbamate **45** (294 mg, 94%) as a white amorphas.

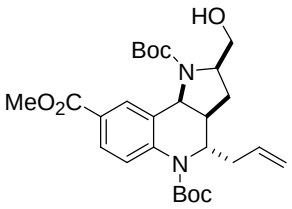
To a cooled (0 ℃) solution of amine **13b** (915 mg, 1.25 mmol) and Boc_2O (2.98 mL, 12.5 mmol) in THF (4.6 mL) was added NaHMDS (1.9 M THF solution, 4.62 mL, 8.75 mmol) slowly and the mixture was stirred for 10 min at that temperature, then allowed to warm up to room temperature. After stirring for 1.5 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 20:1) to give the carbamate **46** (973 mg, 94%) as a white amorphas.

45: $[\alpha]_D^{26}$ –42.5° (c 3.60, $CHCl_3$) ; IR (neat) : 2931, 2858, 1701, 1368, 1326, 1295, 1254, 1166, 1108, 1021, 839, 761, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 0.08 (3H, s), 0.14 (3H, s), 0.73 (9H, s), 0.96 (9H, s), 1.40 (9H, s), 1.47 (9H, s), 1.94 (1H, m), 2.10 (1H, m), 3.27 (1H, m), 3.52-3.72 (3.6H, m), 3.82 (0.4H, br s), 3.92 (1H, br s), 4.05 (1H, br s), 4.71 (0.4H, br s), 4.77 (0.6H, br s), 6.26 (1H, br s), 7.32 (7H, m), 7.52 (2H, d, *J* = 7.1 Hz), 7.58 (2H, br s), 7.77 (0.5H, br s), 7.91 (1H, d, *J* = 8.3 Hz), 7.99 (0.5H, br s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : -5.4, -4.6, 17.9, 19.1, 25.5, 26.8, 28.2, 30.1, 45.9, 46.3, 51.6, 56.7, 57.2, 59.6, 63.9, 65.7, 74.3, 74.8, 77.2, 80.0, 80.2, 81.4, 81.7, 125.0, 125.4, 126.1, 126.4, 126.6, 127.3, 127.4, 127.8, 129.3, 132.8, 133.2, 133.4, 135.16, 135.21, 138.9, 139.2, 151.9, 155.1, 155.5, 166.4 ; MS m/z : 773 (M^+-*t*-Bu), 485 (100%) ; HRMS calad. for $C_{42}H_{57}N_2O_8Si_2$ (M^+-*t*-Bu) : 773.3654, found :

773.3673 ; *Anal.* calad. for $C_{46}H_{66}N_2O_8Si_2$: C, 66.47 ; H, 8.00 ; N, 3.37, found : C, 66.37 ; H, 7.96 ; N, 3.39.

46: $[\alpha]_D^{23}$ +136.3° (c 0.78, $CHCl_3$) ; IR (neat) : 2931, 2858, 1701, 1612, 1472, 1428, 1391, 1368, 1327, 1257, 1167, 1107, 1022, 862, 838, 762, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 0.07 (3H, s), 0.15 (3H, s), 0.73 (9H, s), 1.06 (9H, s), 1.47-1.53 (18H, s x 3), 1.76 (0.34H, m), 1.85-1.94 (1.56H, m), 3.37 (0.60H, m), 3.48 (0.40H, m), 3.63 (0.60H, m), 3.86-3.92 (4H, s x 2, m), 4.02 (1H, m), 4.06 (0.4H, m), 4.56 (0.4H, d, *J* = 8.8 Hz), 4.65 (0.6H, d, *J* = 8.8 Hz), 6.11 (0.4H, d, *J* = 8.8 Hz), 6.22 (0.6H, d, *J* = 8.8 Hz), 7.41 (6H, m), 7.65 (4H, m), 7.76 (0.6H, s), 7.86-7.93 (1.4H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : -5.4, -5.3, -4.63, -4.57, 17.9, 19.3, 25.5, 26.9, 28.0, 28.1, 28.2, 28.3, 44.7, 46.0, 51.9, 56.4, 58.3, 58.4, 63.4, 64.1, 74.6, 75.1, 77.2, 80.2, 81.5, 81.8, 125.6, 126.0, 126.1, 126.4, 126.8, 126.9, 127.76, 127.80, 128.0, 128.1, 129.7, 129.8, 132.4, 132.9, 133.4, 133.5, 133.6, 133.7, 135.5, 135.6, 139.7, 139.9, 152.2, 154.2, 154.7, 166.9 ; MS m/z : 773 (M^+-*t*-Bu), 485 (100%) ; HRMS calad. for $C_{42}H_{57}N_2O_8Si_2$ (M^+-*t*-Bu) : 773.3654, found : 773.3669.

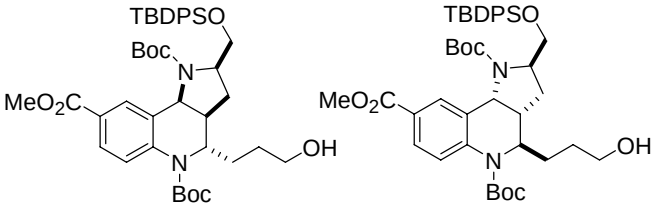
(2*R*,3a*S*,4*S*,9b*S*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl -4-allyl-2-(hydroxymethyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (14)



To a cooled (–40 ℃) solution of carbamate **16** (445 mg, 0.536 mmol) and allyltributylstannane (0.83 mL, 2.680 mmol) in CH_2Cl_2 (5.4 mL) was added $BF_3 \cdot OEt_2$ (0.24 mL, 1.876 mmol) slowly and the mixture was stirred for 5 min at that temperature, then allowed to warm up to －10 ℃. After stirring for 2.5 h, the reaction mixture was quenched with sat. $NaHCO_3$ and stirred for 30 min at room temperature. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water, 10% aq. KF and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was roughly purified by flash silica gel column chromatography (hexane:AcOEt, 20:1) to give the crude carbamate (344 mg) containing the wreckage of tin which was used in the next step without further purification. To a cooled (0 ℃) solution of crude carbamate in THF (5 mL) was added TBAF (1.0 M THF solution, 0.80 mL, 0.804 mmol) and the mixture was allowed to warm up to room temperature. After stirring for 3 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **14** (223 mg, 83% over 2 steps from **16**) as a white amorphas.

14: $[\alpha]_D^{27}$ –14.8° (c 1.07, $CHCl_3$) ; IR (neat) : 3414, 2978, 2360, 1698, 1611, 1498, 1476, 1438, 1368, 1326, 1276, 1166, 1045, 1002, 920, 851, 757, 666 cm^{-1} ; ^{1}H-NMR (600 MHz, toluene, 100 ℃) δ : 1.38 (9H, s), 1.59 (9H, s), 1.83-1.90 (2H, m), 2.03-2.13 (3H, m), 3.30 (1H, dd, *J* = 11.4, 6.0 Hz), 3.37 (1H, dd, *J* = 10.8, 3.6 Hz), 3.56 (3H, s), 3.97 (1H, m), 4.54 (1H, ddd, *J* = 9.0, 6.6, 2.4 Hz), 4.82 (1H, ddd, *J* = 17.4, 3.0, 1.2 Hz), 4.89 (1H, ddd, *J* = 10.2, 1.8, 1.2 Hz), 5.17 (1H, d, *J* = 8.4 Hz), 5.64 (1H, ddt, *J* = 17.4, 10.8, 6.6 Hz), 7.69 (1H, d, *J* = 8.4 Hz), 7.88 (1H, ddd, *J* = 8.4, 1.2, 0.6 Hz), 8.74 (1H, d, *J* = 1.8 Hz) ; ^{13}C-NMR (150 MHz, toluene, 100 ℃) δ : 28.4, 28.7, 31.3, 37.2, 40.7, 51.2, 55.1, 55.7, 61.0, 67.2, 81.4, 81.7, 117.3, 125.3, 126.9, 129.0, 129.7, 132.2, 134.8, 140.2, 154.2, 156.7, 166.3 ; MS m/z : 502 (M^+), 315 (100%) ; HRMS calad. for $C_{27}H_{38}N_2O_7$ (M^+) : 502.2679, found : 502.2671.

(2*R*,3a*S*,4*S*,9b*S*),(2*R*,3a*R*,4*R*,9b*R*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-2-[(*tert*-butyldiphenylsilyloxy)methyl]-4-(3-hydroxypropyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (47),(48)

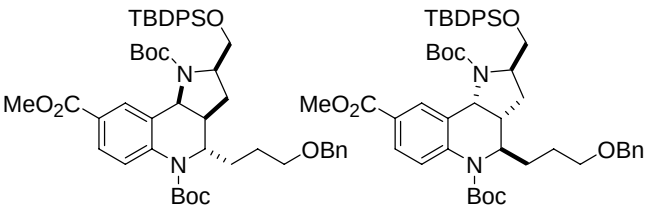


To a cooled (−40℃) solution of carbamate **45** (1.45 g, 1.75 mmol) and allyltributyltin (2.71 mL, 8.75 mmol) in CH_2Cl_2 (30 mL) was added $BF_3 \cdot OEt_2$ (0.67 mL, 5.25 mmol) slowly and the mixture was stirred for 5 min at that temperature, then allowed to warm up to −5 ℃. After stirring for 1 h, the reaction mixture was quenched with sat. $NaHCO_3$ and stirred for 30 min at room temperature. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water, 10% aq. KF and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was roughly purified by flash silica gel column chromatography (hexane:AcOEt, 20:1) to give the crude carbamate containing the wreckage of tin which was used in the next step without further purification. To a cooled (0 ℃) solution of crude carbamate in THF (8.8 mL) was added 9-BBN (0.5 M THF solution, 9.45 mL, 5.25 mmol) slowly. After stirring for 3 h at 0 ℃, the mixture was quenched with dry MeOH (1 mL), 1N NaOH (7.88 mL, 8.75 mmol) and 30% aq. H_2O_2 (2.63 mL) (slowly!), then stirred for 30 min. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **47** (1.07 g, 81% over 2 steps from **45**) as a white amorphas. Following this procedure, carbamate **46** (893 mg, 1.08 mmol) was also converted to the alcohol **48** (677 mg, 83% over 2 steps from **46**).

47: $[\alpha]_D^{25}$ –21.6° (c 1.53, $CHCl_3$) ; IR (neat) : 3483, 2932, 1693, 1368, 1323, 1276, 1163, 1112, 757, 704 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.57 (0.5H, br s), 8.42 (0.5H, br s), 7.80 (1H, dd, *J* = 8.8, 2.1 Hz), 7.68 (1H, br s), 7.52 (2H, br s), 7.48 (2H, d, *J* = 6.6 Hz), 7.26 (6H, m), 5.24 (0.5H, br s), 5.11 (0.5H, br s), 4.68 (1H, m), 4.02 (0.5H, br s), 3.90 (0.5H, br s), 3.84 (3H, s), 3.75-3.52 (4H, m), 2.49 (1H, m), 2.21 (1H, m), 2.03 (1H, m), 1.82-1.15 (22H, m), 0.77(9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.5, 156.3, 155.0, 154.0, 138.8, 135.32, 135.29, 133.4, 133.0, 131.9, 129.3, 128.9, 128.7, 128.1, 127.4, 125.6, 125.3, 124.3, 81.7, 80.6, 80.2, 77.2, 65.5, 64.0, 62.3, 59.1, 55.2, 54.4, 51.8, 40.6, 39.9, 31.7, 30.1, 29.3, 28.9, 28.8, 28.3, 26.5, 18.9 ; MS m/z : 701 (M^+-*t*-Bu), 589 (100%) ; HRMS calad. for $C_{39}H_{49}N_2O_8Si$ (M^+-*t*-Bu) : 701.3258, found : 701.3262 ; *Anal.* calad. for $C_{43}H_{58}N_2O_8Si$: C, 68.04 ; H, 7.70 ; N, 3.69, found : C, 67.96 ; H, 7.71 ; N, 3.63.

48: $[\alpha]_D^{22}$ +27.3° (c 0.63, $CHCl_3$) ; IR (neat) : 3471, 2932, 2360, 1695, 1390, 1368, 1330, 1276, 1239, 1164, 1113, 756, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.82 (0.5H, br s), 8.73 (0.5H, br s), 7.84 (1H, m), 7.65 (4H, m), 7.55 (1H, m), 7.39 (6H, m), 5.22 (0.5H, d, *J* = 7.8 Hz), 5.09 (0.5H, d, *J* = 7.8 Hz), 4.52 (0.5H, br m), 4.46 (0.5H, br m), 4.33 (0.5H, dd, *J* = 10.4, 4.0 Hz), 3.89-3.84 (4.5H, m), 3.69 (1H, m), 3.59 (2H, br m), 2.84 (0.5H, br m), 2.64 (0.5H, br m), 2.16 (0.5H, br m), 2.00 (0.5H, br m), 1.87 (1H, br m), 1.80-1.28 (22H, s x 4, m), 1.08 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.8, 166.7, 155.7, 154.4, 154.3, 154.0, 153.5, 139.4, 138.8, 135.6, 135.5, 133.8, 133.5, 133.4, 132.6, 132.1, 129.8, 129.7, 129.4, 128.5, 128.4, 127.8, 127.7, 125.9, 125.5, 125.1, 124.6, 81.9, 80.8, 80.2, 77.2, 64.4, 63.4, 62.4, 58.4, 58.1, 57.9, 57.0, 54.8, 54.7, 54.4, 54.3, 51.9, 51.8, 40.9, 39.0, 31.2, 30.8, 29.35, 29.29, 28.4, 28.3, 28.2, 26.97, 26.95, 19.4, 19.3 ; MS m/z : 758 (M^+), 333 (100%) ; HRMS calad. for $C_{43}H_{58}N_2O_8Si$ (M^+) : 758.3962, found : 758.3929.

(2*R*,3a*S*,4*S*,9b*S*),(2*R*,3a*R*,4*R*,9b*R*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-[3-(benzyloxy)propyl]-2-[(*tert*-butyldiphenylsilyloxy)methyl]-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (17),(49)



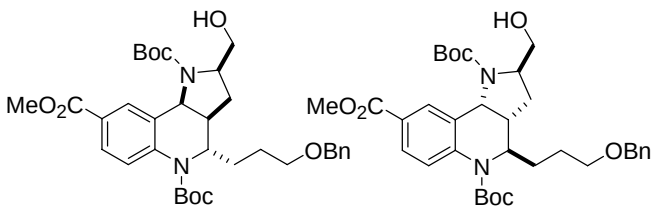
To a cooled (0 ℃) solution of alcohol **47** (1.04 g, 1.37 mmol) in THF (14 mL) was added 60% NaH (548 mg, 13.7 mmol) and the mixture was stirred for 30 min at that temperature. To the mixture were successively added BnBr (2.43 mL, 20.6 mmol) and TBAI (51 mg, 0.137 mmol), then allowed to warm up to 45 ℃. After stirring for 15 h, the reaction mixture was quenched with sat. $NaHCO_3$ and stirred for 5 min at room temperature. The layers were

separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 12:1) to give the ether **17** (209 mg, 71%) as a white amorphas. Following this procedure, alcohol **48** (550 mg, 0.725 mmol) was also converted to the ether **49** (415 mg, 67%).

17: $[\alpha]_D^{21}$ –19.6° (c 0.55, $CHCl_3$) ; IR (neat) : 2931, 2857, 1693, 1367, 1322, 1274, 1165, 1111, 755, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.57 (0.5H, br s), 8.42 (0.5H, br s), 7.80 (1H, dd, *J* = 8.8, 2.0 Hz), 7.70 (1H, br s) , 7.53 (2H, br s), 7.48 (2H, d, *J* = 6.3 Hz), 7.28 (11H, m), 5.25 (0.5H, br s), 5.11 (0.5H, br s), 4.63 (1H, m), 4.44 (2H, s), 4.02 (0.5H, br s), 3.90 (0.5H, br s), 3.85 (3H, s), 3.79-3.20 (4H, m), 2.47 (1H, m), 2.22 (1H, m), 2.01 (1H, m), 1.77-1.18 (22H, m), 0.79 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.7, 166.0, 154.0, 139.0, 138.4, 135.5, 135.4, 133.6, 133.2, 132.0, 129.4, 128.5, 128.3, 128.2, 127.6, 127.5, 125.5, 124.5, 81.6, 80.5, 80.2, 77.2, 72.9, 69.7, 65.8, 64.2, 59.1, 55.2, 54.5, 51.8, 40.6, 40.0, 31.8, 30.1, 29.0, 28.3, 27.7, 26.6, 26.5, 18.9 ; MS m/z : 791 (M^+-*t*-Bu), 679 (100%) ; HRMS calad. for $C_{46}H_{55}N_2O_8Si$ (M^+-*t*-Bu) : 791.3728, found : 701.3721.

49: $[\alpha]_D^{24}$ +5.6° (c 1.01, $CHCl_3$) ; IR (neat) : 2932, 2858, 1694, 1367, 1328, 1276, 1237, 1165, 1113, 754, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.84 (0.5H, br s), 8.74 (0.5H, br s), 7.84 (1H, m), 7.65 (4H, m), 7.56 (1H, m), 7.42-7.36 (6H, m), 7.31-7.23 (5H, m), 5.23 (0.5H, d, *J* = 7.8 Hz), 5.23 (0.5H, d, *J* = 7.8 Hz), 5.10 (0.5H, d, *J* = 7.8 Hz), 4.47 (1H, m), 4.42 (2H, s), 4.31 (0.5H, dd, *J* = 10.2, 3.9 Hz), 3.89 (1.5H, s), 3.86 (1.5H, m), 3.84 (1.5H, s), 3.71 (0.5H, d, *J* = 10.2 Hz), 3.66 (0.5H, dd, *J* = 8.9, 6.7 Hz), 3.48-3.36 (2H, m), 2.83 (0.5H, br m), 2.63 (0.5H, br m), 2.16 (0.5H, dd, *J* = 12.7, 6.0 Hz), 2.16 (0.5H, dd, *J* = 12.7, 6.0 Hz), 1.85 (1H, m), 1.64-1.32 (22H, s x 4, m), 1.08 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.8, 166.6, 155.6, 154.3, 154.2, 154.0, 139.5, 138.9, 138.4, 135.6, 135.5, 133.8, 133.5, 133.3, 132.6, 132.0, 129.8, 129.7, 129.4, 128.5, 128.3, 127.79, 127.76, 127.71, 127.68, 127.6, 127.5, 126.9, 125.8, 125.5, 125.2, 124.7, 81.7, 81.6, 80.8, 80.1, 77.3, 72.9, 72.8, 69.63, 69.59, 64.4, 63.4, 58.1, 57.9, 54.8, 54.7, 54.4, 54.3, 51.8, 51.7, 41.0, 39.1, 31.1, 30.8, 28.7, 28.5, 28.4, 28.3, 28.2, 26.96, 26.93, 26.6, 26.5, 19.34, 19.27 ; MS m/z : 848 (M^+), 379 (100%) ; HRMS calad. for $C_{50}H_{64}N_2O_8Si$ (M^+) : 848.4432, found : 848.4416.

(2*R*,3a*S*,4*S*,9b*S*),(2*R*,3a*R*,4*R*,9b*R*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-[3-(benzyloxy)propyl]-2-(hydroxymethyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (50),(51)



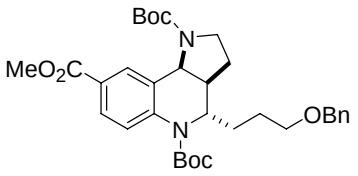
To a cooled (0 ℃) solution of ether **17** (205 mg, 0.242 mmol) in THF (4 mL) was added TBAF (1.0 M THF solution, 0.726 mL, 0.726 mmol) and the mixture was allowed to warm up to room temperature. After stirring for 5 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **50** (146 mg, 99%) as a white amorphas.

To a cooled (0 ℃) solution of ether **49** (410 mg, 0.483 mmol) in THF (4 mL) was added TBAF (1.0 M THF solution, 2.42 mL, 2.42 mmol) and the mixture was allowed to warm up to room temperature. After stirring for 5 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **51** (291 mg, 99%) as a white amorphas.

50: $[\alpha]_D^{29}$ −18.7° (c 1.09, $CHCl_3$) ; IR (neat) : 3415, 2977, 1698, 1610, 1497, 1437, 1368, 1323, 1276, 1164, 1109, 754 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.45 (1H, s), 7.84 (1H, d, *J* = 8.8 Hz), 7.64 (1H, d, *J* = 8.8 Hz), 7.28 (6H, m), 5.13 (1H, br s), 4.54 (1H, m), 4.43 (2H, s), 4.41 (1H, br s), 4.10 (1H, m), 3.89 (3H, s), 3.54-3.36 (3H, m), 3.23 (1H, m), 2.50 (1H, m), 2.23 (1H, m), 1.73-1.28 (22H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.2, 157.1, 153.8, 138.8, 138.1, 131.1, 128.6, 128.3, 128.1, 127.4, 127.3, 125.5, 124.5, 81.9, 81.8, 77.2, 72.7, 69.4, 68.2, 60.5, 55.0, 54.3, 51.7, 40.3, 30.2, 28.8, 28.3, 28.2, 27.7, 26.5 ; MS m/z : 610 (M^+), 423 (100%) ; HRMS calad. for $C_{34}H_{46}N_2O_8$ (M^+) : 610.3254, found : 610.3269.

51: $[\alpha]_D^{24}$ +1.8° (c 1.08, $CHCl_3$) ; IR (neat) : 3440, 2976, 1695, 1610, 1497, 1455, 1437, 1367, 1326, 1277, 1242, 1165, 1127, 754 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.82 (0.17H, br s), 8.57 (0.83H, br s), 7.87 (1H, d, *J* = 8.3 Hz), 7.34-7.22 (5H, m), 5.26 (1H, br s), 5.08 (0.83H, d, *J* = 7.0 Hz), 4.50 (1H, br m), 4.42 (2H, s), 4.36 (1H, br m), 3.89 (3H, s), 3.92-3.77 (2H, m), 3.72 (1H, m), 3.48-3.36 (2H, m), 2.57 (1H, br m), 1.95-1.78 (2H, br m), 1.73-1.45 (22H, s x 2, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.6, 155.7, 154.0, 139.9, 138.3, 131.8, 128.9, 128.8, 128.3, 127.61, 127.57, 125.6, 125.2, 81.9, 81.7, 77.3, 72.8, 69.5, 66.6, 60.0, 55.9, 55.0, 51.8, 41.2, 32.3, 29.1, 28.33, 28.26, 26.5 ; MS m/z : 610 (M^+), 287 (100%) ; HRMS calad. for $C_{34}H_{46}N_2O_8$ (M^+) : 610.3254, found : 610.3223.

(3a*S*,4*S*,9b*S*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-[3-(benzyloxy)propyl]-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (19)

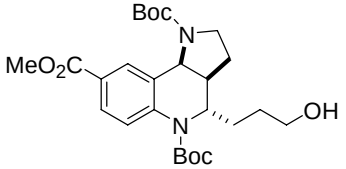


. To a solution of alcohol **50** (465 mg, 0.762 mmol) in CH_2Cl_2 (15.2 mL) were successively added 4ÅMS (465 mg), NMO (134 mg, 1.143 mmol) and TPAP (27 mg, 0.076 mmol). After stirring for 20 min, the reaction mixture was quenched with sat. $Na_2S_2O_3$ (50 μL). The reaction mixture was filtered through a Celite pad eluting with Et_2O. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure to give the crude aldehyde **18** (425 mg) which was used in the next step without further purification. To a solution of crude aldehyde **18** in xylene (15 mL) was added $(Ph_3P)_3RhCl$ (761 mg, 0.914 mmol) and the mixture was heated to reflux for 30 min. After cooled to room temperature, the reaction mixture was filtered through a Celite pad eluting with Et_2O and the filtrate was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1) to give the carbamate **19** (363 mg, 82% over 2 steps from **50**) as a colorless oil.

Crude aldehyde 18: ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 9.16 (0.5H, br s), 9.08 (0.5H, br s), 8.60 (1H, d, *J* = 2.0 Hz), 7.86 (1H, dd, *J* = 8.8, 1.9 Hz), 7.64 (1H, d, *J* = 8.8 Hz), 7.28 (6H, m), 5.31 (0.5H, br s), 5.15 (0.5H, br s), 4.57 (1H, m), 4.43 (2H, s), 4.28 (0.5H, m), 4.13 (0.5H, m), 3.90 (3H, s), 3.47 (1H, m), 3.40 (1H, m), 2.62 (0.9H, m), 2.43 (0.1H, m), 2.29 (1H, m), 1.95-1.25 (23H, m) ; MS m/z : 608 (M^+), 423 (100%) ; HRMS calad. for $C_{34}H_{44}N_2O_8$ (M^+) : 608.3098, found : 608.3099.

19: $[\alpha]_D^{29}$ −17.1° (c 1.38, $CHCl_3$) [for the enantiomer $[\alpha]_D^{24}$ +18.7° (c 1.58, $CHCl_3$)] ; IR (neat) : 2976, 1697, 1610, 1497, 1477, 1455, 1437, 1367, 1323, 1276, 1165, 1104, 755 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.56 (1H, s), 7.84 (1H, d, *J* = 8.8 Hz), 7.58 (1H, d, *J* = 7.8 Hz), 7.30 (6H, m), 5.19 (0.3H, br s), 5.04 (0.7H, br s), 4.57 (1H, m), 4.43 (2H, s), 3.88 (3H, s), 3.60-3.25 (4H, m), 2.52 (1H, m), 2.04 (1H, m),1.82-1.40 (23H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.4, 154.5, 153.9, 145.4, 139.4, 138.2, 132.2, 131.8, 128.9, 128.3, 128.2, 127.5, 127.4, 127.3, 125.4, 124.7, 81.6, 80.6, 77.2, 72.8, 69.5, 55.0, 54.1, 51.8, 45.5, 45.1, 42.6, 41.4, 29.1, 28.4, 28.3, 27.5, 26.9, 26.5 ; MS m/z : 580 (M^+), 379, 336 (100%) ; HRMS calad. for $C_{33}H_{44}N_2O_7$ (M^+) : 580.3149, found : 580.3126.

(3a*S*,4*S*,9b*S*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-(3-hydroxypropyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (52)

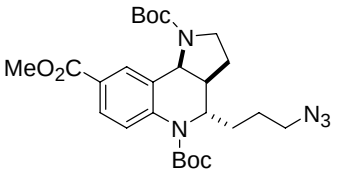


A solution of ether **19** (20 mg, 0.034 mmol) in MeOH (1 mL) was hydrogenated in the presence of Pd-C (10 wt%, 2 mg) under atomospheric pressure of H_2. After stirring for 10 h at room temperature, the reaction mixture was filtered through a Celite pad eluting with AcOEt

and the filtrate was concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **52** (17 mg, quant.) as a colorless oil.

52: $[\alpha]_D^{28}$ −17.9° (c 1.24, $CHCl_3$) [for the enantiomer $[\alpha]_D^{27}$ +20.1° (c 1.42, $CHCl_3$)] ; IR (neat) : 3463, 2977, 1697, 1390, 1368, 1323, 1277, 1243, 1163, 1118, 756 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.55 (1H, s), 7.84 (1H, d, *J* = 8.8 Hz), 7.57 (1H, d, *J* = 8.3 Hz), 5.18 (0.4H, br s), 5.05 (0.6H, br s), 4.59 (1H, m), 3.88 (3H, s), 3.72-3.37 (3H, m), 3.31 (1H, m), 2.54 (1H, m), 2.07 (1H, m), 1.92 (1H, m), 1.75 (1H, m), 1.70-1.40 (21H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.4, 155.9, 154.6, 154.0, 139.3, 138.8, 132.1, 131.8, 129.3, 128.8, 128.3, 125.7, 125.4, 124.6, 124.5, 81.8, 80.7, 79.8, 77.2, 62.1, 55.0, 54.7, 54.0, 53.8, 51.8, 45.4, 45.1, 42.6, 41.4, 29.2, 28.8, 28.7, 28.4, 28.2, 27.5, 26.9 ; MS m/z : 490 (M^+), 334 (100%) ; HRMS calad. for $C_{26}H_{38}N_2O_7$ (M^+) : 490.2679, found : 490.2688.

(3a*S*,4*S*,9b*S*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-(3-azidopropyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (53)

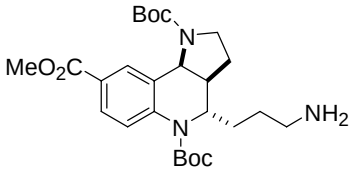


To a cooled (0 ℃) solution of alcohol **52** (314 mg, 0.640 mmol) in CH_2Cl_2 (6.4 mL) were successively added Et_3N (0.27 mL, 1.92 mmol) and MsCl (99 μL, 1.28 mmol). After the mixure was stirring for 40 min at that temperature, water was added and allowed to warm up to room temperature. The mixture was extracted with Et_2O, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give the crude mesylate which was used in the next step without further purification. To a solution of crude mesylate in DMF (6.5 mL) was added NaN_3 (250 mg, 3.84 mmol) and stirred for 1.5 h at 50 ℃. Aftetr the mixture was cooled to room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1) to give the azide **53** (302 mg, 92% over 2 steps from **52**) as a colorless oil.

53: $[\alpha]_D^{28}$ −27.9° (c 1.14, $CHCl_3$) [for the enantiomer $[\alpha]_D^{24}$ +31.5° (c 0.51, $CHCl_3$)] ; IR (neat) : 2976, 2097, 1696, 1610, 1437, 1367, 1276, 1165, 1119, 770 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.56 (1H, s), 7.85 (1H, d, *J* = 8.8 Hz), 7.56 (1H, d, *J* = 8.3 Hz), 5.18 (0.4H, br s), 5.04 (0.6H, br s), 4.58 (1H, m), 3.89 (3H, s), 3.54 (0.6H, m), 3.43 (0.4H, m), 3.32 (1H, m), 3.27 (2H, m), 2.53 (1H, m), 2.08 (1H, m), 1.80-1.40 (23H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 167.2, 156.8, 155.3, 154.7, 139.8, 139.4, 132.9, 132.6, 129.9, 129.5, 129.1, 126.6, 126.2, 125.4, 125.2, 82.4, 81.1, 80.3, 77.6, 55.0, 54.7, 54.3, 54.1, 52.1, 51.0, 45.7, 45.3, 42.9, 41.7, 29.6, 28.6, 28.4, 27.7, 27.1, 25.8 ; MS m/z : 515 (M^+), 57 (100%) ; HRMS calad. for

$C_{26}H_{37}N_5O_6$ (M^+) : 515.2744, found : 515.2761.

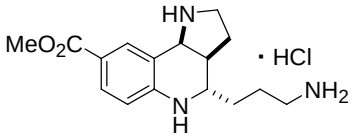
(3a*S*,4*S*,9b*S*)-1,5-Di-(*tert*-butoxycarbonyl)-8-methoxycarbonyl-4-(3-aminopropyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (20)



A solution of azide **53** (300 mg, 0.582 mmol) in MeOH (5 mL) was hydrogenated in the presence of Lindlar's catalyst (Aldrich, 60 mg) under atomospheric pressure of H_2. After stirring for 14 h at room temperature, the reaction mixture was filtered through a Celite pad eluting with $CHCl_3$ and the filtrate was concentrated *in vacuo*. The residue was purified by amine silica gel column chromatography ($CHCl_3$) to give the amine **20** (277 mg, 97%) as a colorless oil.

20: $[\alpha]_D^{28}$ –22.1° (c 0.75, $CHCl_3$) [for the enantiomer $[\alpha]_D^{24}$ +23.2° (c 1.24, $CHCl_3$)] ; IR (neat) : 3378, 2976, 1695, 1610, 1390, 1368, 1323, 1276, 1165, 1111, 753 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$, rotamers) δ : 8.56 (1H, s), 7.84 (1H, d, *J* = 9.0 Hz), 7.59 (1H, d, *J* = 7.8 Hz), 5.19 (0.4H, br s), 5.05 (0.6H, br s), 4.57 (1H, m), 3.88 (3H, s), 3.69-3.21 (2H, m), 2.65 (2H, m), 2.54 (1H, m), 2.08 (1H, m), 2.53 (1H, m), 2.08 (1H, m), 1.96-1.38 (23H, m), 1.28 (2H br s) ; ^{13}C-NMR (100 MHz, $CDCl_3$, rotamers) δ : 166.5, 156.0, 154.6, 154.0, 139.4, 139.0, 132.1, 131.8, 129.3, 128.9, 128.3, 125.7, 125.4, 124.7, 124.5, 81.7, 80.6, 79.8, 77.2, 55.1, 54.8, 54.0, 53.9, 51.8, 45.5, 45.1, 42.5, 41.7, 41.3, 30.4, 29.8, 28.4, 28.3, 27.5, 26.9 ; MS m/z : 489 (M^+), 245 (100%) ; HRMS calad. for $C_{26}H_{39}N_3O_6$ (M^+) : 489.2839, found : 489.2820.

(3a*S*,4*S*,9b*S*)-8-Methoxycarbonyl-4-(3-aminopropyl)-2,3,3a,4-tetrahydro-9b*H*-pyrrolo[3,2-*c*]quinoline (6)

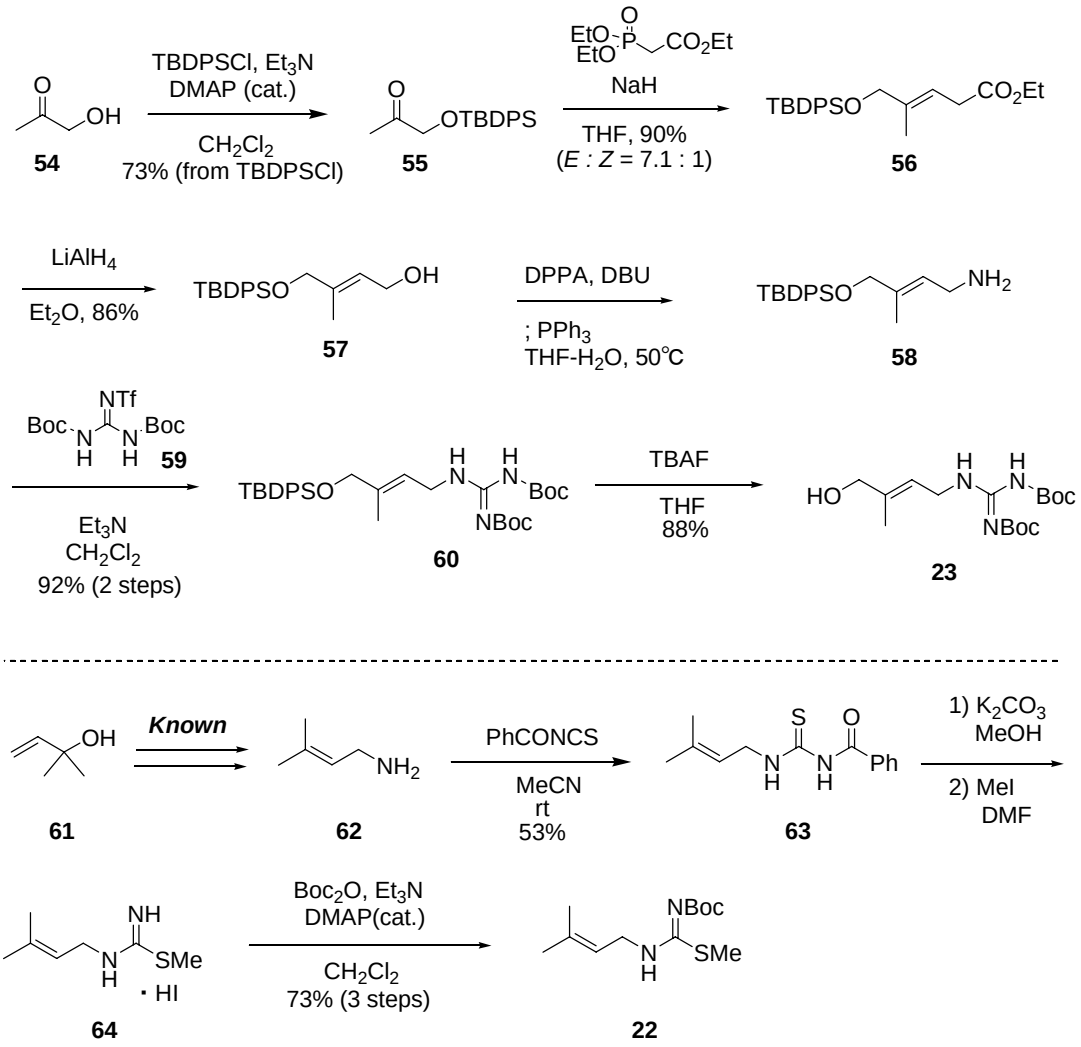


To amine **20** (21 mg, 0.043 mmol) was added a cooled (–15 ℃) HCl-MeOH solution (3 mL). After stirring for 12 h at room temperature, the reaction mixture was concentrated *in vacuo* to give the amine **6** (18 mg, quant. from ^{1}H, ^{13}C-NMR) as a white amorphas. Amine **6** was used in the next step without further purification.

6: $[\alpha]_D^{29}$ –57.7° (c 0.30, MeOH) [lit.[5] $[\alpha]_D^{20}$ –49.9° (c 1.25, MeOH), for the enantiomer $[\alpha]_D^{28}$ +62.4° (c 0.36, MeOH)] ; IR (neat) : 3280, 2950, 1700, 1615, 1523, 1439, 1295 cm^{-1} ; ^{1}H-NMR (400 MHz, CD_3OD) δ : 8.00 (1H, d, *J* = 1.7 Hz), 7.76 (1H, dd, *J* = 8.8, 2.0 Hz), 6.84 (1H, d, *J* = 8.8 Hz), 4.67 (1H, d, *J* = 5.9 Hz), 3.83 (3H, s), 3.38 (2H, m), 3.34 (1H, s), 3.10 (1H, m), 3.00 (2H, m), 2.44 (2H, m), 2.14 (1H, m), 1.99-1.77 (3H, m), 1.73 (1H, m) ; ^{13}C-NMR (100 MHz, CD_3OD) δ : 168.2, 150.9, 133.7, 132.6, 119.2, 115.6, 113.2, 59.2, 52.2, 50.8, 43.5, 40.8, 39.3, 30.4, 27.9, 23.9 ; MS m/z : 289 (M^+), 228 (100%) ; HRMS calad. for $C_{16}H_{23}N_3O_2$ (M^+) :

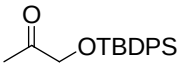
289.1790, found : 289.1773.

・Preparation of Guanidine Chain (22 and 23)[6a,b]



Scheme S-4

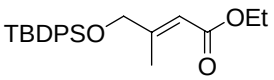
1-(*tert*-Butyldiphenylsilyloxy)propan-2-one (55)



To a solution of hydroxyacetone **54** (5.49 mL, 80.19 mmol) in CH_2Cl_2 (12 mL) were successively added Et_3N (15.22 mL, 108.75 mmol), TBDPSCl (7.48 mL, 29.11 mmol) and DMAP (71 mg, 0.58 mmol). After the mixture was stiired for 10 h at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 50:1) to give the silyl ether **55** (6.64 g, 73% from TBDPSCl) as a colorless oil.

55: IR (neat) : 3071, 2932, 2892, 2858, 1737, 1428, 1113, 824, 742, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 7.67 (4H, dd, *J* = 6.8, 1.0 Hz), 7.38 (6H, m), 4.16 (2H, s), 2.18 (3H, s), 1.11 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 208.1, 135.4, 132.5, 129.9, 127.7, 69.9, 26.8, 26.3, 19.2 ; MS m/z : 255 (M^+-*t*-Bu, 100%) ; HRMS calad. for $C_{15}H_{15}O_2Si$ (M^+-*t*-Bu) : 255.0842, found : 255.0829.

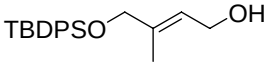
(*E*)-Ethyl4-(*tert*-butyldiphenylsilyloxy)-3-methylbut-2-enoate (56)



To a cooled (0℃) solution of NaH (60%, 10 mg, 0.253 mmol) in THF (1.1 mL) was added ethyl-diethylphosphonoacetate (50 μL, 0.253 mmol). Afer the mixture was stirred for 20 min at that temperature, ether **55** (66 mg, 0.211 mmol) in THF (1.1 mL) was added and the mixture was allowed to warm up to room temperature, then stirred for 1 h. Water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 50:1) to give the ester **56-*E*** (64 mg, 79%) and the ester **56-*Z*** (9 mg, 11%) as a colorless oil.

56 (*E*): IR (neat) : 1716, 1661, 1428, 1318, 1224, 1151, 1112, 825, 741, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 7.66 (4H, dd, *J* = 7.8, 1.5 Hz), 7.41 (6H, m), 6.20 (1H, s),4.19 (2H, q, *J* = 7.1 Hz), 4.13 (2H, s), 2.00 (3H, s), 1.09 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 167.0, 156.5, 135.3, 132.9, 129.7, 127.7, 113.4, 67.5, 59.6, 26.8, 19.3, 15.5, 14.4 ; MS m/z : 382 (M^+), 325 (100%) ; HRMS calad. for $C_{23}H_{30}O_3Si$ (M^+) : 382.1964, found : 382.1958 ; *Anal.* calad. for $C_{23}H_{30}O_3Si$: C, 72.21 ; H, 7.90, found : C, 72.45 ; H, 8.06.

(*E*)-4-(*tert*-Butyldiphenylsilyloxy)-3-methylbut-2-en-1-ol (57)

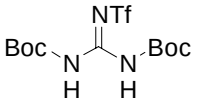


To a cooled (0 ℃) solution of ester **56** (5.2 g, 13.61 mol) in Et_2O (34 mL) was added $LiAlH_4$ (516 mg, 13.61 mmol) slowly. After stirring for 1 h at that temperature, the mixture was quenched with H_2O (0.52 mL) and 15% NaOH (0.52 mL) and stirred for 30 min. H_2O (1.56 mL) and $MgSO_4$ was added and the mixture was stirred for 1 h. The reaction mixture was filtered through a Celite pad eluting with Et_2O and the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 6:1) to give the alcohol **57** (3.96 g, 86%) as a colorless oil.

57: IR (neat) : 3333, 2930, 2857, 1428, 1112, 1007, 823, 741, 702 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 7.68 (4H, dd, *J* = 7.8, 1.7 Hz), 7.39 (6H, m), 5.74 (1H, t, *J* = 6.4 Hz), 4.07 (2H, s), 1.62 (3H, s), 1.24 (1H, br s), 1.07 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 137.9, 135.5, 133.6, 129.6, 127.6, 122.5, 68.1, 59.0, 26.8, 19.3, 13.5 ; MS m/z : 283 (M^+-*t*-Bu), 199 (100%) ; HRMS

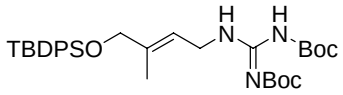
calad. for $C_{17}H_{19}O_2Si$ (M^+-*t*-Bu) : 283.1155, found : 283.1138 ; *Anal.* calad. for $C_{21}H_{28}O_2Si$: C, 74.07 ; H, 8.29, found : C, 74.21 ; H, 8.36.

Compound (59)



Compound **59** was prepared following the known procedure[6a].

Compound (60)

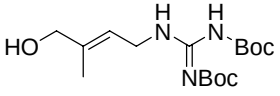


To a solution of alcohol **57** (635 mg, 1.87 mmol) in THF (8 mL) were successively added DBU (0.34 mL, 2.24 mmol) and DPPA (0.48 mL, 2.24 mmol). After stirring for 30 min, PPh_3 (589 mg, 2.24 mmol) and H_2O (1 mL) were added to the mixture and stirred for 5 h at 50 ℃. After cooled to room temperature, the reaction mixture was dried over K_2CO_3 and filtered through a Celite pad eluting with $CHCl_3$, then the filtrate was concentrated *in vacuo*. The residue was purified by amine silica gel column chromatography (hexane:AcOEt, 4:1 to $CHCl_3$) to give the crude amine (700 mg) containing the wreckage of phosphine which was used in the next step without further purification.

To a solution of crude amine **58** (700 mg) in CH_2Cl_2 (5 mL) were successively added Et_3N (0.43 mL, 3.09 mmol) and **59** (686 mg, 1.75 mmol). After the mixure was stirred for 1.5 h at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 12:1) to give the **60** (1.04 g, 92% over 2 steps from **57**) as a colorless oil.

60: IR (neat) : 3336, 2979, 2858, 1720, 1639, 1415, 1334, 1253, 1131, 1029, 822, 758, 703 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 11.50 (1H, br s), 8.23 (1H, br s), 7.67 (4H, dd, *J* = 7.8, 1.7 Hz), 7.38 (6H, m), 5.58 (1H, t, *J* = 6.1 Hz), 4.06 (4H, br s), 1.63 (3H, s), 1.51 (9H, s), 1.50 (9H, s), 1.06 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 163.6, 155.9, 153.2, 139.0, 135.5, 133.6, 129.6, 127.6, 118.6, 82.9, 79.2, 68.1, 38.6, 28.3, 28.1, 26.8, 19.3, 13.7, ; MS m/z : 581 (M^+), 59 (100%) ; HRMS calad. for $C_{32}H_{47}N_3O_5Si$ (M^+) : 581.3285, found : 581.3305.

Compound (23)

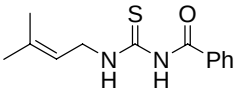


To a cooled (0℃) solution of **60** (508 mg, 0.874 mmol) in THF (1.8 mL) was added TBAF (1.0 M THF solution, 1.30 mL, 1.31 mmol) and the mixture was allowed to warm up to room temperature. After stirring for 2 h, the reaction mixture was quenched with sat. NH_4Cl. The layers were separated and the aqueous phase was extracted with Et_2O and washed with water

and brine, then dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 4:1 to 2:1) to give the alcohol **23** (265 mg, 88%) as a white solid.

23: M.p. = 193-195 ℃ ; IR (neat) : 3338, 2979, 1715, 1632, 1609, 1561, 1412, 1366, 1335, 1312, 1252, 1227, 1154, 1123, 1081, 1054, 1025, 807, 758 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 11.47 (1H, br s), 8.23 (1H, br s), 5.52 (1H, t, *J* = 7.0 Hz), 4.06 (2H, t, *J* = 5.9 Hz), 4.02 (2H, s), 2.17 (1H br s), 1.70 (3H, s), 1.50 (9H, s), 1.49 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 163.4, 155.8, 153.1, 139.4, 119.4, 83.0, 79.2, 67.5, 38.5, 28.2, 27.9, 13.7 ; MS m/z : 343 (M^+), 231 (100%) ; HRMS calad. for $C_{16}H_{29}N_3O_5$ (M^+) : 343.2107, found : 343.2096.

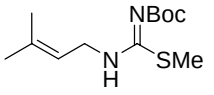
_N_-(3-Methylbut-2-enylcarbamothioyl)benzamide (63)



To a suspension of KSCN (1.14 g, 11.75 mmol) in acetone (9.25 mL) was added benzoyl chloride (1.36 mL, 11.8 mmol) dropwise. After stirring for 1 h at room temperature, the reaction mixture was filtered through a Celite pad eluting with CH_2Cl_2 and the filtrate was concentrated *in vacuo*. To the residue were added successively MeCN (9.25 mL) and prenylamine[6b] **62** (1.00 g, 11.8 mmol) in MeCN (1.85 mL) with stirring. After stirring for 1 h at room temperature, the reaction mixture was concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1) to give the thiourea **63** (1.53 g, 53%) as a white solid.

63: M.p. = 113-115 ℃ ; IR (neat) : 3218, 1663, 1528, 1490, 1443, 1262, 1208, 1164, 758, 689 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 10.55 (1H, br s), 8.99 (1H, br s), 7.83 (2H, d, *J* = 7.3 Hz), 7.62 (1H, t, *J* = 7.3 Hz), 7.51 (2H, t, *J* = 7.7 Hz), 5.36 (1H, m), 4.27 (2H, t, *J* = 5.9 Hz), 1.77 (3H, s), 1.74 (3H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 179.2, 166.7, 138.3, 133.4, 131.8, 129.0, 127.3, 118.0, 44.0, 25.6, 18.1 ; MS m/z : 248 (M^+), 231 (100%) ; HRMS calad. for $C_{13}H_{16}N_2OS$ (M^+) : 248.0983, found : 248.0967 ; *Anal.* calad. for $C_{13}H_{16}N_2OS$: C, 62.87 ; H, 6.49 ; N, 11.28, found : C, 62.76 ; H, 6.44 ; N, 11.26.

***tert*-Butyl-(3-methylbut-2-enylamino)methylthiomethylenecarbamate (22)**



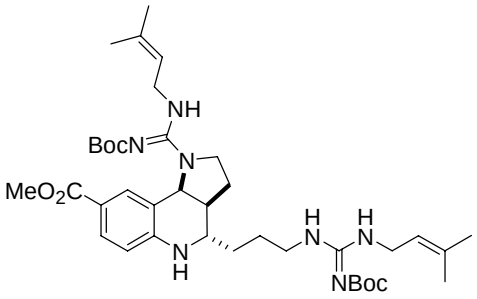
To a solution of thiourea **63** (1.3 g, 5.24 mmol) in MeOH (4.4 mL) was added K_2CO_3 (1.6 g, 11.5 mmol) and the resultant mixture was stirred at room temperature for 6 h. The solvent was removed *in vacuo* and then $CHCl_3$ (10 mL) was added to dissolve the residue. The resultant solution was washed with water and brine, then dried over $MgSO_4$ and concentrated under reduced pressure to give the crude thioamide which was used in the next step without further purification.

A solution of crude thioamide (680 mg) and MeI (0.60 mL, 9.44 mmol) in DMF (4.3 mL) was stirred at room temperature overnight. The solvent was removed *in vacuo* to give the crude **64** which was used in the next step without further purification.

To a solution of crude **64** in CH_2Cl_2 (4.3 mL) were successively added Et_3N (1.38 mL, 9.91 mmol), Boc_2O (1.05 mL, 5.19 mmol) and DMAP (29 mg, 0.237 mmol). After the mixure was stirred for 4 h at room temperature, water was added and the resultant solution was extracted with Et_2O. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane:AcOEt, 10:1) to give the **22** (890 mg, 73% over 3 steps from **63**) as a colorless oil.

22: IR (neat) : 3237, 2977, 2930, 1635, 1575, 1365, 1283, 1162, 1082, 804 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 9.61 (1H, br s), 5.24 (1H, m), 3.88 (2H, m), 2.47 (3H, s), 1.74 (3H, s), 1.68 (3H, s), 1.50 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 172.7, 161.8, 137.1, 118.6, 78.7, 41.4, 28.0, 25.4, 17.7, 13.3 ; MS m/z : 258 (M^+), 57 (100%) ; HRMS calad. for $C_{12}H_{22}N_2O_2S$ (M^+) : 258.1402, found : 258.1392.

(3a*S*,4*S*,9b*S*)-8-Methoxycarbonyl-4-{3-[2-(*tert*-butoxycarbonyl)-3-(3-methylbut-2-enyl)guanidine]propyl}-1-[*N*'-(*tert*-butoxycarbonyl)-*N*-(3-methylbut-2-enyl)carbamimidoyl]-2,3,3a,4,5,9b-hexahydro-1*H*-pyrrolo[3,2-*c*]quinoline (21)

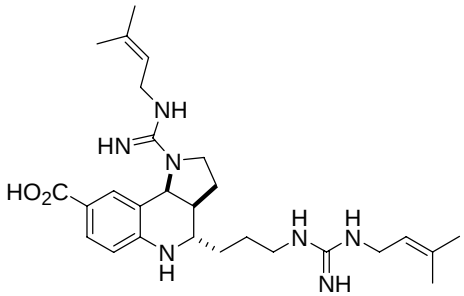


To a solution of amine **6** (40 mg, 0.100 mmol), **22** (126mg, 0.488 mmol) and Et_3N (0.16 mL, 1.170 mmol) in MeCN (2 mL) and MeOH (1 mL) was added a solution of $AgNO_3$ (116 mg, 0.681 mmol) in MeCN (0.5 mL) over 30 min. After the reaction mixture was stirred for 8 h in the dark at 40℃, it was filtered through a Celite pad eluting with $CHCl_3$ and the filtrate was concentrated *in vacuo*. The residue was partitioned between water and $CHCl_3$. The organic layer was separated and the aqueous phase was extracted with $CHCl_3$. The extracts were dried over K_2CO_3 and concentrated under reduced pressure. The crude mixture was purified by amine silica gel column chromatography (hexane:$CHCl_3$ = 1:1 to $CHCl_3$) to give **21** (40 mg, 56%) as a white foam.

21: $[\alpha]_D^{28}$ –179.1° (c 0.80, $CHCl_3$) [lit.[5] $[\alpha]_D^{20}$ –94.2° (c 0.28, $CHCl_3$), for the enantiomer $[\alpha]_D^{27}$ +175.6° (c 0.81, $CHCl_3$)] ; IR (neat) : 3293, 2974, 1607, 1523, 1436, 1320, 1142, 753 cm^{-1} ; ^{1}H-NMR (400 MHz, $CDCl_3$) δ : 7.97 (1H, s), 7.64 (1H, dd, *J* = 8.5, 1.8 Hz), 7.08 (1H, br s), 6.60 (1H, d, *J* = 8.3 Hz), 5.71 (1H, d, *J* = 7.0 Hz), 5.29 (1H, m), 5.19 (1H, m), 3.85 (1H, m), 3.82-3.63 (3H, m), 3.80 (3H, s), 3.50-3.20 (4H, m), 3.13 (1H, m), 2.30 (1H, m), 2.06 (2H, m),

1.72 (6H, s), 1.65 (6H, s), 1.62-1.35 (4H, m), 1.51 (9H, s), 1.48 (9H, s) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 167.2, 163.9, 162.0, 161.5, 160.0, 146.3, 136.9, 136.8, 131.6, 129.8, 120.2, 119.4, 118.1, 117.8, 113.6, 77.8, 77.4, 77.2, 53.2, 51.3, 50.5, 46.7, 42.5, 39.9, 39.5, 39.3, 31.9, 28.5, 28.4, 28.0, 27.9, 26.5, 25.6, 18.0 ; MS (FAB) m/z : 710 ($[M+H]^+$), 69 (100%) ; HRMS (FAB) calad. for $C_{38}H_{60}N_7O_6$ ($[M+H]^+$) : 710.4605, found : 710.4595.

(–)-Martinellic acid (1)



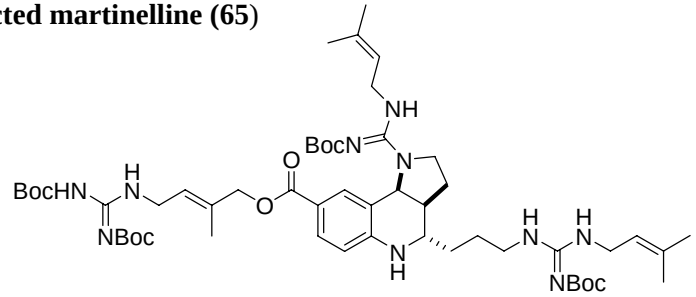
A solution of **21** (37 mg, 0.052 mmol) in 0.2 M NaOH (2 mL) and MeOH (6 mL) was refluxed for 14 h. The reaction mixture was cooled to room temperature and some of the MeOH was removed by concentration under reduced pressure. Sat. NH_4Cl was added to the remaining solution. After the organic layer was separated, the aqueous phase was extracted with $CHCl_3$. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude acid (36 mg) as a yellow foam which was used in the next step without further purification. To a solution of crude acid (36 mg) and anisole (60 μL, 0.552 mmol) in CH_2Cl_2 (3.5 mL) was added TFA (120 μL, 1.62 mmol). The resultant light yellow solution was stirred at room temperature for 16 h and concentrated under reduced pressure. The brown oil was purified by preparative HPLC [YMC-Pack ODS-AM, 250 x 10 mm I.D., S-5 μm, 12 nm, eluting with 80:20 H_2O:MeOH (with 0.1% TFA) to 30:70 H_2O:MeOH (with 0.1% TFA) as a gradient over 90 min and with a flow rate of 4 ml/min ; UV detector : 330 nm ; Retention time : 36.0 min]. This compound was isolated and concentrated by freezed-dry to give **1** (23 mg, 60% over 2 steps from **21**) as a white powder.

1 (TFA salt): $[\alpha]_D^{29}$ –164.3° (c 0.14, MeOH) [lit.[7] natural $[\alpha]_D$ –8.5° (c 0.01, MeOH), [5] $[\alpha]_D^{20}$ –122.7° (c 0.31, MeOH), for the enantiomer $[\alpha]_D^{28}$ +165.5° (c 0.11, MeOH)] ; IR (neat) : 3311, 3186, 2941, 1652, 1605, 1524, 1449, 1318, 1246, 1198, 1177, 1127, 834, 799, 774, 720 cm^{-1} : ^{1}H NMR (600 MHz, d_6-DMSO) δ : 7.75 (1H, br s), 7.69 (2H, br s), 7.63 (1H, s), 7.61 (1H, m), 7.58 (1H, m), 7.57 (1H, dd, *J* = 8.4, 1.8 Hz), 7.42 (2H, br s), 7.04 (1H, d, *J* = 3.6 Hz), 6.57 (1H, *J* = 8.4 Hz), 5.30 (1H, m), 5.27 (1H, d, *J* = 7.2 Hz), 5.16 (1H, m), 3.93 (1H, ddd, *J* = 15.6, 6.0, 6.0 Hz), 3.84 (1H, ddd, *J* = 15.6, 5.4, 5.4 Hz), 3.71 (2H, dd, *J* = 5.4, 5.4 Hz), 3.39 (2H, m), 3.27 (1H,br s), 3.13 (2H, m), 2.42 (1H, m), 2.06 (1H, m), 1.72 (3H, d, *J* = 1.2 Hz), 1.69 (3H, d, *J* = 0.6 Hz), 1.68 (3H, s), 1.68 (1H, m), 1.63 (3H, d, *J* = 0.6 Hz), 1.63 (1H, m), 1.57 (1H, m), 1.42 (2H, m) ; ^{13}C NMR (150 MHz, d_6-DMSO) δ : 167.2, 158.1 (q, *J* = 30.2 Hz), 155.5, 154.3, 146.3,

135.9, 135.5, 130.4, 130.0, 119.6, 119.2, 117.1, 115.6, 113.3, 53.0, 49.2, 45.8, 40.7, 39.8*, 39.3*, 39.0*, 33.4, 26.3, 25.4, 25.27, 25.24, 17.9, 17.8 (3 peaks observed at 39.8, 39.3 and 39.0 by Witherup and co-workers (ref. 7) could not be unequivocally assigned from the ^{13}C NMR as they lied underneath the DMSO peak. These 3 peaks however could be assigned from the DEPT and C-H-COSY data we carried out on synthetic **1**.) ; MS (FAB, glycerol) m/z : 496 ($[M+H]^+$), 93 (100%) ; HRMS (FAB, glycerol) calad. for $C_{27}H_{42}N_7O_2$ ($[M+H]^+$, free guanidine) : 496.3400, found : 496.3398.

^1H NMR and ^{13}C NMR of the isolated compound in d_6-DMSO and MS (FAB) conformed to that of martinelline isolated by Witherup and coworkers (ref 7).

Tetra-Boc protected martinelline (65)

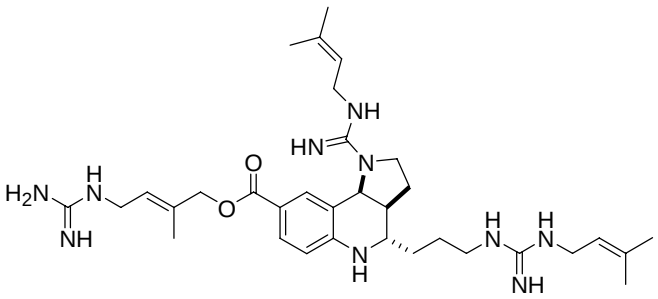


A solution of **21** (39 mg, 0.055 mmol) in 0.2 M NaOH (1.7 mL) and MeOH (5 mL) was refluxed for 14 h. The reaction mixture was cooled to room temperature and some of the MeOH was removed by concentration under reduced pressure. Sat. NH_4Cl was added to the remaining solution. After the organic layer was separated, the aqueous phase was extracted with $CHCl_3$. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude acid (38 mg) as a yellow foam which was used in the next step without further purification. To a solution of crude acid (38 mg, 0.0403 mmol), **23** (21 mg, 0.0605 mmol) and BOPCl (31 mg, 0.121 mmol) in CH_2Cl_2 (2 mL) was added DIEPA (70 μL, 0.403 mmol) and the clear solution was stirred at room temperature for 4 h. The reaction was poured into sat. NH_4Cl (20 mL) and extracted with $CHCl_3$. The extracts were dried over K_2CO_3 and concentrated under reduced pressure. The crude mixture was purified by amine silica gel column chromatography (hexane:AcOEt = 4:1 to $CHCl_3$) to give **65** (42 mg, 75% over 2 steps from **21**) as a white foam.

65: $[\alpha]_D^{27}$ −132.1° (c 0.44, $CHCl_3$) [for the enantiomer $[\alpha]_D^{28}$ +139.3° (c 0.32, $CHCl_3$)] ; IR (neat) : 3330, 2977, 1721, 1608, 1318, 1135, 756 cm^{-1} ; ^1H-NMR (400 MHz, $CDCl_3$) δ :11.48 (1H, br s), 8.23 (1H, m), 7.95 (1H, s), 7.66 (1H, d, *J* = 8.6 Hz), 6.58 (1H,d, *J* = 7.6 Hz), 5.76 (1H, d, *J* = 6.8 Hz), 5.56 (1H, m), 5.27 (1H, m), 5.19 (1H, m), 4.67 (1H, d, *J* = 12.9 Hz), 4.62 (1H, d, *J* = 12.9 Hz), 4.08 (2H, m), 3.90-3.65 (5H, m), 3.52-3.22 (5H, m), 3.14 (1H, br s), 2.33 (1H, m), 2.12-1.92 (3H, m), 1.76 (3H, s), 1.73 (3H, s), 1.70 (3H, s), 1.68-1.55 (2H, m), 1.67

(3H,s), 1.63 (3H, s), 1.50 (9H, s), 1.49 (9H, s), 1.48 (18H, s), 1.45-1.40 (2H, m) ; ^{13}C-NMR (100 MHz, $CDCl_3$) δ : 166.2, 163.8, 163.3, 162.7, 162.1, 160.0, 155.7, 152.9, 146.4, 136.9, 136.7, 135.4, 131.7, 129.8, 122.2, 120.3, 119.4, 118.5, 113.5, 82.9, 79.2, 77.9, 77.6, 77.1, 68.4, 64.8, 53.1, 50.6, 47.0, 42.6, 39.9, 39.4, 39.2, 38.6, 29.7, 28.5, 28.4, 28.3, 28.0, 27.9, 26.5, 25.63, 25.58, 18.0, 14.2 ; MS (FAB) m/z : 1021 ($[M+H]^+$), 69, 57 (100%) ; HRMS (FAB) calad. for $C_{53}H_{85}N_{10}O_{10}$ ($[M+H]^+$) : 1021.6450, found : 1021.6453.

(−)-Martinelline (2)



To a solution of **65** (12 mg, 0.0118 mmol) in CH_2Cl_2 (2 mL) was added TFA (120 μL, 1.62 mmol). The resultant light yellow solution was stirred at room temperature for 24 h and concentrated under reduced pressure. The brown oil was purified by preparative HPLC [YMC-Pack ODS-AM, 250 x 10 mm I.D., S-5 μm, 12 nm, eluting with 80:20 H_2O:MeOH (with 0.1% TFA) to 30:70 H_2O:MeOH (with 0.1% TFA) as a gradient over 90 min and with a flow rate of 4.73 ml/min ; UV detector : 330 nm ; Retention time : 39.5 min]. This compound was isolated and concentrated by freezed-dry to give **2** (8 mg, 70%) as a white powder.

2 (TFA salt): $[\alpha]_D^{28}$ –108.0° (c 0.09, MeOH) [lit.[7] natural $[\alpha]_D$ +9.4° (c 0.02, MeOH), for the enantiomer $[\alpha]_D^{29}$ +98.6° (c 0.02, MeOH)] ; IR (neat) : 3327, 3180, 1663, 1607, 1524, 1455, 1436, 1281, 1252, 1200, 1179, 1129, 836, 801, 768, 722 cm^{-1} : ^{1}H NMR (600 MHz, d_6-DMSO) δ : 7.81-7.67 (4H, br s), 7.65 (1H, br s), 7.57 (1H, dd, *J* = 8.6, 1.7 Hz), 7.52 (1H, br s), 7.40 (2H, br s), 7.19 (1H, d, *J* = 2.0 Hz), 6.60 (1H, d, *J* = 8.3 Hz), 5.49 (1H, t, *J* = 6.5 Hz), 5.39 (1H, d, *J* = 6.2 Hz), 5.29 (1H, m), 5.19 (1H, m), 4.62 (1H, d, *J* = 13.1 Hz), 4.58 (1H, d, *J* = 13.0 Hz), 3.92 (1H, ddd, *J* = 15.1, 5.5, 5.5 Hz), 3.86 (1H, ddd, *J* = 15.8, 5.5, 5.5 Hz), 3.80 (2H, t, *J* = 5.5 Hz), 3.72 (2H, t, *J* = 5.5 Hz), 3.38 (2H, dd, *J* = 9.6, 4.1 Hz), 3.31 (s, H_2O), 3.29 (1H, br s), 3.13 (2H, m), 2.44 (1H, m), 2.06 (1H, m), 1.73 (3H, s), 1.70 (3H, s), 1.69 (3H, s), 1.68 (3H, s), 1.68 (1H, m), 1.63 (3H, s), 1.57 (2H, m), 1.44 (2H, m) ; ^{13}C NMR (150 MHz, d_6-DMSO) δ : 165.1, 157.9 (q, *J* = 30.2 Hz), 156.7, 155.5, 154.3, 146.8, 136.0, 135.5, 134.8, 130.5, 129.7, 121.5, 119.5, 119.2, 116.0, 115.7, 113.3, 67.6, 53.0, 49.1, 45.8, 40.7, 39.9*, 39.2*, 39.0*, 38.4, 33.4, 26.2, 25.34, 25.25, 25.1, 17.9, 17.8, 13.8 (3 peaks observed at 39.9, 39.2 and 39.0 by Witherup and co-workers (ref. 7) could not be unequivocally assigned from the ^{13}C NMR as they lied underneath the DMSO peak. These 3 peaks however could be assigned from the DEPT and C-H-COSY data we carried out on synthetic **2**.) ; MS (FAB, glycerol) m/z : 621 ($[M+H]^+$), 93

(100%) ; HRMS (FAB, glycerol) calad. for $C_{33}H_{53}N_{10}O_2$ ($[M+H]^+$, free guanidine) : 621.4353, found : 621.4347.

^{1}H NMR and ^{13}C NMR of the isolated compound in d_6-DMSO and MS (FAB) conformed to that of martinelline isolated by Witherup and coworkers (ref 7).

References

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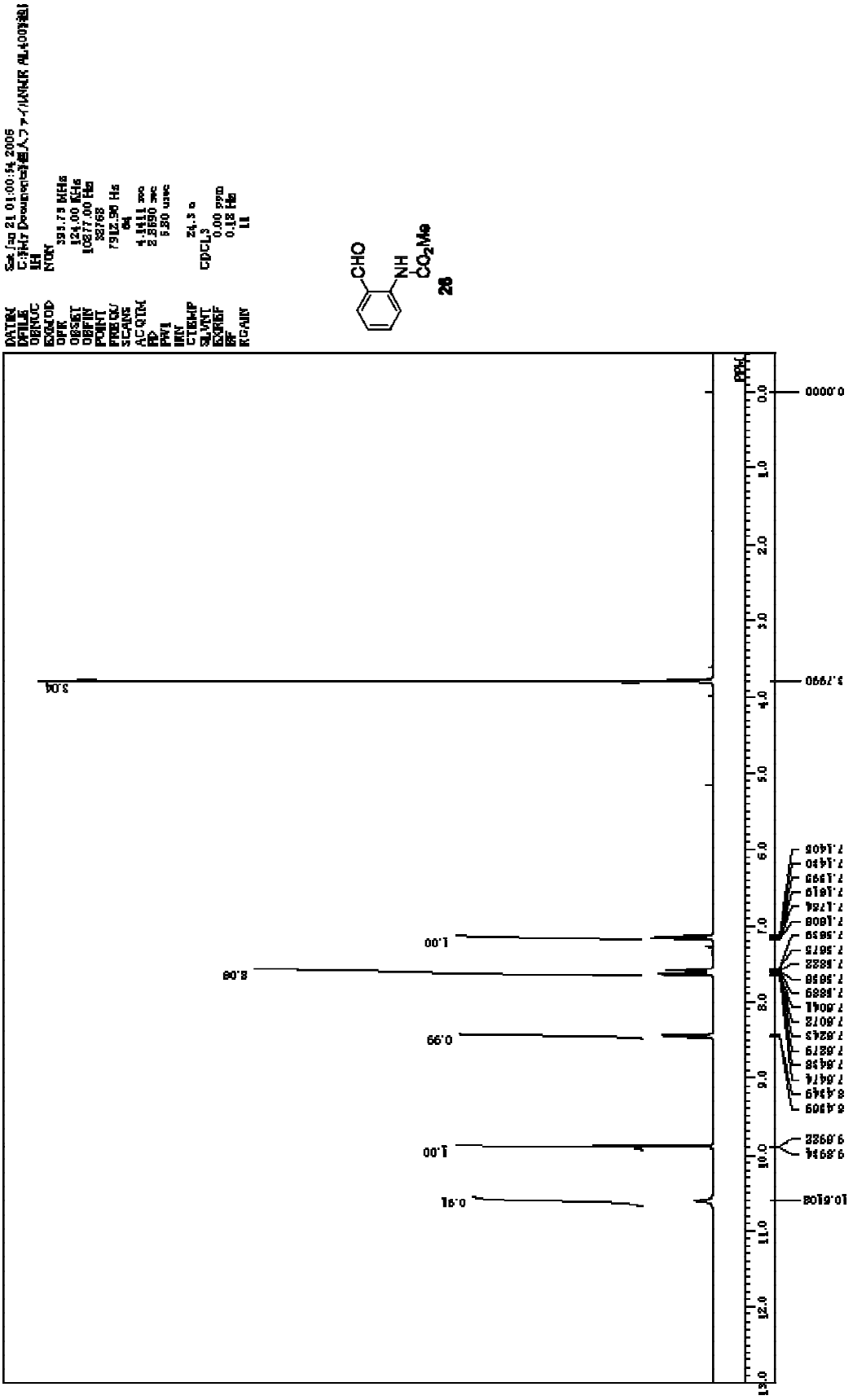
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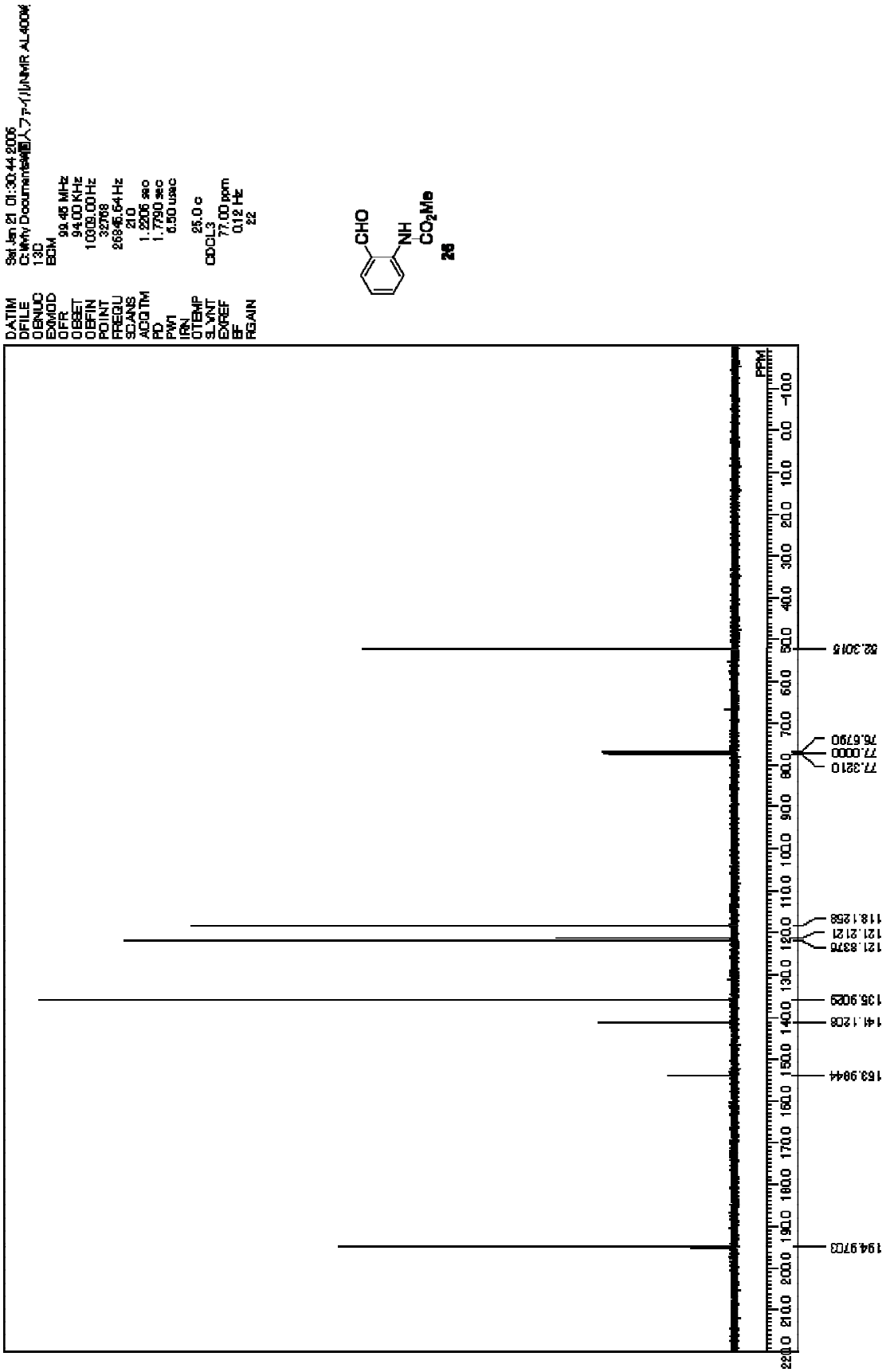
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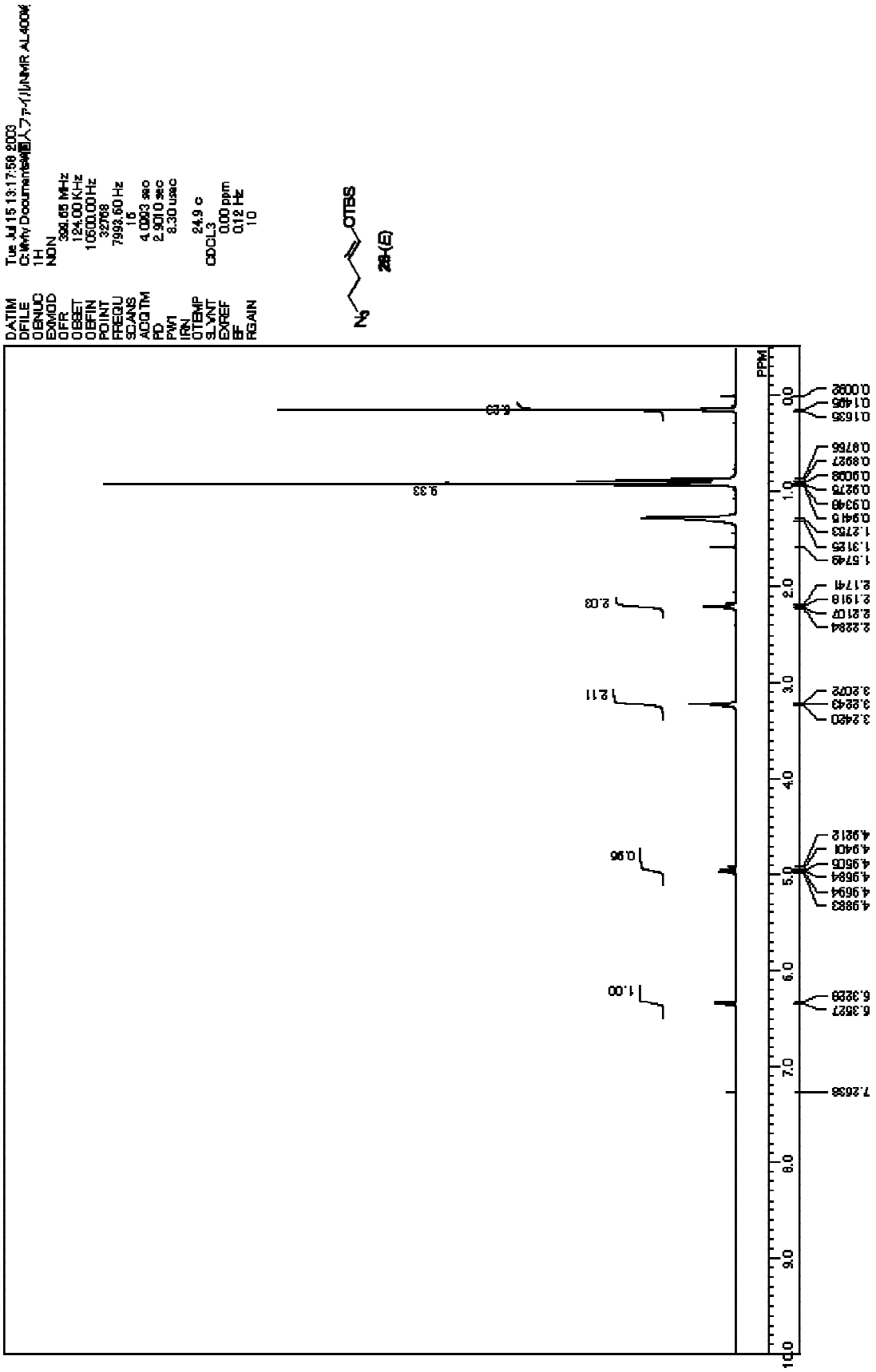
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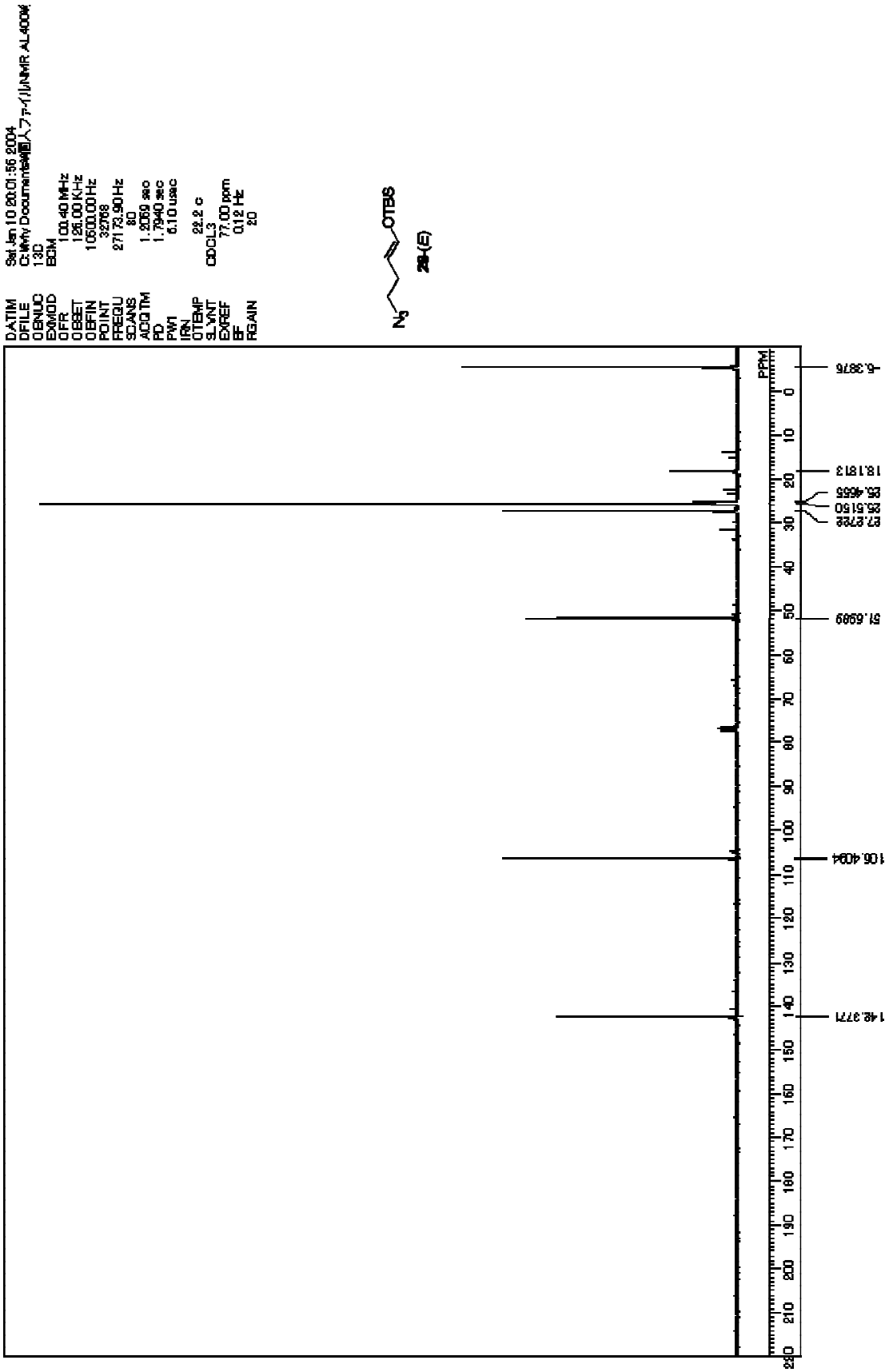
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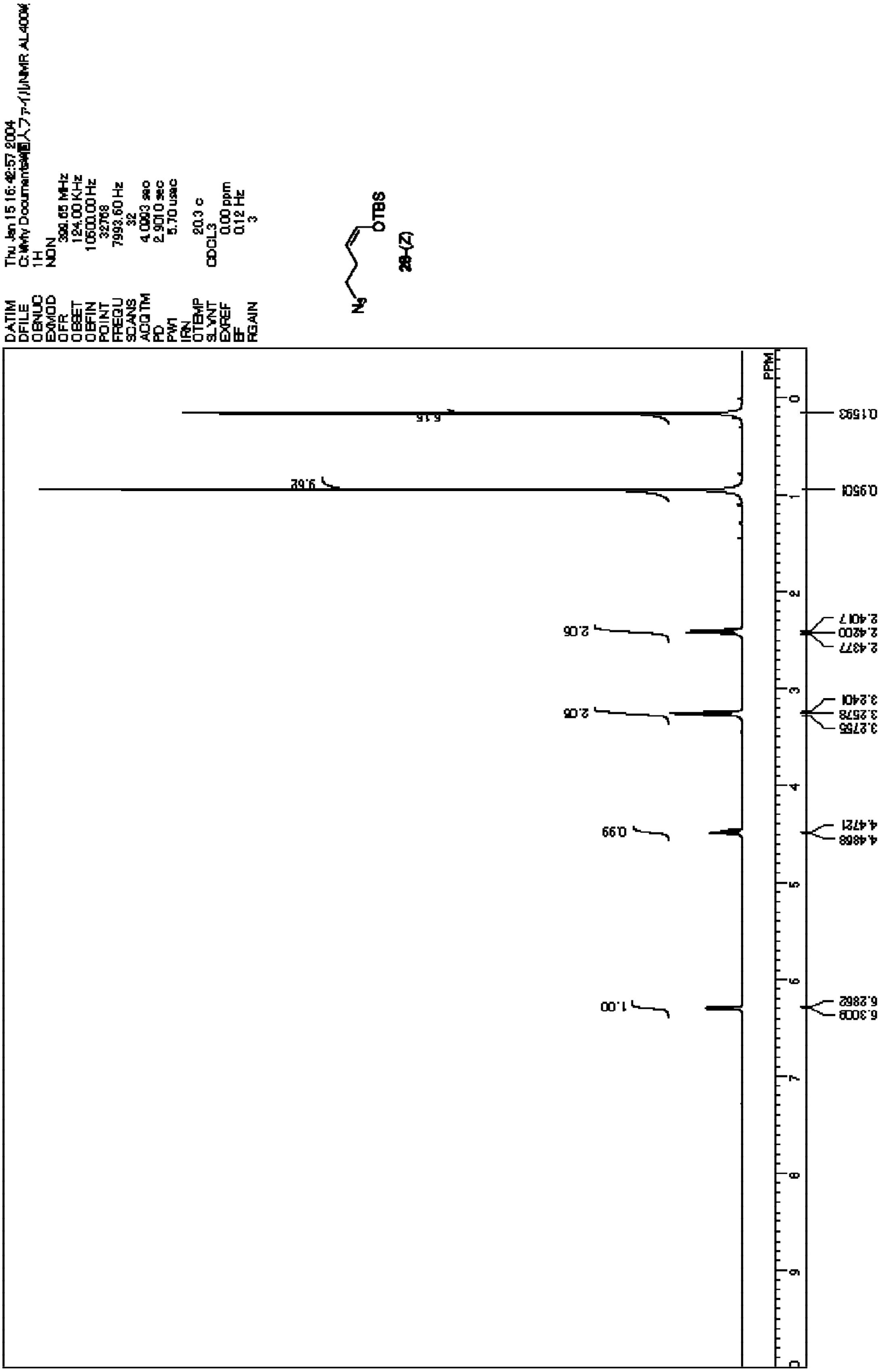
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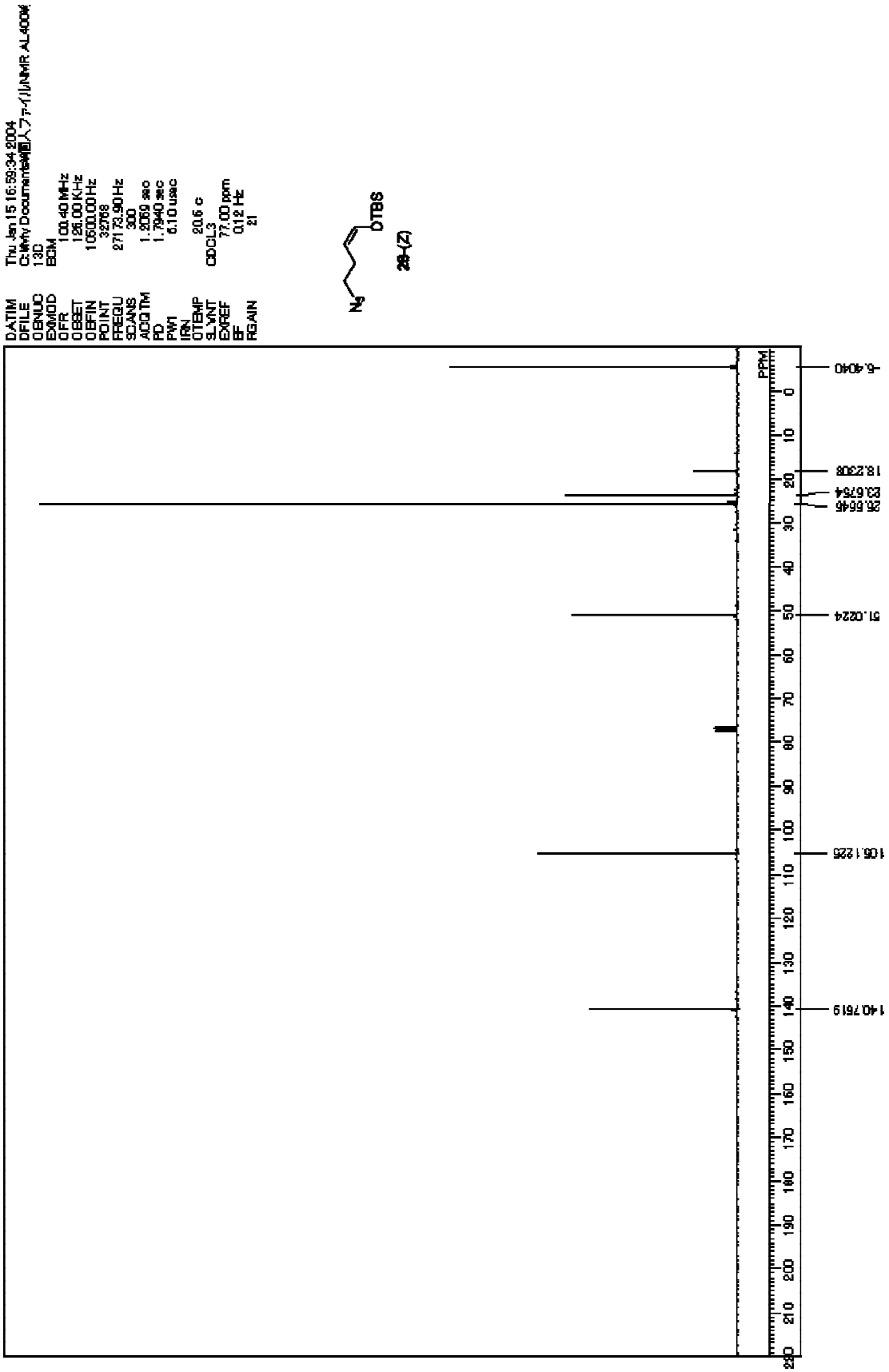
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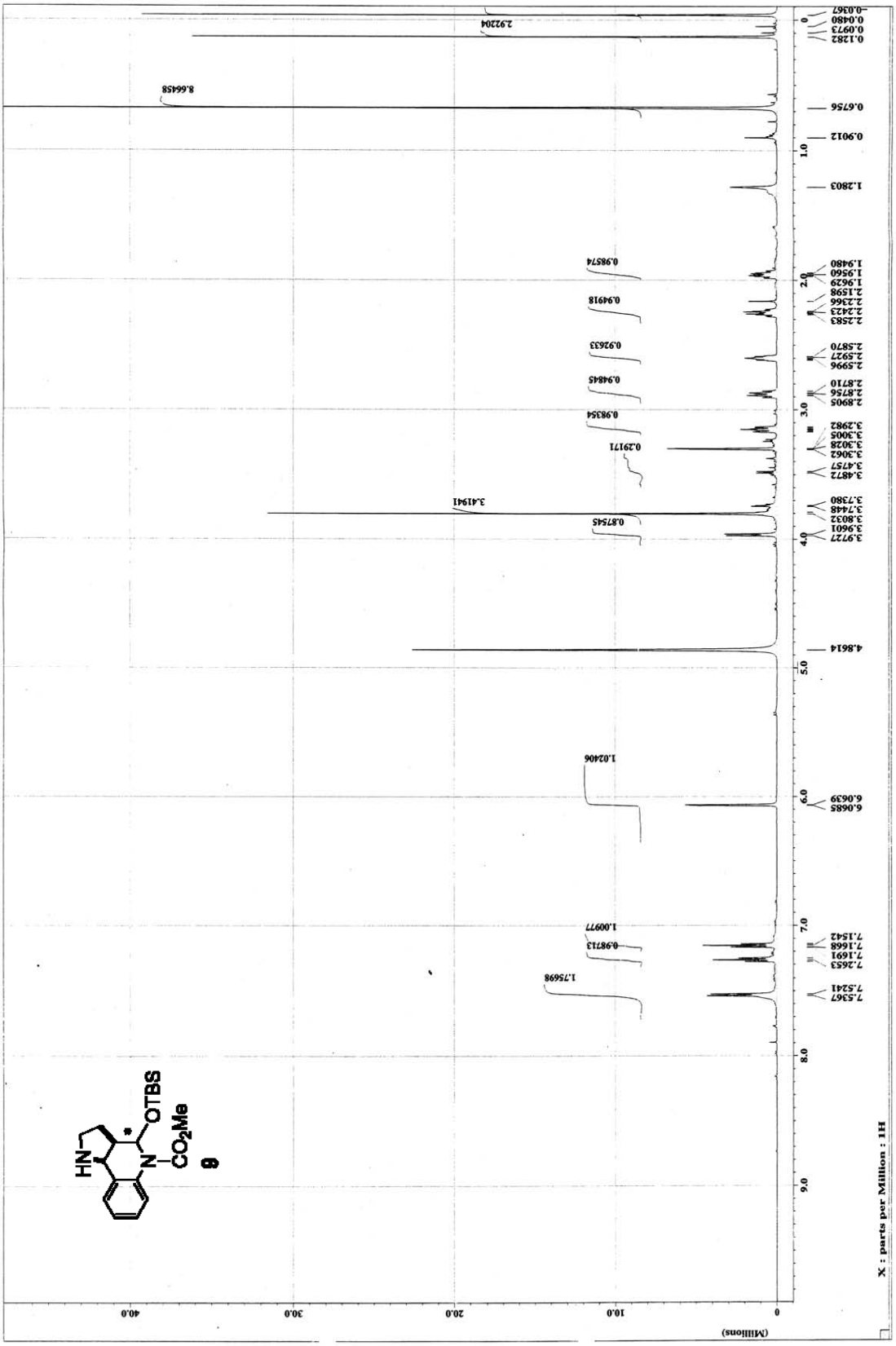
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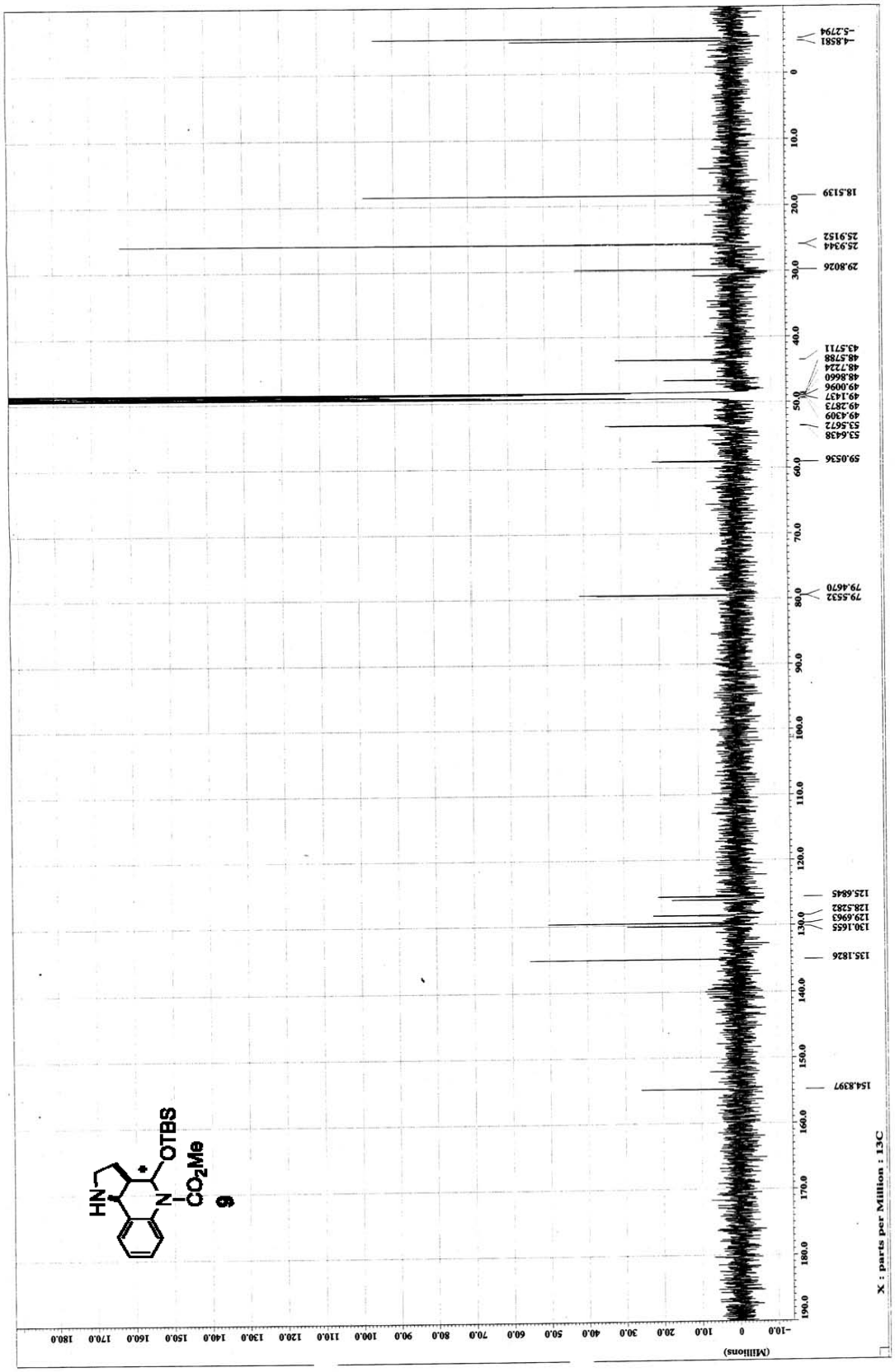
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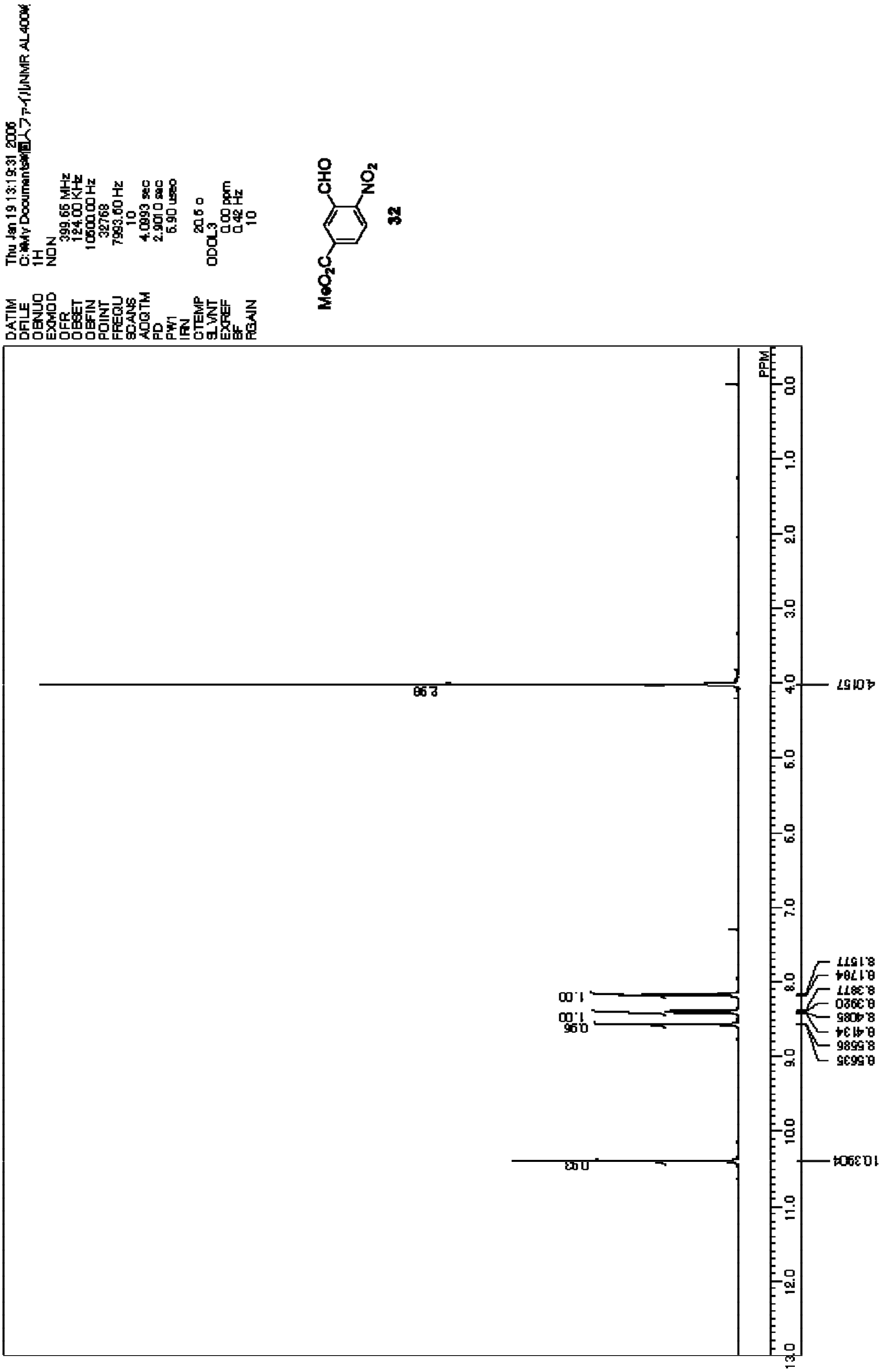
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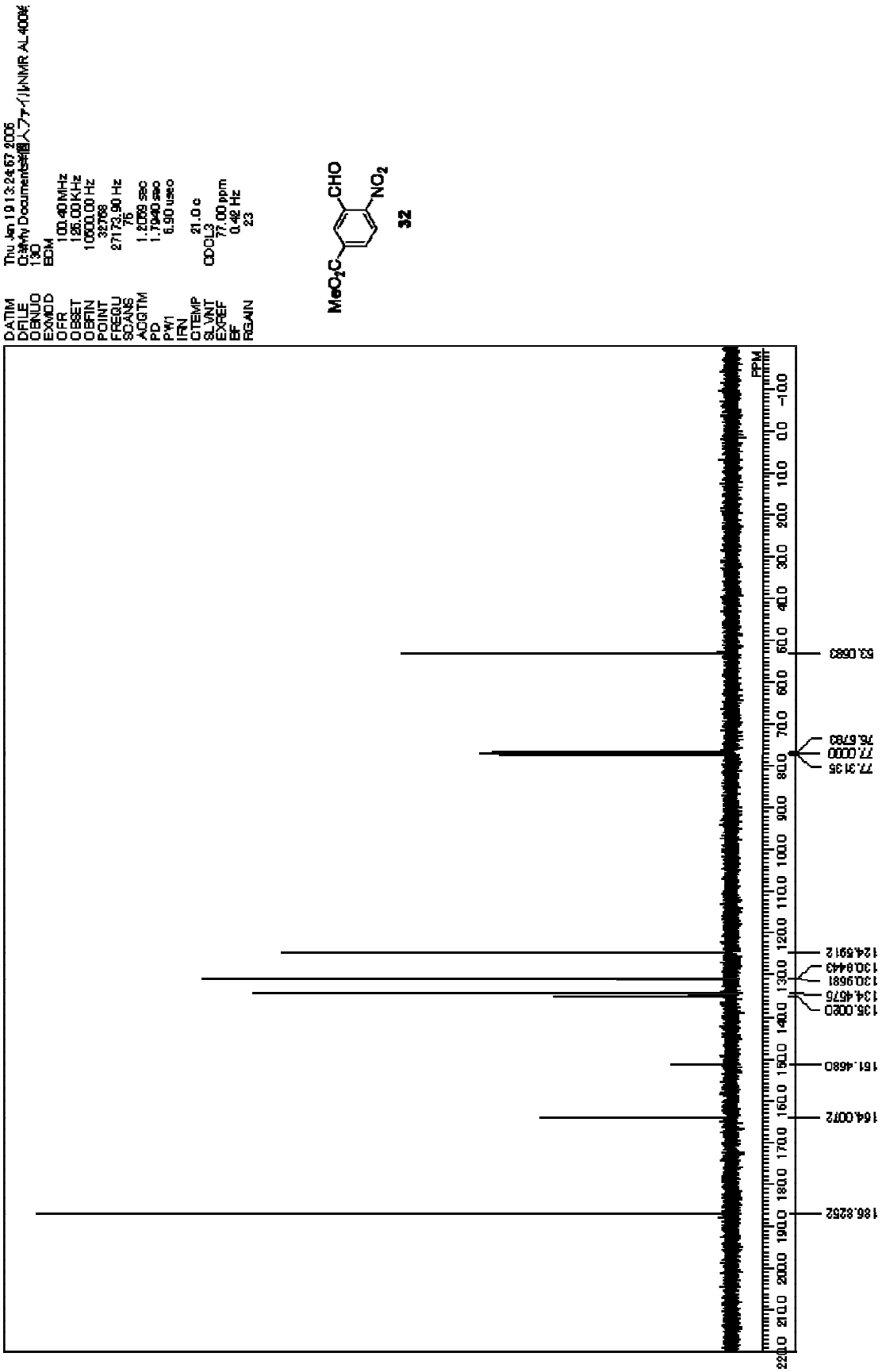
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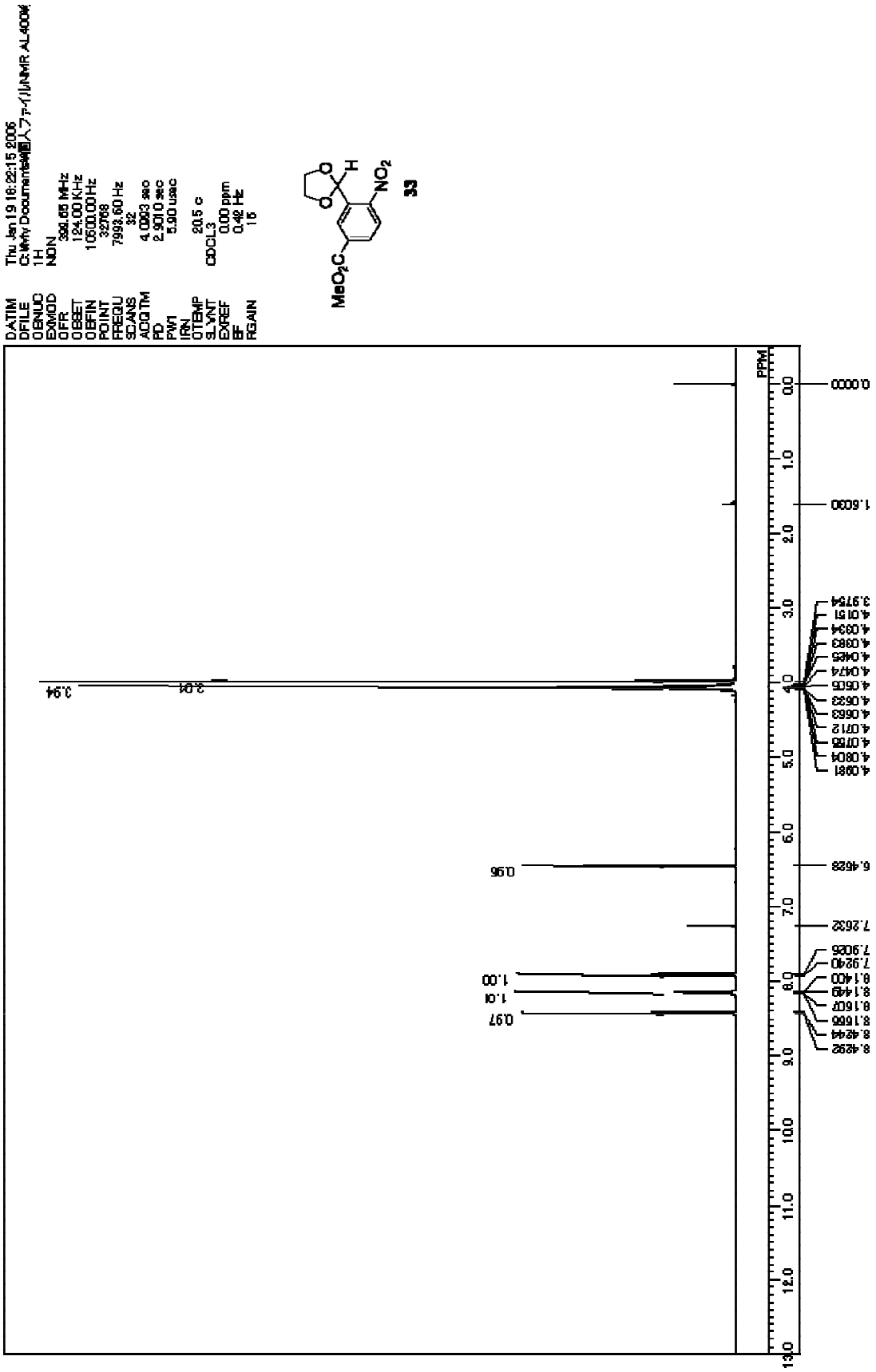
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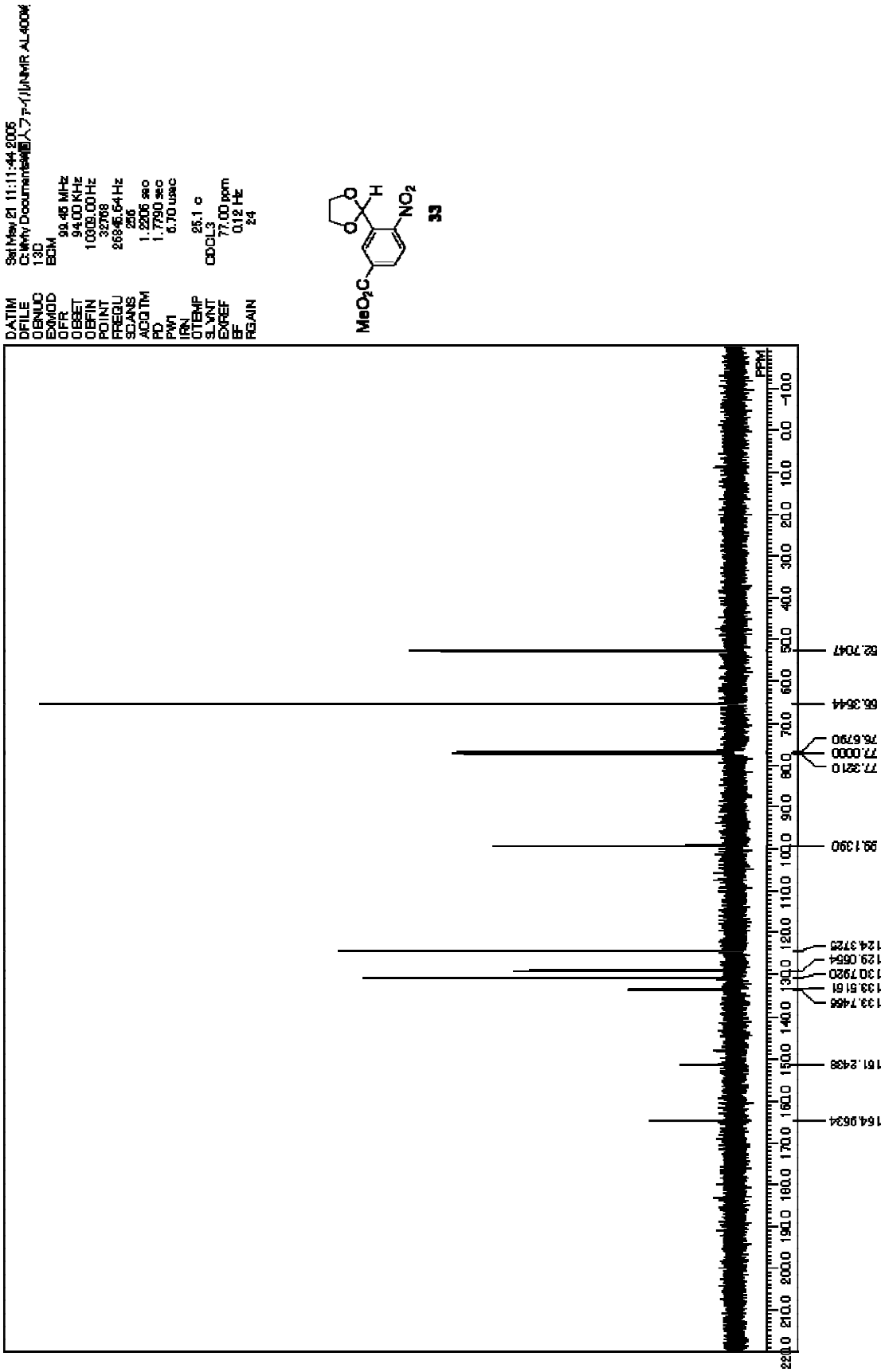
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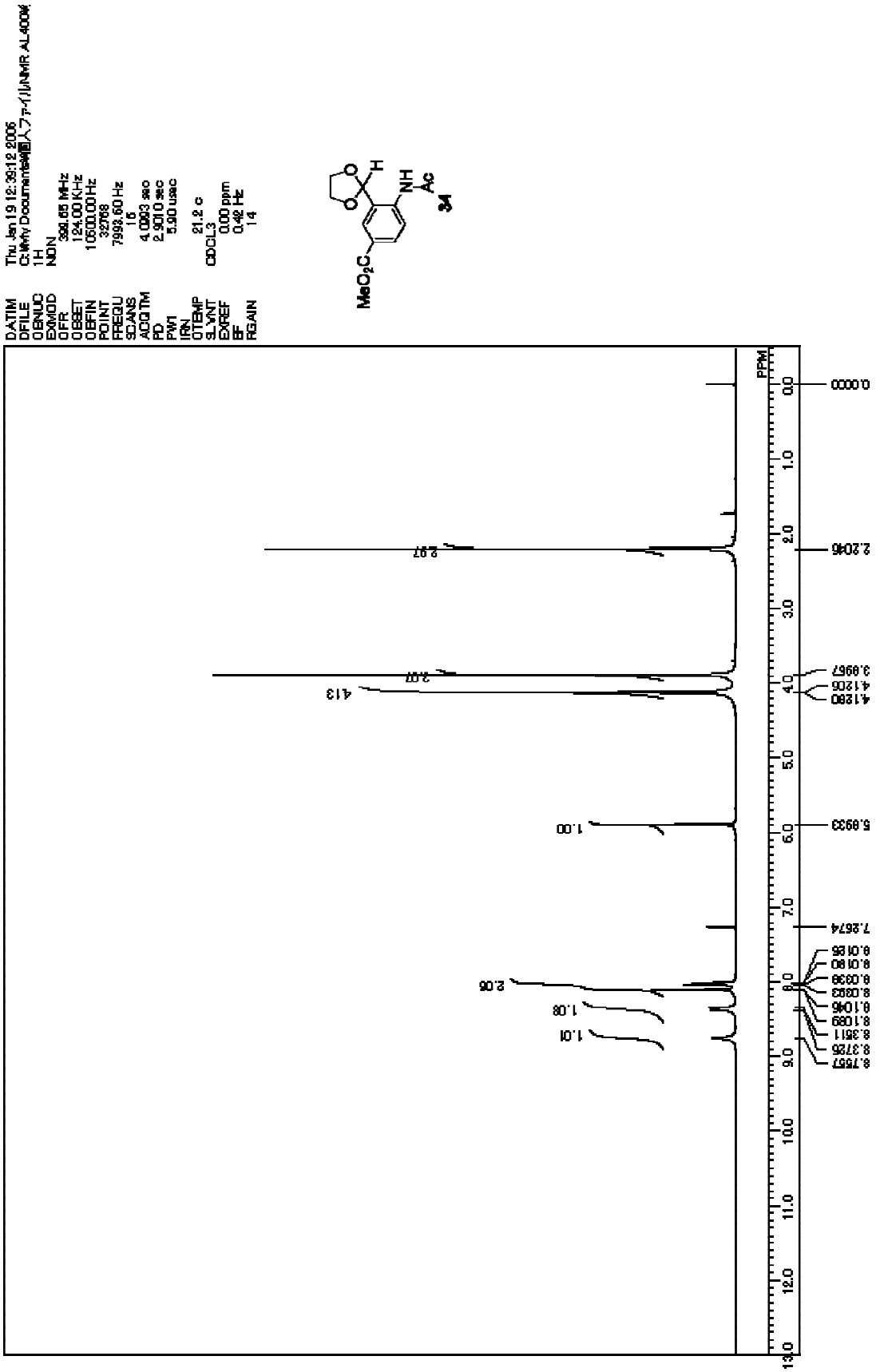
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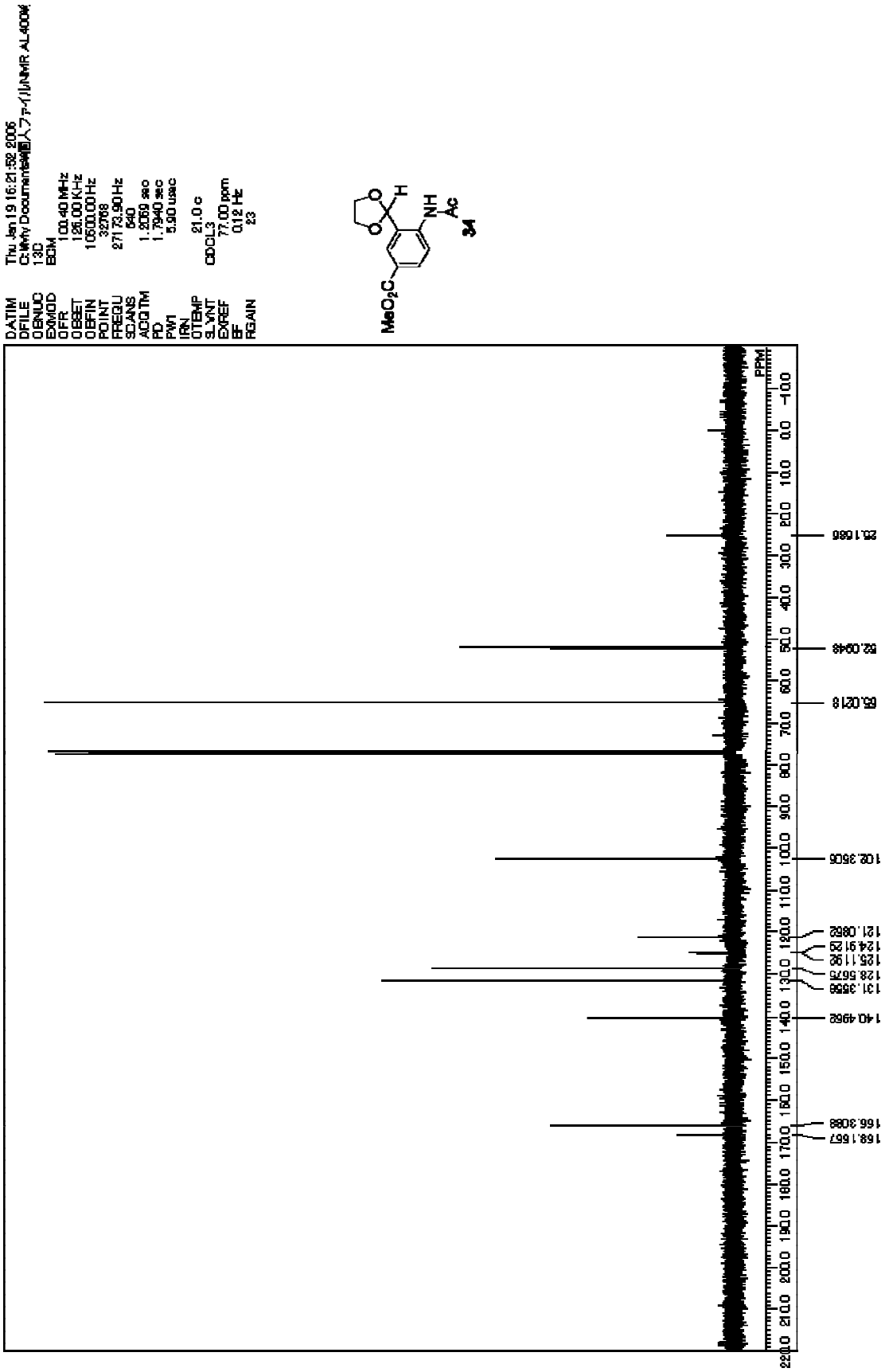
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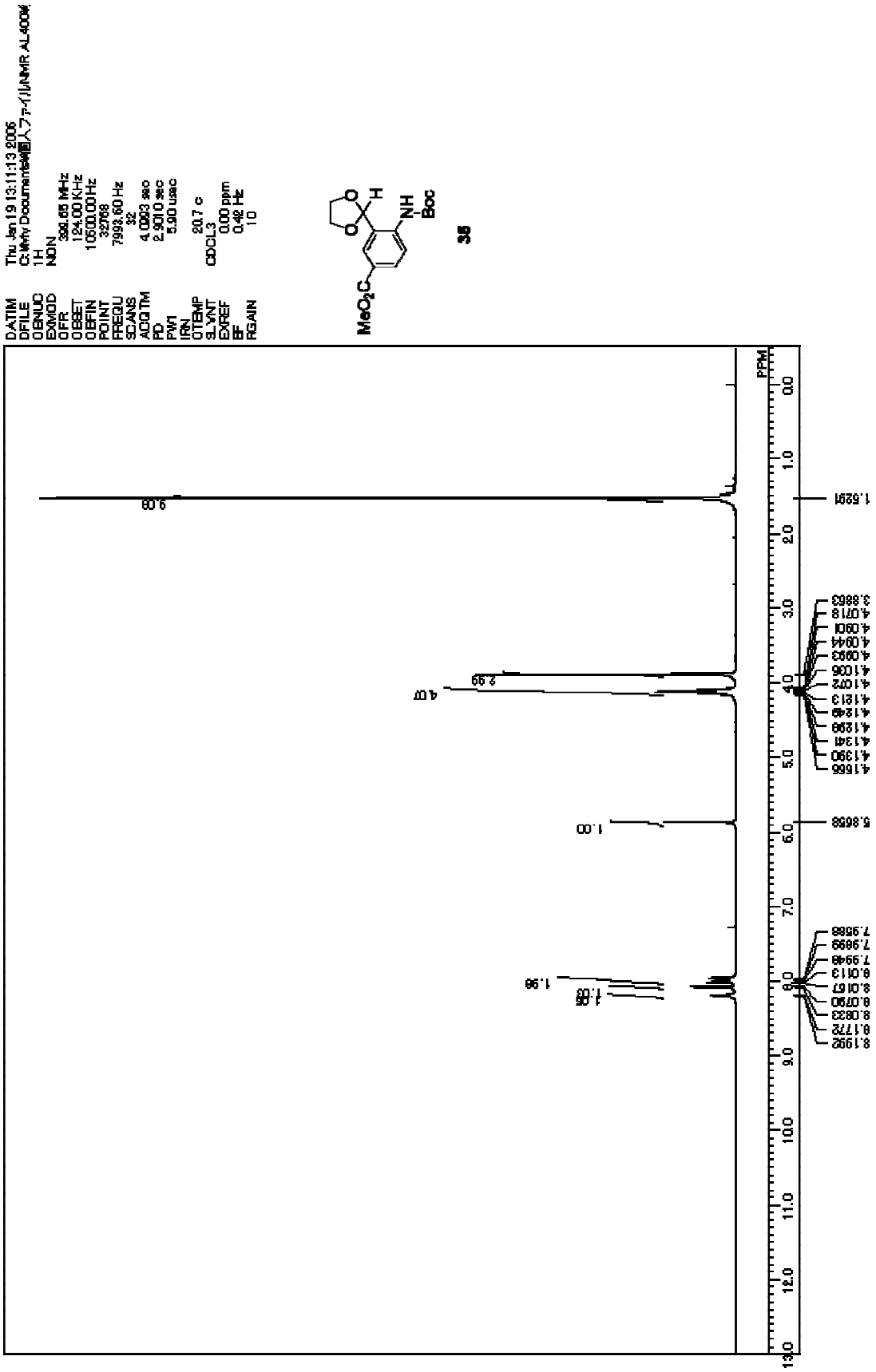
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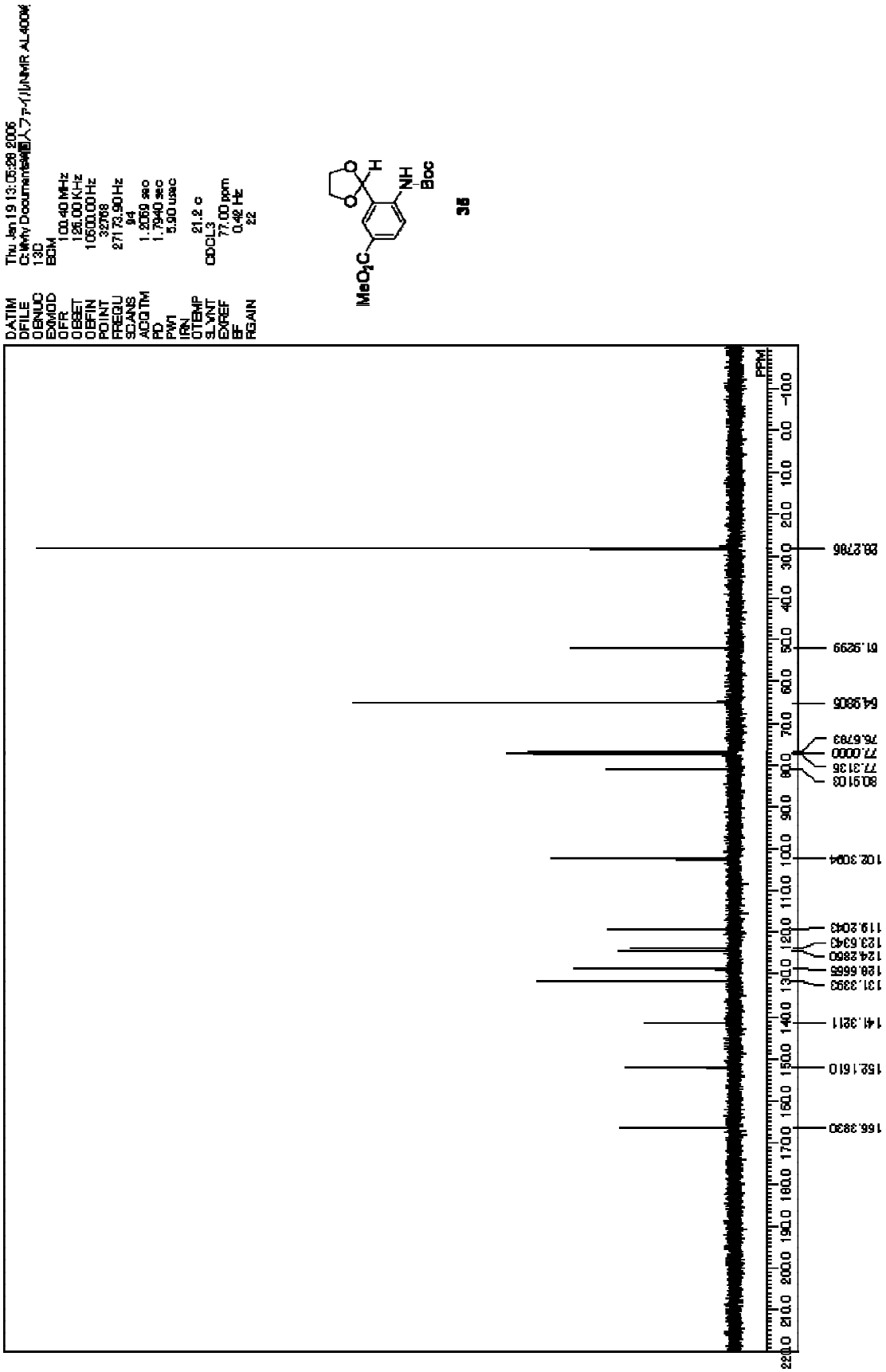
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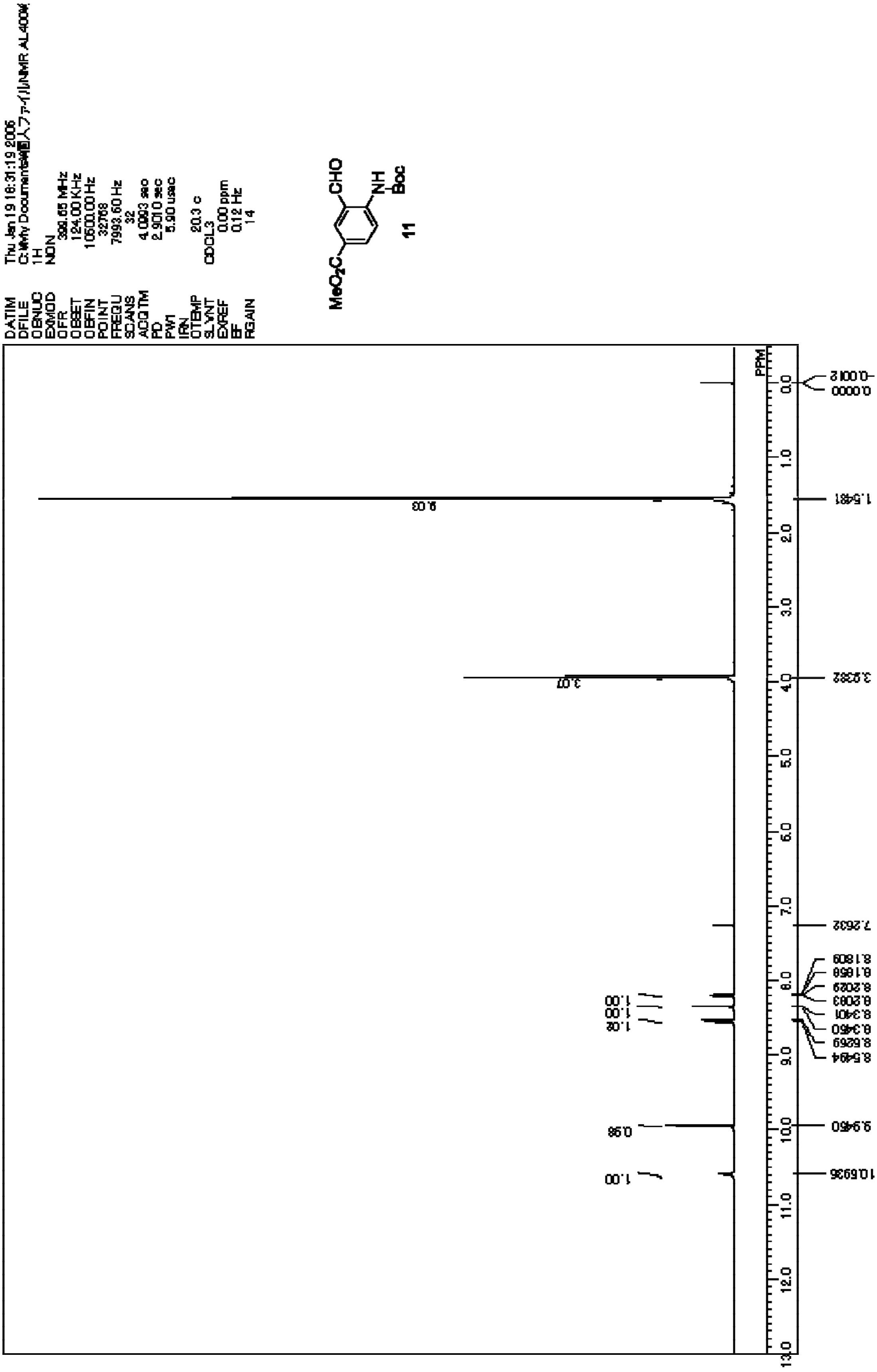
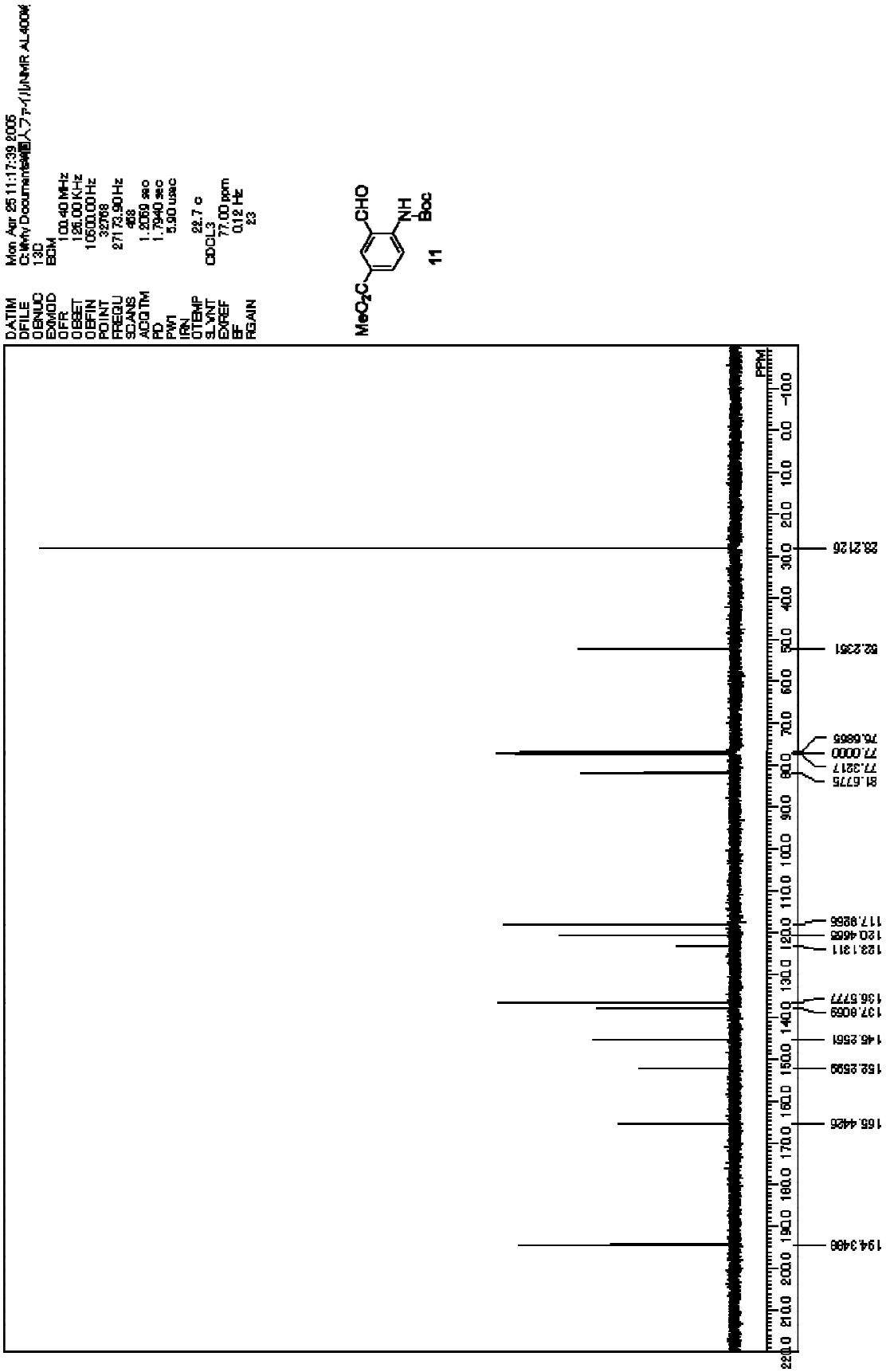
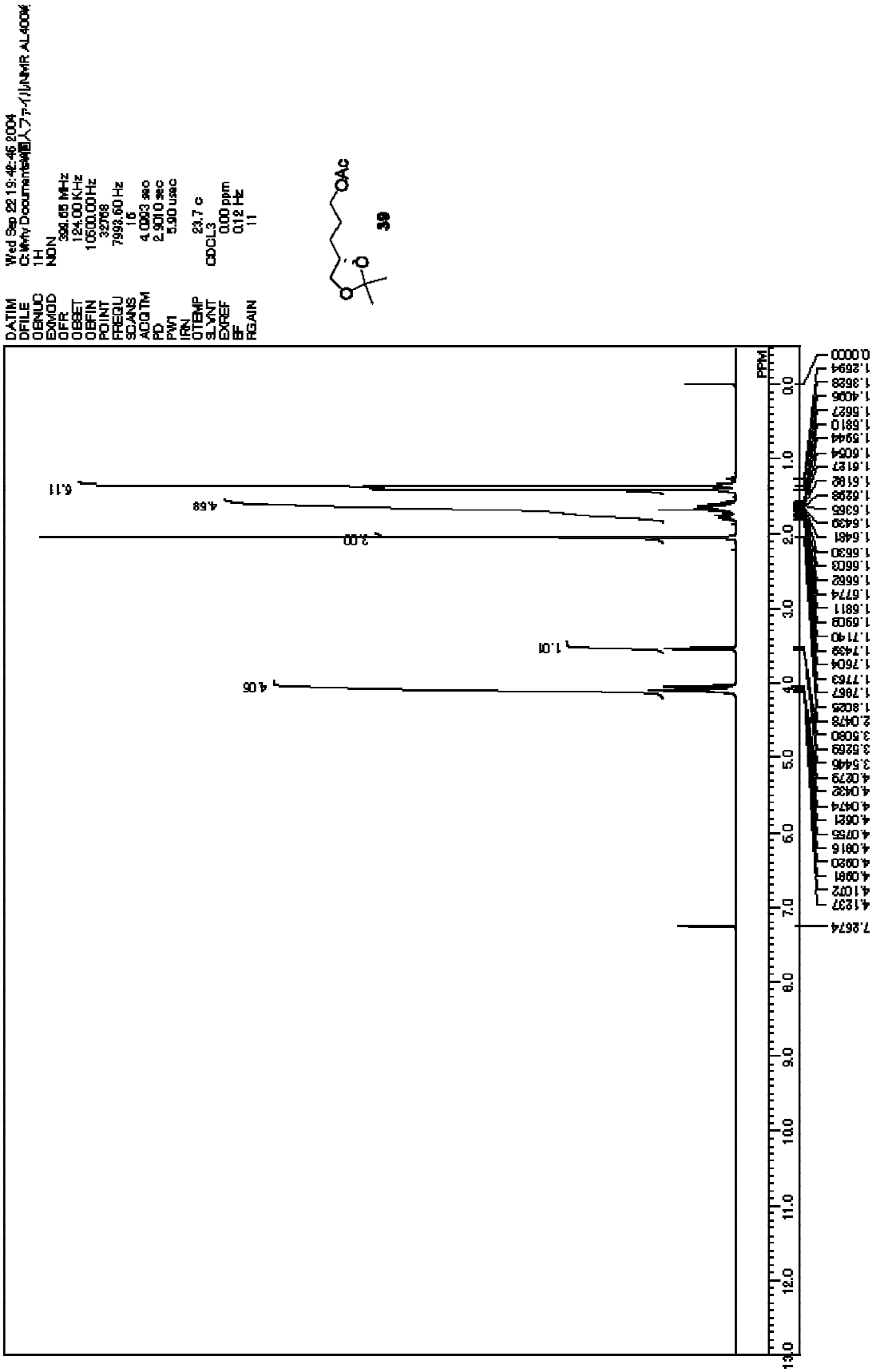
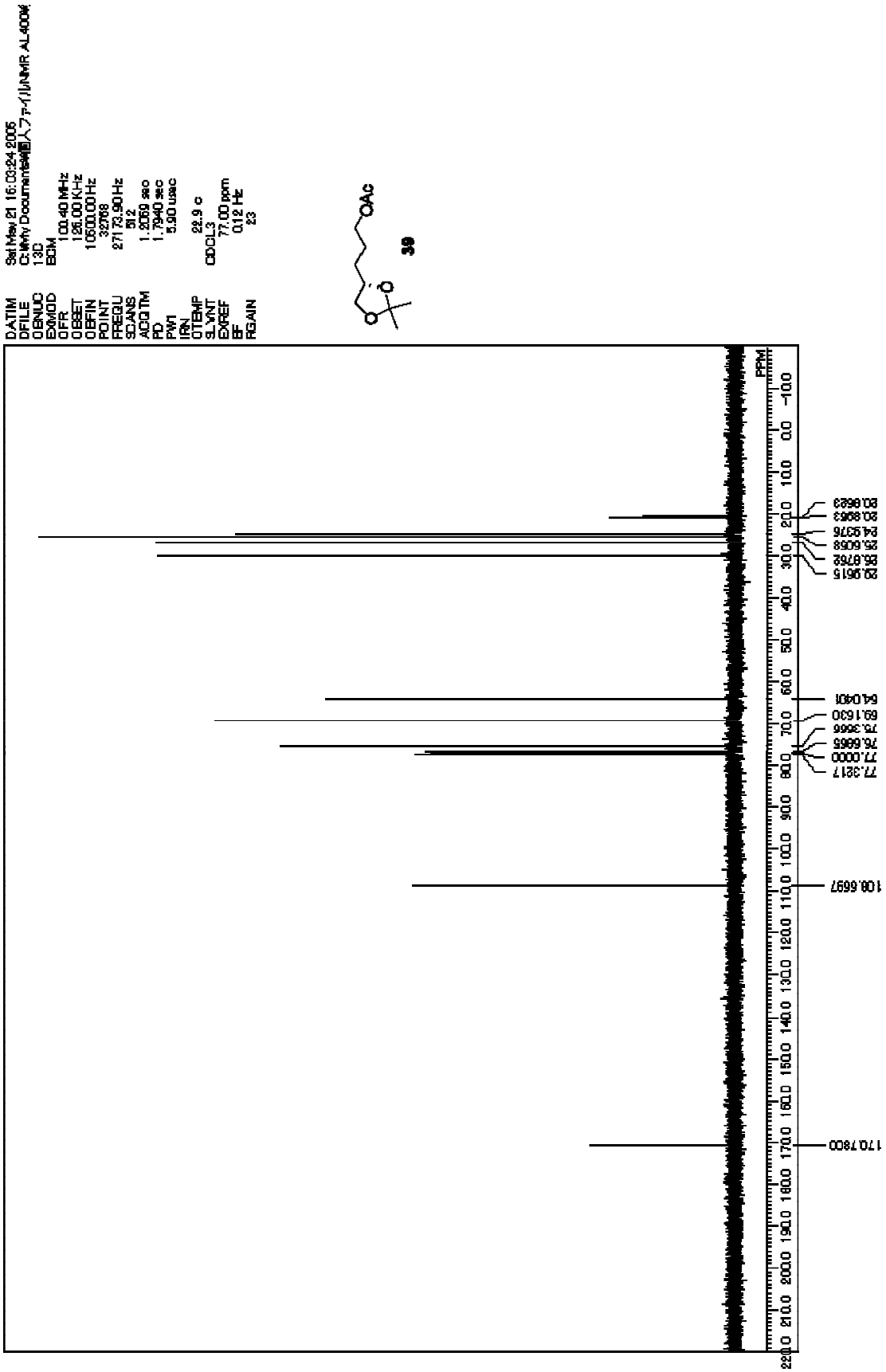
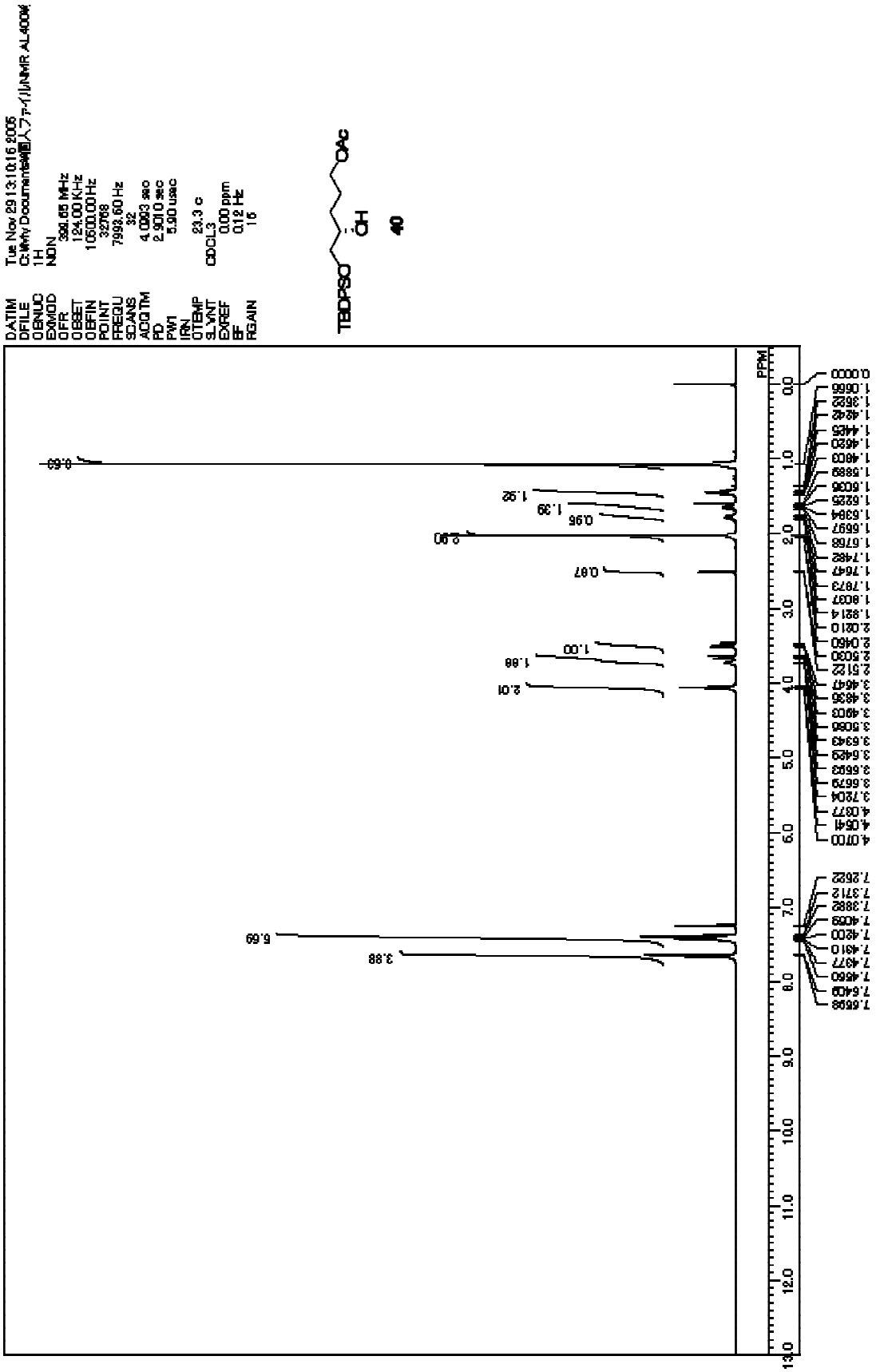
158.1610
166.3830

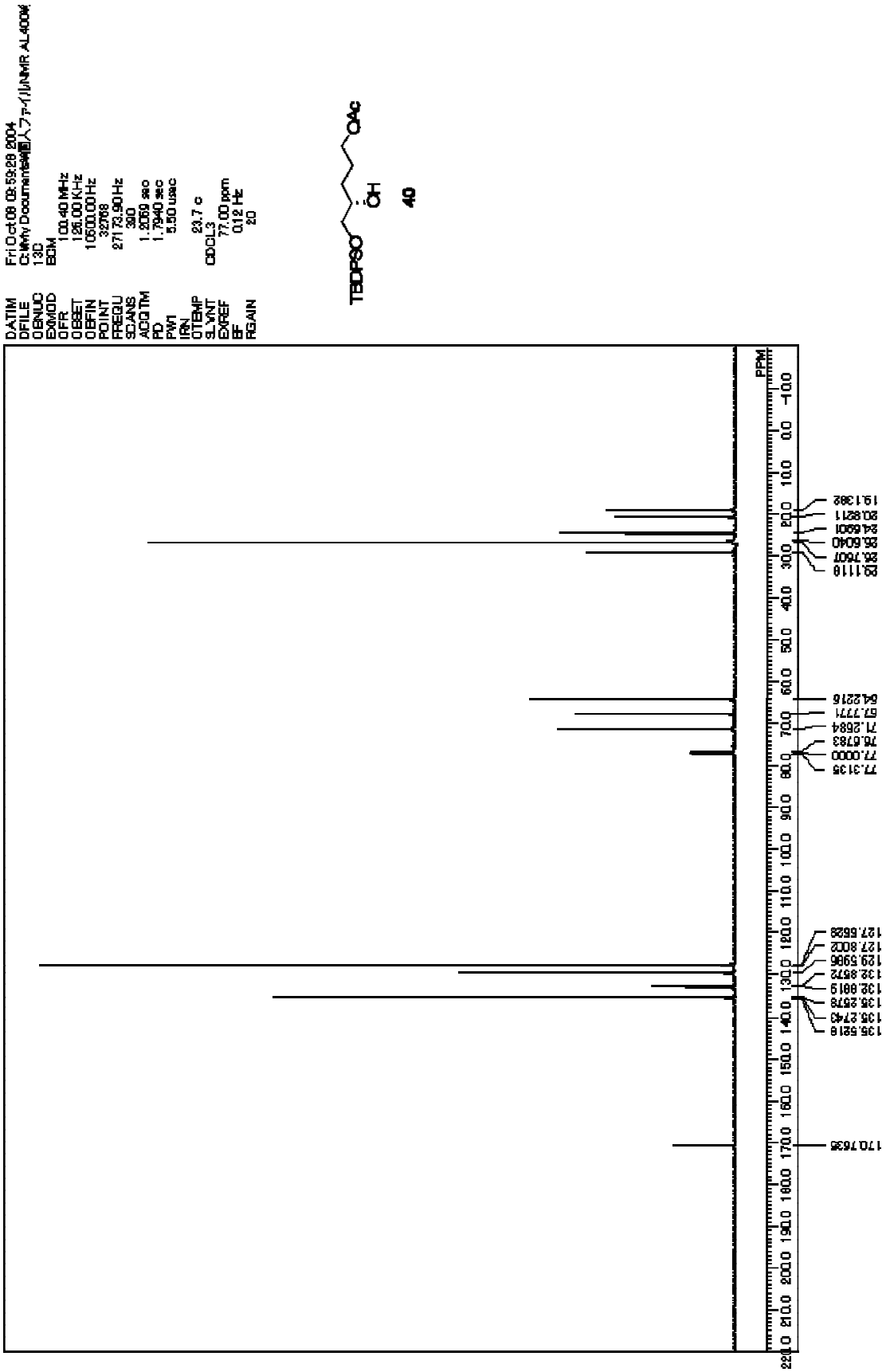

MeO2C
CHO
NH
Boc
11

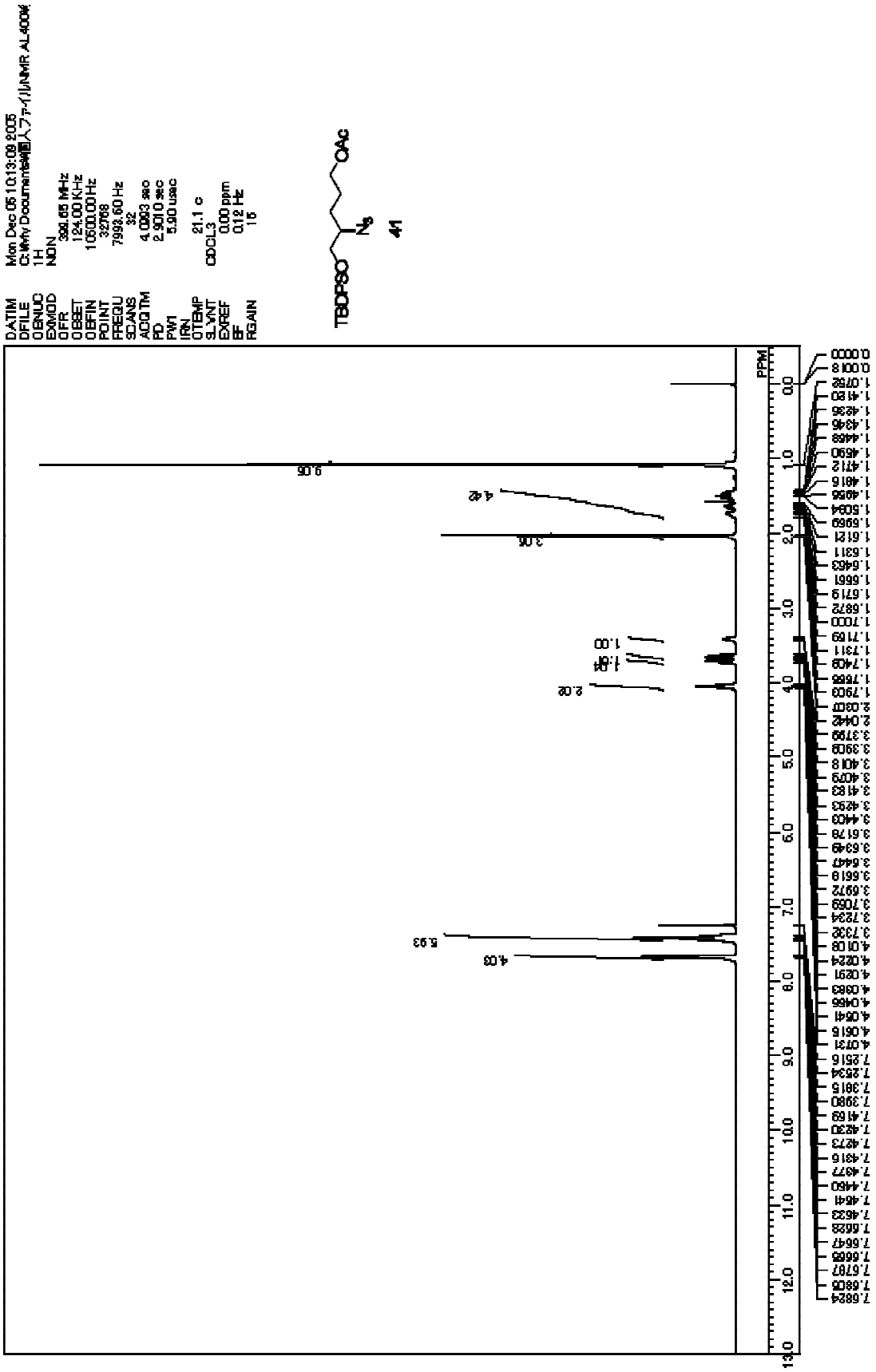

Mon Apr 25 11:17:39 2005
13C
100.40 MHz
125.00 KHz
100000 Hz
32768
271.73 Hz
468
1.2059 sec
1.7940 sec
5.90 usec
22.7 c
CDCl3
77.00 ppm
0.12 Hz
23
CHO
NH
Boc
MeO2C
11
PPM
28.2126
52.2351
76.0865
77.0000
77.3217
81.6775
117.9566
120.4668
123.1211
136.5777
137.8069
146.2561
152.8599
166.4426
194.3488

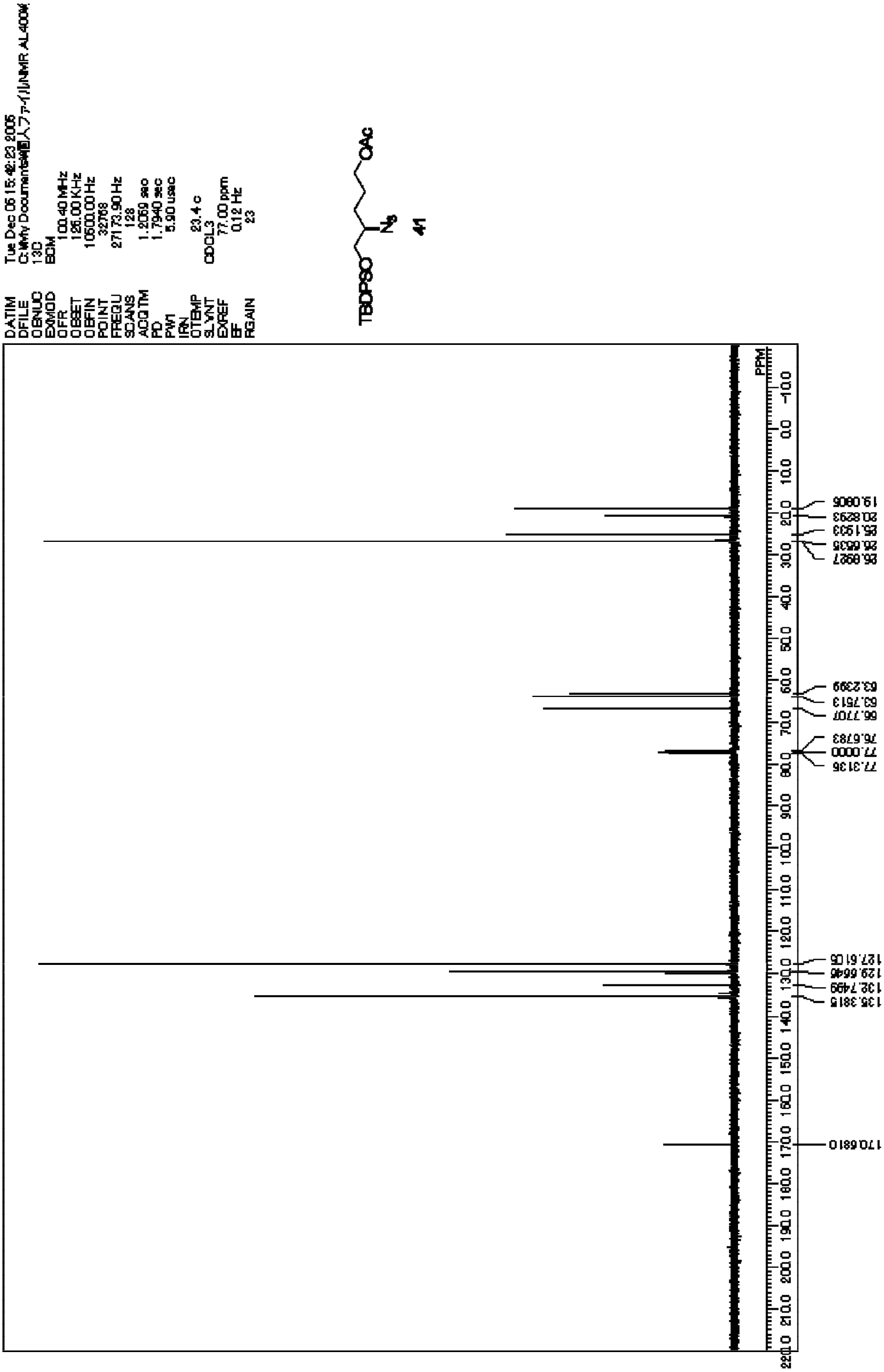

OAc
3g
6.11
4.68
3.00
1.01
4.06
PPM

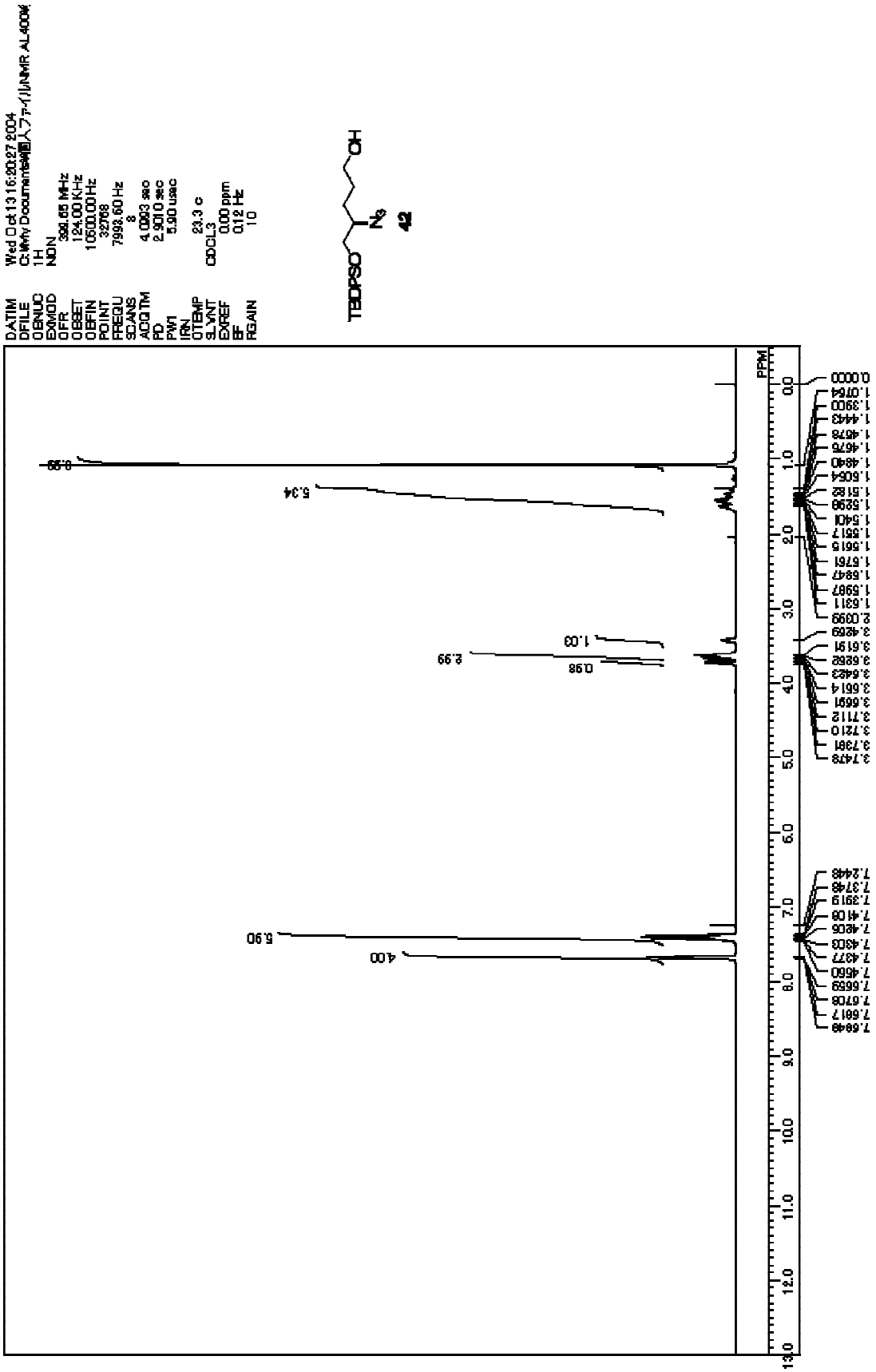

OAc
39
DATIM Sat May 21 16:03:24 2005
DFILE C:¥MyDocuments¥核磁入力データ¥JUNMR AL400¥
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 100010.0 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 512
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 5.90 usec
IRN
OTEMP 22.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 23
PPM
170.7800
108.6697
77.3317
77.0000
76.6665
75.3665
69.1630
64.0401
59.9615
55.6768
55.6058
24.9376
20.8963
20.8663

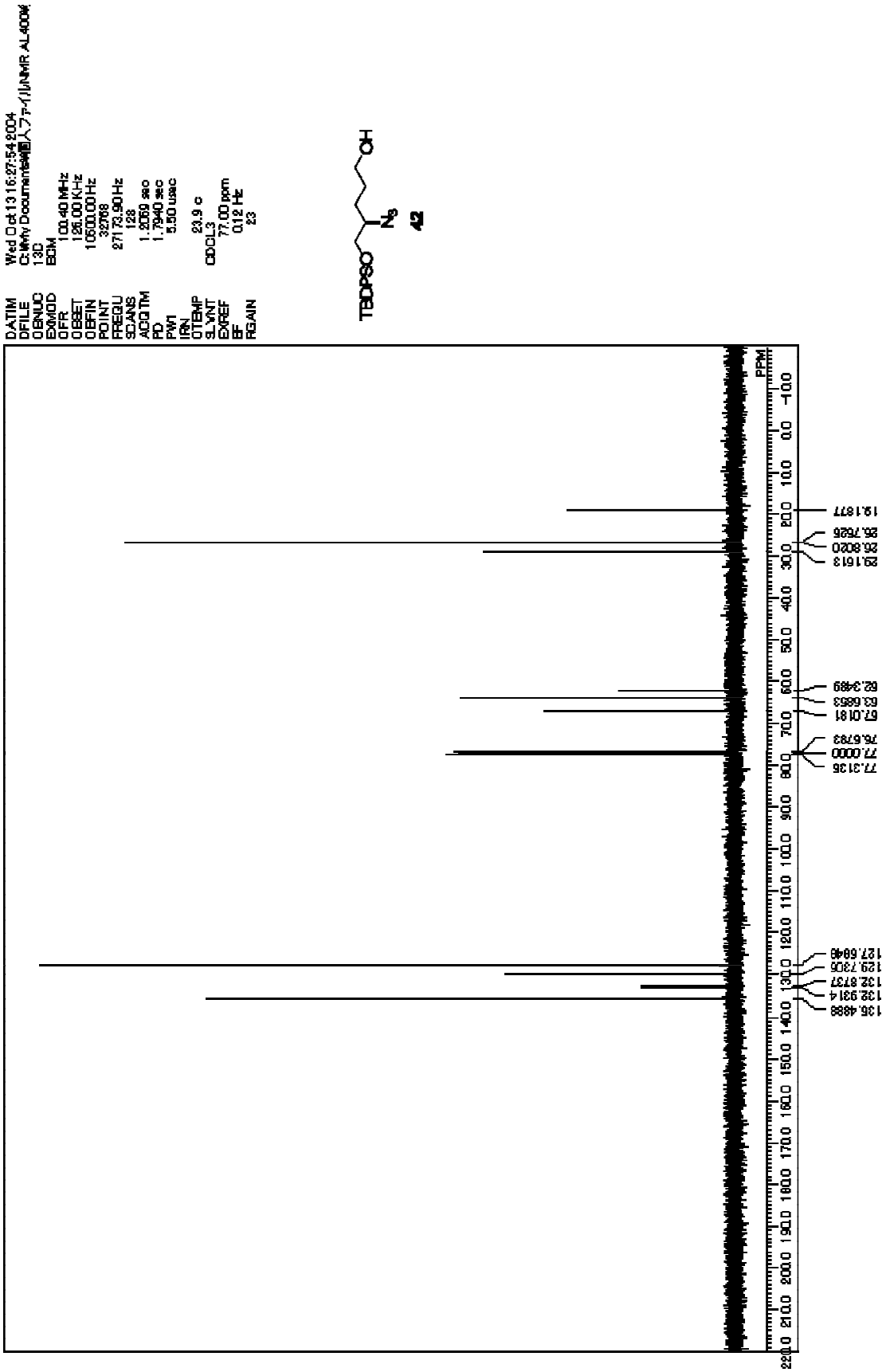

TBDPSO
OH
OAc
40
DATIM Tue Nov 29 13:10:16 2005
DFILE C:¥MyDocuments¥NMR¥データ¥1H-1¥1HNMR AL400M
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 1000100 Hz
POINT 32768
FREQU 7998.60 Hz
SCANS 32
ACQTM 4.0963 sec
PD 2.9010 sec
PW1 5.90 usec
IRN 23.3 c
OTEMP CDCl3
SLVNT 0.00 ppm
EXREF 0.12 Hz
BF 16
RGAIN
0.60
0.90
0.87
1.00
1.66
2.01
1.92
1.39
0.96
5.69
3.88
PPM

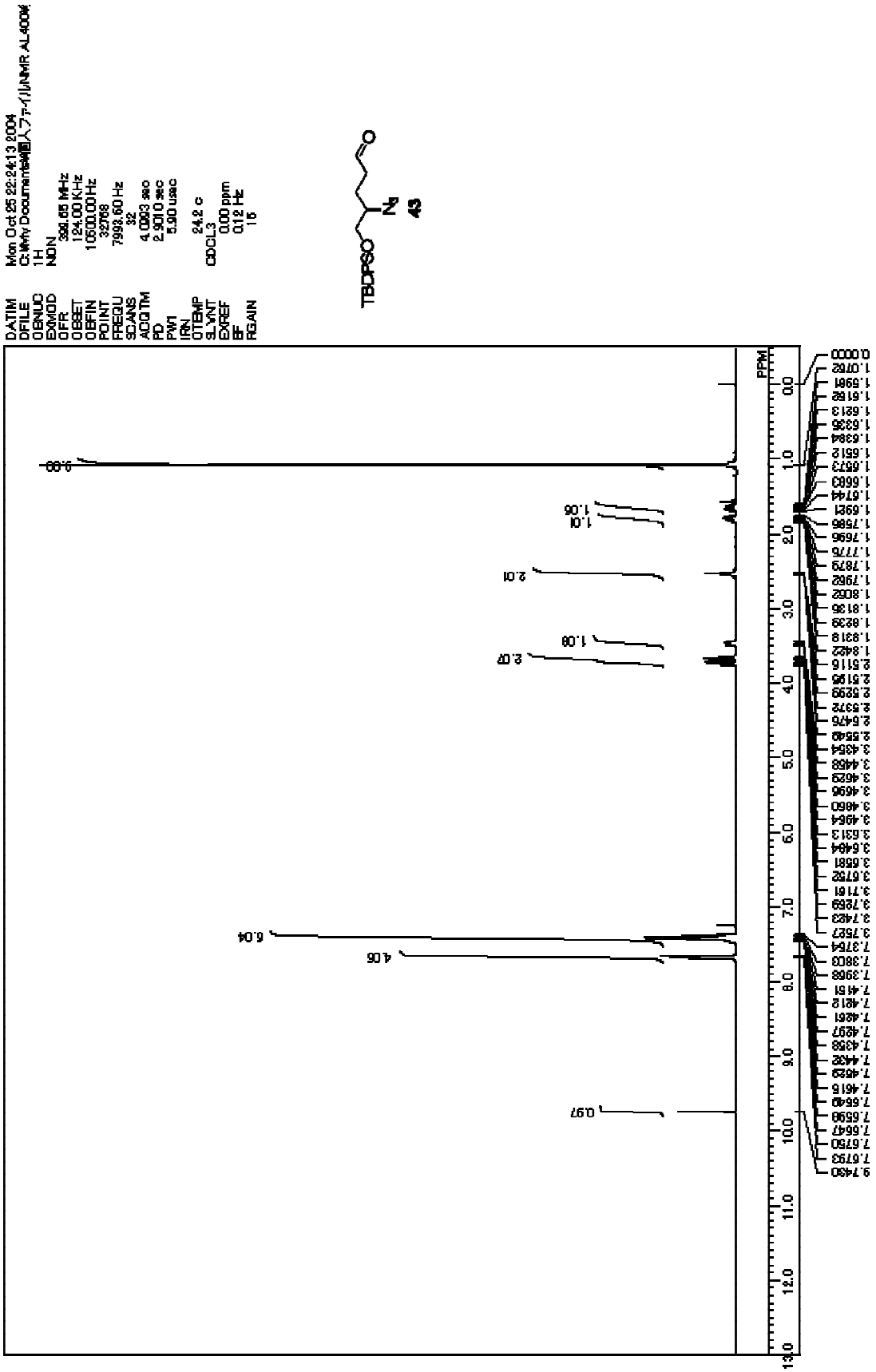

TBDPSO
OAc
OH
40
DATIM Fri Oct 08 09:59:28 2004
DFILE C:¥My Documents¥測定データ¥JUNMR AL400¥
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 126.00 KHz
OBFIN 100,000 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 390
ACQTM 1.2859 sec
PD 1.7940 sec
PW1 5.50 usec
IRN
OTEMP 23.7 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 20
PPM
19.1382
80.8571
84.6901
86.6040
86.7607
89.1119
64.2216
67.7771
71.2684
76.6783
77.0000
77.3135
127.6628
127.8002
129.5986
132.8572
132.8819
135.2578
135.2743
135.5518
170.7638

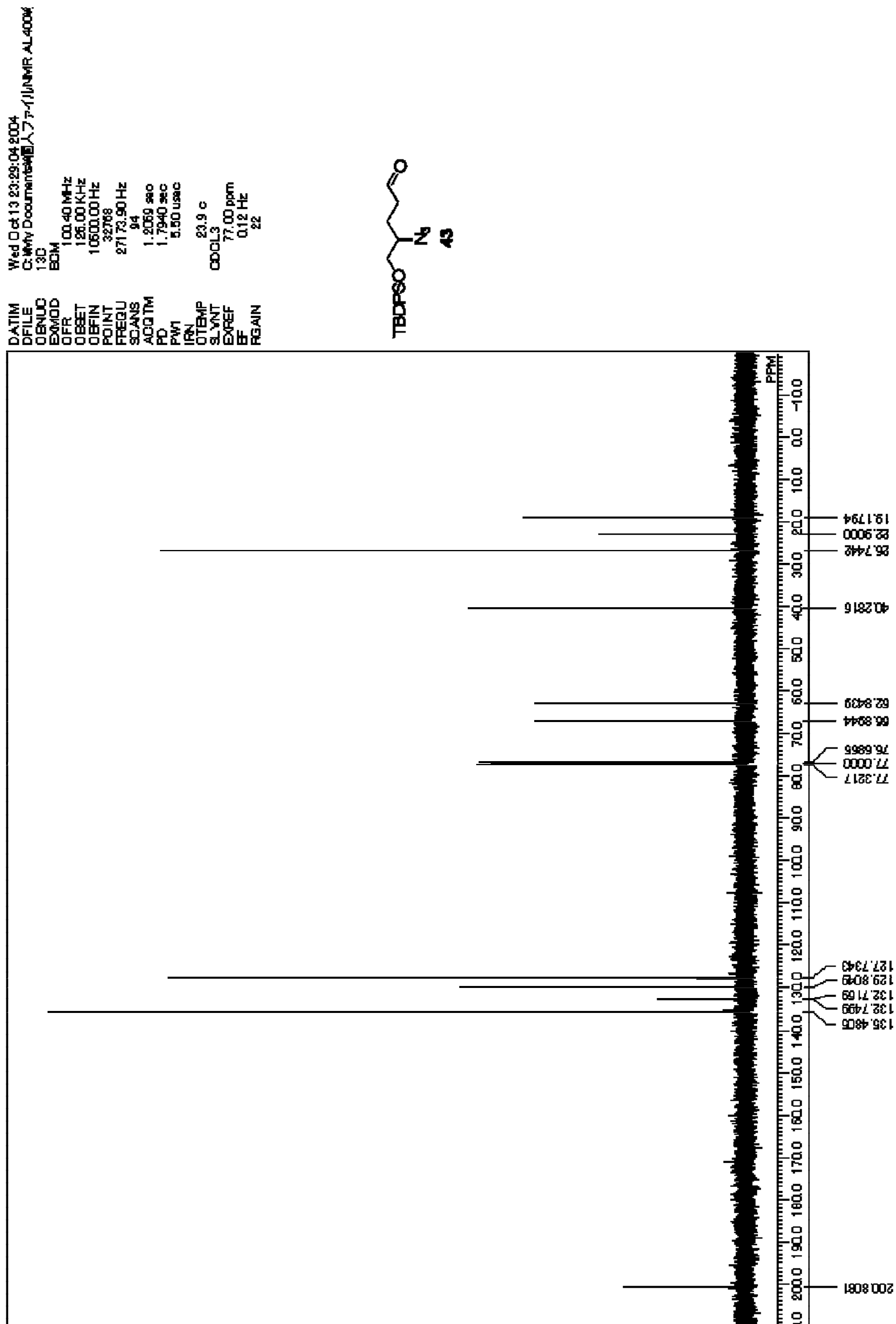

TBDPSO
OAc
N3
4f1
9.05
4.42
3.06
1.00
1.08
2.08
5.03
4.03
PPM

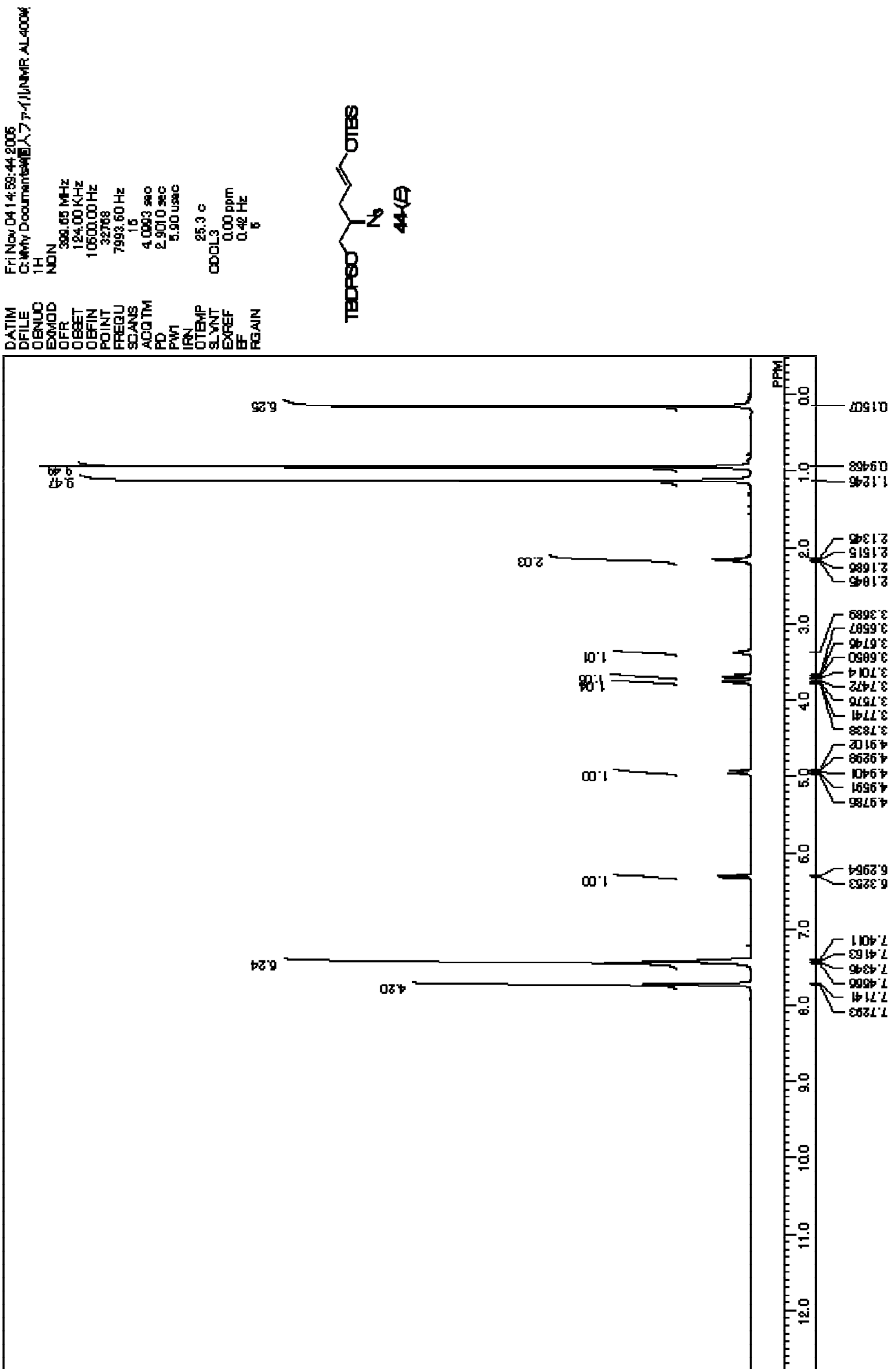

DATIM Tue Dec 06 15:42:23 2005
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 128
ACQTM 1.2059 sec
PD 1.7940 sec
PW1 5.90 usec
IRN
CTEMP 23.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 23
TBDPSO
N3
OAc
41
PPM
19.0806
20.8293
25.1503
26.6535
26.8827
63.2399
63.7513
66.7707
76.6783
77.0000
77.3136
127.6105
129.6646
132.7499
135.3815
170.6810

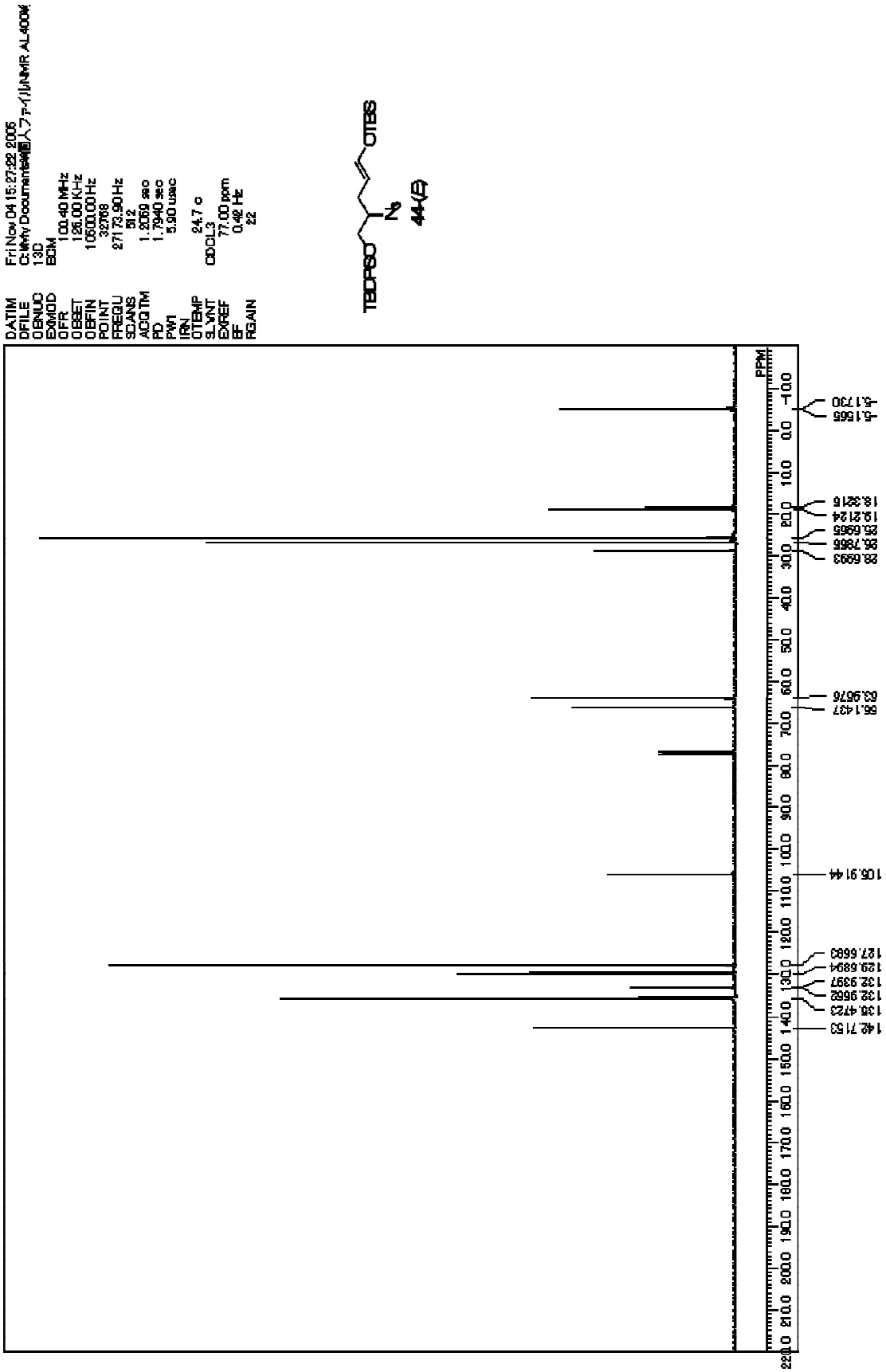

TBDPSO
OH
N3
42
PPM

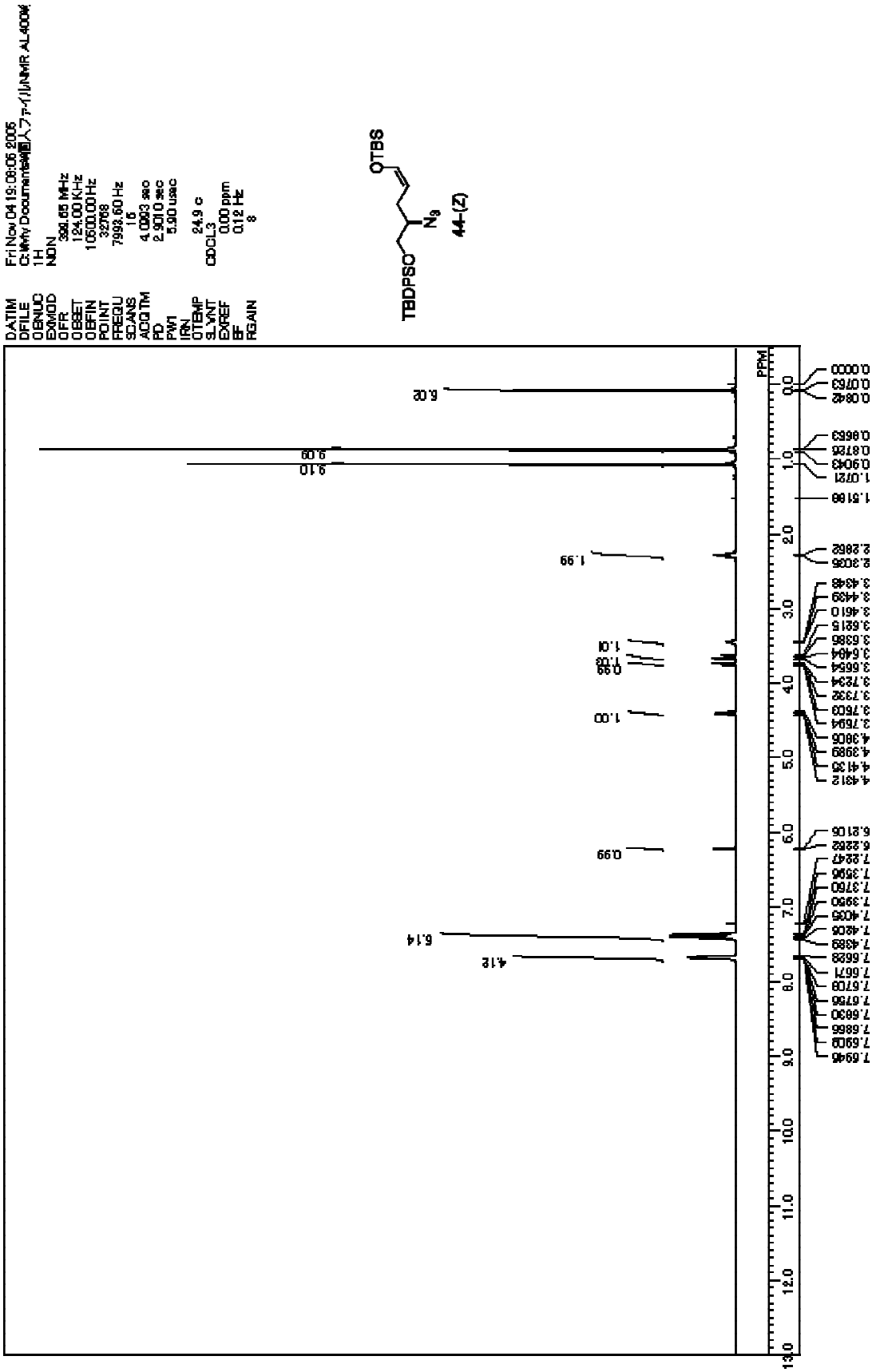

TBDPSO
OH
N3
42
PPM
19.1877
26.7626
26.8020
29.1613
62.3489
63.6653
67.0181
76.6793
77.0000
77.3136
127.6848
129.7305
132.8737
132.9314
136.4888

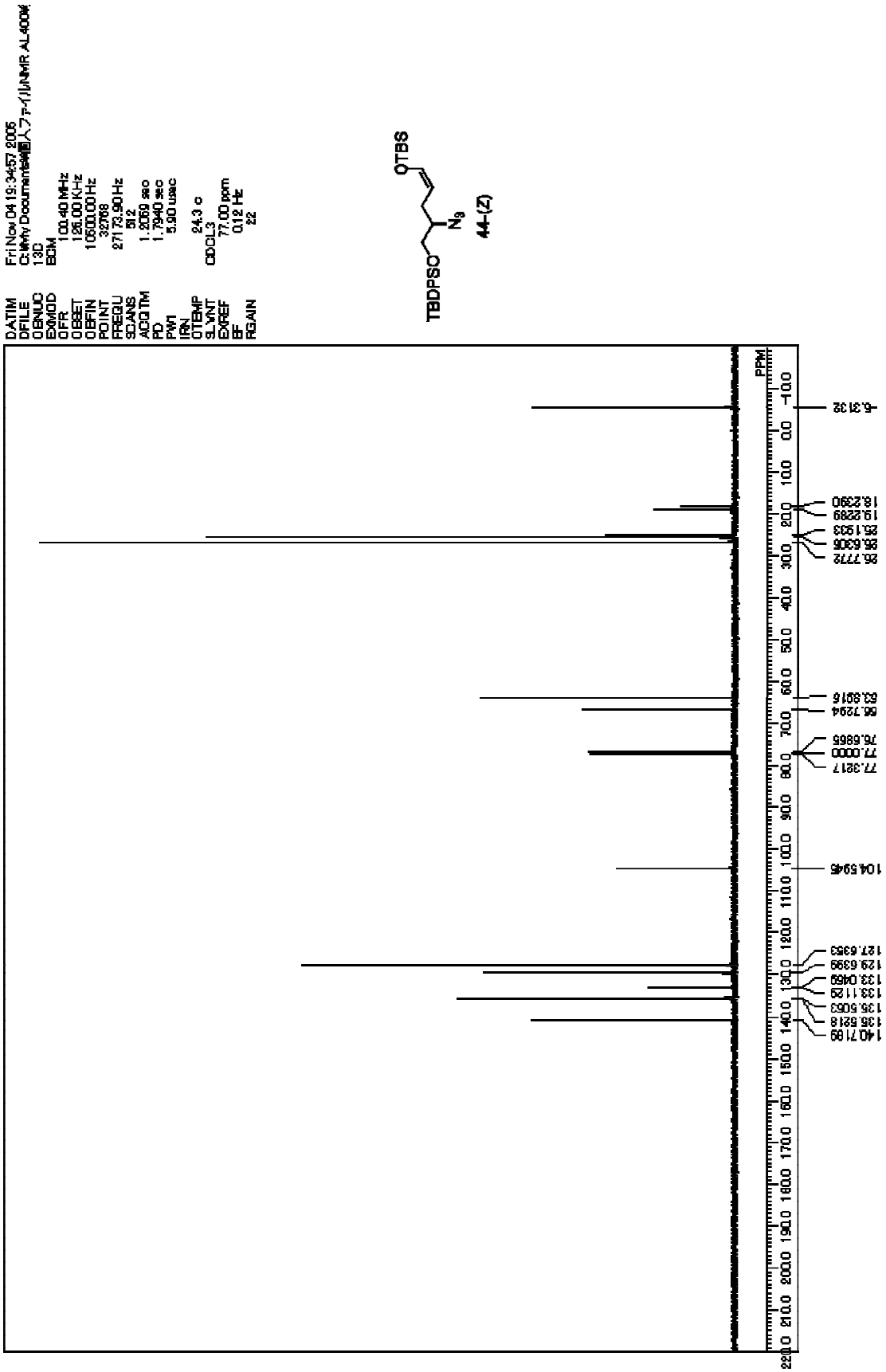

TBDPSO
N3
43
9.00
1.01
1.06
2.01
1.08
2.07
6.04
4.06
0.97
PPM

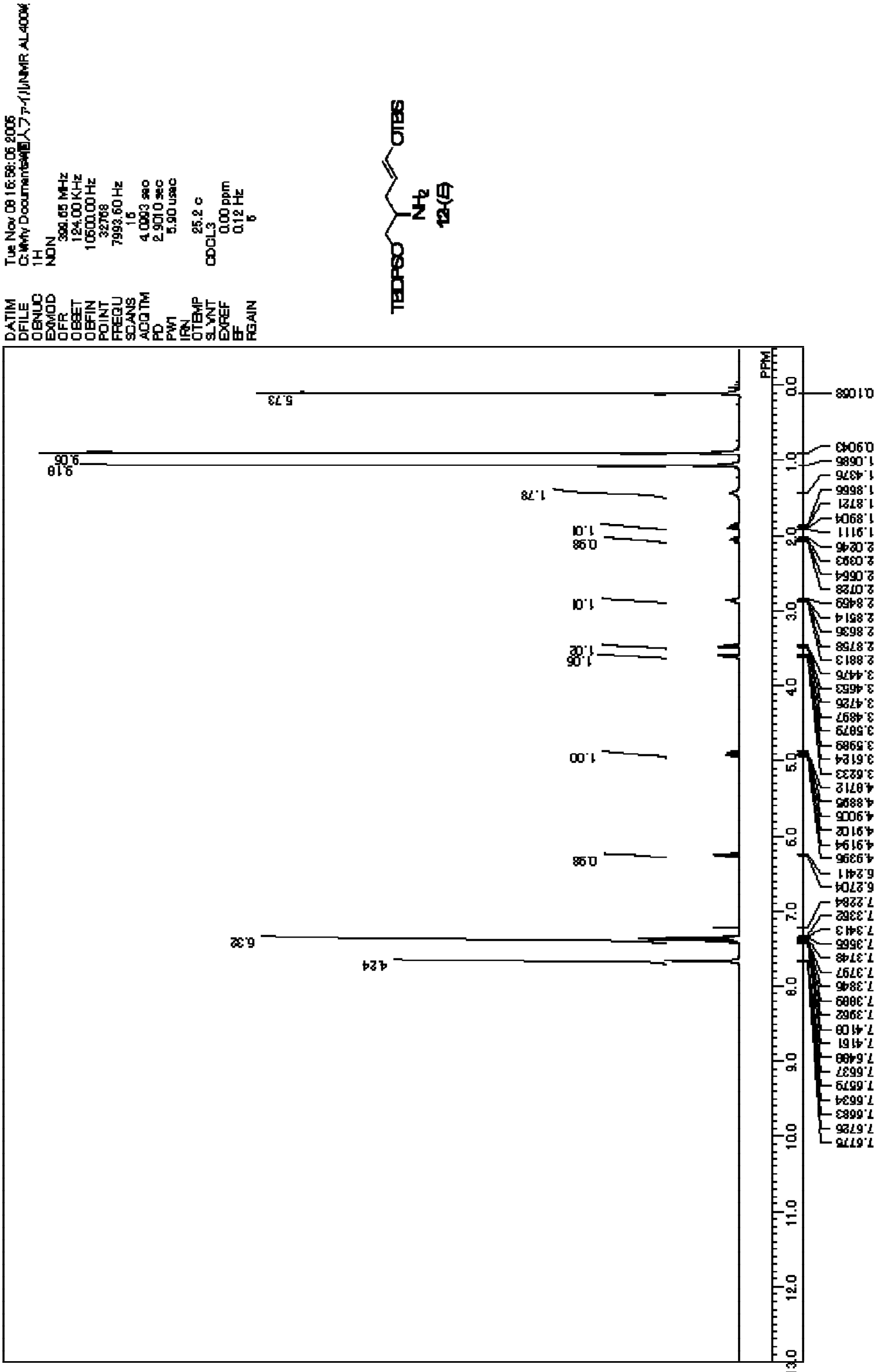

TBDPSO
N3
43
19.1794
22.9000
26.7442
40.2816
62.8439
66.8944
76.6866
77.0000
77.3217
127.7343
129.8049
132.7169
132.7499
135.4805
200.8081
PPM

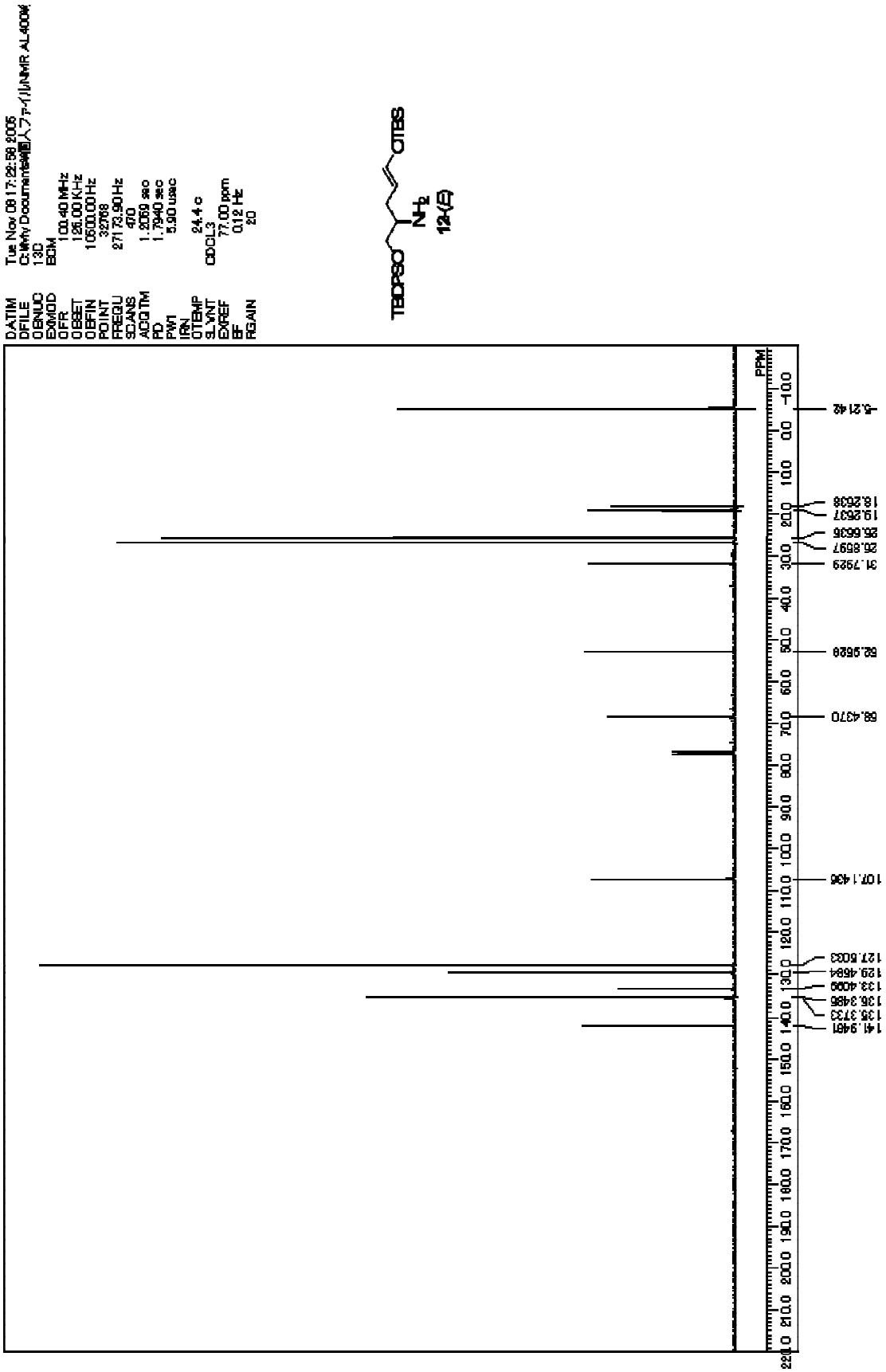


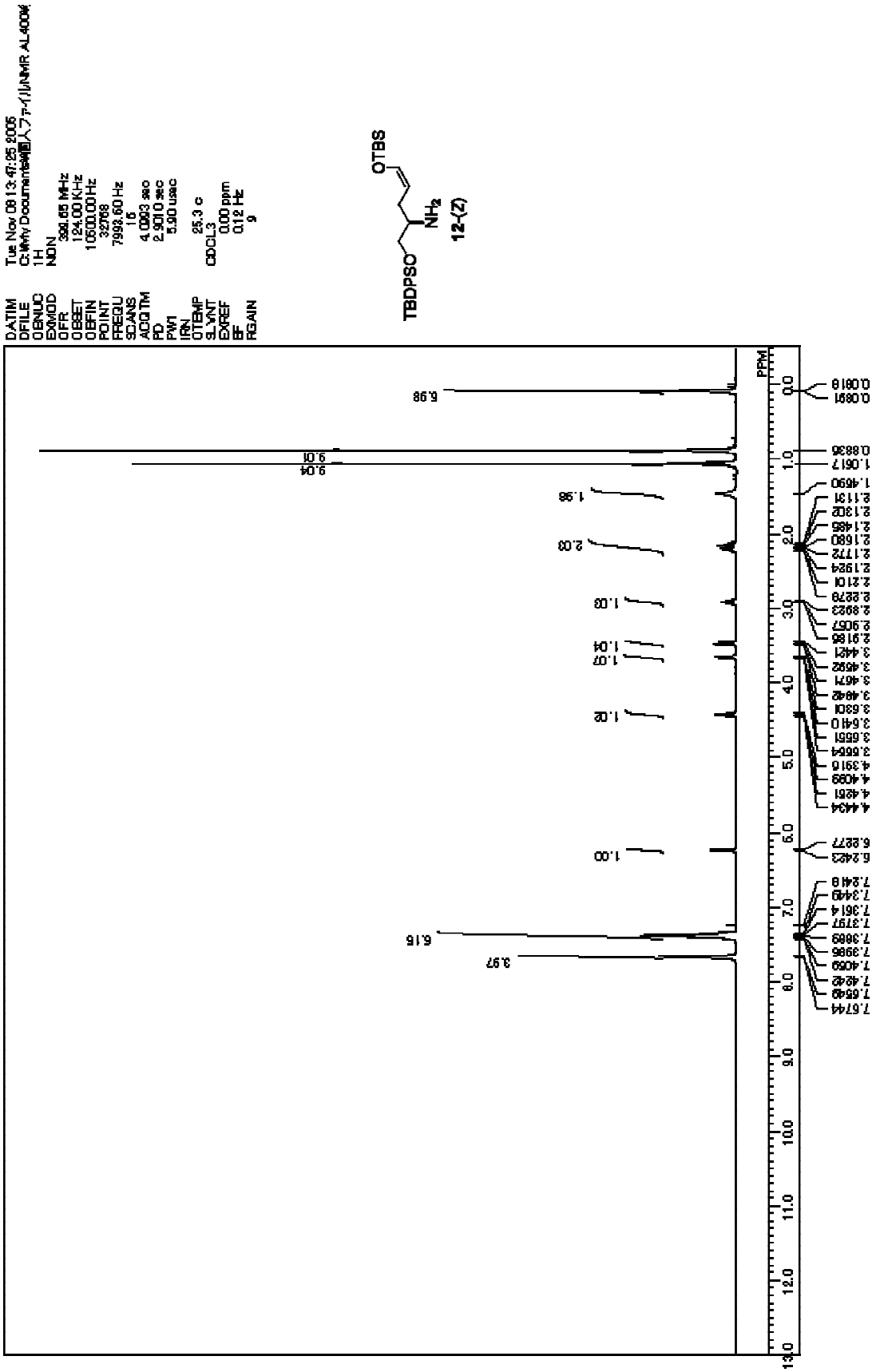

TBDPSO
OTBS
44(E)
-5.1730
-5.1565
18.3215
19.2124
25.6566
25.7866
25.8993
63.9676
66.1437
106.9144
127.6683
129.6894
132.9397
132.9662
135.4723
142.7153
PPM

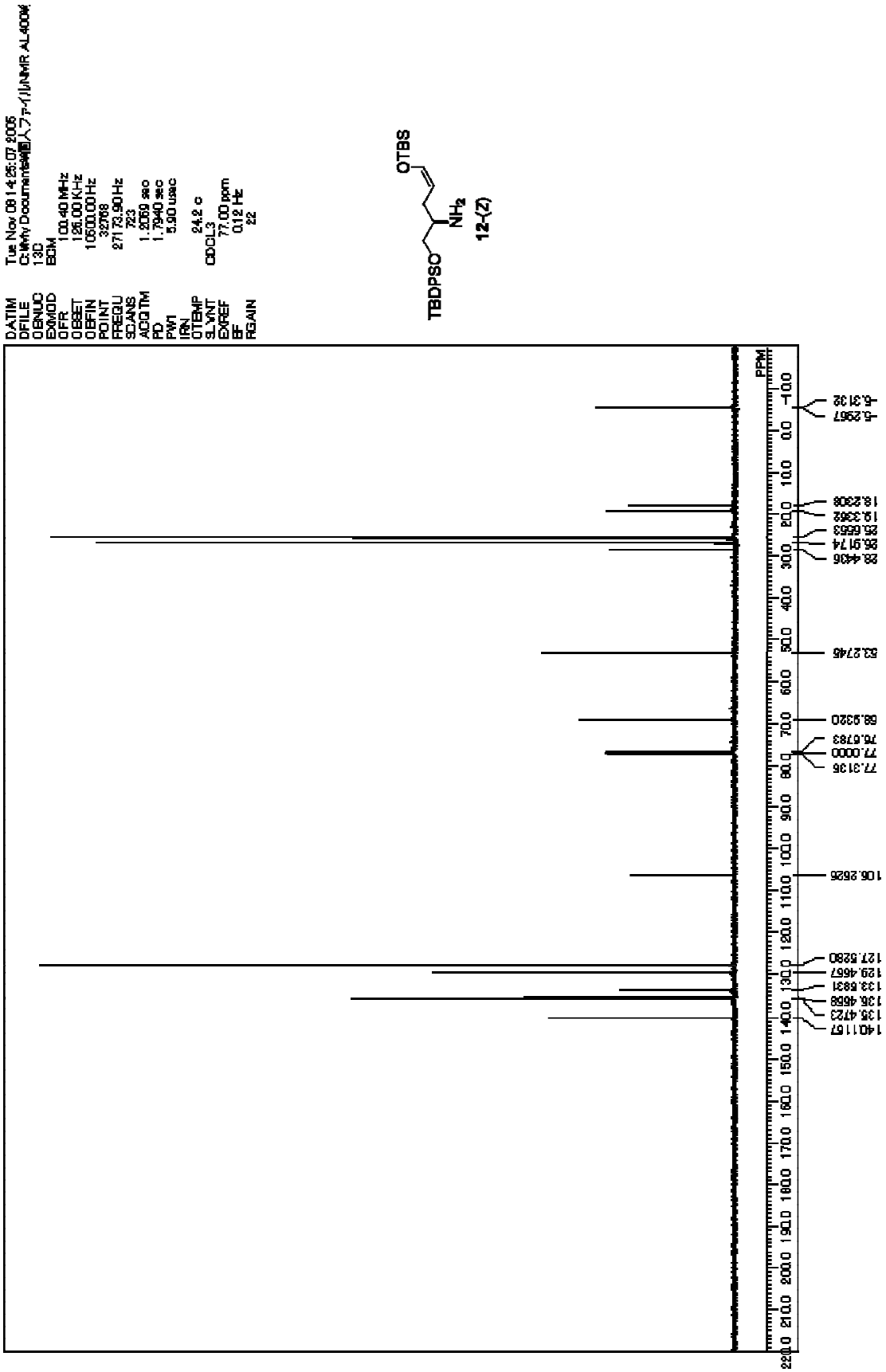

TBDPSO
OTBS
N3
44-(Z)
6.02
9.09
9.10
1.99
1.01
1.08
0.99
1.00
0.99
6.14
4.18
PPM


OTBS
TBDPSO
N3
44-(Z)
-6.3132
18.2290
19.2289
25.1535
25.6306
25.7772
62.8516
66.7294
76.6865
77.0000
77.3817
104.5945
127.6353
129.6899
133.0469
133.1125
135.5063
135.6218
140.7189
PPM




TBDPSO
OTBS
NH2
12-(E)
PPM
-5.2142
18.2638
19.2637
26.6636
26.8697
31.7929
62.9628
68.4370
107.1436
127.5023
129.4684
133.4099
136.3486
136.3733
141.9481


OTBS
NH2
12-(Z)
TBDPSO
6.98
9.04
9.01
1.58
2.08
1.08
1.04
1.09
1.02
1.00
6.16
3.97
PPM


OTBS
NH2
TBDPSO
12-(Z)
Tue Nov 08 14:05:07 2005
13C
BCM
100.40 MHz
126.00 KHz
100000 Hz
32768
271 73.90 Hz
723
1.2059 sec
1.7940 sec
5.90 usec
24.2 c
CDCl3
77.00 ppm
0.12 Hz
22
PPM
-5.3132
-5.2567
18.2308
19.3362
25.6653
25.9174
26.4406
52.2746
68.9320
76.6783
77.0000
77.3136
106.2625
127.5280
129.4667
133.8831
136.4668
136.4723
140.1167