

Supporting Information for

Synthetic Studies on Daphnicyclidin A: Enantiocontrolled Construction of the BCD Ring System

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Experimental Section

S3-S11: Model studies on the tandem cyclization

S12-S26: Synthesis of the chiral tricycle (in manuscript)

S27-S43: X-ray data for compound **30**

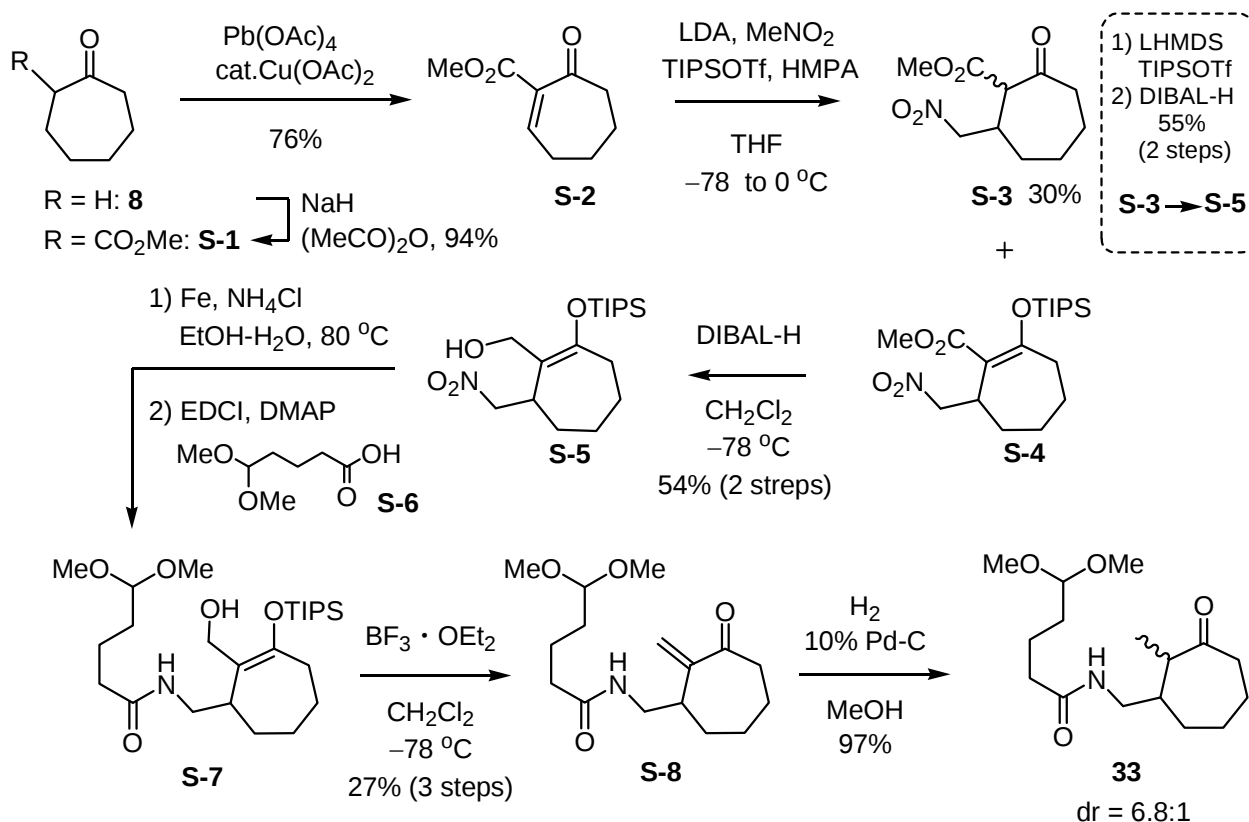
S44-S96: ¹H and ¹³C-NMR spectra

Experimental Section

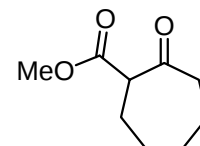
General Procedure. All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated THF and CH₂Cl₂ were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard protocols. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck Kieselgel 60 F₂₅₄). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μ m) and flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μ m). 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 rt, using the sodium D line. IR spectra were recorded on a JASCO FT/IR-410 Fourier Transform Infrared Spectrophotometer. ¹H-NMR (400, 500, and 600 MHz) and ¹³C-NMR spectra (100, 125, and 150 MHz) were recorded on JEOL JNM-AL-400, JEOL JNM-ECP-500 and JEOL JNM-ECA-600 spectrometers, respectively. For ¹H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) in CDCl₃ and from residual non-deuterated solvent peak in the other solvents (DMSO-*d*₆: 2.49 ppm, benzene-*d*₆: 7.15 ppm, toluene-*d*₈: 2.09 ppm, methanol-*d*₄: 3.30 ppm) as internal standards. For ¹³C-NMR spectra, chemical shifts (δ) are given from CDCl₃ (77.0 ppm), DMSO-*d*₆ (39.5 ppm), benzene-*d*₆ (128.0 ppm), toluene-*d*₈ (20.4 ppm), and methanol-*d*₄ (49.0 ppm) as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet, 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.

Model studies on the tandem cyclization

Scheme S-1. Synthesis of the model substrate



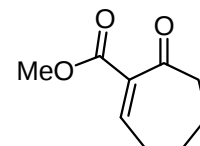
Methyl 2-Oxocycloheptanecarboxylate (S-1) ¹



A three-necked flame-dried 1 L flask equipped with a magnetic stirrer bar was charged with NaH (60% containing mineral oil, 9.60 g, 400 mmol, washed with dry benzene prior to use), benzene (340 mL), and dimethyl carbonate (27.0 mL, 320 mmol). This mixture was heated to reflux and cycloheptanone (**8**) (20.0 g, 178 mmol) in benzene (60 mL) was added dropwise from the dropping funnel over 3.5 h. After the addition was completed, this mixture was refluxed until the evolution of H_2 ceases (20 min). After the reaction mixture was cooled to 0 °C, AcOH (15 mL) was added dropwise to form pasty solids. Then ice-cold water (100 mL) was added and the mixture was stirred until all the solid material has been dissolved. The organic layer was separated and the aqueous layer was extracted with benzene (3 times). The combined organic layers were washed with cold water (3 times). The organic layer was dried over MgSO_4 and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 15:1 to 10:1) to give β -ketoester **S-1** (28.6 g, 94%, keto:enol = 11:6) as a colorless oil.

S-1 (keto-enol mixture = 11:6): IR (neat) : 2931, 1746, 1705, 1643, 1455, 1312, 1199, 1049, 1017, 940, 862 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 12.7 (1 $\times$ 6/17H, s), 3.75 (3 $\times$ 6/17H, s), 3.72 (3 $\times$ 11/17H, s), 3.55 (1 $\times$ 11/17H, dd, J = 10.3, 4.0 Hz), 2.68-2.36 (1 $\times$ 6/17H + 4 $\times$ 11/17H, m), 2.14-1.40 (9 $\times$ 6/17H + 6 $\times$ 11/17H, m) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : keto form : 208.7 (208.5), 170.8 (170.6), 58.6 (58.4), 51.9 (51.7), 42.9 (42.7), 29.5 (29.3), 27.8 (27.7), 27.4 (27.2), 24.20 (24.0) ; enol form : 179.5 (179.3), 173.2 (173.0), 101.3 (101.1), 51.3 (51.1), 35.1 (35.0), 31.8 (31.7), 27.2 (27.1), 24.5 (24.3), 24.17 [Reported $^{13}\text{C-NMR}$ data¹ were presented in the parenthesis. The one peak corresponding to that of reported data (27.5 for enol form) was not observed. Instead, another peak (24.17 for enol form) was abserved.] ; MS m/z : 170 (M^+), 138 (100%) ; HRMS calad. for $\text{C}_9\text{H}_{14}\text{O}_3$ (M^+) : 170.0943, found : 170.0932.

Methyl 7-Oxocyclohept-1-enecarboxylate (S-2) ²



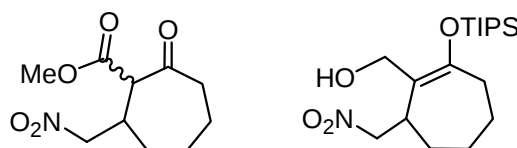
To a solution of β -ketoester **S-1** (2.53 g, 14.9 mmol) in benzene (149 mL) was added $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (74 mg, 0.37 mmol) and the mixture was stirred for 30 min. $\text{Pb}(\text{OAc})_4$ (6.60 g, 14.9 mmol) was added and the mixture was stirred for 3.5 h. Ethylene glycol (4.0 mL) was added until the solution became clear. The solvent was removed under reduced pressure, water was added, and the residue was extracted Et_2O . The extracts were washed with water, sat. NaHCO_3 and brine, then dried over MgSO_4 , and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane: Et_2O , 1:1) to give enoate **S-2** (1.91 g, 76%) as a colorless oil.

S-2: IR (neat) : 2950, 1730, 1697, 1632, 1435, 1379, 1255, 1094, 1032, 906 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.41 (1H, t, J = 5.8 Hz), 3.77 (3H, s), 2.69 (2H, t, J = 6.6 Hz), 2.51 (2H, q, J = 5.8 Hz), 1.87 (2H, m), 1.78 (2H, m) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 202.2, 165.5, 149.0, 136.5, 52.1, 43.6, 28.8, 24.3, 22.5 ; MS m/z : 168 (M^+), 140 (100%) ; HRMS calad. for $\text{C}_9\text{H}_{12}\text{O}_3$ (M^+) : 168.0786, found : 168.0774.

Methyl 2-Nitromethyl-7-oxocycloheptanecarboxylate (S-3)

[(Z)-7-Nitromethyl-2-triisopropylsilyloxycyclohept-

1-enyl]methan-1-ol (S-5)



A three-necked flame-dried 500 mL flask equipped with a magnetic stirrer bar was charged with *i*-Pr₂NH

(6.71 mL, 47.9 mmol) and THF (70 mL) and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. *n*-BuLi (29.0 mL, 45.8 mmol, 1.6 M hexane sol.) was added dropwise and the mixture was allowed to warm up to $0\text{ }^{\circ}\text{C}$. After being stirred for 30 min at that temperature, the reaction mixture was cooled to $-78\text{ }^{\circ}\text{C}$ again. MeNO₂ (2.48 mL, 45.8 mmol) was added dropwise and white precipitates formed immediately. After being stirred for 15 min at that temperature, enoate **S-2** (7.00 g, 41.6 mmol) in THF (34 mL) was added dropwise to the resultant white suspension *via* cannula. After being stirred for 50 min at that temperature, TIPSOTf (16.8 mL, 62.4 mmol) and HMPA (36.2 mL, 208 mmol) were added and the resultant viscous reaction mixture was allowed to warm up to $0\text{ }^{\circ}\text{C}$. After being stirred for 1 h at that temperature, water was added and the reaction mixture was acidified with NaH₂PO₄·2H₂O. The resultant solution was extracted Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 30:1 to 4:1) to give β -ketoester **S-3** (2.86 g, 30%, keto-enol-diastereomeric mixture = 100:43:75), crude silyl enol ether **S-4** including inseparable wreckage of silanol, and a *N*-O-silylated compound. The crude silyl enol ether **S-4** was used in the next step without further purification.

To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of crude silyl enol ether **S-4** in CH₂Cl₂ (40 mL) was added DIBAL-H (118.0 mL, 116.5 mmol, 0.99 M toluene sol.) dropwise. After being stirred for 2 h at that temperature, MeOH (120 mL, slowly!) and sat. Rochelle salt. (240 mL) were added and then the reaction mixture was allowed to warm up to rt. After being stirred for 3 h at rt, the mixture was extracted Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1 to 4:1) to give alcohol **S-5** [8.04 g, 54% (2 steps)] as a colorless oil.

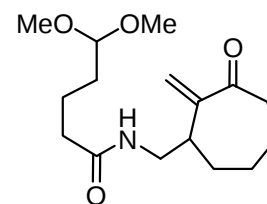
[Recovery from β -ketoester **S-3]:** To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of β -ketoester **S-3** (570 mg, 2.49 mmol) in THF (5 mL) was added LHMDs (2.61 mL, 2.61 mmol, 1.0 M THF sol.) dropwise. After being stirred for 30 min at that temperature, TIPSOTf (700 μ L, 2.61 mmol) and HMPA (2.17 mL, 12.5 mmol) were added and the viscous reaction mixture was allowed to warm up to $-40\text{ }^{\circ}\text{C}$. After an additional stirring for 1 h at $-40\text{ }^{\circ}\text{C}$, the reaction mixture was allowed to warm up to $0\text{ }^{\circ}\text{C}$ and stirred for 2 h. Sat. NaHCO₃ was added and the mixture was extracted with Et₂O. The extracts were washed with brine, then dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 30:1 to 4:1) to give β -ketoester **S-3** (200 mg, 35%), crude silyl enol ether **S-4** including inseparable wreckage of silanol, and a *N*-O-silylated compound. The crude silyl enol ether **S-4** was used in

the next step without further purification. According to the same protocol (reduction of **S-4** with DIBAL-H), **S-5** (490 mg, 55%, 2 steps) was obtained.

β -Ketoester **S-3 (keto-enol-diastereomeric mixture = 100:43:75):** IR (neat) : 2939, 1743, 1710, 1554, 1437, 1236 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 13.2 (1 $\times$ 43/198H, s), 4.74 (1 $\times$ 75/198H, dd, J = 13.0, 5.1 Hz), 4.58 (1 $\times$ 43/198H, dd, J = 11.4, 9.9 Hz), 4.51 (1 $\times$ 100/198H, dd, J = 12.6, 4.4 Hz), 4.45 (1 $\times$ 43/198H, dd, J = 11.4, 6.0 Hz), 4.38 (1 $\times$ 100/198H, dd, J = 12.6, 8.0 Hz), 4.33 (1 $\times$ 75/198H, dd, J = 13.0, 9.8 Hz), 3.81 (1 $\times$ 75/198H, d, J = 2.7 Hz), 3.80 (3 $\times$ 43/198H, s), 3.76 (3 $\times$ 100/198H + 3 $\times$ 75/198H, s), 3.46 (1 $\times$ 100/198H, d, J = 10.4 Hz), 3.0 (1 $\times$ 100/198H + 1 $\times$ 75/198H, m), 2.79-2.44 (2 $\times$ 100/198H + 2 $\times$ 75/198H + 2 $\times$ 43/198H, m), 2.00-1.50 (6 $\times$ 100/198H + 5 $\times$ 75/198H + 6 $\times$ 43/198H, m), 1.40 (1 $\times$ 75/198H + 1 $\times$ 43/198H, m) ; MS m/z : 229 (M^+), 125 (100%) ; HRMS calad. for $\text{C}_{10}\text{H}_{15}\text{NO}_5$ (M^+) : 229.0950, found : 229.0974.

The analytical data of alcohol **S-5** was described in the experiments, page S-15.

(2-Methylene-3-oxocycloheptylmethyl) 5,5-Dimethoxypentanamide (**S-8**)



A mixture of Fe (7.80 g, 140 mmol, 100 mesh), NH_4Cl (996 mg, 18.6 mmol), and alcohol **S-5** (5.55 g, 15.5 mmol) in $\text{EtOH-H}_2\text{O}$ (40 mL, 3:1 v/v) was stirred for 2.5 h at 80 $^\circ\text{C}$. After the mixture was cooled to rt, Et_3N (3.26 mL, 23.3 mmol) was added and the mixture was stirred for 15 min. The mixture was filtered through a Celite pad eluting with CH_2Cl_2 . The filtrate was concentrated under reduced pressure. The residue was diluted with CH_2Cl_2 and dried over Na_2SO_4 . The crude solution was concentrated under reduced pressure to afford corresponding crude amino alcohol (6.19 g), which was used in the next step without further purification.

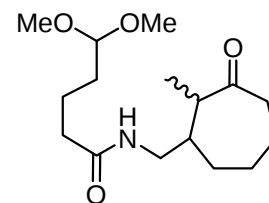
A mixture of the crude amino alcohol, carboxylic acid **S-6**³ (2.52 g, 15.5 mmol), EDCI (2.98 g, 15.5 mmol), and DMAP (1.90 g, 15.5 mmol) in CH_2Cl_2 (30mL) was stirred for 1 h at rt. The reaction mixture was quenched with sat. NaHCO_3 and extracted with Et_2O . The extracts were washed with water and 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, 2:1 to 1:1) to give crude amide **S-7** (2.90 g) including a small amount of inseparable compound (not determined). This crude amide **S-7** was used in the

next step without further purification.

To a cooled (-78°C) solution of crude amide **S-7** in CH_2Cl_2 (25 mL) was added dropwise $\text{BF}_3\cdot\text{OEt}_2$ (1.56 mL, 12.3 mmol). After the mixture was stirred for 5 min at that temperature, sat. NaHCO_3 was added and then the reaction mixture was allowed to warm up to rt. After being stirred for 1 h at rt, the mixture was extracted Et_2O . The extracts were 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, 1:1 to 1:2) to give enone **S-8** [1.25 g, 27% (3 steps)] as a colorless oil.

S-8: IR (neat) : 3500, 3303, 2829, 1688, 1650, 1550, 1446, 1127, 1070, 947 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ : 6.00 (1H, s), 5.81 (1H, br s), 5.25 (1H, s), 4.35 (1H, t, $J = 5.3$ Hz), 3.53 (1H, ddd, $J = 6.8, 13.5, 6.8$ Hz), 3.37 (1H, ddd, $J = 13.5, 8.2, 5.1$ Hz), 3.39 (6H, s), 2.75-2.53 (3H, m), 2.19 (2H, t, $J = 7.1$ Hz), 1.98-1.81 (3H, m), 1.73-1.56 (6H, m), 1.45 (1H, m) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 204.4, 172.7, 150.3, 120.4, 104.3, 52.8, 42.5, 42.0, 41.6, 36.0, 34.8, 31.8, 28.8, 24.6, 20.7 ; MS m/z : 297 (M^+), 71 (100%) ; HRMS calcd. for $\text{C}_{16}\text{H}_{27}\text{NO}_4$ (M^+) : 297.1940, found : 297.1922.

(2-Methyl-3-oxocycloheptylmethyl) 5,5-Dimethoxypentanamide (**33**)

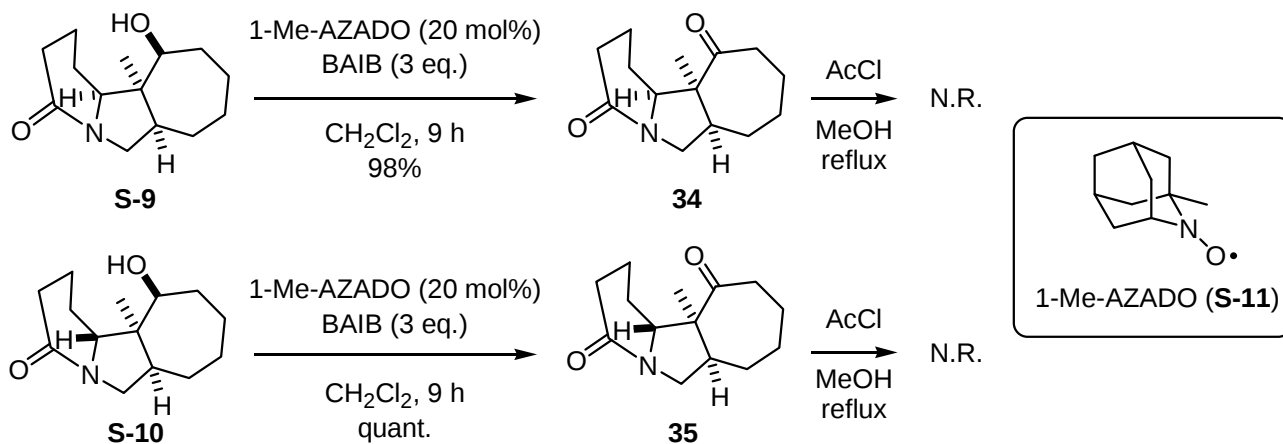
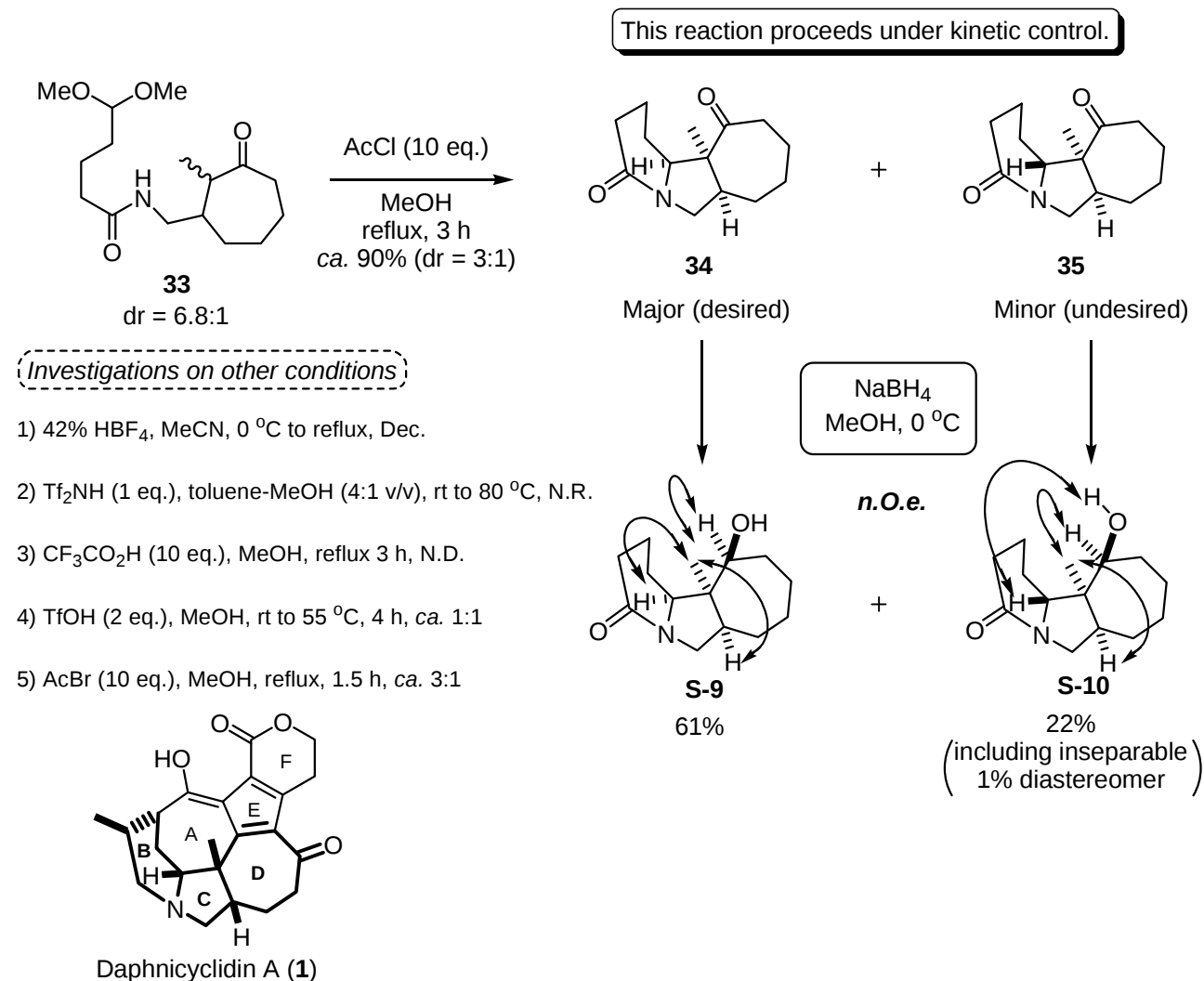


A solution of enone **S-8** (1.20 g, 4.04 mmol) in MeOH (5 mL) was hydrogenated in the presence of 10% Pd-C (120 mg) under atmospheric pressure of H_2 . After being stirred for 2.5 h, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (AcOEt:MeOH, 100:0 to 100:1) to give ketone **33** (1.19 g, 97%) as a colorless oil (dr = 6.8:1 determined by ^1H -NMR spectrum).

33 (diastereomeric mixture = 6.8:1): IR (neat) : 3305, 2931, 1698, 1646, 1546, 1454, 1380, 1127, 1069, 772 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ : 5.79 (1 $\times$ 1/7.8H, br s), 5.67 (1 $\times$ 6.8/7.8H, br s), 4.36 (1 $\times$ 6.8/7.8H + 1 $\times$ 1/7.8H, t, $J = 5.3$ Hz), 3.32 (6 $\times$ 6.8/7.8H + 6 $\times$ 1/7.8H, s), 3.24-3.05 (2 $\times$ 6.8/7.8H + 2 $\times$ 1/7.8H, m), 2.83 (1 $\times$ 6.8/7.8H + 1 $\times$ 1/7.8H, ddd, $J = 14.0, 7.0, 3.1$ Hz), 2.60 (1 $\times$ 6.8/7.8H + 1 $\times$ 1/7.8H, m), 2.42 (1 $\times$ 6.8/7.8H + 1 $\times$ 1/7.8H, m), 2.20 (2 $\times$ 6.8/7.8H + 2 $\times$ 1/7.8H, t, $J = 7.2$ Hz), 2.15-1.50 (8 $\times$ 6.8/7.8H + 8 $\times$ 1/7.8H, m), 1.20 (3 $\times$ 1/7.8H, d, $J = 7.0$ Hz), 1.12 (3 $\times$ 6.8/7.8H, d, $J = 7.0$ Hz) ; ^{13}C -NMR (100 MHz, CDCl_3 , major peaks are shown) δ : 215.4, 172.7, 104.4, 52.9, 47.7, 43.1, 40.6, 40.0, 36.2, 31.9, 30.2, 26.5,

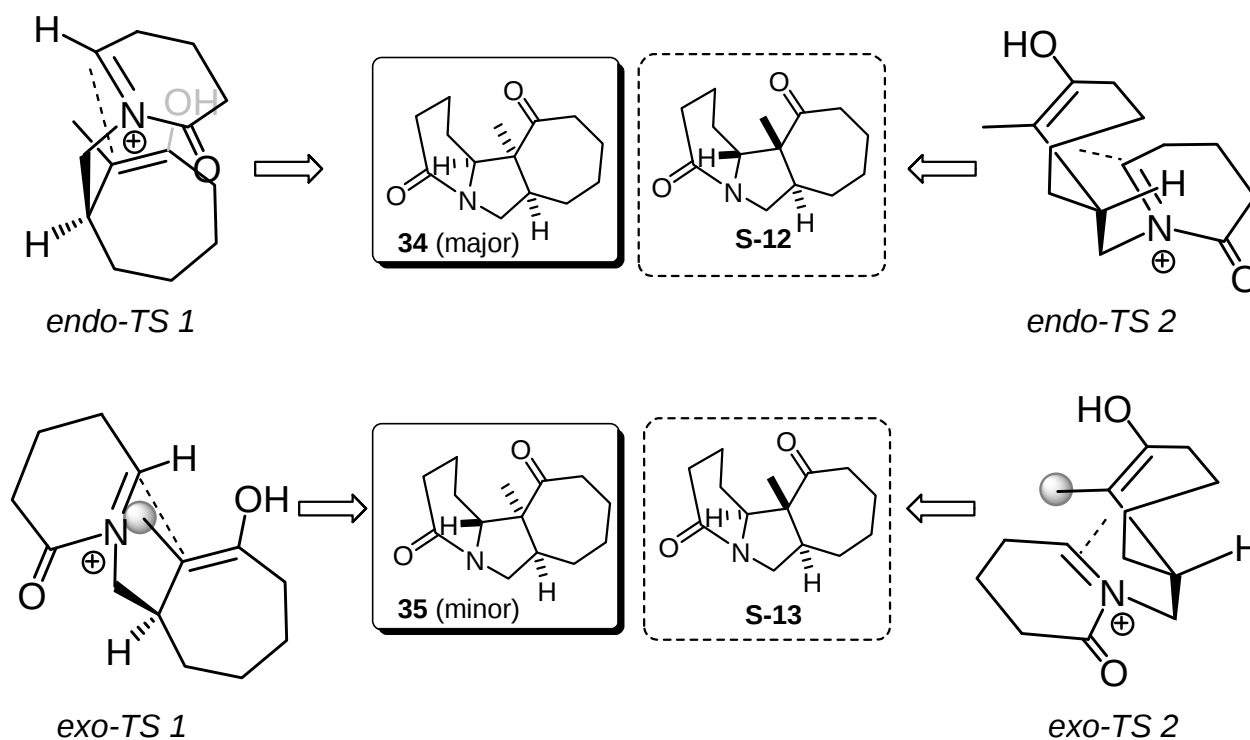
24.1, 20.7, 12.5 ; MS m/z : 284 ($M^+ - Me$), 130 (100%) ; HRMS calcd. for $C_{15}H_{26}NO_4$ ($M^+ - Me$) : 284.1862, found : 284.1855.

Scheme S-2. Examinations of the tandem cyclization



The model experiments of the tandem cyclization are depicted in Scheme S-2. The stereochemistries of **34** and **35** were determined by NOESY correlations after leading them to alcohols **S-9** and **S-10**. Since another subjection of **34** and **35** to the cyclization condition (AcCl, MeOH, reflux) gave no equilibrium between **34** and **35**, it was found that this reaction proceeds under kinetic control.

Figure S-1. Plausible transition states of the tandem cyclization

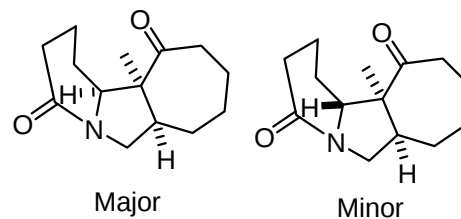


A rationale for the stereoselectivity of the tandem cyclization is described in Figure S-1. Theoretically, four transition states can be considered. Considering the fact that products do not interconvert each other under the reaction conditions, the stereochemical outcome would be rationalized by the transition state models and the predominant formation of **34** can be rationalized by considering the steric repulsion (methyl vs. 6-membered ring) in *exo-TS 1*.

(6a*R**,11a*S**,11b*S**)- and

(6a*R**,11a*S**,11b*R**)-11a-Methyloctahydro-1*H*-cyclohepta[*a*]indolizine-4,11(11a*H*,11b*H*)-dione

(34) and (35)



To a solution of ketone **33** (250 mg, 0.835 mmol) was slowly added AcCl (0.590 mL, 8.35 mmol) and the mixture was heated to reflux. After being stirred for 4 h, the mixture was cooled to rt and the solvent was removed under reduced pressure. Sat. NaHCO₃ was added and the mixture was extracted with CH₂Cl₂. The extracts were washed with brine, then dried over MgSO₄, and concentrated under reduced pressure to give the corresponding lactam [analytically pure but including inseparable diastereomixture (*ca.* 3:1)], which was used in the next step without further purification.

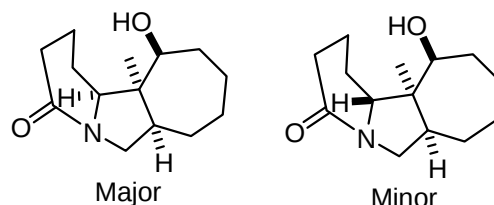
Reoxidation: A mixture of alcohol **S-9** (164 mg, 0.691 mmol), 1-Me-AZADO⁴ (24.0 mg, 0.138 mmol), and BAIB (668 mg, 2.07 mmol) in CH₂Cl₂ (5 mL) was stirred for 9 h at 40 °C. After being cooled to rt, Na₂SO₃ (172 mg, 1.38 mmol) and water were added, then the resultant solution was extracted with Et₂O. The extracts were washed with brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (AcOEt:MeOH, 100:0 to 100:5) to give ketone **34** (159 mg, 98%) as a white solid. Following this procedure, alcohol **S-10** (35.0 mg, 0.147 mmol) was also converted to ketone **35** (36.0 mg, quant.) as a white solid.

34 (major lactam): M.p. = 120-125 °C ; IR (neat) : 2942, 1693, 1634, 1444, 1415, 1392, 1309, 1240, 1173, 1095, 933, 918 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 4.05 (1H, dd, *J* = 12.8, 9.2 Hz), 3.53 (1H, dd, *J* = 12.8, 10.9 Hz), 3.41 (1H, dd, *J* = 11.8, 3.9 Hz), 2.51-2.35 (3H, m), 2.27 (1H, ddd, *J* = 17.9, 12.3, 6.8 Hz), 2.14 (1H, ddd, *J* = 13.3, 11.1, 2.7 Hz), 2.05-1.48 (8H, m), 1.26 (1H, m), 1.20 (3H, s), 1.07 (1H, dtd, *J* = 11.8, 13.3, 2.9 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 213.1, 168.8, 68.0, 60.5, 45.6, 43.4, 42.1, 31.2, 25.8, 25.5, 24.5, 22.7, 21.5, 21.0 ; MS *m/z* : 235 (M⁺), 220 (100%) ; HRMS calad. for C₁₄H₂₁NO₂ (M⁺) : 235.1572, found : 235.1566.

35 (minor lactam): M.p. = 110-112 °C ; IR (neat) : 2924, 1697, 1634, 1448, 1399, 1330, 1316, 1173, 1115, 938 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 4.01 (1H, dd, *J* = 12.8, 8.5 Hz), 3.72 (1H, dd, *J* = 11.1, 3.4 Hz), 3.15 (1H, d, *J* = 12.8 Hz), 2.73 (1H, ddd, *J* = 12.6, 10.9, 2.9 Hz), 2.43 (1H, dd, *J* = 18.1, 6.1 Hz), 2.35 (1H, m), 2.32-2.20 (2H, m), 2.06 (1H, m), 2.02-1.88 (3H, m), 1.77 (1H, tdd, *J* = 13.3, 6.3, 2.9 Hz), 1.67 (1H, dd, *J*

= 13.3, 5.6 Hz), 1.56-1.25 (4H, m), 1.14 (3H, s) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 214.2, 169.5, 60.2, 60.0, 51.6, 44.3, 40.6, 34.8, 31.3, 30.1, 27.7, 24.8, 21.1, 19.0 ; MS m/z : 235 (M^+), 220 (100%) ; HRMS calad. for $\text{C}_{14}\text{H}_{21}\text{NO}_2$ (M^+) : 235.1572, found : 235.1567.

(6a*R,11*R**,11a*S**,11b*S**)- and (6a*R**,11*R**,11a*S**,11b*R**)-11-Hydroxy-11a-methyloctahydro-1*H*-cyclohepta[*a*]indolizin-4-(11b*H*)-one (S-9) and (S-10)**



Reduction (to separate the diastereomeric mixtures of 34 and 35): To a cooled (0 °C) solution of the crude lactam [from ketone **33** (250 mg, 0.835 mmol)] in MeOH (4 mL) was added NaBH_4 (94.0 mg, 2.51 mmol) and the mixture was allowed to warm up to rt. After 2 h, acetone was added and then the solvent was removed under reduced pressure. Sat. NH_4Cl was added to the residue and the mixture was extracted with Et_2O . The extracts were washed with brine, then dried over MgSO_4 , and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography ($\text{AcOEt}:\text{MeOH}$, 100:0 to 100:5) to give alcohols {major: **S-9** [120 mg, 61% (2 steps)] and minor: **S-10** [44 mg, 22% (2 steps, including inseparable 1% diastereomer)]} as white solids.

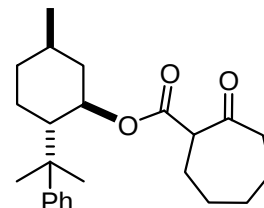
S-9 (major alcohol): M.p. = 178-183 °C ; IR (neat) : 3374, 2936, 1618, 1467, 1098 cm^{-1} ; ^1H -NMR (600 MHz, CDCl_3) δ : 3.90 (1H, s), 3.43 (1H, dd, J = 18.0, 12.0 Hz), 3.41 (1H, dd, J = 18.0, 12.0 Hz), 3.22 (1H, dd, J = 12.0, 3.6 Hz), 2.29 (1H, dd, J = 18.0, 6.0 Hz), 2.26 (1H, d, J = 4.2 Hz), 2.18 (1H, ddd, J = 18.0, 12.0, 6.6 Hz), 2.06 (1H, m), 2.00-1.90 (2H, m), 1.78-1.51 (9H, m), 1.44 (1H, m), 0.96 (3H, s) ; ^{13}C -NMR (150 MHz, CDCl_3) δ : 167.9, 74.3, 70.6, 52.4, 49.9, 44.7, 31.2, 30.7, 30.5, 25.4, 25.1, 23.2, 23.1, 21.5 ; MS m/z : 237 (M^+), 111 (100%) ; HRMS calad. for $\text{C}_{14}\text{H}_{23}\text{NO}_2$ (M^+) : 237.1729, found : 237.1710.

S-10 (minor alcohol): M.p. = 149-153 °C ; IR (neat) : 3376, 2934, 1617, 1473, 1415, 1321, 1173, 1126, 1098, 1010, 936, 731 cm^{-1} ; ^1H -NMR (600 MHz, CDCl_3) δ : 3.96 (1H, dd, J = 13.2, 8.4 Hz), 3.94 (1H, dd, J = 10.8, 3.6 Hz), 3.76 (1H, dd, J = 7.8, 4.2 Hz), 2.90 (1H, dd, J = 13.2, 3.6 Hz), 2.36 (1H, dd, J = 17.4, 5.4 Hz), 2.20 (1H, ddd, J = 17.4, 12.6, 6.6 Hz), 2.00 (1H br s), 1.97-1.64 (9H, m), 1.52 (1H, m), 1.39 (1H, m), 1.36-1.20 (2H, m), 0.83 (3H, s) ; ^{13}C -NMR (150 MHz, CDCl_3) δ : 169.1, 73.9, 60.2, 51.4, 50.9, 47.9, 31.7, 31.5, 30.8, 29.5, 23.5, 22.8, 22.2, 21.3 ; MS m/z : 237 (M^+), 111 (100%) ; HRMS calad. for $\text{C}_{14}\text{H}_{23}\text{NO}_2$ (M^+) : 237.1729, found : 237.1706.

Synthesis of the chiral tricycle (in manuscript)

[(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl]

2-Oxocycloheptanecarboxylate (**9**)



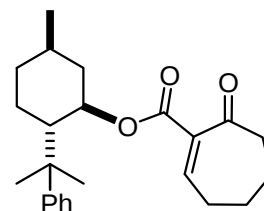
This reaction was executed by total two cycles. (1st cycle → filtered through silica gel column → 2nd cycle)

A mixture of 8-phenylmenthol (7.62 g, 32.8 mmol), β-ketoester **S-1** [10.0 g (1st cycle) + 6.70 g (2nd cycle), 98.1 mmol] and DMAP [800 mg (1st cycle) + 2.00 g (2nd cycle), 22.9 mmol] in toluene [33 mL (1st cycle) + 70 mL (2nd cycle)] was heated to reflux for [2 days (1st cycle) + 2 days (2nd cycle)]. After being cooled to rt, the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 15:1 to 10:1) to give β-ketoester **9** (10.9 g, 90%, keto-enol-diastereomeric mixture = 100:85:43) as a colorless oil.

9 (keto-enol-diastereo mixture = 100:85:43): IR (neat) : 2925, 1737, 1706, 1632, 1496, 1455, 1390, 1366, 1309, 1241, 1214, 1196, 1127, 1040, 996 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 12.9 (1 × 85/228H, s), 7.39-7.22 (4 × 100/228H + 4 × 85/228H + 4 × 43/228H, m), 7.20-7.09 (1 × 100/228H + 1 × 85/228H + 1 × 43/228H, m), 4.88 (1 × 100/228H, td, *J* = 10.6, 4.3 Hz), 4.83 (1 × 85/228H, td, *J* = 8.7, 4.3 Hz), 4.81 (1 × 43/228H, td, *J* = 8.5, 4.1 Hz), 2.98 (1 × 43/228H, dd, *J* = 7.0, 4.1 Hz), 2.61-2.32 (3 × 100/228H + 2 × 85/228H + 2 × 43/228H, m), 2.10-0.75 [25 × 100/228H + 25 × 85/228H + 25 × 43/228H, m, including six singlets C(Ph)(CH₃)(CH₃) × 3; 1.32, 1.30, 1.29, 1.25, 1.21, 1.18] ; MS *m/z* : 370 (M⁺), 119 (100%) ; HRMS calcd. for C₂₄H₃₄O₃ (M⁺) : 370.2508, found : 370.2502.

[(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl]

7-Oxocyclohept-1-enecarboxylate (**11**)



To a cooled (−78 °C) solution of β-ketoester **9** (517 mg, 1.40 mmol) in THF (4 mL) was added dropwise LHMDs (1.47 mL, 1.47 mmol, 1.0 M THF sol.). After being stirred for 10 min at that temperature, *N*-tert-butylbenzenesulfinimidoyl chloride **10** (362 mg, 1.68 mmol) in THF (3.5 mL) was added dropwise over 10 min. After being stirred for 30 min, the reaction mixture was quenched with sat. NaHCO₃ and

allowed to warm up to rt. The resultant solution was extracted Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 15:1 to 8:1) to give enoate **11** (320 mg, 62%).

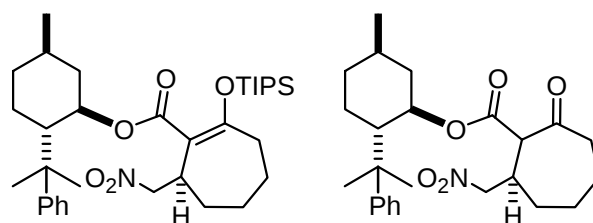
11: [α]_D²⁹ –29.8° (*c* 0.34, CHCl₃) ; IR (neat) : 2951, 1715, 1496, 1456, 1372, 1253, 1093, 1017, 978, 907 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 7.34-7.18 (4H, m), 7.08 (1H, m), 6.49 (1H, t, *J* = 5.7 Hz), 4.91 (1H, td, *J* = 10.7, 4.3 Hz), 2.52 (2H, td, *J* = 6.6, 1.2 Hz), 2.25 (2H, dt, *J* = 6.0, 5.7 Hz), 2.08 (1H, td, *J* = 11.3, 3.4 Hz), 1.94 (1H, m), 1.81-1.59 (6H, m), 1.47 (1H, m), 1.29 (3H, s), 1.18 (3H, s), 1.19-0.82 (3H, m), 0.87 (3H, d, *J* = 6.5 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 201.9, 163.4, 151.8, 148.1, 136.1, 127.8, 125.3, 124.5, 74.8, 50.0, 43.4, 41.3, 39.4, 34.4, 31.1, 28.59, 28.57, 26.4, 24.1, 24.0, 22.5, 21.6 ; MS *m/z* : 368 (M⁺), 154 (100%) ; HRMS calad. for C₂₄H₃₂O₃ (M⁺) : 368.2351, found : 368.2364.

(7R,Z)-[(1R,2S,5R)-5-Methyl-2-(2-phenylpropan-2-yl)cyclohexyl]

7-Nitromethyl-2-triisopropylsilyloxycyclohept-1-enecarboxylate (13)

(2R)-[(1R,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl]

2-Nitromethyl-7-oxocycloheptanecarboxylate (14)



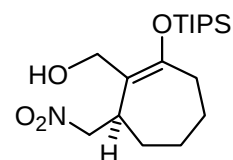
A two-necked flame-dried 100 mL flask equipped with a magnetic stirrer bar was charged with MeNO₂ (0.390 mL, 7.26 mmol) and THF (10 mL) and the solution was cooled to –78 °C. *n*-BuLi (4.16 mL, 6.66 mmol, 1.6 M hexane sol.) was added dropwise to the solution over 7 min. After being stirred for 15 min at that temperature, white precipitates formed immediately. To the resultant white suspension was added enoate **11** (5.38 g, 14.6 mmol) in THF (10 + 3 + 2 mL) dropwise over 20 min *via* cannula. After being stirred for 1.5 h at that temperature, TIPSOTf (2.11 mL, 7.87 mmol) and HMPA (5.26 mL, 30.3 mmol) were added and the viscous reaction mixture (pale yellow) was allowed to warm up to –10 °C (ice-salt bath). After being stirred for 9 h from –10 °C to rt (overnight), the reaction was quenched with sat.NaHCO₃ and the resultant solution was extracted Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 80:1 to 8:1) to give silyl enol ether **13** (2.24 g, 63%), along with β -ketoester **14** (479 mg, 19%, keto-enol-diastereomeric mixture = 100:39:44) and recovered **11** (111 mg, 5%) as

colorless oils.

Silyl enol ether 13: $[\alpha]_D^{24} +45.2^\circ$ (c 0.60, CHCl_3) ; IR (neat) : 2945, 1710, 1602, 1551, 1458, 1372, 1198, 1031, 882 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 7.32-7.21 (4H, m), 7.10 (1H, m), 4.93 (1H, dt, $J = 10.6, 4.3$ Hz), 4.39 (1H, dd, $J = 11.6, 10.1$ Hz), 4.31 (1H, dd, $J = 11.6, 5.6$ Hz), 3.07 (1H, m), 2.41 (1H, m), 2.27 (1H, m), 2.05 (1H, m), 1.89 (1H, dm, $J = 11.8$ Hz), 1.75-1.43 (9H, m), 1.31 (3H, s), 1.28-0.82 (24H, m), 1.20 (3H, s), 0.85 (3H, d, $J = 6.5$ Hz) ; $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 165.1, 164.9, 151.7, 127.8, 125.4, 124.9, 110.8, 76.9, 73.5, 50.2, 41.7, 39.8, 35.8, 34.9, 34.5, 31.3, 27.0, 26.82, 26.77, 25.9, 24.0, 23.3, 21.8, 18.00, 17.99, 13.6 ; MS m/z : 542 ($\text{M}^+ - \text{C}_3\text{H}_7$), 328 (100%) ; HRMS calcd. for $\text{C}_{31}\text{H}_{48}\text{NO}_5\text{Si}$ ($\text{M}^+ - \text{C}_3\text{H}_7$) : 542.3302, found : 542.3268.

β -Ketoester 14 (keto-enol-diastereomeric mixture = 100:39:44): IR (neat) : 2927, 1735, 1711, 1629, 1552, 1457, 1379, 1233 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 13.4 (1 $\times$ 39/183H, s), 7.34-7.22 (4 $\times$ 100/183H + 4 $\times$ 44/183H + 4 $\times$ 39/183H, m), 7.20-7.07 (1 $\times$ 100/183H + 1 $\times$ 44/183H + 1 $\times$ 39/183H, m), 5.01 (1 $\times$ 44/183H, td, $J = 10.6, 4.3$ Hz), 4.89 (1 $\times$ 39/183H, td, $J = 10.6, 4.3$ Hz), 4.80 (1 $\times$ 100/183H, td, $J = 10.6, 4.3$ Hz), 4.39 (1 $\times$ 100/183H, dd, $J = 12.6, 4.1$ Hz), 4.30 (1 $\times$ 44/183H, dd, $J = 11.1, >5.8$ Hz), 4.28 (1 $\times$ 100/183H, dd, $J = 12.6, 8.7$ Hz), 4.18 (1 $\times$ 44/183H, dd, $J = 11.1, 5.8$ Hz), 4.04 (1 $\times$ 39/183H, dd, $J = 13.3, 4.8$ Hz), 3.98 (1 $\times$ 39/183H, dd, $J = 13.3, 9.7$ Hz), 2.91 (1 $\times$ 44/183H, d, $J = 2.4$ Hz), 2.80-2.63 (1 $\times$ 100/183H + 1 $\times$ 44/183H, m), 2.57-0.83 (16 $\times$ 100/183H + 16 $\times$ 44/183H + 17 $\times$ 39/183H, m), 2.47 (1 $\times$ 100/183H, d, $J = 9.9$ Hz), 1.32 (3 $\times$ 39/183H, s), 1.28 (3 $\times$ 44/183H, s), 1.19 (3 $\times$ 39/183H, s), 1.17 (3 $\times$ 100/183H + 3 $\times$ 44/183H, s), 1.04 (3 $\times$ 100/183H, s), 0.91 (3 $\times$ 39/183H, d, $J = 6.8$ Hz), 0.90 (3 $\times$ 44/183H, d, $J = 7.0$ Hz), 0.87 (3 $\times$ 100/183H, d, $J = 6.3$ Hz) ; MS m/z : 429 (M^+), 119 (100%) ; HRMS calcd. for $\text{C}_{25}\text{H}_{35}\text{NO}_5$ (M^+) : 429.2515, found : 429.2537.

[(7*R*,*Z*)-7-Nitromethyl-2-triisopropylsilyloxycyclohept-1-enyl]methan-1-ol (15)

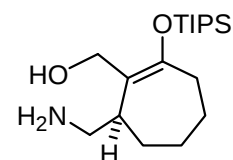


To a cooled (-78°C) solution of silyl enol ether **13** (2.24 g, 3.82 mmol) in toluene (15 mL) was added DIBAL-H (9.00 mL, 8.79 mmol, 0.99 M toluene sol.) dropwise over 10 min (clear $\rightarrow$ yellow $\rightarrow$ orange sol.). After being stirred for 45 min at that temperature, MeOH (9 mL, slowly!) and sat. Rochelle salt. (27 mL) were added and then the reaction mixture was allowed to warm up to rt. After being stirred for 2 h at rt, the mixture was extracted with Et_2O . The extracts were washed with water and brine, then dried over MgSO_4 ,

and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 14:1 to 8:1) to give alcohol **15** (1.20 g, 88%, 96% ee), along with (–)-8-phenylmenthol (800 mg, 90%) as colorless oils. The ee of **15** was determined by HPLC [DICEL CHIRALCEL OD-H (0.46 × 25 cm), *i*-PrOH:Hex (3:97), Flow rate: 0.5 mL/min, UV: 254 nm, Retention time: major, 17.0 min, minor, 19.9 min].

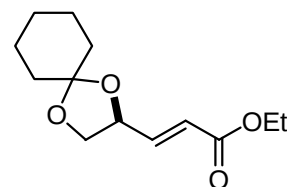
15: $[\alpha]_D^{29} +18.0^\circ$ (*c* 0.46, CH₂Cl₂) ; IR (neat) : 3427, 2943, 1655, 1551, 1463, 1380, 1249, 1174, 1060, 998, 909, 882, 766, 731, 684 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 4.63 (1H, dd, *J* = 11.8, 6.0 Hz), 4.57 (1H, dd, *J* = 11.8, 9.9 Hz), 4.21 (2H, s), 3.29 (1H, m), 2.39 (1H, ddd, *J* = 15.8, 10.4, 2.3 Hz), 2.30 (1H, ddd, *J* = 15.8, 7.5, 3.0 Hz), 1.81-1.52 (6H, m), 1.48 (1H, br s), 1.20-1.06 (21H, m) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 154.7, 116.6, 77.0, 61.9, 38.3, 34.7, 28.6, 25.1, 18.0, 13.4 (one carbom missing) ; MS *m/z* : 357 (M⁺), 103 (100%) ; HRMS calcd. for C₁₈H₃₅NO₄Si (M⁺) : 357.2335, found : 357.2335.

[(7*R,Z*)-7-Aminomethyl-2-triisopropylsilyloxycyclohept-1-enyl]methan-1-ol (16**)**



A mixture of Fe (684 mg, 12.2 mmol, 100 mesh), NH₄Cl (218 mg, 4.08 mmol), and **15** (730 mg, 2.04 mmol) in EtOH-H₂O (14 mL, 3:1 v/v) was stirred under 80 °C for 2.5 h. After being cooled to rt, pyridine (0.33 mL, 4.1 mmol) was added and the mixture was stirred for 10 min. The mixture was filtered through a Celite pad eluting with CH₂Cl₂. The filtrate was concentrated under reduced pressure. The residue was immediately diluted with CH₂Cl₂ and dried over Na₂SO₄. The crude solution was concentrated under reduced pressure to about 2 mL solution (including pyridine) of crude amine **16**, which was used in the next step without further purification.

(4*S,E*)-Ethyl 4,5-Cyclohexylidendioxy-pent-2-enoate (S-14**)**⁵



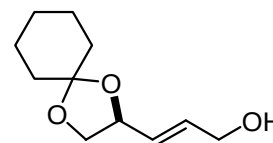
To a cooled (0 °C) suspension of 1,2,5,6-dicyclohexylidene mannitol⁶ (10.0 g, 29.2 mmol) in MeCN (27 mL) and H₂O (18 mL) was added NaIO₄ (12.5 g, 58.4 mmol) in small portions over 40 min with vigorous stirring. After being stirred for 1 h at that temperature, ethyl diethylphosphonoacetate (14.5 mL, 73.0 mmol) and 6 M K₂CO₃ (130 mL) were added. The mixture was allowed to warm up to rt and stirred for 2 h. Water

was added and the resultant solution was extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1 to 9:1) to give esters (*E*:*Z* = 95:4) [major isomer **S-14** (13.3 g, 95%), minor *Z*-isomer (500 mg, 4%)] as colorless oils.

S-14: [α]_D³⁰ +32.5° (c 0.7, CHCl₃) [lit.^{5a} [α]_D²² +31.2° (c 1.2, CHCl₃), ^{5b} [α]_D²² +37.6° (c 1.1, CHCl₃)] ; IR (neat) : 2937, 1722, 1661, 1448, 1366, 1265, 1163, 1098, 1039, 978, 928, 848 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 6.88 (1H, dd, *J* = 15.5, 5.7 Hz), 6.11 (1H, dd, *J* = 15.5, 1.4 Hz), 4.67 (1H, dddd, *J* = 7.0, 6.6, 5.7, 1.4 Hz), 4.21 (2H, q, *J* = 7.1 Hz), 4.18 (1H, dd, *J* = 8.2, 6.6 Hz), 3.67 (1H, dd, *J* = 8.2, 7.0 Hz), 1.69-1.53 (8H, br m), 1.47-1.34 (2H, br m), 1.29 (3H, t, *J* = 7.1 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 165.9, 144.9, 122.2, 110.7, 74.5, 68.4, 60.4, 36.0, 35.2, 25.0, 23.82, 23.76, 14.1 ; MS *m/z* : 240 (M⁺), 197 (100%) ; HRMS calcd. for C₁₃H₂₀O₄ (M⁺) : 240.1362, found : 240.1346.

The ¹H and ¹³C-NMR spectroscopic data of this compound were consistent with those reported (ref 2).

(4*S*,*E*)-4,5-Cyclohexylidendioxypent-2-en-1-ol (**17**)⁷

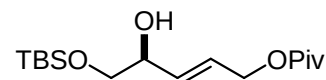


To a cooled (−78 °C) solution of ester **S-14** (11.8 g, 48.9 mmol) in CH₂Cl₂ (49 mL) was added DIBAL-H (138.0 mL, 136.9 mmol, 0.99 M toluene sol.) dropwise over 30 min. After being stirred for 15 min at that temperature, MeOH (140 mL) and sat. Rochelle salt (280 mL) were added. The mixture was allowed to warm up to rt and stirred for 4 h. Water was added and the resultant solution was extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, 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 alcohol **17** (8.30 g, 86%) as a colorless oil.

17: [α]_D²⁸ +14.5° (c 0.36, CHCl₃) ; IR (neat) : 3419, 2937, 1448, 1364, 1280, 848 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 5.93 (1H, dt, *J* = 15.5, 5.1 Hz), 5.70 (1H, ddt, *J* = 15.5, 7.5, 1.7 Hz), 4.53 (1H, dddd, *J* = 7.8, 7.5, 6.3, 1.7 Hz), 4.13 (2H, dd, *J* = 5.1, 1.3 Hz), 4.08 (1H, dd, *J* = 8.2, 6.3 Hz), 3.58 (1H, dd, *J* = 8.2, 7.8 Hz), 2.73 (1H, br s), 1.70-1.54 (8H, br m), 1.46-1.34 (2H, br m) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 133.3, 128.4, 109.8, 76.0, 68.8, 62.2, 36.1, 35.2, 24.9, 23.8, 23.7 ; MS *m/z* : 198 (M⁺), 155 (100%) ; HRMS calcd. for C₁₁H₁₈O₃ (M⁺) : 198.1256, found : 198.1252.

[(4*S,E*)-5-*tert*-Butyldimethylsilyloxy-4-hydroxypent-2-enyl]

2,2-Dimethylpropionate (18)



To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of alcohol **17** (2.25 g, 11.3 mmol) in CH_2Cl_2 (28 mL) were successively added Et_3N (3.20 mL, 22.7 mmol), PivCl (2.10 mL, 17.0 mmol), and DMAP (69 mg, 0.57 mmol). The mixture was allowed to warm up to rt and stirred for 1 h. Water was added and the resultant solution was extracted with Et_2O . The extracts were washed with water and brine, then dried over MgSO_4 , and concentrated under reduced pressure to give corresponding crude pivalate, which was used in the next step without further purification.

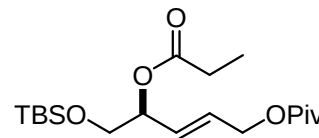
To a solution of the crude pivalate (3.40 g) in MeOH (113 mL) was added Dowex 50WX8 (16 g). After being stirred for 48 h at rt, the mixture was basicified with Et_3N (6 mL). The resultant mixture was filtered through a Celite pad eluting with MeOH and the filtrate was partitioned by hexane (3 times, to remove 1,1-dimethoxycyclohexane). The methanol layer was concentrated under reduced pressure to give a yellow oil. The oil was dissolved in dry toluene (5 mL) and the solvent was removed *in vacuo* (azeotropic MeOH removal). The resultant crude oil (diol) was used in the next step without further purification.

To a cooled ($0\text{ }^{\circ}\text{C}$) solution of the crude diol in DMF (23 mL) were successively added imidazole (1.48 g, 21.8 mmol) and TBSCl (2.15 g, 14.3 mmol). The mixture was allowed to warm up to rt and stirred for 2 h. Water was added and the resultant solution was extracted with Et_2O . The extracts were 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, 8:1 to 6:1) to give alcohol **18** [3.15 g, 88% (3 steps)] as a colorless oil.

18: $[\alpha]_{\text{D}}^{30} +3.5^{\circ}$ (c 0.44, CHCl_3) ; IR (neat) : 3483, 2957, 1731, 1463, 1363, 1283, 1255, 1154, 969, 838 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ : 5.85 (1H, dtd, J = 15.6, 5.6, 1.2 Hz), 5.70 (1H, ddt, J = 15.6, 5.8, 1.2 Hz), 4.53 (2H, dd, J = 5.6, 1.2 Hz), 4.17 (1H, br m), 3.63 (1H, dd, J = 10.0, 3.9 Hz), 3.43 (1H, dd, J = 10.0, 7.5 Hz), 2.63 (1H, s), 1.18 (9H, s), 0.88 (9H, s), 0.05 (6H, s) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 178.1, 131.9, 126.4, 71.9, 66.8, 64.0, 38.7, 27.1, 25.8, 18.2, -5.42 , -5.45 ; MS m/z : 317 ($[\text{M}+\text{H}]^+$), 299, 197, 73 (100%) ; HRMS calcd. for $\text{C}_{16}\text{H}_{33}\text{O}_4\text{Si}$ ($[\text{M}+\text{H}]^+$) : 317.2148, found : 317.2148.

[(4*S,E*)-5-*tert*-Butyldimethylsilyloxy-4-propionyloxypent-2-enyl]

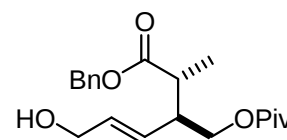
2,2-Dimethylpropionate (19)



To a cooled (0 °C) solution of alcohol **18** (3.15 g, 9.95 mmol) in CH₂Cl₂ (20 mL) were successively added propionic acid (0.960 mL, 12.9 mmol), EDCI (2.48 g, 12.9 mmol), and DMAP (1.58 g, 12.9 mmol). The mixture was allowed to warm up to rt and stirred for 2.5 h. Water was added and the resultant solution was extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 15:1 to 8:1) to give ester **19** (3.70 g, quant.) as a colorless oil.

19: [α]_D³⁰ +13.4° (c 0.44, CHCl₃) ; IR (neat) : 2957, 1737, 1463, 1363, 1281, 1256, 1151, 968, 839 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 5.85 (1H, dt J = 15.7, 5.2 Hz), 5.70 (1H, ddt, J = 15.7, 6.2, 1.2 Hz), 5.35 (1H, ddd, J = 6.2, 6.0, 4.8 Hz), 4.56 (2H, dd, J = 5.2, 1.2 Hz), 3.69 (1H, dd, J = 10.7, 6.0 Hz), 3.66 (1H, dd, J = 10.7, 4.8 Hz), 2.36 (2H, q, J = 7.5 Hz), 1.21 (9H, s), 1.15 (3H, t, J = 7.5 Hz), 0.88 (9H, s), 0.05 (6H, s) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 178.0, 173.4, 128.7, 127.8, 73.8, 64.5, 63.7, 38.7, 27.6, 27.1, 25.7, 18.1, 9.0, -5.5 ; MS (FAB) m/z : 373 ([M+H]⁺), 197, 73 (100%) ; HRMS (FAB) calcd. for C₁₉H₃₇O₅Si ([M+H]⁺) : 373.2410, found : 373.2391.

(2*R*,3*S*,*E*)-3-(2,2-Dimethylpropionyloxymethyl)-6-hydroxy-2-methylhex-4-enoic acid benzyl ester (21)



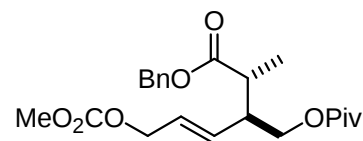
A three-necked flame-dried 1 L flask equipped with a magnetic stirrer bar was charged with TBSCl (7.60 g, 50.5 mmol), 2-Me-THF (90 mL), and THF (70 mL). The resultant solution was cooled to -78 °C. LHMDs [21.0 mL (1.6 M THF sol.) + 19.0 mL (1.0 M THF sol.), total= 52.6 mmol] and HMPA (50 mL) were added to the solution. After being stirred for 20 min, a solution of ester **19** (15.6 g, 42.1 mmol) in THF (40 mL) was added dropwise over 40 min *via* cannula. After being stirred for 4.5 h at that temperature, the mixture was allowed to warm up to rt and stirred for 10 h. AcOH (4 mL) and H₂O (50 mL) were added, then the mixture was stirred for 40 min and extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure to give yellow oil. The oil was dissolved in dry toluene (5 mL) and the solvent was removed *in vacuo* (azeotropic water and AcOH removal). The resultant crude carboxylic acid **20** was used in the next step without further purification.

To a cooled (0 °C) solution of crude carboxylic acid **20** in CH₂Cl₂ (150 mL) were successively added 1-methylimidazole (13.4 mL, 168 mmol) and TsCl (32.0 g, 168 mmol). The mixture was allowed to warm up to rt and stirred for 30 min. BnOH (13.1 mL, 126 mmol) was added to the mixture and stirred for 2 h. Water was added and the resultant solution was extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was roughly purified by flash silica gel column chromatography (hexane:AcOEt, 20:1 to 8:1) to give corresponding crude benzyl ester (15.5 g) including inseparable byproduct (benzyl acetate). The crude oil was used in the next step without further purification.

To a solution of the crude benzyl ester in MeOH (80 mL) was added PPTS (2.53 g, 10.1 mmol) and the mixture was heated at 50-55 °C. After being stirred for 40 min, pyridine (1.00 mL, 12.4 mmol) was added and the mixture was concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 8:1 to 4:1) to give alcohol **21** [10.3 g, 70% (3 steps)] as a colorless oil (diastereomeric mixture).

21 (major): IR (neat) : 3497, 2974, 1731, 1480, 1457, 1397, 1283, 1154, 974 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 7.38-7.32 (5H, m), 5.67 (1H, dt *J* = 15.5, 5.6 Hz), 5.55 (1H, ddt, *J* = 15.5, 8.3, 1.2 Hz), 5.13 (1H, d, *J* = 12.1 Hz), 5.09 (1H, d, *J* = 12.1 Hz), 4.10 (2H, dd, *J* = 5.6 Hz), 4.00 (2H, br m), 2.68 (1H, sext, *J* = 6.8 Hz), 2.64 (1H, m), 1.20 (3H, d, *J* = 6.8 Hz), 1.17 (9H, s) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 178.1, 174.5, 135.8, 132.9, 128.6, 128.4, 128.25, 128.16, 66.2, 64.5, 62.8, 44.6, 40.7, 38.7, 27.0, 14.7 ; MS (FAB) *m/z* : 349 ([M+H]⁺), 91 (100%) ; HRMS (FAB) calcd. for C₂₀H₂₉O₅ ([M+H]⁺) : 349.2015, found : 349.2016.

(2R,3S,E)-3-(2,2-Dimethylpropionyloxymethyl)-6-methoxycarbonyloxy-2-methylhex-4-enoic acid benzyl ester (22)



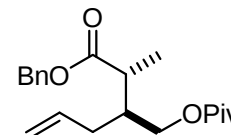
To a cooled (0 °C) solution of alcohol **21** (10.2 g, 29.3 mmol) in CH₂Cl₂ (30 mL) were successively added pyridine (15 mL) and methyl chloroformate (3.40 mL, 43.9 mmol). The mixture was allowed to warm up to rt and stirred for 1 h. Water was added and the resultant solution was extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 9:1 to 7:1) to give carbonate **22** (11.1 g, 93%) as a colorless oil (diastereo mixture, dr = 9:1 determined by ¹H-NMR).

22: IR (neat) : 2973, 1731, 1480, 1455, 1383, 1269, 1151, 1036, 949 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ :

7.39-7.31 (5H, m), 5.74-5.59 (2H, m), 5.10 (2H, s), 4.54 (0.2H, d, $J = 5.3$ Hz), 4.50 (1.8H, d, $J = 5.1$ Hz), 4.10 (2H, d, $J = 5.6$ Hz), 3.76 (3H, s), 2.72-2.62 (2H, m), 1.19 (3H, d, $J = 6.5$ Hz), 1.16 (9H, s) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 178.1, 174.2, 155.4, 135.8, 133.2, 128.5, 128.3, 128.2, 127.0, 67.7, 66.3, 64.2, 54.6, 44.6, 40.7, 38.7, 27.0, 14.7 ; MS (FAB) m/z : 407 ($[\text{M}+\text{H}]^+$), 91 (100%) ; HRMS (FAB) calcd. for $\text{C}_{22}\text{H}_{31}\text{O}_7$ ($[\text{M}+\text{H}]^+$) : 407.2070, found : 407.2093.

(2R,3S)-3-(2,2-Dimethylpropionyloxymethyl)-2-methylhex-

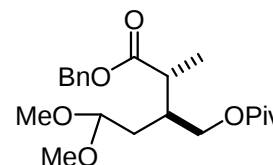
5-enoic acid benzyl ester (23)



A two-necked flame-dried 300 mL flask equipped with a magnetic stirrer bar was charged with HCO_2NH_4 (3.41 g, 54.1 mmol) and degassed DMF (60 mL). $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (840 mg, 0.810 mmol) and $n\text{-Bu}_3\text{P}$ (1.62 mL, 6.49 mmol) were added and the mixture was stirred for 15 min at rt. A solution of carbonate **22** (11.0 g, 27.1 mmol) in degassed DMF (45 mL) was added dropwise *via* cannula. After being stirred for 3 h at rt, the mixture was cooled to 0 °C, diluted with Et_2O , and then sat. NaHCO_3 was added. The resultant solution was extracted with Et_2O and the extracts were 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, 15:1 to 10:1) to give alkene **23** (7.39 g, 82%) as a pale yellow oil (diastereomeric mixture).

23 (major): IR (neat) : 2975, 1731, 1480, 1457, 1283, 1156, 1033, 917 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ : 7.41-7.29 (5H, m), 5.72 (1H, ddt, $J = 17.1, 10.1, 6.9$ Hz), 5.15 (1H, d, $J = 12.4$ Hz), 5.11 (1H, d, $J = 12.4$ Hz), 5.03 (1H, dm, $J = 10.1$ Hz), 5.01 (1H, dm, $J = 17.1$ Hz), 4.05 (2H, d, $J = 4.8$ Hz), 2.63 (1H, quin, $J = 7.0$ Hz), 2.22-2.06 (3H, m), 1.19 (9H, s), 1.18 (3H, d, $J = 7.0$ Hz) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 178.2, 175.3, 135.9, 135.5, 128.5, 128.17, 128.15, 117.2, 66.2, 63.6, 40.5, 39.8, 38.8, 34.1, 27.1, 13.7 ; MS m/z : 332 (M^+), 91 (100%) ; HRMS calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_4$ (M^+) : 332.1988, found : 332.1995.

(2R,3S)-3-(2,2-Dimethylpropionyloxymethyl)-5,5-dimethoxy-2-methylpentanoic acid benzyl ester (24)

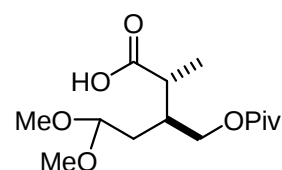


To a cooled (-78 °C) solution of alkene **23** (119 mg, 0.358 mmol, diastereomeric mixture) in MeOH (3 mL) was bubbled O_3 gas for 8 min. After O_2 gas was bubbled for 10 min at that temperature, Me_2S (53.0 μL ,

0.716 mmol) was added and the mixture was allowed to warm up to rt. After being stirred for 30 min, *p*-TsOH·H₂O (3.0 mg, 0.018 mmol) was added and the mixture was stirred for further 2.5 h. Pyridine (100 μL) was added and the solvent was concentrated under reduced pressure. The residual oil was purified by flash silica gel column chromatography (hexane:AcOEt, 10:1 to 8:1) to give acetal **24** (119 mg, 87%) as a colorless oil (diastereomeric mixture).

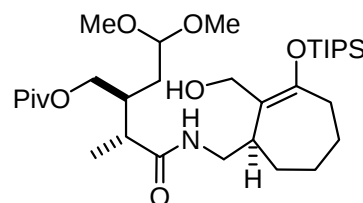
24 (major): $[\alpha]_D^{25} -19.6^\circ$ (c 0.40, CHCl₃) ; IR (neat) : 2973, 1731, 1456, 1366, 1283, 1158, 1058, 973 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 7.38-7.30 (5H, m), 5.15 (1H, d, *J* = 12.4 Hz), 5.11 (1H, d, *J* = 12.4 Hz), 4.43 (1H, t, *J* = 5.7 Hz), 4.09 (2H, d, *J* = 4.8 Hz), 3.29 (3H, s), 3.27 (3H, s), 2.67 (1H, quin, *J* = 7.0 Hz), 2.21 (1H, m), 1.64 (2H, m), 1.18 (9H, s), 1.18 (3H, d, *J* = 7.0 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 178.3, 175.1, 135.9, 128.5, 128.2, 102.9, 66.3, 64.0, 53.1, 52.4, 40.9, 38.8, 36.5, 32.1, 27.1, 14.0 ; MS (FAB) *m/z* : 379 ([M-H]⁺), 91 (100%) ; HRMS (FAB) calcd. for C₂₁H₃₁O₆ ([M-H]⁺) : 379.2121, found : 379.2134 ; *Anal.* calcd. for C₂₁H₃₂O₆ : C, 66.29 ; H, 8.48, found : C, 66.24 ; H, 8.40.

(2*R*,3*S*)-3-(2,2-Dimethylpropionyloxymethyl)-5,5-dimethoxy-2-methylpentanoic acid (25)



A solution of ester **24** (700 mg, 1.84 mmol) in AcOEt (6 mL) was hydrogenated in the presence of 10% Pd-C (70 mg) and NaHCO₃ (15 mg) under atmospheric pressure of H₂. After being stirred for 1.5 h, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated under reduced pressure. The crude carboxylic acid **25** (534 mg) was used in the next step without further purification.

(2*S*,3*R*)-2-(2,2-Dimethoxyethyl)-4-[(1*R*,*Z*)-2-hydroxymethyl-3-triisopropylsilyloxycyclohept-2-enyl]methylamino-3-Methyl-4-oxobutyl pivalate (26)

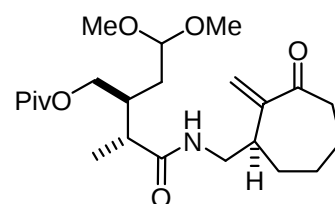


To a mixture of carboxylic acid **25** (534 mg, 1.84 mmol), EDCI (430 mg, 2.24 mmol), and DMAP (274 mg, 2.24 mmol) was added the crude solution of amine **16** in CH₂Cl₂ (2 + 5 mL). After being stirred for 1 h at rt, the reaction mixture was quenched with sat. NaHCO₃ and extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude

mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 2:1 to 1:1) to give amide alcohol **26** [873 mg, 80% (2 steps from **24**)] as a colorless oil including a small amount of diastereomer.

26 (major): $[\alpha]_D^{27} +2.5^\circ$ (*c* 2.60, CHCl₃) ; IR (neat) : 3292, 2932, 1731, 1651, 1550, 1463, 1367, 1168, 1058, 883 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 7.01 (1H, br s), 4.54 (1H, d, *J* = 10.9 Hz), 4.46 (1H, t, *J* = 5.8 Hz), 4.16 (1H, dd, *J* = 11.6, 4.6 Hz), 4.10 (1H, dd, *J* = 11.6, 4.6 Hz), 3.92 (1H, d, *J* = 10.9 Hz), 3.44 (1H, ddd, *J* = 6.0, 13.3, 6.0 Hz), 3.37 (1H, ddd, *J* = 13.3, 9.9, 3.4 Hz), 3.30 (3H, s), 3.29 (3H, s), 2.56-2.42 (2H, m, including broad peak), 2.32-2.15 (3H, m), 2.08 (1H, m), 1.81-1.42 (8H, m), 1.19 (9H, s), 1.13 (3H, d, *J* = 7.0 Hz), 1.20-1.05 (21H, m) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 178.3, 174.8, 153.9, 118.3, 102.8, 64.0, 61.7, 52.9, 52.0, 42.5, 41.2, 39.1, 38.7, 36.7, 34.7, 31.9, 30.0, 27.0, 25.9, 25.3, 17.9, 14.9, 13.2 ; MS *m/z* : 567 ([M–MeOH]⁺), 292 (100%) ; HRMS calcd. for C₃₁H₅₇NO₆Si ([M–MeOH]⁺) : 567.3955, found : 567.3958.

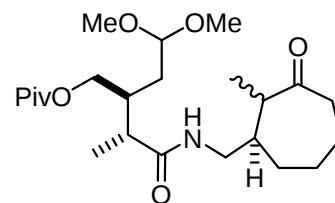
{(2*R*,3*S*)-2-(2,2-Dimethoxyethyl)-3-[(2-methylene-3-oxocycloheptylmethyl) carbamoyl]butyl 2,2-Dimethylpropionate (27)}



To a solution of **26** (640 mg, 1.07 mmol) in CH₂Cl₂ (3 mL) were successively added Et₃N (300 μ L, 2.14 mmol), TsCl (306 mg, 1.61 mmol), and Me₃N·HCl (10 mg, 0.11 mmol). After being stirred for 2 h at rt, TBAF (3.20 mL, 3.20 mmol, 1.0 M THF) was added and the mixture was stirred for 2 h at rt. The reaction mixture was quenched with sat. NH₄Cl and extracted with Et₂O. The extracts were washed with water and brine, then dried over MgSO₄, and concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (hexane:AcOEt, 2:1 to 1:1) to give enone **27** (433 mg, 95%) as a colorless oil including a small amount of diastereomer.

27: $[\alpha]_D^{30} +2.2^\circ$ (*c* 0.22, CH₂Cl₂) ; IR (neat) : 3323, 2932, 1729, 1649, 1541, 1458, 1284, 1160, 1123, 1057, 974 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 6.01 (1H, s), 5.88 (1H, br s), 5.26 (1H, s), 4.44 (1H, t, *J* = 5.8 Hz), 4.19 (1H, dd, *J* = 11.6, 5.1 Hz), 4.06 (1H, dd, *J* = 11.6, 4.6 Hz), 3.53 (1H, ddd, *J* = 6.3, 13.5, 6.3 Hz), 3.40 (1H, ddd, *J* = 13.5, 8.5, 5.1 Hz), 3.31 (3H, s), 3.29 (3H, s), 2.74-2.53 (3H, m), 2.27 (1H, quin, *J* = 7.0 Hz), 2.07 (1H, m), 1.99-1.78 (3H, m), 1.74-1.40 (5H, m), 1.19 (9H, s) 1.12 (3H, d, *J* = 7.0 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 203.9, 178.3, 174.8, 150.1, 120.3, 102.9, 63.8, 53.2, 52.1, 42.3, 41.99, 41.89, 41.4, 38.6, 36.7, 34.6, 31.8, 28.5, 26.9, 24.5, 15.0 ; MS (FAB) *m/z* : 394 (M⁺–OMe), 57 (100%) ; HRMS (FAB) calcd. for C₂₂H₃₆NO₅ (M⁺–OMe) : 394.2593, found : 394.2608.

{(2*R*,3*S*)-2-(2,2-Dimethoxyethyl)-3-[(2-methyl-3-oxocycloheptylmethyl) carbamoyl]butyl 2,2-Dimethylpropionate (28)}

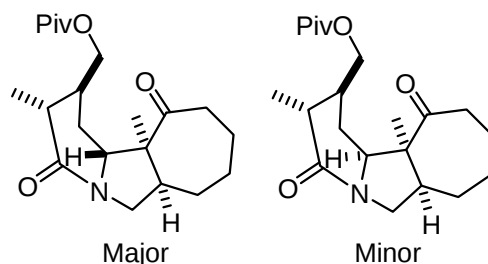


A solution of enone **27** (709 mg, 1.67 mmol) in MeOH (5 mL) was hydrogenated in the presence of 10% Pd-C (71 mg) and NaHCO₃ (35 mg) under atmospheric pressure of H₂. After being stirred for 2 h, the reaction mixture was filtered through a Celite pad eluting with AcOEt and the filtrate was concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 1:1 to 0:100) to give ketone **28** (691 mg, 97%) as a colorless oil (diastereomeric mixture).

28 (major): IR (neat) : 3315, 2934, 1729, 1698, 1651, 1540, 1460, 1369, 1284, 1162, 1056 cm⁻¹ ; ¹H-NMR (400 MHz, CDCl₃) δ : 5.89 (1H, br s), 4.46 (1H, t, *J* = 5.6 Hz), 4.19 (1H, dd, *J* = 11.6, 5.1 Hz), 4.08 (1H, dd, *J* = 11.6, 4.6 Hz), 3.31 (3H, s), 3.29 (3H, s), 3.16 (2H, m), 2.83 (1H, ddd, *J* = 14.5, 7.5, 3.1 Hz), 2.61 (1H, m), 2.41 (1H, m), 2.28 (1H, quin, *J* = 7.2 Hz), 2.07 (2H, m), 1.88-1.54 (8H, m), 1.21 (9H, s) 1.14 (3H, d, *J* = 8.0 Hz), 1.12 (3H, d, *J* = 7.2 Hz) ; ¹³C-NMR (100 MHz, CDCl₃) δ : 215.1, 178.5, 174.7, 103.0, 64.0, 53.3, 52.3, 47.7, 42.9, 42.2, 40.3, 39.9, 38.8, 36.9, 31.9, 30.0, 27.1, 26.4, 24.1, 15.2, 12.3 ; MS *m/z* : 412 (M⁺–Me), 278 (100%) ; HRMS calcd. for C₂₂H₃₈NO₆ (M⁺–Me) : 412.2699, found : 412.2695.

[(2*S*,3*R*,6*aR*,11*aS*,11*bR*)- and

(2*S*,3*R*,6*aR*,11*aS*,11*bS*)-3,11a-Dimethyl-4,11-dioxododecahydro-1*H*-cyclohepta[*a*]indolizin-2-yl)methyl] 2,2-Dimethylpropionate (30) and (31)



From pivalate 28: To a solution of ketone **28** (250 mg, 0.835 mmol) in *i*-PrOH (4 mL) was slowly added AcCl (0.590 mL, 8.35 mmol) and the mixture was heated to reflux. After being stirred for 1 h, the mixture was cooled to rt and the solvent was removed under reduced pressure. sat. NaHCO₃ was added and the mixture was extracted with AcOEt. The extracts were washed with brine, then dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (AcOEt:MeOH, 100:0 to 100:5) to give lactams major: **30** [117 mg, 63% (including inseparable 9%

diastereomer: an analytical pure sample of **30** was obtained by recrystallization from Et₂O-hexane as colorless platelets)] and minor: **31** (58 mg, 31%) as a colorless oil.

Via 29: A solution of ketone **28** (16.0 mg, 0.0379 mmol) and NaOMe (600 µg, 0.114 mmol) in MeOH (1.5 mL) was heated to reflux. After being stirred for 6 h, the solvent was evaporated and sat. NH₄Cl was added. The mixture was extracted with AcOEt. The extracts were washed with brine, then dried over Na₂SO₄, and concentrated under reduced pressure to give crude alcohol **29**, which was used in the next step without further purification.

To a solution of the crude alcohol **29** in MeOH (1 mL) was added AcCl (39.0 µL, 0.569 mmol) slowly and the mixture was heated to reflux. After being stirred for 9 h, the mixture was cooled to rt and the solvent was removed under reduced pressure. sat. NaHCO₃ was added and the mixture was extracted with AcOEt. The extracts were washed with brine, then dried over Na₂SO₄, and concentrated under reduced pressure to give crude tricyclic alcohol, which was used in the next step without further purification.

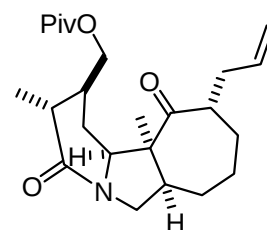
To a solution of crude tricyclic alcohol in CH₂Cl₂ (1 mL) were successively added Et₃N (11 µL, 76 µmol), PivCl (7.0 µL, 57 µmol), and DMAP (1.0 mg, 8.2 µmol). After being stirred for 1 h, water was added and the resultant solution was extracted with AcOEt. The extracts were washed with water and brine, then dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (AcOEt:MeOH, 100:0 to 100:5) to give lactams major: **30** [5 mg, 36% (including inseparable 4% diastereomer)] and minor: **31** (5 mg, 36%).

30 (major): M.p. = 132-134 °C ; [α]_D³⁰ +74.4° (c 0.21, CHCl₃) ; IR (neat) : 2938, 1723, 1632, 1442, 1323, 1283, 1159, 1047, 984, 943 cm⁻¹ ; ¹H-NMR (600 MHz, CDCl₃) δ : 4.07 (1H, dd, *J* = 11.4, 7.8 Hz), 3.98 (1H, dd, *J* = 11.4, 6.6 Hz), 3.92 (1H, dd, *J* = 13.2, 9.0 Hz), 3.72 (1H, dd, *J* = 10.8, 3.6 Hz), 3.03 (1H, d, *J* = 13.2 Hz), 2.64 (1H, ddd, *J* = <13.2, 13.2, 2.4 Hz), 2.29-2.21 (2H, m), 2.11 (1H, dt, *J* = 13.8, 3.6 Hz), 2.05 (1H, m), 2.00 (1H, m), 1.92-1.80 (2H, m), 1.63-1.55 (2H, m), 1.44-1.23 (3H, m), 1.21 (3H, d, *J* = 7.8 Hz), 1.14 (9H, s), 1.06 (3H, s) ; ¹³C-NMR (150 MHz, CDCl₃) δ : 212.9, 178.2, 171.0, 66.6, 65.7, 60.6, 46.2, 43.3, 42.3, 40.4, 38.9, 38.4, 28.0, 27.1, 25.8, 25.6, 22.7, 21.5, 15.7 ; MS *m/z* : 363 (M⁺), 335 (100%) ; HRMS calcd. for C₂₁H₃₃NO₄ (M⁺) : 363.2410, found : 363.2398 ; *Anal.* calcd. for C₂₁H₃₃NO₄ : C, 69.39 ; H, 9.15 ; N, 3.85, found : C, 69.09 ; H, 8.96 ; N, 3.93.

31 (minor): [α]_D²⁹ -81.1° (c 0.5, CHCl₃) ; IR (neat) : 2932, 1730, 1696, 1644, 1447, 1339, 1283, 1160, 1059 cm⁻¹ ; ¹H-NMR (600 MHz, CDCl₃) δ : 4.12 (1H, dd, *J* = 11.4, 3.6 Hz), 4.01 (1H, dd, *J* = 13.2, 9.0 Hz), 3.94 (1H, dd, *J* = 11.4, 6.0 Hz), 3.47 (1H, dd, *J* = 13.2, 10.8 Hz), 3.41 (1H, dd, *J* = 12.0, 3.6 Hz), 2.38 (1H,

m), 2.32 (1H, ddd, $J = 13.2, 7.2, 1.2$ Hz), 2.12 (1H, dq, $J = 10.8, 7.2$ Hz), 2.08 (1H, ddd, $J = 13.2, 10.8, 3.0$ Hz), 1.96 (1H, m), 1.87 (1H, dt, $J = 13.2, 3.6$ Hz), 1.83 (1H, m), 1.80-1.71 (2H, m), 1.66 (1H, m), 1.50 (1H, m), 1.28 (3H, d, $J = 7.2$ Hz), 1.23 (1H, m), 1.14 (3H, s), 1.12 (9H, s), 1.00 (1H, dt, $J = 13.2, 12.0$ Hz) ; ^{13}C -NMR (150 MHz, CDCl_3) δ : 212.9, 178.2, 171.0, 66.6, 65.7, 60.6, 46.2, 43.3, 42.3, 40.4, 38.9, 38.4, 28.0, 27.1, 25.8, 25.6, 22.7, 21.5, 15.7 ; MS m/z : 363 (M^+), 335 (100%) ; HRMS calcd. for $\text{C}_{21}\text{H}_{33}\text{NO}_4$ (M^+) : 363.2410, found : 363.2393.

[(2*S*,3*R*,6*aR*,10*S*,11*aS*,11*bS*)-10-Allyl-3,11*a*-dimethyl-4,11-dioxododecahydro-1*H*-cyclohepta[*a*]indolizin-2-yl)methyl Pivalate (32**)**



To a cooled ($-50\text{ }^{\circ}\text{C}$) solution of ketone **31** (18.0 mg, 0.0495 mmol) and HMPA (43.0 μL , 0.248 mmol) in THF (1 mL) was added KHMDS (0.20 mL, 0.099 mmol, 0.5 M toluene sol.) slowly. After being stirred for 2 h at $-40\text{ }^{\circ}\text{C}$, allyl iodide (7.0 μL , 0.074 mmol) was added. The mixture was stirred for an additional 3 h, and then sat. NH_4Cl was added. The resultant mixture was extracted with AcOEt. The extracts were washed with brine, then dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane:AcOEt, 2:1 to 1:2) to give **32** (12.0 mg, 60%) as a colorless oil.

32: $[\alpha]_{\text{D}}^{22} -68.3^{\circ}$ (c 0.10, CHCl_3) ; IR (neat) : 2931, 1730, 1696, 1644, 1441, 1339, 1283, 1158, 999, 916 cm^{-1} ; ^1H -NMR (600 MHz, CDCl_3) δ : 5.62 (1H, dddd, $J = 18.6, 10.8, 8.4, 6.6$ Hz), 4.99 (1H, dm, $J = 18.6$ Hz), 4.98 (1H dm, $J = 10.8$ Hz), 4.09 (1H, dd, $J = 11.4, 3.6$ Hz), 4.05 (1H, dd, $J = 13.2, 9.6$ Hz), 3.95 (1H, dd, $J = 11.4, 6.6$ Hz), 3.49 (1H, dd, $J = 13.2, 11.4$ Hz), 3.42 (1H, dd, $J = 12.6, 3.6$ Hz), 2.42 (1H, m), 2.30 (1H, m), 2.14 (1H, m), 2.08 (1H, dq, $J = 11.4, 7.2$ Hz), 2.04 (1H, m), 1.98 (1H, m), 1.87 (1H, m), 1.83-1.74 (3H, m), 1.66 (1H, m), 1.53 (1H, m), 1.29 (3H, d, $J = 7.2$ Hz), 1.18 (3H, s), 1.16 (9H, s), 1.04 (1H, dt = 13.2, 12.6 Hz), 0.97 (1H, m) ; ^{13}C -NMR (100 MHz, CDCl_3) δ : 214.5, 178.3, 170.8, 136.2, 117.4, 67.4, 66.1, 60.7, 51.6, 46.2, 42.5, 40.4, 38.9, 38.5, 36.0, 32.3, 28.5, 27.2, 25.0, 22.3, 21.8, 15.6 ; MS m/z : 403 (M^+), 375 (100%) ; HRMS calcd. for $\text{C}_{24}\text{H}_{37}\text{NO}_4$ (M^+) : 403.2723, found : 403.2713.

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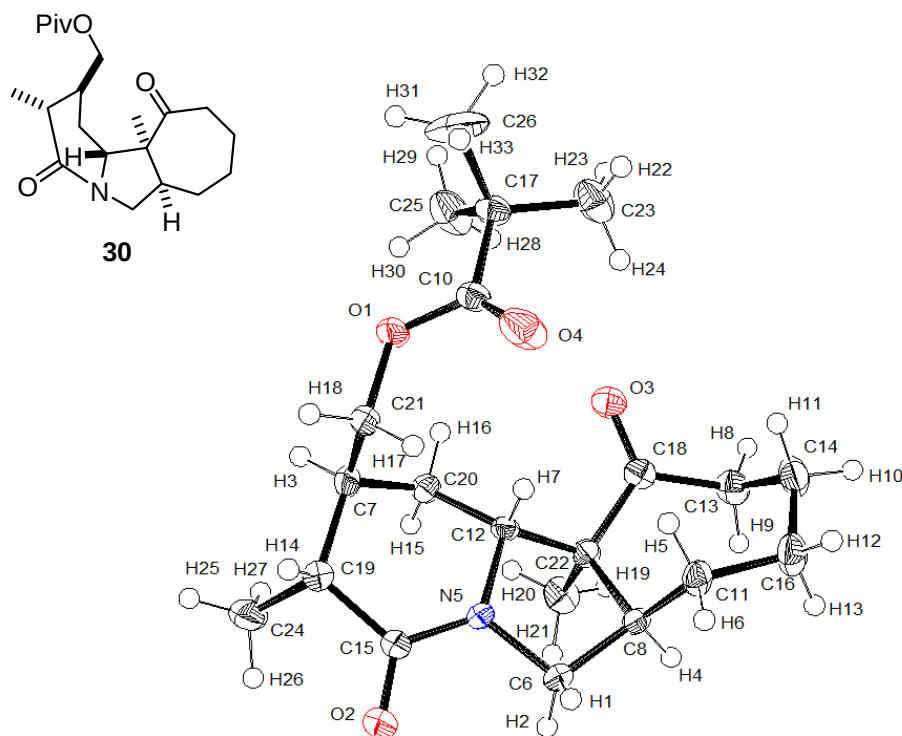


Figure S-2. Displacement ellipsoids are scaled to the 50 % probability level.

Data Collection

A colorless platelet crystal of $C_{21}H_{33}NO_4$ having approximate dimensions of $0.50 \times 0.40 \times 0.20$ mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation.

Indexing was performed from 0 oscillations that were exposed for 0 seconds. The crystal-to-detector distance was 0.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions: $a = 7.152(6)$ Å, $b = 12.354(10)$ Å, $c = 105.52(4)^\circ$, $V = 11.559(13)$ Å³. For $Z = 2$ and F.W. = 363.50, the calculated density is 1.227 g/cm³. Based on the systematic absences of: $0k0: k \pm 2n$ packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $P2_1$ (#4).

The data were collected at a temperature of -100 ± 1 °C to a maximum 2θ value of 54.9° . A total of 0 oscillation images were collected. The crystal-to-detector distance was 0.00 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 0 reflections that were collected, 0 were unique ($R_{int} = 0.050$); equivalent reflections were merged.

The linear absorption coefficient, μ , for Mo-K α radiation is 0.836 cm^{-1} . was applied which resulted in transmission factors ranging from 0.000 to 0.000. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods¹ and expanded using Fourier techniques². The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement³ on F was based on 2350 observed reflections ($I > 2.00\sigma(I)$) and 268 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0755$$

$$R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.1781$$

The standard deviation of an observation of unit weight⁴ was 1.00. Unit weights were used. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.41 and 0.00 $\text{e}^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber⁵. Anomalous dispersion effects were included in F_{calc} ⁶; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley⁷. The values for the mass attenuation coefficients are those of Creagh and Hubbell⁸. All calculations were performed using the CrystalStructure^{9,10} crystallographic software package.

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(3) Least Squares function minimized:

$$\sum w(|F_o| - |F_c|)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(4) Standard deviation of an observation of unit weight:

$$[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

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A. Crystal Data

Empirical Formula	C ₂₁ H ₃₃ NO ₄
Formula Weight	363.50
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.50 × 0.40 × 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
Detector Position	0.00 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 7.152(6) Å b = 12.354(10) Å c = 11.559(13) Å β = 105.52(4)° V = 984.1(16) Å ³
Space Group	P2 ₁ (#4)
Z value	2
D _{calc}	1.227 g/cm ³
F ₀₀₀	396.00
μ(MoKα)	0.836 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Detector Aperture	0 mm × 0 mm
Data Images	0 exposures
Detector Position	0.00 mm
Pixel Size	0.100 mm
2θ _{max}	54.9°
No. of Reflections Measured	Total: 0 Unique: 0 (R _{int} = 0.050)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.000 - 0.000)

C. Structure Solution and Refinement

Structure Solution Direct Methods (SIR92)

Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (F_o - F_c)^2$
Least Squares Weights	1
$2\theta_{\max}$ cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	2350
No. Variables	268
Reflection/Parameter Ratio	8.77
Residuals: R ($I > 2.00\sigma(I)$)	0.0755
Residuals: Rw ($I > 2.00\sigma(I)$)	0.1781
Goodness of Fit Indicator	1.000
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.41 e ⁻ /Å ³
Minimum peak in Final Diff. Map	0.00 e ⁻ /Å ³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
O(1)	0.7952(3)	0.1684(2)	0.0349(2)	2.20(4)
O(2)	0.3068(3)	0.0772(2)	0.3437(2)	2.44(5)
O(3)	0.9478(3)	0.4135(2)	0.2733(2)	2.51(5)
O(4)	0.6259(3)	0.3213(2)	-0.0239(3)	3.62(6)
N(5)	0.5009(3)	0.2136(2)	0.3205(2)	1.60(5)
C(6)	0.4066(4)	0.2933(2)	0.3807(3)	1.71(5)
C(7)	0.7158(4)	0.0816(2)	0.2013(3)	2.06(6)
C(8)	0.5241(4)	0.3980(2)	0.3840(3)	1.58(5)
C(9)	0.7281(4)	0.3532(2)	0.3830(2)	1.56(5)
C(10)	0.7718(4)	0.2702(2)	-0.0084(3)	1.82(6)
C(11)	0.4349(4)	0.4755(2)	0.2804(3)	1.93(6)
C(12)	0.6727(4)	0.2598(2)	0.2906(3)	1.43(5)
C(13)	0.8587(5)	0.5507(3)	0.3918(3)	2.24(6)
C(14)	0.7054(5)	0.6194(2)	0.3044(4)	2.70(7)
C(15)	0.4421(4)	0.1093(2)	0.3074(3)	1.88(6)
C(16)	0.4965(5)	0.5940(3)	0.3049(4)	2.61(6)
C(17)	0.9565(4)	0.3105(3)	-0.0366(3)	1.99(6)
C(18)	0.8547(4)	0.4369(2)	0.3430(3)	1.78(5)
C(19)	0.5500(5)	0.0308(2)	0.2450(3)	2.15(6)
C(20)	0.8173(4)	0.1709(2)	0.2880(3)	1.86(6)
C(21)	0.6374(4)	0.1204(2)	0.0740(3)	2.03(6)
C(22)	0.8392(4)	0.3146(3)	0.5084(3)	2.42(6)
C(23)	0.9706(5)	0.4325(3)	-0.0181(4)	3.11(7)
C(24)	0.6192(7)	-0.0664(3)	0.3260(4)	3.97(9)
C(25)	1.1396(5)	0.2587(3)	0.0434(4)	3.36(7)
C(26)	0.9361(6)	0.2850(5)	-0.1692(4)	4.47(10)

$$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(\text{aa}^*)^2 + U_{22}(\text{bb}^*)^2 + U_{33}(\text{cc}^*)^2 + 2U_{12}(\text{aa}^*\text{bb}^*)\cos \gamma + 2U_{13}(\text{aa}^*\text{cc}^*)\cos \beta + 2U_{23}(\text{bb}^*\text{cc}^*)\cos \alpha)$$

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq}

atom	x	y	z	B _{eq}
H(1)	0.2752	0.3035	0.3366	2.13
H(2)	0.4114	0.2696	0.4597	2.13
H(3)	0.8101	0.0273	0.2019	2.61
H(4)	0.5351	0.4339	0.4582	1.97
H(5)	0.4730	0.4517	0.2119	2.29
H(6)	0.2977	0.4721	0.2642	2.29
H(7)	0.6321	0.2903	0.2124	1.74
H(8)	0.9837	0.5813	0.4016	2.68
H(9)	0.8297	0.5483	0.4673	2.61
H(10)	0.7307	0.6935	0.3247	3.24
H(11)	0.7175	0.6070	0.2256	3.24
H(12)	0.4123	0.6371	0.2450	3.08
H(13)	0.4821	0.6133	0.3816	3.08
H(14)	0.4584	0.0036	0.1758	2.76
H(15)	0.8651	0.1419	0.3665	2.29
H(16)	0.9223	0.1992	0.2615	2.29
H(17)	0.5377	0.1724	0.0695	2.61
H(18)	0.5863	0.0603	0.0243	2.61
H(19)	0.9136	0.3726	0.5514	2.84
H(20)	0.9231	0.2567	0.5017	2.84
H(21)	0.7490	0.2904	0.5500	2.84
H(22)	0.9063	0.4682	-0.0906	3.71
H(23)	1.1027	0.4542	0.0058	3.71
H(24)	0.9099	0.4510	0.0430	3.71
H(25)	0.6102	-0.1308	0.2800	5.37
H(26)	0.5417	-0.0734	0.3808	5.37
H(27)	0.7505	-0.0545	0.3693	5.45
H(28)	1.1847	0.3024	0.1128	4.03
H(29)	1.2374	0.2538	0.0019	4.03
H(30)	1.1102	0.1883	0.0665	4.03
H(31)	0.9895	0.2154	-0.1750	5.68
H(32)	1.0048	0.3377	-0.2015	5.68
H(33)	0.8032	0.2857	-0.2130	5.68

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb*)\cos \gamma + 2U_{13}(aa*cc*)\cos \beta + 2U_{23}(bb*cc*)\cos \alpha)$$

Table 3. Anisotropic displacement parameters

atom	U ₁₁ U ₂₃	U ₂₂	U ₃₃	U ₁₂	U ₁₃
O(1)	0.0259(11) 0.0038(11)	0.0230(11)	0.0414(14)	0.0008(10)	0.0207(10)
O(2)	0.0326(12) 0.0012(11)	0.0251(12)	0.0410(15)	-0.0033(10)	0.0205(10)
O(3)	0.0280(11) 0.0005(11)	0.0301(13)	0.0418(15)	-0.0038(11)	0.0172(10)
O(4)	0.0296(13) 0.0245(16)	0.0453(18)	0.068(2)	0.0084(13)	0.0222(12)
N(5)	0.0207(12) 0.0008(10)	0.0185(12)	0.0251(14)	0.0032(11)	0.0125(10)
C(6)	0.0222(13) -0.0019(12)	0.0211(14)	0.0250(16)	0.0008(13)	0.0121(12)
C(7)	0.0274(15) -0.0009(14)	0.0164(14)	0.0389(19)	0.0022(13)	0.0167(14)
C(8)	0.0196(13) -0.0034(12)	0.0207(15)	0.0220(16)	0.0000(12)	0.0096(11)
C(9)	0.0161(12) 0.0017(12)	0.0198(14)	0.0235(15)	0.0019(12)	0.0054(11)
C(10)	0.0219(14) 0.0003(13)	0.0256(16)	0.0226(16)	-0.0051(13)	0.0076(11)
C(11)	0.0187(14) 0.0009(13)	0.0209(16)	0.0325(19)	0.0039(12)	0.0050(12)
C(12)	0.0165(12) 0.0040(12)	0.0186(14)	0.0212(15)	0.0018(11)	0.0087(11)
C(13)	0.0267(15) -0.0044(14)	0.0277(17)	0.0295(18)	-0.0076(14)	0.0053(13)
C(14)	0.0393(19) 0.0028(15)	0.0196(15)	0.044(2)	-0.0012(15)	0.0118(16)
C(15)	0.0271(15) 0.0016(13)	0.0199(14)	0.0278(17)	-0.0007(13)	0.0135(13)

C(16)	0.0281(17) 0.0015(15)	0.0219(16)	0.047(2)	0.0059(14)	0.0066(15)
C(17)	0.0213(14) 0.0007(14)	0.0287(18)	0.0266(17)	-0.0056(14)	0.0083(12)
C(18)	0.0168(12) 0.0021(13)	0.0258(15)	0.0236(16)	0.0002(13)	0.0031(11)
C(19)	0.0317(16) -0.0018(14)	0.0228(16)	0.0319(18)	-0.0017(14)	0.0166(14)
C(20)	0.0227(14) 0.0027(14)	0.0215(15)	0.0291(17)	0.0037(13)	0.0114(12)
C(21)	0.0273(16) -0.0041(13)	0.0202(15)	0.0351(19)	-0.0053(13)	0.0176(14)
C(22)	0.0266(15) 0.0050(15)	0.0324(18)	0.0295(18)	0.0010(15)	0.0014(13)
C(23)	0.0318(18) 0.0066(18)	0.033(2)	0.052(2)	-0.0086(17)	0.0086(17)
C(24)	0.069(2) 0.017(2)	0.0296(19)	0.072(3)	0.011(2)	0.053(2)
C(25)	0.0208(15) 0.014(2)	0.039(2)	0.067(2)	-0.0022(15)	0.0100(16)
C(26)	0.047(2) -0.024(2)	0.095(4)	0.038(2)	-0.032(2)	0.0291(18)

The general temperature factor expression: $\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom
	distance			
O(1)	C(10)	1.347(3)	O(1)	C(21)
	1.450(4)			
O(2)	C(15)	1.219(4)	O(3)	C(18)
	1.210(4)			
O(4)	C(10)	1.191(3)	N(5)	C(6)
	1.470(4)			
N(5)	C(12)	1.477(3)	N(5)	C(15)

	1.351(3)			
C(6)	C(8)	1.537(3)	C(7)	C(19)
	1.541(4)			
C(7)	C(20)	1.536(3)	C(7)	C(21)
	1.506(4)			
C(8)	C(9)	1.563(4)	C(8)	C(11)
	1.533(4)			
C(9)	C(12)	1.550(3)	C(9)	C(18)
	1.525(4)			
C(9)	C(22)	1.531(3)	C(10)	C(17)
	1.526(4)			
C(11)	C(16)	1.533(4)	C(12)	C(20)
	1.514(3)			
C(13)	C(14)	1.533(4)	C(13)	C(18)
	1.512(4)			
C(14)	C(16)	1.528(5)	C(15)	C(19)
	1.534(4)			
C(17)	C(23)	1.522(5)	C(17)	C(25)
	1.527(4)			
C(17)	C(26)	1.533(5)	C(19)	C(24)
	1.522(4)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom
	distance			
C(6)	H(1)	0.950	C(6)	H(2)
	0.951			
C(7)	H(3)	0.950	C(8)	H(4)
	0.950			
C(11)	H(5)	0.950	C(11)	H(6)
	0.949			
C(12)	H(7)	0.950	C(13)	H(8)
	0.949			
C(13)	H(9)	0.950	C(14)	H(10)
	0.950			

C(14)	H(11)	0.950	C(16)	H(12)
	0.950			
C(16)	H(13)	0.950	C(19)	H(14)
	0.949			
C(20)	H(15)	0.950	C(20)	H(16)
	0.950			
C(21)	H(17)	0.951	C(21)	H(18)
	0.950			
C(22)	H(19)	0.950	C(22)	H(20)
	0.950			
C(22)	H(21)	0.950	C(23)	H(22)
	0.950			
C(23)	H(23)	0.949	C(23)	H(24)
	0.951			
C(24)	H(25)	0.949	C(24)	H(26)
	0.951			
C(24)	H(27)	0.950	C(25)	H(28)
	0.949			
C(25)	H(29)	0.950	C(25)	H(30)
	0.950			
C(26)	H(31)	0.950	C(26)	H(32)
	0.950			
C(26)	H(33)	0.950		

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom
	angle					
C(10)	O(1)	C(21)	117.9(2)	C(6)	N(5)	C(12)
	111.6(2)					
C(6)	N(5)	C(15)	121.6(2)	C(12)	N(5)	C(15)
	126.6(2)					
N(5)	C(6)	C(8)	105.0(2)	C(19)	C(7)	C(20)
	110.4(2)					
C(19)	C(7)	C(21)	109.4(2)	C(20)	C(7)	C(21)
	113.3(2)					

C(6)	C(8)	C(9)	101.9(2)	C(6)	C(8)	C(11)
	113.3(2)					
C(9)	C(8)	C(11)	114.2(2)	C(8)	C(9)	C(12)
	101.6(2)					
C(8)	C(9)	C(18)	113.1(2)	C(8)	C(9)	C(22)
	110.6(2)					
C(12)	C(9)	C(18)	111.0(2)	C(12)	C(9)	C(22)
	113.1(2)					
C(18)	C(9)	C(22)	107.4(2)	O(1)	C(10)	O(4)
	124.6(2)					
O(1)	C(10)	C(17)	110.8(2)	O(4)	C(10)	C(17)
	124.6(2)					
C(8)	C(11)	C(16)	114.4(2)	N(5)	C(12)	C(9)
	101.6(2)					
N(5)	C(12)	C(20)	109.9(2)	C(9)	C(12)	C(20)
	120.2(2)					
C(14)	C(13)	C(18)	109.3(2)	C(13)	C(14)	C(16)
	114.3(3)					
O(2)	C(15)	N(5)	121.6(2)	O(2)	C(15)	C(19)
	120.1(2)					
N(5)	C(15)	C(19)	118.3(2)	C(11)	C(16)	C(14)
	115.4(2)					
C(10)	C(17)	C(23)	108.8(2)	C(10)	C(17)	C(25)
	112.6(2)					
C(10)	C(17)	C(26)	106.9(2)	C(23)	C(17)	C(25)
	108.4(2)					
C(23)	C(17)	C(26)	109.2(3)	C(25)	C(17)	C(26)
	110.9(3)					
O(3)	C(18)	C(9)	121.1(2)	O(3)	C(18)	C(13)
	120.8(2)					
C(9)	C(18)	C(13)	118.1(2)	C(7)	C(19)	C(15)
	115.1(2)					
C(7)	C(19)	C(24)	111.8(3)	C(15)	C(19)	C(24)
	109.3(3)					
C(7)	C(20)	C(12)	109.1(2)	O(1)	C(21)	C(7)
	108.5(2)					

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom
	angle					
N(5)	C(6)	H(1)	110.4	N(5)	C(6)	H(2)
	110.2					
C(8)	C(6)	H(1)	110.9	C(8)	C(6)	H(2)
	110.9					
H(1)	C(6)	H(2)	109.4	C(19)	C(7)	H(3)
	108.5					
C(20)	C(7)	H(3)	107.0	C(21)	C(7)	H(3)
	108.1					
C(6)	C(8)	H(4)	109.1	C(9)	C(8)	H(4)
	108.7					
C(11)	C(8)	H(4)	109.3	C(8)	C(11)	H(5)
	107.8					
C(8)	C(11)	H(6)	108.6	C(16)	C(11)	H(5)
	108.5					
C(16)	C(11)	H(6)	108.0	H(5)	C(11)	H(6)
	109.5					
N(5)	C(12)	H(7)	108.3	C(9)	C(12)	H(7)
	108.5					
C(20)	C(12)	H(7)	107.8	C(14)	C(13)	H(8)
	110.1					
C(14)	C(13)	H(9)	109.2	C(18)	C(13)	H(8)
	109.8					
C(18)	C(13)	H(9)	109.1	H(8)	C(13)	H(9)
	109.5					
C(13)	C(14)	H(10)	108.4	C(13)	C(14)	H(11)
	108.1					
C(16)	C(14)	H(10)	108.6	C(16)	C(14)	H(11)
	108.1					
H(10)	C(14)	H(11)	109.4	C(11)	C(16)	H(12)
	107.8					
C(11)	C(16)	H(13)	108.3	C(14)	C(16)	H(12)
	108.2					

C(14)	C(16)	H(13)	107.6	H(12)	C(16)	H(13)
	109.5					
C(7)	C(19)	H(14)	106.6	C(15)	C(19)	H(14)
	107.4					
C(24)	C(19)	H(14)	106.1	C(7)	C(20)	H(15)
	109.8					
C(7)	C(20)	H(16)	109.3	C(12)	C(20)	H(15)
	109.1					
C(12)	C(20)	H(16)	110.0	H(15)	C(20)	H(16)
	109.5					
O(1)	C(21)	H(17)	110.0	O(1)	C(21)	H(18)
	109.7					
C(7)	C(21)	H(17)	110.3	C(7)	C(21)	H(18)
	108.9					
H(17)	C(21)	H(18)	109.5	C(9)	C(22)	H(19)
	109.7					
C(9)	C(22)	H(20)	109.7	C(9)	C(22)	H(21)
	109.1					
H(19)	C(22)	H(20)	109.5	H(19)	C(22)	H(21)
	109.5					
H(20)	C(22)	H(21)	109.5	C(17)	C(23)	H(22)
	109.7					
C(17)	C(23)	H(23)	110.1	C(17)	C(23)	H(24)
	108.4					
H(22)	C(23)	H(23)	109.6	H(22)	C(23)	H(24)
	109.5					
H(23)	C(23)	H(24)	109.4	C(19)	C(24)	H(25)
	110.8					
C(19)	C(24)	H(26)	109.3	C(19)	C(24)	H(27)
	108.4					
H(25)	C(24)	H(26)	109.4	H(25)	C(24)	H(27)
	109.5					
H(26)	C(24)	H(27)	109.5	C(17)	C(25)	H(28)
	108.4					
C(17)	C(25)	H(29)	110.4	C(17)	C(25)	H(30)
	109.6					

H(28)	C(25)	H(29)	109.5	H(28)	C(25)	H(30)
	109.5					
H(29)	C(25)	H(30)	109.4	C(17)	C(26)	H(31)
	108.9					
C(17)	C(26)	H(32)	109.3	C(17)	C(26)	H(33)
	110.2					
H(31)	C(26)	H(32)	109.4	H(31)	C(26)	H(33)
	109.5					
H(32)	C(26)	H(33)	109.5			

Table 8. Torsion Angles(⁰)

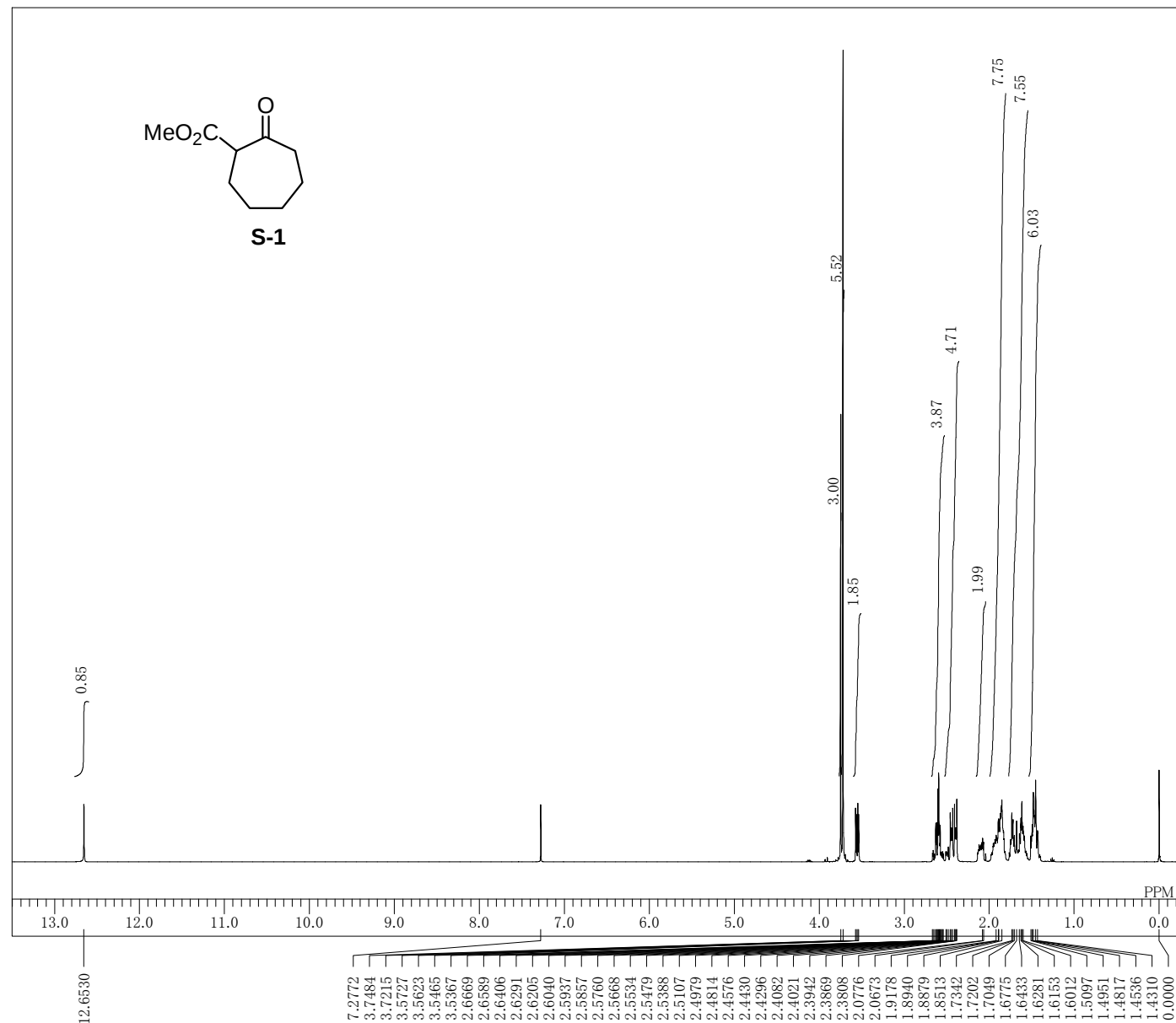
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	angle							
C(10)	O(1)	C(21)	C(7)	-125.6(2)	C(21)	O(1)	C(10)	O(4)
	-4.9(4)							
C(21)	O(1)	C(10)	C(17)	175.9(2)	C(6)	N(5)	C(12)	C(9)
	23.7(2)							
C(6)	N(5)	C(12)	C(20)	152.1(2)	C(12)	N(5)	C(6)	C(8)
	2.3(2)							
C(6)	N(5)	C(15)	O(2)	0.9(4)	C(6)	N(5)	C(15)	C(19)
	-179.2(2)							
C(15)	N(5)	C(6)	C(8)	176.3(2)	C(12)	N(5)	C(15)	O(2)
	174.0(2)							
C(12)	N(5)	C(15)	C(19)	-6.1(3)	C(15)	N(5)	C(12)	C(9)
	-150.0(2)							
C(15)	N(5)	C(12)	C(20)	-21.6(3)	N(5)	C(6)	C(8)	C(9)
	-27.1(2)							
N(5)	C(6)	C(8)	C(11)	96.1(2)	C(19)	C(7)	C(20)	C(12)
	-62.0(3)							
C(20)	C(7)	C(19)	C(15)	34.4(3)	C(20)	C(7)	C(19)	C(24)
	-91.1(2)							
C(19)	C(7)	C(21)	O(1)	179.7(2)	C(21)	C(7)	C(19)	C(15)
	-91.0(2)							
C(21)	C(7)	C(19)	C(24)	143.5(2)	C(20)	C(7)	C(21)	O(1)
	55.9(3)							

C(21)	C(7)	C(20)	C(12)	61.1(3)	C(6)	C(8)	C(9)	C(12)
	41.1(2)							
C(6)	C(8)	C(9)	C(18)	160.2(2)	C(6)	C(8)	C(9)	C(22)
	-79.3(2)							
C(6)	C(8)	C(11)	C(16)	157.5(3)	C(9)	C(8)	C(11)	C(16)
	-86.4(3)							
C(11)	C(8)	C(9)	C(12)	-81.5(2)	C(11)	C(8)	C(9)	C(18)
	37.6(2)							
C(11)	C(8)	C(9)	C(22)	158.1(2)	C(8)	C(9)	C(12)	N(5)
	-39.3(2)							
C(8)	C(9)	C(12)	C(20)	-160.8(2)	C(8)	C(9)	C(18)	O(3)
	-136.1(2)							
C(8)	C(9)	C(18)	C(13)	43.1(3)	C(12)	C(9)	C(18)	O(3)
	-22.6(3)							
C(12)	C(9)	C(18)	C(13)	156.6(2)	C(18)	C(9)	C(12)	N(5)
	-159.9(2)							
C(18)	C(9)	C(12)	C(20)	78.6(3)	C(22)	C(9)	C(12)	N(5)
	79.3(2)							
C(22)	C(9)	C(12)	C(20)	-42.1(3)	C(22)	C(9)	C(18)	O(3)
	101.5(3)							
C(22)	C(9)	C(18)	C(13)	-79.2(3)	O(1)	C(10)	C(17)	C(23)
	-149.3(2)							
O(1)	C(10)	C(17)	C(25)	-29.1(3)	O(1)	C(10)	C(17)	C(26)
	92.9(3)							
O(4)	C(10)	C(17)	C(23)	31.5(4)	O(4)	C(10)	C(17)	C(25)
	151.8(3)							
O(4)	C(10)	C(17)	C(26)	-86.2(4)	C(8)	C(11)	C(16)	C(14)
	72.4(4)							
N(5)	C(12)	C(20)	C(7)	54.7(3)	C(9)	C(12)	C(20)	C(7)
	172.0(2)							
C(14)	C(13)	C(18)	O(3)	86.4(3)	C(14)	C(13)	C(18)	C(9)
	-92.9(3)							
C(18)	C(13)	C(14)	C(16)	73.4(4)	C(13)	C(14)	C(16)	C(11)
	-55.7(4)							
O(2)	C(15)		C(19)	C(7)	179.0(2)	O(2)	C(15)	C(19)
	C(24)		-54.2(3)					

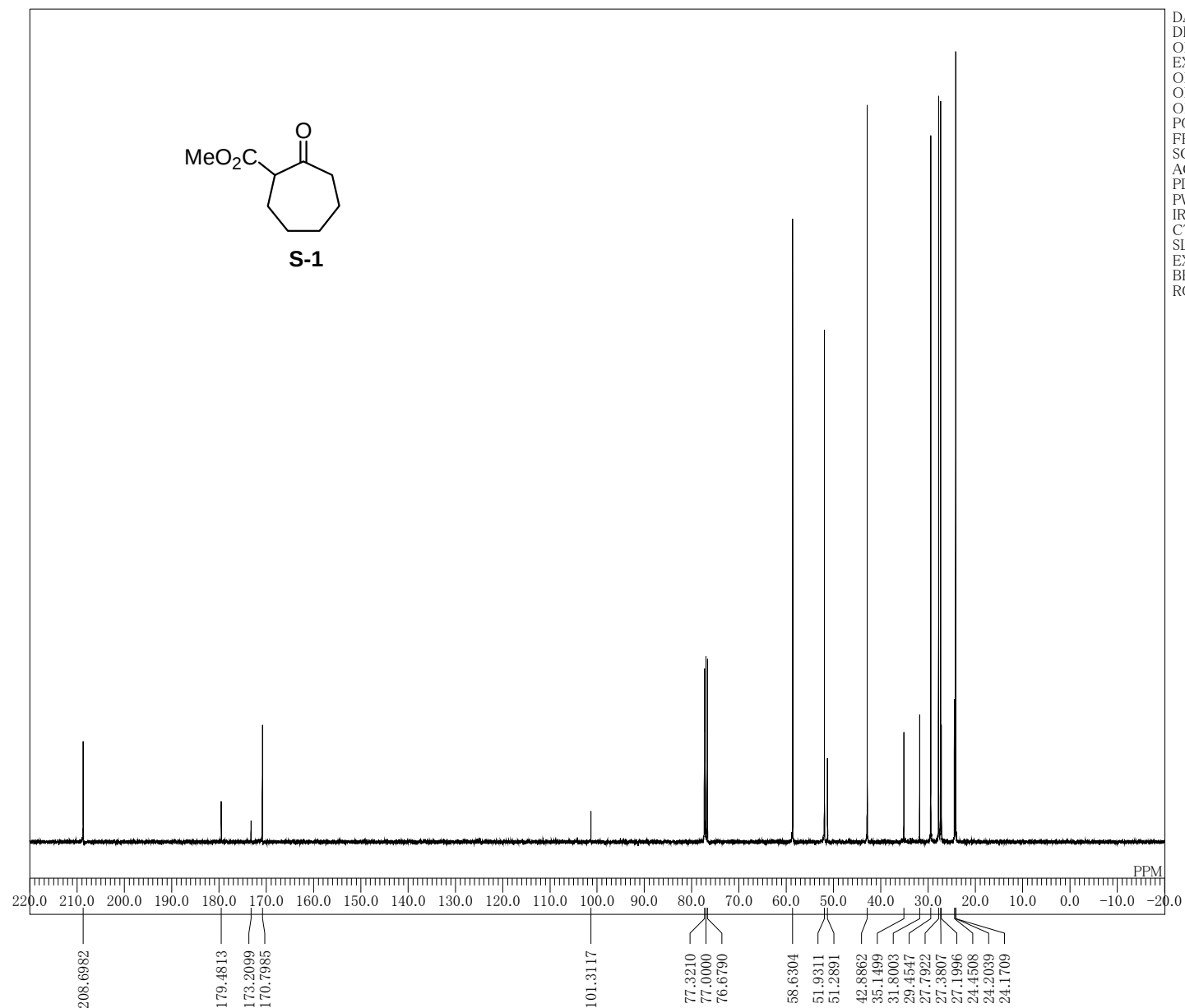
N(5) C(15) C(19) C(7) -1.0(3)
125.8(3)

N(5) C(15) C(19) C(24)

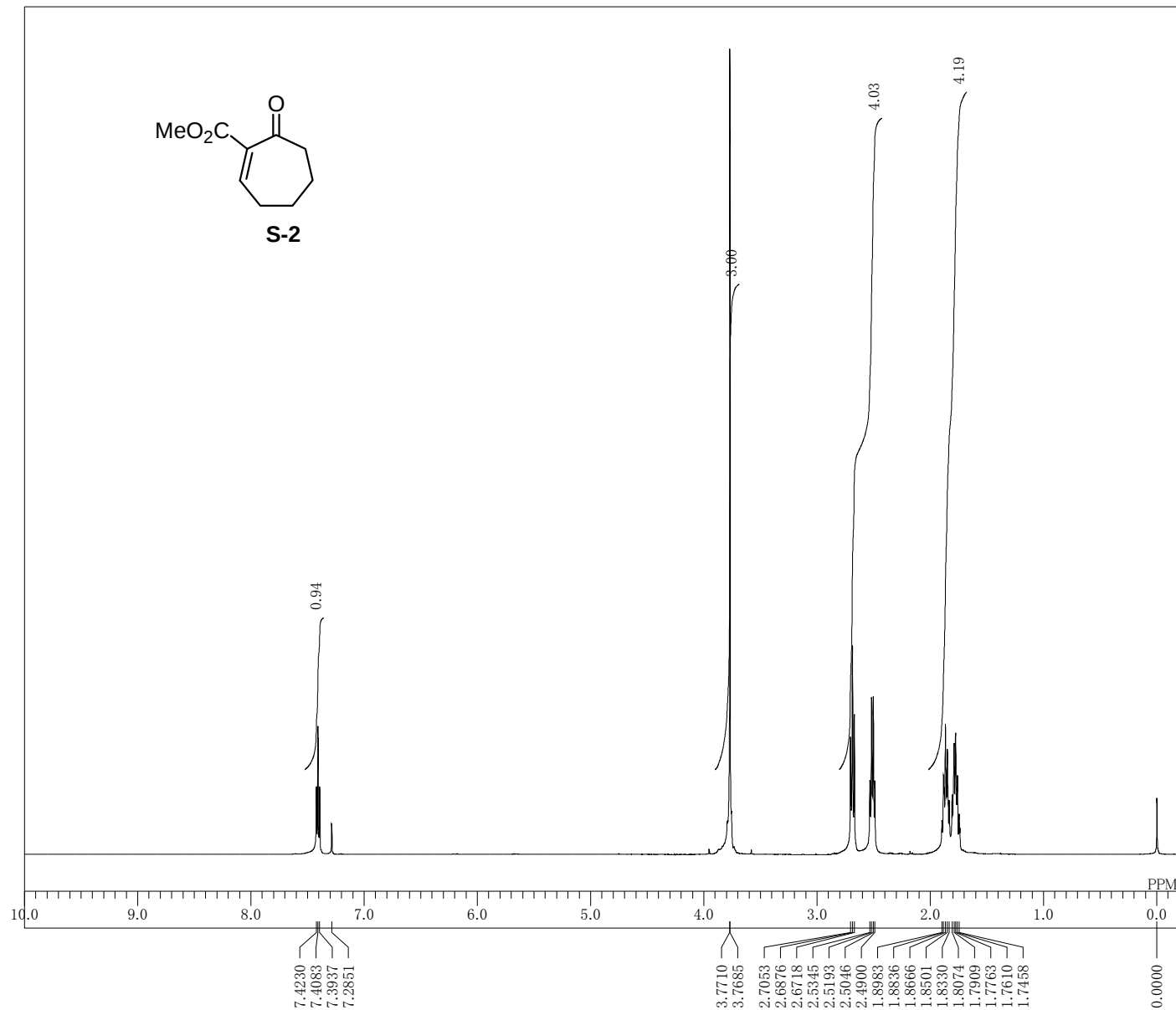
The sign is positive if when looking from atom 2 to atom 3 a clock-wise motion of atom 1 would superimpose it on atom 4.



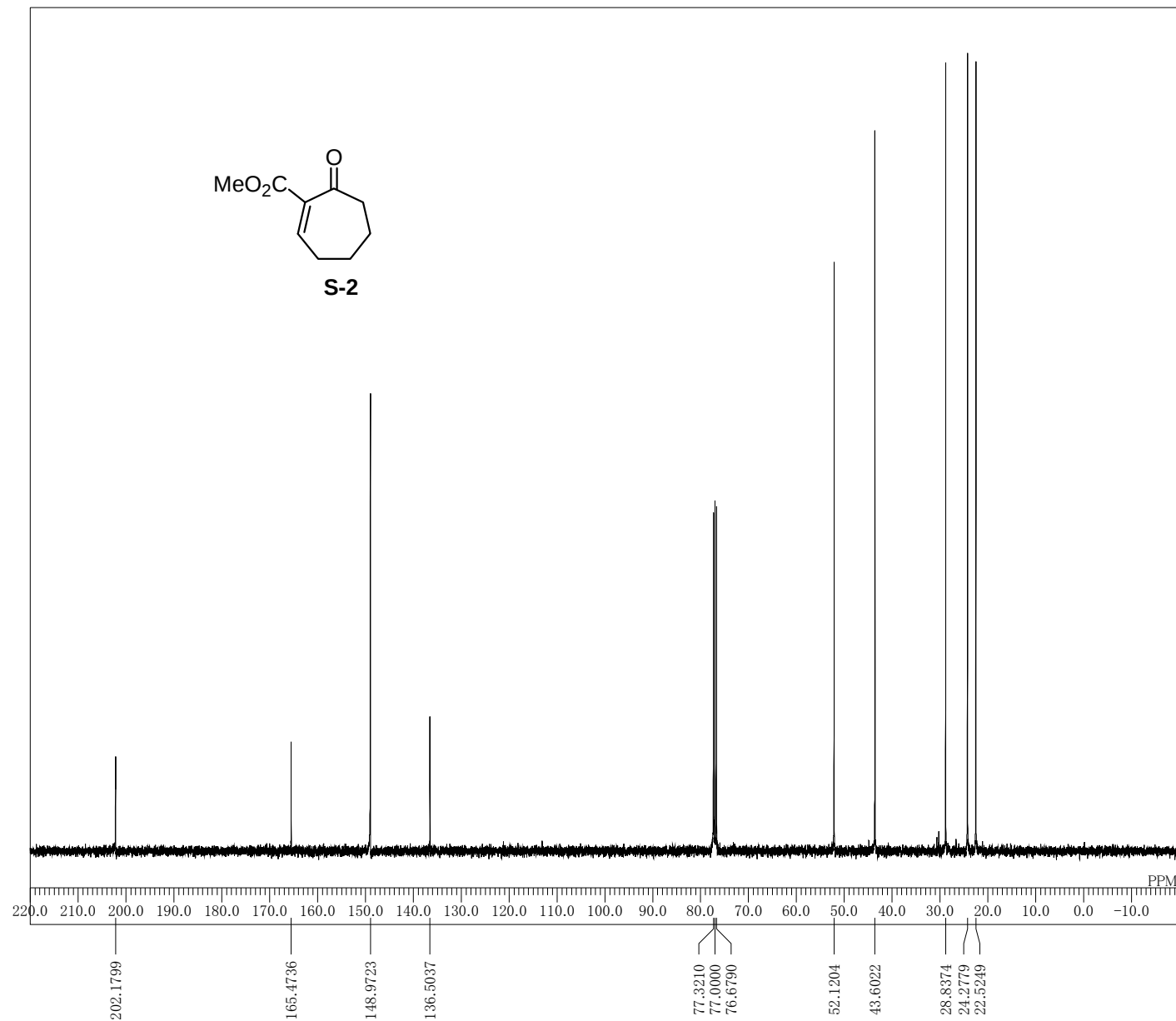
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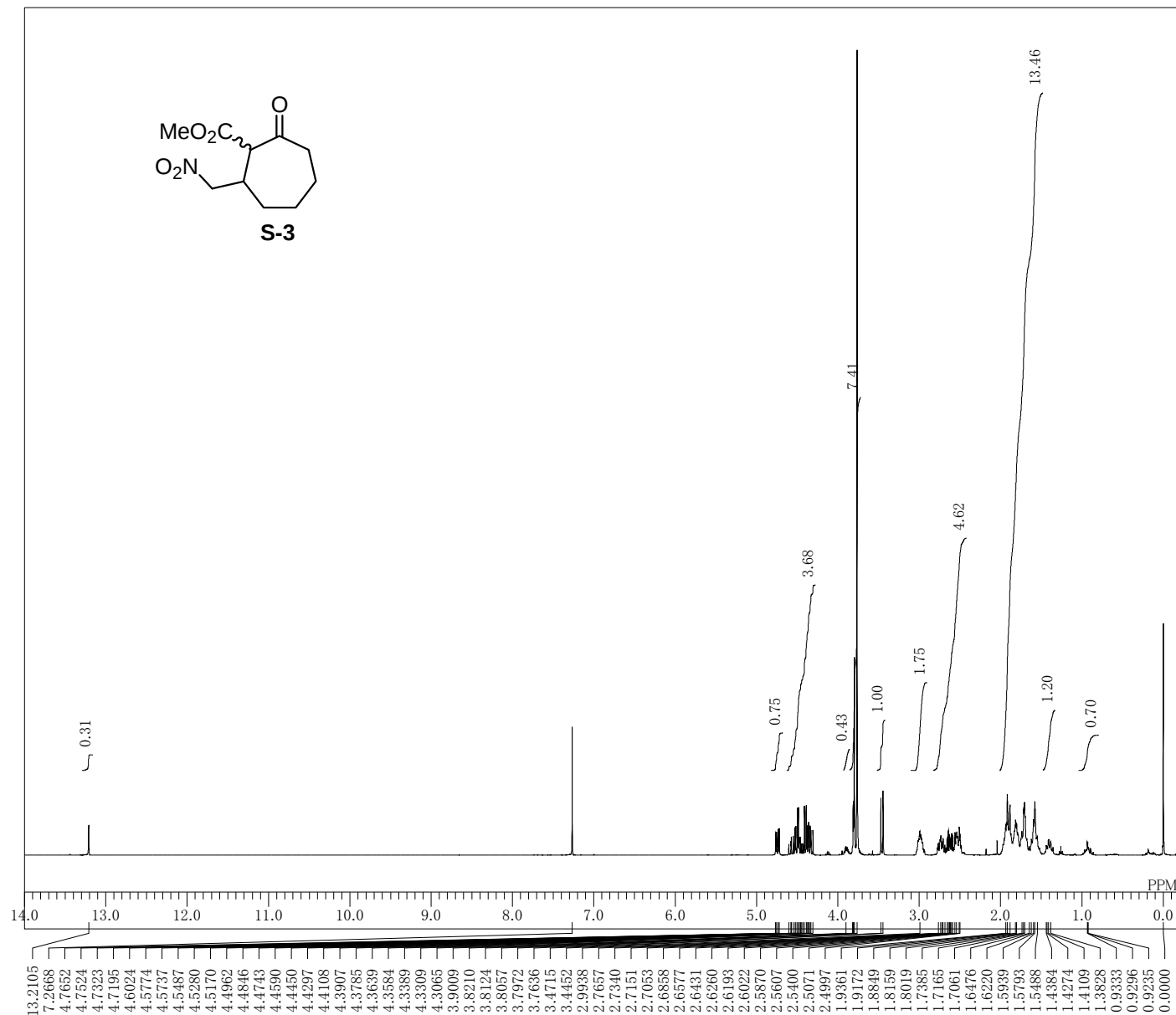
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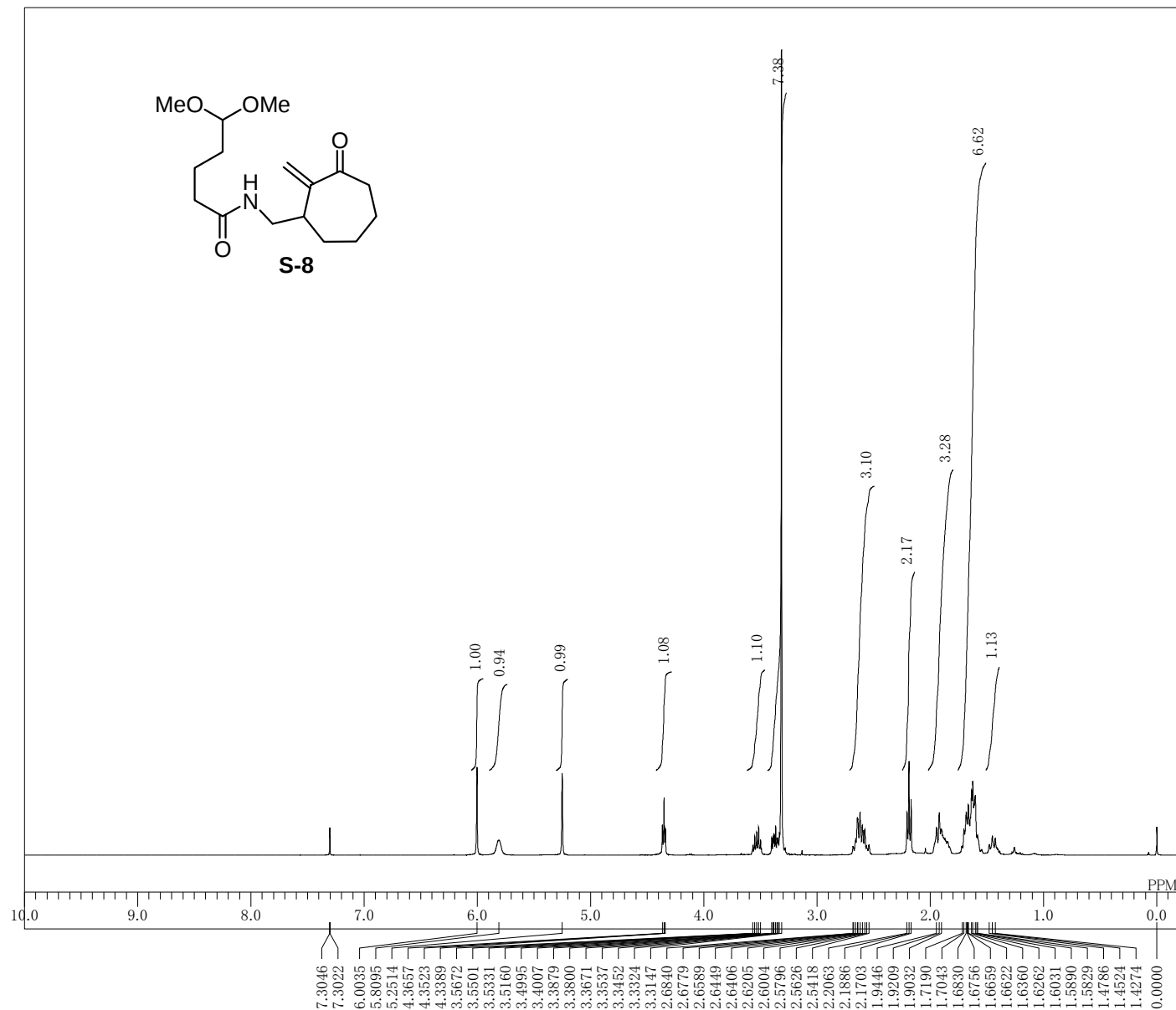
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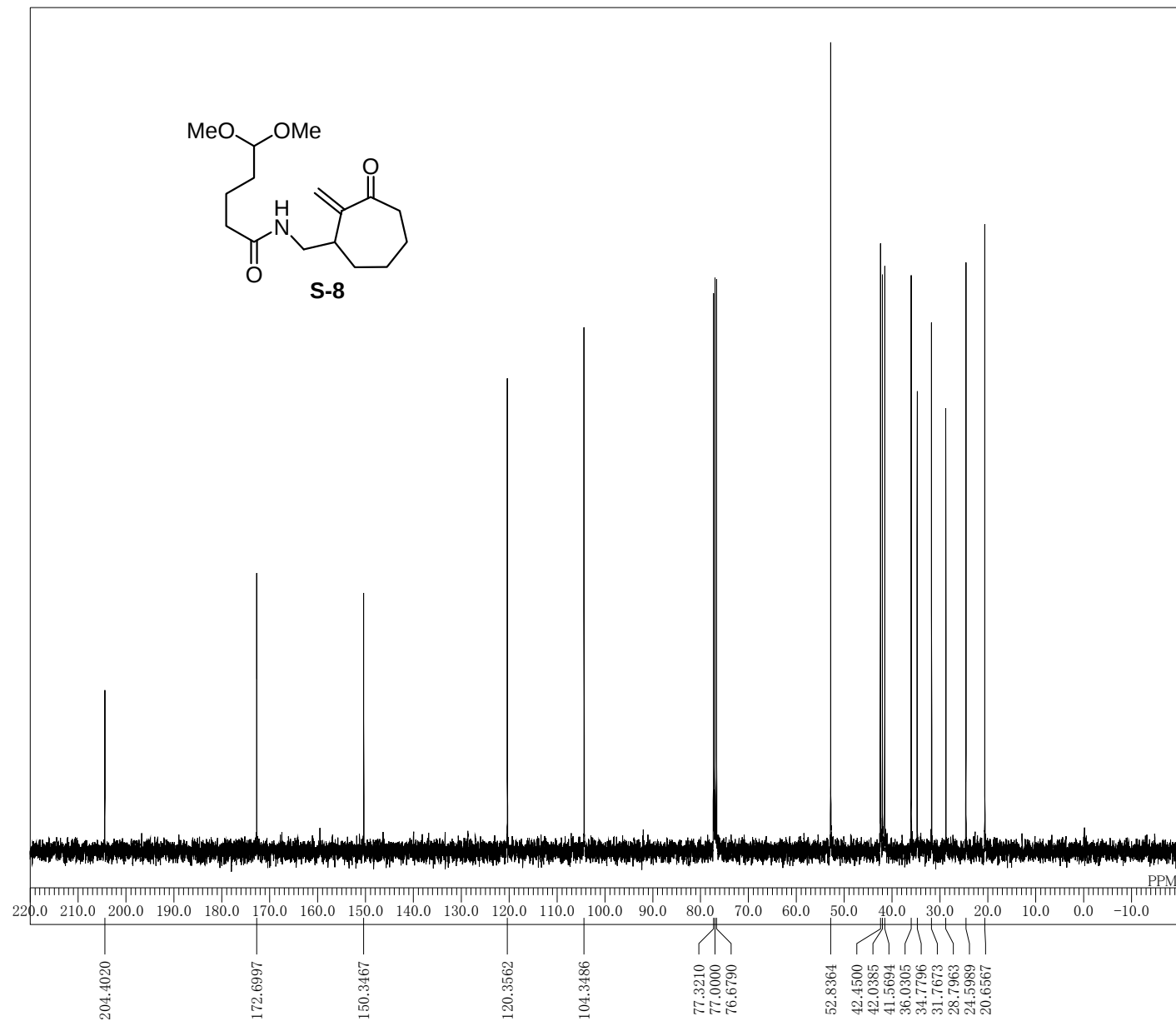
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 ACQTM 1.2206 sec
 PD 1.7790 sec
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 IRN
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 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 24



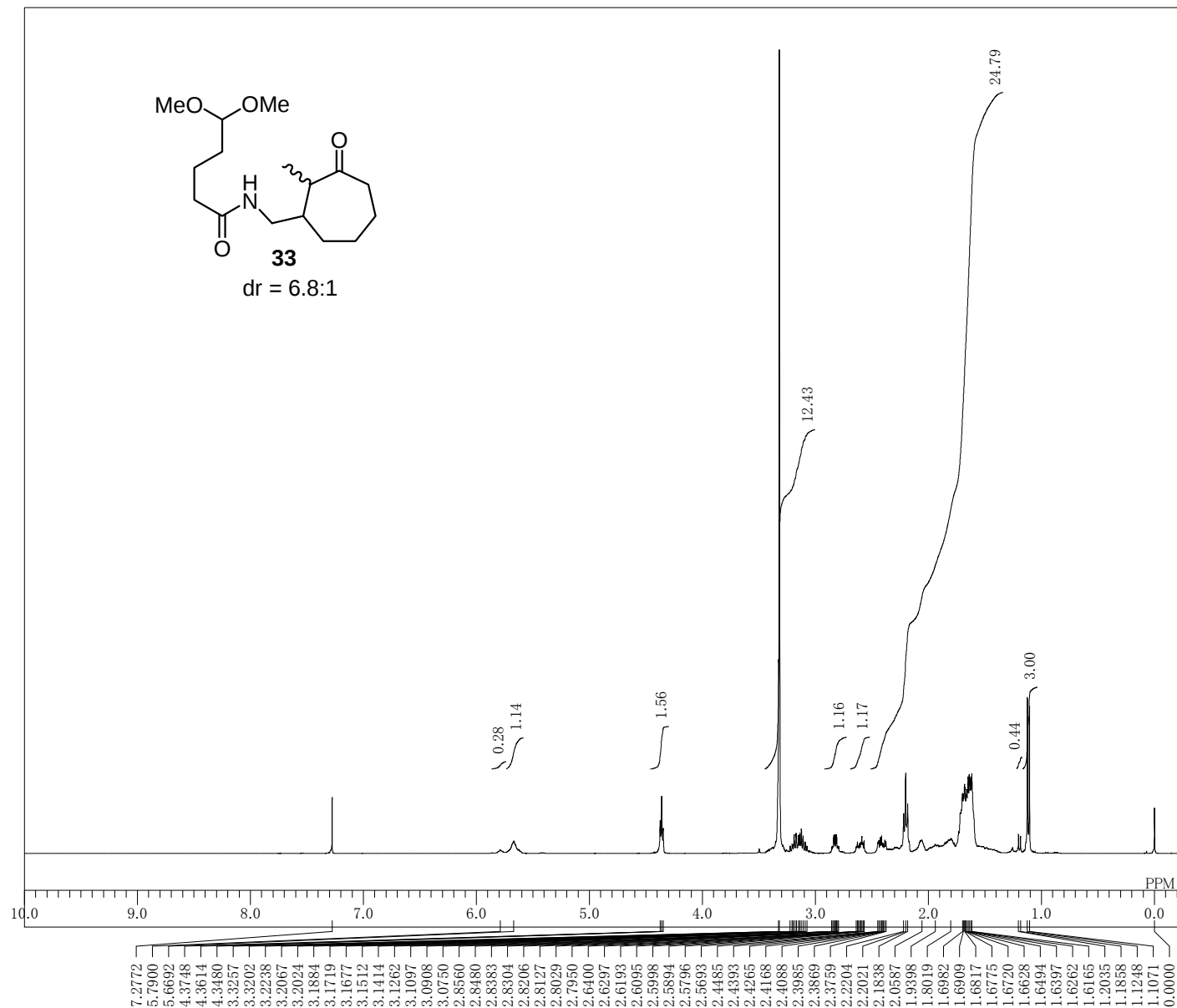
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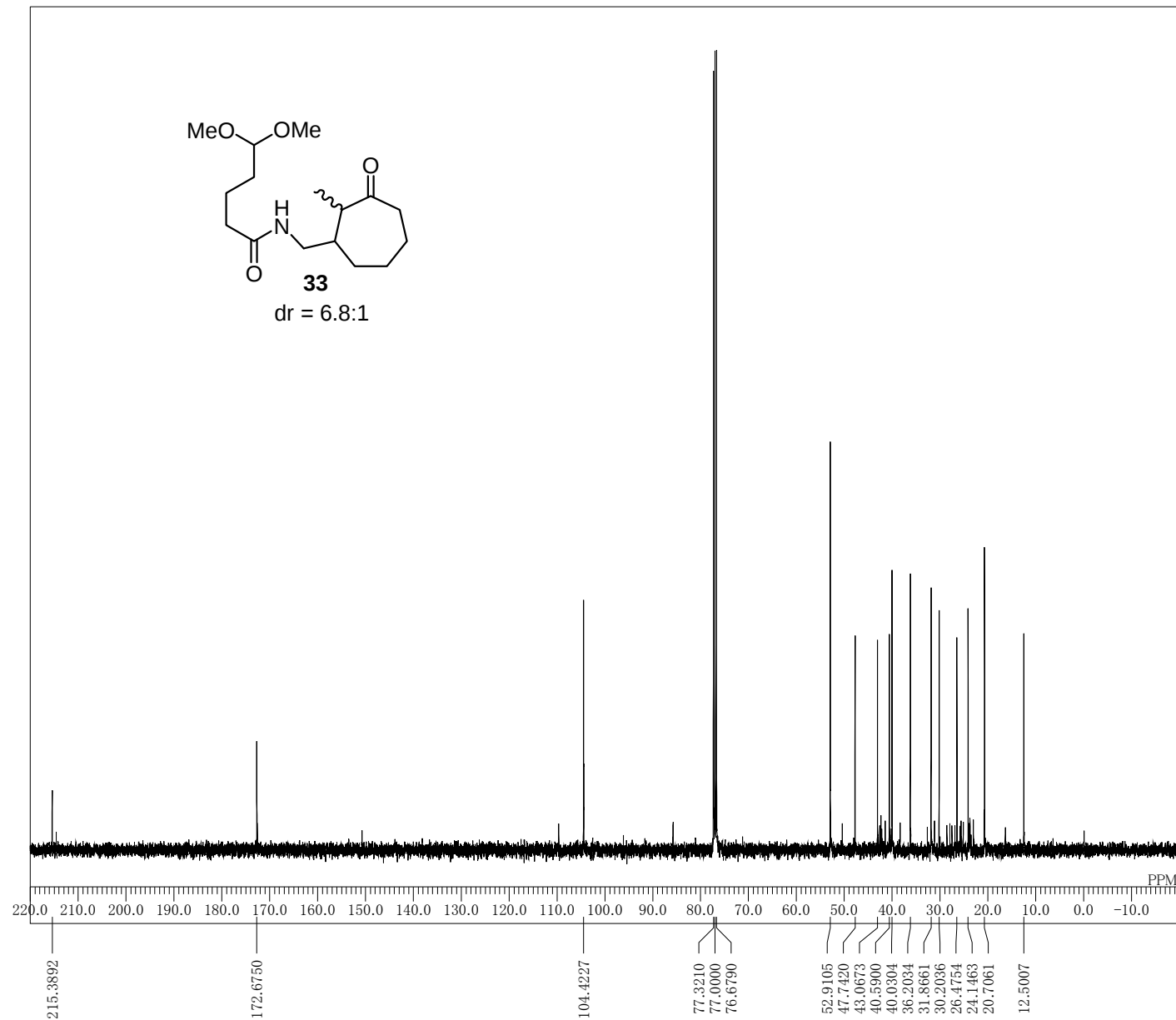
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 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.33 Hz
 RGAIN 11



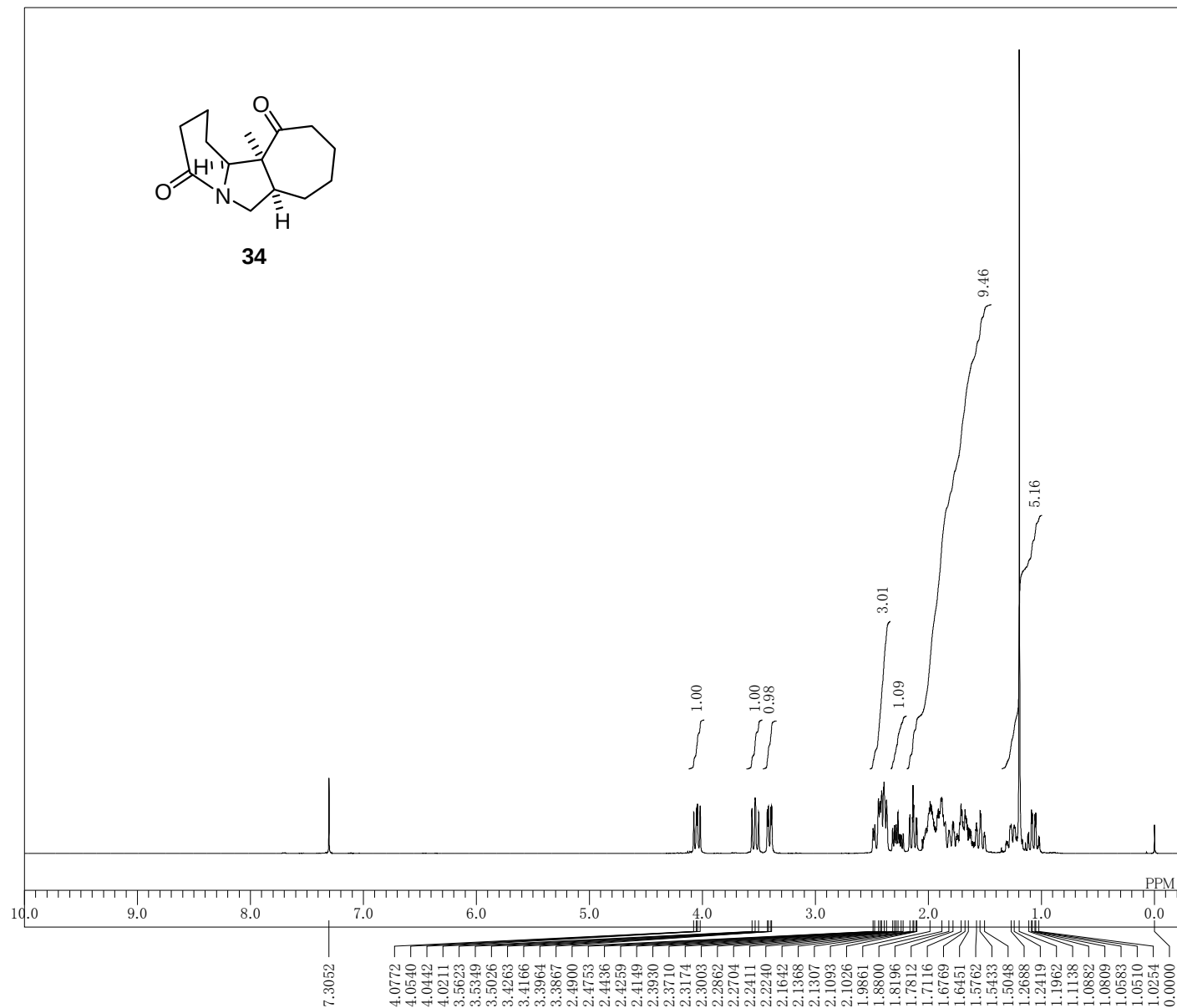
DATIM Thu Sep 13 22:40:13 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1503C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 26.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.23 Hz
 RGAIN 24



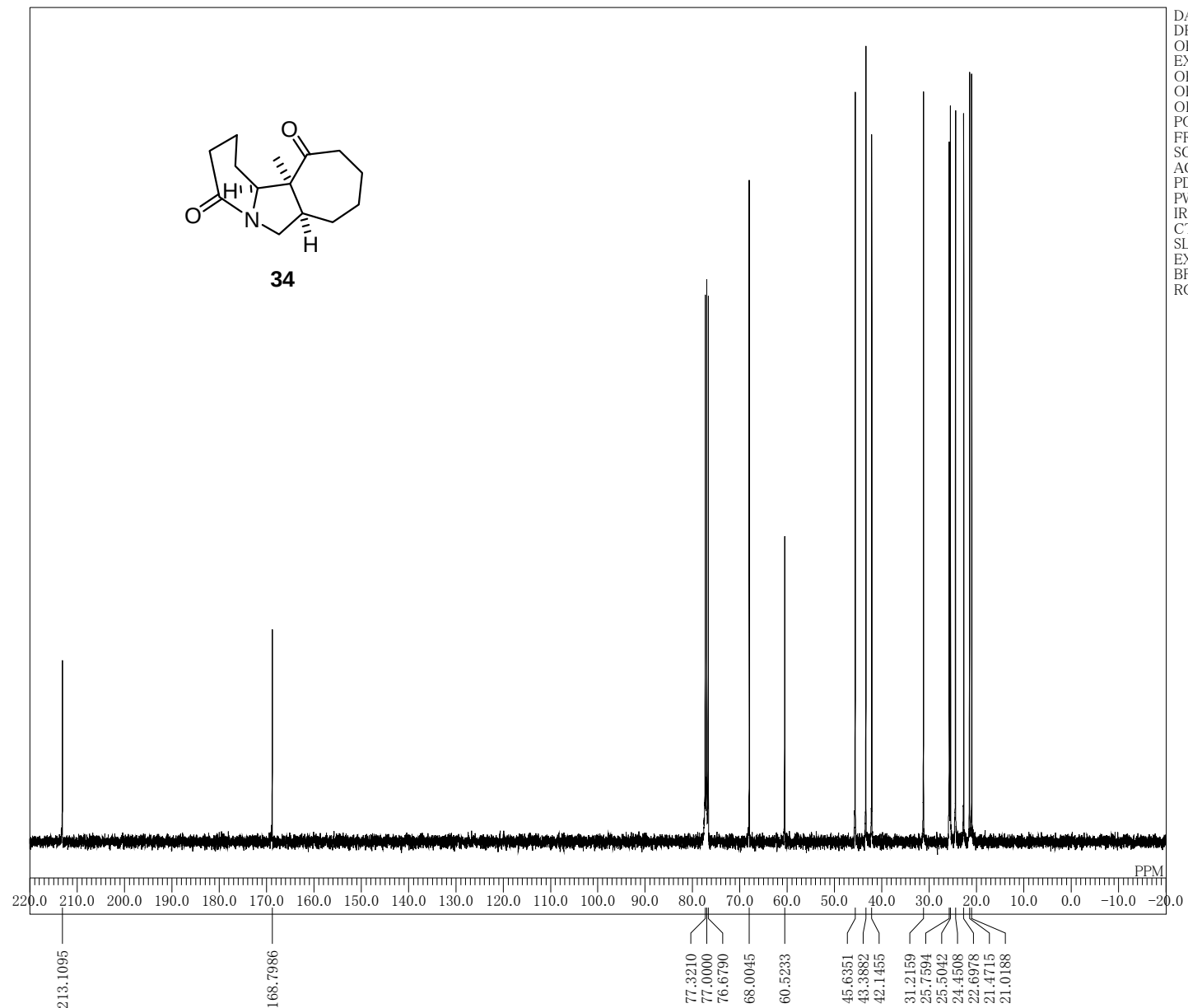
DATIM Sat Oct 25 22:40:25 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1927-H.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 32
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 13



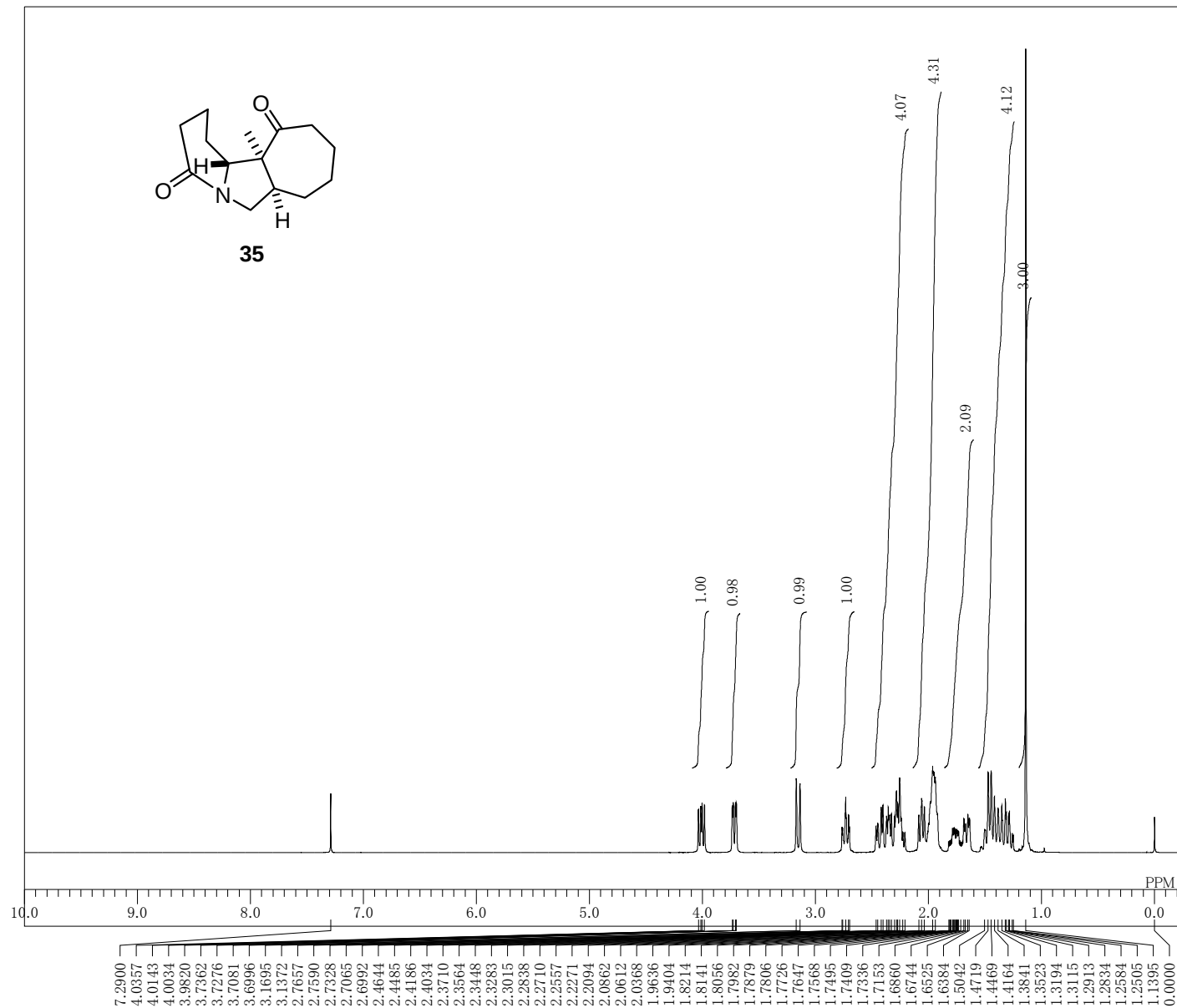
DATIM	Sat Oct 25 23:15:03 2008
DFILE	C:\My Documents\個人ファイル\NMR AL400\
OBNUC	13C
EXMOD	BCM
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	662
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.40 usec
IRN	
CTEMP	26.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.12 Hz
RGAIN	24



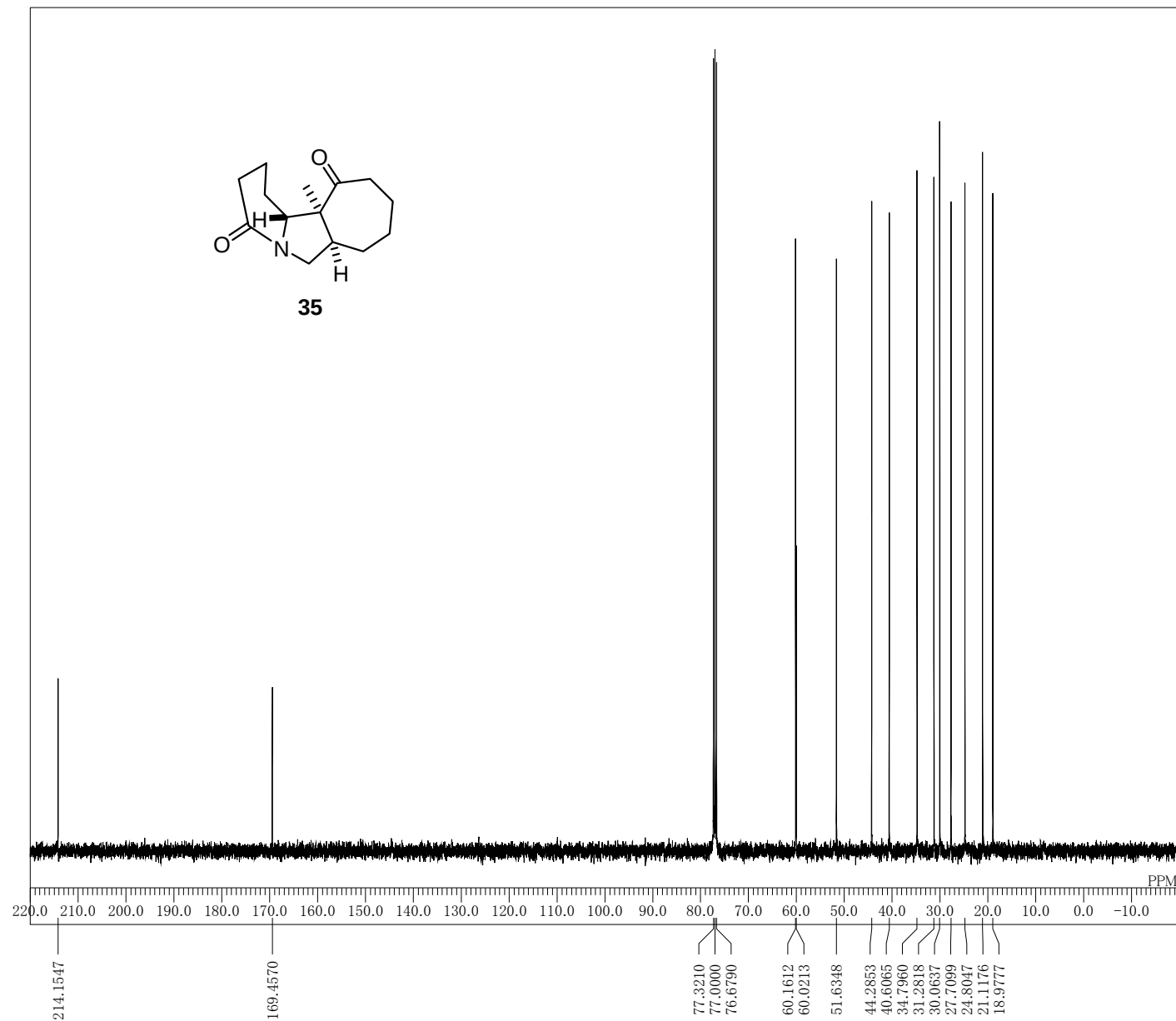
DATIM Thu Apr 10 09:19:41 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1688-H.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.41 Hz
 RGAIN 11



DATIM Thu Apr 10 23:30:45 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1688-C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 546
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 25



DATIM Mon Apr 14 13:06:01 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1697-H.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 12

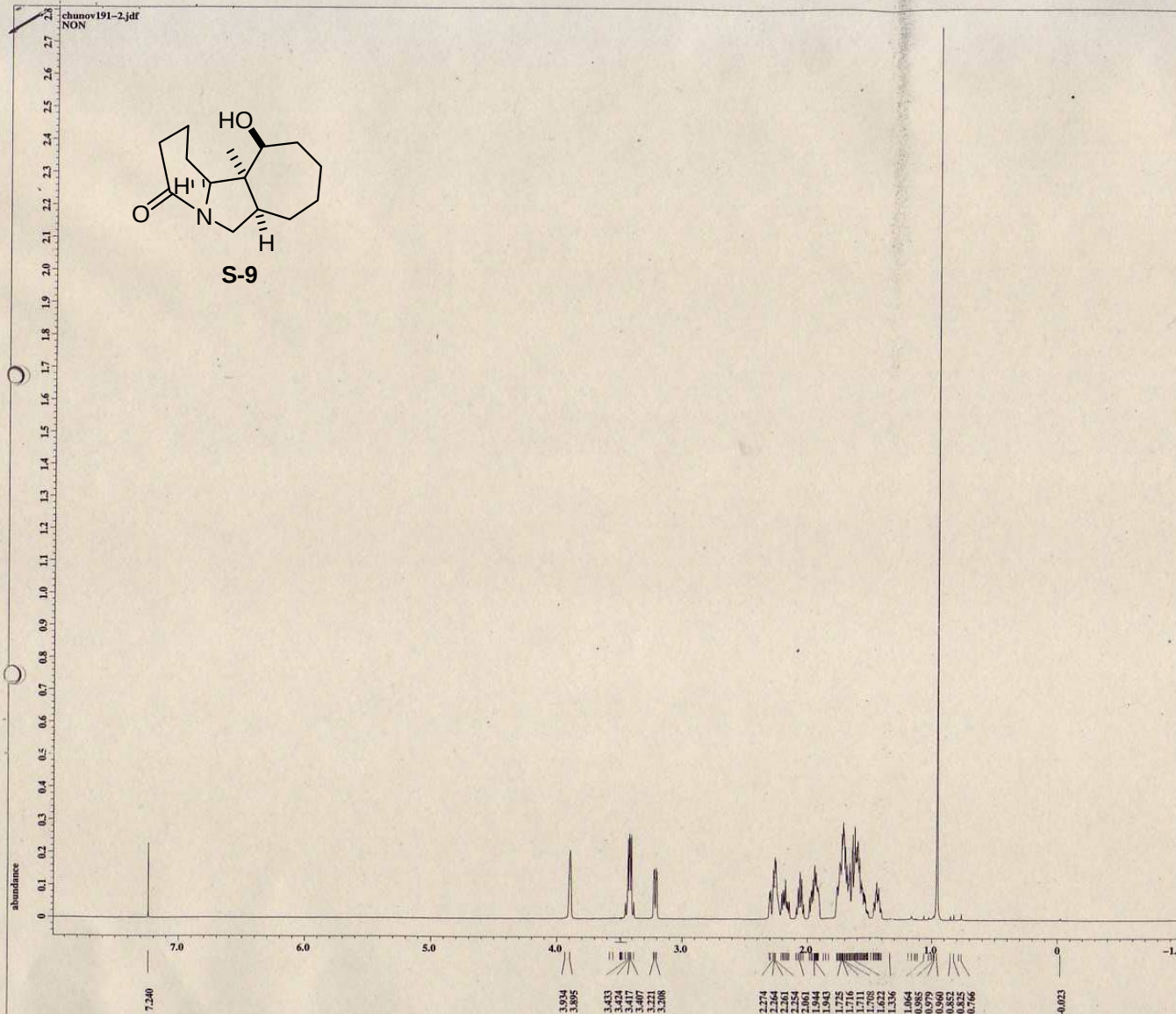
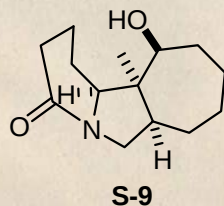


DATIM Mon Apr 14 14:26:05 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1697-C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 403
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 24

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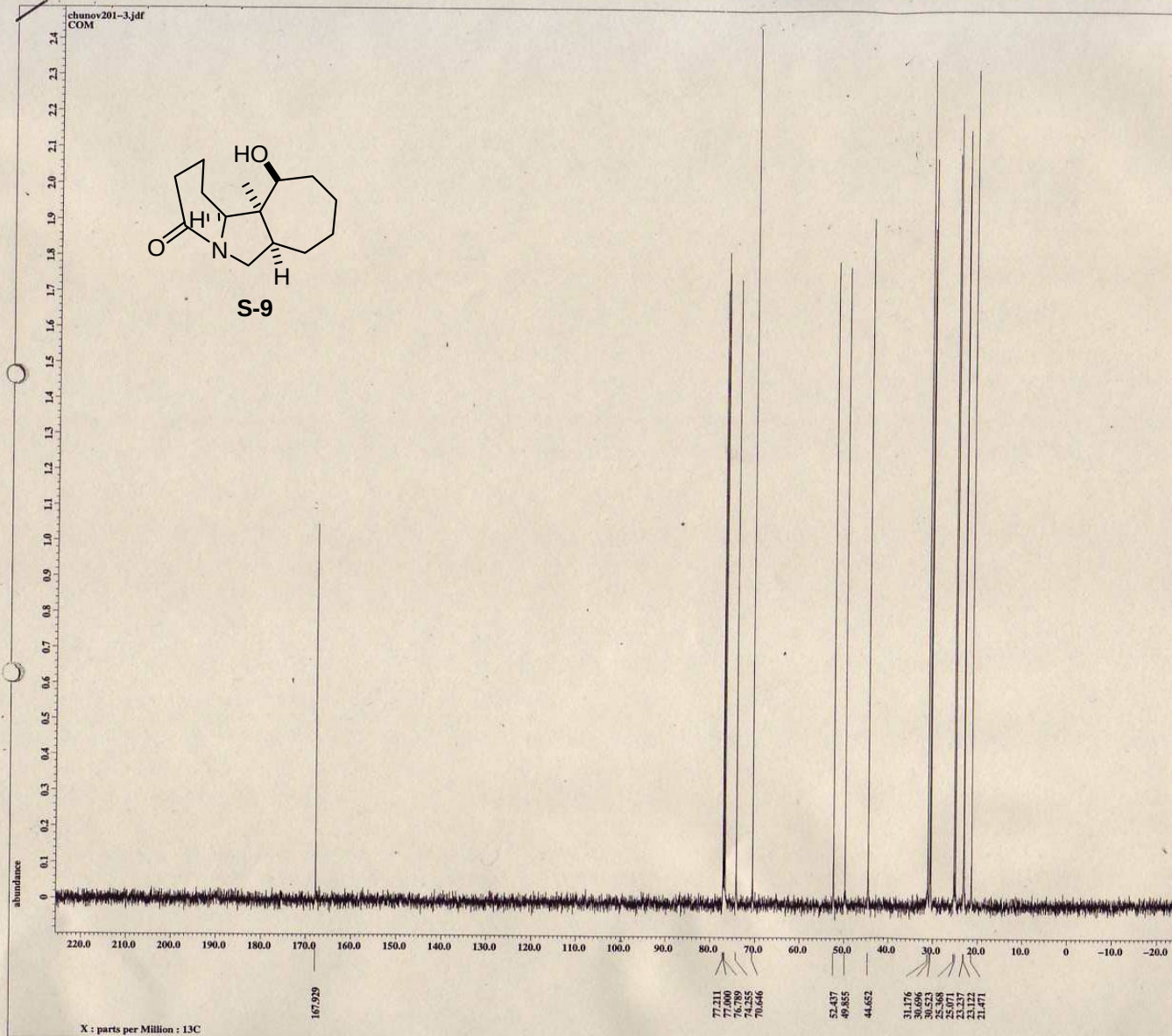


----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 smp : 0.0 [Hz] : 0.0 [s]
 trapezoid : 0 [%] : 80 [%] : 100 [%]
 zero fill : 1
 fft : 1 : TRUE : TRUE
 machine phase
 ppm
 Reference : 7.25 [ppm] : 7.24 [ppm]
 Derived from: chunov191-1.jdf



Filename = chunov191-2.jdf
 Author = delta
 Sample id = ka
 Content = NON
 Creation time = 19-NOV-2007 10:59:34
 Revision time = 19-NOV-2007 12:33:11
 Field strength = 13.95540559 [T] (590 [M]
 X acq duration = 9.8041856 [s]
 X domain = 1H
 X freq = 594.17058168 [MHz]
 X offset = 3.5 [ppm]
 X points = 65836
 X preacans = 0
 X resolution = 0.10199725 [Hz]
 X sweep = 6.68449198 [kHz]
 Irr domain = 1H
 Irr freq = 594.17058168 [MHz]
 Irr offset = 5 [ppm]
 Tri domain = 1H
 Tri freq = 594.17058168 [MHz]
 Tri offset = 5 [ppm]
 Clipped = FALSE
 Mod return = 1
 Scans = 8
 Total scans = 8
 X 90 width = 14.6 [us]
 X acq time = 9.8041856 [s]
 X angle = 45 [deg]
 X attn = 3.5 [dB]
 X pulse = 7.3 [us]
 Irr mode = Off
 Tri mode = Off
 Dante preset = FALSE
 Initial wait = 1 [s]
 Relaxation delay = 5 [s]
 Repetition time = 14.0041856 [s]
 Experiment = single_pulse.ex2
 Recvr gain = 30
 Solvent = CHLOROFORM-D
 Temp get = 24.6 [dC]
 Spin get = 14 [Hz]
 Probe id = 2692

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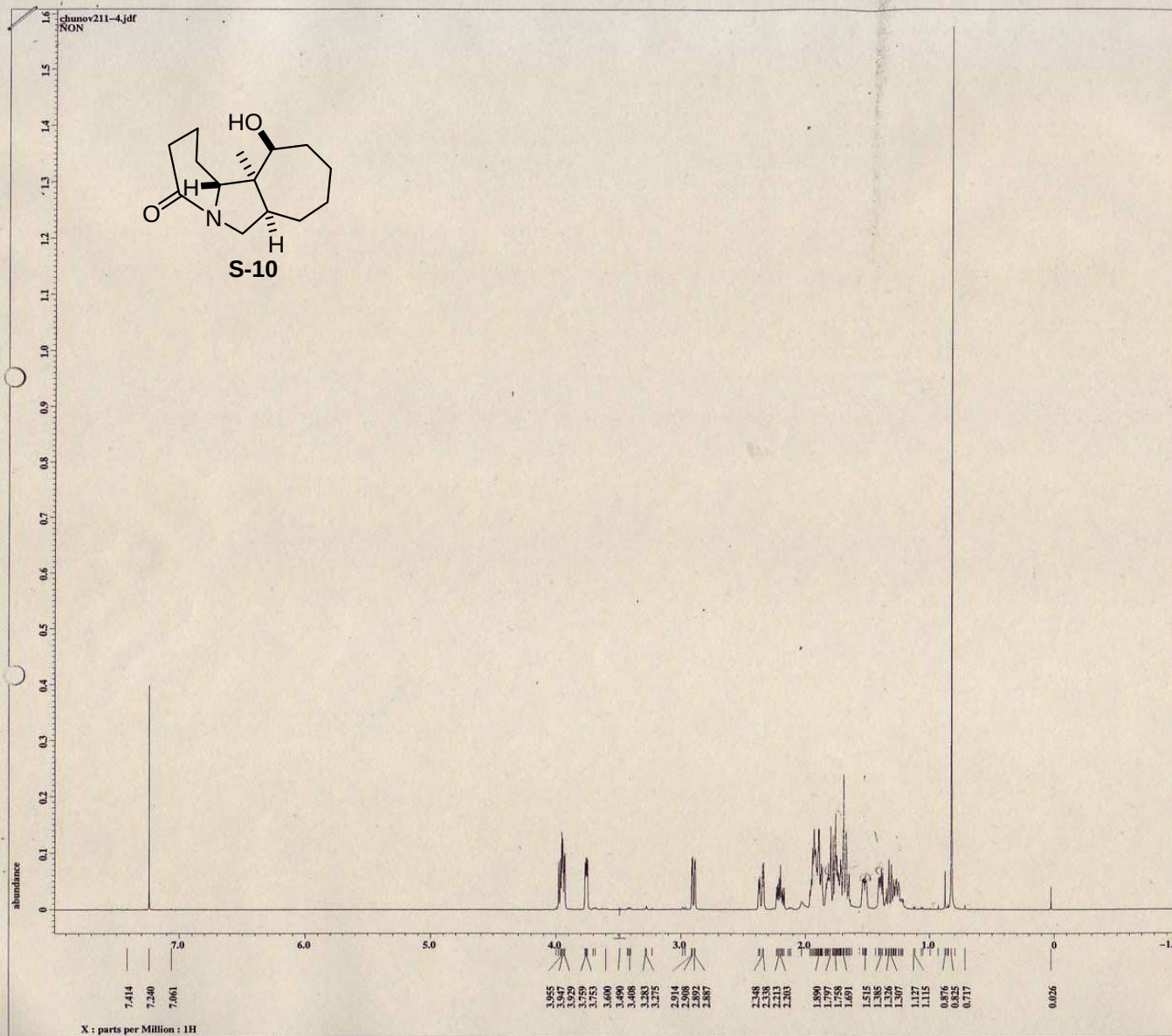
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----- PROCESSING PARAMETERS -----
 dc_balance : 0 : FALSE
 aexp : 2.0 [Hz] : 0.0 [s]
 trapzoid3 : 0 [%] : 80 [%] : 100 [%]
 zerofill : 1
 fft : 1 : TRUE : TRUE
 machinaphase
 ppm
 Derived from: chunov201-1.jdf

Filename = chunov201-3.jdf
 Author = delta
 Sample_id = km
 Content = COM
 Creation_time = 19-NOV-2007 12:50:11
 Revision_time = 19-NOV-2007 13:49:10
 Field_strength = 13.95540559 [T] (590 [M]
 X_acq_duration = 0.69730304 [s]
 X_domain = 13C
 X_freq = 149.40429612 [MHz]
 X_offset = 100 [ppm]
 X_points = 32768
 X_prescans = 4
 X_resolution = 1.43409672 [Hz]
 X_sweep = 46.9924812 [kHz]
 Irr_domain = 1H
 Irr_freq = 500.137058168 [MHz]
 Irr_offset = 5 [ppm]
 Clipped = FALSE
 Mod_return = 1
 Scans = 96
 Total_scans = 96
 X_90_width = 10.2 [us]
 X_acq_time = 0.69730304 [s]
 X_angle = 30 [deg]
 X_atn = 7.9 [dB]
 X_pulse = 3.4 [us]
 Irr_atn_dec = 16 [dB]
 Irr_atn_noe = 16 [dB]
 Irr_noise = WALTZ
 Decoupling = TRUE
 Initial_wait = 1 [s]
 Noe = TRUE
 Noe_time = 2 [s]
 Relaxation_delay = 2 [s]
 Repetition_time = 2.69730304 [s]
 Experiment = single_pulse_dec
 Recvr_gain = 60
 Solvent = CHLOROFORM-D
 Temp_get = 25.7 [dC]
 Spin_get = 14 [Hz]
 Probe_id = 2692

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----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 nexp : 0.0 [Hz] : 0.0 [s]
 trapasoid3 : 0 [Hz] : 80 [Hz] : 100 [Hz]
 zerofill : 1
 eft : 1 : TRUE : TRUE
 machinephase
 ppm
 Derived from: chunov211-1.jdf

Filename = chunov211-4.jdf
 Author = delta
 Sample_id = km
 Content = NON
 Creation time = 20-NOV-2007 11:25:28
 Revision time = 20-NOV-2007 12:32:38
 Field strength = 13.95540559 [T] (590 [M]
 X acq duration = 9.8041856 [s]
 X domain = 1H
 X freq = 594.17058168 [MHz]
 X offset = 3.5 [ppm]
 X points = 65536
 X prescans = 0
 X resolution = 0.10199725 [Hz]
 X sweep = 6.68449198 [kHz]
 Irr domain = 1H
 Irr freq = 594.17058168 [MHz]
 Irr offset = 5 [ppm]
 Tri domain = 1H
 Tri freq = 594.17058168 [MHz]
 Tri offset = 5 [ppm]
 Clipped = FALSE
 Mod return = 1
 Scans = 8
 Total scans = 8
 X 90 width = 14.6 [us]
 X acq time = 9.8041856 [s]
 X angle = 45 [deg]
 X att = 3.5 [dB]
 X pulse = 7.3 [us]
 Irr mode = Off
 Tri mode = Off
 Dante preset = FALSE
 Initial wait = 1 [s]
 Relaxation delay = 5 [s]
 Repetition time = 14.8041856 [s]
 Experiment = single_pulse.ex2
 Recvr gain = 36
 Solvent = CHLOROFORM-D
 Temp get = 24.8 [dC]
 Spin get = 14 [Hz]
 Probe id = 2692

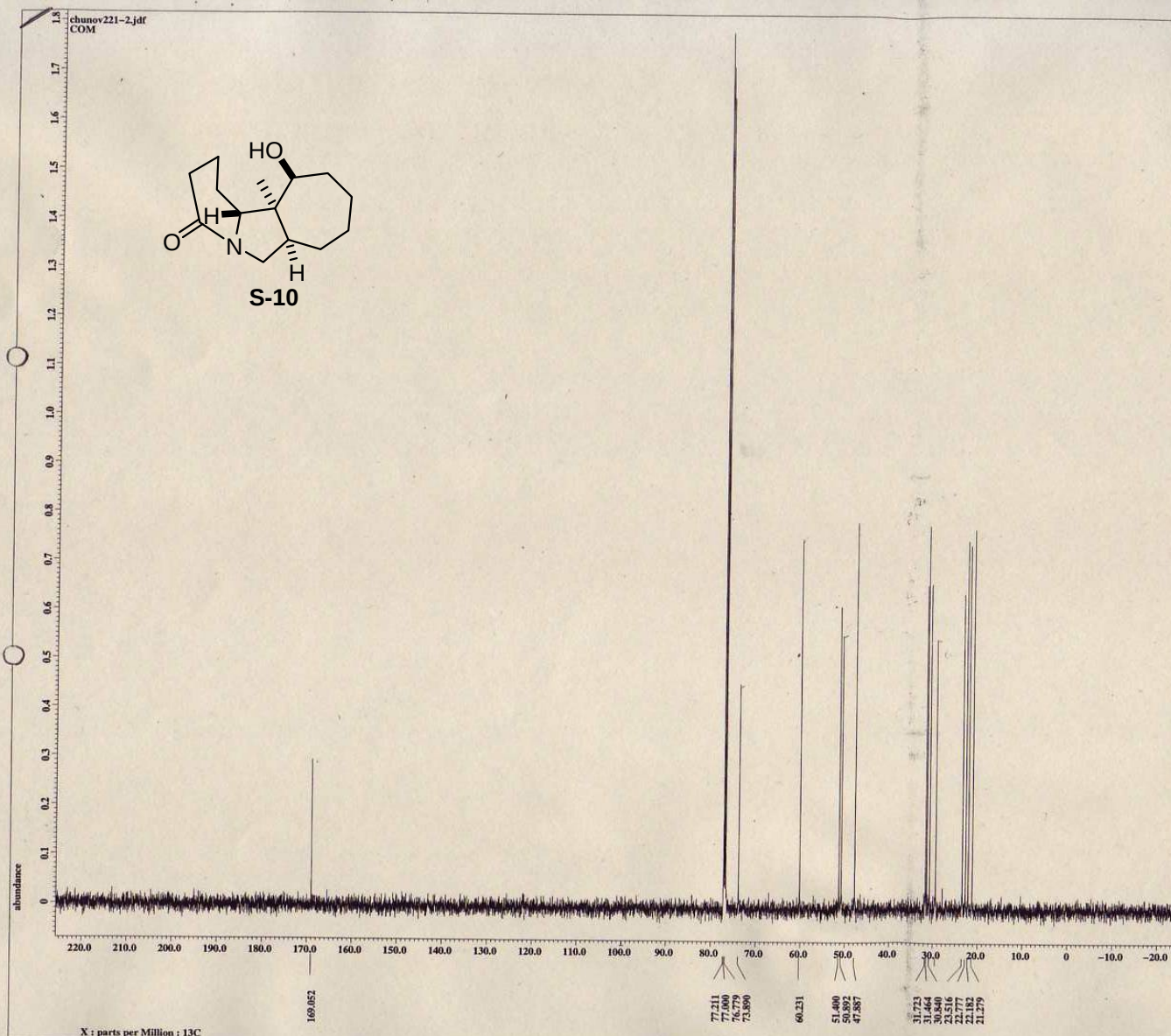
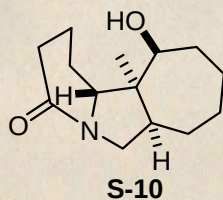
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合成制御化学 254 COM

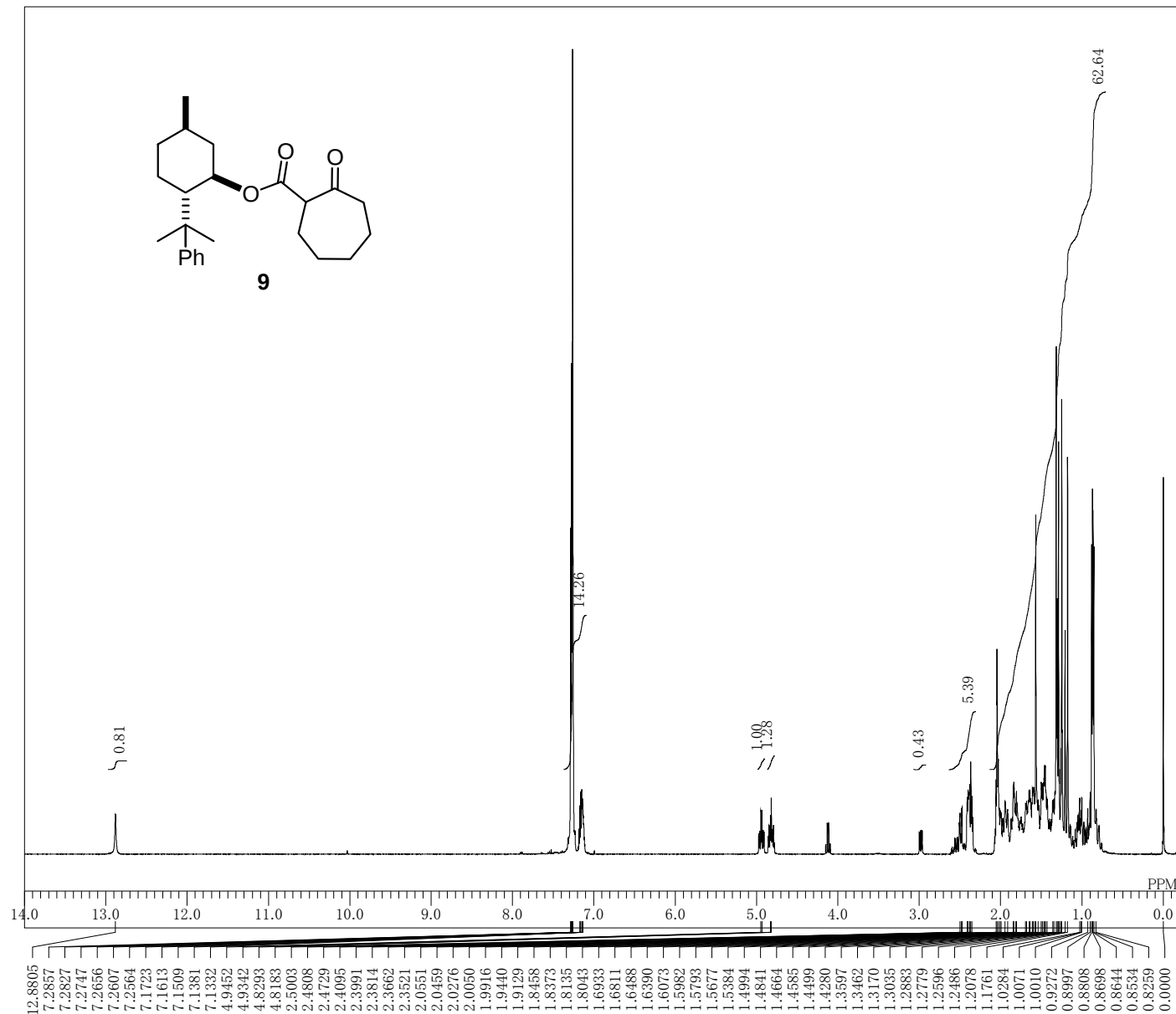


----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 sexp : 2.0 [Hz] : 0.0 [s]
 trapratio : 0.0 (%) : 80 (%) : 100 (%)
 zerofill : 1
 eff : 1 : TRUE : TRUE
 machine : phase
 ppm
 reference : 77.126 [ppm] : 77 [ppm]
 Derived from: chunov221-1.jdf

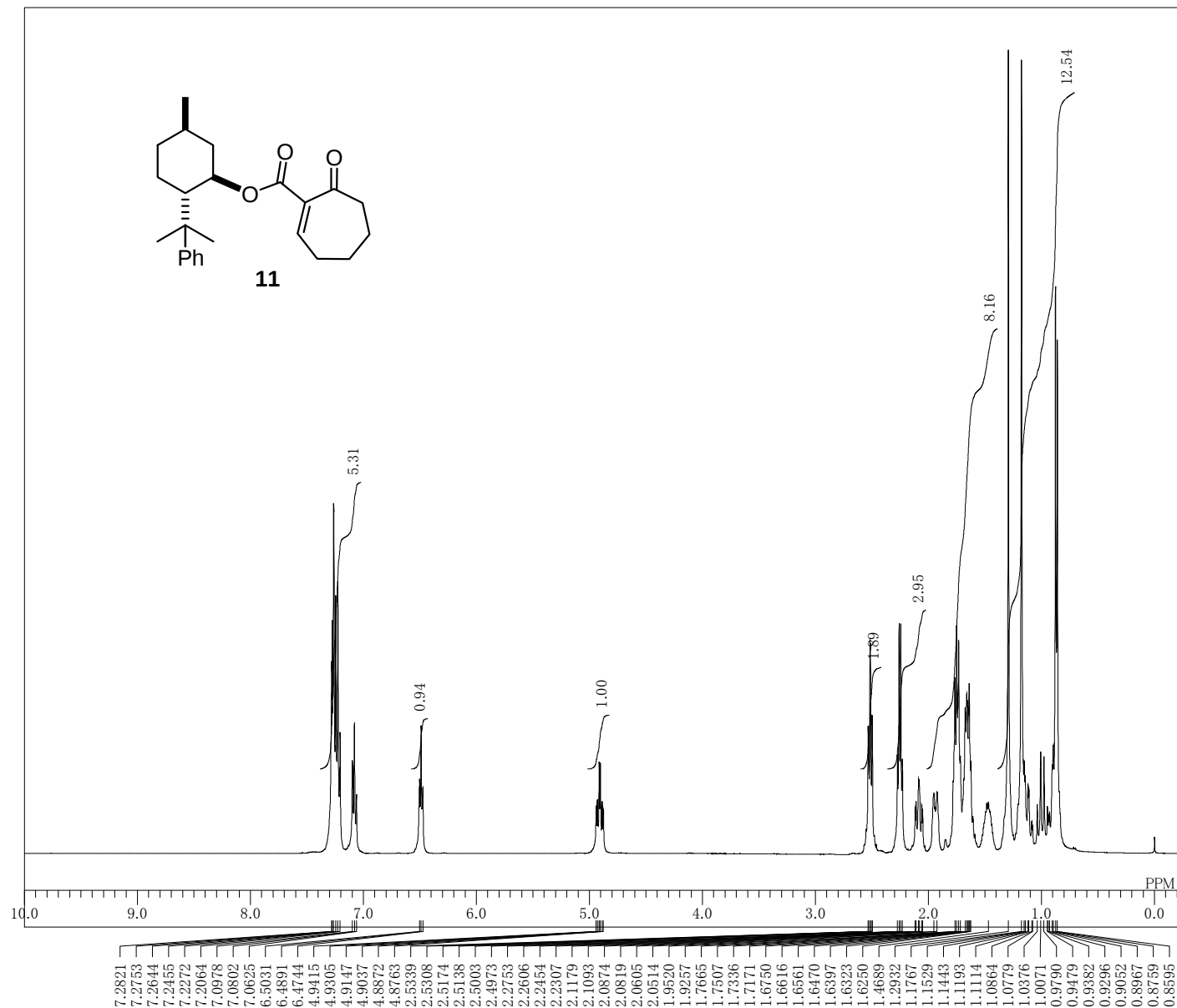
Filename : - chunov221-2.jdf
 Author : delta
 Sample_id : km
 Content : COM
 Creation time : 20-NOV-2007 11:43:17
 Revision time : 20-NOV-2007 12:42:21
 Yield strength : 13.95540559 [Hz] (590 [M]
 X_acq_duration : 0.69730304 [s]
 X_domain : 13C
 X_freq : 149.40429612 [MHz]
 X_offset : 100 [ppm]
 X_points : 32768
 X_prescans : 4
 X_resolution : 1.43409672 [Hz]
 X_sweep : 46.9924812 [kHz]
 irr_domain : 1H
 irr_freq : 594.17058168 [MHz]
 irr_offset : 5 [ppm]
 Clipped : FALSE
 Mod_return : 1
 Scans : 141
 Total_scans : 141
 X_90_width : 10.2 [us]
 X_acq_time : 0.69730304 [s]
 X_angle : 30 [deg]
 X_atn : 7.9 [dB]
 X_pulse : 3.4 [us]
 irr_atn_dec : 16 [dB]
 irr_atn_noe : 16 [dB]
 irr_noise : WALTZ
 Decoupling : TRUE
 Initial_wait : 1 [s]
 Noe : TRUE
 Noe_time : 2 [s]
 Relaxation_delay : 2 [s]
 Repetition_time : 2.69730304 [s]
 Experiment : single_pulse_dec
 Recvr_gain : 60
 Solvent : CHLOROFORM-D
 Temp_get : 26.1 [dC]
 Spin_get : 14 [Hz]
 Probe_id : 2692



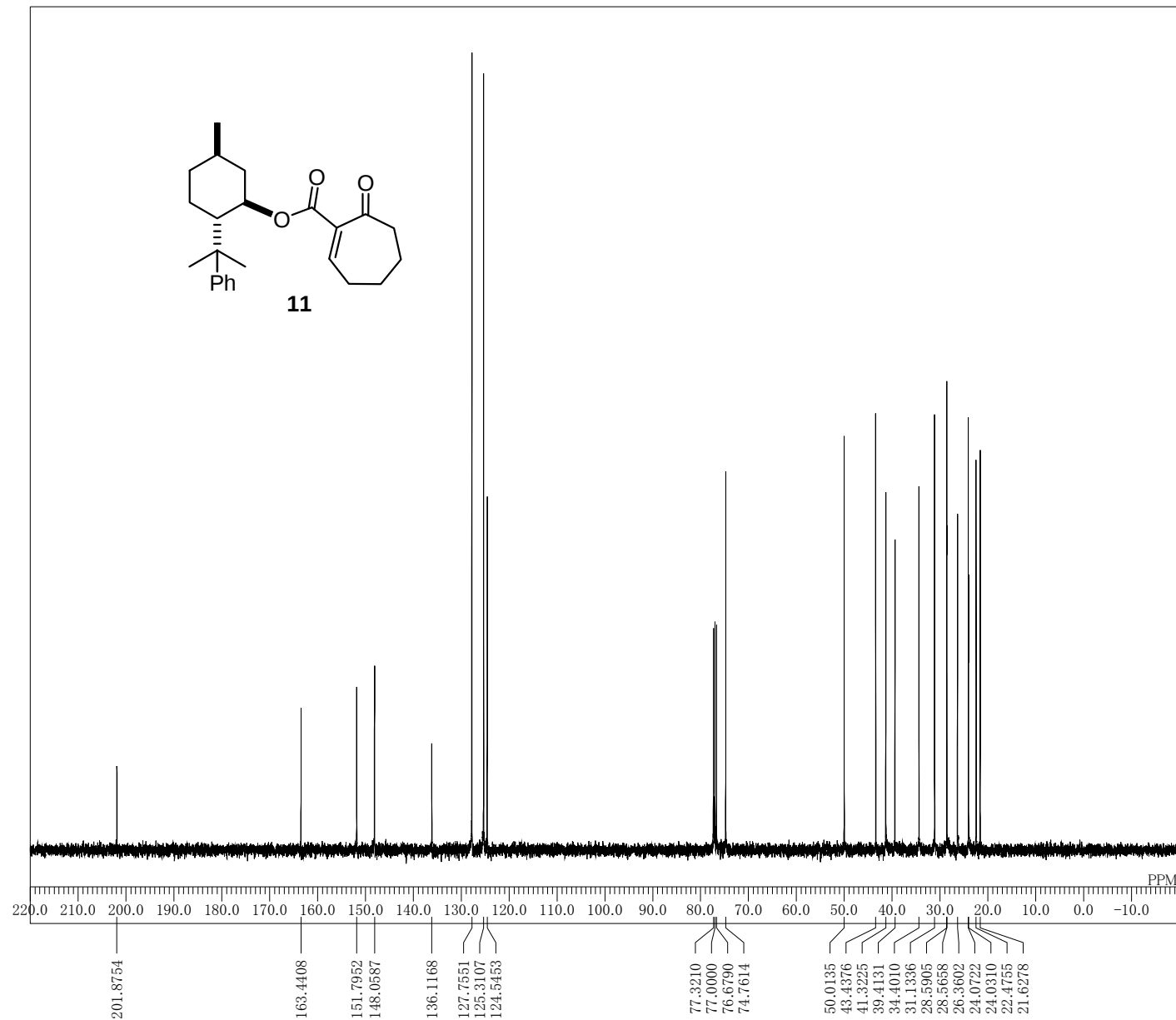
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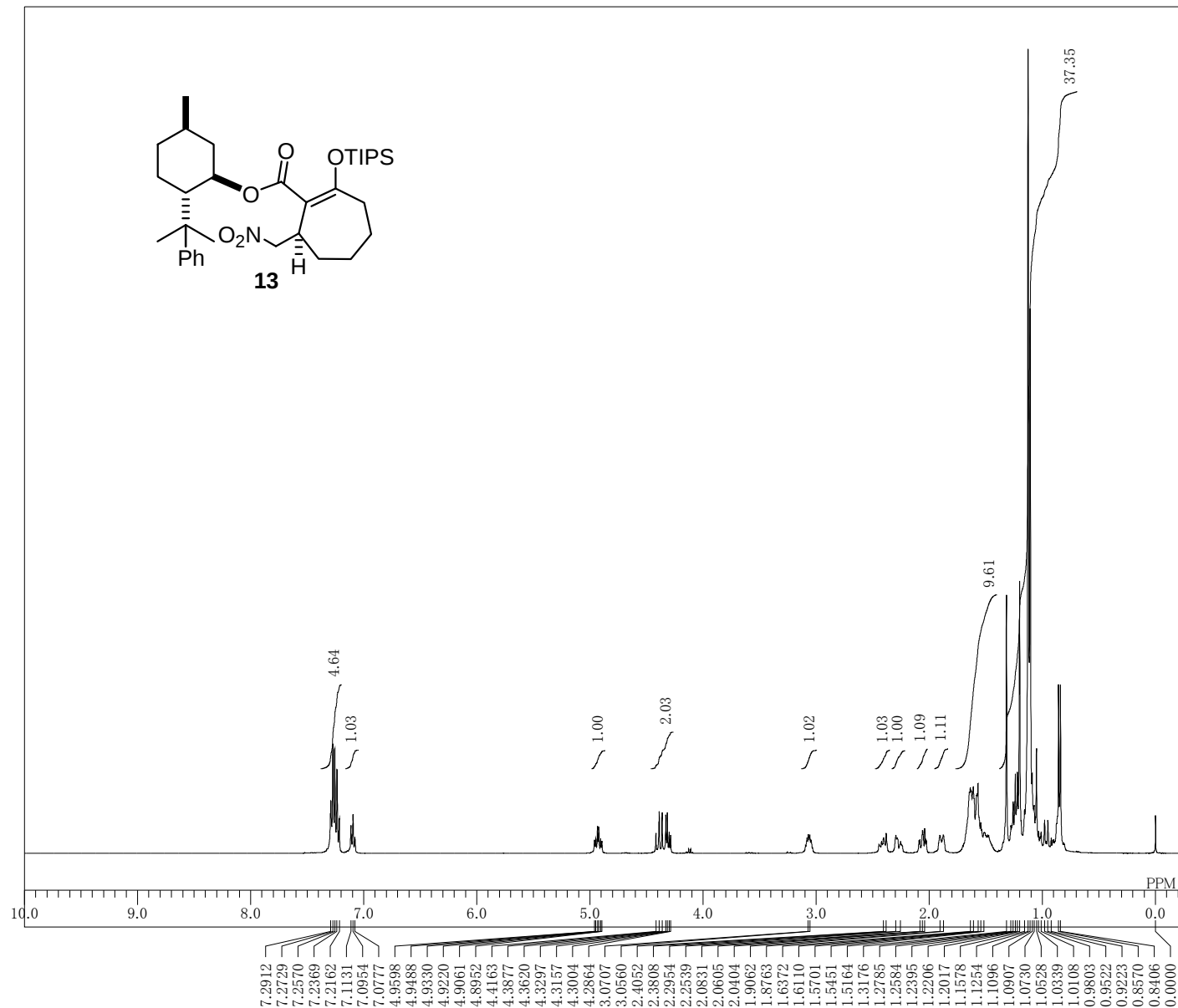
DATIM Mon Dec 03 17:25:47 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\池田\1572.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 21.8 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.40 Hz
 RGAIN 15



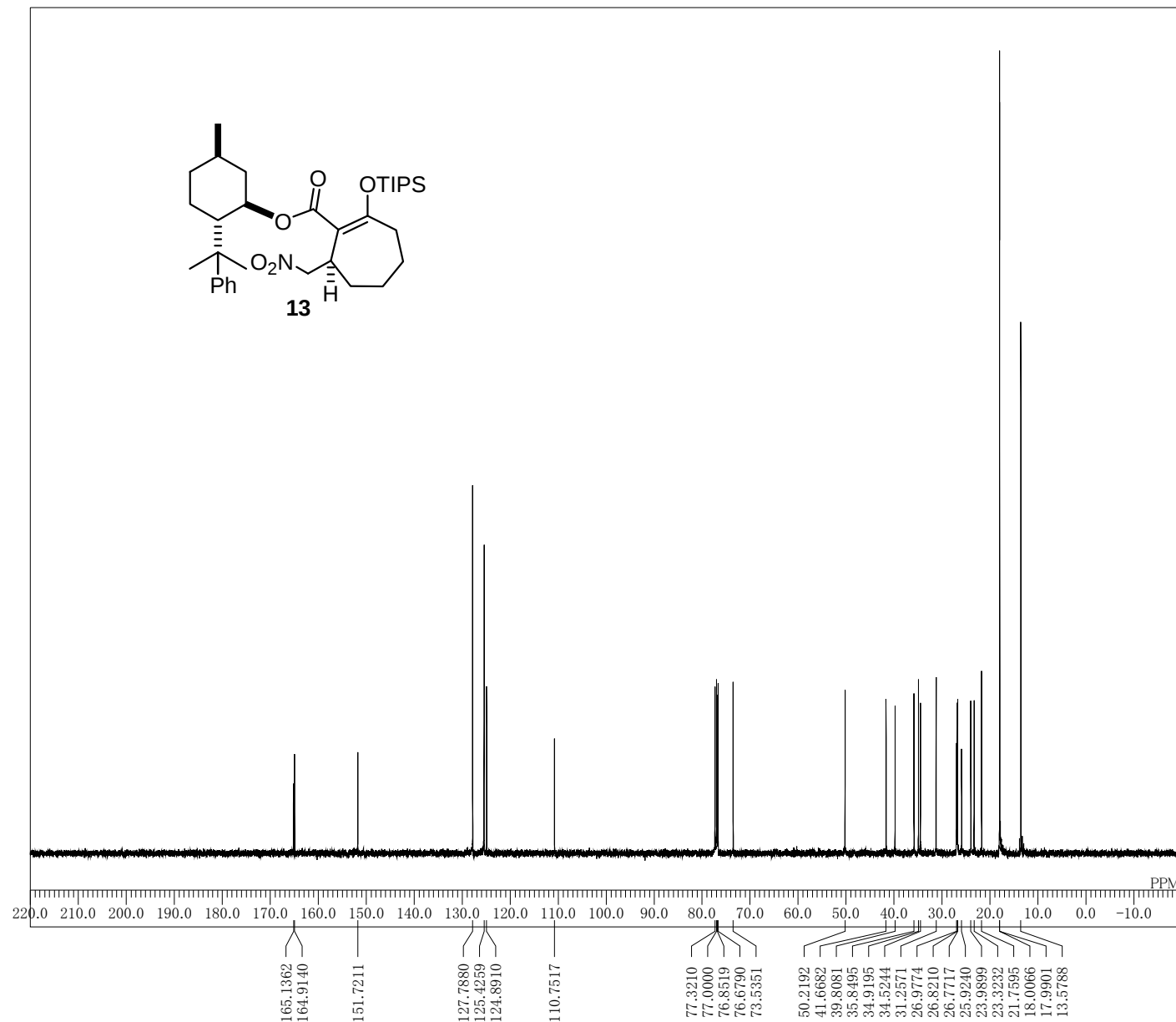
DATIM Tue Dec 04 22:27:51 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1575-2H.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 22.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.43 Hz
 RGAIN 7



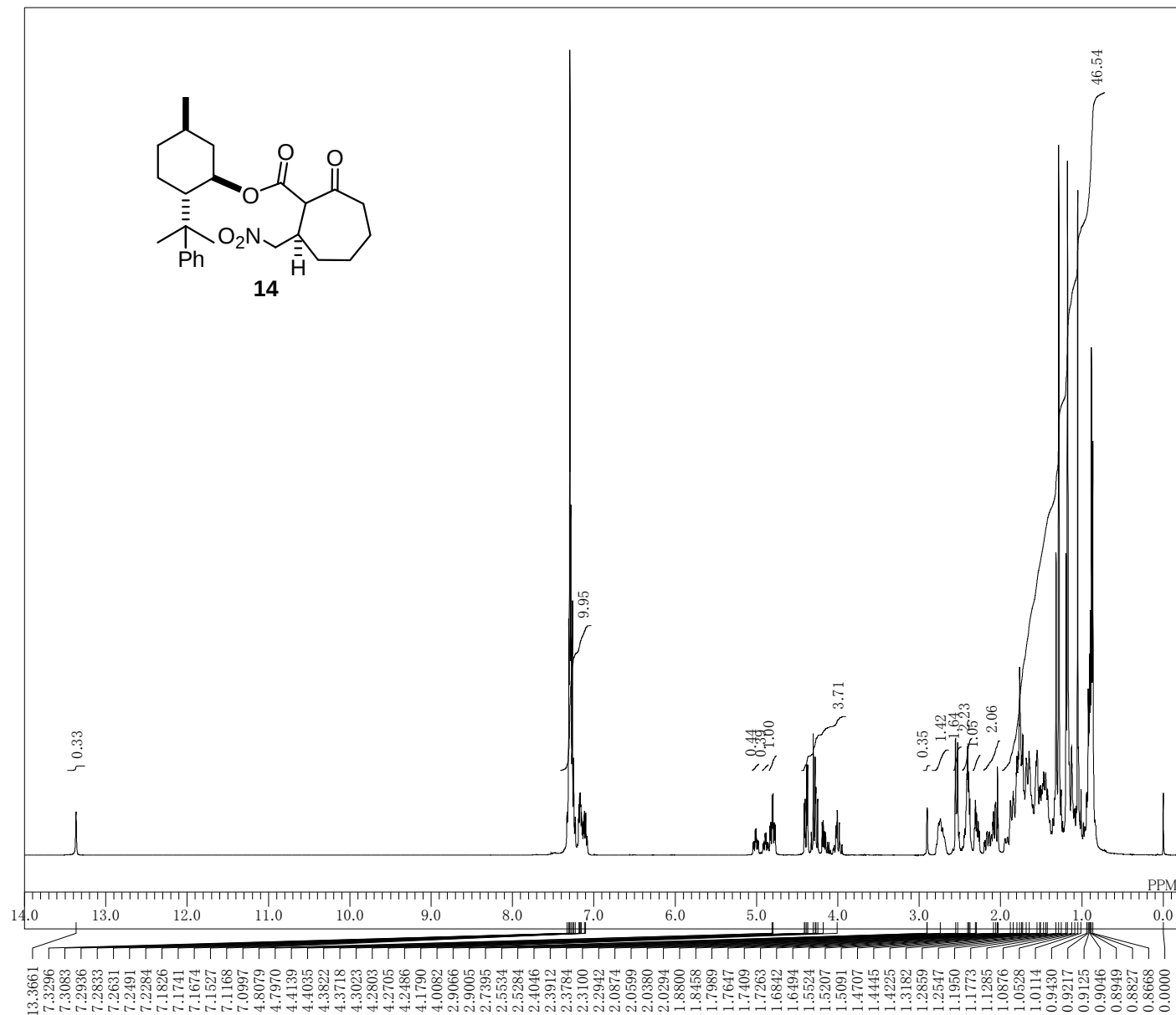
DATIM Tue Dec 04 22:31:28 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1575-2C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 56
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 22.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.13 Hz
 RGAIN 23



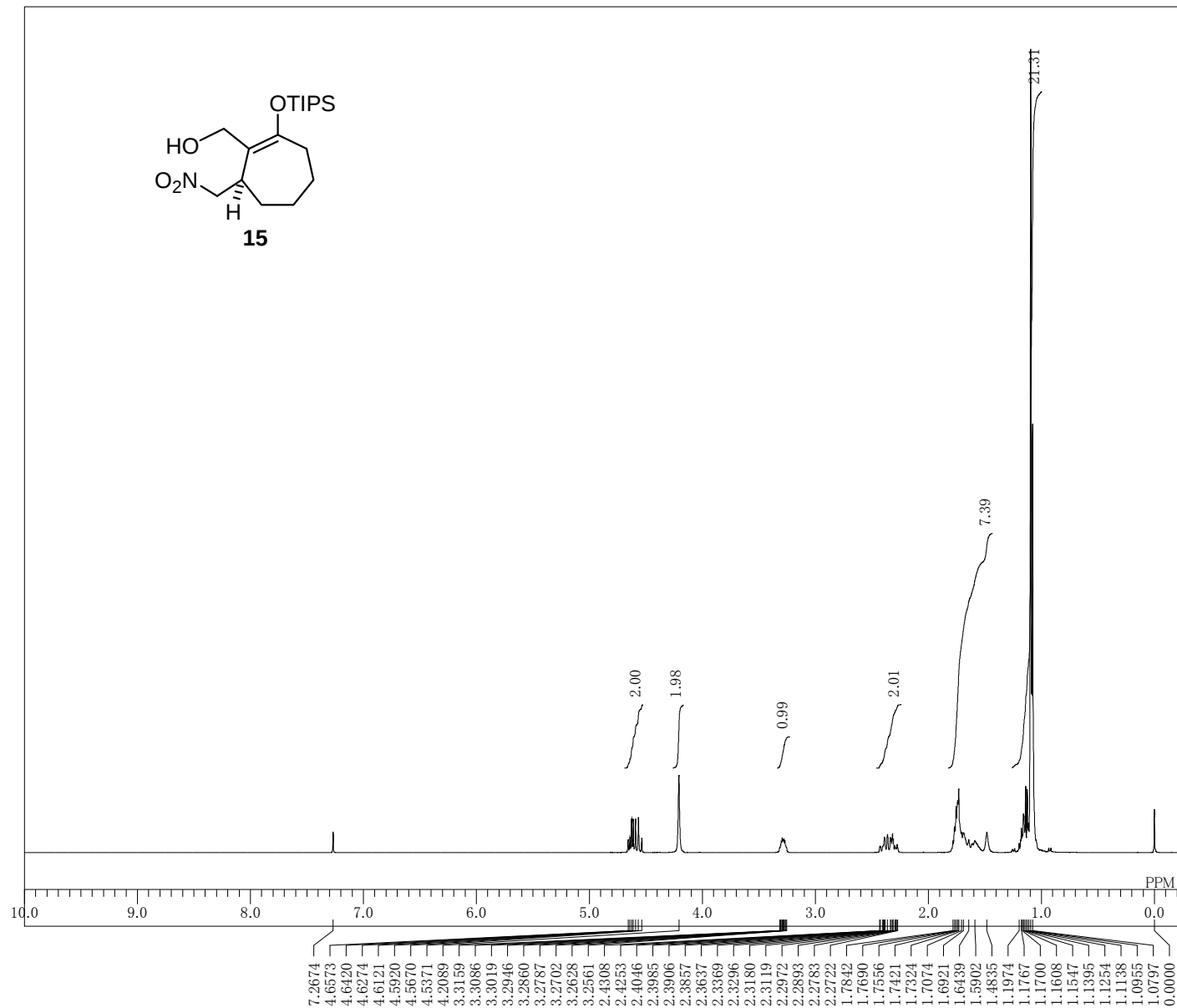
DATIM Thu Jan 22 18:53:53 2009
 DFILE C:\My Documents\個人ファイル\NMR AL400\1982-1.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 10



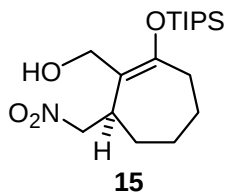
DATIM Thu Dec 06 10:14:48 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1578-1C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.93 Hz
 RGAIN 23



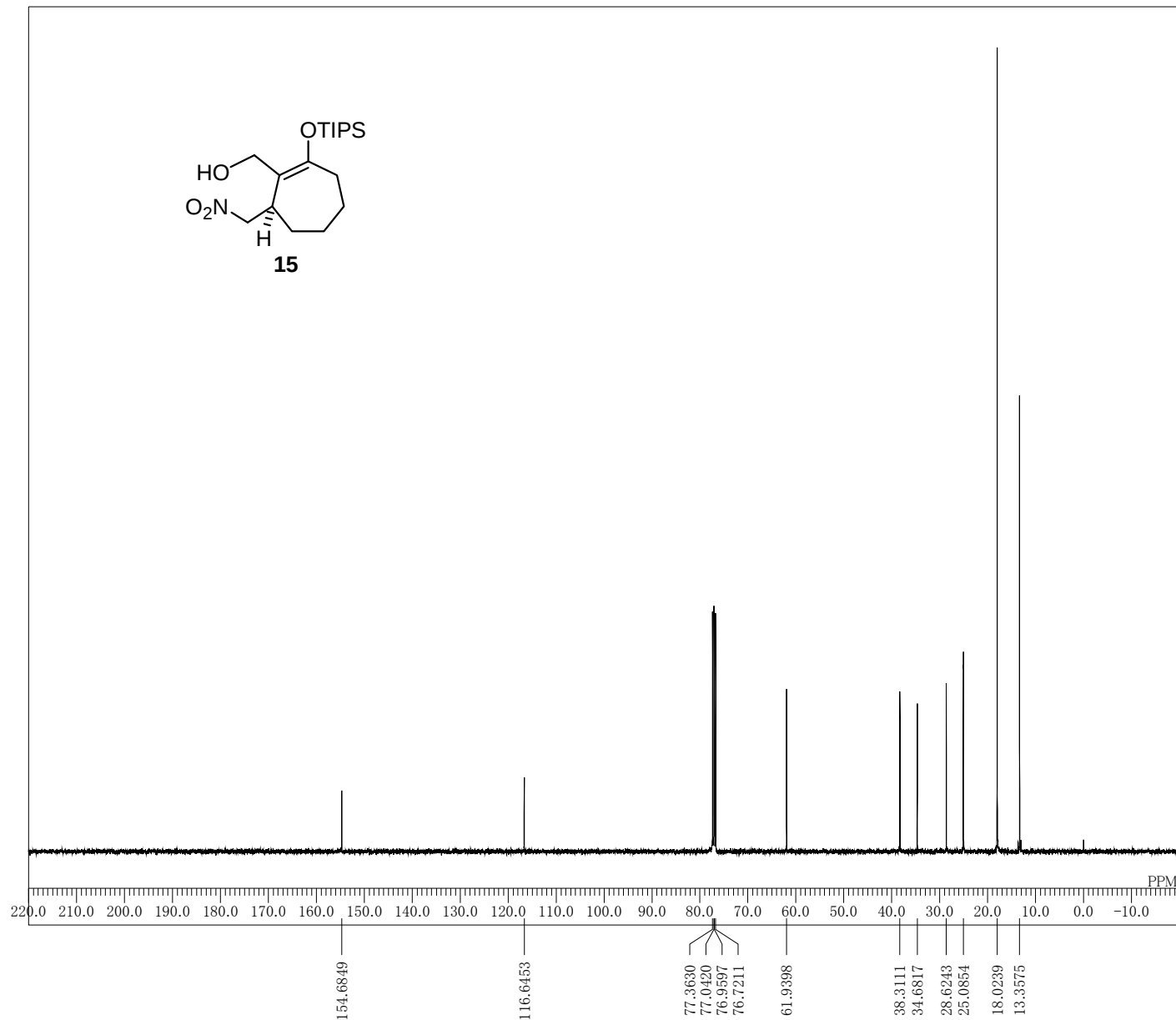
DATIM Thu Dec 06 10:20:30 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1578-2.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.43 Hz
 RGAIN 10

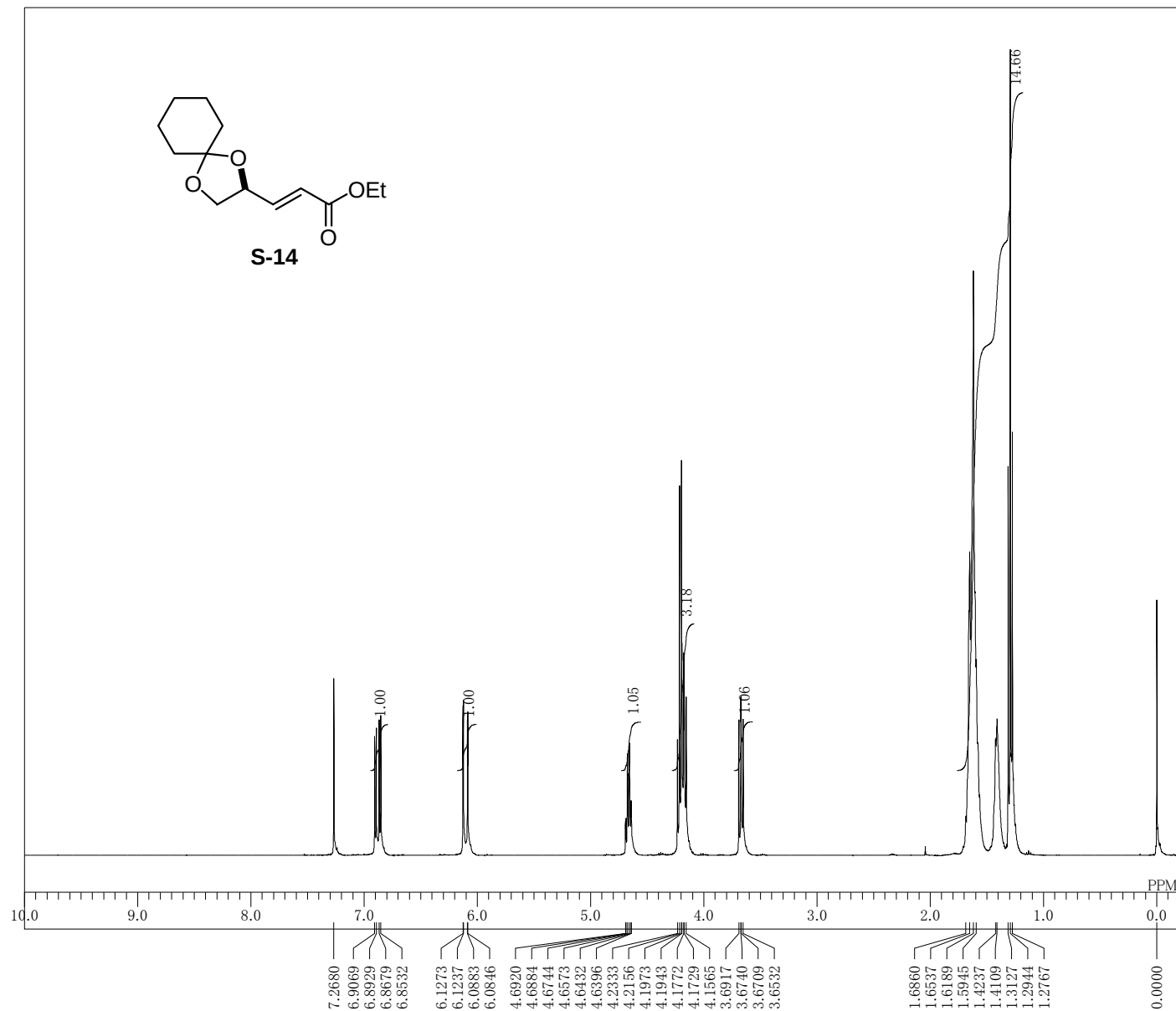


DATIM Sat May 19 18:43:15 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1398.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 26.0 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.32 Hz
 RGAIN 11

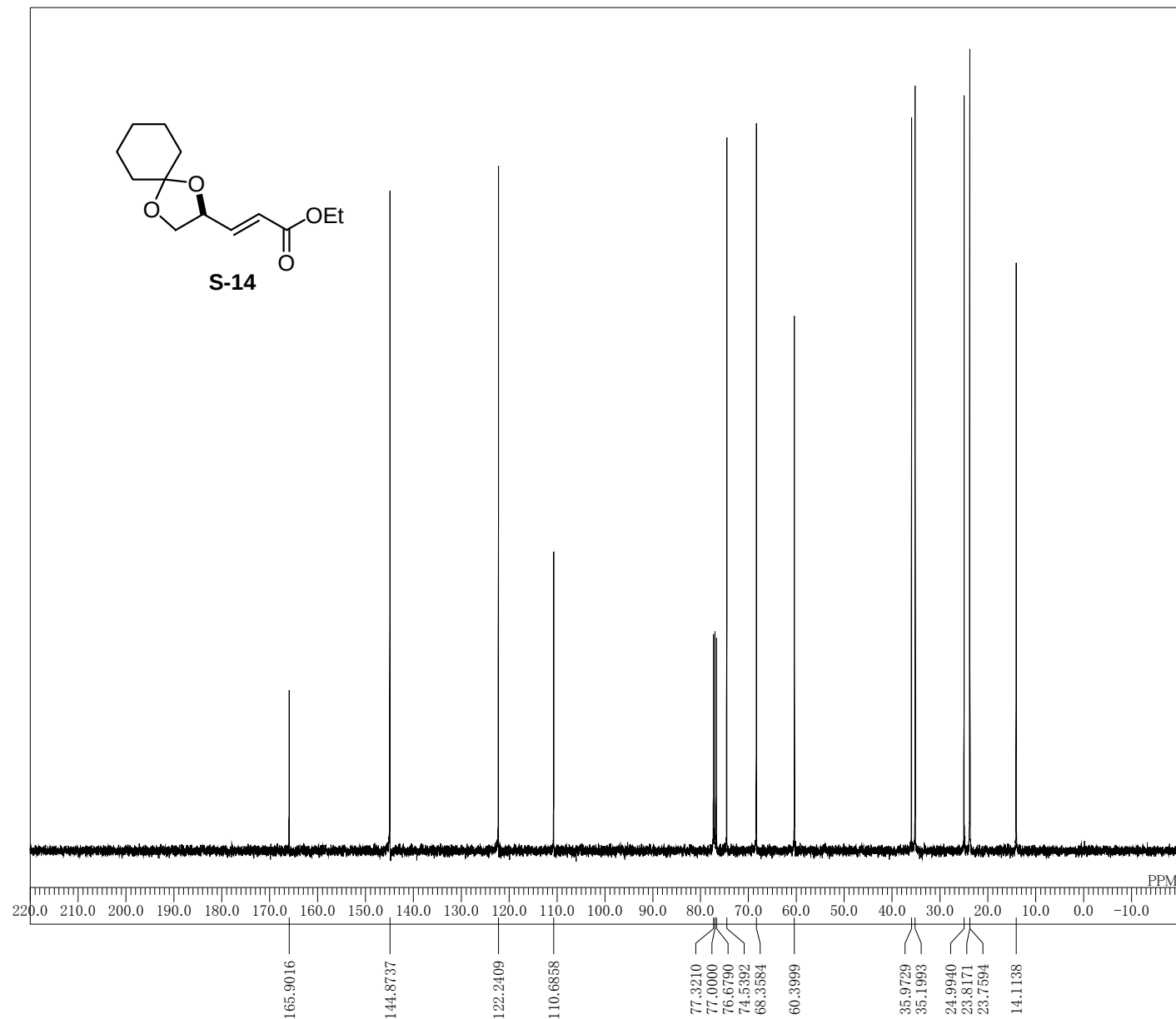


DATIM Sat May 19 21:11:01 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1398C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 777
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 28.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 1.22 Hz
 RGAIN 24

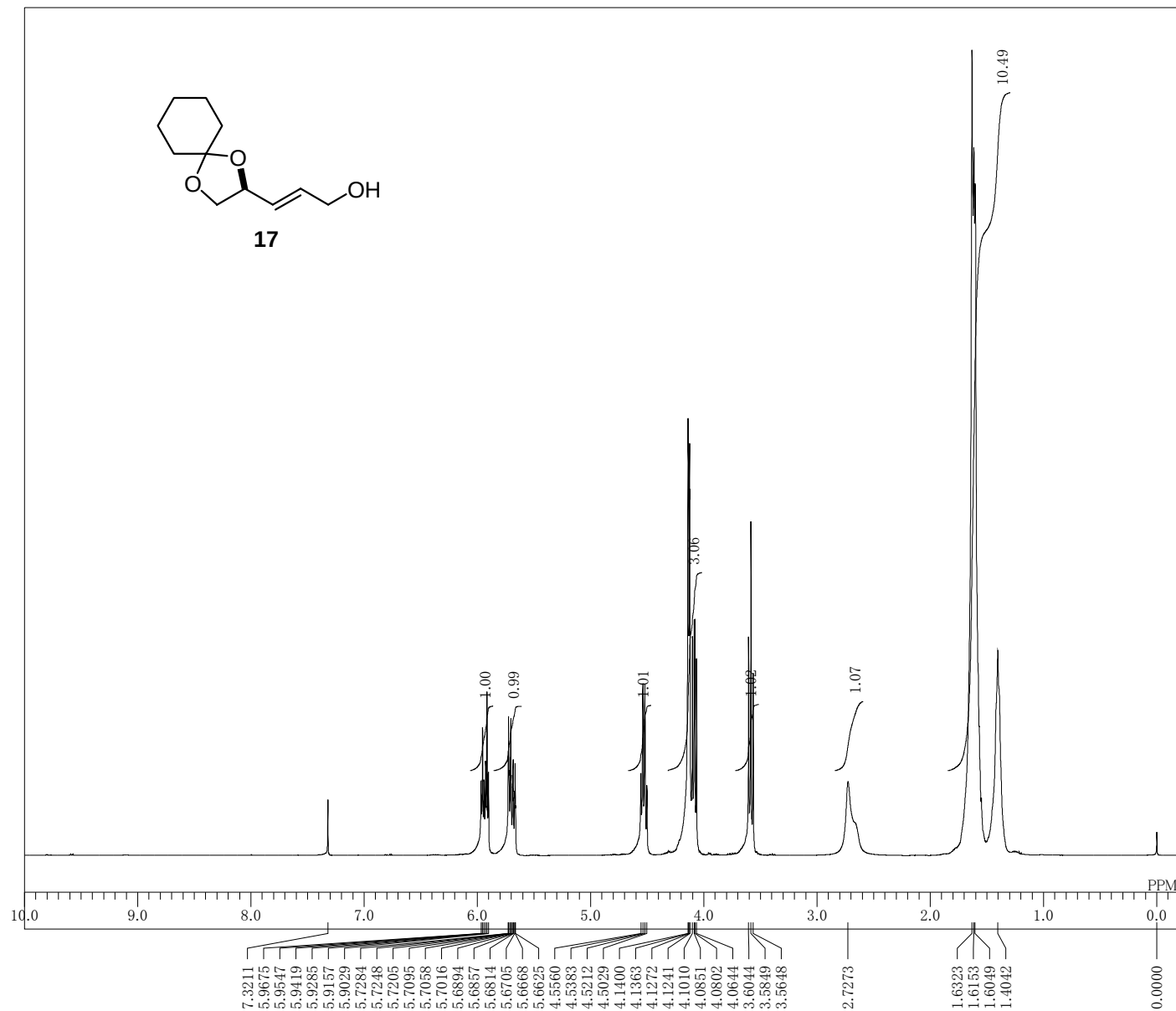




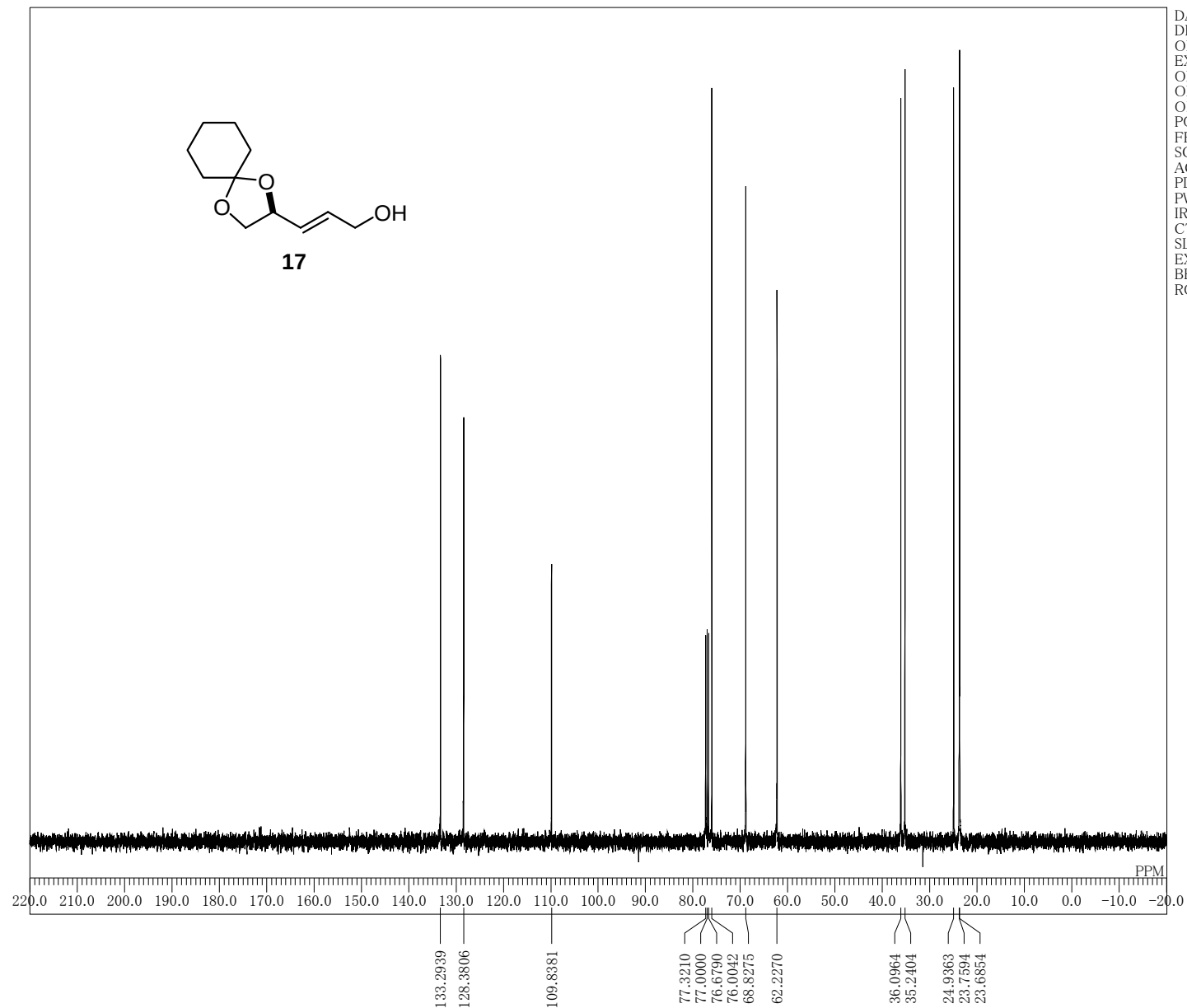
DATIM Wed Oct 03 16:37:51 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1510.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 24.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 13



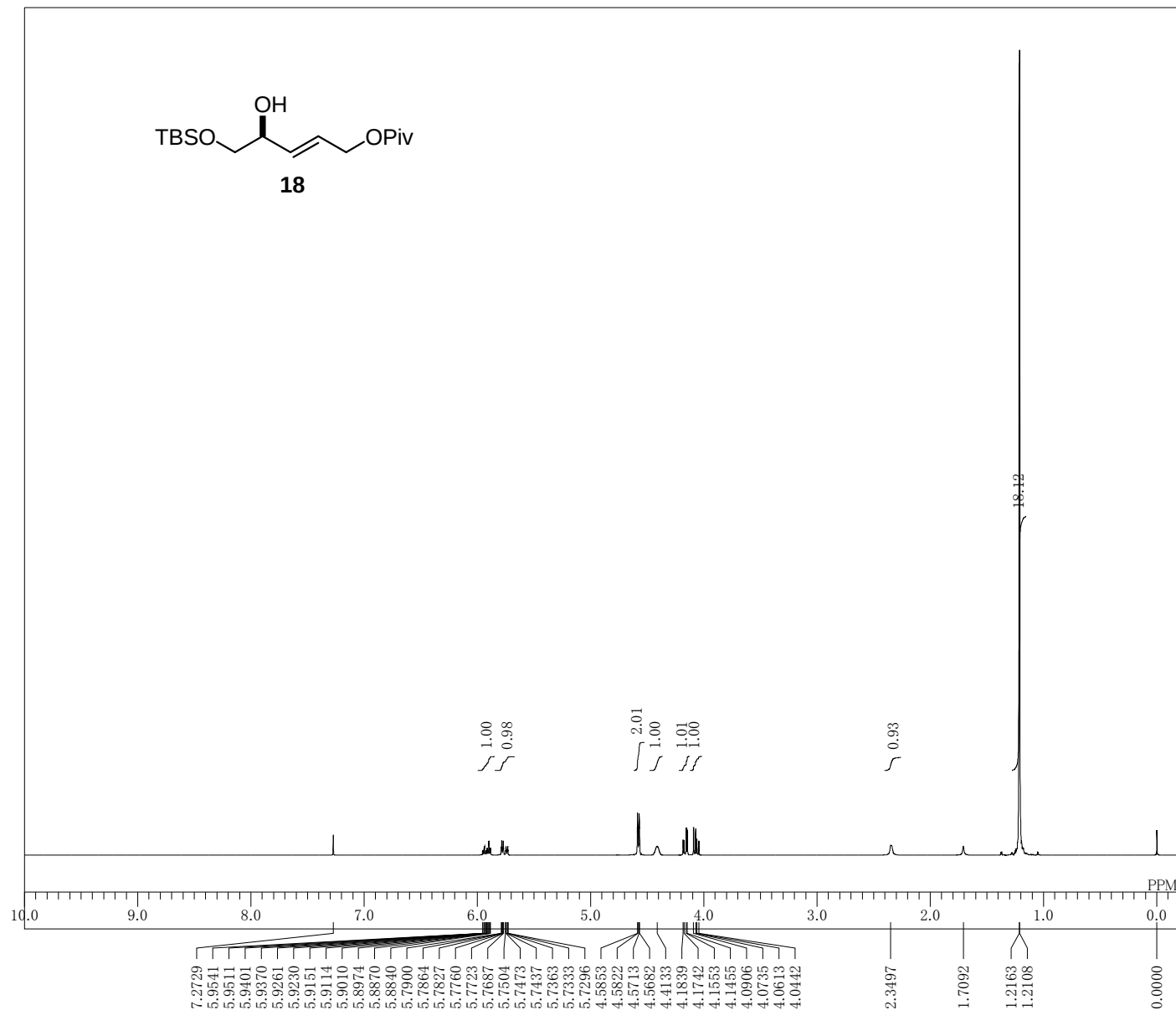
DATIM Tue Jun 24 17:38:59 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\池田\cyclohexylen-ethylesterC.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 28.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 24



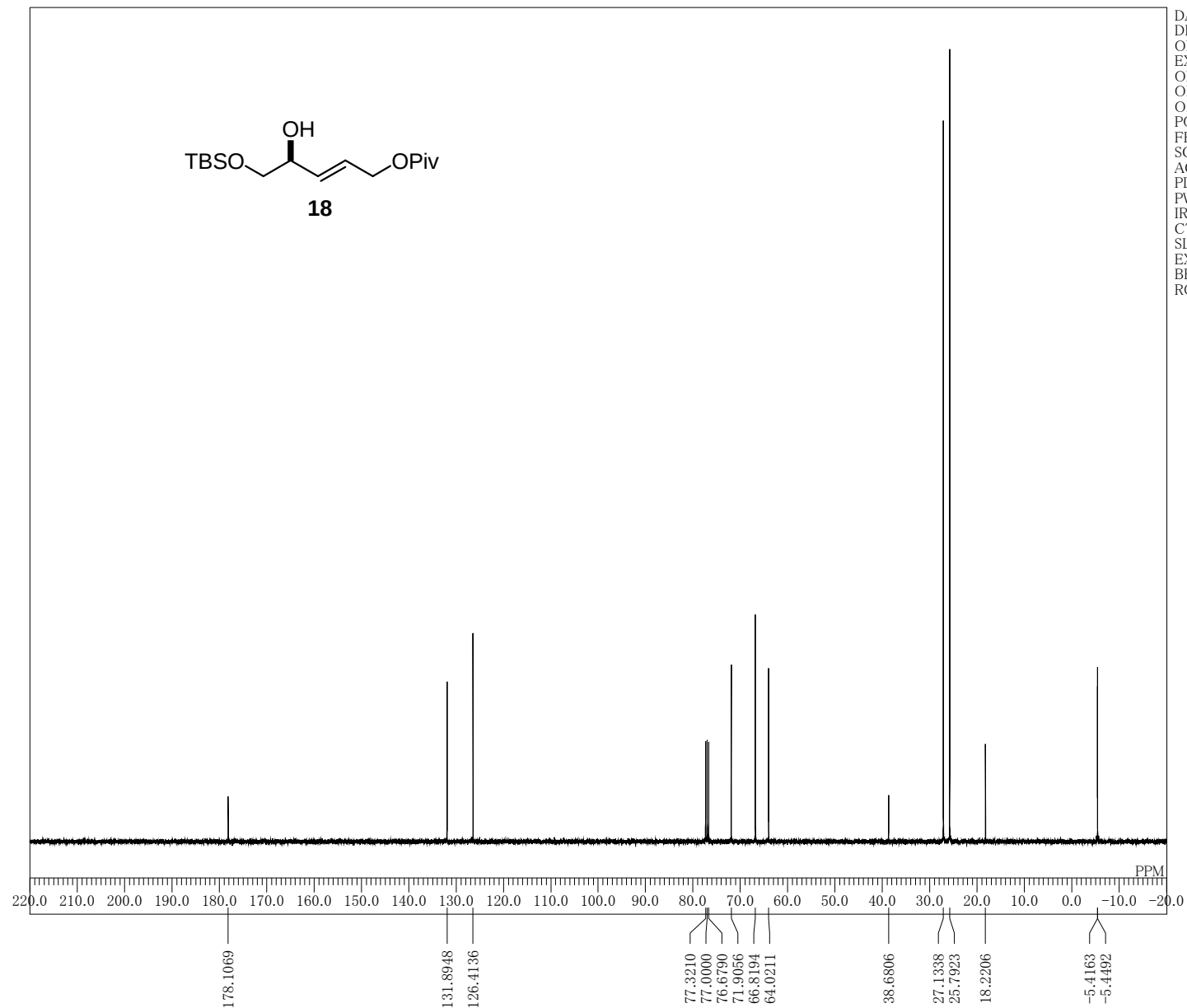
DATIM Thu Aug 28 17:34:12 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\池田\Chiralallyl alcohol-H.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 8



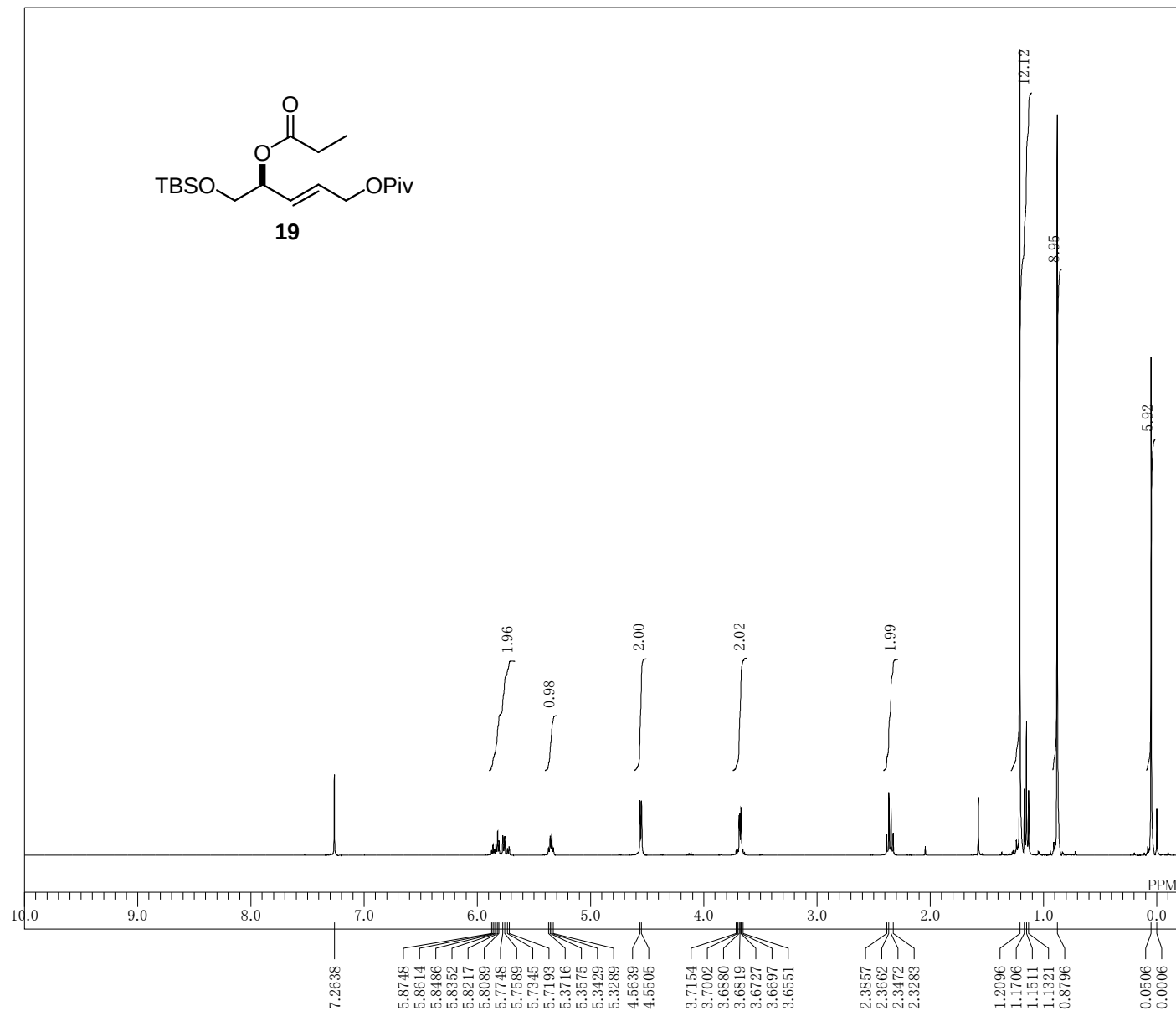
DATIM Thu Aug 28 17:37:00 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\p
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 32
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.0 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 23



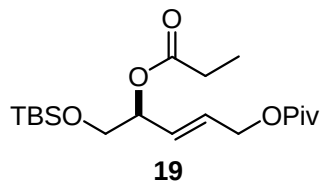
DATIM	Fri Oct 26 18:29:32 2007
DFILE	C:\My Documents\個人ファイル\NMR AL400\
OBNUC	¹ H
EXMOD	NON
OFR	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	32768
FREQU	7912.96 Hz
SCANS	16
ACQTM	4.1411 sec
PD	2.8590 sec
PW1	5.80 usec
IRN	
CTEMP	25.1 c
SLVNT	CDCL ₃
EXREF	0.00 ppm
BF	0.33 Hz
RGAIN	12



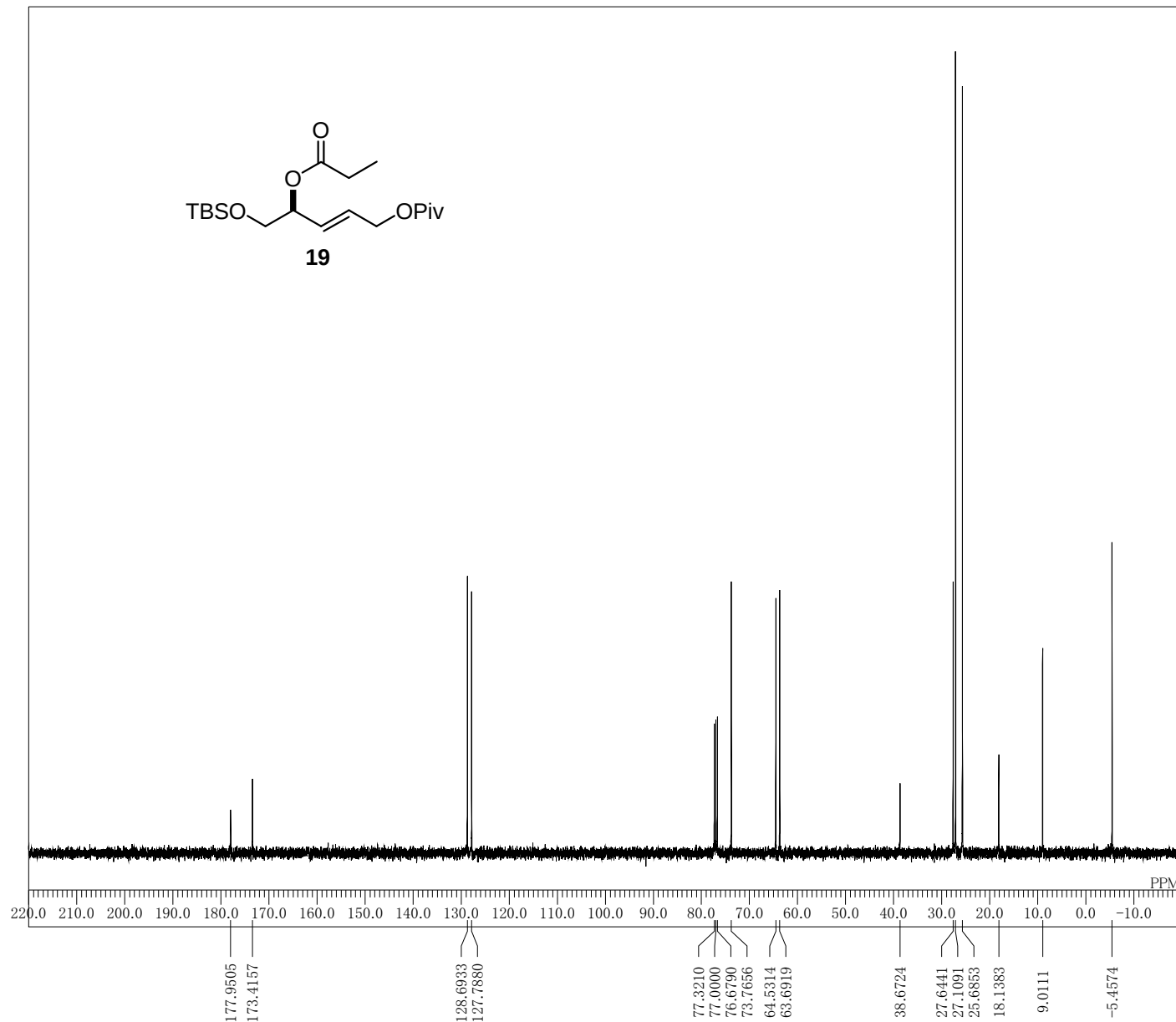
DATIM Wed Oct 31 10:55:19 2007
 DFILE C:\My Documents\個人ファイル\NMR AL400\1527C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 26.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.62 Hz
 RGAIN 22

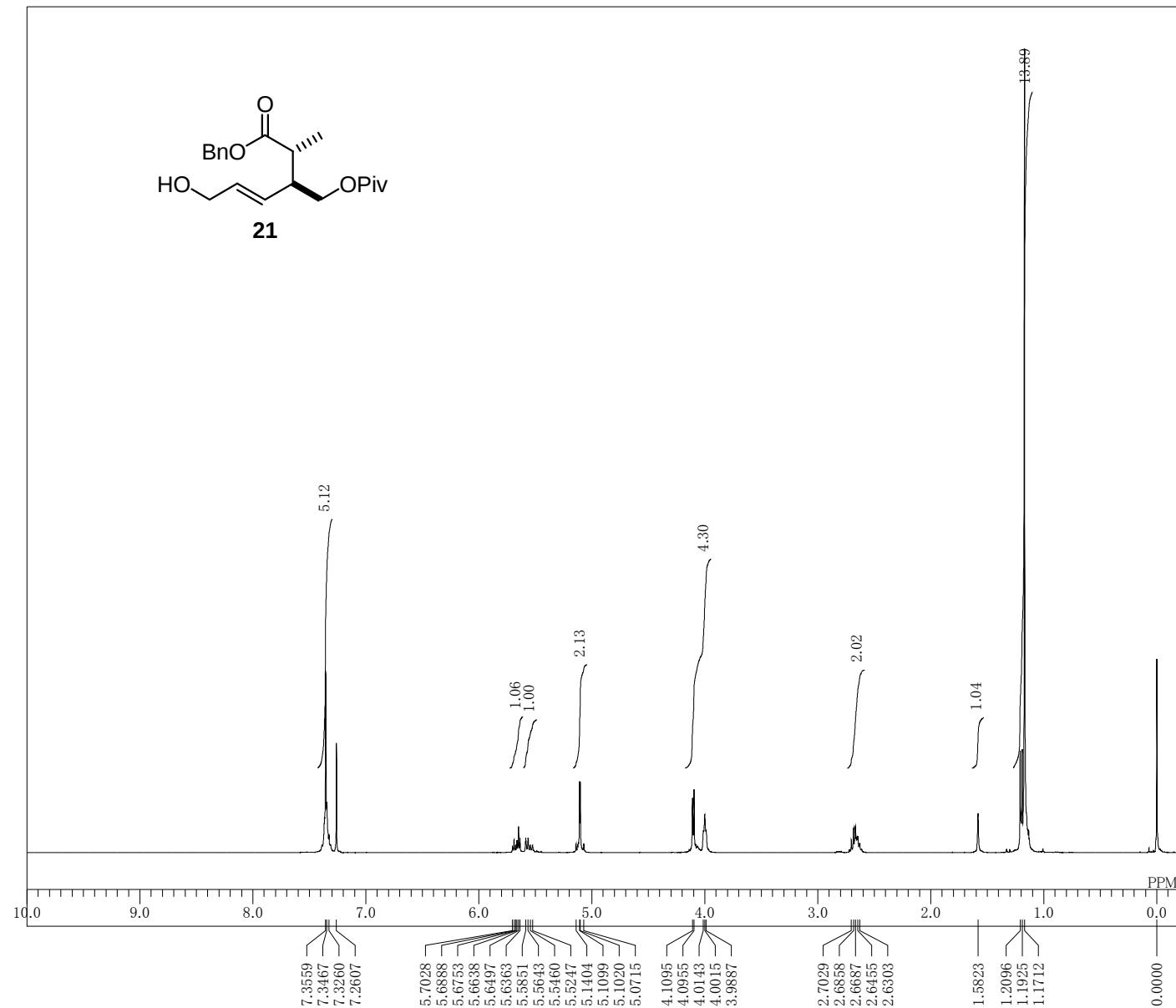
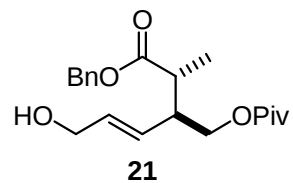


DATIM Tue Apr 15 18:08:15 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1702.als
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 8
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 14

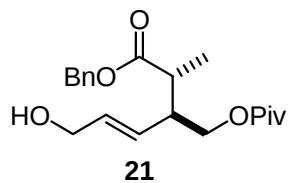


DATIM Thu Aug 28 17:42:16 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\池田\Chiral-ClaisenSM-C.als
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 32
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 22

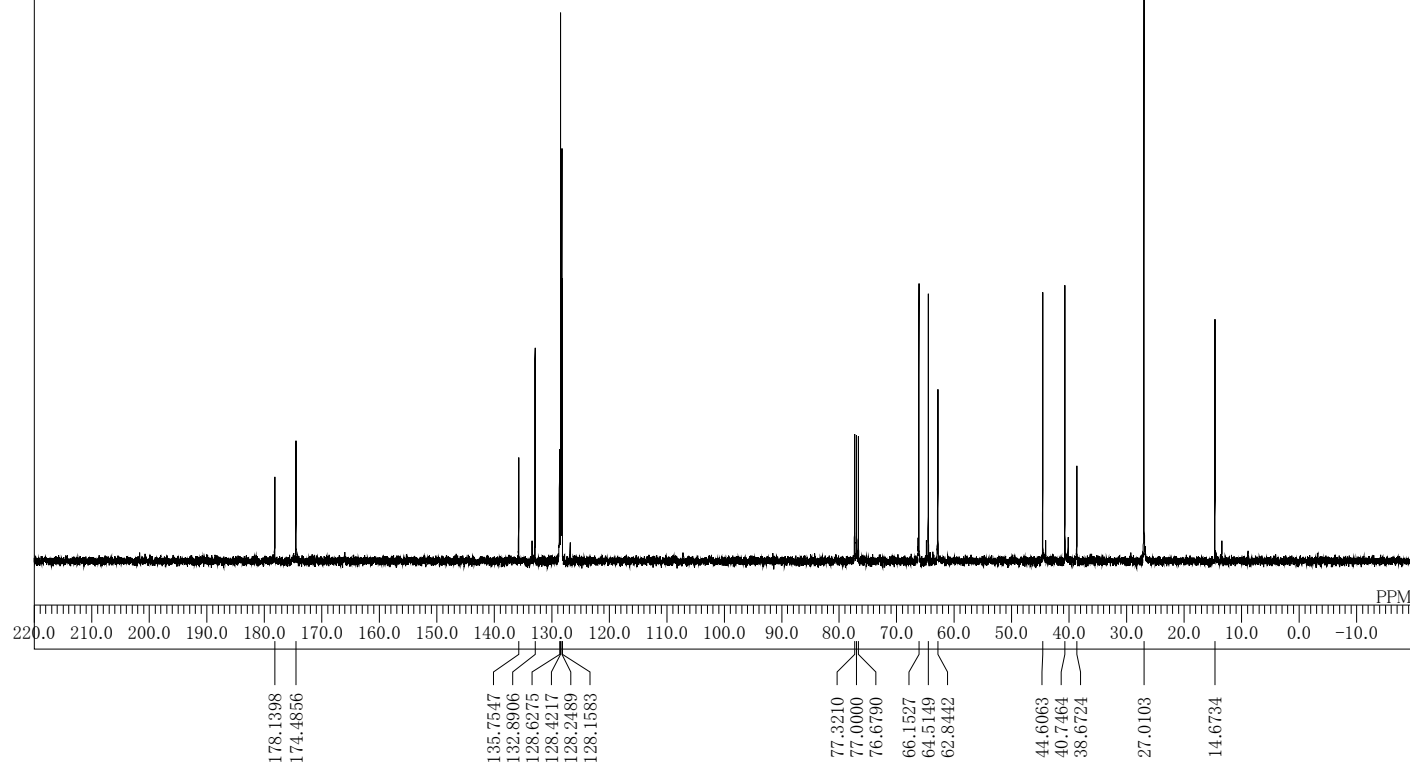


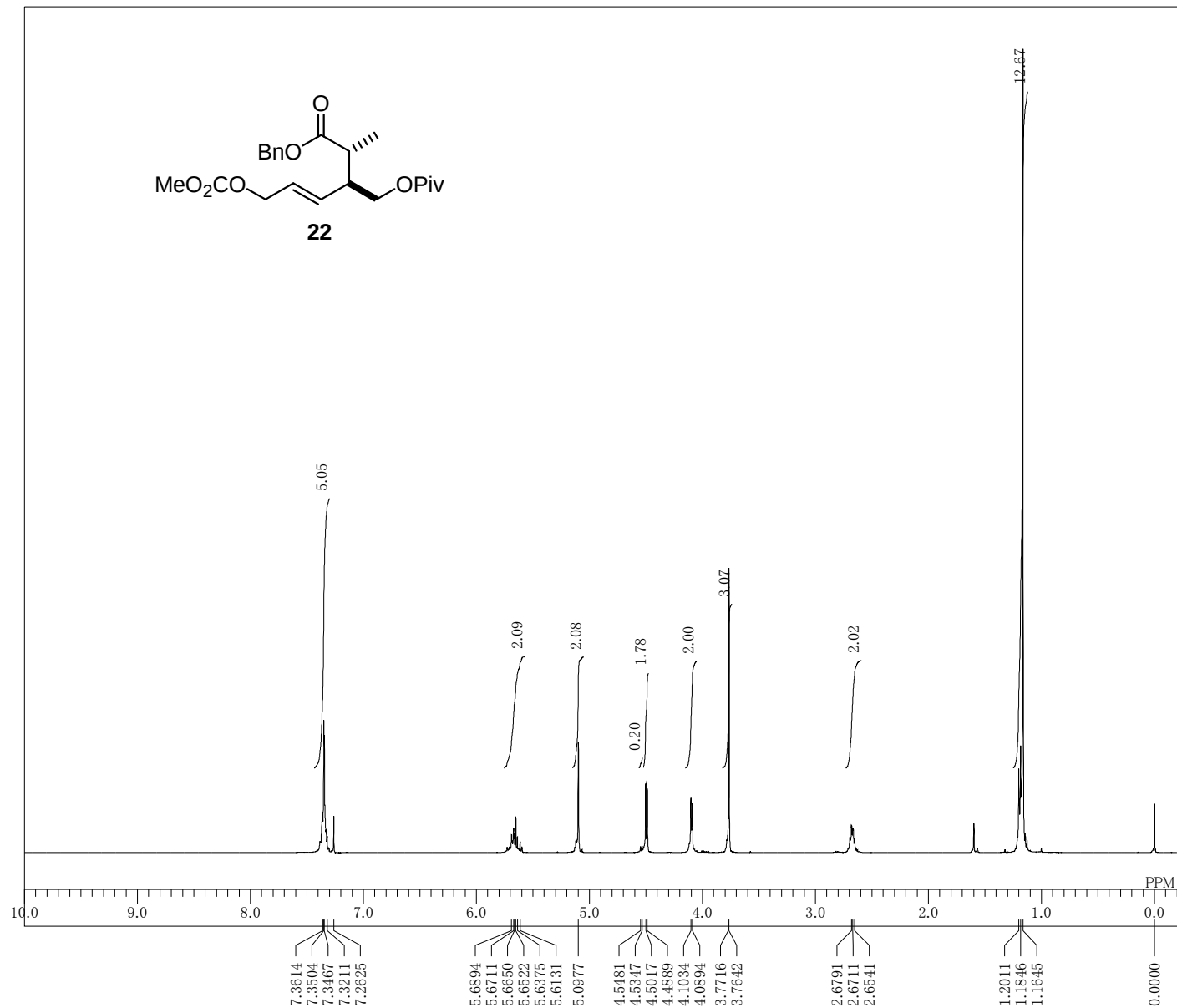
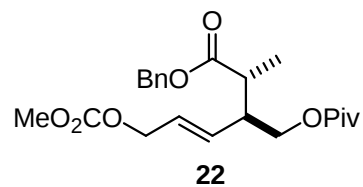


DATIM Wed Jun 11 20:18:52 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 26.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 18

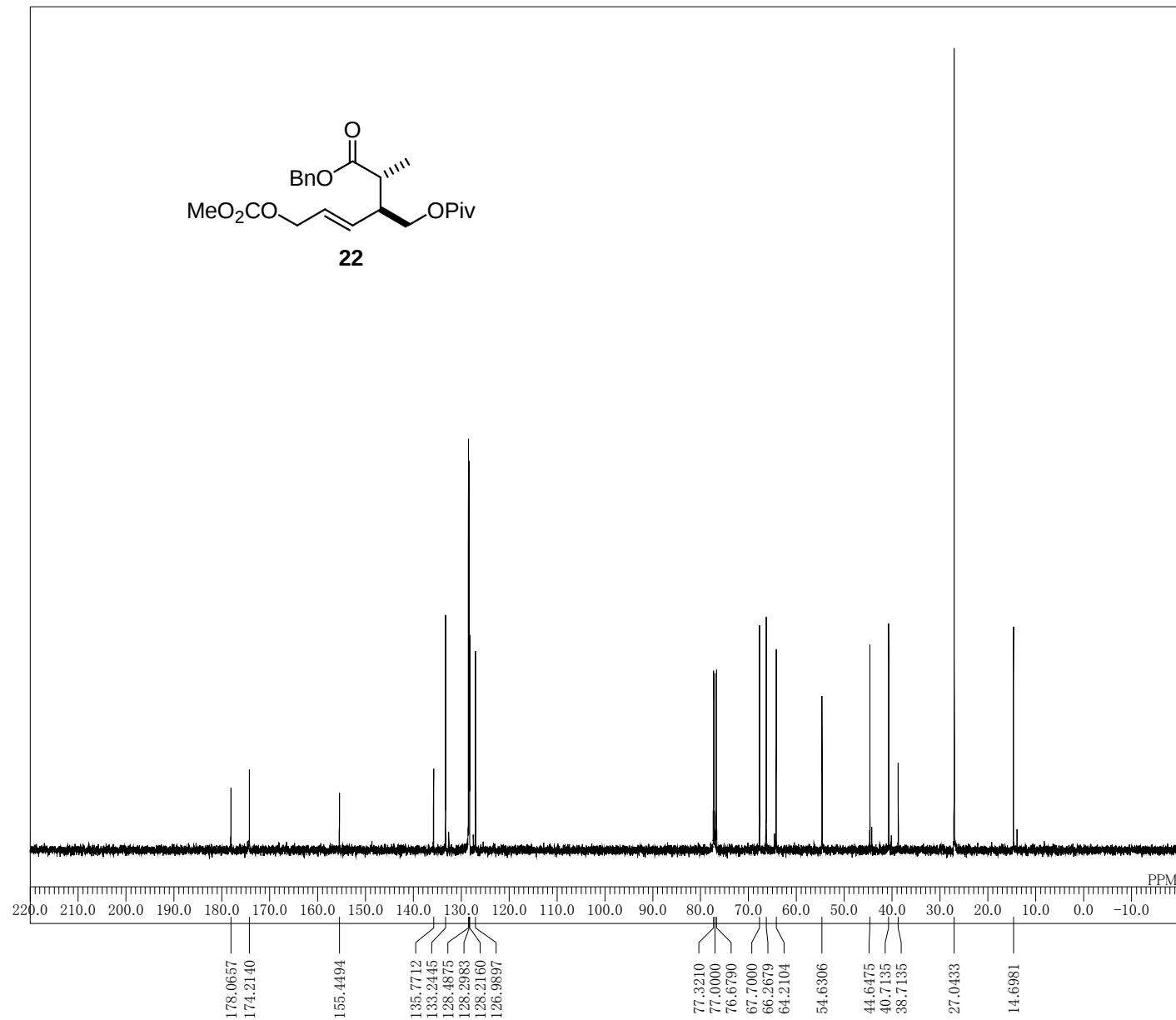
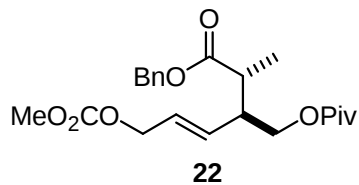


DATIM Thu Aug 28 17:49:09 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 64
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 22

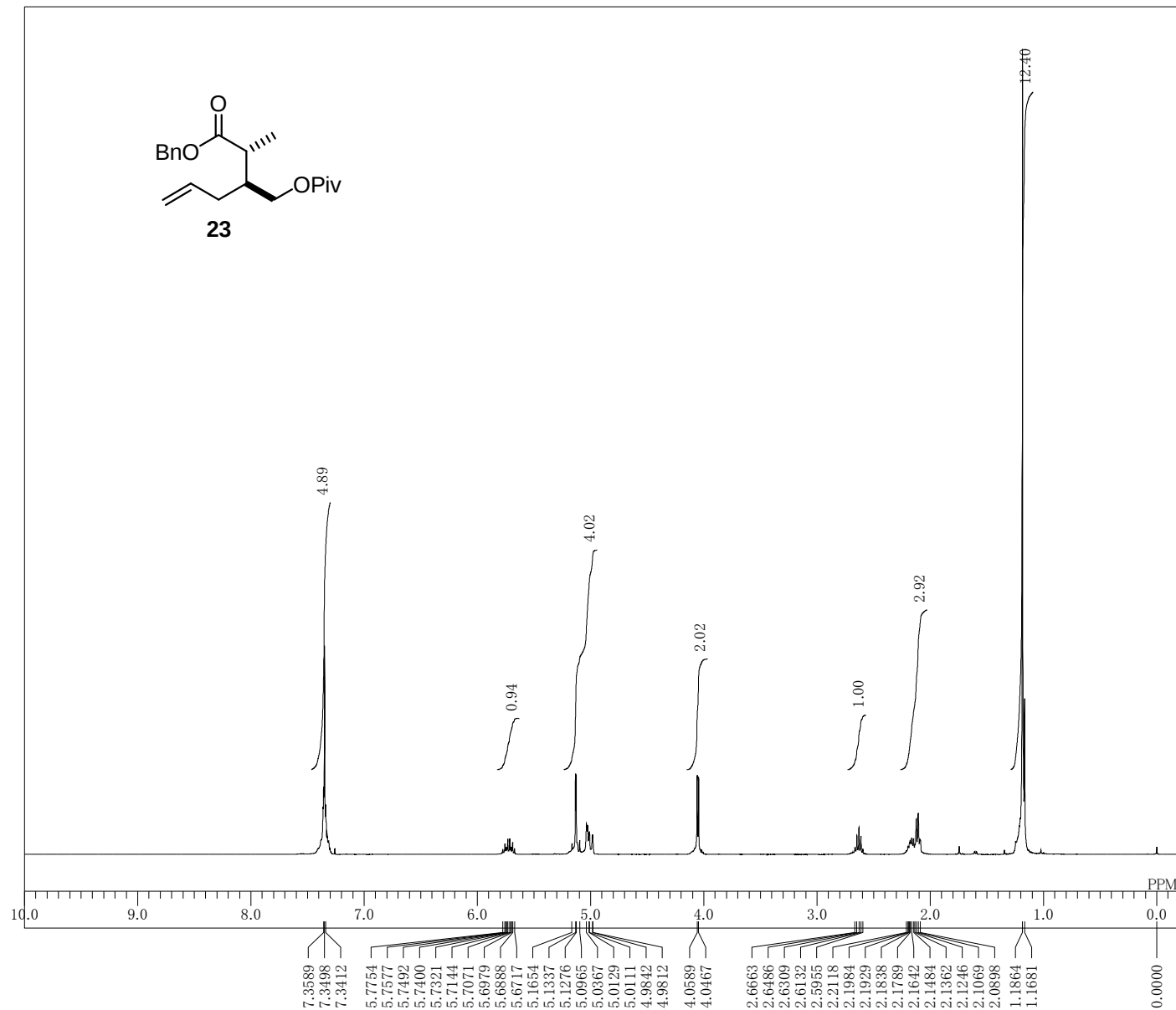
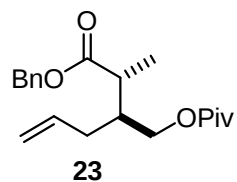




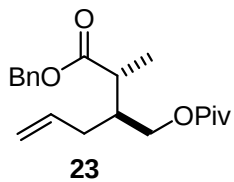
DATIM Fri Aug 29 11:09:01 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 32
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 26.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 14



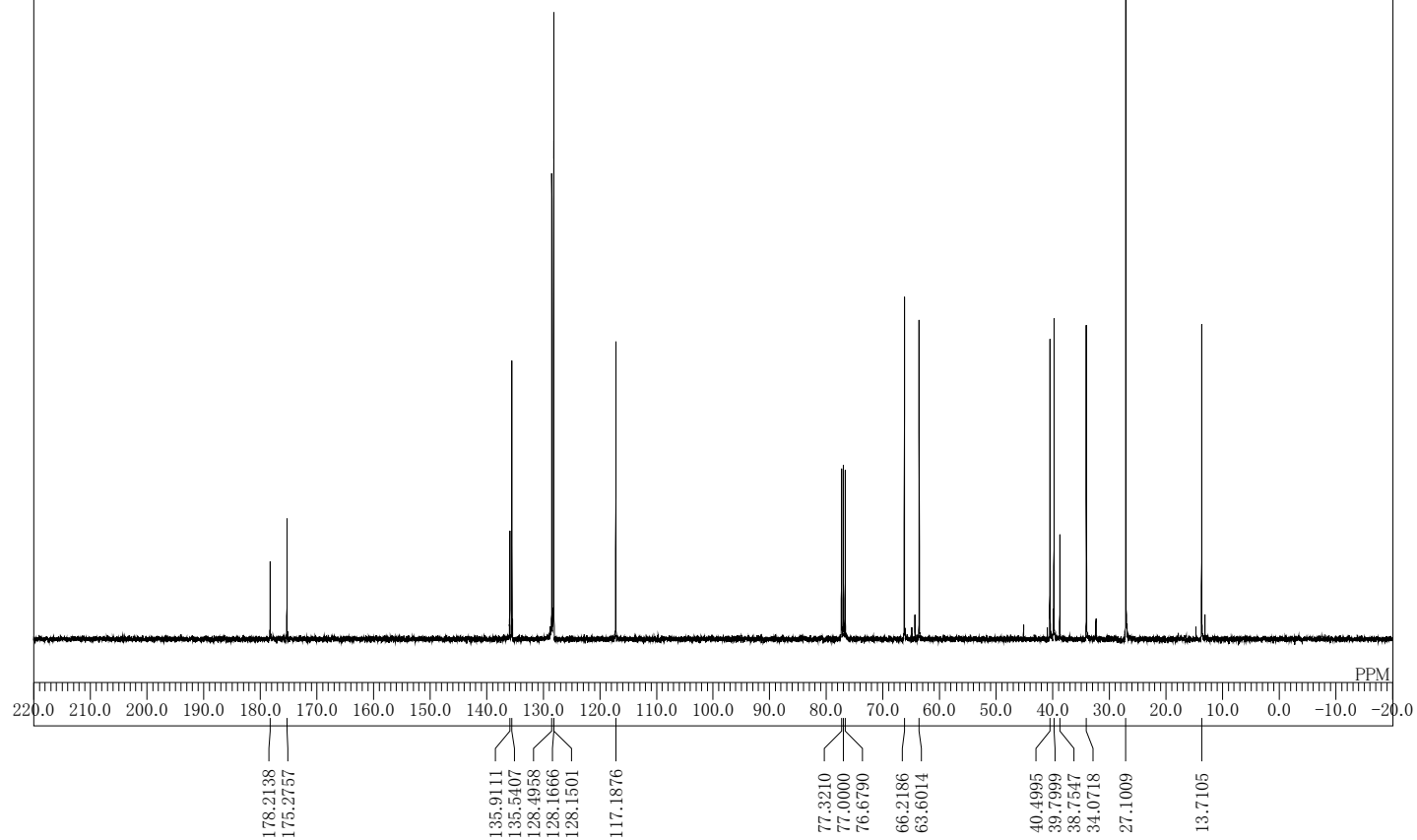
DATIM	Thu Aug 28 18:03:31 2008
DFILE	C:\My Documents\個人ファイル\NMR AL400\
OBNUC	¹³ C
EXMOD	BCM
OFR	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	128
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.40 usec
IRN	
CTEMP	27.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.12 Hz
RGAIN	24

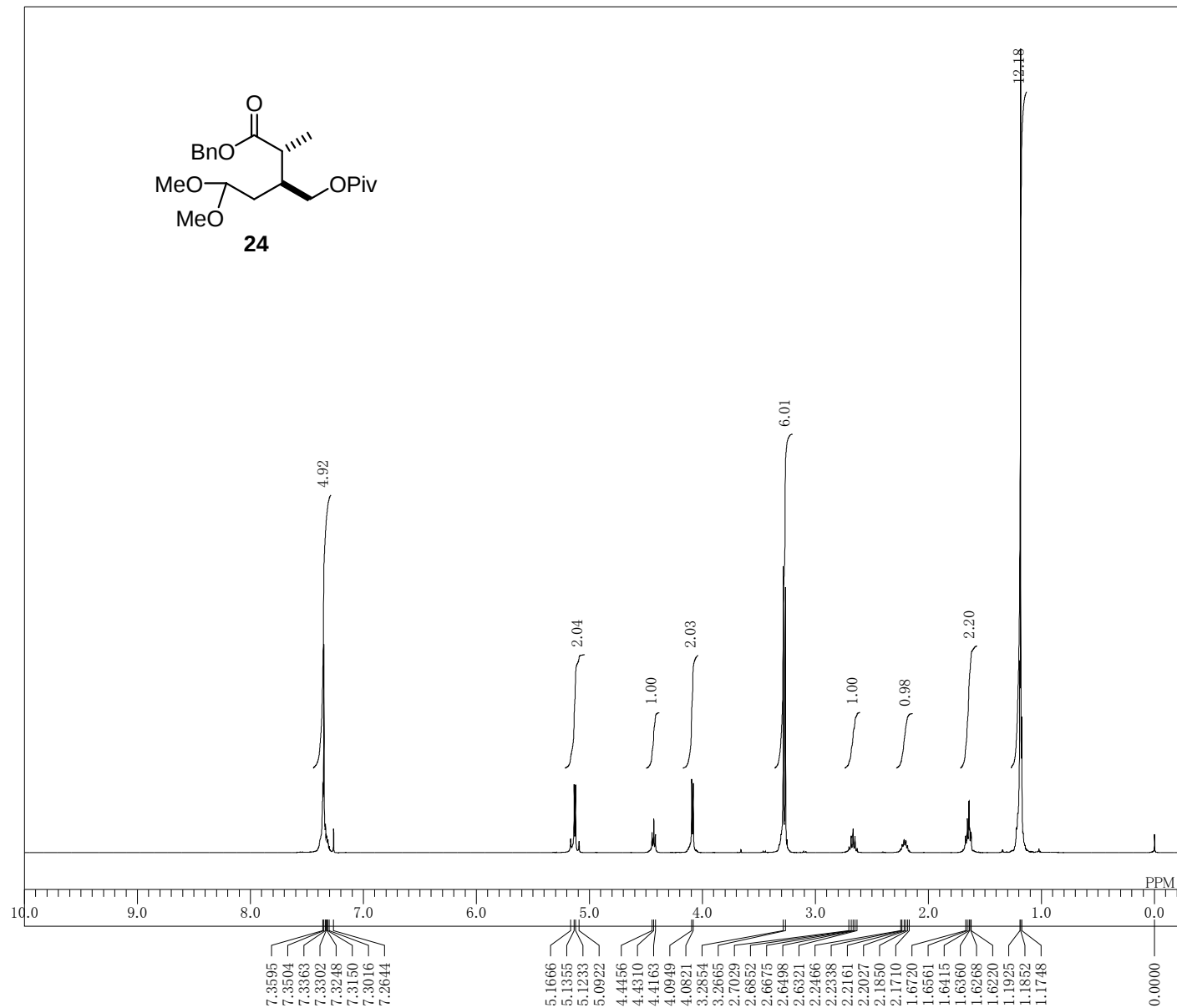
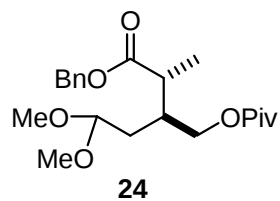


DATIM Tue Sep 02 14:23:37 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 26.7 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 9

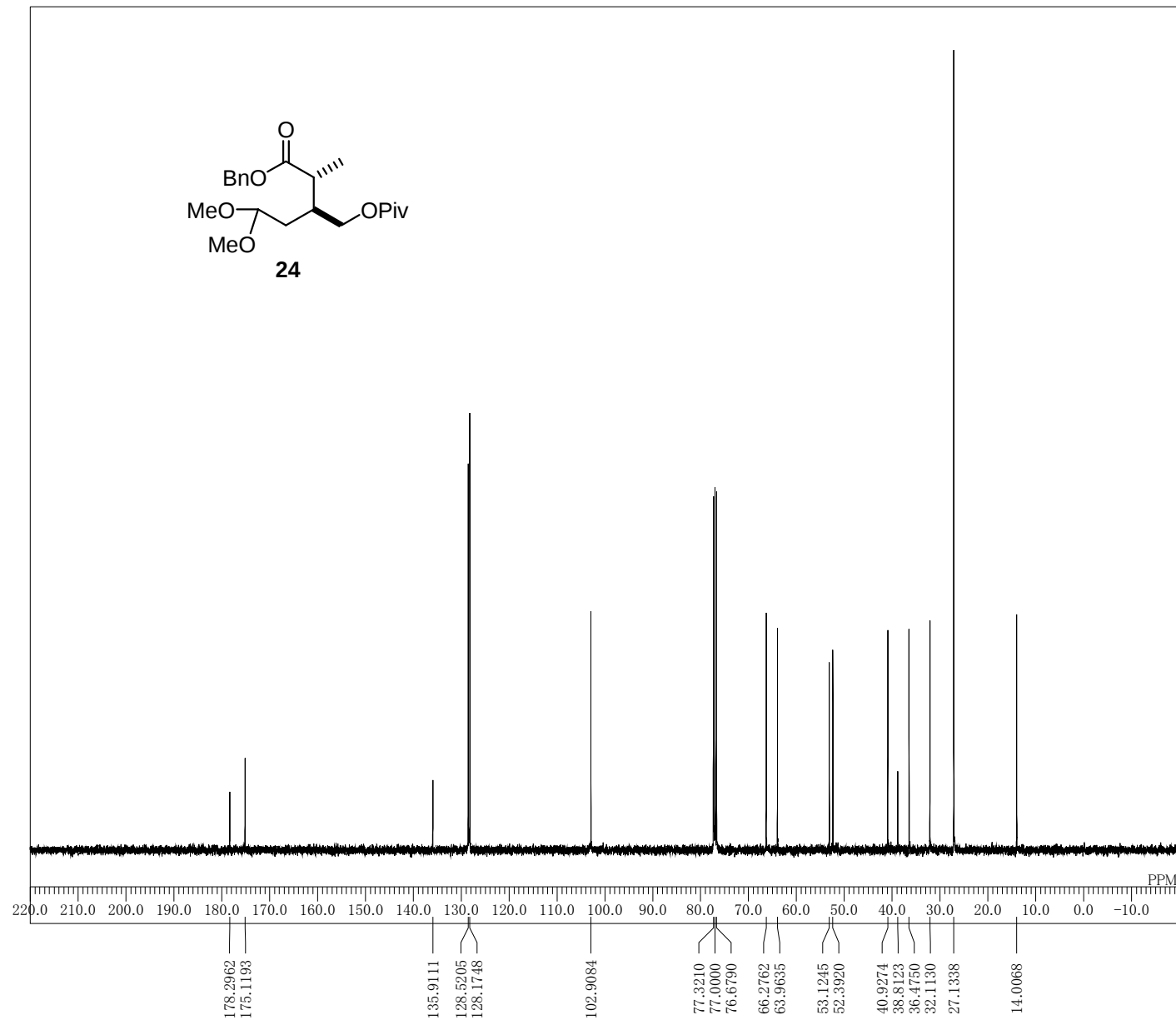
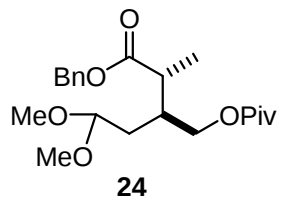


DATIM Tue Sep 02 14:41:39 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 338
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 28.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 24

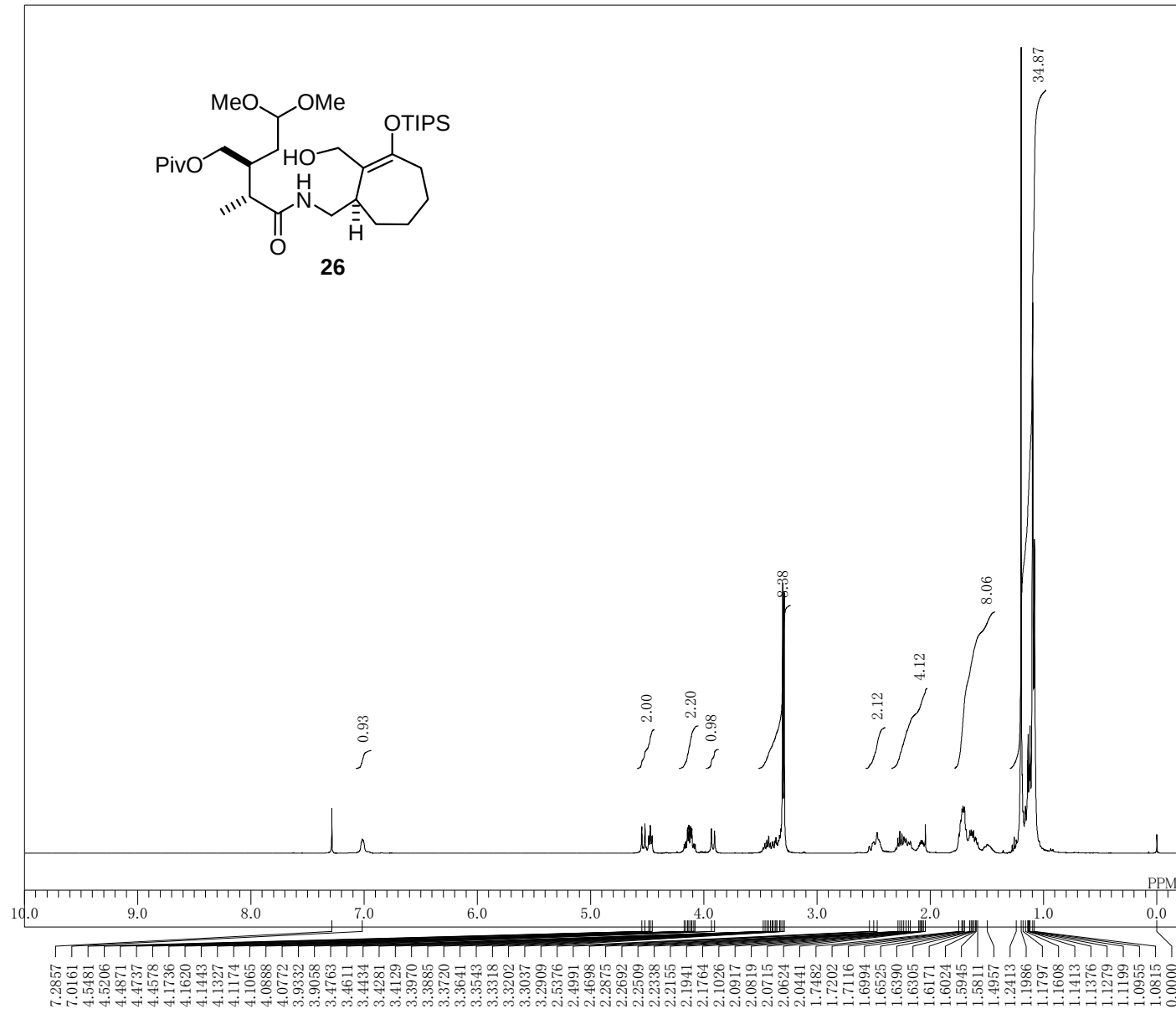




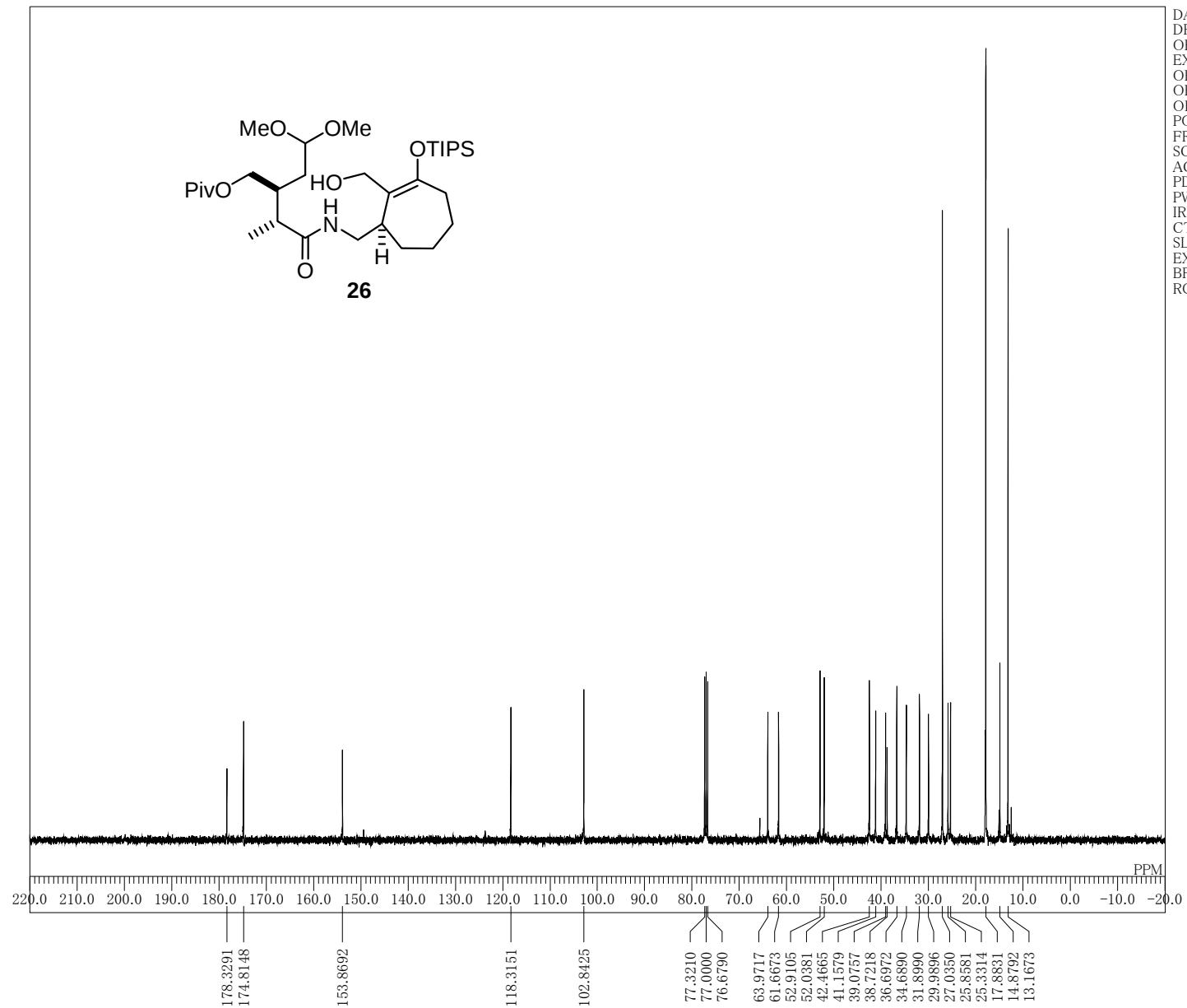
DATIM Wed Nov 05 09:37:50 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 24.2 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 12



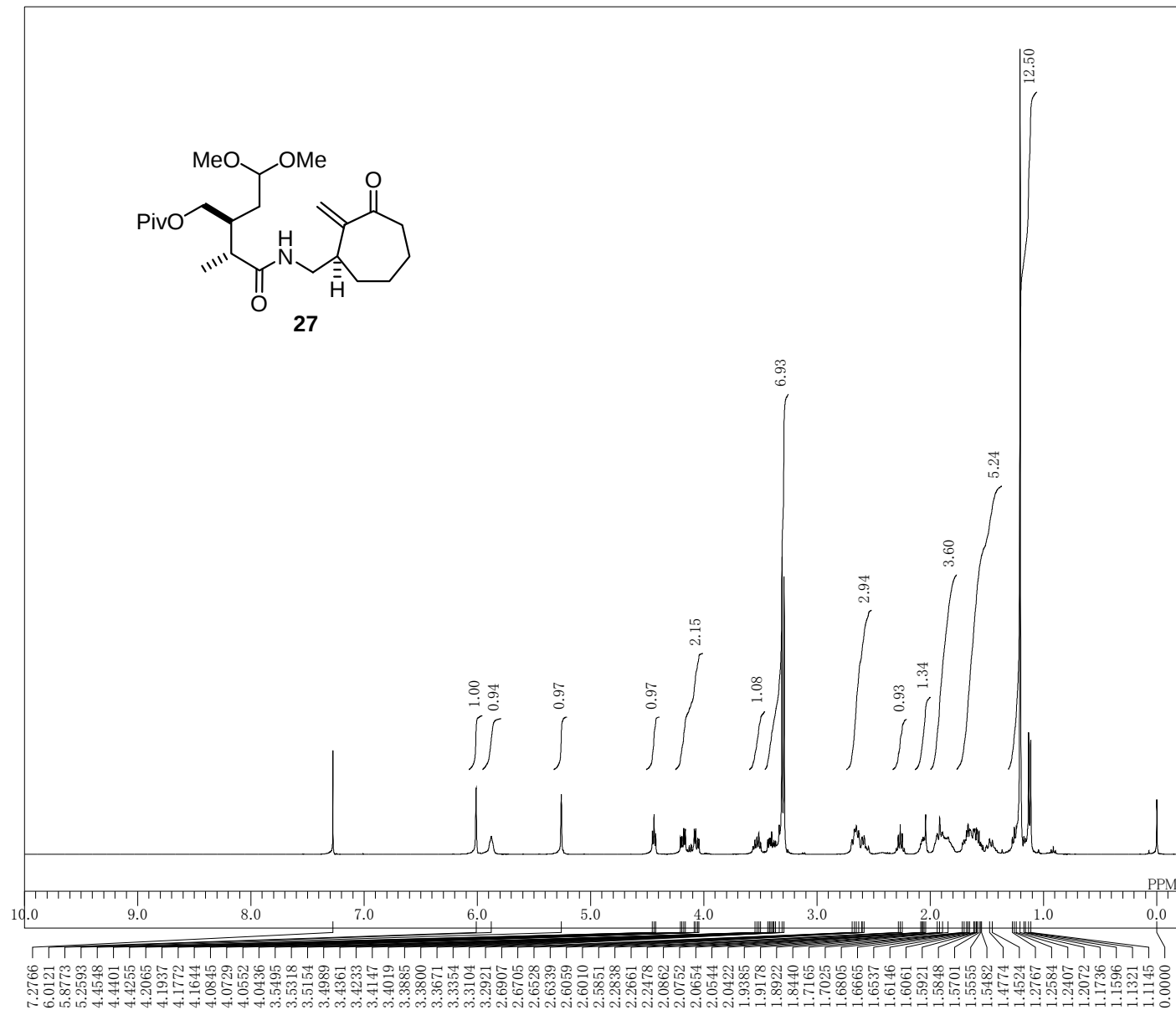
DATIM Wed Nov 05 09:59:22 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 410
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 25.4 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 22



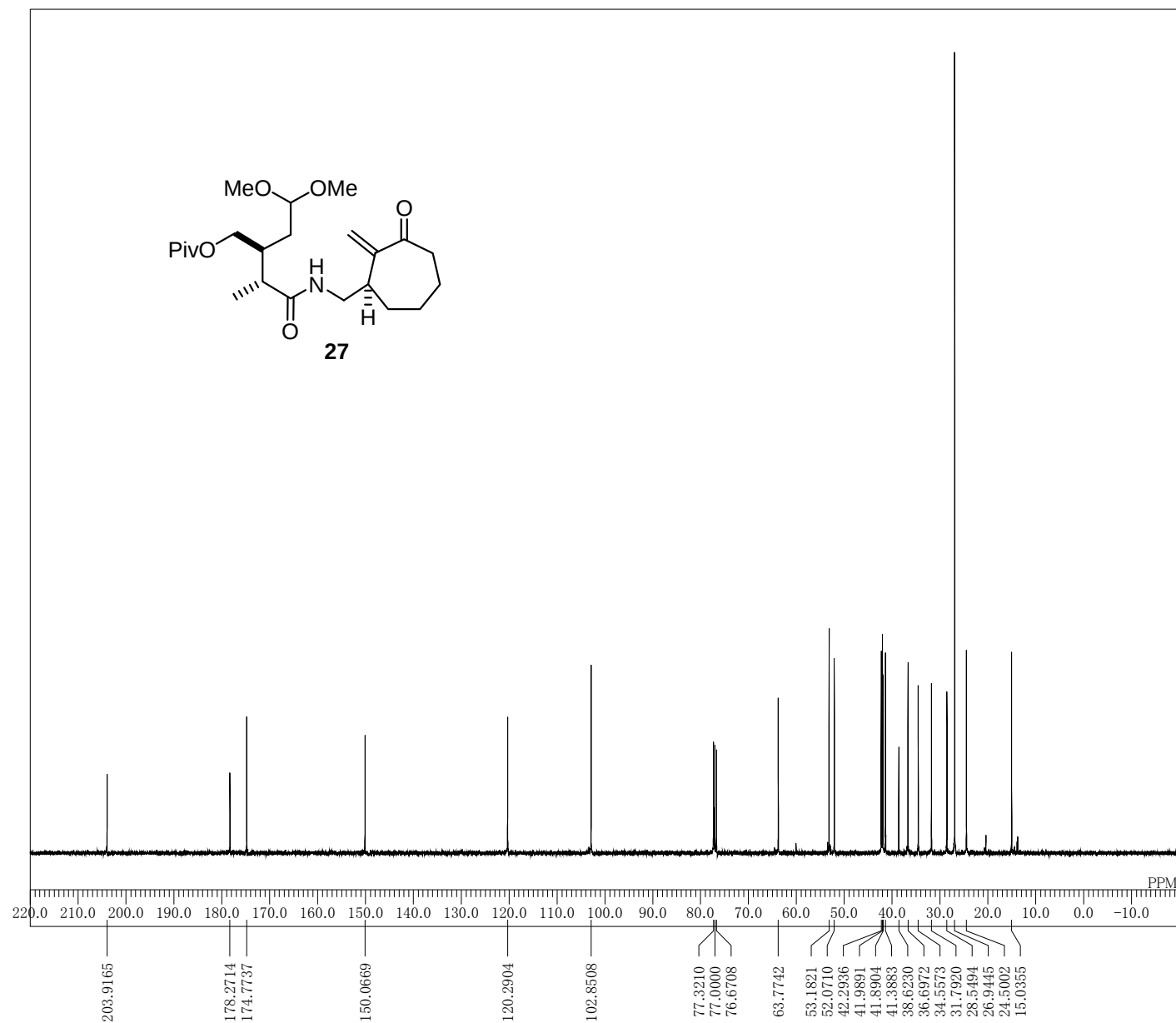
DATIM Tue May 27 09:56:18 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 8
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.2 c
 SLVNT CDCL₃
 EXREF 0.00 ppm
 BF 0.41 Hz
 RGAIN 10



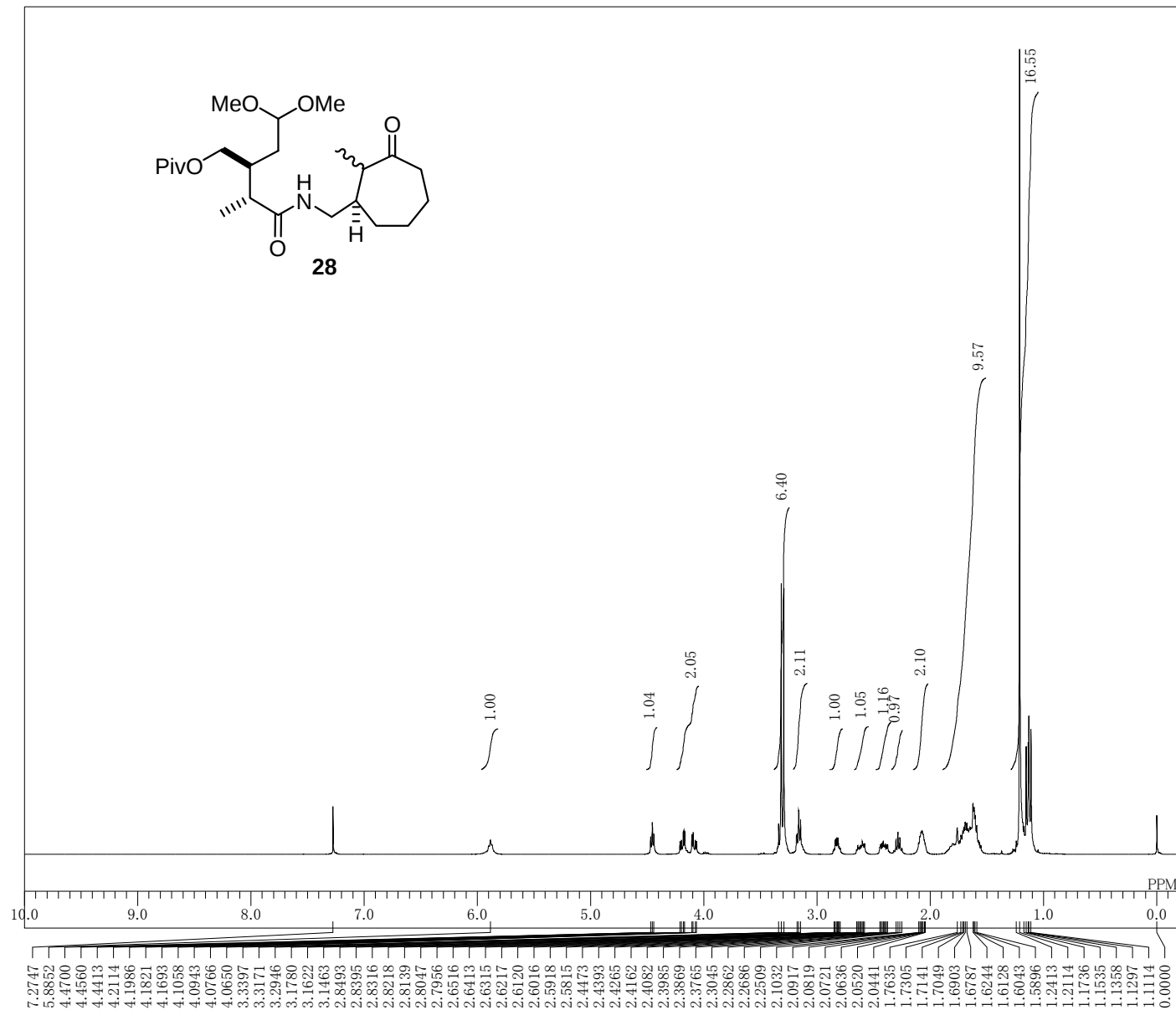
DATIM Fri Oct 10 13:24:51 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\13C
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.13 Hz
 RGAIN 23



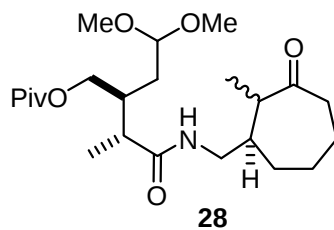
DATIM Fri Jun 27 01:55:28 2008
 DFILE C:\My Documents\¥個人ファイル\NMR AL400¥
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 27.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.42 Hz
 RGAIN 13



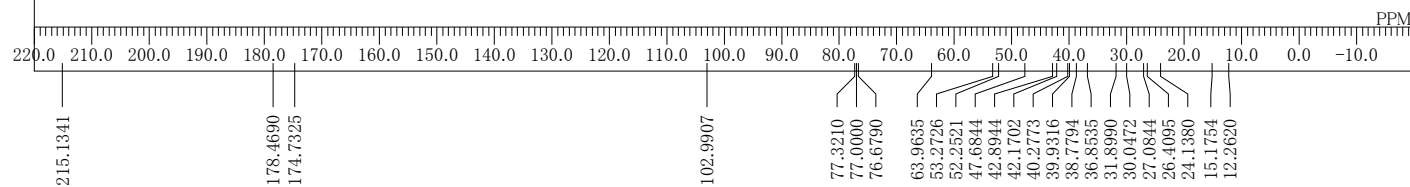
DATIM Wed Oct 15 15:42:15 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 128
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 22



DATIM Wed May 28 15:22:10 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD NON
 OFR 395.75 MHz
 OBSET 124.00 KHz
 OBFIN 10277.00 Hz
 POINT 32768
 FREQU 7912.96 Hz
 SCANS 16
 ACQTM 4.1411 sec
 PD 2.8590 sec
 PW1 5.80 usec
 IRN
 CTEMP 25.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.41 Hz
 RGAIN 13



DATIM Fri Oct 24 18:24:59 2008
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD BCM
 OFR 99.45 MHz
 OBSET 94.00 KHz
 OBFIN 10309.00 Hz
 POINT 32768
 FREQU 26845.64 Hz
 SCANS 301
 ACQTM 1.2206 sec
 PD 1.7790 sec
 PW1 6.40 usec
 IRN
 CTEMP 27.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.12 Hz
 RGAIN 24



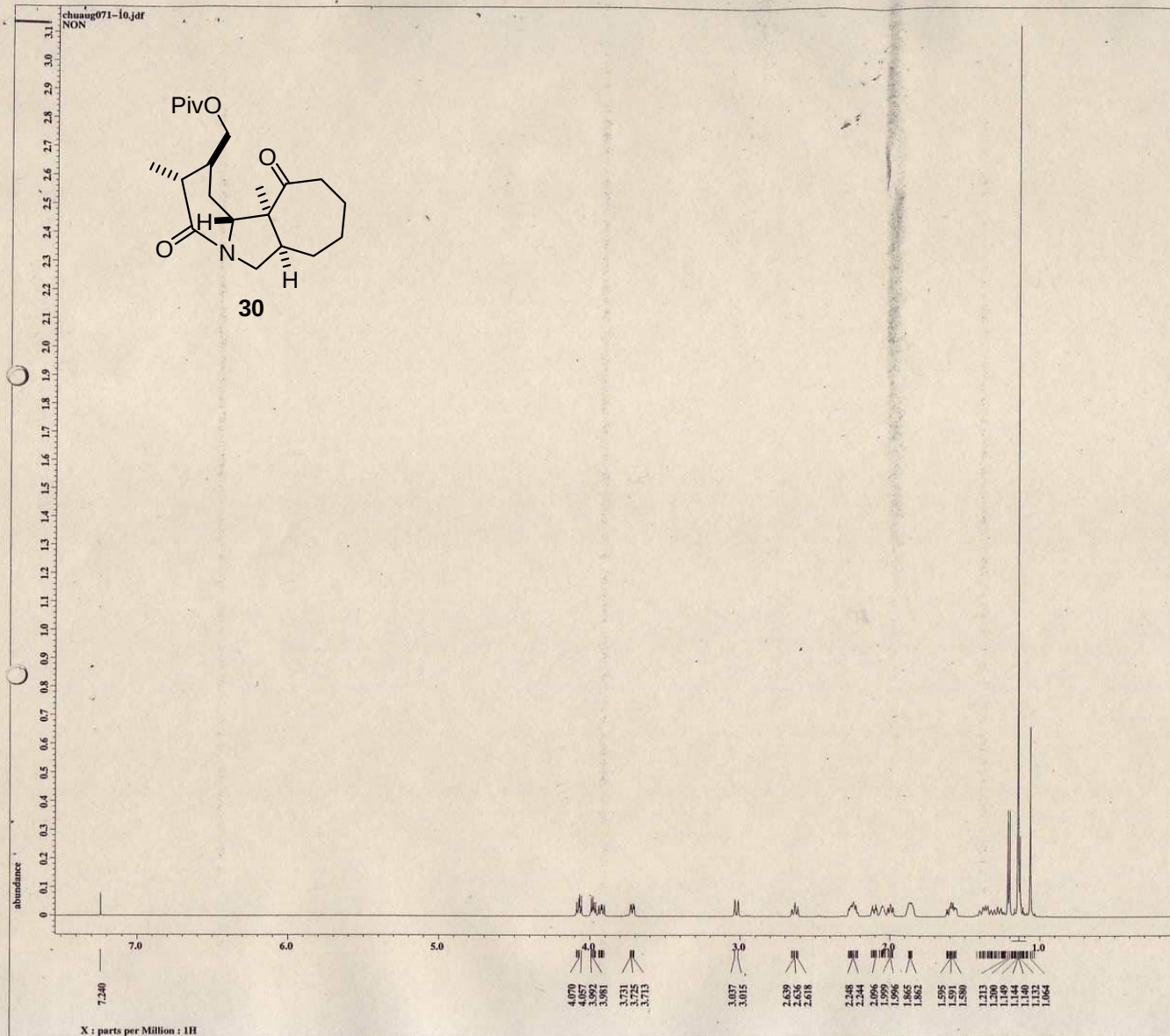
合成制御化学 263 NON



----- PROCESSING PARAMETERS -----
 do_balance : 0 : FALSE
 sweep : 0.0 [Hz] : 0.0 [s]
 trapezoid3 : 0 [%] : 80 [%] : 100 [%]
 zerofill : 1
 fft : 1 : TRUE : TRUE
 machinephase :
 ppm
 Derived from: chuau071-1.jdf

Filename = chuau071-10.jdf
 Author = delta
 Sample_id = km
 Comment = NON
 Creation time = 6-AUG-2008 15:50:12
 Revision time = 6-AUG-2008 14:55:24
 Field strength = 13.95540559 [T] (590 [M]
 X_acq_duration = 11.76502272 [s]
 X_domain = 1M
 X_freq = 594.17058168 [MHz]
 X_offset = 3.0 [ppm]
 X_points = 65536
 X_prescans = 0
 X_resolution = 84.99771091 [MHz]
 X_sweep = 5.57040998 [kHz]
 Irf_domain = 1M
 Irf_freq = 594.17058168 [MHz]
 Irf_offset = 5 [ppm]
 Tri_domain = 1M
 Tri_freq = 594.17058168 [MHz]
 Tri_offset = 5 [ppm]
 Clipped = FALSE
 Mod_return = 1
 Scans = 8
 Total_scans = 8
 X_90_width = 14.6 [us]
 X_acq_time = 11.76502272 [s]
 X_angle = 45 [deg]
 X_atn = 3.5 [dB]
 X_pulse = 7.3 [us]
 Irf_mode = Off
 Tri_mode = Off
 Dmte_preset = FALSE
 Initial_wait = 1 [s]
 Relaxation_delay = 5 [s]
 Repetition_time = 16.76502272 [s]
 Experiment = single_pulse.ex2
 Recvr_gain = 26
 Solvent = CHLOROFORM-D
 Temp_get = 26 [dC]
 Spin_get = 14 [Hz]
 Probe_id = 2692

久野 明

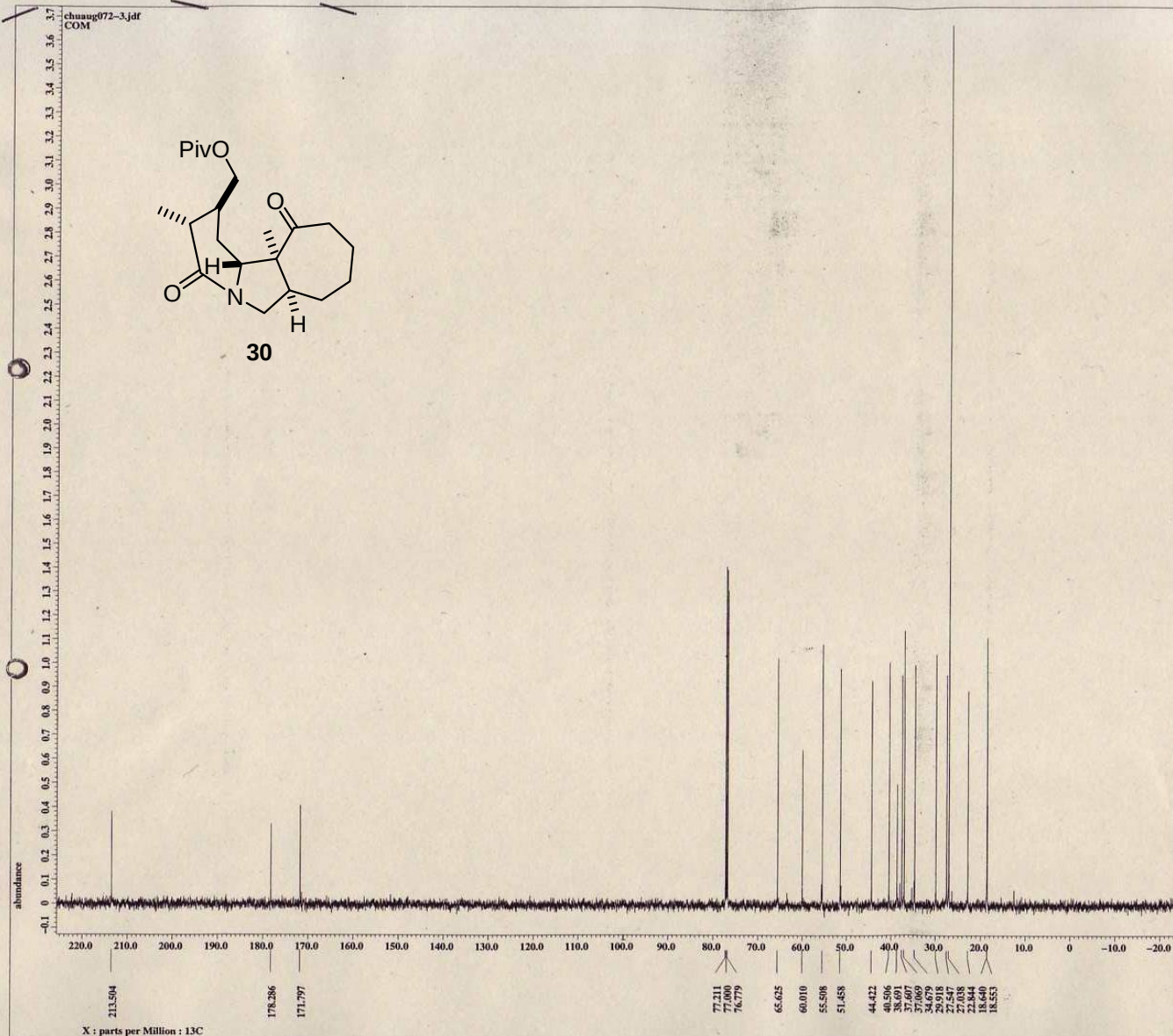


合成制御化学 263 COM



----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 smp : 2.0 [Hz] : 0.0 [s]
 trapezoid3 : 0 [Hz] : 80 [Hz] : 100 [Hz]
 zerofill : 1
 fft : 1 : TRUE : TRUE
 machinephase
 PPS
 Derived from: chuaug072-1.jdf

Filename = chuaug072-3.jdf
 Author = delta
 Sample_id = km
 Comment = COM
 Creation time = 6-AUG-2008 16:08:49
 Revision time = 6-AUG-2008 15:10:15
 Field strength = 13.95540559 [T] (590 [M]
 X acq duration = 0.49730304 [s]
 X domain = 13C
 X freq = 149.40429612 [MHz]
 X offset = 100 [ppm]
 X points = 32768
 X prescans = 4
 X resolution = 1.43409672 [Hz]
 X sweep = 46.9924812 [kHz]
 Irr domain = 1H
 Irr freq = 594.17058168 [MHz]
 Irr offset = 5 [ppm]
 Clipped = FALSE
 Mod return = 1
 Scans = 50
 Total scans = 50
 X 90 width = 10.2 [us]
 X acq time = 0.69730304 [s]
 X angle = 30 [deg]
 X atn = 7.9 [dB]
 X pulse = 3.4 [us]
 Irr atn_dec = 16 [dB]
 Irr atn_noe = 16 [dB]
 Irr noise = WALTZ
 Decoupling = TRUE
 Initial wait = 1 [s]
 Noe = TRUE
 Noe time = 2 [s]
 Relaxation delay = 2 [s]
 Repetition time = 2.69730304 [s]
 Experiment = single_pulse_dec
 Recv gain = 58
 Solvent = CHLOROFORM-D
 Temp_get = 26.9 [dC]
 Spin_get = 15 [Hz]
 Probs_id = 2692



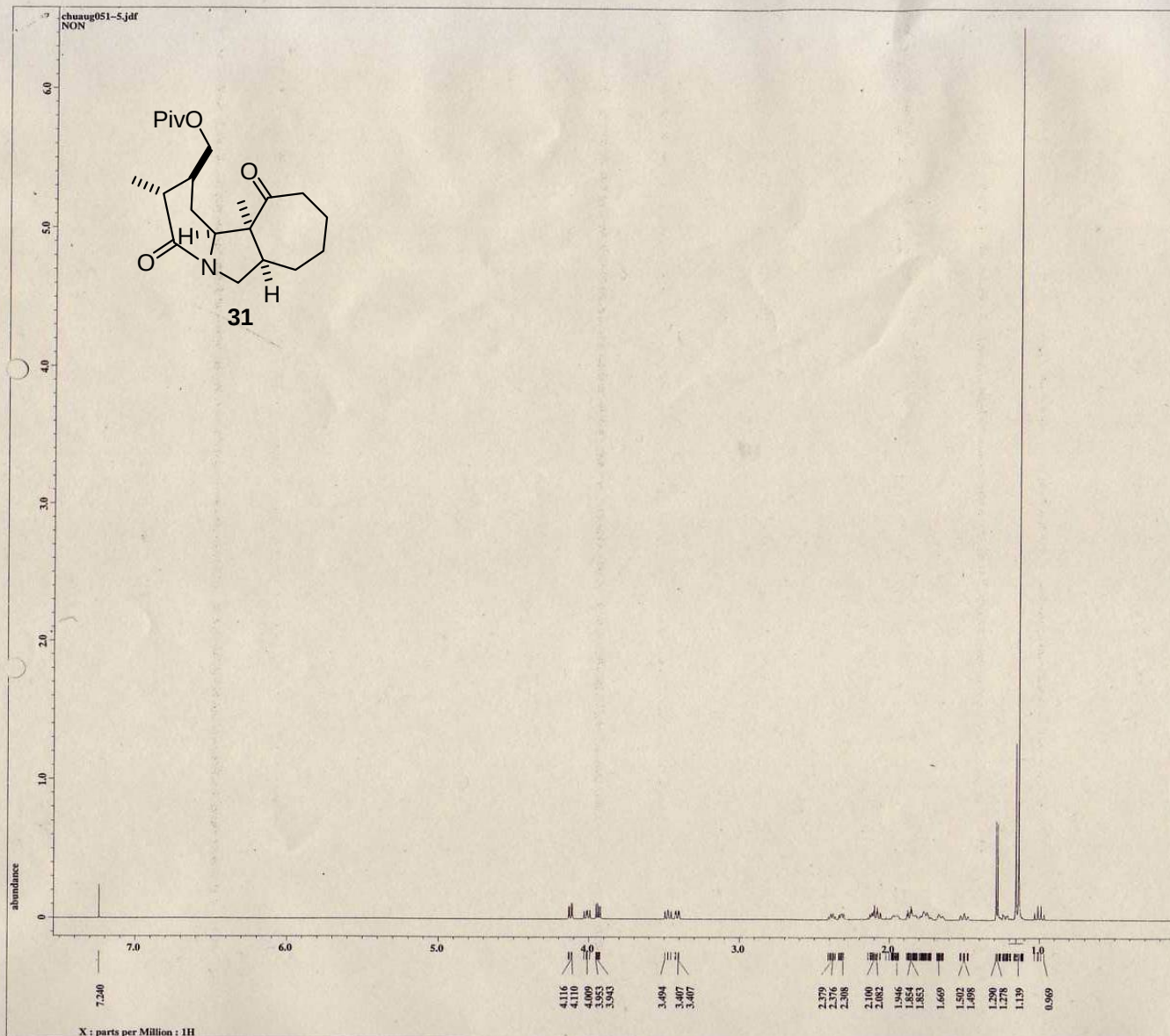
明久化学

合成制御化学 271 NON



----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 exp : 0.0 [Hz] : 0.0 [s]
 trapezoid : 0 [%] : 80 [%] : 100 [%]
 zerofill : 1
 fft : 1 : TRUE : TRUE
 machinephase
 ppm
 Derived from: chuau051-1.jdf

Filename = chuau051-5.jdf
 Author = delta
 Sample_id = ka
 Comment = NON
 Creation_time = 4-AUG-2008 14:29:26
 Revision_time = 4-AUG-2008 13:33:47
 Field_strength = 13.95540559 [T] (590 [M]
 X_acq_duration = 11.76502272 [s]
 X_domain = 1H
 X_freq = 594.17058168 [MHz]
 X_offset = 3.8 [ppm]
 X_points = 65536
 X_prescans = 0
 X_resolution = 84.99771091 [kHz]
 X_sweep = 5.57040998 [kHz]
 Irr_domain = 1H
 Irr_freq = 594.17058168 [MHz]
 Irr_offset = 5 [ppm]
 Tri_domain = 1H
 Tri_freq = 594.17058168 [MHz]
 Tri_offset = 5 [ppm]
 Clipped = FALSE
 Mod_return = 1
 Scans = 8
 Total_scans = 8
 X_90_width = 14.6 [us]
 X_acq_time = 11.76502272 [s]
 X_angle = 45 [deg]
 X_atn = 3.5 [dB]
 X_pulse = 7.3 [us]
 Irr_mode = Off
 Tri_mode = Off
 Danis presat = FALSE
 Initial wait = 1 [s]
 Relaxation delay = 5 [s]
 Repetition_time = 16.76502272 [s]
 Experiment = single_pulse.ex2
 Recvr_gain = 36
 Solvent = CHLOROFORM-D
 Temp_get = 25.9 [dc]
 Spin_get = 14 [Hz]
 Probe_id = 2692



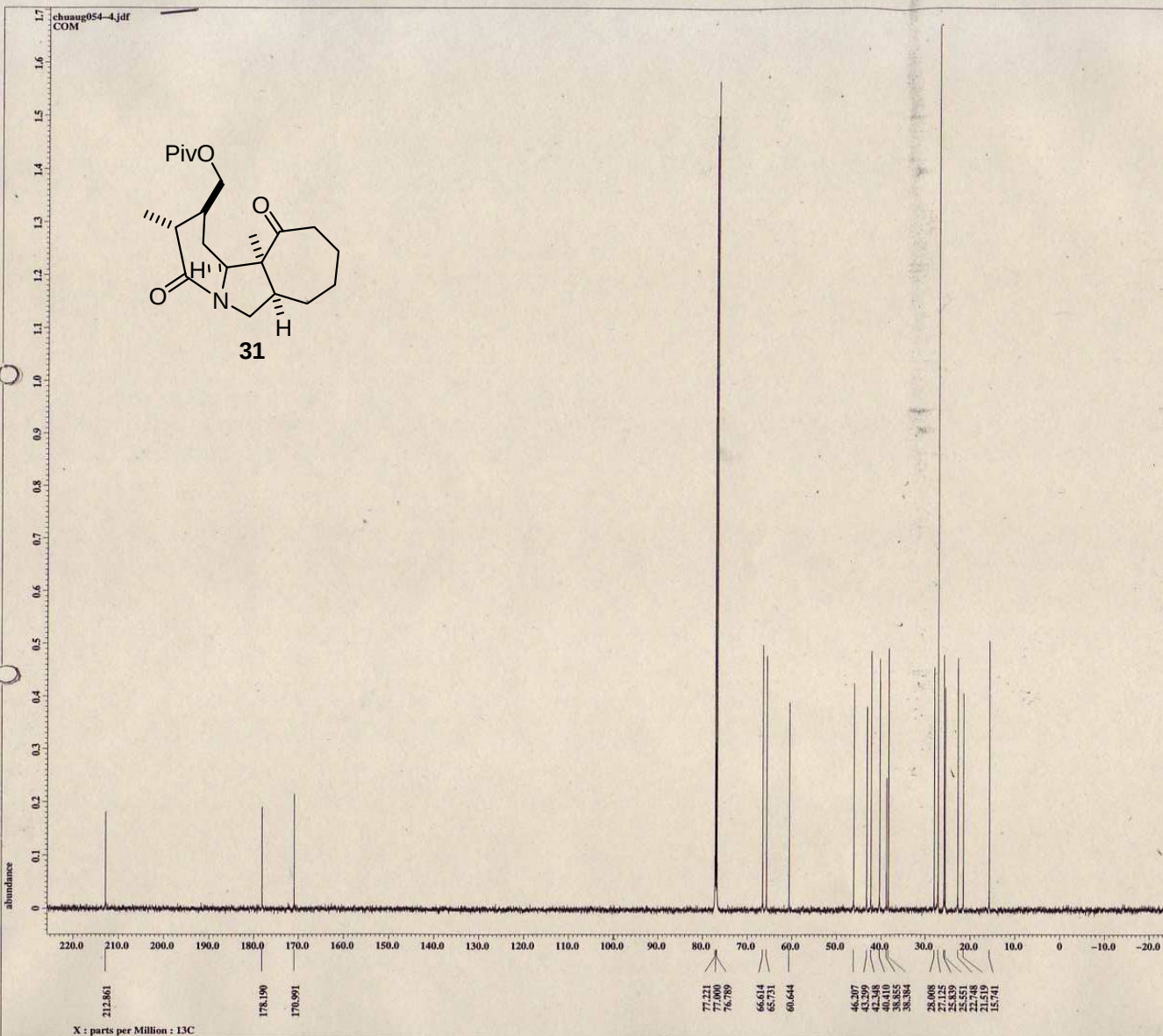
波 南 久 榮 子

台欣制備化學 29/ COM

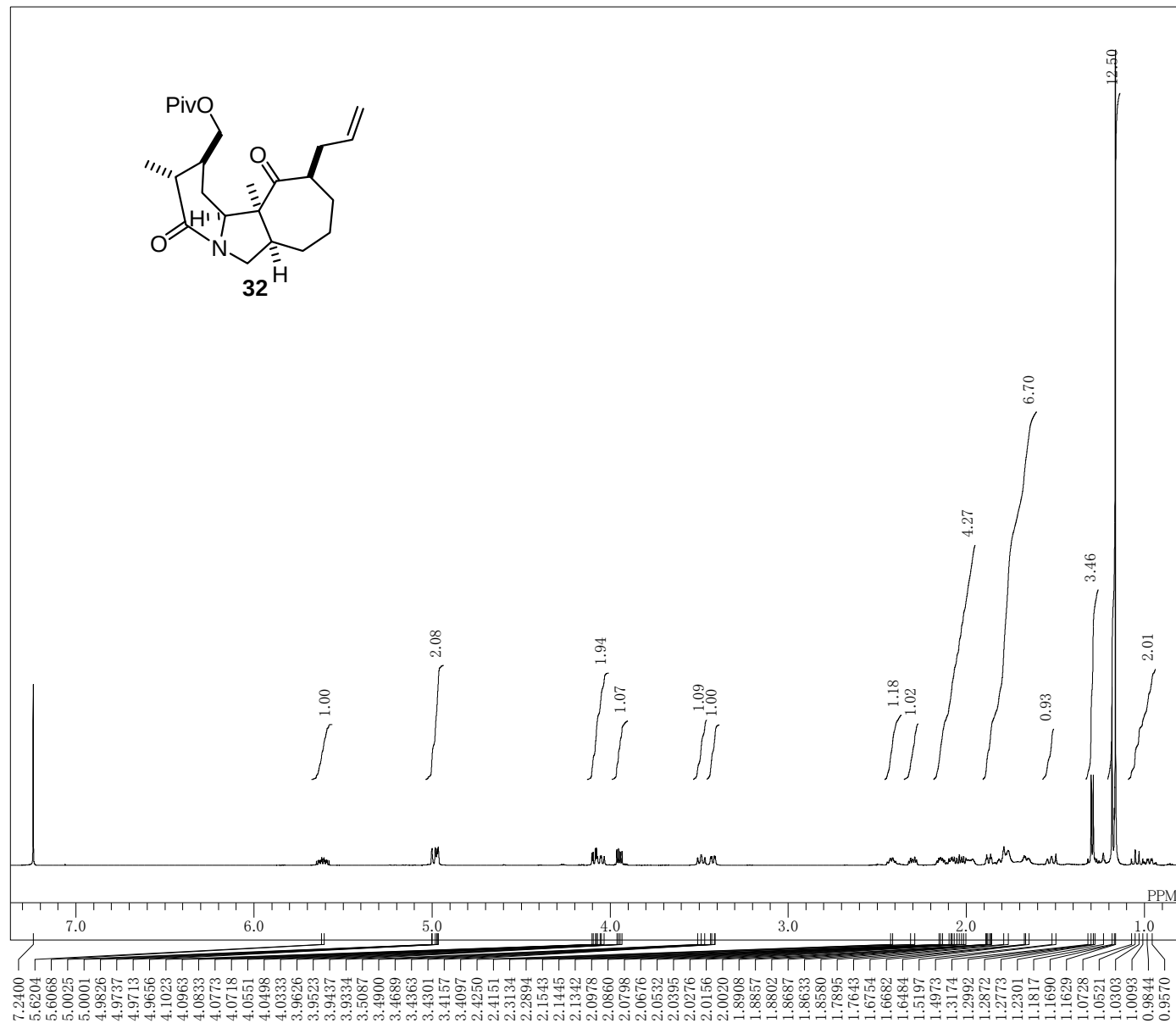


----- PROCESSING PARAMETERS -----
 dc balance : 0 : FALSE
 smp : 2.0[Hz] : 0.0[s]
 trapezoid3 : 0[N] : 80[%] : 100[%]
 zerofill : 1
 f1 : 1 : TRUE : TRUE
 machinphase
 ppm
 Derived from: chuau054-1.jdf

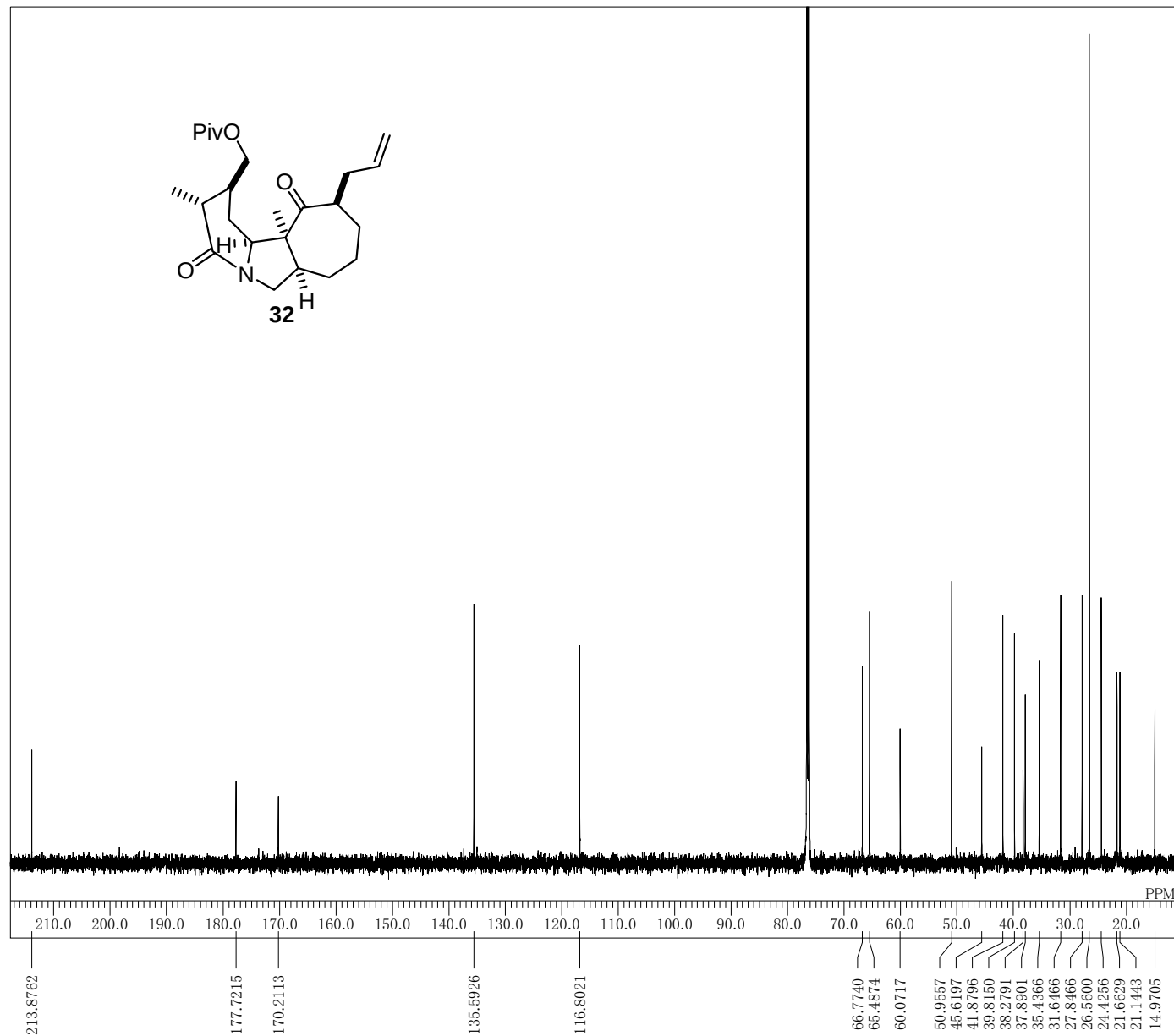
Filename = chuau054-4.jdf
 Author = delta
 Sample id = km
 Comment = COM
 Creation time = 4-AUG-2008 17:07:06
 Revision time = 4-AUG-2008 16:08:51
 Field strength = 13.39540559[T] (590[M]
 X_acq_duration = 0.69730304[s]
 X_domain = 13C
 X_freq = 149.40429612[MHz]
 X_offset = 100[ppm]
 X_points = 32768
 X_prescans = 4
 X_resolution = 1.43409672[Hz]
 X_sweep = 46.9924812[KHz]
 Irf_domain = 1M
 Irf_freq = 594.17058168[MHz]
 Irf_offset = 5[ppm]
 Clipped = FALSE
 Mod return = 1
 Scans = 818
 Total scans = 818
 X_90_width = 10.2[us]
 X_acq_time = 0.69730304[s]
 X_angle = 30[deg]
 X_atn = 7.9[db]
 X_pulse_wdg = 3.4[us]
 Irf_atn_dec = 16[db]
 Irf_atn_noe = 16[db]
 Irf_noise = WALTZ
 Decoupling = TRUE
 Initial wait = 1[s]
 Noe_wait = TRUE
 Noe_time = 2[s]
 Relaxation delay = 2[s]
 Repetition time = 2.69730304[s]
 Experiment = single_pulse_dec
 Recvr_gain = 58
 Solvent = CHLOROFORM-D
 Temp_get = 27.4[deg]
 Spin_get = 13[Hz]
 Probe_id = 2692



血 附 久 純 子



DATIM 19-01-2009 09:51:24
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 1H
 EXMOD single_pulse.ex2
 OFR 594.17 MHz
 OBSET 2.36 KHz
 OBFIN 4.19 Hz
 POINT 65536
 FREQU 6684.49 Hz
 SCANS 8
 ACQTM 9.8042 sec
 PD 5.0000 sec
 PW1 7.30 usec
 IRN
 CTEMP 24.4 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.42 Hz
 RGAIN 46



DATIM 19-01-2009 16:29:20
 DFILE C:\My Documents\個人ファイル\NMR AL400\1
 OBNUC 13C
 EXMOD single.pulse.dec
 OFR 149.42 MHz
 OBSET 1.47 KHz
 OBFIN 7.61 Hz
 POINT 32768
 FREQU 48828.12 Hz
 SCANS 6000
 ACQTM 0.6711 sec
 PD 2.0000 sec
 PW1 3.40 usec
 IRN
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 1.12 Hz
 RGAIN 56