Supporting Information

Highly Discriminative Two-type Transformations of α,β-Unsaturated Esters in the Presence of Enones and Concise Synthesis of Oxacyclic Compounds

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General information

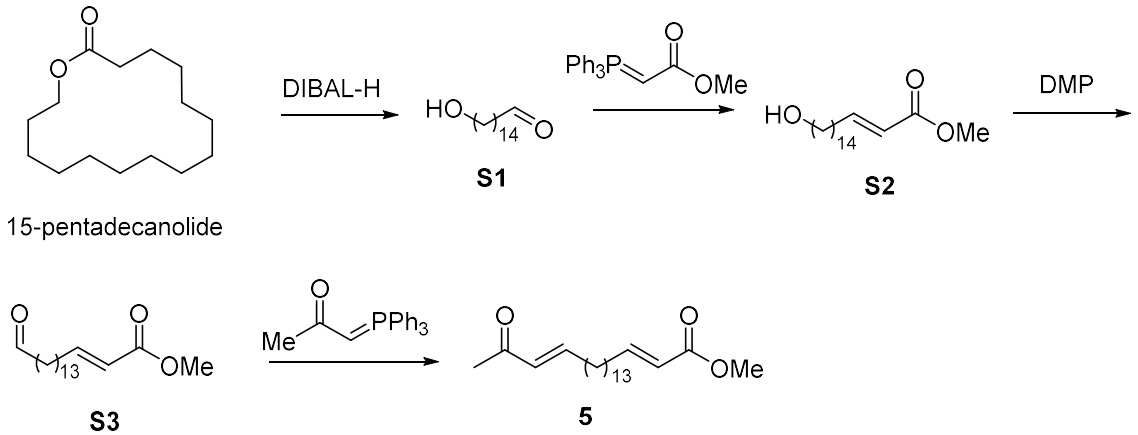
All reagents were purchased from commercial sources and used without further purification, unless otherwise noted. Reactions were performed under a nitrogen atmosphere using purchased anhydrous solvent. All reactions were monitored by thin-layer chromatography using Merck silica gel 60 F254. The products were purified by column chromatography over silica gel Kieselgel 60 (70-230 mesh ASTM) purchased from Merck or Silica Gel 60N (40-50 μm, spherical neutral) purchased from Kanto Chemical. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on a JEOL JNM-AL300 (at 300 MHz and 75 MHz, respectively), a JEOL JNM-ECS 400 (at 400 MHz and 100 MHz, respectively) or a JEOL JNM-LA 500 (at 500 MHz and 125 MHz, respectively), and the chemical shifts are reported relative to internal TMS (^{1}H, δ = 0.00) and $CDCl_3$ (^{13}C, δ = 77.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (integration, multiplicity, coupling constant (Hz)). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra (KBr) were recorded by a SHIMADZU FTIR-8400 or SHIMADZU IRAffinity-1, and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra (MALDI-TOF) were performed by the Elemental Analysis Section of Graduate School of Pharmaceutical Science in Osaka University.

Experimental procedures and characterization data

Synthesis of substrates

The substrates **1**, **2**, **3**, and **4**, are commercially available and compounds **6**[1], **19a**[2], **19b**[3] are known compounds.

Synthesis of methyl (2*E*,18*E*)-20-oxohenicosa-2,18-dienoate (5)



15-Hydroxypentadecanal (S1)

To a solution of 15-Pentadecanolide (2.40 g, 10.0 mmol) in CH_2Cl_2 (100 mL) was added dropwise DIBAL-H (1.0 M in toluene, 25.2 mL, 10.5 mmol, 1.05 equiv.) at -78ºC over 2 h. After the reaction mixture wasstirred for 2 h at the same temperature, saturated sodium potassium tartrate (Rochelle salt, 100 mL) was added. The mixture was allowed to warm to rt. and stirred vigorously for 12 h. The layers were separated and the aqueous layer was extracted with DCM (50 mL × 3). The combined organic layer was washed with brine, dried over $NaSO_4$ and concentrated in vacuo to give **S1** (2.30 g, 96% yield) as a crude product.

IR (KBr) 3632, 1733, 1120 cm^{-1}. **^{1}H-NMR** (300 MHz, BenzenD_6) δ: 9.32 (1H, t, J = 1.7 Hz), 3.40 (2H, t, J = 6.5 Hz), 1.82 (2H, dt, J = 1.7, 7.2 Hz), 1.4-1.75 (24H, m). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 200.9, 62.7, 43.8, 33.2, 30.1, 30.0, 30.0, 29.9, 29.9, 29.8, 29.8, 29.7, 29.4, 26.2, 22.2. **HRMS** (MALDI-TOF) Calcd for $C_{15}H_{30}NaO_2$ $[M+Na]^+$: 265.2138, found 265.2136.

Methyl (*E*)-17-hydroxyheptadec-2-enoate (S2)

To a solution of **S1** (2.00 g, 8.26 mmol) in toluene (41 mL) was added methyl 2-(triphenyl-λ^5-phosphaneylidene)acetate（535mg, 12.4 mmol, 1.5 equiv.）at rt. After being stirred overnight at 80ºC, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 5/1) to afford **S2** (2.30 g, 93%) as a colorless solid.

m.p. 46 °C. **IR** (KBr) 3625, 1718, 1233 cm^{-1}. **^{1}H-NMR** 400 MHz, $CDCl_3$) δ: 6.98 (1H, dt, J = 15.3, 6.9 Hz), 5.82 (1H, dt, J = 15.3, 1.8 Hz), 3.73 (3H, s), 3.64 (2H, t, J = 6.9 Hz), 2.22-2.17 (2H, m), 1.58-1.53 (3H, m), 1.47-1.41 (2H, m), 1.36-1.26 (19H, m). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 167.2, 149.9, 120.7, 63.0, 51.4, 32.7, 32.2, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.1, 28.0, 25.7. Since the carbon chain of the substrate is long and the peak is covered with another carbon peak, the peak of ^{13}C-NMR is two fewer.

HRMS (MALDI-TOF) Calcd for $C_{18}H_{34}NaO_3$ $[M+Na]^+$: 321.2400, found 321.2405.

Methyl (*E*)-17-oxoheptadec-2-enoate (S3)

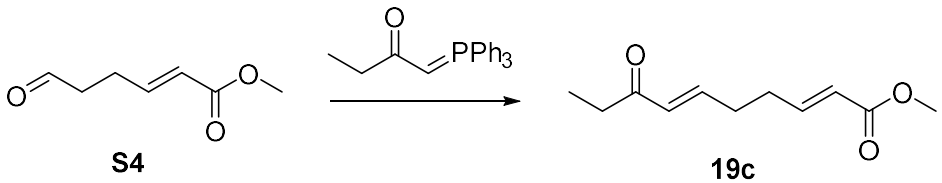
Dess-Martin periodinane (7.11 g, 16.8 mmol, 2.5 equiv.) was added to a solution of **S2** (2.00 g, 6.71 mmol) in CH_2Cl_2 (34 mL) and the mixture was stirred at rt. After 1 h, saturated aqueous $NaHCO_3$ and excess $Na_2S_2O_3$ were added to the reaction mixture. The mixture was extracted with CH_2Cl_2. The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over $NaSO_4$, and filtered. After removal of the solvent (aspirator), the residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 10/1) eluent, to afford **S3** (1.95 g, 98%) as a colorless solid.

m.p. 50 °C. **IR** (KBr) 1725, 1680 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 9.77 (1H, t, J = 1.8 Hz) 6.97 (1H, dt, J = 15.3, 6.9 Hz), 5.83 (1H, dt, J = 15.3, 1.8 Hz), 3.72 (3H, s), 2.44-2.40 (2H, m), 2.22-2.17 (2H, m), 1.64-1.61 (2H, m), 1.46-1.43 (2H, m), 1.30-1.26 (18H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 202.9, 167.1, 149.8, 120.7, 51.3, 43.8, 32.2, 29.5, 29.5, 29.4, 29.3, 29.3, 29.3, 29.1, 29.1, 29.1, 28.0, 22.0. **HRMS** (MALDI-TOF) Calcd for $C_{18}H_{32}NaO_3$ $[M+Na]^+$: 296.2346, found 296.2351.

Methyl (2*E*,18*E*)-20-oxohenicosa-2,18-dienoate (5)

To a solution of **S3** (500 mg, 1.60 mmol) in toluene (16 mL) was added 1-(triphenyl-λ^5-phosphanylidene)propan-2-one（535 mg, 1.68 mmol, 1.05 equiv.） at rt. After being stirred overnight at 80°C, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 25/1) to afford **5** (491 mg, 87%) as a colorless solid.
m.p. 34 °C. **IR** (KBr) 1725, 1680 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 6.97 (1H, dt, J = 15.3, 6.9 Hz), 6.81 (1H, dt, J = 15.3, 6.9 Hz), 6.06 (1H, dt, J = 15.3, 1.7 Hz), 5.83 (1H, dt, J = 15.3, 1.7 Hz), 3.73 (3H, s), 2.24 (3H, s), 2.22-2.15 (4H, m), 1.48-1.42 (4H, m), 1.28-1.26 (18H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.8, 167.2, 149.8, 148.7, 131.2, 120.7, 51.3, 32.4, 32.2, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 29.1, 29.0, 28.0, 28.0, 26.8, 26.8. **HRMS** (MALDI-TOF) Calcd for $C_{21}H_{36}NaO_3$ $[M+Na]^+$: 359.2552, found 359.2557.

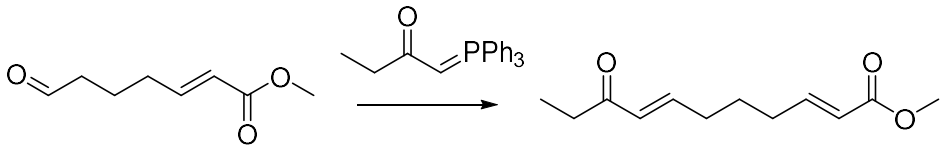
Methyl (2*E*,6*E*)-8-oxodeca-2,6-dienoate (19c)



S4 **19c**

To a solution of methyl (*E*)-6-oxohex-2-enoate (**S4**)[4] (426 mg, 3.00 mmol) in toluene (30 mL) was added 1-(triphenyl-λ^5-phosphaneylidene)butan-2-one (1.49 g, 4.50 mmol, 1.5 equiv.) at rt. After being stirred overnight at 80°C, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 7/1) to afford **19c** (529 mg, 91%) as a colorless oil.
IR (KBr) 1732, 1689 cm^{-1}. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 6.94 (1H, d, J = 15.3 Hz), 6.80 (1H, d, J = 15.3 Hz), 6.14 (1H, d, J = 15.3 Hz), 5.87 (1H, d, J = 15.3 Hz), 3.73 (3H, s), 2.57 (2H, q, J = 7.3 Hz), 2.42-2.40 (4H, m), 1.10 (3H, t, J = 7.3 Hz). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 200.5, 166.5, 147.0, 144.2, 130.5, 121.6, 51.2, 33.1, 30.3, 30.3, 7.4. **HRMS** (MALDI-TOF) Calcd for $C_{11}H_{16}NaO_3$ $[M+Na]^+$: 219.0992, found 219.0990.

Methyl (2*E*,7*E*)-9-oxoundeca-2,7-dienoate (19d)



S5 **19d**

To a solution of methyl (*E*)-7-oxohept-2-enoate (**S5**)[5] (468 mg, 3.00 mmol) in toluene (30 mL) was added 1-(triphenyl-λ^5-phosphaneylidene)butan-2-one (1.49 g, 4.50 mmol, 1.5 equiv.) at rt. After being stirred overnight at 80 °C, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 7/1) to afford **19d** (586 mg, 93%) as a colorless oil.

IR (KBr) 1732, 1686 cm^{-1}. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 6.94 (1H, dt, J = 15.3, 6.9 Hz), 6.80 (1H, dt, J = 15.3, 6.9 Hz), 6.12 (1H, dt, J = 15.3, 1.4 Hz), 5.85 (1H, dt, J = 15.3, 1.4 Hz), 3.73 (3H, s), 2.58 (2H, q, J = 7.3 Hz), 2.27 (4H, m), 1.66 (2H, m), 1.10 (3H, t, J = 7.3 Hz). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 200.7, 166.7, 148.2, 145.5, 130.3, 121.3, 51.2, 33.1, 31.4, 31.3, 26.1, 7.8. **HRMS** (MALDI-TOF) Calcd for $C_{12}H_{18}NaO_3$ $[M+Na]^+$: 233.1148, found 233.1148.

Experimental details in Table 1

Table 1, entry 1: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) and PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (0.50 mL) was added dropwise TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, the reaction mixture was then cooled to -78 °C. To the solution was added DIBAL-H (1.0 M toluene solution, 0.2 mL, 2.0 equiv.). After the starting ester **2** was consumed (TLC check), TBAF (0.30 mL of 1.0 M THF solution, 0.30 mmol) was added, then the resulting solution was stirred for 30 min. After adding H_2O, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane /AcOEt=5/1) to afford the recovered **1** (14.3 mg, 98%) and cinnamyl alcohol (**8Aa**)[7] (11.7 mg, 87%).

Table 1, entry2: A solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol) methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (0.5 mL) was cooled to -78 °C. DIBAL-H (1.0 M toluene solution, 0.20 mL, 2.0 equiv.) was added dropwise and the reaction mixture was stirred for 2 h. After the reaction mixture was quenched with 1 *N* HCl aq. and the solvent volume was reduced under vacuum. The residue left behind was extracted with AcOEt (30 ml x 3). The organic layer was separated and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 5/1) to afford the recovered **1** (5.3 mg,

36%) and **2** (7.0 mg, 43%) and the reduced products **7Aa**[6] (7.1 mg, 48%) and **8Aa**[7] (5.1 mg, 38%).

Table 1, entry 3: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) and PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (0.50 mL) was added dropwise TESOTf (34 μL, 0.15 mmol, 1.5 equiv.) at 0 ºC. After being stirred for 30 min at 0 ºC, $CeCl_3$ (74.0 mg, 0.30 mmol, 3.0 equiv.) and EtMgBr (1.6 M Diethyl ether solution, 0.19 mL, 3.0 equiv.) were added dropwise to the resulting solution. After the starting ester **2** was consumed (TLC check), TBAF (0.20 ml of 1.0 M THF solution, 0.20 mmol, 1.0 equiv.) was added. The resulting solution was stirred for 30 min. After adding H_2O, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 4/1) to afford the recovered **1** (11.7 mg, 80%) and the alcohol **8Ab**[8] (16.7 mg, 88%)

Table 1, entry 4: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) and $CeCl_3$ (74.0 mg, 0.30 mmol, 3.0 equiv.) in CH_2Cl_2 (0.50 mL) was added dropwise EtMgBr (1.6 M THF solution, 0.19 mL, 3.0 equiv.). The resulting solution was stirred for 2 h. After adding H_2O, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 4/1) to afford the recovered **1** (4.5 mg, 31%) and **2** (7.9 mg, 49%) and the reduced products **7Ab**[9] (7.7 mg, 44%) and **8Ab**[8] (5.7 mg, 30%).

Experimental details in Table 2

Table 2, entry 1: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) and PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.) in MeOH/AcOEt (7:1) (0.50 mL) was added dropwise TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.) at 0 ºC. After being stirred for 30 min at 0 ºC, 5% Pd/C (20 wt%) (3.20 mg) was added to the reaction mixture The reaction mixture was stirred at rt under a H_2 balloon. After the starting ester **2** was consumed (TLC check), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol) was added, then the resulting solution was stirred for 30 min. After filtration throug celite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 3/1) to afford the recovered **1** (14.5 mg, 99%) and the hydrogenated **10Aa**[10] (16.1 mg, 98%).

Table 2, entry2 : To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) in MeOH/AcOEt (7:1) (0.50 mL) was added 5% Pd/C (20 wt%, 3.2 0mg). The reaction mixture was stirred at rt for **5 min** under a H_2 balloon. After filtration throug celite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column

chromatography (*n*-Hexane/AcOEt = 3/1) to afford the recovered **1** (13.3 mg, 91%) and **2** (15.1 mg, 93%) and the hydrogenated products **9Aa** [11](1.2 mg, 8%) and **10Aa** [10](1.1 mg, 7%).

Table 2, entry3: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol) in MeOH/AcOEt (7:1) (0.50 mL) was added 5% Pd/C (20 wt%, 3.20 mg). The reaction mixture was stirred at rt for **15 min** under a H_2 balloon. After filtration throug celite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt=3/1) to afford the recovered **1** (6.2 mg, 38%) and **2** (9.9 mg, 61%) and the hydrogenated products **9Aa**[11] (8.7 mg, 59%) and **10Aa**[10] (6.1 mg, 37%).

Table 2, entry 4: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2mg, 0.10 mmol, 1.0 equiv.) and PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.) in Actone/H_2O (50:1) (0.50 mL) was added dropwise TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, $K_2OsO_4/2H_2O$ (3.30 mg, 10 mol%) and NMO (58.6 mg, 5.0 equiv.) were added to the reaction mixture. The resulting solution was stirred at rt under N_2. After the starting ester **2** was consumed, (TLC check), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) were added, then the resulting solution was stirred for 30 min. After filtration throug celite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane /AcOEt=1/3) to afford the recovered **1** (12.0 mg, 82%) and the dihydrogenated **10Ab**[12] (17.5 mg, 89%)).

Table2, entry 5: To a solution of benzalacetone (**1**) (14.6 mg, 0.10 mmol) and methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.) in Acetone/H_2O (50:1) (0.50 mL) were added $K_2OsO_4/2H_2O$ (3.30 mg, 10 mol%) and NMO (58.6 mg, 5.0 equiv.). The reaction mixture was stirred at rt for 2 h under N_2. Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) was added, then the resulting solution was stirred for 30 min. After filtration throug celite padthe filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt = 1/3) to afford the recovered **1** (8.3 mg, 51%) and **2** (9.6 mg, 59%) and the methylated products **9Ab**[13](8.8 mg, 49%) and **10Ab**[12] (8.0 mg, 41%).

Experimental details in Table 3

General procedure for the selective reduction of α,β-unsaturated ester in the presence of enone (Table 3, entries 1, 3, 5, 7, 9 and 11) : To a solution of enone (0.10 mmol) and α,β–unsaturated ester (0.10 mmol, 1.0 equiv.) {or enone-unsaturated ester (0.10 mmol)} and PPh_3 (0.15 mmol, 1.5 equiv.) in CH_2Cl_2 (0.50 mL) was added dropwise TMSOTf (0.15 mmol, 1.5 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, the reaction mixture was then cooled to -78°C. DIBAL-H (0.2 mL, 1.0 M toluene

solution, 2.0 equiv.) was added to the mixture. After the starting α,β-unsaturated ester was consumed (TLC check), TBAF (0.30 mL, 1.0 M THF solution, 0.30 mmol) was added, then the resulting solution was stirred for 30 min. After adding H_2O, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the recovered enone and the reduced alcohol.

(*E*)-3-Phenylprop-2-en-1-ol (8Aa)[7] (Table 3, entries 1 and 5)

Table 3, entry 1 (Same as entry 1 of Table 1): According to the general procedure, benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.), DIBAL-H (0.20 mL of 1.0 M toluene solution, 0.20 mmol, 2.0 equiv.), and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **1** (12.7 mg, 87%) and **8Aa**[7] (11.7 mg, 87%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 5/1).

Table 3, entry 5: According to the general procedure, **3** (14.0 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.), DIBAL-H (0.20 mLof 1.0 M toluene solution, 0.20 mmol, 2.0 equiv.), and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **3** (12.8 mg, 88%) and **8Aa**[7] (12.2 mg, 91%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 5/1).**^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.38 (2H, d, J = 7.3 Hz), 7.31 (2H, t, J = 7.3 Hz), 7.24 (1H, t, J = 7.3 Hz), 6.60 (1H, d, J = 15.6 Hz), 6.35 (1H, dt, J = 16.0, 5.4 Hz), 4.30 (2H, dd, J = 5.4, 1.4 Hz), 2.10 (1H, brs). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ: 136.4, 131.3, 128.4, 128.2, 127.7, 126.6, 63.7.

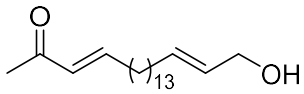
(*E*)-Oct-2-en-1-ol (8Ba)[14] (Table3, entries 3 and 7)

Table 3, entry 3: According to the general procedure, benzalacetone (**1**) (14.6 mg, 0.10 mmol), 4(15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.), DIBAL-H (0.20 mL of 1.0 M toluene solution, 0.20 mmol, 2.0 equiv.), and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **1** (13.0 mg 89%) and **8Ba**[14] (10.9 mg, 85%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 5/1).

Table 3, entry 7: According to the general procedure, **3** (14.0 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.), DIBAL-H (0.20 mL of 1.0 M toluene solution, 0.20 mmol, 2.0 equiv.), and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol) gave recovered **3** (10.2 mg, 73%) and **8Ba**[14] (10.3 mg, 80%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 5/1).

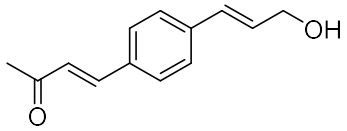
^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.73– 5.54 (2H, m), 4.06 (2H, d, J = 6.0 Hz), 2.01 (2H, dt, J = 7.3, 6.7 Hz), 1.55 (1H, brs), 1.41–1.20 (6H, m), 0.86 (3H, t, J = 6.7 Hz). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ:133.5, 128.7, 63.7, 32.2, 31.7, 28.9, 22.3, 14.0.

(3*E*,18*E*)-20-Hydroxyhenicosa-3,18-dien-2-one (11) (Table 3, entry 9)



According to the general procedure, **5** (35.0 mg, 0.10 mmol), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TMSOTf (27 μL, 0.15 mmol, 1.5 equiv.), DIBAL-H (0.20 mL of 1.0 M toluene solution, 0.20 mmol, 2.0 equiv.), and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave **11** (28.1 mg, 84%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 10/1). **IR** (KBr) 3388, 1669 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 6.80 (1H, dt, J = 15.3, 6.9 Hz), 6.06 (1H, dt, J = 15.3, 1.2 Hz), 5.71-5.60 (2H, m), 4.09 (2H, d, J = 5.7 Hz), 2.24 (3H, s), 2.23-2.20 (2H, m), 2.05-2.01 (2H, m), 1.50-1.43 (2H, m), 1.40-1.24 (2H, m), 1.29-1.22 (19H, m).**^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.9, 148.8, 133.6, 131.2, 128.8, 63.8, 32.5, 32.2, 29.6, 29.6, 29.5, 29.5, 29.4, 29.2, 29.1, 28.0, 26.8. Since the carbon chain of the substrate is long and the peak is covered with another carbon peak, the peak of ^{13}C-NMR is three fewer. **HRMS** (MALDI-TOF) Calcd for $C_{20}H_{36}NaO_2$ $[M+Na]^+$: 331.2613, found 331.2615.

(*E*)-4-(4-((*E*)-3-Hydroxyprop-1-en-1-yl)phenyl)but-3-en-2-one (13) (Table1, entry11)



According to the general procedure, **6** (35.7 mg, 0.15 mmol), PPh_3 (60.0 mg, 0.23 mmol, 1.5 equiv.), TMSOTf (42 μL, 0.23 mmol, 1.5 equiv.), DIBAL-H (0.30 mL of 1.0 M toluene solution, 0.30 mmol, 2.0 equiv.), and TBAF (0.30 mL of 1.0 M THF solution, 0.30 mmol, 2.0 equiv.) gave **13** (25.2 mg, 83%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 3/1). **IR** (KBr) 3413, 1710 cm^{-1}.**^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.50 (1H, d, J = 15.6 Hz), 7.46 (2H, d, J = 8.3 Hz), 7.39 (2H, d, J = 8.3 Hz), 6.68 (1H, d, J = 15.6 Hz), 6.60 (1H, d, J = 15.6 Hz), 6.44 (1H, dt, J = 15.6, 5.6 Hz), 4.35 (2H, dd, J = 5.6, 1.6 Hz), 2.38 (3H, s), 2.01 (1H, s). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.6, 143.0, 139.0, 133.5, 130.4, 129.8, 128.6, 126.9, 126.7, 63.4, 27.5. **HRMS** (MALDI-TOF) Calcd for $C_{13}H_{15}O_2$ $[M]^+$: 203.1067, found 203.1063

General procedure for the selective alkylation of α,β-unsaturated ester in the presence of enone (Table 3, entries 2, 4, 6, 8, 10, 12): To a solution of enone (0.10 mmol), α,β-unsaturated ester (0.10 mmol, 1.0 equiv.) (or enone-unsaturated ester (0.10 mmol)) and PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.) and $CeCl_3$ (74.0 mg, 0.30 mmol, 3.0 equiv.) in CH_2Cl_2 (0.50 mL) was added dropwise TESOTf (34 μL, 0.15 mmol, 1.5 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, Grignard reagent in THF

(1.0 M, 0.20 mL, 2.0 equiv.) was added to the solution. After the α,β-unsaturated ester was consumed (TLC check), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) was added, then the resulting solution was stirred for 30 min. After adding H_2O, the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired products.

(*E*)-3-Ethyl-1-phenylpent-1-en-3-ol (8Ab)[8] (Table 3, entries 2 and 6)

Table 3, entry 2 (Same as entry 3 of Table 1): According to the general procedure, benzalacetone (**1**) (14.6 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TESOTf (34 μL, 0.15 mmol, 1.5 equiv.), $CeCl_3$ (74.0 mg, 0.30 mmol, 3.0 equiv.), EtMgBr (0.13 mL of 1.6 M THF solution, 0.20 mmol, 2.0 equiv.), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **1** (11.7 mg, 80%) and the alcohol **8Ab**[8] (16.7 mg, 88%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 2/1).

Table 3, entry 6: According to the general procedure, **3** (14.0 mg, 0.10 mmol), methyl cinnamate (**2**) (16.2mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TESOTf (34 μL, 0.15 mmol, 1.5 equiv.), EtMgBr (0.13 mL of 1.6 M THF solution, 0.20 mmol, 2.0 equiv.), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **3** (11.5 mg, 82%) and **8Ab** (16.1 mg, 85%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 2/1).

^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.38 (2H, d, J = 7.5 Hz), 7.32 (2H, t, J = 7.5 Hz), 7.24 (1H, t, J = 7.5 Hz), 6.58 (1H, d, J = 16.0 Hz), 6.18 (1H, d, J = 16.0 Hz), 1.64 (4H, q, J = 7.5 Hz), 0.92 (6H, t, J = 7.5 Hz). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 137.1, 135.3, 128.5, 128.1, 127.2, 126.3, 75.8, 33.3, 7.9.

(*E*)-3-Ethyldec-4-en-3-ol (8Bb) (Table 3, entries 4 and 8)

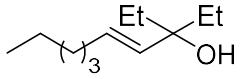


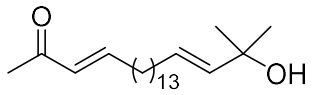
Table3, entry4: According to the general procedure, benzalacetone (**1**) (14.6 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TESOTf (34 μL, 0.15 mmol, 1.5 equiv.), $CeCl_3$ (74.0 mg, 0.30 mmol, 3.0 equiv.), EtMgBr (0.125 mL of 1.6 M THF solution, 0.20 mmol, 2.0 equiv.), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **1** (12.6 mg, 86%) and **8Bb** (16.4 mg, 89%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 30/1).

Table 3, entry 8: According to the general procedure, **3** (14.0 mg, 0.10 mmol), 4 (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (39.3 mg, 0.15 mmol, 1.5 equiv.), TESOTf (34 μL, 0.15 mmol, 1.5 equiv.), EtMgBr (0.13 mL of 1.6 M THF solution, 0.20 mmol, 2.0 equiv.), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **3** (11.3 mg, 81%) and **8Bb** (16.5 mg, 88%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 30/1).

IR (KBr) 3427 cm^{-1}.**^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 5.59 (1H, dt, J = 15.5, 6.9 Hz), 5.39 (1H, dt, J =

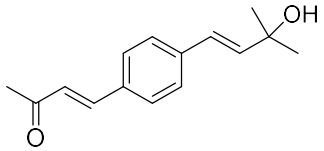
15.5, 1.4 Hz), 2.05 (2H, tdd, *J* = 14.2, 14.2, 1.4 Hz), 1.57-1,26 (10H, m), 1.29-0.83 (9H, m). **^{13}C-NMR** (100 MHz, $CDCl_3$) *δ*: 135.1, 128.9, 75.2, 33.0, 32.3, 31.3, 29.2, 22.5, 14.0, 7.8. **HRMS** (MALDI-TOF) Calcd for $C_{12}H_{24}NaO$ $[M+Na]^+$: 207.1711, found 207.1719.

(3*E*,18*E*)-20-hydroxy-20-methylhenicosa-3,18-dien-2-one (12) (Table 3, entry 10)



According to the general procedure, **5** (60.0 mg, 0.18 mmol), PPh_3 (70.2 mg, 0.27 mmol, 1.5 equiv.), TESOTf (90 μL, 0.27 mmol, 1.5 equiv.), MeMgBr (0.62 mL of 1.0 M THF solution, 0.62 mmol, 3.4 equiv.), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 1.1 equiv.) gave **12** (53.3 mg, 89%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 3/1).
IR (KBr) 3440, 2941, 2851, 1647 cm^{-1}. **^{1}H-NMR** (400 MHz, $CDCl_3$) *δ*: 6.80 (1H, dt, *J* = 16.0, 6.8 Hz), 6.05 (1H, dt, *J* = 16.0, 1.4 Hz), 5.60 (2H, m), 2.25 (3H, s), 2.23-2.20 (2H, m), 2.03-1.98 (2H, m), 1.48-1.43 (2H, m), 1.371.26 (27H, m). **^{13}C-NMR** (100 MHz, $CDCl_3$) *δ*:198.9, 148.7, 137.7, 131.2, 127.3, 70.6, 32.5, 32.1, 29.8, 29.6 (2C), 29.5 (2C), 29.4, 29.3, 29.2, 29.1, 28.0, 26.8. **HRMS** (MALDI-TOF) Calcd for $C_{22}H_{40}NaO_2$ $[M+Na]^+$: 359.2918 found .359.2921.

(*E*)-4-(4-((*E*)-3-Hydroxy-3-methylbut-1-en-1-yl)phenyl)but-3-en-2-one (14) (Table 3, entry 12)



According to the general procedure, **6** (46.0 mg, 0.20 mmol), PPh_3 (78.6 mg, 0.30 mmol, 1.5 equiv.), TESOTf (68 μL, 0.30 mmol, 1.5 equiv.), MeMgBr (0.40 mL of 1.0 M THF solution, 0.40 mmol, 2.0 equiv.), TBAF (0.40 mL of 1.0 M THF solution, 0.40 mmol, 2.0 equiv.) gave **14** (38.6 mg, 84%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 4/1).
IR (KBr) 3461, 2974, 2929, 1663 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) *δ*: 7.50 (2H, d, *J* = 8.2 Hz), 7.48 (1H, d, *J* = 16.0 Hz), 7.41 (2H, d, *J* = 8.2 Hz), 6.71 (1H, d, *J* = 16.0 Hz), 6.60 (1H, d, *J* = 16.0 Hz), 6.43 (1H, d, *J* = 16.0 Hz), 2.38 (3H, s), 1.44 (6H, s). **^{13}C-NMR** (125 MHz, $CDCl_3$) *δ*: 198.5, 143.0, 139.3, 139.2, 133.4, 128.6, 127.0, 126.7, 125.7, 71.1, 29.9, 27.5. **HRMS** (MALDI-TOF) Calcd for $C_{15}H_{18}NaO_2$ $[M+Na]^+$: 253.1204, found 253.1207.

Experimental details in Table 4

General procedure for the selective hydrogenation of α,β-unsaturated ester in the presence of enone (Method A) (Table 4, entries 1, 3, 5, 7, 9, 11)

To a solution of enone (0.10 mmol) and α,β-unsaturated ester (0.10 mmol, 1.0 equiv.) (or enone-unsaturated ester (0.10 mmol)) and PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.) in MeOH/AcOEt (7:1) (0.50 mL) was added dropwise TMSOTf (0.10 mmol, 1.0 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, 5% Pd/C (20 wt%) was added to the reaction mixture. The reaction solution was stirred at rt under a H_2 balloon. After the starting α,β-unsaturated ester was consumed (TLC check), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) was added, then the resulting solution was stirred for 30 min. After filtration through clite pad, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt) to afford the recovered enone and the hydrogenated ester.

Methyl 3-phenylpropanoate (10Aa)[10] (Table 4, entries 1 and 5)

Table 4, entry 1 (Same as entry 1 of Table 2): According to the general procedure, **1** (14.6 mg, 0.10 mmol), **2** (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), 5% Pd/C (20 wt%, 6.2 mg), under H_2 balloon, and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol) gave recovered **1** (13.6 mg, 93%), **10Aa**[10] (16.2 mg, 99%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 15/1).

Table 4, entry 5: According to the general procedure, **3** (14.6 mg, 0.10 mmol), **2** (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol), TMSOTf (18 μL, 0.10 mmol), 5% Pd/C (20 wt%, 6.2 mg), H_2, and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **3** (13.6 mg, 97%) and **10Aa**[10] (16.4 mg, quant) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 15/1).**^{1}H-NMR** (400 MHz, $CDCl_3$) δ : 7.32 (2H, d, J = 7.5 Hz), 7.20 (2H, t, J = 7.5 Hz), 7.17 (1H, t, J = 7.5Hz), 3.64 (3H, s), 2.96 (2H, t, J = 7.5 Hz), 2.63 (2H, t, J = 7.5 Hz,).**^{13}C-NMR** (100 MHz, $CDCl_3$, pp) δ :173.4, 140.5, 128.8, 128.2, 126.5, 51.6, 36.1, 31.2 .

Methyl octanoate (10Ba)[15] (Table 4, entries 3 and 7)

Table 4, entry 3: According to the general procedure, **1** (14.6 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), 5% Pd/C (20 wt%, 6.0 mg), H_2, and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **1** (13.9 mg, 95%) and **10Ba**[15] (15.3 mg, 97%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 20/1).

Table 4, entry 7: According to the general procedure, **3** (14.0 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), 5% Pd/C (20 wt%, 5.9 mg), H_2, and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave recovered **3** (14.0 mg, quant) and **10Ba**[15] (15.7 mg, 99%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 20/1).

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.65 (s, 3H), 2.32 (2H, t, J = 7.9 Hz), 1.6 (2H, m), 1.30 (8H, m), 0.88

(3H, t, J = 6.8 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 174.6, 51.6, 34.3, 31.9, 29.3, 29.1, 25.2, 22.8, 14.3.

Methyl (*E*)-19-oxohenicos-17-enoate (15)

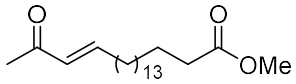


Table 4, entry 9: According to the general procedure, **5** (33.4 mg, 0.10 mmol), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), 5% Pd/C (20 wt%, 6.7 mg), under H_2 balloon, and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) gave **15** (31.9 mg, 95%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 10/1).
IR (KBr) 2927, 2855, 1734, 1696 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 6.80 (1H, dt, J = 15.3, 6.9 Hz), 6.08 (1H, d, J = 15.3 Hz), , 3.67 (3H, s), 2.31-2.24 (2H, m), 2.22 (3H, s), 2.21-2.20 (2H, m), 1.63-1.60 (2H, m), 1.48-1.45 (2H, m), 1.29-1.25 (22H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.9, 174.4, 148.8, 131.3, 51.5, 34.1, 32.5, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 28.1, 27.8, 26.8, 25.0. **HRMS** (MALDI-TOF) Calcd for $C_{21}H_{38}NaO_3$ $[M+Na]^+$: 361.2719, found 361.2711.

Methy (*E*)-3-(4-(3-oxobut-1-en-1-yl)phenyl)propanoat (17)

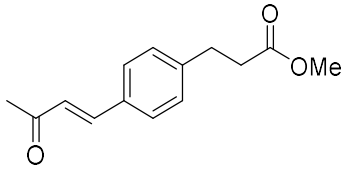


Table 4, entry 11: According to the general procedure, **6** (46.0 mg, 0.20 mmol), PPh_3 (52.4 mg, 0.20 mmol, 1.0 equiv.), TMSOTf (36 μL, 0.20 mmol, 1.0 equiv.), 5% Pd/C (20 wt%, 9.2 mg), under H_2 balloon, and TBAF (0.40 mL of 1.0 M THF solution, 0.40 mmol, 2.0 equiv.) gave **17** (44.4 mg, 96%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 8/1).
IR (KBr) 2958, 1726, 1650 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.42 (2H, d, J = 8.1 Hz), 7.40 (1H, d, J = 16.6 Hz), 7.17 (2H, d, J = 8.1 Hz), 6.62 (1H, d, J = 16.6 Hz), 3.60 (3H, s), 2.90 (2H, t, J = 7.5 Hz), 2.58 (2H, t, J = 7.5 Hz), 2.30 (3H, s). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.4, 173.0, 143.4, 143.2, 132.5, 129.0, 128.5, 126.7, 51.7, 35.2, 30.7, 27.5. **HRMS** (MALDI-TOF) Calcd for $C_{14}H_{16}NaO_3$ $[M+Na]^+$: 255.0992, found 255.0992.

General procedure for the selective dihydroxylation of α,β-unsaturated ester in the presence of enone (Method B) (Tables 4, entry 2, 4, 6, 8, 10, 12) : To a solution of enone (0.10 mmol), α,β-unsaturated ester (0.10 mmol, 1.0 equiv.) (or enone-unsaturated ester (0.10 mmol)) and PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.) in acetone (0.5 mL) was added dropwise TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, H_2O (10 μL), K_2OsO_4 (10 mol%), and NMO

(0.50 mmol, 5.0 equiv.) were added to the mixture. After the starting ester was consumed (TLC check), Na_2SO_3 (0.10 mmol, 1.0 equiv.) and TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) were added to the mixture, then the resulting solution was stirred for 30 min. The mixture was poured into H_2O (10 mL) and extracted with CH_2Cl_2 (20 mL × 3). The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt) to afford the recovered enone and dihydrated ester.

Methyl 2,3-dihydroxy-3-phenylpropanoate (10Ab)[12] (Table 4, entries 2 and 6)

Table 4, entry 2: According to the general procedure, **1** (14.6 mg, 0.10 mmol), **2** (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59.0 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave recovered **1** (12.0 mg, 82%) and **10Ab[12]** (17.5 mg, 89%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/2).

Table 4, entry 6: According to the general procedure, **3** (14.0 mg, 0.10 mmol), **2** (16.2 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59.0 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave recovered **3** (11.5 mg, 77%) and **10Ab[12]** (15.7 mg, 80%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/2).**^{1}H-NMR** (300 MHz, $CDCl_3$) δ:7.42 (2H, d, J = 7.6 Hz), 7.24 (2H, t, J = 7.6 Hz), 7.21 (1H, t, J = 7.6 Hz), 5.05 (1H, d, J = 2.6 Hz), 4.38 (1H, d, J = 2.6 Hz), 3.80 (3H, s), 3.17 (1H, brs), 2.80 (1H, brs).**^{13}C-NMR** (75 MHz, $CDCl_3$) δ:173.0, 139.7, 128.4, 128.1, 126.0, 74.5. 74.4, 52.7.

Methyl 2,3-dihydroxyoctanoate (10Bb)[16] (Table 4, entries 4, 8)Table 4, entry 4: According to the general procedure, **1** (14.6 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave recovered **1** (11.2 mg, 78%) and **10Bb[16]** (15.7 mg, 82%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/4).

Table 4, entry 8: According to the general procedure, **3** (14.0 mg, 0.10 mmol), **4** (15.6 mg, 0.10 mmol, 1.0 equiv.), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59.0 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave recovered **3** (11.1 mg, 79%) and **10Ab[16]** (15.8 mg, 83%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/4).

^{1}H-NMR (300 MHz, $CDCl_3$) δ:4.19-4.08 (1H, m), 3.82–3.90 (1H, m), 3.82 (3H, s), 3.48 (1H, br), 2.56(1H, br), 1.68 (2H, m), 1.58-1.68 (2H, m), 1.47 (1H, m), 1.25–1.41 (5H, m), 0.87 (3H, t, J = 6.8 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$) δ: 169.4, 56.9, 51.4, 48.9, 30.6, 29.2, 29.1, 24.0, 23.3.

Methyl (*E*)-2,3-dihydroxy-19-oxoicos-17-enoate (16)

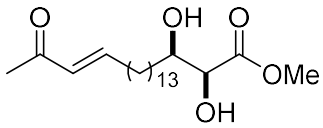


Table 4, entry 10: According to the general procedure, **5** (35.0 mg, 0. 10 mmol), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59.0 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave **16** (28.4 mg, 74%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/3).

IR (KBr) 3480, 2919, 2853, 1734, 1684 cm^{-1}. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 6.81 (1H, dt, J = 15.3, 6.9 Hz), 6.06 (1H, dt, J = 15.3, 1.0 Hz), 4.11 (1H, dt, J = 5.48, 1.0 Hz), 3.84 (3H, s), 3.02 (1H, d, J = 5.48 Hz), 2.25 (3H, s), 2.23-2.20 (2H, m), 1.64-1.58 (2H, m), 1.43-1.29 (22H, m).**^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 207.9, 167.2, 149.9, 120.7, 56.9, 51.4, 48.2, 33.8, 32.2, 31.1, 29.7, 29.6, 29.6, 29.5, 29.4, 29.1, 28.0, 25.0. Since the carbon chain of the substrate is long and the peak is covered with another carbon peak, the peak of ^{13}C NMR is three fewer. **HRMS** (MALDI-TOF) Calcd for $C_{21}H_{38}NaO_5$ $[M+Na]^+$: 393.2612, found 393.2610

Methyl (*E*)- 2,3-dihydroxy-3-(4-(3-oxobut-1-en-1-yl)phenyl)propanoate (18)

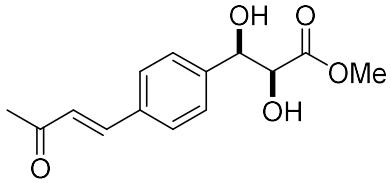


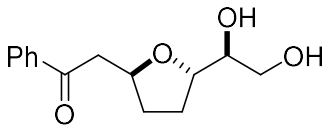
Table 4, entry 12: According to the general procedure, **6** (23.0 mg, 0.10 mmol), PPh_3 (26.2 mg, 0.10 mmol, 1.0 equiv.), TMSOTf (18 μL, 0.10 mmol, 1.0 equiv.), $K_2OsO_4 \cdot 2H_2O$ (3.70 mg, 10 mol%), NMO (59.0 mg, 0.50 mmol, 5.0 equiv.), H_2O (10 μL), TBAF (0.20 mL of 1.0 M THF solution, 0.20 mmol, 2.0 equiv.) and Na_2SO_3 (10.4 mg, 0.10 mmol, 1.0 equiv.) gave **18** (18.7 mg, 71%) as a colorless oil after purification by flash column chromatography (*n*-Hexane/AcOEt = 1/3).

IR (KBr) 3658, 1724, 1695 cm^{-1}. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ: 7.53 (2H, d, J = 8.2 Hz), 7.49 (1H, d, J = 16.5 Hz), 7.44 (2H, d, J = 8.2 Hz), 6.68 (1H, d, J = 16.5 Hz), 5.05 (1H, dd, J = 6.9, 2.8 Hz), 4.38 (1H, dd, J = 6.0, 2.7 Hz), 3.83 (3H, s), 3.36 (1H, d, J = 6.0 Hz), 3.19 (1H, d, J = 7.3 Hz), 2.37 (3H, s). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ: 198.7, 172.9, 143.0, 142.6, 134.0, 128.3, 127.2, 126.8, 74.5, 74.0, 52.9, 27.5. **HRMS** (MALDI-TOF) Calcd for $C_{14}H_{16}NaO_5$ $[M+Na]^+$: 287.0890, found 287.0891

General procedure for the one-pot synthesis of cyclic ethers (Scheme 2)

To a solution of enone-unsaturated ester **19** (0.30 mmol) and PPh_3 (78.9 mg, 0.30 mmol, 1.0 equiv.) in CH_2Cl_2 (1.2 mL) was added dropwise TMSOTf (54 μL, 0.30 mmol, 1.0 equiv.) at 0 °C. After being stirred for 30 min at 0 °C, DIBAL-H (1.0 M toluene solution, 0.90 mL, 3.0 equiv.) was added to the mixture. TLC analysis was conducted after quenching a small amount of the reaction mixture with a drop of TBAF (1.0 M THF solution). 1*N* HCl (100 μL) was added, then the resulting solution was stirred for 2 h. The solvent was evaporated. Acetone/H_2O (50:1) (1.2 mL), $K_2OsO_4 \cdot 2H_2O$ (111 mg, 0.03 mmol, 10 mol%), and NMO (176 mg, 1.5 mmol, 5.0 equiv.) were added to the residue, and the resulting solution was stirred at 0°C. TLC analysis was conducted after quenching a small amount of the reaction mixture with a drop of TBAF (1.0 M THF solution). The solvent was evapolated. After addition of 1,4-dioxane (6.0 mL) and K_2CO_3 (207 mg 1.5 mmol, 5.0 equiv.) at rt, the mixture was refluxed. In the cases of **20c** and **20d**, THF and KO^{t}Bu were used in place of 1,4-dioxane and K_2CO_3. After the enone diol was consumed by TLC check, the reaction was quenched by adding saturated NH_4Cl aq. The mixture was extracted with AcOEt (20 mL × 15). The extract was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (*n*-Hexane/AcOEt) to afford the desired cyclic ether **20**.

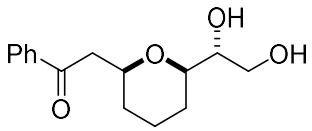
2-(5-(1,2-Dihydroxyethyl)tetrahydrofuran-2-yl)-1-phenylethan-1-one (±)-20a



entry 1: According to the general procedure, **19a** (73.2 mg, 0.30 mmol), PPh_3 (78.9 mg, 0.30 mmol, 1.0 equiv.), CH_2Cl_2 (1.2 mL), TMSOTf (54 μL, 0.3 mmol, 1.0 equiv.), DIBAL-H (1.0 M toluene solution, 0.9 mL, 3.0 equiv.), 1 *N* HCl (100 μL), Acetone/H_2O (50:1) (1.2 mL), $K_2OsO_4 \cdot 2H_2O$ (11.1 mg, 0.03 mmol, 10 mol%), NMO (176 mg, 1.5 mmol, 5.0 equiv.), 1,4-dioxane (6.0 mL) and K_2CO_3 (207 mg, 1.5 mmol, 5.0 equiv.) afforded **20a** (42.8 mg, 57%) as a colorless oil after purification (AcOEt only) by flash column chromatography.

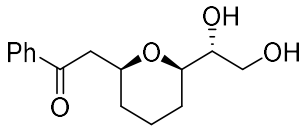
IR (KBr) 3432, 3055, 1683 cm^{-1}. **^{1}H-NMR**. (500 MHz, $CDCl_3$) δ: 7.95 (2H, dd, J = 7.0, 1.2 Hz), 7.56 (1H, tt, J = 7.0, 1.2 Hz) 7.47 (2H, t, J = 7.0 Hz), 4.57-4.54 (1H, m), 4.09-4.05 (1H, m), 3.73-3.63 (2H, m), 3.57-3.54 (1H, m), 3.38 (1H, dd, J = 16.0, 6.3 Hz), 3.08 (1H, dd, J = 16.0, 6.3 Hz), 2.31-2.26 (1H, m), 2.06-2.01 (1H, m), 1.95-1.89 (1H, m), 1.69-1.61 (1H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.1, 136.9, 133.3, 128.6, 128.1, 80.1, 75.9, 73.0, 64.5, 44.4, 32.4, 27.9. **HRMS** (MALDI-TOF) Calcd for $C_{14}H_{18}NaO_4$ $[M+Na]^+$: 273.1097, found 273.1097.

2-(6-(1,2-Dihydroxyethyl)tetrahydro-2H-pyran-2-yl)-1-phenylethan-1-one (±)-20b



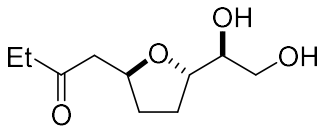
entry 2: According to the general procedure, **19b** (77.4 mg, 0.30 mmol), PPh_3 (78.9 mg, 0.30 mmol, 1.0 equiv.), CH_2Cl_2 (1.2 mL), TMSOTf (54 μL, 0.3 mmol, 1.0 equiv.), DIBAL-H (1.0 M toluene solution, 0.9 mL, 3.0 equiv.), 1N HCl (100 μL), Acetone/H_2O (50:1) (1.2 mL), $K_2OsO_4 \cdot 2H_2O$ (11.1 mg, 0.03 mmol 10 mol%), NMO (176 mg, 1.5 mmol, 5.0 equiv.), 1,4-dioxane (6.0 mL) and K_2CO_3 (207 mg 1.5 mmol, 5.0 equiv.) afford the desired products **20b** (53.9 mg, 68%) as a colorless oil after purification (AcOEt only) by flash column chromatography.

2-((2S,6R)-6-((R)-1,2-Dihydroxyethyl)tetrahydro-2H-pyran-2-yl)-1-phenylethan-1-one (+)-20b



entry 3: According to the general procedure, **19b** (38.7 mg, 0.15 mmol), PPh_3 (39.5 mg, 0.15 mmol, 1.0 equiv.), CH_2Cl_2 (0.6 mL), TMSOTf (27 μL, 0.15 mmol, 1.0 equiv.), DIBAL-H (1.0 M toluene solution, 0.45 mL, 3.0 equiv.), 1N HCl (100 μL), Acetone/H_2O (50:1) (0.6 mL), OsO_4 (1.9 mg, 5 mol%), Hydroquinidine 4-cholorobenzoate (7.0 mg, 10 mol%), NMO (88 mg, 1.5 mmol, 3.0 equiv.), 1,4-dioxane (3.0 mL) and K_2CO_3 (104 mg, 1.50 mmol, 5.0 equiv.) afforded optically active **20b** (23.5 mg, 59%) as a colorless oil after purification (AcOEt only) by flash column chromatography. Optical purity (83% ee) was determined by HPLC using chiral DAICEL CHIRALPAK OD-H $[\alpha]_D^{23} = +2.44$ (c = 1.00, $CHCl_3$). **IR** (KBr) 3345, 1699 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.96 (2H, dd, J = 6.9, 1.3 Hz), 7.57 (1H, tt, J = 6.9, 1.3 Hz), 7.49 (2H, t, J = 6.9 Hz), 4.04-3.98 (1H, m), 3.69-3.60 (2H, m), 3.52-3.44 (2H, m), 3.28 (1H, dd, J = 19.5, 6.8 Hz), 2.97 (1H, dd, J = 19.5, 6.8 Hz), 2.65-2.43 (2H, brs), 1.93-1.33 (6H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.4, 137.0, 133.2, 128.6, 128.1, 78.8, 74.5, 73.8, 63.9, 44.9, 31.2, 26.8, 22.8. **HRMS** (MALDI-TOF) Calcd for $C_{15}H_{20}NaO_4$ $[M+Na]^+$: 287.1254, found 287.1253. **HPLC** (DAICEL CHIRALPAK OD-H, Hexane/iPrOH = 70/30, flow rate = 0.9 ml/ min, 254nm) : t_{major} = 11.5 min, t_{minor} = 16.6 min.

1-(5-(1,2-Dihydroxyethyl)tetrahydrofuran-2-yl)butan-2-one (±)-20c

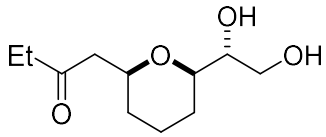


entry 4: According to the general procedure, **19c** (58.8 mg, 0.30 mmol), PPh_3 (78.9 mg, 0.30 mmol, 1.0 equiv.), CH_2Cl_2 (1.2 mL), TMSOTf (54 μL, 0.30 mmol, 1.0 equiv.), DIBAL-H (1.0 M toluene solution, 0.9 mL, 3.0 equiv.), 1 *N* HCl (100 μL), Acetone/H_2O (50:1) (1.2 mL), $K_2OsO_4 \cdot 2H_2O$ (11.1

mg, 0.03 mmol, 10 mol%), NMO (176 mg, 1.5 mmol, 5.0 equiv.), THF (6.0 ml), and KO^{t}Bu (34.0 mg, 0.30 mmol, 1.0 equiv.) afforded **20c**(37.6 mg, 63%) as a colorless oil after purification (AcOEt only) by flash column chromatography.

IR (KBr) 3388, 1706 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ:4.33-4.29 (1H, m), 3.99-3.95 (1H, m), 3.67-3.66 (1H, m), 3.54 (1H, brs), 3.00-2.99 (1H, m), 2.74-2.67 (1H, m), 2.63-2.59 (1H, m), 2.53-2.43 (3H, m), 2.12-2.06 (1H, m), 1.99-1.85 (3H, m), 1.64-1.57 (1H, m), 1.05 (3H, t, J = 7.1 Hz).**^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 209.9, 80.5, 75.8, 73.1, 64.9, 48.1, 36.6, 31.2, 27.2, 7.5. **HRMS** (MALDI-TOF) Calcd for $C_{10}H_{18}NaO_4$ $[M+Na]^+$: 225.1097, found 225.1098

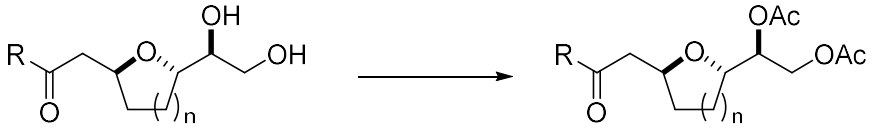
1-(6-(1,2-Dihydroxyethyl)tetrahydro-2H-pyran-2-yl)butan-2-one (±)-20d



entry 5: According to the general procedure, **19d** (63.0 mg, 0.30 mmol), PPh_3 (78.9 mg, 0.30 mmol, 1.0 equiv.), CH_2Cl_2 (1.2 mL), TMSOTf (54 μL, 0.30 mmol, 1.0 equiv.), DIBAL-H (1.0 M toluene solution, 0.9 mL, 3.0 equiv.), 1 *N* HCl (100 μL), Acetone/H_2O (50:1) (1.2 mL), $K_2OsO_4 \cdot 2H_2O$ (11.1 mg, 0.03 mmol, 10 mol%), NMO (176 mg, 1.5 mmol, 5.0 equiv.), THF (6.0 mL), and KO^{t}Bu (34.0 mg 0.30 mmol, 1.0 equiv.) afforded **20d** (38.9 mg, 60%) as a colorless oil after purification (AcOEt only) by flash column chromatography.

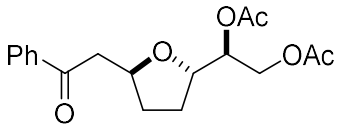
IR (KBr) 3374, 1710 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 3.89-3.84 (1H, m), 3.72-3.64 (2H, m), 3.50-3.47 (2H, m), 2.65 (1H, dd, J = 15.3, 5.5Hz), 2.44 (1H, dd, J = 15.3, 5.0Hz), 2.43, (2H, q, J = 7.1 Hz), 1.90-1.86, (1H, m), 1.62-1.54 (3H, m), 1.47-1.43 (1H, m), 1.27-1.22 (1H, m), 1.05 (3H, t, J = 7.1 Hz). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 209.5, 78.9, 77.2, 73.7, 64.1, 48.7, 36.9, 31.1, 26.8, 22.8, 7.6. **HRMS** (MALDI-TOF) Calcd for $C_{11}H_{20}NaO_4$ $[M+Na]^+$:239.1254 , found 239.1253 .

Compounds **20a-d** were acetylated to give diacetylated products **21a-d**, which were used for NMR study including nOe experiments for determining their structures.



20a-d **21a-d**

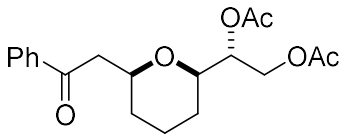
1-(5-(2-Oxo-2-phenylethyl)tetrahydrofuran-2-yl)ethane-1,2-diyl diacetate (21a)



A solution of **20a** (40.0 mg, 0.16 mmol), acetic anhydride (0.30 mL, 3.2 mmol, 20 equiv.) and pyridine (1.6 mL) was stirred until disappearance of the starting material. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with diethyl ether. The combined organic layer was washed with a saturated aqueous $CuSO_4$ solution, water, dried over $NaSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane /AcOEt = 5/1) to give **21a** (52.8 mg, 99%) as a colorless oil.

IR (KBr) 1750, 1690 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.95 (2H, dd, J = 6.9, 1.1 Hz), 7.56 (1H, tt, J = 6.9, 1.1 Hz) 7.47 (2H, t, J = 6.9, 1.1 Hz), 5.11-5.08 (1H, m), 4.53-4.50 (1H, m), 4.33-4.30 (1H, m), 4.16-4.11 (2H, m), 3.43 (1H, dd, J = 16.6, 5.2 Hz), 3.04 (1H, dd, J = 16.6, 5.2 Hz), 2.31-2.29 (1H, m), 2.09 (3H, s), 2.05 (1H, m), 2.04 (3H, s), 1.76-1.72 (1H, m), 1.67-1.59 (1H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.1, 170.7, 170.6, 136.9, 133.2, 128.6, 128.1, 76.1, 72.8, 63.4, 44.5, 44.4, 32.2, 28.0, 21.0, 20.7. **HRMS**(MALDI-TOF) Calcd for $C_{18}H_{22}NaO_6$ $[M+Na]^+$: 357.1306, found 357.1306

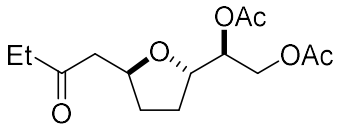
1-(6-(2-Oxo-2-phenylethyl)tetrahydro-2H-pyran-2-yl)ethane-1,2-diyl diacetate (21b)



A solution of **20b** (40.0 mg, 0.15 mmol), acetic anhydride (0.30 mL, 3.0 mmol, 20 equiv.) and pyridine (1.5 mL) was stirred until disappearance of the starting material. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with diethyl ether. The organic layer was washed with a saturated aqueous $CuSO_4$ solution, water, dried over $NaSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane /AcOEt = 5/1) to give **21b** (51.2 mg, 98%) as a colorless oil.

IR (KBr) 2940, 1741, 1241 cm^{-1}. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 7.95 (2H, d, J = 6.9 Hz), 7.56 (1H, t, J = 6.9 Hz) 7.46 (2H, t, J = 6.9 Hz), 5.09-5.06 (1H, m), 4.24 (1H, dd, J = 12.0, 3.4 Hz), 4.04 (1H, dd, J = 12.0, 3.4 Hz), 3.98-3.93 (1H. m), 3.60-3.56 (1H, m), 3.33 (1H, dd, J = 16.0, 7.5 Hz), 2.87 (1H, dd, J = 16.0, 7.5 Hz) 2.02 (3H, s), 1.96 (3H, s), 1.91-1.89 (1H, m), 1.76-1.73 (1H, m), 1.64-1.58 (1H, m), 1.53-1.50 (1H, m), 1.36-1.27 (2H, m). **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 198.6, 170.7, 170.5, 137.4, 133.0, 128.5, 128.3, 76.8, 76.4, 75.3, 72.7, 63.0, 45.0, 31.2, 26.4, 23.0, 20.8. **HRMS**(MALDI-TOF) Calcd for $C_{19}H_{24}NaO_6$ $[M+Na]^+$: 371.1456, found 371.1465

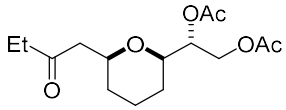
1-(5-(2-Oxobutyl)tetrahydrofuran-2-yl)ethane-1,2-diyl diacetate (21c)



A solution of **20c** (30.0 mg, 0.15 mmol), acetic anhydride (0.30 mL, 3.0 mmol, 20 equiv.) and pyridine (1.5 mL) was stirred until disappearance of the starting material. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with diethyl ether. The organic layer was washed with a saturated aqueous $CuSO_4$ solution, water, dried over $NaSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane /AcOEt = 5/1) to give **21c** (42.5 mg, puant) as a colorless oil.

IR (KBr) 1783, 1242 cm^{-1}.**^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 5.11-5.08 (1H, m), 4.32-4.26 (2H, m), 4.12-4.04 (2H, m), 2.80-2.76 (1H, dd, J = 16.0, 6.9 Hz), 2.53-2.45 (4H, m), 2.08 (3H, s), 2.05 (3H, s), 2.02-1.96 (1H, m), 1.74-1.69 (1H, m), 1.55-1.51 (1H, m), 1.26 (3H, t, J = 7.5 Hz).**^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 209.7, 170.7, 170.5, 77.2, 76.0, 72.8, 63.4, 48.0, 36.9, 31.1, 27.5, 21.0, 20.7, 7.5. **HRMS** (MALDI-TOF) Calcd for $C_{14}H_{22}NaO_6$ $[M+Na]^+$: 309.1305, found 309.1309

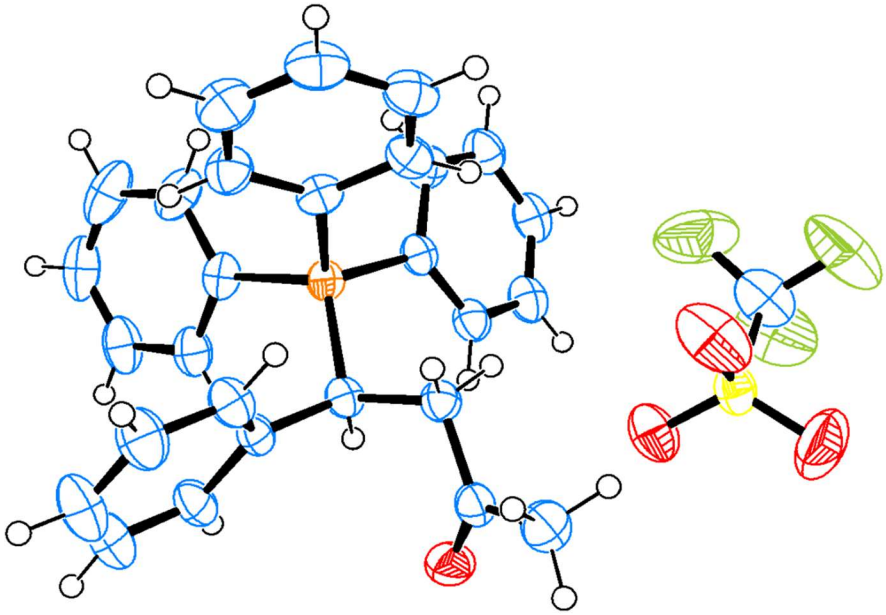
1-(6-(2-Oxobutyl)tetrahydro-2H-pyran-2-yl)ethane-1,2-diyl diacetate (21d)



A solution of **20d** (30.0 mg, 0.15 mmol), acetic anhydride (0.30 mL, 3.0 mmol, 20 equiv.) and pyridine (1.5 mL) was stirred until disappearance of the starting material. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with diethyl ether. The organic layer was washed with a saturated aqueous $CuSO_4$ solution, water, dried over $NaSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane /AcOEt = 5/1) to give **21d** (42.5 mg, quant) as a colorless oil.

IR (KBr) 1743, 1243, 1255 cm^{-1}.**^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 5.10-5.07 (1H, m), 4.28 (1H, dd, J = 12.0, 3.4 Hz), 4.10 (1H, dd, J = 12.0, 3.4 Hz), 3.78 (1H, m), 3.57-3.53 (1H, m), 2.71-2.66 (1H, m), 2.47-2.43 (2H, m), 2.39-2.35 (1H, m), 2.06 (3H, s), 2.04 (3H, s), 1.89-1.86 (1H, m), 1.61-1.48 (2H, m), 1.31-1.21 (3H, m), 1.04 (3H, t, J = 7.5 Hz).**^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 209.8, 170.7, 170.5, 76.3, 75.0, 72.7, 62.9, 48.7, 37.3, 31.0, 26.3, 22.9, 21.0, 20.8, 7.5. **HRMS** (MALDI-TOF) Calcd for $C_{15}H_{24}NaO_6$ $[M+Na]^+$: 323.1466, found 323.1465

X-ray crystallographic analysis of keto phosphonium salt B



Data Collection

A colorless block crystal of $C_{29}H_{26}F_3O_4P$ having approximate dimensions of 0.79 x 0.56 x 0.42 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu-Kα radiation. Indexing was performed from 3 oscillations that were exposed for 135 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 17.1568(3) Å
b = 31.6078(6) Å β = 96.7608(7)°
c = 19.9304(4) Å
V = 10732.9(4) Å^3

For Z = 16 and F.W. = 558.55, the calculated density is 1.383 g/cm^3. The systematic absences of:

h0l: h ± 2n
0k0: k ± 2n

uniquely determine the space group to be: $P2_1/a$

The data were collected at a temperature of -100 ± 1℃ to a maximum 2θ value of 136.5°. A total of 90 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0°

in 10.0° step, at χ = 54.0° and φ = 0.0°. The exposure rate was 50.0 [sec./°]. A second sweep was performed using ω scans from 80.0 to 260.0° in 10.0o step, at χ = 54.0° and φ = 105.0°. The exposure rate was 50.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ = 54.0° and φ = 195.0°. The exposure rate was 50.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ = 54.0° and φ = 285.0°. The exposure rate was 50.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 10.0° step, at χ = 10.0° and φ = 60.0°. The exposure rate was 50.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

The intensity data sets were integrated by CrystalClear software[1]. Of the 19,601 reflections that were collected, 19,601 were unique (R_{int} = 0.082). The linear absorption coefficient, μ, for Cu-Kα radiation is 21.157 cm^{-1}. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structures were solved by direct methods using SIR2004 program[2] and refined by full-matrix least squares on F^2 using SHELXL-97 program[3], implemented in program package WinGX[4]. The final models include anisotropic refinement for the non-hydrogen atoms and a isotropic riding model for H atoms. Further details of the refinements are given table 1.

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC-1507846).

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(1) CrystalClear Rigaku Corporation, The Woodlands, Texas, USA (1999)

(2) Burla MC, Caliandro R, Camalli M, Carrozini B, Cascarano GL, De Caro L, Giacovazzo C, Polidor G, Spagna R *J. Appl. Crystallogr.* (2005) 38,381-338

(3) G. M. Sheldrick *Acta Cryst.,* (2008) A64, 112-122

(4) L.J. Farrugia *J. Appl. Crystallogr*., (1999) 32, 837-838

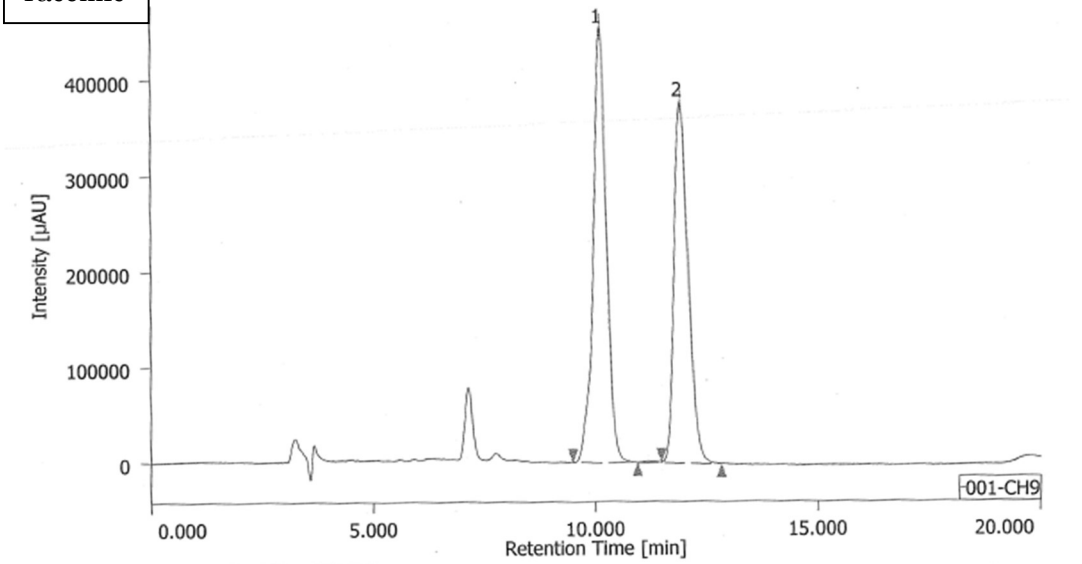
Table 1. Crystallographic data and structure refinement for compound :

Compound	$C_{29}H_{26}F_3O_4PS$
Moiety formula	$C_{28}H_{25}OP$, CF_3O_3S
Sum formula	$C_{29}H_{26}F_3O_4PS$
Formula weight	558.55
Crystal system	monoclinic
Lattice Type	Primitive
Space group	$P2_1/a$
a (Å)	17.1563 (3)
b (Å)	31.6078 (6)
c (Å)	19.9304 (4)
β (°)	96.7608 (7)
V (Å^3)	10732.9 (4)
Z value	16
D_{calcd} (g/cm^3)	1.383
No. of Reflections Measured	19601
No. of Observations (I > 2.00σ(I))	13494
No. of Variables (I > 2.00σ(I))	1369
Reflection/Parameter ratio	9.86
Data completeness	0.998
Residuals : R (I > 2.00σ(I))	0.0672
Residuals : R_w (I > 2.00σ(I))	0.2098
Goodness-of-fit	0.847

HPLC chart for 20b

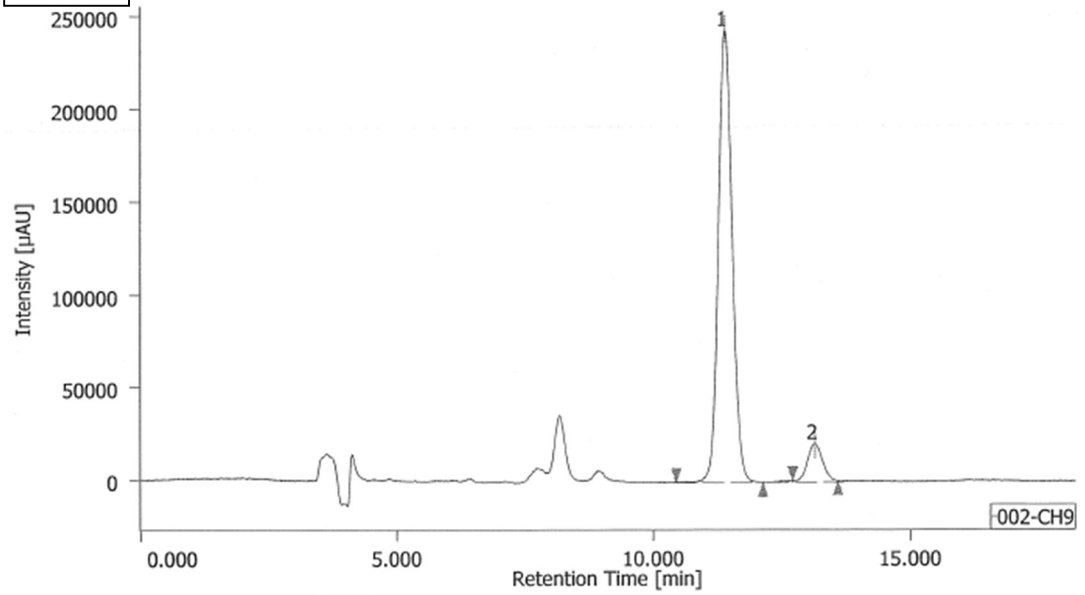
DAICEL CHIRALPAK OD-H, Hexane/iPrOH = 70/30, flow rate = 0.9 ml/ min, 254nm : t_{major} = 11.4 min, t_{minor} = 13.1 min.

racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	10.107	9197549	52.283
2	Unknown	11.907	8394223	47.717

chiral



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	11.373	4535152	91.333
2	Unknown	13.133	430381	8.667

References and Notes

[1] C. Burmester, S and Mataka, T. Thiemann, *Synth. Commun.*, 2010, **40**, 3196-3208.

[2] L. Marques, H. Eugenia and P. Raquel, *Synthesis.,* 2013, **45**, 1016-1028.

[3] K. Li and A. Alexakis, *Chem. Eur. J.,* 2007, **13**, 3765-3771.

[4] M. Yu and S.G. Kim, *Tetrahedron Lett.,* 2015, **56**, 4159-4162.

[5] Y. Sahara, J. Cui, M. Furutachi, J. Chen, T. Watanabe and M. Shibasaki, *Synthesis,* 2017, **49***, 69-75*

[6] T. N. Nguyen, O. Thiel, F. Pape and F. Teichert, *Org Lett*, 2016, **18**, 2455-2458.

[7] R. Tomita, K. Mantani, A. Hamasaki, T. Ishida and M. Tokunaga, *Chem*. *Eur*. *J*., 2014, **20**, 9914-9917.

[8] W. Tuckmantel, K, Oshima and H. Nozaki, *Chem. Ber*., 1986, 119, 1581-1593.

[9] C. A . Parrodi and J. Walsh, *Synlett*, 2004, **13**, 2417-2420.

[10] S. T. Heller and S. Richmond, *Org Lett*, 2010, **12**, 4572-4575.

[11] B. Meryem, T. Sakari and P. M. Petri, *Chem*. *Eur*. *J*., 2011, **17**, 8404-8413.

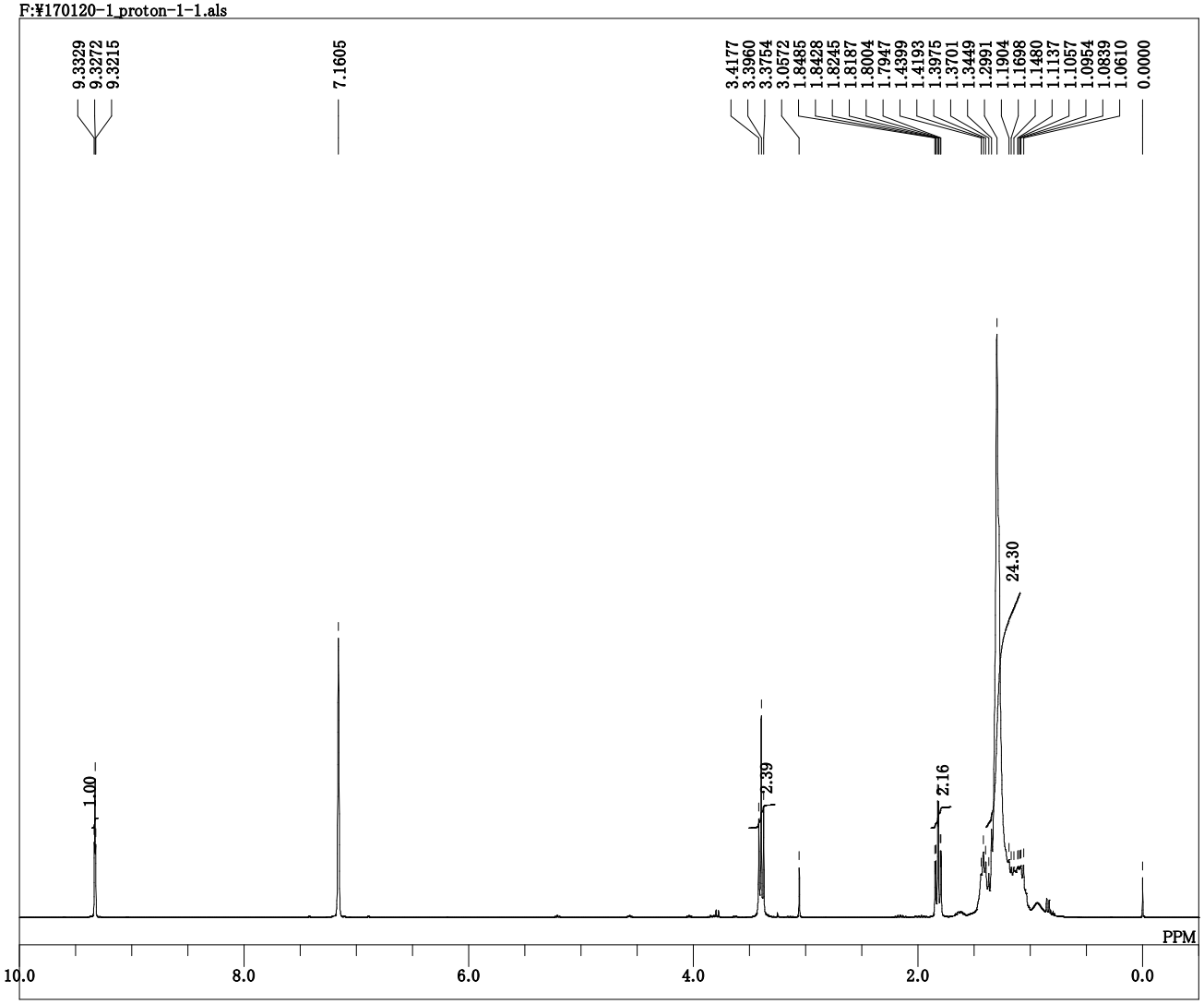
[12] S. Superchi, D. Casarini, C. Summa and C. Rosini, *J. Org*. *Chem*., 2004, **69**, 1685-1694.

[13] Li. L. Y, D. C. Yang, Z. Guan and Y. H. He, *Tetrahedron*, 2015, **71**, 1659-1667.

[14] R. Tomita, K. Mantani, A. Hamasaki, T. Ishida and M. Tokunaga, *Chem*. *Eur*. *J*., 2014, **20**, 9914-9917.

[15] A. B. Powell and S. S. Stahl, *Org Lett*, 2013, **15**, 5072-5075.

[16] K. Mori, K. Osada and M. Amaike, *Tetrahedron Asymmetry*, 2015, **26**, 861-867.



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OBFIN	8.57 Hz
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SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
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CTEMP	19.6 c
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EXREF	0.00 ppm
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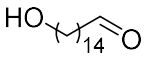
RGAIN	34



S1

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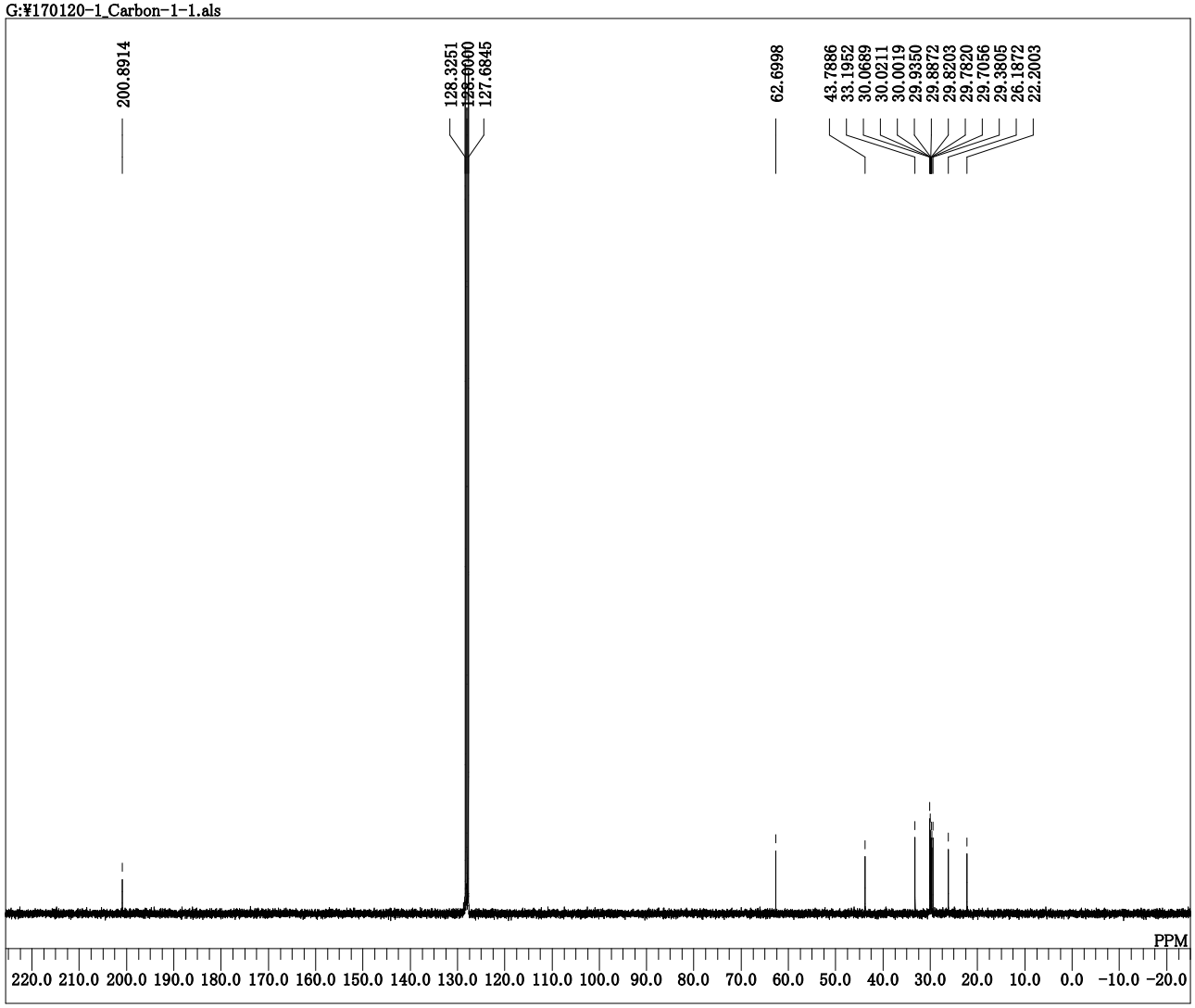

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OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.39 Hz
SCANS	272
ACQTM	1.3841 sec
PD	2.5000 sec
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CTEMP	19.6 c
SLVNT	C6D6
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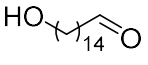
BF	0.12 Hz
RGAIN	60



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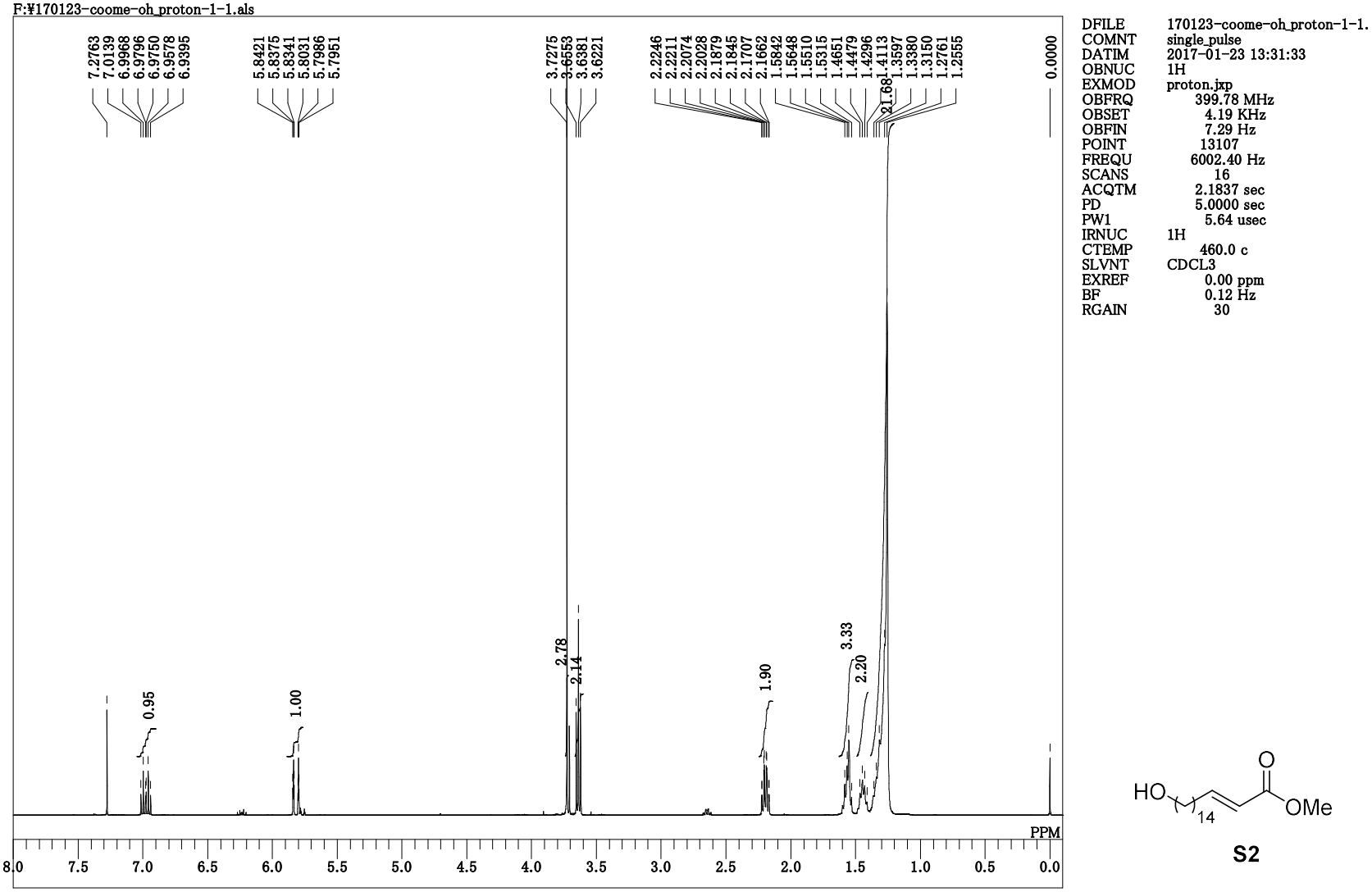

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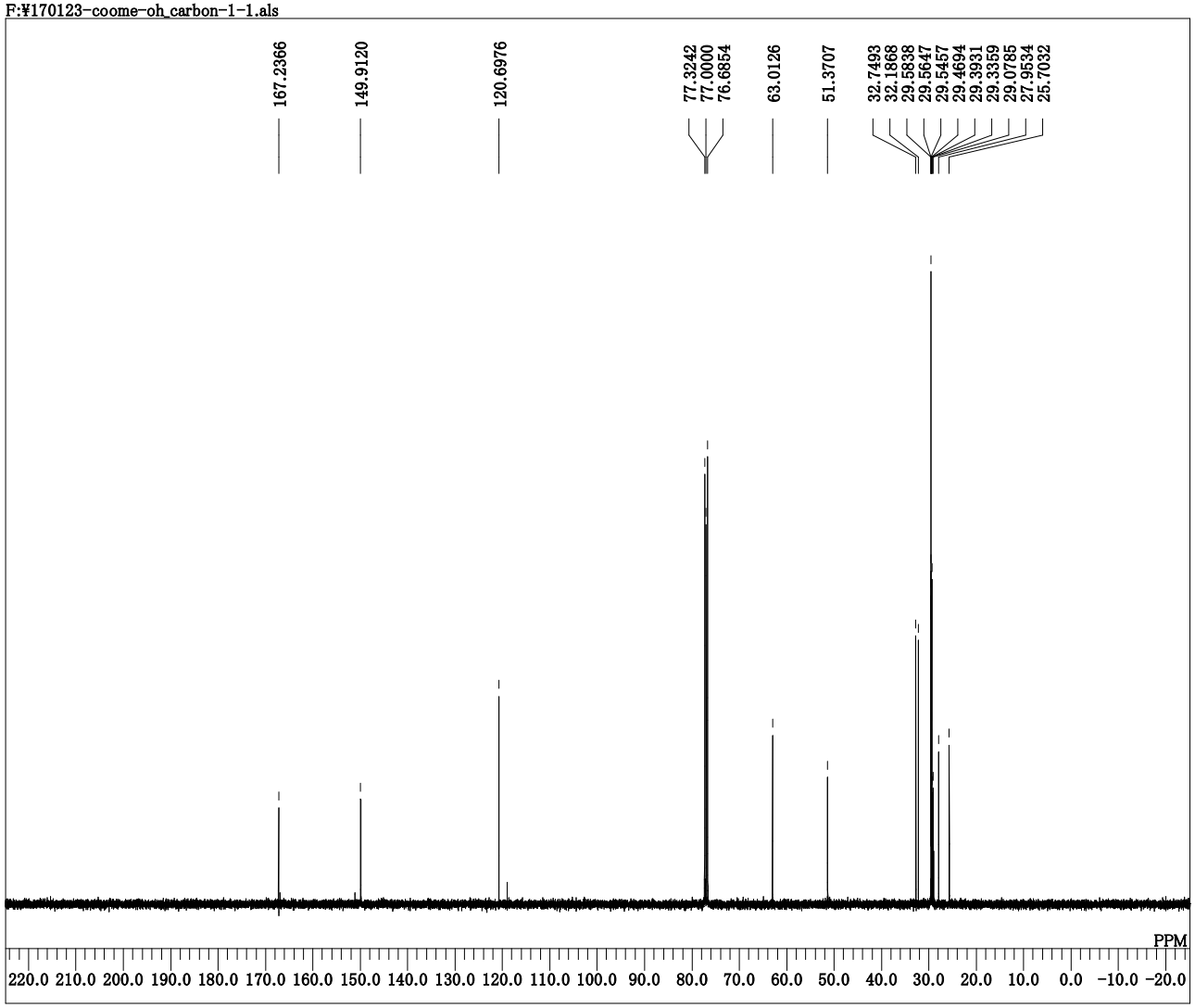
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	30

S2

F:¥170123-coome-oh_carbon-1-1.als



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FREQU	25125.63 Hz
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PD	2.0000 sec
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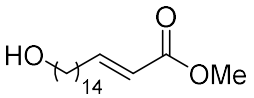
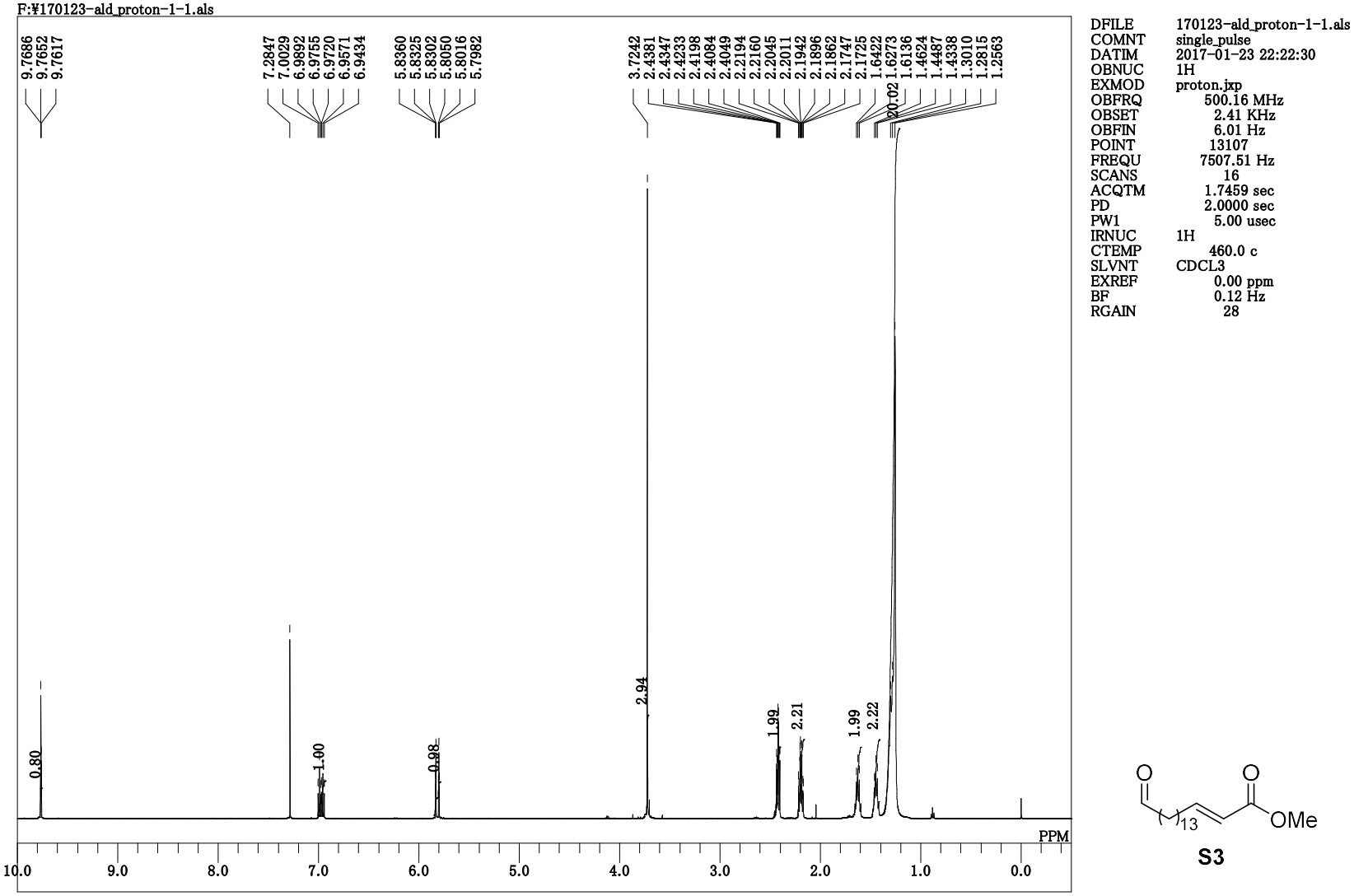
BF	0.12 Hz
RGAIN	60



S2



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OBFIN	6.01 Hz
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FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.00 usec
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CTEMP	460.0 c
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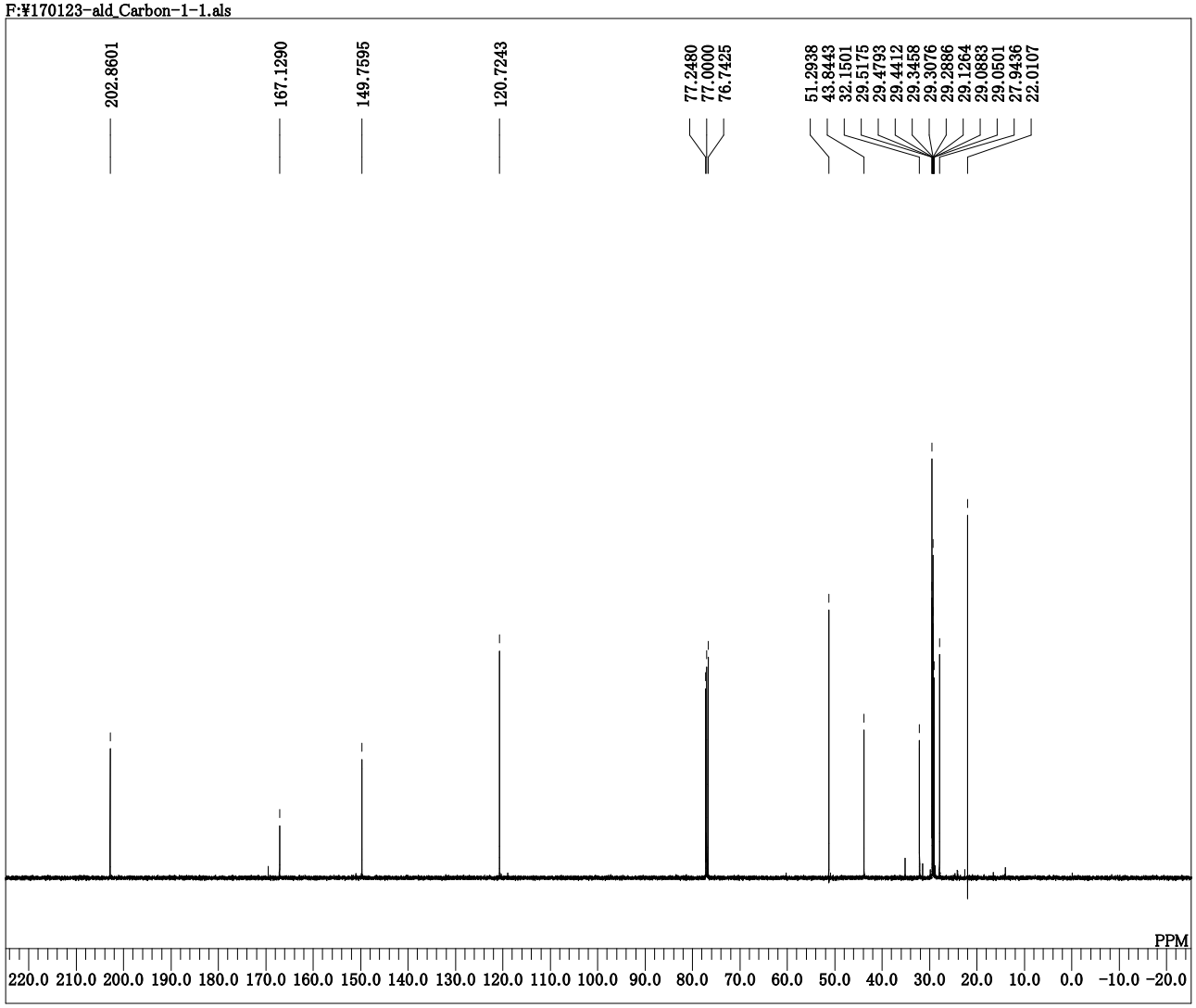
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	28

S3

F:¥170123-ald_Carbon-1-1.als



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OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
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PD	2.0000 sec
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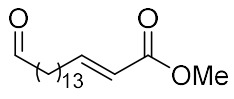
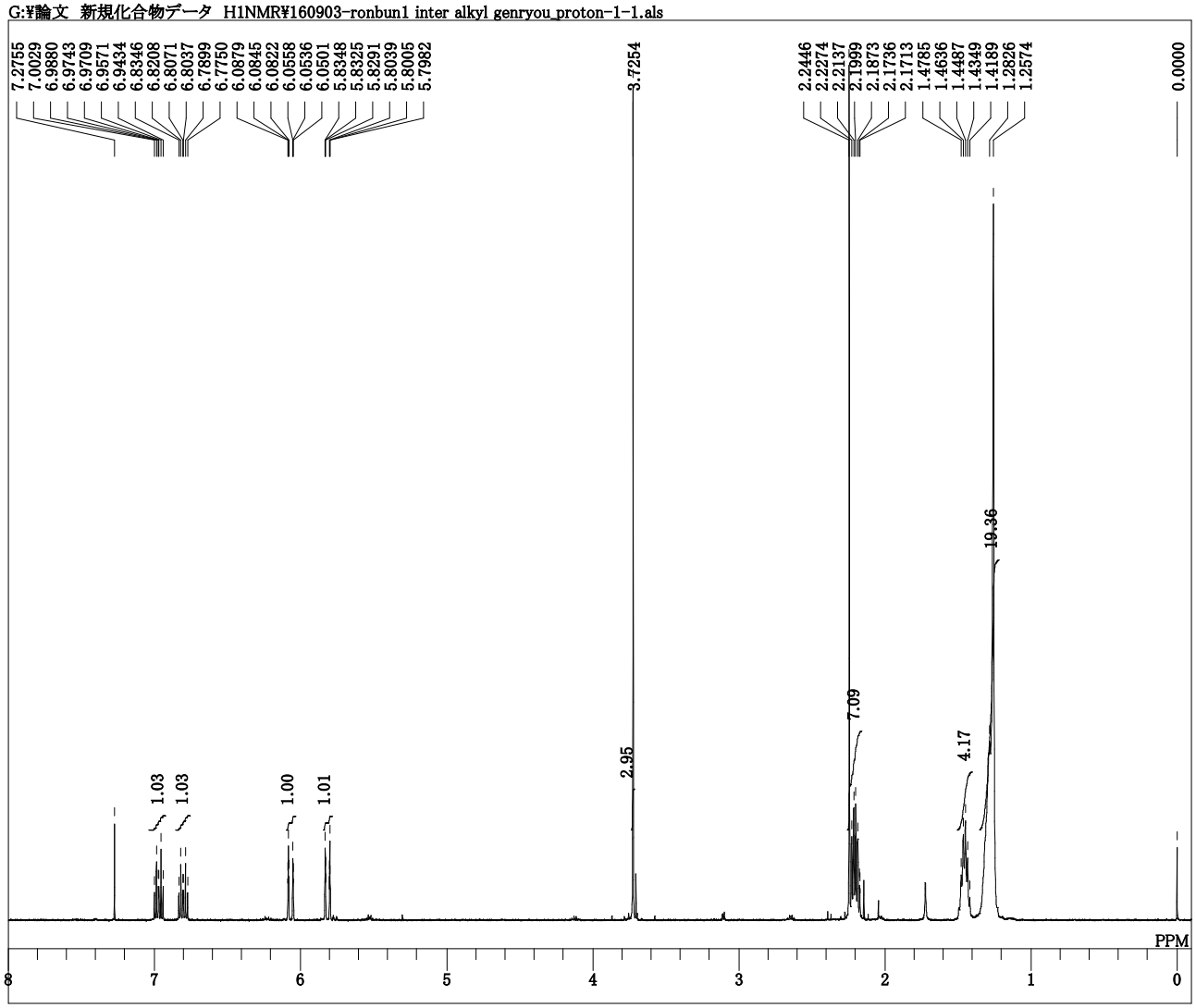
RGAIN	58



S3



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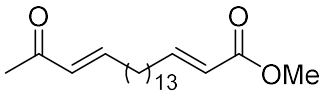
RGAIN	70



5

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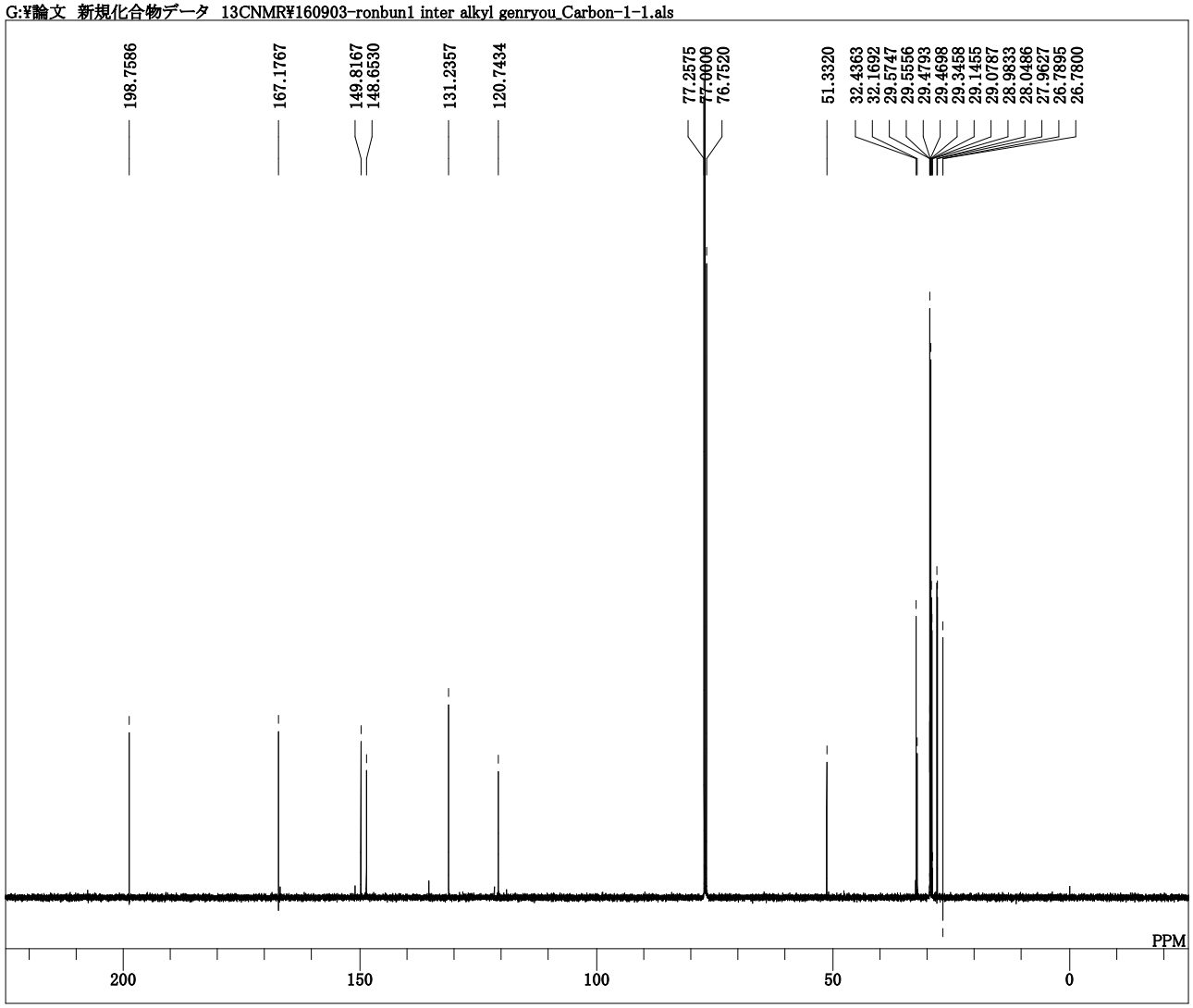

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POINT	26214
FREQU	31446.54 Hz
SCANS	1006
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PD	3.0000 sec
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CTEMP	22.2 c
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EXREF	77.00 ppm
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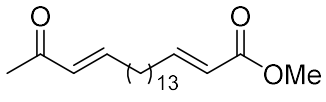
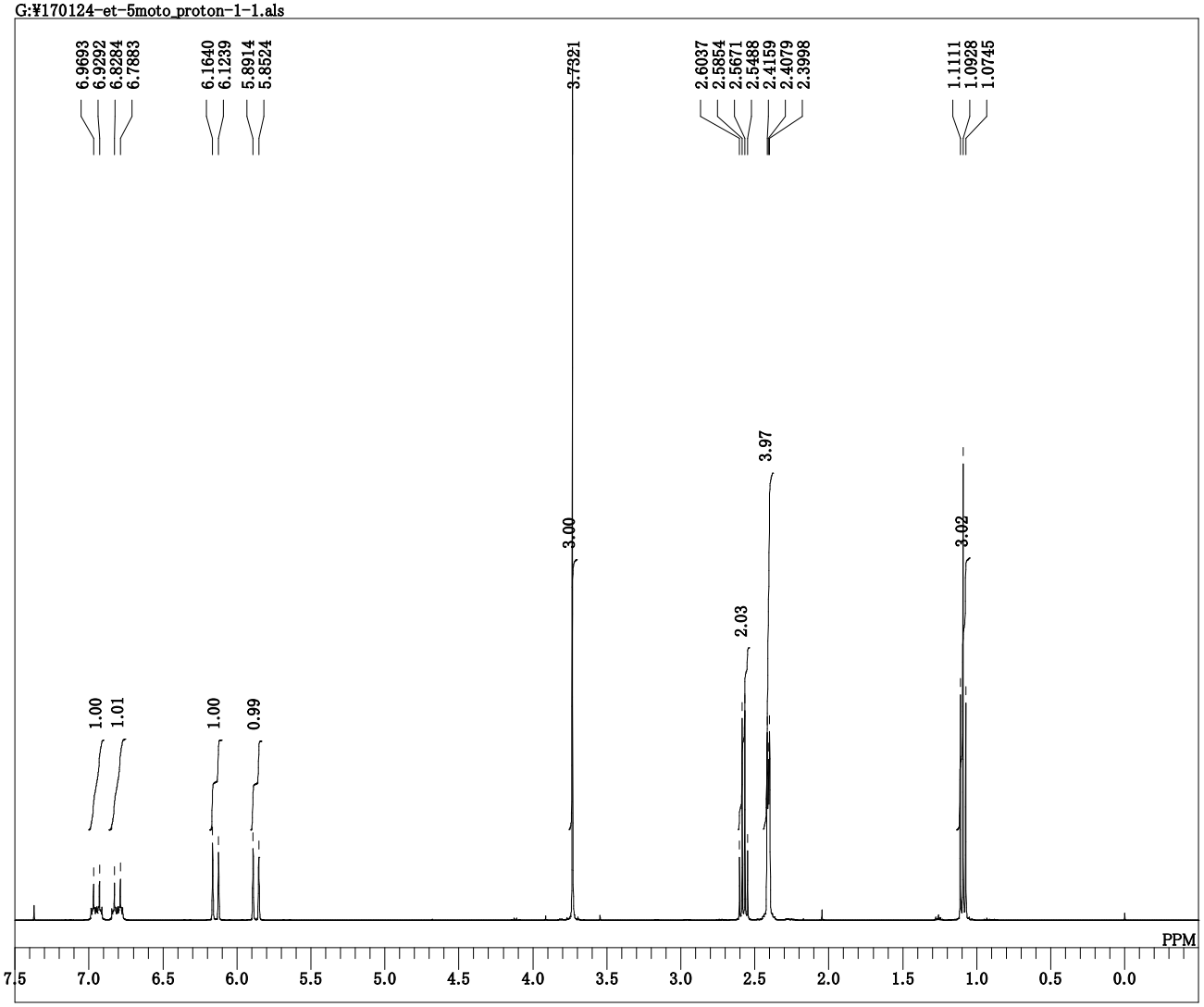
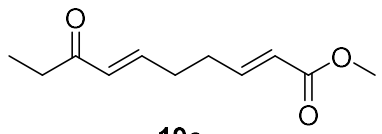
RGAIN	60



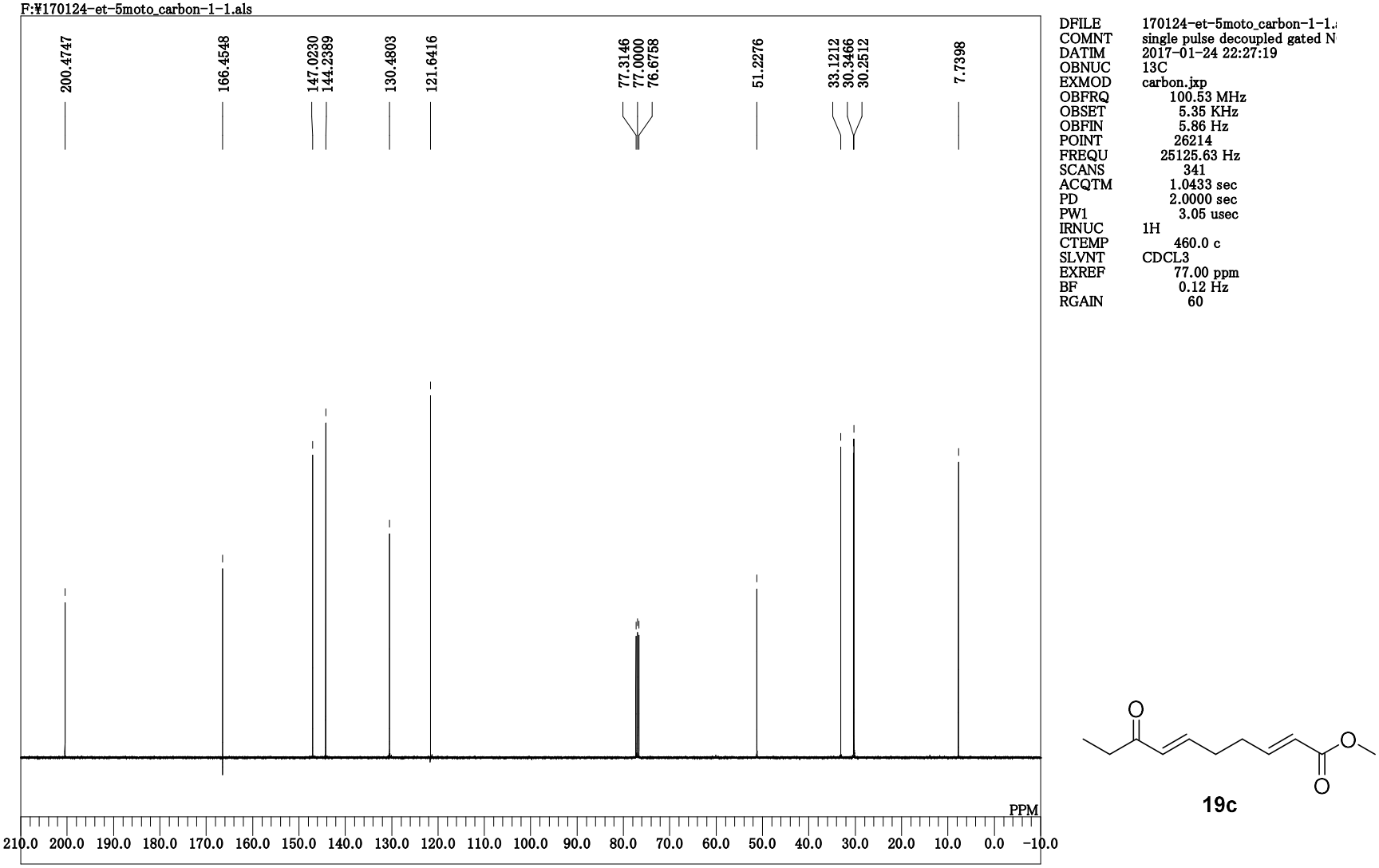
5



DFILE	170124-et-5moto_proton-1-1.a
COMNT	single_pulse
DATIM	2017-01-24 22:22:07
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20

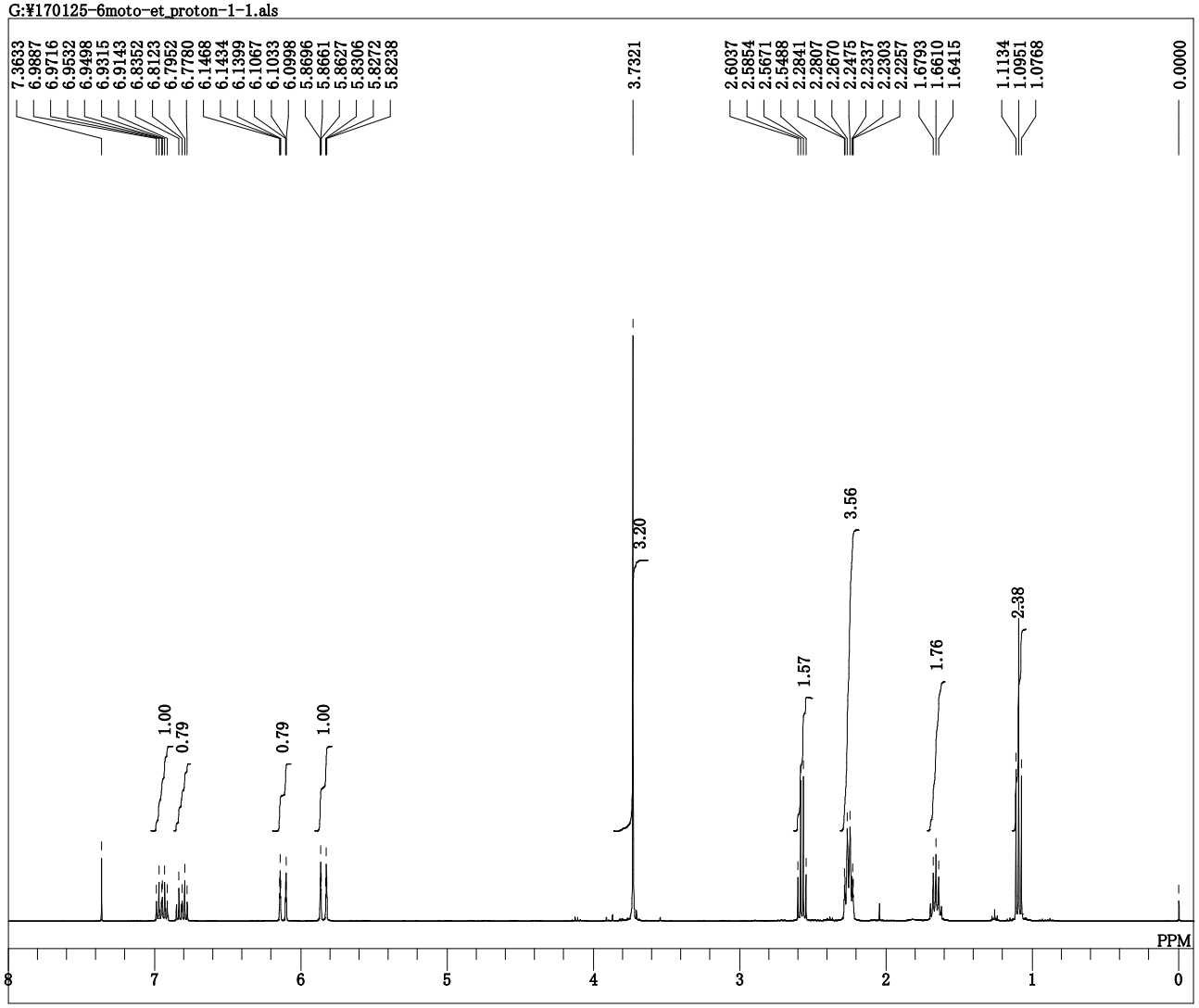


19c

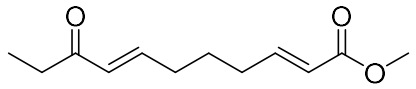


DFILE	170124-et-5moto_carbon-1-1.
COMNT	single pulse decoupled gated N
DATIM	2017-01-24 22:27:19
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	341
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

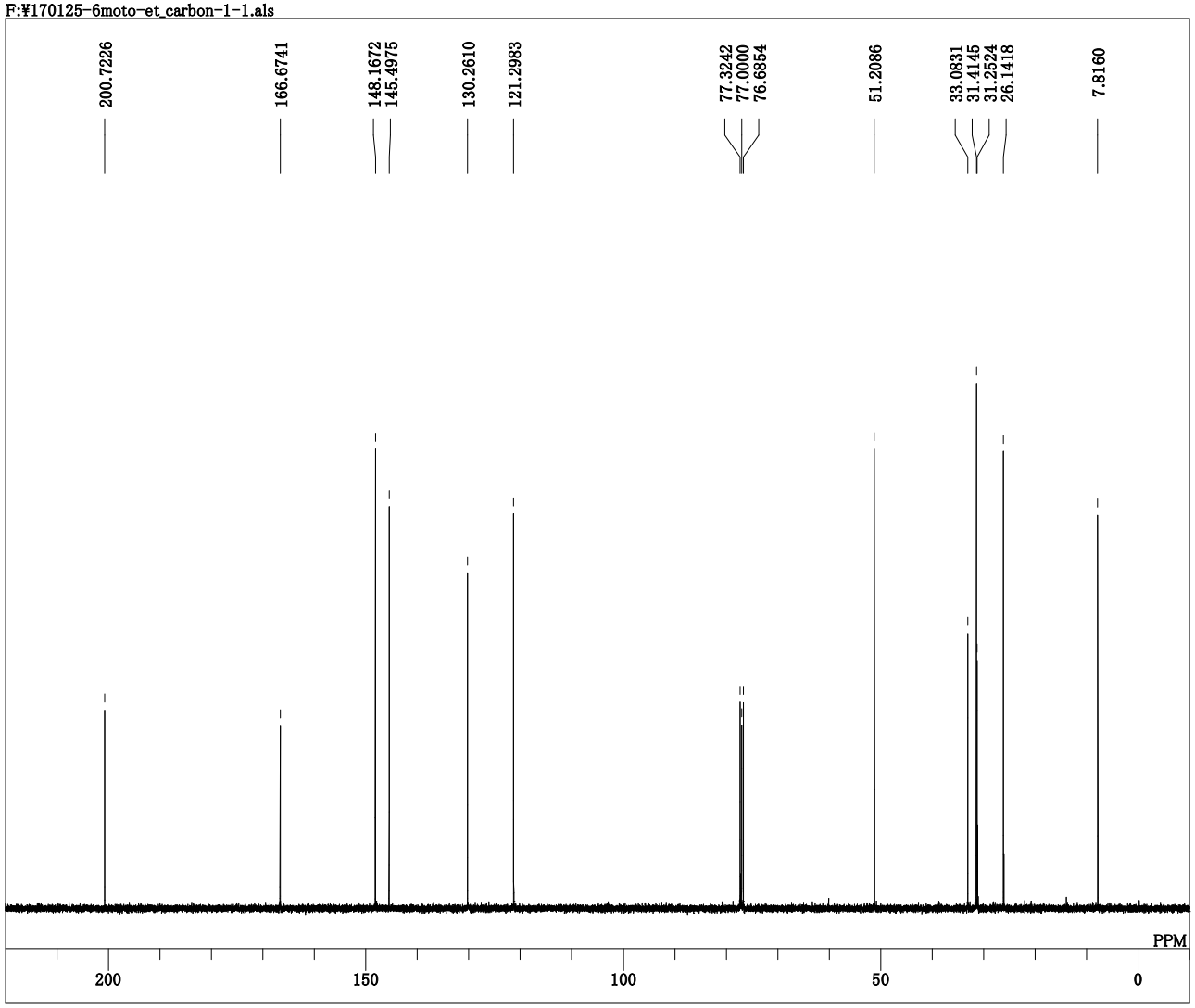
19c



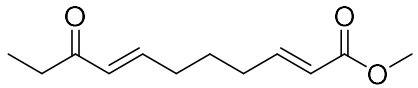
DFILE 170125-6moto-et_proton-1-1.a
COMNT single_pulse
DATIM 2017-01-25 21:09:07
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.64 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20



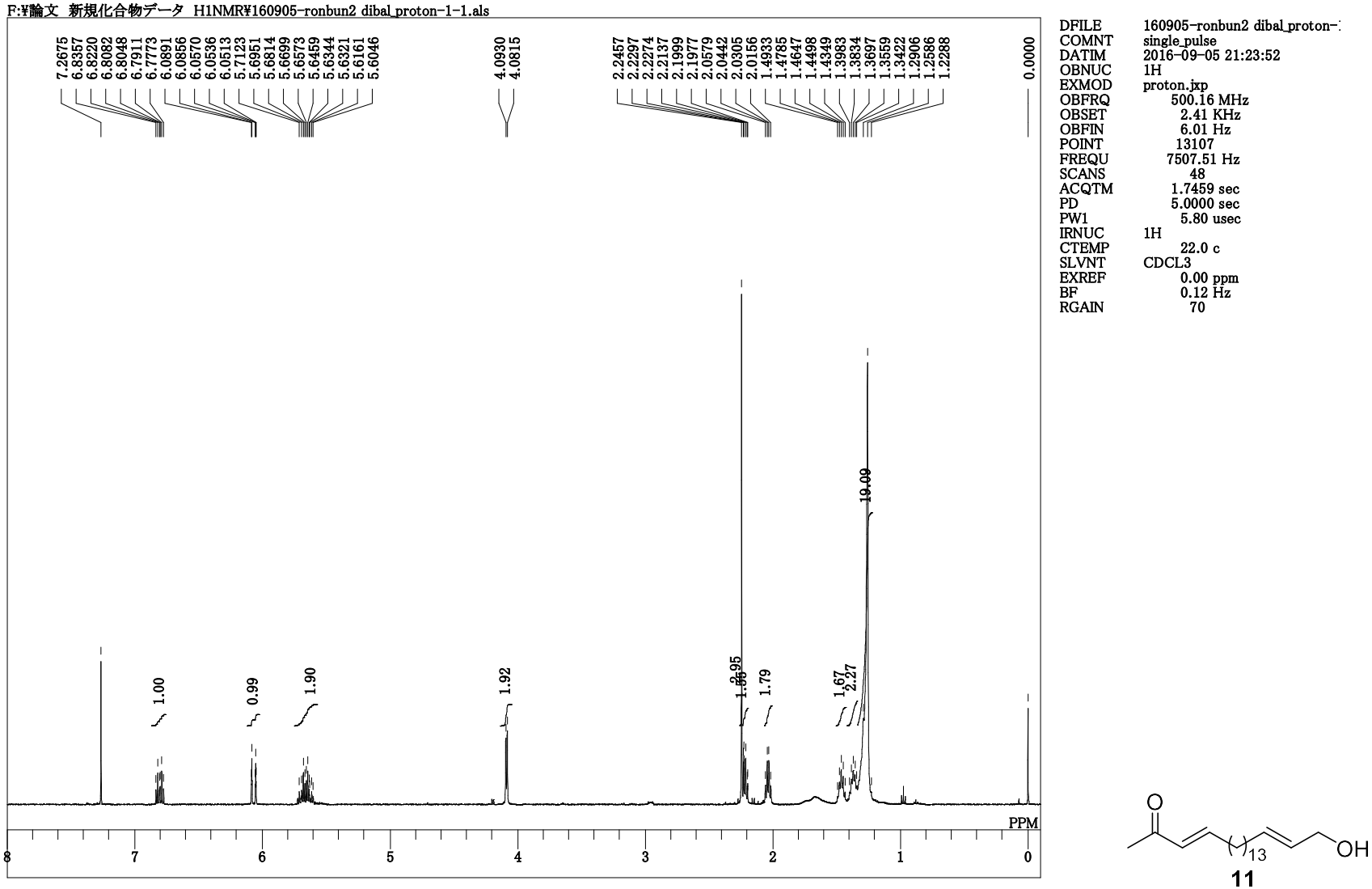
19d



DFILE	170125-6moto-et_carbon-1-1.
COMNT	single pulse decoupled gated N
DATIM	2017-01-25 21:14:19
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	78
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



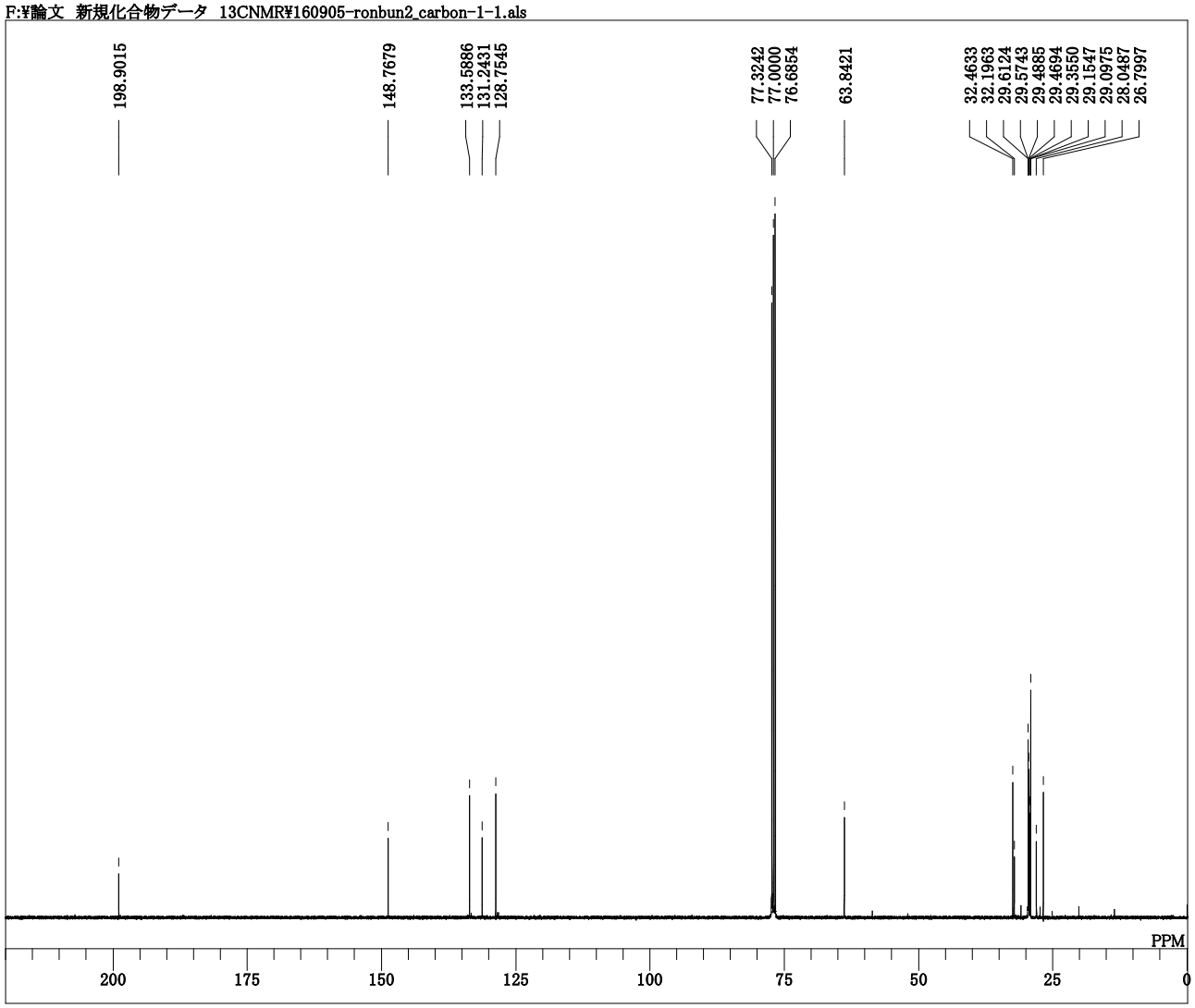
19d



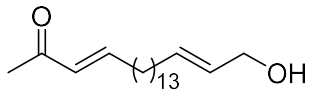
DFILE 160905-ronbun2 dibal_proton-1
COMNT single_pulse
DATIM 2016-09-05 21:23:52
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 48
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.80 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 70

11

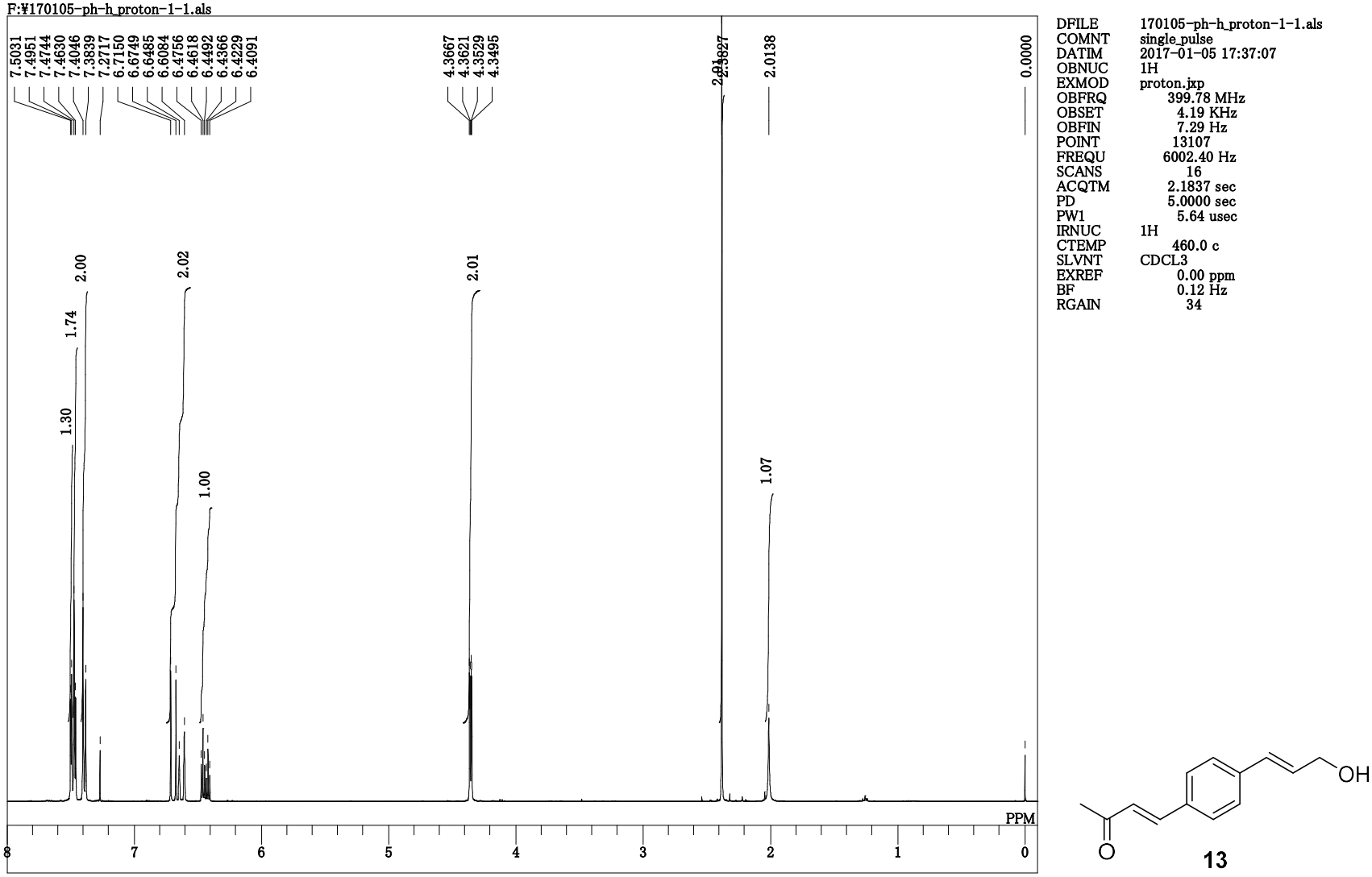
F:¥論文 新規化合物データ 13CNMR¥160905-ronbun2_carbon-1-1.als



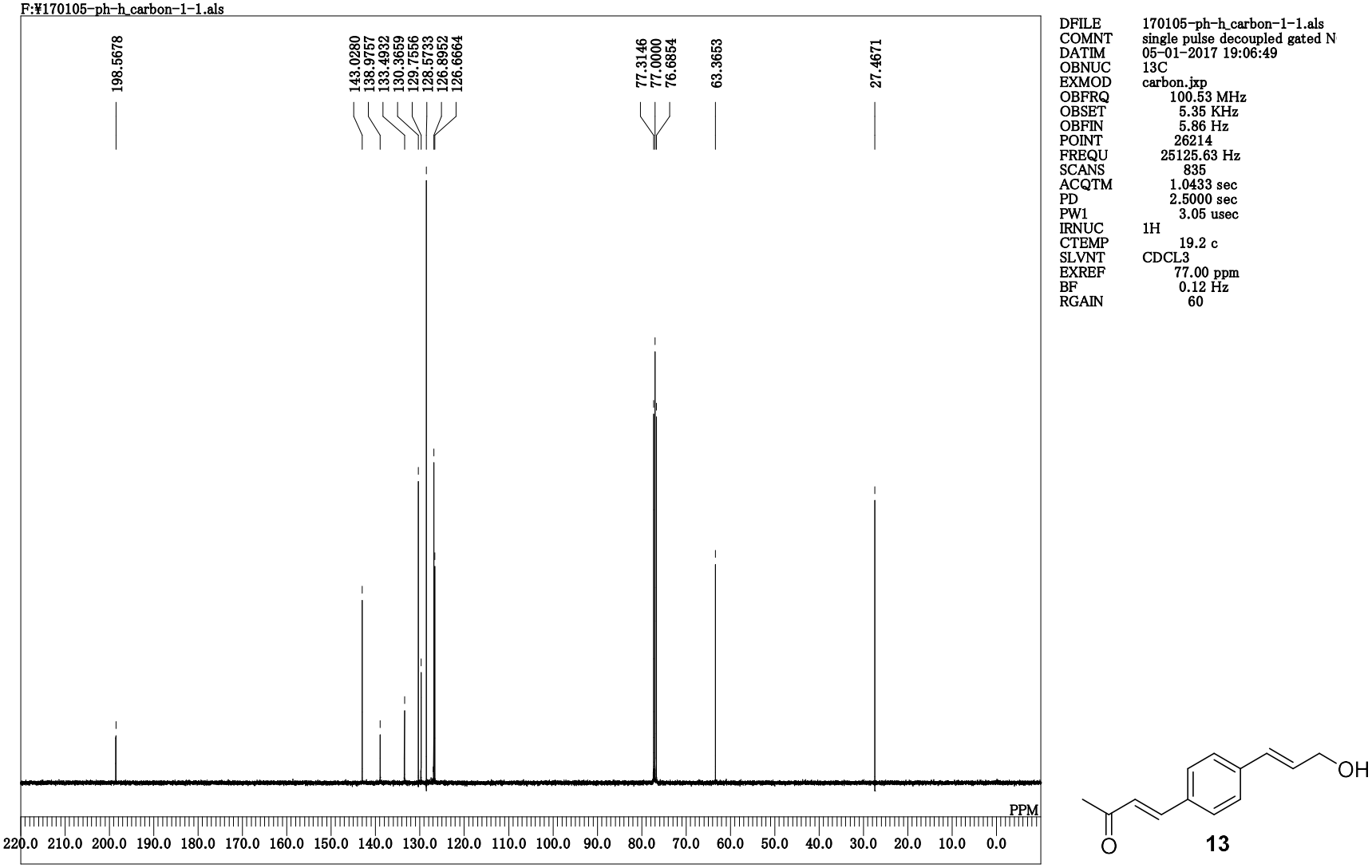
DFILE	160905-ronbun2_carbon-1-1.al
COMNT	single pulse decoupled gated N
DATIM	2016-09-06 00:10:54
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	11774
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



11

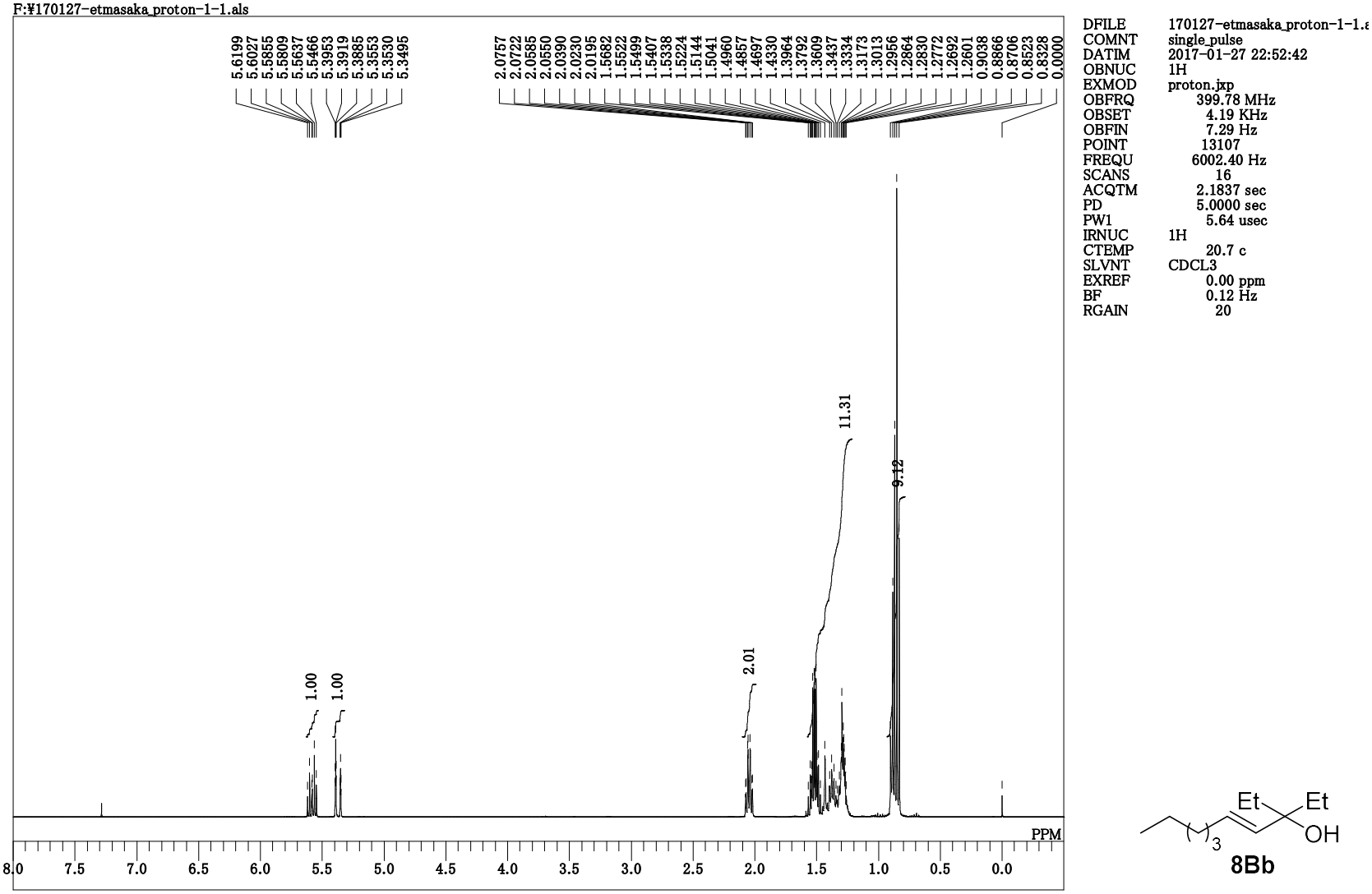

F:¥170105-ph-h_proton-1-1.als
7.5031
7.4951
7.4744
7.4630
7.4046
7.3839
7.2717
6.7150
6.6749
6.6485
6.6084
6.4756
6.4618
6.4492
6.4366
6.4229
6.4091
4.3667
4.3621
4.3529
4.3495
2.3827
2.0138
0.0000
2.00
1.74
1.30
2.02
1.00
2.01
1.07
PPM
8
7
6
5
4
3
2
1
0
DFILE 170105-ph-h_proton-1-1.als
COMNT single_pulse
DATIM 2017-01-05 17:37:07
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.64 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34
OH
O

13



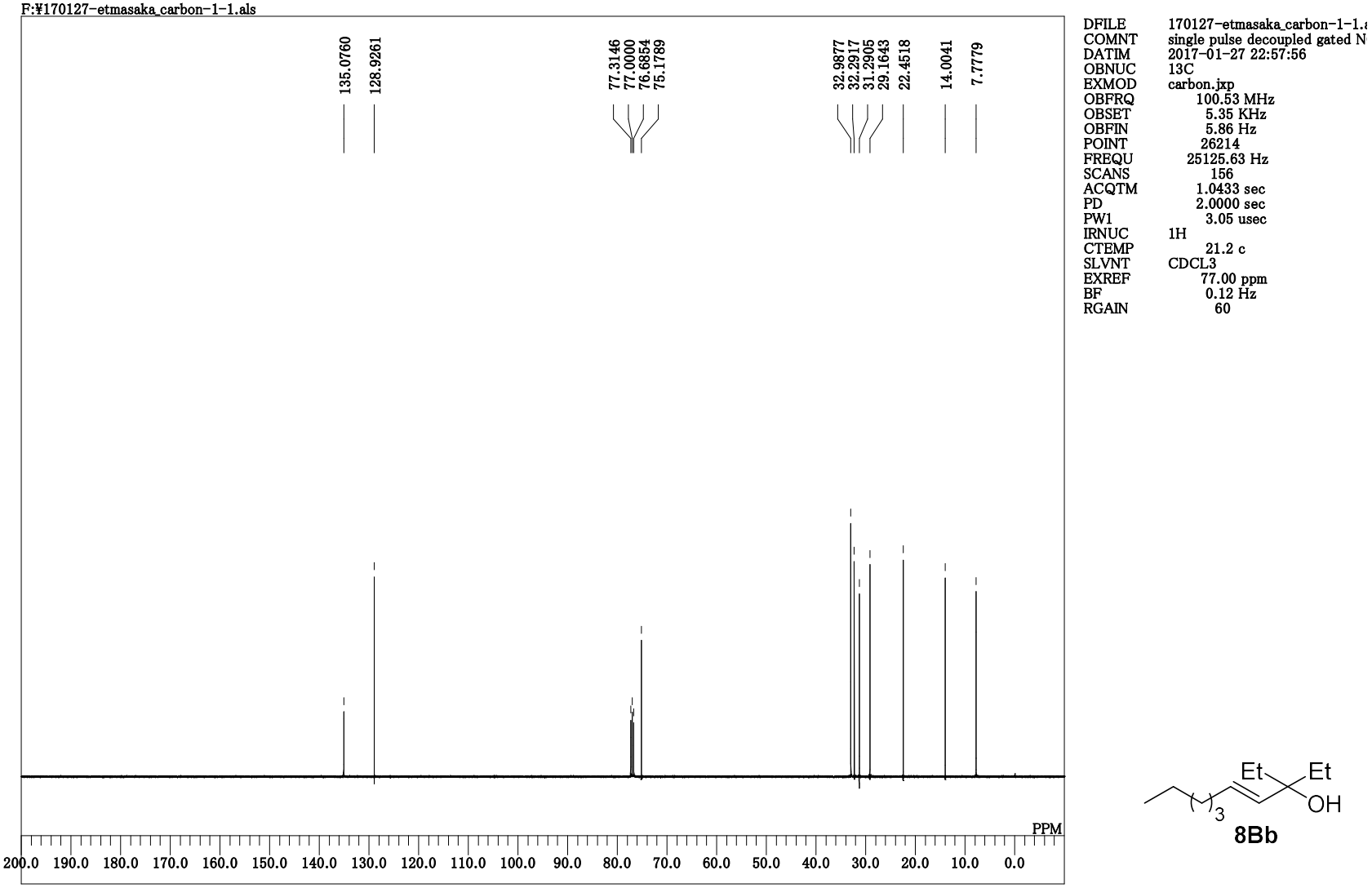
DFILE	170105-ph-h_carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	05-01-2017 19:06:49
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	835
ACQTM	1.0433 sec
PD	2.5000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

13



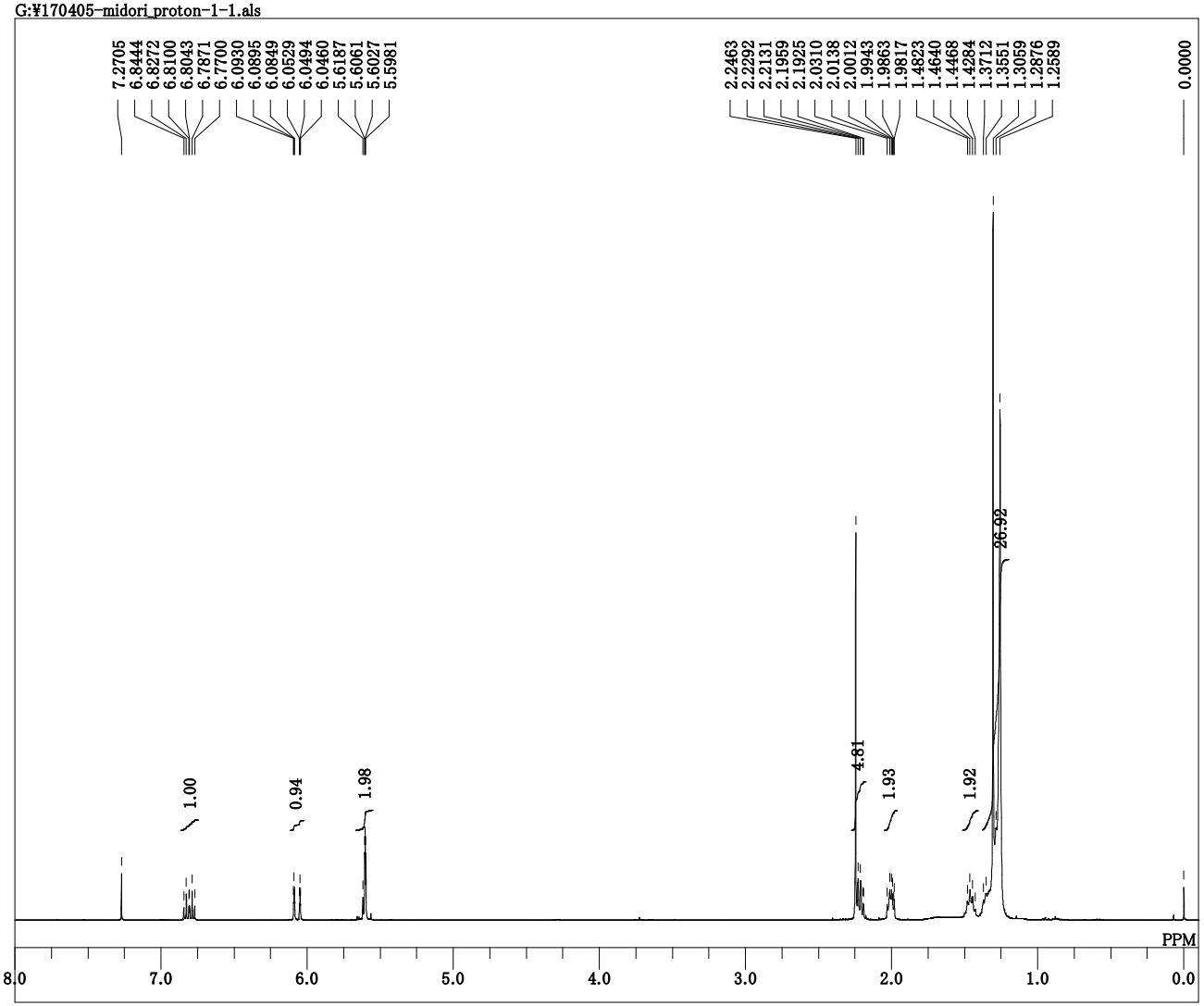
DFILE	170127-etmasaka_proton-1-1.a
COMNT	single_pulse
DATIM	2017-01-27 22:52:42
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20

8Bb

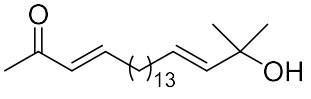


DFILE	170127-etmasaka_carbon-1-1.a
COMNT	single pulse decoupled gated N
DATIM	2017-01-27 22:57:56
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	156
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	21.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

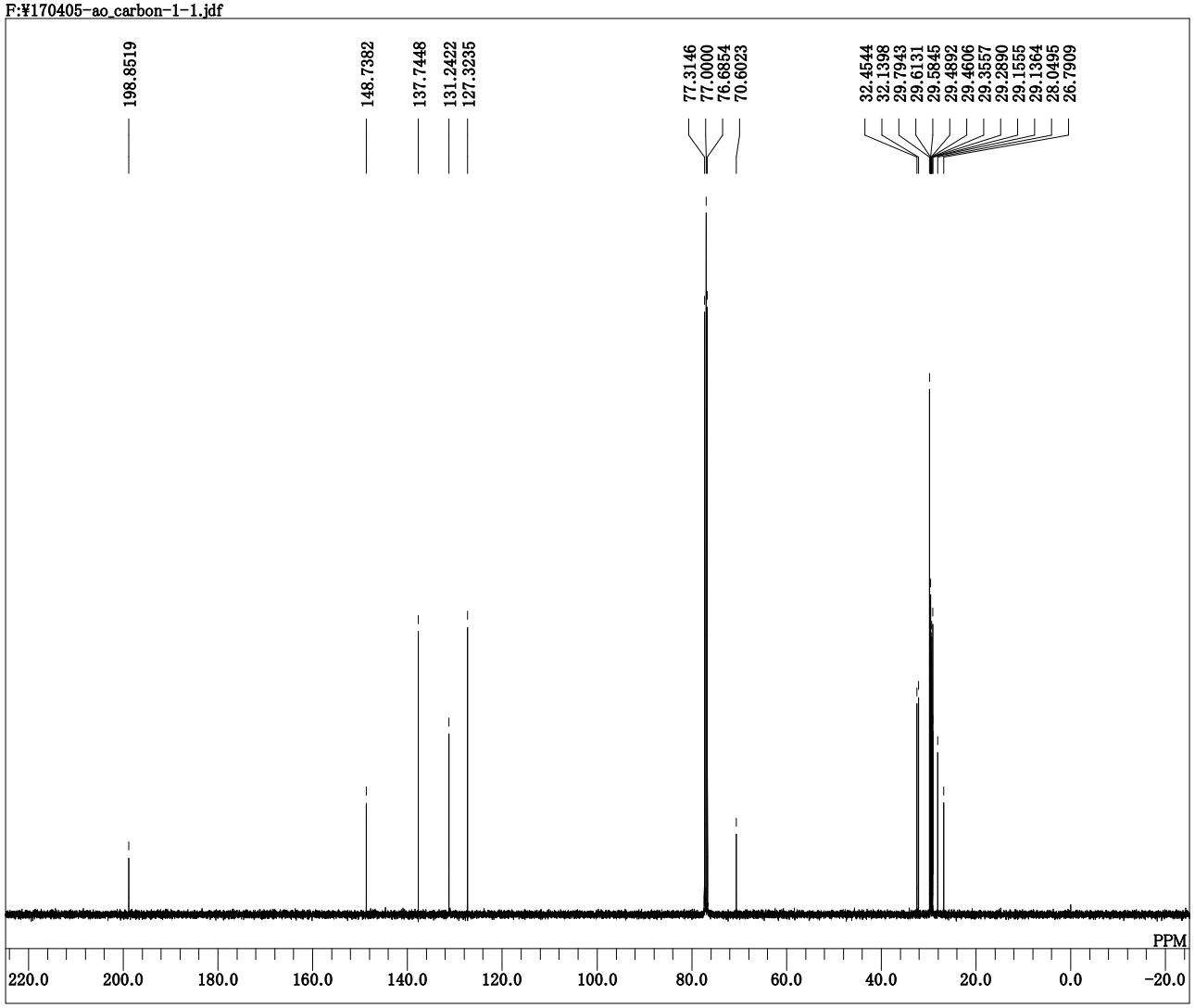
8Bb



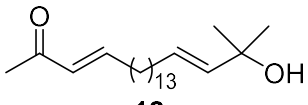
DFILE	170405-midori_proton-1-1.als
COMNT	single_pulse
DATIM	2017-04-05 16:49:54
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	32



12

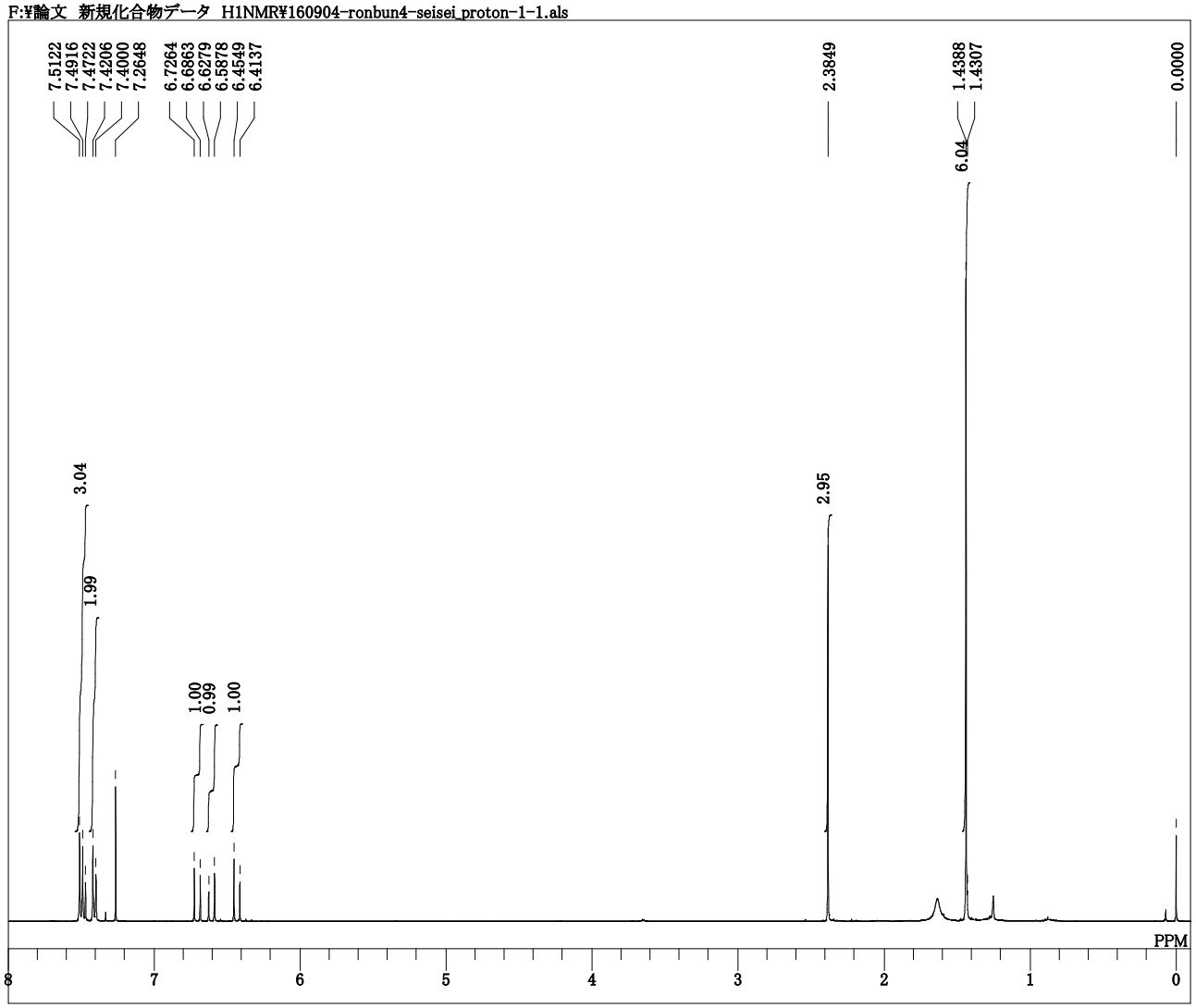


DFILE	170405-ao_carbon-1-1.jdf
COMNT	single pulse decoupled gated N
DATIM	2017-04-05 17:54:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	32767
FREQU	31407.04 Hz
SCANS	1000
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

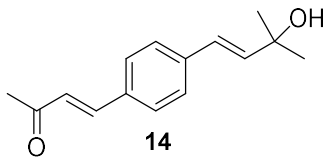


12

F:¥論文 新規化合物データ H1NMR¥160904-ronbun4-seisei_proton-1-1.als

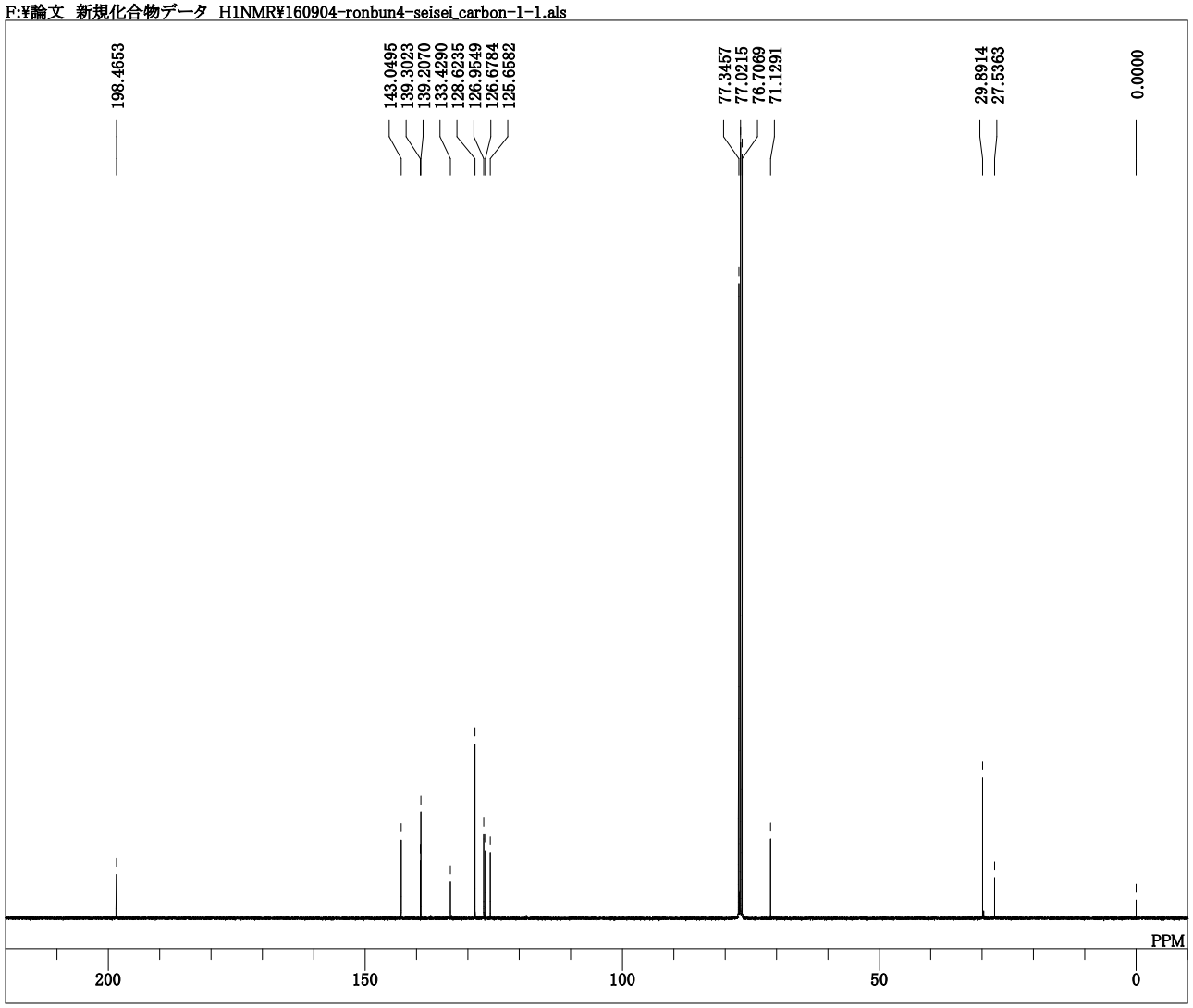


DFILE	160904-ronbun4-seisei_proton-
COMNT	single_pulse
DATIM	2016-09-04 22:19:36
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	48
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46

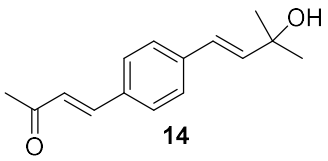


14

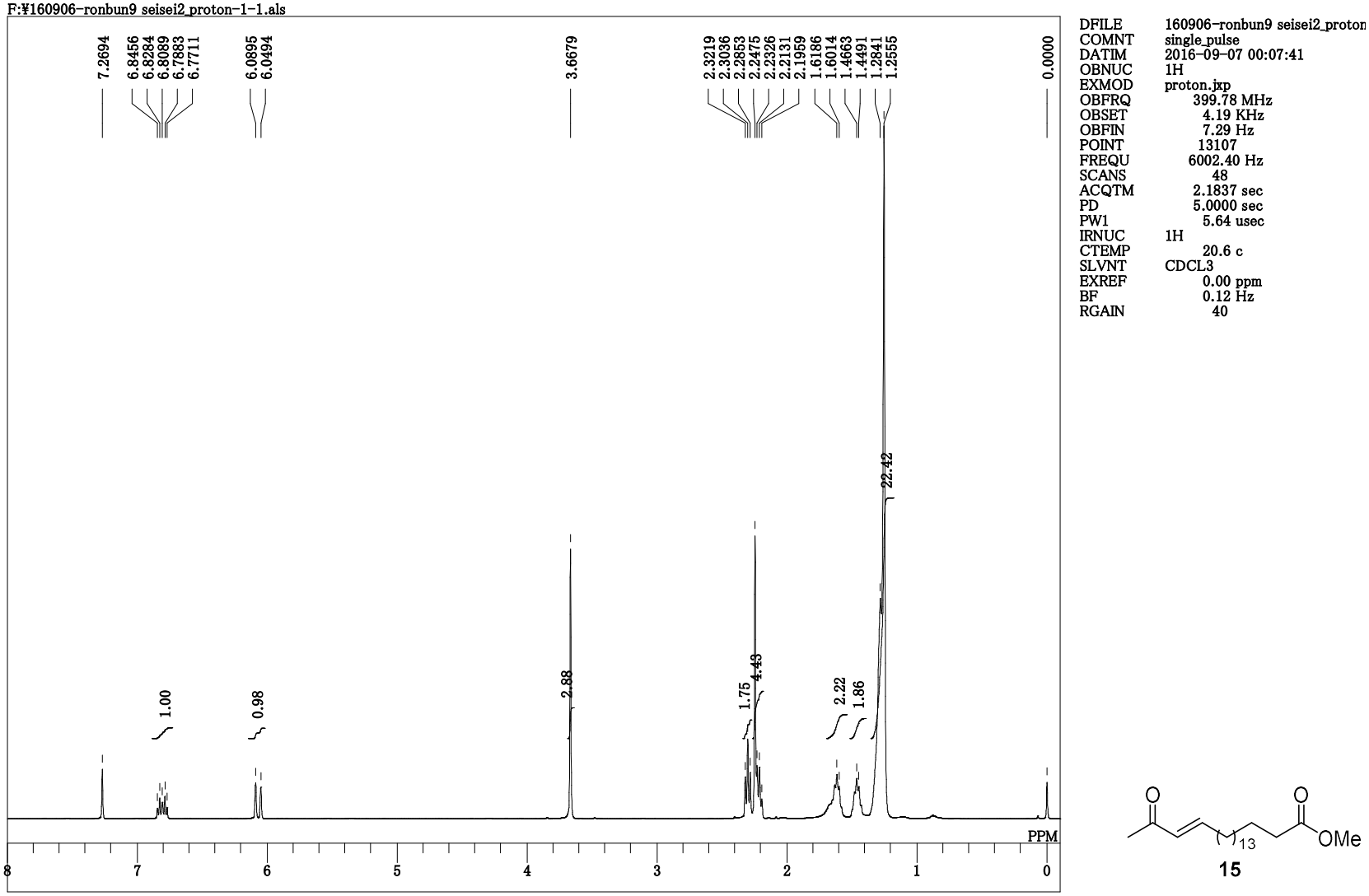
F:¥論文 新規化合物データ H1NMR¥160904-ronbun4-seisei_carbon-1-1.als



DFILE	160904-ronbun4-seisei_carbon
COMNT	single pulse decoupled gated N
DATIM	2016-09-04 22:28:41
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	13335
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	21.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	60

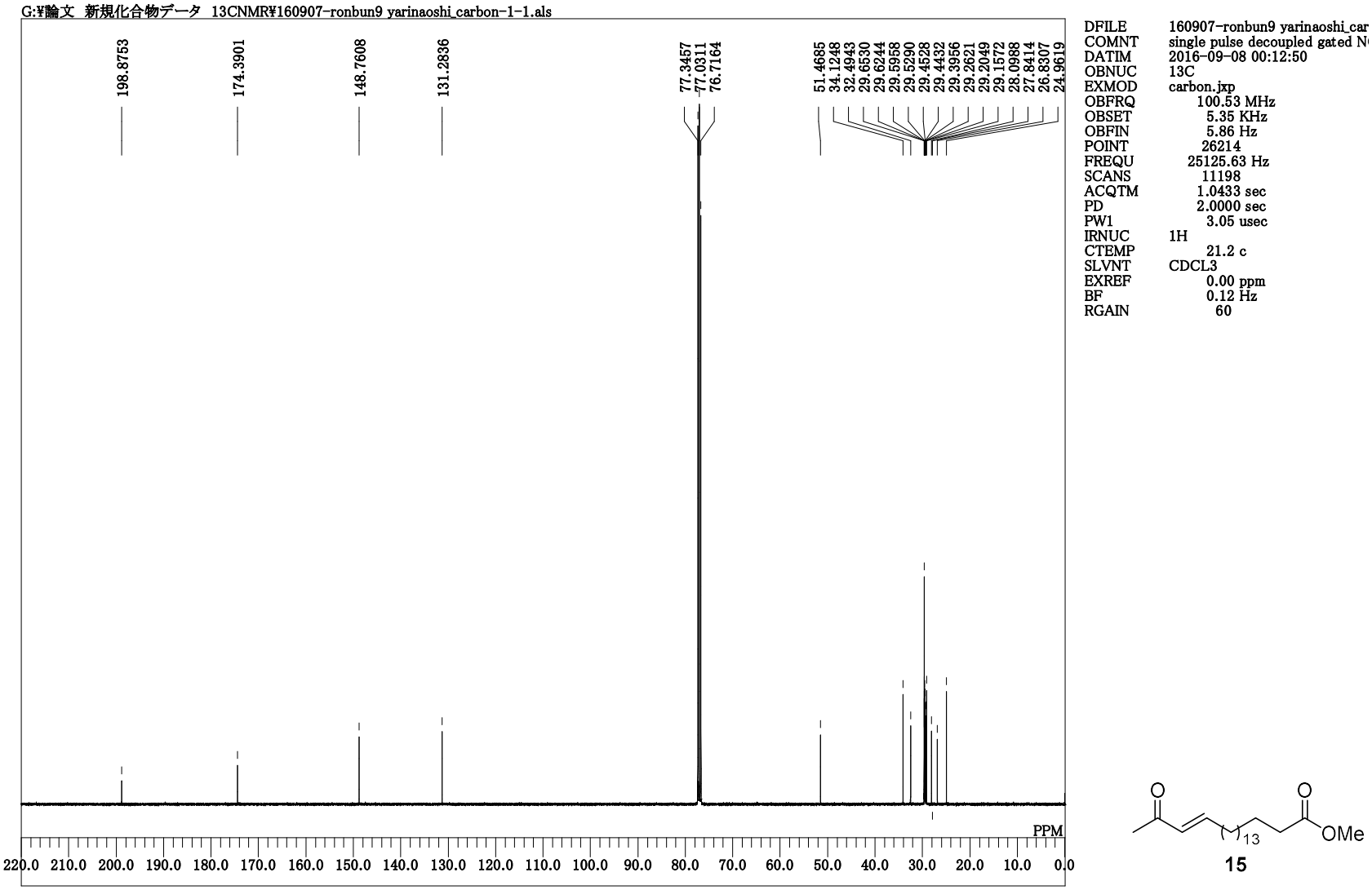


14



DFILE	160906-ronbun9 seisei2_proton
COMNT	single_pulse
DATIM	2016-09-07 00:07:41
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	48
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	20.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

15


G:¥論文 新規化合物データ 13CNMR¥160907-ronbun9 yarinaoshi_carbon-1-1.als
198.8753
174.3901
148.7608
131.2836
77.3457
77.0311
76.7164
51.4685
34.1248
32.4943
29.6530
29.6244
29.5958
29.5290
29.4528
29.4432
29.3956
29.2621
29.2049
29.1572
28.0988
27.8414
26.8307
24.9619
DFILE 160907-ronbun9 yarinaoshi_car
COMNT single pulse decoupled gated N
DATIM 2016-09-08 00:12:50
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 11198
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.05 usec
IRNUC 1H
CTEMP 21.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 60
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

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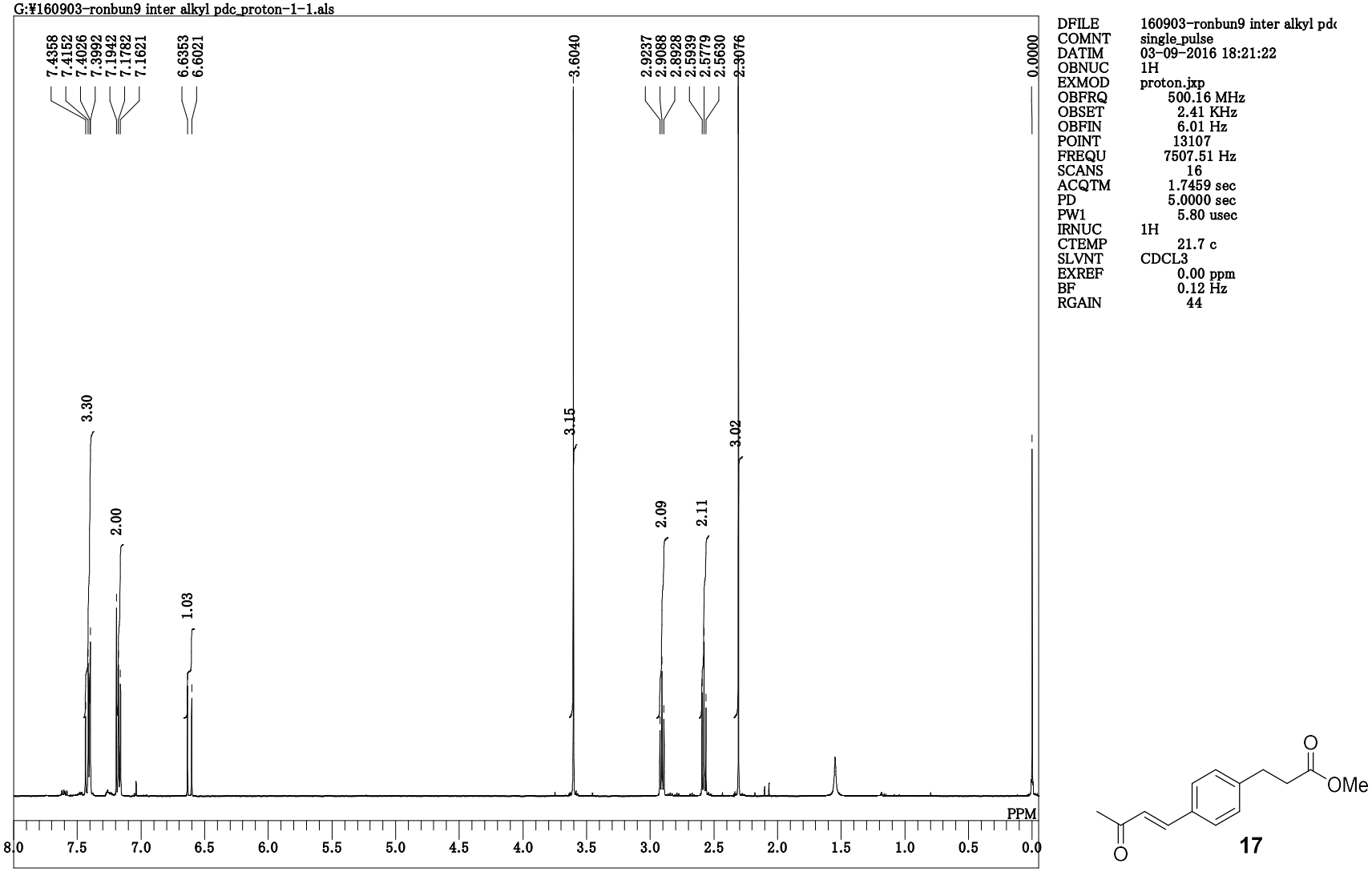
13
OMe

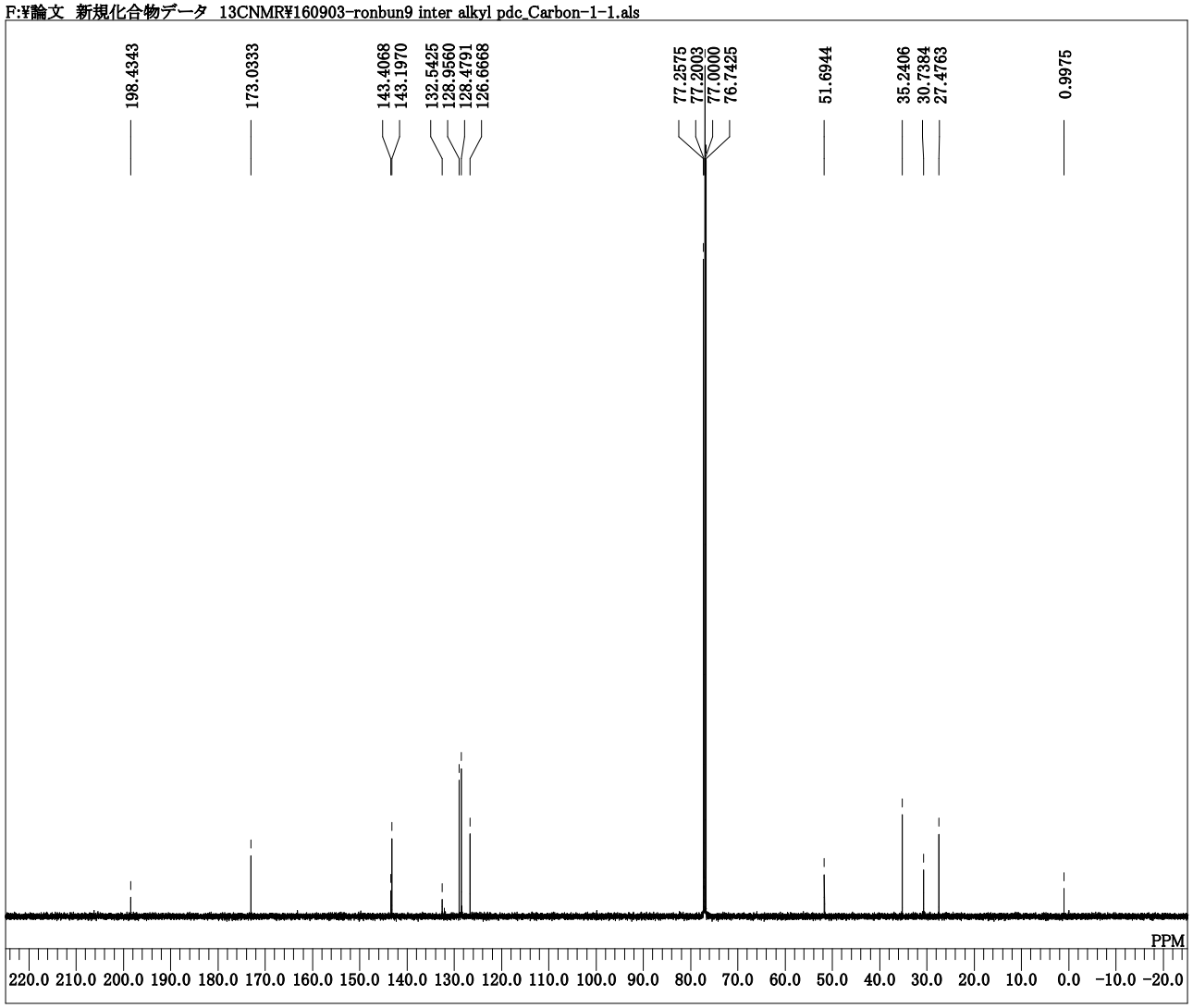
15



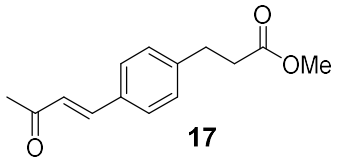
DFILE	160903-ronbun9 inter alkyl pdc
COMNT	single_pulse
DATIM	03-09-2016 18:21:22
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	44

17

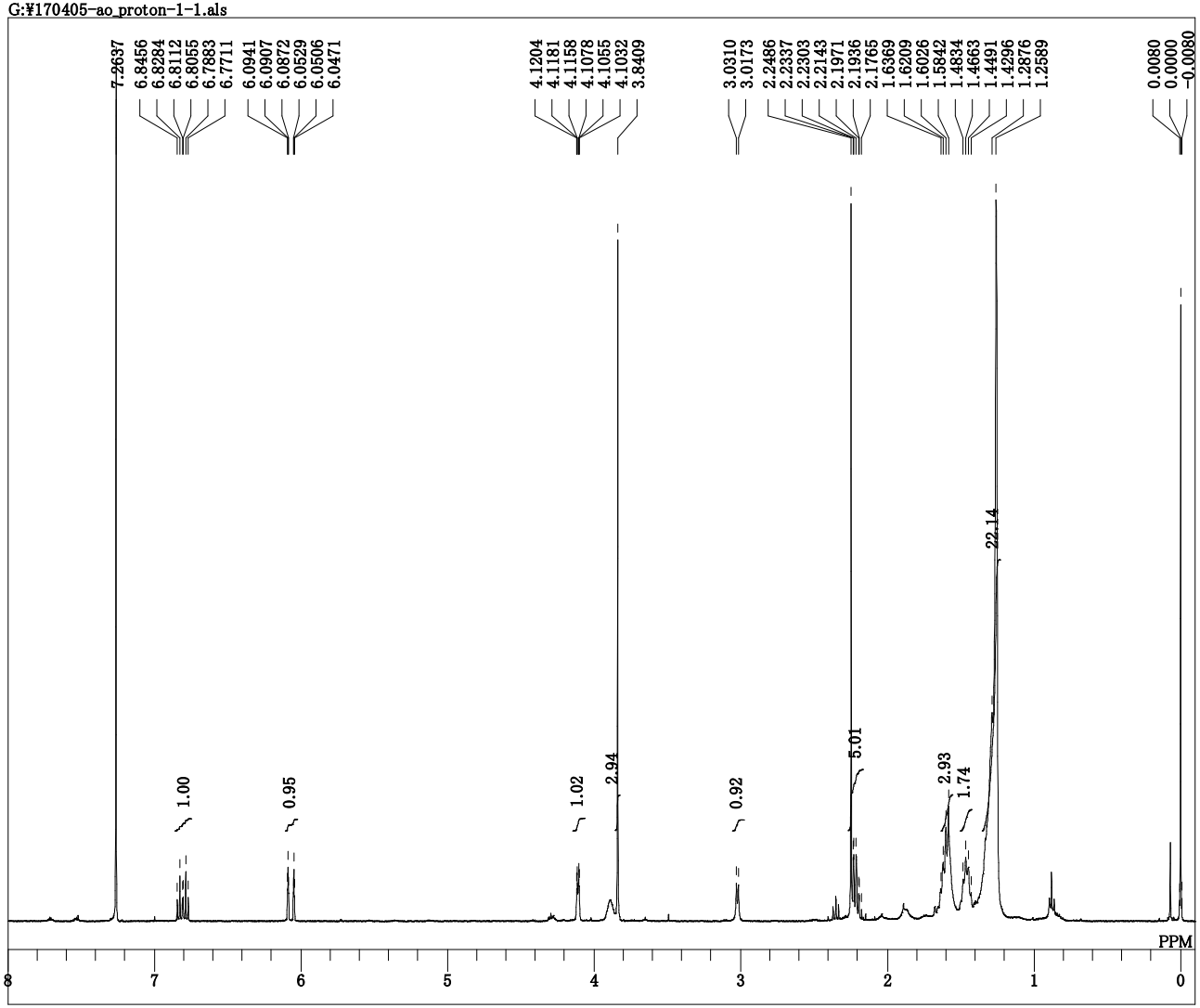
F:¥論文 新規化合物データ 13CNMR¥160903-ronbun9 inter alkyl pdc_Carbon-1-1.als



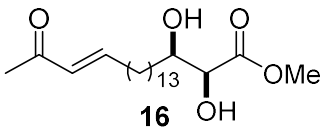
DFILE	160903-ronbun9 inter alkyl pd
COMNT	single pulse decoupled gated N
DATIM	2016-09-03 18:25:36
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1090
ACQTM	0.8336 sec
PD	3.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



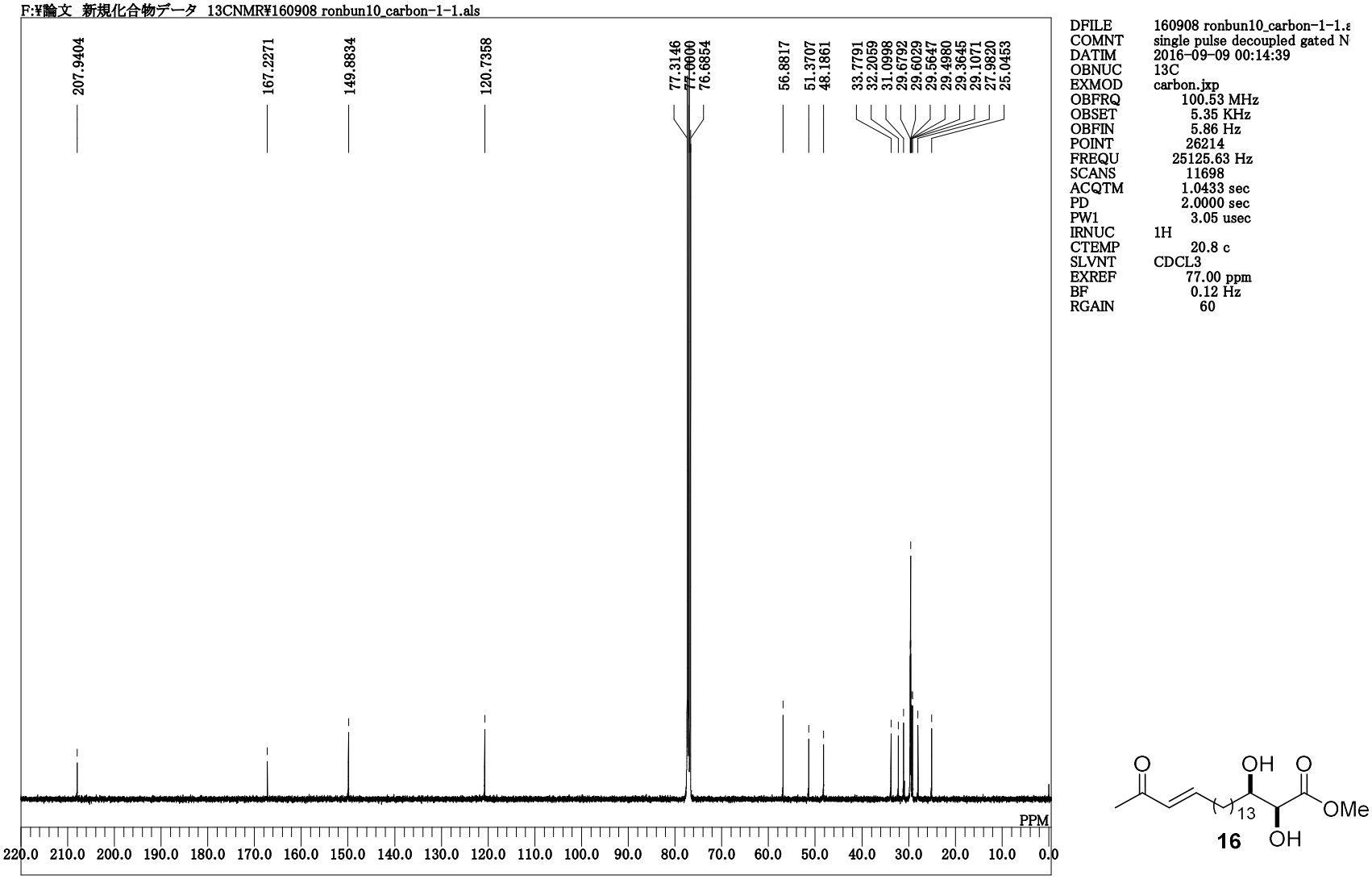
17



DFILE	170405-ao_proton-1-1.als
COMNT	single_pulse
DATIM	2017-04-05 16:42:34
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	46

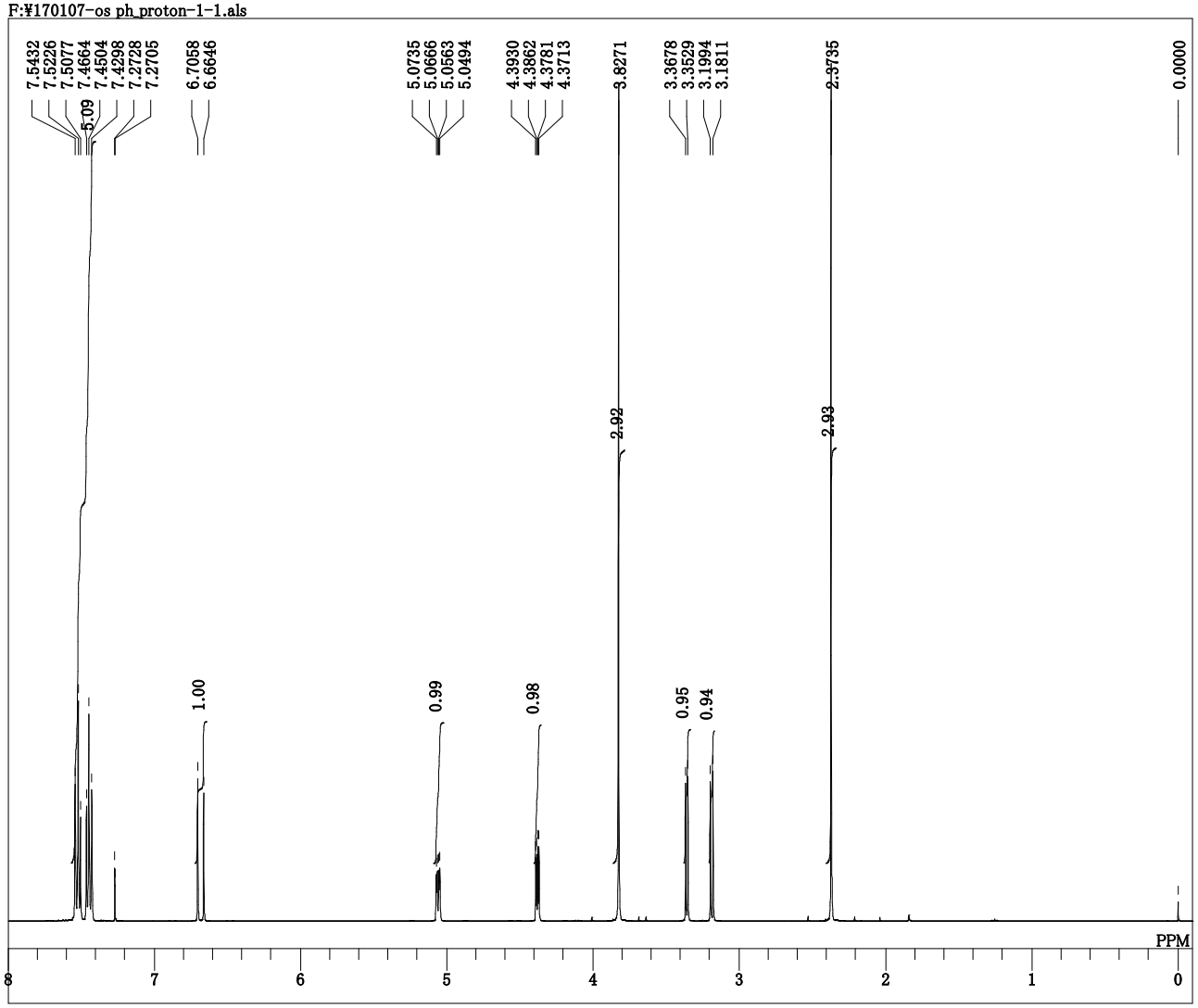


16

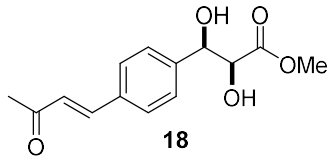

F:¥論文 新規化合物データ 13CNMR¥160908 ronbun10_carbon-1-1.als
207.9404
167.2271
149.8834
120.7358
77.3146
77.0000
76.6854
56.8817
51.3707
48.1861
33.7791
32.2059
31.0998
29.6792
29.6029
29.5647
29.4980
29.3645
29.1071
27.9820
25.0453
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
DFILE 160908 ronbun10_carbon-1-1.a
COMNT single pulse decoupled gated N
DATIM 2016-09-09 00:14:39
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 11698
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.05 usec
IRNUC 1H
CTEMP 20.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

O
OH
O
13
OMe
OH

16

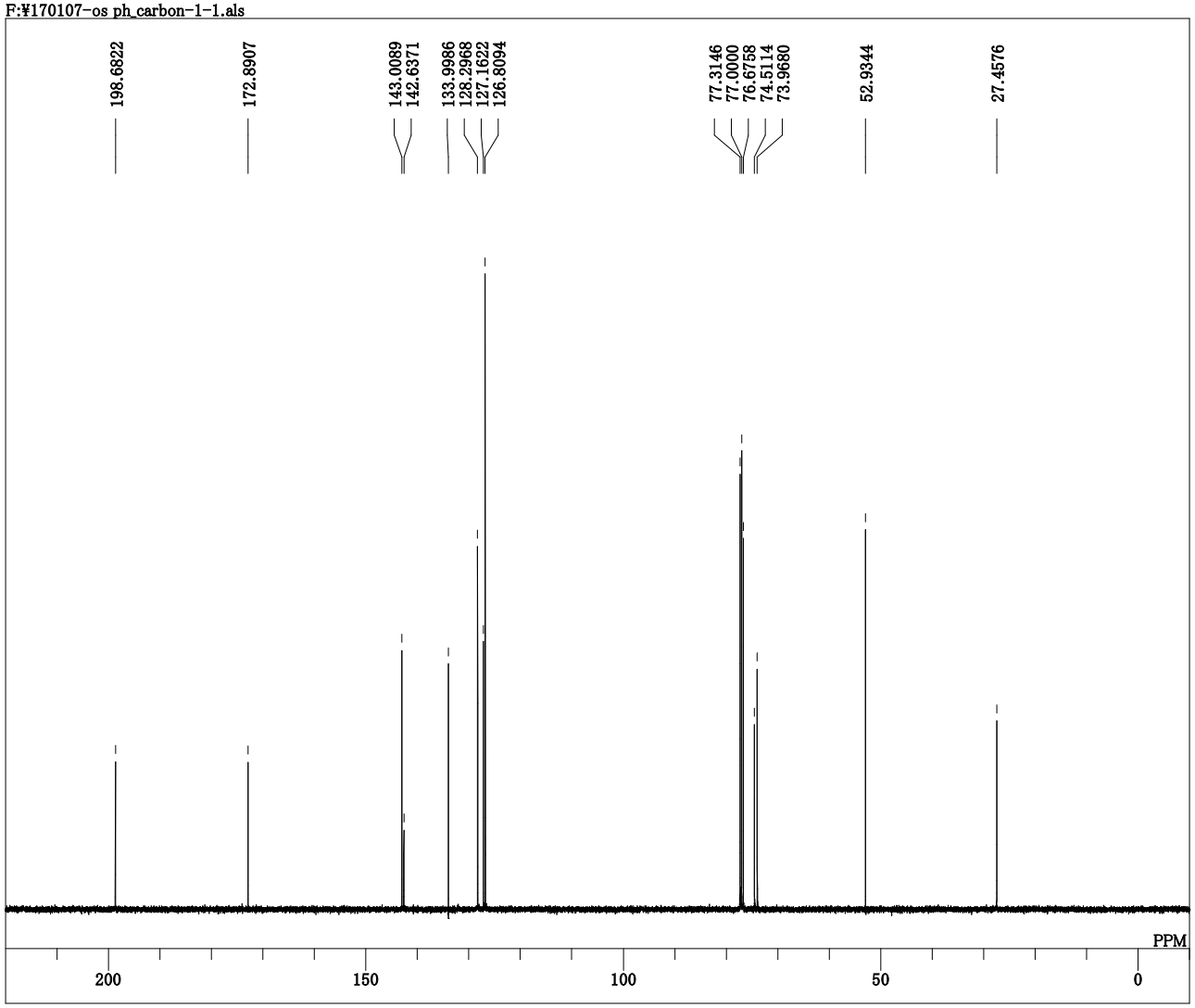


DFILE	170107-os ph_proton-1-1.als
COMNT	single_pulse
DATIM	07-01-2017 15:34:40
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	18.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36

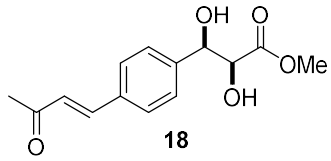


18

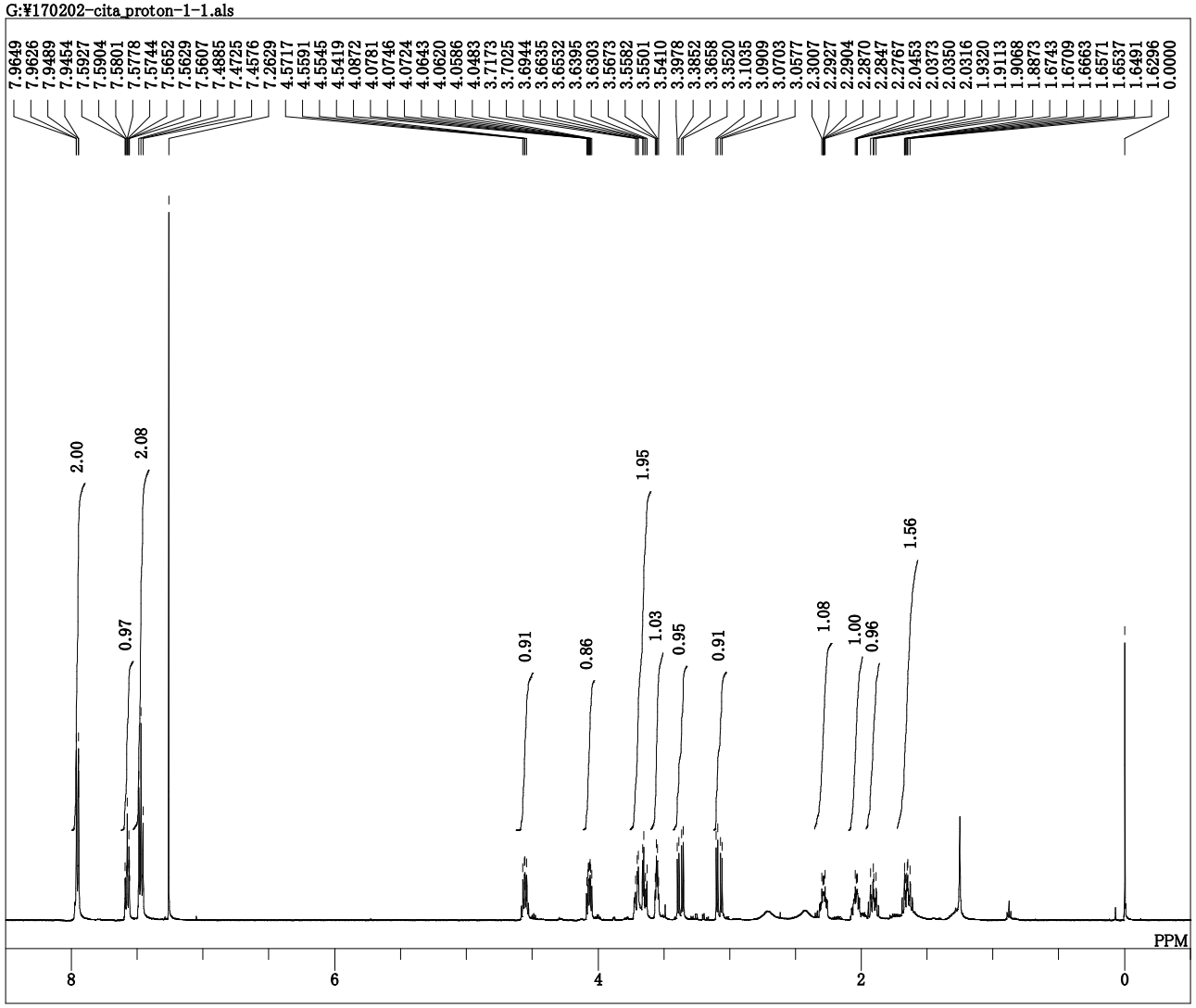
F:¥170107-os ph_carbon-1-1.als



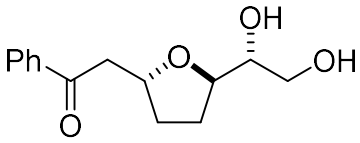
DFILE	170107-os ph_carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	07-01-2017 15:39:52
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	982
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	19.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



18

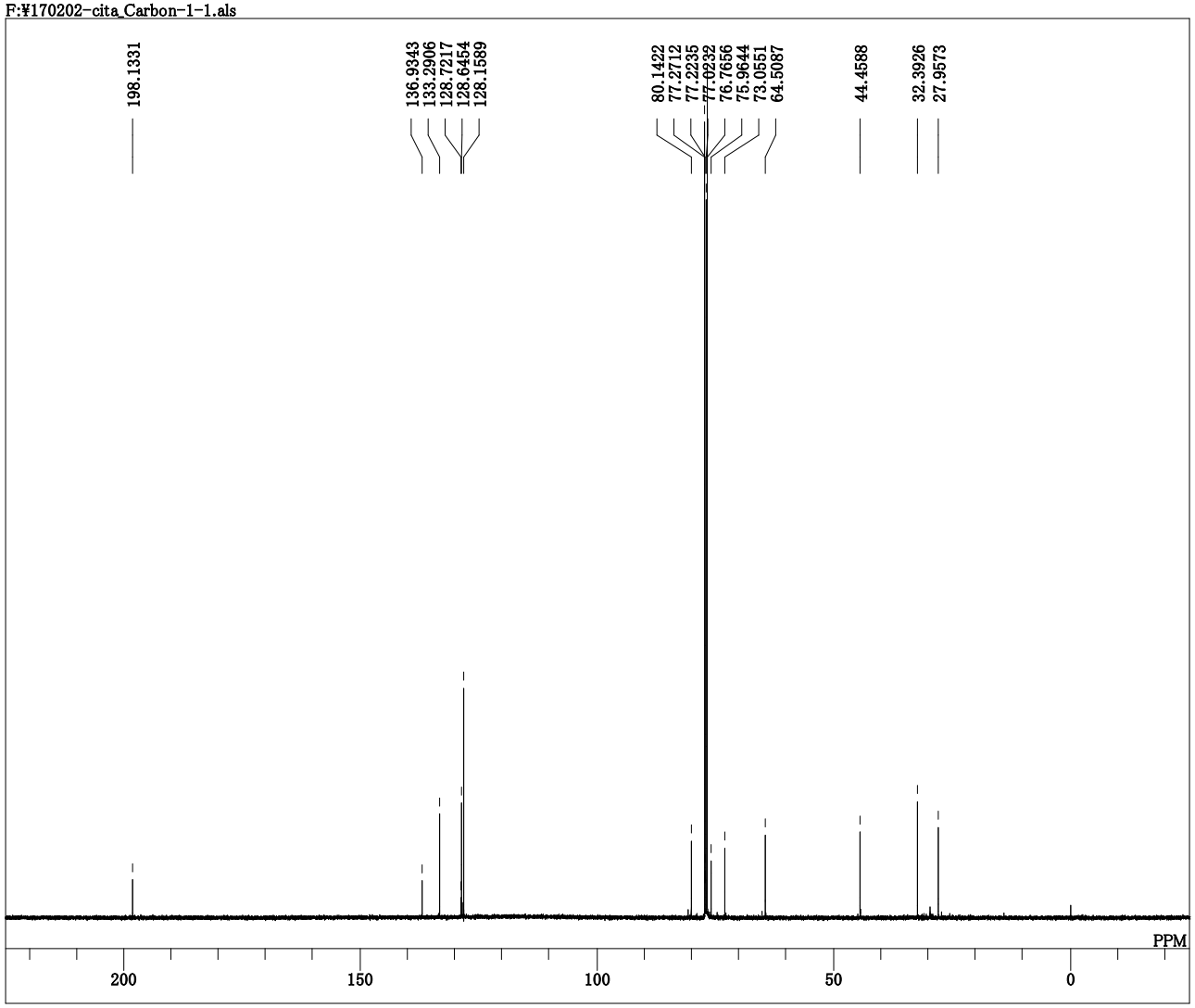


DFILE 170202-cita_proton-1-1.als
COMNT single_pulse
DATIM 2017-02-02 03:26:47
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 16
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

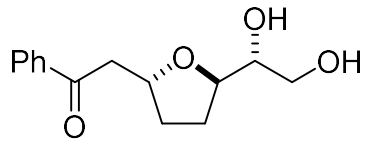


20a

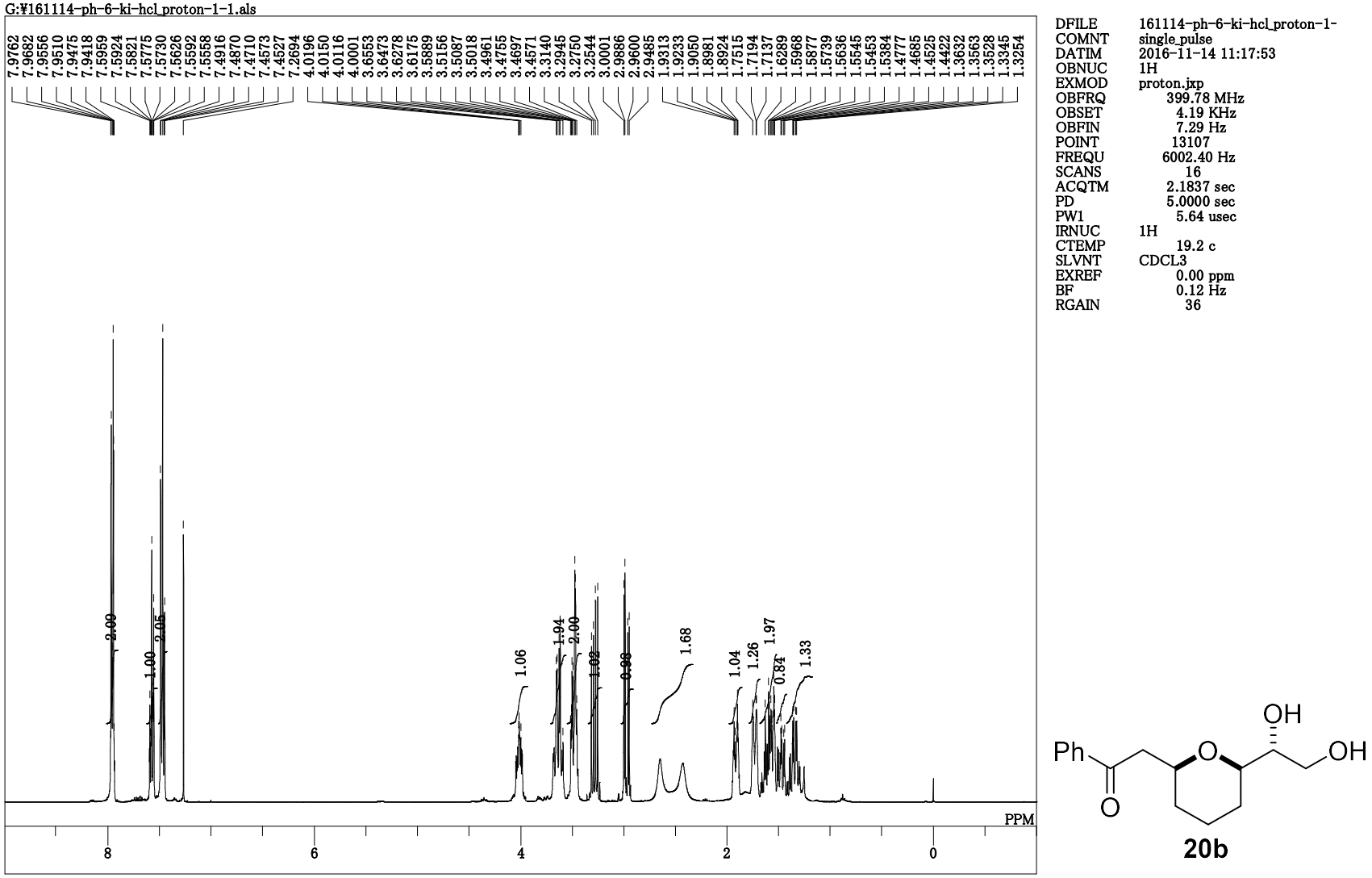
F:¥170202-cita_Carbon-1-1.als



DFILE	170202-cita_Carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	2017-02-02 03:50:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	7811
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.67 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	60

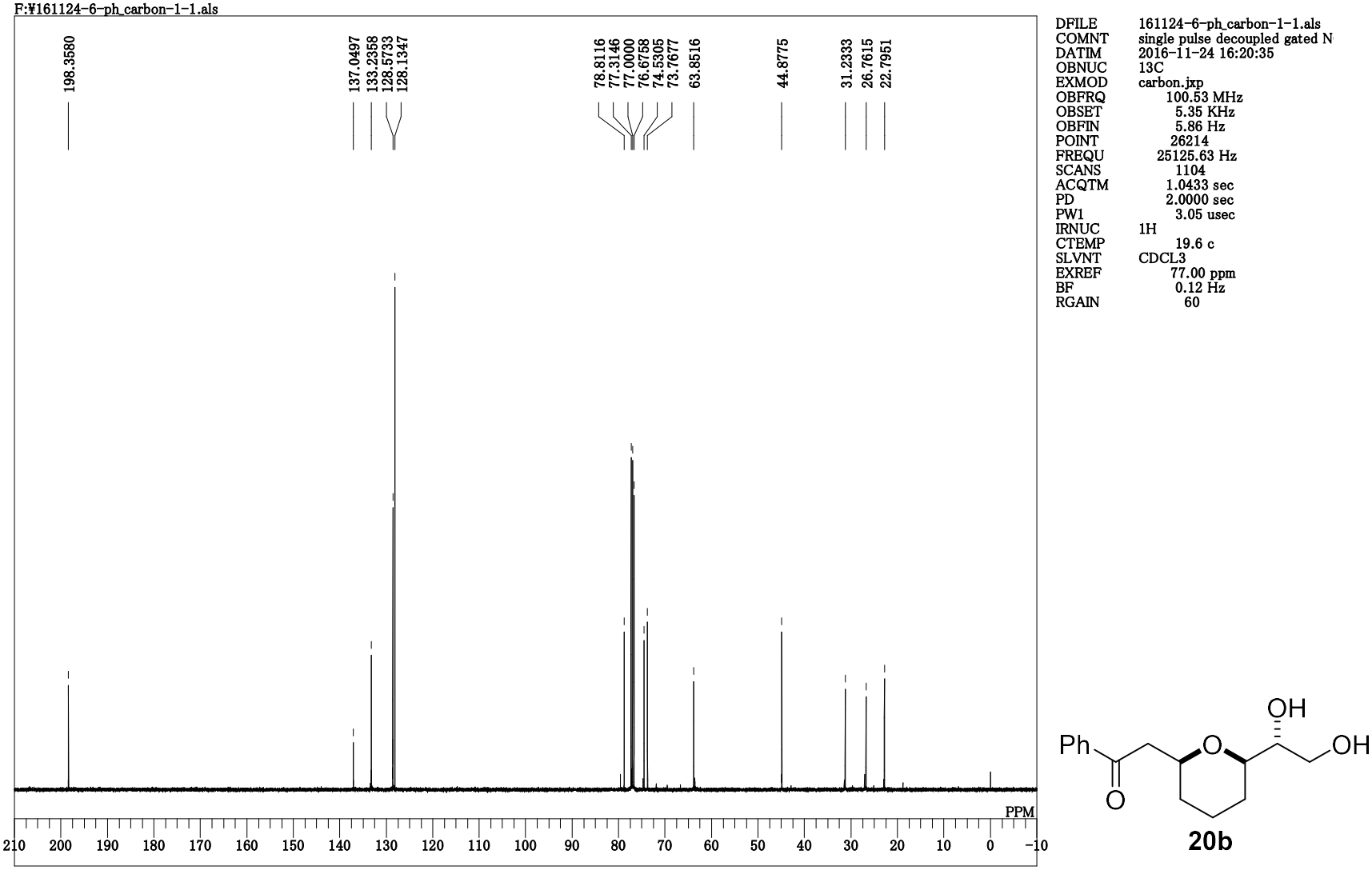


20a



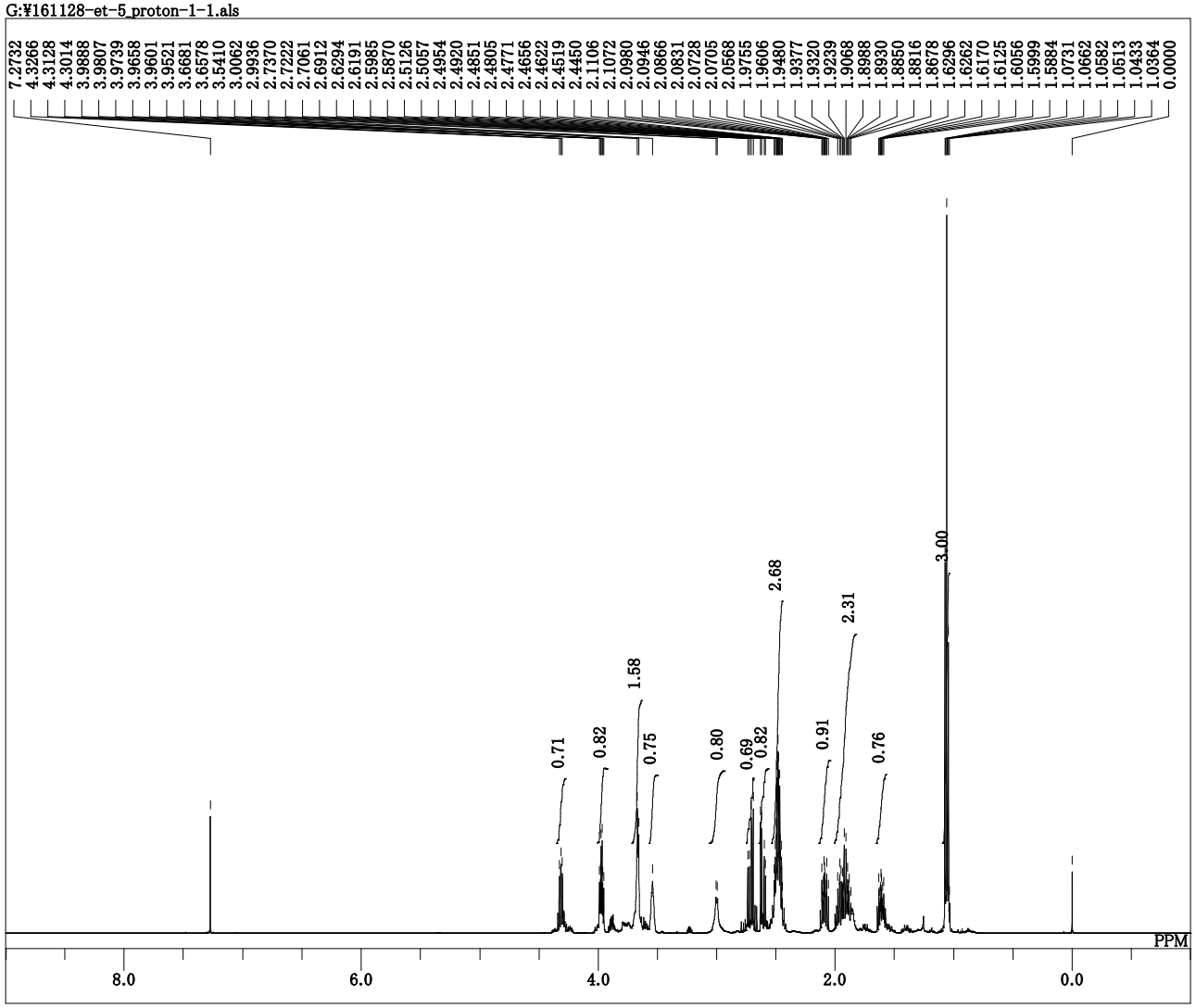
DFILE	161114-ph-6-ki-hcl_proton-1-
COMNT	single_pulse
DATIM	2016-11-14 11:17:53
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.64 usec
IRNUC	1H
CTEMP	19.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36

20b

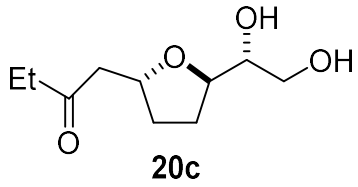


DFILE	161124-6-ph_carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	2016-11-24 16:20:35
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	1104
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.05 usec
IRNUC	1H
CTEMP	19.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

20b

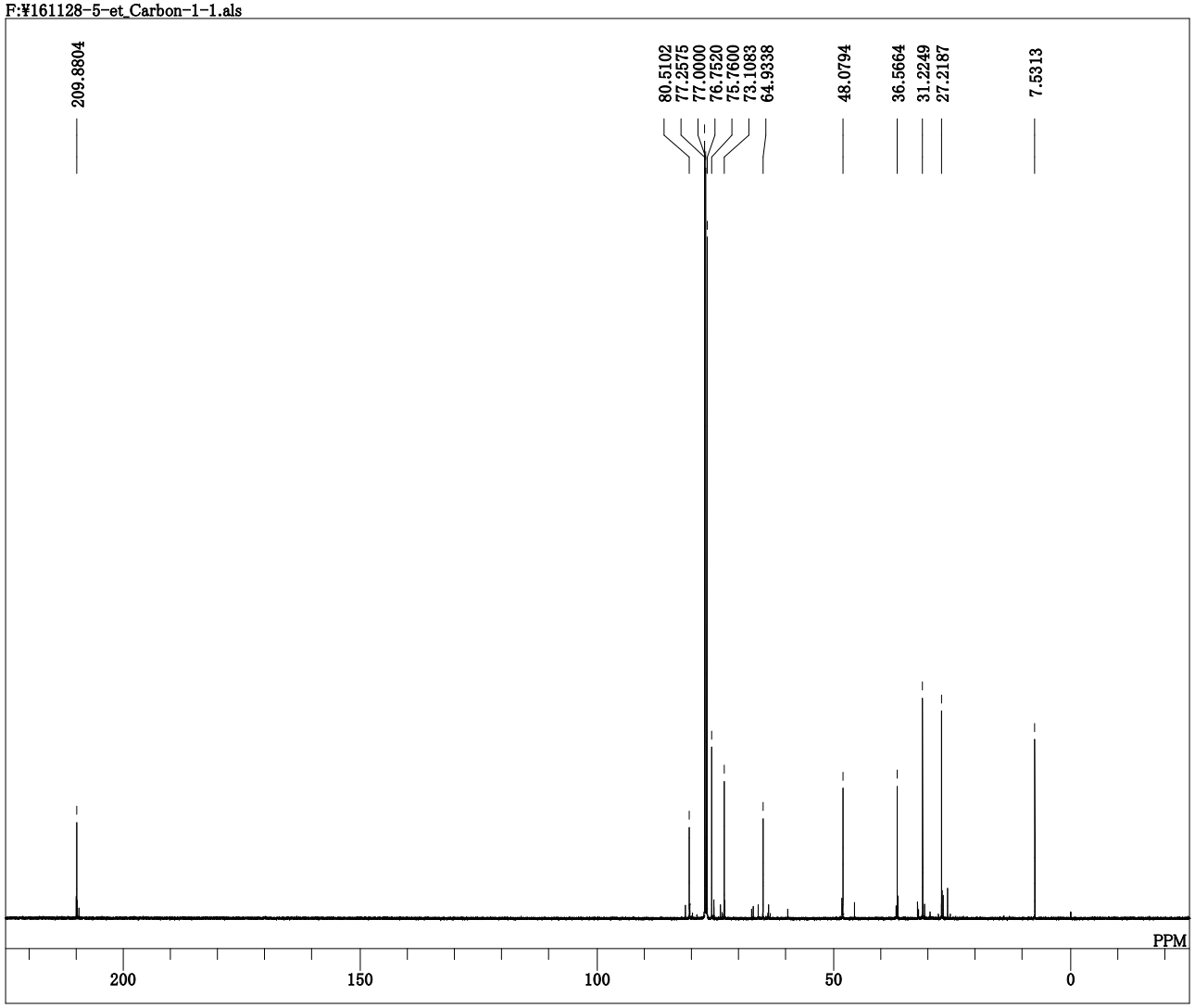


DFILE	161128-et-5_proton-1-1.als
COMNT	single_pulse
DATIM	28-11-2016 17:16:00
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

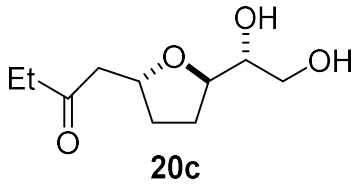


20c

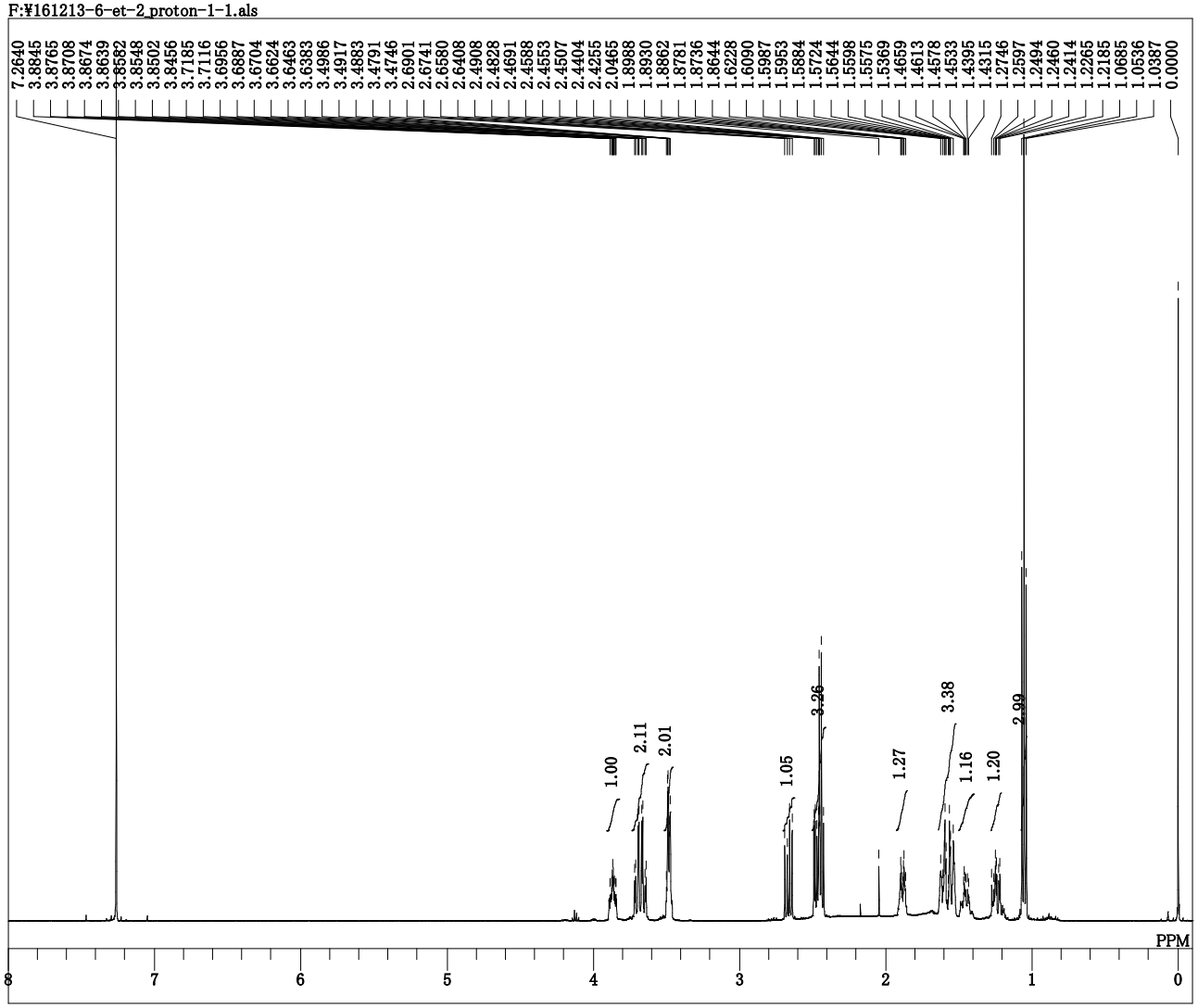
F:¥161128-5-et_Carbon-1-1.als



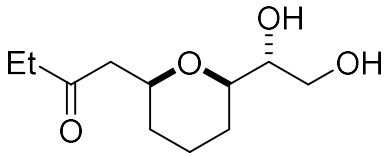
DFILE	161128-5-et_Carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	28-11-2016 23:56:04
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	12394
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	23.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



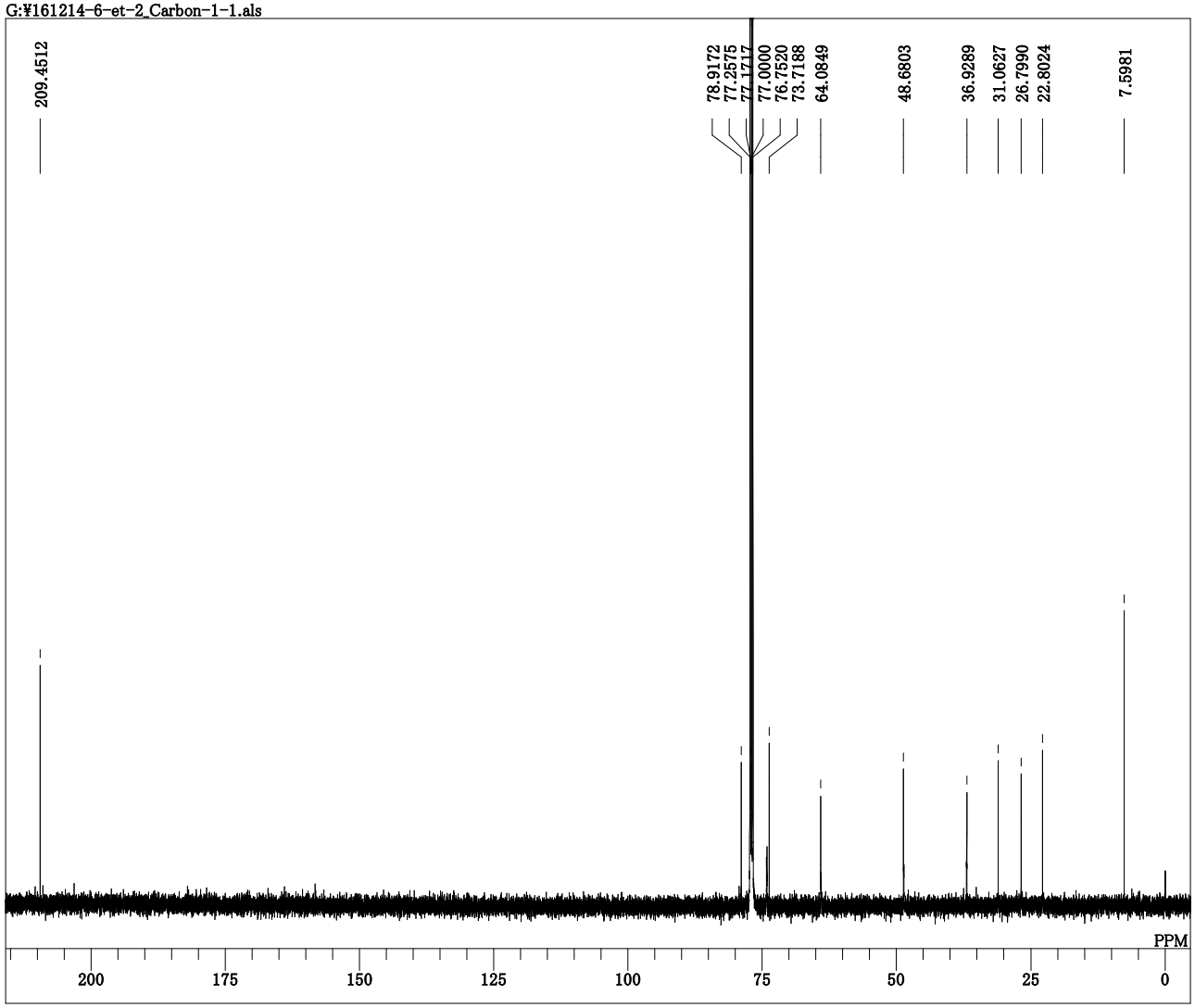
20c



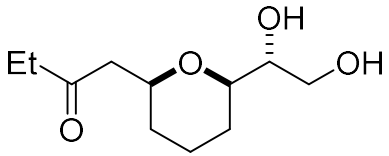
DFILE	161213-6-et-2_proton-1-1.als
COMNT	single_pulse
DATIM	13-12-2016 21:54:24
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	32
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	22.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	54



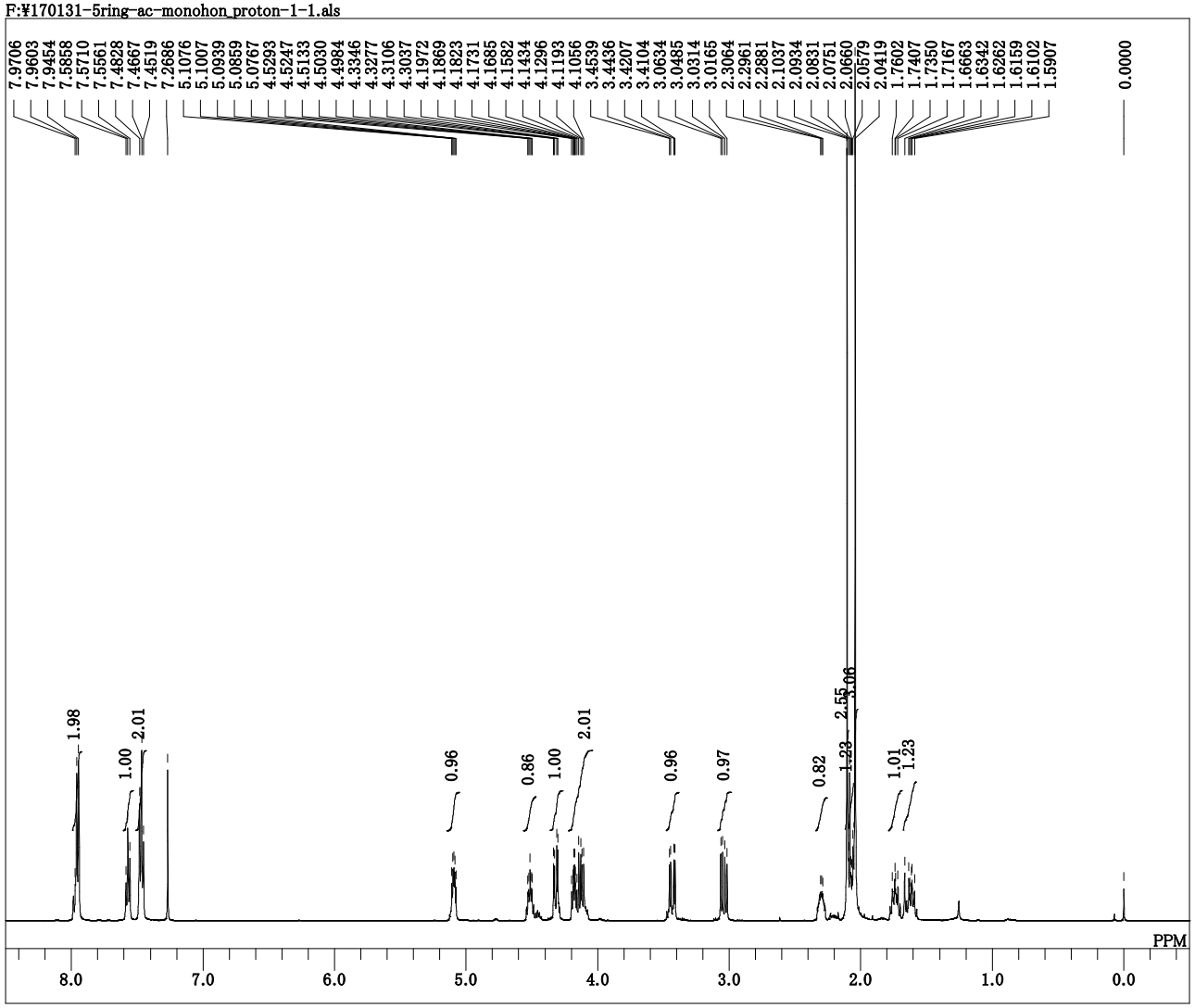
20d



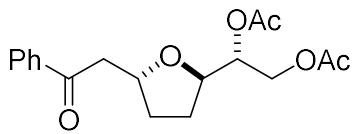
DFILE	161214-6-et-2_Carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	2016-12-14 00:09:20
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	12384
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



20d

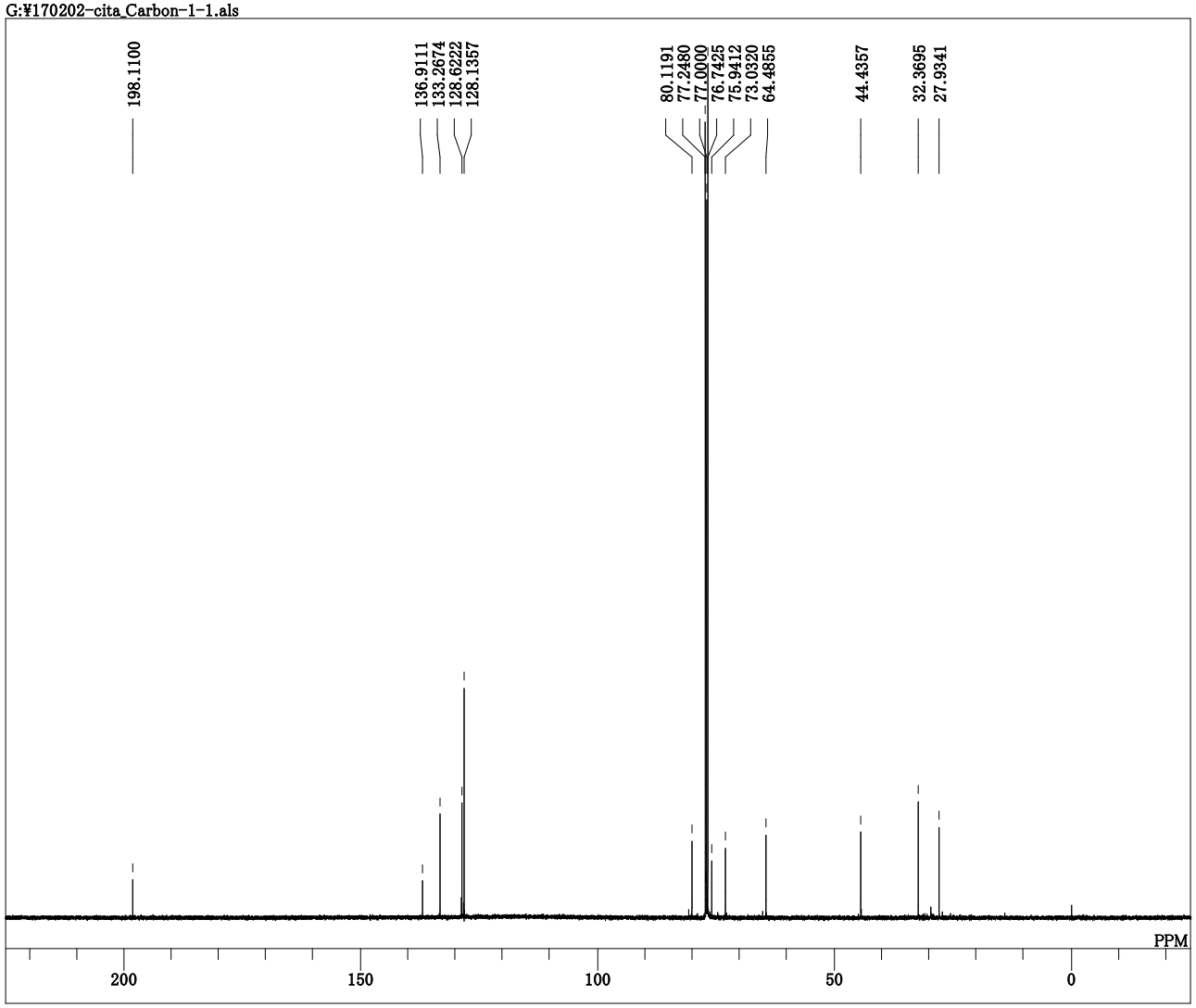


DFILE	170131-5ring-ac-monohon_pro
COMNT	single_pulse
DATIM	2017-01-31 16:45:15
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38

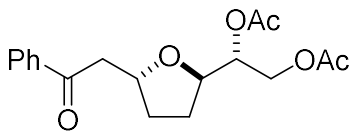


21a

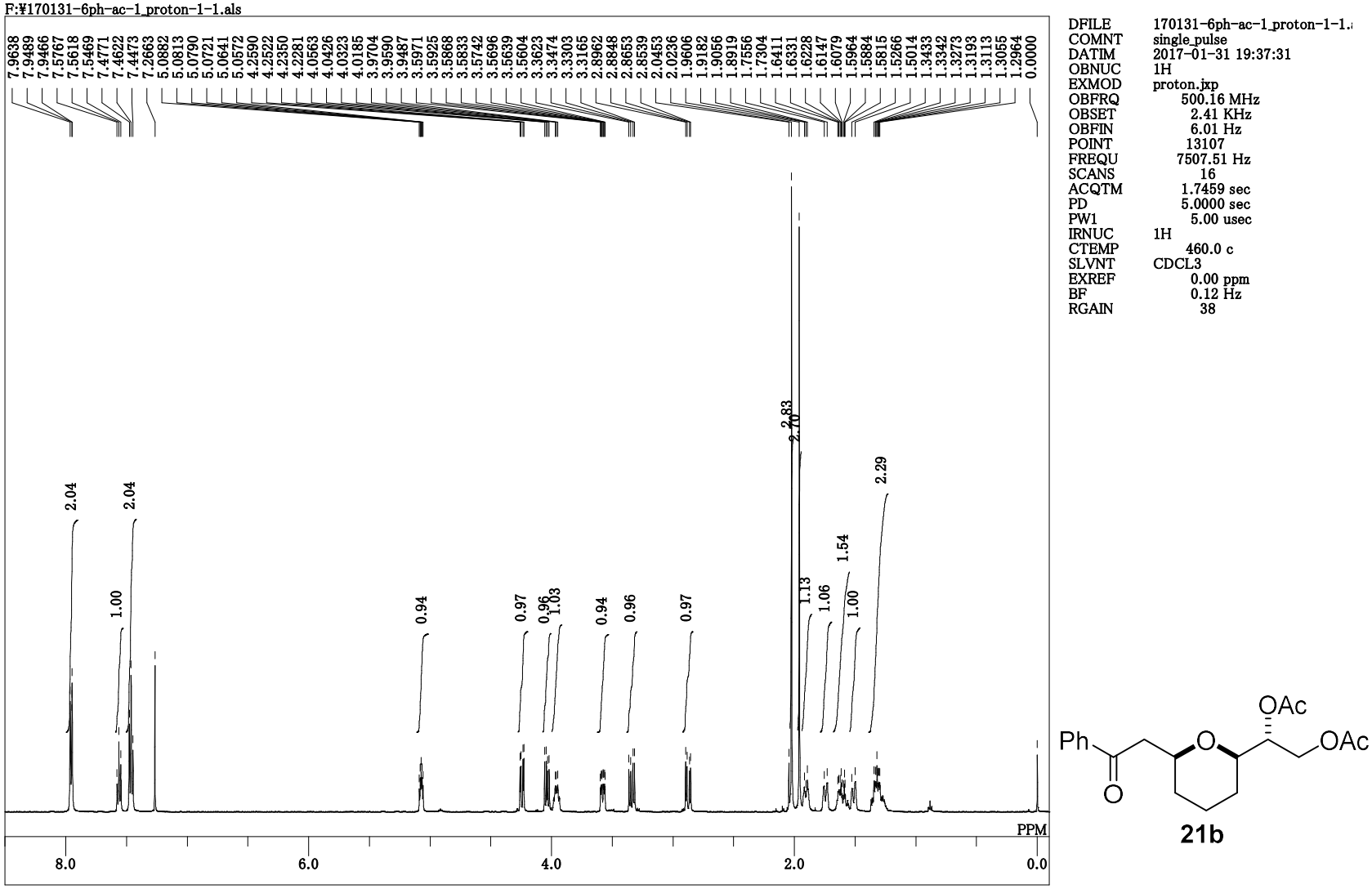
G:¥170202-cita_Carbon-1-1.als



DFILE	170202-cita_Carbon-1-1.als
COMNT	single pulse decoupled gated N
DATIM	2017-02-02 03:50:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	7811
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.67 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

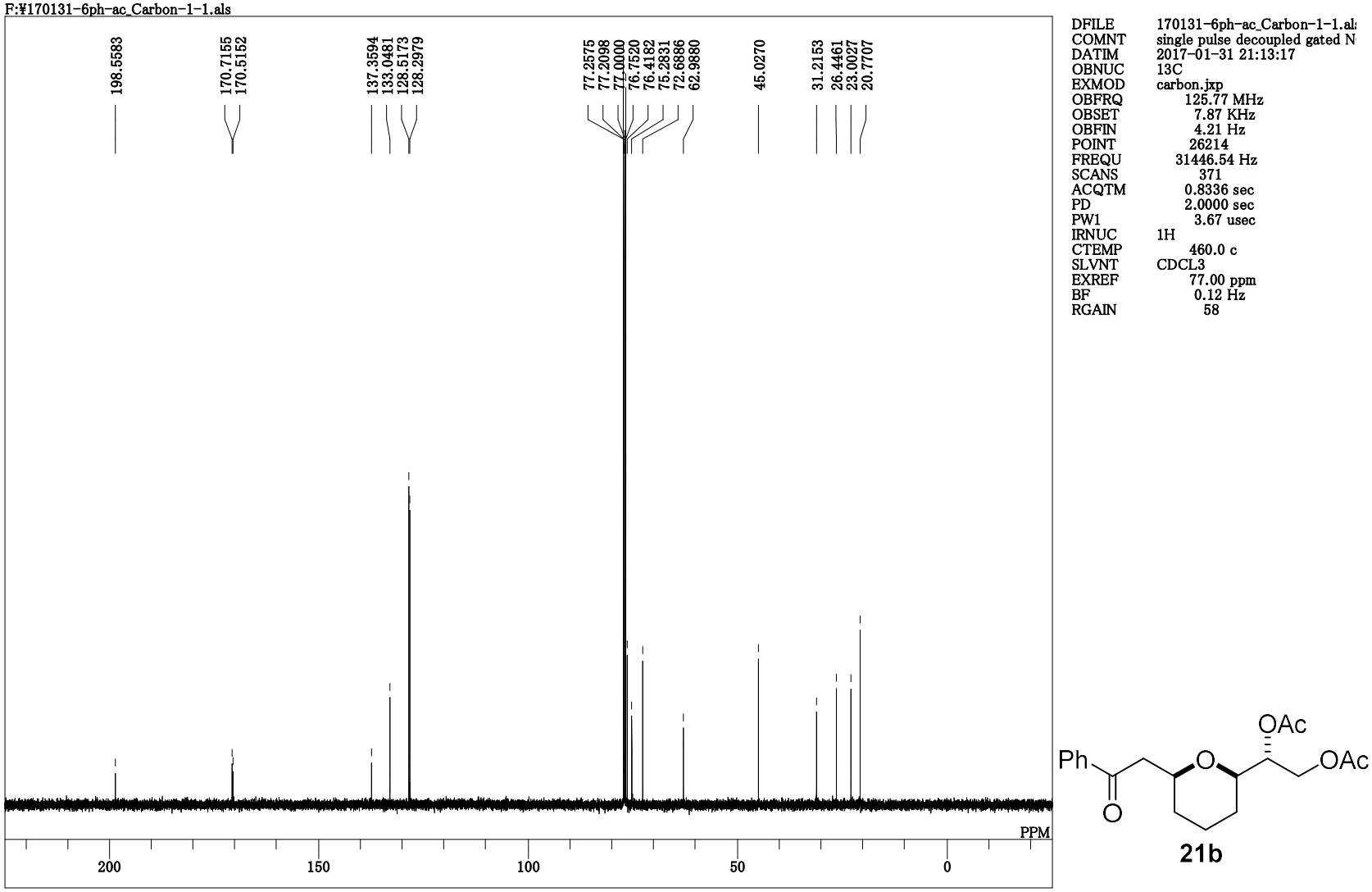


21a

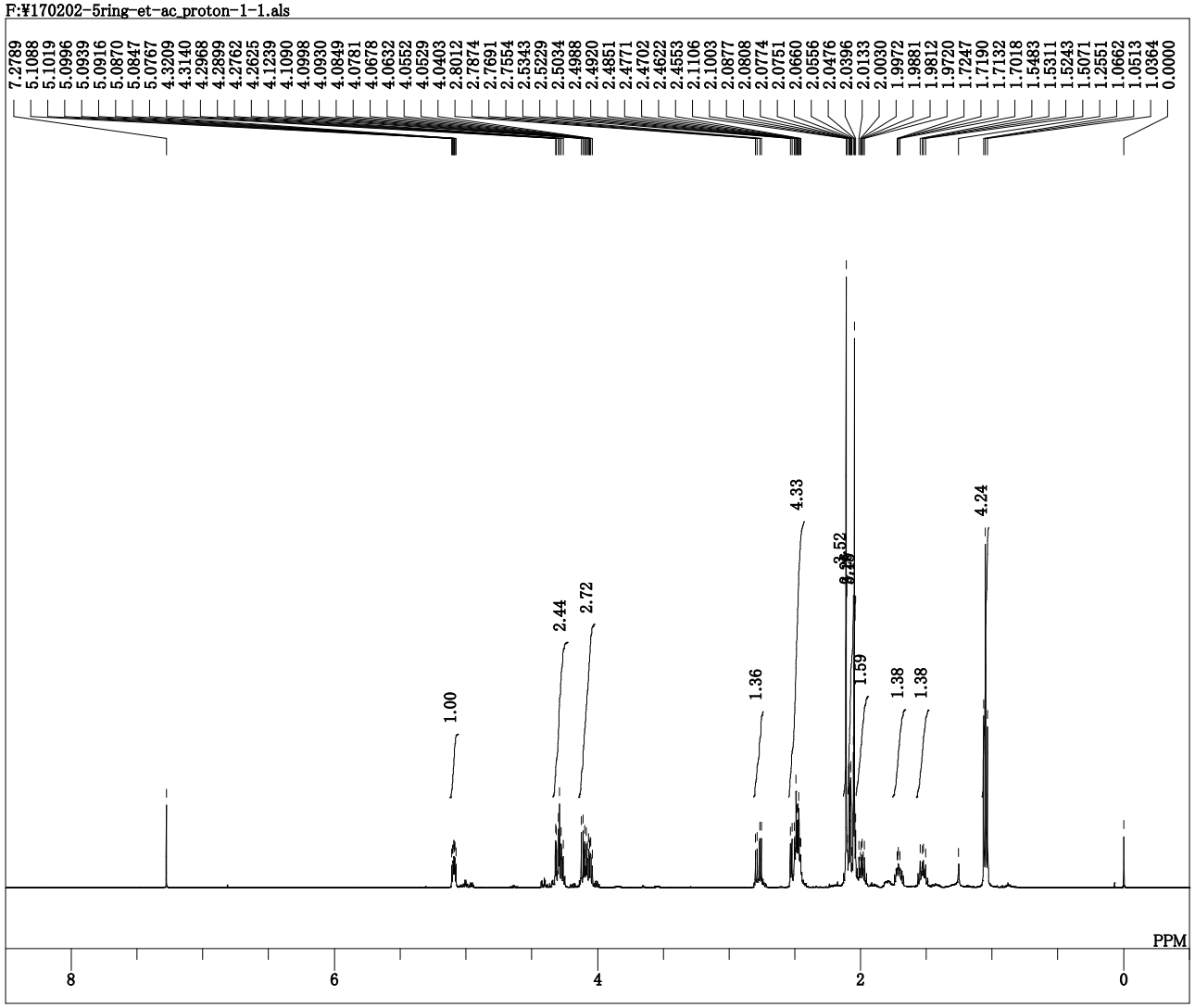


DFILE	170131-6ph-ac-1_proton-1-1.a
COMNT	single_pulse
DATIM	2017-01-31 19:37:31
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38

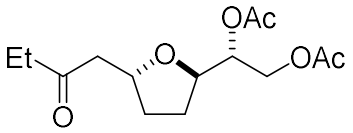
21b


F:¥170131-6ph-ac_Carbon-1-1.als
198.5583
170.7155
170.5152
137.3594
133.0481
128.5173
128.2979
77.2575
77.2098
77.0000
76.7520
76.4182
75.2831
72.6886
62.9880
45.0270
31.2153
26.4461
23.0027
20.7707
PPM
200
150
100
50
0
DFILE 170131-6ph-ac_Carbon-1-1.al
COMNT single pulse decoupled gated N
DATIM 2017-01-31 21:13:17
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 371
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58
Ph
O
O
OAc
OAc

21b

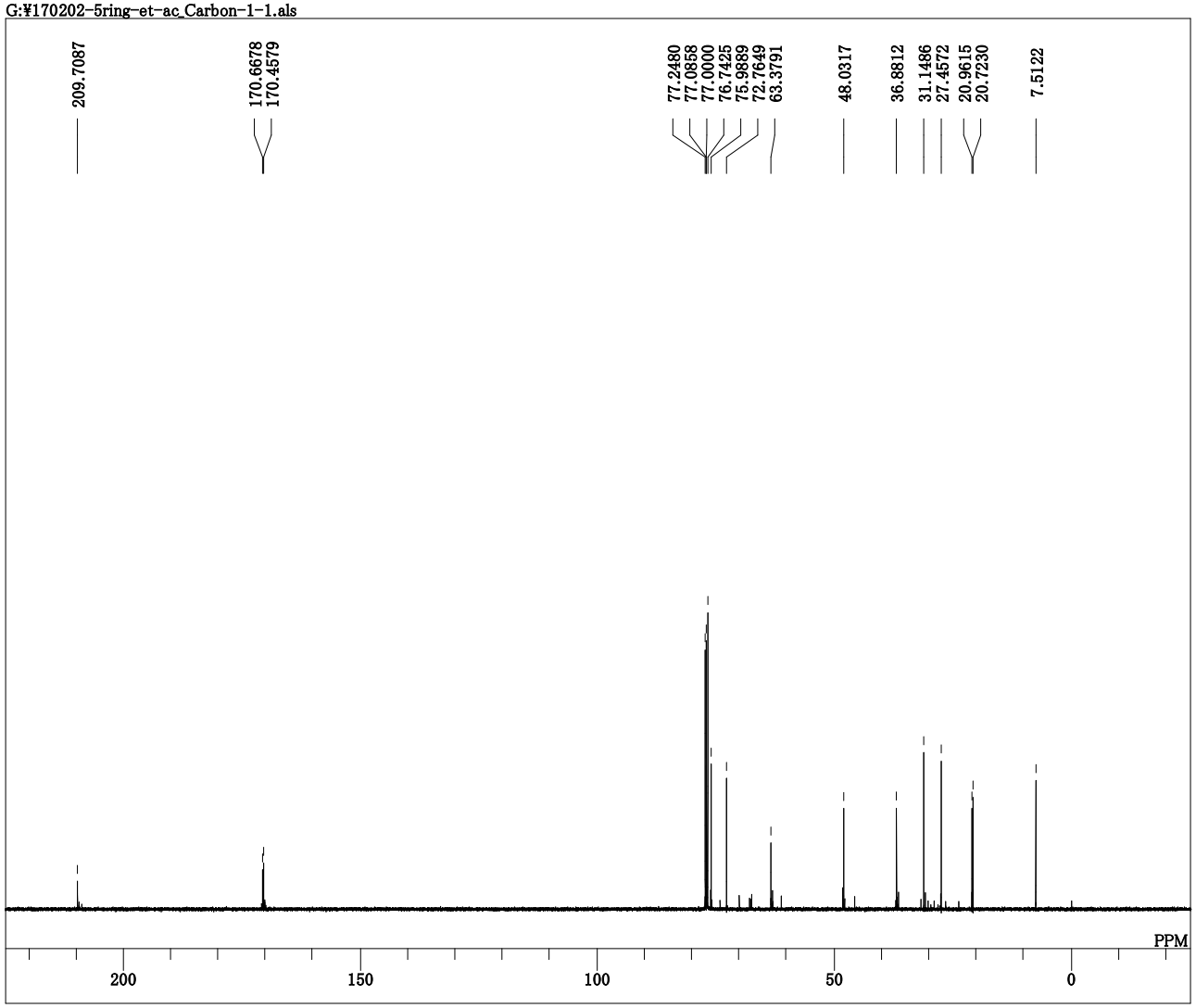


DFILE	170202-5ring-et-ac_proton-1-
COMNT	single_pulse
DATIM	2017-02-02 17:06:02
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	5.0000 sec
PW1	5.00 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36

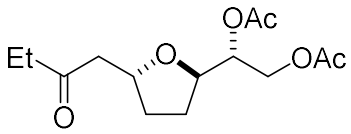


21c

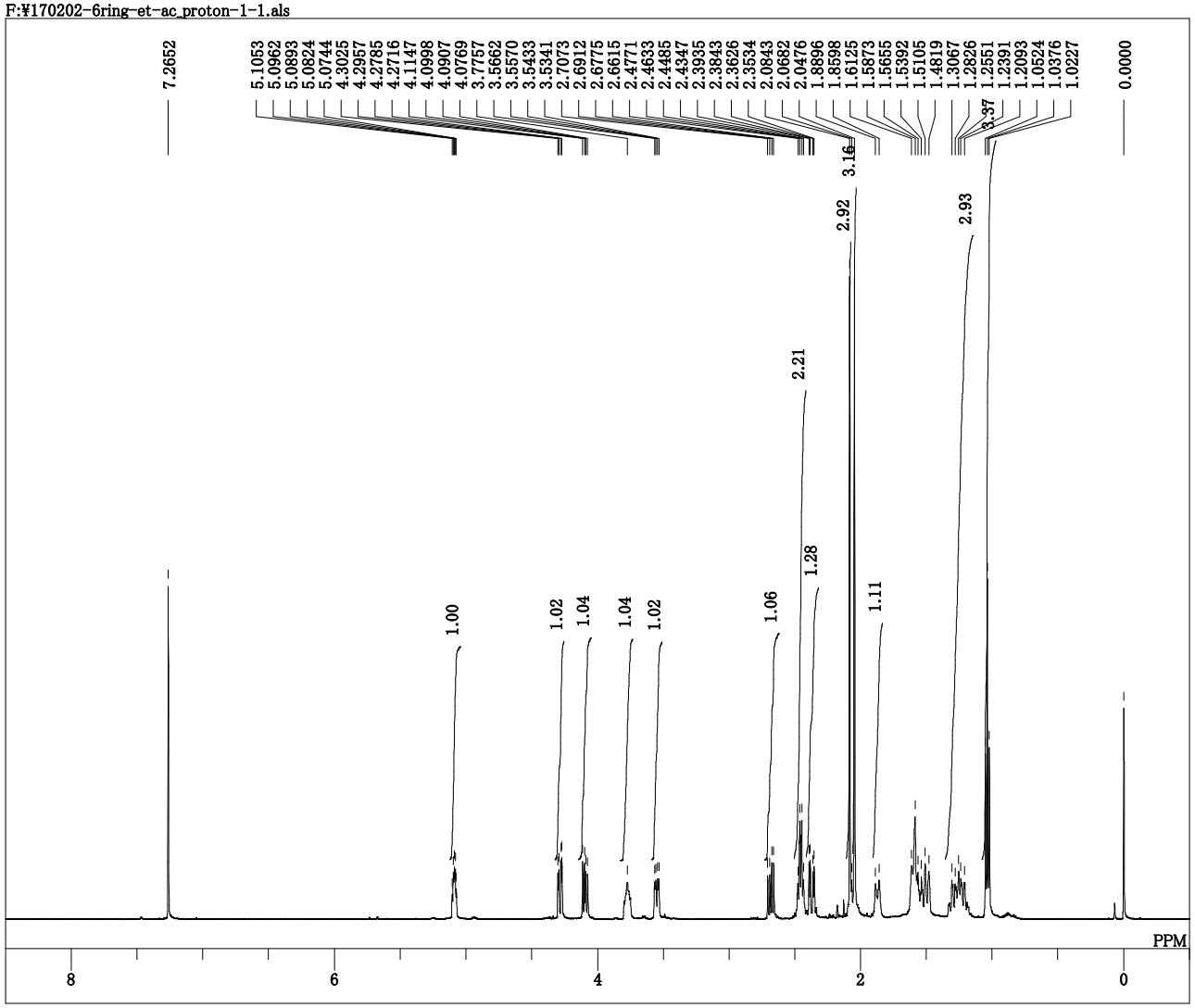
G:¥170202-5ring-et-ac_Carbon-1-1.als



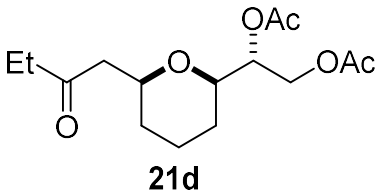
DFILE	170202-5ring-et-ac_Carbon-1-
COMNT	single pulse decoupled gated N
DATIM	2017-02-02 19:50:50
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1098
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.67 usec
IRNUC	1H
CTEMP	460.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



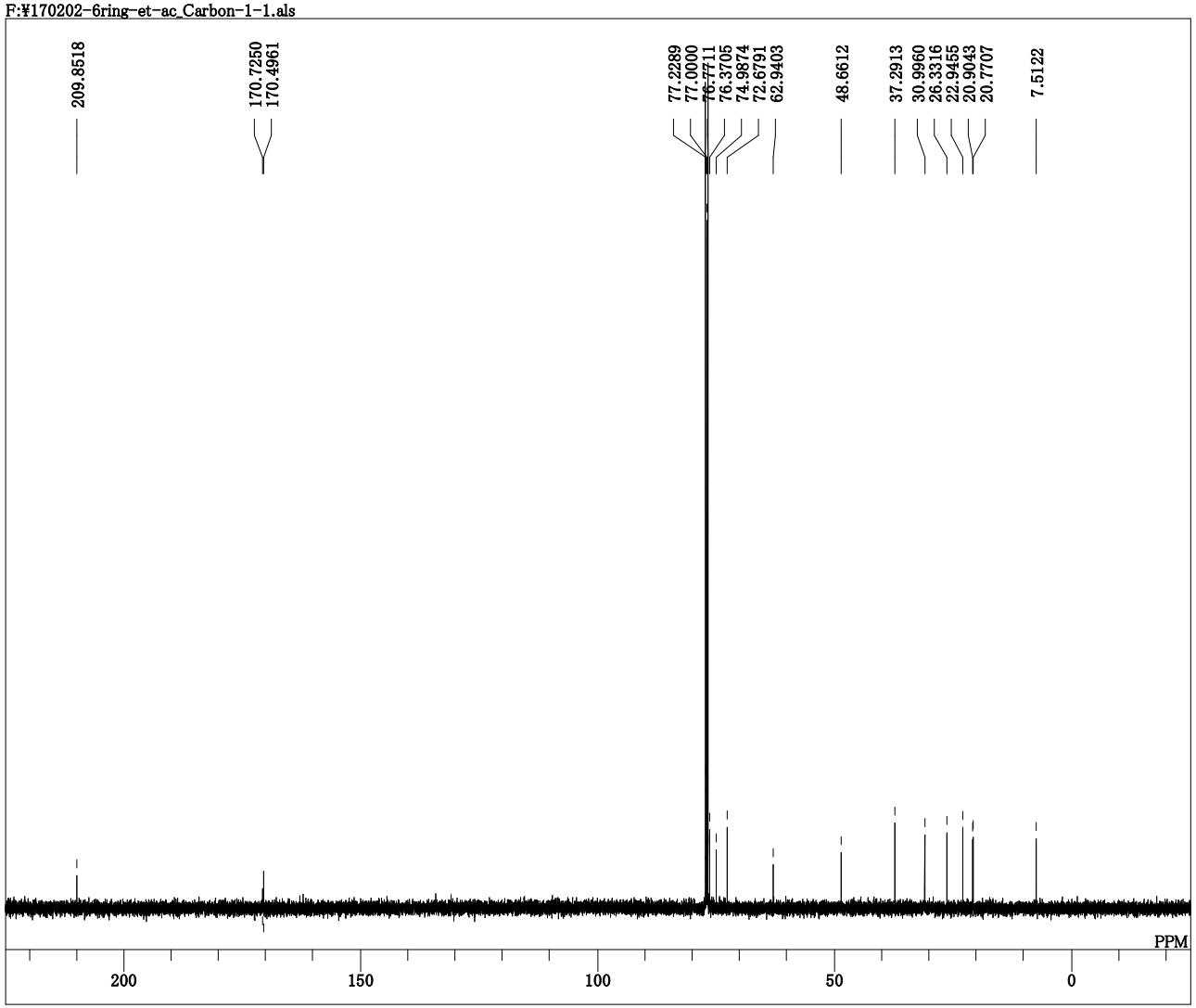
21c



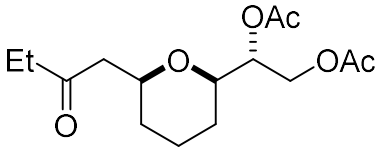
DFILE 170202-6ring-et-ac_proton-1-
COMNT single_pulse
DATIM 2017-02-02 17:14:16
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 13107
FREQU 7507.51 Hz
SCANS 16
ACQTM 1.7459 sec
PD 5.0000 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40



21d

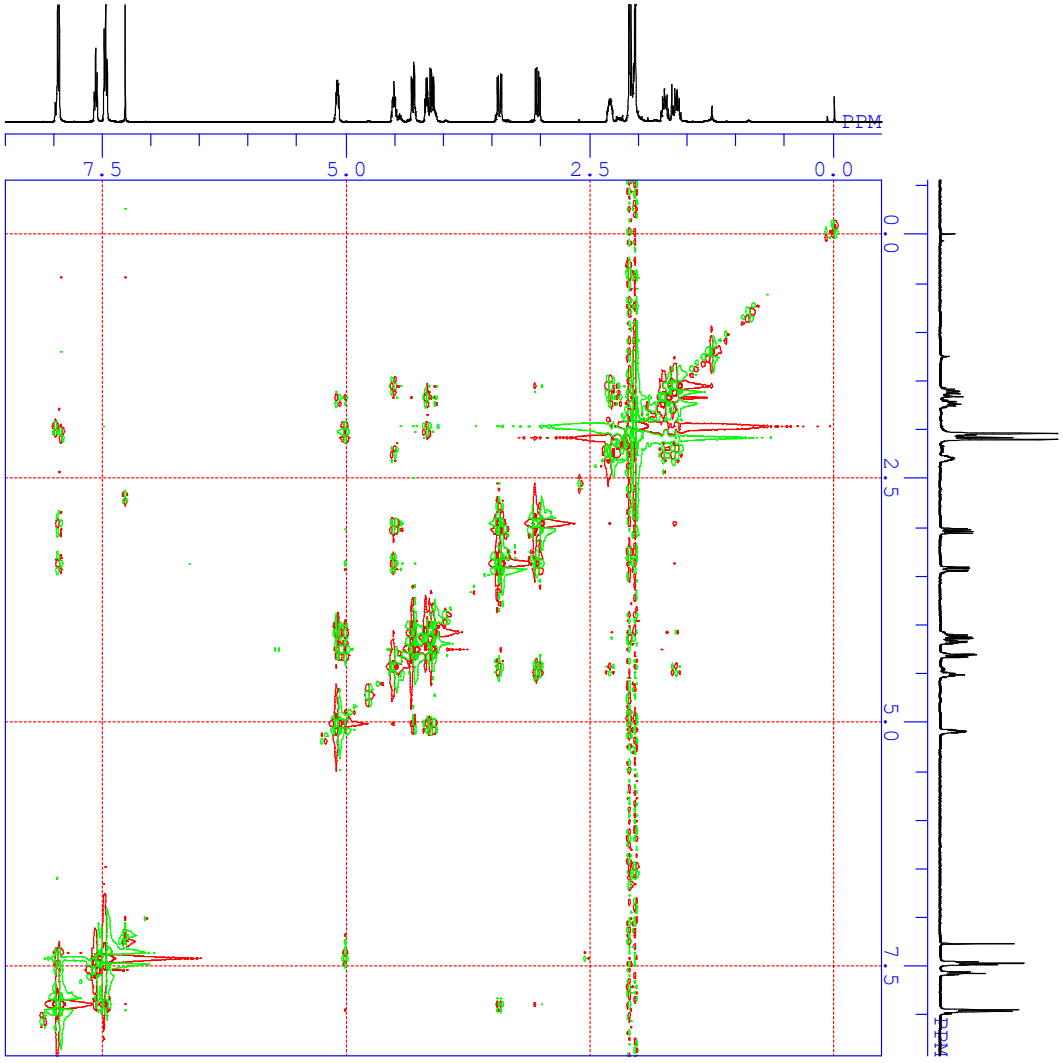


DFILE 170202-6ring-et-ac_Carbon-1-
COMNT single pulse decoupled gated N
DATIM 2017-02-02 18:40:11
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 515
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.67 usec
IRNUC 1H
CTEMP 460.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

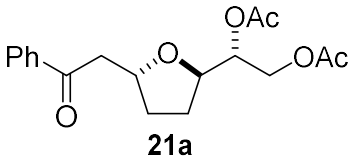


21d

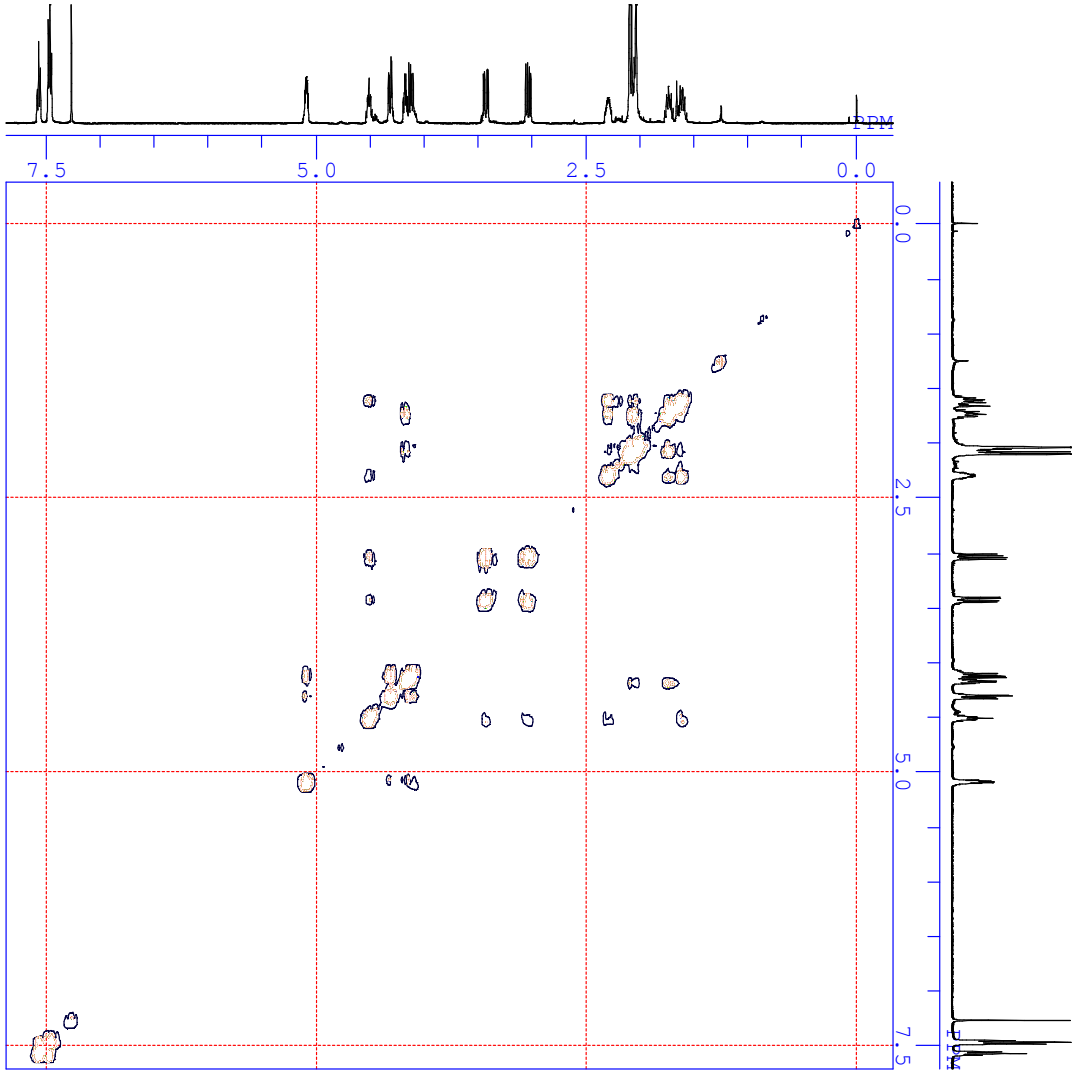
2D spectrum



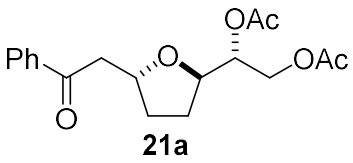

```
DATIM   31-01-2017 16:47:57
DFILE   170131-5ring-ac-monohon
OBNUC   1H
EXMOD   noesy.jxp
OFR          500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT          1024
FREQU       9384.38 Hz
SCANS             2
ACQTM        0.1091 sec
PD           1.5000 sec
PW1           10.00 usec
IRN
CTEMP         460.0 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             4.20 Hz
RGAIN            50
```



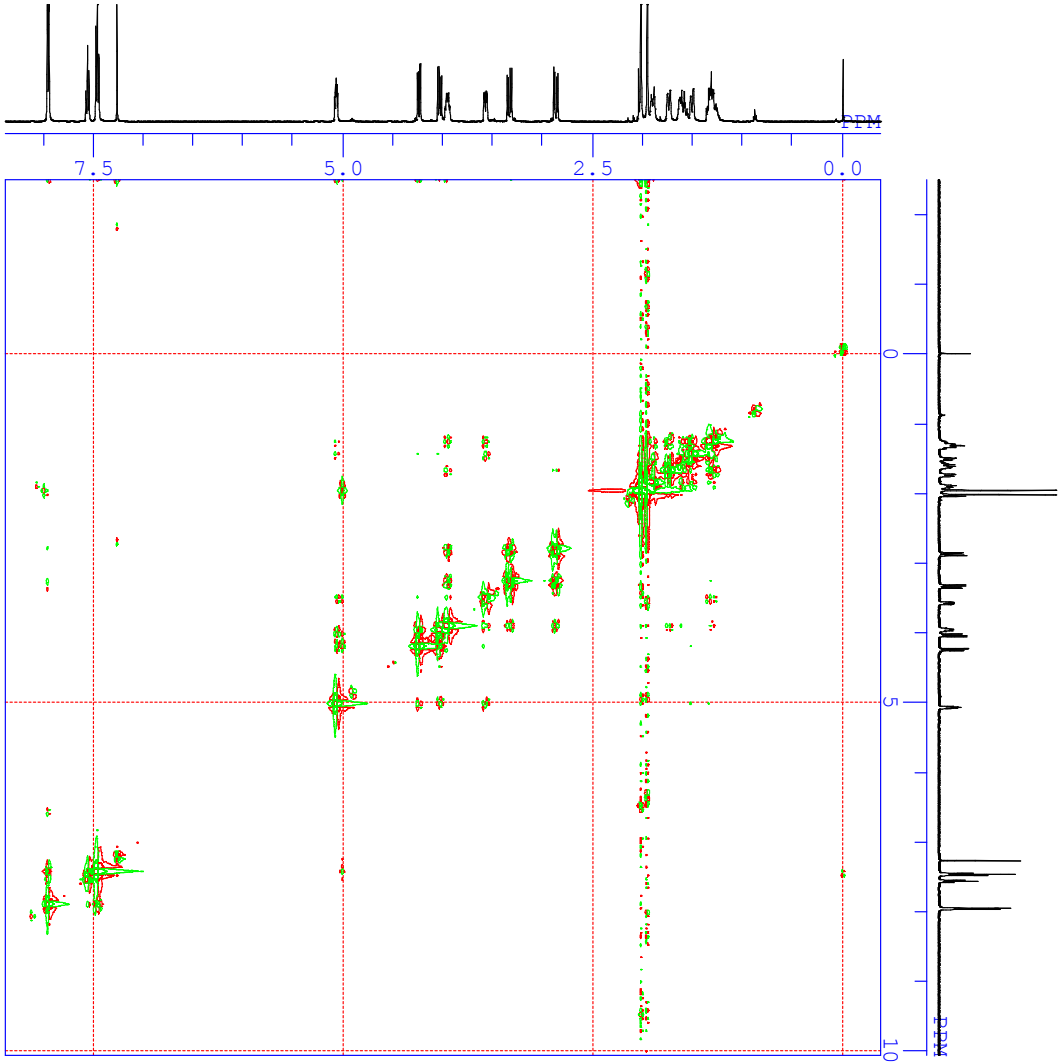
21a



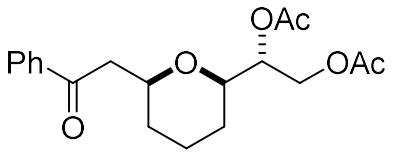

```
DATIM   31-01-2017 17:24:54
DFILE   170131-5ring-ac-monohon
OBNUC   1H
EXMOD   cosy.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           1024
FREQU        7507.51 Hz
SCANS              4
ACQTM         0.1364 sec
PD            1.5000 sec
PW1            10.00 usec
IRN
CTEMP           460.0 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              4.20 Hz
RGAIN             50
```



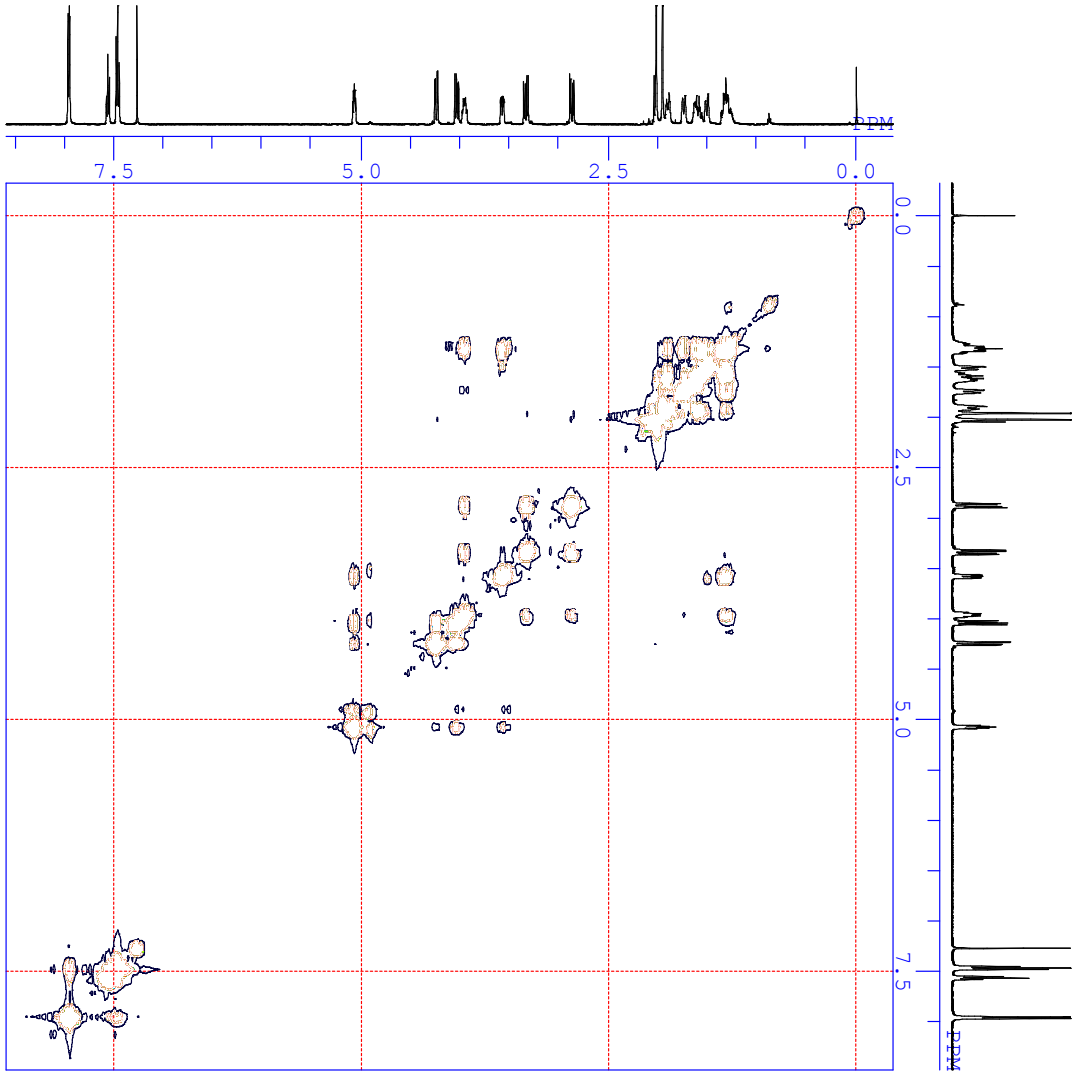
21a



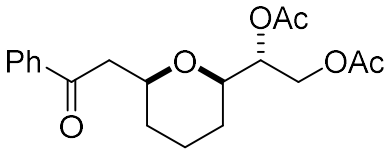

```
DATIM   31-01-2017 19:56:56
DFILE   170131-6ph-ac_NOESY-1-1
OBNUC   1H
EXMOD   noesy.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           1024
FREQU        9384.38 Hz
SCANS              2
ACQTM         0.1091 sec
PD            1.5000 sec
PW1            10.00 usec
IRN
CTEMP           460.0 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              4.20 Hz
RGAIN             52
```



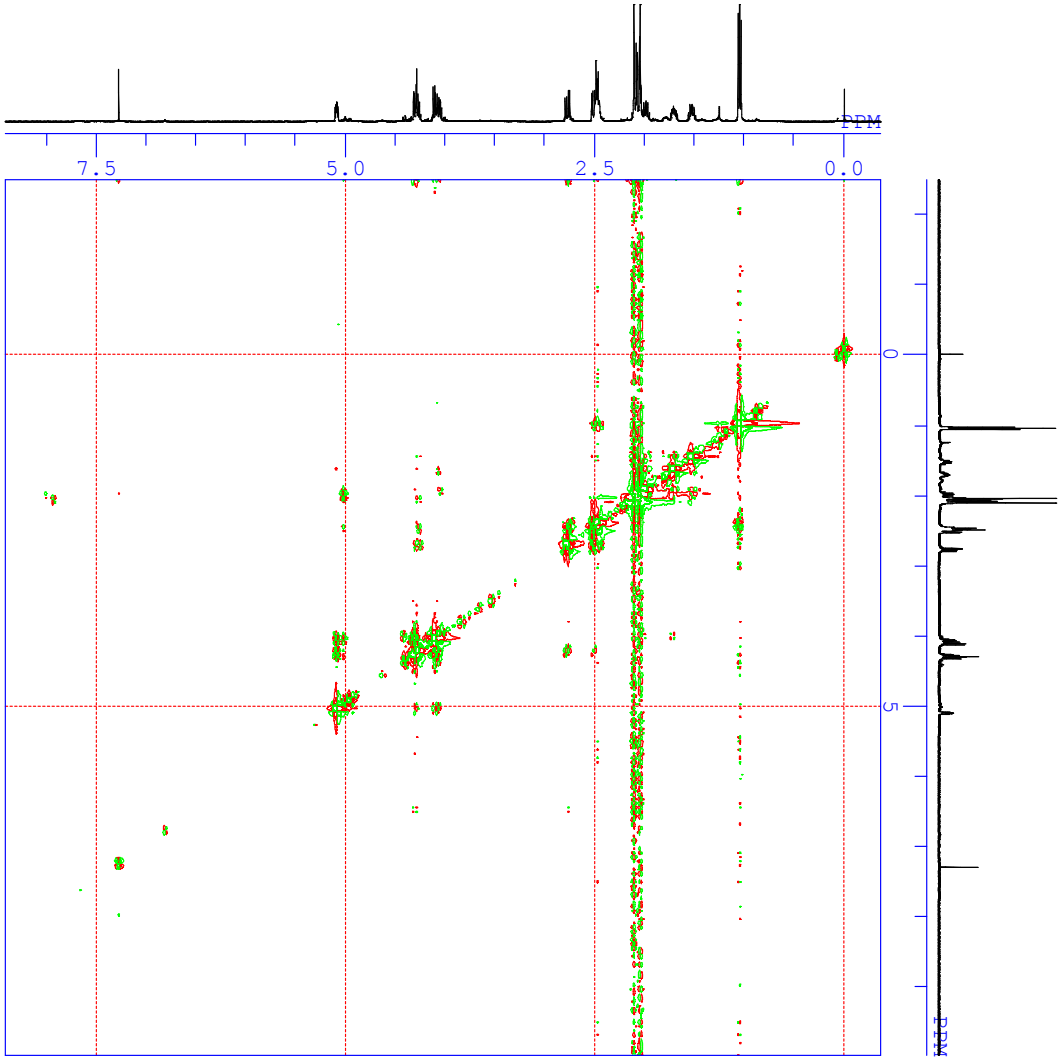
21b



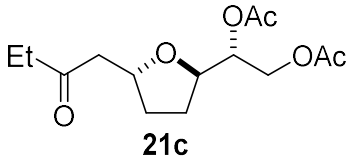

```
DATIM   31-01-2017 20:33:58
DFILE   170131-6ph-ac_cosy-1-1.
OBNUC   1H
EXMOD   cosy.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           1280
FREQU         9384.38 Hz
SCANS              4
ACQTM          0.1364 sec
PD             1.5000 sec
PW1             10.00 usec
IRN
CTEMP           460.0 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               4.20 Hz
RGAIN              52
```



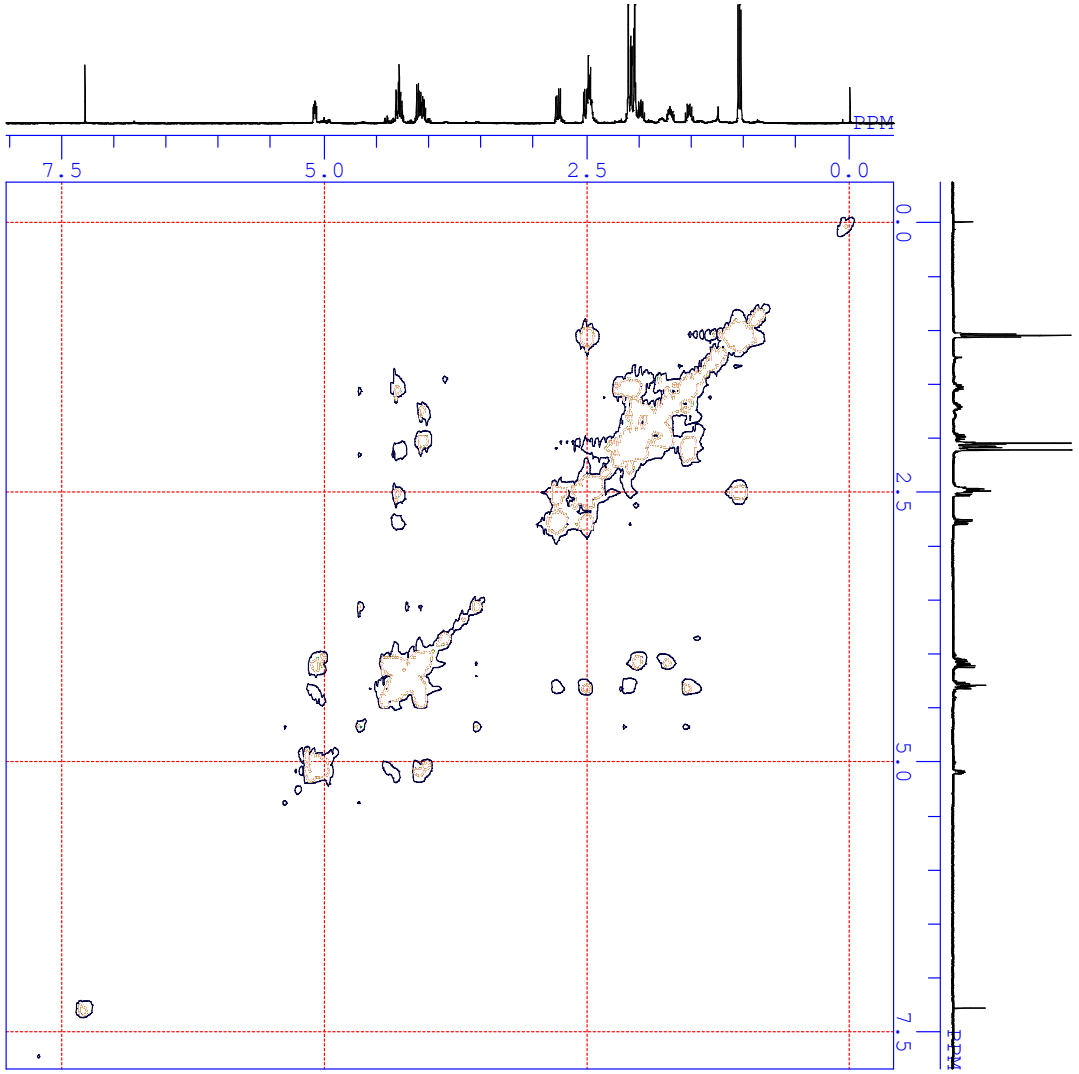
21b



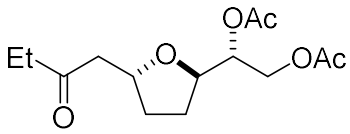

```
DATIM  02-02-2017 20:43:40
DFILE  170202-5ring-et-ac_NOES
OBNUC  1H
EXMOD  noesy.jxp
OFR          500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT          1024
FREQU       9384.38 Hz
SCANS             2
ACQTM        0.1091 sec
PD           1.5000 sec
PW1           10.00 usec
IRN
CTEMP         460.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             4.20 Hz
RGAIN            50
```



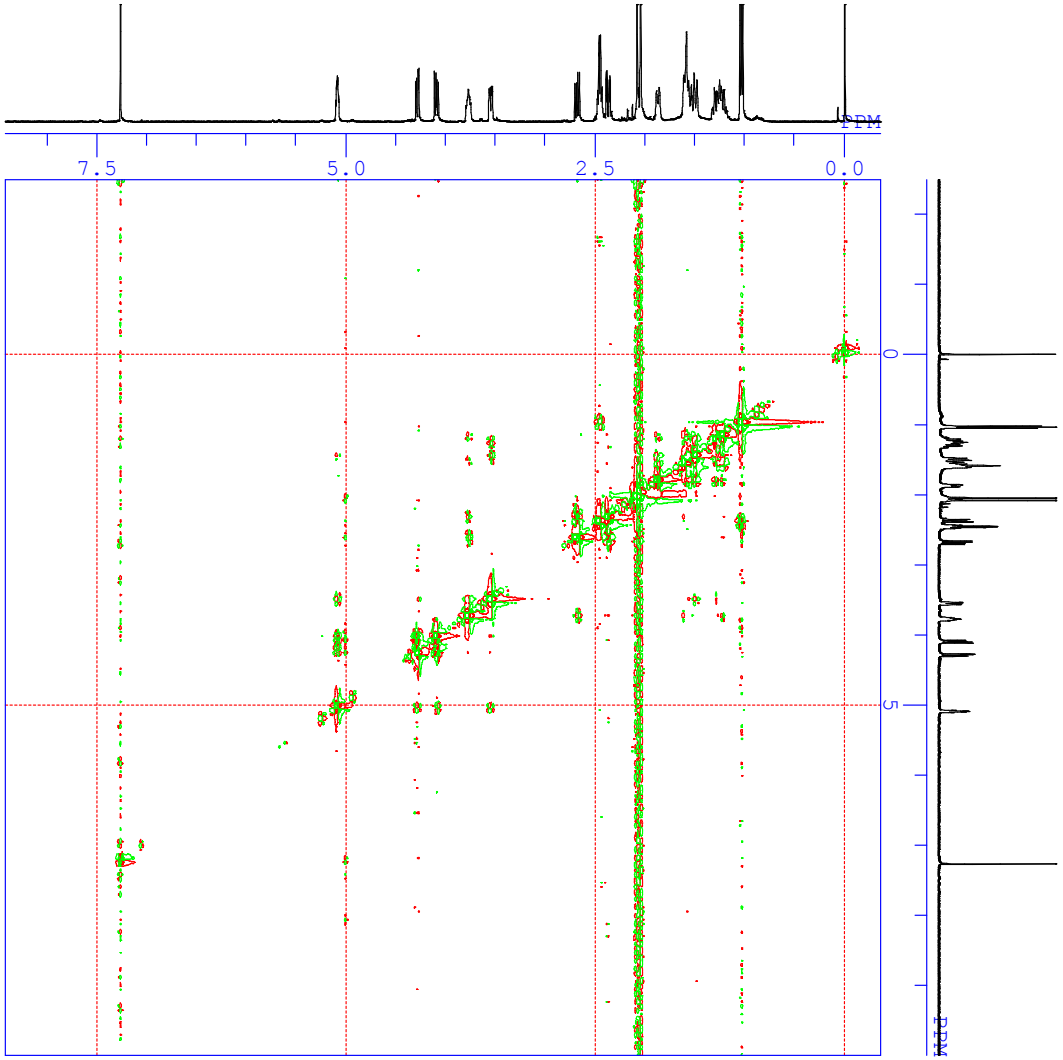
21c



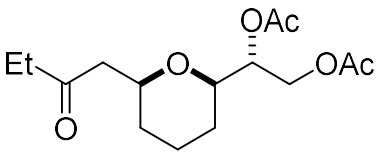

```
DATIM  02-02-2017 21:20:43
DFILE  170202-5ring-et-ac_cosy
OBNUC  1H
EXMOD  cosy.jxp
OFR          500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT          1280
FREQU        9384.38 Hz
SCANS             4
ACQTM         0.1364 sec
PD            1.5000 sec
PW1            10.00 usec
IRN
CTEMP          460.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             4.20 Hz
RGAIN            44
```



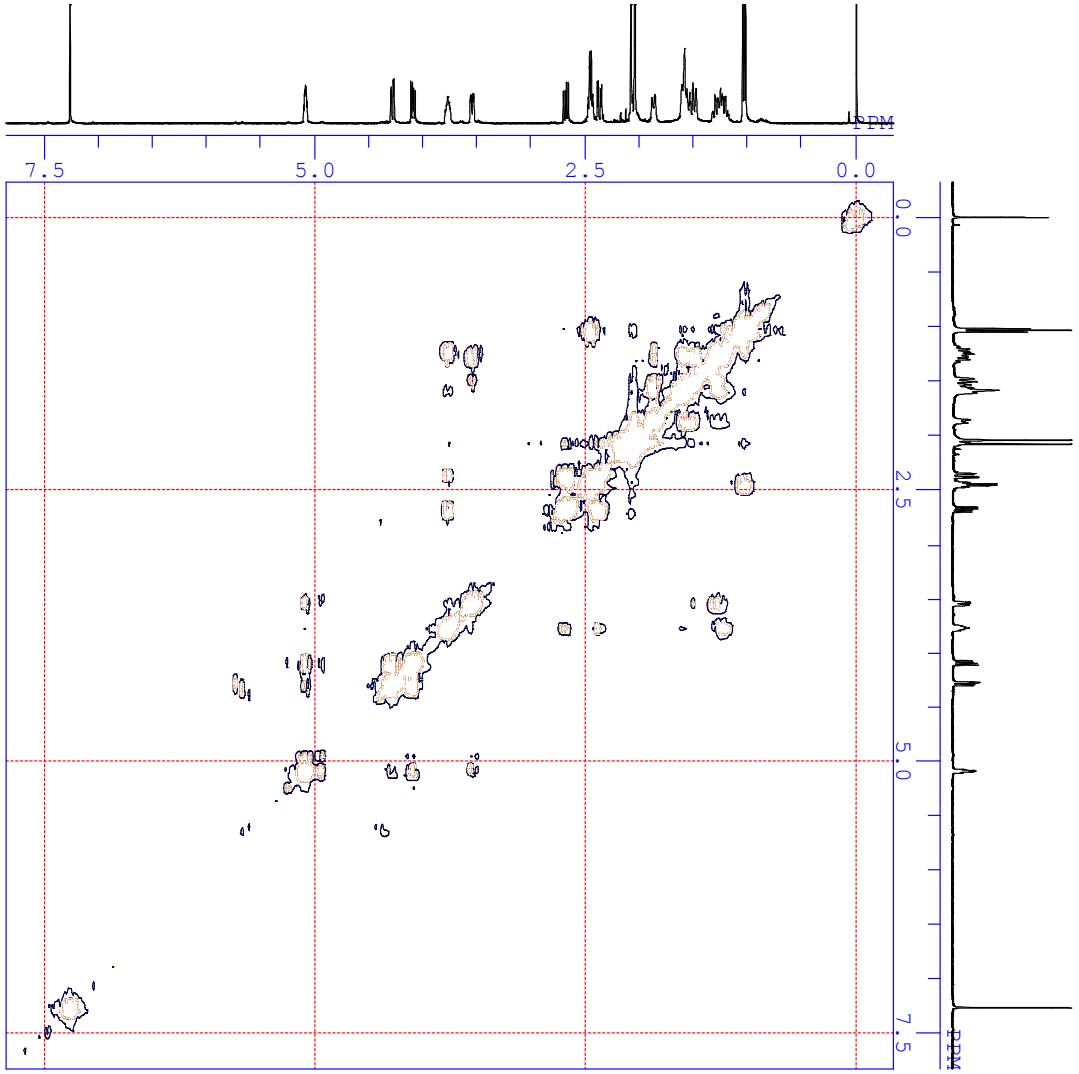
21c



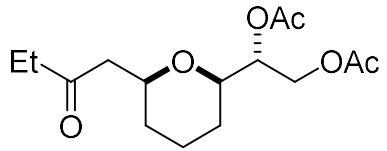

```
DATIM  02-02-2017 17:39:51
DFILE  170202-6ring-et-ac_NOES
OBNUC  1H
EXMOD  noesy.jxp
OFR          500.16 MHz
OBSET          2.41 KHz
OBFIN          6.01 Hz
POINT          1024
FREQU       9384.38 Hz
SCANS             2
ACQTM        0.1091 sec
PD           1.5000 sec
PW1           10.00 usec
IRN
CTEMP         460.0 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             4.20 Hz
RGAIN            50
```



21d




```
DATIM   02-02-2017 18:16:51
DFILE   170202-6ring-et-ac_cosy
OBNUC   1H
EXMOD   cosy.jxp
OFR           500.16 MHz
OBSET           2.41 KHz
OBFIN           6.01 Hz
POINT           1280
FREQU        9384.38 Hz
SCANS              4
ACQTM         0.1364 sec
PD            1.5000 sec
PW1            10.00 usec
IRN
CTEMP           460.0 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               4.20 Hz
RGAIN              60
```



21d