Supporting Information

Cyclization of Non-Terminal Alkynic β-Keto Eaters Catalyzed by Gold(I) Complex with a Semihollow, End-Capped Triethynylphosphine Ligand

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General.

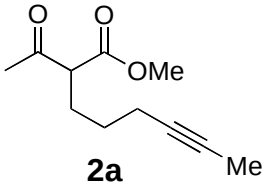
NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR and 121.4 MHz for ^{31}P NMR. Chemical shift values for ^{1}H, ^{13}C and ^{31}P NMR are reference to Me_4Si, the residual solvent resonances and external aqueous 85% H_3PO_4 respectively. Mass spectrometry (JEOL JMS-FABmate for EI-MS, JEOL JMS-700TZ for ESI-MS) and elemental analysis were performed at the Center for Instrument Analysis, Hokkaido University. Triethynylphosphine ligands **1a**, **1b**, and **1c** were prepared according to the reported procedure.[1] $AgNTf_2$ was prepared from Ag_2O and $HN(SO_2CF_3)_2$.[2] Phosphine ligands, PPh_3 and $P(OPh)_3$ were commercially available. Gold complexes {AuCl(ligand)} were synthesized by the reported method.[1] Anhydrous solvents used in synthesis of materials were purchased from Kanto Chemical Co. and used without further purifications. Anhydrous CH_2Cl_2 used in Au-catalyzed cyclizations was purchased from Kanto Chemical Co. and degassed before use. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, $CHCl_3$, 3.5 mL/min, UV and RI detectors). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. PTLC purification was performed on commercial glass plates bearing 1-mm layer of Merck Silica gel $60F_{254}$. All reactions were carried out under argon atmosphere unless otherwise noted.

General Procedure for Alkyne Cyclizations.

{AuCl(ligand)} (1 mol%) was placed in an open vial tube, and was dissolved in CH_2Cl_2 (ca. 0.5 mL). $AgNTf_2$ (3.2 mg) was added, and a mixture was stirred at 25 ˚C for 10 min. The resulting white suspension was filtered through celite to a screw vial. The resulting colorless solution was first concentrated with a stream of Ar gas, and then was dried *in vacuo*. The tube was brought into a glove box. A magnetic stirring bar was placed in the tube, and the gold complex was dissolved in degassed CH_2Cl_2. A substrate (0.4 mmol) was added to the catalyst solution. The tube was sealed with a cap equipped with a Teflon-coated silicon rubber septum. The vial tube was brought out of the glove box, and set into a water bath adjusted at 25 °C. After stirring for a given time, the reaction mixture was passed through a pad of silica gel and concentrated to dryness. Purification by flash chromatography on silica gel gave cyclization products.

Preparation of Substrates

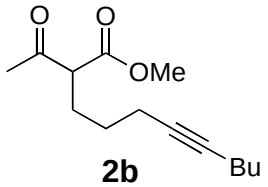
Methyl 2-Acetyl-6-octynoate (2a) (keto/enol = 89/11)



2a

To a suspension of NaH (60 wt. %, 910 mg, 22.8 mmol) in THF (11 mL) and DMF (11 mL) was added dropwise methyl acetoacetate (2.50 mL, 22.8 mmol) at 0 ºC. The mixture was stirred at this temperature for 10 min and at room temperature for 1 h. Then, 6-iodo-2-pentyne (4.65 g, 22.4 mmol) was added, and the reaction mixture was stirred overnight (monitored by TLC). The resulting suspension was diluted with ether, and quenched with saturated aqueous NH_4Cl. The organic layer was washed with saturated aqueous NH_4Cl (3 × 10 mL), and separated. The combined aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 90/10) to afford **2a** as a colorless oil (1.91 g, 44%, keto/enol = 89/11). ^{1}H NMR ($CDCl_3$) δ 1.38–1.61 (m, 2H), 1.77 (t, *J* = 2.4 Hz, 3H), 1.90–2.00 (q, *J* = 7.8 Hz, 2H), 2.04 (s, 0.11×3H), 2.10–2.20 (m, 2H), 2.24 (s, 0.89×3H), 3.47 (t, *J* = 7.5 Hz, 0.89×1H), 3.75 (s, 0.89×3H), 3.78 (s, 0.11H×3H), 12.72 (s, 0.11×1H). ^{13}C NMR of **2a-keto** ($CDCl_3$) δ 3.21, 18.28, 26.49, 27.16, 28.65, 52.30, 59.09, 76.18, 78.04, 170.28, 203.18. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%. Found: C, 67.19; H, 8.17%. HRMS (EI^+) Calcd for $C_{11}H_{16}O_3$ $[M]^+$: *m/z* 196.1099. Found: *m/z* 196.1102.

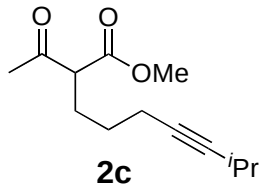
Methyl 2-Acetyl-6-undecynoate (2b) (keto/enol = 87/13)



2b

2b was prepared according to the procedure for the preparation of **2a**, employing methyl acetoacetate (2.0 mL, 18.0 mmol), NaH (804 mg, 20.1 mmol), 9-iodo-5-nonyne (4.72 g, 18.6 mmol) and hexanes/EtOAc (99/1 to 90/10) as the eluent. Colorless oil (1.69 g, 37%, keto/enol = 87/13). ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.33–1.54 (m, 6H), 1.91–2.00 (q, *J* = 7.8 Hz, 2H), 2.04 (s, 0.13×3H), 2.10–2.22 (m, 4H), 2.24 (s, 0.87×3H), 3.47 (t, *J* = 7.5 Hz, 0.87×1H), 3.75 (s, 0.87×3H), 3.75 (s, 0.13×3H), 12.72 (s, 0.13×1H). ^{13}C NMR of **2b-keto** ($CDCl_3$) δ 13.45, 18.23, 18.33, 21.77, 26.59, 27.16, 28.63, 31.00, 52.31, 59.11, 78.84, 81.03, 170.31, 203.23. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30%. Found: C, 70.20; H, 9.24%. HRMS (EI^+) Calcd for $C_{14}H_{22}O_3$ $[M]^+$: *m/z* 238.1569. Found: *m/z* 238.1570.

Methyl 2-Acetyl-8-methyl-6-nonynoate (2c) (keto/enol = 97/3)

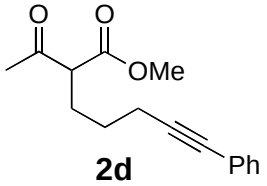


2c

2c was prepared according to the procedure for the preparation of **2a**, employing methyl acetoacetate (1.10 mL, 9.91 mmol), NaH (425 mg, 10.6 mmol), 7-iodo-2-methyl-3-heptyne (2.03 g, 8.60 mmol) for 14 h at 50 ºC and hexanes/EtOAc (99/1 to 90/10) as the eluent. Colorless oil (983 mg, 51%, keto/enol = 97/3). ^{1}H NMR ($CDCl_3$) δ 1.13 (d, *J* = 6.9 Hz, 6H), 1.41–1.53 (m, 2H), 1.95 (q, *J* =

7.5 Hz, 2H), 2.18 (td, *J* = 7.5 Hz, 2.4 Hz, 2H), 2.24 (s, 3H), 2.25 (m, 1H), 3.47 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H) (enol: 12.71 (m, 1H)). ^{13}C NMR of **2c-keto** ($CDCl_3$) δ 18.46, 20.52, 23.41, 26.78, 27.32, 28.81, 52.51, 59.31, 78.22, 87.04, 170.51, 203.44. HRMS (EI^+) Calcd for $C_{13}H_{19}O_3$ $[M–H]^+$: *m/z* 223.1334. Found: *m/z* 223.1325.

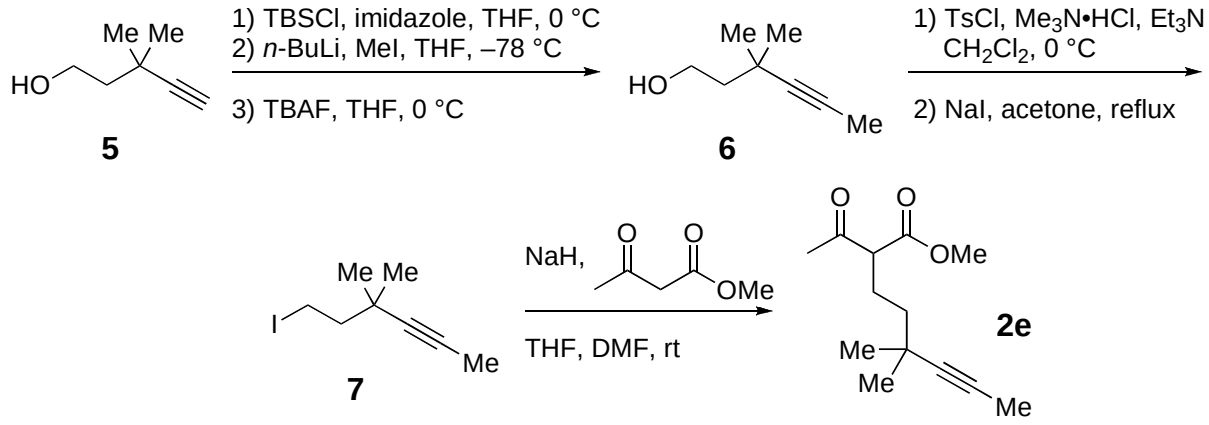
Methyl 2-Acetyl-7-phenyl-6-heptynoate (2d) (keto/enol = 90/10)



2d

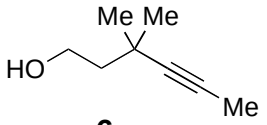
The **2d** was prepared according to the procedure for the preparation of **2a**, employing methyl acetoacetate (1.22 mL, 11.0 mmol), NaH (492 mg, 12.3 mmol), 5-iodo-1-phenyl-1-pentyne[3] (2.86 g, 12.4 mmol) for 15 h and hexanes/EtOAc (99/1 to 90/10) as the eluent. Colorless oil (1.65 g, 58%, keto/enol = 90/10). ^{1}H NMR ($CDCl_3$) δ 1.54–1.74 (m, 2H), 1.99–2.09 (m, 0.90×2H, 0.10×2H), 2.07 (s, 0.10×3H), 2.25 (s, 0.90×3H), 2.45 (t, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 7.2 Hz, 0.90×1H), 3.75 (s, 0.90×3H), 3.77 (s, 0.10×3H), 7.23–7.32 (m, 3H), 7.34–7.43 (m, 2H), 12.75 (s, 0.10×1H). ^{13}C NMR of **2d-keto** ($CDCl_3$) δ 19.04, 26.29, 27.23, 28.77, 52.41, 59.12, 81.27, 89.00, 123.76, 127.76, 128.29, 131.62, 170.29, 203.12. Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02%. HRMS (EI^+) Calcd for $C_{16}H_{18}O_3$ $[M]^+$: *m/z* 258.1256. Found: *m/z* 258.1257.

Scheme 2. Preparation of 2e.



5 **6** **7** **2e**

3,3-Dimethyl-4-hexyn-1-ol (6)



6

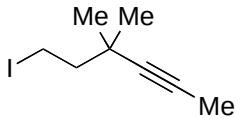
To a solution of TBSCl (2.63 g, 17.1 mmol) in THF (8 mL) was added 3,3-dimethyl-4-pentyn-1-ol (**5**)[4] (1.83 g) in THF (8 mL) at 0 ºC. Then imidazole was added and stirred at this temperature for 20 min (monitored by TLC). The resulting white suspension was quenched with saturated aqueous $NaHCO_3$ at 0 ºC. The organic layer was washed with water (3 × 10 mL), and separated. The combined aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the silylated compound as a crude product (colorless oil, 3.81 g). This crude product was used in the next step without further purification.

To a solution of the silylated compound (3.81 g 16.3 mmol) in THF (16 mL) was added dropwise *n*-BuLi (11.3 mL of 1.52 M in hexane, 17.2 mmol) at 0 ºC under Ar atmosphere. The reaction mixture

was stirred at this temperature for 30 min (white suspension was observed). Then MeI (2.16 mL, 32.7 mmol) was added and the mixture was stirred at –78 ºC for 30 min. The reaction mixture was allowed to warm to room temperature and stirred for 90 min (consumption of starting material was checked by ^{1}H NMR) before being quenched with saturated aqueous NH_4Cl. The organic layer was washed with water (3 × 10 mL), and separated. The combined aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the methylated compound as a crude product (colorless oil, 3.84 g). This crude product was used in the next step without further purification.

To a solution of the methylated compound (3.84 g) in THF (48 mL) was added TBAF (17.9 mL of 1.0 M in THF, 17.9 mmol) at 0 ºC under Ar atmosphere. After stirring at this temperature for 2 h and at rt for 18 h, the reaction mixture was quenched with water. The organic layer was washed with water (3 × 20 mL), and separated. The combined aqueous layer was extracted with ether (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford a mixture of **6** and a small amount of siloxane as a colorless oil (1.71g, 3 steps over all 83%). This mixture was used in the next step without further purification. ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 6H), 1.67 (t, *J* = 6.6 Hz, 2H), 1.78 (s, 3H), 2.14–2.24 (br s, 1H), 3.84 (br q, *J* = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 3.26, 29.19, 29.83, 45.43, 60.55, 76.42, 86.33.

4,4-Dimethyl-6-iodo-2-hexyne (7)

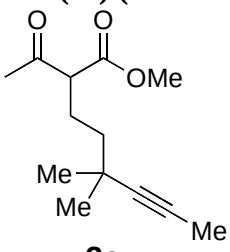


7

Tosylation of alcohol was conducted by using the reported method[5]. To a solution of $Me_3N{\cdot}HCl$ (112 mg, 1.11 mmol), Et_3N (3.08 mL, 22.1 mmol) and **6** (1.39 g, 11.0 mmol, containing trace amount of siloxane) was added TsCl (3.18 g, 16.5 mmol) in two portions at 0 ºC under Ar atmosphere. The resulting orange suspension was stirred at this temperature for 5 min (monitored by TLC), and then quenched with water. The organic layer was washed with water (3 × 10 mL), and separated. The combined aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired tosylated product as a crude product (yellow oil, 3.17 g, >100%). This mixture was used in the next step without further purification.

To a 200 mL-three-necked, round-bottomed flask equipped with a condenser was added NaI (8.40 g, 55.8 mmol), and the mixture was vigorously stirred at 150 ºC for 6 h in *vacuo*. After that, a flask was cooled to rt and charged with Ar. Acetone (55 mL) and the crude tosylated product (3.17 g, 11.0 mmol) was added to a flask, and the mixture was stirred at 80 ºC overnight. The resulting orange suspension was cooled to rt, a half of acetone was removed by the evaporator, and water was added. The organic layer was washed with water (3 × 30 mL), and separated. The combined aqueous layer was extracted with pentane (3 × 30 mL). The organic layer was combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash silica gel column purification (pentane) of the crude product afforded **7** as a colorless oil (2.25 g, 2 steps overall 86%). ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 6H), 1.77 (s, 3H), 1.97–2.05 (m, 2H), 3.25–3.33 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 0.76, 3.30, 28.92, 33.18, 48.11, 76.22, 84.30. HRMS (EI^+) Calcd for $C_8H_{13}I$ $[M]^+$: *m/z* 236.0062. Found: *m/z* 236.0057.

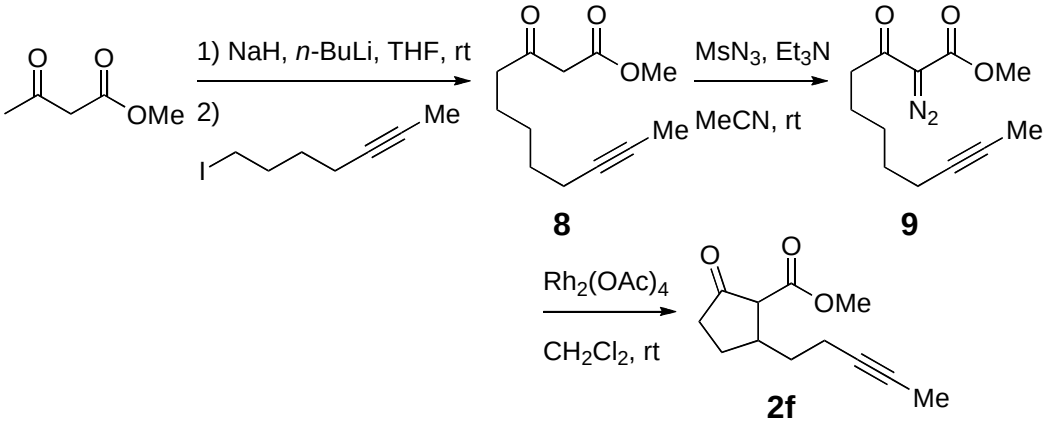
Methyl 2-Acetyl-5,5-dimethy-6-octynoate (2e) (keto/enol = 93/7)



2e

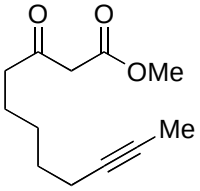
2e was prepared according to the procedure for the preparation of **2a**, employing methyl acetoacetate (1.11 mL, 10.0 mmol), NaH (225 mg, 5.62 mmol), **7** (1.18 g, 5.00 mmol) for 38 h and the eluent (hexanes/EtOAc: 99/1 to 85/15) afforded **2e** as a colorless oil (792 mg, 71%, keto/enol = 93/7). ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 0.93×6H), 1.17 (s, 0.07×6H), 1.26–1.45 (m, 2H), 1.78 (s, 0.93×3H), 1.80 (s, 0.07×3H), 1.95–2.06 (m, 2H, 0.07×3H), 2.25 (s, 0.93×3H), 3.43 (t, *J* = 7.5 Hz, 0.93×1H), 3.75 (s, 0.93×3H), 3.76 (s, 0.07×3H), 12.65 (s, 0.07×1H). ^{13}C NMR of **2e-keto** ($CDCl_3$) δ 3.14, 24.12, 28.47, 28.89, 29.24, 30.59, 40.61, 52.11, 59.64, 75.51, 85.52, 170.26, 203.26. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%. HRMS (EI^+) Calcd for $C_{13}H_{20}O_3$ $[M]^+$: *m/z* 224.1412. Found: *m/z* 224.1410.

Scheme 2. Preparation of 2f[6].



8 **9** **2f**

Methyl 3-Oxo-9-undecynoate (8) (keto/enol = 96/4)

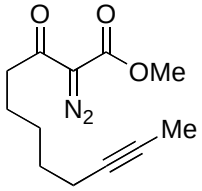


8

To a solution of NaH (60 wt. %, 884 mg, 22.1 mmol) in THF (40 mL) was added dropwise methyl acetoacetate (2.22 mL, 20.0 mmol) at 0 ºC under Ar atmosphere. The mixture was stirred at this temperature for 10 min and at room temperature for 2 h. Then, the solution was cooled to –78 ºC, *n*-BuLi (12.7 mL of 1.65 M in hexane, 20.0 mmol) was added dropwise, and the mixture was stirred at this temperature for 30 min and at 0 ºC for 2 h. 7-Iodo-2-heptyne (4.62 g, 20.8 mmol) was added, and the reaction mixture was stirred at 0 ºC overnight. The resulting suspension was diluted with ether, and quenched with saturated aqueous NH_4Cl. The organic layer was washed with saturated aqueous NH_4Cl (3 × 30 mL), and separated. The combined aqueous layer was extracted with ether (3 × 30 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 93/7) provided **8** as a colorless oil (3.04 g, 72%, keto/enol = 96/4). ^{1}H NMR of **8-keto** ($CDCl_3$) δ 1.32–1.54 (m, 4H), 1.61

(quint, *J* = 7.5 Hz, 2H), 1.77 (t, *J* = 2.4 Hz, 3H), 2.12 (m, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 3.63 (s, 3H), 3.74 (s, 3H) (**8-enol**: 2.21 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H), 5.00 (s, 1H), 12.03 (s, 1H)). ^{13}C NMR of **8-keto** ($CDCl_3$) δ 3.34, 18.43, 22.86, 28.05, 28.61, 42.82, 48.91, 52.24, 75.54, 78.85, 167.61, 202.63. HRMS (EI^+) Calcd for $C_{12}H_{19}O_3$ $[M+H]^+$: *m/z* 211.1334. Found: *m/z* 211.1351.

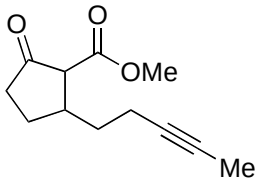
Methyl 2-Diazo-3-oxo-9-undecynoate (9)



9

To a suspension of **8** (2.44 g, 11.6 mmol) and MsN_3 (1.47 g, 12.2 mmol) in MeCN (23 mL) was added Et_3N (3.23 mL, 23.2 mmol) at room temperature under Ar atmosphere. After stirring for 7 h, the reaction mixture was diluted with 1 M NaOH (20 mL), and extracted with EtOAc (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 93/7) to give **9** as a pale yellow oil (2.61 g, 95%): ^{1}H NMR ($CDCl_3$) δ 1.37–1.57 (m, 4H), 1.65 (quint, *J* = 7.5 Hz, 2H), 1.78 (t, *J* = 2.4 Hz, 3H), 2.13 (m, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 3.24, 18.47, 23.67, 28.23, 28.58, 39.91, 52.01, 75.42, 78.97, 161.86, 192.88, 192.90. Anal. Calcd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83; N, 11.86%. Found: C, 61.00; H, 6.76; N 11.75%. HRMS (EI^+) Calcd for $C_{12}H_{16}N_2O_3$ $[M]^+$: *m/z* 236.1161. Found: *m/z* 236.1153.

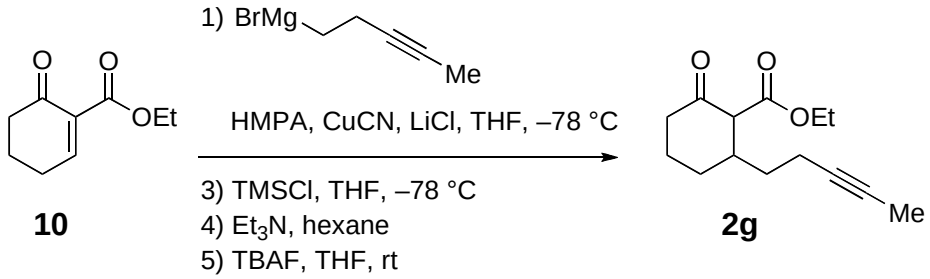
Methyl 2-Oxo-5-(3-pentynyl)cyclopentanecarboxylate (2f) (keto/enol = 97/3)



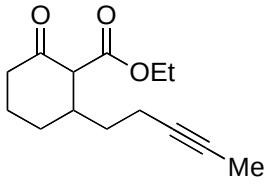
2f

To a suspension of $Rh_2(OAc)_4$ (88.8 mg, 0.201 mmol) in CH_2Cl_2 (33 mL) was added dropwise **9** (1.19 g, 5.03 mmol) in CH_2Cl_2 (33 mL) by a syringe pump (at the rate of 30 mL/h) at room temperature under Ar atmosphere. After stirring for 3.5 h, the mixture was filtered through a suction funnel to recover the catalyst (61.8 mg). The filtrate was concentrated under reduced pressure, and purified by flash chromatography on silica gel (hexanes/EtOAc: 70/30) to afford **2f** as a colorless oil (895 mg, 75%, keto/enol = 97/3). ^{1}H NMR of **2f-keto** ($CDCl_3$) δ 1.41–1.84 (m, 3H), 1.77 (t, *J* = 2.4 Hz, 3H), 2.10–2.50 (m, 5H), 2.64–2.80 (m, 1H), 2.89 (d, *J* = 11.4 Hz, 1H), 3.77 (s, 3H) (**2f-enol**: 3.71 (s, 3H), 10.61 (s, 1H)). ^{13}C NMR of **2f-keto** ($CDCl_3$) δ 3.27, 16.57, 26.88, 33.96, 38.28, 40.44, 52.40, 61.36, 76.24, 77.96, 169.86, 211.78. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H 7.74%. Found: C, 68.87; H, 7.73%. HRMS (EI^+) Calcd for $C_{12}H_{16}O_3$ $[M]^+$: *m/z* 208.1099. Found: *m/z* 208.1086.

Scheme 3. Preparation of 2g[7].



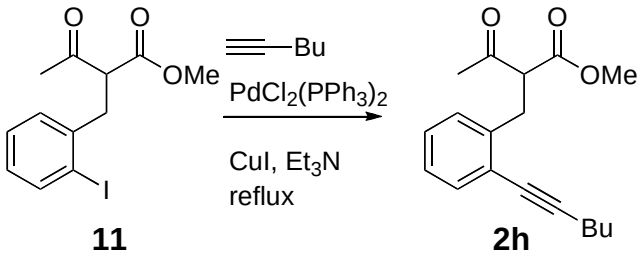
Ethyl 2-Oxo-6-(3-pentynyl)cyclohexanecarboxylate (2g) (keto/enol = 78/22).



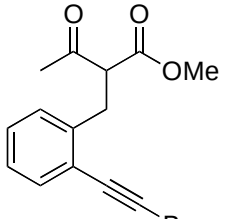
2g

To a 100 mL of two-necked, round-bottomed flask equipped with a condenser and a dropping funnel was added Mg (295 mg, 12.3 mmol), and heated by a heat gun and vigorously stirred for 10 min in *vacuo*. After that, a flask was cooled to rt, and charged with Ar. THF (10 mL) was then added. To this mixture, a solution of 5-bromo-2-pentyne (2.16 mL, 14.8 mmol) in THF (10 mL) was added dropwise over 10 min, and stirred for 20 min. The mixture was cooled to –78 ºC. A dropping funnel was replaced to a septum, CuCN (50.2 mg, 0.50 mmol), LiCl (21.7 mg, 0.50 mmol) and HMPA (3.87 mL, 22.0 mmol) was added to the flask, and the mixture was stirred for 20 min. A solution of **10**[8] (1.54 g, 10.0 mmol) and TMSCl (2.53 mL, 20.0 mmol) in THF (10 mL) was added dropwise over 40 min, and additionally stirred for 3.5 h. Et_3N (10 mL) and hexane (50 mL) were added to the reaction mixture at –78 ºC. The organic layer was washed with water (3 × 20 mL), and separated. The combined aqueous layer was extracted with ether (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was treated with TBAF (12.0 mL of 1.0 M in THF, 12.0 mmol) in THF (30 mL) at room temperature for 9 h, and then purified by flash chromatography on silica gel followed by GPC to afford **2g** as a colorless oil (573 mg, 24%, keto/enol = 78/22). ^{1}H NMR ($CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 0.78H×3H), 1.33 (t, *J* = 7.2 Hz, 0.22×3H), 1.34–1.75 (m, 4H), 1.77 (t, *J* = 2.4 Hz, 0.78×3H), 1.78 (t, *J* = 2.4 Hz, 0.22×3H), 2.07–2.43 (m, 6H), 2.50 (br dt, *J* = 14.1 Hz, 9.3 Hz, 0.78×1H), 2.62 (m, 0.22×1H), 3.13 (dd, *J* = 10.8 Hz, 0.81 Hz, 0.78×1 H), 4.17–4.31 (m, 2H), 12.44 (s, 0.22H×1H). ^{13}C NMR of **2g-keto** ($CDCl_3$) δ 3.10, 13.86, 15.79, 24.31, 28.14, 33.67, 39.89, 40.81, 60.72, 63.18, 75.92, 77.80, 169.58, 205.94. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%. Found: C, 70.87; H, 8.56%. HRMS (EI^+) Calcd for $C_{14}H_{20}O_3$ $[M]^+$: *m/z* 236.1412. Found: *m/z* 236.1406.

Scheme 6. Preparation of 2h.[9]



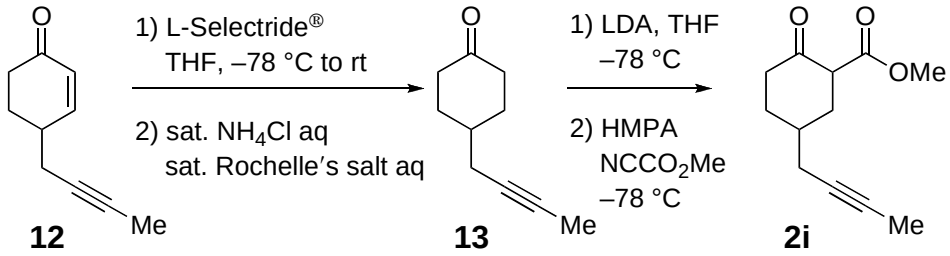
Methyl 2-[2-(1-Hexynyl)benzyl]-3-oxobutanoate (2h) (keto/enol = 98/2)



2h

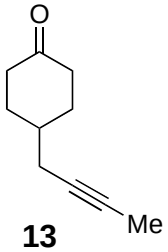
To a solution of methyl 2-(2-iodobenzyl)-3-oxobutanoate (**11**)[9] (1.36 g, 4.08 mmol) and 1-hexyne (0.557 mL, 4.80 mmol) in Et_3N (16 mL) was added $PdCl_2(PPh_3)_2$ (57.7 mg, 0.0797 mmol). The mixture was stirred for 10 min and CuI (7.9 mg, 0.041 mmol) was added. The resulting mixture was then stirred at room temperature under Ar atmosphere for 18 h. The ammonium salt was removed by filtration, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 91/9), followed by GPC to afford **2h** as a pale yellow oil (402 mg, 34%, keto/enol = 98/2). The same product could be prepared from 2-(2-bromobenzyl)-3-oxobutanoate, $PdCl_2(PPh_3)_2$ (5 mol %), CuI (2 mol %) and 1-hexyne (1.5 eq) at 100 ºC for 18 h (31%). ^{1}H NMR of **2h-keto** ($CDCl_3$) δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.40-1.66 (m, 4H), 2.19 (s, 3H), 2.45 (t, *J* = 6.9 Hz, 2H), 3.29 (qd, *J* = 13.5 Hz, 7.5 Hz, 2H), 3.68 (s, 3H), 4.05 (t, *J* = 7.5 Hz, 1H), 7.13–7.19 (m, 3H), 7.37 (m, 1H) (**2h-enol**: 12.97 (s, 1H)). ^{13}C NMR of **2h-keto** ($CDCl_3$) δ 13.37, 19.00, 21.83, 29.43, 30.59, 32.90, 52.13, 59.23, 78.54, 95.15, 123.48, 126.66, 127.70, 129.72, 132.36, 139.61, 169.68, 202.74. Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%. Found: C, 75.51; H, 7.85%. HRMS (EI^+) Calcd for $C_{18}H_{22}O_3$ $[M]^+$: *m/z* 286.1569. Found: *m/z* 286.1557.

Scheme 4. Preparation of 2i.



12 **13** **2i**

4-(2-Butynyl)cyclohexanone (13)

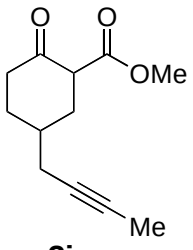


13

To a solution of 4-(2-butynyl)-2-cyclohexenone (**12**)[10] (3.57 g, 24.1 mmol) in Et_2O (96 mL) was added dropwise L-selectride® (25.3 mL of 1.0 M in THF, 25.3 mL) at –78 ºC under Ar atmosphere. After stirring for 1 h at this temperature, the reaction mixture was allowed to warm slowly to room temperature (over 1 h) and stirred for 1 h. The reaction mixture was quenched with sat. NH_4Cl aq and sat. Rochell's salt solution, and stirred for 30 min. The organic layer was washed with sat. Rochell's salt solution (3 × 50 mL), and separated. The combined aqueous layer was extracted with ether (3 × 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 90/10) to afford **13** as a colorless oil (1.36 g, 38%). ^{1}H NMR ($CDCl_3$) δ 1.52 (br dq, *J* = 10.5 Hz, 6.6

Hz, 2H), 1.79 (t, *J* = 2.7 Hz, 3H), 1.93 (m, 1H), 2.08–2.21 (m, 4H), 2.29–2.46 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 3.39, 24.98, 31.92, 35.80, 40.54, 76.89, 77.07, 211.90. HRMS (EI^+) Calcd for $C_{10}H_{14}O$ $[M]^+$: *m/z* 150.1045. Found: *m/z* 150.1043.

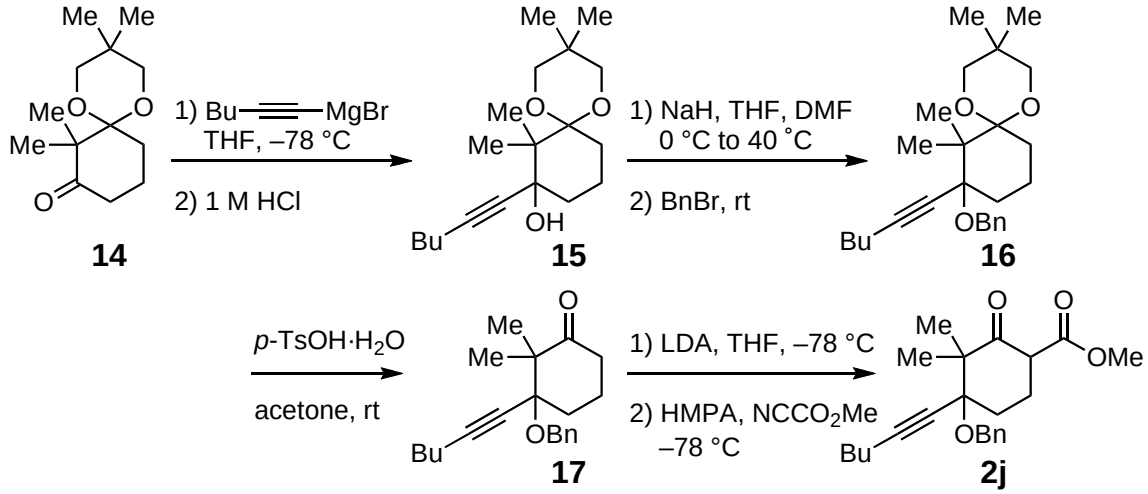
Methyl 5-(2-Butynyl)-2-oxocyclohexanecarboxylate (2i) (keto/enol = 0/100)



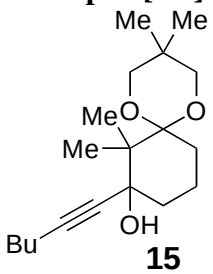
2i

2i was synthesized by the reported method.[11] *n*-Butyl lithium (6.36 ml of 1.65 M in hexane, 10.5 mmol) was added to a stirred solution of diisopropylamine (1.48 mL, 10.5 mmol) in THF (22 ml) at –20 ºC under Ar atmosphere. After 30 min the temperature was lowered to –78 ºC, a solution of **13** (1.31 g, 8.74 mmol) in THF (9 ml) was added through a cannula-tube, and then stirring was continued at 0 ºC for 1 h. The mixture was cooled again to –78 ºC, HMPA (1.55 mL, 8.73 mmol) was added, and methyl cyanoformate (0.840 mL, 10.5 mmol) was added. After stirring for 2 h, the mixture was poured into cold water (20 ml). The organic layer was washed with saturated aqueous NH_4Cl (3 × 20 mL), and separated. The combined aqueous layer was extracted with ether (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 90/10) of the residue gave **2i** as a colorless oil (200 mg, 11%, keto/enol = 0/100). ^{1}H NMR of **2i-enol** ($CDCl_3$) δ 1.42 (m, 1H), 1.70 (m, 1H), 1.80 (t, *J* = 2.7 Hz, 3H), 1.85–1.98 (m, 2H), 2.07–2.26 (m, 2H), 2.31–2.38 (m, 2H), 2.45 (br dd, *J* = 15.3 Hz, 4.8 Hz, 1H), 3.76 (s, 3H), 12.16 (s, 1H). ^{13}C NMR of **2i-enol** ($CDCl_3$) δ 3.49, 25.09, 27.07, 28.24, 28.71, 33.41, 51.39, 76.84, 77.12, 96.73, 171.82, 172.94; Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%. Found: C, 69.27; H, 7.99%. HRMS (EI^+) Calcd for $C_{12}H_{16}O_3$ $[M]^+$: *m/z* 208.1099. Found: *m/z* 208.1089.

Scheme 5. Preparation of 2j.



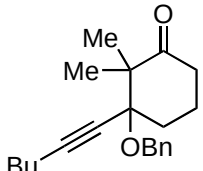
8-(1-Hexynyl)-3,3,7,7-tetramethyl-1,5-dioxaspiro[5.5]undecan-8-ol (15)



15

To a solution of 1-hexyne (16.2 mL, 140 mmol) in THF (40 mL) was added *n*-BuLi (87.0 mL of 1.61 M in hexane, 140 mmol) dropwise at –78 ºC. After stirring for 30 min at this temperature, a solution of 3,3,7,7-tetramethyl-1,5-dioxaspiro[5.5]undecan-8-one (**14**)[12] (15.8 g, 69.9 mmol) and HMPA (12.4 mL, 69.8 mmol) in THF (30 mL) was added dropwise by a cannula-tube over 30 min. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with ether and quenched with saturated aqueous NH_4Cl. The organic layer was washed with saturated aqueous NH_4Cl (3 × 50 mL), and separated. The combined aqueous layer was extracted with ether (3 × 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 90/10) to afford a 17.1 g of mixture of **15** (10.1 g, 32.8 mmol, 47% ^{1}H NMR yield) and unreacted **14** (7.04 g, 31.1 mmol). This mixture was used in the next step without further purification.

3-(Benzyloxy)-3-(1-hexynyl)-2,2-dimethylcyclohexanone (17)



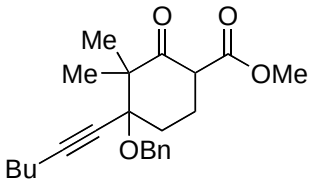
17

To a suspension of NaH (60 wt. %, 469 mg, 11.7 mmol) in DMF (8 mL) was added dropwise a solution of **15** (2.38 mL, 7.72 mmol) in THF (4 mL) and DMF (4 mL) at room temperature. The mixture was stirred at this temperature for 10 min and at 40 ºC for 1 h. The mixture was cooled to room temperature, and then benzyl chloride (1.87 mL, 15.4 mmol) was added. The resulting mixture was stirred for 1 h (monitored by TLC), diluted with ether, and quenched with saturated aqueous NH_4Cl. The organic layer was washed with saturated aqueous NH_4Cl (3 × 15 mL), and separated. The combined aqueous layer was extracted with ether (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexanes/EtOAc: 100/0 to 95/5) afforded **16** as a colorless viscous oil (1.81 g, 59%).

To a solution of **16** (5.29 g, 13.3 mmol) in acetone (130 mL) was added one portion of TsOH· H_2O (3.78 g, 14.8 mmol) at room temperature. After stirring for 9 h, the reaction mixture was concentrated by rotator evaporator to remove a half of acetone, diluted with ether, and quenched with saturated aqueous $NaHCO_3$. The organic layer was washed with saturated aqueous $NaHCO_3$ (3 × 40 mL), and separated. The combined aqueous layer was extracted with ether (3 × 40 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 96/4) to afford **17** as a colorless viscous oil (3.26 g, 79%). ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 3H), 1.31 (s, 3H), 1.34–1.56 (m, 4H), 1.74–1.95 (m, 2H), 2.18 (dd, *J* = 5.1 Hz, 8.4 Hz, 2H), 2.25 (t, *J* = 6.9 Hz, 2H), 2.33 (dt, *J* = 15.0 Hz, 5.1 Hz, 1H), 2.52 (ddd, *J* = 15.0 Hz, 10.5 Hz, 7.2 Hz, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 7.20–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 13.23, 17.96, 18.87, 19.66,

21.59, 23.09, 29.62, 30.47, 36.25, 53.68, 65.13, 77.80, 81.59, 88.59, 126.78, 126.89, 127.99, 139.04, 213.83. Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.37; H, 9.03%. Found: C, 80.74; H, 9.05%. HRMS (EI^+) Calcd for $C_{21}H_{28}O_2$ $[M]^+$: *m/z* 312.2089. Found: *m/z* 312.2089.

Methyl 4-(Benzyloxy)-4-(1-hexynyl)-3,3-dimethyl-2-oxocyclohexanecarboxylate (2j) (keto/enol = 12/88)

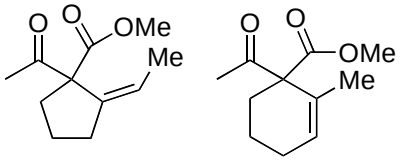


2j

2j was synthesized by the known method.[11] *n*-Butyl lithium (3.90 ml of 1.54M in hexane, 6.01 mmol) was added to a stirred solution of diisopropylamine (0.846 mL, 5.99 mmol) in THF (12.5 ml) at –20 ºC under Ar atmosphere. After 30 min the temperature was lowered to –78 ºC. A solution of **17** (1.58 g, 5.05 mmol) in THF (5 ml) was added through a canula-tube. Stirring was continued at 0 ºC for l h. The mixture was cooled again to –78 ºC, HMPA (0.887 mL, 5.00 mmol) was added, and methyl cyanoformate (0.480 mL, 5.99 mmol) was added. After stirring for 20 min at –78 ºC and for 40 min at room temperature, the mixture was poured into cold water (20 ml). The organic layer was washed with saturated aqueous NH_4Cl (3 × 15 mL), and separated. The combined aqueous layer was extracted with ether (3 × 15 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexanes/EtOAc: 99/1 to 94/6) and PTLC to afford **2j** as a colorless viscous oil (409 mg, 22%, keto/enol = 12/88). ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 0.88×3H), 0.91 (t, *J* = 6.9 Hz, 0.12×3H), 1.27 (s, 0.12×3H), 1.34 (s, 0.88×3H), 1.35 (s, 0.12×3H), 1.39 (s, 0.88×3H), 1.37–1.58 (m, 4H), 1.85–2.19 (m, 2H), 2.19–2.33 (m, 4H), 3.59 (m, 0.12×1H), 3.73 (s, 0.88×3H), 3.74 (s, 0.12×3H), 4.43 (d, *J* = 11.4 Hz, 0.12×1H), 4.49 (d, *J* = 11.4 Hz, 0.88×1H), 4.72 (d, *J* = 11.7 Hz, 0.12×1H), 4.84 (d, *J* = 11.4 Hz, 0.88×1H), 7.18–7.42 (m, 5H), 12.49 (s, 1H). ^{13}C NMR of **2j-enol** ($CDCl_3$) δ 13.40, 18.18, 19.18, 20.44, 21.77, 24.95, 27.24, 30.68, 44.51, 51.38, 65.75, 78.28, 78.52, 88.26, 94.63, 127.07, 127.13, 128.19, 139.67, 173.40, 176.49. Anal. Calcd for $C_{23}H_{30}O_4$: C, 74.56; H, 8.16%. Found: C, 74.55; H, 8.17%. HRMS (EI^+) Calcd for $C_{23}H_{30}O_4$ $[M]^+$: *m/z* 370.2144. Found: *m/z* 370.2154.

Cyclization Products.

Mixture of (*Z*)-Methyl 1-Acetyl-2-ethylidenecyclopentanecarboxylate (3a) and Methyl 1-Acetyl-2-methyl-2-cyclohexenecarboxylate (4a) (3a/4a = 80/20)

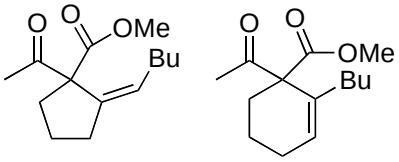


3a **4a**

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.54–1.64 (m, 0.20×3H), 1.60 (dt, *J* = 7.5 Hz, 1.8 Hz, 0.80×3H), 1.66–1.79 (m, 0.80×2H, 0.20×2H), 1.94 (m, 0.20×1H), 2.03–2.15 (m, 0.20×2H), 2.09 (dt, *J* = 13.2 Hz, 7.5 Hz, 0.80×1H), 2.19 (s, 0.20×3H), 2.23 (s, 0.80×3H), 2.34 (m, 0.20×1H), 2.40–2.55 (m, 0.80×3H), 3.75 (s, 0.80×3H), 3.78 (s, 0.20×3H), 5.71 (qt, *J* = 7.2 Hz, 2.1 Hz, 0.80×1H), 5.78 (m, 0.20×1H). ^{13}C NMR ($CDCl_3$) δ 15.28 (0.80×1C), 18.43 (0.20×1C), 21.55 (0.20×1C), 24.38 (0.80×1C), 24.90 (0.20×1C), 26.19 (0.80×1C), 26.49 (0.20×1C), 29.71 (0.20×1C), 35.03 (0.80 ×1C), 37.03 (0.80×1C), 52.11 (0.20×1C), 52.27 (0.80×1C), 65.45 (0.20×1C), 69.08 (0.80×1C), 123.03 (0.80×1C), 128.37

(0.20×1C), 129.62 (0.20×1C), 140.03 (0.80×1C), 172.40 (0.80×1C), 172.53 (0.20×1C), 205.24 (0.80×1C), 206.58 (0.20×1C). HRMS (EI$^+$) Calcd for $C_{11}H_{16}O_3$ [M]$^+$: *m/z* 196.1099. Found: *m/z* 196.1104.

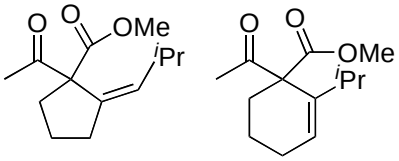
Mixture of (*Z*)-Methyl 1-Acetyl-2-pentylidenecyclopentanecarboxylate (3b) and Methyl 1-Acetyl-2-butyl-2-cyclohexenecarboxylate (4b) (3b/4b = 91/9)



3b **4b**

Colorless oil. ^{1}H NMR of **3b** ($CDCl_3$) δ 0.85–0.93 (m, 3H), 1.26–1.36 (m, 4H), 1.66–1.77 (m, 2H), 1.82–2.13 (m, 3H), 2.23 (s, 3H), 2.41–2.54 (m, 3H), 3.74 (s, 3H), 5.61 (br t, *J* = 7.5 Hz, 1H) (**4b**: 2.18 (s, 3H), 3.75 (s, 3H), 5.791 (m, 1H)). ^{13}C NMR of **3b** ($CDCl_3$) δ 13.83, 22.36, 24.35, 26.23, 29.72, 31.19, 35.06, 37.15, 52.28, 69.11, 129.04, 138.54, 172.46, 205.28. HRMS (EI$^+$) Calcd for $C_{14}H_{22}O_3$ [M]$^+$: *m/z* 238.1569. Found: *m/z* 238.1568.

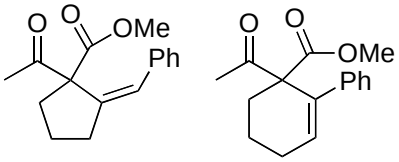
Mixture of (*Z*)-Methyl 1-Acetyl-2-(2-methylpropylidene)cyclopentanecarboxylate (3c) and Methyl 1-Acetyl-2-isopropyl-2-cyclohexenecarboxylate (4c) (3c/4c = 92/8)



3c **4c**

Colorless oil. ^{1}H NMR of **3c** ($CDCl_3$) δ 0.90 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 1.66–1.79 (m, 2H), 2.05 (dt, *J* = 12.9 Hz, 7.5 Hz, 1H), 2.25 (s, 3H), 2.33 (m, 1H), 2.39–2.54 (m, 3H), 3.75 (s, 3H), 5.36 (dt, *J* = 1.8 Hz, 10.8 Hz, 1H) (**4c**: 1.00 (d, *J* = 6.6 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 2.21 (s, 3H), 3.76 (s, 3H), 5.87 (t, *J* = 3.9 Hz, 1H)). ^{13}C NMR of **3c** ($CDCl_3$) δ 21.85, 22.12, 24.39, 26.42, 29.24, 35.18, 37.45, 52.43, 68.98, 135.86, 135.89, 172.73, 205.32. HRMS (EI$^+$) Calcd for $C_{13}H_{20}O_3$ [M]$^+$: *m/z* 224.1412. Found: *m/z* 224.1406.

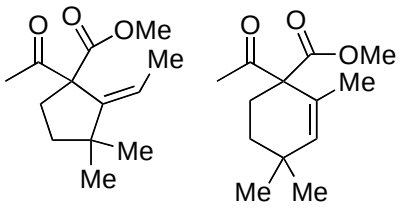
Mixture of (*Z*)-Methyl 1-Acetyl-2-benzylidenecyclopentanecarboxylate (3d) and Methyl 1-Acetyl-2-phenyl-2-cyclohexenecarboxylate (4d) (3d/4d = 45/55)



3d **4d**

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.60–1.88 (m, 2H), 2.02 (s, 0.45×3H), 2.04 (s, 0.55×3H), 2.14–2.53 (m, 4H), 3.43 (s, 0.45×3H), 3.61 (s, 0.55×3H), 6.13 (t, *J* = 3.9 Hz, 0.55×1H), 6.73 (br s, 0.45 ×1H), 7.14–7.28 (m, 5H). All the signal observed were shown; ^{13}C NMR ($CDCl_3$) δ 17.97, 22.96, 25.18, 26.68, 27.27, 30.75, 35.29, 38.30, 52.17 (×2C), 66.33, 70.08, 126.98, 127.05, 127.14, 127.94, 128.00, 128.12, 128.49, 131.05, 135.99, 136.68, 141.16, 142.24, 171.97, 172.78, 205.29, 206.23. HRMS (EI$^+$) Calcd for $C_{16}H_{18}O_3$ [M]$^+$: *m/z* 258.1256. Found: *m/z* 258.1256.

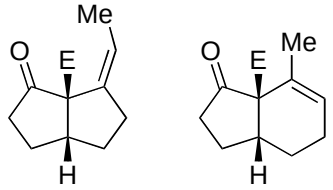
Mixture of (*Z*)-Methyl 1-Acetyl-2-ethylidene-3,3-dimethylcyclopentanecarboxylate (3e) and Methyl 1-Acetyl-2,4,4-trimethyl-2-cyclohexenecarboxylate (4e) (3e/4e = 23/77)



3e **4e**

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 0.77×3H), 0.99 (s, 0.77×3H), 1.08 (s, 0.23×3H), 1.11 (s, 0.23×3H), 1.36–1.42 (m, 0.77×2H), 1.51–1.68 (m, 0.23×2H), 1.61 (d, *J* = 7.5 Hz, 0.23×3H), 1.73 (d, *J* = 1.5 Hz, 0.77×3H), 2.00 (m, 0.77×1H), 2.08 (m, 0.23×1H), 2.19 (s, 0.77×3H), 2.22 (s, 0.23×3H), 2.32 (m, 0.77×1H), 2.45 (sextet, *J* = 6.3 Hz, 0.23×1H), 3.74 (s, 0.23×3H), 3.76 (s, 0.77×3H), 5.49 (distorted q, *J* = 1.5 Hz, 0.77×1H), 5.49 (q, *J* = 7.2 Hz, 0.23×1H). ^{13}C NMR ($CDCl_3$) δ 15.27 (0.23×1C), 21.50 (0.77×1C), 25.99 (0.23×1C), 26.50 (0.77×1C), 27.08 (0.77×1C), 28.74 (0.77×1C), 29.49 (0.23×1C), 29.52 (0.77×1C), 29.60 (0.23×1C), 31.89 (0.77×1C), 32.82 (0.23×1C), 33.06 (0.77×1C), 39.76 (0.23×1C), 43.76 (0.77×1C), 52.15 (0.77×1C), 52.29 (0.23×1C), 65.58 (0.77×1C), 70.71 (0.23×1C), 121.87 (0.23×1C), 127.16 (0.77×1C), 138.85 (0.77×1C), 148.70 (0.23×1C), 172.48 (0.77×1C), 172.61 (0.23×1C), 205.5 (0.23×1C), 206.49 (0.77×1C). HRMS (EI$^+$) Calcd for $C_{13}H_{20}O_3$ [M]$^+$: *m/z* 224.1412. Found: *m/z* 224.1415.

Mixture of (*Z*)-Methyl 3-Ethylidene-4-oxooctahydropentalene-3a-carboxylate (3f) and Methyl 4-Methyl-3-oxo-2,3,3a,6,7,7a-hexahydro-1H-indene-3a-carboxylate (4f) (3f/4f = 49/51)

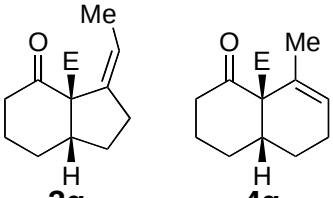


3f **4f**

E = CO_2Me

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.52 (m, 1H), 1.63–2.20 (m, 7H), 2.39–2.58 (m, 3H), 2.77 (m, 0.51×1H), 3.05 (quint, *J* = 6.6 Hz, 0.49 × 1H), 3.73 (s, 3H), 5.71 (qt, *J* = 7.2 Hz, 1.8 Hz, 0.49×1H), 5.76 (m, 0.51×1H). All the signal observed were shown; ^{13}C NMR ($CDCl_3$) δ 15.50, 20.07, 21.71, 21.91, 23.33, 23.74, 29.85, 33.71, 36.67, 37.61, 41.50, 51.44, 52.44, 64.22, 68.14, 123.75, 127.10, 127.80, 138.37, 172.48, 172.52, 212.71, 213.00. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%. Found: C, 69.02; H, 7.69%. HRMS (EI$^+$) Calcd for $C_{12}H_{16}O_3$ [M]$^+$: *m/z* 208.1099. Found: *m/z* 208.1103.

Mixture of (*Z*)-Ethyl 3-Ethylidene-4-oxooctahydro-1H-indene-3a-carboxylate (3g) and Ethyl 5-Methyl-4-oxo-1,2,3,4,4a,7,8,8a-octahydronaphthalene-4a-carboxylate (4g) (3g/4g = 67/33)



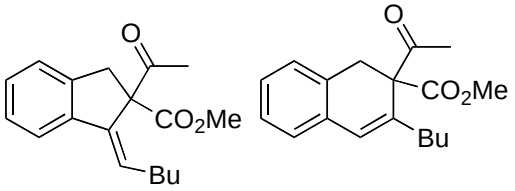
3g **4g**

E = CO_2Et

Colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 0.67×3H), 1.29 (t, *J* = 7.2 Hz, 0.33×3H), 1.37–2.78 (m, 13H, 0.33×1H), 3.01 (quint, *J* = 6.6 Hz, 0.67×1H), 4.15–4.33 (m, 2H), 5.69 (aprox. qt, *J* = 7.2 Hz, 2.1 Hz, 0.67×1H), 5.71 (m, 0.33×1H). All the signal observed were shown; ^{13}C NMR of **3g**

($CDCl_3$) δ 13.94, 13.96, 14.15, 21.28, 23.31, 23.45, 23.80, 24.18, 25.76, 27.07, 28.27, 31.63, 40.05, 40.23, 40.33, 50.50, 61.16, 61.32, 66.59, 69.90, 123.26, 126.09, 129.52, 139.39, 172.38, 172.40, 207.89, 208.98. Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%. Found: C, 69.78; H, 8.44%. HRMS (EI^+) Calcd for $C_{14}H_{20}O_3$ $[M]^+$: *m/z* 238.1569. Found: *m/z* 236.1409.

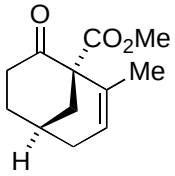
Mixture of (*Z*)-Methyl 2-Acetyl-1-pentylidene-2,3-dihydro-1H-indene-2-carboxylate (3h) and Methyl 2-Acetyl-3-butyl-1,2-dihydronaphthalene-2-carboxylate (4h) (3h/4h = 63/37)



3h **4h**

Colorless oil. ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 0.63×3H), 0.97 (t, *J* = 7.5 Hz, 0.37×3H), 1.31–1.51 (m, 3H), 1.55–1.66 (m, 1H), 2.07–2.33 (m, 2H), 2.19 (s, 0.37×3H), 2.21 (s, 0.63×3H), 3.41 (td, *J* = 19.5 Hz, 15.9 Hz, 0.63×2H), 3.73 (t, *J* = 16.3 Hz, 0.37×2H), 3.74 (s, 0.37×3H), 3.75 (s, 0.37×3H), 6.29 (t, *J* = 7.8 Hz, 0.63×1H), 6.48 (m, 0.37×1H), 7.01–7.45 (m, 4H). All the signal observed were shown; ^{13}C NMR of **3h** ($CDCl_3$) δ 13.89, 22.49, 25.69, 27.93, 29.47, 29.80, 31.33, 33.25, 35.67, 39.94, 52.45, 52.59, 64.95, 69.44, 120.19, 124.90, 125.55, 126.02, 127.13, 127.28, 127.32, 127.37, 127.79, 128.22, 131.66, 132.91, 137.72, 138.15, 140.43, 140.62, 171.72, 172.32, 203.81, 205.25. HRMS (EI^+) Calcd for $C_{18}H_{22}O_3$ $[M]^+$: *m/z* 286.1569. Found: *m/z* 286.1564.

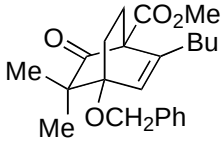
Methyl 2-Methyl-8-oxo-2-bicyclo[3.3.1]nonene-1-carboxylate (4i)



4i

Colorless oil. ^1H NMR ($CDCl_3$) δ 1.77 (m, 3H), 1.87 (m, 1H), 2.00–2.20 (m, 3H), 2.24–2.37 (m, 3H), 2.51–2.72 (m, 2H), 2.75 (s, 3H), 5.81 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 19.86, 24.69, 31.49, 31.74, 34.12, 35.93, 51.96, 61.77, 129.72, 132.17, 171.82, 205.13. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%. Found: C, 69.27; H, 7.99%. HRMS (EI^+) Calcd for $C_{12}H_{16}O_3$ $[M]^+$: *m/z* 208.1099. Found: *m/z* 208.1090.

Methyl 4-(Benzyloxy)-2-butyl-5,5-dimethyl-6-oxo-2-bicyclo[2.2.2]octene-1-carboxylate (4j)



4j

Colorless oil. ^1H NMR ($CDCl_3$) δ 0.89 (br t, *J* = 6.9 Hz, 3H), 1.17 (s, 3H), 1.18 (s, 3H), 1.23–1.40 (m, 4H), 1.80–1.95 (m, 2H), 1.95–2.10 (m, 2H), 2.17–2.36 (m, 2H), 3.83 (s, 3H), 4.67 (q, *J* = 11.7 Hz, 2H), 6.29 (br s, 1H), 7.24–7.43 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 13.76, 20.81, 22.29, 23.83, 24.27, 24.77, 29.76, 32.01, 49.17, 52.01, 63.03, 65.06, 81.44, 126.62, 127.32, 128.39, 131.84, 136.69, 139.48, 170.46, 209.63. HRMS (EI^+) Calcd for $C_{23}H_{30}O_4$ $[M]^+$ *m/z* 370.2144. Found *m/z* 370.2140.

Reference

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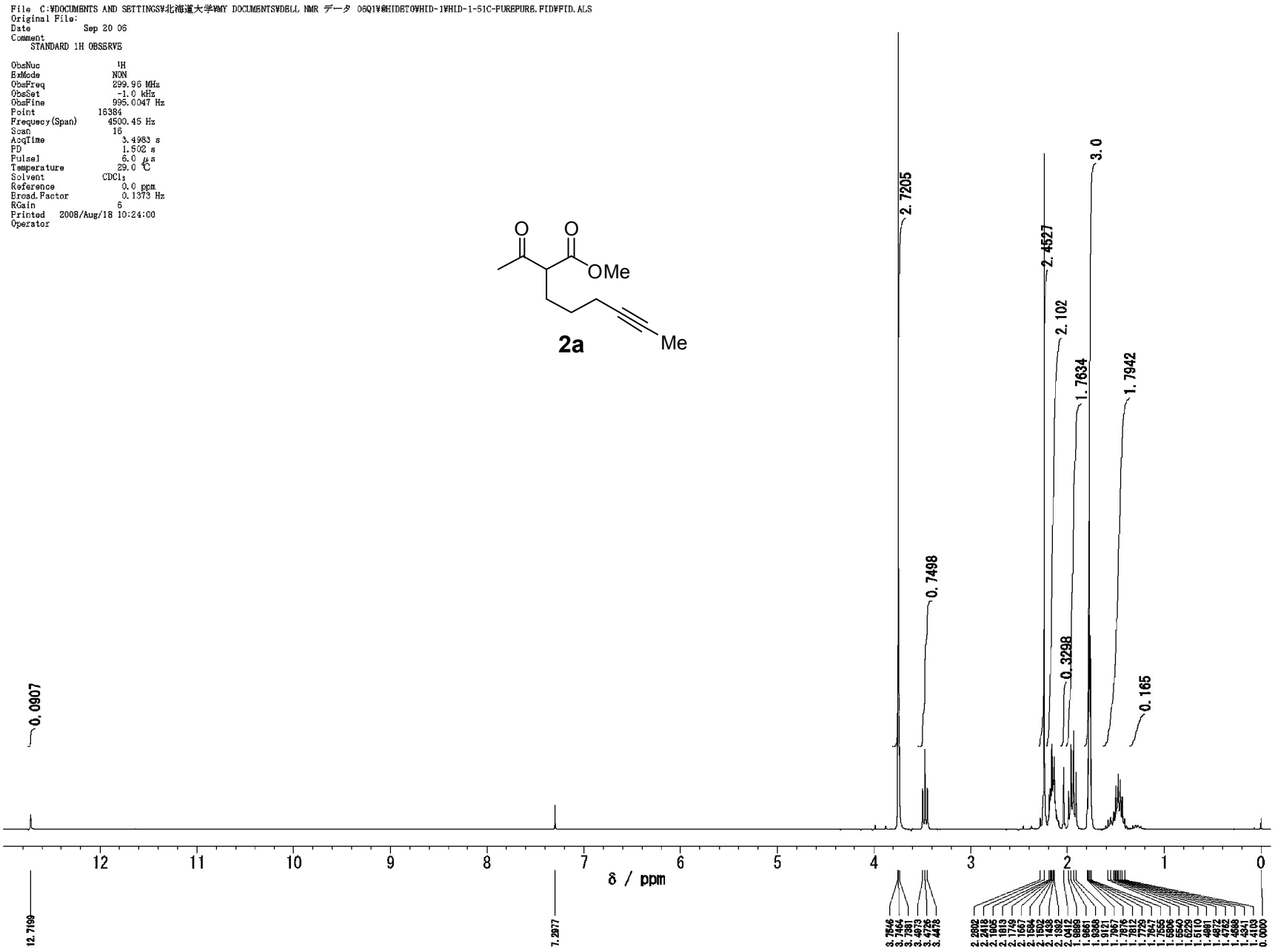
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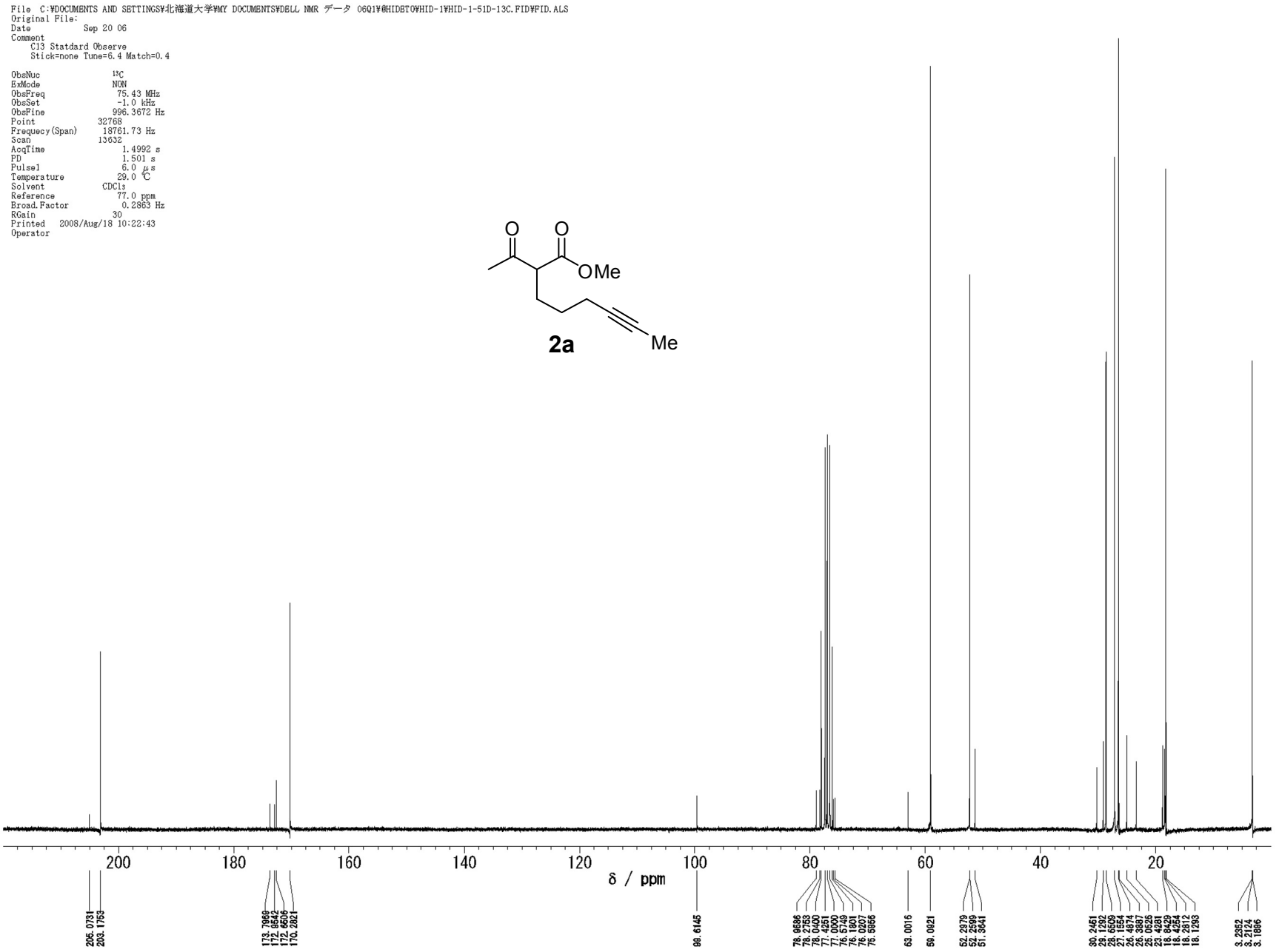
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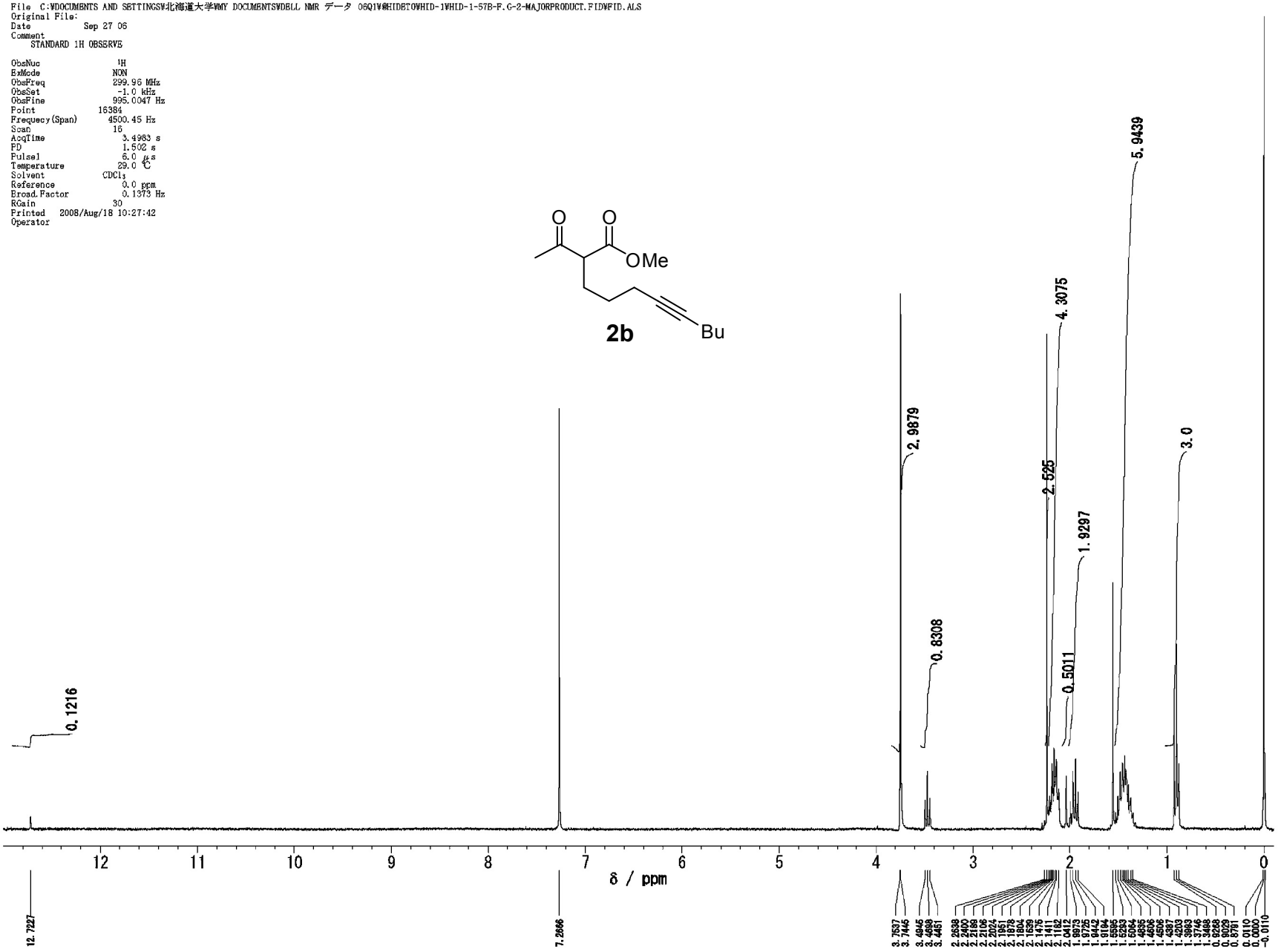
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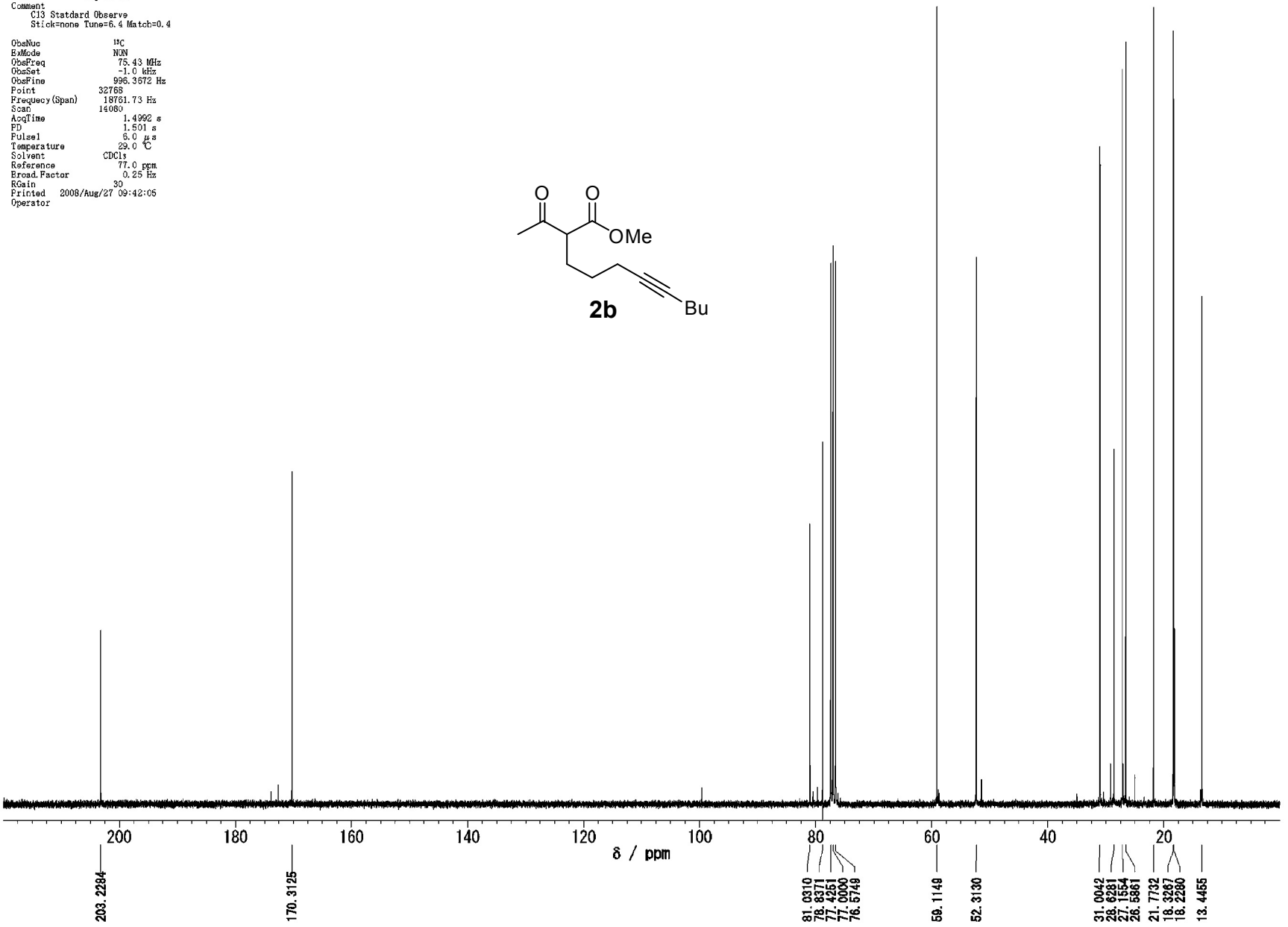
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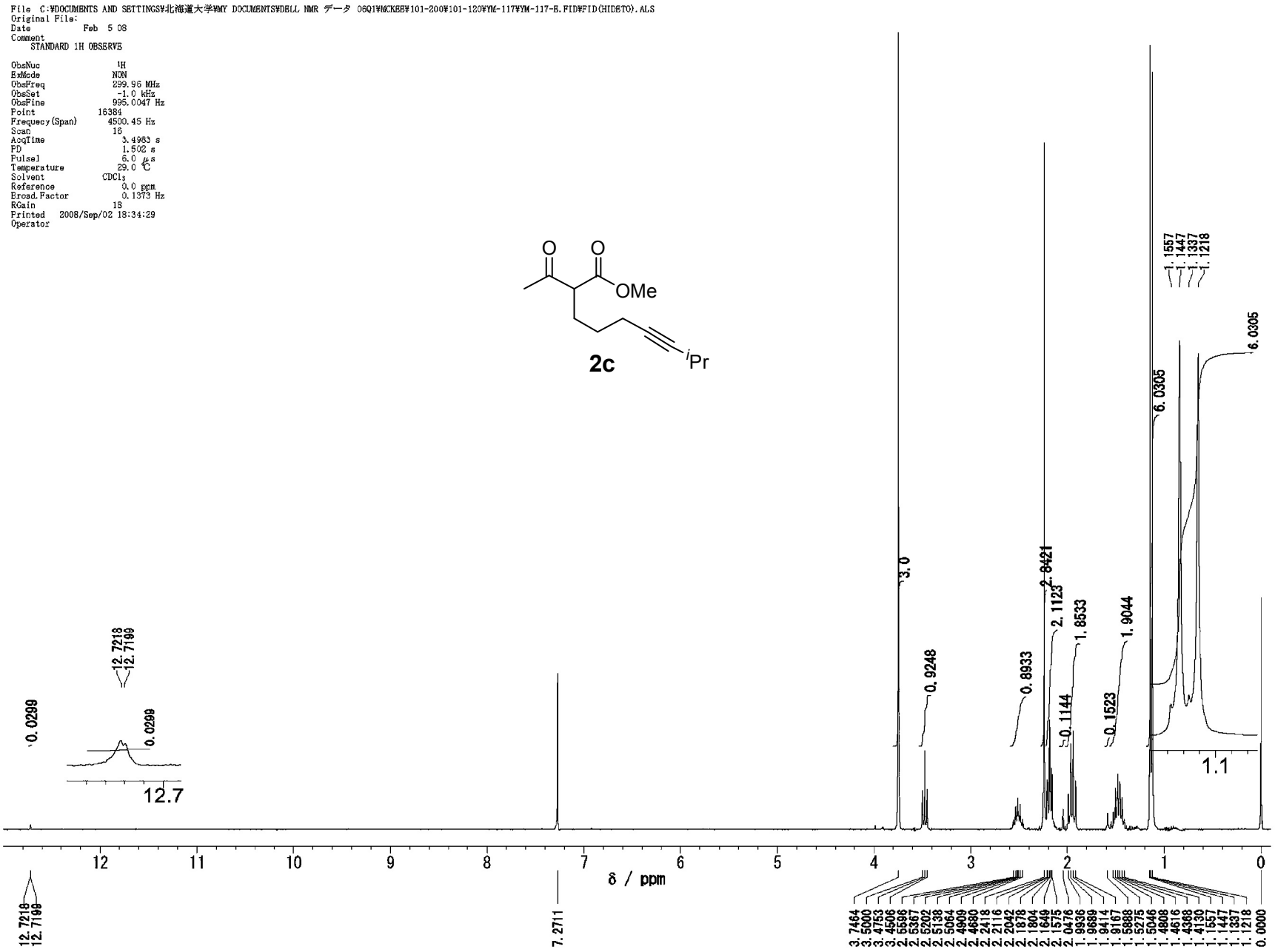
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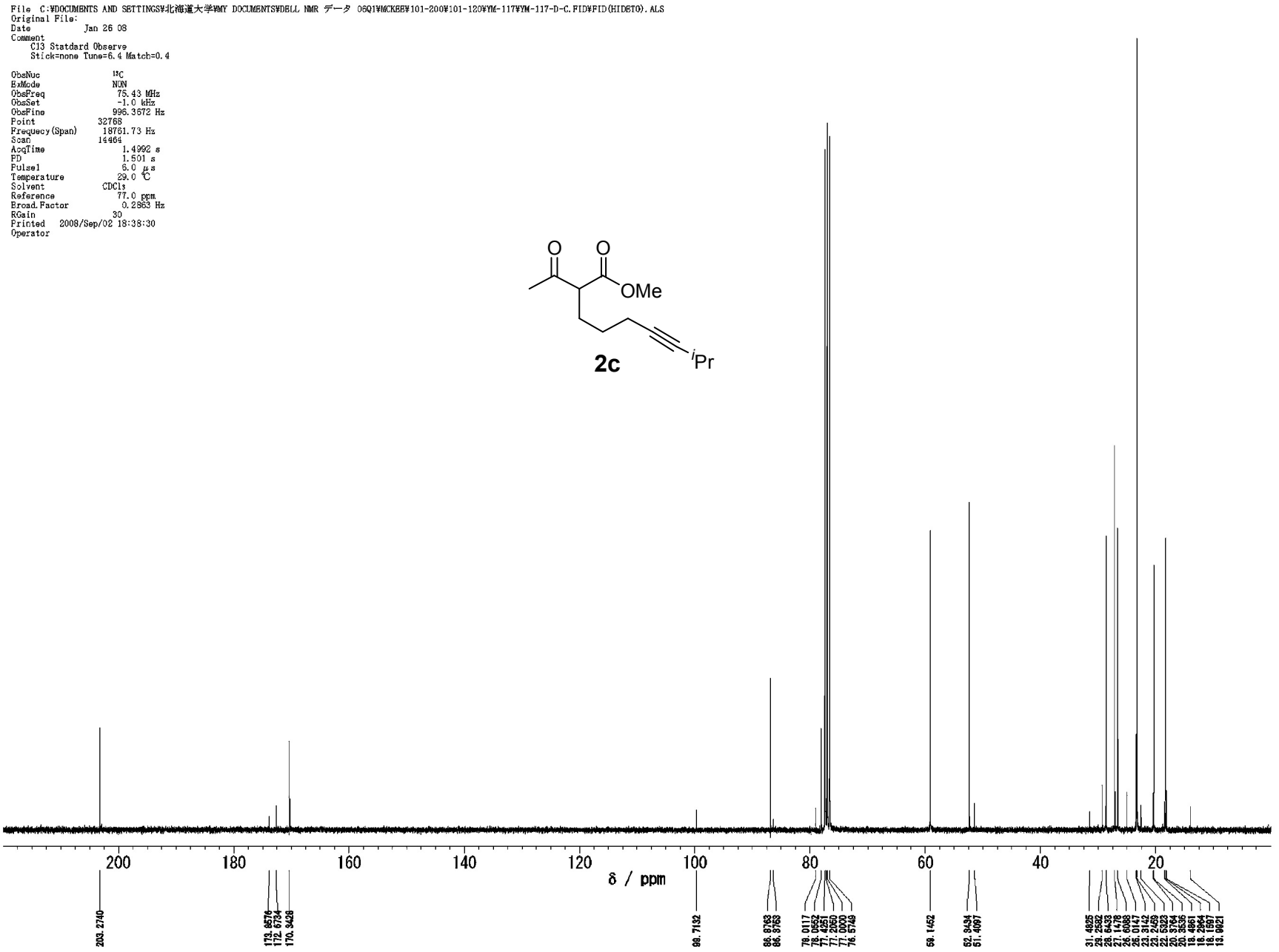
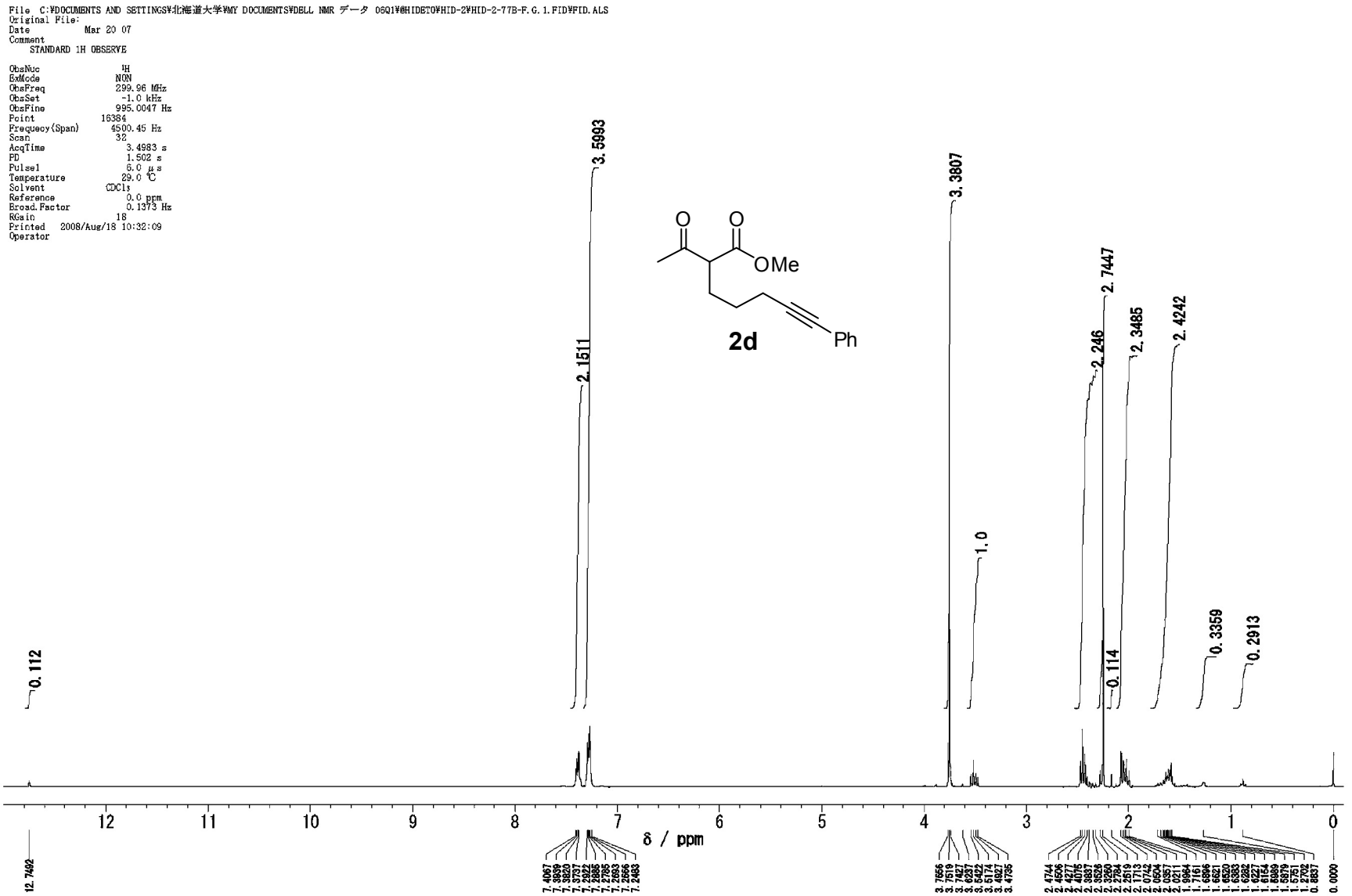

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥MCKEE¥101-200¥101-120¥YM-117¥YM-117-D-C.FID¥FID(HIDETO).ALS
Original File:
Date Jan 26 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 14464
AcqTime 1.4992 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Sep/02 18:38:30
Operator
O
O
OMe
2c
iPr
200
180
160
140
120
100
80
60
40
20
δ / ppm
203.2740
173.8576
172.6734
170.3428
98.7132
86.8763
86.5763
78.0117
78.0552
77.4251
77.2960
77.0000
76.5749
60.1452
52.3434
51.4097
31.4925
29.2592
28.6433
27.1478
26.6088
26.0147
23.3142
23.2469
22.5323
20.3764
20.3515
18.4961
18.2964
18.1597
13.9021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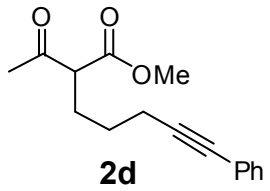
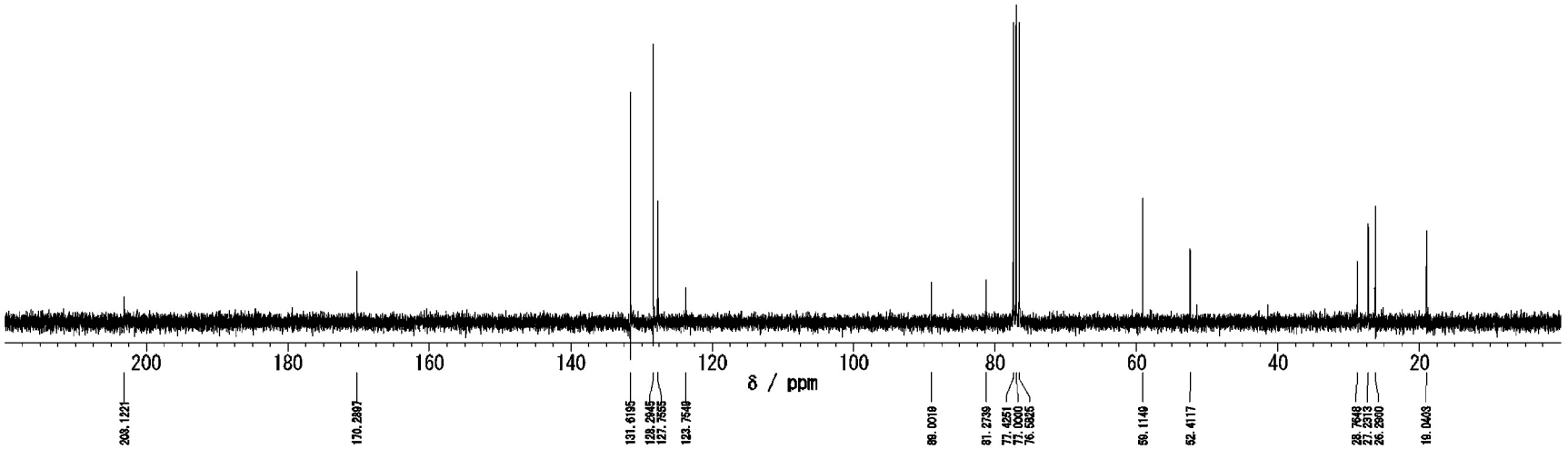
Original File:
Date Mar 20 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2008/Aug/18 10:32:09
Operator
O
O
OMe
Ph
2d
3.5993
3.3807
2.7447
2.4242
2.3485
2.2460
2.1511
1.0
0.3359
0.2913
0.1144
0.1120
δ / ppm
12
11
10
9
8
7
6
5
4
3
2
1
0

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥@HIDETO¥HID-2¥HID-2-77C-13C.FID¥FID.ALS
Original File:
Date Mar 20 07
Comment
C13 Statdard Observe
Stick=none Tune=5.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	320
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2008/Aug/18 10:48:46
Operator	

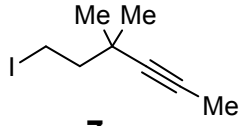


2d



File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥卓HIDETO¥HID-4¥HID-4-97A-FR1-1H.FID¥FID.ALS
Original File:
Date Mar 7 08
Comment
STANDARD 1H OBSERVE

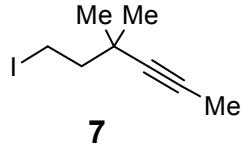
ObsNuc	1H
ExMode	NON
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsFine	995.0047 Hz
Point	16384
Frequecy(Span)	4500.45 Hz
Scan	32
AcqTime	3.4983 s
PD	1.502 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	$CDCl_3$
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	11
Printed	2008/Aug/18 10:58:56
Operator	



7

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-4¥HID-4-97B-FR1-13C.FID¥FID.ALS
Original File:
Date Mar 8 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	256
AcqTime	1.4992 s
PD	1.501 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2008/Aug/18 11:01:40
Operator	



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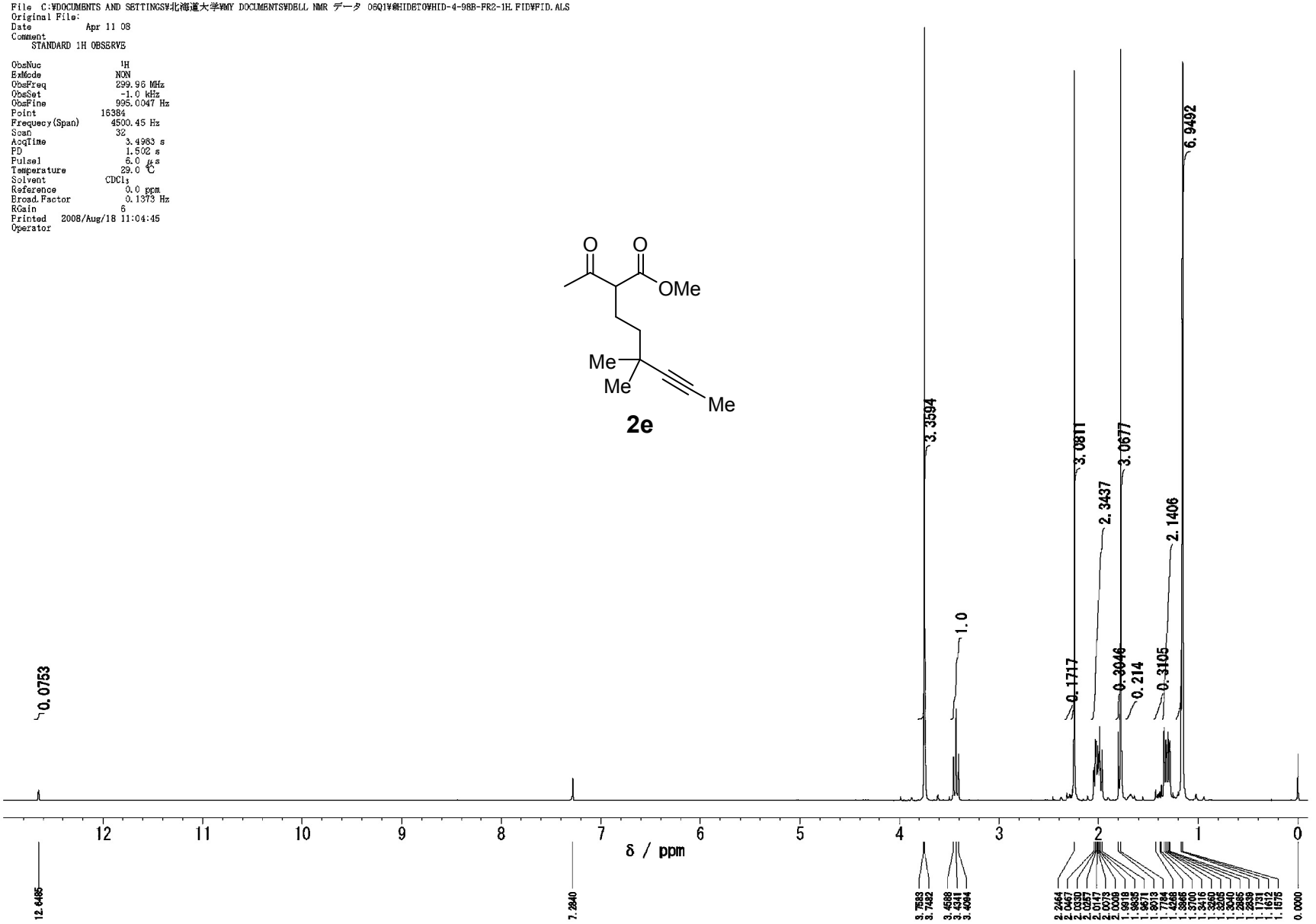
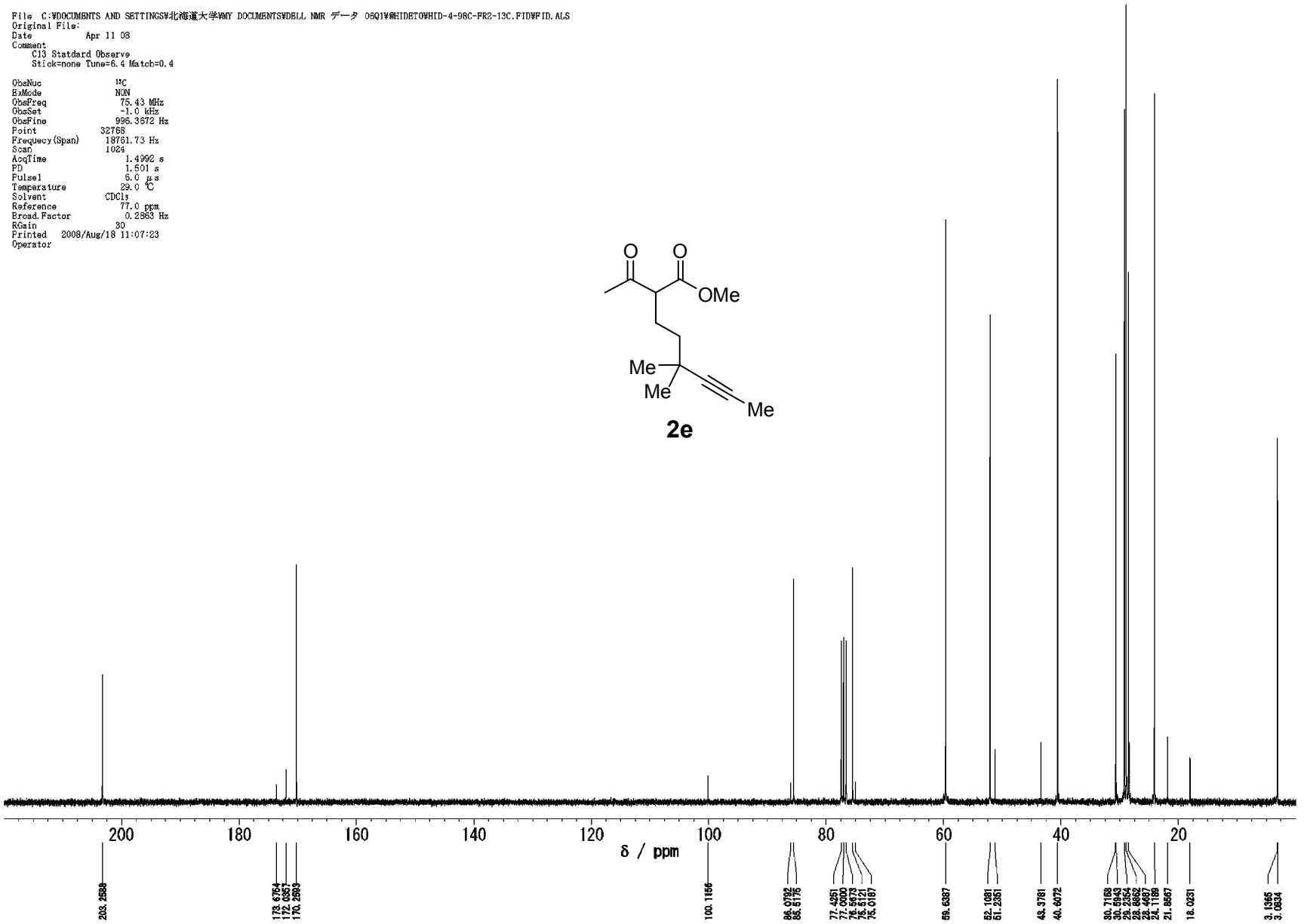
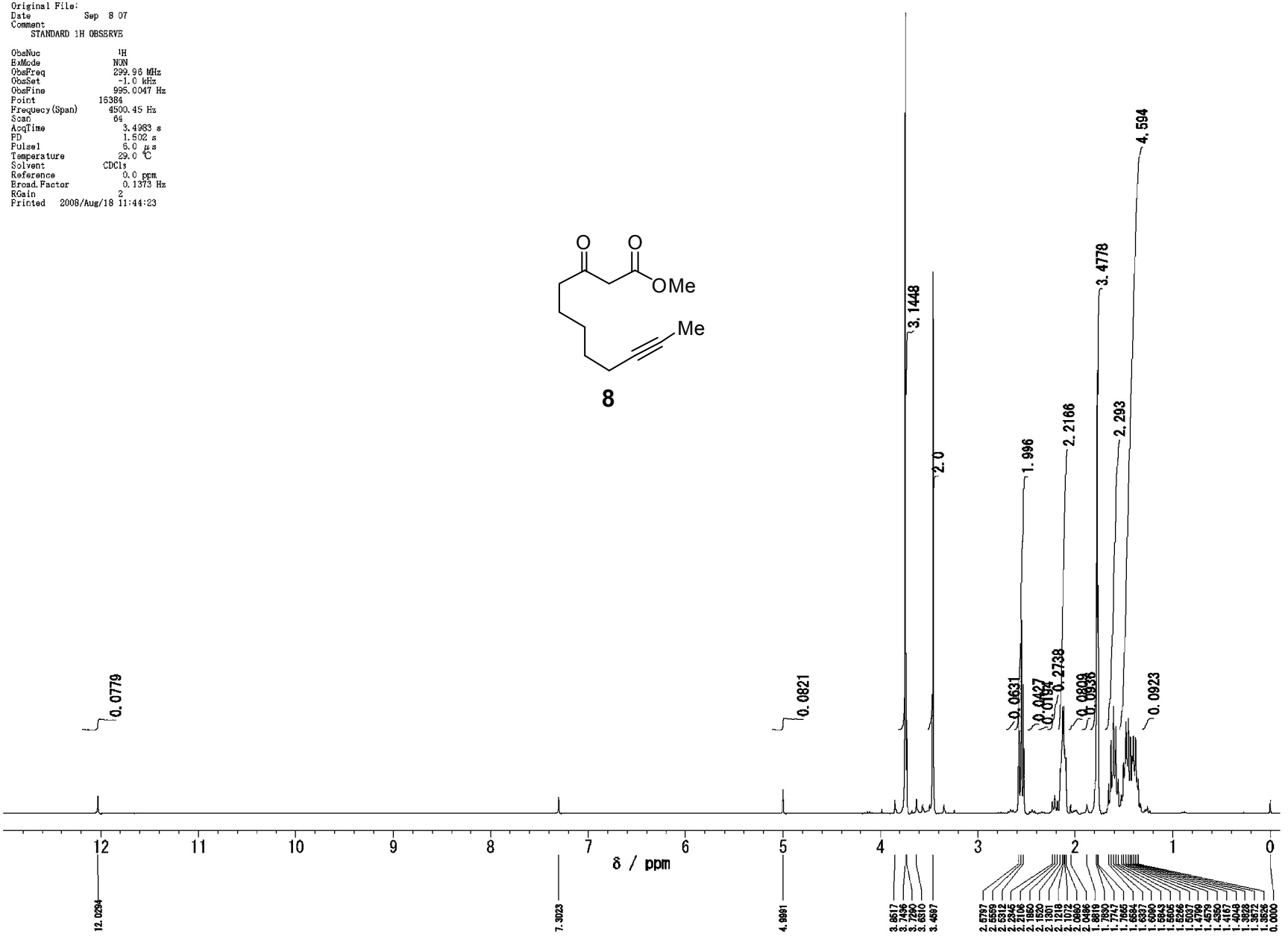
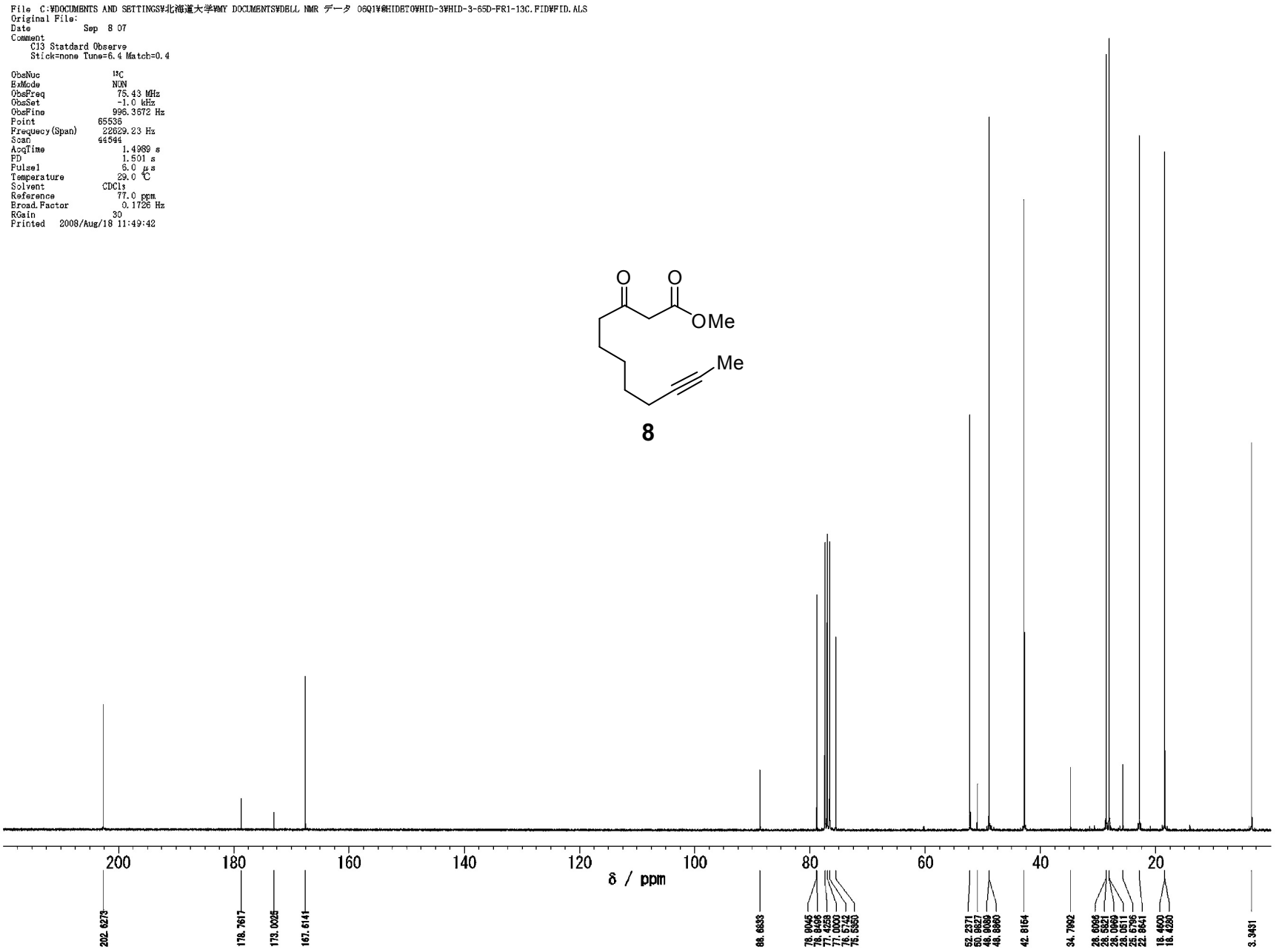

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥森HIDETO¥HID-4-96B-FR2-1H.FID¥FID.ALS
Original File:
Date Apr 11 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/18 11:04:45
Operator
O
O
OMe
Me
Me
Me
2e
0.0753
3.3594
1.0
0.1717
3.0811
0.3046
2.3437
3.0677
0.214
0.3105
2.1406
6.9492
δ / ppm
12.6485
7.2840
3.7583
3.7482
3.4588
3.4341
3.4094
2.2464
2.0467
2.0357
2.0147
2.0073
2.0009
1.9818
1.9835
1.9671
1.9513
1.4744
1.4588
1.3946
1.3700
1.3416
1.3205
1.3040
1.2885
1.2539
1.2371
1.1617
1.1575
0.0000


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-4-96C-FR2-13C.FID¥FID.ALS
Original File:
Date Apr 11 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 1024
AcqTime 1.4992 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 11:07:23
Operator
O
O
OMe
Me
Me
Me
2e
200
180
160
140
120
100
80
60
40
20
δ / ppm
203.2588
173.6764
172.0357
170.2893
100.1156
86.0792
85.5175
77.4251
77.0000
76.5673
75.5121
75.0187
59.6387
52.1081
51.2351
43.3781
40.6072
30.7168
30.5943
29.2354
28.8862
28.4467
24.1188
21.8567
18.0231
3.1365
3.0834

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-65B-FR1-1H.FID
¥FID.ALS
Original File:
Date Sep 8 07
Comment
STANDARD 1H OBSERVE

ObsNuc	1H
ExMode	NON
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsFine	995.0047 Hz
Point	16384
Frequecy(Span)	4500.45 Hz
Scan	64
AcqTime	3.4983 s
PD	1.502 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	2
Printed	2008/Aug/18 11:44:23

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Original File:
Date Sep 8 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 65536
Frequecy(Span) 22629.23 Hz
Scan 44594
AcqTime 1.4989 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.1726 Hz
RGain 30
Printed 2008/Aug/18 11:49:42
O
O
OMe
Me
8
200
180
160
140
120
100
80
60
40
20
δ / ppm
202.6273
178.7617
173.0025
167.6141
88.6633
78.9045
78.8496
77.4258
77.0000
76.5742
75.5350
52.2371
50.9827
48.9080
48.8860
42.8164
34.7992
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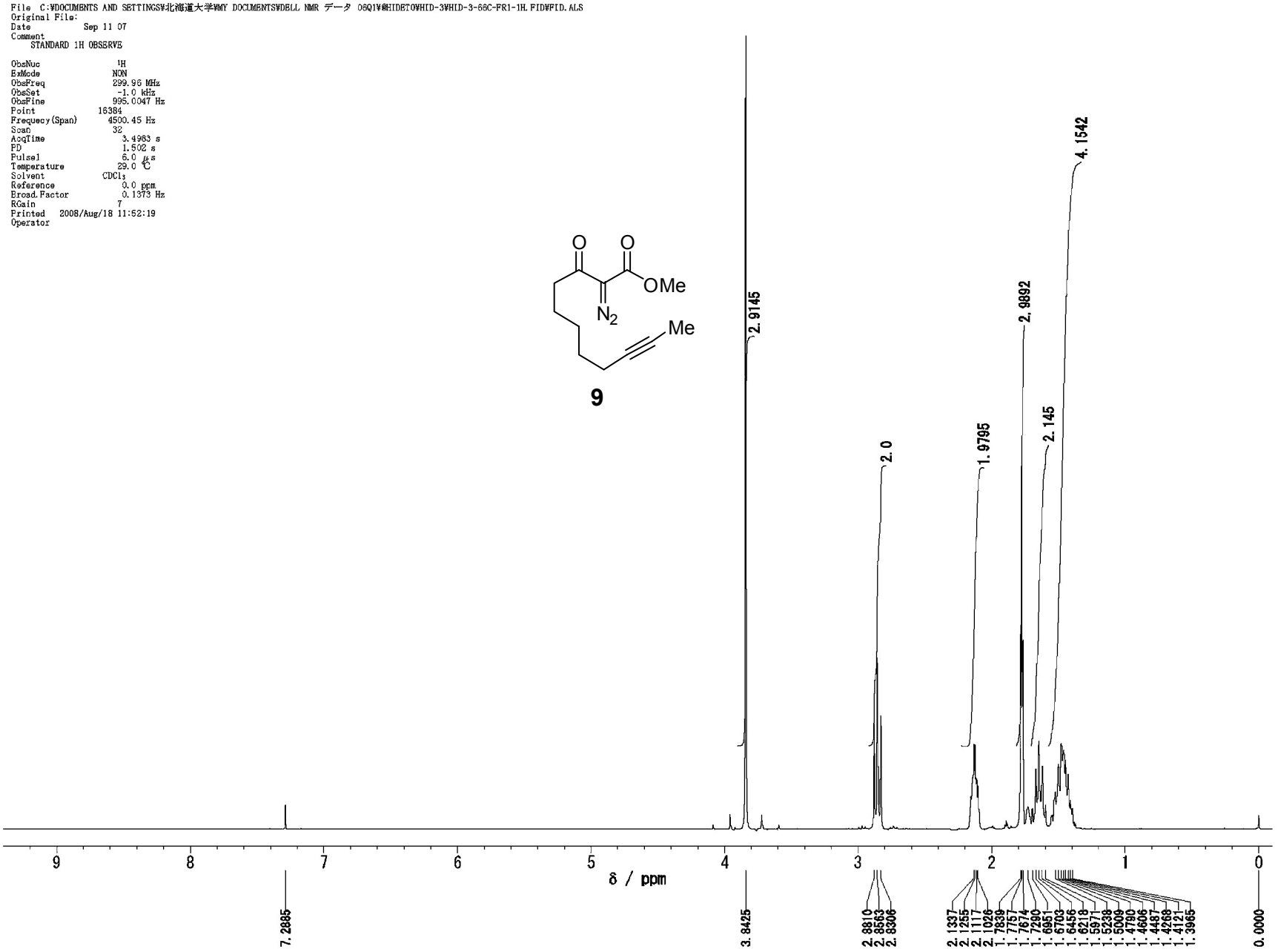
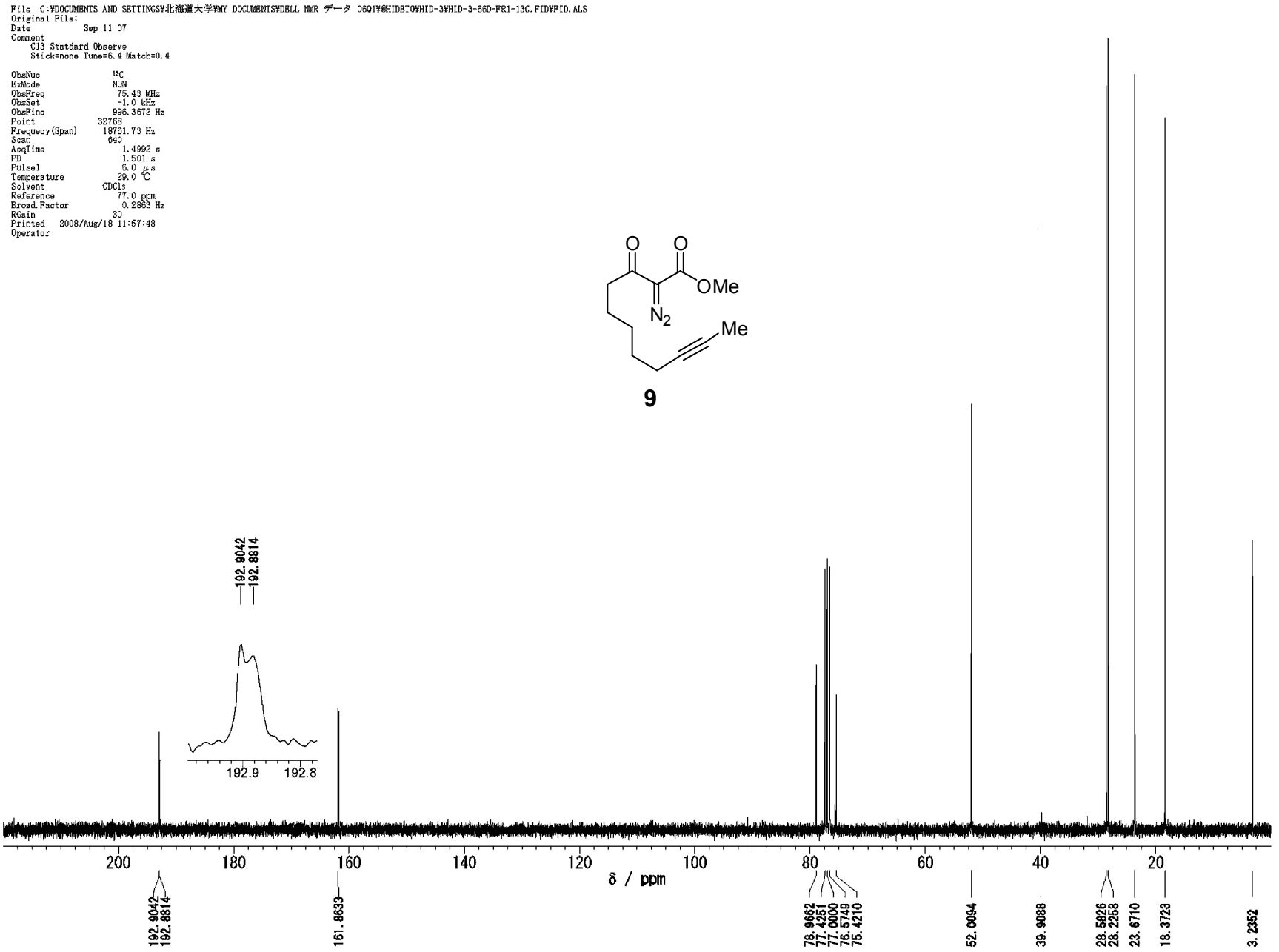
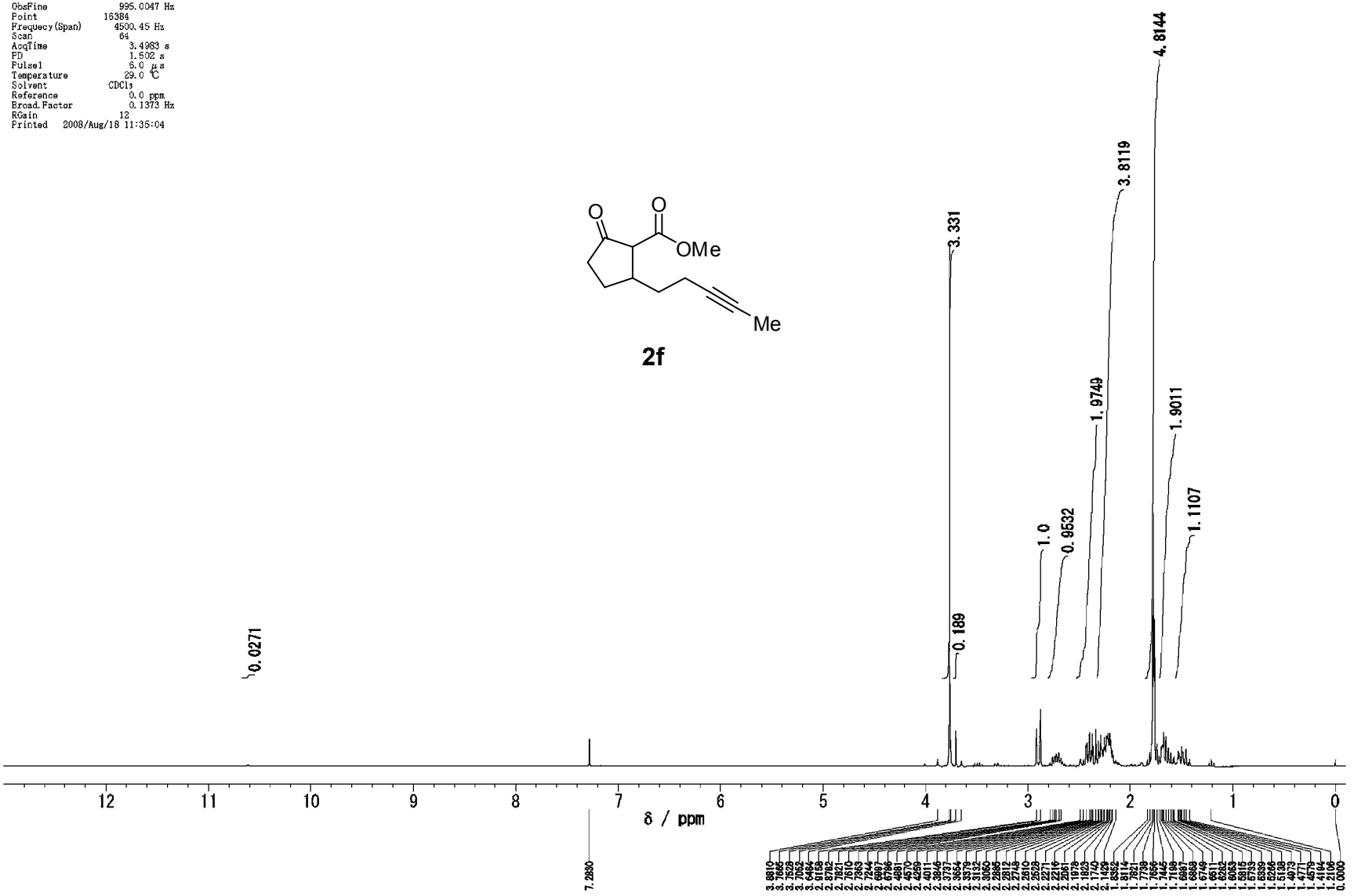
28.5821
28.0069
28.0511
25.5795
22.8641
18.4900
18.4230
3.9431


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-66C-FR1-1H.FID¥FID.ALS
Original File:
Date Sep 11 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 7
Printed 2008/Aug/18 11:52:19
Operator
O
O
OMe
N2
Me
9
2.9145
2.0
1.9795
2.9892
2.145
4.1542
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2885
3.8425
2.8810
2.8563
2.8306
2.1337
2.1255
2.1117
2.1026
1.7839
1.7757
1.7674
1.7290
1.6951
1.6703
1.6456
1.6218
1.5971
1.5238
1.5009
1.4790
1.4606
1.4487
1.4268
1.4121
1.3965
0.0000


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-66D-FR1-13C.FID¥FID.ALS
Original File:
Date Sep 11 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 640
AcqTime 1.4992 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 11:57:48
Operator
O
O
OMe
N2
Me
9
192.9042
192.8814
192.9
192.8
200
180
160
140
120
100
80
60
40
20
δ / ppm
192.9042
192.8814
161.8633
78.9662
77.4251
77.0000
76.5749
75.4210
52.0094
39.9088
28.5826
28.2258
23.6710
18.3723
3.2352

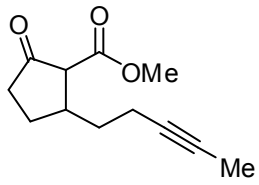
File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-67C-FR1-1H.FID
¥FID.ALS
Original File:
Date Sep 12 07
Comment
STANDARD 1H OBSERVE

ObsNuc	1H
ExMode	NON
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsFine	995.0047 Hz
Point	16384
Frequecy(Span)	4500.45 Hz
Scan	64
AcqTime	3.4983 s
PD	1.502 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	12
Printed	2008/Aug/18 11:35:04



File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-67D-FR1-13C.FI
D¥FID.ALS
Original File:
Date Sep 12 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	14464
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30



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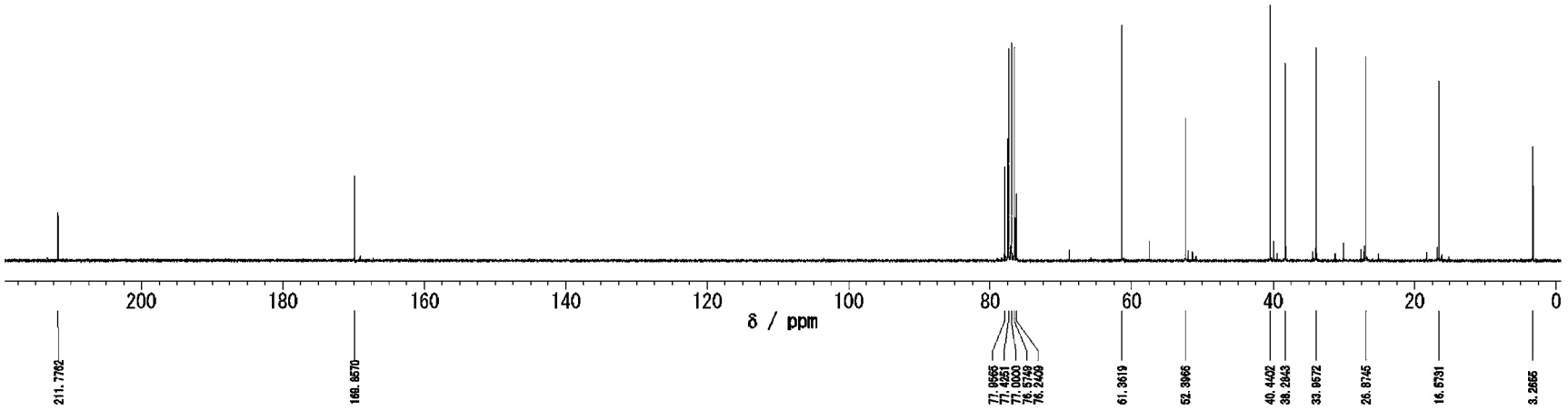
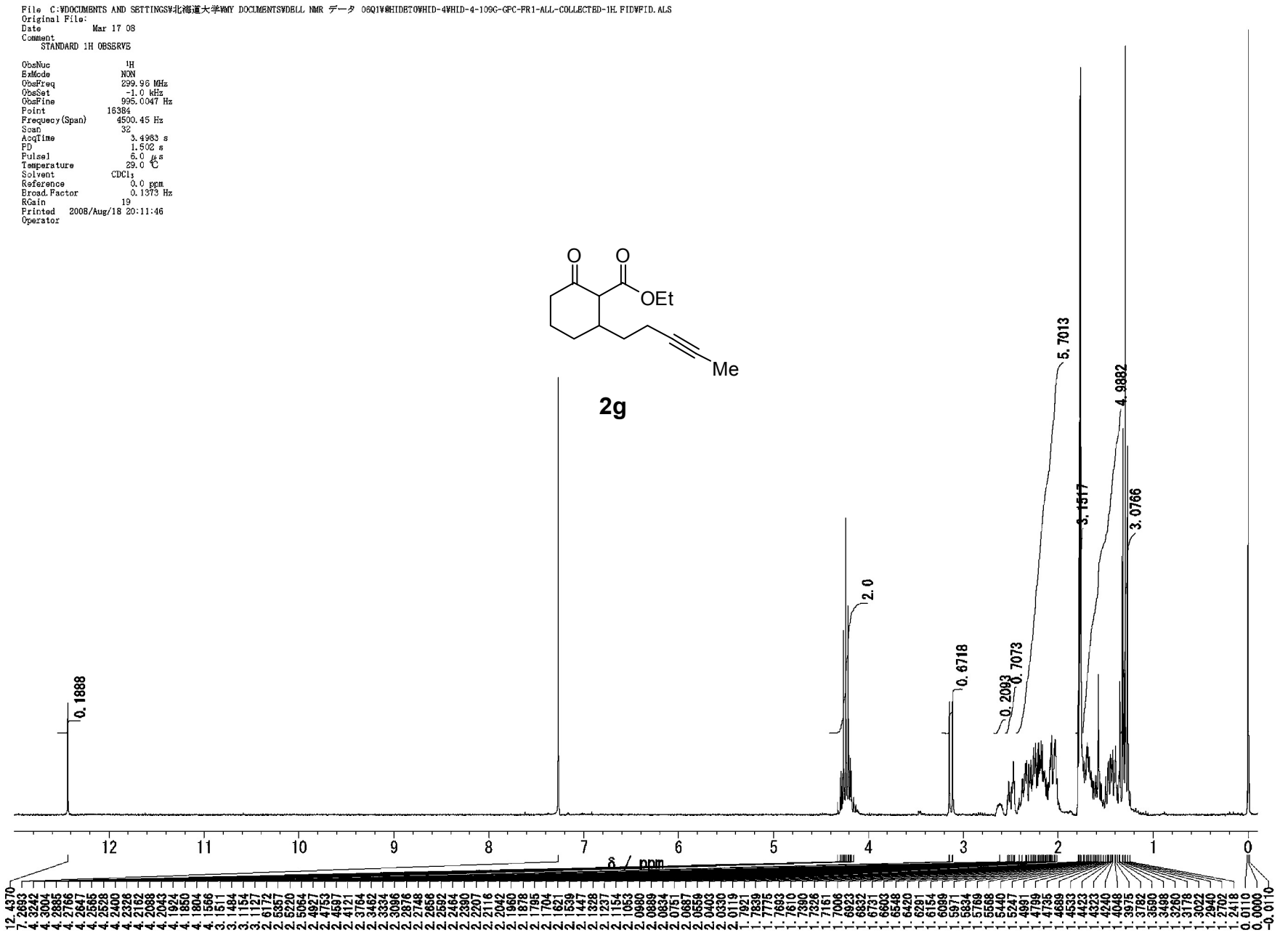
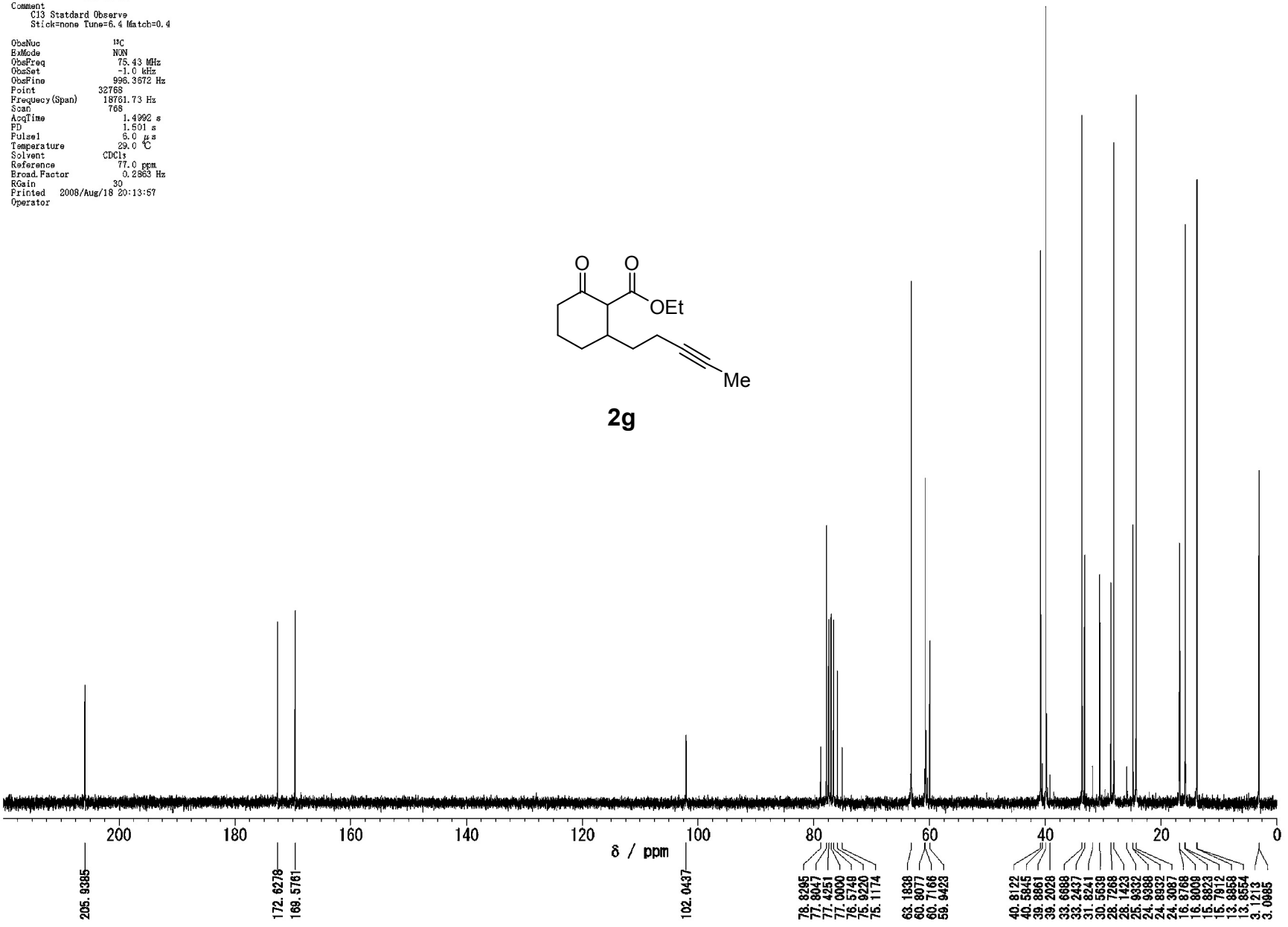


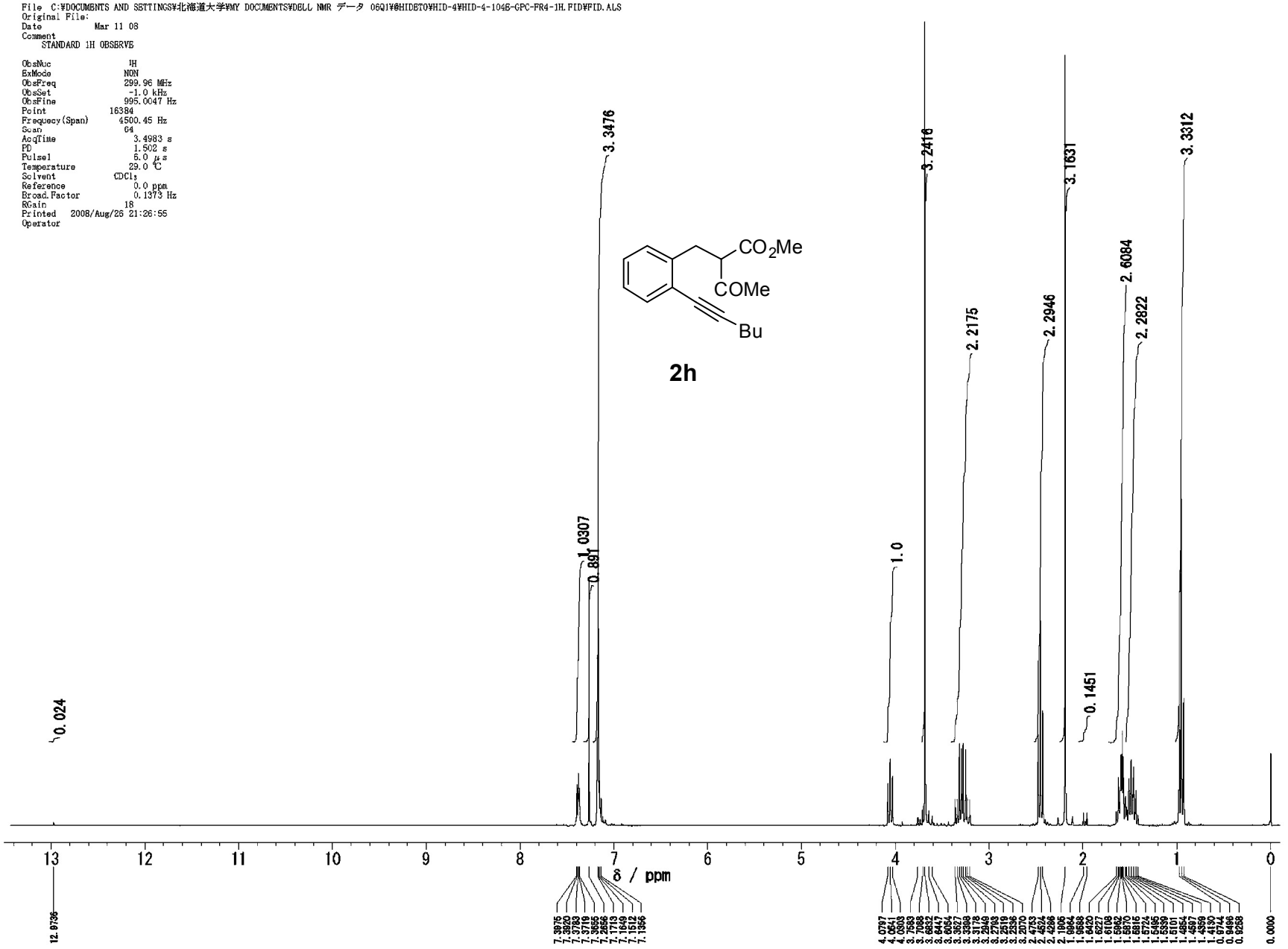

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 08Q1¥各HIDETO¥HID-4¥HID-4-109C-GPC-FR1-ALL-COLLECTED-1H FID¥FID.ALS
Original File:
Date Mar 17 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad Factor 0.1373 Hz
RGain 19
Printed 2008/Aug/18 20:11:46
Operator
O
O
OEt
Me
2g
0.1888
2.0
0.6718
0.2083
0.7073
5.7013
3.1317
4.9882
3.0766
δ / ppm

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-4¥HID-4-109H-GPC-FR1-ALL-COLLECTED-13C.FID¥FID.ALS
Original File:
Date Mar 17 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	768
AcqTime	1.4992 s
PD	1.501 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2008/Aug/18 20:13:57
Operator	



2g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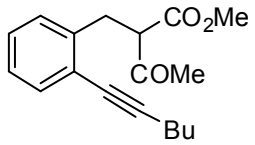
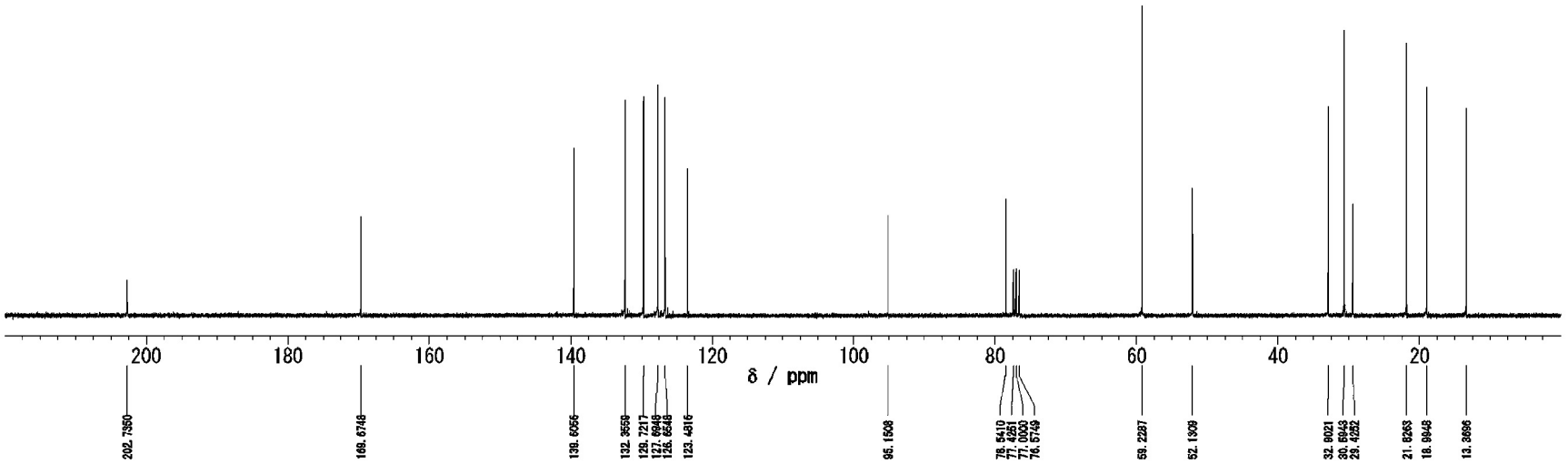
Original File:
Date Mar 11 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulsel 5.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2008/Aug/26 21:26:55
Operator
3.3476
3.2416
3.1631
3.3312
2.6084
2.2822
2.2175
2.2946
1.0307
0.8911
1.0
0.1451
0.024
CO2Me
COMe
Bu
2h
δ / ppm

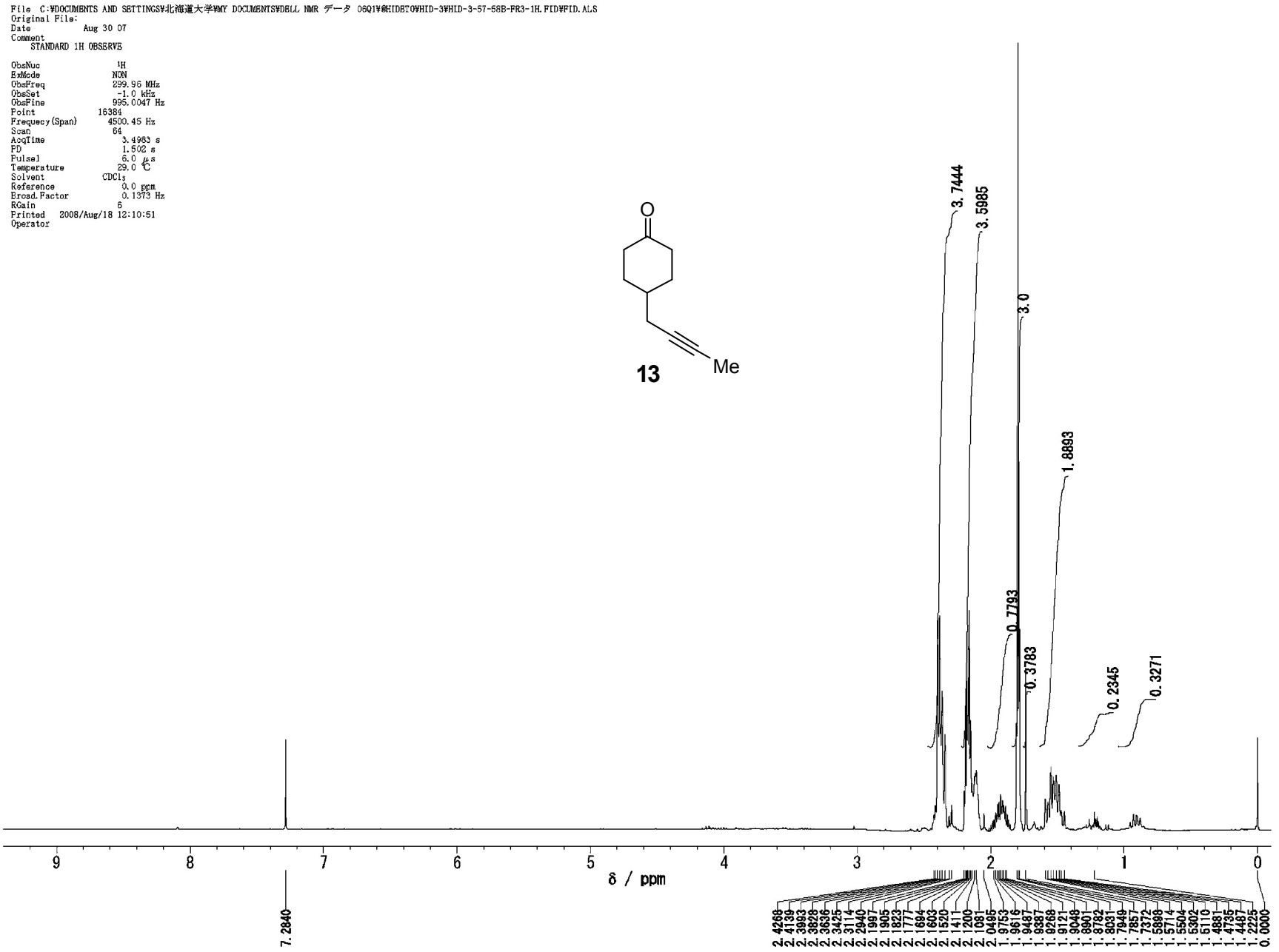
File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥@HIDETO¥HID-4¥HID-4-104F-GPC-FR4-13C.FID¥FID.ALS
Original File:
Date Mar 11 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

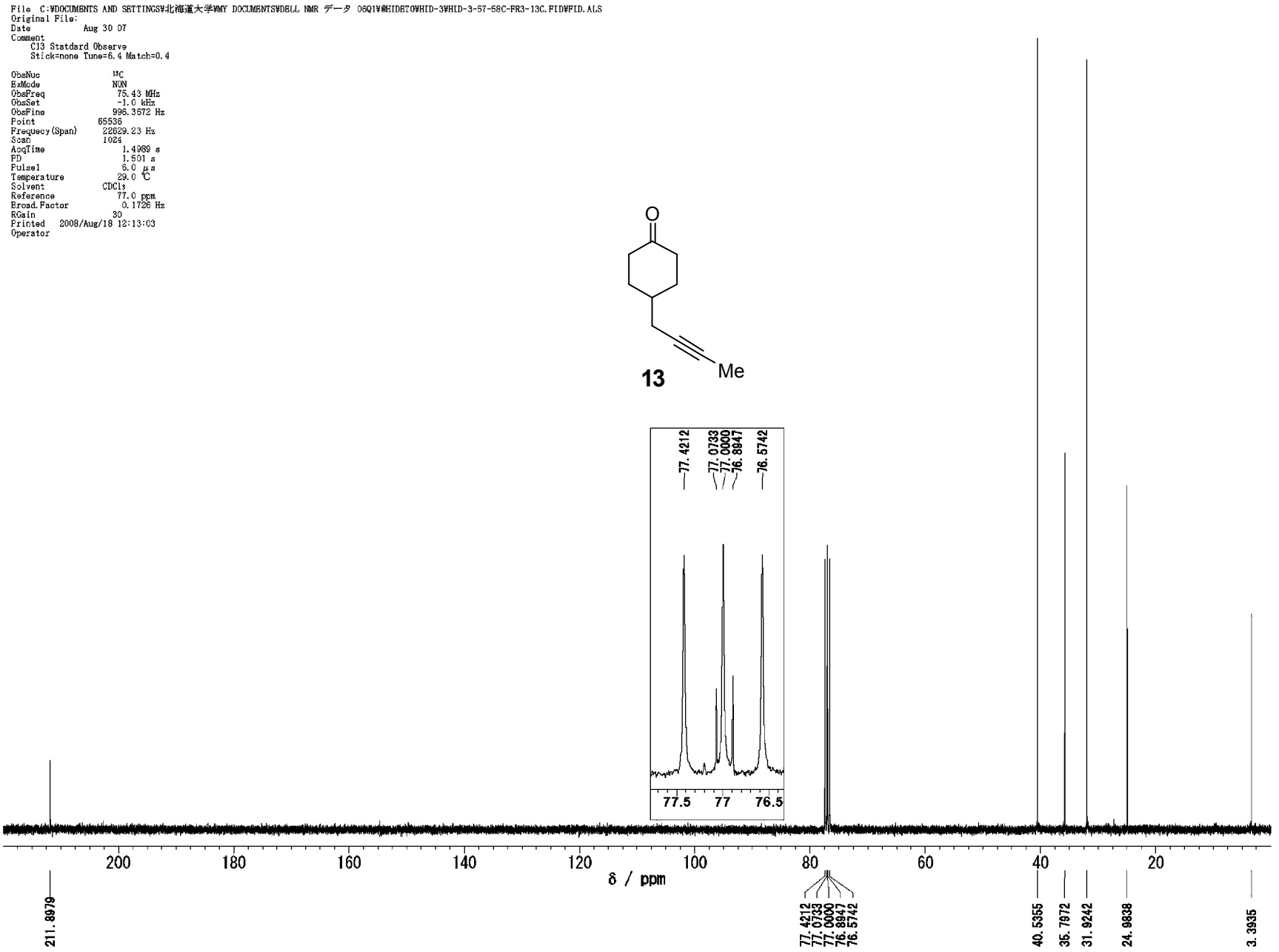
ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	995.3672 Hz
Point	32768
Frequency(Span)	18761.73 Hz
Scan	448
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2008/Aug/26 21:29:11
Operator	

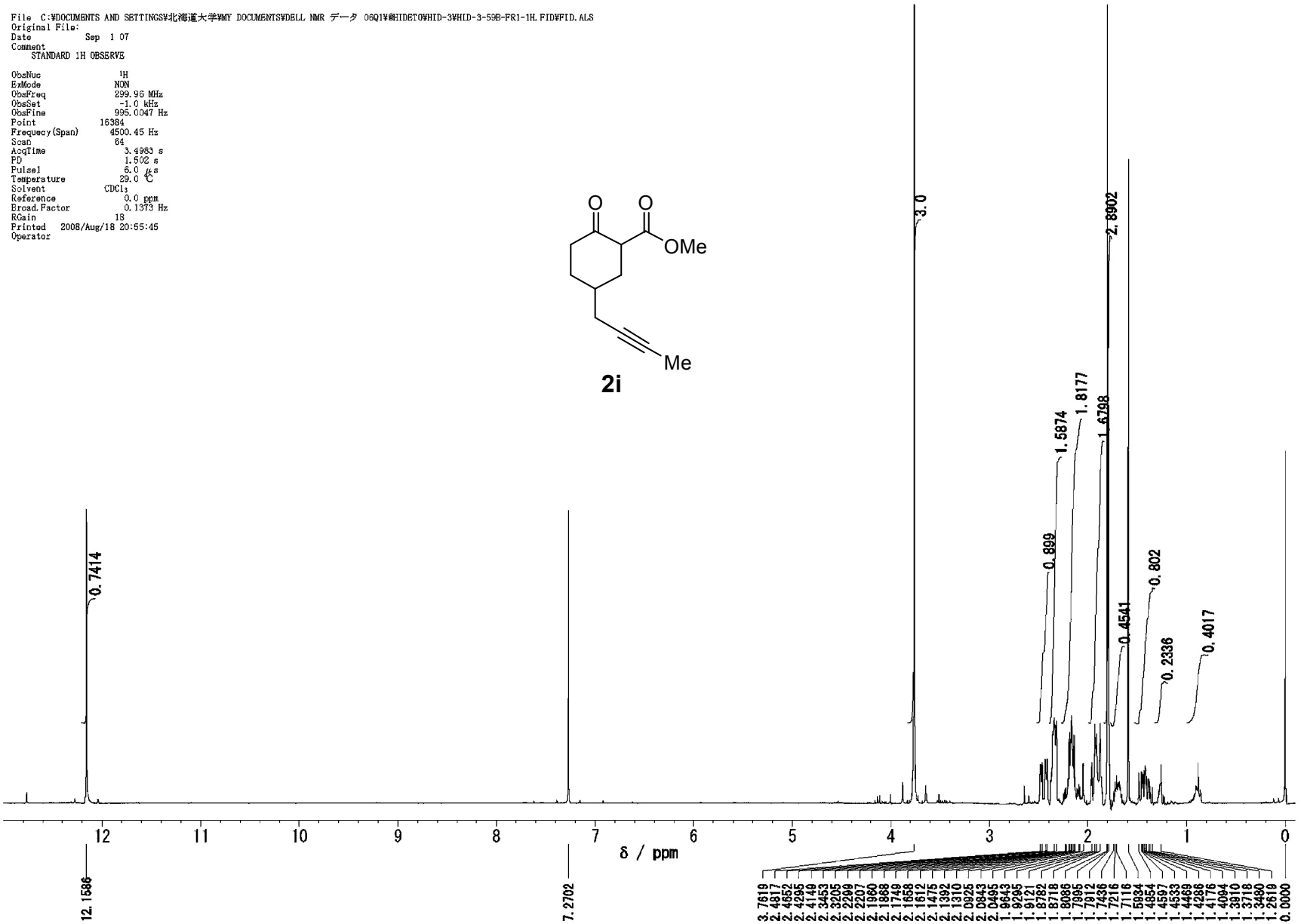


2h



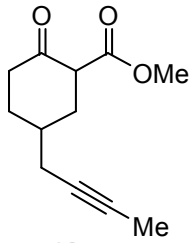

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-57-58B-FR3-1H.FID¥FID.ALS
Original File:
Date Aug 30 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/18 12:10:51
Operator
O
Me
13
3.7444
3.5985
3.0
1.8893
0.7793
0.3783
0.2345
0.3271
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2840
2.4260
2.4139
2.3993
2.3828
2.3636
2.3425
2.3114
2.2940
2.1997
2.1905
2.1823
2.1777
2.1694
2.1603
2.1520
2.1411
2.1200
2.1081
2.0495
1.9753
1.9616
1.9487
1.9387
1.9268
1.9121
1.9048
1.8901
1.8782
1.8631
1.7949
1.7857
1.7372
1.5898
1.5714
1.5504
1.5302
1.5110
1.4881
1.4735
1.4487
1.2225
0.0000


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-57-58C-FR3-13C.FID¥FID.ALS
Original File:
Date Aug 30 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 65536
Frequecy(Span) 22629.23 Hz
Scan 1024
AcqTime 1.4989 s
PD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.1726 Hz
RGain 30
Printed 2008/Aug/18 12:13:03
Operator
O
Me
13
77.4212
77.0733
77.0000
76.8947
76.5742
77.5
77
76.5
200
180
160
140
120
100
80
60
40
20
δ / ppm
211.8979
77.4212
77.0733
77.0000
76.8947
76.5742
40.5355
35.7972
31.9242
24.9838
3.3935


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-59B-FR1-1H.FID¥FID.ALS
Original File:
Date Sep 1 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2008/Aug/18 20:55:45
Operator
O
O
OMe
Me
2i
3.0
2.8902
1.8177
1.6798
1.5874
0.899
0.802
0.7414
0.4541
0.4017
0.2336
12.1586
7.2702
δ / ppm

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-59C-13C.FID¥FID.ALS
Original File:
Date Sep 1 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	65536
Frequecy(Span)	22629.23 Hz
Scan	1216
AcqTime	1.4989 s
PD	1.501 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.1726 Hz
RGain	30
Printed	2008/Aug/18 20:58:43
Operator	



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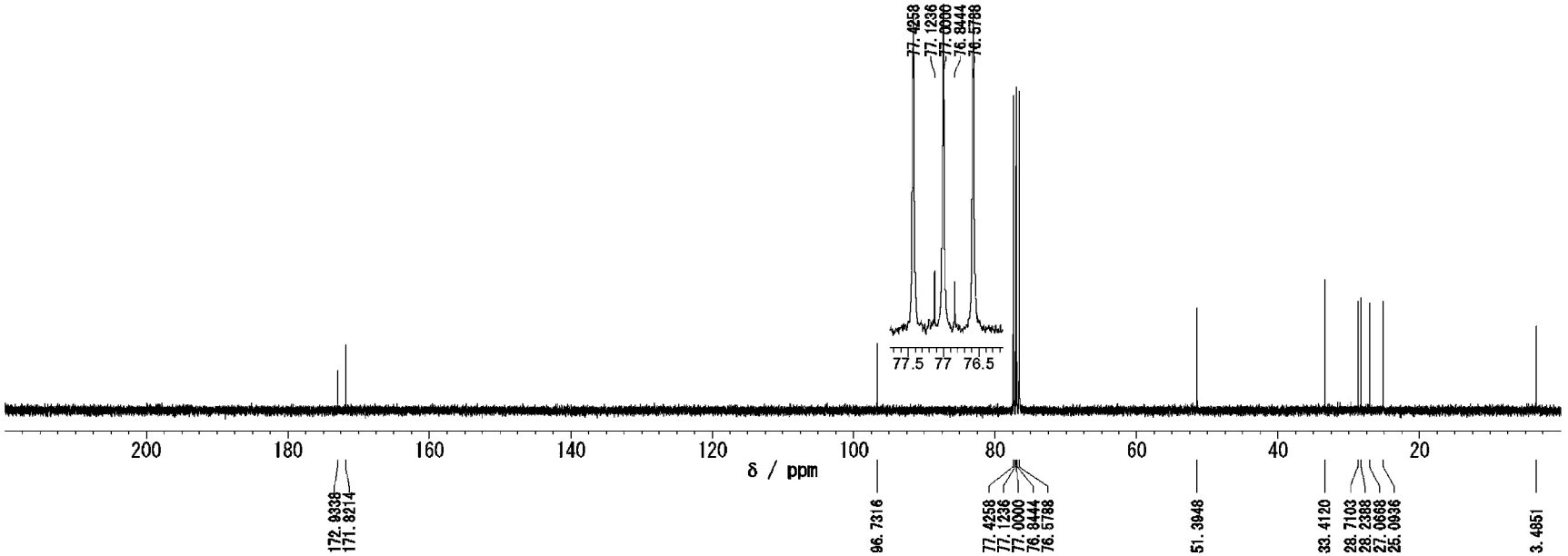
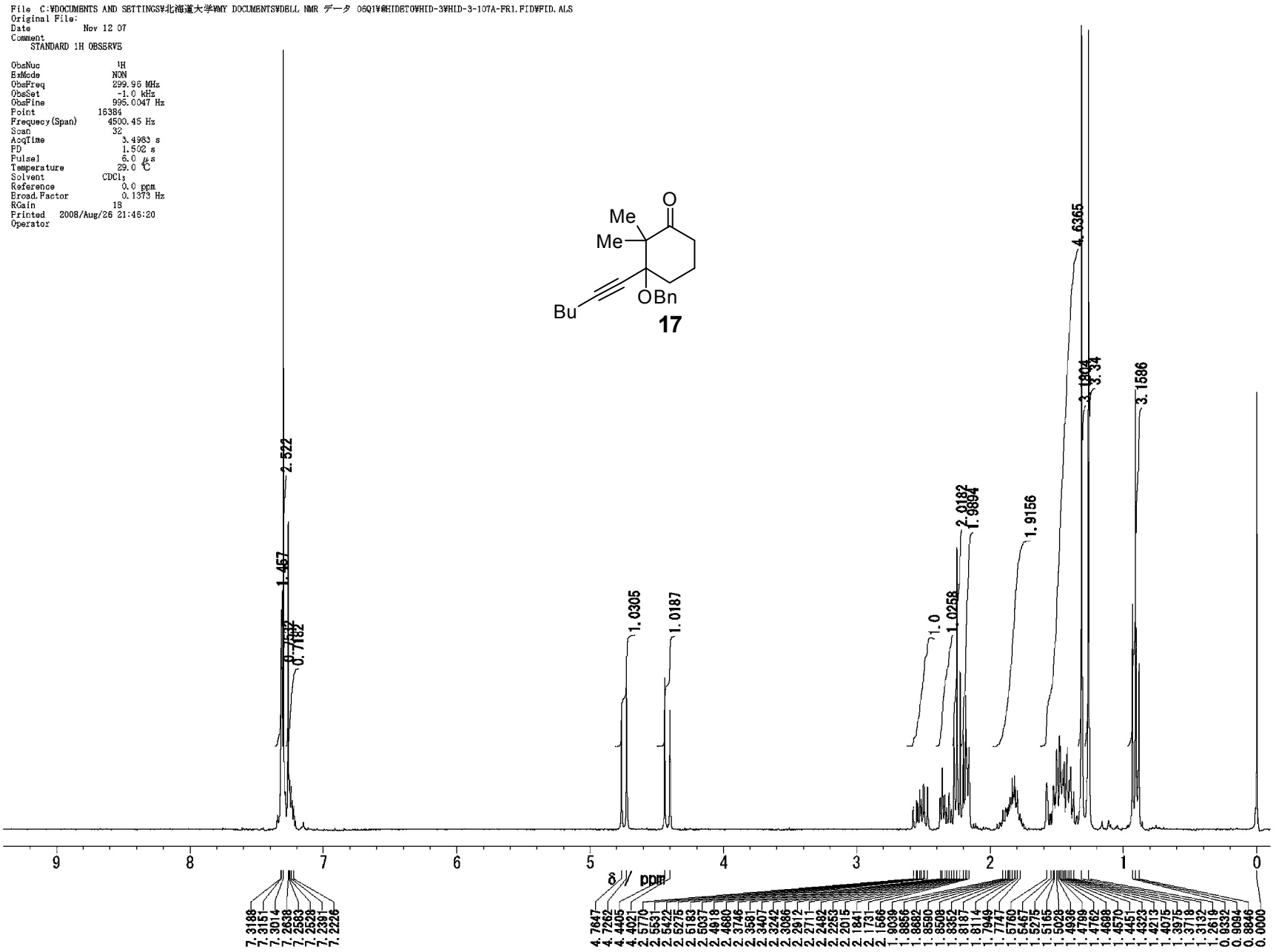
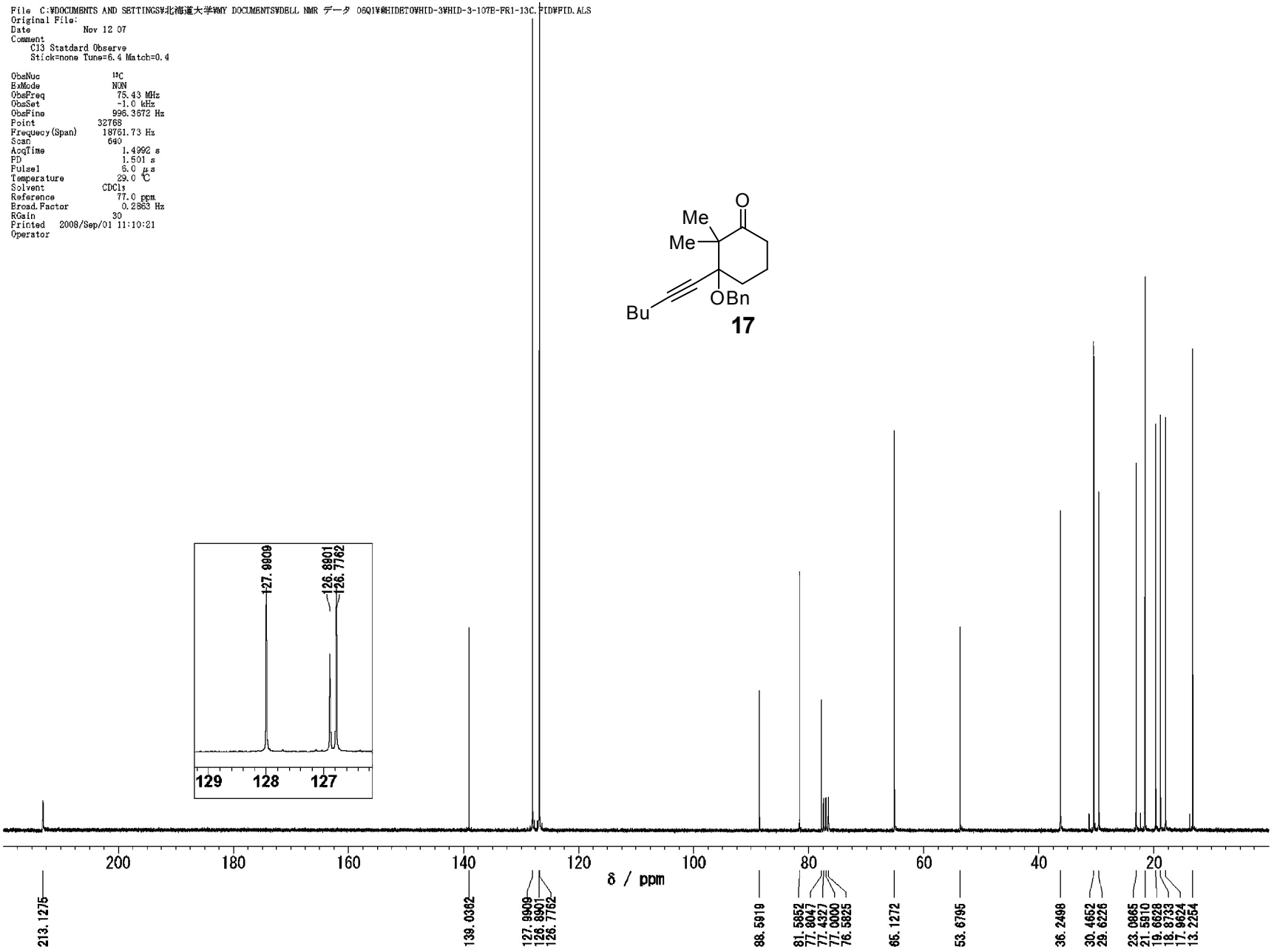



File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-107A-FR1.FID¥FID.ALS
Original File:
Date Nov 12 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 18
Printed 2008/Aug/26 21:46:20
Operator
Me
Me
O
OBn
Bu
17
δ / ppm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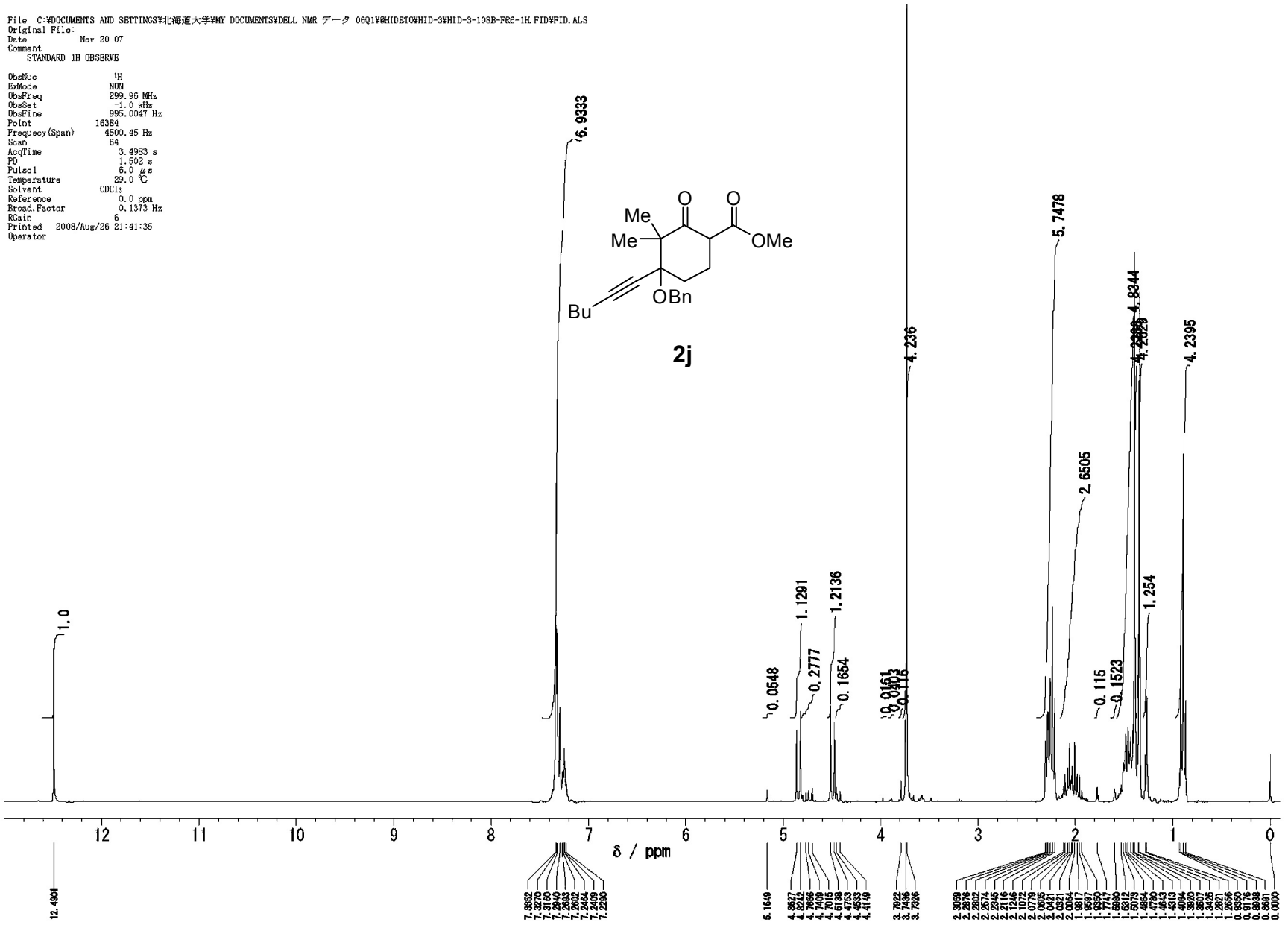
Original File:
Date Nov 12 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 640
AcqTime 1.4992 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Sep/01 11:10:21
Operator
Me
Me
O
OBn
Bu
17
127.9909
126.8801
126.7762
129
128
127
200
180
160
140
120
100
80
60
40
20
δ / ppm
213.1275
139.0362
127.9909
126.8801
126.7762
88.5919
81.5852
77.8047
77.4327
77.0000
76.5825
65.1272
53.6795
36.2498
30.4652
29.6226
23.0865
21.5910
19.6628
18.8733
17.9624
13.2254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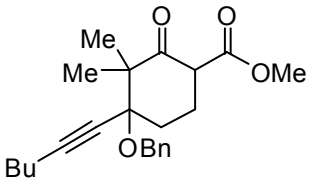
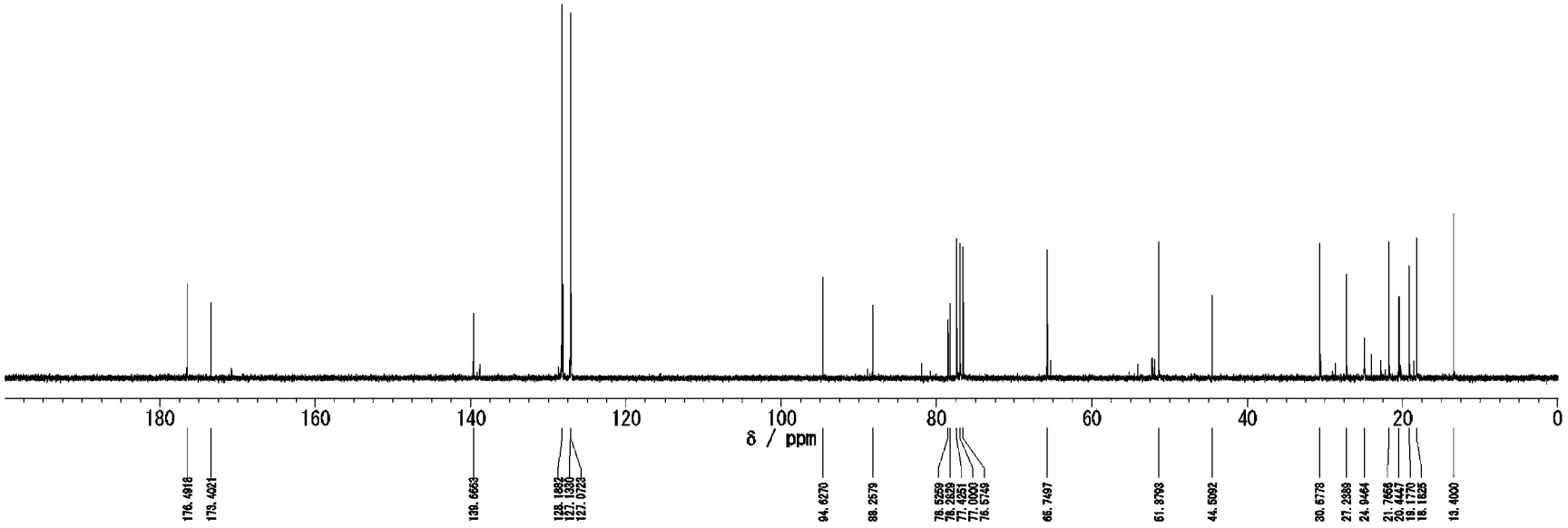
Original File:
Date Nov 20 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet 1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/26 21:41:35
Operator
Me
Me
O
O
OMe
OBn
Bu
2j
δ / ppm

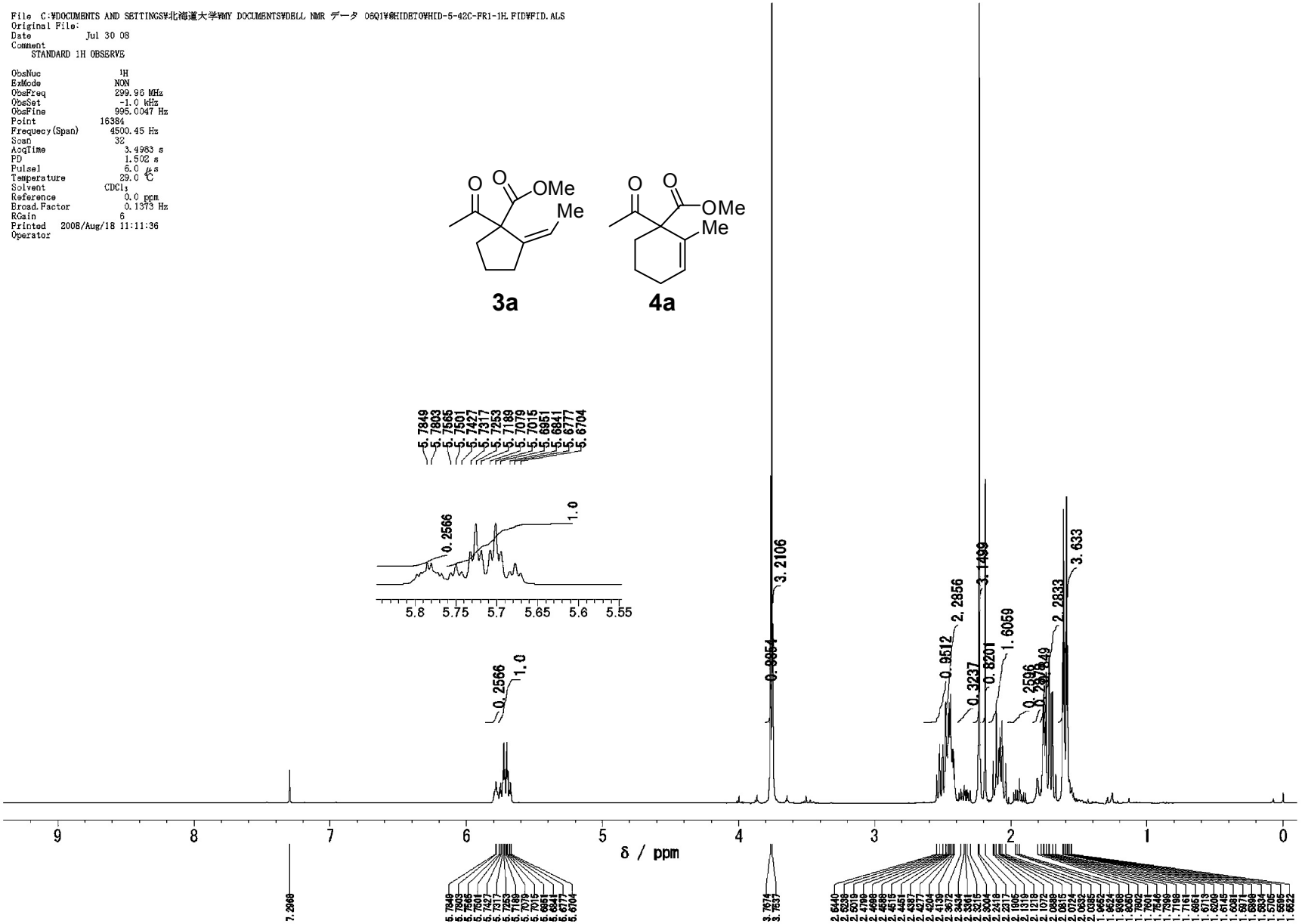
File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-10SC-FR6-13C-BS8.FID¥FID.ALS
Original File:
Date Nov 20 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

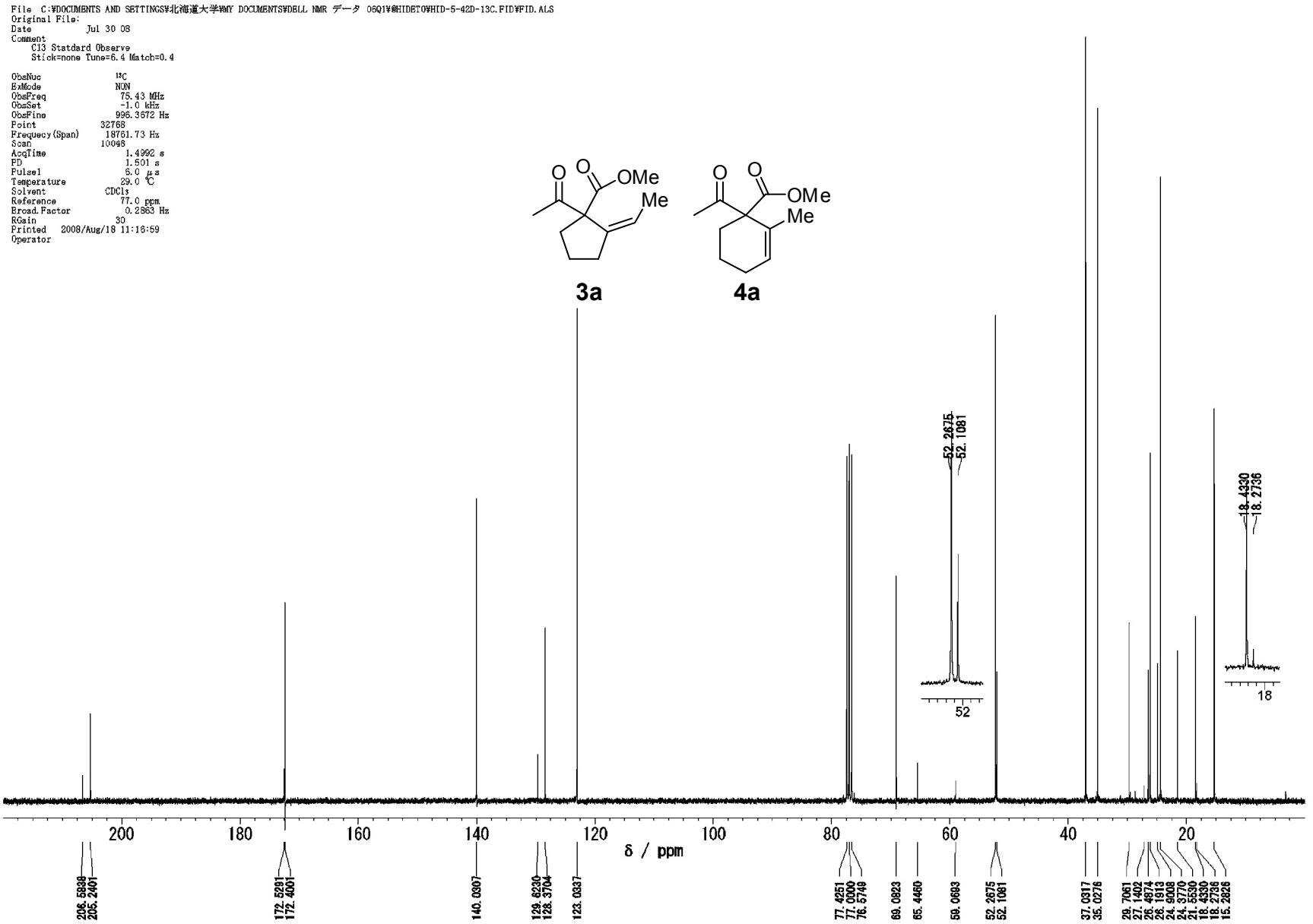
ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	512
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2563 Hz
RGain	30
Printed	2008/Aug/26 21:43:44
Operator	

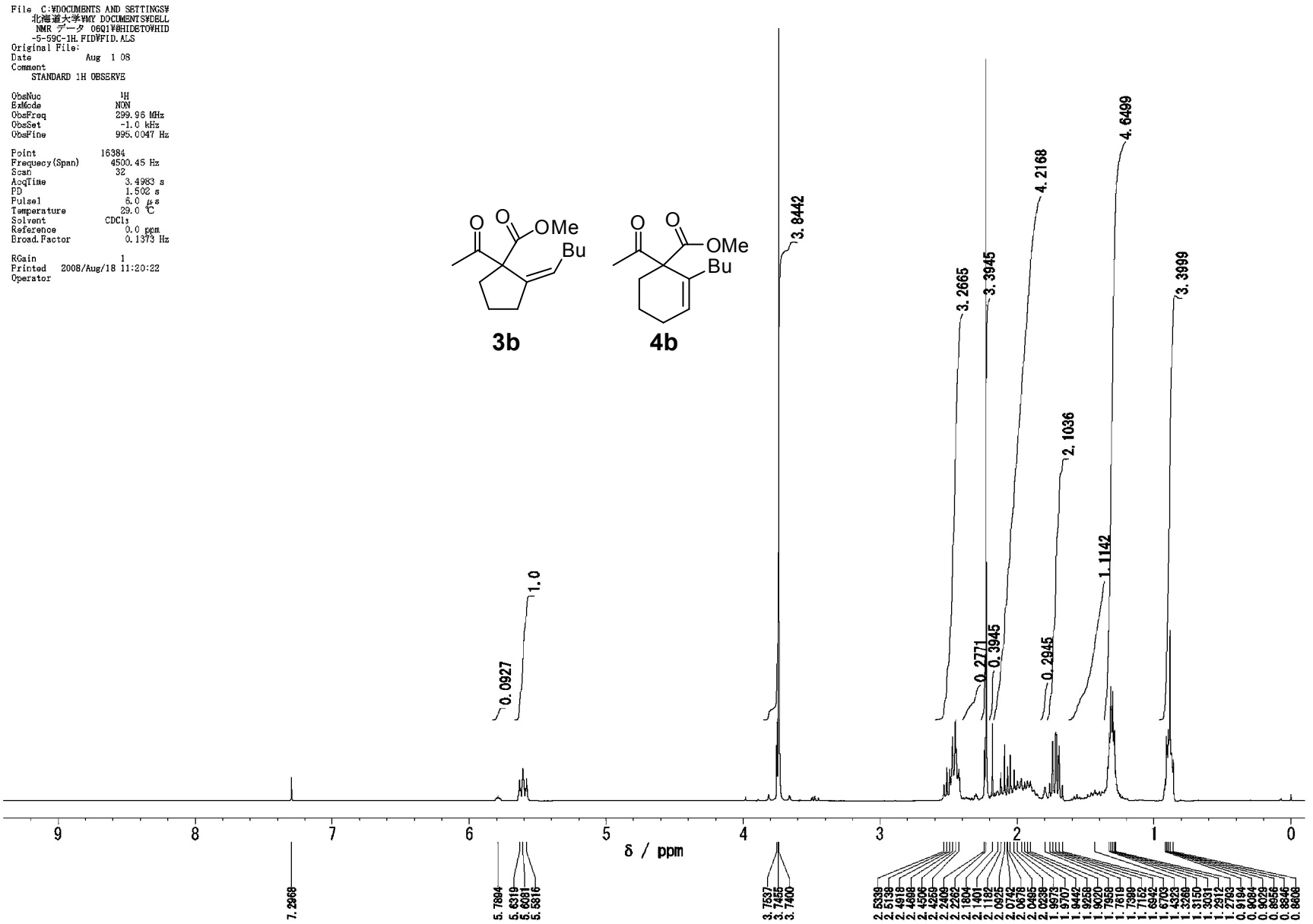


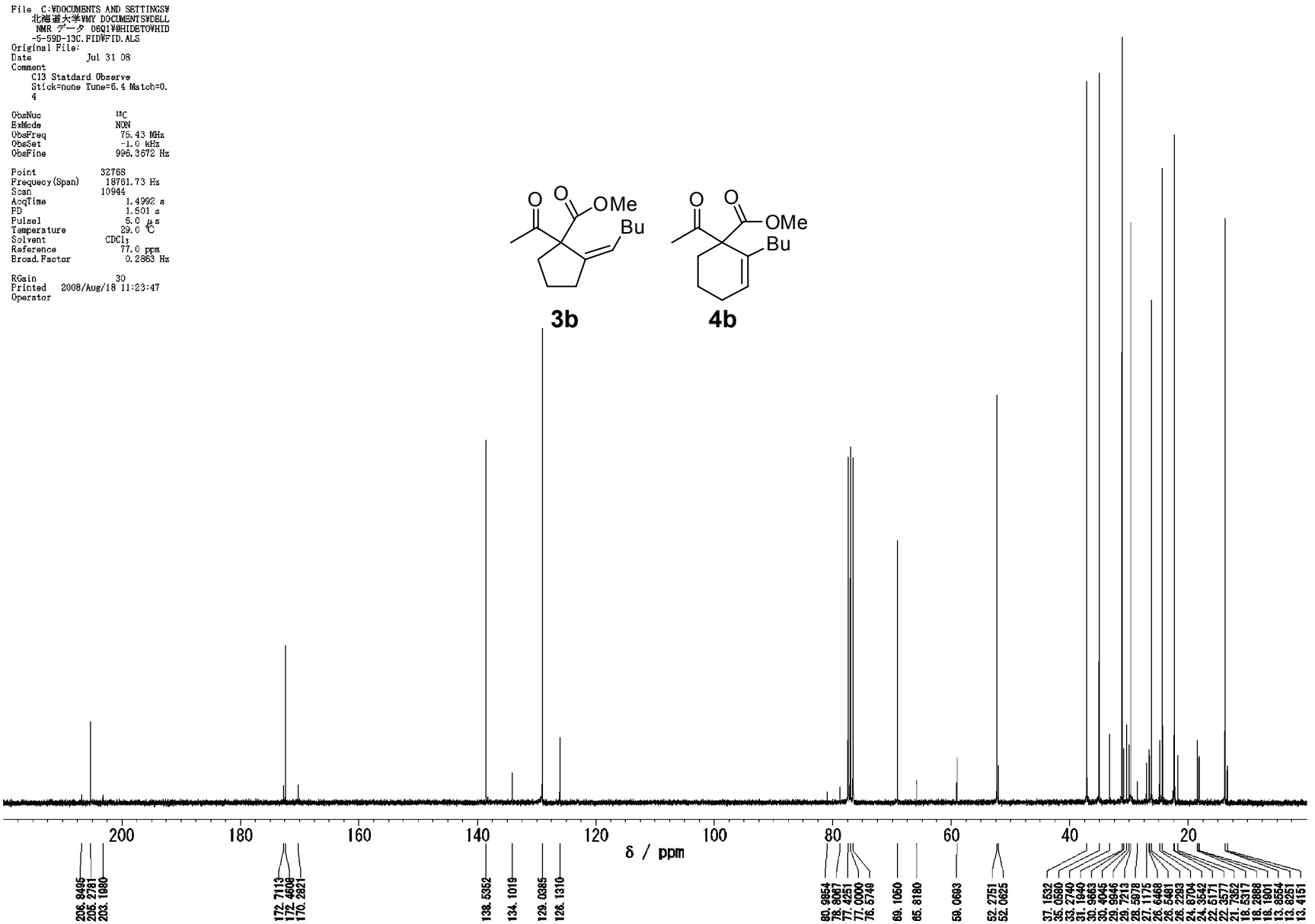
2j




File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-5-42C-FR1-1H.FID¥FID.ALS
Original File:
Date Jul 30 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/18 11:11:36
Operator
O
O
OMe
Me
3a
4a
δ / ppm


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥森HIDETO¥HID-5-42D-13C.FID¥FID.ALS
Original File:
Date Jul 30 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 10098
AcqTime 1.4992 s
PD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 11:16:59
Operator
O
O
OMe
Me
3a
O
O
OMe
Me
4a
52.2675
52.1081
18.4330
18.2736
δ / ppm
206.5838
205.2401
172.5291
172.4001
140.0307
129.6230
128.3704
123.0337
77.4251
77.0000
76.5749
69.0823
65.4460
59.0693
52.2675
52.1081
37.0317
35.0276
29.7061
27.1402
26.4874
26.1914
24.9008
24.3770
21.5530
18.4330
18.2736
15.2826


File C:¥DOCUMENTS AND SETTINGS¥
北海道大学¥MY DOCUMENTS¥DELL
NMR データ 06Q1¥0HIDETO¥HID
-5-59C-1H.FID¥FID.ALS
Original File:
Date Aug 1 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 1
Printed 2008/Aug/18 11:20:22
Operator
O
O
OMe
Bu
3b
O
O
OMe
Bu
4b
3.8442
3.2665
3.3945
4.2168
4.6499
3.3999
2.1036
1.1142
0.0927
1.0
0.2771
0.3945
0.2945
δ / ppm
7.2968
5.7804
5.6319
5.6031
5.5816
3.7537
3.7455
3.7400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北海道大学¥MY DOCUMENTS¥DELL
NMR データ 06Q1¥0HIDETO¥HID
-5-59D-13C.FID¥FID.ALS
Original File:
Date Jul 31 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.
4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 10944
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 11:23:47
Operator
O
O
OMe
Bu
3b
O
O
OMe
Bu
4b
200
180
160
140
120
100
80
60
40
20
δ / ppm
206.8495
205.2781
203.1980
172.7113
172.4608
170.2821
138.5352
134.1019
129.0385
128.1310
80.9854
78.8067
77.4251
77.0000
76.5749
69.1050
65.8180
59.0693
52.2751
52.0625
37.1532
35.0580
33.2740
31.1940
30.9663
30.4045
29.9946
29.7213
28.5978
27.1175
26.6468
26.5481
26.2293
24.8704
24.3542
22.5171
22.3577
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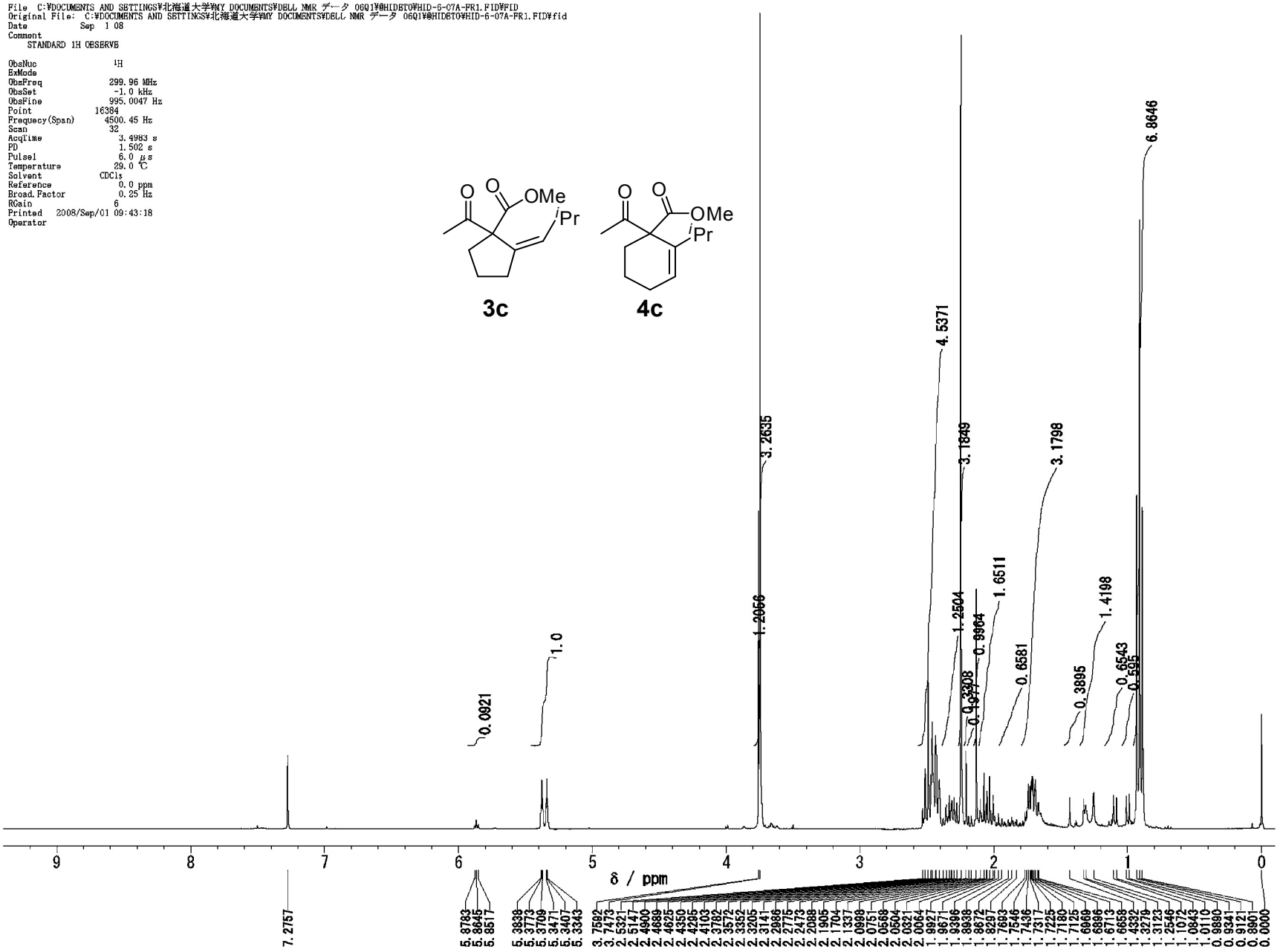
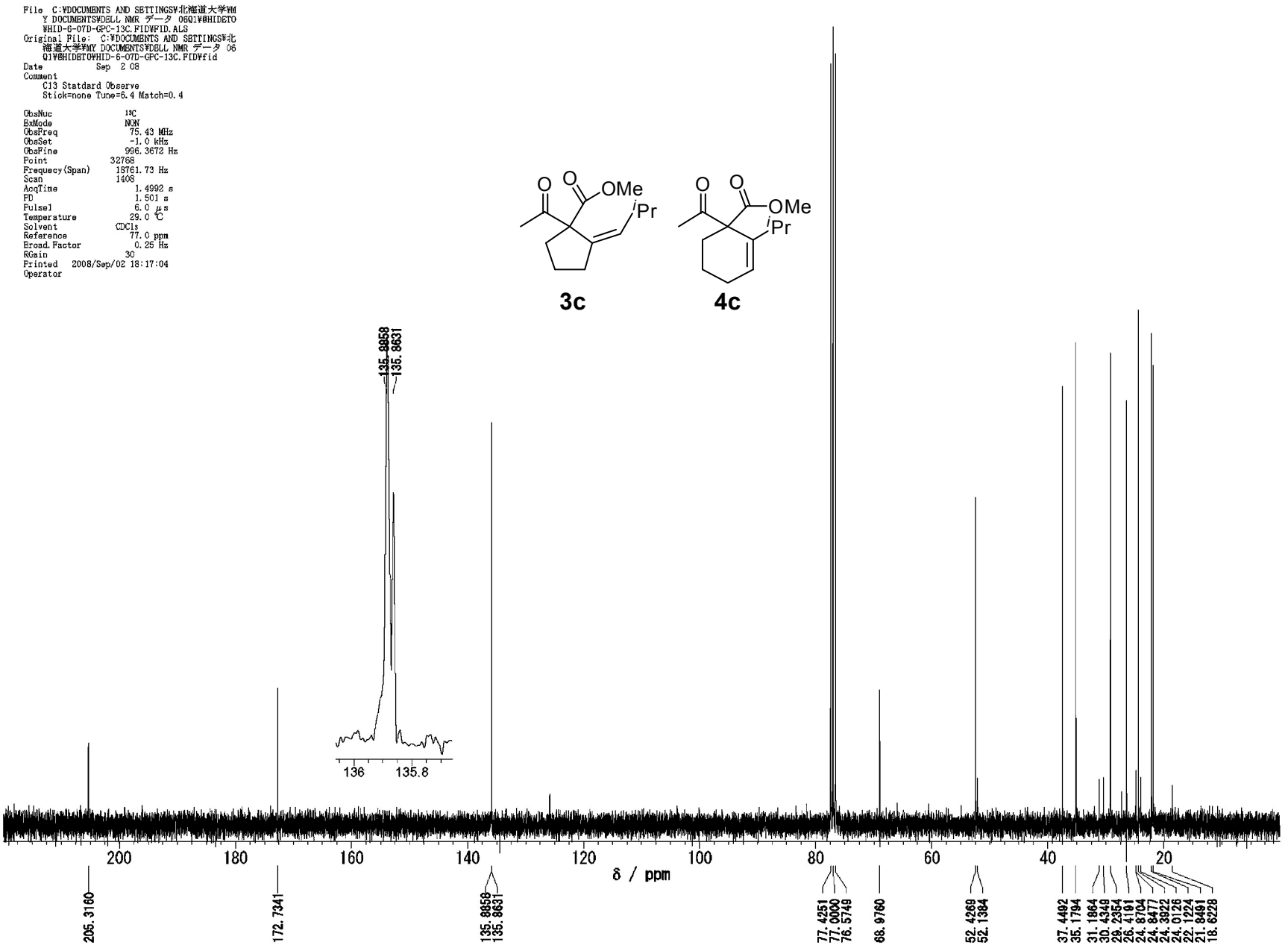
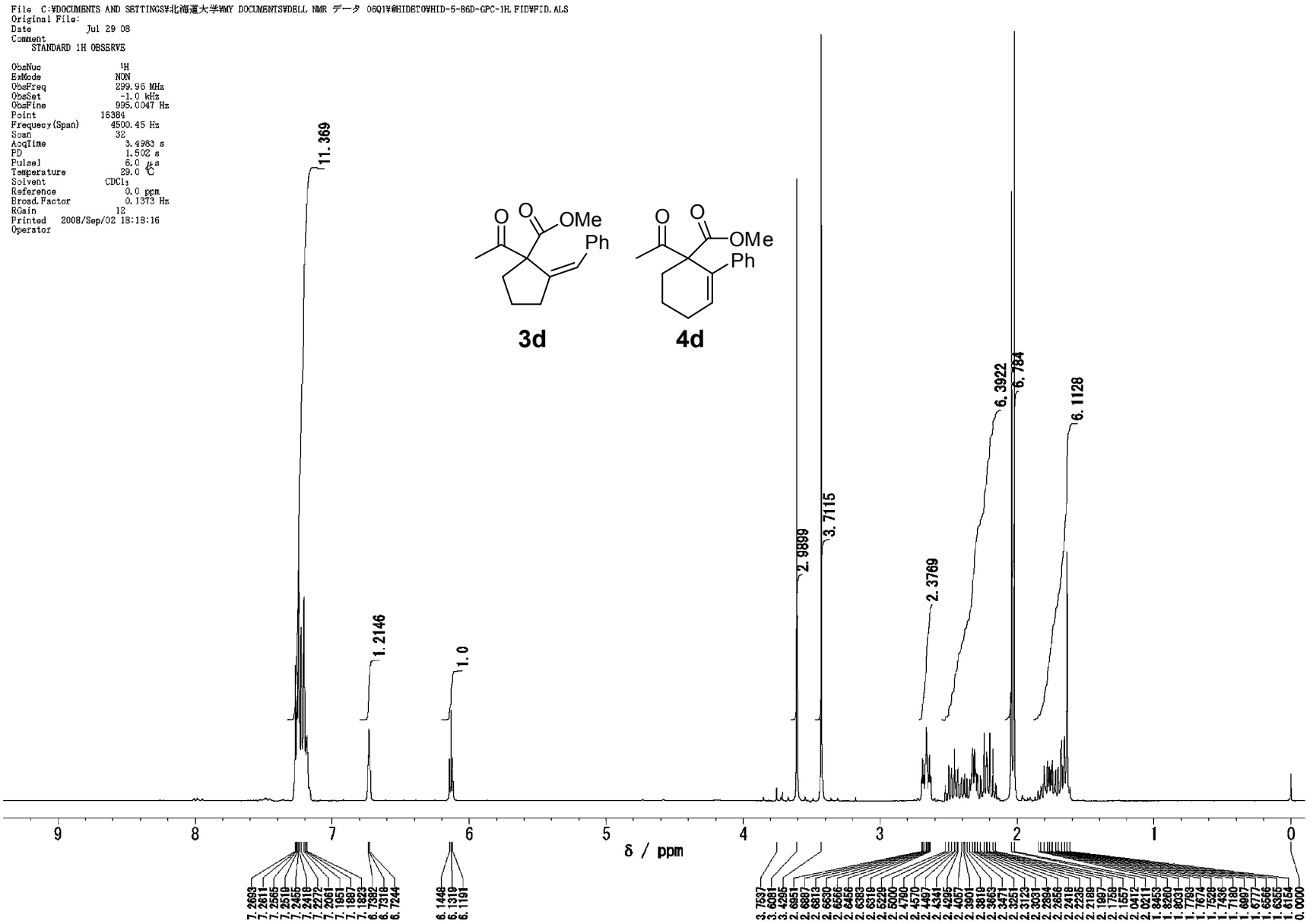
18.2888
18.1901
13.8554
13.8251
13.4151


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥@HIDETO¥HID-6-07A-PR1.FID¥FID
Original File: C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥@HIDETO¥HID-6-07A-PR1.FID¥fid
Date Sep 1 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.25 Hz
RGain 6
Printed 2008/Sep/01 09:43:18
Operator
O
O
OMe
iPr
3c
O
O
OMe
iPr
4c
6.8646
4.5371
3.2635
3.1849
3.1798
1.6511
1.4198
1.2504
1.2056
0.9904
0.6581
0.6543
0.3895
0.0921
1.0
δ / ppm


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥0HIDETO¥HID-6-07D-GPC-13C.FID¥FID.ALS
Original File: C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥0HIDETO¥HID-6-07D-GPC-13C.FID¥fid
Date Sep 2 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 1408
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.25 Hz
RGain 30
Printed 2008/Sep/02 18:17:04
Operator
O
O
OMe
iPr
3c
4c
135.8858
135.8631
136
135.8
200
180
160
140
120
100
80
60
40
20
δ / ppm
205.3160
172.7341
135.8858
135.8631
77.4251
77.0000
76.5749
68.9760
52.4269
52.1384
37.4492
35.1794
31.1864
30.4349
29.2354
26.4191
24.8704
24.8477
24.3922
24.0126
22.1224
21.8461
18.6228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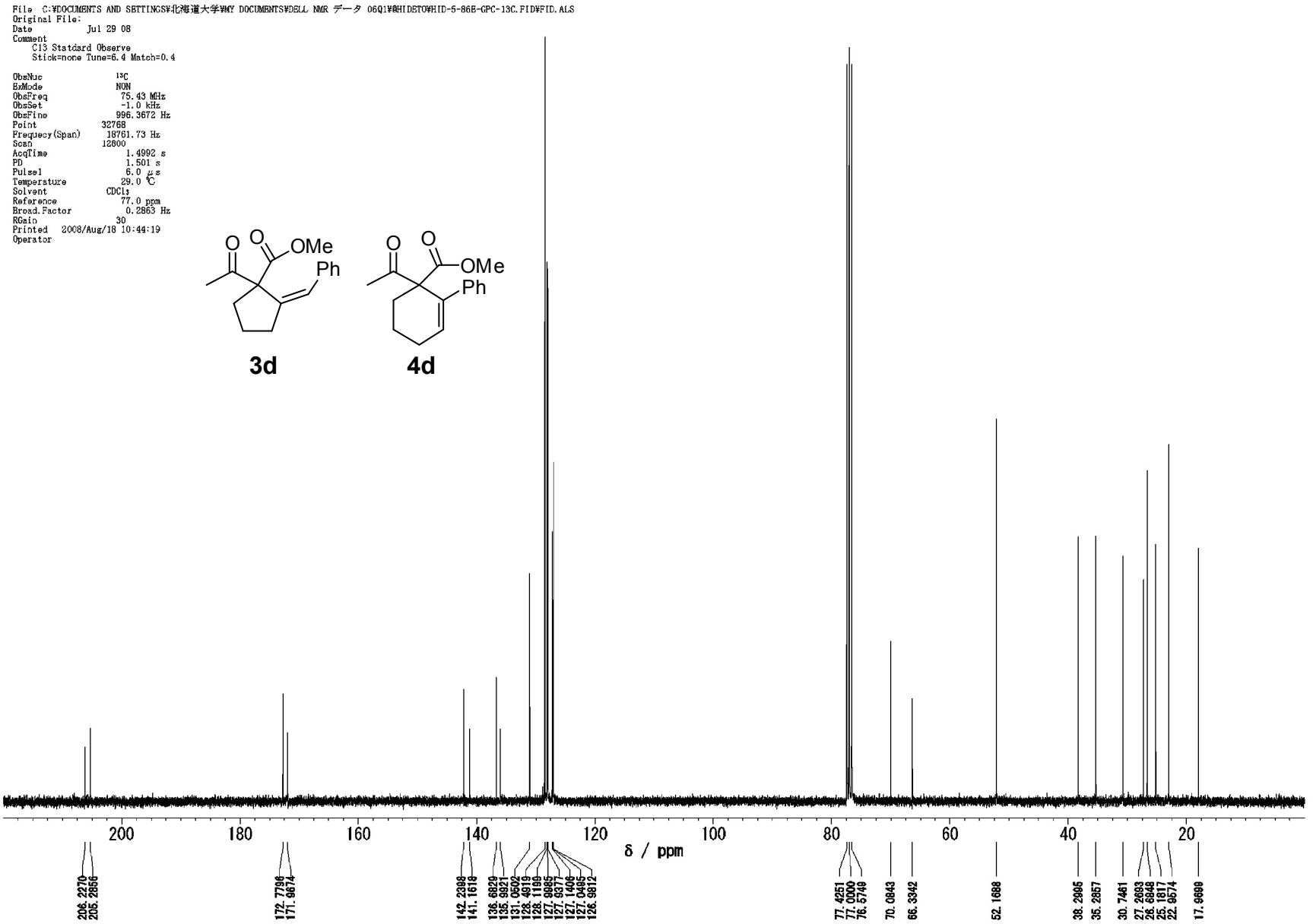
Original File:
Date Jul 29 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 12
Printed 2008/Sep/02 18:18:16
Operator
11.369
1.2146
1.0
2.9899
3.7115
2.3769
6.3922
6.784
6.1128
3d
4d
δ / ppm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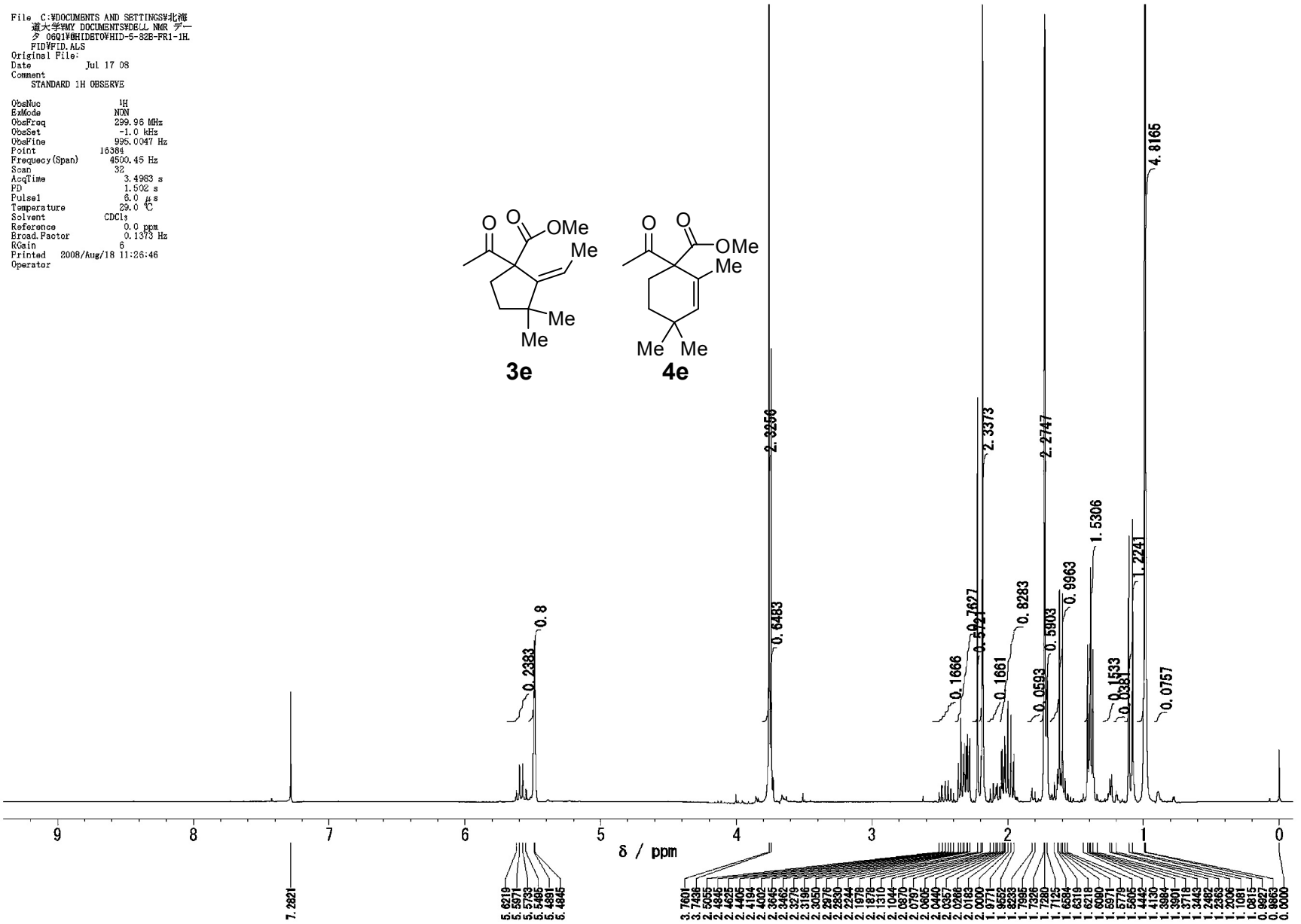
Original File:
Date Jul 29 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 12800
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 10:44:19
Operator
O
O
OMe
Ph
3d
O
O
OMe
Ph
4d
200
180
160
140
120
100
80
60
40
20
δ / ppm
206.2270
205.2856
172.7796
171.9674
142.2398
141.1618
136.6829
135.9921
131.0502
128.4019
128.1199
127.9885
127.8377
127.1406
127.0485
126.9812
77.4251
77.0000
76.5749
70.0843
66.3342
52.1688
38.2985
35.2857
30.7461
27.2693
26.6848
25.1617
22.9574
17.9699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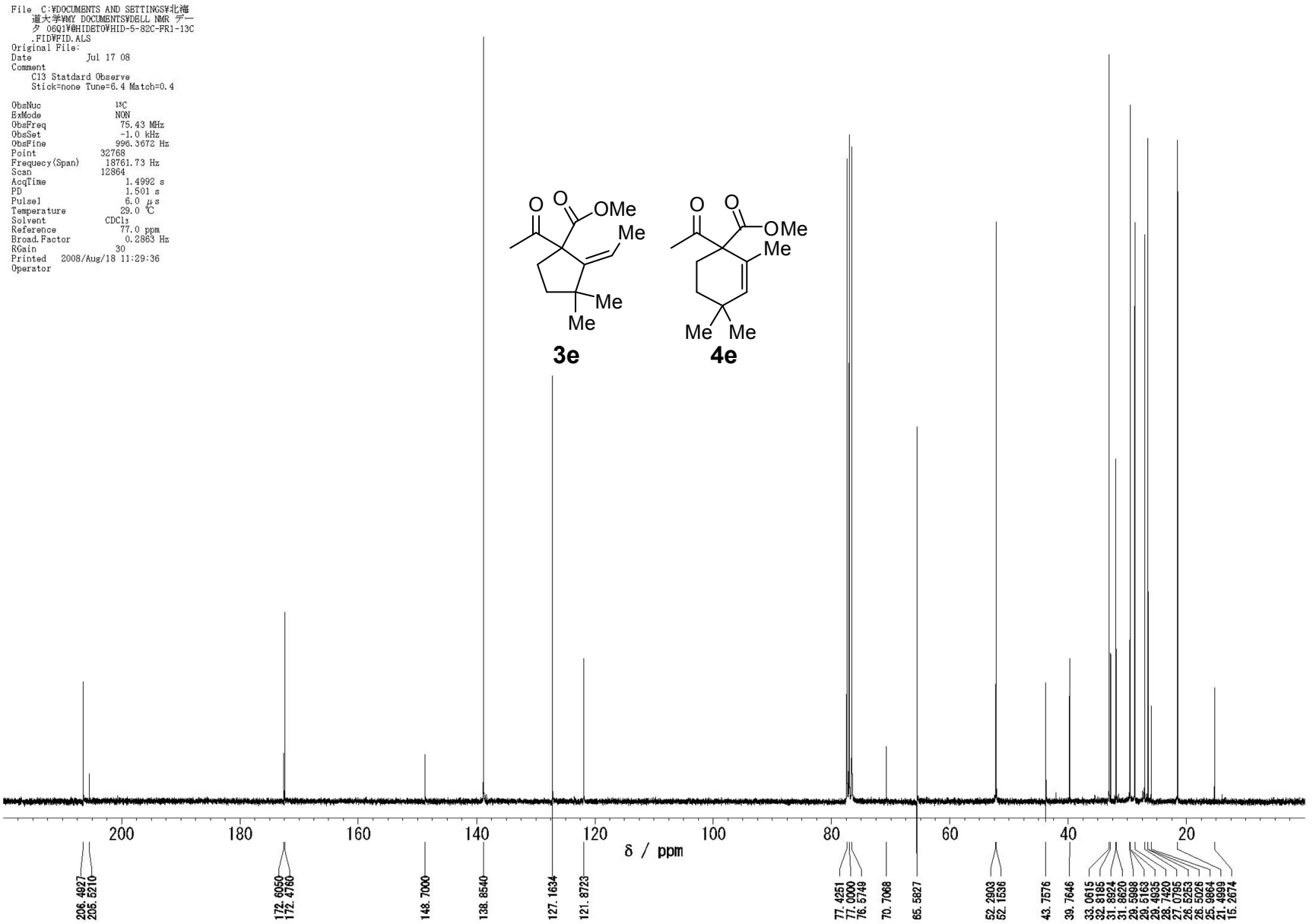
Original File:
Date Jul 17 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/18 11:26:46
Operator
3e
4e
δ / ppm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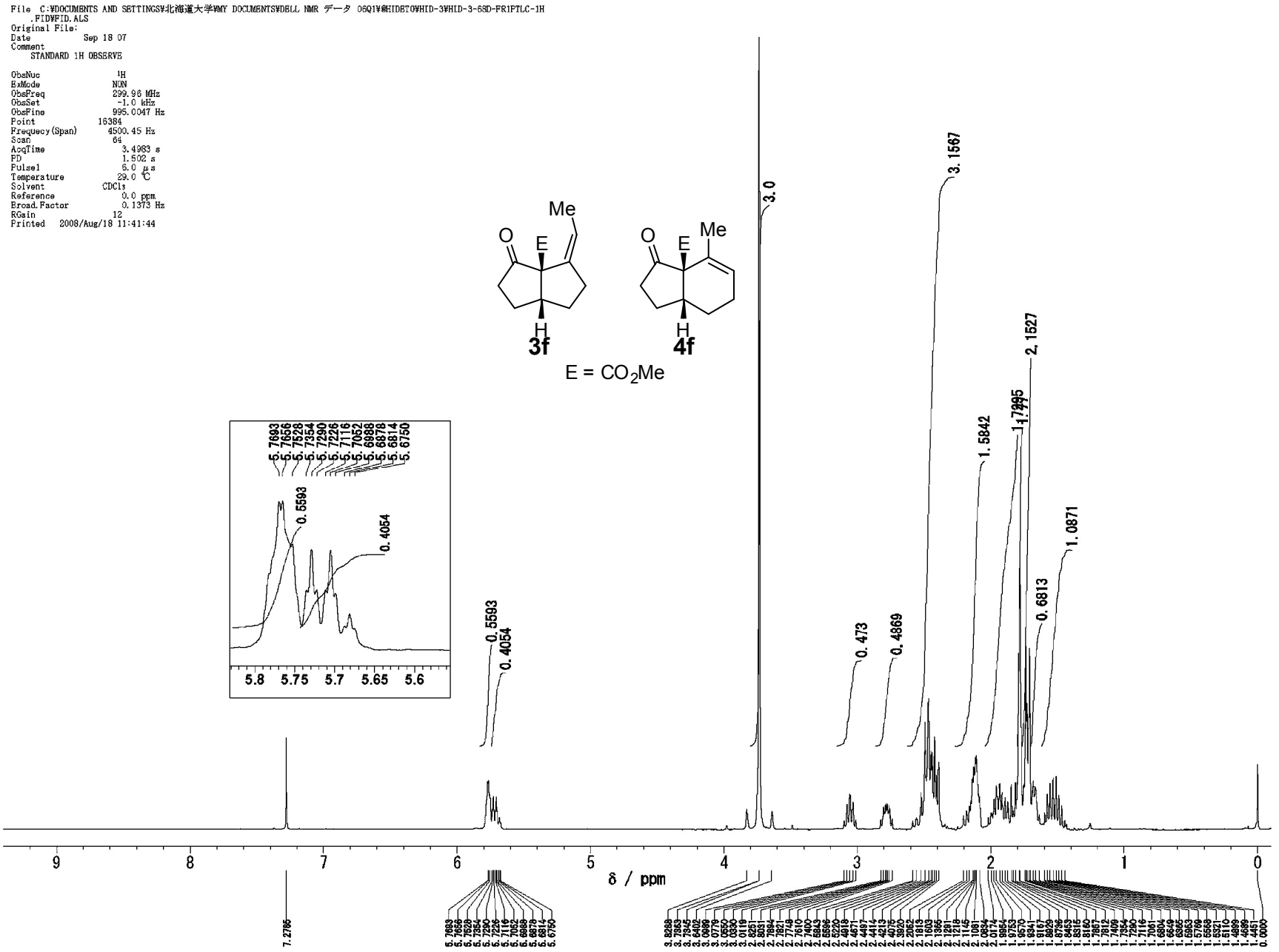
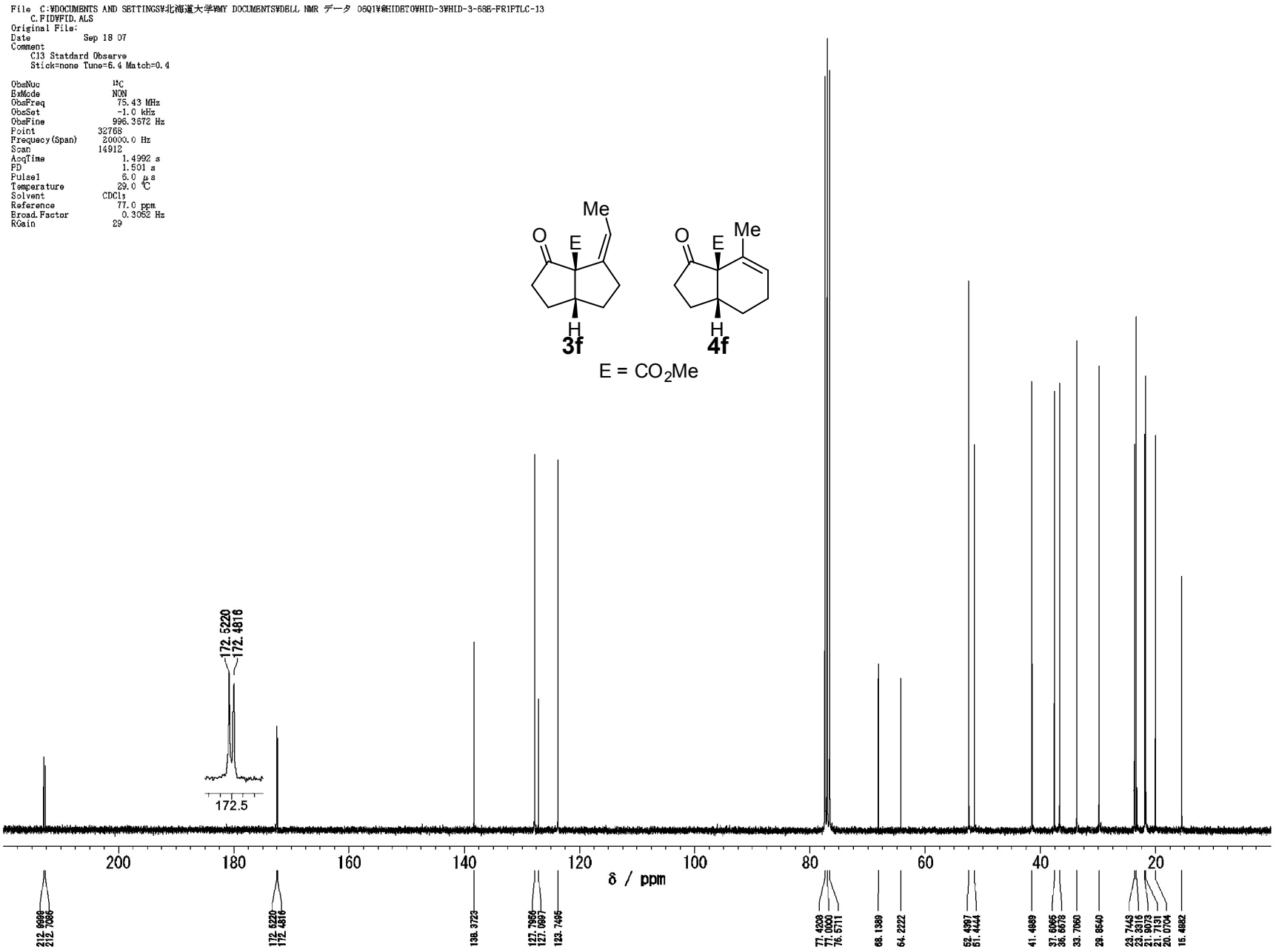
Original File:
Date Jul 17 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 12864
AcqTime 1.4992 s
PD 1.501 s
Pulsel 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 11:29:36
Operator
O
O
OMe
Me
Me
Me
3e
O
O
OMe
Me
Me Me
4e
200
180
160
140
120
100
80
60
40
20
δ / ppm
206.4927
205.5210
172.6050
172.4760
148.7000
138.8540
127.1634
121.8723
77.4251
77.0000
76.5749
70.7068
65.5827
52.2903
52.1536
43.7576
39.7646
33.0615
32.8185
31.8924
31.8620
29.5998
29.5163
29.4935
28.7420
27.0795
26.5253
26.5026
25.9864
21.4999
15.2674


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-3¥HID-3-68D-FR1PTLC-1H
.FID¥FID.ALS
Original File:
Date Sep 18 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 64
AcqTime 3.4983 s
PD 1.502 s
Pulse1 8.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 12
Printed 2008/Aug/18 11:41:44
Me
O
E
H
3f
O
E
Me
H
4f
E = CO2Me
3.0
3.1567
2.1527
1.5842
1.0871
0.6813
0.4869
0.473
0.5593
0.4054
δ / ppm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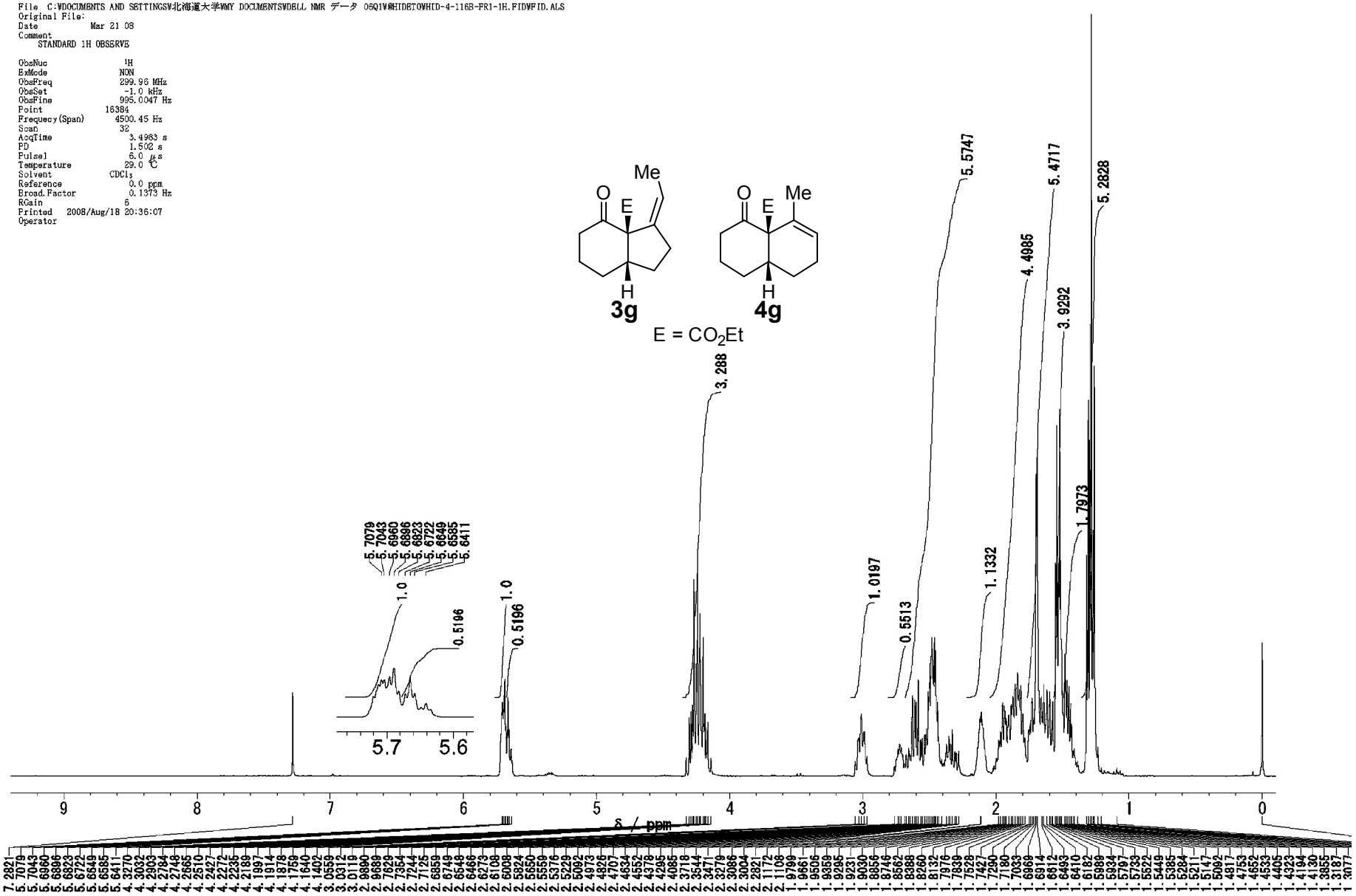
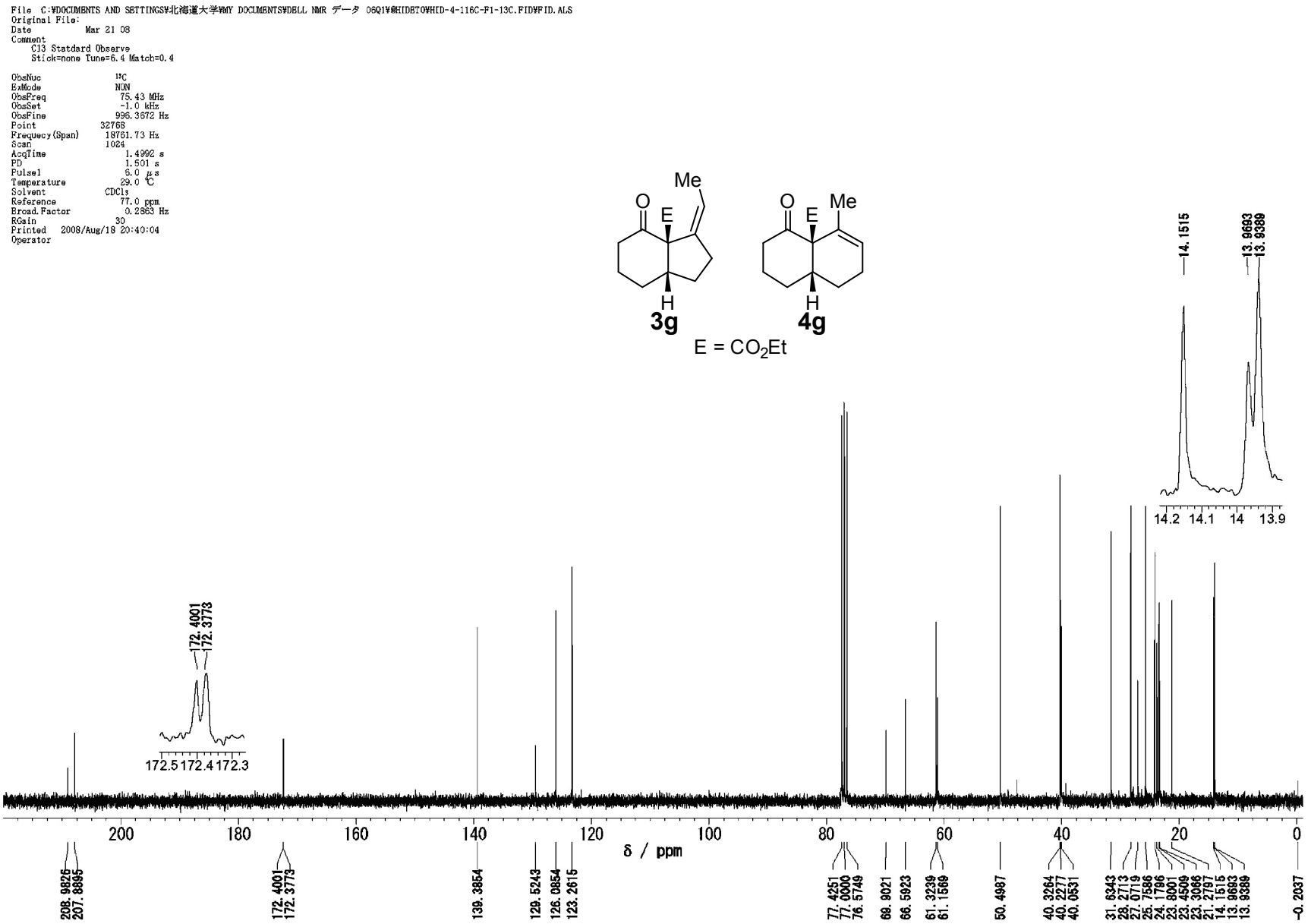
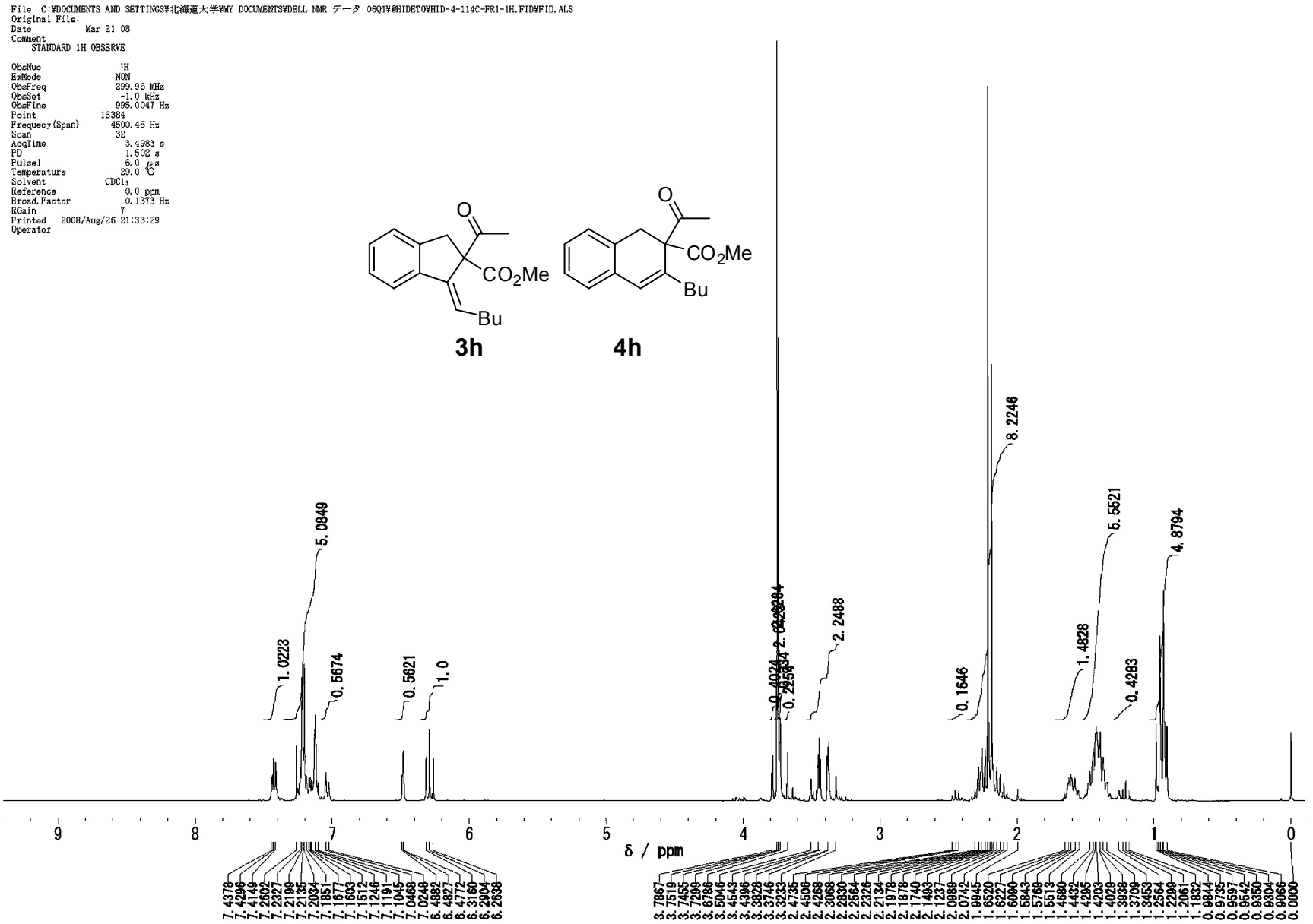
C.FID¥FID.ALS
Original File:
Date Sep 18 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 20000.0 Hz
Scan 14912
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.3052 Hz
RGain 29
Me
O
E
H
3f
Me
O
E
H
4f
E = CO2Me
172.5220
172.4816
172.5
δ / ppm
212.8998
212.7086
172.5220
172.4816
136.3723
127.7966
127.0897
123.7495
77.4208
77.0000
76.5711
68.1388
64.2222
52.4397
51.4444
41.4989
37.6065
36.6678
33.7060
29.8540
23.7443
23.3316
21.9073
21.7131
20.0704
15.4982


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥森HIDETO¥HID-4-116B-FR1-1H.FID¥FID.ALS
Original File:
Date Mar 21 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 6
Printed 2008/Aug/18 20:36:07
Operator
Me
O
E
H
3g
O
E
Me
H
4g
E = CO2Et
5.7079
7043
6960
6896
6823
6722
6649
6585
6411
1.0
0.5196
1.0
0.5196
3.288
1.0197
0.5513
5.5747
1.1332
4.4985
5.4717
3.9292
1.7973
5.2828
5.7
5.6
9
8
7
6
5
4
3
2
1
0
δ / ppm


File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥森HIDETO¥HID-4-116C-F1-13C.FID¥FID.ALS
Original File:
Date Mar 21 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 1024
AcqTime 1.4992 s
FD 1.501 s
Pulse1 9.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 20:40:04
Operator
Me
O
E
H
3g
O
E
Me
H
4g
E = CO2Et
14.1515
13.9693
13.9389
14.2 14.1 14 13.9
172.4001
172.3773
172.5 172.4 172.3
δ / ppm
208.9826
207.8895
172.4001
172.3773
139.3854
129.5243
126.0854
123.2615
77.4251
77.0000
76.5749
68.9021
66.5923
61.3239
61.1569
50.4987
40.3264
40.2277
40.0531
31.6343
28.2713
27.0719
25.7586
24.1796
23.8001
23.4509
23.3086
21.2797
14.1515
13.9693
13.9389
-0.2037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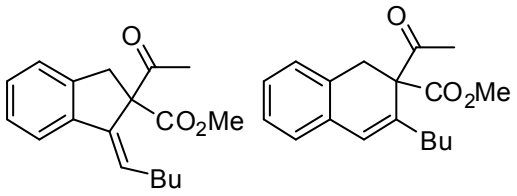
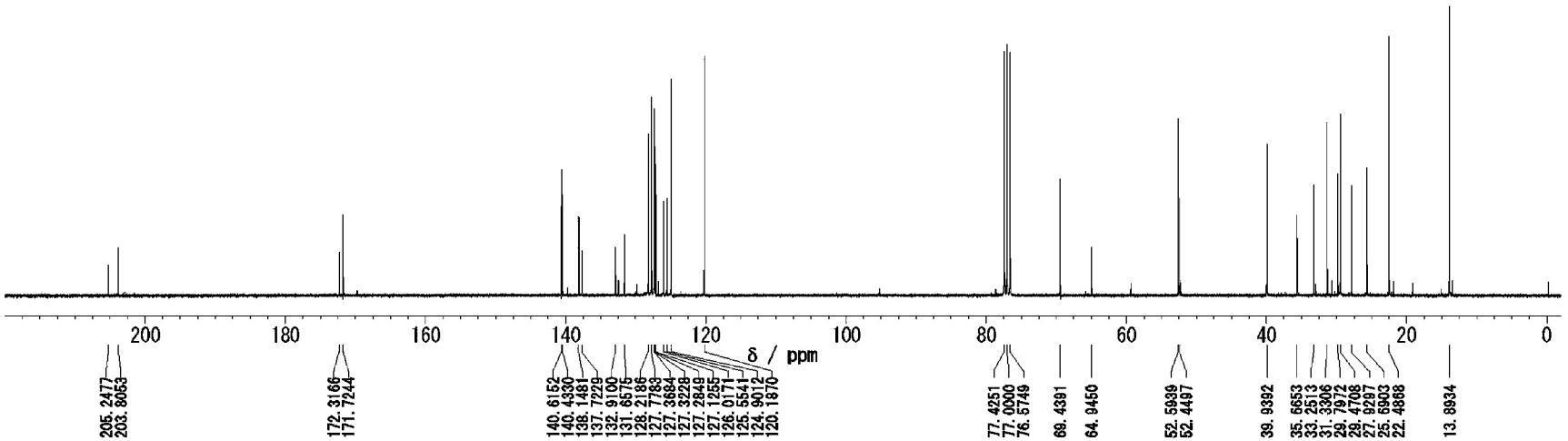
Original File:
Date Mar 21 08
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 7
Printed 2008/Aug/26 21:33:29
Operator
O
CO2Me
Bu
3h
O
CO2Me
Bu
4h
1.0223
5.0849
0.5674
0.5621
1.0
0.4024
2.2488
0.1646
8.2246
1.4828
5.5521
0.4283
4.8794
9
8
7
6
5
4
3
2
1
0
δ / ppm

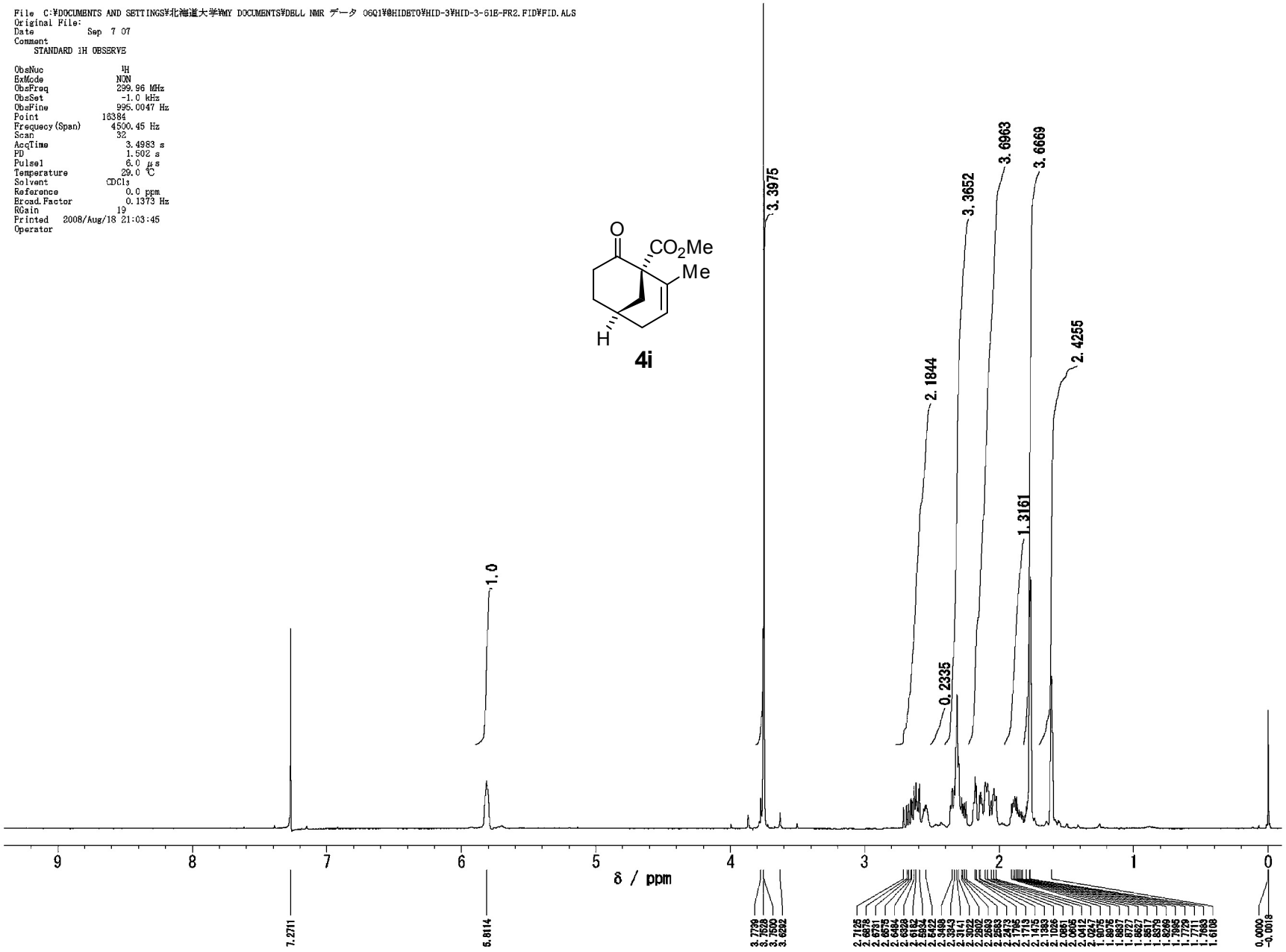
File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥各HIDETO¥HID-4-114D-FR1-13C.FID¥FID.ALS
Original File:
Date Mar 21 08
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4

ObsNuc	^{13}C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsFine	996.3672 Hz
Point	32768
Frequecy(Span)	18761.73 Hz
Scan	8896
AcqTime	1.4992 s
PD	1.501 s
Pulse1	9.0 μs
Temperature	29.0 ℃
Solvent	CDCl3
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2008/Aug/26 21:35:40
Operator	



3h **4h**

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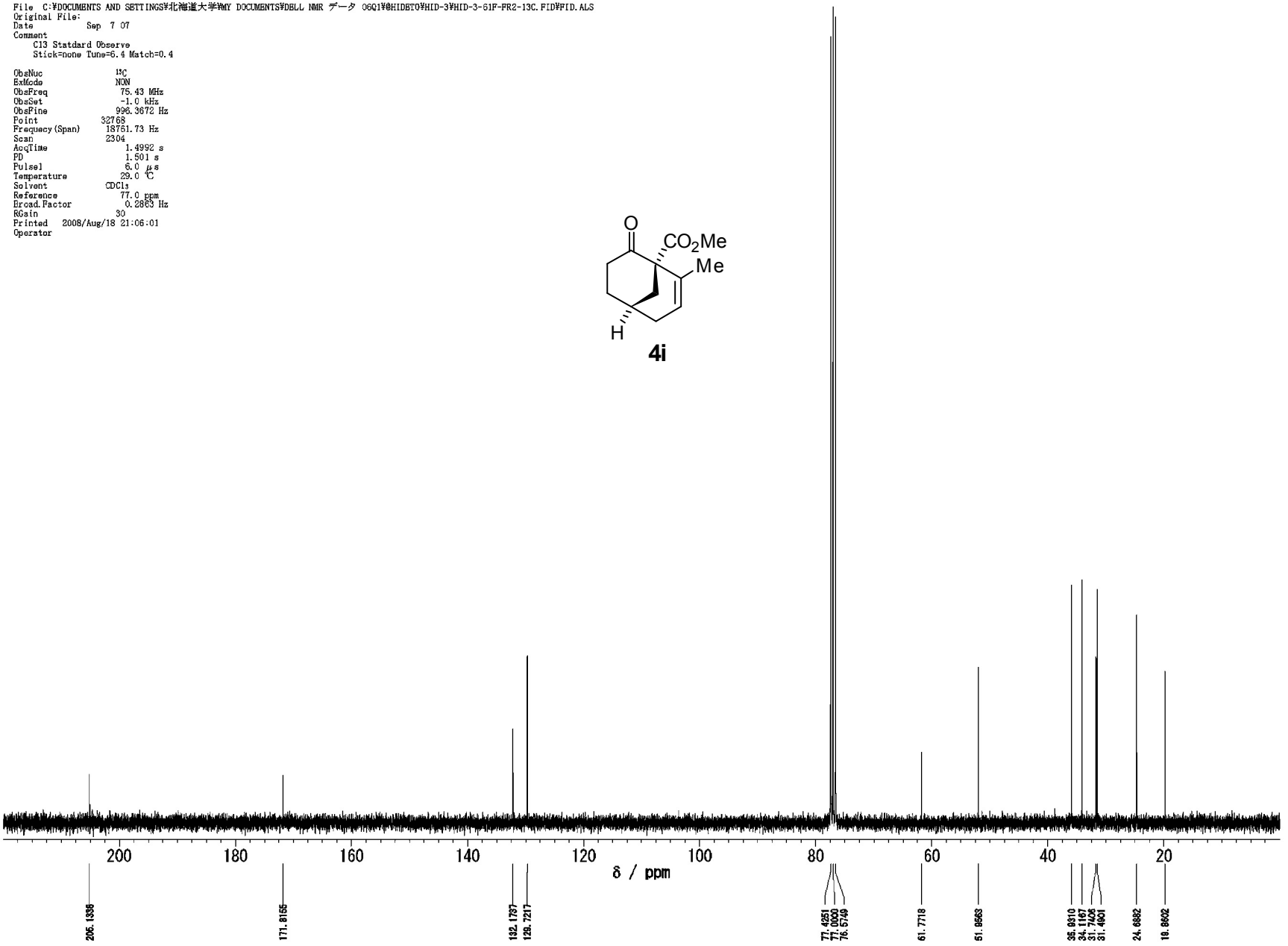
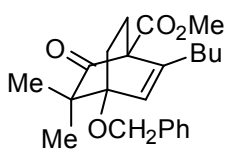
Original File:
Date Sep 7 07
Comment
STANDARD 1H OBSERVE
ObsNuc 1H
ExMode NON
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequecy(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 19
Printed 2008/Aug/18 21:03:45
Operator
O
CO2Me
Me
H
4i
3.3975
3.6963
3.3652
3.6669
2.1844
2.4255
1.3161
0.2335
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2711
6.8114

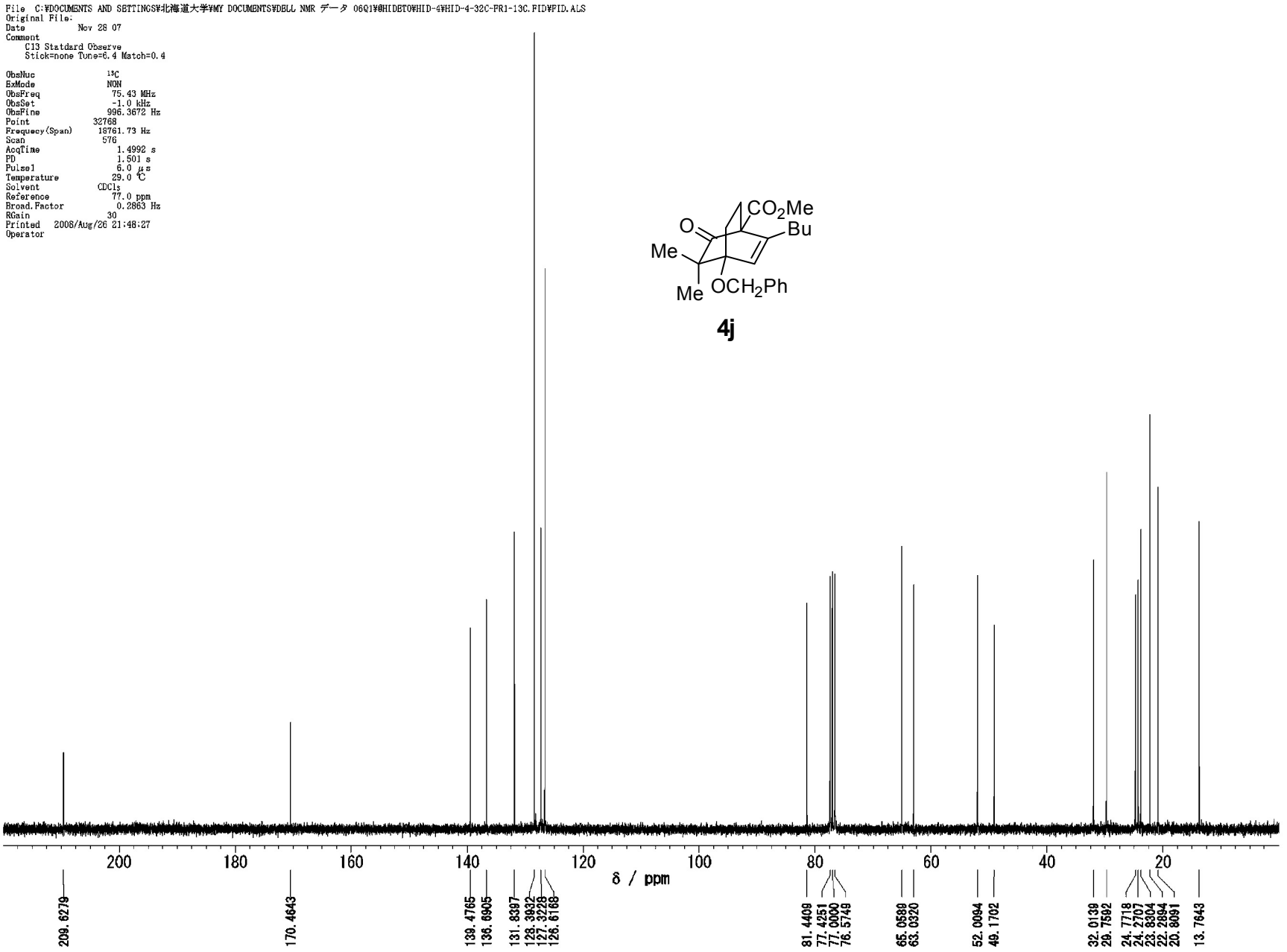

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DELL NMR データ 06Q1¥0HIDETO¥HID-3¥HID-3-61F-FR2-13C.FID¥FID.ALS
Original File:
Date Sep 7 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsPine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 2304
AcqTime 1.4992 s
PD 1.501 s
Pulsel 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/18 21:06:01
Operator
O
CO2Me
Me
H
4i
200
180
160
140
120
100
80
60
40
20
δ / ppm
206.1338
171.8165
132.1737
129.7217
77.4251
77.0000
76.5749
61.7718
51.9563
35.8310
34.1167
31.7406
31.4901
24.6882
18.8602

File C:¥DOCUMENTS AND SETTINGS¥北海道大学¥MY DOCUMENTS¥DBLL NMR データ 06Q1¥0HIDETO¥HID-4¥HID-4-32B-FR1-1H.FID¥FID.ALS
Original File:
Date Nov 28 07
Comment
STANDARD 1H OBSERVE

ObsNuc	^{1}H
ExMode	NON
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsPine	995.0047 Hz
Point	16384
Frequecy(Span)	4500.45 Hz
Scan	32
AcqTime	3.4983 s
PD	1.502 s
Pulse1	6.0 μs
Temperature	29.0 ℃
Solvent	CDCl$_3$
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	6
Printed	2008/Aug/26 21:51:55
Operator	



4j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Original File:
Date Nov 28 07
Comment
C13 Statdard Observe
Stick=none Tune=6.4 Match=0.4
ObsNuc 13C
ExMode NON
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsPine 996.3672 Hz
Point 32768
Frequecy(Span) 18761.73 Hz
Scan 576
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2008/Aug/26 21:48:27
Operator
CO2Me
Bu
O
Me
Me
OCH2Ph
4j
200
180
160
140
120
100
80
60
40
20
δ / ppm
209.6279
170.4643
139.4765
136.6905
131.8397
128.3932
127.3228
126.6168
81.4409
77.4251
77.0000
76.5749
65.0588
63.0320
52.0094
49.1702
32.0139
29.7592
24.7718
24.2707
23.8304
22.2894
20.8091
13.7643