Enantioselective Iodolactonization of Allenoic Acids

*Kenichi Murai**, *Nozomi Shimizu, and Hiromichi Fujioka**

Graduate School of Pharmaceutical Sciences, Osaka University,

1-6, Yamada-oka, Suita, Osaka, 565-0871 (Japan)

Tel: (+81) 6-6879-8225, Fax: (+81) 6-6879-8229

E-mail: *murai@phs.osaka-u.ac.jp, fujioka@phs.osaka-u.ac.jp*

Electronic Supplementary Information

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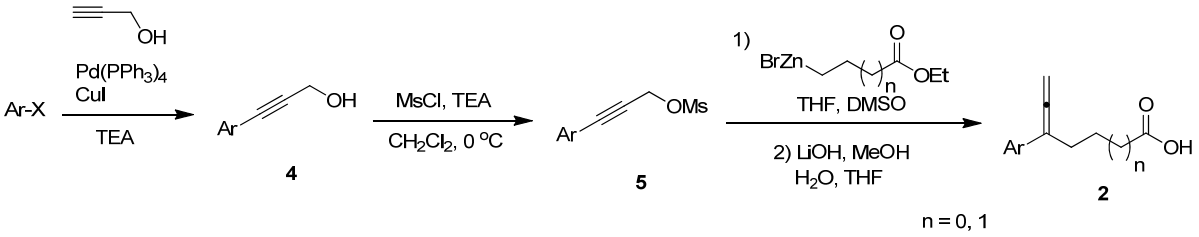
1. General

Melting points were measured by BÜCHI B-545 and all melting points were uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were measured by JEOL JNM-ECS 400, JEOL ECS 300 or JEOL JNM-LA 500 spectrometers with tetramethylsilane as an internal standard. IR spectra were recorded by Shimadzu FTIR 8400 using a diffuse reflectance measurement of samples dispersed in KBr powder. Optical rotation was measured by JASCO P-1020. High resolution mass spectra and elemental analysis were performed by the Elemental Analysis Section of Osaka University. Enantiomeric excesses (ee) were measured by chiral HPLC analysis: DAICEL CHIRALPAK AD-H, IC columns and DAICEL CHIRALCEL OD-H columns using a multiwavelength detector JASCO MD-2010. Column chromatography was performed with SiO_2 (Merck Silica Gel 60 (230-400 mesh) or Kanto Chemical Silicagel 60 (spherical, 63-210 μm).

Unless otherwise noted, materials were purchased from Aldrich Inc., Kanto Kagaku, Wako Chemicals, and other commercial suppliers and were used without purification.

2. Preparation of allenoic acids

Allenoic acids were synthesized by the hydrolysis of corresponding allenoic esters, which were prepared from propargyl mesylates and zinc reagents according to the procedure reported by Kondo et al. [1]



General procedure A (Synthesis of alcohol 4)

To the solution of arylhalide and propargyl alcohol in triethylamine was added $Pd(PPh_3)_4$ and CuI under N_2 and the resulting reaction mixture was stirred at rt (for ArI) or under reflux (for ArBr). After the reaction completed, the reaction mixture was diluted with AcOEt and filtered through short pad SiO_2 (eluent AcOEt). The filtrate was concentrated in vacuo and the residue was purified by SiO_2 column chromatography to give alcohol **4**.

General procedure B (Synthesis of mesylate 5)

To the solution of alcohol **4** and triethylamine in CH_2Cl_2 was added MsCl at 0 ^{o}C under N_2 and the resulting reaction mixture was stirred at the same temperature. After the reaction completed, H_2O was added to the reaction mixture and the resulting solution was extracted with AcOEt. The organic layer was washed with H_2O, 5% HCl aq., sat. $NaHCO_3$ aq, and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography to give mesylate **5**.

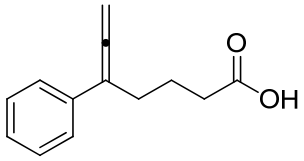
General procedure C (Synthesis of allenoic acid 2)

To the solution of mesylate **2** in DMSO was added 4-ethoxy-4-oxobutylzinc bromide or 3-ethoxy-3-oxopropylzinc bromide (0.5 M solution in THF) at rt under Ar and the resulting reaction mixture

[1] K. Kobayashi, H. Naka, A. E. H. Wheatley, and Y. Kondo, *Org. Lett.*, 2008, **10**, 3375.

was stirred at the same temperature. After the reaction completed, NH_4Cl aq. was added to the reaction mixture at 0 °C and the resulting solution was extracted with AcOEt. The organic layer was washed with H_2O and brine, dried over with Na_2SO_4 and concentrated *in vacuo*. The residue was roughly purified by SiO_2 column chromatography to give allenoic ester. Although the products included impurities, it was subjected subsequent hydrolysis. To the solution of crude allenoic ester in THF/MeOH/H_2O (3/1/1) was added LiOH and the resulting solution was stirred at rt. After the reaction completed, THF was removed by evaporator and the resulting mixture was acidified with 10% HCl aq. at 0 °C and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography to give allenoic acid **2**.

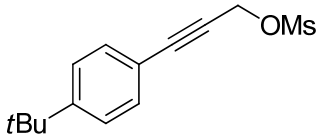
5-Phenylhepta-5,6-dienoic acid (2a)



The reaction was carried out according to the general procedure C (nucleophilic substitution: 3-phenylprop-2-yn-1-yl methanesulfonate[2] (209 mg, 0.994 mmol) and 4-ethoxy-4-oxobutylzinc bromide (2.0 ml, 0.5 M solution in THF, 1.0 mmol) in DMSO (2.0 ml); hydrolysis: LiOH (60 mg, 2.5 mmol) in THF/MeOH/H_2O (3/1/1, 4 ml)) to give **2a** (68.6 mg, 34%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 12/1; 2nd step Hexane/AcOEt = 3/1).

Colorless solid; Mp: 109-110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.41-7.17 (m, 5H), 5.11 (t, *J* = 3.3 Hz, 2H), 2.53-2.44 (m, 4H), 1.97-1.87 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.4, 179.7, 135.9, 128.4, 126.7, 125.9, 104.0, 78.8, 33.4, 28.6, 22.7 ppm; IR (KBr): 3039, 2954, 1938, 1705, 1452, 1286, 1201 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{13}H_{15}O_2$ [*M*+H]$^+$: 203.1066, found 203.1062.

3-(4-*tert*-Butylphenyl)prop-2-yn-1-yl methanesulfonate (5b)



The reaction was carried out according to the general procedure B with 3-(4-*tert*-butylphenyl)prop-2-yn-1-ol[3] (558 mg, 2.96 mmol), MsCl (0.3 ml, 0.39 mmol), and triethylamine (0.8 ml, 5.7 mmol) in CH_2Cl_2 (10 ml) to give **5b** (547 mg, 69%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Colorless solid; Mp: 75-76 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.41-7.35 (m, 4H), 5.09 (s, 2H), 3.16 (s, 3H), 1.31 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 152.9, 131.7, 125.5, 118.0, 89.7, 80.1, 58.7, 39.1, 34.8, 31.0 ppm; IR (KBr): 2964, 2225, 1506, 1365, 1176 cm^{-1}; HRMS ((MALDI-TOF)): calcd for $C_{14}H_{18}O_3NaS$ [*M*+Na]$^+$: 289.0868, found 289.0866.

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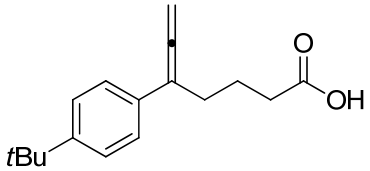
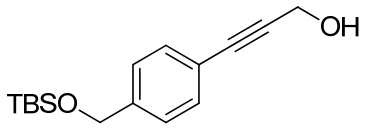
2 A. Claesson, and C. Sahlberg, *Tetrahedron* 1982, **38**, 363.
3 S. Kusaka, R. Sakamoto, Y. Kitagawa, M. Okumura, and H. Nishihara, *Chem. Asian J.* 2013, **8**, 723.

5-(4-*tert*-Butylphenyl)hepta-5,6-dienoic acid (2b)



The reaction was carried out according to the general procedure C (nucleophilic substitution: **5b** (225 mg, 0.845 mmol) and 4-ethoxy-4-oxobutylzinc bromide (3.5 ml, 0.5 M solution in THF, 1.75 mmol) in DMSO (3.5 ml); hydrolysis: LiOH (80 mg, 3.34 mmol) in THF/MeOH/H_2O (3/1/1, 5 ml)) to give **2b** (110.6 mg, 51%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 3/1). Colorless solid; Mp: 75-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.37-7.31 (m, 4H), 5.09 (t, *J* = 3.3 Hz, 2H), 2.52-2.44 (m, 4H), 1.96-1.86 (m, 2H) 1.31 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.3, 179.7, 149.7, 132.9, 125.6, 125.4, 103.7, 78.6, 34.4, 33.4, 31.3, 28.6, 22.7 ppm; IR (KBr): 3047, 2960, 1940, 1699, 1512, 1408, 1203 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{22}O_2Na$ [*M*+Na]$^+$: 281.1512, found 281.1510.

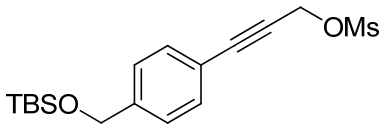
3-(4-((*tert*-Butyldimethylsilyloxy)methyl)phenyl)prop-2-yn-1-ol (4c)



The reaction was carried out according to the general procedure A with *tert*-butyl((4-iodobenzyloxy)dimethylsilane[4] (561 mg, 1.61 mmol), propargyl alcohol (0.3 ml, 5.1 mmol), $Pd(PPh_3)_4$ (18.5 mg, 0.016 mmol) and CuI (13.5 mg, 0.07 mmol) in triethylamine (10 ml) to give **4c** (436 mg, 98%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.38 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.71 (s, 2H), 4.88 (d, *J* = 5.8 Hz, 2H), 0.92 (s, 9H), 0.08 ppm (s, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ= 142.0, 131.6, 125.9, 120.9, 86.7, 85.8, 64.6, 51.7, 25.9, 18.4, -5.3 ppm; IR (KBr): 3280, 2954, 2929, 2858, 1257, 839 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{24}NaO_2Si$ [*M*+Na]$^+$: 299.1443, found 299.1432.

3-(4-((*t*ert-Butyldimethylsilyloxy)methyl)phenyl)prop-2-yn-1-yl methanesulfonate (5c)



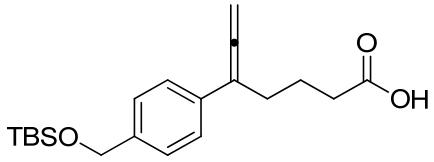
The reaction was carried out according to the general procedure B with **4c** (436.3 mg, 1.58 mmol), MsCl (0.2 ml, 2.58 mmol), and triethylamine (0.5 ml, 3.6 mmol) in CH_2Cl_2 (10 mL) to give **5c** (515.5 mg, 92%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.42-7.39 (m, 2H), 7.29-7.26 (m, 2H), 5.07 (s, 2H), 4.72 (s, 2H), 3.14 (s, 3H), 0.92 (s, 9H), 0.08 ppm (s, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ= 143.2, 131.9, 126.0, 119.5,

[4] T. Sato, K. Sugimoto, A. Inoue, S. Okudaira, J. Aoki, and H. Tokuyama, *Bioorg. Med. Chem. Lett.* 2012, **22**, 4323

89.6, 80.3, 64.5, 58.5, 39.1, 25.9, 18.4, -5.3 ppm; IR (KBr): 2929, 1365, 1259, 1176 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{26}O_4NaSiS$ $[M+Na]^+$: 377.1213, found 377.1213.

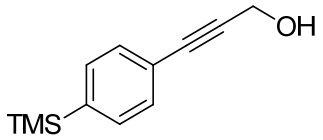
5-(4-((*tert*-Butyldimethylsilyloxy)methyl)phenyl)hepta-5,6-dienoic acid (2c)



The reaction was carried out according to the general procedure C (nucleophilic substitution: **5c** (510 mg, 1.44 mmol) and 4-ethoxy-4-oxobutylzinc bromide (5.8 ml, 0.5 M solution in THF, 2.9 mmol) in DMSO (5.8 ml); hydrolysis: LiOH (133 mg, 5.55 mmol) in THF/MeOH/H_2O (3/1/1, 3 ml)) to give **2c** (160.4 mg, 32%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 12/1; 2nd step Hexane/AcOEt = 4/1).

Colorless solid; Mp: 74-76; ^1H NMR (300 MHz, $CDCl_3$): δ= 7.34 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 5.09-5.07 (m, 2H), 4.70 (s, 2H), 2.49-2.42 (m, 4H), 1.92-1.86 (m, 2H), 0.92 (s, 9H), 0.07 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.4, 178.1, 140.0, 134.5, 126.2, 125.8, 103.9, 78.7, 64.7, 33.1, 28.7, 25.9, 22.7, 18.4, -5.3 ppm; IR (KBr): 2953, 2929, 1707, 1257, 1091, 839 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{30}NaO_3Si$ $[M+Na]^+$: 369.1862, found 369.1867.

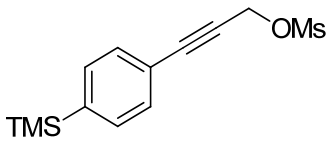
3-(4-Trimethylsilylphenyl)prop-2-yn-1-ol (4d)



The reaction was carried out according to the general procedure A with (4-bromophenyl)trimethylsilane (1.35 g, 5.89 mmol), propargyl alcohol (0.7 ml, 11.8 mmol), $Pd(PPh_3)_4$ (68 mg, 0.059 mmol) and CuI (22 mg, 0.116 mmol) in triethylamine (10 ml) to give **4d** (263.9 mg, 22%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 7/2

Pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ= 7.46-7.43 (m, 2H), 7.40-7.37 (m, 2H), 4.48 (d, J = 5.1 Hz, 2H), 0.24 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 141.4, 133.2, 130.7, 122.7, 87.5, 85.8, 51.7, -1.28 ppm; IR (KBr): 3325, 2954, 1249, 1109 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{12}H_{16}OSiNa$ $[M+Na]^+$: 227.0868, found 227.0878.

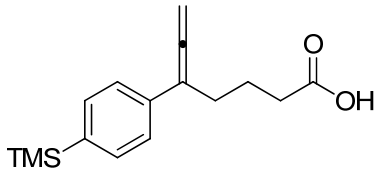
3-(4-Trimethylsilylphenyl)prop-2-yn-1-yl methanesulfonate (5d)



The reaction was carried out according to the general procedure B with **4d** (258.7 mg, 1.27 mmol), MsCl (0.15 ml, 1.94 mmol), and triethylamine (0.4 ml, 2.87 mmol) in CH_2Cl_2 (12 mL) to give **5d** (286.3 mg, 80%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.49-7.40 (m, 4H), 5.07 (s, 2H), 3.14 (s, 3H), 0.25 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 142.8, 133.3, 130.9, 121.3, 89.6, 81.0, 58.5, 39.1, -1.34 ppm; IR (KBr): 2956, 1361, 1176 cm^{-1}; HRMS (FAB): calcd for $C_{13}H_{18}O_3SSiNa$ [*M*+Na]$^+$: 305.0644, found 305.0644.

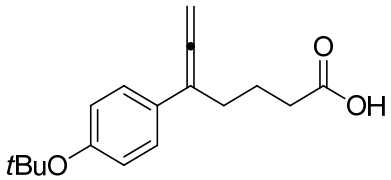
5-(4-Trimethylsilylphenyl)hepta-5,6-dienoic acid (2d)



The reaction was carried out according to the general procedure C (nucleophilic substitution: **5d** (272.9 mg, 0.97 mmol) and 4-ethoxy-4- oxobutylzinc bromide (4 ml, 0.5 M solution in THF, 2 mmol) in DMSO (4 ml); hydrolysis: LiOH (70 mg, 2.92 mmol) in THF/MeOH/H_2O (3/1/1, 5 ml)) to give **2d** (87.1 mg, 33%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 12/1; 2nd step Hexane/AcOEt = 4/1).

Colorless solid; Mp: 104-105 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.47 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 5.12-5.09 (m, 2H), 2.53-2.44 (m, 4H), 1.97-1.87 (m, 2H), 0.26 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.6, 178.3, 138,8, 136.4, 133.5, 125.2, 104.0, 78.7, 33.1, 28.6, 22.7, -1.2 ppm; IR (KBr): 2953, 1712 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{22}O_2SiNa$ [*M*+Na]$^+$: 297.1287, found 297.1281.

5-(4-*tert*-Butoxyphenyl)hepta-5,6-dienoic acid (2e)



The reaction was carried out according to the general procedure B with 3-(4-(*tert*-butoxyphenyl)prop-2-yn-1-ol[5] (450.9 mg, 2.21 mmol), MsCl (0.3 ml, 3.88 mmol), and triethylamine (1.0 ml, 7.2 mmol) in CH_2Cl_2 (6 ml) to give crude 3-(4-*tert*-butoxyphenyl)prop-2-yn-1-yl methanesulfonate. This mesylate was used directly without the purification by SiO_2 column chromatography to the next transformation after the extraction and concentration. The following reaction was carried out according to the general procedure C (nucleophilic substitution: obtained crude mesylate and 4-ethoxy-4-oxobutylzinc bromide (8 ml, 0.5 M solution in THF, 4 mmol) in DMSO (8 ml); hydrolysis: LiOH (300 mg, 12.5 mmol) in THF/MeOH/H_2O (3/1/1, 5 ml)) to give **2e** (228.6 mg, 38%, 3 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 9/1; 2nd step Hexane/AcOEt = 3/1).

Colorless solid; Mp: 84-85^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.29 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 5.10 (t, *J* = 3.0 Hz, 2H), 2.45-2.43 (m, 4H), 1.96-1.86 (m, 2H), 1.34 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.2, 179.3, 154.2, 130.8, 126.3, 124.2, 103.7, 78.8, 78.6, 33.4, 28.8, 28.7, 22.7 ppm; IR (KBr): 3035, 2976, 1938, 1708, 1506, 1238, 1163 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{22}O_3Na$ [*M*+Na]$^+$: 297.1461, found 297.1462.

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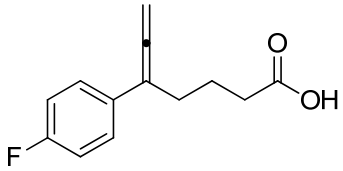
[5] J. P. Davidson, O. Lubman, T. Rose, G. Waksman, and S. F. Martin, *J. Am. Chem. Soc.* 2002, **124**. 205

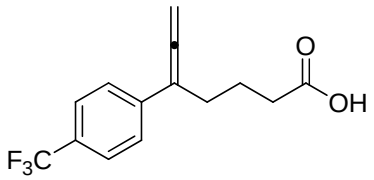
5-(4-Fluorophenyl)hepta-5,6-dienoic acid (2f)



The reaction was carried out according to the general procedure C (nucleophilic substitution: 3-(4-fluorophenyl)prop-2-yn-1-yl methanesulfonate[6] (540 mg, 2.37 mmol) and 4-ethoxy-4-oxobutylzinc bromide (9.5 ml, 0.5 M solution in THF, 4.75 mmol) in DMSO (9.5 ml); hydrolysis: LiOH (227 mg, 9.48 mmol) in THF/MeOH/H_2O (3/1/1, 3 ml)) to give **2f** (127 mg, 24%). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 3/1).

Colorless solid; Mp: 109-110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.37-7.32 (m, 2H), 7.03-6.97 (m, 2H), 5.11 (t, *J* = 3.1 Hz, 2H), 2.49-2.42 (m, 4H), 1.90 ppm (tt, *J* = 7.4 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.2, 179.4, 161.8 (d, *J* = 245.9 Hz), 131.8 (d, *J* = 3.5 Hz), 127.4 (d, *J* = 7.3 Hz), 115.3 (d, *J* = 21.6 Hz), 103.3, 79.0, 33.3, 28.8, 22.6 ppm; IR (KBr): 3070, 1710, 1510, 1232 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{13}H_{13}O_2FNa$ [*M*+Na]$^+$: 243.0791, found 243.0780.

5-(4-Trifluoromethylphenyl)hepta-5,6-dienoic acid (2g)



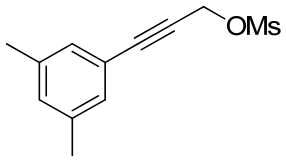
The reaction was carried out according to the general procedure C (nucleophilic substitution: 3-(4-trifluoromethylphenyl)prop-2-yn-1-yl methanesulfonate [7] (949 mg, 3.41 mmol) and 4-ethoxy-4-oxobutylzinc bromide (12 ml, 0.5 M solution in THF, 6 mmol) in DMSO (12 ml); hydrolysis: LiOH (250 mg, 10.4 mmol) in THF/MeOH/H_2O (3/1/1, 5 ml)) to give **2g** (135 mg, 15%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 3/1).

Colorless solid; Mp: 71-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.56 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 5.18 (t, *J* = 3.2 Hz, 2H), 2.52-2.47 (m, 4H), 1.92 ppm (tt, *J* = 7.4 Hz, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.8, 179.5, 139.9, 128.6 (q, *J* = 32.4 Hz), 126.1, 125.3 (q, *J* = 3.0 Hz), 124.2 (q, *J* = 272 Hz), 103.5, 79.4, 33.3, 28.4, 22.6 ppm; IR (KBr): 3041, 1938, 1714, 1325, 1126 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{14}H_{14}O_2F_3$ [*M*+H]$^+$: 271.0940, found 271.0948.

[6] L. Jeppesen, P. H. et al *J. Med. Chem.* 1999, **42**, 1999.

[7] T. J. Martins, K. W. Fowler, J. Odingo, E. A. Kesicki, A. Oliver, L. E. Burgess, J. J. Gaudino, Z. S. Jones, B. J. Newhouse, S. T. Schlachter, U.S. Patent 6423710B1, 2002.

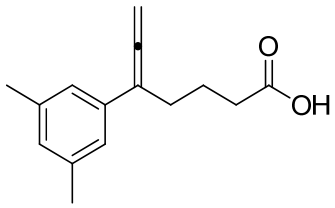
3-(3,5-Dimethylphenyl)prop-2-yn-1-yl methanesulfonate (5h)



The reaction was carried out according to the general procedure B with 3-(3,5-dimethylphenyl)prop-2-yn-1-ol[8] (467.1 mg, 2.92 mmol), MsCl (0.3 ml, 4.4 mmol), and triethylamine (1.2 ml, 8.8 mmol) in CH_2Cl_2 (15 mL) to give **5h** (607.3 mg, 87%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.09 (s, 2H), 7.02 (s, 1H), 5.08 (s, 2H), 3.16 (s, 3H), 2.30 ppm (s, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ= 138.2, 131.4, 129.6, 120.7, 89.9, 80.0, 58.6, 39.2, 21.1 ppm; IR (KBr): 2228, 1599, 1352, 1174 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{12}H_{14}O_3NaS$ [*M*+H]$^+$: 261.0555, found 261.0555.

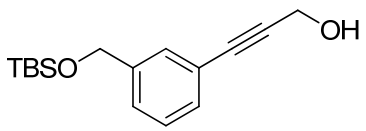
5-(3,5-Dimethylphenyl)hepta-5,6-dienoic acid (2h)



The reaction was carried out according to the general procedure C (nucleophilic substitution: **5h** (603.5 mg, 2.53 mmol) and 4-ethoxy-4-oxobutylzinc bromide (10 ml, 0.5 M solution in THF, 5 mmol) in DMSO (10 ml); hydrolysis: LiOH (240 mg, 10.0 mmol) in THF/MeOH/H_2O (3/1/1, 8 ml)) to give **2h** (267.1 mg, 46%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 12/1; 2nd step Hexane/AcOEt = 4/1).

Colorless solid; Mp: 117-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.01 (s, 2H), 6.85 (s, 1H), 5.08 (d, *J* = 3.7 Hz, 1H), 5.08 (d, *J* = 3.2 Hz, 1H), 2.49-2.43 (m, 4H), 2.30 (s, 6H), 1.94-1.88 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.4, 179.5, 137.9, 135.8, 128.5, 123.8, 104.0, 78.4, 33.4, 28.8, 22.8, 21.3 ppm; IR (KBr): 3041, 2960, 1932, 1710, 1597, 1429, 1273 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{15}H_{19}O_2$ [*M*+H]$^+$: 231.1379, found 231.1379.

3-(3-((*tert*-Butyldimethylsilyloxy)methyl)phenyl)prop-2-yn-1-ol (4i)



The reaction was carried out according to the general procedure A with *tert*-butyl(3-iodobenzyloxy)dimethylsilane[9] (1.49 g, 4.27 mmol), propargyl alcohol (0.76 ml, 12.9 mmol), $Pd(PPh_3)_4$ (25 mg, 0.022 mmol) and CuI (12 mg, 0.063 mmol) in triethylamine (10 ml) to give **4i** (1.16 g, 99%).

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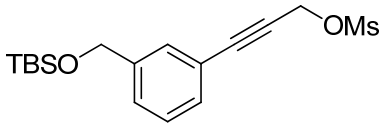
8 H. W. Lee, L. N. Lee, A. S. C. Chan, and F. Y. Kwong, *Eur. J. Org. Chem.* 2008, **19**, 3403.

9 H. Jian, and J. M. Tour, *J. Org. Chem.* 2003, **68**, 5091.

Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.39 (s, 1H), 7.32-7.26 (m, 3H), 4.71 (s, 2H), 4.50 (d, *J* = 3.4 Hz, 2H), 0.94 (s, 9H), 0.10 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 141.6, 130.2, 129.2, 128.2, 126.3, 122.3, 86.9, 85.8, 64.5, 51.7, 25.9, 18.4, -5.3 ppm; IR (KBr): 3302, 2929, 1257, 1105, 1082, 1033, 837 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{24}NaO_2Si$ [*M*+Na]$^+$: 299.1442, found 299.1437.

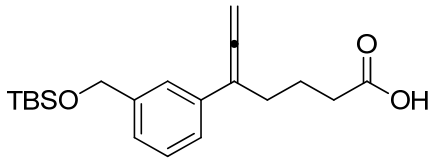
3-(3-((*t*ert-Butyldimethylsilyloxy)methyl)phenyl)prop-2-yn-1-yl methanesulfonate (5i)



The reaction was carried out according to the general procedure B with **4i** (1.16 g, 4.2 mmol), MsCl (0.4 ml, 5.2 mmol), and triethylamine (1.8 ml, 12.9 mmol) in CH_2Cl_2 (12 ml) to give **5i** (781 mg, 52%). Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.42 (s, 1H), 7.35-7.31 (m, 3H), 5.10 (s, 2H), 4.72 (s, 2H), 3.17 (s, 3H), 0.95 (s, 9H), 0.11 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 142.0, 130.4, 129.4, 128.4, 127.1, 121.0, 89.6, 80.5, 64.3, 58.5, 39.1, 25.9, 18.4, -5.3 ppm; IR (KBr): 1355, 1174 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{27}O_4SiS$ [*M*+H]$^+$: 355.1393, found 355.1392.

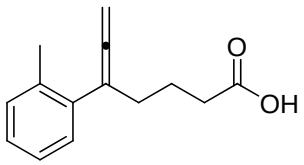
5-(3-((*tert*-Butyldimethylsilyloxy)methyl)phenyl)hepta-5,6-dienoic acid (2i)



The reaction was carried out according to the general procedure C (nucleophilic substitution: **5i** (780 mg, 2.2 mmol) and 4-ethoxy-4-oxobutylzinc bromide (8.8 ml, 0.5 M solution in THF, 4.4 mmol) in DMSO (8.8 ml); hydrolysis: LiOH (250 mg, 10.4 mmol) in THF/MeOH/H_2O (3/1/1, 3 ml)) to give **2i** (160.4 mg, 25%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 4/1).

Colorless solid; Mp: 69-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.38 (s, 1H), 7.29-7.26 (m, 2H), 7.17-7.15 (m, 1H), 5.10 (t, *J* = 3.0 Hz, 2H), 4.74 (s, 2H), 2.51-2.44 (m, 4H), 1.97-1.89 (m, 2H), 0.94 (s, 9H), 0.10 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 208.5, 179.5, 141.6, 135.8, 128.3, 124.4, 123.5, 104.1, 78.7, 64.8, 33.4, 28.6, 25.9, 22.7, 18.4, -5.2 ppm; IR (KBr): 3047, 2954, 1940, 1708, 1257 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{30}NaO_3Si$ [*M*+Na]$^+$: 369.1856, found 369.1856.

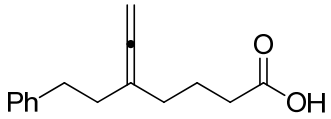
5-(o-Tolyl)hepta-5,6-dienoic acid (2j)



Title compound was prepared from 1-(3-bromoprop-1-yn-1-yl)-2-methylbenzene[10] instead of mesylate. The reaction was carried out according to the general procedure C (nucleophilic substitution: 1-(3-bromoprop-1-yn-1-yl)-2-methylbenzene (550.2 mg, 2.5 mmol) and 4-ethoxy-4-oxobutylzinc bromide (10 ml, 0.5 M solution in THF, 5 mmol) in DMSO (10 ml); hydrolysis: LiOH (126.5 mg, 5.28 mmol) in THF/MeOH/H_2O (3/1/1, 9 ml)) to give **2j** (110.4 mg, 20%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 20/1; 2nd step Hexane/AcOEt = 3/1).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.19-7.15 (m, 4H), 4.83 (t, *J* = 3.5 Hz, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.39-2.33 (m, 5H), 1.85-1.79 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 206.6, 179.7, 136.8, 136.0, 130.5, 127.8, 127.0, 125.9, 102.8, 75.9, 33.4, 32.5, 22.6, 20.2 ppm; IR (KBr): 2951, 1950, 1713, 1454, 1242 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{14}H_{16}O_2Na$ [*M*+Na]$^+$: 239.1042, found 239.1037.

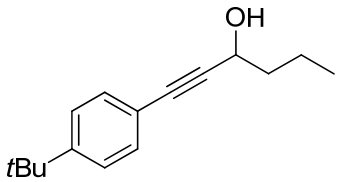
5-Phenethylhepta-5,6-dienoic acid (2k)



The reaction was carried out according to the general procedure C (nucleophilic substitution: 5-phenylpent-2-yn-1-yl methanesulfonate[11] (310 mg, 1.3 mmol) and 4-ethoxy-4-oxobutylzinc bromide (5 ml, 0.5 M solution in THF, 2.5 mmol) in DMSO (5 ml); hydrolysis: LiOH (125 mg, 5.2 mmol) in THF/MeOH/H_2O (3/1/1, 3 ml)) to give **2k** (162.1 mg, 54%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 5/1 to 3/1).

Colorless solid; Mp: <25 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.30-7.15 (m, 5H), 4.73 (tt, *J* = 3.4, 3.4 Hz, 2H), 2.75-2.69 (m, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.25-2.18 (m, 2H), 2.05-1.98 (m, 2H), 1.83-1.73 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 205.6, 180.1, 142.1, 128.4, 128.3, 125.8, 101.9, 76.8, 33.9, 33.8, 33.4, 31.4, 22.3 ppm; IR (KBr): 3026, 2941, 1955, 1699, 1452, 1431, 1411, 1286, 1242 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{15}H18O_2Na$ [*M*+Na]$^+$: 253.1199, found 253.1201.

1-(4-*tert*-Butylphenyl)hex-1-yn-3-ol (4l)



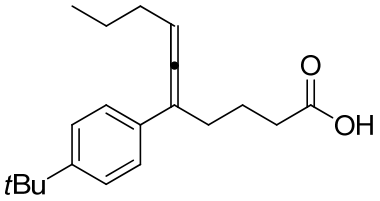
To the solution of 1-*tert*-butyl-4-ethynylbenzene (0.4 ml, 2.2 mmmol) in THF (11 ml) was added *n*BuLi (1.6 M solution in hexane, 1.51 ml, 2.42 mmol) under N_2 at -78 °C and resulting solution was stirred for 1.5 hr at the same temperature. Butyraldehyde (0.26 ml, 2.86 mmol) was added to the solution, and the reaction mixture was stirred for 1 hr at at -78 °C and allowed to warm to 0 °C. After the reaction completed, NH_4Cl aq. was added to the reaction mixture at 0 °C and the resulting solution was extracted with AcOEt. The organic layer was washed

[10] T. Okitsu, T. M. Potewar, K. Sato, and A. Wada, *J. Org. Chem.*, 2011, **76**, 3438.
[11] A. L. Moure, R. G. Arrayás, D. J. Cárdenas, I. Alonsom, and J. C. Carretero, *J. Am. Chem. Soc.* 2012, **134**, 7219.

with H_2O and brine, dried over with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt = 7/1) to give **4l** (342.2 mg, 68%).

Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.38-7.31 (m, 4H), 4.60 (t, *J* = 6.6 Hz, 2H) 1.82-1.74 (m, 2H), 1.58-1.51 (m, 2H), 1.30 (s, 9H), 0.98 ppm (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 151.6, 131.4, 125.3, 119.6, 89.4, 84.9, 62.8, 40.0, 34.7, 31.1, 18.5, 13.8 ppm; IR (KBr): 3317, 2960, 1504, 1462, 1363, 1267 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{22}ONa$ [*M*+Na]$^+$: 253.1562, found 253.1551.

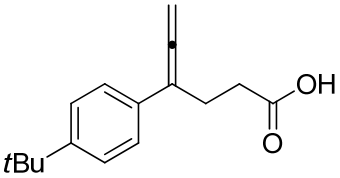
5-(4-*tert*-Butylphenyl)deca-5,6-dienoic acid (2l)



The reaction was carried out according to the general procedure B with **4l** (342 mg, 1.49 mmol), MsCl (0.15 ml, 1.94 mmol), and triethylamine (0.62 ml, 4.45 mmol) in CH_2Cl_2 (7.5 ml) to give crude 1-(4-*tert*-butylphenyl)hex-1-yn-3-yl methanesulfonate. This mesylate was used directly without the purification by SiO_2 column chromatography to the next transformation after the extraction and concentration. The following reaction was carried out according to the general procedure C (nucleophilic substitution: obtained crude mesylate and 4-ethoxy-4-oxobutylzinc bromide (6 ml, 0.5 M solution in THF, 3.0 mmol) in DMSO (6 ml); hydrolysis: LiOH (214 mg, 8.94 mmol) in THF/MeOH/H_2O (3/1/1, 5 ml)) to give **2x** (200.7 mg, 45%, 3 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 19/1; 2nd step Hexane/AcOEt = 3/1 to 2/1).

Colorless solid; Mp: 58-59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.33 (s, 4H), 5.53-5.50 (m, 1H), 2.49-2.45 (m, 4H), 2.09 (dt, *J* = 7.2, 7.2 Hz, 2H), 1.91 (dq, *J* = 7.4, 7.4 Hz, 2H), 1.50 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.31 (s, 9H), 0.96 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 203.5, 179.7, 149.4, 134.0, 125.5, 125.3, 104.1, 94.8, 33.4, 33.5, 31.3, 29.1, 22.9, 22.6, 13.9 ppm; IR (KBr): 2959, 1946, 1713, 1512, 1269 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{18}O_2Na$ [*M*+Na]$^+$: 323.1981, found 323.1973.

4-(4-*tert*-Butylphenyl)hexa-4,5-dienoic acid (2m)

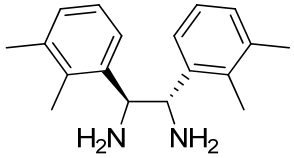


The reaction was carried out according to the general procedure C (nucleophilic substitution: 3-(4-*tert*-butylphenyl)prop-2-yn-1-yl methanesulfonate (308.3 mg, 1.16 mmol) and 3-ethoxy-3-oxopropylzinc bromide (4.6 ml, 0.5 M solution in THF, 2.3 mmol) in DMSO (4.6 ml); hydrolysis: LiOH (120 mg, 5.0 mmol) in THF/MeOH/H_2O (3/1/1, 3 ml)) to give **2m** (46.3 mg, 16%, 2 steps). (Eluent of SiO_2 column chromatography: 1st step: Hexane/AcOEt = 10/1; 2nd step Hexane/AcOEt = 3/1).

Colorless solid; Mp: 127-128 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.35 (s, 4H), 5.14 (t, *J* = 3.4 Hz, 2H), 2.74-2.62 (m, 4H), 1.31 ppm (s, 9H); ^{13}C NMR (75.6 MHz, $CDCl_3$): δ= 207.7, 179.7, 149.9, 132.7, 125.5, 125.4, 103.7, 80.0, 34.4, 32.3, 31.3, 23.8 ppm; IR (KBr): 3030, 2966, 1942, 1708, 1423, 1315, 1288, 1203 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{20}O_2Na$ [*M*+Na]$^+$: 267.1355, found 267.1353.

3. Preparation of DMP-tris

(*1S*,*2S*)-1,2-bis(2,3-dimethylphenyl)ethane-1,2-diamine

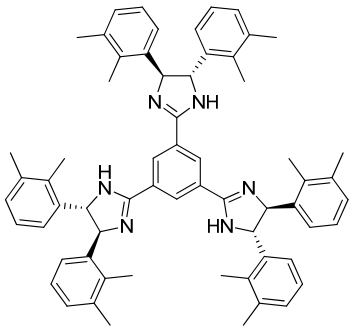


Title diamine was prepared according to the literature procedure from HPEN.[12]

To the solution of 2,3-dimethylbenzaldehyde (680 mg, 5.06 mmol) in DMSO (10 ml) was added (1*R*, 2*R*)-1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane (515 mg, 2.11 mmol) and the reaction mixture was stirred 9 hr at room temperature. The reaction was quenched with distilled water and the resulting solution was extracted with diethyl ether. The organic layer was washed with water and brine, dried over Na_2SO_4, and evaporated in vacuo. The residue was dissolved in THF (20 ml) and *c*HCl (0.6 ml) was added to the solution. The resulting reaction mixture was stirred for 13 hr to produce a white precipitate. The solid was filtered and washed with Et_2O and Hexane. The HCl salt of diamine was treated with 10% NaOH aq. and the solution was extracted with CH_2Cl_2. Organic layer was dried over Na_2SO_4, and evaporated in vacuo to give the title diamine (289.5 mg, 51%).

Colorless solid; Mp: 98-99 °C; $[\alpha]_D^{26}$ = +15.3 (c 0.77, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.5 Hz, 2H), 7.09 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 4.40 (s, 2H), 2.20 (s, 6H), 2.03 (s, 6H), 1.79 ppm (brs, 4H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ: 141.4, 136.6, 133.8, 128.3, 125.3, 124.4, 55.7, 21.0, 14.8 ppm; IR (KBr): 3292, 2941, 1585, 1460, 1381 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{18}H_{25}N_2$ [*M*+H]$^+$: 269.2012, found 269.2013.

DMP-tris 1b



1,3,5-Triformylbenzene[13] (21.4 mg, 0.132 mmol) and (1*S*,2*S*)-1,2-bis(2,3-dimethylphenyl)ethane- 1,2-diamine

12 H. Kim, Y. Nguyen, C. P.-H. Yen, L. Chagal, A. J. Lough, B. M. Kim, and J. Chin, *J. Am. Chem. Soc.*, 2008, **130**, 12184.
13 M. Fourmigué, I. Johannsen, K. Boubekeur, C. Nelson, and P. Batail, *J. Am. Chem. Soc.* 1993, **115**, 3752.

(118.4 mg, 0.441 mmol) was dissolved in CH_2Cl_2 (4 ml) and stired for 2 hr at room temperature under N_2. The resulting solution was added NBS (78 mg, 0.438 mmol) at 0 ^oC and stirred for 20 hr at room temperature. After the reaction was completed (judged by TLC), sat. $Na_2S_2O_5$ aq. and 5% NaOH aq. was added to the reaction mixture and extracted with CH_2Cl_2. Organic layer was dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by SiO_2 column chromatography (2 times: Hexane/AcOEt = 3/1 to 1/1; AcOEt/CH_2Cl_2 = 2/1) to give **1b** (70.6 mg, 59 %).

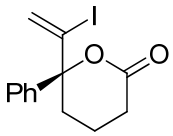
Colorless solid; Mp: 277-278 ^oC; $[\alpha]_D^{27}$ = -27.8 (c= 0.51 , $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ= 8.59 (s, 3H), 7.39-7.35 (m, 3H), 7.27-7.22 (m, 3H), 7.13-7.02 (m, 12H), 5.77 (brs, 3H), 5.46-5.42 (m, 3H), 5.11-5.07 (m, 3H), 2.24 (s, 18H), 1.94-1.91 ppm (m, 18H); ^{13}C NMR (125.8 MHz, $CDCl_3$): 161.5, 141.8, 141.0, 136.9, 136.6, 133.7, 133.5, 130.8, 129.1, 128.7, 128.1, 126.1, 125.9, 124.8, 123.8, 76.4, 66.0, 20.8, 14.9, 14.7 ppm; IR (KBr): 3157, 2941, 2916, 1625, 1581, 1469 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{63}H_{67}N_6$ $[M+H]^+$: 907.5421, found 907.5426.

4. Iodolactonization of allenoic acid

General procedure for iodolactonization of allenoic acid

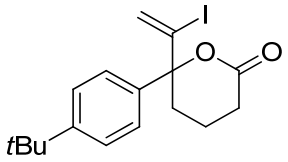
Under the N_2 atmosphere, to the solution of allenoic acid **2** and trisimidazoline **1b** (10 mol%) in touene (0.1 M) was added DTBP (2.5 equiv) at room temperature and the resulting solution was cooled to 0 ^oC. I_2 (2.5 equiv) was added in one portion to the solution and the reaction mixture was stirred at 0 ^oC. After the completion of the reaction (judged by TLC), the reaction was quenched with sat. $Na_2S_2O_3$ aq. at 0 ^oC, and the solution was extracted with AcOEt. The organic layer were washed with H_2O and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography to give lactone **3**.

Lactone 3a



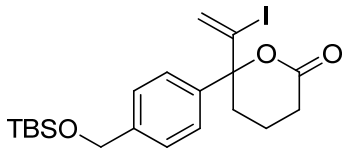
Reaction was carried out according to the typical procedure with **2a** (19.0 mg, 0.0939 mmol), **1b** (8.0 mg, 0.0088 mmol), I_2 (60.2 mg, 0.273 mmol), and DTBP (54 μl, 0.240 mmol) in toluene (0.9 ml) to give **3a** (25.6 mg, 83%) as color less oil. Reaction time: 48 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{21}$ = +49.4 (c= 0.77, $CHCl_3$, 66% ee); ^1H NMR (300 MHz, $CDCl_3$): δ= 7.50-7.35 (m, 5H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 2.72-2.55 (m, 2H), 2.51-2.33 (m, 2H), 1.92-1.82 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.1, 139.5, 128.51, 128.45, 127.8, 126.2, 115.2, 88.4, 30.7, 29.1, 16.2 ppm; IR (KBr): 2951, 1732, 1607, 1447, 1240 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{13}H_{13}O_2NaI$ $[M+Na]^+$: 350.9852, found 350.9851; HPLC (DAICEL CHIRALCEL OD-H, Hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, 218 nm): t_{major} = 16.2 min, t_{minor} = 15.0 min.

Lactone 3b



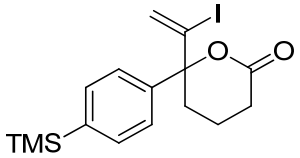
Reaction was carried out according to the typical procedure with **2b** (11.8 mg, 0.0504 mmol), **1b** (4.5 mg, 0.0050 mmol), I_2 (35.8 mg, 0.141 mmol), and DTBP (29 μl, 0.130 mmol) in toluene (0.5 ml) to give **3b** (17.0 mg, 89%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{18}$ = +53.4 (c= 0.79, $CHCl_3$, 82% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.40 (s, 4H), 6.48 (d, *J* = 2.2 Hz, 1H), 6.03 (d, *J* = 2.2 Hz, 1H), 2.71-2.54 (m, 2H), 2.50-2.33 (m, 2H), 1.99-1.76 (m, 2H), 1.32 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.2, 151.5, 136.3, 127.8, 126.0, 125.4, 115.5, 88.4, 34.5, 31.2, 30.8, 29.1, 16.2 ppm; IR (KBr): 2961, 1746, 1244 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{21}O_2NaI$ $[M+Na]^+$: 407.0478, found 407.0477; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 223 nm): t_{major} = 10.3 min, t_{minor} = 8.0 min.

Lactone 3c



Reaction was carried out according to the typical procedure with **2c** (9.4 mg, 0.0271 mmol), **1b** (2.9 mg, 0.0032 mmol), I_2 (18.2 mg, 0.0717 mmol), and DTBP (15 μl, 0.0668 mmol) in toluene (0.3 ml) to give **3c** (11.2 mg, 88%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{21}$ = +39.0 (c= 0.98, $CHCl_3$, 79% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 2.5 Hz, 1H), 6.03 (d, *J* = 2.5 Hz, 1H), 4.75 (s, 2H), 2.67-2.55 (m, 2H), 2.48-2.35 (m, 2H), 1.95-1.77 (m, 2H), 0.94 (s, 9H), 0.10 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.2, 141.9, 138.0, 127.8, 126.2, 126.0, 115.4, 88.4, 64.4, 30.8, 29.1, 25.9, 18.4, 16.2, -5.3 ppm; IR (KBr): 2953, 1746, 1244 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{29}O_3NaSiI$ $[M+Na]^+$: 495.0822, found 495.0826; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 96/4, flow rate = 1.0 mL/min, 223 nm): t_{major} = 7.3 min, t_{minor} = 9.1 min.

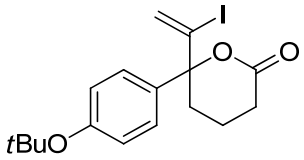
Lactone 3d



Reaction was carried out according to the typical procedure with **2d** (9.6 mg, 0.0350 mmol), **1b** (3.5 mg, 0.0039 mmol), I_2 (22.3 mg, 0.0878 mmol), and DTBP (20 μl, 0.0891 mmol) in toluene (0.4 ml) to give **3d** (10.9 mg, 78%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1.

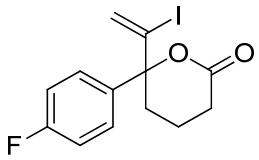
$[\alpha]_D^{17}$ = +47.5 (c= 1.00, $CHCl_3$, 80% ee); ^1H NMR (300 MHz, $CDCl_3$): δ= 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 2.71-2.54 (m, 2H), 2.50-2.33 (m, 2H), 1.99-1.75 (m, 2H), 0.27 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.1, 141.1, 139.8, 133.5, 128.0, 125.4, 115.2, 88.4, 30.9, 29.1, 16.2, -1.2 ppm; IR (KBr): 2953, 1746, 1246 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{21}O_2NaSiI$ [*M*+Na]$^+$: 423.0247, found 423.0247; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 225 nm): t_{major} = 7.4 min, t_{minor} = 6.9 min.

Lactone 3e



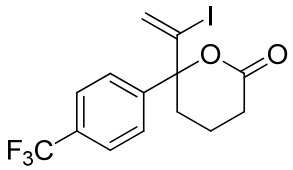
Reaction was carried out according to the typical procedure with **2e** (12.5 mg, 0.0456 mmol), **1b** (5.0 mg, 0.0055 mmol), I_2 (27.8 mg, 0.109 mmol), and DTBP (25 μl, 0.111 mmol) in toluene (0.5 ml) to give **3e** (15.7 mg, 85%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. ^1H NMR (300 MHz, $CDCl_3$): δ= 7.39-7.34 (m, 2H), 7.01-6.96 (m, 2H), 6.47 (d, *J* = 2.4 Hz, 1H), 6.03 (d, *J* = 2.4 Hz, 1H), 2.71-2.30 (m, 4H), 1.99-1.82 (m, 2H), 1.36 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.2, 155.7, 133.9, 127.7, 127.1, 123.5, 115.5, 88.4, 78.8, 30.6, 29.1, 28.9, 16.2 ppm; IR (KBr): 2974, 1744, 1607, 1506, 1366, 1242, 1163 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{17}H_{21}O_3NaI$ [*M*+Na]$^+$: 423.1427, found 423.0425; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 94/6, flow rate = 1.0 mL/min, 227 nm): t_{major} = 16.4 min, t_{minor} = 18.1 min.

Lactone 3f



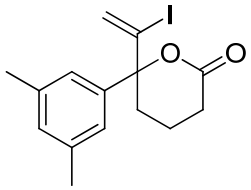
Reaction was carried out according to the typical procedure with **2f** (16.1 mg, 0.0731 mmol), **1b** (6.5 mg, 0.0072 mmol), I_2 (46.1 mg, 0.0181 mmol), and DTBP (40 μl, 0.0178 mmol) in toluene (0.7 ml) to give **3f** (19.1 mg, 78%) as color less oil. Reaction time: 42 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{16}$ = +58.5 (c= 0.88, $CHCl_3$, 68% ee); ^1H NMR (300 MHz, $CDCl_3$): δ= 7.51-7.44 (m, 2H), 7.12-7.04 (m, 2H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 2.75-2.57 (m, 2H), 2.52-2.41 (m, 1H), 2.32 (ddd, *J* = 14.1, 9.3, 4.2 Hz, 1H), 2.01-1.78 ppm (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ= 169.9, 162.5 (d, *J* = 248.5 Hz), 135.5 (d, *J* = 3.6 Hz), 128.2 (d, *J* = 8.6 Hz), 127.9, 115.4 (d, *J* = 21.7 Hz), 114.9, 114.8, 88.0, 30.6, 29.0, 16.1 ppm; IR (KBr): 2951, 1744, 1603, 1508, 1238 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{13}H_{12}O_2FNaI$ [*M*+Na]$^+$: 368.9758, found 368.9759; HPLC (DAICEL CHIRALPAK AD-H, Hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, 217 nm): t_{major} = 15.6 min, t_{minor} = 16.4 min.

Lactone 3g



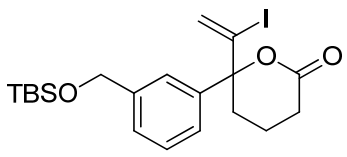
Reaction was carried out according to the typical procedure with **2g** (19.7 mg, 0.0729 mmol), **1b** (6.5 mg, 0.0072 mmol), I_2 (46.3 mg, 0.182 mmol), and DTBP (40 μl, 0.178 mmol) in toluene (0.7 ml) to give **3g** (10.4 mg, 53%) as color less oil. Reaction time: 48 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{22}$ = +39.6 (c= 1.00, $CHCl_3$, 62% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.68-7.61 (m, 4H), 6.59 (d, *J* = 2.6 Hz, 1H), 6.10 (d, *J* = 2.6 Hz, 1H), 2.75 (ddd, *J* = 14.1, 7.2, 4.2 Hz, 1H), 2.69-2.43 (m, 2H), 2.35 (ddd, *J* = 14.1, 9.3, 4.5 Hz, 1H), 2.03-1.77 ppm (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ= 169.5, 143.7, 130.7 (q, *J* = 32.4 Hz), 128.4, 126.7, 125.5 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 272.4 Hz), 113.8, 87.8, 30.8, 29.1, 16.1 ppm; IR (KBr): 1748, 1327 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{14}H_{12}O_2F_3NaI$ [*M*+Na]$^+$: 418.9726, found 418.9731; HPLC (DAICEL CHIRALPAK AD-H, Hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, 218 nm): t_{major} = 12.9 min, t_{minor} = 12.1 min.

Lactone 3h



Reaction was carried out according to the typical procedure with **2h** (20.4 mg, 0.0886 mmol), **1b** (8.0 mg, 0.0088 mmol), I_2 (56.2 mg, 0.221 mmol), and DTBP (50 μl, 0.223 mmol) in toluene (0.9 ml) to give **3h** (27.0 mg, 85%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{22}$ = +41.9 (c= 1.16, $CHCl_3$, 64% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.07 (s, 2H), 6.98 (s, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 2.67-2.31 (m, 4H), 2.33 (s, 6H), 1.98-1.74 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.3, 139.4, 138.0, 130.1, 127.8, 124.0, 115.5, 88.5, 30.9, 29.1, 21.5, 16.3 ppm; IR (KBr): 2949, 2916, 1732, 1234 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{15}H_{17}O_2NaI$ [*M*+Na]$^+$: 379.0165, found 379.0161; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 94/6, flow rate = 1.0 mL/min, 219 nm): t_{major} = 7.6 min, t_{minor} = 6.3 min.

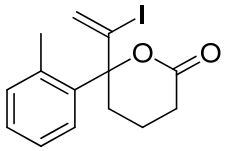
Lactone 3i



Reaction was carried out according to the typical procedure with **2i** (19.9 mg, 0.0574 mmol), **1b** (5.0 mg,

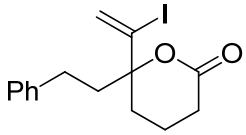
0.0055 mmol), I_2 (36.1 mg, 0.142 mmol), and DTBP (31 μl, 0.138 mmol) in toluene (0.6 ml) to give **3i** (22.0 mg, 82%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{18}$ = +31.8 (c= 1.04, $CHCl_3$, 66% ee); ^1H NMR (500 MHz, $CDCl_3$): δ= 7.42 (s, 1H), 7.36-7.32 (m, 3H), 6.49 (d, *J* = 1.8 Hz, 1H), 6.04 (d, *J* = 1.8 Hz, 1H), 4.76 (s, 2H), 2.67-2.32 (m, 4H), 1.94-1.79 (m, 2H), 0.94 (s, 9H), 0.09 ppm (s, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.1, 141.8, 139.4, 128.4, 127.8, 126.1, 124.8, 123.8, 115.2, 88.4, 64.7, 30.8, 29.1, 25.9, 18.3, 16.2, -5.2 ppm; IR (KBr): 2953, 1748, 1251, 1231 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{29}O_3NaSiI$ $[M+Na]^+$: 495.0822, found 495.0821; HPLC (DAICEL CHIRALPAK IC, Hexane/*i*PrOH = 99/1, flow rate = 1.2 mL/min, 217 nm): t_{major} = 33.7 min, t_{minor} = 31.7 min.

Lactone 3j



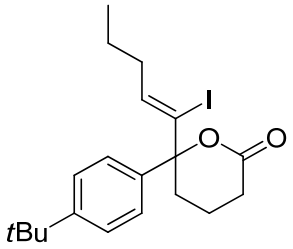
Reaction was carried out according to the typical procedure with **2j** (20.9 mg, 0.0966 mmol), **1b** (9.1 mg, 0.0100 mmol), I_2 (61.2 mg, 0.241 mmol), and DTBP (54 μl, 0.240 mmol) in toluene (1.0 ml) to give **3j** (11.5 mg, 35%) as color less oil. Reaction time: 72 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1. $[\alpha]_D^{24}$ = +49.8 (c= 1.14, $CHCl_3$, 74% ee); ^1H NMR (300 MHz, $CDCl_3$): δ= 7.38 (d, *J* = 7.8 Hz, 1H), 7.28-7.19 (m, 3H), 6.31 (d, *J* = 2.4 Hz, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 2.58-2.50 (m, 3H), 2.46 (s, 3H), 2.39-2.31 (m, 1H) 1.98-1.93 ppm (m, 2H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.3, 137.8, 136.5, 133.3, 128.9, 128.5, 127.4, 125.5, 114.1, 89.5, 31.0, 28.7, 22.2, 16.0 ppm; IR (KBr): 2955, 2926, 1738, 1460, 1238 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{14}H_{15}O_2NaI$ $[M+Na]^+$: 365.0008, found 365.0001; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 217 nm): t_{major} = 10.7 min, t_{minor} = 9.1 min.

Lactone 3k

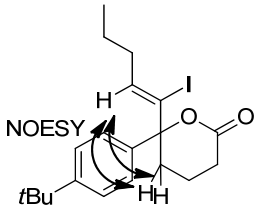


Reaction was carried out according to the typical procedure with **2k** (17.5 mg, 0.0760 mmol), **1b** (7.8 mg, 0.0086 mmol), I_2 (48.0 mg, 0.189 mmol), and DTBP (43 μl, 0.192 mmol) in toluene (0.8 ml) to give **3k** (19.9 mg, 74%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 3/1. $[\alpha]_D^{23}$ = +8.64 (c= 1.32, $CHCl_3$, 34% ee); ^1H NMR (500 MHz, $CDCl_3$): δ= 7.31-7.20 (m, 5H), 6.48 (d, *J* = 2.3 Hz, 1H), 6.11 (d, *J* = 2.3 Hz, 1H), 2.85-2.78 (m, 1H), 2.63-2.56 (m, 2H), 2.49-2.40 (m, 2H), 2.32-2.26 (m, 1H), 2.03-1.96 (m, 1H), 1.83-1.77 (m, 2H), 1.71-1.65 ppm (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.7, 141.3, 129.6, 128.43, 128.39, 126.0, 111.3, 88.0, 41.7, 31.6, 29.2, 28.7, 15.8 ppm; IR (KBr): 2957, 1742, 1236 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{15}H_{17}O_2NaI$ $[M+Na]^+$: 379.0165, found 379.0164; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 94/6, flow rate = 1.0 mL/min, 206 nm): t_{major} = 10.6 min, t_{minor} = 11.5 min.

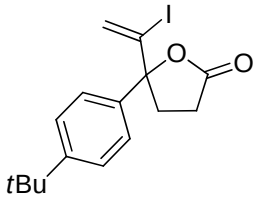
Lactone 3l



Reaction was carried out according to the typical procedure with **2l** (24.1 mg, 0.0802 mmol), **1b** (7.0 mg, 0.0077 mmol), I_2 (49.2 mg, 0.194 mmol), and DTBP (45 μl, 0.200 mmol) in toluene (0.8 mL) to give **3l** (26.1 mg, 76%) as color less oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1. $[\alpha]_D^{23}$ = +35.2 (c= 0.89, $CHCl_3$, 59% ee); ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.37 (s, 4H), 5.97 (t, *J* = 6.6 Hz, 1H), 2.72 (ddd, *J* = 14.4, 7.2, 4.8 Hz, 1H), 2.62-2.32 (m, 3H), 2.19 (dd, *J* = 14.1, 4.5 Hz, 2H), 1.90-1.78 (m, 2H), 1.47 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.32 (s, 9H), 0.93 ppm (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 170.6, 151.2, 137.5, 137.4, 126.1, 125.2, 113.4, 88.6, 38.8, 34.5, 31.6, 31.2, 29.2, 21.5, 16.2, 13.7 ppm; IR (KBr): 2959, 1732, 1242 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{20}H_{27}O_2NaI$ $[M+Na]^+$: 449.0947, found 449.0945; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 98/2, flow rate = 1.0 mL/min, 221 nm): t_{major} = 11.1 min, t_{minor} = 7.6 min.



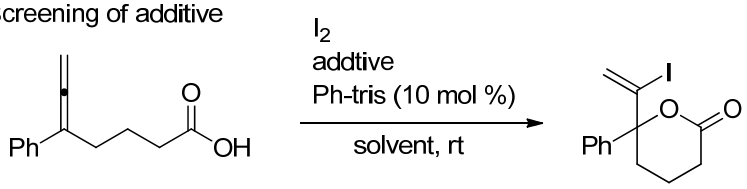
Lactone 3m



Reaction was carried out according to the typical procedure with **2m** (19.5 mg, 0.0798 mmol), **1b** (7.6 mg, 0.0084 mmol), I_2 (51.9 mg, 0.204 mmol), and DTBP (45 μl, 0.200 mmol) in toluene (0.8 mL) to give **3m** (25.7 mg, 87%) as color less oil. Reaction time: 7 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1. $[\alpha]_D^{23}$ = +18.9 (c= 1.11, $CHCl_3$, 21% ee); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.41-7.37 (m, 4H), 6.47 (d, *J* = 2.3 Hz, 1H), 5.97 (d, *J* = 2.3 Hz, 1H), 2.86-2.79 (m, 1H), 2.77-2.65 (m, 2H), 2.58-2.50 (m, 1H), 1.32 ppm (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 175.2, 151.7, 135.5, 127.1, 126.0, 125.3, 114.1, 90.4, 34.6, 33.3, 31.2, 28.7 ppm; IR (KBr): 2961, 1782 cm^{-1}; HRMS (MALDI-TOF): calcd for $C_{16}H_{19}O_2NaI$ $[M+Na]^+$: 393.0321, found 393.0322; HPLC (DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 222 nm): t_{major} = 8.1 min, t_{minor} = 7.0 min.

5. Optimization study

Table S1. Screening of additive



entry	solvent	I_2 (eq.)	additive	time (h)	yield (%)	er
1	$CHCl_3$	1.2	Na_2CO_3 (1.2 eq.)	23	75	33
2	$CHCl_3$	1.2	CaO (3.1 eq.)	24	32	23
3	dry $CHCl_3$	1.2	MS 4A (200 mg/0.09 mmol)	48	61	35
4	$CHCl_3$	1.2	TsOH (0.3 eq.)	24	-	0
5	toluene	2.5	K_2CO_3 (2.5 eq.)	5	86	23
6	toluene	2.5	Li_2CO_3 (2.5 eq.)	24	76	21
7	toluene	2.5	DOWEX (100 mg/ 0.1 mmol)	24	32	29
8	toluene	2.5	DTBP (2.5 eq.)	7	85	48
9	toluene	2.5	2,4,6-collidine (2.5 eq.)	1	69	33
10	toluene	2.5	protone sponge (2.5 eq.)	1	N.D.	-

DOWEX: Wako Chem 230-400 mesh basic, DTBP: 2,6-di-*tert*-butylpyridine

protone sponge:

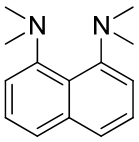
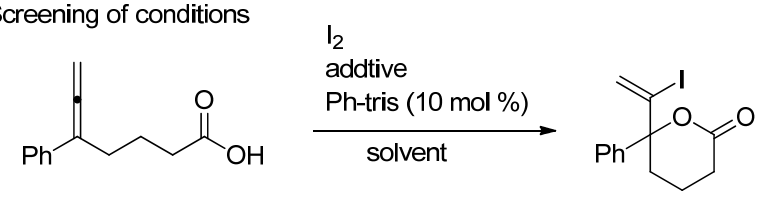


Table S2. Screening of conditions

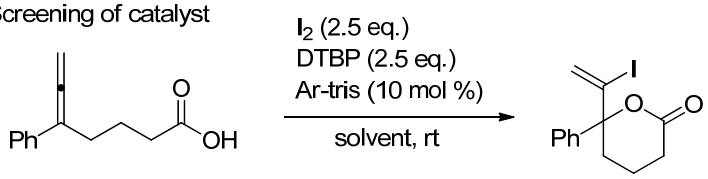


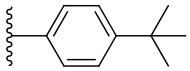
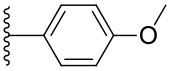
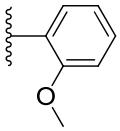
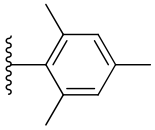
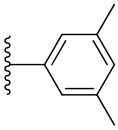
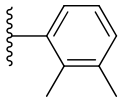
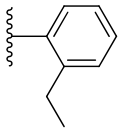
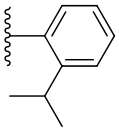
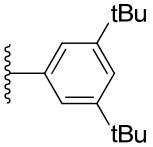
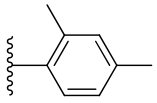
1 **5**

entry	solvent	I_2 (eq.)	DTBP (eq.)	time (h)	yield (%)	ee (%)
1	toluene, rt	2.5	2.5	7	85	48
2	$CHCl_3$, rt	2.5	2.5	18	91	42
3	MeCy, rt	2.5	2.5	10	75	10
4	toluene/CH_2Cl_2 (1/1), rt	2.5	2.5	17	58	47
5	toluene, -20 °C	2.5	2.5	48	62	57
6	toluene, rt	2.5	1.2	16	91	45
7	toluene, rt	1.2	2.5	23	72	52
8	toluene, rt	1.2	5.0	22	81	51
9[a)]	toluene, rt	2.5	2.5	20	76	47

a) Ph-tris (5 mol%)

Table S3. Screening of catalyst

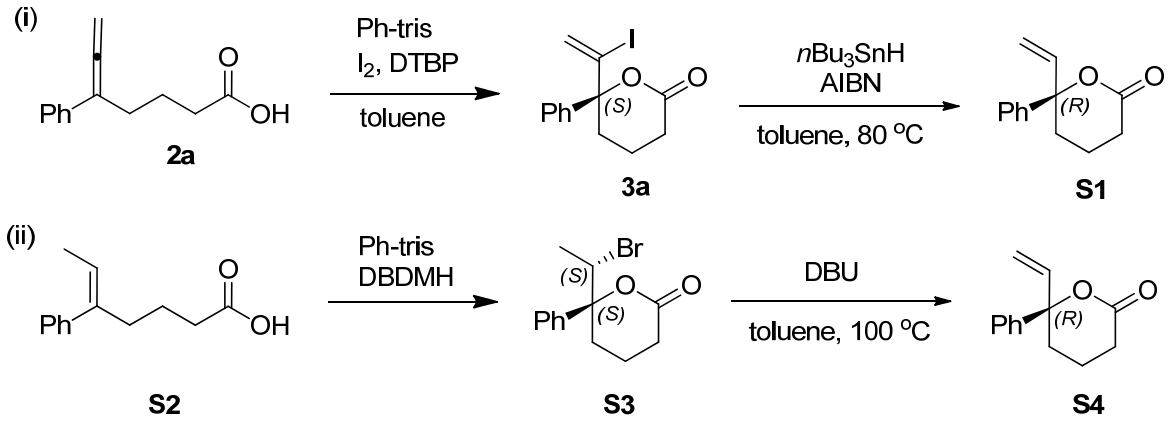


entry	Ar	time (h)	yield (%)	ee (%)
1	Ph	7	85	48
2		17	94	49
3		19	82	41
4		16	87	59
5		19	90	31
6		15	85	55
7		9	77	62
8		19	90	58
9		15	95	55
10		17	91	43
11		9	89	61

6. Determination of stereochemistry of 3a

(i) Vinyl lactone **S1** was prepared from **3a** using radical reduction conditions with *n*Bu_3SnH and AIBN.

(ii) Vinyl lactone **S4** was prepared from bromolactone **S3**[14] by DBU mediated elimination of HBr.



By comparison of HPLC data between **S1** and **S4**, it was revealed that the produced major enantiomer using Ph-tris in iodolactonization of allenoic acid **2a** and bromolactonization of ene-carboxylic acid **S2** have the same absolute configuration. Consequently, stereochemistry of major enantiomer of **3a** was determined to be *S* as shown in above scheme.

Procedure for S1 (S4)

From 3a

To the solution of lactone **3a** (20.7 mg, 0.063 mmol, 75 : 25 er) in toluene (1.2 ml) was added *n*Bu_3SnH (0.1 ml, 3.7 mmol) and AIBN (4 mg, 0.024 mmol) at rt under N_2 and the resulting solution was heated at 80 °C for 30 min. After cooling, the reaction mixture was purified by column chromatography (2 times. 1st column: KF-SiO_2[15], eluent Hexane/AcOEt= 2/1; 2nd column: SiO_2, eluent Hexane/AcOEt= 5/2) to give lactone **S1** (12.0 mg, 94%, 75.5 : 24.5 er).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.41-7.28 (m, 5H), 6.05 (dd, *J* = 16.5, 10.5 Hz, 1H), 5.32 (d, *J* = 16.5 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 2.58 (ddd, *J* = 18.0, 6.5, 6.5 Hz, 1H), 2.46 (ddd, *J* = 18.0, 7.5, 7.5 Hz, 1H), 2.28-2.17 (m, 2H), 1.92-1.87 (m, 1H), 1.77-1.72 ppm (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ= 171.0, 142.3, 140.9, 128.6, 127.6, 125.1, 114.8, 86.4, 32.5, 29.3, 16.4 ppm; IR (KBr): 2954, 1732, 1492, 1446, 1246 cm^{-1}; HRMS ((MALDI-TOF)): calcd for $C_{13}H_{15}O_2$ $[M+H]^+$: 203.1066, found 203.1066; HPLC (DAICEL CHIRALCEL OD-H, Hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, 210 nm): t_{major} = 9.8 min, t_{minor} = 10.3 min.

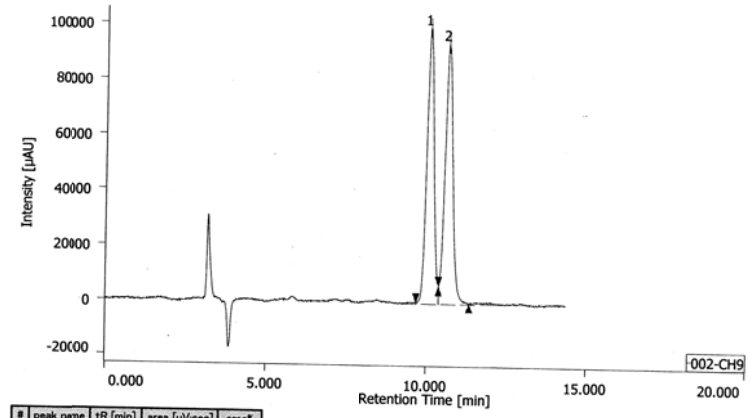
From S3

To the solution of lactone **S3** (14.8 mg, 0.052 mmol, 89 : 11 er) in toluene (1.2 ml) was added DBU (0.12 ml, 8.0 mmol) at rt under N_2 and the resulting solution was heated at 100 °C for 3 hr. After the reaction completed, H_2O was added to the reaction mixture and the resulting solution was extracted with AcOEt. The organic layer

[14] K. Murai, A. Nakamura, T. Matsushita, M. Shimura, and H. Fujioka, *Chem. Eur. J.* 2012, **18**, 8448.
[15] D. C. Harrowven, and I. L. Guy, *Chem. Commun.* 2004, 1968.

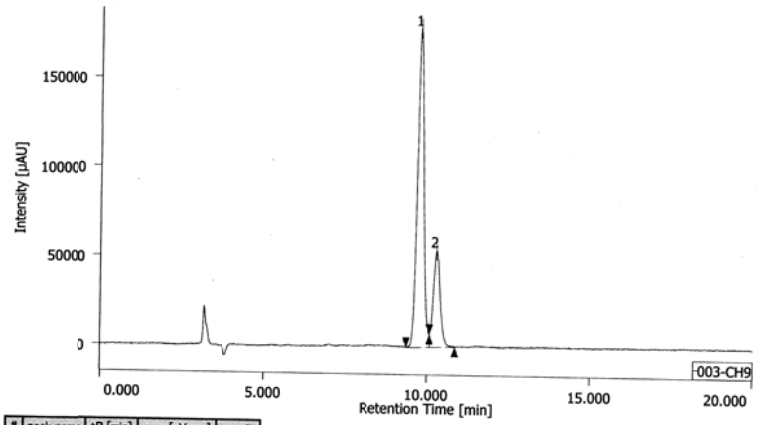
was washed with H_2O and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (Hexane/AcOEt= 3/1) to give **S4** (2.7 mg, 25%, 89.5 : 10.5 er).

HPLC data



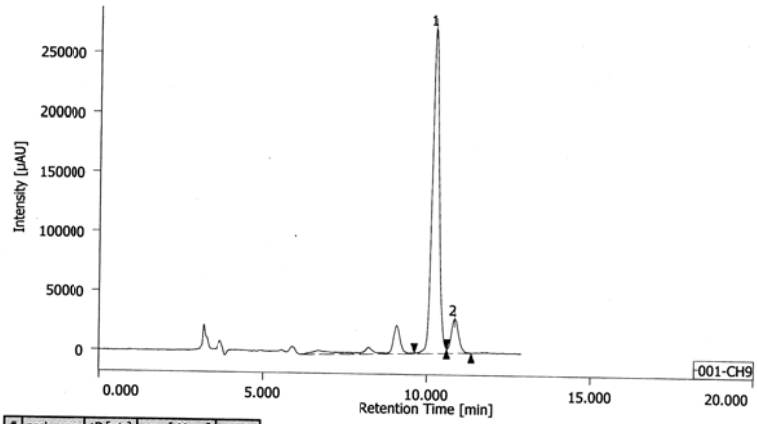
#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	10.067	1549028	49.359
2	Unknown	10.640	1589230	50.641

racemic



#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	9.760	2448362	75.508
2	Unknown	10.280	794149	24.492

S1



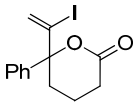
#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	10.213	3984765	89.619
2	Unknown	10.840	461584	10.381

S4

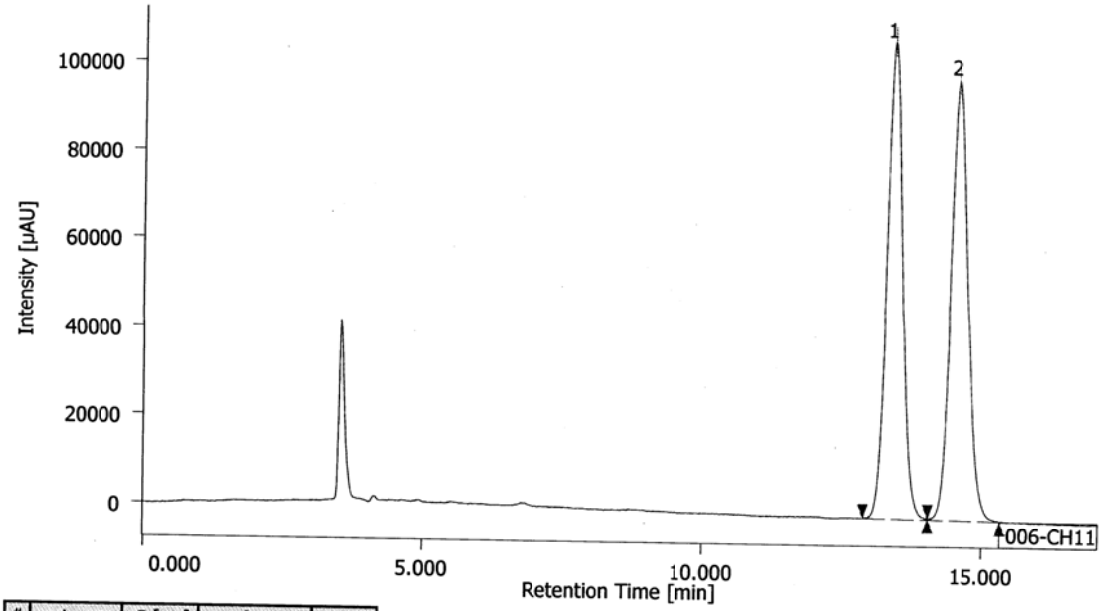
7. HPLC Data

HPLC chart for **3a**

DAICEL CHIRALCEL OD-H, Hexane/*i*PrOH = 90/10, flow rate = 1.0 mL/min, 218 nm

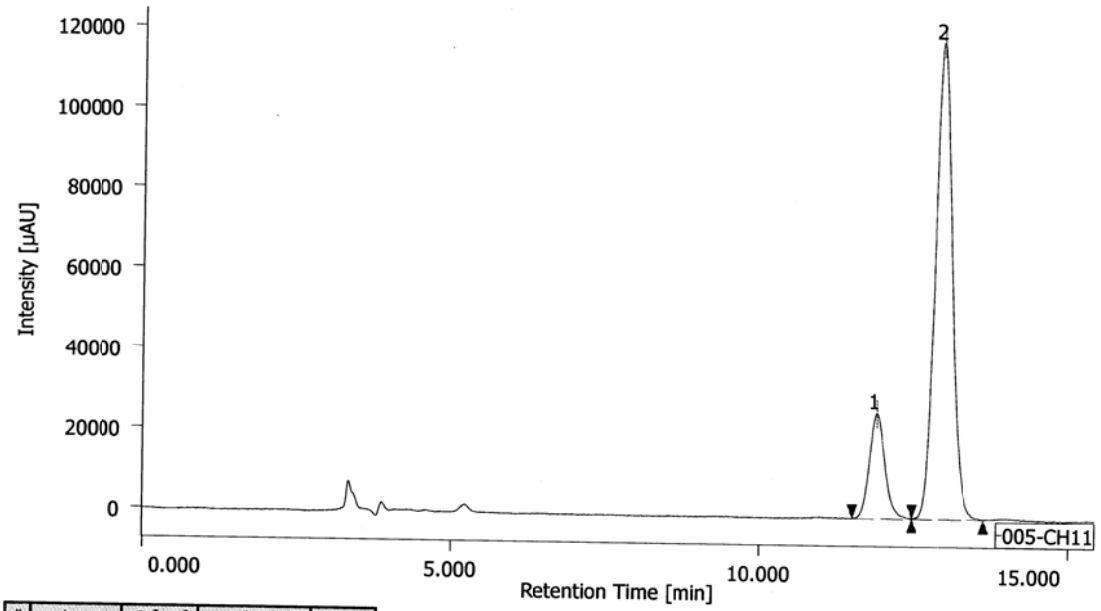


racemic



#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	13.400	2072759	49.145
2	Unknown	14.547	2144857	50.855

chiral

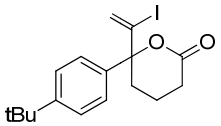


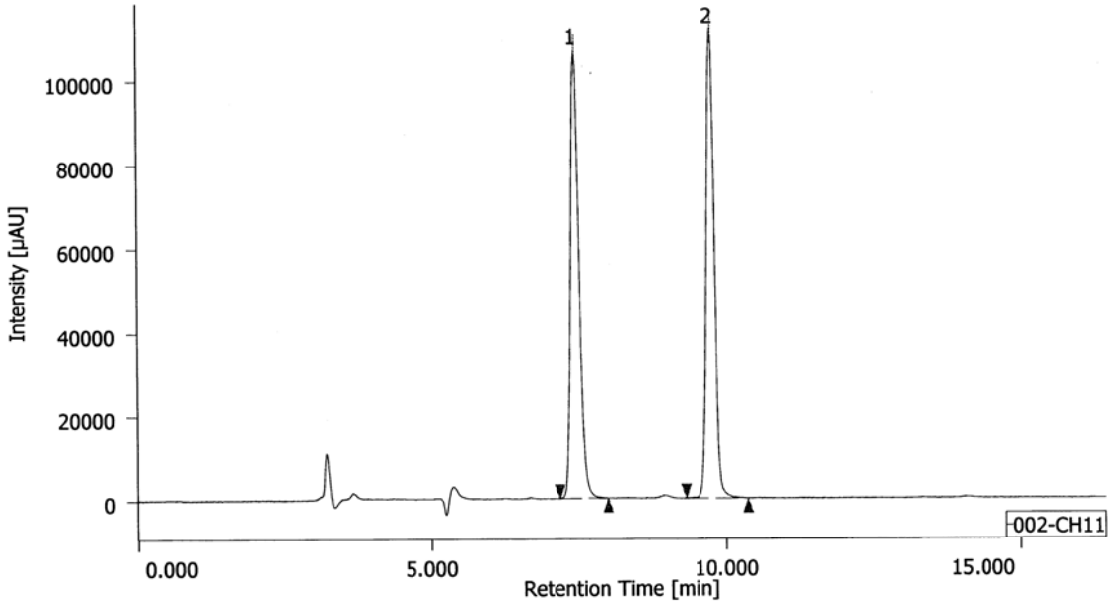
#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	11.893	456891	16.878
2	Unknown	12.933	2250160	83.122

HPLC chart for **3b**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 223 nm

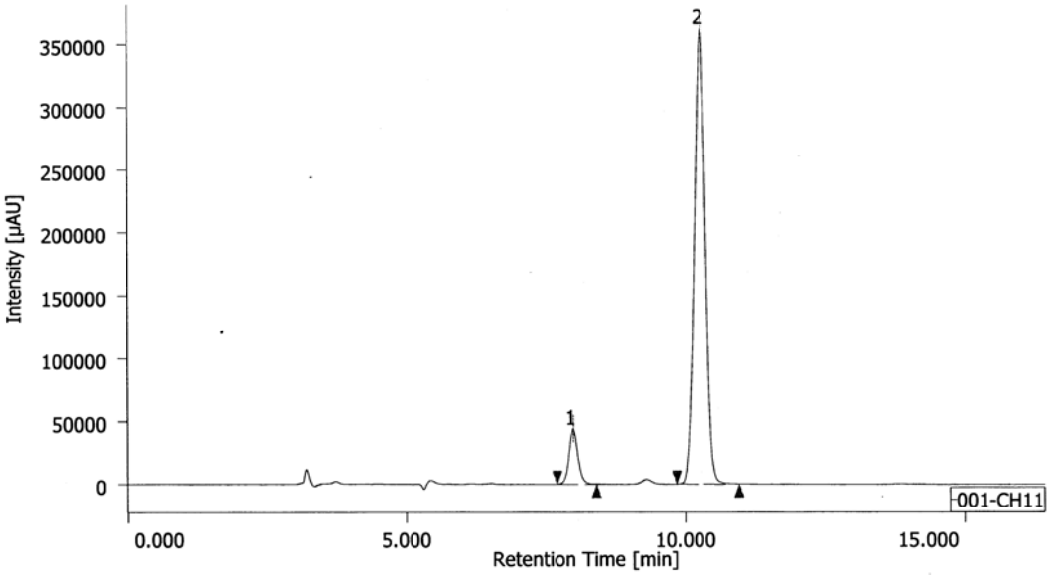
racemic





#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.440	1075349	50.129
2	Unknown	9.760	1069829	49.871

chiral

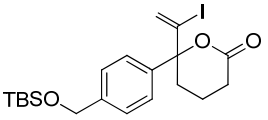


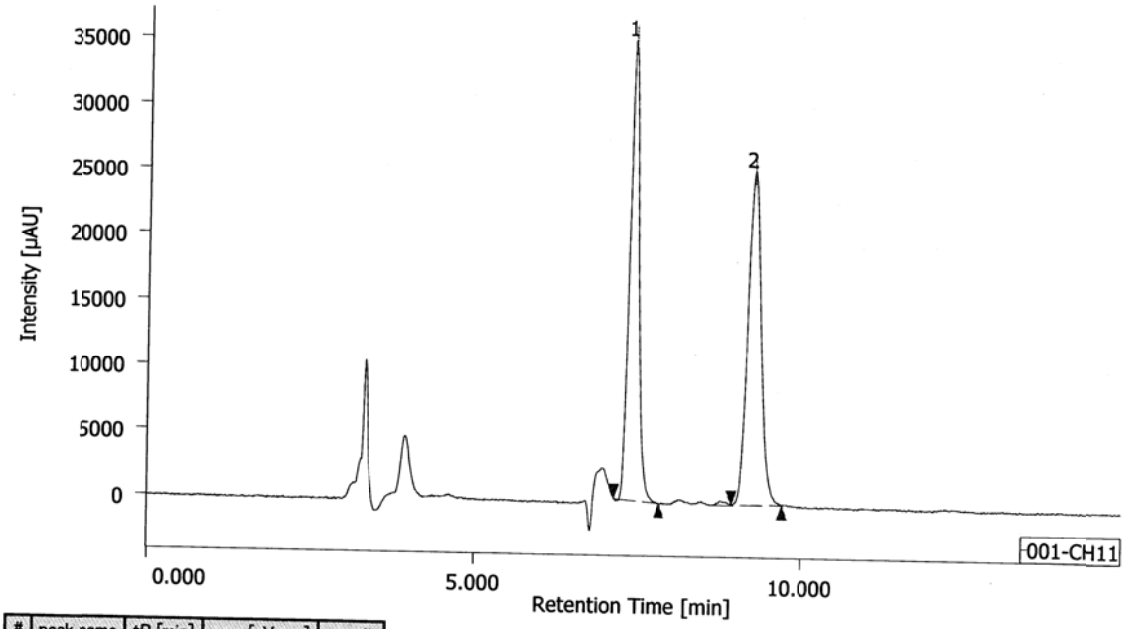
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.987	500322	9.104
2	Unknown	10.280	4995530	90.896

HPLC chart for **3c**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 96/4, flow rate = 1.0 mL/min, 223 nm

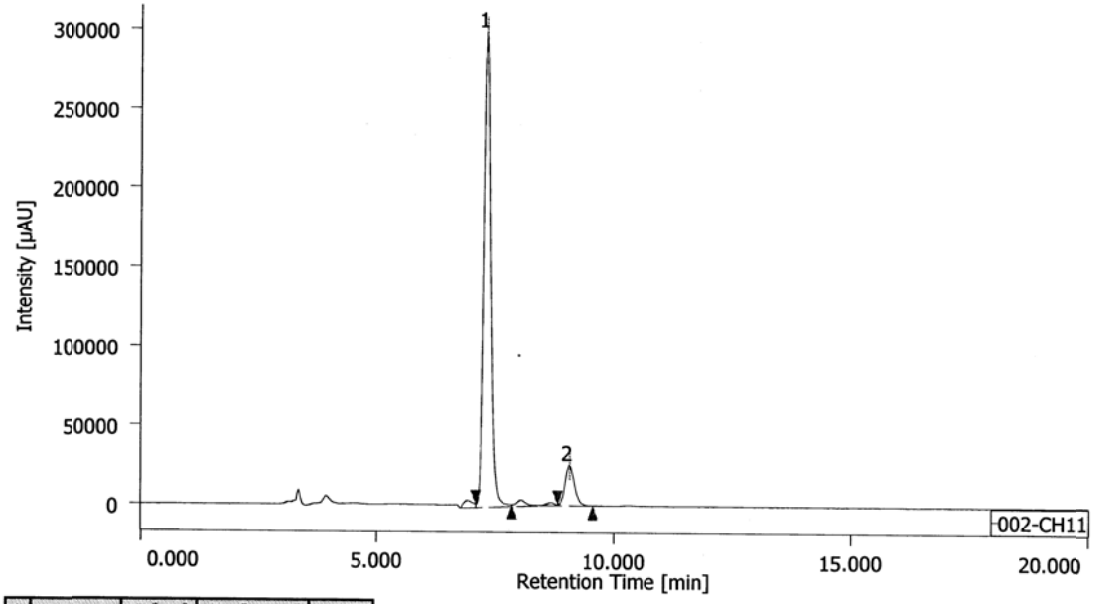
racemic





#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.400	353966	49.782
2	Unknown	9.240	357065	50.218

chiral

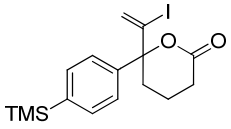


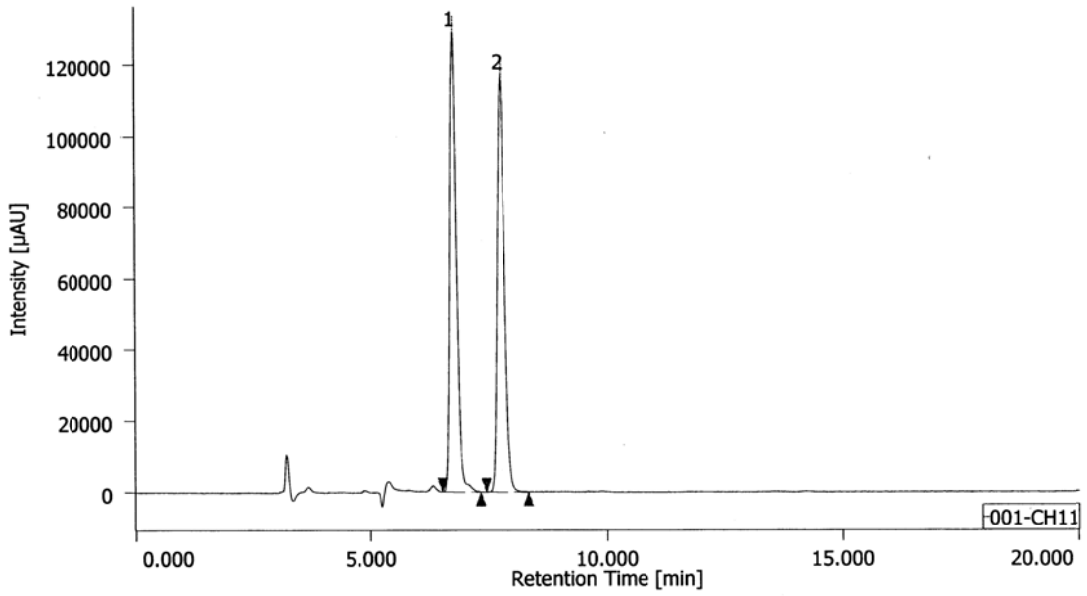
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.293	3019741	89.631
2	Unknown	9.067	349345	10.369

HPLC chart for **3d**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 225 nm

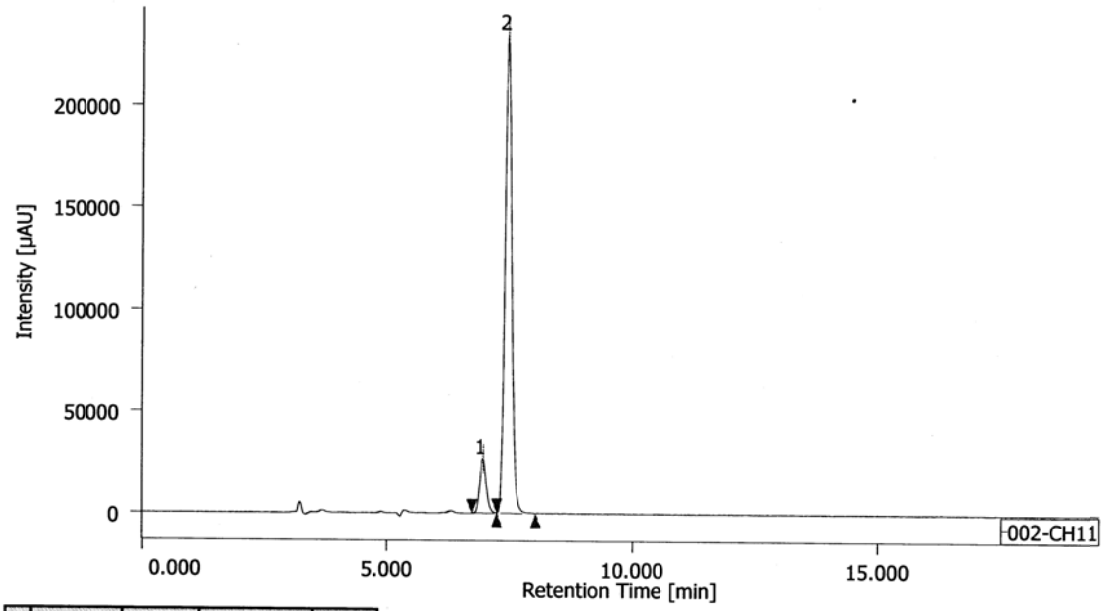
racemic





#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	6.747	1244060	50.243
2	Unknown	7.760	1232024	49.757

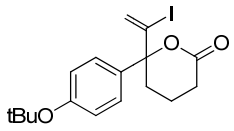
chiral



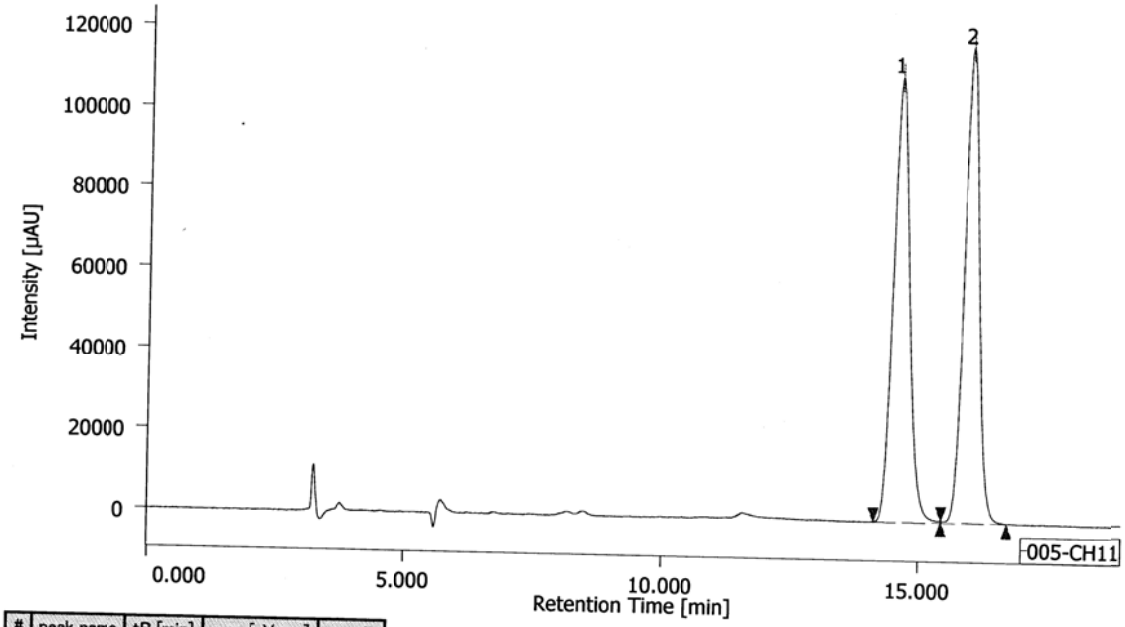
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	6.947	255712	9.982
2	Unknown	7.440	2305933	90.018

HPLC chart for **3e**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 96/4, flow rate = 1.0 mL/min, 227 nm

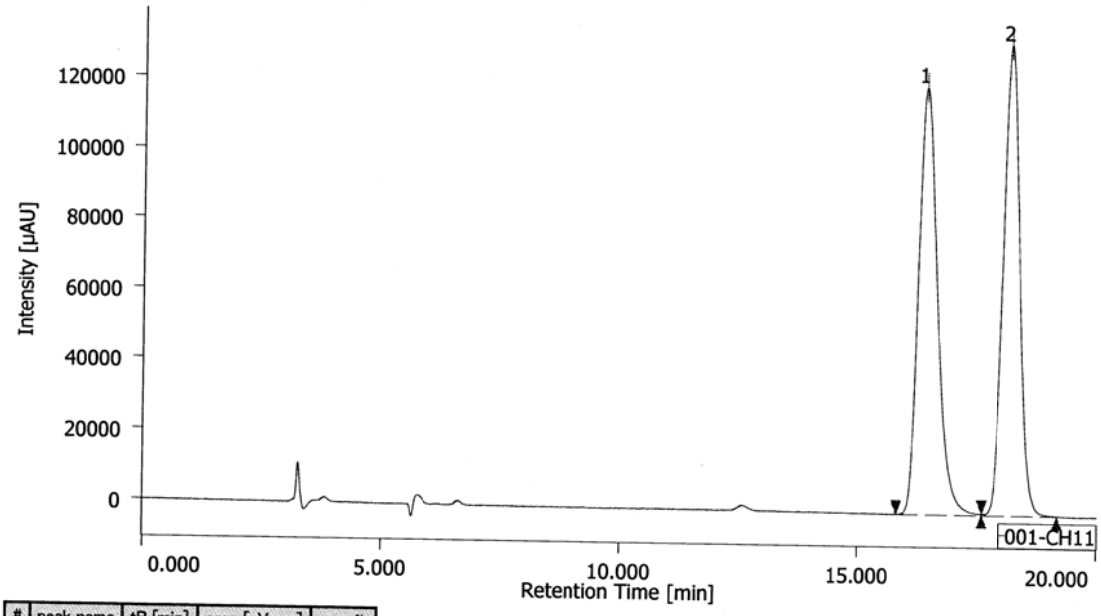


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	14.573	2398760	49.963
2	Unknown	15.947	2402292	50.037

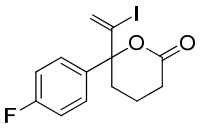
chiral



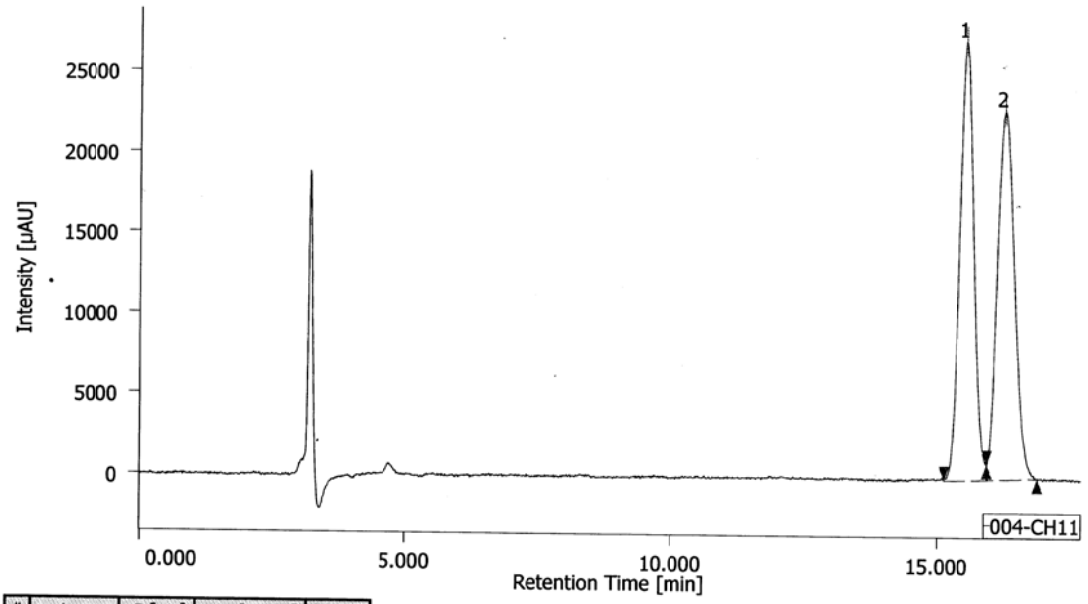
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	16.373	3286692	50.647
2	Unknown	18.147	3202717	49.353

HPLC chart for **3f**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 217 nm

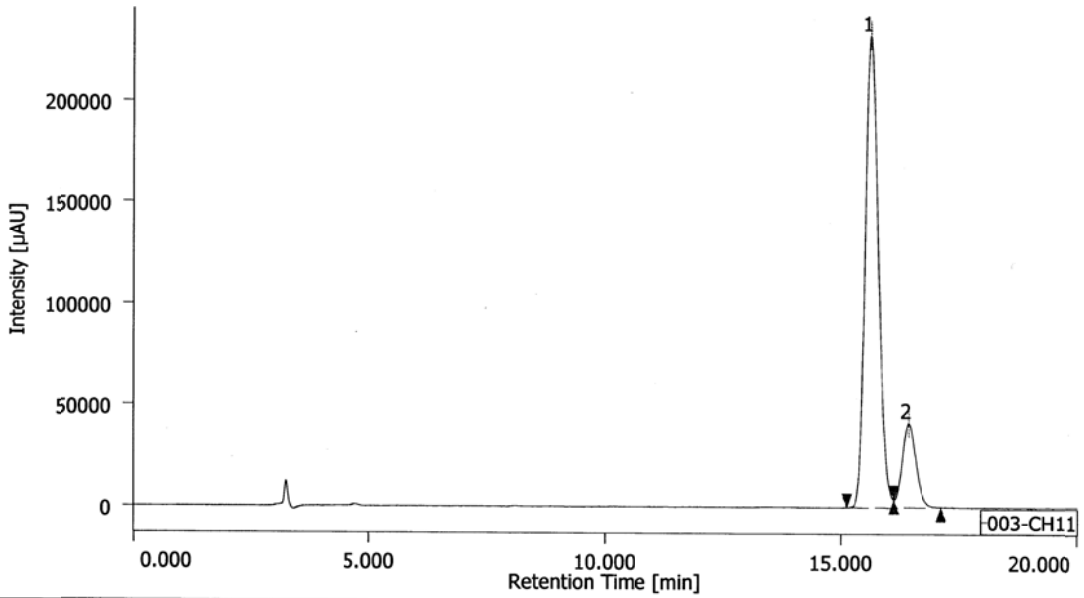


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	15.533	508795	50.120
2	Unknown	16.253	506363	49.880

chiral

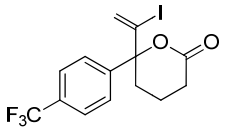


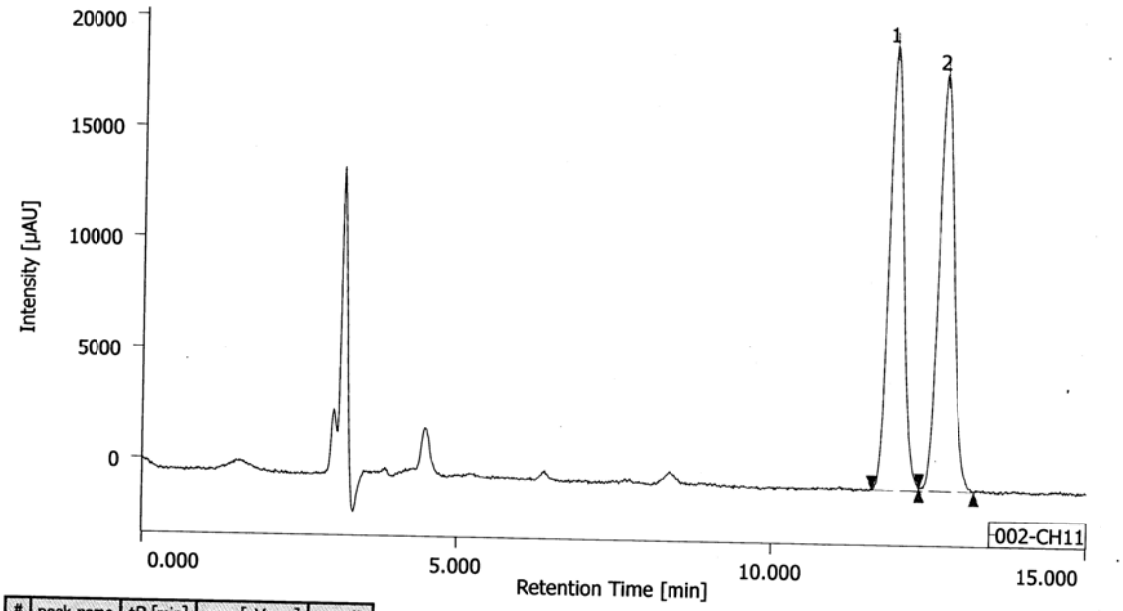
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	15.627	4461015	83.902
2	Unknown	16.413	855945	16.098

HPLC chart for **3g**

DAICEL CHIRALPAK AD-H, Hexane/*i*PrOH = 95/5, flow rate = 1.0 mL/min, 218 nm

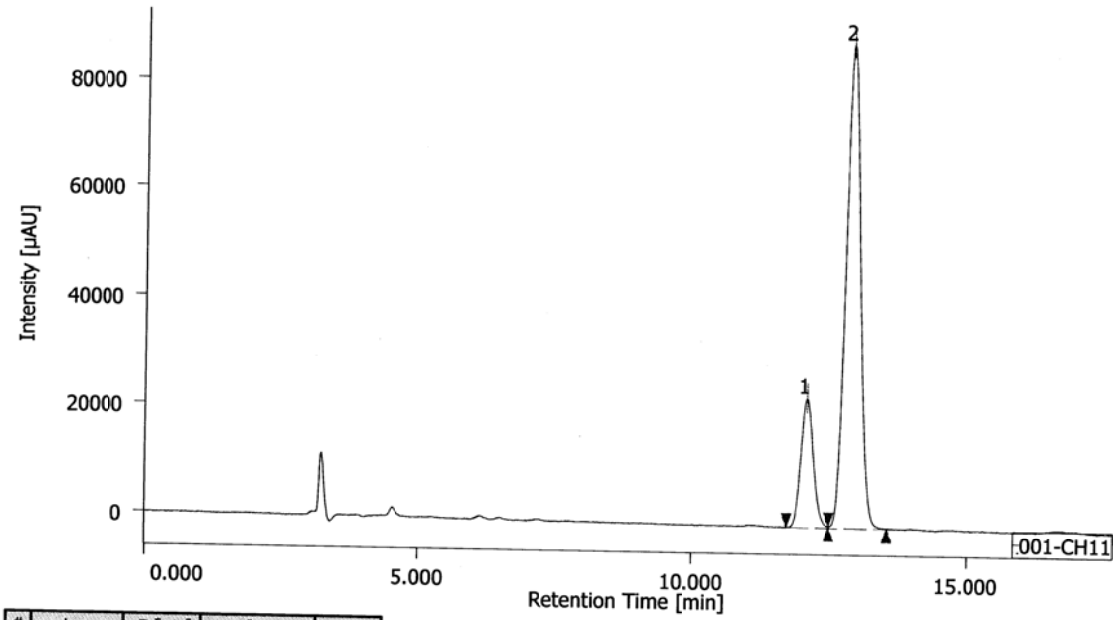
racemic





#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	11.920	315154	49.669
2	Unknown	12.720	319352	50.331

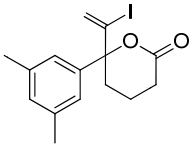
chiral



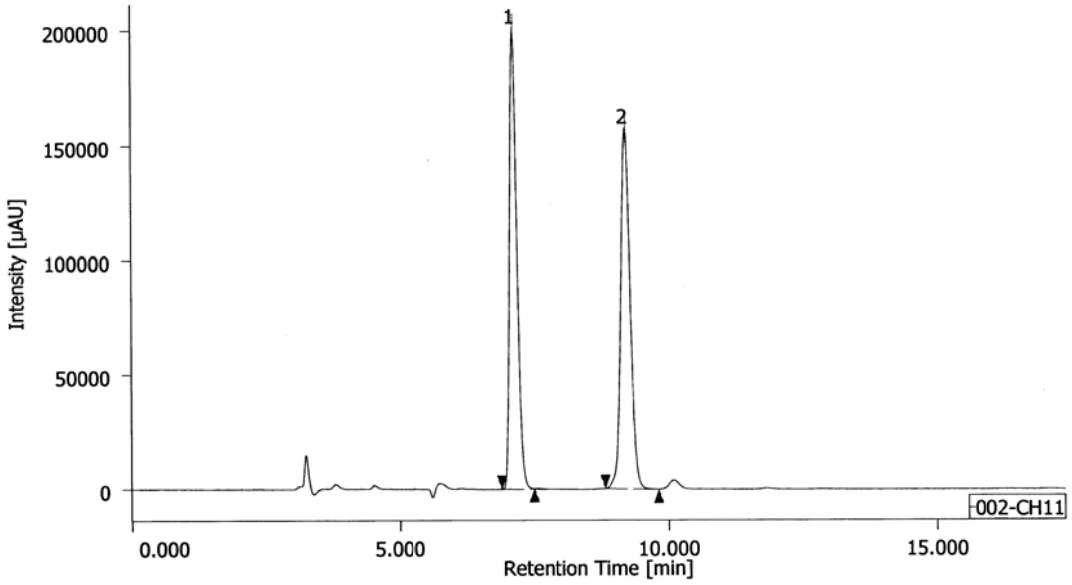
#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	12.080	375168	18.799
2	Unknown	12.880	1620549	81.201

HPLC chart for **3h**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 94/6, flow rate = 1.0 mL/min, 219 nm

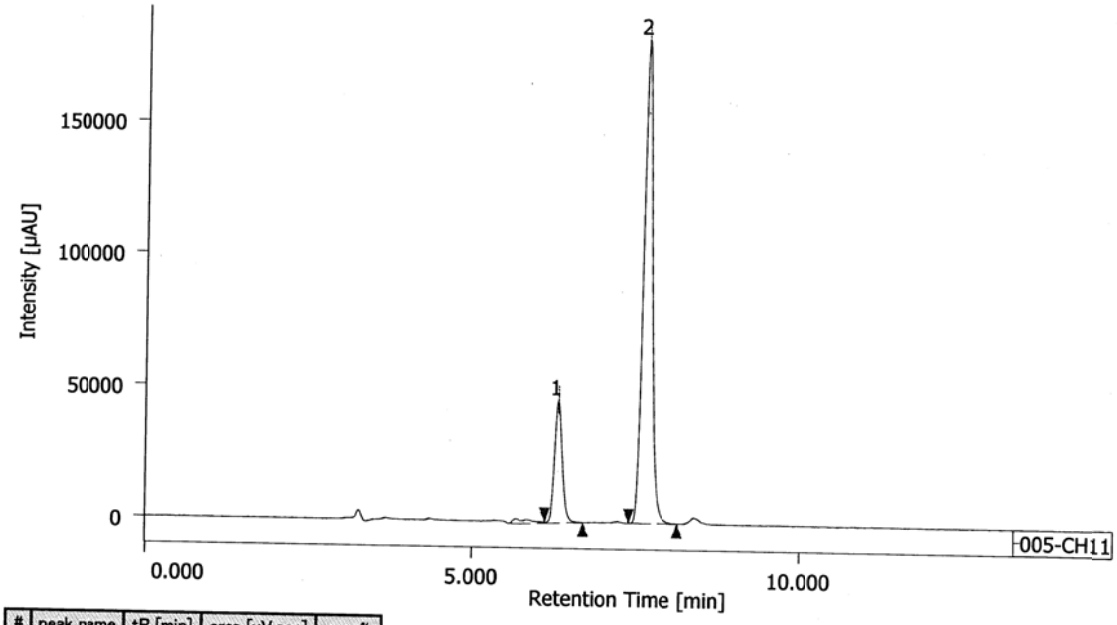


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.120	1866528	49.348
2	Unknown	9.213	1915852	50.652

chiral

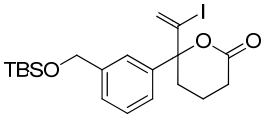


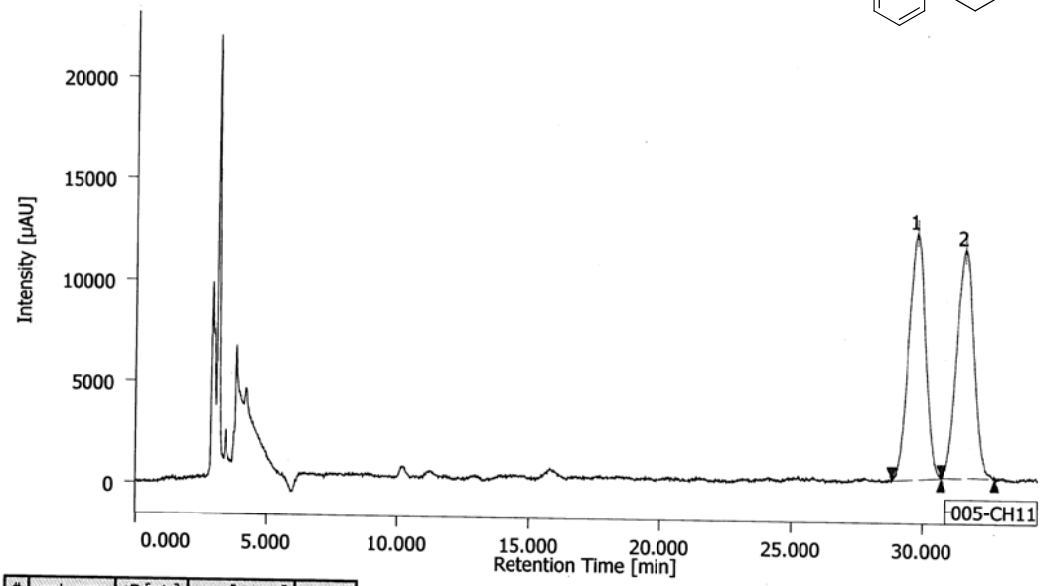
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	6.307	375544	17.824
2	Unknown	7.627	1731400	82.176

HPLC chart for **3i**

DAICEL CHIRALPAK AD-H, Hexane/*i*PrOH = 99/1, flow rate = 1.2 mL/min, 217 nm

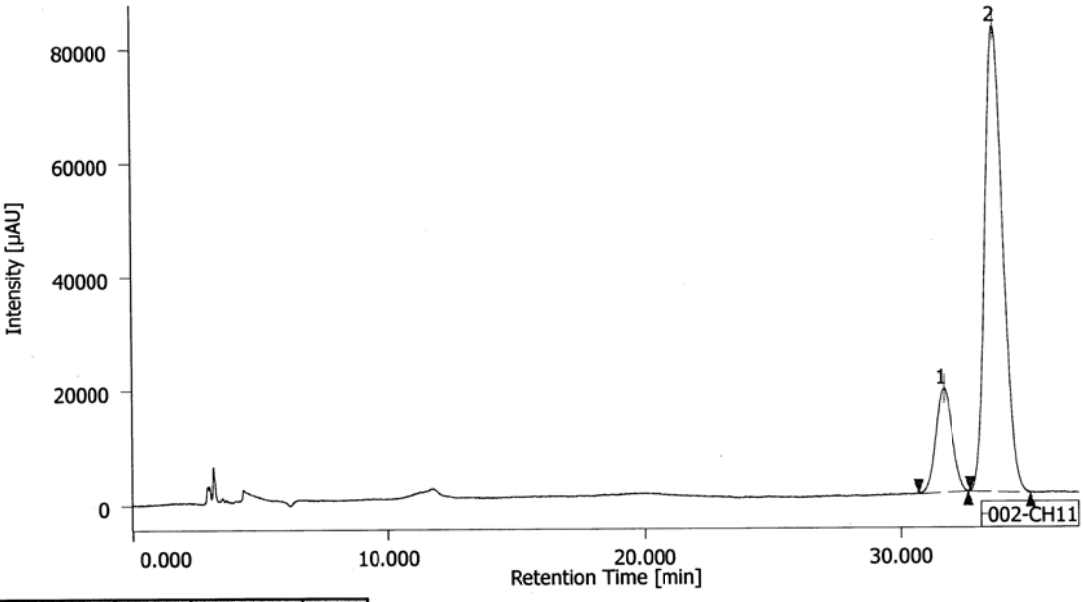
racemic





#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	29.693	532618	50.800
2	Unknown	31.547	515840	49.200

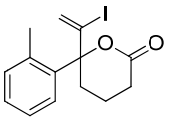
chiral



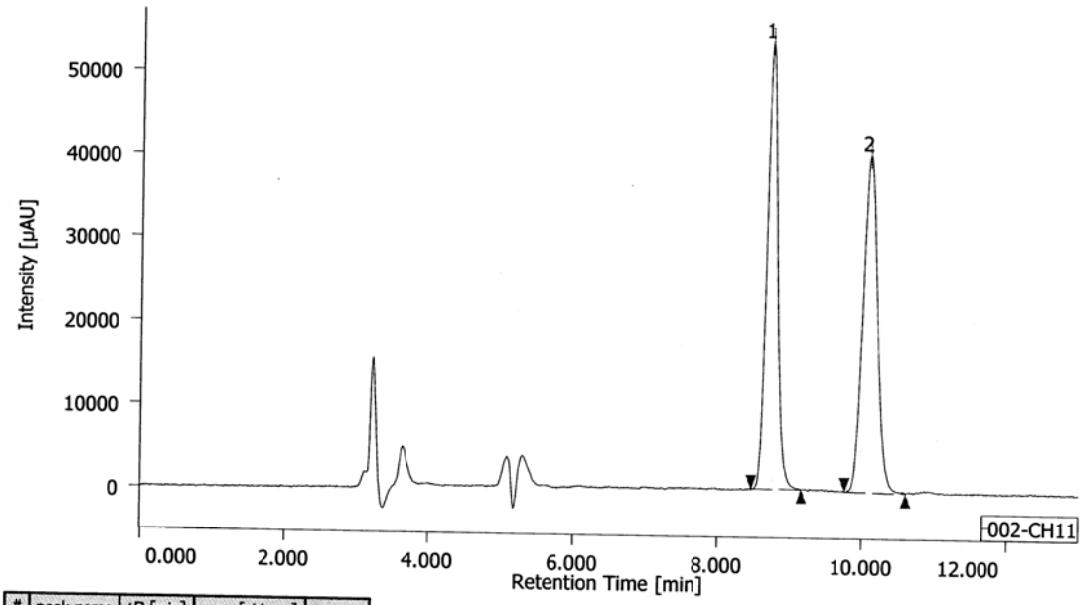
#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	31.667	815858	16.939
2	Unknown	33.680	4000583	83.061

HPLC chart for **3j**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 217 nm

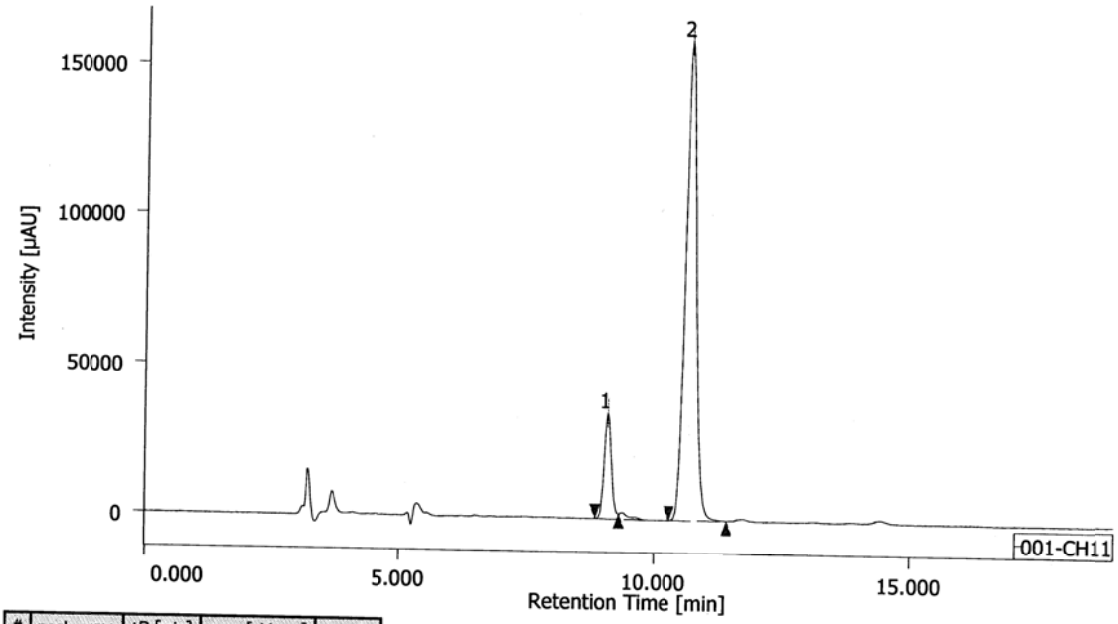


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	8.720	555222	49.936
2	Unknown	10.080	556654	50.064

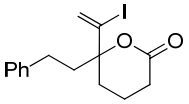
chiral



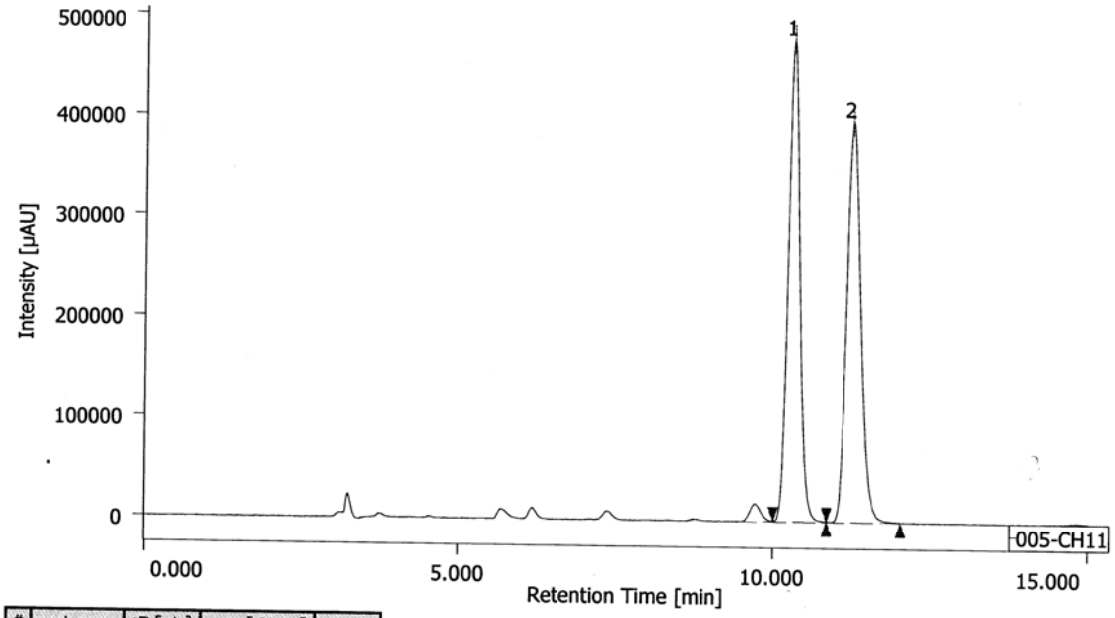
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	9.080	354786	12.953
2	Unknown	10.667	2384182	87.047

HPLC chart for **3k**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 94/6, flow rate = 1.0 mL/min, 206 nm

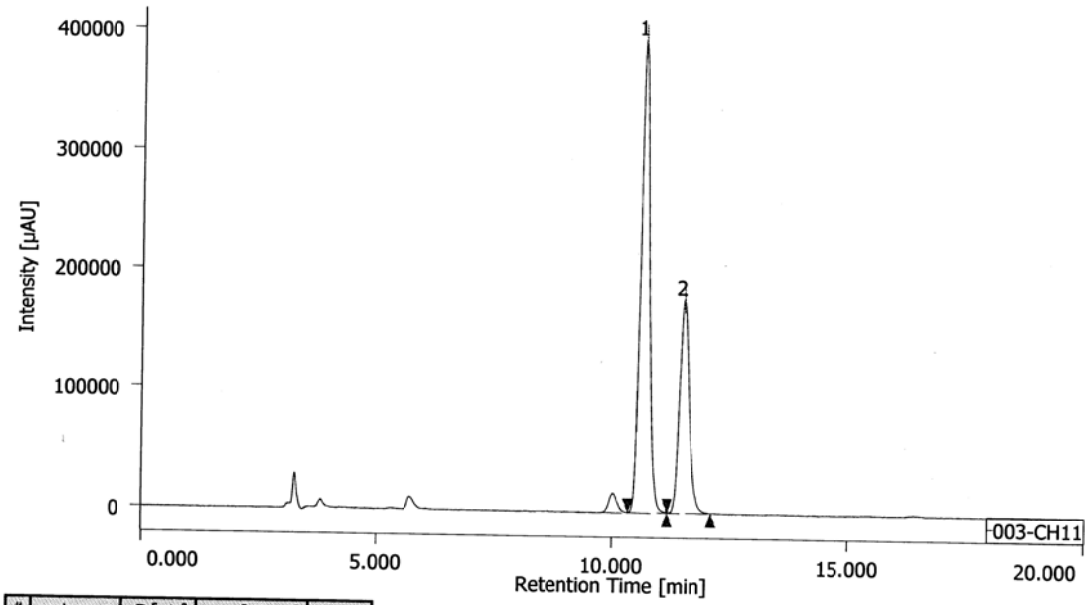


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	10.293	6203433	50.093
2	Unknown	11.240	6180507	49.907

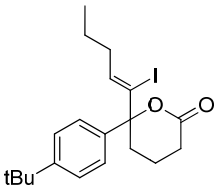
chiral



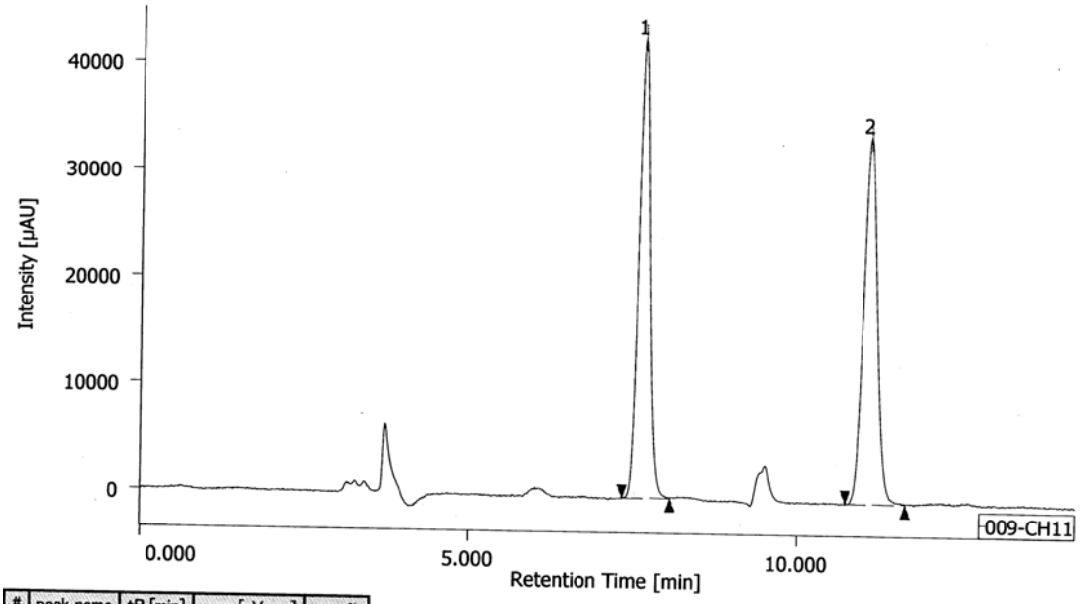
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	10.640	5195041	67.008
2	Unknown	11.507	2557776	32.992

HPLC chart for **3l**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 221 nm

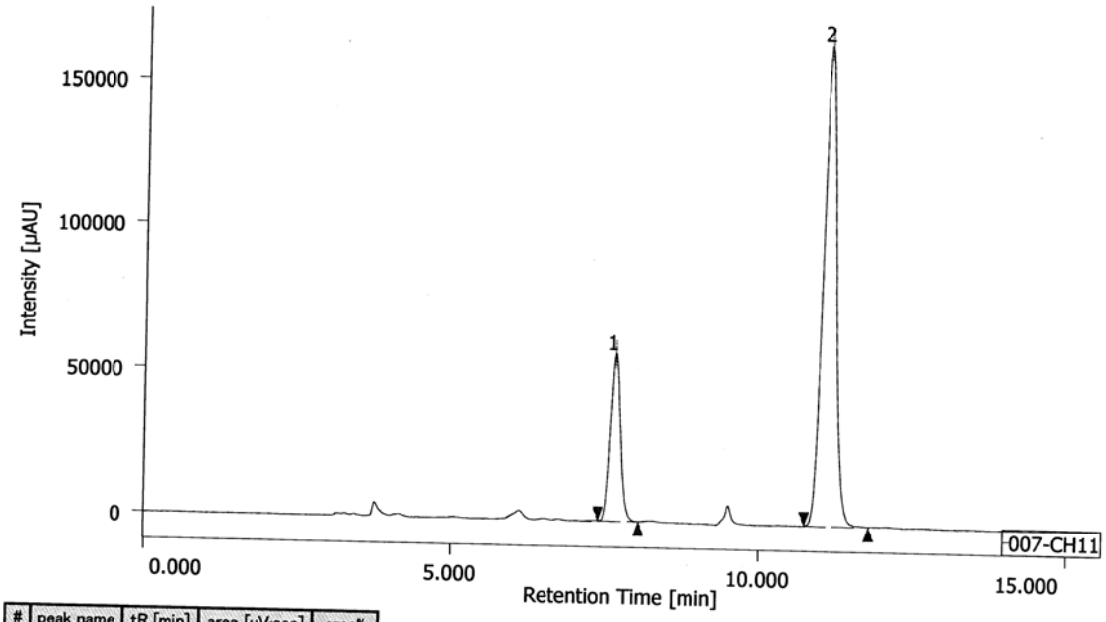


racemic



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.627	496039	49.714
2	Unknown	11.080	501750	50.286

chiral

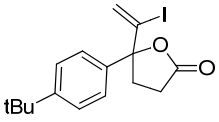


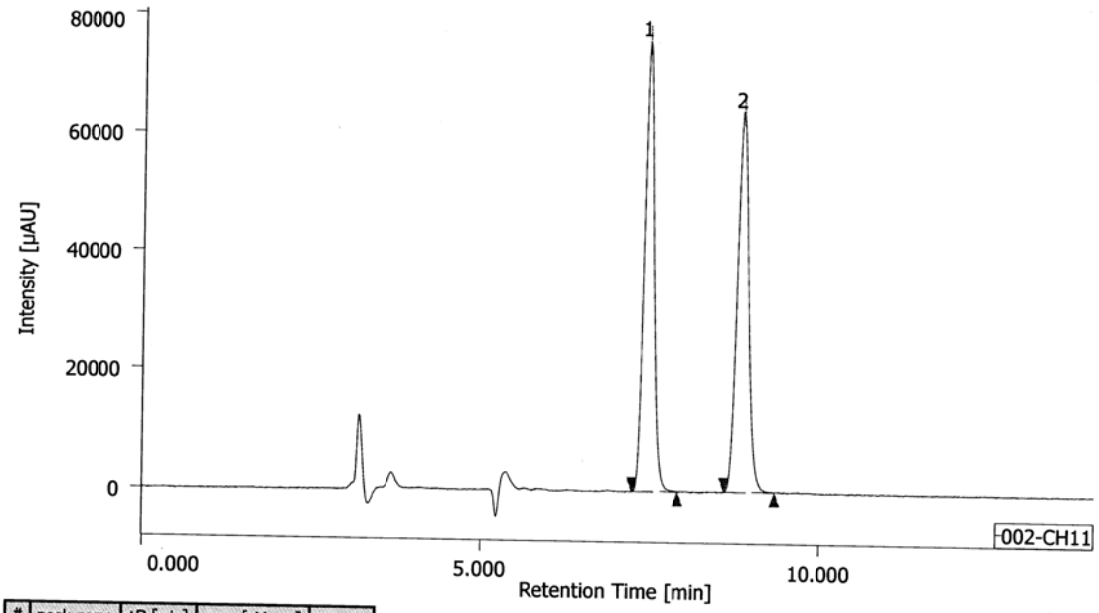
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.640	644387	20.662
2	Unknown	11.093	2474302	79.338

HPLC chart for **3m**

DAICEL CHIRALPAK AD-H, Hexane/EtOH = 93/7, flow rate = 1.0 mL/min, 222 nm

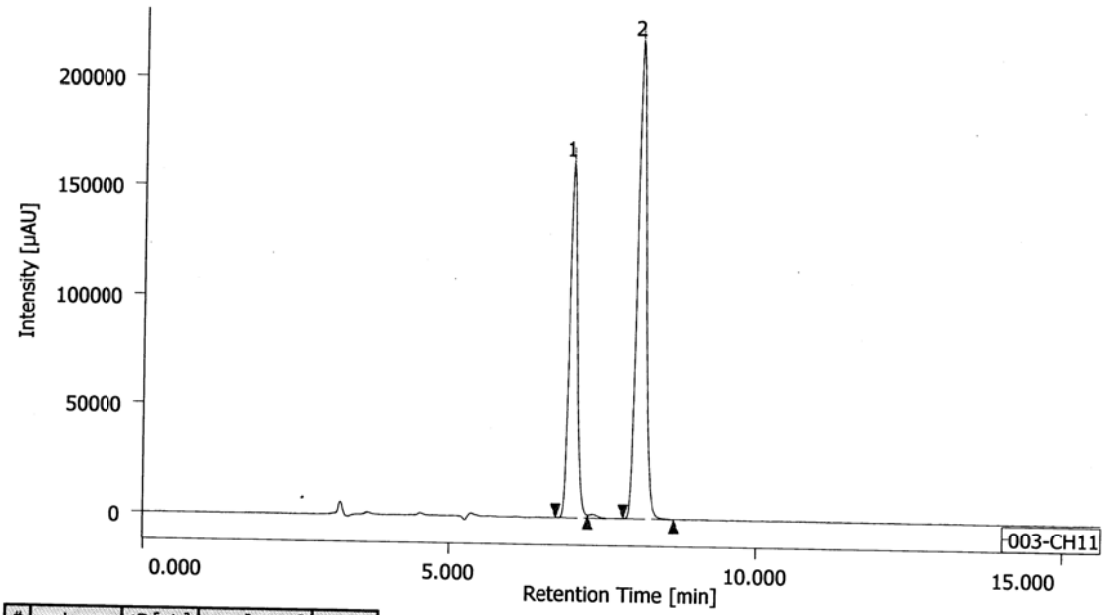
racemic





#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	7.440	749466	50.000
2	Unknown	8.840	749469	50.000

chiral



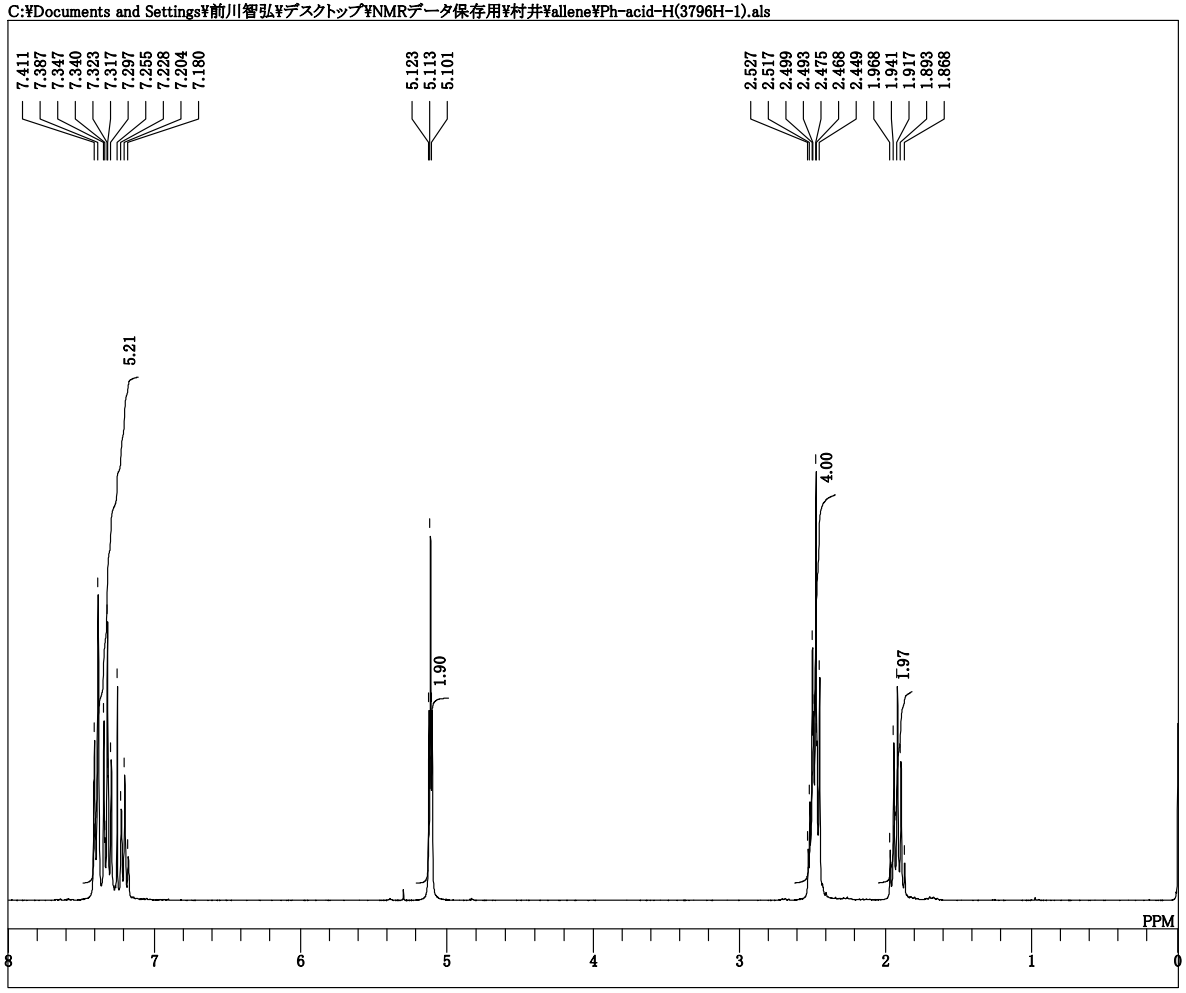
#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	6.987	1437605	39.564
2	Unknown	8.080	2195976	60.436

8. ^{1}H and ^{13}C NMR Data

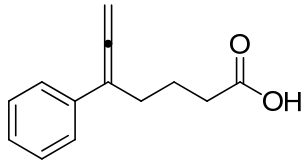
^{1}H NMR chart of **2a**

3796H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥Ph-acid-H(3796H-1).als



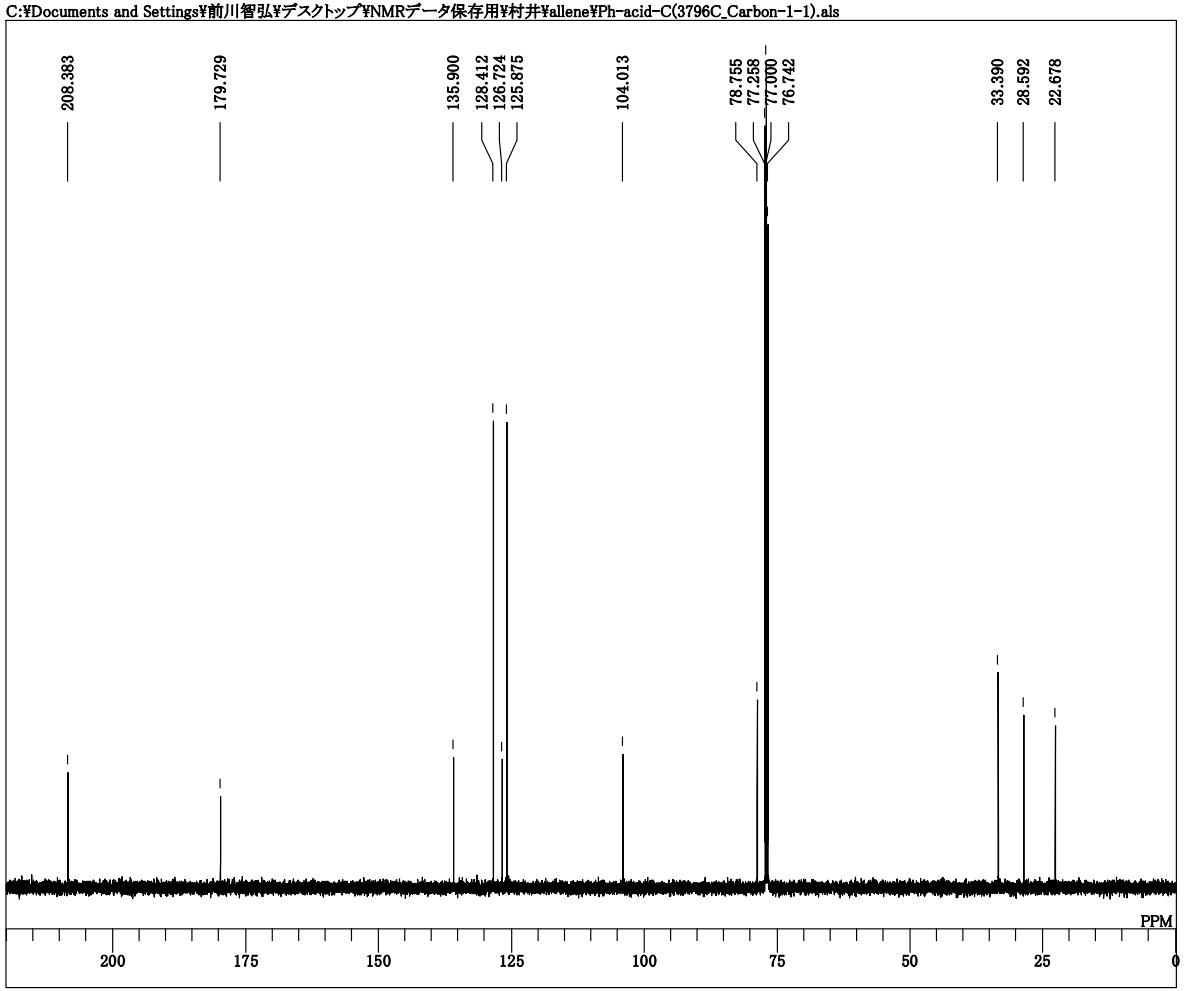
DFILE	Ph-acid-H(3796H-1).als
COMNT	3796H
DATIM	27-02-2014 16:18:42
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	16.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



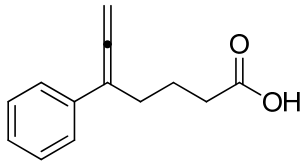
^{13}C NMR chart of **2a**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥Ph-acid-C(3796C_Carbon-1-1).als



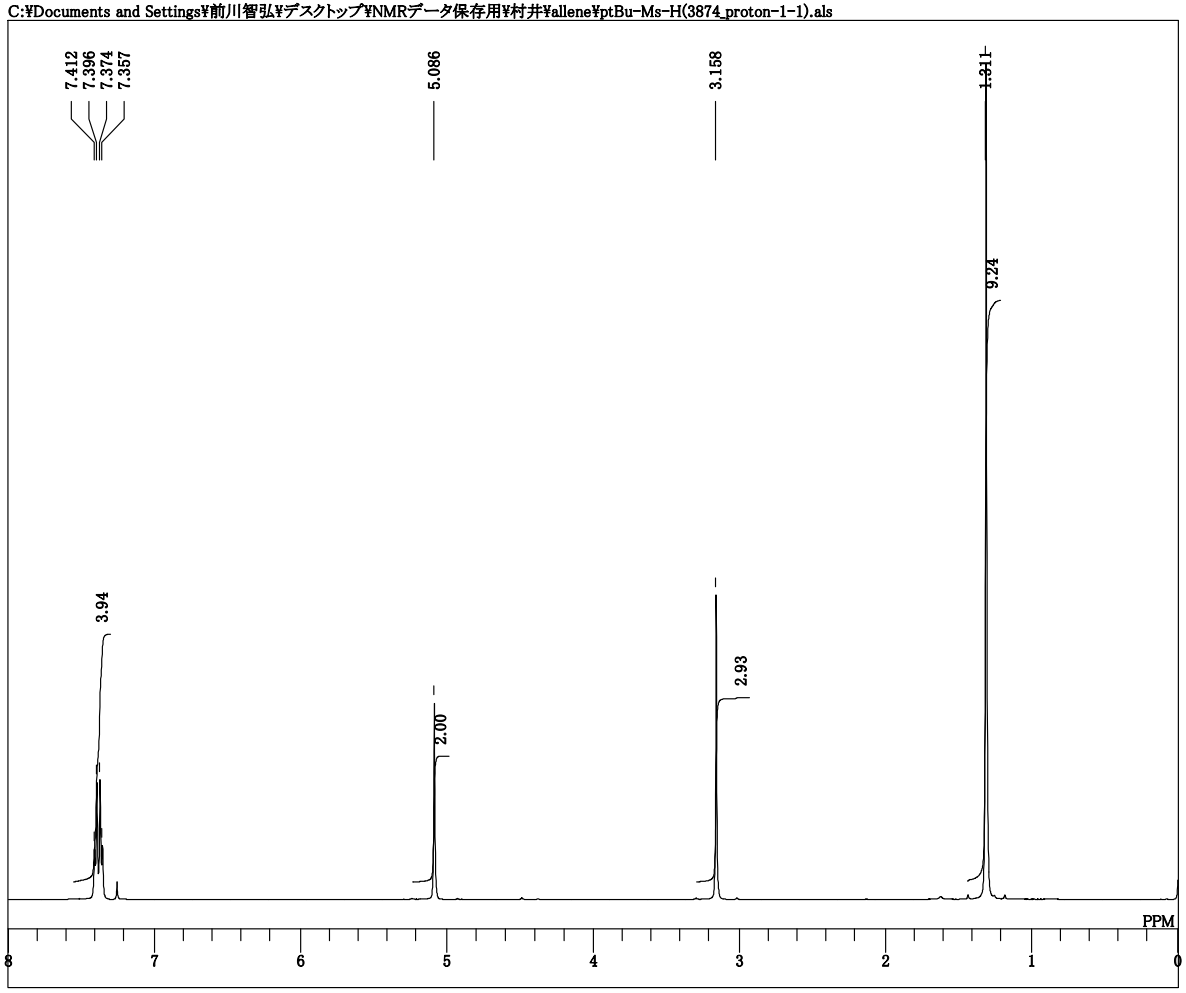
DFILE	Ph-acid-C(3796C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	27-02-2014 17:14:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	463
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



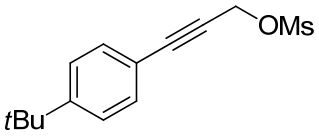
^{1}H NMR chart of **5b**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥ptBu-Ms-H(3874_proton-1-1).als



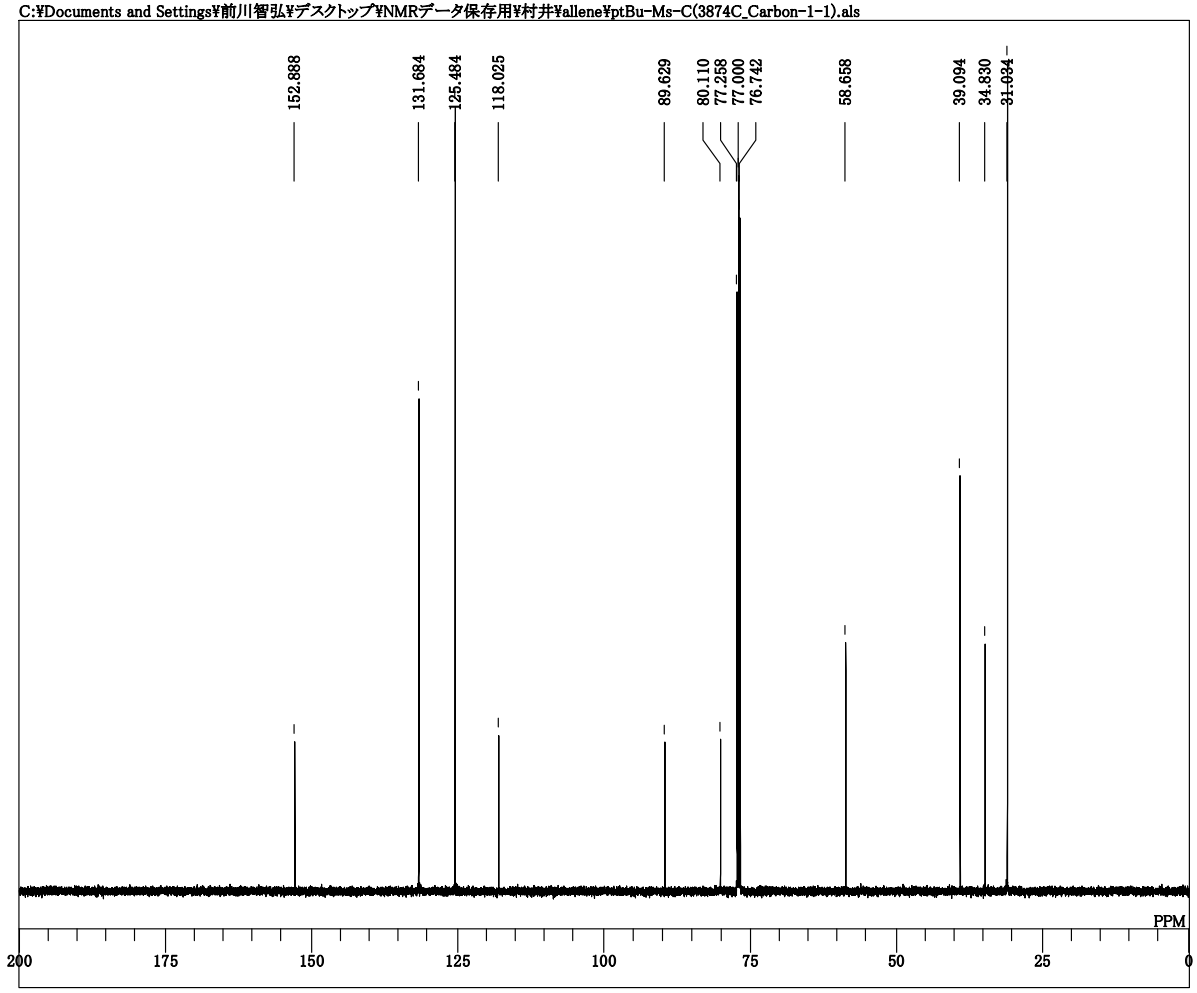
DFILE	ptBu-Ms-H(3874_proton-1-1).als
COMNT	single_pulse
DATIM	28-02-2014 10:41:55
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.91 KHz
OBFIN	6.17 Hz
POINT	13107
FREQU	8503.40 Hz
SCANS	16
ACQTM	1.5414 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	17.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	30



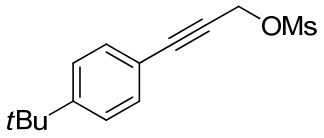
^{13}C NMR chart of **5b**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥ptBu-Ms-C(3874C_Carbon-1-1).als

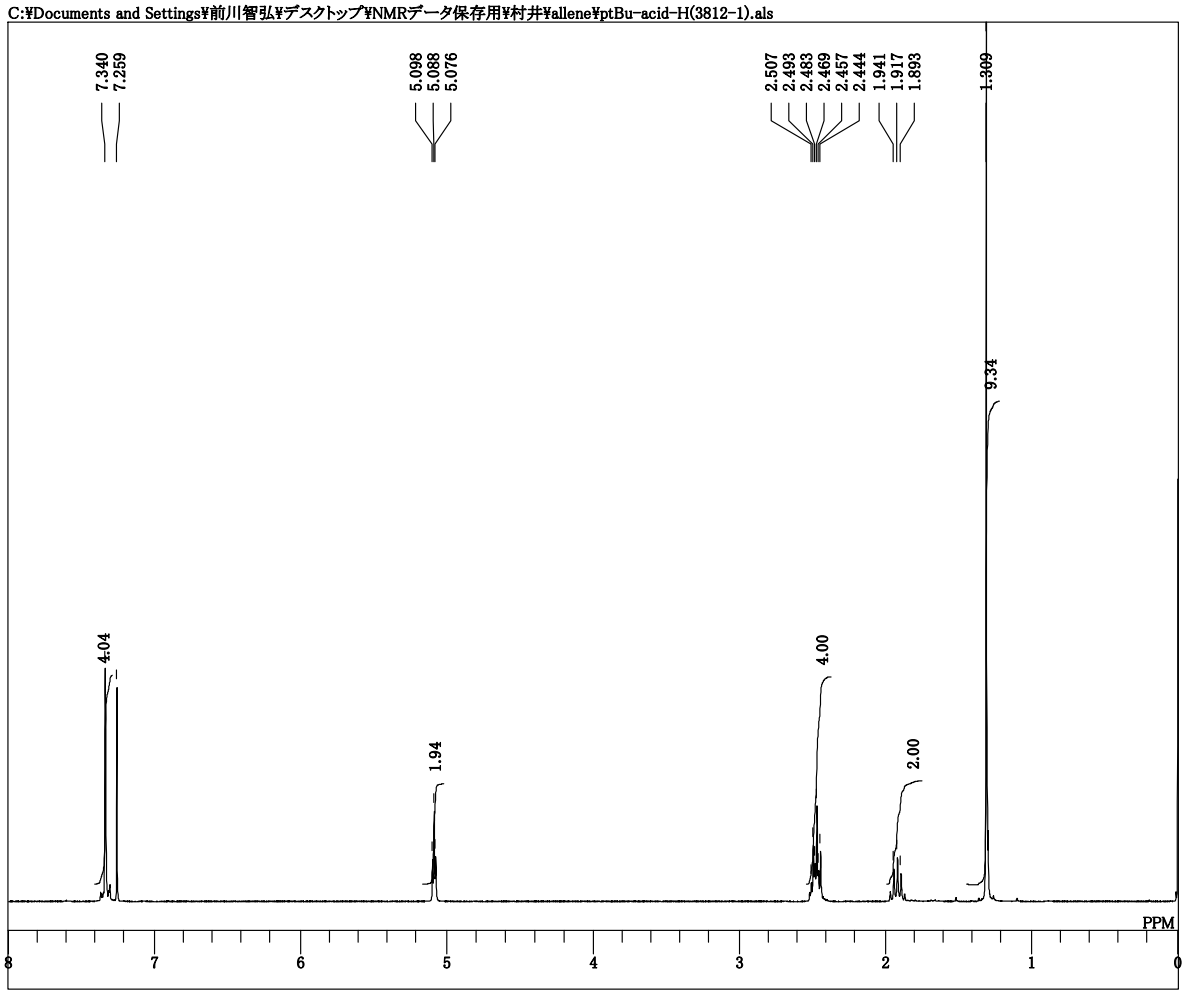


DFILE	ptBu-Ms-C(3874C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	28-02-2014 11:17:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	405
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

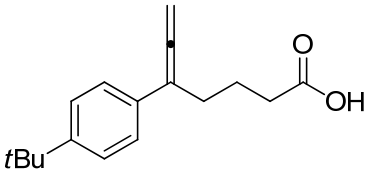


^{1}H NMR chart of **2b**

3812

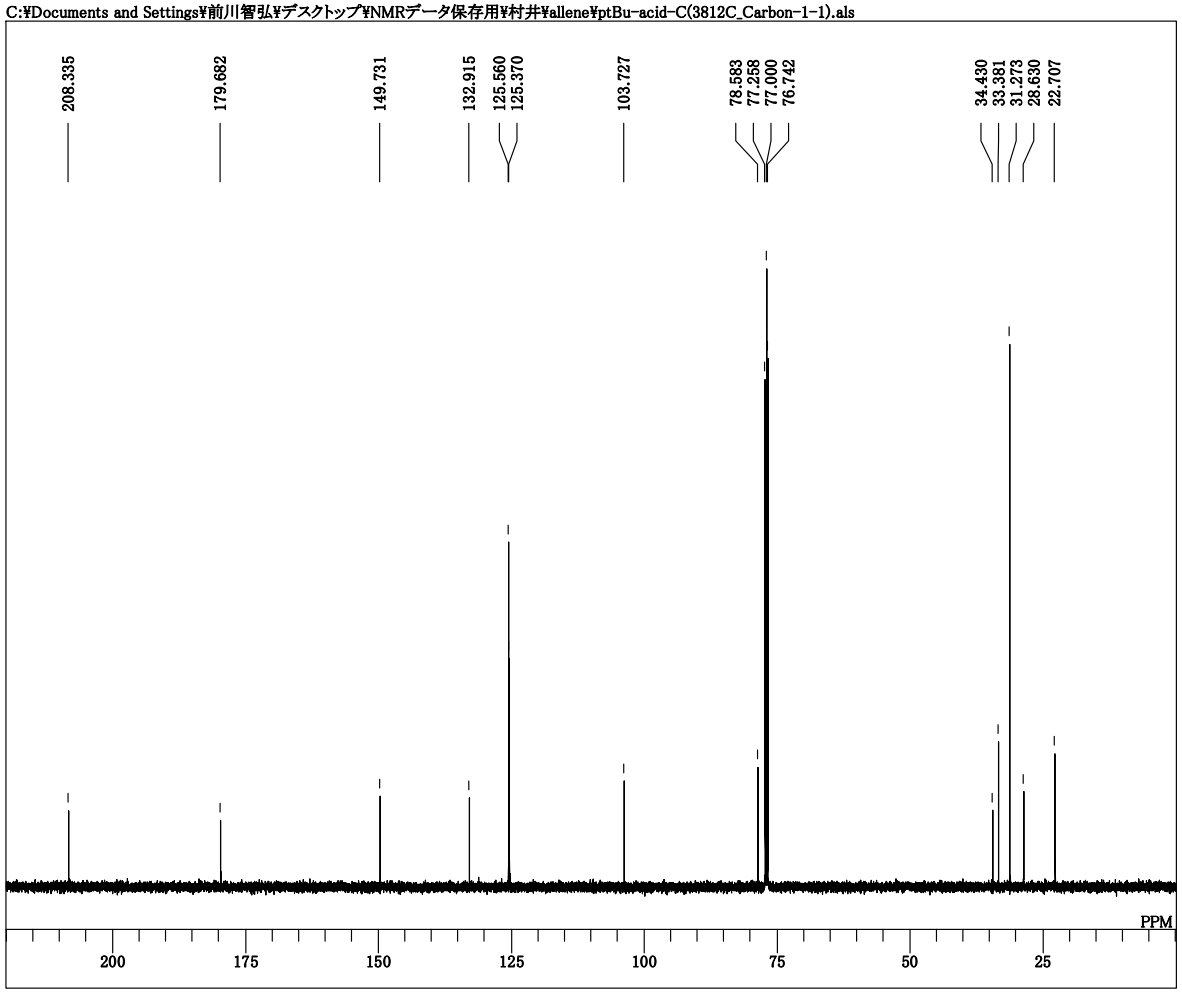


DFILE	ptBu-acid-H(3812-1).als
COMNT	3812
DATIM	11-11-2013 14:39:35
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

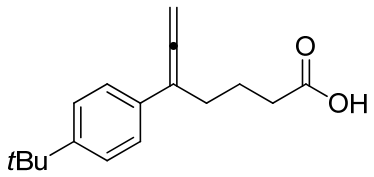


^{13}C NMR chart of **2b**

single pulse decoupled gated NOE

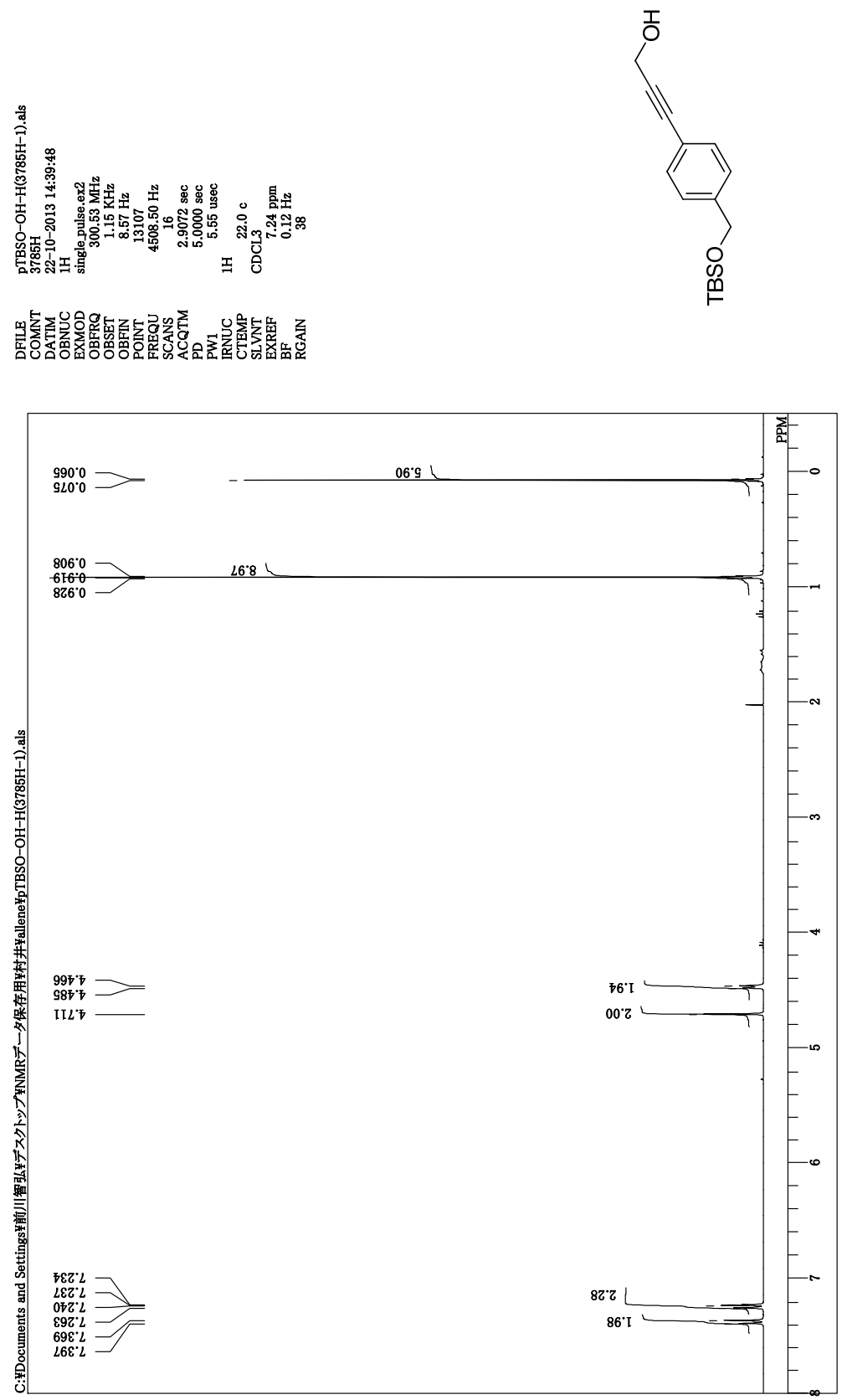


DFILE	ptBu-acid-C(3812C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	27-02-2014 21:35:12
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	370
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



^{1}H NMR chart of **4c**

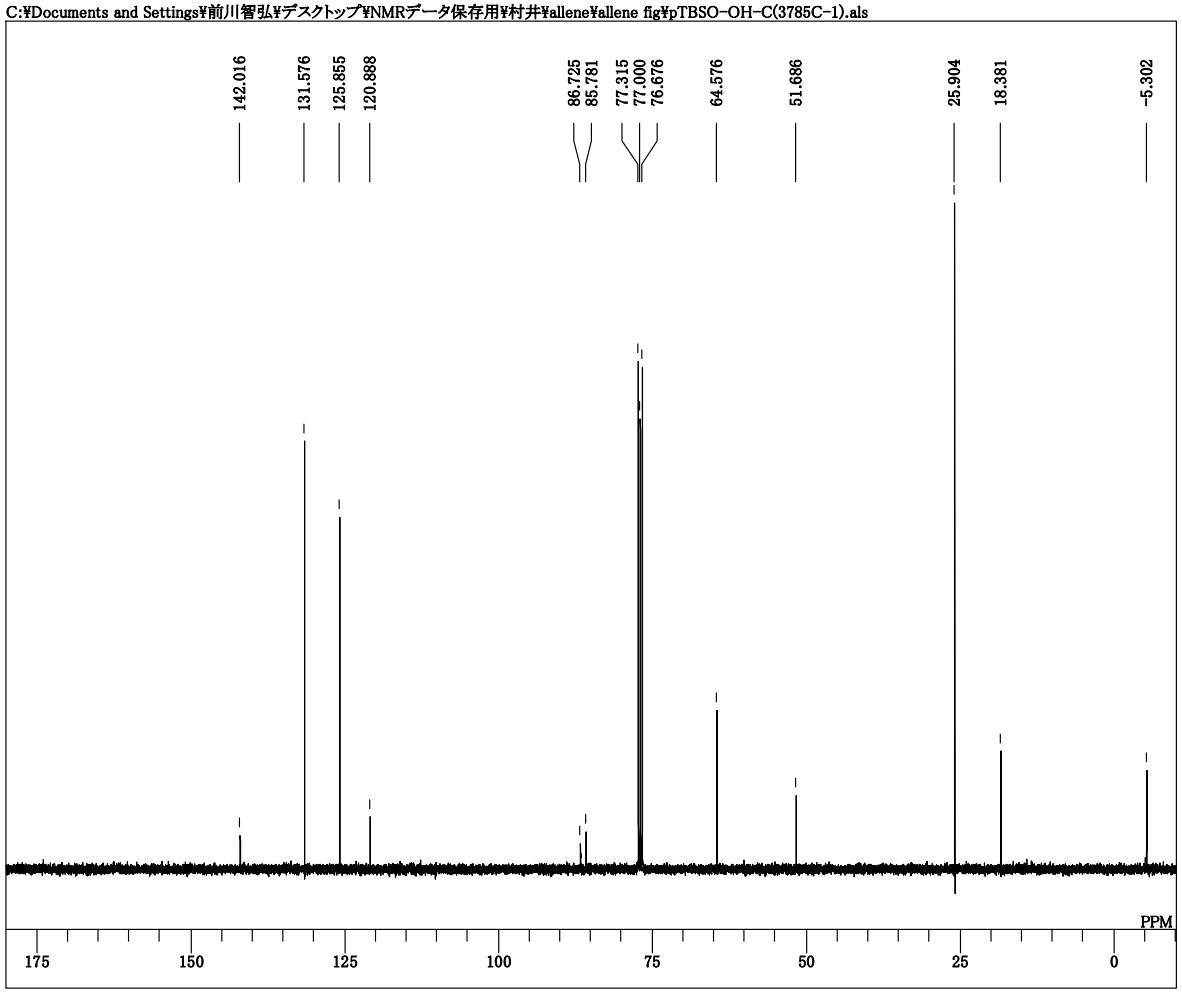
3785H



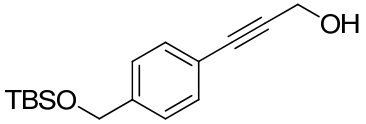
^{13}C NMR chart of **4c**

3785C

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥allene fig¥pTBSO-OH-C(3785C-1).als



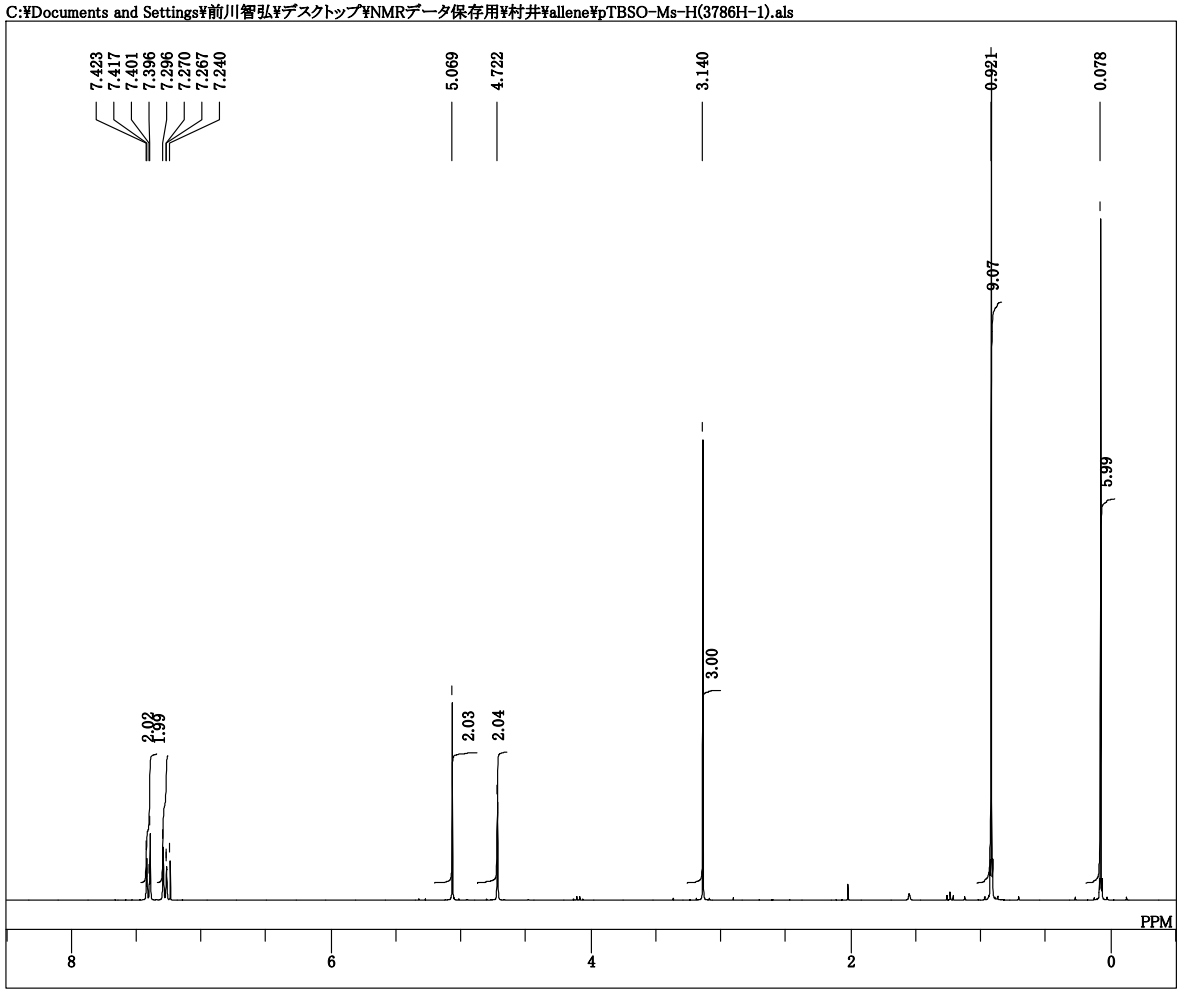
DFILE	pTBSO-OH-C(3785C-1).als
COMNT	3785C
DATIM	22-10-2013 14:58:32
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	471
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



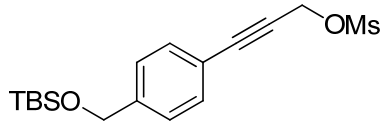
^{1}H NMR chart of **5c**

3786H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥pTBSO-Ms-H(3786H-1).als

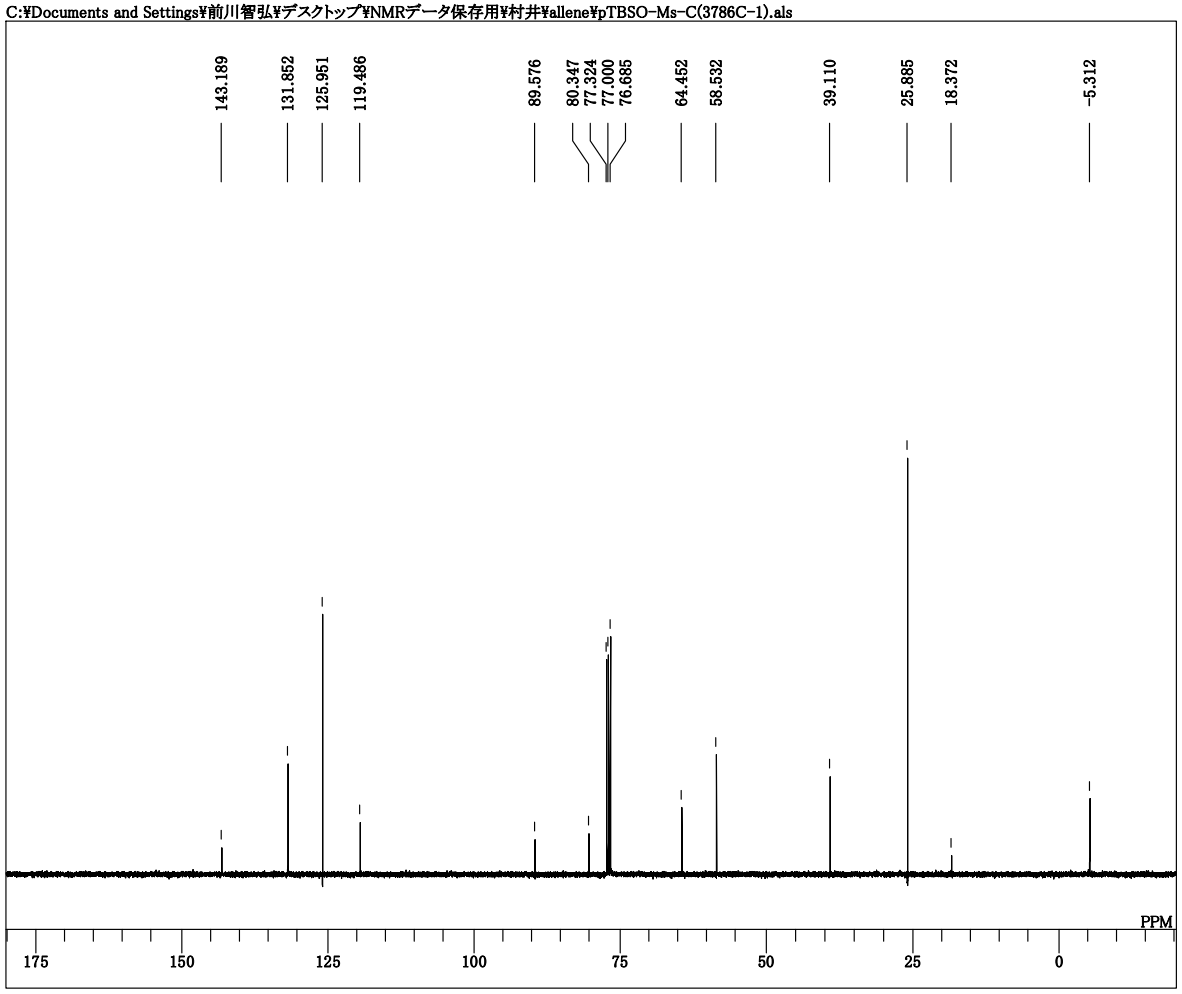


DFILE	pTBSO-Ms-H(3786H-1).als
COMNT	3786H
DATIM	22-10-2013 18:28:01
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	36

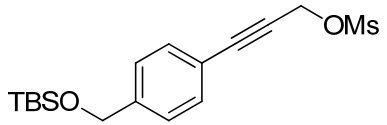


^{13}C NMR chart of **5c**

3786C



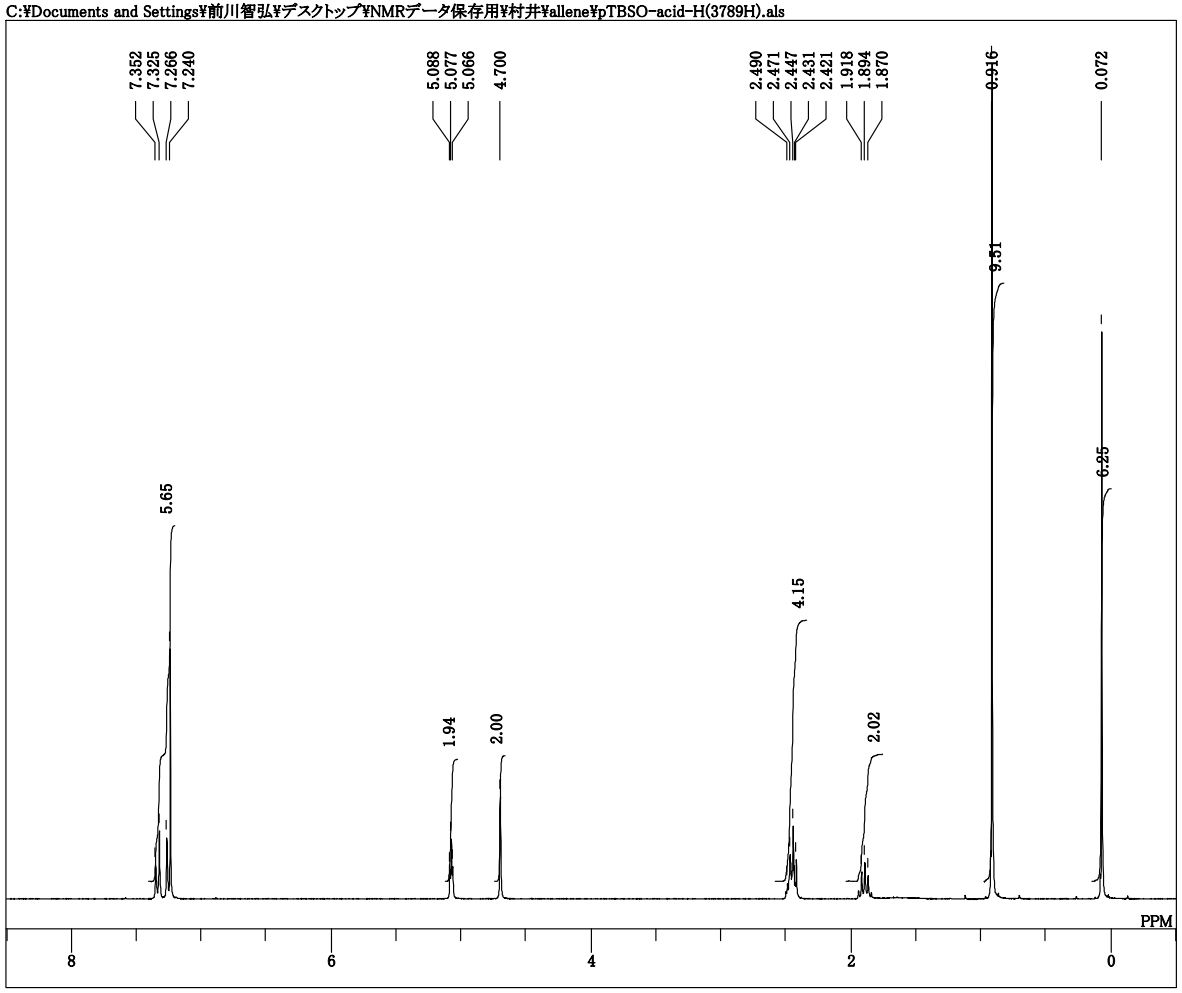
DFILE	pTBSO-Ms-C(3786C-1).als
COMNT	3786C
DATIM	22-10-2013 19:08:41
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.24 Hz
SCANS	411
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



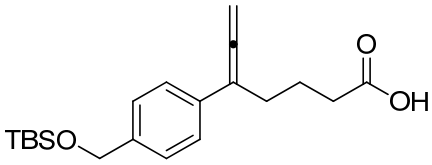
^{1}H NMR chart of **2c**

3789

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥pTBSO-acid-H(3789H).als

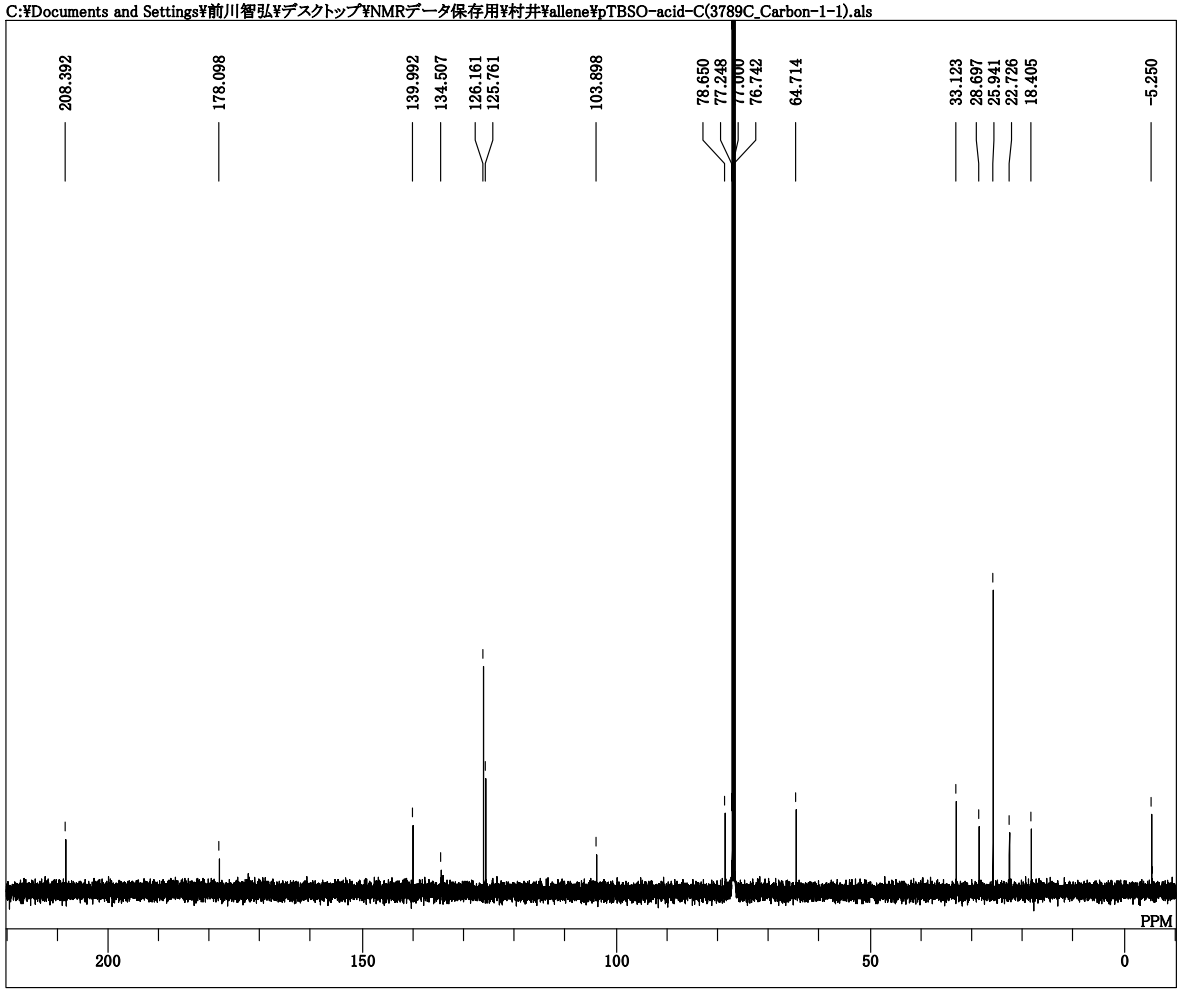


DFILE	pTBSO-acid-H(3789H).als
COMNT	3789
DATIM	24-10-2013 14:39:00
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	42

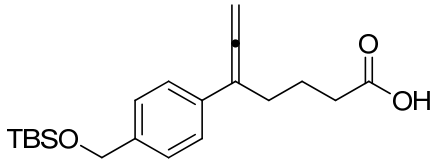


^{13}C NMR chart of **2c**

single pulse decoupled gated NOE



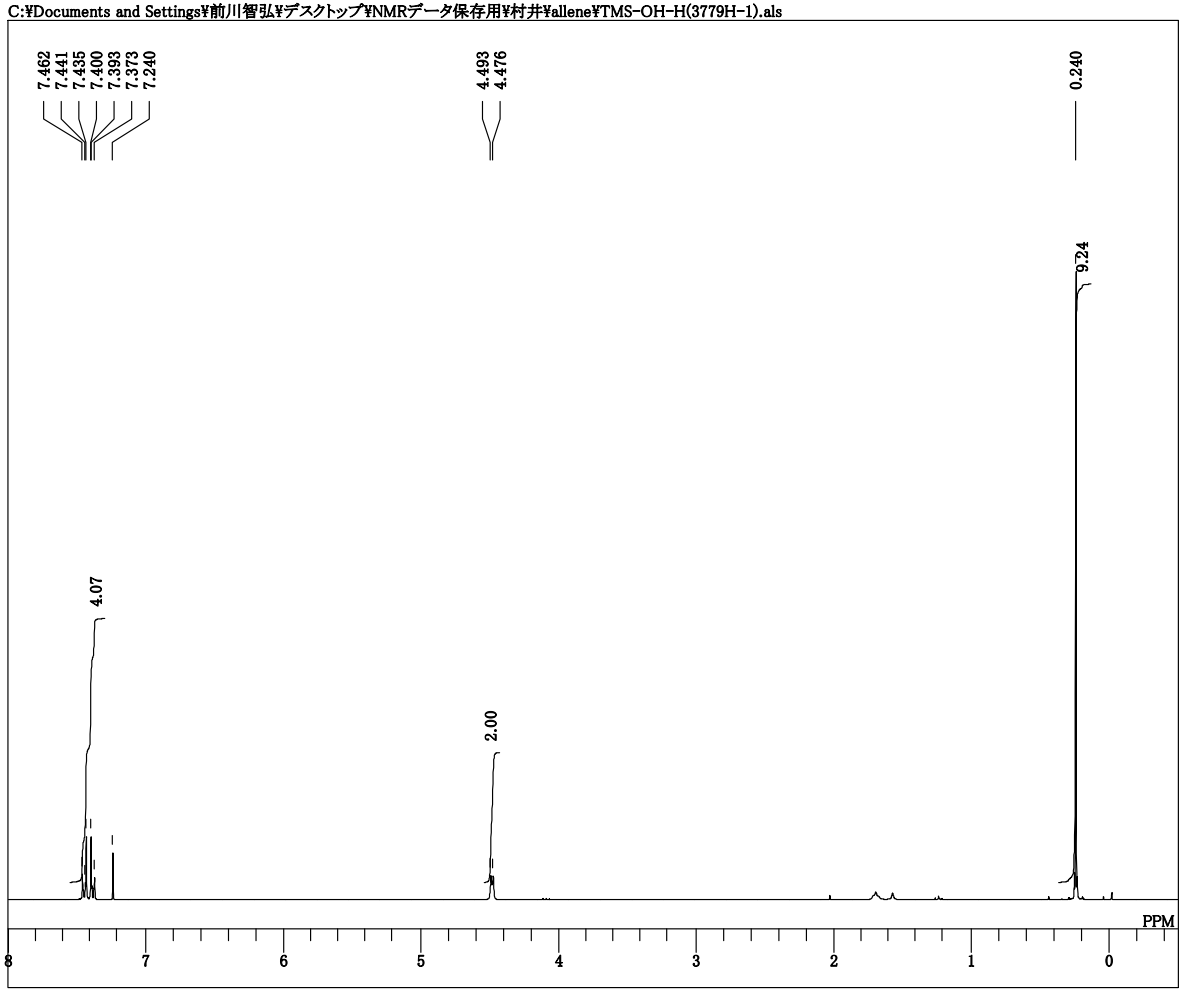
DFILE	pTBSO-acid-C(3789C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	24-10-2013 15:32:15
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	988
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



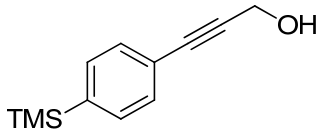
^{1}H NMR chart of **4d**

3779H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥TMS-OH-H(3779H-1).als

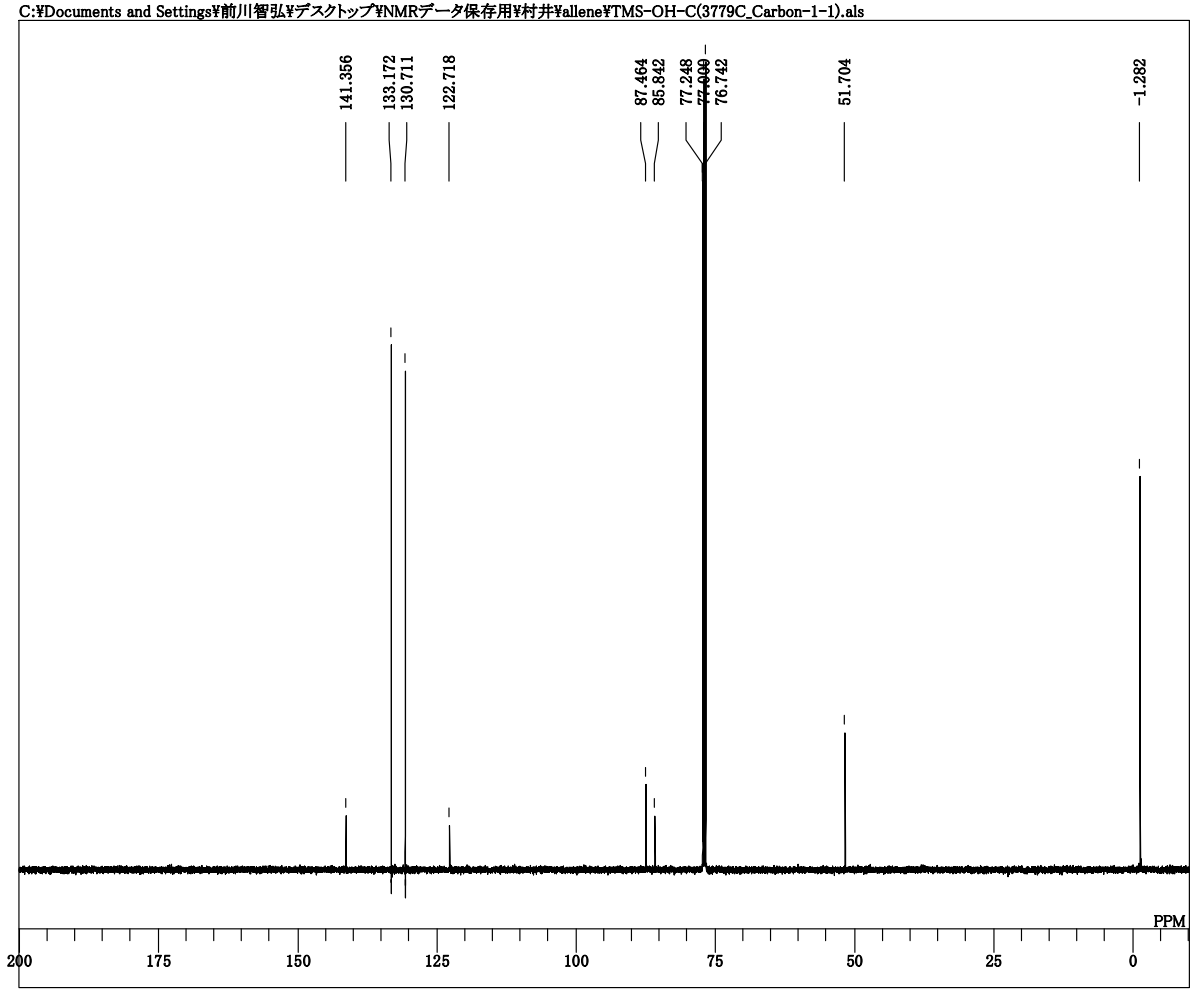


DFILE	TMS-OH-H(3779H-1).als
COMNT	3779H
DATIM	18-10-2013 19:56:51
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.2 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	38

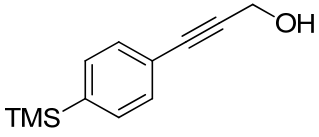


^{13}C NMR chart of **4d**

single pulse decoupled gated NOE



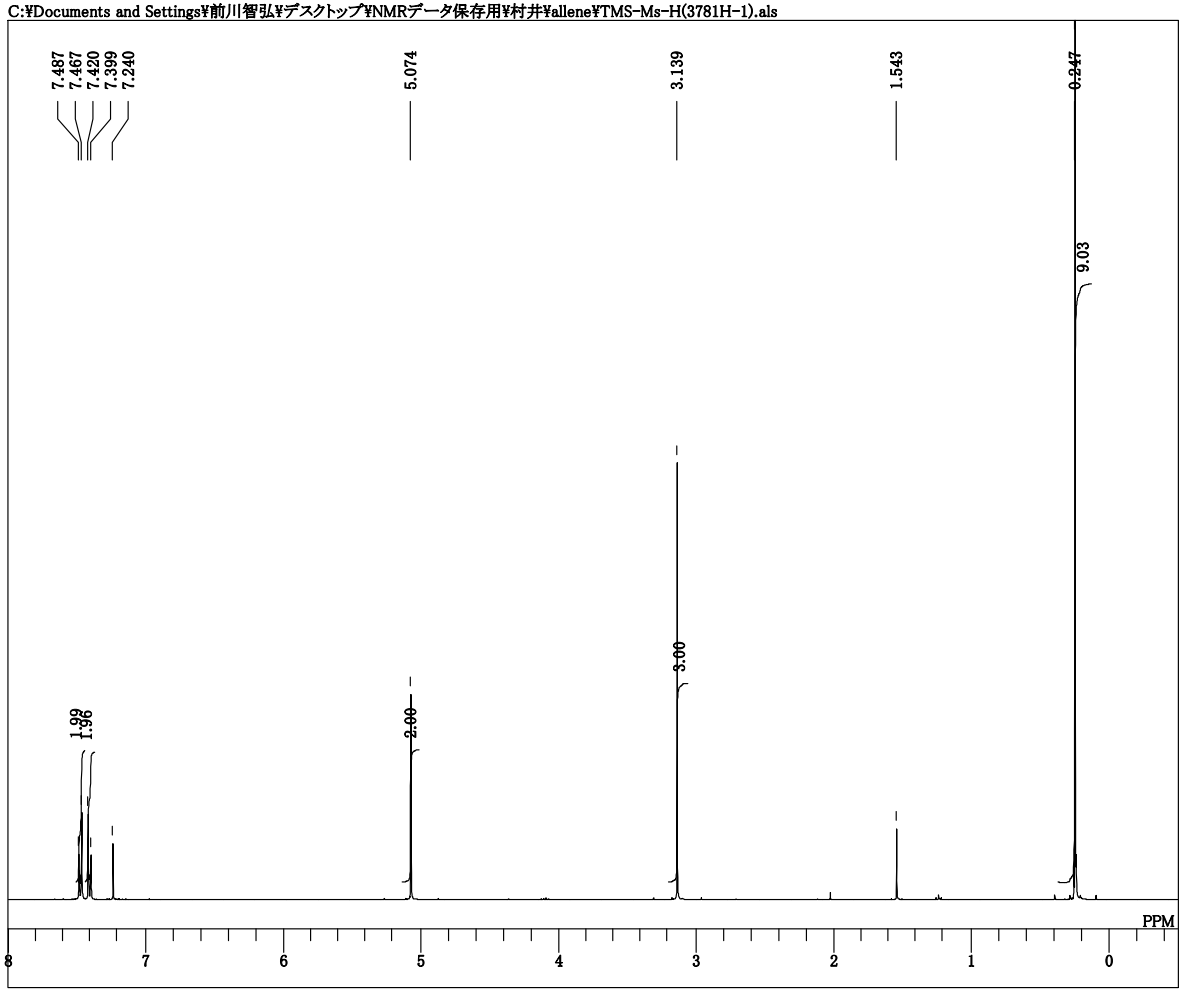
DFILE	TMS-OH-C(3779C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	19-10-2013 09:42:34
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1439
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



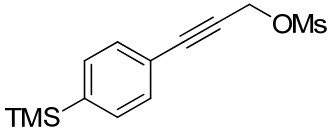
^{1}H NMR chart of **5d**

3781H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥TMS-Ms-H(3781H-1).als

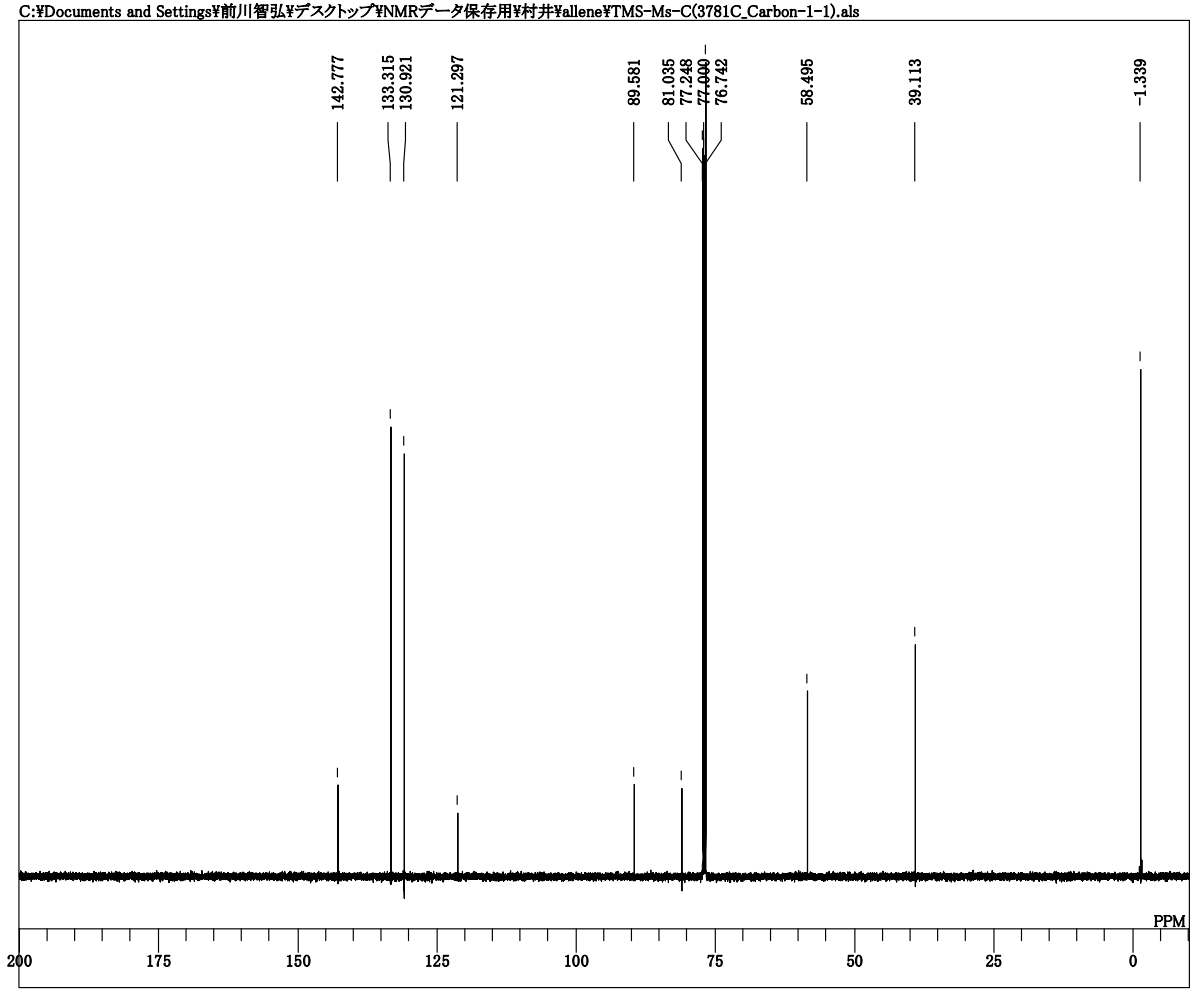


DFILE	TMS-Ms-H(3781H-1).als
COMNT	3781H
DATIM	19-10-2013 11:31:08
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.35 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	7.24 ppm
BF	0.12 Hz
RGAIN	42

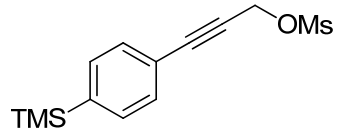


^{13}C NMR chart of **5d**

single pulse decoupled gated NOE



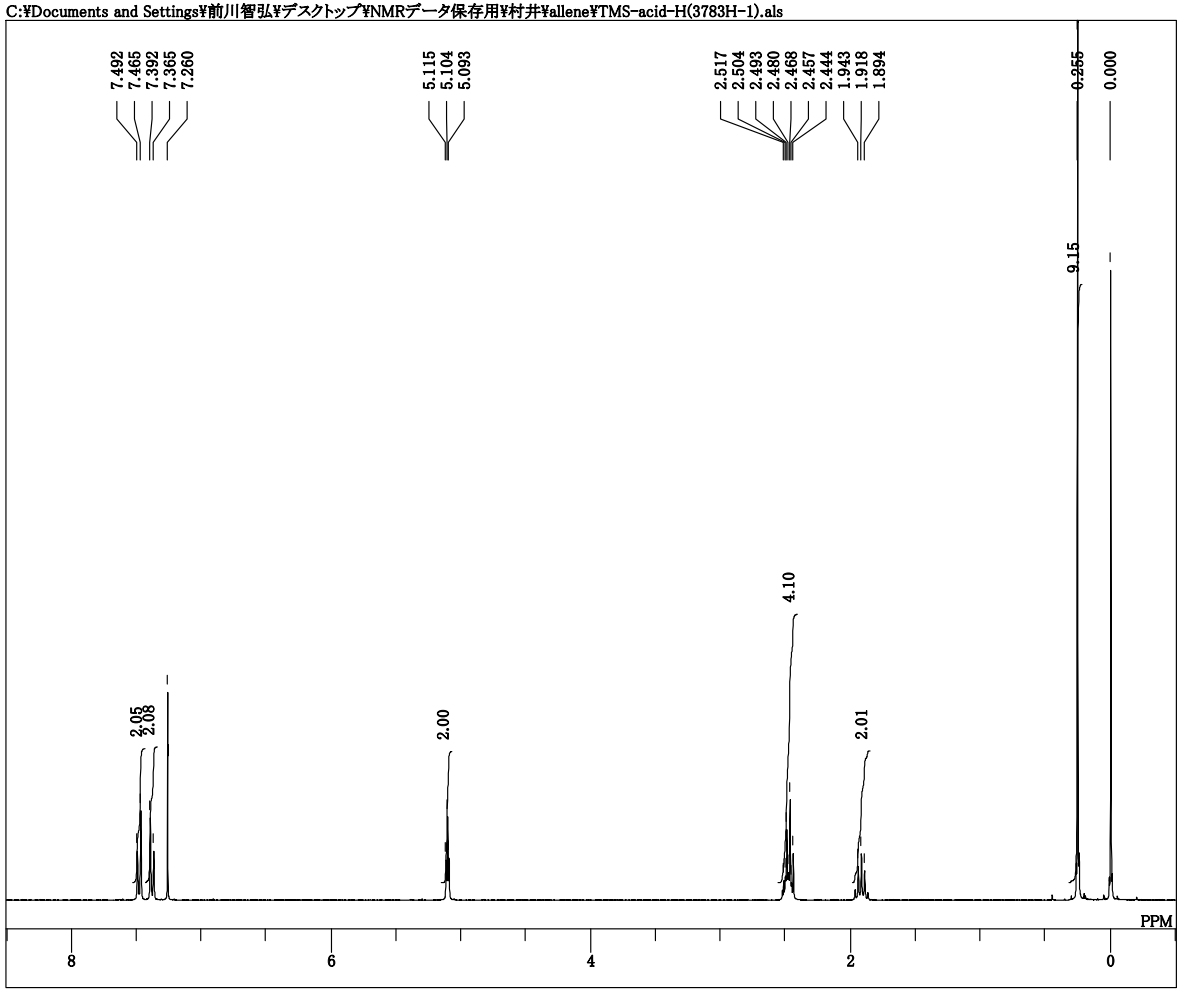
DFILE	TMS-Ms-C(3781C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	19-10-2013 12:52:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	895
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



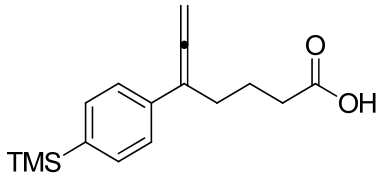
^{1}H NMR chart of **2d**

3783H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥TMS-acid-H(3783H-1).als

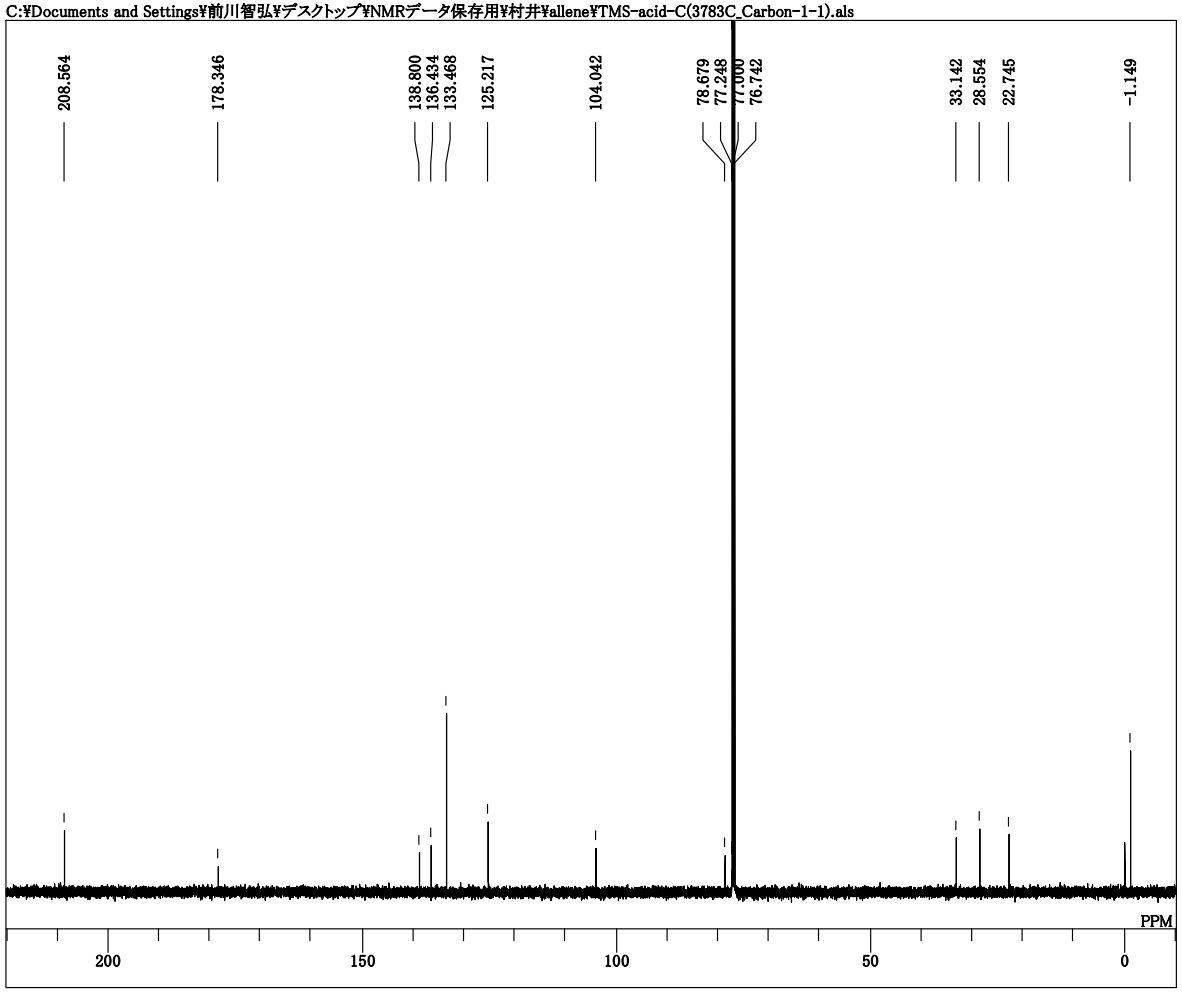


DFILE	TMS-acid-H(3783H-1).als
COMNT	3783H
DATIM	21-10-2013 16:37:46
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	21.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	42

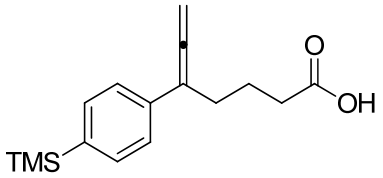


^{13}C NMR chart of **2d**

single pulse decoupled gated NOE



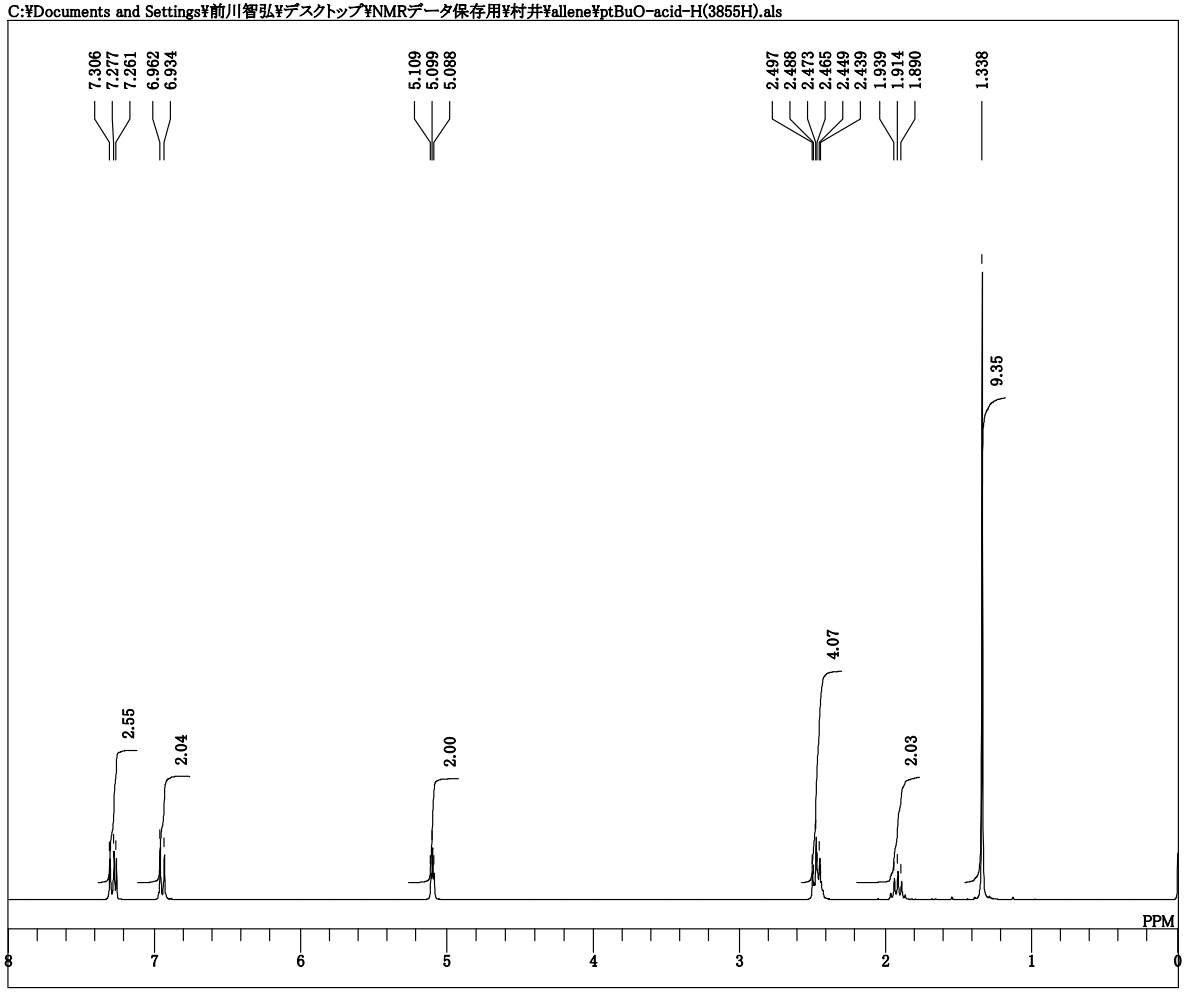
DFILE	TMS-acid-C(3783C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	21-10-2013 17:44:38
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1056
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



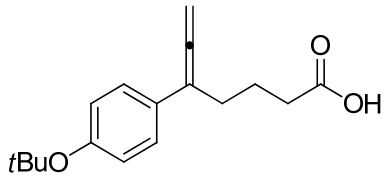
^{1}H NMR chart of **2e**

3855

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥ptBuO-acid-H(3855H).als



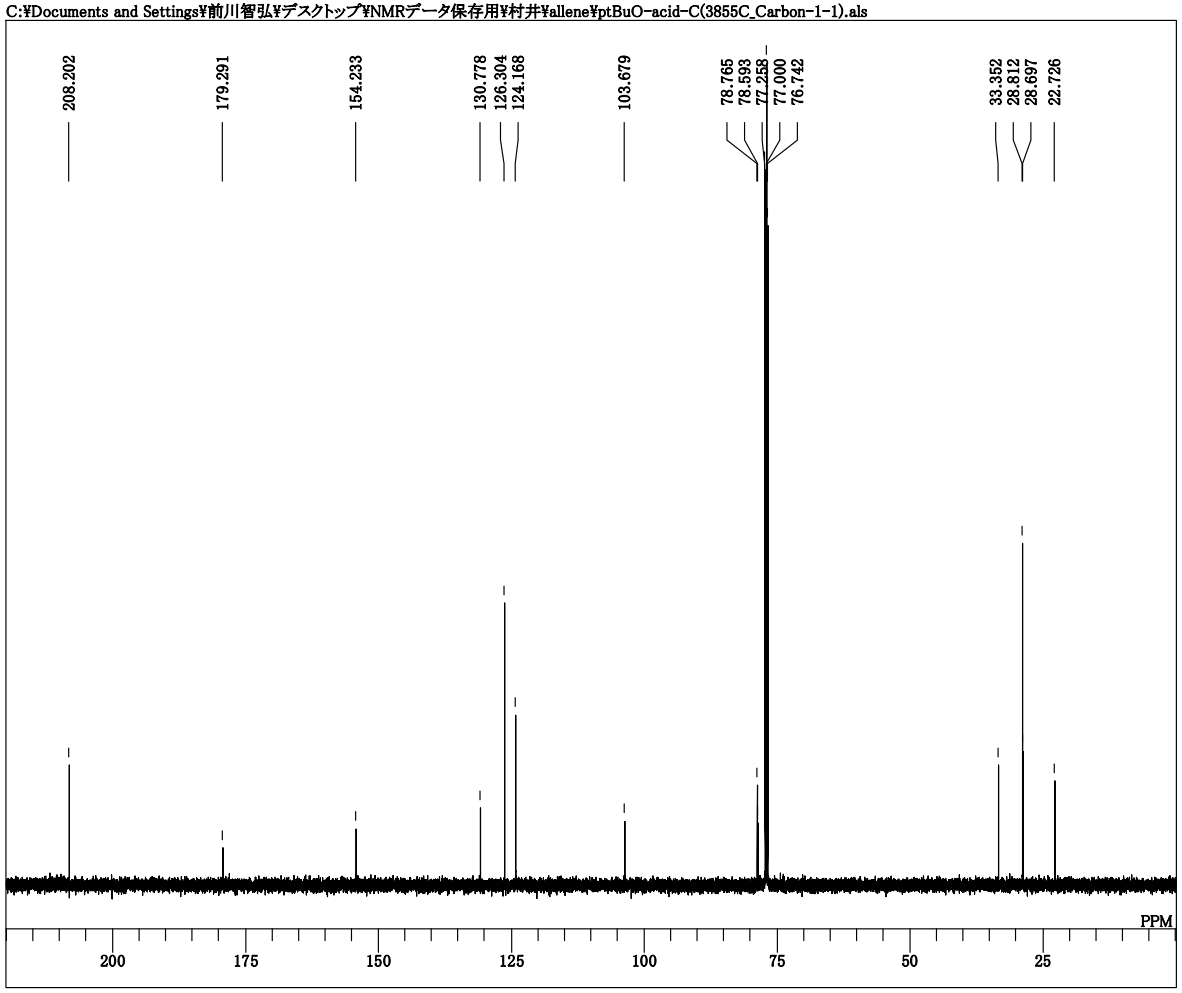
DFILE	ptBuO-acid-H(3855H).als
COMNT	3855
DATIM	15-01-2014 13:56:33
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	19.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



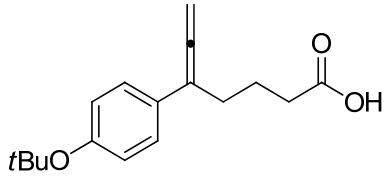
^{13}C NMR chart of **2e**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥ptBuO-acid-C(3855C_Carbon-1-1).als



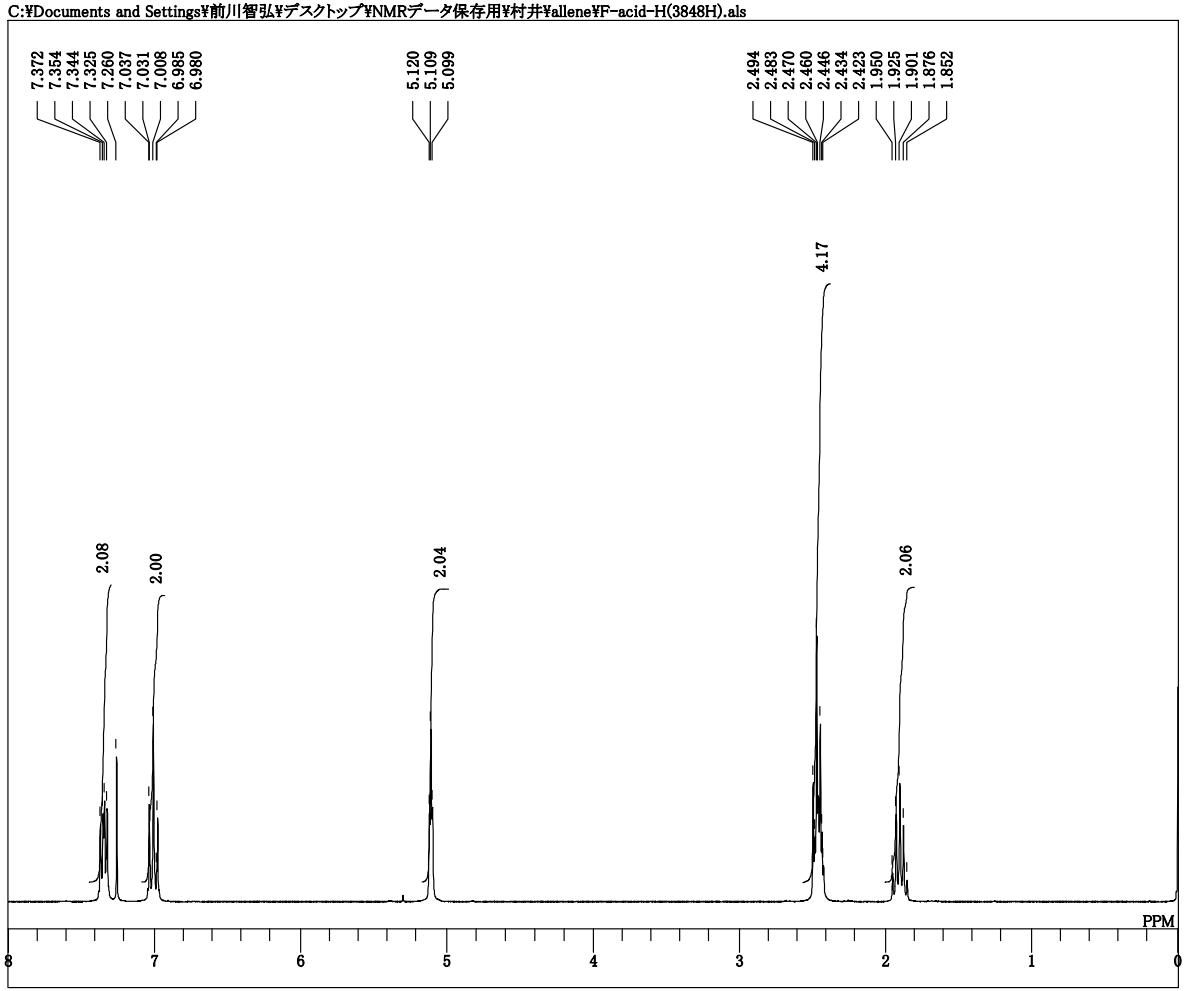
DFILE	ptBuO-acid-C(3855C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	15-01-2014 15:01:57
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	324
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



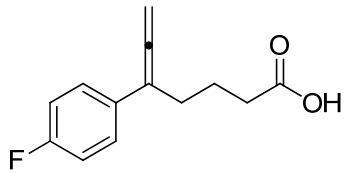
^{1}H NMR chart of **2f**

3848

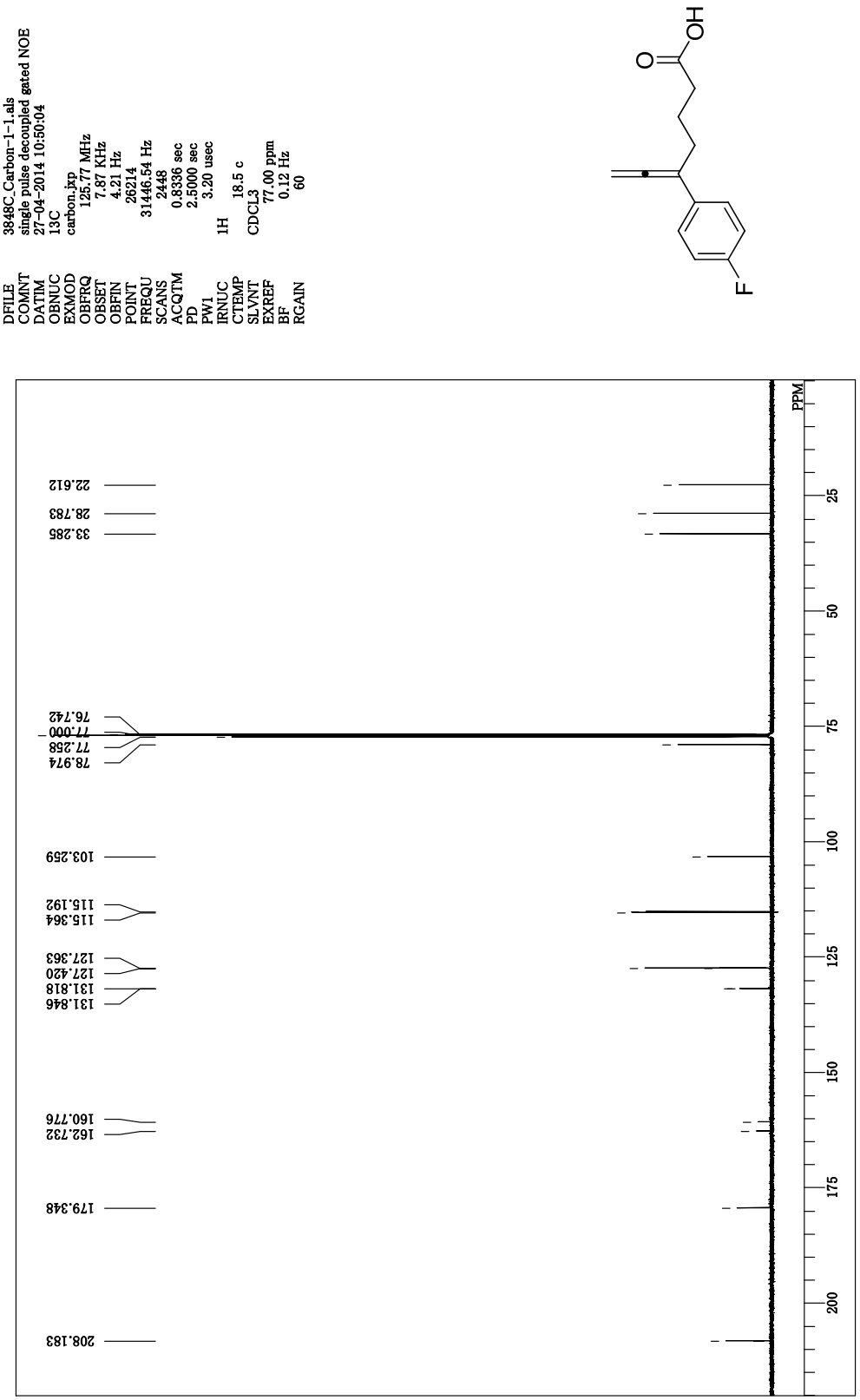
C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥F-acid-H(3848H).als



DFILE	F-acid-H(3848H).als
COMNT	3848
DATIM	09-01-2014 14:43:23
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	19.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



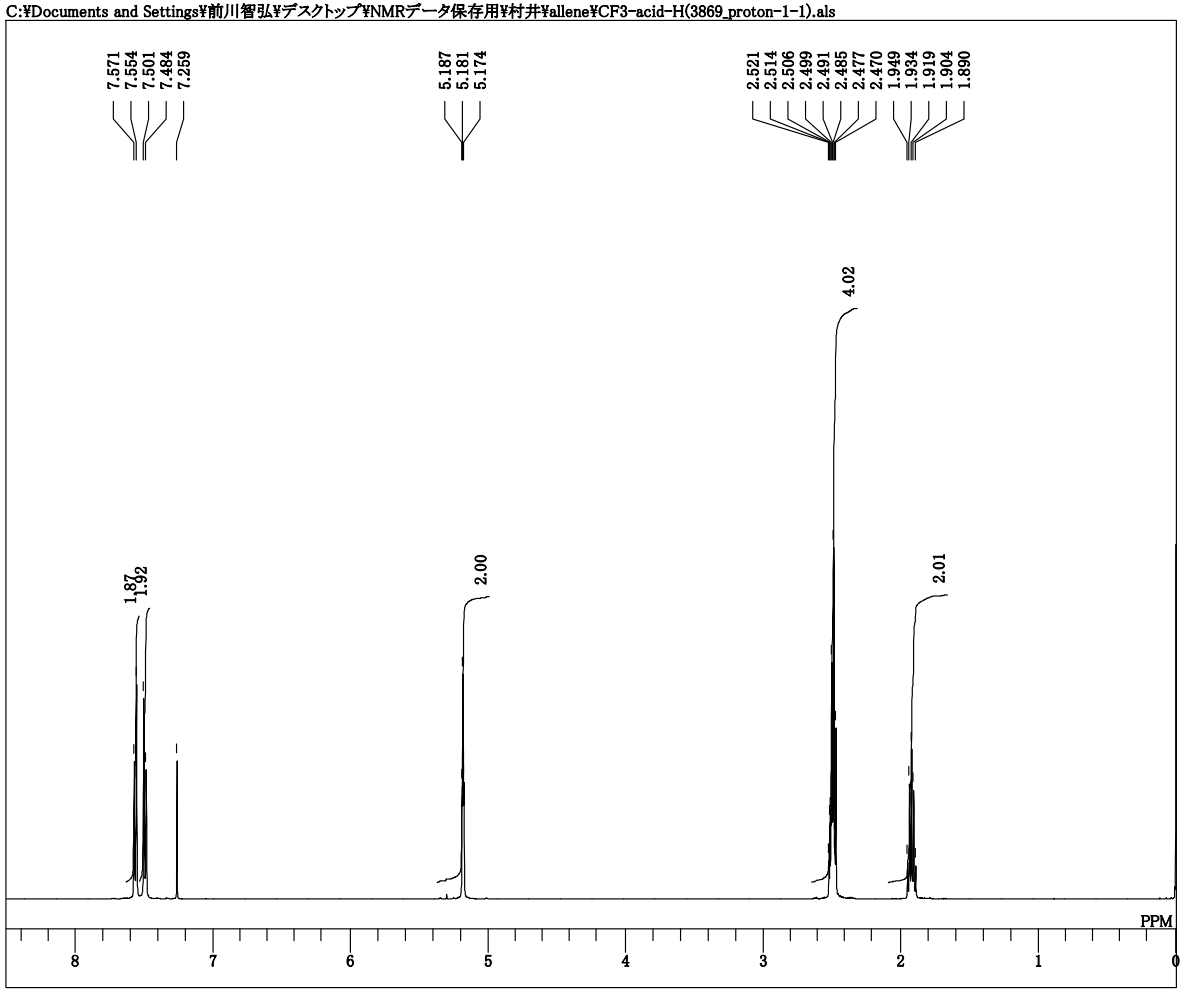
^{13}C NMR chart of **2f**



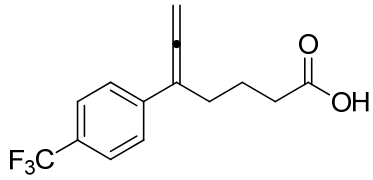
^{1}H NMR chart of **2g**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥CF3-acid-H(3869_proton-1-1).als

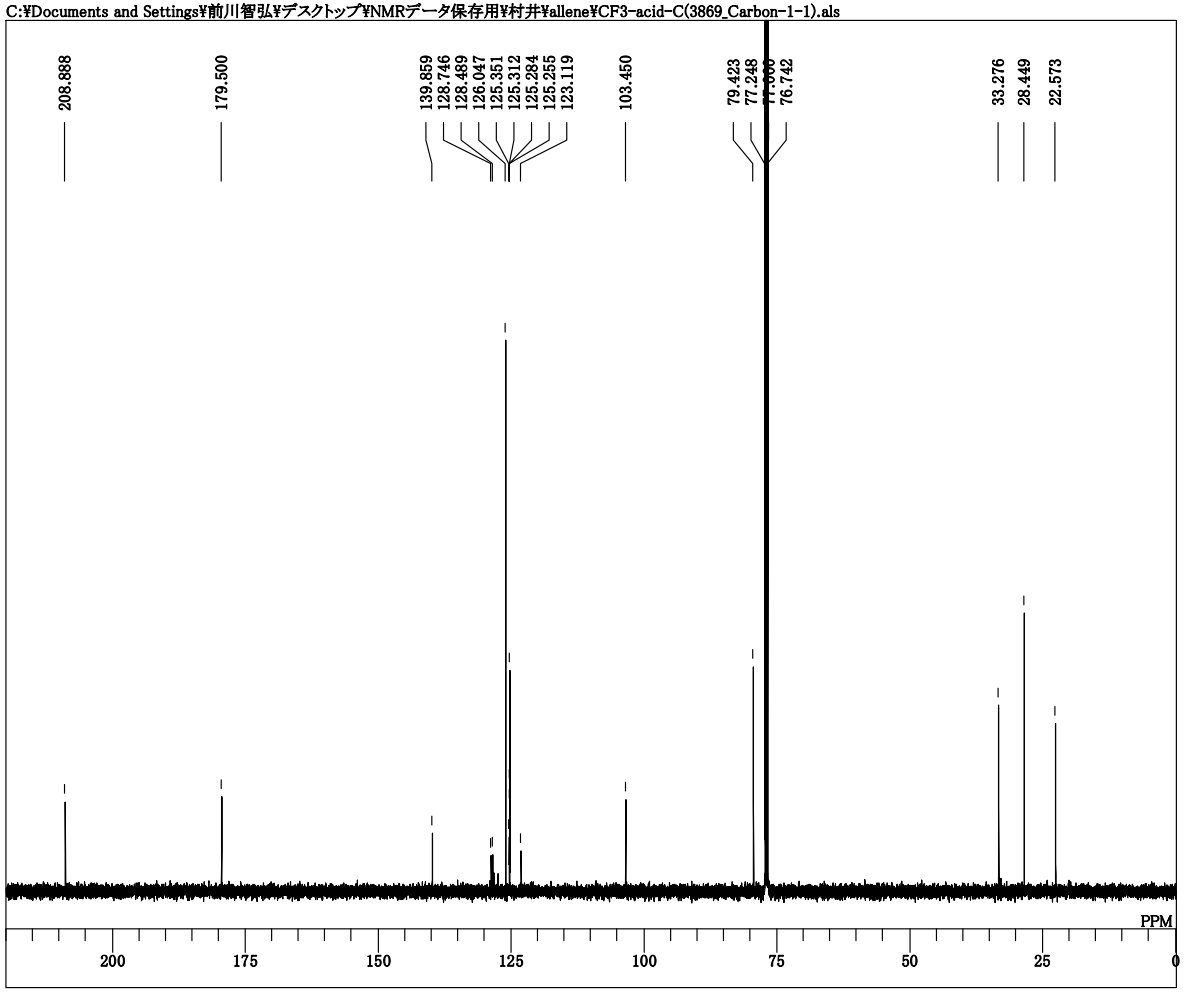


DFILE	CF3-acid-H(3869_proton-1-1).als
COMNT	single_pulse
DATIM	28-01-2014 14:20:28
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	42

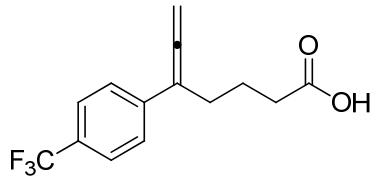


^{13}C NMR chart of **2g**

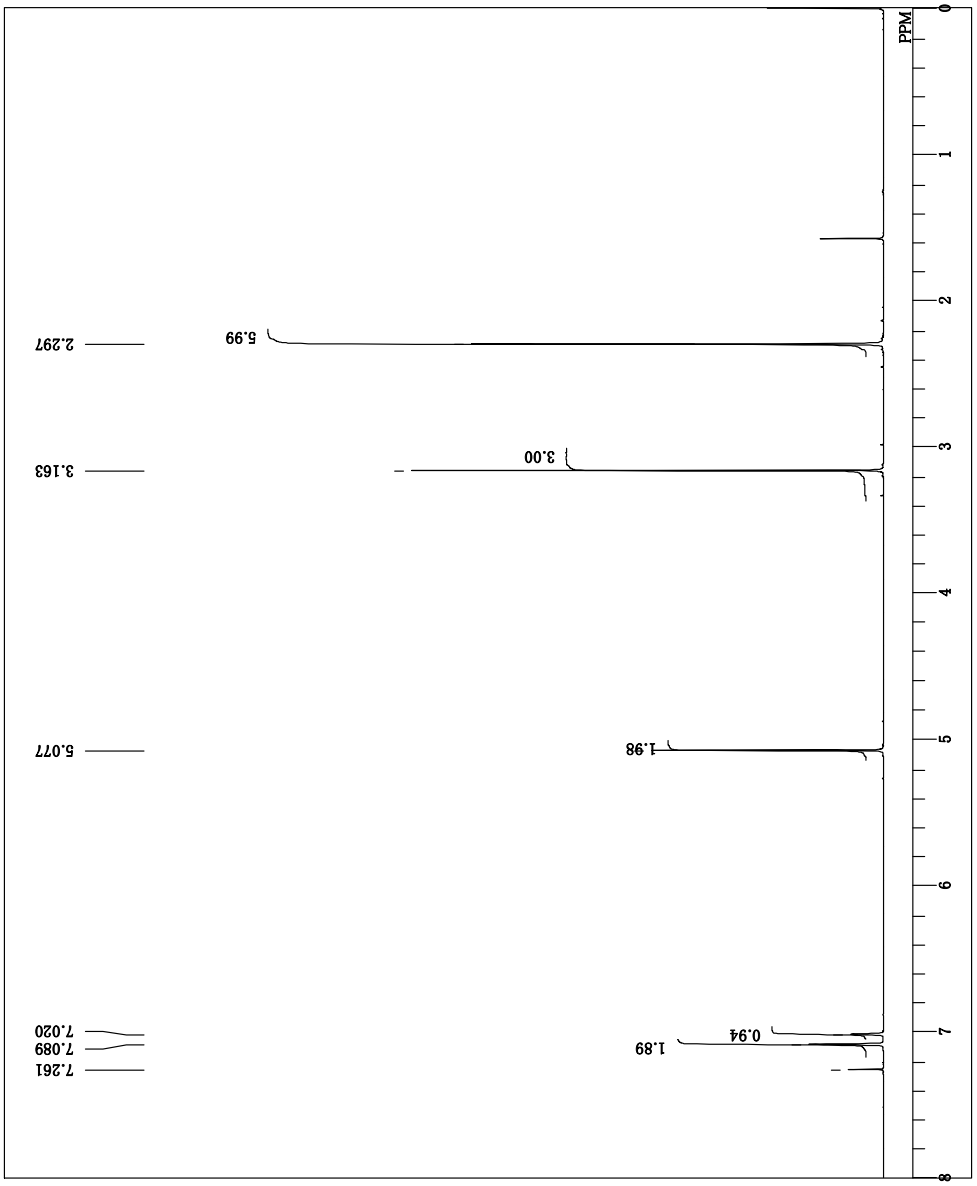
single pulse decoupled gated NOE



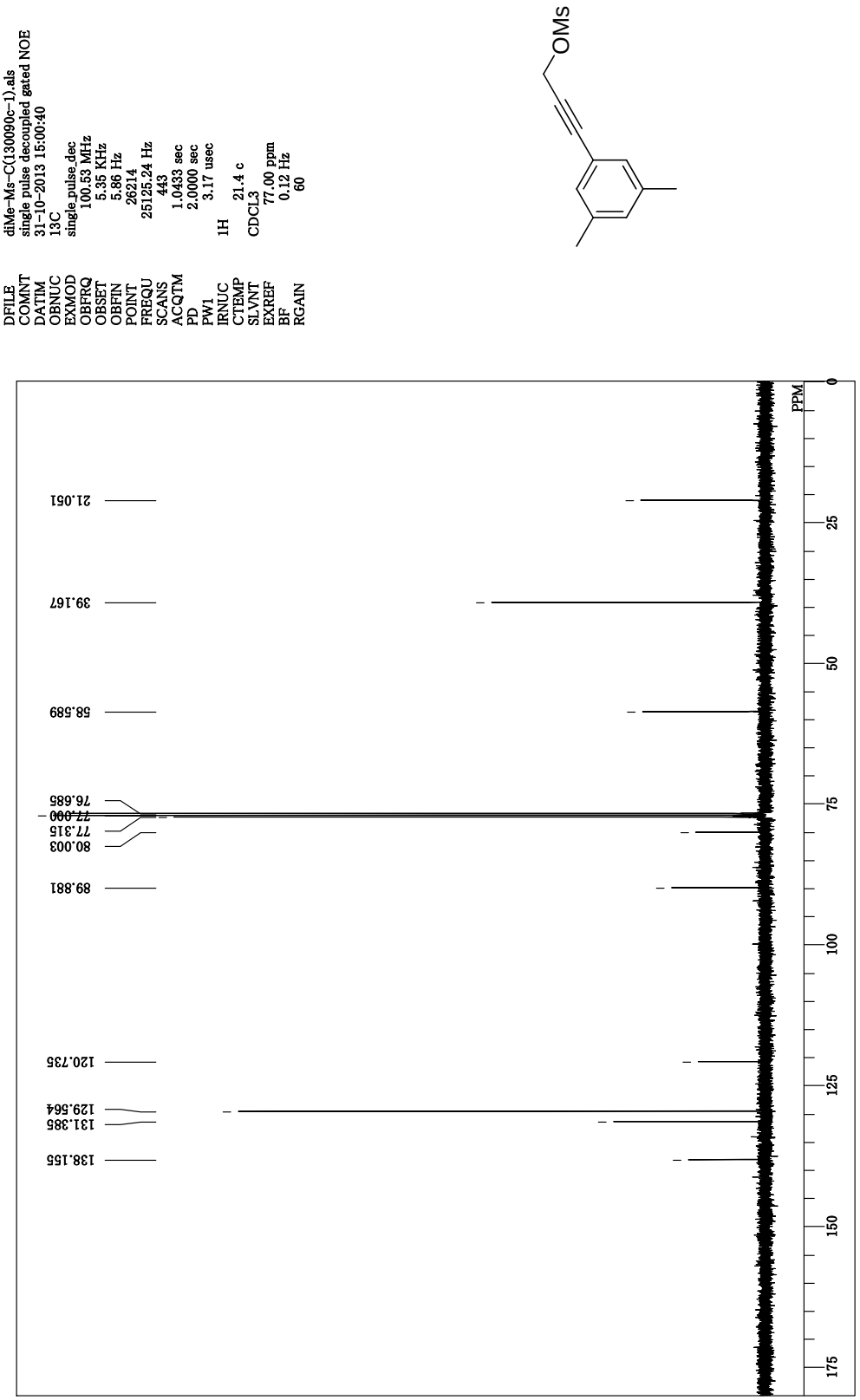
DFILE	CF3-acid-C(3869_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	28-01-2014 14:23:39
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	685
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



^{1}H NMR chart of **4h**



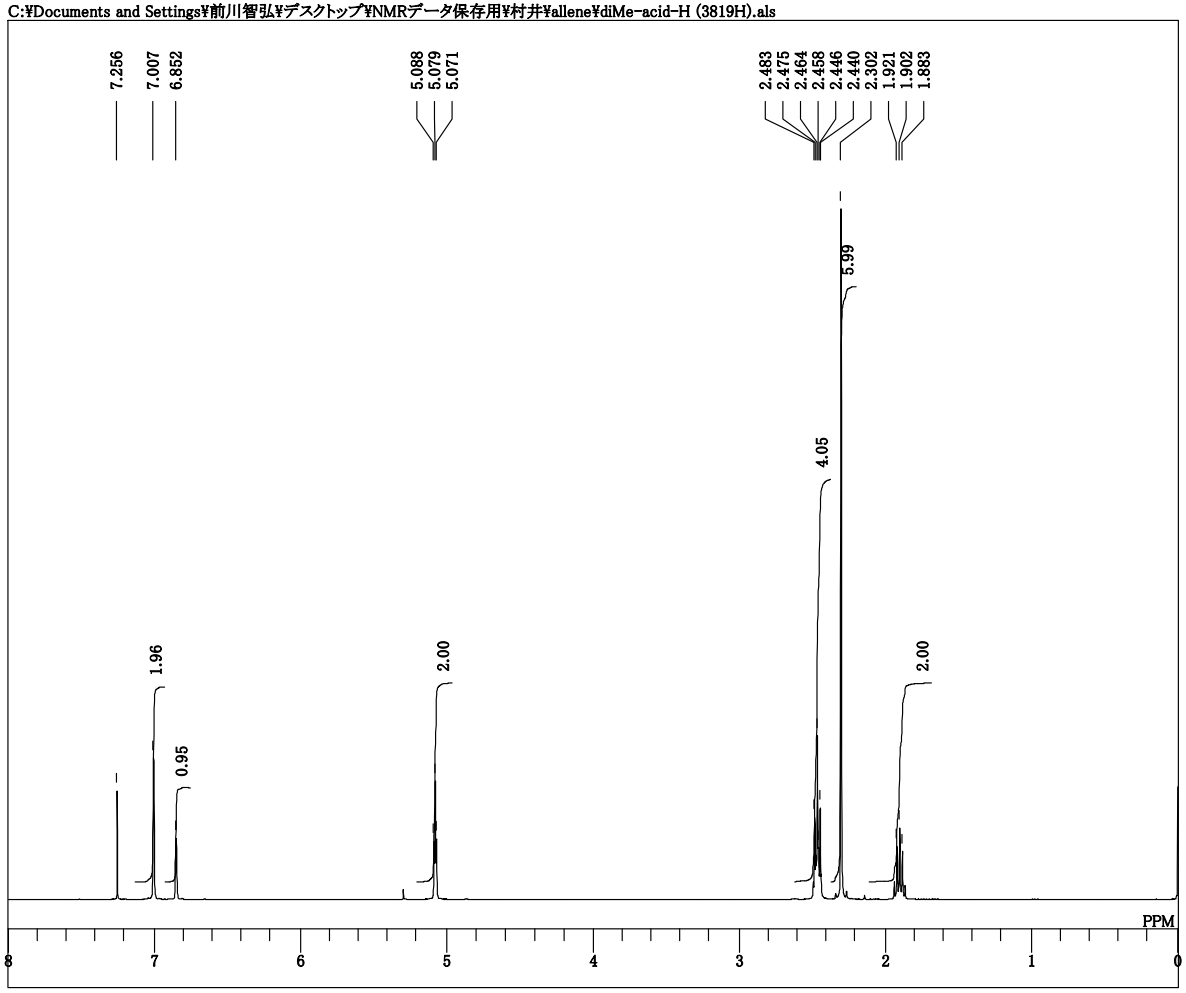
^{13}C NMR chart of **4h**



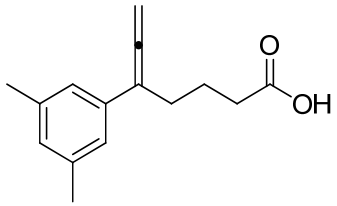
^{1}H NMR chart of **2h**

3819

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥diMe-acid-H (3819H).als



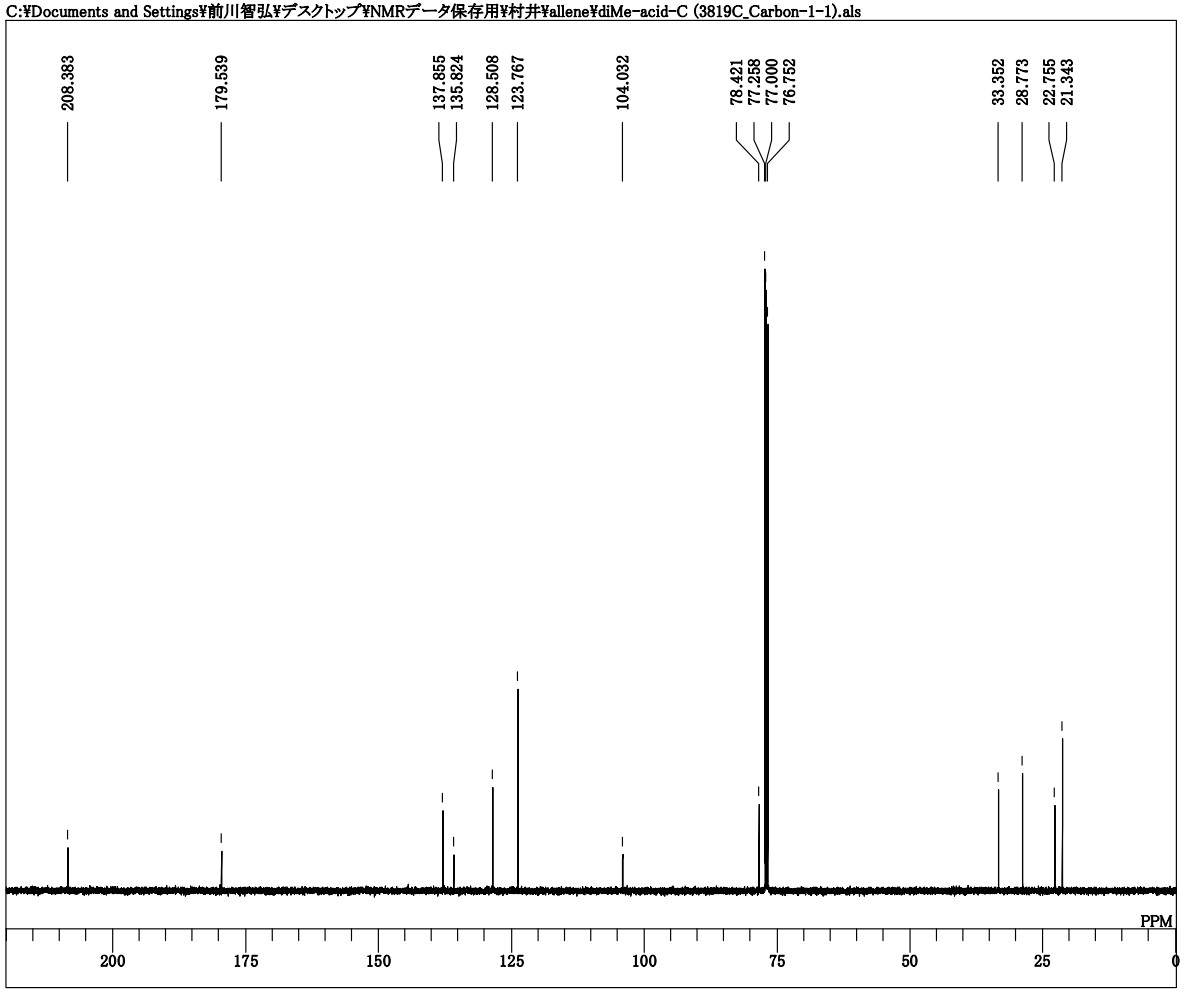
DFILE	diMe-acid-H (3819H).als
COMNT	3819
DATIM	14-11-2013 19:49:32
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.31 Hz
SCANS	16
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.35 usec
IRNUC	1H
CTEMP	19.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



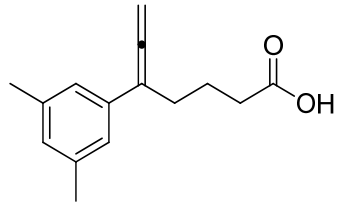
^{13}C NMR chart of **2h**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥diMe-acid-C (3819C_Carbon-1-1).als



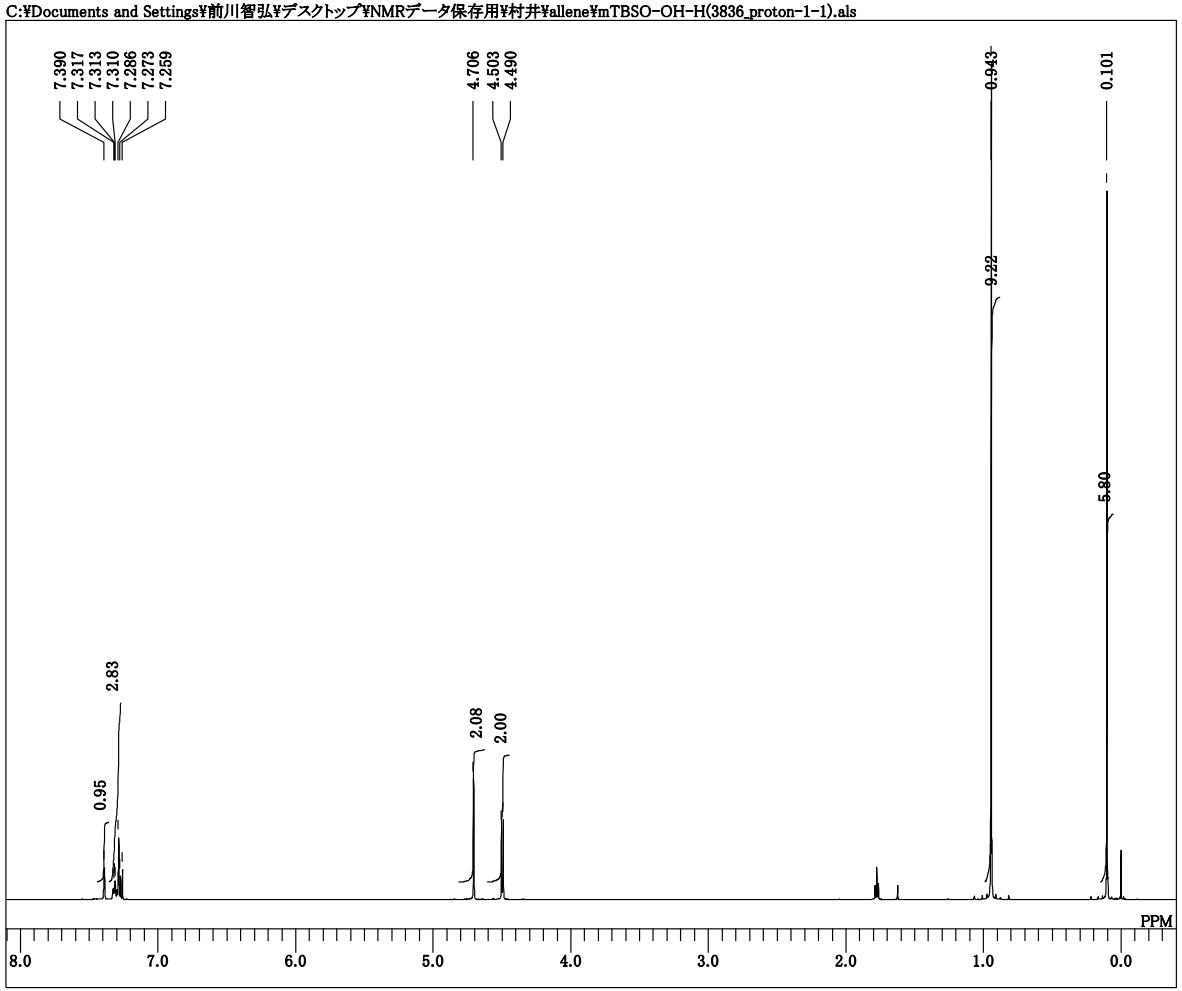
DFILE	diMe-acid-C (3819C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	14-11-2013 21:18:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	648
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



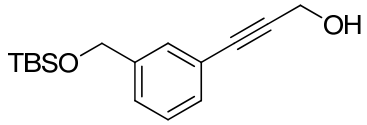
^{1}H NMR chart of **4i**

120356-11-upper_spot

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥mTBSO-OH-H(3836_proton-1-1).als



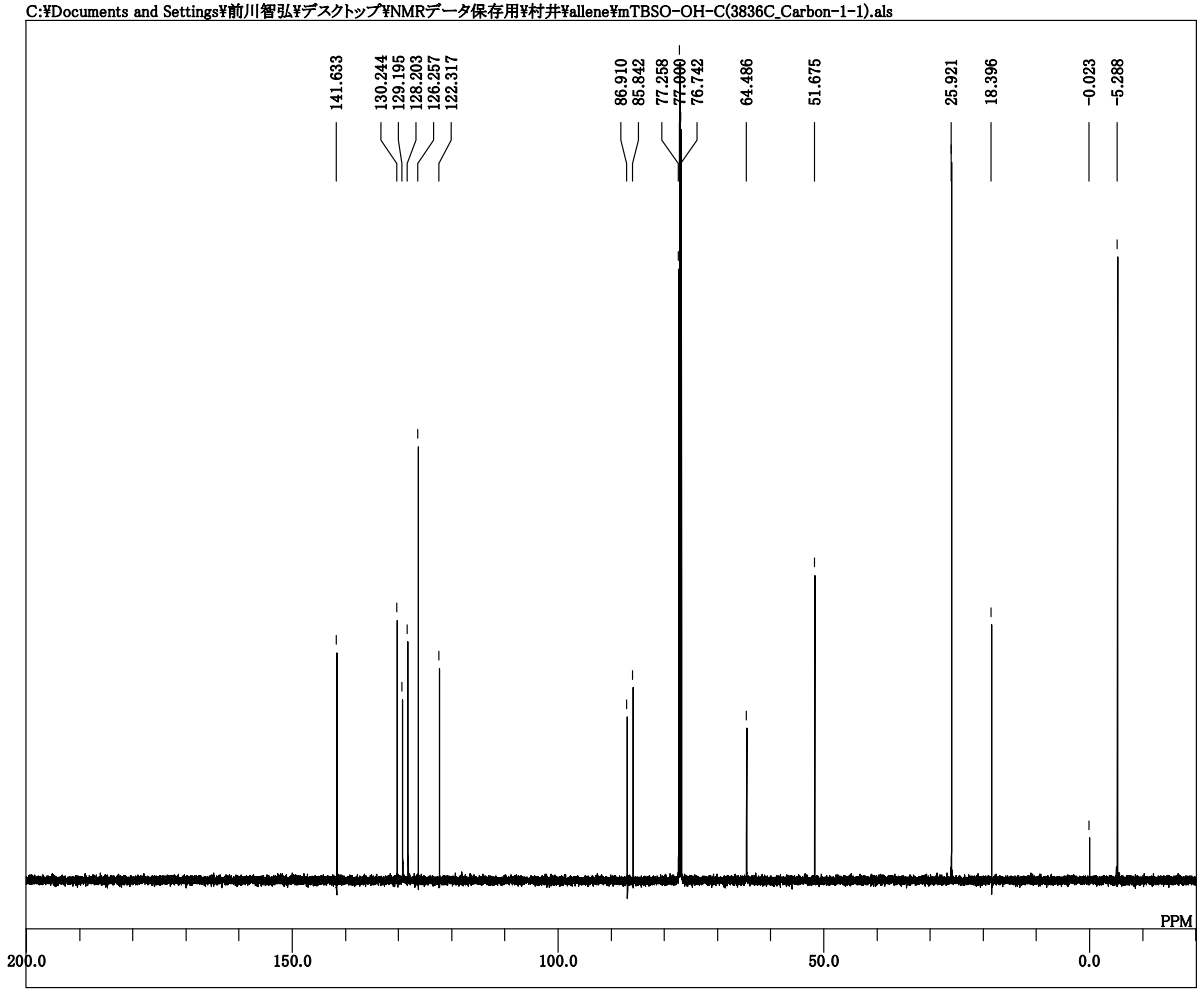
DFILE	mTBSO-OH-H(3836_proton-1-1).als
COMNT	120356-11-upper_spot
DATIM	18-12-2013 10:58:34
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



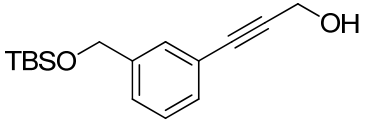
^{13}C NMR chart of **4i**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥mTBSO-OH-C(3836C_Carbon-1-1).als



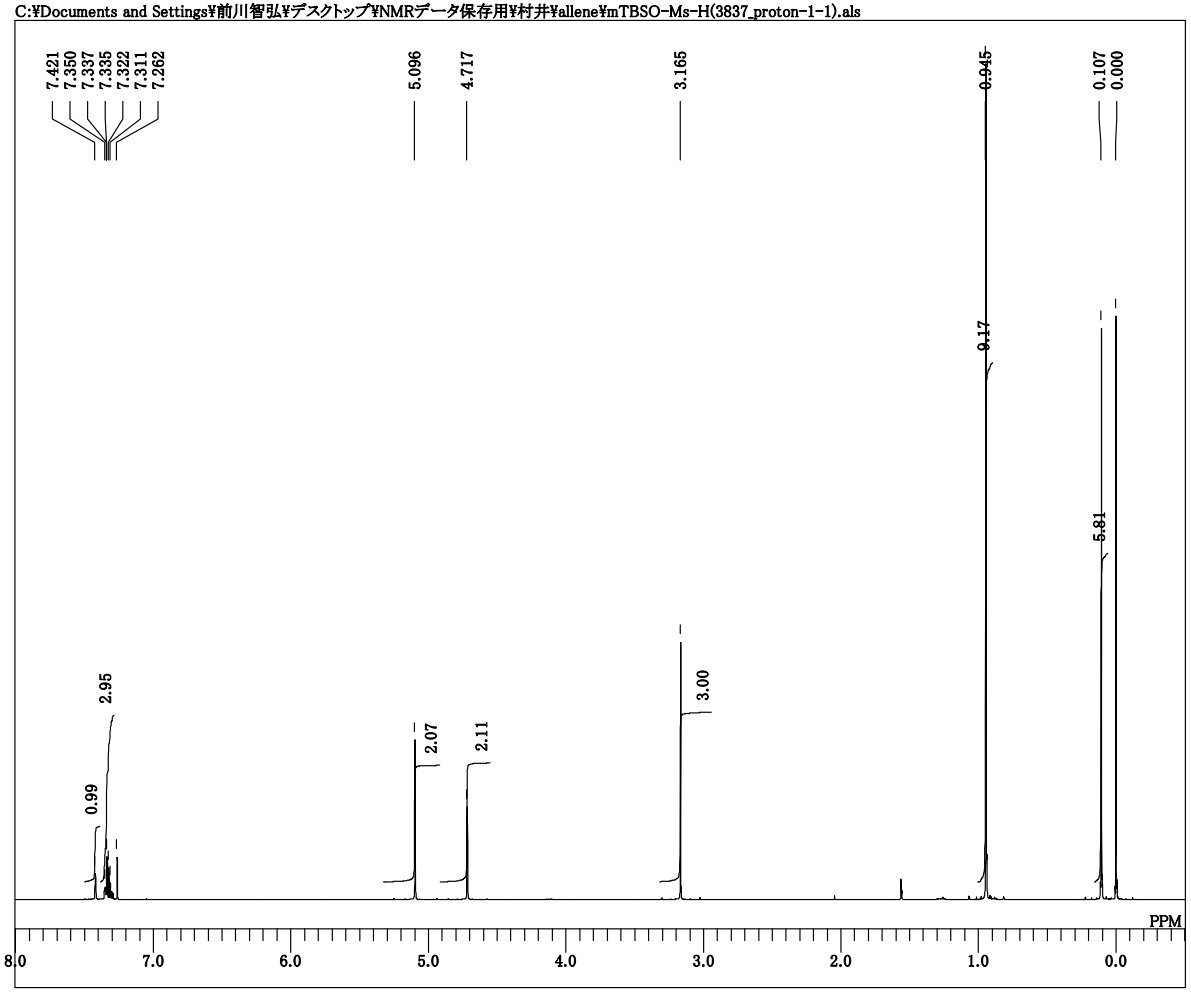
DFILE	mTBSO-OH-C(3836C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	18-12-2013 11:01:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	759
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



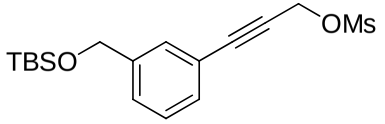
^{1}H NMR chart of **4i**

120356-11-upper_spot

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥mTBSO-Ms-H(3837_proton-1-1).als



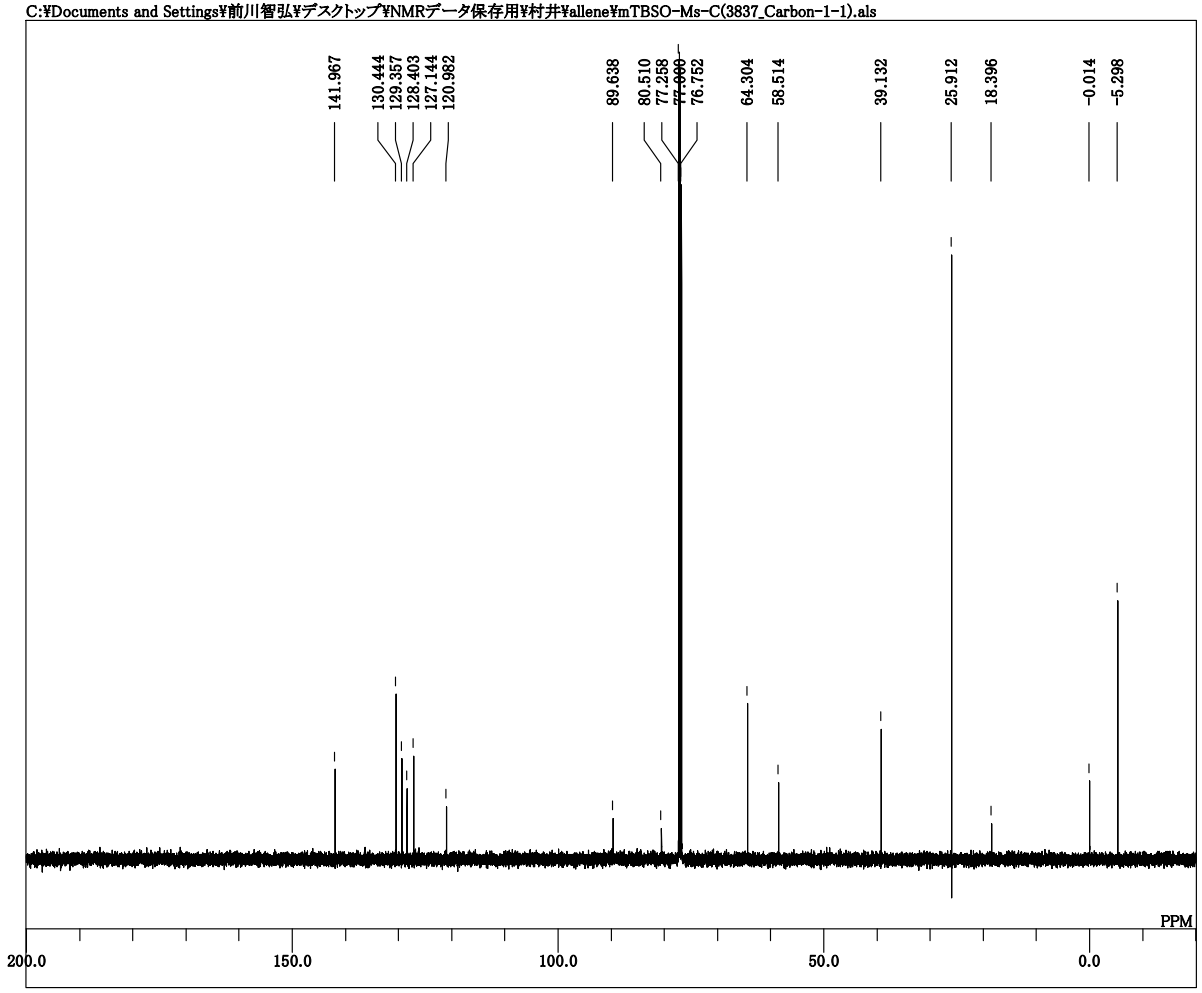
DFILE	mTBSO-Ms-H(3837_proton-1-1).als
COMNT	120356-11-upper_spot
DATIM	18-12-2013 15:07:00
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	20.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



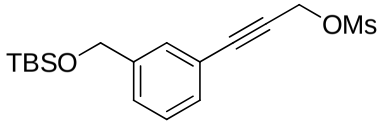
^{13}C NMR chart of **4i**

single pulse decoupled gated NOE

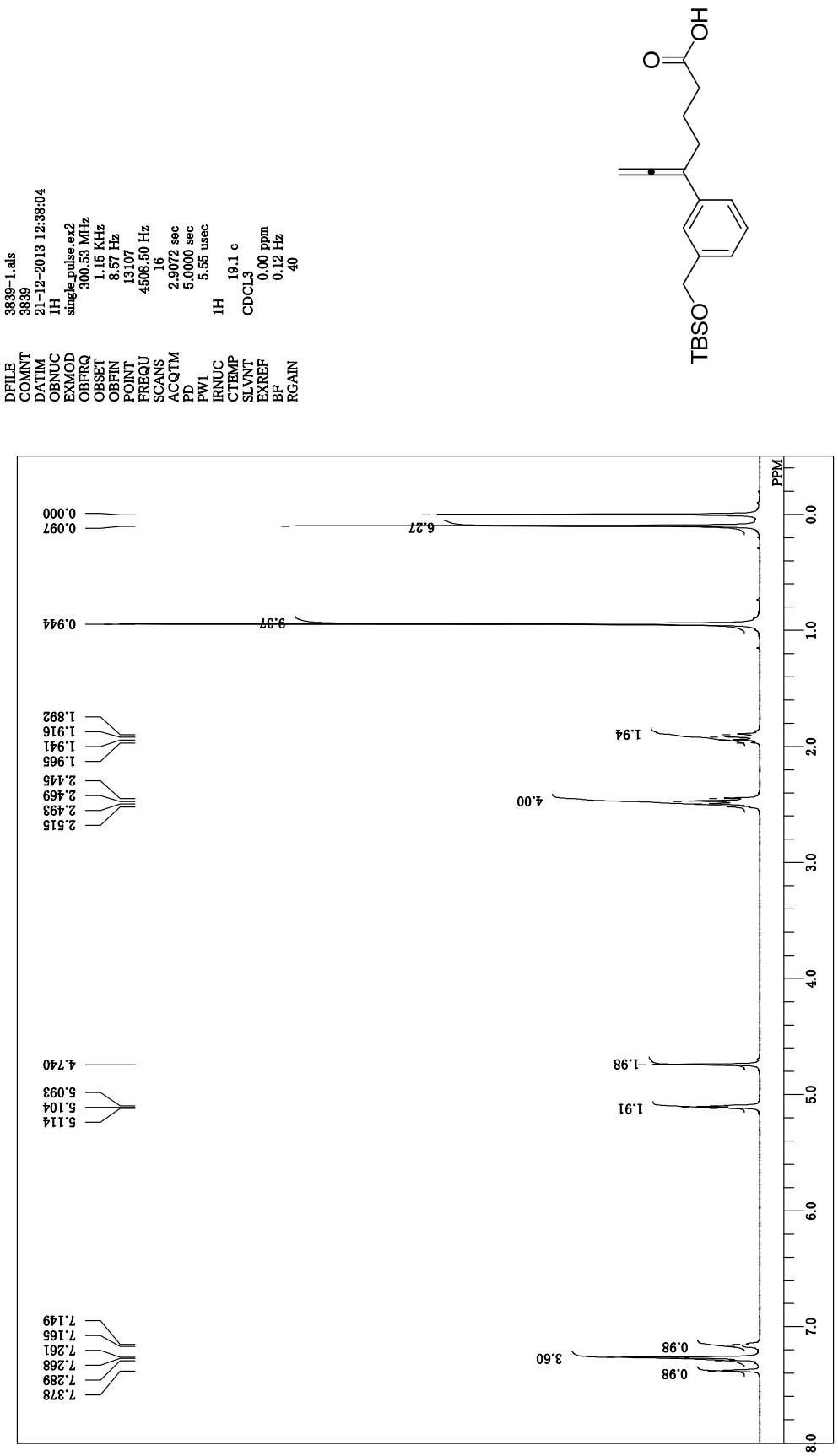
C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥mTBSO-Ms-C(3837_Carbon-1-1).als



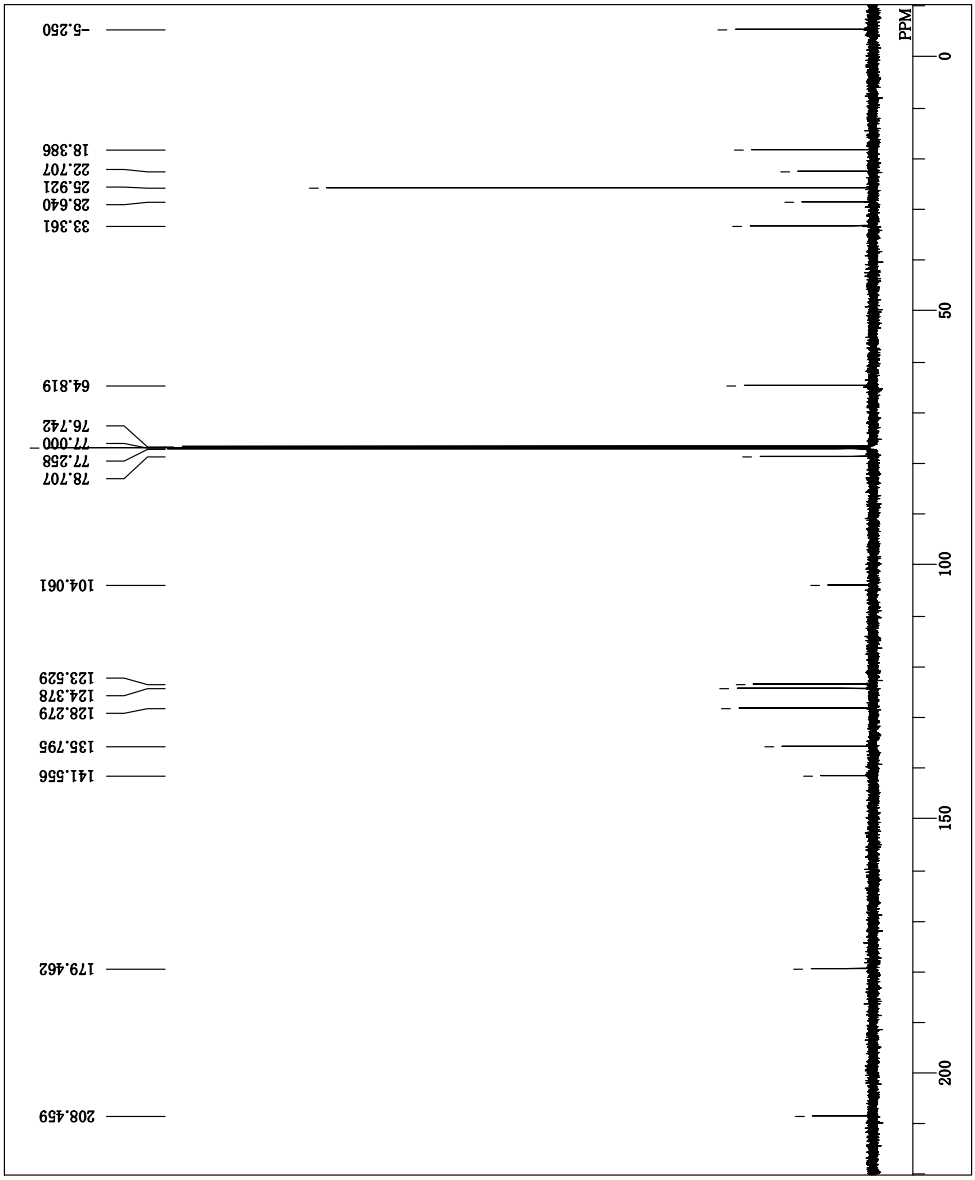
DFILE	mTBSO-Ms-C(3837_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	18-12-2013 15:10:19
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	318
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



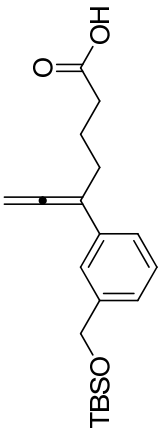
^{1}H NMR chart of **2i**



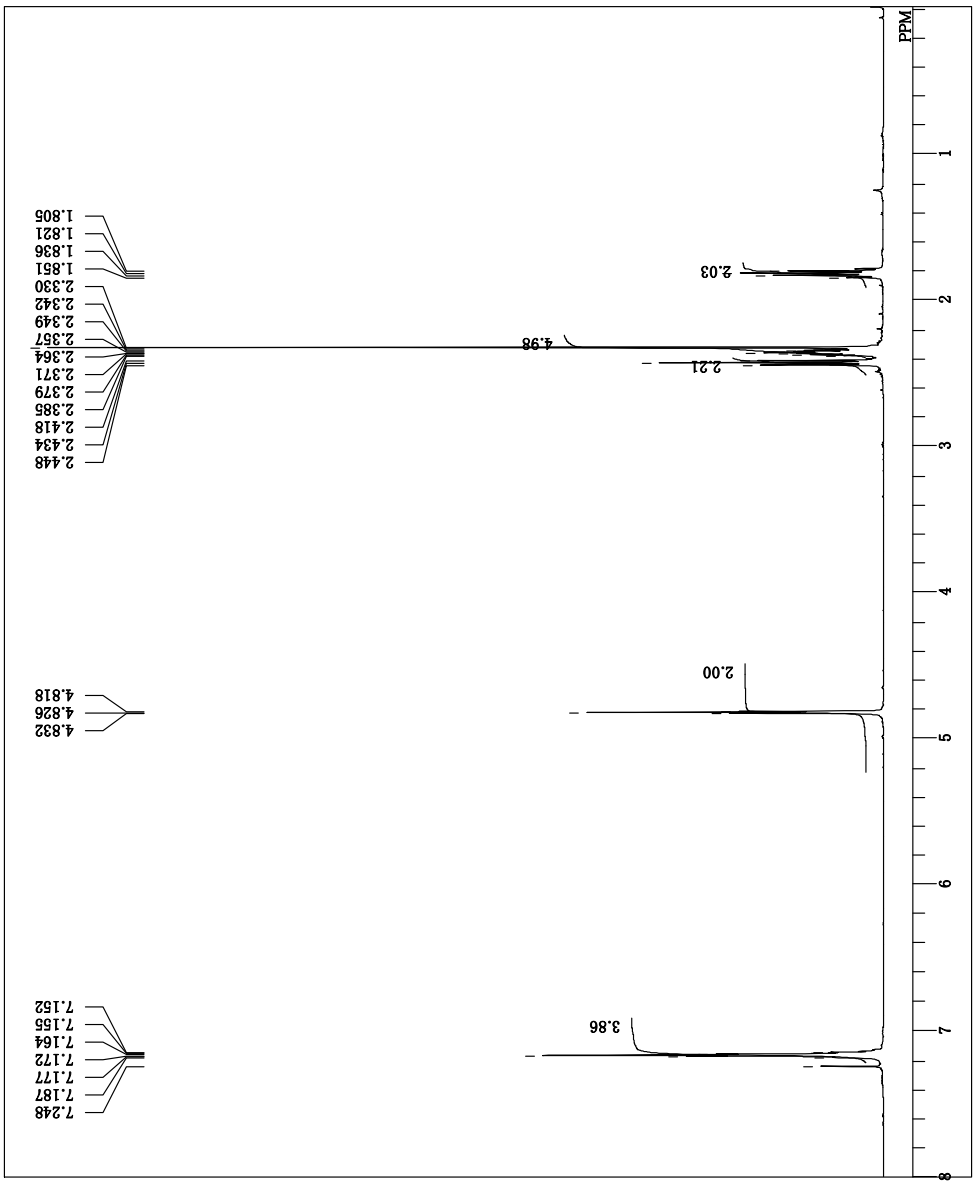
^{13}C NMR chart of **2i**



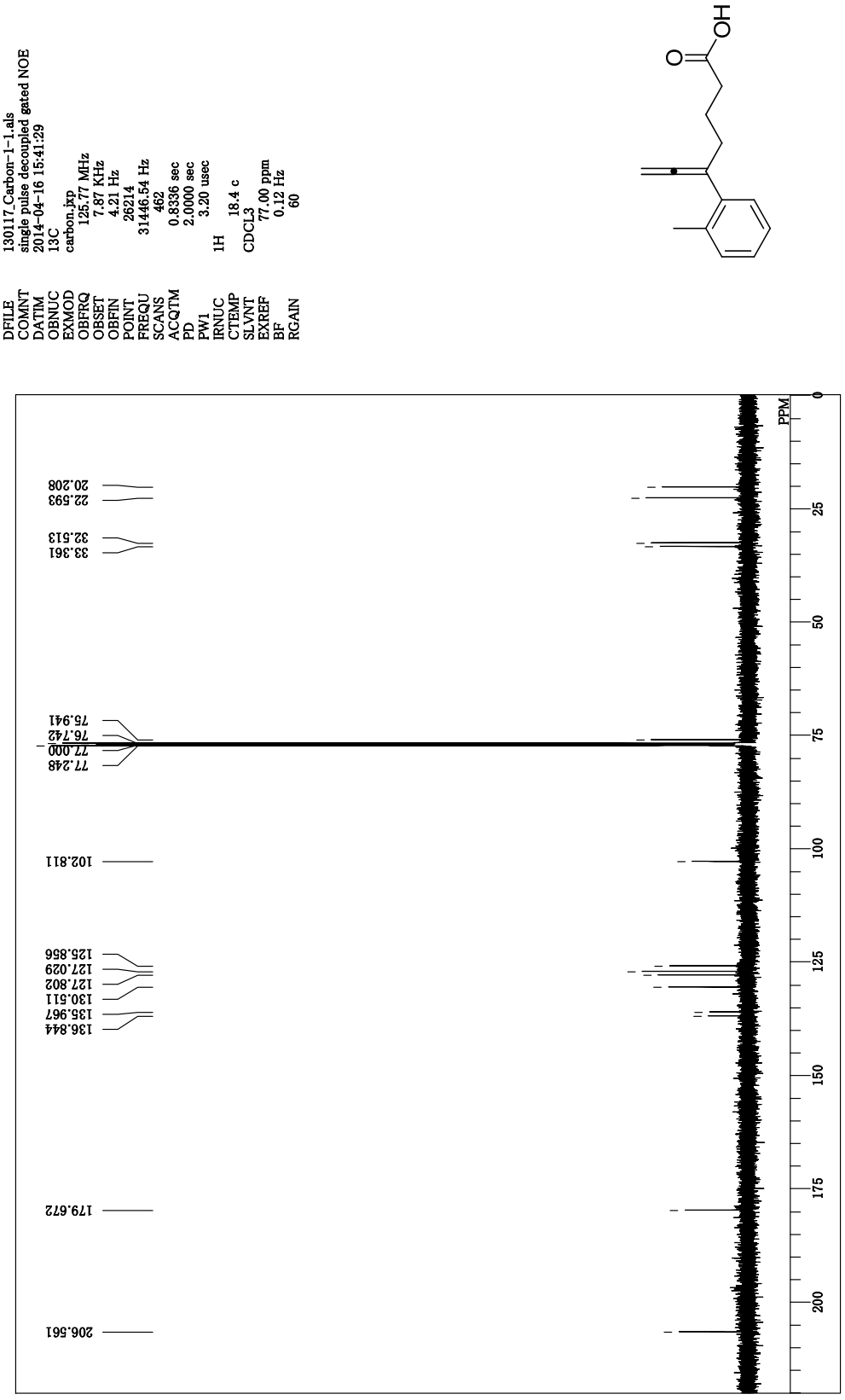
DFILE 3839C_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 26-04-2014 17:45:40
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 521
ACQTM 0.8336 sec
PD 2.5000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 19.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



^{1}H NMR chart of **2j**



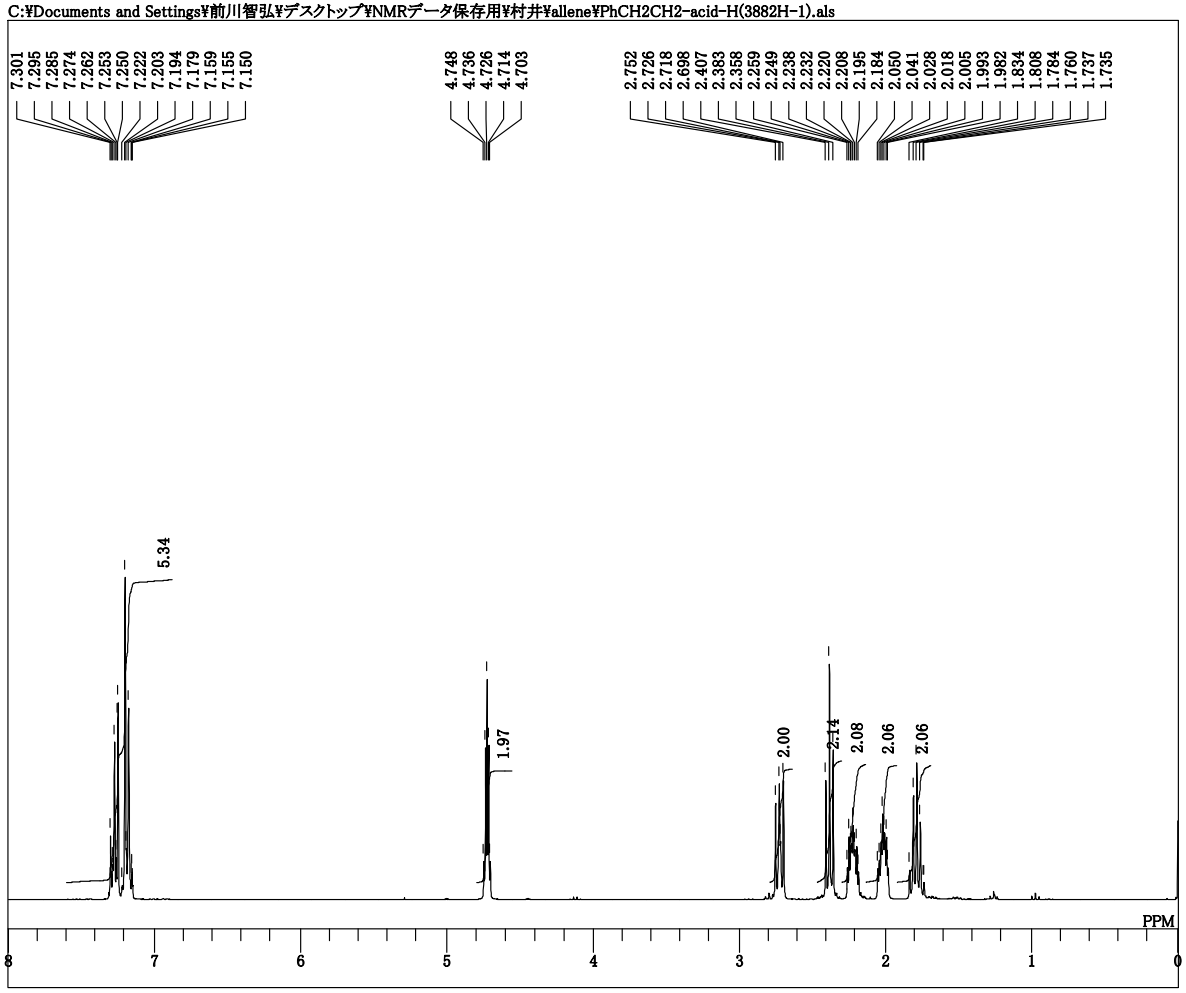
^{1}H NMR chart of **2j**



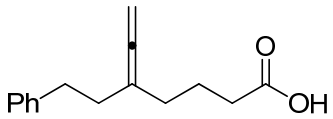
^{1}H NMR chart of **2k**

3882H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥PhCH2CH2-acid-H(3882H-1).als



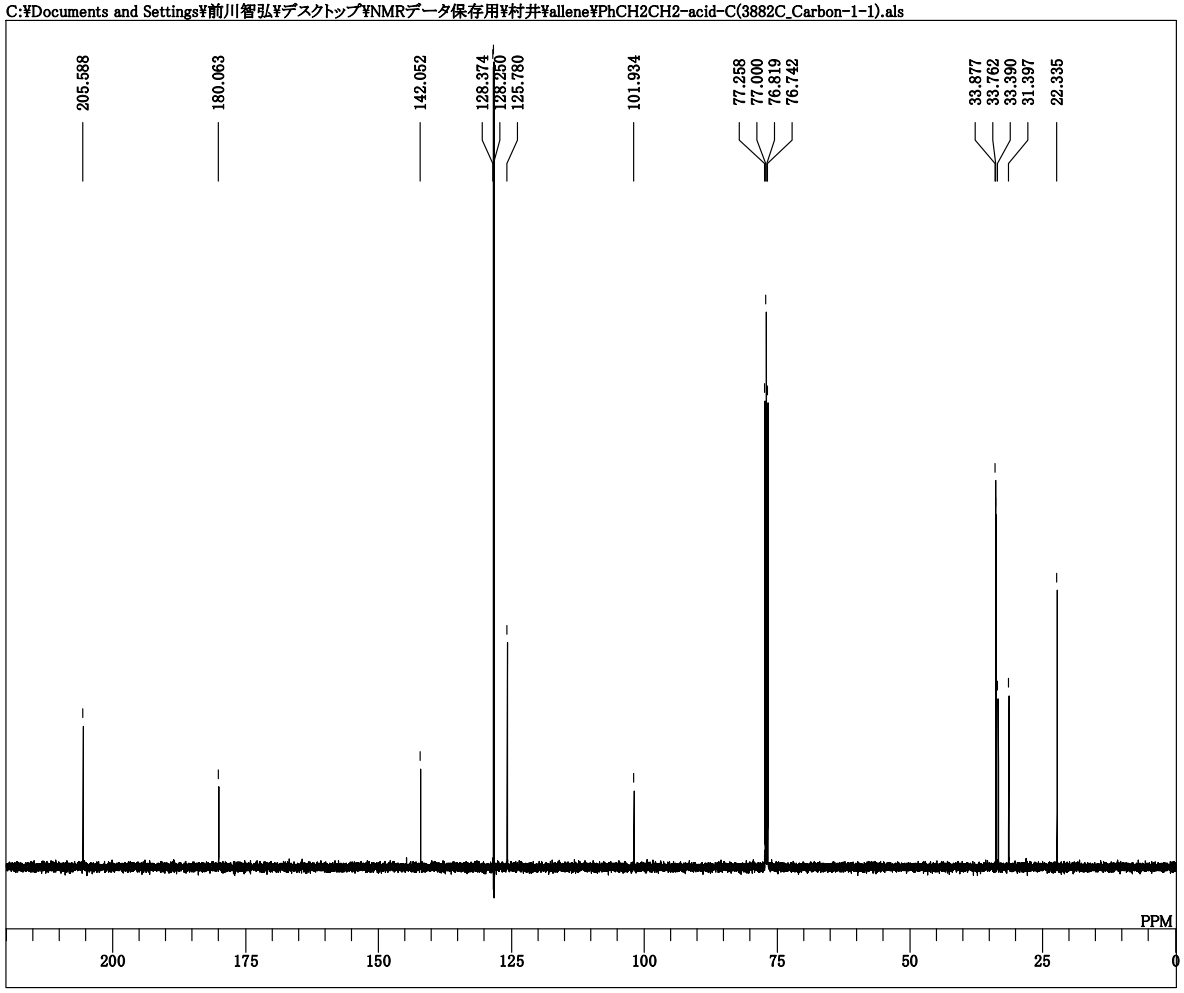
DFILE	PhCH2CH2-acid-H(3882H-1).als
COMNT	3882H
DATIM	12-02-2014 21:30:10
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	16.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



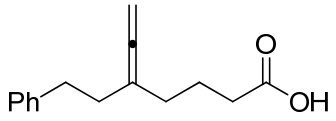
^{13}C NMR chart of **2k**

single pulse decoupled gated NOE

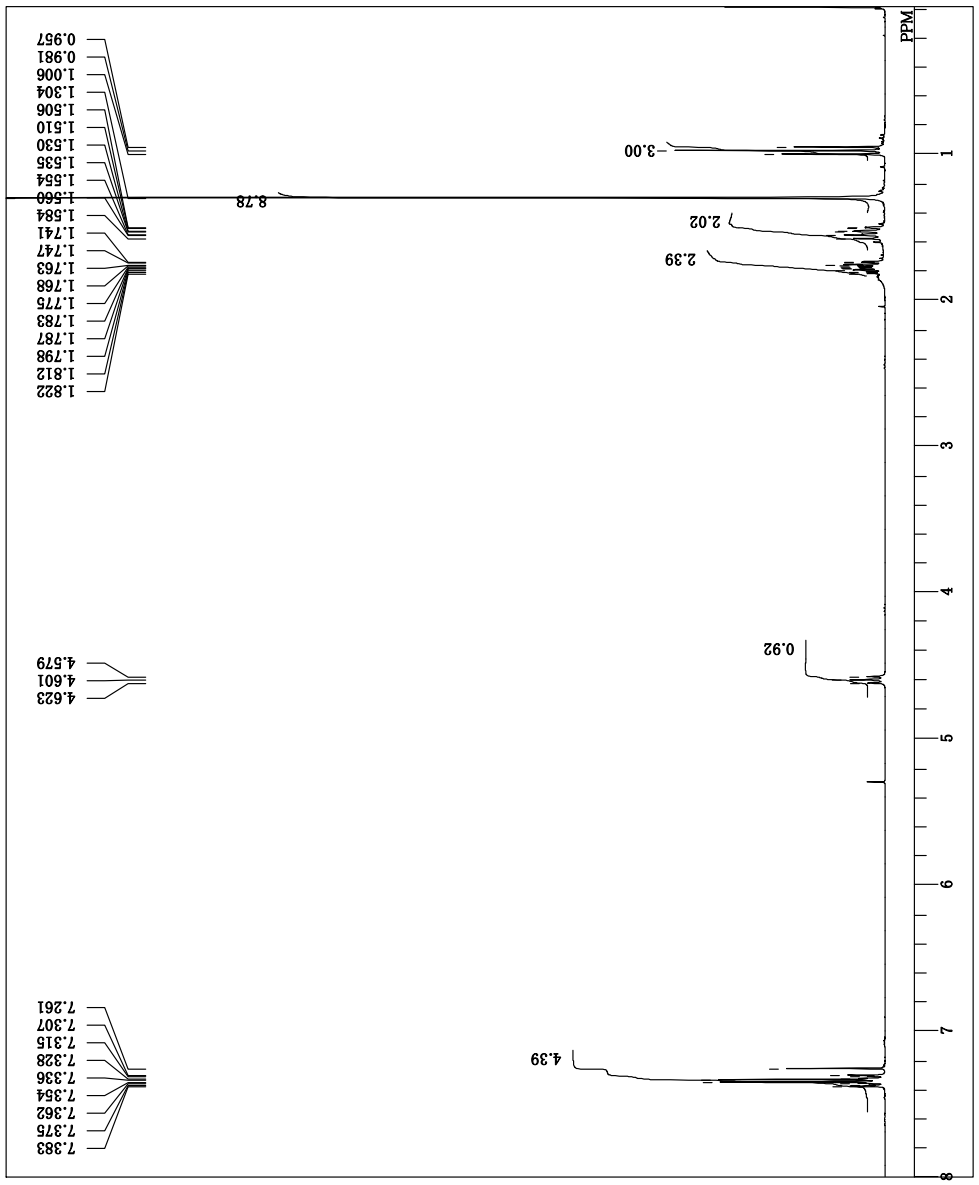
C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥PhCH2CH2-acid-C(3882C_Carbon-1-1).als



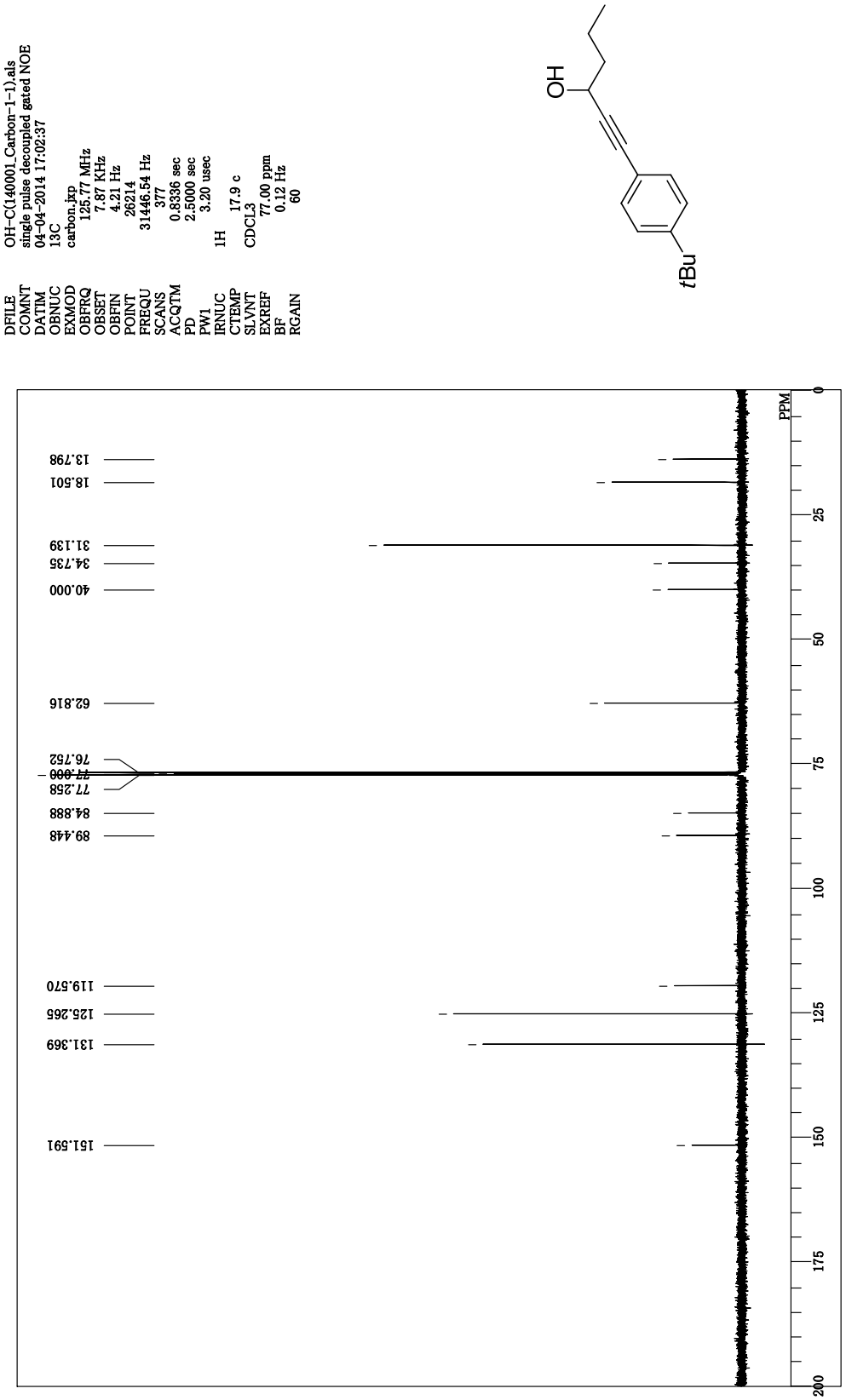
DFILE	PhCH2CH2-acid-C(3882C_Carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	12-02-2014 22:17:43
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	318
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



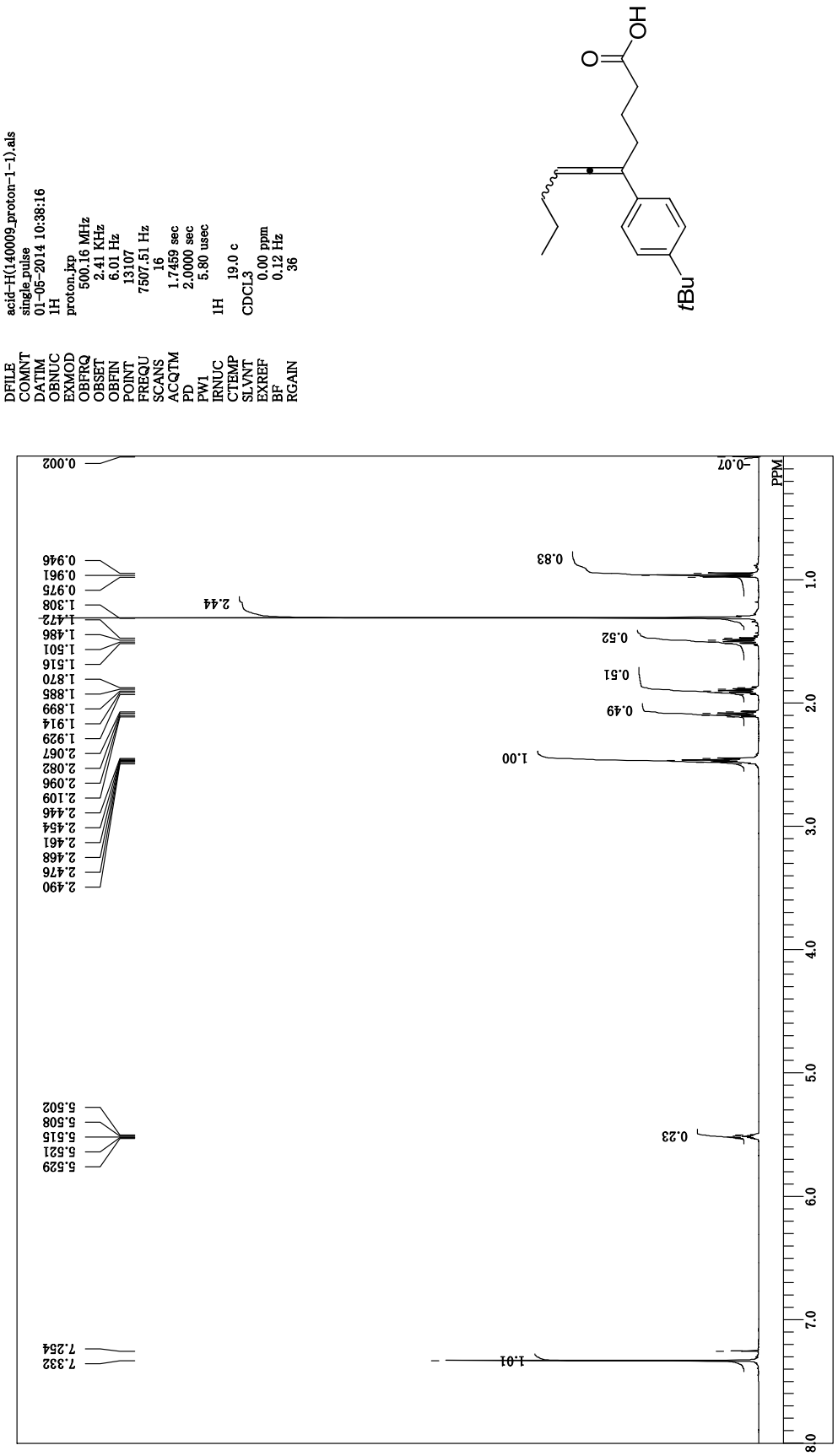
^{1}H NMR chart of **4l**



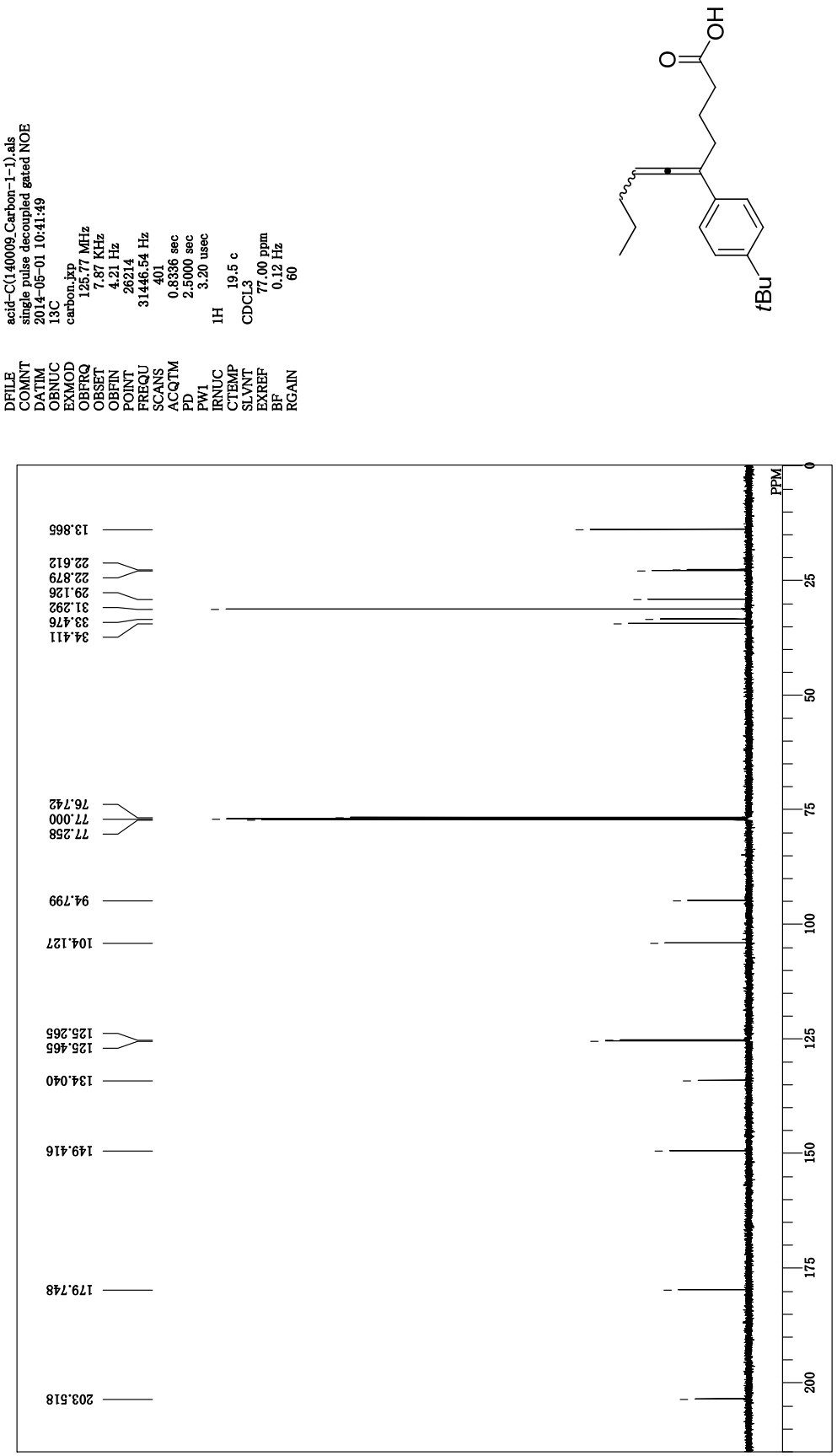
^{13}C NMR chart of **4l**



^{1}H NMR chart of **2l**



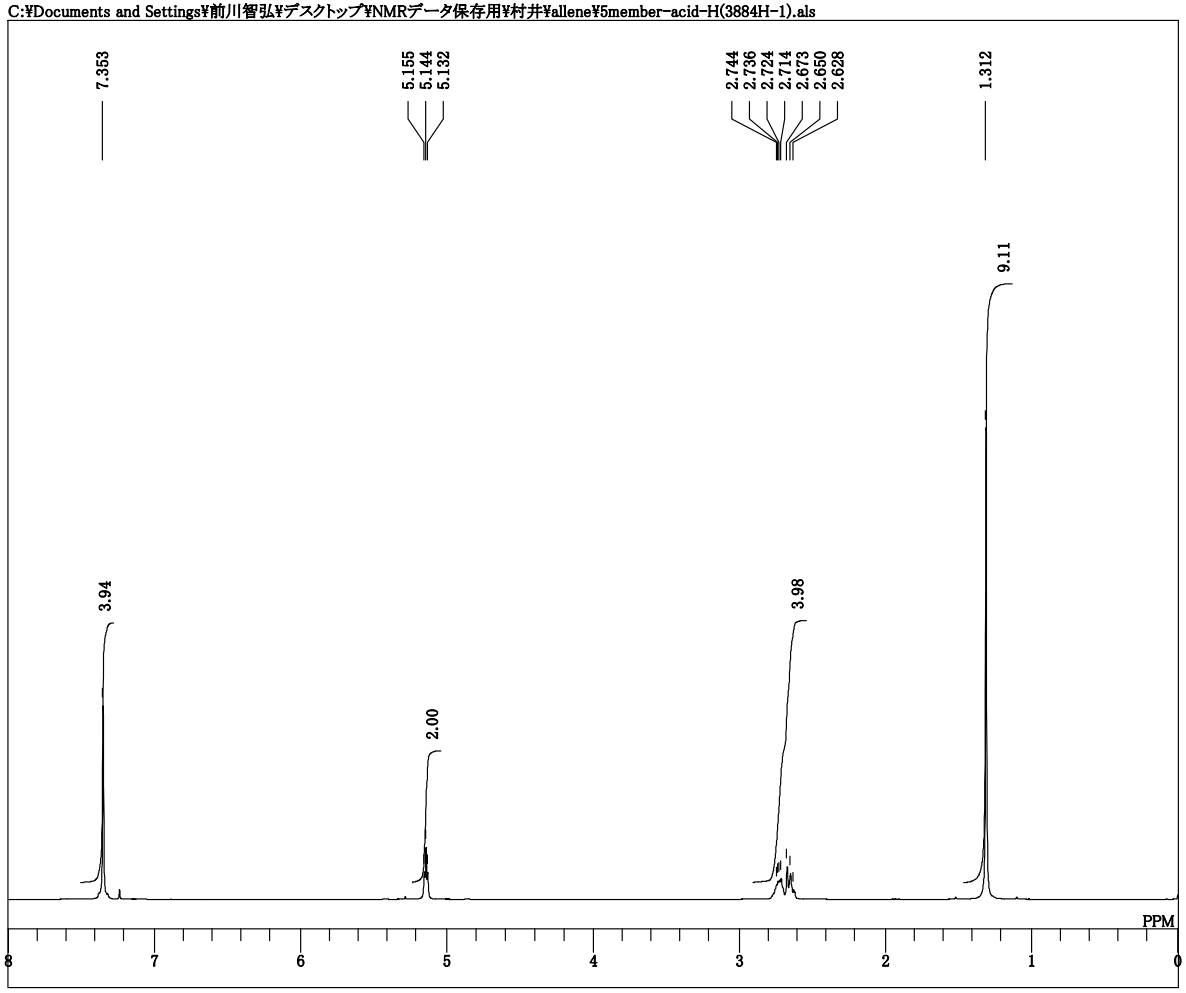
^{13}C NMR chart of **21**



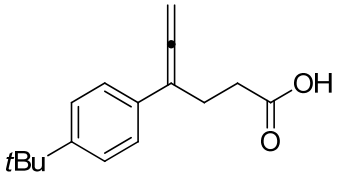
^{1}H NMR chart of **2m**

3884H

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥5member-acid-H(3884H-1).als



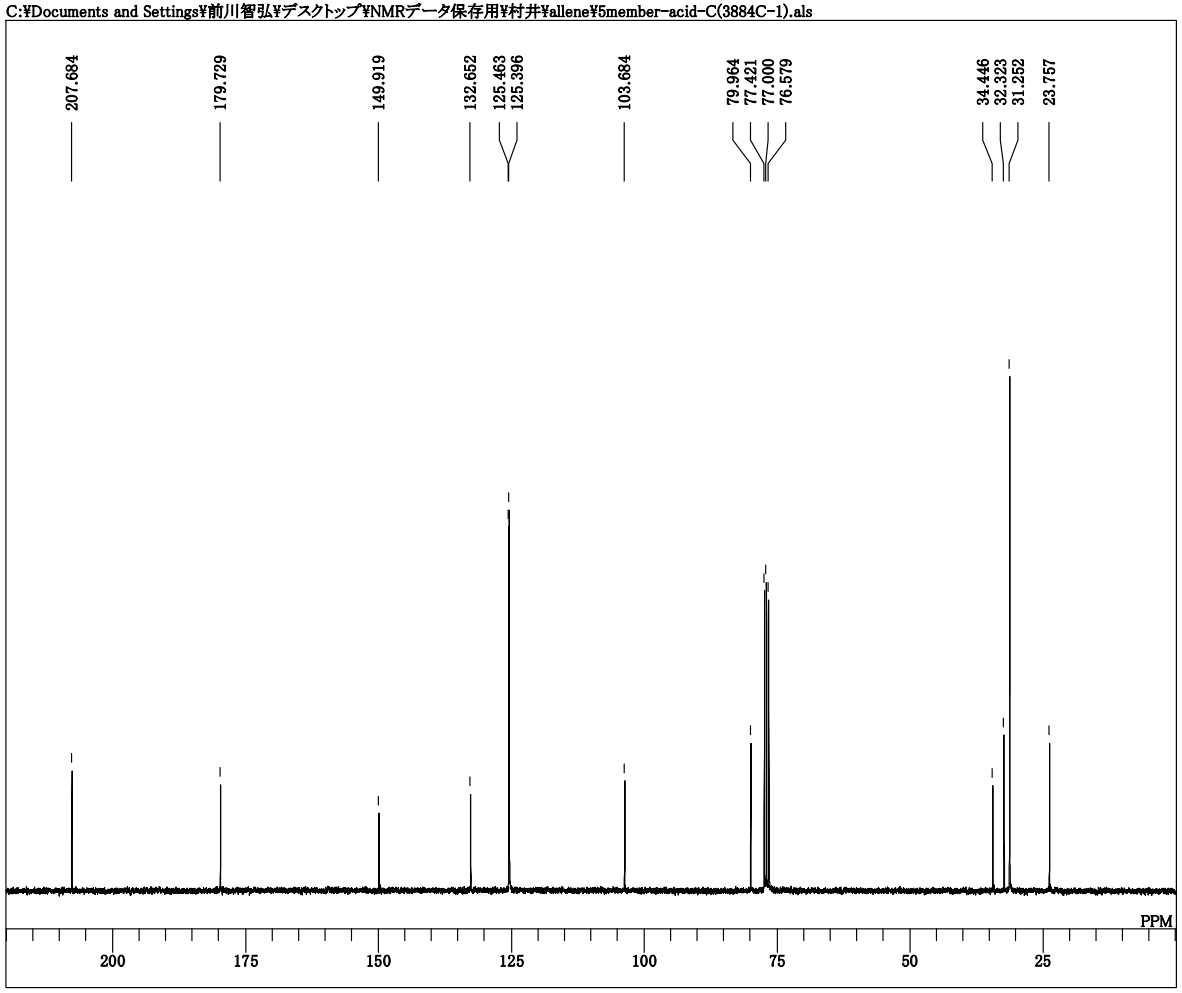
DFILE	5member-acid-H(3884H-1).als
COMNT	3884H
DATIM	15-02-2014 11:04:55
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	16
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	15.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	30



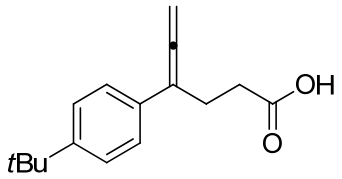
^{13}C NMR chart of **2m**

3884C

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene¥5member-acid-C(3884C-1).als

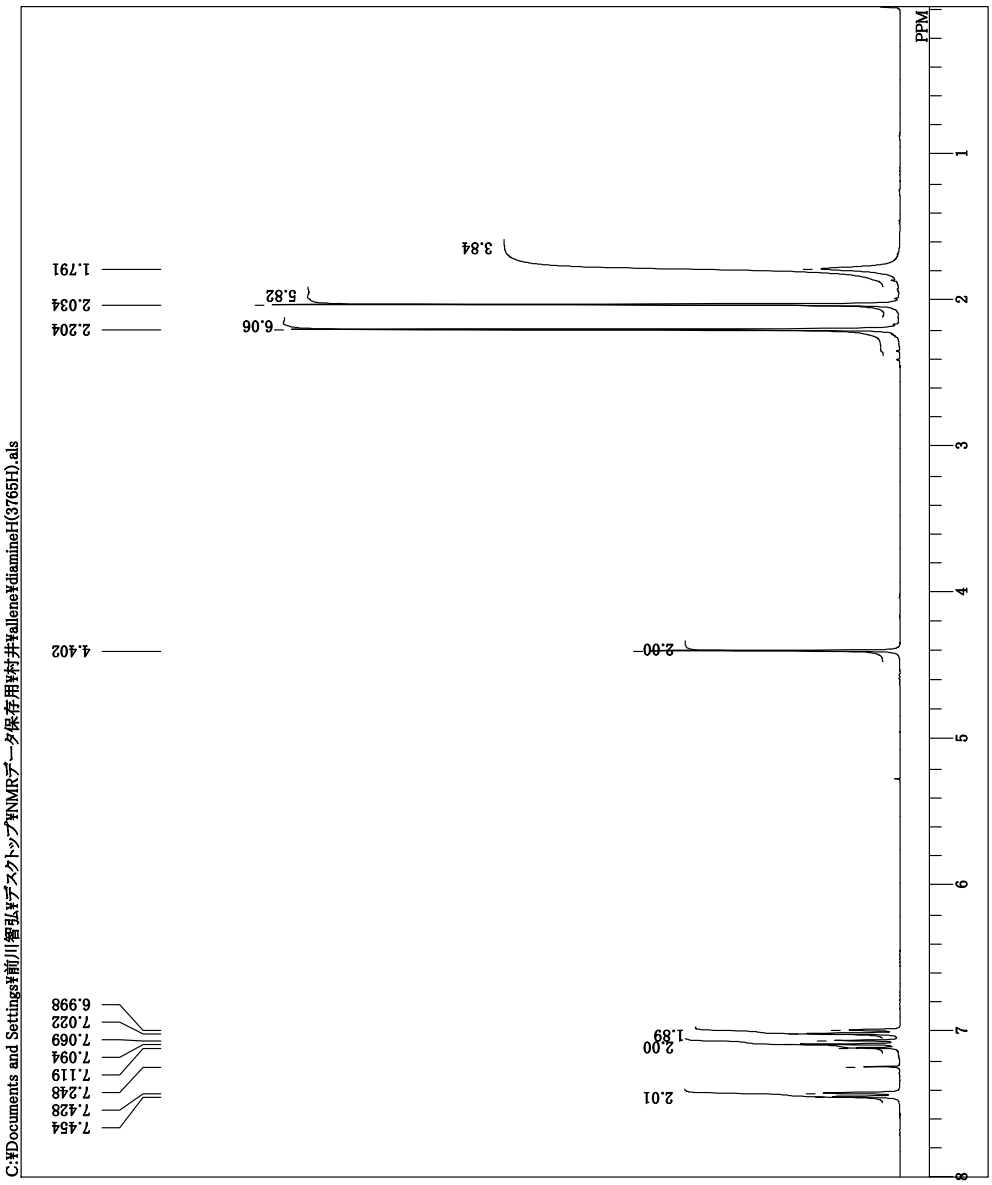


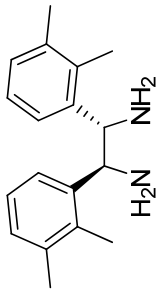
DFILE	5member-acid-C(3884C-1).als
COMNT	3884C
DATIM	15-02-2014 12:43:06
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.11 Hz
SCANS	490
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.13 usec
IRNUC	1H
CTEMP	16.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	60



^{1}H NMR chart of **(*1S*,2*S*)-1,2-bis(2,3-dimethylphenyl)ethane-1,2-diamine**

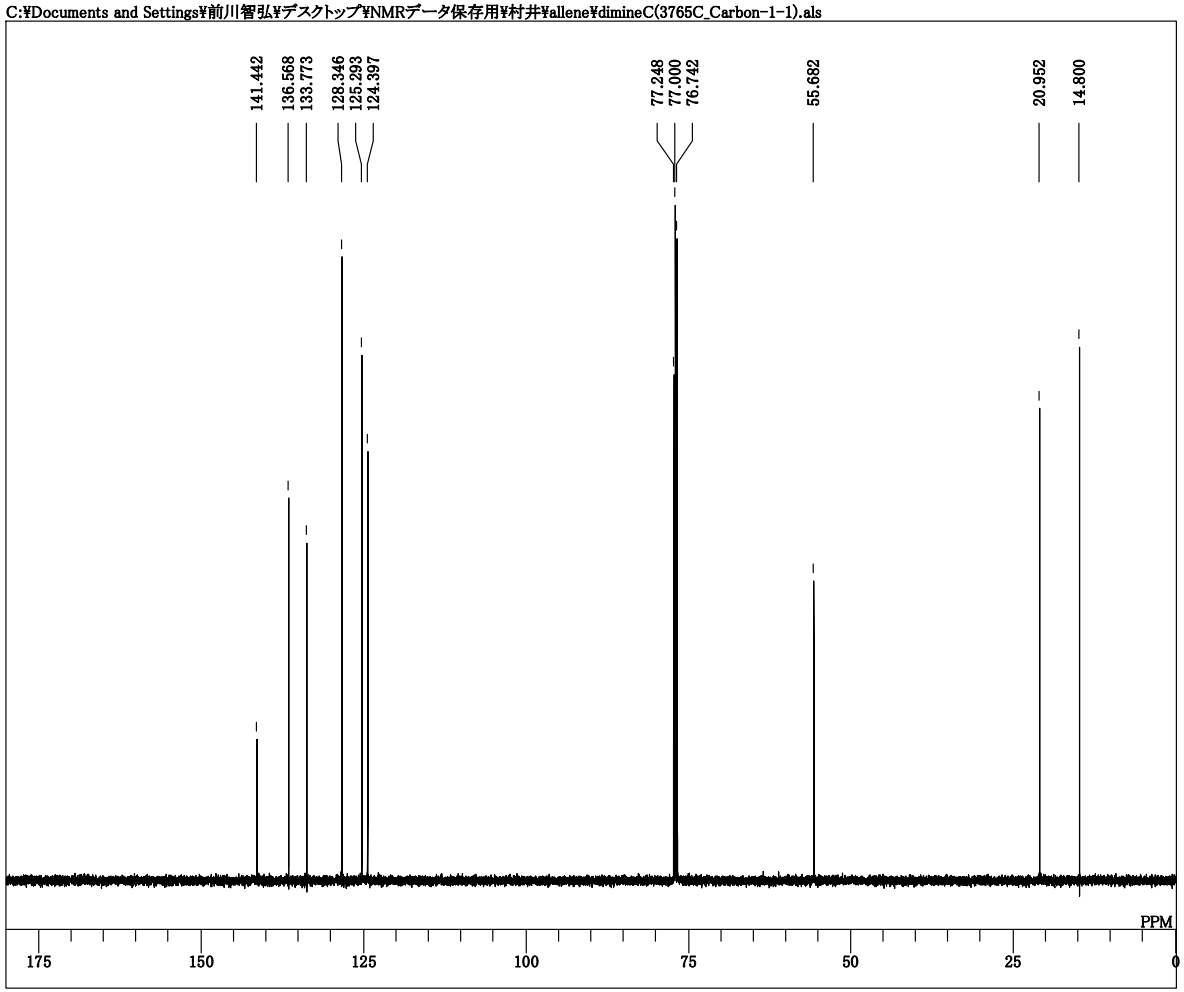
1H 300MHz CDCl3



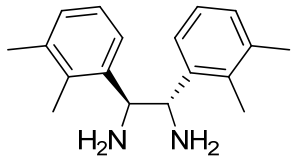


^{13}C NMR chart of ***(1S,2S)*-1,2-bis(2,3-dimethylphenyl)ethane-1,2-diamine**

single pulse decoupled gated NOE

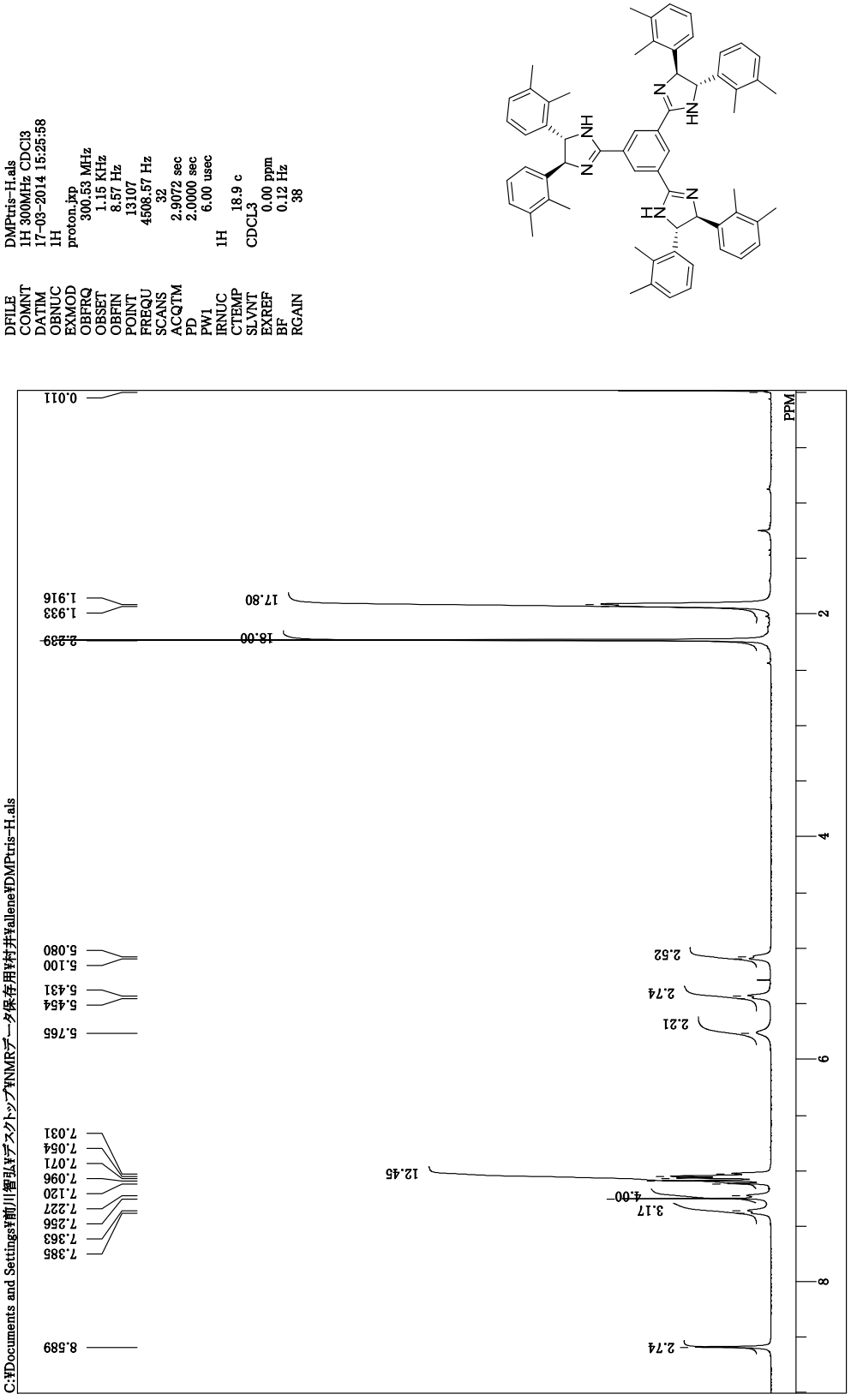


DFILE	dimineC(3765C_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	15-03-2014 16:10:46
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	419
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



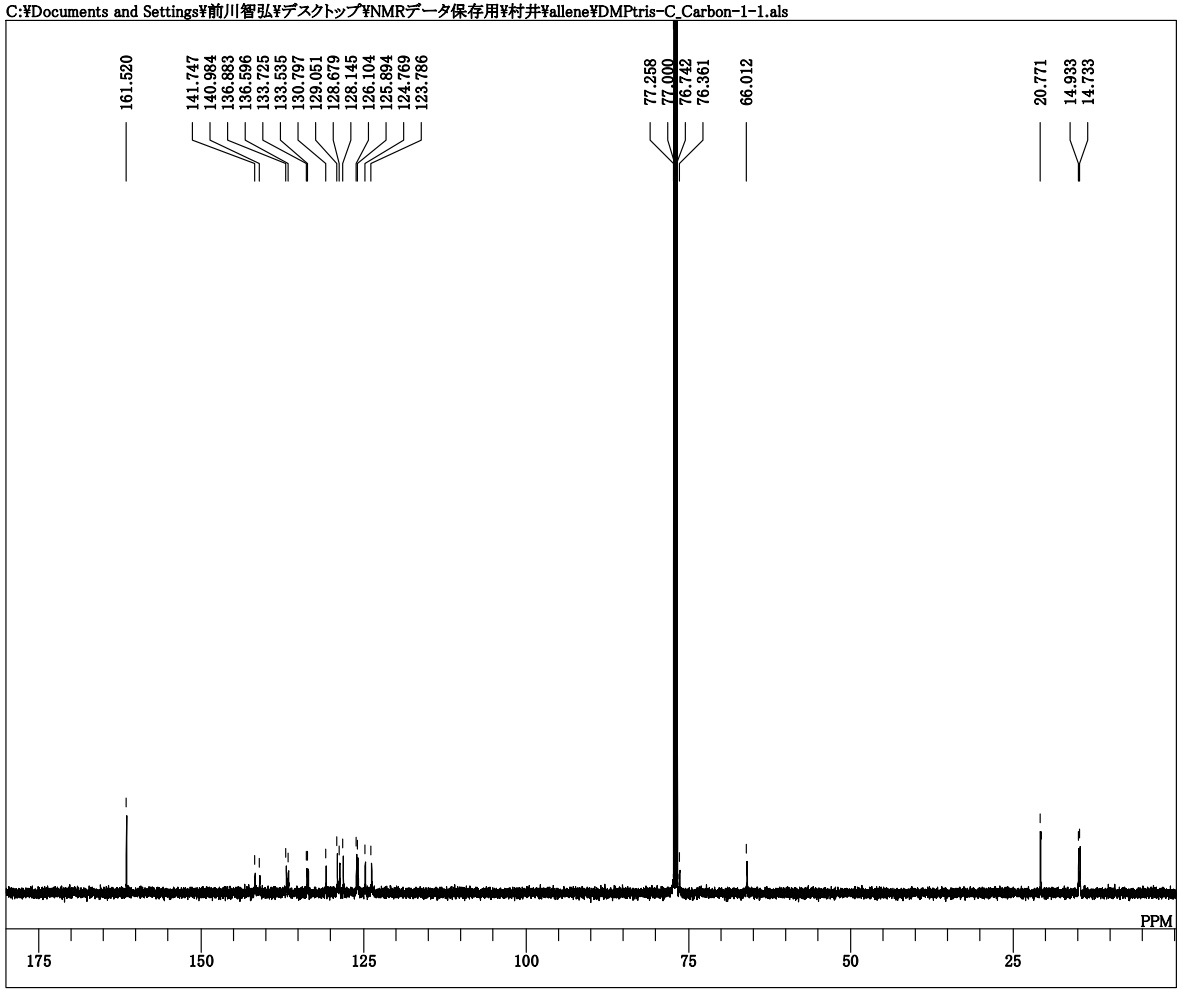
^{1}H NMR chart of DMP-tris (**1b**)

1H 300MHz CDCl3

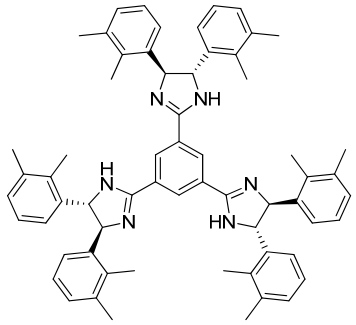


^{13}C NMR chart of DMP-tris (**1b**)

single pulse decoupled gated NOE



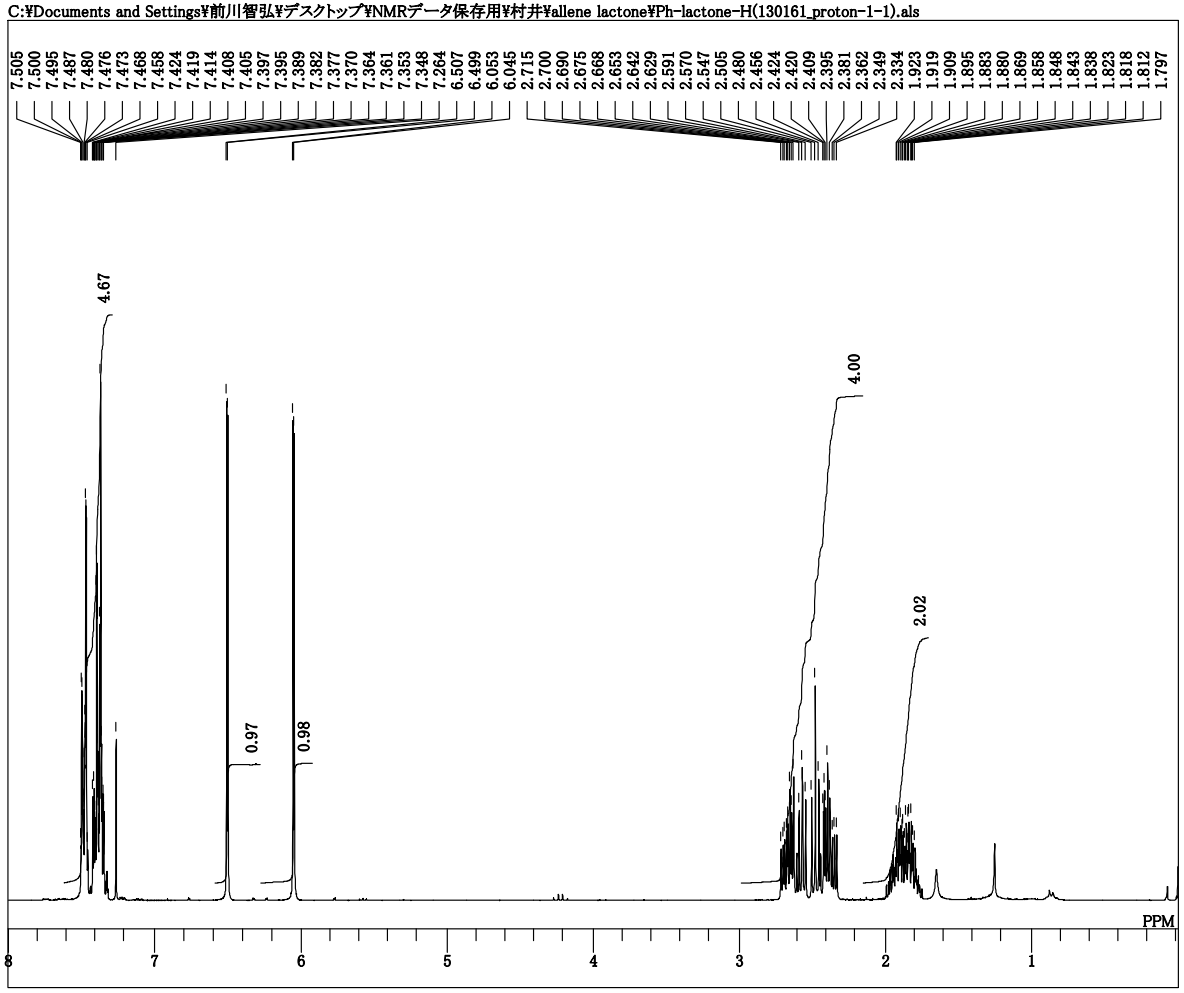
DFILE	DMPtris-C_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	17-03-2014 14:06:21
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1057
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	54



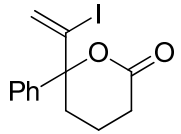
^{1}H NMR chart of **3a**

300MHz CDCl3

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥Ph-lactone-H(130161_proton-1-1).als



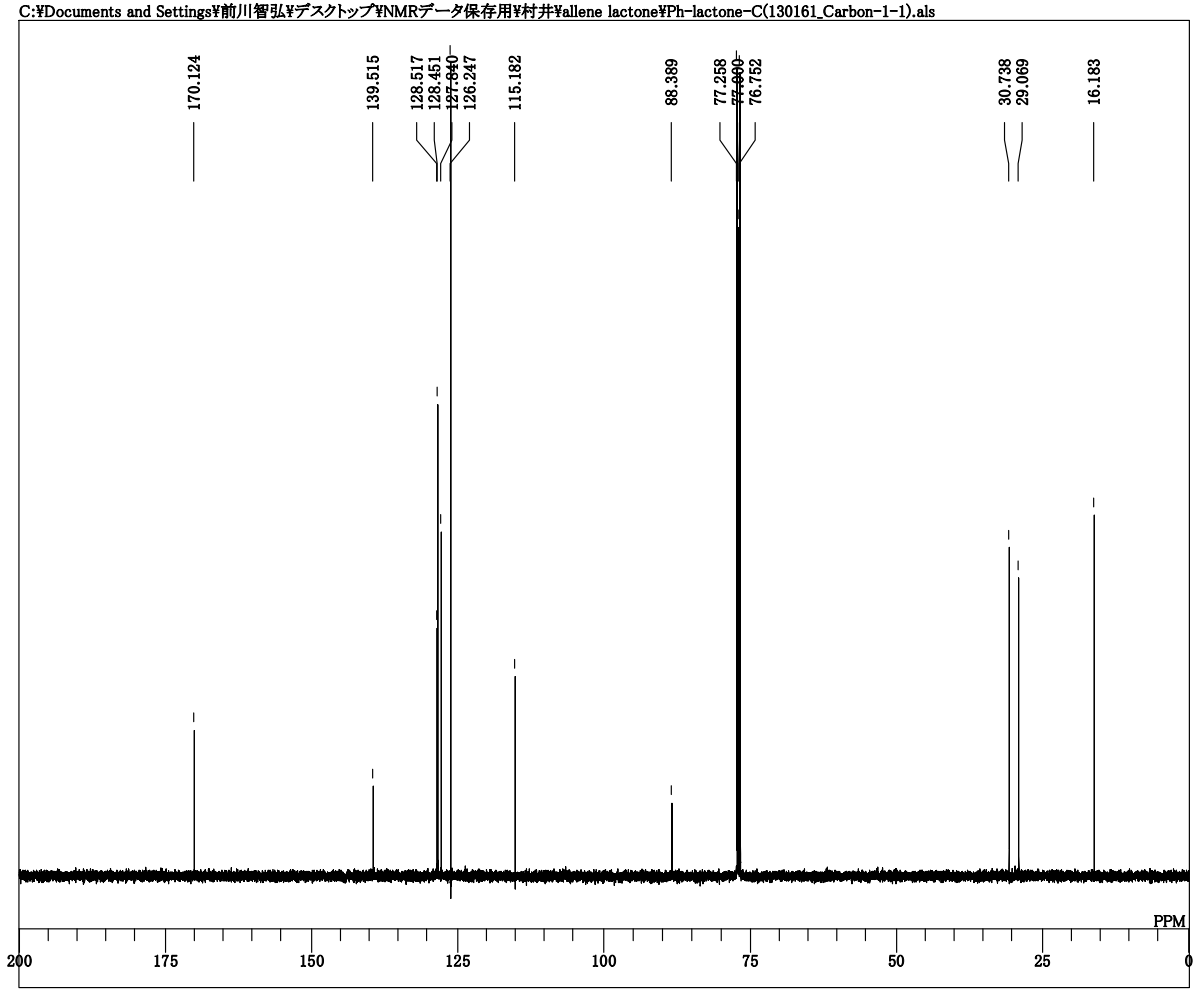
DFILE	Ph-lactone-H(130161_proton-1-1).als
COMNT	300MHz CDCl3
DATIM	2014-04-09 18:14:32
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4512.64 Hz
SCANS	16
ACQTM	2.9046 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	18.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



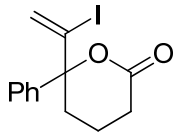
^{13}C NMR chart of **3a**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥Ph-lactone-C(130161_Carbon-1-1).als



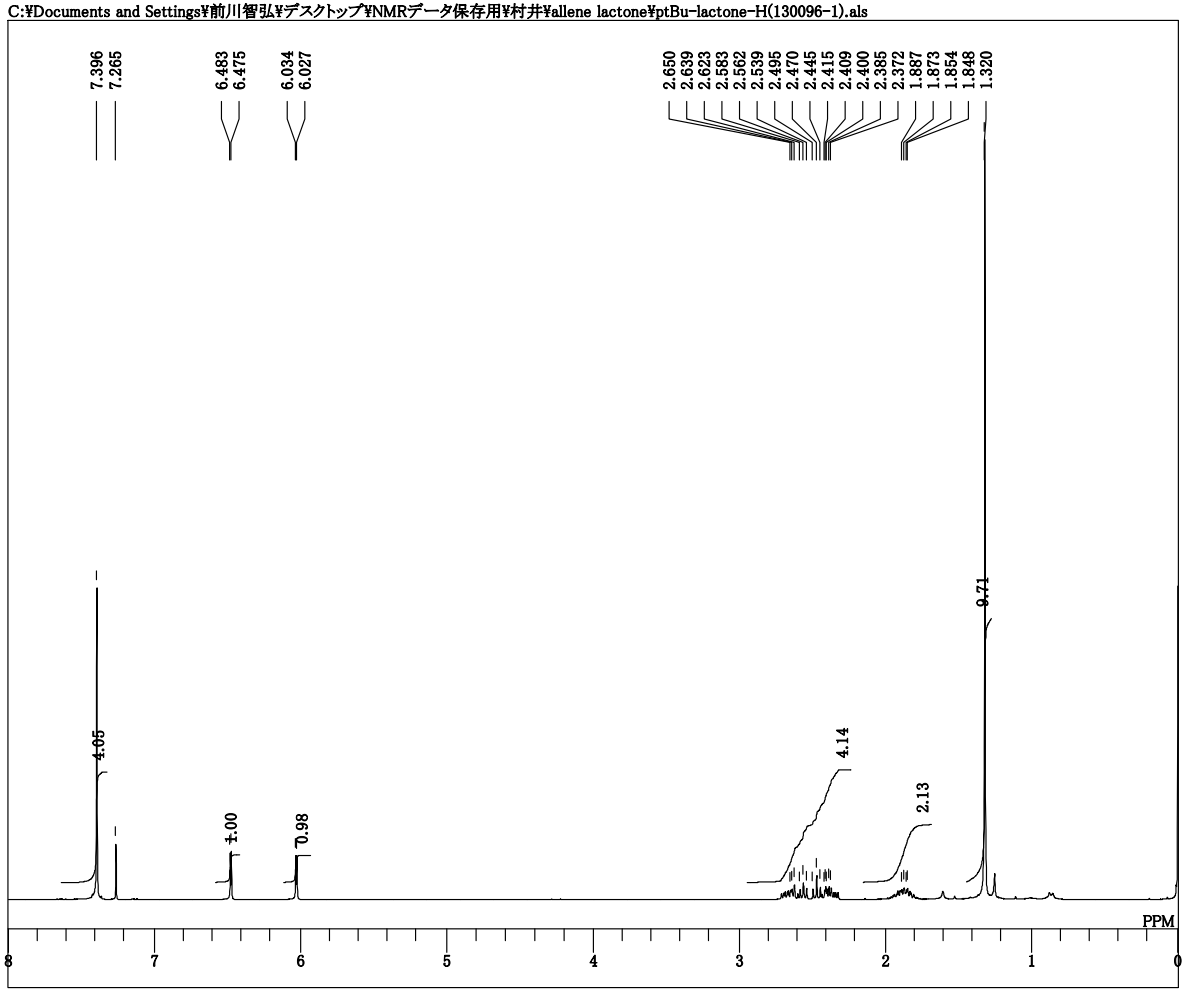
DFILE	Ph-lactone-C(130161_Carbon-1-1).als
COMNT	single pulse decoupled gated NOE
DATIM	2014-04-10 10:09:13
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	424
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



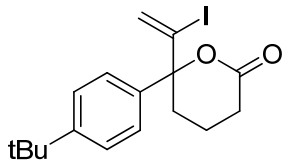
^{1}H NMR chart of **3b**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥ptBu-lactone-H(130096-1).als



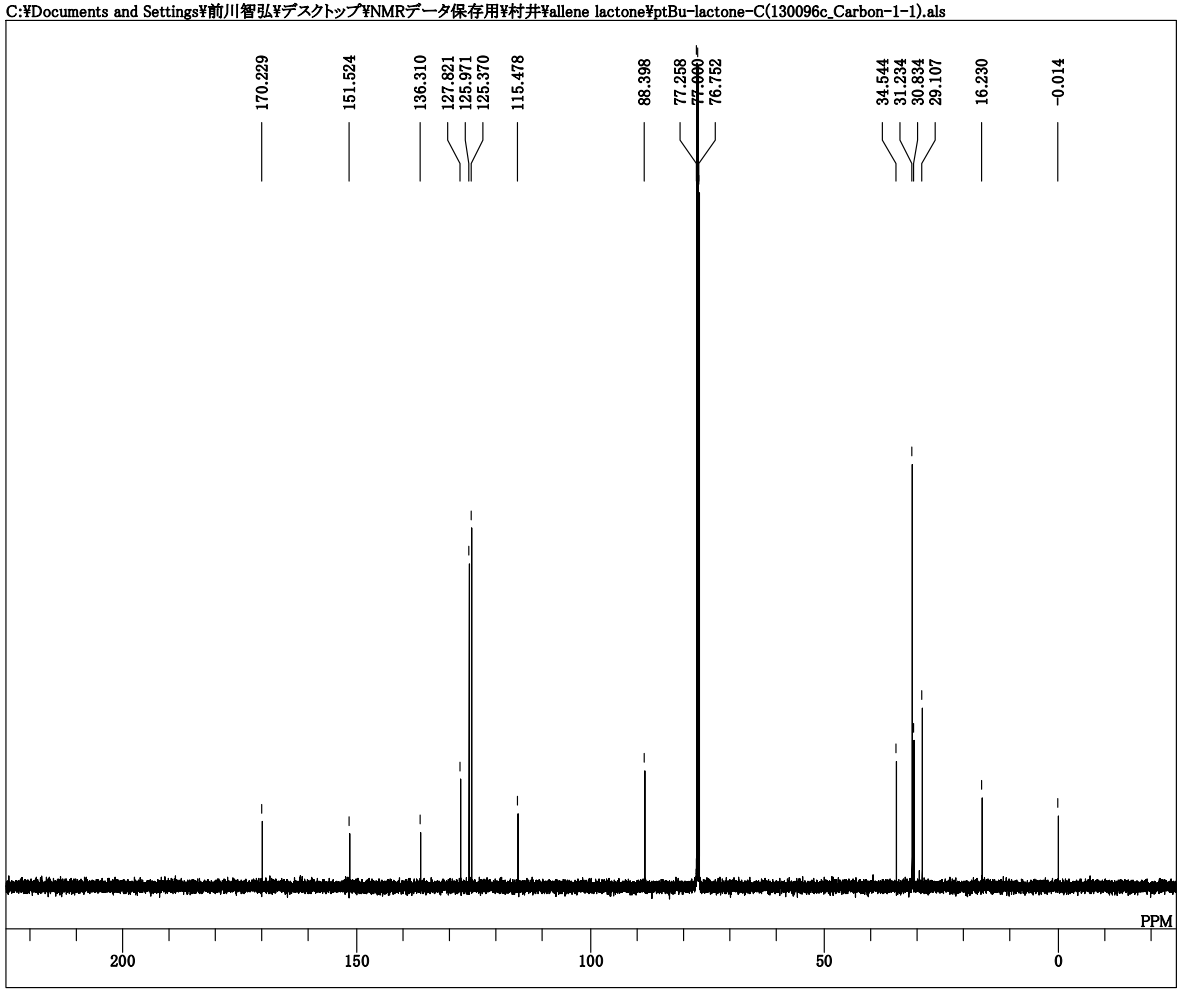
DFILE	ptBu-lactone-H(130096-1).als
COMNT	single_pulse
DATIM	28-01-2014 15:07:59
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	16.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



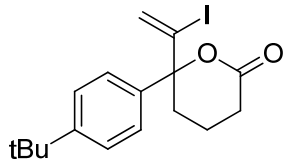
^{13}C NMR chart of **3b**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥ptBu-lactone-C(130096c_Carbon-1-1).als

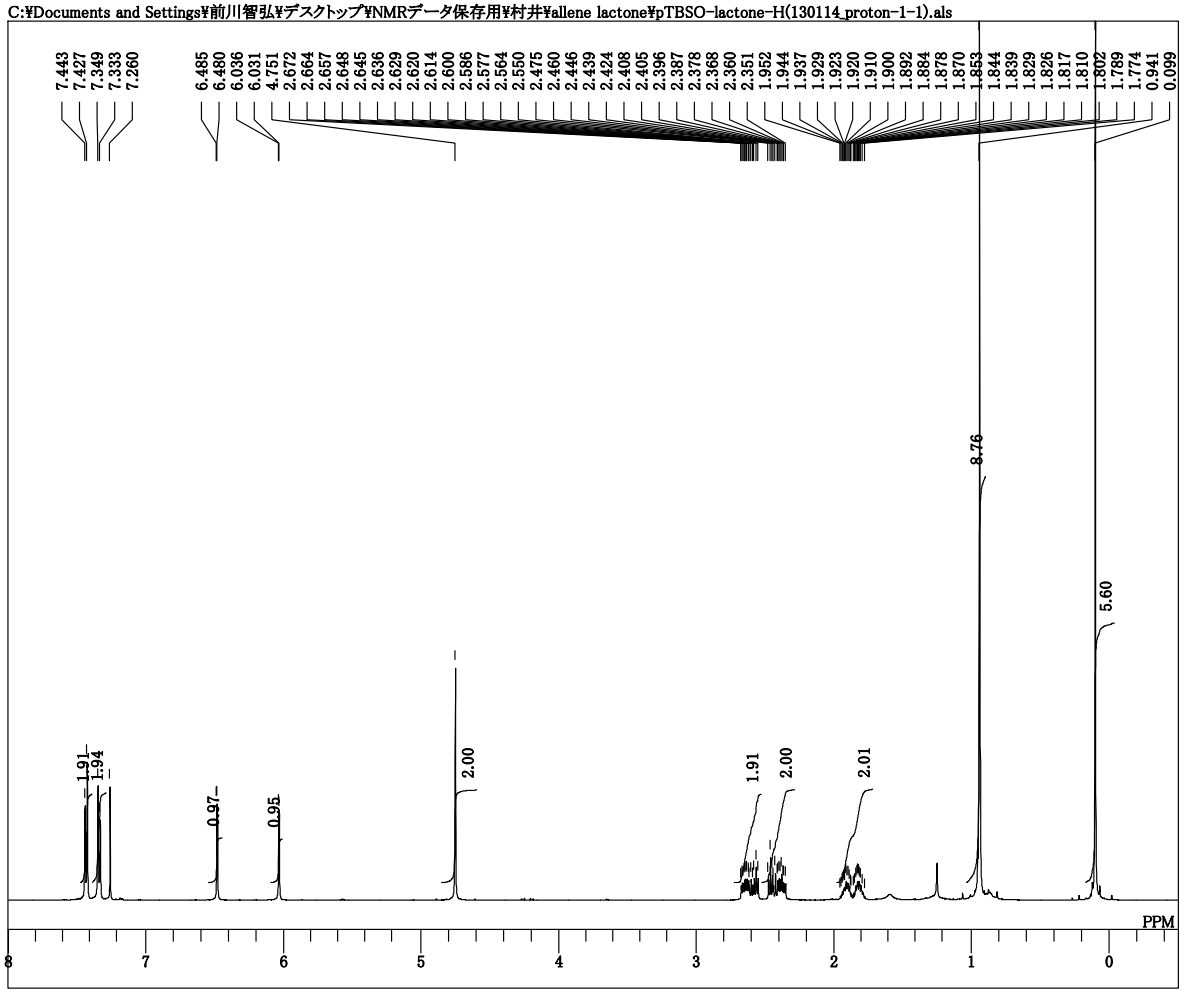


DFILE	ptBu-lactone-C(130096c_Carbon-1-1).
COMNT	single pulse decoupled gated NOE
DATIM	28-01-2014 16:50:60
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	436
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	18.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

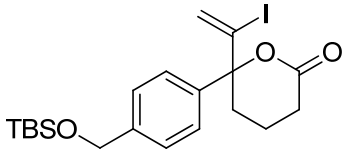


^{1}H NMR chart of **3c**

single_pulse



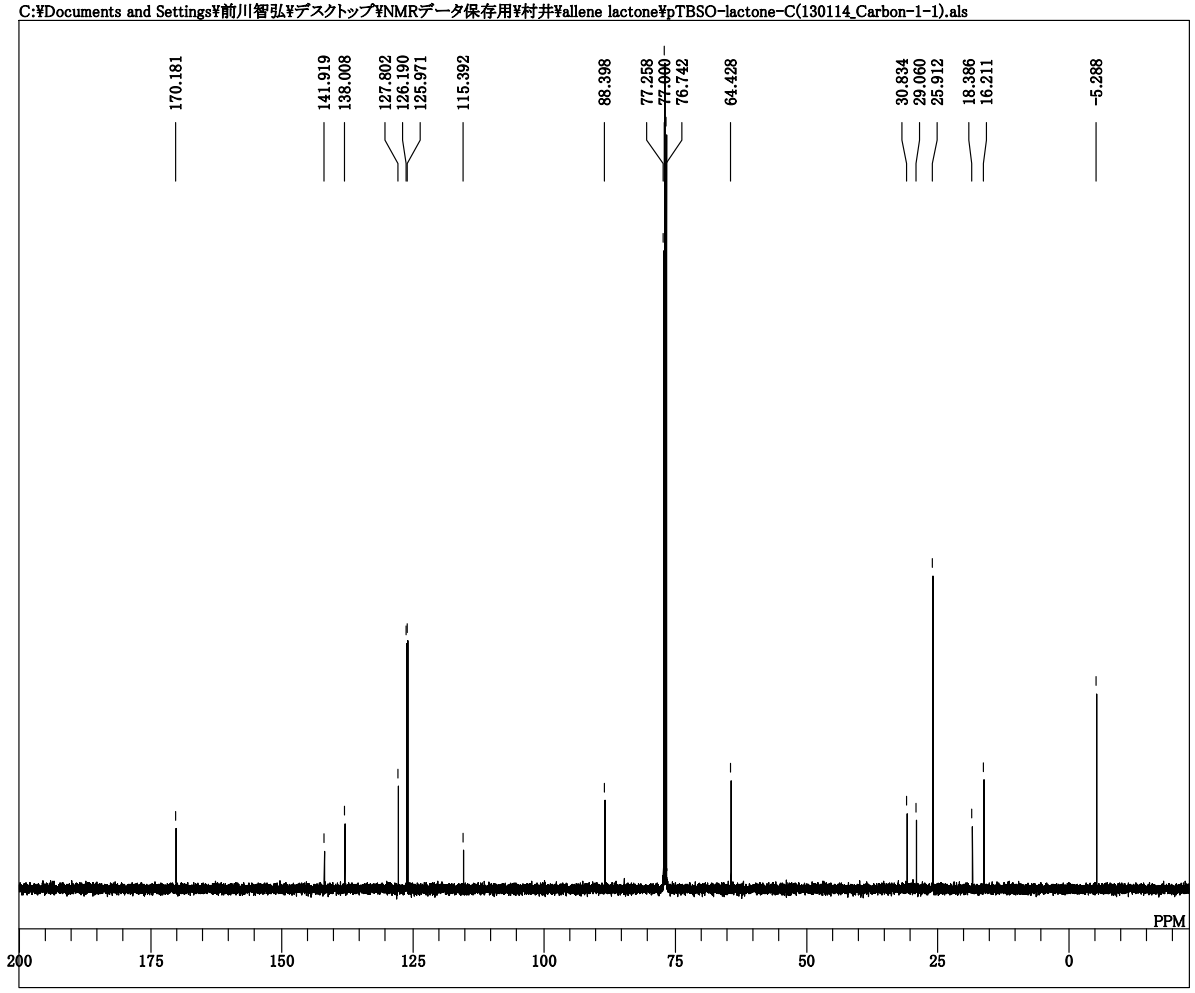
DFILE	pTBSO-lactone-H(130114_proton-1-1)
COMNT	single_pulse
DATIM	2014-02-26 14:34:43
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	13107
FREQU	7507.51 Hz
SCANS	16
ACQTM	1.7459 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	17.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



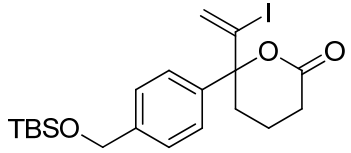
^{13}C NMR chart of **3c**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥pTBSO-lactone-C(130114_Carbon-1-1).als



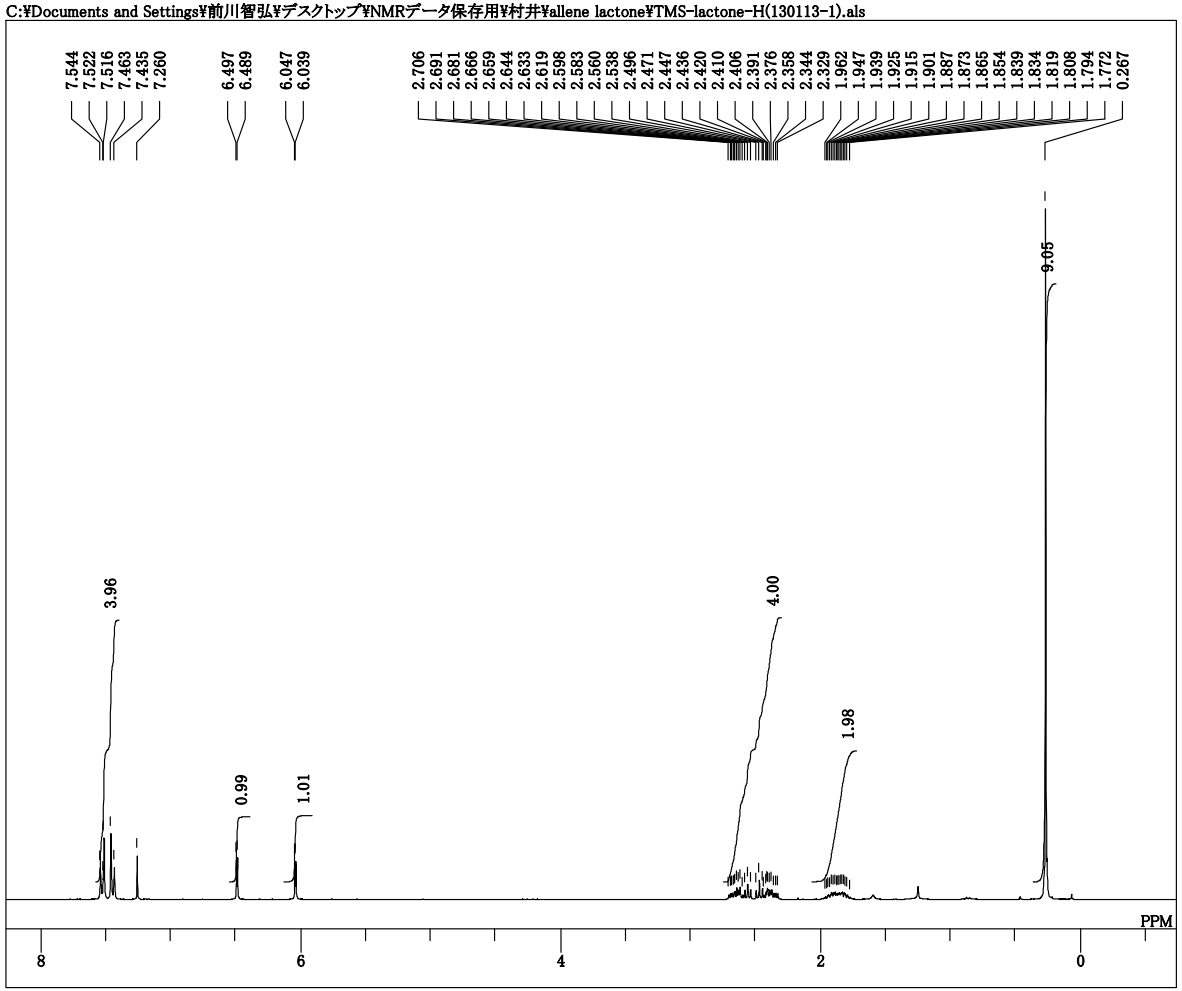
DFILE	pTBSO-lactone-C(130114_Carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	2014-02-26 14:56:56
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	606
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



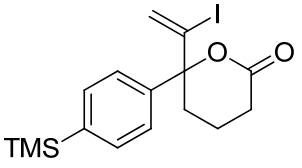
^{1}H NMR chart of **3d**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥TMS-lactone-H(130113-1).als



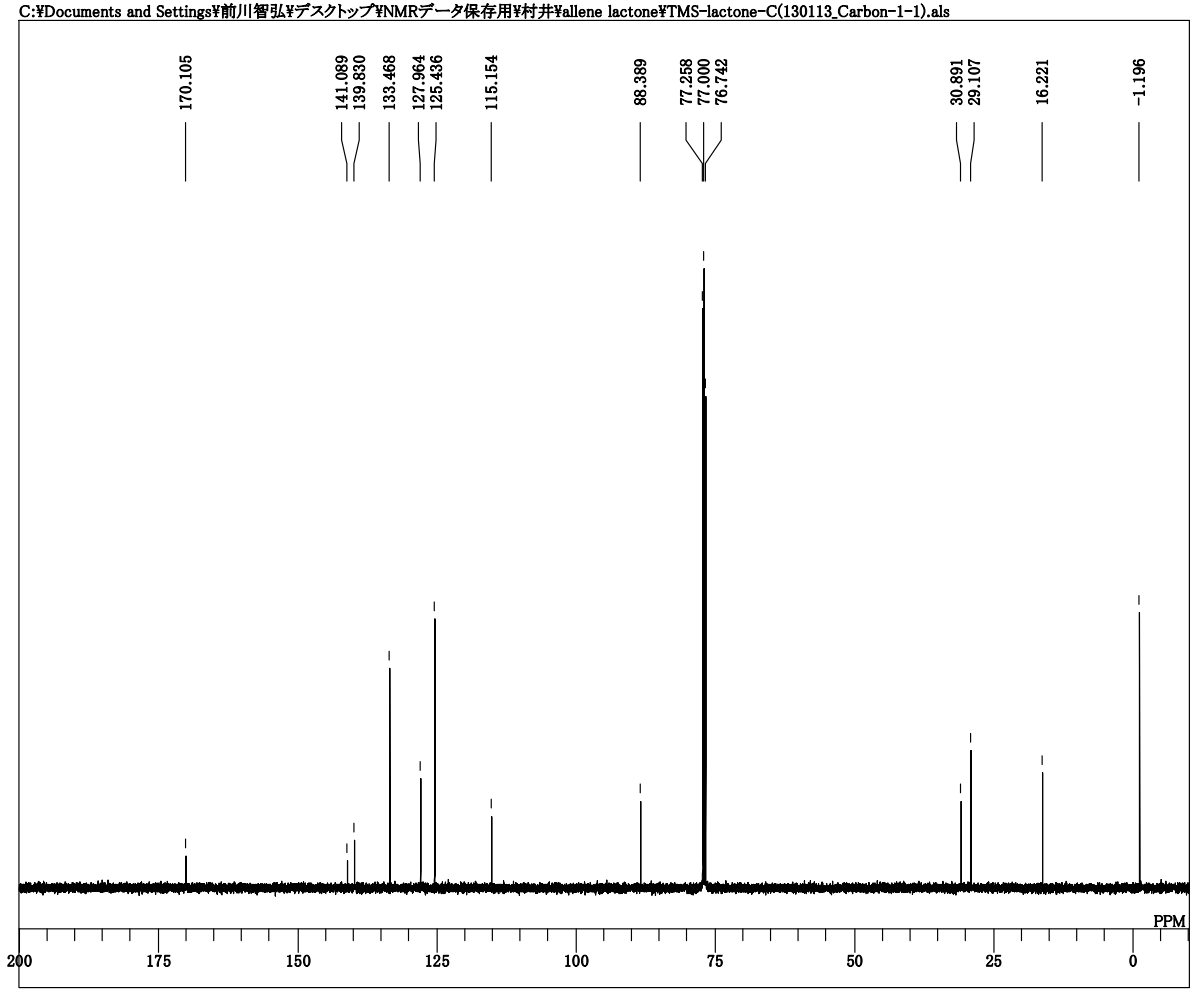
DFILE	TMS-lactone-H(130113-1).als
COMNT	single_pulse
DATIM	2014-02-25 13:54:48
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	16.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



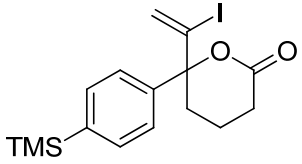
^{13}C NMR chart of **3d**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥TMS-lactone-C(130113_Carbon-1-1).als



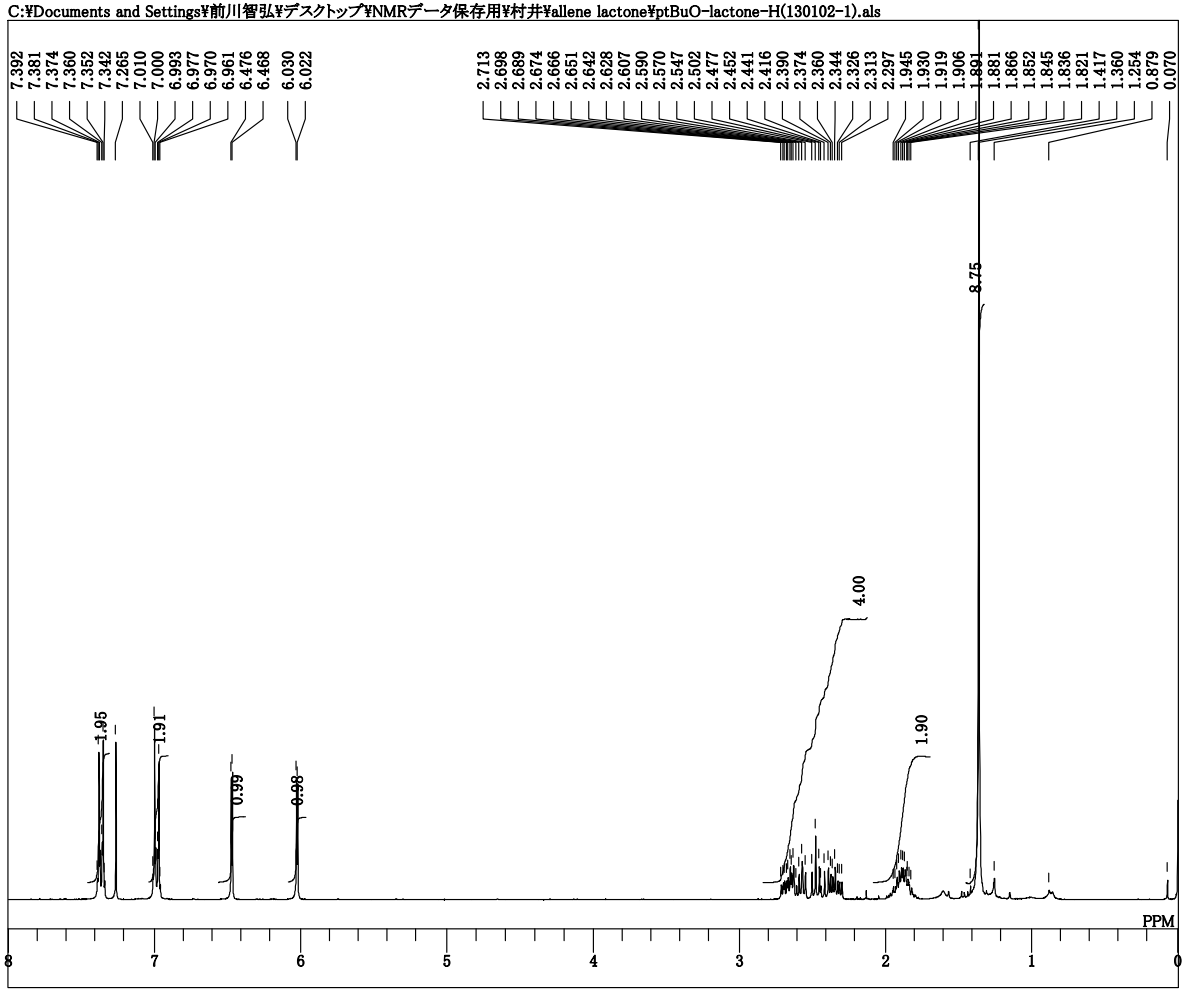
DFILE	TMS-lactone-C(130113_Carbon-1-1).a
COMNT	single pulse decoupled gated NOE
DATIM	2014-02-25 15:19:17
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	466
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



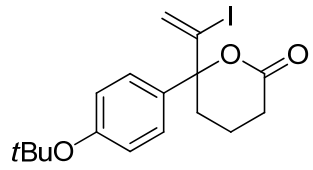
^{1}H NMR chart of **3e**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥ptBuO-lactone-H(130102-1).als



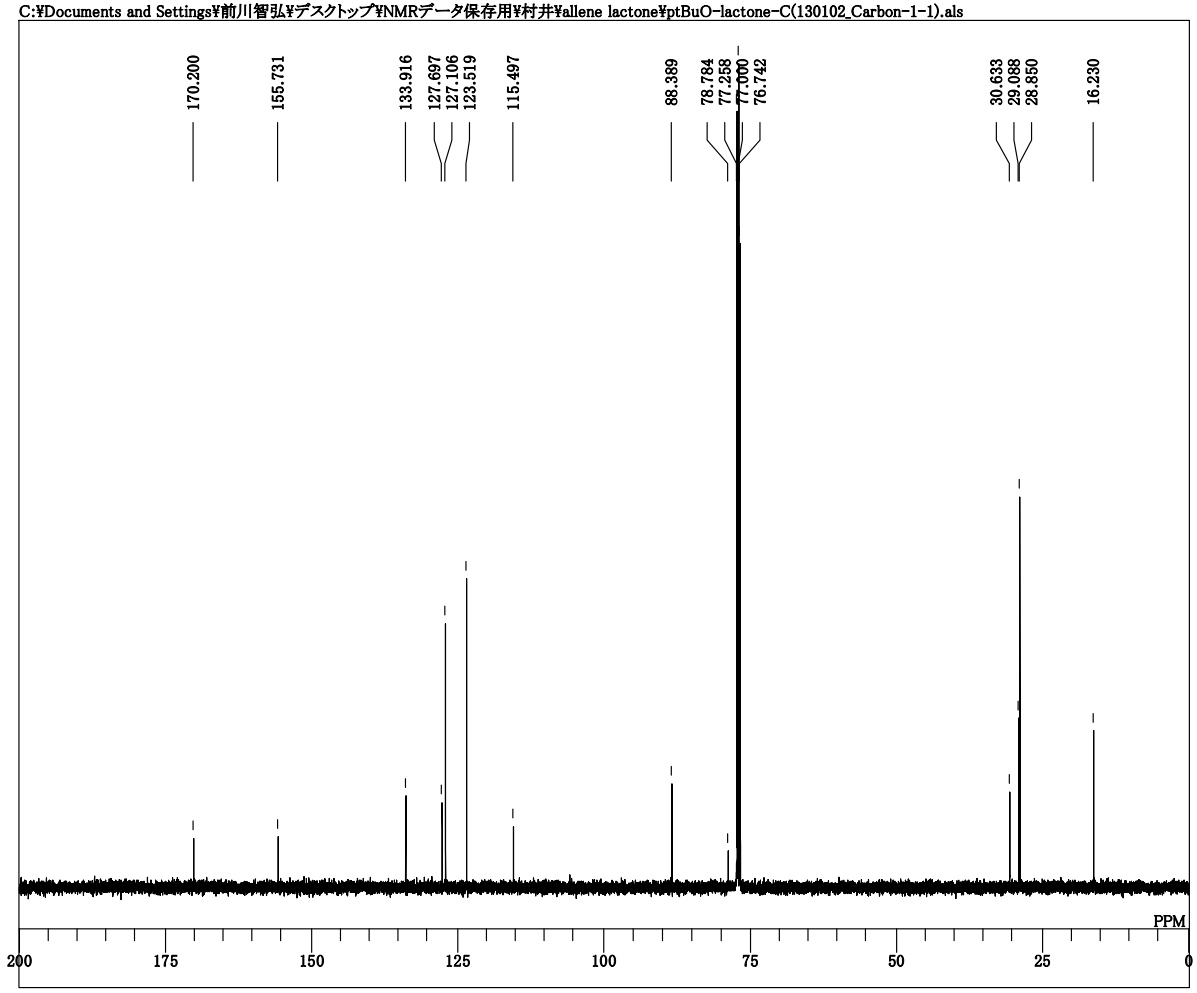
DFILE	ptBuO-lactone-H(130102-1).als
COMNT	single_pulse
DATIM	06-02-2014 17:30:25
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



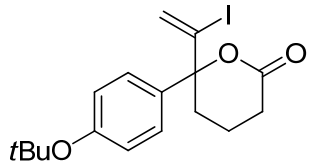
^{13}C NMR chart of **3e**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥ptBuO-lactone-C(130102_Carbon-1-1).als

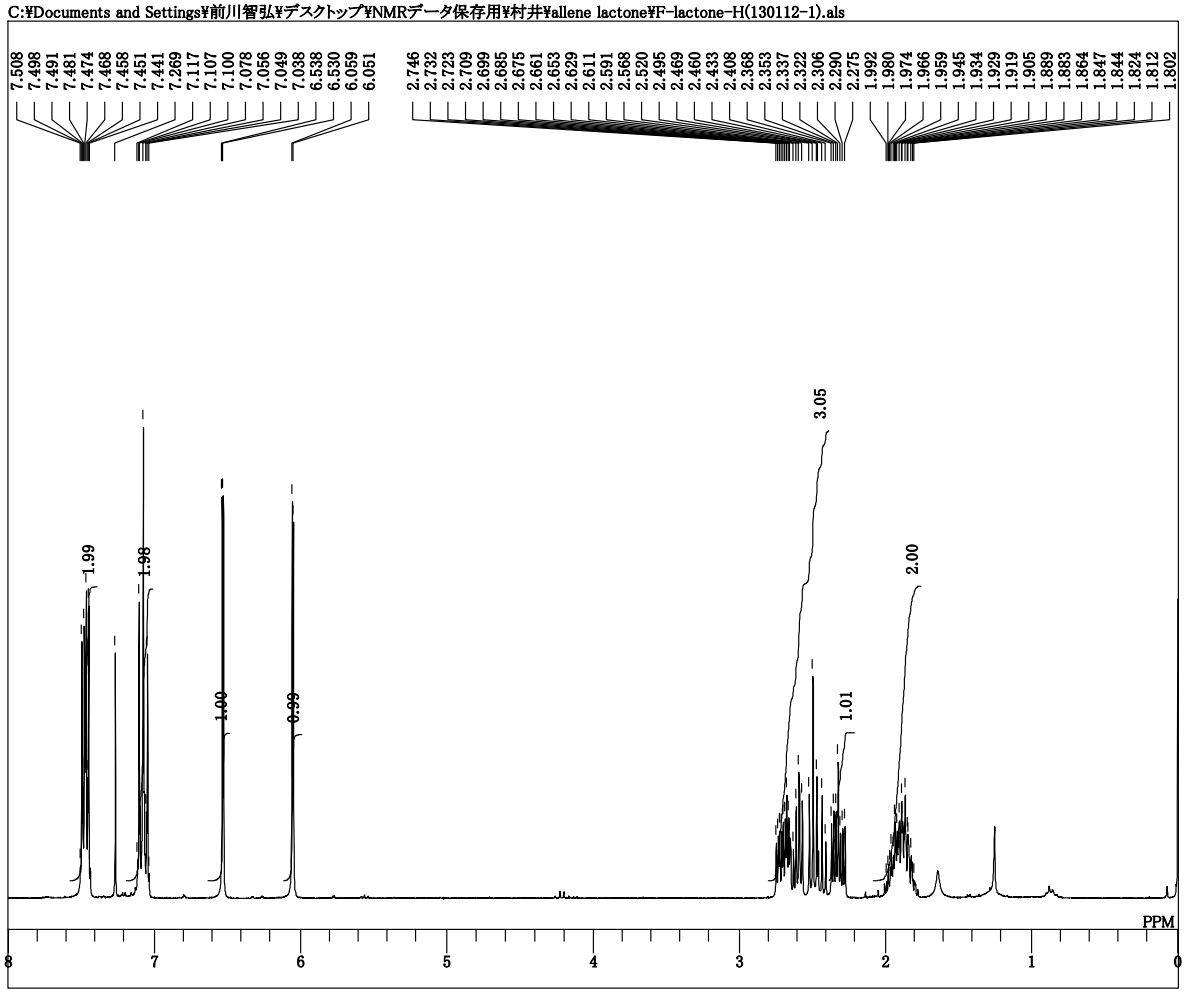


DFILE	ptBuO-lactone-C(130102_Carbon-1-1)
COMNT	single pulse decoupled gated NOE
DATIM	2014-02-07 15:44:13
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	559
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

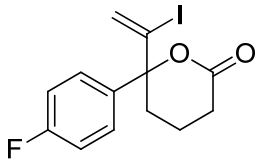


^{1}H NMR chart of **3f**

single_pulse

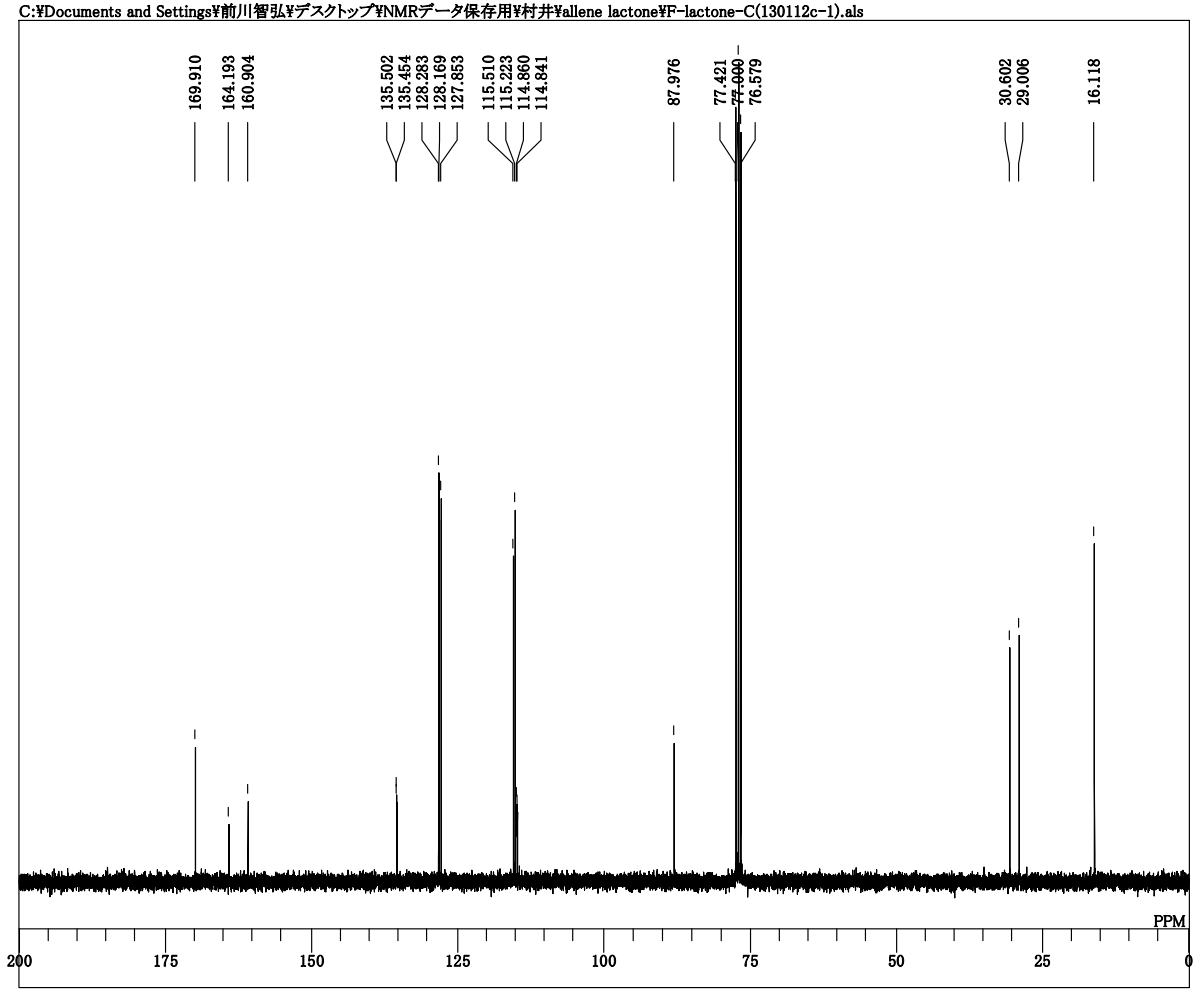


DFILE	F-lactone-H(130112-1).als
COMNT	single_pulse
DATIM	21-02-2014 13:47:18
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	16.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38

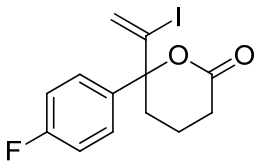


^{13}C NMR chart of **3f**

single pulse decoupled gated NOE

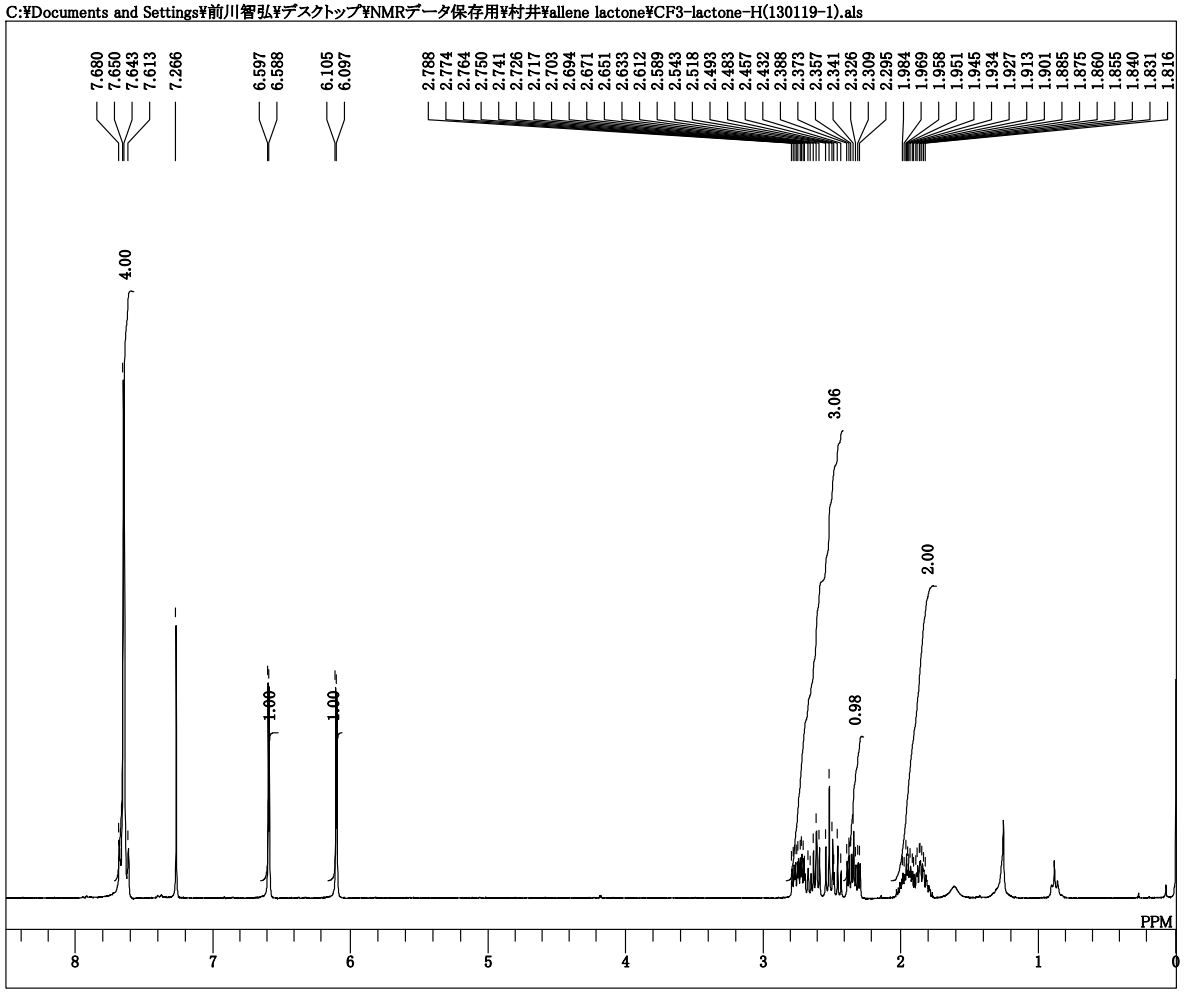


DFILE	F-lactone-C(130112c-1).als
COMNT	single pulse decoupled gated NOE
DATIM	21-02-2014 15:47:14
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	75.57 MHz
OBSET	5.79 KHz
OBFIN	1.08 Hz
POINT	26214
FREQU	18939.11 Hz
SCANS	1000
ACQTM	1.3841 sec
PD	2.0000 sec
PW1	3.13 usec
IRNUC	1H
CTEMP	16.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

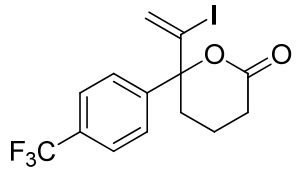


^{1}H NMR chart of **3g**

single_pulse

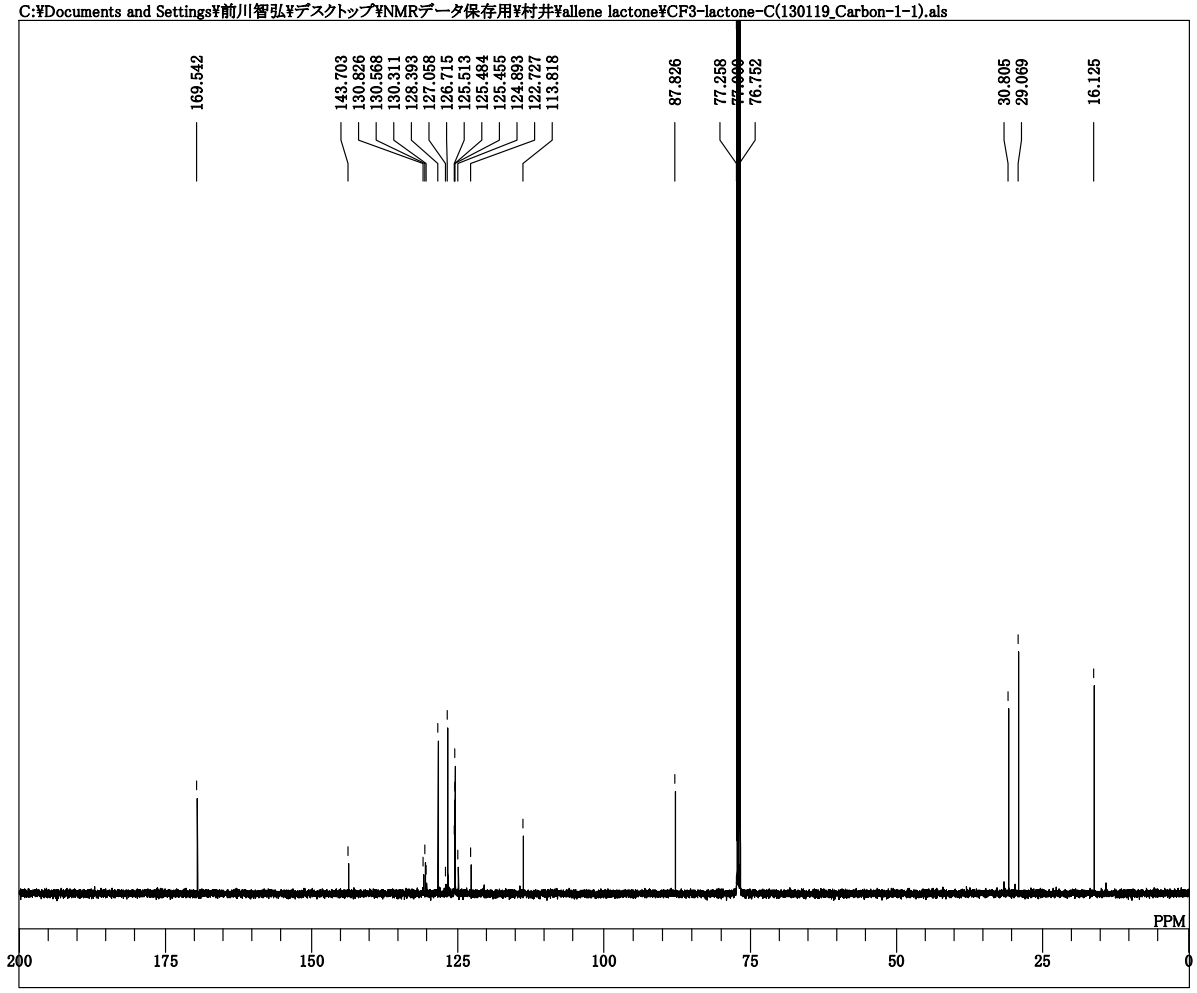


DFILE	CF3-lactone-H(130119-1).als
COMNT	single_pulse
DATIM	06-03-2014 09:38:37
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	15.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40

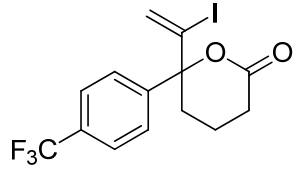


^{13}C NMR chart of **3g**

single pulse decoupled gated NOE



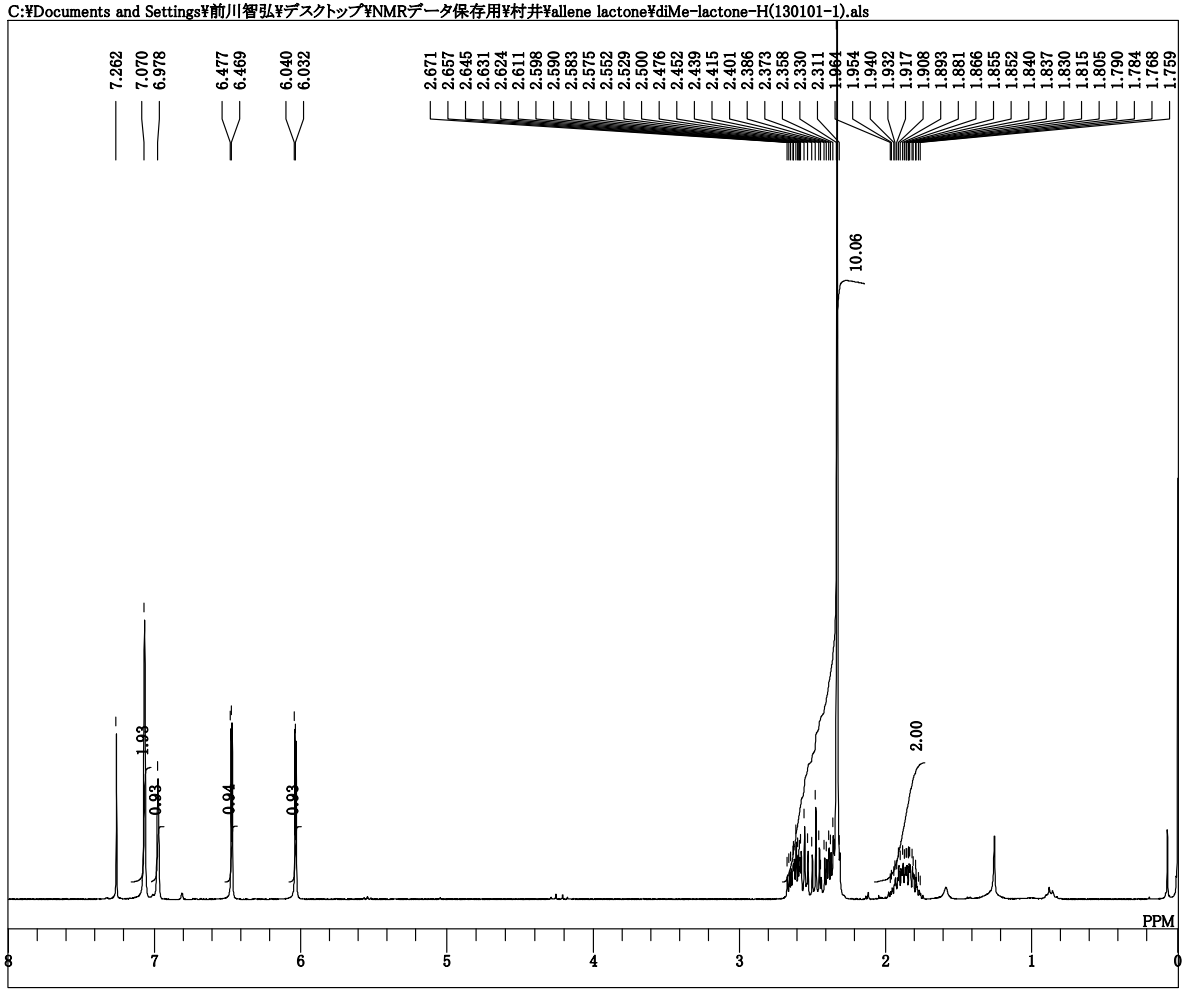
DFILE	CF3-lactone-C(130119_Carbon-1-1).a
COMNT	single pulse decoupled gated NOE
DATIM	2014-03-06 11:20:43
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	2443
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



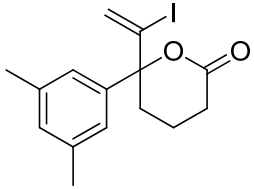
^{1}H NMR chart of **3h**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥diMe-lactone-H(130101-1).als



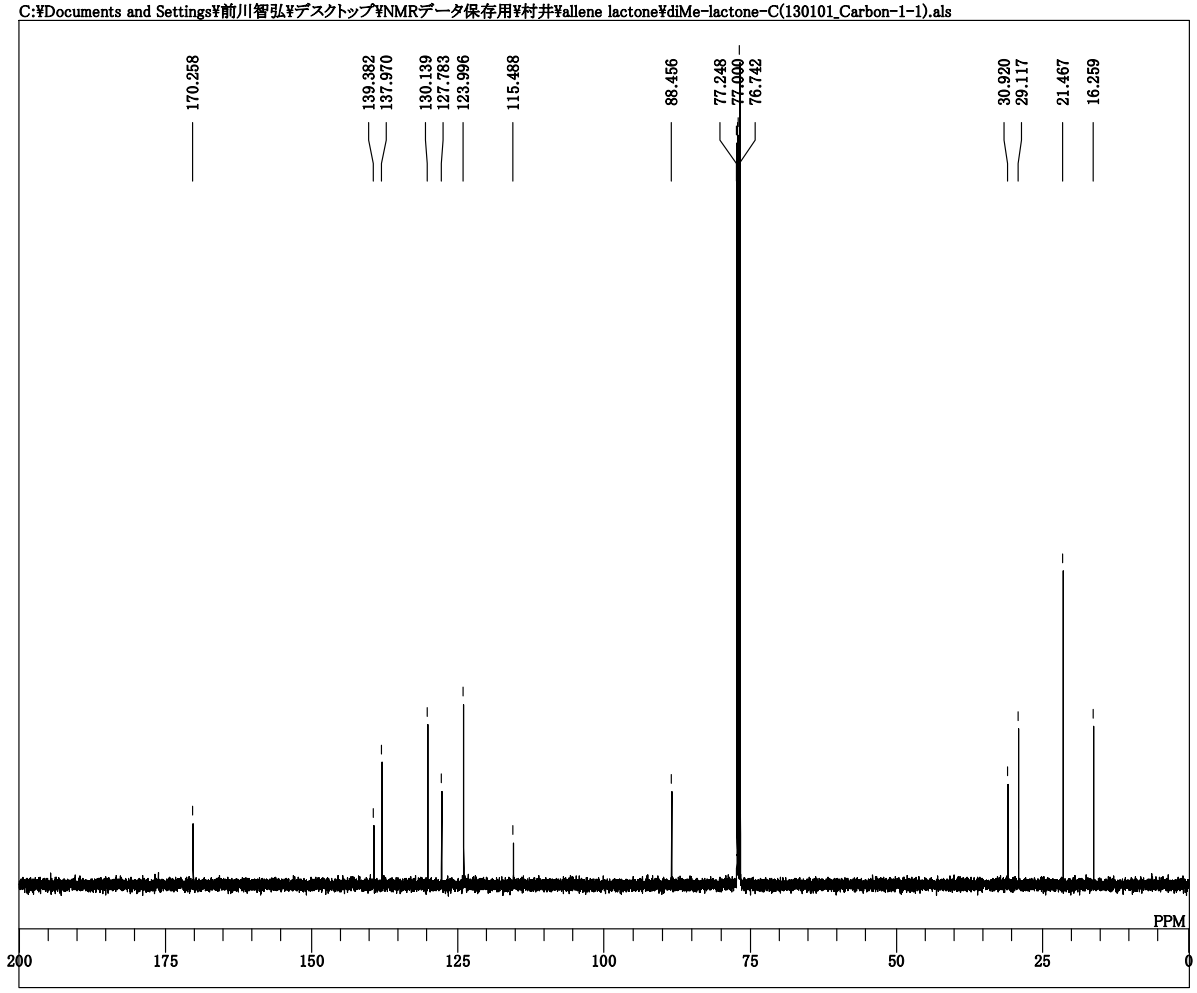
DFILE	diMe-lactone-H(130101-1).als
COMNT	single_pulse
DATIM	2014-02-06 17:35:30
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.50 Hz
SCANS	8
ACQTM	2.9072 sec
PD	5.0000 sec
PW1	5.55 usec
IRNUC	1H
CTEMP	22.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	38



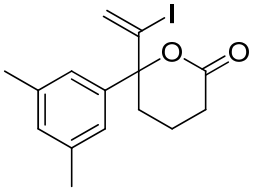
^{13}C NMR chart of **3h**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥diMe-lactone-C(130101_Carbon-1-1).als



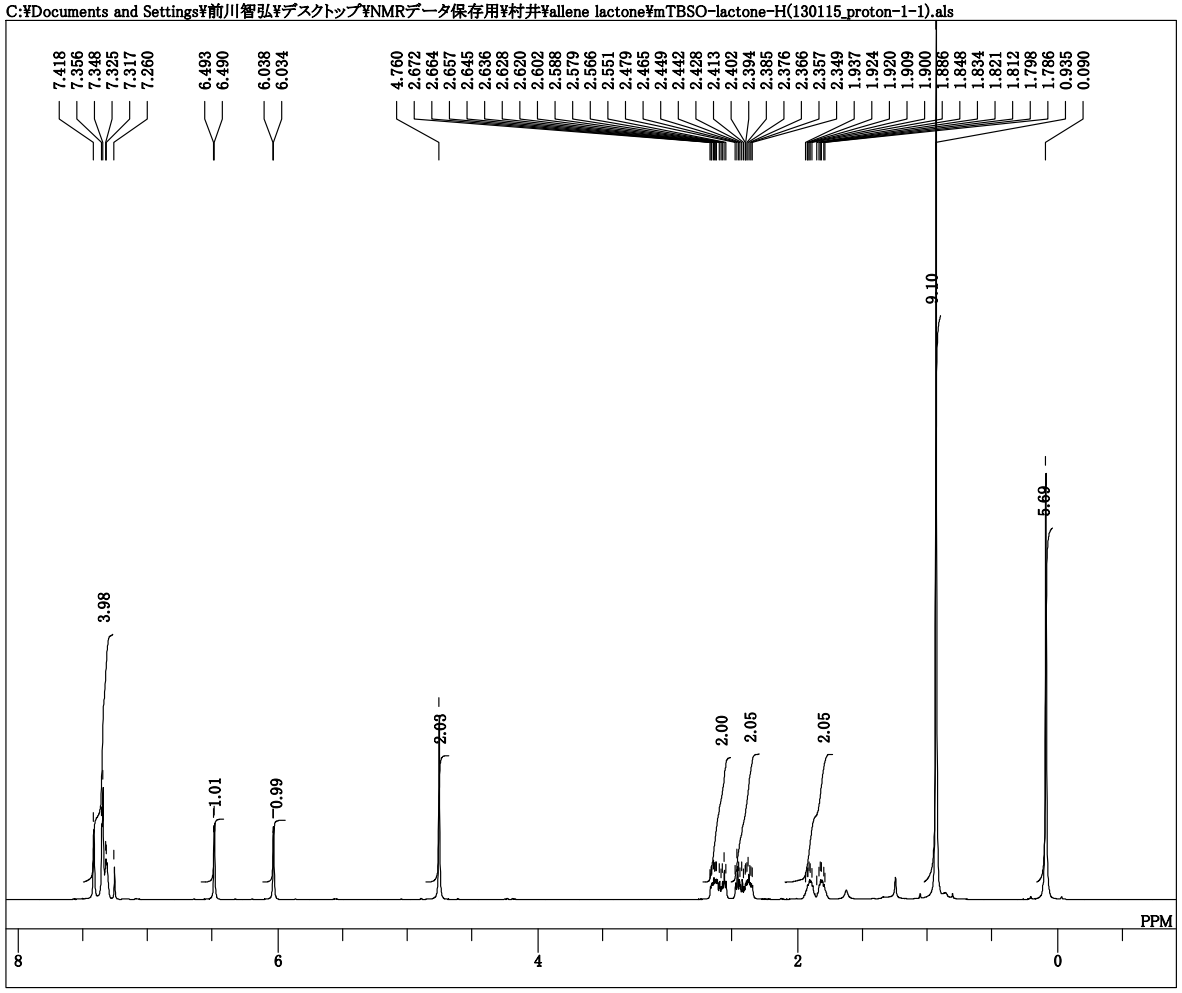
DFILE	diMe-lactone-C(130101_Carbon-1-1).a
COMNT	single pulse decoupled gated NOE
DATIM	2014-02-07 14:30:06
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	504
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



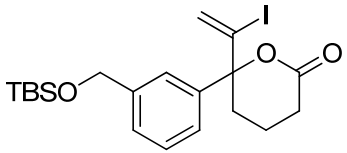
^{1}H NMR chart of **3i**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥mTBSO-lactone-H(130115_proton-1-1).als



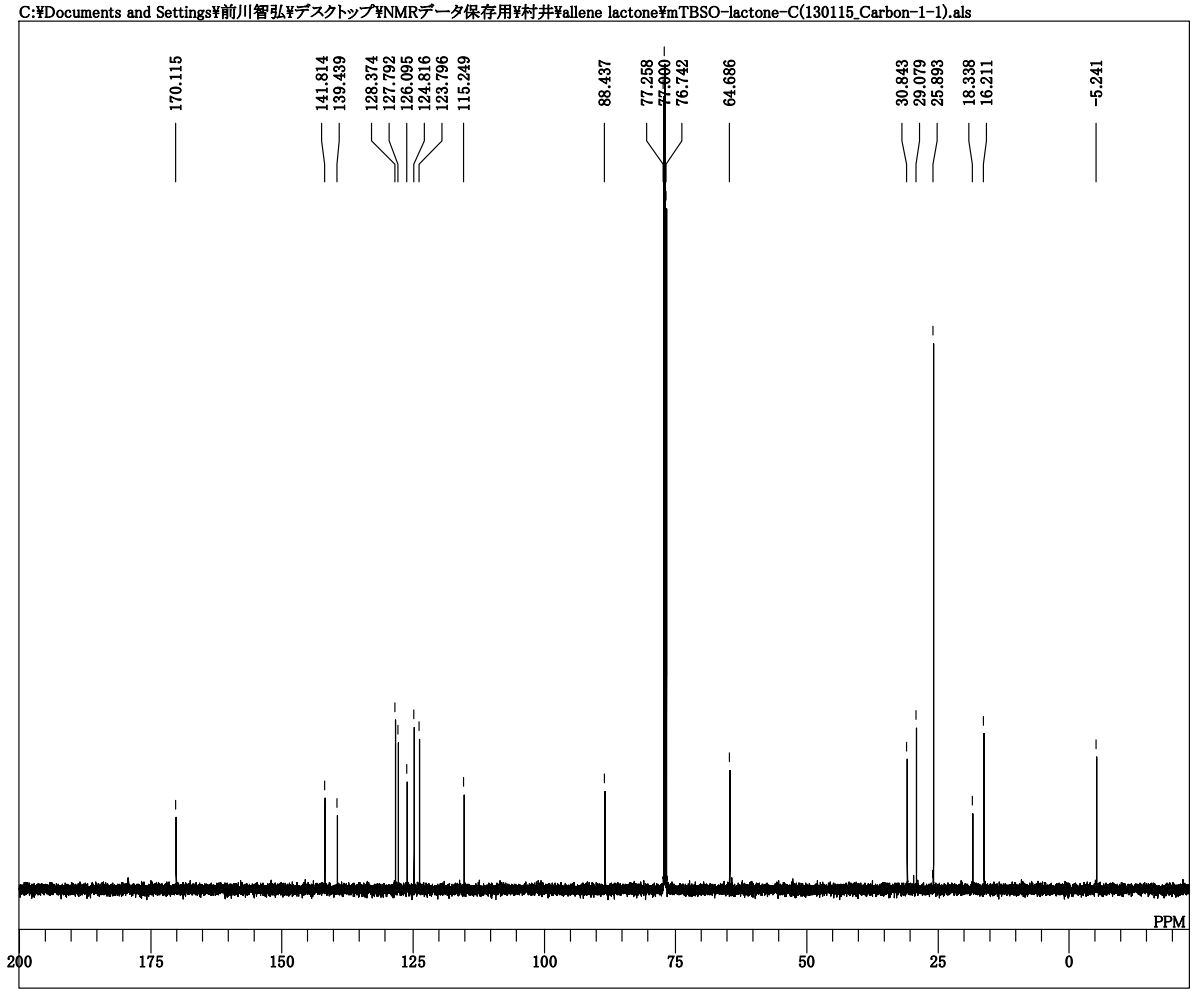
DFILE	mTBSO-lactone-H(130115_proton-1-1
COMNT	single_pulse
DATIM	28-02-2014 17:18:52
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.91 KHz
OBFIN	6.17 Hz
POINT	13107
FREQU	8503.40 Hz
SCANS	16
ACQTM	1.5414 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	16.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



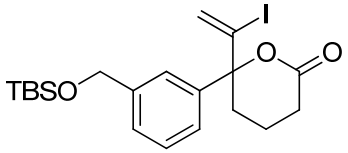
^{13}C NMR chart of **3i**

single pulse decoupled gated NOE

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥mTBSO-lactone-C(130115_Carbon-1-1).als

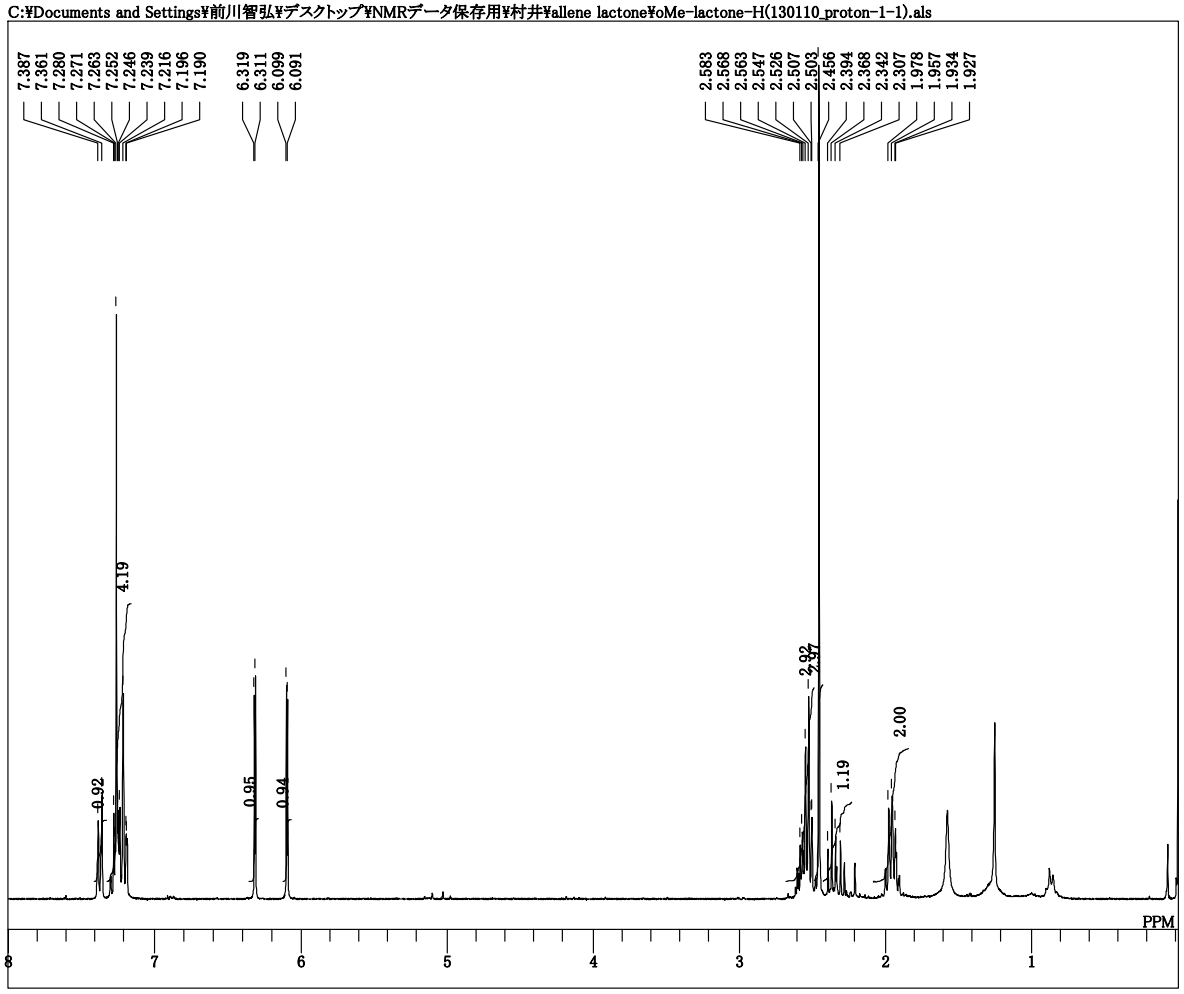


DFILE	mTBSO-lactone-C(130115_Carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	28-02-2014 17:22:16
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	386
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

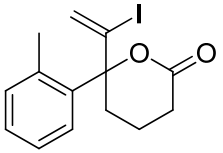


^{1}H NMR chart of **3j**

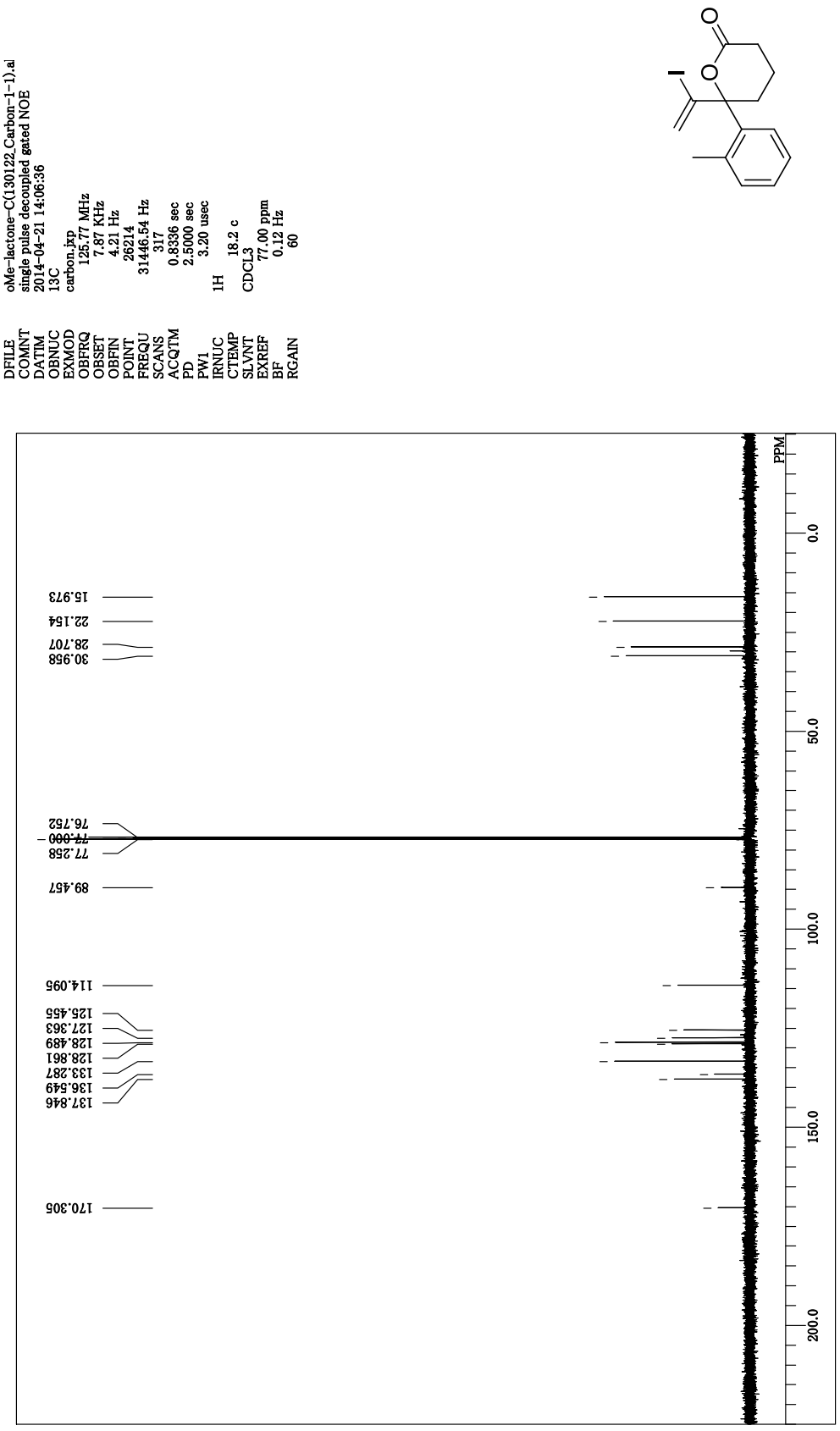
300MHz CDCl3



DFILE	oMe-lactone-H(130110_proton-1-1).al
COMNT	300MHz CDCl3
DATIM	09-04-2014 18:06:07
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4512.64 Hz
SCANS	16
ACQTM	2.9046 sec
PD	2.0000 sec
PW1	6.00 usec
IRNUC	1H
CTEMP	18.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	36



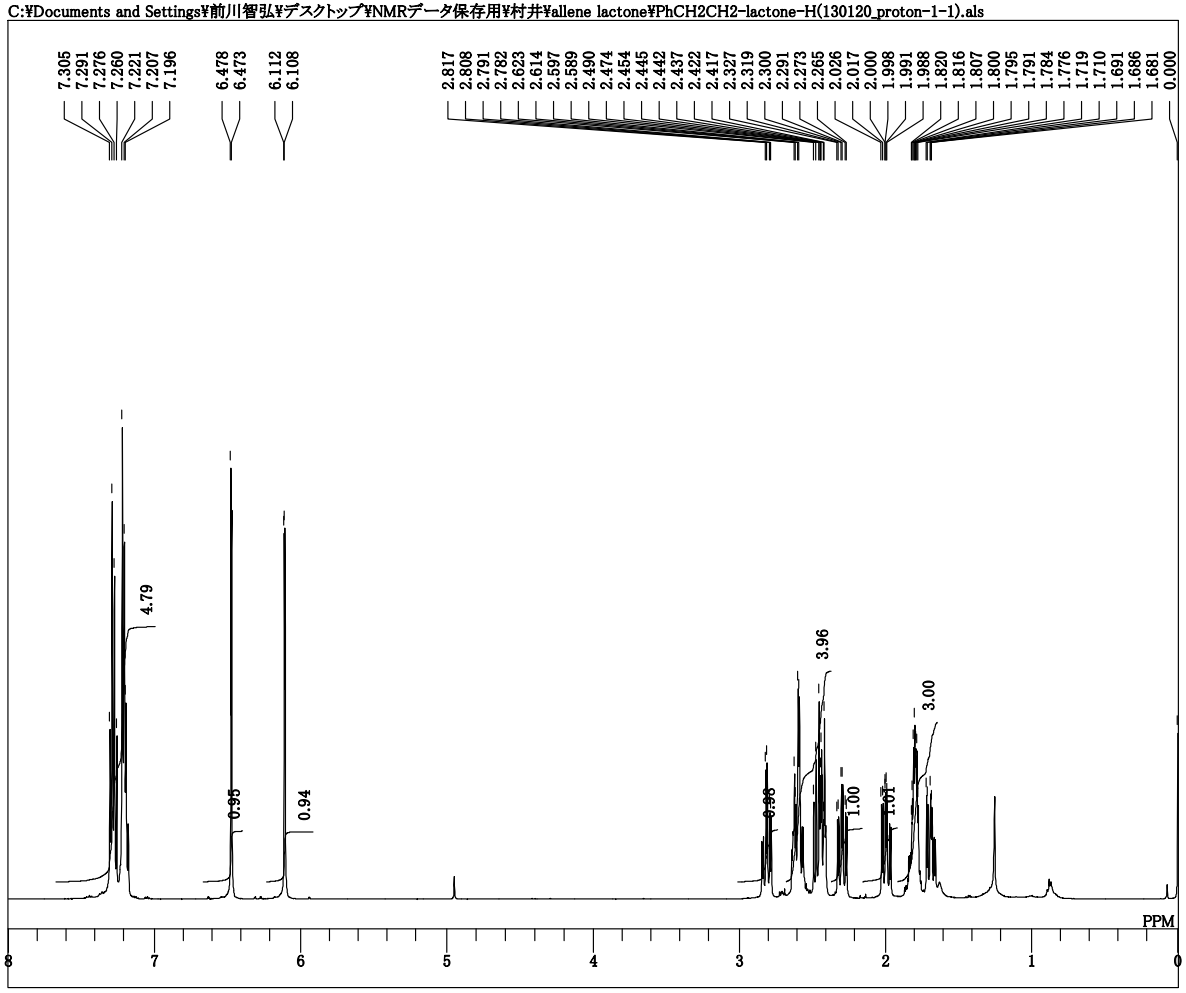
^{13}C NMR chart of **3j**



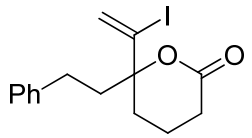
^{1}H NMR chart of **3k**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥PhCH2CH2-lactone-H(130120_proton-1-1).als



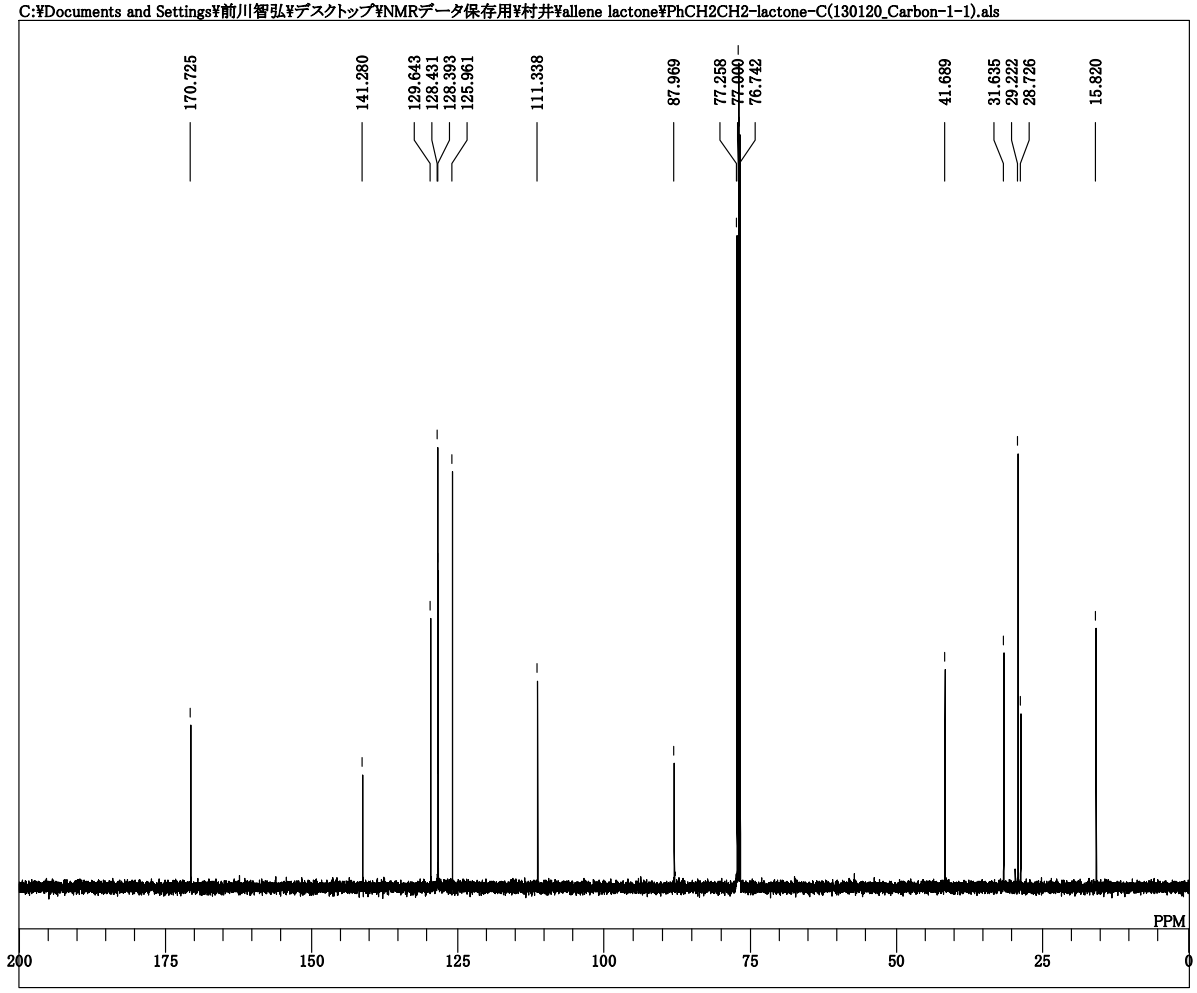
DFILE	PhCH2CH2-lactone-H(130120_proton-
COMNT	single_pulse
DATIM	06-03-2014 17:28:52
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	2.91 KHz
OBFIN	6.17 Hz
POINT	13107
FREQU	8503.40 Hz
SCANS	16
ACQTM	1.5414 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	17.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



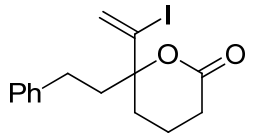
^{13}C NMR chart of **3k**

single pulse decoupled gated NOE

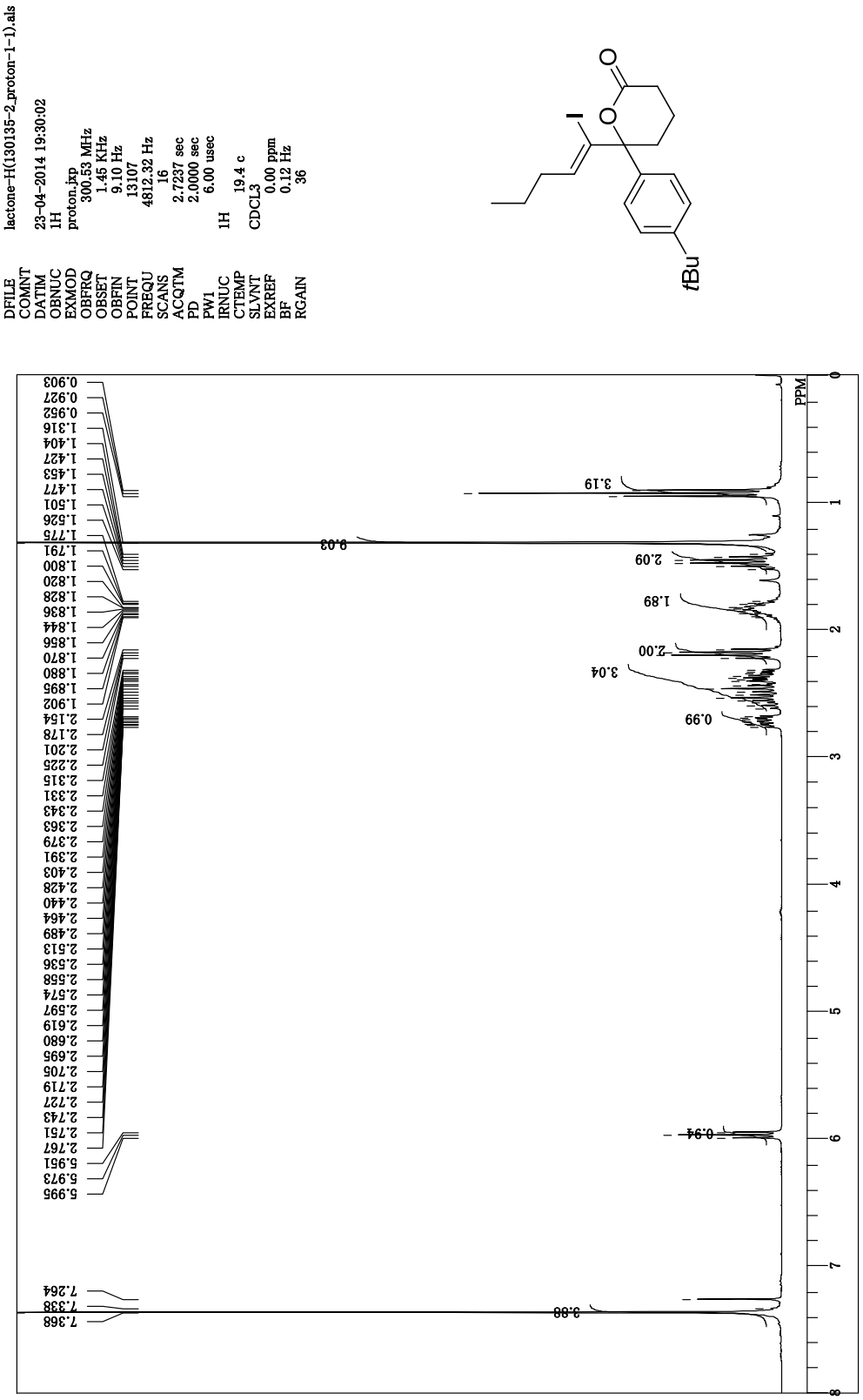
C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥PhCH2CH2-lactone-C(130120_Carbon-1-1).als



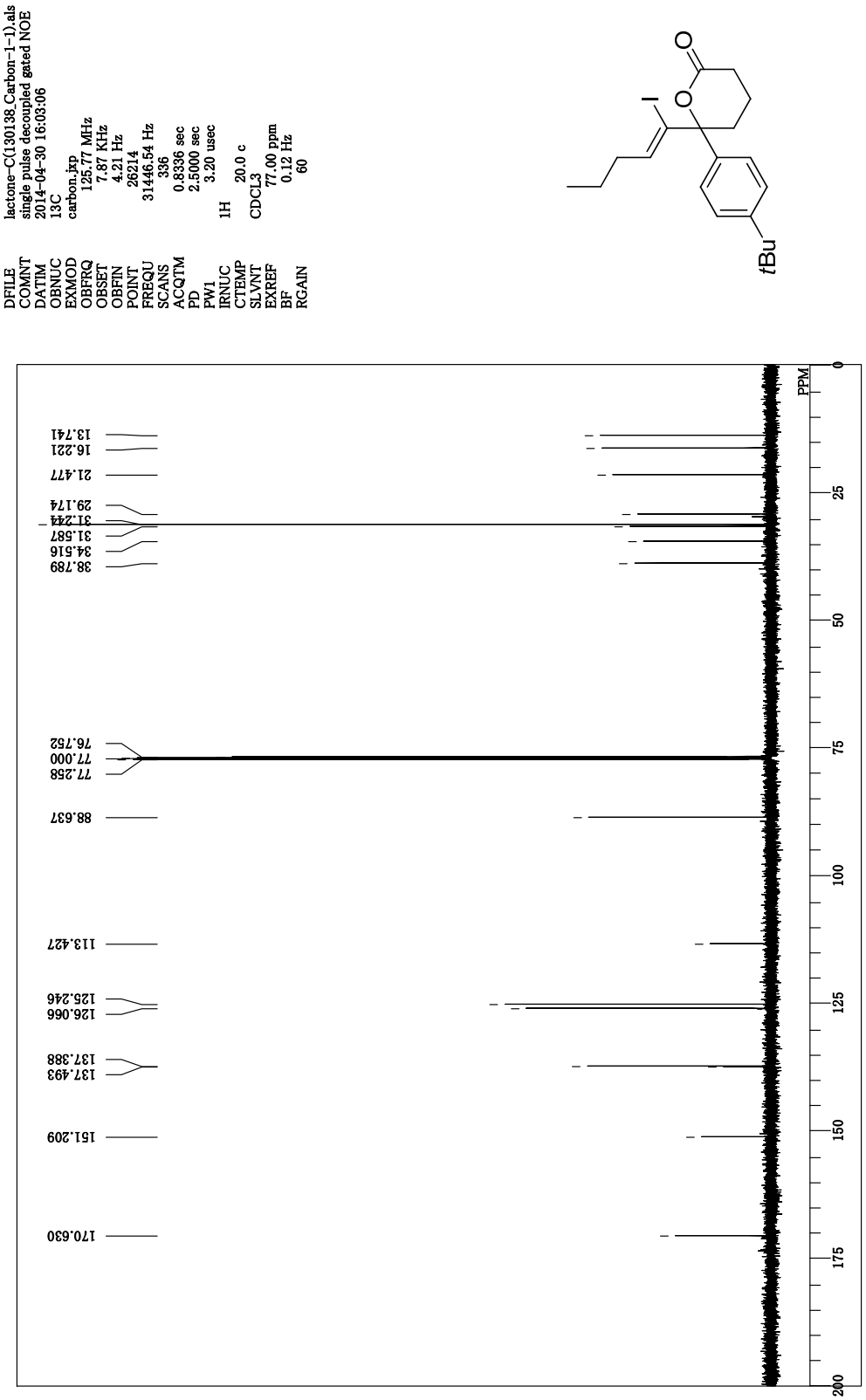
DFILE	PhCH2CH2-lactone-C(130120_Carbon
COMNT	single pulse decoupled gated NOE
DATIM	2014-03-06 17:32:28
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	468
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



^{1}H NMR chart of **3l**

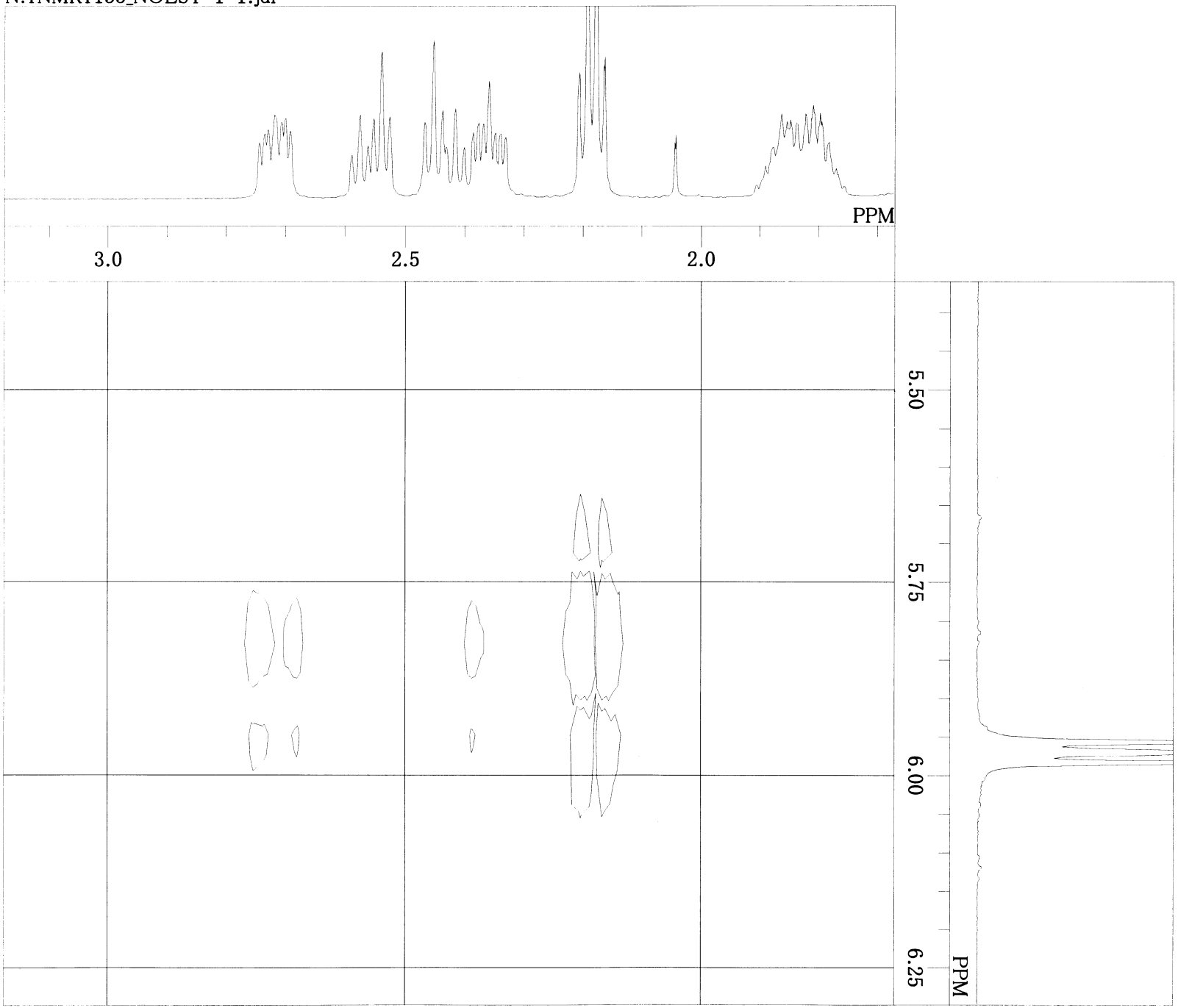


^{13}C NMR chart of **3l**



phase sensitive noesy

N:¥NMR¥135_NOESY-1-1.jdf



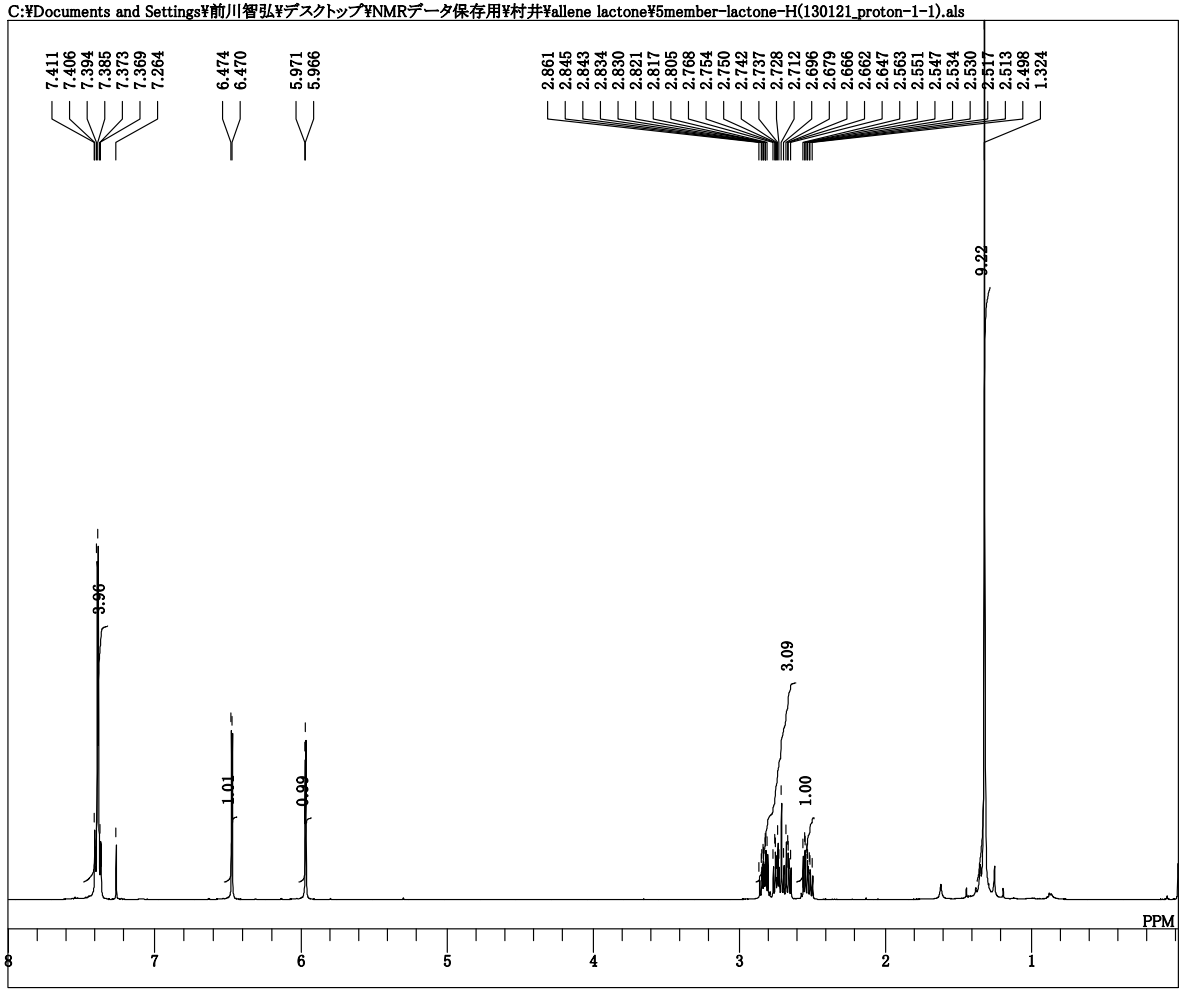
DFILE	135_NOESY-1-1.jdf
COMNT	phase sensitive noesy
DATIM	02-05-2014 01:05:05
EXMOD	noesy.jxp
OBNUC	1H
OBFRQ	500.16 MHz
OBSET	2.41 KHz
OBFIN	6.01 Hz
POINT	1024
FREQU	9384.38 Hz
CLPNT	128
TODAT	128
CLFRQ	7503.00 Hz
SCANS	40
ACQTM	0.1091 sec
PD	1.5000 sec
PW1	11.60 usec
PW2	0.00 usec
PW3	0.00 usec
PI1	0.0000 msec
PI2	0.0000 msec
PI3	0.0000 msec
IRNUC	1H
CTEMP	18.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
CLEXR	0.00
RGAIN	40

part of NOESY data for **3l**

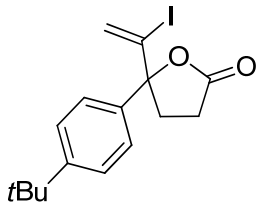
^{1}H NMR chart of **3m**

single_pulse

C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥5member-lactone-H(130121_proton-1-1).als



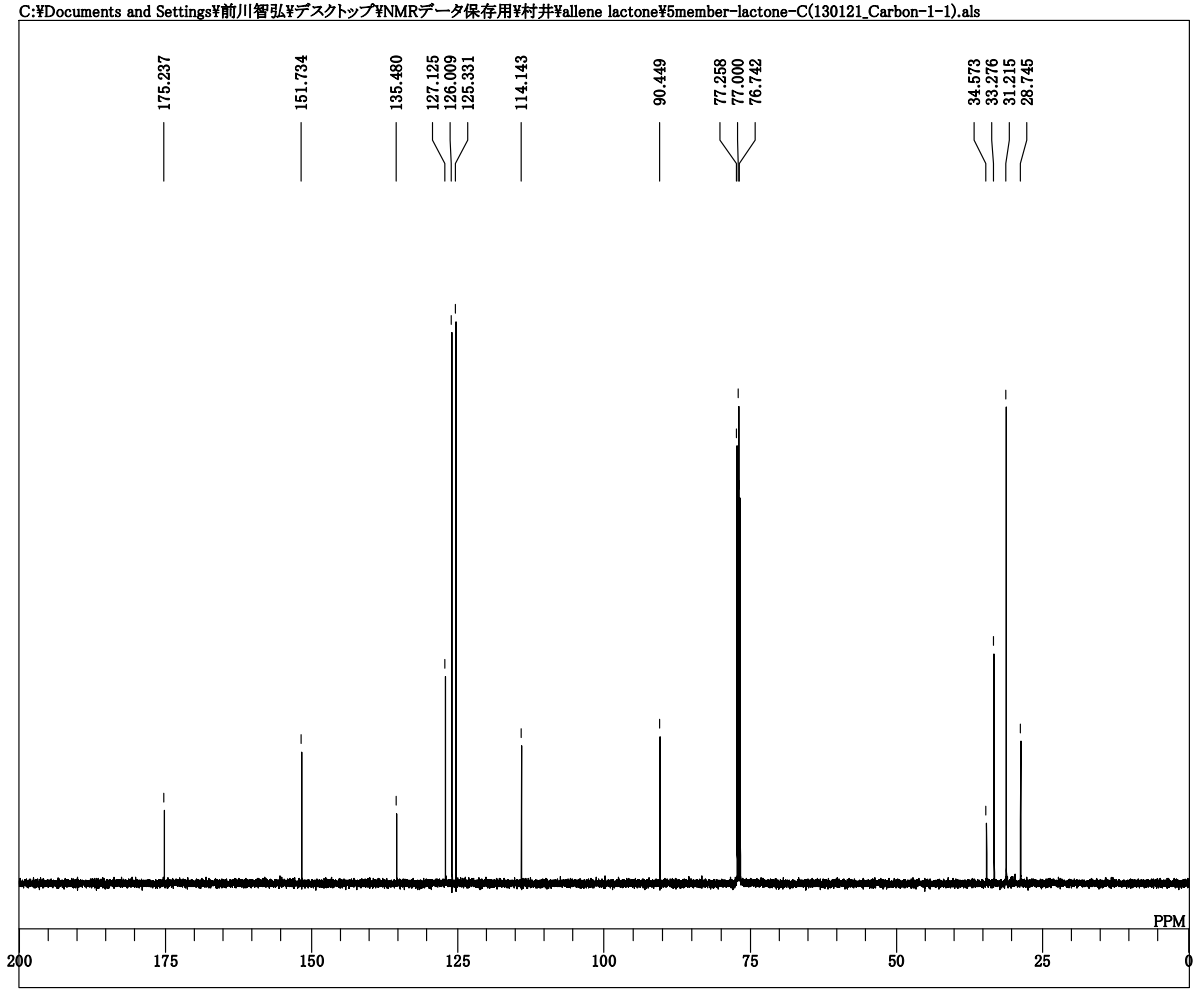
DFILE	5member-lactone-H(130121_proton-1-
COMNT	single_pulse
DATIM	13-03-2014 14:02:12
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	500.16 MHz
OBSET	3.41 KHz
OBFIN	6.33 Hz
POINT	13107
FREQU	8012.82 Hz
SCANS	16
ACQTM	1.6358 sec
PD	2.0000 sec
PW1	5.80 usec
IRNUC	1H
CTEMP	17.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	34



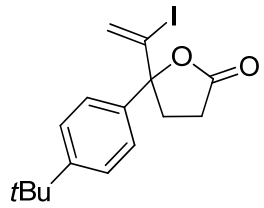
^{13}C NMR chart of **3m**

single pulse decoupled gated NOE

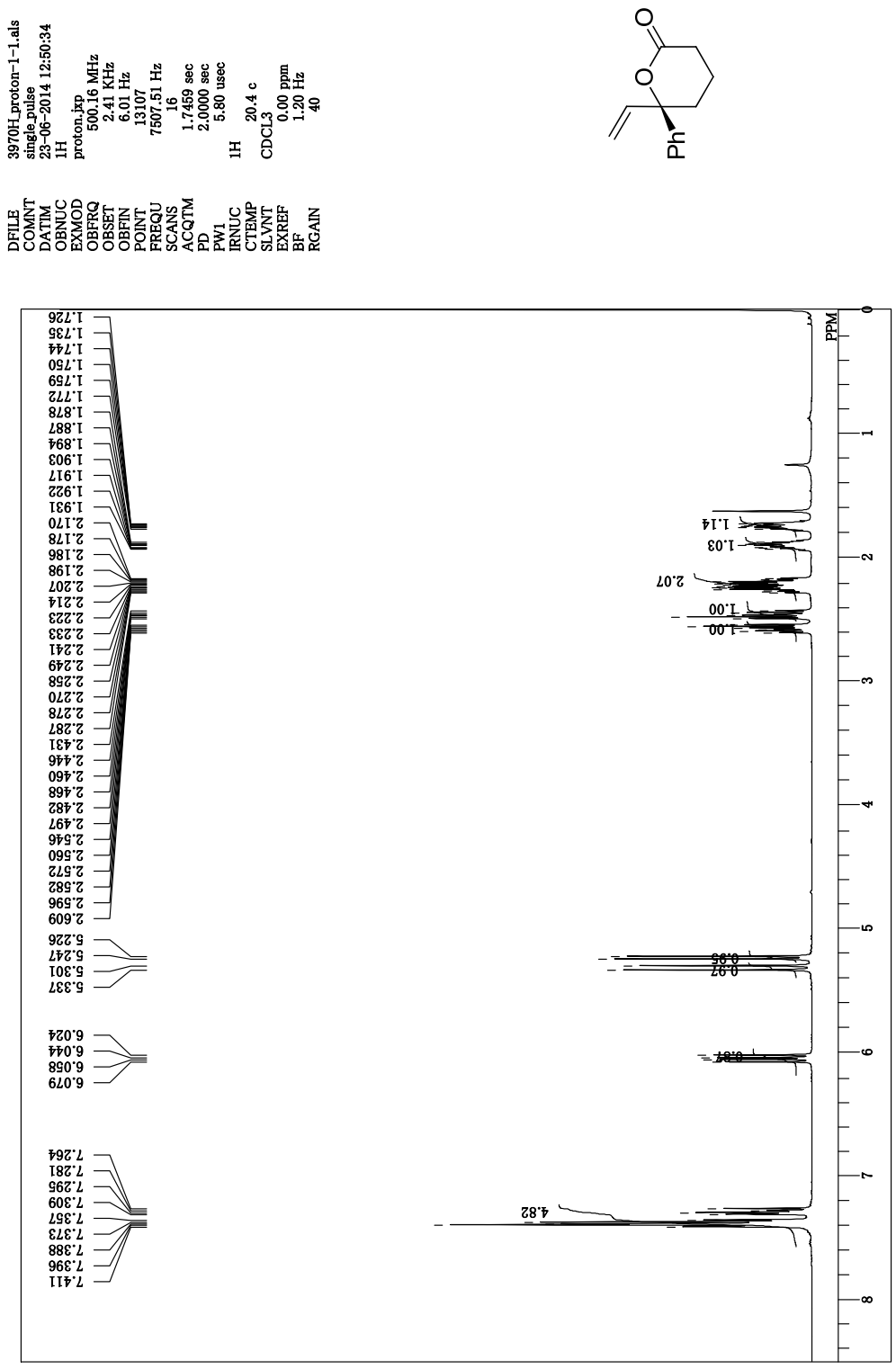
C:¥Documents and Settings¥前川智弘¥デスクトップ¥NMRデータ保存用¥村井¥allene lactone¥5member-lactone-C(130121_Carbon-1-1).als



DFILE	5member-lactone-C(130121_Carbon-1-
COMNT	single pulse decoupled gated NOE
DATIM	2014-03-13 14:05:39
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	379
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.20 usec
IRNUC	1H
CTEMP	17.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60



^{1}H NMR chart of **S1**



^{13}C NMR chart of **S1**