Supporting Information

Niobium(V)-Catalyzed Defluorinative Triallylation of α,α,α–Trifluorotoluene Derivatives by Triple C-F Bond Activation

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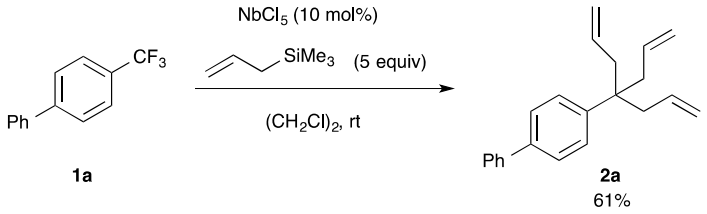
General. NMR spectra were recorded on Unity Inova-400 instrument (Varian Inc., 400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F) or AVANCE III HD Nano Bay (Bruker Co., 400 MHz for ^{1}H, 100 MHz for ^{13}C) using $CDCl_3$ as a solvent. Tetramethylsilane (TMS) ($\delta = 0$) or $CHCl_3$ ($\delta = 7.26$) served as an internal standard for ^{1}H NMR, $CDCl_3$ was used as an internal standard ($\delta = 77.0$) for ^{13}C NMR and hexafluorobenzene (C_6F_6) was used as an external standard ($\delta = -164.9$) for ^{19}F NMR. Melting point (mp) determinations were performed by using AS ONE ATM-01 instrument and are uncorrected. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). EI mass spectra were recorded on JEOL GCmate™ II GC/MS Double-Focusing Mass Spectrometer. ESI mass spectra were recorded on Bruker Daltonics microTOF_15 focus. Elemental analyses were performed by Flash2000 instrument (Amco Inc). Purification of the products was performed by column chromatography on silica gel (Fuji sylisia PSQ-60B) or preparative TLC on silica gel (Wako gel B-5F). All solvents were purified according to the standard procedures.

1. Representative procedure for the defluorinative triallylation of α,α,α–trifluorotoluene derivatives

The preparation of **2a** is described below as a representative procedure. The reaction time and the amount of $NbCl_5$ were optimized for each substrate (See Table 2). The reactions were carried out in 0.16-0.39 mmol scale.



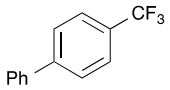
To a dried 20 mL two-necked flask, **1a** (44.8 mg, 0.201 mmol) and 1,2-dichloroethane (0.2 mL) were added. Then, allyltrimethylsilane (0.16 mL, 1.01 mmol) and $NbCl_5$ (5.4 mg, 0.020 mmol) were added in this manner, and the mixture was stirred for 0.5 h at room temperature. The resulting mixture was treated with aqueous 1M HCl and extracted with CH_2Cl_2 three times. The combined organic layer was filtered and concentrated. Purification by preparative TLC (hexane) afforded **2a** in 61% yield (35.6 mg, 0.123 mmol).

2. Preparation and analytical data of substrates and products

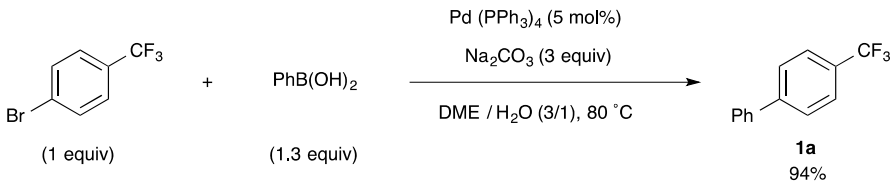
2-1. Substrates

Substrate **1c**, **1i**, **1j** were purchased from Sigma-Aldrich Co. Llc., Tokyo Chemical Industry Co., Ltd. and Wako Pure Chemical Industries Ltd., respectively.

Trifluorotoluene 1a



Trifluorotoluene **1a** was prepared according to the reported procedure.[1]



In a 110 mL test tube, 4-bromobenzotrifluoride (0.50 mL, 3.6 mmol), phenylboronic acid (0.57 g, 4.6 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol), Na_2CO_3 (1.13 g, 10.7 mmol) were dissolved to a mixture of 1,2-dimethoxyethane (9 mL) and water (3 mL). The mixture was stirred at 80 ºC for 13.5 h. After

being cooled to room temperature, the resulting mixture was filtered through Celite with AcOEt, and the filtrate was extracted by AcOEt three times. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded **1a** in 94% yield (0.75 g, 3.4 mmol).

White solid

Mp = 79-80 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.43 (m, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.58-7.62 (m, 2H), 7.70 (s, 4H)

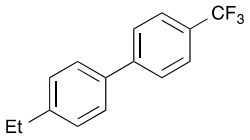
^{13}C NMR (100 MHz, $CDCl_3$) δ 124.3 (q, $J_{C\text{-}F}$ = 273.7 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.5 Hz), 127.3, 127.4, 128.2, 129.0, 129.3 (q, $J_{C\text{-}F}$ = 32.4 Hz), 139.8, 144.7

^{19}F NMR (376 Hz, $CDCl_3$) δ -65.0 (s, 3F)

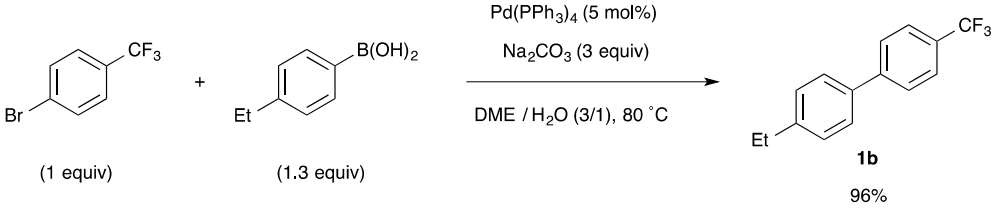
IR (KBr) 3446, 3084, 2359, 1614, 1329, 1169, 1113, 1074, 843, 768, 727, 690 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[2]

Trifluorotoluene 1b



Trifluorotoluene **1b** was prepared according to the reported procedure.[1]



In a 110 mL test tube, 4-bromobenzotrifluoride (0.32 mL, 2.3 mmol), phenylboronic acid (0.44 g, 3.0 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol), Na_2CO_3 (0.73 g, 6.8 mmol) were dissolved to a mixture of 1,2-dimethoxyethane (9 mL) and water (3 mL). The mixture was stirred at 80 ºC for 12 h. After being cooled to room temperature, the resulting mixture was filtered through Celite with AcOEt, and the filtrate was extracted with AcOEt three times. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded **1b** in 96% yield (0.55 g, 2.2 mmol).

White solid

Mp=143-144 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.6 Hz, 3H), 2.71 (q, J = 7.6 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.68 (s, 4H)

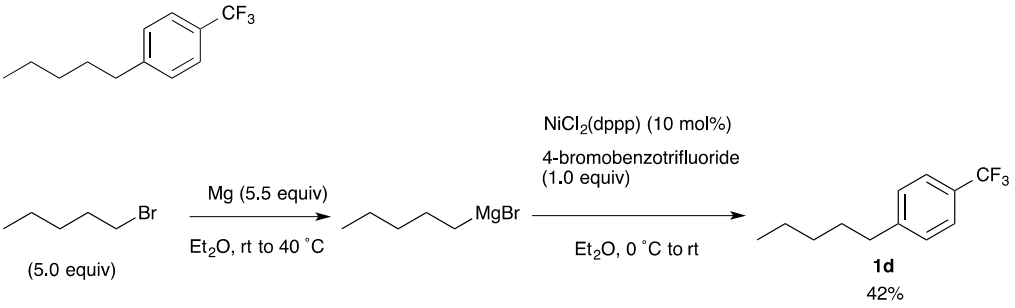
^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 28.5, 124.3 (q, $J_{C\text{-}F}$ = 273.7 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.9, 127.2, 128.5, 129.0 (q, $J_{C\text{-}F}$ = 32.4 Hz), 137.1, 144.5, 144.6

^{19}F NMR (376 Hz, $CDCl_3$) δ -65.0 (s, 3F)

IR (KBr) 3435, 2976, 2937, 2883, 1616, 1398, 1329, 1171, 1126, 1072, 823, 596 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[1]

Trifluorotoluene 1d



To a 30 mL two-neck flask equipped with a dropping funnel, Mg turning (0.12 g, 4.9 mmol) was added and it was heated to dryness *in vacuo*. After cooling, Et_2O (1 mL) and a small piece of iodine were added under nitrogen. Then, Et_2O (3 mL) solution of 1-bromopentane (0.55 mL, 4.5 mmol) was slowly added through a dropping funnel. The mixture was stirred for 12 h at 40 ºC to afford a solution of pentylmagnesium bromide.

To another 30 mL two-neck flask, 4-bromobenzotrifluoride (0.12 mL, 0.89 mmol), $NiCl_2$(dppp) (dppp = 1,2-bis(diphenylphosphino)propane) (48 mg, 0.089 mmol) and Et_2O (3 mL) were added. Pentyl magnesium bromide was added dropwise via cannula and the mixture was stirred for 32 h at room temperature. The resulting mixture was treated with 1M aqueous HCl, and extracted with Et_2O three times. The combined organic layer was filtered through a short pad of Celite on silica gel with AcOEt. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford **1d** in 42% yield (80 mg, 0.37 mmol).

Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85-0.93 (m, 3H), 1.26-1.40 (m, 4H), 1.58-1.67 (m, 2H), 2.65 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H)

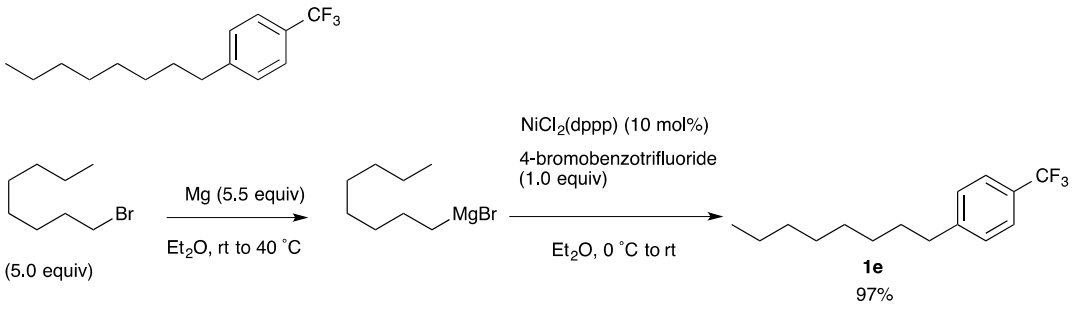
^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.5, 30.9, 31.4, 35.8, 124.5 (q, $J_{C\text{-}F}$ = 272.9 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.6 Hz), 128.0 (q, $J_{C\text{-}F}$ = 31.2 Hz), 128.7, 147.0

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F)

IR (neat) 2960, 2933, 2860, 1618, 1466, 1417, 1327, 1165, 1126, 1068, 1018, 843 cm^{-1}

HRMS (EI) m/z calcd for $C_{12}H_{15}F_3$ $(M)^+$ 216.1120, found 216.1126.

Trifluorotoluene 1e



To a 30 mL two-neck flask equipped with a dropping funnel, Mg turning (0.44 g, 18 mmol) was added and it was heated to dryness *in vacuo*. After cooling, Et_2O (3 mL) and a small piece of iodine were added under nitrogen. Then, Et_2O (11 mL) solution of 1-bromooctane (2.9 mL, 17 mmol) was slowly added through a dropping funnel. The mixture was stirred for 5 h at 40 ºC to afford a solution of octylmagnesium bromide.

To a dried 100 mL two-neck flask, 4-bromobenzotrifluoride (0.47 mL, 3.3 mmol), $NiCl_2$(dppp) (0.18 g, 0.33 mmol) and Et_2O (5 mL) were added. Octylmagnesium bromide was added dropwise via cannula at 0 ºC, and the mixture was stirred for 13 h at room temperature. The resulting mixture was treated with 1M aqueous HCl, and extracted with CH_2Cl_2 three times. The combined organic layer was filtered through a pad of Celite on silica gel with CH_2Cl_2. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford **1e** in 97% yield (0.839 g, 0.325 mmol).

Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.20-1.38 (m, 10H), 1.57-1.67 (m, 2H), 2.65 (t, J = 8.0 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 29.2, 29.4, 29.7, 31.2, 31.9, 35.8, 124.4 (q, $J_{C\text{-}F}$ = 272.9 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 127.9 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.7, 147.0

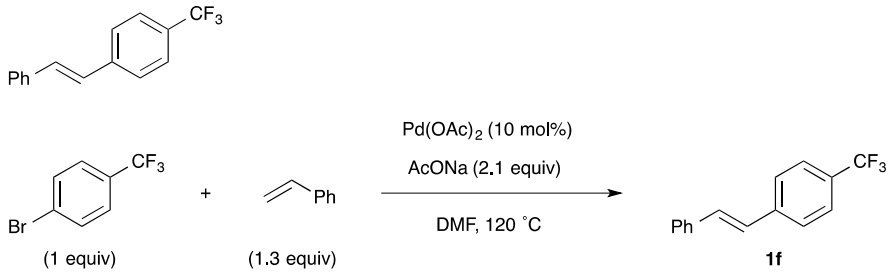
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, 3F)

IR (neat) 2956, 2925, 2856, 2360, 1618, 1466, 1327, 1165, 1126, 1068, 1018, 843 cm^{-1}

HRMS (EI) m/z calcd for $C_{15}H_{21}F_3$ $(M)^+$ 258.1587, found 258.1595.

The analytical data were in accordance with those reported in the literature.[3]

Trifluorotoluene 1f



To a dried 110 mL test tube, 4-bromobenzotrifluoride (0.62 mL, 4.4 mmol), styrene (0.60 g, 5.8 mmol), $Pd(OAc)_2$ (0.10 g, 0.44 mmol) and DMF (5 mL) were added, and the mixture was stirred at 120 ºC for 8 h. The resulting mixture was filtered through a short pad of Celite on silica gel with AcOEt. After removal of the solvent, the crude mixture was purified by silica gel column chromatography (hexane) to afford **1f** in 33% yield (0.37 g, 1.5 mmol).

White solid

Mp = 169-170 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 16.2 Hz, 1H), 7.20 (d, J = 16.2 Hz, 1H), 7.28-7.33 (m, 1H), 7.36-7.41 (m, 2H), 7.51-7.56 (m, 2H), 7.61 (s, 4H)

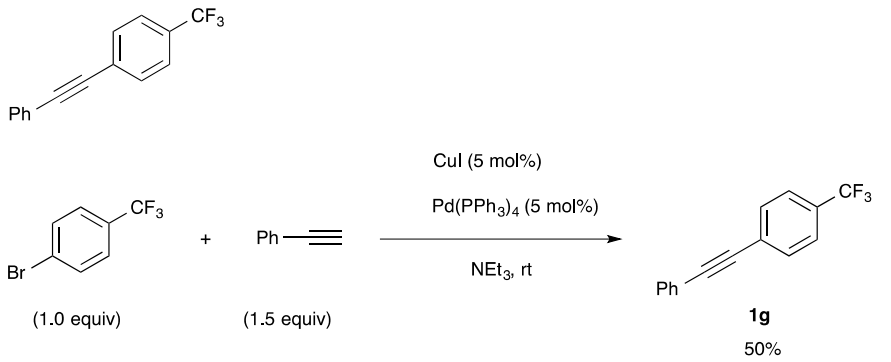
^{13}C NMR (100 MHz, $CDCl_3$) δ 124.2 (q, $J_{C\text{-}F}$ = 280.8 Hz), 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 126.6, 126.8, 127.1, 128.3, 128.8, 129.3 (q, $J_{C\text{-}F}$ = 32.6 Hz), 131,2, 136.6, 140.8

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0 (s, 3F)

IR (KBr) 3446, 3028, 2360, 1612, 1325, 1167, 1155, 1111, 1068, 827, 758, 694 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[4]

Trifluorotoluene 1g



To a dried 30mL two-necked flask, CuCl (21 mg, 0.11 mmol), $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol),

4-bromobenzotrifluoride (0.31 mL, 2.2 mmol) and NEt_3 (7.4 mL) were added. Then, phenylacetylene (0.37 mL, 3.3 mmol) was added to the mixture and it was stirred for 20.5 h at room temperature. The resulting mixture was filtered through Celite with CH_2Cl_2 and concentrated. Purification by silica gel column chromatography (hexane) afforded **1g** in 50% yield (0.28 g, 1.1 mmol).

White solid

Mp = 129-130˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.40 (m, 3H), 7.53-7.58 (m, 2H), 7.59-7.66 (m, 4H)

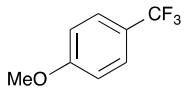
^{13}C NMR (100 MHz, $CDCl_3$) δ 88.0, 91.8, 122.6, 123.9 (q, J_{C-F} = 273.0 Hz), 125.3 (q, J_{C-F} = 3.7 Hz), 127.1 (d, J_{C-F} = 1.2 Hz), 128.5, 128.9, 129.9 (q, J_{C-F} = 32.8 Hz), 131.8, 131.8

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.4 (s, 3F)

IR (KBr) 3444, 2220, 1608, 1325, 1167, 1155, 1105, 1066, 1018, 843, 760, 690 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[5]

Trifluorotoluene 1h



1h was prepared according to the reported procedure.[6,7]

Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.96 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H)

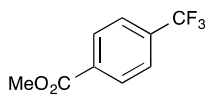
^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 113.9, 122.8 (q, J_{C-F} = 32.7 Hz), 124.5 (q, J_{C-F} = 272.4 Hz), 126.9 (q, J_{C-F} = 3.8 Hz), 162.0

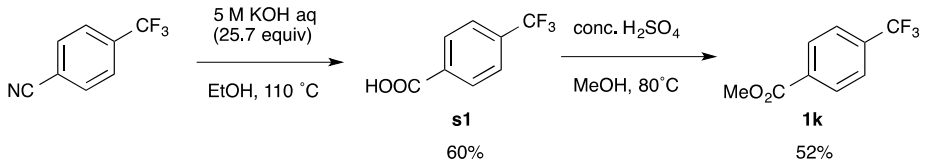
^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1 (s, 3F)

IR (neat) 2844, 2362, 1618, 1522, 1331, 1261, 1180, 1163, 1109, 1068, 1032, 837 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[6]

Trifluorotoluene **1k**

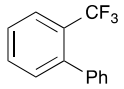




To a 100 mL two-necked flask, 4-(trifluoromethyl)benzonitrile (0.765 g, 4.47 mmol), ethanol (23 mL) and aqueous 5M KOH (23 mL) were added. After the mixture was stirred at 110 ºC for 16 h, it was cooled to room temperature and acidified by aqueous 6 M HCl. The mixture was extracted with CH_2Cl_2 3 times and the combined organic layer was dried over $MgSO_4$, filtered and concentrated. Recrystallization from hexane/AcOEt afforded carboxylic acid **s1** in 60% yield (508 mg, 2.67 mmol).

To a dried 30 mL two-neck flask, carboxylic acid **s1** (0.400 g, 2.10 mmol), methanol (12 mL), conc. sulfuric acid (1.2 mL) were added, and the mixture was stirred at 80 ºC for 22 h. The resulting mixture was cooled to 0 ºC and diluted with water, then the most part of organic solvent was removed *in vacuo*. After the addition of AcOEt, the mixture was extracted with AcOEt twice and the combined organic layer was concentrated. Purification by silica gel column chromatography (hexane : AcOEt = 5 : 1) afforded **1k** in 52% yield (0.222 g, 1.09 mmol).

Trifluorotoluene 3b



3b was prepared according to the reported procedure.[8]

Colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.36 (m, 3H), 7.37-7.42 (m, 3H), 7.46 (dd, J = 7.6, 7.8 Hz, 1H), 7.56 (dd, J = 7.6, 7.6 Hz, 1H), 7.75 (d, J = 7.6 Hz, 1H)

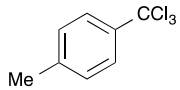
^{13}C NMR (100 MHz, $CDCl_3$) δ 124.1 (q, $J_{C\text{-}F}$ = 275.2 Hz), 126.0 (q, $J_{C\text{-}F}$ = 5.4 Hz), 127.3, 127.6, 127.7, 128.4 (q, $J_{C\text{-}F}$ = 29.9 Hz), 128.9 (d, $J_{C\text{-}F}$ = 1.5 Hz), 131.2, 132.0, 139.8, 141.4

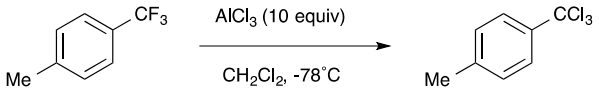
^{19}F NMR (376 MHz, $CDCl_3$) δ -59.5 (s, 3F)

IR (neat) 3066, 1483, 1315, 1261, 1173, 1128, 1110, 1072, 1036, 768, 748, 702 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[8]

Trichlorotoluene 6





6

96%

To a dried 30 mL two-necked flask, $AlCl_3$ (832 mg, 8.17 mmol) and CH_2Cl_2 were added. CH_2Cl_2 (3 mL) solution of 4-methylbenzotrifluoride (0.114 mL, 0.817 mmol) was added at –78 ºC, and the mixture was stirred overnight. The resulting mixture was treated with 1 M aqueous HCl and extracted with CH_2Cl_2 three times. The organic layer was filtered through Celite with CH_2Cl_2, and the filtrate was concentrated to afford analytically pure **6** in 96% yield (0.164 g, 0.781 mmol).

Brown solid

Mp = 54-55 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.23 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 97.9, 125.5, 129.0, 140.7, 141.7

IR (KBr) 2925, 1914, 1715, 1506, 1276, 1179, 1017, 874, 804, 742, 695, 514 cm^{-1}

HRMS (EI) m/z calcd for $C_8H_7Cl_3$ $(M)^+$ 207.9610, found 207.9614.

Monofluorotoluene 7

s2 95%

7 36%

To a dried 100 mL two-necked flask, 4-phenylbenzaldehyde (0.500 g, 2.74 mmol) and methanol (15 mL) were added. $NaBH_4$ (0.125 g, 3.29 mmol) was added in one portion at 0 ºC, and the mixture was stirred at room temperature for 15.5 h. The resulting mixture was cooled to 0 ºC and diluted with water, then the most part of organic solvent was removed *in vacuo*. the mixture was extracted with AcOEt three times. Concentration of the combined organic layer afforded alcohol **s2** in 95% yield (478 mg, 2.59 mmol). This material was used in the next step without further purification.

To a dried 100 mL one-necked flask, alcohol **s2** (0.477 g, 2.59 mmol), CH_2Cl_2 (12 mL), and (*N*,*N*-diethylamino)sulfur trifluoride (DAST) (1.2 mL, 9.1 mmol) were added. The mixture was stirred for 24 h at room temperature. The resulting mixture was treated with ice and stirred at room temperature. The organic layer was extracted with CH_2Cl_2 three times and concentrated. Purification by silica gel column chromatography (hexane : AcOEt = 5 : 1) and further purification by

preparative TLC (hexane : AcOEt = 5 : 1) afforded **7** in 36% yield (0.173 g, 0.931 mmol).

White solid

Mp = 84-85 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (d, $J_{H\text{-}F}$ = 48.1 Hz, 2H), 7.34-7.39 (m, 1H), 7.42-7.49 (m, 4H), 7.57-7.65 (m, 4H)

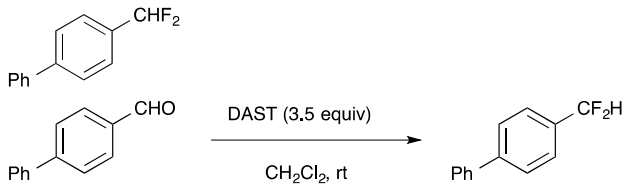
^{13}C NMR (100 MHz, $CDCl_3$) δ 84.3 (d, $J_{C\text{-}F}$ = 165.5 Hz), 127.1, 127.4, 127.5, 128.0 (d, $J_{C\text{-}F}$ = 5.4 Hz), 128.8, 135.1 (d, $J_{C\text{-}F}$ = 16.9 Hz), 140.6, 141.7 (d, $J_{C\text{-}F}$ = 3.0 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ -208.8 (t, $J_{F\text{-}H}$ = 48.1 Hz, 1F)

IR (KBr) 3438, 2962, 1614, 1487, 1408, 1225, 968, 849, 822, 762, 733, 696 cm^{-1}.

The analytical data were in accordance with those reported in the literature.[9]

Difluorotoluene 8



8

79%

To a dried 30 mL two-necked flask, 4-phenylbenzaldehyde (0.500 g, 2.24 mmol), CH_2Cl_2 (12 mL), and (*N*,*N*-diethylamino)sulfur trifluoride (DAST) (1.3 mL, 9.6 mmol) were added. The mixture was stirred for 20.5 h at room temperature. The resulting mixture was treated with water at 0 ºC, and was extracted with CH_2Cl_2 three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. Purification by silica gel column chromatography (hexane) afforded **8** in 79% yield (0.442 g, 2.16 mmol).

White solid

Mp= 88-89 ˚C

^{1}H NMR (400 MHz, $CDCl_3$) 6.70 (t, $J_{H\text{-}F}$ = 56.0 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.57-7.62 (m, 4H), 7.68 (d, J = 8.0 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 114.7 (t, $J_{C\text{-}F}$ = 237.2 Hz), 126.0 (t, $J_{C\text{-}F}$ = 6.1 Hz), 127.2, 127.4, 127.9, 128.9, 133.2 (t, $J_{C\text{-}F}$ = 22.3 Hz), 140.2, 143.7

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9 (d, $J_{F\text{-}H}$ = 56.0 Hz, 2F)

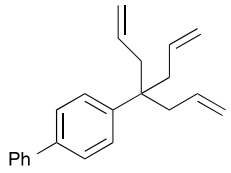
IR(KBr) 3440, 2970, 2359, 1925, 1614, 1381, 1227, 1078, 1022, 839, 766, 690 cm^{-1}

HRMS (EI) m/z calcd for $C_{13}H_{10}F_2$ $(M)^+$ 204.0769, found 204.0751.

The analytical data were in accordance with those reported in the literature.[10]

2-2. Products

Product 2a



35.6 mg, 61% from 0.201 mmol **1a**, colorless oil

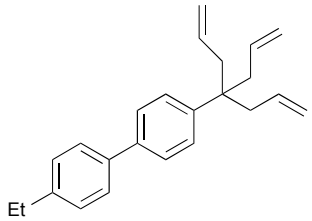
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (d, *J* = 7.2 Hz, 6H), 5.02-5.12 (m, 6H), 5.63 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 3H), 7.32-7.37 (m, 1H), 7.39-7.48 (m, 4H), 7.57-7.66 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.9, 43.2, 117.7, 126.6, 126.9, 127.1, 127.1, 128.7, 134.5, 138.3, 140.8, 144.9

IR (neat) 3074, 2978, 2925, 1638, 1487, 1447, 997, 913, 835, 768, 737, 696 cm^{-1}

HRMS (EI) m/z calcd for $C_{22}H_{24}$ $(M)^+$ 288.1886, found 288.1878.

Product 2b



45.5 mg, 78% from 0.184 mmol **1b**, colorless oil

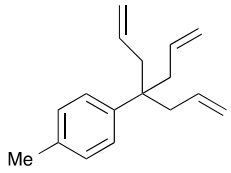
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.6 Hz, 3H), 2.51 (d, *J* = 7.1 Hz, 6H), 2.71 (q, *J* = 7.6 Hz, 2H), 5.01-5.10 (m, 6H), 5.63 (ddt, *J* = 17.2, 10.4 Hz, 7.1 Hz, 3H), 7.26-7.30 (m, 2H), 7.36-7.40 (m, 2H), 7.51-7.59 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 28.5, 41.9, 43.1, 117.6, 126.4, 126.8, 127.0, 128.2, 134.5, 138.1, 138.3, 143.1, 144.5

IR (neat) 3074, 2965, 2928, 1638, 1497, 1449, 1331, 1119, 1003, 913, 820, 626 cm^{-1}

HRMS (EI) m/z calcd for $C_{24}H_{28}$ $(M)^+$ 317.2183, found 317.2191.

Product 2c



47.8 mg, 71% from 0.296 mmol **1c**, 7.9 mg, 21% from 0.20 mmol **6**, colorless oil

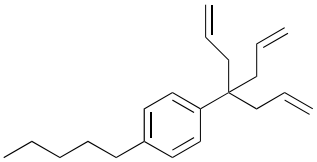
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.47 (d, *J* = 7.2 Hz, 6H), 4.98-5.08 (m, 6H), 5.59 (ddt, *J*= 17.2, 10.0 Hz, 7.2 Hz, 3H), 7.12-7.17 (m, 2H), 7.19-7.25 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 41.9, 42.9, 117.5, 126.5, 128.7, 134.7, 135.1 142.6

IR (neat) 3074, 3008, 2978, 2923, 1638, 1515, 1448, 1248, 998, 912, 816, 731 cm^{-1}

HRMS (EI) m/z calcd for $C_{17}H_{22}$ $(M)^+$ 226.1723, found 226.1722.

Product 2d



33.0 mg, 71% from 0.164 mmol **1d**, colorless oil

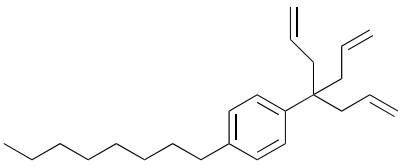
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.26-1.40 (m, 4H), 1.56-1.66 (m, 2H), 2.44 (d, *J* = 6.8 Hz, 6H), 2.57 (t, *J* = 7.5 Hz, 2H), 4.96-5.06 (m, 6H), 5.56 (ddt, *J* =16.0, 10.0 Hz, 7.5 Hz, 3H), 6.99-7.14 (m, 2H), 7.18-7.23 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 31.0, 31.6, 35.4, 41.9, 42.9, 117.4, 126.5, 128.0, 134.7, 140.1, 142.8

IR (neat) 3075, 3005, 2956, 2927, 2857, 1638, 1515, 1448, 1415, 998, 912, 835 cm^{-1}

HRMS (ESI) m/z calcd for $C_{21}H_{30}(M+Na)^+$ 305.2240, found 305.2259.

Product 2e



28.2 mg, 53%, from 0.164 mmol **1e**, colorless oil

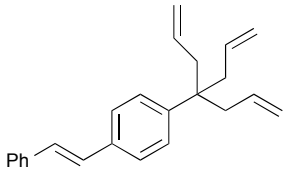
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.20-1.38 (m, 10H), 1.55-1.65 (m, 2H), 2.44 (d, *J* = 7.2 Hz, 6H), 2.57 (t, *J* = 7.8 Hz, 2H), 4.95-5.05 (m, 6H), 5.56 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 3H) 7.12 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 29.3, 29.4, 29.5, 31.3, 31.9, 35.4, 41.9, 42.9, 117.4, 126.5, 128.0, 134.7, 140.2, 142.8

IR (neat) 3583, 3075, 2925, 2854, 1638, 1515, 1449, 1326, 1126, 998, 912, 836 cm^{-1}

Anal. Calcd for $C_{24}H_{36}$: C, 88.82; H, 11.18; Found C, 88.76; H, 11.26.

Product 2f



20.9 mg, 35%, from 0.191 mmol **1f**, colorless oil

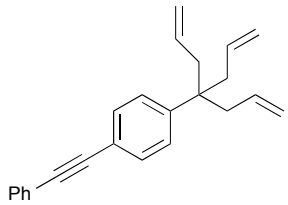
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (d, *J* = 7.2 Hz, 6H), 4.98-5.07 (m, 6H), 5.58 (ddt, *J* = 16.8, 10.2, 7.2 Hz, 3H), 7.10 (s, 2H), 7.23-7.28 (m, 1H), 7.28-7.39 (m, 4H), 7.45-7.53 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.8, 43.4, 117.7, 126.2, 126.5, 127.1, 127.5, 128.2, 128.4, 128.7, 134.5, 134.8, 137.5, 145.4

IR (neat) 3074, 3026, 2926, 1638, 1514, 1448, 998, 962, 913, 817, 756, 691 cm^{-1}

HRMS (EI) m/z calcd for $C_{24}H_{26}(M)^+$ 314.2037, found 314.2035.

Product 2g



18.9 mg, 42% from 0.182 mmol **1g**, colorless oil

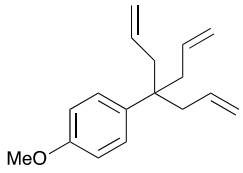
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (d, *J* = 7.3 Hz, 6H), 4.99-5.06 (m, 6H), 5.56 (ddt, *J* = 16.8, 10.4, 7.3 Hz, 3H), 7.27-7.38 (m, 5H), 7.47-7.56 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.7, 43.5, 89.1, 89.3, 117.9, 120.5, 123.4, 126.8, 128.1, 128.3, 131.3, 131.6, 134.2, 146.3

IR (neat) 3074, 2978, 2925, 1638, 1515, 1443, 1415, 997, 913, 832, 755, 689 cm^{-1}

HRMS (EI) m/z calcd for $C_{24}H_{24}(M)^+$ 312.1894, found 312.1878.

Product 2h



30 mg, 44%, from 0.281 mmol **1h**, colorless oil

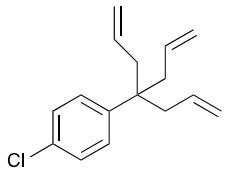
^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (d, *J* = 7.2 Hz, 6H), 3.80 (s, 3H), 4.97-5.05 (m, 6H), 5.56 (ddt, *J* = 17.2, 10.0, 7.2 Hz, 3H), 6.80-6.89 (m, 2H), 7.20-7.25 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.9, 42.7, 55.1, 113.3, 117.4, 127.6, 134.6, 137.7, 157.4

IR (neat) 3074, 2978, 2926, 1638, 1515, 1442, 1250, 1186, 1038, 999, 912, 828 cm^{-1}

HRMS (ESI) m/z calcd for $C_{17}H_{22}O$ $(M+Na)^+$ 265.1563, found 265.1542.

Product 2i



15.8 mg, 34% from 0.276 mmol **1i**, colorless oil

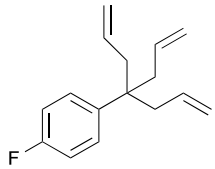
^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (d, *J* = 7.6 Hz, 6H), 4.97-5.05 (m, 6H), 5.48-5.60 (m, 3H), 7.21-7.31 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 41.7, 43.2, 118.0, 128.1, 128.2, 131.5, 134.0, 144.3

IR (neat) 3075, 2979, 2925, 1638, 1496, 1449, 1096, 1012, 997, 914, 824, 622 cm^{-1}

HRMS (EI) m/z calcd for $C_{16}H_{19}Cl$ $(M)^+$ 246.1183, found 246.1175.

Product 2j



36.1 mg, 40% from 0.39 mmol **1j**, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (d, J = 7.2 Hz, 6H), 4.97-5.04 (m, 6H), 5.49-5.60 (m, 3H), 6.97-7.03 (m, 2H), 7.23-7.30 (m, 2H)

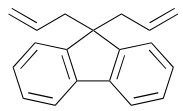
^{13}C NMR (100 MHz, $CDCl_3$) δ 41.9, 43.0, 114.7 (d, $J_{C\text{-}F}$ = 21.2 Hz), 117.8, 128.2 (d, $J_{C\text{-}F}$ = 7.1 Hz), 134.2, 141.3 (d, $J_{C\text{-}F}$ = 3.0 Hz), 160.9 (d, $J_{C\text{-}F}$ = 242.0 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ -120.5 (s, 1F)

IR (neat) 3076, 2979, 2926, 1638, 1603, 1512, 1449, 1235, 1165, 998, 914, 831 cm^{-1}

Anal. Calcd for $C_{16}H_{19}F$: C, 83.44; H, 8.32; Found C, 83.28; H, 8.46.

Product 5



20.3 mg, 40% 0.206 mmol from **3b**, colorless oil

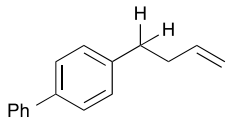
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70 (d, J = 7.2 Hz, 4H), 4.74 (d, J = 10.0 Hz, 2H), 4.82 (d, J = 17.2 Hz, 2H), 5.19-5.31 (m, 2H), 7.25-7.36 (m, 4H), 7.40 (d, J = 6.8 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 43.5, 54.1, 117.5, 119.7, 123.6, 126.9, 127.1, 133.7, 140.7, 149.3

IR (neat) 3072, 3013, 2978, 2920, 2342, 1637, 1475, 1447, 1221, 994, 915, 736 cm^{-1}

HRMS (ESI) m/z calcd for $C_{19}H_{18}(M+Na)^+$ 269.1301, found 269.1298.

Product 9



21.9 mg, 48% from 0.217 mmol **7**, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37-2.45 (m, 2H), 2.75 (t, J = 7.8 Hz, 2H), 4.97-5.11 (m, 2H), 5.89 (ddt, J

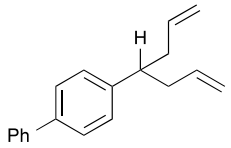
= 17.2, 10.4, 6.6 Hz, 1H), 7.26-7.29 (m, 2H), 7.29-7.35 (m, 1H), 7.38-7.45 (m, 2H), 7.48-7.54 (m, 2H), 7.55-7.60 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 35.0, 35.4, 115.0, 126.4, 126.8, 127.2, 128.5, 128.6, 129.0, 138.2, 138.8, 141.0

IR (neat) 3077, 3028, 2925, 2853, 1639, 1487, 1449, 1408, 911, 837, 761, 697 cm^{-1}

HRMS (EI) m/z calcd for $C_{16}H_{16}(M)^+$ 208.1255, found 208.1252.

Product 10



16.3 mg, 33%, from 0.199 mmol **8**, colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34-2.49 (m, 4H), 2.72-2.80 (m, 1H), 4.93-5.03 (m, 4H), 5.70 (ddt, *J* = 16.8 Hz, 10.2 Hz, 7.0 Hz, 2H), 7.20-7.25 (m, 2H), 7.29-7.34 (m, 1H), 7.39-7.45 (m, 2H), 7.50-7.55 (m, 2H), 7.57-7.61 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 45.2, 116.1, 126.9, 126.9, 127.0, 128.1, 128.7, 136.7, 138.9, 141.0, 143.8

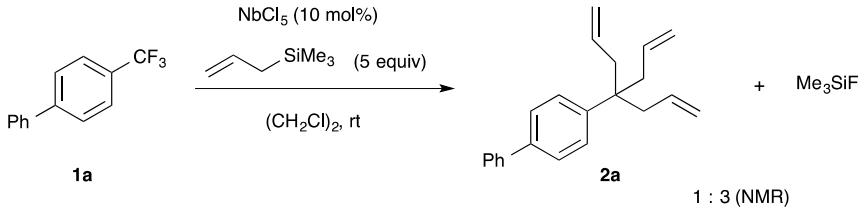
IR (neat) 3075, 3028, 2977, 2921, 1639, 1486, 994, 912, 834, 765, 734, 697 cm^{-1}

HRMS (EI) m/z calcd for $C_{19}H_{20}$ $(M)^+$ 248.1572, found 248.1565.

3. Appendix

2-1. Detection and Quantification of Me_3SiF (Scheme 5)

Detection and quantification of Me_3SiF were carried out by ^1H and ^{19}F NMR analyses of the reaction mixture.



In a dried 1.5 mL glass tube, trifluorotoluene **1a** (44.4 mg, 0.200 mmol) was dissolved to dichloroethane (0.2 mL). Subsequently, allyltrimethylsilane (0.16 mL, 1.0 mmol) and $NbCl_5$ (5.4 mg, 0.020 mmol) were added in this manner. After the mixture was stirred for 30 minutes at room temperature, it was diluted with $CDCl_3$ at 0 ºC (to prevent volatile compounds from evaporation) and rapidly transferred into NMR sample tube. The sample was analyzed by ^1H NMR, and then by ^{19}F NMR using fluorobenzene (13.7 mg, 0.143 mmol) as an internal standard at room temperature. The ^1H NMR spectrum exhibited the formation of **2a** (representatively δ 2.5) and Me_3SiF (δ 0.2) evidently in 1 : 3 ratio (Figure S1). The amount of Me_3SiF was estimated to 0.48 mmol (240% based on **1a**) by ^{19}F NMR analysis (Figure S2). No other fluorine-containing species were observed.

The mixture was treated with 1 M aqueous HCl, extracted with AcOEt three times, and the insoluble residue was filtered off. After removal of the solvent, the product was purified by preparative TLC (hexane) to afford **2a** in 69% yield (39.6 mg, 0.14 mmol).

The NMR spectra of Me_3SiF were as follows;

^1H NMR (400 MHz, $CDCl_3$) δ 0.23 (d, $J_{H\text{-}F}$ = 7.2 Hz, 9H)

^{19}F NMR (376 MHz, $CDCl_3$) δ -160.3 (m, 1F).

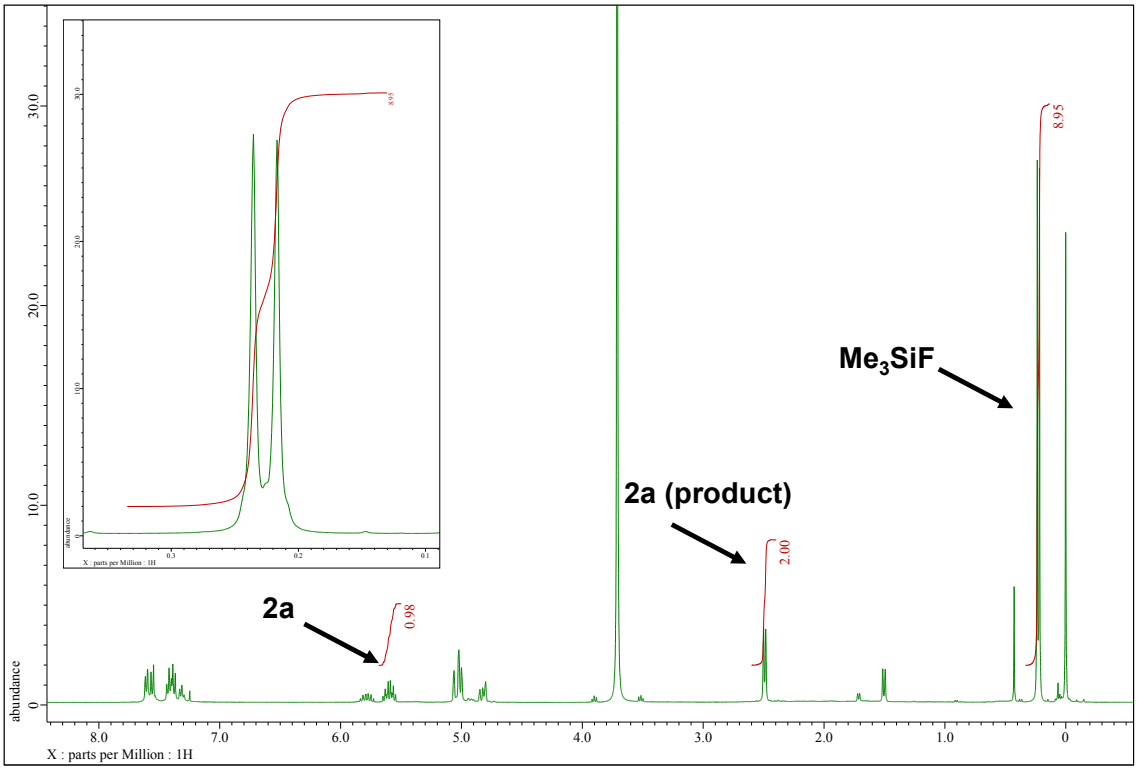


Figure S1. ^{1}H NMR spectrum of the reaction mixture (diluted with $CDCl_3$).

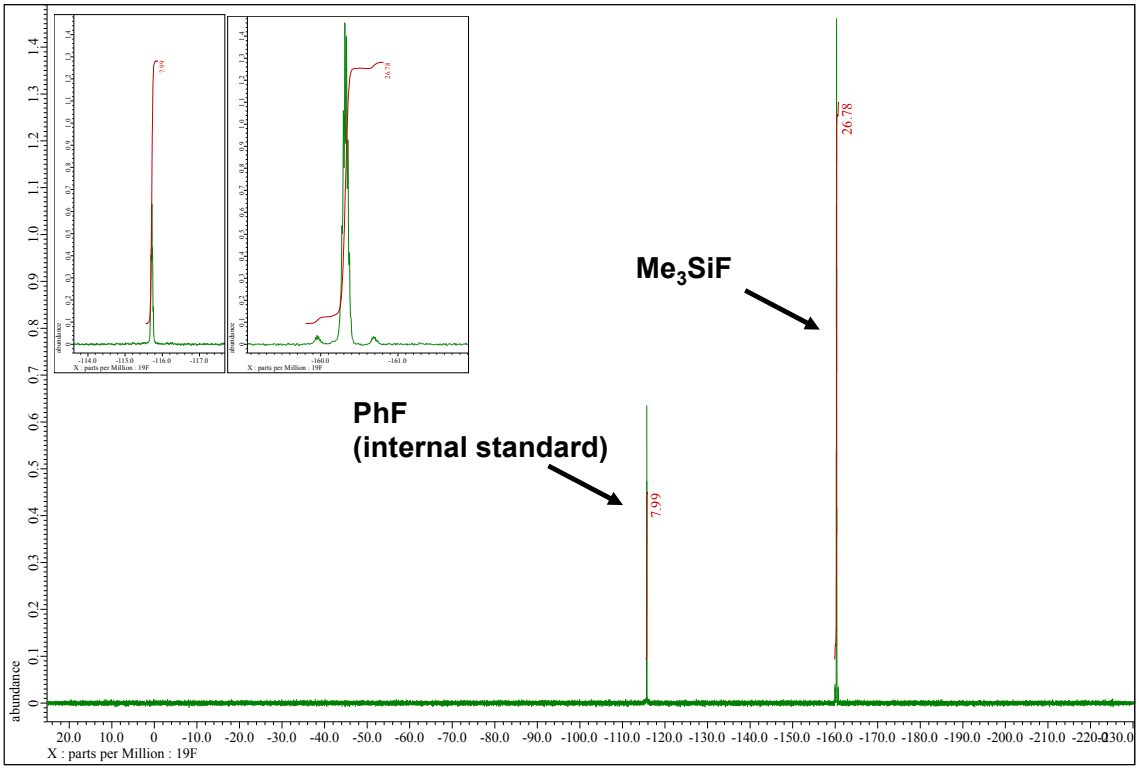
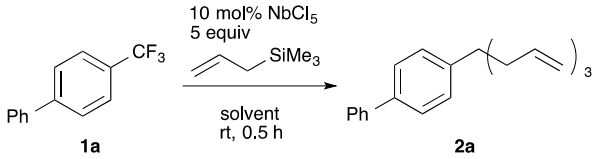


Figure S2. ^{19}F NMR spectrum of the reaction mixture (diluted with $CDCl_3$).

2-2. Solvent Effect

The solvent effect was investigated by using substrate **1a** (Table S1). The yield was found to be significantly dependent on the solvent. Not only coordinative MeCN, Et_2O and THF, but also non-coordinative CH_2Cl_2 were unsuitable to the reaction. Cyclohexane was not as effective as dichloroethane because of insolubility of $NbCl_5$.



entry	solvent	yield (%)
1	$(CH_2Cl)_2$	61
2	MeCN	0
3	Et_2O	0
4	THF	0
5	CH_2Cl_2	5
6	cyclohexane	16

Table S1. Solvent effect.

4. References

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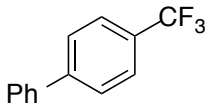
(10) K. Fujikawa, Y. Fujioka, A. Kobayashi and H. Amii, *Org. Lett.*, 2011, **13**, 5560–5563.

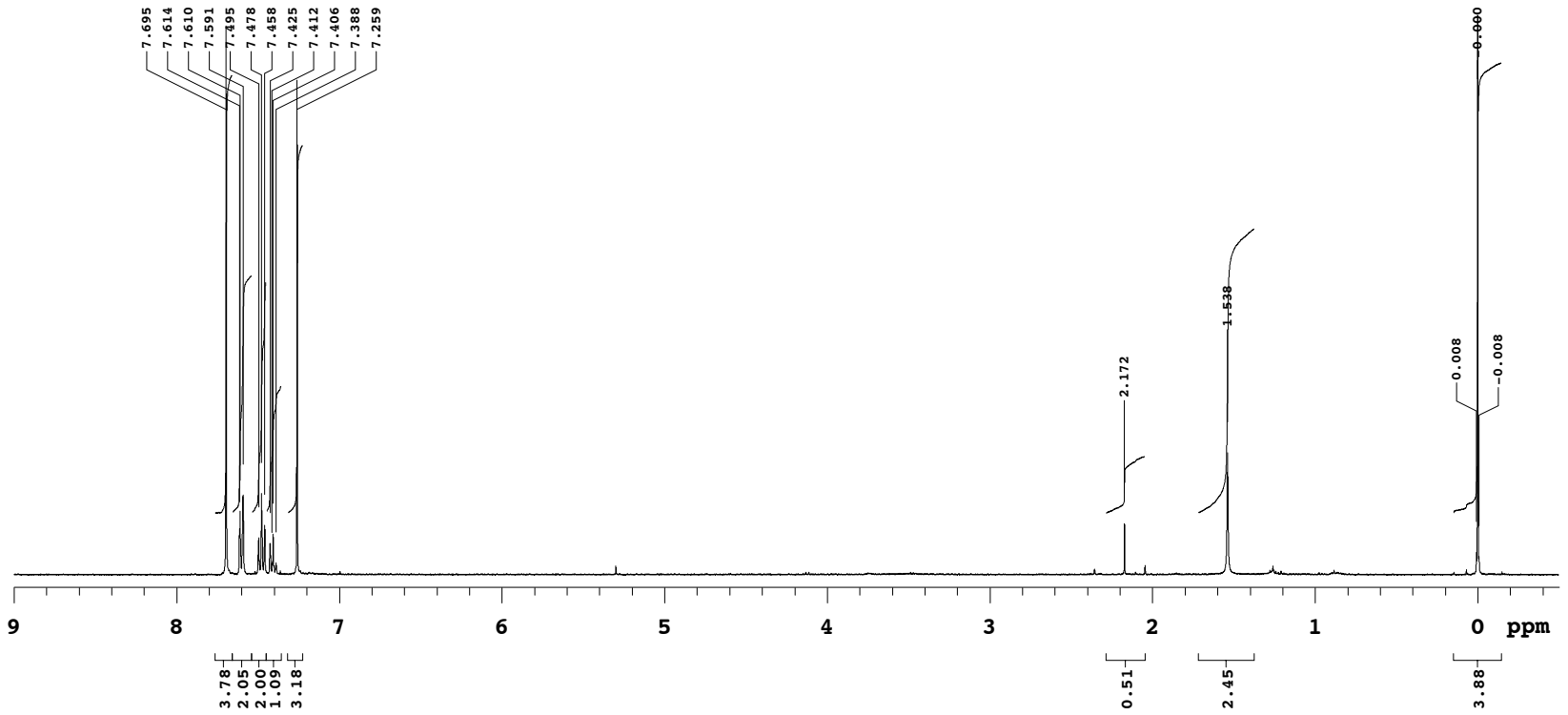
5. ^{1}H, ^{13}C NMR and IR spectral data

^{1}H NMR spectrum of **1a**.



KI_762-3

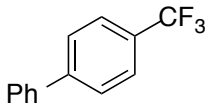
Sample Name	KI_762-3	Pulse sequence	PROTON	Temperature	40	Study owner	vnmr1
Date collected	2016-01-20	Solvent	cdcl3	Spectrometer	Varian400-vnmrs400	Operator	vnmr1



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CF3_1H.fid

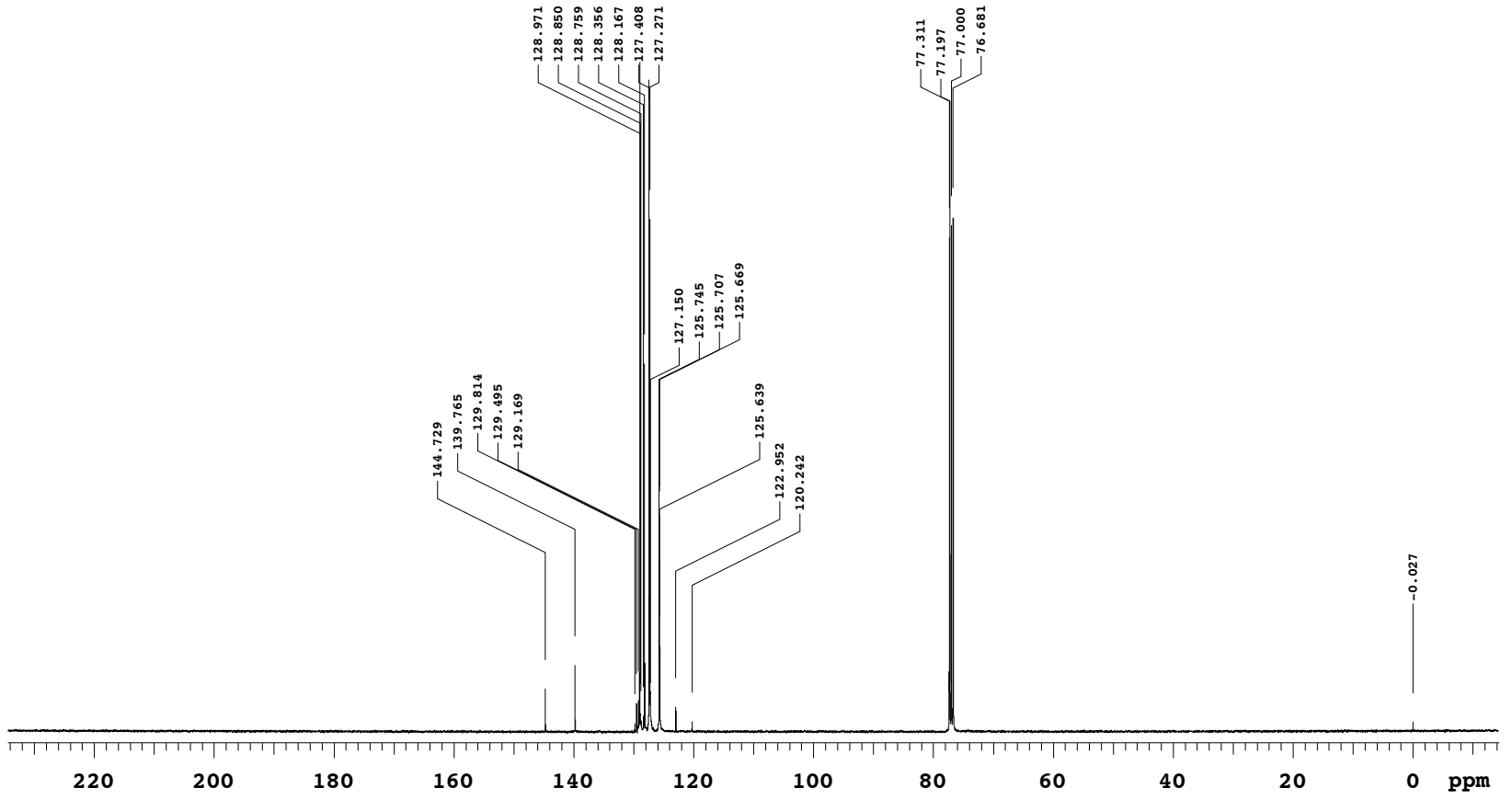
Plot date 2016-07-15

^{13}C NMR spectrum of **1a**.



RM_380_24h

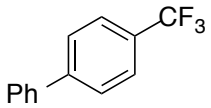
Sample Name	RM_380_24h	Pulse sequence	CARBON	Temperature	25	Study owner	vnmr1
Date collected	2016-04-07	Solvent	cdcl3	Spectrometer	Varian400-vnmrs400	Operator	vnmr1



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CF3_13C.fid

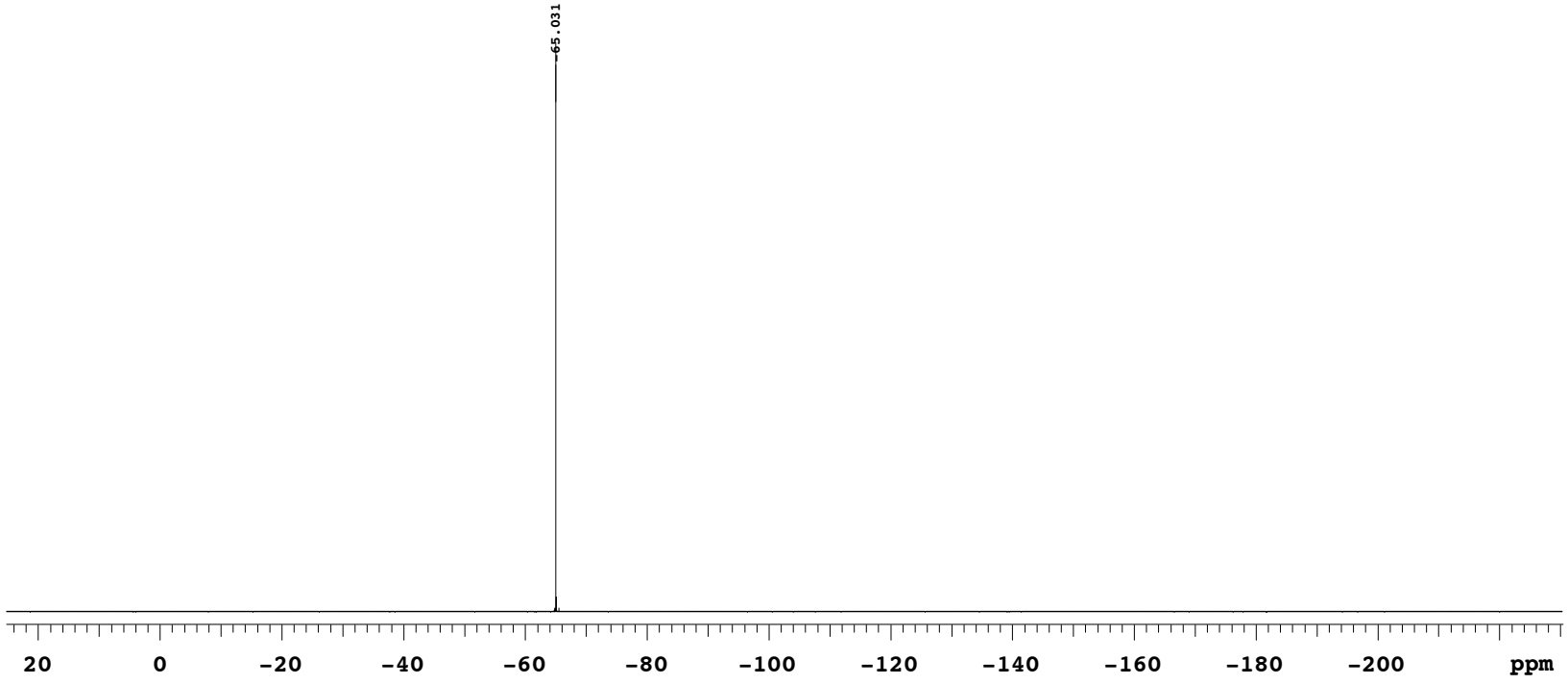
Plot date 2016-04-18

^{19}F NMR spectrum of **1a**.



RM_380_24h

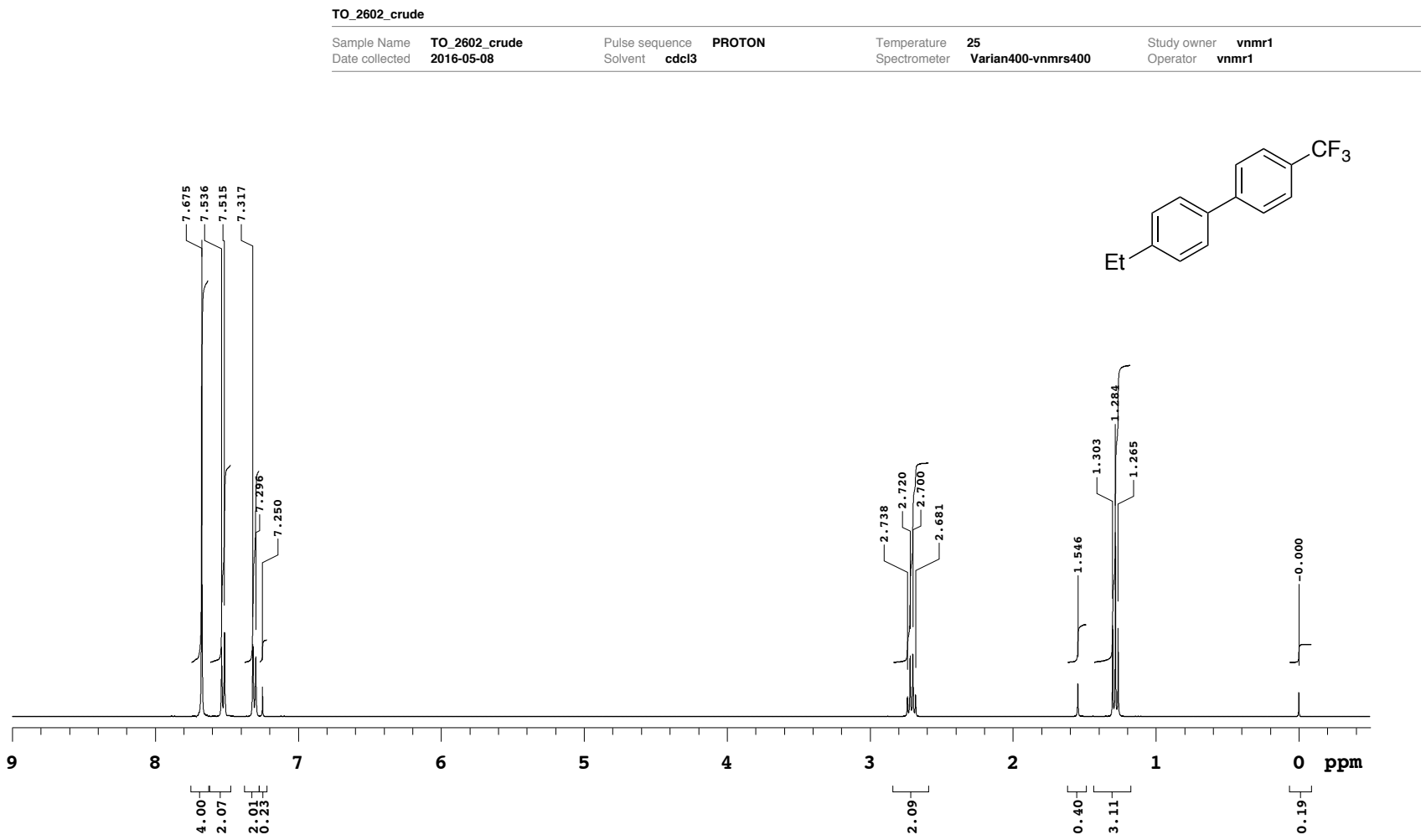
Sample Name	**RM_380_24h**	Pulse sequence	**FLUORINE**	Temperature	**25**	Study owner	**vnmr1**
Date collected	**2016-04-07**	Solvent	**cdcl3**	Spectrometer	**Varian400-vnmrs400**	Operator	**vnmr1**



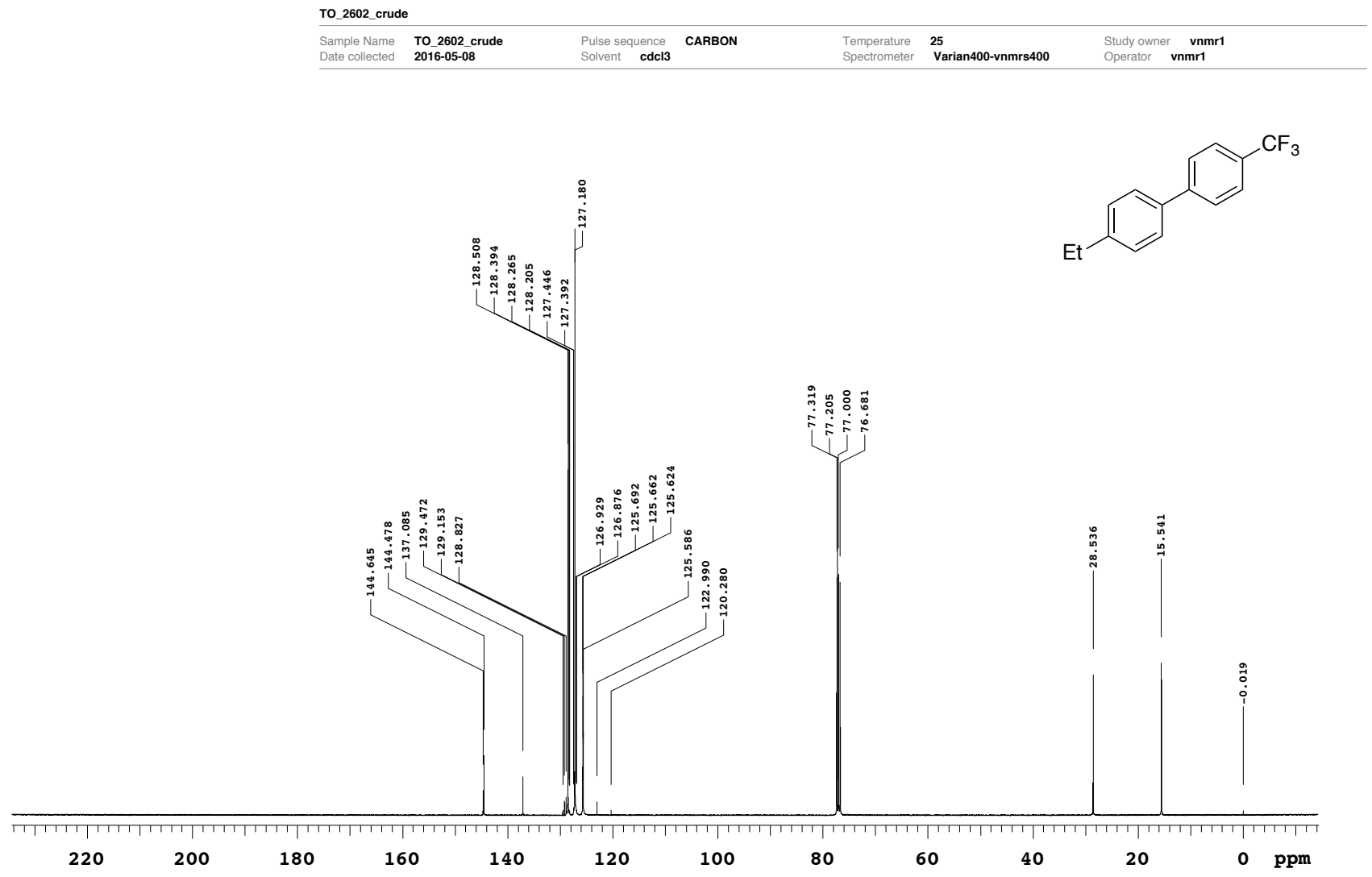
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CF3_19F.fid

Plot date 2016-04-18

^{1}H NMR spectrum of **1b**.



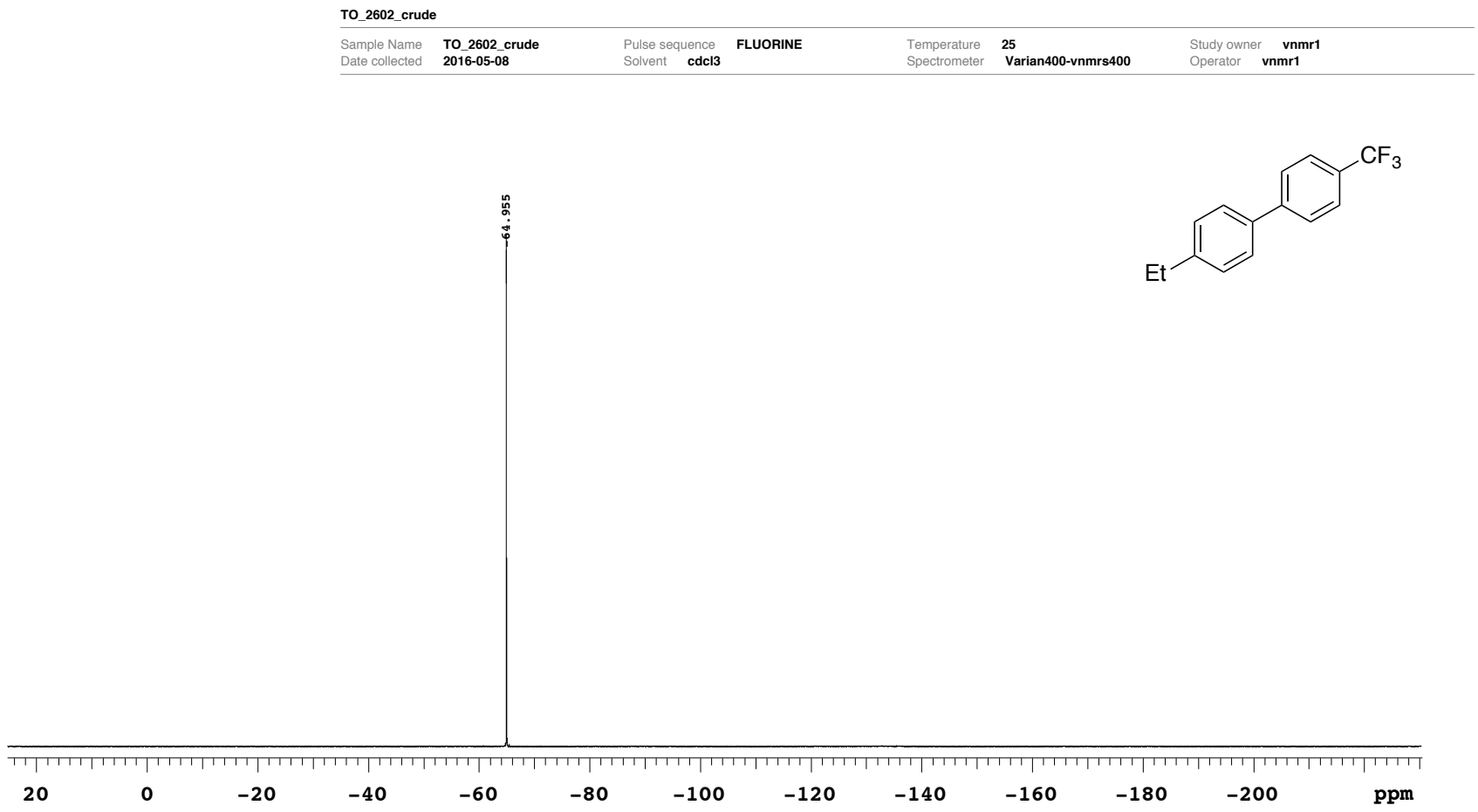
^{13}C NMR spectrum of **1b**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_ethyl_phenyl_CF3_13C.fid

Plot date 2016-10-17

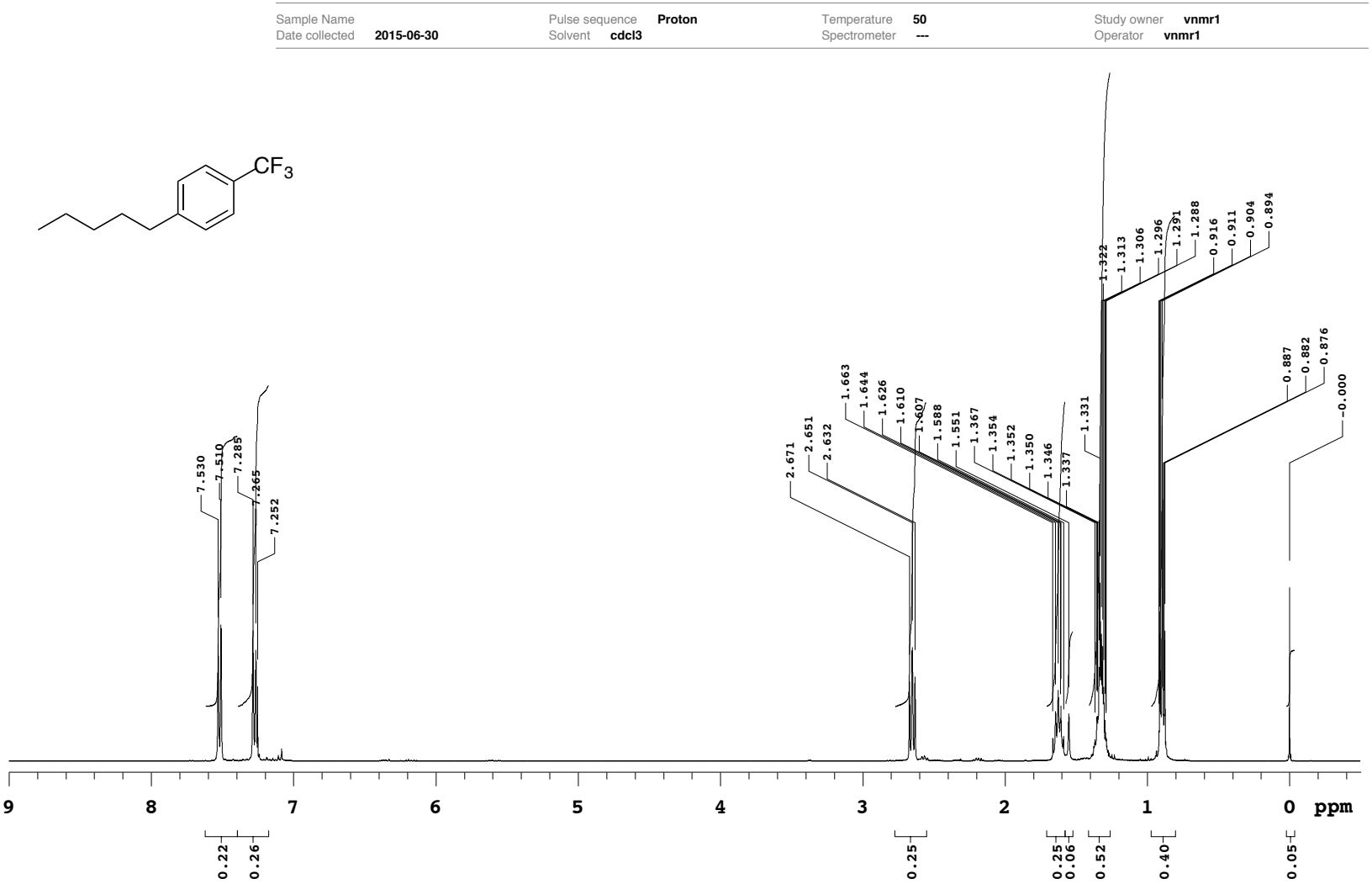
^{19}F NMR spectrum of **1b**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_ethyl_phenyl_CF3_19F.fid

Plot date 2016-05-12

^{1}H NMR spectrum of **1d**.

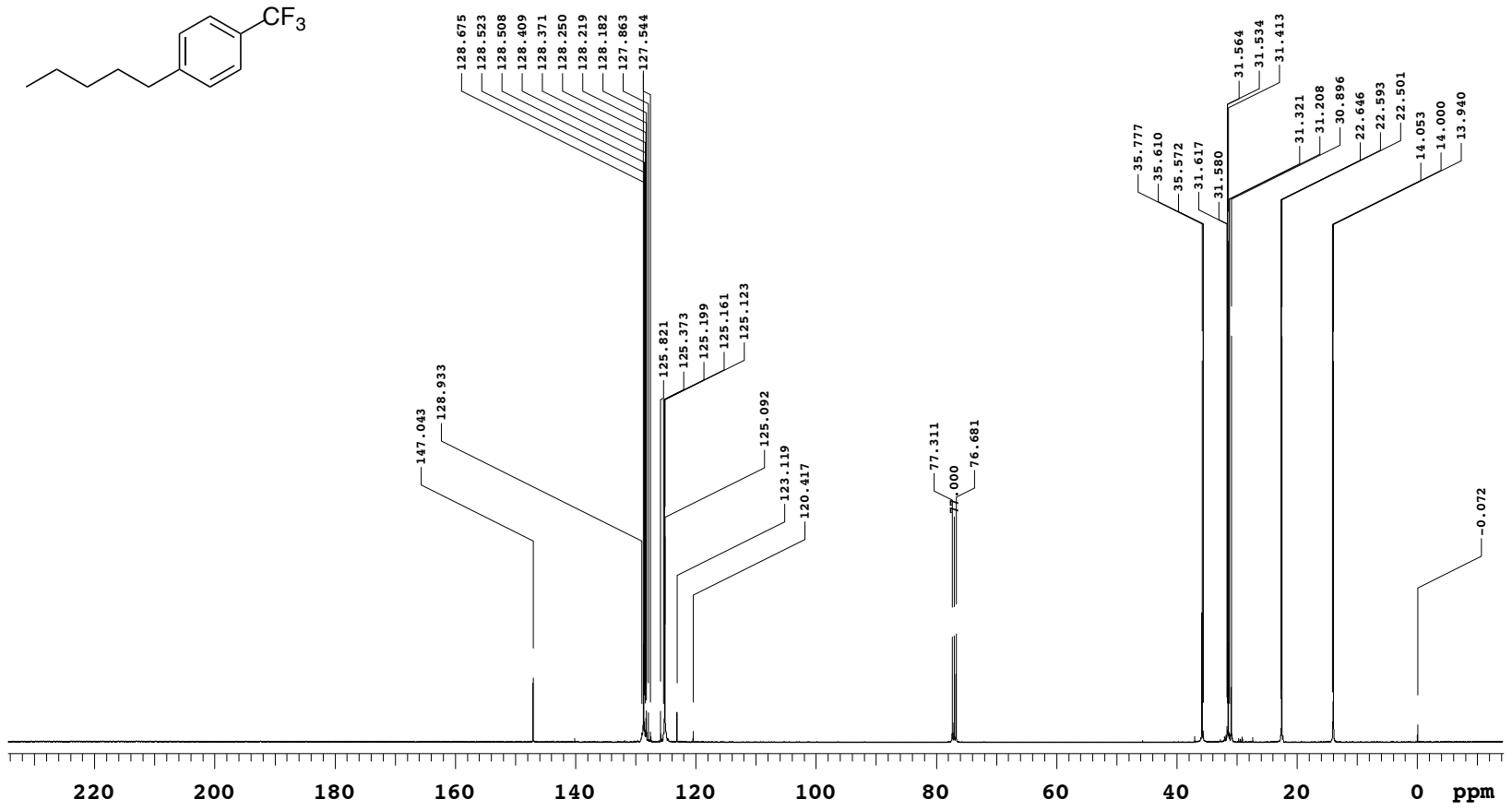


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_pentyl_CF3_1H.fid

Plot date 2016-04-18

^{13}C NMR spectrum of **1d**.

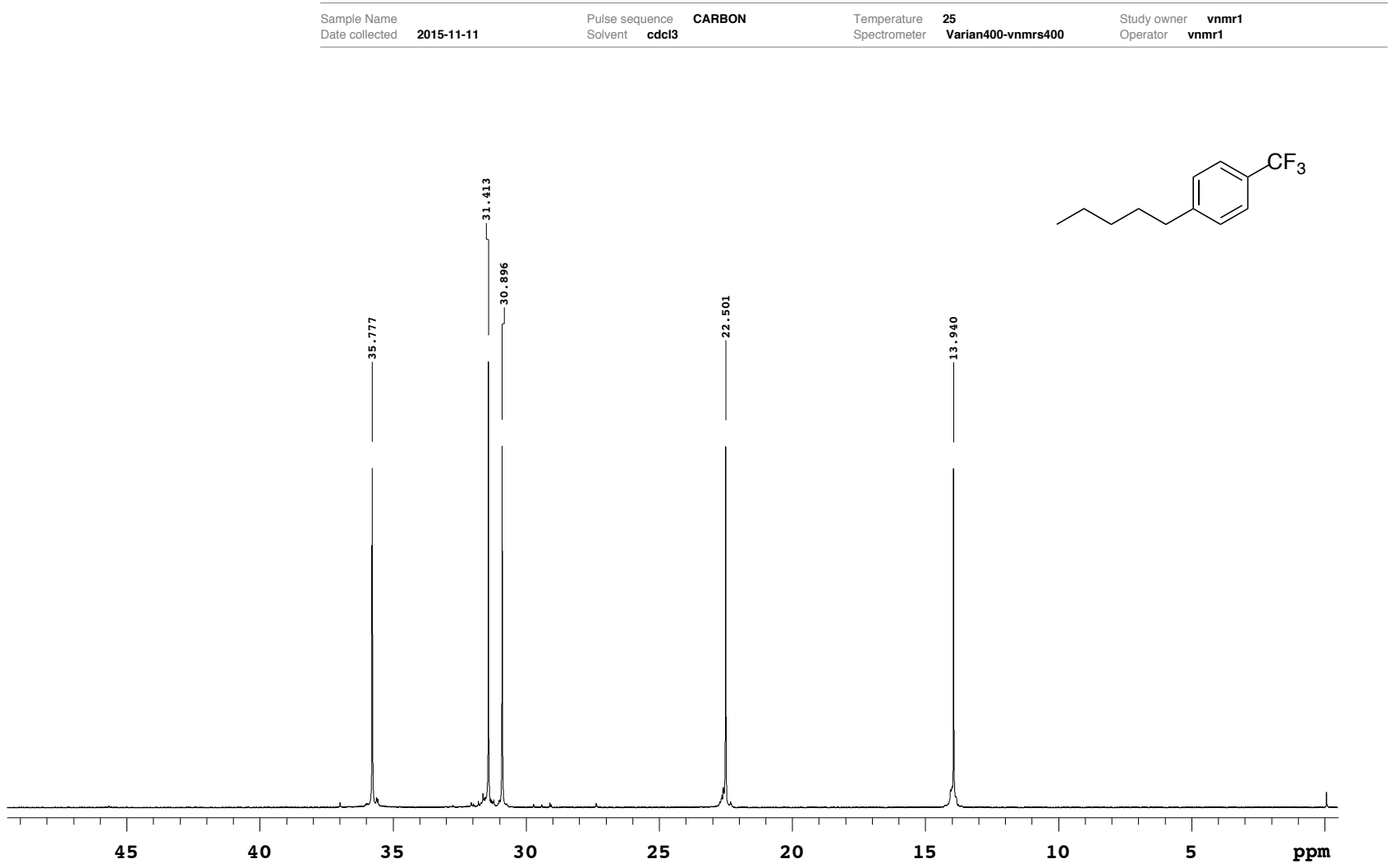
Sample Name		Pulse sequence	**CARBON**	Temperature	**25**	Study owner	**vnmr1**
Date collected	**2015-11-11**	Solvent	**cdcl3**	Spectrometer	**Varian400-vnmrs400**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_propyl_CF3_13C.fid

Plot date 2015-11-12

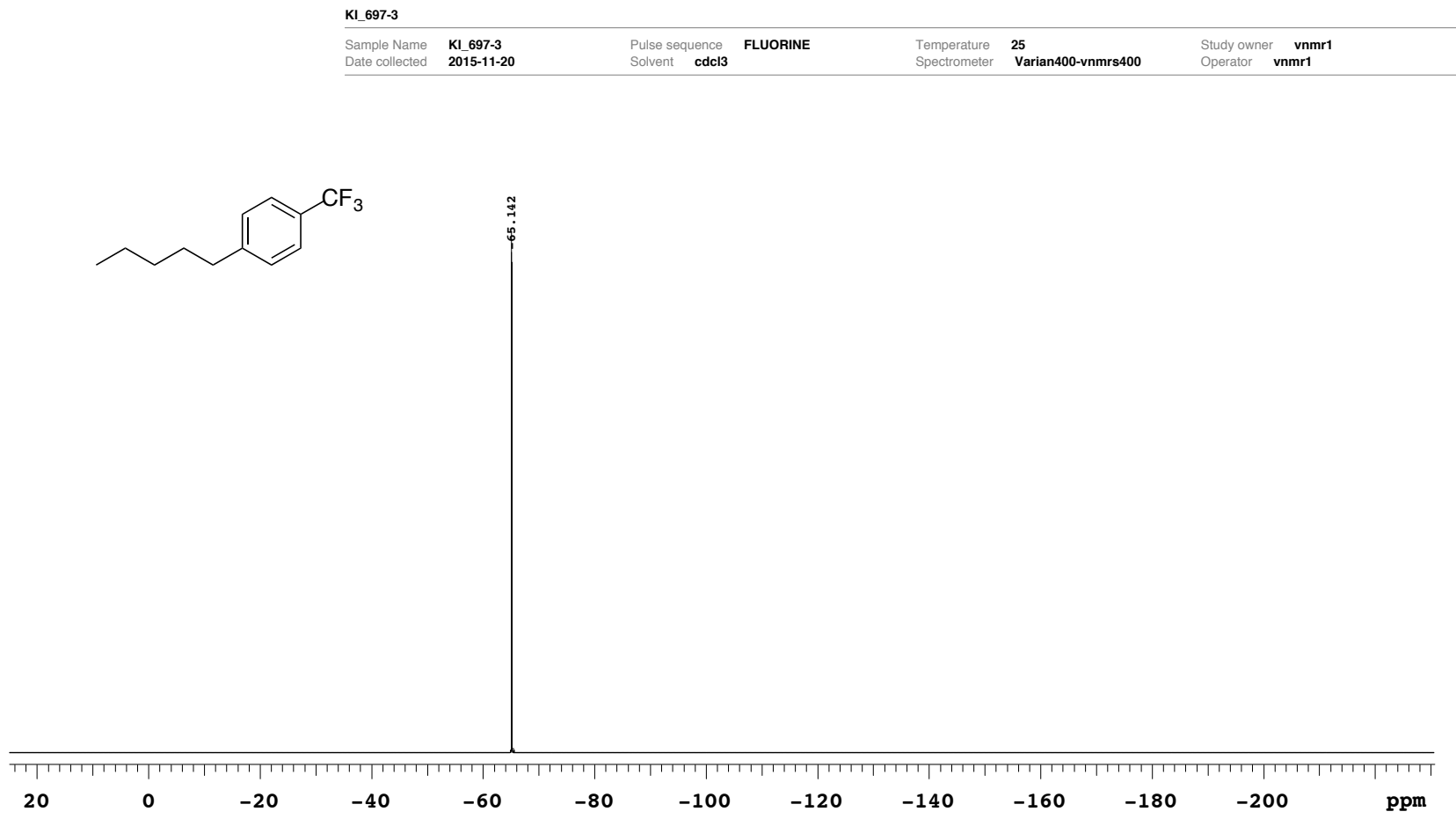
^{13}C NMR spectrum of **1d** (magnified).



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_pentyl_CF3_13C.fid

Plot date 2016-10-29

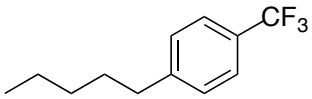
^{19}F NMR spectrum of **1d**.

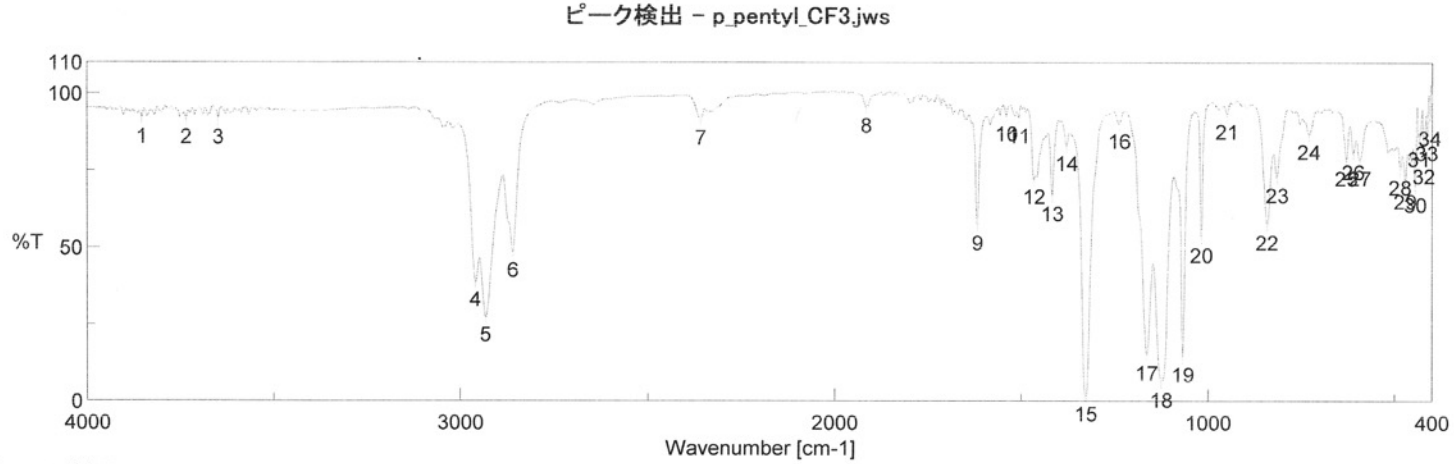


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_pentyl_CF3_19F.fid

Plot date 2016-02-19

IR spectrum of **1d**.





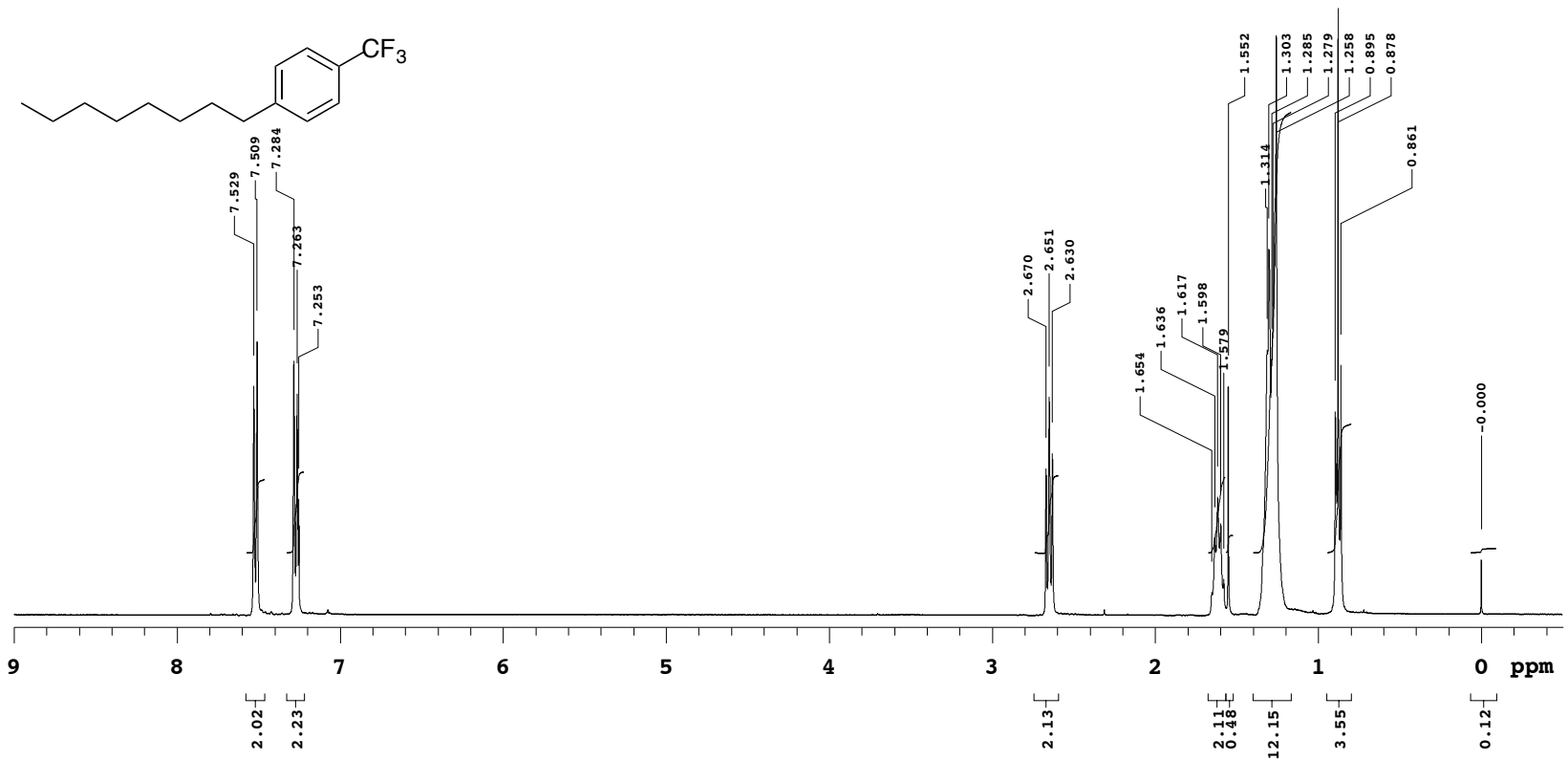
[コメント情報]
試料名 p_pentyl_CF3
コメント
測定者
所属
会社 学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3853.08	91.7345	2	3733.51	91.5651	3	3648.66	91.5027	4	2960.2	38.7061
5	2933.2	27.3004	6	2859.92	48.2204	7	2360.44	91.2683	8	1916.9	95.274
9	1617.98	57.1295	10	1540.85	92.548	11	1508.06	91.9178	12	1465.63	72.1956
13	1417.42	66.6467	14	1378.85	82.9861	15	1326.79	1.52521	16	1238.08	90.1606
17	1164.79	14.8311	18	1126.22	5.97998	19	1068.37	14.3095	20	1018.23	53.0949
21	950.734	93.1915	22	842.74	57.1858	23	815.742	72.6502	24	730.889	86.6393
25	630.609	78.1485	26	611.324	80.2417	27	593.968	78.1666	28	485.974	75.2226
29	472.474	70.6969	30	445.476	69.6401	31	435.834	84.5272	32	422.334	78.9596
33	414.62	86.4535	34	406.907	91.2318						

^{1}H NMR spectrum of **1e**.

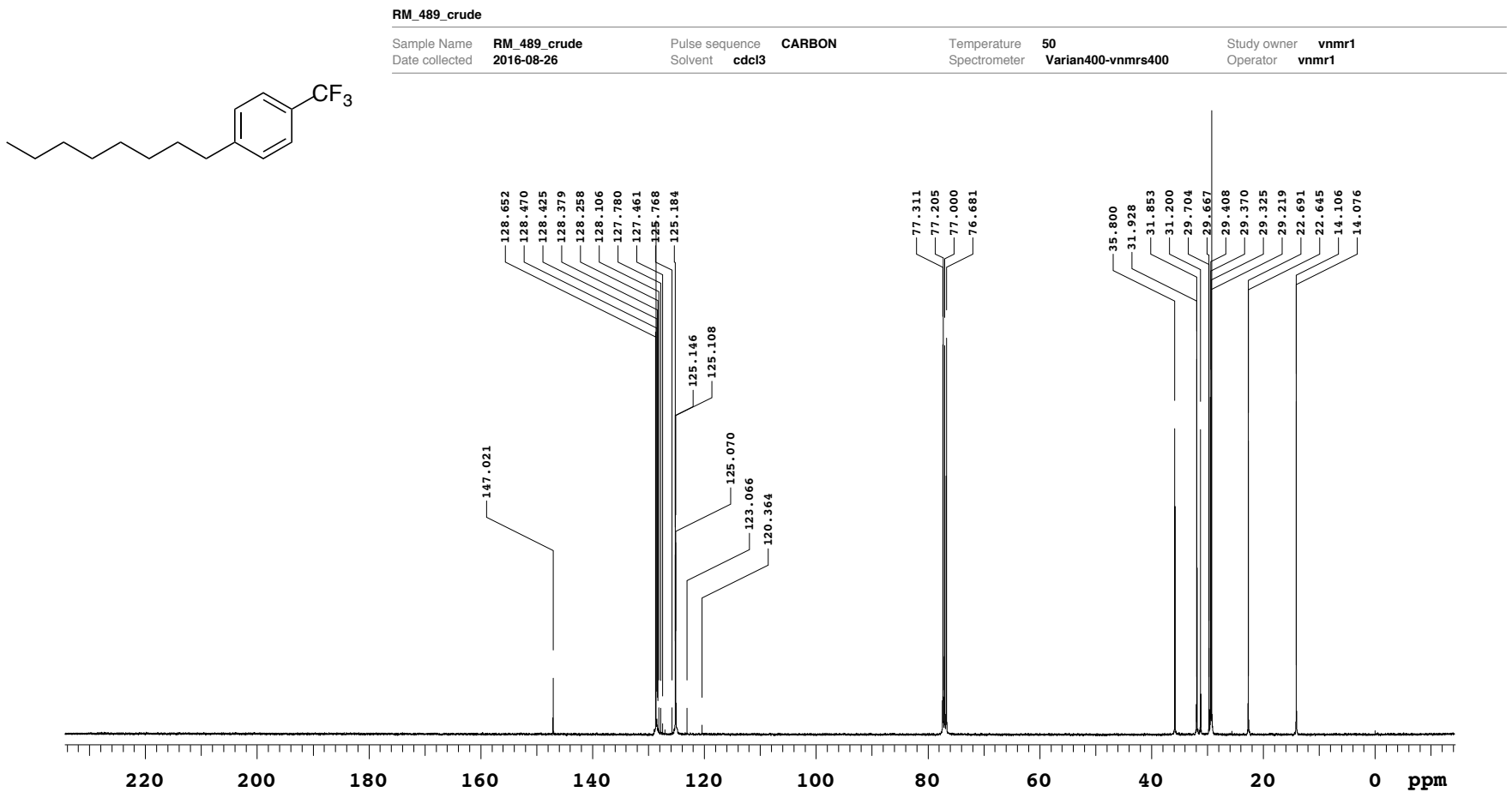
Sample Name		Pulse sequence	**PROTON**	Temperature	**50**	Study owner	**vnmr1**
Date collected	**2016-07-30**	Solvent	**cdcl3**	Spectrometer	**Varian400-vnmrs400**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_octyl_CF3_1H.fid

Plot date 2016-10-18

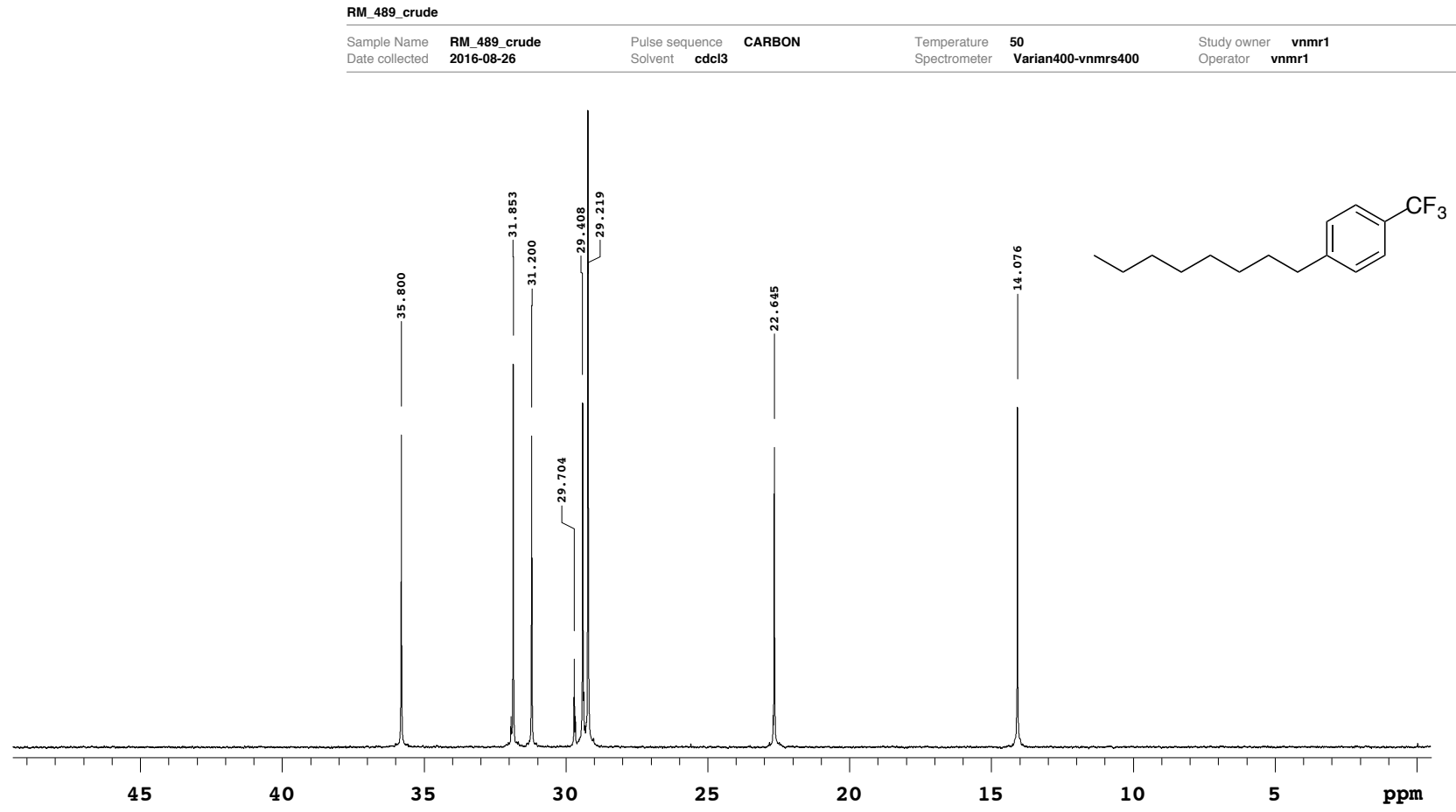
^{13}C NMR spectrum of **1e**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_octyl_CF3_13C_2.fid

Plot date 2016-11-10

^{13}C NMR spectrum of **1e** (magnified).

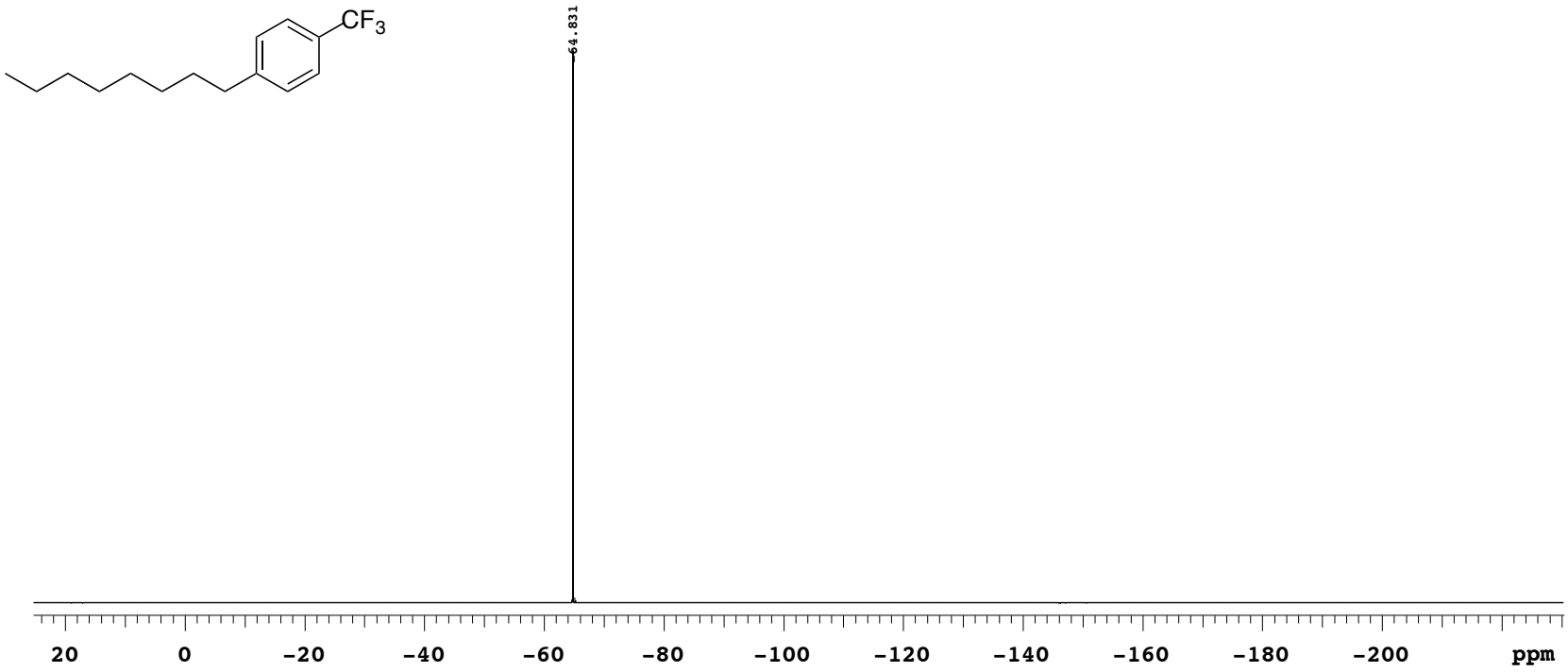


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_octyl_CF3_13C_2.fid

Plot date 2016-11-10

^{19}F NMR spectrum of **1e**.

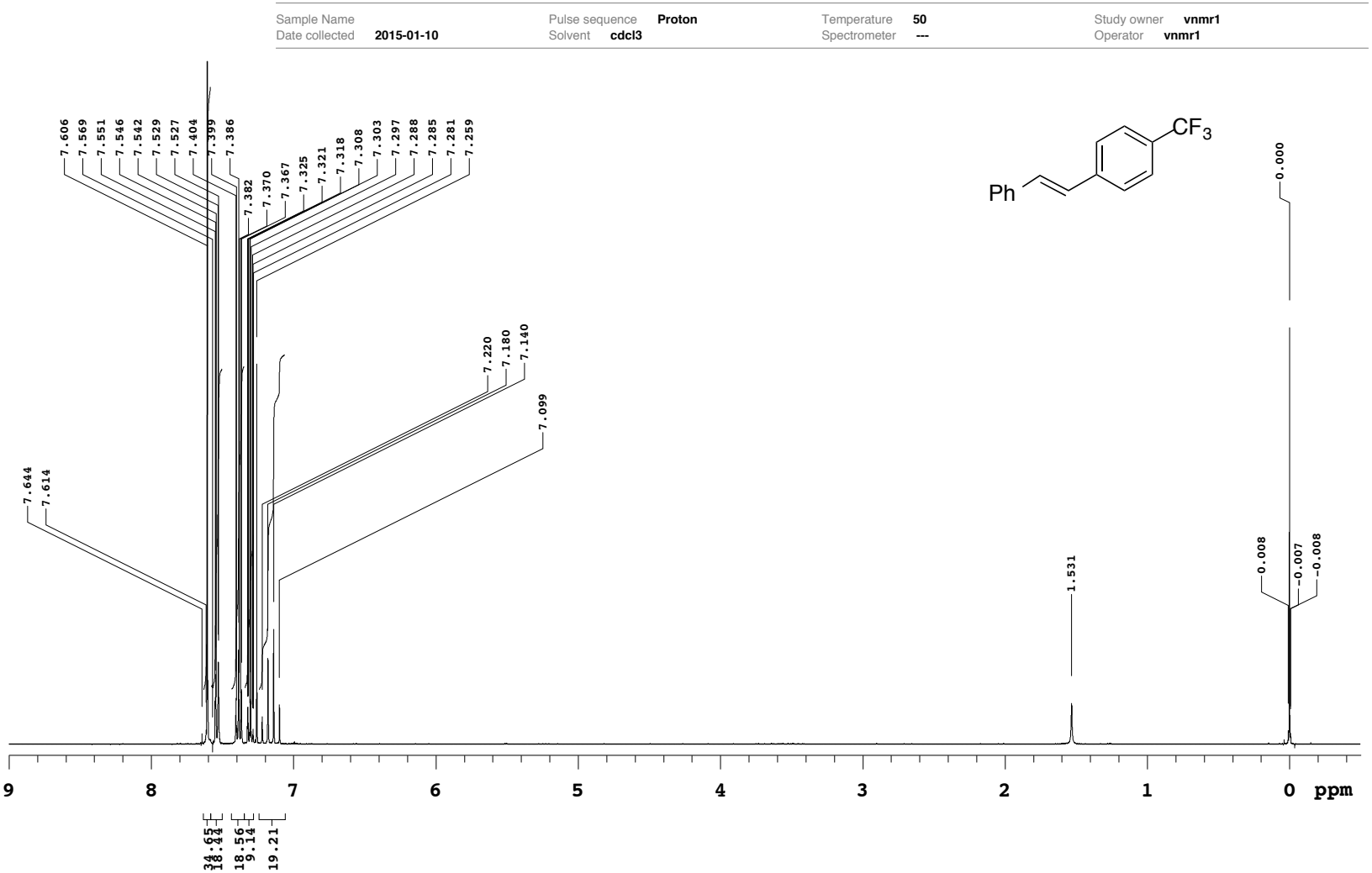
Sample Name		Pulse sequence	**FLUORINE**	Temperature	**25**	Study owner	**vnmr1**
Date collected	**2015-10-30**	Solvent	**cdcl3**	Spectrometer	**Varian400-vnmrs400**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_octyl_CF3_19F.fid

Plot date 2015-11-20

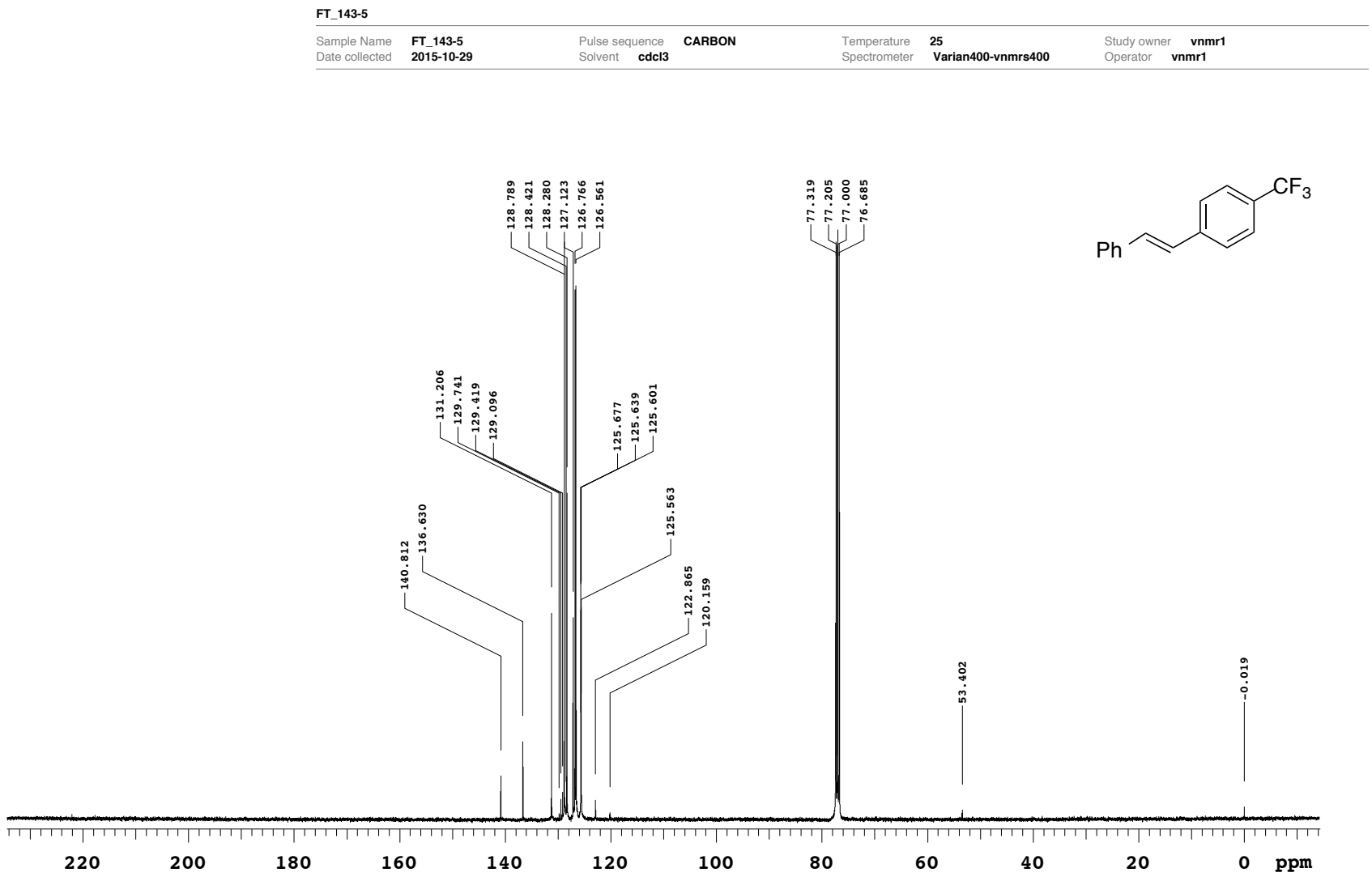
^{1}H NMR spectrum of **1f**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/yamada/1300_/Exp.1351_column_H1.fid

Plot date 2015-10-29

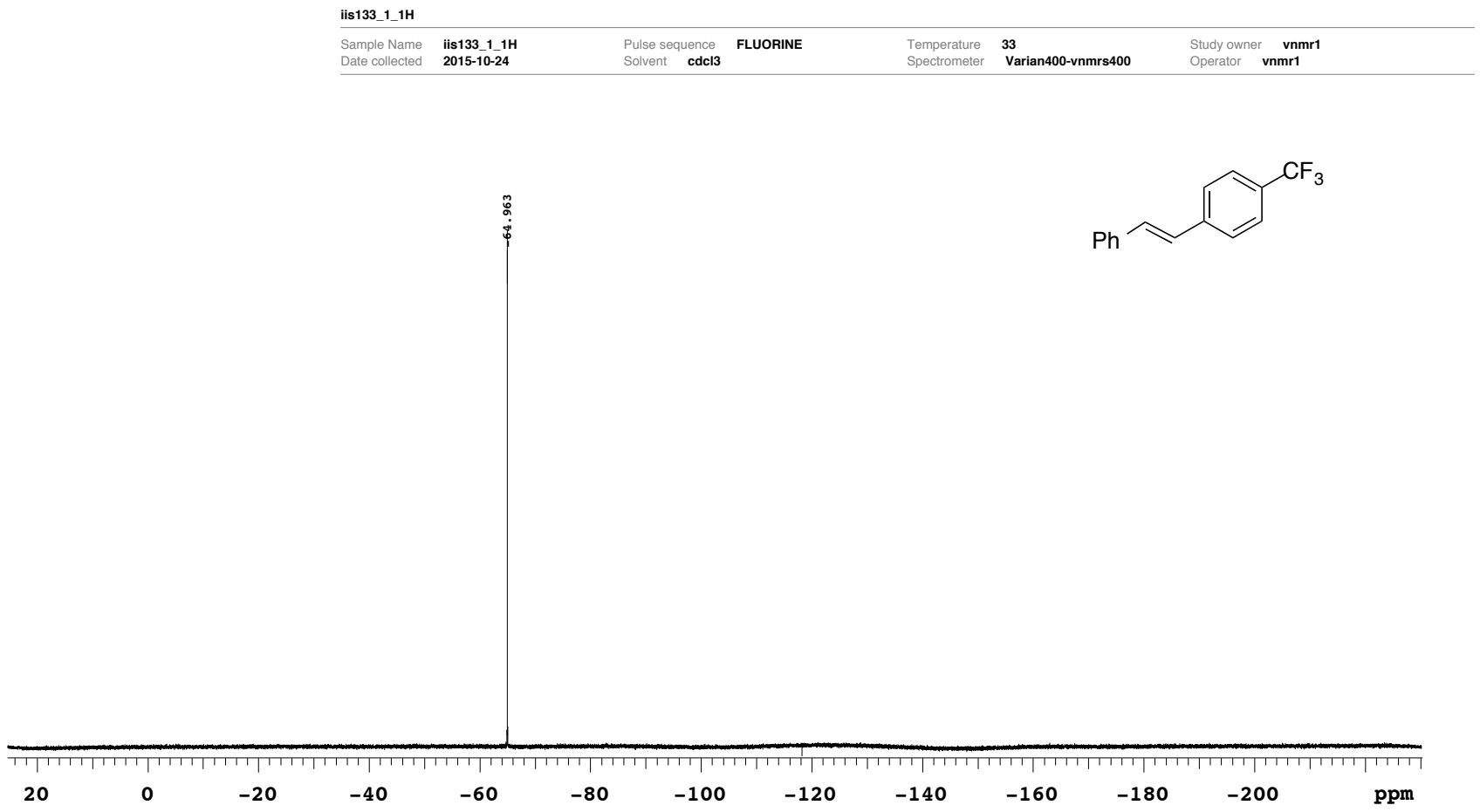
^{13}C NMR spectrum of **1f**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_alkene_CF3_13C.fid

Plot date 2016-10-18

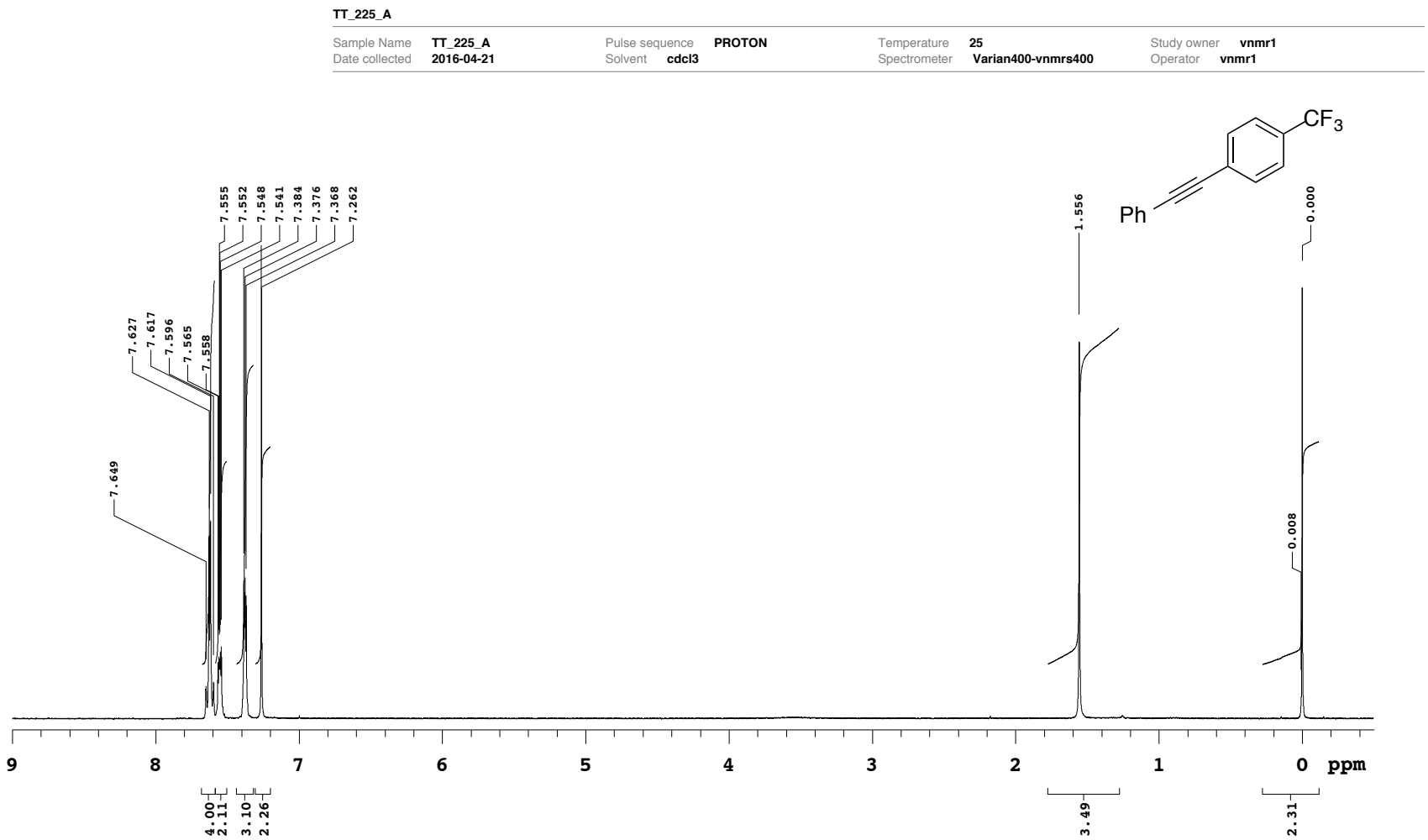
^{19}F NMR spectrum of **1f**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/alkene_phenyl_CF3_19F.fid

Plot date 2015-10-29

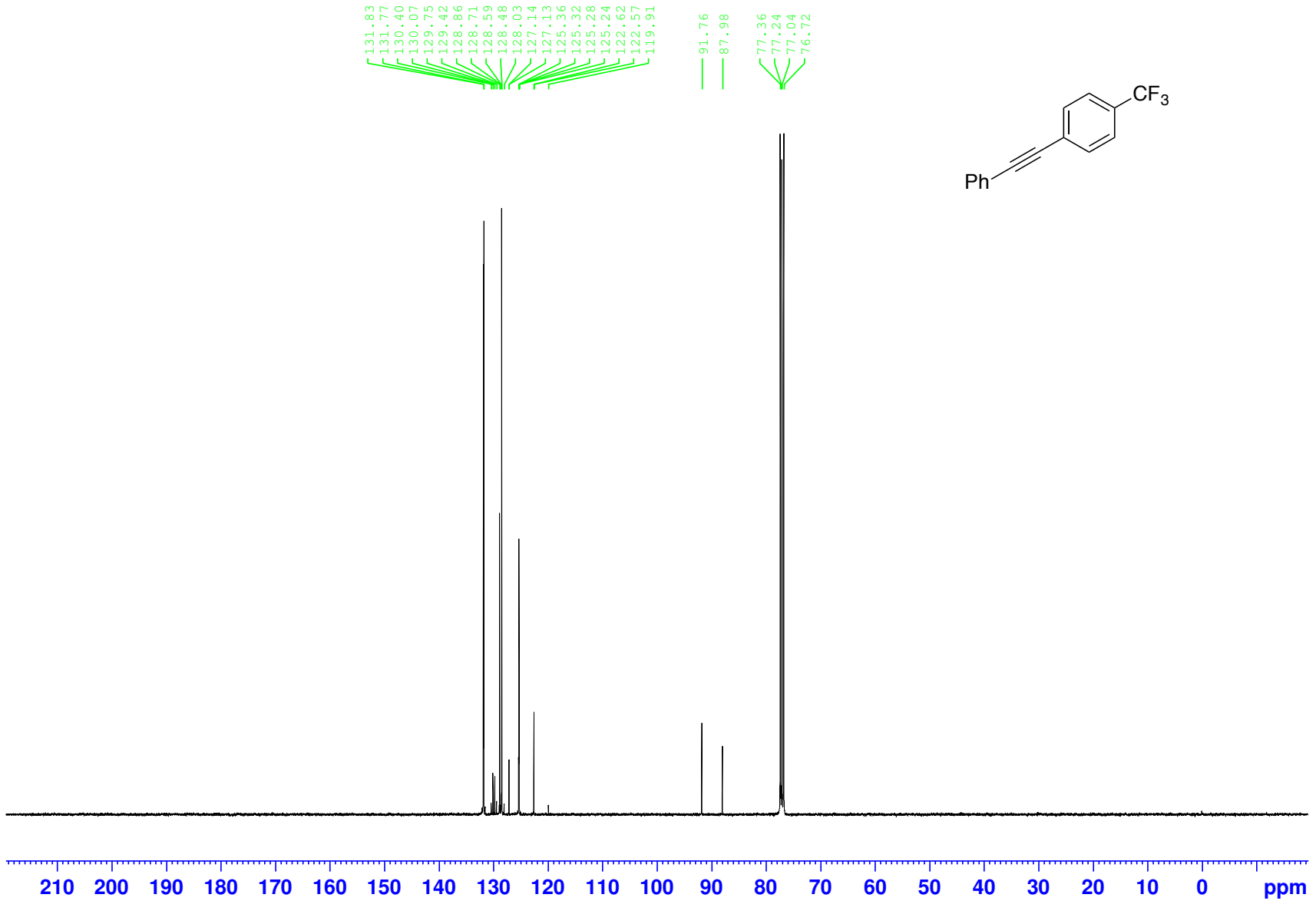
^{1}H NMR spectrum of **1g**.



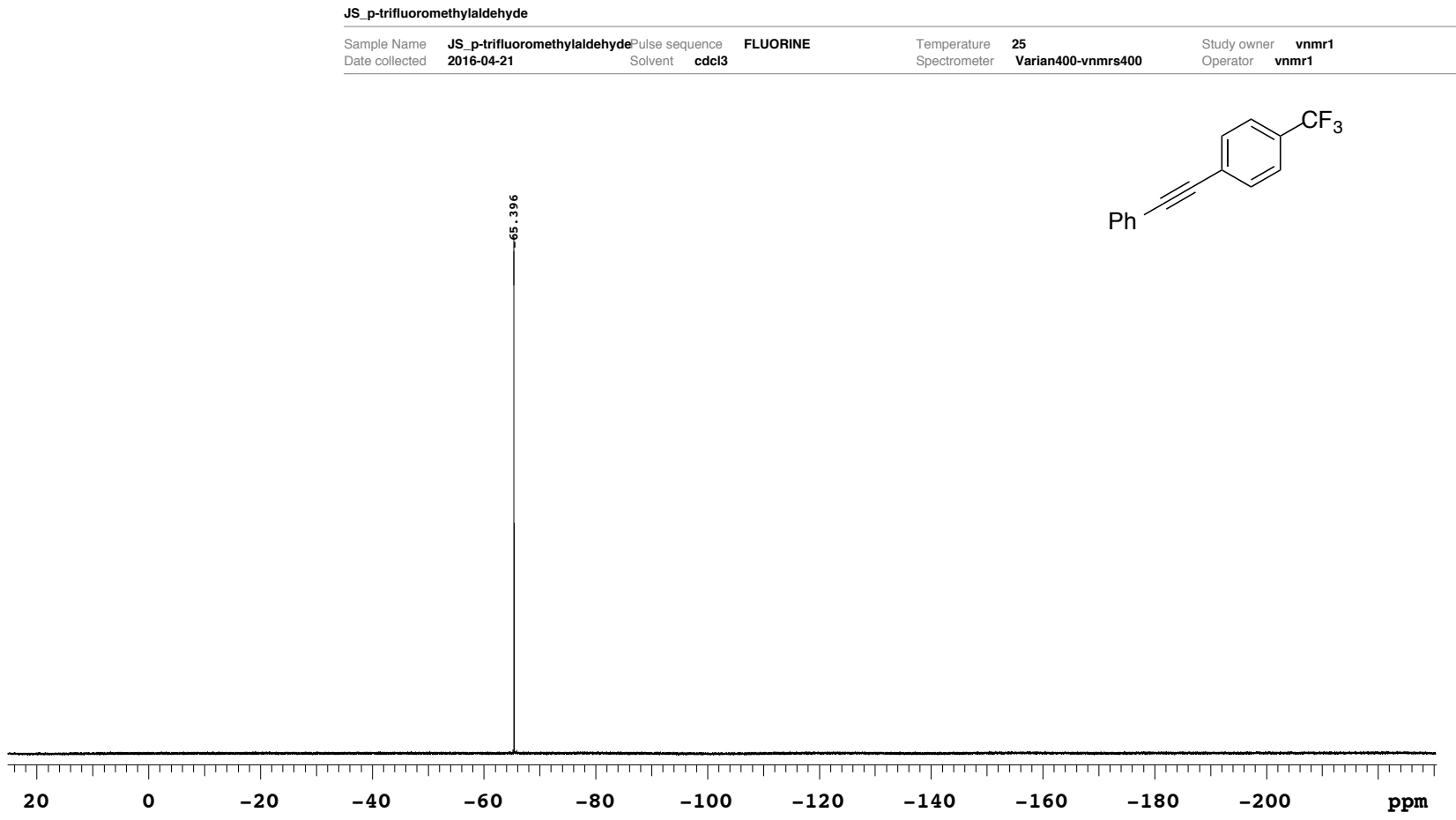
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_phenyl_alkyne_CF3_1H.fid

Plot date 2016-04-21

^{13}C NMR spectrum of **1g**.



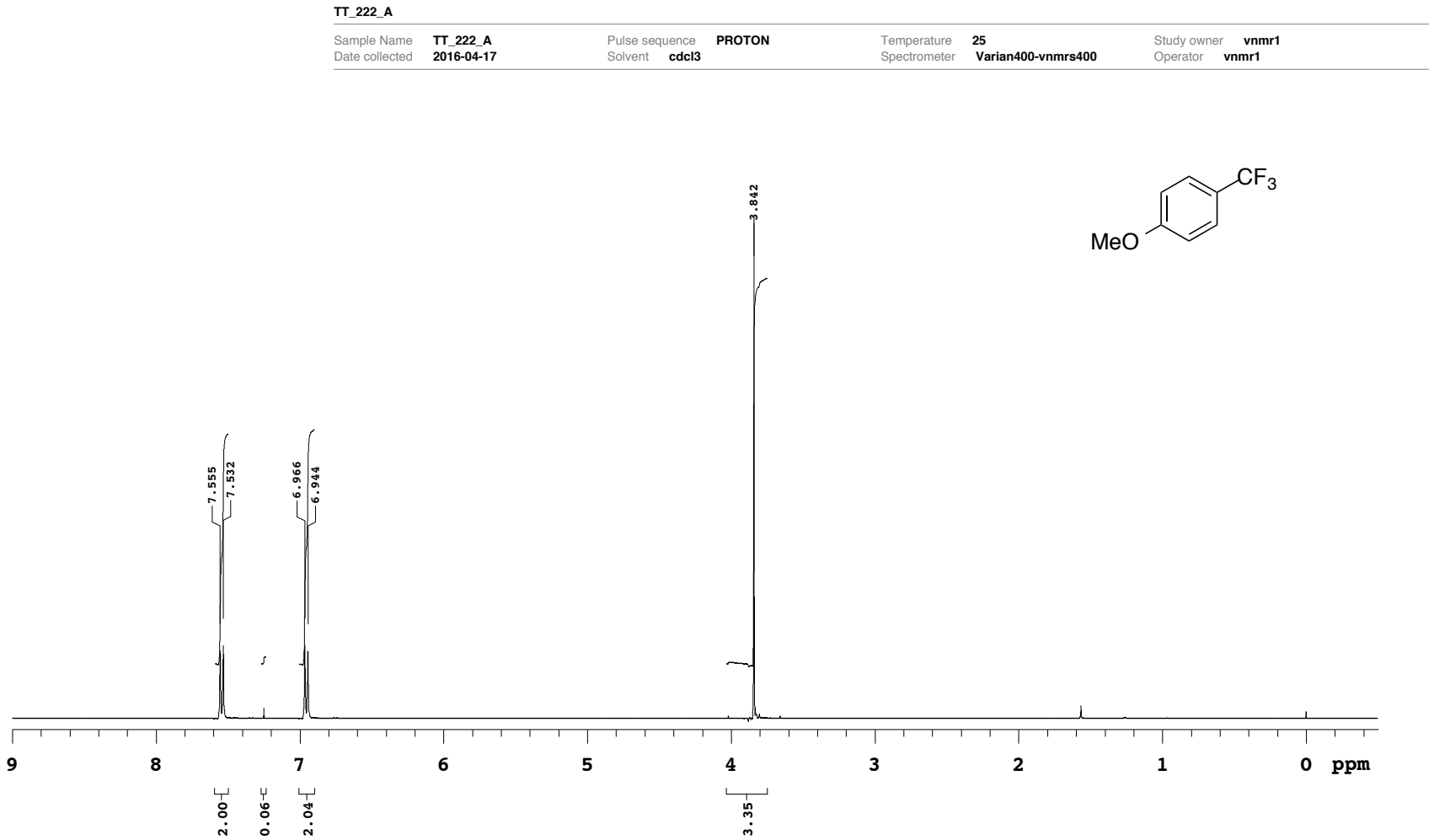
^{19}F NMR spectrum of **1g**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_phenyl_alkyne_CF3_19F.fid

Plot date 2016-04-21

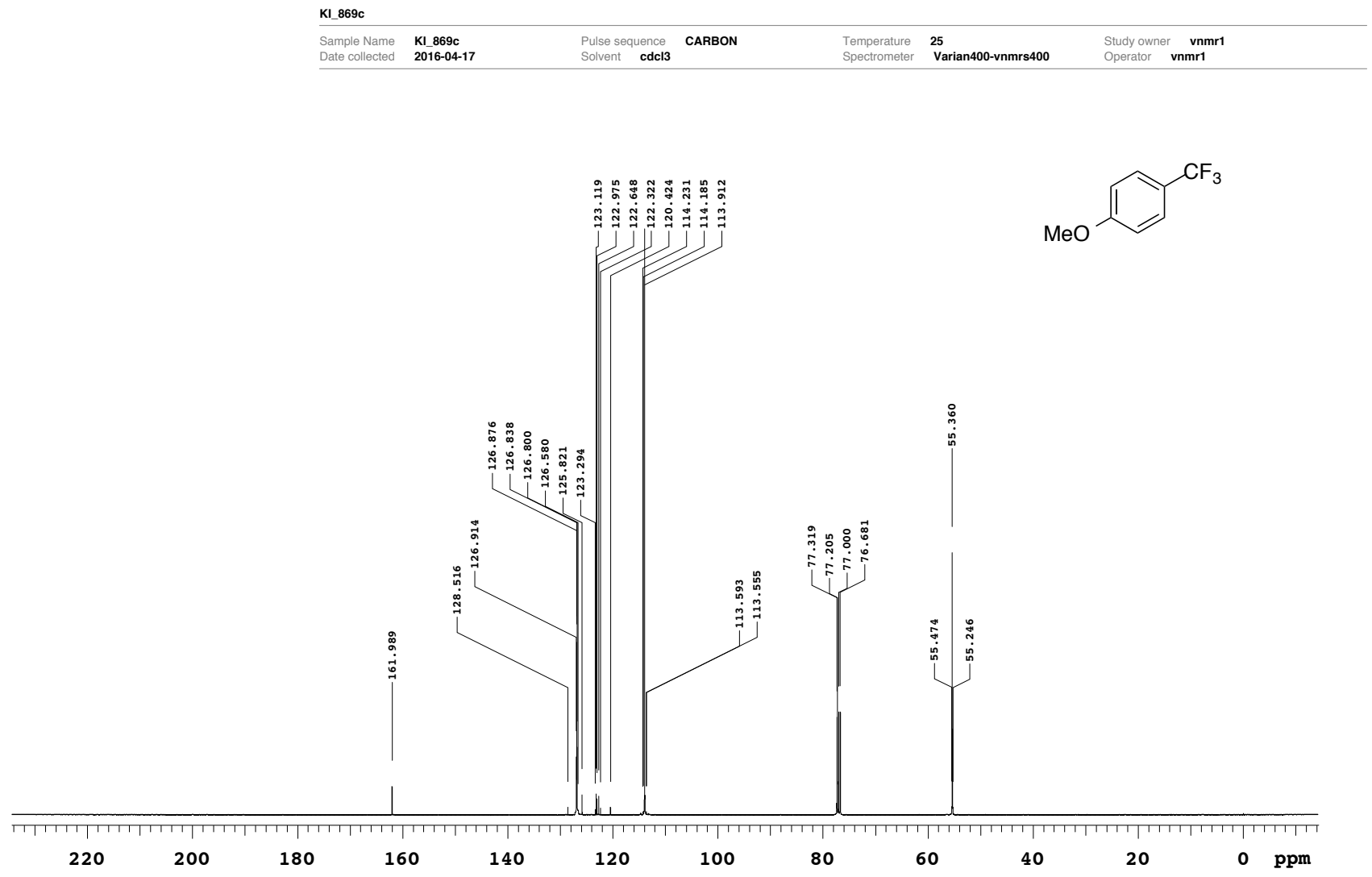
^{1}H NMR spectrum of **1h**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_methoxy_CF3_1H.fid

Plot date 2016-11-10

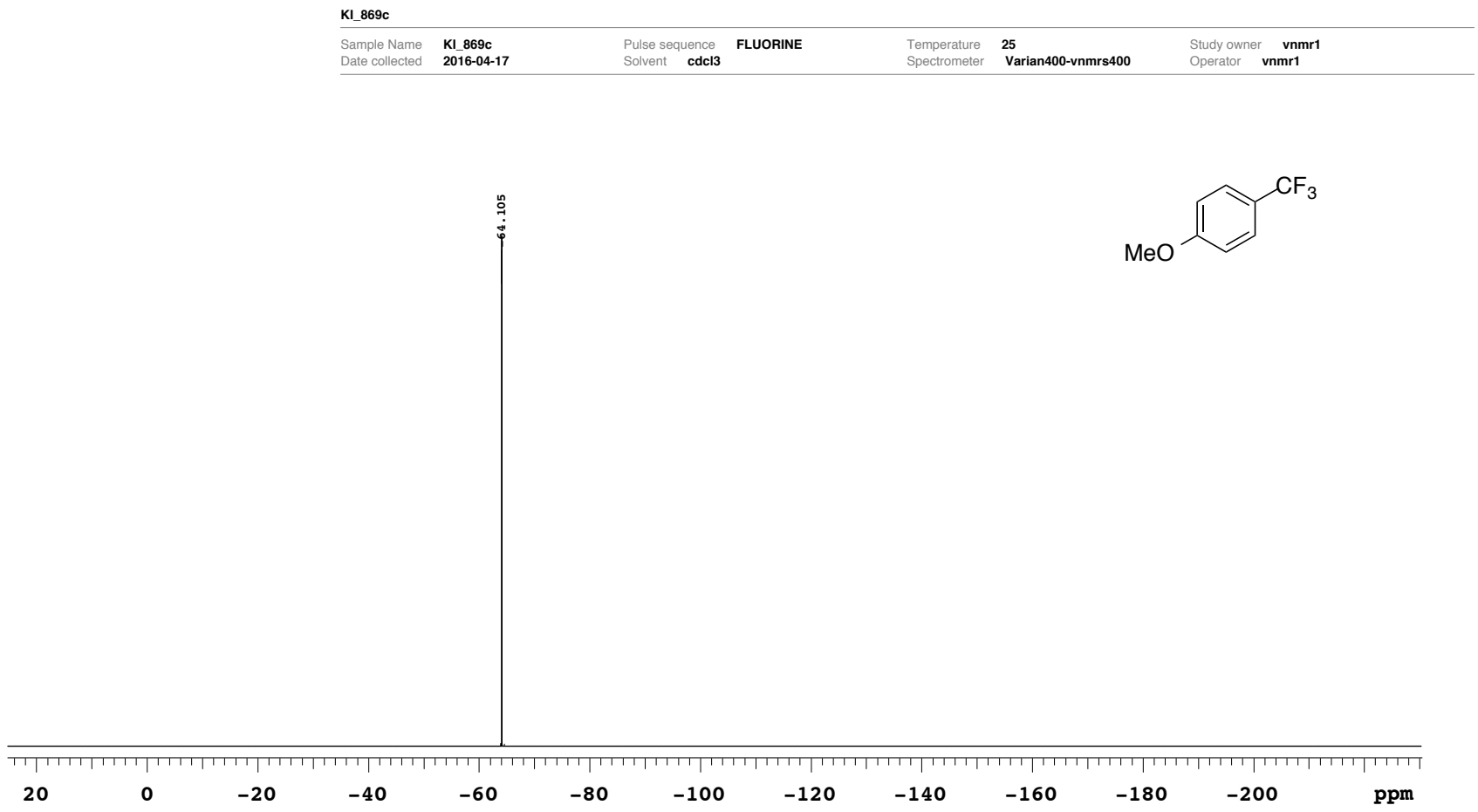
^{13}C NMR spectrum of **1h**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_methoxy_CF3_13C.fid

Plot date 2016-04-18

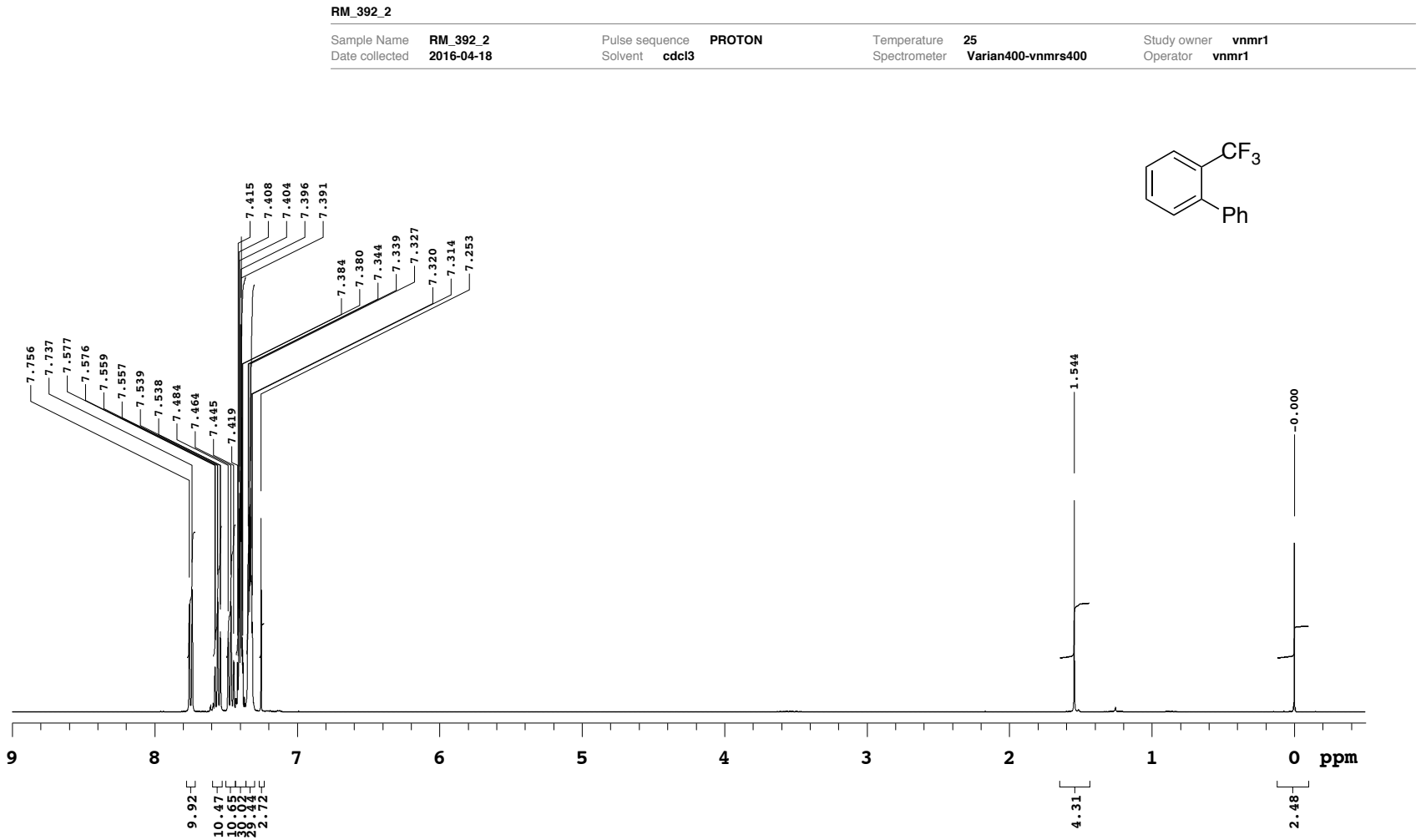
^{19}F NMR spectrum of **1h**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_methoxy_CF3_19F.fid

Plot date 2016-04-18

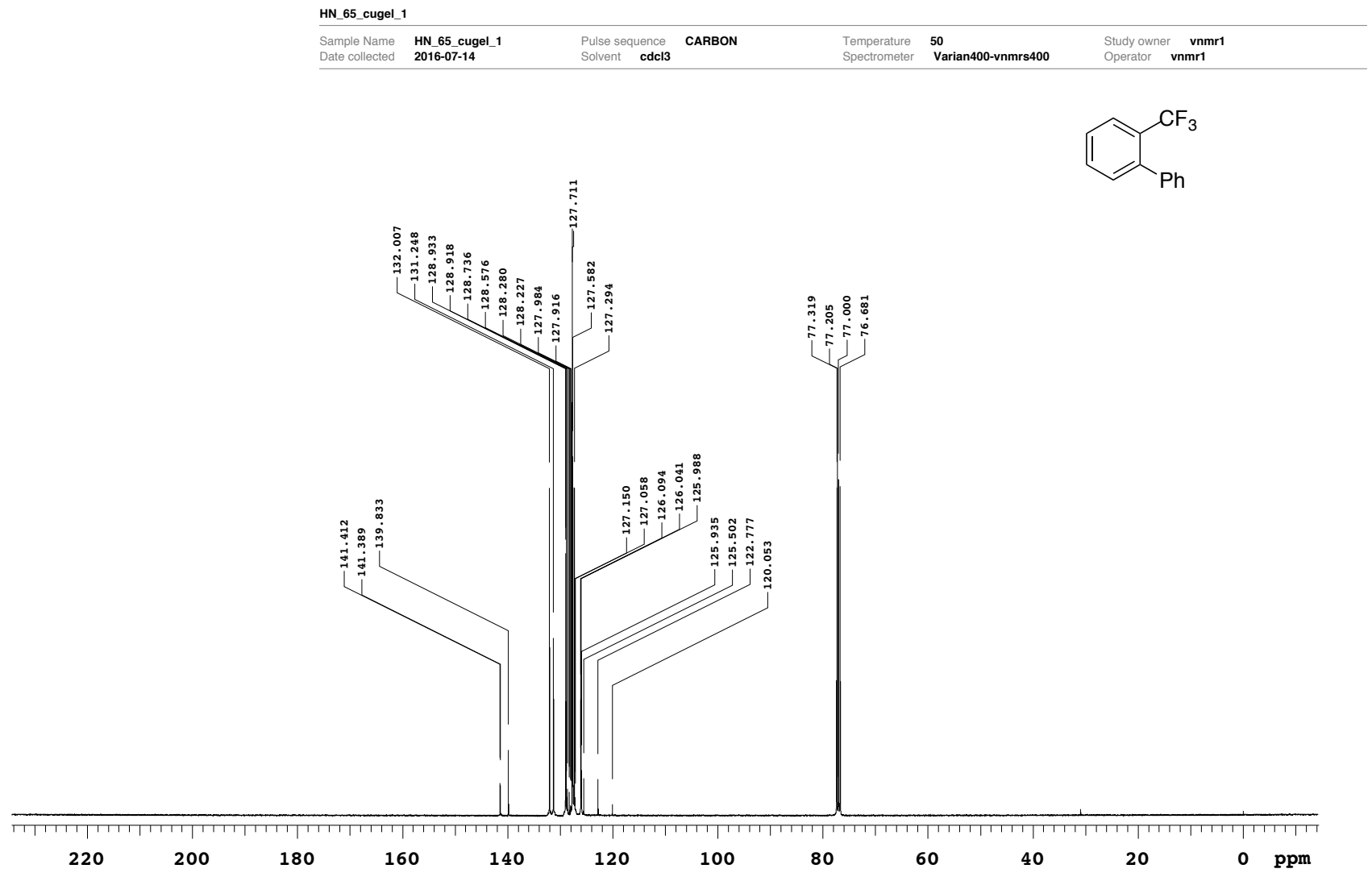
^{1}H NMR spectrum of **3b**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/o_phenyl_CF3_1H.fid

Plot date 2016-04-18

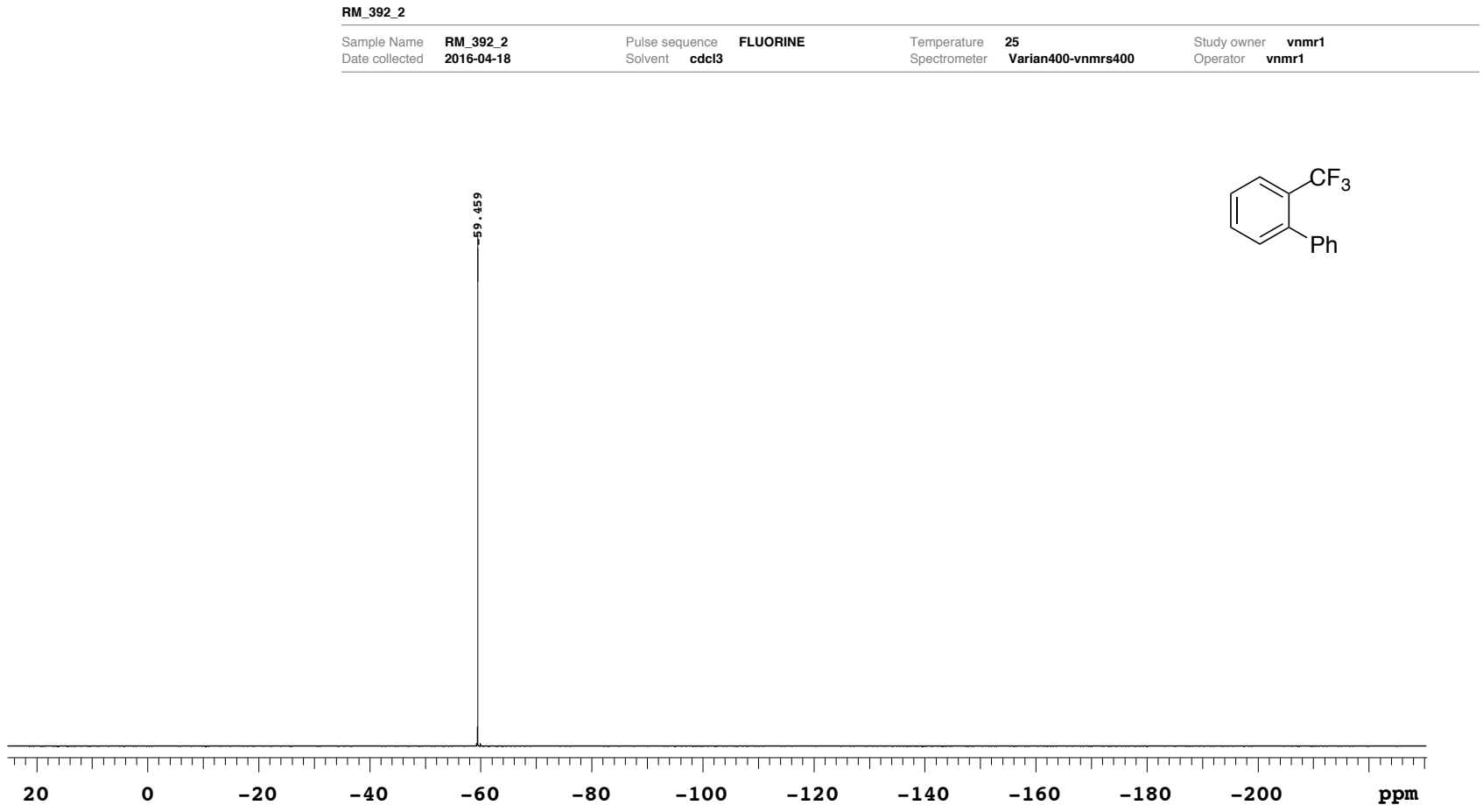
^{13}C NMR spectrum of **3b**.



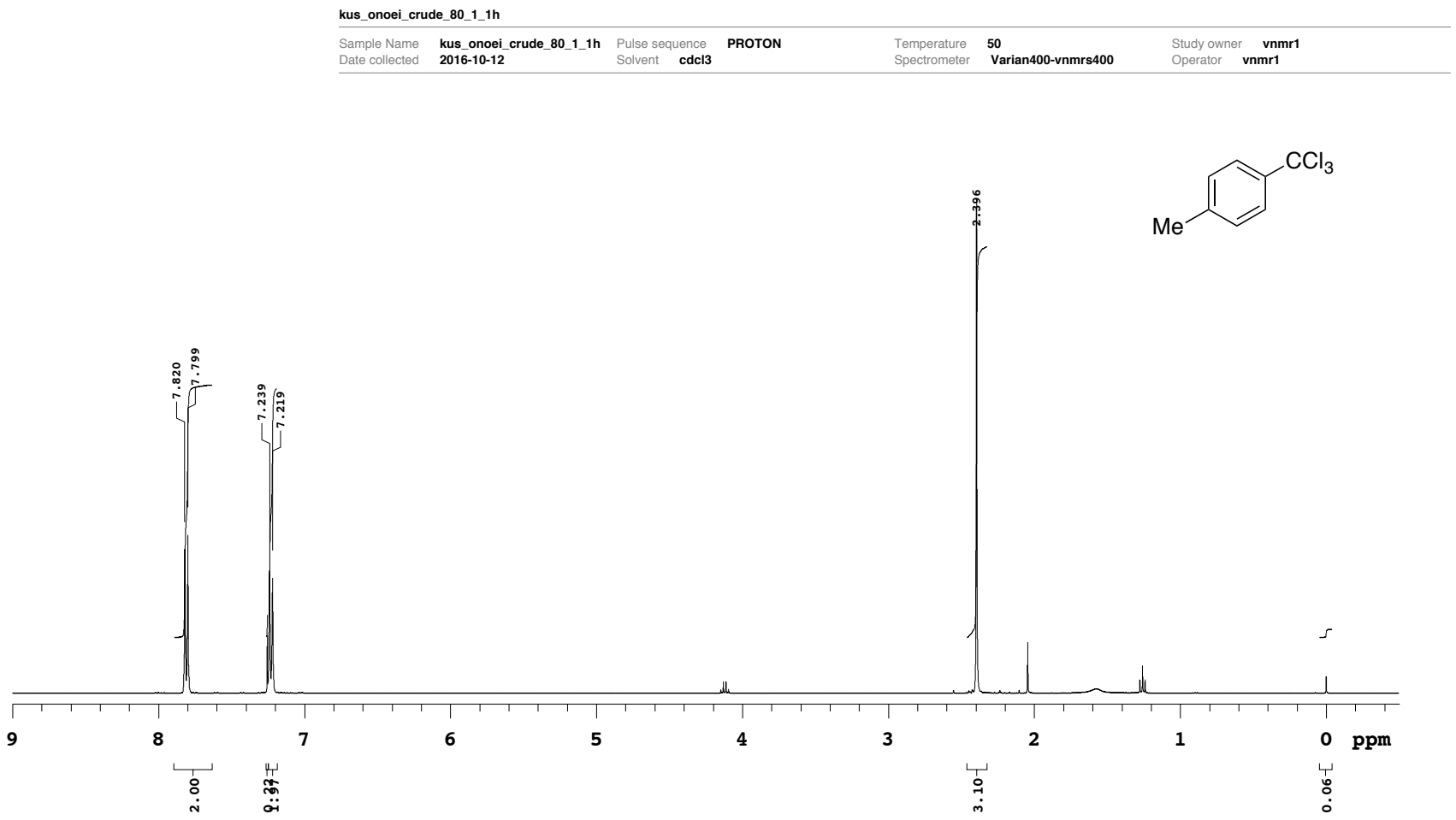
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/o_phenyl_CF3_13C_overnight.fid

Plot date 2016-07-15

^{19}F NMR spectrum of **3b**.



^{1}H NMR spectrum of **6**.



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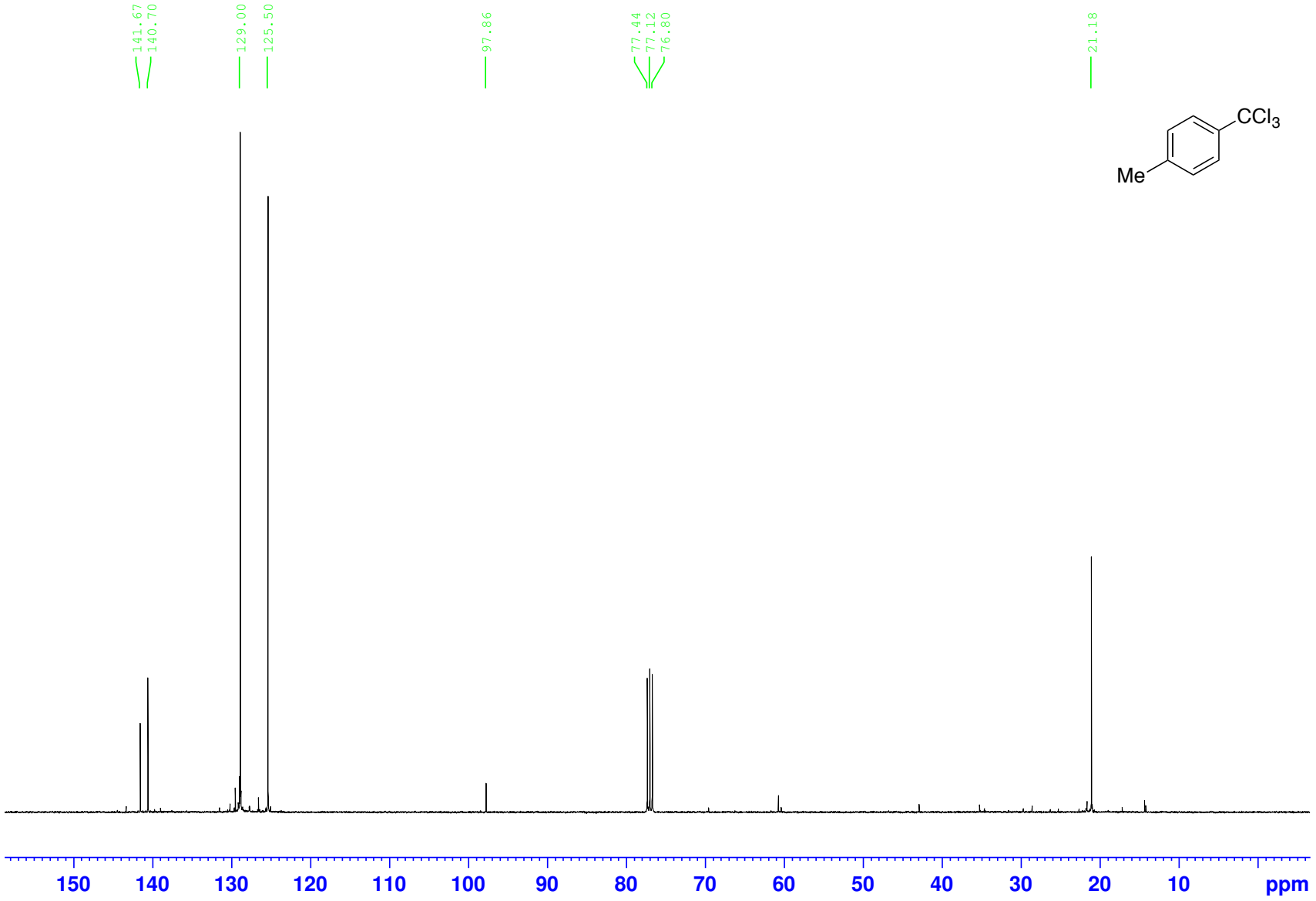
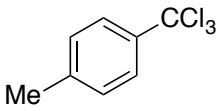
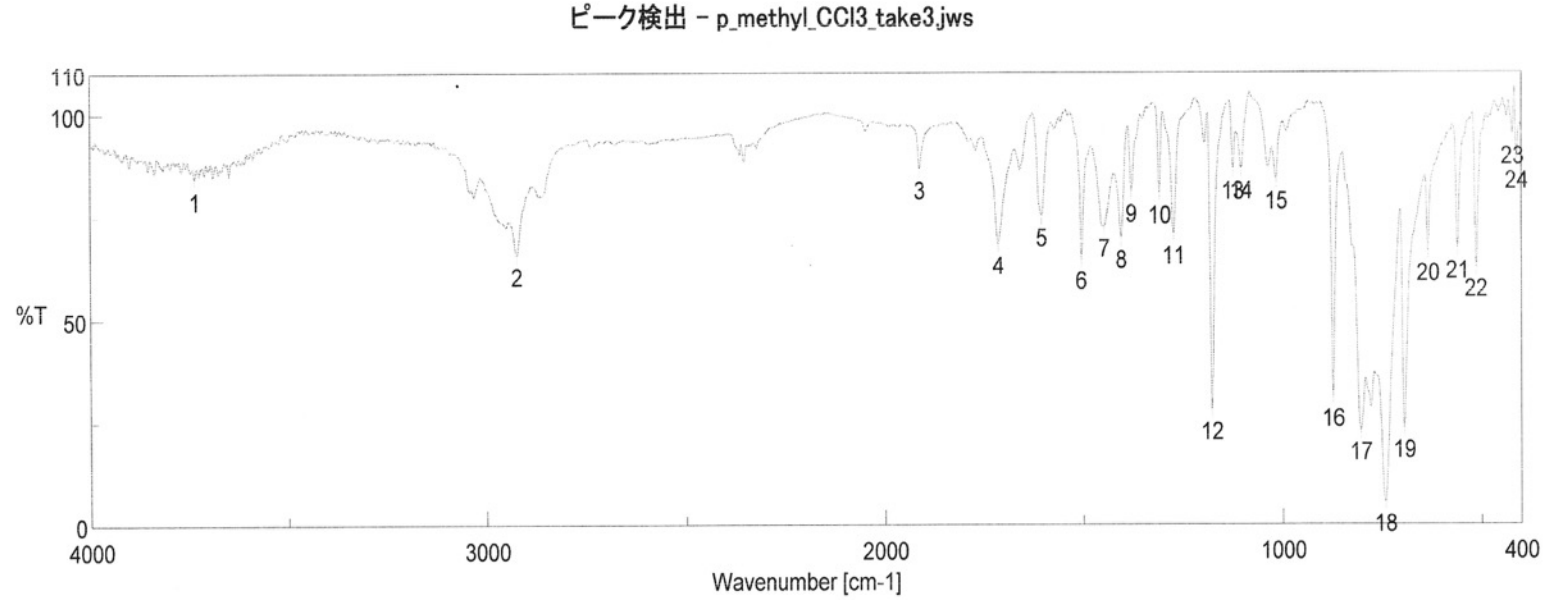
Plot date 2016-10-14

^{13}C NMR spectrum of **6**.



IR spectrum of **6**.





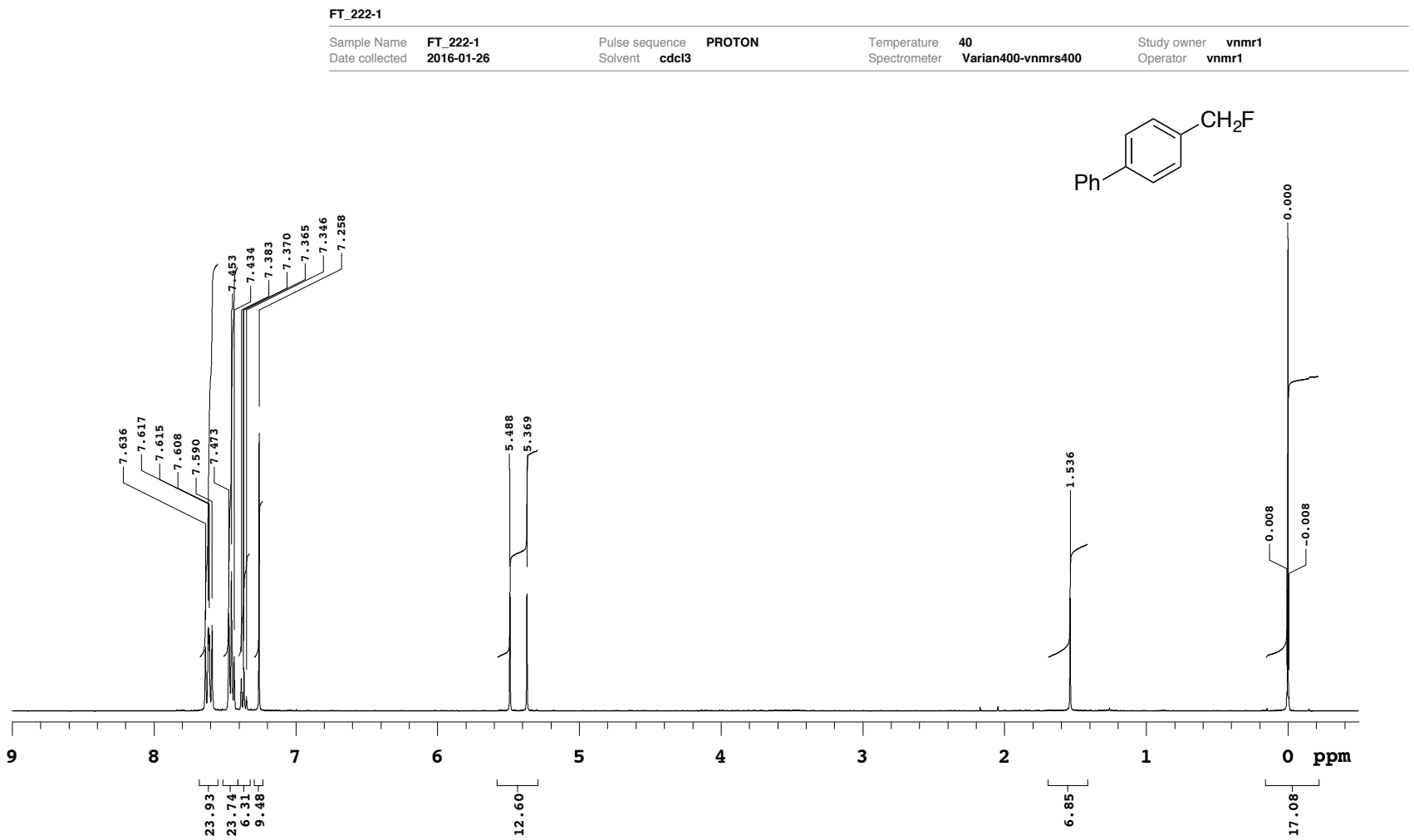
[コメント情報]

試料名	p_methyl_CCl3
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3735.44	84.3132	2	2924.52	65.7506	3	1914	86.6666	4	1715.37	68.4243
5	1606.41	75.1175	6	1506.13	64.7264	7	1449.24	72.5745	8	1405.85	69.875
9	1380.78	81.0051	10	1310.39	80.653	11	1275.68	70.8308	12	1179.26	28.0693
13	1127.19	86.5196	14	1105.98	86.5751	15	1017.27	84.067	16	873.596	31.1847
17	804.171	23.0599	18	742.46	5.51536	19	695.212	23.5757	20	634.466	66.558
21	560.22	67.1487	22	513.936	62.6884	23	422.334	94.9269	24	411.728	88.9335

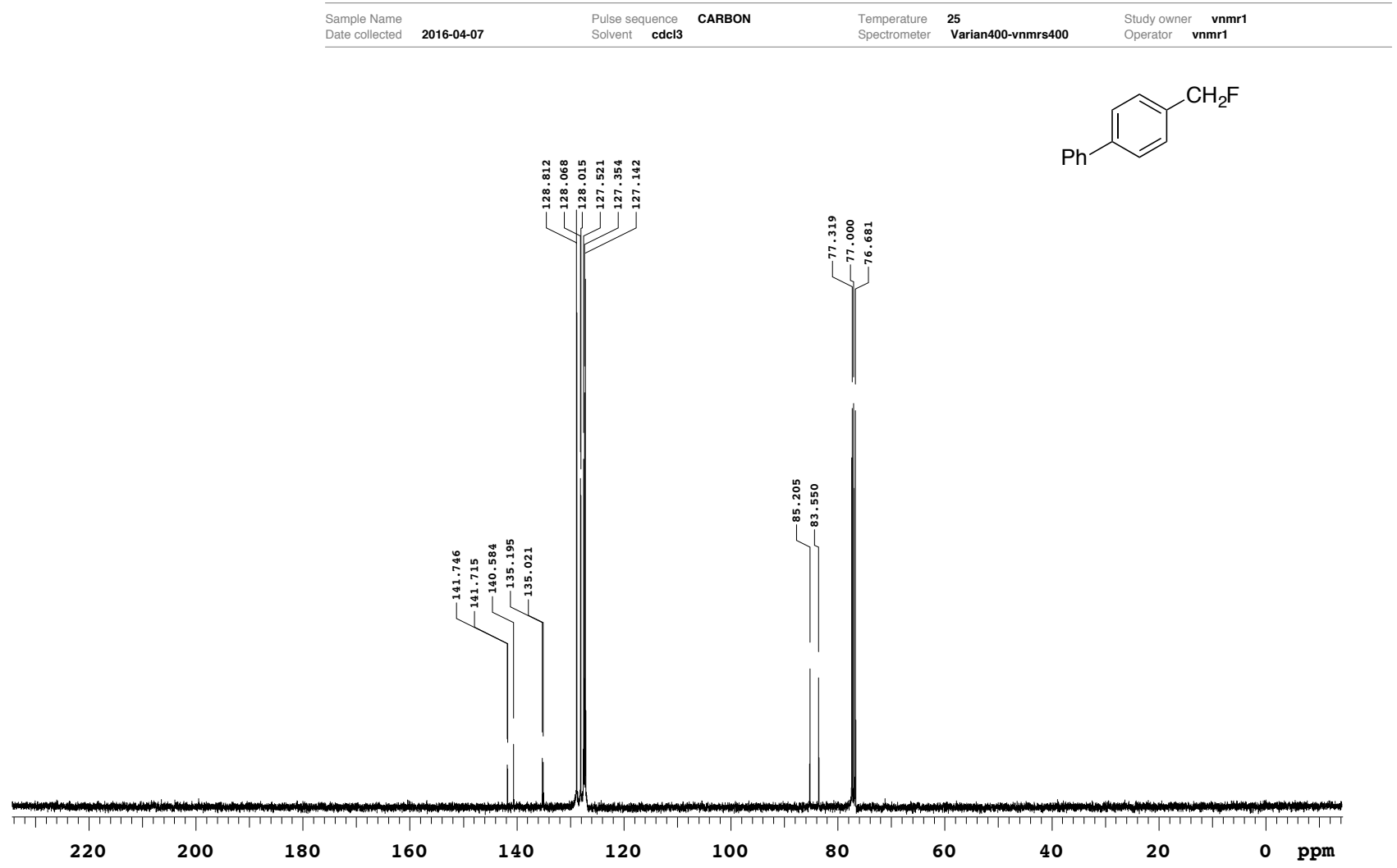
^{1}H NMR spectrum of **7**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CFH2_1H.fid

Plot date 2016-04-18

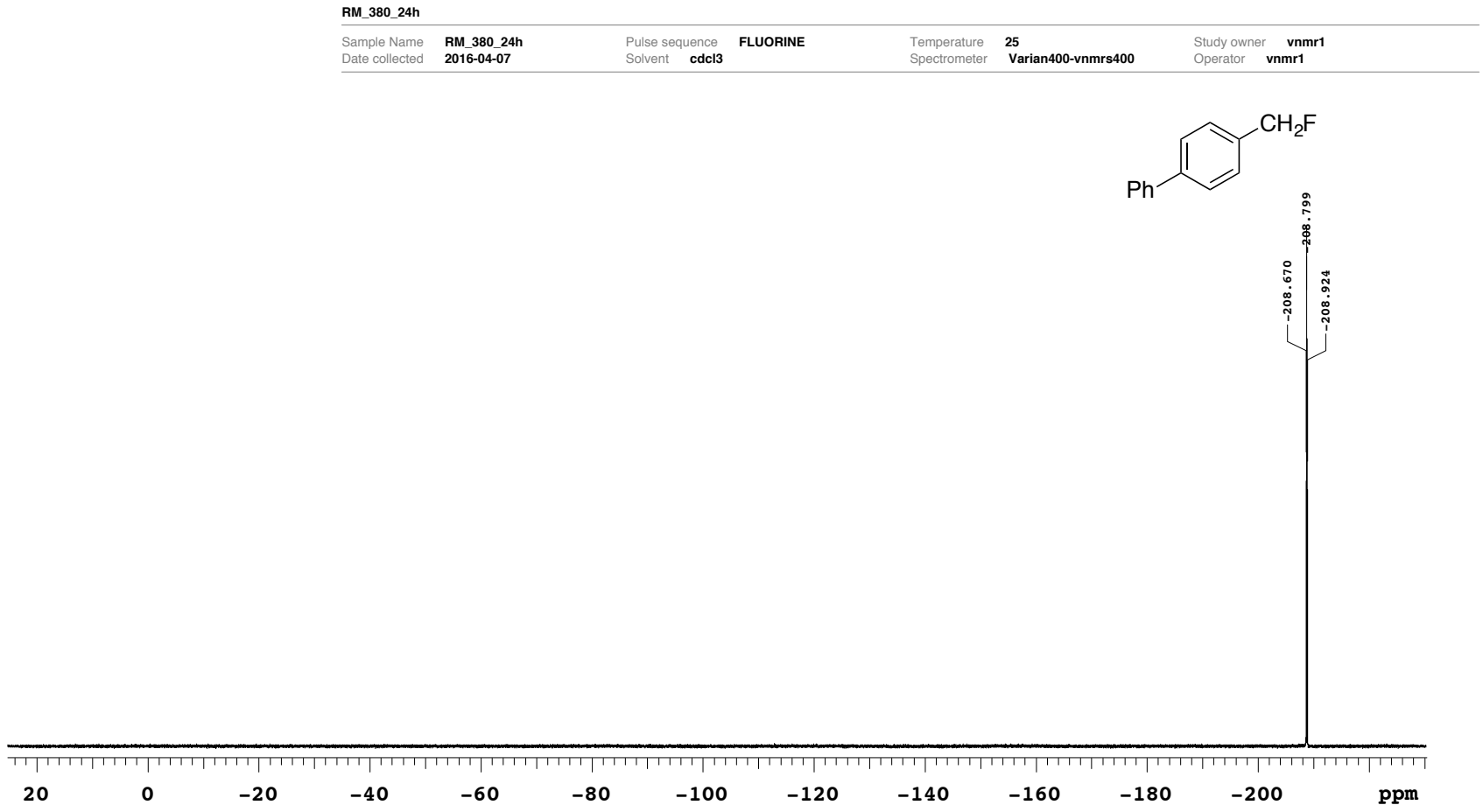
^{13}C NMR spectrum of **7**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CFH2_13C.fid

Plot date 2016-04-18

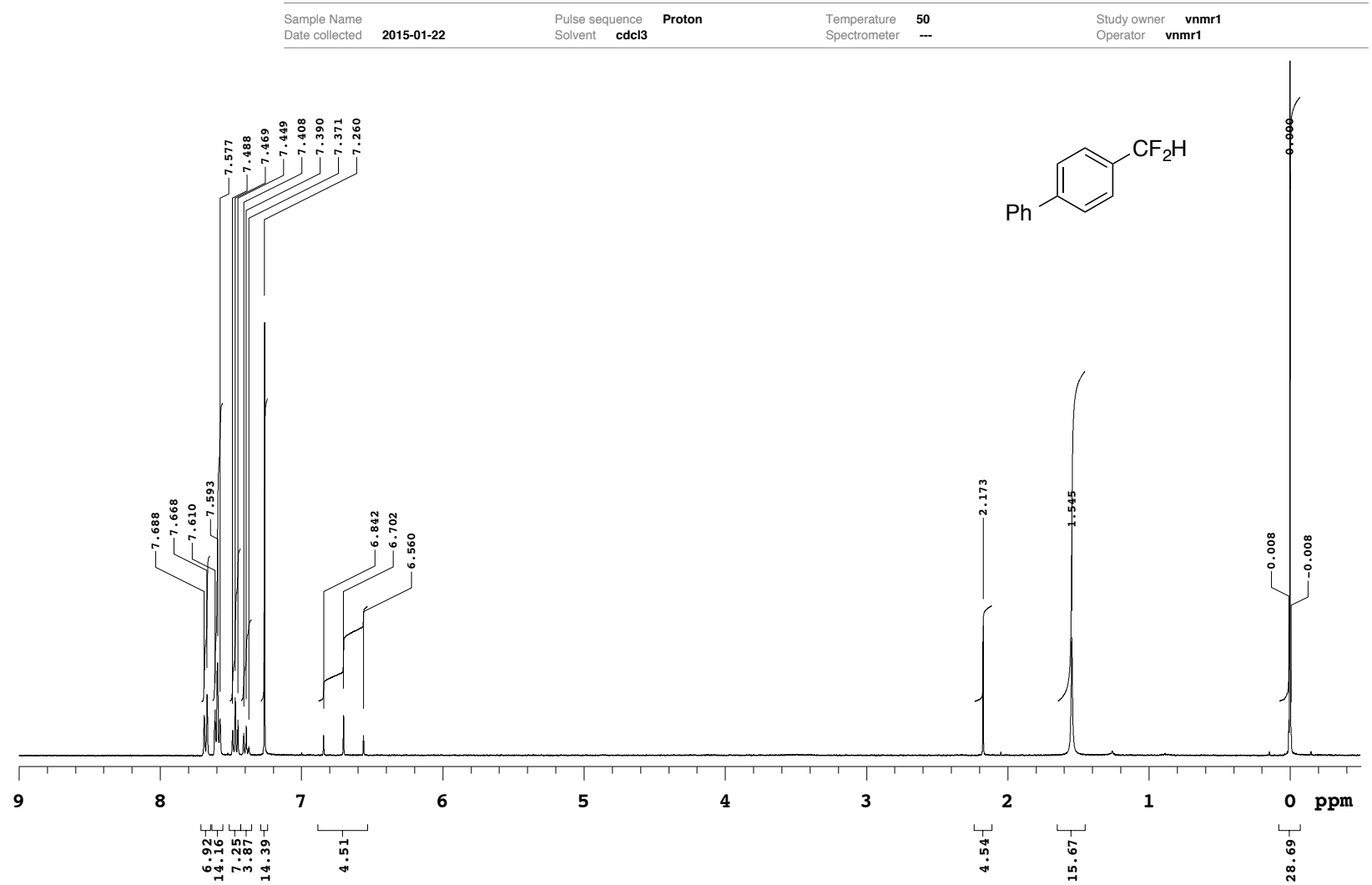
^{19}F NMR spectrum of **7**.



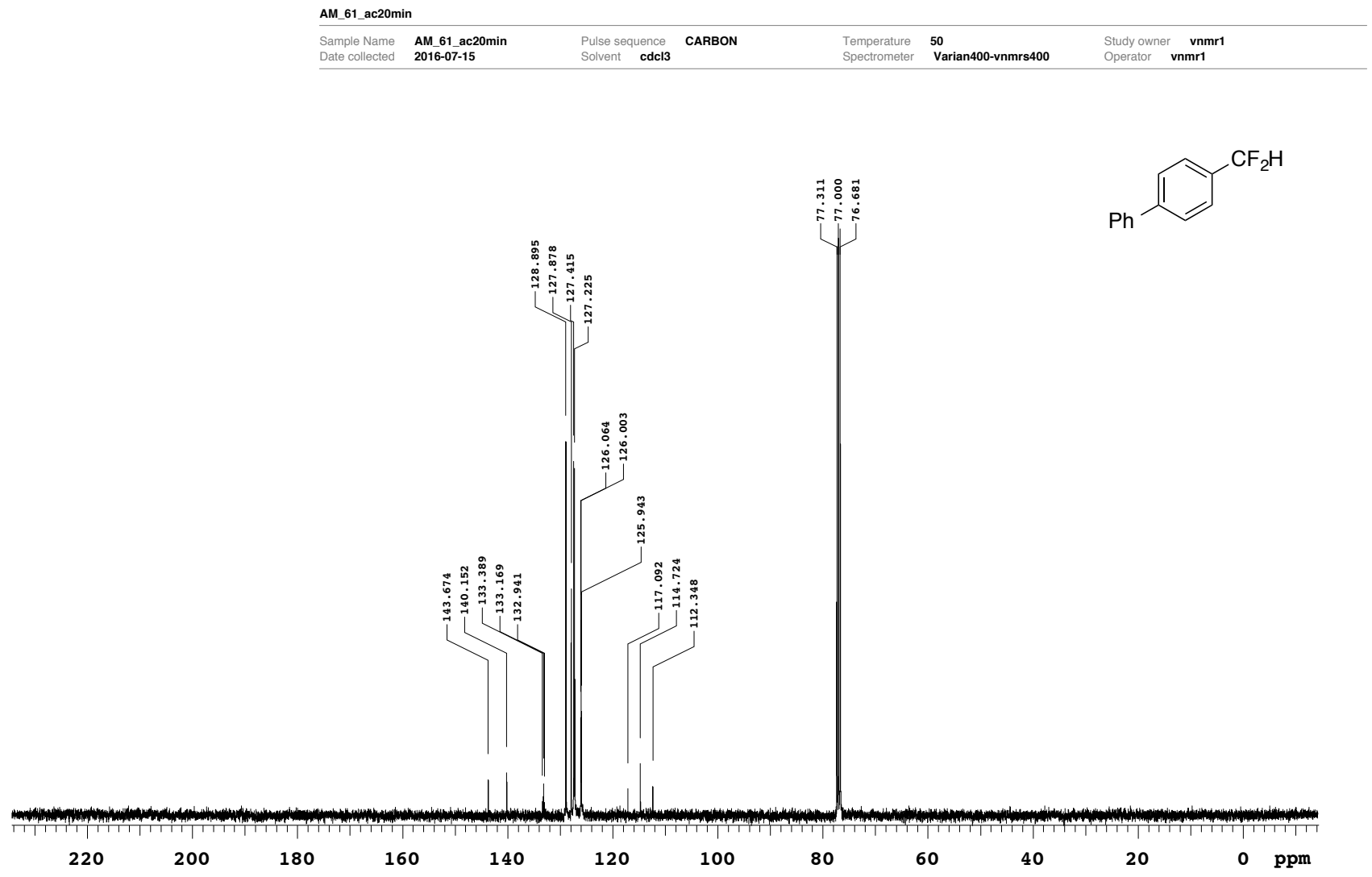
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/p_phenyl_CFH2_19F.fid

Plot date 2016-04-18

^{1}H NMR spectrum of **8**.



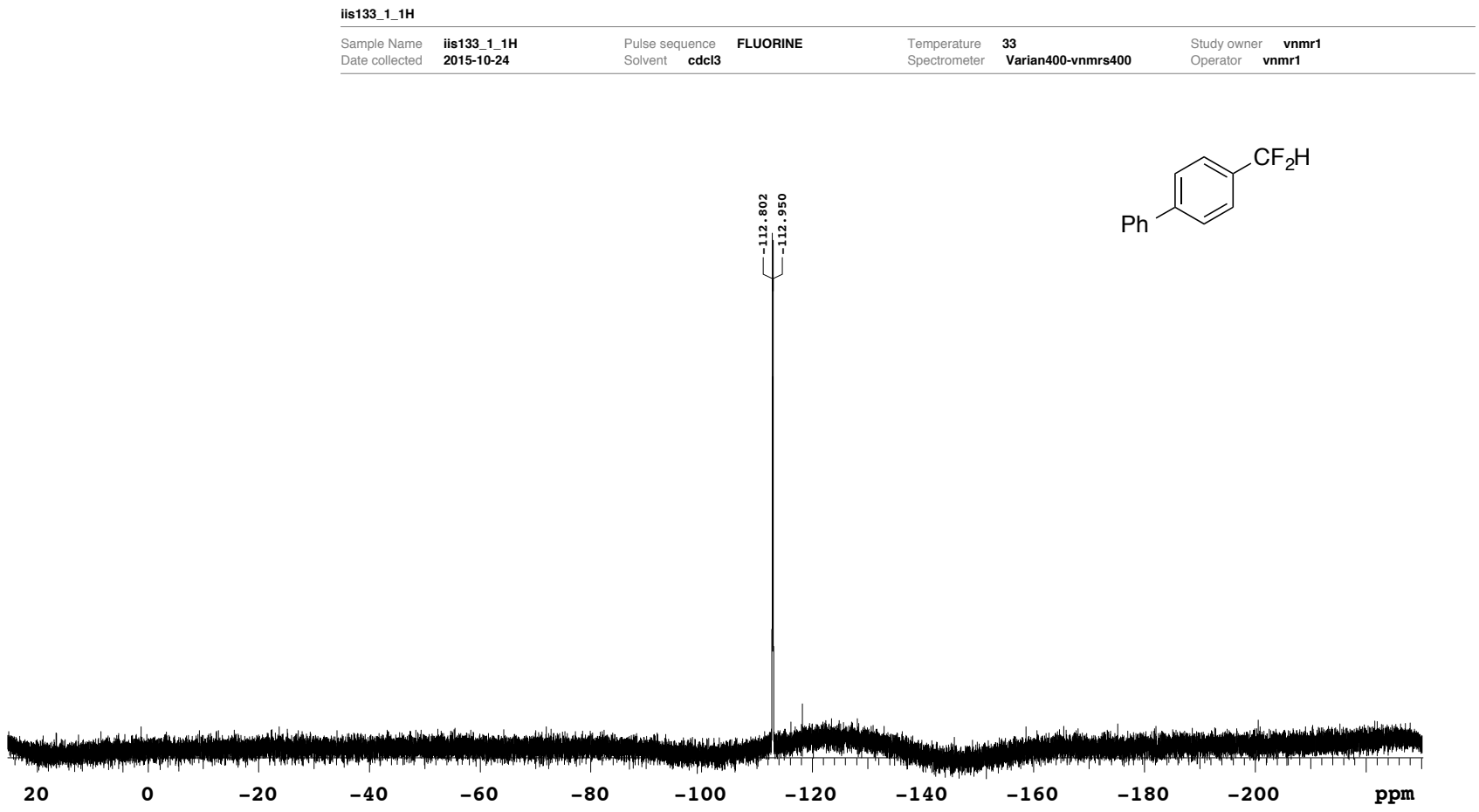
^{13}C NMR spectrum of **8**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_phenyl_CF2H_13C.fid

Plot date 2016-11-12

^{19}F NMR spectrum of **8**.

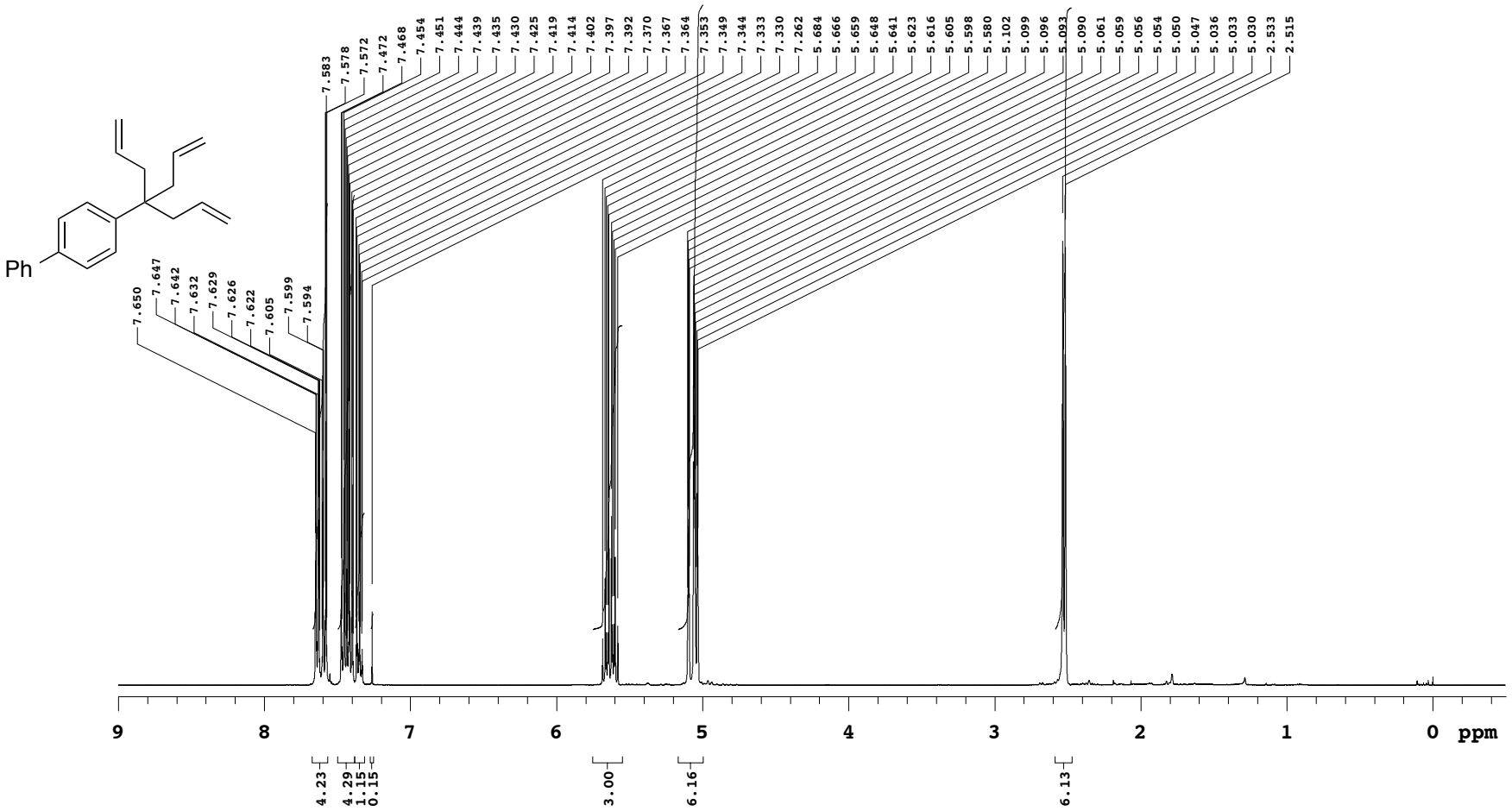


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/NMR data/phenyl_CF2H_19F.fid

Plot date 2015-11-20

^{1}H NMR spectrum of **2a**.

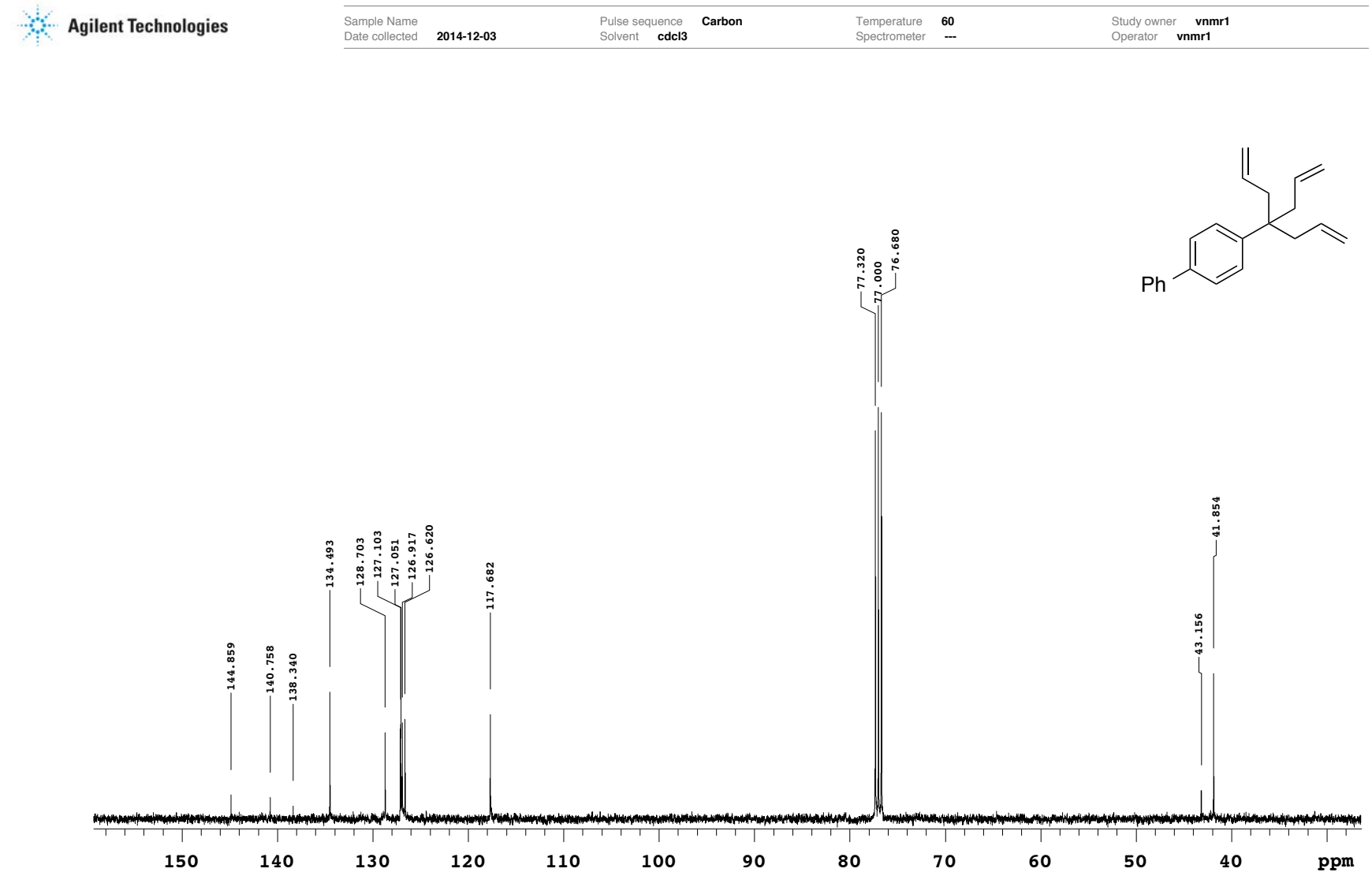
Sample Name		Pulse sequence	**Proton**	Temperature	**50**	Study owner	**vnmr1**
Date collected	**2015-01-10**	Solvent	**cdcl3**	Spectrometer	**---**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/101-200/EXP187-PTLC-H1-1.fid

Plot date 2016-05-24

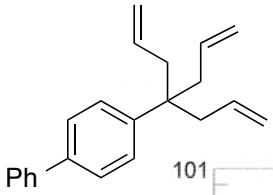
^{13}C NMR spectrum of **2a**.

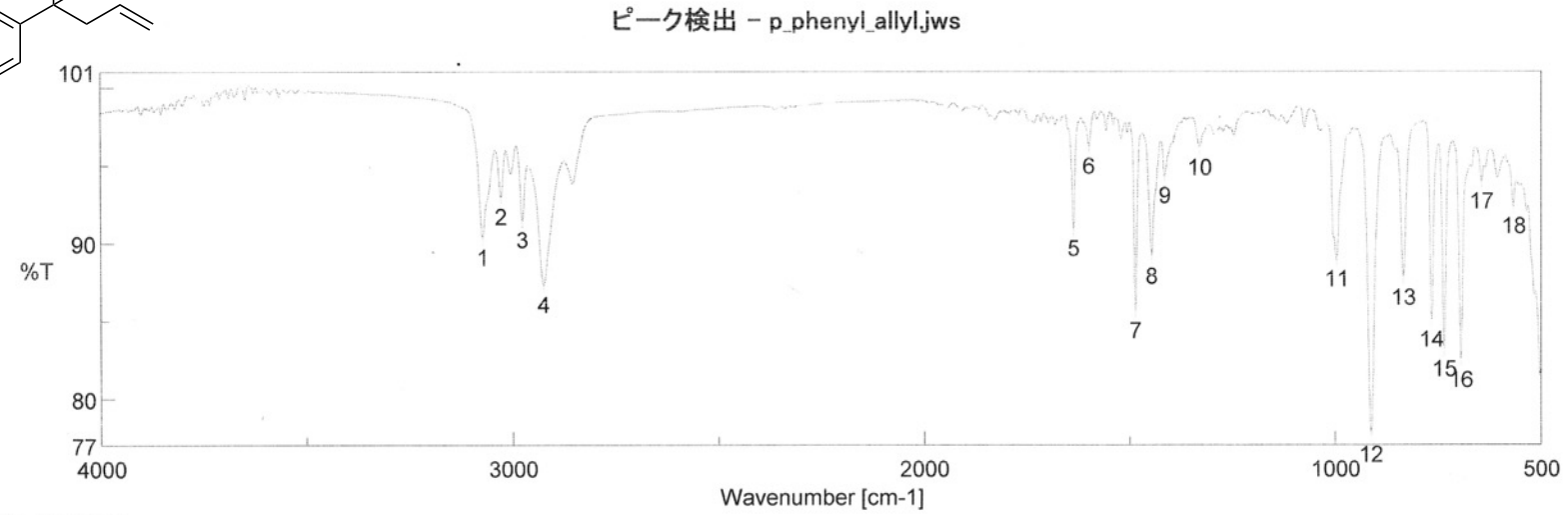


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/101-200/EXP167-PTLC-13C-2.fid

Plot date 2015-10-10

IR spectrum of **2a**.





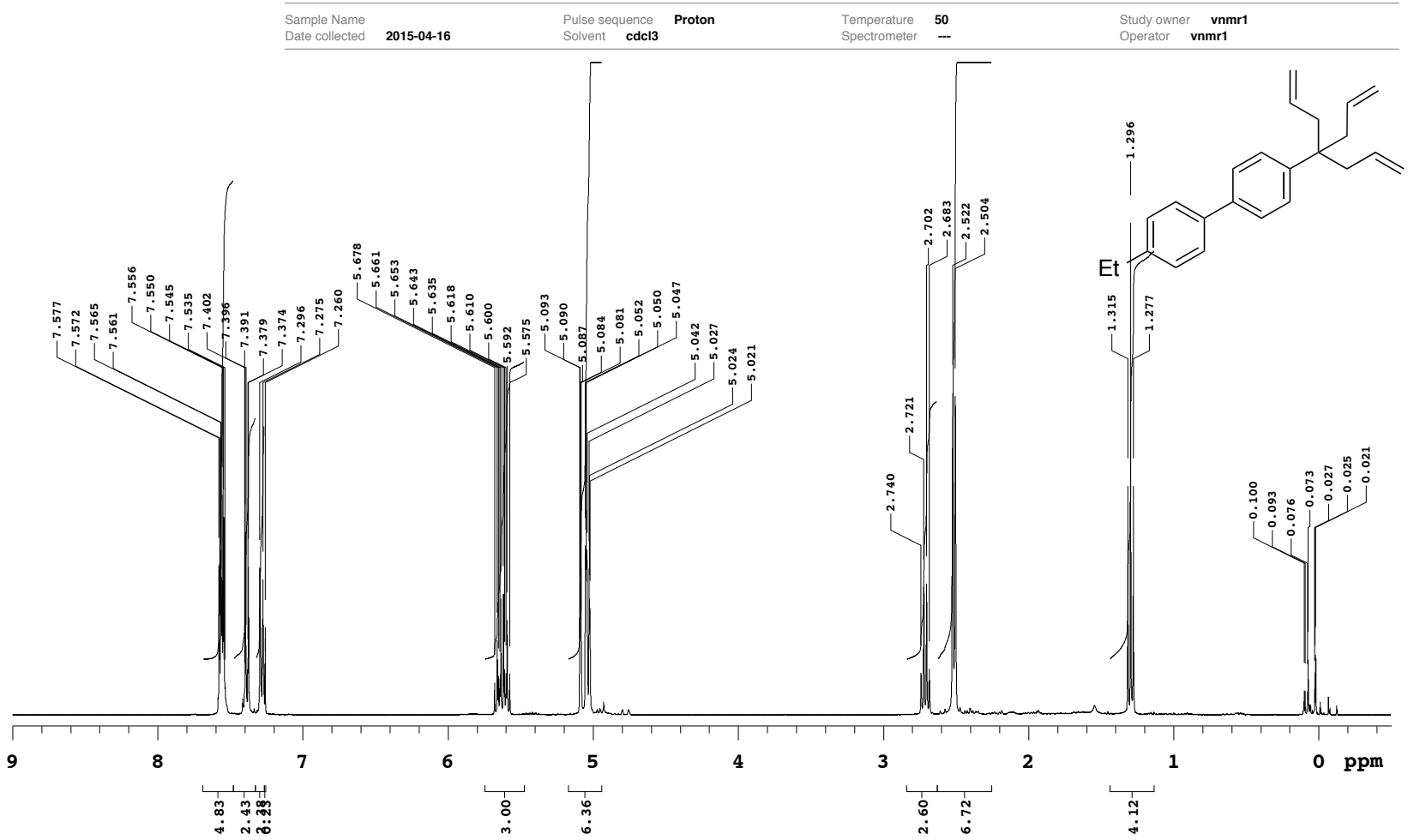
[コメント情報]

試料名	p_phenyl_allyl
コメント	
測定者	
所属	
会社	学習院大学

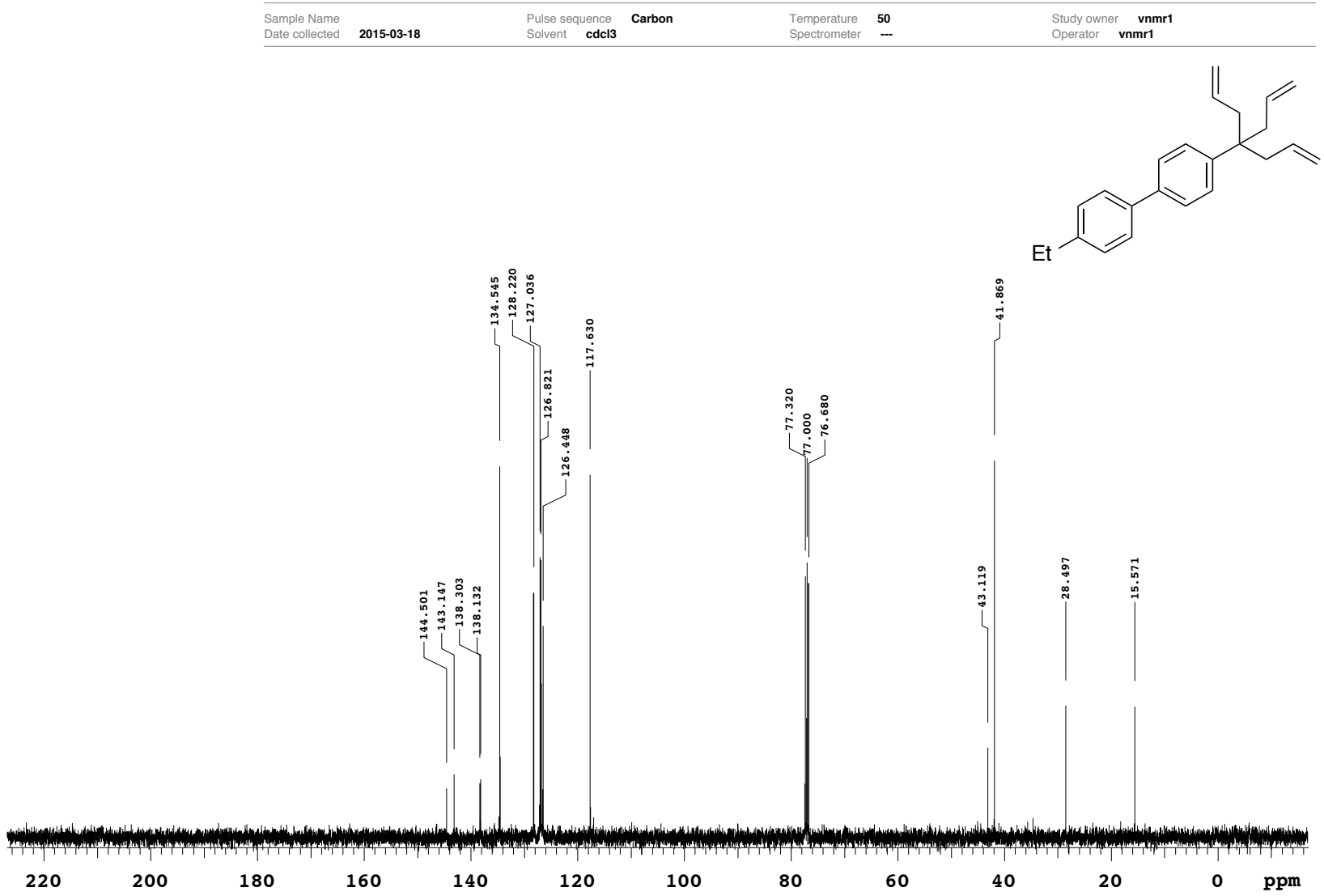
[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3073.98	90.3238	2	3028.66	92.9475	3	2977.55	91.4573	4	2925.48	87.2879
5	1638.23	90.8877	6	1600.63	96.183	7	1486.85	85.6342	8	1447.31	89.1146
9	1415.49	94.3094	10	1330.64	96.0988	11	997.017	88.936	12	913.129	77.6459
13	835.026	87.7545	14	767.53	85.0542	15	736.674	83.1444	16	696.177	82.4612
17	646.036	93.9496	18	567.934	92.3635						

^{1}H NMR spectrum of **2b**.



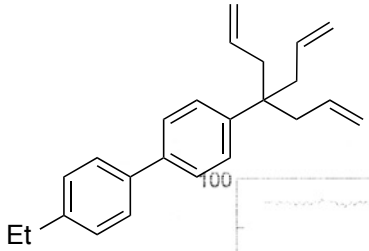
^{13}C NMR spectrum of **2b**.

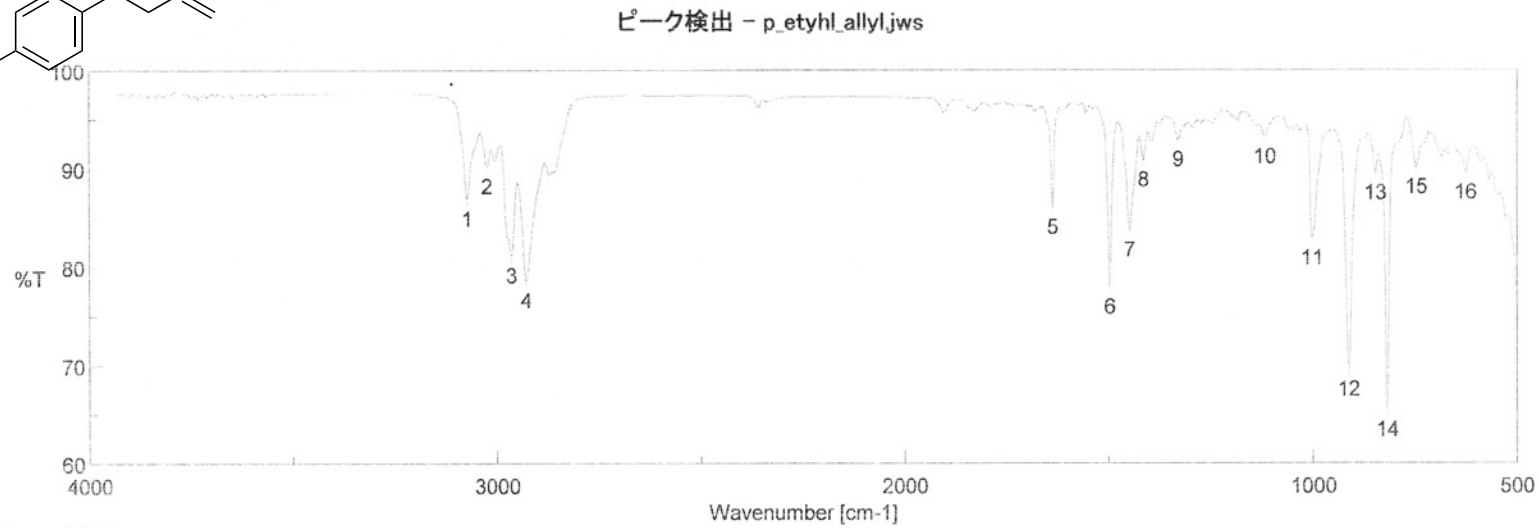


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP203-PTLC-C13-2.fid

Plot date 2015-10-31

IR spectrum of **2b**.





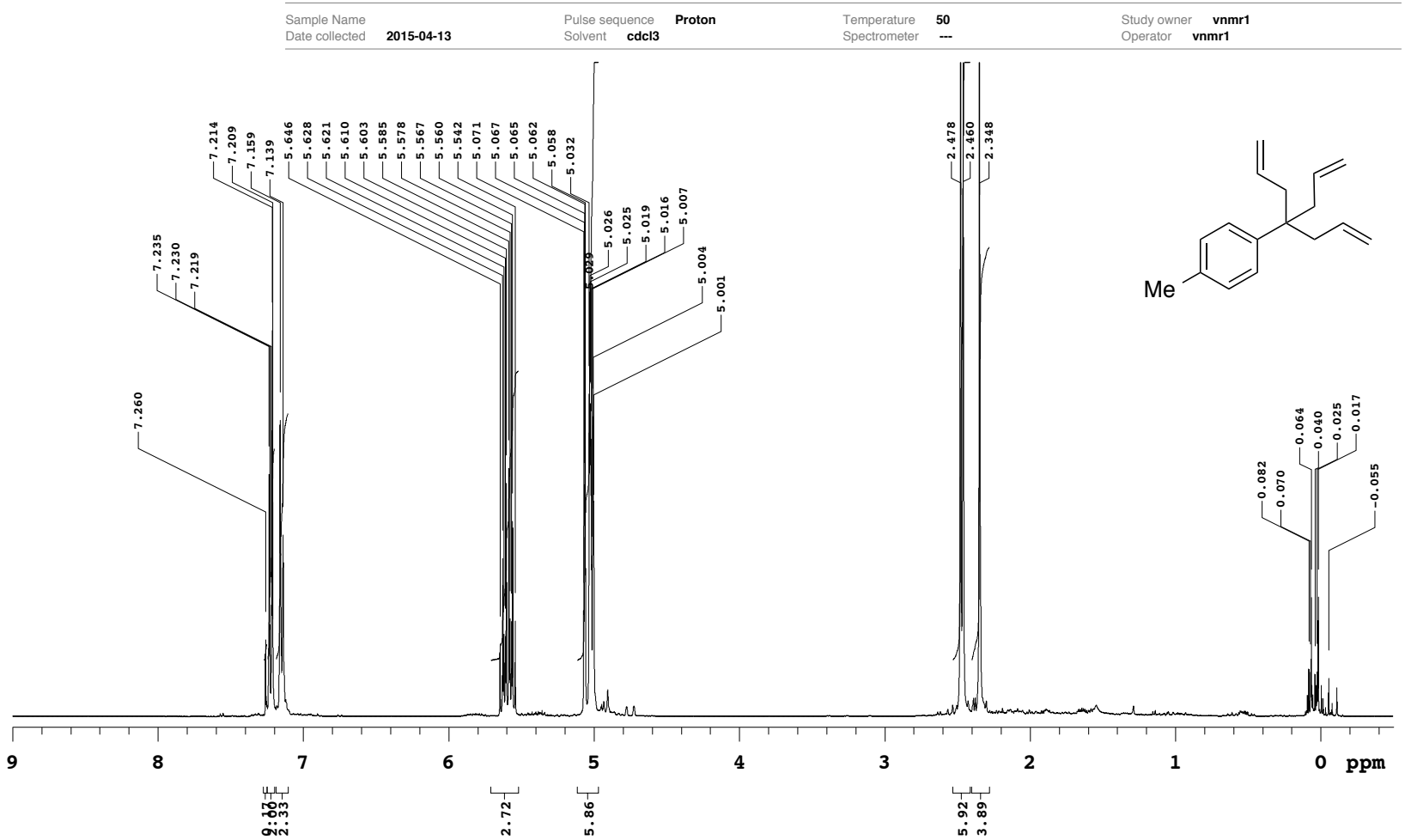
[コメント情報]

試料名	p_ethyl_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3073.98	86.8562	2	3024.8	90.16	3	2965.02	81.0744	4	2928.38	78.5481
5	1638.23	86.0376	6	1497.45	77.9061	7	1449.24	83.6976	8	1415.49	90.8271
9	1330.64	92.8903	10	1118.51	93.1919	11	1002.8	82.8624	12	913.129	69.5329
13	848.525	89.4744	14	819.598	65.3862	15	748.245	90.1178	16	625.788	89.5659

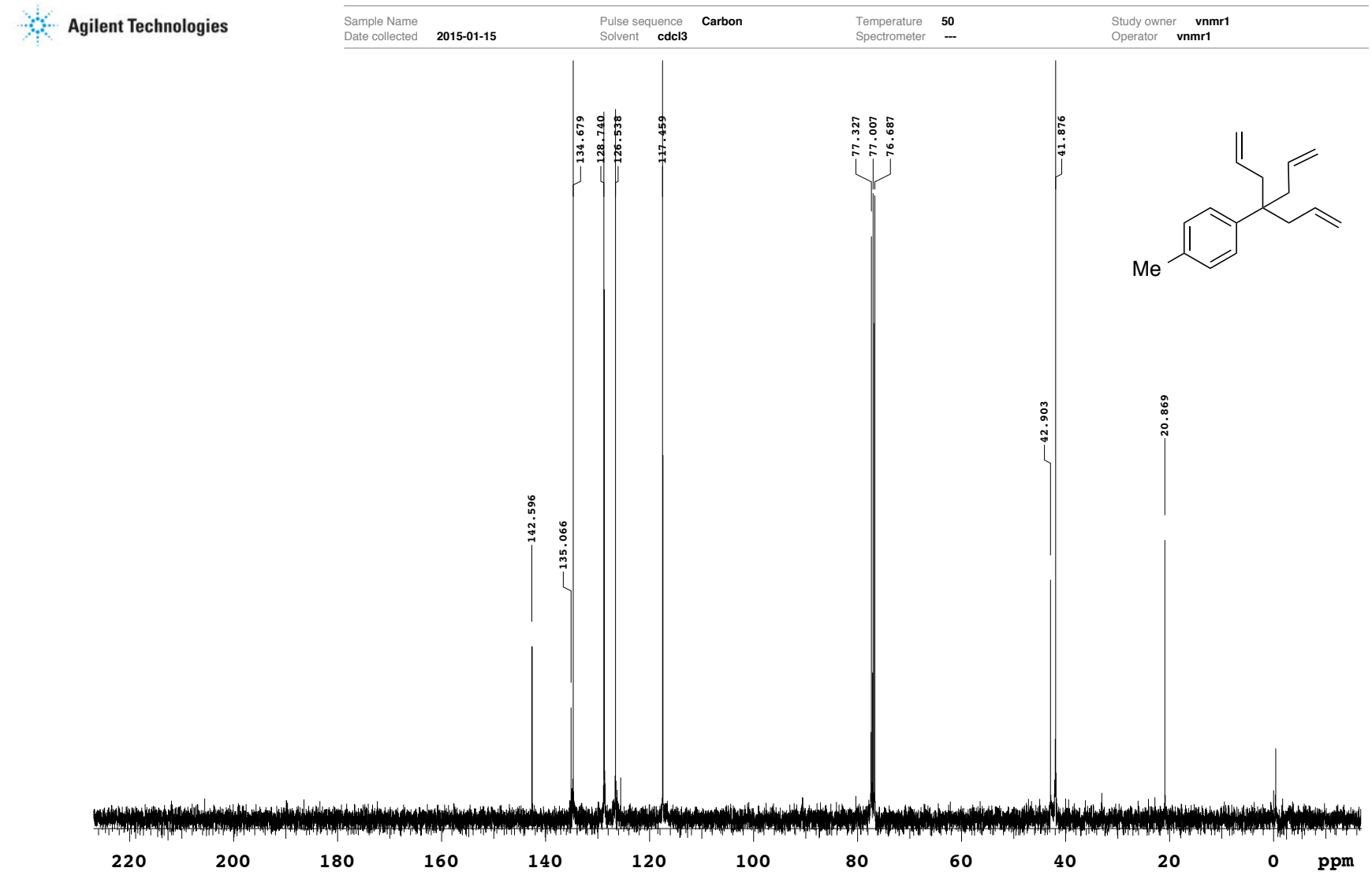
^{1}H NMR spectrum of **2c**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_methyl_allyl_1H.fid

Plot date 2016-07-13

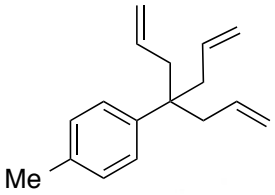
^{13}C NMR spectrum of **2c**.

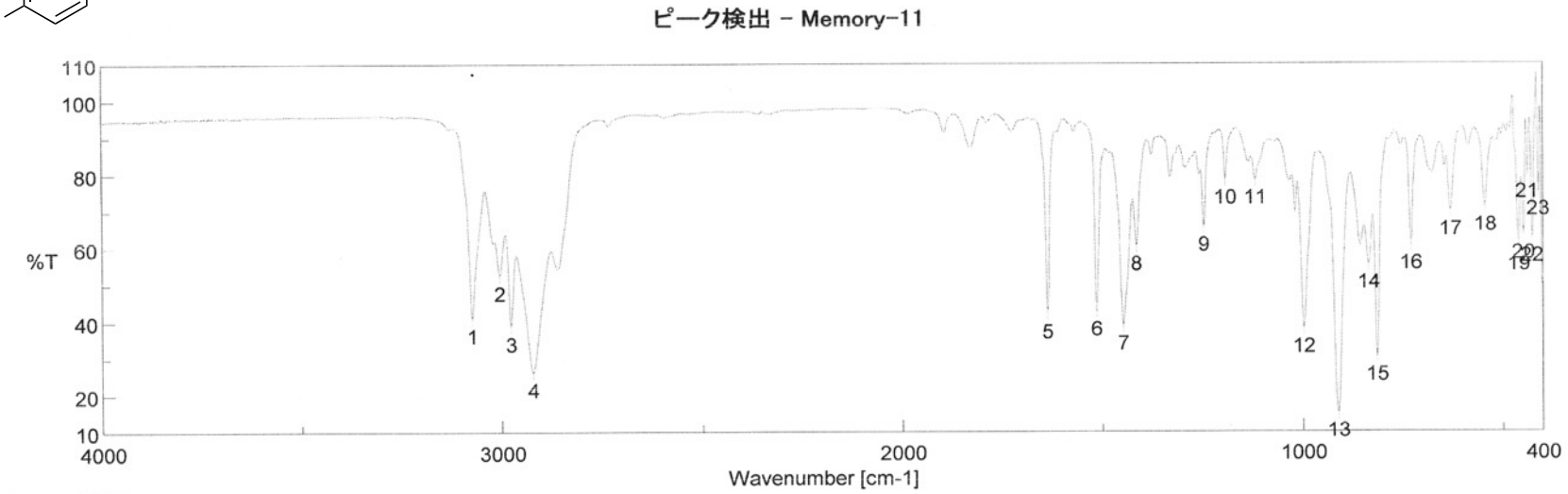


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/101-200/EXP188-PTLC-C13-1.fid

Plot date 2015-10-10

IR spectrum of **2c**.





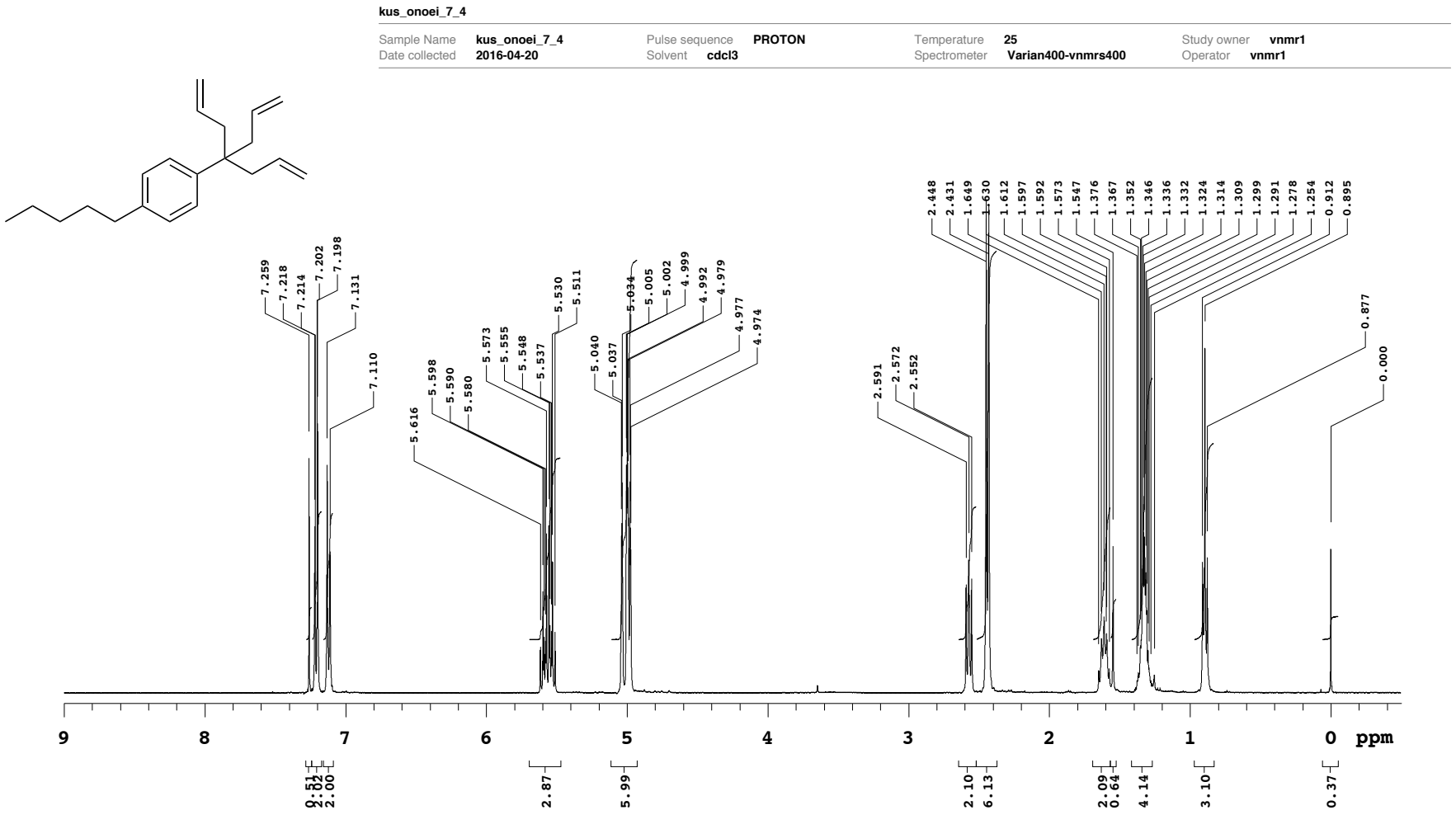
[コメント情報]

試料名	p_methyl_allyl
コメント	
測定者	
所属	
会社	学習院大学

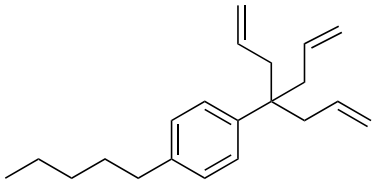
[ピーク検出結果]

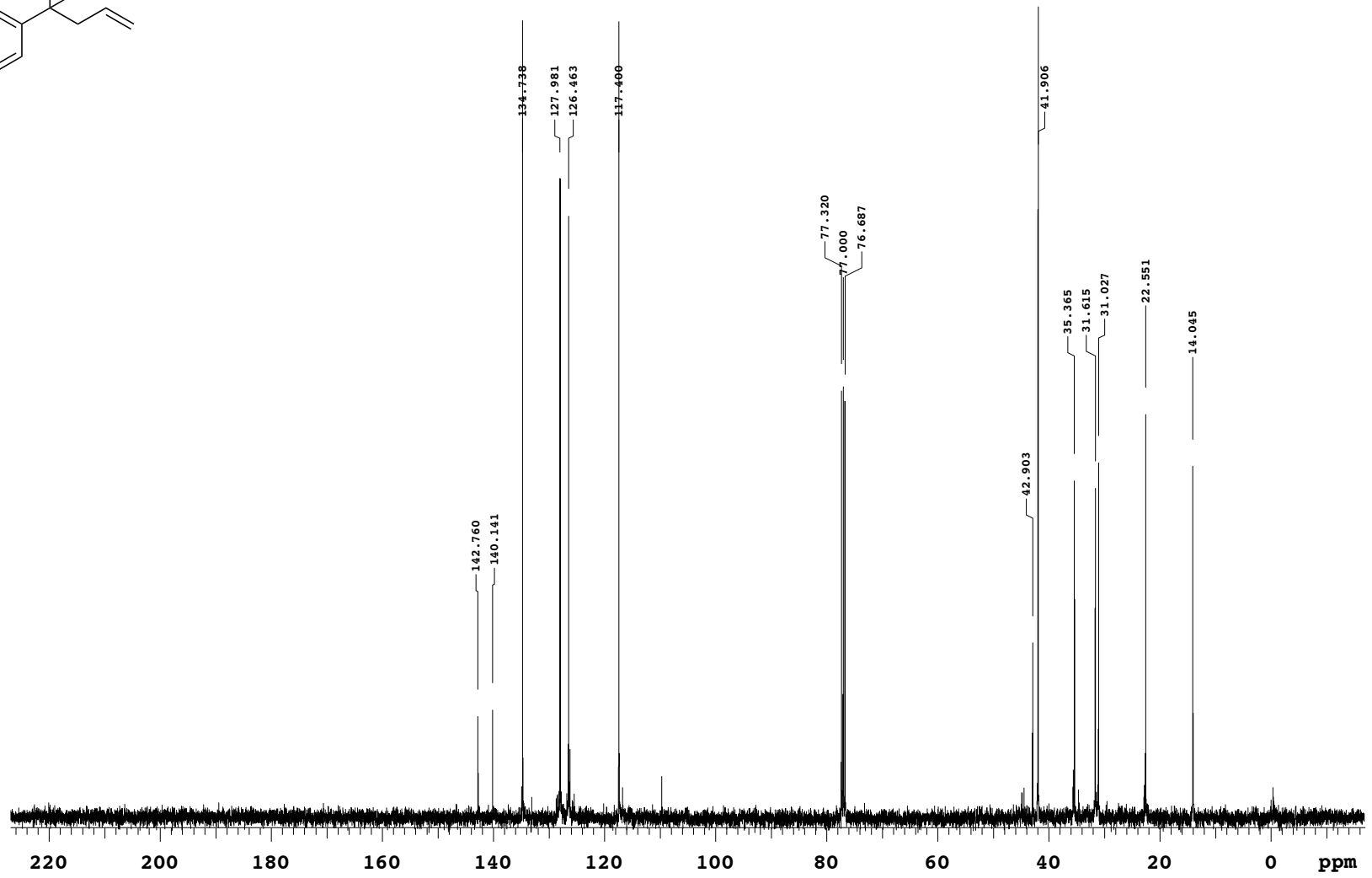
No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3074.94	41.0473	2	3005.52	52.5545	3	2977.55	38.7597	4	2922.59	26.2535
5	1638.23	41.9919	6	1514.81	42.773	7	1448.28	38.9269	8	1415.49	60.4963
9	1247.72	65.6767	10	1194.69	78.525	11	1119.48	78.5199	12	997.982	38.0819
13	912.165	15.1538	14	836.955	55.484	15	815.742	30.4351	16	730.889	60.6904
17	631.573	69.9467	18	544.792	71.0622	19	460.904	60.3072	20	448.369	63.4661
21	439.69	80.0064	22	427.155	62.6065	23	411.728	75.3419			

^{1}H NMR spectrum of **2d**.

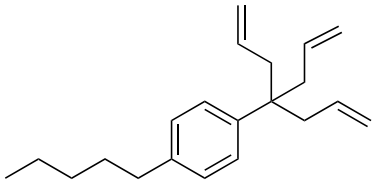


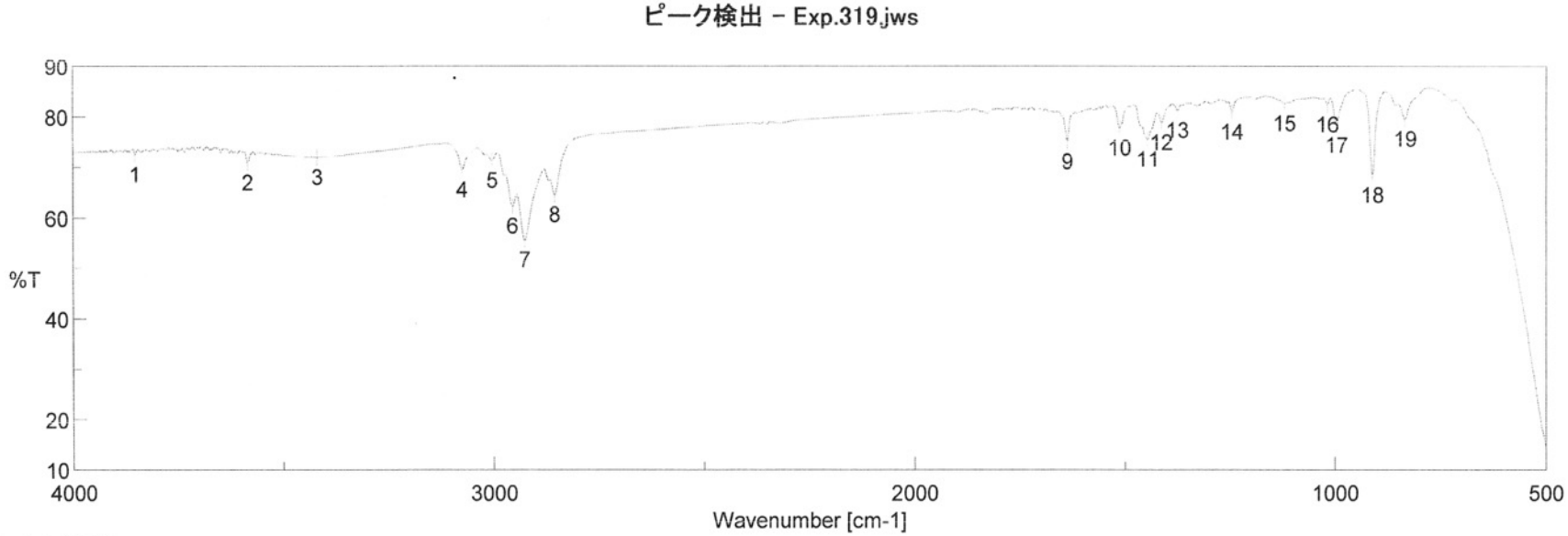
^{13}C NMR spectrum of **2d**.





IR spectrum of **2d**.





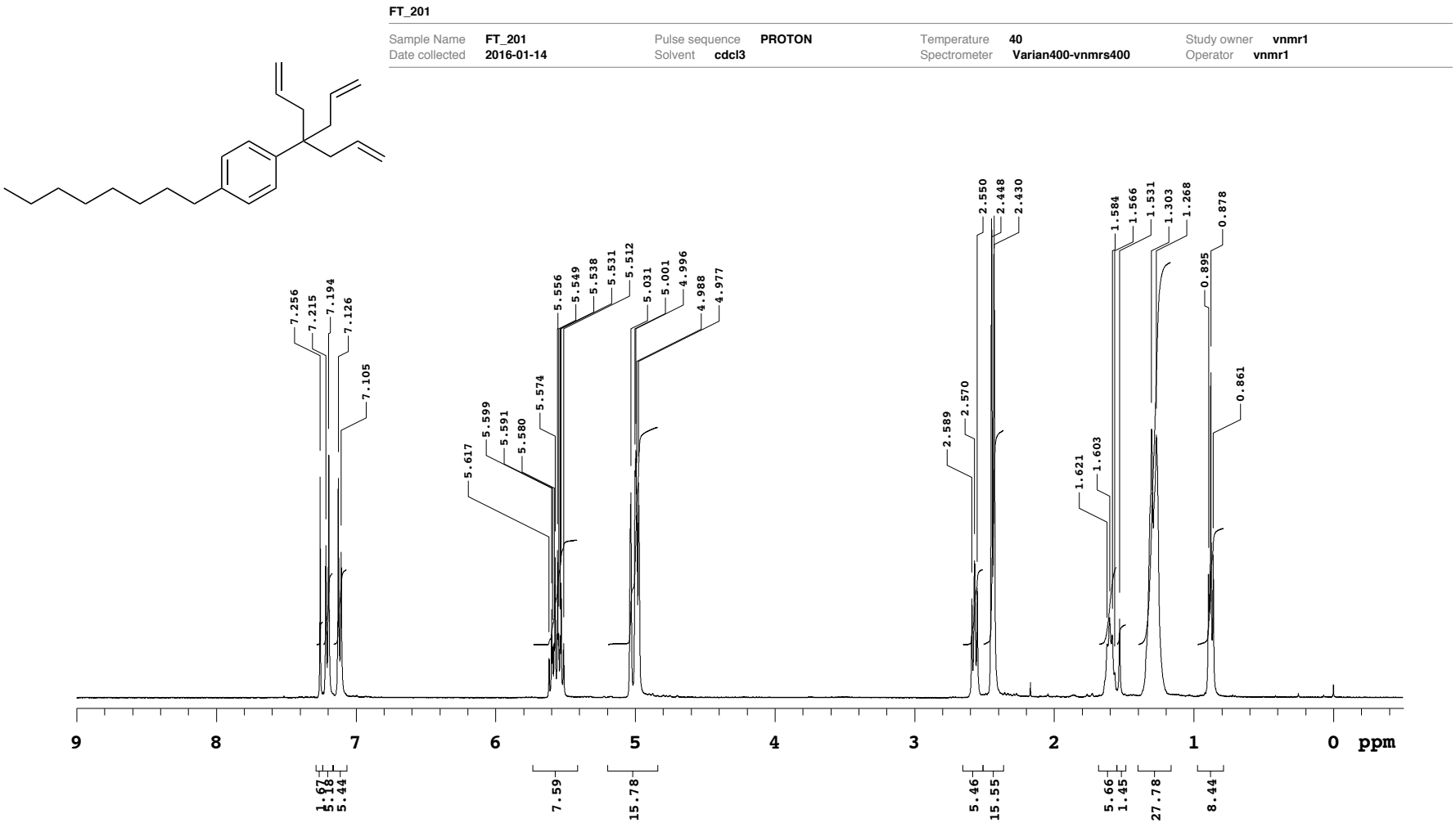
[コメント情報]

試料名	p_pentyl_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3852.11	72.4353	2	3584.06	70.8344	3	3419.17	71.9441	4	3074.94	69.5052
5	3004.55	71.329	6	2956.34	62.3079	7	2927.41	55.604	8	2857.02	64.5714
9	1638.23	75.0179	10	1514.81	77.7087	11	1448.28	75.4085	12	1415.49	78.831
13	1377.89	81.1973	14	1247.72	80.9071	15	1122.37	82.5616	16	1019.19	82.3236
17	997.982	78.3011	18	912.165	68.381	19	835.026	79.4732			

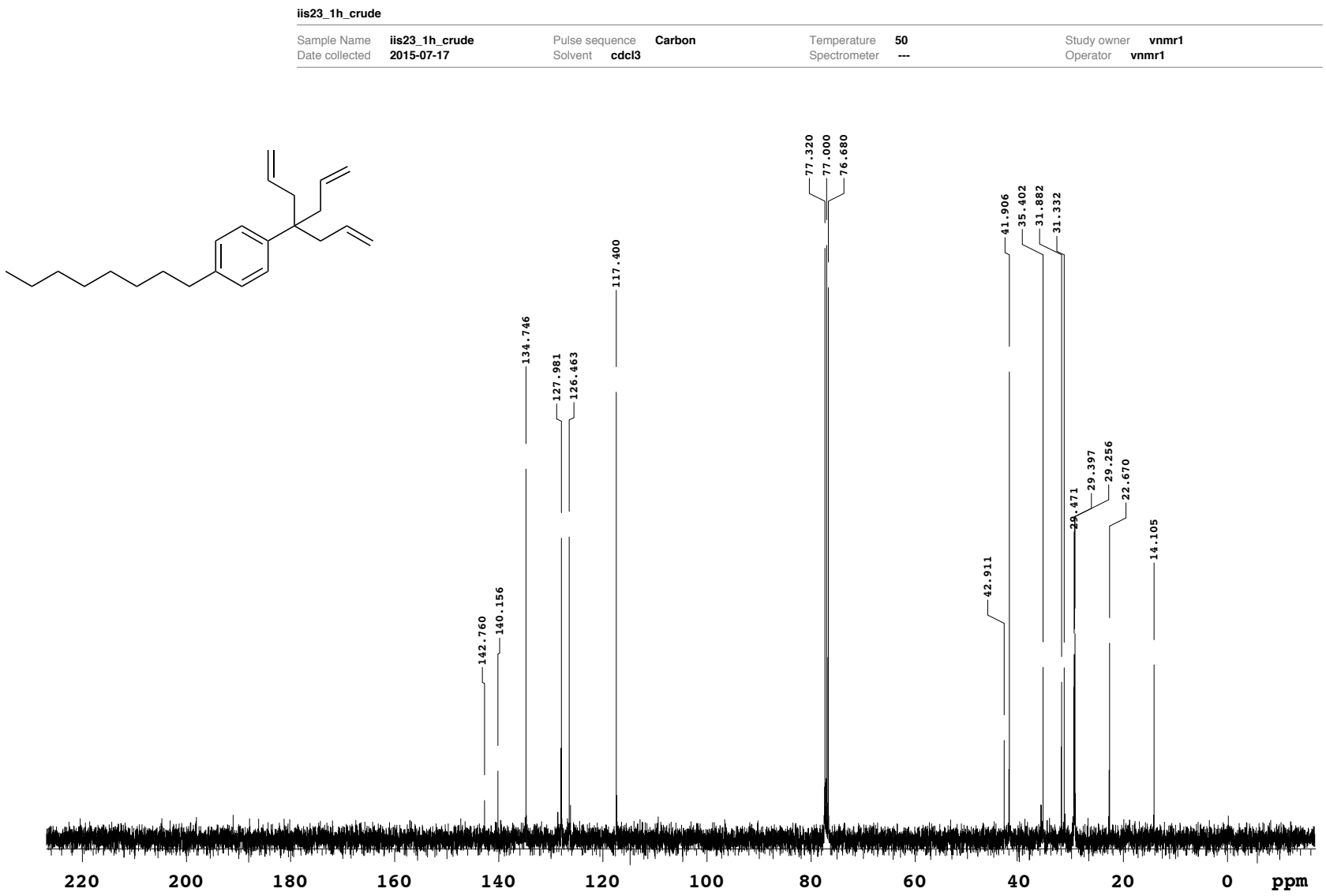
^{1}H NMR spectrum of **2e**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/401-500/Exp.412_PTLC_1_H1_take2.fid

Plot date 2016-02-19

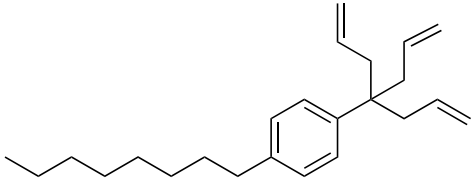
^{13}C NMR spectrum of **2e**.

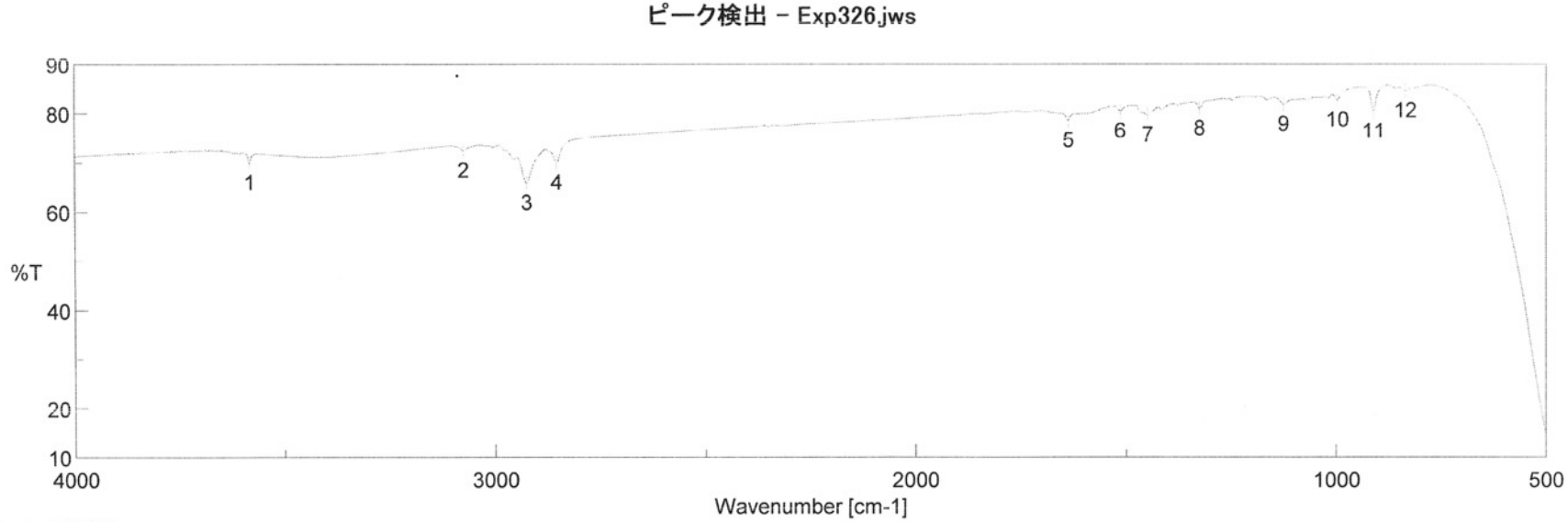


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/301-400/EXP326-PTLC-C13-2.fid

Plot date 2015-10-14

IR spectrum of **2e**.



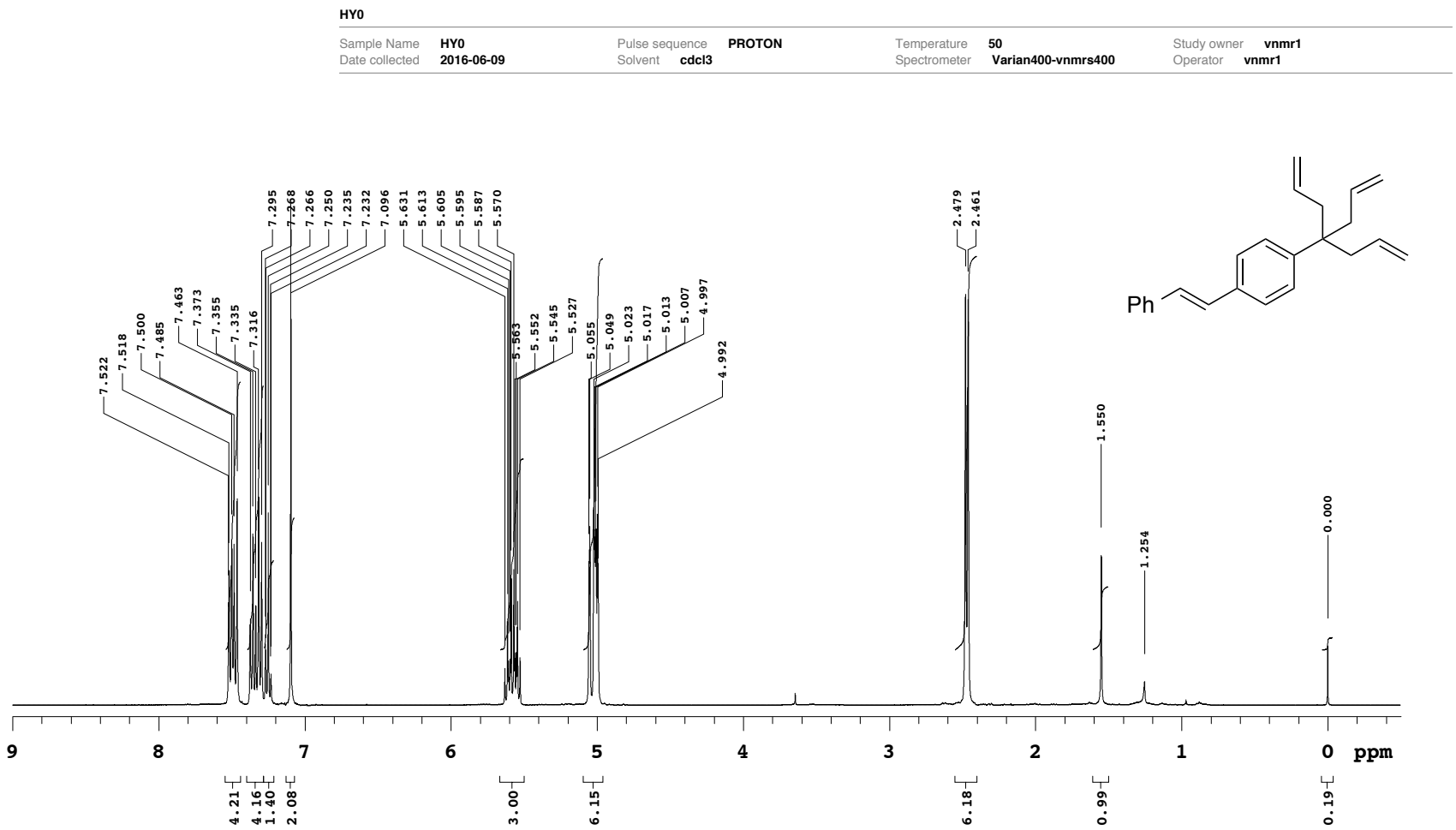


[コメント情報]
試料名 p_octyl_allyl
コメント
測定者
所属
会社 学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3583.09	69.8892	2	3074.94	72.4055	3	2925.48	65.8157	4	2854.13	69.9331
5	1638.23	78.5009	6	1514.81	80.389	7	1449.24	79.6042	8	1325.82	80.8795
9	1126.22	81.7692	10	997.982	82.6655	11	912.165	80.3019	12	835.99	84.5368

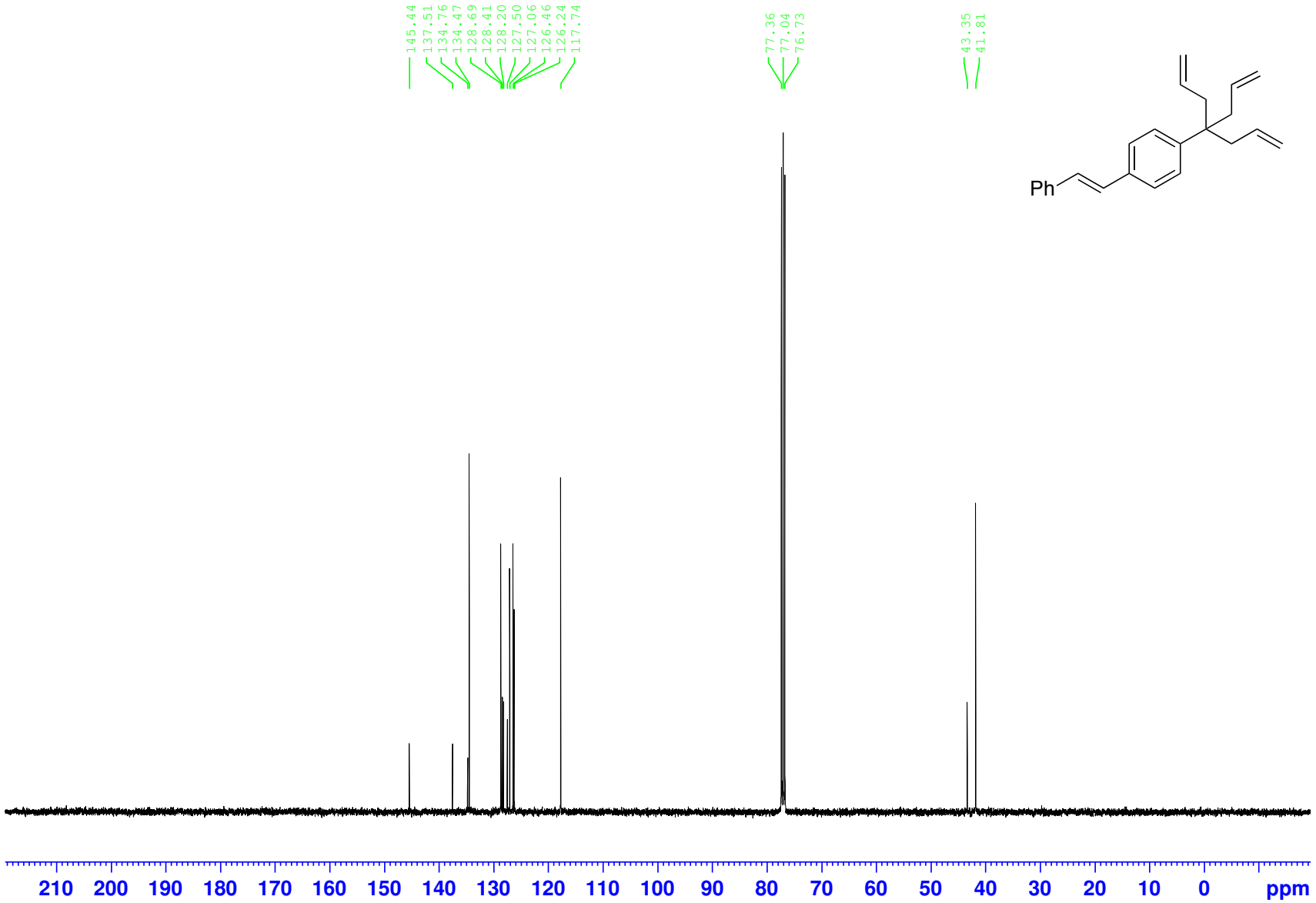
^{1}H NMR spectrum of **2f**.



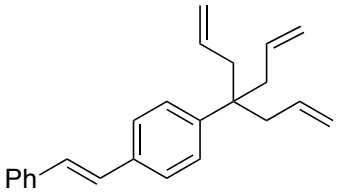
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_phenyl_alkene_allyl_1H.fid

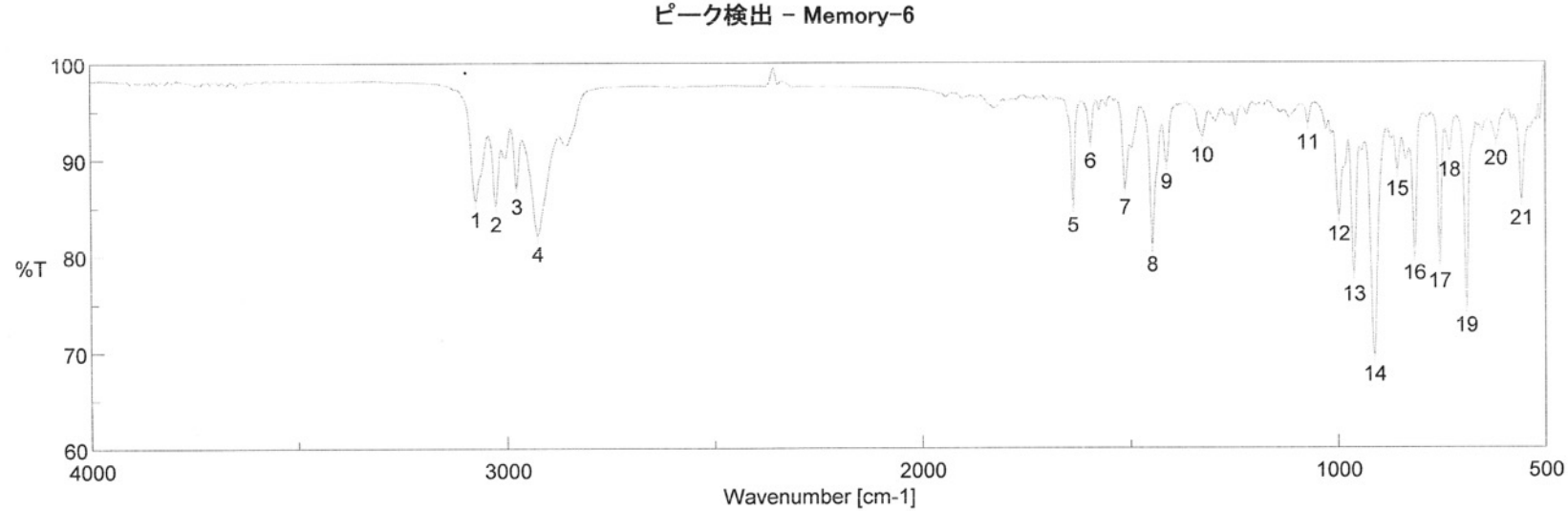
Plot date 2016-10-18

^{13}C NMR spectrum of **2f**.



IR spectrum of **2f**.





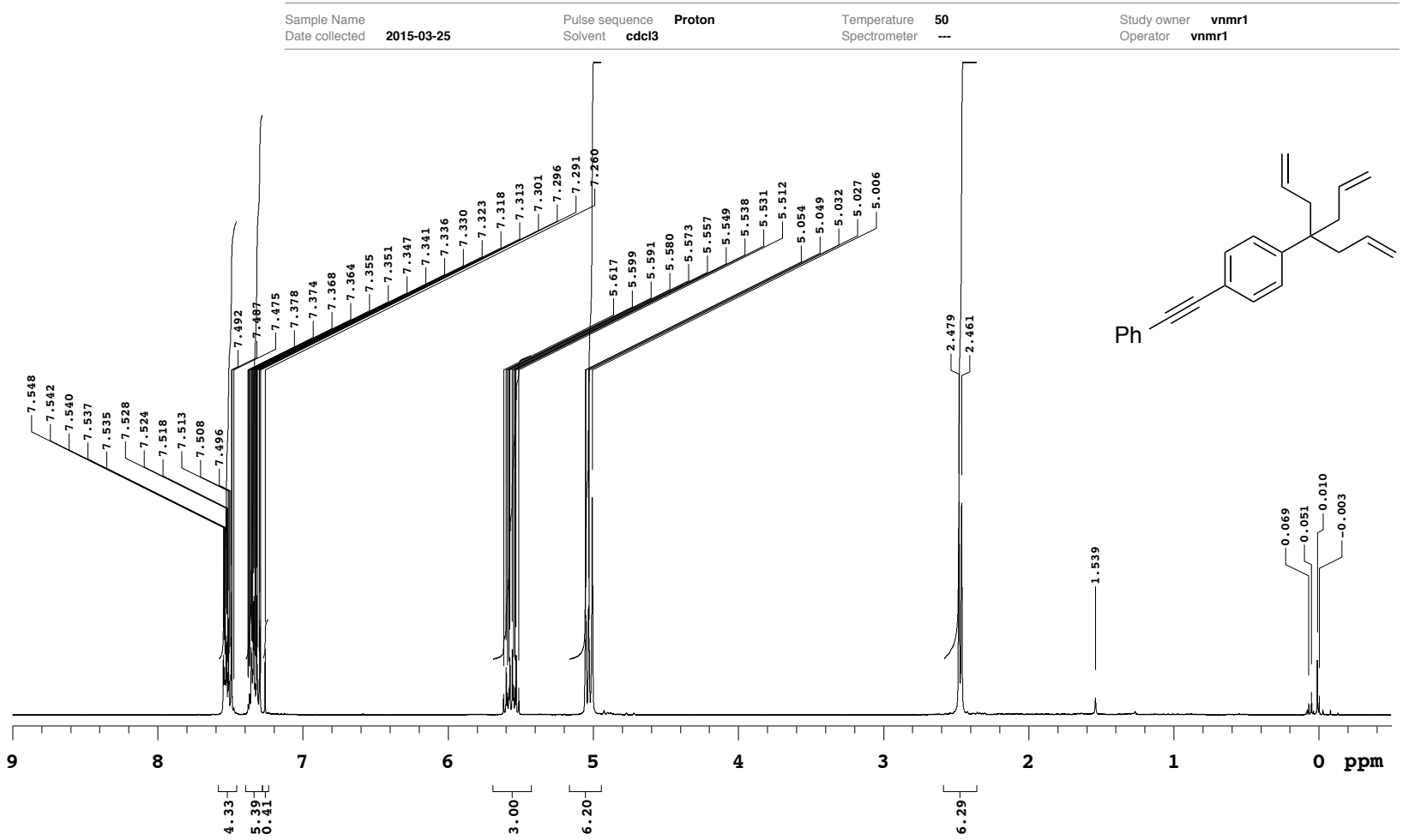
[コメント情報]

試料名	p_phenyl_alkene_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3073.98	85.71	2	3025.76	85.2389	3	2976.59	87.066	4	2926.45	82.1191
5	1638.23	85.085	6	1596.77	91.717	7	1513.85	86.9485	8	1448.28	80.9643
9	1413.57	89.5621	10	1327.75	92.3344	11	1072.23	93.6319	12	997.982	84.1568
13	962.305	77.8956	14	913.129	69.6073	15	858.168	88.82	16	816.706	80.1029
17	755.959	79.2211	18	732.817	90.764	19	691.355	74.6455	20	619.038	91.9457
21	557.327	85.775									

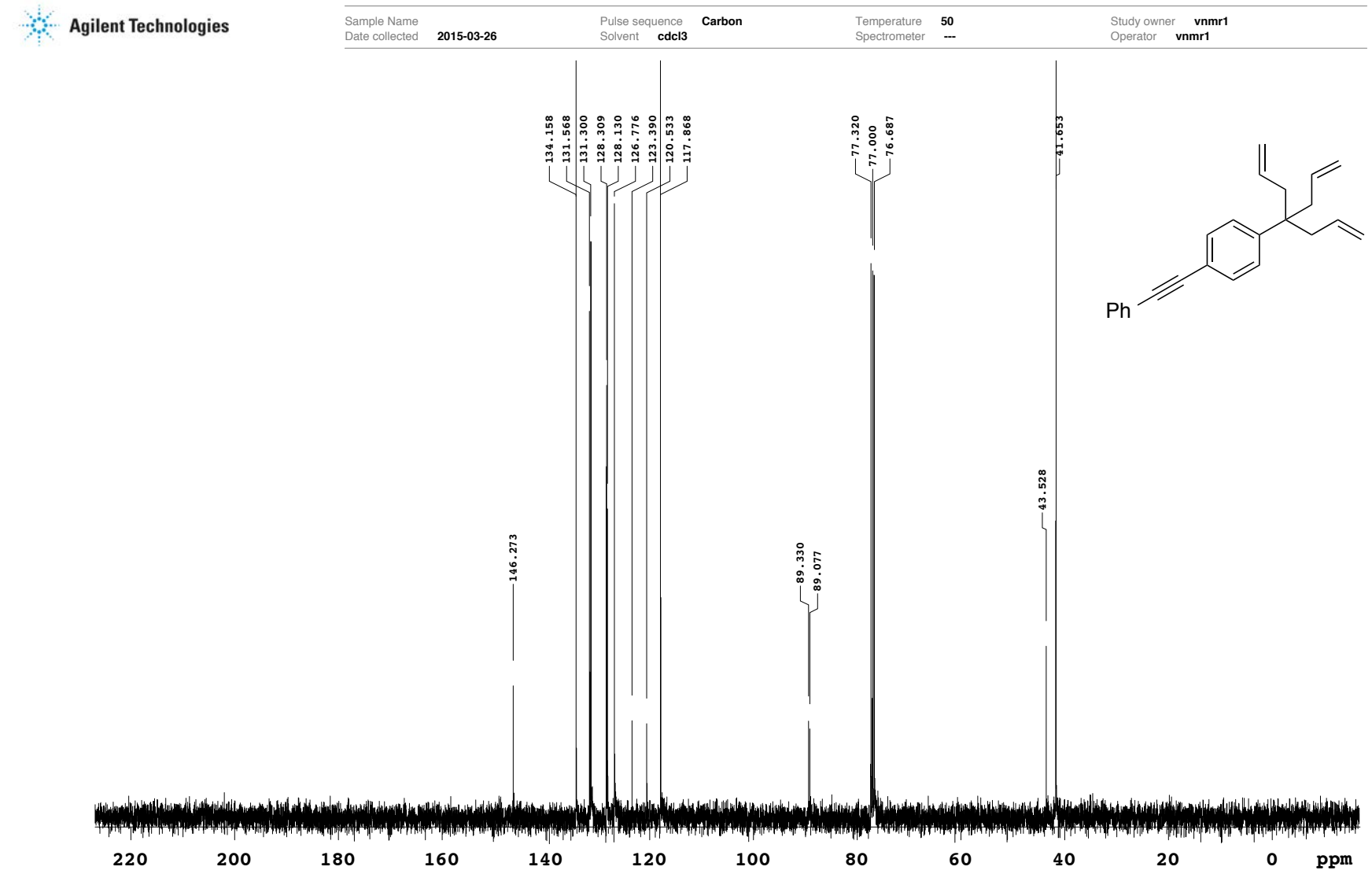
^{1}H NMR spectrum of **2g**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP231-PTLC-H1-3.fid

Plot date 2016-07-13

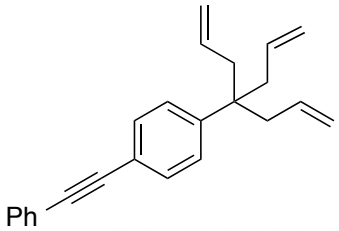
^{13}C NMR spectrum of **2g**.

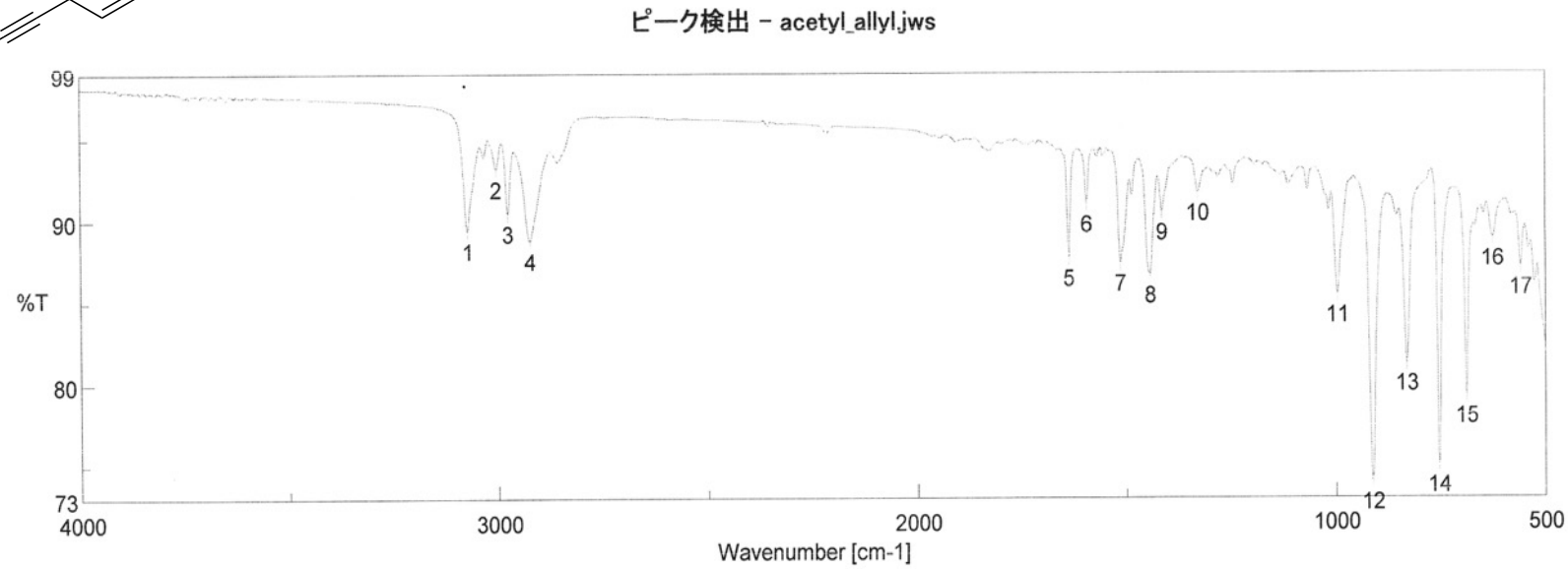


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP231-PTLC-C13-3.fid

Plot date 2015-10-10

IR spectrum of **2g**.





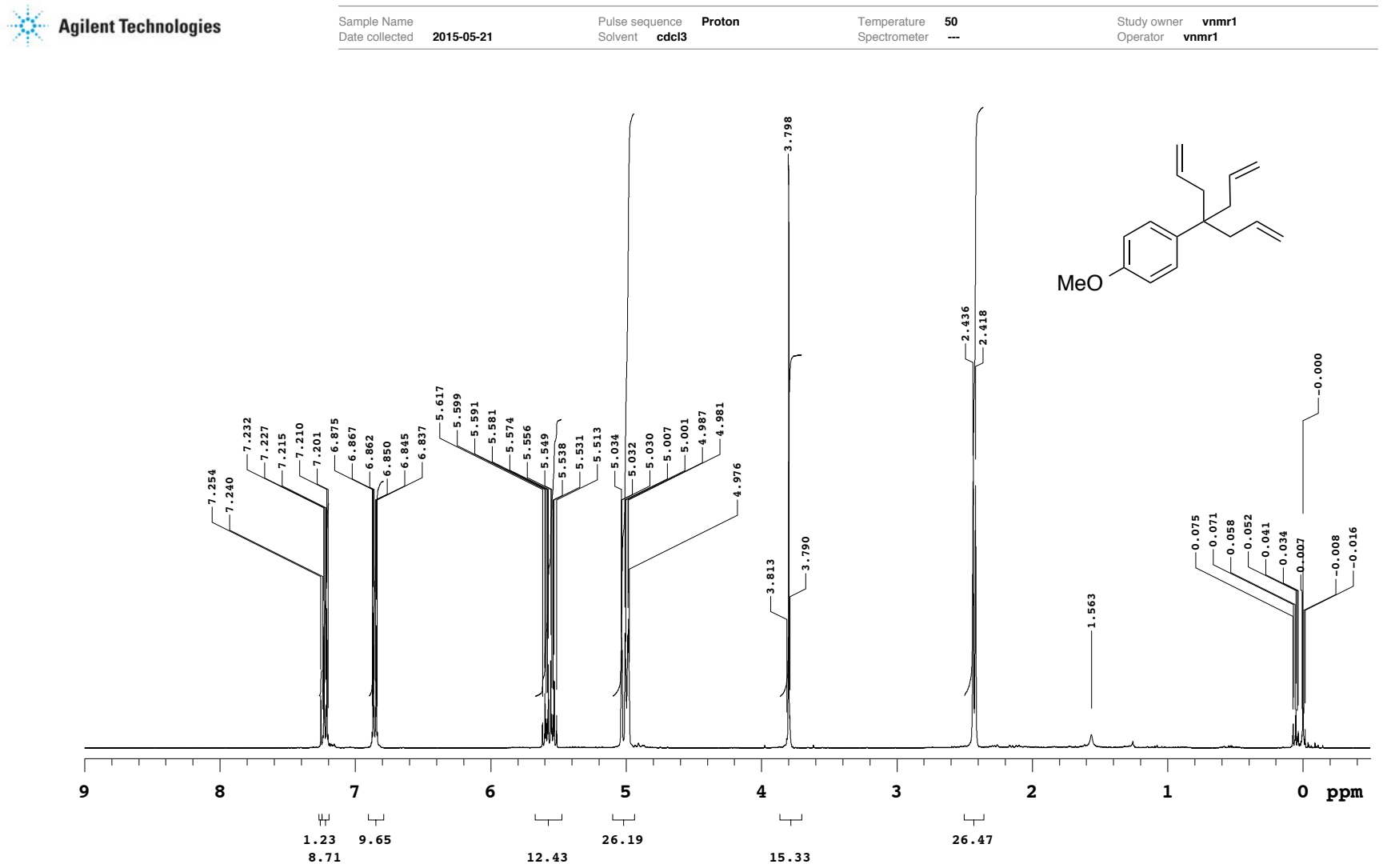
[コメント情報]

試料名	p_phenyl_alkyne_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3073.98	89.4249	2	3005.52	93.1984	3	2977.55	90.4995	4	2924.52	88.8047
5	1638.23	87.7013	6	1595.81	91.0124	7	1514.81	87.4034	8	1443.46	86.6752
9	1415.49	90.5329	10	1330.64	91.7052	11	997.017	85.4536	12	913.129	73.9794
13	832.133	81.2583	14	754.995	75.0358	15	689.427	79.2632	16	626.752	88.888
17	559.255	87.1232									

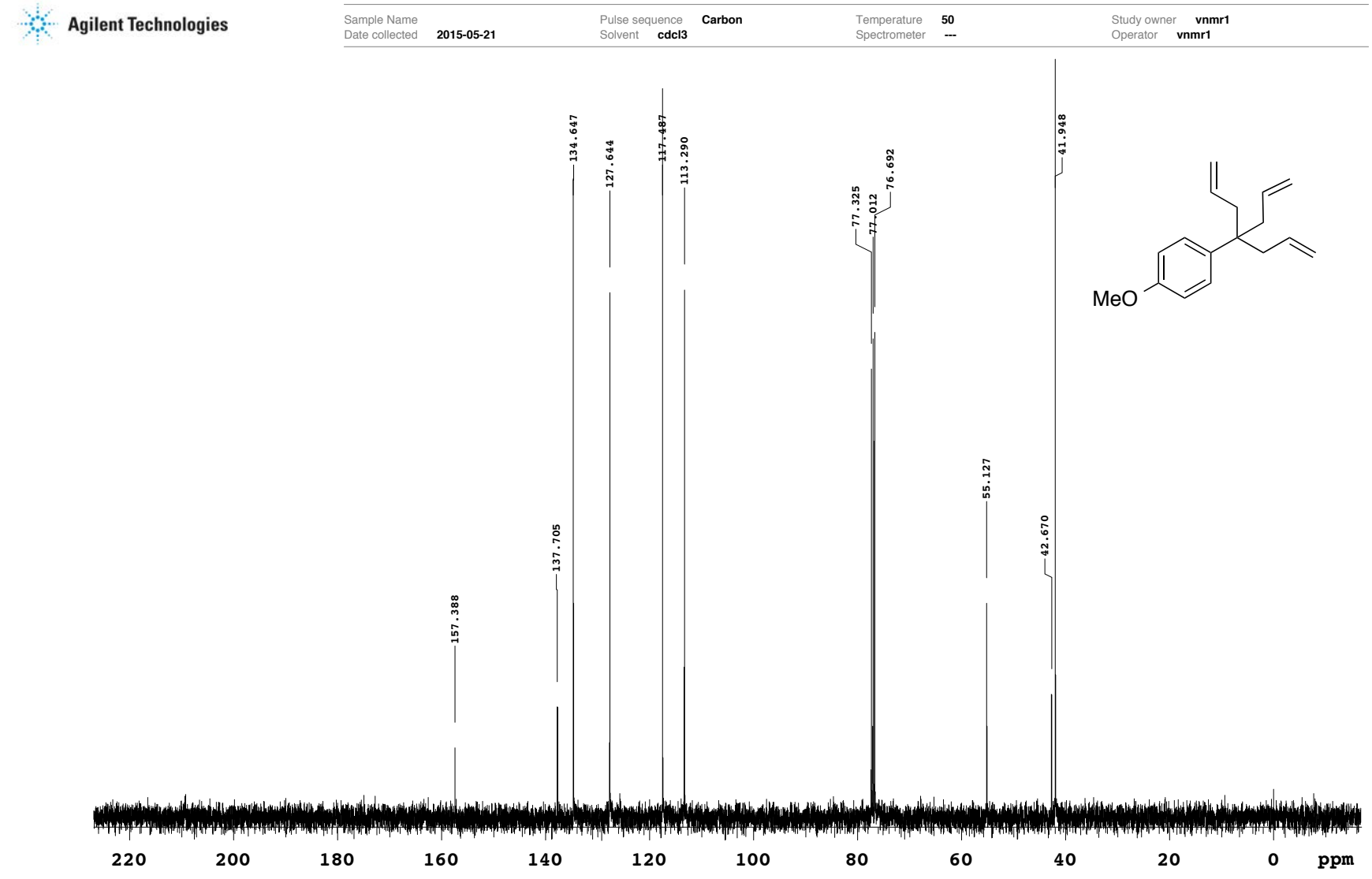
^{1}H NMR spectrum of **2h**.



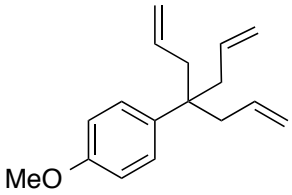
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP276-PTLC-H1-2.fid

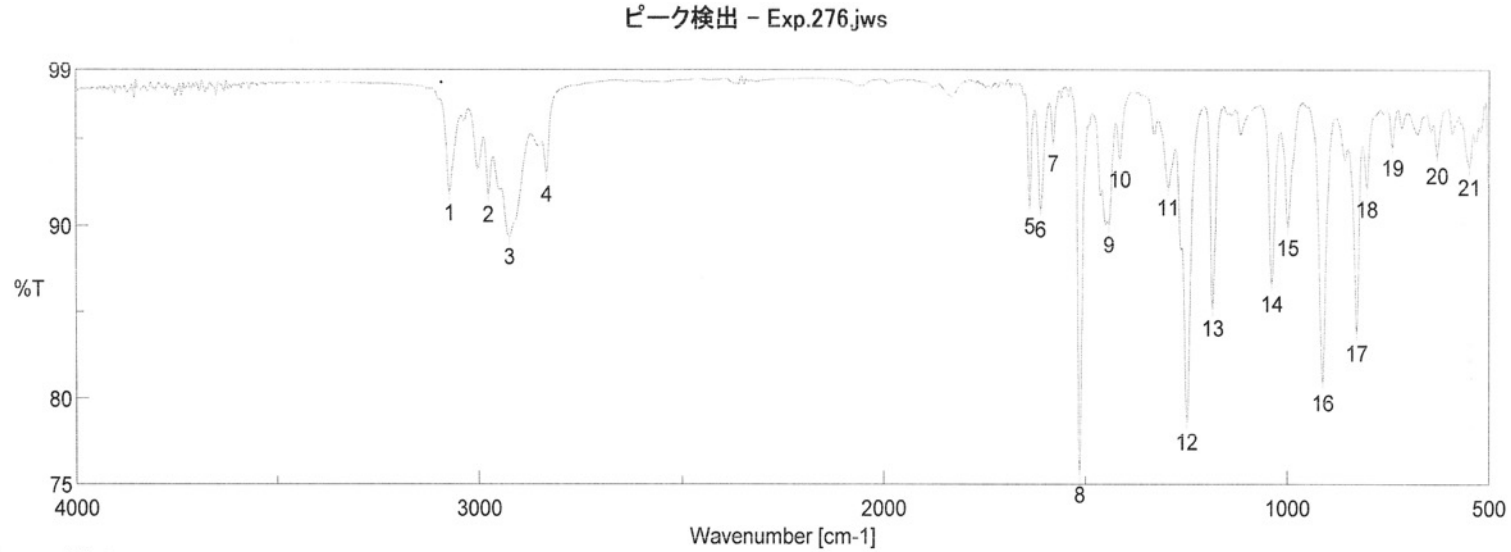
Plot date 2015-10-10

^{13}C NMR spectrum of **2h**.



^{13}C NMR spectrum of **2h**.





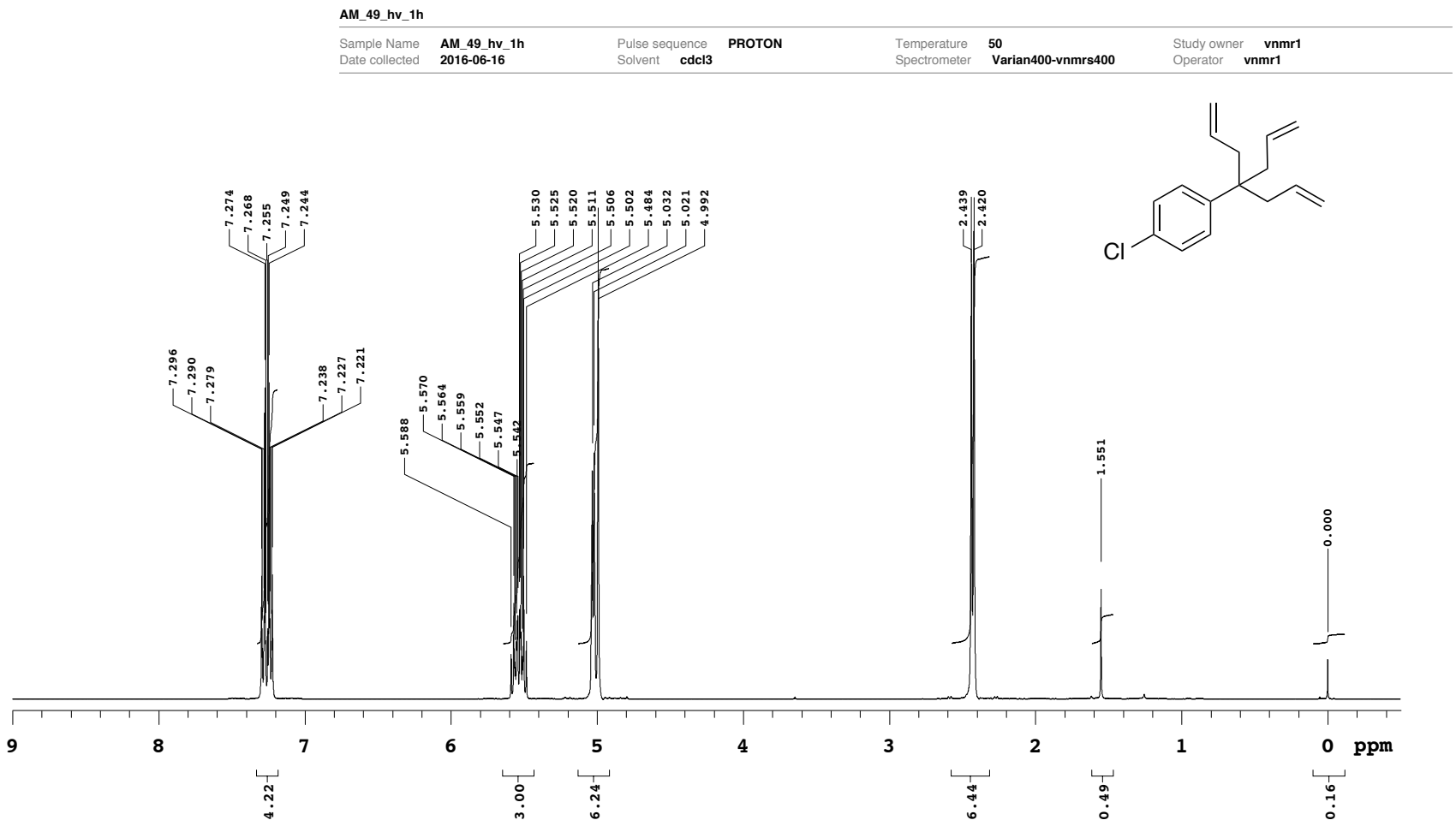
[コメント情報]

試料名	p_methoxy_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3073.98	91.8961	2	2977.55	91.8004	3	2926.45	89.3443	4	2834.85	92.9805
5	1638.23	91.1422	6	1611.23	90.9436	7	1580.38	94.7511	8	1514.81	75.5598
9	1442.49	90.0553	10	1415.49	93.8319	11	1296.89	92.1973	12	1249.65	78.6298
13	1186.01	85.2092	14	1038.48	86.6218	15	998.946	89.859	16	912.165	80.88
17	828.277	83.7572	18	803.206	92.1053	19	739.567	94.4998	20	628.68	94.0432
21	548.649	93.3715									

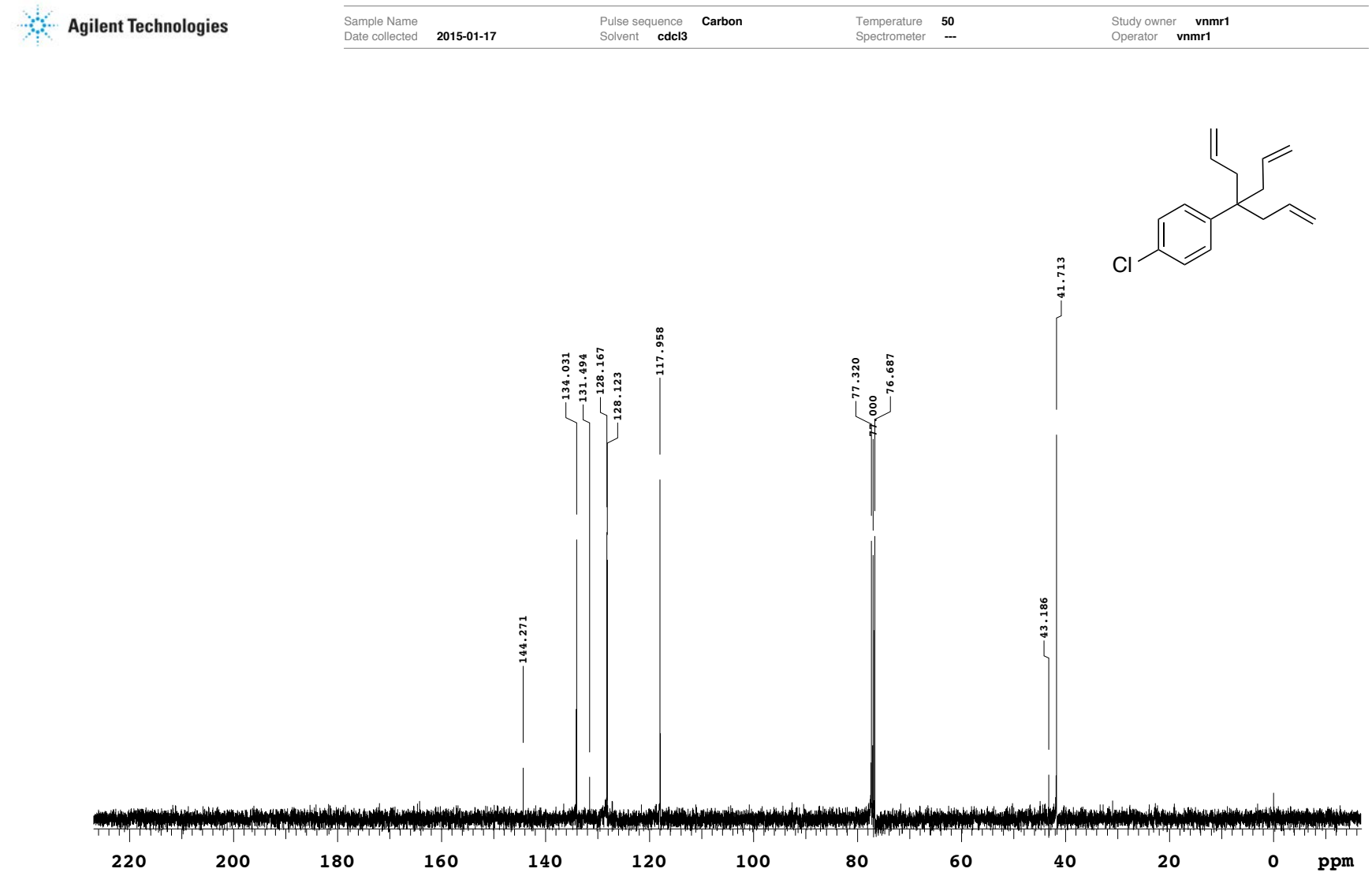
^{1}H NMR spectrum of **2i**.



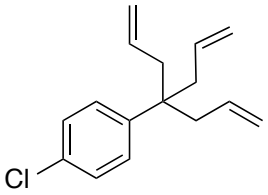
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_chloro_allyl_1H.fid

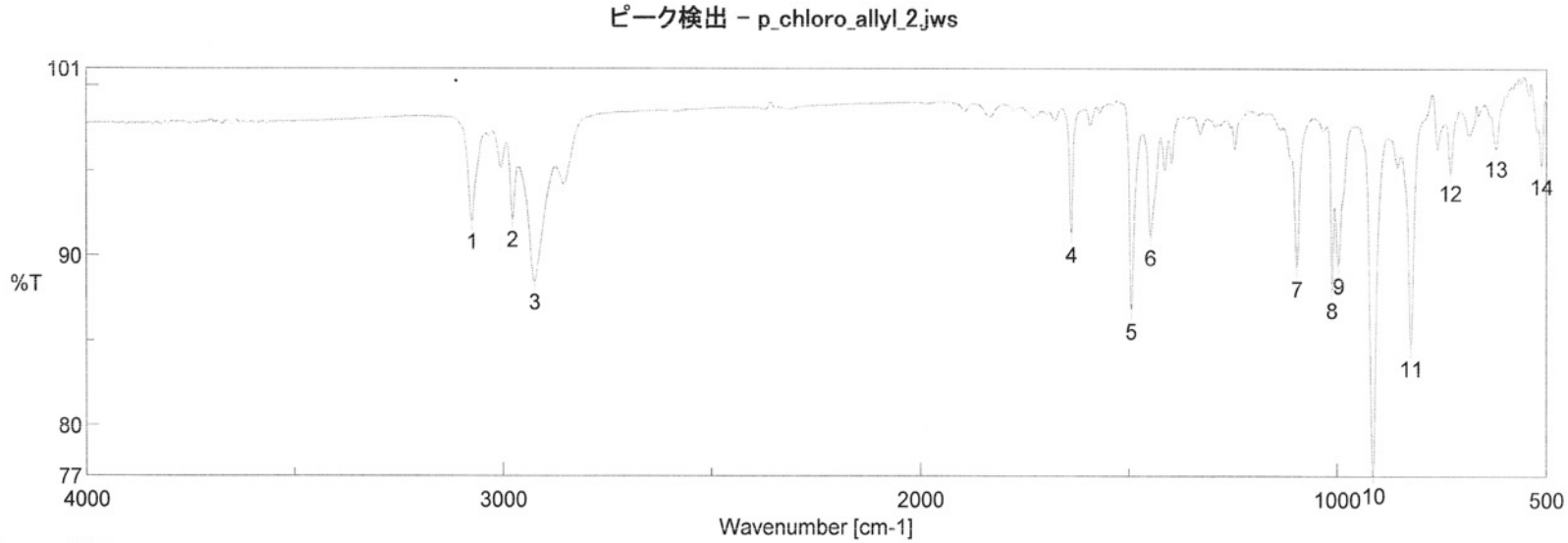
Plot date 2016-07-12

^{13}C NMR spectrum of **2i**.



IR spectrum of **2i**.





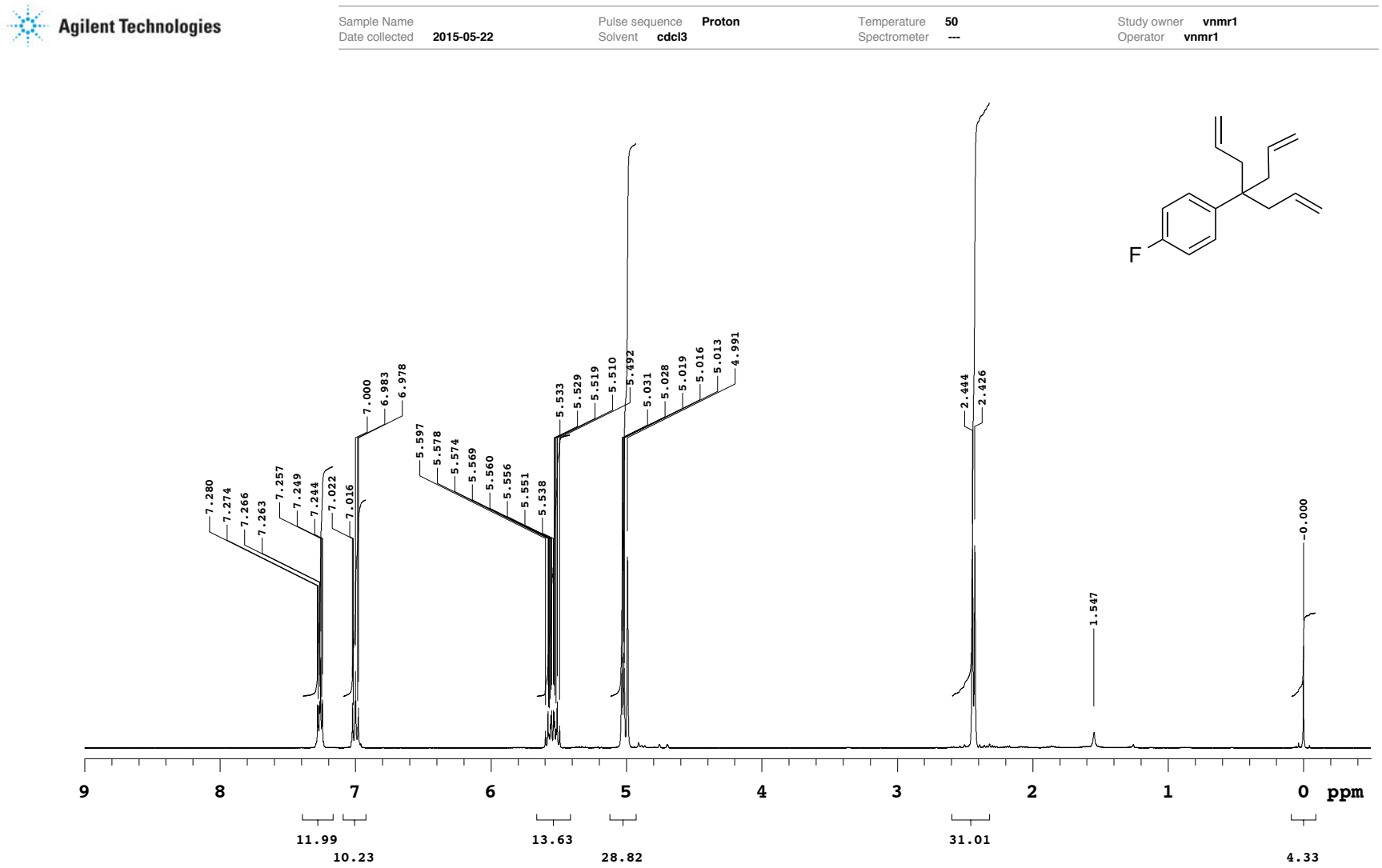
[コメント情報]

試料名	p_chloro_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3074.94	91.9715	2	2978.52	92.1202	3	2925.48	88.4207	4	1638.23	91.2038
5	1495.53	86.7034	6	1449.24	91.0296	7	1096.33	89.191	8	1012.45	87.933
9	997.017	89.3846	10	914.093	77.0291	11	824.42	84.5086	12	730.889	94.8677
13	621.931	96.2919	14	512.008	95.2437						

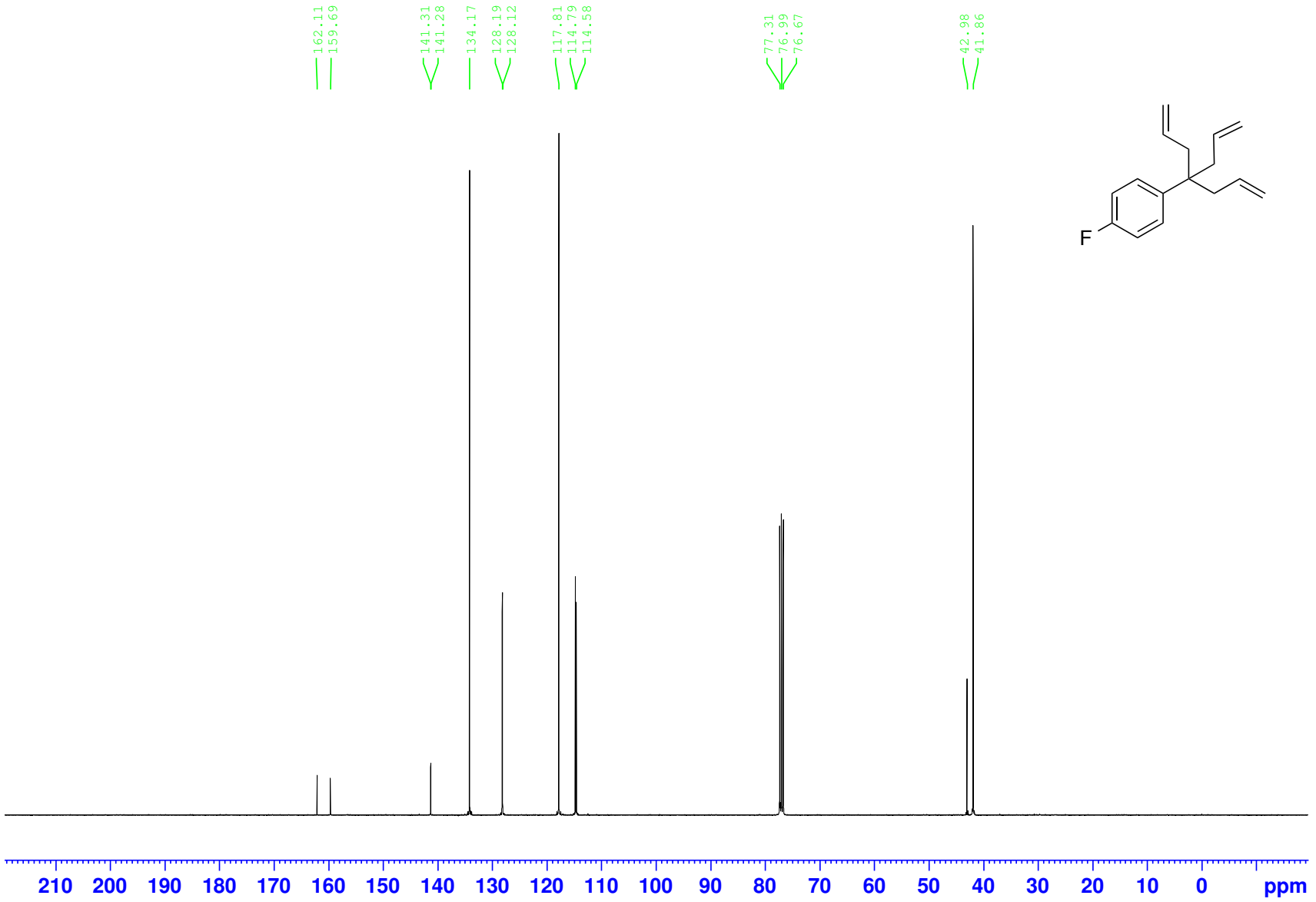
^{1}H NMR spectrum of **2j**.



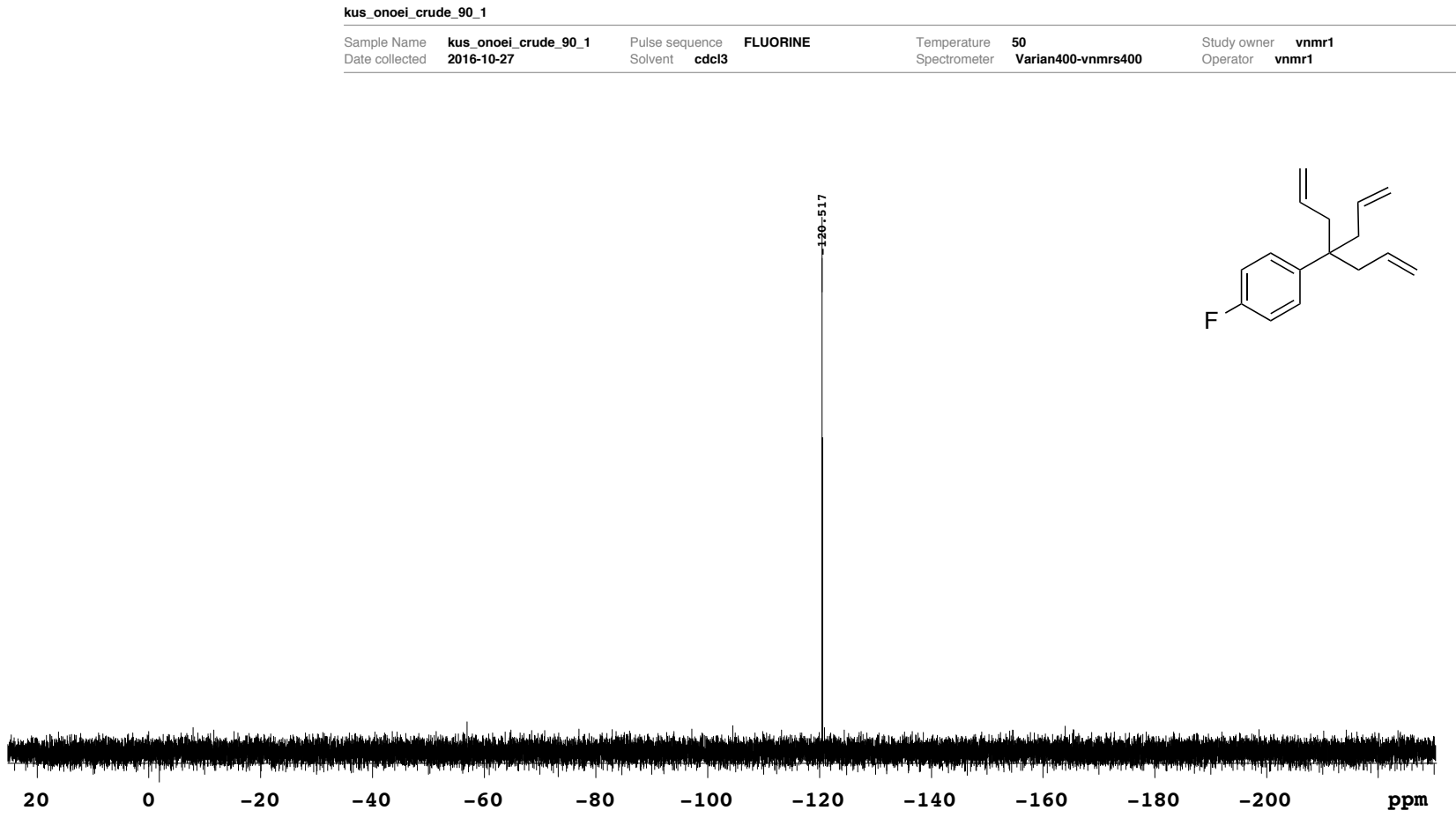
Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP280-PTLC-H1-2.fid

Plot date 2015-10-10

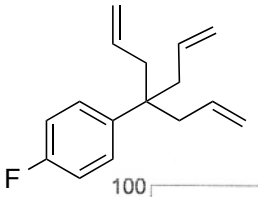
^{13}C NMR spectrum of **2j**.

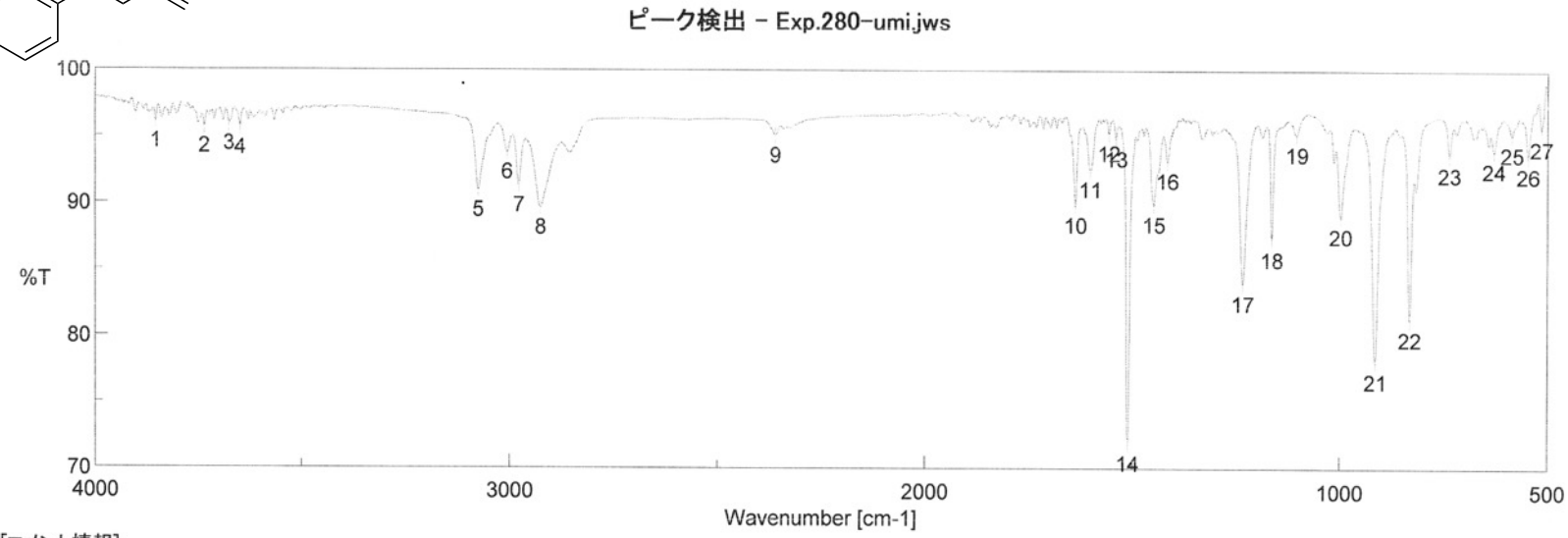


^{19}F NMR spectrum of **2j**.



IR spectrum of **2j**.





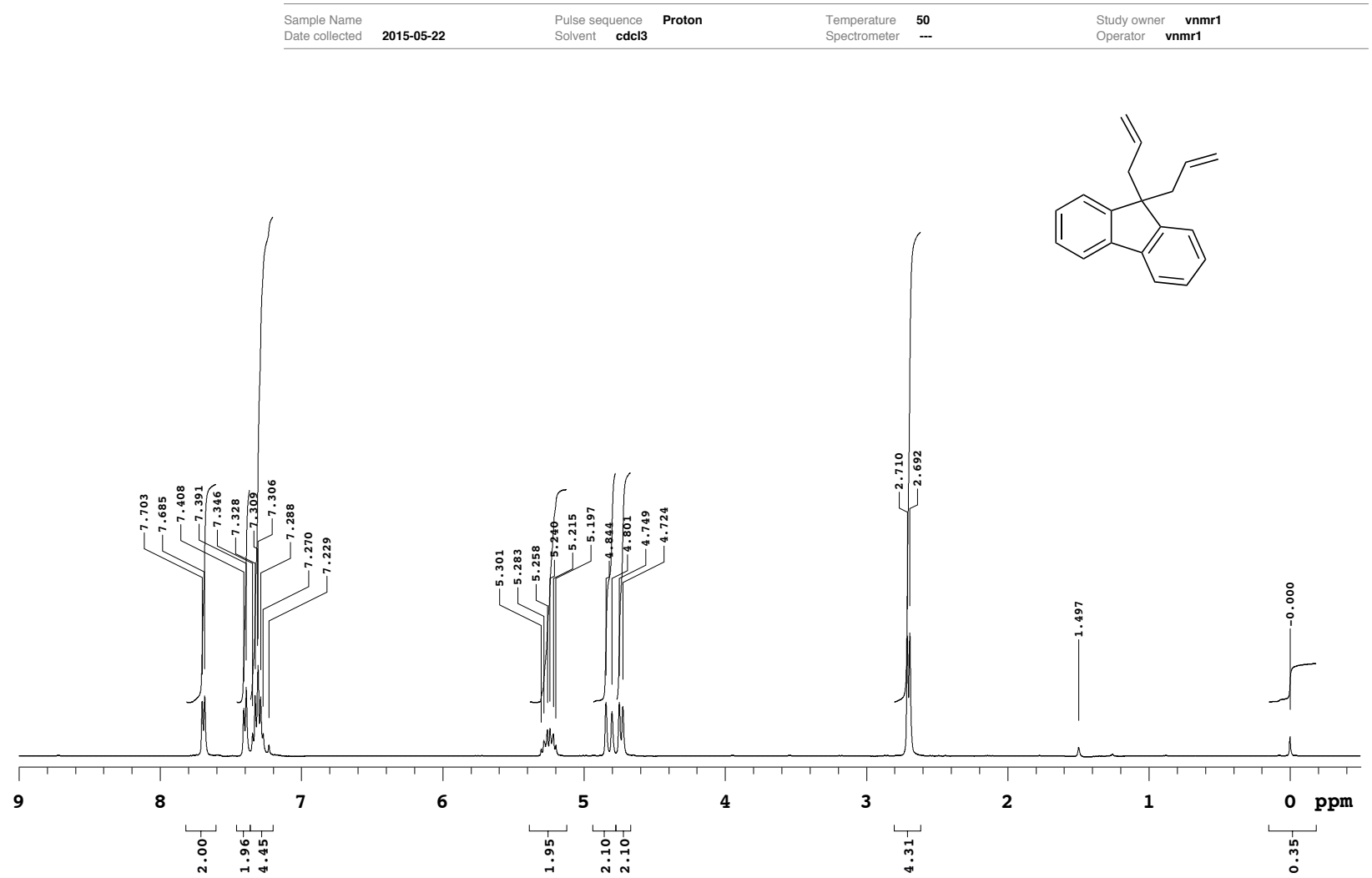
[コメント情報]

試料名	p_fluoro_allyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3853.08	96.0788	2	3734.48	95.7116	3	3675.66	95.9101	4	3648.66	95.5887
5	3075.9	90.9419	6	3006.48	93.8014	7	2978.52	91.3031	8	2926.45	89.6383
9	2361.41	95.0571	10	1638.23	89.8144	11	1602.56	92.5146	12	1558.2	95.2135
13	1540.85	94.8118	14	1511.92	71.8628	15	1449.24	89.8668	16	1416.46	93.146
17	1235.18	83.9167	18	1164.79	87.2056	19	1105.01	95.1304	20	997.982	88.9632
21	914.093	78.0452	22	831.169	81.2297	23	735.71	93.6233	24	628.68	93.9431
25	585.29	95.1806	26	546.72	93.554	27	514.901	95.6165			

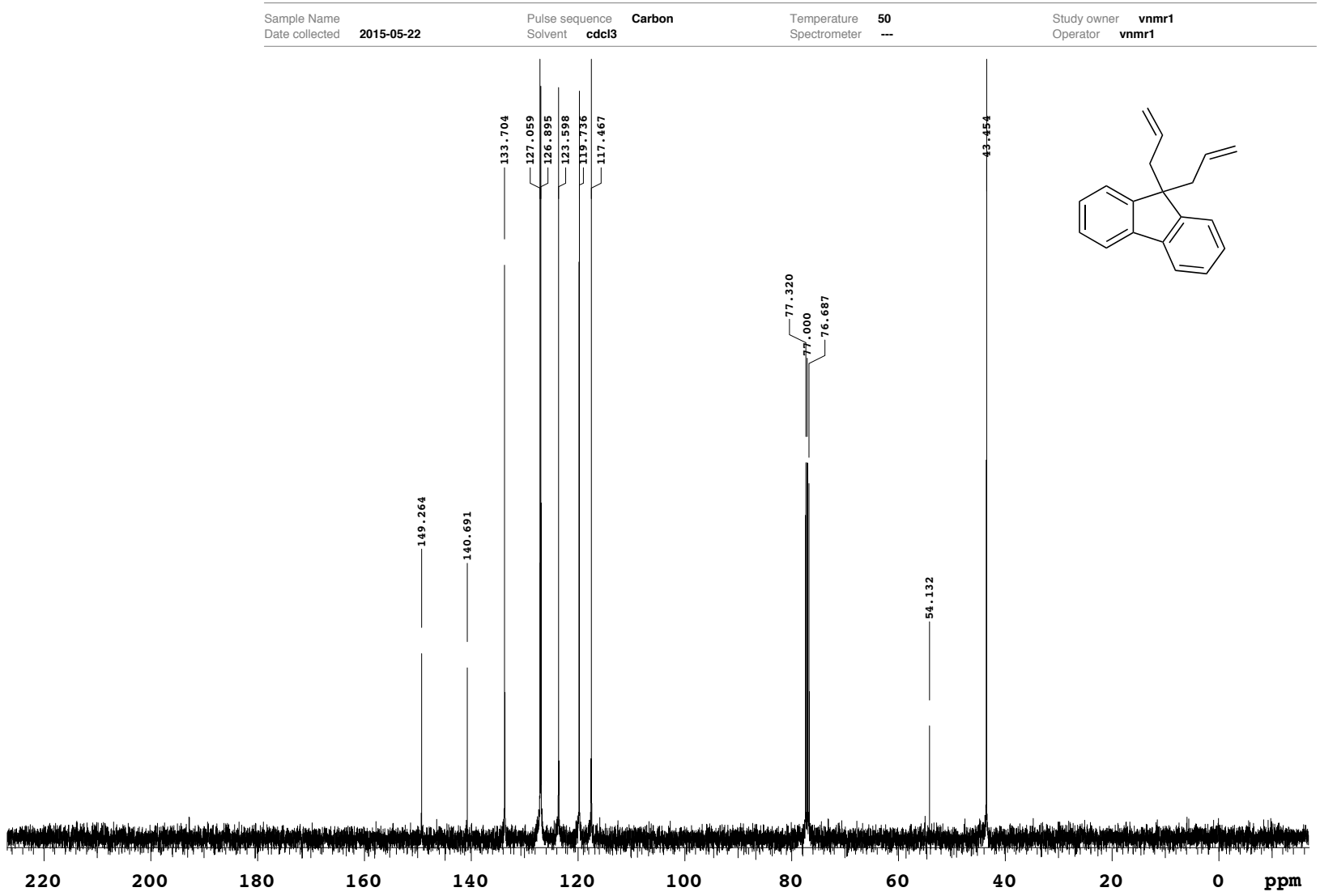
^{1}H NMR spectrum of **5**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP281-PTLC-H1-2.fid

Plot date 2016-10-29

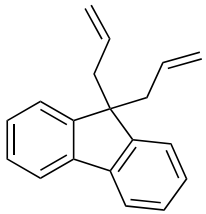
^{13}C NMR spectrum of **5**.

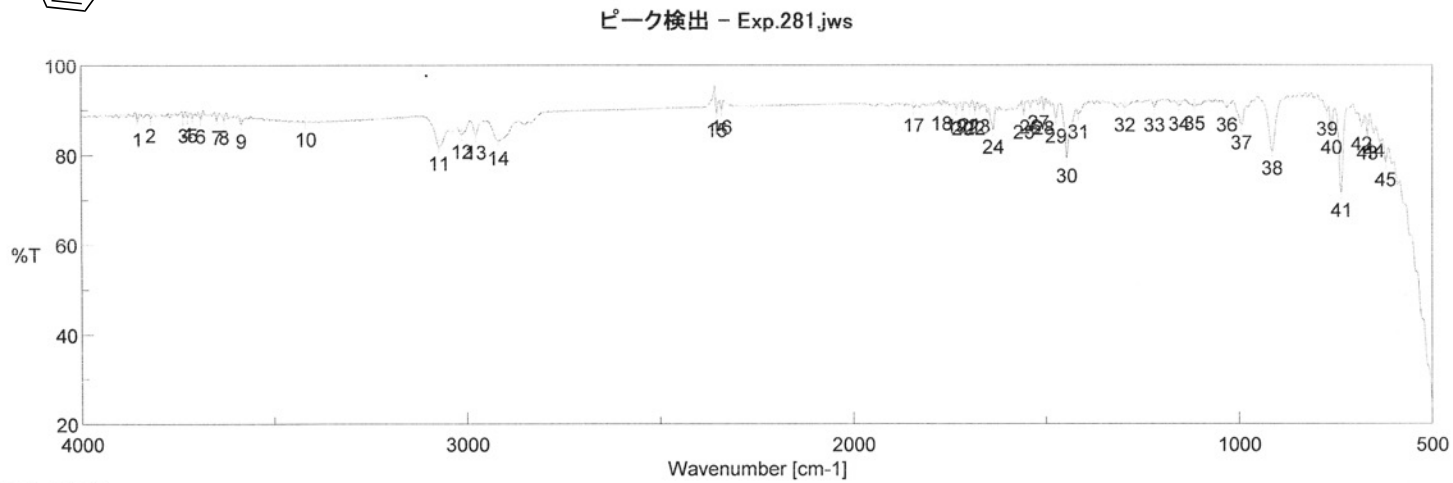


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP281-PTLC-C13-2.fid

Plot date 2016-11-10

IR spectrum of **5**.





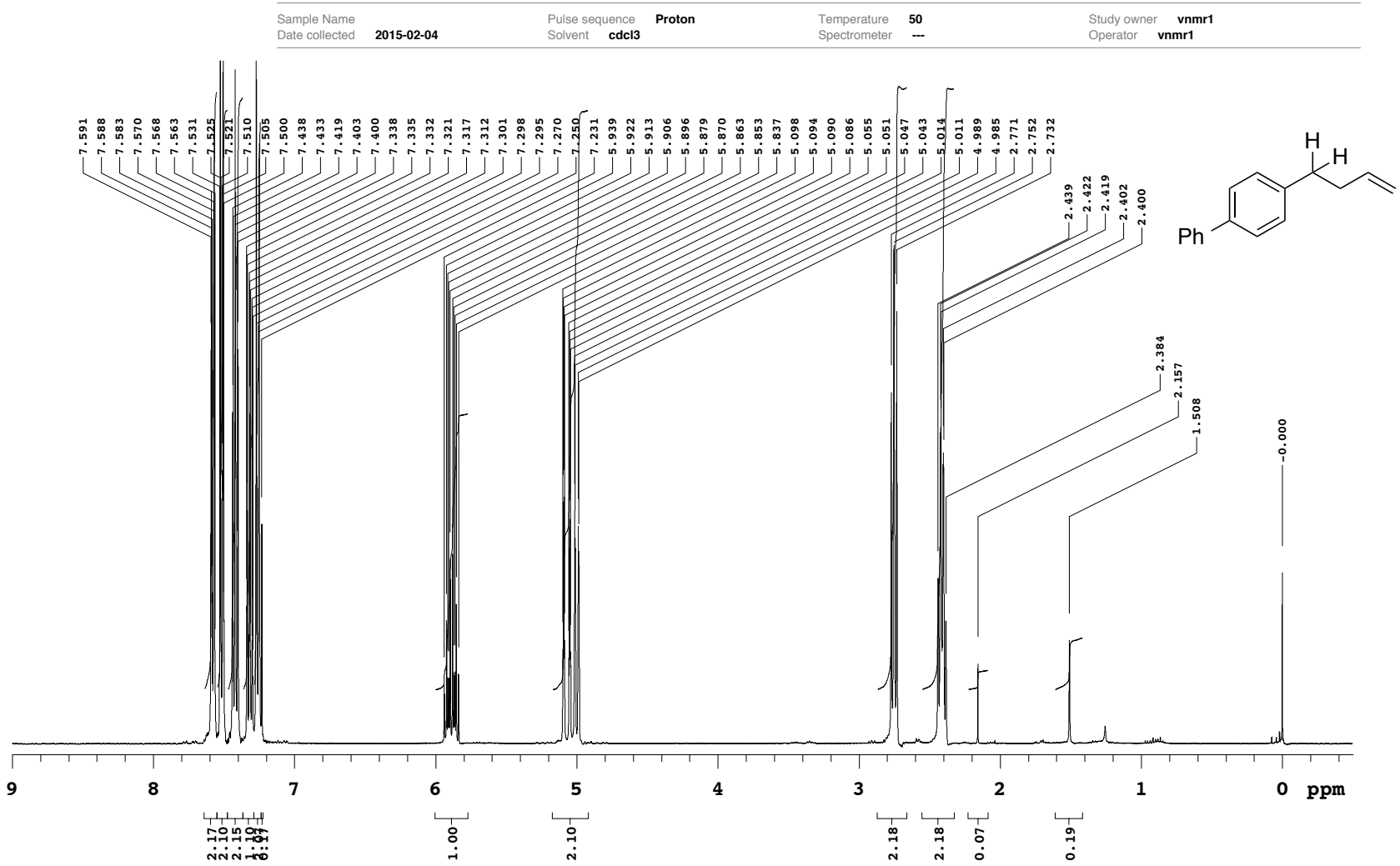
[コメント情報]

試料名	fluorene_diallyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3853.08	87.3687	2	3818.36	88.2581	3	3734.48	88.2533	4	3722.91	88.5387
5	3710.37	88.2821	6	3689.16	88.0624	7	3647.7	87.7535	8	3629.37	87.832
9	3585.02	86.918	10	3418.21	87.2958	11	3072.05	81.9352	12	3013.23	84.5947
13	2977.55	84.418	14	2919.7	83.1407	15	2354.66	89.3345	16	2342.12	90.0087
17	1843.61	90.3959	18	1771.3	90.8509	19	1732.73	90.2028	20	1716.34	89.7557
21	1698.02	90.4246	22	1684.52	89.7859	23	1671.98	90.2139	24	1637.27	85.6572
25	1558.2	88.9338	26	1540.85	90.0497	27	1519.63	91.1115	28	1507.1	89.8673
29	1475.28	88.0247	30	1447.31	79.167	31	1417.42	88.9783	32	1297.86	90.4904
33	1220.72	90.4889	34	1156.12	90.7368	35	1115.62	90.8147	36	1031.73	90.5485
37	994.125	86.5629	38	915.058	90.8988	39	773.315	89.6369	40	761.744	85.532
41	735.71	71.5273	42	682.677	86.3367	43	668.214	84.2884	44	650.858	84.7988
45	620.966	78.3373									

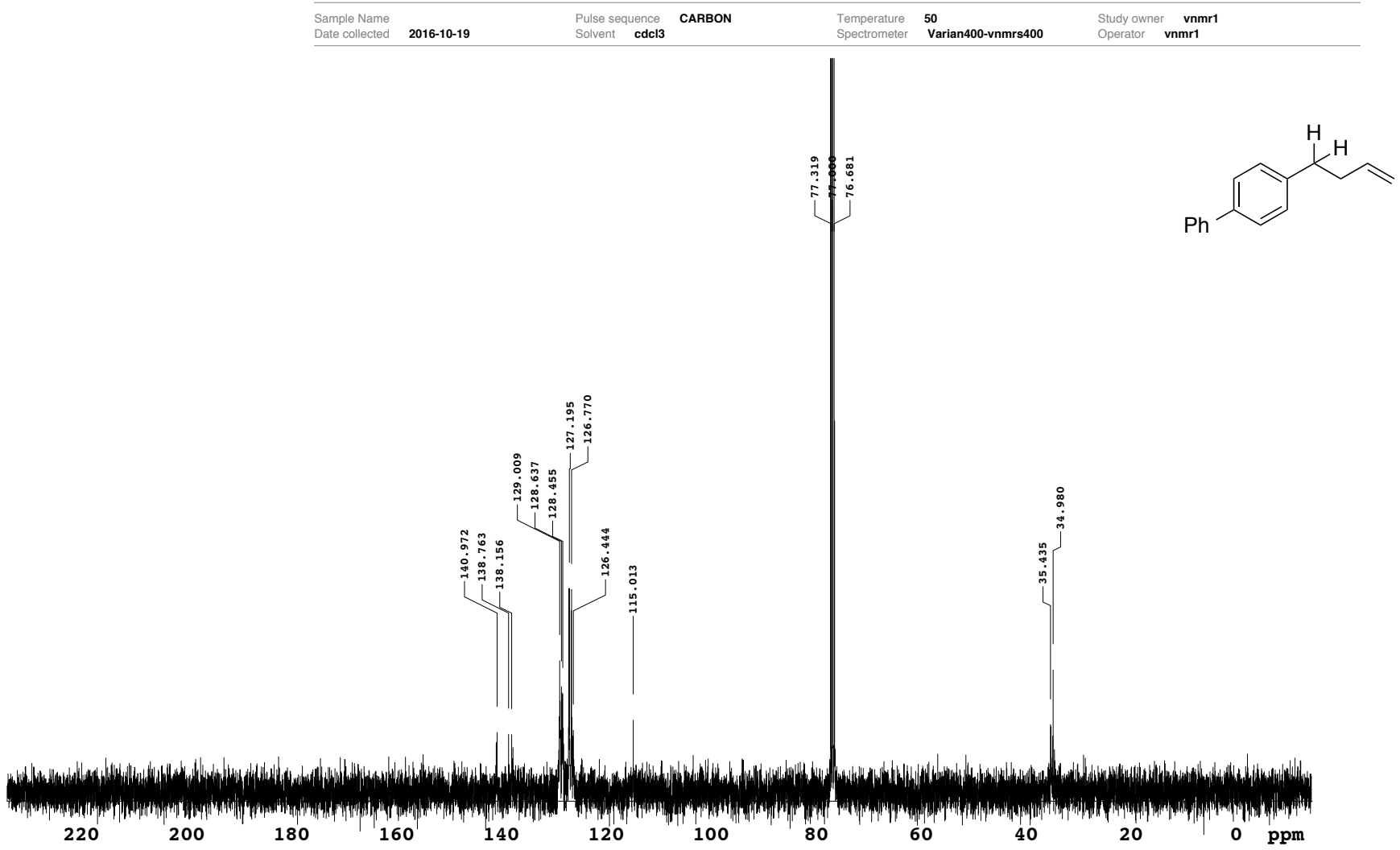
^{1}H NMR spectrum of **9**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP211-PTLC-H1-1.fid

Plot date 2016-10-18

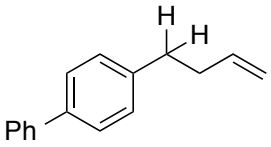
^{13}C NMR spectrum of **9**.

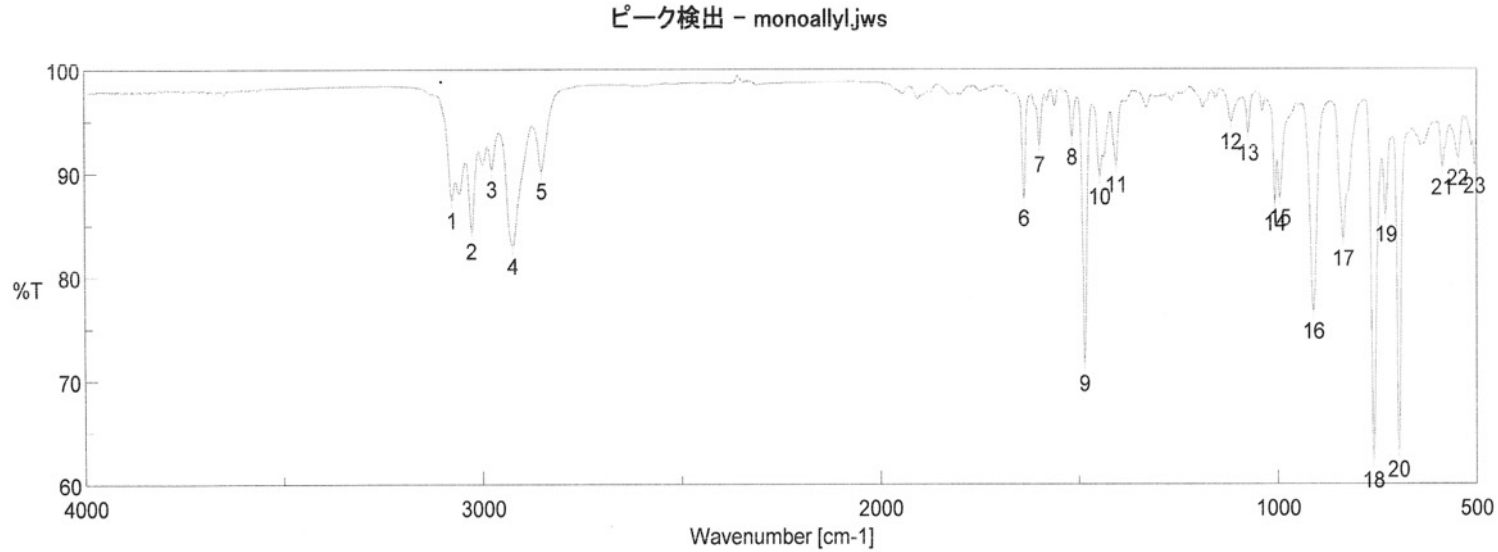


Data file exp

Plot date 2016-10-19

IR spectrum of **9**.





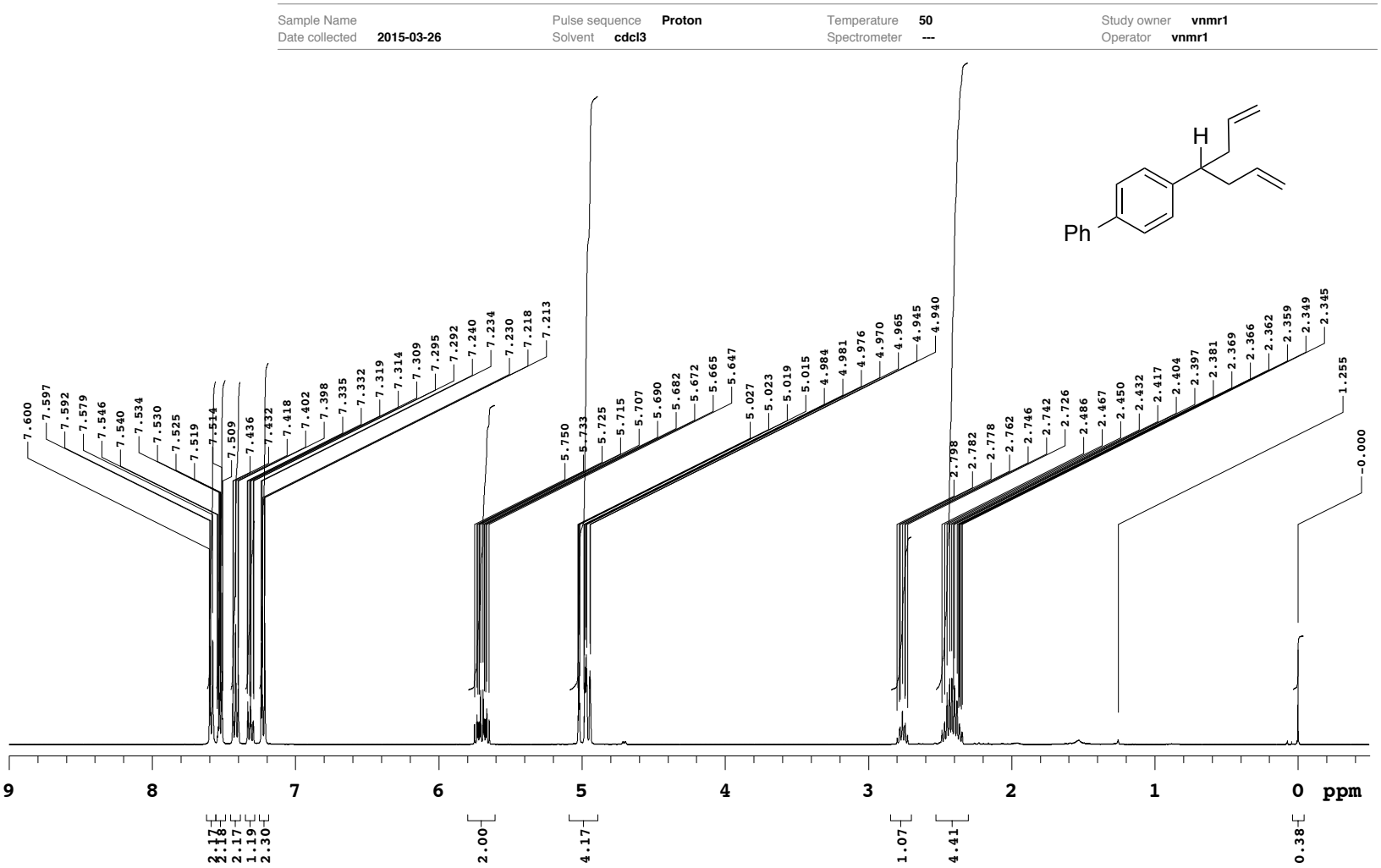
[コメント情報]

試料名	p_phenyl_monoallyl
コメント	
測定者	
所属	
会社	学習院大学

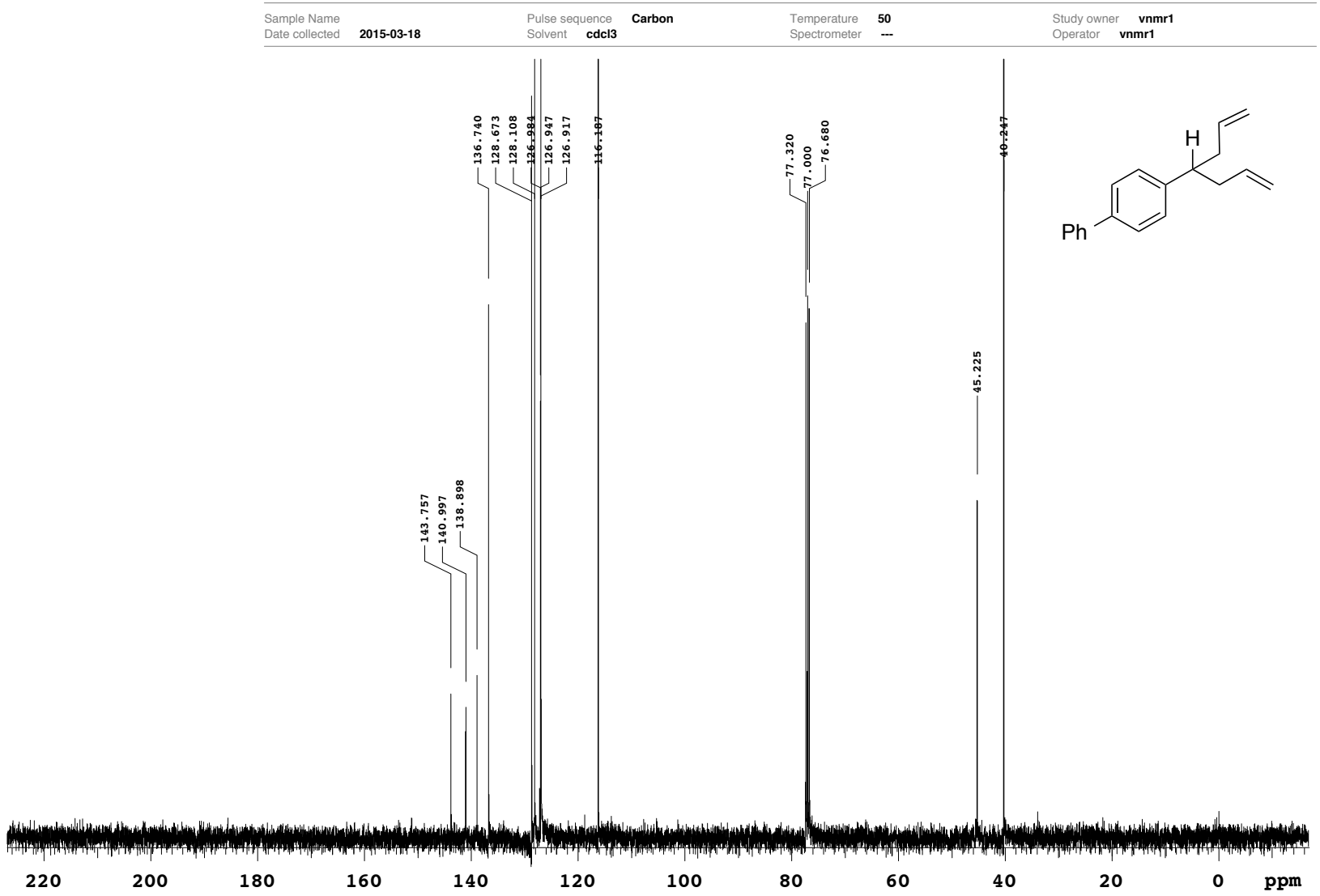
[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3076.87	87.4001	2	3027.69	84.4387	3	2977.55	90.407	4	2925.48	82.979
5	2853.17	90.2134	6	1639.2	87.5891	7	1600.63	92.7117	8	1518.67	93.4796
9	1486.85	71.6697	10	1449.24	89.6465	11	1407.78	90.7804	12	1118.51	94.9195
13	1075.12	93.8258	14	1007.62	87.0948	15	995.089	87.6042	16	911.201	76.6864
17	836.955	83.6704	18	760.78	62.2893	19	729.925	86.0106	20	697.141	63.3374
21	587.218	90.5207	22	547.685	91.4253	23	505.258	90.6523			

^{1}H NMR spectrum of **10**.



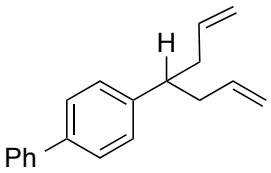
^{13}C NMR spectrum of **10**.

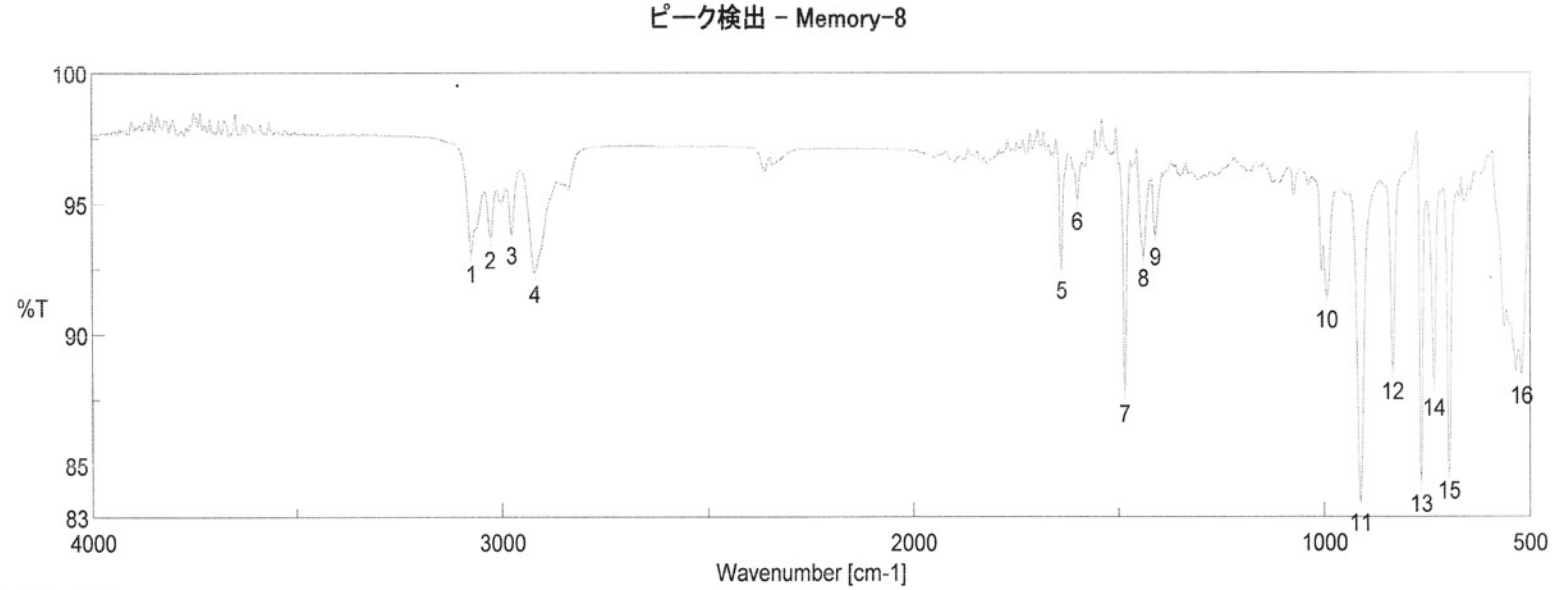


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/201-300/EXP201-PTLC-C13-2-1.fid

Plot date 2015-11-20

IR spectrum of **10**.





[コメント情報]

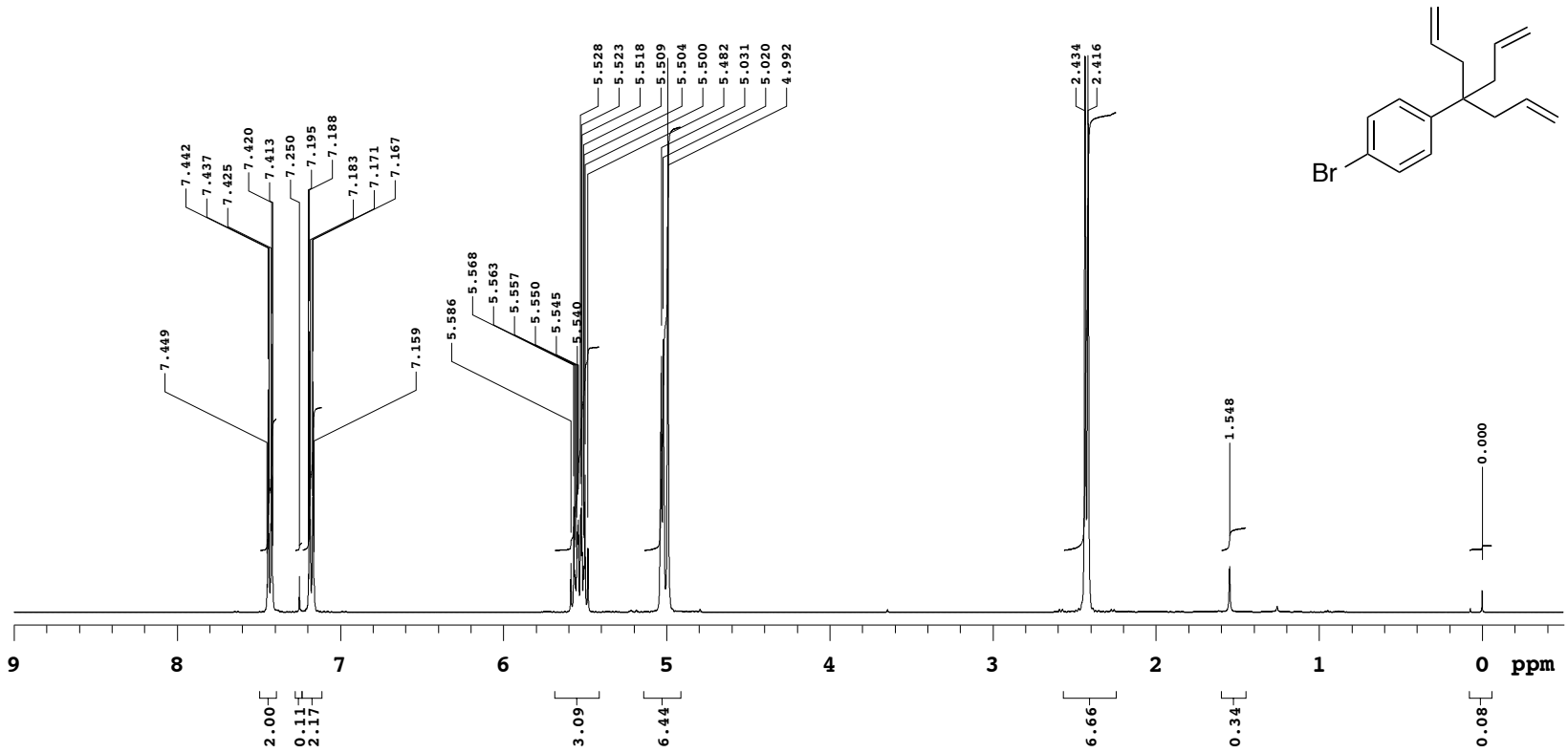
試料名	p_phenyl_diallyl
コメント	
測定者	
所属	
会社	学習院大学

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3074.94	93.1361	2	3027.69	93.658	3	2976.59	93.8522	4	2920.66	92.3549
5	1639.2	92.4844	6	1600.63	95.1356	7	1485.88	87.7822	8	1440.56	92.9544
9	1411.64	93.7793	10	994.125	91.3712	11	912.165	83.5943	12	834.062	88.6461
13	764.637	84.3276	14	733.782	88.015	15	697.141	84.8357	16	520.686	88.4734

^{1}H NMR spectrum of **2x**.

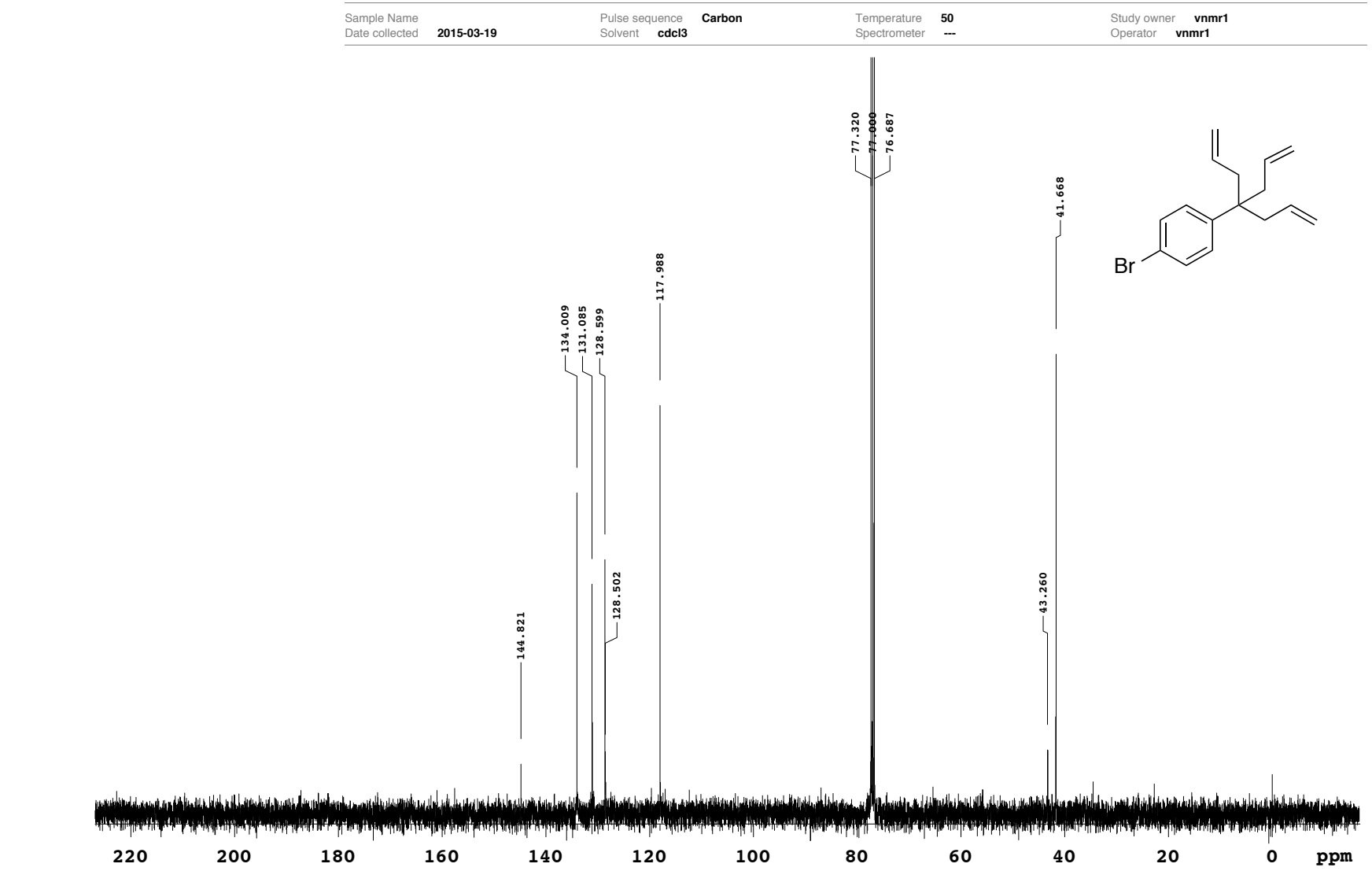
Sample Name		Pulse sequence	**PROTON**	Temperature	**50**	Study owner	**vnmr1**
Date collected	**2016-06-23**	Solvent	**cdcl3**	Spectrometer	**Varian400-vnmrs400**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/p_bromo_allyl_1H.fid

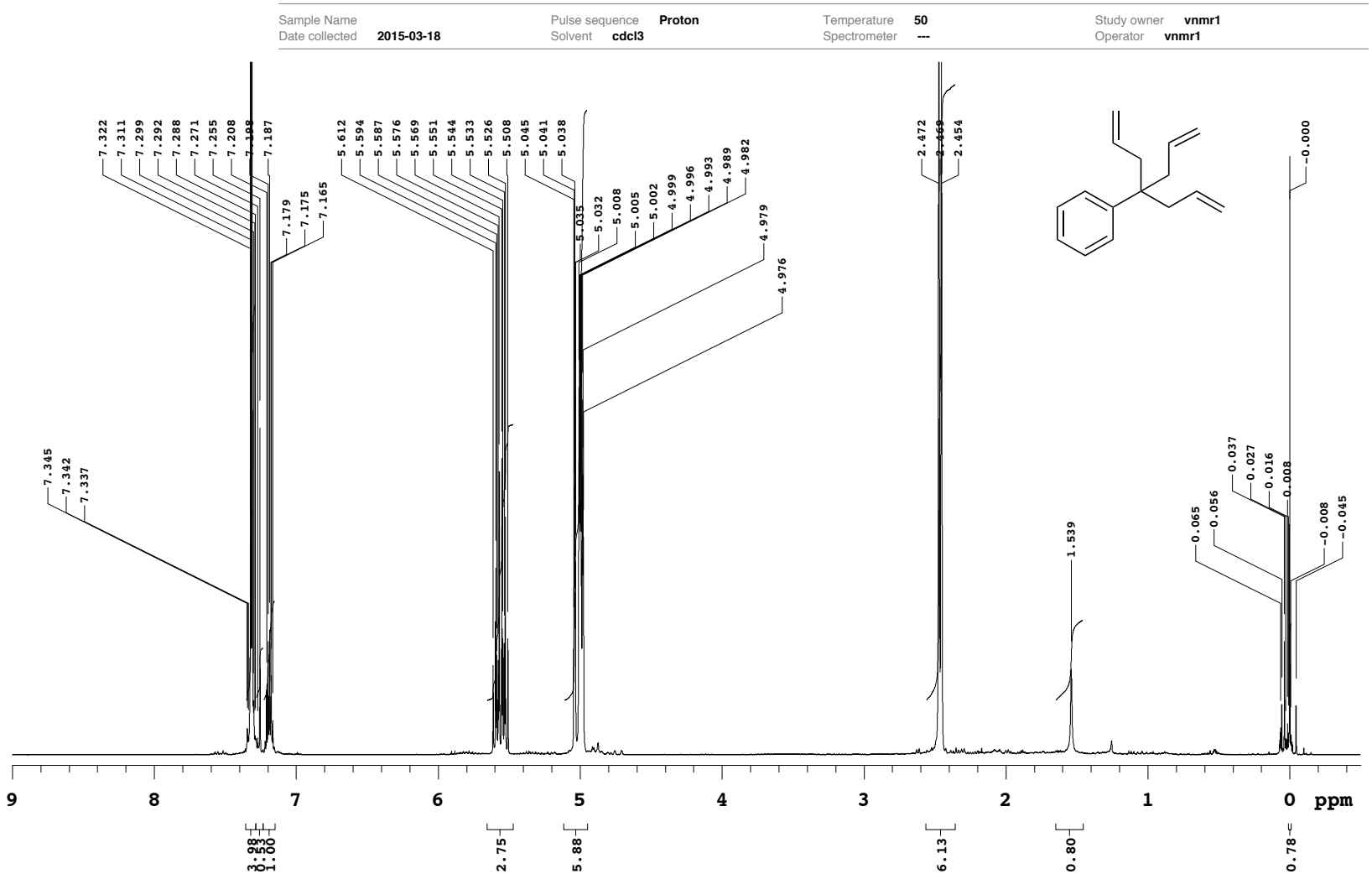
Plot date 2016-07-12

^{13}C NMR spectrum of **2x**.



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/yamada/1400_/Exp.1438_pTLC_C13_pure.fid

Plot date 2015-10-14

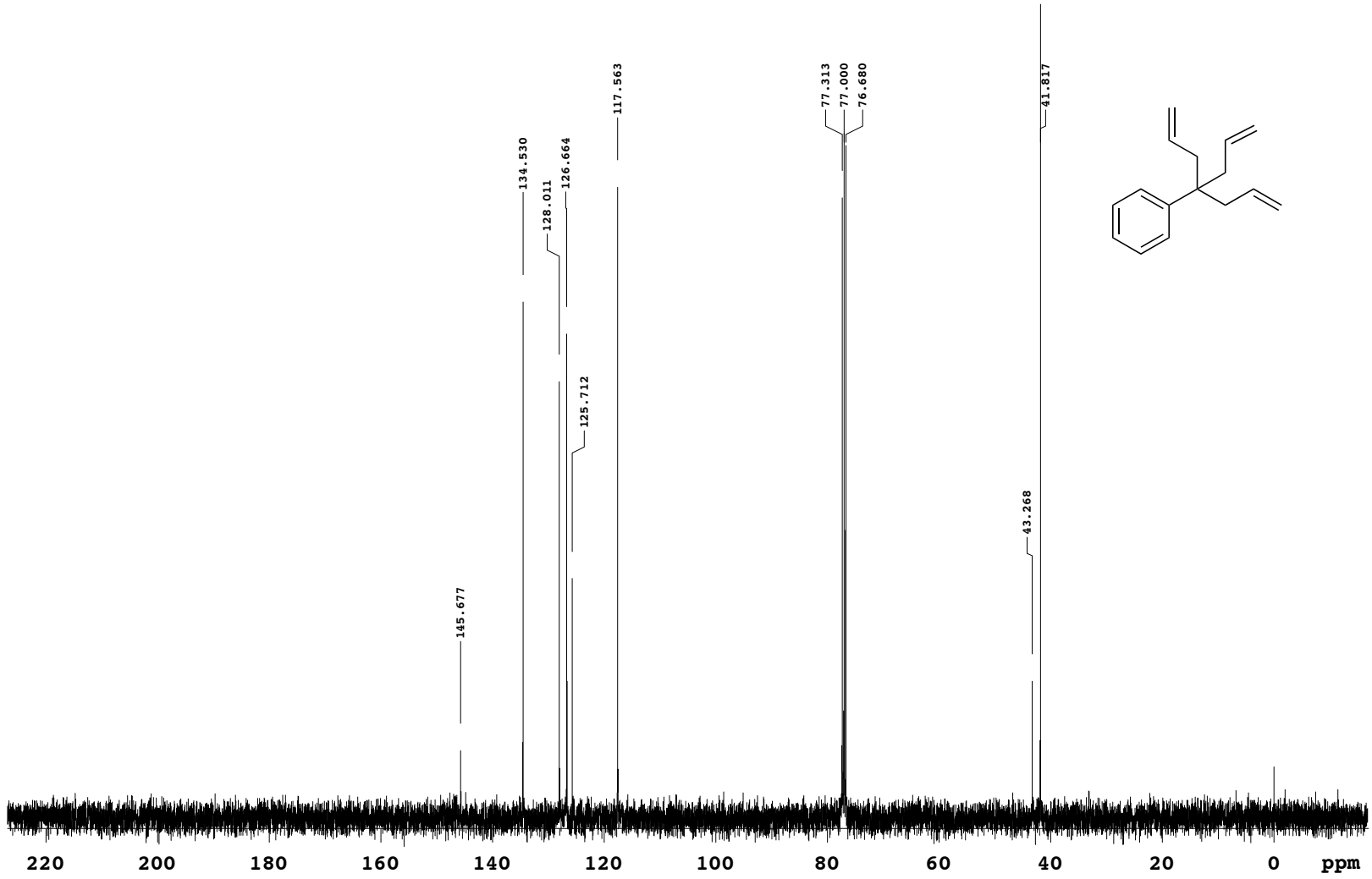


Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/101-200/EXP192-PTLC-H1-1-2.fid

Plot date 2016-10-18

Agilent Technologies

Sample Name		Pulse sequence	**Carbon**	Temperature	**50**	Study owner	**vnmr1**
Date collected	**2015-03-18**	Solvent	**cdcl3**	Spectrometer	**---**	Operator	**vnmr1**



Data file /home/vnmr1/vnmrsys/data/Organic_Chemistry/Akiyama/Umi/101-200/EXP192-PTLC-C13-1-2.fid

Plot date 2015-10-10