Ni- and Pd-Catalyzed Synthesis of Substituted and Functionalized Allylic Boronates

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Supporting Information

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GENERAL INFORMATION

^{1}H NMR spectra were recorded on either a Varian Gemini-400 (400 MHz), a Varian Gemini-500 (500 MHz) or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the reference ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on either a Varian Gemini-400 (100 MHz), or a Varian Gemini-500 (125 MHz) or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the reference ($CDCl_3$: 77.0 ppm). Carbons with directly attached boron atoms were not observed in some compounds, most likely due to quadrupolar relaxation.[1] Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, ν_{max} cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). High-resolution mass spectra (ESI) were obtained at the Mass Spectrometry Facility, Boston College. The melting point was recorded on a laboratory Melt-Temp device, ºC.

Liquid Chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230×450 mesh) purchased from Silicycle. Thin Layer Chromatography was performed on 25 μm silica gel plates purchased from Silicycle. Visualization was performed using ultraviolet light (254 nm) or potassium permanganate ($KMnO_4$) in water.

All reactions were conducted in oven- or flame-dried glasswares under an inert atmosphere of nitrogen or argon unless stated otherwise. Tetrahydrofuran (THF) was purified using a Pure Solv MD-4 solvent purification system from Innovative Technology Inc. Ethyl acetate was purified by drying with calcium hydride and distilled under N_2. Dimethyl sulfoxide (DMSO) was purified by drying with calcium hydride and distilled under high vacuum. Benzaldehyde was freshly distilled under high vacuum prior to use. Tricyclohexylphosphine (PCy_3), tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(dba)_3$], bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$] were purchased from Strem Chemicals, Inc. 2-Methylallyl acetate was purchased form Tokyo Chemical Industry (TCI).

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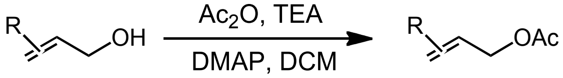
[1] Wrackmeyer, B. *Prog. NMR Spectrosc.* **1979**, *12*, 227.

Bis(pinacolato)diboron [$B_2(pin)_2$] was obtained from Allylchem Co., Ltd. and recrystallized from pentane prior to use. All other reagents were purchased from either Fisher or Aldrich and used without further purification.

EXPERIMENTAL PROCEDURES

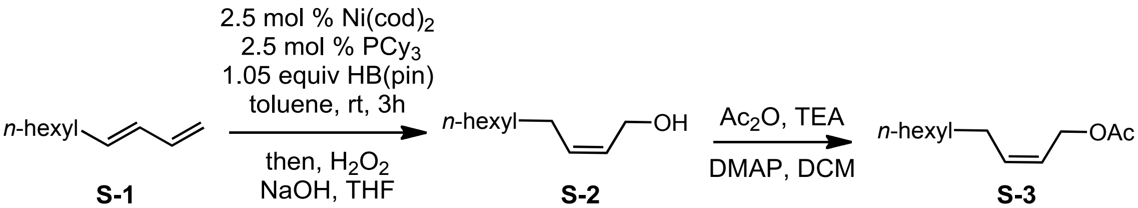
Preparation and Characterization of Allylic Acetates

Representative Procedure for the Synthesis of Allylic Acetates. The non-commercially available allylic acetate substrates were generally prepared by the acetylation of the corresponding allylic alcohols as shown below.



The following allylic acetates were prepared from commercially available allylic alcohols: hex-1-en-3-yl acetate (Table 2, entry 3),[2] (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)allyl acetate (Table 2, entry 6)[3] and (*E*)-2-methylbut-2-en-1-yl acetate (Table 4, entry 5).[4] Spectral data are in accordance with the literature references.

Preparation of (Z)-dec-2-en-1-yl acetate. From allylic alcohol **S-2**, which was synthesized through Ni-catalyzed hydroboration of decadiene as shown below.[5]



S-1 **S-2** **S-3**

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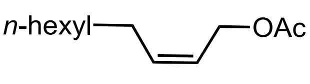
[2] Strazzolini, P.; Giumanin, A. G.; Verardo, G. *Tetrahedron* **1994**, *50*, 217.

[3] Kumar, V.; Sharma, A.; Sharma, M.; Sharma, U. K.; Shiha, A. K. *Tetrahedron* **2007**, *63*, 9718.

[4] Rowan, D. D.; Heather, P.; Allen, J. M.; Fielder, S.; Hunt, M. B. *J. Agric. Food. Chem.* **1996**, *44*, 3276.

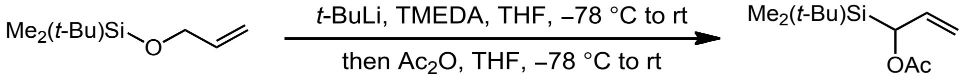
[5] Ely, R. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 2534.



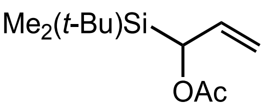
S-3

(*Z*)-dec-2-en-1-yl acetate (Table 2, entry 5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 7.0 Hz, $CH_2C\mathbf{H_3}$), 1.27-1.39 (10H, m, $(C\mathbf{H_2})_5CH_3$), 2.06 (3H, s, $COC\mathbf{H_3}$), 2.09 (2H, dt, *J* = 7.4, 7.4 Hz, $CH_2C\mathbf{H_2}CH{=}CH$), 4.61 (2H, dd, *J* = 6.3, 0.6 Hz, $CH{=}CHC\mathbf{H_2}O$), 5.49-5.55 (1H, m, $C\mathbf{H_a}{=}CH_b$), 5.62-5.67 (1H, m, $CH_a{=}C\mathbf{H_b}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 21.0, 22.6, 27.5, 29.12, 29.14, 29.4, 31.8, 60.4, 123.2, 135.5, 171.0; IR (neat): 2956.4 (w), 2924.9 (m), 2855.2 (w), 1740.0 (s), 1459.1 (w), 1371.5 (m), 1225.0 (s), 1024.6 (m), 962.8 (w), 840.5 (w), 643.4 (w), 606.8 (w) cm^{-1}; HRMS (ESI+) for $C_{12}H_{26}NO_2$ [M+NH_4]: calculated: 216.1964, found: 216.1969. The crude reaction mixture was purified on silica gel (flashed with 100:1 hexanes/EtOAc) to afford 2.13 g (95% yield) of (*Z*)-dec-2-en-1-yl acetate as a colorless oil. R_f = 0.53 (8:1 hexanes/EtOAc, stain in $KMnO_4$).

Preparation of 1-(tert-butyldimethylsilyl)allyl acetate. From commercially available (allyloxy)(*tert*-butyl)dimethylsilane, procedure was modified from the literature procedure.[6]



S-4 **S-5**



S-5

1-(*tert*-butyldimethylsilyl)allyl acetate (Table 2, entry 8). To a flame-dried round-bottom flask equipped with a stir bar was added (allyloxy)(*tert*-butyl)dimethylsilane (345 mg, 2.0 mmol), tetramethylethylenediamine (TMEDA, 326 mg, 2.8 mmol) and THF (4 mL). The reaction was cooled to −78 °C and 1.6 M *tert*-butyllithium in pentane (1.5 mL, 2.4 mmol) was added dropwise over 10 minutes, *via* syringe. The reaction was allowed to slowly warm up to room temperature. After stirring for another 30 minutes, the reaction was cooled to −78 °C and quenched with acetic anhydride (283 mg, 2.8 mmol) in THF (0.25 mL). The reaction was allowed to warm to room temperature and stir for one hour. Water was then slowly added, and the reaction was extracted into diethyl ether three times. The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (50:1

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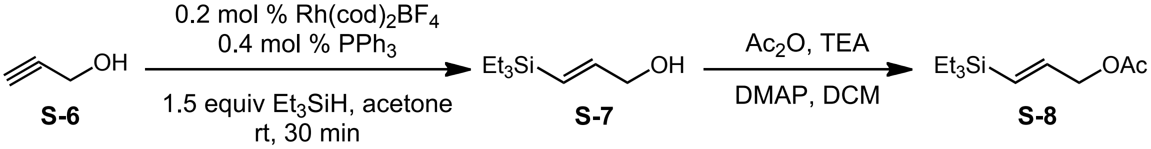
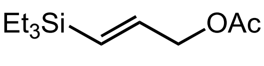
[6] Han, S. B.; Gao, X.; Krische, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 9153.

hexanes/Et_2O) to afford 162 mg (38% yield) of 1-(tert-butyldimethylsilyl)allyl acetate as colorless oil. R*f* = 0.52 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature references.[7]

Preparation of (E)-3-(triethylsilyl)allyl acetate. From (*E*)-3-(triethylsilyl)prop-2-en-1-ol (**S-7**), which was synthesized through the Rh-catalyzed hydrosilyation of prop-2-yn-1-ol as shown below.[8]




S-8

(*E*)-3-(triethylsilyl)allyl acetate (Table 2, entry 9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.58 (6H, q, *J* = 8.1 Hz, Si(C$\mathbf{H_2}$$CH_3$)$_3$), 0.93 (9H, t, *J* = 8.1 Hz, Si(CH_2C$\mathbf{H_3}$)$_3$), 2.10 (3H, s, COC$\mathbf{H_3}$), 4.60 (2H, dd, *J* = 5.1, 1.5 Hz, CH=C**H**CH_2OAc), 5.87 (1H, dt, *J* = 19.0, 1.5 Hz, C**H**=CHCH_2OAc), 6.07 (1H, dt, *J* = 18.9, 5.1 Hz, CH=C**H**CH_2OAc); ^{13}C NMR (125 MHz, $CDCl_3$): δ 3.3, 7.3, 21.0, 67.1, 129.8, 140.5, 170.7; IR (neat): 2953.2 (w), 2910.9 (w), 2875.3 (w), 1743.3 (s), 1623.7 (w), 1458.1 (w), 1416.2 (w), 1376.2 (w), 1226.6 (s), 1068.7 (w), 1014.8 (m), 985.9 (m), 845.2 (w), 777.7 (m), 760.1 (m), 718.0 (s), 637.1 (w), 606.2 (w); HRMS (ESI+) for $C_{11}H_{23}O_2Si$ [M+H]: calculated: 215.1467, found: 215.1463. The crude reaction mixture was purified on silica gel (flashed with 30:1 hexanes/EtOAc) to afford 1.21 g (90% yield) of (*E*)-3-(triethylsilyl)allyl acetate as a colorless oil. R*f* = 0.54 (8:1 hexanes/EtOAc, stain in $KMnO_4$).

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[7] Panek, J. S.; Cirillo, P. F. *J. Am. Chem. Soc.* **1990**, *112*, 4873.

[8] Takeuchi, R.; Nitta, S.; Watanabe, D. *J. Org. Chem*. **1995**, *60*, 3045.

Representative Procedures for Allylic Borylation

Representative Procedure for $Pd_2(dba)_3$ Catalyzed Allylic Borylation (Table 1, entries 1-3 and Table 3, entries 1-4, 6).

In a dry-box under an argon atmosphere, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with tris(dibenzylideneacetone) dipalladium(0) (2.3 mg, 0.0025 mmol), bis(pinacolato)diboron (254 mg, 1.0 mmol), THF (0.5 mL) and lastly, cinnamylchloride (153 mg, 1.0 mmol). The vial was capped and taped with electrical tape, removed from the dry-box, and allowed to stir at 60 °C for 12 hours. The vial was then cooled to ambient temperature, and the reaction mixture was directly analyzed using ^{1}H NMR to determine the conversion of reaction. Silica gel chromatography (50:1 pentane/Et_2O) afforded 220 mg (90% yield) of 2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a colorless oil.

Representative Procedures for $Pd_2(dba)_3$ Catalyzed Allylic Borylation with Bases (Table 1, entries 4-6).

In a dry-box under an argon atmosphere, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with tris(dibenzylideneacetone) dipalladium(0) (22.9 mg, 0.025 mmol), bis(pinacolato)diboron (127 mg, 0.5 mmol), THF (1 mL), 2-methylallyl acetate (57.1 mg, 0.5 mml) and cesium carbonate (489 mg, 1.5 mmol). The vial was capped and taped with electrical tape, removed from the dry-box, and allowed to stir at 60 °C for 12 hours. The vial was then cooled to ambient temperature. The reaction was diluted with diethyl ether, filtered through a plug of silica gel, washed with more diethyl ether, and concentrated in *vacuo*. An 84% reaction conversion was determined by ^{1}H NMR analysis of the crude reaction mixture. No purification was performed.

Representative Procedures for $PdCl_2$ Catalyzed Allylic Borylation (Table 3, entries 1-4 and 6).

An oven-dried 2-dram vial equipped with a magnetic stir bar was charged with palladium(II) chloride (0.9 mg, 0.005 mmol) and bis(pinacolato)diboron (254 mg, 1.0 mmol) . The vial was sealed with a septum and purged three times with N_2. THF (0.5 mL) was added by syringe, followed by the addition of cinnamylchloride (153 mg, 1.0 mmol). The septum was quickly replaced with a cap, and the reaction was allowed to stir at 60 °C for 12 hours. The reaction was then cooled to ambient temperature, and the reaction mixture was directly analyzed using ^{1}H NMR to determine the conversion of reaction. Silica gel chromatography (50:1 pentane/Et_2O) afforded 237 mg (97% yield) of 2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as colorless oil.

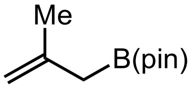
Representative Procedures for $PdCl_2$ Catalyzed Allylic Borylation with KOAc (Table 3, entry 5).

An oven-dried 2-dram vial equipped with a magnetic stir bar was charged with palladium(II) chloride (0.9 mg, 0.005 mmol), bis(pinacolato)diboron (254 mg, 1.0 mmol) and potassium acetate (98.2 mg, 1.0 mmol). The vial was sealed with a septum and purge three times with N_2. THF (0.5 mL) was added by syringe, followed by the addition of 2-methylallyl chloride (90.1 mg, 1.0 mmol). The septum was quickly replaced with a cap, and the reaction was allowed to stir at 60 °C for 12 hours. The reaction was then cooled to ambient temperature. The reaction was diluted with diethyl ether, filtered through a plug of silica gel, washed with more diethyl ether, and concentrated in *vacuo*. The reaction conversion was determined by ^{1}H NMR of the crude reaction mixture. Silica gel chromatography (50:1 pentane/Et_2O) afforded 127 mg (70% yield) of (*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as colorless oil.

Representative Procedures for Ni(cod)$_2$/Phosphine Allylic Borylation (Table 1, entires7-10, Table 2 and Scheme 2).

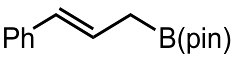
In a dry-box under an argon atmosphere, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (6.9 mg, 0.025 mmol), tricyclohexylphosphine (7.0 mg, 0.025 mmol) and EtOAc (1.0 mL) . Cinnamyl acetate (88.1 mg, 0.5 mmol) was then added, followed by bis(pinacolato)diboron (127 mg, 0.5 mmol). The vial was capped and sealed, removed from the dry-box, and allowed to stir at 60 °C for 12 hours. The vial was then cooled to ambient temperature, and the crude reaction mixture was directly analyzed using ^{1}H NMR to determine the conversion of reaction. Silica gel chromatography (50:1 pentane/Et_2O) afforded 224 mg (92% yield) of 2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as colorless oil.

Characterization and Proof of Stereochemistry



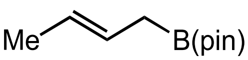
4

4,4,5,5-tetramethyl-2-(2-methylallyl)-1,3,2-dioxaborolane (Table 1). The crude reaction mixture was purified on silica gel (50:1 pentane/Et_2O) to afford a clear, colorless oil (60.0 mg, 67% yield). R_f = 0.49 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature references.[9]



S-9

2-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 1). The crude reaction mixture was purified on silica gel (50:1 pentane/Et_2O) to afford a clear, colorless oil (109.9 mg, 90% yield). R_f = 0.45 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature reference.[10]



S-10

(*E*)-2-(but-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 2 and Table 3, entries 2-3). The crude reaction mixture was purified on silica gel (50:1 pentane/Et_2O) to afford a clear, colorless oil (76.5 mg, 84% yield) with 5% (*Z*)-2-(cyclooct-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as impurity from ^{1}H NMR analysis. R_f = 0.55 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature reference.[11]

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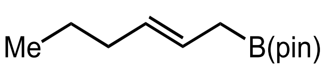
[9] (a) Ishiyama, T.; Ahiko, T.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 6889. (b) Zhang, P.; Brozek, L. A.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 10686.

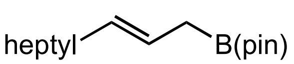
[10] Selander, N.; Szabó, K. J. J. *Org. Lett.* **2009**, *74*, 5695.

[11] Roush, W. R.; Adam, M. A.; Walts, A. E.; Harris, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 3422.



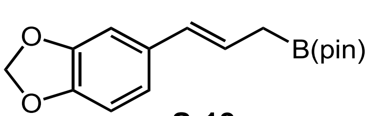
S-11

(*E*)-2-(hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entries 3-4). ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.86 (3H, t, *J* = 9 Hz, CH$_2$C**H$_3$**), 1.21 (12 H, s, (C(C**H$_3$**)$_2$)$_2$), 1.29-1.39 (2H, m, C**H$_2$**CH$_3$), 1.62 (2H, d, *J* = 8.0 Hz, C**H$_2$**B), 1.95 (2H, app q, J = 8.5 Hz, CH$_2$C**H$_2$**CH=CH), 5.33-5.47 (2H, m, CH$_2$CH$_2$C**H**=C**H**); ^{13}C NMR (125 MHz, CDCl$_3$): δ 13.6, 22.7, 24.7, 34.8, 83.1, 124.8, 130.8; IR (neat): 2978.1 (w), 2959.3 (w), 2929.4 (w), 2872.7 (w), 1457.7 (w), 1359.0 (m), 1323.3 (s), 1142.9 (s), 965.8 (s), 846.8 (m), 673.8 (m), 520.0 (w) cm^{-1}; HRMS (ESI+) for $C_{12}H_{24}BO_2$ [M+H]: calculated: 211.1869, found: 211.1876. The crude reaction mixture was purified on silica gel (50:1 pentane/Et$_2$O) to afford a clear, colorless oil (99.3 mg, 94% yield). R$_f$ = 0.6 (8:1 hexanes/EtOAc, stain in KMnO$_4$).



S-12

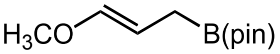
(*E*)-2-(dec-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 5). ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.87 (3H, t, *J* = 7.0 Hz, CH$_2$C**H$_3$**), 1.20-1.37 (22 H, m, CH$_3$(C**H$_2$**)$_5$ and (C(C**H$_3$**)$_2$)$_2$), 1.63 (2H, d, *J* = 6.0 Hz, C**H$_2$**B), 1.96 (2H, app q, J = 6.5 Hz, CH$_2$C**H$_2$**CH=CH), 5.31-5.46 (2H, m, CH$_2$CH$_2$C**H**=C**H**); ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1, 22.7, 24.7, 29.1, 29.2, 29.7, 31.9, 32.7, 83.1, 124.6, 131.1 ppm; IR (neat): 2976.1 (w), 2956.3 (w), 2928.4 (w), 1460.7 (w), 1356.3 (m), 1321.2 (s), 1141.0 (s), 962.3 (s), 842.3 (m), 671.1 (m), 654.2 (m), 431.2 (w) cm^{-1}; HRMS (ESI+) for $C_{16}H_{32}BO_2$ [M+H]: calculated: 267.2469, found: 267.2472. The crude reaction mixture was purified on silica gel (50:1 pentane/Et$_2$O) to afford a clear, colorless oil (122.5 mg, 92% yield). R$_f$ = 0.66 (8:1 hexanes/EtOAc, stain in KMnO$_4$).



S-13

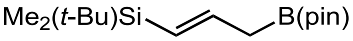
(*E*)-2-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.26 (12H, s, (C(C**H$_3$**)$_2$)$_2$), 1.84 (2H, d, *J* = 7.3 Hz, CH=CHC**H$_2$**B), 5.93 (2H, s, OC**H$_2$**O), 6.10 (1H, dt, *J* = 15.6, 7.6 Hz, CH=C**H**CH$_2$B), 6.28 (1H, d, *J* = 15.6 Hz, C**H**=CHCH$_2$B), 6.70-6.75 (2H, m, Ar**H**), 6.89 (1H, s, Ar**H**); ^{13}C NMR (125 MHz, CDCl$_3$): δ 24.8, 83.4, 100.8, 105.4, 108.1, 120.0, 124.9, 129.8, 132.8, 146.3, 147.8; IR (neat): 2977.6 (w), 2930.4 (w), 2877.4 (w), 1488.8 (m), 1442.3 (m), 1360.4 (m), 1326.8 (s), 1276.2 (s), 1248.0 (s), 1140.5 (s), 1119.6 (s), 1033.3 (s), 963.3 (s), 929.1 (s), 876.8 (s), 844.9 (m), 799.8 (s), 521.2 (m) cm^{-1}; HRMS (ESI+) for $C_{16}H_{22}BO_4$ [M+H]:

calculated: 289.1611, found: 289.1612. The crude reaction mixture was purified on silica gel (10:1 pentane/Et$_2$O) to afford a white solid (108.4 mg, 95% yield). R_f = 0.33 (8:1 hexanes/EtOAc, stain in KMnO$_4$). Melting point: 48 °C.



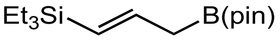
S-14

(*E*)-2-(3-methoxyallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 2, entry 7). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.26 (12H, s, (C(C$\mathbf{H_3}$)$_2$)$_2$), 1.51 (2H, d, *J* = 7.4 Hz, CH=CHC$\mathbf{H_2}$B), 3.49 (3H, s, OC$\mathbf{H_3}$), 4.76 (1H, dt, *J* = 12.7, 7.3 Hz, CH=C**H**CH$_2$B), 6.27 (1H, d, *J* = 12.7 Hz, C**H**=CHCH$_2$B); ^{13}C NMR (100 MHz, CDCl$_3$): δ 24.8, 55.9, 83.2, 97.8, 147.0; IR (neat): 2978.5 (w), 2934.0 (w), 1653.3 (w), 1358.5 (m), 1321.9 (s), 1272.5 (w), 1212.0 (m), 1143.5 (s), 1123.0 (s), 1105.6 (m), 967.2 (m), 881.2 (m), 845.7 (m), 673.2 (w), 539.8 (w) cm^{-1}; HRMS (ESI+) for $C_{10}H_{20}BO_3$ [M+H]: calculated: 199.1506, found: 199.1497. The crude reaction mixture was purified on silica gel (100:1 → 25:1 pentane/Et$_2$O) to afford a clear, colorless oil (51.5 mg, 52% yield). R_f = 0.38 (8:1 hexanes/EtOAc, stain in KMnO$_4$).



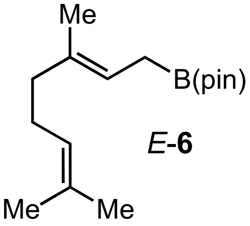
S-15

***tert*-butyldimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (Table 2, entry 8).** ^{1}H NMR (500 MHz, CDCl$_3$): δ –0.01 (*E*, 6H, s, Si(C$\mathbf{H_3}$)$_2$), 0.09 (*Z*, 6H, s, Si(C$\mathbf{H_3}$)$_2$), 0.85 (*E*, 9H, s, SiC(C$\mathbf{H_3}$)$_3$), 0.88 (*Z*, 9H, s, SiC(C$\mathbf{H_3}$)$_3$), 1.236 (*E*, 12H, s, (C(C$\mathbf{H_3}$)$_2$)$_2$), 1.243 (*Z*, 12H, s, (C(C$\mathbf{H_3}$)$_2$)$_2$), 1.82-1.85 (2H, m, CH=CHC$\mathbf{H_2}$B), 5.47 (*Z*, 1H, dt, *J* = 14.2, 1.3 Hz, C**H**=CHCH$_2$B), 5.60 (*E*, 1H, dt, *J* = 18.5, 1.5 Hz, C**H**=CHCH$_2$B), 6.08 (*E*, 1H, dt, *J* = 18.5, 7.2 Hz, CH=C**H**CH$_2$B), 6.51 (*Z*, 1H, dt, *J* = 14.2, 8.3 Hz, CH=C**H**CH$_2$B); ^{13}C NMR (125 MHz, CDCl$_3$): δ –6.1, –4.1, 10.6, 16.5, 24.6, 24.71, 24.74, 26.4, 26.5, 30.9, 83.2, 82.3, 125.2, 127.5, 143.4, 144.7; IR (neat): 2978.7 (w), 2952.5 (w), 2927.7 (w), 2884.2 (w), 2855.3 (w), 2040.0 (w), 1744.4 (w), 1608.6 (w), 1470.0 (w), 1370.5 (w), 1323.6 (s), 1272.0 (w), 1247.2 (m), 1214.7 (w), 1164.7 (w), 1143.7 (s), 1105.0 (w), 1006.7 (w), 986.9 (w), 967.0 (w), 938.0 (w), 885.2 (w), 847.9 (w), 825.5 (s), 810.0 (m), 773.8 (m), 715.8 (w), 576.9 (w), 545.7 (w) cm^{-1}; HRMS (ESI+) for $C_{15}H_{32}BO_2Si$ [M+H]: calculated: 283.2265, found: 283.2257. The crude reaction mixture was purified on silica gel (pentane → 100:1 pentane/Et$_2$O) to afford a clear, colorless oil (98.7 mg, 70% yield) as a mixture of *E* and *Z* isomers (2.5:1 *E*:*Z*). R_f = 0.61 (8:1 hexanes/EtOAc, stain in $KMnO_4$).



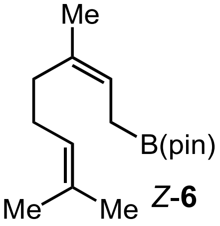
S-16

triethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (Table 2, entry 9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.53 (*E*, 6H, q, *J* = 8.0 Hz, $(CH_3C\mathbf{H_2})_3Si$), 0.62 (*Z*, 6H, q, *J* = 8.0 Hz, $(CH_3C\mathbf{H_2})_3Si$), 0.88-0.96 (9H, m, $(C\mathbf{H_3}CH_2)_3Si$), 1.24 (*E*, 12H, s, $(C(C\mathbf{H_3})_2)_2$), 1.26 (*Z*, 12H, s, $(C(C\mathbf{H_3})_2)_2$), 1.83 (2H, d, *J* = 7.5 Hz, $CH{=}CHC\mathbf{H_2}B$), 5.38 (*Z*, d, *J* = 14.0 Hz, $SiC\mathbf{H}{=}CHCH_2$), 5.53 (*E*, d, *J* = 18.5 Hz, $SiC\mathbf{H}{=}CHCH_2$), 6.08 (*E*, dt, *J* = 18.5, 7.5 Hz, $SiCH{=}C\mathbf{H}CH_2$), 6.08 (*Z*, dt, *J* = 14.0, 7.5 Hz, $SiCH{=}C\mathbf{H}CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 3.6, 4.6, 7.3, 7.5, 24.8, 83.2, 124.6, 126.3, 143.5, 145.0; IR (neat): 2978. 8 (w), 2952.2 (w), 2910.4 (w), 2874.3 (w), 1609.1 (w), 1323.0 (s), 1143.5 (s), 1013.9 (w), 987.1 (w), 966.7 (w), 847.8 (w), 716.0 (s) cm^{-1}; HRMS (ESI+) for $C_{15}H_{32}BO_2Si$ [M+H]: calculated: 283.2265, found: 283.2258. The crude reaction mixture was purified on silica gel (pentane ⟶ 100:1 pentane/Et_2O) to afford a clear, colorless oil (131.2 mg, 93% yield) as a mixture of *E* and *Z* isomers (2.2:1 *E*:*Z*). R_f = 0.60 (8:1 hexanes/EtOAc, stain in $KMnO_4$).



E-**6**

(*E*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*-6). The crude reaction mixture was purified on silica gel (50:1 pentane/Et_2O) to afford a clear, colorless oil (131.9 mg, quat. yield). R_f = 0.55 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature references.[12]



Z-**6**

(*Z*)-2-(3,7-dimethylocta-2,6-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*Z*-6). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (12H, s, $(C(C\mathbf{H_3})_2)_2$), 1.61 (5H, m, $(C\mathbf{H_3})_{\mathbf{a}}C{=}CH$ and $C\mathbf{H_2}B$), 1.68 (3H, s, $(C\mathbf{H_3})_{\mathbf{b}}C{=}CH$), 1.69 (3H, s, $(C\mathbf{H_3})_{\mathbf{c}}C{=}CH$), 2.00-2.06 (4H, m, $C\mathbf{CH_2CH_2}C$), 5.13 (1H, tq, *J* = 7.0, 1.5 Hz, $(C{=}C\mathbf{H})_{\mathbf{a}}CH_2$), 5.24 (1H, tq, *J* = 7.5, 1.5 Hz, $(C{=}C\mathbf{H})_{\mathbf{b}}CH_2$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.6, 23.5, 24.8, 25.7, 26.4, 31.8, 83.1, 119.1, 124.5, 131.3, 135.2; IR (neat): 2976.9 (w),

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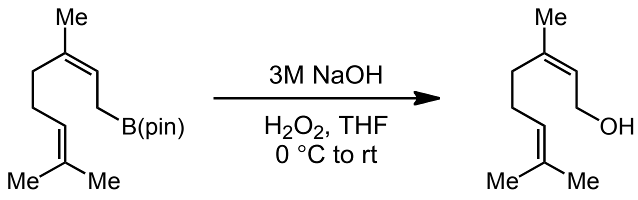
[12] (a) Wu, J.; Moreau, B.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 12915. (b) Dutheuil, G.; Aggarwal, V. K.; Selander, N.; Szabó, K. J. *Synthesis*, **2008**, *14*, 2293.

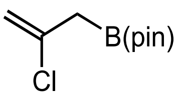
2925.8 (w), 2856.7 (w), 1448.1 (w), 1370.6 (w), 1340.6 (s), 1322.2 (s), 1272.6 (w), 1214.3 (w), 1143.2 (s), 1106.4 (w), 1074.8 (w), 967.4 (m), 884.5 (m), 845.2 (m), 674.5 (w) 577.8 (w) cm^{-1}; HRMS (ESI+) for $C_{16}H_{30}BO_2$ [M+H]: calculated: 265.2339, found: 265.2350. The crude reaction mixture was purified on silica gel (pentane ⟶ 100:1 pentane/Et_2O) to afford a clear, colorless oil (131.5 mg, >95% yield). R_f = 0.55 (8:1 hexanes/EtOAc, stain in $KMnO_4$).

Proof of Stereochemistry. The relative configuration was assigned by oxidizing the title compound to the corresponding allylic alcohol **S-17**. The ^{1}H and ^{13}C spectral of **S-17** are in accordance with commercial nerol.



Z-**6**

S-17

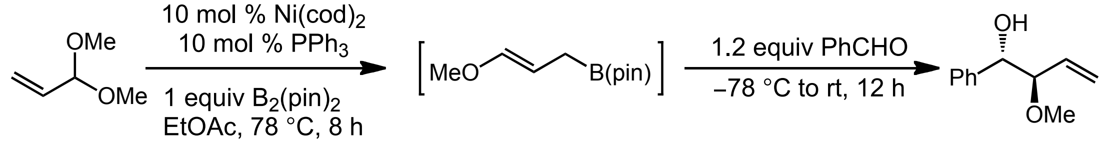


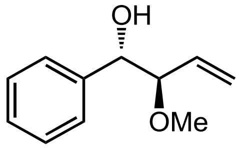
S-18

2-(2-chloroallyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Table 3, entry 5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (12H, s, $(C(C\mathbf{H_3})_2)_2$), 2.12 (2H, s, $CH_2{=}CClC\mathbf{H_2}B$), 5.11 (1H, s, $C\mathbf{H_a}H_b{=}CCl$), 5.14 (1H, s, $CH_a\mathbf{H_b}{=}CCl$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.7, 83.9, 112.2, 139.2; IR (neat): 2979.6 (w), 2930.8 (w), 1634.1 (w), 1331.1 (w), 1272.9 (w), 1141.4 (s), 968.5 (m), 871.7 (m), 845.6 (m), 671.6 (w), 631.9 (w), 548.6 (w) cm^{-1}; HRMS (ESI+) for $C_9H_{17}BClO_2$ [M+H]: calculated: 203.1010, found: 203.1015. The crude reaction mixture was purified on silica gel (50:1 pentane/Et_2O) to afford a clear, colorless oil (69.8 mg, 69% yield). R_f = 0.52 (8:1 hexanes/EtOAc, stain in $KMnO_4$).

Representative Procedures for the One-Pot Borylation/Allylboration (Table 4)

Representative Procedure A:



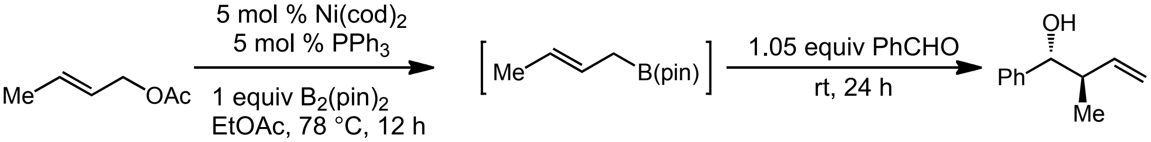


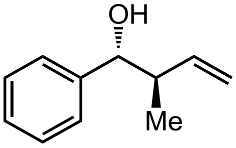
S-19

2-methoxy-1-phenylbut-3-en-1-ol (Table 4, entry 1). In a dry-box under an argon atmosphere, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (13.8 mg, 0.05mmol), triphenylphosphine (13.1 mg, 0.05 mmol) and EtOAc (1.0 mL). 3,3-Dimethoxyprop-1-ene (51.1 mg, 0.5 mmol) was then added, followed by bis(pinacolato)diboron (127 mg, 0.5 mmol). The vial was capped and taped with electrical tape, removed from the dry-box, and allowed to stir at 60 °C for 8 hours. The reaction was then concentrated *in vacuo*, cooled to -78 °C and charged with freshly distilled benzylaldehyde (63.6 mg, 0.6 mmol) dropwise. The reaction was capped, allowed to warm to room temperature and stir for 12 hours. The reaction was then diluted with 1:1 mixture of diethyl ether and water, and extracted with diethyl ether three times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Analysis of the crude reaction mixture using ^{1}H NMR was used to determine the conversion and the diastereoselectivity of the reaction. The crude reaction mixture was purified on silica gel (10:1 hexanes:EtOAc) to afford a clear, colorless oil (78.1 mg, 80% yield). R_f = 0.25 (8:1 hexanes/EtOAc, stain in $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.56 (1H, m, O**H**), 3.33 (3H, s, OC**H₃**), 3.78 (1H, m, MeOC**H**CH=CH₂), 4.83 (1H, t, *J* = 4.0 Hz, ArC**H**OH), 5.19 (1H, dq, *J* = 17.5, 1.0 Hz, C**H*trans***H*cis*=CH), 5.28 (1H, dq, *J* = 11.0, 1.0 Hz, CH*trans***H*cis***=CH), 5.65 (1H, ddd, *J* = 17.5, 11.0, 8.0 Hz, CH₂=C**H**), 7.25-7.28 (1H, m, Ar-**H**), 7.31-7.35 (4H, m, Ar-**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 56.7, 75.3, 86.6, 120.2, 126.7, 127.5, 128.0, 133.6, 140.1; IR (neat): 3448.7 (w), 2982.0 (w), 2929.4 (w), 2880.7 (w), 2823.7 (w), 1452.1 (m), 1189.1 (m), 1100.8 (m), 1081.6 (m), 1065.1 (m), 989.5 (m), 926.6 (m), 725.1 (m), 697.9 (s) cm^{-1}; HRMS (ESI+) for $C_{11}H_{18}NO_2$ [M+NH₄]: calculated: 196.1337, found: 196.1347.

Proof of Stereochemistry. The relative configuration was assigned by comparison of the ^{1}H with the literature references.[13]

Representative Procedure B:





S-20

2-methyl-1-phenylbut-3-en-1-ol (Table 4, entry 3). In a dry-box under an argon atmosphere, an oven-dried 2-dram vial equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (6.9 mg, 0.025 mmol), triphenylphosphine (13.1 mg, 0.025 mmol) and EtOAc (1.0 mL). Crotyl acetate (57.1 mg, 0.5 mmol) was then added, followed by bis(pinacolato)diboron (127 mg, 0.5 mmol). The vial was capped and taped with electrical tape, removed from the dry-box, and allowed to stir at 60 °C for 12 hours. The reaction was allowed to cool to ambient temperature and then charged with freshly distilled benzylaldehyde (55.7 mg, 0.53 mmol). The reaction was capped again and allowed to stir for another 24 hours. The reaction was then diluted with a 1:1 mixture of diethyl ether and water, and extracted with diethyl ether for three times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Analysis of the crude reaction mixture using ^{1}H NMR was used to determine the conversion and the diastereoselectivity of the reaction. The crude reaction mixture was purified on silica gel (12:1 hexanes:EtOAc) to afford a clear, colorless oil (64.9 mg, 80% yield). $R_f = 0.24$ (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature reference.[14]

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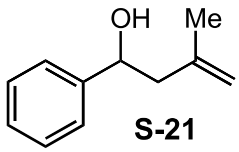
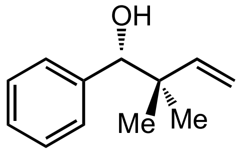
[13] The *syn*-diastereomer of this molecule has been reported: Brown, H. C.; Jadhav, P. K.; Bhat, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 1535.

[14] Katsukiyo, M.; Wang, D.; Hosomi, A.; *J. Am. Chem. Soc.* **2005**, *127*, 9366.



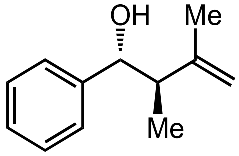
S-21

3-methyl-1-phenylbut-3-en-1-ol (Table 4, entry 2). Procedure B was followed. The crude reaction mixture was purified on silica gel (12:1 hexanes:EtOAc) to afford a clear, colorless oil (71.3 mg, 88% yield). R_f = 0.25 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature reference.[15]



S-22

2,2-dimethyl-1-phenylbut-3-en-1-ol (Table 4, entry 4). Procedure B was followed. The crude reaction mixture was purified on silica gel (40:1 hexanes:EtOAc) to afford a clear, colorless oil (44.1 mg, 50% yield). R_f = 0.38 (8:1 hexanes/EtOAc, stain in $KMnO_4$). Spectral data are in accordance with the literature reference.[15]



S-23

2,3-dimethyl-1-phenylbut-3-en-1-ol (Table 4, entry 5). Procedure B was followed. The crude reaction mixture was purified on silica gel (40:1 hexanes:EtOAc) to afford a clear, colorless oil (70 mg, 50% yield) as a mixture of *anti* and *syn* diastereomers (15:1 *anti*:*syn*). R_f = 0.27 (8:1 hexanes/EtOAc, stain in $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.79 (3H, d, J = 7.1 Hz, $CHC\mathbf{H_3}$), 1.79 (3H, m, $C\mathbf{H_3}C{=}CH_2$), 2.27 (1H, d, J = 1.7 Hz, $O\mathbf{H}$), 2.48 (1H, dq, J = 9.5, 7.0 Hz, $CH_3C\mathbf{H}C{=}CH_2$), 4.38 (1H, dd, J = 9.5, 1.7 Hz, $ArC\mathbf{H}OH$), 4.99 (2H, m, $C{=}C\mathbf{H_2}$), 7.29-7.37 (5H, m, Ar-**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.9, 18.5, 50.1, 76.2, 113.7, 127.1, 127.7, 128.3, 142.5, 147.3; IR (neat): 3442.9 (w), 3066.1 (w), 3029.8 (w), 2967.2 (w), 2935.8 (w), 2899.9 (w), 1644.3 (w), 1493.6 (w), 1453.0 (w), 1373.5 (w), 1318.3 (w), 1271.0 (w), 1193.2 (w), 1086.6 (w), 1072.8 (w), 1053.0 (w), 1017.3 (m), 889.4 (s), 834.7 (w), 751.2 (m), 698.3 (s), 628.8 (w), 568.8 (m), 541.3 (w) cm^{-1}; HRMS (ESI+) for $C_{12}H_{15}$ $[M+H-H_2O]$: calculated: 159.1174, found: 159.1172.

Proof of Stereochemistry. The relative configuration was assigned by comparison of the ^1H with the literature reference.[16]

SPECTRAL DATA

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[15] Han, S. B.; Kim, I. S.; Han, H.; Krische, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 6916.

[16] Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577.

S-3

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Sep 9 2010

Temp. 25.0 C / 298.1 K
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INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
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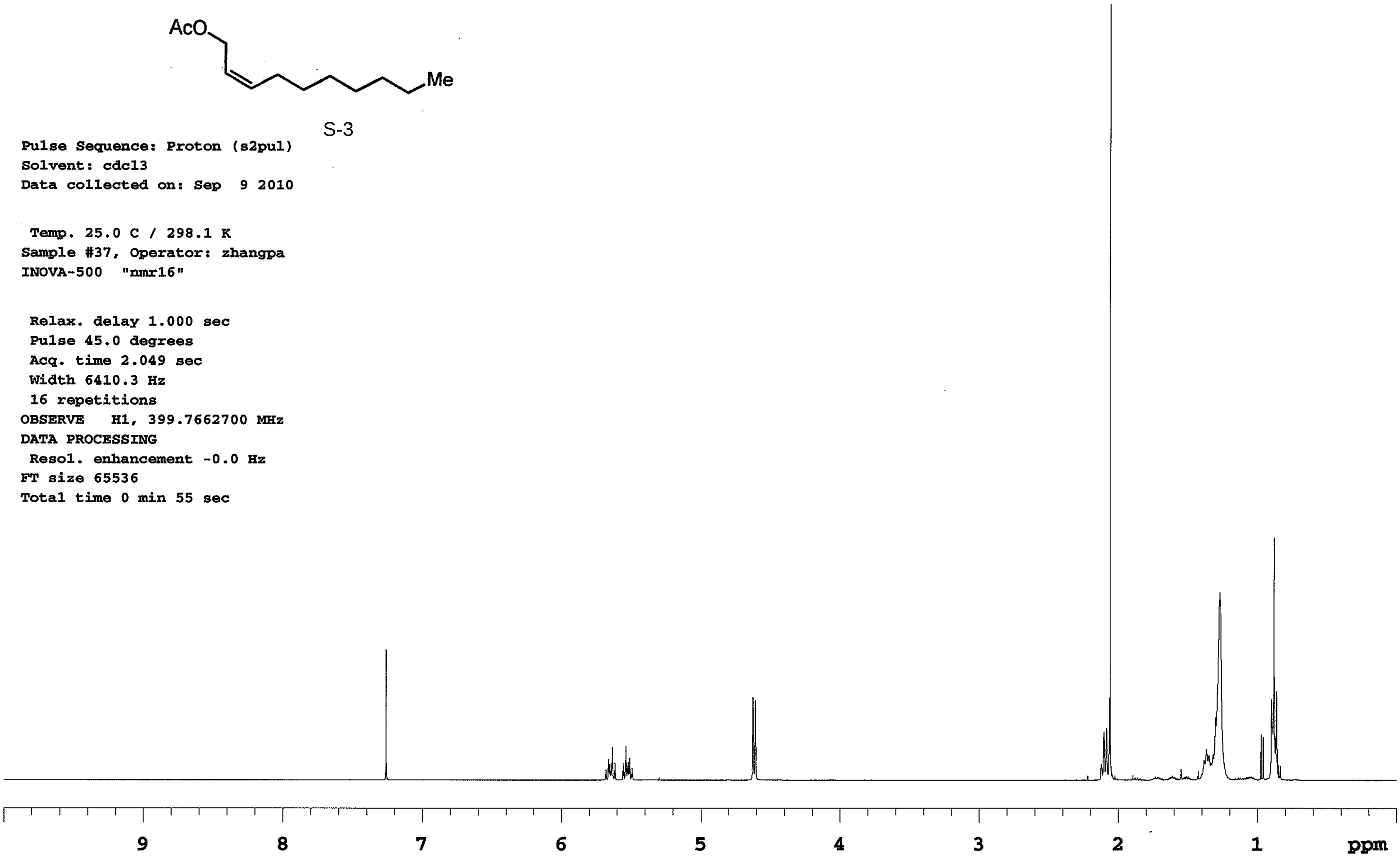
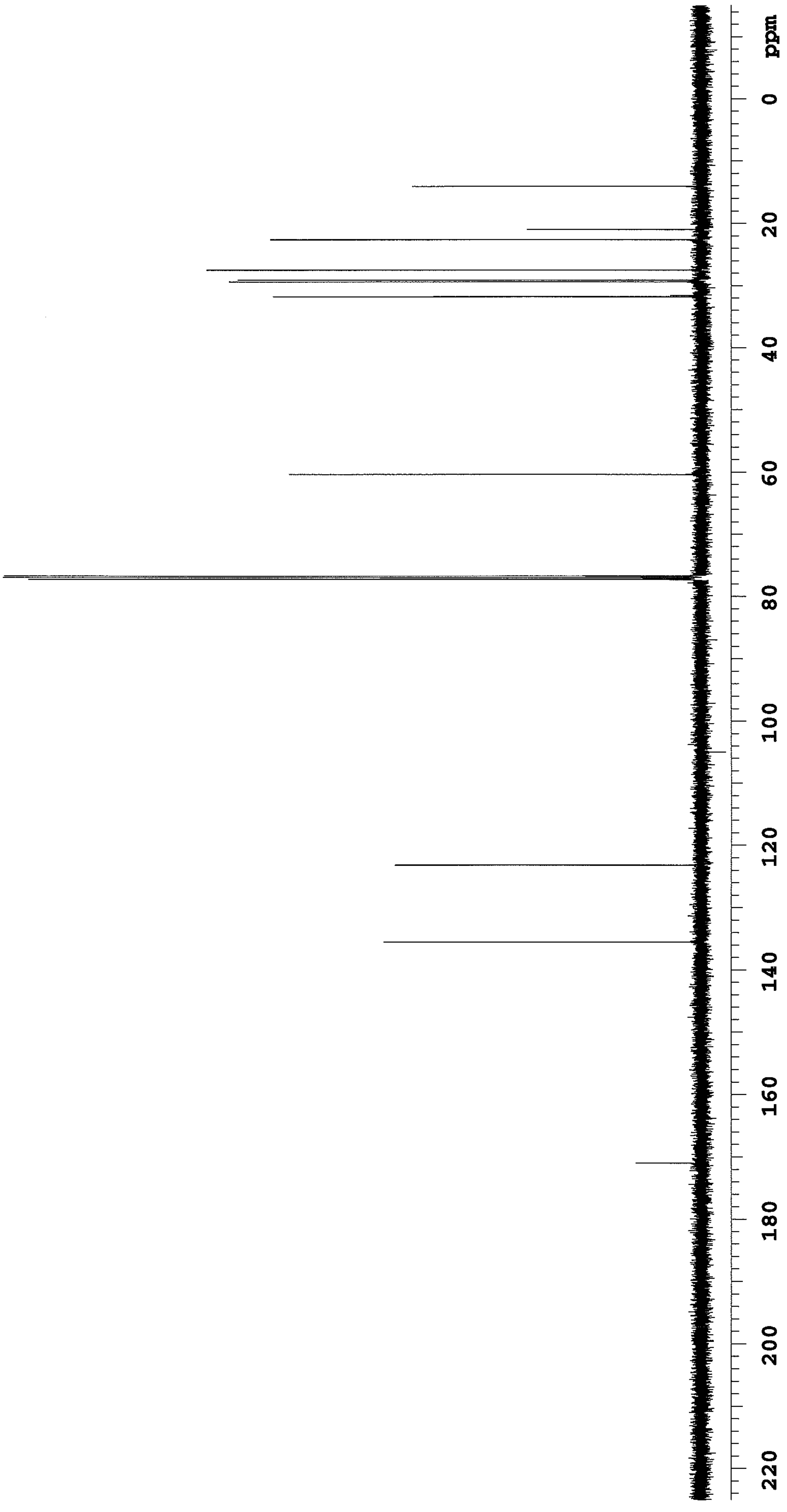
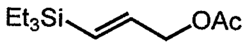
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec

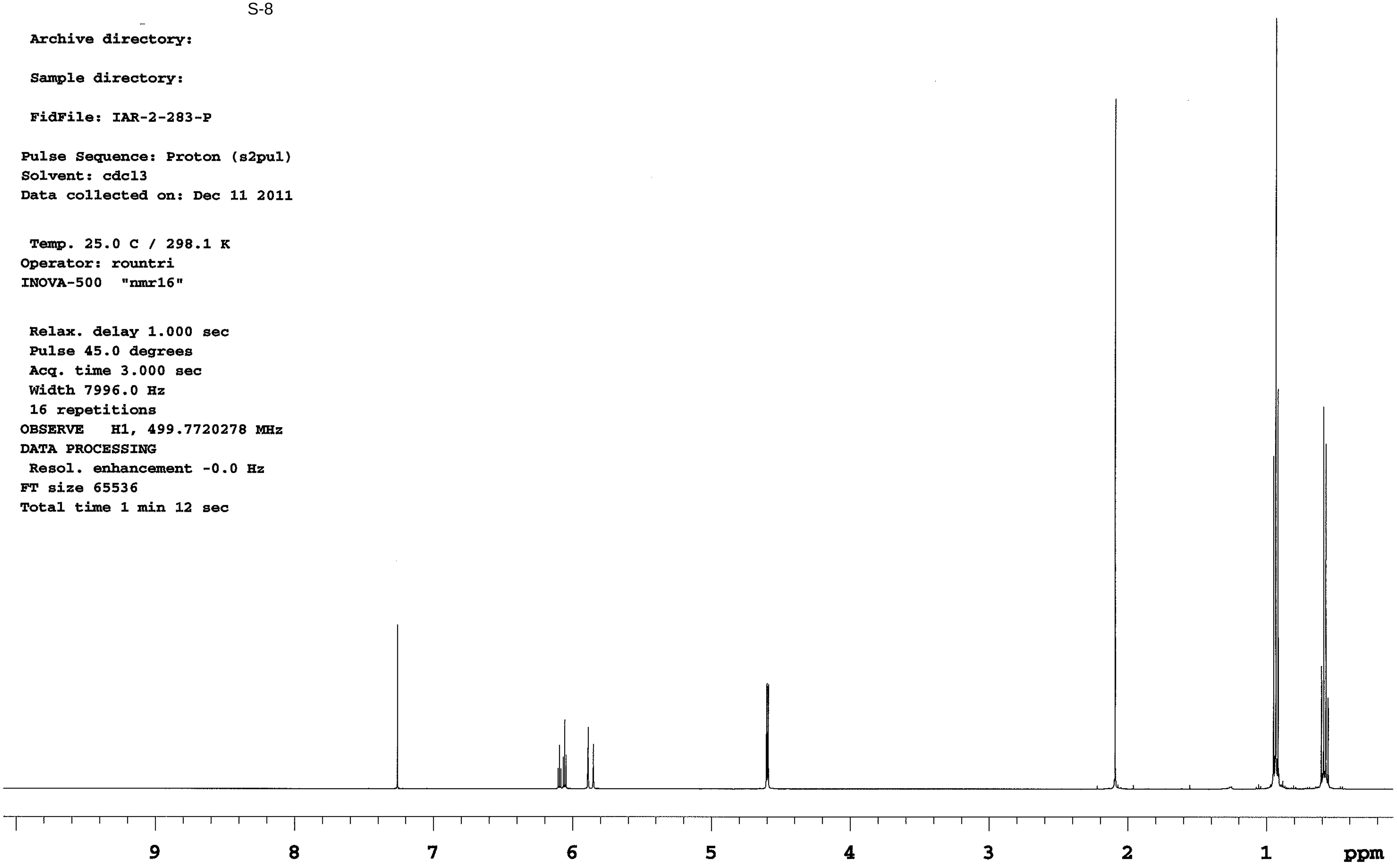


S-3





S-8



Archive directory:

Sample directory:

FidFile: IAR-2-283-P

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Solvent: cdcl3
Data collected on: Dec 11 2011

Temp. 25.0 C / 298.1 K
Operator: rountri
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
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DATA PROCESSING
Resol. enhancement -0.0 Hz
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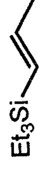
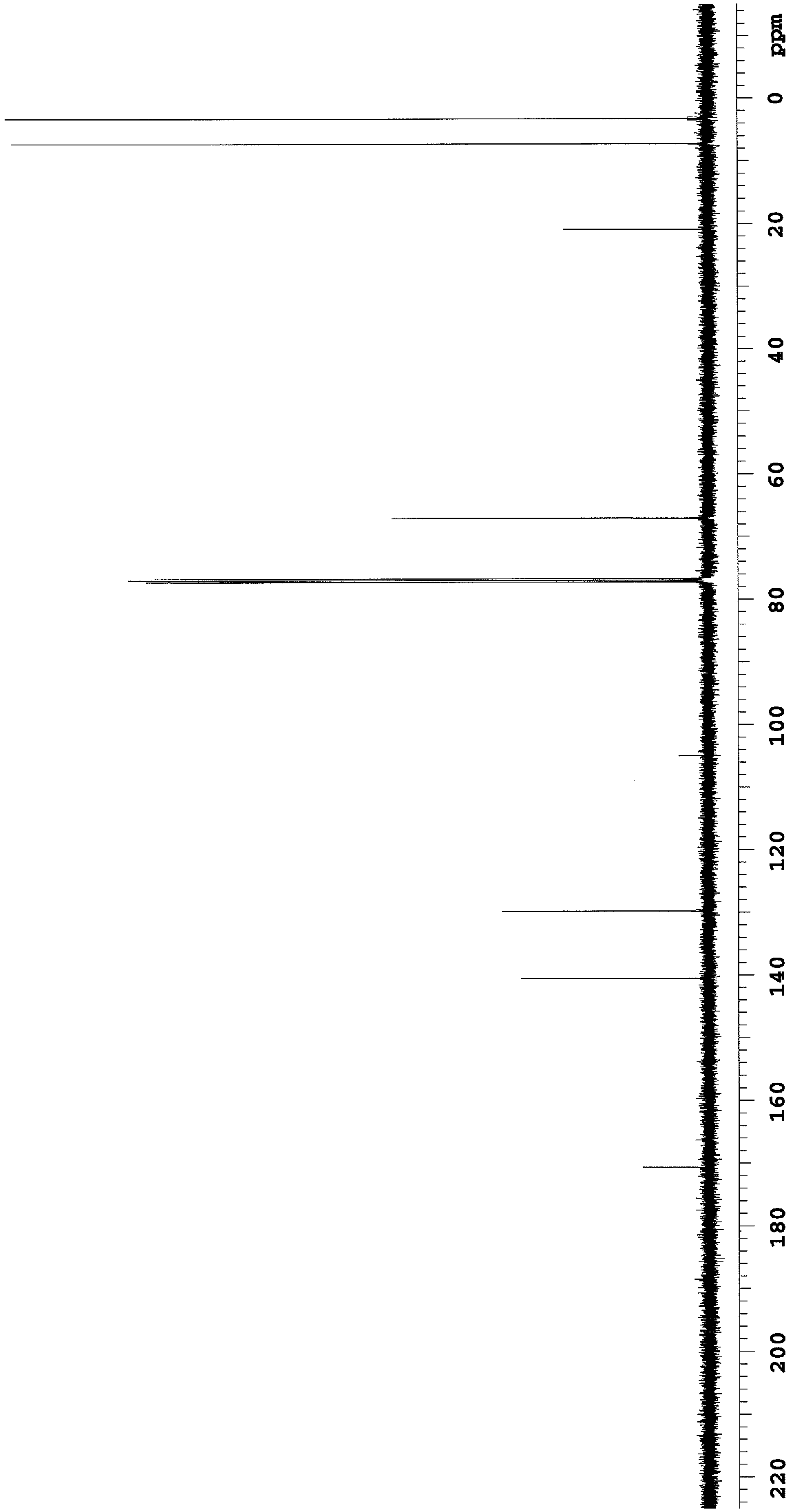
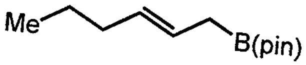
Total time 1 min 12 sec



S-8





S-11

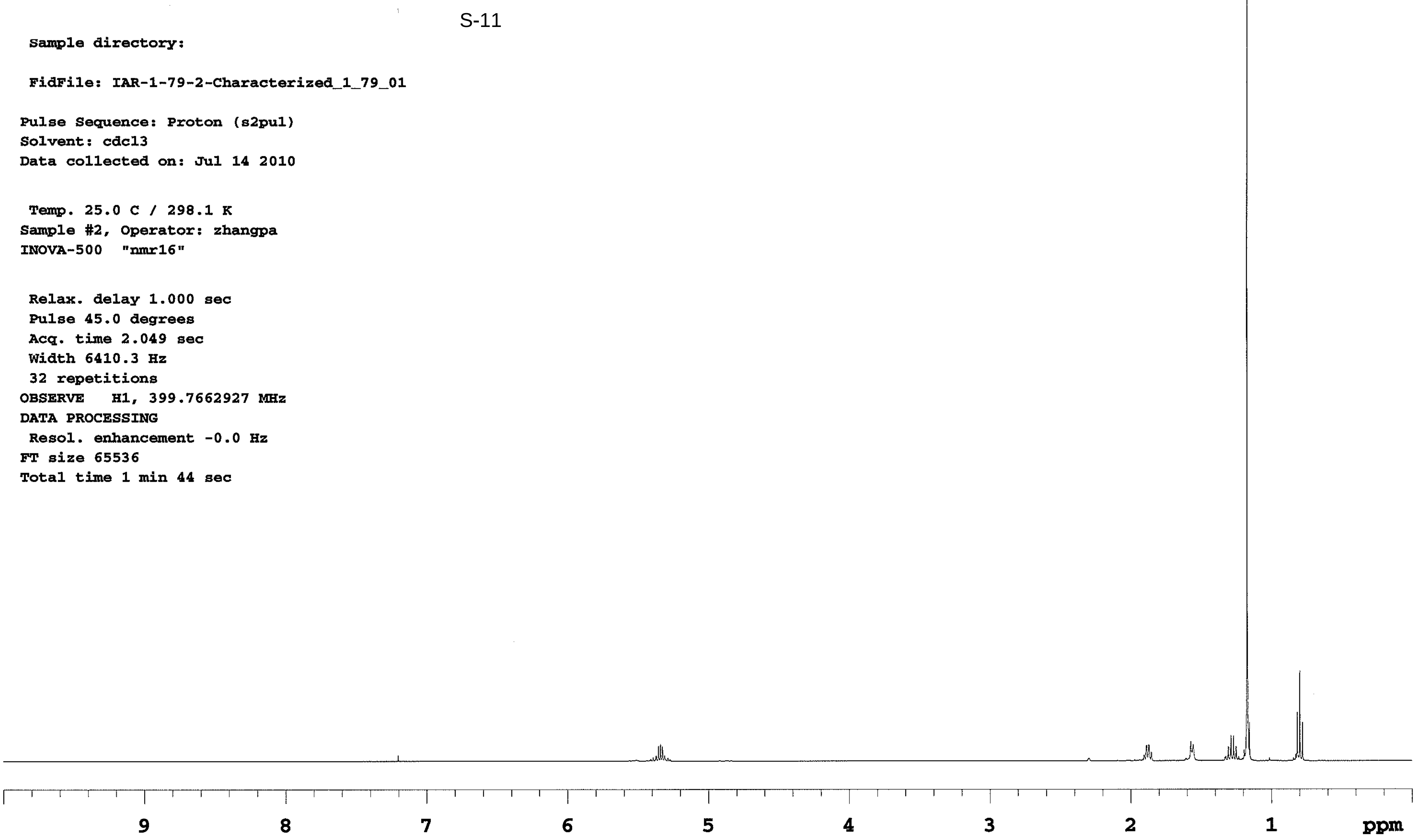
Sample directory:

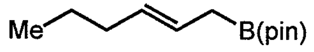
FidFile: IAR-1-79-2-Characterized_1_79_01

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 14 2010

Temp. 25.0 C / 298.1 K
Sample #2, Operator: zhangpa
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
32 repetitions
OBSERVE H1, 399.7662927 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min 44 sec





S-11

Archive directory:

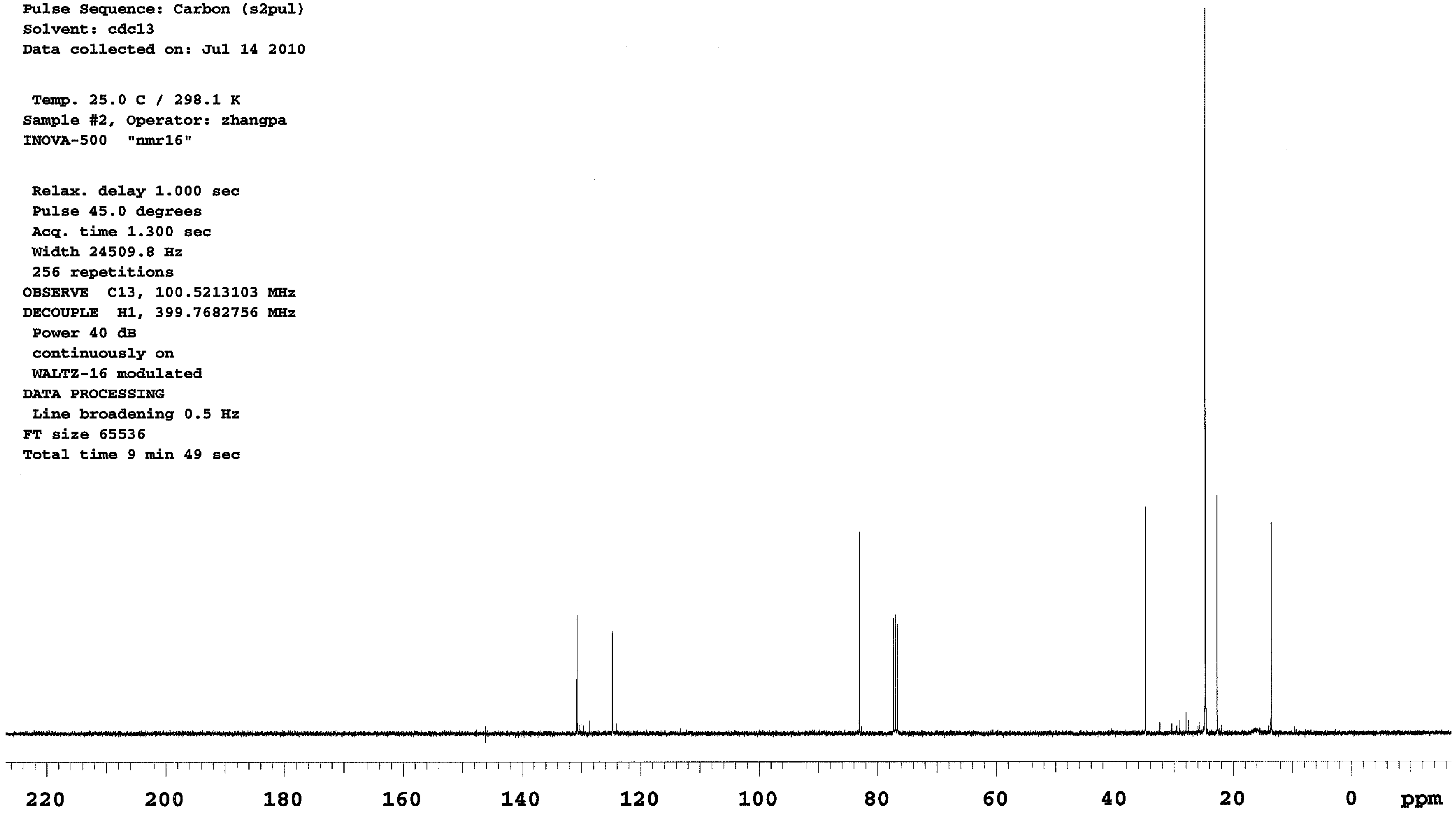
Sample directory:

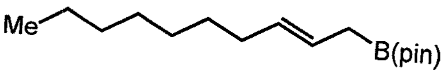
FidFile: IAR-1-79-2-Characterized_1_79_02

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Jul 14 2010

Temp. 25.0 C / 298.1 K
Sample #2, Operator: zhangpa
INOVA-500 "nmr16"

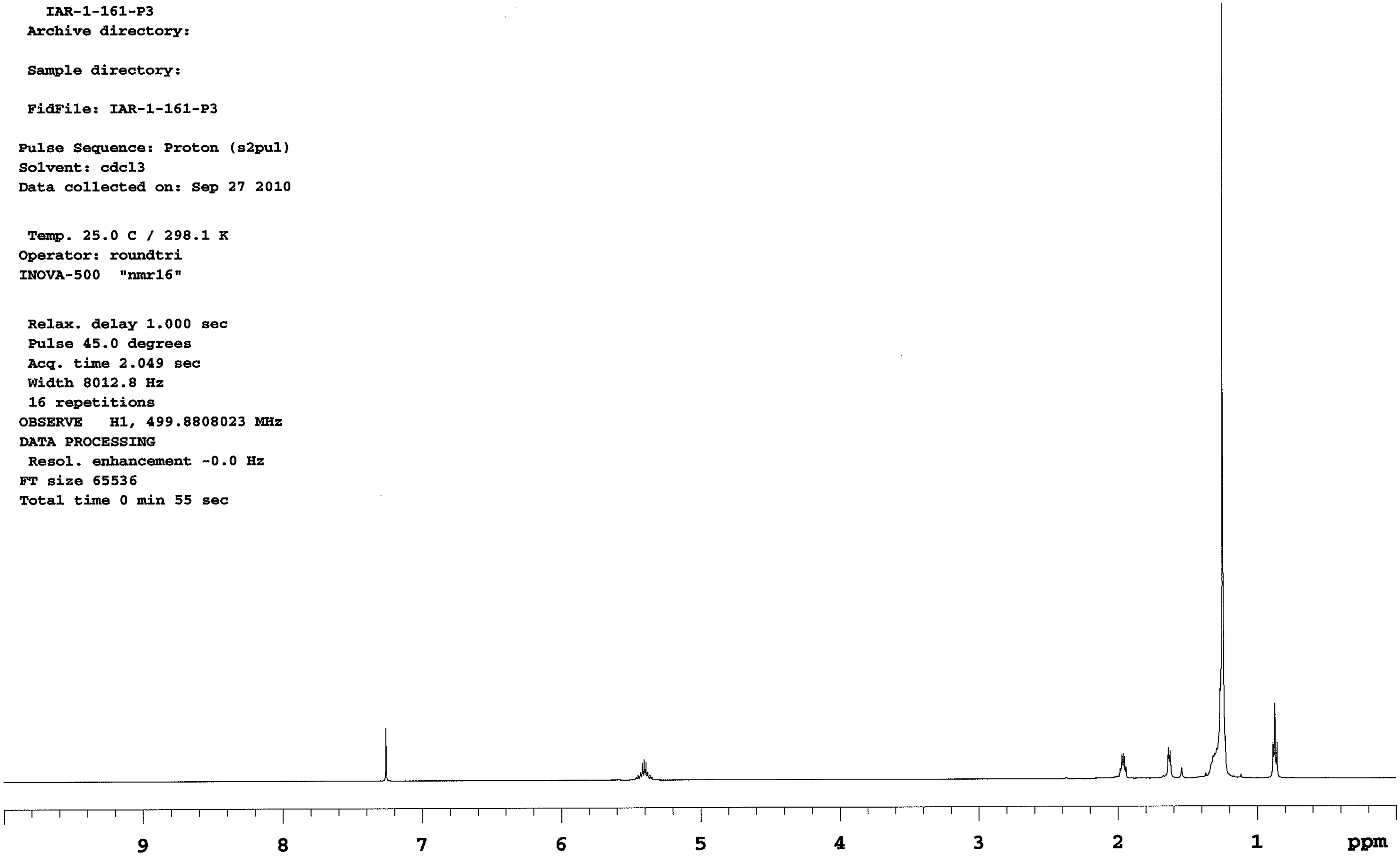
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions
OBSERVE C13, 100.5213103 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 49 sec

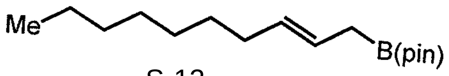




S-12

```
  IAR-1-161-P3
 Archive directory:

 Sample directory:

 FidFile: IAR-1-161-P3

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Sep 27 2010

 Temp. 25.0 C / 298.1 K
Operator: roundtri
INOVA-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 8012.8 Hz
 16 repetitions
OBSERVE   H1, 499.8808023 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec
```





S-12

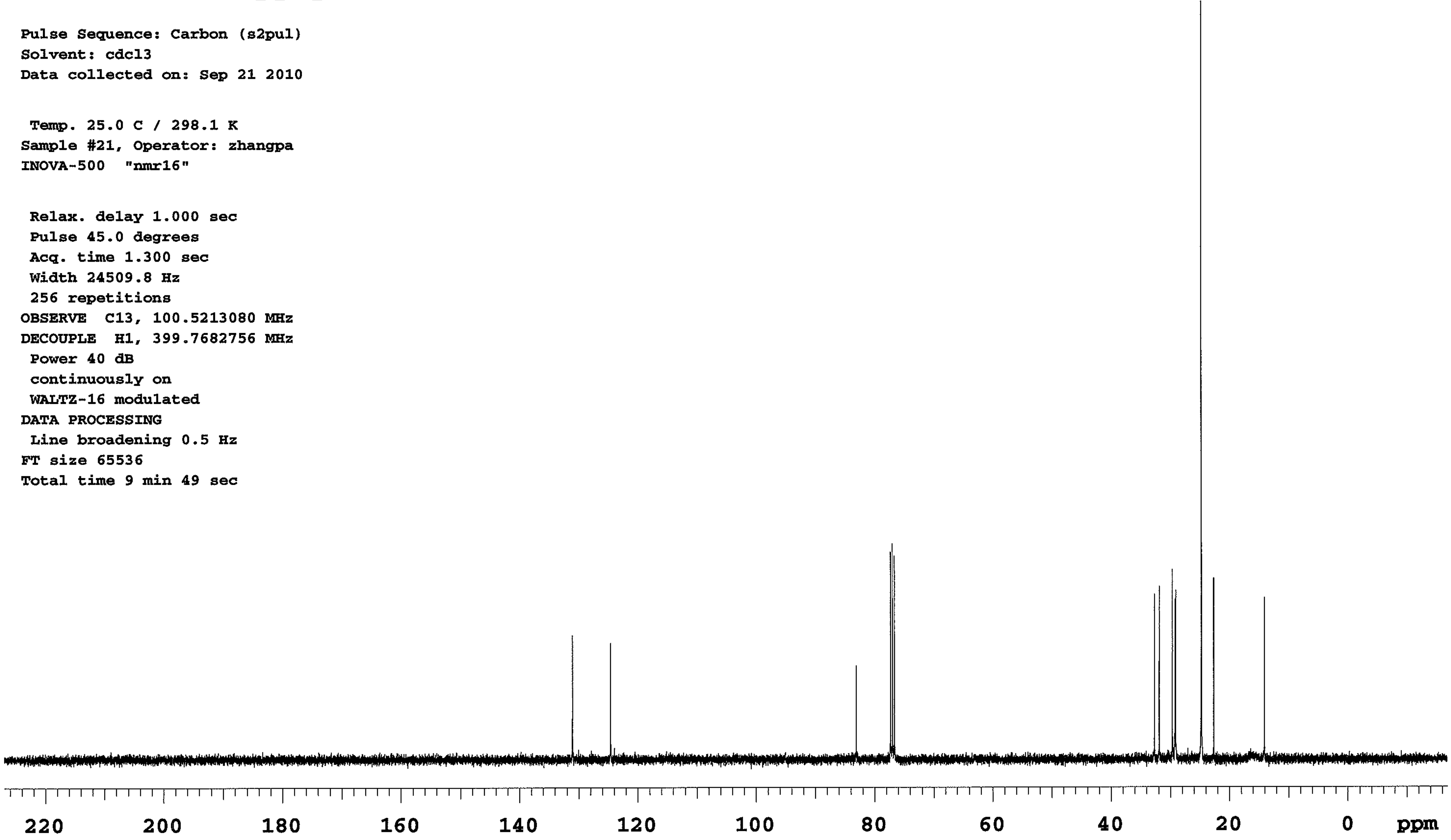
Sample directory:

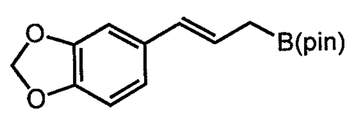
FidFile: IAR-1-161-P-C13_1_161_01

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Sep 21 2010

Temp. 25.0 C / 298.1 K
Sample #21, Operator: zhangpa
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
256 repetitions
OBSERVE C13, 100.5213080 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min 49 sec

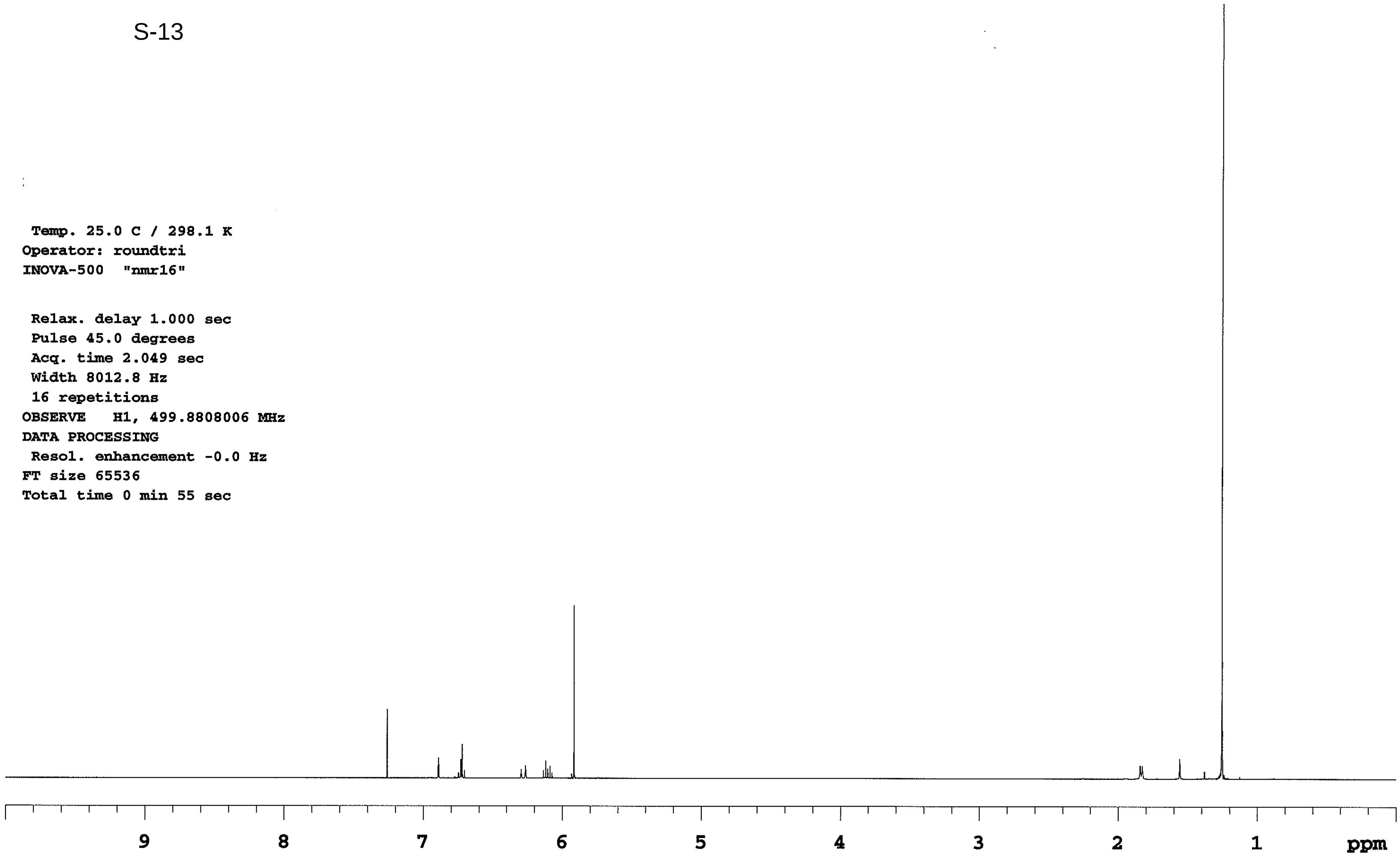


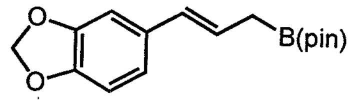


S-13

Temp. 25.0 C / 298.1 K
Operator: roundtri
INOVA-500 "nmr16"

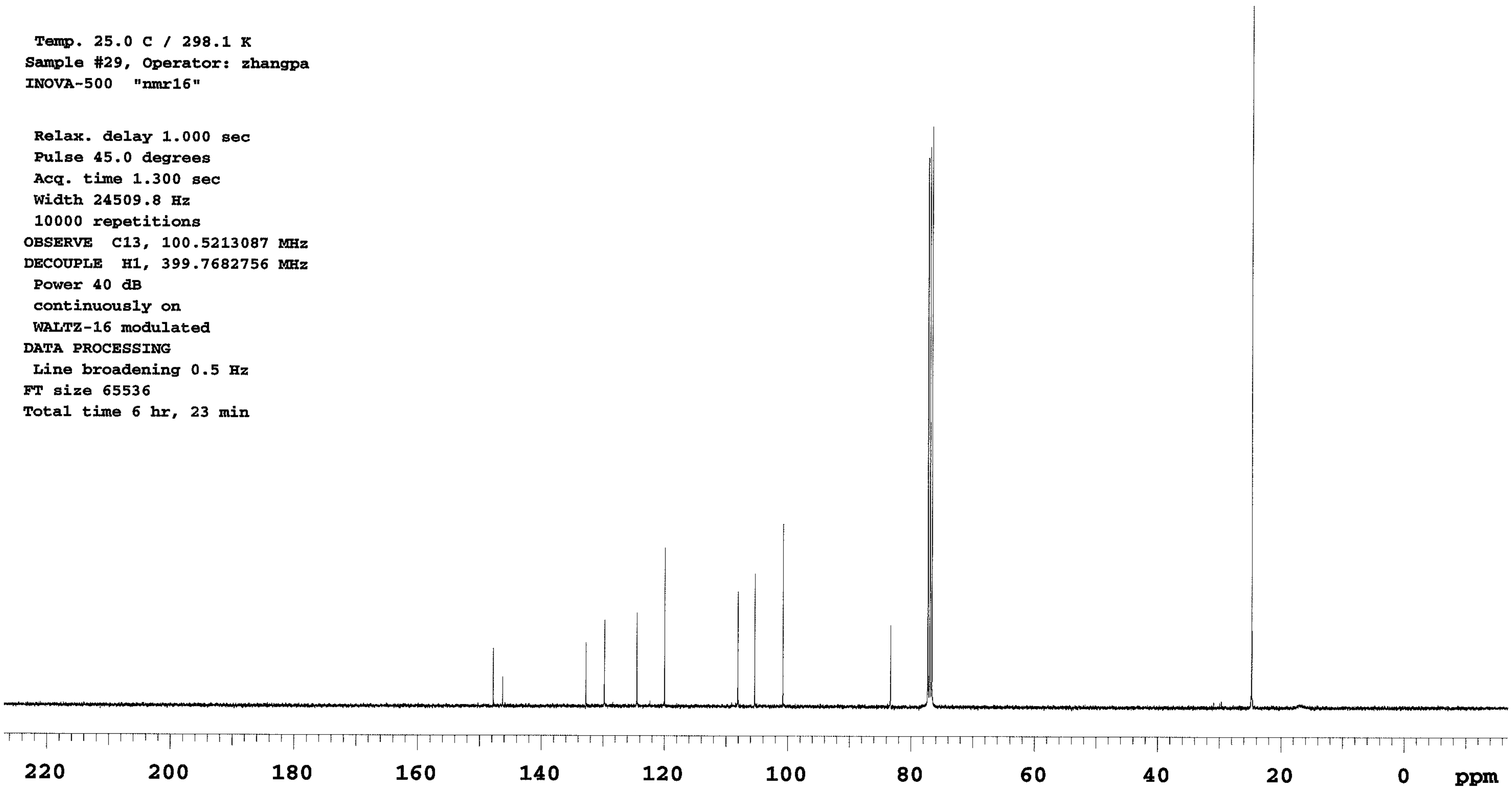
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.8808006 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec

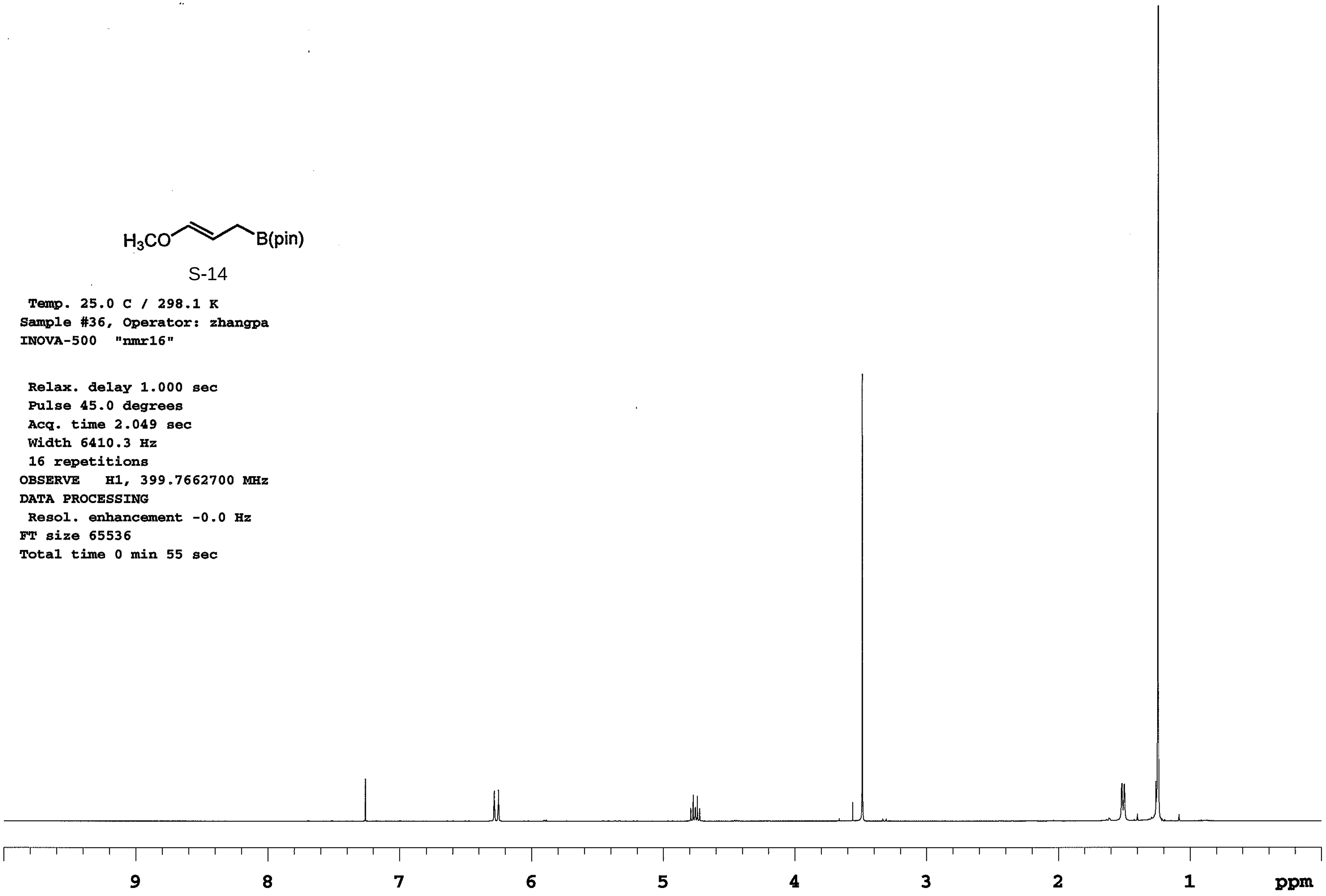




S-13

```
 Temp. 25.0 C / 298.1 K
Sample #29, Operator: zhangpa
INOVA-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 10000 repetitions
OBSERVE  C13, 100.5213087 MHz
DECOUPLE  H1, 399.7682756 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 23 min
```

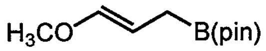




S-14

Temp. 25.0 C / 298.1 K
Sample #36, Operator: zhangpa
INOVA-500 "nmr16"

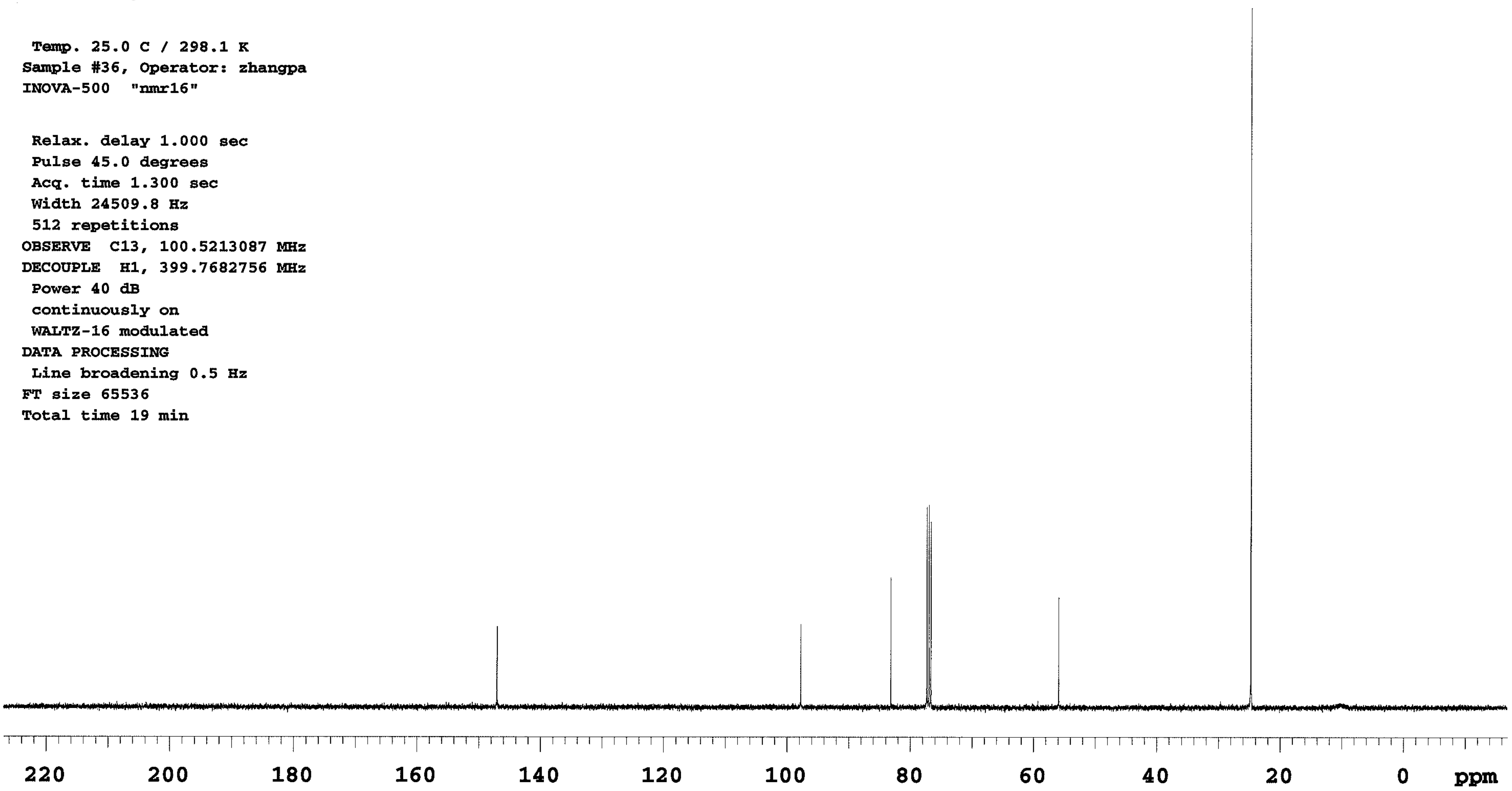
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7662700 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec



S-14

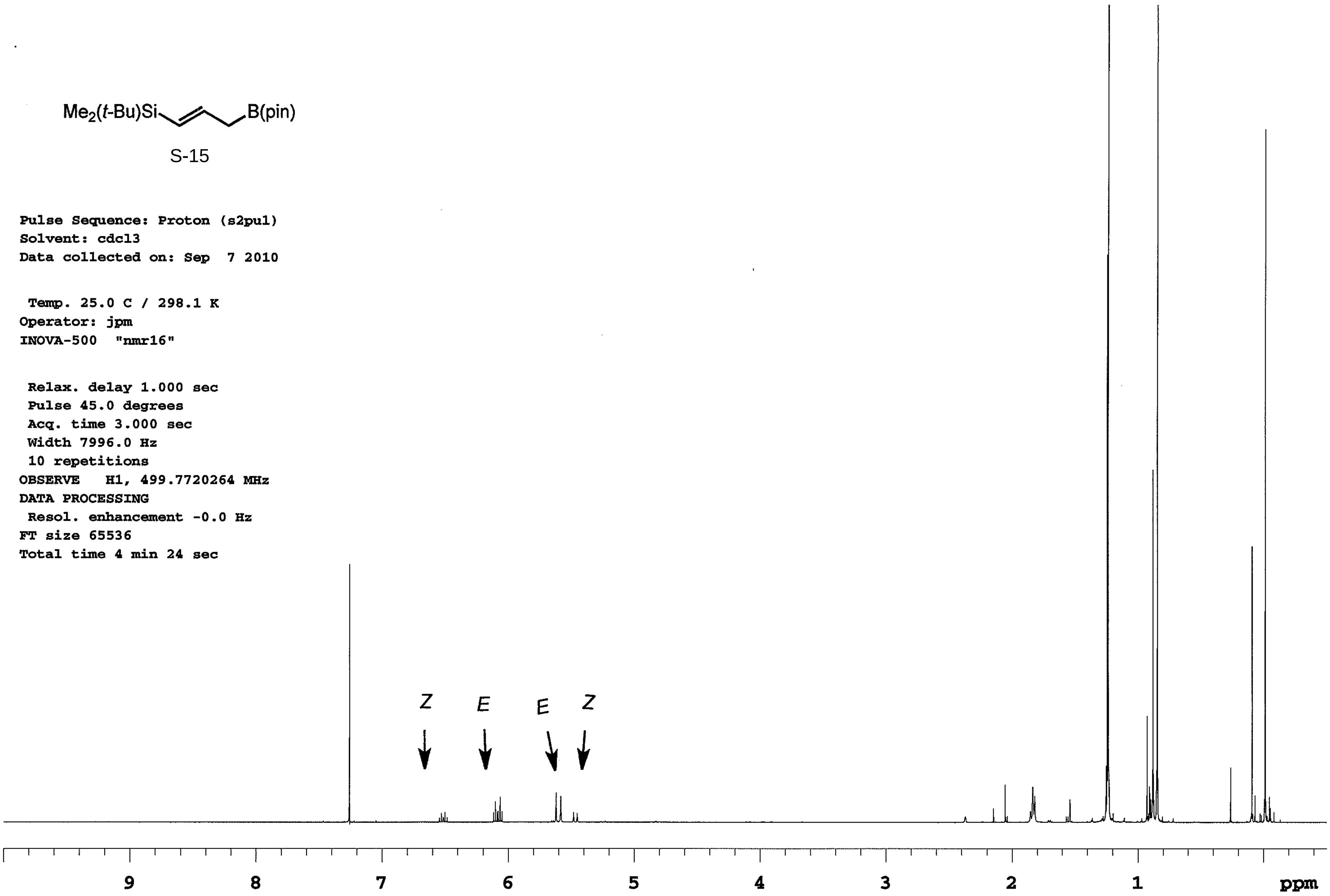
Temp. 25.0 C / 298.1 K
Sample #36, Operator: zhangpa
INOVA-500 "nmr16"

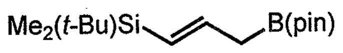
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5213087 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



S-15

```
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Sep  7 2010

 Temp. 25.0 C / 298.1 K
Operator: jpm
INOVA-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 10 repetitions
OBSERVE   H1, 499.7720264 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 4 min 24 sec
```



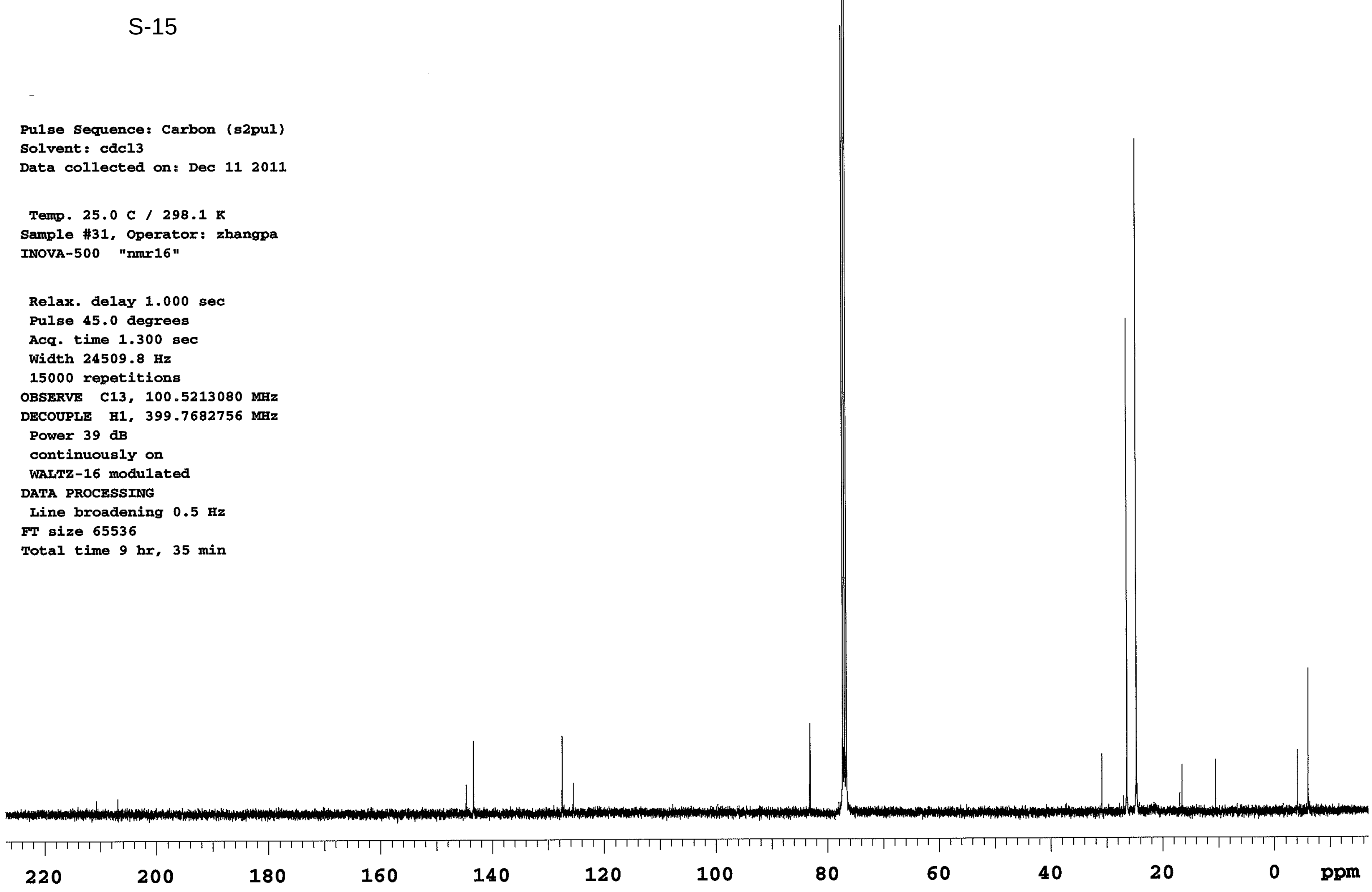


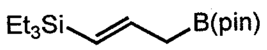
S-15

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Dec 11 2011

Temp. 25.0 C / 298.1 K
Sample #31, Operator: zhangpa
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
15000 repetitions
OBSERVE C13, 100.5213080 MHz
DECOUPLE H1, 399.7682756 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 hr, 35 min



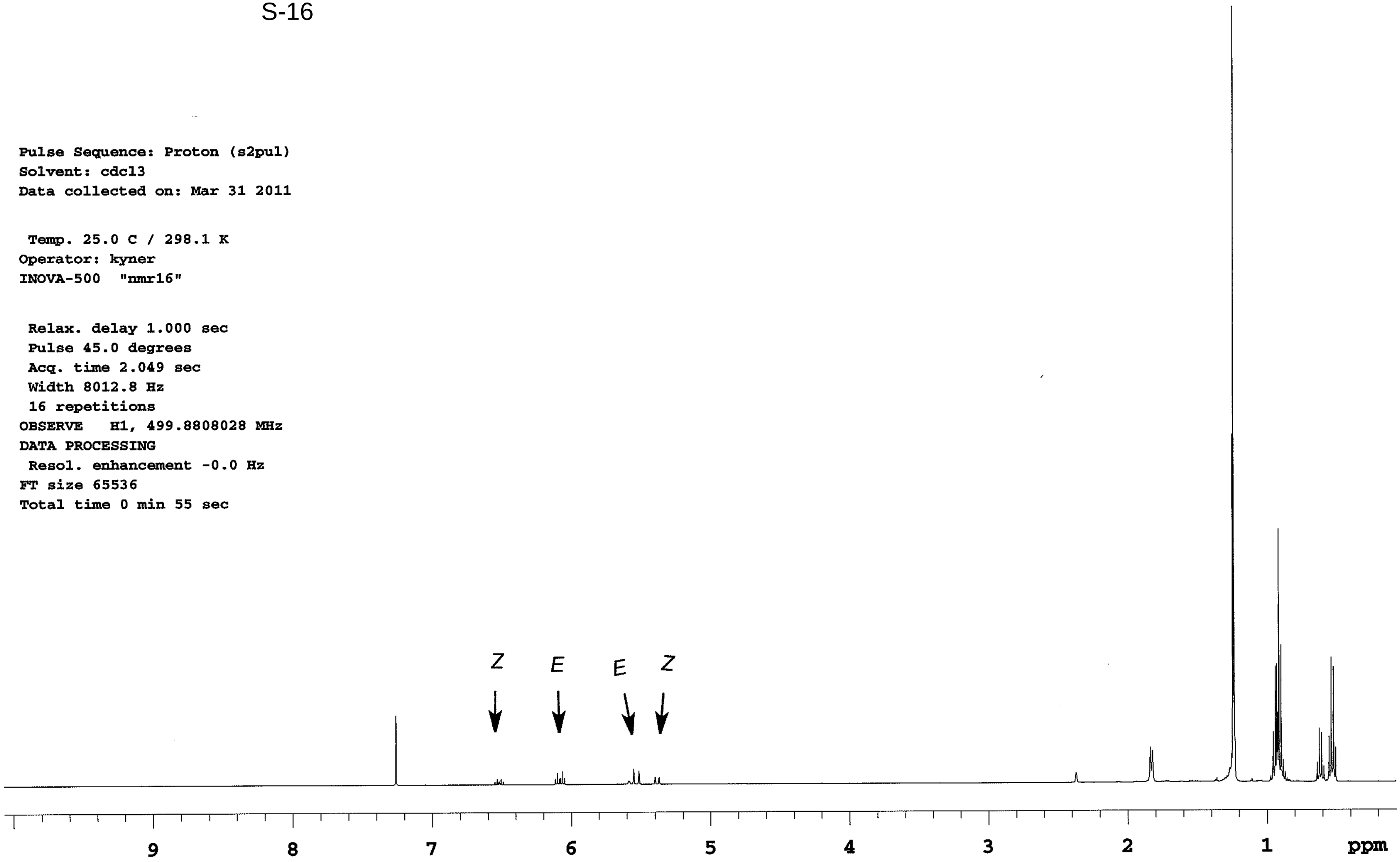


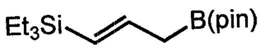
S-16

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Mar 31 2011

Temp. 25.0 C / 298.1 K
Operator: kyner
INOVA-500 "nmr16"

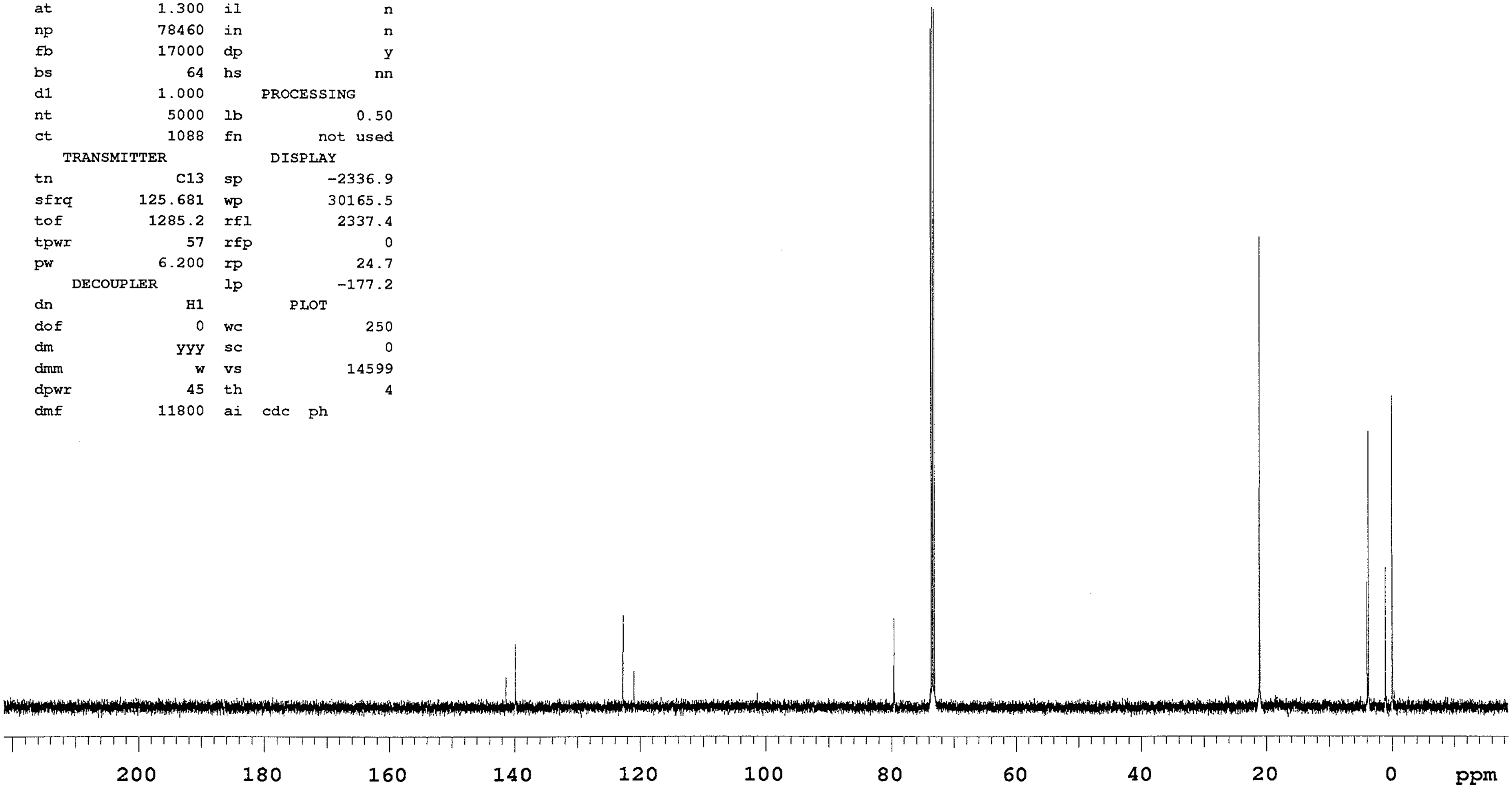
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.8808028 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec

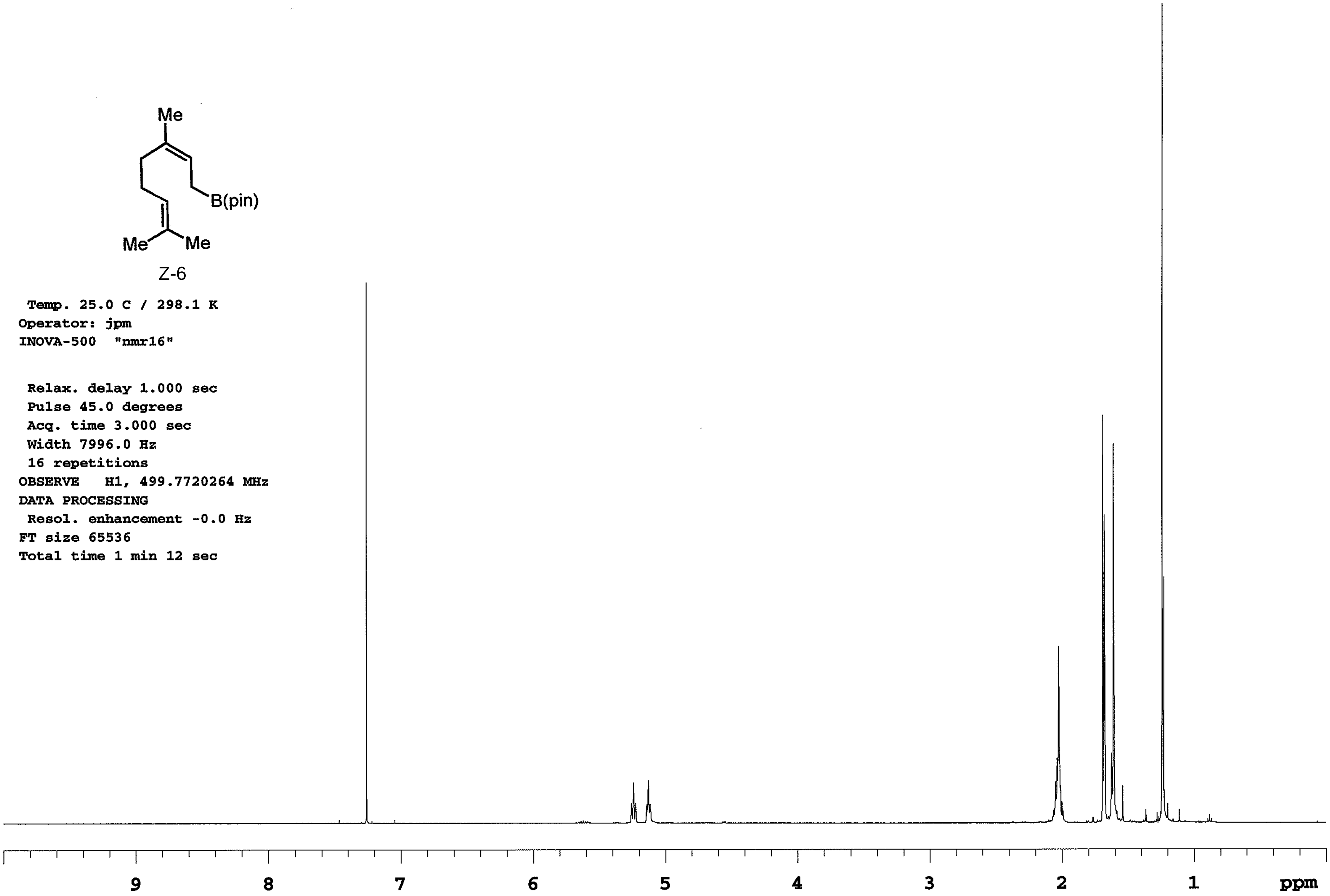




S-16

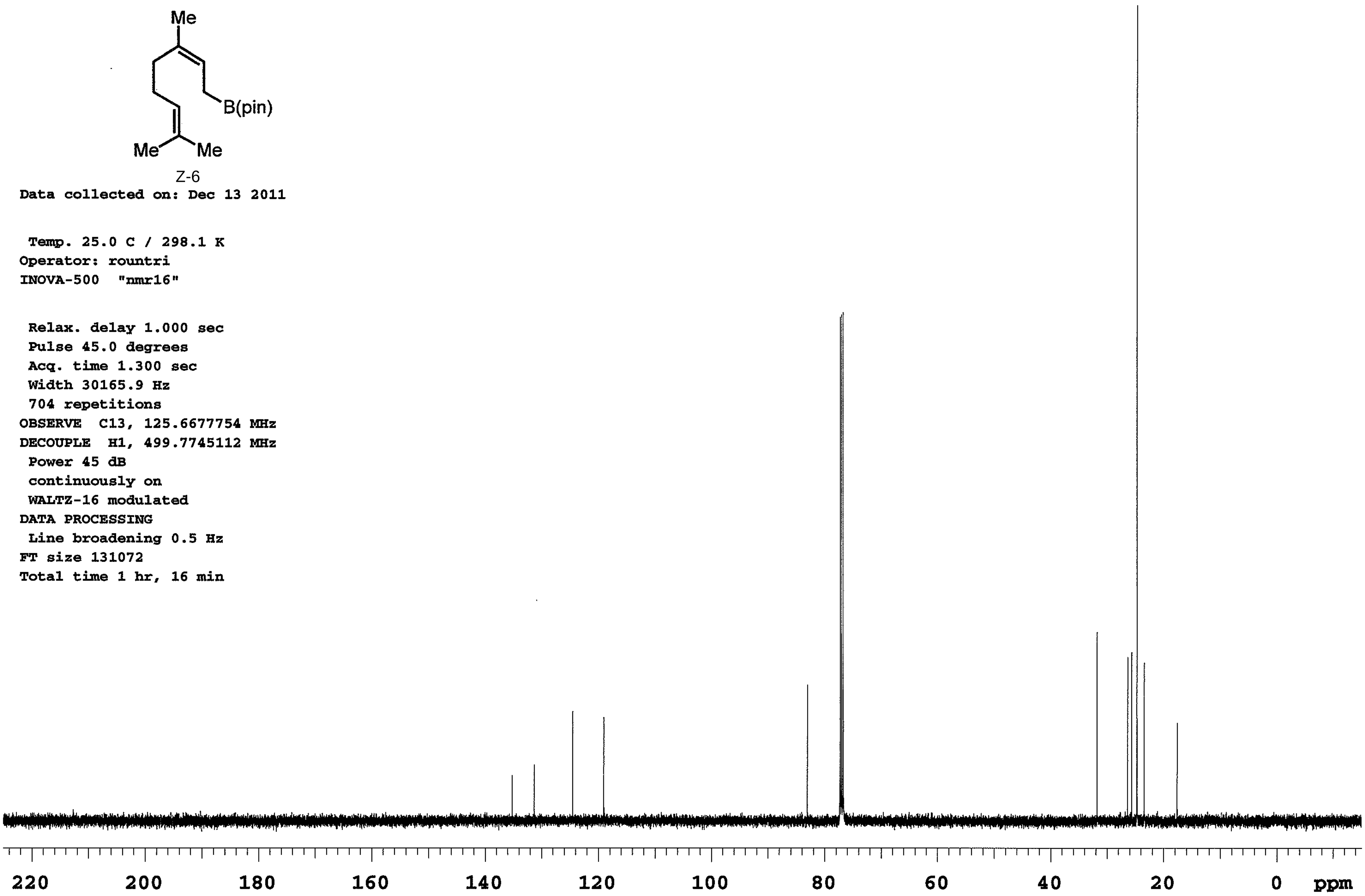
```
      SAMPLE              SPECIAL
date   Apr  1 2011  temp          25.0
solvent       cdcl3 gain            30
file /home/All/jpm~ spin            20
/IAR/IAR-2-81-P3-C~ hst          0.008
            13.fid  pw90        12.400
   ACQUISITION      alfa         6.600
sw          30165.9         FLAGS
at            1.300 il               n
np            78460 in               n
fb            17000 dp               y
bs               64 hs              nn
d1            1.000        PROCESSING
nt             5000 lb            0.50
ct             1088 fn        not used
   TRANSMITTER              DISPLAY
tn              C13 sp         -2336.9
sfrq        125.681 wp         30165.5
tof          1285.2 rfl         2337.4
tpwr             57 rfp              0
pw            6.200 rp            24.7
    DECOUPLER       lp          -177.2
dn               H1          PLOT
dof               0 wc             250
dm              yyy sc               0
dmm               w vs           14599
dpwr             45 th               4
dmf           11800 ai   cdc  ph
```





Z-6

```
 Temp. 25.0 C / 298.1 K
Operator: jpm
INOVA-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 16 repetitions
OBSERVE   H1, 499.7720264 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min 12 sec
```



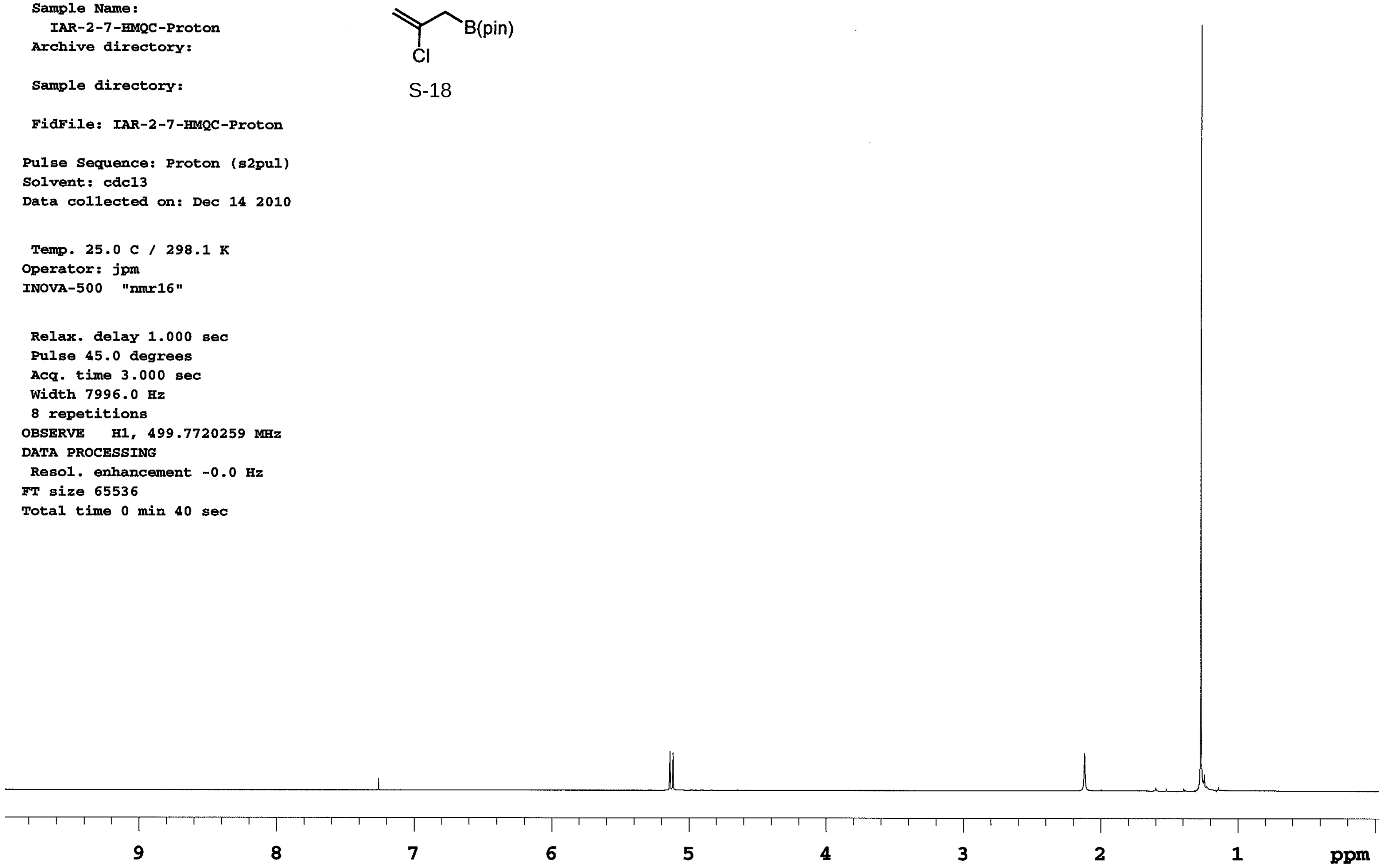
Z-6

Data collected on: Dec 13 2011

Temp. 25.0 C / 298.1 K
Operator: rountri
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
704 repetitions
OBSERVE C13, 125.6677754 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 1 hr, 16 min

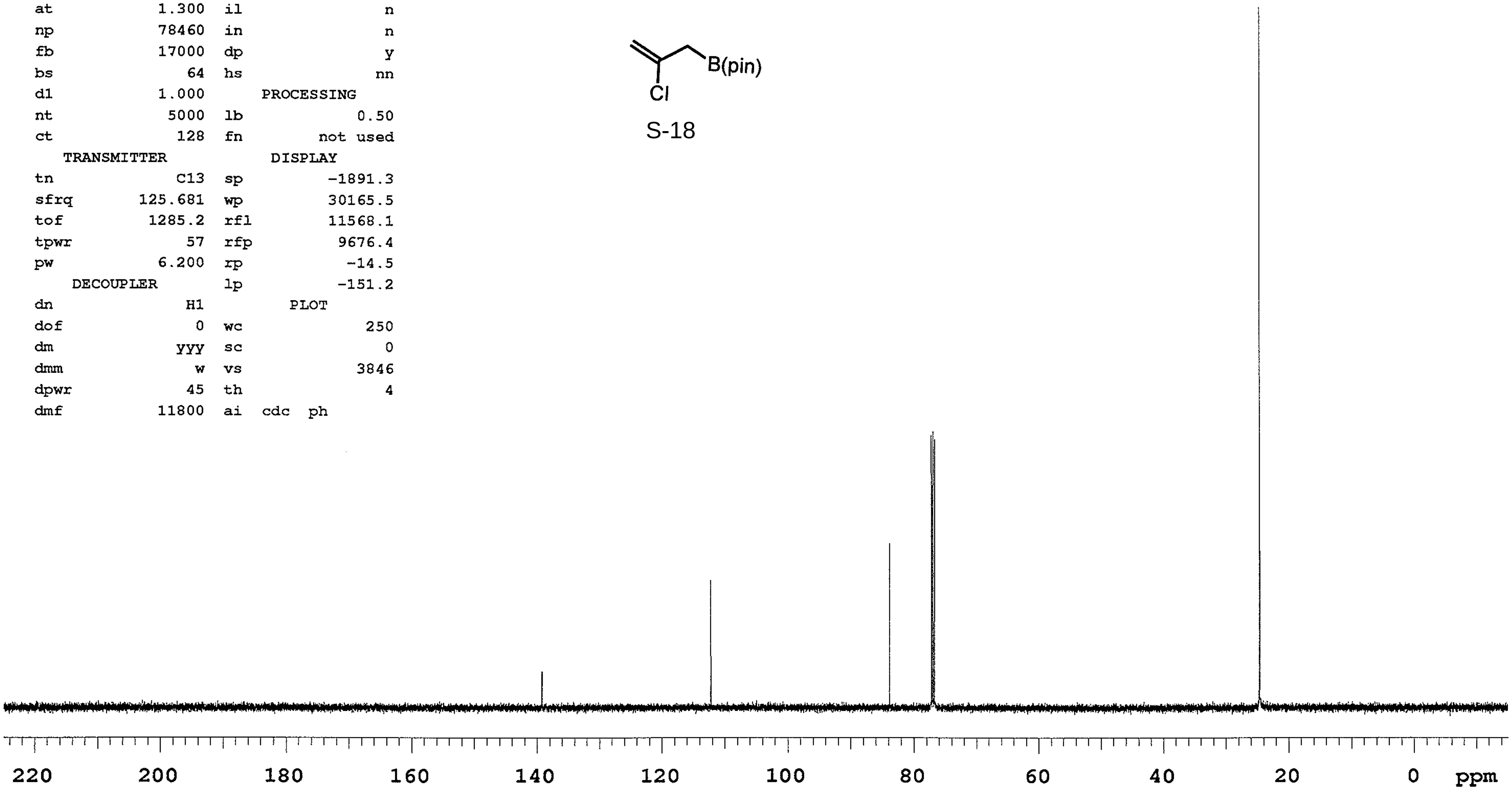
```
IAR-2-7-HMQC-Proton

 Sample Name:
   IAR-2-7-HMQC-Proton
 Archive directory:

 Sample directory:

 FidFile: IAR-2-7-HMQC-Proton

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Dec 14 2010

 Temp. 25.0 C / 298.1 K
Operator: jpm
INOVA-500  "nmr16"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 7996.0 Hz
 8 repetitions
OBSERVE   H1, 499.7720259 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 40 sec
```

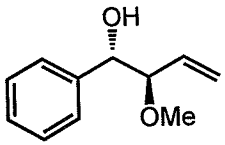


S-18

```
IAR-2-7-HMQC-Carbon

exp2  Carbon

      SAMPLE              SPECIAL
date   Dec 14 2010  temp          25.0
solvent      cdcl3  gain            30
file /home/All/jpm~ spin            20
/IAR/IAR-2-7-HMQC-~ hst          0.008
        Carbon.fid  pw90        12.400
   ACQUISITION      alfa         6.600
sw         30165.9         FLAGS
at           1.300  il               n
np           78460  in               n
fb           17000  dp               y
bs              64  hs              nn
d1           1.000       PROCESSING
nt            5000  lb            0.50
ct             128  fn        not used
   TRANSMITTER            DISPLAY
tn             C13  sp         -1891.3
sfrq       125.681  wp         30165.5
tof         1285.2  rfl        11568.1
tpwr            57  rfp         9676.4
pw           6.200  rp           -14.5
    DECOUPLER       lp          -151.2
dn              H1         PLOT
dof              0  wc             250
dm             yyy  sc               0
dmm              w  vs            3846
dpwr            45  th               4
dmf          11800  ai   cdc  ph
```

S-18



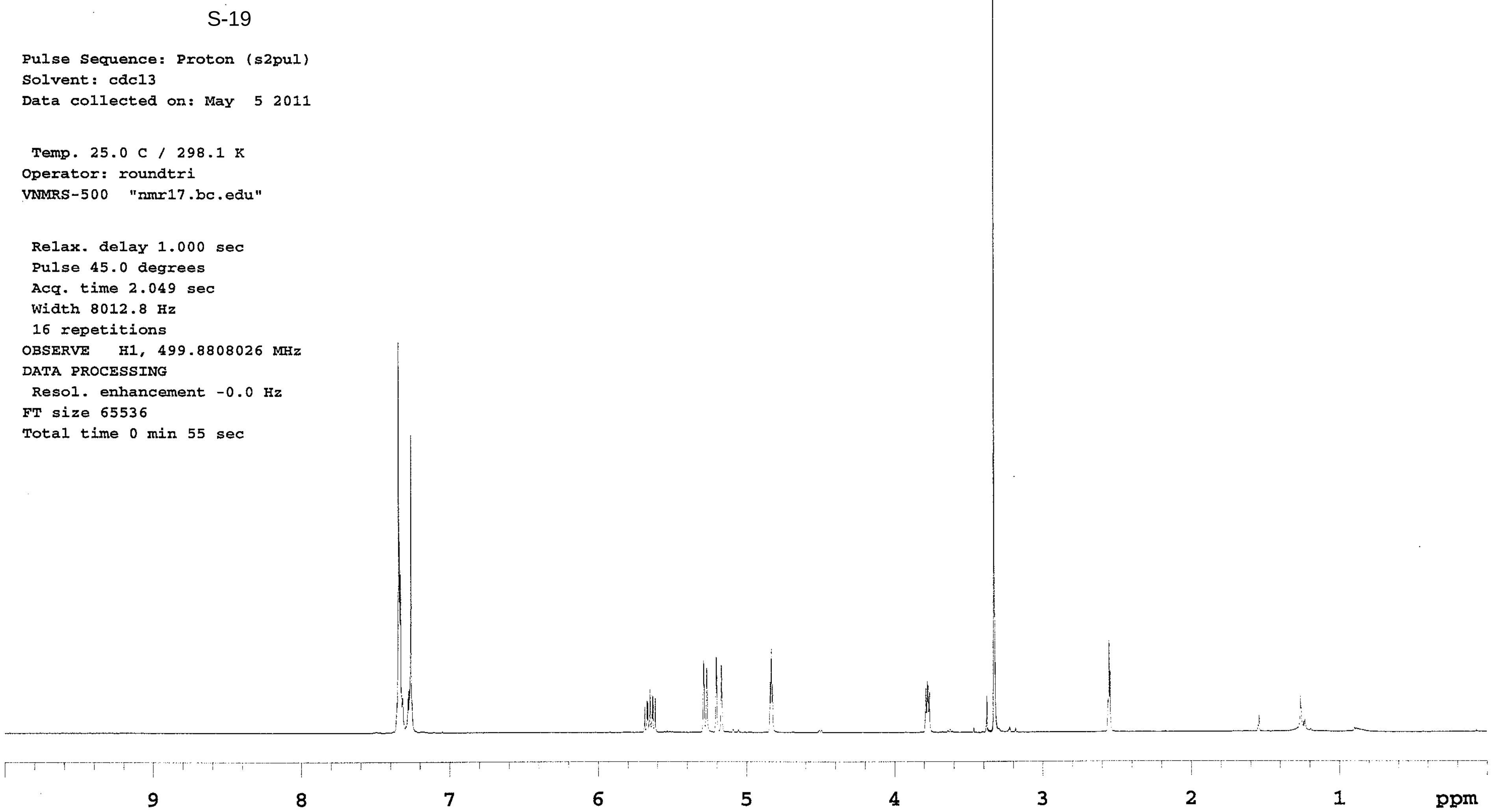


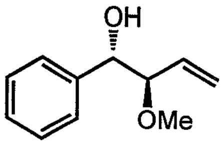
S-19

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: May 5 2011

Temp. 25.0 C / 298.1 K
Operator: roundtri
VNMRS-500 "nmr17.bc.edu"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.049 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 499.8808026 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min 55 sec





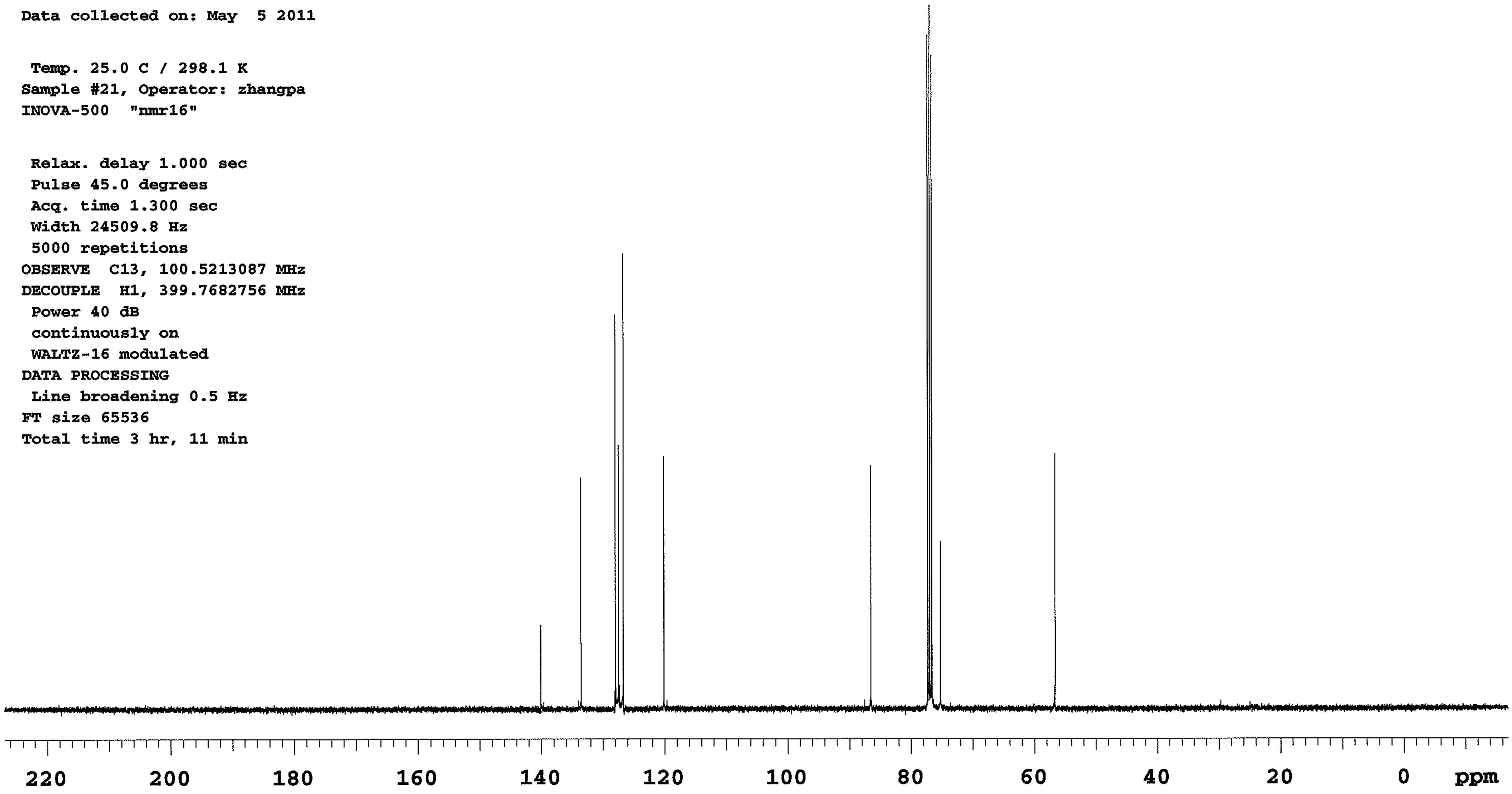
S-19

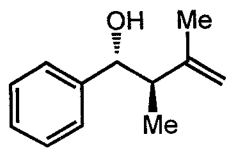
FidFile: IAR-2-101-P2-C13_2_101_01

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: May 5 2011

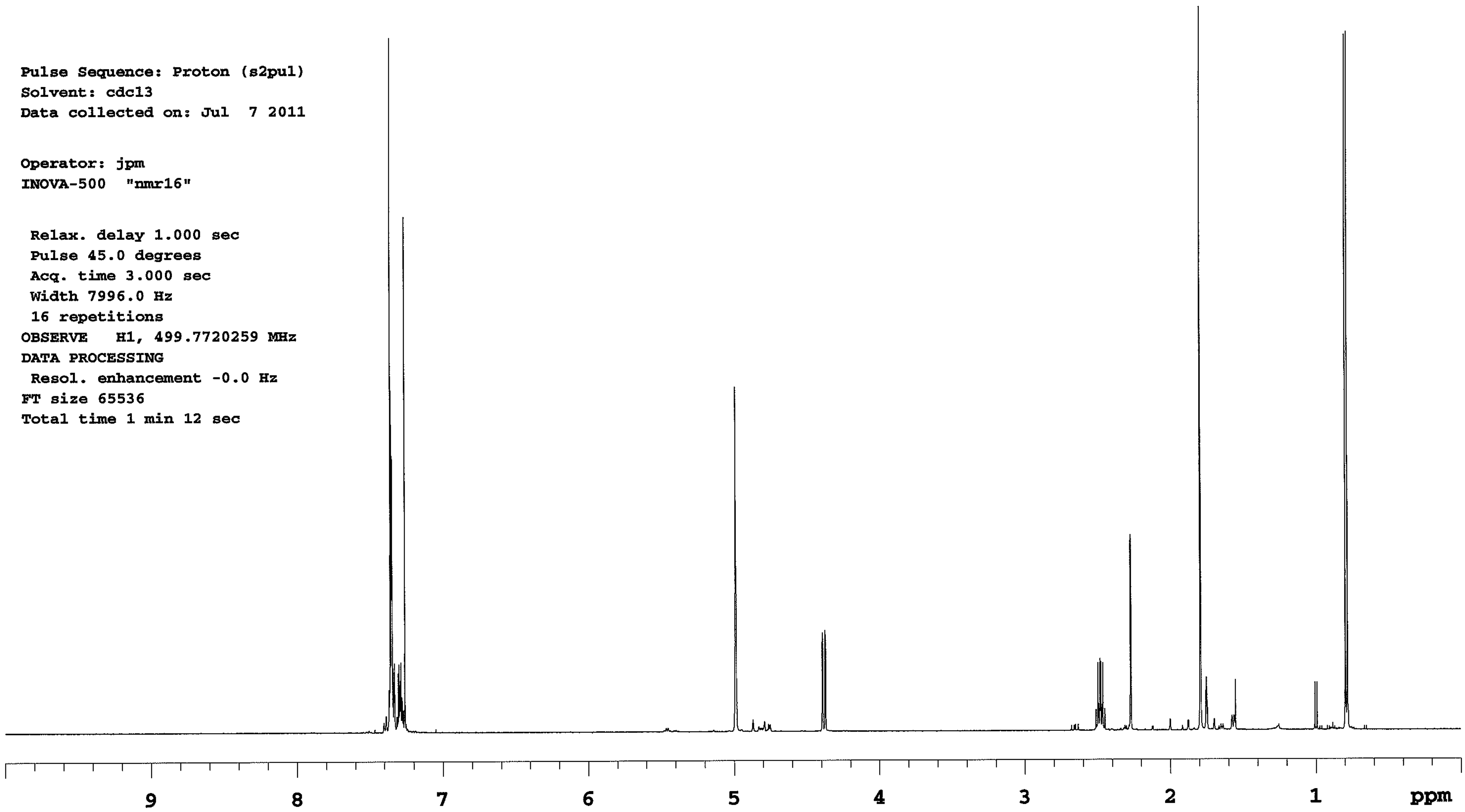
Temp. 25.0 C / 298.1 K
Sample #21, Operator: zhangpa
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
5000 repetitions
OBSERVE C13, 100.5213087 MHz
DECOUPLE H1, 399.7682756 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 11 min





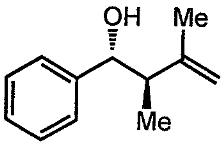
S-23



Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Jul 7 2011

Operator: jpm
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 7996.0 Hz
16 repetitions
OBSERVE H1, 499.7720259 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 1 min 12 sec



S-23

Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Dec 11 2011

Temp. 25.0 C / 298.1 K
Operator: rountri
INOVA-500 "nmr16"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 30165.9 Hz
256 repetitions
OBSERVE C13, 125.6677773 MHz
DECOUPLE H1, 499.7745112 MHz
Power 45 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 19 min