Supporting Information. Mechanistic Variations in Ionic Hydrogenation of Unsaturated Phosphine and Amine Boranes Timothy S. De Vries, Supriyo Majumder, Angela M. Sandelin, Guoqiang Wang, and Edwin Vedejs*

Experimental

The following chemicals were commercially available and used as received: trimethylamine borane; tributylphosphine borane; trifluoroacetic acid; methanesulfonic acid; borane tetrahydrofuran, 1.0 M solution in tetrahydrofuran; methyltriphenylphosphonium bromide; sodium bis(trimethylsilyl)amide; 3-methylcyclohexanol (mixture of *cis* and *trans*); *p*-toluenesulfonyl chloride; diphenylphosphine; (+)-camphorsulfonic acid; 3-methyl-2-cyclohexen-1-ol; methanesulfonyl chloride; dimethylamine, 33% in absolute ethanol. Chloroform-*d* and methylene chloride-d_2 were dried by storing over activated 4Å molecular sieves; dichloromethane (DCM) and tetrahydrofuran (THF) were dried by passing through a column of activated alumina; triethylamine was distilled from CaH_2 and pyridine from KOH under an N_2 atmosphere. All reactions were performed at room temperature under an N_2 atmosphere unless otherwise stated. Nuclear magnetic resonance experiments were performed on Varian Inova 500 and Inova 400 spectrometers at the following frequencies: ^{1}H 500 MHz; {^{1}H}^{13}C 101 MHz; ^{11}B 160 MHz; ^{19}F 376 MHz, unless otherwise stated. All spectra were recorded in $CDCl_3$ and referenced to the ^{1}H signal of internal Me_4Si (unless otherwise stated) according to recommendations,[1] using a Ξ of 25.145020 for Me_4Si (^{13}C), a Ξ of 32.083974 for $BF_3{\cdot}OEt_2$ (^{11}B), and a Ξ of 94.094011 for CCl_3F (^{19}F).

Hydrogen Evolution from $Me_3N{\cdot}BH_3$ (37) vs. $Bu_3P{\cdot}BH_3$ with CF_3CO_2H

Neat CF_3CO_2H (6 μL, 78 μmol) was added by syringe to a stirred solution of $Me_3N{\cdot}BH_3$ (4.8 mg, 66 μmol) in anhydrous CD_2Cl_2 (1.0 mL) under an N_2 atmosphere. After 45 min, this solution was transferred via syringe to an N_2-flushed NMR tube. Assay by ^{1}H NMR showed ca. 45% of $Me_3N{\cdot}BH_3$ remaining by integration of its B–*H* signal at δ 2.0-1.3 ppm relative to the methyl singlet at δ 2.61 ppm (overlapping $Me_3N{\cdot}BH_3$ and $Me_3N{\cdot}BH_2(O_2CCF_3)$ signals). The formation of trifluoroacetoxyborane complex was confirmed by reaction of $Me_3N{\cdot}BH_3$ with 10 equiv CF_3CO_2H

(50 μL, 650 μmol) under the same conditions, giving $Me_3N{\cdot}BH_2(O_2CCF_3)$ as the major product after 1 h: ^{1}H NMR: δ 3.1-2.0 (2H br s), 2.63 (9H, s).

The reaction of $Bu_3P{\cdot}BH_3$ (20 μL, 75 μmol) with CF_3CO_2H (6 μL, 78 μmol) in 1.0 mL CD_2Cl_2 was performed under the same conditions, assay by 1H NMR after 45 min showing less than 2% conversion to $Bu_3P{\cdot}BH_2(O_2CCF_3)$ by integration of its α-C*H*$_2$ at δ 1.76-1.67 ppm relative to the α-C*H*$_2$ peak for unreacted $Bu_3P{\cdot}BH_3$ at δ 1.60-1.50 ppm. This product trifluoroacetoxyborane complex was also confirmed by reaction of $Bu_3P{\cdot}BH_3$ with 10 equiv CF_3CO_2H (50 μL, 650 μmol) under the same conditions, giving $Bu_3P{\cdot}BH_2(O_2CCF_3)$ as the major product after 1 h: ^{1}H NMR: δ 3.4-2.3 (2H br s), 1.76-1.67 (6H, m), 1.53-1.37 (6H, m), 0.94 (9H, t, J = 7.1 Hz); ^{31}P NMR: δ 3.1-0.4 (br m).

Representative Procedure for Ionic Hydrogenation of Phosphine Borane 4

Neat MsOH (100 μL, 1.54 mmol) was added by syringe to a stirred solution of **4** (138 mg, 0.51 mmol) in anhydrous DCM (5 mL) under an N_2 atmosphere. After 10 min, this solution was quenched by addition of 10 mL MeOH, 1 mL 20% aq. NaOH and 1 mL 35% aq. H_2O_2. After an additional 1 h, this mixture was diluted with 10 mL H_2O, separated and the aqueous layer extracted with 2 x 10 mL DCM. The combined organic layers were dried over Na_2SO_4 and reduced by rotatory evaporation. The product was purified by flash chromatography (FC) on silica gel (15 cm x 20 mm diameter, 19:1 DCM/EtOH), isolating 110 mg product **5** (Rf = 0.3, 78% y) and recovering 18 mg **6** (Rf = 0.07, 12% y). ^{1}H and ^{13}C NMR spectral data matched those reported for **5** and **6**.[2]

Preparation and Ionic Hydrogenation of Phosphine Borane 12

Methyltriphenylphosphonium bromide (520 mg, 1.46 mmol) and sodium bis(trimethylsilyl)-amide (242 mg, 1.32 mmol) were transferred under an N_2 atmosphere to an oven-dried 50 mL round-bottom flask fused to a reflux condenser and dissolved in anhydrous THF (20 mL). After 30 min the now yellow solution was heated to reflux, cooling after 1 h and filtering through an N_2-flushed fritted filter into a flask containing a stirred solution of 3-diphenylphosphinylcyclohexanone borane[3] (355 mg, 1.20 mmol) in anhydrous THF (10 mL), rinsing the flask in which the phosphonium ylide was formed with 10 mL THF. After 1 d the reaction mixture was washed with H_2O (50 mL) and brine (50 mL), dried over $MgSO_4$, and reduced by rotatory evaporation. The product was purified by FC on silica gel (15 cm x 30 mm diameter, 2:1 hexanes/Et_2O), isolating 337 mg (3-Methylenecyclohexyl)-diphenylphosphine borane (**12**): analytical thin layer chromatography (TLC) on K6F silica gel 60Å, 2:1 hexanes/Et_2O, Rf = 0.53. Molecular ion calculated for $C_{19}H_{24}BNaP$: 317.1606; [M+Na], ESMS found *m/z* = 317.1591; IR (neat, cm^{-1}) 2381, B–H; 2348, B–H; 1650, C=C; ^{1}H NMR: δ 7.78-7.70 (4H, m), 7.52-7.41 (6H, m), 4.66 (1H, s), 4.57 (1H, s), 2.55-2.45 (1H, m), 2.31 (1H, br d, J = 13.1 Hz), 2.28-2.17 (2H, m), 2.00 (1H, td, J = 13.4, 4.4 Hz), 1.95-1.87 (1H, m), 1.73-1.66 (1H, m), 1.61 (1H, qt, J = 12.7, 4.4 Hz), 1.35 (1H, qt, J = 13.0, 3.9 Hz), 1.3-0.5 (3H, br m); ^{13}C NMR: δ 147.4 (d, J = 12 Hz), 132.6 (d, J = 9 Hz), 132.6 (d, J = 8 Hz), 131.2 (d, J = 2 Hz), 131.1 (d, J = 2 Hz), 128.8 (d, J = 10 Hz), 128.8 (d, J = 10 Hz), 128.3 (d, J = 54 Hz), 128.0 (d, J = 53 Hz), 108.6, 35.0 (d, J = 10 Hz), 34.8 (d, J = 27 Hz), 34.4 (d, J = 2 Hz), 27.9 (d, J = 12 Hz), 26.1; ^{11}B NMR: δ -42.1 (qd, J = 93, 30 Hz); ^{31}P NMR: δ 19.7-18.0 (br m).

Reaction of **12** under the same conditions as for **4** above gave ionic hydrogenation product **14b** (76% y), and a minor byproduct resulting from hydroboration (14%). *trans*-(3-Methylcyclohexyl)-diphenylphosphine oxide (**14b**): TLC on K6F silica gel 60Å, 19:1 DCM/EtOH, Rf = 0.18. Molecular ion calculated for $C_{19}H_{23}NaOP$: 298.1486; [$M^{\bullet+}$], EIMS found *m/z* = 298.1478; IR (neat, cm^{-1}) 1181, P=O; ^{1}H NMR: δ 7.82-7.74 (4H, m), 7.52-7.41 (6H, m), 2.55-2.45 (1H, m), 2.15-2.06 (1H, m), 1.87-1.77 (1H, m), 1.71-1.40 (6H, m), 1.38-1.30 (1H, m), 0.96 (3H, d, J = 7.1 Hz); ^{13}C NMR: δ 132.6 (d, J = 94 Hz), 132.4 (d, J = 94 Hz), 131.4 (d, J = 3 Hz), 131.4 (d, J = 3 Hz), 131.0 (d, J = 8 Hz), 131.0 (d, J = 8 Hz), 128.6 (d, J

= 11 Hz), 128.5 (d, J = 11 Hz), 31.7, 31.5 (d, J = 73 Hz), 31.0 (d, J = 3 Hz), 27.1 (d, J = 10 Hz), 25.0 (d, J = 3 Hz), 20.8 (d, J = 11 Hz), 18.5; ^{31}P NMR: δ 36.4.

Independent Synthesis of Minor Diastereomer 14a

Pyridine (5 mL, 62 mmol) was added to *p*-toluenesulfonyl chloride (1.63 g, 8.5 mmol) at 0 °C under an N_2 atmosphere to dissolve; the solution developed a yellow color. To this was added the commercially available mixture of *cis*- and *trans*-3-methylcyclohexanol (**15**), the yellow color fading on alcohol addition. After 20 h at 0 °C, the reaction was quenched by pouring onto 150 mL iced 1 M aq. HCl, extracting with ethyl ether (3 x 20 mL), drying the combined organic layers over $MgSO_4$ before reducing by rotatory evaporation, leaving 1.74 g (88% y) of residue. ^{1}H NMR assay shows a mixture of *cis*- and *trans*-3-methylcyclohexyl-*p*-toluenesulfonates (**16**) in a ratio of 2.6:1 by integration of the methyl doublets at 0.89 and 0.82 ppm, respectively. This crude tosylate mixture was taken on without purification.

Diphenylphosphine (0.62 g, 3.3 mmol) was charged to a 50 mL round-bottom flask under an N_2 atmosphere and dissolved in anhydrous THF (17 mL). After cooling the solution to -40 °C, a solution of *n*BuLi (1.98 M in hexane, 1.7 mL, 3.4 mmol) was added slowly, the resulting solution developing a deep red color. After stirring 4 h, the solution was warmed to 0 °C and a mixture of *cis*- and *trans*-3-methylcyclohexyl-*p*-toluenesulfonate (**16**, 0.96 g, 3.6 mmol) was added by syringe. After 2 h the deep red color had mostly faded to a light orange, and the mixture was oxidized by the addition of 5 mL 35% aq. H_2O_2. After warming to rt, the layers were separated and the aqueous layer washed with ethyl ether (2 x 20 mL), the combined organic layers dried over $MgSO_4$ and reduced by rotatory evaporation. Assay of the crude product mixture (1.14 g) by ^{1}H NMR showed unreacted tosylate **16** further enriched in the *cis*-isomer as well as the desired *cis*-diastereomer (**14a**); no trace of *trans*-(3-methylcyclohexyl)-diphenylphosphine oxide (**14b**) was observed. Purification of a portion of the crude product (176 mg) by preparative thin layer

chromatography (PLC) on silica gel (20 x 20 cm x 1000 μm, EtOAc) gave pure *cis*-(3-methylcyclohexyl)-diphenylphosphine oxide (**14a**, 23 mg, 50% based on *trans*-3-methylcyclohexyl-*p*-toluenesulfonate): TLC on K6F silica gel 60Å, EtOAc, Rf = 0.42. Molecular ion calculated for $C_{19}H_{23}NaOP$: 298.1486; [$M^{\bullet+}$], EIMS found *m*/*z* = 298.1490; IR (neat, cm^{-1}) 1181, P=O; ^{1}H NMR: δ 7.82-7.74 (4H, m), 7.54-7.43 (6H, m), 2.33-2.24 (1H, m), 1.86-1.79 (1H, m), 1.74-1.65 (3H, m), 1.54-1.17 (4H, m), 0.92 (1H, qd, J = 12.6, 3.7 Hz), 0.86 (3H, d, J = 6.6 Hz); ^{13}C NMR: δ 132.2 (d, J = 94 Hz), 132.1 (d, J = 94 Hz), 131.4 (d, J = 3 Hz), 131.4 (d, J = 3 Hz), 131.1 (d, J = 9 Hz), 128.6 (d, J = 11 Hz), 128.5 (d, J = 12 Hz), 37.1 (d, J = 73 Hz), 36.6, 32.9 (d, J = 13 Hz), 32.7 (d, J = 3 Hz), 26.3 (d, J = 14 Hz), 24.3 (d, J = 3 Hz), 22.7; ^{31}P NMR: δ 34.1.

General Procedure for the Synthesis of Unsaturated Phosphinite Boranes: To a solution of homoallylic alcohol in ether at 0 °C was added Et_3N followed by the dropwise addition of chlorodiphenyl phosphine. The resulting mixture was warmed to room temperature and stirred for 1 h. The progress of the reaction was monitored by TLC and upon completion the solution was filtered through a plug of silica and concentrated. 20% EtOAc in hexanes was added to the concentrate and filtered once again to remove the remaining ammonium salts. The filtrate was concentrated under reduced pressure and dried under vacuum. The crude material was dissolved in THF and cooled to 0 °C. THF·BH_3 (1M solution in THF) was added dropwise and the resulting solution was slowly warmed to room temperature and stirred overnight. The solution was concentrated under reduced pressure and the crude material was purified by column chromatography on silica.

3-Methylenecyclohexyl Diphenylphosphinite Borane 18. The general procedure was followed from 3-methylenecyclohexanol (672 mg, 6 mmol), Et_3N (1.7 mL, 12 mmol), chlorodiphenyl phosphine (1.72 mL, 9.6 mmol) and THF·BH_3 (4.7 mL, 4.7 mmol). The crude product was purified by column chromatography using 1:19 EtOAc/hexanes to yield **18** (1.0 g, 68%) as colorless oil which slowly crystalized to a white solid, mp 49-50 °C. Molecular ion calculated for $C_{19}H_{24}BOP$: 309.1574; [M-H], ESMS found *m*/*z* = 309.1573; IR (neat, cm^{-1}) 2384, B–H; 2344, B–H;

1653, C=C; ^{1}H NMR: δ 7.80-7.74 (4H, m), 7.52-7.48 (2H, m), 7.46-7.42 (4H, m), 4.73 (1H, s), 4.64 (1H, s), 4.51-4.44 (1H, m), 2.52 (1H, dd, J = 13.0 and 4 Hz), 2.28 (1H, dd, J = 13.5 and 8.0 Hz), 2.17-2.12 (1H, m), 2.07-2.02 (1H, m), 1.94-1.90 (1H, m), 1.83-1.76 (1H, m), 1.70-1.62 (1H, m), 1.44-1.36 (1H, m), 1.28-0.72 (3H, br m); ^{13}C NMR: δ 144.7, 133.3 (d, J = 64.8 Hz), 133.2 (d, J = 64.4 Hz), 131.5, 131.2 (d, J = 7.1 Hz), 131.1 (d, J = 7.1 Hz), 128.5 (d, J = 1.9 Hz), 128.4 (d, J = 1.9 Hz), 77.0 (d, J = 2.4 Hz), 42.4 (d, J = 3.4 Hz), 33.9, 33.1 (d, J = 3.4 Hz), 23.5; ^{11}B NMR: δ -38.6 to -41.3 (m); ^{31}P NMR: δ 102.1-101.9 (br m).

Ionic hydrogenation of phosphinate 19 using TfOH activation. To a solution of phosphinite borane **18** (62 mg, 0.2 mmol) at −78 °C in CH_2Cl_2 (5 mL) was added CF_3SO_3H (18 μL, 0.2 mmol) dropwise under nitrogen. The solution was stirred at that temperature for 4 h. Then the solution was treated with a premixed solution of H_2O_2 (0.5 mL) and 20% NaOH (0.5 mL) in methanol 4 mL) and stirred for further 4h. The reaction mixture was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered and concentrated. NMR analysis of the crude sample showed diastereoselectivity of 19:1 according to a comparison of methyl signals vs. independently synthesized diastereomers. The crude product was purified by PLC using 40% EtOAc in hexanes to yield **19** (27 mg, 43%) as a pure diastereomer, mp 80-81 °C. Molecular ion calcd for $C_{19}H_{23}O_2P$: 315.1508; [M+H], ESMS found *m/z* = 315.1505; IR (neat, cm^{-1}) 1221, P=O; ^{1}H NMR: δ 7.84-7.80 (4H, m), 7.52-7.49 (2H, m), 7.46-7.42 (4H, m), 4.76-4.74 (1H, m), 1.94-1.86 (3H, m), 1.82-1.76 (1H, m), 1.75-1.69 (1H, m), 1.59-1.54 (1H, m), 1.43-1.37 (1H, m), 1.14 (1H, t, J = 7.5 Hz), 0.98-0.88 (1H, m), 0.86 (3H, d, J = 6.5 Hz); ^{13}C NMR (175 MHz): δ 132.5 (interpreted as two carbon signals, d, J = 136.8 Hz), 131.8 (interpreted as two overlapping carbon signals, d, J = 2.6 Hz), 131.6 (d, J = 10.1 Hz), 131.5 (d, J = 10.1 Hz), 128.3 (interpreted as two overlapping carbon signals, d, J = 12.9 Hz), 72.7 (d, J = 5.4 Hz), 40.4 (d, J = 3.0 Hz), 34.1, 31.8 (d, J = 4.0 Hz), 26.6, 22.1, 20.3; ^{31}P NMR: δ 29.4 (s).

Independent Synthesis of 19 and 20

Both the major and the minor diastereomers (**19** and **20**) ware independently synthesized by the oxidation of the phosphonite borane of *trans* and *cis* 3-methylcychohexanol. To a solution of *Cis*-3-methylcyclohexanol (1 equiv, commertially available as a pure diastereomer) or *trans*-3-methylcyclohexanol (1 equiv, 80:20 mixture of trans:cis) at 0 °C in diethyl ether was added Et_3N (2 equiv) followed by the dropwise addition of chlorodiphenyl phosphine (1.5 equiv). The resulting mixture was warmed to room temperature and stirred for 1 h. The progress of the reaction was monitored by TLC and upon completion the solution was filtered through a plug of silica and concentrated. 20% EtOAc in hexanes was added to the concentrate and filtered once again to remove the remaining ammonium salts. The filtrate was concentrated under reduced pressure and dried under vacuum. The crude material was dissolved in THF and cooled to 0 °C. $THF{\cdot}BH_3$ (1 equiv, 1M solution in THF) was added dropwise and the resulting solution was slowly warmed to room temperature and stirred overnight. The solution was concentrated under reduced pressure and the crude material was purified by flash column chromatography on silica using 5% acetone in hexanes. **Oxidation procedure**: The phosphinite borane (1 equiv) was dissolved in dry dichloromethane and was treated with 0.5 equiv I_2. The solution was stirred under N_2 until the iodine color vanishes and then was poured in a premixed solution of H_2O_2 and NaOH. The solution was stirred at room temperature for 4h. Usual work-up followed by PLC using 30-40% EtOAc in hexanes produced pure samples of both *trans* (**19**) and *cis* (**20**) diastereomer. **Phosphinate 20:** R_f: 0.34 in 30% EtOAc hexanes. Molecular ion calcd for $C_{19}H_{23}O_2P$: 315.1508; [M+H], ESMS found *m/z* = 315.1504; IR (neat, cm^{-1}) 1229, P=O; ^1H NMR: δ 7.81-7.76 (4H, m), 7.49-7.45 (2H, m), 7.42-7.38 (4H, m), 4.34-4.26 (1H, m), 2.07-2.00 (2H, m), 1.70-1.66 (1H, m), 1.54-1.51 (1H, m), 1.42-1.33 (2H, m), 1.23-1.14 (2H, m), 0.85 (3H, d, J = 6.5 Hz), 0.81-0.73 (1H, m); ^{13}C NMR (175 MHz): δ 132.57 (d, J = 136.8 Hz), 132.53 (d, J = 136.3 Hz), 131.8 (interpreted as two overlapping carbon signals, d, J = 2.6 Hz), 131.6 (d, J = 10.1 Hz), 131.5 (d, J = 10.1 Hz), 128.3 (interpreted as two

overlapping carbon signals, d, J = 12.9 Hz), 75.6 (d, J = 6.8 Hz), 42.9 (d, J = 4.2 Hz), 33.9 (d, J = 4.2 Hz), 33.6, 31.3, 23.9, 22.1; ^{31}P NMR: δ 29.8 (s).

Phosphinite borane 22a. The general procedure was followed from 4-phenylpent-4-en-2-ol (972 mg, 6 mmol), Et_3N (1.4 mL, 10 mmol), chlorodiphenyl phosphine (1.62 mL, 9 mmol) and THF·BH_3 (4 mL, 4 mmol). The crude product was purified by column chromatography using 1:19 acetone/hexanes to yield **22a** (900 mg, 63%) as colorless oil. Molecular ion calcd for $C_{23}H_{23}OP$: 346.1487; [M-BH_3], ESMS found *m/z* = 346.1478; IR (neat, cm^{-1}) 2384, B–H; 2344, B–H; 1626, C=C; ^{1}H NMR: δ 7.75-7.69 (4H, m), 7.52-7.42 (6H, m), 7.31-7.27 (4H, m), 5.33 (1H, d, J = 1.5 Hz), 5.14 (1H, d, J = 1.0 Hz), 4.65-4.60 (1H, m), 3.08 (1H, dd, J = 14.0 and 6.0 Hz), 2.70 (1H, dd, J = 14.0 and 7.5 Hz), 1.25 (3H, d, J = 6 Hz), 1.2-0.70 (3H, br m); ^{13}C NMR: δ 144.2, 140.1, 133.1 (d, J = 63.9 Hz), 132.9 (d, J = 65.4 Hz), 131.5 (interpreted as two overlapping carbon signals, d, J = 2.9 Hz), 131.3 (d, J = 10.8 Hz), 131.1 (d, J = 11 Hz), 128.4 (d, J = 10.5 Hz), 128.3 (d, J = 11.5), 128.3, 127.5, 126.1, 115.6, 74.5 (d, J = 1.8 Hz), 43.8 (d, J = 4.4 Hz), 21.6 (d, J = 2.9 Hz); ^{11}B NMR: δ -39.9 to -40.0 (m); ^{31}P NMR: δ 102-101.5 (br m).

Phosphinite borane 22b. This compound was prepared following a similar procedure to that of phosphinite borane **22c**. The reaction was carried out with 2,2-dimethyl-5-phenylhex-5-en-3-ol (612 mg, 3 mmol), *n*-BuLi (2.4 mL, 3.84 mmol), chlorodiphenyl phosphine (0.72 mL, 4 mmol) and THF·BH_3 (2.7 mL, 2.7 mmol). The crude product was purified by column chromatography using 1:19 acetone/hexanes to yield **22b** (864 mg, 79%) as colorless oil. Molecular ion calculated for $C_{26}H_{32}BOP$: 401.2200; [M-H], ESMS found *m/z* = 401.2198; IR (neat, cm^{-1}) 2386, B–H; 2347, B–H; 1627, C=C; ^{1}H NMR: δ 7.80-7.74 (4H, m), 7.47-7.36 (6H, m), 7.30-7.26 (3H, m), 7.17-7.16 (2H, m), 4.96 (1H, s), 4.87 (1H, d, J = 1.0 Hz), 4.42-4.46 (1H, m), 2.98 (1H, dd, J = 15.0 and 4 Hz), 2.69 (1H, dd, J = 15.5 and 7.5 Hz), 0.93 (9H, s), 1.28-0.75 (3H, br m); ^{13}C NMR: δ 144.1, 140.3, 134.3 (d, J = 82.9 Hz), 133.9 (d, J = 87.3 Hz), 131.3 (d, J = 11.0 Hz), 131.1 (d, J = 2.4 Hz), 130.8 (d, J = 10.4 Hz), 128.5 (d, J =

10.5 Hz), 128.3 (d, J = 11.0 Hz), 128.1, 128.0 (d, J = 11.9 Hz), 127.4, 126.4, 115.8, 86.7 (d, J = 4.2 Hz), 38.0 (d, J = 2.0 Hz), 36.2 (d, J = 3.4 Hz), 26.4; ^{11}B NMR: δ -40.8 (br s); ^{31}P NMR: δ 102.2-101.8 (br m).

Phosphinite borane 22c: To a solution of 2,2,5-trimethylhex-5-en-3-ol (650 mg, 4.57 mmol) in THF (30 mL) at 0 °C was added *n*-BuLi (3.57 mL, 5.7 mmol) dropwise. The resulting dark red solution was stirred at that temperature for 1 h and then chlorodiphenyl phosphine (1.02 mL, 5.7 mmol) was added keeping the temperature at 0 °C. The solution was slowly warmed to room temperature and stirred for 2 h. The resulting light yellow solution was filtered and concentrated under reduced pressure. The crude material was dissolved in THF (25 mL) and cooled to 0 °C. THF·BH_3 (4.3 mL, 4.3 mmol) was added dropwise and the resulting solution was slowly warmed to room temperature and stirred overnight. The solution was concentrated under reduced pressure and the crude product was purified by column chromatography using 1:19 acetone/hexanes to yield **22c** (670 mg, 46%) as colorless oil. Molecular ion calculated for $C_{21}H_{27}OP$: 326.1800; [M-BH_3], ESMS found *m*/*z* = 326.1798; IR (neat, cm^{-1}) 2386, B–H; 2347, B–H; 1651, C=C; ^{1}H NMR: δ 7.82-7.74 (4H, m), 7.48-7.36 (6H, m), 4.47-4.52 (1H, m), 4.41 (2H, d, J = 0.5 Hz), 2.37 (1H, dd, J = 14.5 and 3.5 Hz), 2.25 (1H, dd, J = 15.0 and 7.5 Hz), 1.67 (3H, s), 0.94 (9H, s), 1.47-0.97 (3H, br m); ^{13}C NMR: δ 141.4, 134.5 (d, J = 85 Hz), 133.8 (d, J = 89 Hz), 131.3 (d, J = 11.5 Hz), 131.2 (d, J = 2.4 Hz), 131.1 (d, J = 2.5 Hz), 130.9 (d, J = 11 Hz), 128.3 (d, J = 10.5 Hz), 128.1 (d, J = 10.5 Hz), 113.7, 86.3 (d, J = 4.2 Hz), 40.9 (d, J = 1.9 Hz), 36.1 (d, J = 3.9 Hz), 26.2, 22.2; ^{11}B NMR: δ -39.3 to -40.0 (m); ^{31}P NMR: δ 102.1-101.6 (br m).

Phosphinite borane 22d: The general procedure was followed from 4-methylpent-4-en-2-ol (1 g, 10 mmol), Et_3N (2.1 mL, 15 mmol), chlorodiphenyl phosphine (2.16 mL, 12 mmol) and THF·BH_3 (7 mL, 7 mmol). The crude product was purified by column chromatography using 1:9 EtOAc/hexanes to yield **22d** (790 mg, 38%) as colorless oil. Molecular ion calculated for $C_{18}H_{23}BOP$: 297.1580; [M-H], ESMS found *m*/*z* = 297.1585; IR (neat, cm^{-1}) 2384, B–H; 2344, B–H; 1650, C=C; ^{1}H NMR: δ 7.77-7.69 (4H, m), 7.52-7.40 (6H, m), 4.76 (1H, s), 4.74 (1H, s), 4.73-

4.69 (1H, m), 2.48 (1H, dd, J = 14.0 and 6.5 Hz), 2.22 (1H, dd, J = 13.5 and 7.0 Hz), 1.67 (3H, s), 1.26 (3H, d, J = 6.5 Hz), 1.42-0.88 (3H, br m); ^{13}C NMR: δ 141.5, 133.5 (d, J = 63.9 Hz), 133.1 (d, J = 66.8 Hz), 131.5 (d, J = 7.6 Hz), 131.4 (d, J = 7.6 Hz), 131.3 (d, J = 1.9 Hz), 131.2 (d, J = 1.5 Hz), 128.4 (d, J = 14.2 Hz), 128.3 (d, J = 14.8 Hz), 113.7, 74.3 (d, J = 2.4 Hz), 46.6 (d, J = 4.8 Hz), 22.4, 21.8 (d, J = 2.4 Hz); ^{11}B NMR: δ -39.4 to -40.6 (m); ^{31}P NMR: δ 101.9-101.0 (br m).

General Procedure for the Ionic Hydrogenation of Unsaturated Acyclic Phosphinite Boranes. To a solution of phosphinite borane in CH_2Cl_2 (ca. 0.1 M) was added $MeSO_3H$ (3 equiv) at room temperature under nitrogen. The solution was stirred at that temperature for 15-60 min until TLC assay indicated completion, and the solution was then treated with a premixed solution of H_2O_2 and 20%NaOH in methanol and stirred for an additional 4h. The reaction mixture was extracted with CH_2Cl_2 (3x), dried over $MgSO_4$, filtered and concentrated. The crude product was purified either by column chromatography or by PLC.

Phosphinate 24a: The general procedure was followed from phosphinite borane **22a** (144 mg, 0.4 mmol) and $MeSO_3H$ (80 μL, 1.2 mmol) in 4 mL CH_2Cl_2. The solution was oxidized with a premixed solution of 30% H_2O_2 (1 mL) and 20% NaOH (1 mL) in methanol (8 mL). The crude product was purified by column chromatography using 40% EtOAc in hexanes to yield **24a** (112 mg, 77%) as a mixture of two diastereomers (dr ~ 2.6:1). Molecular ion calcd for $C_{23}H_{25}O_2P$: 365.1665; [M+H], ESMS found *m/z* = 365.1655; IR (neat, cm^{-1}) 1230, P=O; Major diastereomer (signals based on a mixture of two inseparable diastereomers): ^{1}H NMR: δ 7.81-7.73 (4H, m), 7.52-7.38 (6H, m), 7.25-7.00 (5H, m), 4.43-4.37 (1H, m), 2.79-2.74 (1H, m), 2.15-2.09 (1H, m), 1.79-1.74 (1H, m), 1.31 (3H, d, J = 6.5 Hz), 1.15 (3H, d, J = 7 Hz); ^{13}C NMR: 146.2, 132.3 (d, J = 132.0 Hz), 132.2 (d, J = 109.2 Hz), 131.8 (d, J = 2.5 Hz), 131.6 (d, J = 10.0 Hz), 131.5 (d, J = 10.0 Hz), 128.4 (d, J = 4.3 Hz), 128.3 (d, J = 1.9 Hz), 128.2 (d, J = 3.4 Hz), 126.9, 126.5, 125.9, 71.7 (d, J = 6.1 Hz), 45.8 (d, J = 5.3 Hz), 36.0, 22.5, 22.1 (d, J = 2.4 Hz); ^{31}P NMR: δ 29.3 (s).

Phosphinate 24b: The general procedure was followed from phosphinite borane **22b** (80.4 mg, 0.2 mmol) and $MeSO_3H$ (40 μL, 0.6 mmol) in 2 mL CH_2Cl_2. The solution was oxidized with a premixed solution of 30% H_2O_2 (0.5 mL) and 20%NaOH (0.5 mL) in methanol (4 mL). The crude product was purified by column chromatography using 30% EtOAc in hexanes to yield **24b** (49 mg, 60%) as a mixture of two diastereomers (dr ~ 1:0.85). Two diastereomers were separated by repeated PLC using 30% EtOAc in hexanes. Major diastereomer: Molecular ion calcd for $C_{26}H_{31}O_2P$: 407.2134; [M+H], ESMS found *m/z* = 407.2136; IR (neat, cm^{-1}) 1229, P=O; ^1H NMR (700 MHz): δ 7.91-7.88 (2H, m), 7.76-7.73 (2H, m), 7.51-7.49 (1H, m), 7.47-7.43 (3H, m), 7.39-7.36 (2H, m), 7.22 (2H, t, J = 7.7 Hz), 7.11 (1H, t, J = 7.7 Hz), 7.08 (2H, d, J = 7.0 Hz), 4.00-3.98 (1H, m), 2.76-2.73 (1H, m), 1.92-1.88 (1H, m), 1.83-1.79 (1H, m), 0.97 (3H, d, J = 7.0 Hz), 0.71 (9H, s); ^{13}C NMR (175 MHz): δ 146.1, 134.0 (d, J = 134.7 Hz), 133.2 (d, J = 133.3 Hz), 131.7 (d, J = 2.8 Hz), 131.6 (d, J = 10.1 Hz), 131.5 (d, J = 2.6 Hz), 131.3 (d, J = 10.1Hz), 128.4 (d, J = 12.7 Hz), 128.3 (d, J = 12.9 Hz), 128.2, 127.6, 125.9, 84.0 (d, J = 8.0 Hz), 40.7 (d, J = 1.4 Hz), 36.6, 35.3 (d, J = 4.7 Hz), 25.8 (3C), 23.1; ^{31}P NMR: δ 28.5 (s). Minor diastereomer: mp 101-102 °C. Molecular ion calcd for $C_{26}H_{31}O_2P$: 407.2134; [M+H], ESMS found *m/z* = 407.2136; IR (neat, cm^{-1}) 1228, P=O; ^1H NMR (700 MHz): δ 7.87-7.84 (2H, m), 7.81-7.78 (2H, m), 7.50 (1H, t, J = 7.0 Hz), 7.47-7.39 (5H, m), 7.16 (2H, t, J = 7.0 Hz), 7.11 (1H, t, J = 7.0 Hz), 6.77 (2H, d, J = 7.7 Hz), 4.51 (1H, t, J = 9.0 Hz), 2.51-2.48 (1H, m), 1.89-1.85 (1H, m), 1.73 (1H, t, J = 13.3 Hz), 1.13 (3H, d, J = 7.0 Hz), 0.90 (9H, s); ^{13}C NMR (175 MHz): δ 148.1, 134.2 (d, J = 136.9 Hz), 133.4 (d, J = 137.4 Hz), 131.7 (d, J = 2.8 Hz), 131.6 (d, J = 2.8 Hz), 131.4 (d, J = 9.6 Hz), 131.3 (d, J = 9.5 Hz), 128.4 (d, J = 12.9 Hz), 128.3 (d, J = 12.9 Hz), 128.2, 126.5, 125.7, 84.4 (d, J = 8.0 Hz), 40.5 (d, J = 2.1 Hz), 35.4 (d, J = 4.2 Hz), 35.3, 26.3 (3C), 20.1; ^{31}P NMR: δ 29.5 (s).

Phosphinate 24c: The general procedure was followed from phosphinite borane **22c** (68 mg, 0.2 mmol) and $MeSO_3H$ (40 μL, 0.6 mmol) in 2 mL CH_2Cl_2. The solution was oxidized with a premixed solution of 30% H_2O_2 (0.5 mL) and 20% NaOH (0.5 mL) in methanol (4 mL). The crude

product was purified by column chromatography using 30% EtOAc in hexanes to yield **24c** (42 mg, 61%) as a white solid, mp 94-95 °C. Molecular ion calculated for $C_{21}H_{29}O_2P$: 345.1978; [M+H], ESMS found *m/z* = 345.1972; IR (neat, cm^{-1}) 1222, P=O; ^1H NMR: δ 7.83-7.78 (4H, m), 7.48-7.39 (6H, m), 4.37-4.33 (1H, m), 1.62-1.56 (1H, m), 1.45-1.37 (1H, m), 1.33-1.26 (1H, m), 0.90 (9H, s), 0.75 (3H, d, J = 6.5 Hz), 0.65 (3H, d, J = 6.5 Hz); ^{13}C NMR: δ 134.0 (d, J = 136.4 Hz), 133.5 (d, J = 137.9 Hz), 131.5 (d, J = 2.9 Hz), 131.4 (d, J = 2.9 Hz), 131.3 (d, J = 10.0 Hz), 131.2 (d, J = 10.0 Hz), 128.2 (d, J = 6.8 Hz), 128.1 (d, J = 6.8 Hz), 83.8 (d, J = 8.1 Hz), 40.9 (d, J = 2.4 Hz), 35.3 (d, J = 3.8 Hz), 26.2 (3C), 24.7, 23.6, 21.3; ^{31}P NMR: δ 28.9 (s).

Phosphinate 24d and Phosphinite borane 25: The general procedure was followed from phosphinite borane **22d** (298 mg, 1 mmol) and $MeSO_3H$ (200 μL, 3 mmol) in 10 mL CH_2Cl_2. The solution was oxidized with a premixed solution of 30% H_2O_2 (2.5 mL) and 20% NaOH (2.5 mL) in methanol (20 mL). The crude product was chromatographed on silica gel using 40% EtOAc in hexanes. The nonpolar fractions were collected and saved for further isolation of pure phosphinite borane **25**. The more polar fractions provided pure **24d** (195 mg, 65%) as viscous oil. Molecular ion calcd for $C_{18}H_{23}O_2P$: 303.1508; [M+H], ESMS found *m/z* = 303.1509; IR (neat, cm^{-1}) 1230, P=O; ^1H NMR: δ 7.85-7.83 (4H, m), 7.52-7.48 (2H, m), 7.46-7.41 (4H, m), 4.63-4.56 (1H, m), 1.73-1.62 (2H, m), 1.39-1.33 (1H, m), 1.31 (3H, d, J = 6 Hz), 0.81 (6H, app. t, J = 6.5 Hz); ^{13}C NMR: δ 132.7 (d, J = 136.9 Hz), 132.3 (d, J = 132.5 Hz), 131.8 (d, J = 2.4 Hz), 131.6 (d, J = 10.0 Hz), 131.5 (d, J = 10.0 Hz), 128.3 (d, J = 12.9 Hz), 128.2 (d, J = 12.9 Hz), 72.1 (d, J = 6.8 Hz), 47.2 (d, J = 5.8 Hz), 24.4, 22.7, 22.6 (d, J = 2.4 Hz), 22.3; ^{31}P NMR: δ 29.3 (s). The upper nonpolar fractions were concentrated and purified twice by PLC. In the second PLC using 2% Et_2O in hexanes, the upper nonpolar band was roughly divided into two halves. Extraction of the upper half provided the pure phosphinite borane **25**. Molecular ion calculated for $C_{18}H_{23}OP$: 286.1486; [M-BH_3], EIMS found *m/z* = 286.1483; IR (neat, cm^{-1}) 2383, B–H; 2345, B–H; ^1H NMR: δ 7.75-7.64 (4H, m), 7.49-7.37 (6H, m), 4.65-4.55 (1H, m), 1.66-1.54 (2H, m), 1.32-1.27 (1H, m), 1.20 (3H, d, J = 6.0 Hz), 0.81 (3H, d, J = 6.4 Hz), 0.81 (3H, d, J = 6.4 Hz); ^{13}C NMR: δ 133.5 (d, J = 63.7

Hz), 133.3 (d, J = 67.0 Hz), 131.5 (2C), 131.2 (d, J = 12.9 Hz), 131.1 (d, J = 12.9 Hz), 128.4 (d, J = 10.1 Hz), 128.3 (d, J = 10.8 Hz), 74.9 (d, J = 2.1 Hz), 47.3 (d, J = 5.4 Hz), 24.5, 22.8, 22.5 (d, J = 2.1 Hz), 22.3; ^{11}B NMR: δ -38.6 to -41.4 (m); ^{31}P NMR: δ 101.6-100.4 (br m).

Preparation of Amine Borane Complexes; 26a and 26b

BH_3·THF (6.3 mL, 6.3 mmol) was added by syringe under an N_2 atmosphere to the known (3-methyl-3-butenyl)-dimethylamine[4] (1.0 mL, 6.8 mmol) in anhydrous DCM (20 mL). After 1 h, the solution was filtered through a plug of silica gel, flushing with DCM and removing solvent by rotary evaporation, yielding 0.78 g (3-methyl-3-butenyl)-dimethylamine borane **26a** (97% y): TLC on K6F silica gel 60Å, 9:1 hexanes/Et_2O, Rf = 0.26. Molecular ion calculated for $C_7H_{17}BN$: 126.1454; [M-H], EIMS found *m/z* = 126.1452; IR (neat, cm^{-1}) 2366, B–H; 2319, B–H; 2273, B–H; 1650, C=C; 1459, B–N; 1167, C–N; ^{1}H NMR: δ 4.81 (1H, s), 4.73 (1H, s), 2.90-2.85 (2H, m), 2.61 (6H, s), 2.46-2.41 (2H, m), 2.1-1.3 (3H, br m), 1.77 (3H, s); ^{13}C NMR: δ 141.9, 112.1, 63.0, 51.4, 32.1, 22.7; ^{11}B NMR: δ -9.9 (q, J = 98 Hz).

Borane complexation from (3-phenyl-3-butenyl)-dimethylamine[5] under the same conditions gave **26b** (67%): TLC on K6F silica gel 60Å, 2:1 hexanes/EtOAc, Rf = 0.27. Molecular ion calculated for $C_{12}H_{20}BNNa$: 212.1586; [M+Na], ESMS found *m/z* = 212.1582; IR (neat, cm^{-1}) 2366, B–H; 2319, B–H; 2273, B–H; 1627, C=C; 1461, B–N; 1167, C–N; ^{1}H NMR: δ 7.44-7.41 (2H, m), 7.37-7.33 (2H, m), 7.32-7.28 (1H, m), 5.38 (1H, d, J = 1.0 Hz), 5.15 (1H, q, J = 1.0 Hz), 3.02-2.97 (2H, m), 2.85-2.80 (2H, m), 2.61 (6H, s), 2.1-1.3 (3H, br m); ^{13}C NMR: δ 144.8, 139.8, 128.6, 128.0, 126.0, 114.6, 63.6, 51.8, 30.4; ^{11}B NMR: δ -10.2 (q, J = 97 Hz).

Ionic Hydrogenation of Amine Boranes 26; Isolation of 29a and 29b

Neat MsOH (100 μL, 1.54 mmol) was added by syringe to a stirred solution of **26a** (64 mg, 0.50 mmol) in anhydrous DCM (5 mL) under an N_2 atmosphere. After 1 h, the reaction was quenched by addition of 5 mL 5% aq. NaOH, separated and the aqueous layer extracted with 2 x 5 mL DCM. The combined organic layers were dried over Na_2SO_4 and reduced by rotatory evaporation. The product was purified by flash chromatography (FC) on silica gel (15 cm x 20 mm diameter, 1:2 hexanes/EtOAc), isolating 71 mg (3-methylbutyl)-dimethylamine bis(methylsulfonyloxy)borane (**29a**, 44%): TLC on K6F silica gel 60Å, 1:2 hexanes/EtOAc, Rf = 0.20. Molecular ion calculated for $C_9H_{24}BNNaO_6S_2$: 340.1036; [M+Na], ESMS found *m/z* = 340.1027; IR (neat, cm^{-1}) 2508, B–H; 1484, B–N; 1318, B–O; 1173, C–N; ^{1}H NMR: δ 3.8-2.8 (1H, br m), 3.07 (6H, s), 2.95-2.90 (2H, m), 2.61 (6H, s), 1.65-1.52 (3H, m), 0.96 (6H, d, J = 6.4 Hz); ^{13}C NMR: δ 57.8, 44.5, 38.9, 30.4, 26.6, 22.4; ^{11}B NMR: δ 1.0 (d, J = 134 Hz).

The same rocedure was used from **26b** and afforded 3-phenylbutyl)-dimethylamine bis(methylsulfonyloxy)borane **29b**, was purified by reverse-phase PLC on K18F silica gel (70%): TLC on K18F silica gel 60Å, 4:1 MeOH/H_2O buffered with 0.5% Et_3N and 0.5% CF_3CO_2H, Rf = 0.62. Molecular ion calculated for $C_{14}H_{25}BNO_6S_2$: 378.1216; [M-H], EIMS found *m/z* = 378.1215; IR (neat, cm^{-1}) 2512, B–H; 1484, B–N; 1322, B–O; 1177, C–N; ^{1}H NMR: δ 7.33 (2H, t, J = 7.5 Hz), 7.23 (1H, t, J = 7.3 Hz), 7.18 (2H, d, J = 7.3 Hz), 3.02 (3H, s), 3.01 (3H, s), 2.95 (1H, td, J = 12.7, 4.9 Hz), 2.74-2.66 (1H m), 2.60 (1H, td, J = 12.7, 4.4 Hz), 2.56 (3H, s), 2.52 (3H, s), 2.07-1.90 (2H, m), 1.32 (3H, d, J = 7.1 Hz); ^{13}C NMR: δ 145.0, 128.9, 126.8, 126.7, 58.3, 45.0, 44.7, 38.9, 38.9, 38.2, 30.3, 22.5; ^{11}B NMR: δ 0.8 (d, J = 111 Hz).

Conversion of 26a to 27a Using Stoichiometric MsOH

Neat MsOH (40 μL, 0.62 mmol) was added by syringe to a stirred solution of **26a** (64 mg, 0.50 mmol) in anhydrous DCM (5 mL) under an N_2 atmosphere. After 1 h, the reaction was quenched by addition of 2 mL 5% aq. NaOH, diluted with 3 mL H_2O, separated and the aqueous layer extracted with 2 x 5 mL DCM. The combined organic layers were dried over Na_2SO_4 and reduced by rotatory evaporation. The product was purified by flash chromatography (FC) on silica gel (15 cm x 20 mm diameter, 1:2 hexanes/EtOAc), isolating 57 mg (3-methyl-3-butenyl)-dimethylamine methylsulfonyloxy-borane (**27a**, 52%): TLC on K6F silica gel 60Å, 1:2 hexanes/EtOAc, Rf = 0.37. Molecular ion calculated for $C_8H_{20}BNNaO_3S$: 244.1155; [M+Na], ESMS found *m/z* = 244.1156; IR (neat, cm^{-1}) 2347, B–H; 2325, B–H; 1466, B–N; 1314, B–O; 1146, C–N; ^1H NMR: δ 4.85 (1H, s), 4.76 (1H, s), 3.0-2.1 (2H, br m), 2.97-2.92 (2H, m), 2.91 (3H, s), 2.61 (6H, s), 2.42-2.36 (2H, m), 1.77 (3H, s); ^{13}C NMR: δ 141.1, 112.9, 59.0, 46.9, 37.7, 30.9, 22.6; ^{11}B NMR: δ 3.2 to -1.2 (br m).

4-(Dimethylamino)-2-phenylbutan-2-yl Acetate Borane Complex (30). To a solution of amine (120 mg, 0.51 mmol) in THF (2 mL) was slowly added BH_3·THF (0.85 M, 0.9 mL) at 0 °C. The resulting mixture was stirred for 2 h at rt. After removal of solvent, flash chromatography (hexane-ethyl acetate, 5:1) of the residue afforded 107 mg (84%) of the amine borane **30**: IR (neat) 3053, 1733, 2985, 1419, 1095, 895, 704 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.20-2.00 (br m, 3H), 1.87 (s, 3H), 2.10 (s, 3H), 2.38-2.44 (m, 1H), 2.49 (s, 3H), 2.50 (s, 3H), 2.53-2.59 (m, 1H), 2.62-2.73 (m, 2H), 7.26-7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.2, 25.8, 35.9, 51.3, 51.4, 59.7, 82.7, 124.3, 127.4, 128.5, 143.7, 169.5; HRMS (ESI) *m/z* $C_{14}H_{24}BNO_2Na$ 272.1798 $[M+Na]^+$, found 272.1794.

Ionic Hydrogenation of 30 Activated by TMSOTf; N,N-Dimethyl-3-phenylbutanamine (33).[6] To a solution of amine borane complex **30** (18 mg, 0.072 mmol) in CH_3CN (2 mL) was added TMSOTf (25 μL) at 0 °C. The mixture was stirred overnight at rt, and quenched by addition of

NaOH (2N). After separation, the aqueous layer was extracted with DCM, the combined organic layers were dried over sodium sulfate and concentrated (vacuum) to give 10.5 mg (83%) of **33**[6] after preparatory TLC using 3 : 1 : 0.02 hexane : ether : triethylamine; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (d, *J* = 7.0 Hz), 1.71-1.83 (m, 2H), 2.11-2.27 (m, 2H), 2.20 (s, 6H), 2.71-2.79 (m, 1H), 7.17-7.22 (m, 3H), 7.26-7.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.4, 36.0, 38.0, 45.4, 57.9, 125.8, 126.9, 128.3, 147.3.

2-((Dimethylamino)methyl)-1-methyl-1,2,3,4-tetrahydronaphthalen-1-yl Acetate Borane Complex (Footnote 7, *i*). The same procedure was used as for the preparation of **30** to give *I*; IR (neat) 3052, 1733, 1456, cm $^{-1}$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20-2.10 (br m, 3H), 1.92 (s, 3H), 2.08 (s, 3H), 2.17-2.24 (m, 1H), 2.33-2.41 (m, 1H), 2.60 (s, 3H), 2.61 (s, 3H), 2.70-2.75 (m, 1H), 2.82-2.90 (m, 2H), 2.94-3.02 (m, 2H), 7.10-7.15 (m, 1H), 7.18-7.24 (m, 2H), 7.60-7.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.5, 24.7, 25.7, 28.1, 38.4, 51.5, 52.9, 63.2, 83.0, 126.0, 126.6, 127.6, 129.0, 135.1, 138.8, 170.1; HRMS (ESI) *m/z* $C_{16}H_{26}BNO_2Na$ 298.1954 $[M+Na]^+$, found 298.1951.

N,N-Dimethyl(1-methyl-1,2,3,4-tetrahydronaphthalen-2-yl)methanamine (Footnote 7, *ii*). The same procedure was used as for the ionic hydrogenation of **30** and gave ***ii*** in 52% yield as a mixture of diastereoisomer (dr = 2.7:1) from ***i*** (starting *dr* = 3.5:1): major isomer IR (neat) 3052, 2985, 1419 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (d, *J* = 7.4 Hz, 3H), 1.60-1.68 (m, 1H), 1.76-1.84 (m, 1H), 1.96-2.08 (m, 1H), 2.12-2.28 (m, 2H), 2.24 (s, 3H), 2.27 (s, 3H), 2.64-2.76 (m, 2H), 2.82-2.88 (m, 1H), 7.05-7.18 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.5, 22.5, 24.1, 26.2, 36.2, 37.4, 46.0, 63.5, 125.4, 129.4, 136.1, 141.1; HRMS (ESI) *m/z* $C_{14}H_{22}N$ 204.1752 $[M+H]^+$, found 204.1745.

Reaction of 26b with (+)-Camphorsulfonic Acid

Solid (+)-camphorsulfonic acid (CSA, **34**, 35 mg, 0.15 mmol) was added to a stirred solution of **26b** (25 mg, 0.13 mmol) in anhydrous DCM (5 mL) which was then quickly capped with a septum and an N_2 inlet. After stirring 2 h, neat MsOH (15 μL, 0.23 mmol) was added by syringe, monitoring the reaction by MS. After 1 h, the major peak corresponded to **36**. The solvent was then removed by a stream of N_2, and the residue was dissolved in MeOH (1.0 mL) which was then acidified by addition of 0.10 mL 6M aq. HCl before heating to reflux 16 h. The mixture was cooled to rt, made alkaline with 5% aq. NaOH and extracted with Et_2O (2 x 5 mL), the organic layers dried over $MgSO_4$ and reduced by rotatory evaporation. The product was purified by PLC on silica gel (20 x 20 cm x 250 μm, 65:33:2 hexanes/acetone/Et_3N), isolating 12 mg (3-phenylbutyl)-dimethylamine (**33**, 53%, 68% ee). Conditions for enantiomeric excess assay by HPLC (Chiralcel OD column, 0.1% *i*PrOH/hexane, 1 mL/min) were optimized using racemic **33**, obtained by hydrolysis of *rac*-**29b** with HCl, with peaks at 13 and 23 minutes (peak at 40 minutes for (3-phenyl-3-butenyl)-dimethylamine impurity).

Reaction of $Me_3N{\cdot}BH_3$ (37) with (–)-Camphorsulfonic Acid

Solid (–)-camphorsulfonic acid (*ent*-CSA, *ent*-**34**, 152 mg, 0.65 mmol) was added to a stirred solution of $Me_3N{\cdot}BH_3$ (**37**, 43 mg, 0.59 mmol) in anhydrous DCM (2.2 mL) which was then quickly capped with a septum and an N_2 inlet. After stirring 4 h the solution was washed with H_2O (5 mL), the layers separated and the aqueous layer extracted with 5 mL DCM. The combined organic layers were dried over Na_2SO_4 and reduced by rotatory evaporation. The residue was taken up in minimal DCM (ca. 1 mL) and hexanes was added until the solution started to turn cloudy (ca. 15 mL). The flask was left open to allow solvent evaporation, collecting the long needles that formed after 1 d, rinsing with hexanes and collecting 41 mg trimethylamine ((1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethyl-bicyclo[2.2.1]hept-1-yl)-methylsulfonyloxyborane (**38**, 27%):

Molecular ion calculated for $C_{13}H_{25}BNO_4S$: 302.1597; [M-H_2-H^-], EIMS found *m/z* = 302.1595; IR (neat, cm^{-1}) 3512, O–H, 2427, B–H; 2342, B–H; 1468, B–N; 1316, B–O; 1138, C–N; ^{1}H NMR: δ 4.15-4.08 (1H, m), 3.44 (1H, d, J = 14.0 Hz), 3.37 (1H, d, J = 3.3 Hz), 2.93 (1H, d, J = 14.0 Hz), 2.90 (1H, d, J = 4.0 Hz), 2.8-2.0 (2H, br m), 2.64 (9H, s), 1.88-1.47 (6H, m), 1.08 (3H, s), 0.83 (3H, s); ^{13}C NMR: δ 76.4, 50.0, 49.9, 49.7, 48.5, 44.5, 38.8, 30.5, 27.4, 20.6, 19.9; ^{11}B NMR: δ 3.4 to -0.2 (br m).

References for Supporting Information

(1) Harris, R. K.; Becker, E. D.; Cabral De Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

(2) Shapland, P.; Vedejs, E. *J. Org. Chem.* **2004**, *69*, 4094.

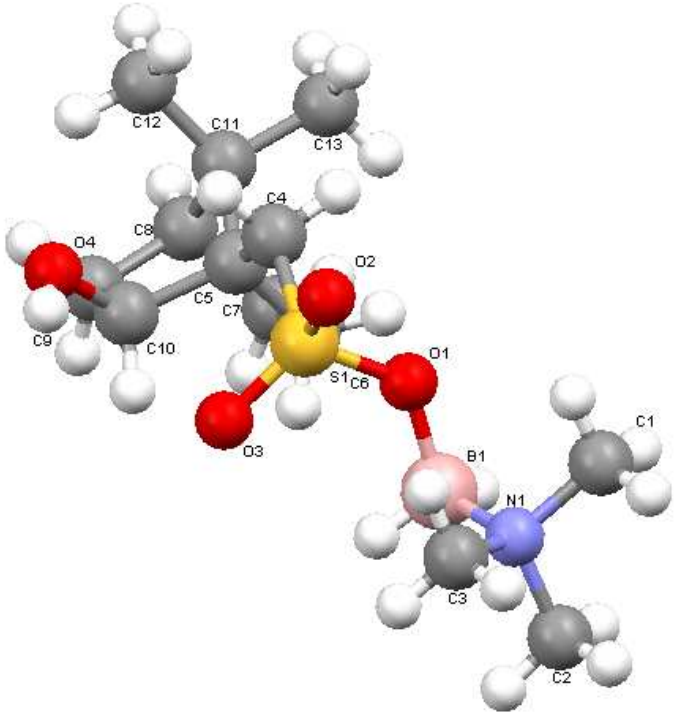
(3) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

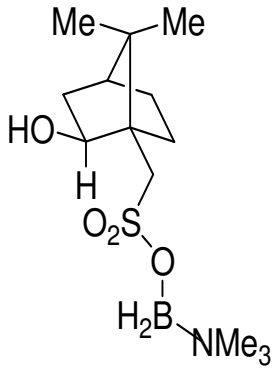
(4) Krafft, M. E.; Juliano, C. A.; Scott, I. L.; Wright, C.; McEachin, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 1693.

(5) Aoyama, H.; Sugiyama, J.-I.; Yoshida, M.; Hatori, H.; Hosomi, A. *J. Org. Chem.* **1992**, *57*, 3037.

(6) Bussas, R.; Muenster, H.; Kresze, G. *J. Org. Chem.* **1983**, *48*, 2828.

X-ray Crystal Structure of **38**





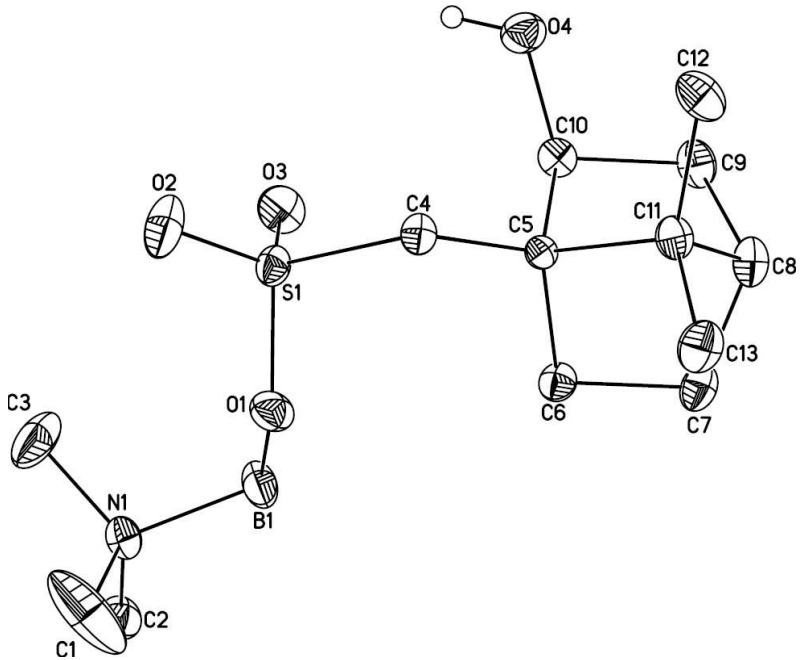


Table 1. Crystal data and structure refinement for **38**.

Identification code	**38**
Empirical formula	C13 H28 B N O4 S
Formula weight	305.23
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.8265(5) A alpha = 90 deg. b = 9.4699(8) A beta = 90 deg. c = 24.772(2) A gamma = 90 deg.
Volume	1601.4(2) A^3
Z, Calculated density	4, 1.266 Mg/m^3
Absorption coefficient	0.214 mm^-1
F(000)	664
Crystal size	0.50 x 0.34 x 0.22 mm
Theta range for data collection	1.64 to 28.34 deg.
Limiting indices	-9<=h<=9, -12<=k<=12, -33<=l<=33
Reflections collected / unique	57330 / 3997 [R(int) = 0.0376]
Completeness to theta = 28.34	100.0 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9545 and 0.9007
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3997 / 0 / 190
Goodness-of-fit on F^2	1.171
Final R indices [I>2sigma(I)]	R1 = 0.0330, wR2 = 0.0892
R indices (all data)	R1 = 0.0332, wR2 = 0.0893
Absolute structure parameter	0.04(6)
Largest diff. peak and hole	0.356 and -0.189 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **4-25**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	3664(3)	6617(2)	8546(1)	26(1)
N(1)	4294(2)	5263(1)	8193(1)	18(1)
S(1)	502(1)	7984(1)	8102(1)	17(1)
O(1)	1510(2)	6860(1)	8448(1)	22(1)
O(2)	-633(2)	7258(2)	7697(1)	30(1)
O(3)	1845(2)	9044(1)	7918(1)	26(1)
O(4)	-708(2)	11747(1)	8363(1)	23(1)

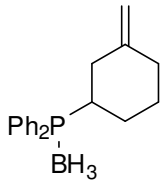
C(1)	2985(3)	4063(2)	8310(1)	59(1)
C(2)	6321(3)	4857(2)	8345(1)	26(1)
C(3)	4276(3)	5583(3)	7609(1)	45(1)
C(4)	-1217(2)	8733(2)	8555(1)	15(1)
C(5)	-429(2)	9704(1)	8990(1)	12(1)
C(6)	1174(2)	9081(2)	9361(1)	17(1)
C(7)	1072(2)	10025(2)	9875(1)	22(1)
C(8)	-559(2)	11080(2)	9733(1)	20(1)
C(9)	260(2)	12077(2)	9299(1)	22(1)
C(10)	396(2)	11134(2)	8787(1)	16(1)
C(11)	-2028(2)	10165(2)	9410(1)	16(1)
C(12)	-3744(2)	11000(2)	9172(1)	23(1)
C(13)	-2899(2)	8950(2)	9737(1)	21(1)

Table 3. Bond lengths [A] and angles [deg] for **38**.

B(1)-O(1)	1.507(2)
B(1)-N(1)	1.610(2)
N(1)-C(1)	1.474(2)
N(1)-C(3)	1.478(2)
N(1)-C(2)	1.485(2)
S(1)-O(3)	1.4340(12)
S(1)-O(2)	1.4428(12)
S(1)-O(1)	1.5306(11)
S(1)-C(4)	1.7716(14)
O(4)-C(10)	1.4174(18)
C(4)-C(5)	1.5162(18)
C(5)-C(6)	1.5458(19)
C(5)-C(10)	1.5510(19)
C(5)-C(11)	1.5692(19)
C(6)-C(7)	1.556(2)
C(7)-C(8)	1.536(2)
C(8)-C(9)	1.536(2)
C(8)-C(11)	1.548(2)
C(9)-C(10)	1.554(2)
C(11)-C(13)	1.527(2)
C(11)-C(12)	1.532(2)
O(1)-B(1)-N(1)	107.18(13)
C(1)-N(1)-C(3)	110.3(2)
C(1)-N(1)-C(2)	108.39(15)
C(3)-N(1)-C(2)	108.03(14)
C(1)-N(1)-B(1)	110.15(15)
C(3)-N(1)-B(1)	111.43(14)
C(2)-N(1)-B(1)	108.48(12)
O(3)-S(1)-O(2)	117.10(8)
O(3)-S(1)-O(1)	112.21(7)
O(2)-S(1)-O(1)	107.45(7)

O(3)-S(1)-C(4)	110.20(7)
O(2)-S(1)-C(4)	105.97(7)
O(1)-S(1)-C(4)	102.78(6)
B(1)-O(1)-S(1)	129.38(12)
C(5)-C(4)-S(1)	117.27(10)
C(4)-C(5)-C(6)	116.26(11)
C(4)-C(5)-C(10)	115.32(11)
C(6)-C(5)-C(10)	105.60(11)
C(4)-C(5)-C(11)	113.19(12)
C(6)-C(5)-C(11)	101.81(11)
C(10)-C(5)-C(11)	102.98(10)
C(5)-C(6)-C(7)	103.59(12)
C(8)-C(7)-C(6)	102.69(12)
C(7)-C(8)-C(9)	107.17(13)
C(7)-C(8)-C(11)	102.92(12)
C(9)-C(8)-C(11)	102.57(12)
C(8)-C(9)-C(10)	103.89(12)
O(4)-C(10)-C(5)	113.89(12)
O(4)-C(10)-C(9)	109.76(12)
C(5)-C(10)-C(9)	102.41(11)
C(13)-C(11)-C(12)	107.18(12)
C(13)-C(11)-C(8)	113.56(12)
C(12)-C(11)-C(8)	113.95(13)
C(13)-C(11)-C(5)	114.34(12)
C(12)-C(11)-C(5)	114.82(12)
C(8)-C(11)-C(5)	92.76(11)

Symmetry transformations used to generate equivalent atoms:



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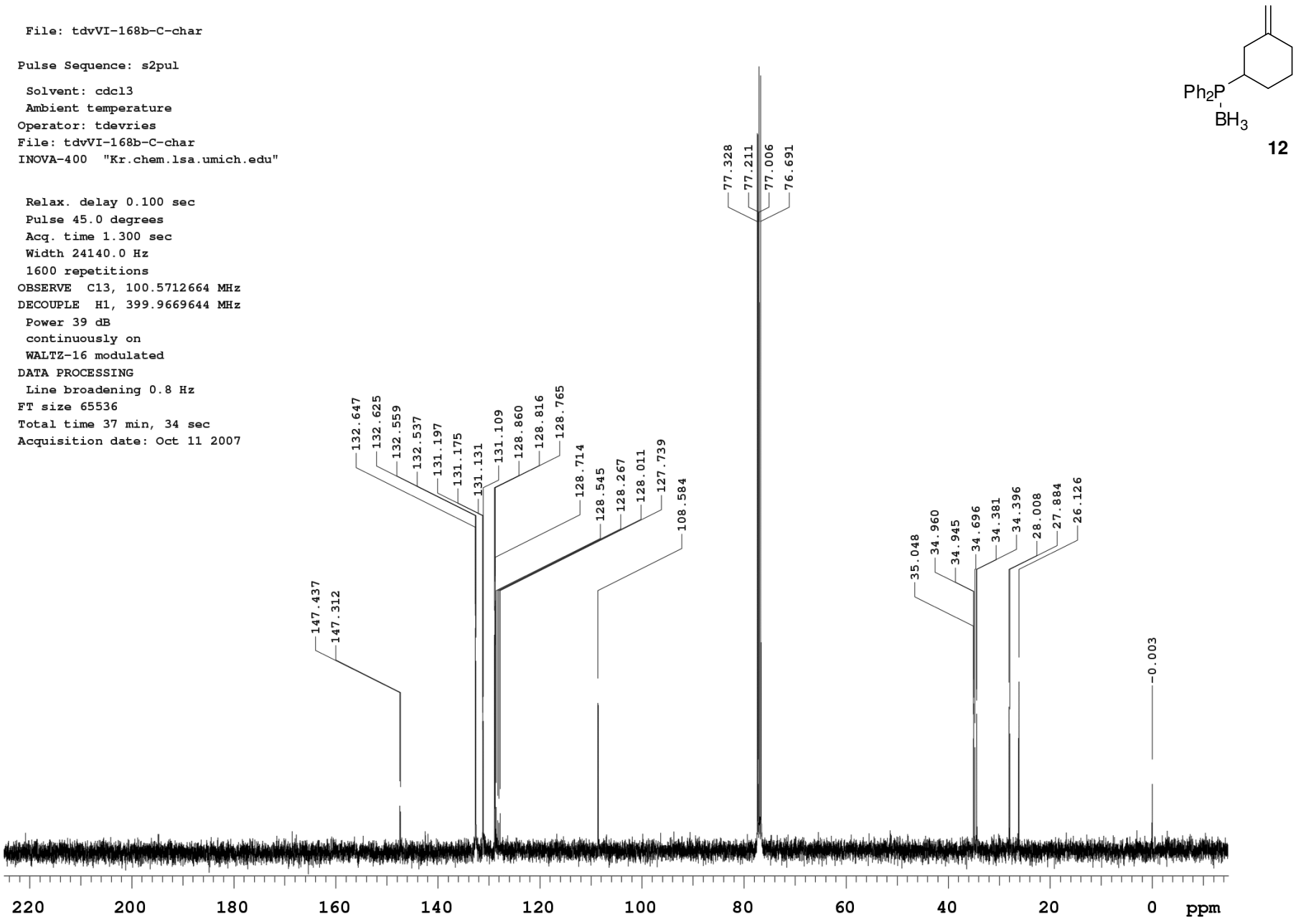
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Power 39 dB
continuously on
WALTZ-16 modulated
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131.109
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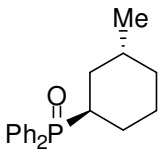

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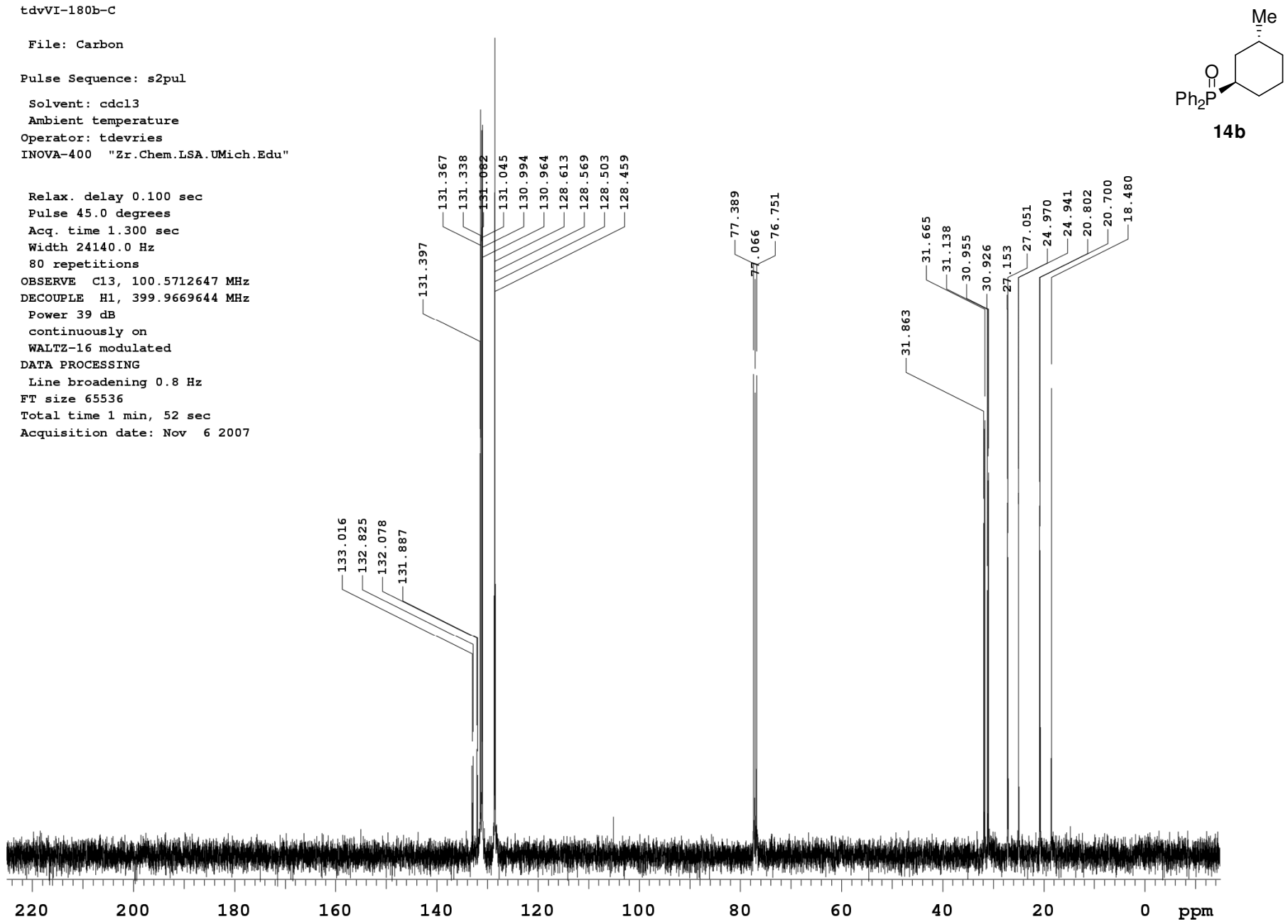
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DECOUPLE H1, 399.9669644 MHz
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continuously on
WALTZ-16 modulated
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128.503
128.459
77.389
77.066
76.751
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31.665
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30.955
30.926
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24.970
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120
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60
40
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0
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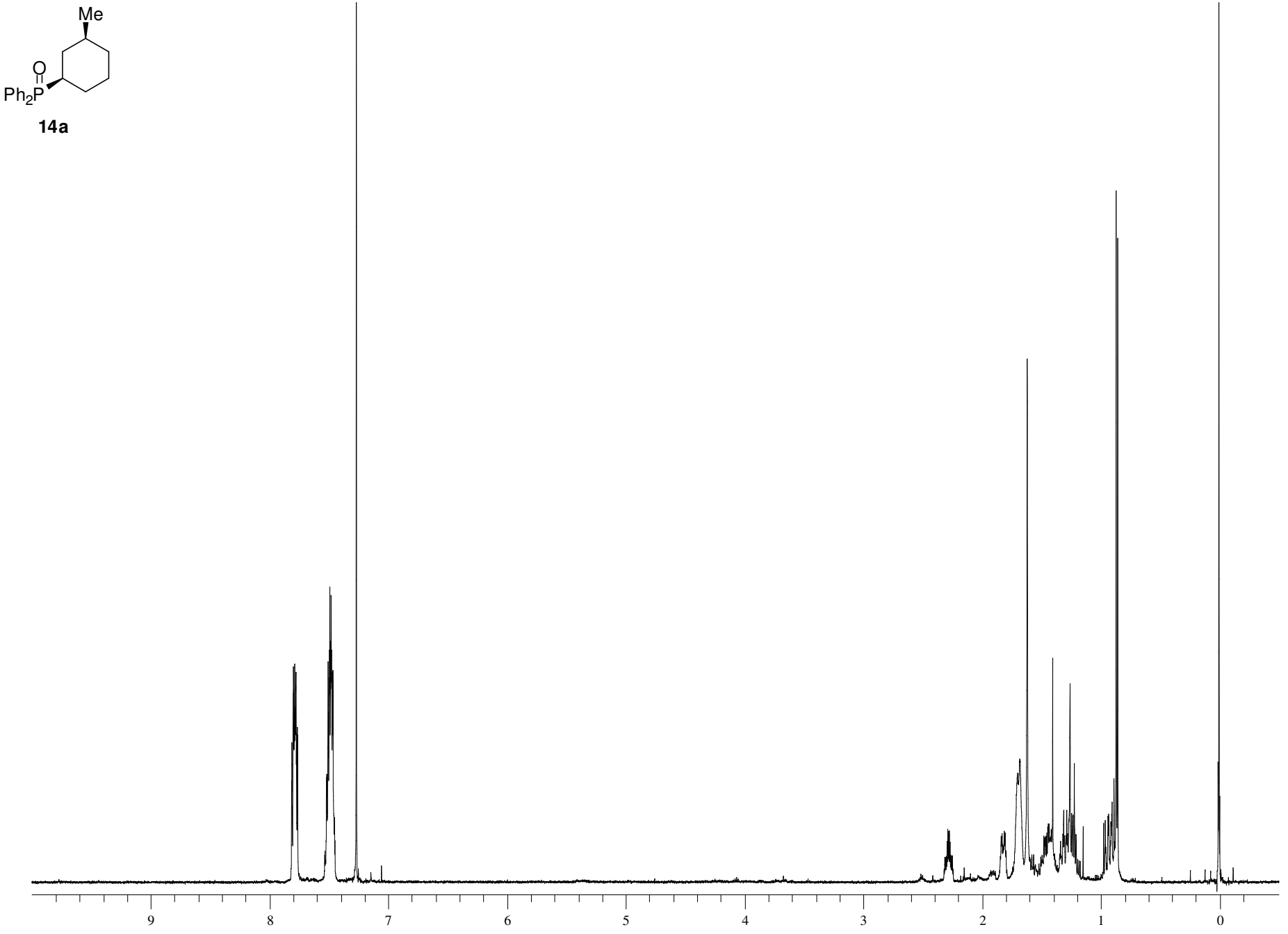
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8
7
6
5
4
3
2
1
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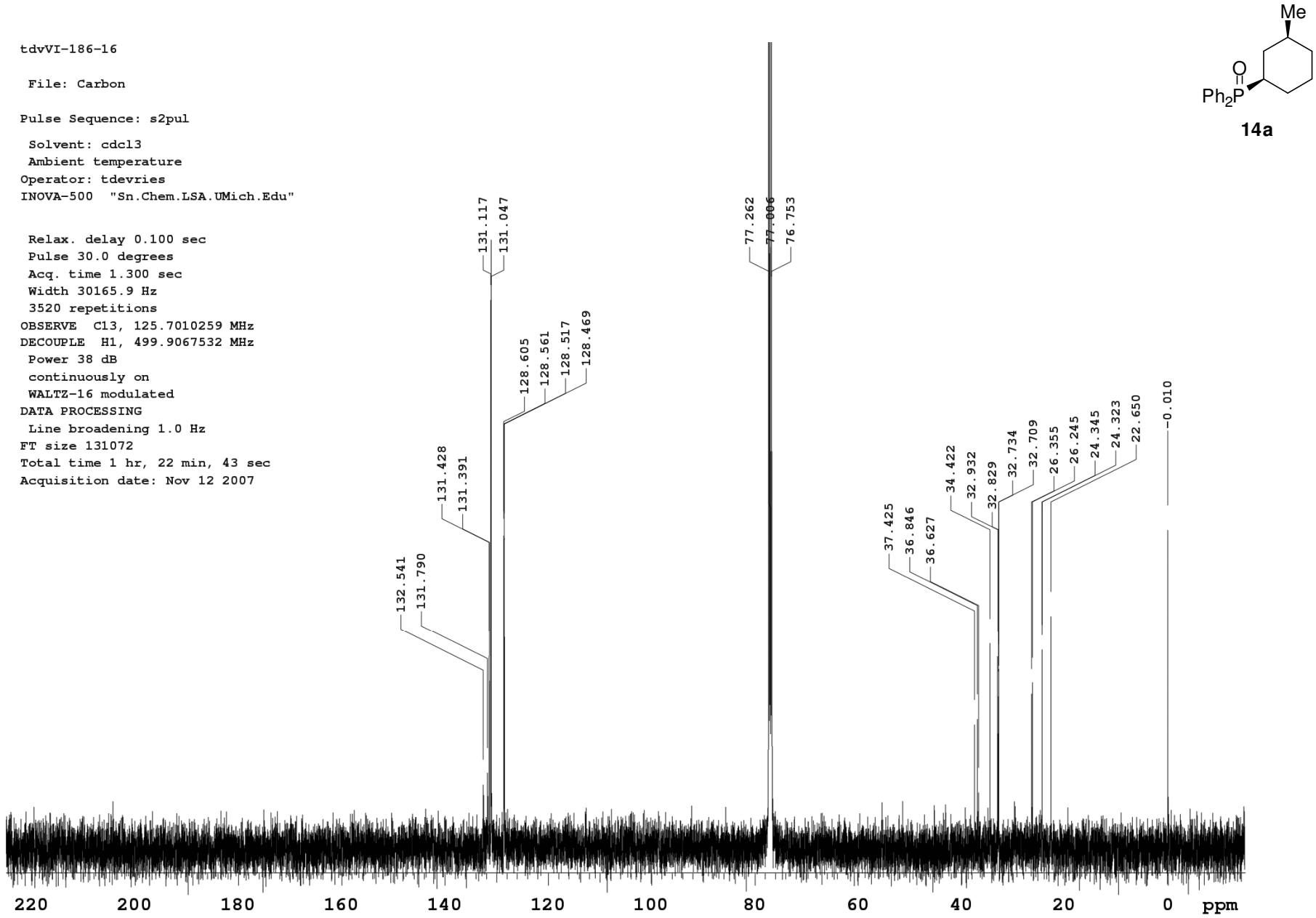
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Operator: tdevries
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Pulse 30.0 degrees
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Width 30165.9 Hz
3520 repetitions
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DECOUPLE H1, 499.9067532 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
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Total time 1 hr, 22 min, 43 sec
Acquisition date: Nov 12 2007
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O
Ph2P
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32.734
32.709
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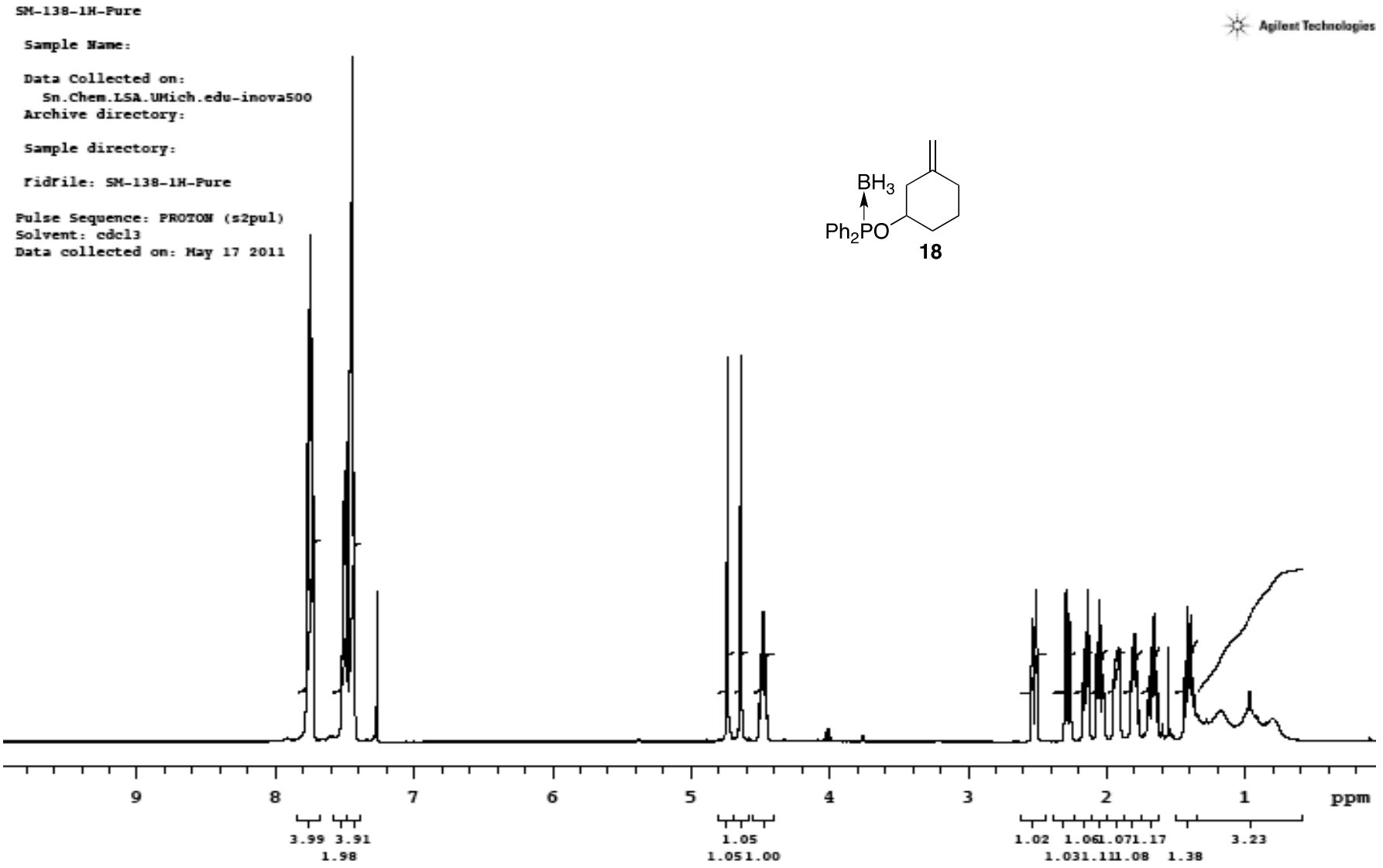
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Agilent Technologies
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8
7
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5
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3
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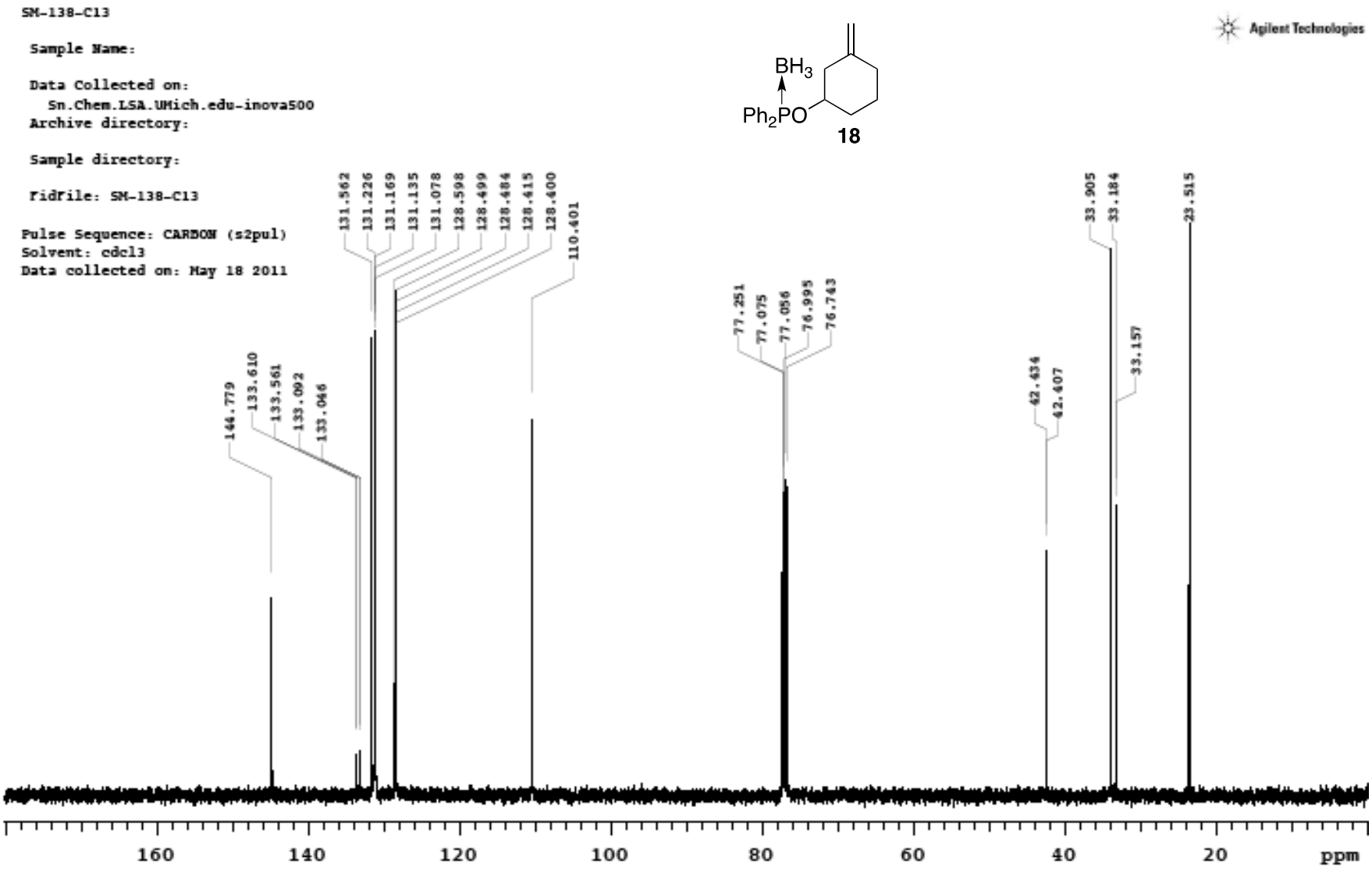
3.23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Agilent Technologies
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76.995
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SM-155-1H-minorisomer-pure

Sample Name:

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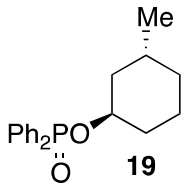
Agilent Technologies



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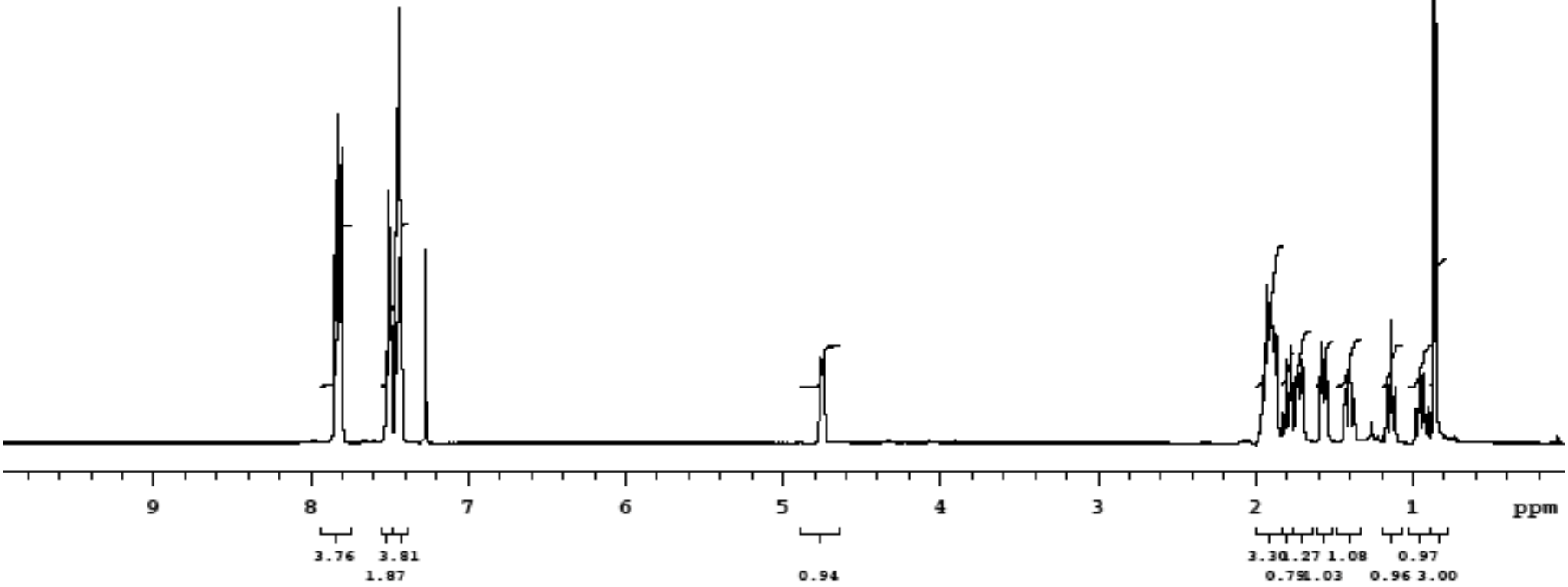

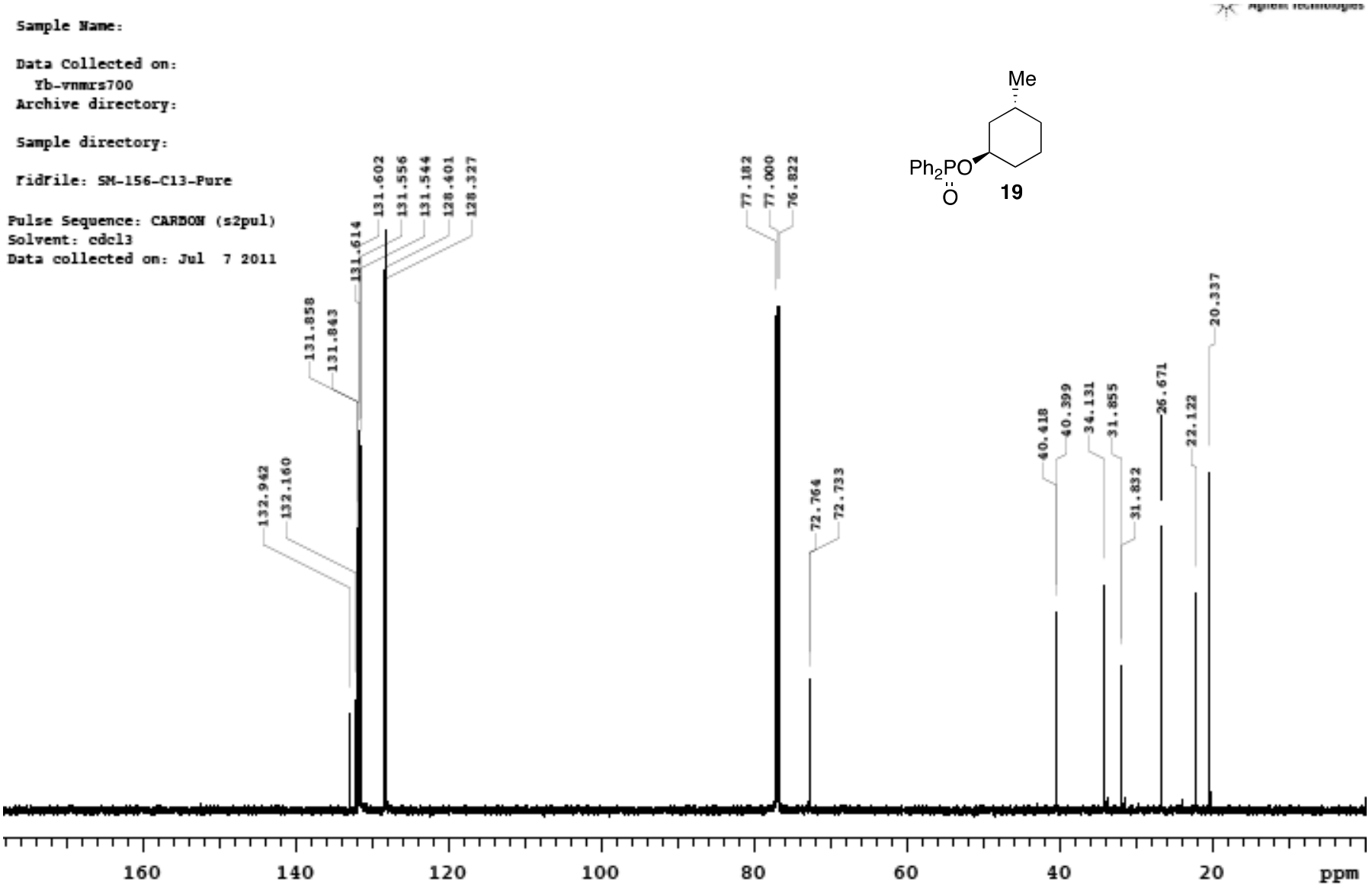
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Solvent: cdcl3
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76.822
72.764
72.733
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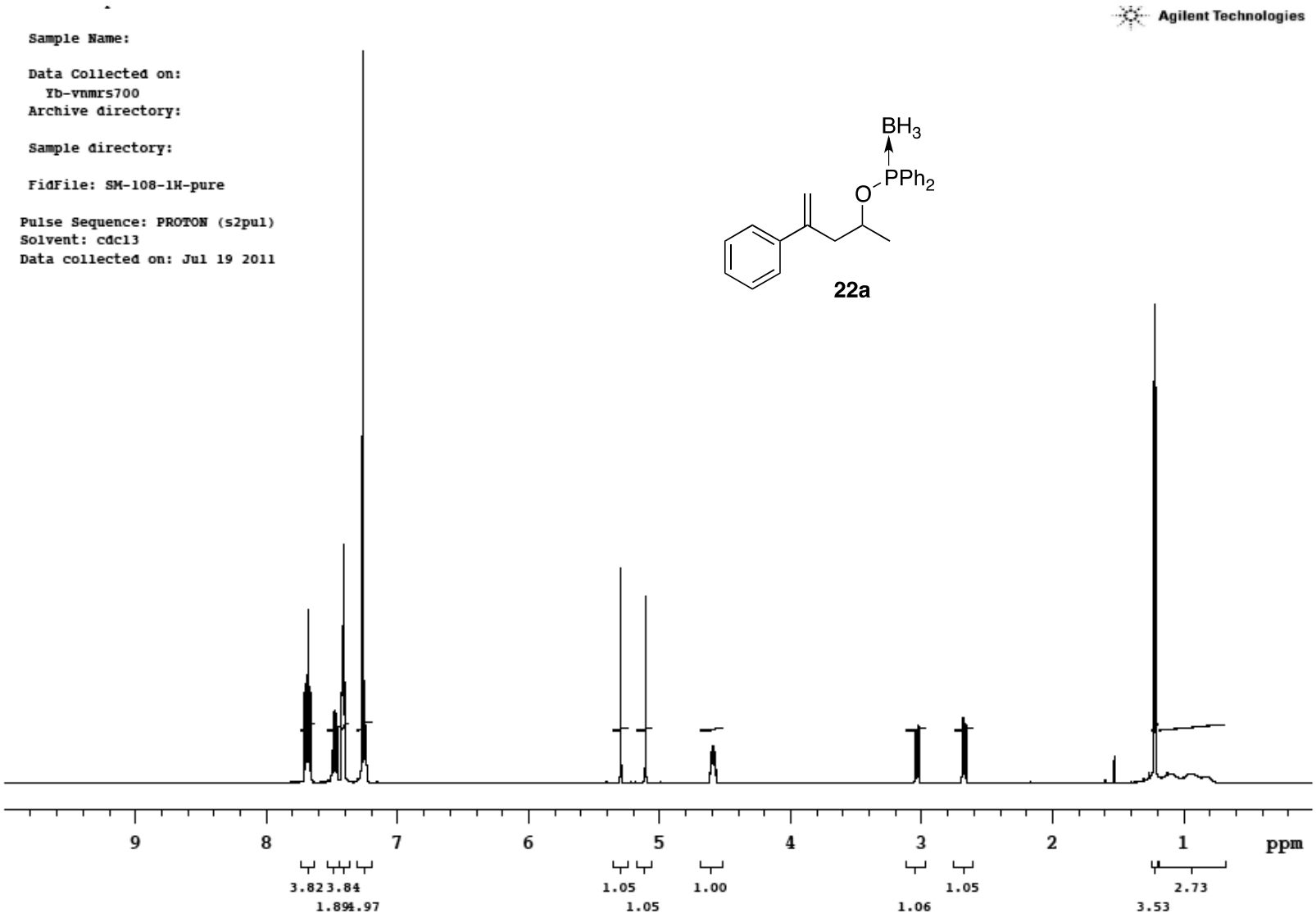
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8
7
6
5
4
3
2
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1.05
1.00
1.06
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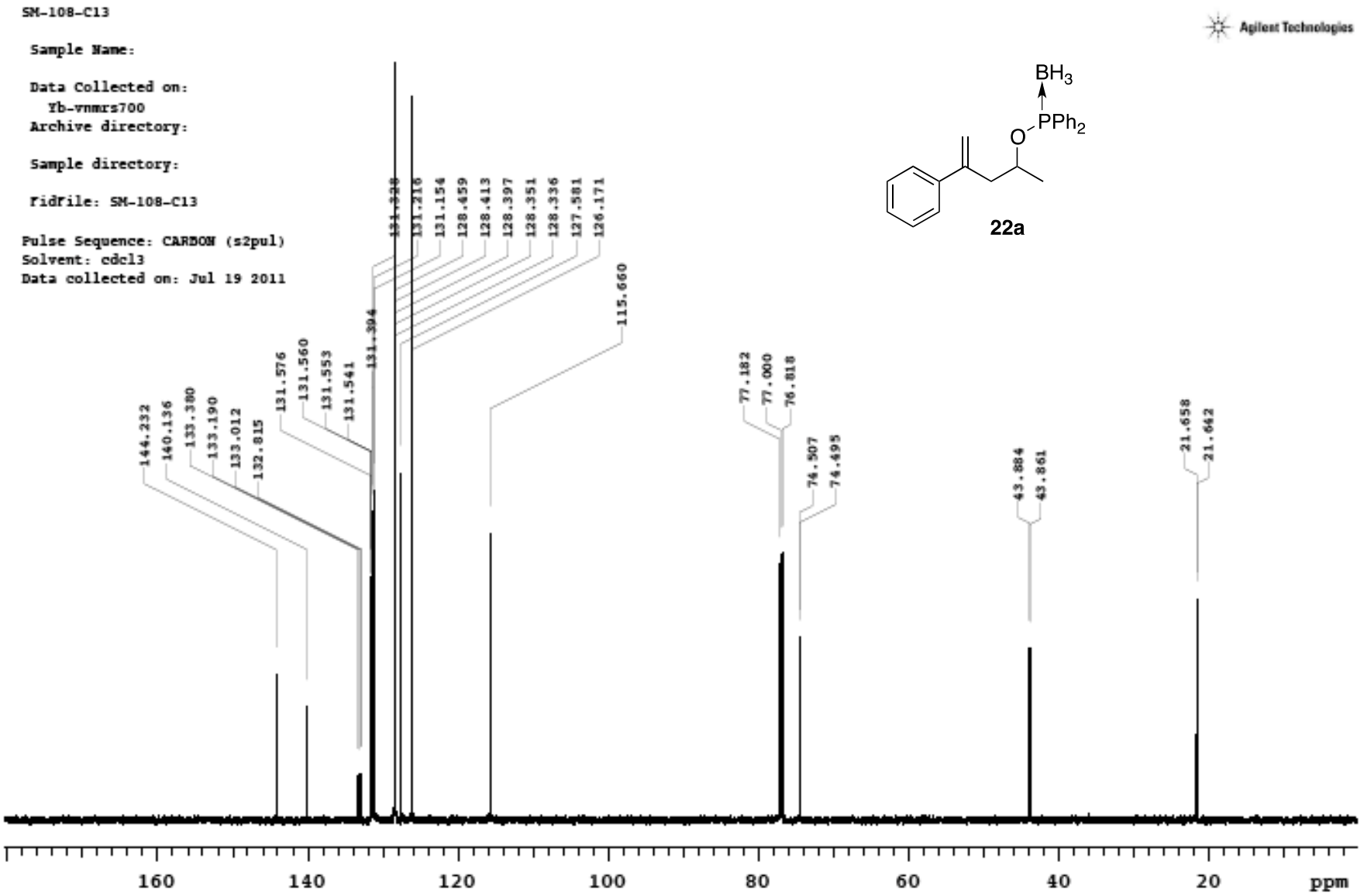
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Agilent Technologies
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115.660
131.394
131.576
131.560
131.553
131.541
144.232
140.136
133.380
133.190
133.012
132.815
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77.000
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80
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40
20
ppm

SM-145-1H-Pure

Sample Name:

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Archive directory:

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FidFile: SM-145-1H-Pure

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Solvent: cdcl3
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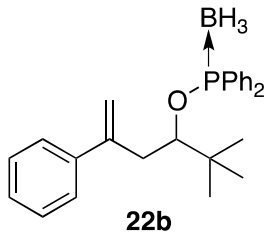
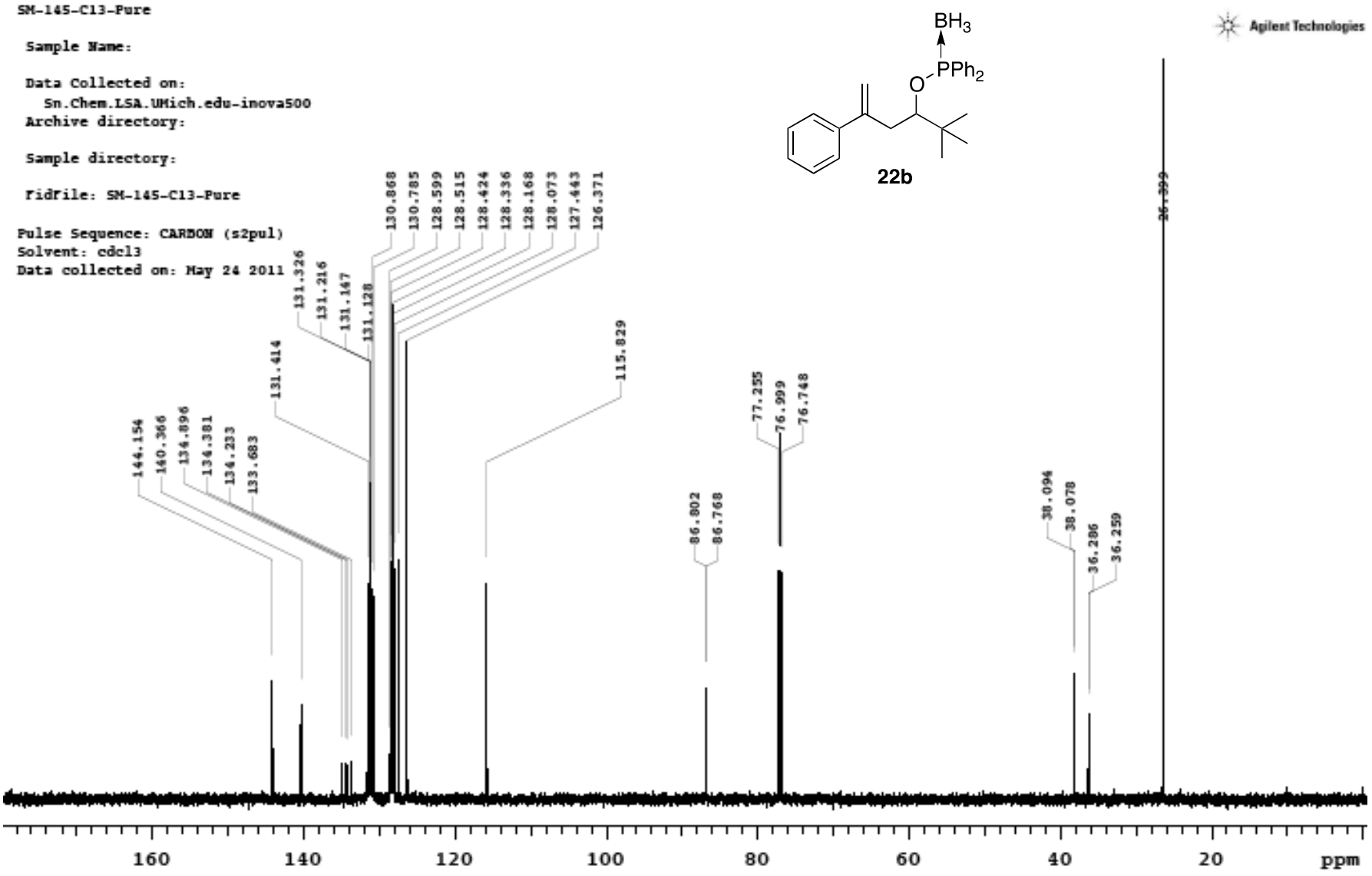


22b


SM-145-C13-Pure
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-145-C13-Pure
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2011
Agilent Technologies
BH3
PPh2
O
22b
144.154
140.366
134.896
134.381
134.233
133.683
131.414
131.326
131.216
131.147
131.128
130.868
130.785
128.599
128.515
128.424
128.336
128.168
128.073
127.443
126.371
115.829
86.802
86.768
77.255
76.999
76.748
38.094
38.078
36.286
36.259
26.399
160
140
120
100
80
60
40
20
ppm

SM-96-1H

Sample Name:

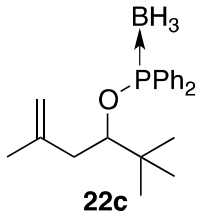
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

Sample directory:

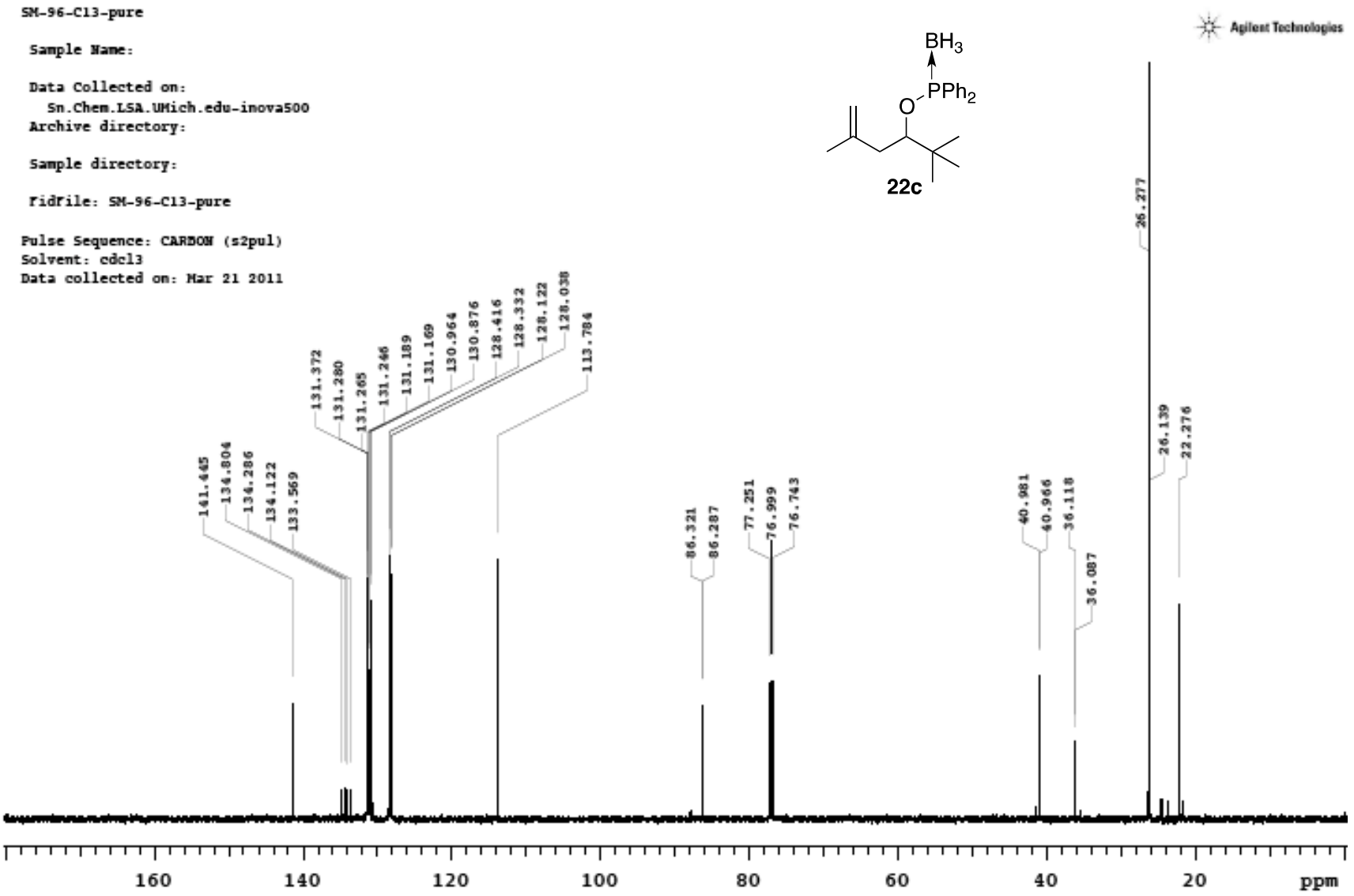
fidfile: SM-96-1H-Pure

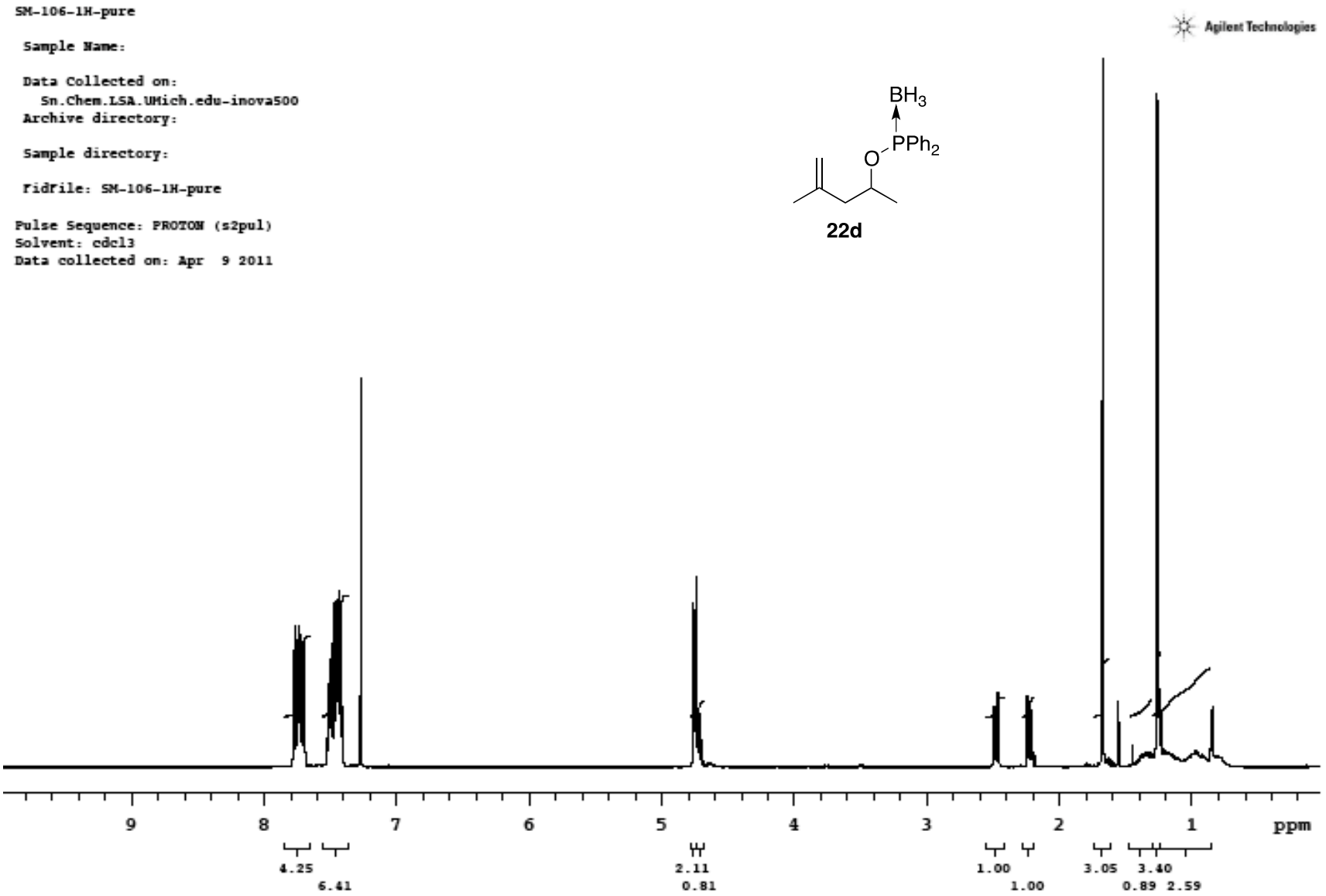
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 21 2011

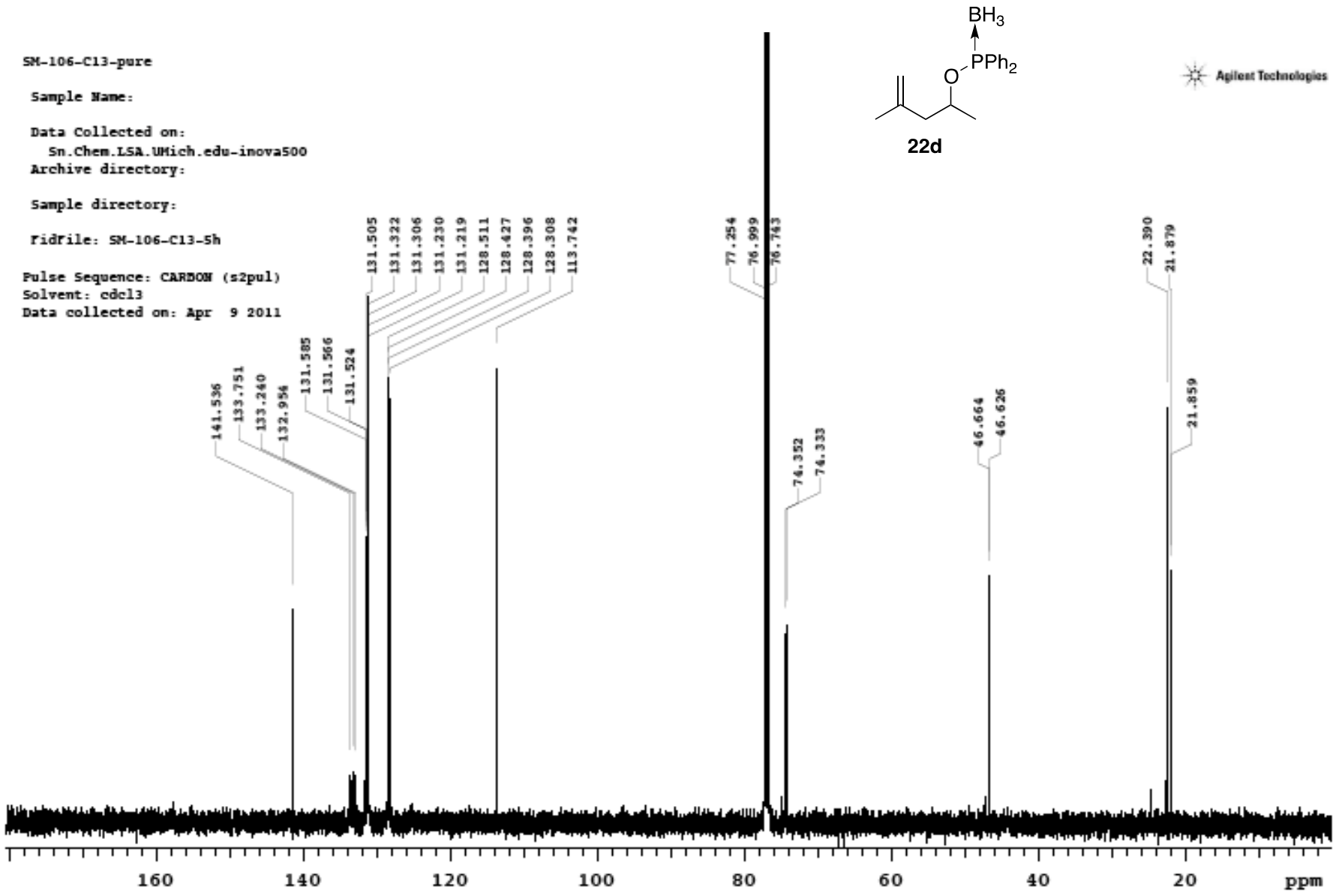
Agilent Technologies

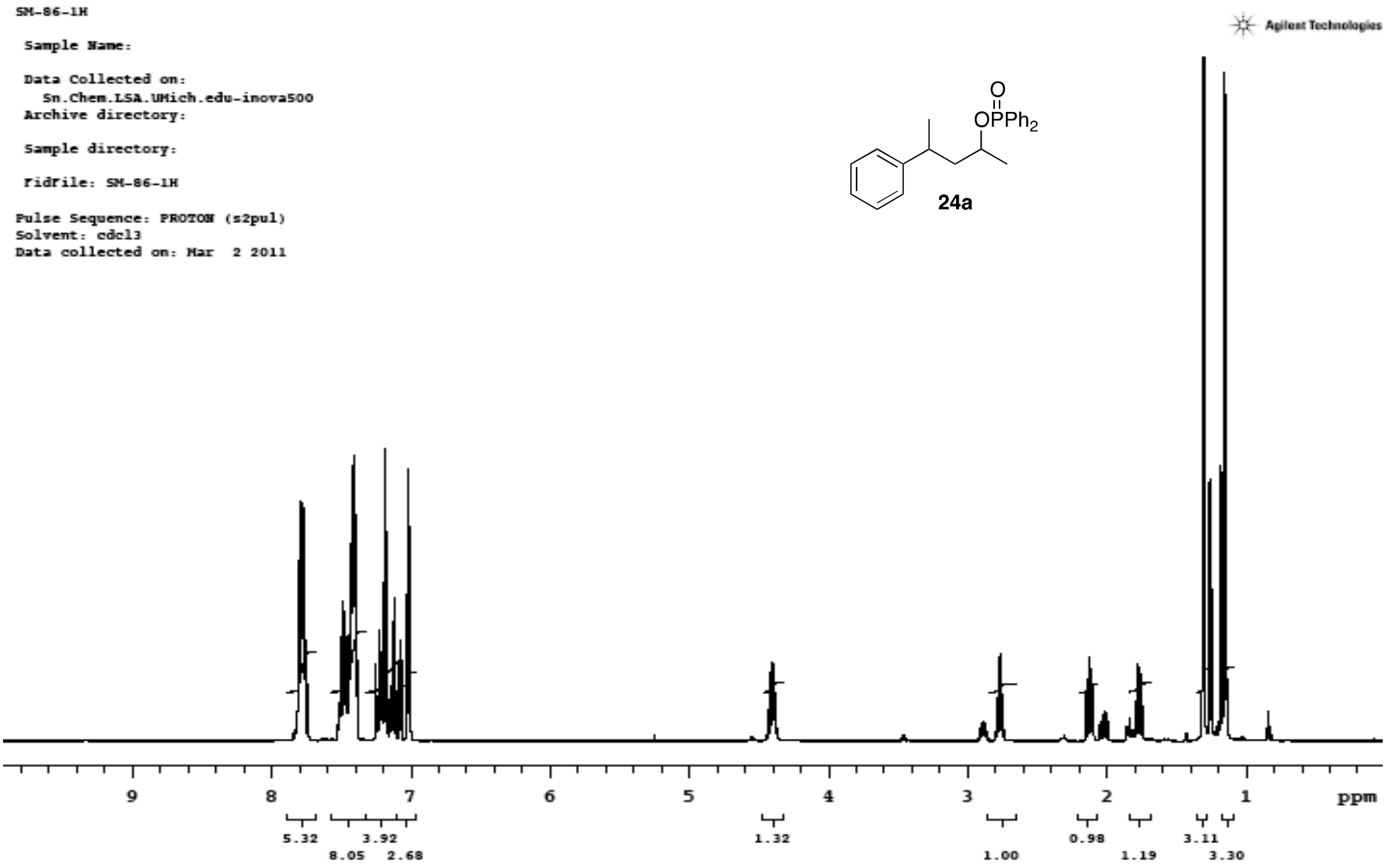


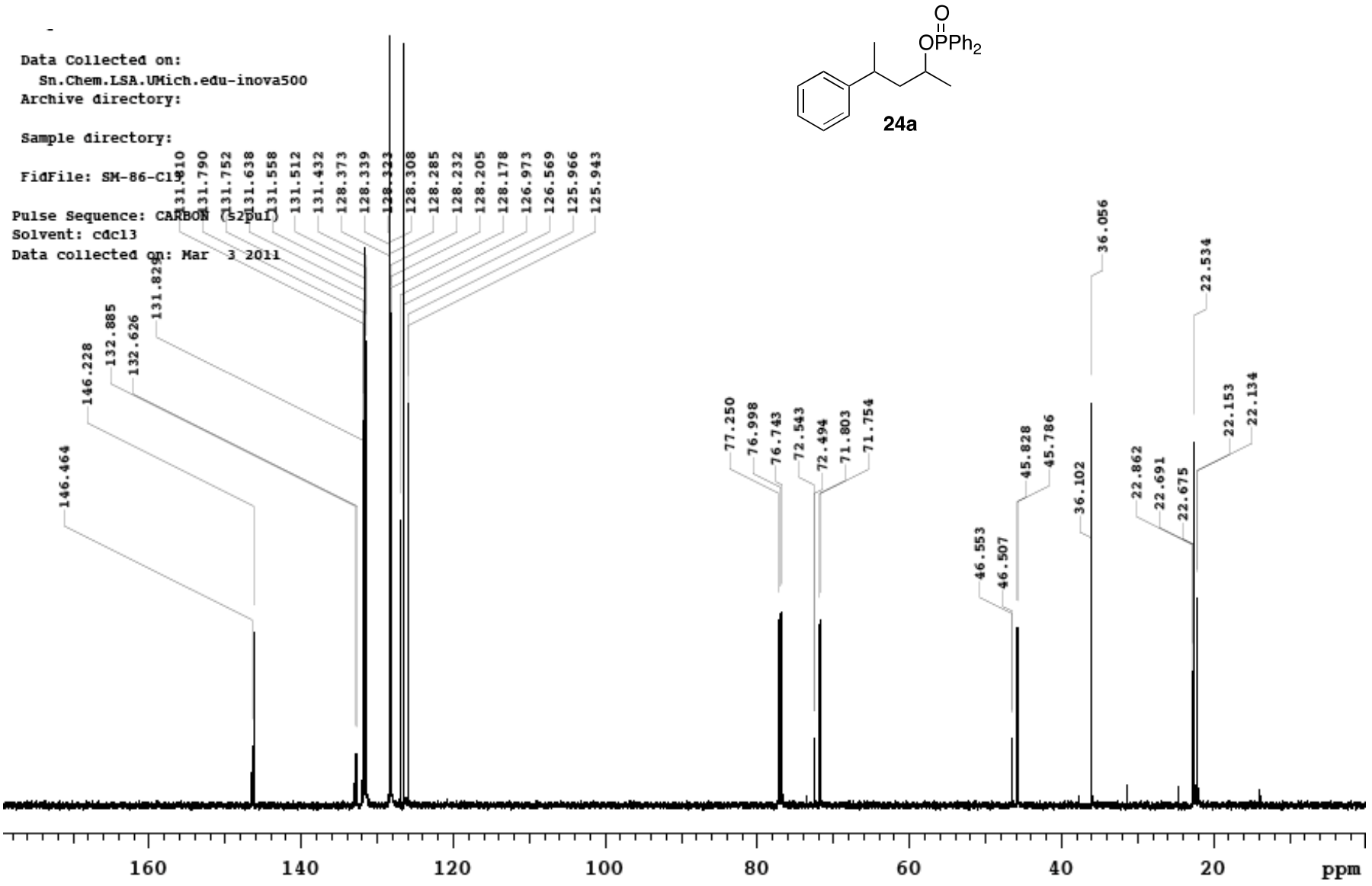
22c


SM-96-C13-pure
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-96-C13-pure
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 21 2011
Agilent Technologies
BH3
PPh2
O
22c
141.445
134.804
134.286
134.122
133.569
131.372
131.280
131.265
131.246
131.189
131.169
130.964
130.876
128.416
128.332
128.122
128.038
113.784
86.321
86.287
77.251
76.999
76.743
40.981
40.966
36.118
36.087
26.277
26.139
22.276
160
140
120
100
80
60
40
20
ppm


SM-106-1H-pure
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-106-1H-pure
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 9 2011
Agilent Technologies
BH3
PPh2
O
22d
9
8
7
6
5
4
3
2
1
ppm
4.25
6.41
2.11
0.81
1.00
1.00
3.05
3.40
0.89
2.59


SM-106-C13-pure
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-106-C13-5h
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 9 2011
BH3
PPh2
O
22d
Agilent Technologies
131.505
131.322
131.306
131.230
131.219
128.511
128.427
128.396
128.308
113.742
77.254
76.999
76.743
22.390
21.879
21.859
141.536
133.751
133.240
132.954
131.585
131.566
131.524
74.352
74.333
46.664
46.626
160
140
120
100
80
60
40
20
ppm


SM-86-1H
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-86-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 2 2011
Agilent Technologies
O
OPPh2
24a
9
8
7
6
5
4
3
2
1
ppm
5.32
3.92
8.05
2.68
1.32
1.00
0.98
1.19
3.11
3.30


Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: SM-86-C13
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 3 2011
O
OPPh2
24a
131.810
131.790
131.752
131.638
131.558
131.512
131.432
128.373
128.339
128.323
128.308
128.285
128.232
128.205
128.178
126.973
126.569
125.966
125.943
131.829
132.885
132.626
146.228
146.464
77.250
76.998
76.743
72.543
72.494
71.803
71.754
46.553
46.507
45.828
45.786
36.102
36.056
22.862
22.691
22.675
22.534
22.153
22.134
160
140
120
100
80
60
40
20
ppm

SM-147-1H-Upper-diastereomer-major

Sample Name:

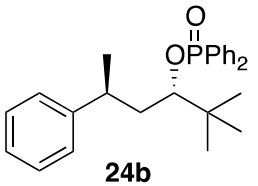
Data Collected on:
Yb-vnmrs700
Archive directory:

Sample directory:

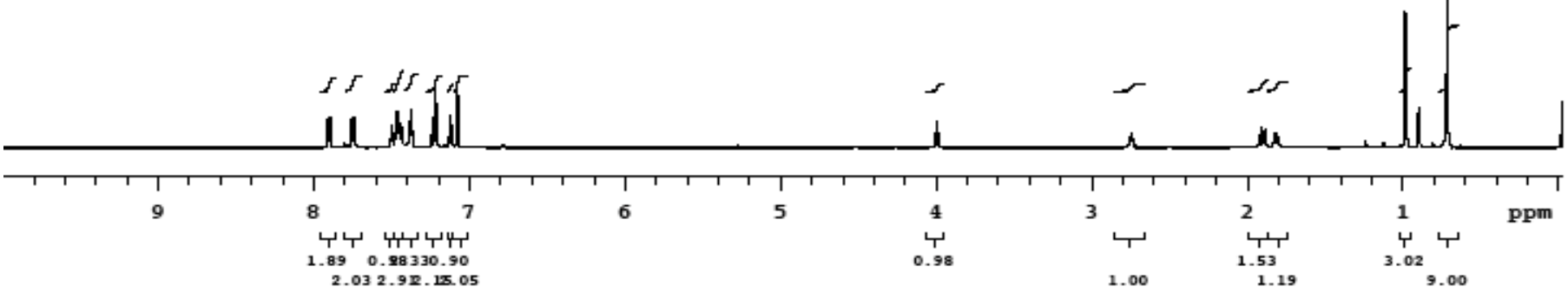
FidFile: SM-147-1H-Upper-diastereomer-major

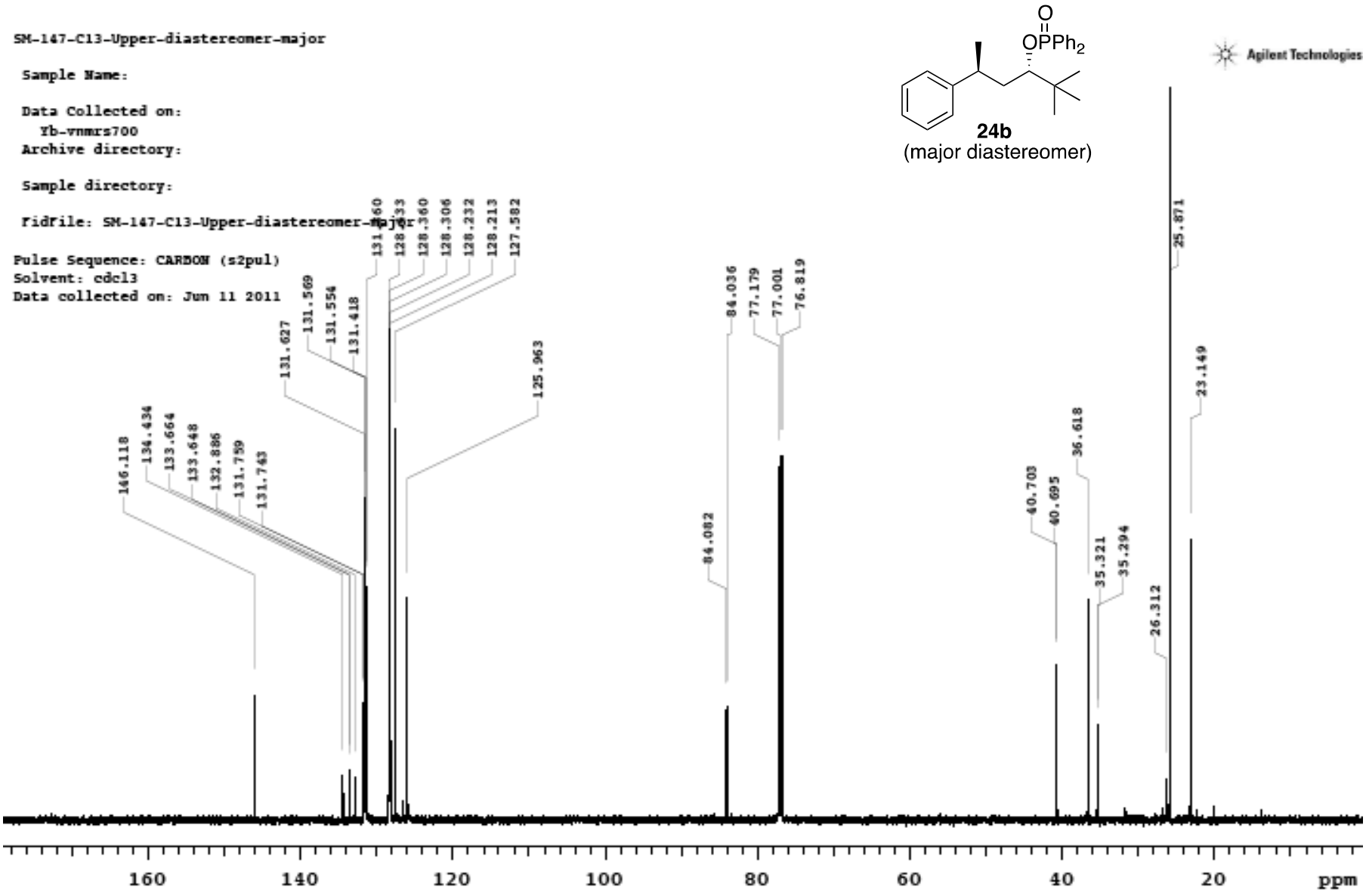
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

Agilent Technologies



24b
(major diastereomer)




SM-147-C13-Upper-diastereomer-major
Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
fidfile: SM-147-C13-Upper-diastereomer-major
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011
O
OPPh2
24b
(major diastereomer)
Agilent Technologies
146.118
134.434
133.664
133.648
132.886
131.759
131.743
131.627
131.569
131.554
131.418
131.160
128.433
128.360
128.306
128.232
128.213
127.582
125.963
84.082
84.036
77.179
77.001
76.819
40.703
40.695
36.618
35.321
35.294
26.312
25.871
23.149
160
140
120
100
80
60
40
20
ppm

SM-147-1H-Lower-diastereomer-minor

Sample Name:

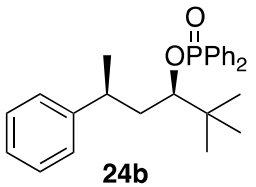
Data Collected on:
Yb-vnmrs700
Archive directory:

Sample directory:

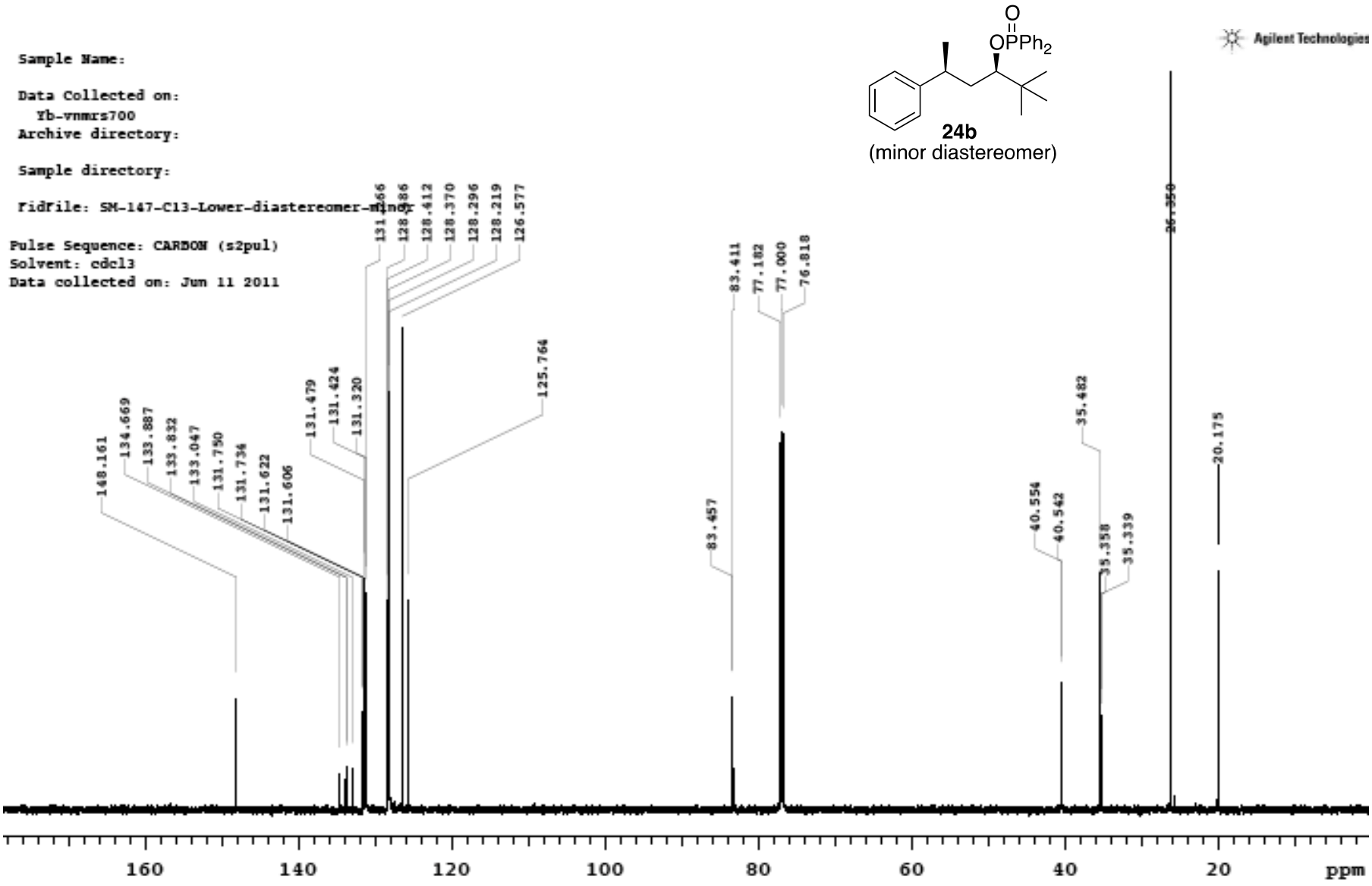
fidfile: SM-147-1H-Lower-diastereomer-minor

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011

Agilent Technologies



24b
(minor diastereomer)


Sample Name:
Data Collected on:
Yb-vnmrs700
Archive directory:
Sample directory:
fidfile: SM-147-C13-Lower-diastereomer-minor
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 11 2011
Agilent Technologies
O
OPPh2
24b
(minor diastereomer)
148.161
134.669
133.887
133.832
133.047
131.750
131.734
131.622
131.606
131.479
131.424
131.320
131.266
128.486
128.412
128.370
128.296
128.219
126.577
125.764
83.457
83.411
77.182
77.000
76.818
40.554
40.542
35.482
35.358
35.339
26.350
20.175
160
140
120
100
80
60
40
20
ppm

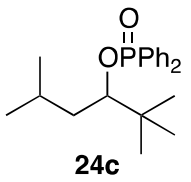
Sample Name:

Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

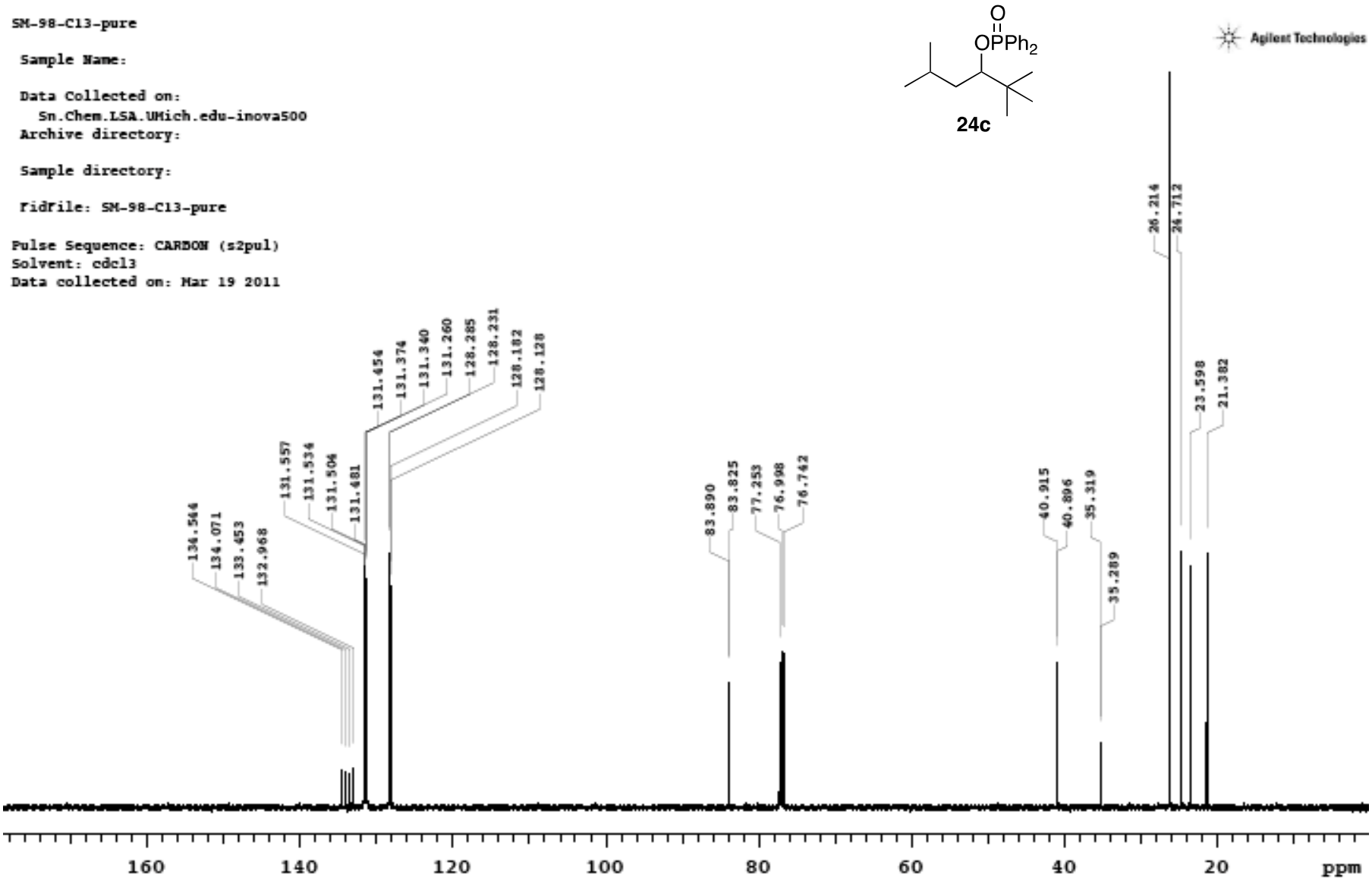
Sample directory:

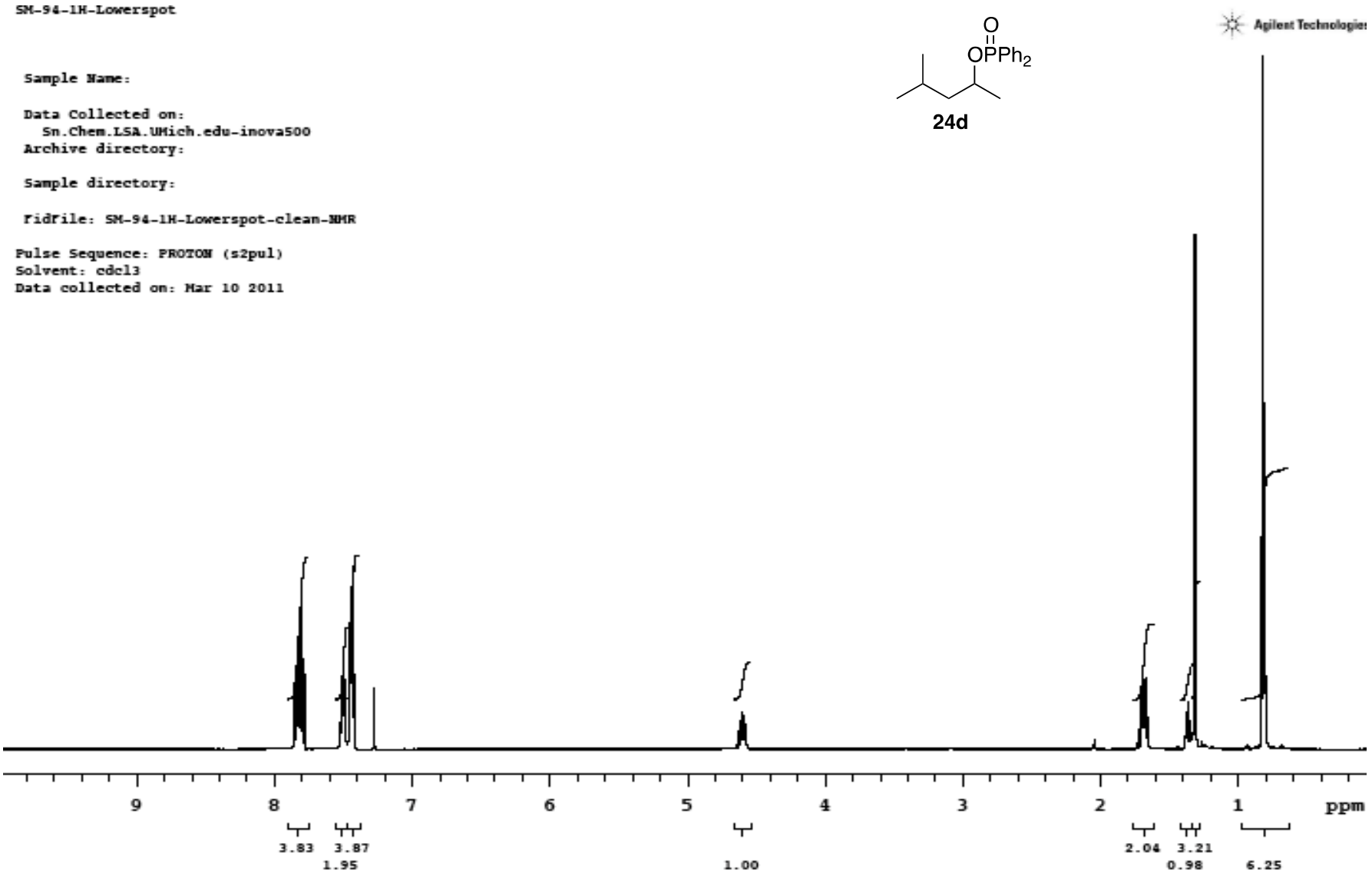
FidFile: SM-98-1H-pure

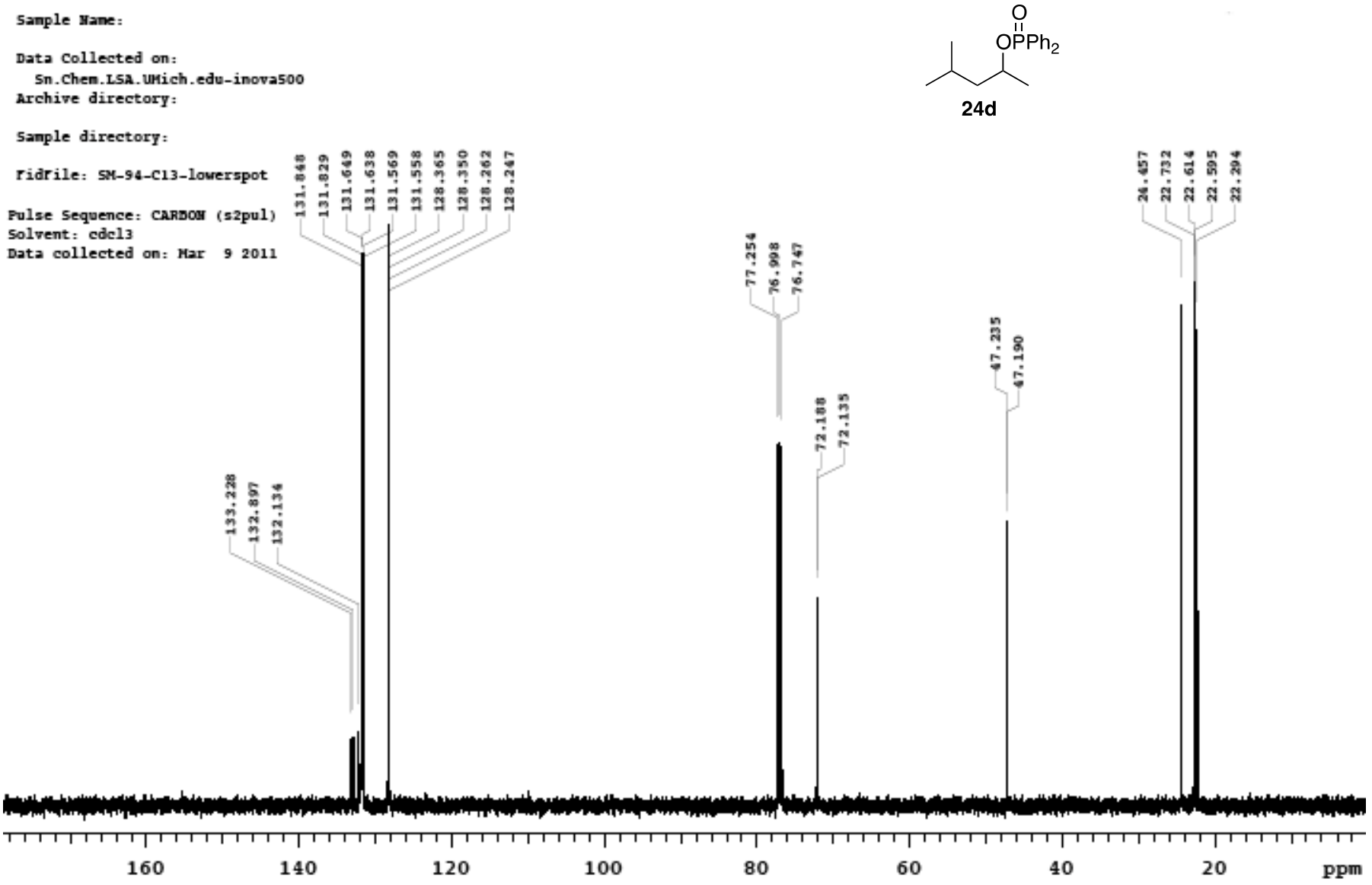
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2011

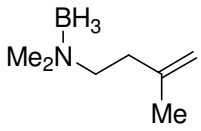


24c

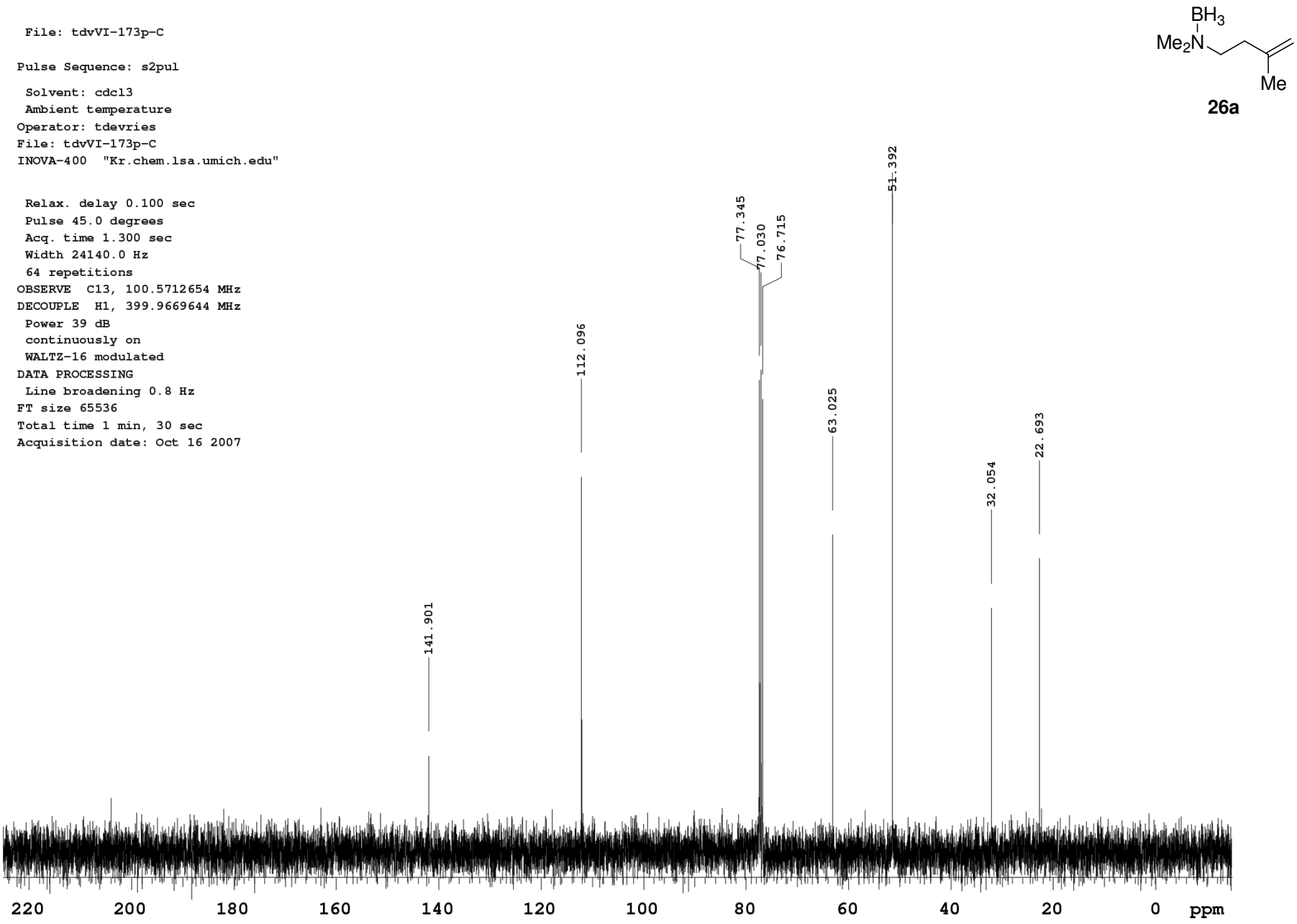

SM-98-C13-pure
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-98-C13-pure
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 19 2011
O
OPPh2
24c
Agilent Technologies
134.544
134.071
133.453
132.968
131.557
131.534
131.504
131.481
131.454
131.374
131.340
131.260
128.285
128.231
128.182
128.128
83.890
83.825
77.253
76.998
76.742
40.915
40.896
35.319
35.289
26.214
24.712
23.598
21.382
160
140
120
100
80
60
40
20
ppm


SM-94-1H-Lowerspot
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-94-1H-Lowerspot-clean-NMR
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2011
Agilent Technologies
O
OPPh2
24d
9
8
7
6
5
4
3
2
1
ppm
3.83
3.87
1.95
1.00
2.04
3.21
0.98
6.25


Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
fidfile: SM-94-C13-lowerspot
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 9 2011
O
OPPh2
24d
131.848
131.829
131.649
131.638
131.569
131.558
128.365
128.350
128.262
128.247
133.228
132.897
132.134
77.254
76.998
76.747
72.188
72.135
47.235
47.190
24.457
22.732
22.614
22.595
22.294
160
140
120
100
80
60
40
20
ppm

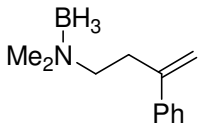


26a

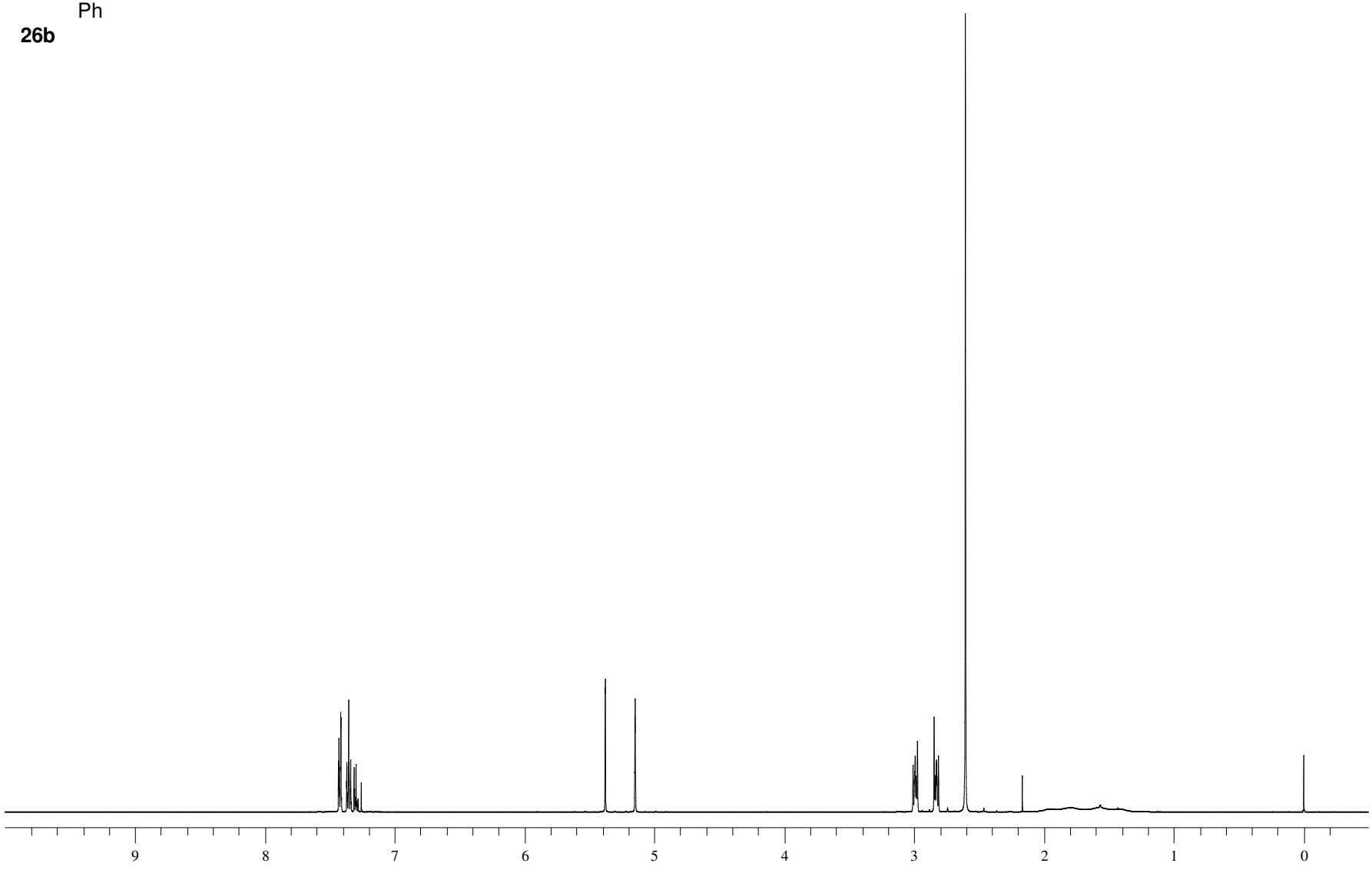

File: tdvVI-173p-C
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: tdevries
File: tdvVI-173p-C
INOVA-400 "Kr.chem.lsa.umich.edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
64 repetitions
OBSERVE C13, 100.5712654 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 1 min, 30 sec
Acquisition date: Oct 16 2007
141.901
112.096
77.345
77.030
76.715
63.025
51.392
32.054
22.693
220
200
180
160
140
120
100
80
60
40
20
0
ppm

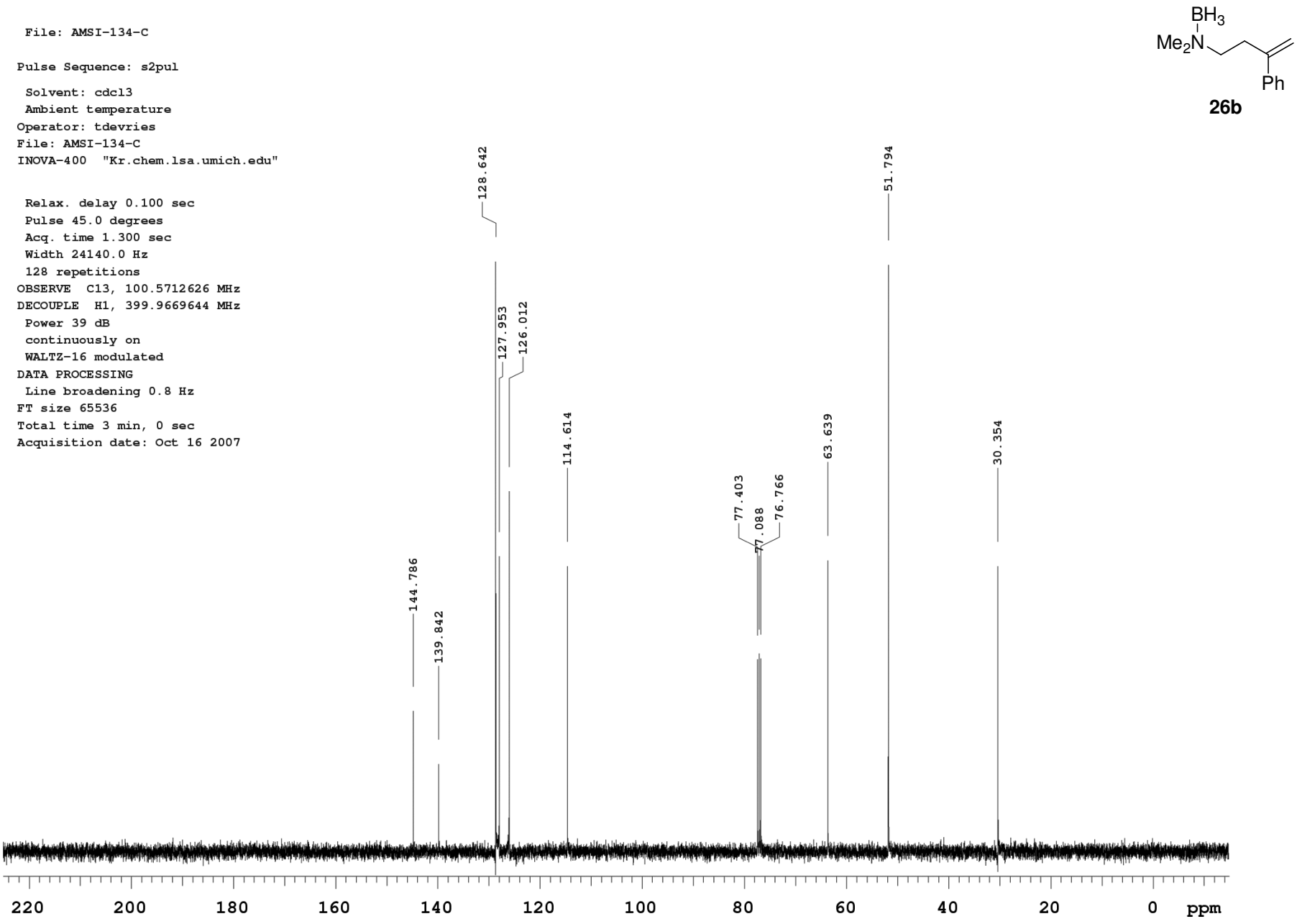
BH3
Me2N
Me

26a



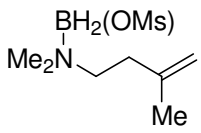
26b



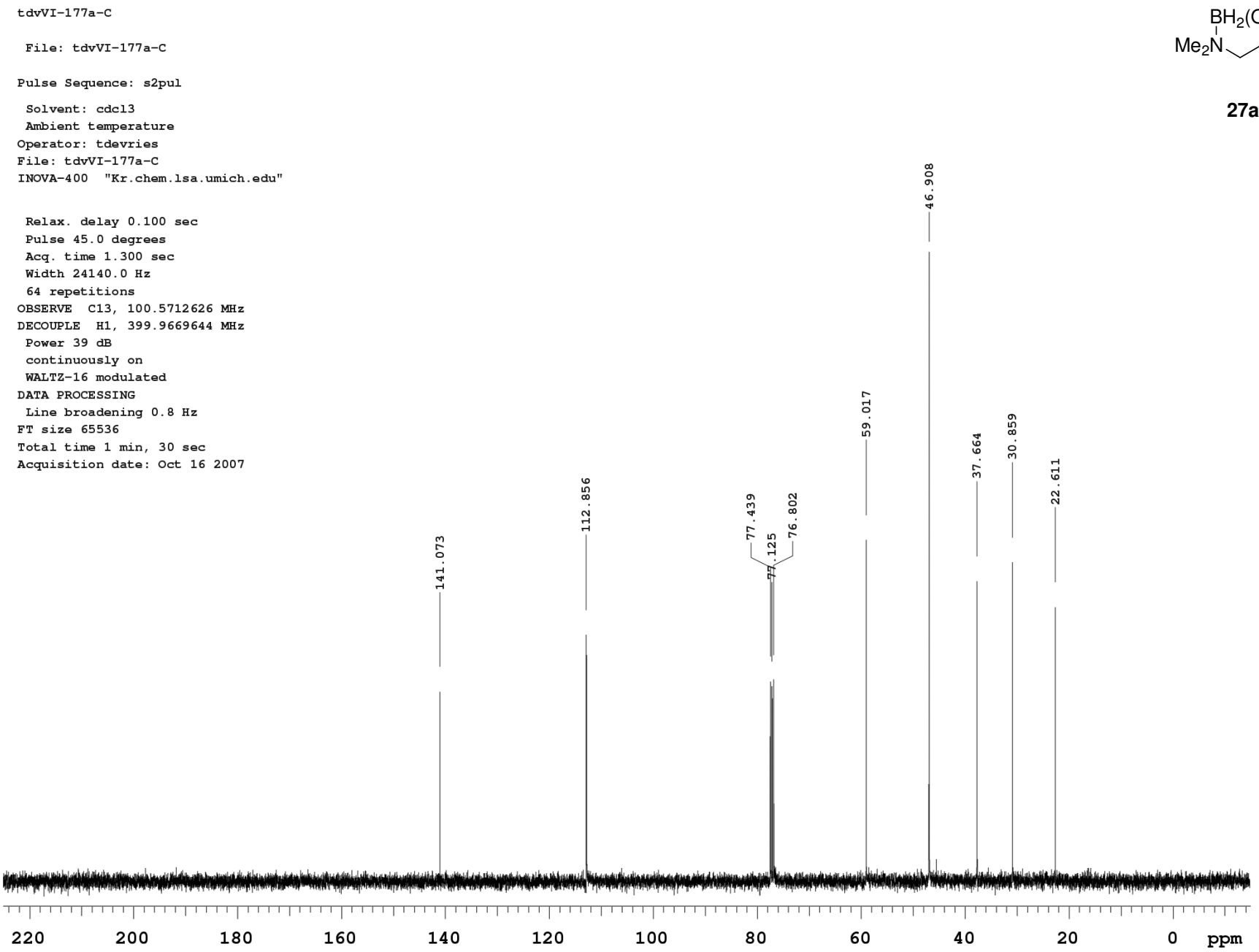

File: AMSI-134-C
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: tdevries
File: AMSI-134-C
INOVA-400 "Kr.chem.lsa.umich.edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
128 repetitions
OBSERVE C13, 100.5712626 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 3 min, 0 sec
Acquisition date: Oct 16 2007
128.642
127.953
126.012
114.614
77.403
77.088
76.766
63.639
51.794
30.354
144.786
139.842
220
200
180
160
140
120
100
80
60
40
20
0
ppm

BH3
Me2N
Ph

26b

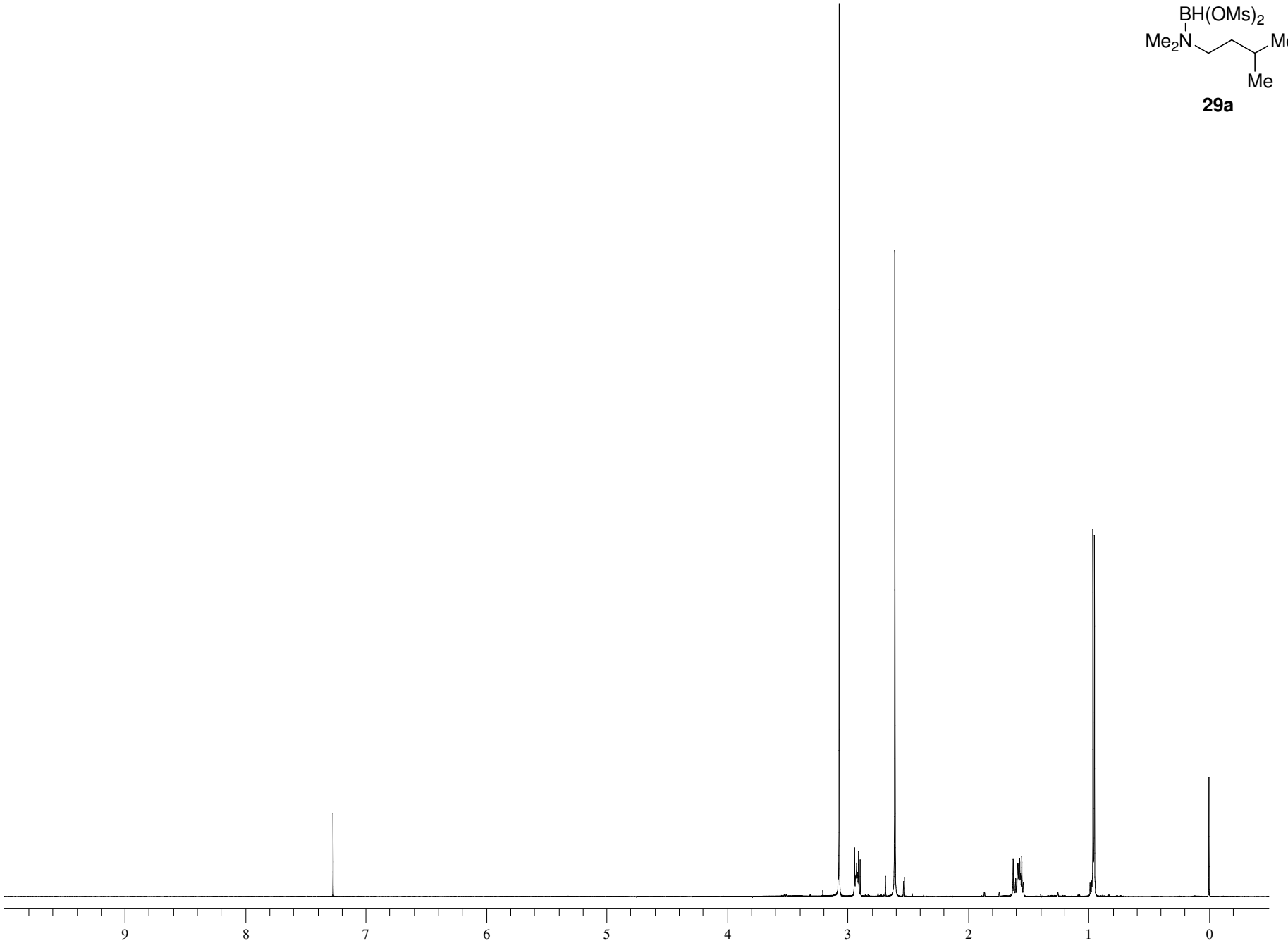


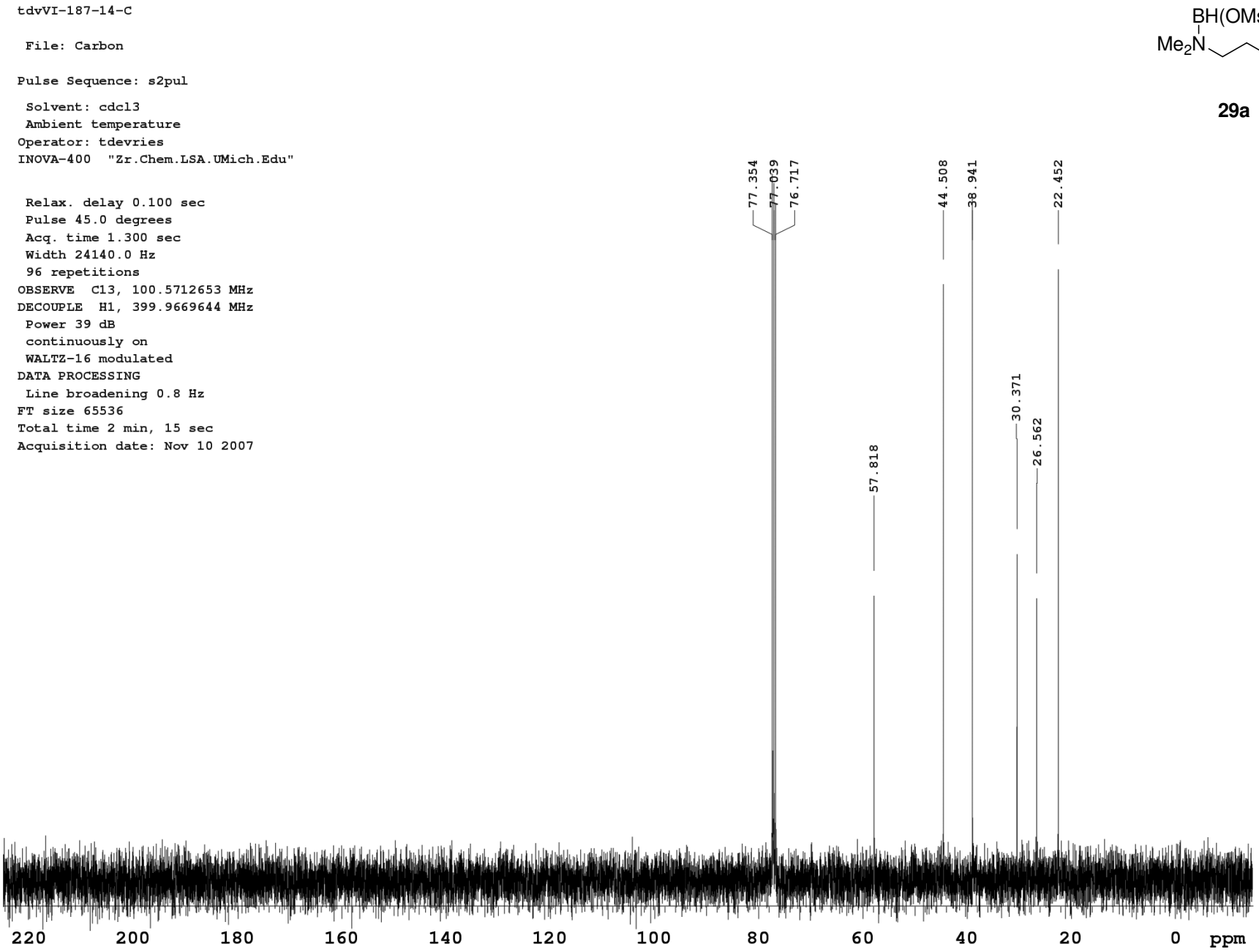
27a



$BH_2(OMs)$
Me_2N
Me

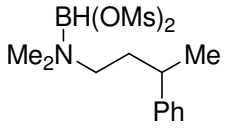
27a


BH(OMs)2
Me2N
Me
Me
29a
9
8
7
6
5
4
3
2
1
0

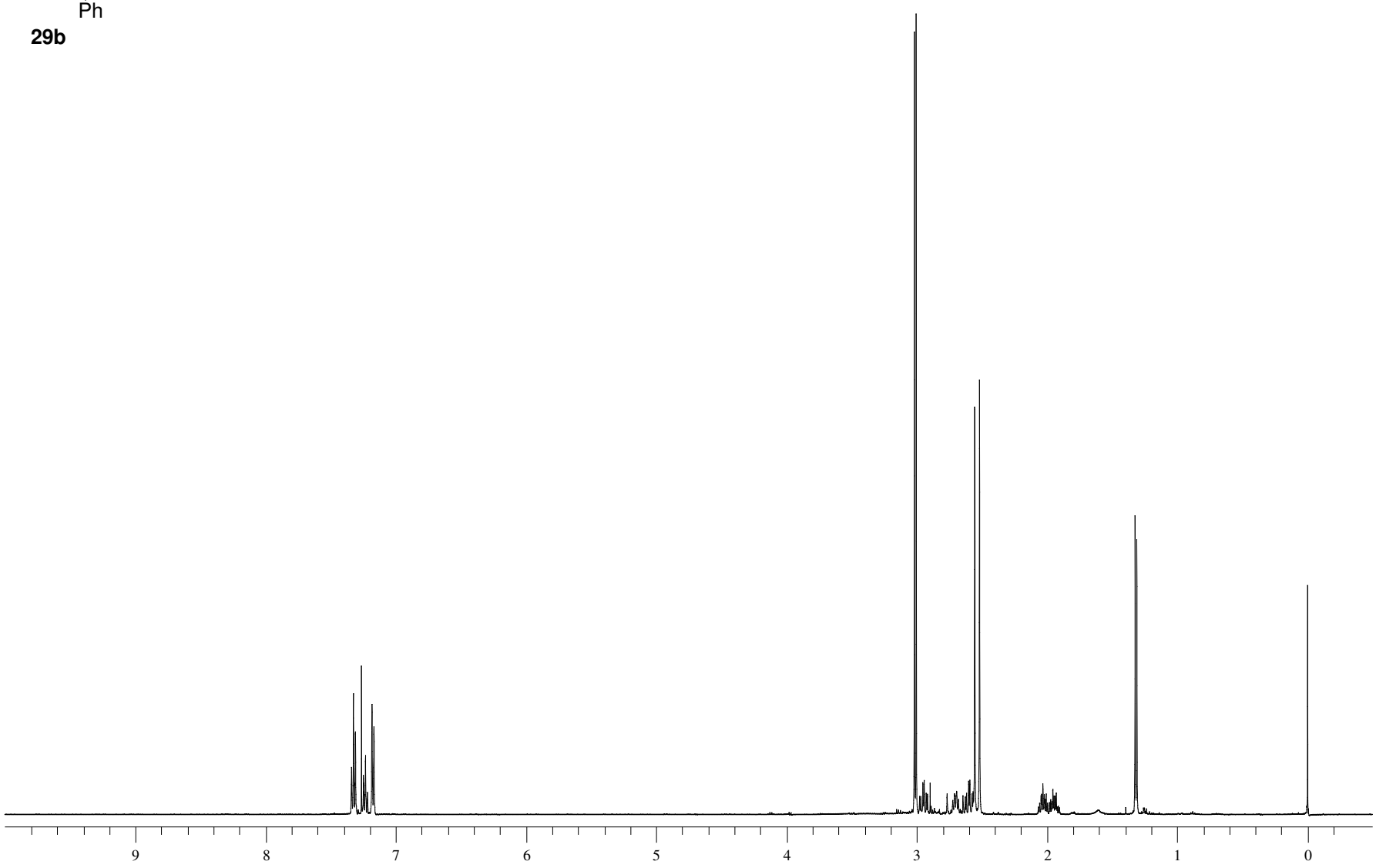

tdvVI-187-14-C
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: tdevries
INOVA-400 "Zr.Chem.LSA.UMich.Edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
96 repetitions
OBSERVE C13, 100.5712653 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 2 min, 15 sec
Acquisition date: Nov 10 2007
77.354
77.039
76.717
44.508
38.941
30.371
26.562
22.452
57.818
220
200
180
160
140
120
100
80
60
40
20
0
ppm

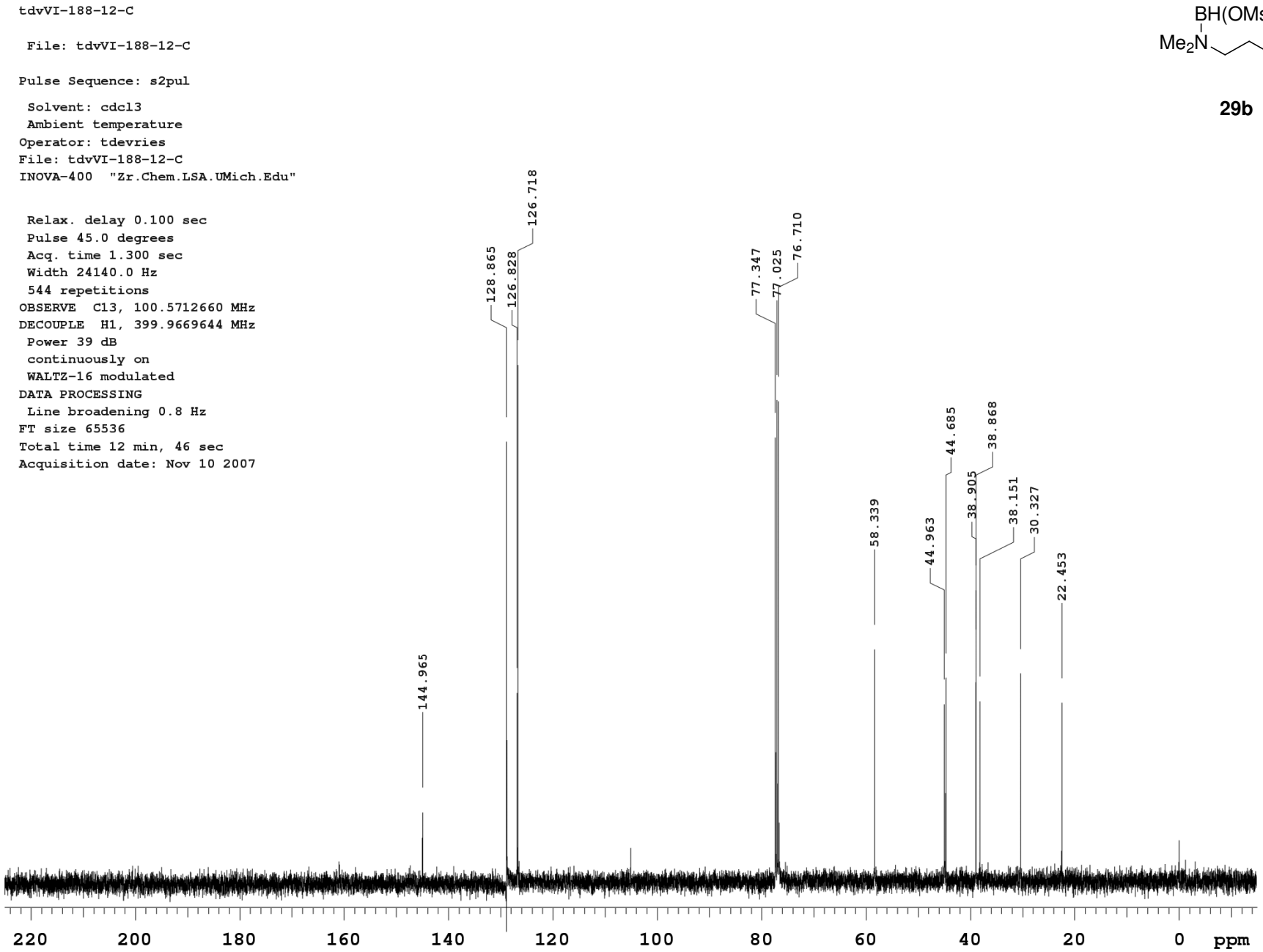
BH(OMs)2
Me2N
Me
Me

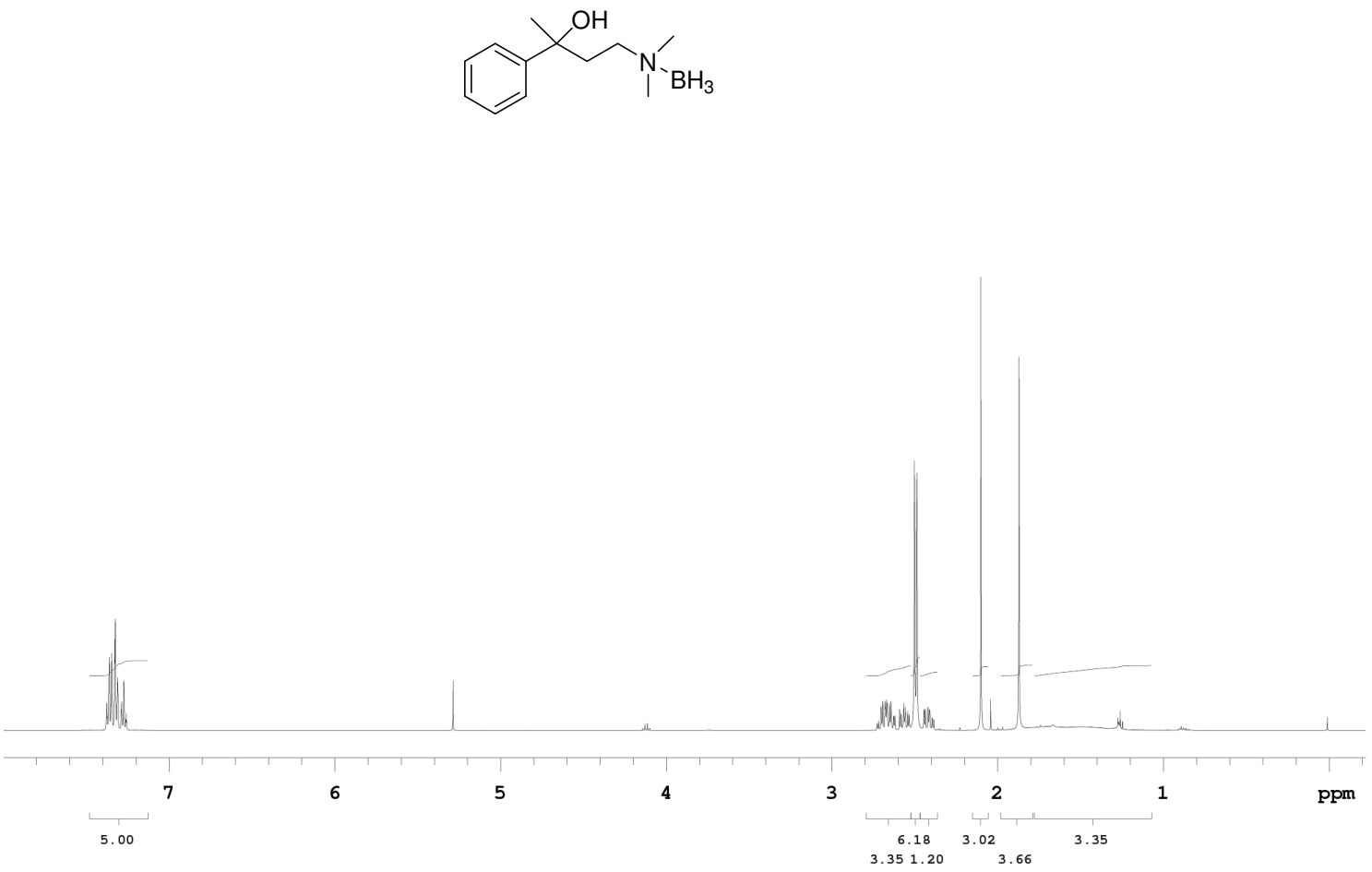
29a

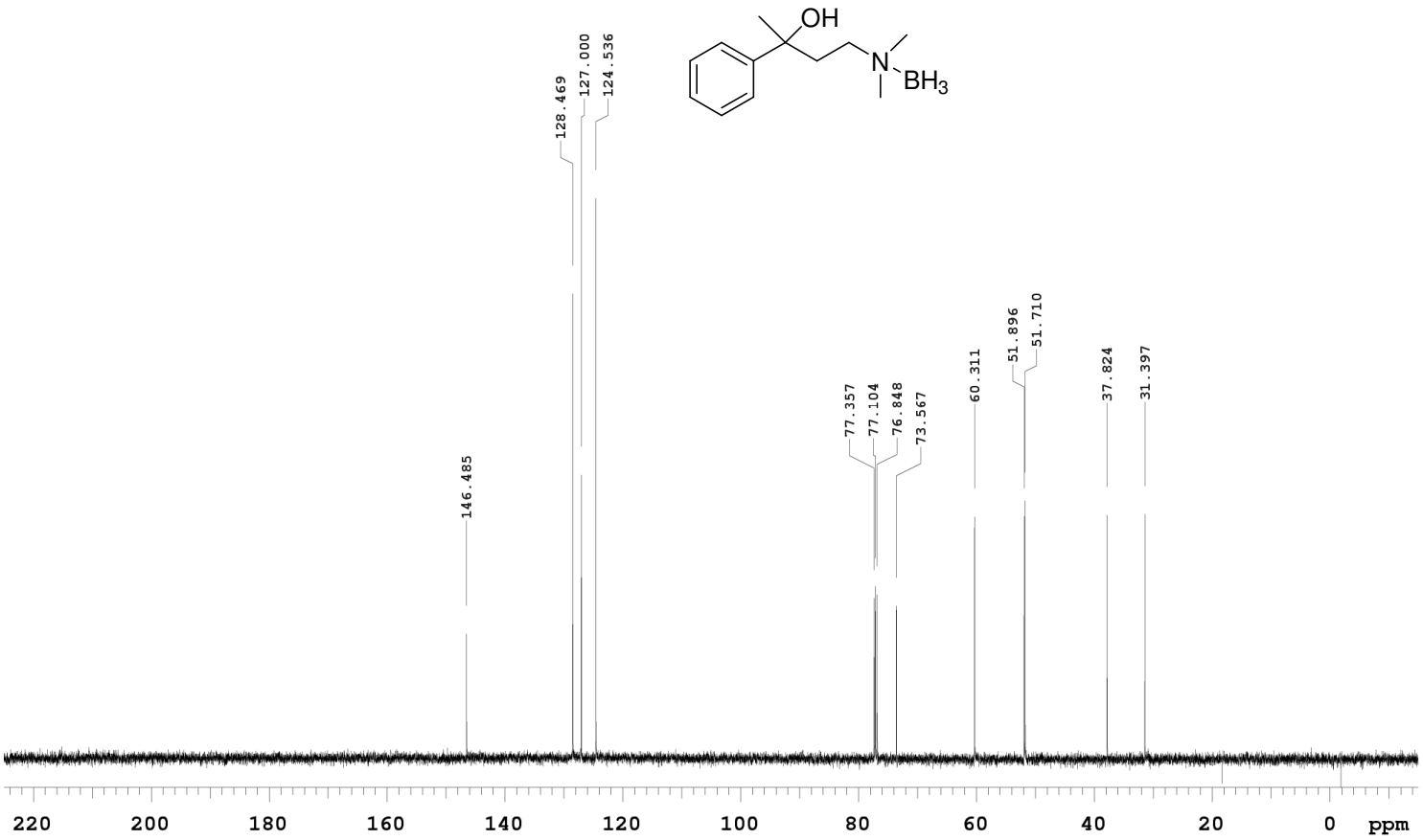


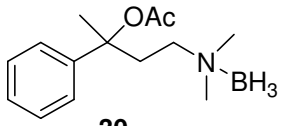
29b



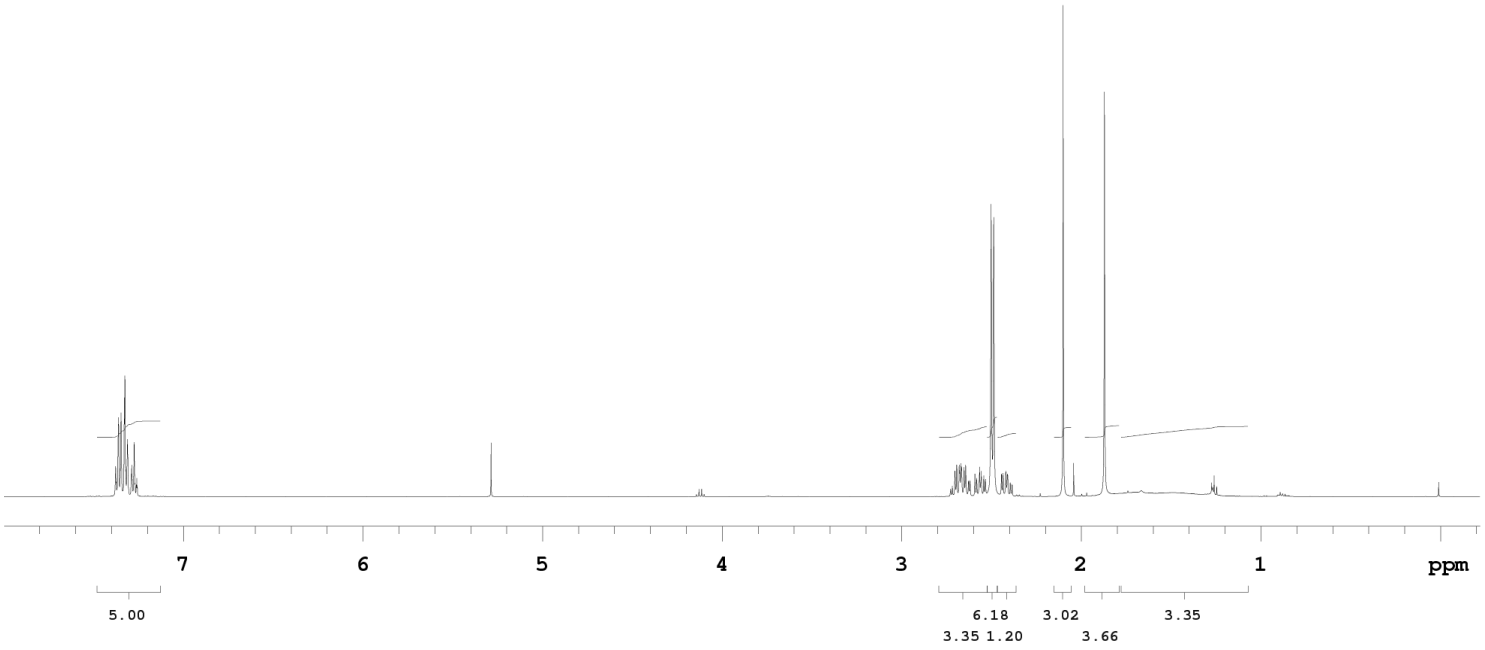

tdvVI-188-12-C
File: tdvVI-188-12-C
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: tdevries
File: tdvVI-188-12-C
INOVA-400 "Zr.Chem.LSA.UMich.Edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
544 repetitions
OBSERVE C13, 100.5712660 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 12 min, 46 sec
Acquisition date: Nov 10 2007
BH(OMs)2
Me2N
Me
Ph
29b
144.965
128.865
126.828
126.718
77.347
77.025
76.710
58.339
44.963
44.685
38.905
38.868
38.151
30.327
22.453
220
200
180
160
140
120
100
80
60
40
20
0
ppm

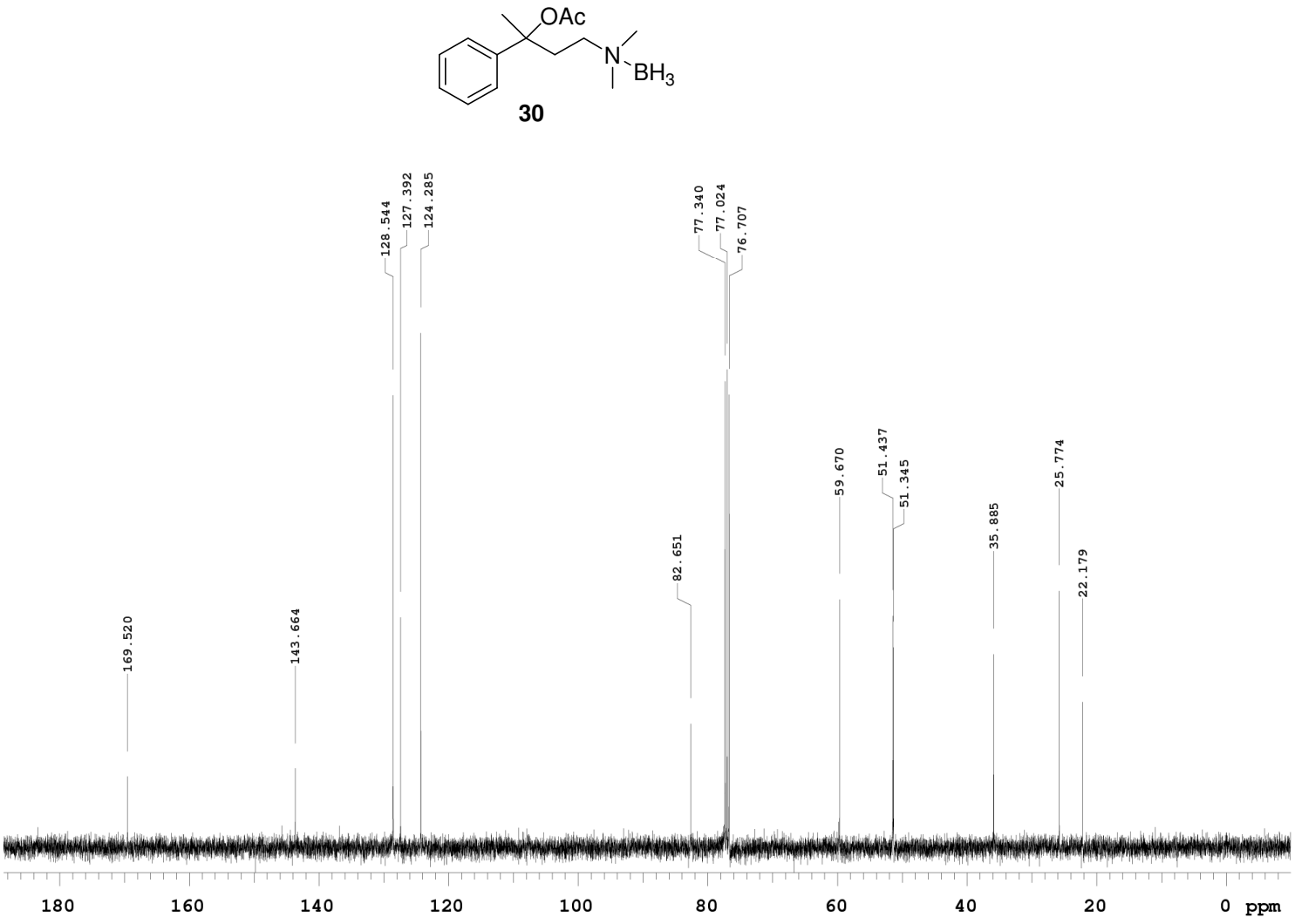

OH
N
BH3
7
6
5
4
3
2
1
ppm
5.00
6.18
3.35 1.20
3.02
3.66
3.35

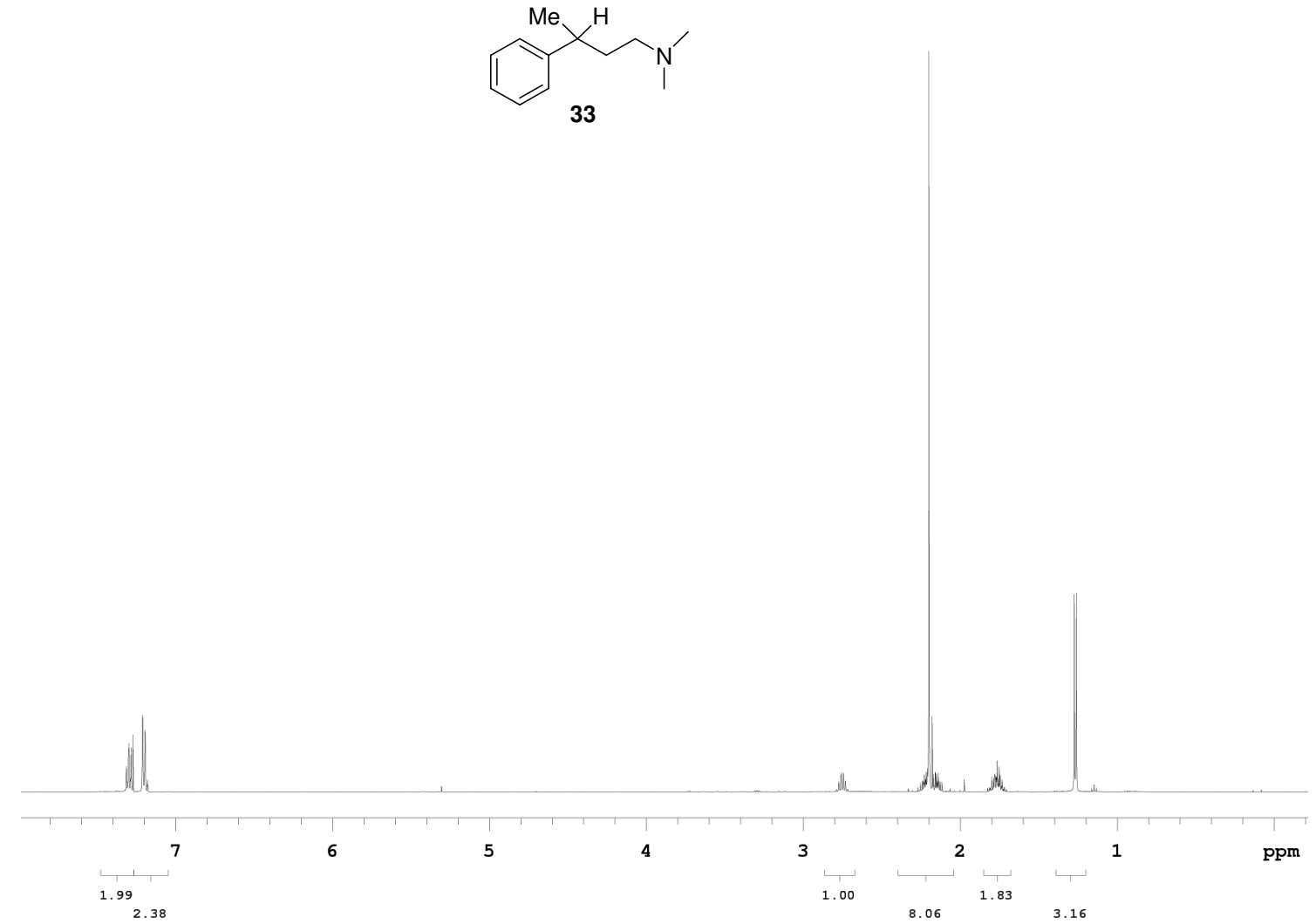

OH
N
BH3
128.469
127.000
124.536
146.485
77.357
77.104
76.848
73.567
60.311
51.896
51.710
37.824
31.397
220
200
180
160
140
120
100
80
60
40
20
0
ppm



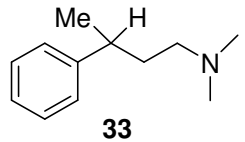
30



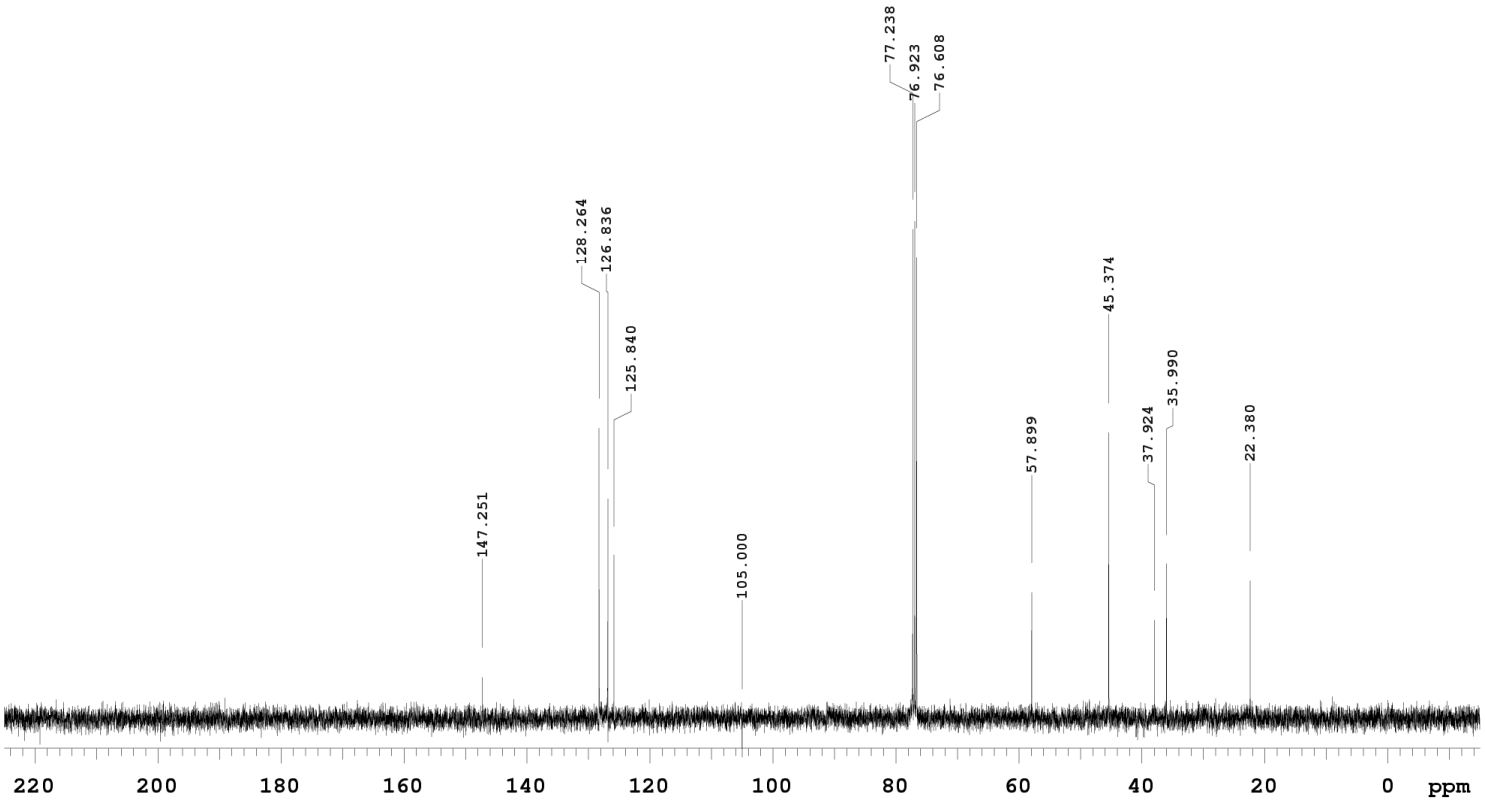

OAc
N
BH3
30
169.520
143.664
128.544
127.392
124.285
82.651
77.340
77.024
76.707
59.670
51.437
51.345
35.885
25.774
22.179
180
160
140
120
100
80
60
40
20
0 ppm

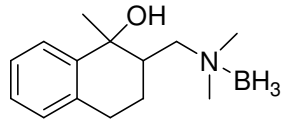

Me
H
N
33
7
6
5
4
3
2
1
ppm
1.99
2.38
1.00
8.06
1.83
3.16

=


Me
H
N

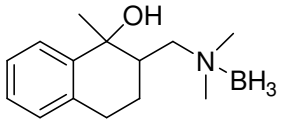
33


77.238
76.923
76.608
128.264
126.836
125.840
147.251
105.000
57.899
45.374
37.924
35.990
22.380
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OH
N
BH3

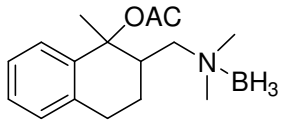
footnote 7

7
6
5
4
3
2
1
ppm
1.28
1.21
3.67
1.09
0.30
2.55
9.17
2.56
2.60
2.71
3.54
1.00

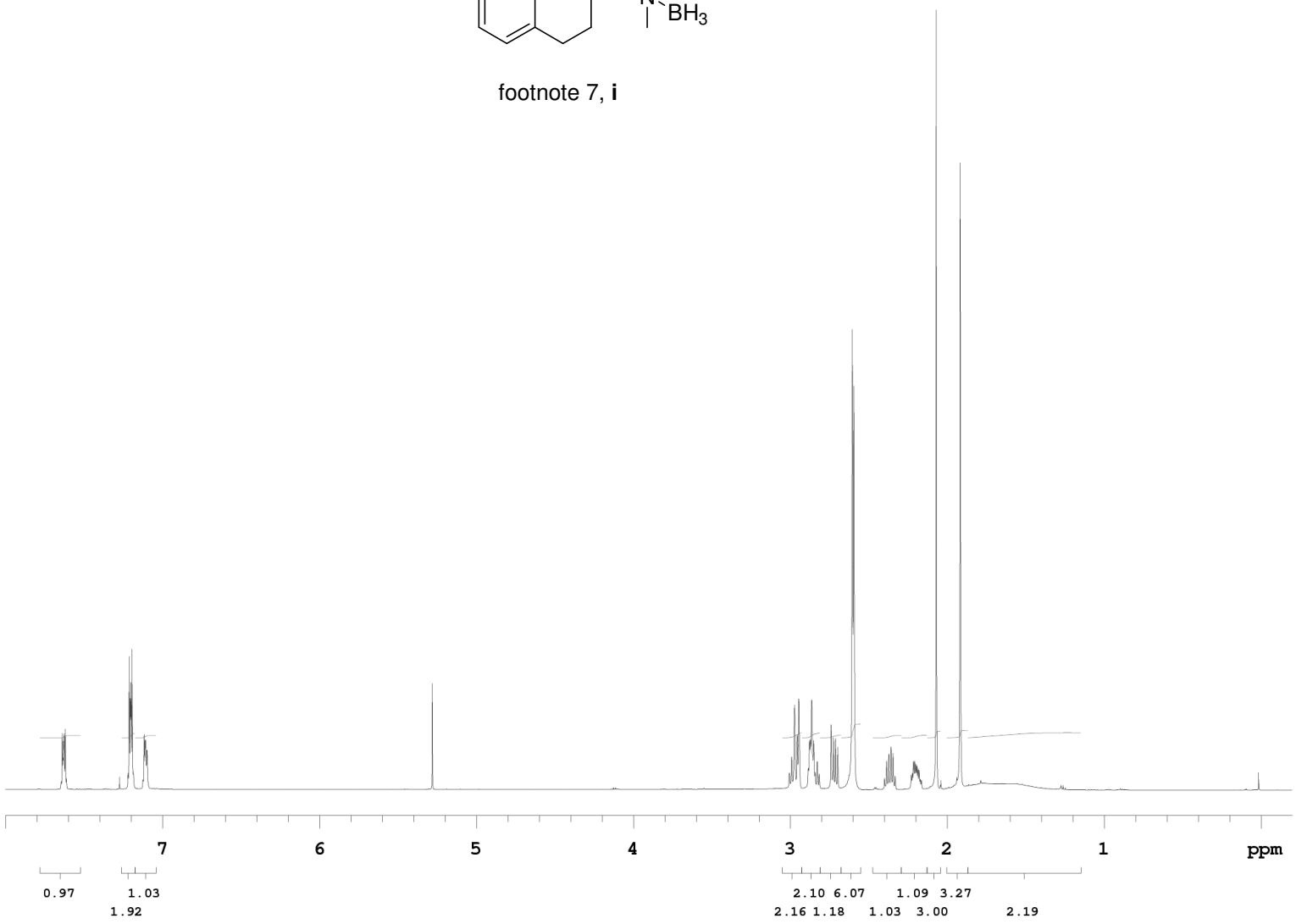

OH
N
BH3

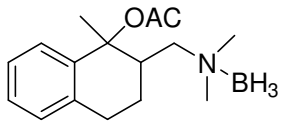
footnote 7

77.317
77.317
77.000
77.000
76.683
76.683
71.991
64.679
64.679
52.821
52.666
52.520
40.932
30.590
30.590
27.274
26.477
141.785
135.362
128.776
127.261
127.191
126.580
126.580
126.511
126.511
220
200
180
160
140
120
100
80
60
40
20
0
ppm

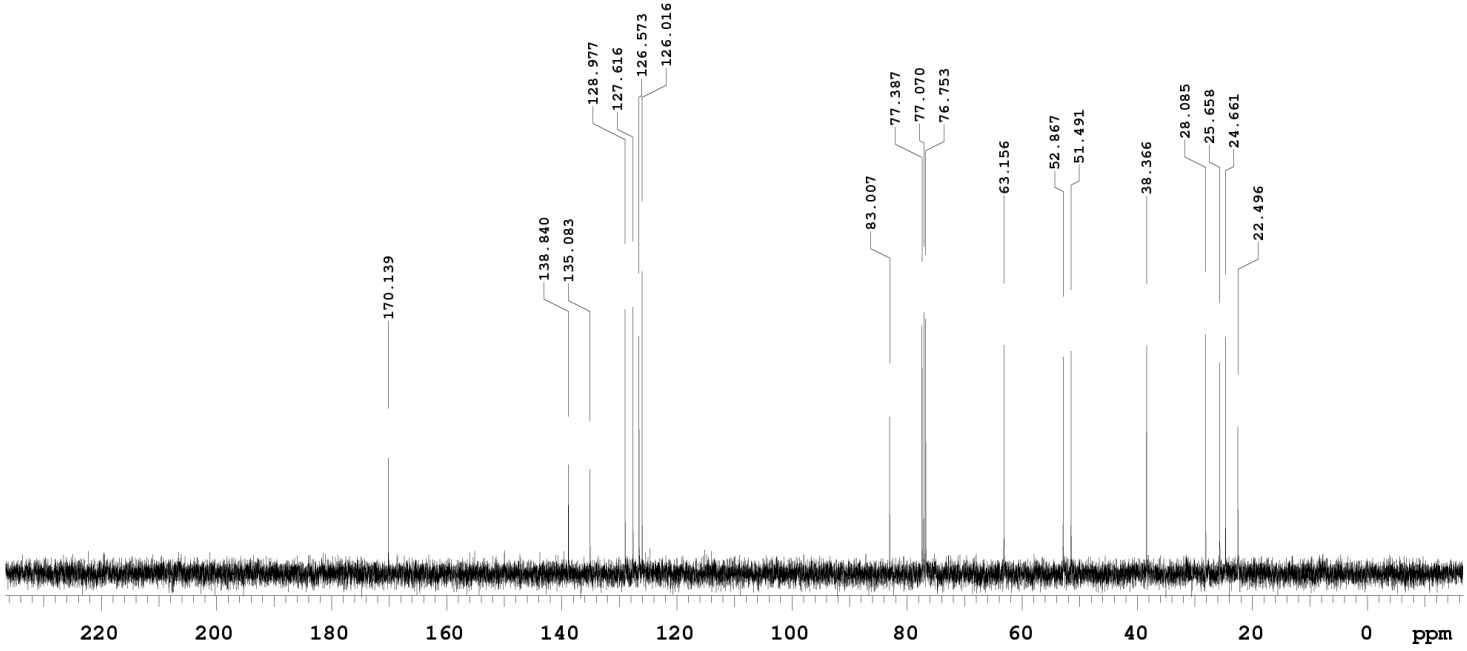

OAC
N
BH3

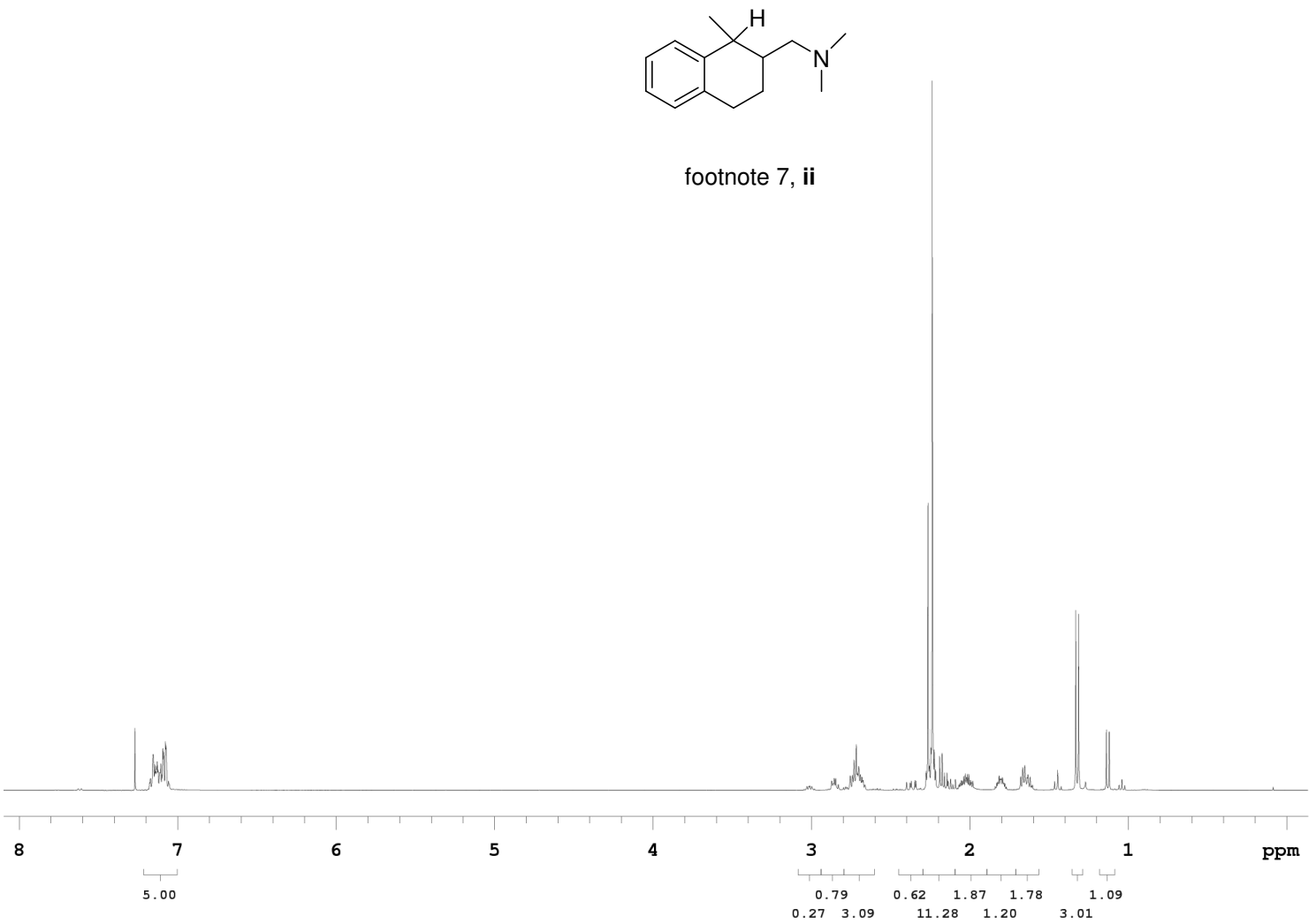
footnote 7, **i**


7
6
5
4
3
2
1
ppm
0.97
1.03
1.92
2.10 6.07
2.16 1.18
1.09 3.27
1.03 3.00
2.19

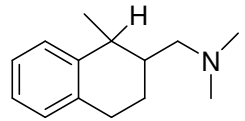

OAC
N
BH3

footnote 7, **i**

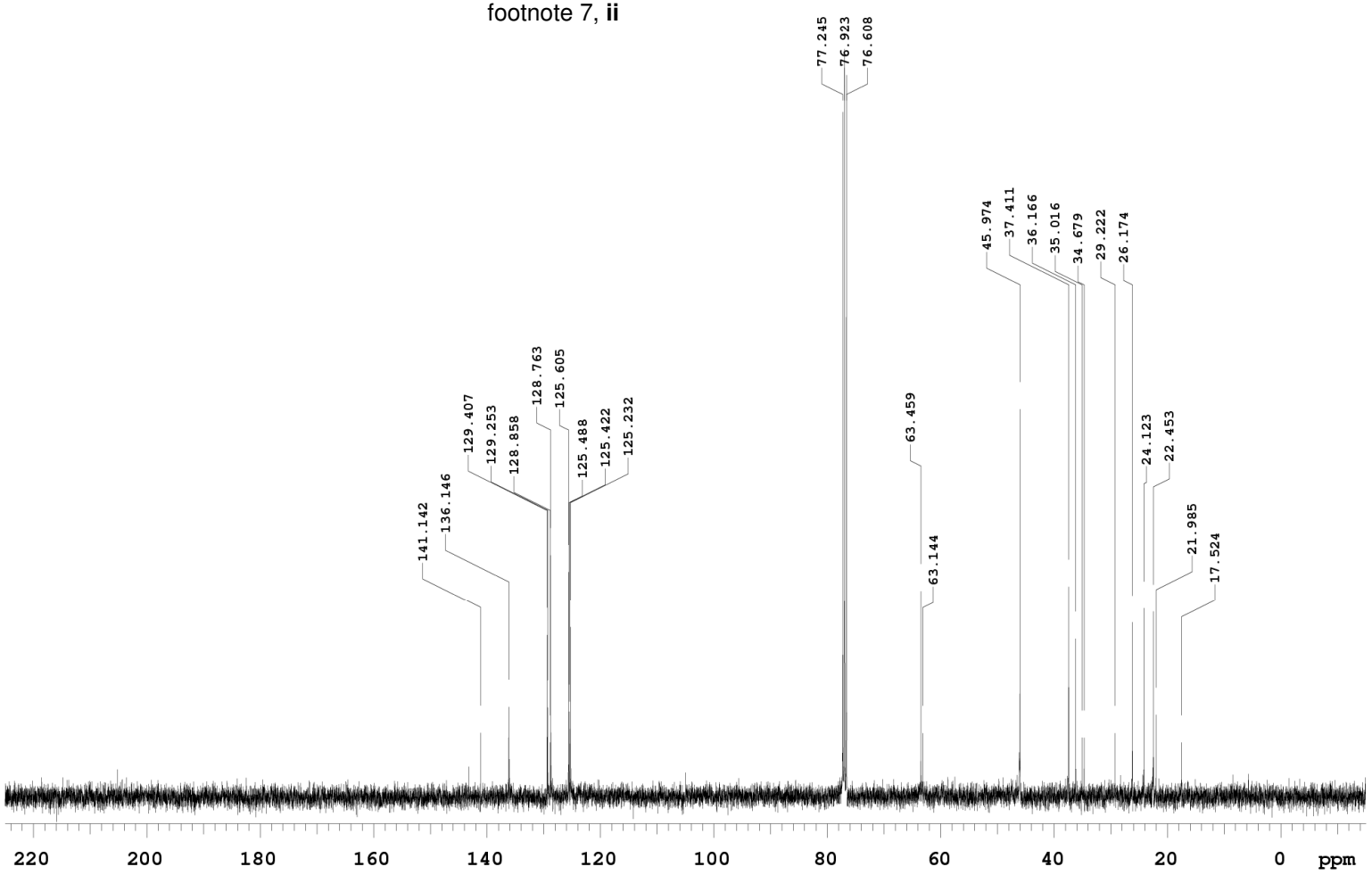

170.139
138.840
135.083
128.977
127.616
126.573
126.016
83.007
77.387
77.070
76.753
63.156
52.867
51.491
38.366
28.085
25.658
24.661
22.496
220
200
180
160
140
120
100
80
60
40
20
0
ppm

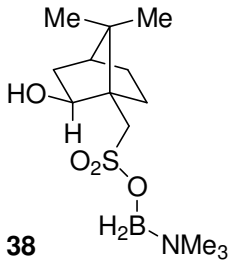


footnote 7, **ii**

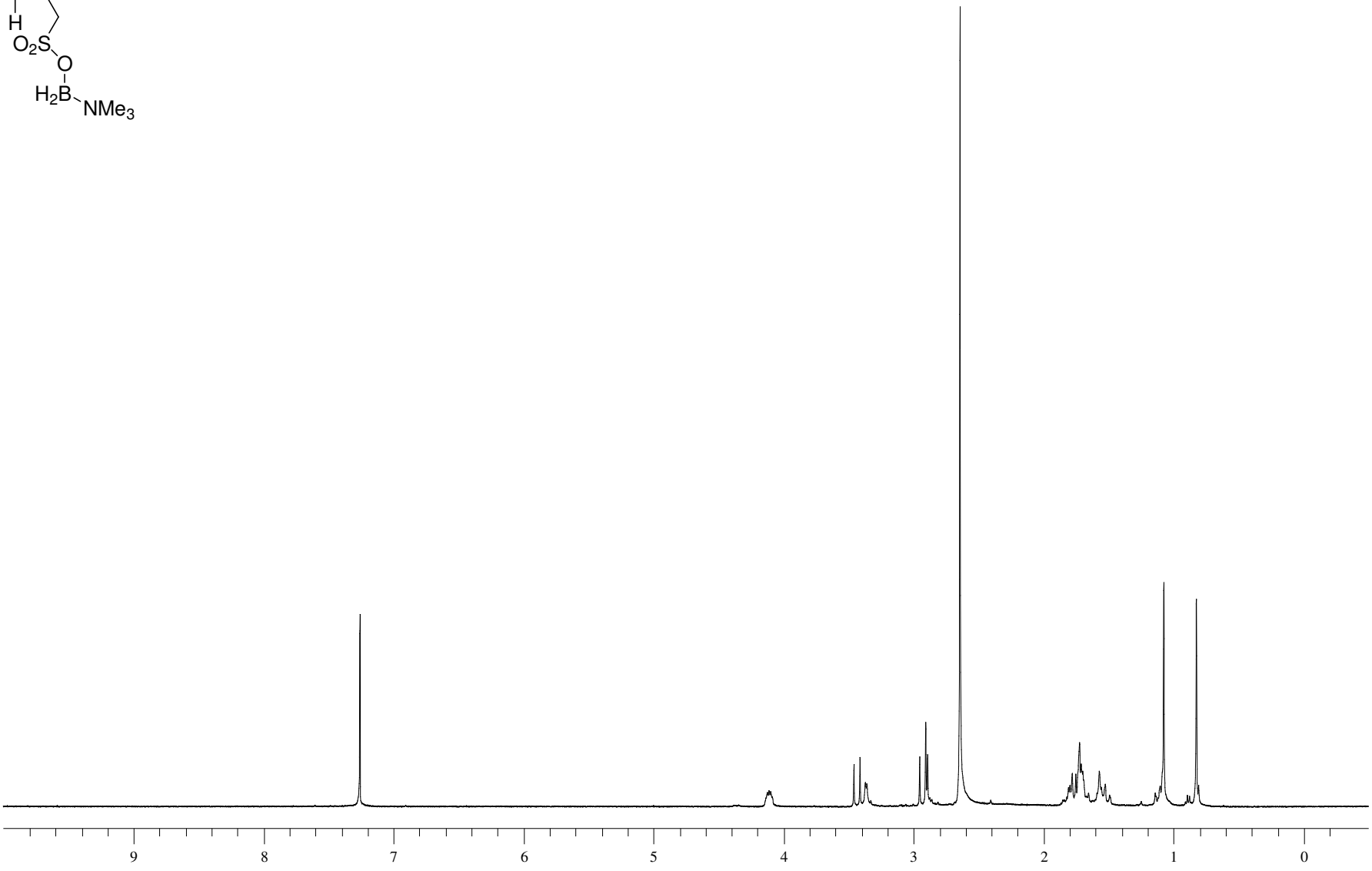


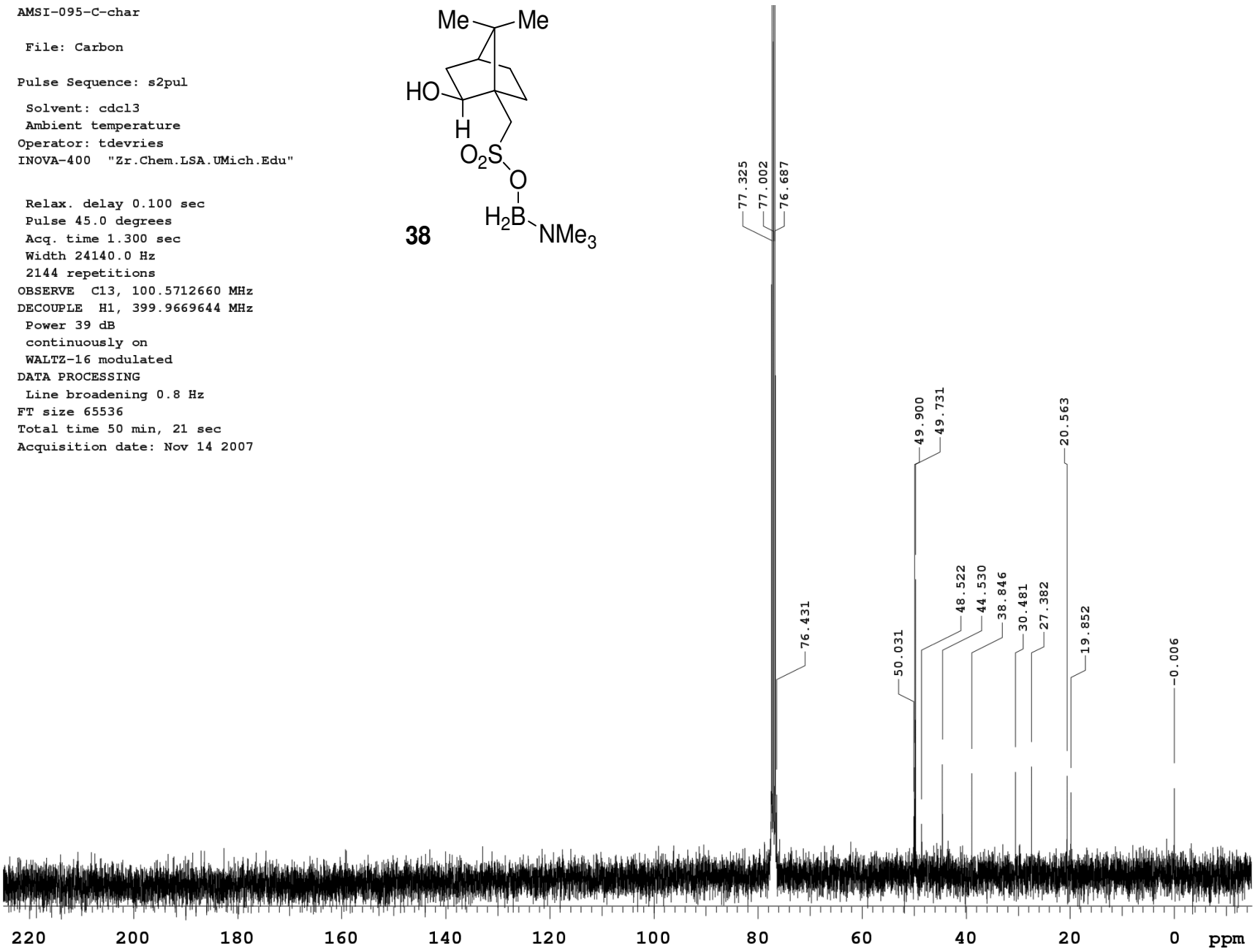
footnote 7, **ii**





38




AMSI-095-C-char
File: Carbon
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: tdevries
INOVA-400 "Zr.Chem.LSA.UMich.Edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
2144 repetitions
OBSERVE C13, 100.5712660 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 50 min, 21 sec
Acquisition date: Nov 14 2007
Me
Me
HO
H
O2S
O
H2B
NMe3
38
77.325
77.002
76.687
76.431
50.031
49.900
49.731
48.522
44.530
38.846
30.481
27.382
20.563
19.852
0.006
220
200
180
160
140
120
100
80
60
40
20
0
ppm