Supporting Information

Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (R)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels-Alder Reaction of α,β-Unsaturated Aldehydes with Amidodienes

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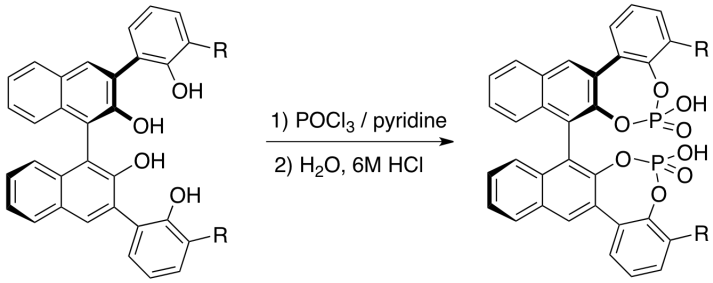
Experimental Section.

General. All reactions were carried out under an atmosphere of standard grade nitrogen gas (oxygen <10 ppm) in flame-dried glassware with magnetic stirring. Toluene was used as anhydrous in solvent line system KANTO. α, β-Unsaturated aldehydes were distilled over calcium hydride before used. Purification of reaction products was carried out by flash column chromatography on silica gel 60 (spherical, neutral, 100-210 μm; KANTO). Analytical thin layer chromatography (TLC) was performed on E. Merck precoated (0.25 mm) silica gel 60-F_{254} plates. Visualization was accomplished with UV light and phosphomolybdic acid solution in ethanol by heating.

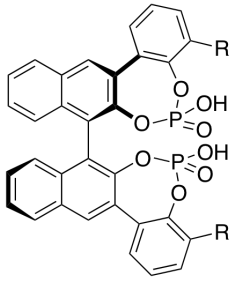
Infrared (IR) spectra were recorded on a Shimazu FTIR-8600PC spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-A-500 (500 MHz) spectrometer at ambient temperature. NMR solvents were purchased from ACROS ($CDCl_3$), CIL, Inc. (DMSO-d_6), and used as received. Data are reported as follows: chemical shifts are reported in ppm from tetramethylsilane on the δ scale, with solvent resonance employed as internal standard ($CDCl_3$ 7.26 ppm, DMSO-d_6 2.49 ppm), multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, coupling constant (Hz) and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-A-500 (125.7 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from tetramethylsilane on the δ scale, with solvent resonance employed as internal standard ($CDCl_3$ 77.0 ppm, DMSO-d_6 39.50 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-A-300 (121.5 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from 85% H_3PO_4 on the δ scale, with solvent resonance employed as internal standard (DMSO-d_6 0.4 ppm). High-performance liquid chromatography (HPLC) was performed on a Jasco equipped with a variable wavelength detector using Chiralcel OD-H column (0.46 cm x 25 cm), AD-3 column (0.46 cm x 25 cm), and IA column (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]_D^{T\,°C}$ (*c* = g/100 mL, solvent). Mass spectra were obtained on Bruker Daltonics APEX III FT-ICR-MS spectrometer and HITACHI M-2500 spectrometer in Instrumental Analysis Center for Department of Chemistry, Graduate School of Science, Tohoku University.

General Procedure for Synthesis of Chiral Bis-Phosphoric Acid 1



Corresponding tetraphenol was synthesized based on reported procedure.[1] A flame-dried 20mL two-necked round bottom flask equipped with a magnetic stir bar was charged with tetraphenol (0.84 mmol, 1 equiv), and pyridine (8.0 mL) was added. To the resulting solution was added phosphorus oxychloride (4.2 mmol, 5 equiv) at room temperature, then stirred at 70 °C for 24 h. After cooling to room temperature, H_2O (8.0 mL) was added and the resulting suspension was further stirred at 70 °C for 12 h. The resulting mixture was diluted with CH_2Cl_2 (30 mL), followed by washed with 6N HCl (3×20 mL), and combined organic layers were concentrated under reduced pressure. The resultant solids were dissolved in MeOH (10 mL). To the resulting solution was added conc. HCl (5 mL) at room temperature, and stirred further at this temperature for 1 h. The mixture was extracted with CH_2Cl_2 (3×20 mL), and then, the organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was purified by column chromatography on silica gel (Silica gel 60 extra pure for column chromatography: Catalogue No. 107754 Merck KgaA) with elution by dichloromethane:methanol (100:1) to give metal- or HCl-free chiral phosphoric acid as white solid.*

***IMPORTANCE**: To exclude the contamination of metals and HCl, short pass column chromatography was conducted on Silica gel 60 extra pure (Catalogue No. 107754 Merck KgaA). The present purification procedure is valid to produce "metal- and/or HCl-free chiral phosphoric acid". Details were reported in our recent publication "Metal-Free Chiral Phosphoric Acid or Chiral Metal Phosphate as Active Catalyst in the Activation of *N*-Acyl Aldimines" *(Synlett* **2011**, 1255-1258.)[2]



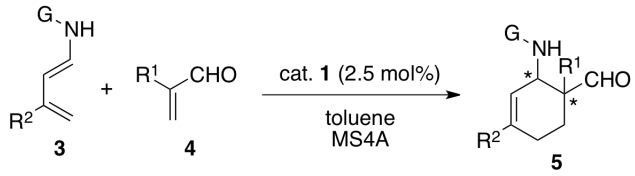
1e: R = 2,4,6-*i*-$Pr_3C_6H_2$

Chiral Bis-Phosphoric Acid 1e

White solid; TLC R_f = 0.48 (10:1 dichloromethane:methanol); IR (KBr) 3432(br), 2961, 2869, 1605, 1448, 1423, 1211, 1194, 1095, 996, 895 cm^{-1}; ^1H NMR (DMSO, 500 MHz) δ 8.43 (s, 1H, Ar-*H*), 8.14 (d, 1H, *J* = 8.1 Hz, Ar-*H*), 7.90 (d, 1H, *J* = 7.7 Hz, Ar-*H*), 7.52 (t, 1H, *J* = 7.5 Hz, Ar-*H*), 7.44 (t, 1H, *J* = 7.7 Hz, Ar-*H*), 7.38 (t, 1H, *J* = 7.7 Hz, Ar-*H*), 7.22

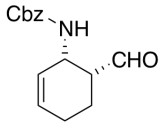
(d, 1H, *J* = 7.7 Hz, Ar-*H*), 7.16 (d, 1H, *J* = 8.5 Hz, Ar-*H*), 7.01 (s, 1H, Ar-*H*), 6.95 (s, 1H, Ar-*H*), 3.77 (bs, O*H*), 2.86 (m, 1H, C*H*), 2.69 (m, 1H, C*H*), 2.29 (m, 1H, C*H*), 1.21 (d, 6H, *J* = 6.8 Hz, CH_3), 1.06 (d, 6H, *J* = 6.8 Hz, CH_3), 0.98 (d, 3H, *J* = 6.8 Hz, CH_3), 0.82 (d, 3H, *J* = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125.65 MHz) δ 147.1, 146.9, 146.5 (d, $J_{P\text{-}C}$ = 7.6 Hz), 146.2, 144.8 (d, $J_{P\text{-}C}$ = 9.4 Hz), 133.0, 132.6, 132.3, 132.0, 130.8, 130.5, 129.6, 129.3, 128.6, 127.1, 125.5, 125.4, 124.8, 122.6, 122.5, 120.7, 119.9, 33.4, 30.5, 30.1, 25.9, 24.6, 24.0, 23.9, 23.4, 23.0; ^{31}P NMR (DMSO, 121.5 MHz) δ -3.34; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{62}H_{64}O_8P_2$ ([M-H]$^-$) 997.4004. Found: 997.4001.

General Procedure for Reactions of α,β-Unsaturated Aldehydes with Amidodienes.



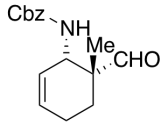
To the solution of catalyst (2.5 mol%, 0.005 mmol) and MS4A (150 mg) in toluene was added α,β-unsaturated aldehyde **4** (0.3 mmol) at room temperature, and the resulting solution was stirred at this temperature for 30 min. Then, amidodiene **3** (0.2 mmol) in toluene (0.5mL) was added at -80 °C, and the resulting solution was stirred at this temperature for 48 h. The reaction mixture was quenched by saturated $NaHCO_3$ aq. (10 mL) and the aqueous layer was extracted with EtOAc (20 mLx3). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was chromatographed on silica gel using a mixture of ethyl acetate and hexane as the eluant to give the amido aldehyde **5**.

Benzyl (1*S*, 6*R*)-6-formylcyclohex-2-enylcarbamate (5aa)



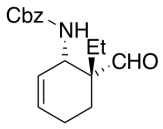
Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.40 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 111.1° (*c* = 1.11 , $CHCl_3$); IR (ATR) 3319, 3030, 2935, 2837, 1715, 1518, 1236, 1062 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 9.81 (s, 1H, C*H*O), 7.37-7.30 (m, 5H, Ar-*H*), 5.86-5.84 (m, 1H, C*H*), 5.71-5.68 (m, 1H, C*H*), 5.11-5.03 (m, 3H, N*H*, CH_2), 4.74 (bs, 1H, C*H*), 2.79-2.77 (m, 1H, CH_2), 2.09-2.05 (m, 2H, CH_2), 2.00-1.96 (m, 1H, CH_2), 1.77-1.74 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 202.5, 155.7, 136.1, 130.6, 128.4 (2C), 128.1, 128.0 (2C), 126.2, 66.9, 50.9, 45.5, 23.3, 18.5; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{15}H_{17}NO_3$ ([M+Na]$^+$): 282.1106. Found: 282.1101. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (95:5 hexane:ethanol), 0.6 mL/min; minor enantiomer t_r = 24.1 min, major enantiomer t_r = 35.5 min.

Benzyl (1*S*, 6*R*)-6-formyl-6-methylcyclohex-2-enylcarbamate (5ab)



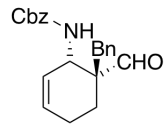
Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.28 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 60.1° (*c* = 0.84 , $CHCl_3$); IR (ATR) 3324, 3031, 2931, 1720, 1500, 1455, 1325, 1234, 1132 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.47 (s, 1H, C*H*O), 7.38-7.29 (m, 5H, Ar-*H*), 5.75-5.72 (m, 1H, C*H*), 5.62-5.59 (m, 1H, C*H*), 5.40 (d, 1H, *J* = 9.5 Hz, N*H)*, 5.12 (d, 1H, *J* = 12.0 Hz, CH_2), 5.07 (d, 1H, *J* = 12.0 Hz, CH_2), 4.30 (d, 1H, *J* = 10.0 Hz, C*H*), 2.14-2.07 (m, 1H, CH_2), 2.01-1.89 (m, 2H, CH_2), 1.70-1.66 (m, 1H, CH_2), 1.17 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 204.2, 156.3, 136.4, 128.5, 128.1, 128.0, 127.4, 66.9, 51.8, 49.3, 31.6, 27.8, 22.6, 22.2, 18.8, 14.1; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{16}H_{19}NO_3$ ($[M+Na]^+$): 296.1263. Found: 296.1257. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 12.9 min, major enantiomer t_r = 23.8 min.

Benzyl (1*S*, 6*R*)-6-ethyl-6-formylcyclohex-2-enylcarbamate (5ac)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.30 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 101.8° (*c* = 1.00 , $CHCl_3$); IR (ATR) 3319, 2965, 2926, 1721, 1499, 1455, 1326, 1234, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.52 (s, 1H, C*H*O), 7.37-7.28 (m, 5H, Ar-*H*), 5.77-5.75 (m, 1H, C*H*), 5.63-5.59 (m, 1H, C*H*), 5.26 (d, 1H, *J* = 9.4 Hz, N*H)*, 5.11 (d, 1H, *J* = 12.2 Hz, CH_2), 5.05 (d, 1H, *J* = 12.2 Hz, CH_2), 4.35 (d, 1H, *J* = 9.8 Hz, C*H*), 2.01 (m, 2H, CH_2), 1.81-1.74 (m, 2H, CH_2), 1.72-1.62 (m, 1H, CH_2), 1.65-1.57 (m, 1H, CH_2), 0.91 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 205.0, 156.1, 136.3, 129.0, 128.5 (2C), 128.1, 128.0 (2C), 127.0, 66.9, 52.6, 50.0, 24.3, 22.6, 21.9, 8.2; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{17}H_{21}NO_3$ ($[M+Na]^+$): 310.1419. Found: 310.1413. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 12.1 min, major enantiomer t_r = 21.7 min.

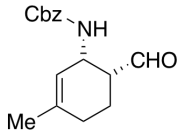
Benzyl (1*S*, 6*R*)-6-benzyl-6-formylcyclohex-2-enylcarbamate (5ad)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.35 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 25.7° (*c* = 1.29 , $CHCl_3$); IR (ATR) 3423, 3321, 3029, 2941, 2839,

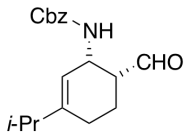
1718, 1496, 1455, 1323, 1055, 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.54 (s, 1H, C*H*O), 7.37-7.15 (m, 10H, Ar-*H*), 5.72-5.70 (m, 1H, C*H*), 5.63-5.60 (m, 2H, C*H*, N*H*), 5.14 (d, 1H, *J* = 12.0 Hz, C*H2)*, 5.10 (d, 1H, *J* = 12.0 Hz, CH_2), 4.42 (d, 1H, *J* = 9.8 Hz, C*H*), 3.01 (d, 1H, *J* = 14.1 Hz, CH_2), 2.84 (d, 1H, *J* = 13.7 Hz, CH_2), 2.14-2.10 (m, 1H, CH_2), 1.96-1.92 (m, 2H, CH_2), 1.55-1.49 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 205.1, 156.2, 136.4, 135.1, 130.4 (2C), 128.5 (2C), 128.4 (2C), 128.1, 128.0 (2C), 127.8, 126.9, 66.9, 52.6, 50.5, 38.5, 25.0, 22.0(2C); Anal. HRMS (ESI) Exact Mass Calcd. for $C_{22}H_{23}NO_3$ ([M+Na]$^+$): 372.1576. Found: 372.1568. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 15.3 min, major enantiomer t_r = 18.6 min

Benzyl (1*S*, 6*R*)-6-formyl-3-methylcyclohex-2-en-1-ylcarbamate (5ba)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.24 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 100.0° (*c* = 1.20 , $CHCl_3$); IR (ATR) 3318, 2931, 1694, 1517, 1454, 1376, 1224, 1067, 966 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.82 (s, 1H, C*H*O), 7.32-7.30 (m, 5H, Ar-*H*), 5.45-5.42 (m, 1H, C*H*), 5.10 (d, 1H, *J* = 8.2 Hz, CH_2), 5.04 (d, 1H, *J* = 8.2 Hz, CH_2), 4.96 (d, 1H, *J* = 8.1 Hz, C*H)*, 4.72 (bs, 1H, N*H*), 2.69 (m, 1H, C*H*), 1.97-1.91 (m, 3H, CH_2), 1.85-1.72 (m, 1H, CH_2), 1.68 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 202.8, 155.8, 138.9, 136.3, 128.5 (2C), 128.1, 128.0 (2C), 120.6, 66.9, 50.9, 46.0, 28.4, 23.3, 18.6; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{16}H_{19}NO_3$ ([M+Na]$^+$): 296.1257. Found: 296.1256. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 14.8 min, major enantiomer t_r = 25.7 min.

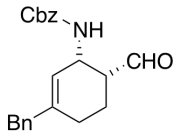
Benzyl (1*S*, 6*R*)-6-formyl-3-isopropylcyclohex-2-enylcarbamate (5ca)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.34 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 95.6° (*c* = 1.28, $CHCl_3$); IR (ATR) 3324, 2959, 2871, 1715, 1517, 1455, 1330, 1227, 1064 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.82 (s, 1H, C*H*O), 7.37-7.26 (m, 5H, Ar-*H*), 5.43 (d, 1H, *J* = 4.25 Hz, C*H*), 5.11 (d, 1H, *J* = 12.4 Hz, CH_2), 5.04 (d, 1H, *J* = 12.4 Hz, CH_2), 4.95 (d, 1H, *J* = 8.5 Hz, N*H)*, 4.75-4.72 (m, 1H, CH_2), 2.70 (d, 1H, *J* = 11.1 Hz, CH_2), 2.21-2.16 (m, 1H, C*H*), 2.05-1.93 (m, 3H, CH_2), 1.71-1.67 (m, 1H, CH_2), 0.99 (d, 6H, *J* = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 202.8, 155.7, 148.3, 136.2, 128.5(2C), 128.2, 128.1(2C), 118.0, 66.9, 51.3, 45.9, 34.8, 24.5, 21.3, 21.0, 18.7; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{18}H_{23}NO_3$ ([M+Na]$^+$): 324.1570. Found: 324.1570. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 20.4 min, major

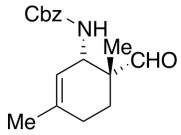
enantiomer t_r = 30.9 min.

Benzyl (1*S*, 6*R*)-3-benzyl-6-formylcyclohex-2-enylcarbamate (5da)



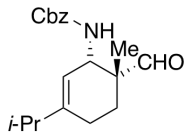
Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as white solid. TLC R_f = 0.26 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 88.6° (*c* = 0.90, $CHCl_3$); IR (ATR) 3325, 3029, 2900, 2834, 1715, 1517, 1496, 1454, 1230, 1064 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.79 (s, 1H, C*H*O), 7.39-7.26 (m, 7H, Ar-*H*), 7.23-7.19 (m, 1H, Ar-*H*), 7.11 (d, 2H, *J* = 6.80 Hz, Ar-*H*), 5.49 (d, 1H, *J* = 4.3 Hz, C*H*), 5.10 (d, 1H, *J* = 12.0 Hz, CH_2), 5.05-5.02 (m, 2H, CH_2, N*H*), 4.76 (bs, 1H, CH_2), 3.27 (s, 2H, CH_2), 2.72 (d, 1H, *J* = 4.7 Hz, CH_2), 1.95-1.92 (m, 3H, CH_2), 1.74-1.69 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 202.6, 155.8, 141.8, 138.7, 136.2, 128.8(2C), 128.5(2C), 128.4(2C), 128.2, 128.1(2C), 126.4, 122.1, 67.0, 50.9, 46.1, 43.8, 26.4, 18.8; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{22}H_{23}NO_3$ ($[M+Na]^+$): 372.1570. Found: 372.1569. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 24.3 min, major enantiomer t_r = 42.5 min.

Benzyl (1*S*, 6*R*)-6-formyl-3,6-dimethylcyclohex-2-enylcarbamate (5bb)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.30 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 72.1° (*c* = 1.57, $CHCl_3$); IR (ATR) 3324, 2965, 2930, 2728, 1721, 1499, 1455, 1231, 1041 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.49 (s, 1H, C*H*O), 7.37-7.30 (m, 5H, Ar-*H*), 5.33 (d, 1H, *J* = 1.3 Hz, N*H*), 5.28 (d, 1H, *J* = 8.5 Hz, C*H*), 5.11 (d, 1H, *J* = 12.2 Hz, CH_2), 5.06 (d, 1H, *J* = 12.2 Hz, CH_2), 4.26 (d, 1H, *J* = 9.8 Hz, C*H*), 1.99-1.87 (m, 3H, CH_2), 1.68-1.65 (m, 4H, CH_3, CH_2), 1.15 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 204.5, 156.6, 136.5, 136.4, 128.5(2C), 128.1, 128.0(2C), 121.4, 66.8, 52.1, 49.0, 27.6, 27.0, 23.0, 18.5; Anal. HRMS (ESI) Exact Mass Calcd. for $C_{17}H_{21}NO_3$ ($[M+Na]^+$): 310.1414. Found: 310.1414. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 14.7 min, major enantiomer t_r = 22.8 min.

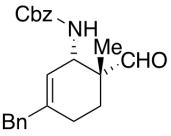
Benzyl (1*S*, 6*R*)-6-formyl-3-isopropyl-6-methylcyclohex-2-enylcarbamate (5cb)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless

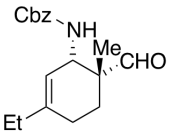
oil. TLC R_f = 0.30 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 75.0° (*c* = 1.50 , $CHCl_3$); IR (ATR) 3439, 3327, 2960, 2930, 1719, 1498, 1455, 1229, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.49 (s, 1H, C*H*O), 7.38-7.26 (m, 5H, Ar-*H*), 5.33-5.29 (m, 2H, C*H,* N*H*), 5.12 (d, 1H, J = 12.2 Hz, CH_2), 5.06 (d, 1H, J = 12.2 Hz, CH_2), 4.28 (d, 1H, J = 9.0 Hz, C*H)*, 2.20-2.14 (m, 1H, C*H*), 2.04-1.88 (m, 3H, CH_2), 1.68-1.63 (m, 1H, CH_2), 1.14 (s, 3H, CH_3), 0.97 (d, 6H, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 204.4, 156.3, 145.9, 136.4, 128.5 (2C), 128.1, 128.0 (2C), 118.9, 66.8, 52.2, 49.2, 34.5, 27.7, 22.9, 21.2, 21.1, 18.6; Anal. HRMS (ESI) Exact Mass Calcd for $C_{19}H_{25}NO_3$ $(M+Na)^+$**:** 338.1727. Found: 338.1726. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 7.3 min, major enantiomer t_r = 11.2 min.

Benzyl (1*S*, 6*R*)-3-benzyl-6-formyl-6-methylcyclohex-2-enylcarbamate (5db)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.27 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 54.8° (*c* = 1.73 , $CHCl_3$); IR (ATR) 3324, 3027, 2927, 2834, 2721, 1718, 1495, 1454, 1226, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.44 (s, 1H, C*H*O), 7.38-7.27 (m, 7H, Ar-*H*), 7.20 (t, 1H, J = 7.3 Hz, Ar-*H*), 7.11 (d, 2H, J = 7.3 Hz, Ar-*H*), 5.43 (s, 1H, N*H*), 5.40 (d, 1H, J = 9.8 Hz, C*H*), 5.12 (d, 1H, J = 12.4 Hz, CH_2), 5.07 (d, 1H, J = 12.4 Hz, CH_2), 4.33 (d, 1H, J = 9.4 Hz, C*H)*, 3.26 (d, 1H, J = 15.2 Hz, CH_2), 3.22 (d, 1H, J = 15.2 Hz, CH_2), 1.93-1.80 (m, 3H, CH_2), 1.66-1.60 (m, 1H, CH_2), 1.15 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 204.3, 156.3, 139.3, 138.9, 136.4, 128.7 (2C), 128.5 (2C), 128.4 (2C), 128.1, 128.0 (2C), 126.3, 123.3, 66.9, 52.3, 49.2, 43.6, 28.0, 25.0, 18.6; Anal. HRMS (ESI) Exact Mass Calcd for $C_{23}H_{25}NO_3$ $(M+Na)^+$: 386.1727. Found: 386.1726. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0 mL/min; minor enantiomer t_r = 16.5 min, major enantiomer t_r = 35.4 min.

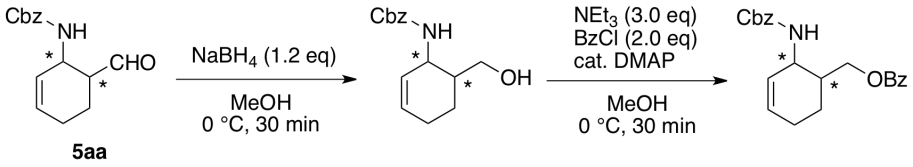
Benzyl (1*S*, 6*R*)-3-ethyl-6-formyl-6-methylcyclohex-2-enylcarbamate (5eb)



Purification by silica gel column chromatography with elution by hexane:ethyl acetate (12:1) provided as colorless oil. TLC R_f = 0.28 (4:1 hexane:ethyl acetate); $[\alpha]_D^{24}$ 78.4° (*c* = 1.57 , $CHCl_3$); IR (ATR) 3324, 2964, 2932, 1719, 1499, 1456, 1229, 1037 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.50 (s, 1H, C*H*O), 7.38-7.27 (m, 5H, Ar-*H*), 5.32-5.28 (m, 2H, C*H,* N*H*), 5.12 (d, 1H, J = 12.2 Hz, CH_2), 5.06 (d, 1H, J = 12.2 Hz, CH_2), 4.28 (d, 1H, J = 9.8 Hz, C*H)*, 1.95 (m, 5H, CH_2), 1.69-1.63 (m, 1H, CH_2), 1.15 (s, 3H, CH_3), 0.98 (t, 3H, J = 7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125.6 MHz) δ 204.5, 156.3, 141.8, 136.4, 128.5 (2C), 128.1, 128.0 (2C), 119.7, 66.8, 52.2, 49.1, 29.6, 27.7, 25.3, 18.6, 12.0; Anal. HRMS (ESI) Exact Mass Calcd for $C_{18}H_{23}NO_3$ $(M+Na)^+$: 324.1570. Found: 324.1570. Enantiomeric excess was determined by HPLC analysis of the corresponding benzoylether with a Chiralcel OD-H column (97:3 hexane:ethanol), 1.0

mL/min; minor enantiomer t_r = 7.9 min, major enantiomer t_r = 12.8 min.

Representative Procedure for Derivatization of Amido Aldehyde to Benzoylether.



To the solution of **5aa** (22.5 mg, 0.10 mmol) in MeOH (2.0 mL) was added $NaBH_4$ (45.0 mg, 0.12 mmol) at 0 °C. The resulting mixture was stirred at this temperature for 30 min. The reaction mixture was quenched by water, then the aqueous layer was extracted with EtOAc (10 mLx3). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration, used in next step without purification.

To the solution of amido alcohol and 4-dimethylaminopyridine (1.0 mg) in CH_2Cl_2 (2.0 mL) was added triethylamine (42 μL, 0.30 mmol) and benzoyl chloride (23.0 μL, 0.20 mmol) at room temperature. The resulting solution was stirred at room temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (5.0 mL) and quenched by water. The aqueous layer was extracted with CH_2Cl_2 (10 mLx3), the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was chromatographed on silica gel using a mixture of ethyl acetate and hexane as the eluant to give the product as a white solid.

Determination of Absolute Configuration.

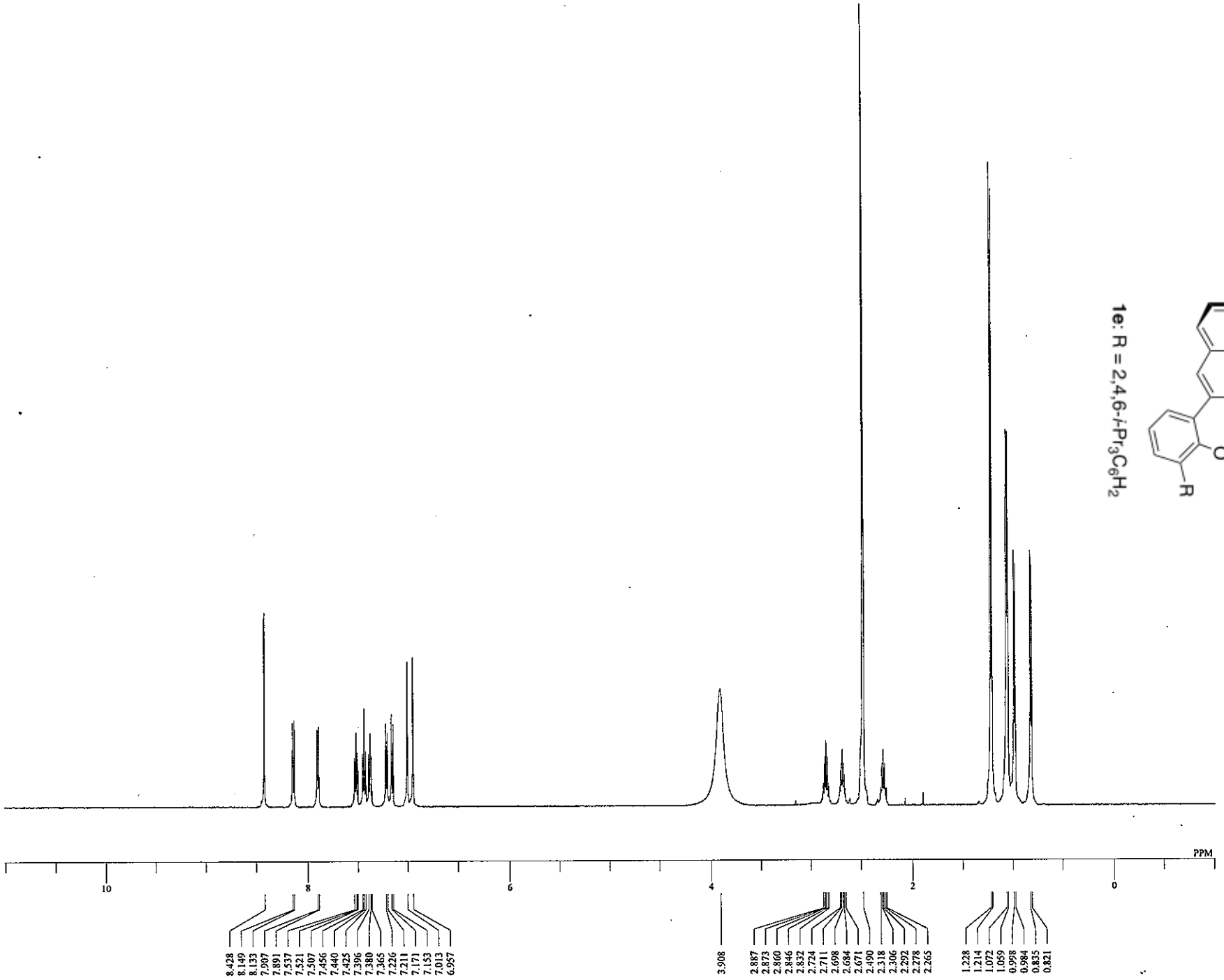
Benzyl (1*R*, 6*S*)-6-formylcyclohex-2-enylcarbamate **5aa** was synthesized based on reported procedure.[3] Enantiomeric excess of **5aa** was determined by HPLC analysis after derivatization to the corresponding benzoylether based on above procedure. Absolute configuration was determined by comparison with HPLC analysis of reported benzyl (1*R*, 6*S*)-6-formylcyclohex-2-enylcarbamate **5aa**. Absolute configuration of other products was determined by analogy.

Reference

(1) Ishihara, K.; Kurihara, H.; Matsumoto, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 6920-6930.

(2) Terada, M.; Kanomata, K. *Synlett* **2011**, 1255-1258.

(3) Wipf, P.; Wang, X. *Tetrahedron Lett.* **2000**, *41*, 8747-8751.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OBSET 0.00 KHz
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POINT 16384
FREQU 6997.90 Hz
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PD 1.6587 sec
PW1 6.75 usec
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BF 0.10 Hz
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6
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2
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8.149
8.133
7.907
7.891
7.537
7.521
7.507
7.456
7.440
7.425
7.396
7.380
7.365
7.226
7.211
7.171
7.153
7.013
6.957
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2.873
2.860
2.846
2.832
2.724
2.711
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2.671
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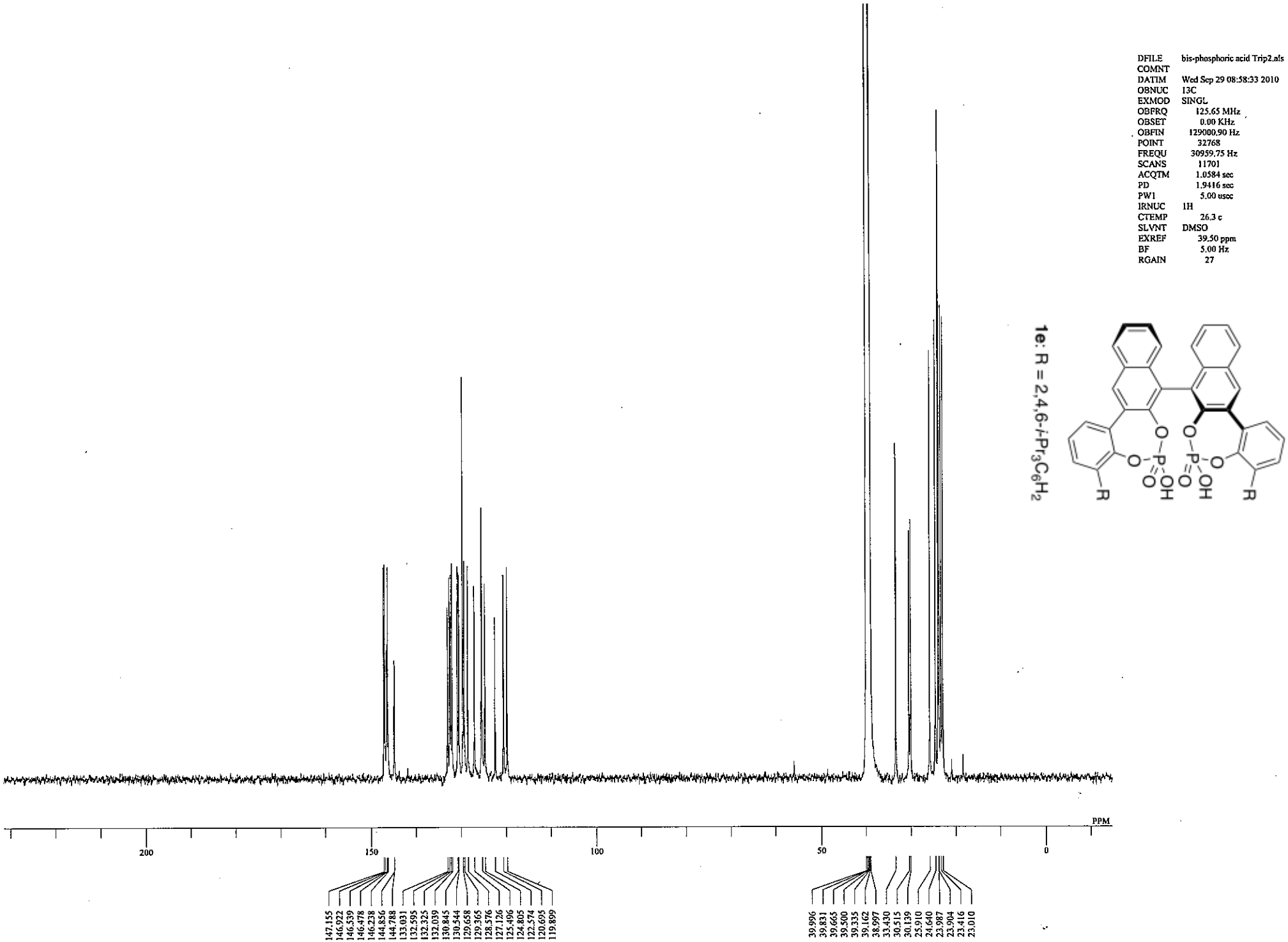
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OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 11701
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT DMSO
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BF 5.00 Hz
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127.126
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124.805
122.574
120.695
119.899
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39.831
39.665
39.500
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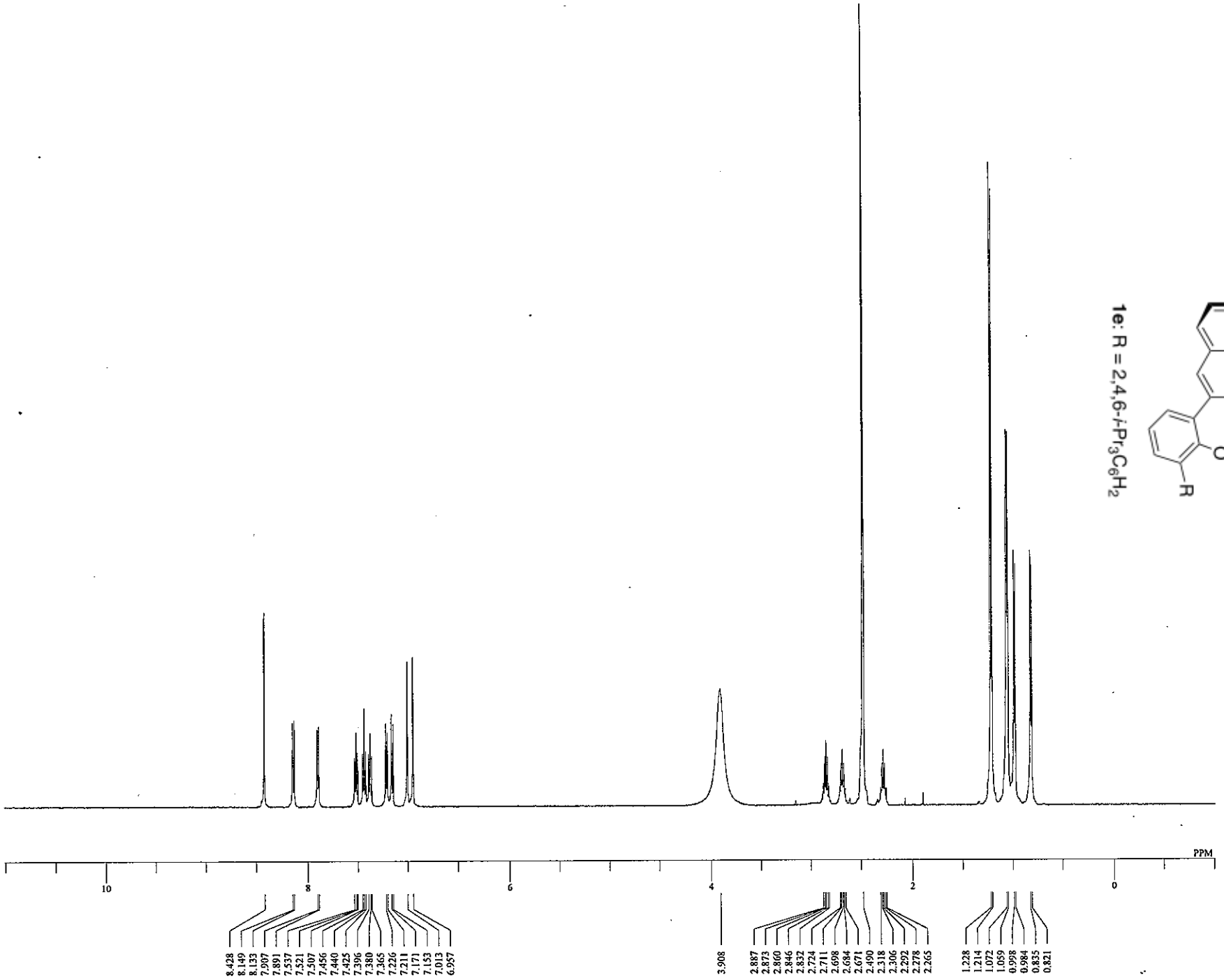
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POINT 16384
FREQU 6997.90 Hz
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ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 26.2 c
SLVNT DMSO
EXREF 2.49 ppm
BF 0.10 Hz
RGAIN 22
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PPM
10
8
6
4
2
0
8.428
8.149
8.133
7.907
7.891
7.537
7.521
7.507
7.456
7.440
7.425
7.396
7.380
7.365
7.226
7.211
7.171
7.153
7.013
6.957
3.908
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2.265
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DFILE	bis phosphoric acid Trip.als
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FREQU	40000.00 Hz
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PD	2.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	DMSO
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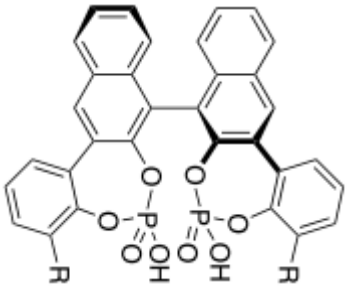
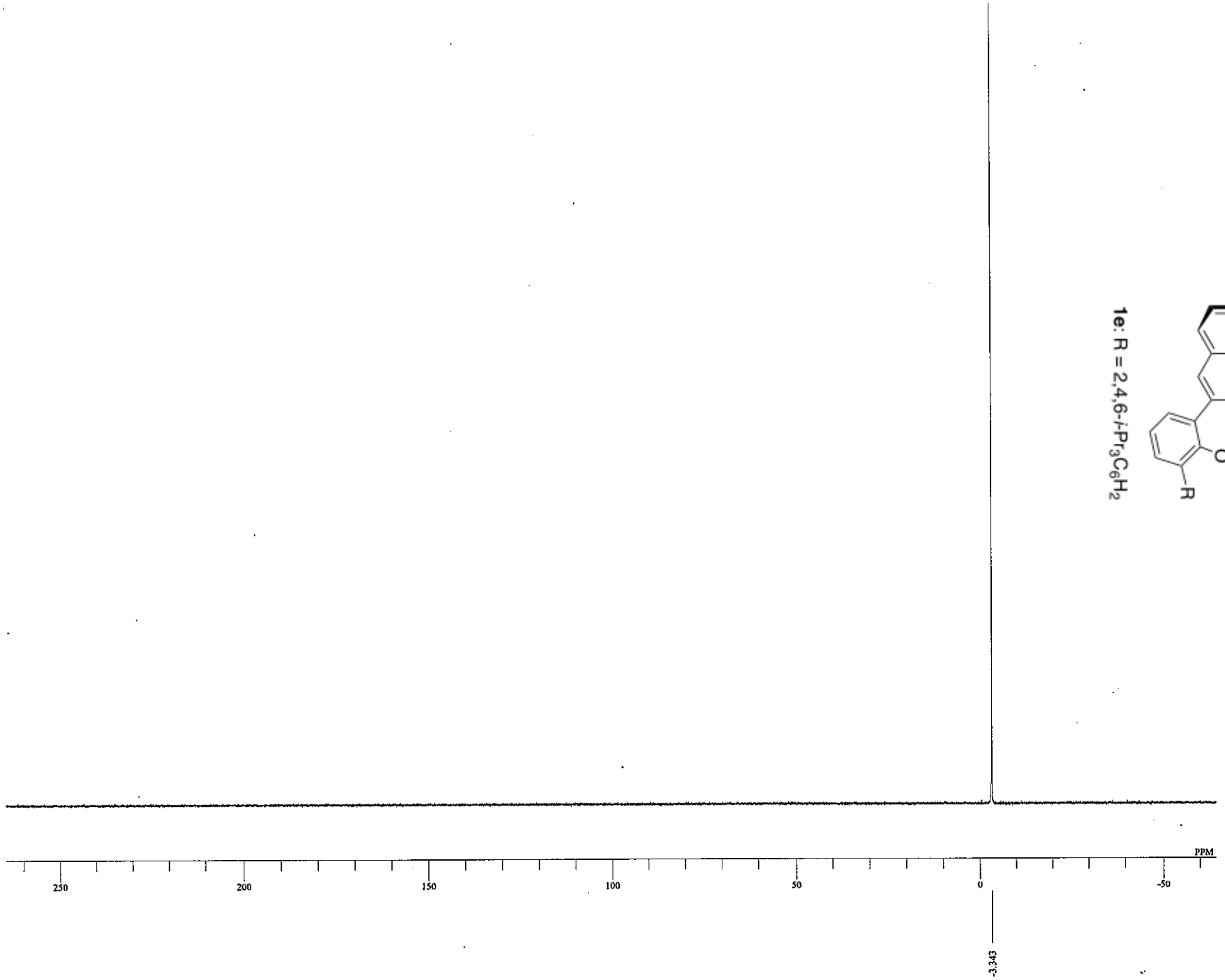
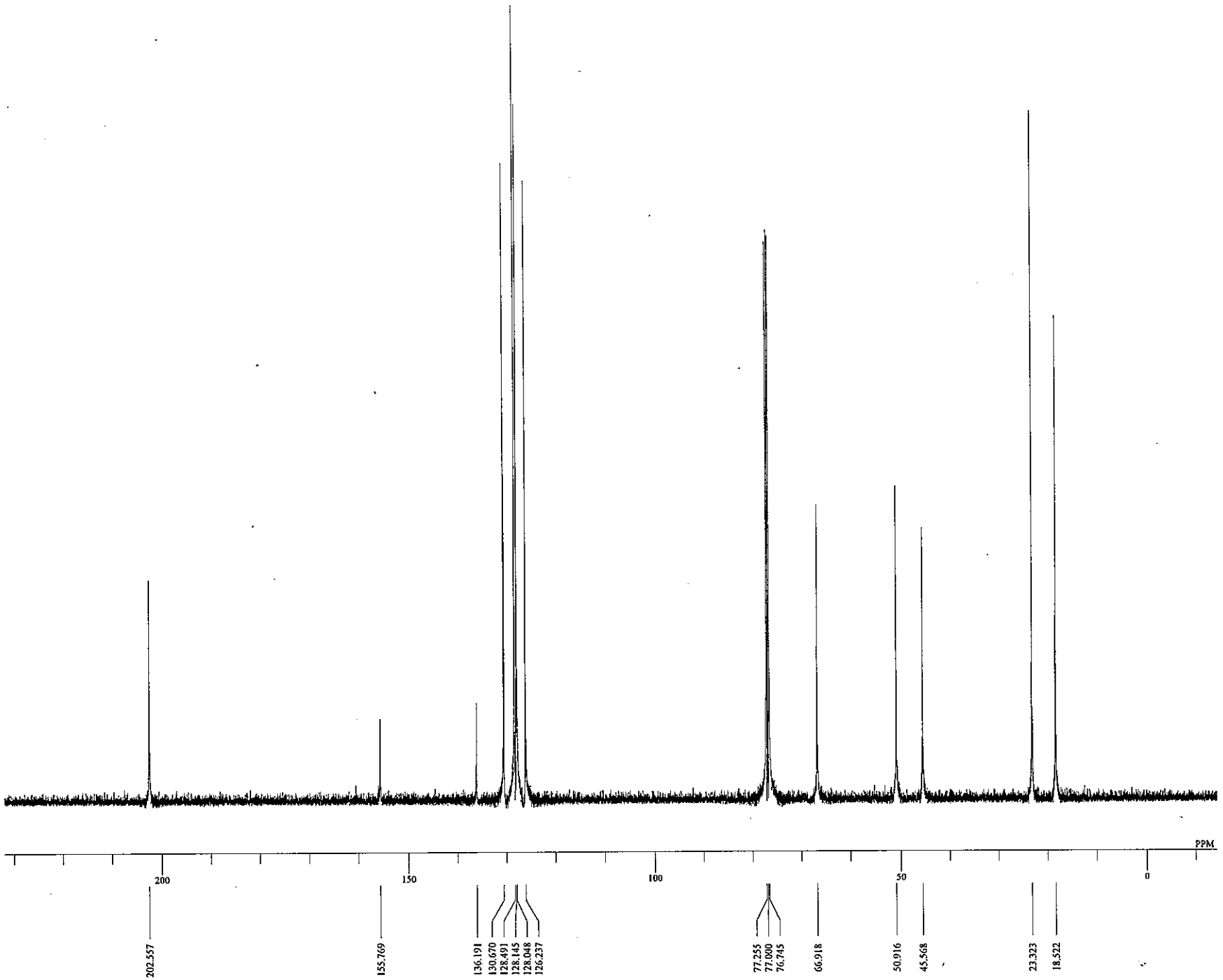
BF	1.00 Hz
RGAIN	25

1e: R = 2,4,6-*i*-Pr$_3$C$_6$H$_2$



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POINT 32768
FREQU 30959.75 Hz
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PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
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BF 1.00 Hz
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Cbz
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CHO
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POINT	16384
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PD	1.6587 sec
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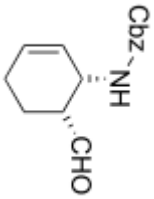

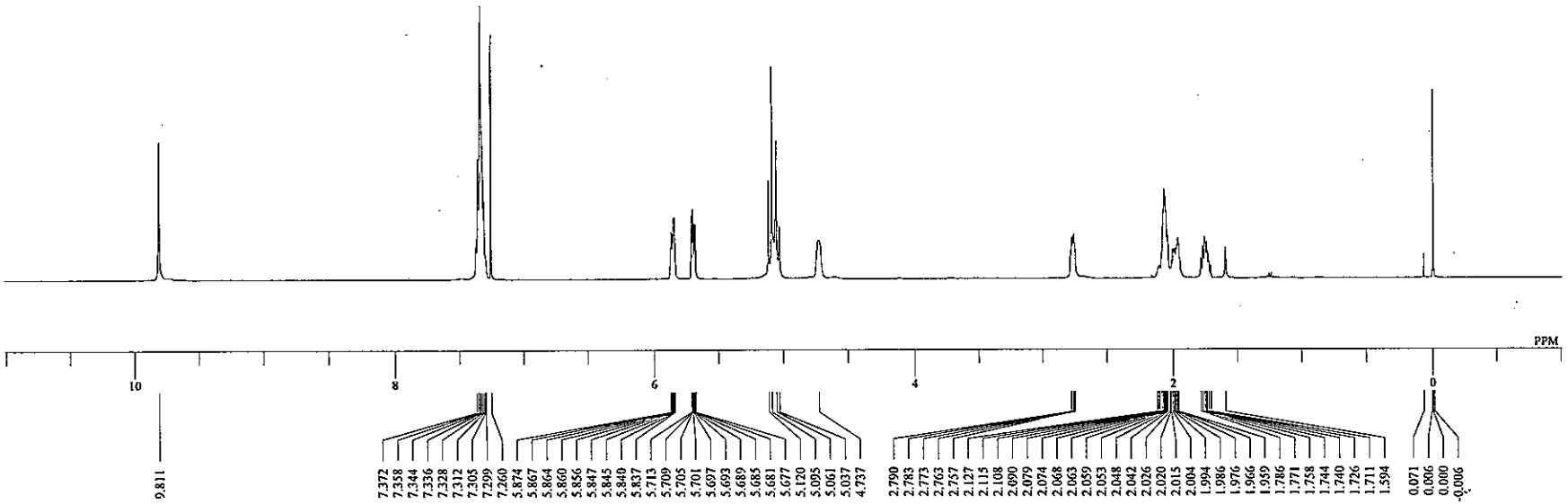

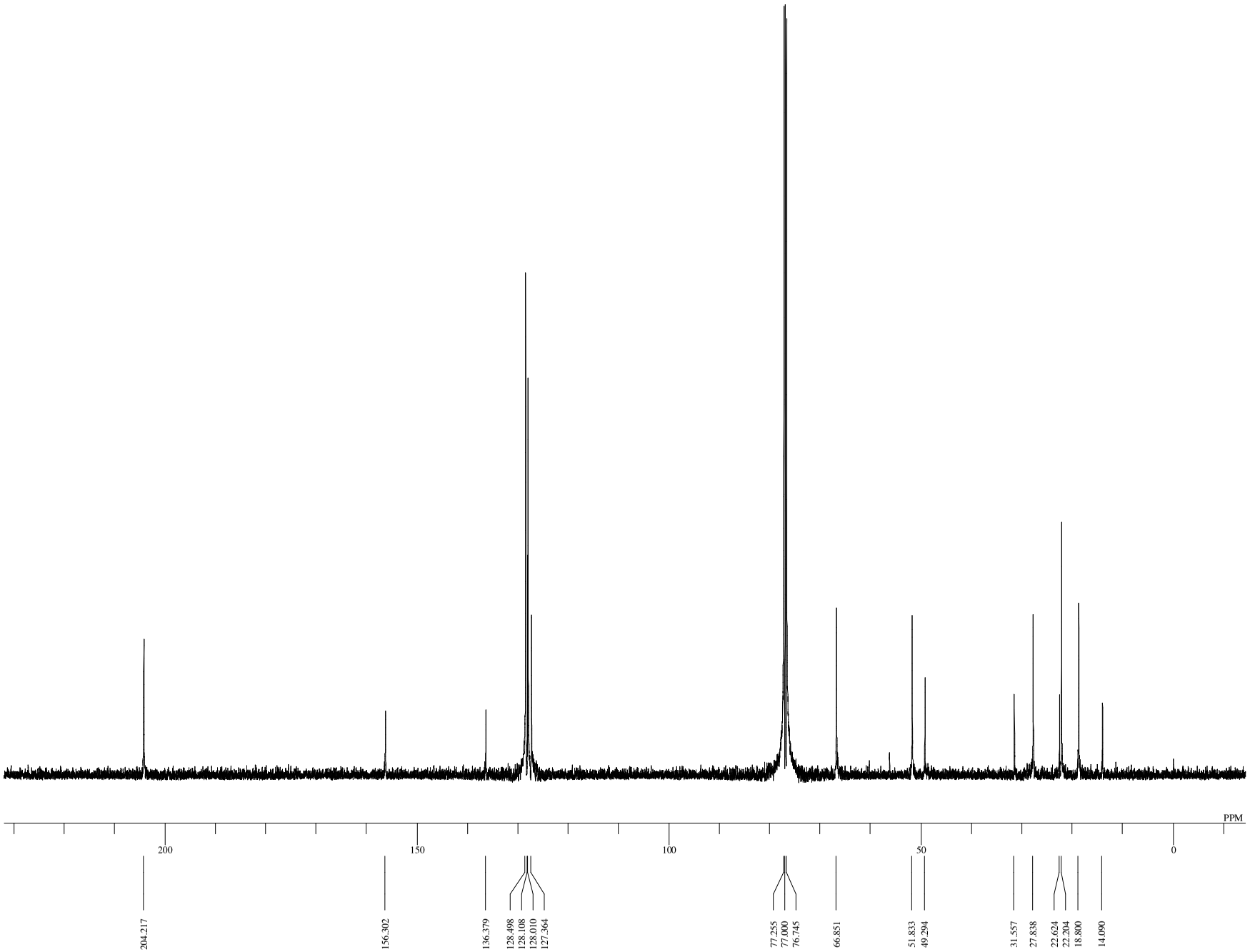
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PD 1.9416 sec
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CTEMP 25.2 c
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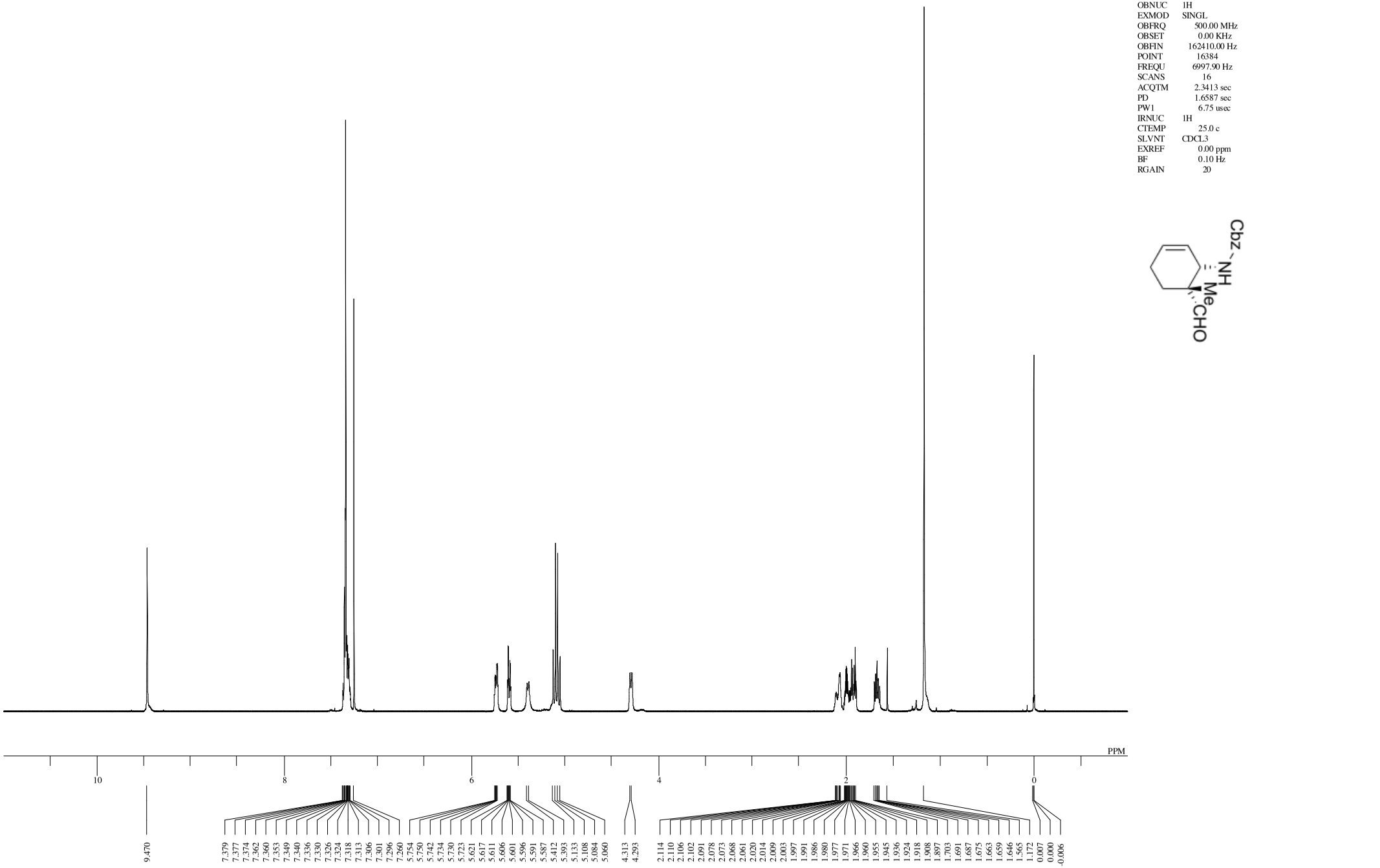
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PW1 6.75 usec
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CTEMP 25.0 c
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BF 0.10 Hz
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Cbz
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Me
CHO
PPM
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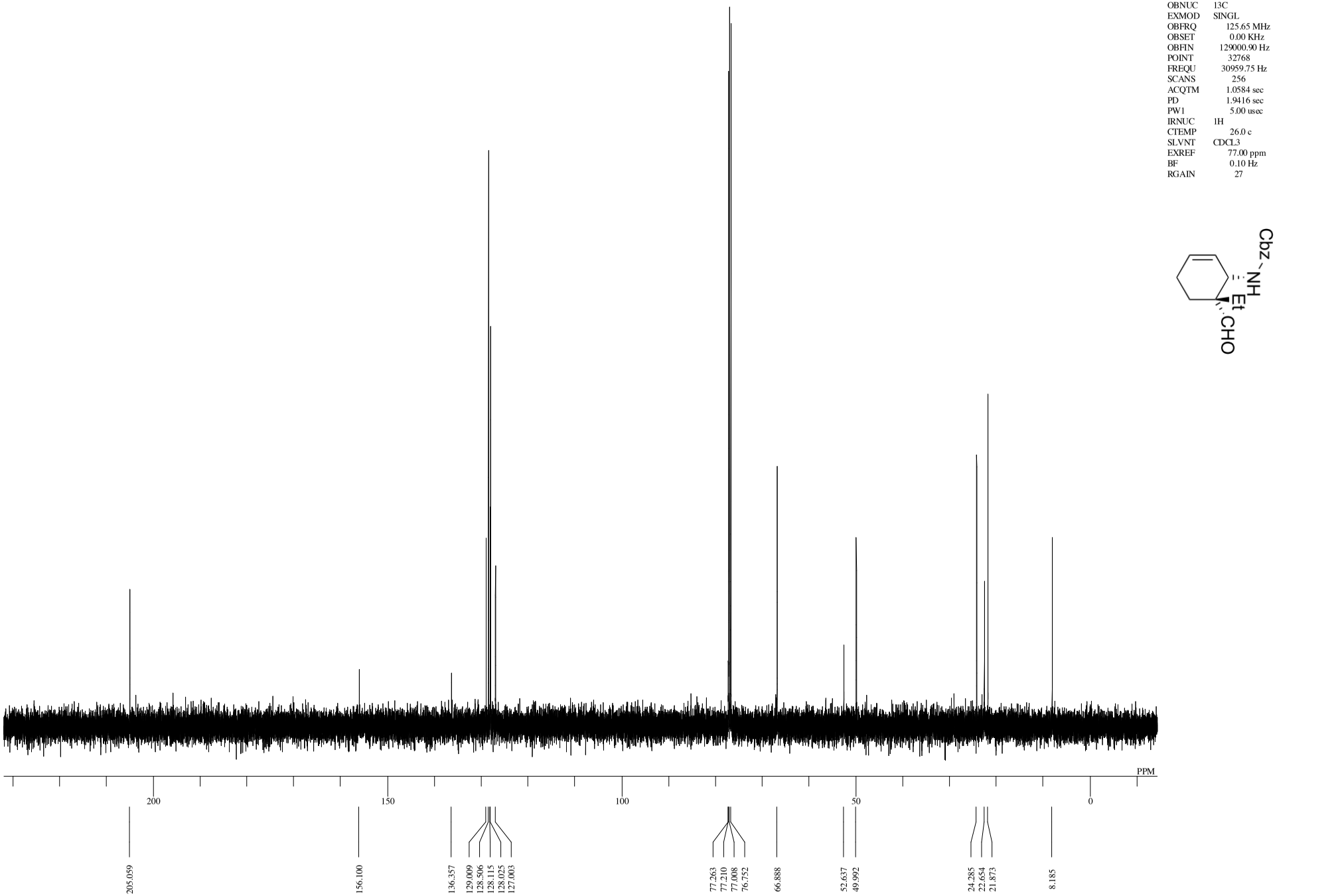
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PD 1.9416 sec
PW1 5.00 usec
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BF 0.10 Hz
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PPM
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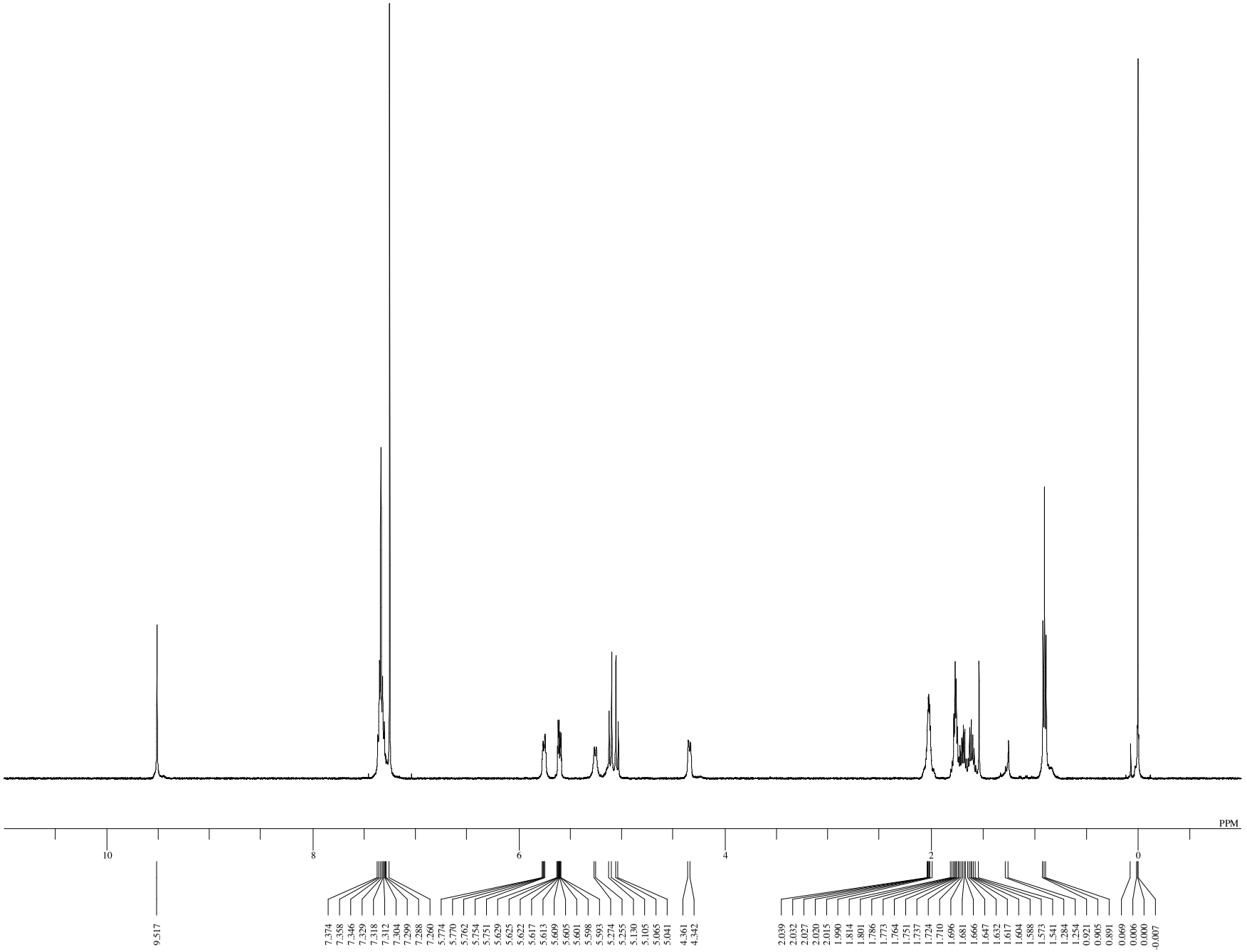
21.873
8.185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EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 24.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 24
Cbz
NH
Et
CHO
PPM
10
8
6
4
2
0
9.517
7.374
7.358
7.346
7.329
7.318
7.312
7.304
7.299
7.288
7.260
5.774
5.770
5.762
5.754
5.751
5.629
5.625
5.622
5.617
5.613
5.609
5.605
5.601
5.598
5.593
5.274
5.255
5.130
5.105
5.065
5.041
4.361
4.342
2.039
2.032
2.027
2.020
2.015
1.990
1.814
1.801
1.786
1.773
1.764
1.751
1.737
1.724
1.710
1.696
1.681
1.666
1.647
1.632
1.617
1.604
1.588
1.573
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1.284
1.254
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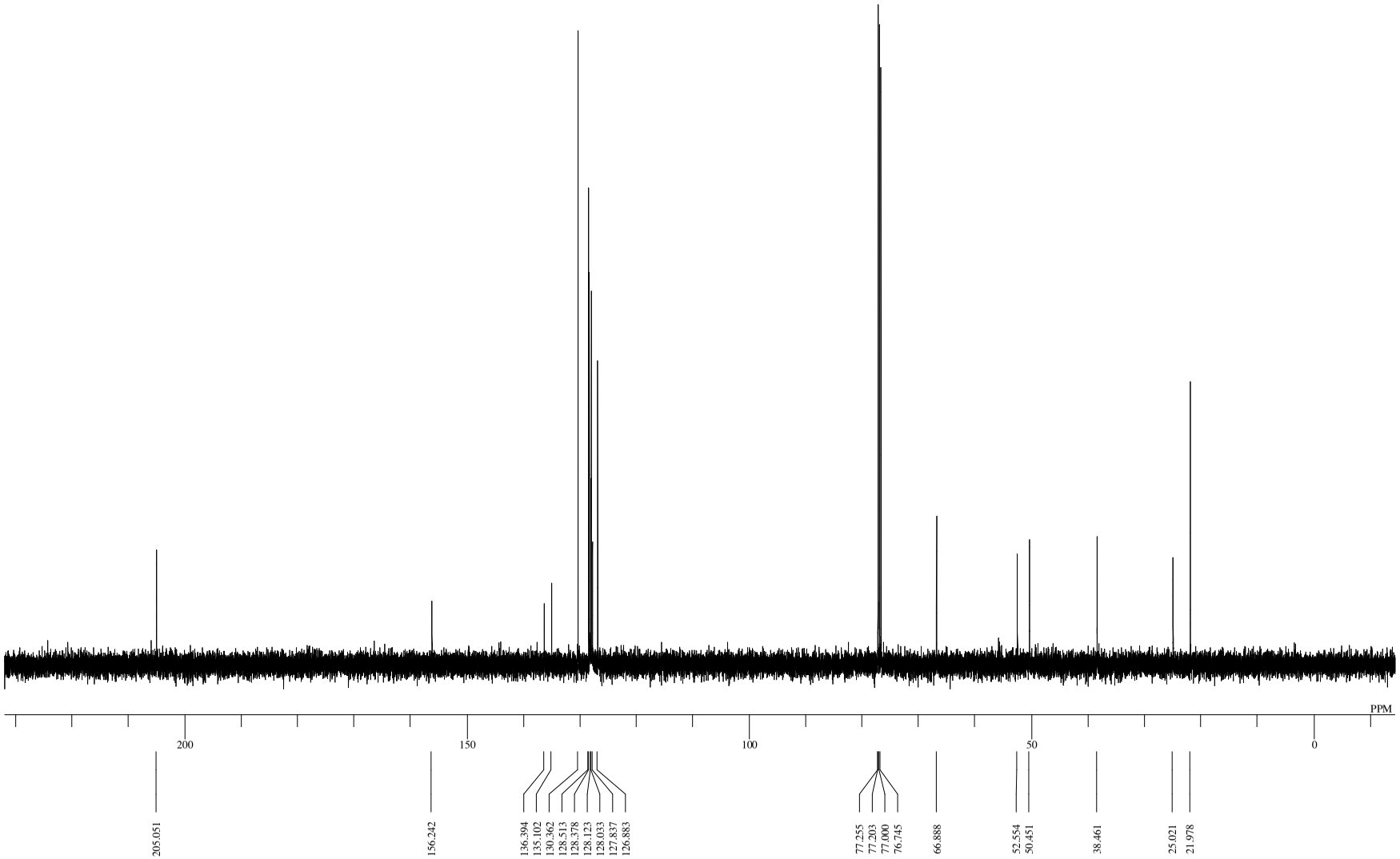
0.905
0.891
0.069
0.006
0.000
-0.007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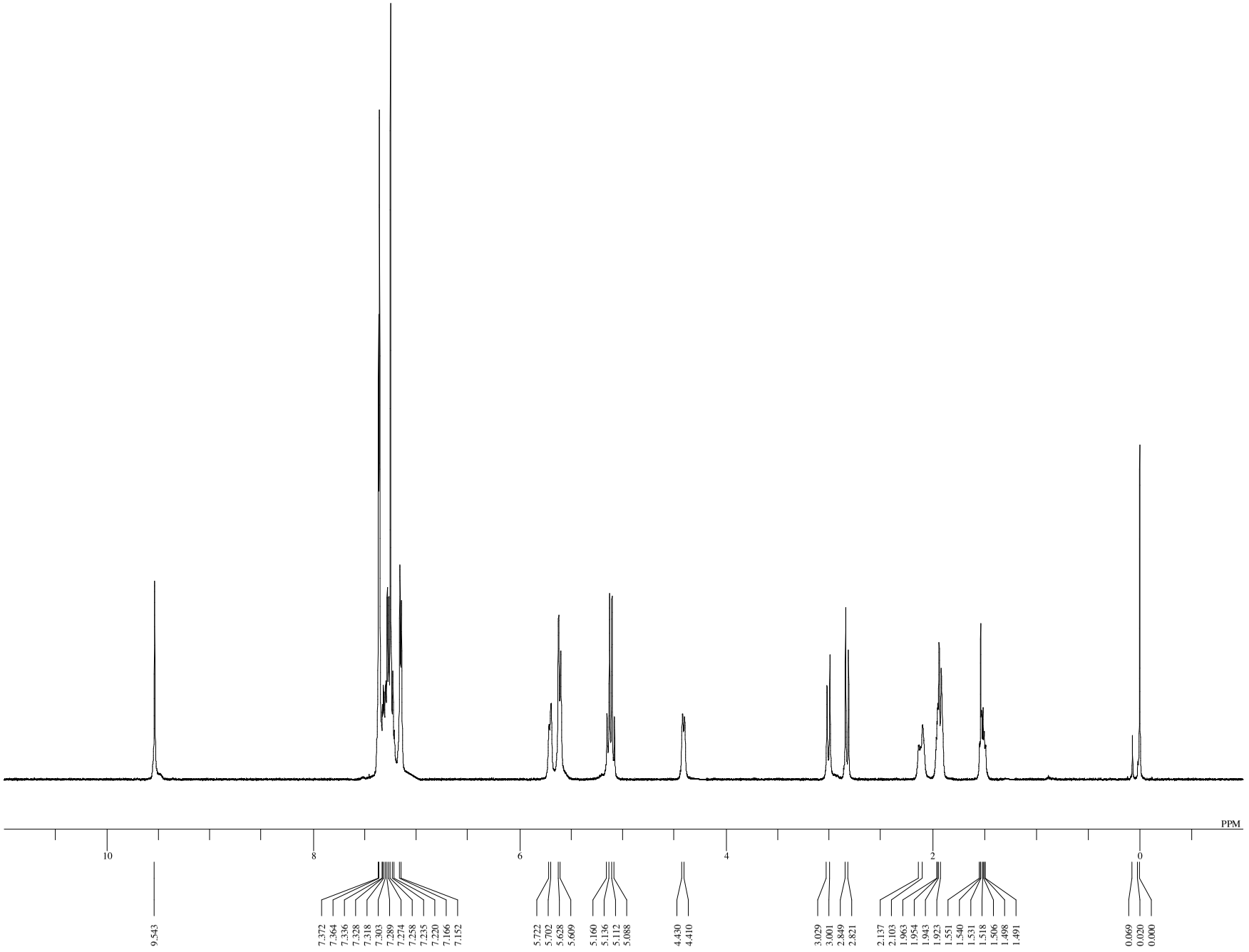
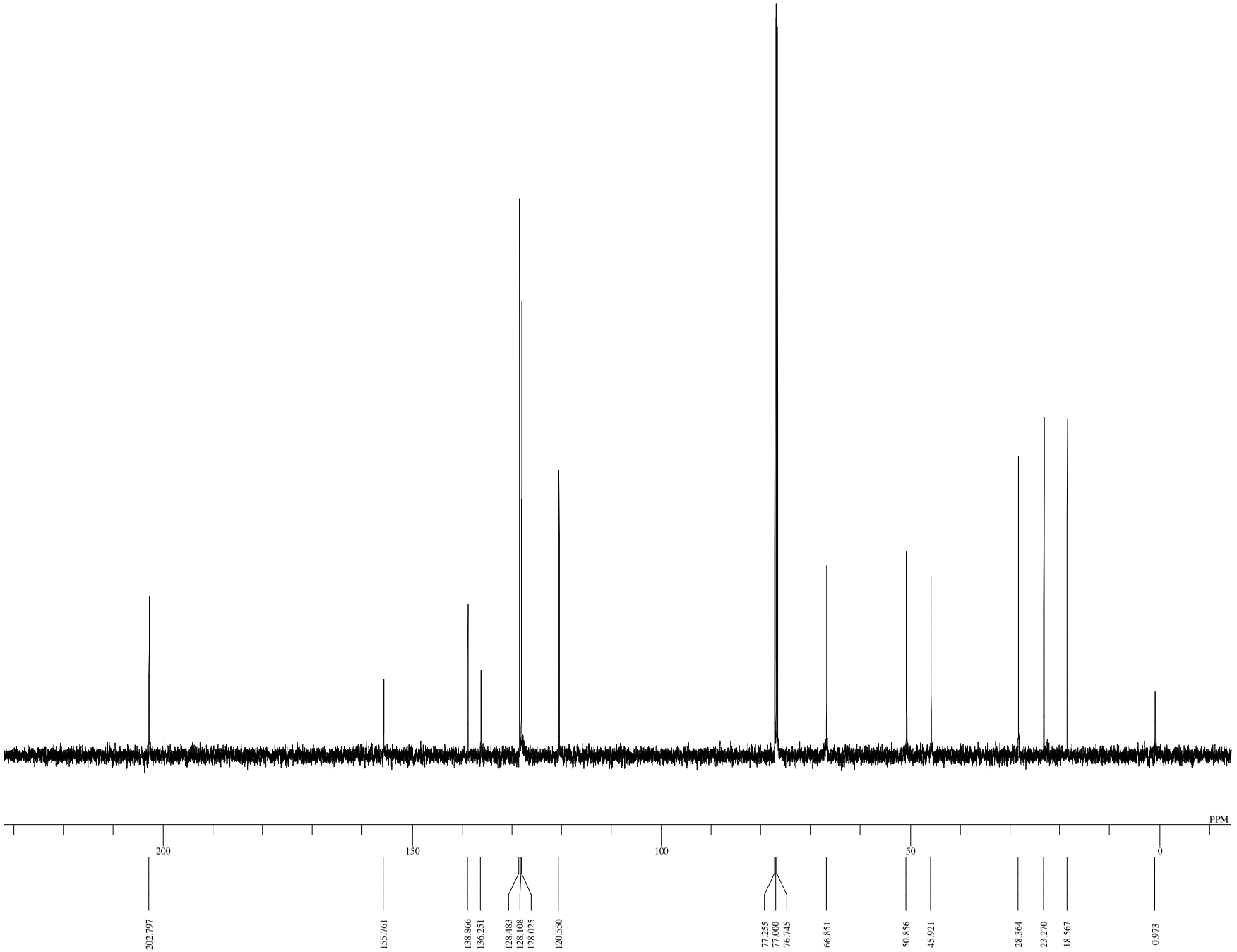
DATIM Tue Dec 07 19:58:10 2010
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 256
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 28
Cbz
NH
Bn
CHO
PPM
200
150
100
50
0
205.051
156.242
136.394
135.102
130.362
128.513
128.378
128.123
128.033
127.837
126.883
77.255
77.203
77.000
76.745
66.888
52.554
50.451
38.461
25.021
21.978


DFILE E:\Group C\¡¬i\NMR\101021-\ex552 P.als
COMNT
DATIM Tue Dec 07 19:37:48 2010
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 22
Cbz
NH
Bn
CHO
PPM
10
8
6
4
2
0
9.543
7.372
7.364
7.336
7.328
7.318
7.303
7.289
7.274
7.258
7.235
7.220
7.166
7.152
5.722
5.702
5.628
5.609
5.160
5.136
5.112
5.088
4.430
4.410
3.029
3.001
2.849
2.821
2.137
2.103
1.963
1.954
1.943
1.923
1.551
1.540
1.531
1.518
1.506
1.498
1.491
0.069
0.020
0.000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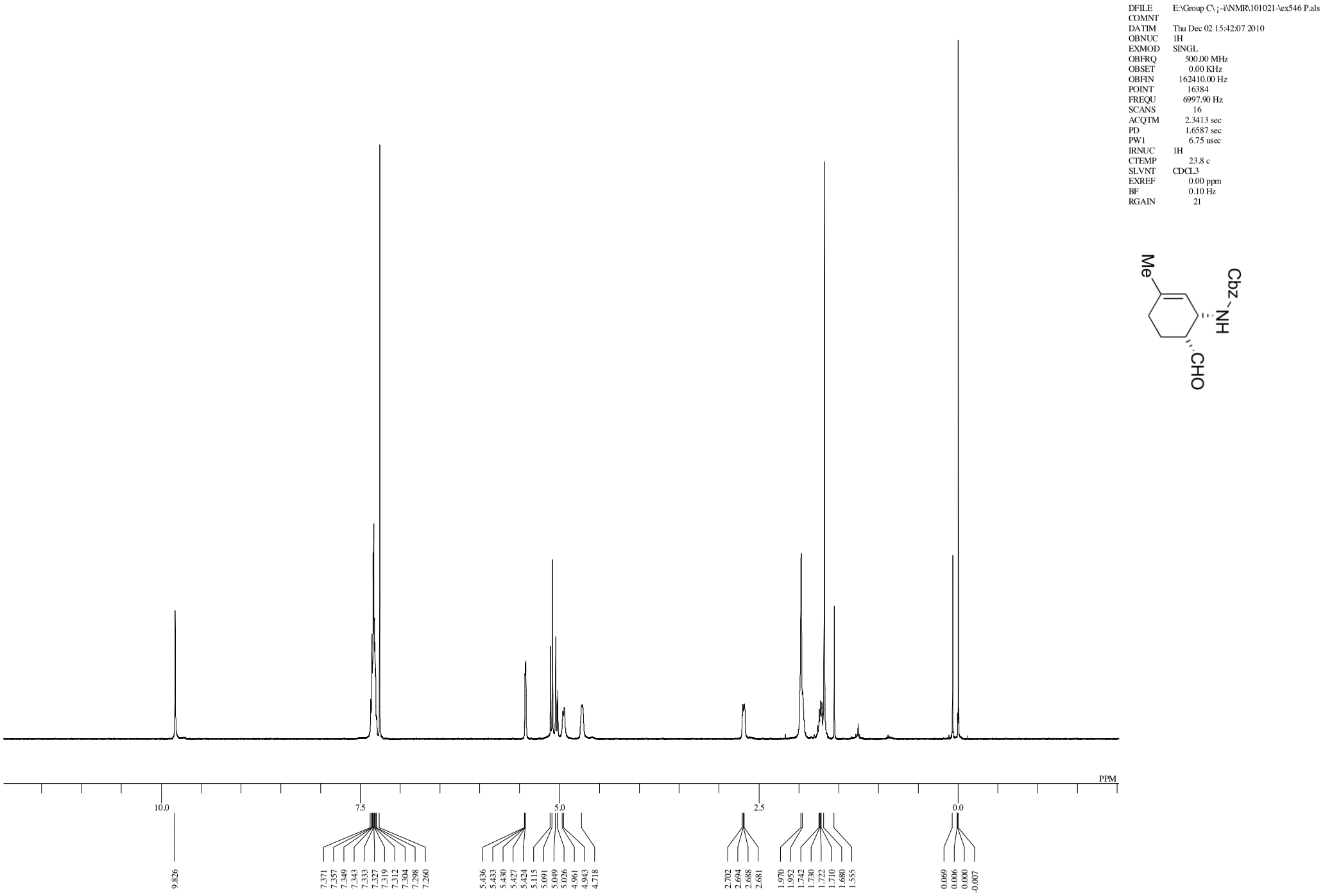
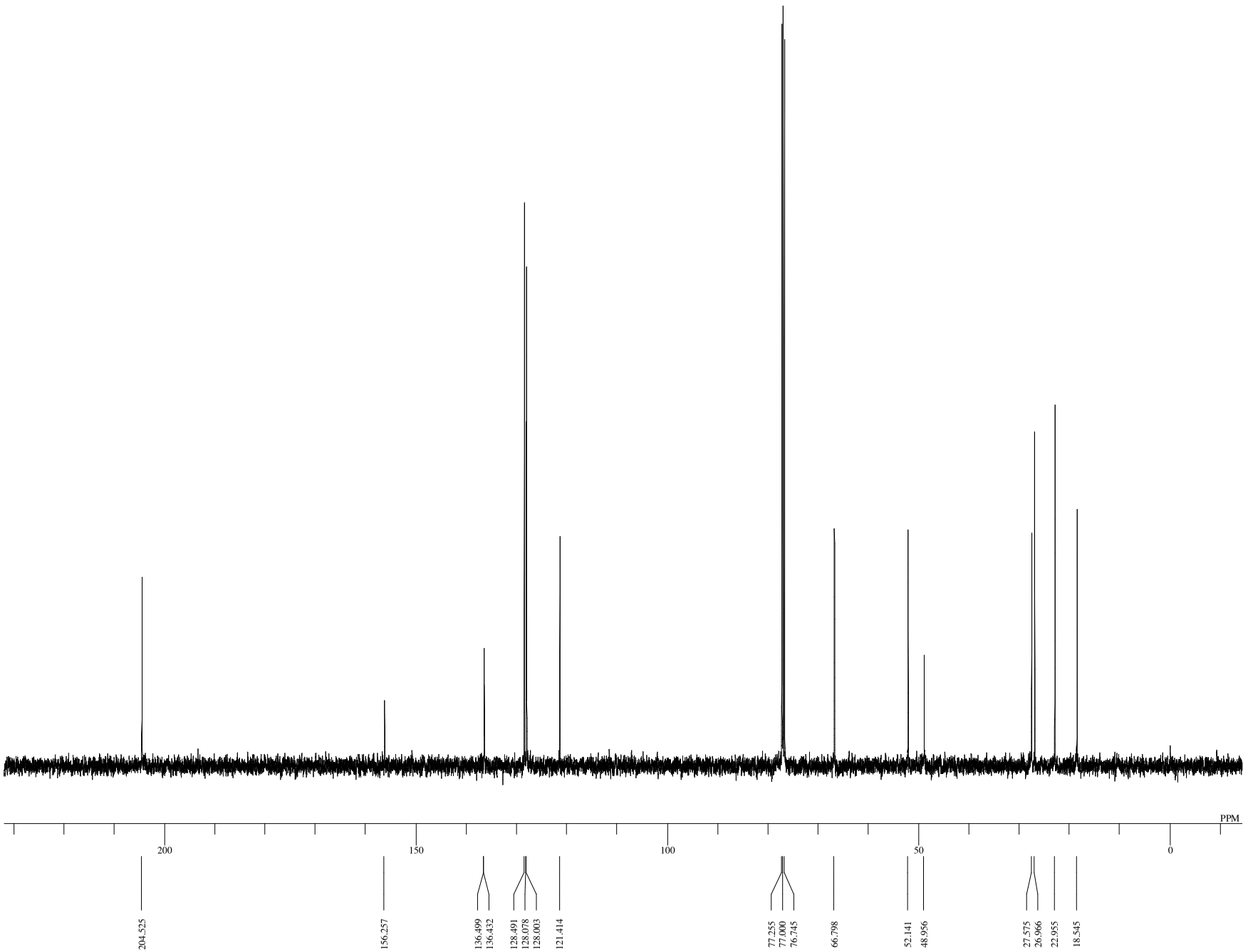
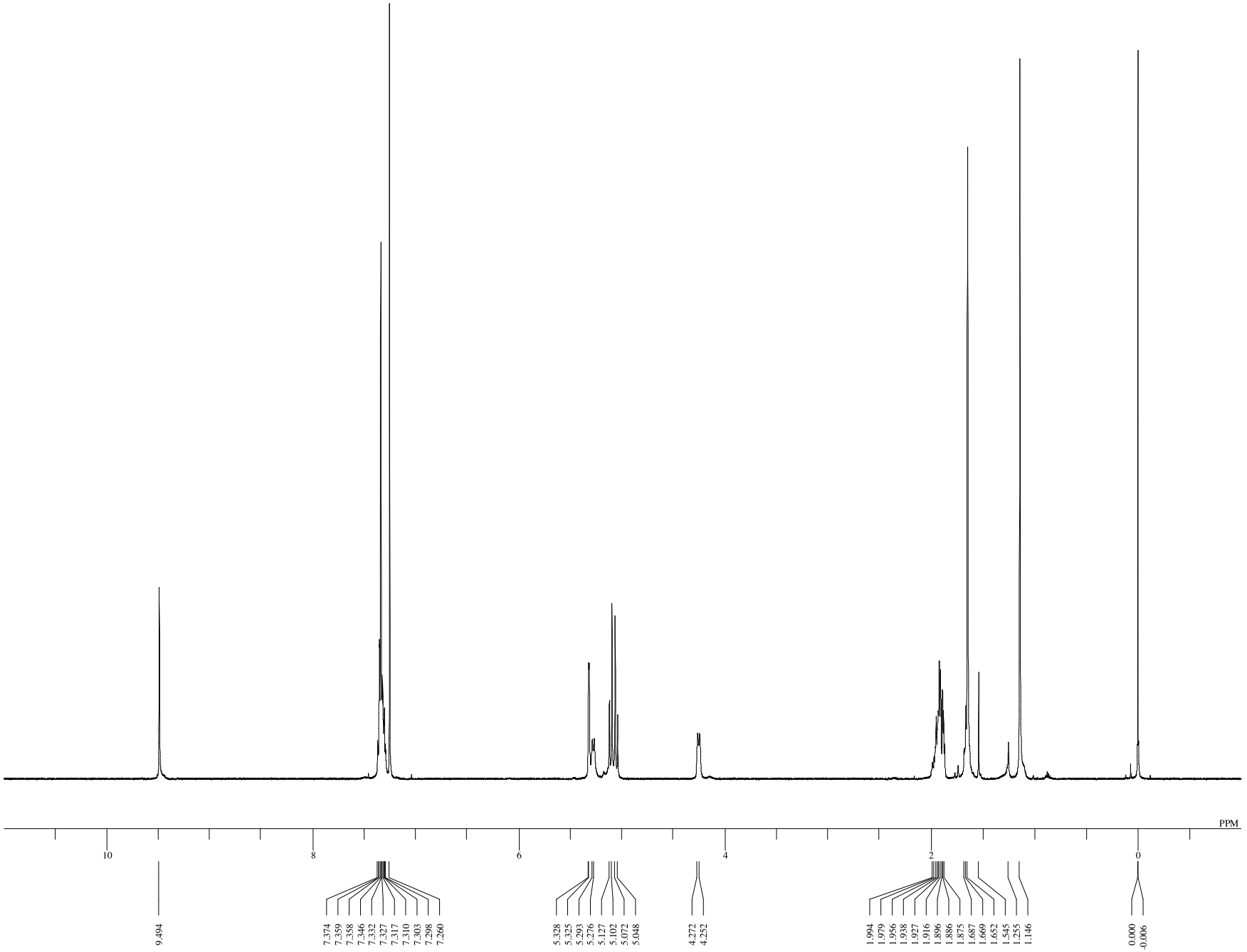
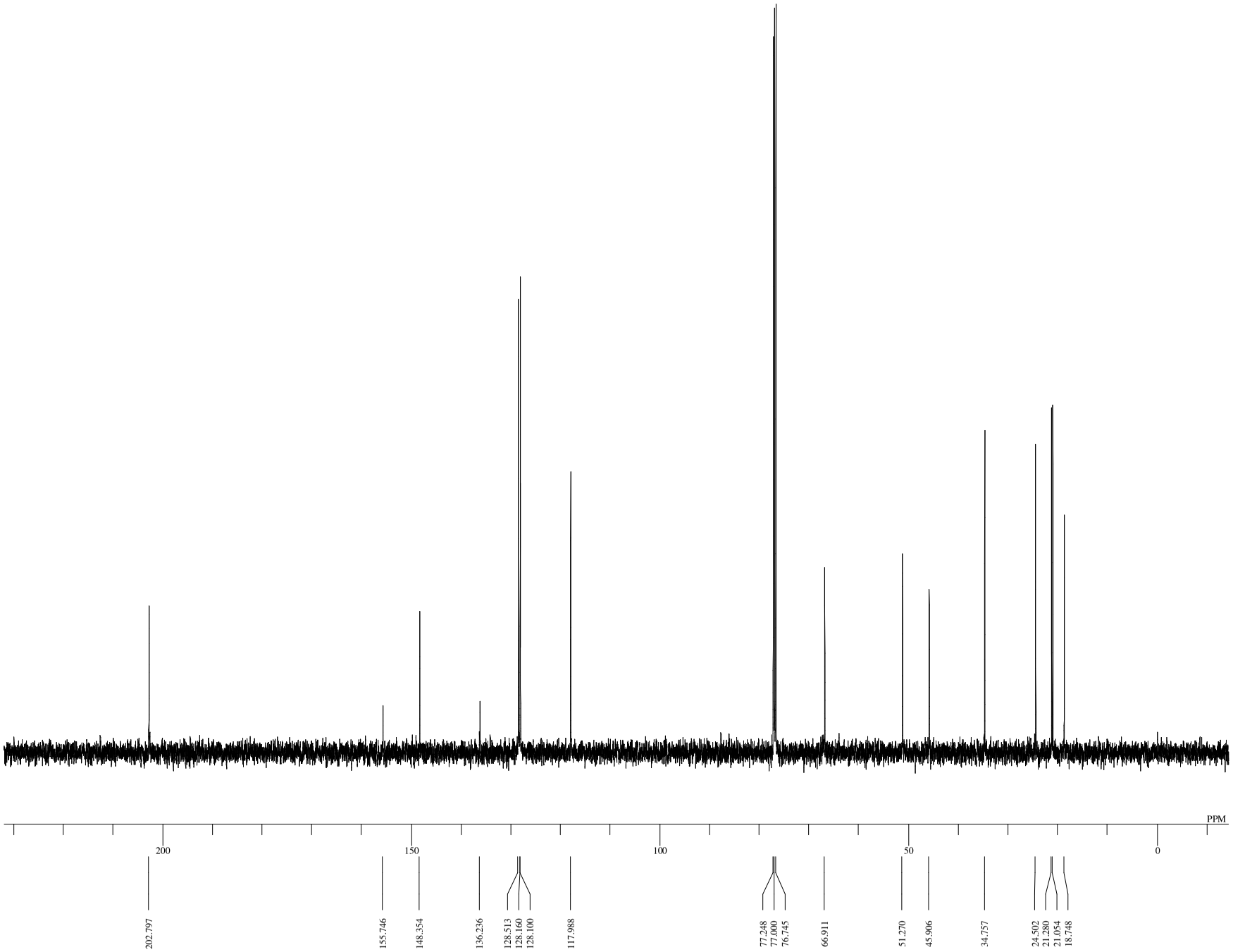
COMNT
DATIM Thu Dec 02 18:06:13 2010
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 256
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
Me
Cbz
NH
CHO
PPM
200
150
100
50
0
202.797
155.761
138.866
136.251
128.483
128.108
128.025
120.550
77.255
77.000
76.745
66.851
50.856
45.921
28.364
23.270
18.567
0.973


DFILE E:\Group C\ ¡-i\NMR\101021-\ex546 P.als
COMNT
DATIM Thu Dec 02 15:42:07 2010
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 21
Me
Cbz
NH
CHO
PPM
10.0
7.5
5.0
2.5
0.0
9.826
7.371
7.357
7.349
7.343
7.333
7.327
7.319
7.312
7.304
7.298
7.260
5.436
5.433
5.430
5.427
5.424
5.115
5.091
5.049
5.026
4.961
4.943
4.718
2.702
2.694
2.688
2.681
1.970
1.952
1.742
1.730
1.722
1.710
1.680
1.555
0.069
0.006
0.000
-0.007


DFILE E:\Group C\ ¡¬i\NMR\carbon\ex587 Me.als
COMNT
DATIM Tue Feb 01 18:20:45 2011
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 256
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
Me
Cbz
NH
Me
CHO
PPM
200
150
100
50
0
204.525
156.257
136.499
136.432
128.491
128.078
128.003
121.414
77.255
77.000
76.745
66.798
52.141
48.956
27.575
26.966
22.955
18.545


DFILE E:\Group C\¡¬i\NMR\101021-\ex587 Me P.als
COMNT
DATIM Tue Feb 01 15:04:35 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 25.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 22
Me
Cbz
NH
Me
CHO
PPM
10
8
6
4
2
0
9.494
7.374
7.359
7.358
7.346
7.332
7.327
7.317
7.310
7.303
7.298
7.260
5.328
5.325
5.293
5.276
5.127
5.102
5.072
5.048
4.272
4.252
1.994
1.979
1.956
1.938
1.927
1.916
1.896
1.886
1.875
1.687
1.669
1.652
1.545
1.255
1.146
0.000
-0.006


DFILE E:\Group C\ ¡–i\NMR\carbon\Cbz(i-Pr)-acrolein.als
COMNT
DATIM Fri Feb 18 15:14:20 2011
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 160
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
i-Pr
Cbz
NH
CHO
PPM
200
150
100
50
0
202.797
155.746
148.354
136.236
128.513
128.160
128.100
117.988
77.248
77.000
76.745
66.911
51.270
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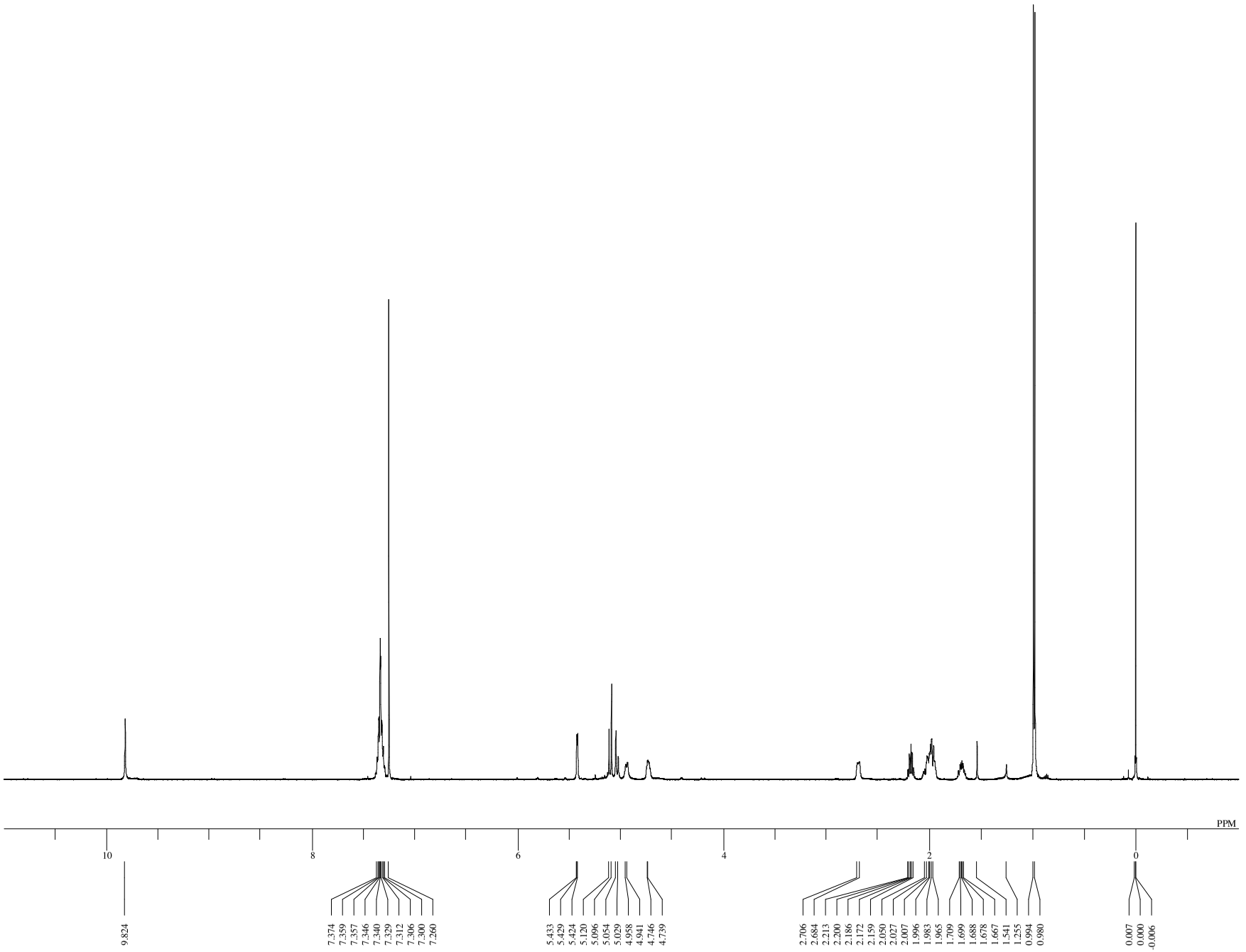
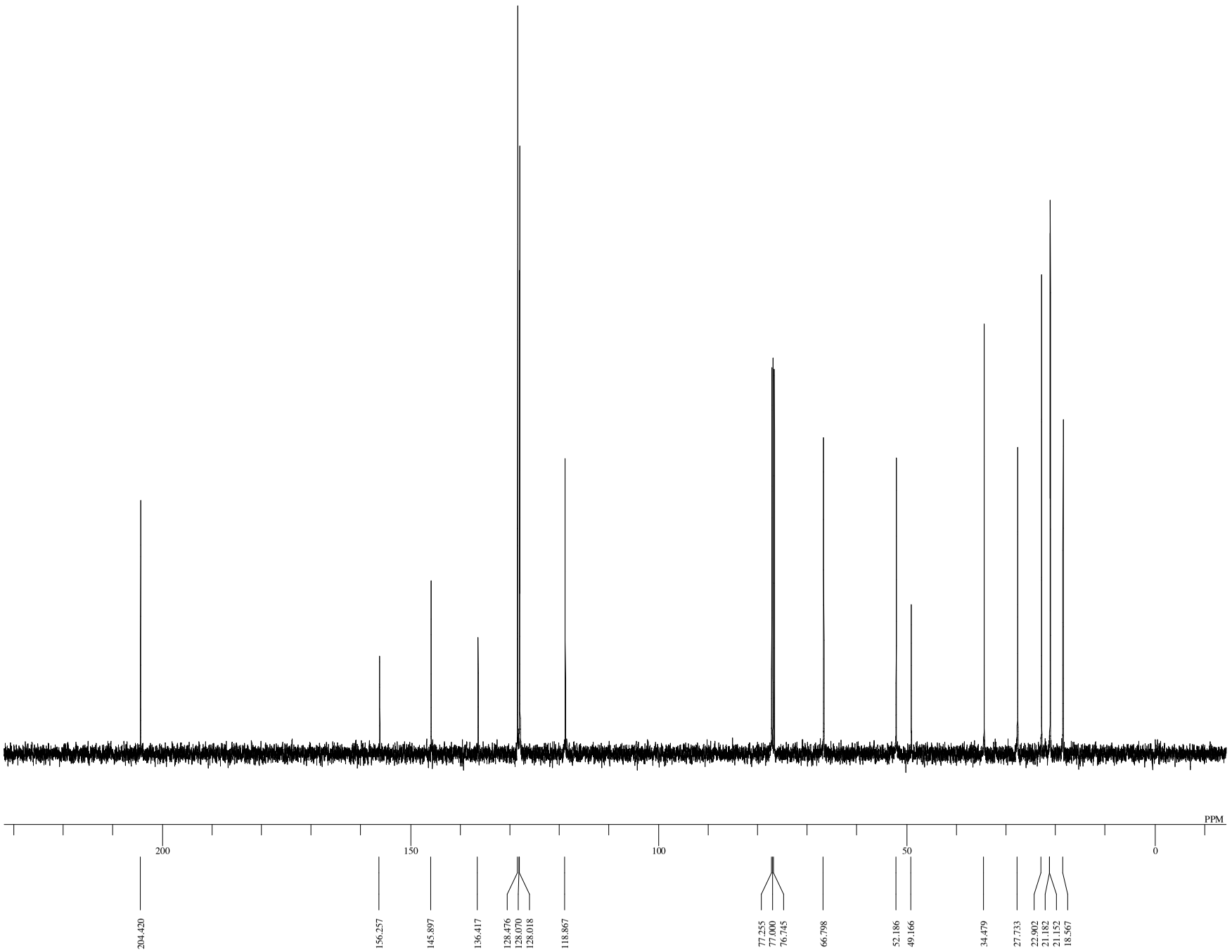
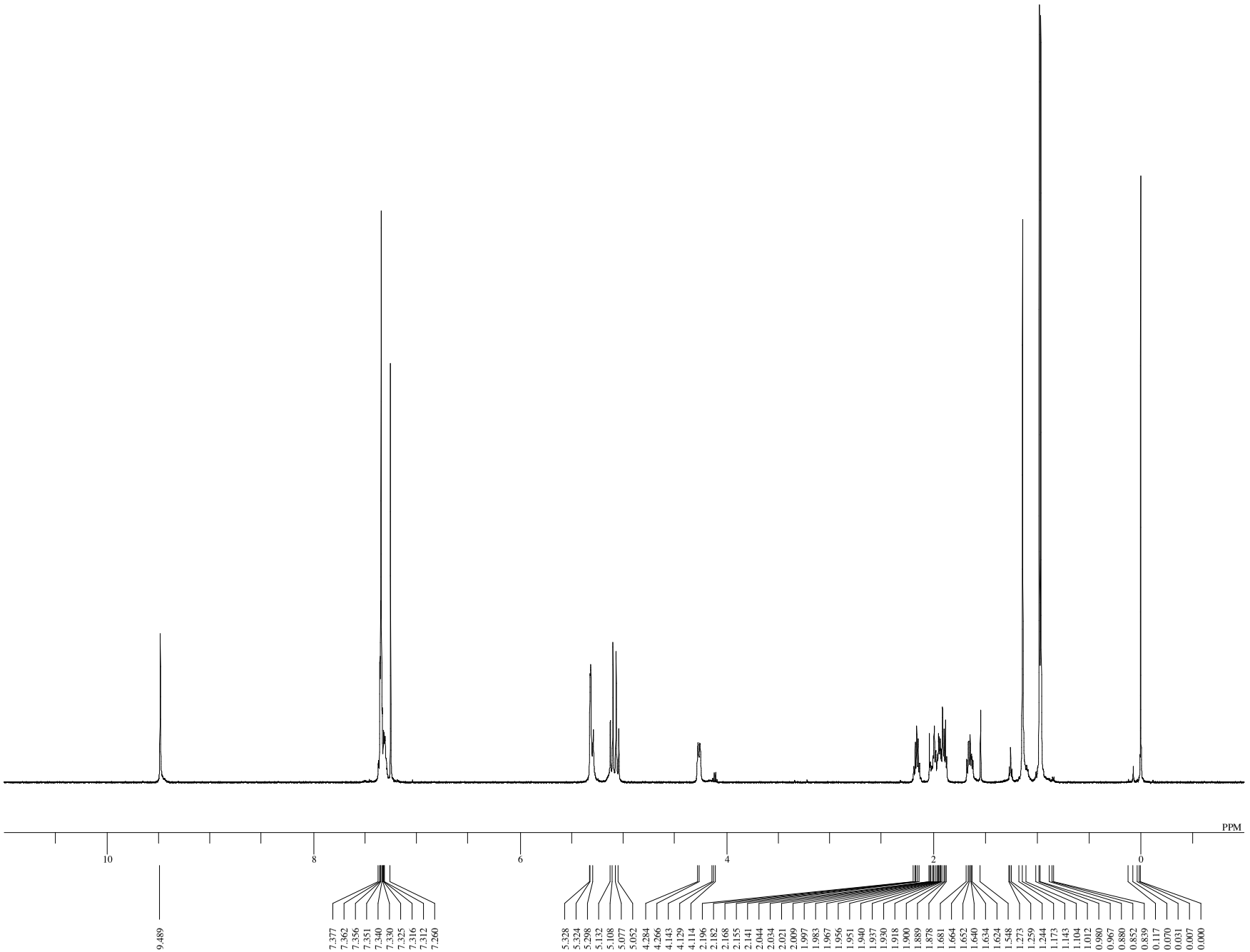
34.757
24.502
21.280
21.054
18.748


DFILE E:\Group C\ ¡–i\NMR\101021-\ex591 i-Pr data.als
COMNT
DATIM Thu Feb 17 21:13:24 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 23
i-Pr
Cbz
NH
CHO
PPM
10
8
6
4
2
0
9.824
7.374
7.359
7.357
7.346
7.340
7.329
7.312
7.306
7.300
7.260
5.433
5.429
5.424
5.120
5.096
5.054
5.029
4.958
4.941
4.746
4.739
2.706
2.684
2.213
2.200
2.186
2.172
2.159
2.050
2.027
2.007
1.996
1.983
1.965
1.709
1.699
1.688
1.678
1.667
1.541
1.255
0.994
0.980
0.007
0.000
-0.006


DFILE E:\Group C\ ¡–i\NMR\carbon\ex578 i-Pr.als
COMNT
DATIM Wed Jan 26 21:04:01 2011
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 120
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
i-Pr
Cbz
NH
Me
CHO
PPM
200
150
100
50
0
204.420
156.257
145.897
136.417
128.476
128.070
128.018
118.867
77.255
77.000
76.745
66.798
52.186
49.166
34.479
27.733
22.902
21.182
21.152
18.567


DFILE E:\Group C\ ¡–i\NMR\101021-\ex587 i-Pr P.als
COMNT
DATIM Tue Feb 01 14:20:26 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 8
ACQTM 2.3413 sec
PD 0.9040 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 21
i-Pr
Cbz
NH
Me
CHO
PPM
10
8
6
4
2
0
9.489
7.377
7.362
7.356
7.351
7.340
7.330
7.325
7.316
7.312
7.260
5.328
5.324
5.298
5.132
5.108
5.077
5.052
4.284
4.266
4.143
4.129
4.114
2.196
2.182
2.168
2.155
2.141
2.044
2.034
2.021
2.009
1.997
1.983
1.967
1.956
1.951
1.940
1.937
1.930
1.918
1.900
1.889
1.878
1.681
1.664
1.652
1.640
1.634
1.624
1.548
1.273
1.259
1.244
1.173
1.143
1.104
1.012
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0.967
0.880
0.852
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0.117
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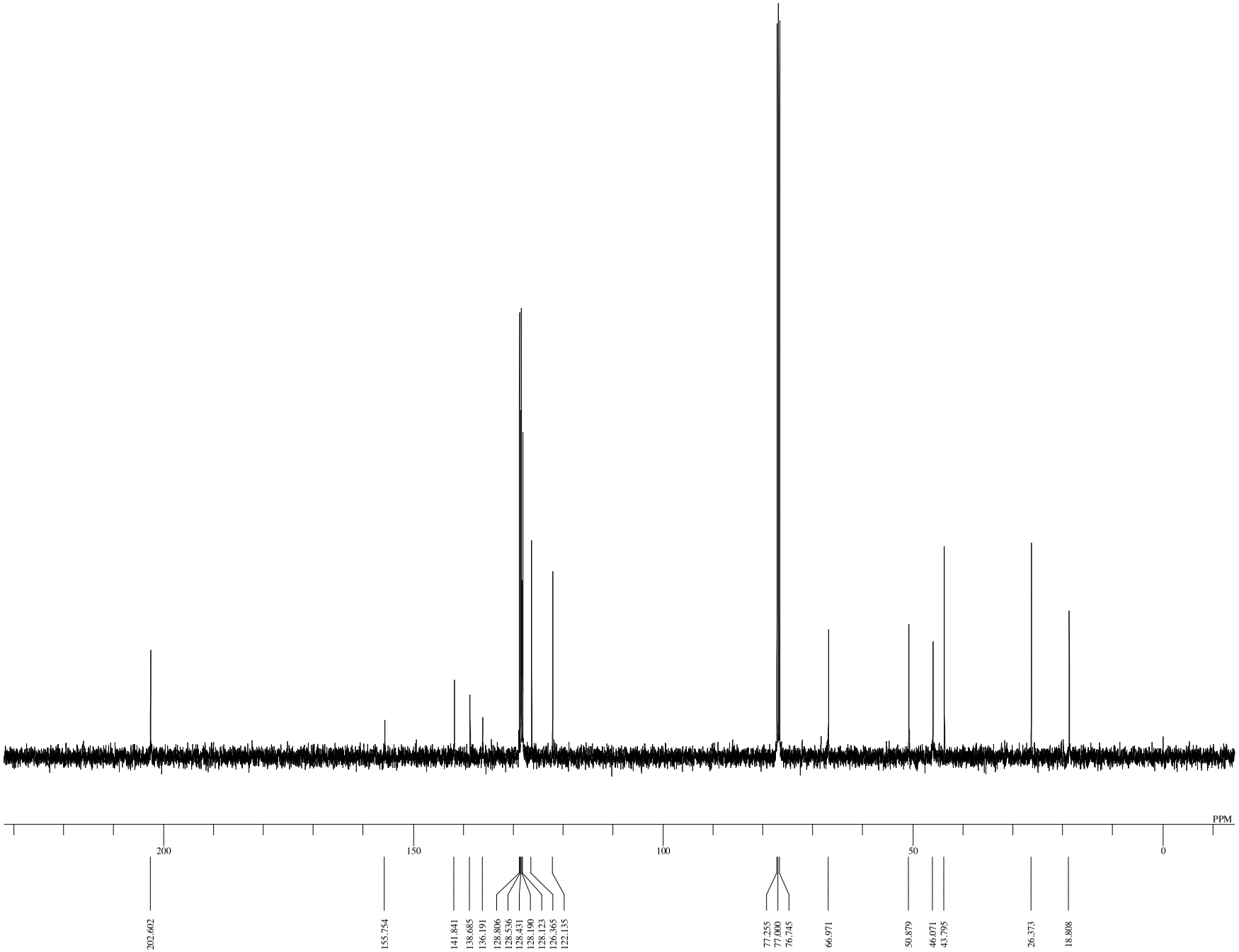
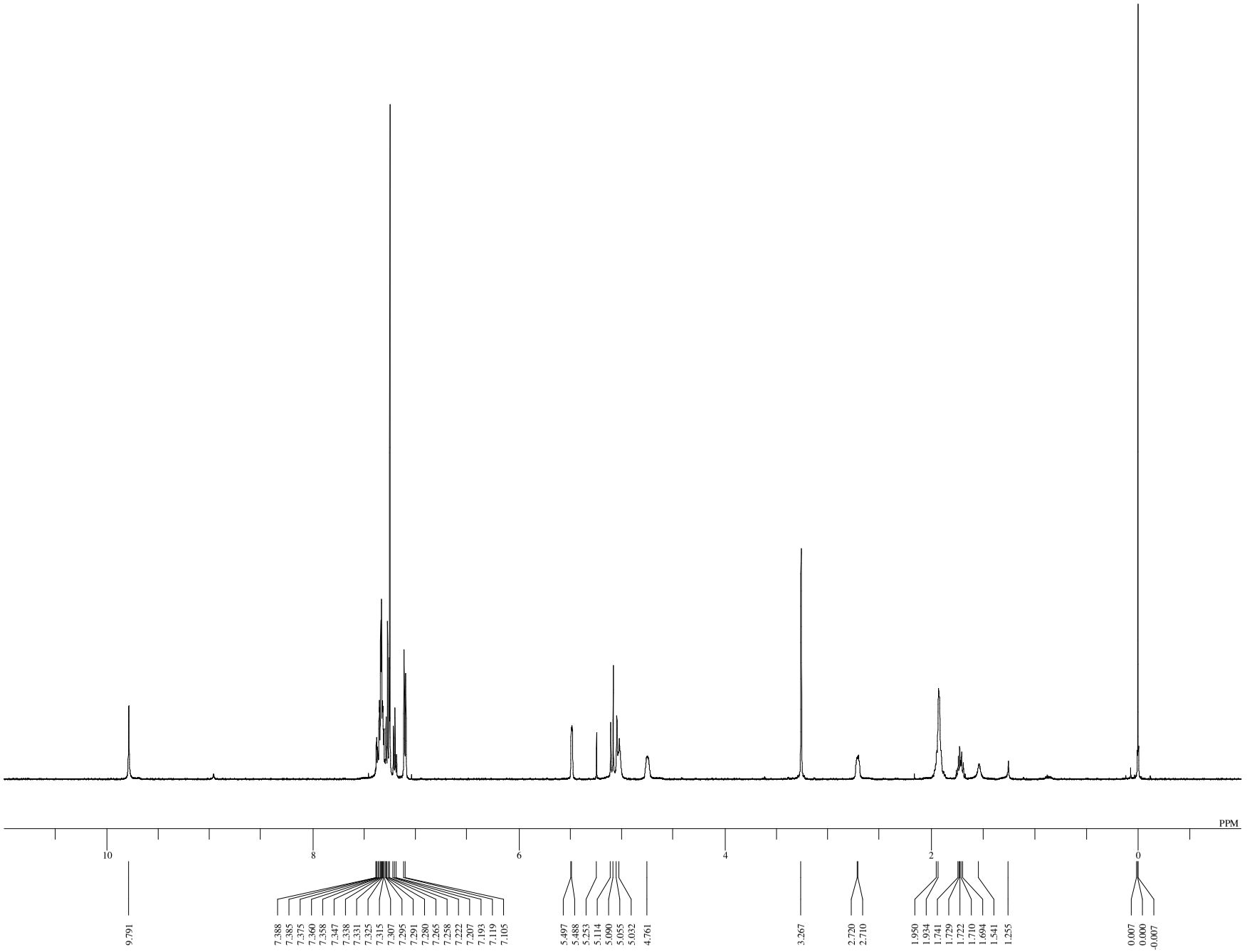
0.007
0.000


DFILE E:\Group C\ ¡–i\NMR\carbon\Cbz(Bn)-acrolein.als
COMNT
DATIM Fri Feb 18 15:30:48 2011
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 200
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 24.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
Bn
Cbz
NH
CHO
PPM
200
150
100
50
0
202.602
155.754
141.841
138.685
136.191
128.806
128.536
128.431
128.190
128.123
126.365
122.135
77.255
77.000
76.745
66.971
50.879
46.071
43.795
26.373
18.808


DFILE E:\Group C\ ¡–i\NMR\101021-\ex591 Bn.als
COMNT
DATIM Thu Feb 17 21:24:21 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 16
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 23
Bn
Cbz
NH
CHO
PPM
10
8
6
4
2
0
9.791
7.388
7.385
7.375
7.360
7.358
7.347
7.338
7.331
7.325
7.315
7.307
7.295
7.291
7.280
7.265
7.258
7.222
7.207
7.193
7.119
7.105
5.497
5.488
5.253
5.114
5.090
5.055
5.032
4.761
3.267
2.720
2.710
1.950
1.934
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1.729
1.722
1.710
1.694
1.541
1.255
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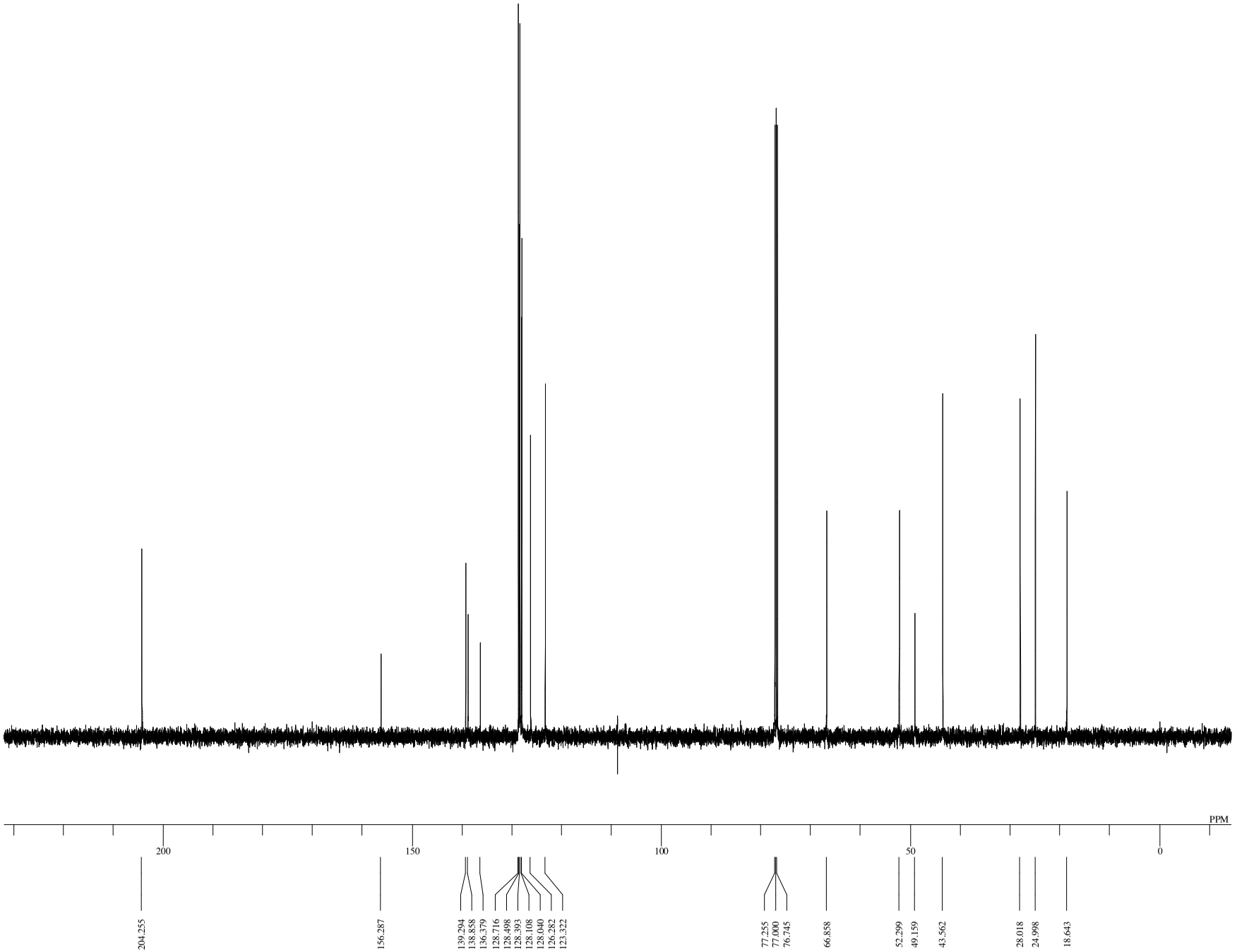
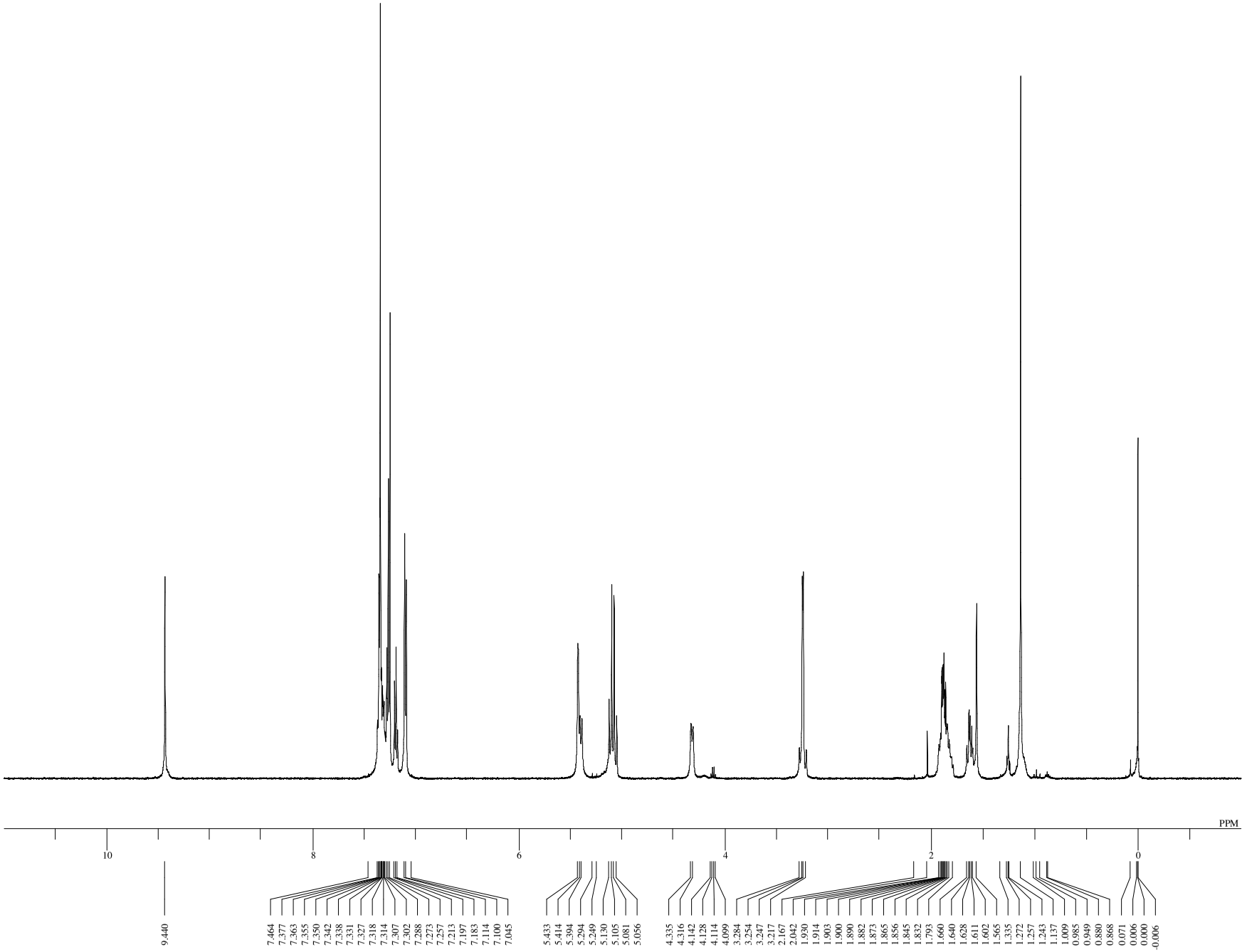

DFILE E:\Group C\ ¡–i\NMR\carbon\ex578 Bn.als
COMNT
DATIM Wed Jan 26 20:53:24 2011
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 206
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 28
Bn
Cbz
NH
Me
CHO
PPM
200
150
100
50
0
204.255
156.287
139.294
138.858
136.379
128.716
128.498
128.393
128.108
128.040
126.282
123.322
77.255
77.000
76.745
66.858
52.299
49.159
43.562
28.018
24.998
18.643


DFILE E:\Group C\ ¡–i\NMR\101021-\ex578 Bn P.als
COMNT
DATIM Wed Jan 26 10:31:28 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 8
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 25.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 20
Bn
Cbz
NH
Me
CHO
PPM
10
8
6
4
2
0
9.440
7.464
7.377
7.363
7.355
7.350
7.342
7.338
7.331
7.327
7.318
7.314
7.307
7.302
7.288
7.273
7.257
7.213
7.197
7.183
7.114
7.100
7.045
5.433
5.414
5.394
5.294
5.249
5.130
5.105
5.081
5.056
4.335
4.316
4.142
4.128
4.114
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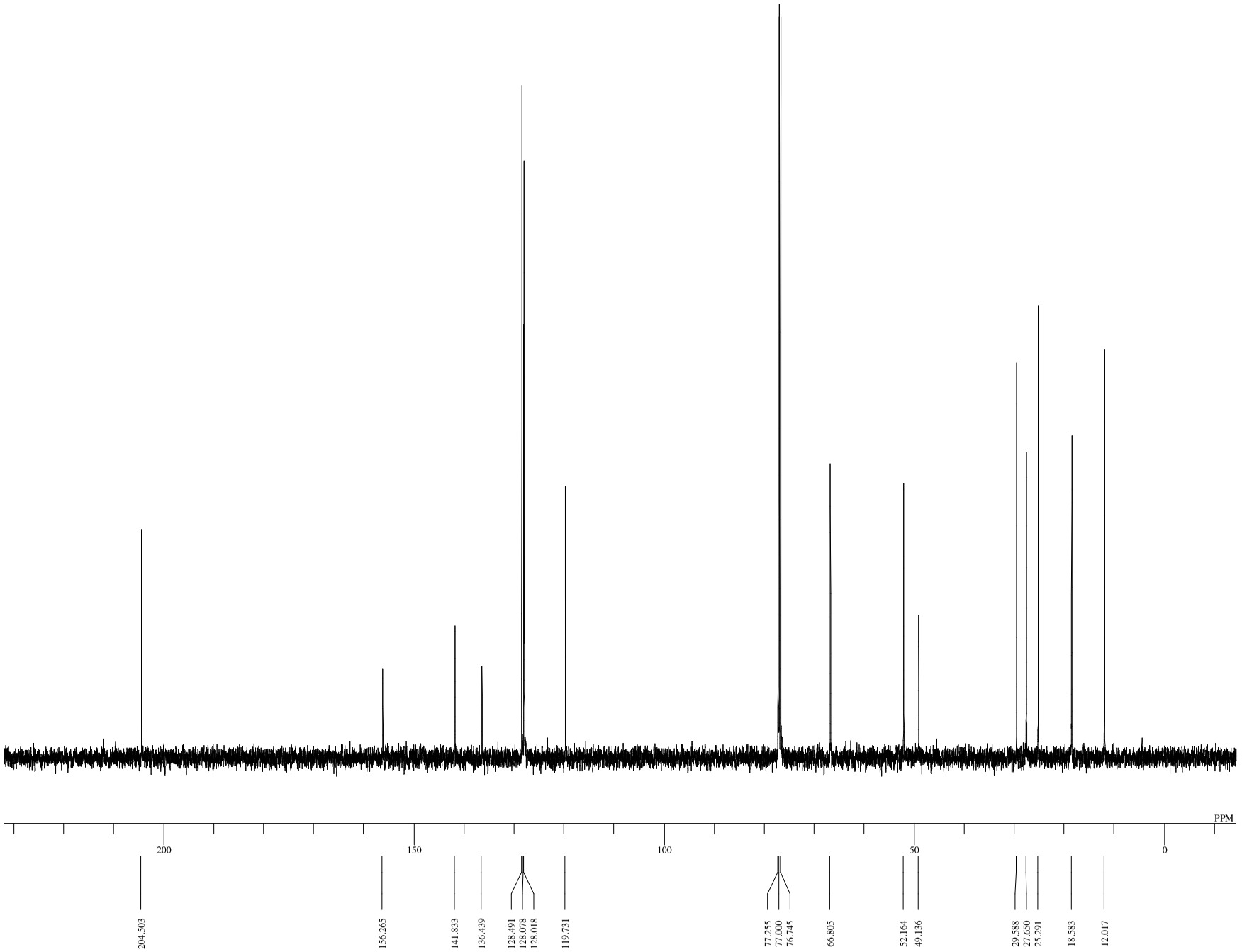
3.284
3.254
3.247
3.217
2.167
2.042
1.930
1.914
1.903
1.900
1.890
1.882
1.873
1.865
1.856
1.845
1.832
1.793
1.660
1.640
1.628
1.611
1.602
1.565
1.335
1.272
1.257
1.243
1.137
1.009
0.985
0.949
0.880
0.868
0.071
0.006
0.000
-0.006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DATIM Wed Jan 26 21:19:07 2011
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OBSET 0.00 KHz
OBFIN 129000.90 Hz
POINT 32768
FREQU 30959.75 Hz
SCANS 200
ACQTM 1.0584 sec
PD 1.9416 sec
PW1 5.00 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 28
Et
Cbz
NH
Me
CHO
PPM
200
150
100
50
0
204.503
156.265
141.833
136.439
128.491
128.078
128.018
119.731
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52.164
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25.291
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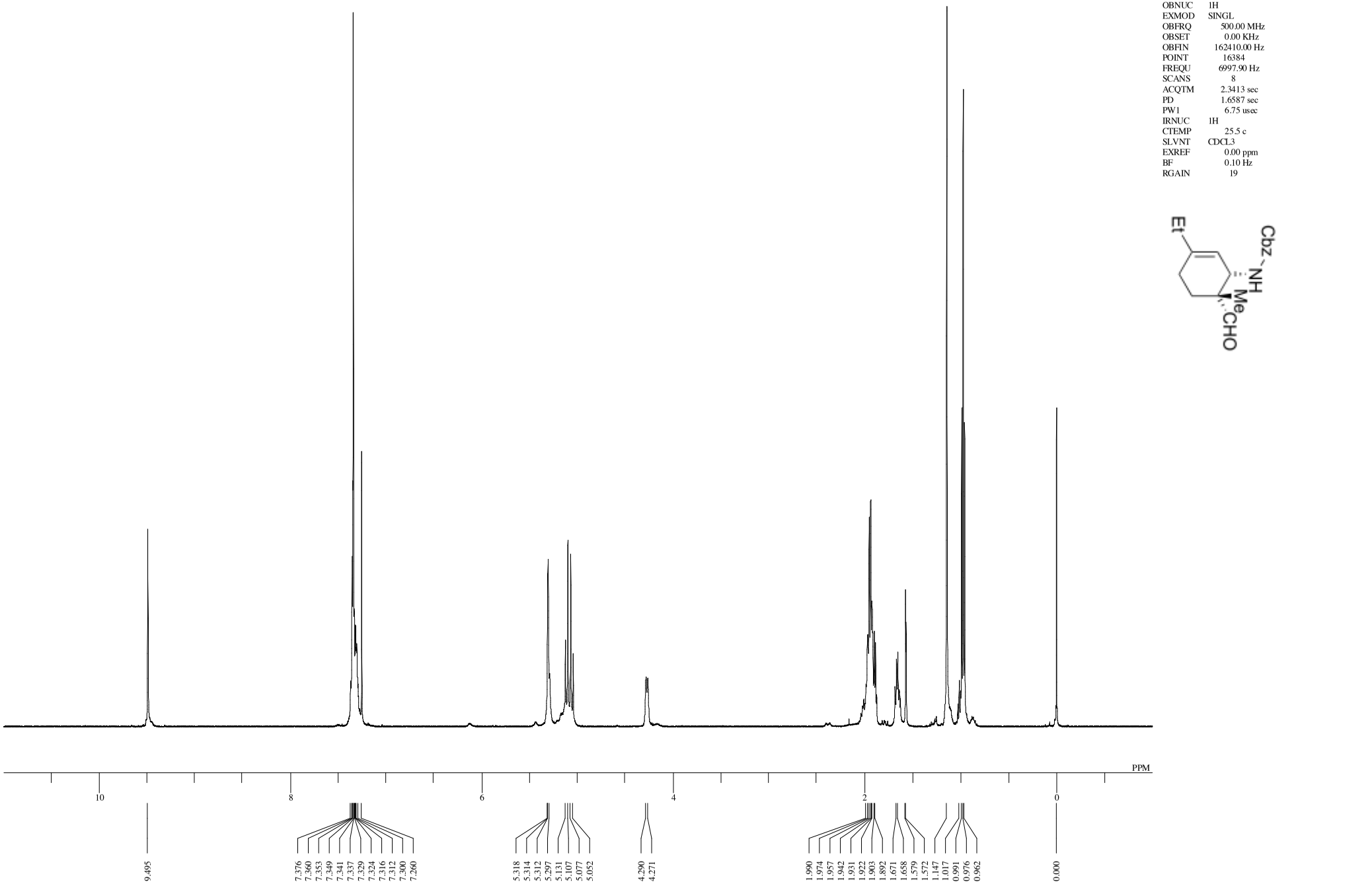
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COMNT
DATIM Tue Jan 25 16:47:42 2011
OBNUC 1H
EXMOD SINGL
OBFRQ 500.00 MHz
OBSET 0.00 KHz
OBFIN 162410.00 Hz
POINT 16384
FREQU 6997.90 Hz
SCANS 8
ACQTM 2.3413 sec
PD 1.6587 sec
PW1 6.75 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 19
Et
Cbz
NH
Me
CHO
PPM
10
8
6
4
2
0
9.495
7.376
7.360
7.353
7.349
7.341
7.337
7.329
7.324
7.316
7.312
7.300
7.260
5.318
5.314
5.312
5.297
5.131
5.107
5.077
5.052
4.290
4.271
1.990
1.974
1.957
1.942
1.931
1.922
1.903
1.892
1.671
1.658
1.579
1.572
1.147
1.017
0.991
0.976
0.962
0.000