Regioselective Reactions for Programmable Resveratrol Oligomer Synthesis

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Supporting Information

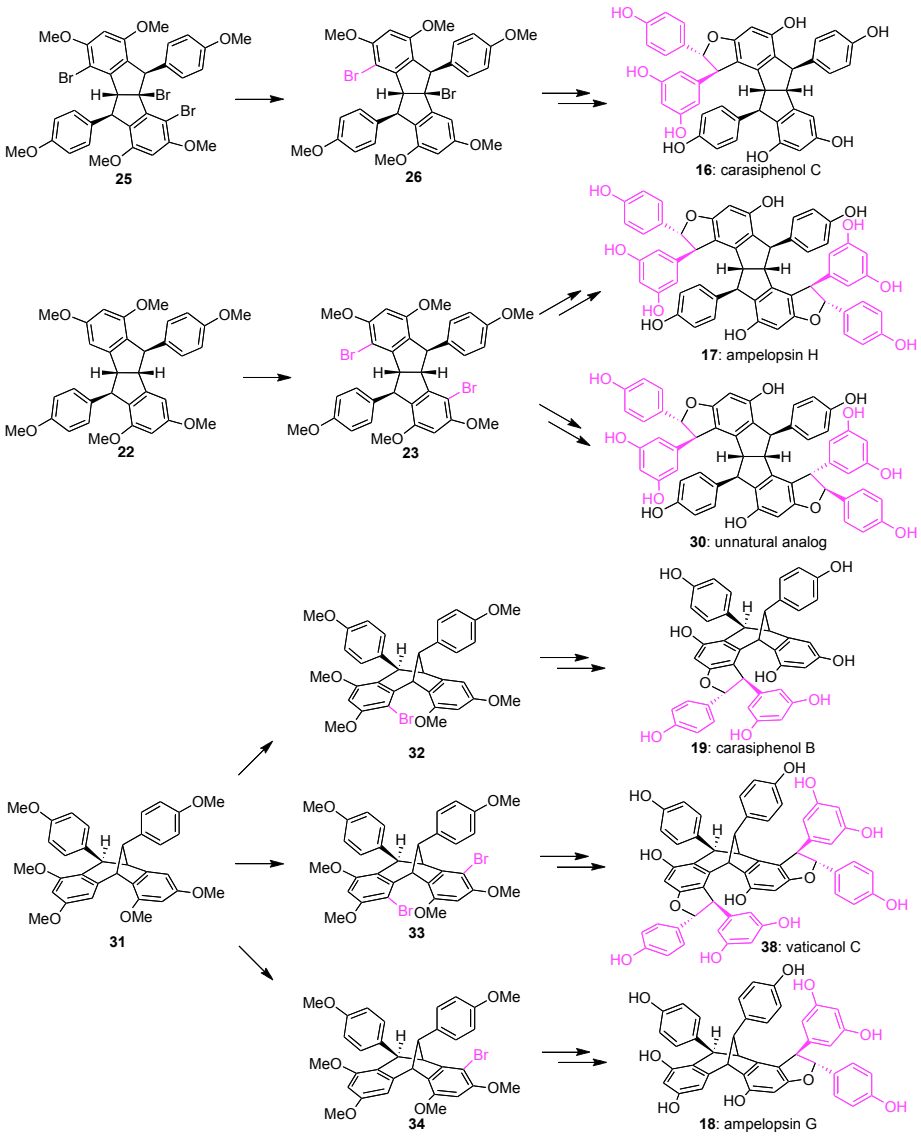

Figure S1. Overarching synthetic scheme for the prapration of 5 natural and 1 non-natural resveratrol oligomers.

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Experimental Data for Compounds

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran, toluene, benzene, diethyl ether and dichloromethane were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H and ^{13}C NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent, and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. SiliCycle silica gel (60, academic grade, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography separations were carried out on 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker 300, 400, 500, 600 and 800 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, br = broad, app = apparent. IR spectra were recorded on a Perkin-Elmer 1000 series FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded in the Columbia University Mass Spectral Core facility on a JOEL HX110 mass spectrometer using FAB (fast atom bombardment) and APCI (atmospheric pressure chemical ionization) techniques.

Abbreviations. NBS = *N*-bromosuccinimide, EtOAc = ethyl acetate, bpy = 2,2'-bipyridine, *i*-Pr_2NEt = *N,N*-diisopropylethylamine, DMF = *N,N*-dimethylformamide, *n*-BuLi = *n*-butyllithium, *t*-BuLi = *tert*-butyllithium, DMP = Dess – Martin periodinane, BnBr = benzyl bromide, TBAI = tetrabutylammonium iodide, Me_3SI = trimethylsulfonium iodide, KHMDS = potassium bis(trimethylsilyl)amide, MeOH = methanol, BDSB = bromodiethylsulfonium bromopentachloroantimonate, KO*t*-Bu = potassium *tert*-butoxide, DMSO = dimethylsulfoxide.

Permethylated Pallidol (22). Tribromide **25** (0.280 g, 0.361 mmol, 1.0 equiv; prepared according to published procedures[1]) was dissolved in THF (5 mL), degassed by argon sparging for 20 min, and cooled to –78 °C. Next, *t*-BuLi (1.7 M in THF, 1.2 mL, 2.04 mmol, 5.7 equiv) was added dropwise over the course of 5 min and the reaction was stirred at –78 °C for an additional 10 min. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (10 mL) at –78 °C, warmed to 25 °C, poured into water (10 mL) extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to afford permethylated pallidol (**22**, 0.193 g, 99% yield) as a colorless oil. **22**: R_f = 0.55 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2998, 2908, 2835, 1560, 1510, 1463, 1328, 1248, 1142, 1037, 829, 731 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.8 Hz, 4 H), 6.80 (d, *J* = 8.4 Hz, 4 H), 6.69 (d, *J* = 1.6 Hz, 2 H), 6.26 (d, *J* = 1.6 Hz, 2 H), 4.61 (s, 2 H), 4.00 (s, 2 H), 3.86 (s, 6 H), 3.77 (s, 6 H), 3.61 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 157.8, 156.9, 148.6, 137.9, 128.1, 124.8, 113.6, 100.1, 97.7, 59.6, 55.5, 55.2 (2 C), 53.4; HRMS (FAB) calcd for $C_{34}H_{34}O_6^+$ [M^+] 538.6302, found 538.2354.

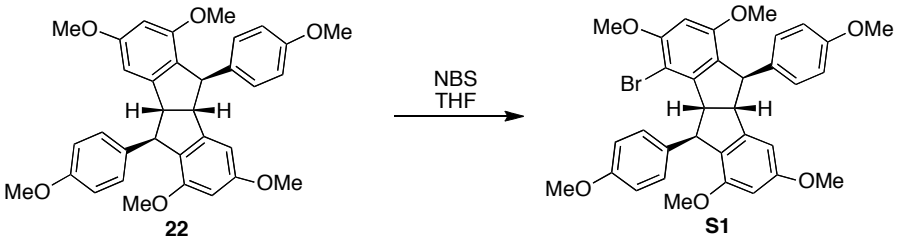


Figure S2. Synthesis of monobromide **S1** from intermediate **22**. Reagents and Conditions: NBS (1.0 equiv), THF, -78 ºC, 4 h, -78 ºC to 25 ºC, 2 h, 47%.

Monobromide S1. Permethylated pallidol (**22**, 0.295 g, 0.564 mmol, 1.0 equiv) was dissolved in THF (10 mL), cooled to –78 °C, and then NBS (0.100 g, 0.564 mmol, 1.0 equiv) was added in three portions over the course of 40 min at –78 °C. The resultant solution was stirred at –78 °C for an additional 4 h and then slowly warmed to 25 °C over the course of 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (15 mL), poured into water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford monobromide **S1** (0.163 g, 47% yield, 62% based on recovered starting material) as a colorless oil, dibromide **23** (0.090 g, 23% yield, 30% based on recovered starting material) as a colorless oil, and starting material (**22**, 0.073 g, 24% yield) as a colorless oil. **S1**: R_f = 0.40 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2999, 2934, 2835, 1598, 1510, 1461, 1330, 1248, 1215, 1175, 1144, 1079, 1035, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.6 Hz, 2 H), 7.02 (d, J = 8.6 Hz, 2 H), 6.80 (d, J = 8.6 Hz, 2 H), 6.78 (d, J = 8.6 Hz, 2 H), 6.66 (s, 1 H), 6.31 (s, 1 H), 6.23 (s, 1 H), 5.03 (s, 1 H), 4.68 (s, 1 H), 4.16 (d, J = 6.8 Hz, 1 H), 4.09 (d, J = 6.8 Hz, 1 H), 3.88 (s, 3 H), 3.86 (s, 3 H), 3.77 (s, 3 H), 3.76 (s, 3 H), 3.63 (s, 3 H), 3.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 157.9, 157.7, 156.8, 156.8, 156.0, 147.9, 146.9, 138.4, 137.9, 128.5, 128.0, 127.2, 125.7, 113.7, 113.4, 100.1, 100.0, 97.7, 96.0, 61.5, 58.9, 56.7, 55.5, 55.2, 55.1, 54.7, 51.3; HRMS (FAB) calcd for $C_{34}H_{33}O_6Br^+$ [M^+] 616.1461, found 616.1456 (for ^{79}Br).

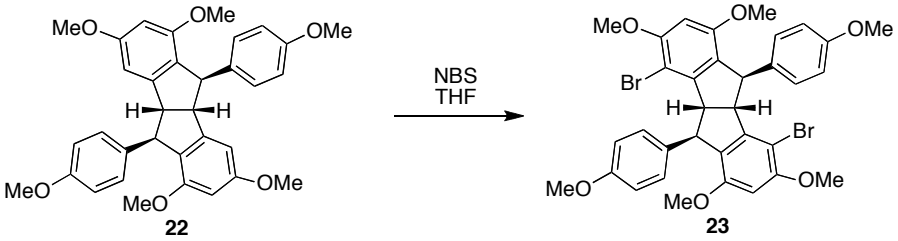


Figure S3. Synthesis of dibromide **23** from intermediate **22**. Reagents and Conditions: NBS (2.0 equiv), THF, -78 ºC, 2 h, 99%.

Dibromide 23. Permethylated pallidol (**22**, 0.123 g, 0.235 mmol, 1.0 equiv) was dissolved in THF (4 mL), cooled to –78 °C, and then NBS (0.084 g, 0.471 mmol, 2.0 equiv) was added in a single portion. The resultant solution was stirred at –78 °C for 2 h and then warmed up to 25 ºC over 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (10 mL), poured into water (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford dibromide **23** (0.163 g, 99% yield) as a white solid. **23**: R_f = 0.35 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2999, 2934, 2835, 1581, 1509, 1461, 1433, 1330, 1249,

1214, 1177, 1080, 1035, 822 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 8.6 Hz, 4 H), 6.79 (d, J = 8.6 Hz, 4 H), 6.27 (s, 2 H), 5.01 (s, 2 H), 4.28 (s, 2 H), 3.87 (s, 6 H), 3.77 (s, 6 H), 3.59 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.7, 155.8, 146.4, 138.2, 128.5, 127.9, 113.4, 99.5, 96.0, 60.5, 56.7, 55.5, 55.1, 52.9; HRMS (FAB) calcd for $C_{34}H_{32}O_6Br_2^+$ [M^+] 694.0566, found 694.0569 (for ^{79}Br).

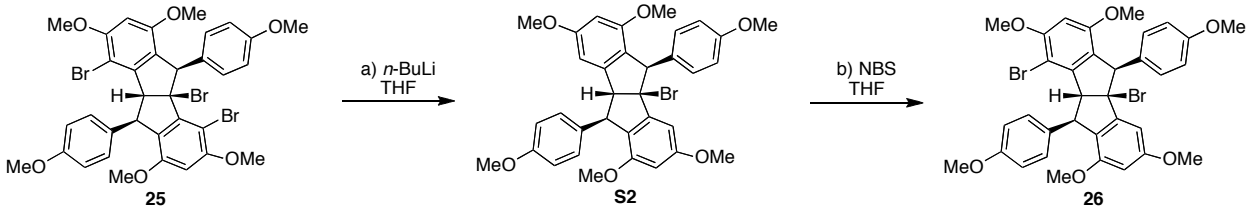


Figure S4. Synthesis of dibromide **26** from intermediate **25**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 2.1 equiv), THF, -78 ºC, 20 min, 94%; b) NBS (1.0 equiv), THF, -78 ºC, 4 h, -78 ºC to 25 ºC, 2 h, 84%.

Monoalkyl Bromide S2. Tribromide **25** (1.00 g, 1.290 mmol, 1.0 equiv) was dissolved in THF (20 mL) and cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 1.61 mL, 2.58 mmol, 2.0 equiv) was added dropwise over the course of 3 min and the reaction was stirred at –78 °C for an additional 5 min. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (15 mL) at –78 °C, warmed to 25 °C, poured into water (50 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 12:1→5:1) to afford monoalkyl bromide **S2** (0.750 g, 94% yield) as a white solid. **S2**: R_f = 0.39 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2998, 2994, 2835, 1604, 1511, 1490, 1462, 1327, 1303, 1246, 1205, 1174, 1143, 1104, 1038, 831, 784 cm^{-1}; ^1H NMR (400 MHz, 55 °C, $CDCl_3$) δ 7.25 (d, J = 8.8 Hz, 2 H), 7.00 (br s, 2 H), 6.89–6.77 (m, 5 H), 6.66 (s, 3 H), 6.35 (s, 1 H), 6.26 (s, 1 H), 4.88 (s, 1 H), 4.65 (s, 1 H), 4.29 (s, 1 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.62 (s, 3 H), 3.54 (s, 3 H); ^{13}C NMR (100 MHz, 55 °C, $CDCl_3$) δ 162.0, 161.7, 158.5, 158.2, 157.1, 156.6, 151.0, 146.6, 136.5, 135.5, 130.1, 129.1, 124.3, 123.4, 113.7, 113.2, 100.0, 99.9, 99.7, 98.5, 78.3, 69.0, 58.9, 55.7, 55.6, 55.4, 55.2, 55.1, 54.0; HRMS (FAB) calcd for $C_{34}H_{33}O_6Br^+$ [M^+] 616.1461, found 616.1475 (for ^{79}Br).

Dibromide 26. Monoalkyl bromide **S2** (0.700 g, 1.136 mmol, 1.0 equiv) was dissolved in THF (20 mL), cooled to –78 °C, and then NBS (0.202 g, 1.136 mmol, 1.0 equiv) in THF (2 mL was added in a dropwise in 15 min. The resultant solution was stirred at –78 °C for 8 h and then was warmed to 25 °C over the course of 4 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (20 mL), poured into water (80 mL), and extracted with EtOAc (3 × 50 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was recrystallized from acetonitrile to give dibromide **26** (0.561 g, 71% yield) as white crystals. The mother liquor was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford additional **26** (0.102 g, 13%) as a white solid (combined 84% yield). **26**: R_f = 0.30 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3000, 2934, 2836, 1603, 1583, 1511, 1491, 1462, 1434, 1331, 1303, 1246, 1210, 1177, 1147, 1080, 1036, 829, 811, 784, 733 cm^{-1}; ^1H NMR (400 MHz, 55 °C, $CDCl_3$) δ 7.51 (d, J = 8.7 Hz, 2 H), 6.94 (br s, 2 H), 6.83–6.75 (m, 5 H), 6.32–6.28 (m, 2 H), 5.01 (s, 1 H), 4.97 (s, 1 H), 4.47 (s, 1 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.78 (br s, 6 H), 3.58 (s, 3 H), 3.55 (s, 3 H); ^{13}C NMR (100 MHz, 55 °C, $CDCl_3$) δ 161.9, 158.6, 158.1, 157.4, 156.9, 155.7, 150.1, 145.5, 136.5, 136.0, 130.1, 129.8, 126.3, 124.5, 113.3, 113.2, 99.8 (2 C), 97.0, 77.8, 70.6, 60.3, 56.8, 55.8,

55.7, 55.4, 55.2 (2 C), 51.9; HRMS (FAB) calcd for $C_{34}H_{32}O_6Br_2^+$ [M^+] 694.0566, found 694.0579 (for ^{79}Br).

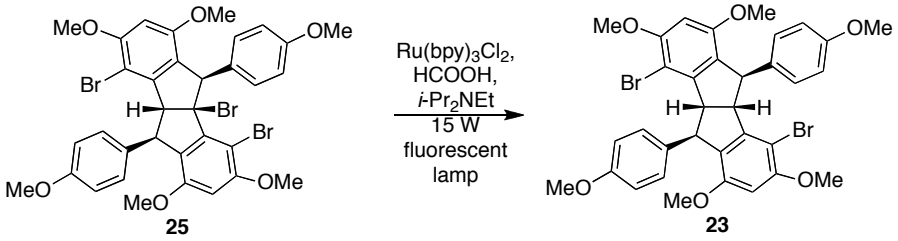


Figure S5. Alternate synthesis of dibromide **23** from intermediate **25**. Reagents and Conditions: $Ru(bpy)_3Cl_2 \cdot 7H_2O$ (0.1 equiv), *i*-Pr_2NEt (20.0 equiv), HCOOH (20.0 equiv), DMF, degassed, 15 W fluorescent lamp, 25º C, 14 h, 85%.

Dibromide 23. A round-bottomed flask was charged sequentially with $Ru(bpy)_3Cl_2 \cdot 7H_2O$ (2.0 mg, 0.003 mmol, 0.1 equiv), tribromide **25** (0.020 g, 0.026 mmol, 1.0 equiv), *i*-Pr_2NEt (0.086 mL, 0.520 mmol, 20 equiv), and formic acid (0.020 mL, 0.520 mmol, 20 equiv). Finally, DMF (1.5 mL) was added at 25 °C and the resultant mixture was degassed by argon sparging for 20 min and placed at a distance of ~10 cm from a 15 W fluorescent lamp.[2] After turning the lamp on and stirring at 25 °C for 14 h, the reaction contents were poured into saturated aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford dibromide **23** (0.015 g, 85% yield) as a white solid.

Total Synthesis of Carasiphenol C (16).

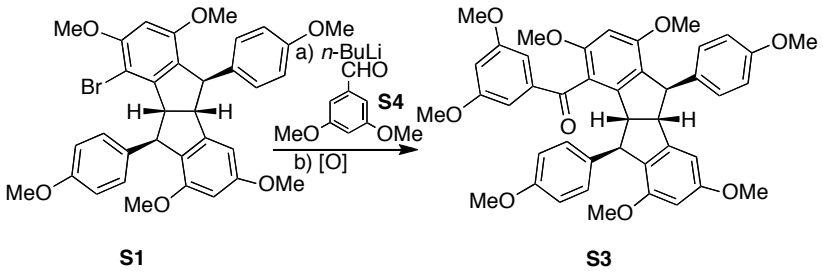


Figure S6. Synthesis of ketone **S3** starting from monobromide **S1**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 1.1 equiv), THF, -78 ºC, 10 min, then **S4** (3.0 equiv), THF, -78 ºC, 2h, -78 ºC to 25 ºC, 1.5 h, 88%; b) $NaHCO_3$ (10.0 equiv), DMP (1.4 equiv), CH_2Cl_2, 25 ºC, 1 h, 99%.

Ketone S3. Monobromide **S1** (0.150 g, 0.243 mmol, 1.0 equiv) was azeotroped with benzene (3 × 10 mL), dissolved in THF (3 mL), and then cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 0.267 mL, 0.267 mmol, 1.1 equiv) was added dropwise over the course of 5 min and the reaction mixture was stirred at –78 °C for an additional 10 min, ultimately yielding a solution with a slight yellow color. A solution of benzene-azeotroped (3 × 5 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.121 g, 0.729 mmol, 3.0 equiv) in THF (1.5 mL) was then added dropwise over 4 min at –78 °C. After stirring the resultant solution for an additional 2 h at –78 °C, the reaction was then allowed to slowly warm to 25 °C over the course of 1.5 h. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (5 mL), poured into water (20 mL), and extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→1:1) to afford the

corresponding alcohol as a mixture of diastereomers (0.151 g, 88% yield) as a colorless oil. Pressing forward, this newly synthesized material (0.151 g, 0.214 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and solid $NaHCO_3$ (0.180 g, 2.14 mmol, 10 equiv) and Dess–Martin periodinane (0.127 g, 0.300 mmol, 1.4 equiv) were added sequentially at 25 °C. The resultant mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (10 mL) and the resultant slurry was stirred for an additional 20 min at 25 °C before being poured into water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated to afford ketone **S3** (0.150 g, 99% yield) as a colorless oil. **S3**: R_f = 0.27 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2999, 2935, 2836, 1662, 1593, 1510, 1462, 1426, 1325, 1300, 1249, 1204, 1155, 1033, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2 H), 7.06 (d, *J* = 2.3 Hz, 2 H), 6.81 (d, *J* = 8.7 Hz, 2 H), 6.72 (d, *J* = 8.7 Hz, 2 H), 6.68 (t, *J* = 2.0 Hz, 1 H), 6.66 (d, *J* = 2.2 Hz, 1 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.30 (s, 1 H), 6.23 (d, *J* = 1.9 Hz, 1 H), 4.63 (s, 1 H), 4.33 (s, 1 H), 4.16 (d, *J* = 6.3 Hz, 1 H), 3.94 (d, *J* = 6.4 Hz, 1 H), 3.86 (s, 3 H), 3.79 (s, 6 H), 3.77 (s, 3 H), 3.69 (s, 6 H), 3.66 (s, 3 H), 3.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 161.1, 157.9 (2 C), 157.5, 156.9, 148.4, 147.2, 141.2, 137.4, 137.1, 128.1, 127.9, 125.8, 124.8, 118.4, 113.7, 113.3 106.9, 105.8, 100.1, 97.6, 94.4, 58.9, 58.8, 55.5, 55.3, 55.2, 55.0 (2 C), 52.9, 51.8; HRMS (FAB) calcd for $C_{43}H_{42}O_9^+$ [M^+] 702.2829, found 702.2811.

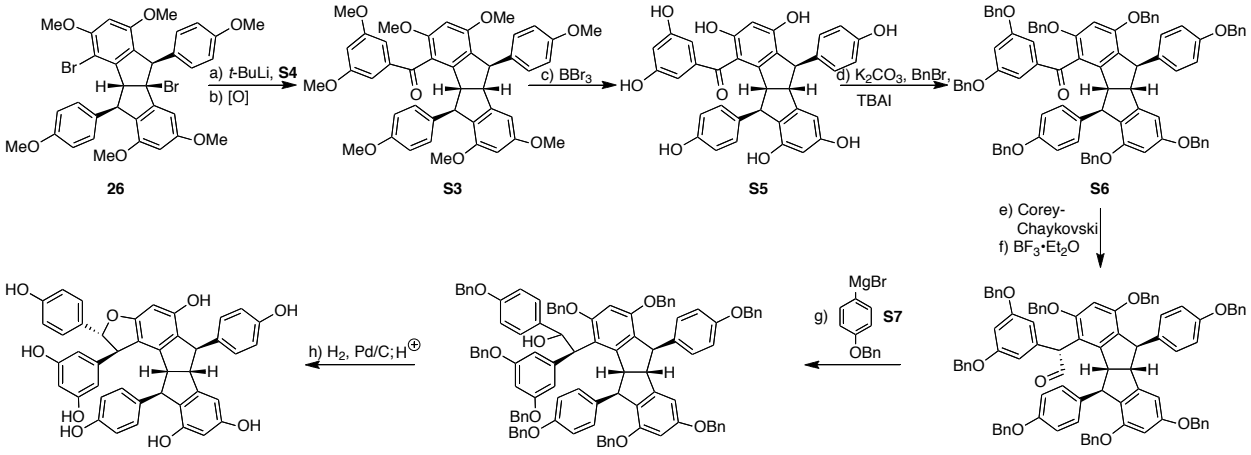


Figure S7. Total synthesis of carasiphenol C (**16**) from dibromide **26**. Reagents and Conditions: a) *t*-BuLi (1.7 M in THF, 3.0 equiv), THF, -78 ºC, 4 min, then **S4** (3.0 equiv), THF, -78 ºC, 1.5 h, 77%; b) $NaHCO_3$ (10.0 equiv), DMP (1.4 equiv), CH_2Cl_2, 25 ºC, 1 h, 99%; c) BBr_3 (1.0 M in CH_2Cl_2, 35 equiv), CH_2Cl_2, sealed tube, 70 ºC, 3 d, 86%; d) K_2CO_3 (50.0 equiv), BnBr (50.0 equiv), *n*-Bu_4NI (2.0 equiv), acetone, 70 ºC, 24 h, 85%, e) Me_3SI (10.0 equiv), *n*-BuLi (1.6 M in THF, 8.0 equiv), THF, 0 ºC, 2 min, then **S6**, 0 ºC, 30 min; f) BF_3•Et_2O (3.0 equiv), THF, 0 ºC, 30 min, 78% (over 2 steps); g) **S7** (1.0 M in THF, 5.0 equiv), THF, 25 ºC, 45 min, 93%; h) H_2, 30% Pd/C, EtOAc:MeOH (1:1) to MeOH, 25 ºC, 12 h, then Amberlite IR-12OH, 25 ºC, 1 h, 73% (over 2 steps).

Ketone S3. Dibromide **26** (0.550 g, 0.790 mmol, 1.0 equiv) was azeotroped with benzene (3 × 15 mL), dissolved in THF (10 mL), and then cooled to –78 °C. Next, *t*-BuLi (1.7 M in THF, 1.39 mL, 2.37 mmol, 3.0 equiv) was added dropwise over the course of 3 min and the reaction mixture was stirred at –78 °C for an additional 2 min, ultimately yielding a solution with a deeply yellow/orange color. A solution of benzene-azeotroped (2 × 10 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.151 g, 0.91 mmol, 1.15 equiv) in THF (2 mL) was then added dropwise over 3 min at –78 °C. After stirring the resultant solution for an additional 1.5 h at –78 °C, the bright yellow reaction contents were quenched with saturated aqueous NH_4Cl (20 mL) at –78 °C, warmed to 25 °C, poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc,

4:1→1:1) to afford the desired alcohol product as a mixture of diastereomers (0.428 g, 77% yield) as a colorless oil. Pressing forward, the material (combined from two different batches) (0.650 g, 0.923 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (15 mL), and solid $NaHCO_3$ (0.775 g, 9.23 mmol, 10 equiv) and Dess–Martin periodinane (0.545 g, 1.29 mmol, 1.4 equiv) were added sequentially at 25 °C. The resultant mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (20 mL) and the resultant slurry was stirred for an additional 20 min at 25 °C before being poured into water (50 mL) and extracted with EtOAc (3 × 25 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered, and concentrated afford ketone **S3** (0.642 g, 99% yield) as a colorless oil.

Deprotected Ketone S5. Permethylated ketone **S3** (0.123 g, 0.175 mmol, 1.0 equiv) was dissolved in a minimum amount of CH_2Cl_2 (1 mL), transferred to a sealable reaction vessel, and then BBr_3 (1.0 M in CH_2Cl_2, 6.13 mL, 6.13 mmol, 35 equiv) was added quickly in a single portion at 25 °C. The resulting black reaction mixture was then heated at 70 °C for 3 d. Upon completion, the reaction contents were cooled to 25 °C and quenched with the addition of water (5 ml). After stirring the resultant biphasic mixture for an additional 10 min at 25 °C, the reaction contents were poured into water (15 mL), extracted with EtOAc (5 × 10 mL), dried ($MgSO_4$), filtered, and concentrated. The resultant dark orange oil was purified by flash column chromatography (silica gel, CH_2Cl_2:MeOH, 10:1→3:1) to afford the deprotected ketone **S5** (0.089 g, 86% yield) as an orange oil. **S5** R_f = 0.30 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3291, 2917, 2849, 1697, 1511, 1445, 1342, 1239, 1168, 1105, 1005, 831 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 9.33 (br s, 1 H), 8.63 (br s, 1 H), 8.44 (br s, 2 H), 8.09 (br s, 1 H), 8.03 (br s, 1 H), 7.86 (br s, 1 H), 7.74 (br s, 1 H), 7.09 (d, J = 8.2 Hz, 2 H), 6.93 (d, J = 1.5 Hz, 2 H), 6.77 (d, J = 8.2 Hz, 2 H), 6.65 (d, J = 8.4 Hz, 2 H), 6.61 (s, 1 H), 6.53 (d, J = 8.4 Hz, 2 H), 6.50 (s, 1 H), 6.32 (s, 1 H), 6.15 (s, 1 H), 4.62 (s, 1 H), 4.27 (s, 1 H), 4.18 (d, J = 6.2 Hz, 1 H), 3.80 (d, J = 6.1 Hz, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 197.7, 159.2, 158.5, 158.3, 157.1, 155.6, 155.1, 154.2, 149.0, 148.9, 141.4, 136.4, 136.1, 128.2, 124.6, 122.6, 115.1, 114.7, 114.3, 108.4, 106.8, 102.2, 101.8, 101.7, 59.7, 59.0, 52.6, 52.4; HRMS (FAB) calcd for $C_{35}H_{26}O_9^+$ [M^+] 590.1577, found 590.1575.

Perbenzylated Ketone S6. Solid K_2CO_3 (1.04 g, 7.54 mmol, 50 equiv), BnBr (1.29 g, 7.54 mmol, 50 equiv) and *n*-Bu_4NI (0.111 g, 0.301 mmol, 2.0 equiv) were added sequentially to a solution of deprotected ketone **S5** (0.089 g, 0.151 mmol, 1.0 equiv) in dry acetone (1 mL) at 25 °C. The resultant reaction mixture was then heated at 70 °C for 24 h. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of water (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→5:1) to afford perbenzylated ketone **S6** (0.168 g, 85% yield) as a yellow oil. **S6**: R_f = 0.45 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 3062, 3031, 2917, 1662, 1594, 1508, 1453, 1377, 1322, 1242, 1176, 1151, 1109, 1063, 1026, 736, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.42 (m, 4 H), 7.41–7.36 (m, 7 H), 7.34–7.28 (m, 14 H), 7.26–7.24 (m, 2 H), 7.19–7.09 (m, 11 H), 7.04–7.00 (m, 2 H), 6.93–6.90 (m, 2 H), 6.89 (d, J = 8.6 Hz, 2 H), 6.86–6.82 (m, 2 H), 6.78 (d, J = 8.8 Hz, 2 H), 6.76 (d, J = 1.7 Hz, 1H), 6.74–6.70 (m, 3 H), 6.33 (d, J = 1.7 Hz, 1 H), 6.29 (s, 1 H), 5.07–5.01 (m, 4 H), 4.97–4.87 (m, 8 H), 4.86 (d, J = 11.9 Hz, 1 H), 4.80 (d, J = 11.9 Hz, 1 H), 4.73–4.69 (m, 2 H), 4.64 (s, 1 H), 4.48 (s, 1 H), 4.38 (d, J = 7.0 Hz, 1 H), 4.09 (d, J = 7.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 160.4, 160.0, 157.9, 157.3, 157.0, 156.8, 155.6, 148.6, 147.8, 142.0, 138.0, 137.7, 137.4, 137.2, 137.0, 136.9,

136.7, 136.6, 136.5, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0 (2 C), 127.9, 127.8 (2 C), 127.6 (2 C), 127.5 (2 C), 127.2, 127.1, 126.9, 126.8, 126.3, 126.0, 118.9, 114.7, 114.3, 108.1, 107.1, 101.7, 99.7, 97.2, 70.7, 70.4, 70.2, 70.1, 69.9, 69.7, 69.1, 59.0, 58.8, 53.8, 53.0; MS (FAB) calcd for $C_{91}H_{74}O_9^+$ [M^+] 1310.5, found 1310.8.

Aldehyde 27. To a slurry of Me_3SI (0.134 g, 0.656 mmol, 10 equiv) in THF (4 mL) at 0 °C was added *n*-BuLi (1.6 M in THF, 0.328 mL, 0.525 mmol, 8.0 equiv) dropwise over a period of 2 min, and the reaction mixture was stirred at 0 °C for an additional 2 min.[3] A solution of ketone **S6** (0.086 g, 0.066 mmol, 1.0 equiv) in THF (1 mL) was then added dropwise over the course of 2 min at 0 °C, and the resultant solution was stirred for an additional 30 min at 0 °C. Upon completion, the reaction contents were quenched at 0 °C with the addition of saturated aqueous NH_4Cl (10 mL), poured into water (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), and concentrated to give the crude epoxide as light yellow oil. Next, the crude epoxide was immediately dissolved in THF (3 mL), cooled to 0 °C, and BF_3•Et_2O (0.028 g, 0.198 mmol, 3.0 equiv) in THF (0.5 mL) was added dropwise over a period of 3 min. The resultant reaction mixture was stirred at 0 °C for 30 min. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 15:1→5:1) to afford aldehyde **27** (0.068 g, 78% yield) as a mixture of diastereomers (5.5:1.0 as determined by ^{1}H NMR). The stereoisomers could not be separated at this stage by flash column chromatography. An analytical sample of aldehyde **27** was obtained by reverse-phase HPLC (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 42 min, 5% H_2O in MeCN). **27**: R_f = 0.40 (silica gel, hexanes:EtOAc, 3:1); IR (film) ν_{max} 3031, 2920, 1716, 1597, 1507, 1453, 1377, 1323, 1240, 1146, 1026, 826, 734, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1 H), 7.46–7.35 (m, 9 H), 7.34–7.26 (m, 18 H), 7.25–7.16 (m, 11 H), 6.98–6.93 (m, 4 H), 6.92–6.89 (m, 2 H), 6.87 (d, *J* = 6.6 Hz, 2 H), 6.85 (d, *J* = 6.8 Hz, 2 H), 6.60 (d, *J* = 1.4 Hz, 1 H), 6.46 (t, *J* = 2.2 Hz, 1 H), 6.37 (s, 1 H), 6.32 (d, *J* = 1.6 Hz, 1 H), 6.16 (d, *J* = 2.0 Hz, 2 H), 5.02 (s, 2 H), 5.00 (s, 2 H), 4.93 (d, *J* = 11.7 Hz, 1 H), 4.91–4.85 (m, 4 H), 4.83 (d, *J* = 11.9 Hz, 1 H), 4.83–4.73 (m, 5 H), 4.70 (d, *J* = 11.4 Hz, 2 H), 4.62 (d, *J* = 2.6 Hz, 1 H), 4.50 (d, *J* = 2.6 Hz, 1 H), 4.22 (dd, *J* = 8.1, 2.8 Hz, 1 H), 4.17 (dd, *J* = 8.1, 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 160.4, 159.9, 157.3, 157.2, 157.1, 155.7, 155.3, 149.3, 148.1, 140.0, 139.3, 139.2, 137.2, 137.1, 137.0, 136.8, 136.7 (2 C), 136.4, 129.2, 128.6, 128.5 (2 C), 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 127.0, 126.8, 126.4, 116.0, 114.7, 114.6, 107.6, 101.3, 101.1, 99.4, 97.5, 71.1, 70.3, 70.0, 69.9 (2 C), 69.6, 69.4, 60.5, 59.8, 58.4, 56.3, 56.2; MS (FAB) calcd for $C_{92}H_{76}O_9^+$ [M+H^+] 1325.5, found 1325.9.

Alcohol S8. To a solution of aldehyde **27** (0.022 g, 0.014 mmol, 1.0 equiv, 5.5:1 mixture of diastereomers) in THF (1 mL) at 25 °C was added 4–benzyloxyphenylmagnesium bromide (**S7**, 1.0 M in THF, 0.072 mL, 0.072 mmol, 5.0 equiv), and the resultant reaction mixture was stirred for 45 min at 25 °C. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (4 mL), poured into water (4 mL), and extracted with EtOAc (3 × 3 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→1:1) to afford alcohol **S8** (0.017 g, 93% yield, mixture of diastereomers, 4:1 based on ^{1}H NMR, separable from the diastereomers resulting from the minor aldehyde stereoisomer) as a white solid. An analytical sample of the major diastereomer was obtained by preparative thin layer chromatography (hexanes:EtOAc, 1:1). **S8**: R_f = 0.40 (silica gel,

hexanes:EtOAc, 3:1); IR (film) ν_{max} 3062, 3030, 2917, 1596, 1508, 1454, 1378, 1312, 1242, 1146, 1066, 1027, 828, 736, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.21 (m, 30 H), 7.12–7.19 (m, 10 H), 7.18–7.11 (m, 5 H), 7.01 (d, *J* = 8.6 Hz, 2 H), 7.98–7.95 (m, 2 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 8.9 Hz, 2 H), 6.73 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 6.49 (s, 1 H), 6.34 (s, 1 H), 6.30 (t, *J* = 2.2 Hz, 1 H), 6.02 (d, *J* = 2.2 Hz, 2 H), 5.78 (dd, *J* = 10.2, 2.1 Hz, 1 H), 5.14 (d, *J* = 11.4 Hz, 1 H), 5.07 (d, *J* = 11.4 Hz, 1 H), 5.05–5.02 (m, 2 H), 4.99–4.95 (m, 4 H), 4.88 (d, *J* = 11.6 Hz, 1 H), 4.83 (d, *J* = 10.6 Hz, 2 H), 4.78 (d, *J* = 11.5 Hz, 1 H), 4.71 (s, 2 H), 4.59 (d, *J* = 10.4 Hz, 1 H), 4.57 (s, 1 H), 4.49 (s, 4 H), 4.22 (d, *J* = 7.9 Hz, 1 H), 4.13 (d, *J* = 7.9 Hz, 1 H), 2.84 (d, *J* = 2.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 158.0, 157.9, 157.1, 157.0, 155.6, 154.6, 149.2, 147.9, 144.1, 139.2, 138.7, 137.3, 137.1, 137.0, 136.9, 136.5, 135.5, 129.4, 128.8, 128.6, 128.5 (4 C), 128.4 (2 C), 128.3 (3 C), 127.9 (3 C), 127.8, 127.7 (2 C), 127.6 (2 C), 127.4 (2 C), 127.1, 126.9, 114.6, 114.1, 113.8, 108.0, 101.3, 101.0, 99.3, 98.0, 75.2, 71.5, 70.4, 70.0 (2 C), 69.7, 69.5, 59.8, 59.3, 56.9, 55.5, 54.8; MS (FAB) calcd for $C_{105}H_{88}O_{10}^+$ [M^+] 1508.6, found 1508.7.

Carasiphenol C (16). Alcohol **S8** (9.0 mg**,** 0.006 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc:MeOH (1:1, 3 mL) and solid Pd/C (30%, 6.0 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to rereach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) for 2 h. H_2 was bubbled through the stirred reaction mixture again for 30 min and the reaction mixture again was refilled with MeOH to account for lost solvent. The reaction was then stirred under H_2 for 12 h.[5] Upon completion, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g, pre-washed with MeOH five times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 1 h. When this operation was complete, the solution was filtered through simple filtration papered to remove the Amberlite, and the filtrate was concentrated directly to afford carasiphenol C (**16**, 3.0 mg, 73%) as a white solid, with a scrupulously pure analytical sample obtained by reverse-phase HPLC[7] (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 11.7 min, 45% MeOH in H_2O). **16**: R_f = 0.45 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3343, 2924, 2853, 1659, 1600, 1511, 1461, 1342, 1259, 1160, 1087, 1027, 834 cm^{-1}; ^1H NMR (600 MHz, acetone-d_6) δ 8.45 (s, 1 H), 8.18 (s, 2 H), 8.05 (s, 1 H), 8.01 (s, 2 H), 7.80 (s, 1 H), 7.70 (s, 1 H), 7.23 (d, *J* = 8.5 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 6.70 (d, *J* = 8.6 Hz, 2 H), 6.61 (d, *J* = 1.8 Hz, 1 H), 6.43 (d, *J* = 8.6, 2 H), 6.35 (d, *J* = 8.6 Hz, 2 H), 6.30 (t, *J* = 2.2 Hz, 1 H), 6.25 (d, *J* = 2.2 Hz, 2 H), 6.24 (s, 1 H), 6.16 (d, *J* = 1.8 Hz, 1 H), 5.26 (d, *J* = 7.5 Hz, 1 H), 4.83 (d, *J* = 7.5 Hz, 1 H), 4.62 (s, 1 H), 4.53 (s, 1 H), 3.67 (d, *J* = 5.9 Hz, 1 H), 3.62 (d, *J* = 5.9 Hz, 1 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 162.9, 160.2, 159.4, 158.4, 157.7, 156.4, 156.1, 155.5, 150.9, 145.5, 145.1, 137.7, 136.7, 133.4, 130.6 (2 C), 129.2 (2 C), 128.8, 125.8, 123.0, 116.4, 116.2, 116.0, 115.4, 107.6, 103.5, 102.6, 102.4, 96.9, 94.8, 60.1, 59.9, 57.2, 53.4, 50.0; HRMS (FAB) calcd for $C_{42}H_{42}O_9^+$ [M^+] 680.2046, found 680.2028. All spectroscopic data for **16** match that reported by Hu and co-workers. For a direct comparison, see Table S1. For a larger scale synthesis of this natural product, see end of this section before the physical NMR spectra.

Total Synthesis of Ampelopsin H (17) and Unnatural Analog 30.

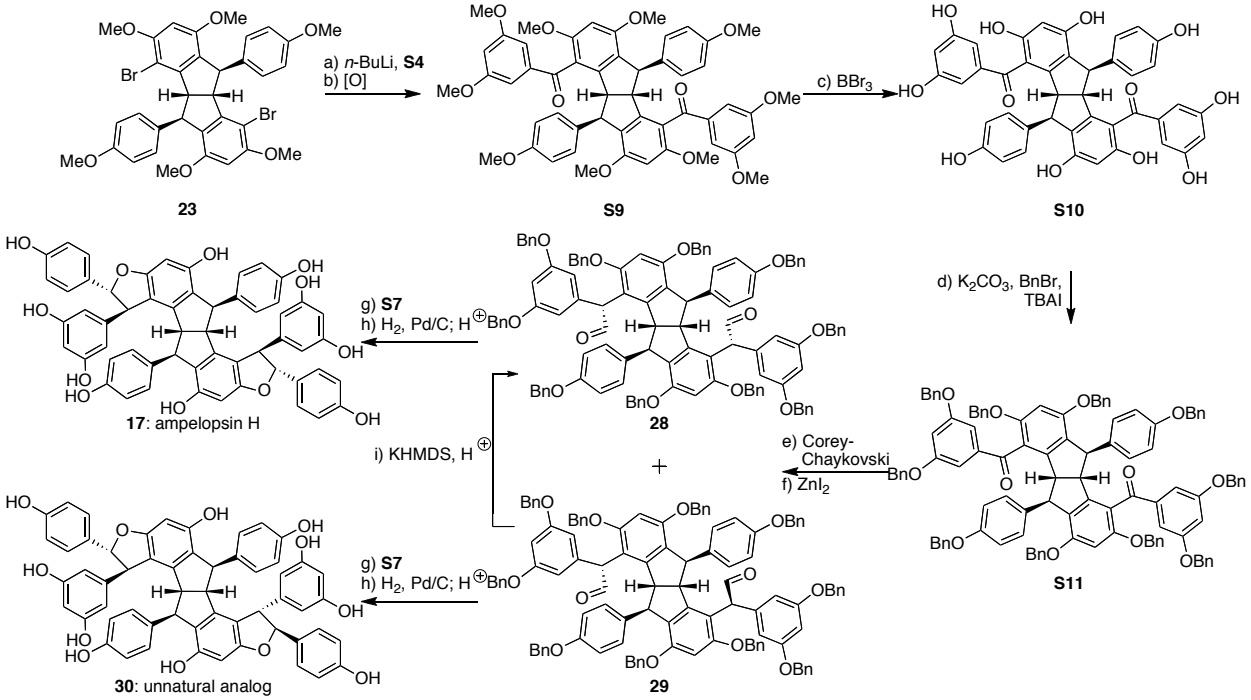


Figure S8. Total syntheses of ampelopsin H (**17**) and unnatural analog **30** from dibromide **23**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 2.2 equiv), THF, -78 ºC, 10 min, then **S4** (6.0 equiv), THF, -78 ºC, 2 h, -78 ºC to 25 ºC, 1.5 h, 87%; b) $NaHCO_3$ (10.0 equiv), DMP (2.8 equiv), CH_2Cl_2, 25 ºC, 1 h, 99%; c) BBr_3 (1.0 M in CH_2Cl_2, 45 equiv), CH_2Cl_2, sealed tube, 70 ºC, 3.5 d, 94%; d) K_2CO_3 (50.0 equiv), BnBr (50.0 equiv), *n*-Bu_4NI (2.0 equiv), acetone, 70 ºC, 24 h, 87%, e) Me_3SI (15.0 equiv), *n*-BuLi (1.6 M in THF, 12.0 equiv), THF, 0 ºC, 4 min, then **S11**, 0 ºC, 30 min; f) ZnI_2 (6.0 equiv), benzene, 25 ºC, 20 min, 77% (over 2 steps); g) **S7** (1.0 M in THF, 8.0 equiv), THF, 25 ºC, 45 min, 86% (from **28**) and 78% (from **29**) ; h) H_2, 30% Pd/C, EtOAc:MeOH (1:1) to MeOH, 25 ºC, 12 h, then Amberlite IR-12OH, 25 ºC, 1 h, 71% (from **28**) and 65% (from **29**) over 2 steps, i) KHMDS (1.0 M in THF, 1.1 equiv), -78 ºC, 10 min, 61%.

Ketone S9. Dibromide **23** (0.110 g, 0.156 mmol, 1.0 equiv) was azeotroped with benzene (3 × 5 mL), dissolved in THF (5 mL), and then cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 0.217 mL, 0.348 mmol, 2.2 equiv) was added dropwise over the course of 5 min and the reaction mixture was stirred at –78 °C for an additional 10 min, ultimately yielding a solution with a slight yellow color. A solution of benzene-azeotroped (3 × 3 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.156 g, 0.936 mmol, 6.0 equiv) in THF (2 mL) was then added dropwise over 5 min at –78 °C. After stirring the resultant solution for an additional 2 h at –78 °C, the reaction was then allowed to slowly warm to 25 °C over the course of 1.5 h. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (10 mL), poured into water (10 mL), and extracted with EtOAc (4 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→1:1) to afford the desired alcohol as a mixture of diastereomers (0.118 g, 87% yield) as a colorless oil. Pressing forward, the mixture of alcohol diastereomers (0.118 g, 0.136 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (5 mL) and solid $NaHCO_3$ (0.113 g, 1.36 mmol, 10 equiv) and Dess–Martin periodinane (0.161 g, 0.379 mmol, 2.8 equiv) were added sequentially at 25 °C. The resultant mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (3 mL) and the resultant slurry was stirred for an additional 20 min before being poured into water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$),

filtered, and concentrated to afford ketone **S9** (0.117 g, 99% yield) as a colorless oil. **S9**: R_f = 0.23 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3000, 2935, 2836, 1664, 1592, 1510, 1459, 1426, 1324, 1300, 1250, 1204, 1155, 1081, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 2.4 Hz, 4 H), 6.73 (d, *J* = 8.6 Hz, 4 H), 6.66 (t, *J* = 2.4 Hz, 2 H), 6.64 (d, *J* = 8.6 Hz, 4 H), 6.27 (s, 2 H), 4.36 (s, 2 H), 4.05 (s, 2 H), 3.80 (s, 12 H), 3.70 (s, 6 H), 3.66 (s, 6 H), 3.56 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 160.7, 158.8, 157.8, 157.6, 146.8, 141.0, 136.7, 125.6, 118.0, 113.3, 107.0, 105.8, 94.5, 58.3, 56.1, 55.5, 55.1, 55.0, 51.4; HRMS (FAB) calcd for $C_{52}H_{50}O_{12}^+$ [M^+] 866.3302, found 866.3306.

Deprotected Ketone S10. Permethylated ketone **S9** (0.095 g, 0.110 mmol, 1.0 equiv) was dissolved in a minimal amount of CH_2Cl_2 (1 mL), transferred to a sealable reaction vessel, and BBr_3 (1.0 M in CH_2Cl_2, 4.93 mL, 4.93 mmol, 45 equiv) was added quickly in a single portion. The resulting black reaction mixture was then heated at 70 °C for 3.5 d. Upon completion, the reaction contents were cooled to 25 °C, quenched with water (15 mL), and extracted with EtOAc (5 × 10 mL). The resultant crude product was purified by flash column chromatography (silica gel, CH_2Cl_2:MeOH, 10:1→3:1) to afford the desired deprotected ketone **S10** (0.075 g, 94% yield) as an orange oil. **S10**: R_f = 0.25 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3270, 1694, 1511, 1445, 1341, 1302, 1233, 1154, 1105, 1003, 818 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 9.43 (br s, 2 H), 8.57 (br s, 2 H), 8.39 (br s, 4 H), 7.89 (br s, 2 H), 6.88 (d, *J* = 1.7 Hz, 4 H), 6.74 (d, *J* = 8.4 Hz, 4 H), 6.58 (d, *J* = 8.4 Hz, 4 H), 6.46 (s, 2 H), 6.23 (s, 2 H), 4.27 (s, 2 H), 4.13 (s, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 197.8, 159.4, 158.5, 157.1, 155.3, 148.5, 141.4, 135.7, 128.1, 124.8, 114.6, 114.2, 108.4, 106.8, 101.8, 59.3, 52.2; HRMS (FAB) calcd for $C_{42}H_{30}O_{12}^+$ [M^+] 726.1737, found 726.1754.

Perbenzylated Ketone S11. Solid K_2CO_3 (0.719 g, 5.20 mmol, 60 equiv), BnBr (0.890 g, 5.20 mmol, 60 equiv), and *n*-Bu_4NI (0.080 g, 0.217 mmol, 2.5 equiv) were added to a solution of deprotected ketone **S10** (0.063 g, 0.087 mmol, 1.0 equiv) in dry acetone (1 mL) at 25 °C. The resultant reaction mixture was then heated at 70 ºC for 24 h. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of water (10 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→5:1) to afford perbenzylated ketone **S11** (0.123 g, 87% yield) as a yellow oil. **S11**: R_f = 0.61 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3063, 3032, 2931, 1660, 1592, 1508, 1454, 1441, 1323, 1295, 1243, 1220, 1155, 1060, 1027, 910, 829, 736, 696 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 7.41–7.25 (m, 30 H), 7.24–7.10 (m, 16 H), 6.96–7.90 (m, 4 H), 6.88 (d, *J* = 6.8 Hz, 4 H), 6.84 (d, *J* = 8.8 Hz, 4 H), 6.73 (d, *J* = 8.8 Hz, 4 H), 6.76–6.69 (m, 3 H), 6.34 (s, 2 H), 4.93 (s, 8 H), 4.91 (s, 4 H), 4.83 (d, *J* = 12.4 Hz, 2 H), 4.78 (d, *J* = 12.1 Hz, 2 H), 4.75 (d, *J* = 12.8 Hz, 2 H), 4.71 (d, *J* = 12.0 Hz, 2 H), 4.53 (s, 2 H), 4.35 (s, 2 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 196.8, 159.9, 157.9, 157.0, 156.5, 147.7, 141.8, 137.3, 137.2, 136.6, 136.5, 136.4, 128.6, 128.5, 128.3, 128.2, 128.0, 127.7, 127.6, 127.4, 126.9, 126.8, 126.4, 118.7, 114.4, 108.1, 106.9, 97.4, 70.7, 70.2, 69.9, 69.3, 58.2, 52.7; MS (FAB) calcd for $C_{112}H_{90}O_{12}^+$ [$M+H^+$] 1627.6, found 1628.1.

Aldehydes 28 and 29. To a slurry of Me_3SI (0.433 g, 2.12 mmol, 15 equiv) in THF (6 mL) at 0 °C was added *n*-BuLi (1.6 M in THF, 1.06 mL, 1.70 mmol, 12 equiv) dropwise at 0 °C over the course of 3 min, and the reaction mixture was stirred at 0 °C for an additional 4 min. A solution of ketone **S11** (0.236 g, 0.145 mmol, 1.0 equiv) in THF (4 mL) was then added dropwise over the course of 3 min at 0 °C, and the resultant solution was stirred for an additional 30 min at 0 °C.[3] Upon completion, the reaction contents were quenched with the addition of

saturated aqueous NH_4Cl (10 mL), poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give the crude product as light yellow oil. Pressing forward without any additional purification, the crude epoxide was immediately dissolved in benzene (5 mL) and solid ZnI_2 (0.280 g, 0.879 mmol, 6.0 equiv) was added at 25 °C in a single portion.[8] The resultant reaction mixture was stirred at 25 °C for 20 min. Upon completion, the reaction contents were quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to afford aldehydes **28** and **29** (0.182 g, 77% yield) as a mixture of diastereomers (1.8:1.0 based on ^{1}H NMR) and as a white solid. The major diastereomer **28** could be selectively crystallized using hexanes:EtOAc (3:1) to afford clean **28** (0.061 g). The mother liquor was concentrated and purified further by flash column chromatography (silica gel, hexanes:EtOAc, 15:1→10:1) to give additional **28** (0.051 g) and **29** (0.061 g). An analytical sample of the minor aldehyde **29** was obtained by reverse-phase HPLC (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 48.0 min, 5% H_2O in MeCN). **28**: R_f = 0.60 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3062, 3031, 2918, 1716, 1595, 1508, 1453, 1323, 1242, 1155, 1062, 1027, 829, 735, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 2 H), 7.31–7.19 (m, 50 H), 7.06 (d, *J* = 8.6 Hz, 4 H), 6.87–6.84 (m, 4 H), 6.85 (d, *J* = 8.6 Hz, 4 H), 6.44 (t, *J* = 2.2 Hz, 2 H), 6.36 (s, 2 H), 6.06 (d, *J* = 2.2 Hz, 4 H), 4.95 (d, *J* = 11.8 Hz, 2 H), 4.90 (d, *J* = 11.8 Hz, 2 Hz), 4.89 (s, 4 H), 4.79 (s, 2 H), 4.76 (s, 4 H), 4.73 (s, 4 H), 4.72 (d, *J* = 11.6 Hz, 2 H), 4.52 (t, *J* = 2.8 Hz, 2 H), 4.50 (s, 2 H), 4.15 (t, *J* = 2.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 159.9, 157.4, 156.9, 155.1, 148.9, 139.9, 139.3, 137.0, 136.8, 136.5, 136.4, 129.5, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127.1, 115.6, 114.7, 107.9, 101.3, 97.5, 71.1, 70.0, 69.9, 69.7, 60.7, 58.7, 56.8; MS (FAB) calcd for $C_{114}H_{94}O_{12}^+$ [M+H$^+$] 1655.7, found 1656.1. **29**: R_f = 0.62 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3031, 2920, 1719, 1597, 1454, 1324, 1241, 1156, 1119, 1067, 1027, 830, 736, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1 H), 9.79 (s, 1 H), 7.36–7.26 (m, 30 H), 7.25–7.15 (m, 16 H), 7.02–6.99 (m, 2 H), 6.95–6.87 (m, 4 H), 6.87–6.81 (m, 2 H), 6.58–6.54 (m, 3 H), 6.49 (d, *J* = 8.7 Hz, 2 H), 6.46 (t, *J* = 2.2 Hz, 1 H), 6.38 (d, *J* = 2.2 Hz, 2 H), 6.30 (s, 1 H), 6.24 (s, 1 H), 6.13 (d, *J* = 2.1 Hz, 2 H), 4.95–4.89 (m, 6 H), 4.86 (d, *J* = 3.9 Hz, 1 H), 4.84–4.81 (m, 4 H), 4.79 (s, 2 H), 4.76 (s, 1 H), 4.75 (d, *J* = 12.0 Hz, 1 H), 4.73–4.67 (m, 4 H), 4.64 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.45 (dd, *J* = 8.2, 2.2 Hz, 1 H), 4.42 (s, 1 H), 4.32 (dd, *J* = 8.3, 2.3 Hz, 1 H), 4.15 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 160.0, 159.9, 157.6, 157.4 (2 C), 156.9 (2 C), 155.3, 154.9 (2 C), 148.6, 148.4, 140.0, 139.2, 139.0, 138.0, 137.0 (2 C), 136.8, 136.6 (2 C), 136.5, 136.4, 136.3, 129.4, 128.8, 128.6, 128.5 (3 C), 128.4, 128.3, 128.2, 128.0, 127.9 (2 C), 127.8 (3 C), 127.7, 127.6, 127.5, 127.4, 127.1, 127.0, 126.9, 115.7, 114.7, 114.0, 113.4, 108.0, 107.5, 101.3, 101.2, 97.6, 97.3, 71.0, 70.5, 70.1, 70.0, 69.9, 69.8, 69.6, 69.4, 60.0, 59.7, 58.3 (2 C), 57.0, 54.3; MS (FAB) calcd for $C_{114}H_{94}O_{12}^+$ [M+H$^+$] 1655.7, found 1656.1.

Epimerization of Aldehyde 29 into 28. A mixture of aldehydes **28** and **29** (d.r. = 1:10, based on ^{1}H NMR, 0.052 g, 0.031 mmol, 1.0 equiv) was dissolved in THF (3 mL) and cooled to –78 °C. KHMDS (1.0 M in THF, 0.035 mL, 0.035 mmol, 1.1 equiv) was then added dropwise over the course of 4 min and the resultant yellow solution was stirred at –78 °C for an additional 10 min. Upon completion, the reaction contents were quenched at –78 °C with the addition of saturated aqueous NH_4Cl (4 mL), warmed to 25 °C, poured into water (4 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated

to give the crude mixture of recovered aldehydes as a light yellow oil which was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to afford aldehyde **28** (0.031 g, 61% yield) as a white solid and as primarily a single diastereomer (d.r. = 21:1 based on ^{1}H NMR).

Ampelopsin H (17). To a solution of aldehyde **28** (0.047 g, 0.028 mmol, 1.0 equiv) in THF (1 mL) at 25 °C was added 4–benzyloxyphenylmagnesium bromide (**S7**, 1.0 M in THF, 0.227 mL, 0.227 mmol, 8.0 equiv), and the resultant solution was stirred for 45 min at 25 °C. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (3 mL), poured into water (3 mL), and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→1:1) to afford the desired alcohol product (0.049 g, 86% yield) as a mixture of diastereomers (d.r. = 2:1 based on ^{1}H NMR analysis). The major diastereomer could be crystallized from hexanes:EtOAc (2:1) to afford an analytical sample. [Note: this compound was used as a mixture of diastereomers for the final transformation]. R_f = 0.31 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2919, 2851, 1594, 1509, 1454, 1379, 1316, 1242, 1156, 1113, 1027, 829, 735, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 4 H), 7.36–7.19 (m, 48 H), 7.16–7.10 (m, 8 H), 6.96 (d, *J* = 8.7 Hz, 4 H), 6.91 (d, *J* = 8.6 Hz, 4 H), 6.73 (d, *J* = 8.8 Hz, 4 H), 6.66 (s, 1 H), 6.61 (d, *J* = 8.7 Hz, 4 H), 6.45 (s, 2 H), 6.27 (t, *J* = 2.2 Hz, 2 H), 5.86 (d, *J* = 2.2 Hz, 4 H), 5.73 (dd, *J* = 10.1, 2.6 Hz, 2 H), 5.12 (d, *J* = 11.4 Hz, 2 H), 5.03 (d, *J* = 11.4 Hz, 2 H), 4.96 (s, 4 H), 4.89 (d, *J* = 11.7 Hz, 2 H), 4.88 (s, 2 H), 4.81 (d, *J* = 11.8 Hz, 2 H), 4.63 (s, 4 H), 4.46 (d, *J* = 11.6 Hz, 2 H), 4.45 (s, 4 H), 4.43 (*J* = 11.6 Hz, 4 H), 4.15 (s, 2 H), 3.01 (d, *J* = 2.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.9, 157.7, 156.9, 154.2, 148.6, 144.0, 139.0, 137.1, 137.0, 136.9, 136.5, 135.4, 129.6, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8 (2 C), 127.6, 127.4 (2 C), 118.0, 114.0, 113.7, 108.1, 101.1, 98.1, 75.4, 71.6, 70.0, 69.7 (2 C), 58.9, 57.0, 55.6; MS (FAB) calcd for $C_{140}H_{117}NaO_{14}^+$ [M+Na$^+$] 2044.8, found 2044.9 This intermediate alcohol (0.021 g, 0.010 mmol, 1.0 equiv, utilized as a mixture of diastereomers) was dissolved in a mixture of EtOAc:MeOH (1:1, 3 mL) and solid Pd/C (30%, 15 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to reach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) for 2 h. H_2 was bubbled through the stirred reaction mixture again for 30 min and the reaction mixture again was refilled with MeOH to account for lost solvent. This process was repeated one more time after stirring the reaction under H_2 for 2 h and finally the reaction was stirred under H_2 for 12 h.[5] Upon completion of the reaction, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g, pre-washed with MeOH five times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 1 h. When this operation was complete, the solution was filtered through simple filtration papered to remove the Amberlite and the filtrate was concentrated directly to afford ampelopsin H (**17**) as a white solid. This was purified by reverse-phase HPLC[7] (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 15.0 min, 45% MeOH in H_2O) to give ampelopsin H (**17**, 6.7 mg, 71% yield) as a white solid. **17**: R_f = 0.28 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3372, 1602, 1512, 1462, 1347,1248, 1203, 1156, 1087, 828 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.46 (s, 2 H), 8.15 (s, 4 H), 7.91 (s, 2 H), 7.79 (s, 2 H), 7.25 (d, *J* = 8.5 Hz, 4 H), 6.88 (d, *J* = 8.5 Hz, 4 H), 6.46 (d, *J* = 8.6 Hz, 4 H), 6.38 (d, *J* = 8.6 Hz, 4 H), 6.29 (t, *J* = 2.2 Hz, 2 H), 6.25 (d, *J* = 2.2 Hz, 4 H), 6.24 (s, 2 H), 5.27 (d, *J* = 7.6 Hz, 2 H), 4.86 (d, *J* = 7.6 Hz, 2 H), 4.61 (s, 2 H), 3.52 (s, 2 H); ^{13}C NMR (100 MHz,

acetone–d_6) δ 162.9, 160.1, 158.4, 156.1, 155.5, 145.4, 145.2, 136.6, 133.3, 129.2, 128.8, 125.3, 116.6, 116.2, 115.5, 107.6, 102.3, 97.0, 94.8, 59.5, 57.1, 49.4; HRMS (FAB) calcd for $C_{56}H_{43}O_{12}^+$ [M+H$^+$] 907.2755, found 907.2726. All spectroscopic data for **17** match that reported by Tanaka and co-workers.[9] For a direct comparison, see Table S2.

Unnatural Analog 30. To a solution of aldehyde **29** (0.022 g, 0.013 mmol, 1.0 equiv) in THF (1 mL) at 25 °C was added 4–benzyloxyphenylmagnesium bromide (**S7**, 1.0 M in THF, 0.106 mL, 0.106 mmol, 8.0 equiv), and the resultant solution was stirred for 45 min at 25 °C. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (3 mL), poured into water (3 mL), and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→1:1) to afford the desired intermediate alcohol (0.021 g, 78% yield) as a complex mixture of diastereomers based on ^{1}H NMR analysis. Pressing forward, a portion of this newly synthesized alcohol (0.015 g, 0.007 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc:MeOH (1:1, 3 mL) and solid Pd/C (30%, 15 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to rereach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) for 2 h. H_2 was bubbled through the stirred reaction mixture again for 30 min and the reaction mixture again was refilled with MeOH to account for lost solvent. This process was repeated one more time after stirring the reaction under H_2 for 2 h and finally the reaction was stirred under H_2 for 12 h.[5] Upon completion of the reaction, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g, pre-washed with MeOH five times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 1 h. When this operation was complete, the solution was filtered through simple filtration paper to remove the Amberlite and the filtrate was concentrated directly to afford ampelopsin H analog (**30**) as a white solid which was purified by preparative TLC (CH_2Cl_2:MeOH, 3:1) to give ampelopsin H analog **30** (4.3 mg, 65% yield) as a white solid. **30**: R_f = 0.30 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3323, 1611, 1512, 1455, 1343, 1259, 1161, 1084, 1008, 832 cm^{-1}; ^{1}H NMR (800 MHz, acetone-d_6) δ 8.61 (s, 1 H), 8.48 (s, 1 H), 8.29 (s, 4 H), 8.11 (s, 1 H), 8.03 (s, 1 H), 7.94 (s, 1 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.5, 2 H), 7.19 (s, 1 H), 6.94 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 8.0 Hz, 4 H), 6.61 (d, J = 8.4 Hz, 2 H), 6.47 (d, J = 8.4 Hz, 2 H), 6.36 (d, J = 8.1 Hz, 2 H), 6.34 (s, 1 H), 6.32 (t, J = 2.0 Hz, 1 H), 6.29–6.26 (m, 4 H), 6.19 (s, 1 H), 5.37 (s, 1 H), 5.29 (d, J = 7.5 Hz, 1 H), 4.93 (d, J = 7.5 Hz, 1 H), 4.64 (s, 1 H), 4.48 (s, 1 H), 4.37 (s, 1 H), 3.74 (d, J = 6.0 Hz, 1 H), 3.60 (d, J = 6.0 Hz, 1 H); ^{13}C NMR (200 MHz, acetone-d_6) δ 162.6, 162.4, 161.7, 159.3, 159.2, 157.5, 157.1, 155.1, 154.7, 154.5, 148.0, 147.6, 144.6, 144.5, 143.5, 137.2, 136.0, 133.8, 132.6, 132.5, 128.2, 128.1, 127.8, 126.5, 125.3, 124.4, 115.7, 115.3, 115.2, 114.7, 114.5, 106.6, 105.4, 101.3, 96.1, 95.8, 93.7, 92.9, 59.2, 59.0, 56.1, 55.9, 49.3, 48.2; HRMS (FAB) calcd for $C_{56}H_{43}O_{12}^+$ [M$^+$] 906.3, found 906.4.

Permethylated Ampelopsin F (31). Synthesized according to published procedures.[1] **31**: R_f = 0.69 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2997, 2936, 2835, 1604, 1511, 1487, 1462, 1319, 1248, 1206, 1176, 1140, 1091, 1037, 832 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.4 Hz, 2 H), 6.84 (d, J = 8.4 Hz, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 6.66 (d, J = 8.8 Hz, 2 H), 6.58 (d, J = 1.6 Hz, 1 H), 6.53 (d, J = 2.0 Hz, 1 H), 6.26 (d, J = 2.4 Hz, 1 H), 6.19 (d, J = 1.6 Hz, 1 H), 4.22 (s, 1 H), 4.19 (s, 1 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.77 (s, 3 H), 3.75 (s, 4 H), 3.74 (s, 1 H), 3.68 (s, 3 H), 3.44 (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 159.6, 159.0, 157.7, 157.6, 155.0, 146.2, 145.6, 139.2, 135.6, 129.8, 128.8, 128.6, 115.9, 113.5, 103.1, 101.5,

97.1 (2 C), 57.3, 55.6, 55.5, 55.4, 55.3, 55.2, 49.9, 49.1, 46.3; HRMS (FAB) calcd for $C_{34}H_{34}O_6^+$ [M^+] 538.6302, found 538.2374.

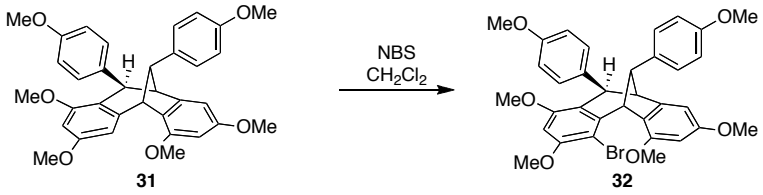


Figure S9. Synthesis of monobromide **32** from intermediate **31**. Reagents and Conditions: NBS (0.9 equiv), CH_2Cl_2, -78 ºC, 1 h, -78 ºC to 25 ºC, 2 h, 88-95%.

Monobromide 32. Permethylated ampelopsin F (**31**, 0.034 g, 0.063 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (1.5 mL), cooled to –78 °C, and then NBS (0.010 g, 0.056 mmol, 0.9 equiv) was added in a single portion. The resultant solution was stirred at –78 °C for 1 h and then was warmed to 25 °C over the course of 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (5 mL) and saturated aqueous Na_2SO_3 (5 mL), poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant amorphous product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 9:1→1:1) to afford bromide **32** (0.037 g, 95% yield) as an off-white foam. In general in these experiments, it is worth noting that the NBS used was not recrystallized from the commercial sample; upon dissolution we always observed some yellow coloration indicating the presence of Br_2 which had the same selectivity in bromination pattern as NBS. For this reason, we always observed some over halogenation relative to the amount of NBS used, accounting here for the yield observed. **32**: R_f = 0.64 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2935, 2835, 1598, 1511, 1488, 1461, 1434, 1321, 1249, 1204, 1178, 1148, 1133, 1075, 1036, 830, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.4 Hz, 2 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.56 (d, *J* = 1.6 Hz, 1 H), 6.30 (s, 1 H), 6.18 (d, *J* = 2.0 Hz, 1 H), 4.98 (s, 1 H), 4.24 (d, *J* = 1.6 Hz, 1 H), 3.88 (s, 3 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 3.72 (s, 3 H), 3.68 (s, 4 H), 3.44 (s, 3 H), 3.38 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 158.5, 157.8, 157.7, 155.7, 155.2, 146.3, 145.2, 139.1, 135,3, 128.8, 128.7 (2 C), 118.3, 113.9, 113.5, 102.3, 101.1, 97.1, 95.4, 57.1, 56.5, 55.6 (2 C), 55.3 (2 C), 49.8, 47.9, 46.4; HRMS (FAB) calcd for $C_{34}H_{33}BrO_6^+$ [M^+] 617.5262, found 616.1471 (for ^{79}Br). We note that a large-scale run of this reaction performed with 0.590 g of **31** provided 0.730 g of an 8:1 mixture of **32** and **33** following extraction that was free of other impurities; this result accounts for a total of 0.640 g of **32** (88% yield) and 0.090 g (12% yield) of **33**. Again, the overall level of purity for the NBS here dictated the amount of halogenation observed using 0.9 equivalents of NBS.

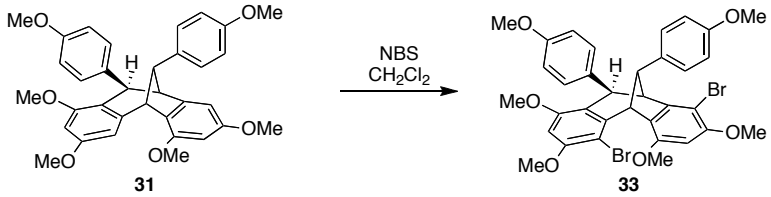


Figure S10. Synthesis of dibromide **33** from intermediate **31**. Reagents and Conditions: NBS (2.0 equiv), CH_2Cl_2, -78 ºC, 2 h, 99%.

Dibromide 33. Permethylated ampelopsin F (**31**, 0.178 g, 0.330 mmol, 1.0 equiv) was dissolved in THF (6 mL), cooled to –78 °C, and then NBS (0.117 g, 0.660 mmol, 2.0 equiv) was

added in a single portion. The resultant solution was stirred at –78 °C for 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (15 mL), poured into water (5 mL), and extracted with EtOAc (2 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford dibromide **33** (0.229 g, 99% yield) as a colorless oil. **33**: R_f = 0.32 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 2999, 2935, 2835, 1607, 1585, 1510, 1461, 1433, 1321, 1249, 1218, 1204, 1179, 1151, 1140, 1076, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.2 Hz, 2 H), 6.87 (d, *J* = 8.3 Hz, 2 H), 6.82 (d, *J* = 8.3 Hz, 2 H), 6.68 (d, *J* = 8.3 Hz, 2 H), 6.32 (s, 1 H), 6.19 (s, 1 H), 5.08 (s, 1 H), 4.37 (s, 1 H), 3.88 (s, 3 H), 3.83 (s, 3 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 3.68 (br s, 5 H), 3.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 157.8, 157.5, 156.0, 155.1, 154.6, 145.9, 144.4, 138.5, 134.4, 128.8, 128.5, 128.4, 117.8, 113.5, 113.4, 102.0, 99.1, 95.6, 95.3, 56.7, 56.4, 56.3, 55.5, 55.4, 55.2, 55.1, 49.7, 48.8, 43.6; HRMS (FAB) calcd for $C_{34}H_{32}O_6Br_2^+$ [M^+] 694.0566, found 694.0543 (for ^{79}Br).

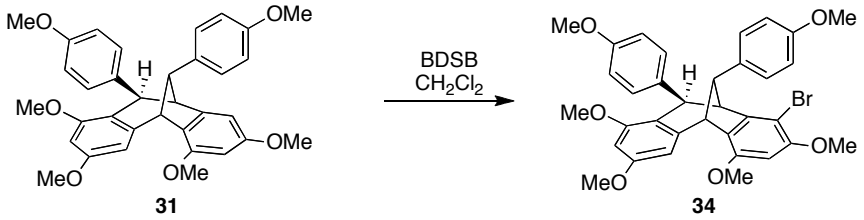


Figure S11. Synthesis of monobromide **34** from intermediate **31**. Reagents and Conditions: BDSB (0.9 equiv), CH_2Cl_2, -78 ºC, 2 h, 78%.

Monobromide 34. Permethylated ampelopsin F (**31**, 0.560 g, 1.04 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (20 mL), cooled to –78 °C, and then BDSB (0.516 g, 0.94 mmol, 0.9 equiv) was added in a single portion. The resultant solution was stirred at –78 °C for 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (20 mL) and saturated aqueous Na_2SO_3 (50 mL), and extracted with EtOAc (2 × 50 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant amorphous product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford bromide **34** contaminated with a trace of dibromide **33** (0.560 g total, 0.500 g **34** based on NMR integration, 78%, 85% yield based on recovered starting material) as an amorphous off-white solid and recovered permethylated ampelopsin F (**34**, 0.045 g, 8%). An analytical sample was obtained by running the reaction less to completion as the dibromide cannot be separated. [Note: the large scale reaction was run to test the robustness of the method; key is to note that monobromide **32** was not detected by NMR analysis]. **34**: R_f = 0.56 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2935, 2835, 1606, 1583, 1510, 1462, 1434, 1336, 1320, 1248, 1209, 1178, 1140, 1080, 1036, 966, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 2.4 Hz, 1 H), 6.27 (d, *J* = 2.4 Hz, 1 H), 6.19 (s, 1 H), 4.34 (s, 1 H), 4.25 (s, 1 H), 3.83 (s, 3 H), 3.83 (s, 3 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 3.69 (s, 1 H), 3.69 (s, 4 H), 3.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.1, 157.9, 157.7, 156.0, 154.1, 145.6, 145.5, 138.8, 135.0, 130.0, 128.8, 128.6, 115.7, 113.7, 113.6, 113.5, 103.1, 97.2, 95.8, 57.2, 56.7, 55.8, 55.5, 55.4, 55.3 (2 C), 51.0, 49.2, 43.7; HRMS (FAB) calcd for $C_{34}H_{33}BrO_6^+$ [M^+] 617.5262, found 616.1465 (for ^{79}Br).

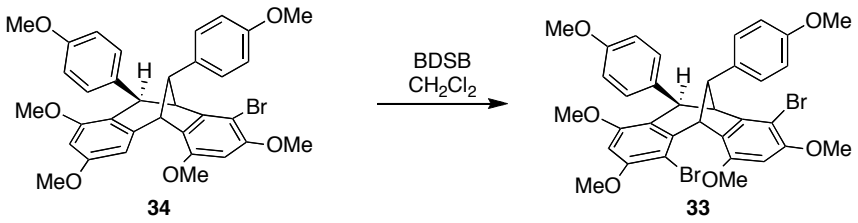


Figure S12. Synthesis of dibromide **33** from monobromide **34**. Reagents and Conditions: BDSB (1.1 equiv), CH_2Cl_2, -78 ºC, 2 h, 99%.

Dibromide 33. Monobromide **34** (0.015 g, 0.024 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL), cooled to –78 °C, and then BDSB (0.014 g, 0.025 mmol, 1.1 equiv) was added in a single portion. The resultant solution was stirred at –78 °C for 2 h. Upon completion, the reaction contents were quenched with saturated aqueous $NaHCO_3$ (10 mL) and saturated aqueous Na_2SO_3 (10 mL), and extracted with EtOAc (2 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant amorphous product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford dibromide **33** (0.016 g, 99% yield) as an amorphous off-white solid.

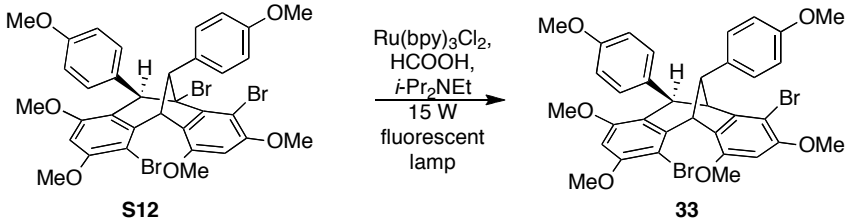


Figure S13. Alternate synthesis of dibromide **33** from intermediate **S12**. Reagents and Conditions: $Ru(bpy)_3Cl_2$•$7H_2O$ (0.1 equiv), *i*-Pr_2NEt (20.0 equiv), HCOOH (20.0 equiv), DMF, degassed, 15 W fluorescent lamp, 25º C, 15 h, 89%.

Dibromide 33. A round-bottomed flask was charged sequentially with $Ru(bpy)_3Cl_2$•$7H_2O$ (2.0 mg, 0.003 mmol, 0.1 equiv), tribromide **S12** (0.025 g, 0.033 mmol, 1.0 equiv), *i*-Pr_2NEt (0.011 mL, 0.650 mmol, 20 equiv), and formic acid (0.032 mL, 0.650 mmol, 20 equiv). Finally, DMF (2.5 mL) was added at 25 °C and the resultant mixture was degassed by argon sparging for 20 min, and placed at a distance of ~10 cm from a 15 W fluorescent lamp.[2] After turning the lamp on and stirring at 25 °C for 15 h, the reaction contents were poured into saturated aqueous $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→4:1) to afford dibromide **33** (0.020 g, 89% yield) as a white solid.

Total Synthesis of Carasiphenol B (19).

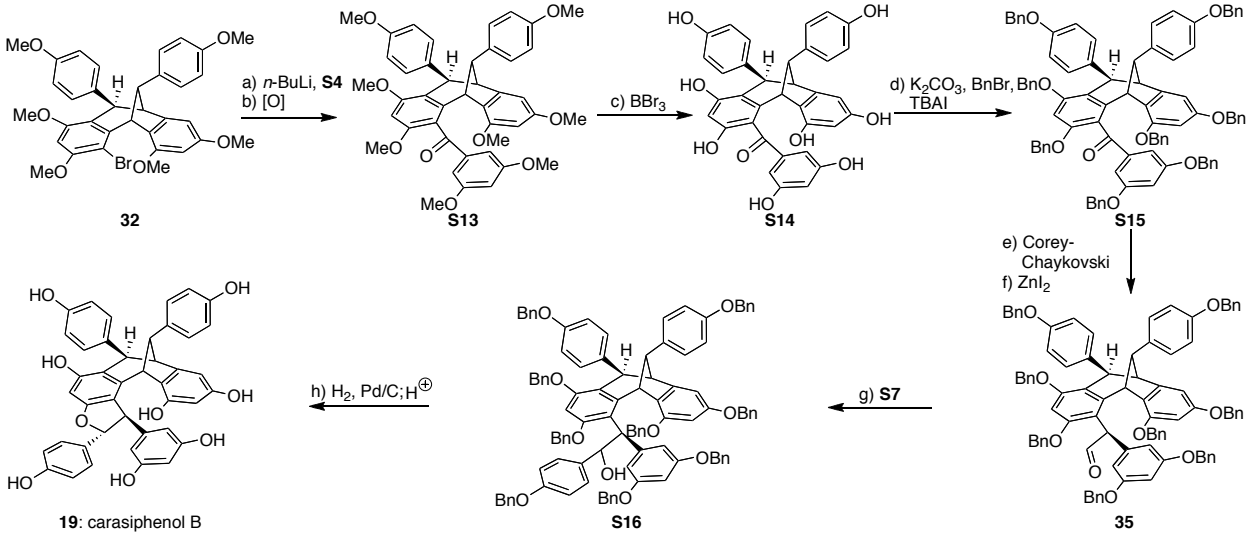


Figure S14. Total synthesis of carasiphenol B (**19**) from monobromide **32**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 1.3 equiv), THF, -78 ºC, 10 min, then **S4** (3.0 equiv), THF, -78 ºC, 2h, -78 ºC to 25 ºC, 2 h, 58%; b) $NaHCO_3$ (21.0 equiv), DMP (2.3 equiv), CH_2Cl_2, 25 ºC, 1 h, 97%; c) BBr_3 (1.0 M in CH_2Cl_2, 40.0 equiv), CH_2Cl_2, sealed tube, 70 ºC, 5 d, 96%; d) K_2CO_3 (40.0 equiv), BnBr (43 equiv), *n*-Bu_4NI (2.0 equiv), acetone, 70 ºC, 15 h, 78%, e) Me_3SI (20.0 equiv), *n*-BuLi (1.6 M in THF, 16.0 equiv), THF, 0 ºC, 2 min, then **S15**, 0 ºC, 1 h; f) ZnI_2 (31.0 equiv), benzene, 25 ºC, 1 h, 94% (over 2 steps); g) **S7** (1.0 M in THF, 6.0 equiv), THF, 25 ºC, 1 h, 68%; h) H_2, 30% Pd/C, EtOAc:MeOH (1:1) to MeOH, 25 ºC, 12 h, then Amberlite IR-12OH, 25 ºC, 1 h, 89% (over 2 steps).

Ketone S13. Monobromide **32** (0.053 g, 0.086 mmol, 1.0 equiv) was azeotroped with benzene (3 × 3 mL), dissolved in THF (1.5 mL), and then cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 0.067 mL, 0.107 mmol, 1.25 equiv) was added dropwise over the course of 5 min and the reaction mixture was stirred at –78 °C for an additional 10 min, ultimately yielding a solution with a slight yellow color. A solution of benzene-azeotroped (3 × 3 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.043 g, 0.257 mmol, 3.0 equiv) in THF (1.5 mL) was then added dropwise over 5 min at –78 °C. After stirring the resultant solution for an additional 2 h at –78 °C, the reaction was then allowed to slowly warm to 25 °C over the course of 2 h. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (5 mL), poured into water (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude yellow oil was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→1:1) to afford the desired alcohol product as a mixture of diastereomers (0.035 g, 58% yield) as an off-white solid, alongside debrominated permethylated ampelopsin F **31** (0.012 g, 26% yield). After repeating this reaction several times, the mixture of alcohol diastereomers (0.237 g, 0.336 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (8 mL) and solid $NaHCO_3$ (0.600 g, 7.14 mmol, 21 equiv) and Dess–Martin periodinane (0.330 g, 0.778 mmol, 2.3 equiv) were added sequentially at 25 °C. The resultant mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (40 mL) and the resultant slurry was stirred for an additional 20 min at 25 °C before being poured into water (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were then washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered, and concentrated to afford ketone **S13** (0.230 g, 97% yield) as a white amorphous solid. **S13**: R_f = 0.38 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2935, 2836, 1723, 1661, 1589, 1511, 1460, 1428, 1316, 1249, 1204, 1178, 1155, 1111, 1080, 1036, 832, 758, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2 H), 7.04 (br s, 2 H), 6.82 (d, *J* = 8.4 Hz, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.65 (t, *J* = 2.4 Hz, 1 H), 6.58 (d, *J* = 8.8 Hz, 2 H), 6.56 (d, *J* = 1.6 Hz, 1 H), 6.27 (s, 1 H), 5.99 (d, *J* = 2.0 Hz, 1H), 4.46 (br s, 1 H), 4.28 (d, *J* = 1.6 Hz,

1 H), 3.80 (s, 9 H), 3.78 (s, 1 H), 3.76 (s, 3 H), 3.64 (s, 3 H), 3.62 (s, 3 H), 3.50 (s, 3 H), 3.41 (s, 1 H), 2.97 (br s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 160.9, 160.8, 160.7, 157.9, 157.8, 157.6, 155.1, 146.4, 145.4, 141.9, 139.4, 135.4, 129.2, 129.0, 128.8, 118.9, 117.4, 113.7, 113.6, 107.6, 105.4, 100.8, 96.4, 94.1, 56.5, 56.0, 55.9, 55.7, 55.6 (2 C), 55.4, 54.0, 49.9, 46.8, 44.7; HRMS (FAB) calcd for $C_{43}H_{42}O_9^+$ [M^+] 702.7882, found 702.2816.

Deprotected Ketone S14. Permethylated ketone **S13** (0.230 g, 0.327 mmol, 1.0 equiv) was dissolved in a minimal amount of CH_2Cl_2 (1 mL), transferred to a sealable reaction vessel, and then BBr_3 (1.0 M in CH_2Cl_2, 13.0 mL, 13.0 mmol, 40 equiv) was added quickly in a single portion at 25 °C. The resulting reddish-brown reaction mixture was then heated at 70 °C for 5 d. Upon completion, the reaction contents were cooled to 25 °C and quenched with the addition of saturated aqueous $NaHCO_3$ (20 mL). After stirring the resultant biphasic mixture for an additional 10 min at 25 °C, the reaction contents were poured into water (20 mL), extracted with EtOAc (5 × 40 mL), dried ($MgSO_4$), filtered, and concentrated. The resultant orange oil was purified by flash column chromatography (silica gel, CH_2Cl_2:MeOH, 10:1→3:1) to afford the deprotected ketone **S14** (0.185 g, 96% yield) as a yellow amorphous solid. **S14**: R_f = 0.66 (CH_2Cl_2:MeOH, 4:1); IR (film) ν_{max} 3297, 2978, 2937, 1697, 1596, 1512, 1443, 1358, 1343, 1237, 1159, 1005, 836, 792 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.32 (s, 1 H), 8.65 (br s, 4 H), 8.06 (br s, 2H), 7.19 (d, J = 8.4 Hz, 2 H), 7.01 (d, J = 2.0 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 6.70 (d, J = 8.4 Hz, 2 H), 6.66 (t, J = 2.2 Hz, 1 H), 6.59 (d, J = 2.0 Hz, 1 H), 6.56 (d, J = 8.4 Hz, 2 H), 6.37 (s, 1 H), 6.11 (d, J = 2.0 Hz, 1 H), 4.32 (d, J = 1.6 Hz, 1 H), 4.16 (s, 1 H), 3.71 (s, 1 H), 3.41 (s, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 200.6, 159.6, 158.5, 158.4, 155.8, 155.4, 154.7, 153.2, 146.8, 145.6, 141.9, 137.3, 134.0, 128.9, 128.2, 124.9, 114.9, 114.7, 114.4, 108.3, 107.5, 103.2, 101.6, 101.1, 56.3, 49.2, 46.6, 46.0; HRMS (FAB) calcd for $C_{35}H_{26}O_9^+$ [M^+] 590.5755, found 590.1580.

Perbenzylated Ketone S15. Solid K_2CO_3 (0.430 g, 3.11 mmol, 40 equiv), BnBr (0.576 g, 3.368 mmol, 43 equiv) and *n*-Bu_4NI (0.058 g, 0.157 mmol, 2.0 equiv) were added sequentially to a solution of the deprotected ketone **S14** (0.046 g, 0.078 mmol, 1.0 equiv) in dry acetone (1 mL) at 25 °C. The resultant reaction mixture was then heated at 70 ºC for 15 h. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of saturated NH_4Cl (5 mL), poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The resultant crude orange oil was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→5:1) to afford perbenzylated ketone **S15** (0.080 g, 78% yield) as a yellow oil. **S15**: R_f = 0.65 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3031, 2927, 1661, 1588, 1508, 1454, 1377, 1295, 1244, 1156, 1110, 1083, 1061, 1028, 833, 736, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 1.6 Hz, 1 H), 7.39–7.29 (m, 37 H), 7.23–7.12 (m, 13 H), 7.02–6.99 (m, 5 H), 6.95 (d, J = 8.8 Hz, 2 H), 6.85 (d, J = 8.0 Hz, 2 H), 6.76 (d, J = 8.8 Hz, 2 H), 6.72 (d, J = 7.2 Hz, 2 H), 6.68–6.74 (m, 2 H), 6.66–6.65 (m, 2 H), 6.64 (d, J = 1.6 Hz, 1 H), 6.32 (s, 1 H), 6.14 (d, J = 2.0 Hz, 1 H), 5.08 (s, 2 H), 4.98–4.95 (m, 5 H), 4.91–4.87 (m, 6 H), 4.83–4.62 (m, 6 H), 4.40 (d, J = 1.6 Hz, 1 H), 3.90 (s, 1 H), 3.43 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 159.9, 159.6, 159.4, 157.2, 157.0, 156.5, 153.6, 146.4, 145.5, 142.4, 139.6, 137.5, 137.4, 137.1 (2 C), 137.0, 136.6, 136.5 (2 C), 130.4, 129.1, 128.7 (2 C), 128.6, 128.3, 128.2, 128.1, 128.0 (2 C), 127.9, 127.8, 127.7 (2 C), 127.6, 127.5, 127.2, 127.1, 126.5, 119.7, 117.6, 114.8, 114.4, 106.7, 102.6, 99.2, 96.2, 70.5 (2 C), 70.3 (2 C), 70.0, 69.9, 68.7, 56.7, 50.0, 46.8, 44.2; MS (FAB) calcd for $C_{91}H_{74}O_9^+$ [M+H^+] 1311.5, found 1311.4.

Aldehyde 35. To a slurry of Me_3SI (0.032 g, 0.156 mmol, 20 equiv) in THF (1 mL) at 0 °C was added *n*-BuLi (1.6 M in THF, 0.080 mL, 0.128 mmol, 16 equiv) dropwise over the course of 2 min, and the reaction mixture was stirred at 0 °C for an additional 2 min. A solution of ketone **S15** (0.011 g, 0.008 mmol, 1.0 equiv) in THF (1 mL) was then added dropwise over the course of 2 min at 0 °C, and the resultant solution was stirred for an additional 1 h at 0 °C.[3] Upon completion, the reaction contents were quenched at 0 °C with the addition of saturated aqueous NH_4Cl (5 mL), poured into water (5 mL), and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated to give the desired crude epoxide as a yellow oil. Next, the crude epoxide was immediately dissolved in benzene (0.5 mL) and solid ZnI_2 (0.080 g, 0.251 mmol, 31 equiv) was added at 25 °C.[8] The resultant reaction mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with water (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude yellow oil was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→3:1) to afford aldehyde **35** as an amorphous solid (0.010 g, 94% yield) as a single diastereoisomer. **35**: R_f = 0.61 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3031, 2922, 1724, 1594, 1509, 1454, 1378, 1300, 1243, 1157, 1124, 1060, 1027, 830, 737, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1 H), 7.45 – 7.27 (m, 36 H), 7.22 - 7.13 (m, 2 H), 7.15 (d, *J* = 7.6 Hz, 2 H), 7.08 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 1.6 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 2 H), 6.67 (s, 3 H), 6.54 (t, *J* = 2.0 Hz, 1 H), 6.42 (d, *J* = 2.0 Hz, 2 H), 6.40 (d, *J* = 1.6 Hz, 1 H), 5.44 (s, 1 H), 5.03 – 4.85 (m, 15 H), 4.68 (d, *J* = 11.6 Hz, 1 H), 4.60 (d, *J* = 11.6 Hz, 1 H), 4.43 (s, 1 H), 4.33 (s, 1 H), 3.58 (s, 1H), 3.42 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 160.1, 157.9, 157.1 (2 C), 155.3, 154.2, 146.7, 146.2, 140.9, 139.9, 137.3, 137.1, 136.8, 136.6, 135.6, 129.0, 128.9, 128.7 (3 C), 128.6, 128.3 (2 C), 128.2, 128.1 (2 C), 128.0 (2 C), 127.8, 127.7, 127.6, 127.5, 127.2, 117.8, 115.3, 114.7, 114.4, 108.7, 102.8, 100.9, 98.9, 96.7, 70.9, 70.6, 70.4, 70.2 (2 C), 69.9, 69.8, 57.2, 55.8, 50.0, 46.8, 45.9; MS (FAB) calcd for $C_{92}H_{77}O_9^+$ [M+H$^+$] 1324.6, found 1325.4.

Carasiphenol B (19). To a solution of aldehyde **35** (0.045 g, 0.034 mmol, 1.0 equiv) in THF (4 mL) at 25 °C was added 4-benzyloxyphenylmagnesium bromide (**S7**, 1.0 M in THF, 0.200 mL, 0.2 mmol, 6 equiv), and the resultant solution was stirred for 1 h at 25 °C. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (10 mL), poured into water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant colorless crude oil was purified by flash column chromatography (silica gel, hexanes:EtOAc, 5:1→1:1) to afford alcohol **S16** as a white solid (0.035 g, 68% yield) and as a single diastereomer. **S16**: R_f = 0.50 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3493, 3062, 3031, 2922, 2866, 1592, 1509, 1454, 1377, 1298, 1241, 1173, 1117, 1061, 1026, 829, 736, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (δ, *J* = 7.2 Hz, 5 H), 7.36–7.32 (m, 30 H), 7.20 (d, *J* = 8.8 Hz, 2 H), 7.20–7.08 (m, 10 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.72 (d, *J* = 1.6 Hz, 1 H), 6.69 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 6.48 (d, *J* = 2.4 Hz, 2 H), 6.47 (s, 1 H), 6.38 (t, *J* = 2.4 Hz, 1 H), 6.28 (d, *J* = 1.6 Hz, 1 H), 5.45 (d, *J* = 10.0 Hz, 1 H), 5.13–5.00 (m, 7 H), 4.91 (s, 4 H), 4.86 (s, 3 H), 4.74–4.69 (m, 5 H), 4.58 (d, *J* = 11.6 Hz, 1 H), 4.38 (s, 1 H), 3.67 (s, 1 H), 3.39 (s, 1 H), 3.19 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 159.5, 157.9, 157.2, 157.1 (2 C), 147.7, 145.7, 140.3, 137.5, 137.4, 137.2 (2 C), 137.1, 137.0, 136.9, 136.0, 129.8, 129.0, 128.9, 128.7 (2 C), 128.6, 128.4, 128.3 (2 C), 128.1, 128.0, 127.8 (2 C), 127.7, 127.6 (3 C), 127.5, 127.3, 126.8, 118.3, 117.9, 114.7, 114.5 (2 C), 108.5, 103.7, 100.3, 97.2, 73.9, 71.2, 70.6, 70.2, 70.0 (2 C), 69.9, 69.8, 55.8, 52.0, 50.7, 47.2, 46.6, 29.8; MS (FAB) calcd for $C_{105}H_{88}O_{10}^+$ [M$^+$]

1509.8, found 1508.4. This intermediate alcohol (6.0 mg**,** 0.004 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc:MeOH (1:1, 3 mL) and solid Pd/C (30%, 5.0 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to rereach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) for 2 h. H_2 was bubbled through the stirred reaction mixture again for 30 min and the reaction mixture again was refilled with MeOH to account for lost solvent. The reaction was stirred under H_2 at 25 ºC for 12 h.[5] Upon completion, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g, pre-washed with MeOH 5 times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 1 h. When this operation was complete, the solution was filtered through simple filtration paper to remove the Amberlite, and the filtrate was concentrated directly to afford carasiphenol B (**19**, 2.4 mg, 89%) as a white solid, with a scrupulously pure analytical sample obtained by reverse-phase HPLC[7] (Shimadzu Epic C18, 5µ, 250 × 9.6 mm, retention time = 10.3 min, 55% water in MeOH). **19**: R_f = 0.74 (silica gel, CH_2Cl_2:MeOH, 4:1); IR (film) ν_{max} 3323, 2968, 2925, 2853, 1696, 1606, 1512, 1453, 1366, 1333, 1238, 1165, 1120, 1084, 1013, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 8.22 (s, 2 H), 8.12 (s, 1 H), 8.06 (s, 1 H), 7.94 (s, 1 H), 7.88 (s, 1 H), 7.57 (s, 1 H), 7.25 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.4 Hz, 2 H), 6.61 (d, *J* = 2.0 Hz, 1 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 6.49 (d, *J* = 8.4 Hz, 2 H), 6.43 (d, *J* = 2.4 Hz, 2 H), 6.35 (t, *J* = 2.0 Hz, 1 H), 6.19 (s, 1 H), 6.14 (d, *J* = 2.0 Hz, 1 H), 5.44 (d, *J* = 6.0 Hz, 1 H), 4.97 (d, *J* = 6.4 Hz, 1 H), 4.26 (d, *J* = 1.6 Hz, 1 H), 4.06 (s, 1 H), 3.56 (s, 1 H), 3.43 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 159.8, 158.6, 158.2, 157.9, 156.2, 156.1, 153.5, 153.4, 148.5, 144.1, 138.8, 135.2, 134.3, 130.0, 129.3, 128.6, 127.1, 117.8, 116.1, 115.7, 115.4, 114.8, 107.4, 103.9, 102.0, 101.8, 95.9, 94.4, 56.8, 56.4, 49.6, 47.8, 46.7; HRMS (FAB) calcd for $C_{42}H_{32}O_9^+$ [M^+] 680.6981, found 680.2025. All spectroscopic data for **19** match that reported by Hu and co-workers. For a direct comparison, see Table S3.

Total Synthesis of Ampelopsin G (18).

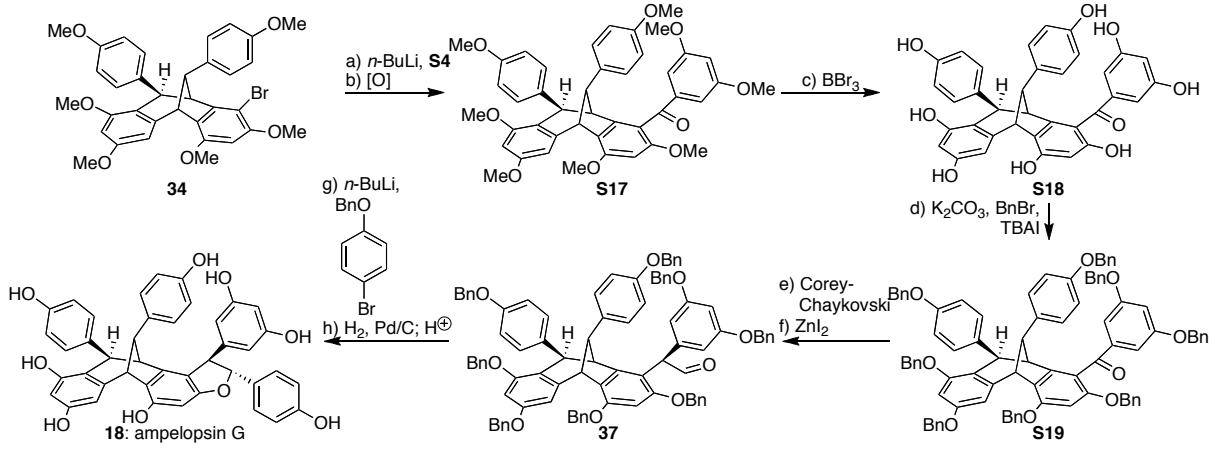


Figure S15. Total synthesis of ampelopsin G (**18**) from monobromide **34**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 1.1 equiv), THF, -78 ºC, 10 min, then **S4** (2.5 equiv), THF, -78 ºC, 2 h, -78 ºC to 25 ºC, 1.5 h, 83%; b) $NaHCO_3$ (16.0 equiv), DMP (4.3 equiv), CH_2Cl_2, 25 ºC, 10 min, 89%; c) BBr_3 (1.0 M in CH_2Cl_2, 117.0 equiv), CH_2Cl_2, sealed tube, 70 ºC, 7 d, 44%; d) K_2CO_3 (40 equiv), BnBr (43 equiv), *n*-Bu_4NI (2.0 equiv), acetone, 70 ºC, 12 h, 86%, e) Me_3SI (3.5 equiv), KO*t*-Bu (1.0 M in THF, 3.0 equiv), THF:DMSO 1:3, 12 ºC, 1 min, then **S19**, 12 ºC, 15 min; f) ZnI_2 (4.0 equiv), benzene, 25 ºC, 1 h, 73% (over 2 steps); g) 4-benzyloxyphenyl bromide (20.0 equiv), *n*-BuLi (1.6 M in THF, 18 equiv), THF, -78 ºC, 20 min, then **37**, -78 ºC, 15 min, -78 ºC to 25 ºC, 2 min, 76%; h) H_2, 30% Pd/C, EtOAc:MeOH (1:1) to MeOH, 25 ºC, 12 h, then Amberlite IR-12OH, 25 ºC, 1 h, 69% (over 2 steps).

Permethylated Ketone S17. Monobromide **34** (0.360 g, 0.583 mmol, 1.0 equiv) was azeotroped with benzene (3 × 10 mL), dissolved in THF (20 mL), and then cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 0.4 mL, 0.6413 mmol, 1.1 equiv) was added dropwise over the

course of 5 min and the reaction mixture was stirred at –78 °C for an additional 10 min, ultimately yielding a solution with a slight yellow color. A solution of benzene-azeotroped (3 × 5 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.242 g, 1.457 mmol, 2.5 equiv) in THF (4 mL) was then added dropwise over 5 min at –78 °C. After stirring the resulting solution for an additional 2 h at –78 °C, the reaction was then allowed to slowly warm to 25 ºC over the course of 1.5 h. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (30 mL), and extracted with EtOAc (4 × 20 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude yellow oil was purified by flash column chromatography (silica gel, hexanes:EtOAc, 4:1→1:1) to afford the desired alcohol as a mixture of diastereomers (0.340 g, 83% yield) as a white solid. The mixture of diastereomers (0.340 g, 0.482 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (10 mL) and solid $NaHCO_3$ (0.632 g, 7.578 mmol, 16 equiv) and Dess–Martin periodinane (0.876 g, 2.064 mmol, 4.3 equiv) were added sequentially at 25 °C. The resultant reaction mixture was stirred at 25 °C for 10 min. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (30 mL) and the resulting slurry was stirred for an additional 20 min at 25 ºC before being poured into water (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and concentrated to afford ketone **S17** (0.303 g, 89% yield) as an off-white foam. **S17**: R_f = 0.42 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2937, 2836, 1735, 1659, 1599, 1511, 1461, 1318, 1300, 1249, 1206, 1156, 1034, 829, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 2.0 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 8.8 Hz, 2 H), 6.63 (t, *J* = 2.0 Hz, 1 H), 6.53 (d, *J* = 2.0 Hz, 1 H), 6.26 (d, *J* = 2.4 Hz, 1 H), 6.19 (s, 1 H), 4.36 (br s, 1 H), 4.21 (s, 1 H), 3.84 (s, 3 H), 3.82 (s, 3 H), 3.74 (s, 9 H), 3.68 (s, 3 H), 3.67 (s, 1 H), 3.60 (s, 3 H), 3.44 (s, 1 H), 3.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 160.8, 159.8, 159.0, 158.5, 157.8, 157.4, 156.3, 145.4, 145.3, 141.5, 139.1, 135.0, 129.1, 128.8, 128.6, 118.8, 116.1, 113.5, 113.3, 107.0, 105.7, 103.1, 97.1, 94.3, 56.2, 55.6, 55.5 (2 C), 55.3 (2 C), 55.2, 54.8, 49.7, 49.4, 45.1; HRMS (FAB) calcd for $C_{43}H_{42}O_9^+$ [M^+] 702.7882, found 702.2835.

Deprotected Ketone S18. Permethylated ketone **S17** (0.300 g, 0.430 mmol, 1.0 equiv) was dissolved in a minimal amount of CH_2Cl_2 (1.0 mL), transferred to a sealable reaction vessel, and then BBr_3 (1.0 M in CH_2Cl_2, 50 mL, 50 mmol, 117 equiv) was added quickly in a single portion at 25 ºC. The resulting reddish-brown reaction mixture was then heated to 70 °C for 1 week. Upon completion, the reaction contents were cooled to 25 °C and quenched with the addition of H_2O (100 mL). After stirring the biphasic mixture for an additional 10 min at 25 ºC, the reaction contents were poured into water (30 mL), extracted with EtOAc (5 × 40 mL), dried ($MgSO_4$), filtered, and concentrated. The resultant orange oil was purified by preparative thin layer chromatography (silica gel, CH_2Cl_2:MeOH, 6:1) to afford the deprotected ketone **S18** (0.110 g, 44% yield) as a yellow foam, along with a monomethylated congener (0.140 g, 54% yield); this latter material could be recycled through a reprotection/deprotection sequence. **S18**: R_f = 0.68 (silica gel, CH_2Cl_2:MeOH, 4:1); IR (film) ν_{max} 3338, 3027, 2971, 2924, 1697, 1595, 1512, 1453, 1448, 1364, 1340, 1297, 1229, 1171, 1142, 867 cm^{-1}; ^1H NMR (400 MHz, acetone) δ 6.90–6.85 (m, 4 H), 6.74–6.63 (m, 7 H), 6.52 (br s, 1 H), 6.24 (s, 1 H), 6.21(d, *J* = 2.0 Hz, 1 H), 4.27 (s, 1 H), 4.20 (s, 1 H), 3.64 (s, 1 H), 3.60 (s, 1 H); ^{13}C NMR (100 MHz, acetone) δ 198.2, 160.3, 158.5, 156.8, 156.2, 155.2, 155.1, 146.8, 145.6, 142.5, 137.1, 133.4, 128.8, 128.3, 128.2, 114.8, 114.7, 114.5, 114.4, 112.2, 107.2, 106.0, 104.9, 101.6, 101.1, 55.7, 48.8, 48.3, 44.7; HRMS (FAB) calcd for $C_{35}H_{26}O_9^-$ [M^-] 590.58, found 589.01

Perbenzylated Ketone S19. Solid K_2CO_3 (1.00 g, 7.237 mmol, 39 equiv), BnBr (1.48 g, 8.408 mmol, 45 equiv) and *n*-Bu_4NI (0.140 g, 0.191 mmol, 1.1 equiv) were added sequentially to a solution of the deprotected ketone **S18** (0.110 g, 0.187 mmol, 1.0 equiv) in dry acetone (4 mL) at 25 °C. The resultant reaction mixture was heated at 70 ºC for 12 h. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of saturated aqueous NH_4Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The resultant crude orange oil was purified by preparative thin layer chromatography (silica gel, hexanes:EtOAc, 3:2) to afford perbenzylated ketone **S19** (0.210 g, 86% yield) as a yellow oil. **S19**: R_f = 0.63 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3031, 2868, 1659, 1599, 1508, 1453, 1295, 1241, 1175, 1147, 1058, 1026, 736, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.43–7.29 (m, 32 H), 7.16–7.06 (m, 9 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 2.4 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.84–6.82 (m, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 6.83 (t, *J* = Hz, 1 H), 6.66 (d, *J* = 7.2 Hz, 2 H), 6.63 (d, *J* = 2.4 Hz, 1 H), 6.43 (d, *J* = 2.0 Hz, 1 H), 6.22 (s, 1 H), 5.05 (s, 4 H), 5.02 (s, 1 H), 4.98 (s, 1 H), 4.91 (s, 4 H), 4.86 (s, 2 H), 4.72–4.60 (m, 4 H), 4.54 (br s, 1 H), 4.30 (s, 1 H), 3.81 (s, 1 H), 3.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 160.1, 158.7, 158.3, 157.9, 157.1, 155.6, 146.4, 145.5, 142.4, 139.6, 137.6, 137.3, 137.0, 136.9 (2 C), 136.6, 135.3, 130.4, 129.2, 128.8, 128.7 (2 C), 128.6, 128.3, 128.2, 128.1 (2 C), 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 126.9 (2 C), 119.2, 116.6, 114.6, 114.5, 107.8, 107.0, 103.7, 99.1, 96.7, 70.7, 70.3 (2 C), 70.2, 70.0 (2 C), 69.5, 54.5, 50.1, 49.7, 45.6; MS (FAB) calcd for $C_{91}H_{74}O_9^+$ [M+H^+] 1311.5, found 1312.2.

Aldehyde 37. To a slurry of Me_3SI (4 mg, 0.019 mmol, 3.5 equiv) in THF/DMSO 1:3 (2 mL) at 12 ºC was added KO*t*-Bu (1.0 M in THF, 0.016 mL, 0.016 mmol, 3.0 equiv) dropwise over the course of 1 min, and the reaction mixture was stirred at 12 ºC for an additional 1 min. A solution of ketone **S19** (7 mg, 0.005 mmol, 1.0 equiv) in DMSO (0.25 mL) was then added dropwise over the course of 1 min, and the resultant solution was stirred for an additional 15 min at 12 ºC.[3] Upon completion, the reaction contents were quenched at 12 ºC with the addition of water (5 mL) and brine (5 mL), and extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with water (5 × 20 mL) and brine (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated to give the desired crude epoxide as a yellow oil. Next, the crude epoxide was immediately dissolved in benzene (0.75 mL) and solid ZnI_2 (7 mg, 0.02 mmol, 4 equiv) was added at 25 ºC.[8] The resultant solution was stirred at 25 ºC for 1 h. Upon completion, the reaction contents were quenched with water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were then washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), filtered, and concentrated. The resulting crude yellow oil was purified by preparative thin layer chromatography (EtOAc:hexanes, 7:3) to afford aldehyde **37** and its diastereomer (epimeric at the α carbon of the aldehyde, 5.2 mg, 73% yield) as a mixture of diastereomers (1:1 based on ^1H NMR) and as a white solid. The pure aldehydes were obtained by reverse-phase HPLC (Shimadzu Epic C18, 5μ, 250 × 9.6 mm; retention time for **37** = 39.0 min, the diastereomer of **37** = 36.0 min, 5% H_2O in MeCN). **37**: R_f = 0.61 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3031, 2918, 1718, 1602, 1508, 1454, 1378, 1314, 1242, 1147, 1110, 1063, 1027, 737, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.43–7.24 (m, 25 H), 7.18–7.10 (m, 6 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 7.2 Hz, 2 H), 6.65 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 2.0 Hz, 1 H), 6.56 (d, *J* = 8.4 Hz, 2 H), 6.50–6.48 (m, 2 H), 6.43 (d, *J* = 2.4 Hz, 1 H), 6.32 (s, 1 H), 5.03–4.78 (m, 13 H), 4.70 (dd, *J* = 28 Hz, 16.4 Hz, 2 H), 4.34 (s, 1 H), 4.25 (s, 1 H), 3.80 (s, 1 H), 3.56 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 160.3, 158.7, 158.5, 157.3, 157.0, 156.3, 153.8, 146.6. 145.7,

139.6, 139.4, 137.5, 137.3, 136.9, 136.5, 134.9, 130.0, 129.0, 128.9, 128.8, 128.7 (3 C), 128.6, 128.2, 128.1, 128.0 (2 C), 127.9, 127.8, 127.7, 127.6, 127.5 (2 C), 127.1, 116.2, 115.5, 114.8, 114.3, 114.1, 108.1, 105.6, 103.7, 101.3, 99.1, 97.4, 71.1, 70.3, 70.2, 70.0 (2 C), 69.8, 69.6, 59.1, 53.5, 50.7, 49.6, 45.5; MS (FAB) calcd for $C_{92}H_{77}O_9^+$ [M+H$^+$] 1324.6, found 1325.7. The other diastereomer of **37**: R_f = 0.61 (silica gel, hexanes:EtOAc, 7:3); IR (film) ν_{max} 3063, 3032, 1721, 1603, 1508, 1454, 1379, 1313, 1297, 1241, 1176, 1155, 1111, 1063, 1027, 734, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.45–7.28 (m, 25 H), 7.24–7.22 (m, 6 H), 7.13–7.04 (m, 5 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 1.6 Hz, 2 H), 6.76 (d, *J* = 8.8 Hz, 2 H), 6.63 (d, *J* = 2.0 Hz, 1 H), 6.57 (d, *J* = 7.2 Hz, 2 H), 6.39 (d, *J* = 8.8 Hz, 2 H), 6.35 (d, *J* = 2.4 Hz, 1 H), 6.29 (s, 1 H), 6.28 (t, *J* = 2.0 Hz, 1 H), 5.04–4.90 (m, 9 H), 4.81-4.73 m, 3H), 4.68-4.64 (m, 3 H), 4.53 (dd, *J* = 23.2, 11.6 Hz, 2 H), 4.31 (s, 1 H), 3.90 (s, 1 H), 3.82 (s, 1 H), 3.58 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 160.1, 158.3, 158.2, 157.0, 156.9, 156.5, 153.4, 145.9, 145.8, 139.4, 139.1, 137.3, 137.2, 137.1, 136.8, 136.4, 135.2, 130.4, 128.9, 128.6, 128.5 (3 C), 128.4, 128.0, 127.9 (2 C), 127.8 (2 C), 127.7, 127.6, 127.4 (2 C), 127.3 (3 C), 127.1, 126.6, 116.2, 115.5, 114.5, 114.4, 107.8, 103.6, 101.0, 99.0, 97.3, 71.0, 70.0 (2 C), 69.9, 69.8 (2 C), 69.2, 58.2, 54.8, 50.1, 49.2, 44.7; MS (FAB) calcd for $C_{92}H_{77}O_9^+$ [M+H$^+$] 1324.6, found 1325.7.

Ampelopsin G (18). To a degassed solution of 4-benzyloxyphenyl bromide (0.020 g, 0.12 mmol, 20 equiv) in THF (0.5 mL) at −78 ºC was added *n*-BuLi (1.6 M in THF, 0.074 mL, 0.11 mmol, 18 equiv) dropwise over the course of 1 min, and the resultant solution was stirred at −78 ºC for 20 min. A degassed solution of aldehyde **37** (7.5 mg, 0.006 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise to the above solution over the course of 2 min at −78 ºC. The reaction was stirred at −78 ºC for 15 min, before being removed from the ice bath for 2 min. Upon completion, the reaction contents were quenched with water (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered and concentrated. The resultant yellow crude oil was purified by preparative thin layer chromatography (EtOAc:hexanes, 3:7) to afford the desired alcohol as a mixture of diastereomers (6.5 mg, 76% yield) and as a white solid. This intermediate alcohol mixture (6.5 mg**,** 0.004 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc:MeOH (1:1, 2 mL) and solid Pd/C (30%, 4.0 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to rereach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) at 25 ºC for 12 h.[5] Upon completion, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g pre-washed with MeOH 5 times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 20 min. When this operation was complete, the solution was filtered through simple filtration paper to remove the Amberlite (IR-12OH, 0.100 g pre-washed with MeOH five times), and the filtrate was concentrated directly to afford ampelopsin G (**18**, 2.0 mg, 69%) as a white solid, with a scrupulously pure analytical sample obtained by reverse-phase HPLC[7] (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 10.5 min, 55% water in MeOH). **18**: R_f = 0.62 (silica gel, CH_2Cl_2:MeOH, 7:3); IR (film) ν_{max} 3352, 2923, 2853, 1694, 1662, 1611, 1513, 1449, 1365, 1258, 1158, 1083, 1015, 834, 800 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.37 (s, 1 H), 8.27 (s, 1 H), 7.99 (s, 1 H), 7.90 (s, 1 H), 7.88 (s, 1 H), 7.28 (s, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.72 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 8.4 Hz, 2 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.56 (d, *J* = 2.0 Hz, 2 H), 6.50 (d, *J* = 2.0 Hz, 1 H), 6.37 (t, *J* = 2.0 Hz, 1 H), 6.19 (d, *J* = 2.4 Hz, 1 H), 6.11 (s, 1 H), 5.62 (d, *J* = 8.0

Hz, 1 H), 4.58 (d, J = 7.6 Hz, 1 H), 4.18 (s, 1 H), 4.12 (s, 1 H), 3.56 (s, 1 H), 3.18 (s, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 161.2, 160.0, 159.9, 158.2, 157.9, 157.3, 156.1, 156.0, 153.3, 147.8, 146.0, 142.5, 138.1, 134.6, 133.5, 130.0, 129.6, 128.9, 128.2, 118.8, 116.2, 116.1, 115.7, 115.6, 115.5, 113.3, 108.1, 108.0, 105.8, 102.4, 102.0, 96.3, 94.2, 57.7, 52.0, 51.5, 50.5, 45.0; HRMS (FAB) calcd for $C_{42}H_{32}O_9^+$ [M^+] 680.7, found 680.4. All spectroscopic data for **18** match that reported by Oshima and co-workers. For a direct comparison, see Table S4.

Unnatural Isomer of Ampelopsin G (obtained from the diastereomer of **37**)**:** R_f = 0.64 (silica gel, CH_2Cl_2:MeOH, 7:3); IR (film) ν_{max} 3363, 2919, 2853, 1737, 1653, 1559, 1444, 1231, 821 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.41 (s, 1 H), 8.24 (s, 2 H), 8.02 (s, 1 H), 7.99 (s, 1 H), 7.97 (s, 1 H), 7.91 (s, 1 H), 7.17 (d, J = 8.8 Hz, 2 H), 6.84 (d, J = 8.8 Hz, 2 H), 6.78 (d, J = 8.4 Hz, 2 H), 6.61 (d, J = 8.4 Hz, 2 H), 6.49 (d, J = 2.4 Hz, 1 H), 6.45 (d, J = 2.0 Hz, 2 H), 6.36 (t, J = 2.0 Hz, 1 H), 6.16 (d, J = 2.0 Hz, 1 H), 6.16 (s, 1 H), 5.49 (d, J = 6.4 Hz, 1 H), 4.44 (d, J = 6.8 Hz, 1 H), 4.14 (s, 1 H), 3.76 (s, 1 H), 3.64 (s, 1 H), 3.24 (s, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 161.4, 160.1, 160.0, 158.3, 157.8, 157.2, 156.4, 156.0, 153.2, 146.9 (2 C), 142.4, 138.4, 135.3, 133.7, 130.1, 129.4, 129.3, 128.1, 119.2, 116.1 (2 C), 115.7, 115.6, 115.5, 113.7, 107.9, 105.6, 102.5 (2 C), 101.9, 96.2, 94.3, 57.6, 55.7, 51.1, 50.2, 44.2; HRMS (FAB) calcd for $C_{42}H_{32}O_9^-$ [M^-] 680.7, found 680.4.

Total Synthesis of Vaticanol C (38).

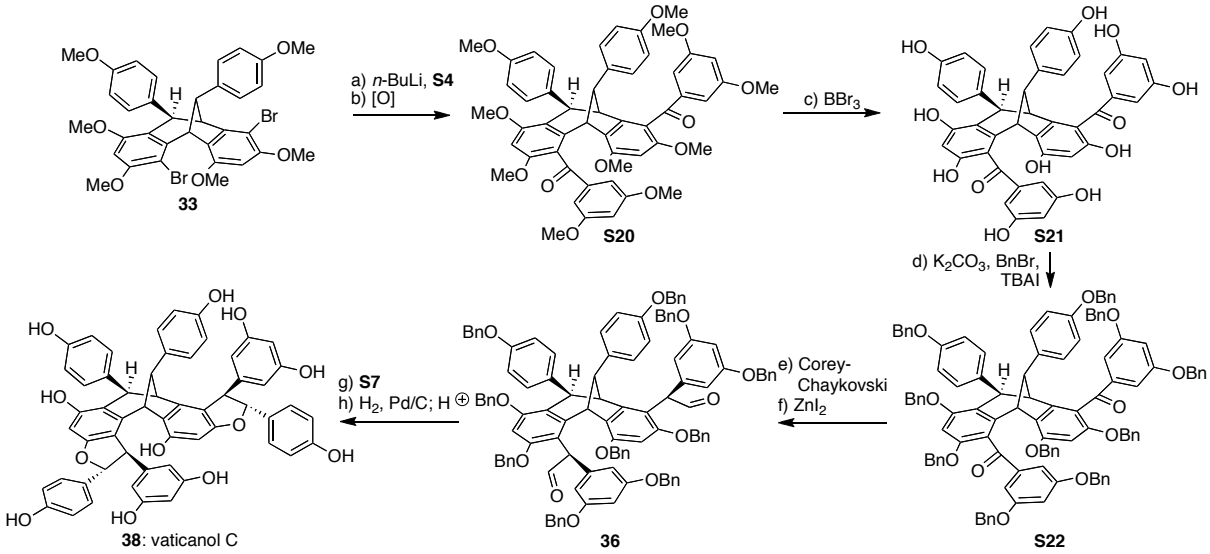


Figure S16. Total synthesis of vaticanol C (**38**) from dibromide **33**. Reagents and Conditions: a) *n*-BuLi (1.6 M in THF, 2.2 equiv), THF, -78 ºC, 4 min, then **S4** (6.0 equiv), THF, -78 ºC, 2 h, -78 ºC to 25 ºC, 3 h, 86%; b) $NaHCO_3$ (10.0 equiv), DMP (3.0 equiv), CH_2Cl_2, 25 ºC, 1 h, 99%; c) BBr_3 (1.0 M in CH_2Cl_2, 205 equiv), CH_2Cl_2, sealed tube, 100 ºC, 14 d, 60%; d) K_2CO_3 (60.0 equiv), BnBr (60.0 equiv), *n*-BuN_4I (2.5 equiv), acetone, 70 ºC, 24 h, 85%, e) *n*-BuLi (1.6 M in THF, 15.0 equiv), Me_3SI (20.0 equiv), THF, 0 ºC, 3 min, then **S22**, 0 ºC, 30 min, then 25 ºC, 6 h; f) ZnI_2 (10.0 equiv), benzene, 25 ºC, 1 h, 52% (over 2 steps); g) **S7** (1.0 M in THF, 10 equiv), THF, 25 ºC, 1 h, 83%; h) H_2, 30% Pd/C, EtOAc:MeOH (1:1) to MeOH, 25 ºC, 12 h, then Amberlite IR-12OH, 25 ºC, 1 h, 68% (over 2 steps).

Permethylated Ketone S20. Dibromide **33** (0.260 g, 0.375 mmol, 1.0 equiv) was azeotroped with benzene (3 × 5 mL), dissolved in THF (10 mL), and then cooled to –78 °C. Next, *n*-BuLi (1.6 M in THF, 0.515 mL, 0.824 mmol, 2.2 equiv) was added dropwise over the course of 4 min and the reaction mixture was stirred at –78 °C for an additional 4 min, ultimately yielding a solution with a slight yellow color. A solution of benzene-azeotroped (3 × 5 mL) 3,5-dimethoxybenzaldehyde (**S4**, 0.374 g, 2.25 mmol, 6.0 equiv) in THF (1.5 mL) was then added dropwise over the course of 5 min at –78 °C. After stirring the resultant solution for an additional 2 h at –78 °C, the reaction was then allowed to slowly warm to 25 °C over the course of 3 h. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl

(10 mL), poured into water (5 mL) and extracted with EtOAc (4 × 15 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by flash column chromatography (silica gel, hexanes:EtOAc, 10:1→1:1) to afford the desired diol (0.275 g, 86% yield) as a colorless oil and as a mixture of diastereomers based on ^{1}H NMR analysis. This alcohol mixture (0.275 g, 0.321 mmol, 1.0 equiv) was then dissolved in CH_2Cl_2 (10 mL) and solid $NaHCO_3$ (0.270 g, 3.21 mmol, 10 equiv) and Dess–Martin periodinane (0.406 g, 0.963 mmol, 3.0 equiv) were added sequentially at 25 °C. The resultant reaction mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with saturated aqueous Na_2SO_3 (15 mL) and the resultant slurry was stirred for an additional 20 min at 25 °C before being poured into water (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), filtered, and concentrated to afford ketone **S20** (0.274 g, 99% yield) as a colorless oil. **S20**: R_f = 0.50 (silica gel, hexanes:EtOAc, 1:1); IR (film) ν_{max} 2961, 1726, 1665, 1590, 1510, 1459, 1375, 1299, 1246, 1204, 1155, 1076, 1030, 830, 731, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (br s, 2 H), 7.03 (d, *J* = 8.6 Hz, 2 H), 6.92 (d, *J* = 2.2 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 6.73 (d, *J* = 8.6 Hz, 2 H), 6.68 (t, *J* = 2.2 Hz, 1 H), 6.64 (t, *J* = 2.1 Hz, 1 H), 6.57 (d, *J* = 8.4 Hz, 2 H), 6.30 (s, 1 H), 6.01 (s, 1 H), 4.52 (br s, 1 H), 4.49 (s, 1 H), 3.83 (s, 6 H), 3.75 (s, 6 H), 3.74 (s, 3 H), 3.73 (s, 1 H), 3.64 (s, 6 H), 3.57 (s, 3 H), 3.50 (s, 3 H), 3.43 (s, 1 H), 3.07 (br s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.2, 160.8, 160.7, 160.6, 158.6, 157.6, 157.5, 157.4, 156.2, 145.8, 144.3, 141.8, 141.4, 139.1, 134.6, 129.1, 128.7, 128.6, 118.4, 118.1, 117.3, 113.3, 106.9, 105.5, 105.3, 93.9, 93.2, 56.0, 55.8, 55.7, 55.6 (2 C), 55.4, 55.2, 55.1, 54.0, 53.9, 49.4, 45.3; HRMS (FAB) calcd for $C_{52}H_{50}O_{12}^+$ [M^+] 866.3302, found 866.3306.

Deprotected Ketone S21. Permethylated ketone **S20** (0.270 g, 0.317 mmol, 1.0 equiv) was dissolved in a minimal amount of CH_2Cl_2 (2 mL), transferred to a sealable reaction vessel, and then BBr_3 (1.0 M in CH_2Cl_2, 65.0 mL, 65.0 mmol, 205 equiv) was added in a single portion. The resulting black reaction mixture was then heated at 100 °C for 14 d. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of water (100 mL), and extracted with EtOAc (5 × 40 mL). The resultant crude product mixture was purified by preparative thin layer chromatography (silica gel, CH_2Cl_2:MeOH, 3:1) to afford the desired deprotected ketone **S21** (0.144 g, 60% yield) as an orange oil along with a monomethylated congener (0.066 g, 28% yield); this latter material could be recycled through a reprotection/deprotection sequence. **S21**: R_f = 0.25 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3001, 2936, 2836, 1662, 1589, 1511, 1460, 1426, 1316, 1299, 1249, 1204, 1180, 1156, 1110, 1081, 1065, 1033, 964, 926, 830 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.95 (br s, 1 H), 9.46 (br s, 1 H), 8.88 (br s, 1 H), 8.61 (br s, 2 H), 8.48 (br s, 2 H), 8.42 (br s, 1 H), 8.04 (br s, 1 H), 7.98 (br s, 1 H), 6.99–6.94 (m, 4 H), 6.77 (d, *J* = 2.2 Hz, 2 H), 6.70 (d, *J* = 8.6 Hz, 4 H), 6.63 (t, *J* = 2.2 Hz, 1 H), 6.56 (t, *J* = 2.2 Hz, 1 H), 6.54 (d, *J* = 8.6 Hz, 2 H), 6.35 (s, 1 H), 6.16 (s, 1 H), 4.36 (d, *J* = 1.3 Hz, 1 H), 4.20 (s, 1 H), 3.62 (s, 1 H), 3.52 (s, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 201.6, 198.4, 160.8, 159.9, 159.5, 159.4, 157.2, 157.0, 156.4, 156.2, 148.3, 145.8, 143.1, 142.8, 138.0, 134.0, 129.7, 129.1, 127.1, 116.2, 115.7, 115.6, 115.3, 109.2, 108.5, 108.3, 107.2, 103.0, 102.2, 55.2, 49.6, 47.1, 46.0; HRMS (FAB) calcd for $C_{42}H_{30}O_{12}^+$ [M^+] 726.1737, found 726.1713.

Perbenzylated Ketone S22. Solid K_2CO_3 (1.00 g, 7.29 mmol, 60 equiv), BnBr (1.25 g, 7.29 mmol, 60 equiv) and *n*-Bu_4NI (0.110 g, 0.305 mmol, 2.5 equiv) were added sequentially to a solution of the deprotected ketone **S21** (0.090 g, 0.122 mmol, 1.0 equiv) in dry acetone (2 mL)

at 25 °C. The resultant reaction mixture was then heated at 70 °C for 24 h. Upon completion, the reaction contents were cooled to 25 °C, quenched with the addition of water (30 mL), and extracted with EtOAc (3 × 25 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, 20:1→5:1) to afford perbenzylated ketone **S22** (0.170 g, 85% yield) as a yellow oil. **S22**: R_f = 0.62 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3062, 3031, 2923, 1658, 1588, 1508, 1453, 1415, 1377, 1295, 1242, 1178, 1154, 1108, 1058, 1027, 910, 840, 737, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2 H), 7.38–7.28 (m, 19 H), 7.27–7.22 (m, 8 H), 7.19–7.08 (m, 16 H), 7.04–6.95 (m, 4 H), 6.90 (d, *J* = 2.2 Hz, 2 H), 6.88–6.81 (m, 6 H), 6.73 (d, *J* = 8.6 Hz, 2 H), 6.71 (t, *J* = 2.2 Hz, 1 H), 6.89–6.65 (m, 5 H), 6.34 (s, 1 H), 6.00 (s, 1 H), 5.00 (br s, 2 H), 4.93–4.84 (m, 9 H), 4.83–4.79 (m, 3 H), 4.77 (d, *J* = 11.8 Hz, 2 H), 4.72–4.62 (m, 4 H), 4.54 (d, *J* = 11.8 Hz, 1 H), 4.43 (d, *J* = 11.8 Hz, 1 H), 3.87 (s, 1 H), 3.57 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 196.3, 159.9, 159.5, 159.4, 157.6, 157.0, 156.9, 156.3, 155.0, 146.7, 144.4, 142.3, 142.2, 139.6, 137.4, 137.1, 136.7, 136.6, 136.5, 136.4, 136.3, 134.8, 130.3, 129.0, 128.6, 128.5 (3 C), 128.4, 128.2 (2 C), 128.1 (2 C), 128.0, 127.9, 127.8 (2 C), 127.6, 127.5 (2 C), 127.4, 127.3, 126.9 (2 C), 126.7, 126.4, 119.3, 118.9, 117.7, 114.5, 114.3, 107.5, 106.9, 106.7, 96.7, 96.3, 70.4, 70.3, 70.1 (3 C), 69.8, 69.7, 69.0, 54.0, 49.7, 45.6, 44.8; MS (FAB) calcd for $C_{112}H_{90}O_{12}^+$ [M+H$^+$] 1627.6, found 1627.8.

Aldehyde 36. To a slurry of Me_3SI (0.104 g, 0.511 mmol, 20 equiv) in THF (5 mL) at 0 °C was added *n*-BuLi (1.6 M in THF, 0.240 mL, 0.384 mmol, 15.0 equiv) dropwise over the course of 3 min, and the reaction mixture was stirred at 0 °C for additional 3 min. A solution of ketone **S22** (0.050 g, 0.031 mmol, 1.0 equiv) in THF (2 mL) was added dropwise over the course of 3 min at 0 °C, and the resultant solution was stirred for an additional 30 min at 0 °C and then warmed to 25 °C and stirred for another 6 h.[3] Upon completion, the reaction contents were quenched with the addition of saturated aqueous NH_4Cl (10 mL), poured into water (5 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated to give the desired crude epoxide as a light yellow oil. Pressing forward without any additional purification, the crude epoxide was immediately dissolved in benzene (5 mL) and solid ZnI_2 (0.100 g, 0.313 mmol, 10 equiv) was added at 25 °C in a single portion.[8] The resultant reaction mixture was stirred at 25 °C for 1 h. Upon completion, the reaction contents were quenched with water (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product was purified by preparative thin layer chromatography (silica gel, hexanes:EtOAc, 2:1) to afford aldehyde diastereomer **36** (0.013 g, 26% yield) and a second stereoisomer of unknown configuration (0.013 g, 26% yield). Analytical samples were obtained by semi-preparative reverse-phase HPLC (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time for **36** = 35 min, other isomer of **36** = 45 min, 5% H_2O in MeCN). **36**: R_f = 0.53 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3031, 2920, 1723, 1593, 1508, 1454, 1379, 1299, 1241, 1156, 1108, 1063, 1027, 830, 736, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.96 (d, *J* = 0.9 Hz, 1 H), 9.51 (s, 1 H), 7.41–7.35 (m, 13 H), 7.34–7.27 (m, 28 H), 7.21–7.14 (m, 8 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 6.86 (d, *J* = 8.6 Hz, 2 H), 6.68 (d, *J* = 8.6 Hz, 2 H), 6.56 (t, *J* = 2.2 Hz, 1 H), 6.54–6.51 (m, 3 H), 6.47 (d, *J* = 8.6 Hz, 2 H), 6.43–6.41 (m, 3 H), 6.37 – 6.35 (m, 3 H), 5.39 (s, 1 H), 4.98 (s, 2 H), 4.97 (d, *J* = 12.0 Hz, 1 H), 4.95–4.92 (m, 3 H), 4.90–4.89 (m, 3 H), 4.88 (s, 2 H), 4.86 (s, 2 H), 4.84 (s, 2 H), 4.80 (d, *J* = 10.5 Hz, 1 H), 4.73–4.66 (m, 4 H), 4.60 (d, *J* = 11.7 Hz, 1 H), 4.42 (s, 1 H), 4.39 (s, 1 H), 3.53 (s, 1 H), 3.51 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 199.5, 160.2, 160.1, 157.8, 157.2, 156.8, 156.4, 155.1, 153.7, 147.2, 145.5, 140.9, 139.5,

139.3, 137.3, 137.1, 137.0, 136.7, 136.6, 136.4, 136.3, 136.1, 134.5, 129.1, 128.8, 128.6 (2 C), 128.5, 128.4, 128.2 (2 C), 128.0 (2 C), 127.9 (2 C), 127.8, 127.7, 127.6, 127.5, 127.4 (2 C), 127.1, 117.6, 115.4, 115.3, 114.7 (2 C), 114.1 (2 C), 108.6, 108.1, 101.1, 100.1, 96.9, 96.8, 71.0, 70.8, 70.4, 70.1 (2 C), 70.0, 69.7, 69.6, 59.1, 57.2, 52.1, 49.6, 47.0, 45.6; MS (FAB) calcd for $C_{114}H_{94}O_{12}^{+}$ [M+H^{+}] 1655.7, found 1655.8. The other diastereoisomer of **36**: R_f = 0.58 (silica gel, hexanes:EtOAc, 2:1); IR (film) ν_{max} 3062, 3031, 2923, 2854, 1722, 1593, 1508, 1454, 1379, 1299, 1242, 1156, 1109, 1062, 1027, 829, 736, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (d, *J* = 1.1 Hz, 1 H), 9.59 (s, 1 H), 7.41–7.27 (m, 33 H), 7.25–7.21 (m, 10 H), 7.14–7.05 (m, 5 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 6.74 (d, *J* = 8.6 Hz, 2 H), 6.70–6.64 (m, 4 H), 6.58 (s, 1 H), 6.56 (s, 1 H), 6.54 (t, *J* = 2.2 Hz, 1 H), 6.43 (d, *J* = 2.2 Hz, 2 H), 6.40 (d, *J* = 2.2 Hz, 2 H), 6.35–6.31 (m, 3 H), 5.45 (s, 1 H), 5.01 (d, *J* = 11.0 Hz, 1 H), 4.97 (d, *J* = 11.0 Hz, 1 H), 4.96 (s, 1 H), 4.92 (d, *J* = 11.9 Hz, 1 H), 4.92 (s, 2 H), 4.89–4.83 (m, 7 H), 4.81 (d, *J* = 11.7 Hz, 1 H), 4.79 (d, *J* = 11.7 Hz, 2 H), 4.71 (d, *J* = 11.7 Hz, 2 H), 4.66 (d, *J* = 11.7 Hz, 1 H), 4.53 (d, *J* = 11.9 Hz, 1 H), 4.47 (s, 1 H), 4.42 (d, *J* = 11.9 Hz, 1 H), 3.96 (s, 1 H), 3.57 (s, 1 H), 3.53 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ. 200.1, 199.9, 160.2, 160.0, 157.6, 157.0, 156.9, 156.7, 155.0, 153.6, 146.6, 145.7, 140.8, 139.4, 137.3, 137.2. 137.1, 136.9, 136.6, 136.4, 136.3 (2 C), 135.3, 135.0, 129.2, 128.8, 128.7, 128.6, 128.5 (2 C), 128.4, 128.2, 128.0 (2 C), 127.9, 127.8 (2 C), 127.7, 127.4 (2 C), 127.3 (3 C), 126.6, 117.8, 115.6, 115.5, 114.5, 114.4, 108.5, 107.9, 101.2, 100.8, 97.2, 96.9, 71.1, 70.7, 70.6, 70.1, 70.0, 69.9, 69.8, 69.5, 58.2, 57.0, 53.5, 49.3, 46.5, 45.0; MS (FAB) calcd for $C_{114}H_{94}O_{12}^{+}$ [M+H^{+}] 1655.7, found 1655.7.

Vaticanol C (38). To a solution of aldehyde **36** (5.0 mg, 0.003 mmol, 1.0 equiv) in THF (1 mL) at 25 °C was added 4–benzyloxyphenylmagnesium bromide (**S7**, 1.0 M in THF, 0.030 mL, 0.003 mmol, 10 equiv), and the resultant solution was stirred for 1 h at 25 °C. Upon completion, the reaction contents were quenched with saturated aqueous NH_4Cl (3 mL), poured into water (3 mL), and extracted with EtOAc (3 × 5 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated. The resultant crude product mixture was purified by preparative thin layer chromatography (silica gel, hexanes:EtOAc, 2:1) to afford the desired intermediate alcohol (5.0 mg, 83% yield) as a colorless oil and as a complex mixture of diastereomers based on ^{1}H NMR analysis. Carrying this mixture of diastereomeric alcohols forward, the material (5.0 mg, 0.003 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc:MeOH (1:1, 3 mL) and solid Pd/C (30%, 5 mg) was added. H_2 was then bubbled directly through the stirred reaction mixture for 30 min.[4] Once complete, some additional MeOH was added to replace any evaporated solvent to rereach ~3 mL reaction volume and the reaction mixture was stirred under H_2 (balloon) for 2 h. H_2 was bubbled through the stirred reaction mixture again for 30 min and the reaction mixture again was refilled with MeOH to account for lost solvent. This process was repeated one more time after stirring the reaction under H_2 for 2 h and finally the reaction was stirred under H_2 at 25 °C for 12 h.[5] Upon completion of the reaction, the reaction solution was filtered through simple filtration paper to remove Pd/C and washed with MeOH (2 mL).[6] Next, Amberlite (IR-12OH, 0.100 g pre-washed with MeOH five times) was added to the filtrate and the resultant mixture was stirred at 25 °C for 1 h. When this operation was complete, the solution was filtered through simple filtration papered to remove the Amberlite and the filtrate was concentrated directly to afford crude vaticanol C (**35**) as a white solid. This was purified by semi-preparative reverse-phase HPLC[7] (Shimadzu Epic C18, 5μ, 250 × 9.6 mm, retention time = 13.5 min, 45% MeOH in H_2O) to give vaticanol C (**38**, 1.2 mg, 68% yield) as a white solid. **38**: R_f = 0.28 (silica gel, CH_2Cl_2:MeOH, 3:1); IR (film) ν_{max} 3354, 2926, 2855, 1660, 1609, 1513, 1452, 1342, 1240, 1159, 1079, 1003, 832 cm^{-1}; ^{1}H NMR (400 MHz,

acetone-d_6) δ 8.44 (br s, 2 H), 8.36 (br s, 2 H), 8.26 (br s, 3 H), 7.98 (br s, 1 H), 7.84 (br s, 1 H), 7.51 (br s, 1 H), 7.27 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.6 Hz, 2 H), 7.04 (d, J = 8.6 Hz, 2 H), 6.87 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 6.68 (d, J = 8.6 Hz, 2 H), 6.58 (d, J = 2.2 Hz, 2 H), 6.48 (d, J = 8.6 Hz, 2 H), 6.43 (d, J = 2.2 Hz, 2 H), 6.39 (t, J = 2.2 Hz, 1 H), 6.38 (d, J = 8.6 Hz, 2 H), 6.36 (t, J = 2.2 Hz, 1 H), 6.19 (s, 1 H), 6.15 (s, 1 H), 5.64 (d, J = 7.9 Hz, 1 H), 5.46 (d, J = 6.6 Hz, 1 H), 4.96 (d, J = 6.6 Hz, 1 H), 4.59 (d, J = 7.9 Hz, 1 H), 4.20 (s, 1 H), 4.03 (s, 1 H), 3.41 (s, 1 H), 3.14 (s, 1 H); ^{13}C NMR (150 MHz, acetone-d_6) δ 161.1, 160.1, 160.0, 159.9, 158.3, 157.9, 156.2, 155.9, 153.6, 148.5, 146.1, 144.2, 143.3, 138.4, 134.3 (2 C), 133.6, 130.1, 129.6128.7, 128.4, 128.2, 118.7, 117.9, 116.2 (2 C), 115.7, 115.6, 114.8, 108.2, 107.6, 102.5, 102.0, 96.0, 95.9, 94.3, 57.9, 56.9, 51.1, 49.8, 47.7, 45.7, ; HRMS (FAB) calcd for $C_{56}H_{43}O_{12+}$ [M+H$^+$] 906.2755, found 906.2642. All spectroscopic data for **38** match that reported by Tanaka and co-workers. For a direct comparison, see Table S5.

Larger Scale Synthesis of Carasiphenol C (16): on ~50 mg scale

All reactions were performed as described above if not otherwise stated.

Deprotected Ketone S5. Permethylated ketone **S3** (0.510 g, 0.725 mmol, 1.0 equiv); split in two sealable reaction vessels; 70 °C for 2 d. Deprotected ketone **S5** (0.611 g, 84% yield) as an orange oil.

Perbenzylated Ketone S6. Deprotected ketone **S5** (0.285 g, 0.483 mmol, 1.0 equiv). Perbenzylated ketone **S6** (0.526 g, 83% yield) as a yellow oil.

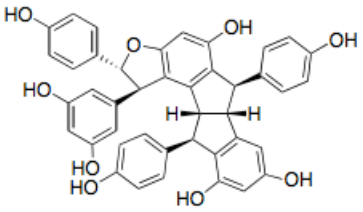
Aldehyde 27. Ketone **S6** (0.185 g, 0.141 mmol, 1.0 equiv). Aldehyde **27** (0.147 g, 79% yield).

Alcohol S8. Aldehyde **27** (0.147 g, 0.014 mmol, 1.0 equiv, 5.5:1 mixture of diastereomers); the crude product was purified by preparative thin layer chromatography (Et_2O/toluene, 19/1) to afford alcohol **S8** (0.112 g, 90% yield, mixture of diastereomers, 4:1 based on ^{1}H NMR) as a white solid.

Carasiphenol C (16). HPLC grade solvents were used for all operations performed in the final reaction. Alcohol **S8** (55 mg**,** 0.036 mmol, 1.0 equiv) was dissolved in a mixture of EtOAc/MeOH (1/2, 8 mL,), solid Pd/C (10%, 120 mg); 7 h total reaction time (deprotection); crude ^{1}H NMR of the deprotected alcohol intermediate obtained indicating 100% conversion, ~90% pure crude carasiphenol C (**16**, 25 mg) as a slight orange solid. The reaction was performed two times at this scale and one time on 12 mg scale. In total 55 mg of material containing **16** in at least 90% purity (if not better) have been obtained from this process. ^{1}H NMR of all three batches of this material, the ^{13}C spectrum for a portion of the material after 100 scans, and the alcohol precursor to the final cyclization can be found at the very end of the Supporting Information Section.

^{1}H Literature Chemical Shift	^{1}H Literature Appearance	^{1}H Observed Chemical Shift	^{1}H Observed Appearance
		8.45	s, 1 H
		8.18	s, 2 H
		8.05	s, 1 H
		8.01	s, 2 H
		7.80	s, 1 H
		7.80	s, 1 H
		7.70	s, 1 H
7.22	d, *J* = 8.5 Hz, 2 H	7.23	d, *J* = 8.5 Hz, 2 H
6.98	d, *J* = 8.3 Hz, 2 H	6.98	d, *J* = 8.6 Hz, 2 H
6.86	d, *J* = 8.5 Hz, 2 H	6.85	d, *J* = 8.6 Hz, 2 H
6.70	d, *J* = 8.3 Hz, 2 H	6.70	d, *J* = 8.6 Hz, 2 H
6.61	d, *J* = 1.3 Hz, 1 H	6.61	d, *J* = 1.8 Hz, 1 H
6.44	d, *J* = 8.6 Hz, 2 H	6.43	d, *J* = 8.6 Hz, 2 H
6.35	d, *J* = 8.4 Hz, 2 H	6.35	d, *J* = 8.6 Hz, 2 H
6.31	d, *J* = 2.1 Hz, 1 H	6.30	t, *J* = 2.2 Hz, 1 H
6.25	d, *J* = 2.3 Hz, 1 H	6.25	d, *J* = 2.2 Hz, 2 H
6.25	s, 1 H	6.24	s, 1 H
6.17	d, *J* = 1.3 Hz, 1 H	6.16	d, *J* = 1.8 Hz, 1 H
5.25	d, *J* = 7.5 Hz, 1 H	5.26	d, *J* = 7.5 Hz, 1 H
4.82	d, *J* = 7.5 Hz, 1 H	4.83	d, *J* = 7.5 Hz, 1 H
4.61	br s, 1 H	4.62	s, 1 H
4.51	br s, 1 H	4.53	s, 1 H
3.66	d, *J* = 5.9 Hz, 1 H	3.67	d, *J* = 5.9 Hz, 1 H
3.61	d, *J* = 5.9 Hz, 1 H	3.62	d, *J* = 5.9 Hz, 1 H

^{13}C Literature	^{13}C Observed Recalibrated	^{13}C Observed Acetone at 29.8 ppm
163.1	163.2	162.9
160.3	160.5	160.2
159.6	159.7	159.4
158.7	158.7	158.4
156.3	156.7	156.4
156.2	156.4	156.1
155.6	155.8	155.5
150.7	151.2	150.9
145.8	145.8	145.5
145.4	145.4	145.1
138.0	138.0	137.7
137.0	137.0	136.7
133.5	133.7	133.4
129.6	130.9	130.6
129.4	129.5	129.2
129.4	129.5	129.2
129.4	129.2	128.9
126.1	126.1	125.8
123.3	123.3	123.0
116.6	116.7	116.4
116.5	116.5	116.2
116.2	116.3	116.0
115.6	115.7	115.4
107.8	107.9	107.6
103.6	103.8	103.5
102.8	102.9	102.6
102.6	102.7	102.4
97.2	97.2	96.9
95.1	95.1	94.8
60.4	60.4	60.1
60.3	60.2	59.9
57.4	57.5	57.2
53.7	53.7	53.4
50.4	50.3	50.0

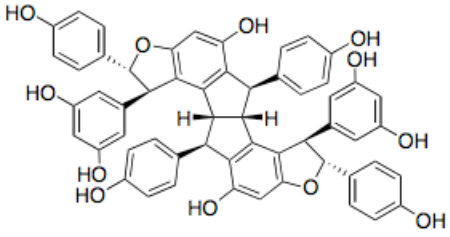


16: carasiphenol C

Table 1 Comparison of ^{1}H and ^{13}C NMR spectra of **16** with reported literature data.

^{1}H Literature		^{1}H Observed	
Chemical Shift	Appearance	Chemical Shift	Appearance
8.41	br s, 2 H	8.46	s, 2 H
8.11	br s, 4 H	8.15	s, 4 H
7.88	br s, 2 H	7.91	s, 2 H
7.75	br s, 2 H	7.79	s, 2 H
7.21	d, *J* = 8.6 Hz, 4H	7.25	d, *J* = 8.5 Hz, 4 H
6.84	d, *J* = 8.6 Hz, 4 H	6.88	d, *J* = 8.5 Hz, 4 H
6.42	d, *J* = 8.8 Hz, 4 H	6.46	d, *J* = 8.6 Hz, 4 H
6.34	d, *J* = 8.8 Hz, 4 H	6.38	d, *J* = 8.6 Hz, 4 H
6.25	t, *J* = 2.2 Hz, 2 H	6.29	t, *J* = 2.2 Hz, 2 H
6.21	d, *J* = 2.2 Hz, 4 H	6.25	d, *J* = 2.2 Hz, 4 H
6.20	s, 2 H	6.24	s, 2 H
5.23	d, *J* = 7.7 Hz, 2 H	5.27	d, *J* = 7.6 Hz, 2 H
4.82	d, *J* = 7.7 Hz, 2 H	4.86	d, *J* = 7.6 Hz, 2 H
4.57	s, 2 H	4.61	s, 2 H
3.47	s, 2 H	3.52	s, 2 H

^{13}C Literature	^{13}C Observed Recalibrated	^{13}C Observed Acetone at 29.8 ppm
162.8	162.8	163.3
160.0	160.0	160.5
158.3	158.3	158.8
156.0	156.0	156.5
155.4	155.4	155.9
145.4	145.3	145.8
145.2	145.1	145.6
136.5	136.5	137.0
133.3	133.7	134.2
129.1	129.1	129.6
128.7	128.7	129.2
125.3	125.2	125.7
116.5	116.5	117.0
116.2	116.1	116.6
115.4	115.4	115.9
107.5	107.5	108.0
102.3	102.0	102.5
96.9	96.9	97.4
94.7	94.7	95.2
59.4	59.4	59.9
57.6	57.1	57.6
49.4	49.4	49.9

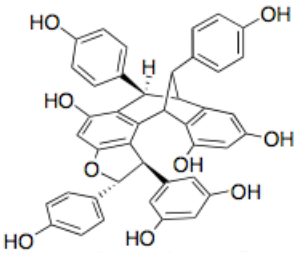


17: ampelopsin H

Table 2 Comparison of ^{1}H and ^{13}C NMR spectra of **17** with reported literature data.

^{1}H Literature		^{1}H Observed	
Chemical Shift	Appearance	Chemical Shift	Appearance
		8.43	s, 1 H
		8.22	s, 2 H
		8.12	s, 1 H
		8.06	s, 1 H
		7.94	s, 1 H
		7.88	s, 1 H
		7.57	s, 1 H
7.20	d, *J* = 8.3 Hz, 2 H	7.25	d, *J* = 8.8 Hz, 2 H
7.10	d, *J* = 8.2 Hz, 2 H	7.16	d, *J* = 8.4 Hz, 2 H
6.81	d, *J* = 8.5 Hz, 2 H	6.84	d, *J* = 8.4 Hz, 2 H
6.74	d, *J* = 8.2 Hz, 2 H	6.79	d, *J* = 8.4 Hz, 2 H
6.56	d, *J* = 1.4 Hz, 1 H	6.61	d, *J* = 2.0 Hz, 1 H
6.56	d, *J* = 8.6 Hz, 2 H	6.61	d, *J* = 8.4 Hz, 2 H
6.45	d, *J* = 8.6 Hz, 2 H	6.49	d, *J* = 8.4 Hz, 2 H
6.37	d, *J* = 1.8 Hz, 1 H	6.43	d, *J* = 2.4 Hz, 2 H
6.31	t, *J* = 1.8 Hz, 1 H	6.35	t, *J* = 2.0 Hz, 1 H
6.15	s, 1H	6.19	s, 1 H
6.09	d, *J* = 1.1 Hz, 1 H	6.14	d, *J* = 2.0 Hz, 1 H
5.38	d, *J* = 6.3 Hz, 1 H	5.44	d, *J* = 6.0 Hz, 1 H
4.93	d, *J* = 6.3 Hz, 1 H	4.97	d, *J* = 6.4 Hz, 1 H
4.20	bs, 1 H	4.26	d, *J* = 1.6 Hz, 1 H
4.01	s, 1 H	4.06	s, 1 H
3.51	s, 1 H	3.56	s, 1 H
3.37	bs, 1 H	3.43	s, 1 H

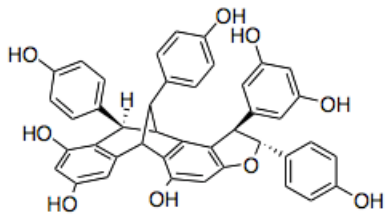
^{13}C Literature	^{13}C Observed Recalibrated	^{13}C Observed Acetone at 29.8 ppm
160.1	160.1	159.9
160.0	160.0	159.8
158.5	158.8	158.6
158.1	158.4	158.2
158.1	158.1	157.9
156.4	156.5	156.3
156.3	156.3	156.1
153.7	153.7	153.5
148.7	148.7	148.5
144.4	144.3	144.1
139.0	139.0	138.8
135.4	135.4	135.2
134.4	134.6	134.4
130.2	130.2	130.0
129.6	129.5	129.3
128.9	128.8	128.6
127.0	127.3	127.1
118.0	118.0	117.8
116.4	116.3	116.1
116.0	115.9	115.7
115.7	115.6	115.4
115.0	115.0	114.8
107.6	107.6	107.4
104.0	104.1	103.9
102.2	102.2	102.0
102.0	102.0	101.8
96.0	96.1	95.9
94.7	94.6	94.4
56.9	57.0	56.8
56.8	56.6	56.4
49.9	49.8	49.6
48.1	48.0	47.8
46.9	46.9	46.7



19: carasiphenol B

Table 3 Comparison of ^{1}H and ^{13}C NMR spectra of **38** with reported literature data.

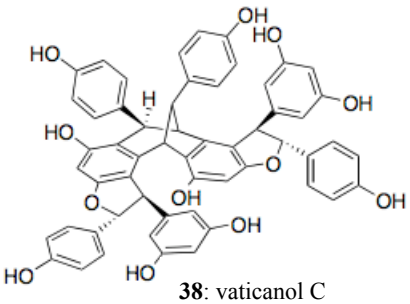
^{1}H Literature Chemical Shift	^{1}H Literature Appearance	^{13}C Literature	^{13}C Observed Recalibrated	^{13}C Observed Acetone at 29.8 ppm
		163.6	161.6	161.2
		160.4	160.4	160.0
		160.4	160.3	159.9
		158.6	158.6	158.2
		158.3	158.3	157.9
		157.7	157.7	157.3
		156.5	156.5	156.1
7.24	d, *J* = 8.5 Hz, 2 H	156.5	156.4	156.0
6.99	d, *J* = 7.5 Hz, 2 H	153.7	153.7	153.3
6.84	d, *J* = 7.5 Hz, 2 H	148.2	148.2	147.8
6.70	d, *J* = 8.5 Hz, 2 H	146.3	146.4	146.0
6.66	d, *J* = 7.5 Hz, 2 H	142.9	142.9	142.5
6.60	d, *J* = 8.5 Hz, 2 H	138.5	138.5	138.1
6.54	d, *J* = 2.0 Hz, 2 H	134.9	135.0	134.6
6.48	d, *J* =I 2.0 Hz, 1 H	133.8	133.9	133.5
6.35	t, *J* = 2.0 Hz, 1 H	130.4	130.4	130.0
6.18	d, *J* = 2.0 Hz, 1 H	130.0	130.0	129.6
6.10	s, 1 H	129.3	129.3	128.9
5.60	d, *J* = 8.0 Hz, 1 H	128.5	128.6	128.2
4.55	d, *J* = 8.0 Hz, 1 H	119.2	119.2	118.8
4.15	br d, *J* = 1.0 Hz, 1 H	116.5	116.6	116.2
4.09	bs, 1 H	116.5	116.5	116.1
3.53	bs, 1 H	116.1	116.1	115.7
3.15	bs, 1 H	116.0	116.0	115.6
^{1}H Observed Chemical Shift	^{1}H Observed Chemical Shift	116.0	115.9	115.5
		113.7	113.7	113.3
		108.5	108.5	108.1
8.37	s, 1 H	108.5	108.4	108.0
8.27	s, 1 H	106.2	106.2	105.8
7.99	s, 1 H	102.8	102.8	102.4
7.90	s, 1 H	102.4	102.4	102.0
7.88	s, 1 H	96.6	96.7	96.3
7.28	s, 1 H	94.6	94.6	94.2
7.26	d, *J* = 8.4 Hz, 2 H	58.1	58.1	57.7
7.01	d, *J* = 8.4 Hz, 2 H	52.4	52.4	52.0
6.86	d, *J* = 8.4 *Hz*, 2 H	51.0	51.9	51.5
6.72	d, *J* = 8.4 Hz, 2 H	50.9	50.9	50.5
6.68	d, *J* = 8.4 Hz, 2 H	45.4	45.4	45.0
6.62	d, *J* = 8.8 Hz, 2 H			
6.56	d, *J* = 2.0 Hz, 2 H			
6.50	d, *J* = 2.0 Hz, 1 H			
6.37	t, *J* = 2.0 Hz, 1 H			
6.19	d, *J* = 2.4 Hz, 1 H			
6.11	s, 1 H			
5.62	d, *J* = 8.0 Hz, 1 H			
4.58	d, *J* = 7.6 Hz, 1 H			
4.18	s, 1 H			
4.12	s, 1 H			
3.56	s, 1 H			
3.18	s, 1 H			



18: ampelopsin G

Table 4 Comparison of ^{1}H and ^{13}C NMR spectra of **18** with reported literature data.

^{1}H Literature		^{1}H Observed		^{13}C Literature	^{13}C Observed
Chemical Shift	**Appearance**	**Chemical Shift**	**Appearance**		**Acetone at 29.8 ppm**
8.49	s, 1H	8.44	br s, 2 H	161.1	161.1
8.46	s, 1 H	8.36	br s, 2 H	160.1	160.1
8.35	s, 2 H	8.36	br s, 2 H	160.1	160.1
8.26	s, 2 H	8.26	br s, 3 H	160.0	160.0
8.23	s, 1 H			160.0	159.9
7.98	s, 1 H	7.98	br s, 1 H	158.3	158.3
7.81	s, 1 H	7.84	br s, 1 H	158.3	158.3
7.51	s, 1 H	7.51	br s, 1 H	157.9	157.9
7.24	d, *J* = 8.8 Hz, 2 H	7.27	d, *J* = 8.4 Hz, 2 H	156.1	156.2
7.23	d, *J* = 8.8 Hz, 2 H	7.26	d, *J* = 8.6 Hz, 2 H	155.9	155.9
7.01	d, *J* = 8.3 Hz, 2 H	7.04	d, *J* = 8.6 Hz, 2 H	153.5	153.6
6.84	d, *J* = 8.8 Hz, 2 H	6.87	d, *J* = 8.6 Hz, 2 H	148.5	148.5
6.83	d, *J* = 8.8 Hz, 2 H	6.86	d, *J* = 8.6 Hz, 2 H	146.1	146.1
6.65	d, *J* = 8.3 Hz, 2 H	6.68	d, *J* = 8.6 Hz, 2 H	144.2	144.2
6.55	d, *J* = 2.0 Hz, 2 H	6.58	d, *J* = 2.2 Hz, 2 H	143.3	143.3
6.45	d, *J* = 8.8 Hz, 2 H	6.48	d, *J* = 8.6 Hz, 2 H	138.4	138.4
6.40	d, *J* = 2.0 Hz, 2 H	6.43	d, *J* = 2.2 Hz, 2 H	134.4	134.3
6.36	t, *J* = 2.0 Hz, 1 H	6.39	t, *J* = 2.2 Hz, 1 H	134.3	134.3
6.35	d, *J* = 8.8 Hz, 2 H	6.38	d, *J* = 8.6 Hz, 2 H	133.6	133.6
6.33	t, *J* = 2.0 Hz, 1 H	6.36	t, J = 2.2 Hz, 1 H	130.1	130.1
6.16	s, 1 H	6.19	s, 1 H	129.6	129.6
6.12	s, 1 H	6.15	s, 1 H	128.7	128.7
5.61	d, *J* = 7.8 Hz, 1 H	5.64	d, *J* = 7.9 Hz, 1 H	128.4	128.4
5.43	d, *J* = 6.5 Hz, 1 H	5.46	d, *J* = 6.6 Hz, 1 H	128.2	128.2
4.93	d, *J* = 6.5 Hz, 1 H	4.96	d, *J* = 6.6 Hz, 1 H	118.7	118.7
4.56	d, *J* = 7.8 Hz, 1 H	4.59	d, *J* = 7.9 Hz, 1 H	118.0	117.9
4.16	s, 1 H	4.20	s, 1 H	116.3	116.2
3.99	s, 1 H	4.03	s, 1 H	116.2	116.2
3.38	s, 1 H	3.41	s, 1 H	115.7	115.7
3.10	s, 1 H	3.14	s, 1 H	115.6	115.6
				114.8	114.8
				108.2	108.2
				108.2	108.2
				107.6	107.6
				102.5	102.5
				102.0	102.0
				96.1	96.0
				96.0	95.9
				94.3	94.3
				94.3	94.3
				57.9	57.9
				56.9	56.9
				51.2	51.1
				49.8	49.8
				47.7	47.7
				45.7	45.7



38: vaticanol C

Table 5 Comparison of ^{1}H and ^{13}C NMR spectra of **38** with reported literature data.

References

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4. The debenzylation proceeds much faster in MeOH than in a mixture of MeOH and EOAc. Since the starting material does not dissolve in pure MeOH the use of a mixture of EtOAc and MeOH is required at the start of the reaction. By refilling the evaporated solvent with MeOH its proportion increases slowly with the increase of the polarity of the partly deprotected substrate.
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6. Generally, the last step can be performed without filtering the Pd/C and simply adding Amberlite to the reaction mixture.
7. Preparative thin layer chromatography or flash column chromatography in our hands turned out not to be the method of choice for the purification of the target molecules since a significant amount of material is lost.
8. Bach, N. J., Kornfeld, E. C., Jones, N. D., Chaney, M. O., Dorman, D. E., Paschal. J. W., Clemens, J. A. & Smalstig, E. B. Bicyclic and tricyclic ergoline partial structures. Rigid 3-(2-aminoethyl)pyrroles and 3- and 4-(2-aminoethyl)pyrazoles as dopamine agonists. *J. Med. Chem.* **23**, 481–491 (1980).
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Regioselective Reactions for Programmable Resveratrol Oligomer Synthesis

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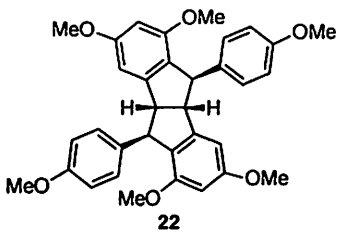
^{1}H and ^{13}C Spectra



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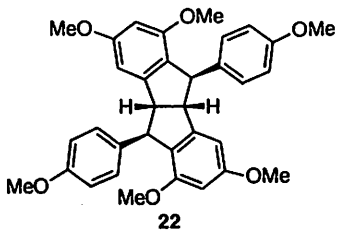

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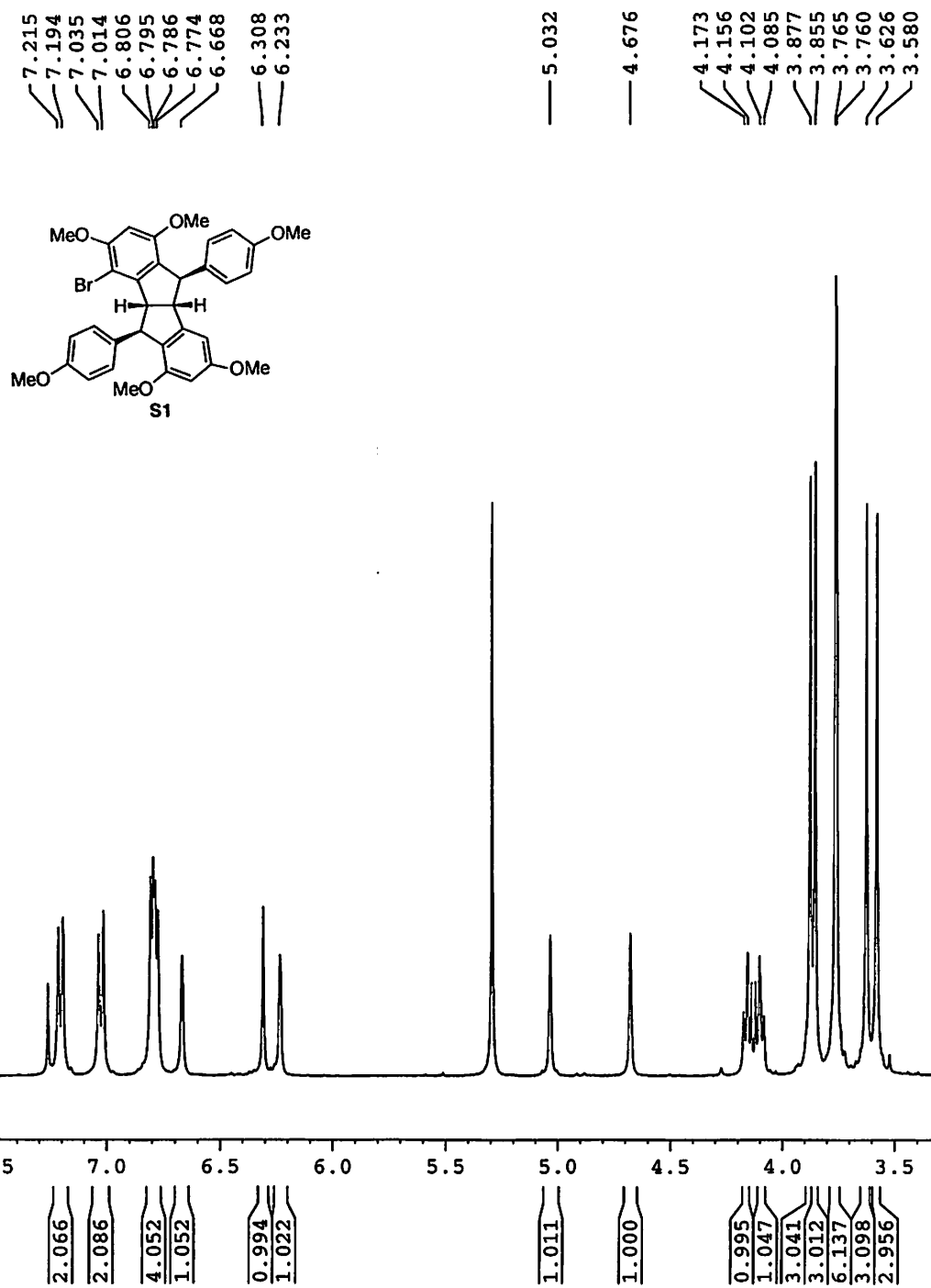
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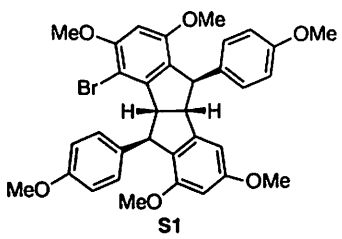

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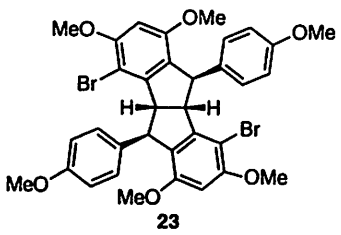

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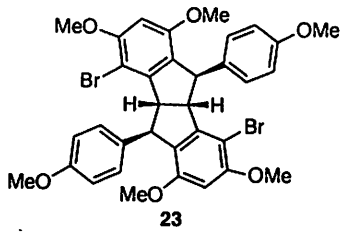
6.098
6.010

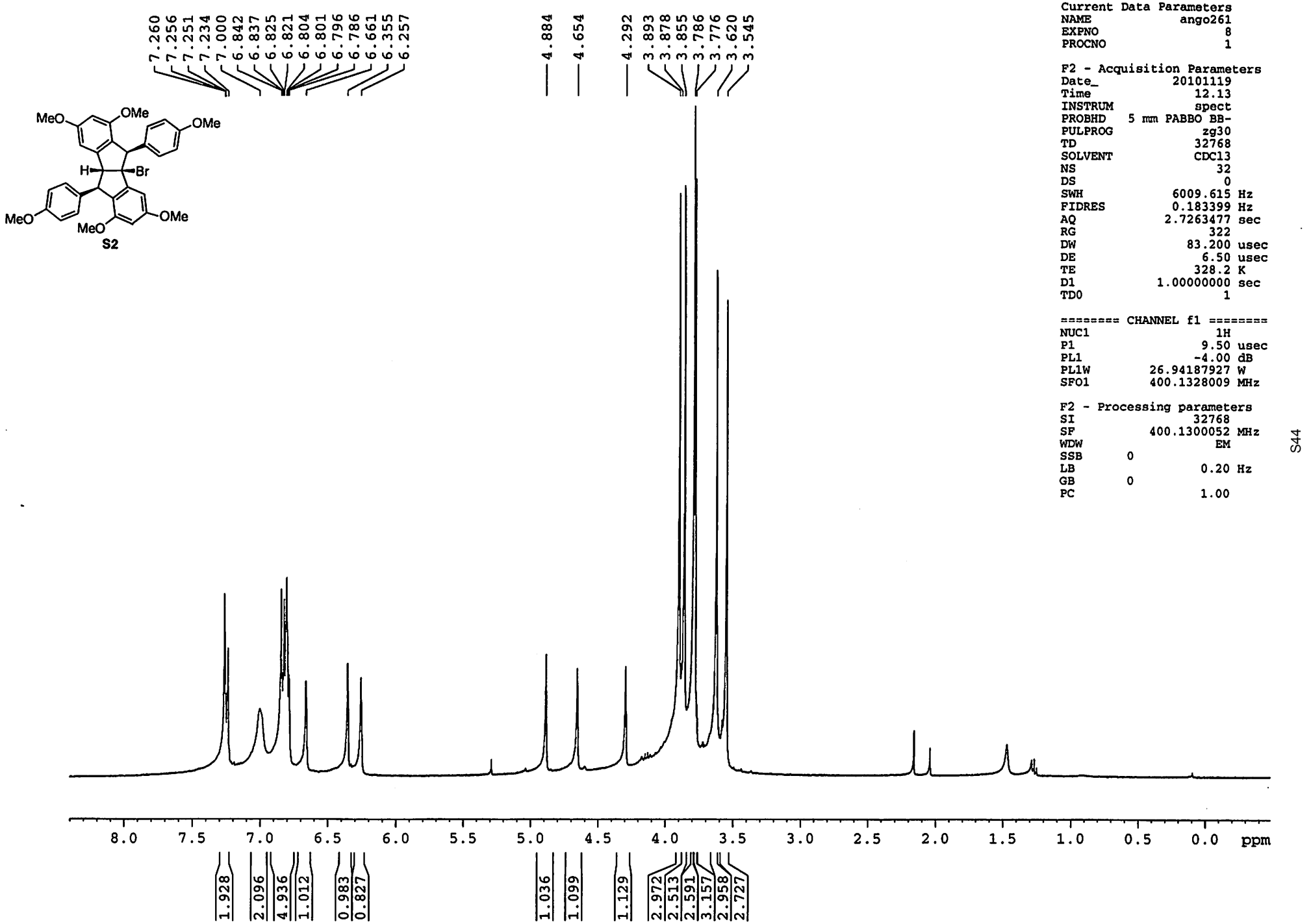


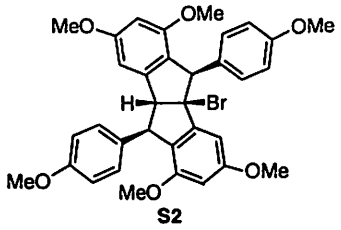
23

157.714
156.723
155.773
146.384
138.183
128.529
127.900
113.369
99.537
96.034
60.546
56.667
55.482
55.108
52.919

NAME	angol26dibromol2C
EXPNO	1
PROCNO	1
Date_	20100512
Time	16.52
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	653
DS	0
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	0.6816244 sec
RG	1820
DW	20.800 usec
DE	6.50 usec
TE	295.9 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127757 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
7.256
7.251
7.234
7.000
6.842
6.837
6.825
6.821
6.804
6.801
6.796
6.786
6.661
6.355
6.257
4.884
4.654
4.292
3.893
3.878
3.855
3.786
3.776
3.620
3.545
MeO
OMe
OMe
H
Br
MeO
OMe
MeO
S2
Current Data Parameters
NAME ango261
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101119
Time 12.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 322
DW 83.200 usec
DE 6.50 usec
TE 328.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.928
2.096
4.936
1.012
0.983
0.827
1.036
1.099
1.129
2.972
2.513
2.591
3.157
2.958
2.727



S2

161.953
161.692
158.506
158.221
157.096
156.593
151.041
146.571
136.472
135.466
130.095
129.109
124.286
123.439
113.660
113.176
100.022
99.938
99.737
98.463
78.334
68.957
58.860
55.699
55.603
55.407
55.246
55.144
53.975

Current Data Parameters
NAME ango261
EXPNO 9
PROCNO 1

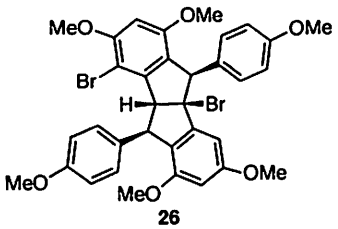
F2 - Acquisition Parameters
Date_ 20101119
Time 12.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2909
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 328.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127601 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



26

7.518 7.496 7.260 6.941 6.821 6.816 6.805 6.799 6.786 6.778 6.773 6.316 6.307

5.012 4.974 4.473 3.890 3.875 3.779 3.584 3.549

```
Current Data Parameters
NAME                  ango274C
EXPNO                        1
PROCNO                       1

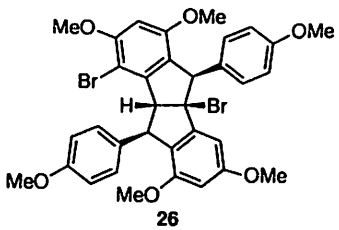
F2 - Acquisition Parameters
Date_                 20101122
Time                     17.35
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      32768
SOLVENT                 CDCl3
NS                         32
DS                          0
SWH                  6009.615 Hz
FIDRES               0.183399 Hz
AQ                 2.7263477 sec
RG                        228
DW                   83.200 usec
DE                    6.50 usec
TE                    329.3 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    9.50 usec
PL1                   -4.00 dB
PL1W            26.94187927 W
SFO1            400.1328009 MHz

F2 - Processing parameters
SI                      32768
SF              400.1300084 MHz
WDW                        EM
SSB          0
LB                    0.20 Hz
GB           0
PC                    1.00
```


8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2.159 1.934 5.473 2.116 0.942 1.043 0.982 2.755 3.330 6.366 2.971 3.045



26

161.882
158.590
158.109
157.396
156.887
155.686
150.138
145.498
136.496
136.014
130.084
129.802
126.262
124.489
113.274
113.236
99.843
99.813
96.984
77.785
70.560
60.265
56.828
55.762
55.710
55.418
55.199
55.168
51.925

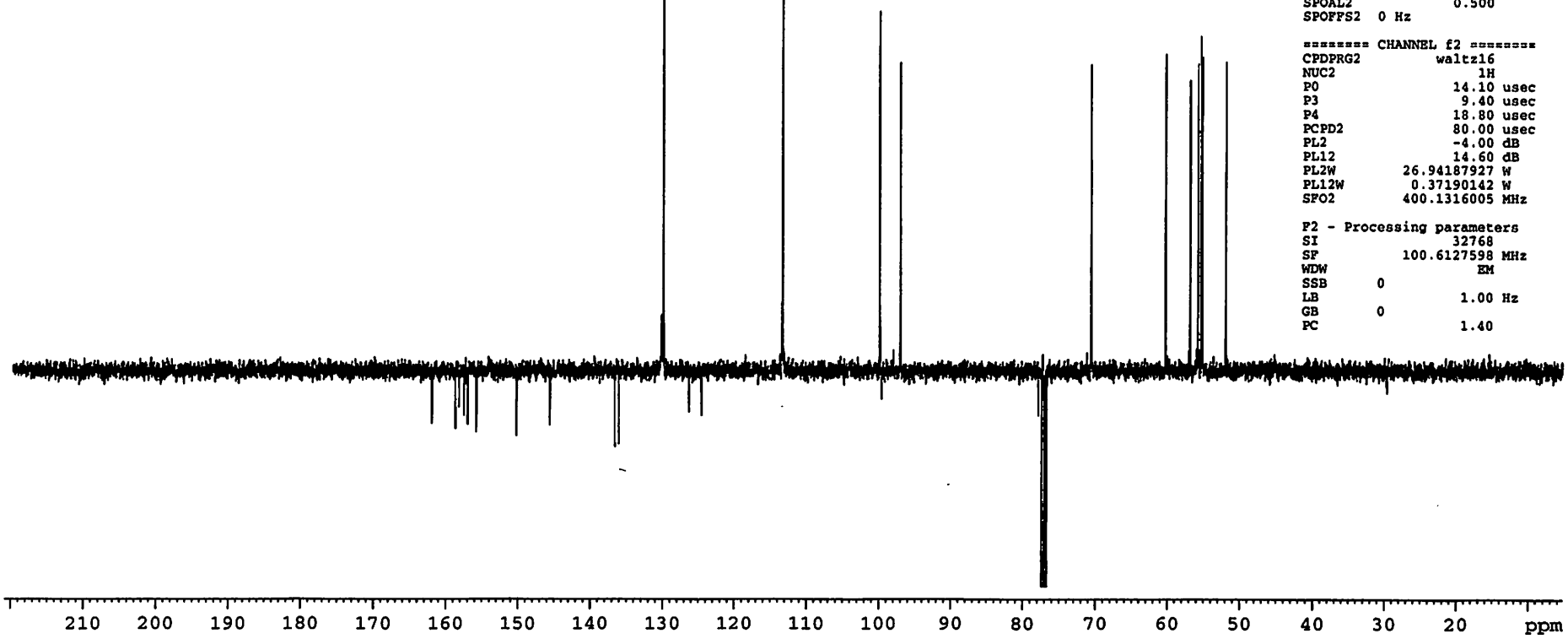
```
Current Data Parameters
NAME                 ango274C
EXPNO                       3
PROCNO                      1

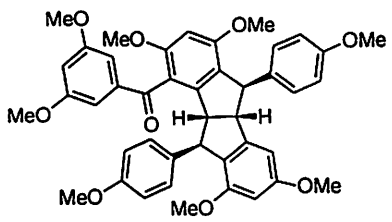
F2 - Acquisition Parameters
Date_               20101122
Time                   17.47
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             deptqsp
TD                      33650
SOLVENT                 CDCl3
NS                       1227
DS                          4
SWH                24038.461 Hz
FIDRES             0.714367 Hz
AQ                 0.6999700 sec
RG                       1820
DW                   20.800 usec
DE                    6.50 usec
TE                    328.3 K
CNST2              145.0000000
CNST12               1.5000000
D1                 2.00000000 sec
D2                 0.00344828 sec
D12                0.00002000 sec
TD0                         1
ZGOPTNS

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
P12                 2000.00 usec
PL0                  120.00 dB
PL1                    3.20 dB
PL0W       0 W
PL1W           49.53329468 W
SFO1           100.6228298 MHz
SP2                   11.07 dB
SPNAM2          Crp60comp.4
SPOAL2                0.500
SPOFFS2    0 Hz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
P0                   14.10 usec
P3                    9.40 usec
P4                   18.80 usec
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 14.60 dB
PL2W           26.94187927 W
PL12W           0.37190142 W
SFO2           400.1316005 MHz

P2 - Processing parameters
SI                      32768
SF                100.6127598 MHz
WDW                        EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
```





S3

7.120 7.098 7.069 7.063 6.830 6.808 6.731 6.709 6.686 6.683 6.673 6.667 6.661 6.639 6.308 6.237 6.233

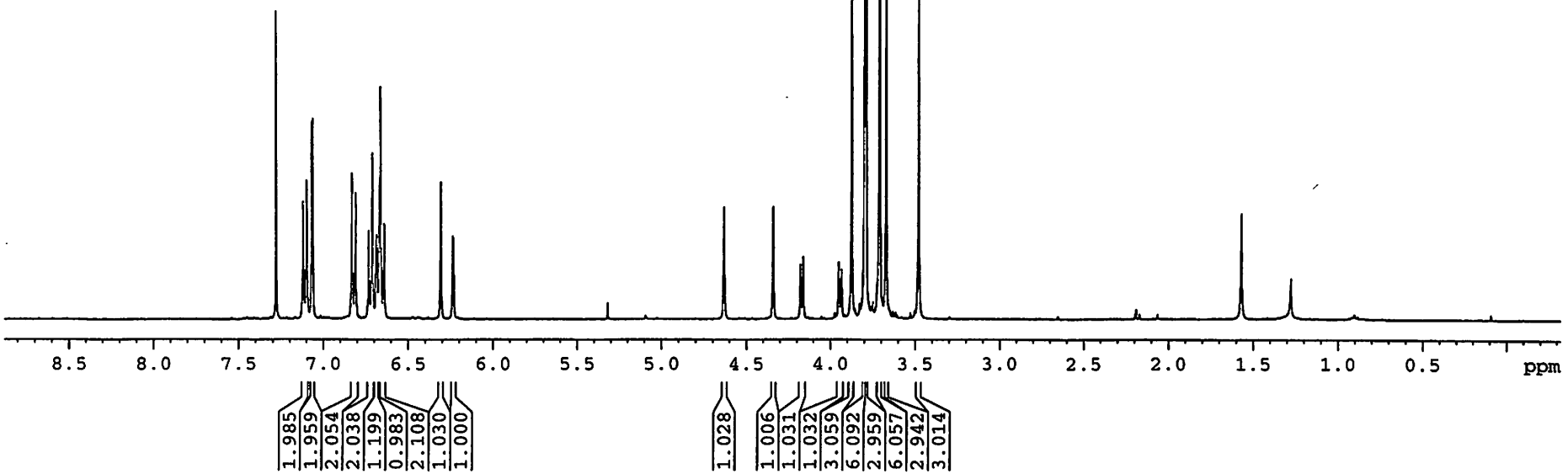
4.632 4.339 4.176 4.160 3.953 3.937 3.877 3.799 3.790 3.711 3.673 3.481

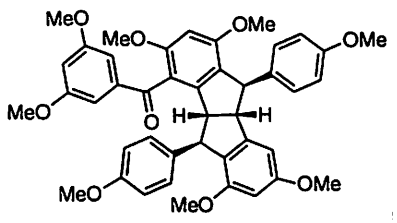
```
Current Data Parameters
NAME                  ango277
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20101119
Time                  17.47
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        0
SWH                6009.615 Hz
FIDRES            0.183399 Hz
AQ                2.7263477 sec
RG                      287
DW                 83.200 usec
DE                  6.50 usec
TE                  298.2 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  9.50 usec
PL1                -4.00 dB
PL1W         26.94187927 W
SFO1         400.1328009 MHz

F2 - Processing parameters
SI                    32768
SF           400.1300010 MHz
WDW                     EM
SSB       0
LB                  0.20 Hz
GB        0
PC                  1.00
```





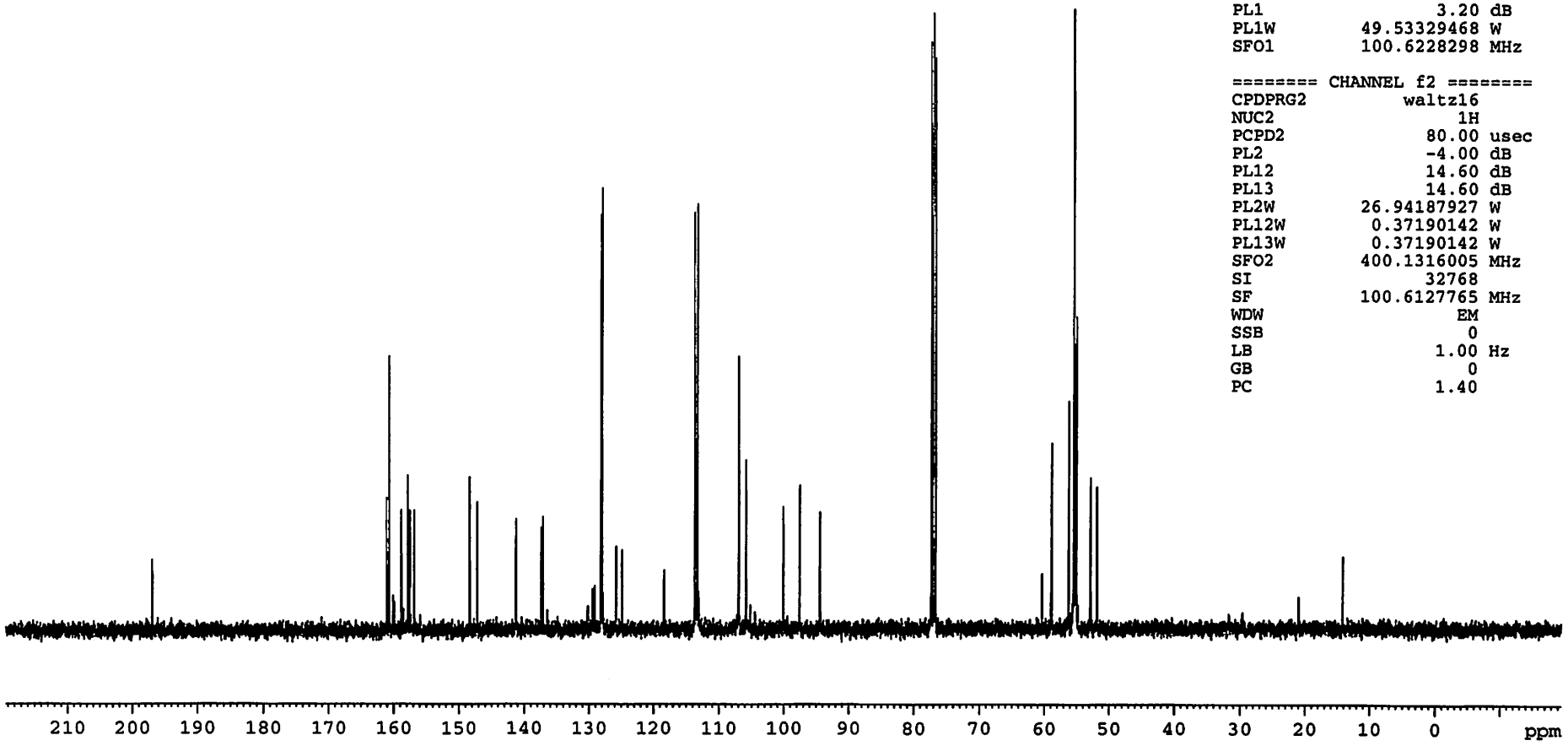
S3

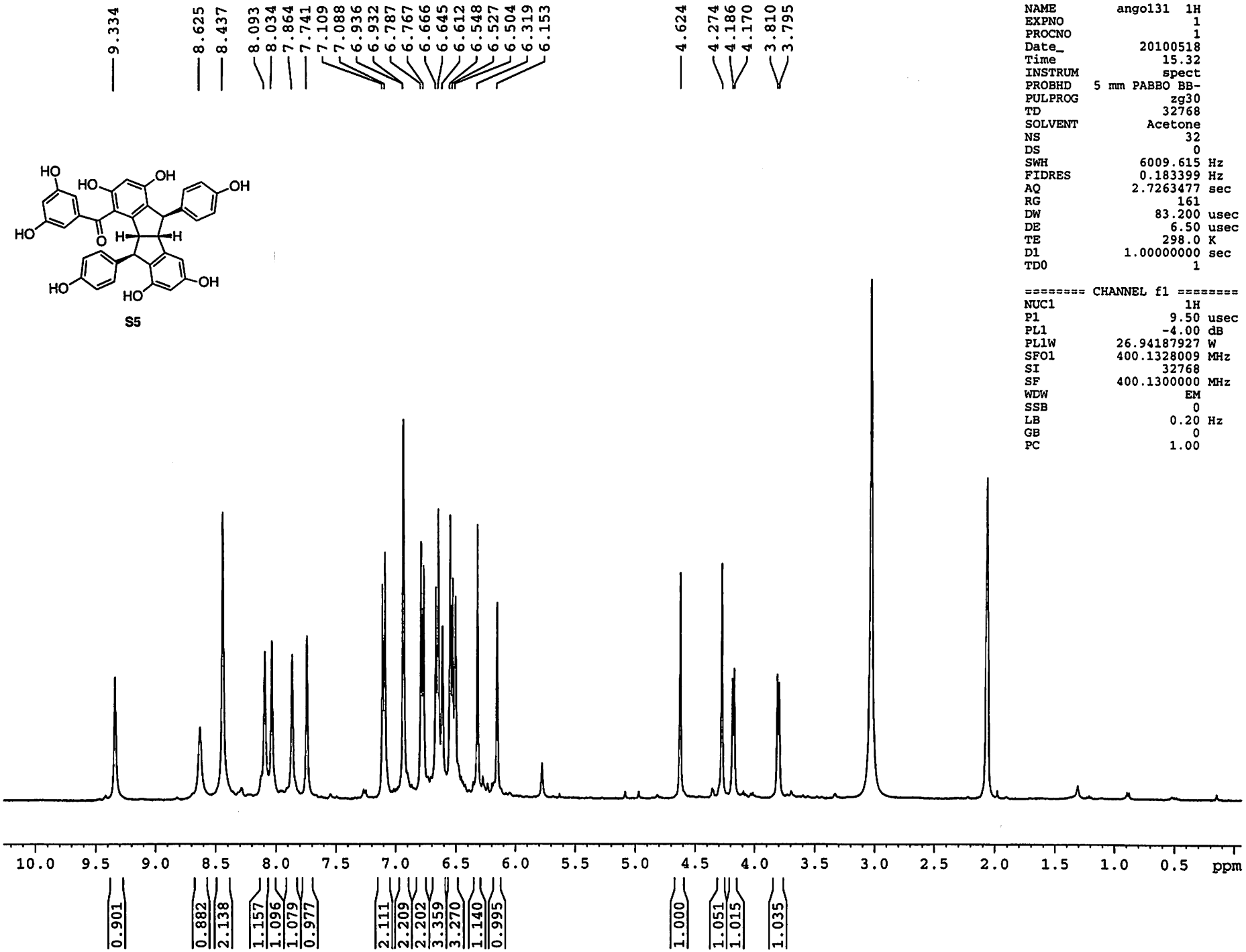
196.911

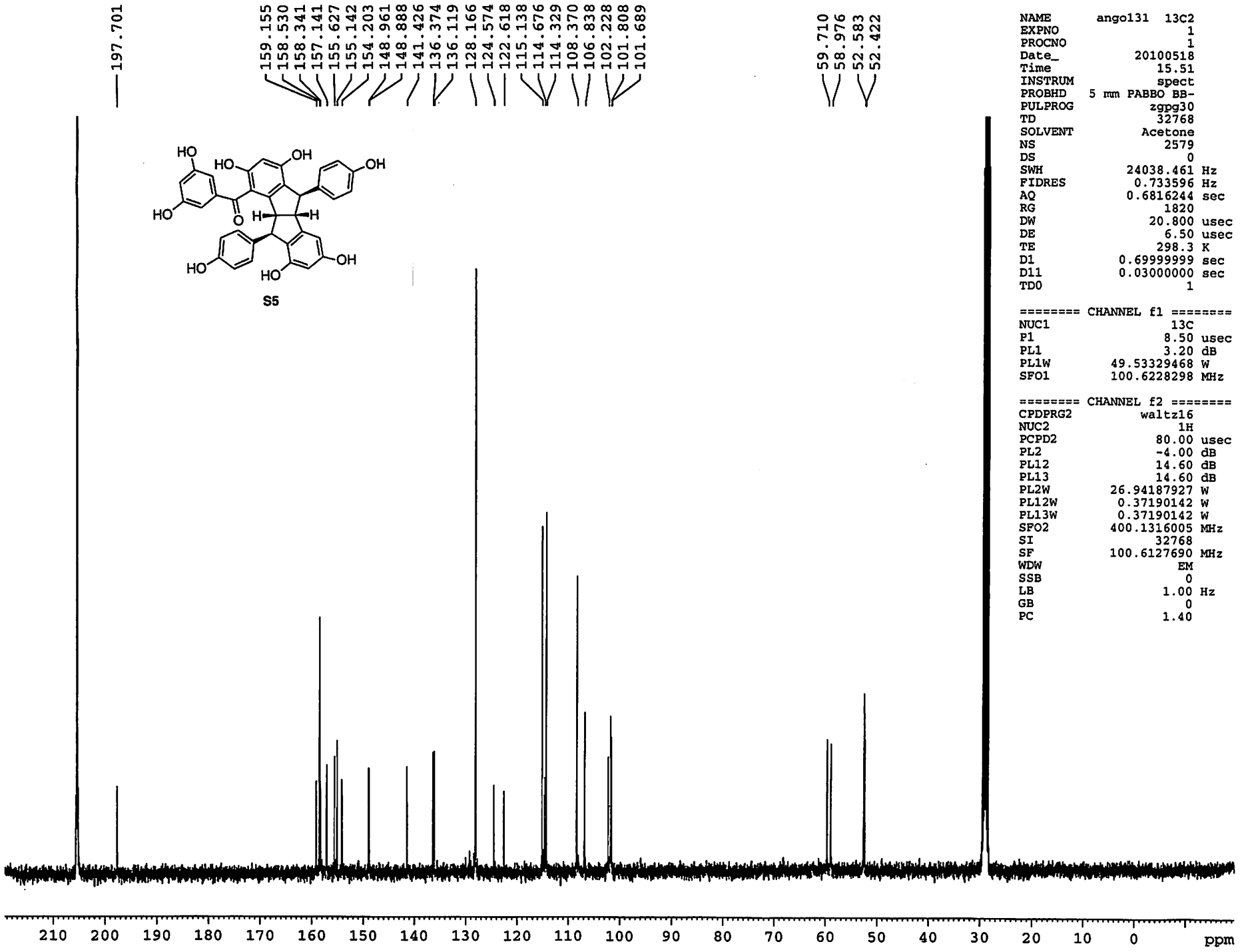
161.061
157.882
157.853
157.510
156.864
148.361
147.185
141.248
137.398
137.125
128.136
127.937
125.784
124.833
118.353
113.676
113.303
106.942
105.848
100.066
97.556
94.423

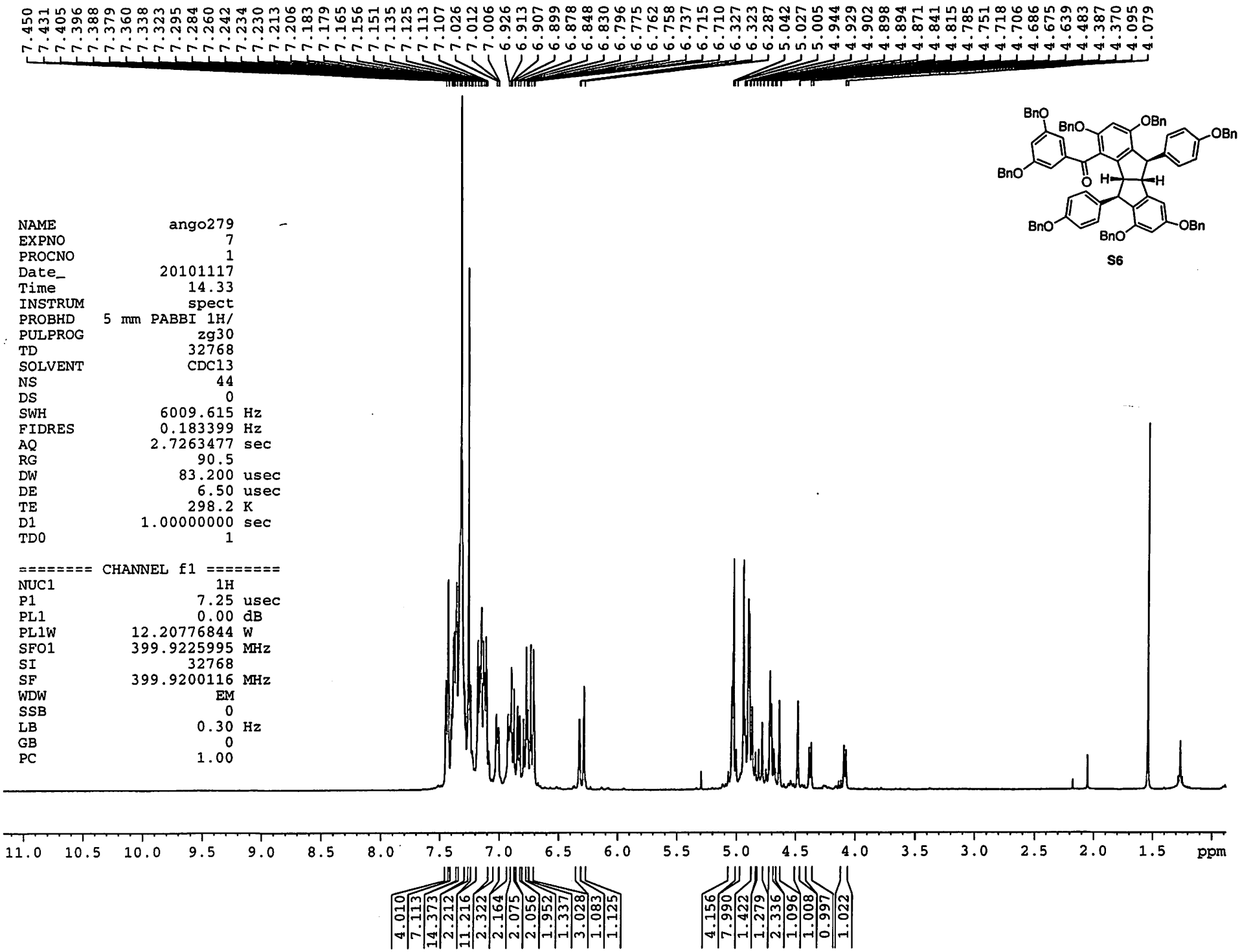
58.894
58.840
55.463
55.279
55.164
55.031
55.003
52.851
51.848

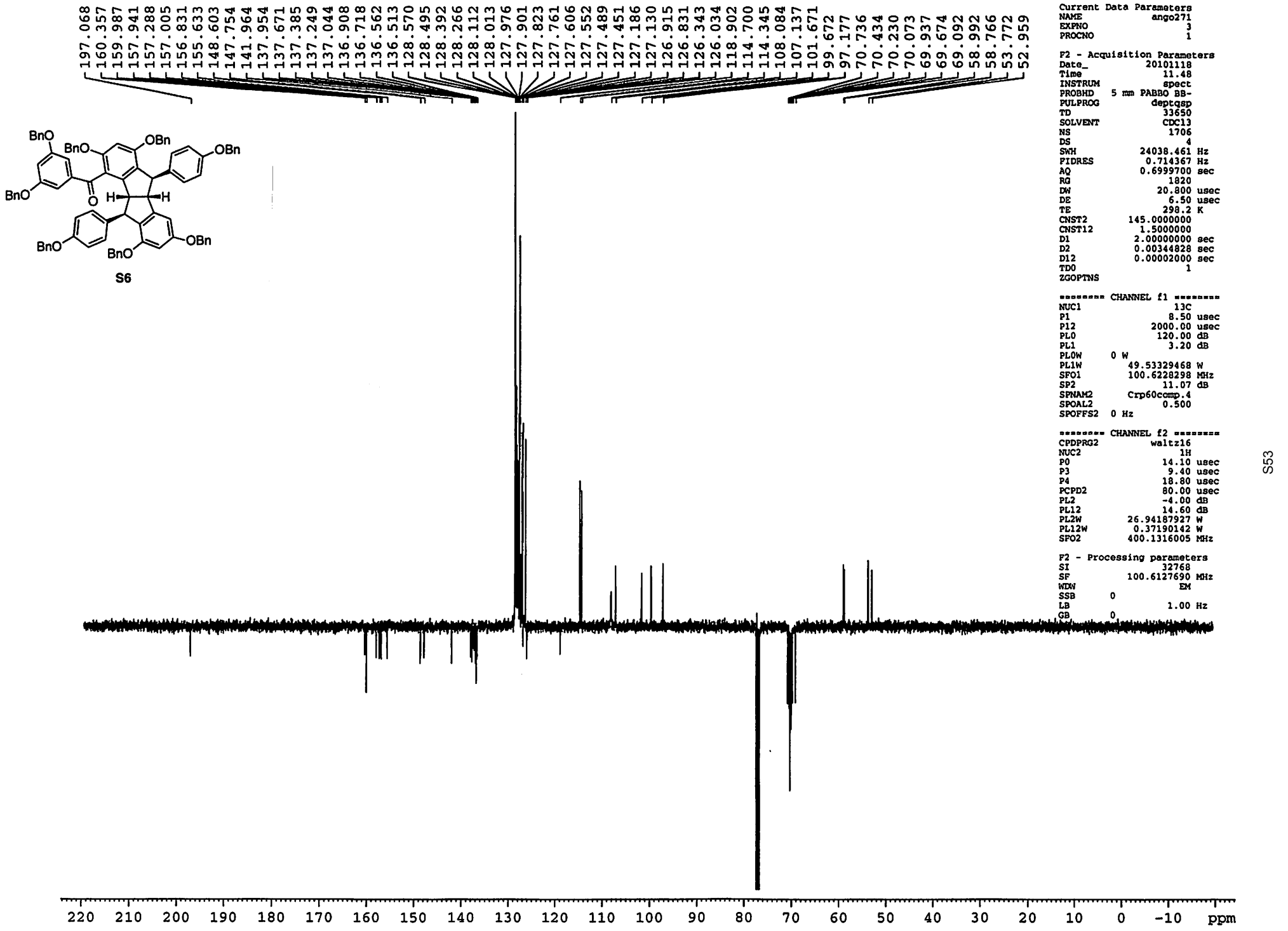
NAME	ango129 13C
EXPNO	1
PROCNO	1
Date_	20100514
Time	18.17
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	365
DS	0
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	0.6816244 sec
RG	1820
DW	20.800 usec
DE	6.50 usec
TE	295.8 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127765 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40




9.334
8.625
8.437
8.093
8.034
7.864
7.741
7.109
7.088
6.936
6.932
6.787
6.767
6.666
6.645
6.612
6.548
6.527
6.504
6.319
6.153
4.624
4.274
4.186
4.170
3.810
3.795
NAME angol31 1H
EXPNO 1
PROCNO 1
Date_ 20100518
Time 15.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 161
DW 83.200 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
HO
HO
OH
OH
HO
O
H
H
HO
HO
OH
S5
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.901
0.882
2.138
1.157
1.096
1.079
0.977
2.111
2.209
2.202
3.359
3.270
1.140
0.995
1.000
1.051
1.015
1.035


197.701
159.155
158.530
158.341
157.141
155.627
155.142
154.203
148.961
148.888
141.426
136.374
136.119
128.166
124.574
122.618
115.138
114.676
114.329
108.370
106.838
102.228
101.808
101.689
59.710
58.976
52.583
52.422
HO
HO
OH
OH
HO
O
H
H
HO
HO
OH
S5
NAME ango131 13C2
EXPNO 1
PROCNO 1
Date_ 20100518
Time 15.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT Acetone
NS 2579
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.450 7.431 7.405 7.396 7.388 7.379 7.360 7.338 7.323 7.295 7.284 7.260 7.242 7.234 7.230 7.213 7.206 7.183 7.179 7.165 7.156 7.151 7.135 7.125 7.113 7.107 7.026 7.012 7.006 6.926 6.913 6.907 6.899 6.878 6.848 6.830 6.796 6.775 6.762 6.758 6.737 6.715 6.710 6.327 6.323 6.287 5.042 5.027 5.005 4.944 4.929 4.902 4.898 4.894 4.871 4.841 4.815 4.785 4.751 4.718 4.706 4.686 4.675 4.639 4.483 4.387 4.370 4.095 4.079
BnO
BnO
OBn
OBn
BnO
O
H
H
BnO
BnO
OBn
S6
NAME ango279
EXPNO 7
PROCNO 1
Date_ 20101117
Time 14.33
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 44
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 90.5
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200116 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
S52
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
4.010 7.113 14.373 2.212 11.216 2.322 2.164 2.075 2.056 1.952 1.337 3.028 1.083 1.125
4.156 7.990 1.422 1.279 2.336 1.096 1.008 0.997 1.022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157.941
157.288
157.005
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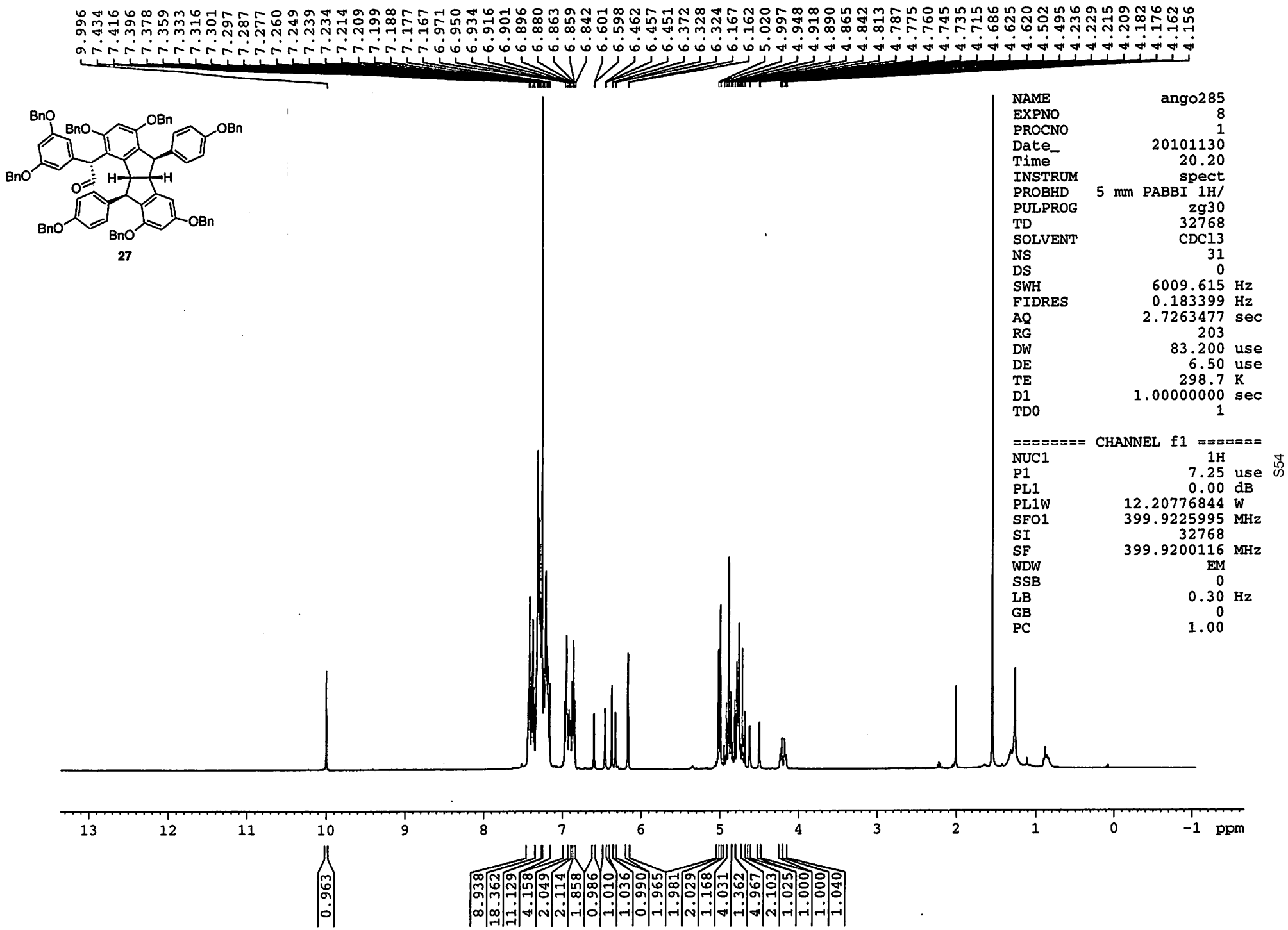
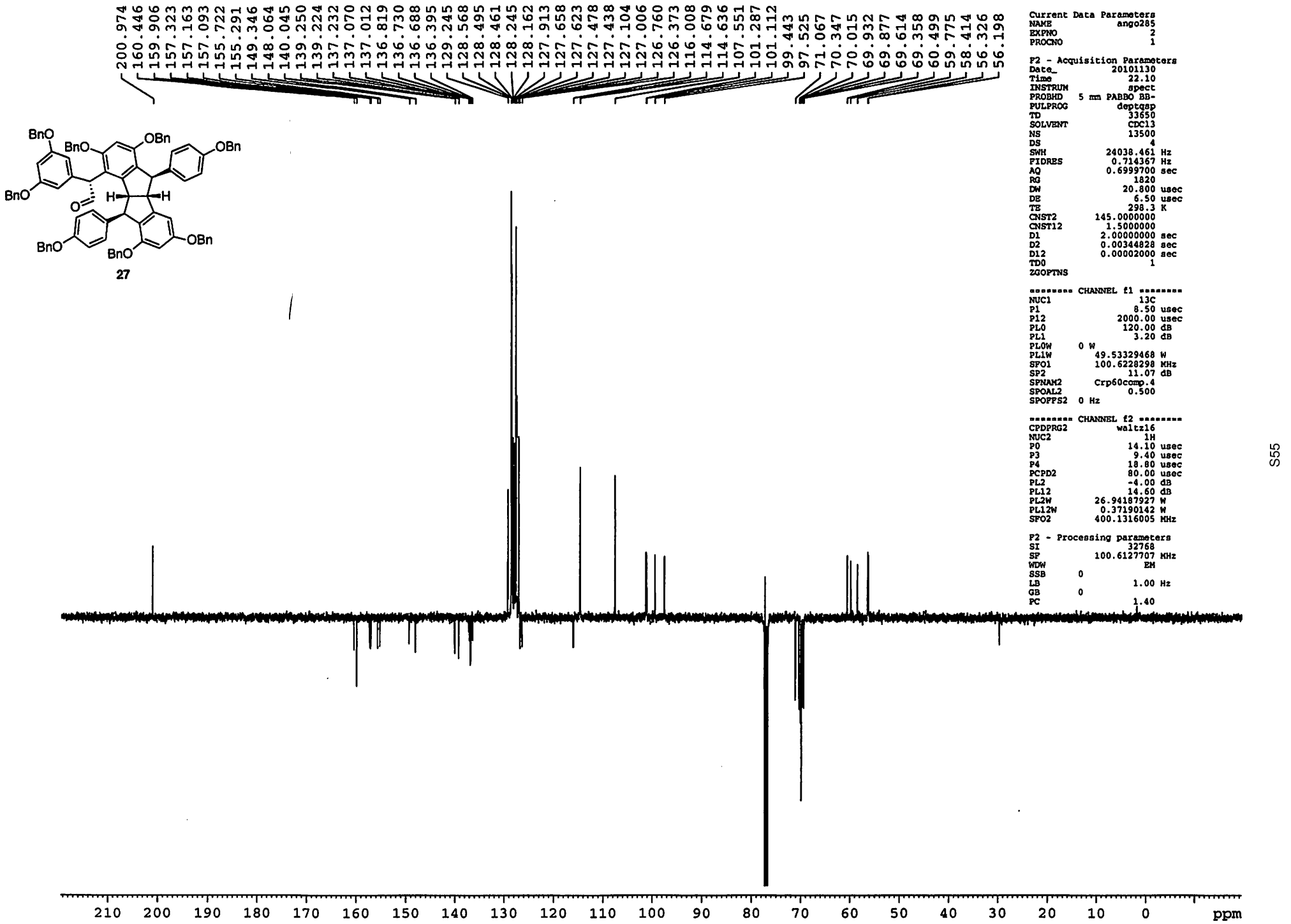
147.754
141.964
137.954
137.671
137.385
137.249
137.044
136.908
136.718
136.562
136.513
128.570
128.495
128.392
128.266
128.112
128.013
127.976
127.901
127.823
127.761
127.606
127.552
127.489
127.451
127.186
127.130
126.915
126.831
126.343
126.034
118.902
114.700
114.345
108.084
107.137
101.671
99.672
97.177
70.736
70.434
70.230
70.073
69.937
69.674
69.092
58.992
58.766
53.772
52.959
BnO
BnO
OBn
OBn
BnO
O
H
H
BnO
BnO
OBn
S6
Current Data Parameters
NAME ango271
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101118
Time 11.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 1706
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


9.996 7.434 7.416 7.396 7.378 7.359 7.333 7.316 7.301 7.297 7.287 7.277 7.260 7.249 7.239 7.234 7.214 7.209 7.199 7.188 7.177 7.167 6.971 6.950 6.934 6.916 6.901 6.896 6.880 6.863 6.859 6.842 6.601 6.598 6.462 6.457 6.451 6.372 6.328 6.324 6.167 6.162 5.020 4.997 4.948 4.918 4.890 4.865 4.842 4.813 4.787 4.775 4.760 4.745 4.735 4.715 4.686 4.625 4.620 4.502 4.495 4.236 4.229 4.215 4.209 4.182 4.176 4.162 4.156
BnO
BnO
OBn
OBn
BnO
O
H
H
BnO
BnO
OBn
27
NAME ango285
EXPNO 8
PROCNO 1
Date_ 20101130
Time 20.20
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 31
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 use
DE 6.50 use
TE 298.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 =======
NUC1 1H
P1 7.25 use
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200116 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
0.963
8.938 18.362 11.129 4.158 2.049 2.114 1.858 0.986 1.010 1.036 0.990 1.965 1.981 2.029 1.168 4.031 1.362 4.967 2.103 1.025 1.000 1.000 1.040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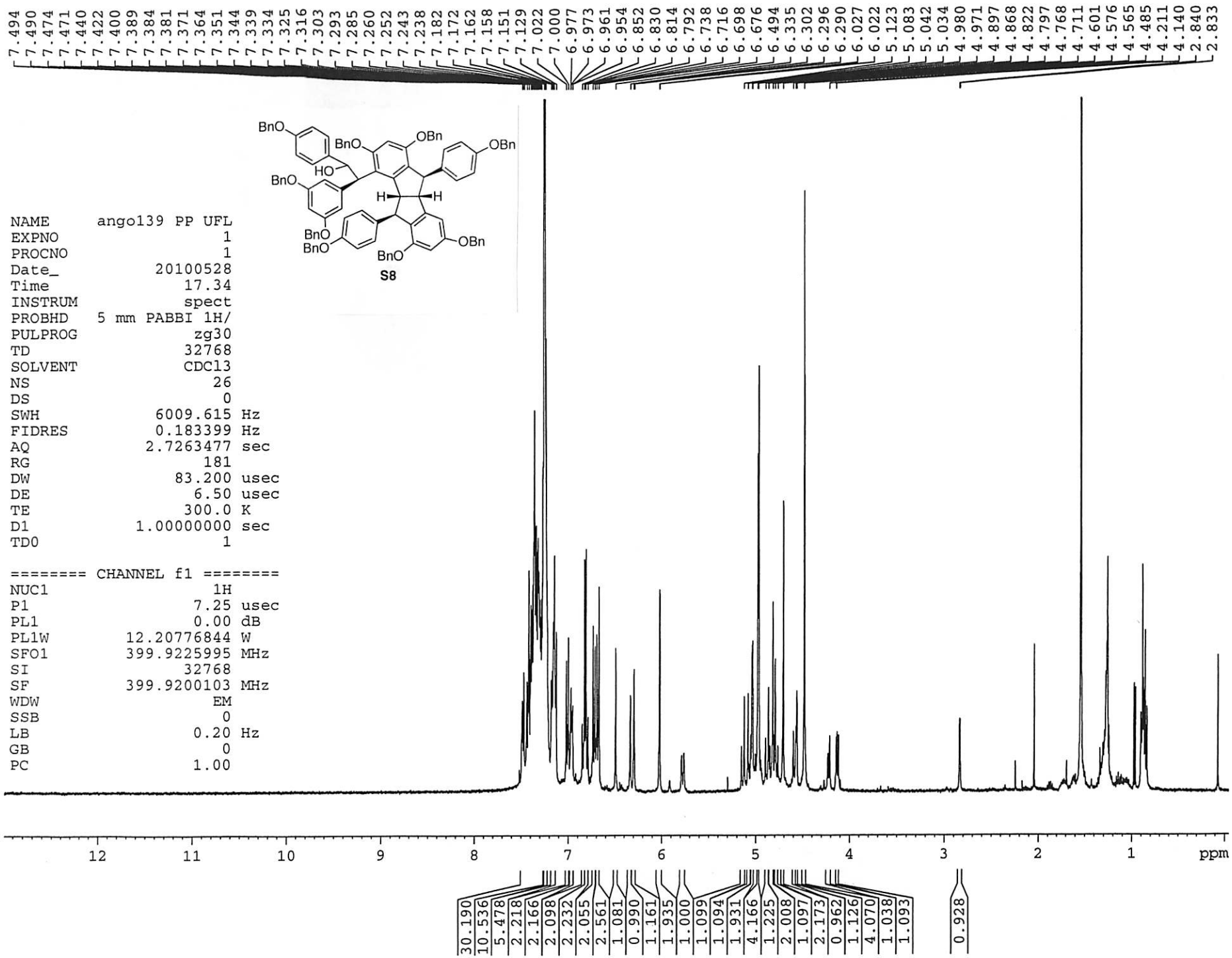
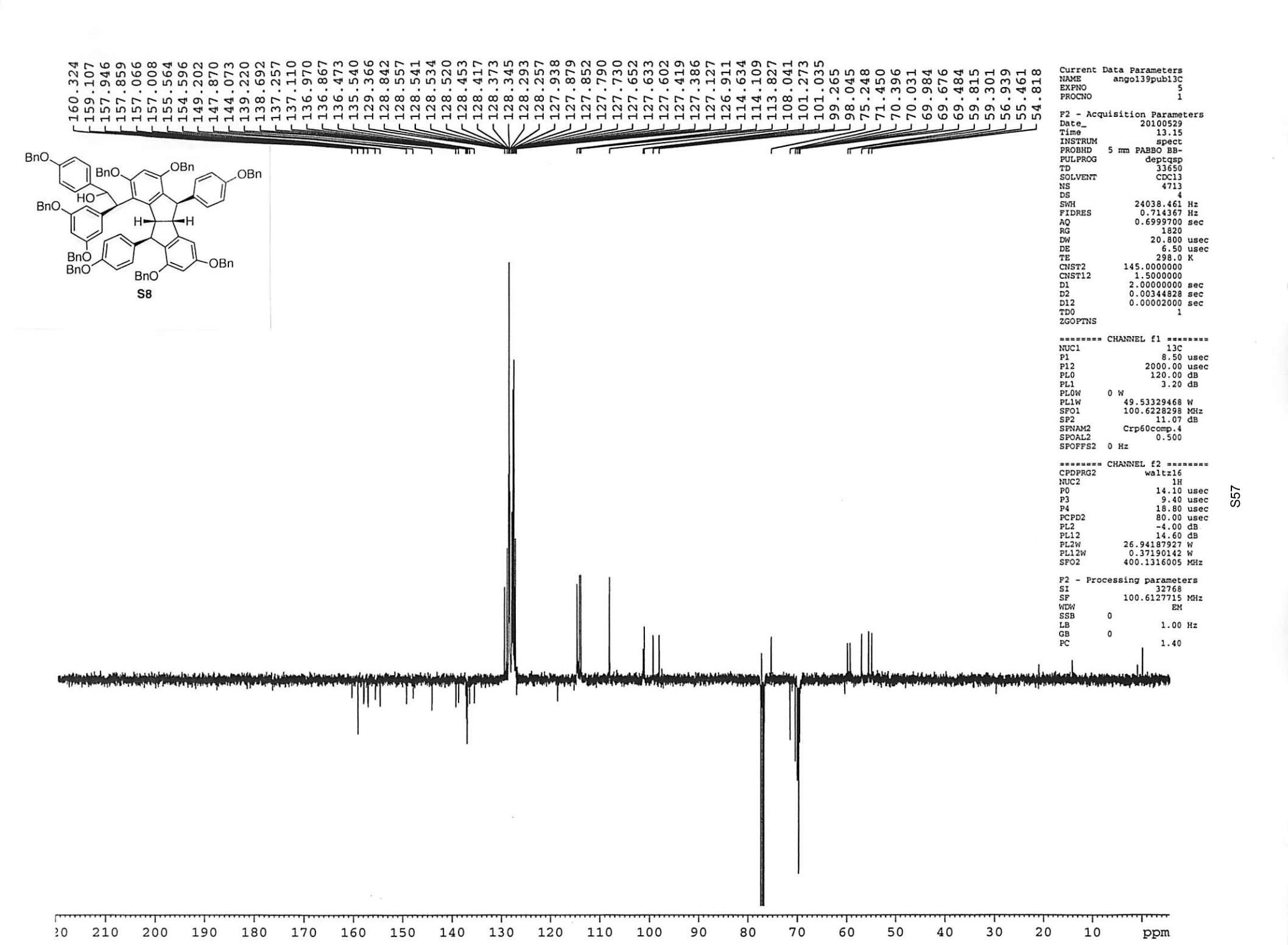
159.906
157.323
157.163
157.093
155.722
155.291
149.346
148.064
140.045
139.250
139.224
137.232
137.070
137.012
136.819
136.730
136.688
136.395
129.245
128.568
128.495
128.461
128.245
128.162
127.913
127.658
127.623
127.478
127.438
127.104
127.006
126.760
126.373
116.008
114.679
114.636
107.551
101.287
101.112
99.443
97.525
71.067
70.347
70.015
69.932
69.877
69.614
69.358
60.499
59.775
58.414
56.326
56.198
BnO
BnO
OBn
OBn
BnO
O
H
H
BnO
BnO
OBn
27
Current Data Parameters
NAME ango285
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101130
Time 22.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 13500
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.494 7.490 7.474 7.471 7.440 7.422 7.400 7.389 7.384 7.381 7.371 7.364 7.351 7.344 7.339 7.334 7.325 7.316 7.303 7.293 7.285 7.260 7.252 7.243 7.238 7.182 7.172 7.162 7.158 7.151 7.129 7.022 7.000 6.977 6.973 6.961 6.954 6.852 6.830 6.814 6.792 6.738 6.716 6.698 6.676 6.494 6.335 6.302 6.296 6.290 6.027 6.022 5.123 5.083 5.042 5.034 4.980 4.971 4.897 4.868 4.822 4.797 4.768 4.711 4.601 4.576 4.565 4.485 4.211 4.140 2.840 2.833
BnO
BnO
OBn
OBn
HO
BnO
H
H
BnO
BnO
OBn
BnO
S8
NAME ango139 PP UFL
EXPNO 1
PROCNO 1
Date_ 20100528
Time 17.34
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 26
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 181
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200103 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
12 11 10 9 8 7 6 5 4 3 2 1 ppm
30.190 10.536 5.478 2.218 2.166 2.098 2.232 2.055 2.561 1.081 0.990 1.161 1.935 1.000 1.099 1.094 1.931 4.166 1.225 2.008 1.097 2.173 0.962 1.126 4.070 1.038 1.093
0.928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159.107
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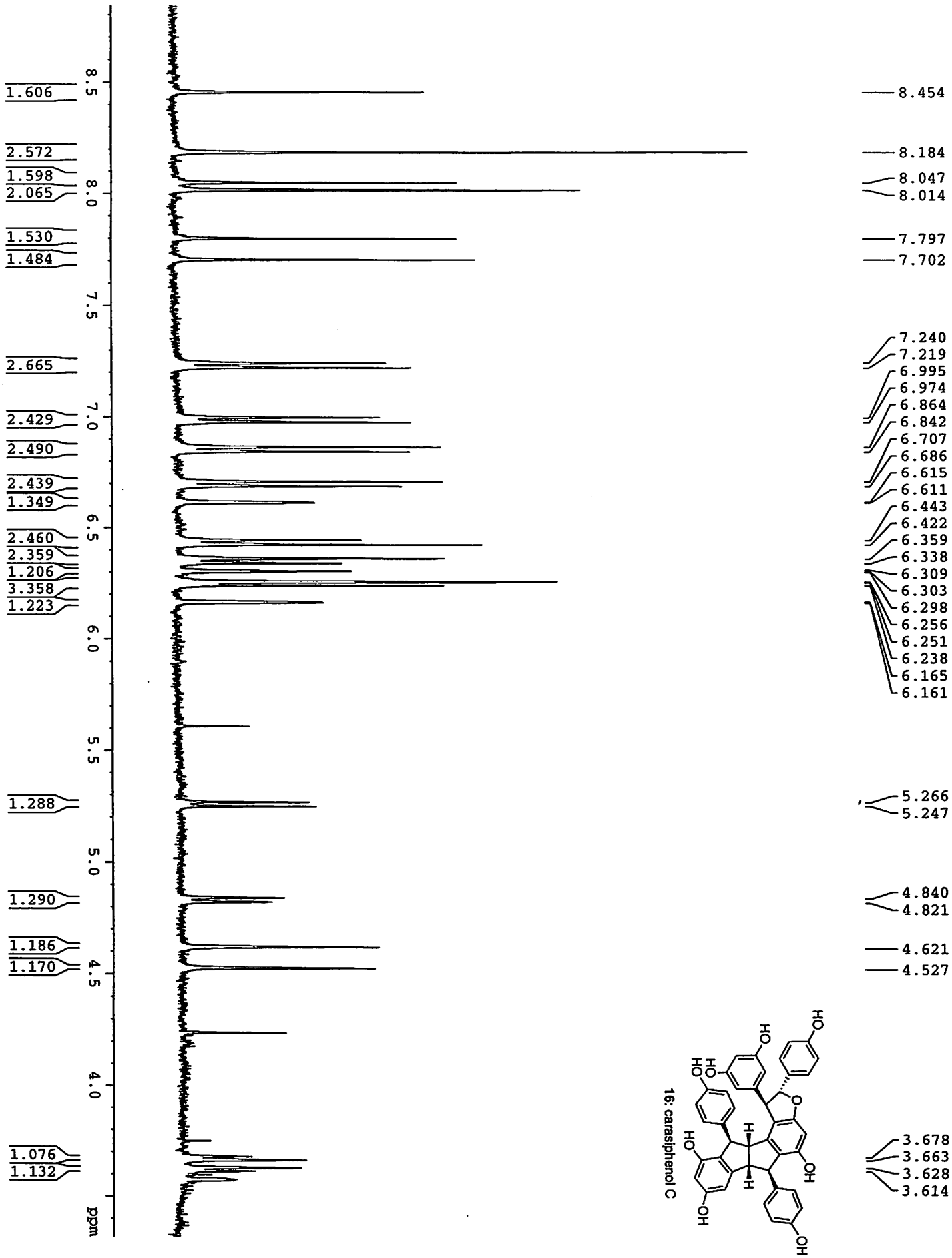
157.859
157.066
157.008
155.564
154.596
149.202
147.870
144.073
139.220
138.692
137.257
137.110
136.970
136.867
136.473
135.540
129.366
128.842
128.557
128.541
128.534
128.520
128.453
128.417
128.373
128.345
128.293
128.257
127.938
127.879
127.852
127.790
127.730
127.652
127.633
127.602
127.419
127.386
127.127
126.911
114.634
114.109
113.827
108.041
101.273
101.035
99.265
98.045
75.248
71.450
70.396
70.031
69.984
69.676
69.484
59.815
59.301
56.939
55.461
54.818
BnO
BnO
OBn
OBn
HO
BnO
H
H
BnO
BnO
OBn
BnO
S8
Current Data Parameters
NAME ango139pub13C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100529
Time 13.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 4713
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.0 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127715 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


1.606
2.572
1.598
2.065
1.530
1.484
2.665
2.429
2.490
2.439
1.349
2.460
2.359
1.206
3.358
1.223
1.288
1.290
1.186
1.170
1.076
1.132
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
8.454
8.184
8.047
8.014
7.797
7.702
7.240
7.219
6.995
6.974
6.864
6.842
6.707
6.686
6.615
6.611
6.443
6.422
6.359
6.338
6.309
6.303
6.298
6.256
6.251
6.238
6.165
6.161
5.266
5.247
4.840
4.821
4.621
4.527
3.678
3.663
3.628
3.614
16: carasiphenol C

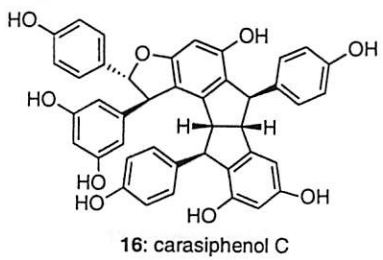
```
Current Data Parameters
NAME      Carasiphenol-C
EXPNO                 13
PROCNO               999

F2 - Acquisition Parameters
Date_           20100811
Time                6.59
INSTRUM            spect
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD               134144
SOLVENT         Acetone
NS                  9216
DS                     2
SWH            39062.500 Hz
FIDRES          0.291198 Hz
AQ              1.7170932 sec
RG                   203
DW                12.800 usec
DE                25.82 usec
TE                297.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.25 usec
PL1                 3.10 dB
PL1W         32.60212326 W
SFO1        150.9209173 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              70.00 usec
PL2                 3.40 dB
PL12               16.00 dB
PL13               16.00 dB
PL2W          7.46299839 W
PL12W         0.41012228 W
PL13W         0.41012228 W
SFO2        600.1324005 MHz

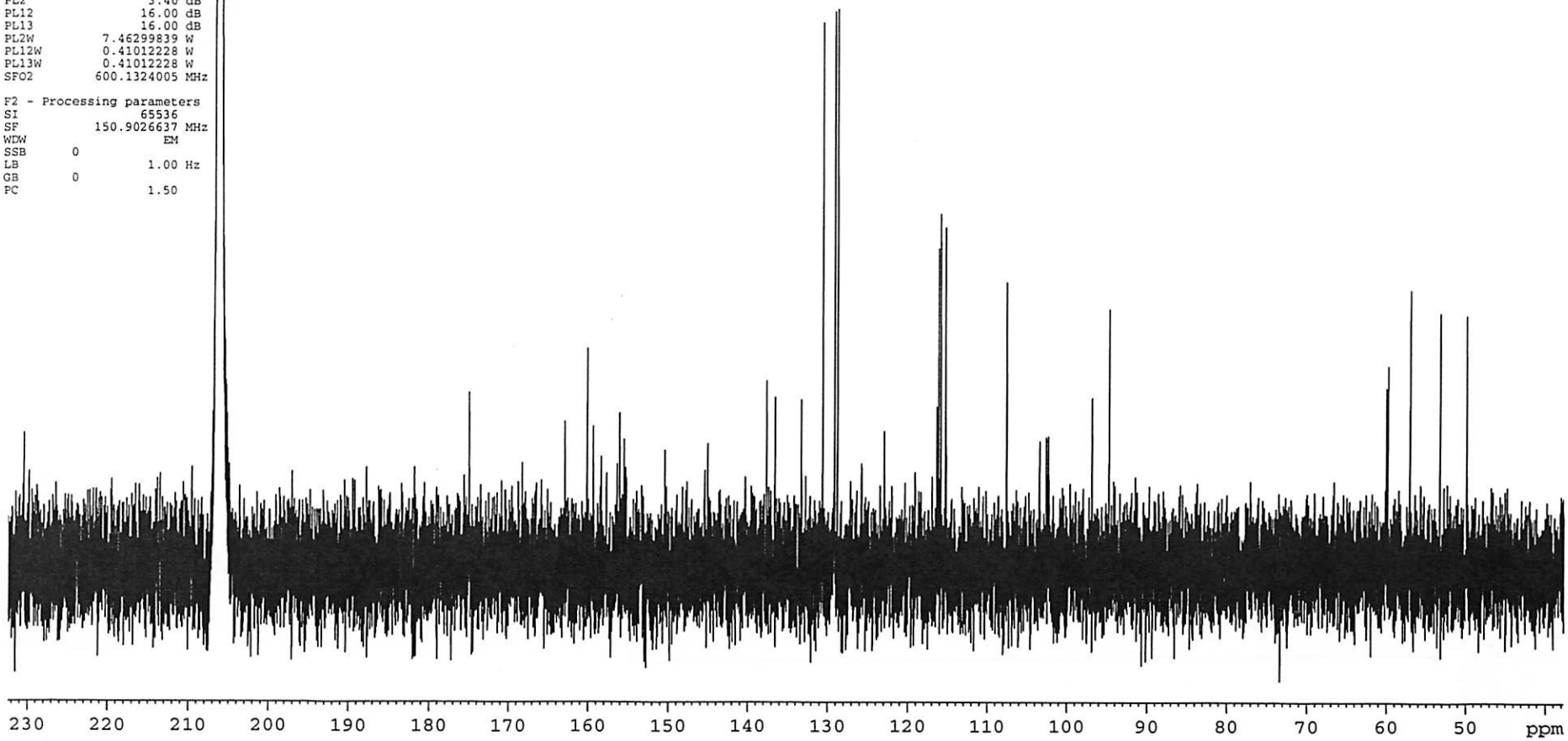
F2 - Processing parameters
SI                 65536
SF          150.9026637 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.50
```

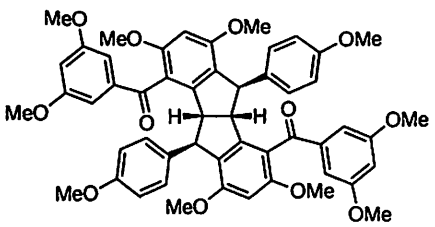


16: carasiphenol C

162.946
160.168
159.398
158.409
157.739
156.424
156.111
155.535
150.851
145.490
145.120
137.720
136.651
133.362
130.642
130.623
129.201
129.159
128.797
125.838
122.987
116.421
116.215
115.959
115.365
107.609
103.460
102.623
102.364
96.946
94.787

60.116
59.923
57.169
53.351
50.016





S9

7.076 7.070 6.747 6.725 6.668 6.662 6.656 6.652 6.630 6.266

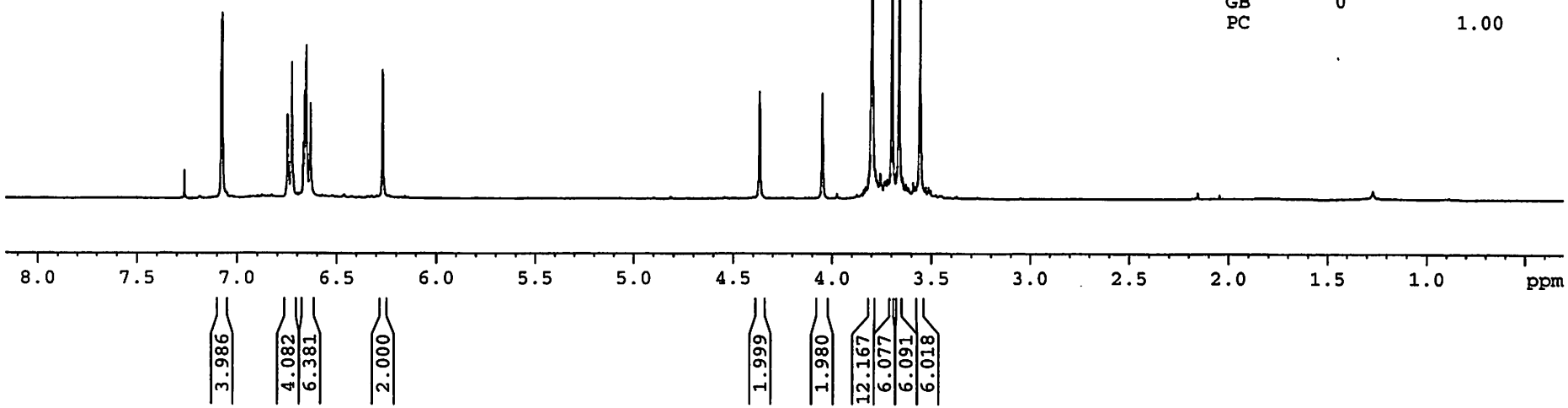
4.364 4.049 3.798 3.697 3.662 3.557

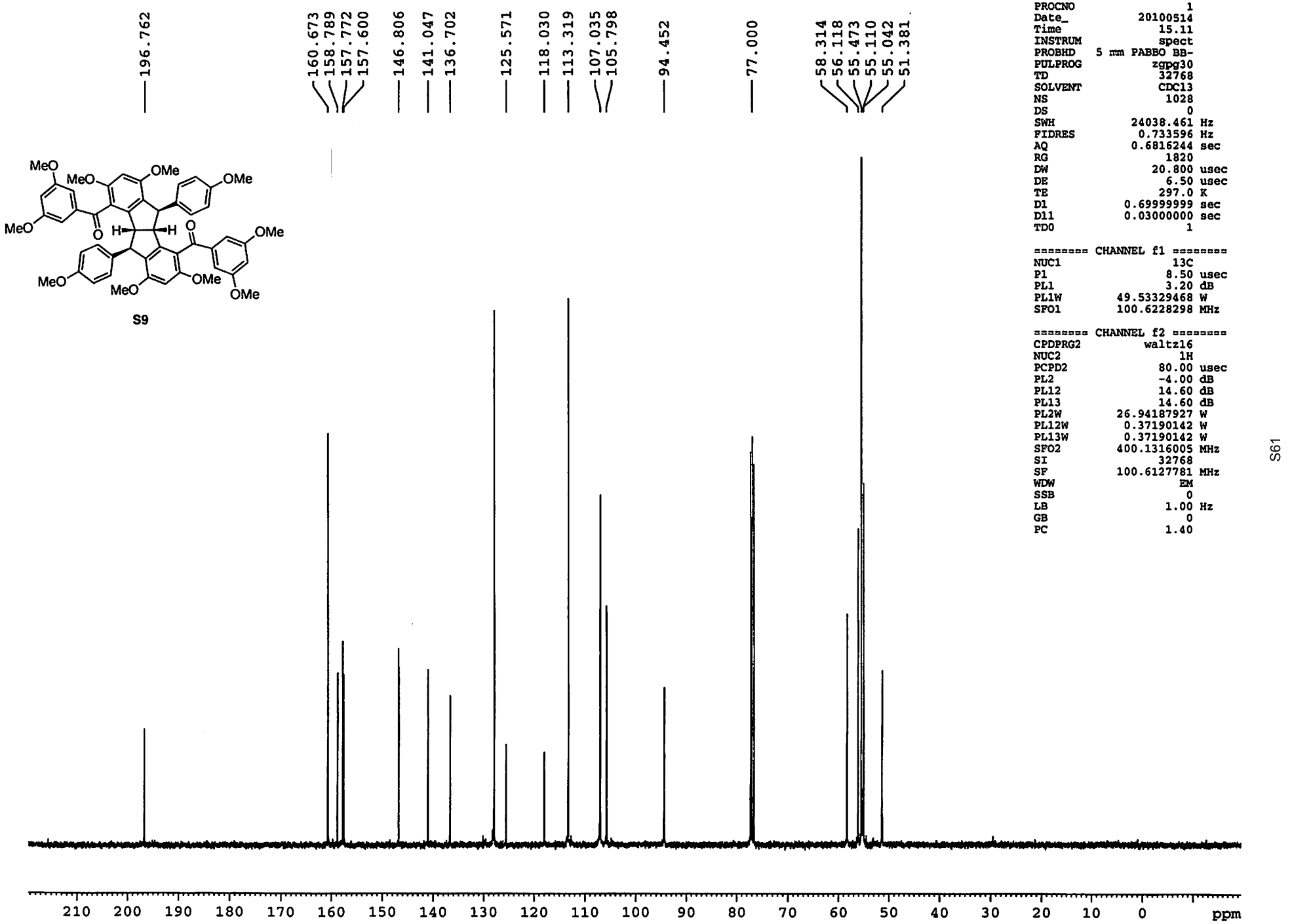
Current Data Parameters
NAME ango128 1H
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100514
Time 15.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 17
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 32
DW 83.200 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz

F2 - Processing parameters
SI 32768
SF 400.1300085 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

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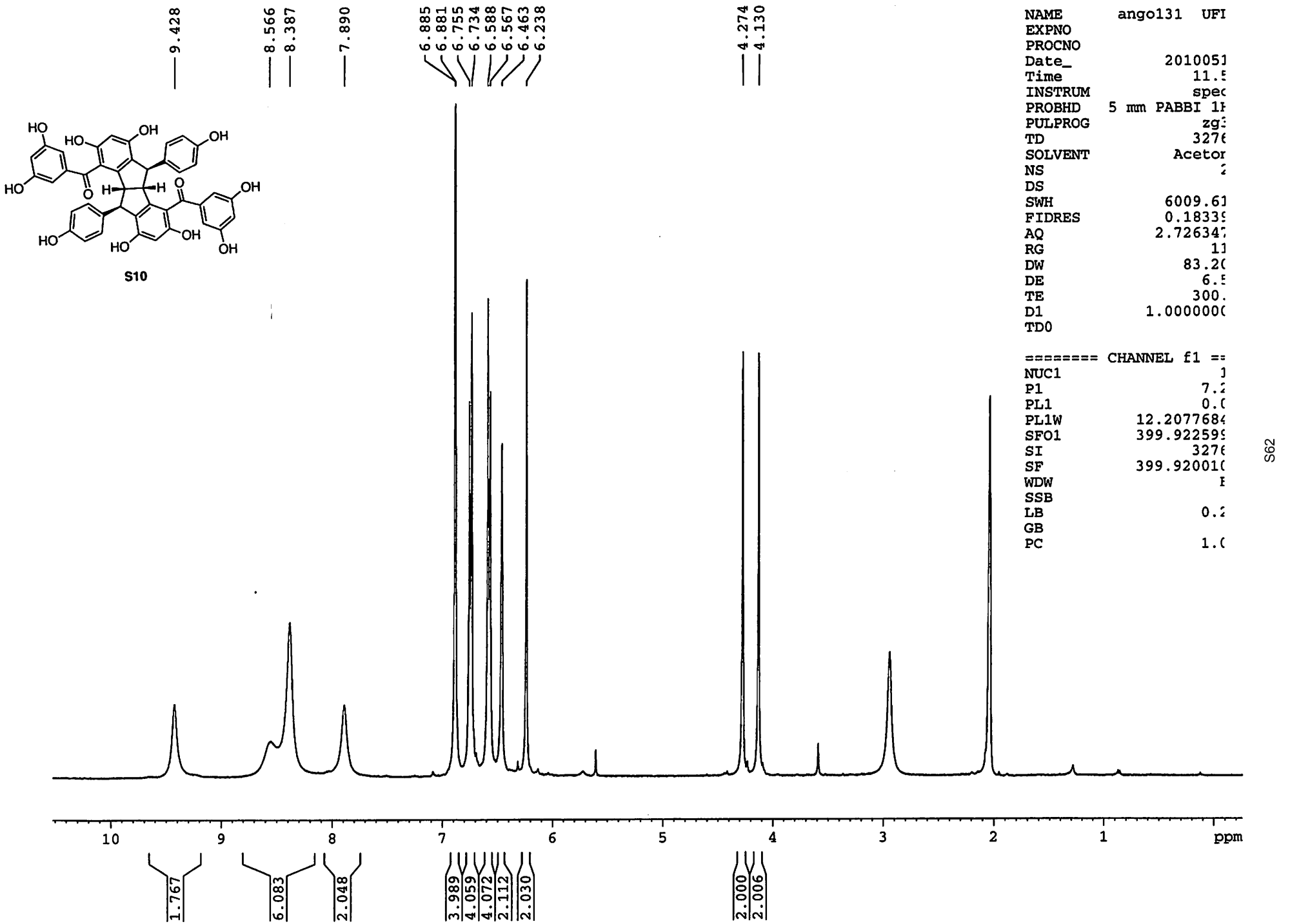
157.772
157.600
146.806
141.047
136.702
125.571
118.030
113.319
107.035
105.798
94.452
77.000
58.314
56.118
55.473
55.110
55.042
51.381
MeO
MeO
OMe
OMe
MeO
O
H
H
O
OMe
MeO
MeO
OMe
OMe
S9
NAME angol28 13C
EXPNO 1
PROCNO 1
Date_ 20100514
Time 15.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1028
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 297.0 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127781 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.566
8.387
7.890
6.885
6.881
6.755
6.734
6.588
6.567
6.463
6.238
4.274
4.130
S10
NAME ango131 UFI
EXPNO
PROCNO
Date_ 2010051
Time 11.5
INSTRUM spec
PROBHD 5 mm PABBI 1H
PULPROG zg3
TD 3276
SOLVENT Acetor
NS 2
DS
SWH 6009.61
FIDRES 0.18339
AQ 2.726347
RG 11
DW 83.20
DE 6.5
TE 300.
D1 1.000000
TD0
======== CHANNEL f1 ==
NUC1 1
P1 7.2
PL1 0.0
PL1W 12.2077684
SFO1 399.922599
SI 3276
SF 399.92001
WDW E
SSB
LB 0.2
GB
PC 1.0
10
9
8
7
6
5
4
3
2
1
ppm
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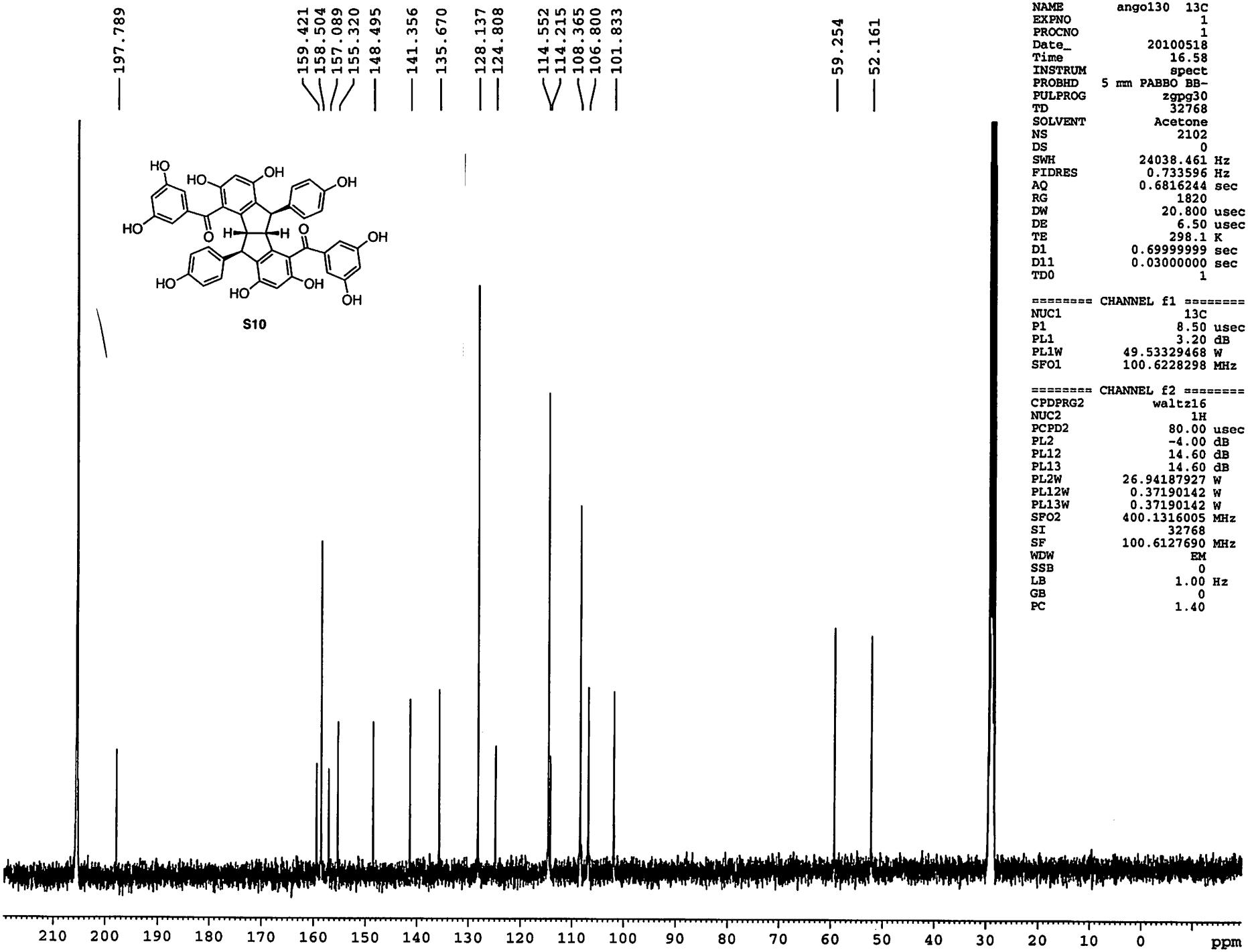
4.059
4.072
2.112
2.030
2.000
2.006


197.789
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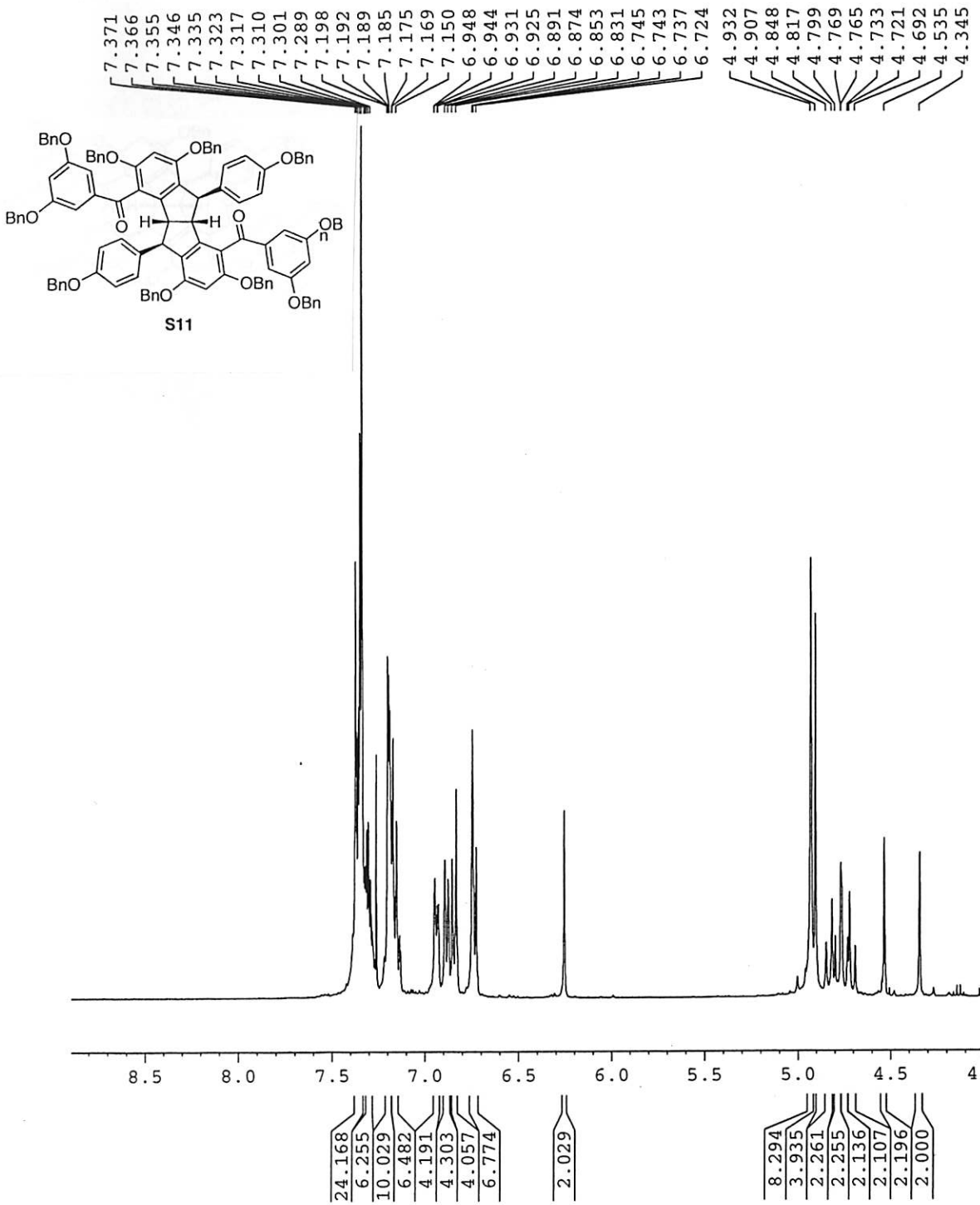
158.504
157.089
155.320
148.495
141.356
135.670
128.137
124.808
114.552
114.215
108.365
106.800
101.833
59.254
52.161
S10
NAME ango130 13C
EXPNO 1
PROCNO 1
Date_ 20100518
Time 16.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT Acetone
NS 2102
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.1 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.301
7.289
7.198
7.192
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7.185
7.175
7.169
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6.944
6.931
6.925
6.891
6.874
6.853
6.831
6.745
6.743
6.737
6.724
4.932
4.907
4.848
4.817
4.799
4.769
4.765
4.733
4.721
4.692
4.535
4.345
BnO
BnO
OBn
OBn
BnO
O
H
H
O
OBn
BnO
BnO
OBn
OBn
S11
NAME ango132 F2
EXPNO 1
PROCNO 1
Date_ 20100519
Time 20.45
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 26
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 28.5
DW 83.200 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200103 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
24.168
6.255
10.029
6.482
4.191
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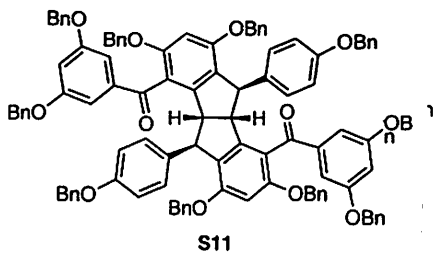
2.255
2.136
2.107
2.196
2.000



S11

196.846

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157.933
157.044
156.534
147.721
141.833
137.292
137.197
136.611
136.520
136.432
128.557
128.452
128.311
128.232
127.989
127.740
127.578
127.420
126.871
126.788
126.376
118.745
114.350
108.125
106.945
97.380

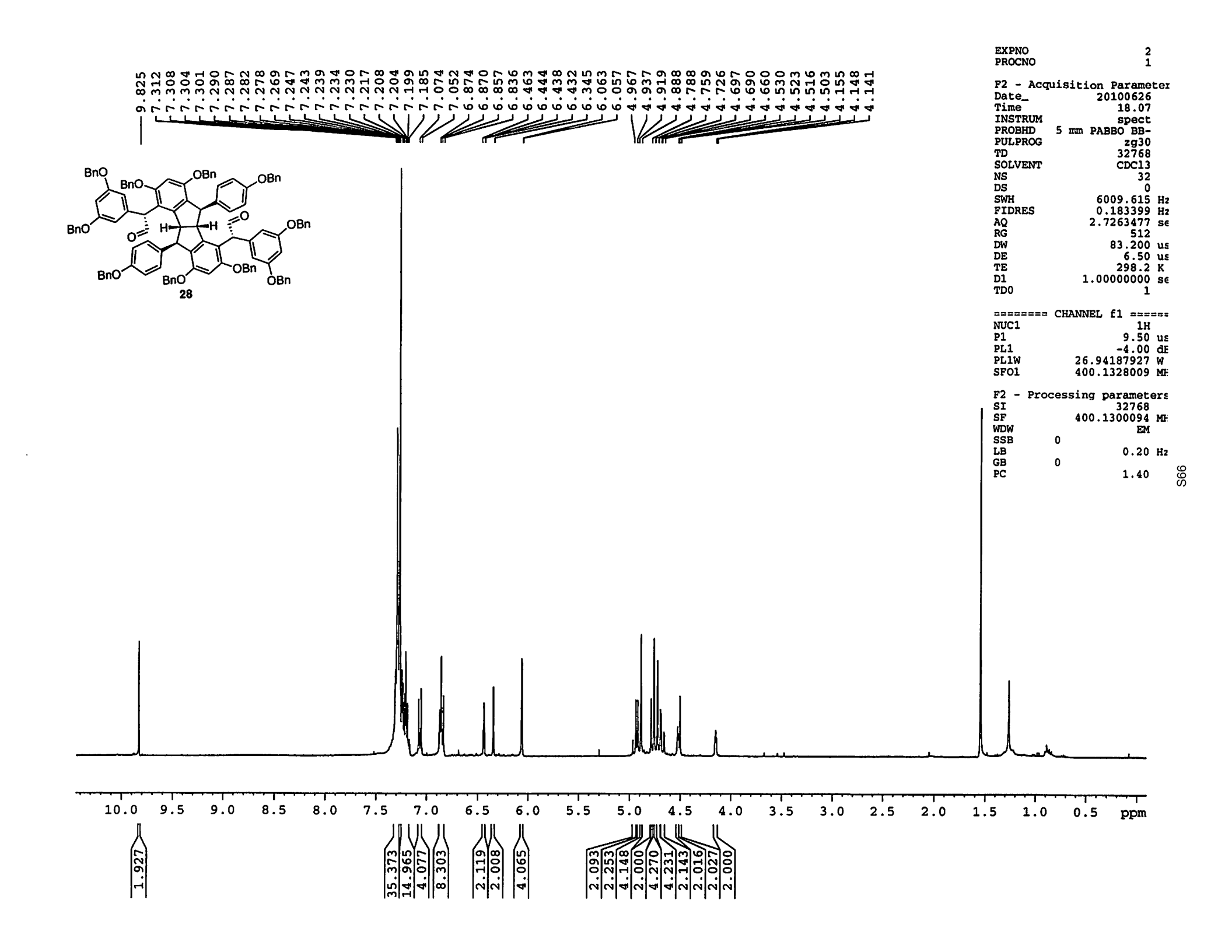
70.730
70.243
69.856
69.263

58.161

52.747

NAME	ango132 13C
EXPNO	1
PROCNO	1
Date_	20100519
Time	21.07
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	2135
DS	0
SWH	24038.461 Hz
FIDRES	0.733596 Hz
AQ	0.6816244 sec
RG	1820
DW	20.800 usec
DE	6.50 usec
TE	298.3 K
D1	0.69999999 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	3.20 dB
PL1W	49.53329468 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-4.00 dB
PL12	14.60 dB
PL13	14.60 dB
PL2W	26.94187927 W
PL12W	0.37190142 W
PL13W	0.37190142 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127736 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.290
7.287
7.282
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7.247
7.243
7.239
7.234
7.230
7.217
7.208
7.204
7.199
7.185
7.074
7.052
6.874
6.870
6.857
6.836
6.463
6.444
6.438
6.432
6.345
6.063
6.057
4.967
4.937
4.919
4.888
4.788
4.759
4.726
4.697
4.690
4.660
4.530
4.523
4.516
4.503
4.155
4.148
4.141
BnO
OBn
H
O
28
EXPNO 2
PROCNO 1
F2 - Acquisition Parameter
Date_ 20100626
Time 18.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 se
RG 512
DW 83.200 us
DE 6.50 us
TE 298.2 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 9.50 us
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MH
F2 - Processing parameters
SI 32768
SF 400.1300094 MH
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.927
35.373
14.965
4.077
8.303
2.119
2.008
4.065
2.093
2.253
4.148
2.000
4.270
4.231
2.143
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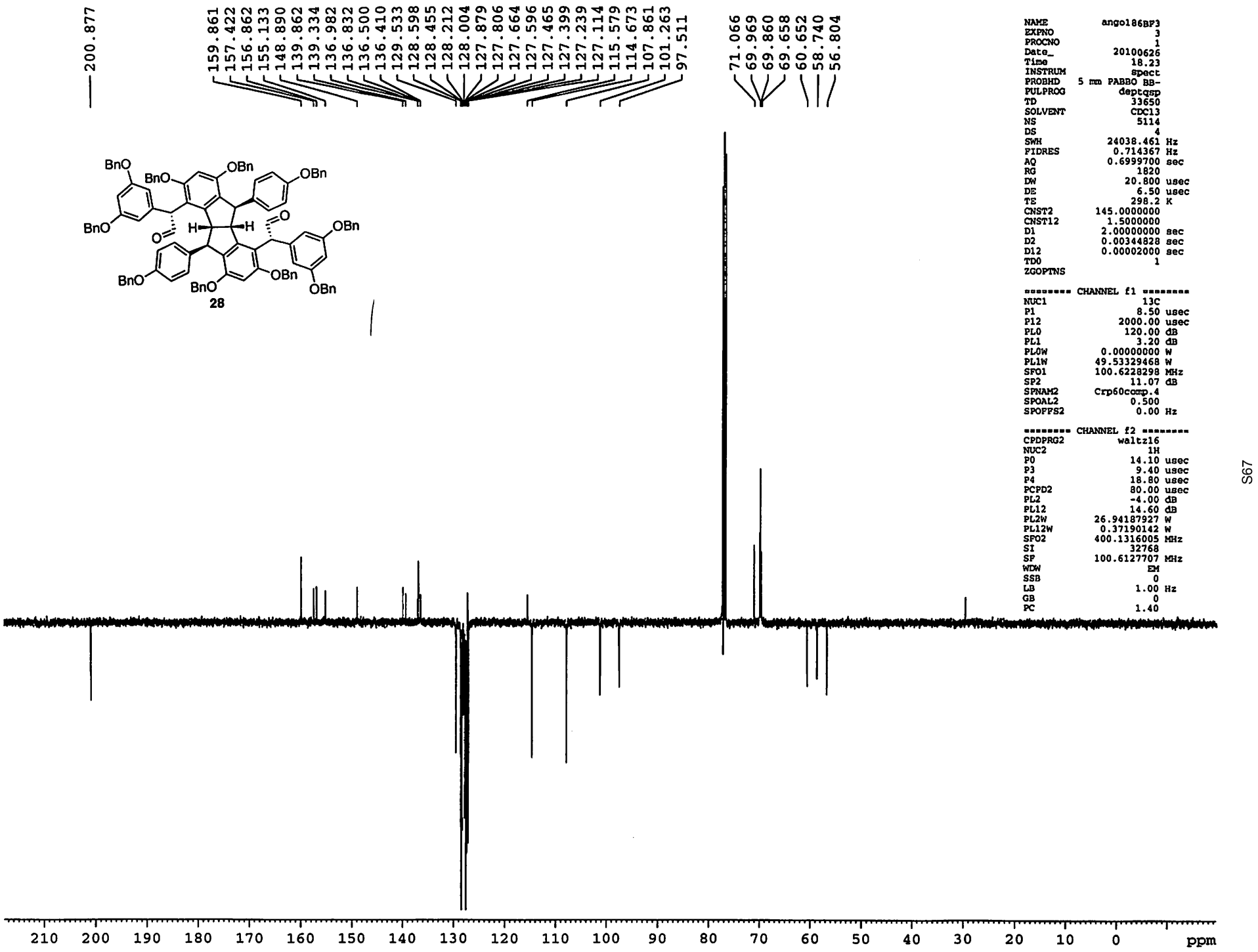
2.027
2.000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128.598
128.455
128.212
128.004
127.879
127.806
127.664
127.596
127.465
127.399
127.239
127.114
115.579
114.673
107.861
101.263
97.511
71.066
69.969
69.860
69.658
60.652
58.740
56.804
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BnO
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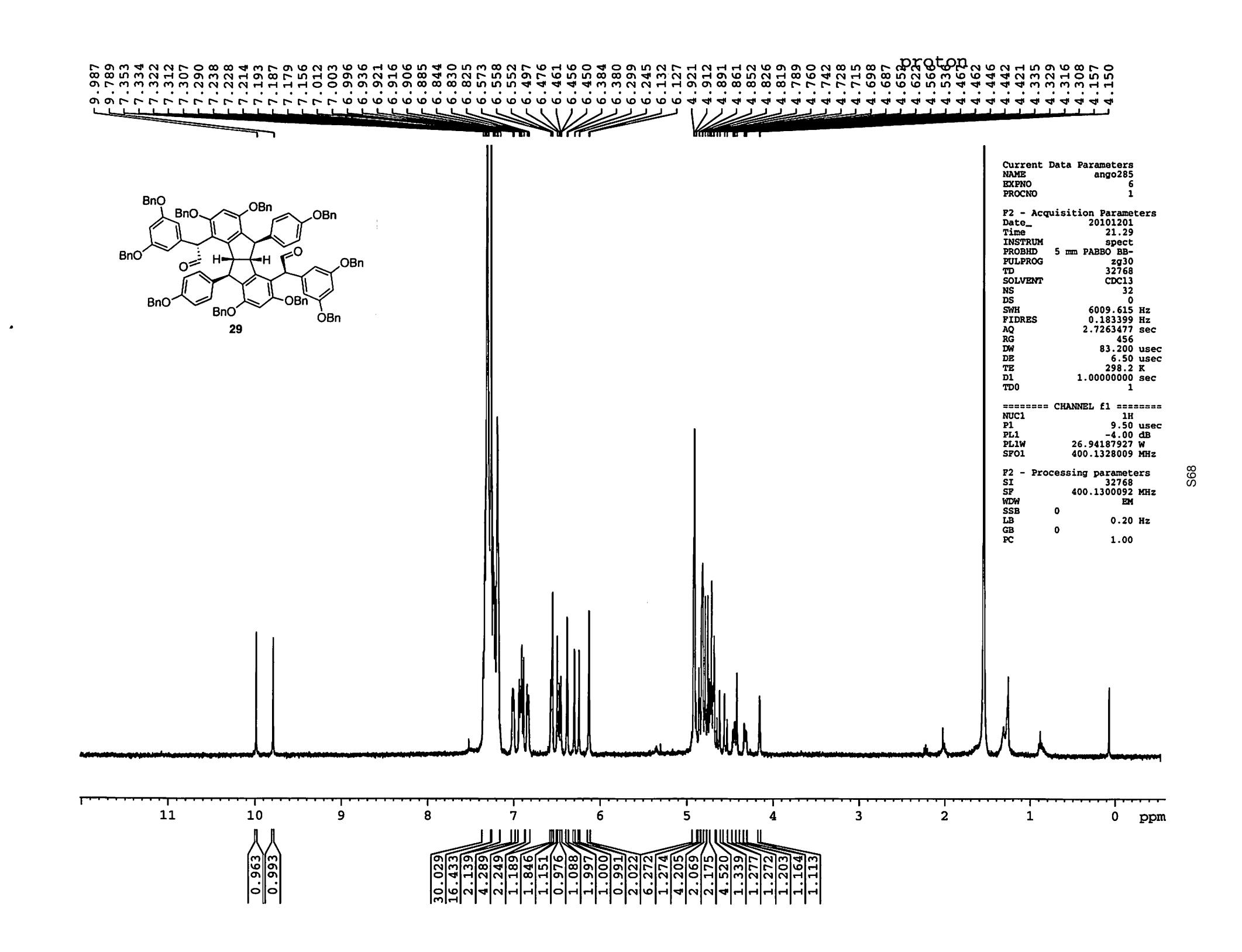
H
H
O
OBn
BnO
BnO
OBn
OBn
28
NAME ango186BP3
EXPNO 3
PROCNO 1
Date_ 20100626
Time 18.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 5114
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0.00000000 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127707 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


proton
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7.322
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7.307
7.290
7.238
7.228
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7.193
7.187
7.179
7.156
7.012
7.003
6.996
6.936
6.921
6.916
6.906
6.885
6.844
6.830
6.825
6.573
6.558
6.552
6.497
6.476
6.461
6.456
6.450
6.384
6.380
6.299
6.245
6.132
6.127
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4.912
4.891
4.861
4.852
4.826
4.819
4.789
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4.742
4.728
4.715
4.698
4.687
4.653
4.622
4.566
4.536
4.467
4.462
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4.442
4.421
4.335
4.329
4.316
4.308
4.157
4.150
BnO
BnO
OBn
OBn
BnO
O
H
H
O
OBn
BnO
BnO
OBn
OBn
29
Current Data Parameters
NAME ango285
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101201
Time 21.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 456
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.963
0.993
30.029
16.433
2.139
4.289
2.249
1.189
1.846
1.151
0.976
1.088
1.997
1.000
0.991
2.022
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4.205
2.069
2.175
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1.277
1.272
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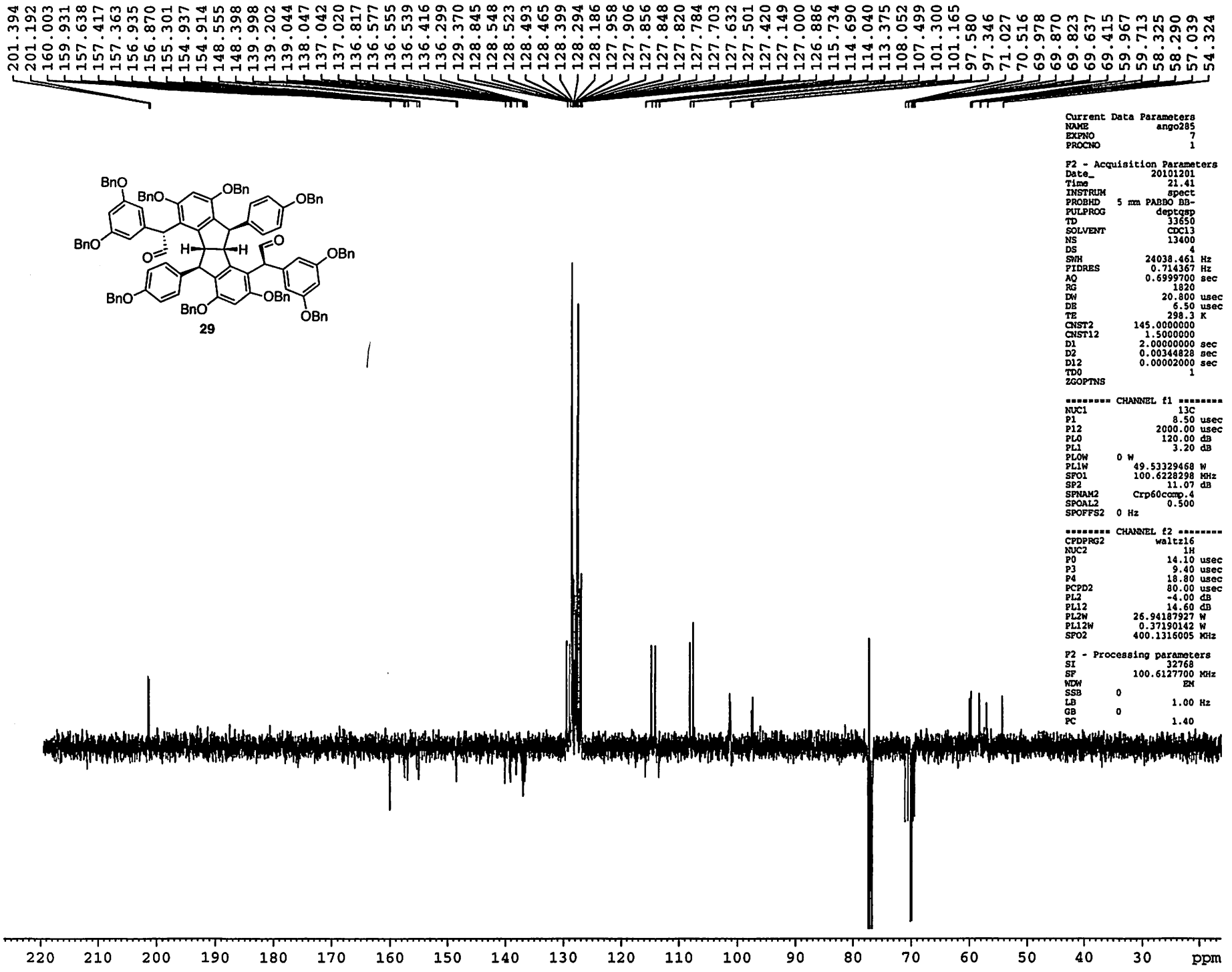
1.164
1.113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148.555
148.398
139.998
139.202
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138.047
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127.848
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127.784
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127.149
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58.290
57.039
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BnO
BnO
OBn
OBn
BnO
H
H
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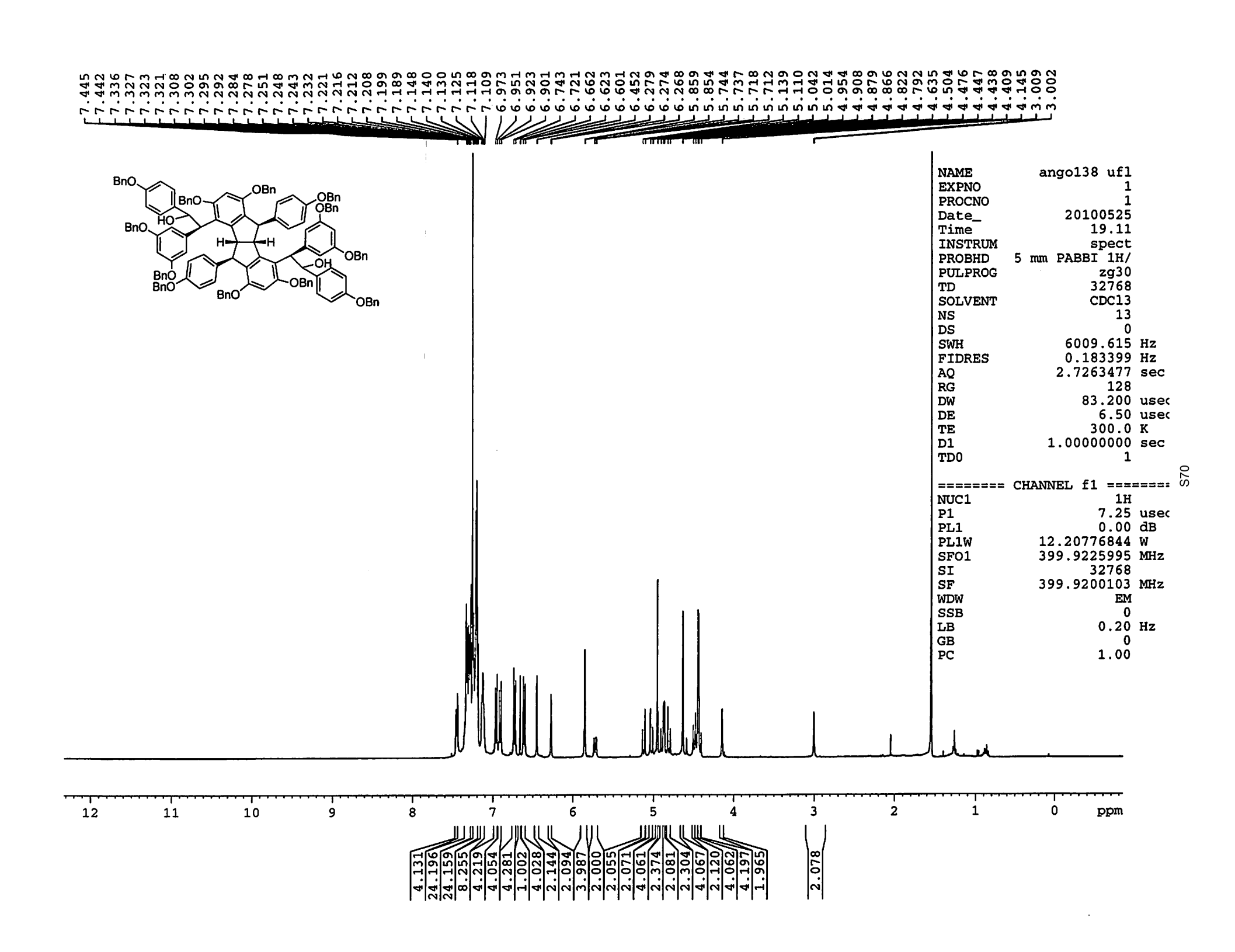
OBn
BnO
BnO
OBn
OBn
29
Current Data Parameters
NAME ango285
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101201
Time 21.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 13400
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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7.278
7.251
7.248
7.243
7.232
7.221
7.216
7.212
7.208
7.199
7.189
7.148
7.140
7.130
7.125
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7.109
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6.951
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6.662
6.623
6.601
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6.274
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5.854
5.744
5.737
5.718
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5.139
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5.014
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4.866
4.822
4.792
4.635
4.504
4.476
4.447
4.438
4.409
4.145
3.009
3.002
BnO
BnO
OBn
OBn
OBn
HO
BnO
H
H
OBn
OH
BnO
BnO
OBn
BnO
OBn
NAME ango138 ufl
EXPNO 1
PROCNO 1
Date_ 20100525
Time 19.11
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 13
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 128
DW 83.200 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200103 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S70
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.131
24.196
24.159
8.255
4.219
4.054
4.281
1.002
4.028
2.144
2.094
3.987
2.000
2.055
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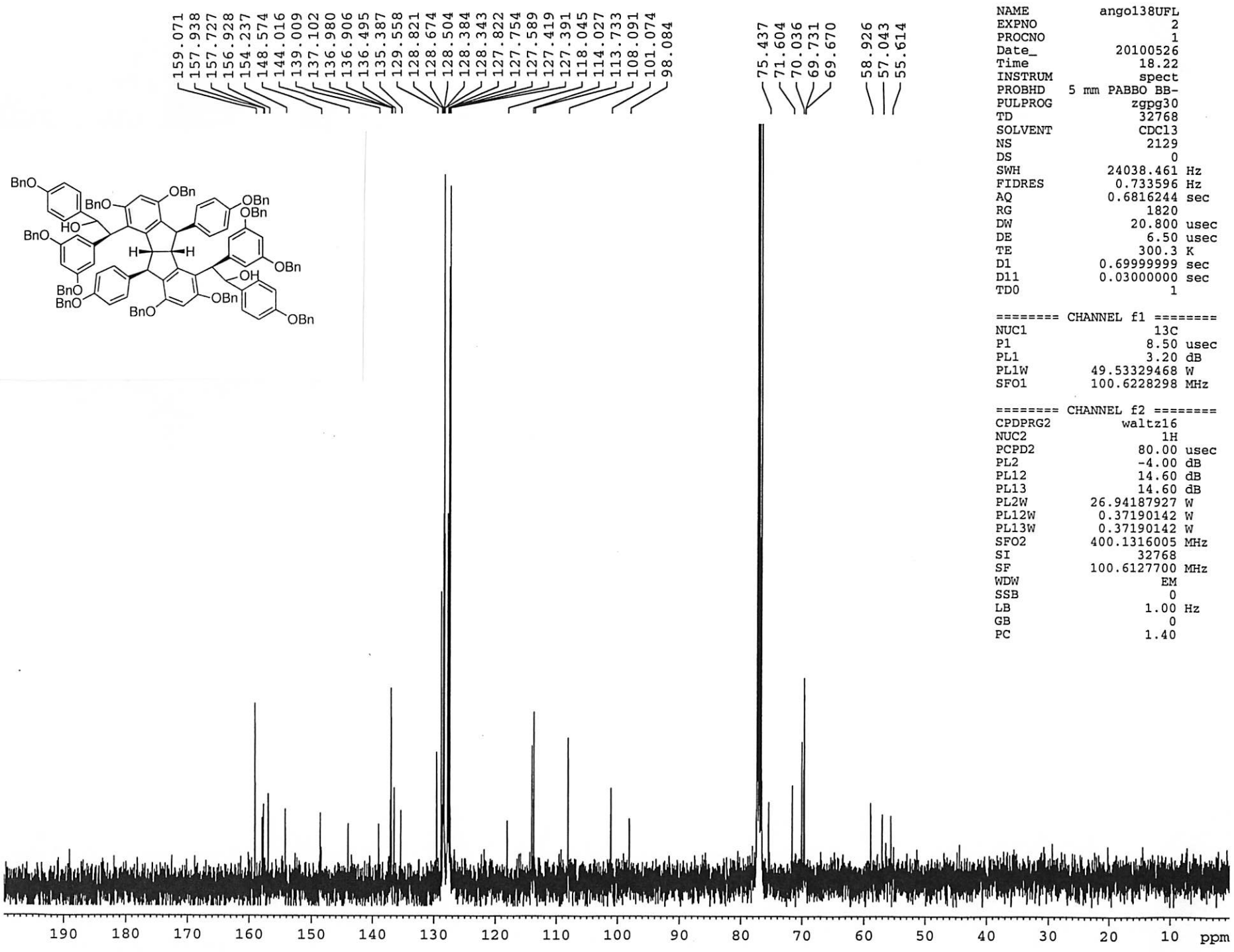
2.374
2.081
2.304
4.067
2.120
4.062
4.197
1.965
2.078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129.558
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128.674
128.504
128.384
128.343
127.822
127.754
127.589
127.419
127.391
118.045
114.027
113.733
108.091
101.074
98.084
75.437
71.604
70.036
69.731
69.670
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57.043
55.614
BnO
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BnO
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H
OBn
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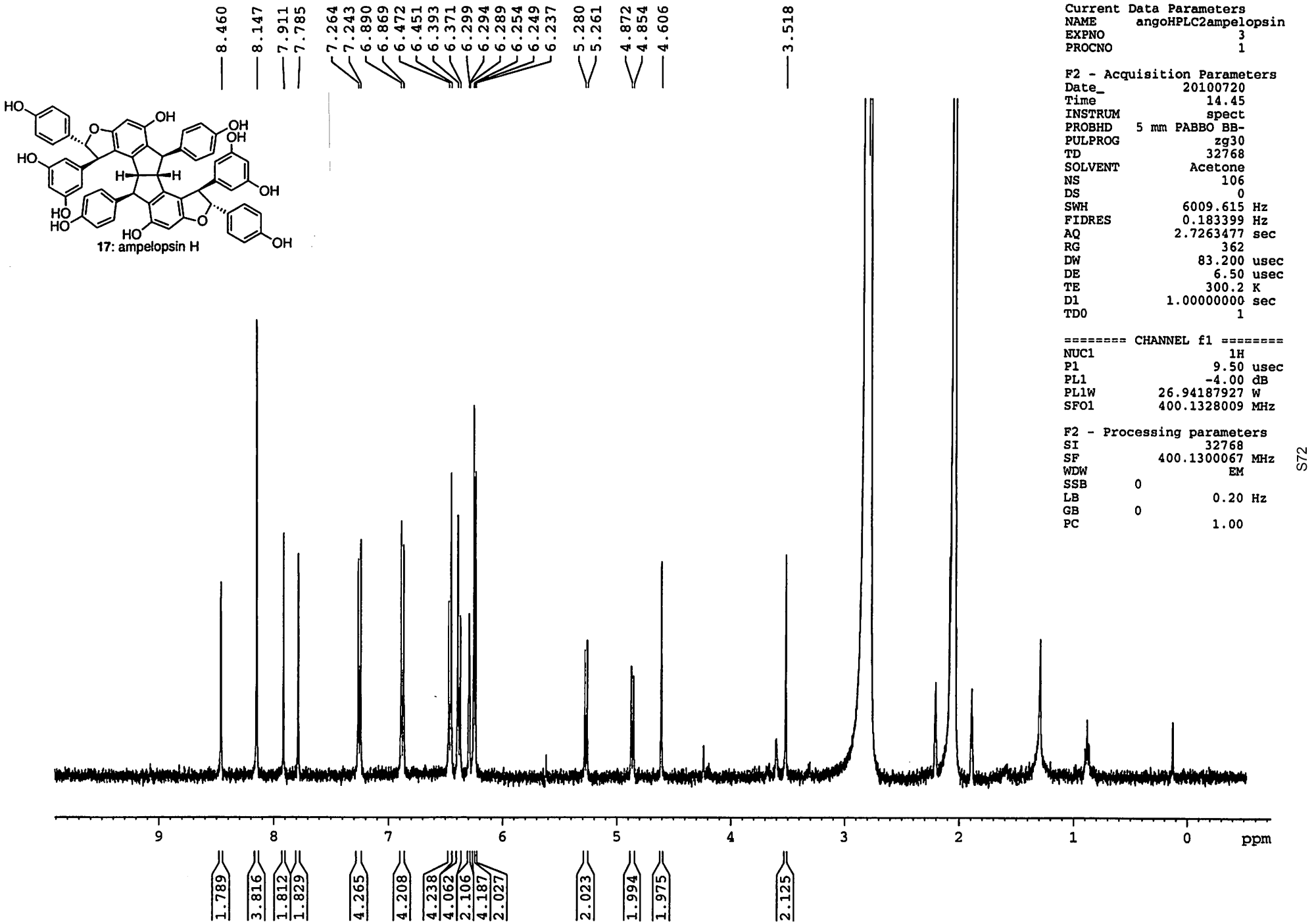
OBn
BnO
OBn
NAME ango138UFL
EXPNO 2
PROCNO 1
Date_ 20100526
Time 18.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2129
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 300.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.243
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6.869
6.472
6.451
6.393
6.371
6.299
6.294
6.289
6.254
6.249
6.237
5.280
5.261
4.872
4.854
4.606
3.518
17: ampelopsin H
Current Data Parameters
NAME angoHPLC2ampelopsin
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100720
Time 14.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 106
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
1.789
3.816
1.812
1.829
4.265
4.208
4.238
4.062
2.106
4.187
2.027
2.023
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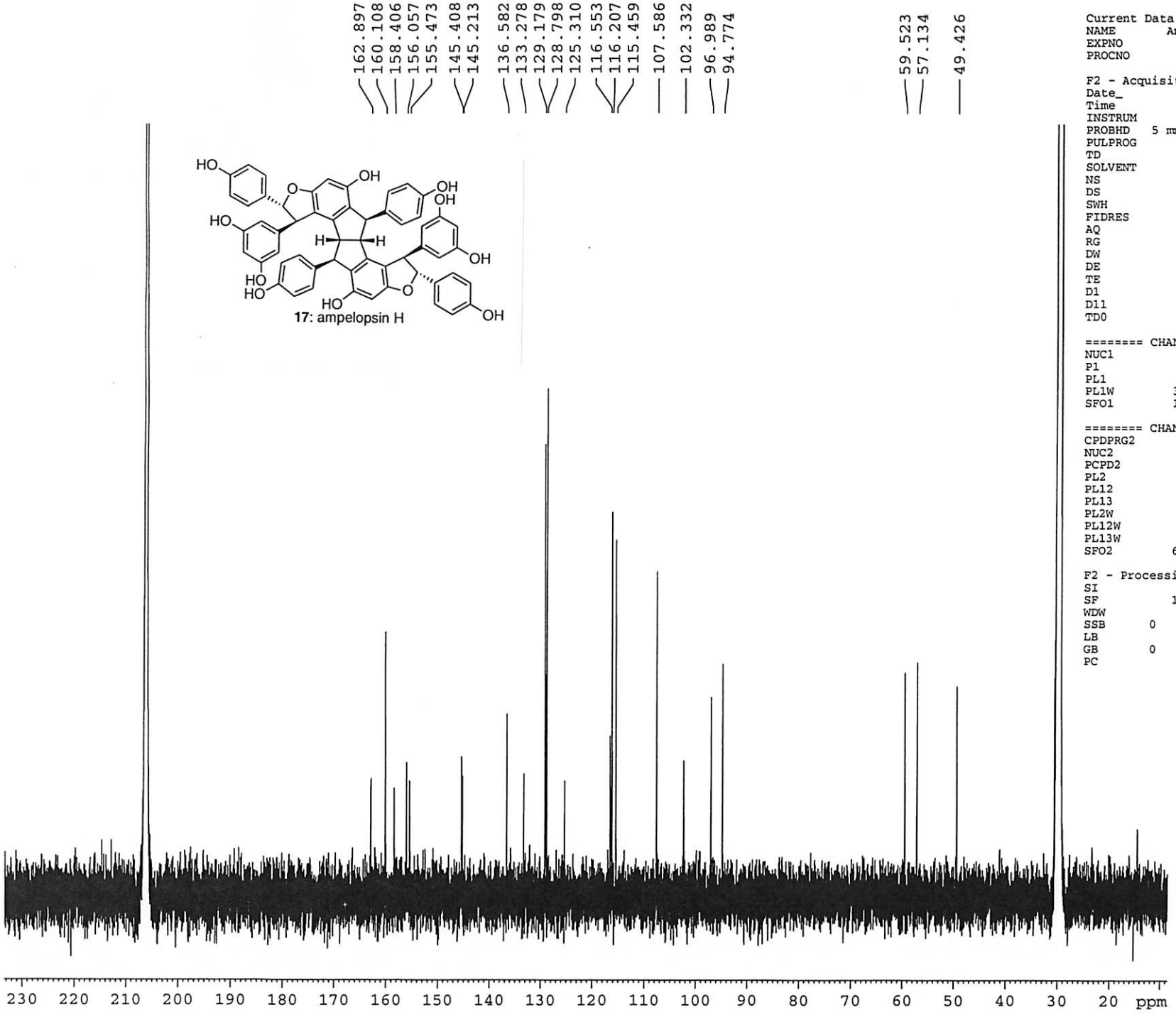
1.975
2.125




```
Current Data Parameters
NAME        Ampelopsin-H
EXPNO                 12
PROCNO               999

F2 - Acquisition Parameters
Date_          20100810
Time               2.30
INSTRUM           spect
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD               134144
SOLVENT         Acetone
NS                 5120
DS                    2
SWH          39062.500 Hz
FIDRES        0.291198 Hz
AQ            1.7170932 sec
RG                  203
DW               12.800 usec
DE               25.82 usec
TE               297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               10.25 usec
PL1               3.10 dB
PL1W        32.60212326 W
SFO1       150.9209173 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            70.00 usec
PL2               3.40 dB
PL12             16.00 dB
PL13             16.00 dB
PL2W         7.46299839 W
PL12W        0.41012228 W
PL13W        0.41012228 W
SFO2       600.1324005 MHz

F2 - Processing parameters
SI                 65536
SF         150.9026668 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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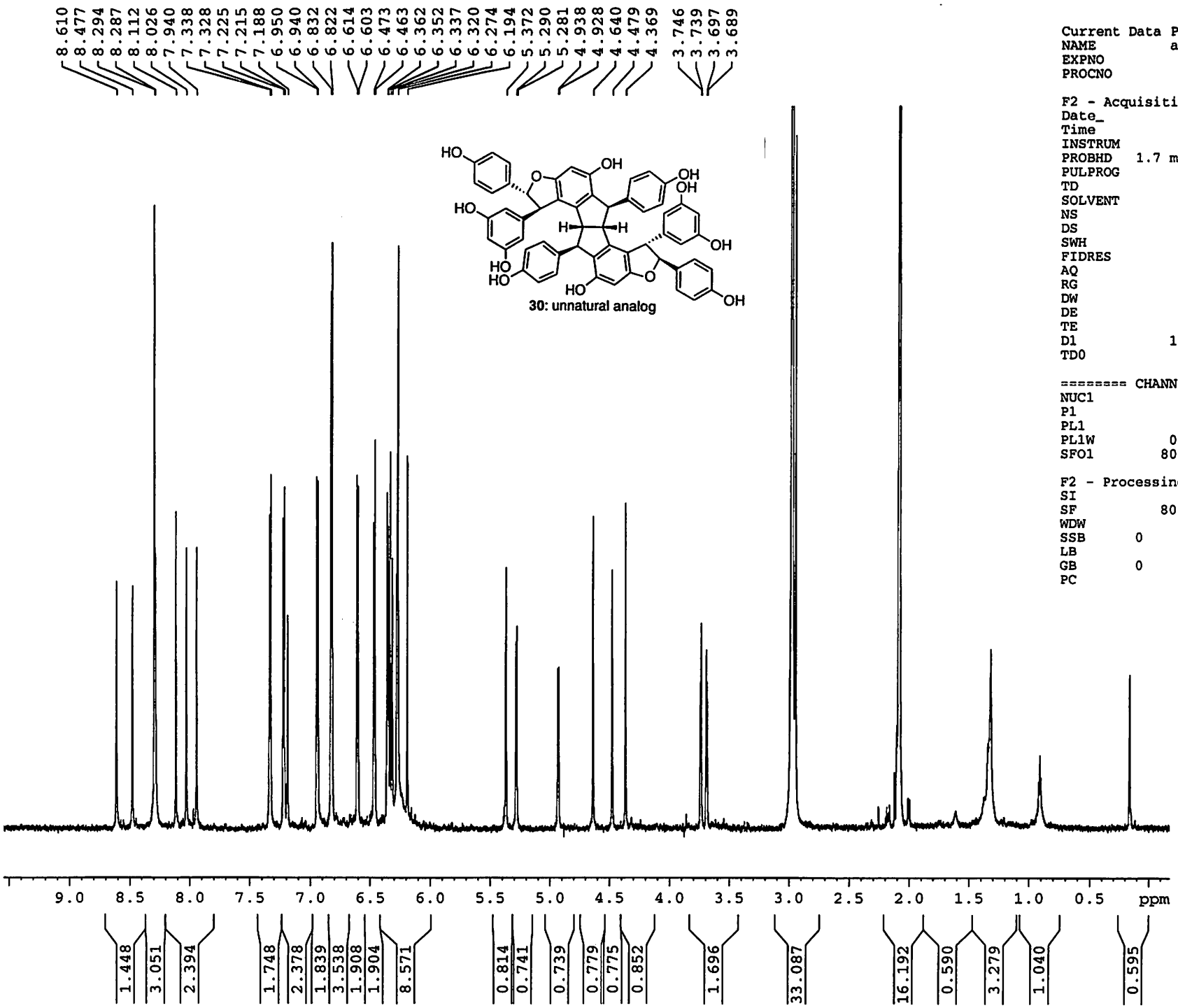
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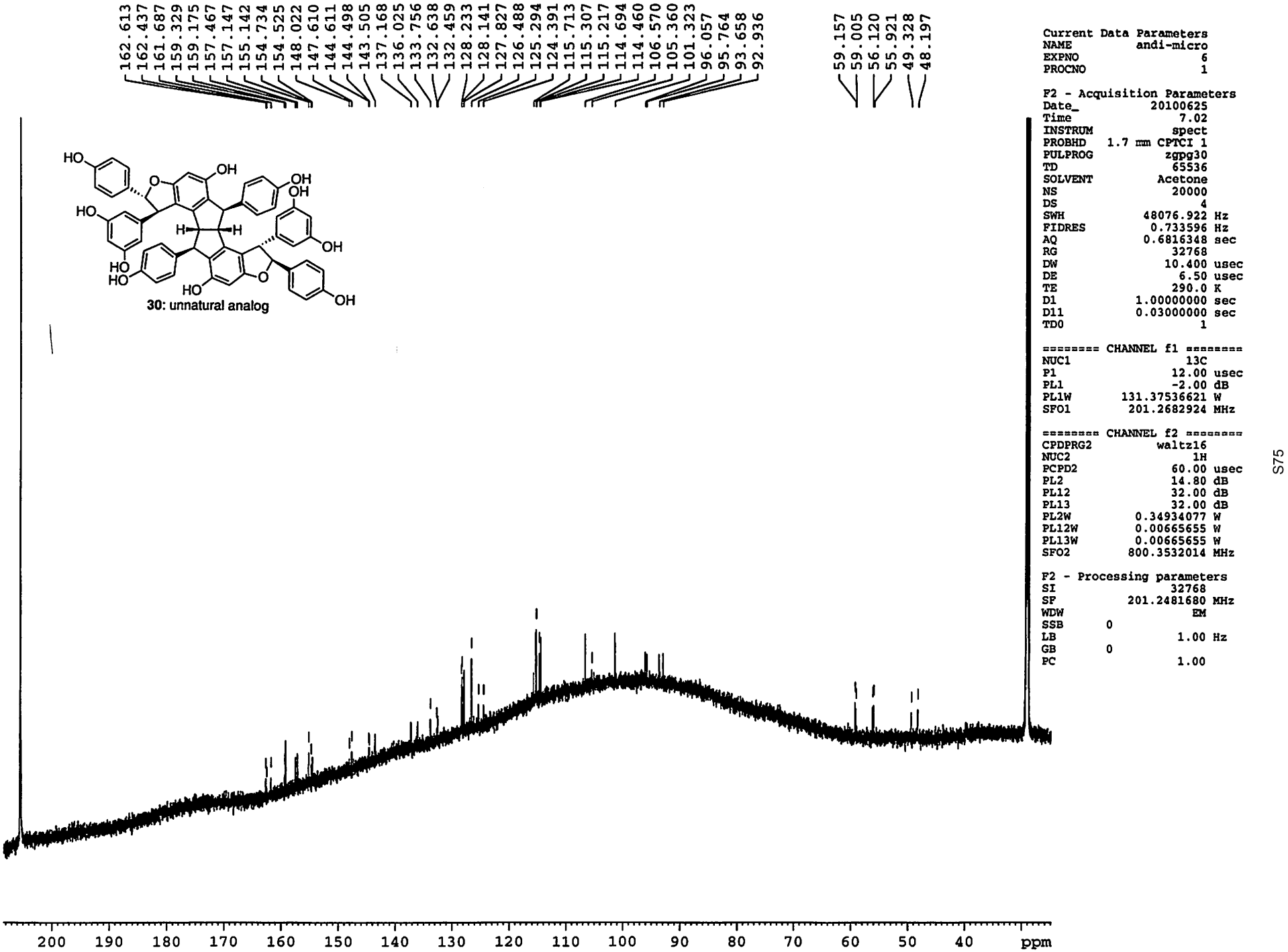
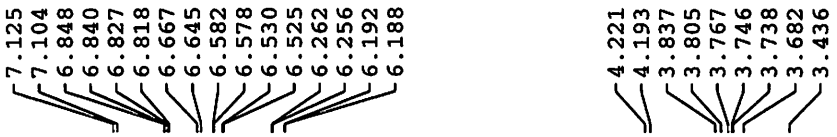
8.287
8.112
8.026
7.940
7.338
7.328
7.225
7.215
7.188
6.950
6.940
6.832
6.822
6.614
6.603
6.473
6.463
6.362
6.352
6.337
6.320
6.274
6.194
5.372
5.290
5.281
4.938
4.928
4.640
4.479
4.369
3.746
3.739
3.697
3.689
30: unnatural analog
Current Data Parameters
NAME andi-micro
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100624
Time 11.29
INSTRUM spect
PROBHD 1.7 mm CPTCI 1
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 90
DS 2
SWH 16501.650 Hz
FIDRES 0.251795 Hz
AQ 1.9858211 sec
RG 4
DW 30.300 usec
DE 6.50 usec
TE 289.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.40 usec
PL1 14.80 dB
PL1W 0.34934077 W
SFO1 800.3549425 MHz
F2 - Processing parameters
SI 32768
SF 800.3499845 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.448
3.051
2.394
1.748
2.378
1.839
3.538
1.908
1.904
8.571
0.814
0.741
0.739
0.779
0.775
0.852
1.696
33.087
16.192
0.590
3.279
1.040
0.595


162.613
162.437
161.687
159.329
159.175
157.467
157.147
155.142
154.734
154.525
148.022
147.610
144.611
144.498
143.505
137.168
136.025
133.756
132.638
132.459
128.233
128.141
127.827
126.488
125.294
124.391
115.713
115.307
115.217
114.694
114.460
106.570
105.360
101.323
96.057
95.764
93.658
92.936
59.157
59.005
56.120
55.921
49.328
48.197
30: unnatural analog
Current Data Parameters
NAME andi-micro
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100625
Time 7.02
INSTRUM spect
PROBHD 1.7 mm CPTCI 1
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 20000
DS 4
SWH 48076.922 Hz
FIDRES 0.733596 Hz
AQ 0.6816348 sec
RG 32768
DW 10.400 usec
DE 6.50 usec
TE 290.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 -2.00 dB
PL1W 131.37536621 W
SFO1 201.2682924 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL2 14.80 dB
PL12 32.00 dB
PL13 32.00 dB
PL2W 0.34934077 W
PL12W 0.00665655 W
PL13W 0.00665655 W
SFO2 800.3532014 MHz
F2 - Processing parameters
SI 32768
SF 201.2481680 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

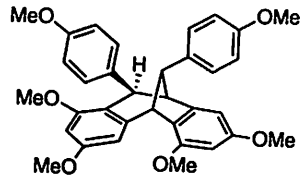



```
Current Data Parameters
NAME      mic_III_perme_amp_f_2
EXPNO                     5
PROCNO                    1

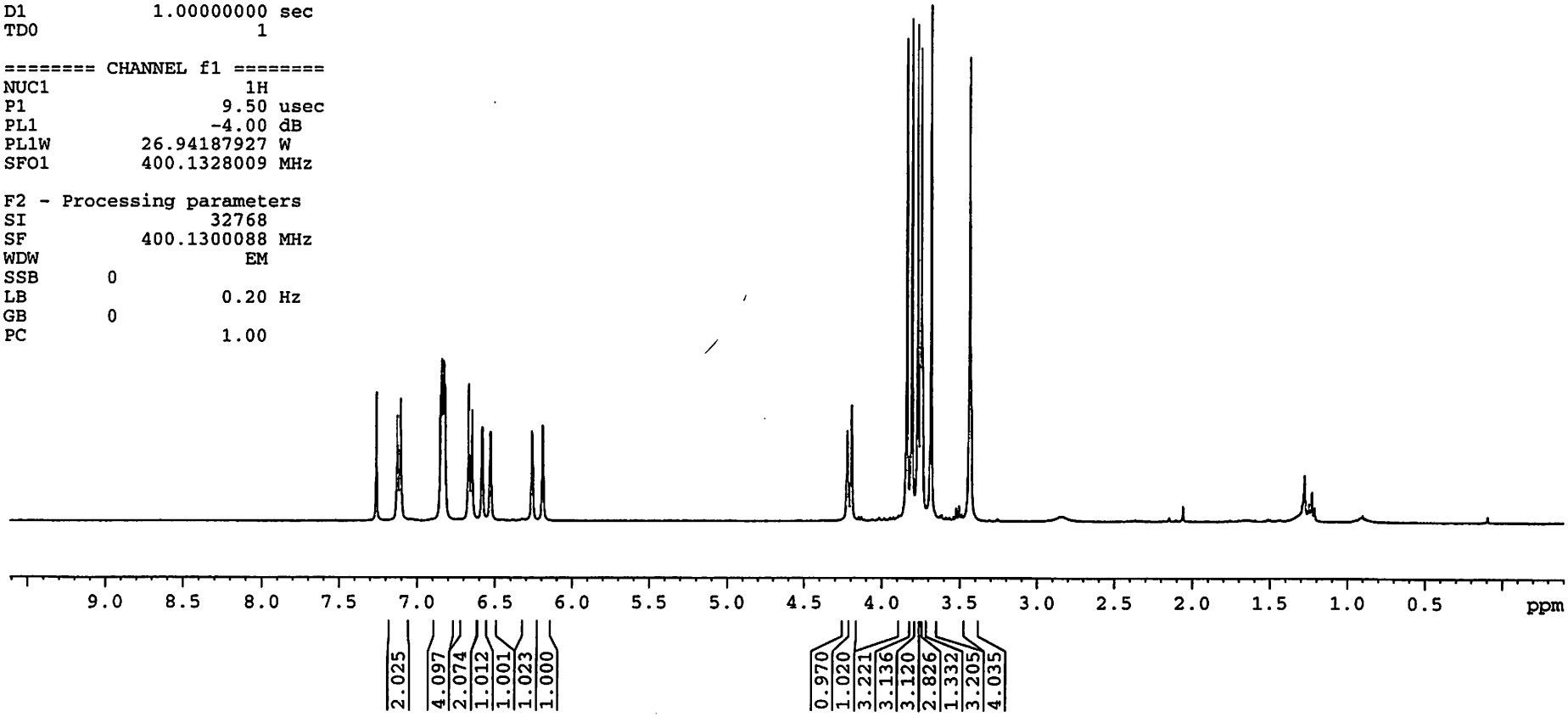
F2 - Acquisition Parameters
Date_           20100915
Time               11.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     6
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   144
DW                83.200 usec
DE                 6.50 usec
TE                298.2 K
D1           1.00000000 sec
TD0                    1

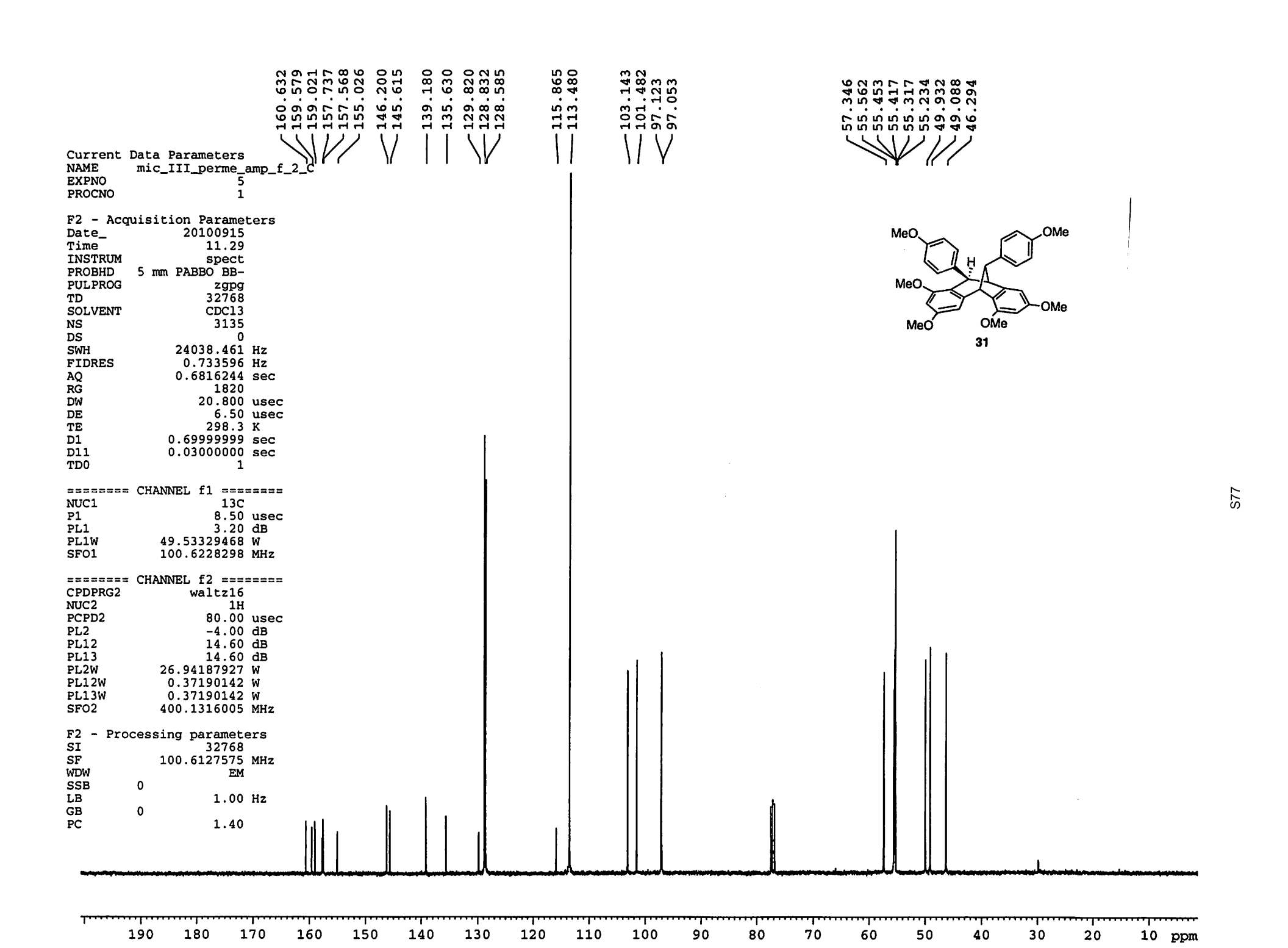
======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W         26.94187927 W
SFO1         400.1328009 MHz

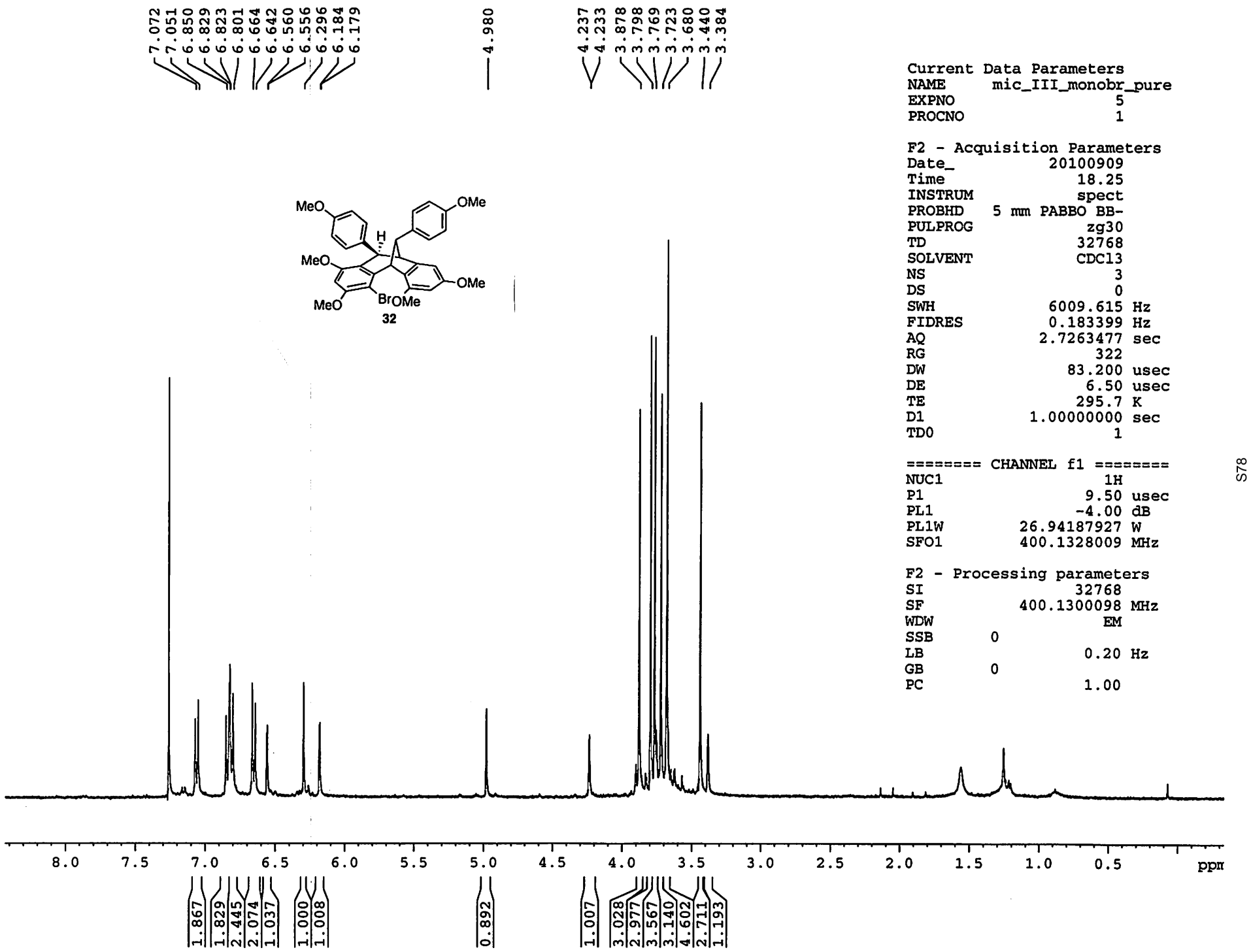
F2 - Processing parameters
SI                 32768
SF           400.1300088 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.00
```

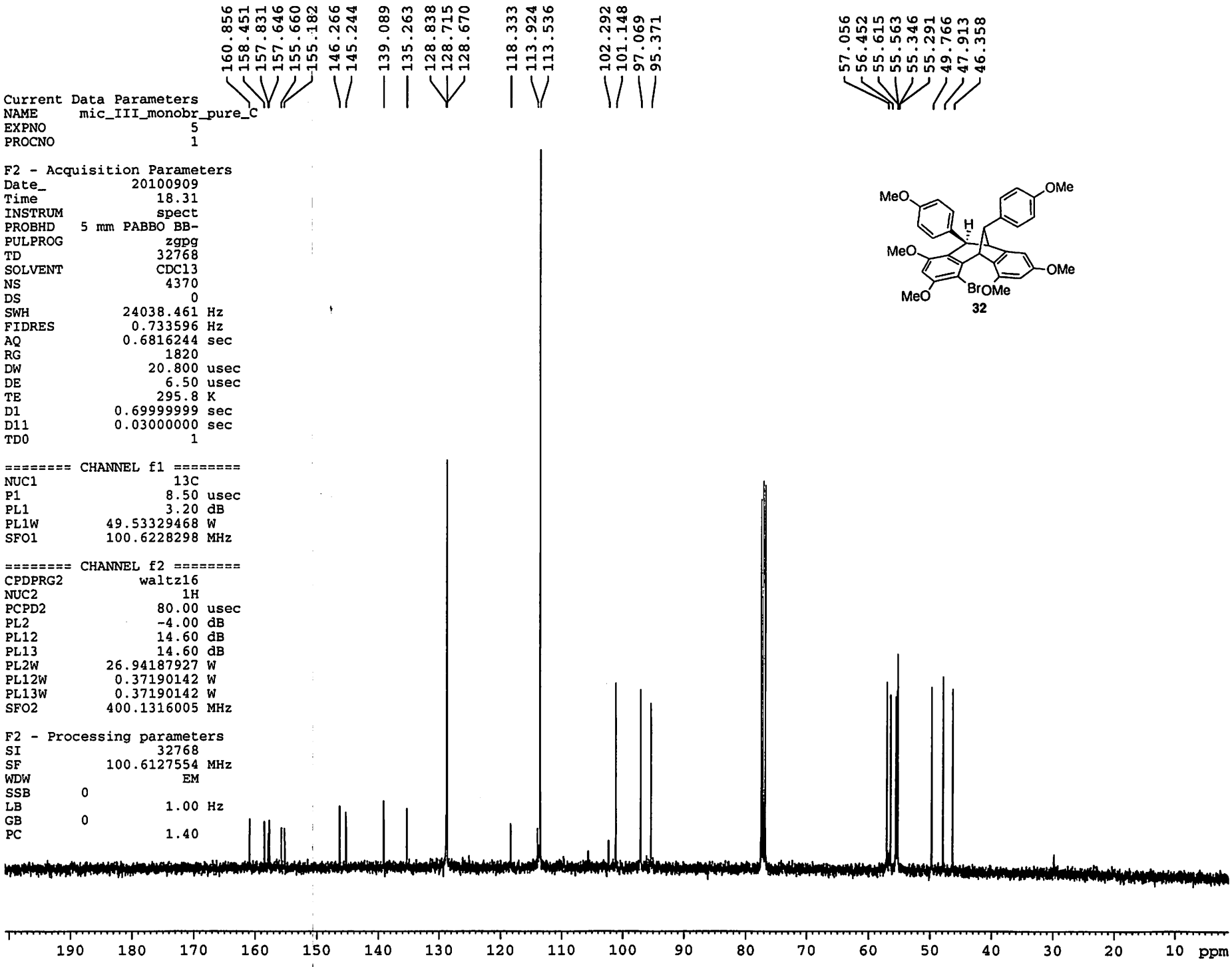


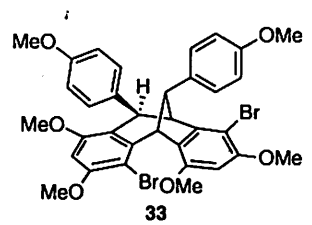
31




160.632
159.579
159.021
157.737
157.568
155.026
146.200
145.615
139.180
135.630
129.820
128.832
128.585
115.865
113.480
103.143
101.482
97.123
97.053
57.346
55.562
55.453
55.417
55.317
55.234
49.932
49.088
46.294
Current Data Parameters
NAME mic_III_perme_amp_f_2_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100915
Time 11.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 3135
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127575 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
OMe
MeO
OMe
MeO
OMe
31
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.072
7.051
6.850
6.829
6.823
6.801
6.664
6.642
6.560
6.556
6.296
6.184
6.179
4.980
4.237
4.233
3.878
3.798
3.769
3.723
3.680
3.440
3.384
MeO
OMe
H
MeO
OMe
MeO
BrOMe
32
Current Data Parameters
NAME mic_III_monobr_pure
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100909
Time 18.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 3
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 322
DW 83.200 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.867
1.829
2.445
2.074
1.037
1.000
1.008
0.892
1.007
3.028
2.977
3.567
3.140
4.602
2.711
1.193


160.856
158.451
157.831
157.646
155.660
155.182
146.266
145.244
139.089
135.263
128.838
128.715
128.670
118.333
113.924
113.536
102.292
101.148
97.069
95.371
57.056
56.452
55.615
55.563
55.346
55.291
49.766
47.913
46.358
Current Data Parameters
NAME mic_III_monobr_pure_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100909
Time 18.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 4370
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 295.8 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127554 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
OMe
H
MeO
OMe
MeO
BrOMe
32
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



33

7.136
7.115
6.882
6.861
6.826
6.805
6.687
6.666
6.320
6.193
5.075
4.372
3.884
3.827
3.789
3.730
3.684
3.453

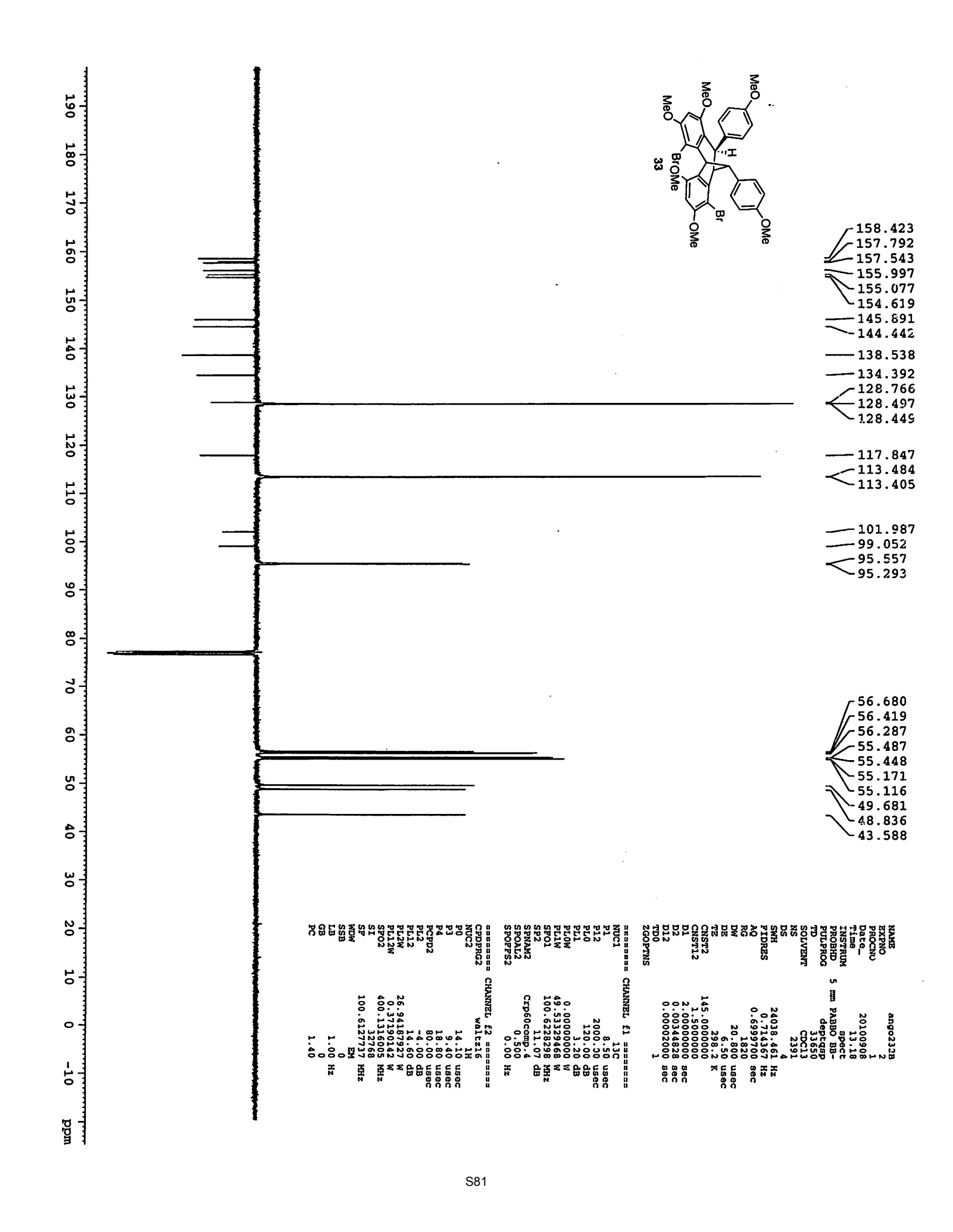
```
Current Data Parameters
NAME                 ango232B
EXPNO                       1
PROCNO                      1

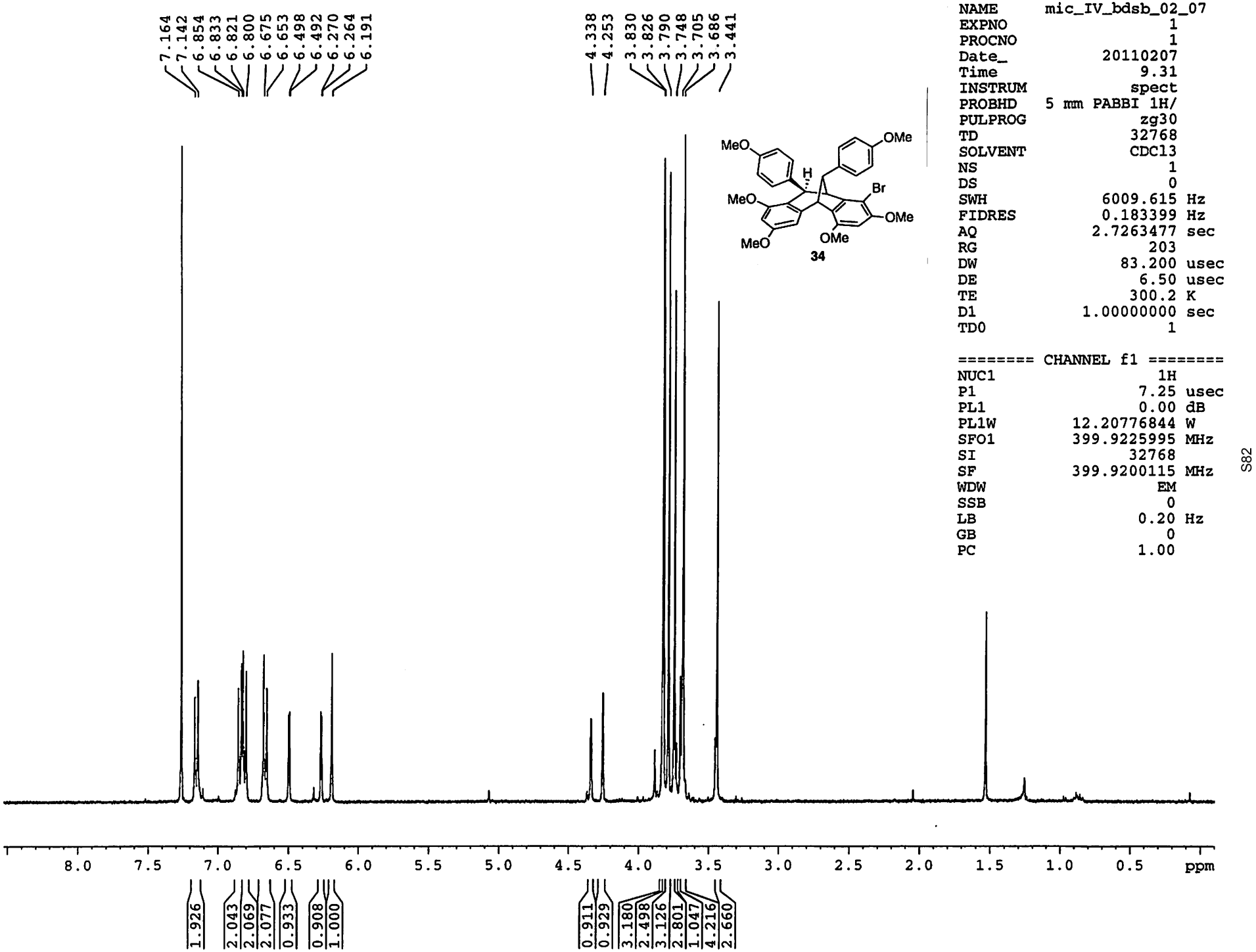
F2 - Acquisition Parameters
Date_               20100908
Time                   13.10
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        32
DS                         0
SWH                 6009.615 Hz
FIDRES                0.183399 Hz
AQ                 2.7263477 sec
RG                       114
DW                    83.200 usec
DE                     6.50 usec
TE                     298.2 K
D1                1.00000000 sec
TD0                         1

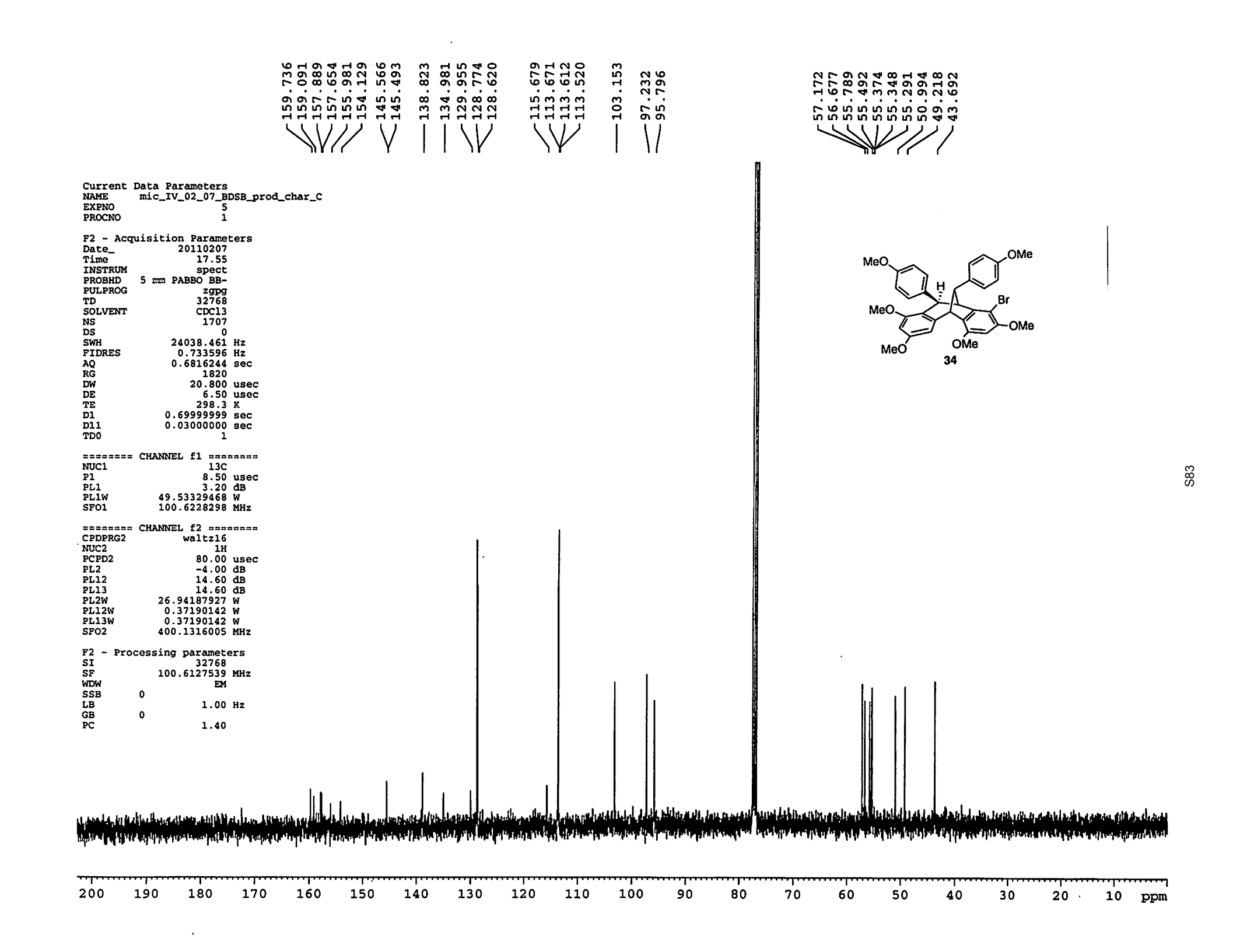
======== CHANNEL f1 ========
NUC1                       1H
P1                      9.50 usec
PL1                    -4.00 dB
PL1W              26.94187927 W
SFO1              400.1328009 MHz

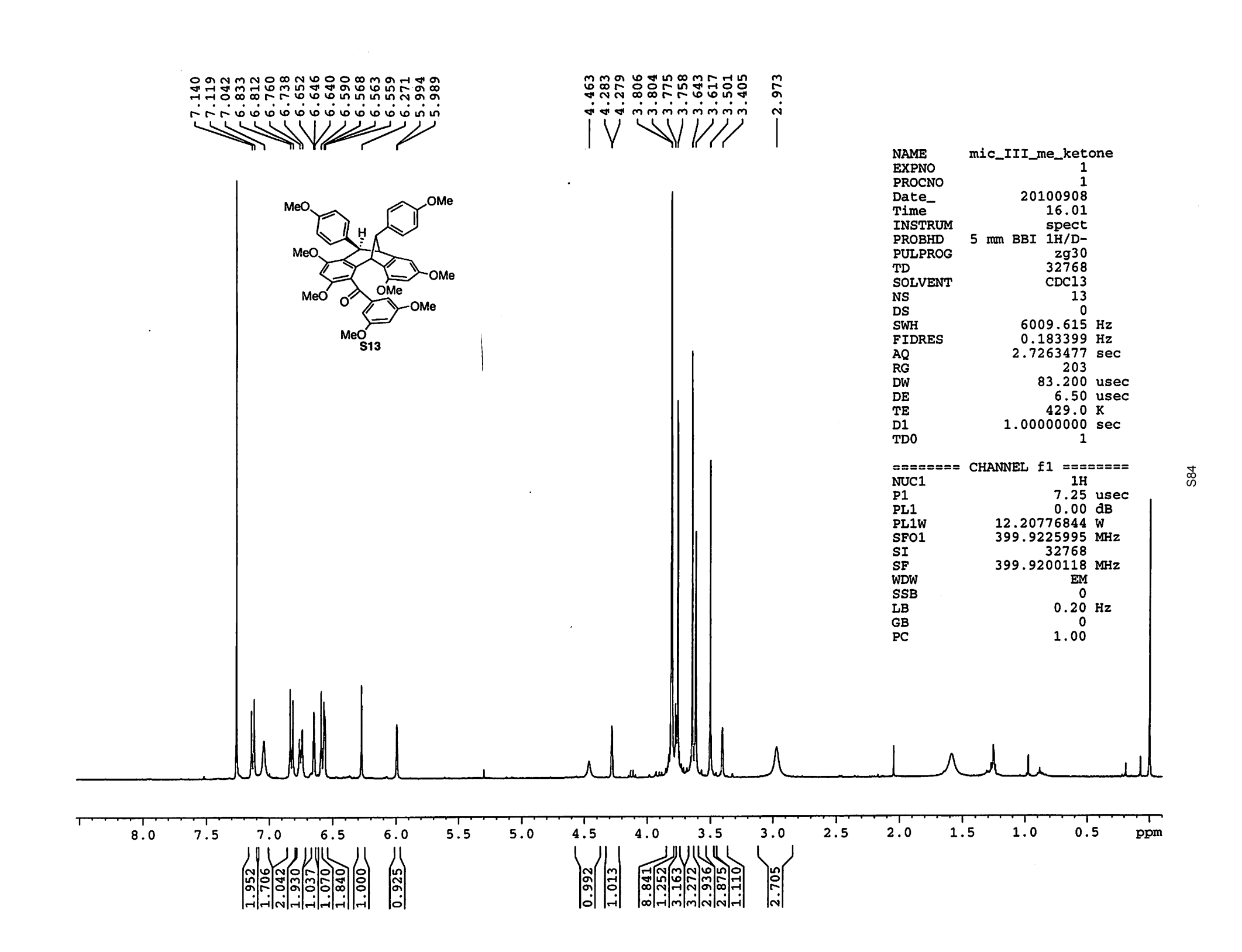
F2 - Processing parameters
SI                        32768
SF                400.1300080 MHz
WDW                          EM
SSB          0
LB                      0.20 Hz
GB           0
PC                        1.00
```


1.990
2.034
2.022
2.032
1.025
1.008
1.000
1.041
3.135
3.076
3.003
3.186
4.801
2.988


MeO
MeO
MeO
H
Br
OMe
OMe
Br
OMe
33
158.423
157.792
157.543
155.997
155.077
154.619
145.891
144.442
138.538
134.392
128.766
128.497
128.449
117.847
113.484
113.405
101.987
99.052
95.557
95.293
56.680
56.419
56.287
55.487
55.448
55.171
55.116
49.681
48.836
43.588
NAME ango232B
EXPNO 2
PROCNO 1
Date_ 20100908
Time 13.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 2391
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0.00000000 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
SI 32768
SP 100.6127737 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


7.164
7.142
6.854
6.833
6.821
6.800
6.675
6.653
6.498
6.492
6.270
6.264
6.191
4.338
4.253
3.830
3.826
3.790
3.748
3.705
3.686
3.441
MeO
OMe
H
Br
MeO
OMe
MeO
OMe
34
NAME mic_IV_bdsb_02_07
EXPNO 1
PROCNO 1
Date_ 20110207
Time 9.31
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 1
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200115 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.926
2.043
2.069
2.077
0.933
0.908
1.000
0.911
0.929
3.180
2.498
3.126
2.801
1.047
4.216
2.660


159.736
159.091
157.889
157.654
155.981
154.129
145.566
145.493
138.823
134.981
129.955
128.774
128.620
115.679
113.671
113.612
113.520
103.153
97.232
95.796
57.172
56.677
55.789
55.492
55.374
55.348
55.291
50.994
49.218
43.692
Current Data Parameters
NAME mic_IV_02_07_BDSB_prod_char_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110207
Time 17.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 1707
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127539 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
OMe
H
Br
MeO
OMe
MeO
OMe
34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.140
7.119
7.042
6.833
6.812
6.760
6.738
6.652
6.646
6.640
6.590
6.568
6.563
6.559
6.271
5.994
5.989
4.463
4.283
4.279
3.806
3.804
3.775
3.758
3.643
3.617
3.501
3.405
2.973
MeO
OMe
MeO
OMe
MeO
OMe
OMe
MeO
S13
NAME mic_III_me_ketone
EXPNO 1
PROCNO 1
Date_ 20100908
Time 16.01
INSTRUM spect
PROBHD 5 mm BBI 1H/D-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 13
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 429.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200118 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.952
1.706
2.042
1.930
1.037
1.070
1.840
1.000
0.925
0.992
1.013
8.841
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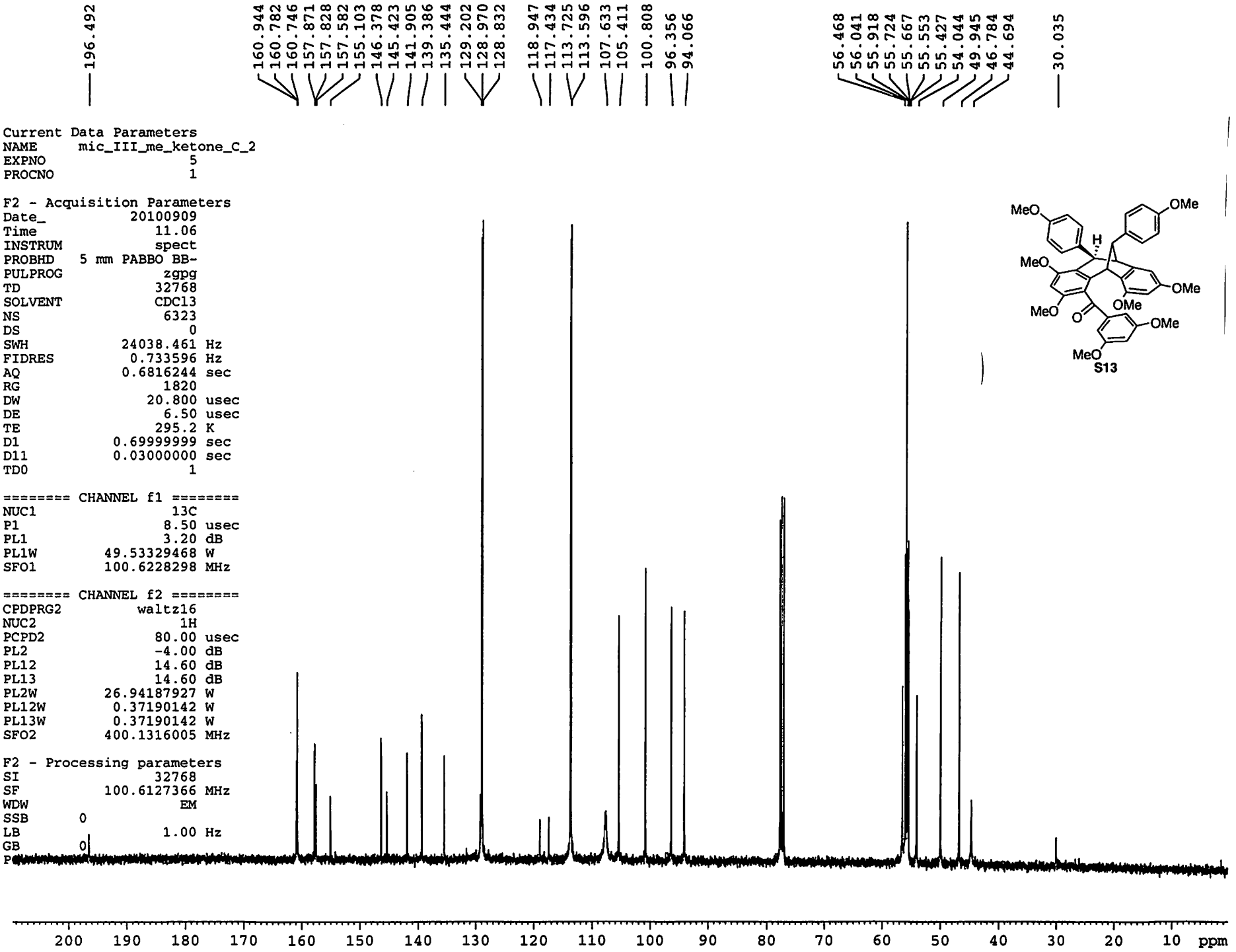
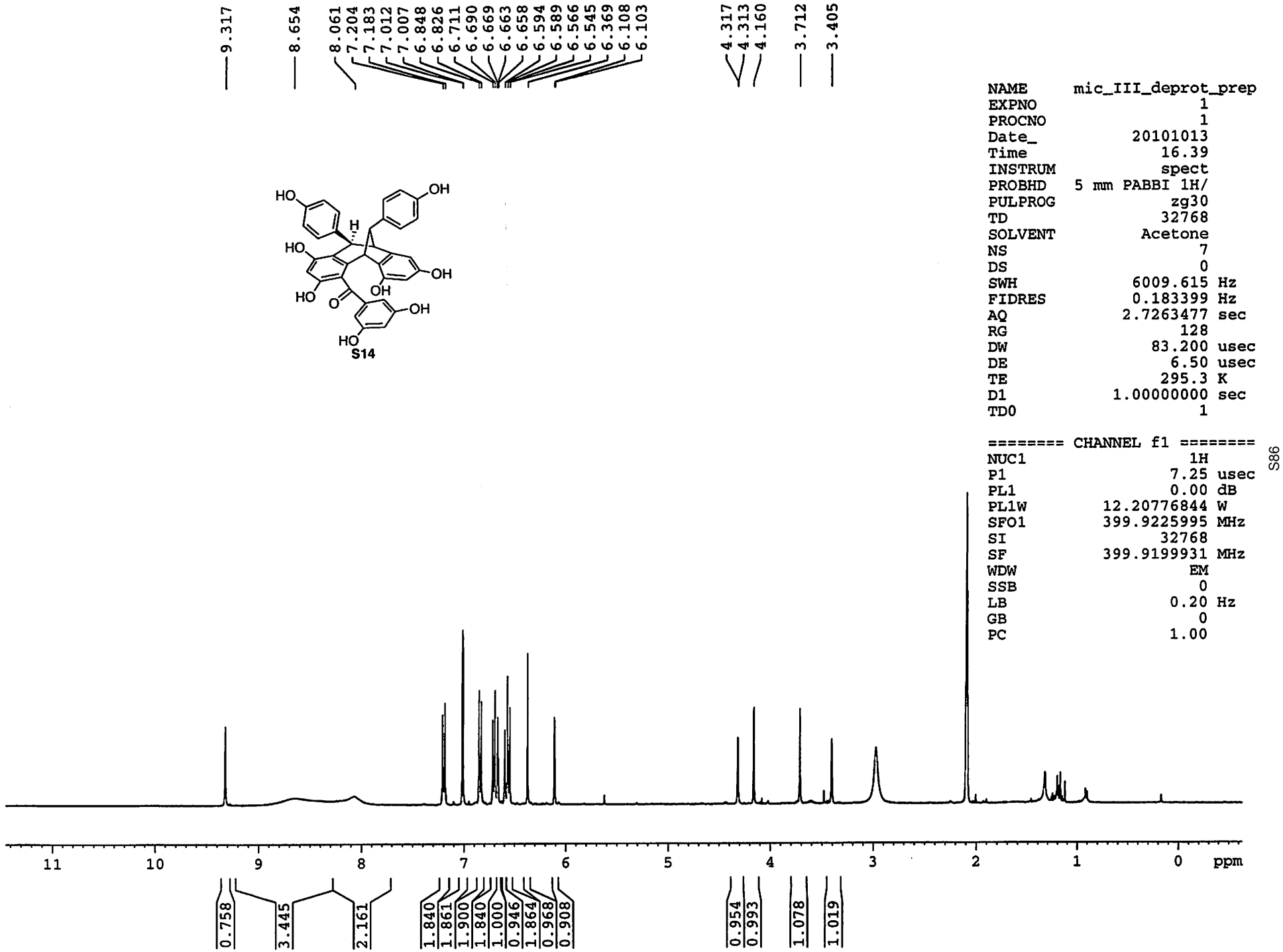
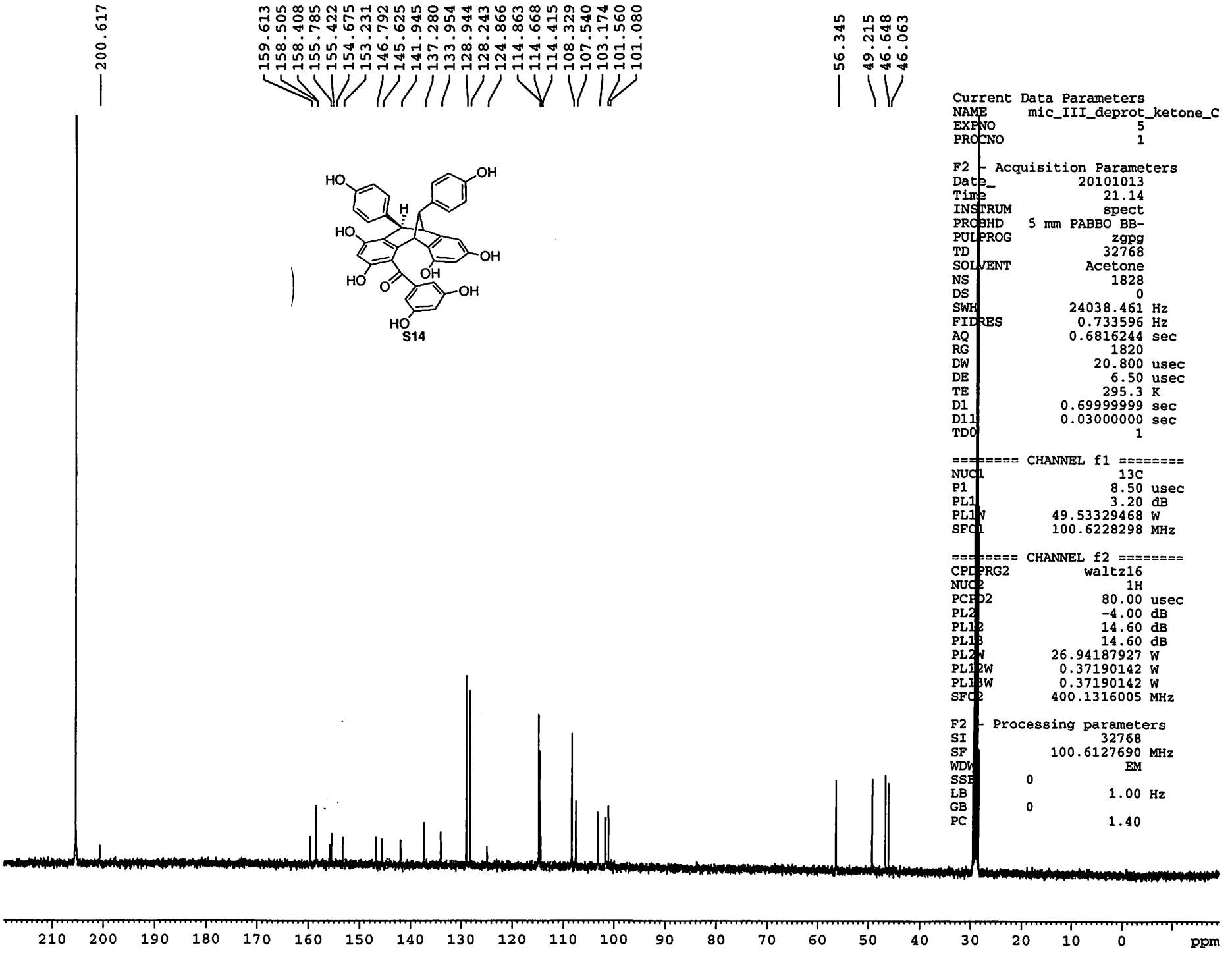
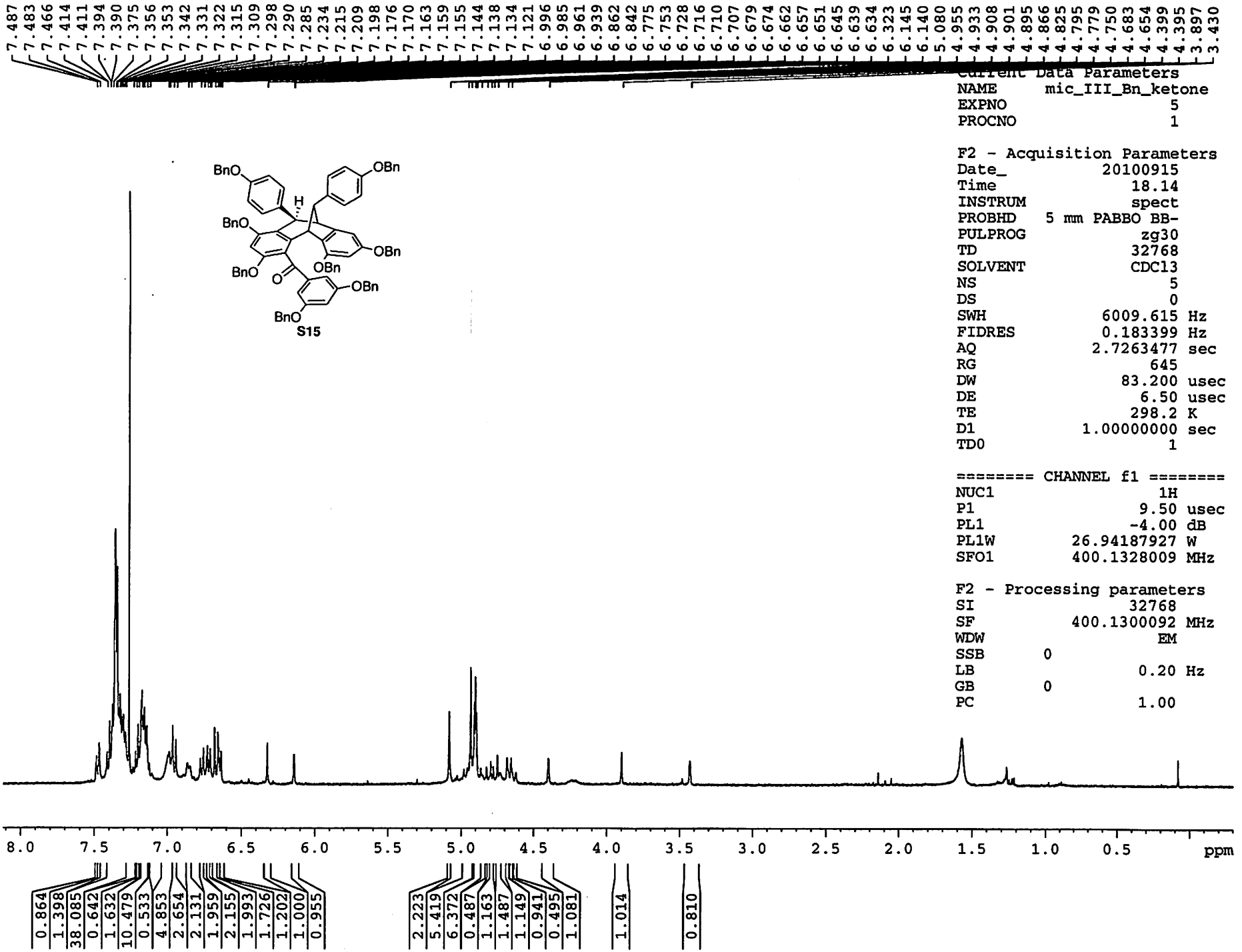
3.272
2.936
2.875
1.110
2.705

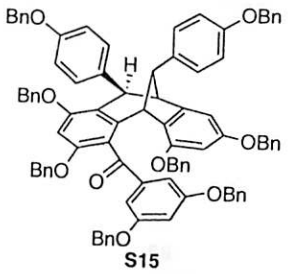

196.492
160.944
160.782
160.746
157.871
157.828
157.582
155.103
146.378
145.423
141.905
139.386
135.444
129.202
128.970
128.832
118.947
117.434
113.725
113.596
107.633
105.411
100.808
96.356
94.066
56.468
56.041
55.918
55.724
55.667
55.553
55.427
54.044
49.945
46.784
44.694
30.035
Current Data Parameters
NAME mic_III_me_ketone_C_2
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100909
Time 11.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 6323
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 295.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127366 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
MeO
OMe
H
MeO
OMe
MeO
OMe
O
OMe
MeO
S13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.317
8.654
8.061
7.204
7.183
7.012
7.007
6.848
6.826
6.711
6.690
6.669
6.663
6.658
6.594
6.589
6.566
6.545
6.369
6.108
6.103
4.317
4.313
4.160
3.712
3.405
S14
NAME mic_III_deprot_prep
EXPNO 1
PROCNO 1
Date_ 20101013
Time 16.39
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 7
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 128
DW 83.200 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9199931 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S86
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.758
3.445
2.161
1.840
1.861
1.900
1.840
1.000
0.946
1.864
0.968
0.908
0.954
0.993
1.078
1.019


200.617
159.613
158.505
158.408
155.785
155.422
154.675
153.231
146.792
145.625
141.945
137.280
133.954
128.944
128.243
124.866
114.863
114.668
114.415
108.329
107.540
103.174
101.560
101.080
56.345
49.215
46.648
46.063
S14
Current Data Parameters
NAME mic_III_deprot_ketone_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101013
Time 21.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT Acetone
NS 1828
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 295.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.487 7.483 7.466 7.414 7.411 7.394 7.390 7.375 7.356 7.353 7.342 7.331 7.322 7.315 7.309 7.298 7.290 7.285 7.234 7.215 7.209 7.198 7.176 7.170 7.163 7.159 7.155 7.144 7.138 7.134 7.121 6.996 6.985 6.961 6.939 6.862 6.842 6.775 6.753 6.728 6.716 6.710 6.707 6.679 6.674 6.662 6.657 6.651 6.645 6.639 6.634 6.323 6.145 6.140 5.080 4.955 4.933 4.908 4.901 4.895 4.866 4.825 4.795 4.779 4.750 4.683 4.654 4.399 4.395 3.897 3.430
BnO
OBn
H
O
S15
Current Data Parameters
NAME mic_III_Bn_ketone
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100915
Time 18.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 5
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 645
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.864 1.398 38.085 0.642 1.632 10.479 0.533 4.853 2.654 2.131 1.959 2.155 1.993 1.726 1.202 1.000 0.955
2.223 5.419 6.372 0.487 1.163 1.487 1.149 0.941 0.495 1.081
1.014
0.810

196.591
159.933
159.552
159.357
157.235
157.003
156.472
153.598
146.386
145.484
142.392
139.647
137.473
137.397
137.146
137.076
136.965
136.579
136.504
135.502
130.383
129.100
128.722
128.656
128.624
128.333
128.188
128.107
128.018
127.946
127.850
127.799
127.718
127.667
127.647
127.523
127.244
127.103
126.451
119.663
117.564
114.761
114.427
106.662
102.567
99.167
96.242
70.501
70.453
70.278
70.256
70.043
69.885
68.692
56.684
49.968
46.822
44.220



S15

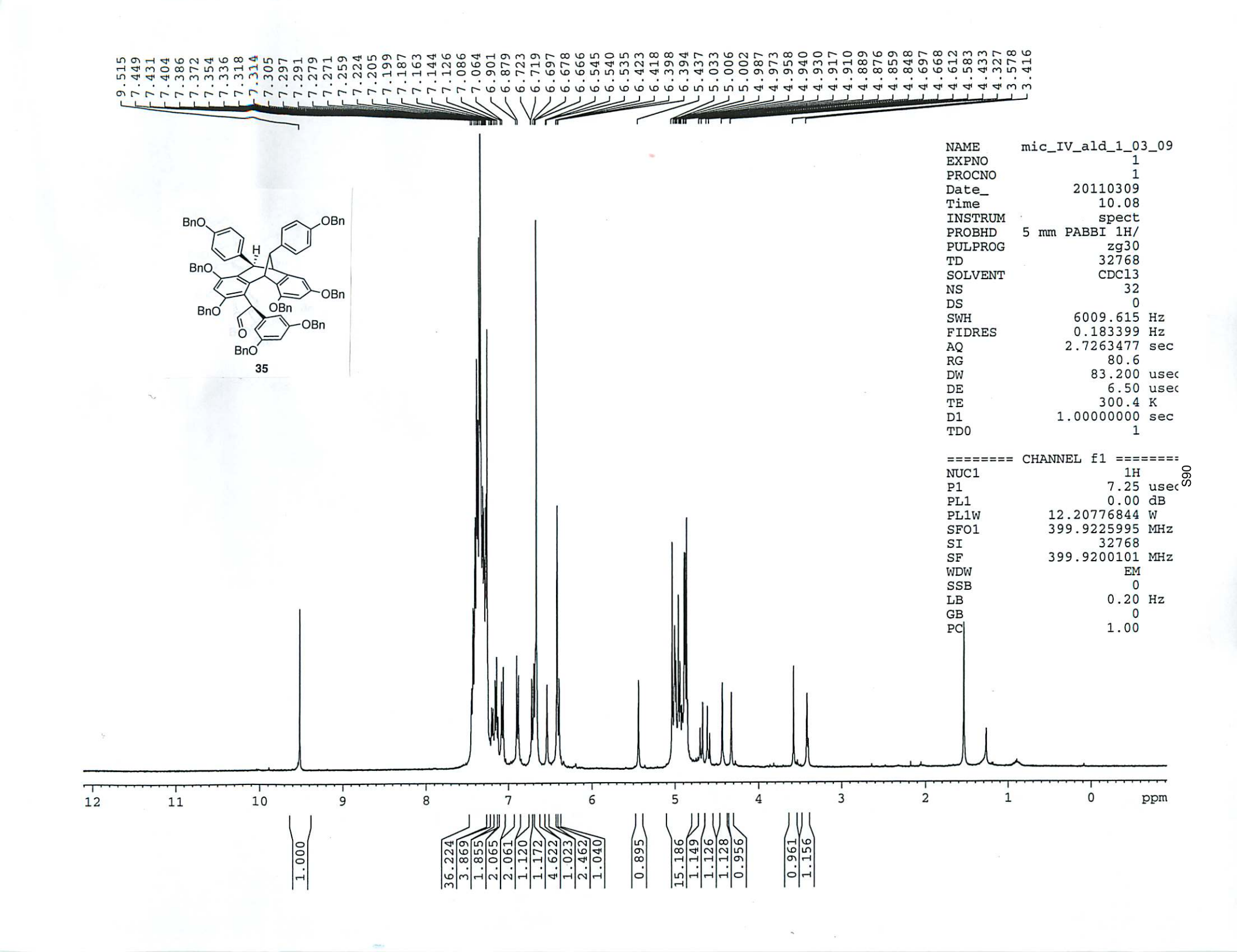
```
Current Data Parameters
NAME      mic_III_Bn_ketone_2_C
EXPNO                         5
PROCNO                        1

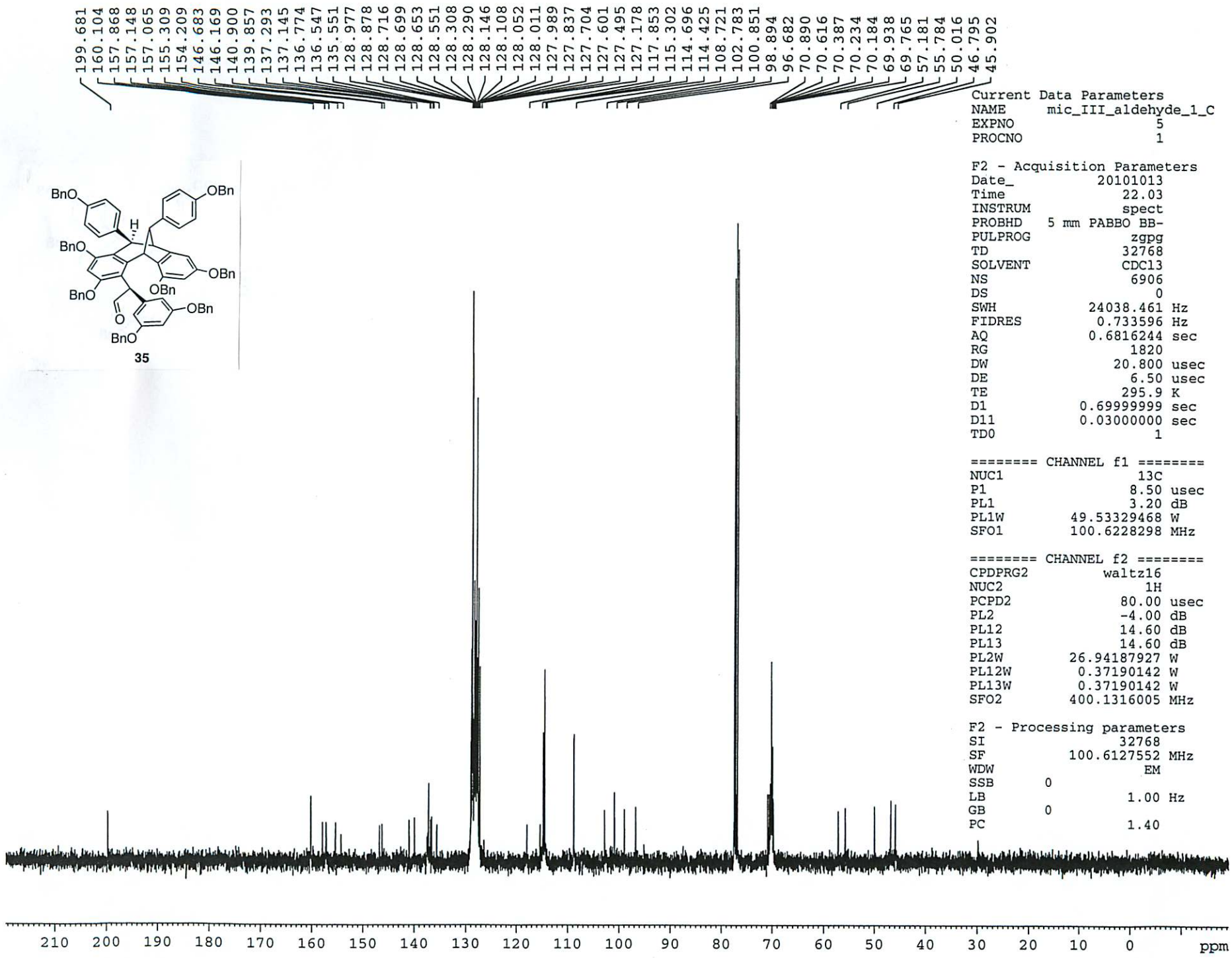
F2 - Acquisition Parameters
Date_              20100922
Time                 13.23
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg
TD                  32768
SOLVENT             CDCl3
NS                   2759
DS                      0
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6816244 sec
RG                   1820
DW                 20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1              0.69999999 sec
D11             0.03000000 sec
TD0                     1

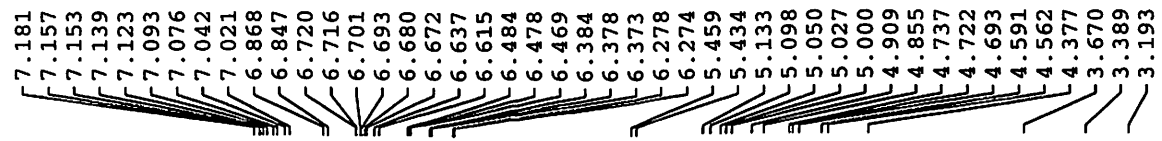
======== CHANNEL f1 ========
NUC1                  13C
P1                  8.50 usec
PL1                 3.20 dB
PL1W          49.53329468 W
SFO1         100.6228298 MHz

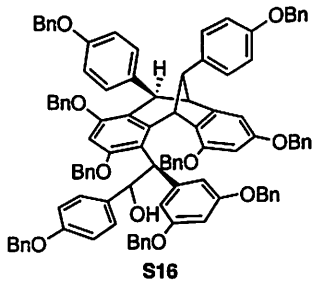
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -4.00 dB
PL12               14.60 dB
PL13               14.60 dB
PL2W          26.94187927 W
PL12W          0.37190142 W
PL13W          0.37190142 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127567 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```


9.515
7.449
7.431
7.404
7.386
7.372
7.354
7.336
7.318
7.314
7.305
7.297
7.291
7.279
7.271
7.259
7.224
7.205
7.199
7.187
7.163
7.144
7.126
7.086
7.064
6.901
6.879
6.723
6.719
6.697
6.678
6.666
6.545
6.540
6.535
6.423
6.418
6.398
6.394
5.437
5.033
5.006
5.002
4.987
4.973
4.958
4.940
4.930
4.917
4.910
4.889
4.876
4.859
4.848
4.697
4.668
4.612
4.583
4.433
4.327
3.578
3.416
BnO
OBn
H
BnO
OBn
BnO
OBn
OBn
O
BnO
35
NAME mic_IV_ald_1_03_09
EXPNO 1
PROCNO 1
Date_ 20110309
Time 10.08
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 80.6
DW 83.200 usec
DE 6.50 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200101 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S90
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
36.224
3.869
1.855
2.065
2.061
1.120
1.172
4.622
1.023
2.462
1.040
0.895
15.186
1.149
1.126
1.128
0.956
0.961
1.156


199.681
160.104
157.868
157.148
157.065
155.309
154.209
146.683
146.169
140.900
139.857
137.293
137.145
136.774
136.547
135.551
128.977
128.878
128.716
128.699
128.653
128.551
128.308
128.290
128.146
128.108
128.052
128.011
127.989
127.837
127.704
127.601
127.495
127.178
117.853
115.302
114.696
114.425
108.721
102.783
100.851
98.894
96.682
70.890
70.616
70.387
70.234
70.184
69.938
69.765
57.181
55.784
50.016
46.795
45.902
BnO
OBn
H
O
35
Current Data Parameters
NAME mic_III_aldehyde_1_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101013
Time 22.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 6906
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127552 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





S16

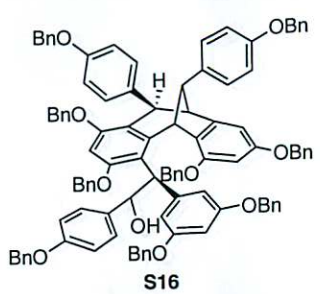
```
Current Data Parameters
NAME      mic_III_grignard_alcohol_2
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100911
Time               11.49
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDC13
NS                    13
DS                     0
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ              2.7263477 sec
RG                   287
DW                83.200 usec
DE                 6.50 usec
TE                298.2 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.50 usec
PL1               -4.00 dB
PL1W          26.94187927 W
SFO1          400.1328009 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300097 MHz
WDW                   EM
SSB       0
LB                 0.20 Hz
GB        0
PC                 1.00
```

159.908
159.501
157.915
157.174
157.095
157.079
147.676
145.732
140.256
137.485
137.361
137.216
137.165
137.088
137.001
136.861
136.010
129.798
128.959
128.850
128.714
128.684
128.629
128.367
128.315
128.273
128.098
127.991
127.812
127.753
127.695
127.645
127.592
127.579
127.470
127.284
126.812
118.346
117.927
114.659
114.521
114.484
108.497
103.693
100.309
97.166
73.913
71.202
70.570
70.208
70.027
69.950
69.889
69.770
55.750
51.996
50.665
47.160
46.616
29.847



S16

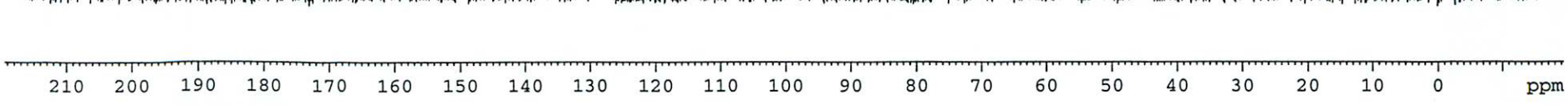
```
Current Data Parameters
NAME      mic_III_grignard_alcohol_2_C
EXPNO                5
PROCNO               1

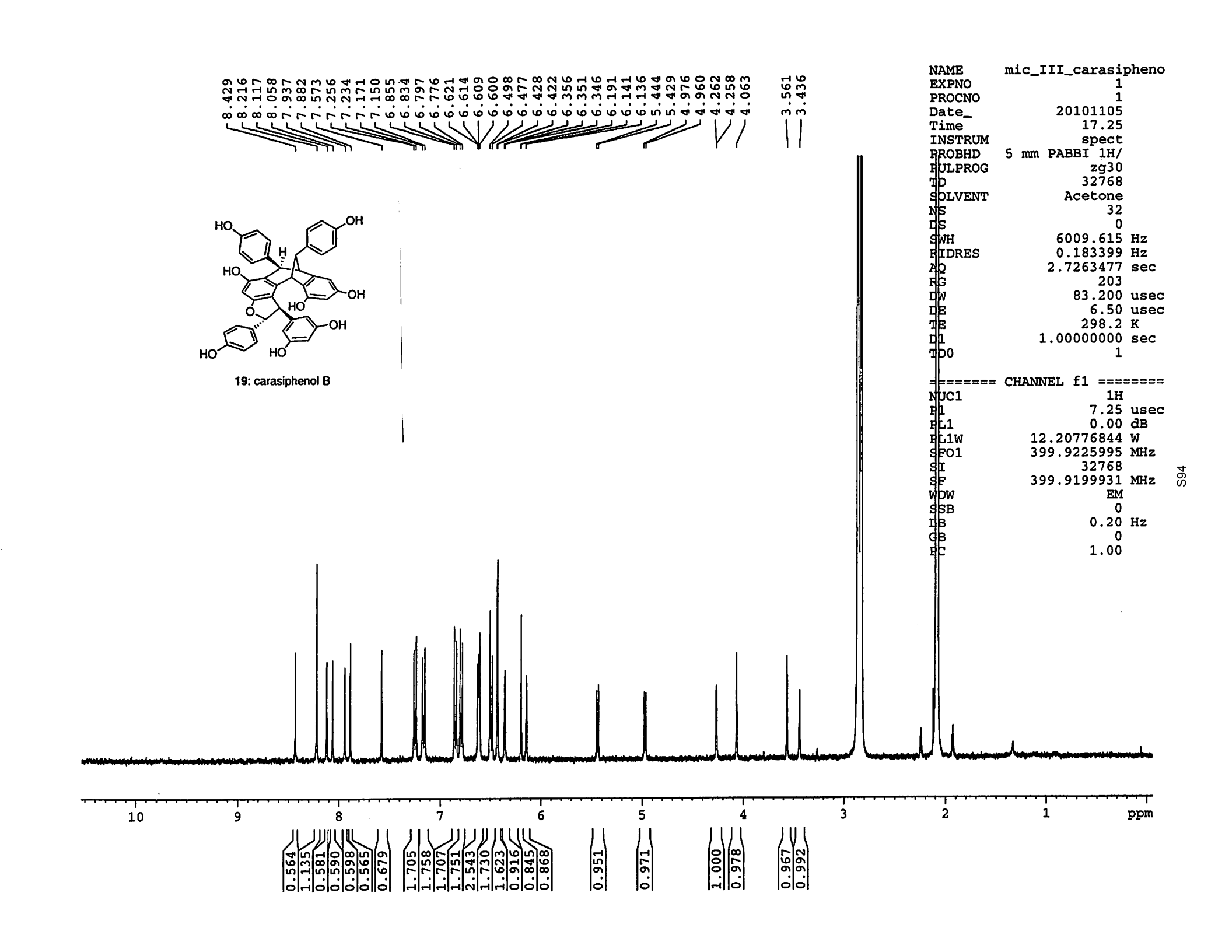
F2 - Acquisition Parameters
Date_          20100911
Time              11.53
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg
TD               32768
SOLVENT          CDCl3
NS                7881
DS                   0
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ            0.6816244 sec
RG                1820
DW              20.800 usec
DE               6.50 usec
TE              298.2 K
D1           0.69999999 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               8.50 usec
PL1              3.20 dB
PL1W       49.53329468 W
SFO1      100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2           80.00 usec
PL2             -4.00 dB
PL12            14.60 dB
PL13            14.60 dB
PL2W       26.94187927 W
PL12W       0.37190142 W
PL13W       0.37190142 W
SFO2      400.1316005 MHz

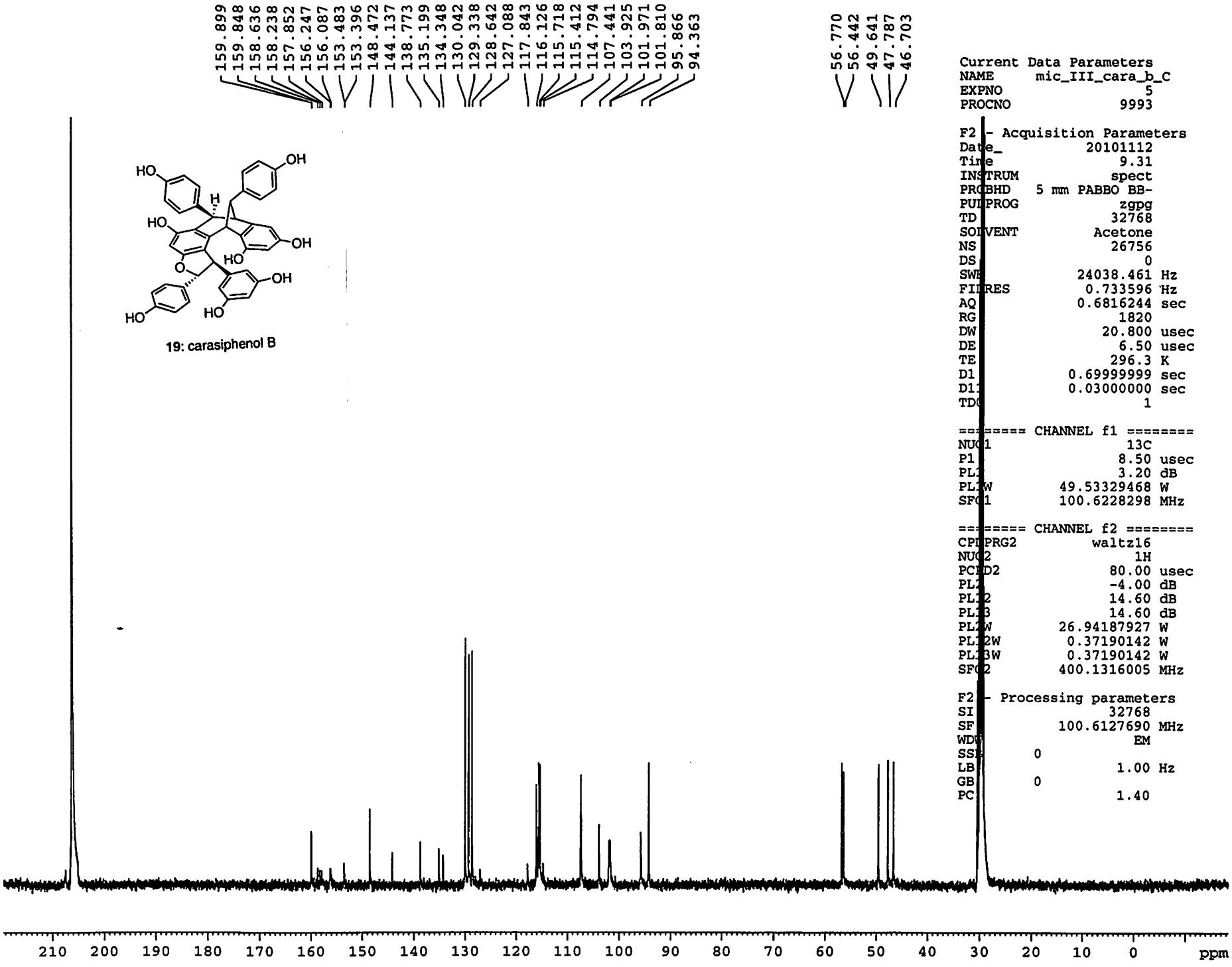
F2 - Processing parameters
SI               32768
SF        100.6127554 MHz
WDW                EM
SSB      0
LB              1.00 Hz
GB       0
PC              1.40
```



HO
OH
H
HO
OH
HO
O
OH
HO
HO

19: carasiphenol B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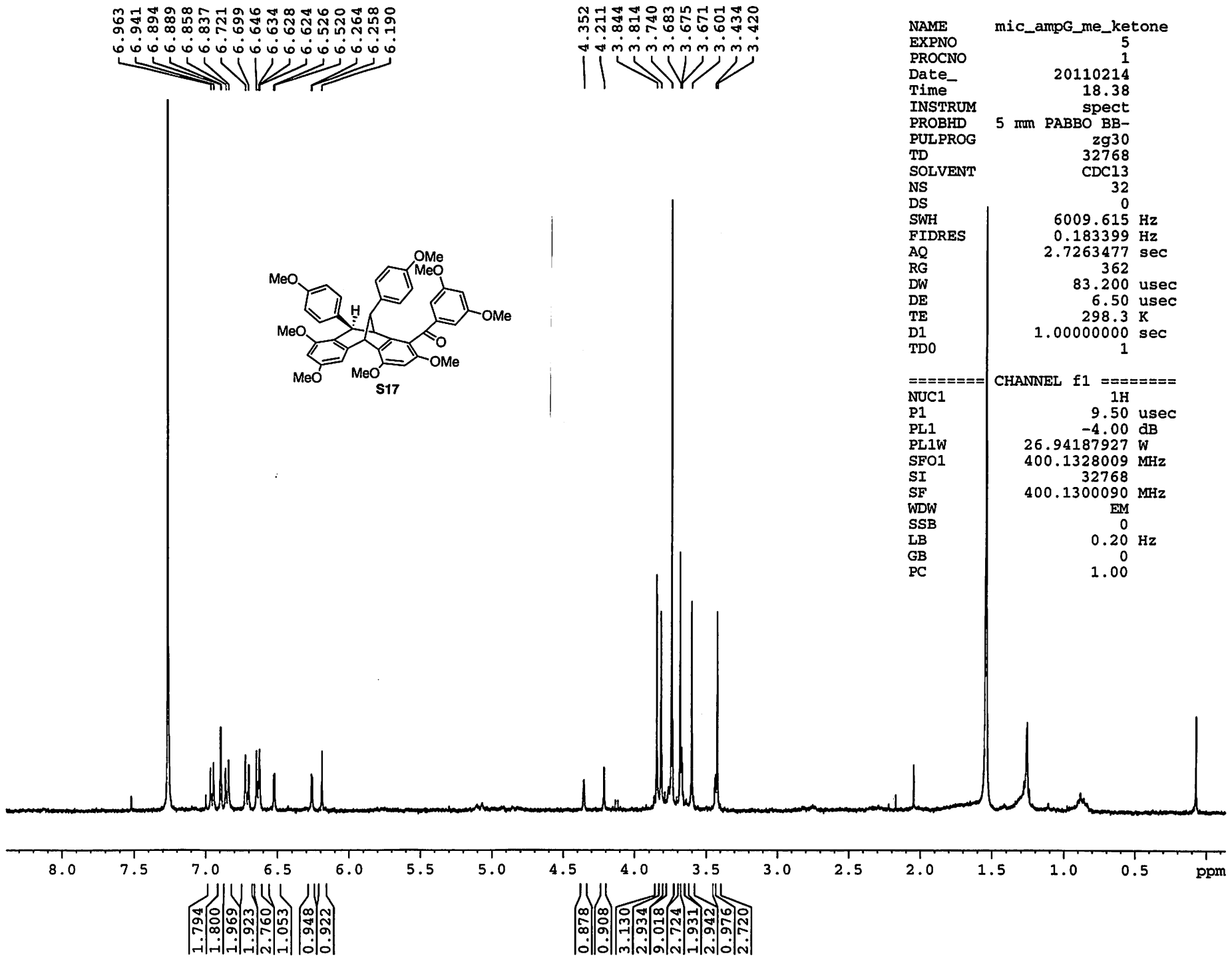
135.199
134.348
130.042
129.338
128.642
127.088
117.843
116.126
115.718
115.412
114.794
107.441
103.925
101.971
101.810
95.866
94.363
56.770
56.442
49.641
47.787
46.703
19: carasiphenol B
Current Data Parameters
NAME mic_III_cara_b_C
EXPNO 5
PROCNO 9993
F2 - Acquisition Parameters
Date_ 20101112
Time 9.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT Acetone
NS 26756
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 296.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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6.699
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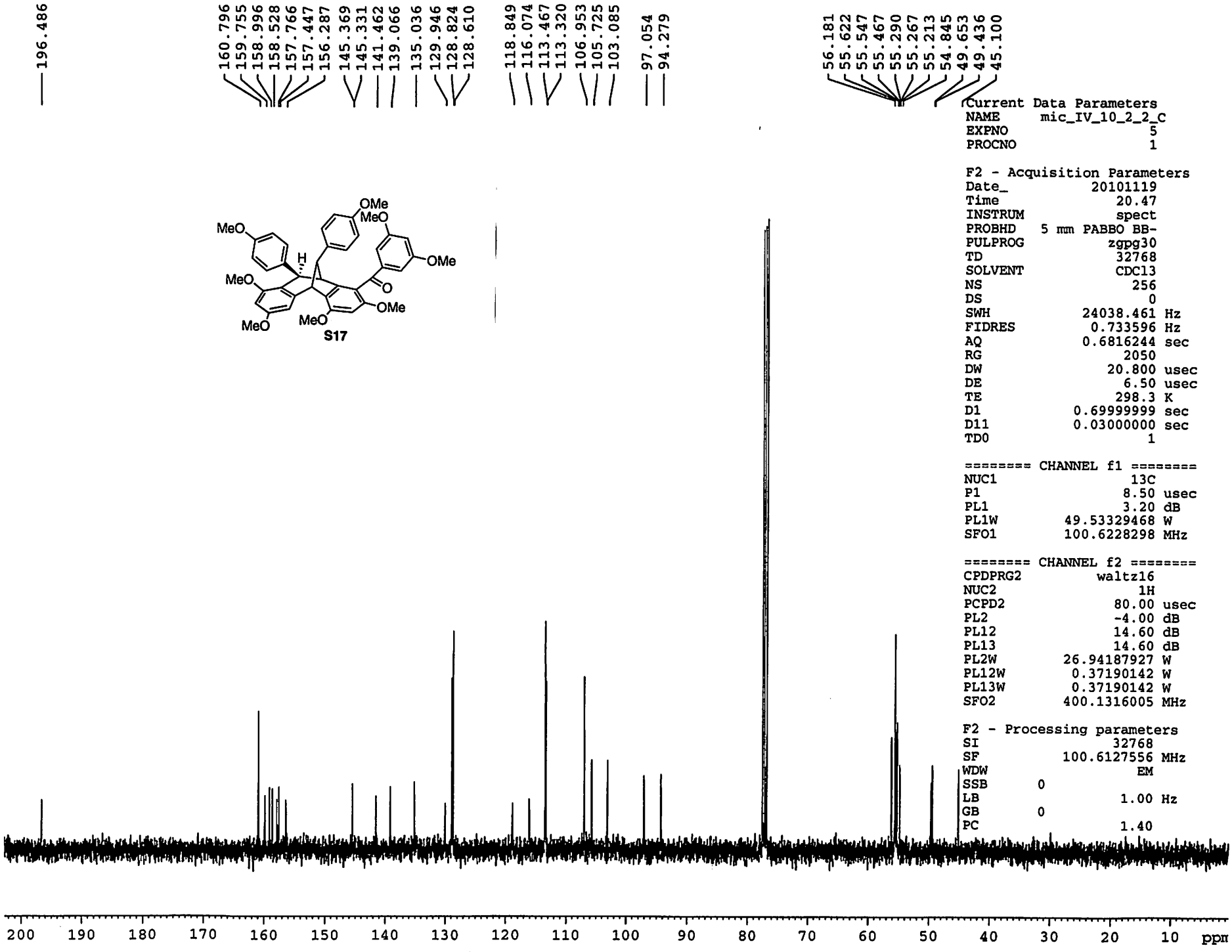
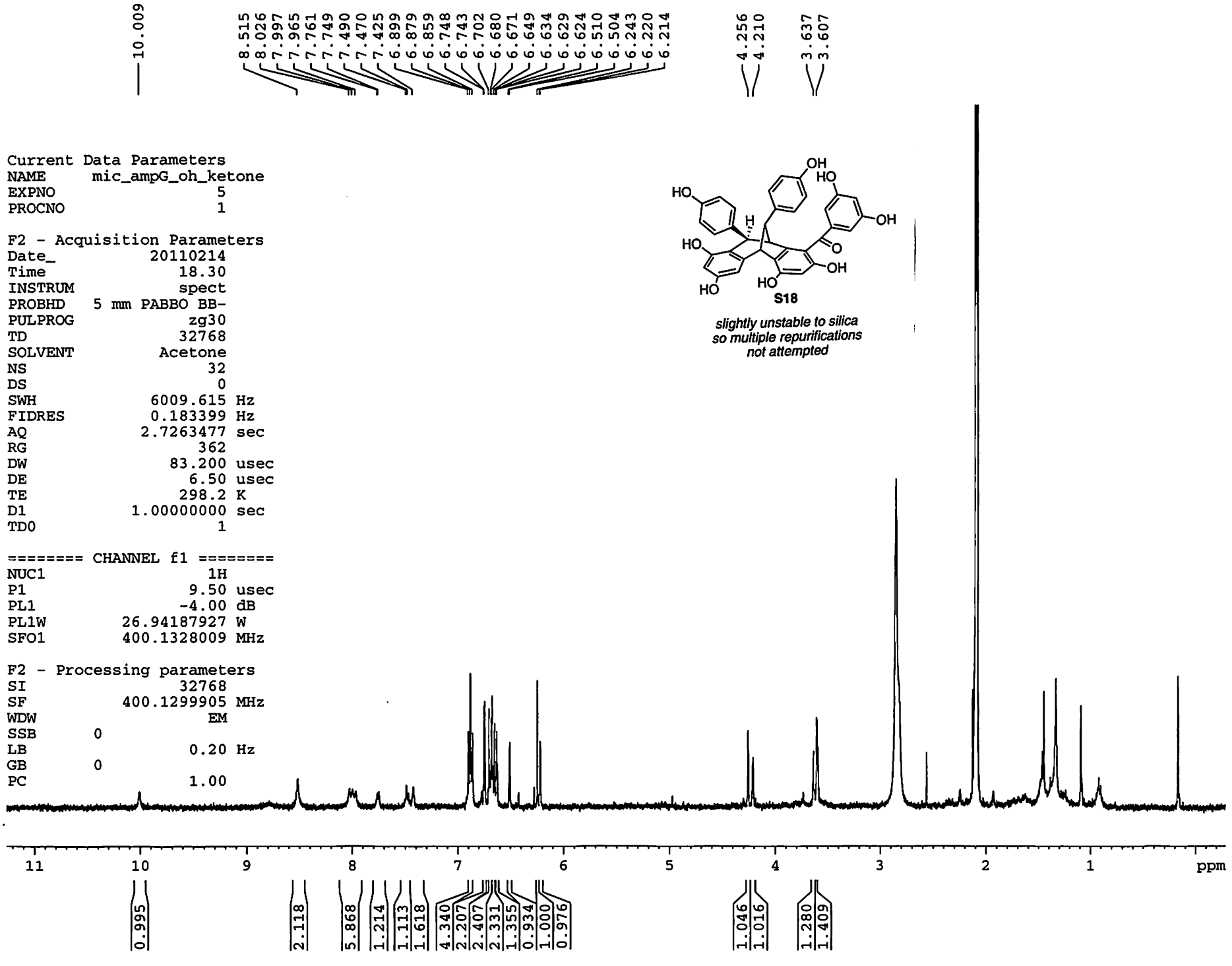
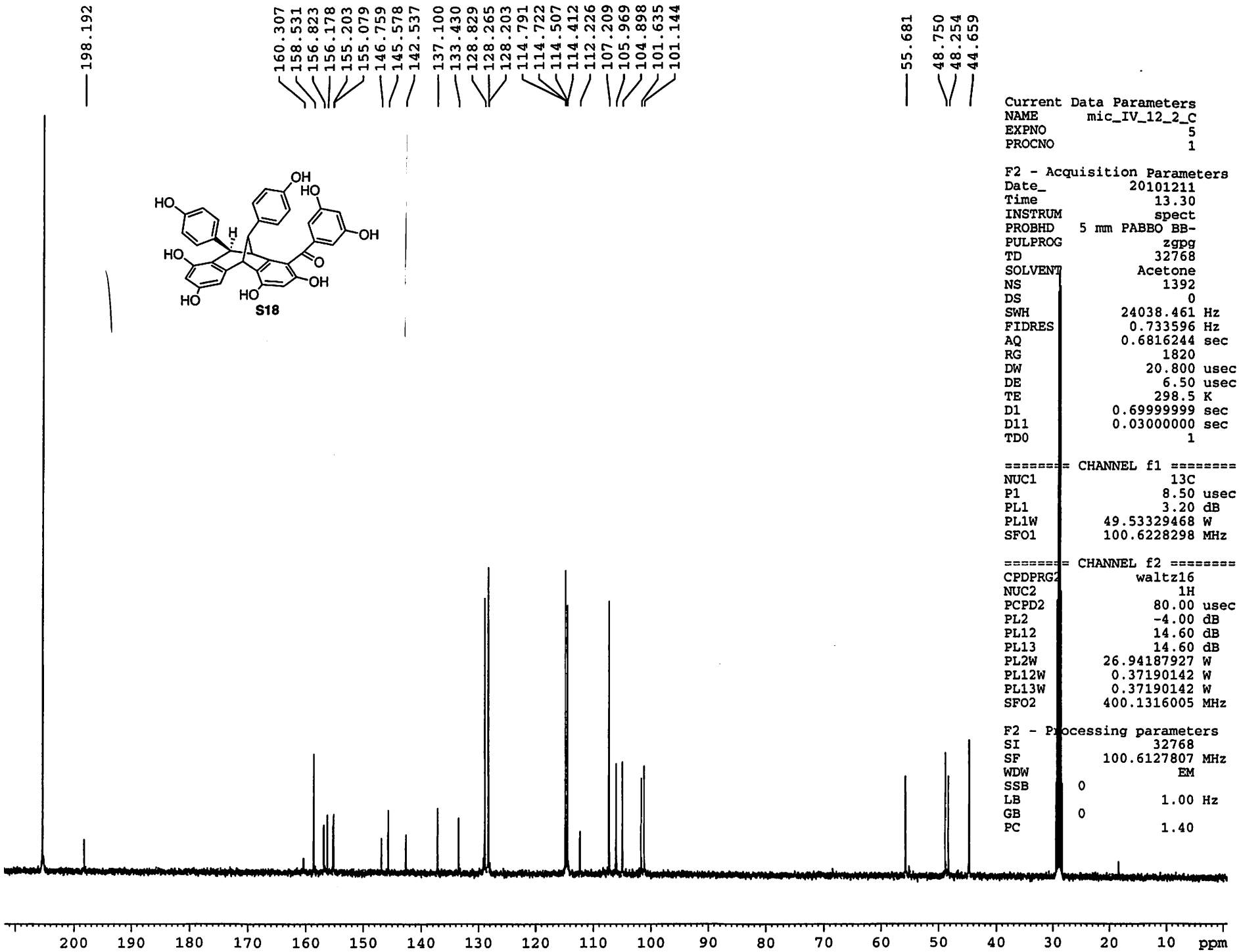
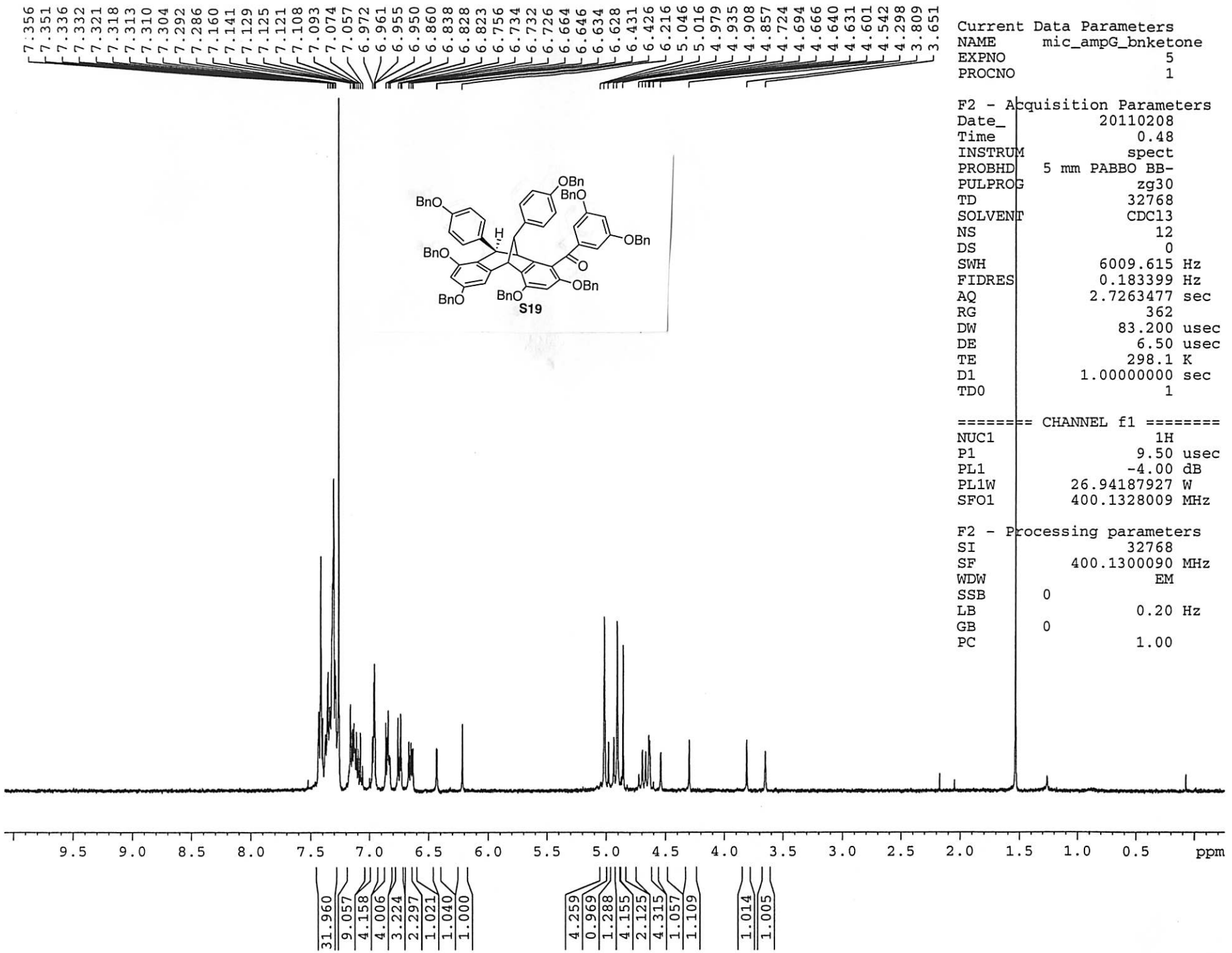
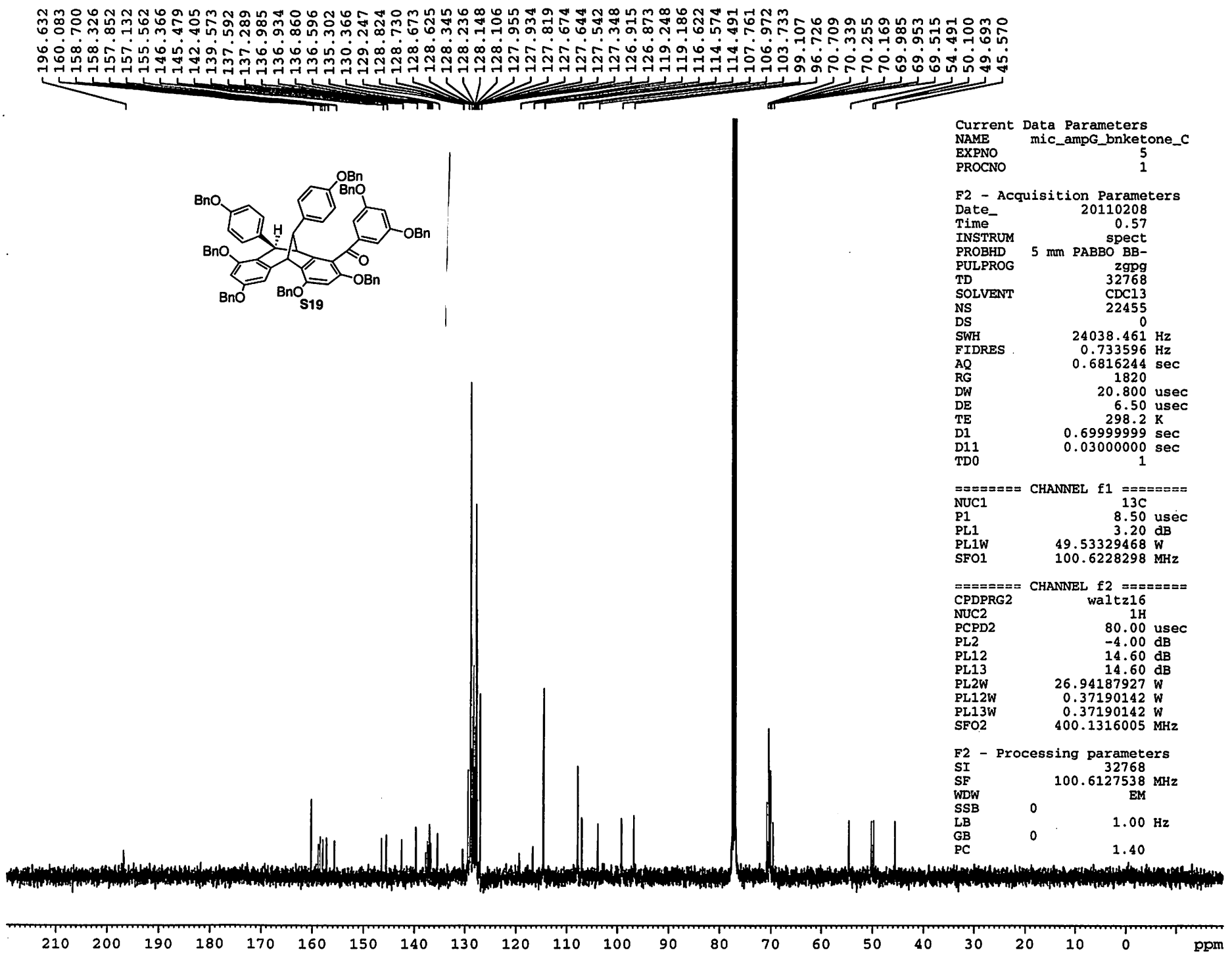
6.634
6.628
6.624
6.526
6.520
6.264
6.258
6.190
4.352
4.211
3.844
3.814
3.740
3.683
3.675
3.671
3.601
3.434
3.420
OMe
MeO
MeO
OMe
MeO
H
O
OMe
MeO
MeO
S17
NAME mic_ampG_me_ketone
EXPNO 5
PROCNO 1
Date_ 20110214
Time 18.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.794
1.800
1.969
1.923
2.760
1.053
0.948
0.922
0.878
0.908
3.130
2.934
9.018
2.724
1.931
2.942
0.976
2.720

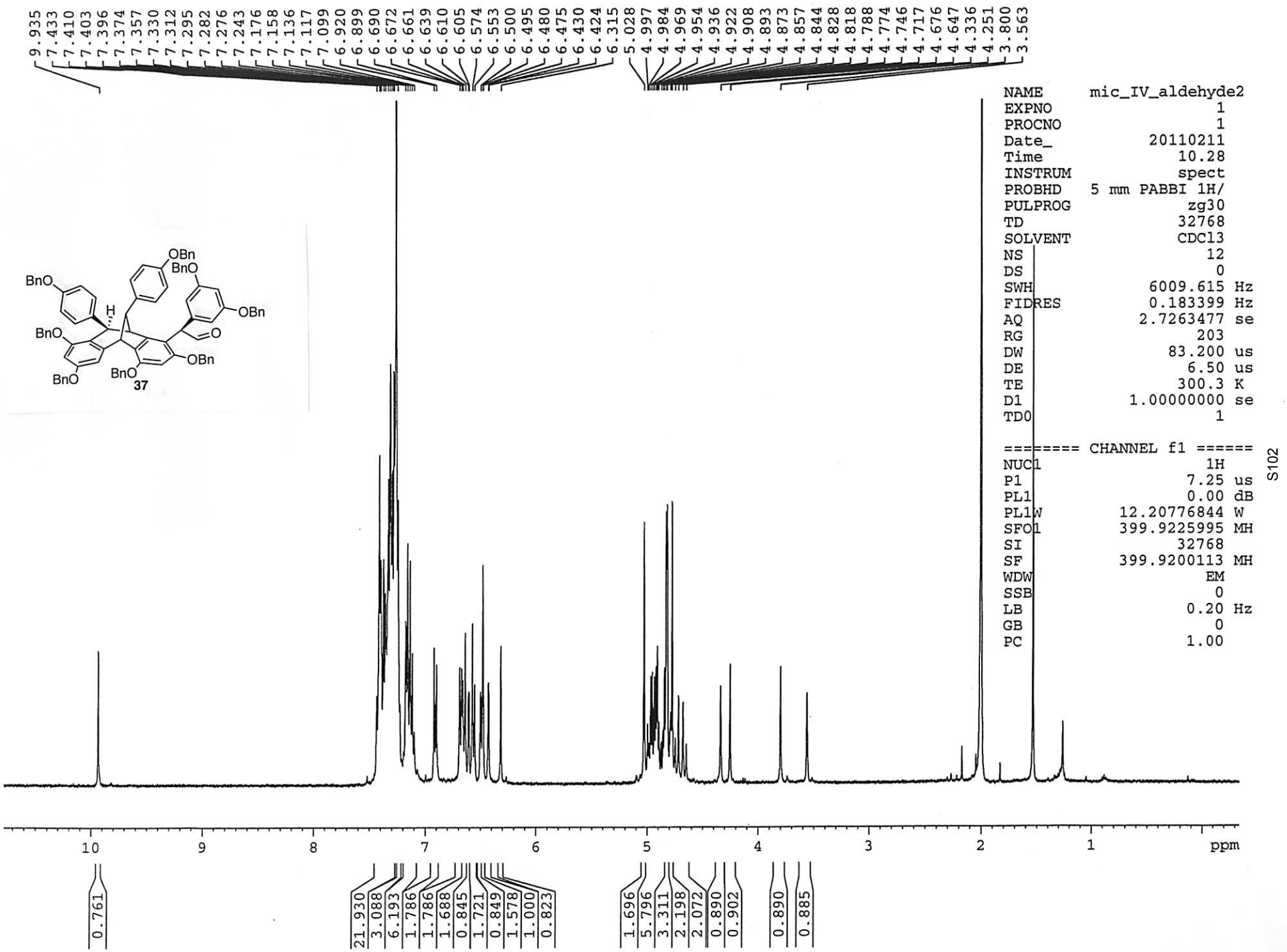

196.486
160.796
159.755
158.996
158.528
157.766
157.447
156.287
145.369
145.331
141.462
139.066
135.036
129.946
128.824
128.610
118.849
116.074
113.467
113.320
106.953
105.725
103.085
97.054
94.279
56.181
55.622
55.547
55.467
55.290
55.267
55.213
54.845
49.653
49.436
45.100
OMe
MeO
MeO
OMe
H
MeO
O
OMe
MeO
MeO
S17
Current Data Parameters
NAME mic_IV_10_2_2_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101119
Time 20.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 298.3 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127556 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

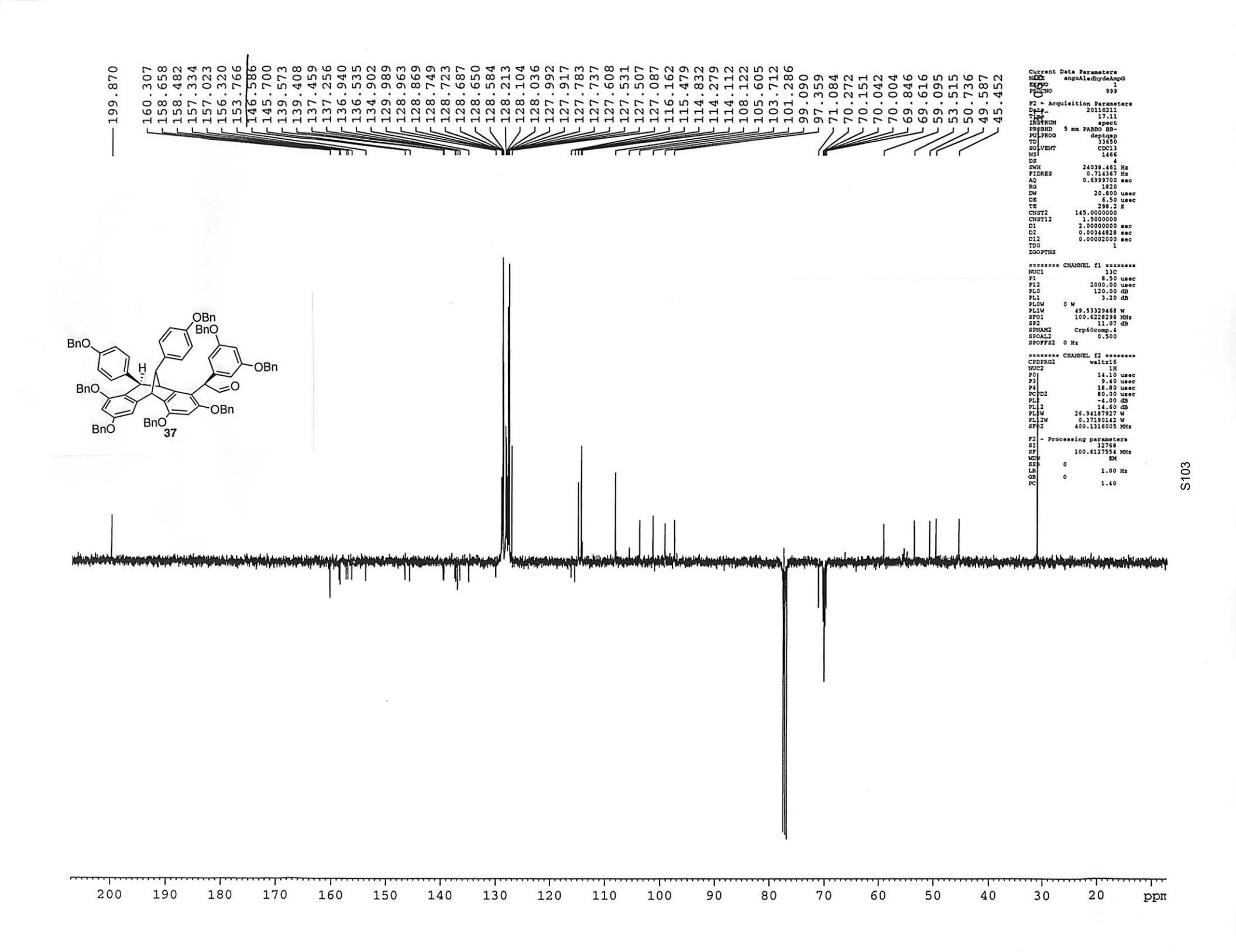

10.009
8.515
8.026
7.997
7.965
7.761
7.749
7.490
7.470
7.425
6.899
6.879
6.859
6.748
6.743
6.702
6.680
6.671
6.649
6.634
6.629
6.624
6.510
6.504
6.243
6.220
6.214
4.256
4.210
3.637
3.607
Current Data Parameters
NAME mic_ampG_oh_ketone
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110214
Time 18.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1299905 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S18
slightly unstable to silica
so multiple repurifications
not attempted
11
10
9
8
7
6
5
4
3
2
1
ppm
0.995
2.118
5.868
1.214
1.113
1.618
4.340
2.207
2.407
2.331
1.355
0.934
1.000
0.976
1.046
1.016
1.280
1.409

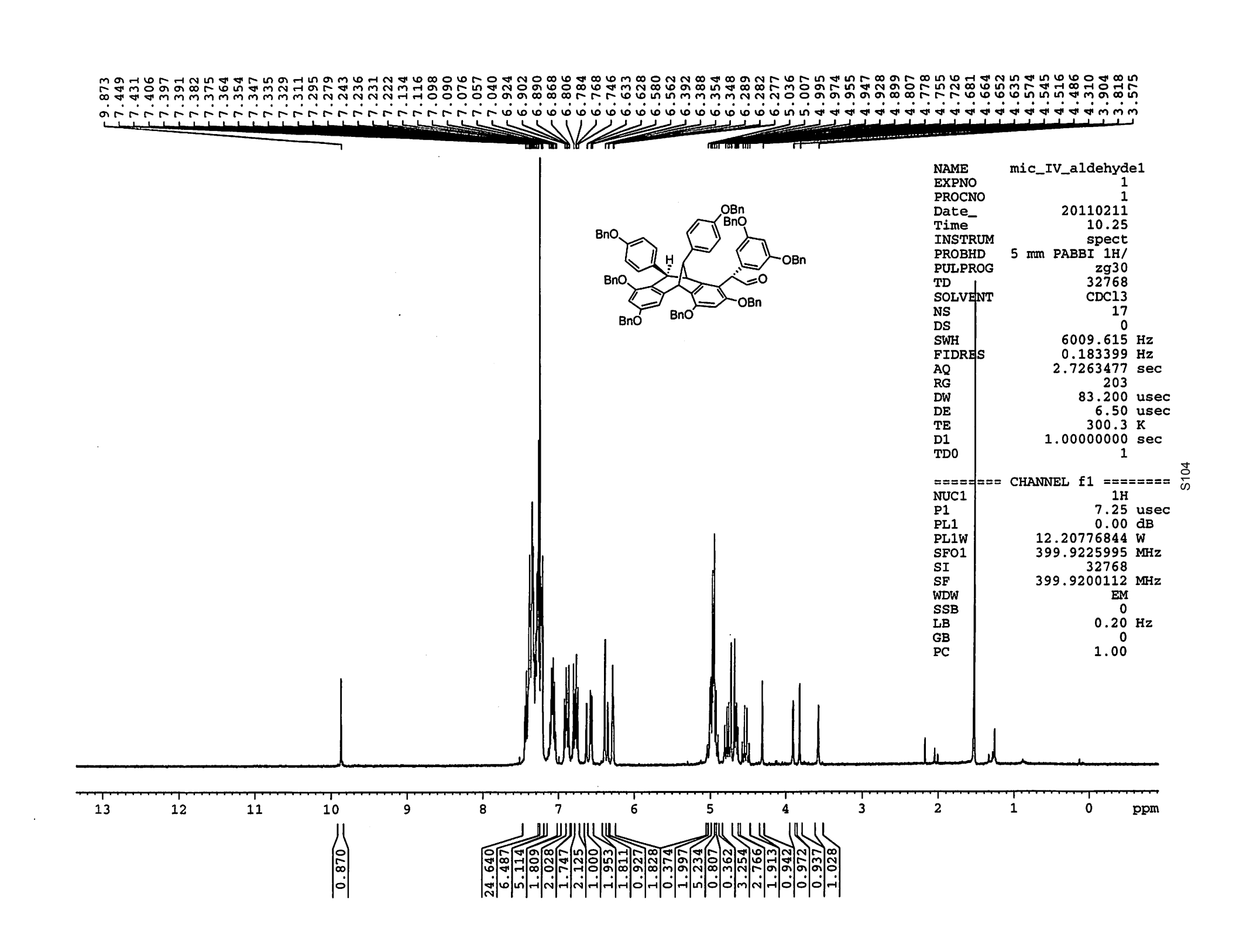

198.192
160.307
158.531
156.823
156.178
155.203
155.079
146.759
145.578
142.537
137.100
133.430
128.829
128.265
128.203
114.791
114.722
114.507
114.412
112.226
107.209
105.969
104.898
101.635
101.144
55.681
48.750
48.254
44.659
S18
Current Data Parameters
NAME mic_IV_12_2_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101211
Time 13.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT Acetone
NS 1392
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.5 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127807 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
S99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

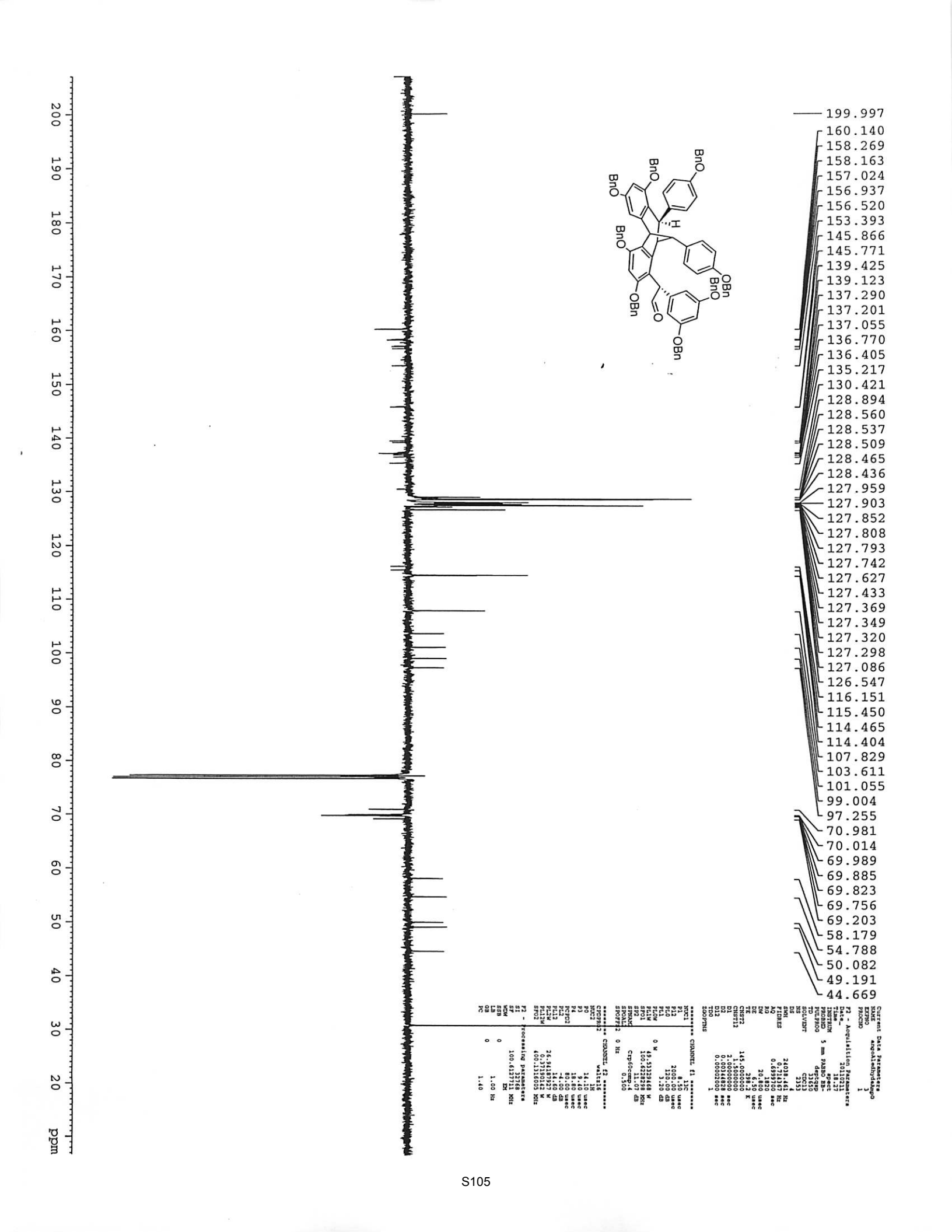

7.356
7.351
7.336
7.332
7.321
7.318
7.313
7.310
7.304
7.292
7.286
7.160
7.141
7.129
7.125
7.121
7.108
7.093
7.074
7.057
6.972
6.961
6.955
6.950
6.860
6.838
6.828
6.823
6.756
6.734
6.732
6.726
6.664
6.646
6.634
6.628
6.431
6.426
6.216
5.046
5.016
4.979
4.935
4.908
4.857
4.724
4.694
4.666
4.640
4.631
4.601
4.542
4.298
3.809
3.651
BnO
OBn
BnO
OBn
BnO
O
OBn
BnO
BnO
H
S19
Current Data Parameters
NAME mic_ampG_bnketone
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110208
Time 0.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 362
DW 83.200 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -4.00 dB
PL1W 26.94187927 W
SFO1 400.1328009 MHz
F2 - Processing parameters
SI 32768
SF 400.1300090 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
31.960
9.057
4.158
4.006
3.224
2.297
1.021
1.040
1.000
4.259
0.969
1.288
4.155
2.125
4.315
1.057
1.109
1.014
1.005

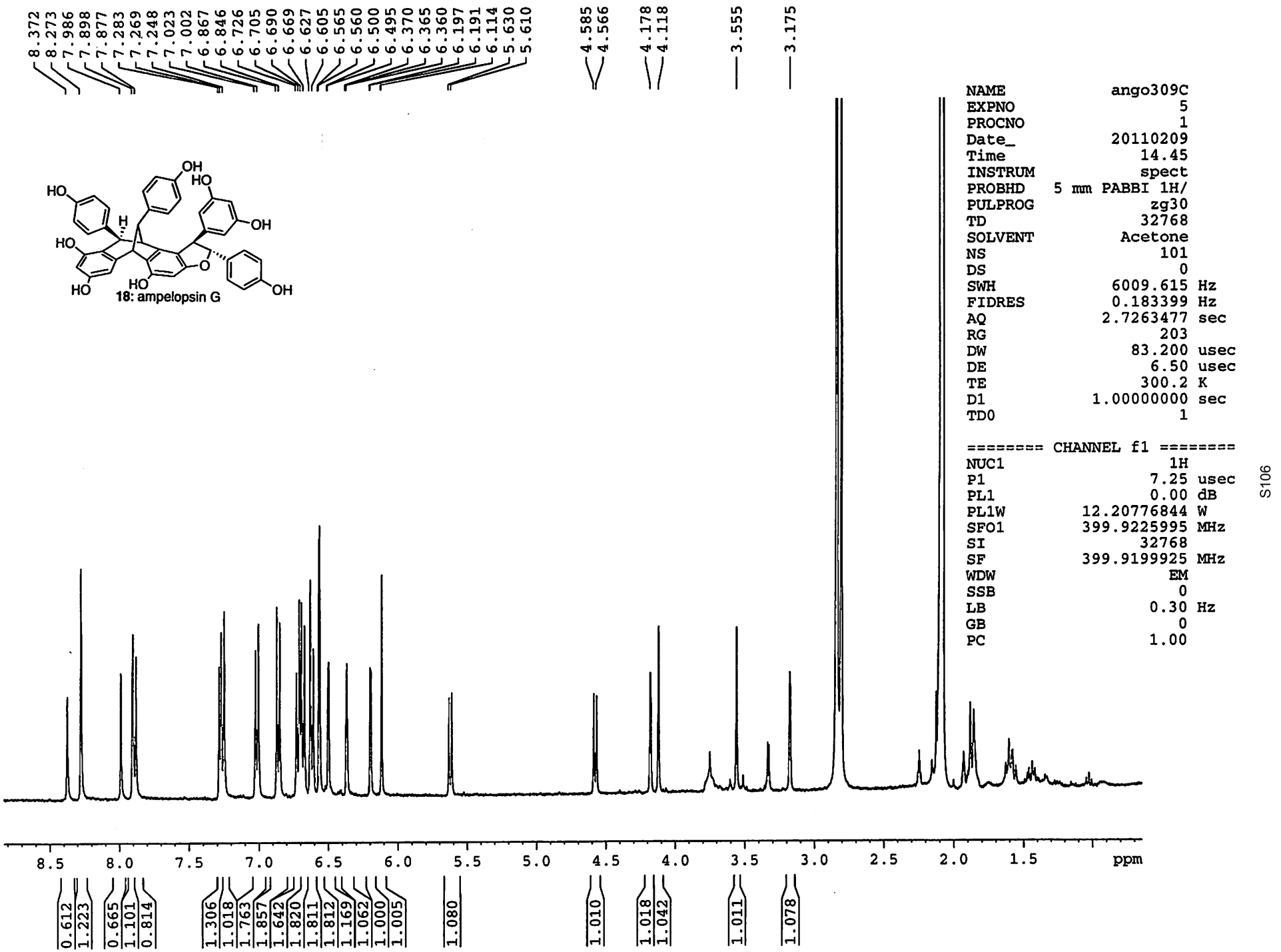

196.632
160.083
158.700
158.326
157.852
157.132
155.562
146.366
145.479
142.405
139.573
137.592
137.289
136.985
136.934
136.860
136.596
135.302
130.366
129.247
128.824
128.730
128.673
128.625
128.345
128.236
128.148
128.106
127.955
127.934
127.819
127.674
127.644
127.542
127.348
126.915
126.873
119.248
119.186
116.622
114.574
114.491
107.761
106.972
103.733
99.107
96.726
70.709
70.339
70.255
70.169
69.985
69.953
69.515
54.491
50.100
49.693
45.570
OBn
BnO
BnO
OBn
H
BnO
O
OBn
BnO
BnO
S19
Current Data Parameters
NAME mic_ampG_bnketone_C
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110208
Time 0.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 22455
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6816244 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
D1 0.69999999 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 3.20 dB
PL1W 49.53329468 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL13 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
PL13W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127538 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

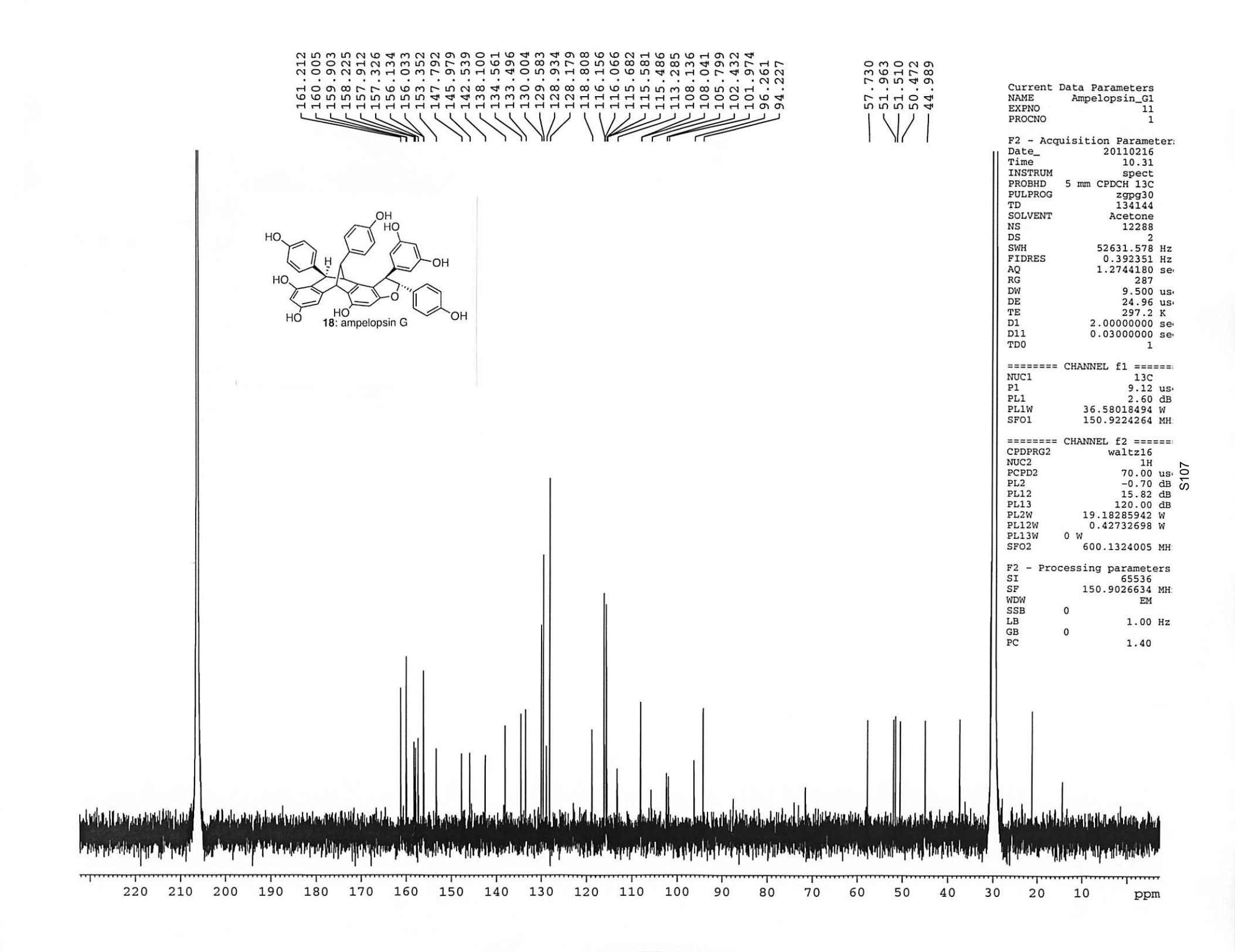

9.935
7.433
7.410
7.403
7.396
7.374
7.357
7.330
7.312
7.295
7.282
7.276
7.243
7.176
7.158
7.136
7.117
7.099
6.920
6.899
6.690
6.672
6.661
6.639
6.610
6.605
6.574
6.553
6.500
6.495
6.480
6.475
6.430
6.424
6.315
5.028
4.997
4.984
4.969
4.954
4.936
4.922
4.908
4.893
4.873
4.857
4.844
4.828
4.818
4.788
4.774
4.746
4.717
4.676
4.647
4.336
4.251
3.800
3.563
OBn
BnO
BnO
OBn
H
O
BnO
OBn
BnO
BnO
37
NAME mic_IV_aldehyde2
EXPNO 1
PROCNO 1
Date_ 20110211
Time 10.28
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 se
RG 203
DW 83.200 us
DE 6.50 us
TE 300.3 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 7.25 us
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MH
SI 32768
SF 399.9200113 MH
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S102
10
9
8
7
6
5
4
3
2
1
ppm
0.761
21.930
3.088
6.193
1.786
1.786
1.688
0.845
1.721
0.849
1.578
1.000
0.823
1.696
5.796
3.311
2.198
2.072
0.890
0.902
0.890
0.885

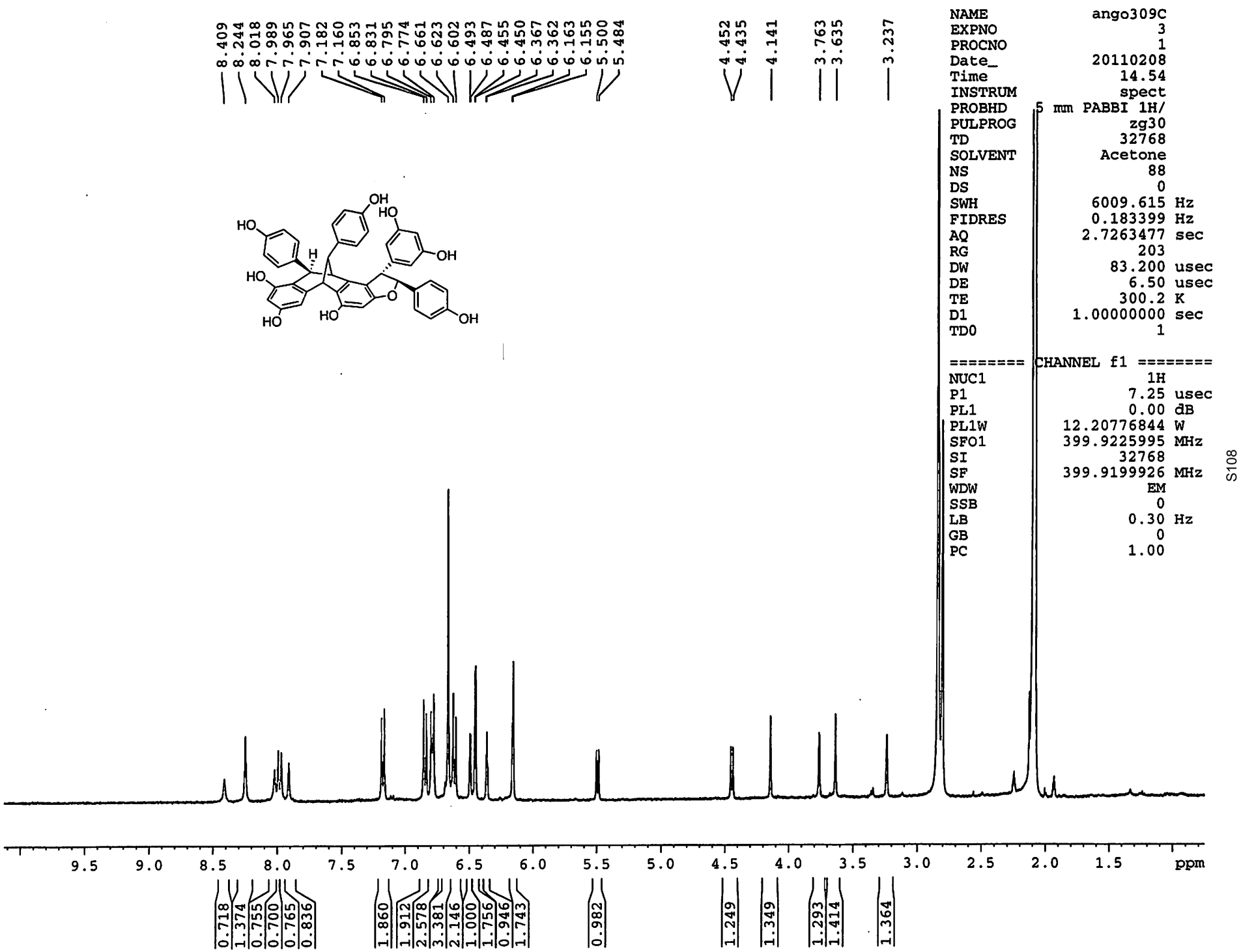

199.870
160.307
158.658
158.482
157.334
157.023
156.320
153.766
146.586
145.700
139.573
139.408
137.459
137.256
136.940
136.535
134.902
129.989
128.963
128.869
128.749
128.723
128.687
128.650
128.584
128.213
128.104
128.036
127.992
127.917
127.783
127.737
127.608
127.531
127.507
127.087
116.162
115.479
114.832
114.279
114.112
108.122
105.605
103.712
101.286
99.090
97.359
71.084
70.272
70.151
70.042
70.004
69.846
69.616
59.095
53.515
50.736
49.587
45.452
OBn
BnO
BnO
OBn
H
O
BnO
OBn
BnO
BnO
37
Current Data Parameters
angoAledhydeAmpG
1
999
F2 - Acquisition Parameters
20110211
17.11
spect
5 mm PABBO BB-
deptqsp
33650
CDCl3
1466
4
24038.461 Hz
0.714367 Hz
0.6999700 sec
1820
20.800 usec
6.50 usec
298.2 K
CNST2 145.0000000
CNST12 1.5000000
2.00000000 sec
0.00344828 sec
0.00002000 sec
1
ZGOPTNS
CHANNEL f1
13C
8.50 usec
2000.00 usec
120.00 dB
3.20 dB
0 W
49.53329468 W
100.6228298 MHz
11.07 dB
Crp60comp.4
0.500
0 Hz
CHANNEL f2
waltz16
1H
14.10 usec
9.40 usec
18.80 usec
80.00 usec
-4.00 dB
14.60 dB
26.94187927 W
0.37190142 W
400.1316005 MHz
F2 - Processing parameters
32768
100.6127554 MHz
EM
0
1.00 Hz
0
1.40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

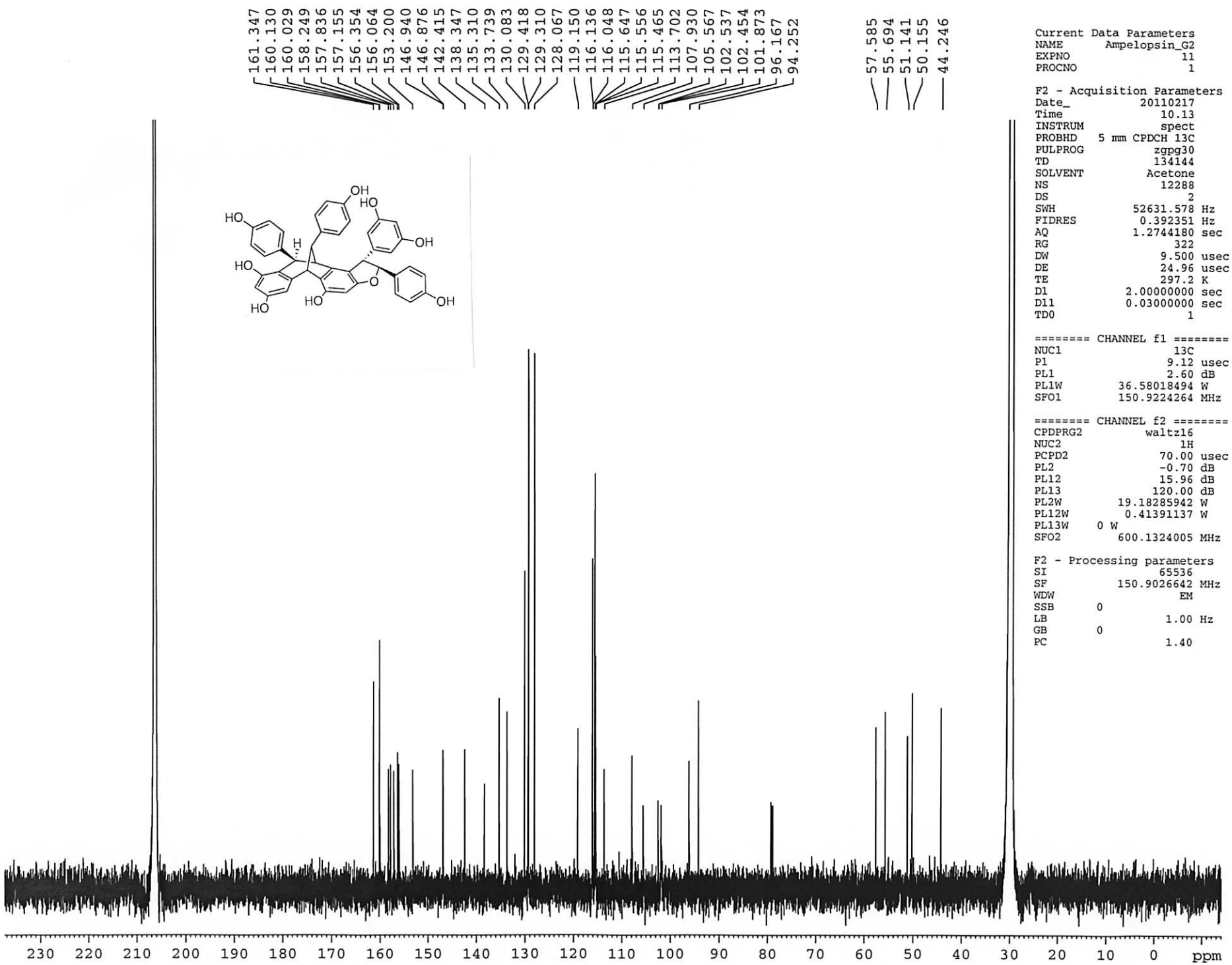

9.873 7.449 7.431 7.406 7.397 7.391 7.382 7.375 7.364 7.354 7.347 7.335 7.329 7.311 7.295 7.279 7.243 7.236 7.231 7.222 7.134 7.116 7.098 7.090 7.076 7.057 7.040 6.924 6.902 6.890 6.868 6.806 6.784 6.768 6.746 6.633 6.628 6.580 6.562 6.392 6.388 6.354 6.348 6.289 6.282 6.277 5.036 5.007 4.995 4.974 4.955 4.947 4.928 4.899 4.807 4.778 4.755 4.726 4.681 4.664 4.652 4.635 4.574 4.545 4.516 4.486 4.310 3.904 3.818 3.575
OBn
BnO
BnO
OBn
H
O
BnO
OBn
BnO
BnO
NAME mic_IV_aldehyde1
EXPNO 1
PROCNO 1
Date_ 20110211
Time 10.25
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 17
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 300.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200112 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
S104
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.870
24.640 6.487 5.114 1.809 2.028 1.747 2.125 1.000 1.953 1.811 0.927 1.828 0.374 1.997 5.234 0.807 0.362 3.254 2.766 1.913 0.942 0.972 0.937 1.028

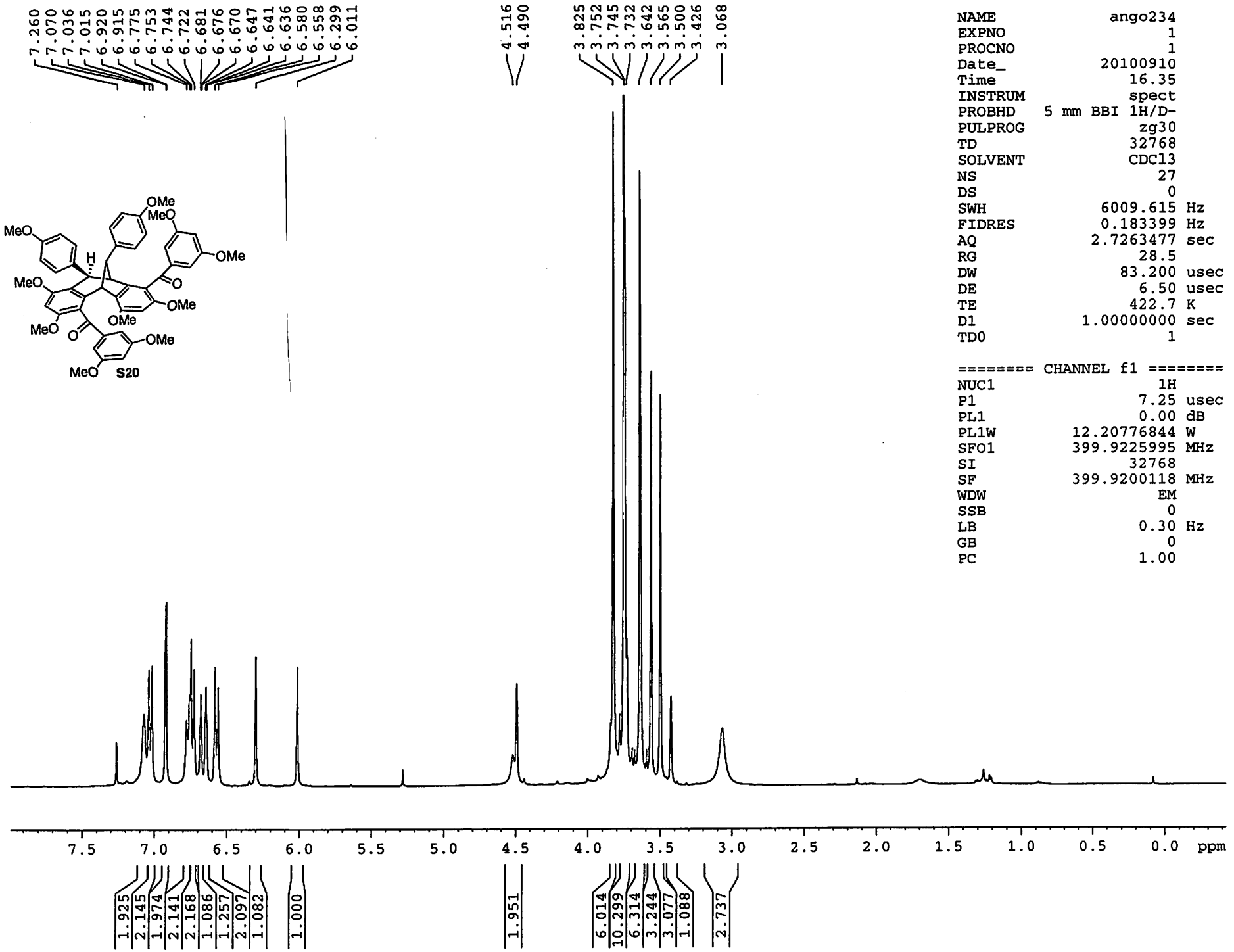

BnO
BnO
BnO
BnO
OBn
OBn
OBn
OBn
H
O
199.997
160.140
158.269
158.163
157.024
156.937
156.520
153.393
145.866
145.771
139.425
139.123
137.290
137.201
137.055
136.770
136.405
135.217
130.421
128.894
128.560
128.537
128.509
128.465
128.436
127.959
127.903
127.852
127.808
127.793
127.742
127.627
127.433
127.369
127.349
127.320
127.298
127.086
126.547
116.151
115.450
114.465
114.404
107.829
103.611
101.055
99.004
97.255
70.981
70.014
69.989
69.885
69.823
69.756
69.203
58.179
54.788
50.082
49.191
44.669
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

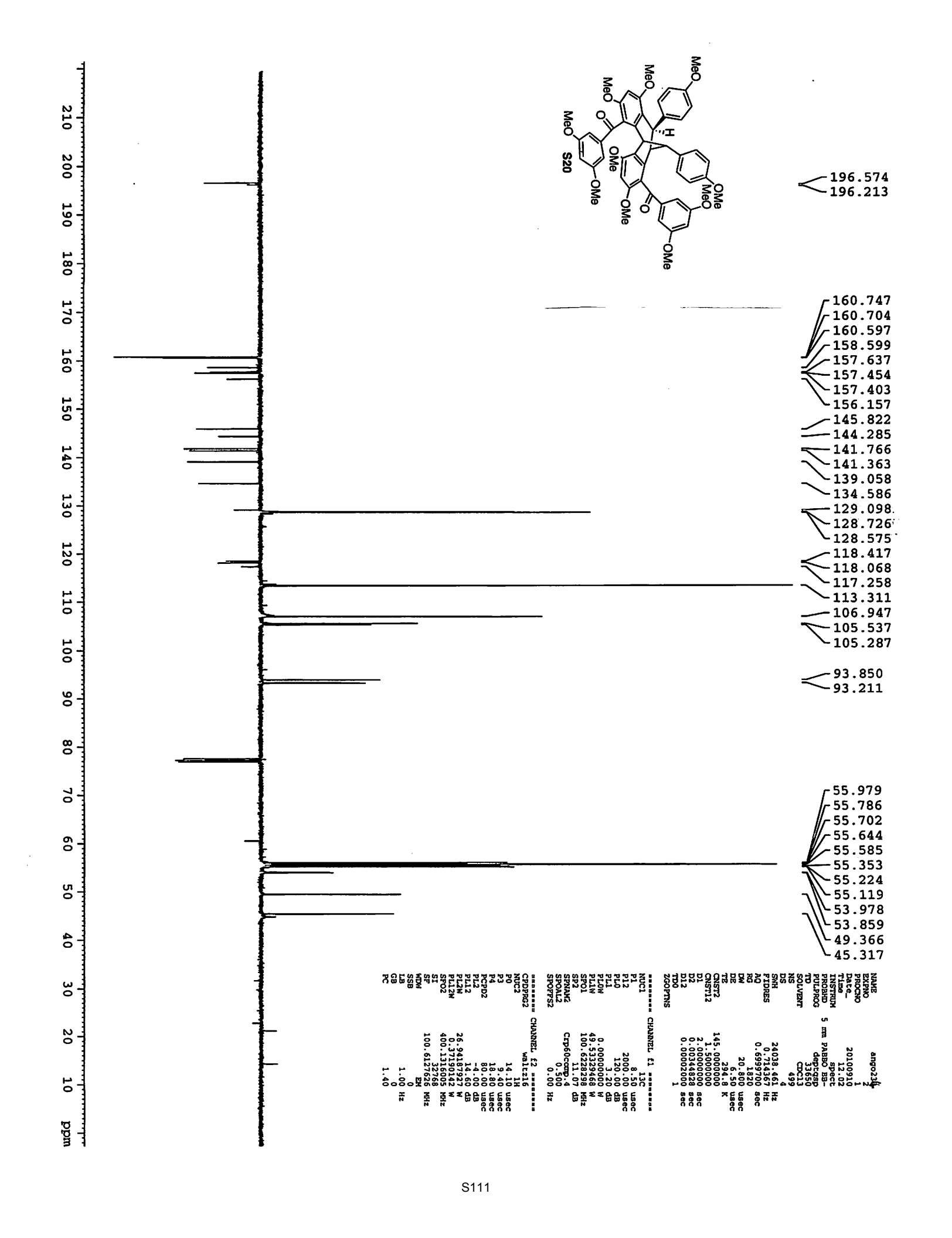

8.372
8.273
7.986
7.898
7.877
7.283
7.269
7.248
7.023
7.002
6.867
6.846
6.726
6.705
6.690
6.669
6.627
6.605
6.565
6.560
6.500
6.495
6.370
6.365
6.360
6.197
6.191
6.114
5.630
5.610
4.585
4.566
4.178
4.118
3.555
3.175
18: ampelopsin G
NAME ango309C
EXPNO 5
PROCNO 1
Date_ 20110209
Time 14.45
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 101
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9199925 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
0.612 1.223 0.665 1.101 0.814 1.306 1.018 1.763 1.857 1.642 1.820 1.811 1.812 1.169 1.062 1.000 1.005 1.080 1.010 1.018 1.042 1.011 1.078


161.212
160.005
159.903
158.225
157.912
157.326
156.134
156.033
153.352
147.792
145.979
142.539
138.100
134.561
133.496
130.004
129.583
128.934
128.179
118.808
116.156
116.066
115.682
115.581
115.486
113.285
108.136
108.041
105.799
102.432
101.974
96.261
94.227
57.730
51.963
51.510
50.472
44.989
18: ampelopsin G
Current Data Parameters
NAME Ampelopsin_G1
EXPNO 11
PROCNO 1
F2 - Acquisition Parameter
Date_ 20110216
Time 10.31
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 134144
SOLVENT Acetone
NS 12288
DS 2
SWH 52631.578 Hz
FIDRES 0.392351 Hz
AQ 1.2744180 se
RG 287
DW 9.500 us
DE 24.96 us
TE 297.2 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 9.12 us
PL1 2.60 dB
PL1W 36.58018494 W
SFO1 150.9224264 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 us
PL2 -0.70 dB
PL12 15.82 dB
PL13 120.00 dB
PL2W 19.18285942 W
PL12W 0.42732698 W
PL13W 0 W
SFO2 600.1324005 MH
F2 - Processing parameters
SI 65536
SF 150.9026634 MH
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.409
8.244
8.018
7.989
7.965
7.907
7.182
7.160
6.853
6.831
6.795
6.774
6.661
6.623
6.602
6.493
6.487
6.455
6.450
6.367
6.362
6.163
6.155
5.500
5.484
4.452
4.435
4.141
3.763
3.635
3.237
NAME ango309C
EXPNO 3
PROCNO 1
Date_ 20110208
Time 14.54
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 88
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9199926 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
HO
HO
HO
H
HO
HO
O
OH
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.718
1.374
0.755
0.700
0.765
0.836
1.860
1.912
2.578
3.381
2.146
1.000
1.756
0.946
1.743
0.982
1.249
1.349
1.293
1.414
1.364


161.347
160.130
160.029
158.249
157.836
157.155
156.354
156.064
153.200
146.940
146.876
142.415
138.347
135.310
133.739
130.083
129.418
129.310
128.067
119.150
116.136
116.048
115.647
115.556
115.465
113.702
107.930
105.567
102.537
102.454
101.873
96.167
94.252
57.585
55.694
51.141
50.155
44.246
OH
HO
HO
OH
H
HO
HO
O
OH
Current Data Parameters
NAME Ampelopsin_G2
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110217
Time 10.13
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 134144
SOLVENT Acetone
NS 12288
DS 2
SWH 52631.578 Hz
FIDRES 0.392351 Hz
AQ 1.2744180 sec
RG 322
DW 9.500 usec
DE 24.96 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.12 usec
PL1 2.60 dB
PL1W 36.58018494 W
SFO1 150.9224264 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -0.70 dB
PL12 15.96 dB
PL13 120.00 dB
PL2W 19.18285942 W
PL12W 0.41391137 W
PL13W 0 W
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 65536
SF 150.9026642 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.260
7.070
7.036
7.015
6.920
6.915
6.775
6.753
6.744
6.722
6.681
6.676
6.670
6.647
6.641
6.636
6.580
6.558
6.299
6.011
4.516
4.490
3.825
3.752
3.745
3.732
3.642
3.565
3.500
3.426
3.068
OMe
MeO
MeO
OMe
H
MeO
O
OMe
MeO
OMe
O
OMe
MeO
S20
NAME ango234
EXPNO 1
PROCNO 1
Date_ 20100910
Time 16.35
INSTRUM spect
PROBHD 5 mm BBI 1H/D-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 27
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 28.5
DW 83.200 usec
DE 6.50 usec
TE 422.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200118 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.925
2.145
1.974
2.141
2.168
1.086
1.257
2.097
1.082
1.000
1.951
6.014
10.299
6.314
3.244
3.077
1.088
2.737


MeO
MeO
MeO
MeO
OMe
OMe
OMe
OMe
OMe
OMe
H
O
O
S20
196.574
196.213
160.747
160.704
160.597
158.599
157.637
157.454
157.403
156.157
145.822
144.285
141.766
141.363
139.058
134.586
129.098
128.726
128.575
118.417
118.068
117.258
113.311
106.947
105.537
105.287
93.850
93.211
55.979
55.786
55.702
55.644
55.585
55.353
55.224
55.119
53.978
53.859
49.366
45.317
NAME ango234
EXPNO 2
PROCNO 1
Date_ 20100910
Time 12.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 499
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 294.8 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.0000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
2GOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PLIN 0.00000000 W
SP01 49.51329468 W
SP2 100.62228298 MHz
SPNAM2 11.07 dB
SPOAL2 Crp60comp.4
SPOFFS2 0.500
0.00 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 9.40 usec
P3 18.80 usec
P4 80.00 usec
PL2 14.00 dB
PL12 14.60 dB
PLIN 26.94187927 W
PLIN2 0.37190142 W
SFO2 400.1316005 MHz
SF 32768
WDW EM
SSB 0
LB 1.00 Hz
GB
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

9.953 9.456 8.880 8.607 8.483 8.416 8.038 7.977 6.981 6.964 6.959 6.775 6.769 6.710 6.688 6.636 6.631 6.625 6.566 6.561 6.555 6.548 6.543 6.531 6.527 6.352 6.157 4.366 4.363 4.204 3.615 3.521

```
Current Data Parameters
NAME                  ango235
EXPNO                       3
PROCNO                      1

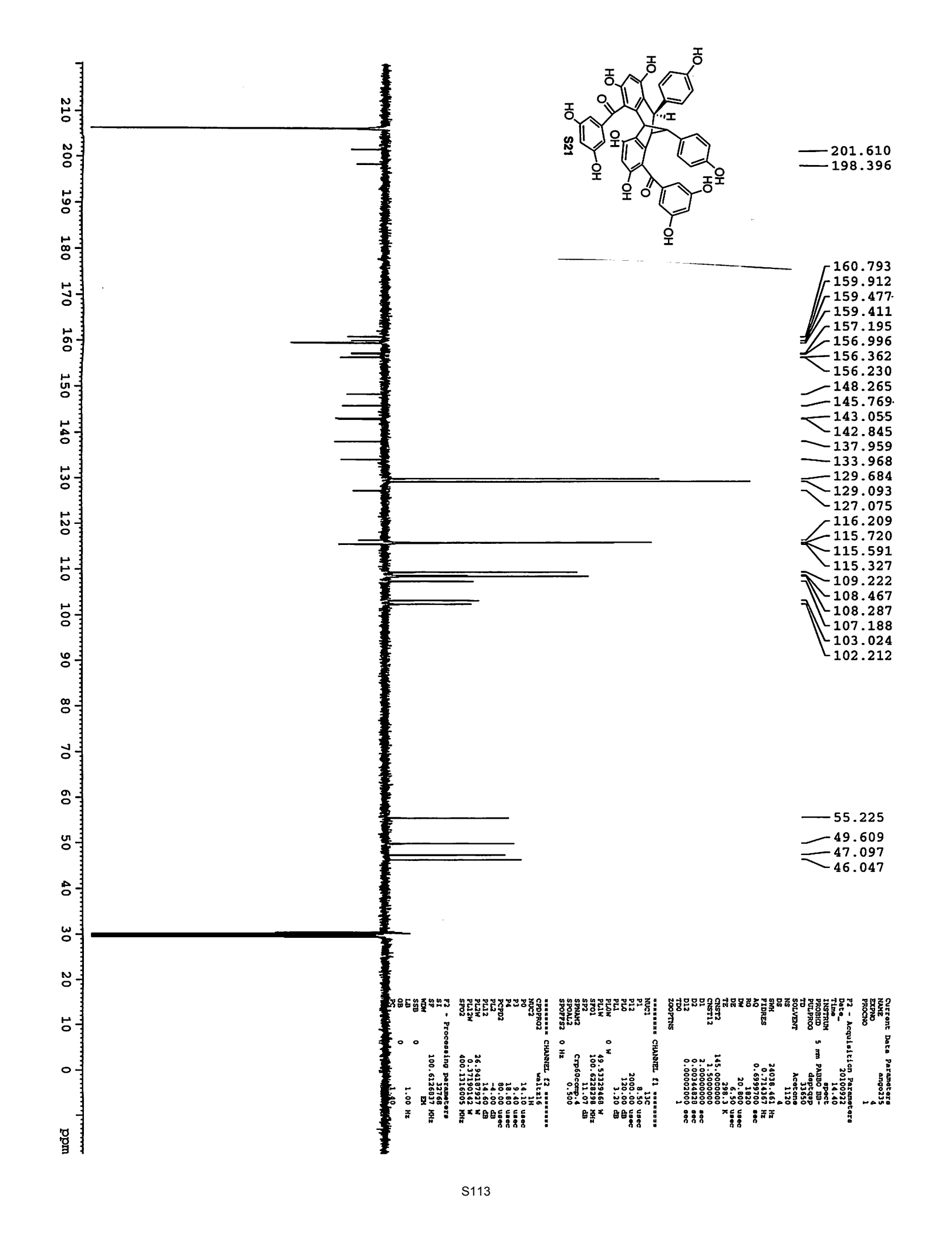
F2 - Acquisition Parameters
Date_              20100922
Time                  14.34
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT             Acetone
NS                         32
DS                          0
SWH                6009.615 Hz
FIDRES             0.183399 Hz
AQ                 2.7263477 sec
RG                       456
DW                  83.200 usec
DE                   6.50 usec
TE                   298.2 K
D1                1.00000000 sec
TD0                         1

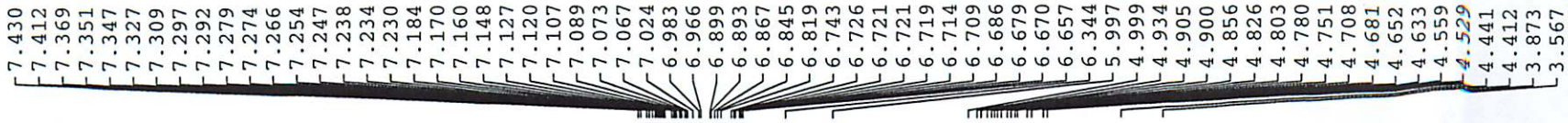
======== CHANNEL f1 ========
NUC1                       1H
P1                    9.50 usec
PL1                  -4.00 dB
PL1W           26.94187927 W
SFO1           400.1328009 MHz

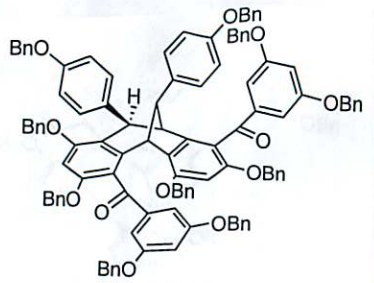
F2 - Processing parameters
SI                      32768
SF             400.1300105 MHz
WDW                        EM
SSB         0
LB                    0.20 Hz
GB          0
PC                     1.00
```

10 9 8 7 6 5 4 3 2 1 0 ppm

0.826 0.813 0.812 2.045 2.085 0.867 0.906 0.906 3.855 1.864 4.237 1.189 1.126 2.179 1.012 0.937 0.975 1.019 1.014 1.073

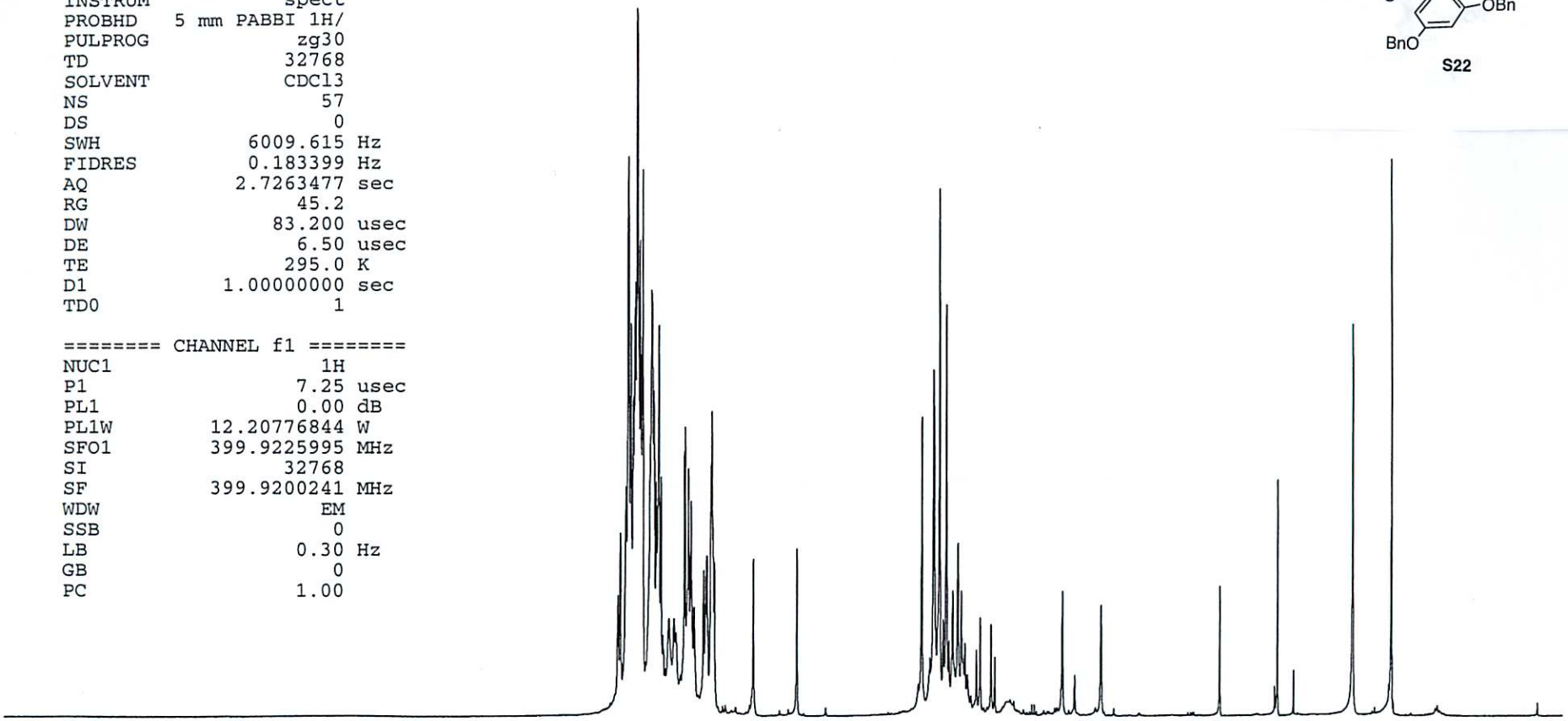

S21
201.610
198.396
160.793
159.912
159.477
159.411
157.195
156.996
156.362
156.230
148.265
145.769
143.055
142.845
137.959
133.968
129.684
129.093
127.075
116.209
115.720
115.591
115.327
109.222
108.467
108.287
107.188
103.024
102.212
55.225
49.609
47.097
46.047
ppm

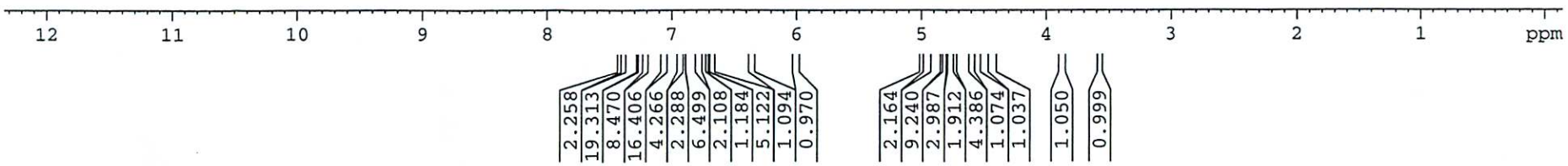


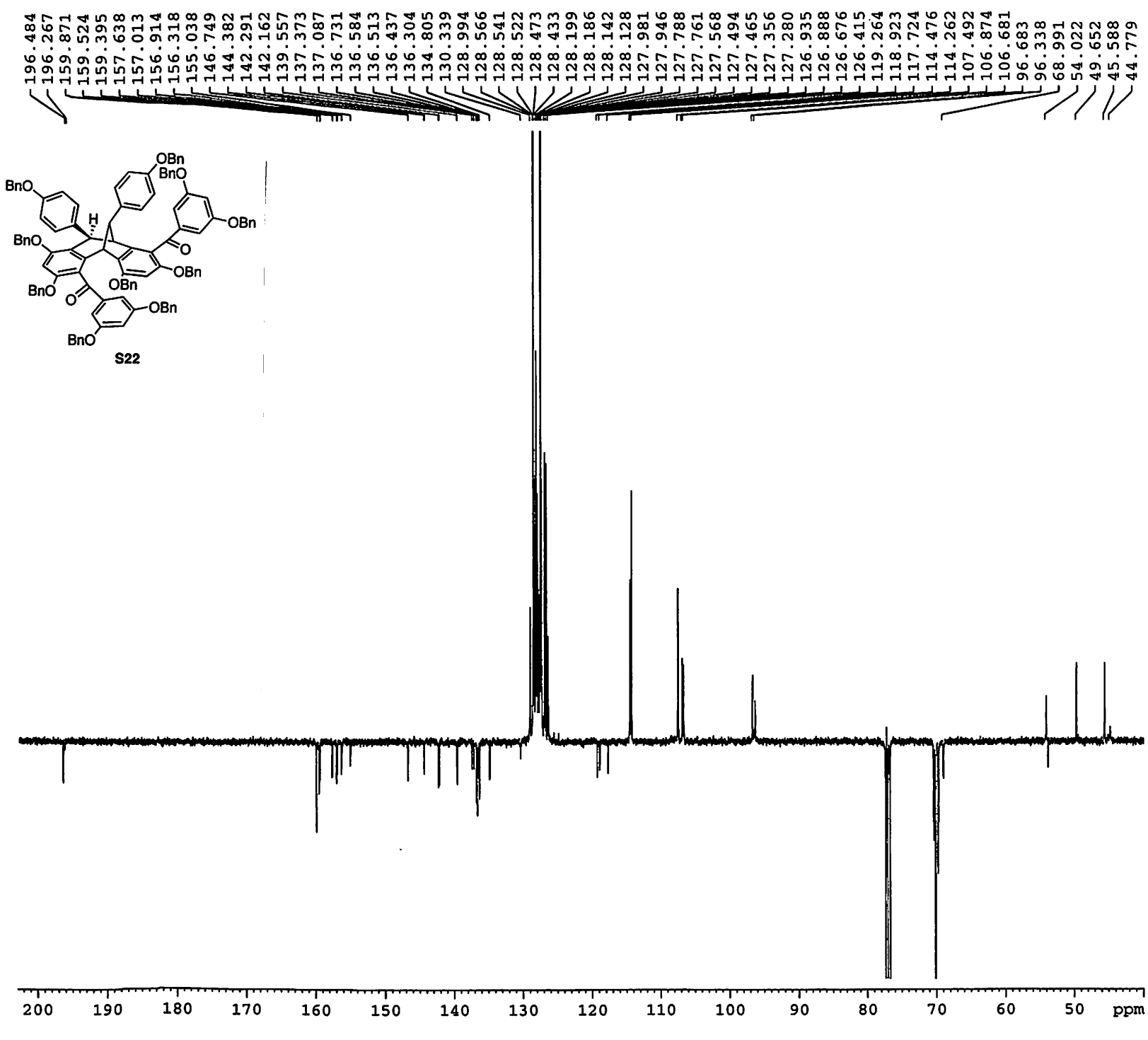


S22

NAME	ango228B
EXPNO	1
PROCNO	1
Date_	20100923
Time	14.48
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	57
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	45.2
DW	83.200 usec
DE	6.50 usec
TE	295.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	7.25 usec
PL1	0.00 dB
PL1W	12.20776844 W
SFO1	399.9225995 MHz
SI	32768
SF	399.9200241 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00







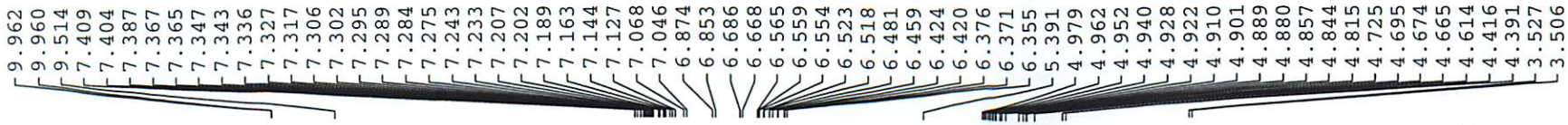

```
Current Data Parameters
NAME                 ango228B
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20100923
Time                   16.15
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             deptqsp
TD                      33650
SOLVENT                 CDCl3
NS                       2746
DS                          4
SWH                24038.461 Hz
FIDRES             0.714367 Hz
AQ                 0.6999700 sec
RG                       1820
DW                    20.800 usec
DE                     6.50 usec
TE                    298.2 K
CNST2             145.0000000
CNST12              1.5000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                         1
ZGOPTNS

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
P12                 2000.00 usec
PL0                  120.00 dB
PL1                    3.20 dB
PL0W        0 W
PL1W           49.53329468 W
SFO1           100.6228298 MHz
SP2                   11.07 dB
SPNAM2         Crp60comp.4
SPOAL2                0.500
SPOFFS2     0 Hz

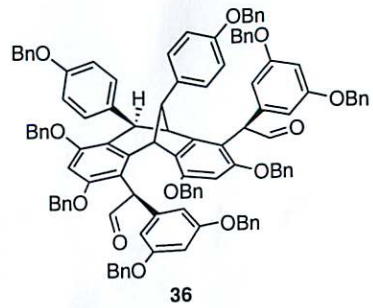
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
P0                    14.10 usec
P3                     9.40 usec
P4                    18.80 usec
PCPD2                 80.00 usec
PL2                   -4.00 dB
PL12                  14.60 dB
PL2W           26.94187927 W
PL12W           0.37190142 W
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127735 MHz
WDW                         EM
SSB         0
LB                    1.00 Hz
GB          0
PC                    1.40
```

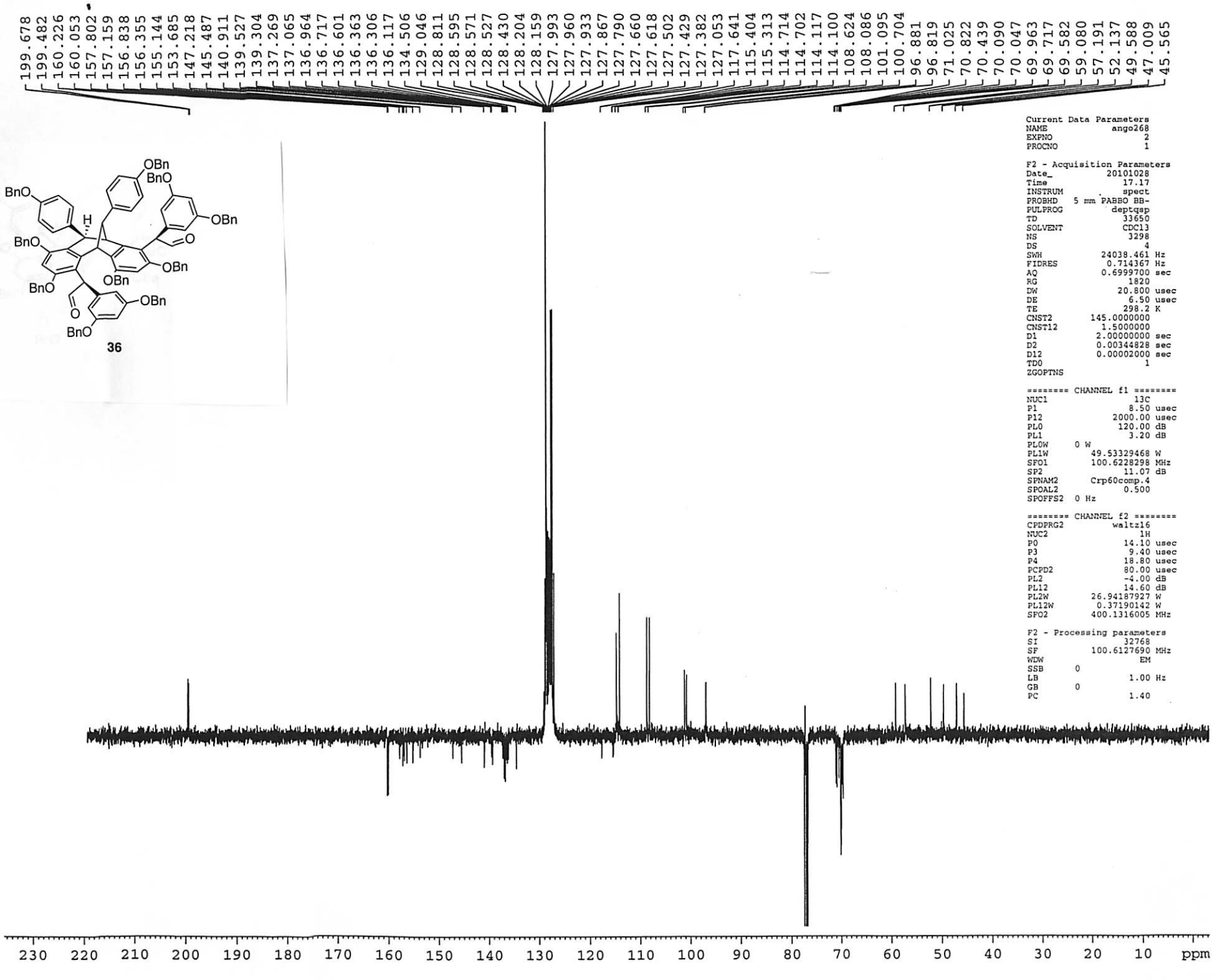


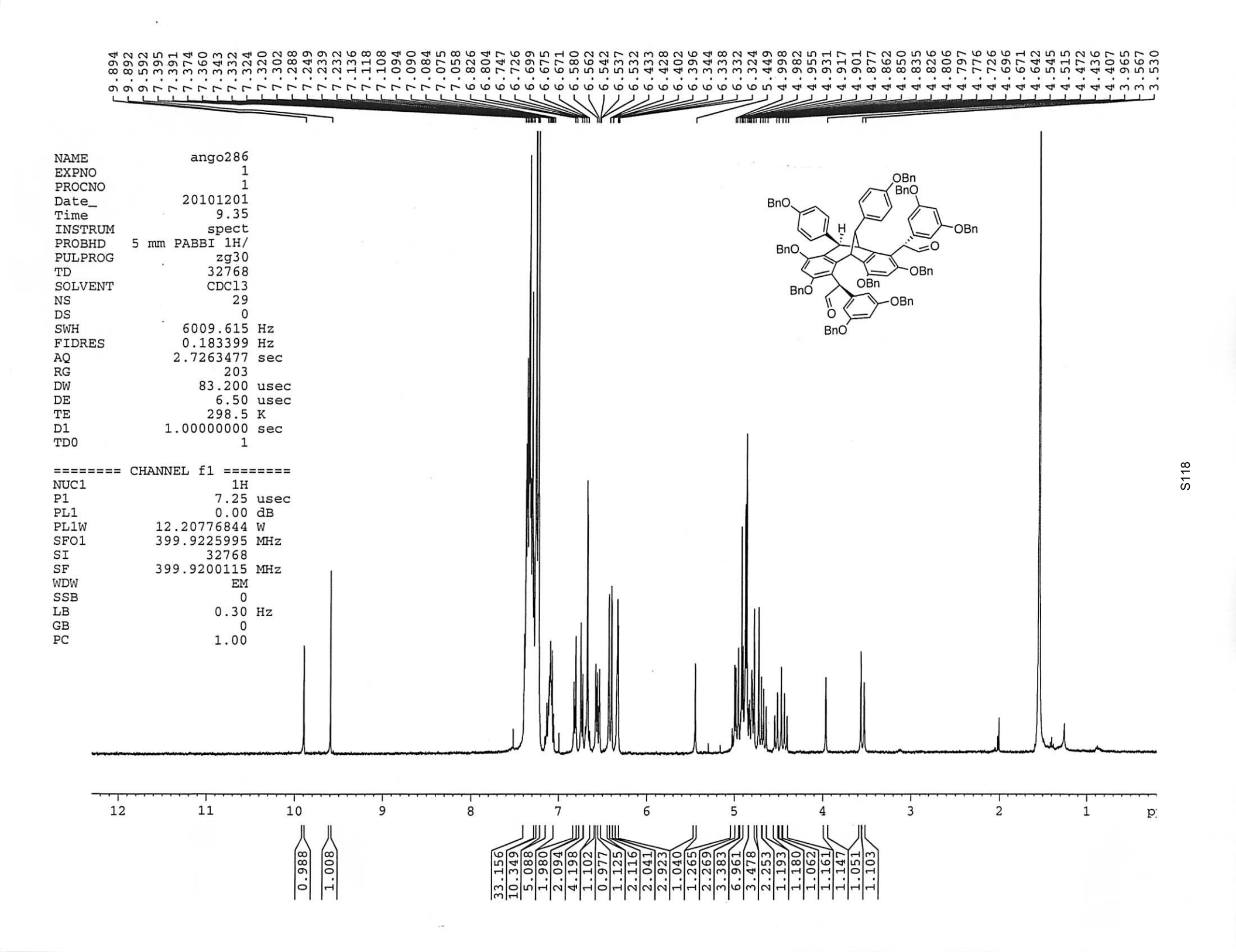

```
NAME              ango268
EXPNO                   4
PROCNO                  1
Date_            20101028
Time                13.05
INSTRUM             spect
PROBHD   5 mm PABBI 1H/
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     36
DS                      0
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ               2.7263477 sec
RG                    101
DW                 83.200 use
DE                  6.50 use
TE                 295.1 K
D1            1.00000000 sec
TD0                     1

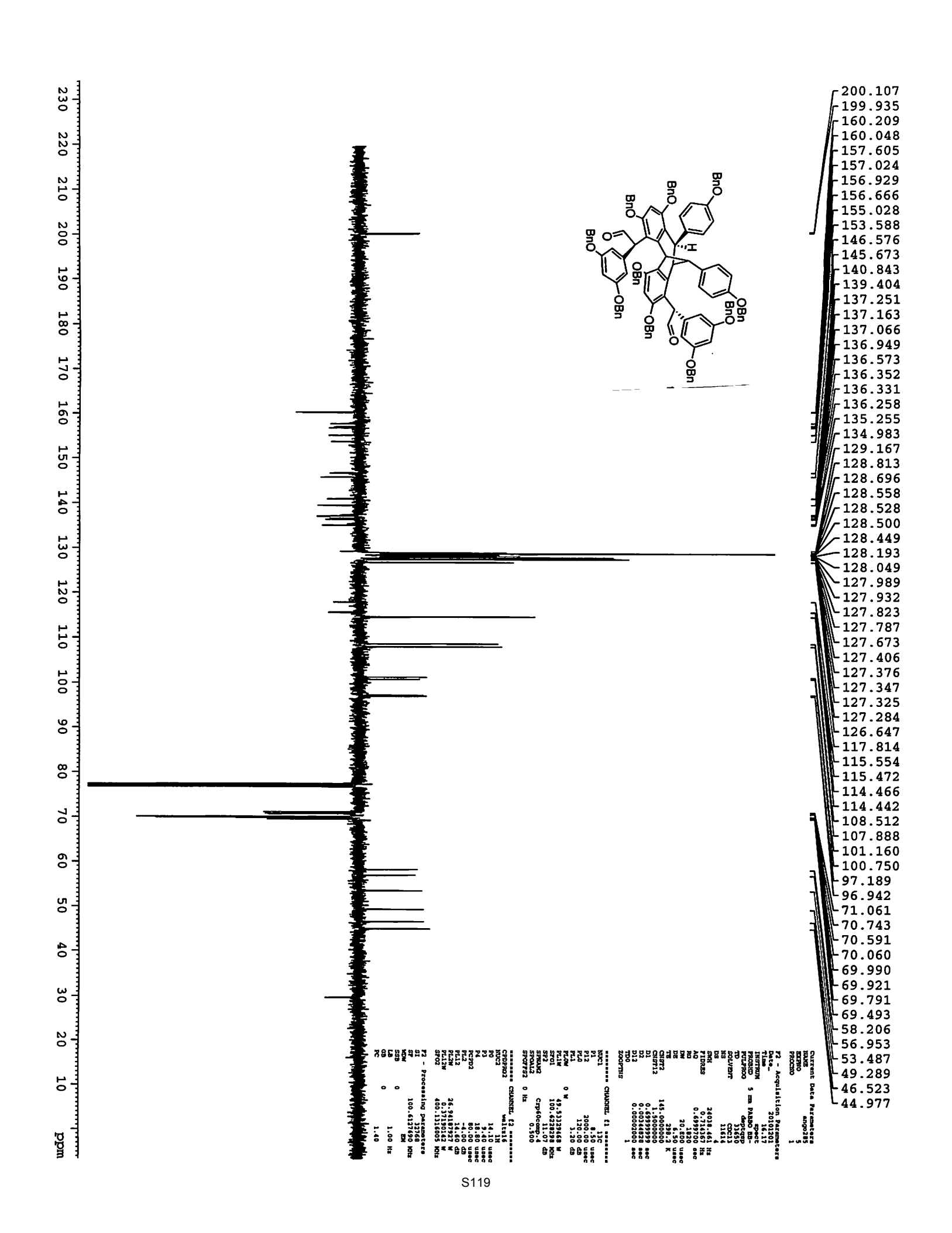
======== CHANNEL f1 ========
NUC1                   1H
P1                   7.25 use
PL1                  0.00 dB
PL1W         12.20776844 W
SFO1         399.9225995 MHz
SI                  32768
SF           399.9200125 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

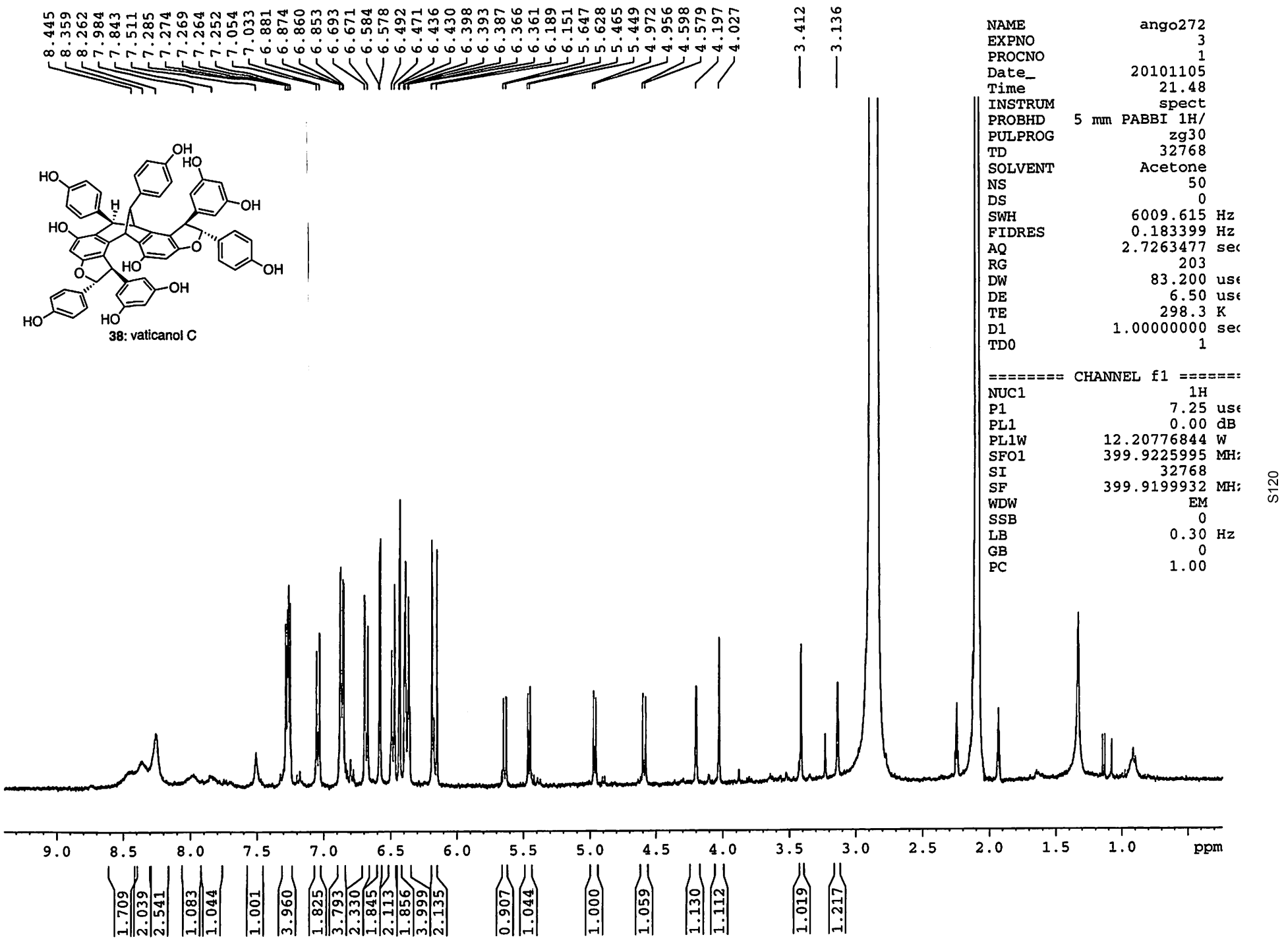


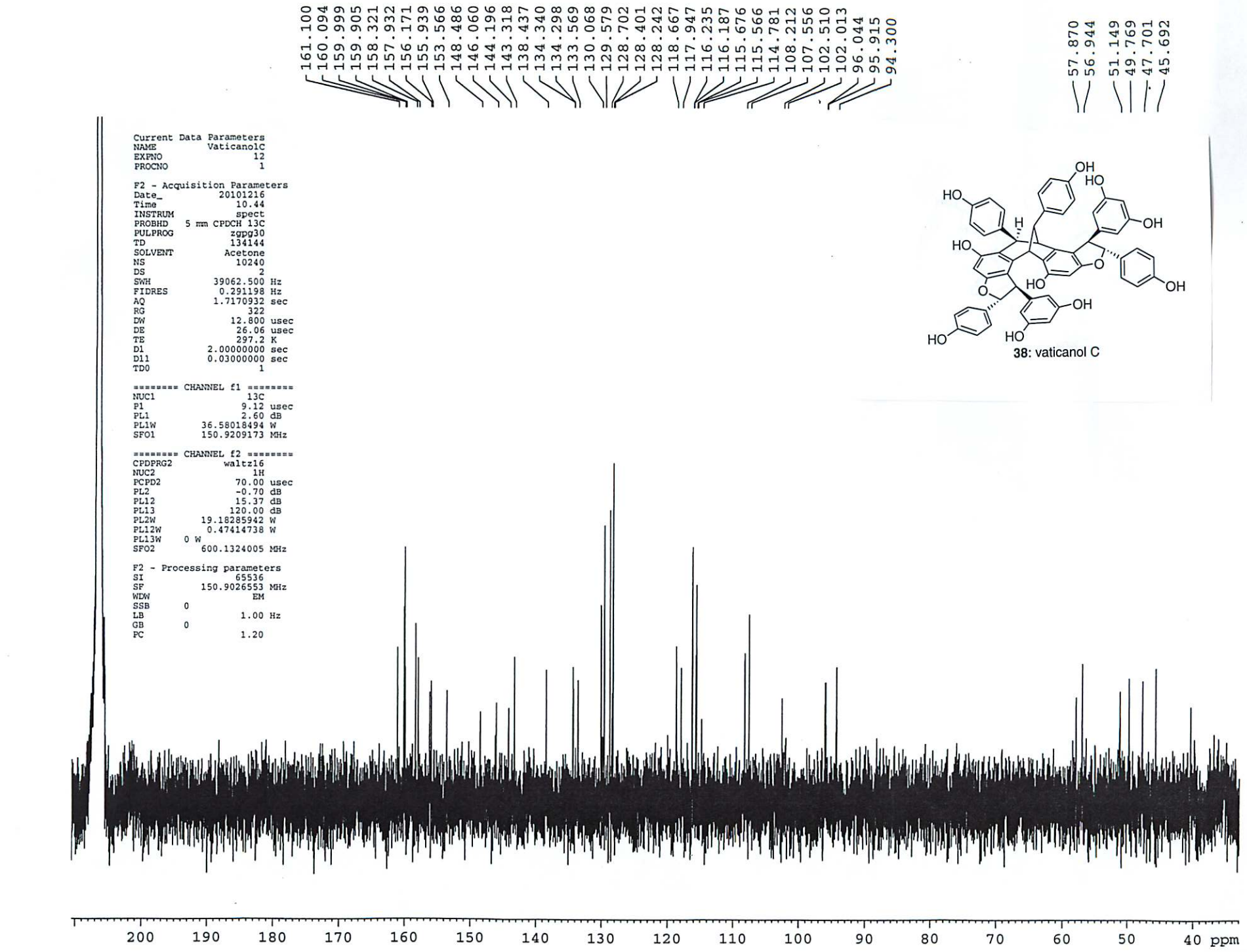
36

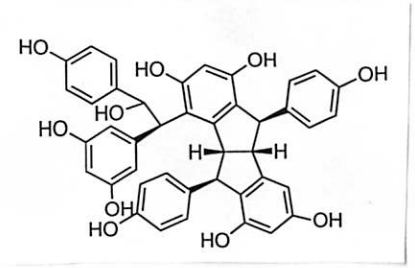

199.678
199.482
160.226
160.053
157.802
157.159
156.838
156.355
155.144
153.685
147.218
145.487
140.911
139.527
139.304
137.269
137.065
136.964
136.717
136.601
136.363
136.306
136.117
134.506
129.046
128.811
128.595
128.571
128.527
128.430
128.204
128.159
127.993
127.960
127.933
127.867
127.790
127.660
127.618
127.502
127.429
127.382
127.053
117.641
115.404
115.313
114.714
114.702
114.117
114.100
108.624
108.086
101.095
100.704
96.881
96.819
71.025
70.822
70.439
70.090
70.047
69.963
69.717
69.582
59.080
57.191
52.137
49.588
47.009
45.565
OBn
BnO
BnO
OBn
H
BnO
O
OBn
BnO
OBn
OBn
O
BnO
36
Current Data Parameters
NAME ango268
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101028
Time 17.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG deptqsp
TD 33650
SOLVENT CDCl3
NS 3298
DS 4
SWH 24038.461 Hz
FIDRES 0.714367 Hz
AQ 0.6999700 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 298.2 K
CNST2 145.0000000
CNST12 1.5000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
ZGOPTNS
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 3.20 dB
PL0W 0 W
PL1W 49.53329468 W
SFO1 100.6228298 MHz
SP2 11.07 dB
SPNAM2 Crp60comp.4
SPOAL2 0.500
SPOFFS2 0 Hz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P0 14.10 usec
P3 9.40 usec
P4 18.80 usec
PCPD2 80.00 usec
PL2 -4.00 dB
PL12 14.60 dB
PL2W 26.94187927 W
PL12W 0.37190142 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.894 9.892 9.592 7.395 7.391 7.374 7.360 7.343 7.332 7.324 7.320 7.302 7.288 7.249 7.239 7.232 7.136 7.118 7.108 7.094 7.090 7.084 7.075 7.058 6.826 6.804 6.747 6.726 6.699 6.675 6.671 6.580 6.562 6.542 6.537 6.532 6.433 6.428 6.402 6.396 6.344 6.338 6.332 6.324 5.449 4.998 4.982 4.955 4.931 4.917 4.901 4.877 4.862 4.850 4.835 4.826 4.806 4.797 4.776 4.726 4.696 4.671 4.642 4.545 4.515 4.472 4.436 4.407 3.965 3.567 3.530
NAME ango286
EXPNO 1
PROCNO 1
Date_ 20101201
Time 9.35
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 29
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 298.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.25 usec
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MHz
SI 32768
SF 399.9200115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OBn
BnO
H
O
12 11 10 9 8 7 6 5 4 3 2 1 p
0.988 1.008
33.156 10.349 5.088 1.980 2.094 4.198 1.102 0.977 1.125 2.116 2.041 2.923 1.040 1.265 2.269 3.383 6.961 3.478 2.253 1.193 1.180 1.062 1.161 1.147 1.051 1.103

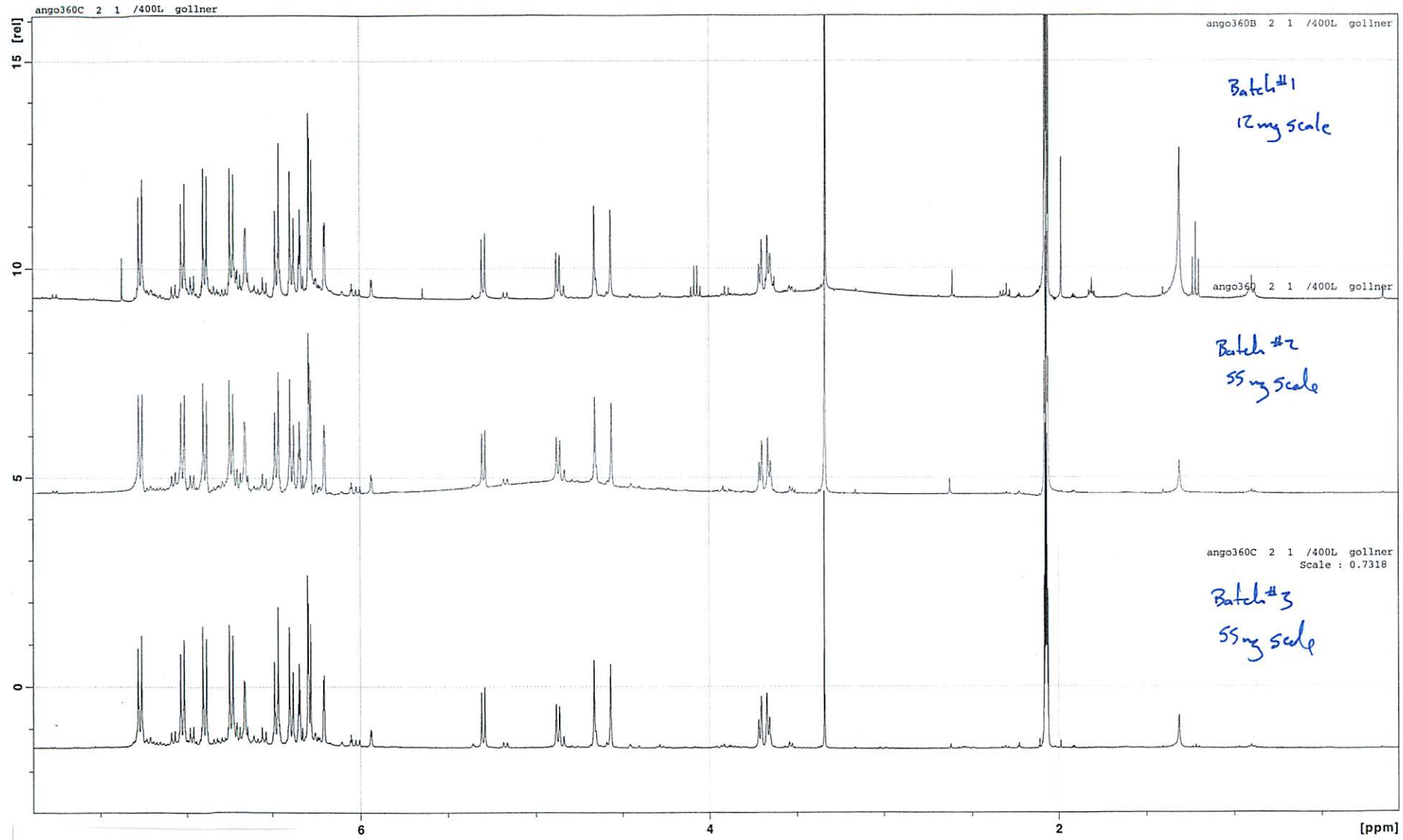

200.107
199.935
160.209
160.048
157.605
157.024
156.929
156.666
155.028
153.588
146.576
145.673
140.843
139.404
137.251
137.163
137.066
136.949
136.573
136.352
136.331
136.258
135.255
134.983
129.167
128.813
128.696
128.558
128.528
128.500
128.449
128.193
128.049
127.989
127.932
127.823
127.787
127.673
127.406
127.376
127.347
127.325
127.284
126.647
117.814
115.554
115.472
114.466
114.442
108.512
107.888
101.160
100.750
97.189
96.942
71.061
70.743
70.591
70.060
69.990
69.921
69.791
69.493
58.206
56.953
53.487
49.289
46.523
44.977
BnO
OBn
H
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

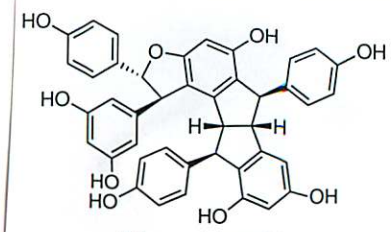

8.445
8.359
8.262
7.984
7.843
7.511
7.285
7.274
7.269
7.264
7.252
7.054
7.033
6.881
6.874
6.860
6.853
6.693
6.671
6.584
6.578
6.492
6.471
6.436
6.430
6.398
6.393
6.387
6.366
6.361
6.189
6.151
5.647
5.628
5.465
5.449
4.972
4.956
4.598
4.579
4.197
4.027
3.412
3.136
38: vaticanol C
NAME ango272
EXPNO 3
PROCNO 1
Date_ 20101105
Time 21.48
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT Acetone
NS 50
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 use
DE 6.50 use
TE 298.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 7.25 use
PL1 0.00 dB
PL1W 12.20776844 W
SFO1 399.9225995 MH
SI 32768
SF 399.9199932 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.709
2.039
2.541
1.083
1.044
1.001
3.960
1.825
3.793
2.330
1.845
2.113
1.856
3.999
2.135
0.907
1.044
1.000
1.059
1.130
1.112
1.019
1.217


161.100
160.094
159.999
159.905
158.321
157.932
156.171
155.939
153.566
148.486
146.060
144.196
143.318
138.437
134.340
134.298
133.569
130.068
129.579
128.702
128.401
128.242
118.667
117.947
116.235
116.187
115.676
115.566
114.781
108.212
107.556
102.510
102.013
96.044
95.915
94.300
57.870
56.944
51.149
49.769
47.701
45.692
Current Data Parameters
NAME Vaticanol C
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20101216
Time 10.44
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 134144
SOLVENT Acetone
NS 10240
DS 2
SWH 39062.500 Hz
FIDRES 0.291198 Hz
AQ 1.7170932 sec
RG 322
DW 12.800 usec
DE 26.06 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.12 usec
PL1 2.60 dB
PL1W 36.58018494 W
SFO1 150.9209173 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -0.70 dB
PL12 15.37 dB
PL13 120.00 dB
PL2W 19.18285942 W
PL12W 0.47414738 W
PL13W 0 W
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 65536
SF 150.9026553 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.20
OH
HO
HO
OH
H
HO
O
O
HO
OH
OH
HO
HO
38: vaticanol C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40 ppm



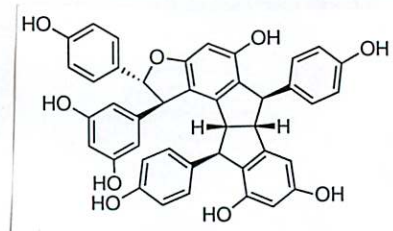
NAME	ango360C
EXPNO	1
PROCNO	1
Date_	20110506
Time	15.39
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg30
TD	32768
SOLVENT	MeOD
NS	20
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	114
DW	83.200 usec
DE	6.50 usec
TE	300.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	7.25 usec
PL1	0.00 dB
PL1W	12.20776844 W
SFO1	399.9225995 MHz
SI	32768
SF	399.9200000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00





16: carasiphenol C
scale-up
crude ^{1}H NMR
3 batches

NAME	ango360C
EXPNO	2
PROCNO	1
Date_	20110506
Time	18.22
INSTRUM	spect
PROBHD	5 mm PABBI 1H/
PULPROG	zg30
TD	32768
SOLVENT	Acetone
NS	32
DS	0
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	36
DW	83.200 usec
DE	6.50 usec
TE	300.3 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	7.25 usec
PL1	0.00 dB
PL1W	12.20776844 W
SFO1	399.9225995 MHz
SI	32768
SF	399.9200000 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00



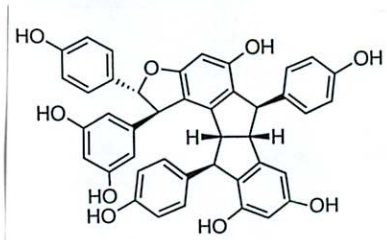
16: carasiphenol C
scale-up
crude ^{1}H NMR

Batch #3

```
NAME              ango360
EXPNO                   3
PROCNO                  1
Date_            20110507
Time                15.18
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   32768
SOLVENT            Acetone
NS                     101
DS                       0
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ               0.6816244 sec
RG                    1820
DW                  20.800 usec
DE                   6.50 usec
TE                  298.3 K
D1              0.69999999 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.50 usec
PL1                   3.20 dB
PL1W         49.53329468 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -4.00 dB
PL12                 14.60 dB
PL13                 14.60 dB
PL2W         26.94187927 W
PL12W         0.37190142 W
PL13W         0.37190142 W
SFO2        400.1316005 MHz
SI                   32768
SF          100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



16: carasiphenol C
scale-up
crude ^{13}C NMR
100 scans
Batch 2 + 3