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Electronic Supplementary Information

Synthesis of ferrocenylmethylidene and arylidene substituted camphane based compounds as potential anticancer agents

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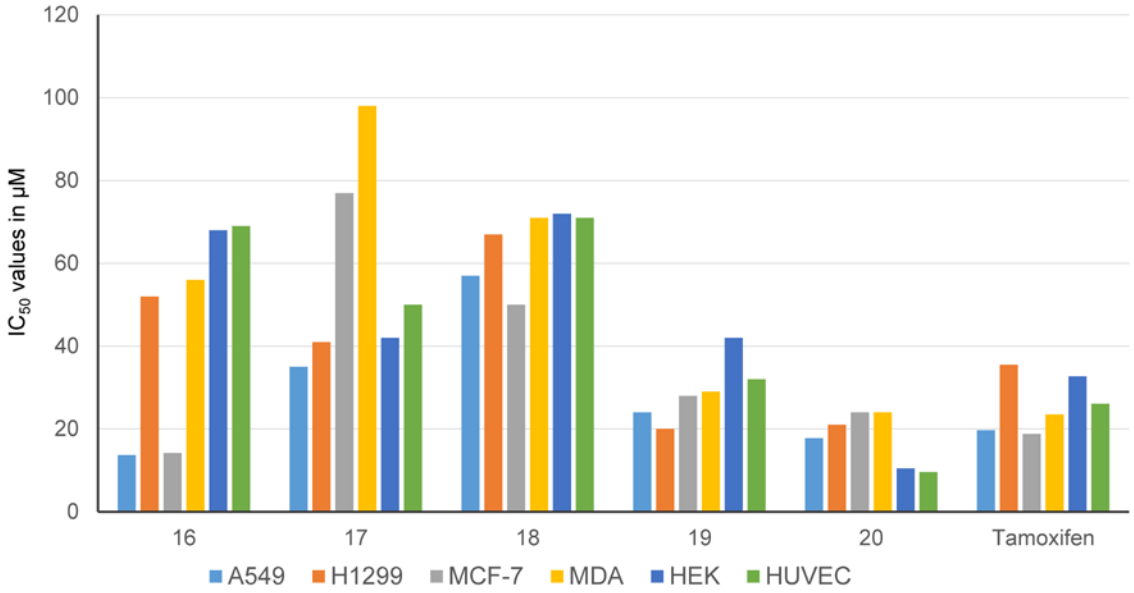
S1. General information and methodology

Chemistry:

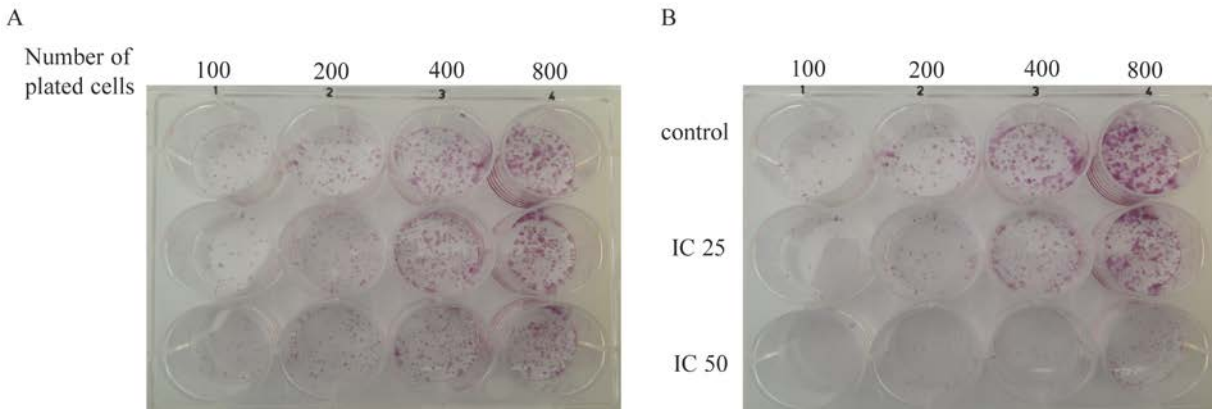
For thin layer chromatography (TLC) aluminum sheets precoated with silica gel 60 F_{254} (Merck) were used. Flash column chromatography was carried out using silica gel 60 (0.040-0.063 mm, 230-400 mesh ASTM, Merck). Commercially available solvents for TLC and column chromatography were used after distillation (and were dried when needed) - hexane, heptane, light petroleum ether – fraction 40-60°C (PE), diethyl ether (Et_2O), dichloromethane (DCM), methyl *tert*-butyl ether (MTBE), tetrahydrofurane (THF), methanol (MeOH), ethanol (EtOH), ethylacetate (EtOAc). Toluene for *Claisen-Shmidt* type condensation was with 99.5 % purity (contains ca. 0.05% water) and was used without distillation. *N*,*N*-Diisopropylethylamine (DIEA) and trimethylamine were commercially available. Melting temperatures were determined in capillary tubes on an Electrothermal MEL-TEMP 1102D-230 VAC apparatus without corrections. The NMR spectra were recorded on a Bruker Avance DRX-250 (250.13 for ^{1}H and 62.90 MHz for ^{13}C) and on a Bruker Avance II+ 600 (600.13 for ^{1}H and 150.92 MHz and for ^{13}C NMR) spectrometers. In case of $CDCl_3$ TMS was used as internal standard for chemical shifts (δ, ppm) and ^{1}H spectra were calibrated to the signal of TMS (δ = 0.0000). ^{13}C spectra were calibrated in all cases to the residual solvent peaks ($CDCl_3$, δ = 77.00). The following additional NMR techniques were used: DEPT135, COSY, HSQC and HMBC. ^{1}H and ^{13}C NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), integration, identification, and coupling constants (in Hz). For numbering of the atoms see section *S2* in this supplementary material. Mass spectra (MS) were recorded on a Thermo Scientific High Resolution Magnetic Sector MS DFS by chemical ionization (CI) or electrospray ionization (ESI), and are reported as fragmentation in *m/z* with relative intensities (%). Elemental analyses were performed by the Microanalytical Laboratory for Elemental Analysis of the Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences.

The names of the compounds are in agreement with the IUPAC nomenclature. The numbering of atoms in formulas is not in conformity with the IUPAC names of the compounds. Chemical shifts of carbon atoms in ^{13}C NMR spectra assigned with asterisk (*) are tentative. The assignments of protons as H_a and H_b are tentative. Some other assignments: Cp – cyclopentadienyl ring, Fc – ferrocene.

Biology:



Supplementary figure 1. Comparison of cytotoxicity of the ferrocenylmethylidene derivatives studied by MTT assay in four cancer and two normal cell lines after exposure to studied compounds for 72 h; the data are plotted as the IC_{50} values. The mean values of three independent experiments are presented the standard deviation is about 5% over most data, and is not shown to avoid clutter.



Supplementary figure 2. ***Panel A.*** An example plate layout for illustration how PE was calculated - the ratio of the number of colonies to the number of cells seeded according the formula:

PE = no. of colonies formed/ no. of cells seeded x 100%.

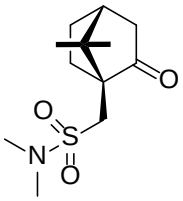
Panel B. A typical plate layout for SF calculation according the formula:

SF = no. of colonies formed after treatment/ no. of cells seeded x PE.

In every experiment, the PE was determined, as small changes in conditions may influence this factor. The surviving fraction of cells after each treatment was always calculated taking into account the PE of control cells in the same experiment.

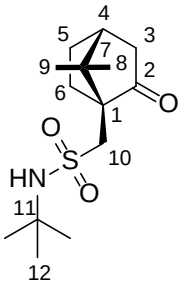
S2. Synthesis and analytical data of compounds

1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*,*N*-dimethylmethanesulfonamide (8):



For preparation and analytical data of this compound see references [1,2].

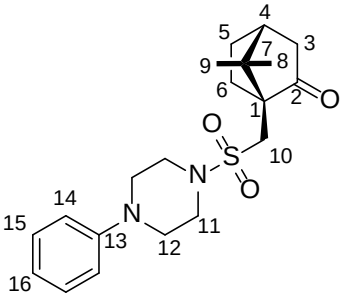
***N*-(*tert*-butyl)-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonamide (9):**



To a solution of 1.94 ml (18.35 mmol) *tert*-butylamine (**2**) in 50 ml dry DCM was added at 0°C in small portions (1*S*)-(+)-10-camphorsulfonyl chloride (**1**) as a solid (2.00 g, 7.98 mmol). The reaction mixture was stirred at r.t. for 24 h, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was crystallized from heptane:acetone = 10:1 ml. The crystals obtained were washed with hexane and dried *in vacuo* to give 1.57 g (69%) pure **9** as white crystals. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 3.49 (d, 1H, 10-H_a, *J* = 15.0 Hz), 2.99 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.40 (m, 1H, 3-H_{exo}), 2.32 (m, 1H, 6-H_{exo}), 2.12 (br t, 1H, 4-H, *J* = 4.5 Hz), 2.03 (tdd, 1H, 5-H_{exo}, *J* = 16.2, 12.1, 4.1 Hz), 1.94 (d, 1H, 3-H_{endo}, *J* = 18.7 Hz), 1.90 (m, 1H, 6-H_{endo}), 1.44 (m, 1H, 5-H_{endo}), 1.41 (s, 9H, 12-H), 1.05 (s, 3H, 9-H), 0.91 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 216.89 (1C, 2-C), 59.28 (1C, 1-C), 54.86 (1C, 11-C), 53.77 (1C, 10-C), 48.54 (1C, 7-C), 42.91 (1C, 3-C), 42.71 (1C, 4-C), 30.25 (3C, 12-C), 27.00 (1C, 5-C), 26.31 (1C, 6-C), 19.87 (1C, 8-C), 19.64 (1C, 9-C).

For other properties of this compound see references [3-5].

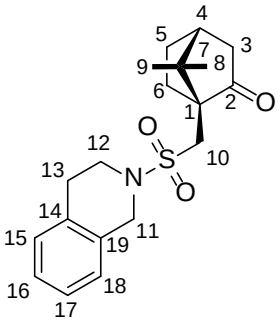
(1*S*,4*R*)-7,7-dimethyl-1-(((4-phenylpiperazin-1-yl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (10):



A modified literature procedure was used for this reaction [6].

To a solution of 1-phenylpiperazine (**4**) (3.03 ml, 19.94 mmol) and DIEA (3.63 ml, 21.93 mmol) in 40 ml dry DCM was added at 0°C in small portions (1*S*)-(+)-10-camphorsulfonyl chloride (**1**) (5.0 g, 19.94 mmol). The reaction mixture was stirred at r.t. for 24 h and washed with 5% aqueous HCl, water, saturated aqueous $NaHCO_3$, and water again. The organic phase was dried over anhydrous Na_2SO_4 and solvent was evaporated *in vacuo*. The product was washed with hot heptane (40 ml) and hexane (5 ml) and dried *in vacuo* to give 7.17 g (95%) pure **10** as white crystals. M.p. 154-155 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.29 (m, 2H, 15-H), 6.94 (m, 2H, 14-H), 6.91 (br dt, 1H, 16-H, *J* = 7.4, 1.0 Hz), 3.47 (m, 4H, 11-H), 3.38 (d, 1H, 10-H_a, *J* = 14.6 Hz), 3.27 (br t, 4H, 12-H, *J* = 5.0 Hz), 2.78 (d, 1H, 10-H_b, *J* = 14.6 Hz), 2.54 (m, 1H, 6-H_{exo}), 2.39 (m, 1H, 3-H_{exo}), 2.13 (br t, 1H, 4-H, *J* = 4.5 Hz), 2.06 (m, 1H, 5-H_{exo}), 1.95 (d, 1H, 3-H_{endo}, *J* = 18.5 Hz), 1.67 (ddd, 1H, 6-H_{endo}, *J* = 14.1, 9.4, 4.8 Hz), 1.44 (ddd, 1H, 5-H_{endo}, *J* = 13.0, 9.4, 4.0 Hz), 1.15 (s, 3H, 9-H), 0.89 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 215.17 (1C, 2-C), 150.77 (1C, 13-C), 129.23 (2C, 15-C), 120.70 (1C, 16-C), 116.92 (2C, 14-C), 58.15 (1C, 1-C), 49.52 (2C, 12-C), 47.92 (1C, 7-C), 45.69 (2C, 11-C), 44.62 (1C, 10-C), 42.74 (1C, 4-C), 42.55 (1C, 3-C), 26.89 (1C, 5-C), 25.08 (1C, 6-C), 19.98 (1C, 9-C), 19.76 (1C, 8-C). MS (CI) *m/z* (rel. int.): 378 (26, M+2), 377 (100, M+1), 376 (38, M), 161 (32). Anal. calcd. for $C_{20}H_{28}N_2O_3S$ (376.51): C, 63.80; H, 7.50; N, 7.44; S, 8.52. Found: C, 63.74; H, 7.54; N, 7.49; S, 8.50 %.

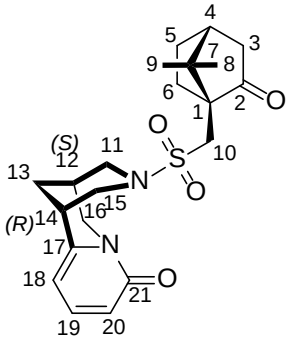
(1*S*,4*R*)-1-(((3,4-dihydroisoquinolin-2(1*H*)-yl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1] heptan-2-one (11):



To a solution of 2.50 ml (19.94 mmol) **5** and 3.06 ml (21.93 mmol) Et_3N in 80 ml dry DCM was added at 0°C in small portions (1*S*)-(+)-10-camphorsulfonyl chloride (**1**) as a solid (5.00 g, 19.94 mmol). The reaction mixture was stirred at r.t. for 48 h, washed with aqueous citric acid and water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was crystallized from heptane:EtOH = 40:30 ml. The crystals were washed with hot hexane and dried *in vacuo* to give 5.99 g (86%) pure **11** as white crystals. M.p. 150-151 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.19 (m, 2H, 16-H, 17-H), 7.15 (m, 1H, 15-H), 7.10 (m, 1H, 18-H), 4.55 (d, 1H, 11-H_a, *J* = 15.4 Hz), 4.51 (d, 1H, 11-H_b, *J* = 15.4 Hz), 3.63 (td, 1H, 12-H_a, *J* = 12.0, 5.9 Hz), 3.59 (td, 1H, 12-H_b, *J* = 12.0, 5.9 Hz), 3.41 (d, 1H, 10-H_a, *J* = 14.6 Hz), 2.98 (t, 2H, 13-H, *J* = 5.9 Hz), 2.81 (d, 1H, 10-H_b, *J* = 14.6 Hz), 2.56 (m, 1H, 6-H_{exo}), 2.38 (m, 1H, 3-H_{exo}), 2.11 (br t, 1H, 4-H, *J* = 4.5 Hz), 2.06 (m, 1H, 5-H_{exo}), 1.94 (d, 1H, 3-H_{endo}, *J* = 18.5 Hz), 1.67 (ddd, 1H, 6-H_{endo}, *J* = 14.1, 9.4, 4.8 Hz), 1.44 (ddd, 1H, 5-H_{endo}, *J* = 13.0, 9.4, 4.0 Hz), 1.15 (s, 3H, 9-H), 0.88 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 215.31 (1C, 2-C), 133.31 (1C, 14-C), 132.03 (1C, 19-C), 128.98 (1C, 15-C), 126.77* (1C, 17-C), 126.39* (1C, 18-C), 126.30* (1C, 16-C), 58.24 (1C, 1-C), 47.95 (1C, 7-C), 47.04 (1C, 11-C), 45.52 (1C, 10-C), 43.32 (1C, 12-C), 42.73 (1C, 4-C), 42.57 (1C, 3-C), 29.10 (1C, 13-C), 26.90 (1C, 5-C), 25.10 (1C, 6-C), 19.97 (1C, 9-C), 19.76 (1C, 8-C). MS (CI) *m/z* (rel. int.): 349 (12, M+2), 348 (53, M+1), 216 (12), 215 (100, camphor-SO_2), 133 (11, tetrahydroisoquinoline), 132 (86, tetrahydroisoquinoline-1). Anal. calcd. for $C_{19}H_{25}NO_3S$ (347.47): C, 65.68; H, 7.25; N, 4.03; S, 9.23. Found: C, 65.61; H, 7.29; N, 4.08; S, 9.25 %.

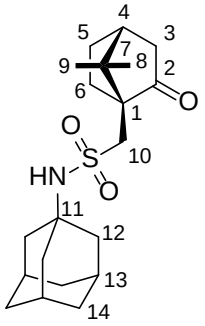
For preparation of this compound see also reference [7].

(1*R*,5*R*)-3-((((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)sulfonyl)-1,2,3,4,5,6-hexahydro-8*H*-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (12):



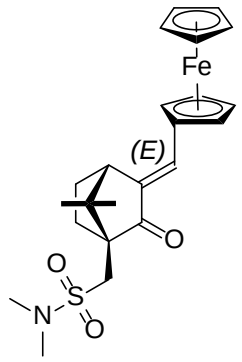
To a solution of 0.835 g (4.39 mmol) cytisine (**6)** and 0.67 ml (4.79 mmol) Et_3N in 20 ml dry DCM was added at 0°C in small portions (1*S*)-(+)-10-camphorsulfonyl chloride (**1**) as a solid (1.00 g, 3.99 mmol). The reaction mixture was stirred at r.t. for 20 h (TLC monitoring – DCM:MTBE = 3:1), washed with aqueous citric acid and water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography (40 g silica gel, phase - DCM:MTBE = 3:1) to give 1.11 g (68%) pure **12** as white crystals. M.p. 173-174 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.29 (dd, 1H, 19-H, *J* = 9.1, 6.9 Hz), 6.45 (dd, 1H, 20-H, *J* = 9.1, 1.2 Hz), 6.06 (dd, 1H, 18-H, *J* = 6.9, 1.2 Hz), 4.17 (d, 1H, 16-H_a, *J* = 15.7 Hz), 3.93 (m, 1H, 16-H_b), 3.91 (m, 1H, 11-H_a), 3.82 (m, 1H, 15-H_a), 3.20 (m, 1H, 11-H_b), 3.18 (d, 1H, 10-H_a, *J* = 14.7 Hz), 3.14 (dd, 1H, 15-H_b, *J* = 11.7, 2.1 Hz), 3.12 (br s, 1H, 14-H), 2.59 (m, 1H, 12-H), 2.54 (d, 1H, 10-H_b, *J* = 14.7 Hz), 2.34 (m, 1H, 3-H_{exo}), 2.29 (m, 1H, 6-H_{exo}), 2.07 (br t, 1H, 4-H, *J* = 4.5 Hz), 2.03 (m, 1H, 13-H_a), 1.98 (m, 1H, 5-H_{exo}), 1.92 (m, 1H, 13-H_b), 1.88 (d, 1H, 3-H_{endo}, *J* = 18.5 Hz), 1.48 (ddd, 1H, 6-H_{endo}, *J* = 14.0, 9.4, 4.7 Hz), 1.36 (ddd, 1H, 5-H_{endo}, *J* = 13.0, 9.4, 3.9 Hz), 1.02 (s, 3H, 9-H), 0.82 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 215.00 (1C, 2-C), 163.23 (1C, 21-C), 148.42 (1C, 17-C), 138.72 (1C, 19-C), 117.64 (1C, 20-C), 105.36 (1C, 18-C), 57.99 (1C, 1-C), 52.76 (1C, 15-C), 51.54 (1C, 11-C), 48.83 (1C, 16-C), 47.96 (1C, 7-C), 46.18 (1C, 10-C), 42.65 (1C, 4-C), 42.50 (1C, 3-C), 34.33 (1C, 14-C), 27.09 (1C, 12-C), 26.86 (1C, 5-C), 25.27 (1C, 13-C), 24.92 (1C, 6-C), 19.70* (1C, 8-C), 19.66* (1C, 9-C). MS (CI) *m/z* (rel. int.): 406 (26, M+2), 405 (100, M+1), 404 (20, M), 189 (11). Anal. calcd. for $C_{21}H_{28}N_2O_4S$ (404.52): C, 62.35; H, 6.98; N, 6.93; S, 7.93. Found: C, 62.30; H, 6.92; N, 6.98; S, 7.88 %.

_N_-adamantan-1-yl-1-((1_S_,4_R_)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl) methanesulfonamide (13):



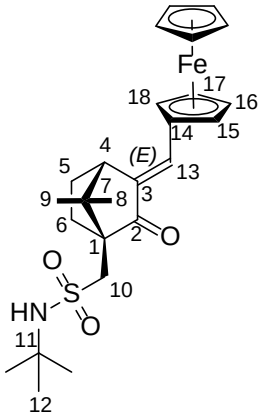
To a solution of 0.995 g (6.58 mmol) 1-adamantylamine (**7**) and 1.00 ml (7.18 mmol) Et_3N in 20 ml dry DCM was added at 0°C in small portions (1*S*)-(+)-10-camphorsulfonyl chloride (**1**) as a solid (1.50 g, 5.98 mmol). The reaction mixture was stirred at r.t. for 24 h (TLC monitoring – DCM), washed with aqueous citric acid and water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography (70 g silica gel, phase – a) DCM, b) DCM:MTBE = 10:1) to give 1.30 g (60%) pure **13** as white crystals. M.p. 196-197 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 5.00 (br s, 1H, $SO_2N\underline{H}$), 3.50 (d, 1H, 10-H_a, *J* = 15.0 Hz), 3.01 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.40 (m, 1H, 3-H_{exo}), 2.33 (m, 1H, 6-H_{exo}), 2.11 (m, 4H, 4-H, 13-H), 2.03 (m, 1H, 5-H_{exo}) 2.01 (br s, 6H, 12-H), 1.94 (d, 1H, 3-H_{endo}, *J* = 18.5 Hz), 1.89 (ddd, 1H, 6-H_{endo}, *J* = 14.3, 9.4, 4.9 Hz), 1.67 (br t, 6H, 14-H, *J* = 3.0 Hz), 1.44 (ddd, 1H, 5-H_{endo}, *J* = 13.0, 9.4, 4.0 Hz), 1.05 (s, 3H, 9-H), 0.91 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 216.83 (1C, 2-C), 59.34 (1C, 1-C), 55.38 (1C, 11-C), 54.46 (1C, 10-C), 48.49 (1C, 7-C), 43.14 (3C, 12-C), 42.91 (1C, 3-C), 42.73 (1C, 4-C), 35.96 (3C, 14-C), 29.62 (3C, 13-C), 26.99 (1C, 5-C), 26.26 (1C, 6-C), 19.93 (8-C), 19.70 (1C, 9-C). MS (CI) *m/z* (rel. int.): 366 (7, M+1), 364 (10, M-1), 135 (100, adamantyl). Anal. calcd. for $C_{20}H_{31}NO_3S$ (365.53): C, 65.72; H, 8.55; N, 3.83; S, 8.77. Found: C, 65.77; H, 8.50; N, 3.86; S, 8.71 %.

1-((1_S_,4_S_,)-3-((_E_)-3-ferrocenylmethylidene)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-_N_,_N_-dimethylmethanesulfonamide (15):



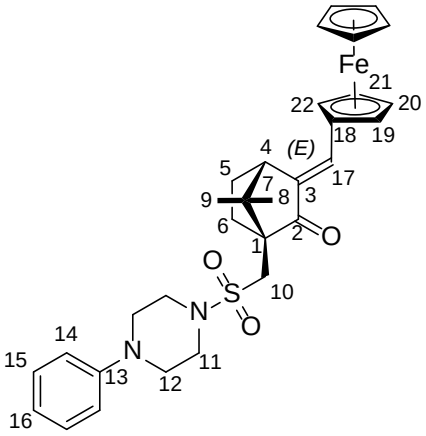
For preparation and analytical data of this compound see references [1,2].

1-((1*S*,4*S*)-3-((*E*)-ferrocenylmethylidene)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(*tert*-butyl)methanesulfonamide (16):



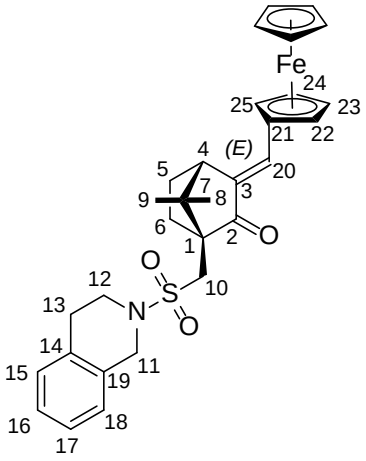
To a solution of 0.500 g (1.74 mmol) **9** and 0.372 g (1.74 mmol) ferrocenecarbaldehyde (**14**) in 25 ml dry toluene were added powdered KOH (0.195 g, 3.48) and a crystal of 18-crown-6. The mixture was refluxed for 3 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (80 g silica gel, phase – a) DCM, b) DCM:MTBE = 10:1) to give 0.779 g (93%) pure **16** as red crystals. M.p. 133-134 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.13 (s, 1H, 13-H), 5.65 (s, 1H, N<u>H</u>) 4.52 (m, 1H, 15-H), 4.51 (m, 1H, 18-H), 4.45 (m, 1H, 17-H), 4.43 (dt, 1H, 16-H, *J* = 2.5, 1.3 Hz), 4.15 (s, 5H, Cp), 3.58 (d, 1H, 10-H_a, *J* = 15.0 Hz), 3.06 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.93 (br d, 1H, 4-H, *J* = 4.0 Hz), 2.32 (m, 1H, 6-H_{exo}), 2.17 (tt, 1H, 5-H_{exo}, *J* = 11.4, 4.5 Hz), 2.03 (ddd, 1H, 6-H_{endo}, *J* = 14.1, 9.3, 4.8 Hz), 1.56 (m, 1H, 5-H_{endo}), 1.45 (s, 9H, 12-H), 1.05 (s, 3H, 9-H), 0.89 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 204.91 (1C, 2-C), 136.48 (1C, 3-C), 130.75 (1C, 13-C), 78.06 (1C, 14-C), 71.83 (1C, 15-C), 71.05* (1C, 16-C or 17-C), 71.03* (1C, 16-C or 17-C), 69.47 (5C, Cp), 68.91 (1C, 18-C), 58.68 (1C, 1-C), 54.89 (1C, 11-C), 54.12 (1C, 10-C), 48.92 (1C, 4-C), 48.28 (1C, 7-C), 30.30 (3C, 12-C), 27.81 (1C, 6-C), 25.62 (1C, 5-C), 20.74 (1C, 9-C), 18.89 (1C, 8-C). MS (CI) *m/z* (rel. int.): 484 (96, M+1), 483 (55, M), 428 (60), 411 (100), 347 (25). Anal. calcd. for $C_{25}H_{33}FeNO_3S$ (483.44): C, 62.11; H, 6.88; Fe, 11.55; N, 2.90; S, 6.63. Found: C, 62.19; H, 6.92; Fe, 11.50; N, 2.88; S, 6.67 %.

(1*S*,4*S*)-3-((*E*)-ferrocenylmethylidene)-7,7-dimethyl-1-(((4-phenylpiperazin-1-yl)sulfonyl)methyl)bicyclo[2.2.1]heptan-2-one (17):



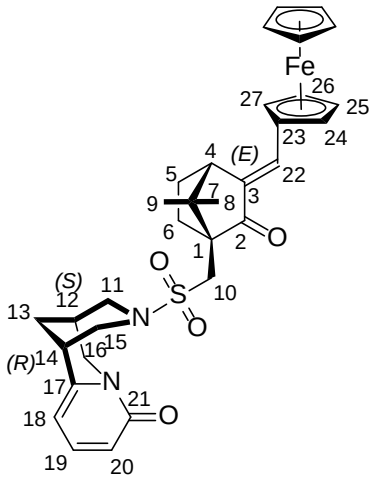
A mixture of **10** (1.00 g, 2.66 mmol), powdered KOH (0.224 g, 3.99 mmol) and 18-crown-6 (0.071 g, 0.27 mmol) in 20 ml dry toluene was stirred for 30 min and ferrocenecarbaldehyde (**14**) (0.569 g, 2.66 mmol) was added. The mixture was heated for 5 h at 80°C and 1 h at 120°C. The reaction was cooled, quenched with water and extracted with CH_2Cl_2 (3x30 ml). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography (160 g silica gel, phase - hexane/MTBE = 5:1) to give (1.404 g) (92%) of pure **17** as red crystals. $[\alpha]_D^{20}$ = -31.3 (*c* 0.11, $CHCl_3$). M.p. 211-212 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$, 293 K): δ = 7.30 (t, 2H, 15-H, *J* = 7.6 Hz), 7.12 (s, 1H, 17-H), 6.96-6.91 (m, 3H, 14-H, 16-H), 4.52* (s, br, 1H, 22-H), 4.51* (s, br, 1H, 19-H), 4.44* (s, br, 1H, 20-H), 4.42* (s, br 1H, 21-H), 4.15 (s, 5H, Cp), 3.55-3.52 (m, 5H, 11-H, 10-H_a), 3.30-3.29 (m, 4H, 12-H), 2.93 (d, 1H, 4-H, *J* = 3.7 Hz), 2.88 (d, 1H, 10-H_b, *J* = 14.6 Hz), 2.64-2.59 (m, 1H, 6-H_{exo}), 2.24-2.18 (m, 1H, 5-H_{exo}), 1.75-1.70 (m, 1H, 6-H_{endo}), 1.59-1.53 (m, 1H, 5-H_{endo}), 1.18 (s, 3H, 9-H), 0.87 (s, 3H, 8-H). ^{13}C NMR (150.9 MHz, $CDCl_3$, 293 K): δ = 203.56 (1C, 2-C), 150.83 (1C, 3`-C), 136.30 (1C, 3-C), 130.15 (1C, 11-C), 129.24 (2C, 5`-C), 120.68 (1C, 6`-C), 116.93 (2C, 4`-C), 78.22 (1C, 12-C), 71.62 (1C, 13-C), 70.91 (2C, 14-C, 15-C), 69.44 (5C, Cp), 69.02 (1C, 16-C), 57.48 (1C, 1-C), 49.56 (2C, 1`-C), 49.07 (1C, 4-C), 47.66 (1C, 7-C), 45.73 (2C, 2`-C), 44.87 (1C, 10-C), 26.07 (1C, 6-C), 25.57 (1C, 5-C), 20.62 (1C, 8-C), 19.39 (1C, 9-C). MS (CI) *m/z* (rel. int.): 572 (42, M), 411 (100, M-phenylpiperazine). Anal. calcd. for $C_{31}H_{36}FeN_2O_3S$ (572.54): C, 65.03; H, 6.34; Fe, 9.75; N, 4.89; S, 5.60. Found: C, 65.03; H, 6.34; Fe, 9.75; N, 4.89; S, 5.60 %.

(1*S*,4*S*)-3-((*E*)-ferrocenylmethylidene)-1-(((3,4-dihydroisoquinolin-2(1*H*)-yl)sulfonyl)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-one (18):



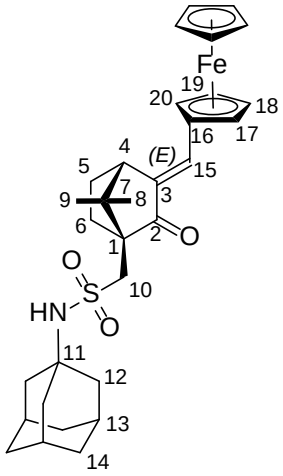
To a solution of 0.800 g (2.30 mmol) **11** and 0.493 g (2.30 mmol) ferrocenecarbaldehyde (**14**) in 30 ml dry toluene were added powdered KOH (0.195 g, 3.48) and a crystal of 18-crown-6. The mixture was refluxed for 3 h (TLC monitoring – PE:MTBE = 5:1) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (80 silica gel, phase – a) PE:MTBE = 10:1; b) PE:MTBE = 5:1) to give 0.886 g (71%) pure **18** as red crystals. M.p. 81-82 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.20 (m, 2H, 17-H, 18-H), 7.15 (m, 1H, 15-H), 7.12 (m, 1H, 16-H), 7.10 (s, 1H, 20-H), 4.60 (d, 1H, 11-H_a, *J* = 15.4 Hz), 4.56 (d, 1H, 11-H_b, *J* = 15.4 Hz), 4.51 (td, 1H, 22-H, *J* = 2.5, 1.2 Hz), 4.50 (td, 1H, 25-H, *J* = 2.5, 1.2 Hz), 4.44* (dt, 1H, 23-H or 24-H, *J* = 2.5, 1.2 Hz), 4.42* (dt, 1H, 23-H or 24-H, *J* = 2.5, 1.2 Hz), 4.14 (s, 5H, Cp), 3.68 (td, 1H, 12-H_a, *J* = 11.9, 5.9 Hz), 3.62 (td, 1H, 12-H_b, *J* = 11.9, 5.9 Hz), 3.55 (d, 1H, 10-H_a, *J* = 14.7 Hz), 3.00 (br t, 2H, 13-H, *J* = 5.9 Hz), 2.92 (m, 1H, 4-H), 2.91 (d, 1H, 10-H_b, *J* = 14.7 Hz), 2.63 (ddd, 1H, 6-H_{exo}, *J* = 14.0, 11.5, 3.7 Hz), 2.21 (tt, 1H, 5-H_{exo}, *J* = 11.5, 4.7 Hz), 1.73 (ddd, 1H, 6-H_{endo}, *J* = 14.0, 9.3, 4.7 Hz), 1.56 (m, 1H, 5-H_{endo}), 1.18 (s, 3H, 9-H), 0.86 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 203.71 (1C, 2-C), 136.38 (1C, 3-C), 133.38 (1C, 14-C), 132.12 (1C, 19-C), 130.06 (1C, 20-C), 128.99 (1C, 15-C), 126.75 (1C, 12-C), 126.38* (1C, 17-C or 18-C), 126.33* (1C, 17-C or 18-C), 78.23 (1C, 21-C), 71.59 (1C, 22-C), 70.89 (2C, 23-C, 24-C), 69.43 (5C, Cp), 69.04 (1C, 25-C), 57.58 (1C, 1-C), 49.07 (1C, 4-C), 47.68 (1C, 7-C), 47.08 (1C, 11-C), 45.74 (1C, 10-C), 43.37 (1C, 12-C), 29.17 (1C, 13-C), 26.09 (1C, 6-C), 25.58 (1C, 5-C), 20.63 (1C, 8-C), 19.39 (1C, 9-C). MS (CI) *m/z* (rel. int.): 545 (20, M+2), 544 (57 (M+1), 543 (100, M), 412 (25), 411 (91, M-tetrahydroisoquinoline), 347 (35, M-FcCHO). Anal. calcd. for $C_{30}H_{33}FeNO_3S$ (543.50): C, 66.30; H, 6.12; Fe, 10.28; N, 2.58; S, 5.90. Found: C, 66.22; H, 6.17; Fe, 10.34; N, 2.59; S, 5.94 %.

(1*R*,5*R*)-*3*-((((1*S*,4*S*)-3-((*E*)-ferrocenylmethylidene)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)sulfonyl)-1,2,3,4,5,6-hexahydro-8*H*-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (19):



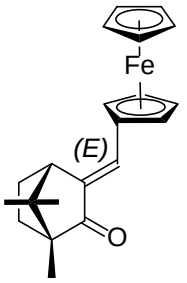
To a solution of 0.500 g (1.24 mmol) **12** and 0.265 g (1.24 mmol) ferrocenecarbaldehyde (**14**) in 30 ml dry toluene were added powdered KOH (0.195 g, 3.48) and a crystal of 18-crown-6. The mixture was refluxed for 1.5 h (TLC monitoring – DCM:MeOH = 50:1) and cooled. The solvent was evaporated *in vacuo* without workup and crude product was purified by column chromatography (70 silica gel, phase –a) DCM:MTBE = 10:1; b) DCM:MeOH = 50:1) to give 0.684 g (92%) pure **19** as deep red crystals. M.p. 265-270 °C (with decomp.). ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.29 (dd, 1H, 19-H, *J* = 9.1, 6.8 Hz), 7.08 (s, 1H, 22-H), 6.46 (dd, 1H, 20-H, *J* = 9.1, 1.2 Hz), 6.06 (dd, 1H, 18-H, *J* = 6.8, 1.2 Hz), 4.51 (m, 1H, 24-H), 4.48 (m, 1H, 27-H), 4.43 (m, 1H, 26-H), 4.41 (dt, 1H, 25-H, *J* = 2.5, 1.2 Hz), 4.18 (br d, 1H, 16-H_a, *J* = 15.6 Hz), 4.14 (s, 5H, Cp), 3.96 (m, 1H, 16-H_b), 3.93 (m, 1H, 15-H_a), 3.85 (m, 1H, 11-H_a), 3.31 (d, 1H, 10-H_a, *J* = 14.7 Hz), 3.26 (m, 1H, 15-H_b), 3.19 (dd, 1H, 11-H_b, *J* = 11.7, 2.1 Hz), 3.13 (br s, 1H, 14-H), 2.88 (br d, 1H, 4-H, *J* = 4.2 Hz), 2.67 (d, 1H, 10-H_b, *J* = 14.7 Hz), 2.60 (br s, 1H, 12-H), 2.37 (m, 1H, 6-H_{exo}), 2.13 (tt, 1H, 5-H_{exo}, *J* = 11.9, 4.2 Hz), 2.04 (m, 1H, 13-H_a), 1.95 (m, 1H, 13-H_b), 1.54 (dt, 1H, 6-H_{endo}, *J* = 9.2, 5.0 Hz), 1.48 (m, 1H, 5-H_{endo}), 1.06 (s, 3H, 9-H), 0.80 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 203.46 (1C, 2-C), 163.26 (1C, 21-C), 148.45 (1C, 17-C), 138.67 (1C, 19-C), 136.32 (1C, 3-C), 130.05 (1C, 22-C), 117.67 (1C, 20-C), 105.31 (1C, 18-C), 78.16 (1C, 23-C), 71.57 (1C, 24-C), 70.91* (1C, 25-C or 26-C), 70.89* (1C, 25-C or 26-C), 69.41 (5C, Cp), 69.02 (1C, 27-C), 57.38 (1C, 1-C), 52.77 (1C, 15-C), 51.56 (1C, 11-C), 48.98 (1C, 4-C), 48.82 (1C, 16-C), 47.70 (1C, 7-C), 46.26 (1C, 10-C), 34.38 (1C, 14-C), 27.13 (1C, 12-C), 25.97 (1C, 6-C), 25.52 (1C, 5-C), 25.31 (1C, 13-C), 20.55 (1C, 8-C), 19.12 (1C, 9-C). MS (CI) *m/z* (rel. int.): 603 (15, M+3), 602 (36, M+2), 601 (100, M+1), 600 (68, M), 536 (18), 535 (54), 411 (40). Anal. calcd. for $C_{32}H_{36}FeN_2O_4S$ (600.55): C, 64.00; H, 6.04; Fe, 9.30; N, 4.66; S, 5.34. Found: C, 64.07; H, 6.08; Fe, 9.33; N, 4.60; S, 5.31 %.

_N_-adamantan-1-yl-1-((1_S_,4_S_)-3-((_E_)-ferrocenylmethylidene)-7,7-dimethyl-2-oxobicyclo[2.2.1] heptan-1-yl)methanesulfonamide (20):



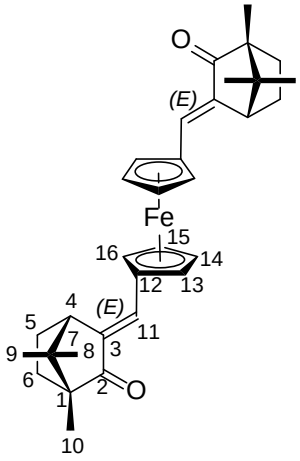
To a solution of 0.700 g (1.92 mmol) **13** and 0.410 g (1.92 mmol) ferrocenecarbaldehyde (**14**) in 30 ml dry toluene were added powdered KOH (0.195 g, 3.48) and a crystal of 18-crown-6. The mixture was refluxed for 2 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (70 silica gel, phase DCM) to give 0.830 g (77%) pure **20** as red crystals. M.p. >220 °C (with decomp.). ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.13 (s, 1H, 15-H), 5.54 (br s, 1H, NH), 4.50-4.52 (m, 2H, 17-H, 20-H), 4.45* (m, 1H, 18-H or 19-H), 4.43* (dt, 1H, 18-H or 19-H, *J* = 2.5, 1.3 Hz), 4.15 (s, 5H, Cp), 3.59 (d, 1H, 10-H_a, *J* = 15.0 Hz), 3.08 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.93 (br d, 1H, 4-H, *J* = 4.0 Hz), 2.32 (m, 1H, 6-H_{exo}), 2.17 (m, 1H, 5-H_{exo}), 2.12 (m, 3H, 13-H), 2.06 (m, 6H, 12-H), 2.03 (m, 1H, 6-H_{endo}), 1.68 (m, 6H, 14-H), 1.56 (m, 1H, 5-H_{endo}), 1.06 (s, 3H, 9-H), 0.89 (s, 3H, 8-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 204.84 (1C, 2-C), 136.51 (1C, 3-C), 130.68 (1C, 15-C), 78.08 (1C, 16-C), 71.83* (1C, 17-C or 20-C), 71.03* (1C, 18-C or 19-C), 71.00* (1C, 18-C or 19-C), 69.47 (5C, Cp), 68.89* (1C, 17-C or 20-C), 58.72 (1C, 1-C), 55.43 (1C, 11-C), 54.82 (1C, 10-C), 48.93 (1C, 4-C), 48.24 (1C, 7-C), 43.15 (3C, 12-C), 36.01 (3C, 14-C), 29.66 (3C, 13-C), 27.77 (1C, 6-C), 25.62 (1C, 5-C), 20.79 (1C, 8-C), 18.94 (1C, 9-C). MS (CI) *m/z* (rel. int.): 562 (44, M+1), 411 (100, M-adamantylamine). Anal. calcd. for $C_{31}H_{39}FeNO_3S$ (561.56): C, 66.30; H, 7.00; Fe, 9.94; N, 2.49; S, 5.71. Found: C, 66.35; H, 7.10; Fe, 9.91; N, 2.42; S, 5.70 %.

(1*R*,4*S*)-3-((*E*)-ferrocenylmethylidene)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (23):



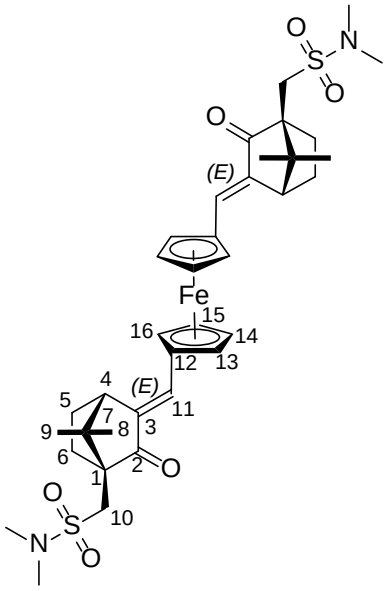
For preparation and analytical data of this compound see reference [2].

(1*R*,1'*R*,3*E*,3'*E*,4*S*,4'*S*)-3,3'-(ferrocene-1,1`-diylbis(methaneylylidene))bis(1,7,7-trimethylbicyclo [2.2.1]heptan-2-one) (24):



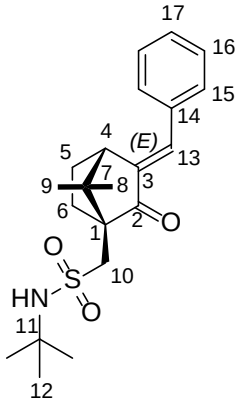
To a solution of (+)-camphor (0.686 g, 4.51 mmol) and 1,1`-ferrocenedicarboxaldehyde (**22**) (0.500 g, 2.25 mmol) in anhydrous toluene (30 ml), were added KOH (0.258 g, 4.51 mmol) and a crystal of 18-crown-6. The mixture was refluxed for 2 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (70 silica gel, phase DCM:MTBE = 100:1) to give 0.468 g (40%) pure **24** as dark red crystals. M.p. 237-238 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 6.96 (s, 2H, 11-H), 4.46* (m, 2H, 13-H or 16-H), 4.44* (m, 2H, 13-H or 16-H), 4.36* (m, 2H, 14-H or 15-H), 4.33* (dt, 2H, 14-H or 15-H, *J* = 2.5, 1.3 Hz), 2.88 (br d, 2H, 4-H, *J* = 4.1 Hz), 2.10 (tt, 2H, 5-H$_{exo}$, *J* = 11.6, 4.1 Hz), 1.75 (ddd, 2H, 6-H$_{exo}$, *J* = 12.8, 11.6, 3.5 Hz), 1.51 (dt, 2H, 6-H$_{endo}$, *J* = 9.0, 4.9 Hz), 1.46 (m, 2H, 5-H$_{endo}$), 1.01 (s, 6H, 10-C), 0.99 (s, 6H, 8-H), 0.81 (s, 6H, 9-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 207.23 (2C, 2-C), 139.66 (2C, 3-C), 126.44 (2C, 11-C), 80.07 (2C, 12-C), 72.21* (2C, 13-C or 16-C), 71.96* (2C, 14-C or 15-C), 71.76* (2C, 14-C or 15-C), 69.81* (2C, 13-C or 16-C), 57.12 (2C, 1-C), 49.30 (2C, 4-C), 46.41 (2C, 7-C), 30.64 (2C, 6-C), 25.70 (2C, 5-C), 20.66 (2C, 9-C), 18.37 (2C, 8-C), 9.30 (2C, 10-C). MS (CI) m/z (rel. int.): 511 (100, M+1). Anal. calcd. for $C_{32}H_{38}FeO_2$ (510.50): C, 75.29; H, 7.50; Fe, 10.94. Found: C, 75.20; H, 7.58; Fe, 10.99 %.

1,1'-((1*S*,1'*S*,3*E*,3'*E*,4*S*,4'*S*)-(ferrocene-1,1`-diylbis(methaneylylidene))bis(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl-3-ylidene))bis(*N*,*N*-dimethylmethanesulfonamide) (25):



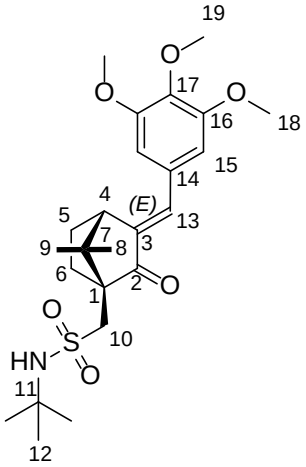
A mixture of **8** (0.200 g, 0.77 mmol), KOH (0.07 g, 1.17 mmol) and 18-crown-6 (0.02 g, 0.08 mmol) in 5 ml dry toluene was stirred for 30 min and **22** (0.094 g, 0.39 mmol) was added. The mixture was heated for 1 h at 120°C, then was cooled, quenched with water and extracted with CH_2Cl_2 (3x10 ml). The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography (50 g silica gel, phase: hexane/MTBE = 5:1) to give 0.117 g (60%) of pure **25** as red crystals. $[\alpha]_D^{20}$ = -1071.1 (*c* 0.02, $CHCl_3$). M.p. 97-98 °C. ^{1}H NMR (600.1 MHz, $CDCl_3$, 293 K): δ = 6.99 (s, 2H, 11-H), 4.46-4.45 (m, 4H, 13-H, 16-H), 4.39-4.38* (m, 2H, 14-H), 4.37-4.36* (m, 2H, 15-H), 3.43 (d, 2H, 10-H_a, *J* = 14.6 Hz), 2.94 (s, 12H, SO_2NMe_2), 2.85 (d, 2H, 4-H, *J* = 3.4 Hz), 2.84 (d, 2H, 10-H_b, *J* = 14.6 Hz), 2.61 (ddd, 2H, 6-H_{exo}, *J* = 14.7, 11.5, 4.9 Hz), 2.22-2.16 (m, 2H, 5-H_{exo}), 1.72-1.68 (m, 2H, 6-H_{endo}), 1.53-1.49 (m, 2H, 5-H_{endo}), 1.17 (s, 6H, 9-H), 0.85 (s, 6H, 8-H). ^{13}C NMR (150.9 MHz, $CDCl_3$, 293 K): δ = 203.58 (2C, 2-C), 137.74 (2C, 3-C), 128.32 (2C, 11-C), 79.56 (2C, 12-C), 72.68* (2C, 16-C), 72.39* (2C, 13-C), 72.24* (2C, 14-C), 69.73* (2C, 15-C), 57.44 (2C, 1-C), 49.11 (2C, 4-C), 47.64 (2C, 7-C), 43.69 (2C, 10-C), 37.52 (4C, SO_2NMe_2), 25.95 (2C, 6-C), 25.55 (2C, 5-C), 20.57 (2C, 9-C), 19.32 (2C, 8-C). MS (CI) m/z (rel. int.): 725 (60, M+1), 680 (100, M-Me_2N). Anal. calcd. for $C_{36}H_{48}FeN_2O_6S_2$ (724.75): C, 59.66; H, 6.68; Fe, 7.71; N, 3.87; S, 8.85. Found: C, 59.60; H, 6.73; Fe, 7.66; N, 3.89; S, 8.82 %.

1-((1*S*,4*S*)-3-((*E*)-benzylidene)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-(*tert*-butyl) methanesulfonamide (29):



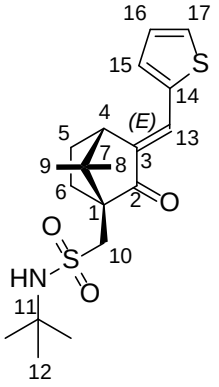
To a solution of **9** (0.200 g, 0.70 mmol) and benzaldehyde (**26**) (0.074 g, 0.70 mmol) in anhydrous toluene (15 ml), were added KOH (0.078 g, 1.39 mmol) and a crystal of 18-crown-6. The mixture was refluxed for 3 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (50 silica gel, phase DCM) to give 0.173 g (77%) pure **29** as white crystals. M.p. 84-85 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.48 (m, 2H, 15-H), 7.42 (m, 2H, 16-H), 7.37 (m, 1H, 17-H), 7.30 (s, 1H, 13-H), 5.41 (s, 1H, NH), 3.61 (d, 1H, 10-H_a, *J* = 15.0 Hz), 3.13 (d, 1H, 4-H, *J* = 4.2 Hz), 3.08 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.40 (m, 1H, 6-H_{exo}), 2.26 (tt, 1H, 5-H_{exo}, *J* = 11.6, 4.7 Hz), 2.04 (ddd, 1H, 6-H_{endo}, *J* = 14.1, 9.3, 4.7 Hz), 1.69 (m, 1H, 5-H_{endo}), 1.45 (s, 9H, 12-H), 1.08 (s, 3H, 8-H), 0.87 (s, 3H, 9-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 205.68 (1C, 2-C), 140.33 (1C, 3-C), 134.96 (1C, 14-C), 129.89 (2C, 15-C), 129.70 (1C, 13-C), 129.28 (1C, 17-C), 128.79 (2C, 16-C), 58.55 (1C, 1-C), 54.94 (1C, 11-C), 53.88 (1C, 10-C), 48.80 (1C, 4-C), 48.48 (1C, 7-C), 30.29 (3C, 12-C), 27.39 (1C, 6-C), 25.86 (1C, 5-C), 20.63 (1C, 9-C), 18.83 (1C, 8-C). MS (ESI+) m/z (rel. int.): 398 (100, M+Na), 342 (40, M+Na-*t*-Bu). Anal. calcd. for $C_{21}H_{29}NO_3S$ (375.53): C, 67.17; H, 7.78; N, 3.73; S, 8.54. Found: C, 67.12; H, 7.72; N, 3.79; S, 8.59 %.

_N_-(_tert_-butyl)-1-((1_S_,4_S_)-7,7-dimethyl-2-oxo-3-((_E_)-3,4,5-trimethoxybenzylidene)bicyclo [2.2.1]heptan-1-yl)methanesulfonamide (30):



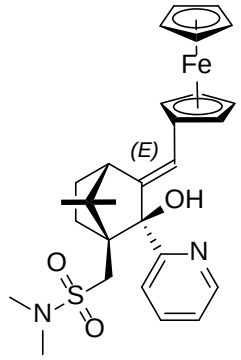
To a solution of **9** (0.200 g, 0.70 mmol) and 3,4,5-trimethoxybenzaldehyde (**27**) (0.137 g, 0.70 mmol) in anhydrous toluene (15 ml), were added KOH (78 mg, 1.39 mmol) and a crystal of 18-crown-6. The mixture was refluxed for 3 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (50 silica gel, phase DCM:MTBE = 50:1) to give 0.200 g (62%) pure **30** as white crystals. M.p. 64-65 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.22 (s, 1H, 13-H), 6.71 (s, 2H, 15-H), 5.42 (br s, 1H, NH), 3.89 (br s, 9H, 18-H, 19-H), 3.61 (d, 1H, 10-H_a, J = 15.0 Hz), 3.10 (overlapped m, 1H, 4-H), 3.08 (d, 1H, 10-H_b, J = 15.0 Hz), 2.41 (m, 1H, 6-H_{exo}), 2.27 (m, 1H, 5-H_{exo}), 2.04 (ddd, 1H, 6-H_{endo}, J = 14.0, 9.3, 4.8 Hz), 1.70 (m, 1H, 5-H_{endo}), 1.45 (s, 9H, 12-H), 1.09 (s, 3H, 8-H), 0.89 (s, 3H, 9-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 205.42 (1C, 2-C), 153.29 (2C, 16-C), 139.48 (1C, 3-C), 139.30 (1C, 17-C), 130.41 (1C, 14-C), 129.94 (1C, 13-C), 107.18 (2C, 15-C), 60.96 (1C, 19-C), 58.44 (1C, 1-C), 56.13 (2C, 18-C), 54.93 (1C, 11-C), 53.85 (1C, 10-C), 48.99 (1C, 4-C), 48.57 (1C, 7-C), 30.28 (3C, 12-C), 27.42 (1C, 6-C), 25.70 (1C, 5-C), 20.62 (1C, 9-C), 18.89 (1C, 8-C). MS (ESI+) m/z (rel. int.): 488 (100, M+Na), 432 (14, M+Na-_t_-Bu). Anal. calcd. for $C_{24}H_{35}NO_6S$ (465.60): C, 61.91; H, 7.58; N, 3.01; S, 6.89. Found: C, 61.98; H, 7.54; N, 2.97; S, 6.83 %.

_N_-(_tert_-butyl)-1-((1_S_,4_S_,_E_)-7,7-dimethyl-2-oxo-3-(thiophen-2-ylmethylene)bicyclo[2.2.1]heptan-1-yl)methanesulfonamide (31):



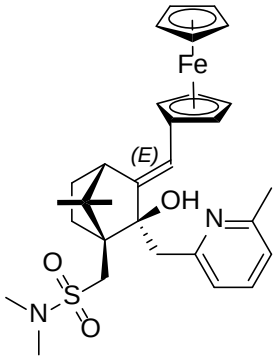
To a solution of **9** (0.200 g, 0.70 mmol) and thiophene-2-carbaldehyde (**28**) (0.078 g, 0.70 mmol) in anhydrous toluene (15 ml), were added KOH (78 mg, 1.39 mmol) and a crystal of 18-crown-6. The mixture was refluxed for 3 h (TLC monitoring – DCM) and cooled. 30 ml Et_2O was added, washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and crude product was purified by column chromatography (50 silica gel, phase DCM) to give 0.162 g (61%) pure **31** as white crystals. M.p. 76-77 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$, 293 K): δ = 7.49 (d, 1H, 17-H, *J* = 5.0 Hz), 7.44 (s, 1H, 13-H), 7.30 (d, 1H, 15-H, *J* = 3.4 Hz), 7.11 (dd, 1H, 16-H, *J* = 5.0, 3.4 Hz), 5.47 (s, 1H, NH), 3.60 (d, 1H, 10-H_a, *J* = 15.0 Hz), 3.20 (d, 1H, 4-H, *J* = 4.0 Hz), 3.07 (d, 1H, 10-H_b, *J* = 15.0 Hz), 2.36 (m, 1H, 6-H_{exo}), 2.22 (tt, 1H, 5-H_{exo}, *J* = 11.6, 4.7 Hz), 2.01 (ddd, 1H, 6-H_{endo}, *J* = 14.1, 9.3, 4.7 Hz), 1.56 (ddd, 1H, 5-H_{endo}, *J* = 12.7, 9.3, 3.7 Hz), 1.44 (s, 9H, 12-H), 1.09 (s, 3H, 8-H), 0.90 (s, 3H, 9-H). ^{13}C NMR (150.92 MHz, $CDCl_3$, 293 K): δ = 205.40 (1C, 2-C), 138.75 (1C, 3-C), 137.78 (1C, 14-C), 132.83 (1C, 15-C), 129.47 (1C, 17-C), 127.89 (1C, 16-C), 122.54 (1C, 13-C), 58.82 (1C, 1-C), 54.92 (1C, 11-C), 53.93 (1C, 10-C), 49.25 (1C, 4-C), 48.60 (1C, 7-C), 30.28 (3C, 12-C), 27.81 (1C, 6-C), 25.59 (1C, 5-C), 20.65 (1C, 9-C), 18.90 (1C, 8-C). MS (ESI+) m/z (rel. int.): 404 (100, M+Na), 348 (13, M+Na-*t*-Bu). Anal. calcd. for $C_{19}H_{27}NO_3S_2$ (381.55): C, 59.81; H, 7.13; N, 3.67; S, 16.81. Found: C, 59.89; H, 7.19; N, 3.62; S, 16.76 %.

1-((1*S*,2*R*,4*S*)-3-((*E*)-ferrocenylmethylidene)-2-hydroxy-7,7-dimethyl-2-(pyridin-2-yl)bicyclo[2.2.1]heptan-1-yl)-*N*,*N*-dimethylmethanesulfonamide (35):



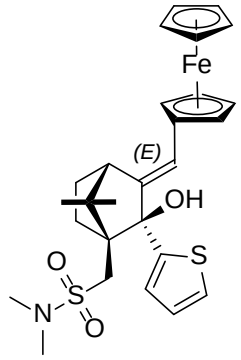
For preparation and analytical data of this compound see references [1].

1-((1*S*,2*R*,4*S*)-3-((*E*)-ferrocenylmethylidene)-2-hydroxy-7,7-dimethyl-2-((6-methylpyridin-2-yl)methyl)bicyclo[2.2.1]heptan-1-yl)-*N*,*N*-dimethylmethanesulfonamide (36):



For preparation and analytical data of this compound see references [2].

1-((1*S*,2*R*,4*S*)-3-((*E*)-ferrocenylmethylidene)-2-hydroxy-7,7-dimethyl-2-(thiophen-2-yl)bicyclo[2.2.1]heptan-1-yl)-*N*,*N*-dimethylmethanesulfonamide (37):



For preparation and analytical data of this compound see references [1].

S3. Additional X-ray crystallographic data

Supplementary Table 1. Most important crystallographic and refinement details for compound **16**.

Crystal data	
Chemical formula	$C_{25}H_{33}FeNO_3S$
M_r	483.43
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	290
a, *b*, *c* (Å)	7.6676 (2), 10.8399 (4), 57.6299 (16)
V (Å^3)	4790.0 (3)
Z	8
Radiation type, λ (Å)	Mo *Kα*, 0.71073
μ (mm^{-1})	0.74
Crystal size (mm)	0.35 × 0.32 × 0.18
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan, *CrysAlis PRO* [8]
T_{min}, T_{max}	0.739, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26053, 10641, 8062
R_{int}	0.036
$(\sin\theta/\lambda)_{max}$ (Å^{-1}), $\theta_{max}/\theta_{min}$ (°)	0.679, 28.9/2.8
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.060, 0.152, 1.06
No. of reflections	10641
No. of parameters	648
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.61, −0.32
Absolute structure	Flack x determined using 2484 quotients [(I+)-(I-)]/[(I+)+(I-)] [9]
Absolute structure parameter	−0.006 (8)

Supplementary Table 2. Hydrogen-bond and weak interactions (CH…..O) geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N12*A*—H12*A*···O12	0.85	2.26	3.076 (13)	159
N12*B*—H12*E*···O11	0.86	2.58	3.054 (11)	116
C101—H10*B*···O11	0.97	2.35	2.855 (10)	112
C121—H12*I*···O31	0.96	2.42	3.048 (11)	123
C131—H13*H*···O21^{i}	0.96	2.56	3.165 (9)	121
C12*A*—H12*D*···O32*A*^{i}	0.96	2.08	2.94 (2)	148
C14*B*—H14*C*···O22*A*	0.96	2.44	3.09 (4)	125
C12*B*—H12*F*···O32*B*	0.96	2.36	3.02 (2)	126
C13*B*—H13*E*···O11	0.96	2.56	3.378 (15)	143
C13*B*—H13*F*···O22*B*^{i}	0.96	2.31	2.974 (16)	125

Symmetry code: (i) *x*+1, *y*, *z*.

S4. References

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[2] M. Kamenova-Nacheva, G.M. Dobrikov and V. Dimitrov, *Tetrahedron: Asymmetry*, 2016, **27**, 852-864.

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[4] A. Shaabani, E. Soleimani and A.H. Rezayan, *Tetrahedron Lett.*, 2007, **48**, 2185-2188.

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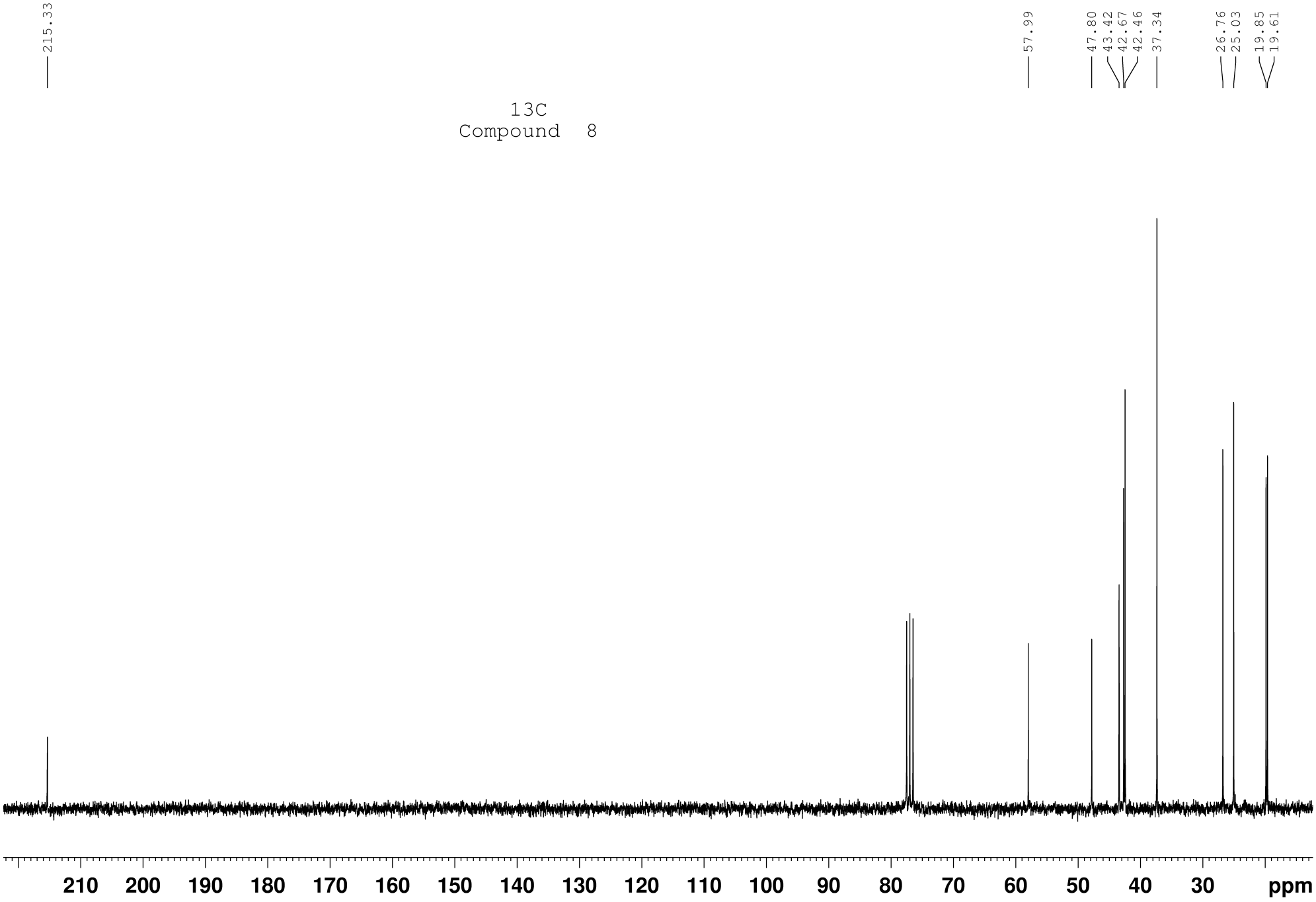
[6] P.D. Williams, P.S. Anderson, R.G. Ball, M.G. Bock, L. Carroll, S.H.L. Chiu, B.V. Clineschmidt, J. Chris Culberson, J.M. Erb, B.E. Evans, S.L. Fitzpatrick, R.M. Freidinger, M.J. Kaufman, G.F. Lundell, J.S. Murphy, J.M. Pawluczyk, D.S. Perlow, D.J. Pettibone, S.M. Pitzenberger, K.L. Thompson and D.F. Veber, *J. Med. Chem.*, 1994, **37**, 565-571.

[7] K. Ito and H. Tanaka, *Chem. Pharm. Bull.*, 1977, **25**, 1732-1739.

[8] Agilent Technologies, CrysalisPro Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET).

[9] S. Parsons, H. D. Flack and T. Wagner, *Acta Cryst.*, 2013, **B69**, 249-259.

S5. ^{1}H and ^{13}C NMR spectra of synthesized compounds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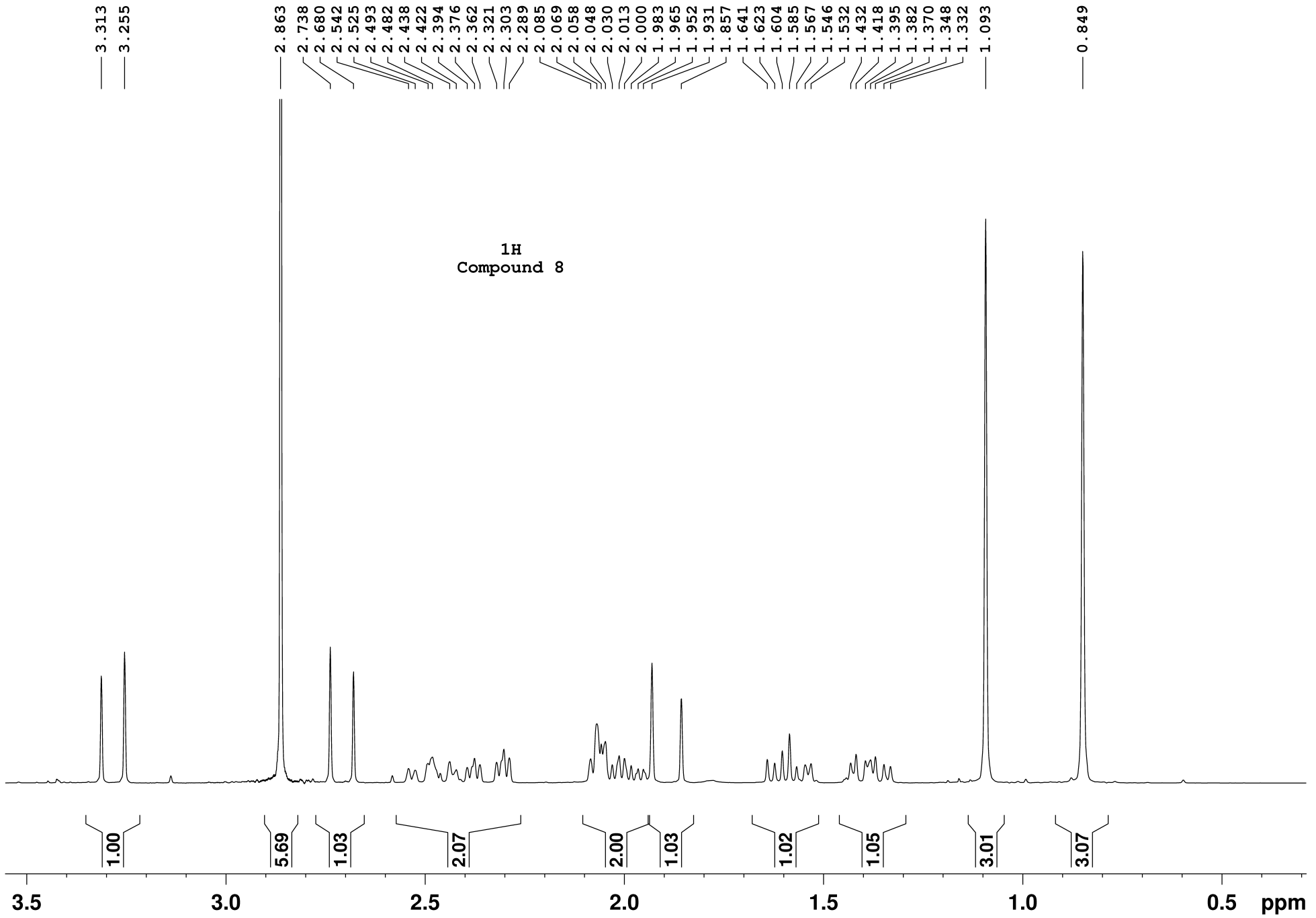
57.99
47.80
43.42
42.67
42.46
37.34
26.76
25.03
19.85
19.61
13C
Compound 8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm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3.255
2.863
2.738
2.680
2.542
2.525
2.493
2.482
2.438
2.422
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2.362
2.321
2.303
2.289
2.085
2.069
2.058
2.048
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2.013
2.000
1.983
1.965
1.952
1.931
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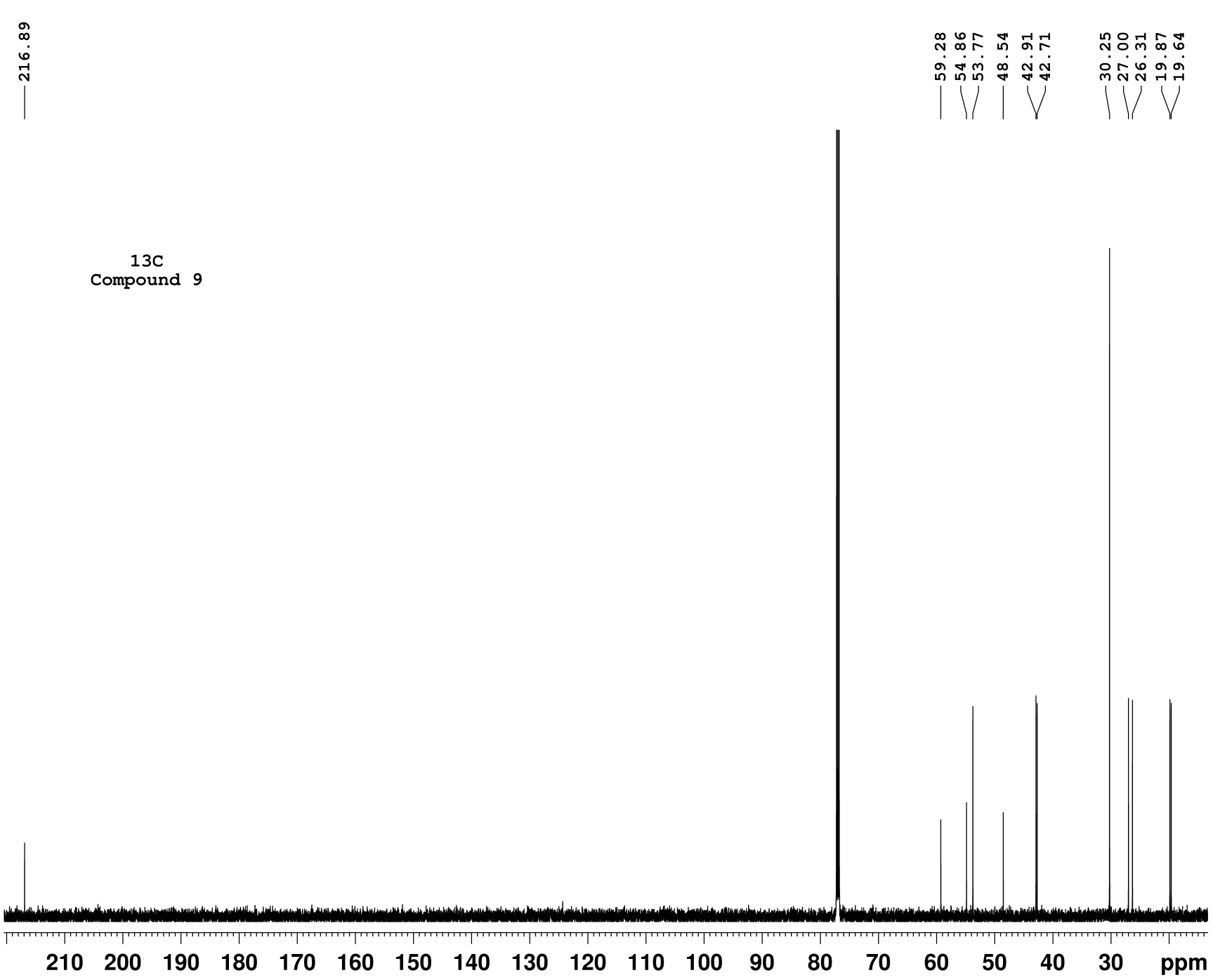
1.641
1.623
1.604
1.585
1.567
1.546
1.532
1.432
1.418
1.395
1.382
1.370
1.348
1.332
1.093
0.849
1H
Compound 8
1.00
5.69
1.03
2.07
2.00
1.03
1.02
1.05
3.01
3.07
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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53.77
48.54
42.91
42.71
30.25
27.00
26.31
19.87
19.64
13C
Compound 9
NAME DK-160-02
EXPNO 12
PROCNO 1
Date_ 20120110
Time 17.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDC13
NS 256
DS 0
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4544329 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 293.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
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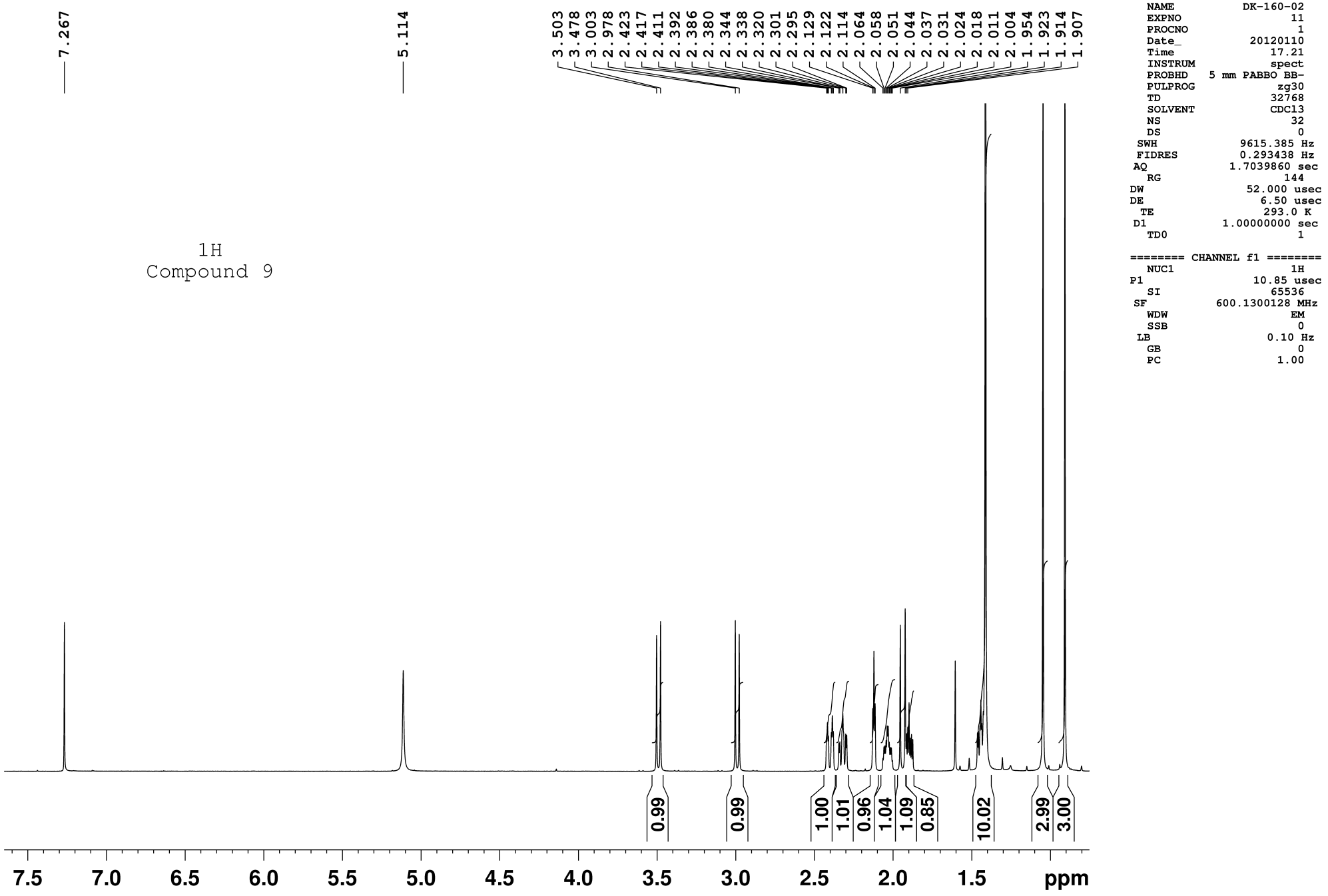
P1 10.75 usec
SI 65536
SF 150.9028161 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm



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TD	32768
SOLVENT	CDCl3
NS	32
DS	0
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FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

NUC1	1H
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SSB	0
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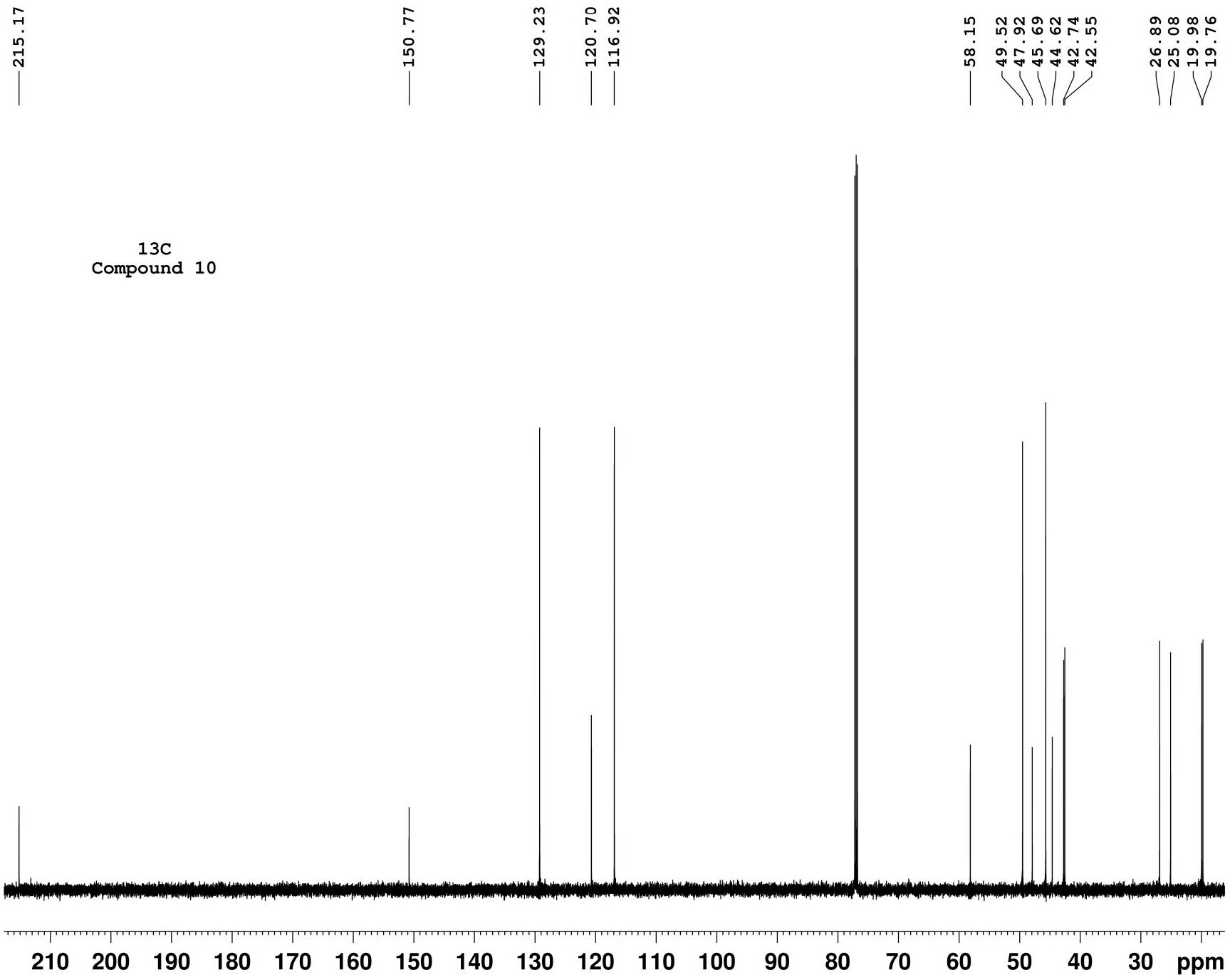
GB	0
PC	1.00



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TD0	1
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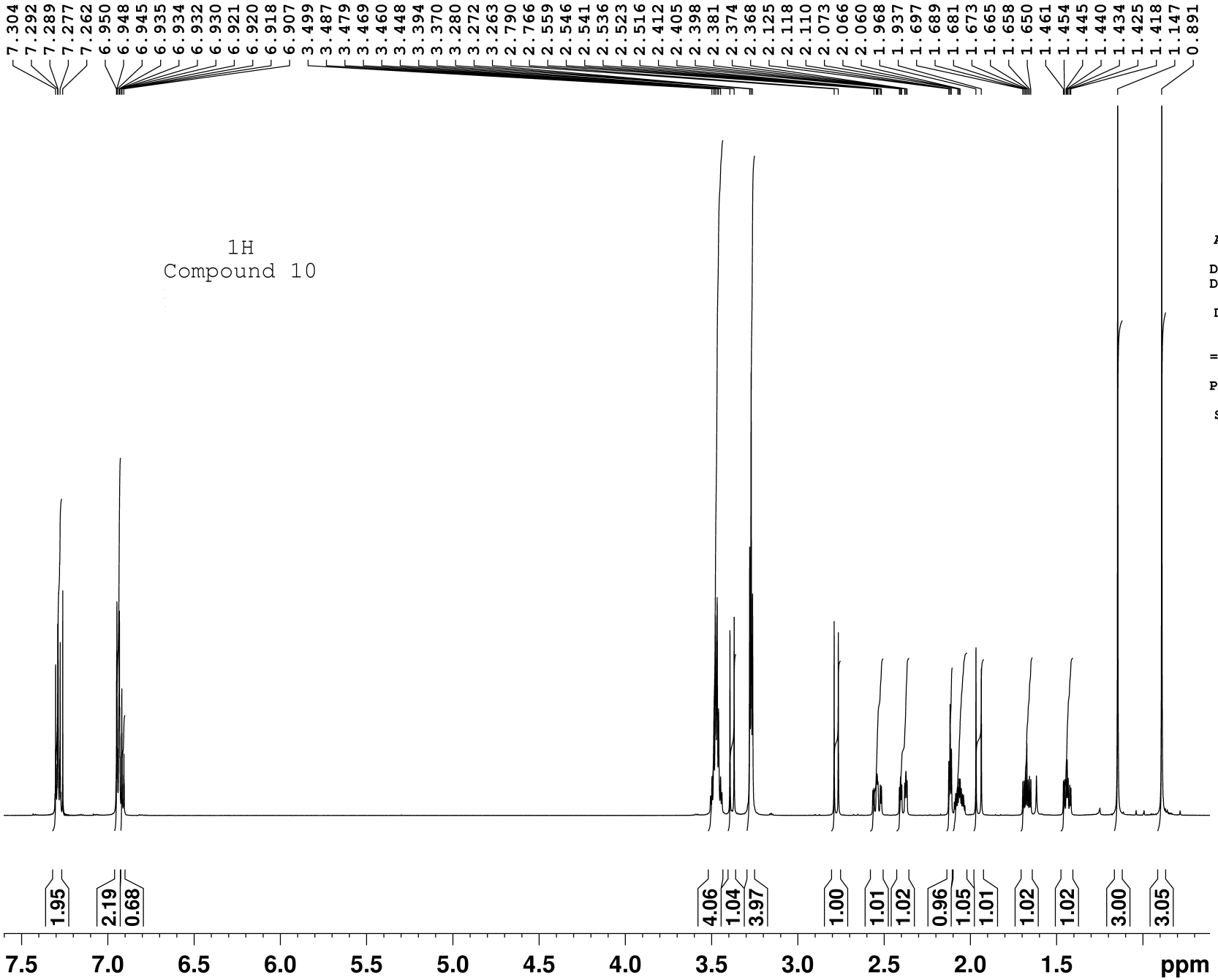
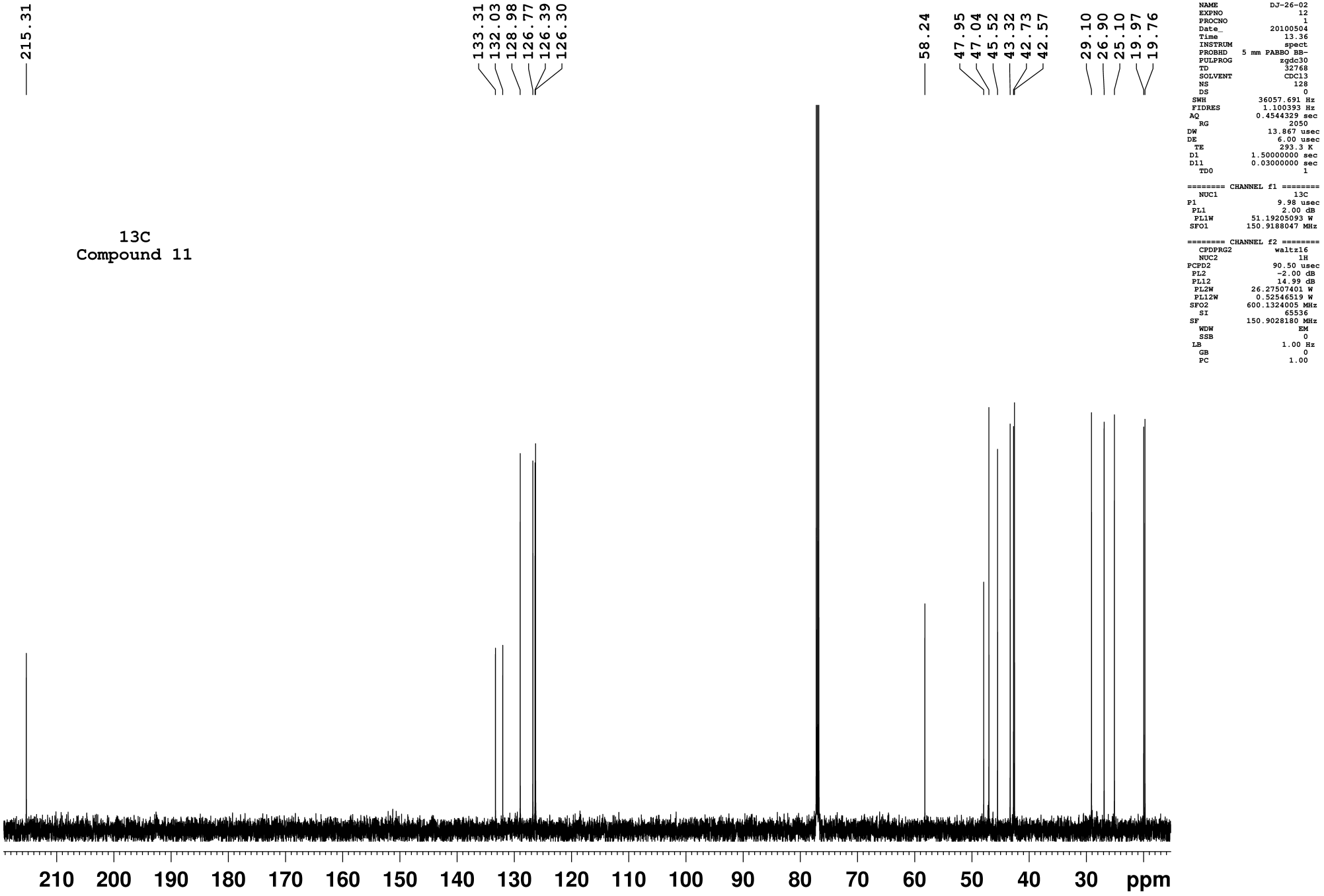
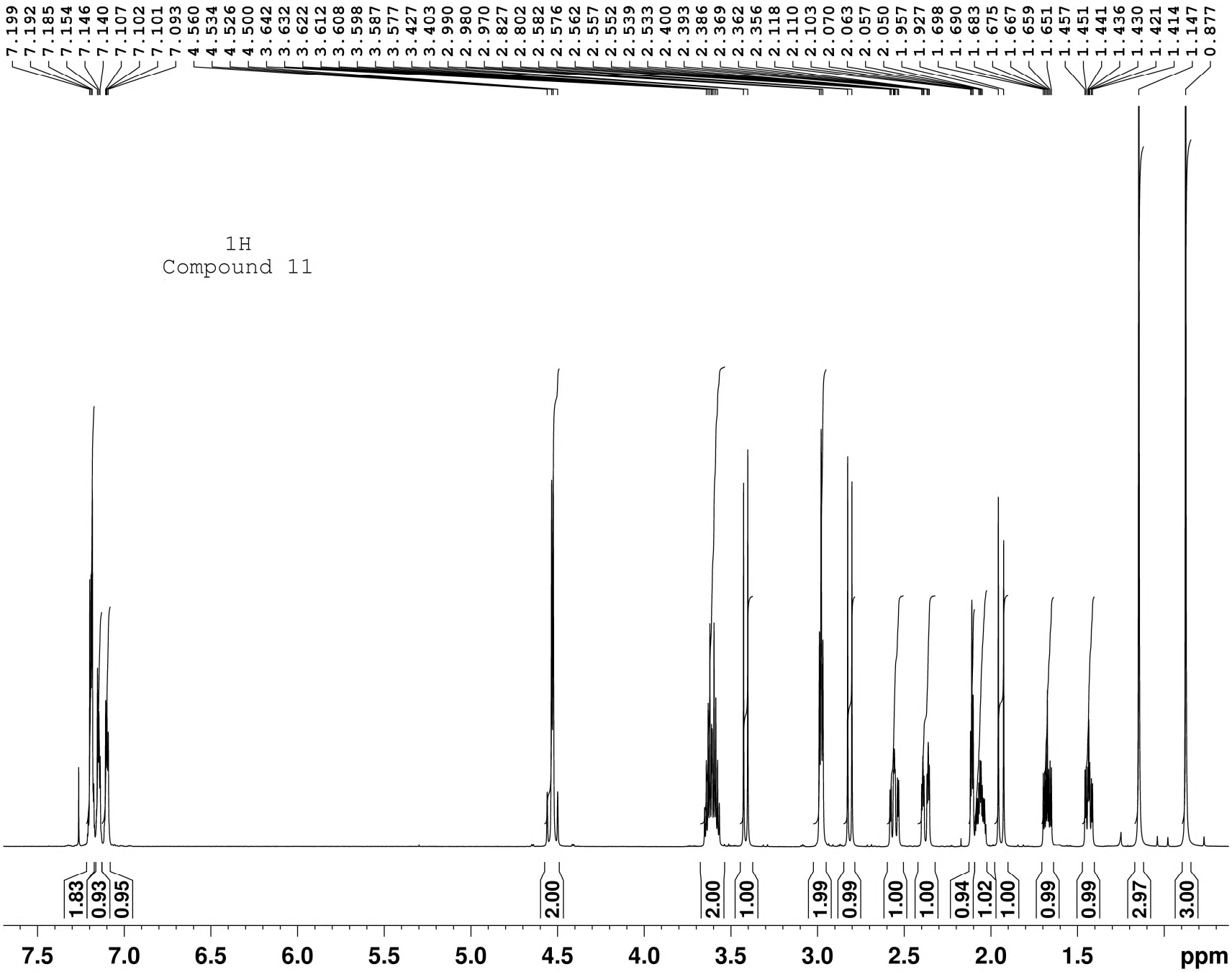
SI	65536
SF	150.9028180 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



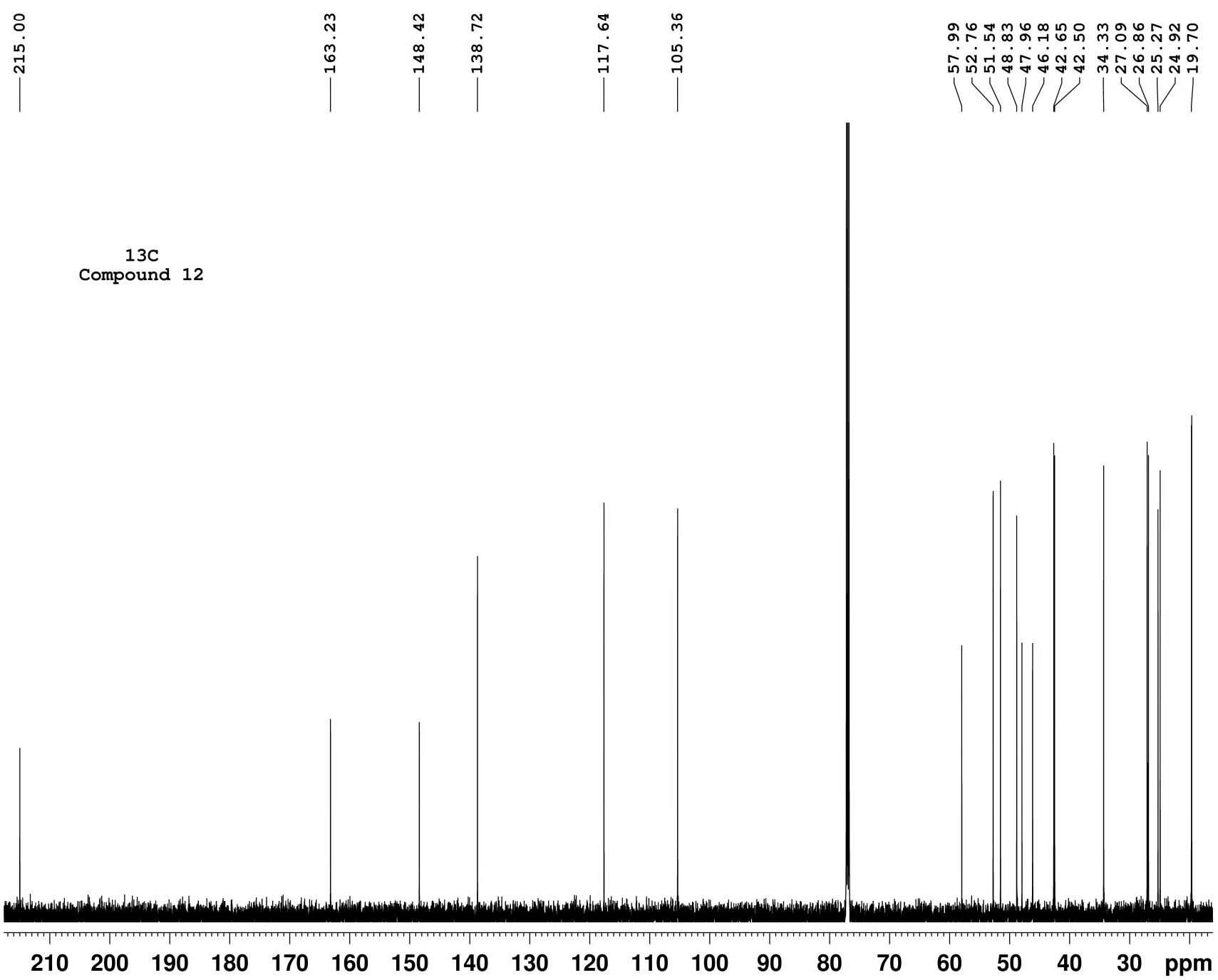
NAME	DG-199-02A
EXPNO	2
PROCNO	1
Date_	20111205
Time	14.15
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300157 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00



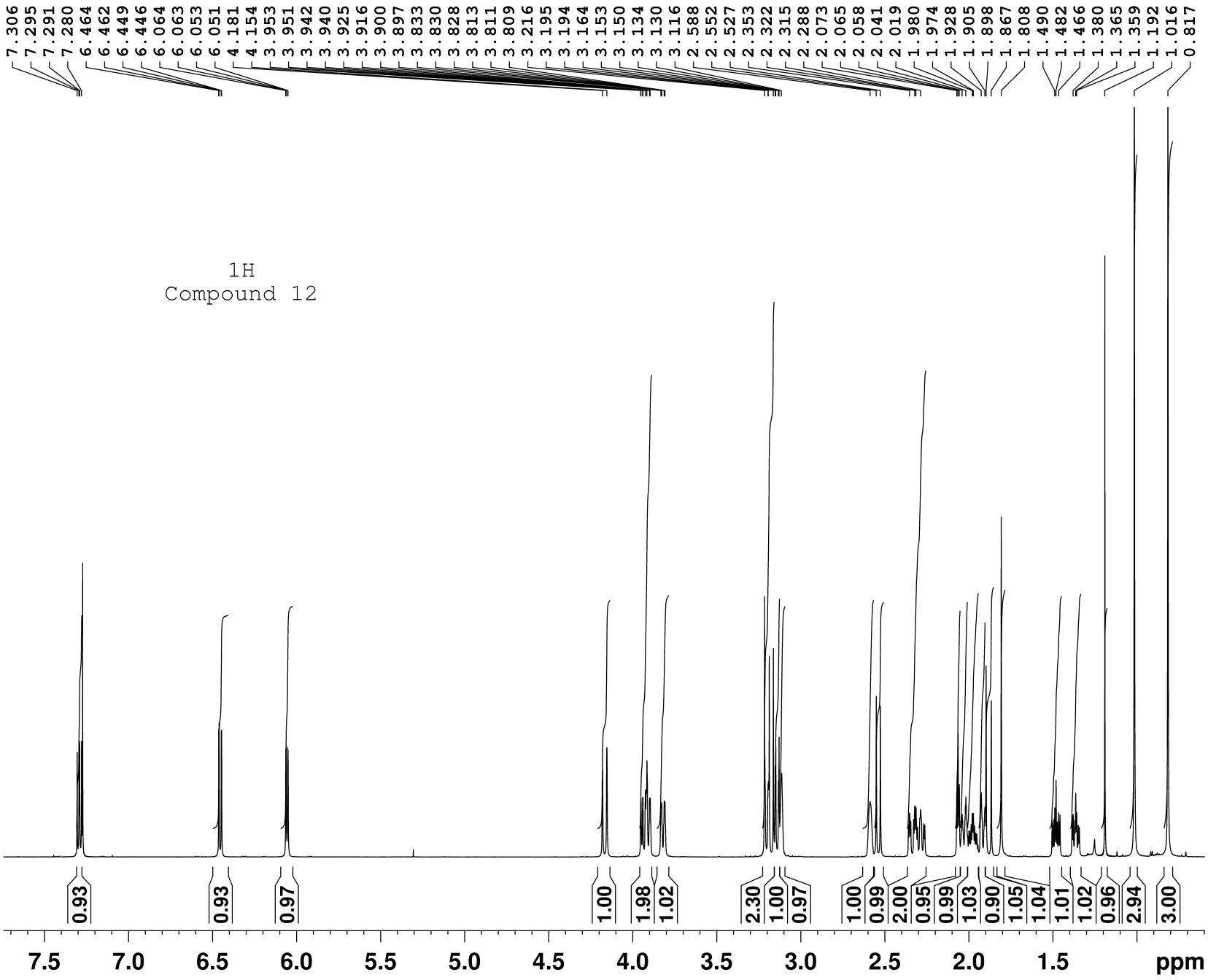
NAME	DJ-26-02
EXPNO	12
PROCNO	1
Date_	20100504
Time	13.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDC13
NS	128
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.00 usec
TE	293.3 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.98 usec
PL1	2.00 dB
PL1W	51.19205093 W
SFO1	150.9188047 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.50 usec
PL2	-2.00 dB
PL12	14.99 dB
PL2W	26.27507401 W
PL12W	0.52546519 W
SFO2	600.1324005 MHz
SI	65536
SF	150.9028180 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



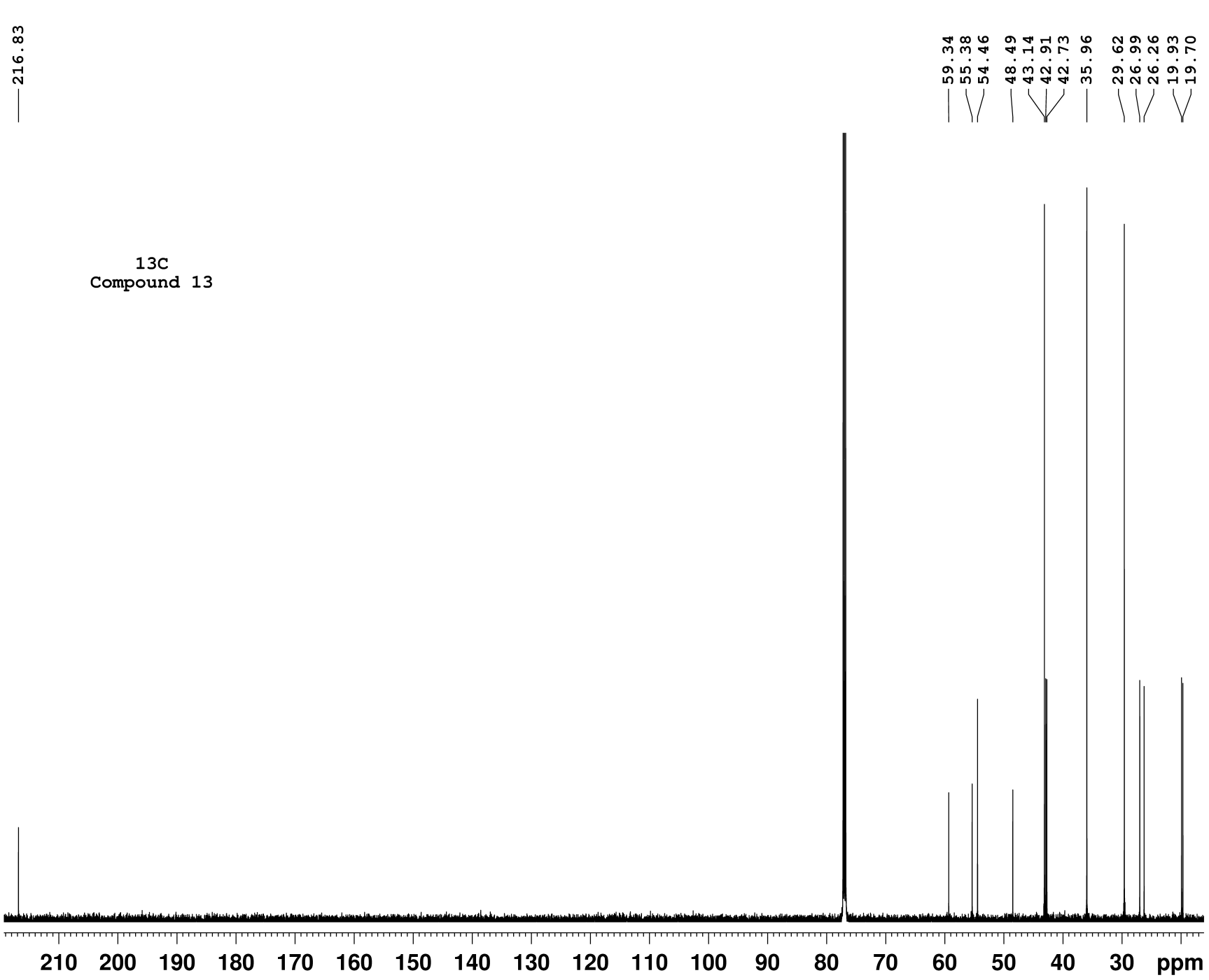
NAME	DJ-26-02
EXPNO	11
PROCNO	1
Date_	20100504
Time	13.35
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	161
DW	52.000 usec
DE	6.00 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.90 usec
PL1	-2.00 dB
PL1W	26.27507401 W
SFO1	600.1345610 MHz
SI	65536
SF	600.1300154 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

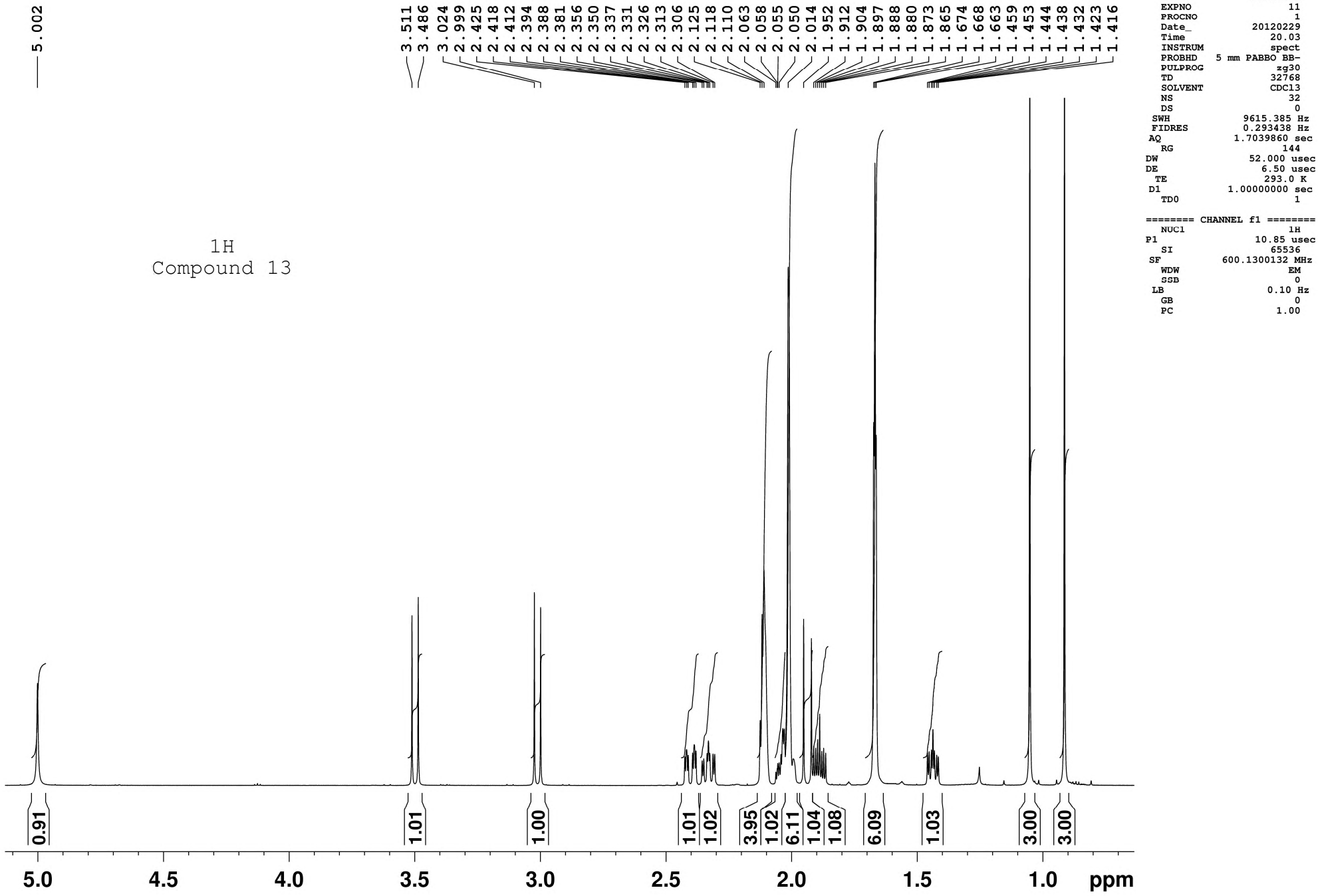


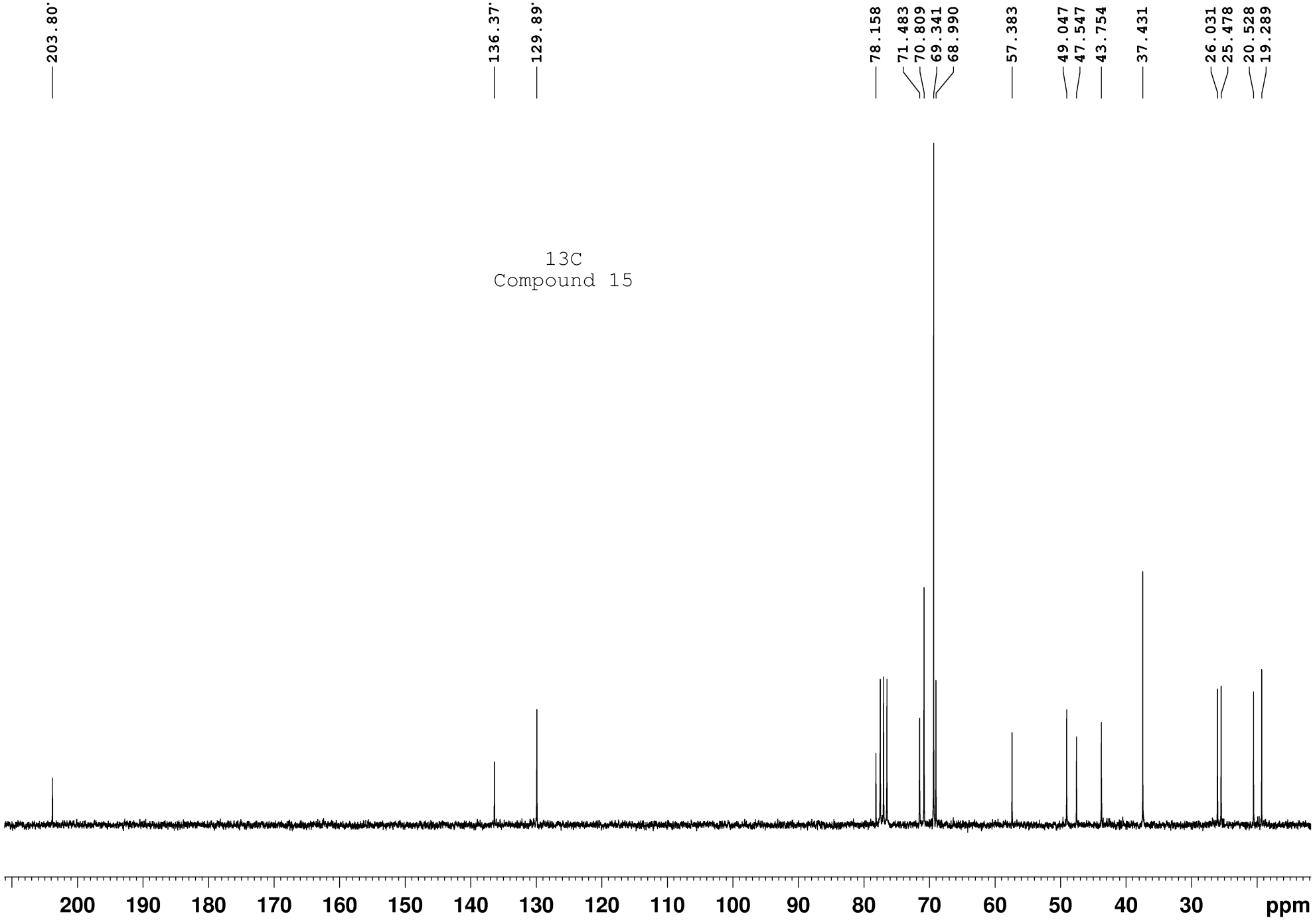
NAME	DK-133-02A
EXPNO	12
PROCNO	1
Date_	20111114
Time	11.48
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	360
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.1 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028180 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

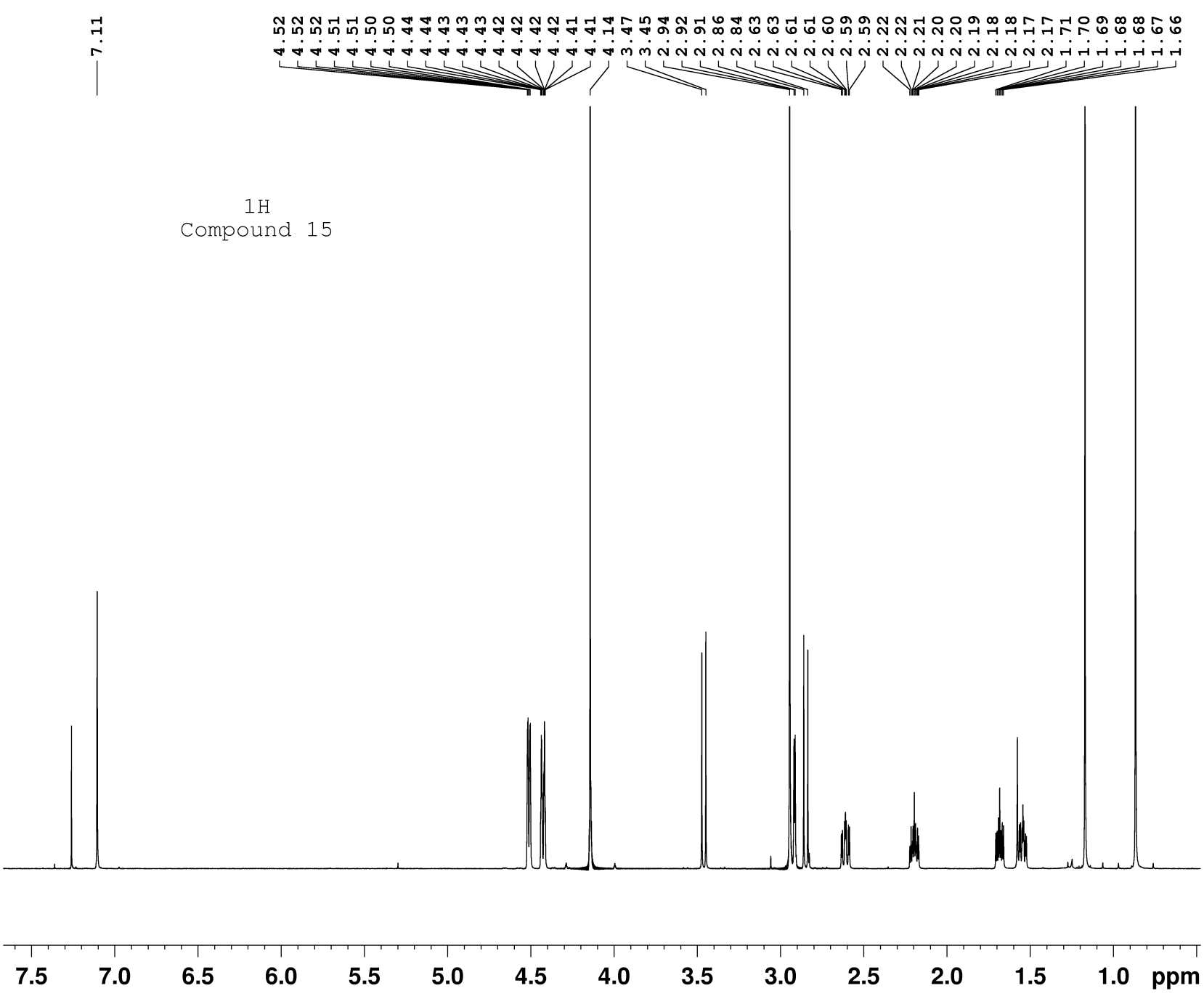


NAME	DK-133-02A
EXPNO	11
PROCNO	1
Date_	20111114
Time	11.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300091 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

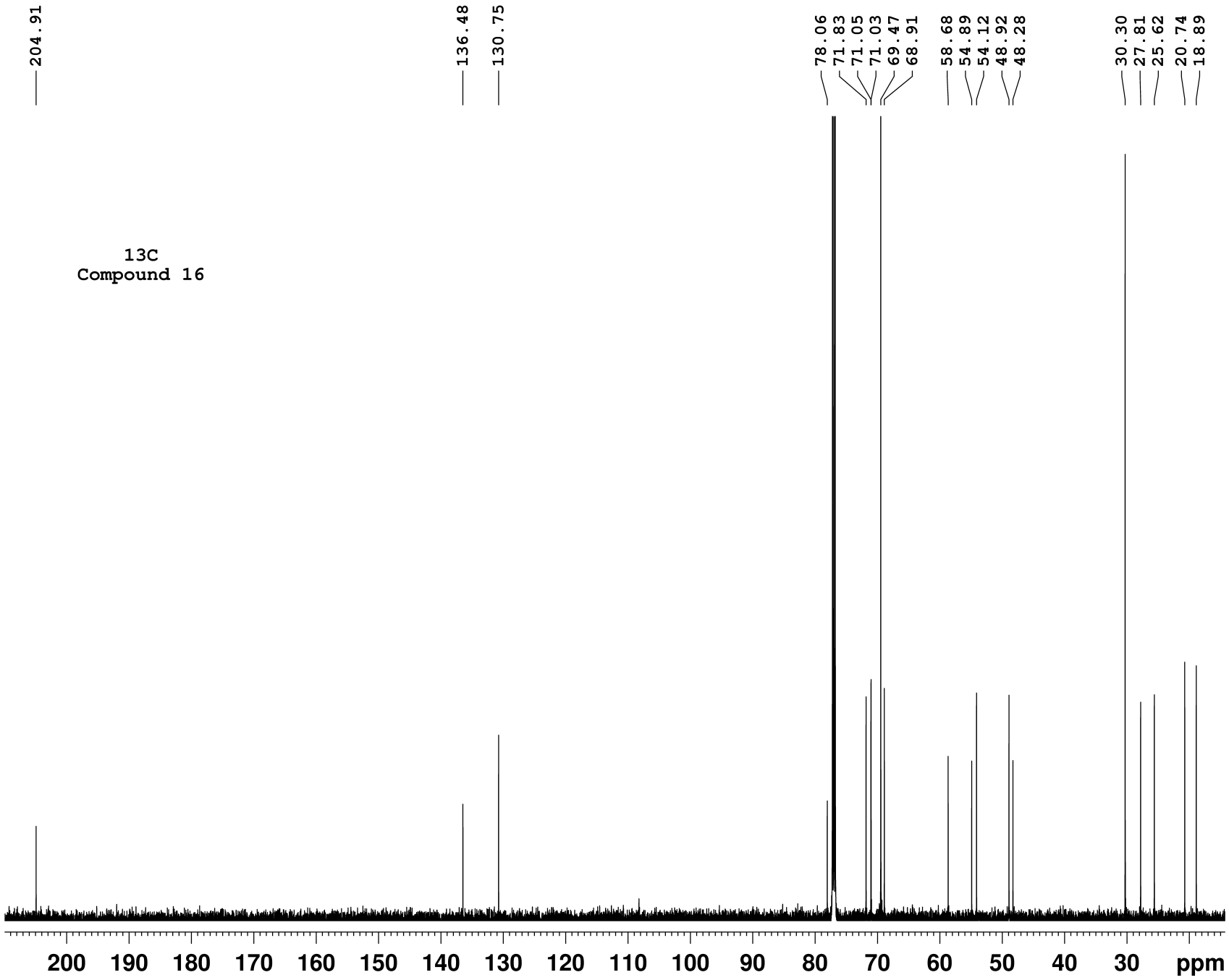

216.83
59.34
55.38
54.46
48.49
43.14
42.91
42.73
35.96
29.62
26.99
26.26
19.93
19.70
13C
Compound 13
NAME DK-173-A
EXPNO 12
PROCNO 1
Date_ 20120229
Time 20.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 512
DS 0
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4544329 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 293.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.75 usec
SI 65536
SF 150.9028158 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


5.002
3.511
3.486
3.024
2.999
2.425
2.418
2.412
2.394
2.388
2.381
2.356
2.350
2.337
2.331
2.326
2.313
2.306
2.125
2.118
2.110
2.063
2.058
2.055
2.050
2.014
1.952
1.912
1.904
1.897
1.888
1.880
1.873
1.865
1.674
1.668
1.663
1.459
1.453
1.444
1.438
1.432
1.423
1.416
1H
Compound 13
NAME DK-173-A
EXPNO 11
PROCNO 1
Date_ 20120229
Time 20.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 144
DW 52.000 usec
DE 6.50 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.85 usec
SI 65536
SF 600.1300132 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
0.91
1.01
1.00
1.01
1.02
3.95
1.02
6.11
1.04
1.08
6.09
1.03
3.00
3.00
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

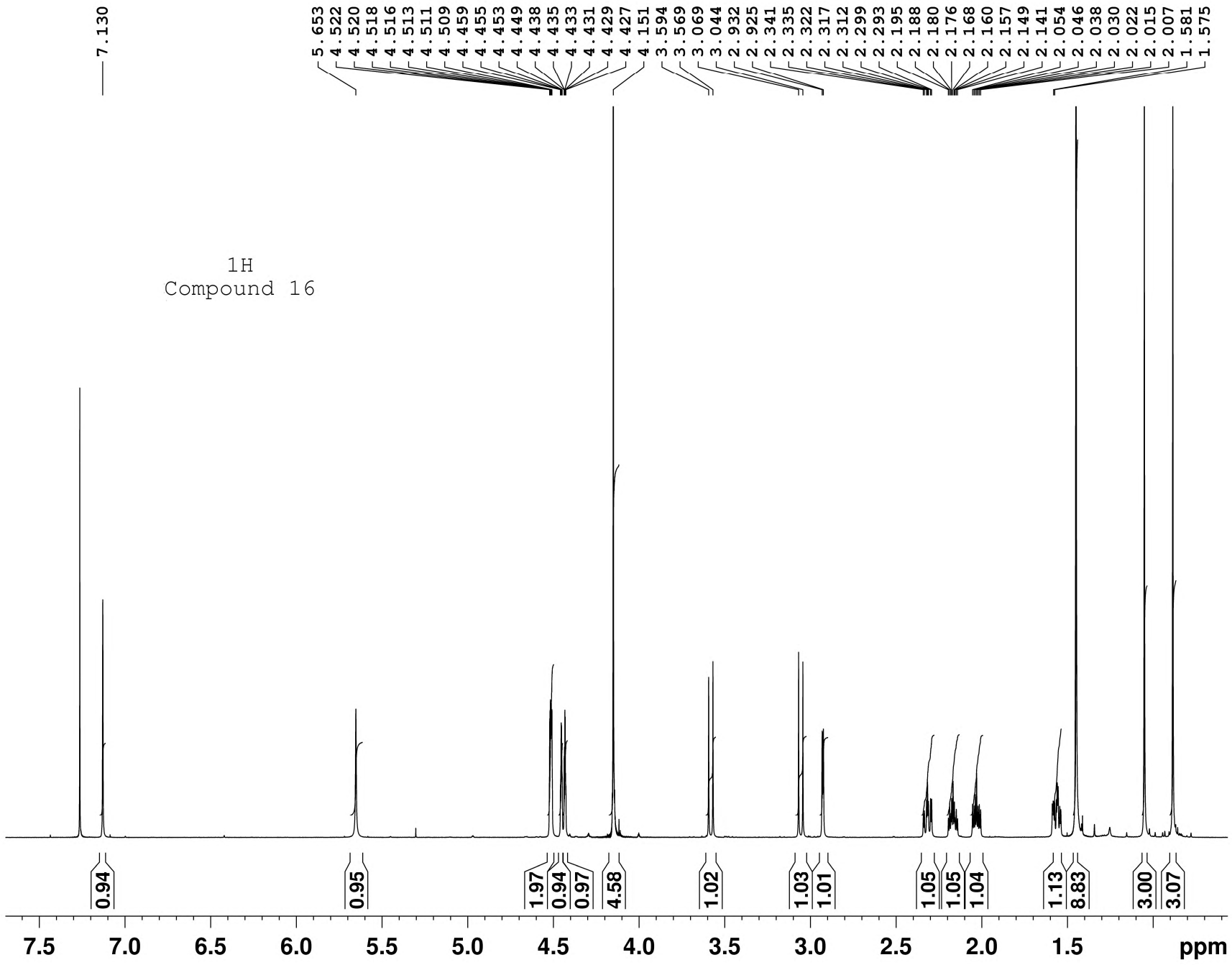

203.80
136.37
129.89
78.158
71.483
70.809
69.341
68.990
57.383
49.047
47.547
43.754
37.431
26.031
25.478
20.528
19.289
13C
Compound 15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm



NAME	MKC5308D	
EXPNO	11	
PROCNO	1	
Date_	20100302	
Time	14.21	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	32768	
SOLVENT	CDCl3	
NS	32	
DS	0	
SWH	9615.385	Hz
FIDRES	0.293438	Hz
AQ	1.7039860	sec
RG	287	
DW	52.000	usec
DE	6.00	usec
TE	293.0	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1	========
NUC1	1H	
P1	11.90	usec
PL1	-2.00	dB
PL1W	26.27507401	W
SFO1	600.1345610	MHz
SI	65536	
SF	600.1300173	MHz
WDW	EM	
SSB	0	
LB	0.10	Hz
GB	0	
PC	1.00	



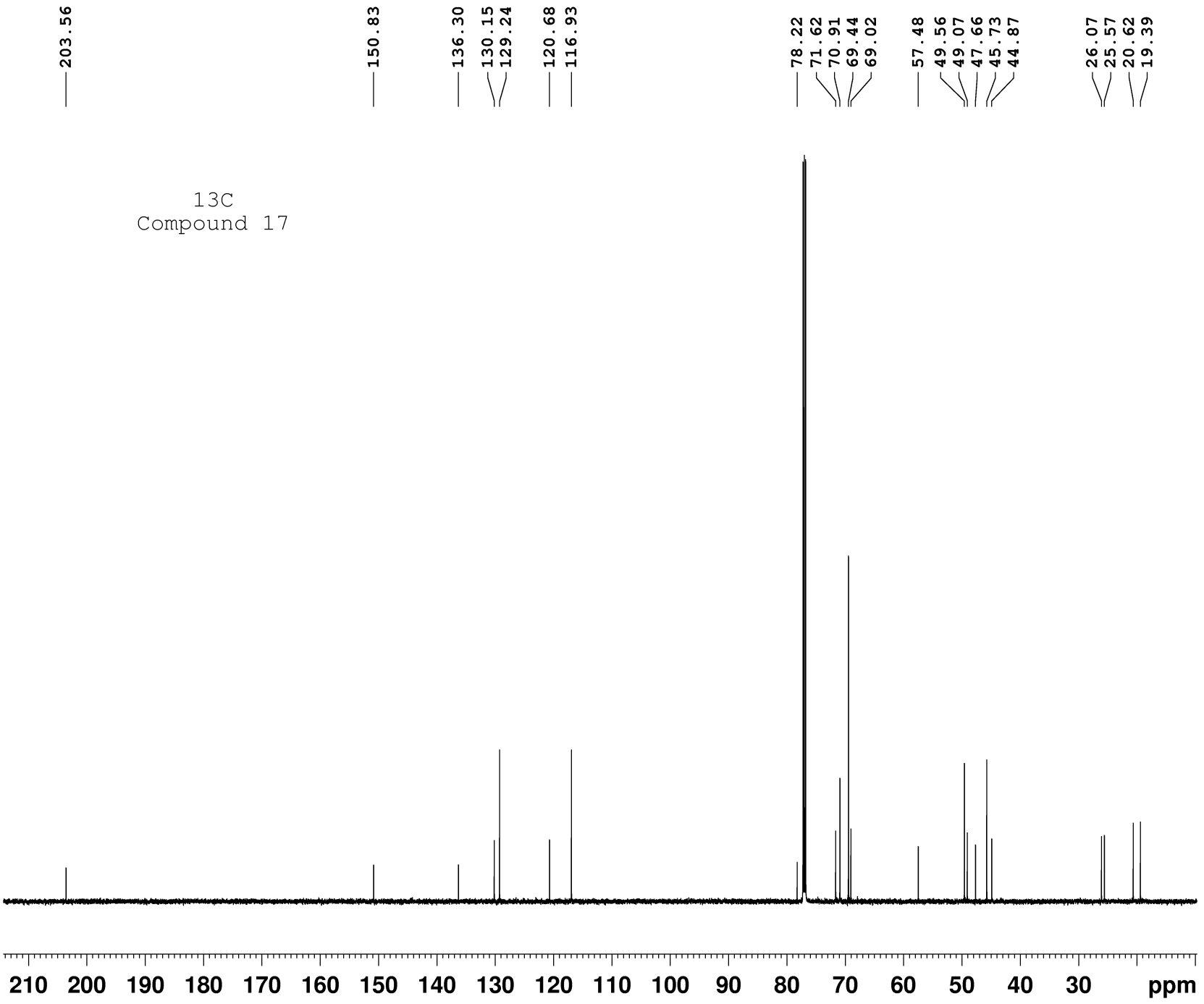
NAME	DK-164-02
EXPNO	3
PROCNO	1
Date_	20120116
Time	19.30
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	512
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.3 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028158 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



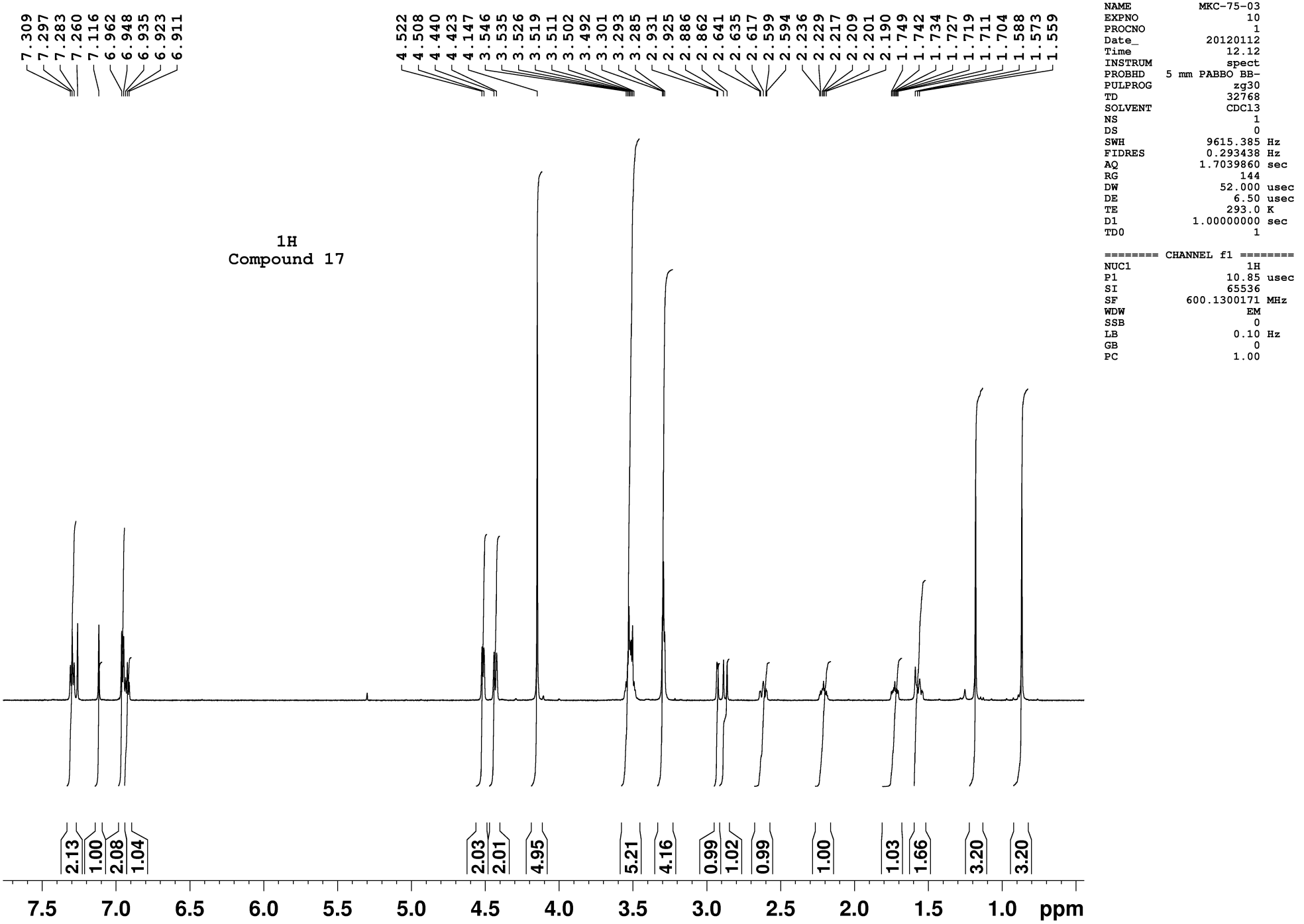
NAME	DK-164-02
EXPNO	2
PROCNO	1
Date_	20120116
Time	19.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

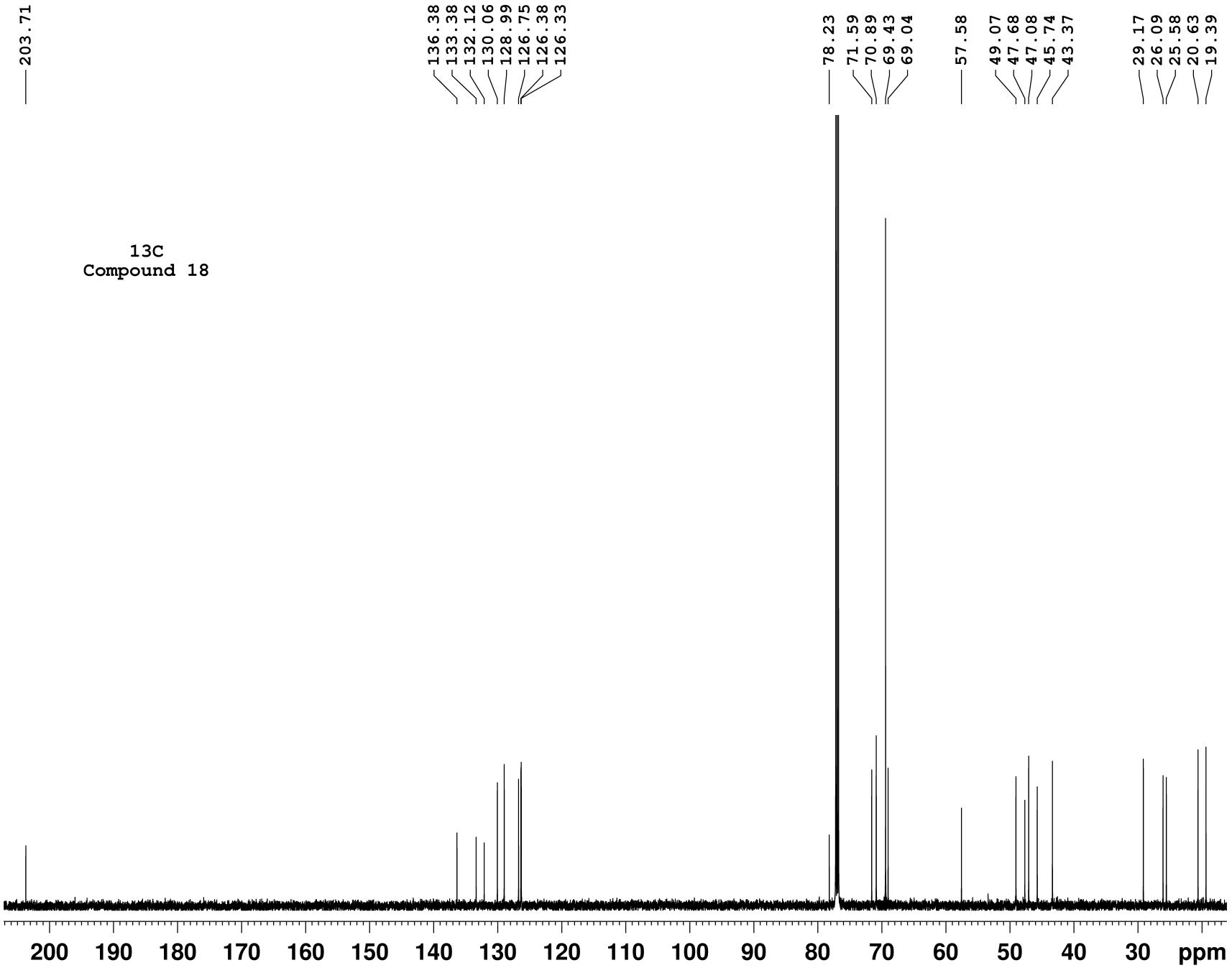
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300149 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00



NAME	MKC-75-03
EXPNO	12
PROCNO	1
Date_	20120112
Time	12.48
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	1024
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 use
DE	6.50 use
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 =======	
NUC1	13C
P1	10.75 use
SI	65536
SF	150.9028170 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



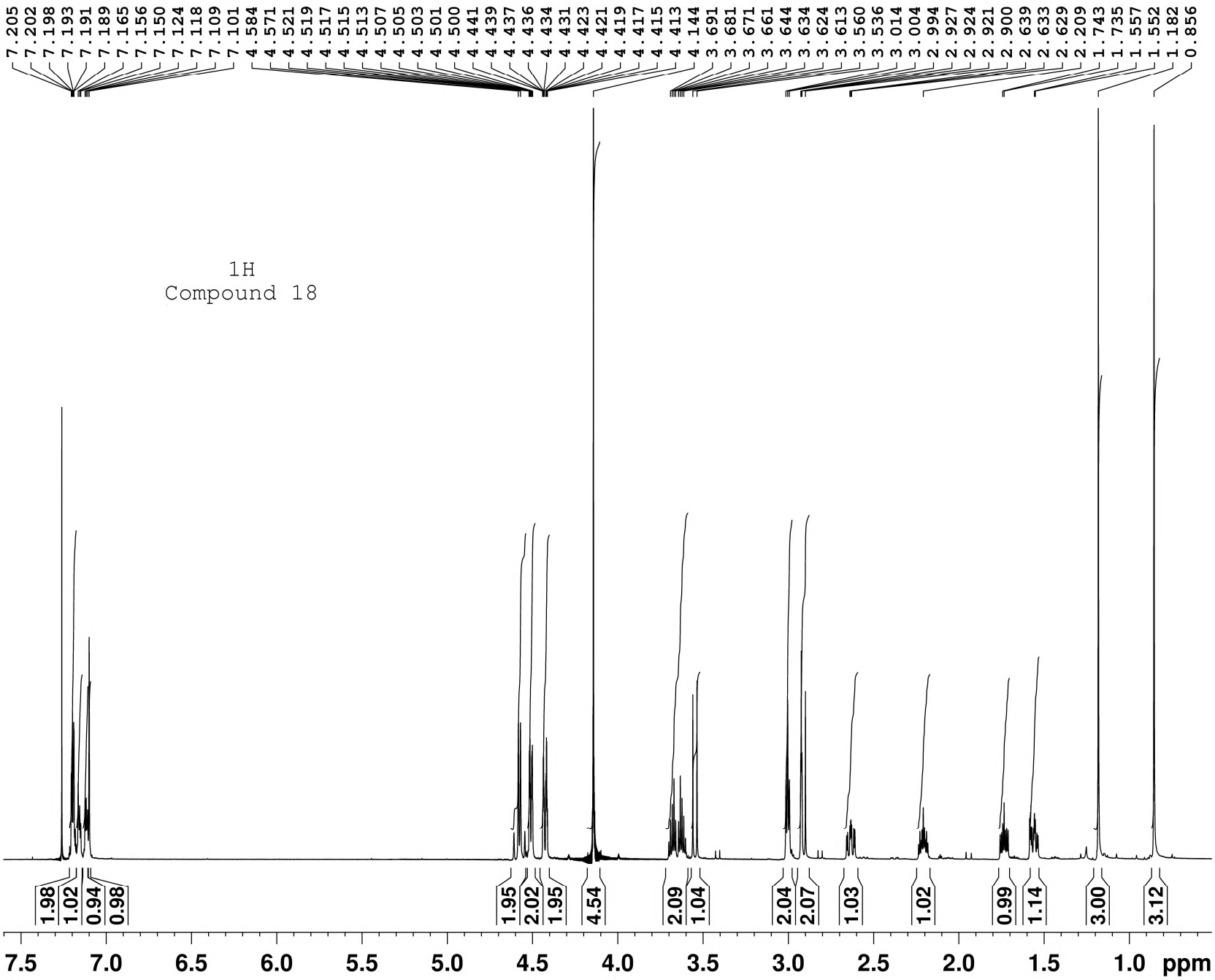
NAME	MKC-75-03
EXPNO	10
PROCNO	1
Date_	20120112
Time	12.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	1
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300171 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00



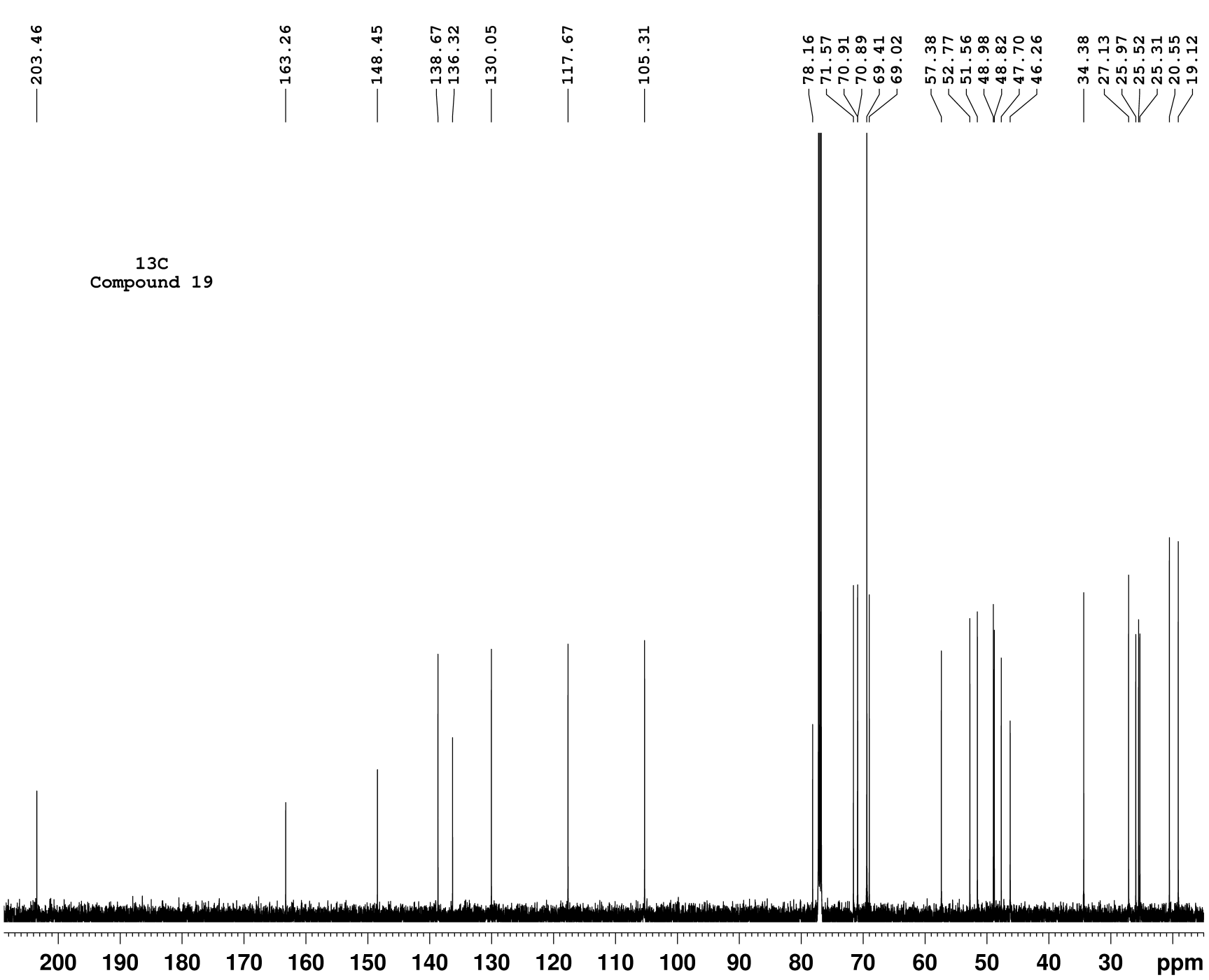
NAME	DK-141-02
EXPNO	3
PROCNO	1
Date_	20111121
Time	14.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	512
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

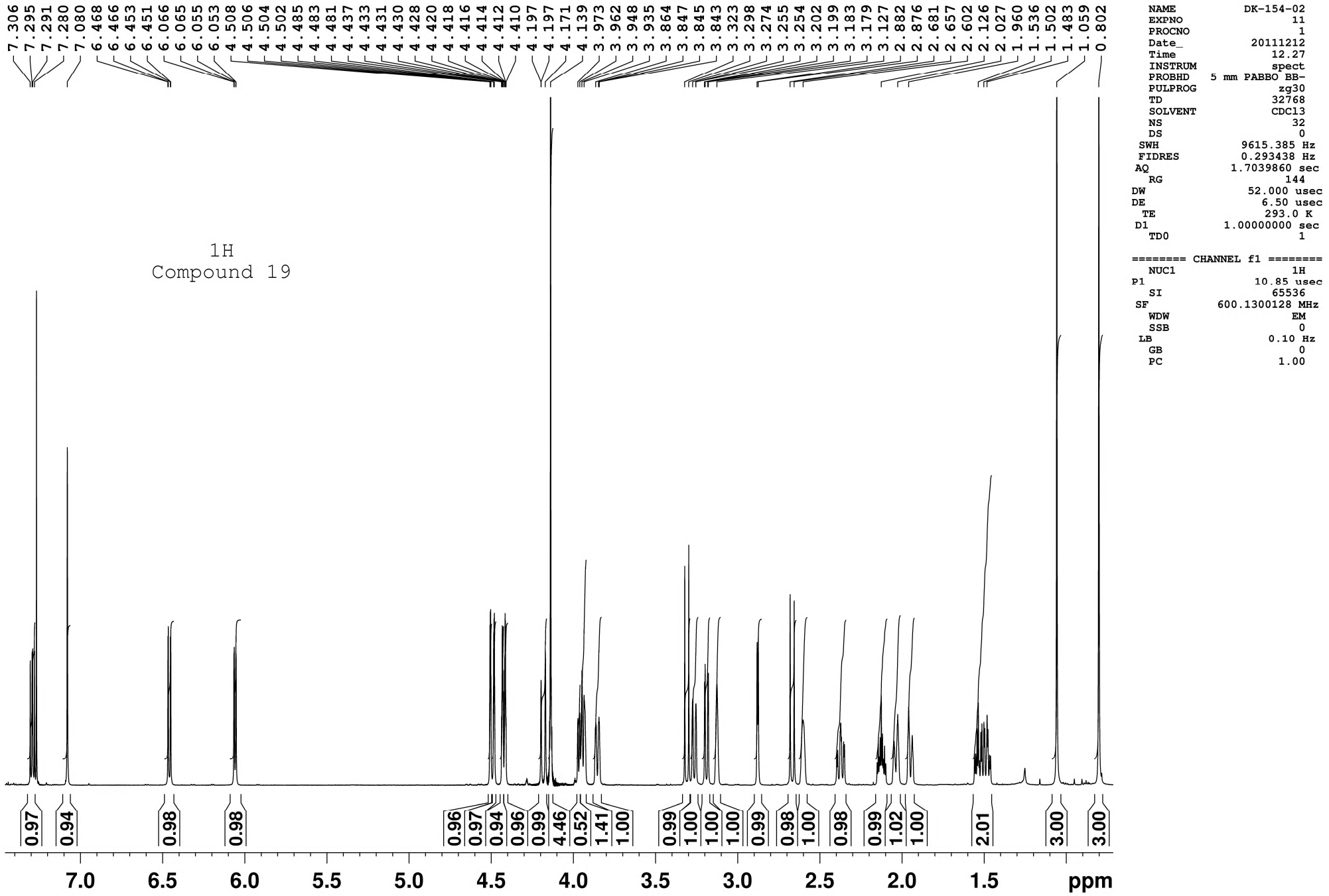
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028168 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



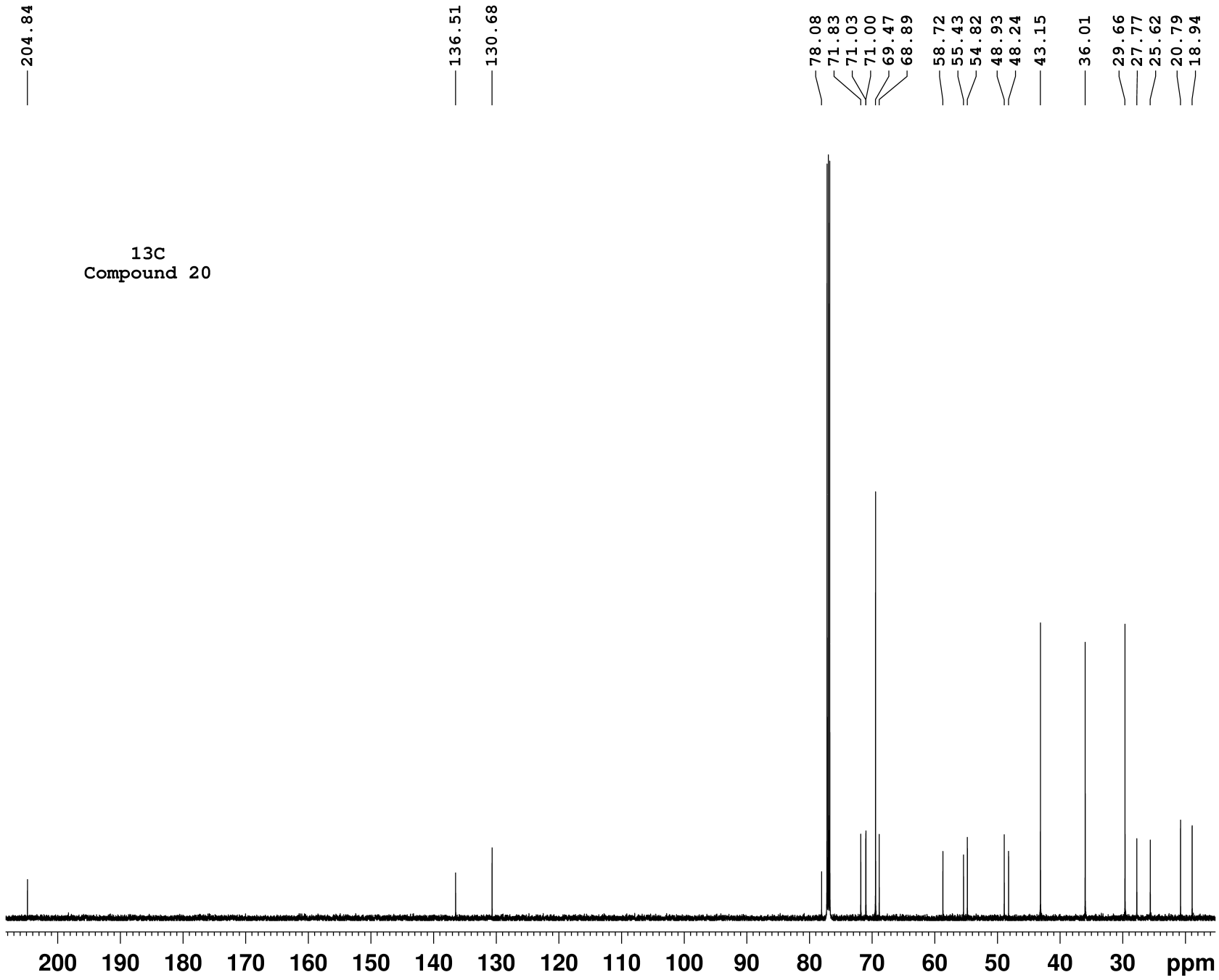
NAME	DK-141-02
EXPNO	2
PROCNO	1
Date_	20111121
Time	14.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300169 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00



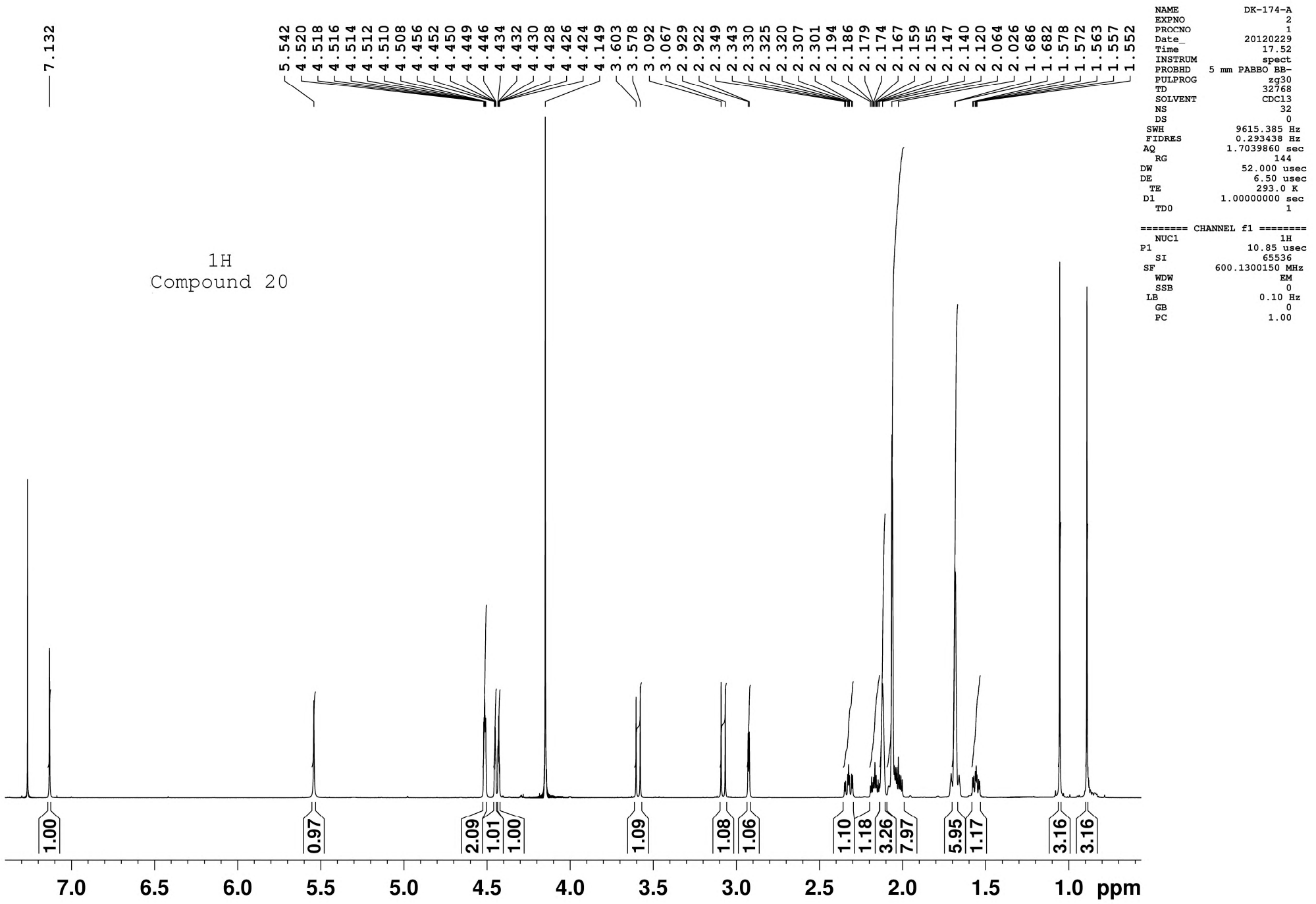
NAME	DK-154-02
EXPNO	12
PROCNO	1
Date_	20111212
Time	12.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	512
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028180 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

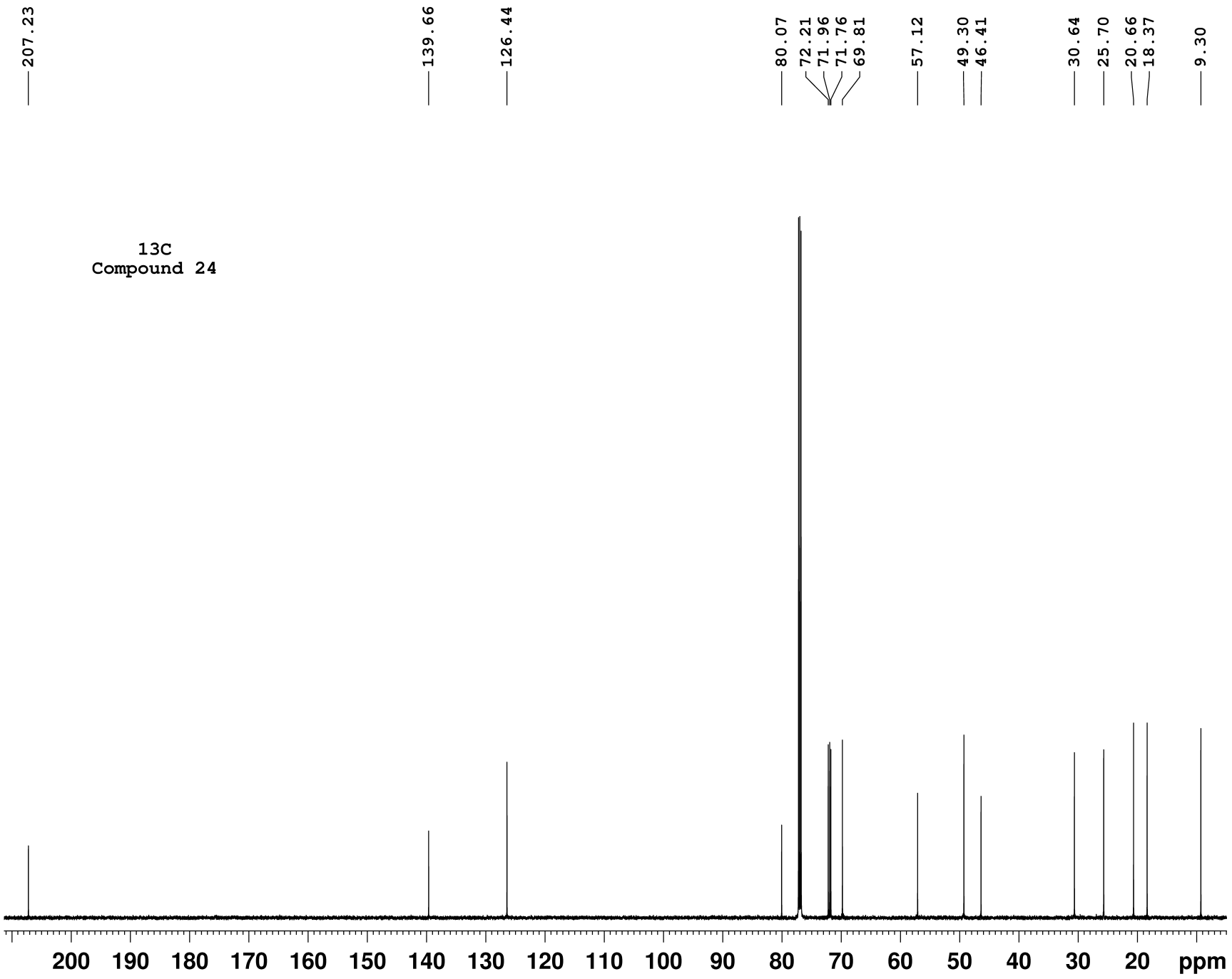


NAME	DK-154-02
EXPNO	11
PROCNO	1
Date_	20111212
Time	12.27
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300128 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

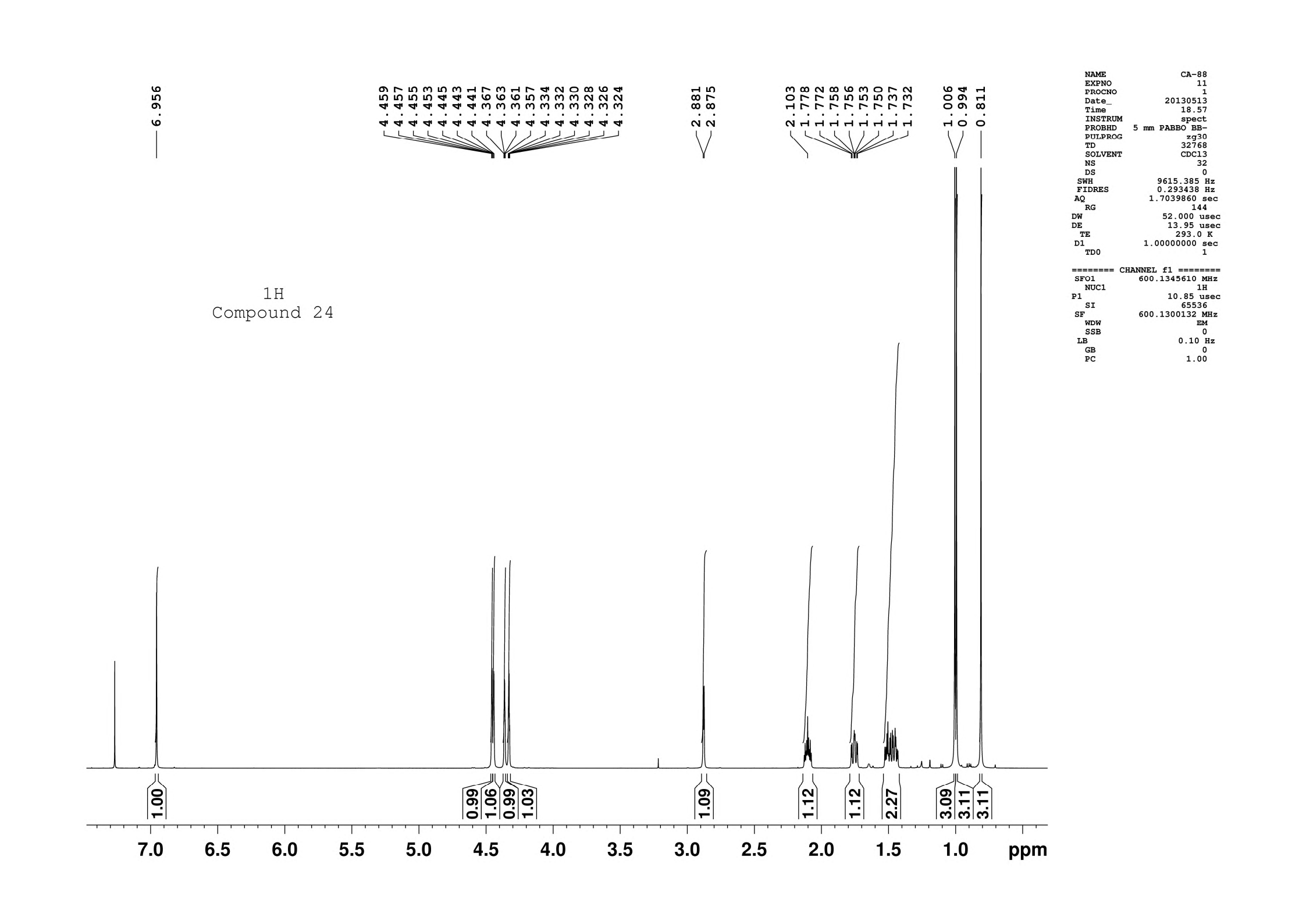


NAME	DK-174-A
EXPNO	11
PROCNO	1
Date_	20120229
Time	17.55
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	512
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.1 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028164 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

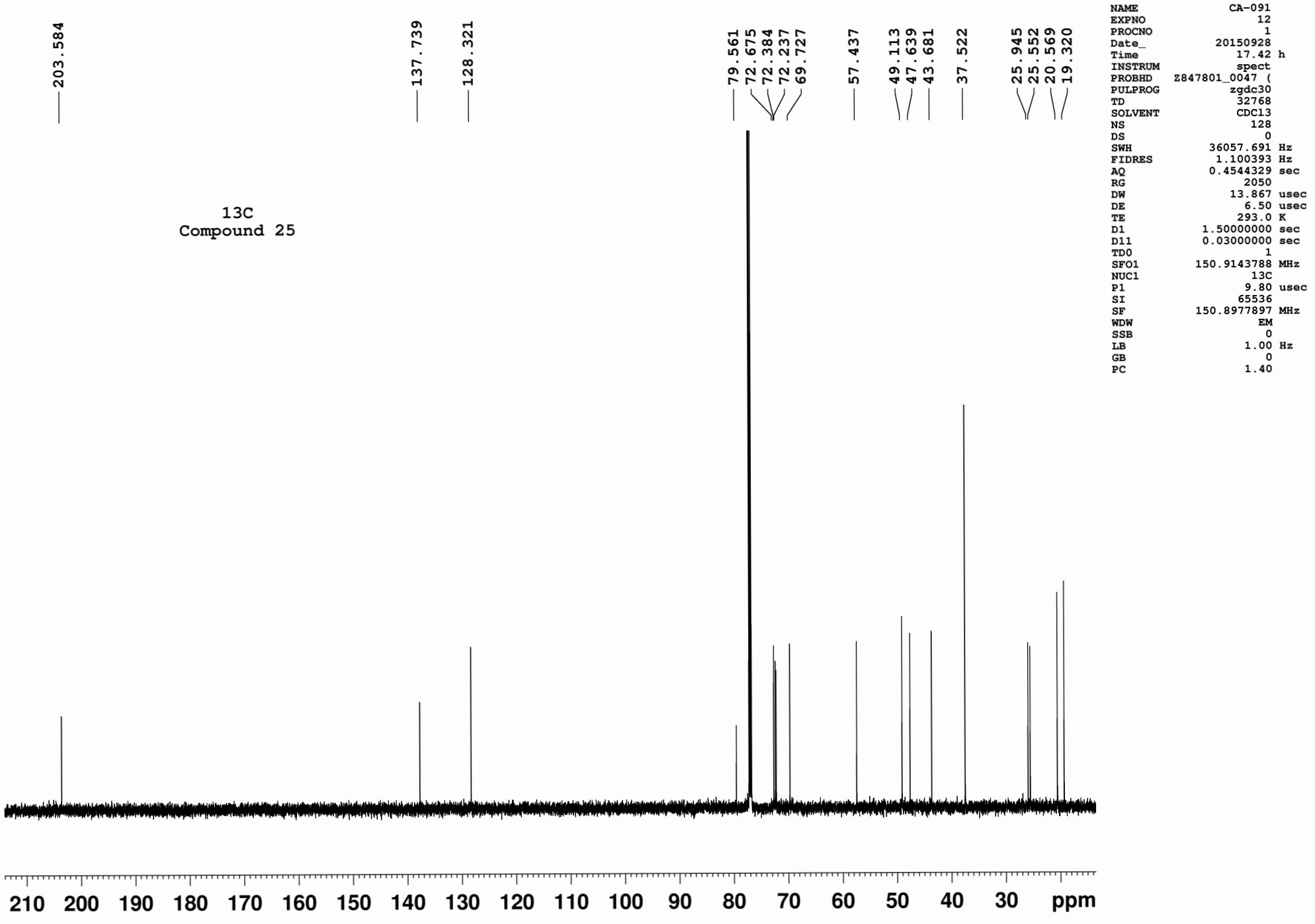

7.132
5.542
4.520
4.518
4.516
4.514
4.512
4.510
4.508
4.456
4.452
4.450
4.449
4.446
4.434
4.432
4.430
4.428
4.426
4.424
4.149
3.603
3.578
3.092
3.067
2.929
2.922
2.349
2.343
2.330
2.325
2.320
2.307
2.301
2.194
2.186
2.179
2.174
2.167
2.159
2.155
2.147
2.140
2.120
2.064
2.026
1.686
1.682
1.578
1.572
1.563
1.557
1.552
1H
Compound 20
NAME DK-174-A
EXPNO 2
PROCNO 1
Date_ 20120229
Time 17.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 9615.385 Hz
FIDRES 0.293438 Hz
AQ 1.7039860 sec
RG 144
DW 52.000 usec
DE 6.50 usec
TE 293.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.85 usec
SI 65536
SF 600.1300150 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1.00
0.97
2.09
1.01
1.00
1.09
1.08
1.06
1.10
1.18
3.26
7.97
5.95
1.17
3.16
3.16
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

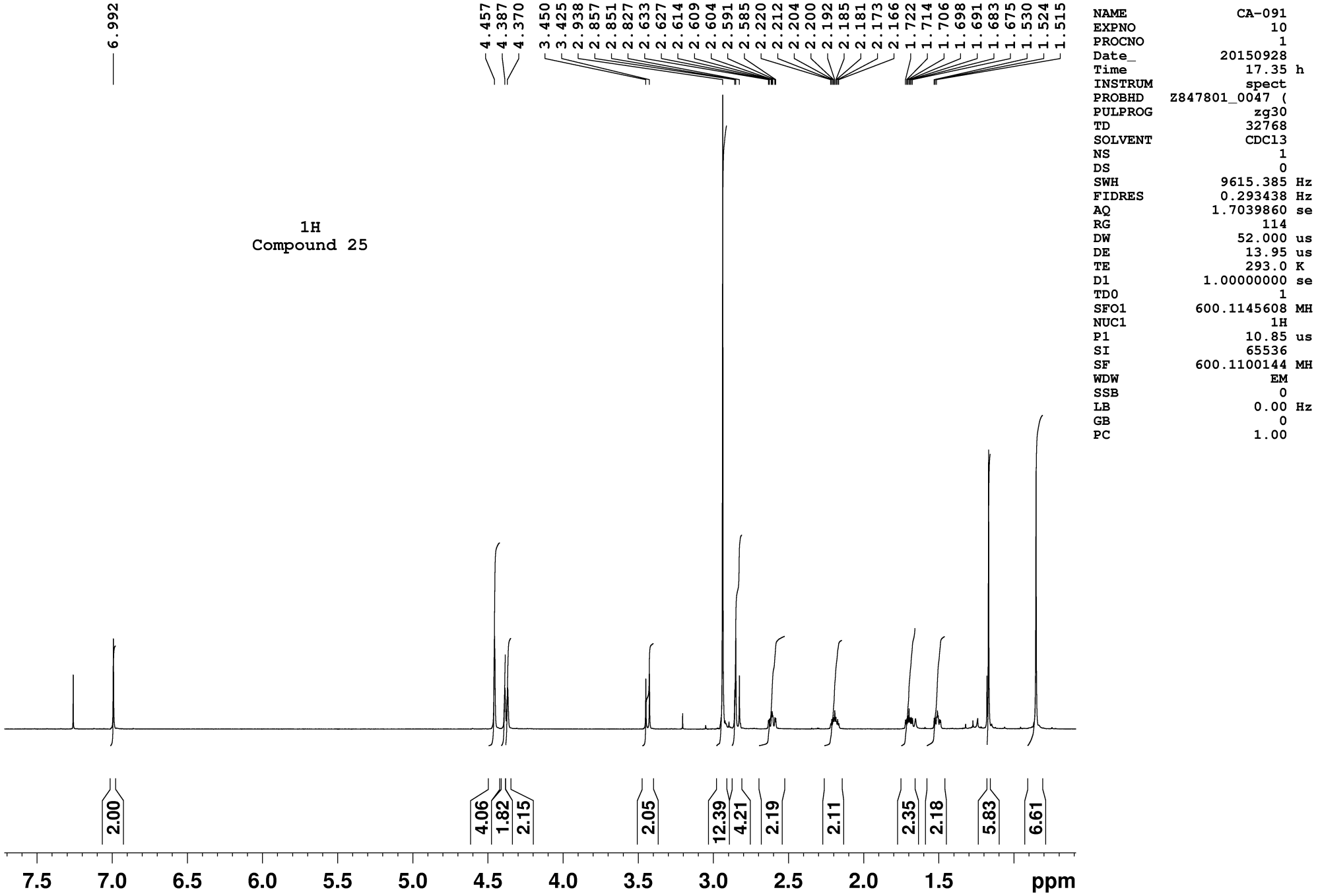


NAME	CA-88
EXPNO	12
PROCNO	1
Date_	20130513
Time	19.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	1024
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 use
DE	7.48 use
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 =======	
SFO1	150.9188042 MHz
NUC1	13C
P1	10.75 use
SI	65536
SF	150.9028167 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	10.00

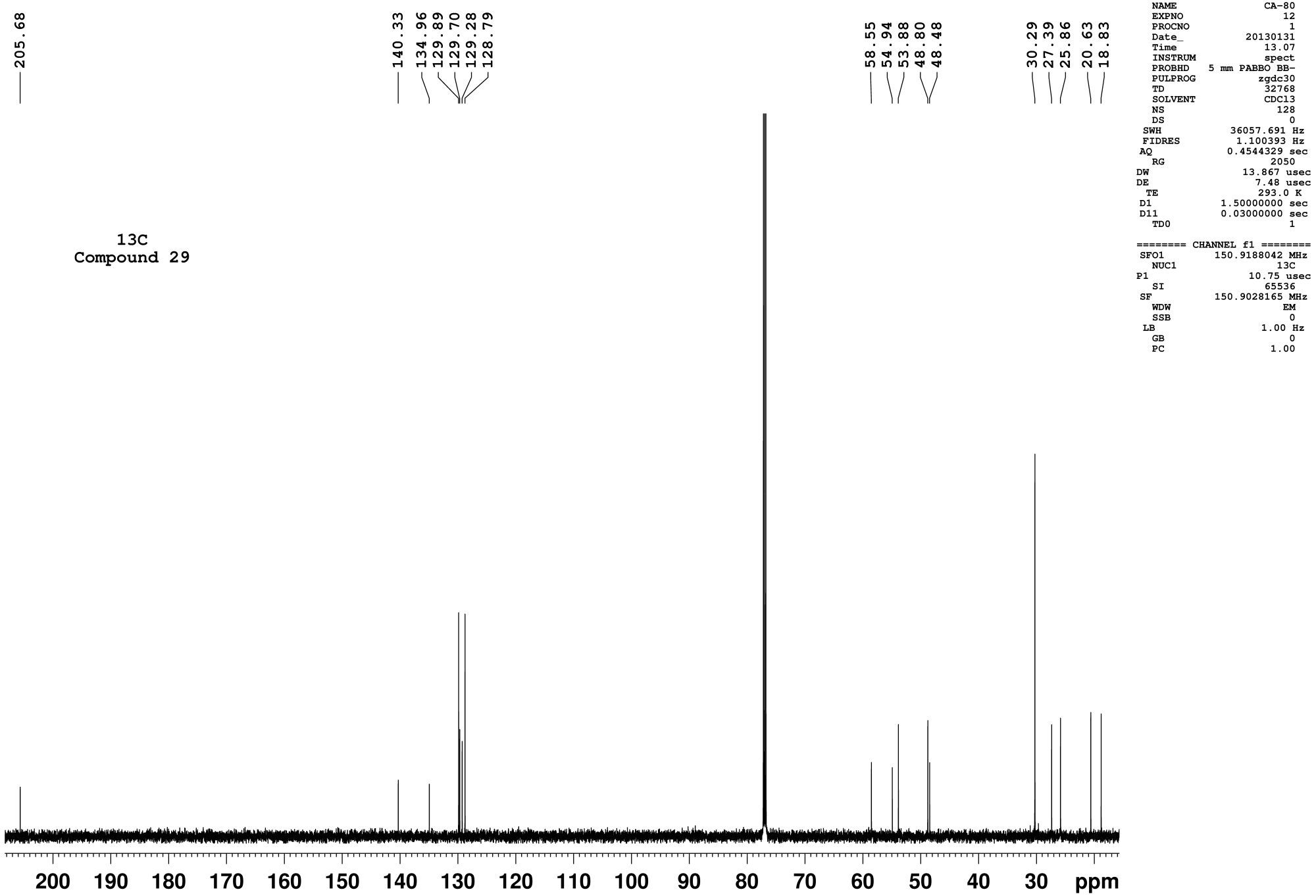


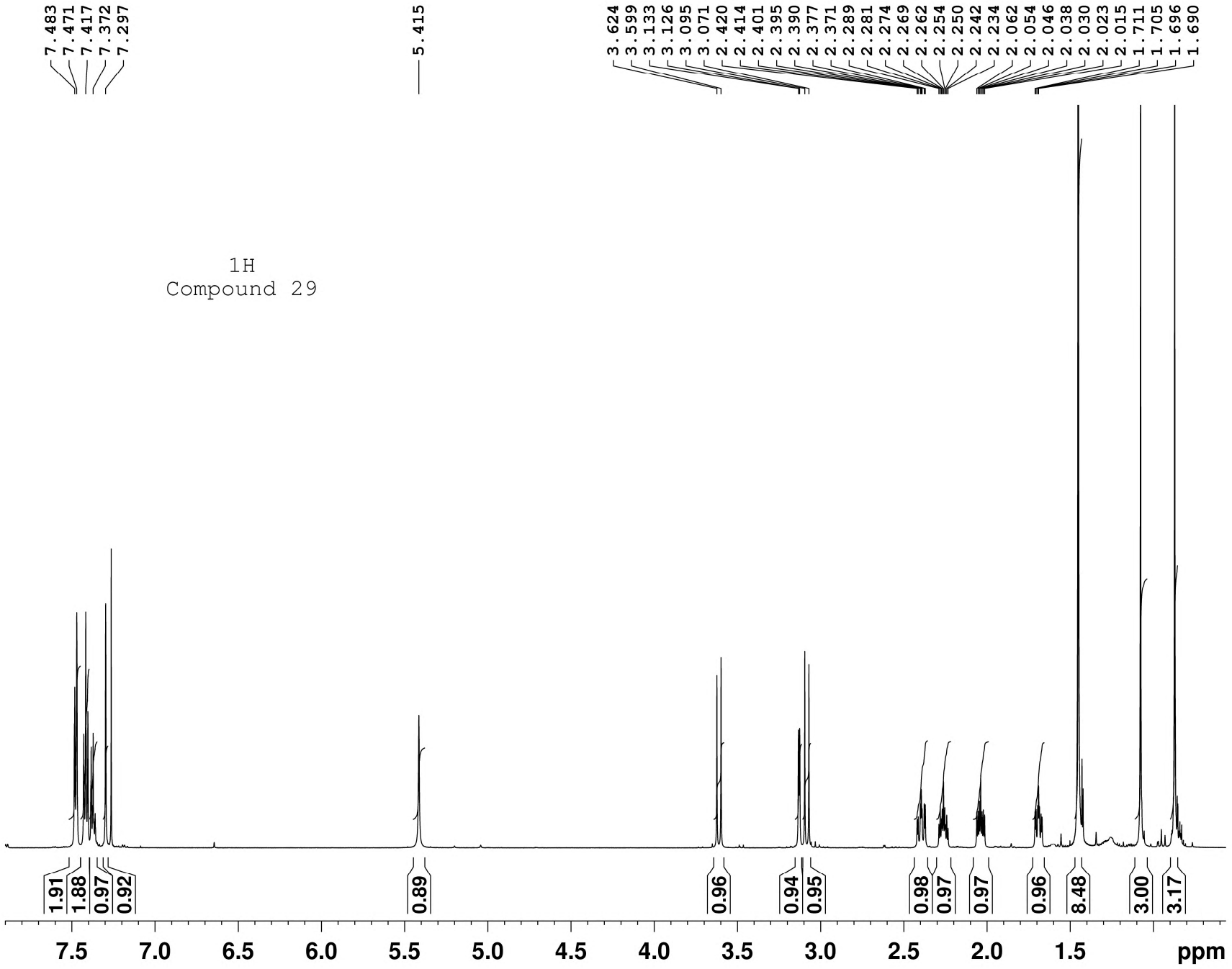
NAME	CA-88
EXPNO	11
PROCNO	1
Date_	20130513
Time	18.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	13.95 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	600.1345610 MHz
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300132 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00


203.584
137.739
128.321
79.561
72.675
72.384
72.237
69.727
57.437
49.113
47.639
43.681
37.522
25.945
25.552
20.569
19.320
13C
Compound 25
NAME CA-091
EXPNO 12
PROCNO 1
Date_ 20150928
Time 17.42 h
INSTRUM spect
PROBHD Z847801_0047 (
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 128
DS 0
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4544329 sec
RG 2050
DW 13.867 usec
DE 6.50 usec
TE 293.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
SFO1 150.9143788 MHz
NUC1 13C
P1 9.80 usec
SI 65536
SF 150.8977897 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 ppm

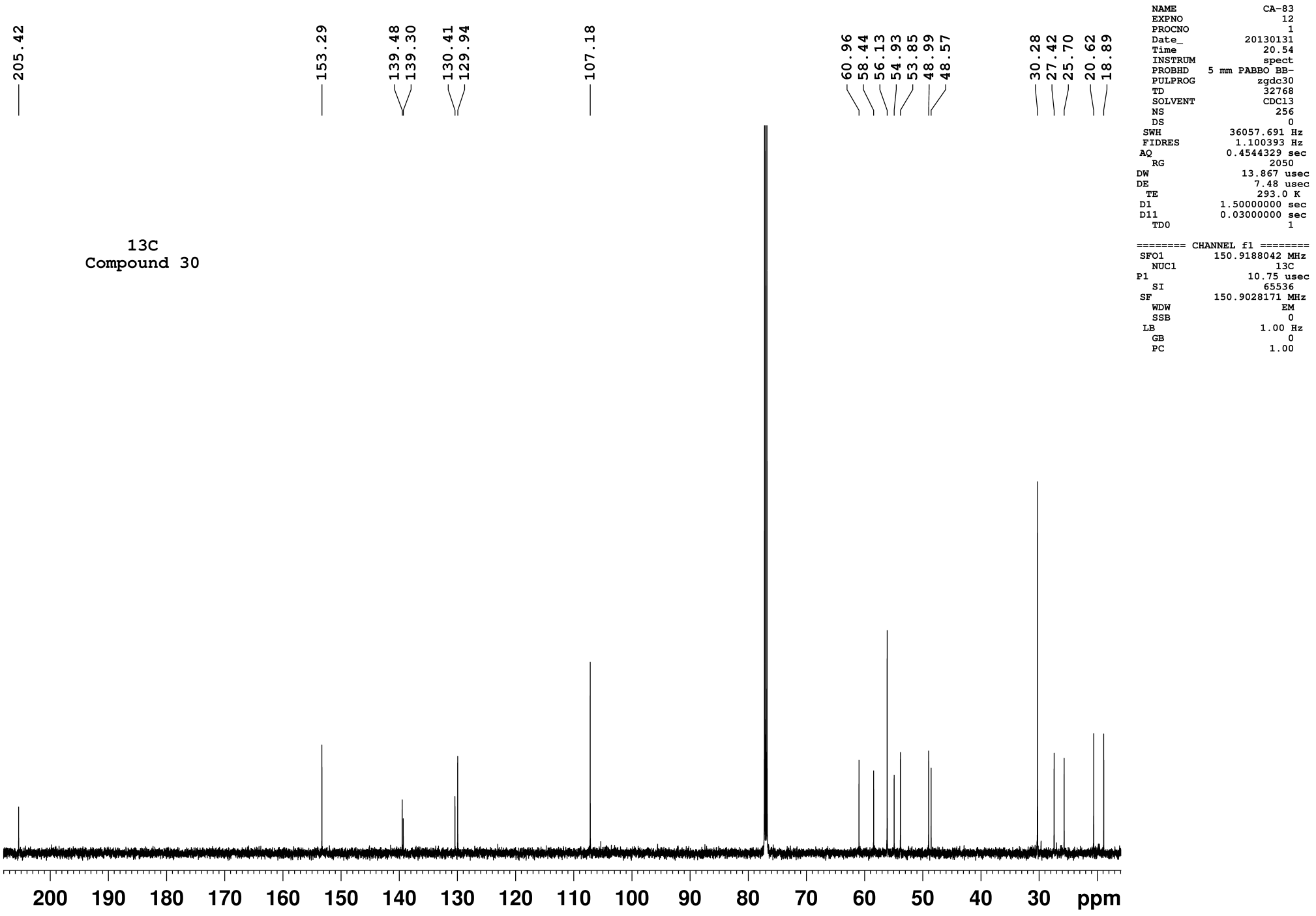


NAME	CA-091
EXPNO	10
PROCNO	1
Date_	20150928
Time	17.35 h
INSTRUM	spect
PROBHD	Z847801_0047 (
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	1
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 se
RG	114
DW	52.000 us
DE	13.95 us
TE	293.0 K
D1	1.00000000 se
TD0	1
SFO1	600.1145608 MH
NUC1	1H
P1	10.85 us
SI	65536
SF	600.1100144 MH
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	1.00


205.68
140.33
134.96
129.89
129.70
129.28
128.79
58.55
54.94
53.88
48.80
48.48
30.29
27.39
25.86
20.63
18.83
13C
Compound 29
NAME CA-80
EXPNO 12
PROCNO 1
Date_ 20130131
Time 13.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDC13
NS 128
DS 0
SWH 36057.691 Hz
FIDRES 1.100393 Hz
AQ 0.4544329 sec
RG 2050
DW 13.867 usec
DE 7.48 usec
TE 293.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 150.9188042 MHz
NUC1 13C
P1 10.75 usec
SI 65536
SF 150.9028165 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 30 ppm



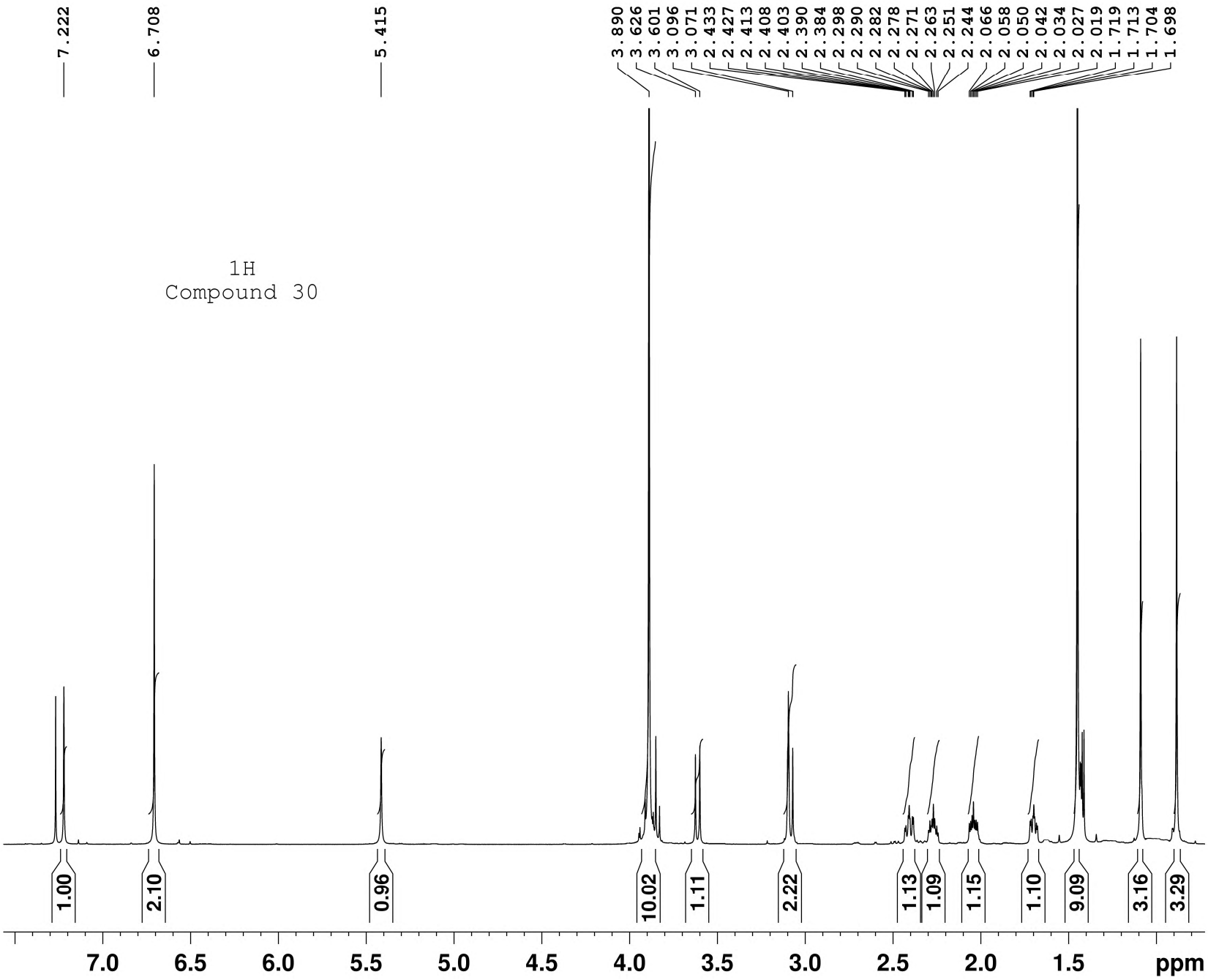
NAME	CA-80
EXPNO	11
PROCNO	1
Date_	20130131
Time	13.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	13.95 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	600.1345610 MHz
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300154 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00



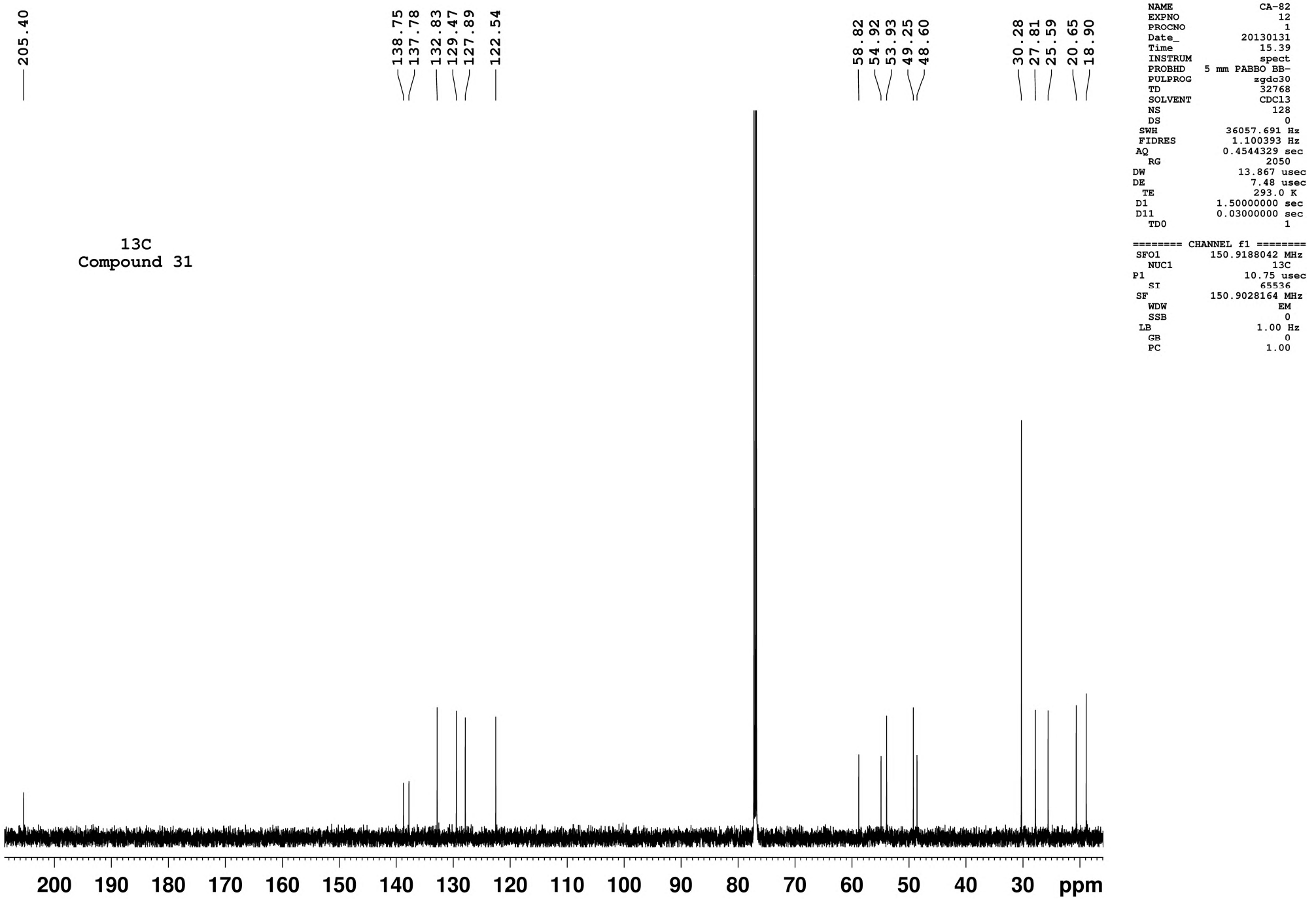
NAME	CA-83
EXPNO	12
PROCNO	1
Date_	20130131
Time	20.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	256
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	7.48 usec
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1

======== CHANNEL f1 ========

SFO1	150.9188042 MHz
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028171 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

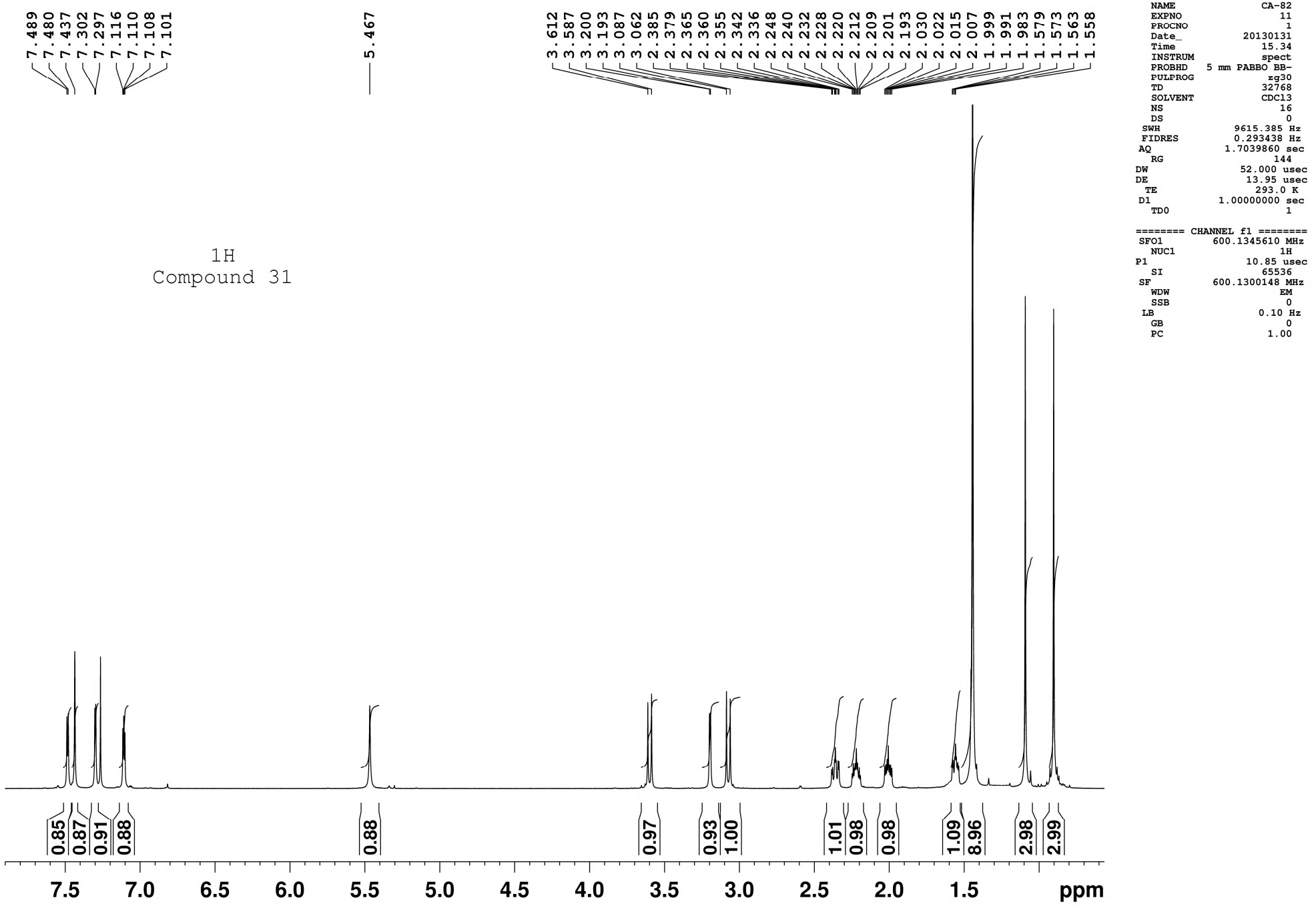


NAME	CA-83
EXPNO	11
PROCNO	1
Date_	20130131
Time	20.45
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	13.95 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	600.1345610 MHz
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300126 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

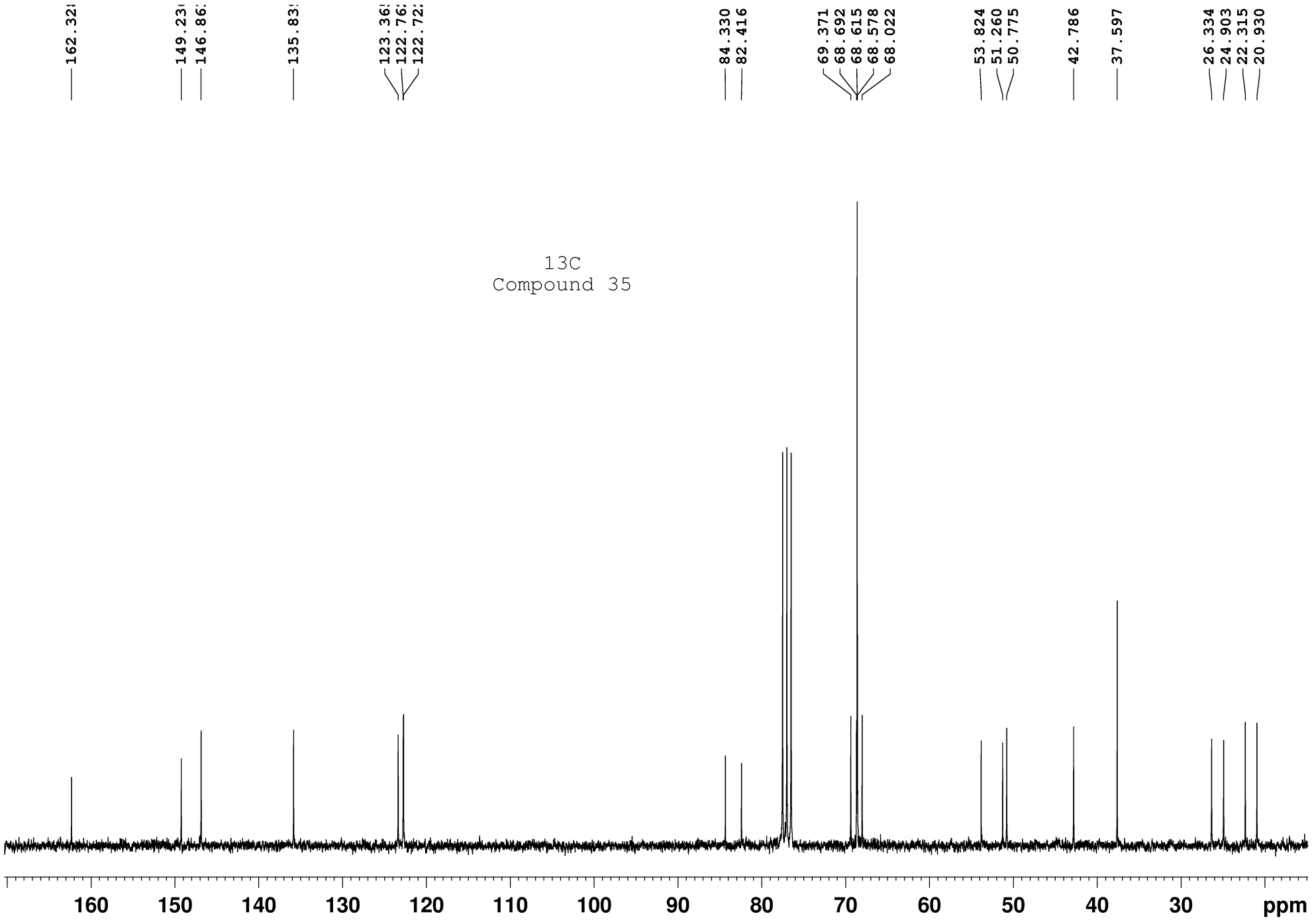


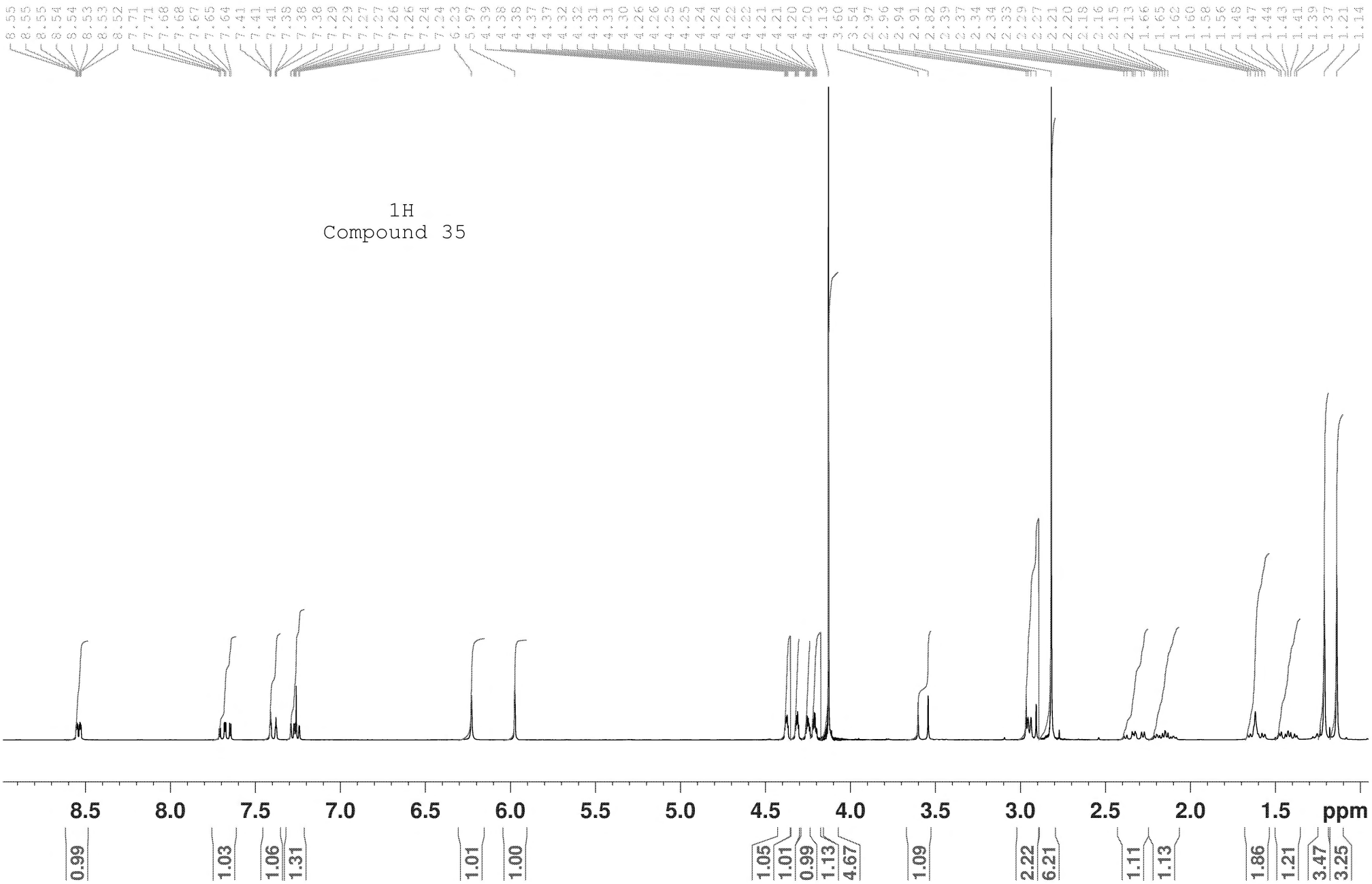
NAME	CA-82
EXPNO	12
PROCNO	1
Date_	20130131
Time	15.39
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	128
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	7.48 usec
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1

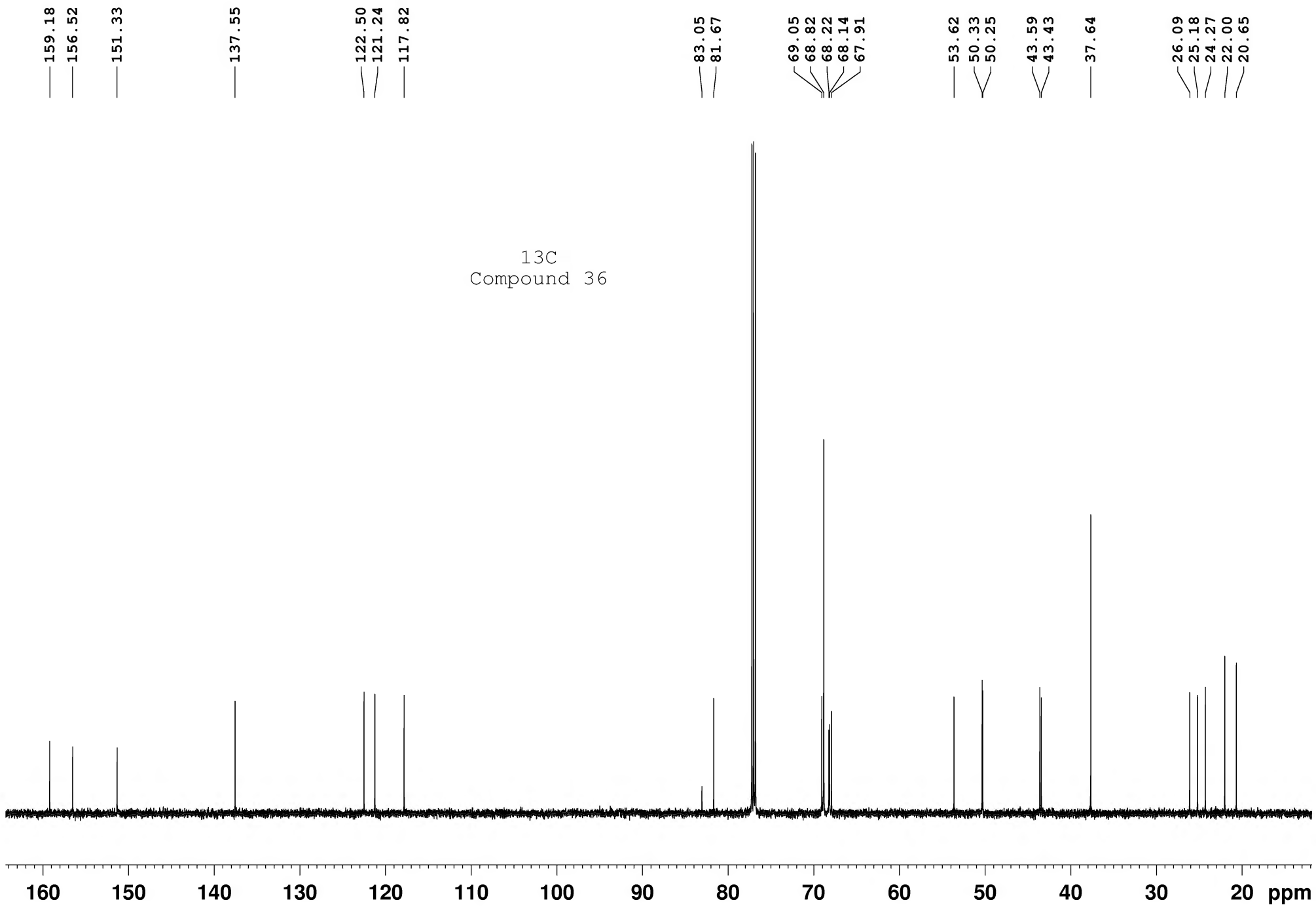
======== CHANNEL f1 ========	
SFO1	150.9188042 MHz
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028164 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

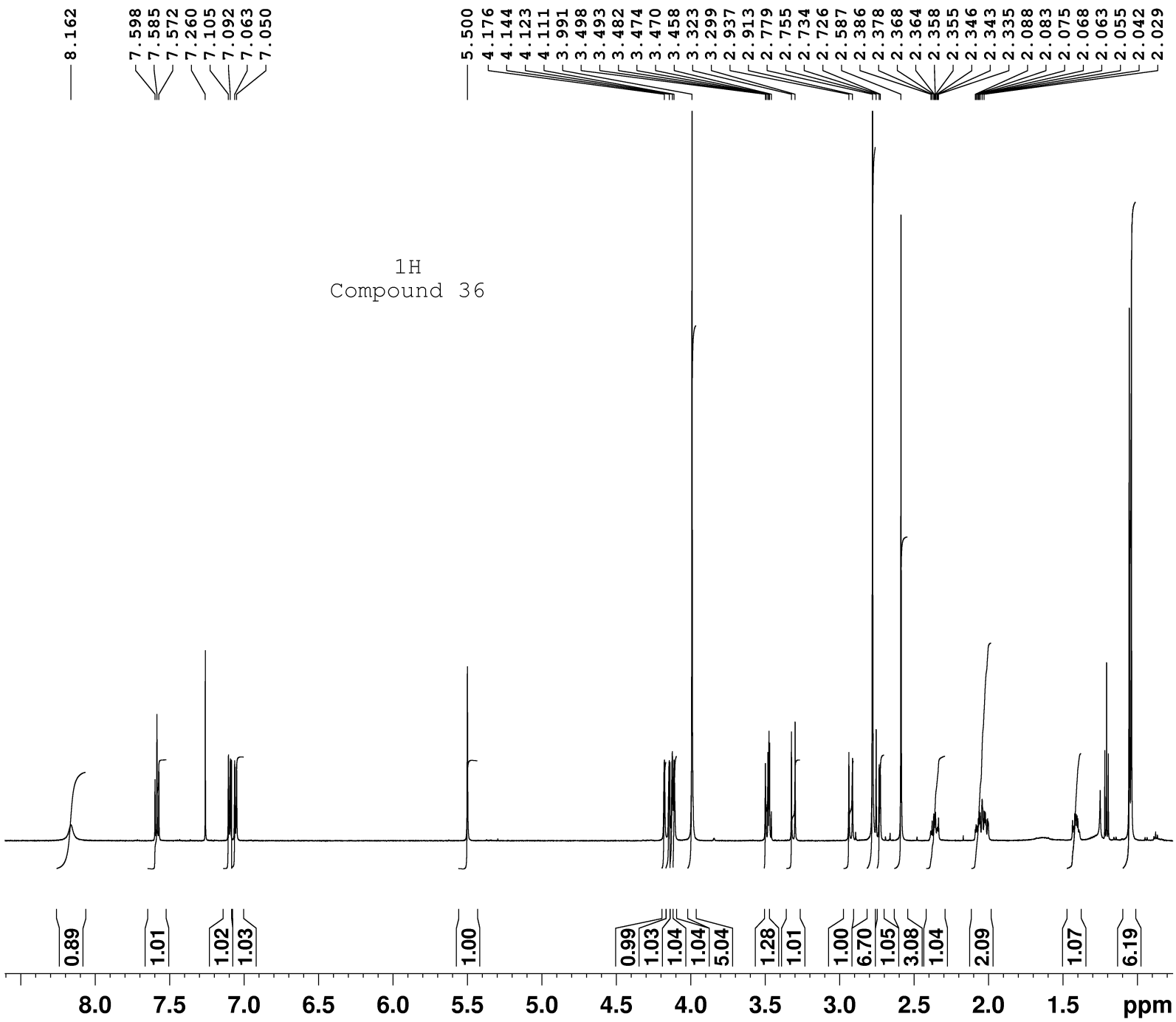


NAME	CA-82
EXPNO	11
PROCNO	1
Date_	20130131
Time	15.34
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	16
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	13.95 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	600.1345610 MHz
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300148 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

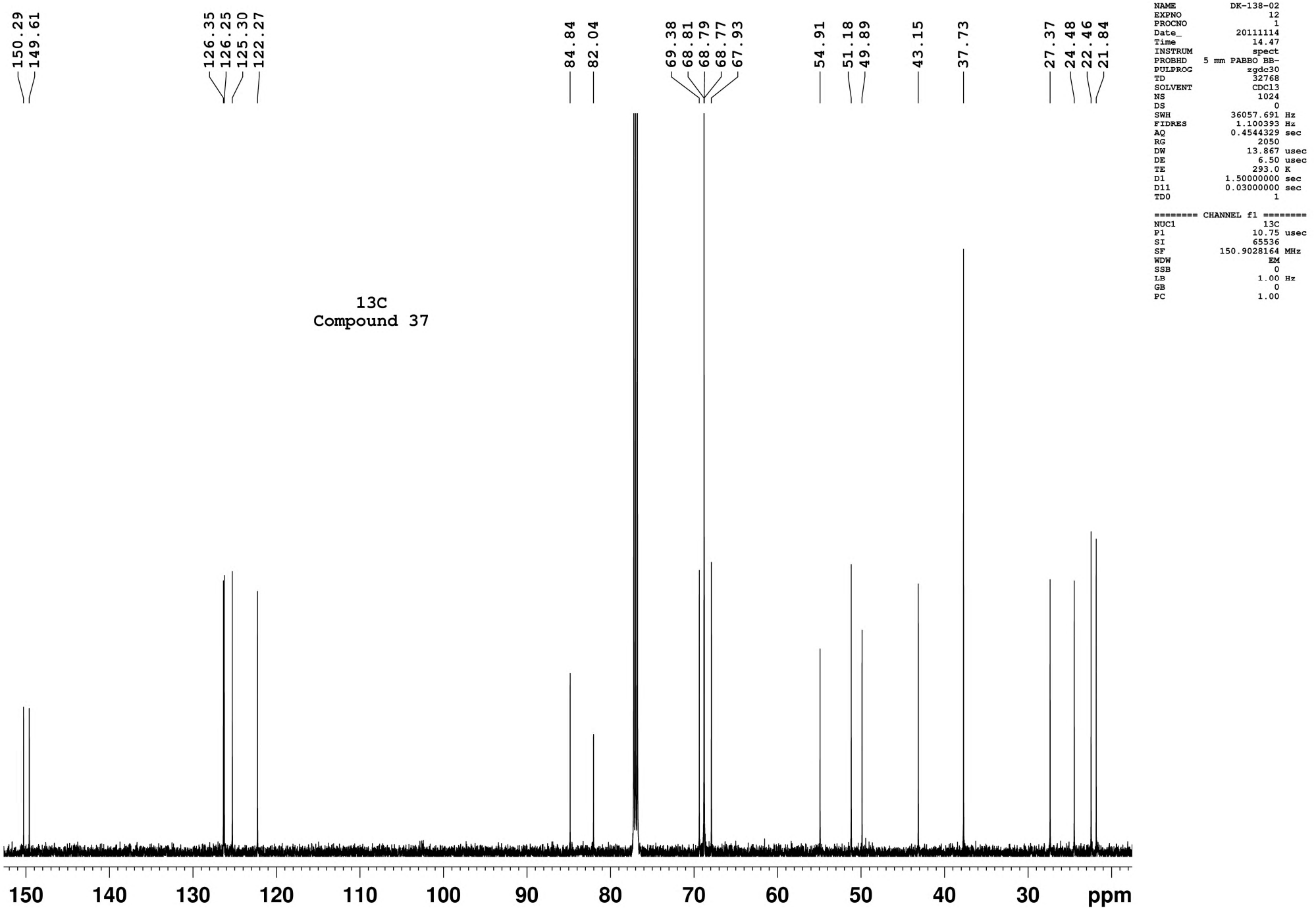

162.32
149.23
146.86
135.83
123.36
122.76
122.72
84.330
82.416
69.371
68.692
68.615
68.578
68.022
53.824
51.260
50.775
42.786
37.597
26.334
24.903
22.315
20.930
13C
Compound 35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


8.55
8.55
8.55
8.54
8.54
8.53
8.53
8.52
7.71
7.71
7.68
7.68
7.67
7.65
7.64
7.41
7.41
7.41
7.38
7.38
7.38
7.29
7.29
7.27
7.27
7.26
7.25
7.24
7.24
6.23
5.97
4.39
4.38
4.38
4.37
4.37
4.32
4.32
4.31
4.31
4.30
4.26
4.26
4.25
4.25
4.24
4.24
4.22
4.22
4.21
4.21
4.20
4.20
4.13
3.60
3.54
2.97
2.96
2.94
2.91
2.82
2.39
2.37
2.34
2.34
2.33
2.29
2.27
2.21
2.20
2.18
2.16
2.15
2.13
1.66
1.65
1.62
1.60
1.58
1.56
1.48
1.47
1.44
1.43
1.41
1.39
1.37
1.21
1.14
1H
Compound 35
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
0.99
1.03
1.06
1.31
1.01
1.00
1.05
1.01
0.99
1.13
4.67
1.09
2.22
6.21
1.11
1.13
1.86
1.21
3.47
3.25

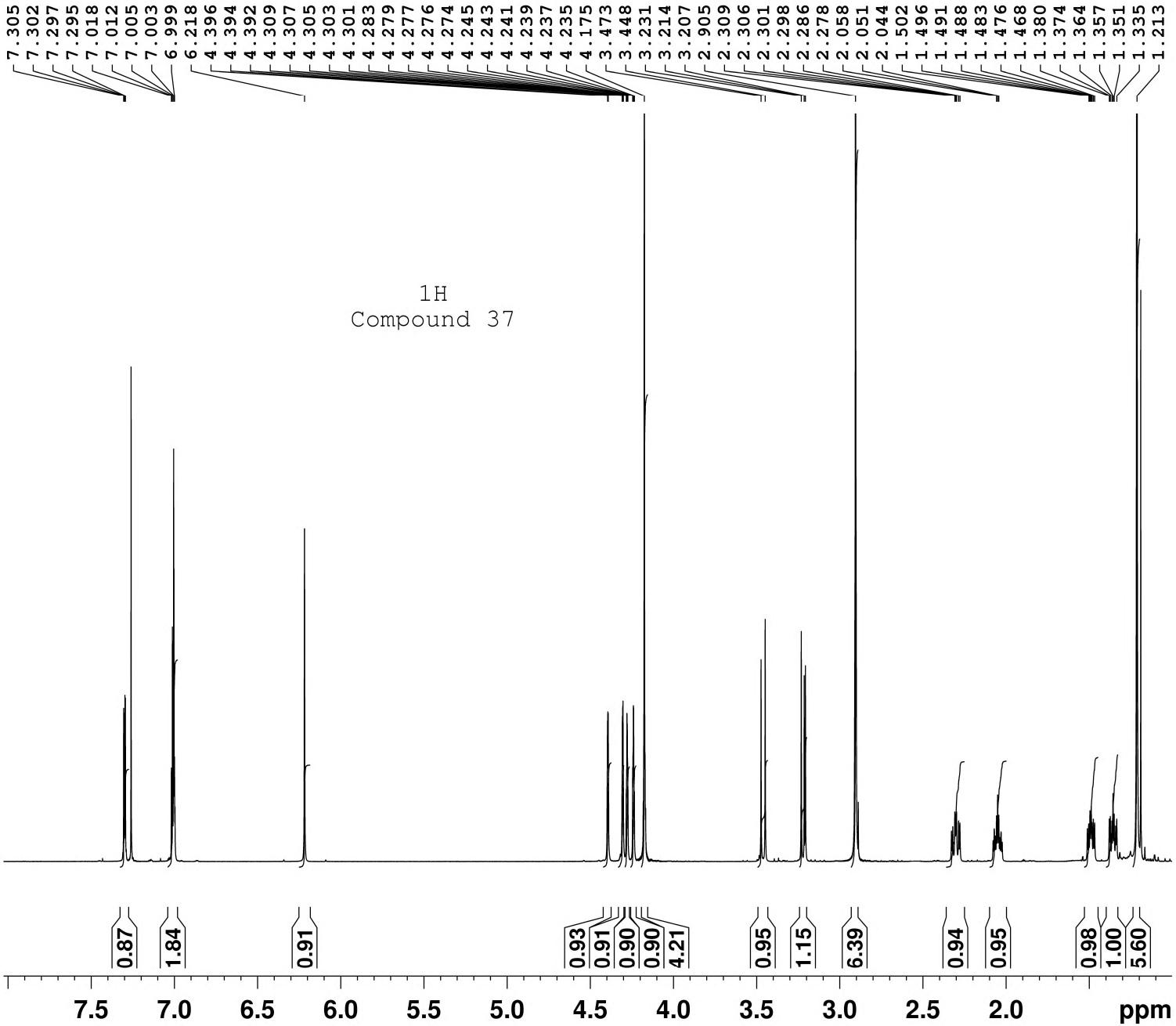

159.18
156.52
151.33
137.55
122.50
121.24
117.82
83.05
81.67
69.05
68.82
68.22
68.14
67.91
53.62
50.33
50.25
43.59
43.43
37.64
26.09
25.18
24.27
22.00
20.65
13C
Compound 36
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



NAME	MKB6807D
EXPNO	1
PROCNO	1
Date_	20081014
Time	17.57
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	1
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.00 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	11.90 usec
PL1	-2.00 dB
PL1W	26.27507401 W
SFO1	600.1345610 MHz
SI	65536
SF	600.1300174 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



NAME	DK-138-02
EXPNO	12
PROCNO	1
Date_	20111114
Time	14.47
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgdc30
TD	32768
SOLVENT	CDCl3
NS	1024
DS	0
SWH	36057.691 Hz
FIDRES	1.100393 Hz
AQ	0.4544329 sec
RG	2050
DW	13.867 usec
DE	6.50 usec
TE	293.0 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.75 usec
SI	65536
SF	150.9028164 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



NAME	DK-138-02
EXPNO	11
PROCNO	1
Date_	20111114
Time	14.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	9615.385 Hz
FIDRES	0.293438 Hz
AQ	1.7039860 sec
RG	144
DW	52.000 usec
DE	6.50 usec
TE	293.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.85 usec
SI	65536
SF	600.1300171 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00