SUPPORTING INFORMATION

Synthesis of Copolymers with Alternating ROMP (AROMP)

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General Information

All reactions were performed under an N_2 or Ar atmosphere. CH_2Cl_2 was dried in a GlassContour solvent pushstill system. CD_2Cl_2 was degassed before use for reactions. Second generation Grubbs' catalyst [$(H_2IMes)(PCy_3)Cl_2Ru$=CHPh], ethyl 1-bromocyclobutane-carboxylate and 3-cyclohexene-1-methanol **6** were purchased from Aldrich (Cat #: 56974-7, 19729-7 and 162167). Cyclohexene **4a** was purchased from Fisher Scientific. Cyclohexene-D_{10} **4a-D_{10}** was purchased from CDN Isotope Inc. (Cat #: D0173). The synthesis of precatalyst **1** was performed with the procedure of Love, J.A. et al.[1] Mallinckrodt silica gel 60 (230-400 mesh) was used for column chromatography. Aluminum TLC (thin layer chromatography) plates were silica gel 60 (F254). ^{1}H NMR spectra were reported as chemical shift in ppm (multiplicity, coupling constant in Hz, and integration). ^{13}C NMR spectra were reported as chemical shift in ppm. The solvent peak was used as an internal reference. LC-MS spectra were acquired on a Waters ACQUITY Ultra Performance Liquid Chromatography system with an SQD detector and using a 10 cm×2.1 mm ACQUITY™ 1.7 μm column (Waters Corp, Milford, USA) with elution by a linear gradient of 20-100% *B* at 0.5 mL/min, where *A* = water and *B* = methanol. The molecular weights of the polymers were assessed by gel permeation chromatography (Phenogel 5 μ MXL GPC column, Phenomenex) eluting with THF.

Cyclobut-1-enecarboxylic acid[2, 3]

Cyclobut-1-enecarboxylic acid was prepared according to the procedure for the preparation of 3,3-dimethylcylobutene carboxylic acid as described by Campbell et al.[2] with minor modifications. KOH (6.00 g, 107 mmol) and toluene (90 mL) were mixed and then heated to

reflux until the KOH dissolved. Ethyl 1-bromocyclobutanecarboxylate (4.90 g, 23.7 mmol) was added dropwise without heating. The reaction mixture was heated at reflux for 1 h, then cooled to RT. Cold water (60 mL) was added, the aqueous layer was washed with pentane (2 x 40 mL), and the pH was adjusted to 2.5 with 30% aq H_2SO_4. The product was then extracted from the aqueous layer with Et_2O (4 x 40 mL) and dried over anhydrous Na_2SO_4. The Et_2O was evaporated to give a yellow oil. The oil was dissolved in pentane (50 mL) and the upper layer was separated from the lower layer. The upper layer was cooled in an acetone-dry ice bath and stirred for 20 min. The resulting precipitate was filtered and dried under vacuum (1.14 g, 49% yield). The dried solid was stored at -20 °C to prevent decomposition. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.23 (bs, 1H), 6.94 (t, J=1.2 Hz, 1H), 2.76 (t, J=3.2 Hz, 2H), 2.51 (td, J=3.2 Hz, 1.2 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 167.5, 150.1, 138.4, 29.1, 27.5.

Methyl cyclobut-1-enecarboxylate, (2a)[4, 5]

The ester **2a** was prepared according to the literature.[4, 5] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 3.68 (s, 3H), 2.69 (m, 2H), 2.46 (m, 2H). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 162.7, 146.5, 138.8, 51.2, 29.3, 27.3.

Phenyl cyclobut-1-enecarboxylate, (2b)

Cyclobut-1-enecarboxylic acid (0.51 mmol, 50 mg) was dissolved in 0.5 mL dry CH_2Cl_2. The solution was cooled to 0 ºC and oxalyl dichloride (0.51 mmol, 43 μL) was added. The temperature of the solution was raised to rt, and the mixture was allowed to react for 1 h. The solvent was evaporated to generate a viscous oil. Phenol (0.51 mmol, 48 mg) and triethylamine

(1.02 mmol, 142 μL) were dissolved in 0.5 mL dry CH_2Cl_2, and the solution was stirred at 0 ºC for 45 min before being added to a vial containing the cyclobut-1-enecarboxylic chloride. The reaction mixture was stirred for 16 h at rt. The reaction was quenched with 1 N HCl, and was extracted with CH_2Cl_2 (30 mL). The CH_2Cl_2 solution was washed with 5 % $NaHCO_3$ (2×10 mL), dried over Na_2SO_4, concentrated by rotary evaporation, and then purified by flash column chromatography (100% CH_2Cl_2) to yield **2b** as a colorless oil (42 mg, 47%). ^{1}H-NMR (100 MHz) δ 7.42 (m, 2H), 7.28 (m, 1H), 7.14 (m, 2H), 7.02 (s, 1H), 2.88 (t, J=3.0 Hz, 2H), 2.60 (m, 2H). ^{13}C-NMR (400 MHz) δ 160.5, 150.8, 149.2, 138.3, 129.6, 125.9, 121.8, 29.5, 27.7. HRMS (EI) calcd. for $C_{11}H_{10}O_2$ $[M]^+$ 174.0679, found 174.0681.

4-(Methoxymethyl)cyclohexene, (4b)

3-Cyclohexene-1-methanol **6** (8.92 mmol, 1.00 g) and NaH (17.8 mmol, 428 mg) were mixed in THF (30 mL) at rt, and the THF solution was stirred for 1 h at rt. MeI (17.8 mmol, 1.10 mL) was added slowly into the above THF solution. After stirring for 16 h at rt, the solution was diluted with water (30 mL), and then was extracted with diethyl ether (2×30 mL). The organic layer was dried over Na_2SO_4, was concentrated by rotary evaporation, and then was distilled to generate the final product **4b** as a colorless liquid (460 mg, 41%). ^{1}H-NMR (500 MHz) δ 5.68 (m, 2H), 3.36 (s, 3H), 3.28 (dd, J=6.5 Hz, J=4 Hz), 2.06-2.14 (m, 3H), 1.92 (m, 1H), 1.83 (m, 1H), 1.75 (m, 1H), 1.29 (m, 1H). ^{13}C-NMR (100 MHz) δ 127.2, 126.1, 78.0, 58.9, 34.0, 28.6, 25.8, 24.7. LC-MS (APCI): peak time = 1.59 min, M/z calcd for $C_8H_{15}O$ $[M+H]^+$ 127.11, found 127.10.

PDI (Polydispersity Index) determination

Polymers were dissolved in THF (0.5 mg/mL). An aliquot (100 μL) of the polymer solution was analyzed by gel permeation chromatography using a Phenogel column (300 x 7.80 mm, 5 μm, linear mixed bed, 0-40k MW range). Elution was performed at 0.7 mL/min with THF and detection at 220 nm at 30 °C. Narrowly dispersed polystyrene standards from Aldrich were used as molecular weight calibrants. The number average and weighted average molecular weights were calculated from the chromatogram.

General Procedure for AROMP

An NMR tube was evacuated under high vacuum for 15 min, and then was purged with Ar gas for another 15 min. Under an Ar atmosphere, a solution of monomer **A** (1-cyclobutenecarboxylate ester) in CD_2Cl_2 (300 μL) was added to the NMR tube. Then a solution of precatalyst $(H_2IMes)(3\text{-Br-Py})_2Cl_2Ru{=}CHPh$ **1** in CD_2Cl_2 (300 μL) was added to the NMR tube. After complete mixing of the solution, the NMR tube was spun for 4-30 min at 25 °C in the NMR spectrometer (400, 500 or 600 MHz) until the precatalyst had reacted. Then monomer **B** (cyclohexene derivatives) in CD_2Cl_2 (300 μL) was added to the NMR tube. After all of monomer **A** was converted, the reaction was quenched with ethylvinyl ether (50 μL) and was stirred for 1 h.

(2a-4a)$_{10}$:

Cyclobutene **2a** (0.06 mmol), cyclohexene **4a** (0.12 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 98%

completion. Degree of polymerization (DP) = 98. M_n^{calc} = 2044. M_n^{GPC} = 376. M_w^{GPC} = 962. PDI = 2.6.

(2a-4a)$_{20}$:

Cyclobutene **2a** (0.12 mmol), cyclohexene **4a** (0.24 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 98% completion. DP = 98. M_n^{calc} = 3984. M_n^{GPC} = 668. M_w^{GPC} = 1816. PDI = 2.7.

(2a-4a)$_{50}$:

Cyclobutene **2a** (0.30 mmol), cyclohexene **4a** (0.60 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 98% completion. DP = 98. M_n^{calc} = 9804. M_n^{GPC} = 652. M_w^{GPC} = 2634. PDI = 4.0.

(2a-4a)$_{100}$:

Cyclobutene **2a** (0.60 mmol), cyclohexene **4a** (1.20 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 97% completion. The crude solution was evaporated to remove solvent, and the residue was purified by flash column chromatography (acetone:CH_2Cl_2/3:97) to provide polymer **(2a-4a)$_{100}$** (72 mg, 62%). DP = 97. According to GPC chromatographic analysis, the copolymer had a bimodal molecular weight distribution (Figure S6). M_n^{calc} = 19504. M_n^{GPC} = 1869. M_w^{GPC} = 10872. PDI = 5.8.

(2a-4a)$_{200}$:

Cyclobutene **2a** (0.60 mmol), cyclohexene **4a** (1.20 mmol) and **1** (0.003 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 6 h to reach 73% completion. The crude solution was evaporated to remove solvents, and was purified by flash column chromatography (acetone:CH_2Cl_2/3:97) to generate polymer **(2a-4a)$_{200}$** (48 mg, 41%). DP = 74. According to GPC chromatographic analysis, the copolymer had a bimodal molecular weight distribution (Figure S6). M_n^{calc} = 29010. The overall GPC result: M_n^{GPC} = 7749, M_w^{GPC} = 18501, PDI = 2.4. The individual peaks were fitted using OriginPro 7.5 (OriginLab Corp.), and the molecular weight and PDI data of each peak were calculated (Figure S7). Peak **A**: M_n^{GPC} = 17703. M_w^{GPC} = 20388. PDI = 1.2. Peak **B**: M_n^{GPC} = 1038. M_w^{GPC} = 3539. PDI = 3.4.

Cyclobutene **2a** (0.60 mmol), cyclohexene **4a** (1.20 mmol) and **1** (0.003 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 1.5 h and quenched at 50% completion. DP = 50. According to GPC chromatographic analysis, the copolymer had a bimodal molecular weight distribution (Figure S6). M_n^{calc} = 29010. The overall GPC result: M_n^{GPC} = 3201. M_w^{GPC} = 18106. PDI = 5.7. Peak A: M_n^{GPC} = 25088. M_w^{GPC} = 28697. PDI = 1.1. Peak B: M_n^{GPC} = 1383. M_w^{GPC} = 2143. PDI = 1.5.

(2b-4a)$_{20}$:

Cyclobutene **2b** (0.12 mmol), cyclohexene **4a** (0.24 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 4 h to reach 96% completion. The solvent was removed from the crude mixture in vacuo and the residue was

purified by flash column chromatography (100% CH_2Cl_2) to provide polymer **(2b-4a)$_{20}$** (16 mg, 55%). ^{1}H (500 MHz, CD_2Cl_2) δ 7.44-6.95 (m, 125H), 6.40 (m, 0.5H+0.5H), 6.31 (b, 0.5H), 6.03 (b, 1H), 5.78 (b, 0.5H), 5.60-5.40 (b, m, 38H), 5.03 (m, 2H), 2.66-2.10 (b, m, 160H), 1.73-1.42 (b, m, 80H). DP = 96. M_n^{calc} = 5224. M_n^{GPC} = 1572. M_w^{GPC} = 3302. PDI = 2.1.

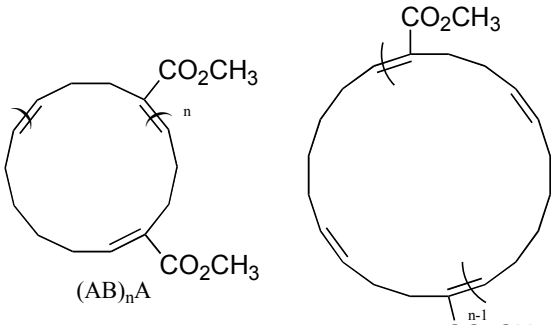
(2a-4b)$_{20}$:

Cyclobutene **2a** (0.12 mmol), cyclohexene **4b** (0.24 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 4 h to reach 95% completion. The solvent was removed from the crude mixture in vacuo and the residue was purified by flash column chromatography (100% CH_2Cl_2) to generate polymer **(2a-4b)$_{20}$** (15 mg, 59%). ^{1}H (500 MHz, CD_2Cl_2) δ 7.41-7.21 (m, 5H), 6.83 (m, 20H), 6.42 (m, 1H), 6.27 (m, 1H), 5.83 (m, 1H), 5.42 (m, 38H), 5.02 (m, 2H), 3.72 (bs, 60H), 3.34-3.17 (m, 100H), 2.47-2.06 (m, 160H), 1.78-1.24 (m, 60H). DP = 95. M_n^{calc} = 4264. M_n^{GPC} = 1506. M_w^{GPC} = 3719. PDI = 2.5.

(2a-4a-D10)$_{20}$ (24 equiv. of 4a-D$_{10}$):

Cyclobutene **2a** (0.12 mmol), cyclohexene **4a-D$_{10}$** (0.144 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 97% completion. The solvent was evaporated, and the residue was purified by flash column chromatography (acetone:CH_2Cl_2/4:96) to provide polymer **(2a-4a-D$_{10}$)$_{20}$** as a sticky oil (17.4 mg, 71%). ^{1}H (500 MHz, CD_2Cl_2) δ 7.41-7.21 (m, 5H), 6.78 (t, J=2.5 Hz, 2H), 6.39 (m, 1H), 6.27 (m, 1H), 5.43 (m, 20H), 5.06-5.02 (d, J=2.0 Hz, 1H), 4.98-4.97 (d, J=0.5 Hz, 1H), 3.72 (s,

60H), 2.36-2.09 (m, 80H). Polymer **(2a-4a-D_{10})$_{20}$** was further purified by flash chromatography (acetone:CH_2Cl_2/4:96) to provide cyclic polymer **cyc-(2a-4a-D_{10})$_{20}$** as a sticky oil (3.3 mg). Polymer **cyc-(2a-4a-D10)$_{20}$** was characterized by ^{1}H-NMR spectroscopy and the structures are shown below. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.84 (t, J=1.0 Hz, 1H) 5.48-5.36 (m, 5H), 3.75 (m, 18H), 2.47-2.12 (m, 24H).



A: ring-opened cyclobutene subunit
B: ring-opened cyclohexene subunit

(2a-4a-D10)$_{20}$ (160 equiv. of 4a-D_{10}):

Cyclobutene **2a** (0.12 mmol), cyclohexene **4a-D_{10}** (0.96 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. The reaction was maintained for 3 h to reach 97% completion.

(4a)$_{20}$:

Cyclohexene **4a** (0.12 mmol) and **1** (0.006 mmol) were mixed in CD_2Cl_2 (600 μL) in an NMR tube. No ROMP or ROM was observed.

(2a)$_{10}$:

Methyl cyclobut-1-enecarboxylate **2a** (0.06 mmol) and **1** (0.006 mmol) were mixed in

CD_2Cl_2 (600 μL) in an NMR tube. The reaction was monitored for 5 h and only reaction of 10% of **2a** was observed.

Preparative Scale AROMP

(2a$_1$): (7a and 7b)

A solution of **2a** (40.0 mg, 0.357 mmol) in dry CH_2Cl_2 (4 mL) was added to a solution of precatalyst **1** (474 mg, 0.536 mmol) in dry CH_2Cl_2 (4 mL) at rt. The solution was stirred at rt for 20 h and ethylvinyl ether (5 mL, 52.2 mmol) was added to the reaction mixture. After 60 min, the solvent was evaporated and the residue was purified by silica column chromatography with CH_2Cl_2. The purified fractions were evaporated to afford the products **7a** (*Z*) and **7b** (*E*) (42.1 mg, 55%) in a 1:2.3 molar ratio. ^{1}H-NMR (600 MHz, CD_2Cl_2) 1-mer **7a** *Z*-isomer δ 7.36-7.19 (m, 5H), 6.47 (d, J=12.6 Hz, 1H), 6.15 (s, 1H), 5.68 (dt, J=11.4, 7.8 Hz, 1H), 5.60 (s,1H), 3.72 (s, 3H), 2.50 (m, 2H), 2.43 (m, 2H). 1-mer **7b** *E*-isomer δ 7.36-7.19 (m, 5H), 6.42 (d, J=16.2 Hz, 1H), 6.25 (dt, J=22.8, 6.0 Hz, 1H), 6.17 (s, 1H), 5.60 (s, 1H), 3.75 (s, 3H), 2.50 (m, 2H), 2.43 (m, 2H). ^{13}C-NMR (100 MHz, CD_2Cl_2) 1-mer **7a** *Z*-isomer δ 167.9, 140.6, 138.1, 132.1, 130.8, 130.0, 129.3, 128.6, 127.2, 125.5, 52.2, 32.6, 28.0. 1-mer **7b** *E*-isomer δ 168.0, 140.7, 138.1, 131.0, 130.3, 129.0, 128.7, 127.5, 126.5, 52.2, 32.4, 32.3. LC-MS (APCI): peak time=2.18 min, M/Z calcd for $C_{14}H_{16}O_2$ $[M+H]^+$ 217.12, found 217.21.

(2a-4a)$_3$:

Cyclobutene **2a** (0.28 mmol, 31 mg) and **1** (0.093 mmol, 82 mg) were mixed in CH_2Cl_2 (2 mL) and stirred for 3 h at rt. Then cyclohexene **4a** (0.56 mmol, 56 μL) was added to the

solution, which was stirred for 3 h. The reaction was quenched with ethylvinyl ether (500 μL) and was stirred for 1 h. The solvent was evaporated, and the residue was purified by flash column chromatography (acetone:CH_2Cl_2/4:96) to provide polymer (**2a**-**4a**)$_3$ as a sticky oil (47 mg, 74%). ^{1}H-NMR (125 MHz, CD_2Cl_2) δ 7.35-7.21 (m, 5H), 6.80 (m, 6H), 6.42 (d, J=16 Hz, 1H), 6.26 (m, 1H), 5.84 (b, 1H), 5.44 (b, 4 H), 5.04 (d, J=17 Hz, 1H), 4.97 (d, J=15 Hz, 1H), 3.73 (b, 9H), 2.61-2.04 (b, 24H), 1.54 (b, 12H). ^{13}C (500 MHz, CD_2Cl_2) δ 170.70 (m), 146.00-145.08 (m), 134.30-132.03 (m), 131.10, 130.77, 129.51, 128.53, 127.51, 126.91, 54.00, 36.20-34.11 (m), 32.34-28.48 (m).

(2a-4a)$_{10}$:

Cyclobutene **2a** (0.23 mmol, 26 mg) and **1** (0.024 mmol, 21 mg) were mixed in CH_2Cl_2 (2.3 mL) and stirred for 25 min at rt. Then cyclohexene **4a** (0.47 mmol, 47 μL) was added to the solution, which was stirred for 4 h. The reaction was quenched with ethylvinyl ether (350 μL), and was stirred for 1 h. The solvent was evaporated, and the residue was purified by flash column chromatography (acetone:CH_2Cl_2/1:99) to provide polymer (**2a**-**4a**)$_{10}$ as a sticky oil (32 mg, 71 %). ^{1}H-NMR (500 MHz, CD_2Cl_2) δ 7.41-7.21 (m, 5H), 6.77 (b, 10H), 6.41 (d, J=15.5 Hz, 1H), 6.26 (d, J=16.0 Hz, 1H), 5.84 (b, 1H), 5.49 (b, 18H), 5.04 (d, J=17.0 Hz, 1H), 4.97 (d, J= 10.0 Hz, 1H), 3.72 (s, 30H), 2.56- 2.02 (b, m, 80H), 1.46 (b, 40H). The broad signal centered at 7.29 ppm was assigned to the phenyl group. All the internal trisubstituted olefinic protons exhibited a broad signal centered at 6.78 ppm, which confirmed all the internal trisubstituted olefin bonds carried the *E*-configuration. All the internal disubstituted olefinic protons also showed a broad signal centered at 5.39 ppm. The peaks at 5.87 ppm and 5.02 ppm

correspond to the terminal vinyl protons, while the peaks at 6.42 ppm and 6.30 ppm could be assigned to the two styrenyl olefinic protons with *E*-configuration. The relative intensities of all these signals were (5: 11: 18: 1: 1: 2: 1) (7.29, 6.78, 5.39, 6.42, 6.30, 5.02, 5.89 ppm), which clearly indicated that polymer (**2a**-**4a**)$_{10}$ contained nearly equal amounts of repeating units A and B generated from monomers **2a** and **4a**, respectively.

(2a-4a)$_{20}$:

Cyclobutene **2a** (0.47 mmol, 53 mg) and **1** (0.024 mmol, 21 mg) were mixed in CH_2Cl_2 (2 mL) and stirred for 25 min at rt. Then cyclohexene **4a** (0.94 mmol, 95 μL) was added to the solution, which was stirred for 5 h thereafter. The reaction was quenched with ethylvinyl ether (350 μL), and was stirred for 1 h. The solvent was evaporated, and the residue was purified by flash column chromatography (acetone:CH_2Cl_2/4:96) to provide polymer (**2a**-**4a**)$_{20}$ as a sticky oil (67 mg, 74%). Polymer (**2a**-**4a**)$_{20}$ was characterized by ^{1}H-NMR, ^{13}C-NMR, gHMQC, ^{1}H -^{1}H gCOSY and ^{13}C-APT spectroscopy (Table S1).

Table S1. ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H gCOSY, ^{13}C-APT, and ^{1}H-^{13}C gHMQC data for compound (**2a**-**4a**)$_{20}$ (500, 100, 500, 100 and 500/125 MHz, CD_2Cl_2).[a]

No.	δ_H (J in Hz)	δ_C	^{1}H-^{1}H gCOSY	^{13}C-APT
1	4.97 d (15)			
	5.04 d (17)			
2	5.79 b	129.5-132.5		CH
3	2.04-2.50 b	26.7-32.5		CH_2
4	1.42 b	29.2-29.9		CH_2
5	1.42 b	29.2-29.9		CH_2
6	2.04-2.50 b	26.7-32.5		CH_2
7	6.74 b	142.7-143.7		CH
8		131.8		q
9	2.04-2.50 b	26.7-32.5		CH_2
10	2.04-2.50 b	26.7-32.5	11	CH_2
11	5.40 m	129.5-131.1	10	CH
12	5.40 m	129.9-131.0	13	CH
13	2.04-2.50 b	26.7-32.5	12, 14, 16	CH_2
14	1.42 b	29.2-29.9	13, 15	CH_2
15	1.42 b	29.2-29.9	14, 16	CH_2
16	2.04-2.50 b	26.7-32.5	13, 15, 17	CH_2
17	6.74 b	142.7-143.7	16	CH
18		131.8		q
19	2.04-2.50 b	26.7-32.5		CH_2
20	2.04-2.50 b	26.7-32.5		CH_2
21	6.24 b	129.7		CH
22	6.39 d (16)	129.7		CH
23		131.9		q
24-28	7.19-7.33 m	128.3-129.7		CH
29		168.2		q
30	3.70 s	51.8		CH_3

[a]Shaded rows correspond to the atoms in the repeating polymer unit (see Figure S1).

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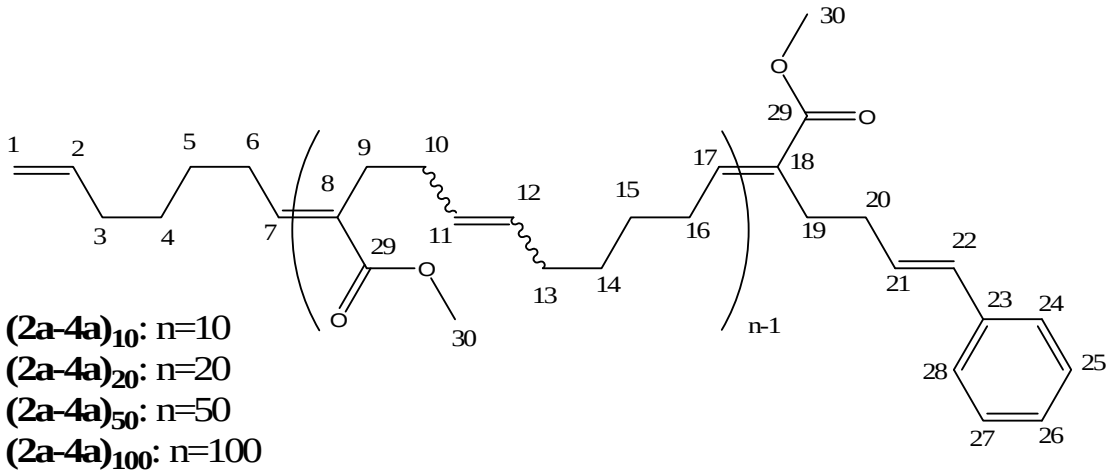
Figure S1. ^{1}H-NMR spectra of alternating ROMP polymers.



(2a-4a)$_{10}$: n=10
(2a-4a)$_{20}$: n=20
(2a-4a)$_{50}$: n=50
(2a-4a)$_{100}$: n=100
(2a-4a)$_{200}$: n=200

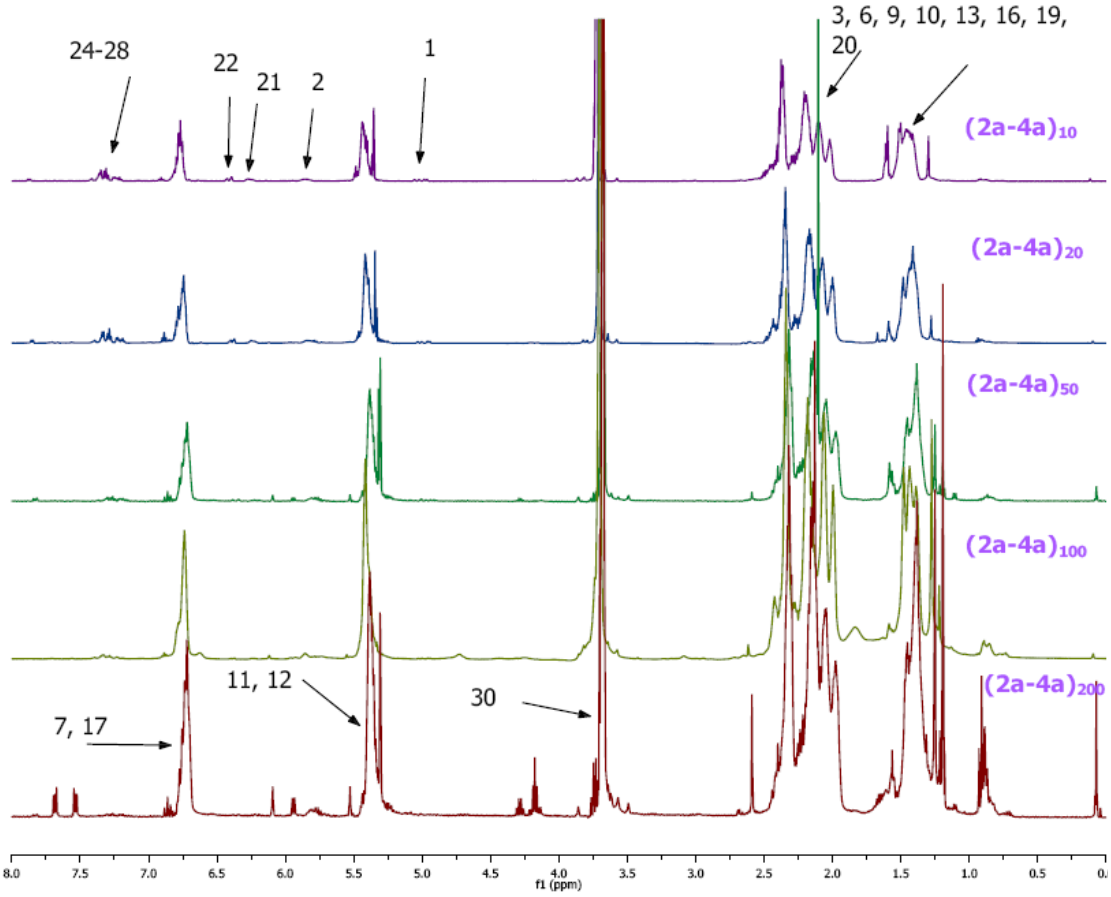


Figure S2. ^{13}C-APT-NMR spectrum of alternating ROMP polymer **(2a-4a)$_{20}$**.

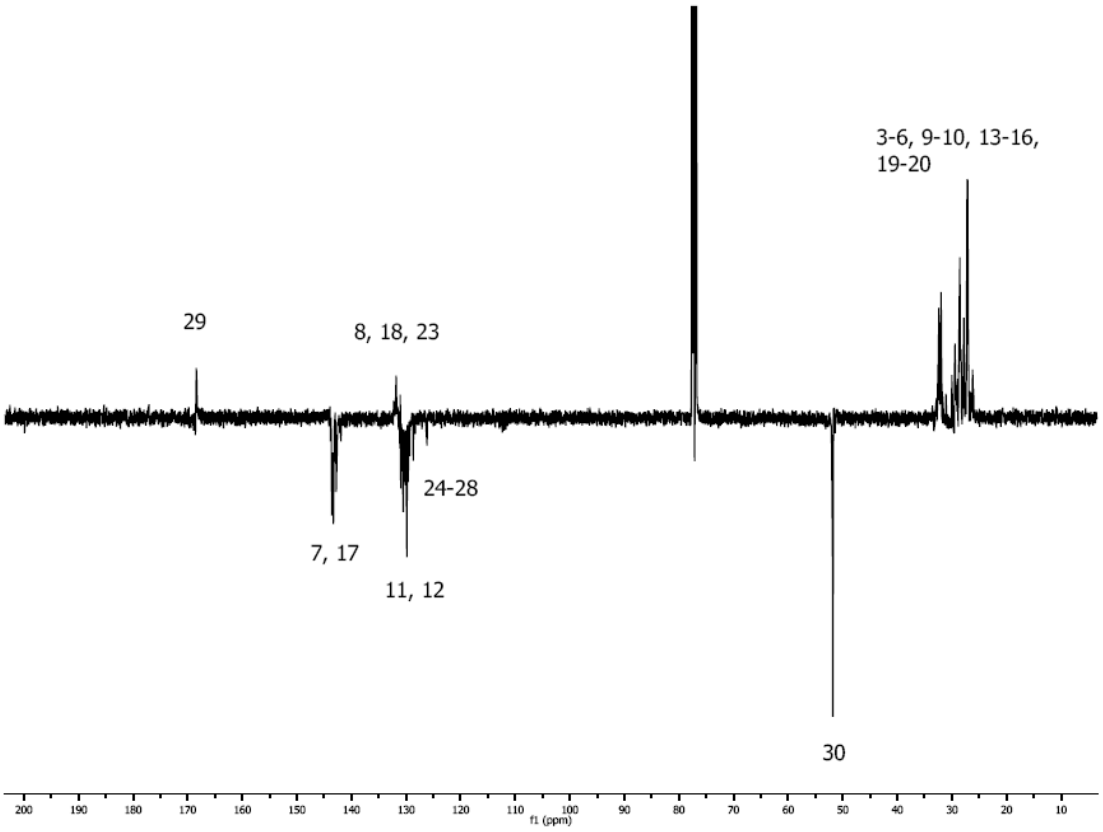


Figure S3. ^{1}H-^{1}H-gCOSY-NMR spectrum of alternating ROMP polymer **(2a-4a)$_{20}$**.

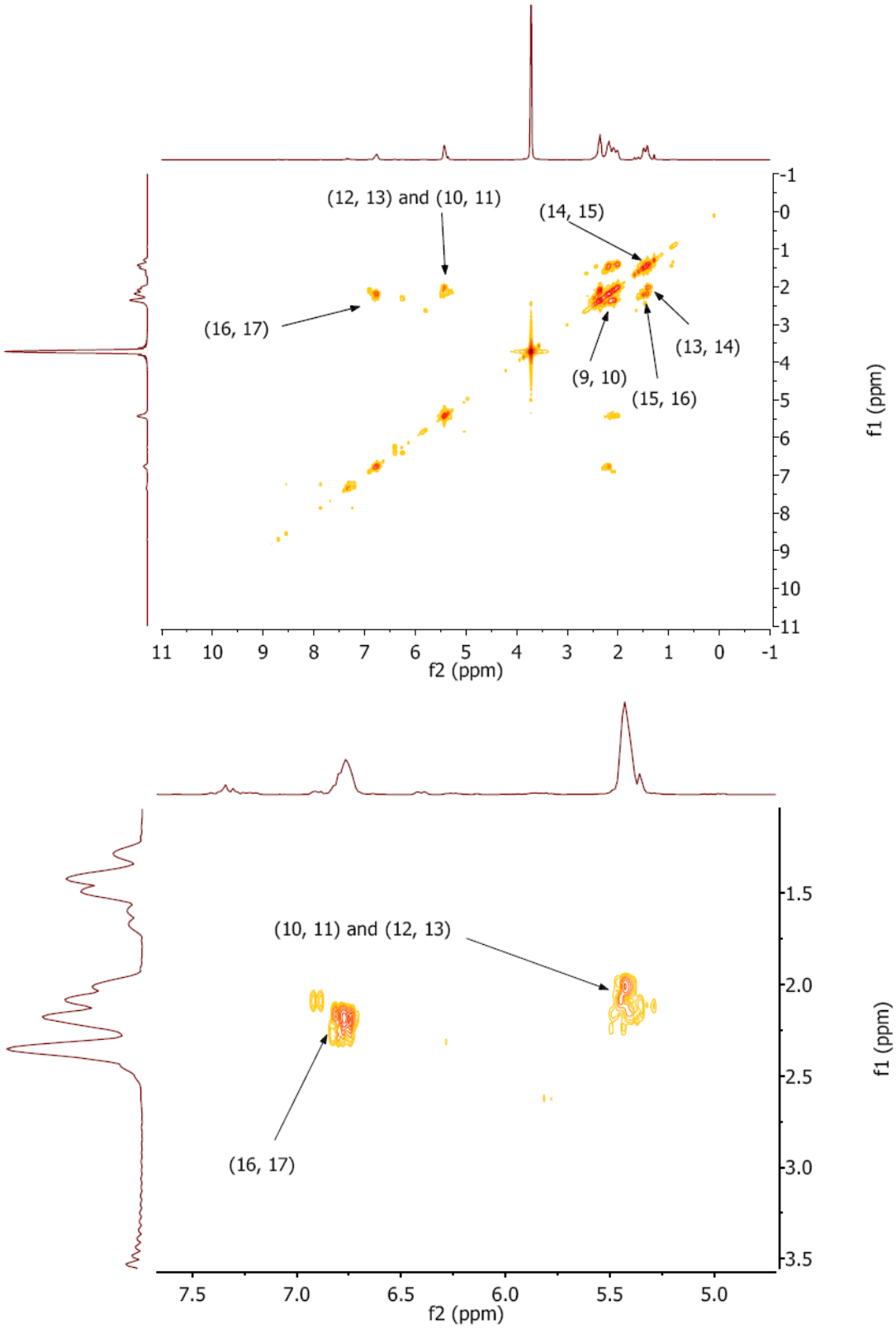


Figure S4. Kinetic NMR-monitoring experiment of **(2a-4a)$_{100}$**

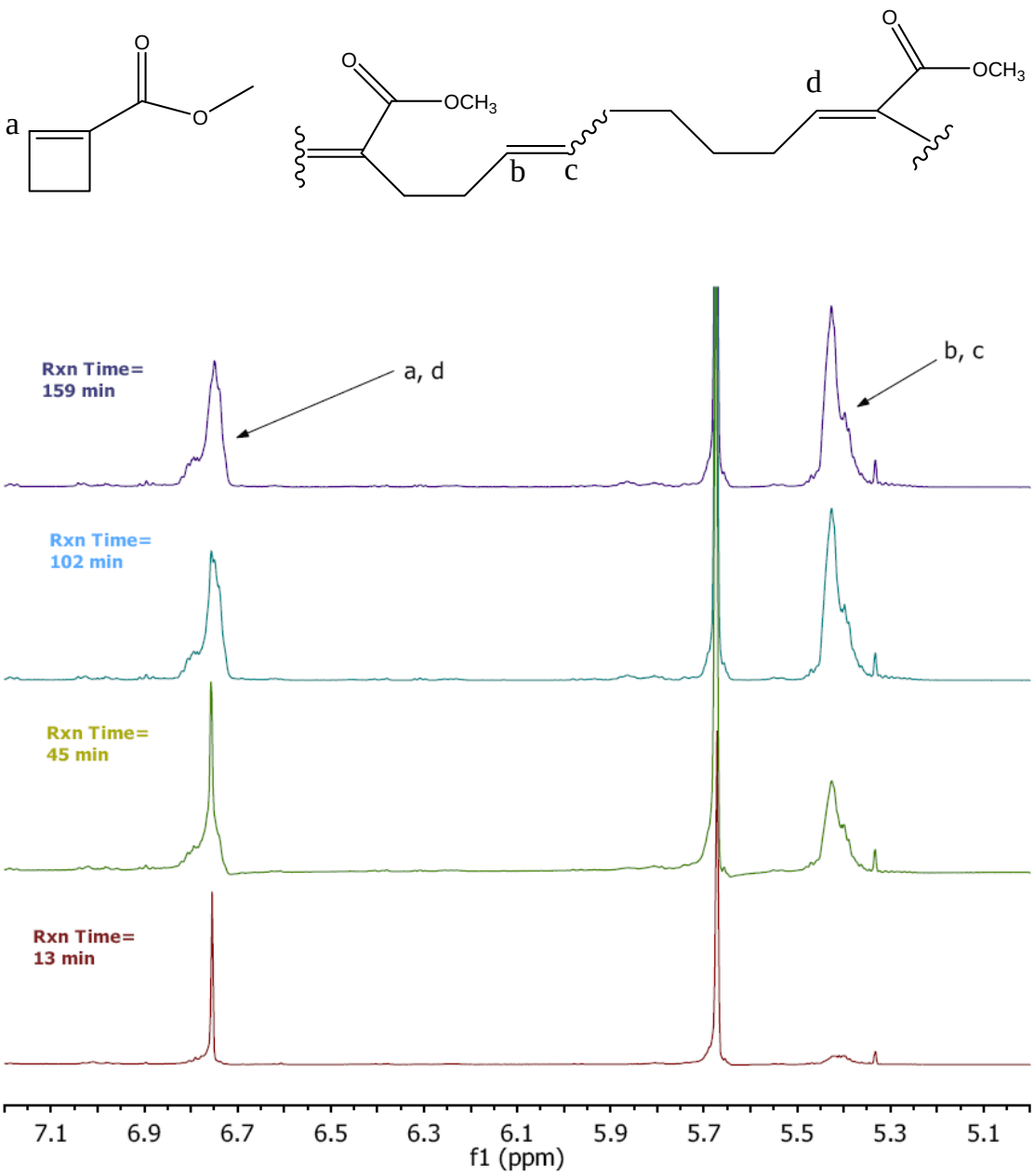
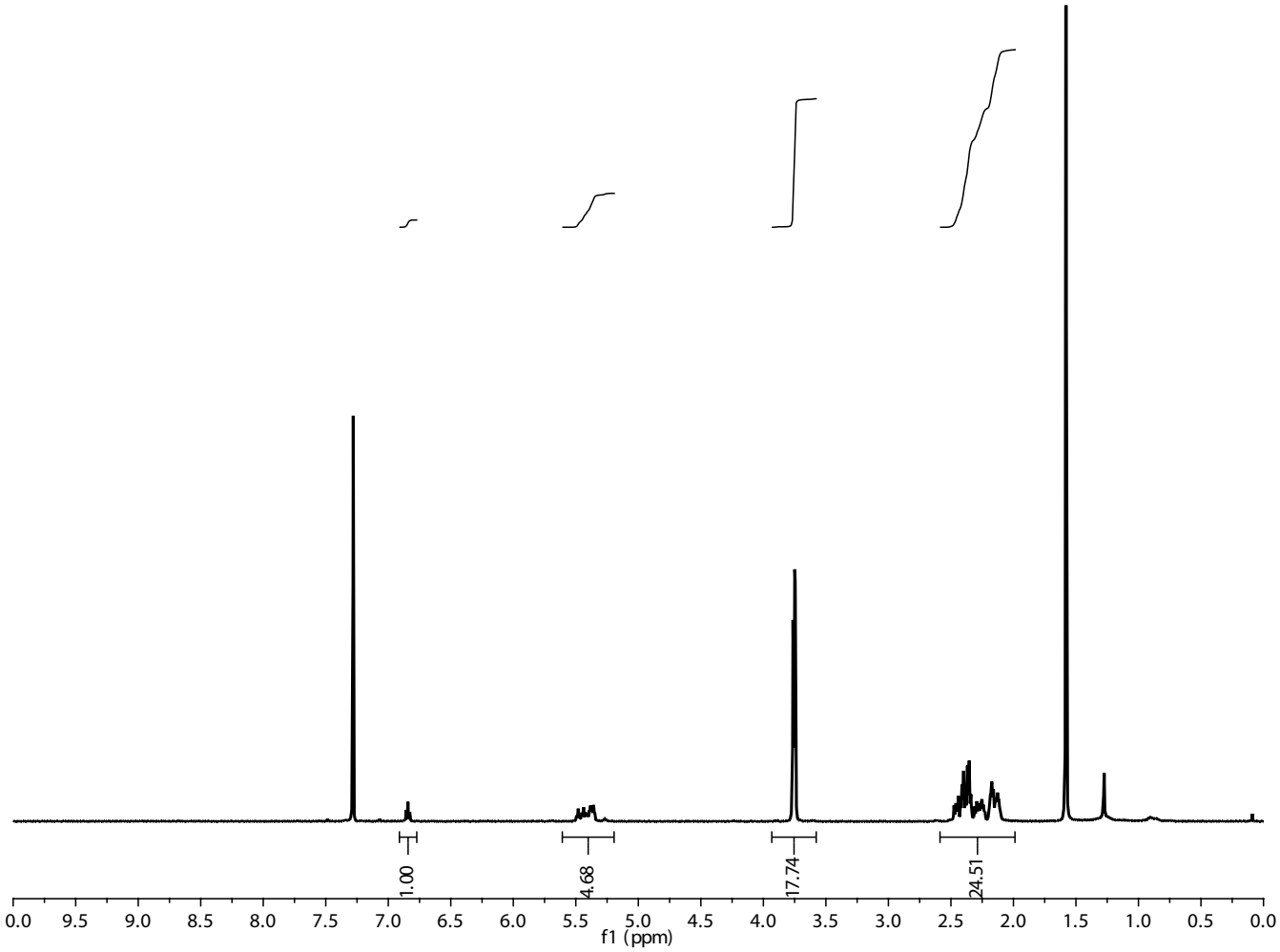
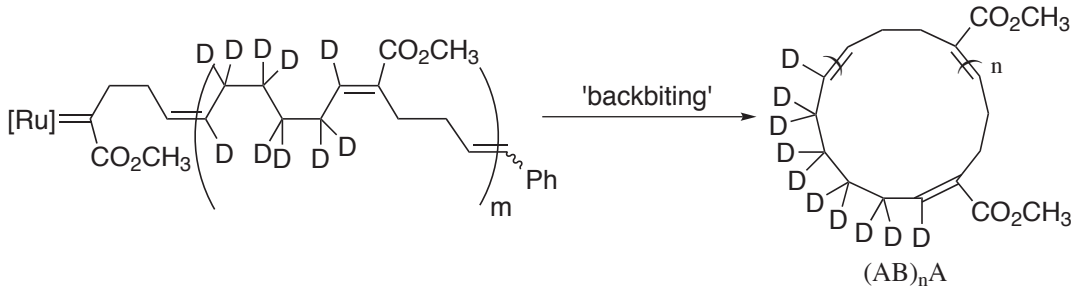
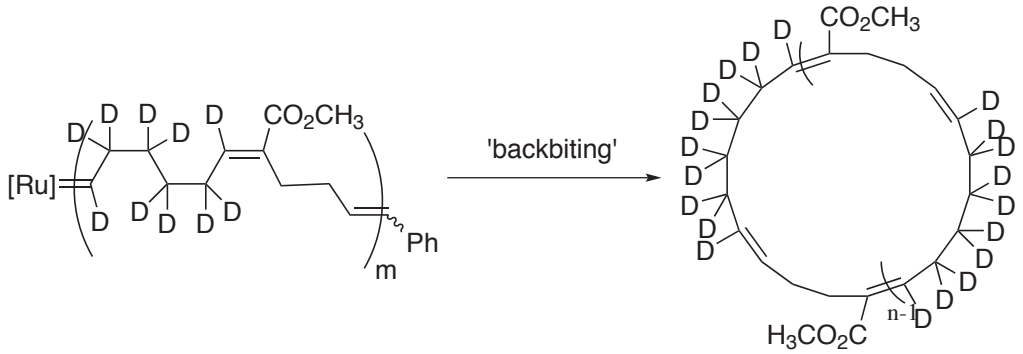


Figure S5. ^{1}H-NMR spectrum of cyclic polymer cyc-(2a-4a-D_{10})$_{20}$





(AB)$_n$A



A: ring-opened cyclobutene subunit
B: ring-opened cyclohexene subunit

(AB)$_n$

Figure S6. GPC traces of $(\mathbf{2a\text{-}4a})_{100}$ and $(\mathbf{2a\text{-}4a})_{200}$

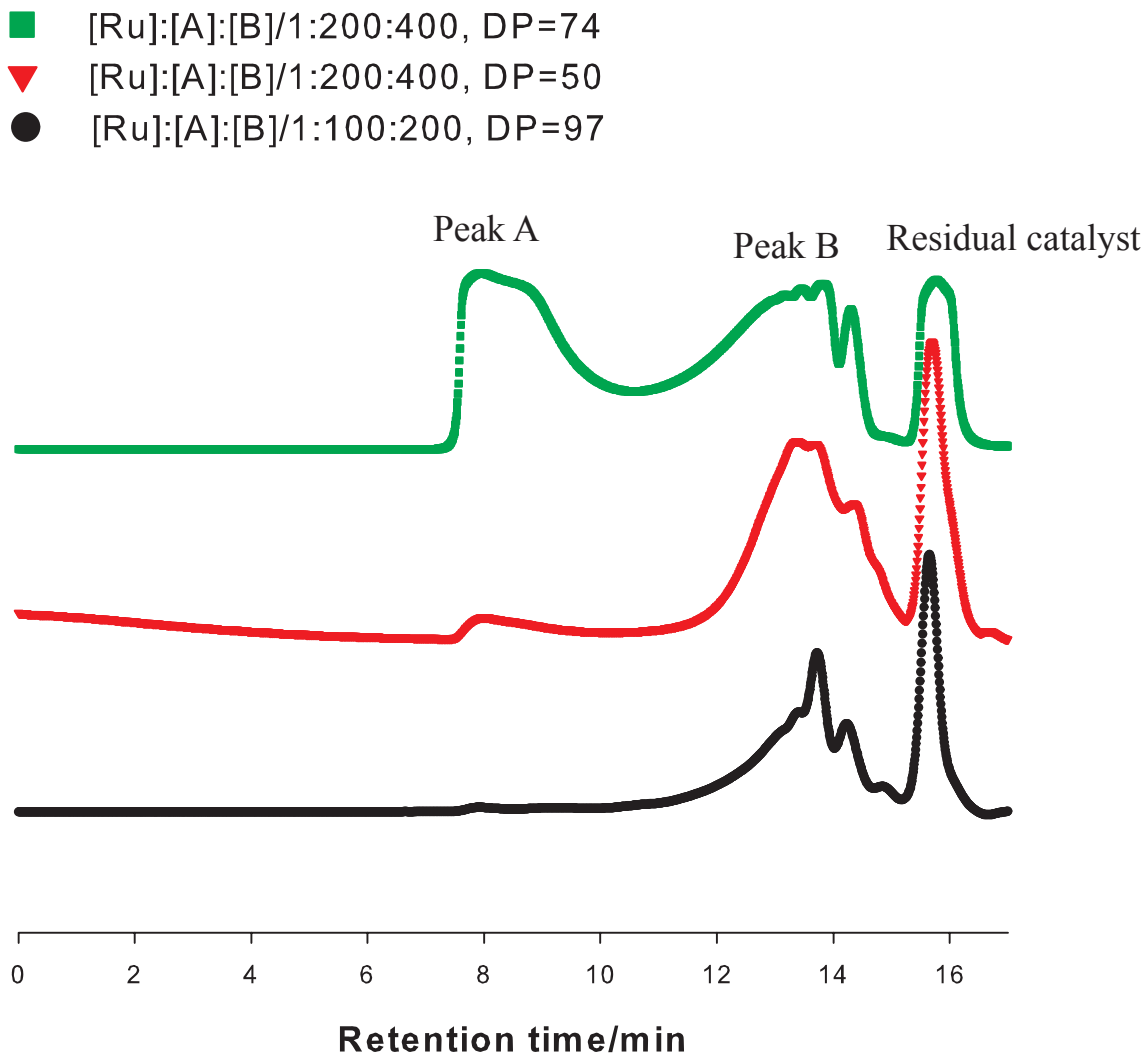
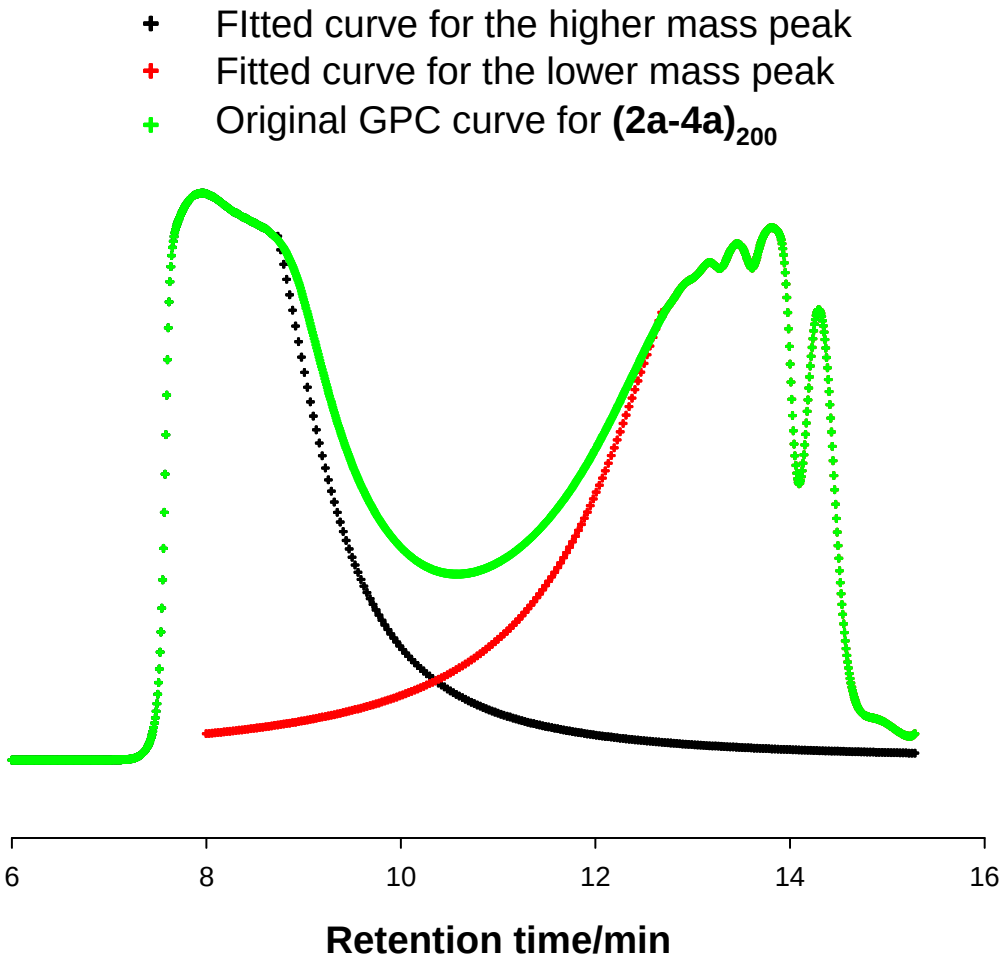
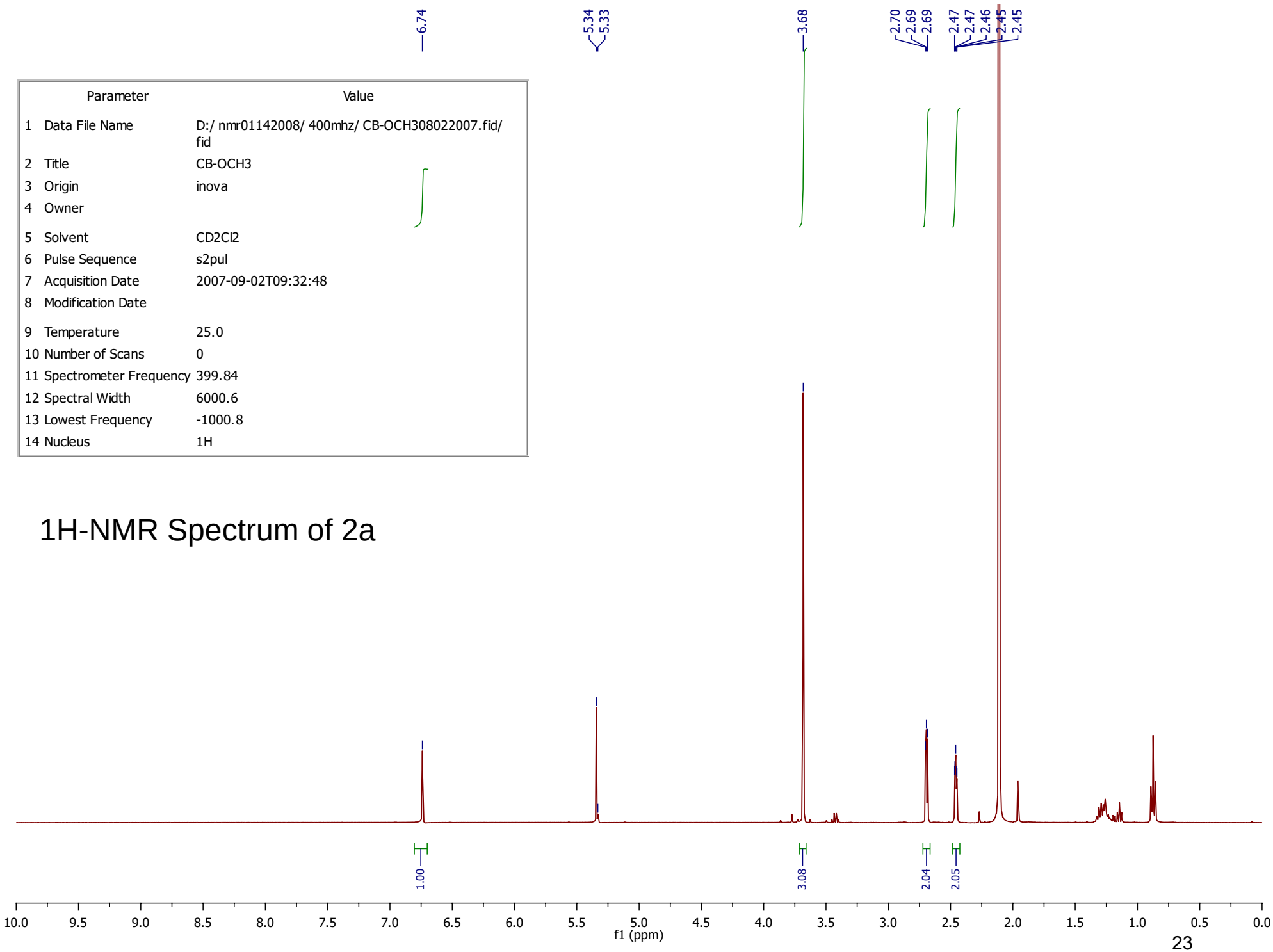


Figure S7. Bimodal peak fitting of GPC trace of $(\mathbf{2a\text{-}4a})_{200}$

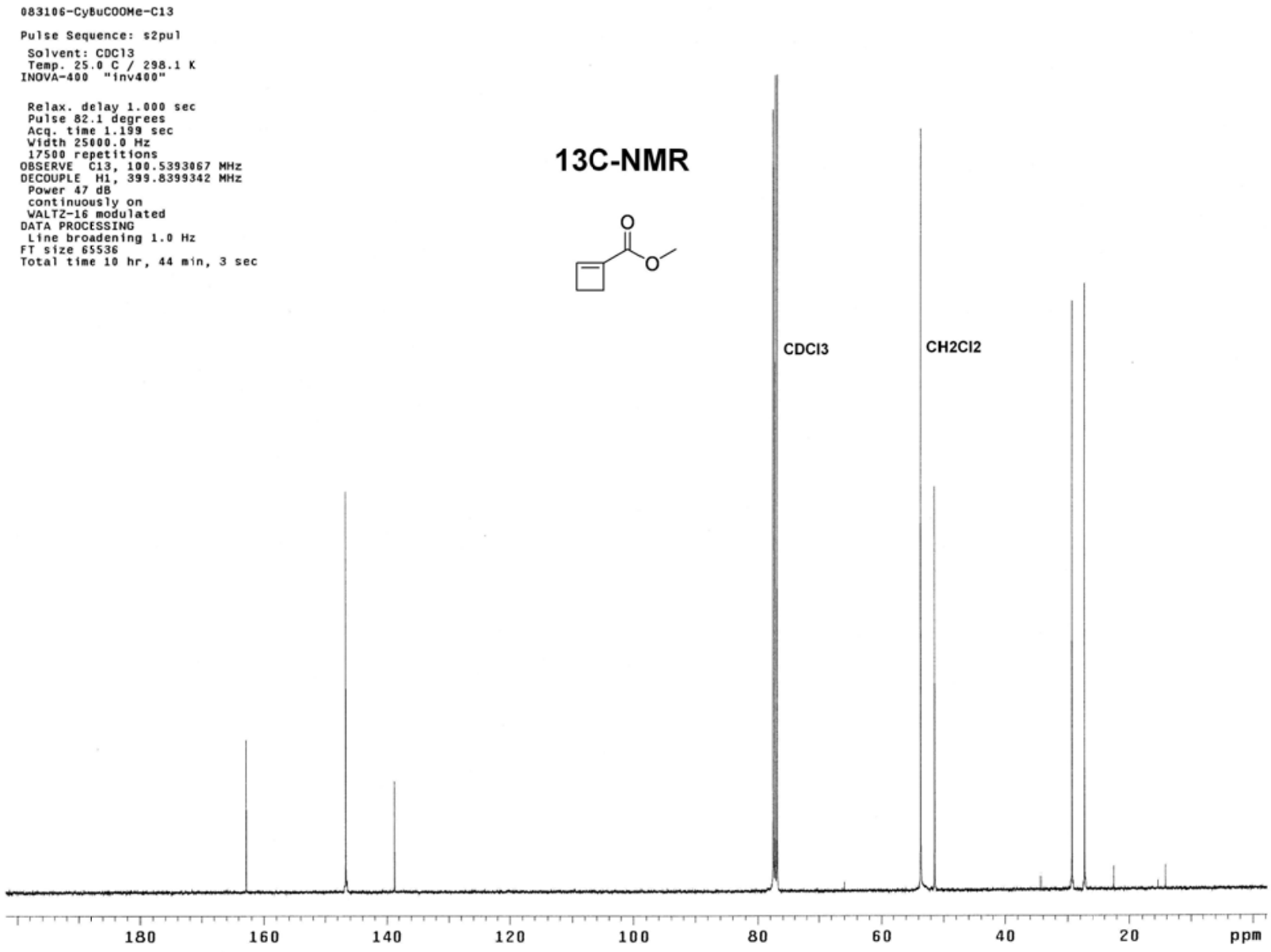


	Parameter	Value
1	Data File Name	D:/ nmr01142008/ 400mhz/ CB-OCH308022007.fid/ fid
2	Title	CB-OCH3
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-09-02T09:32:48
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	0
11	Spectrometer Frequency	399.84
12	Spectral Width	6000.6
13	Lowest Frequency	-1000.8
14	Nucleus	1H

1H-NMR Spectrum of 2a

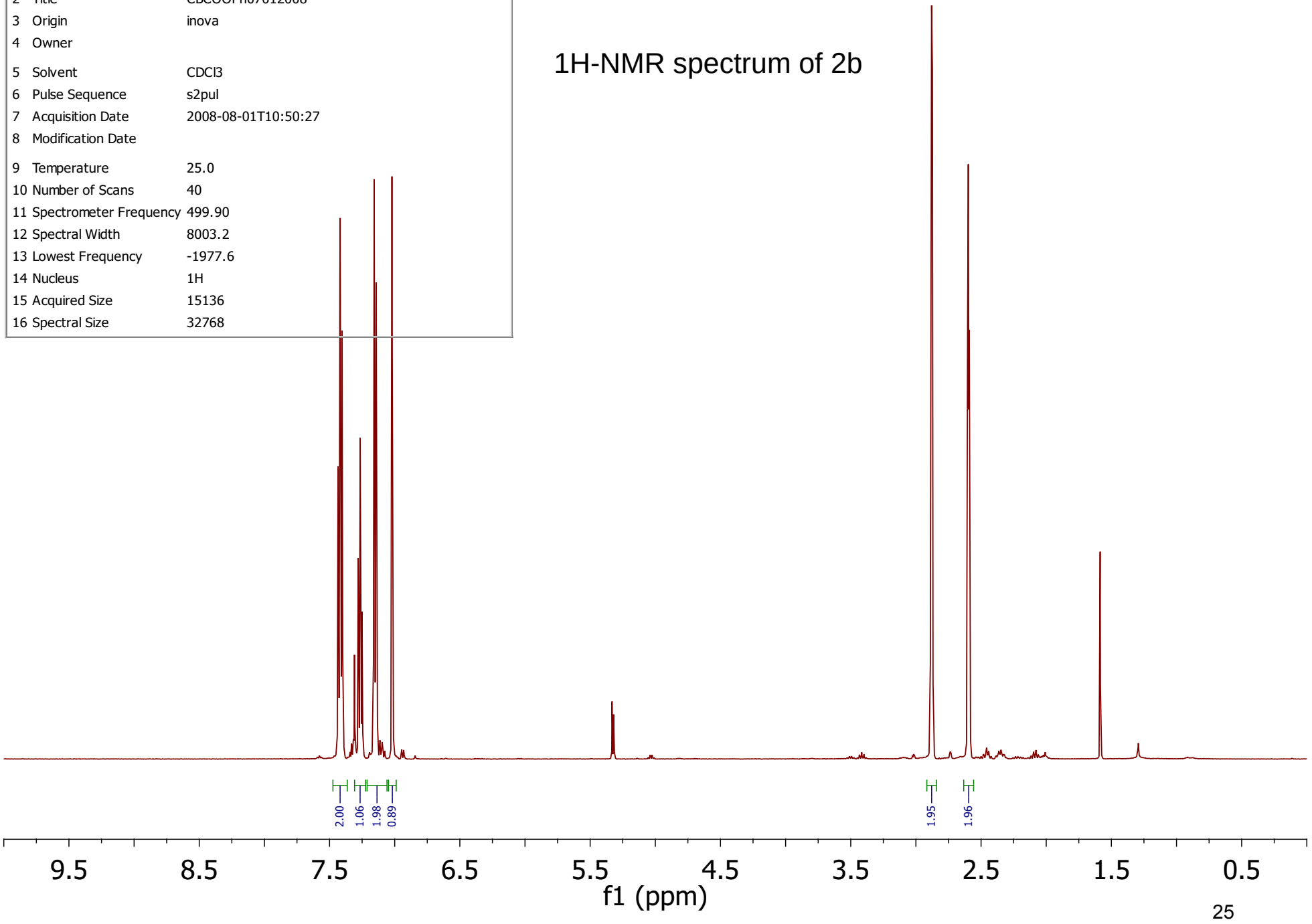


13C-NMR Spectrum of 2a



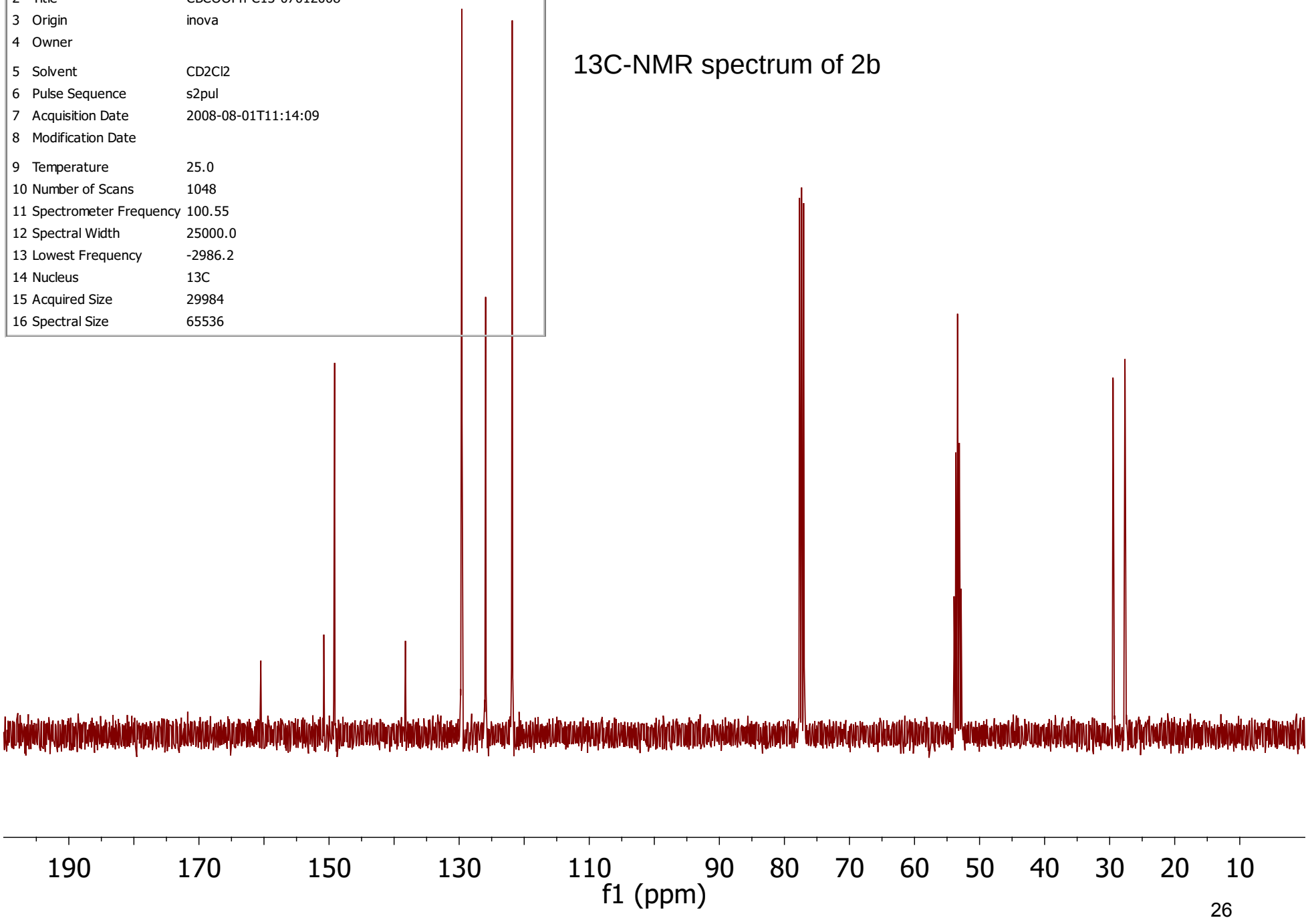
	Parameter	Value
1	Data File Name	L:/ 07012008-07112008/ CBCOOPh07012008.fid/ fid
2	Title	CBCOOPh07012008
3	Origin	inova
4	Owner	
5	Solvent	CDCl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-08-01T10:50:27
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	40
11	Spectrometer Frequency	499.90
12	Spectral Width	8003.2
13	Lowest Frequency	-1977.6
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768

1H-NMR spectrum of 2b



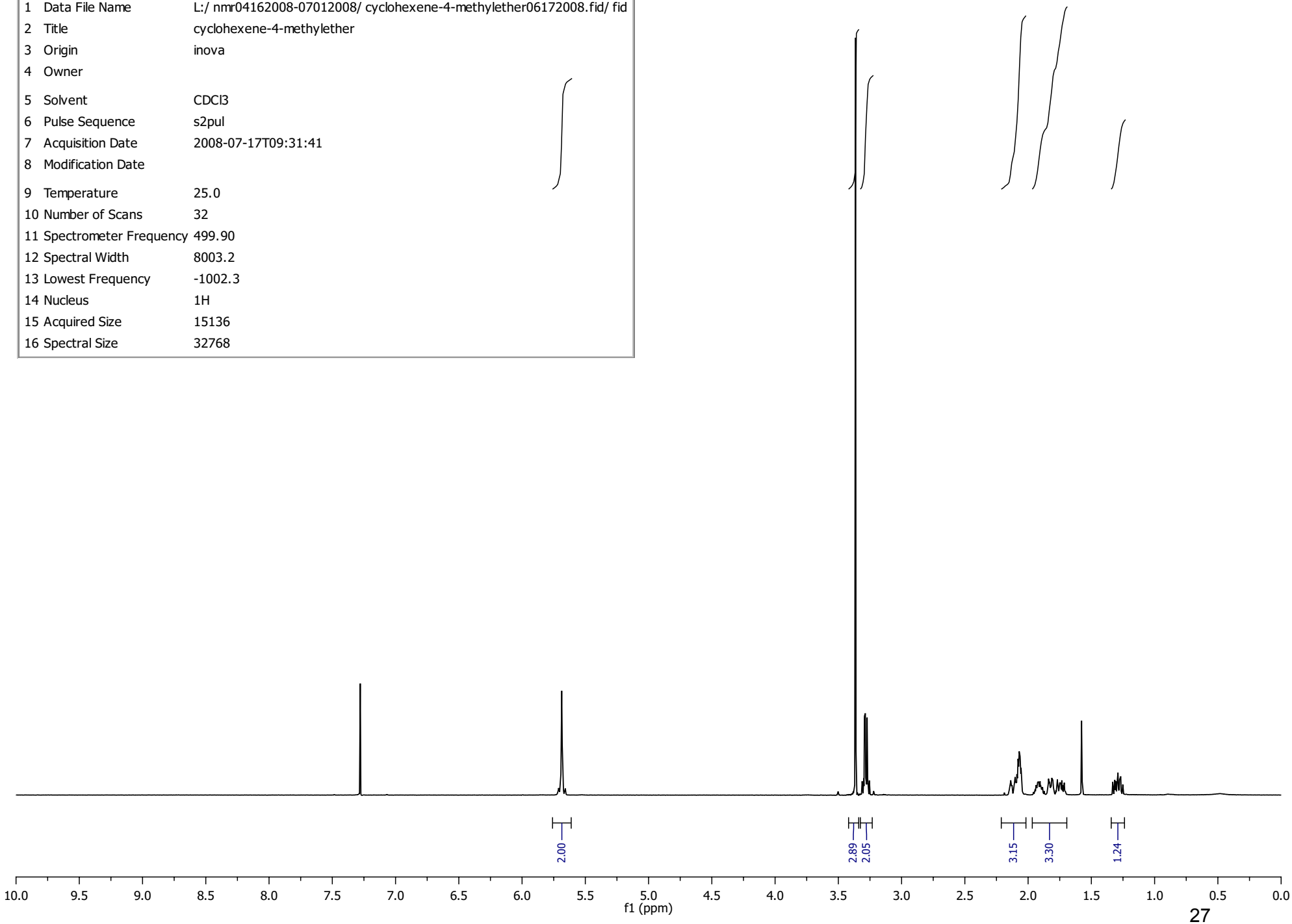
	Parameter	Value
1	Data File Name	L:/ 07012008-07112008/ CBCOOPh-C13-07012008.fid/ fid
2	Title	CBCOOPh-C13-07012008
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-08-01T11:14:09
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	1048
11	Spectrometer Frequency	100.55
12	Spectral Width	25000.0
13	Lowest Frequency	-2986.2
14	Nucleus	13C
15	Acquired Size	29984
16	Spectral Size	65536

13C-NMR spectrum of 2b



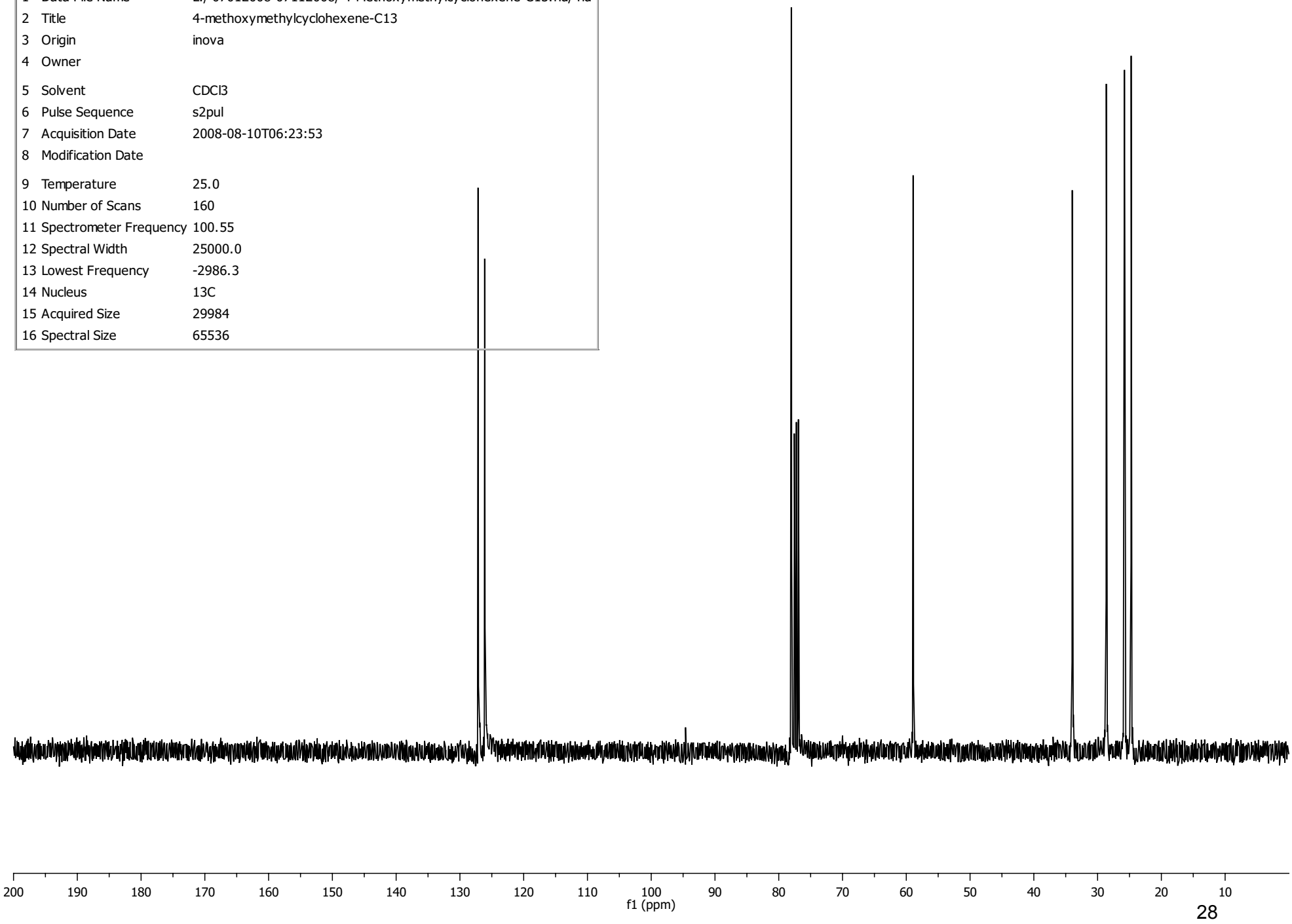
1H-NMR spectrum of 4b

	Parameter	Value
1	Data File Name	L:/ nmr04162008-07012008/ cyclohexene-4-methylether06172008.fid/ fid
2	Title	cyclohexene-4-methylether
3	Origin	inova
4	Owner	
5	Solvent	CDCl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-07-17T09:31:41
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	32
11	Spectrometer Frequency	499.90
12	Spectral Width	8003.2
13	Lowest Frequency	-1002.3
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768



13C-NMR spectrum of 4b

	Parameter	Value
1	Data File Name	L:/ 07012008-07112008/ 4-Methoxymethylcyclohexene-C13.fid/ fid
2	Title	4-methoxymethylcyclohexene-C13
3	Origin	inova
4	Owner	
5	Solvent	CDCl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-08-10T06:23:53
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	160
11	Spectrometer Frequency	100.55
12	Spectral Width	25000.0
13	Lowest Frequency	-2986.3
14	Nucleus	13C
15	Acquired Size	29984
16	Spectral Size	65536



1H-NMR spectrum of (2a-4a)3

CBCOOCH3-cyclohexene-3mer

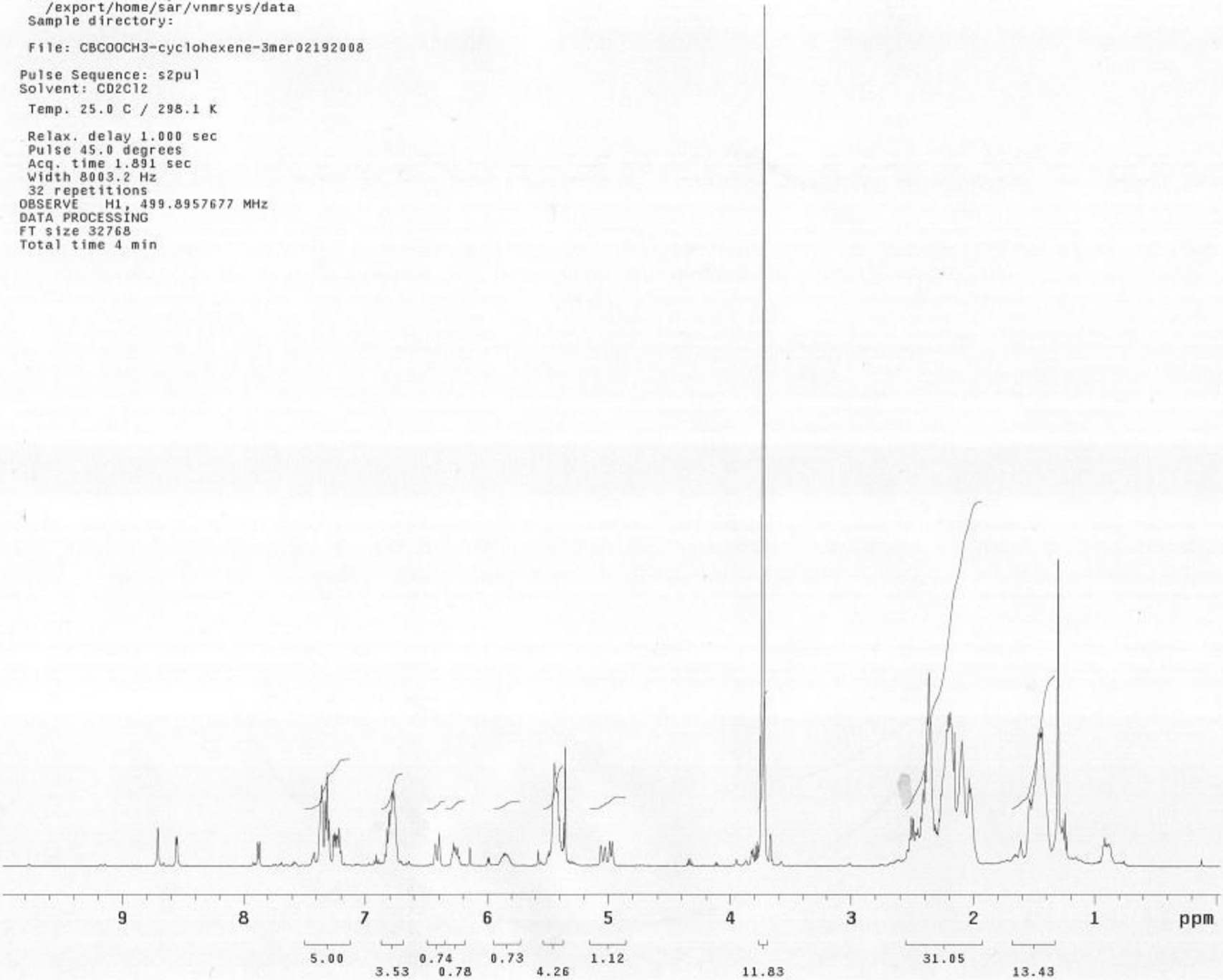
Data Collected on:
inv500-inova500
Archive directory:
/export/home/sar/vnmrsys/data
Sample directory:

File: CBCOOCH3-cyclohexene-3mer02192008

Pulse Sequence: s2pul
Solvent: CD2Cl2

Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.891 sec
Width 8003.2 Hz
32 repetitions
OBSERVE H1, 499.8957677 MHz
DATA PROCESSING
FT size 32768
Total time 4 min



13C-NMR spectrum of (2a-4a)3

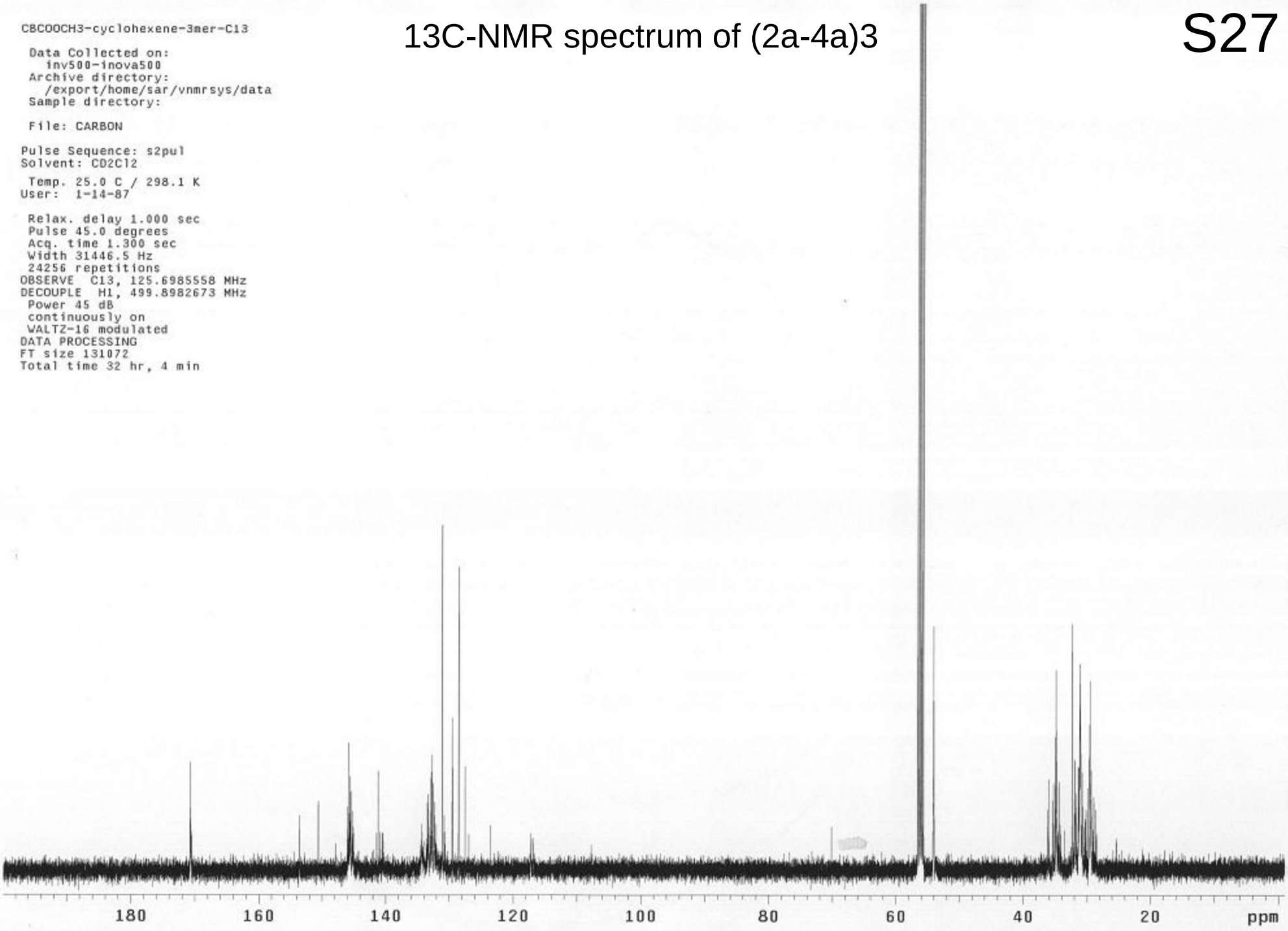

```
CBCOOCH3-cyclohexene-3mer-C13

 Data Collected on:
   inv500-inova500
 Archive directory:
   /export/home/sar/vnmrsys/data
 Sample directory:

 File: CARBON

Pulse Sequence: s2pul
Solvent: CD2Cl2
 Temp. 25.0 C / 298.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 31446.5 Hz
 24256 repetitions
OBSERVE  C13, 125.6985558 MHz
DECOUPLE  H1, 499.8982673 MHz
 Power 45 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
FT size 131072
Total time 32 hr, 4 min
```



1H-NMR spectrum of (2a-4a)10

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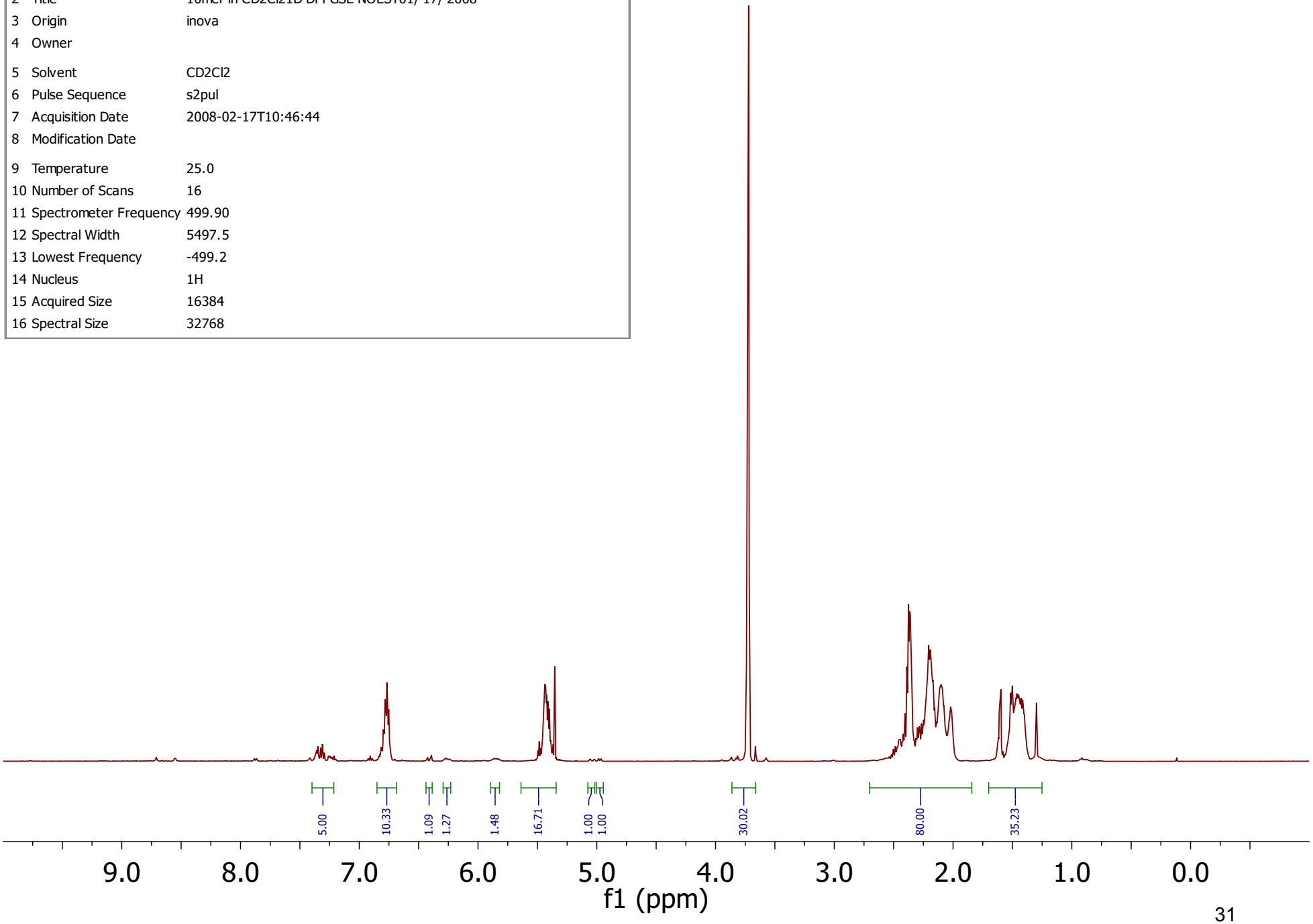
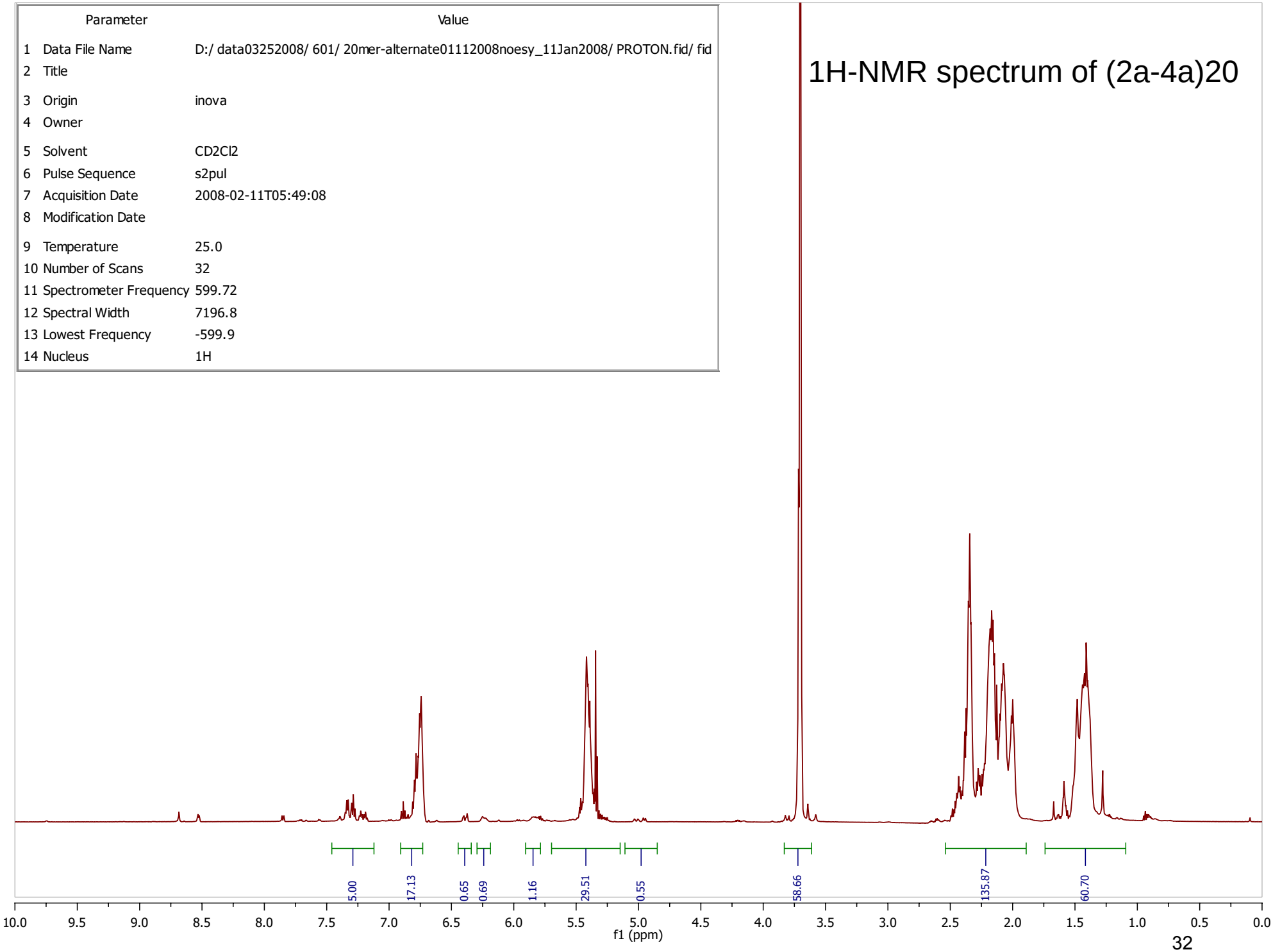
1	Data File Name	L:/ data03252008/ 500mhz/ 20mer-alternate01172008_a/ 10mer.fid/ fid
2	Title	10mer in CD2Cl21D DPFGSE NOESY01/ 17/ 2008
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-02-17T10:46:44
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	16
11	Spectrometer Frequency	499.90
12	Spectral Width	5497.5
13	Lowest Frequency	-499.2
14	Nucleus	1H
15	Acquired Size	16384
16	Spectral Size	32768



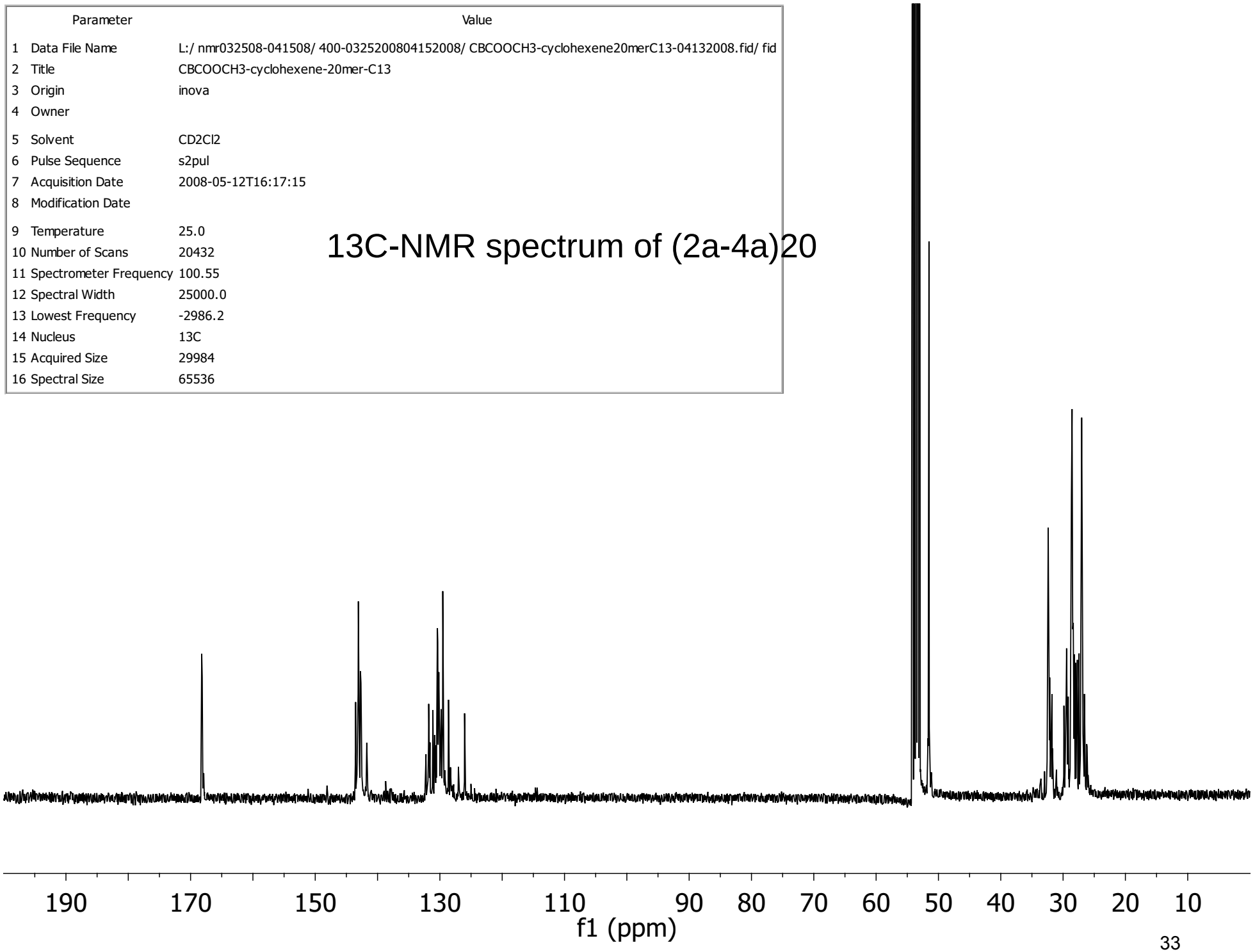
Parameter		Value
1	Data File Name	D:/ data03252008/ 601/ 20mer-alternate01112008noesy_11Jan2008/ PROTON.fid/ fid
2	Title	
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-02-11T05:49:08
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	32
11	Spectrometer Frequency	599.72
12	Spectral Width	7196.8
13	Lowest Frequency	-599.9
14	Nucleus	1H

1H-NMR spectrum of (2a-4a)20



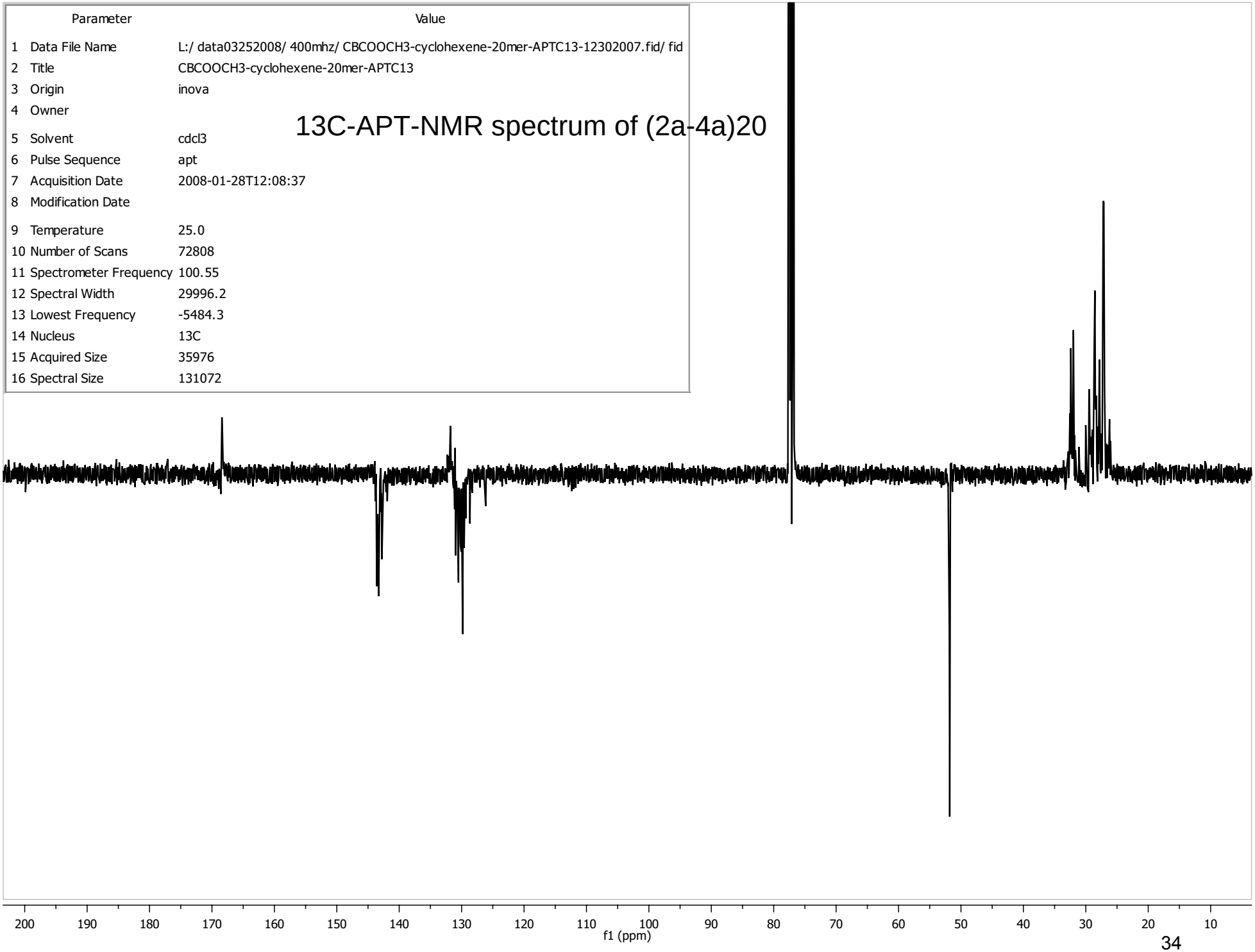
	Parameter	Value
1	Data File Name	L:/ nmr032508-041508/ 400-0325200804152008/ CBCOOCH3-cyclohexene20merC13-04132008.fid/ fid
2	Title	CBCOOCH3-cyclohexene-20mer-C13
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-05-12T16:17:15
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	20432
11	Spectrometer Frequency	100.55
12	Spectral Width	25000.0
13	Lowest Frequency	-2986.2
14	Nucleus	13C
15	Acquired Size	29984
16	Spectral Size	65536

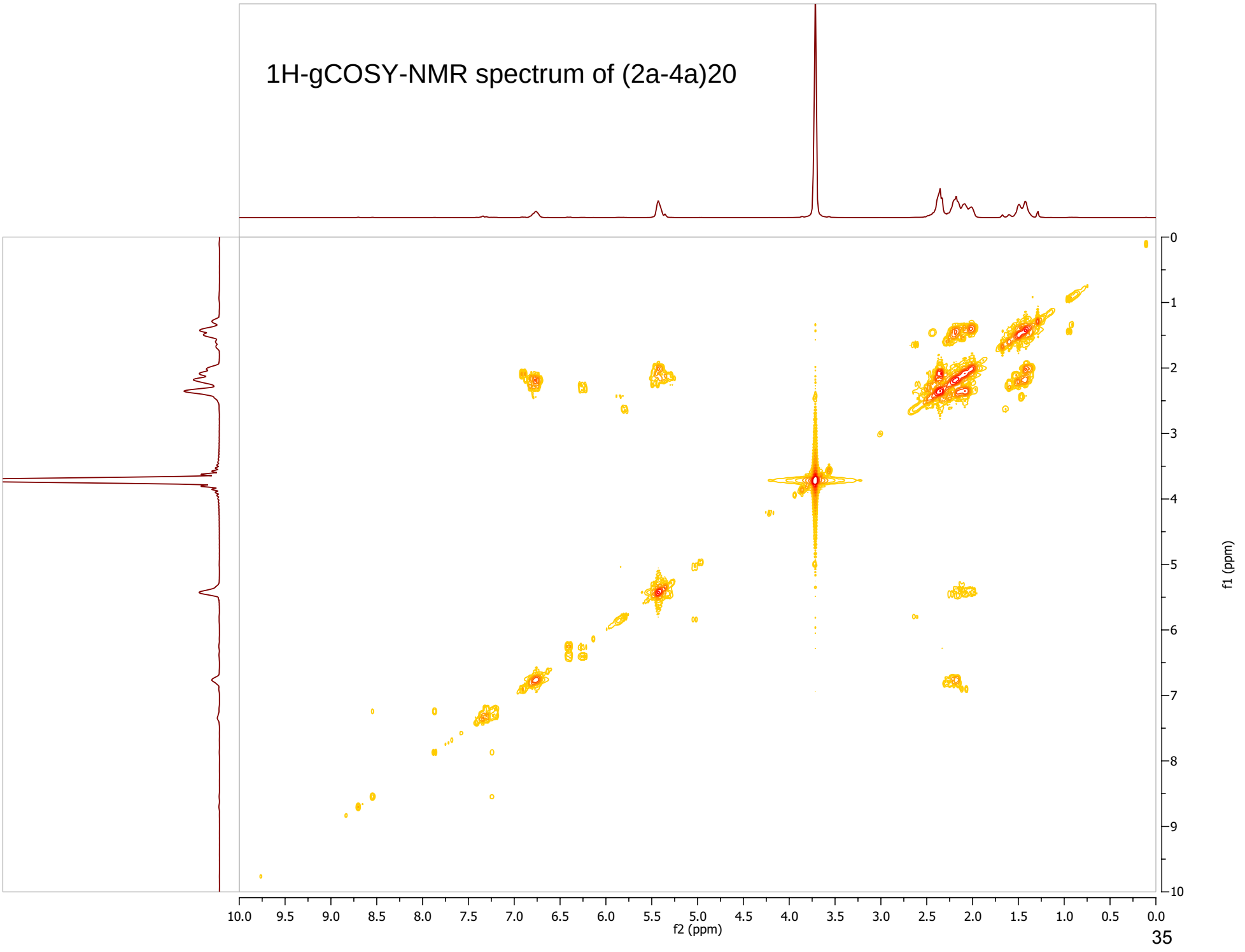
13C-NMR spectrum of (2a-4a)20

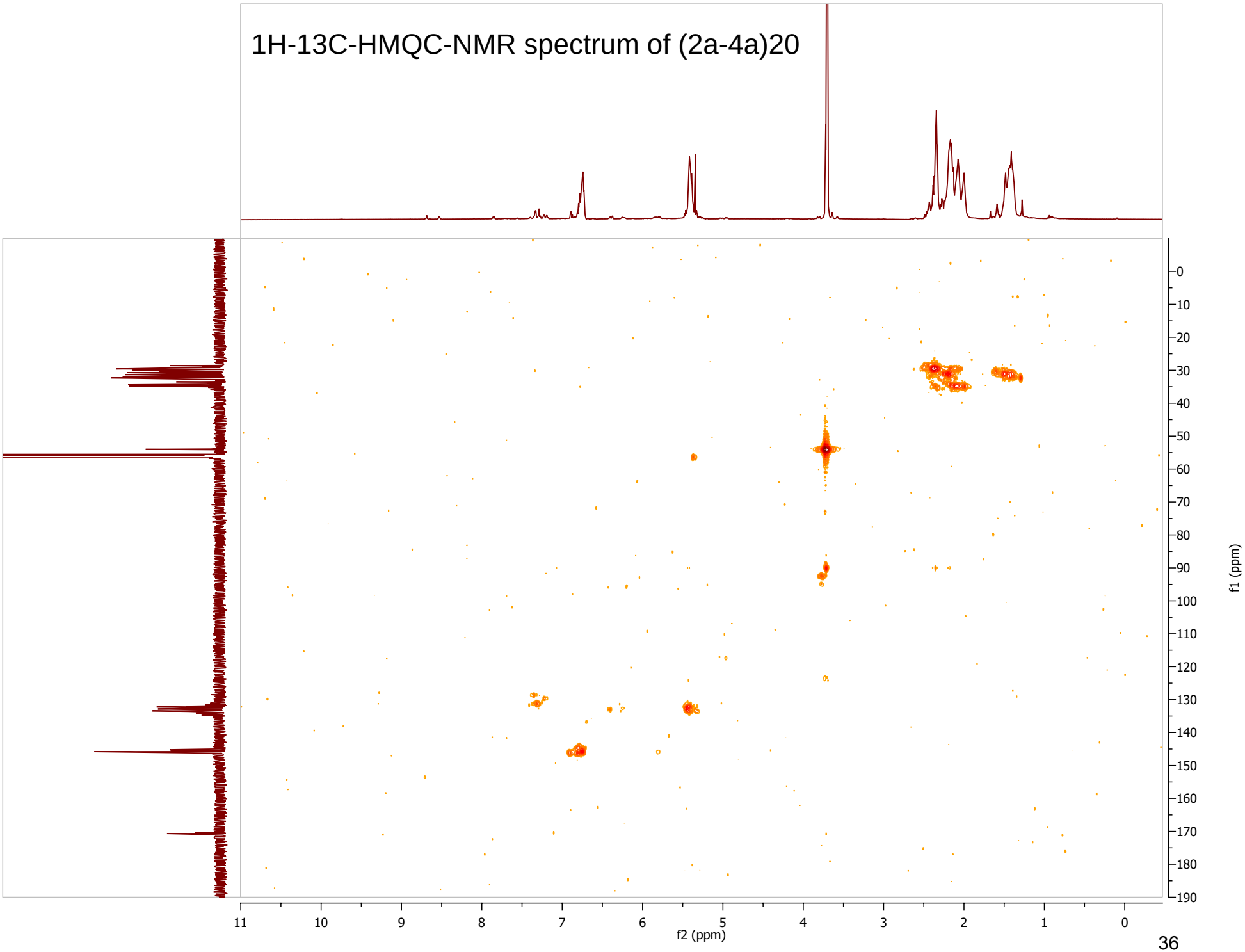


13C-APT-NMR spectrum of (2a-4a)20

	Parameter	Value
1	Data File Name	L:/ data03252008/ 400mhz/ CBCOOCH3-cyclohexene-20mer-APTC13-12302007.fid/ fid
2	Title	CBCOOCH3-cyclohexene-20mer-APTC13
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	apt
7	Acquisition Date	2008-01-28T12:08:37
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	72808
11	Spectrometer Frequency	100.55
12	Spectral Width	29996.2
13	Lowest Frequency	-5484.3
14	Nucleus	13C
15	Acquired Size	35976
16	Spectral Size	131072

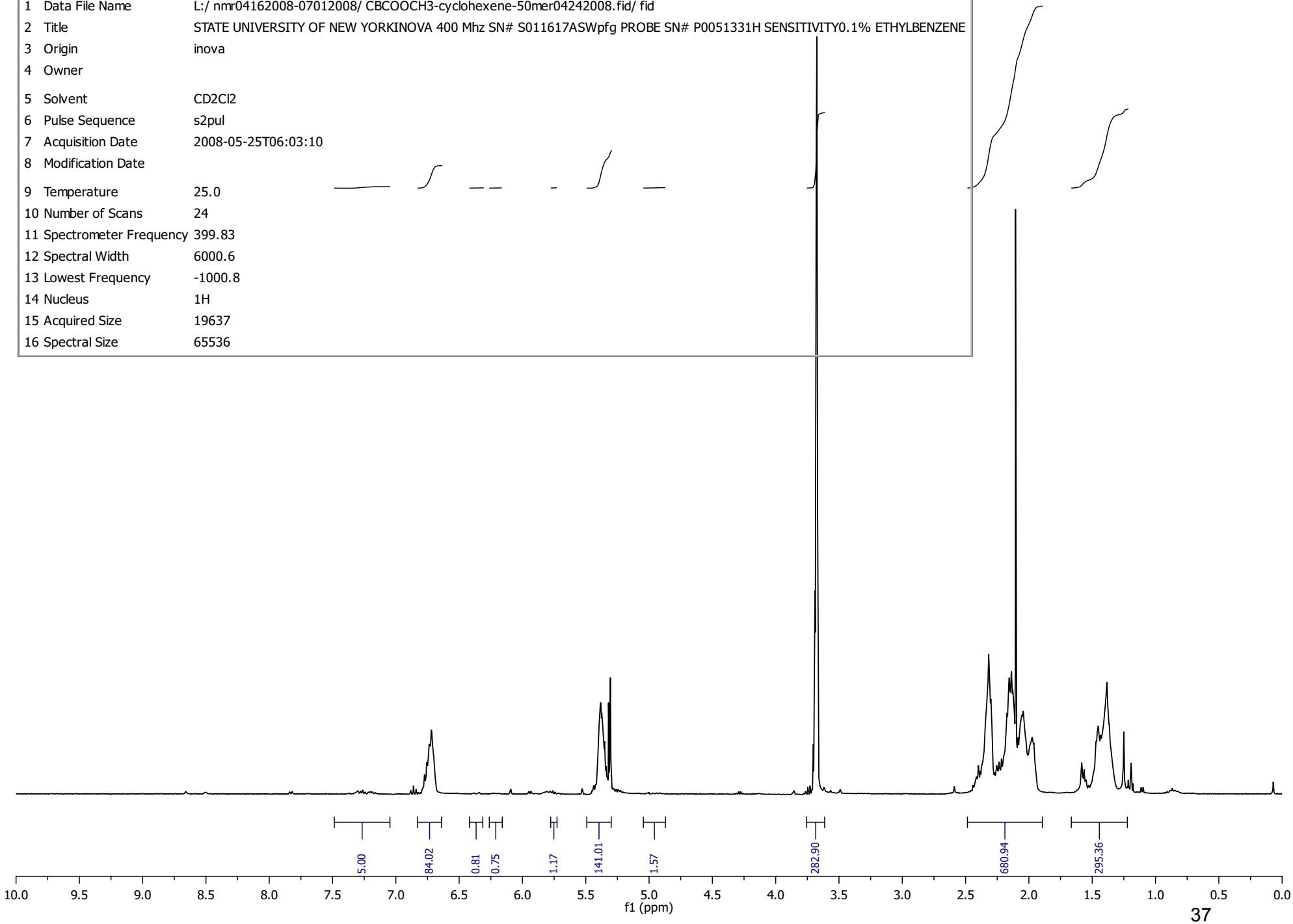



1H-gCOSY-NMR spectrum of (2a-4a)20
f1 (ppm)
f2 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8
9
10


1H-13C-HMQC-NMR spectrum of (2a-4a)20
f2 (ppm)
f1 (ppm)

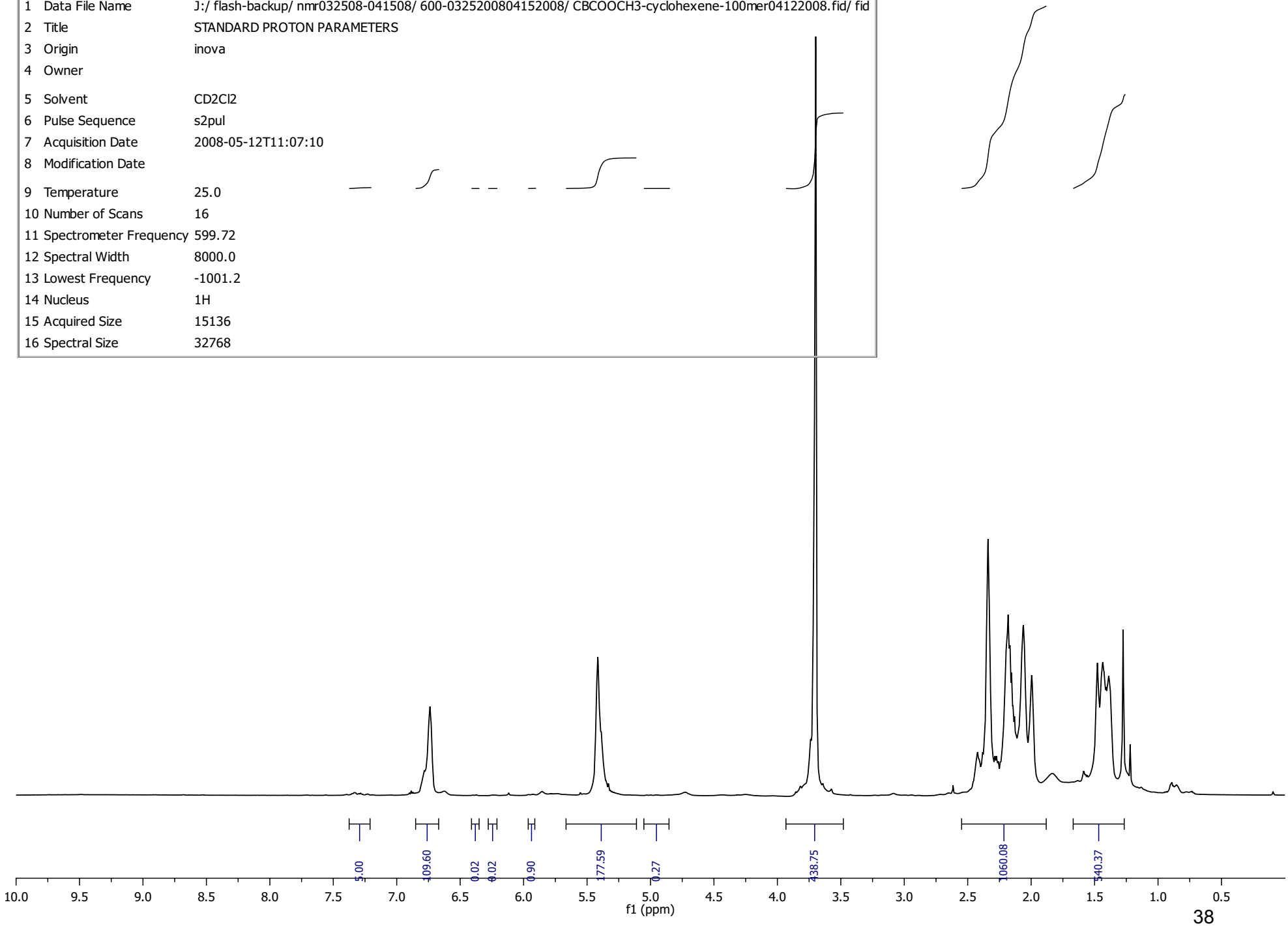
1H-NMR spectrum of (2a-4a)50

	Parameter	Value
1	Data File Name	L:/ nmr04162008-07012008/ CBCOOCH3-cyclohexene-50mer04242008.fid/ fid
2	Title	STATE UNIVERSITY OF NEW YORKINOVA 400 Mhz SN# S011617ASWpfg PROBE SN# P0051331H SENSITIVITY0.1% ETHYLBENZENE
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-05-25T06:03:10
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	24
11	Spectrometer Frequency	399.83
12	Spectral Width	6000.6
13	Lowest Frequency	-1000.8
14	Nucleus	1H
15	Acquired Size	19637
16	Spectral Size	65536

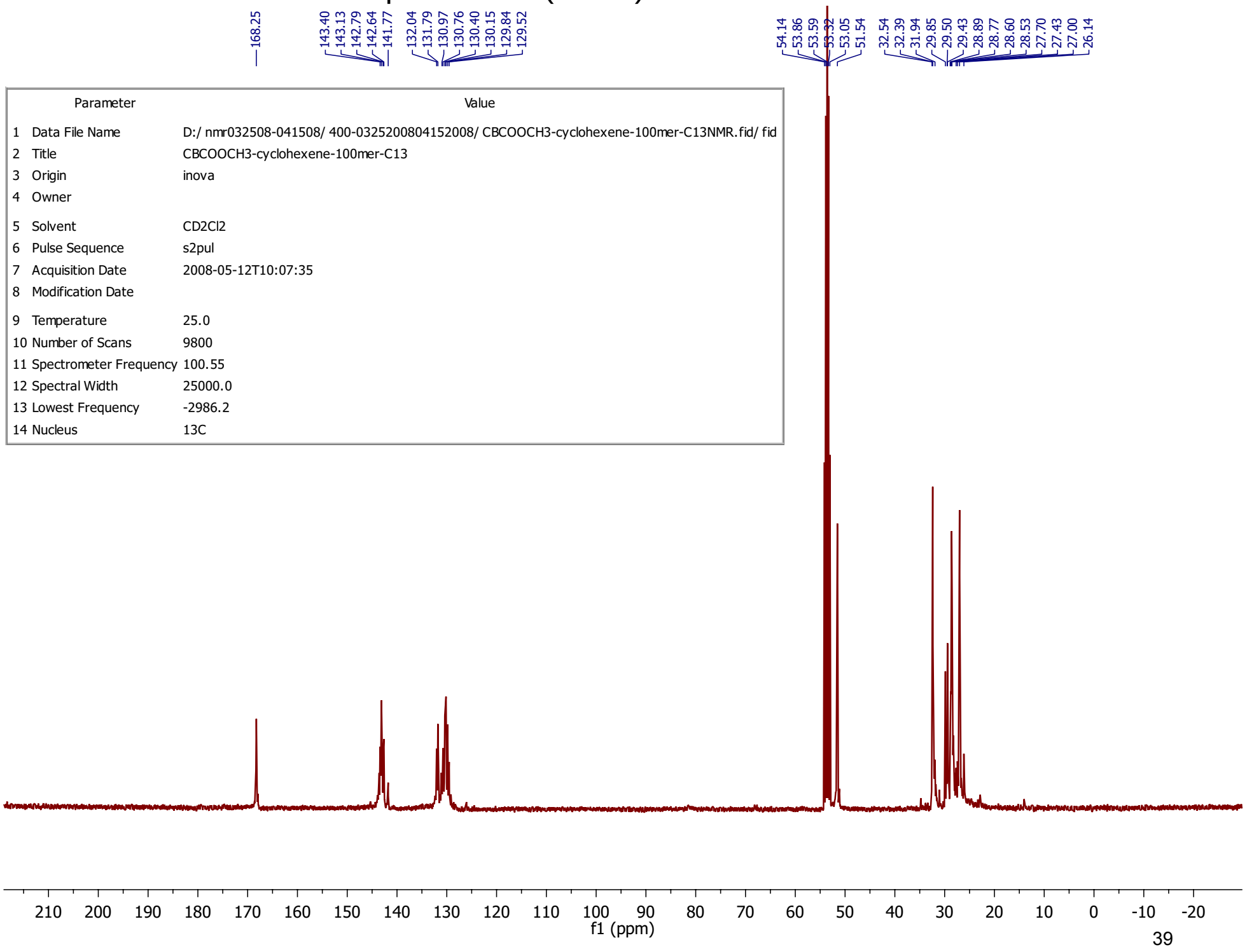


1H-NMR spectrum of (2a-4a)100

	Parameter	Value
1	Data File Name	J:/ flash-backup/ nmr032508-041508/ 600-0325200804152008/ CBCOOCH3-cyclohexene-100mer04122008.fid/ fid
2	Title	STANDARD PROTON PARAMETERS
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-05-12T11:07:10
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	16
11	Spectrometer Frequency	599.72
12	Spectral Width	8000.0
13	Lowest Frequency	-1001.2
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768



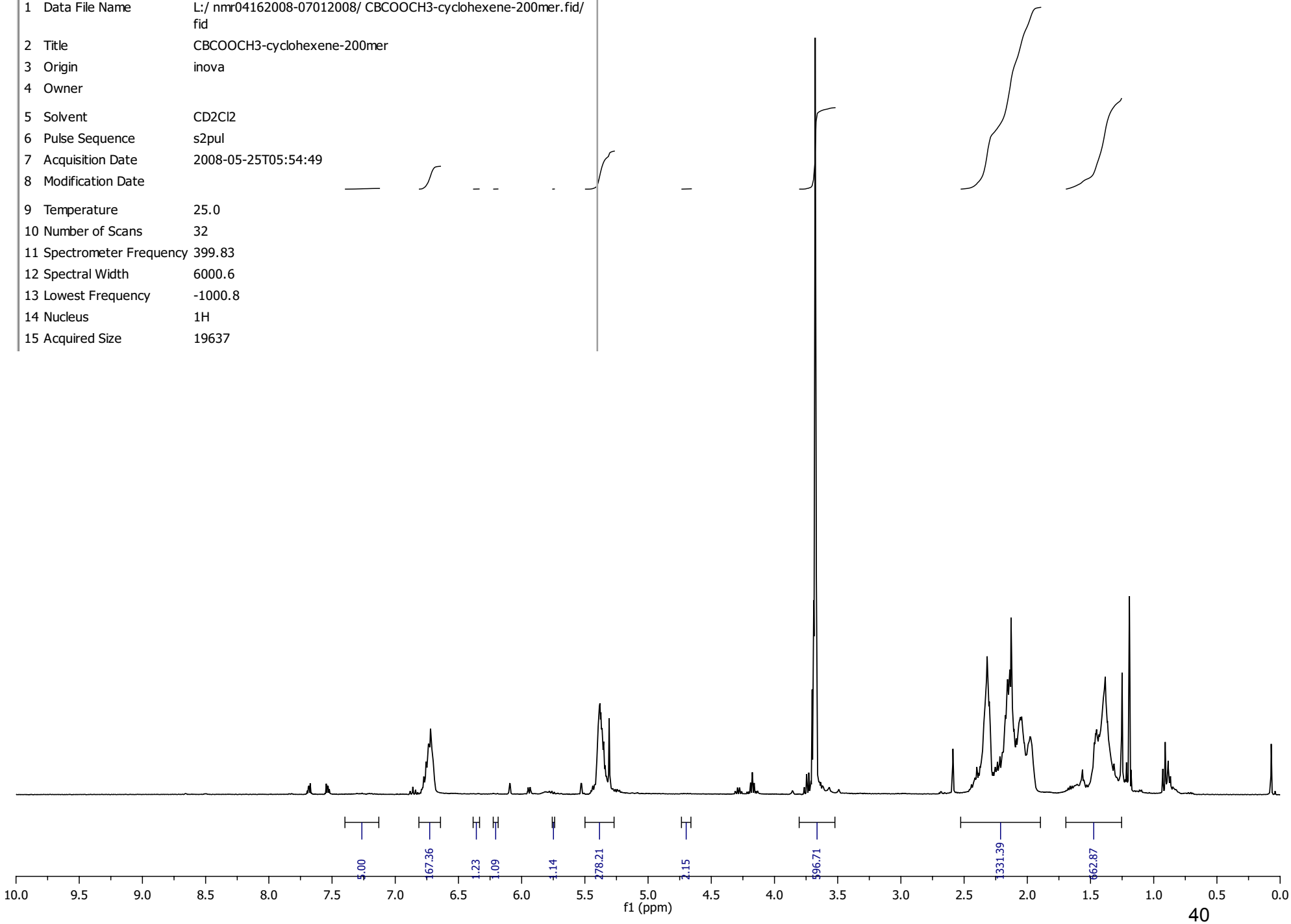
13C-NMR spectrum of (2a-4a)100



	Parameter	Value
1	Data File Name	D:/ nmr032508-041508/ 400-0325200804152008/ CBCOOCH3-cyclohexene-100mer-C13NMR.fid/ fid
2	Title	CBCOOCH3-cyclohexene-100mer-C13
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-05-12T10:07:35
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	9800
11	Spectrometer Frequency	100.55
12	Spectral Width	25000.0
13	Lowest Frequency	-2986.2
14	Nucleus	13C

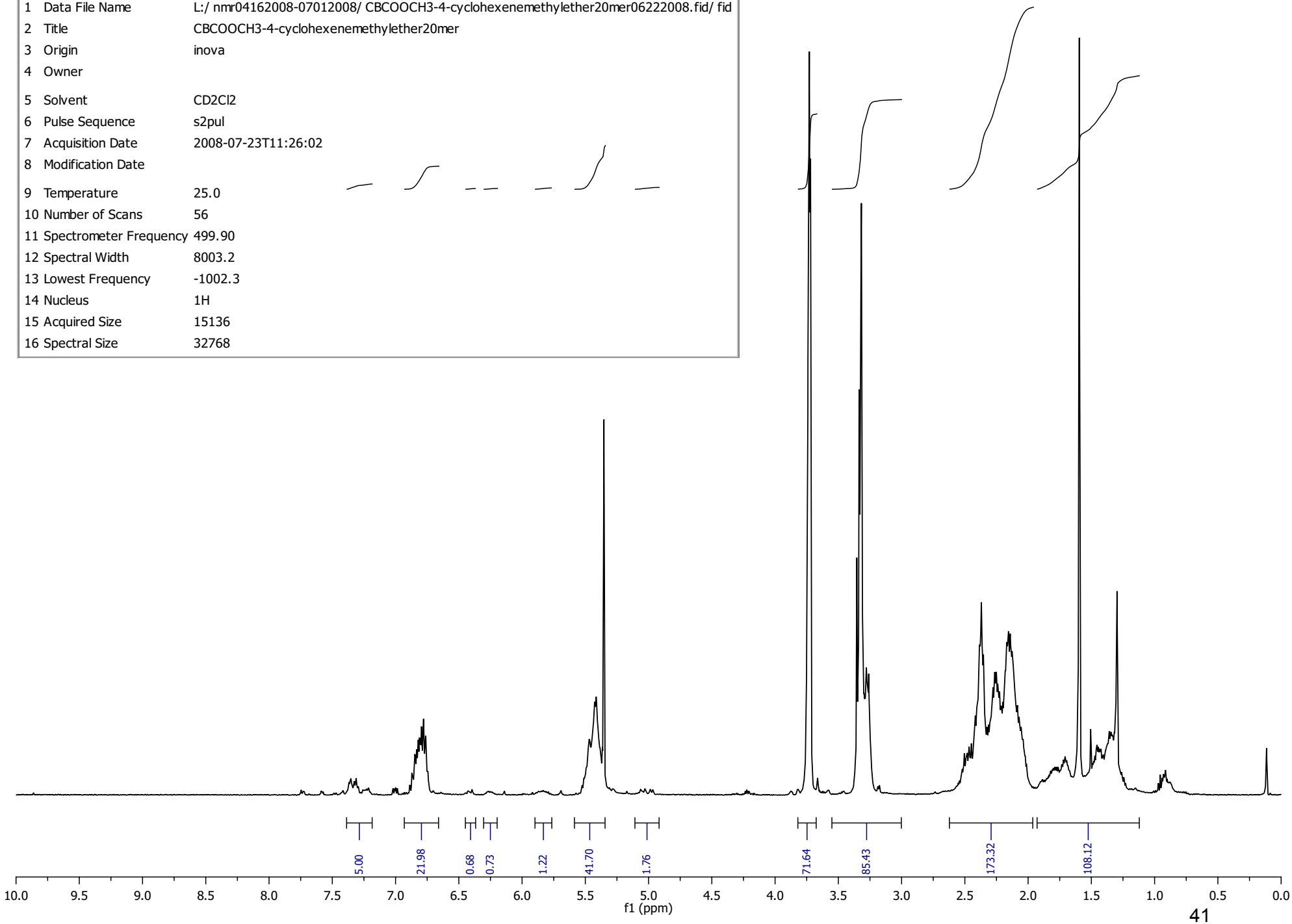
1H-NMR spectrum of (2a-4a)200

	Parameter	Value
1	Data File Name	L:/ nmr04162008-07012008/ CBCOOCH3-cyclohexene-200mer.fid/ fid
2	Title	CBCOOCH3-cyclohexene-200mer
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-05-25T05:54:49
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	32
11	Spectrometer Frequency	399.83
12	Spectral Width	6000.6
13	Lowest Frequency	-1000.8
14	Nucleus	1H
15	Acquired Size	19637



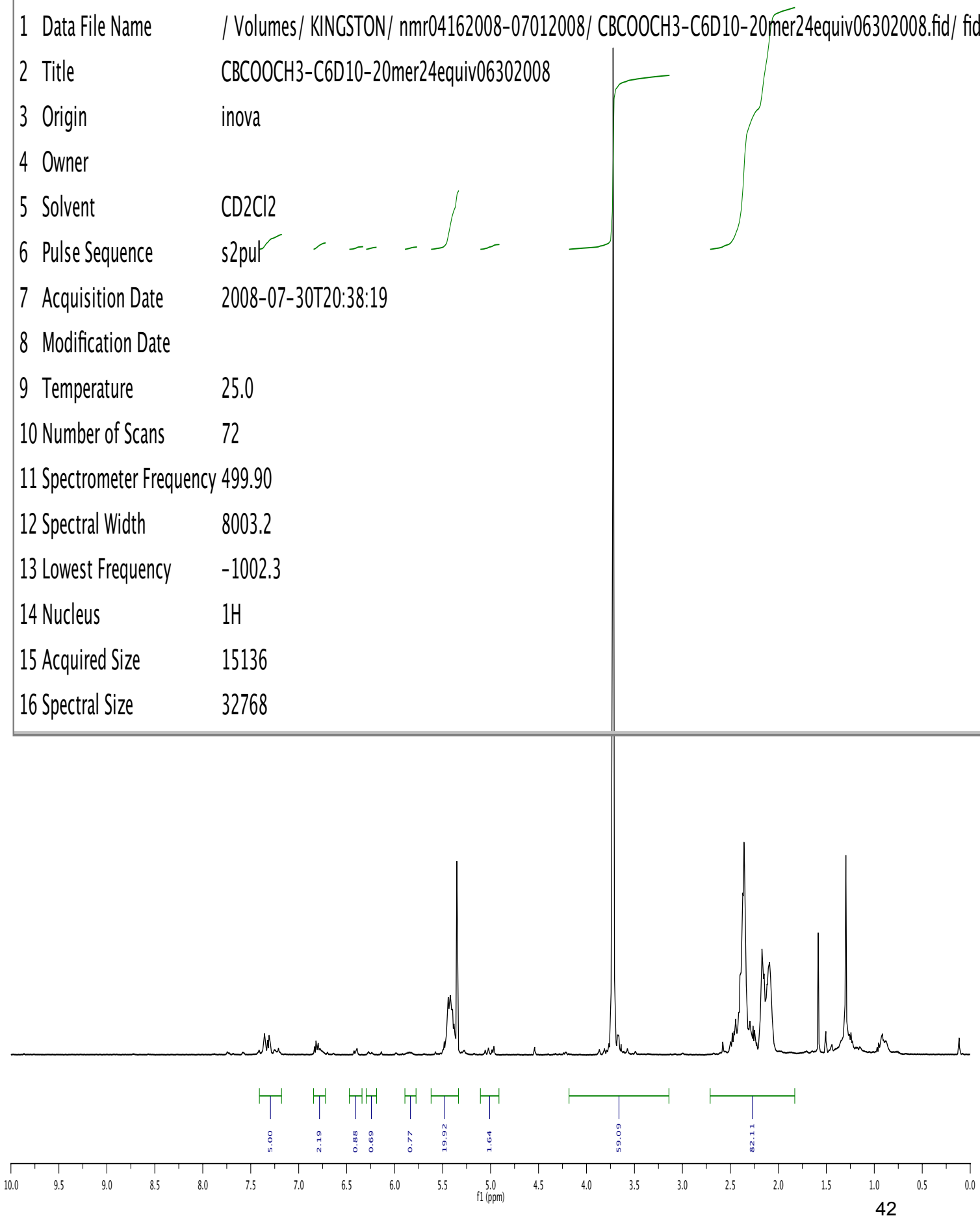
1H-NMR spectrum of (2a-4b)20

	Parameter	Value
1	Data File Name	L:/ nmr04162008-07012008/ CBCOOCH3-4-cyclohexenemethylether20mer06222008.fid/ fid
2	Title	CBCOOCH3-4-cyclohexenemethylether20mer
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-07-23T11:26:02
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	56
11	Spectrometer Frequency	499.90
12	Spectral Width	8003.2
13	Lowest Frequency	-1002.3
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768



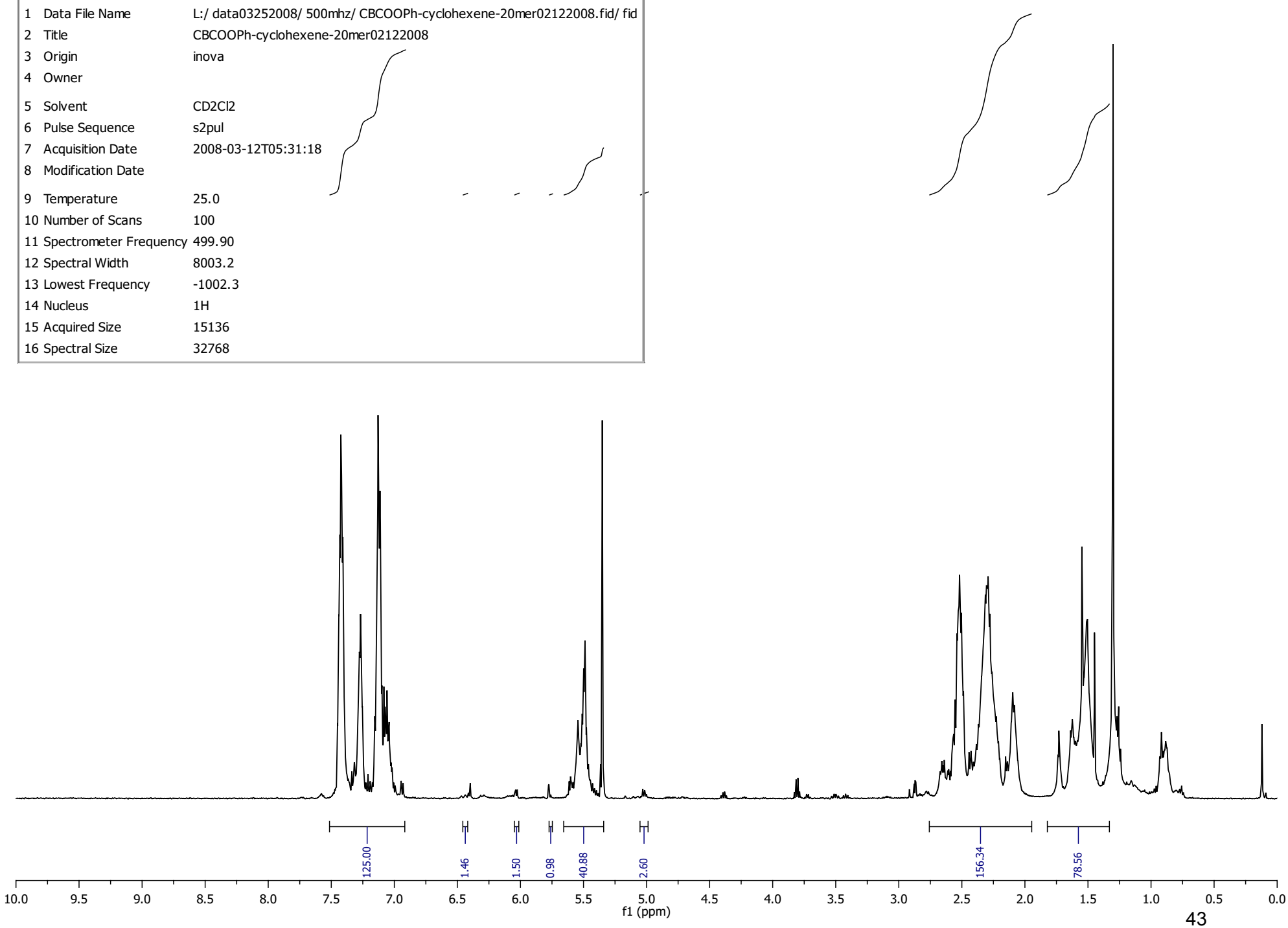
1H-NMR spectrum of (2a-4a-D10)20

Parameter	Value
1 Data File Name	/ Volumes/ KINGSTON/ nmr04162008-07012008/ CBCOOCH3-C6D10-20mer24equiv06302008.fid/ fid
2 Title	CBCOOCH3-C6D10-20mer24equiv06302008
3 Origin	inova
4 Owner	
5 Solvent	CD2Cl2
6 Pulse Sequence	s2pul
7 Acquisition Date	2008-07-30T20:38:19
8 Modification Date	
9 Temperature	25.0
10 Number of Scans	72
11 Spectrometer Frequency	499.90
12 Spectral Width	8003.2
13 Lowest Frequency	-1002.3
14 Nucleus	1H
15 Acquired Size	15136
16 Spectral Size	32768

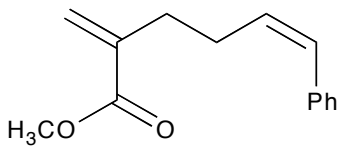


1H-NMR spectrum of (2b-4a)20

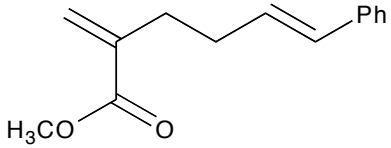
	Parameter	Value
1	Data File Name	L:/ data03252008/ 500mhz/ CBCOOPh-cyclohexene-20mer02122008.fid/ fid
2	Title	CBCOOPh-cyclohexene-20mer02122008
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-03-12T05:31:18
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	100
11	Spectrometer Frequency	499.90
12	Spectral Width	8003.2
13	Lowest Frequency	-1002.3
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768



	Parameter	Value
1	Data File Name	L:/ 07012008-07112008/ CBCOOCH3-1mer07112008.fid/ fid
2	Title	CBCOOCH3-1mer07112008
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-08-11T07:20:11
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	24
11	Spectrometer Frequency	599.72
12	Spectral Width	8000.0
13	Lowest Frequency	-1001.2
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768

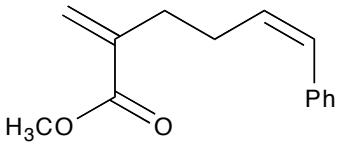


7a

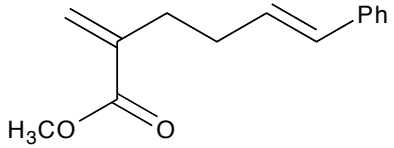


7b

	Parameter	Value
1	Data File Name	F:/ 07012008-07112008/ CBCOOCH3-1merC13-07112008.fid/ fid
2	Title	CBCOOCH3-1merC13-07112008
3	Origin	inova
4	Owner	
5	Solvent	CD2Cl2
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-08-11T07:22:49
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	1760
11	Spectrometer Frequency	100.55
12	Spectral Width	25000.0
13	Lowest Frequency	-2986.2
14	Nucleus	13C
15	Acquired Size	29984
16	Spectral Size	65536



7a



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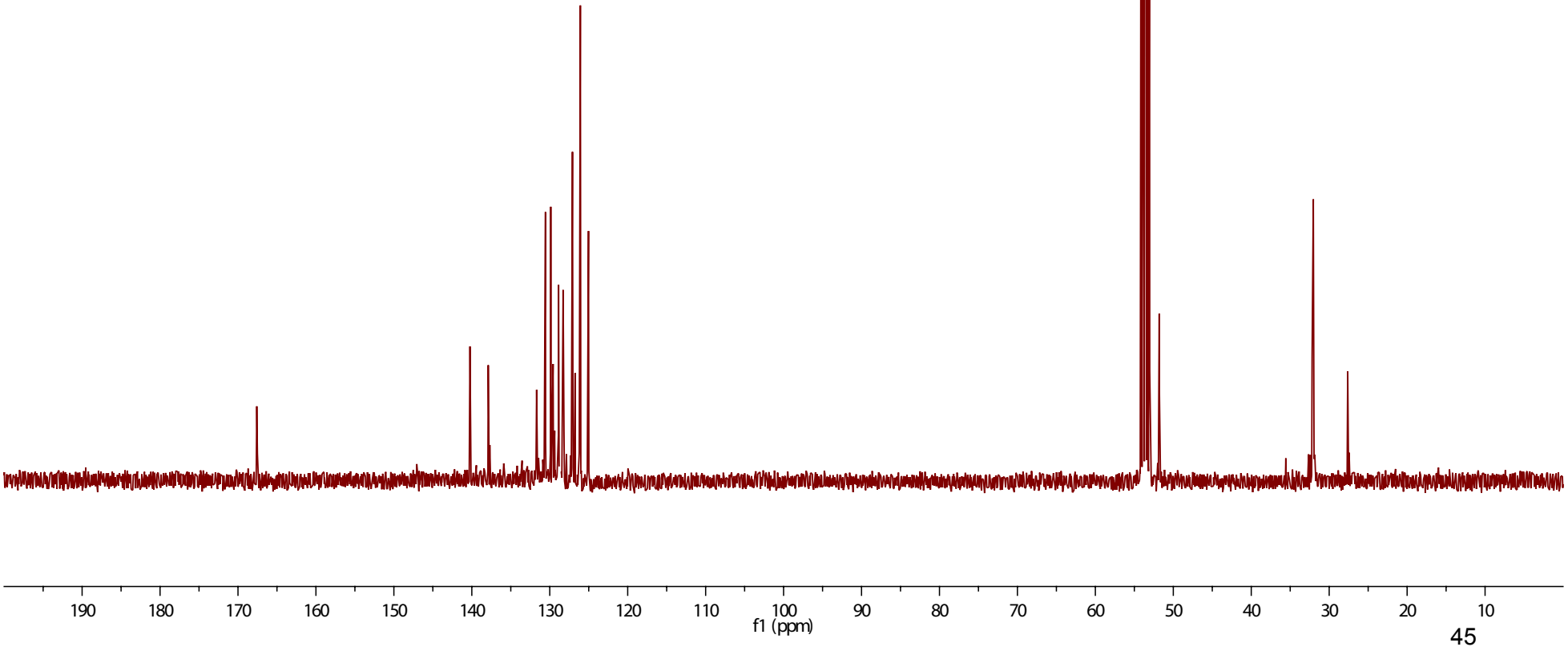
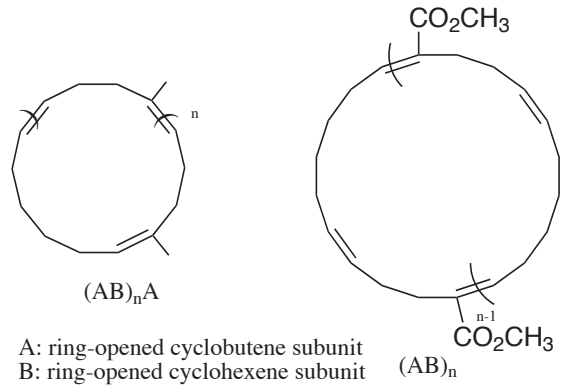


	Parameter	Value
1	Data File Name	F:/ 07262008-10012008/ 500/ CBCOOCH3-C6D10-benzoquinone20merA1-09032008.fid/ fid
2	Title	STANDARD PROTON PARAMETERS
3	Origin	inova
4	Owner	
5	Solvent	CDCl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-10-03T05:39:42
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	136
11	Spectrometer Frequency	499.90
12	Spectral Width	8003.2
13	Lowest Frequency	-1002.3
14	Nucleus	1H
15	Acquired Size	15136
16	Spectral Size	32768



A: ring-opened cyclobutene subunit
B: ring-opened cyclohexene subunit

^{1}H-NMR spectrum of cyclic polymer cyc-(2a-4a-D_{10})$_{20}$