Electronic Supplementary Material (ESI)

Efficient Synthesis of Trifluoromethylated Cyclopentadienes/Fulvenes/Norbornenes from Divinyl Ketones

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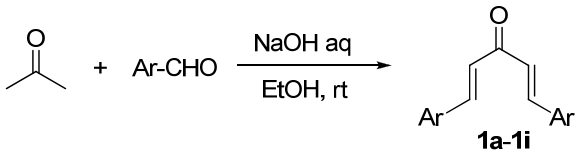
I. General information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC and the products were purified by column chromatography on flash silica gel (300−400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 500 spectrometer (500 MHz for ^{1}H NMR; 125 MHz for ^{13}C NMR; 470 MHz for ^{19}F NMR). ^{1}H NMR and ^{13}C NMR were determined with TMS as the internal standard. ^{19}F NMR was determined with C_6H_5F as the external standard. All shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

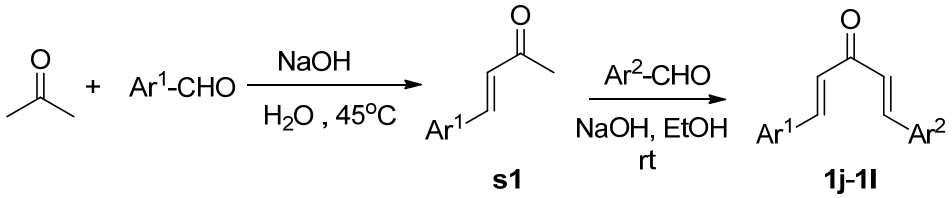
II. Preparation of **1**



1a-1i

General procedure (with **1b** as an example):

To the solution of acetone (0.58 mL, 8.0 mmol) and benzaldehyde (1.63 mL, 16.1 mmol) in ethanol (10 mL), NaOH (15 mL, 10% aqueous solution) was added dropwise and stirred at room temperature to the completion of the reaction (monitored by TLC). The resulted mixture was poured into water (30 mL). The solid was collected by filtration, washed with water (15 mL ×3), and dried under vacuum to afford the crude product, which was recrystallized (petroleum ether : EtOAc = 50:1, v/v) to give **1b** (1.74 g, 93% yield).



s1 **1j-1l**

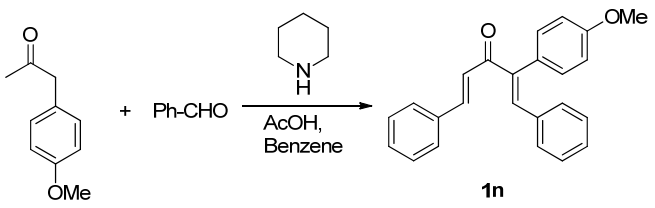
General procedure (with **1j** as an example):

To the solution of acetone (2 mL, 27.5 mmol) and 4-chlorobenzaldehyde (1.4 g, 10 mmol) in water (4 mL), NaOH (0.8 mL, 5% aqueous solution) was added dropwise and stirred at 45 °C for 7 h. After 4-chlorobenzaldehyde was consumed as monitored by TLC, the resulted mixture was poured into water (30 mL). The solid was collected by filtration, washed with water (15 mL ×3), and dried under vacuum to afford the crude product, which was recrystallized (petroleum ether : EtOAc = 50:1, v/v) to give **s1** (1.61 g, 89% yield).

To the solution of **s1** (0.72 g, 4.0 mmol) and 4-bromobenzaldehyde (0.76 g, 4.1 mmol) in ethanol (5 mL), NaOH (0.32 g, 8 mmol) was added and stirred at room temperature to the consumption of **s1** (monitored by TLC). The resulted mixture was poured into water (30 mL). The solid was collected by filtration, washed with water (15 mL ×3) and dried under vacuum to afford the crude product, which was purified by column chromatography (silica gel, petroleum ether : EtOAc = 10:1, v/v) to give **1j** (0.58 g, 42% yield).

Substrate **1m** was prepared following the method of D. R. Carbery (see: *Org. Lett.*, **2009**, *11*, 1175-1178).

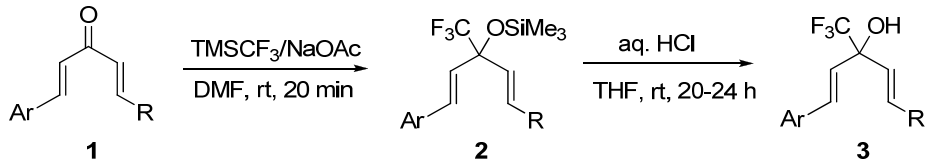
Substrate **1n**



Procedure:

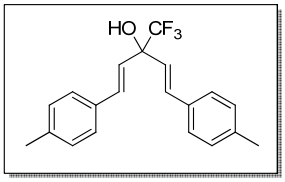
To the solution of 1-(4-methoxyphenyl)propan-2-one (1.37 mL, 8.88 mmol) and piperidine (0.36 mL, 3.6 mmol) in benzene (20 mL), benzaldehyde (3.55 mL, 35.5 mmol) and acetic acid (0.51 mL, 8.95 mmol) were added. The reaction was performed under reflux (equipped with a Dean-Stark trap) to the consumption of 1-(4-methoxyphenyl)propan-2-one (monitored by TLC). The resulted mixture was diluted by EtOAc (30 mL), washed with water (15 mL ×3), aqueous $NaHCO_3$ solution (15 mL ×3). The organic phase then dried under vacuum to afford the crude product, which was purified by column chromatography (silica gel, petroleum ether : EtOAc =6:1, v/v) to give **1n** (2.12g, 70% yield).

III. Synthetic procedures and analytical data of **3**



General procedure (**3a** as an example):

To the solution of **1a** (524 mg, 2.0 mmol) in anhydrous DMF (2 mL) was added anhydrous NaOAc (328 mg, 4.0 mmol) at room temperature. Trimethyl(trifluoromethyl)silane ($TMSCF_3$, 0.44 mL, 3.0 mmol) was added to the mixture after 5 min's stirring. After **1a** was consumed as indicated by TLC, the resulting mixture was poured into water (30 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum) to give **2a** (769 mg, 95%). To a solution of resulted **2a** (607 mg, 1.5 mmol) in THF (8 mL) was added hydrochloric acid (6 N) slowly. After **2a** was consumed as indicated by TLC, the mixture was poured into water and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether : EtOAc = 6:1, V/V) to give **3a** (459mg, 92%).



3a: 1,5-di-*p*-tolyl-3-(trifluoromethyl)penta-1,4-dien-3-ol

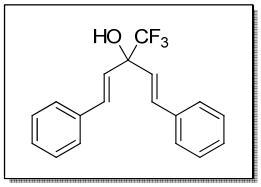
Colorless crystals, m.p. 66–68 °C, 92% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27 (s, 6H), 2.42 (s, 1H), 6.29 (d, *J* = 16.0 Hz, 2H), 6.82 (d, *J* = 16.0 Hz,

2H), 7.07 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 76.4 (q, *J* = 30.0 Hz), 123.3, 124.9 (CF_3, q, *J* = 283.8 Hz), 126.8, 129.4, 132.7, 133.7, 138.6.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3^+$ ($[M\text{-}OH]^+$) 315.1355. Found 315.1369.



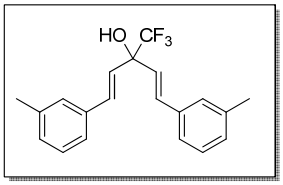
3b: 1,5-diphenyl-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 92–94 °C, 93% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.55 (s, 1H), 6.42 (d, *J* = 16.0 Hz, 2H), 6.94 (d, *J* = 16.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 4H), 7.43 (d, *J* = 7.5 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.4 (q, *J* = 30.0 Hz), 124.3, 124.9 (CF_3, q, *J* = 285.0 Hz), 126.9, 128.6, 128.7, 133.8, 135.5.

HRMS (ESI-TOF) Calcd for $C_{18}H_{14}F_3^+$ ($[M\text{-}OH]^+$) 287.1042. Found 287.1046.



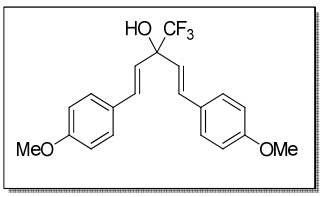
3c: 1,5-di-*m*-tolyl-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 64–66 °C, 91% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 6H), 2.61 (s, 1H), 6.39 (d, *J* = 16.0 Hz, 2H), 6.89 (d, *J* = 16.0 Hz, 2H), 7.08 (t, *J* = 3.5 Hz, 2H), 7.20 (d, *J* = 5.0 Hz, 4H), 7.23 (s, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 76.4 (q, *J* = 28.8 Hz), 124.0, 124.1, 124.8 (CF_3, q, *J* = 283.8 Hz), 127.5, 128.6, 129.4, 133.9, 135.4, 138.3.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3^+$ ($[M\text{-}OH]^+$) 315.1355. Found 315.1370.



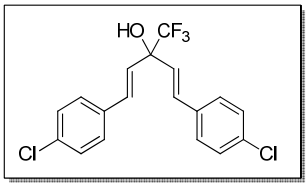
3d: 1,5-bis(4-methoxyphenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 70–72 °C, 96% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.62 (s, 1H), 3.81 (s, 6H), 6.28 (d, *J* = 16.0 Hz, 2H), 6.85–6.88 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.3, 76.4 (q, *J* = 28.8 Hz), 114.0, 122.1, 125.0 (CF_3, q, *J* = 283.8 Hz), 128.2, 128.3, 133.2, 159.8.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3O_2^+$ ($[M\text{-}OH]^+$) 347.1253. Found 347.1265.



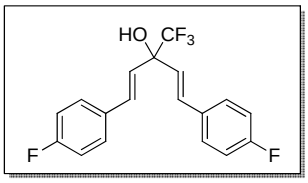
3e: 1,5-bis(4-chlorophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 77–79 ^{o}C, 95% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.69 (s, 1H), 6.37 (d, *J* = 16.0 Hz, 2H), 6.87 (d, *J* = 16.0 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.3 (q, *J* = 28.8 Hz), 124.6, 124.7 (CF_3, q, *J* = 283.8 Hz), 128.1, 128.9, 132.7, 133.8, 134.4.

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}Cl_2F_3^+$ ($[M\text{-}OH]^+$) 355.0263. Found 355.0267.



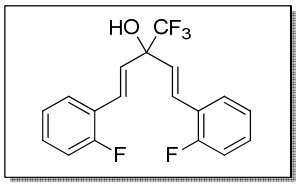
3f: 1,5-bis(4-fluorophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless viscous oil, 90% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.78 (s, 1H), 6.61 (d, *J* = 16.0 Hz, 2H), 7.17 (d, *J* = 16.0 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 4H), 7.56 (t, *J* = 6.0 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.3 (q, *J* = 28.8 Hz), 115.5 (d), 123.7, 124.9 (CF_3, q, *J* = 285.0 Hz), 128.5 (d), 131.6 (d), 132.6, 162.8 (d).

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}F_5^+$ ($[M\text{-}OH]^+$) 323.0854. Found 323.0859



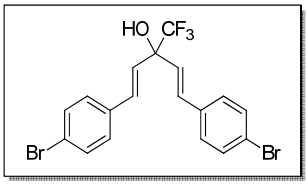
3g: 1,5-bis(2-fluorophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless viscous oil, 88% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.05 (s, 1H), 6.63 (d, *J* = 16.0 Hz, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 16.0 Hz, 2H), 7.29 (dd, *J* = 13.5, 7.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.6 (q, *J* = 28.8 Hz), 115.8 (d), 123.4 (d), 124.2 (d), 124.8 (CF_3, q, *J* = 285.0 Hz), 126.6, 126.7 (d), 128.0 (d), 129.9 (d), 160.5 (d).

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}F_5^+$ ($[M\text{-}OH]^+$) 323.0854. Found 323.0859.



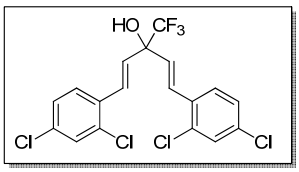
3h: 1,5-bis(4-bromophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 120–122 ^{o}C, 89% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 2H), 6.88 (d, *J* = 16.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.3 (q, *J* = 30.0 Hz), 122.6, 124.6 (CF_3, q, *J* = 283.8 Hz), 124.7, 128.4, 131.9, 132.7, 134.3.

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}Br_2F_3^+$ ($[M\text{-}OH]^+$) 442.9252. Found 442.9245.



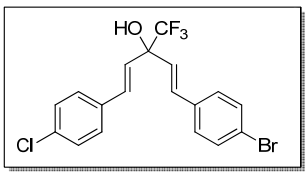
3i: 1,5-bis(2,4-dichlorophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless viscous oil, 87% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.92 (s, 1H), 6.38 (d, *J* = 16.0 Hz, 2H), 7.18 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.28 (d, *J* = 16.0 Hz, 2H), 7.33 (d, *J* = 1.5 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.6 (q, *J* = 30.0 Hz), 124.5 (CF_3, q, *J* = 285.0 Hz), 127.0, 127.3, 127.7, 129.4, 129.5, 132.1, 134.1, 134.7.

HRMS (ESI-TOF) Calcd for $C_{18}H_{10}Cl_4F_3^+$ ($[M\text{-}OH]^+$) 422.9483. Found 422.9483.



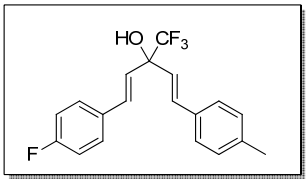
3j: 1-(4-bromophenyl)-5-(4-chlorophenyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless crystals, m.p. 104–106 ^{o}C, 90% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.50 (s, 2H), 6.37 (d, *J* = 8.5 Hz, 2H), 6.40 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 6.5 Hz, 2H), 6.90 (d, *J* = 6.0 H z, 2H), 7.30 (d, *J* = 9.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 9.0 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.3 (q, *J* = 28.8 Hz), 122.6, 124.5, 124.6 (CF_3, q, *J* = 285.0 Hz), 124.7, 128.1, 128.4, 128.9, 131.8, 132.6, 132.7, 133.8, 134.3, 134.4.

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}BrClF_3^+$ ($[M\text{-}OH]^+$) 398.9758. Found 398.9745.



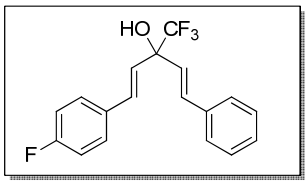
3k: 1-(4-fluorophenyl)-5-(*p*-tolyl)-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless viscous oil, 88% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.35 (s, 6H), 2.48 (s, 2H), 6.33 (d, *J* = 16.0 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 2H), 6.90 (d, *J* = 16.0 Hz, 2H), 6.91 (d, *J* = 16.0 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 7.5 Hz, 4H), 7.33 (d, *J* = 7.5 Hz, 4H), 7.41 (t, *J* = 8.5 Hz, 4H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 76.3 (q, *J* = 28.8 Hz), 115.6 (d), 123.0, 123.9, 124.8 (CF_3, q, *J* = 284.3 Hz), 126.8, 127.1, 127.4, 127.9, 128.5 (d), 129.4, 129.6, 131.6 (d), 132.2, 132.5, 133.7, 134.2, 134.7, 138.6, 162.8(d).

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}BrClF_3^+$ ($[M\text{-}OH]^+$) 319.1104. Found 319.1109.



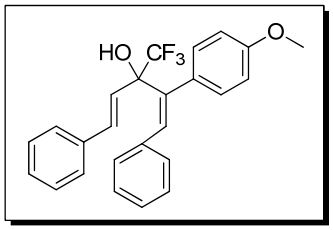
3l: 1-(4-fluorophenyl)-5-phenyl-3-(trifluoromethyl)penta-1,4-dien-3-ol

Colorless viscous oil, 85% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.56 (s, 2H), 6.34 (d, *J* = 16.0 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 2H), 6.91 (d, *J* = 16.0 Hz, 2H), 6.94 (d, *J* = 16.0 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 4H), 7.30 (t, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 4H), 7.39–7.45 (m, 8H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.3 (q, *J* = 28.8 Hz), 115.7 (d), 124.0 (d), 124.8 (CF_3, q, *J* = 285.0 Hz), 126.9, 128.5, 128.6, 128.7, 128.8, 131.6 (d), 132.7, 133.8, 135.4, 162.8 (d).

HRMS (ESI-TOF) Calcd for $C_{18}H_{13}F_4^+$ ($[M\text{-}OH]^+$) 305.0948. Found 305.0958.



3n: 2-(4-methoxyphenyl)-1,5-diphenyl-3-(trifluoromethyl)penta-1,4-dien-3-ol

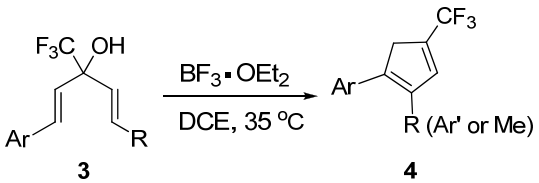
Colorless crystals, m.p.128–129°C, 88% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.56 (s, 1H), 3.76 (s, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.79-6.81 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 7.02-7.05 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.2, 114.3, 125.0 (CF_3, q, *J* = 285.1 Hz), 126.0, 126.9, 127.5, 127.8, 128.0, 128.4, 128.7, 129.5, 131.7, 132.0, 132.2, 135.7 (d, *J* = 11.0 Hz), 138.0, 159.4.

HRMS (ESI-TOF) Calcd for $C_{25}H_{21}F_3O_2^+$ ($[M\text{-}OH]^+$) 393.1561. Found 393.1570.

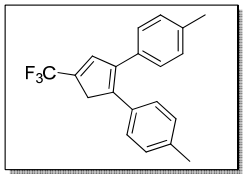
IV. Synthetic procedures and analytical data of **4**



3 **4**

General procedure (**4e** as an example):

To a solution of **3e** (373 mg, 1.0 mmol) in DCE (1.5 mL) was added boron trifluoride etherate (2.0 equiv) and stirred at 35 °C. After **3e** was consumed as indicated by TLC, the reaction mixture was poured into water (30 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : EtOAc = 30 : 1, V/V) to give **4e** (337 mg, 95% yield).



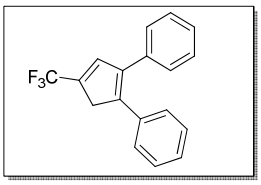
4a: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene)

Colorless crystals, m.p. 89–91 °C, 83% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.31 (s, 3H), 2.35 (s, 3H), 3.70 (s, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 21.2, 42.9, 125.2 (CF_3, q, *J* = 251.3 Hz), 127.8, 128.1, 129.1, 129.3, 132.3 (q, *J* = 35.0 Hz), 132.8, 132.9, 137.3, 137.4, 138.6, 139.5 (q, *J* = 5.0 Hz), 142.7.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3^+$ ($[M+H]^+$) 315.1355. Found 315.1362.



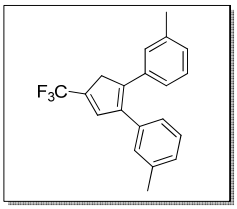
4b: (4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)dibenzene

Colorless crystals, m.p. 88–90 °C, 85% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.75 (s, 2H), 7.11 (s, 1H), 7.24 (m, 5H), 7.30 (m, 5H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 123.0 (CF_3, q, *J* = 266.3 Hz), 127.5, 127.6, 128.0, 128.2, 128.4, 128.6, 132.8 (q, *J* = 35.0 Hz), 135.5, 139.2, 139.3 (q, *J* = 5.0 Hz), 139.4, 143.1.

HRMS (ESI-TOF) Calcd for $C_{18}H_{14}F_3^+$ ($[M+H]^+$) 287.1042. Found 287.1049.



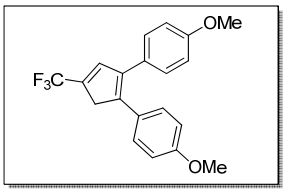
4c: 3,3'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene)

Yellowish viscous oil, 82% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.25 (s, 3H), 2.29 (s, 3H), 3.70 (s, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 7.08 (m, 5H), 7.13 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.3, 43.0, 123.1 (CF_3, q, *J* = 265.0 Hz), 125.2, 125.5, 128.2, 128.3, 128.4, 128.5, 128.6, 128.8, 132.6 (q, *J* = 35.9 Hz), 135.5, 135.6, 138.0, 138.2, 139.2, 139.5 (q, *J* = 5.0 Hz), 143.1.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3^+$ ($[M+H]^+$) 315.1355. Found 315.1359.



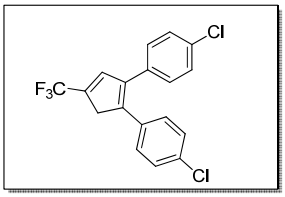
4d: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(methoxybenzene)

Colorless crystals, m.p. 127–129 °C, 79% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.68 (s, 2H), 3.79 (s, 3H), 3.81 (s, 3H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 42.8, 55.1, 55.2, 113.8, 114.0, 123.2 (CF_3, q, *J* = 265.0 Hz), 128.2, 128.3, 129.2, 129.5, 131.9 (q, *J* = 35.0 Hz), 137.5, 139.6, 139.7 (q, *J* = 5.0 Hz), 141.8, 158.9.

HRMS (ESI-TOF) Calcd for $C_{20}H_{18}F_3O_2^+$ ($[M+H]^+$) 347.1253. Found 347.1246.



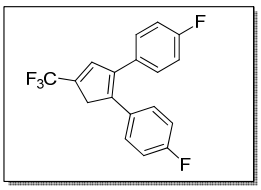
4e: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(chlorobenzene)

Colorless crystals m.p. 104–106 °C, 95% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.72 (s, 2H), 7.06 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 9.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 122.8 (CF_3, q, *J* = 266.3 Hz), 128.9, 129.0, 129.3, 129.6, 133.4 (q, *J* = 26.3 Hz), 133.5, 133.6, 133.7, 133.8, 138.7, 138.8 (q, *J* = 5.0 Hz), 142.3.

HRMS (ESI-TOF) Calcd for $C_{18}H_{12}Cl_2F_3^+$ ($[M+H]^+$) 355.0263. Found 355.0270.



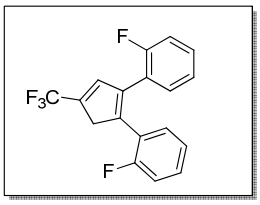
4f: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(fluorobenzene)

Colorless crystals, m.p. 97–99 °C, 97% yield.

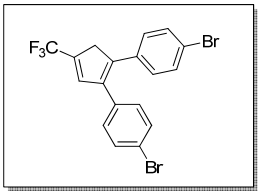
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.71 (s, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 1.5 Hz, 1H), 7.20 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.25 (dd, *J* = 8.5, 5.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.1, 115.6 (d), 115.7, 122.9 (CF_3, q, *J* = 266.3 Hz), 129.7 (d), 130.0 (d), 131.3 (d), 131.5 (d), 133.1 (q, *J* = 35.0 Hz), 138.2, 139.0 (q, *J* = 6.3 Hz), 142.1, 161.2 (d), 163.2 (d).

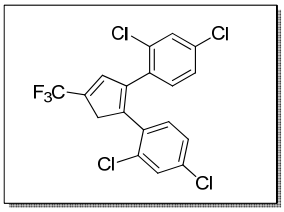
HRMS (ESI-TOF) Calcd for $C_{18}H_{12}F_5^+$ ($[M+H]^+$) 323.0854. Found 323.0848.



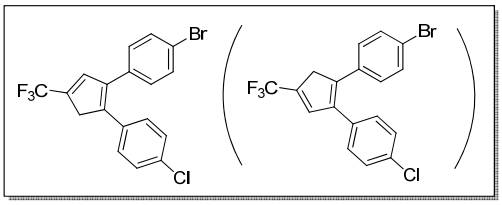
4g: 2,2'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(fluorobenzene)
Colorless crystals, m.p. 67–68 °C, 95% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.66 (s, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.81–6.99 (m, 5H), 7.03 (s, 1H), 7.07–7.11 (m, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.1, 43.2, 116.0 (d), 116.2 (d), 123.0 (CF_3, q, *J* = 266.3 Hz), 123.1 (d), 123.4 (d), 124.0 (d), 124.1 (d), 129.6 (d), 129.7 (d), 130.5 (d), 130.6 (d), 134.1 (q, *J* = 35.0 Hz), 136.1, 138.5 (m), 140.3, 158.9 (d), 160.9(d).
HRMS (ESI-TOF) Calcd for $C_{18}H_{12}F_5^+$ ($[M+H]^+$) 323.0854. Found 323.0845.



4h: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(bromobenzene)
Colorless crystals, m.p. 115–117 °C, 90% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.69 (s, 2H), 7.04 (s, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 121.9, 122.0, 122.8 (CF_3, q, *J* = 265.0 Hz), 129.5, 129.9, 131.8, 132.0, 133.6 (q, *J* = 36.3 Hz), 134.0, 134.1, 138.7 (q, *J* = 6.3 Hz), 138.8, 142.4.
HRMS (ESI-TOF) Calcd for $C_{18}H_{10}Br_2F_3^-$ ($[M-H]^-$) 444.9232 Found 442.8791.



4i: 4,4'-(4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)bis(1,3-dichlorobenzene)
Colorless crystals, m.p. 83–85 °C, 89% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.68 (s, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 7.27 (d, *J* = 13.5 Hz, 2H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 122.7 (CF_3, q, *J* = 266.3 Hz), 127.2, 127.3, 129.8, 129.9 , 131.7, 131.9, 132.4, 133.0, 134.2 (q, *J* = 36.3 Hz), 133.9, 134.0, 134.6, 134.7, 137.7 (q, *J* = 6.3 Hz), 140.1, 143.6.
HRMS (ESI-TOF) Calcd for $C_{18}H_8Cl_4F_3^-$ ($[M-H]^-$) 422.9298. Found 422.8682.



4j: 1-bromo-4-(2-(4-chlorophenyl)-4-(trifluoromethyl)cyclopenta-1,4-dien-1-yl)benzene

4j': 1-bromo-4-(2-(4-chlorophenyl)-4-(trifluoromethyl)cyclopenta-1,3-dien-1-yl)benzene

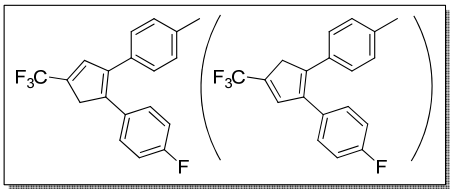
Colorless crystals, 4j/4j' = 1.0/1.0, 96% yield.

^{1}H NMR ($CDCl_3$, 500 MHz):

4j+4j', δ 3.71 (s, 4H), 7.06 (s, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.16 (dd, *J* = 9.0, 6.5 Hz, 4H), 7.20–7.29 (m, 4H), 7.29–7.31 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 42.9, 43.0, 122.8 (CF_3, q, *J* = 266.3 Hz), 121.9 (d), 128.9, 129.0, 129.2, 129.5, 129.6, 129.9, 131.8, 132.0, 133.6 (d), 133.7 (d), 134.1 (d), 138.7 (m), 142.4.

HRMS (ESI-TOF) Calcd for $C_{18}H_{10}BrClF_3^-$ ($[M-H]^-$) 398.9579. Found 398.8560.



4k: 1-fluoro-4-(2-(p-tolyl)-4-(trifluoromethyl)cyclopenta-1,3-dien-1-yl)benzene

4k': 1-fluoro-4-(2-(p-tolyl)-4-(trifluoromethyl)cyclopenta-1,4-dien-1-yl)benzene

Colorless viscous oil. 4k/ 4k' = 1.0/1.0, 87% yield.

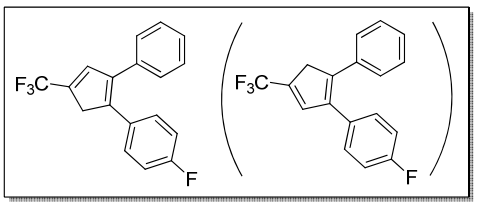
^{1}H NMR ($CDCl_3$, 500 MHz):

4k, δ 2.38 (s, 3H), 3.76 (s, 2H), 6.98 (t, *J* = 10.0 Hz, 2H), 7.11–7.14 (m, 4H), 7.23 (s, 1H), 7.27–7.30 (m, 2H).

4k', δ 2.41 (s, 3H), 3.74 (s, 2H), 7.04 (t, *J* = 10.0 Hz, 2H), 7.17–7.20 (m, 4H), 7.24 (s, 1H), 7.30–7.34 (m, 2H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1, 21.2, 43.0, 115.4 (d), 115.6 (d), 123.1 (CF_3, q, *J* = 265.0 Hz), 127.9, 128.2, 129.3, 129.4, 129.7 (d), 130.2 (d), 131.7 (m), 132.4 (d), 132.7 (m), 137.7 (d), 139.2 (q, *J* = 6.3 Hz), 139.4 (q, *J* = 5.0 Hz), 141.4, 143.4, 161.2 (d), 161.2 (d).

HRMS (ESI-TOF) Calcd for $C_{19}H_{15}F_4^+$ ($[M+H]^+$) 319.1104. Found 319.1110.



4l: 1-fluoro-4-(2-phenyl-4-(trifluoromethyl)cyclopenta-1,3-dien-1-yl)benzene

4l': 1-fluoro-4-(2-phenyl-4-(trifluoromethyl)cyclopenta-1,4-dien-1-yl)benzene

Colorless viscous oil, 4l/ 4l' = 1.0/1.0, 92% yield.

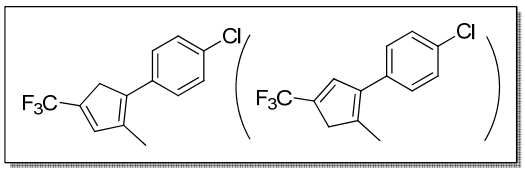
^{1}H NMR ($CDCl_3$, 500 MHz):

4l, δ 3.70 (s, 2H), 6.91 (t, J = 8.5 Hz, 2H), 7.06 (s, 1H), 7.19–7.24 (m, 7H).

4l', δ 3.72 (s, 2H), 6.97 (t, J = 8.5 Hz, 2H), 7.08 (s, 1H), 7.25–7.30 (m, 7H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 115.4 (d), 115.6 (d), 123.0 (CF_3, q, J = 265.0 Hz), 127.8 (d), 128.0, 128.3, 128.5, 128.7, 129.7 (d), 130.0 (d), 135.4, 138.2, 139.0 (q, J = 6.3 Hz), 139.3 (q, J = 5.0 Hz), 141.9, 143.2, 161.2 (d), 163.1 (d).

HRMS (ESI-TOF) Calcd for $C_{18}H_{11}F_4^-$ ([M-H]$^-$) 303.0791. Found 303.0077.



4m: 1-chloro-4-(2-methyl-4-(trifluoromethyl)cyclopenta-1,3-dien-1-yl)benzene

4m': 1-chloro-4-(2-methyl-4-(trifluoromethyl)cyclopenta-1,4-dien-1-yl)benzene

Colorless viscous oil. 4m/ 4m' = 3.0/1.0, 86% yield.

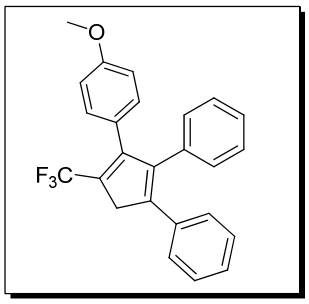
To a solution of **3m** (111 mg, 0.4 mmol) in THF (5 mL) was added TsOH (5.0 equiv) and stirred at 75 °C for 3 h. After **3m** was consumed as indicated by TLC, the reaction mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : EtOAc = 30 : 1, V/V) to give **4m** (89 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 500 MHz):

4m, δ 2.14 (s, 3H), 3.54 (s, 2H), 6.85 (d, J = 2.0 Hz, 1H), 7.28–7.31 (m, 2H), 7.31–7.36 (m, 2H).

4m', δ 2.17 (s, 3H), 3.34 (s, 2H), 7.01 (d, J = 1.5 Hz, 1H), 7.25–7.27 (m, 2H), 7.36–7.38 (m, 2H).

HRMS (ESI-TOF) Calcd for $C_{13}H_{11}ClF_3^+$ ([M+H]$^+$) 259.0496. Found 259.0468.



4n: (3-(4-methoxyphenyl)-4-(trifluoromethyl)cyclopenta-1,3-diene-1,2-diyl)dibenzene

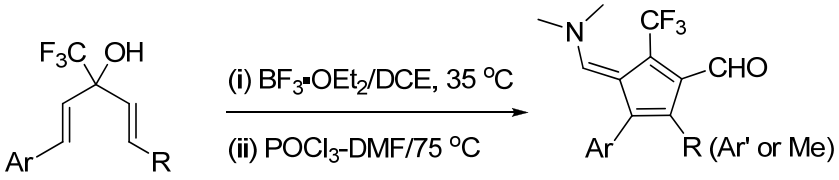
Colorless crystals, m.p.139–140^{o}C, 83% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.77 (s, 3H), 3.87 (s, 2H), 6.74 (d, J = 8.5 Hz, 2H), 6.90-6.92 (m, 2H), 6.96 (d, J = 8.5 Hz, 2H), 7.15-7.18 (m, 8H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 42.6, 55.1, 113.0, 123.5 (CF_3, q, J = 267.5 Hz), 125.9, 126.8 (q, J = 32.6 Hz), 127.1, 127.3, 128.1, 128.2, 128.3, 129.9, 130.2 (q, J = 1.4 Hz), 135.1, 135.4, 142.7, 143.1, 151.6, 159.0.

HRMS (ESI-TOF) Calcd for $C_{25}H_{19}F_3O^+$ ([M+H]$^+$) 393.1461. Found 393.1447.

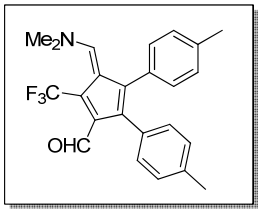
V. Synthetic procedures and analytical data of **5**



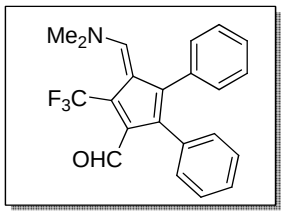
3 **5**

General procedure (**5e** as an example):

To a solution of **3e** (373 mg, 1 mmol) in DCE (3 mL) at 35 °C, was added boron trifluoride etherate (2.0 equiv) slowly. After **3e** was consumed as indicated by TLC, DMF (10 mL) and $POCl_3$ (3.0 equiv) was added, respectively, and the reaction mixture was stirred at 75 °C for 30 min. After cooling to the room temperature, the reaction mixture was poured into water (30 mL), neutralized with saturated $NaHCO_3$ to pH 7, and extracted with CH_2Cl_2 (15 mL × 3). The combined organic phase was washed with water (15 mL ×3), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : EtOAc = 4 : 1, V/V) to give **5e** (408 mg, 93%).

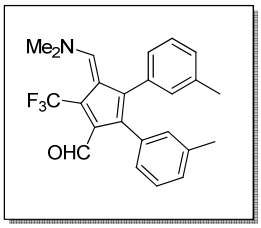


5a: (E)-3-((dimethylamino)methylene)-4,5-di-*p*-tolyl-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 138–140 °C, 78% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 2.30 (s, 3H), 2.64 (s, 3H), 3.33 (s, 3H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.99 (m, 6H), 8.32 (s, 1H), 9.95 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 21.2, 43.0, 47.9, 112.1, 125.5 (CF_3, q, *J* = 230.0 Hz), 128.1, 128.8, 128.9, 129.0, 129.8, 130.7, 133.0, 134.2, 134.6, 135.3, 135.4, 161.6, 187.4.
HRMS (ESI-TOF) Calcd for $C_{24}H_{23}F_3NO^+$ ($[M+H]^+$) 398.1726. Found 398.1718.

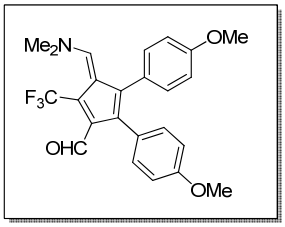


5b: (E)-3-((dimethylamino)methylene)-4,5-diphenyl-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 228–230 °C, 83% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.63 (s, 3H), 3.34 (s, 3H), 6.92 (d, *J* = 7.0 Hz, 2H), 7.09 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.17 (m, 6H), 8.35 (s, 1H), 9.98 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.1, 48.0, 125.9, 126.1, 127.4, 128.3, 130.0, 130.9, 134.5, 136.1, 137.7, 161.5, 187.3.

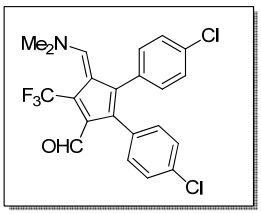
^{19}F NMR (DMSO-d6, 470 MHz) δ -50.5.
HRMS (ESI-TOF) Calcd for $C_{22}H_{19}F_3NO^+$ ($[M+H]^+$) 370.1413. Found 370.1412.



5c: (E)-3-((dimethylamino)methylene)-4,5-di-*m*-tolyl-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 198–200 °C, 80% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.20 (s, 3H), 2.23 (s, 3H), 2.65 (s, 3H), 3.32 (s, 3H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.74 (s, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.93 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 7.06 (m, 2H), 8.35 (s, 1H), 9.92 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.4, 43.1, 48.0, 112.2, 124.9 (CF_3, q, *J* = 268.8 Hz), 126.6, 126.8, 127.1, 127.2, 128.1, 128.2, 129.6, 130.6, 130.7, 131.8, 134.8, 136.0, 136.6, 137.5, 137.7, 161.8, 187.5.
HRMS (ESI-TOF) Calcd for $C_{24}H_{23}F_3NO^+$ ($[M+H]^+$) 398.1726. Found 398.1741.

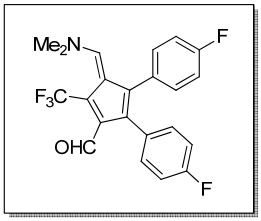


5d: (Z)-3-((dimethylamino)methylene)-4,5-bis(4-methoxyphenyl)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 179–181 °C, 76% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.65 (s, 3H), 3.31 (s, 3H), 3.74 (s, 3H), 3.75 (s, 3H), 6.72–6.75 (m, 4H), 6.82 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 8.34 (s, 1H), 9.93 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 42.8, 47.8, 54.8, 54.9, 112.0, 112.6, 113.7, 118.6 (q), 124.8 (CF_3, q, *J* = 268.8 Hz), 128.4, 128.8, 129.6, 129.9, 130.8, 131.9, 133.4, 157.5, 157.6, 162.1, 187.0.
HRMS (ESI-TOF) Calcd for $C_{24}H_{23}F_3NO_3^+$ ($[M+H]^+$) 430.1624. Found 430.1216.

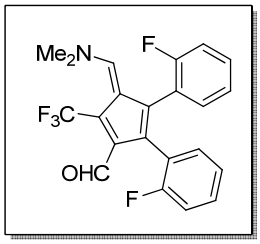


5e: (Z)-4,5-bis(4-chlorophenyl)-3-((dimethylamino)methylene)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 163–164 °C, 94% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.69 (s, 3H), 3.37 (s, 3H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 7.16–7.19 (m, 4H), 8.32 (s, 1H), 10.01 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.2, 48.1, 111.4, 121.2, 121.5, 124.6 (CF_3, q, *J* = 268.8 Hz), 127.6, 128.7, 129.4, 131.0, 132.0, 132.1, 132.6, 134.6, 135.8, 161.2, 186.7.

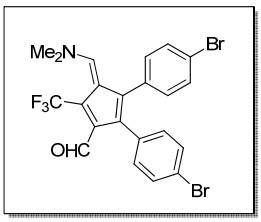
HRMS (ESI-TOF) Calcd for $C_{22}H_{17}Cl_2F_3NO^+$ ($[M+H]^+$) 438.0634. Found 438.0638.



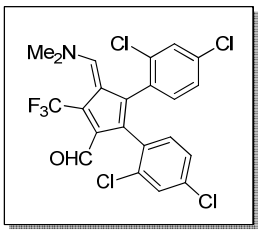
5f: (Z)-3-((dimethylamino)methylene)-4,5-bis(4-fluorophenyl)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 185–187 °C, 84% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.69 (s, 3H), 3.37 (s, 3H), 6.85–6.93 (m, 6H), 7.02 (dd, *J* = 8.5 Hz, 5.5 Hz, 2H), 8.30 (s, 1H), 10.01 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.1, 48.0, 111.6, 114.2 (d), 115.4 (d), 120.9 (q), 124.7 (CF_3, q, *J* = 268.8 Hz), 127.9, 129.7, 131.3 (d), 132.1 (d), 132.3 (d), 133.0, 133.4 (d), 160.3 (d), 161.0, 162.3 (d), 186.9.
HRMS (ESI-TOF) Calcd for $C_{22}H_{17}F_5NO^+$ ($[M+H]^+$) 406.1225. Found 406.1206.



5g: (Z)-3-((dimethylamino)methylene)-4,5-bis(2-fluorophenyl)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 239–241 °C, 92% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.71 (s, 3H), 3.35 (s, 3H), 6.90–6.97 (m, 6H), 7.15 (q, *J* = 7.0 Hz, 2H), 8.29 (s, 1H), 10.03 (s, 1H).
^{13}C NMR (C_3D_6O, 125 MHz) δ 43.3, 48.4, 112.5, 115.3 (d), 116.3 (d), 119.6 (d), 123.7, 124.3, 125.0, 125.1 (d), 126.0, 126.2, 126.3, 127.2, 127.3 (q), 128.9 (d), 129.4 (d), 133.2 (d), 133.3 (d), 165.0, 185.0.
HRMS (ESI-TOF) Calcd for $C_{22}H_{17}F_5NO^+$ ($[M+H]^+$) 406.1225. Found 406.1220.



5h: (Z)-4,5-bis(4-bromophenyl)-3-((dimethylamino)methylene)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde
Green crystals, m.p. 279–281 °C, 85% yield.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.70 (s, 3H), 3.38 (s, 3H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 7.32–7.35 (m, 4H), 8.30 (s, 1H), 10.02 (s, 1H).
^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.3, 48.2, 120.3, 120.4, 128.8, 129.4, 130.6, 130.9, 131.4, 131.7, 132.5, 132.6, 135.1, 136.3, 161.2, 186.8.
HRMS (ESI-TOF) Calcd for $C_{22}H_{17}Br_2F_3NO^+$ ($[M+H]^+$) 525.9624. Found 525.9625.



5i+5i':

(Z)-4,5-bis(2,4-dichlorophenyl)-3-((dimethylamino)methylene)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

Green crystals, 84% yield.

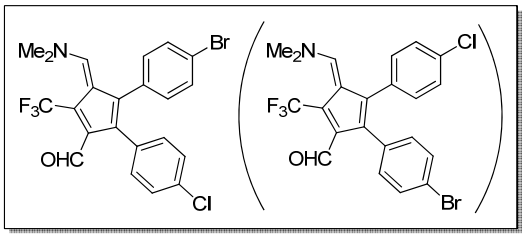
^{1}H NMR ($CDCl_3$, 500 MHz):

5i, δ 2.72 (s, 3H), 3.39 (s, 3H), 6.81 (d, *J* = 8.5 Hz, 1H), 7.03–7.07 (m, 2H), 7.30–7.33 (m, 3H), 8.16 (s, 1H), 10.01 (s, 1H).

5i', δ 2.80 (s, 3H), 3.38 (s, 3H), 6.91–6.99 (m, 4H), 7.11 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 7.27 (d, *J* = 2.0 Hz, 1H), 8.24 (s, 1H), 10.01 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 43.2, 48.3, 111.1, 111.3, 124.6 (CF_3, q, *J* = 268.8 Hz), 125.9, 126.4, 126.9, 127.0, 127.5, 128.4, 128.9, 129.1, 129.4, 129.7, 129.8, 130.3, 132.3, 132.7, 132.8, 132.9, 133.1, 133.2, 133.4, 133.5, 134.3, 134.4, 134.5, 134.8, 134.9, 135.0, 135.3, 135.6, 160.9, 185.9, 186.1.

HRMS (ESI-TOF) Calcd for $C_{22}H_{15}Cl_4F_3NO^+$ ($[M+H]^+$) 505.9854. Found 505.9879.



5j: (Z)-4-(4-bromophenyl)-5-(4-chlorophenyl)-3-((dimethylamino)methylene)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

5j': (Z)-4-(4-bromophenyl)-5-(4-chlorophenyl)-3-((dimethylamino)methylene)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

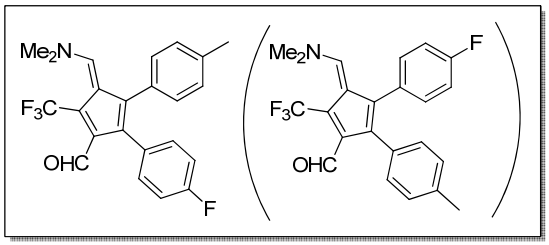
Green crystals, 5j/ 5j' = 1.0/1.0, 92% yield.

^{1}H NMR ($CDCl_3$, 500 MHz):

5j +**5j'**, δ 2.69 (s, 3H), 3.38 (s, 3H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz,1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 7.20 (m, 2H), 7.33 (m, 2H), 8.31 (s, 1H), 10.02 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.2, 48.1, 120.2, 120.3, 124.6 (CF_3, q, *J* = 268.8 Hz), 127.6, 128.7, 129.3, 130.5, 131.0, 131.3, 131.6, 132.0, 132.1, 132.4, 132.4. 132.5, 134.5, 135.1, 135.8, 136.3, 161.1, 186.7.

HRMS (ESI-TOF) Calcd for $C_{22}H_{17}BrClF_3NO^+$ ($[M+H]^+$) 482.0129. Found 482.0134.



5k: (Z)-3-((dimethylamino)methylene)-5-(4-fluorophenyl)-4-(p-tolyl)-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

5k': (Z)-3-((dimethylamino)methylene)-4-(4-fluorophenyl)-5-(p-tolyl)-2-(trifluoromethyl)cyclopenta -1,4-dienecarbaldehyde

Green crystals, 5k/ 5k' = 1.5/1.0, 81% yield.

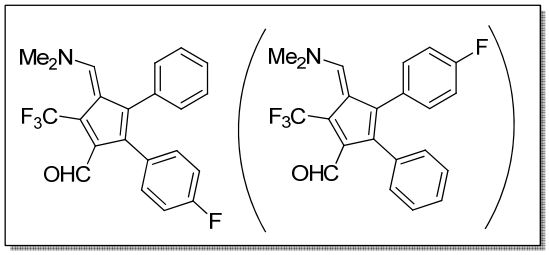
^{1}H NMR ($CDCl_3$, 500 MHz):

5k, δ 2.28 (s, 3H), 2.63 (s, 3H), 3.34 (s, 3H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.86–6.90 (m, 6H), 8.30 (s, 1H), 9.96 (s, 1H).

5k', δ 2.30 (s, 3H), 2.70 (s, 3H), 3.35 (s, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.99 (m, 3H), 7.02–7.06 (m, 3H), 8.32 (s, 1H), 10.0 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 21.1, 29.6, 43.0, 48.0, 111.8 (d), 114.1 (d), 115.3 (d), 122.8 (CF_3, q, *J* = 270.0 Hz), 128.2, 129.1, 129.2, 129.7, 130.7, 130.9, 131.3 (d), 132.3 (d), 132.8, 133.6 (d), 134.3, 134.6, 135.5(d), 160.4 (d), 161.6, 162.3 (d), 186.9, 187.2.

HRMS (ESI-TOF) Calcd for $C_{23}H_{20}F_4NO^+$ ($[M+H]^+$) 402.1476. Found 402.1479.



5l: (Z)-3-((dimethylamino)methylene)-5-(4-fluorophenyl)-4-phenyl-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

5l':(Z)-3-((dimethylamino)methylene)-4-(4-fluorophenyl)-5-phenyl-2-(trifluoromethyl)cyclopenta-1,4-dienecarbaldehyde

Green crystals, 5l/ 5l' = 1.1/1.0, 86% yield.

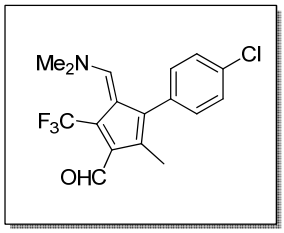
^{1}H NMR ($CDCl_3$, 500 MHz):

5l, δ 2.60 (s, 3H), 3.35 (s, 3H), 6.88–6.89 (m, 9H), 8.35 (s, 1H), 10.01 (s, 1H).

5l' , δ 2.70 (s, 3H), 3.36 (s, 3H), 7.04–7.07 (m, 3H), 7.16– 7.19 (m, 6H), 8.33 (s, 1H), 9.96 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 43.0, 43.2, 48.0, 48.1, 111.8 (d), 114.2 (d), 115.4 (d), 124.7 (CF_3, q, *J* = 268.0 Hz), 126.1 (d), 127.4, 128.4, 129.0 (q), 129.9, 130.9, 131.3 (d), 132.2, 132.4 (d), 132.8, 133.5 (d), 134.6, 136.0, 137.5, 160.3 (d), 161.4, 161.5, 162.2 (d), 187.0, 187.2.

HRMS (ESI-TOF) Calcd for $C_{22}H_{18}F_4NO^+$ ($[M+H]^+$) 388.1319. Found 388.1307 .



5m:(Z)-4-(4-chlorophenyl)-3-((dimethylamino)methylene)-5-methyl-2-(trifluoromethyl)cyclopenta-1,4-die necarbaldehyde

To a solution of **4m** (78 mg, 0.3 mmol) in DMF (3 mL) was added $POCl_3$ (3.0 equiv), and the reaction mixture was stirred at 75 °C for 0.5 h. After cooling to the room temperature, the reaction mixture was poured into water (10 mL), neutralized with saturated $NaHCO_3$ to pH 7, and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phase was washed with water (0.5 mL ×3), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : EtOAc = 4 : 1, V/V) to give **5m** (86.1 mg, 84%).

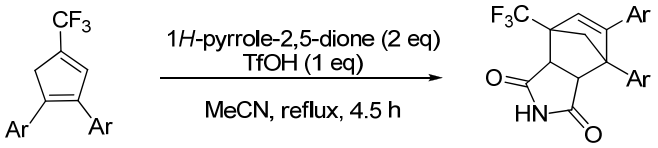
Green crystals, m.p. 145–147 °C, 84% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3H), 2.55 (s, 3H), 3.30 (s, 3H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 8.13 (s, 1H), 10.25 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 M Hz) δ 13.3, 65.5, 111.7, 124.6 (q, *J* = 32.4 Hz), 124.9 (CF_3, q, *J* = 269.0 Hz), 128.8, 129.9, 130.9, 131.0, 132.1, 136.9, 158.3, 188.0.

HRMS (ESI-TOF) Calcd for $C_{17}H_{16}ClF_3NO^+$ ($[M+H]^+$) 342.0067. Found 342.0096.

VI. Synthetic procedures and analytical data of **6**

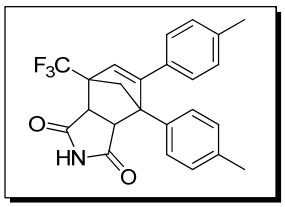


4a: R = 4-MePh;
4e: R = 4-ClPh)

6a (95%)
6e (91%)

General procedure (**6a** as an example):

To a solution of **4a** (315 mg, 1.0 mmol) and 1*H*-pyrrole-2,5-dione (194 mg, 2.0 mmol) in CH_3CN (10 mL), was added CF_3SO_3H (87 μL, 1.0 mmol), and stirred under reflux. After **4a** was consumed as indicated by TLC, the reaction mixture was cooled to the room temperature and poured into water (10 mL), and extracted with CH_2Cl_2 (10 mL × 3). The combined organic phase was washed with water (0.5 mL ×3), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether : EtOAc = 30 : 1, V/V) to give **6a** (391 mg, 95%).



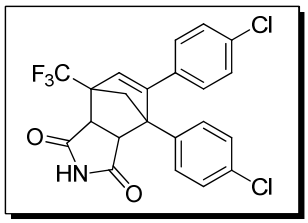
6a: 4,5-di-*p*-tolyl-7-(trifluoromethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione

Colorless crystal, m.p. 233–234°C, 95% yield.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.06 (9.0 Hz, 1H), 2.22 (s, 3H), 2.33 (s, 3H), 2.53 (d, *J* = 9.0 Hz, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 4.23 (d, *J* = 7.5 Hz, 1H), 6.42 (s, 1H), 6.90 (s, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.74 (s, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.0, 21.1, 50.1 (d, *J* = 8.8 Hz), 57.8 (q, *J* = 31.8 Hz), 60.6, 64.0, 123.3, 125.5 (CF_3, q, *J* = 266.3 Hz), 127.0, 128.2, 128.7, 129.2, 129.5, 134.5, 135.0, 137.2, 138.1, 152.3, 173.6, 175.6.

HRMS (ESI-TOF) Calcd for $C_{24}H_{20}F_3NO_2^+$ ($[M+H]^+$) 412.1519. Found 412.1563.



6e:

4,5-bis(4-chlorophenyl)-7-(trifluoromethyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione

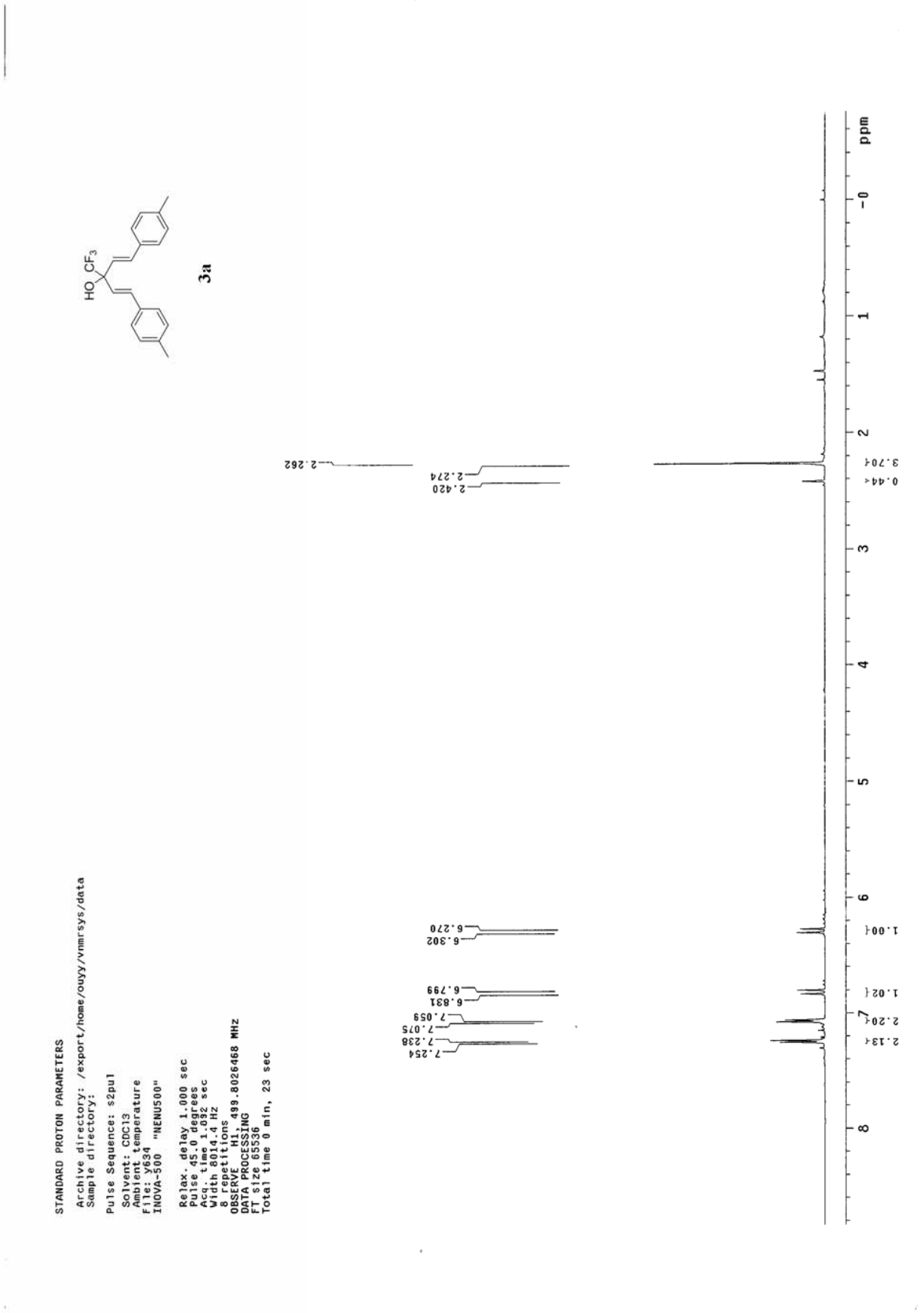
Colorless crystal, m.p. 245–246 ^{o}C, 91% yield.

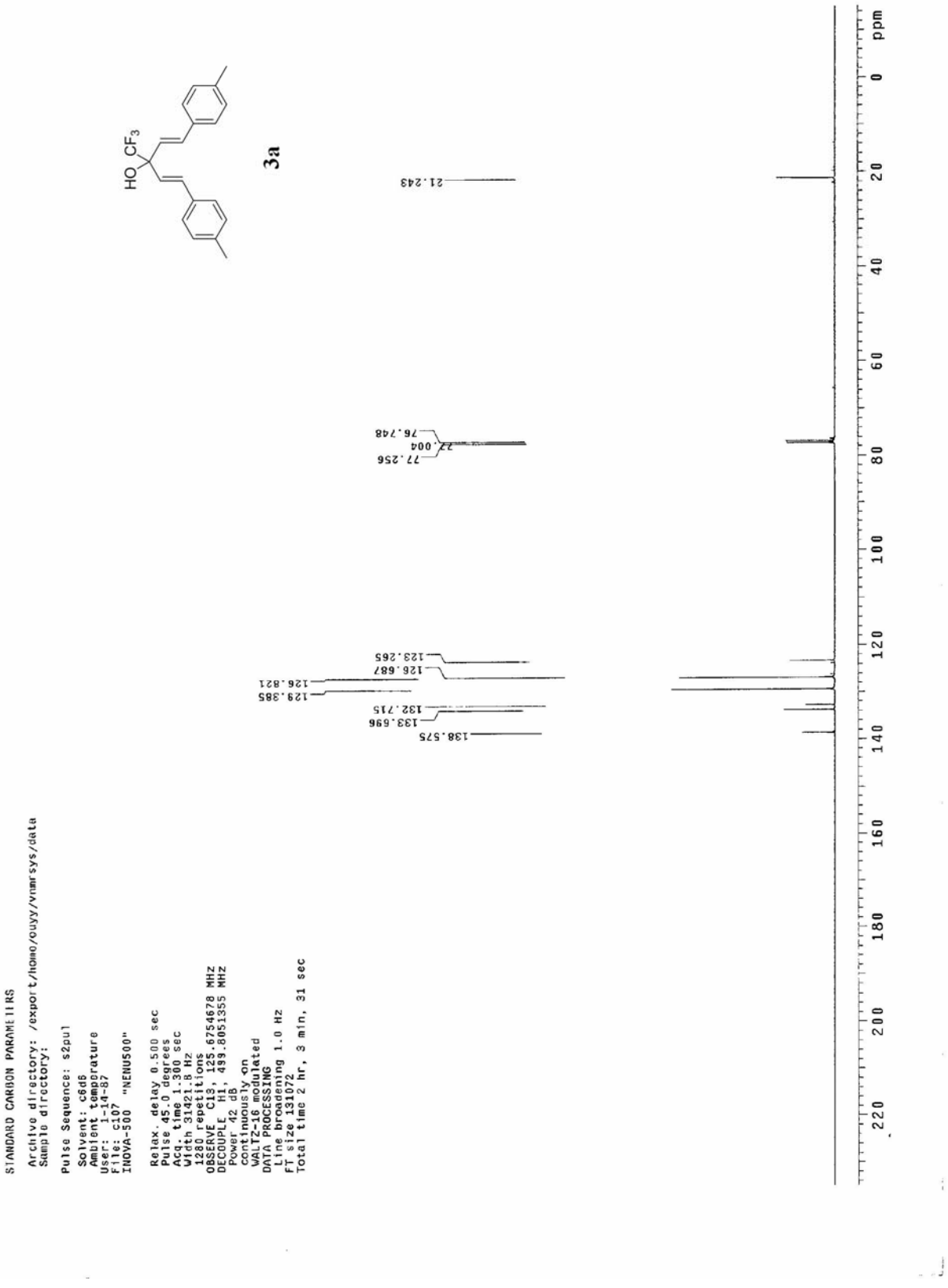
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.13 (d, *J* = 9.0 Hz, 1H), 2.54 (d, *J* = 9.0 Hz, 1H), 3.94 (d, *J* = 8.0 Hz, 1H), 4.23 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.63 (s, 1H).

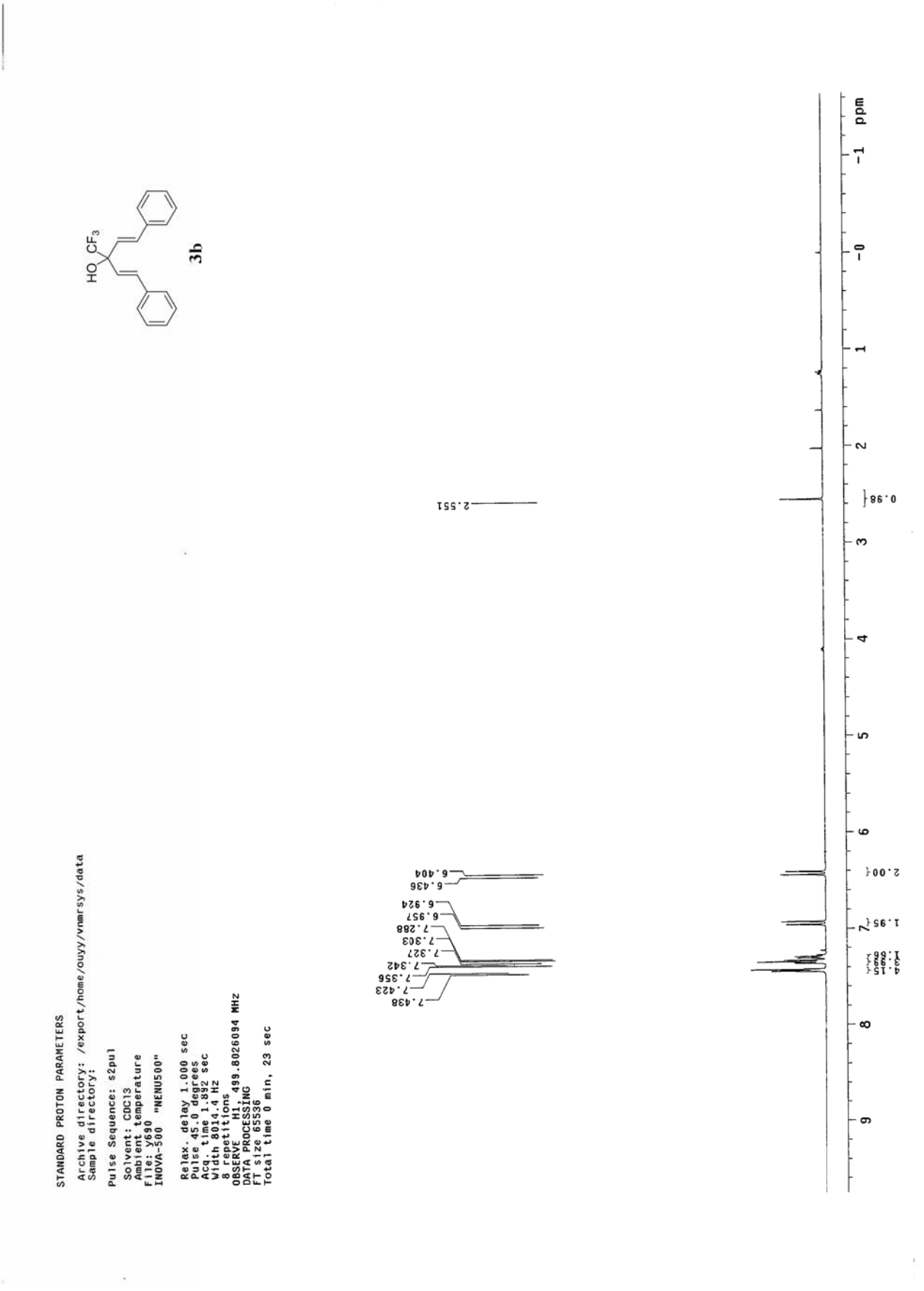
^{13}C NMR ($CDCl_3$, 125 MHz) δ 50.0 (d, *J* = 7.0 Hz), 58.1 (q, *J* = 32.1 Hz), 60.7, 63.8, 125.2 (CF_3, q, *J* = 275.1 Hz), 125.3, 128.4, 128.5, 128.9, 129.7, 130.5, 133.8, 134.5, 135.5, 151.3, 172.7, 174.4.

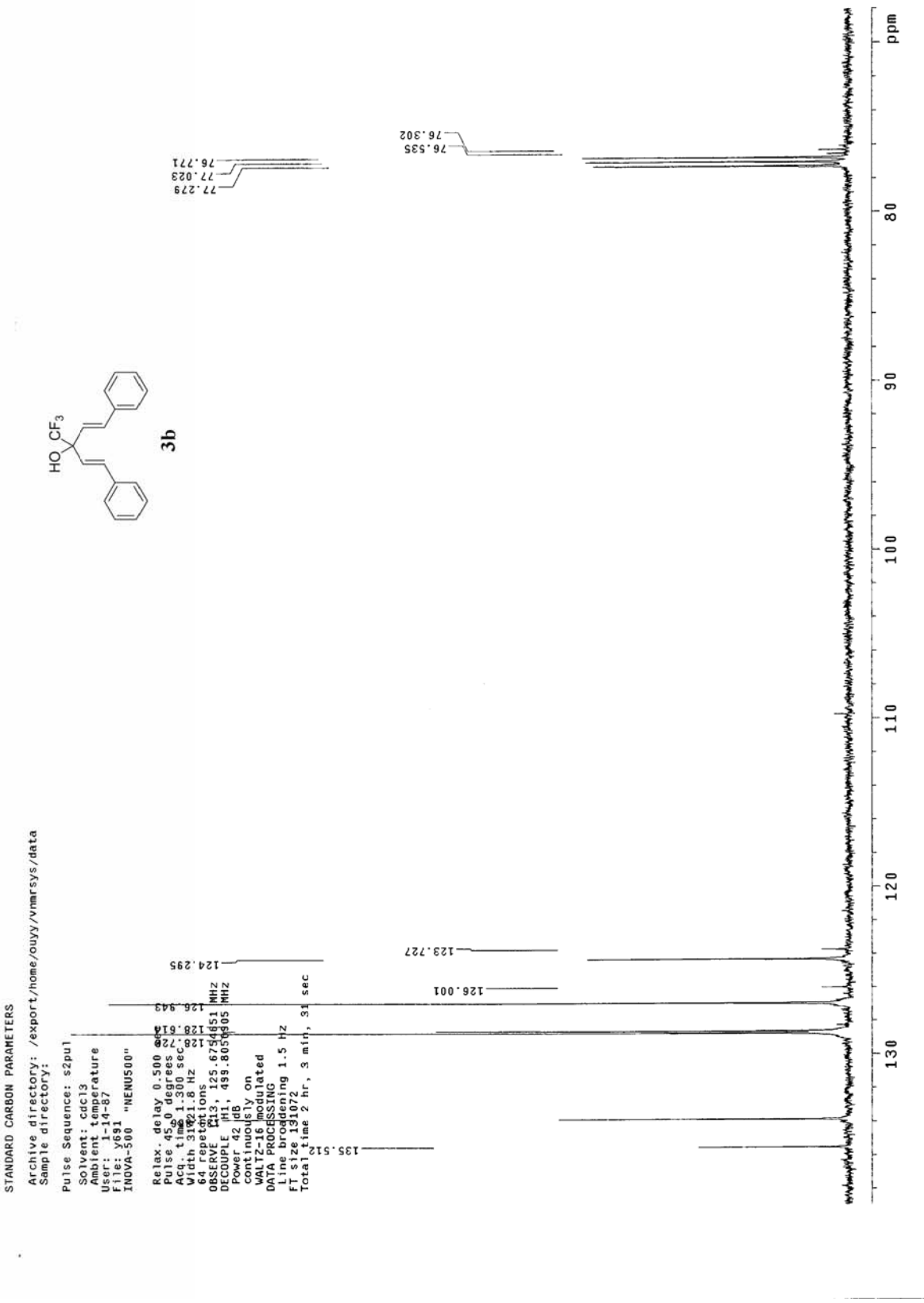
HRMS (ESI-TOF) Calcd for $C_{22}H_{16}Cl_2F_3NO_2^+$ ($[M+H]^+$) 453.0505. Found 453.0571.

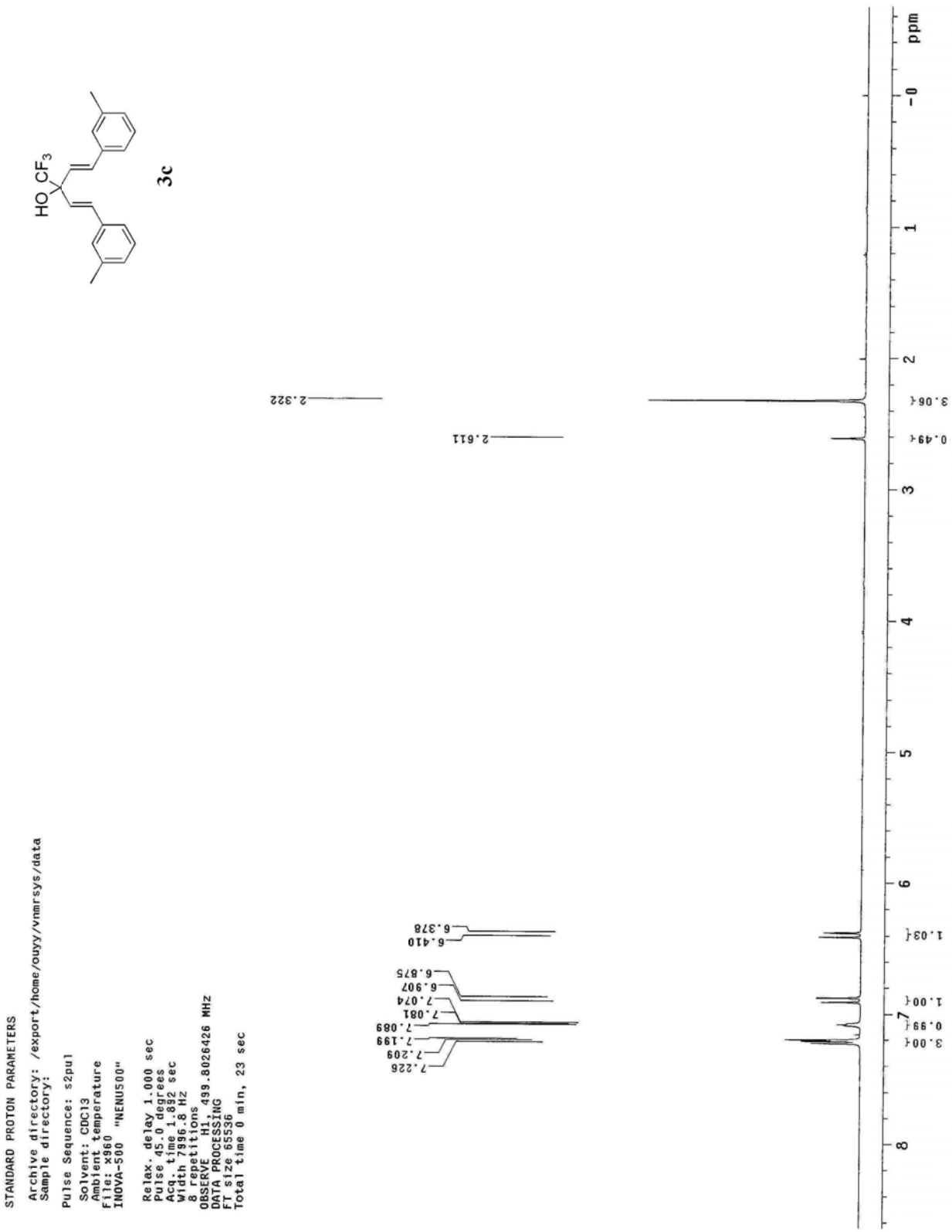
VII. Copies of ^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra

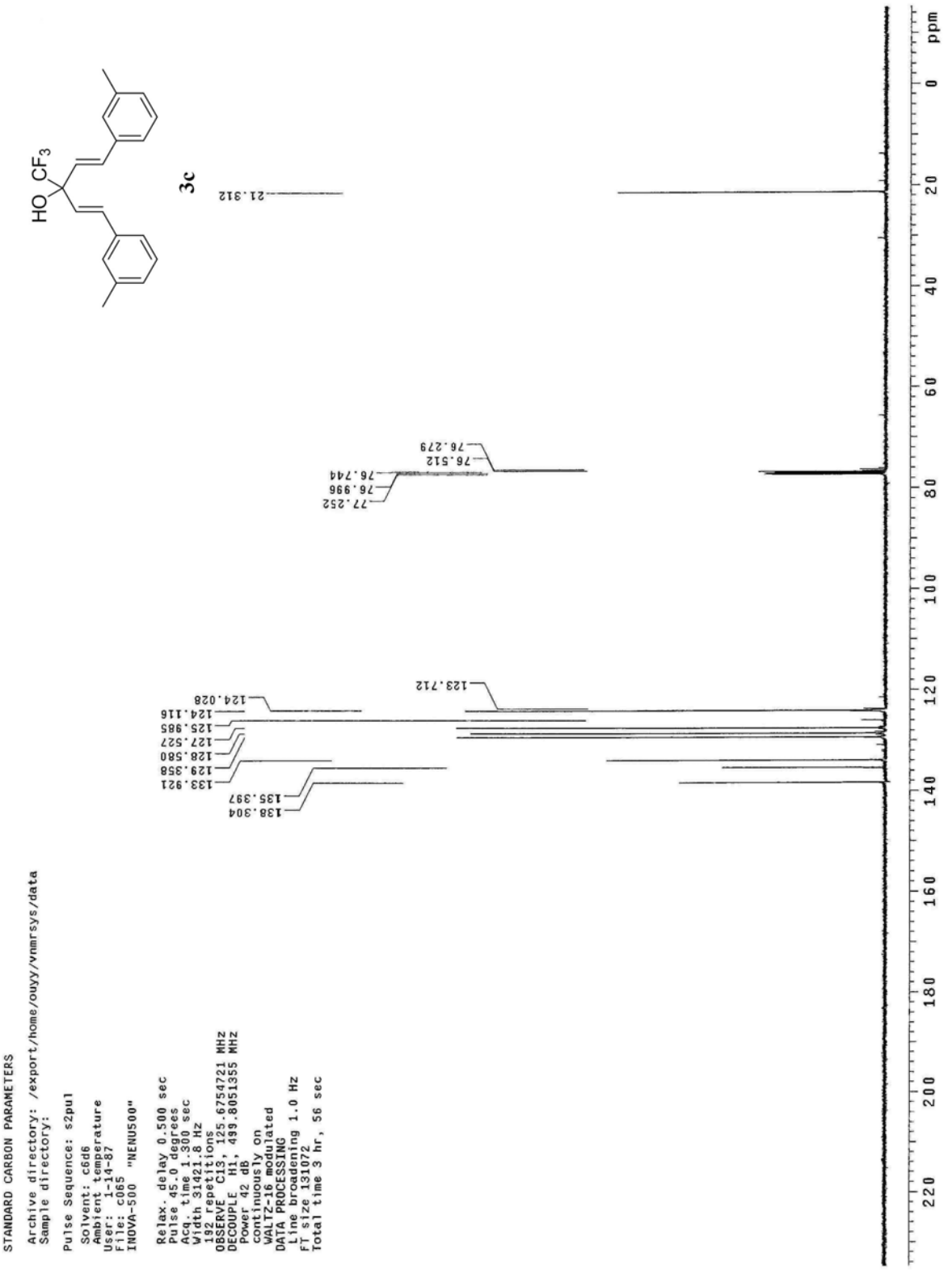


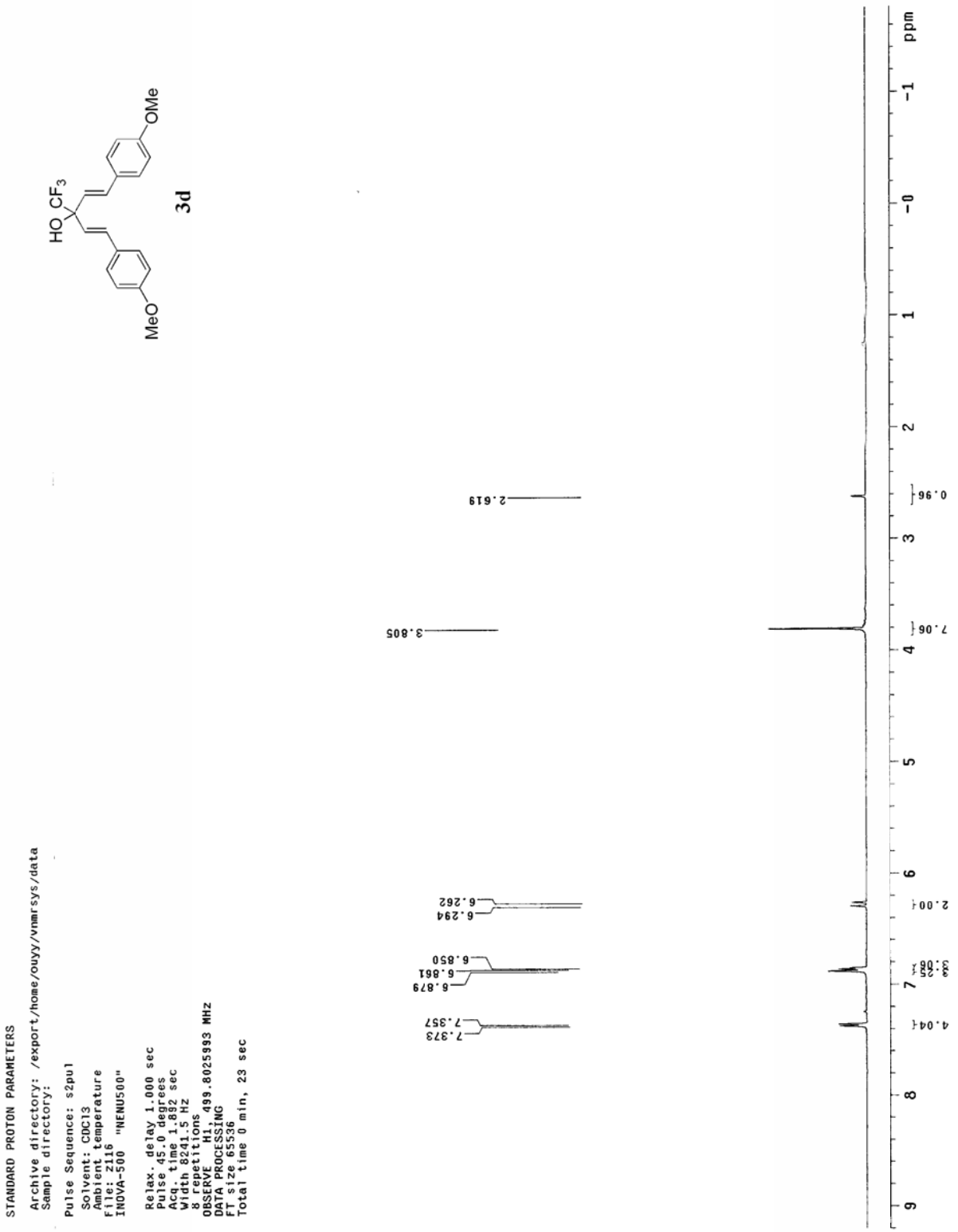


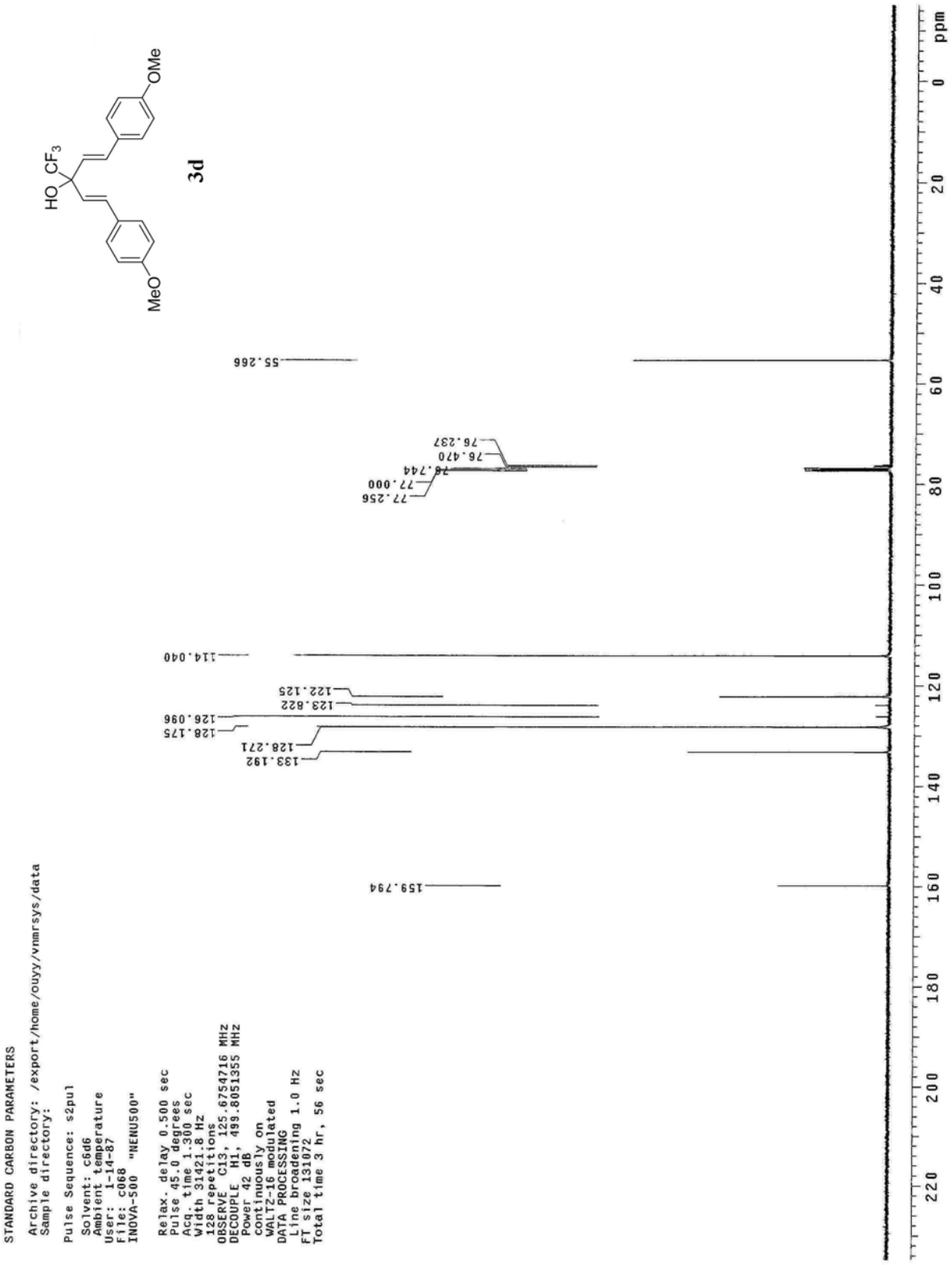


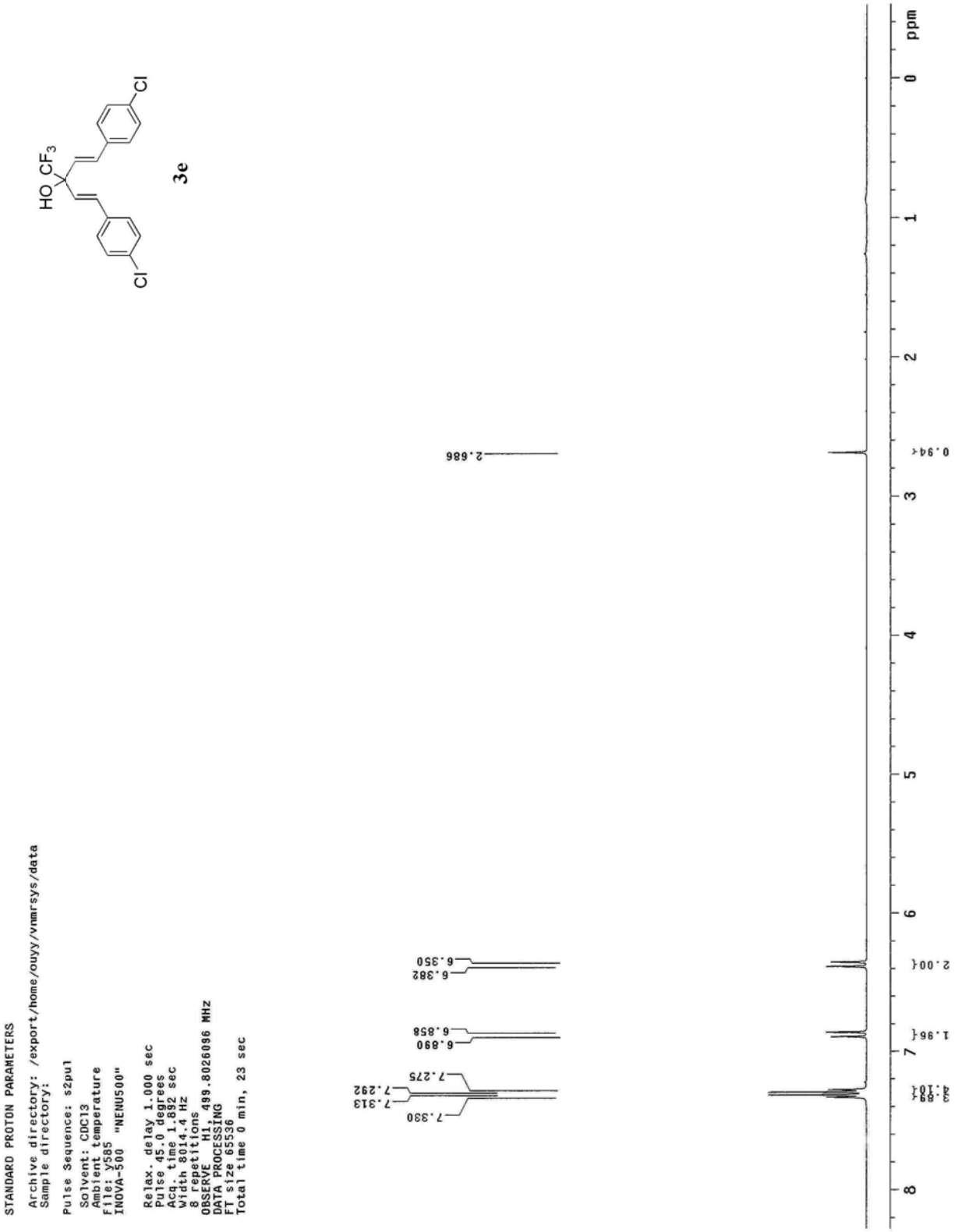


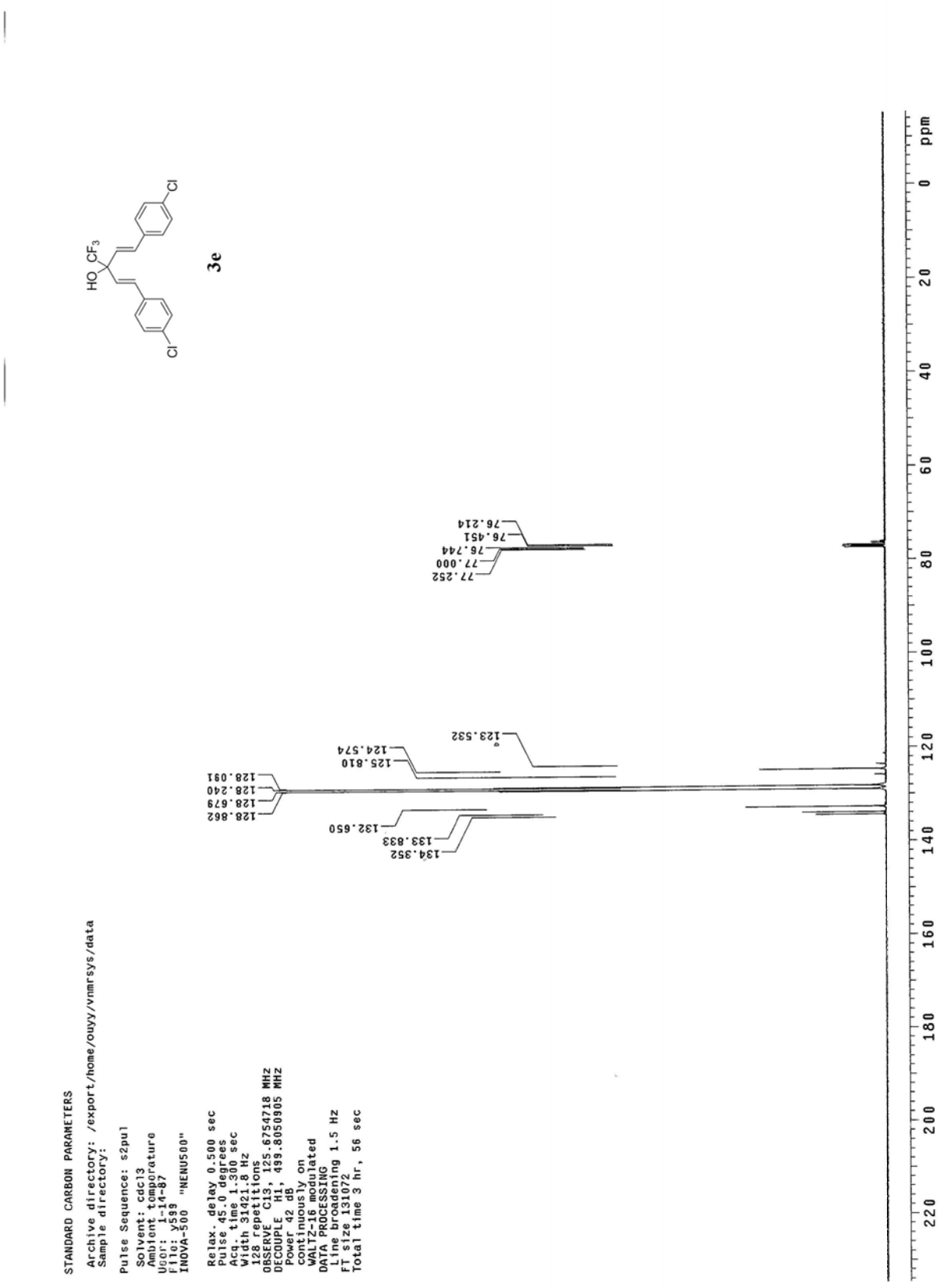

HO CF3
3c
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: x960
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8026426 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2.322
2.611
6.410
6.378
6.875
6.907
7.074
7.081
7.089
7.199
7.209
7.226
3.06
0.49
1.03
1.00
0.99
3.00
ppm

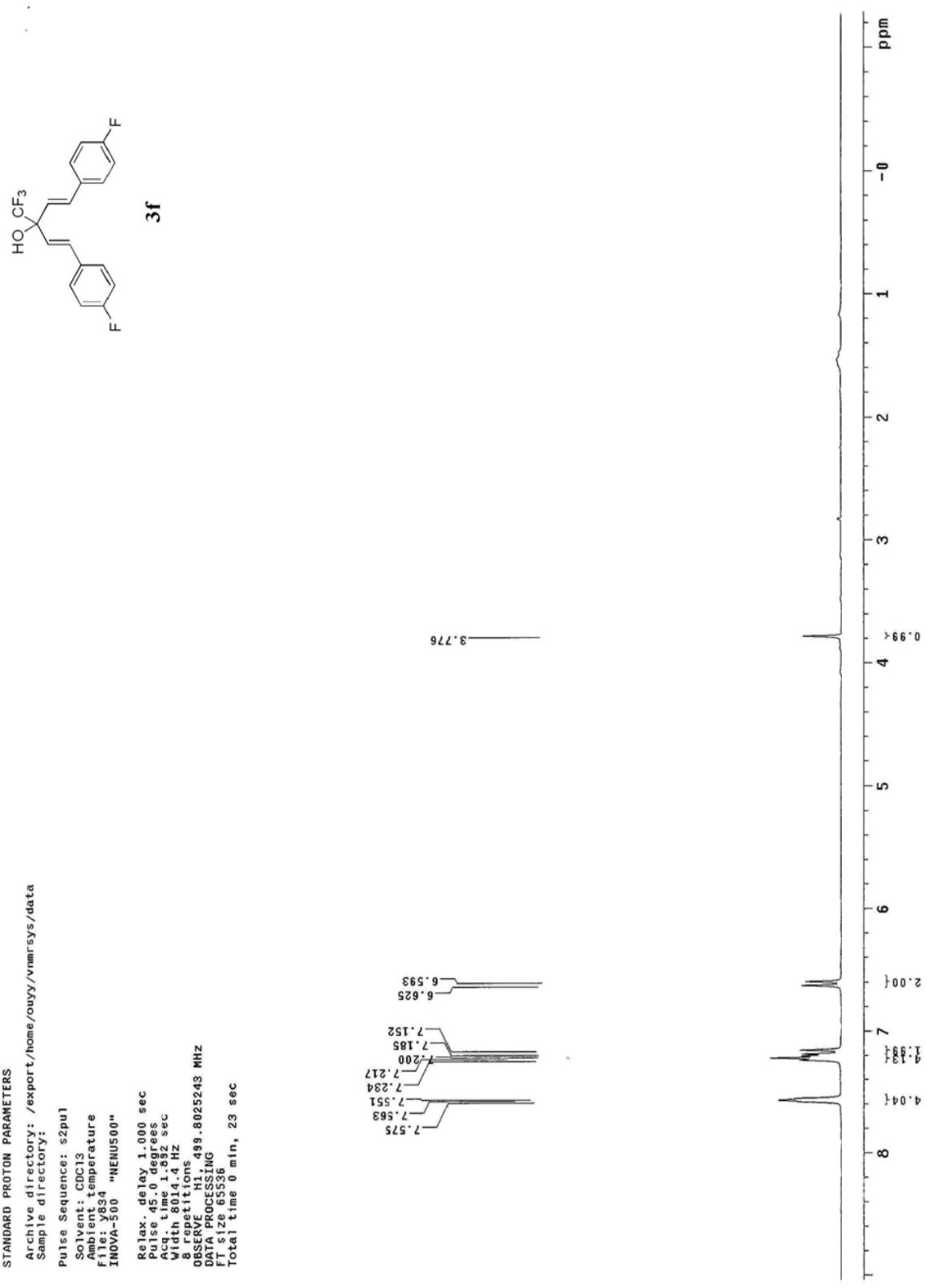

HO
CF3
3c
21.312
76.279
76.512
76.744
76.996
77.252
123.712
124.028
124.116
125.985
127.527
128.580
129.358
133.921
135.397
138.304
ppm
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: 1-14-87
File: c065 "NENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
192 repetitions
OBSERVE C13, 125.6754721 MHz
DECOUPLE H1, 499.8051355 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 hr, 56 sec

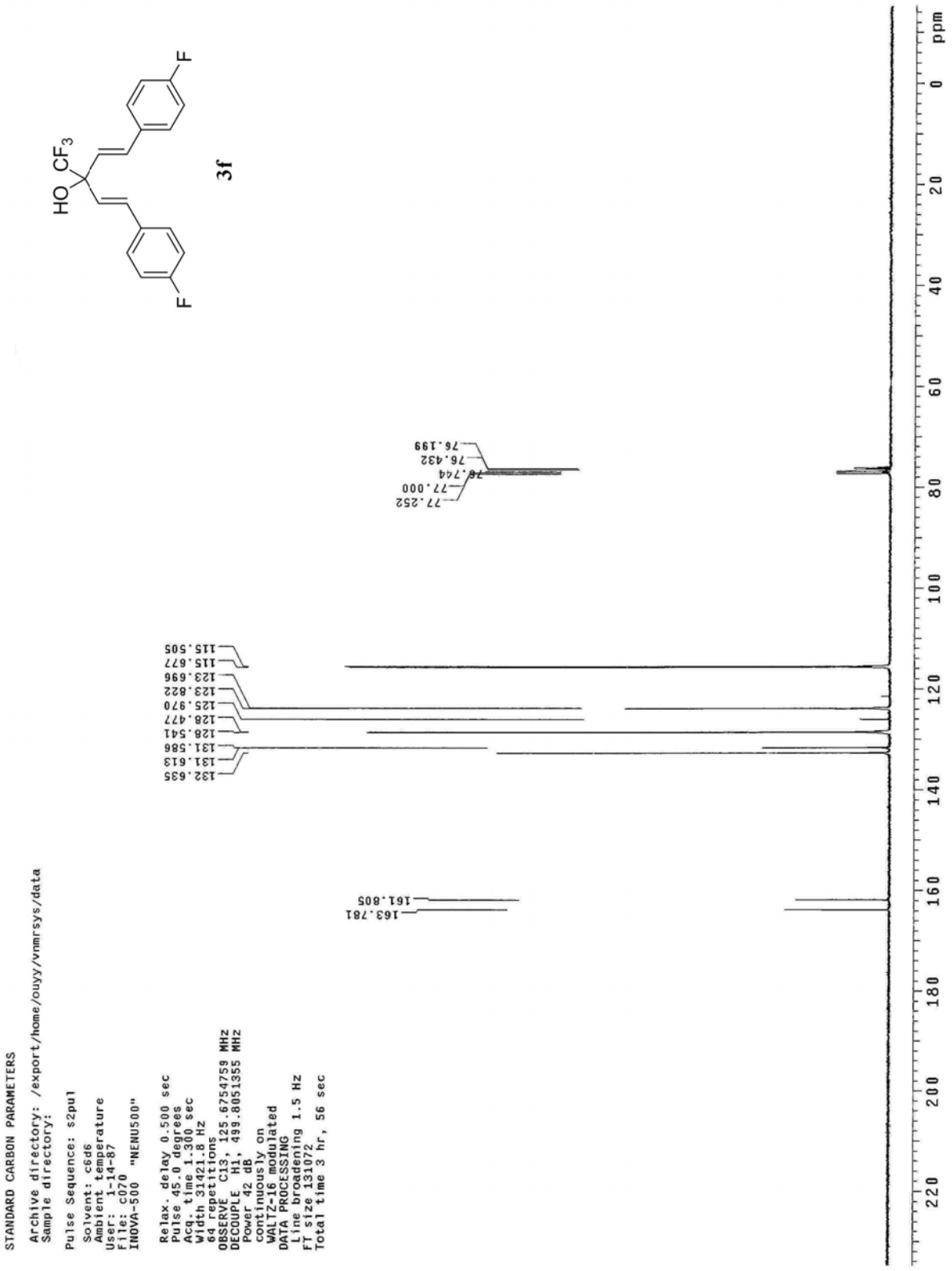

HO CF3
OMe
MeO
3d
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: z116 "NENU500"
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 8241.5 Hz
8 repetitions
OBSERVE H1, 499.8025993 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
7.373
7.357
6.879
6.861
6.850
6.294
6.262
3.805
2.619
4.04
2.00
7.06
0.96
ppm

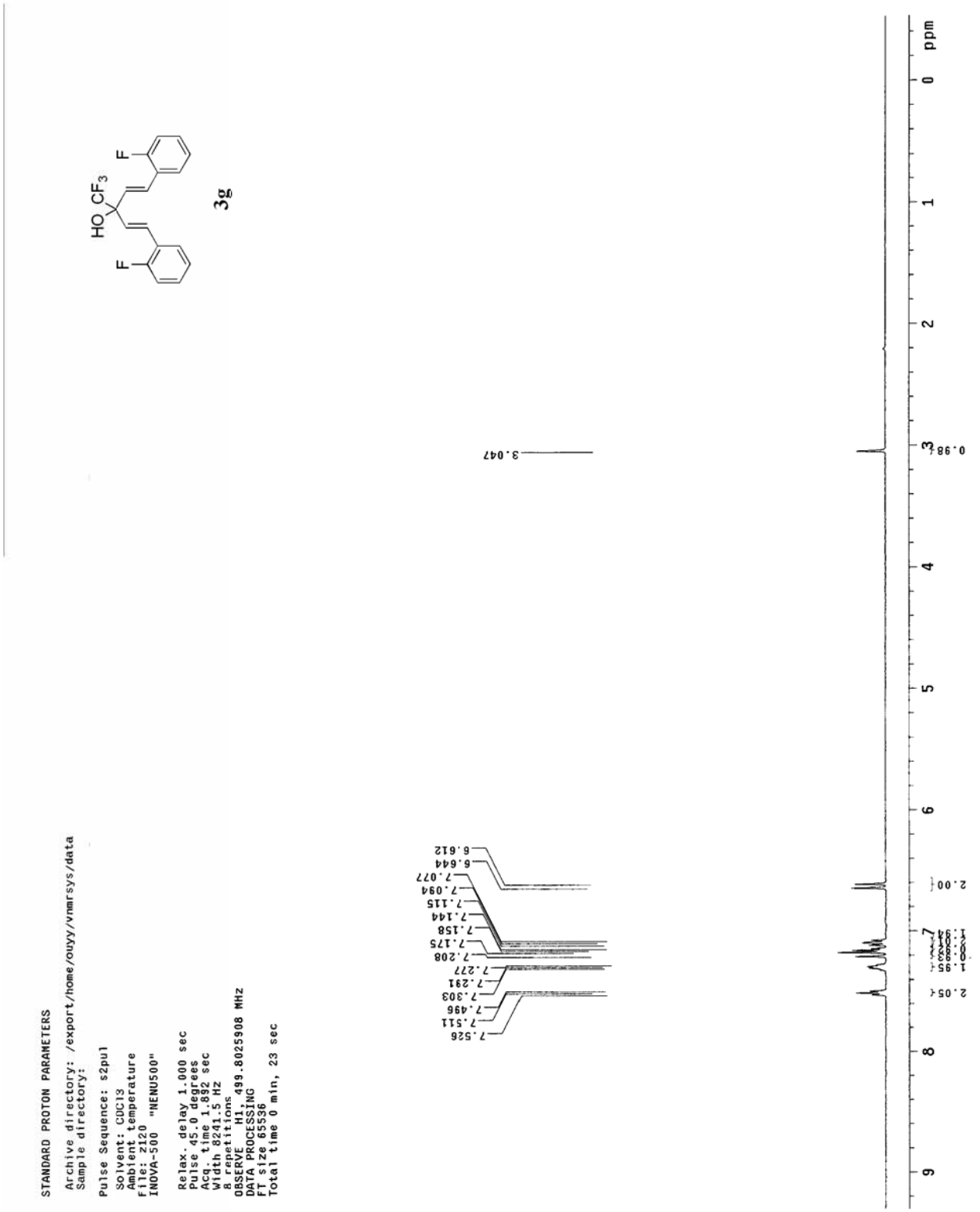


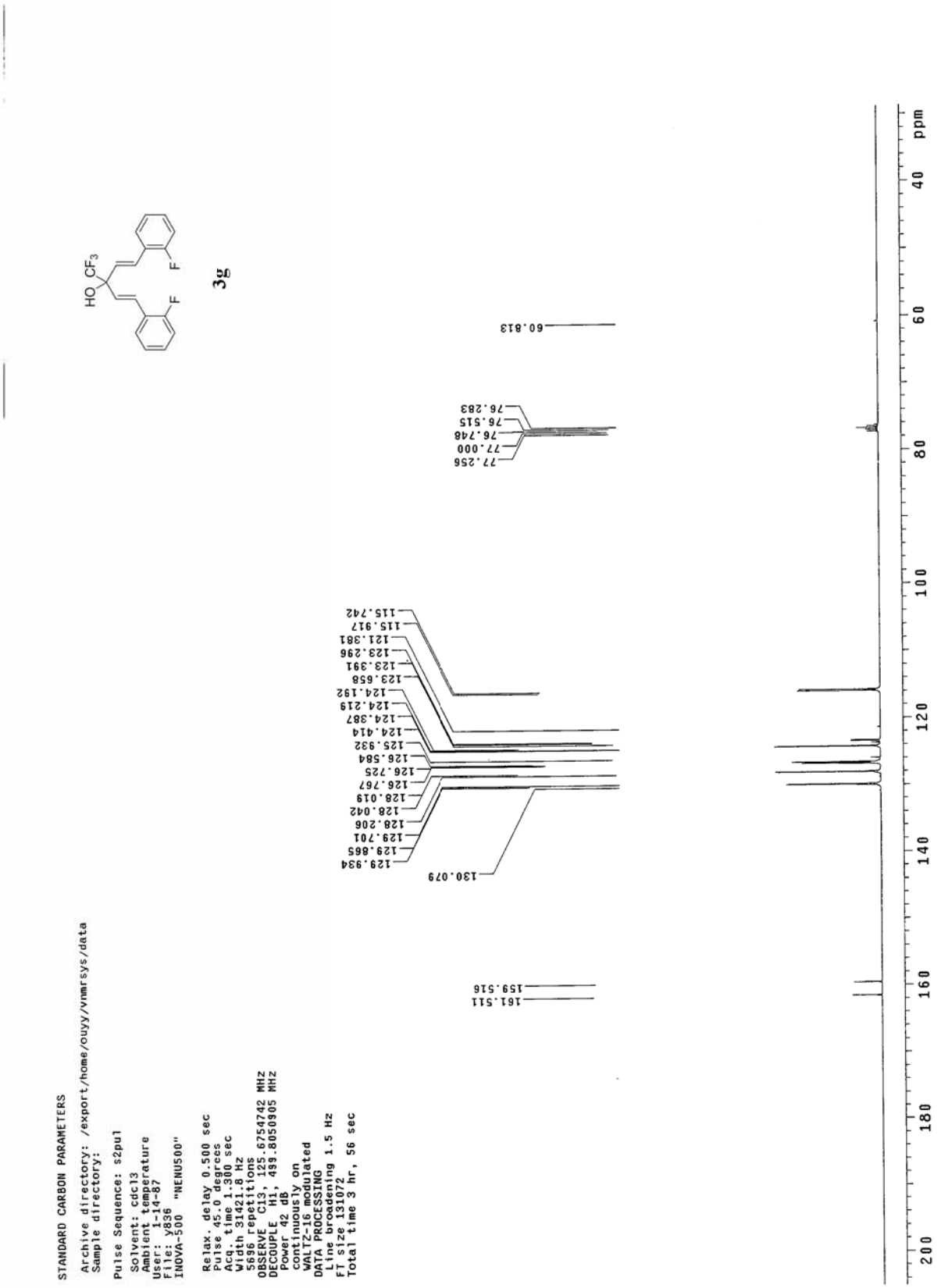


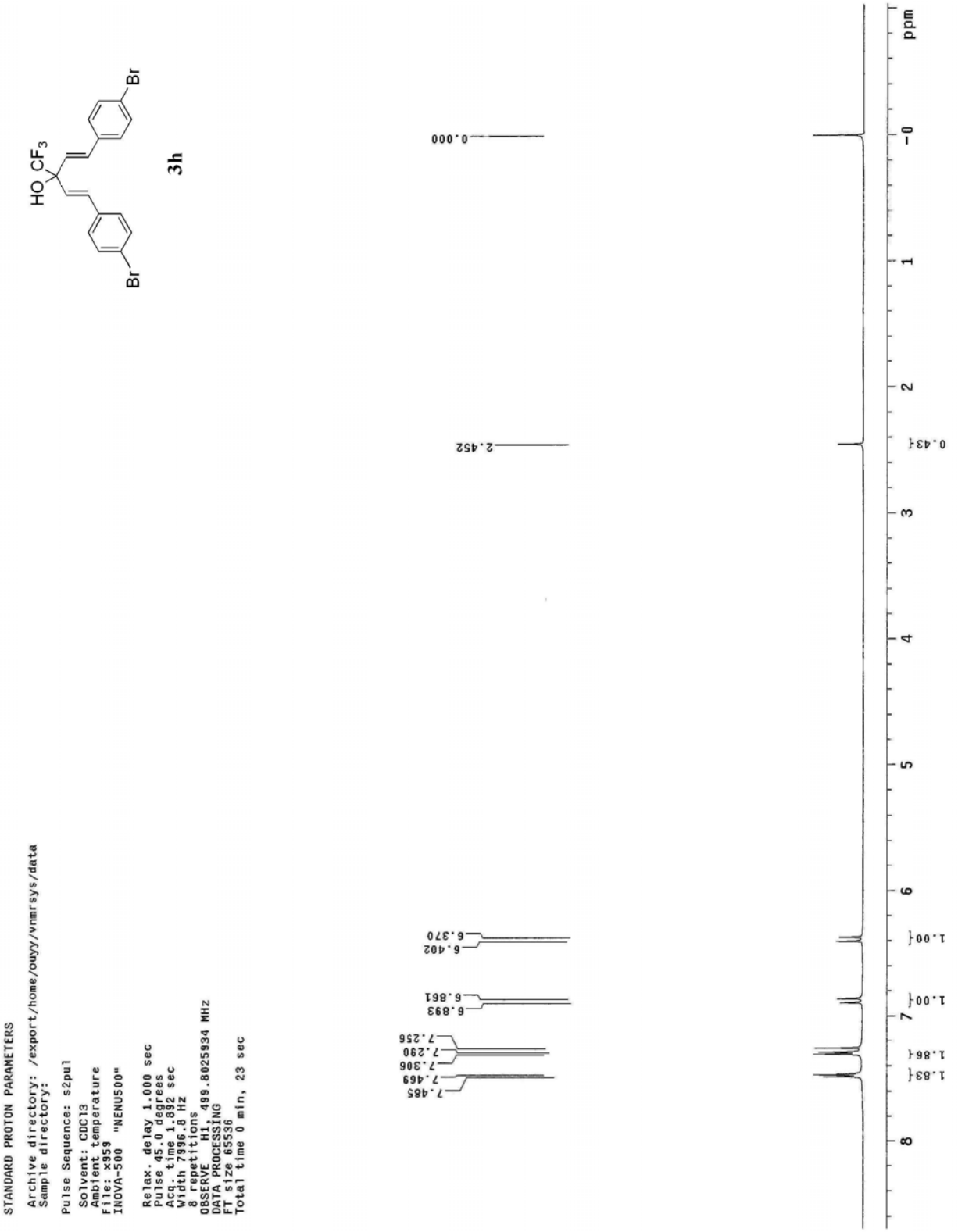


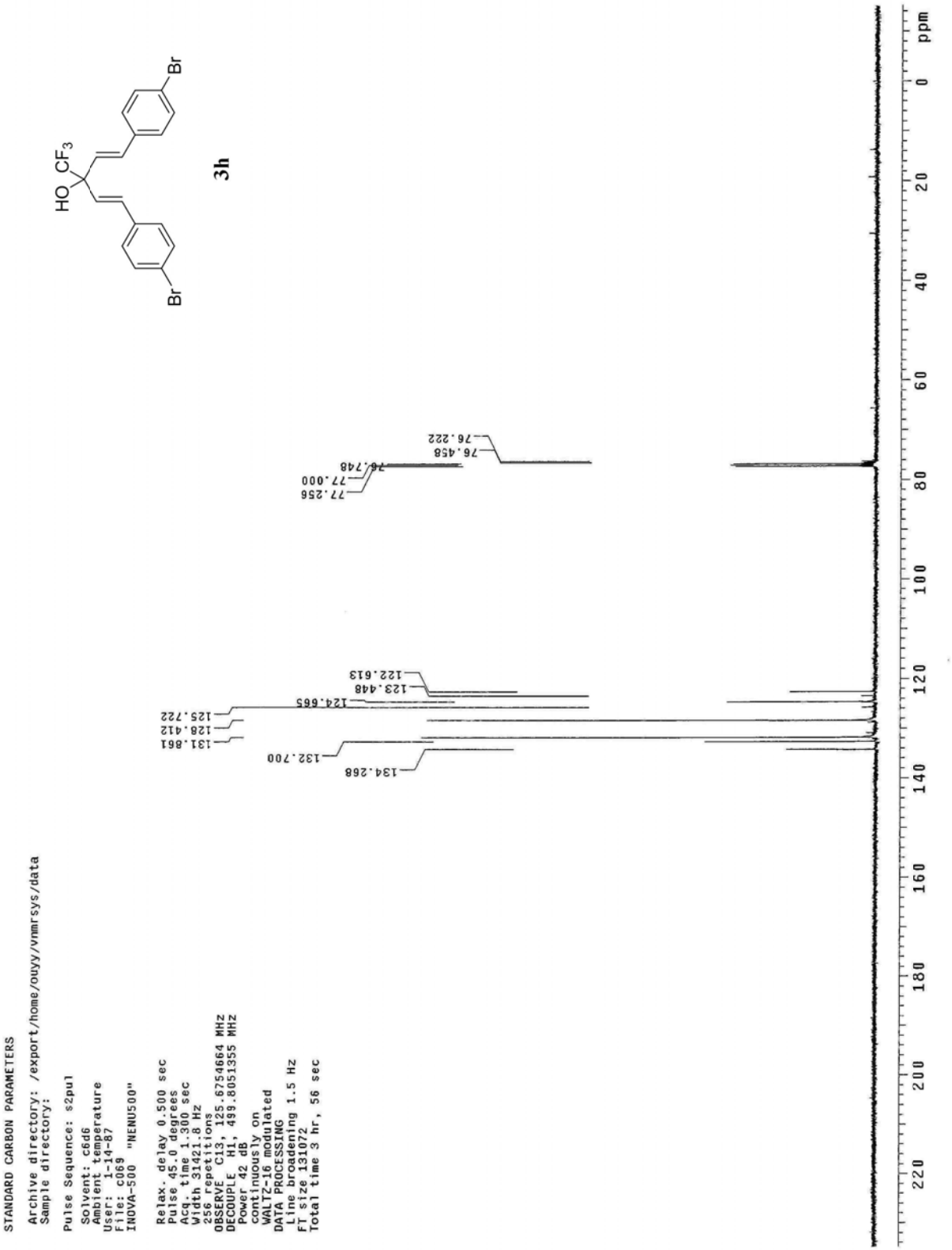

HO
CF3
F
F
3f
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y834
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1, 499.8025243 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
7.575
7.563
7.551
7.284
7.217
7.200
7.185
7.152
6.625
6.593
3.776
ppm
0.99
2.00
1.98
1.93
4.04

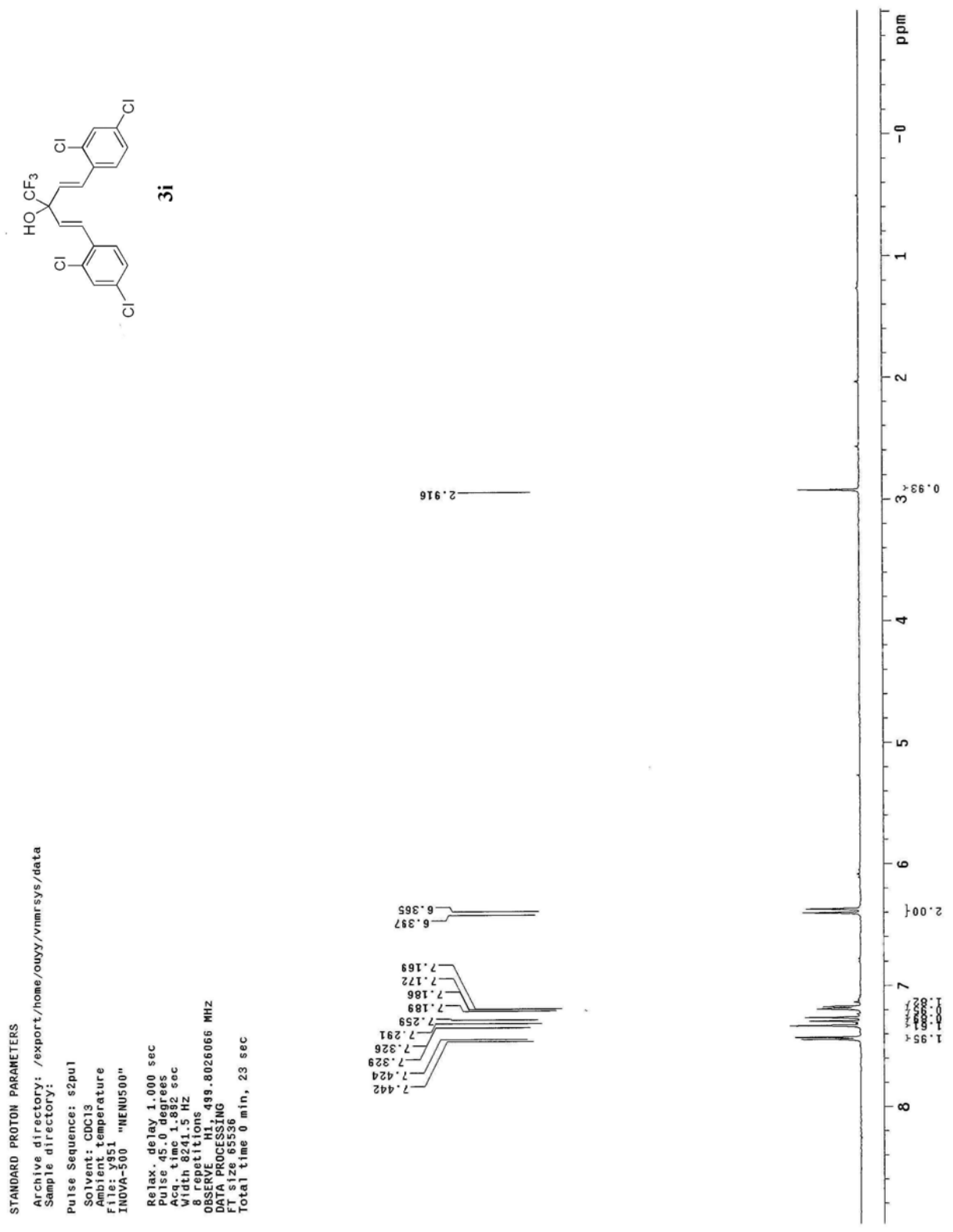


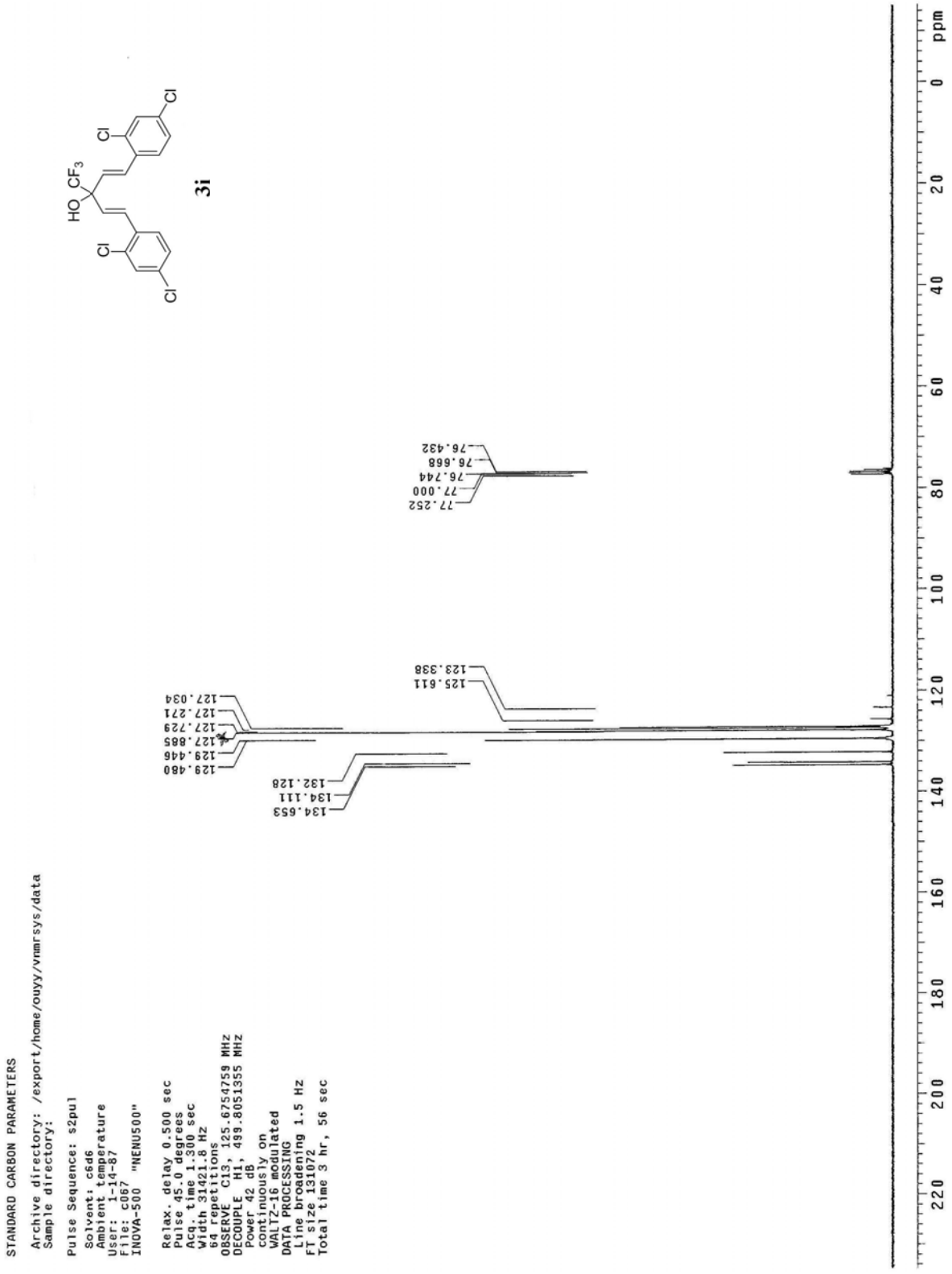

HO CF3
F
F
3g
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: z120
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8241.5 Hz
8 repetitions
OBSERVE H1, 499.8025908 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
7.526
7.511
7.496
7.303
7.291
7.277
7.208
7.175
7.158
7.144
7.115
7.094
7.077
6.644
6.612
3.047
0.98
2.00
1.95
2.05
ppm

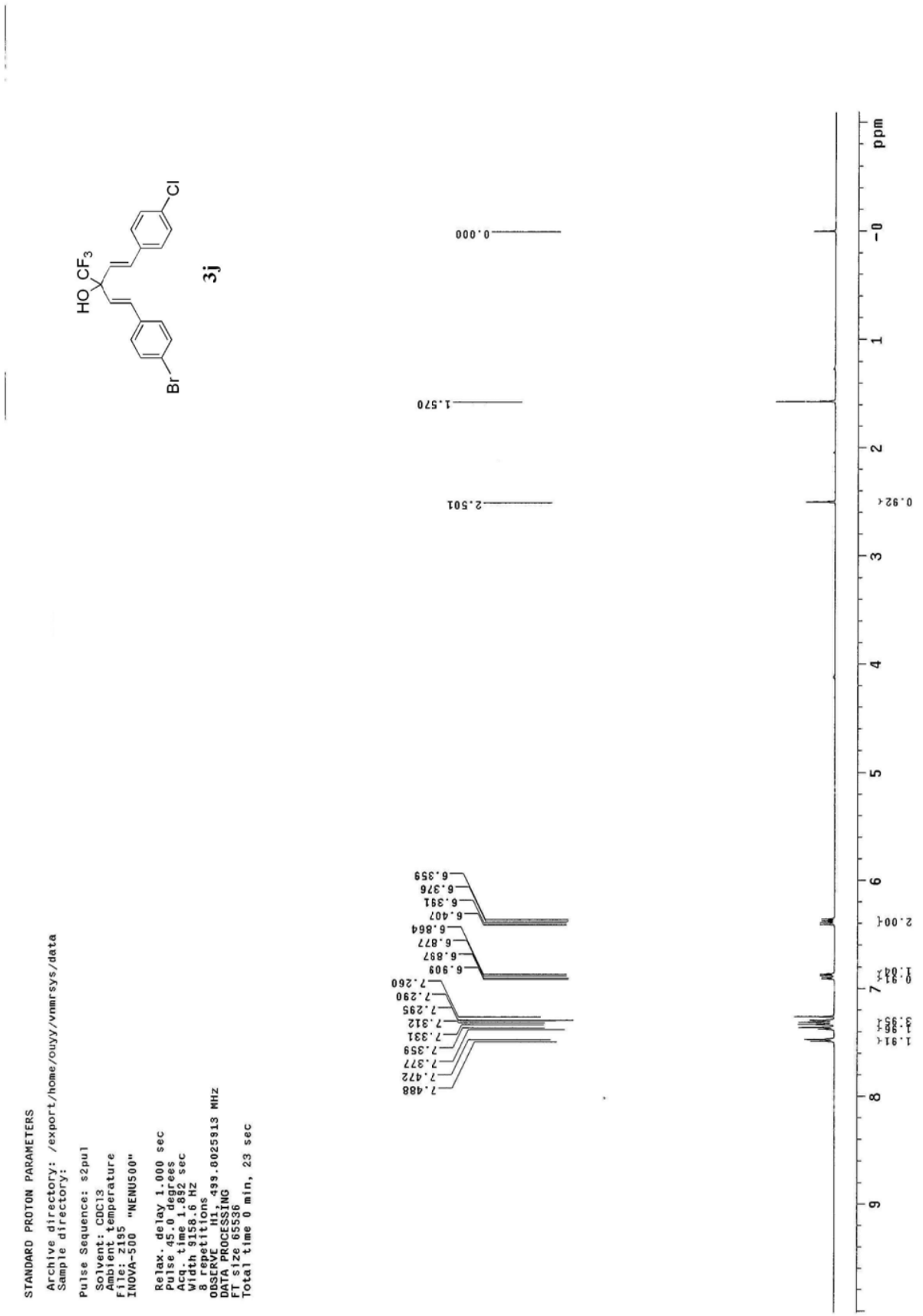

HO
CF3
F
F
3g
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: y836
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
5696 repetitions
OBSERVE C13, 125.6754742 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec
60.813
77.256
77.000
76.748
76.515
76.283
130.079
129.934
129.865
129.701
128.206
128.042
128.019
126.767
126.725
126.584
125.932
124.414
124.387
124.219
124.192
123.658
123.391
123.296
121.381
115.917
115.742
161.511
159.516
200
180
160
140
120
100
80
60
40
ppm

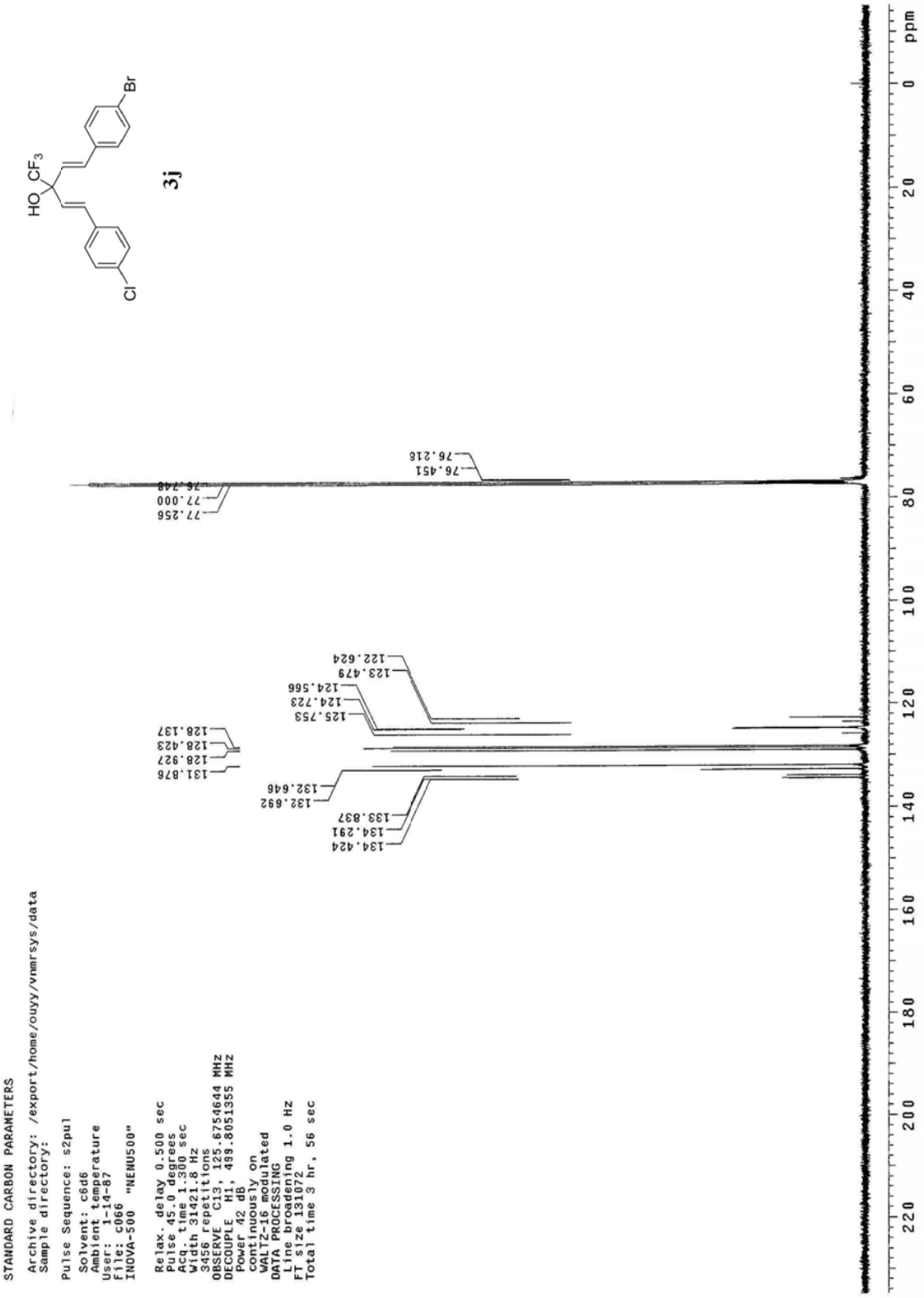


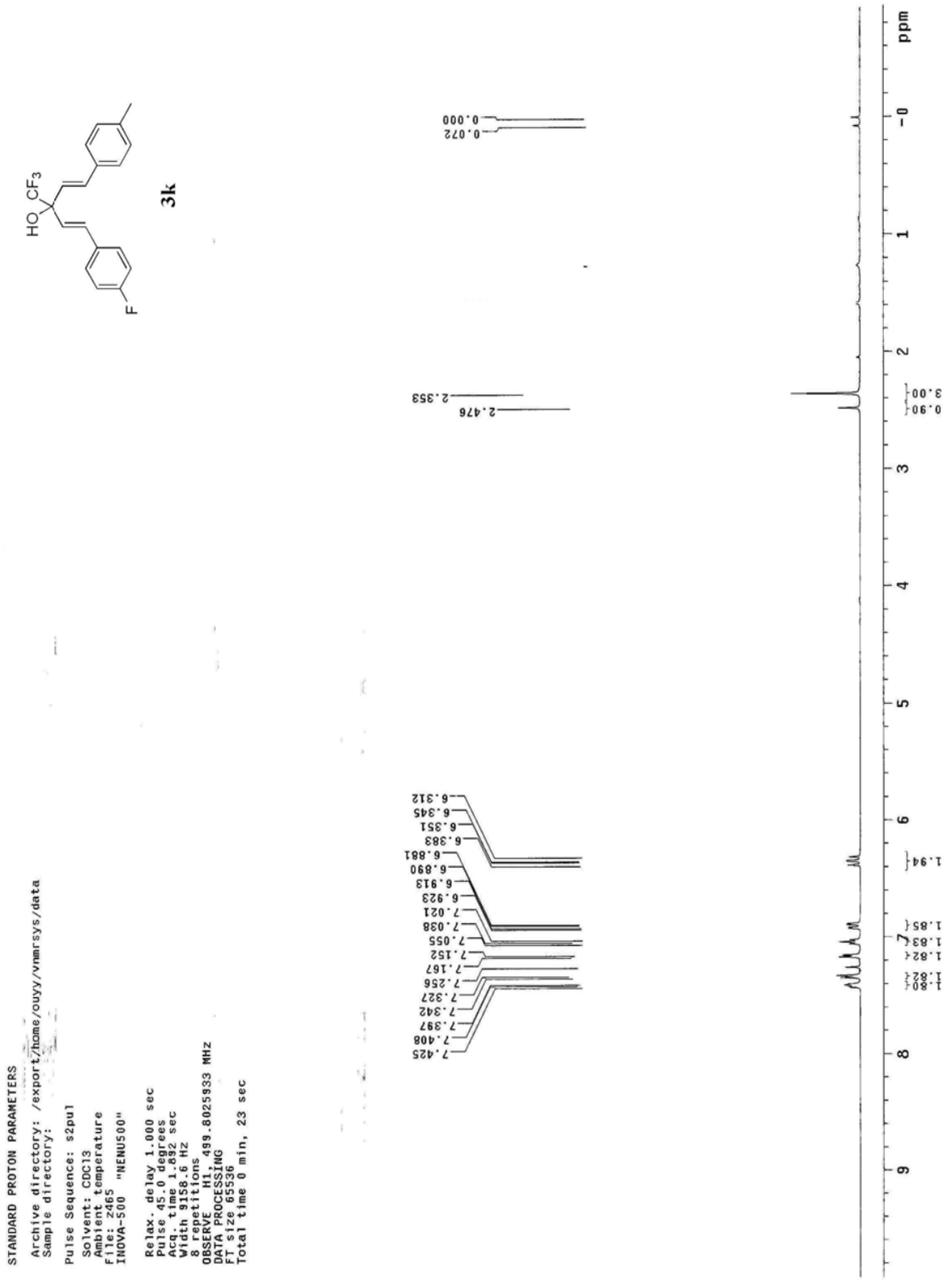


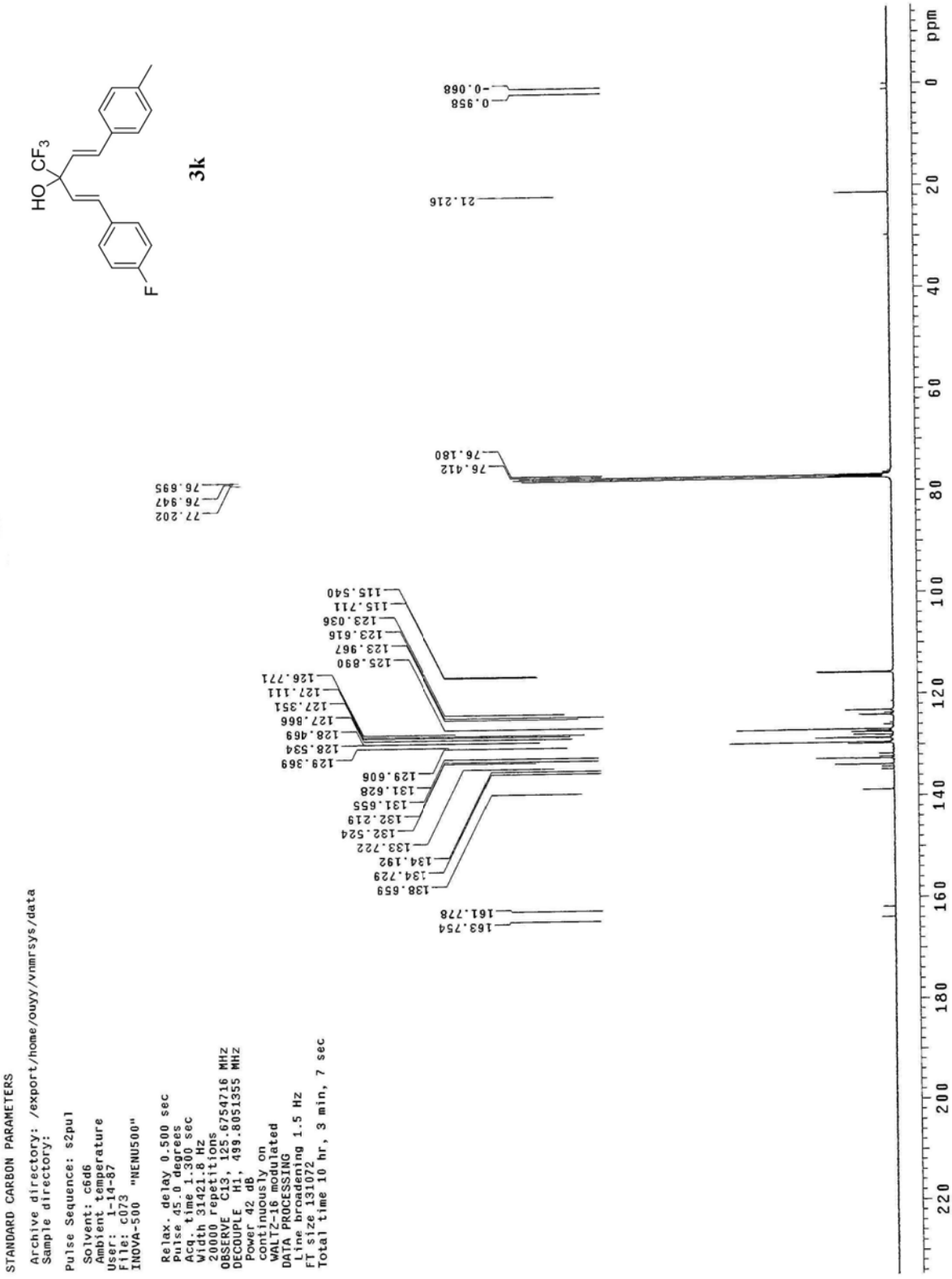

3i
HO
CF3
Cl
Cl
Cl
Cl
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y951 "NENU500"
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8241.5 Hz
8 repetitions
OBSERVE H1, 499.8026066 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
2.916
6.397
6.365
7.442
7.424
7.329
7.326
7.291
7.259
7.189
7.186
7.172
7.169
0.93
2.00
1.95
ppm




HO
CF3
Cl
Br
3j
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: z195
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9158.6 Hz
8 repetitions
OBSERVE H1, 499.8025913 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
0.000
1.570
2.501
6.359
6.376
6.391
6.407
6.864
6.877
6.897
6.909
7.260
7.290
7.295
7.312
7.331
7.359
7.377
7.472
7.488
ppm





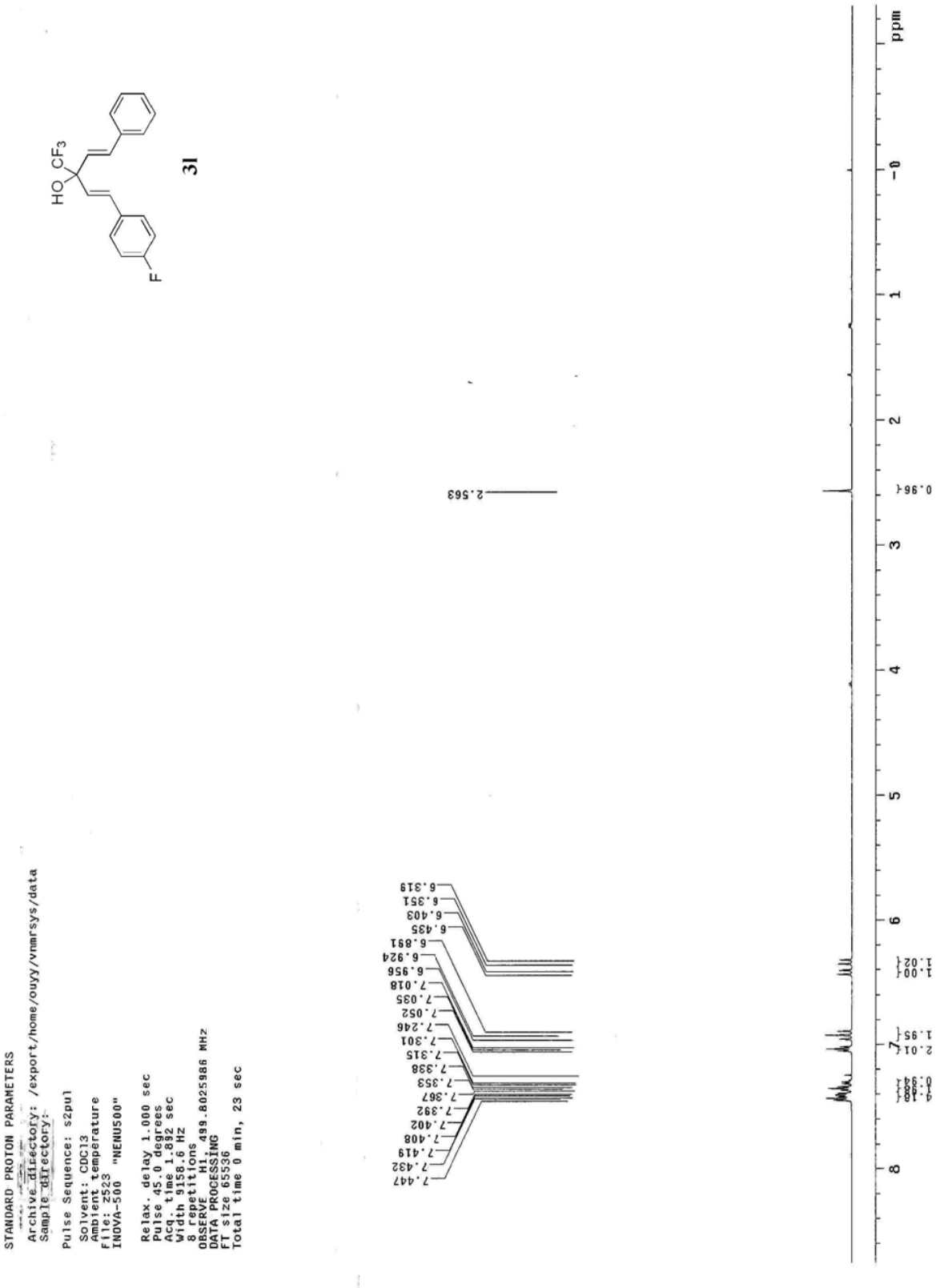


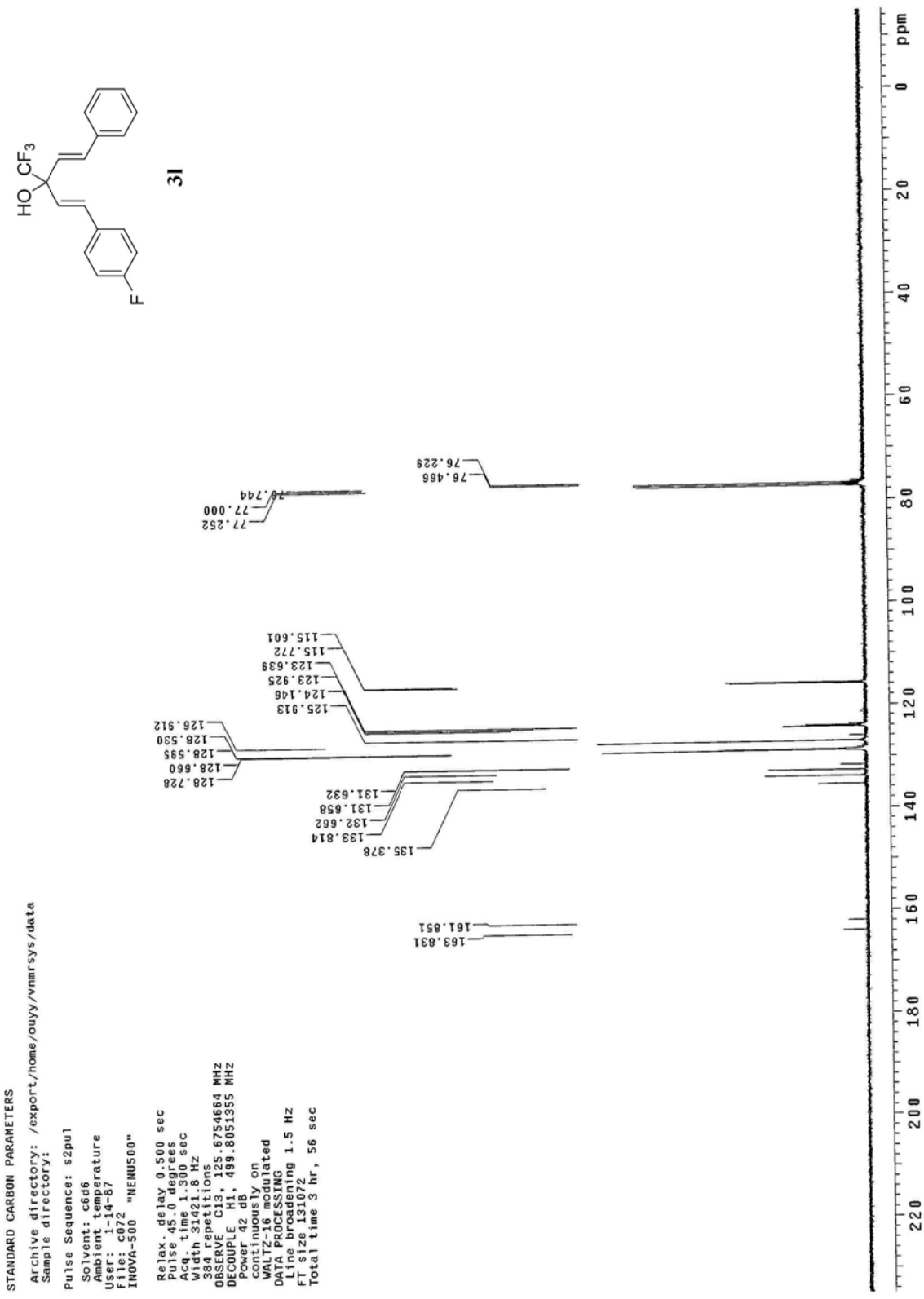
STANDARD CARBON PARAMETERS

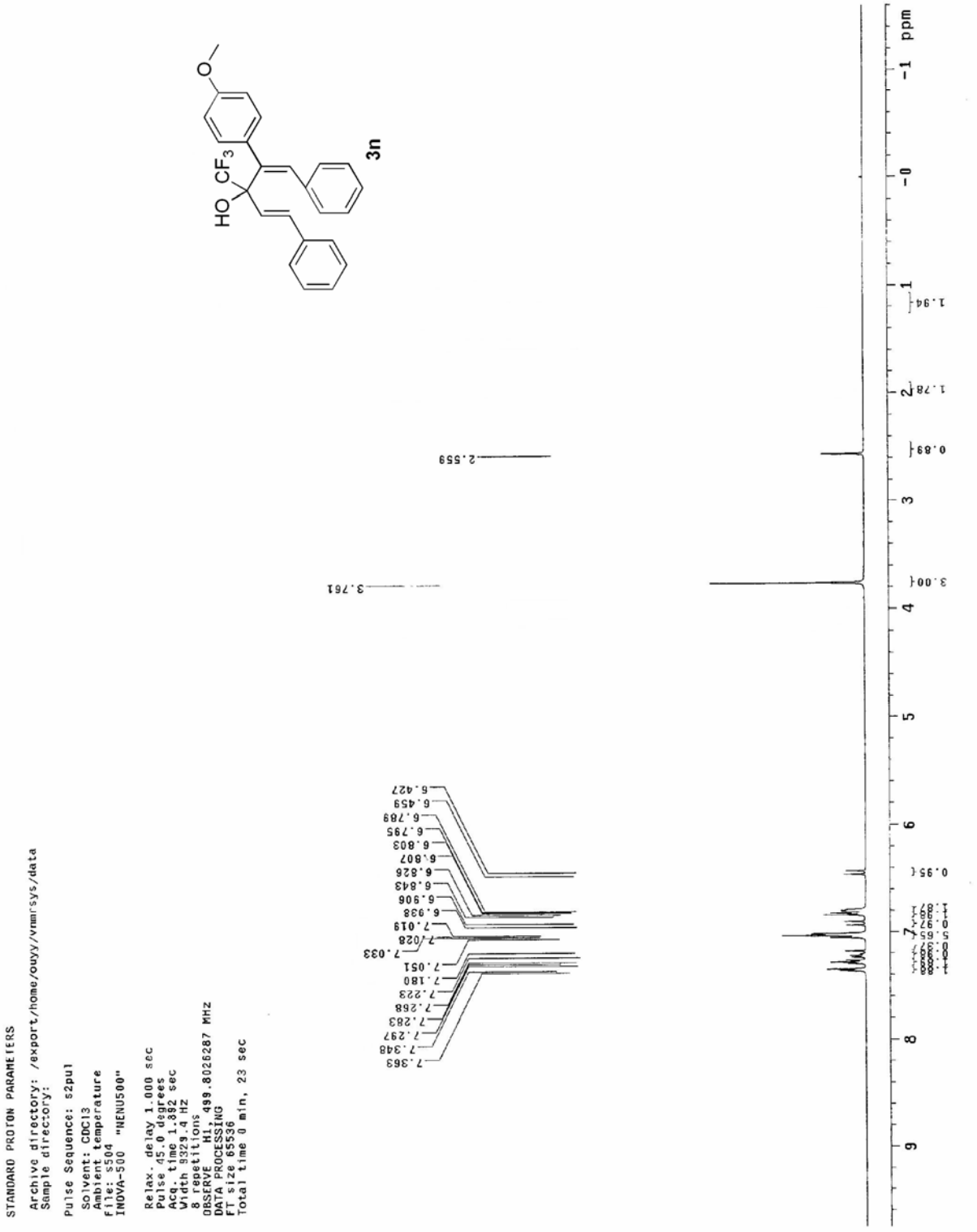
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

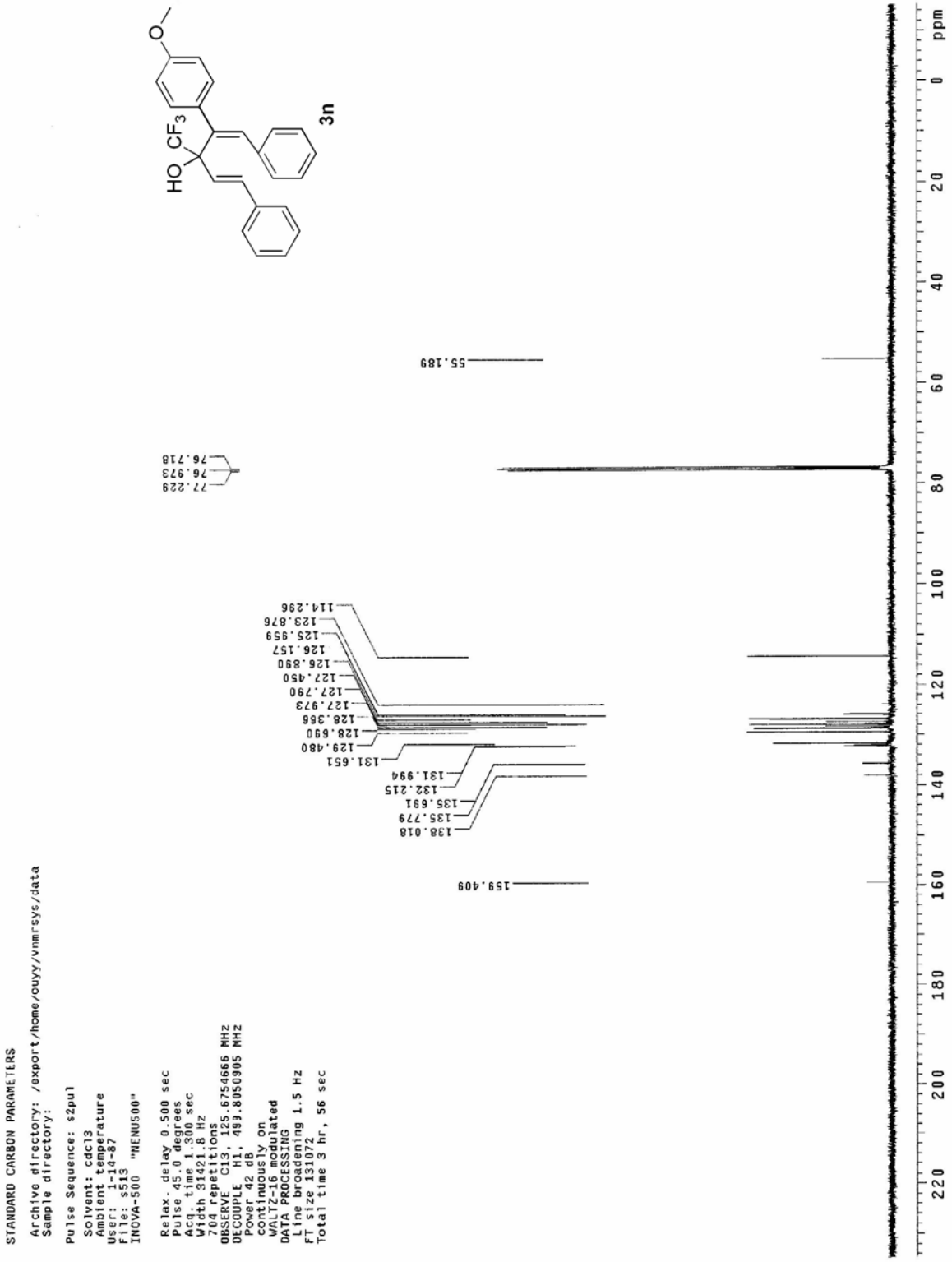
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: 1-14-87
File: c073 "NENU500"
INOVA-500

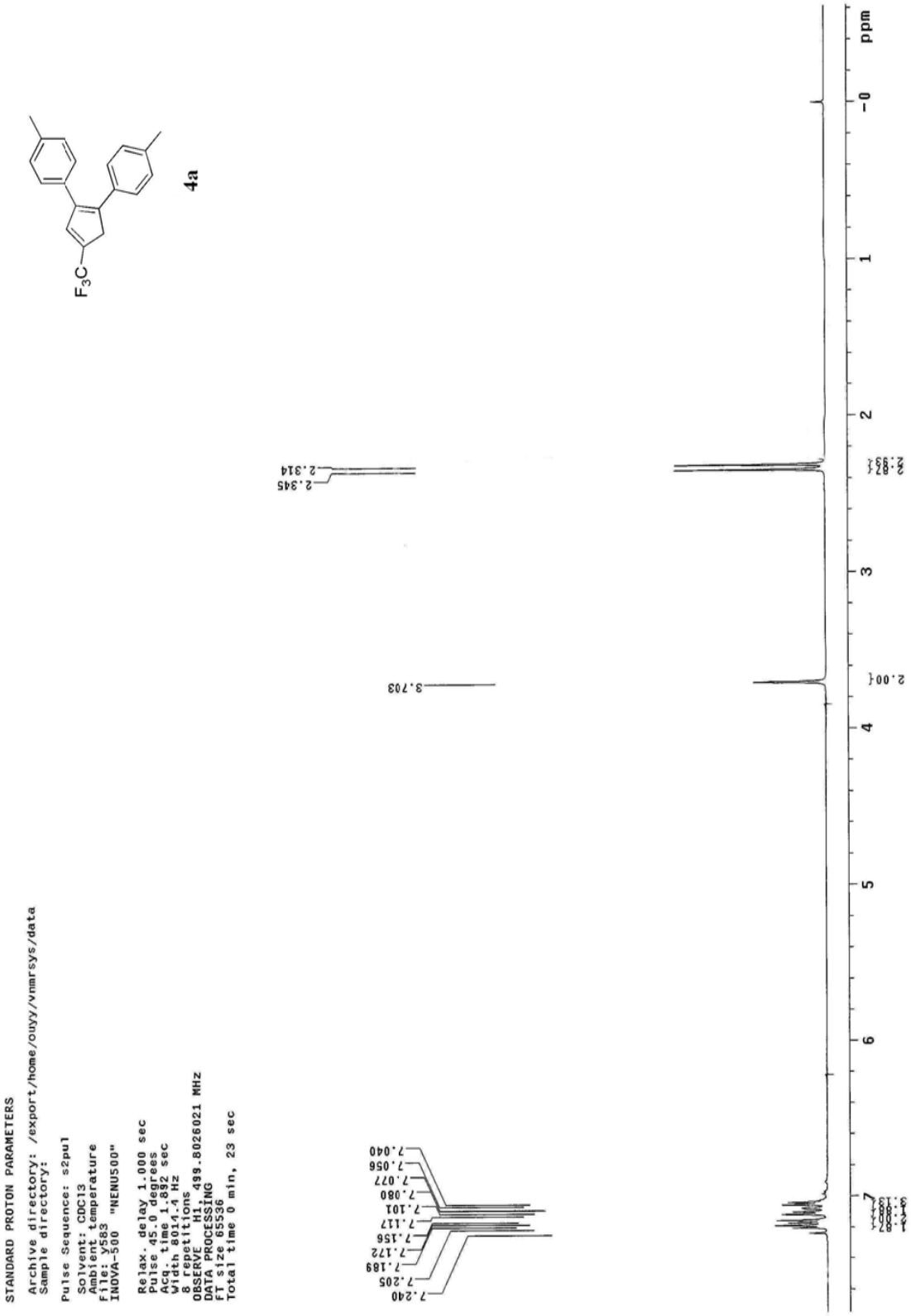
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
20000 repetitions
OBSERVE C13, 125.6754716 MHz
DECOUPLE H1, 499.8051355 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 10 hr, 3 min, 7 sec

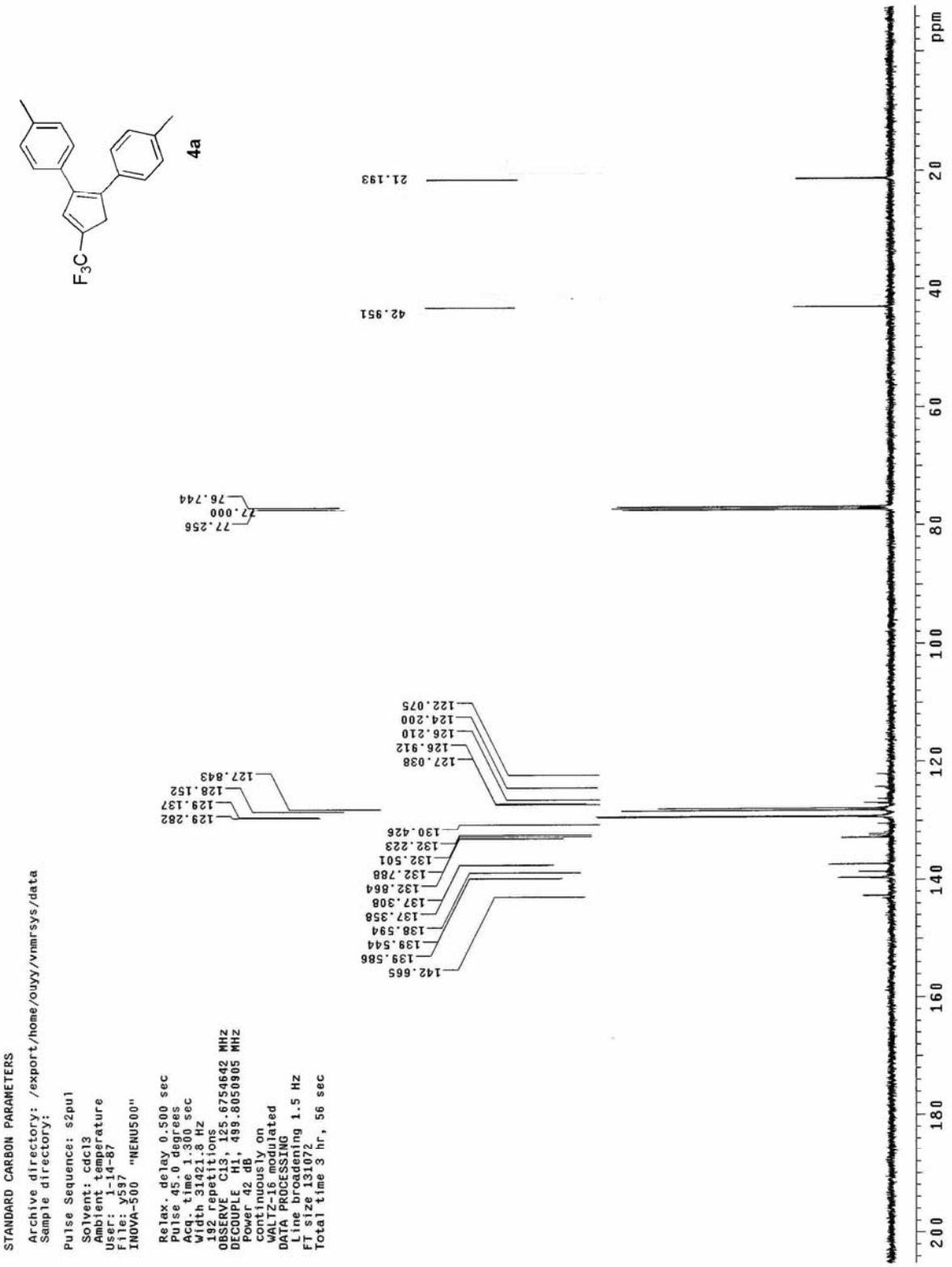

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: Z523
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 9158.6 Hz
8 repetitions
OBSERVE H1 499.8025986 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
HO
CF3
F
3l
2.563
7.447
7.432
7.419
7.408
7.402
7.392
7.367
7.353
7.338
7.315
7.301
7.246
7.052
7.035
7.018
6.956
6.924
6.891
6.435
6.403
6.351
6.319
ppm

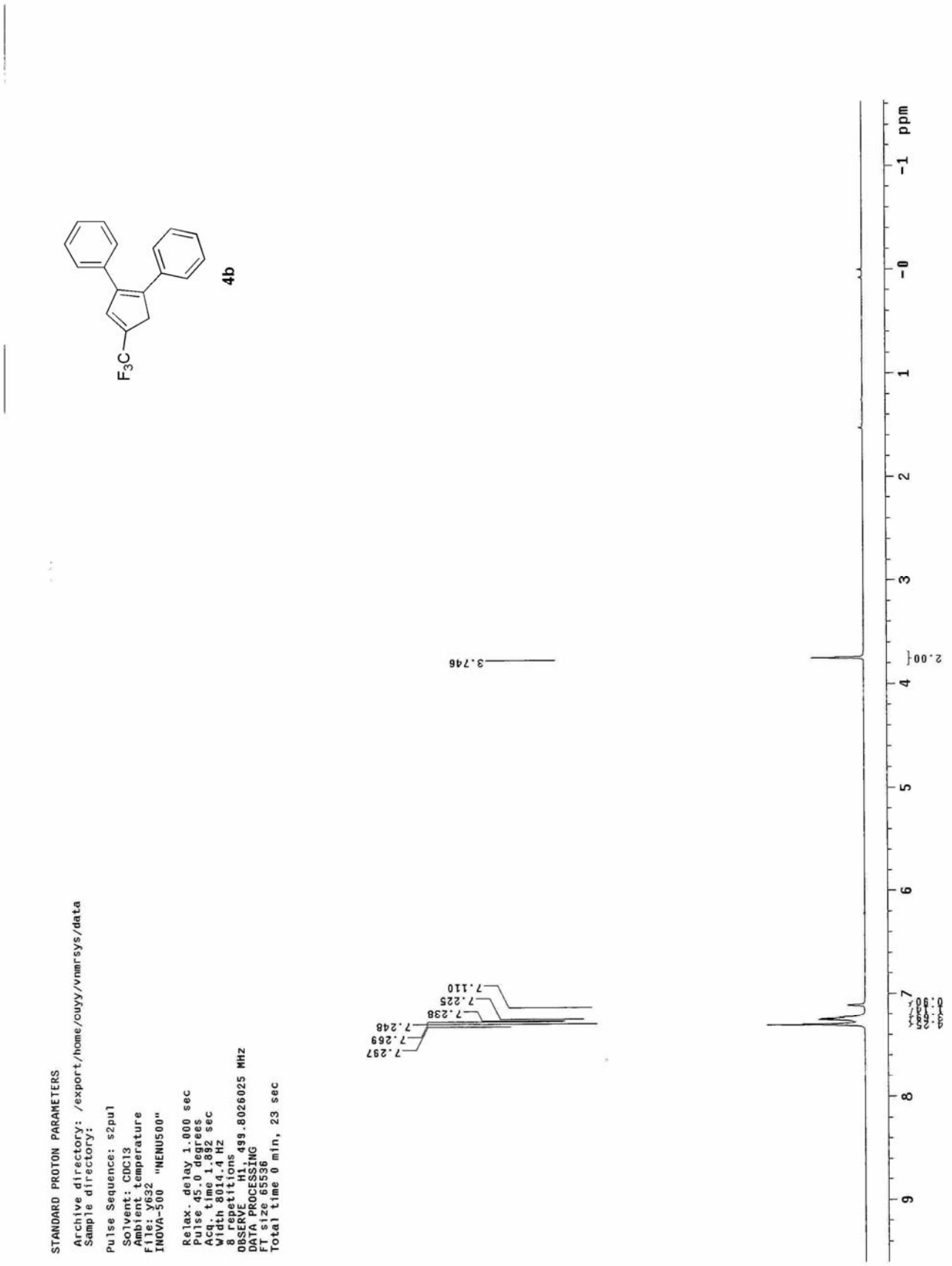

3l
HO
CF3
F
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: 1-14-87
File: c072 "NENU500"
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6754664 MHz
DECOUPLE H1, 499.8051355 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec
76.229
76.466
76.744
77.000
77.252
115.601
115.772
123.639
123.925
124.146
125.913
126.912
128.530
128.595
128.660
128.728
131.632
131.658
132.662
133.814
135.378
161.851
163.831
ppm

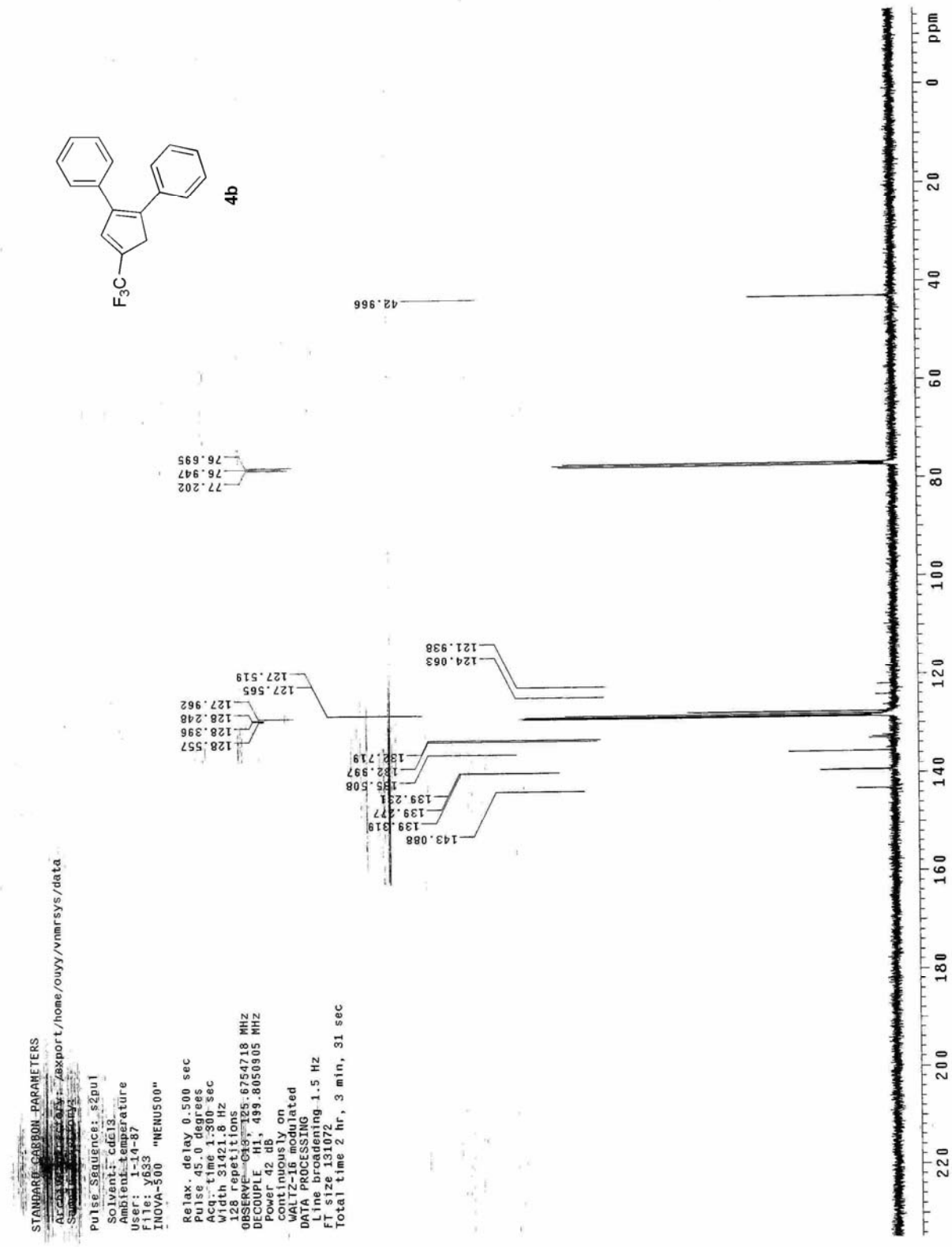


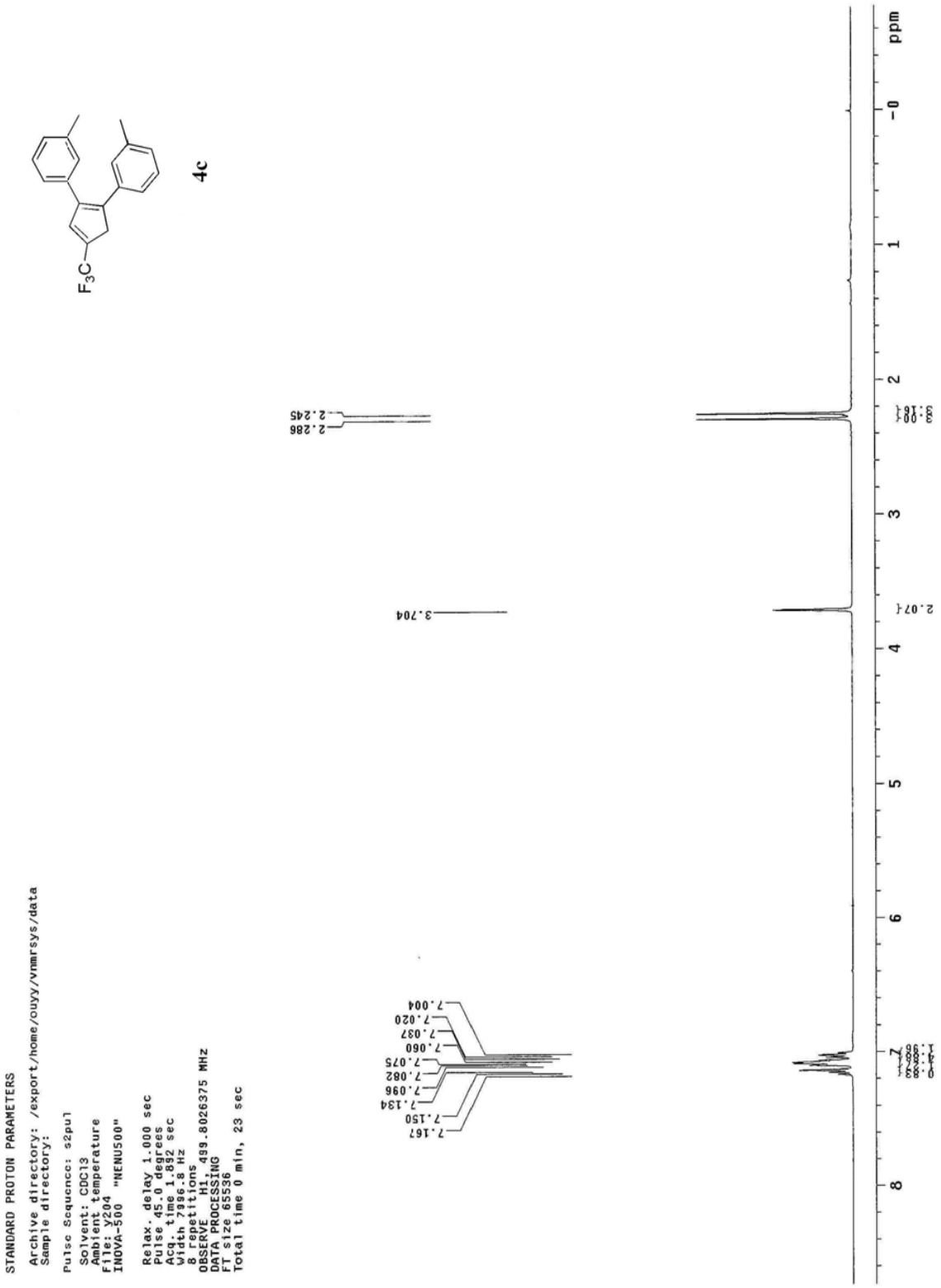


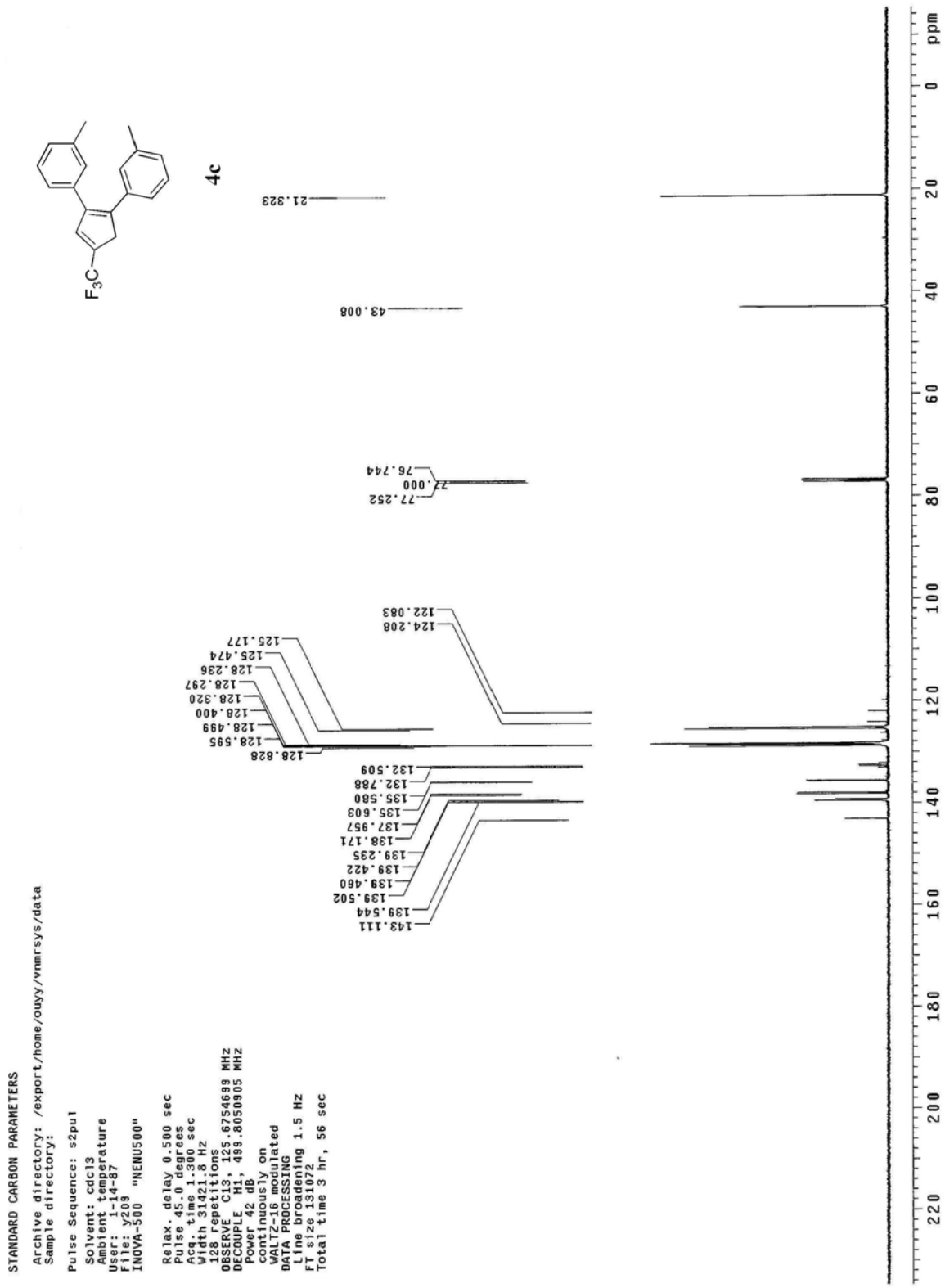

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y583 "NENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1, 499.8026021 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
F3C
4a
2.345
2.314
3.703
7.240
7.205
7.189
7.172
7.156
7.117
7.101
7.080
7.077
7.056
7.040
2.884
2.001
ppm

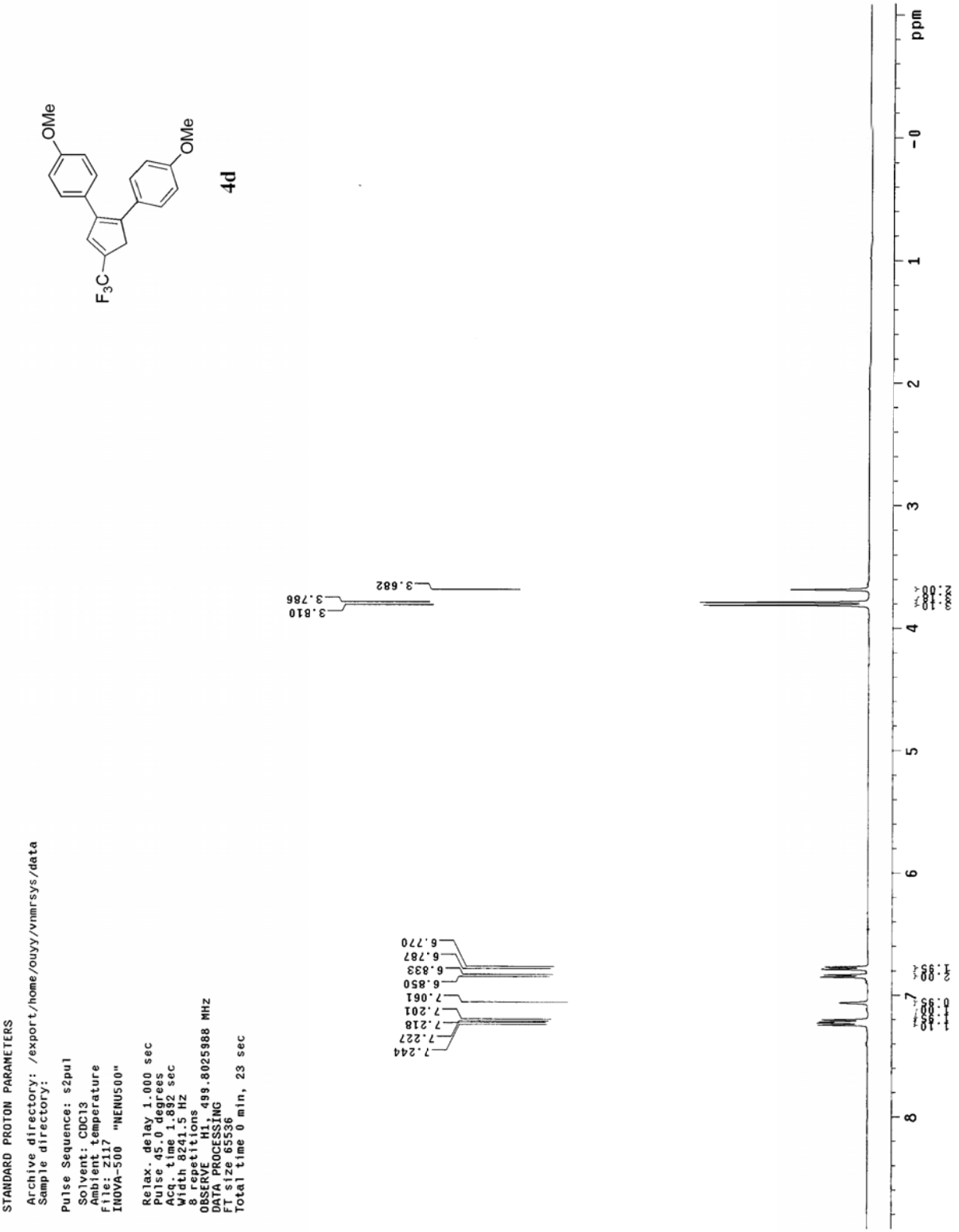


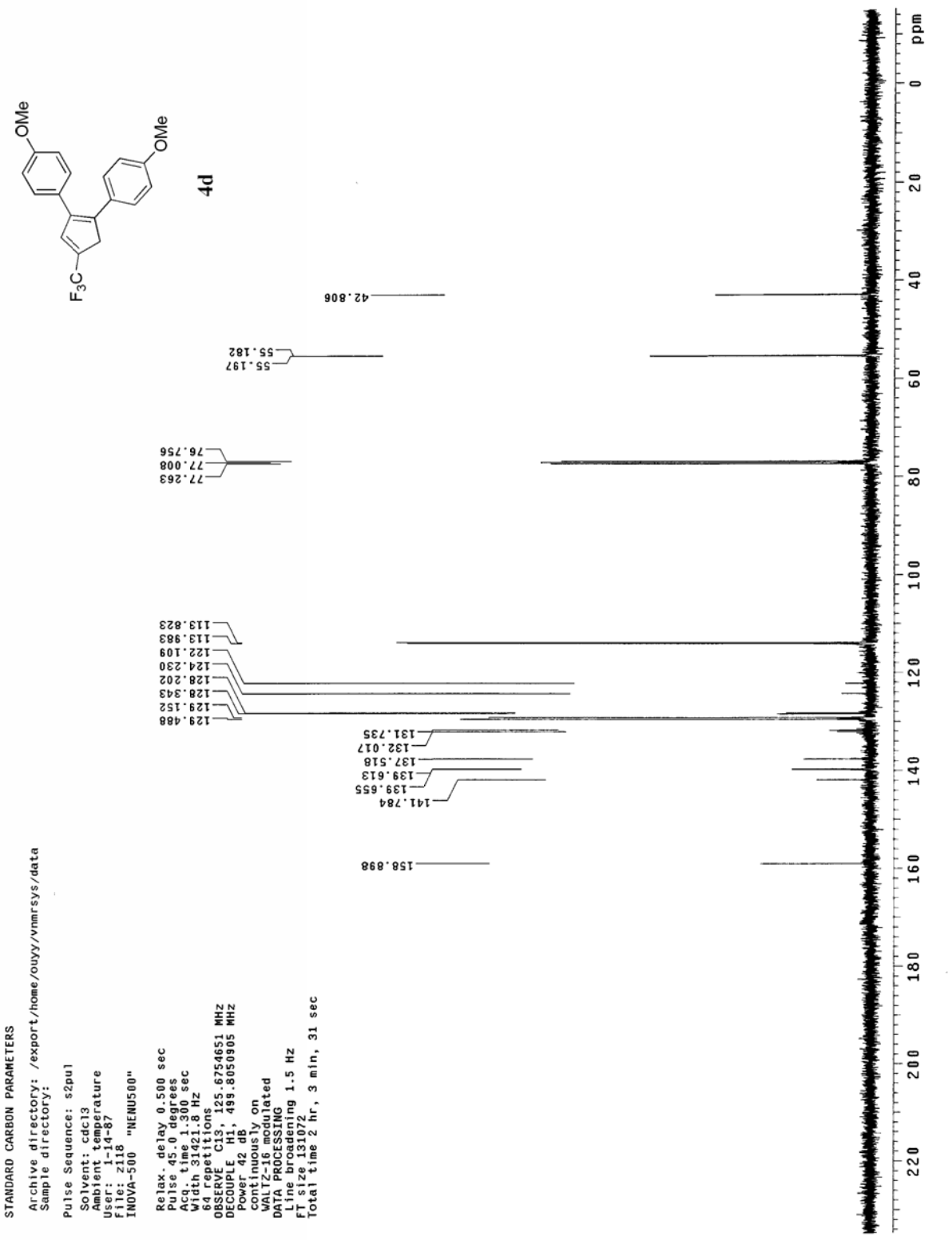

4b
F3C
STANDARD PROTON PARAMETERS
Archive directory: /export/home/cuyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y632
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1, 499.8026025 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
8.746
7.297
7.269
7.248
7.238
7.225
7.110
2.00
ppm

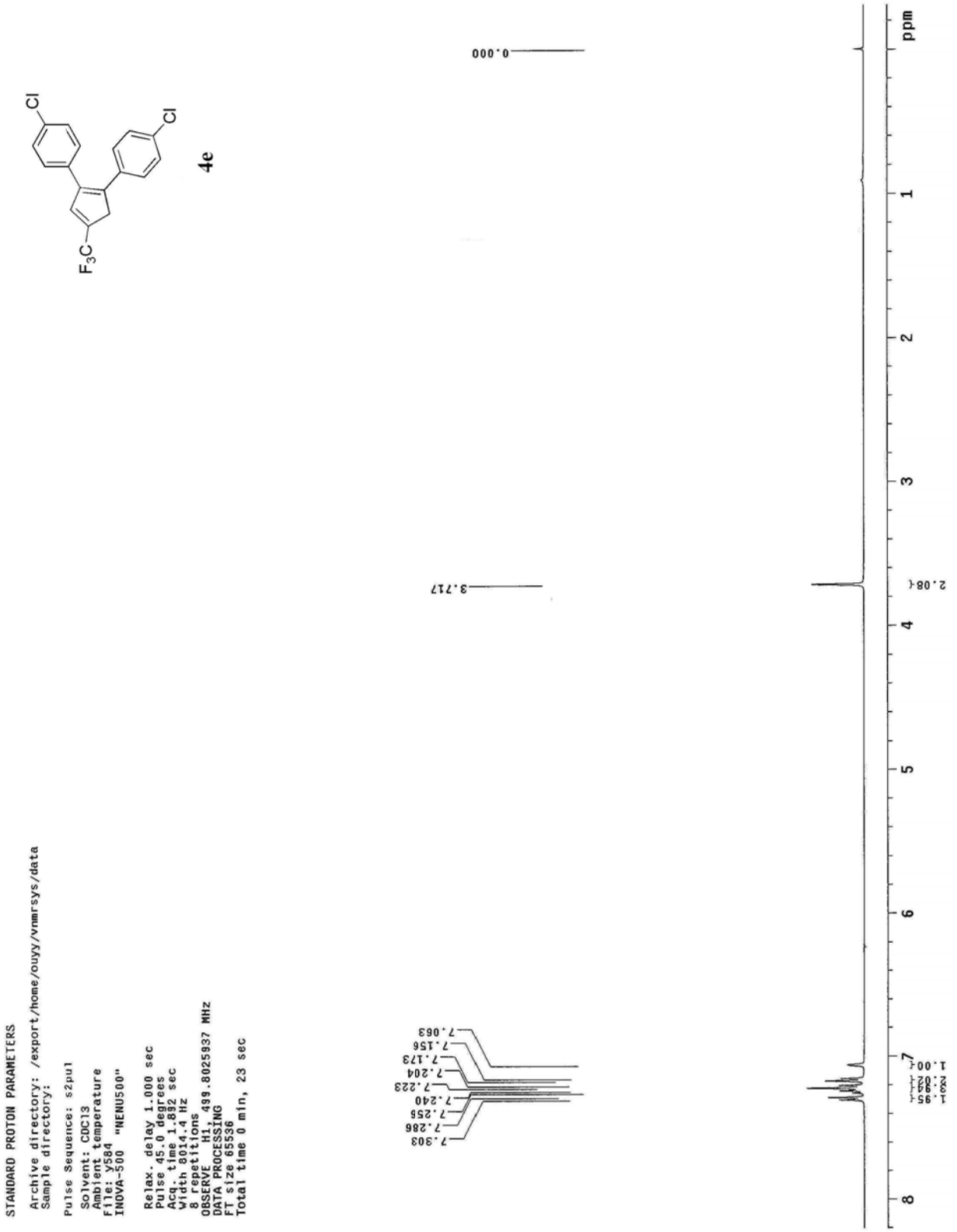


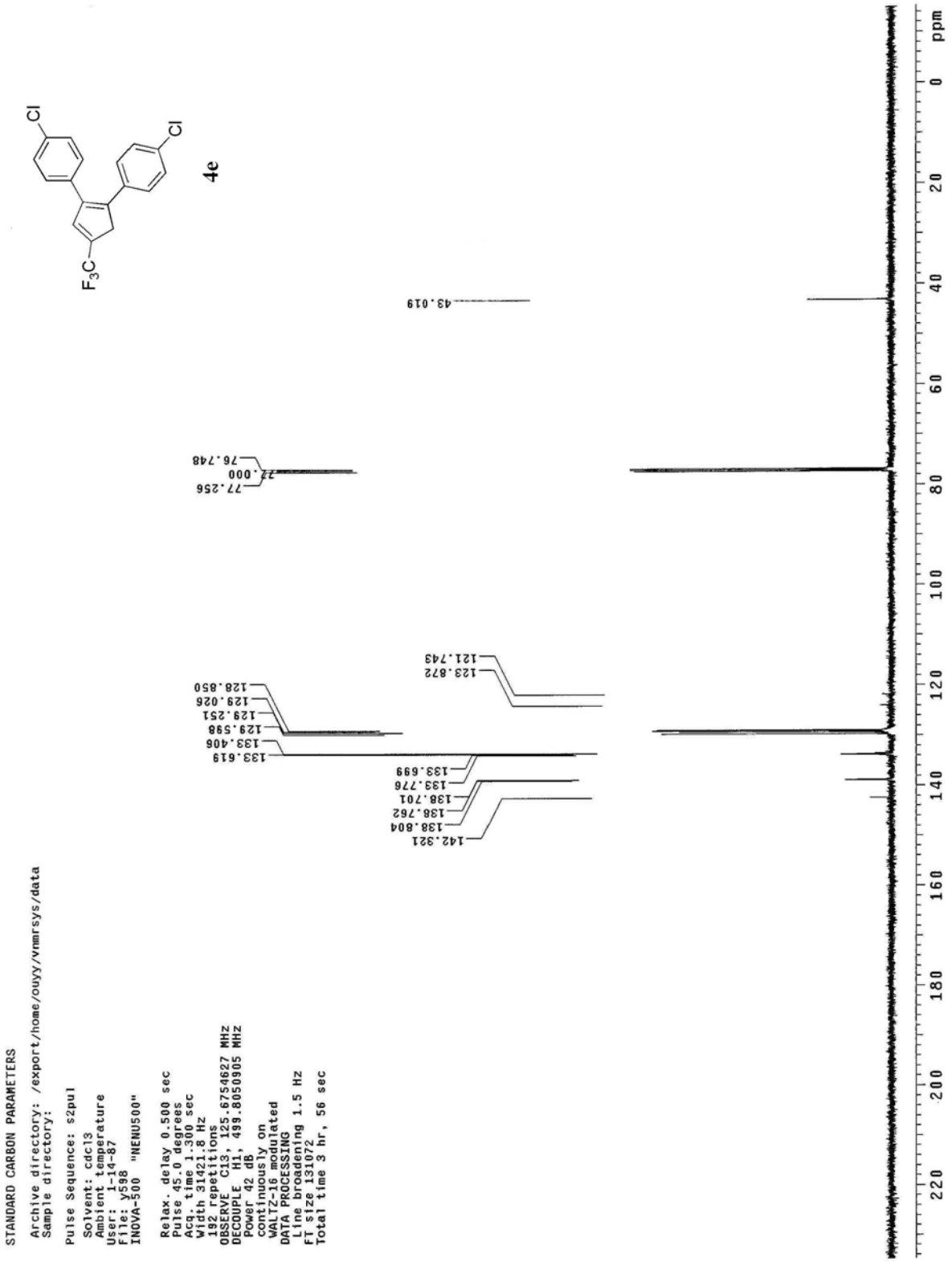

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y204
INOVA-500 "MENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 7996.8 Hz
8 repetitions
OBSERVE H1, 499.8026375 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
F3C
4c
2.286
2.245
3.704
7.167
7.150
7.134
7.096
7.082
7.075
7.060
7.037
7.020
7.004
2.074
ppm

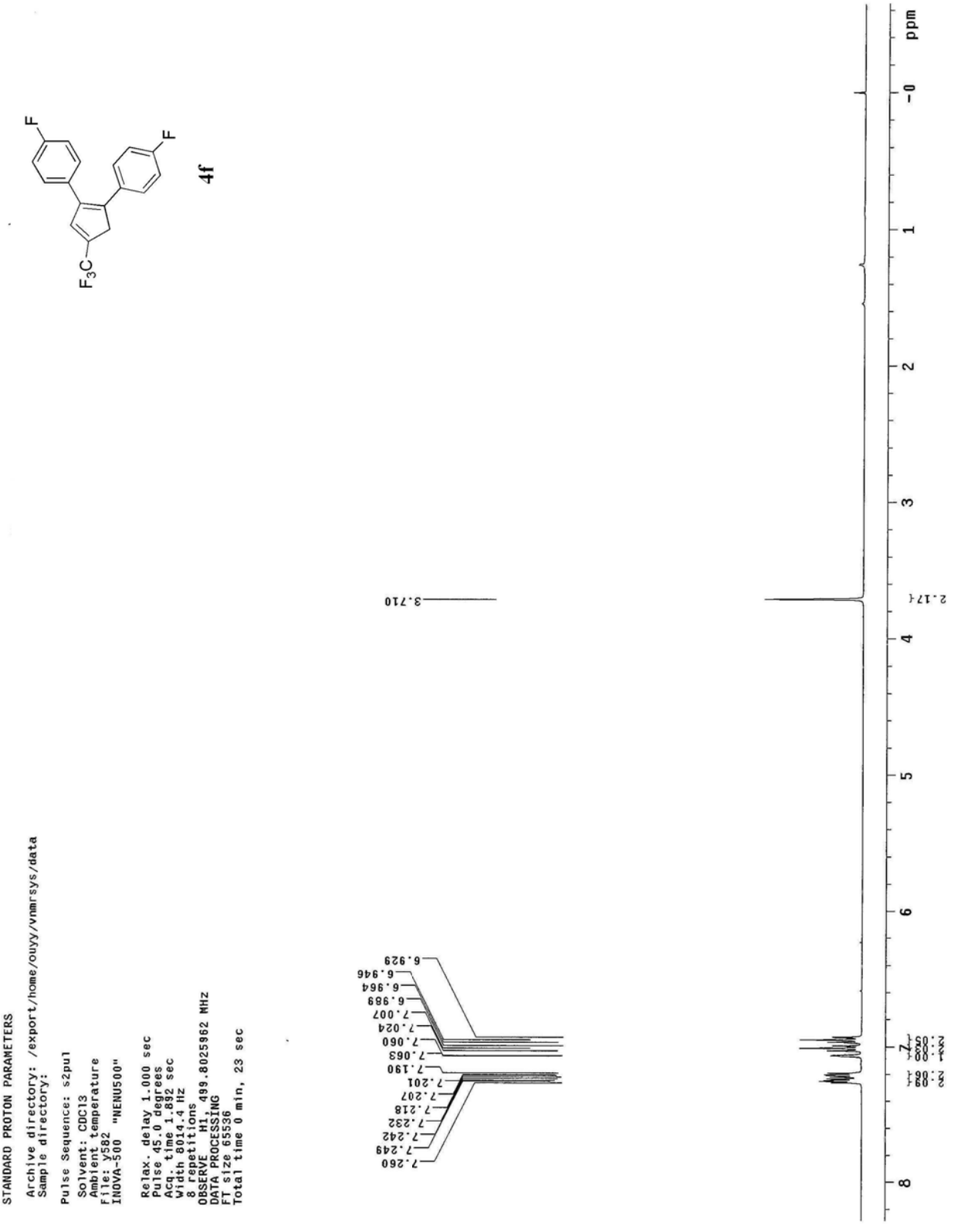


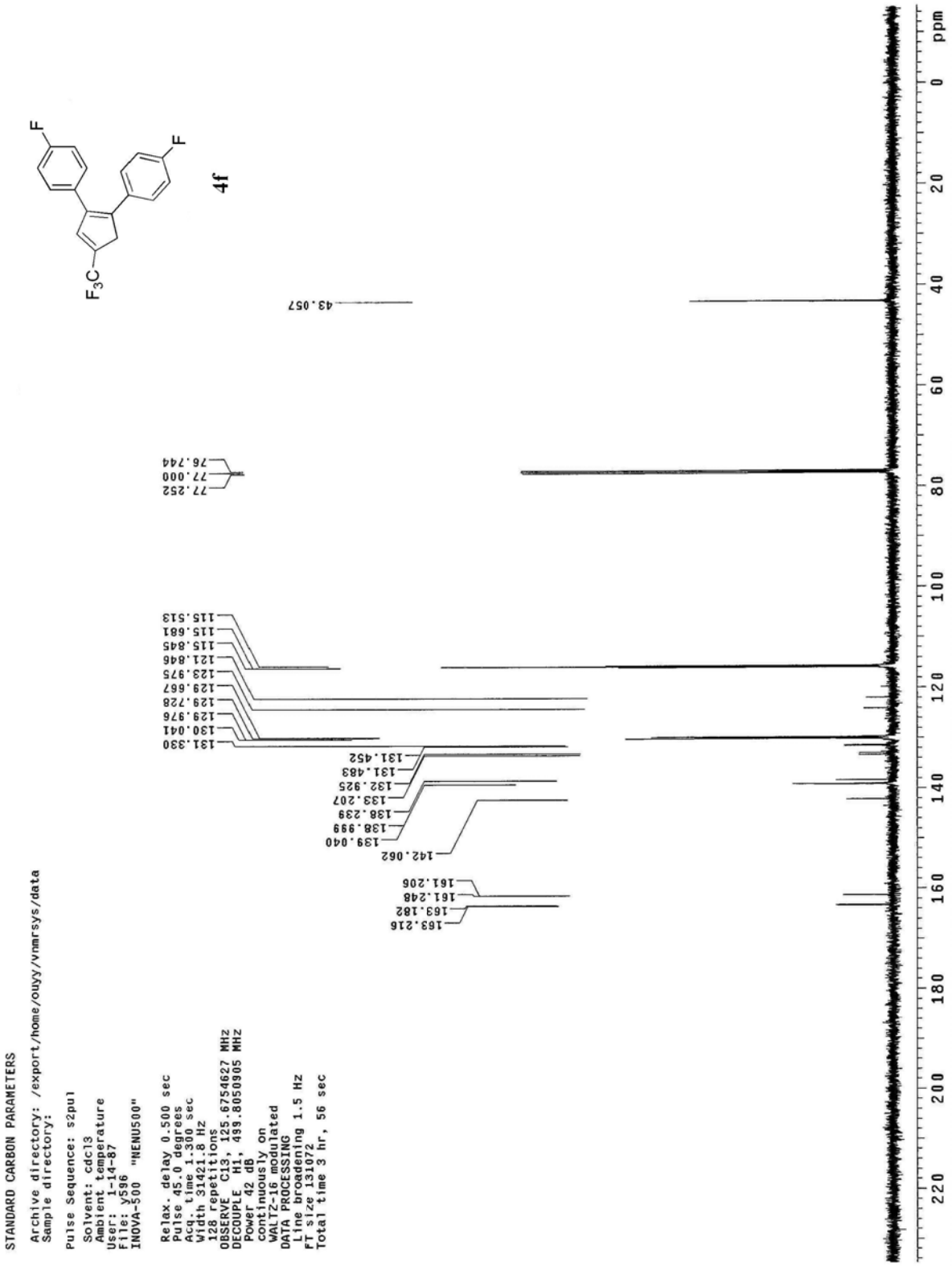


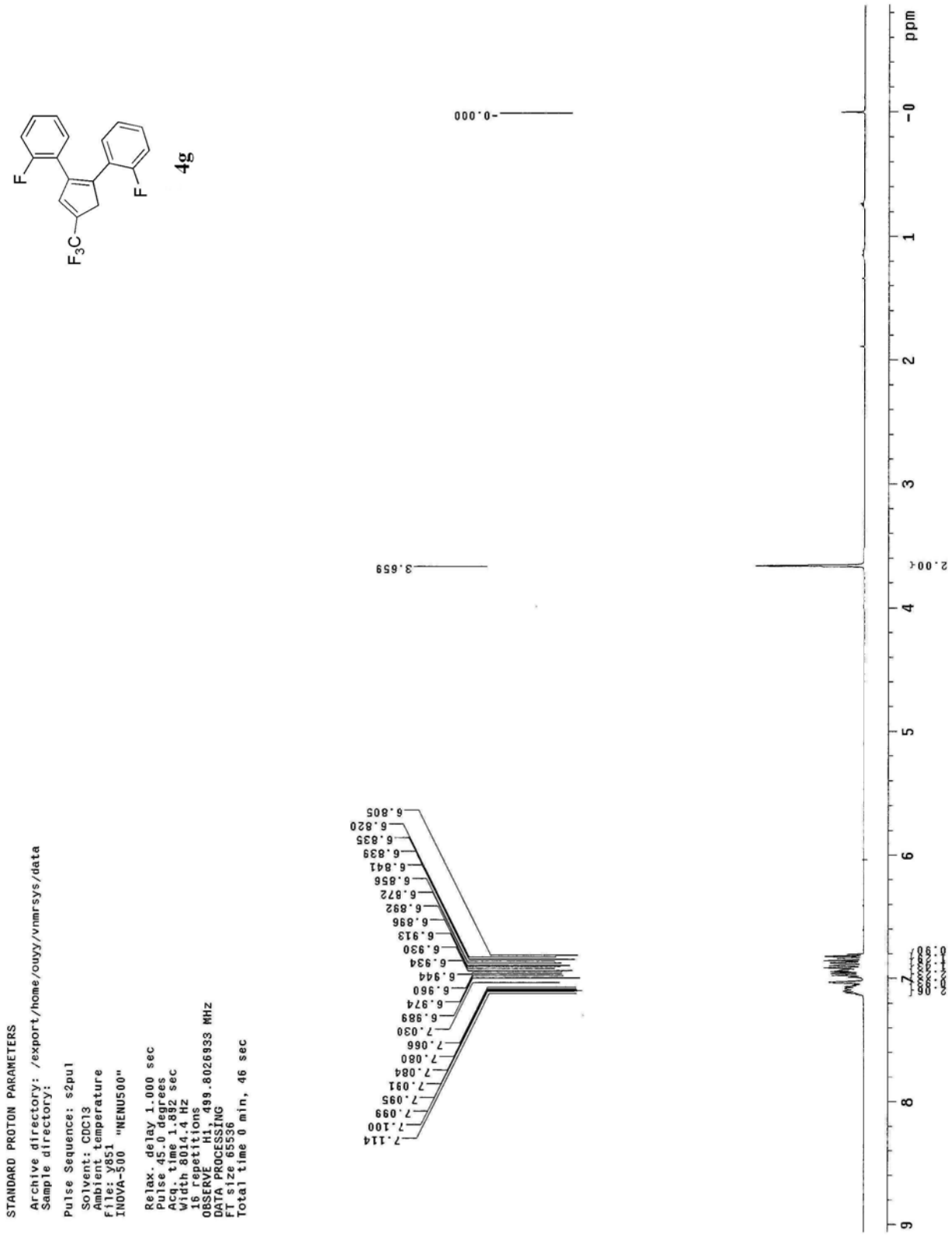


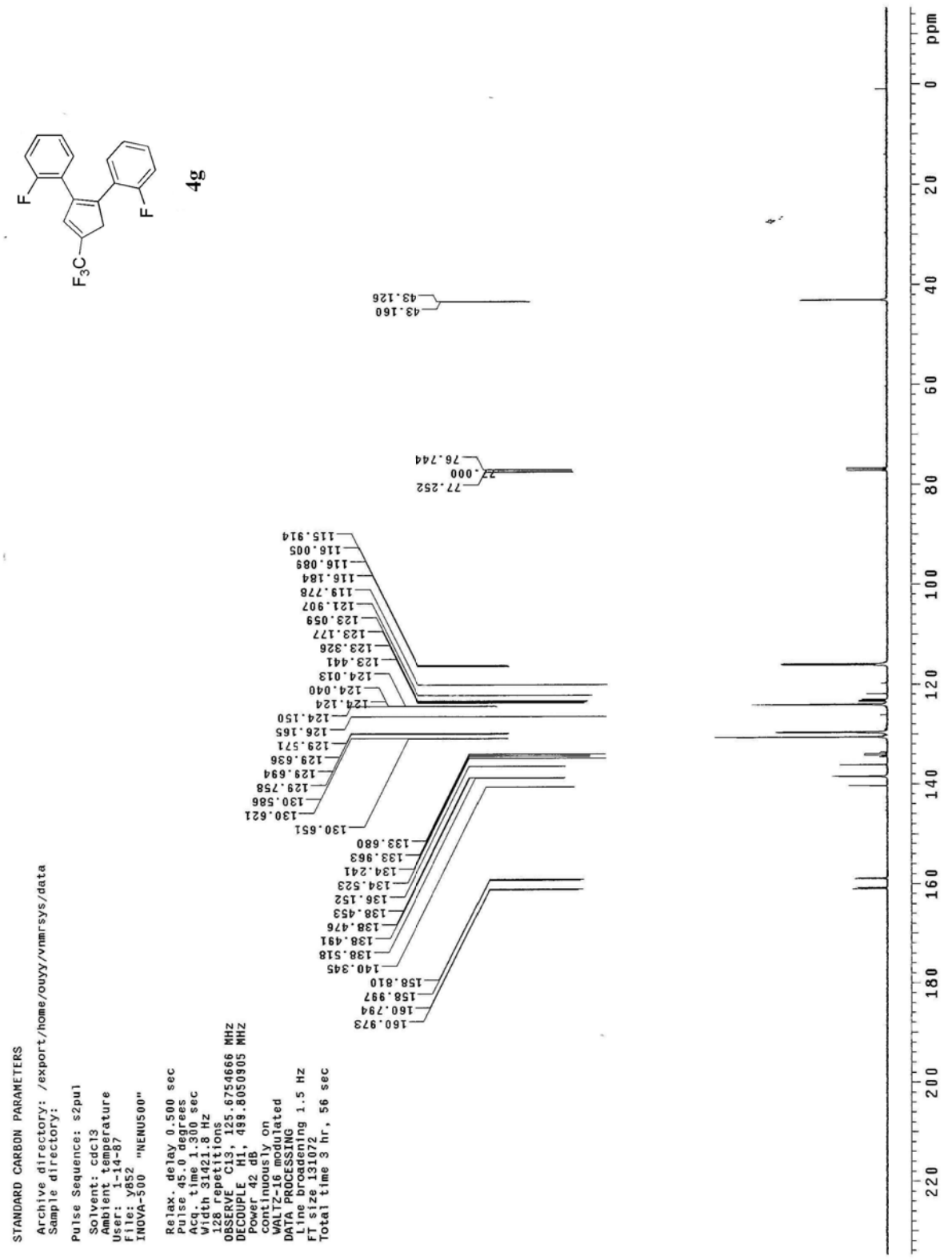

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y584 "NENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1, 499.8025937 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
Cl
Cl
F3C
4e
0.000
3.717
7.303
7.286
7.256
7.240
7.223
7.204
7.173
7.156
7.063
2.08
1.00
ppm

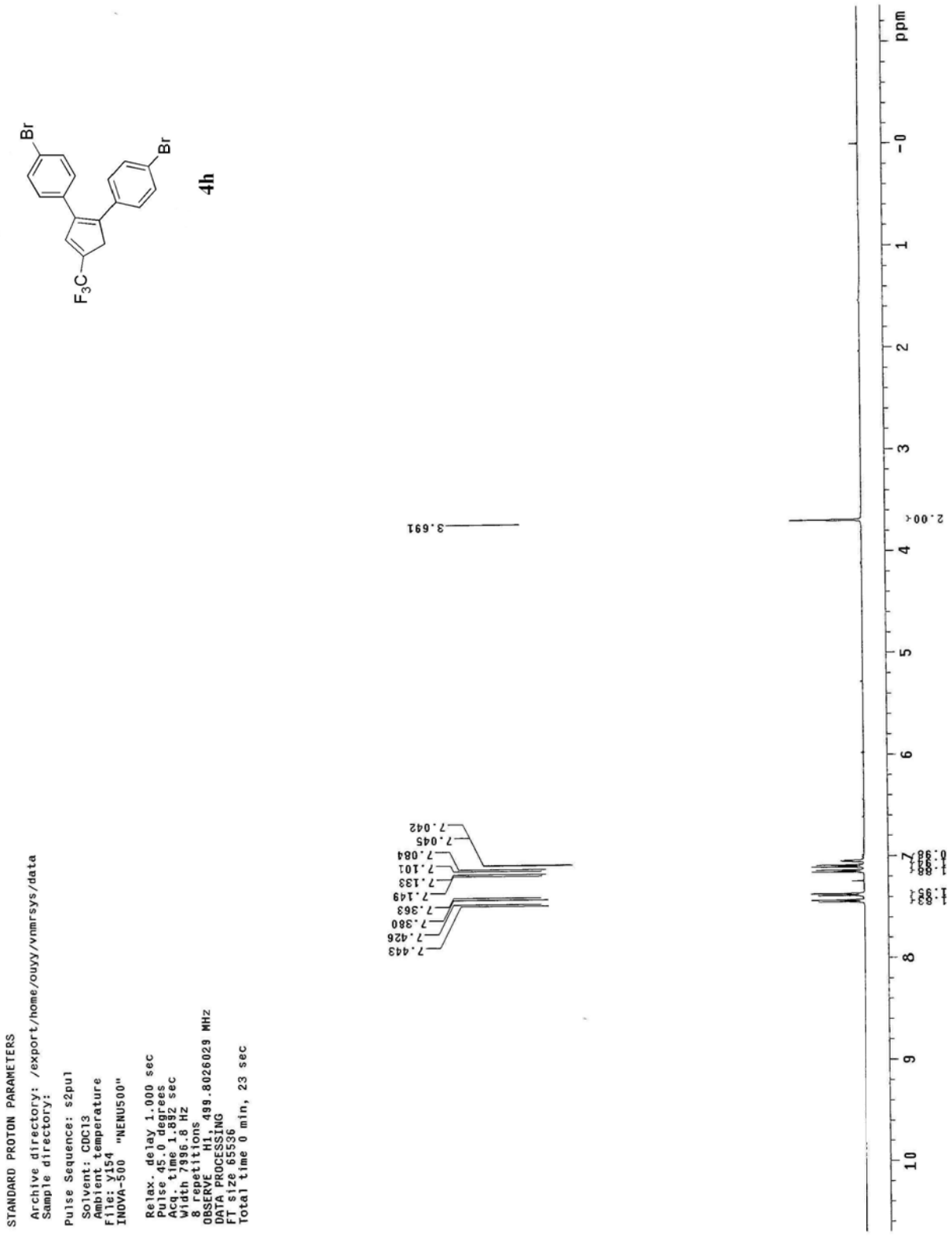


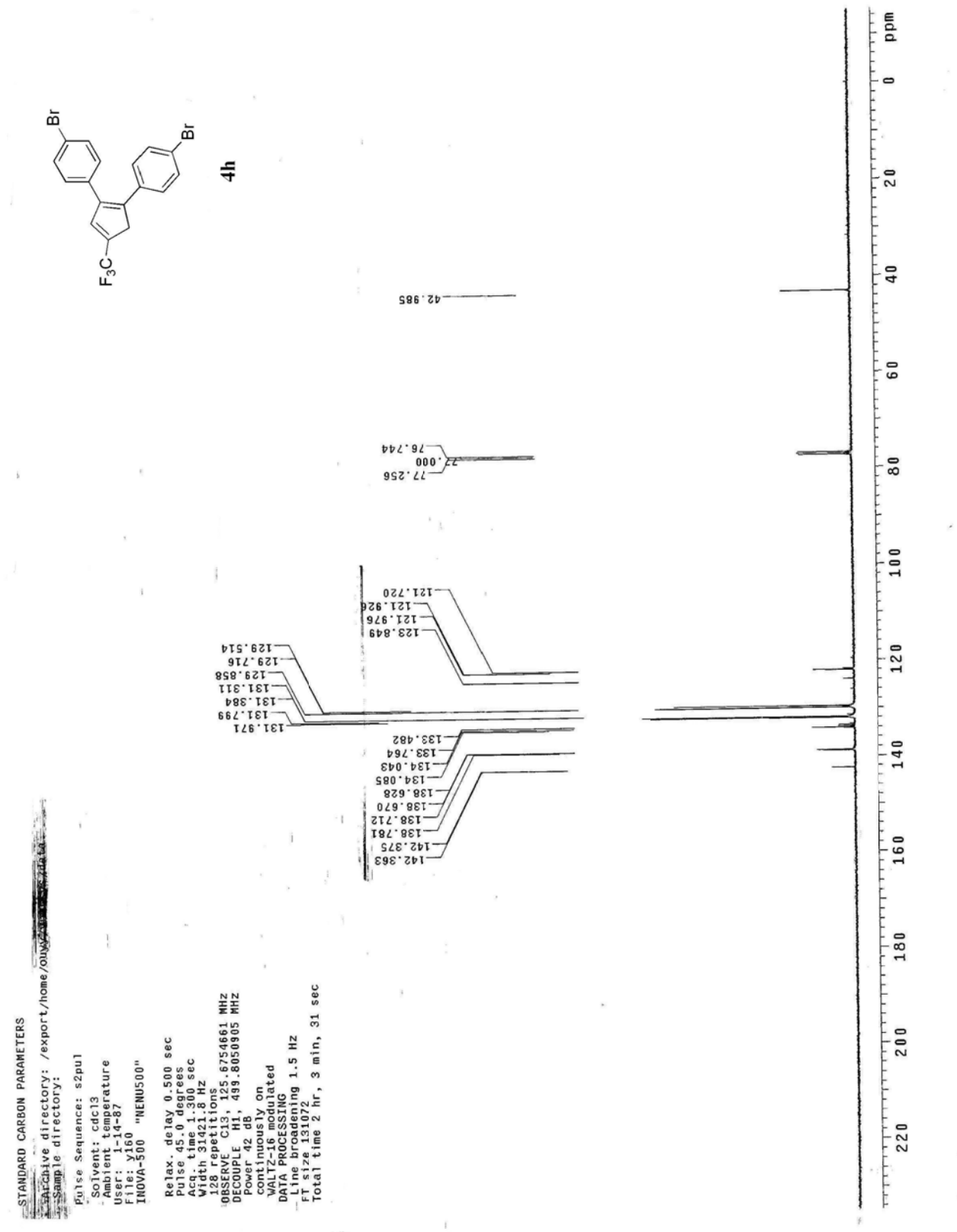

F
F
F3C
4f
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y582 "WENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1, 499.8025962 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
7.260
7.249
7.242
7.232
7.218
7.207
7.201
7.190
7.063
7.060
7.024
7.007
6.989
6.964
6.946
6.929
3.710
2.174
ppm

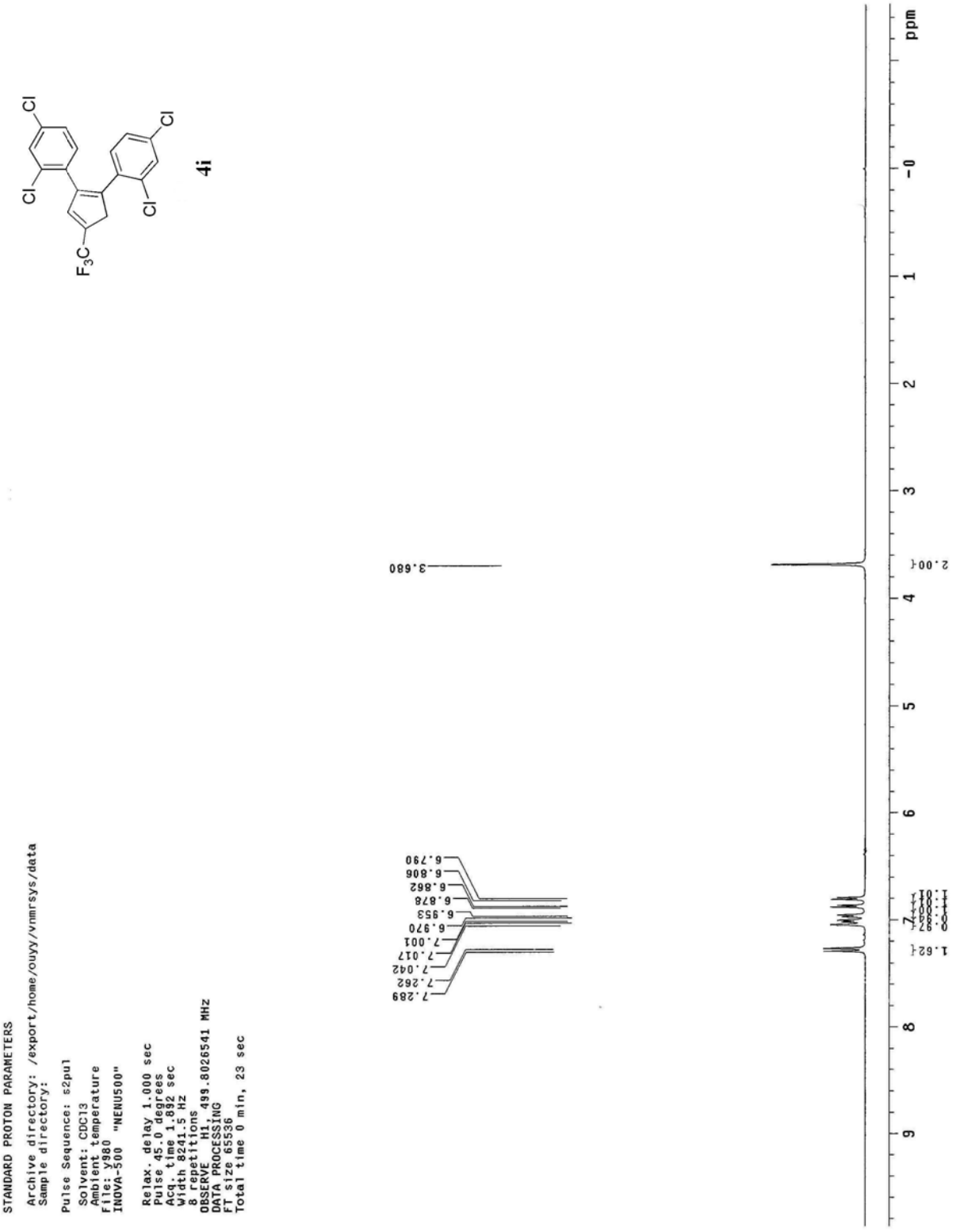

4f
F
F
F3C
43.057
76.744
77.000
77.252
115.513
115.681
115.845
121.846
123.975
129.667
129.728
129.976
130.041
131.330
131.452
131.483
132.925
133.207
138.239
138.999
139.040
142.062
161.206
161.248
163.182
163.216
ppm
0
20
40
60
80
100
120
140
160
180
200
220
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: y596
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754627 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

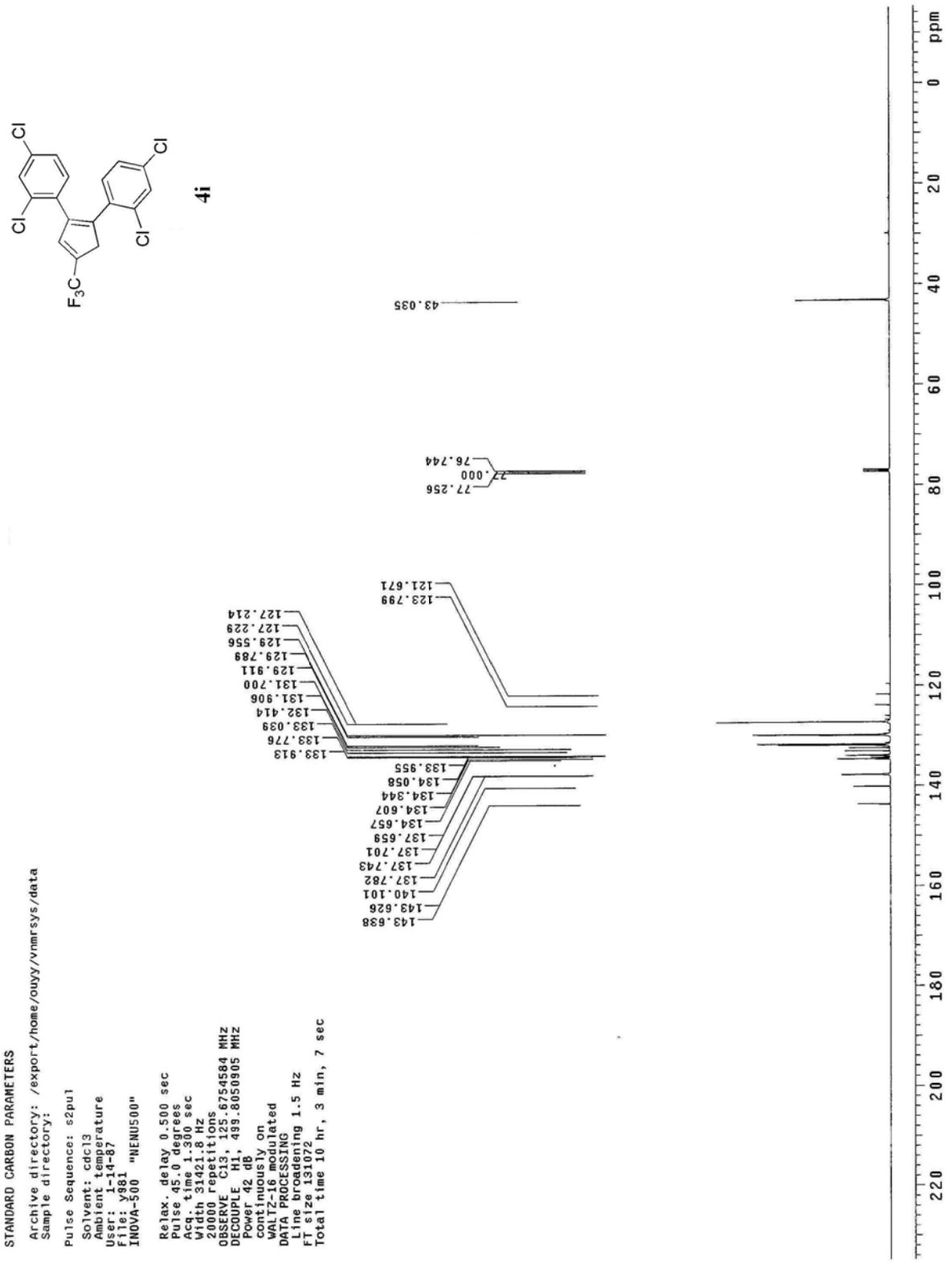

4g
F
F
F3C
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y851
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
16 repetitions
OBSERVE H1, 499.8026933 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec
7.114
7.100
7.099
7.095
7.091
7.084
7.080
7.066
7.030
6.989
6.974
6.960
6.944
6.934
6.930
6.913
6.896
6.892
6.872
6.856
6.841
6.839
6.835
6.820
6.805
3.659
-0.000
2.00
ppm

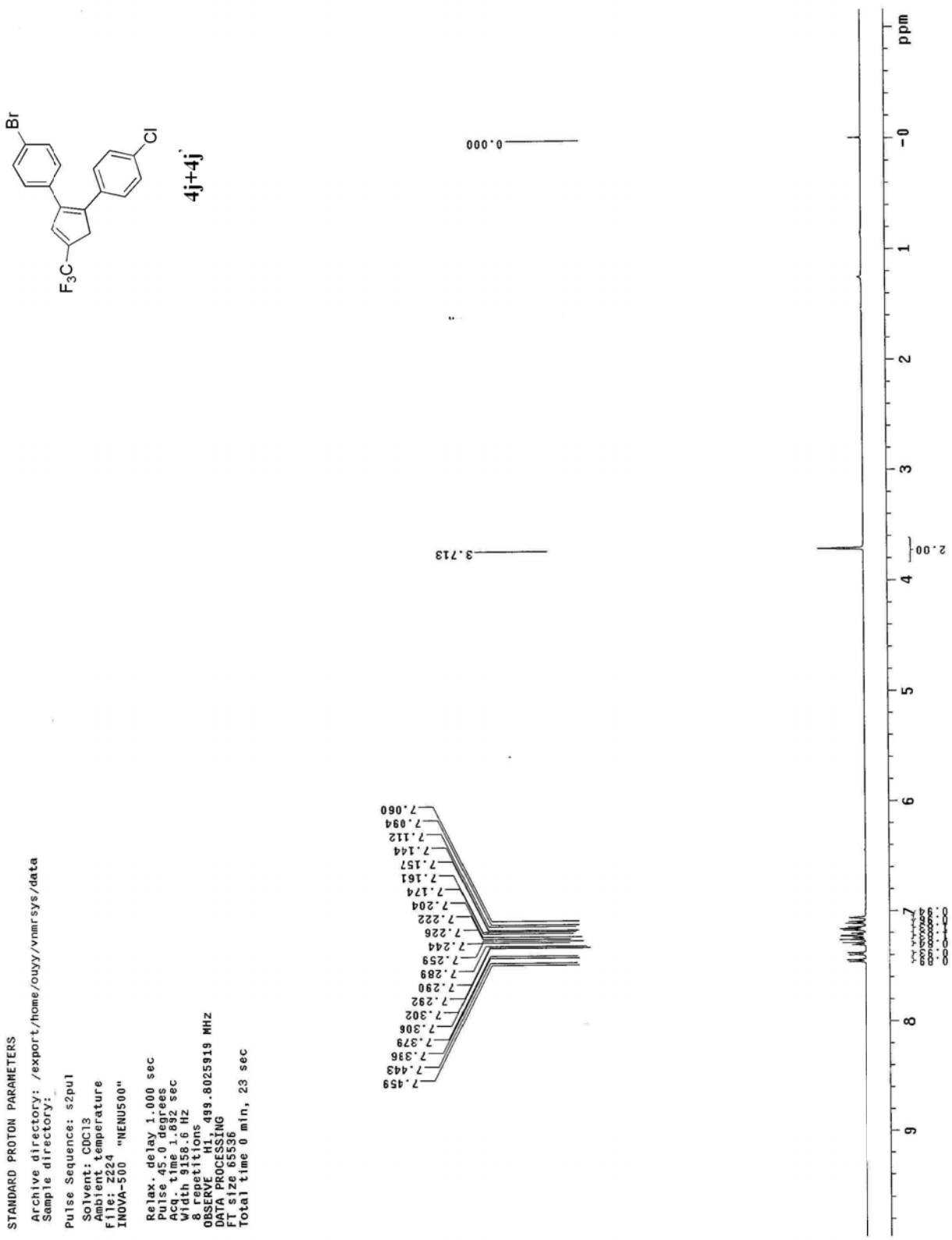

4g
F
F
F3C
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: y852 "NENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754666 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec
43.160
43.126
77.252
77.000
76.744
115.914
116.005
116.089
116.184
119.778
121.907
123.059
123.177
123.326
123.441
124.013
124.040
124.124
124.150
126.165
129.571
129.636
129.694
129.758
130.586
130.621
130.651
133.680
133.963
134.241
134.523
136.152
138.453
138.476
138.491
138.518
140.345
158.810
158.997
160.794
160.973
220
200
180
160
140
120
100
80
60
40
20
0
ppm

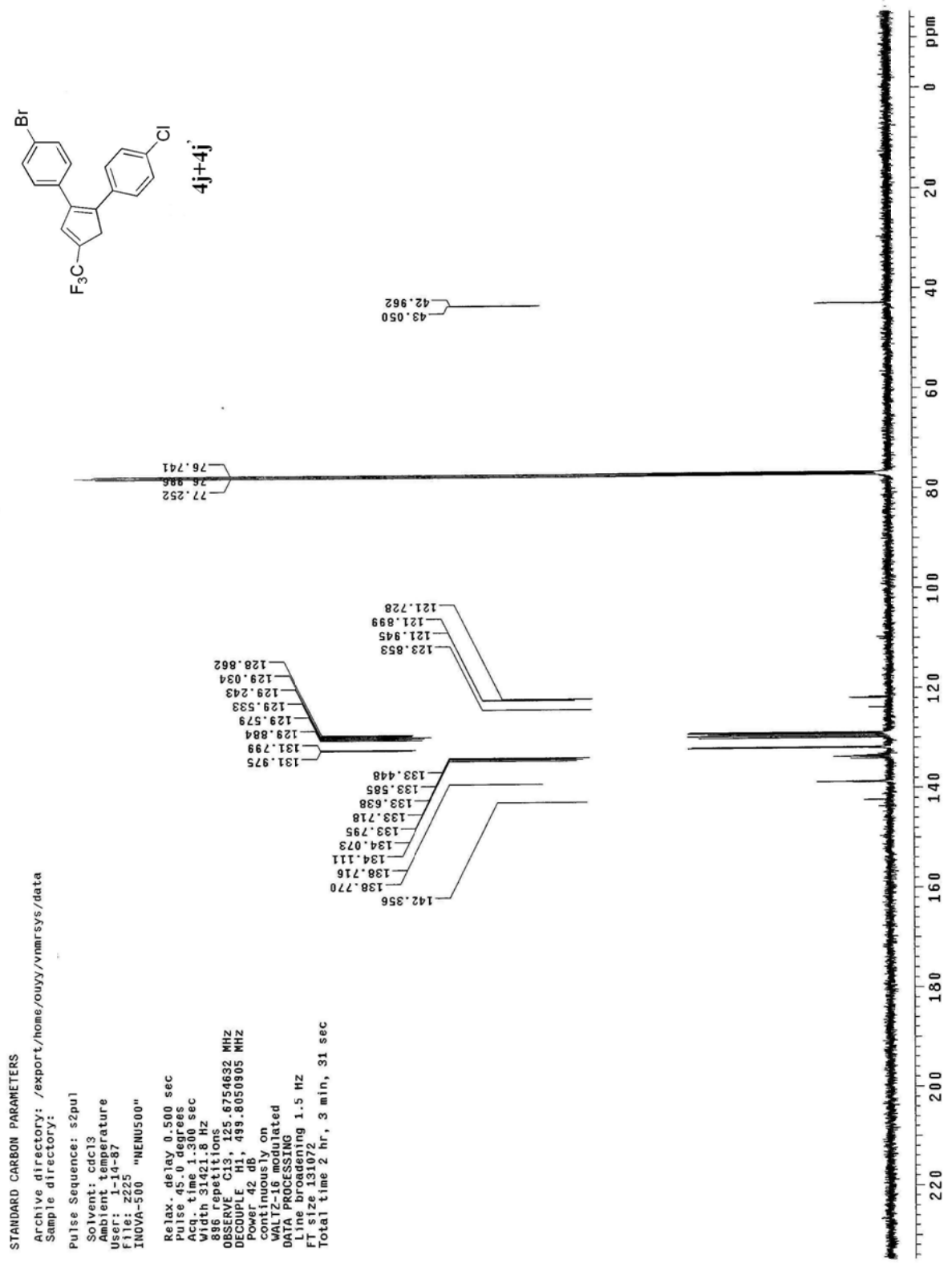


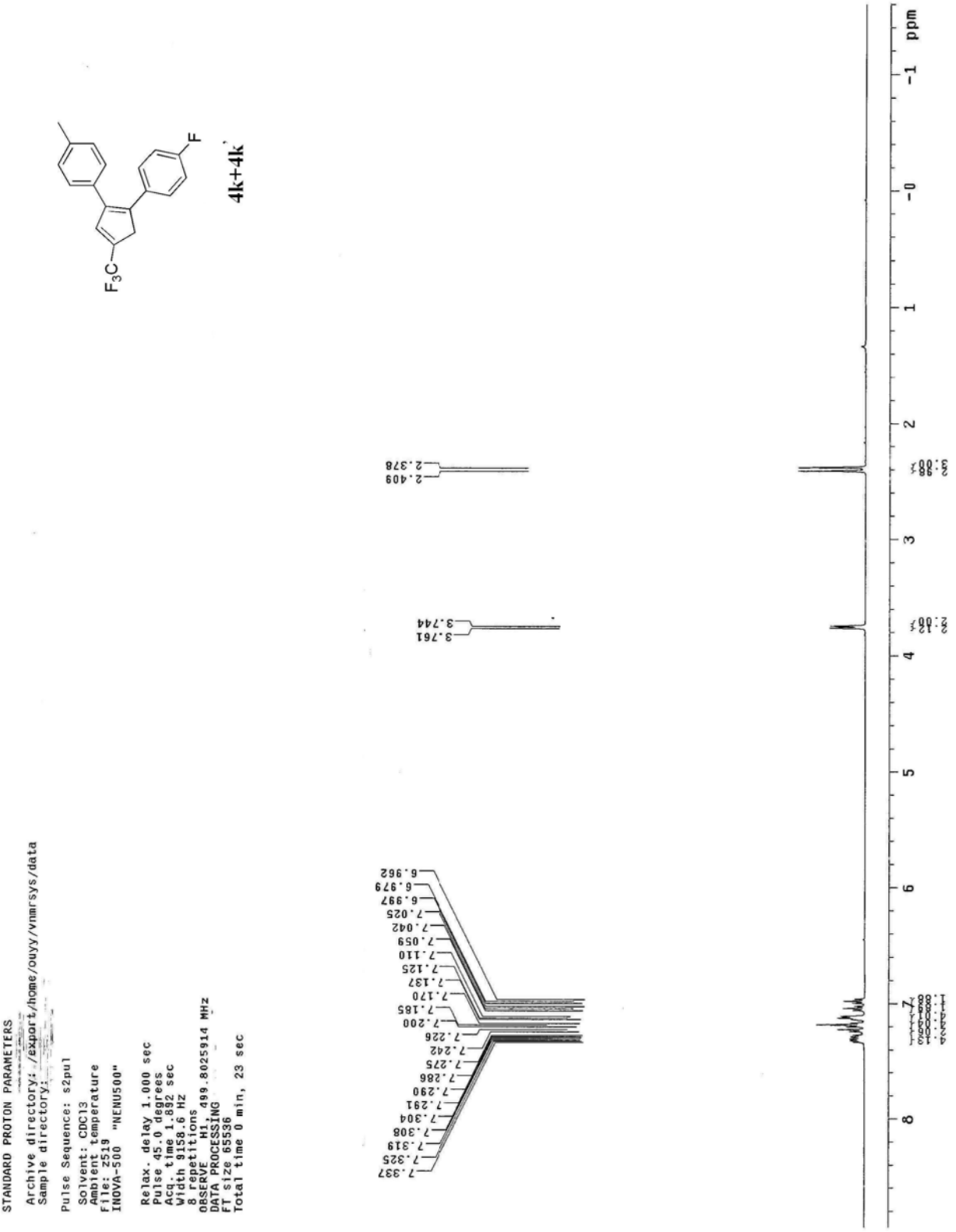


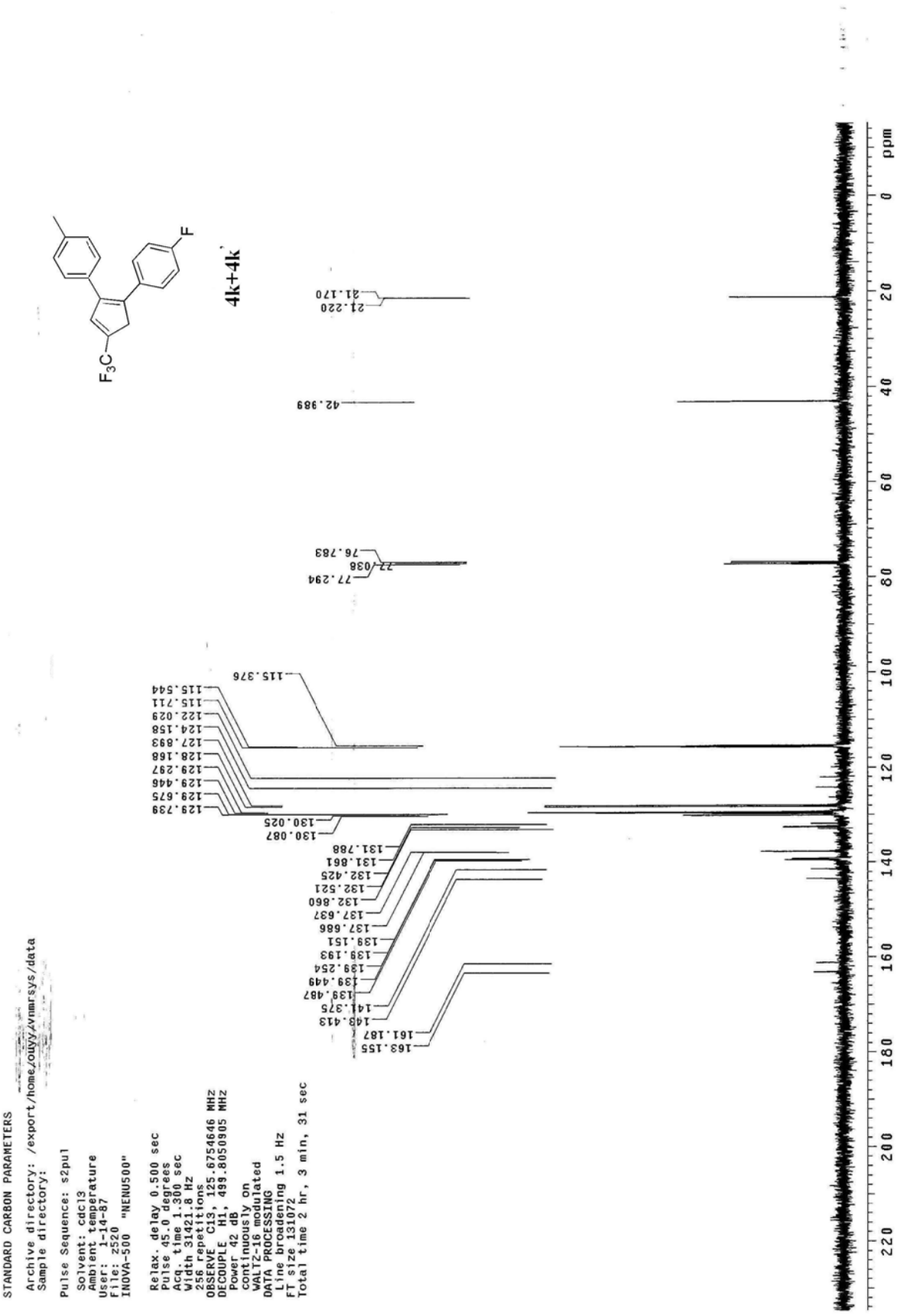

Cl
Cl
Cl
Cl
F3C
4i
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y980 "NENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8241.5 Hz
8 repetitions
OBSERVE H1, 499.8026541 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
3.680
7.289
7.262
7.042
7.017
7.001
6.970
6.953
6.878
6.862
6.806
6.790
2.00
1.62
ppm

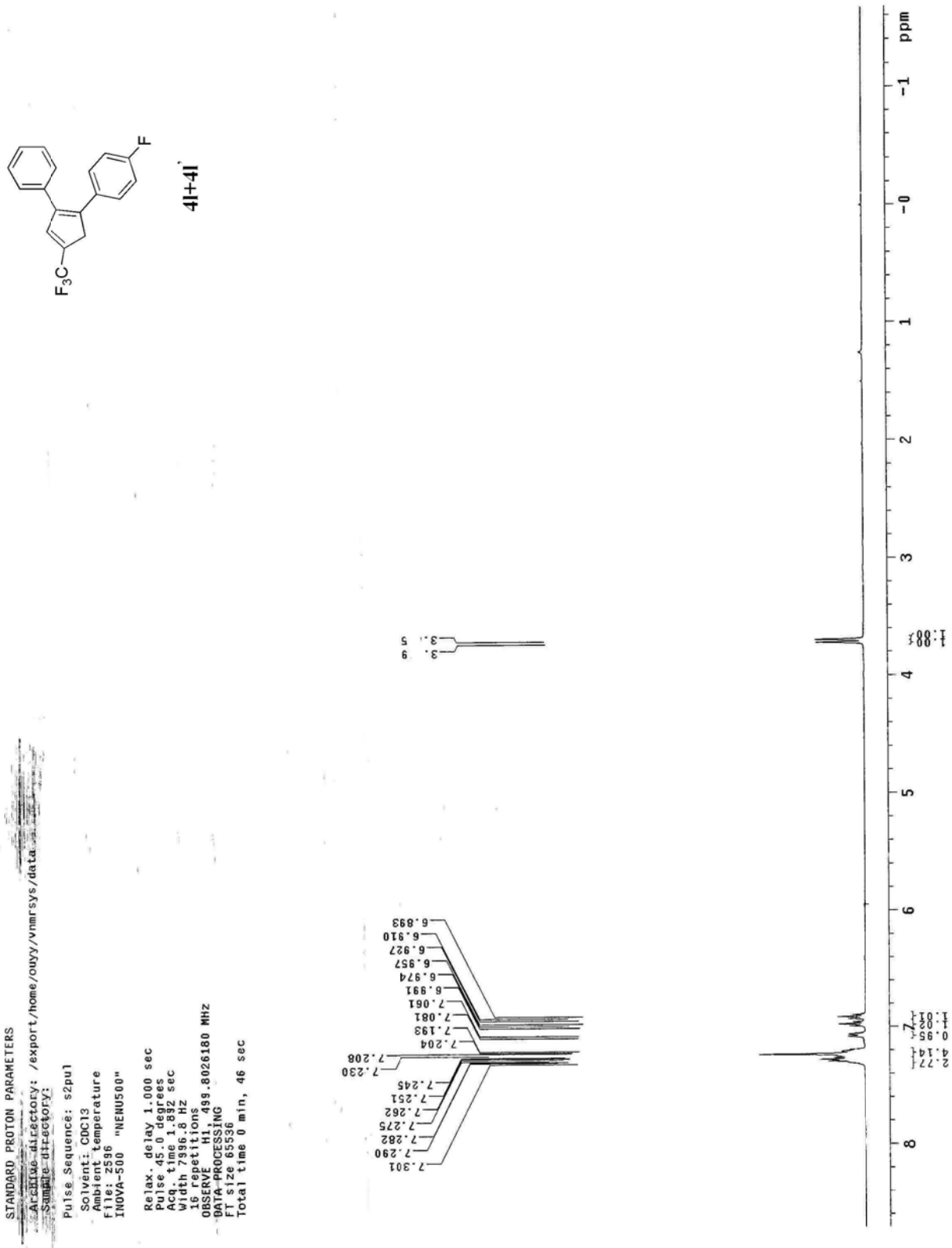


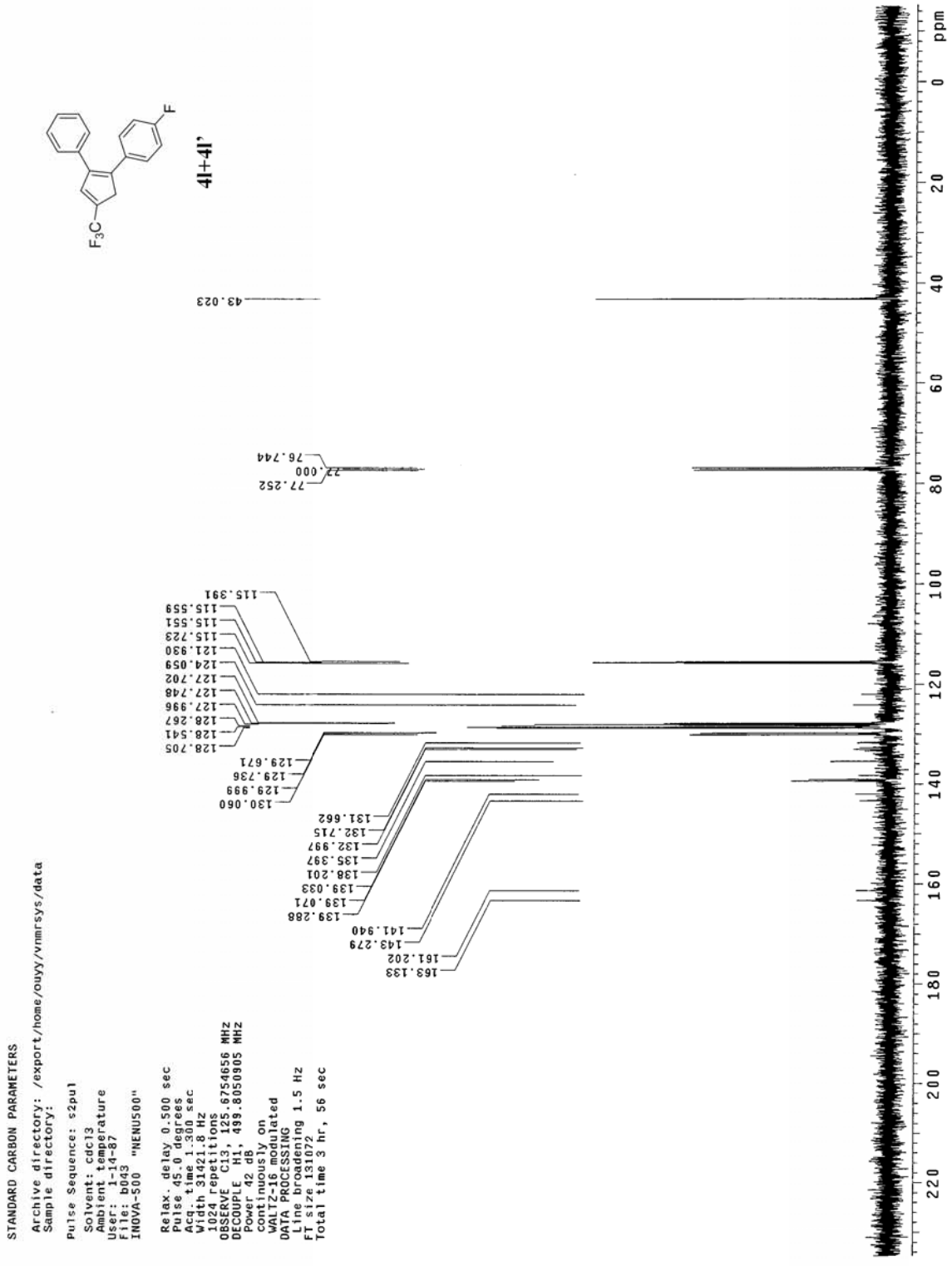

Br
Cl
F3C
4j+4j'
0.000
3.713
7.459
7.443
7.396
7.379
7.306
7.302
7.292
7.290
7.289
7.259
7.244
7.226
7.222
7.204
7.174
7.161
7.157
7.144
7.112
7.094
7.060
2.00
ppm
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: Z224
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9158.6 Hz
8 repetitions
OBSERVE H1, 499.8025919 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec

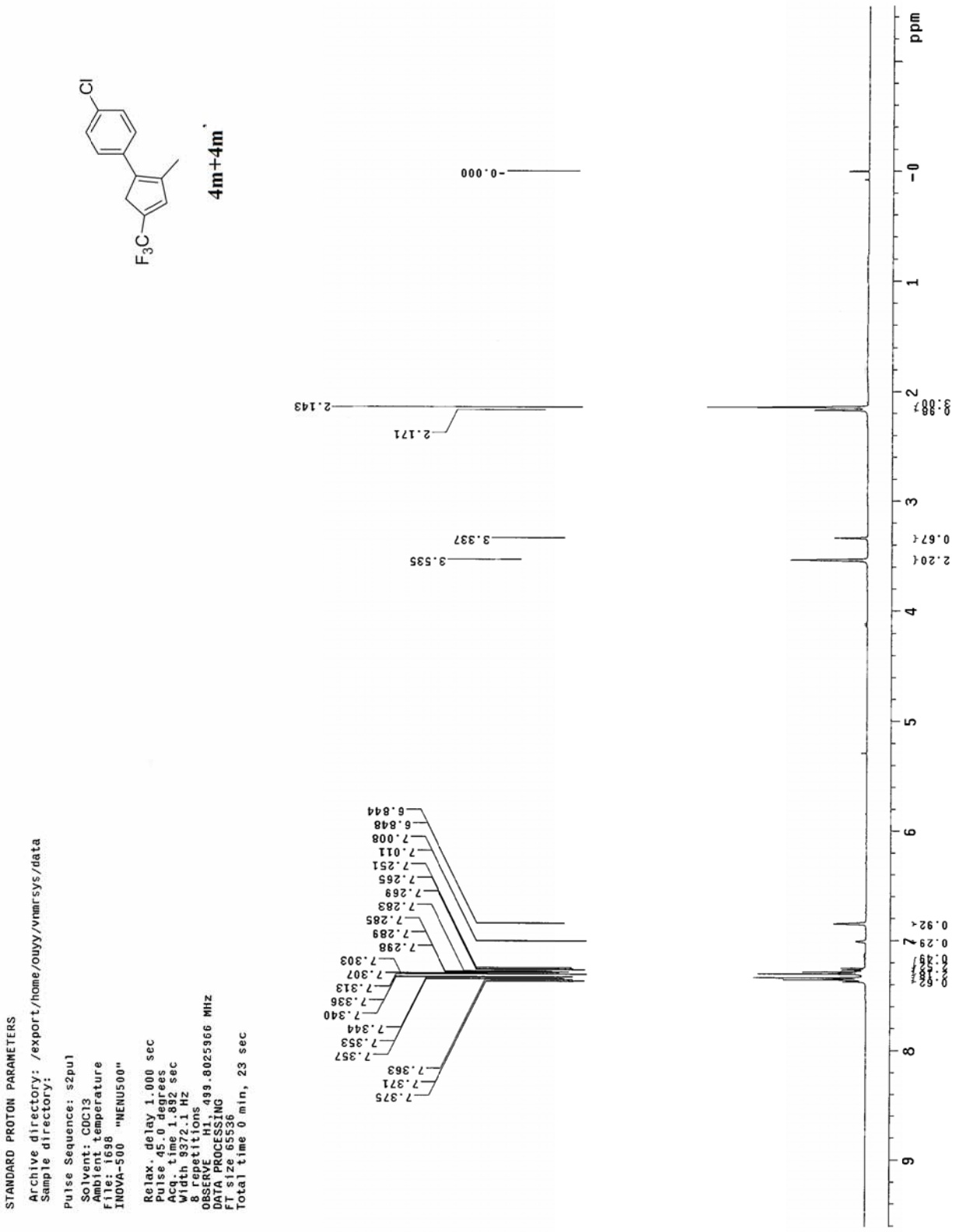


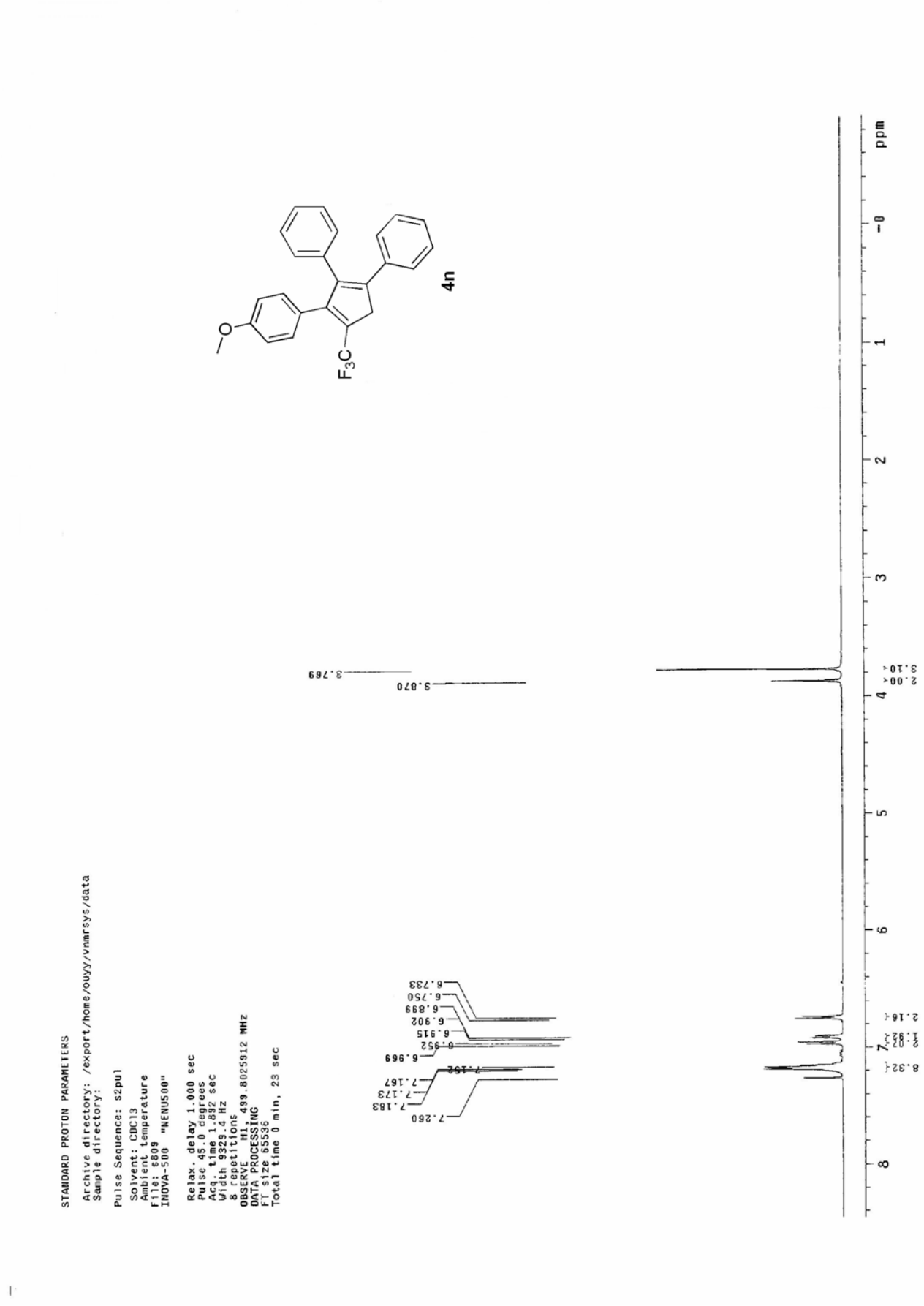


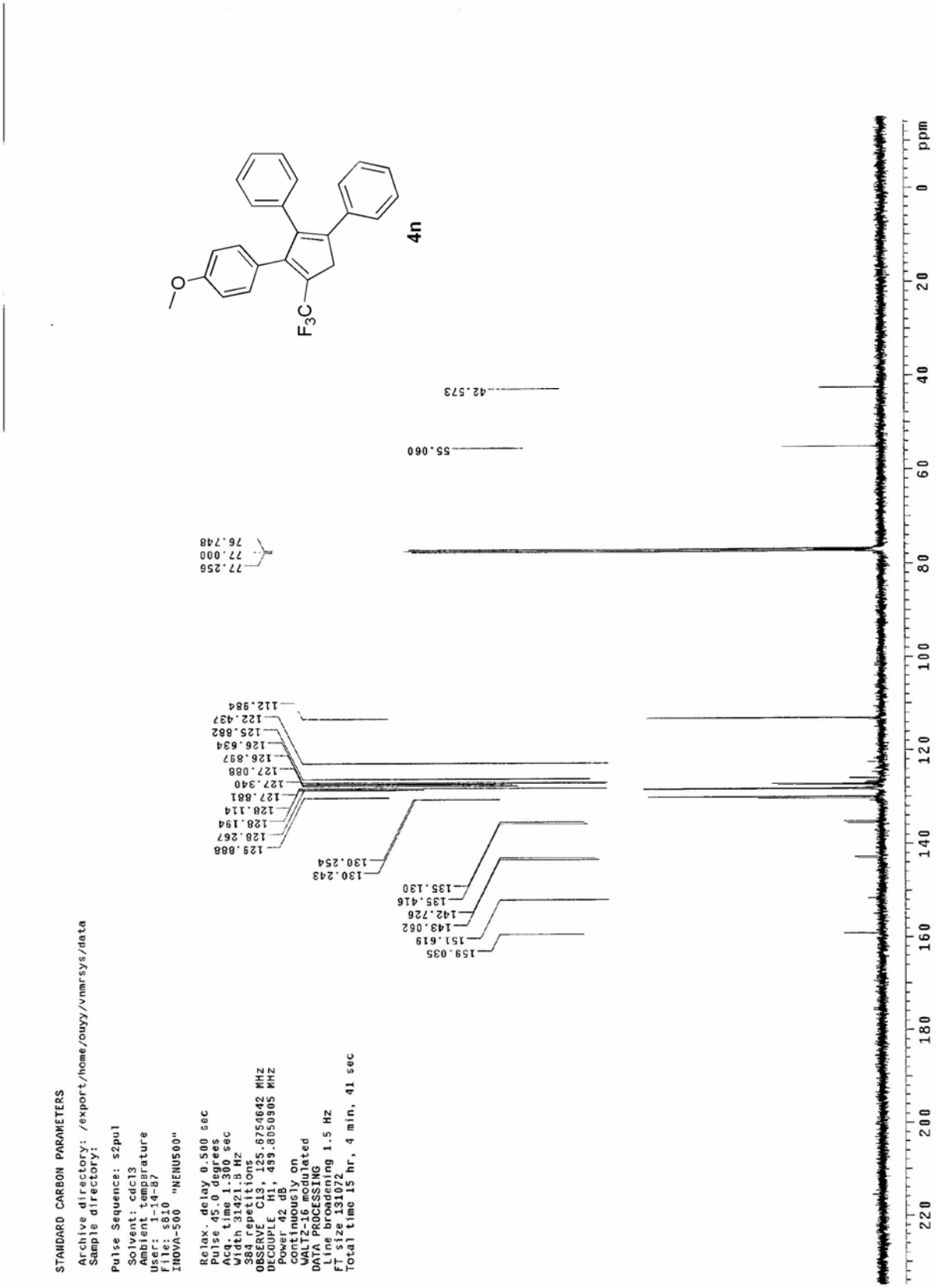

4k+4k'
F
F3C
21.170
21.220
42.389
76.783
77.038
77.294
115.376
115.544
115.711
122.029
124.158
127.893
128.168
129.297
129.446
129.675
129.739
130.025
130.087
131.788
131.861
132.425
132.521
132.860
137.637
137.686
139.151
139.193
139.254
139.449
139.487
141.375
143.413
161.187
163.155
ppm
0
20
40
60
80
100
120
140
160
180
200
220
STANDARD CARBON PARAMETERS
Archive directory: /export/home/couyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: z520 "MENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
256 repetitions
OBSERVE C13, 125.6754646 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec

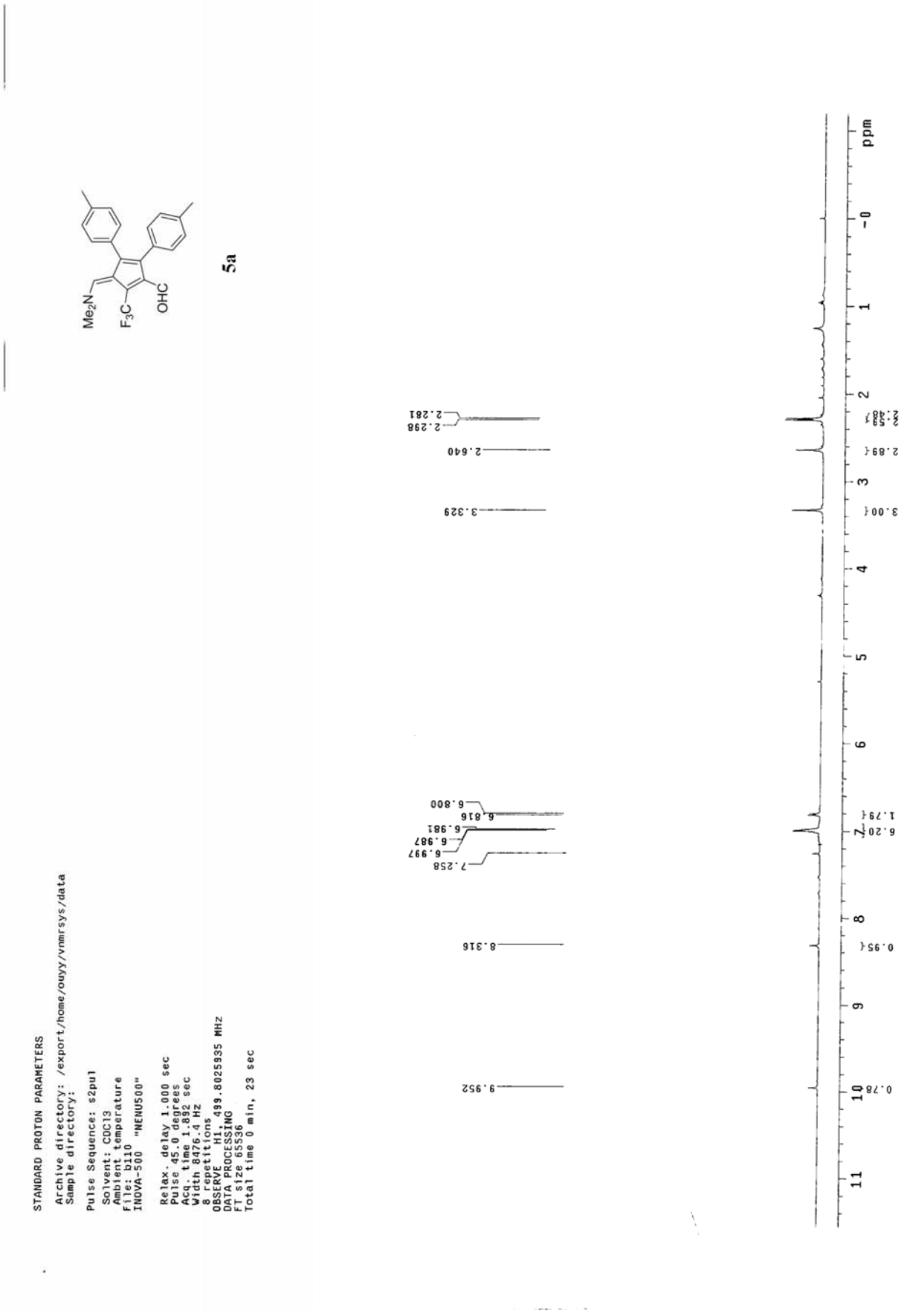

F
F3C
4l+4l'
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 2596 "NENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 7996.8 Hz
16 repetitions
OBSERVE H1, 499.8026180 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec
7.301
7.290
7.282
7.275
7.262
7.251
7.245
7.230
7.208
7.204
7.193
7.081
7.061
6.991
6.974
6.957
6.927
6.910
6.893
3.9
3.5
ppm

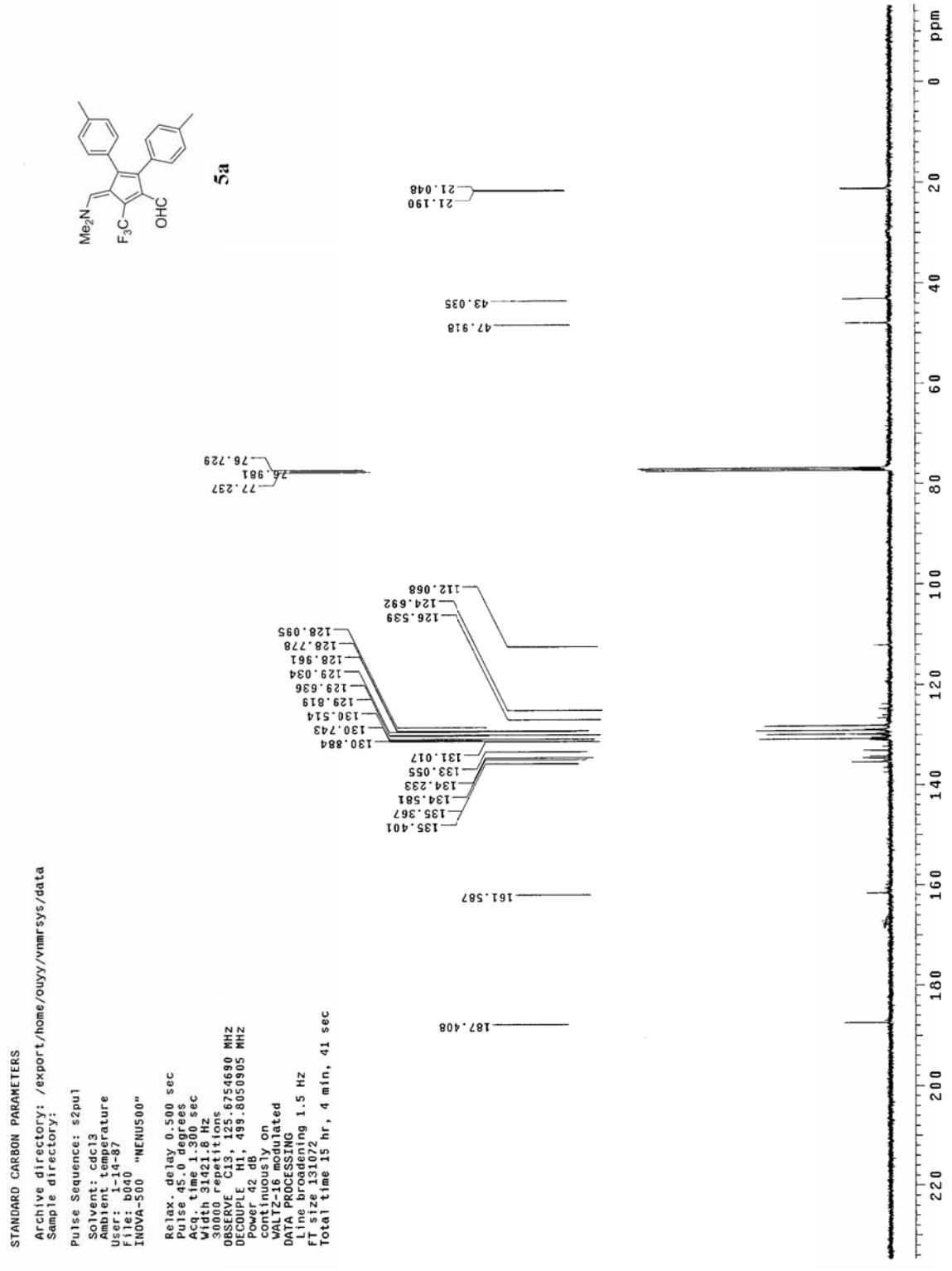

41+41'
F
F3C
43.023
76.744
77.000
77.252
115.391
115.559
115.551
115.723
121.930
124.059
127.702
127.748
127.996
128.267
128.541
128.705
129.671
129.736
129.999
130.060
131.662
132.715
132.997
135.397
138.201
139.033
139.071
139.288
141.940
143.279
161.202
163.133
ppm
0
20
40
60
80
100
120
140
160
180
200
220
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: b043
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
1024 repetitions
OBSERVE C13, 125.6754656 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec


STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 168 "NENU500"
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 9372.1 Hz
8 repetitions
OBSERVE H1, 499.8025966 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
Cl
F3C
4m+4m'
0.000
2.143
2.171
3.337
3.535
6.844
6.848
7.008
7.011
7.251
7.265
7.269
7.283
7.285
7.289
7.298
7.303
7.307
7.313
7.336
7.340
7.344
7.353
7.357
7.363
7.371
7.375
ppm


4n
F3C
O
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: s809
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.392 sec
Width 9329.4 Hz
8 repetitions
OBSERVE H1, 499.8025912 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
3.769
3.870
7.260
7.183
7.173
7.167
6.969
6.952
6.915
6.902
6.899
6.750
6.733
ppm




Me2N
F3C
OHC
5a
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: b110
INOVA-500 "WENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8476.4 Hz
8 repetitions
OBSERVE H1, 499.8025935 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
9.952
8.316
7.258
6.997
6.987
6.981
6.816
6.800
3.329
2.640
2.298
2.281
ppm

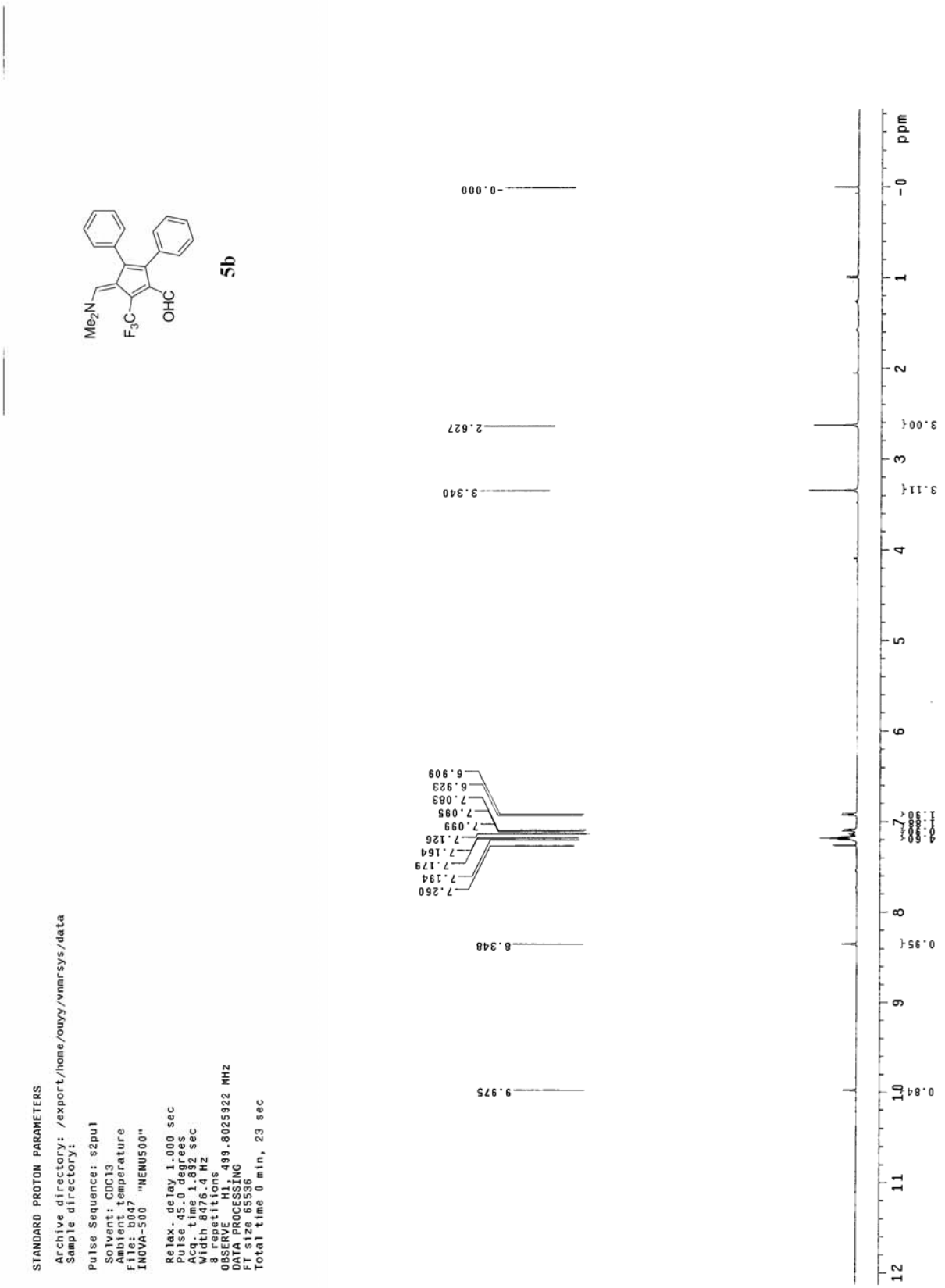


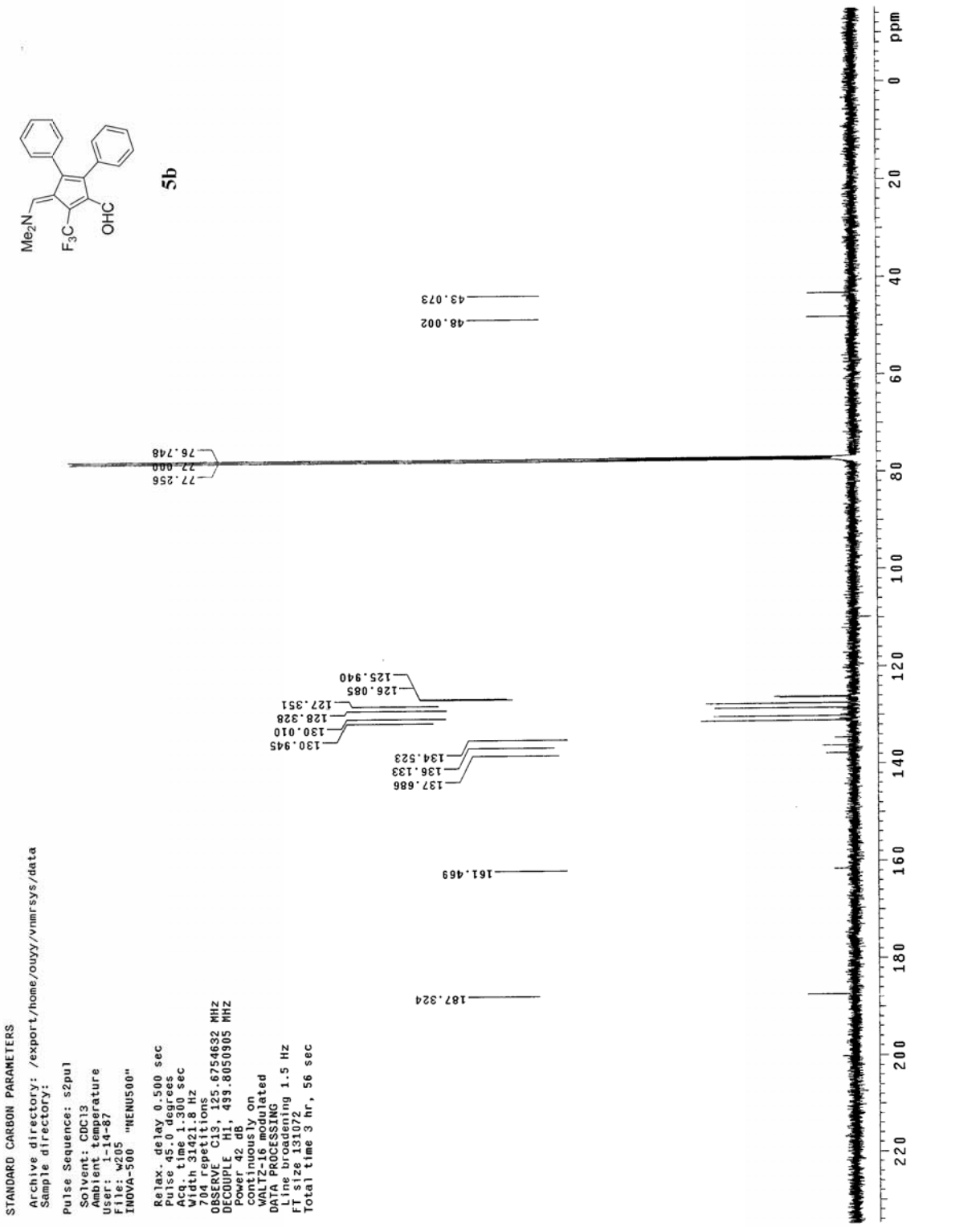
STANDARD CARBON PARAMETERS

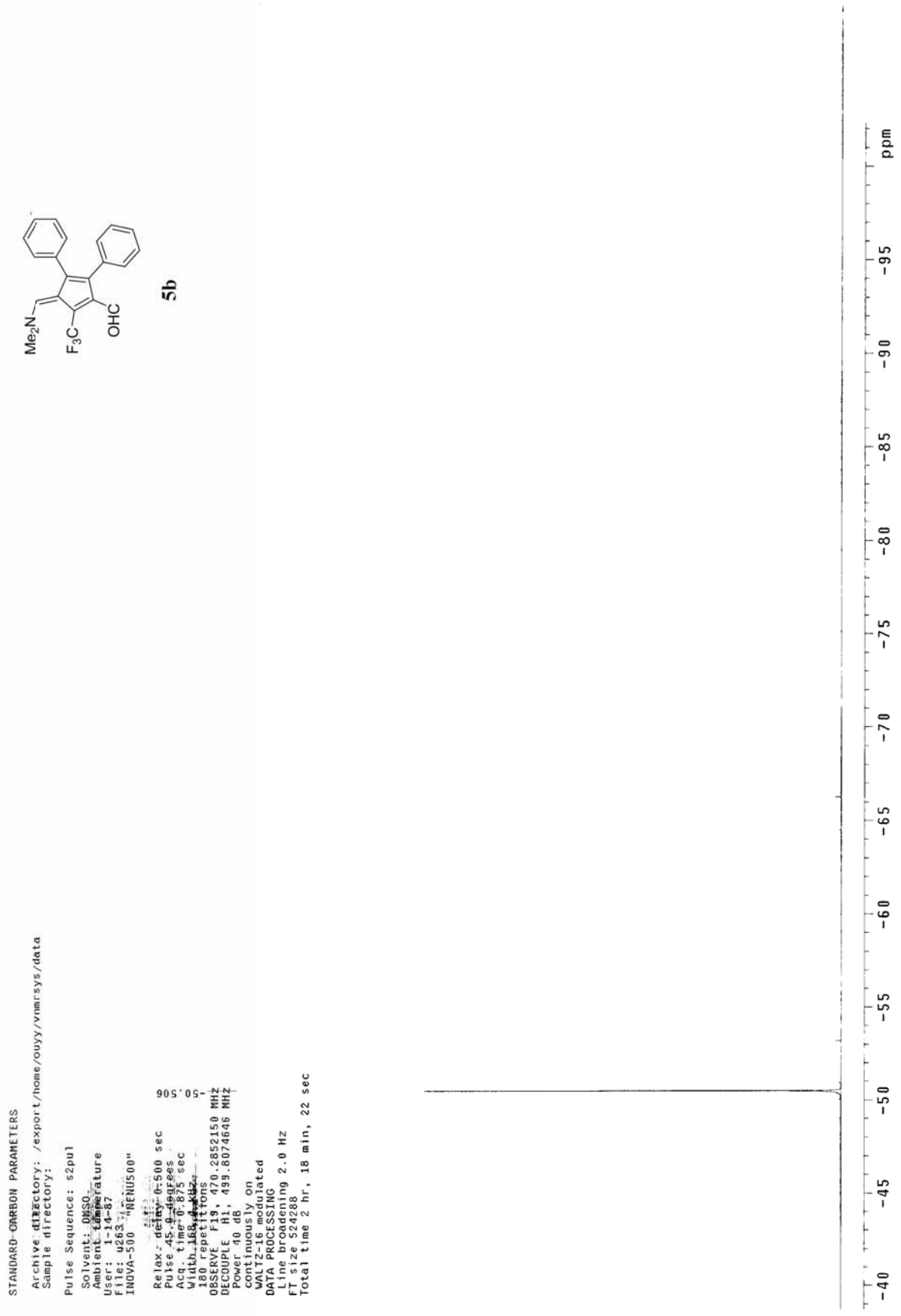
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

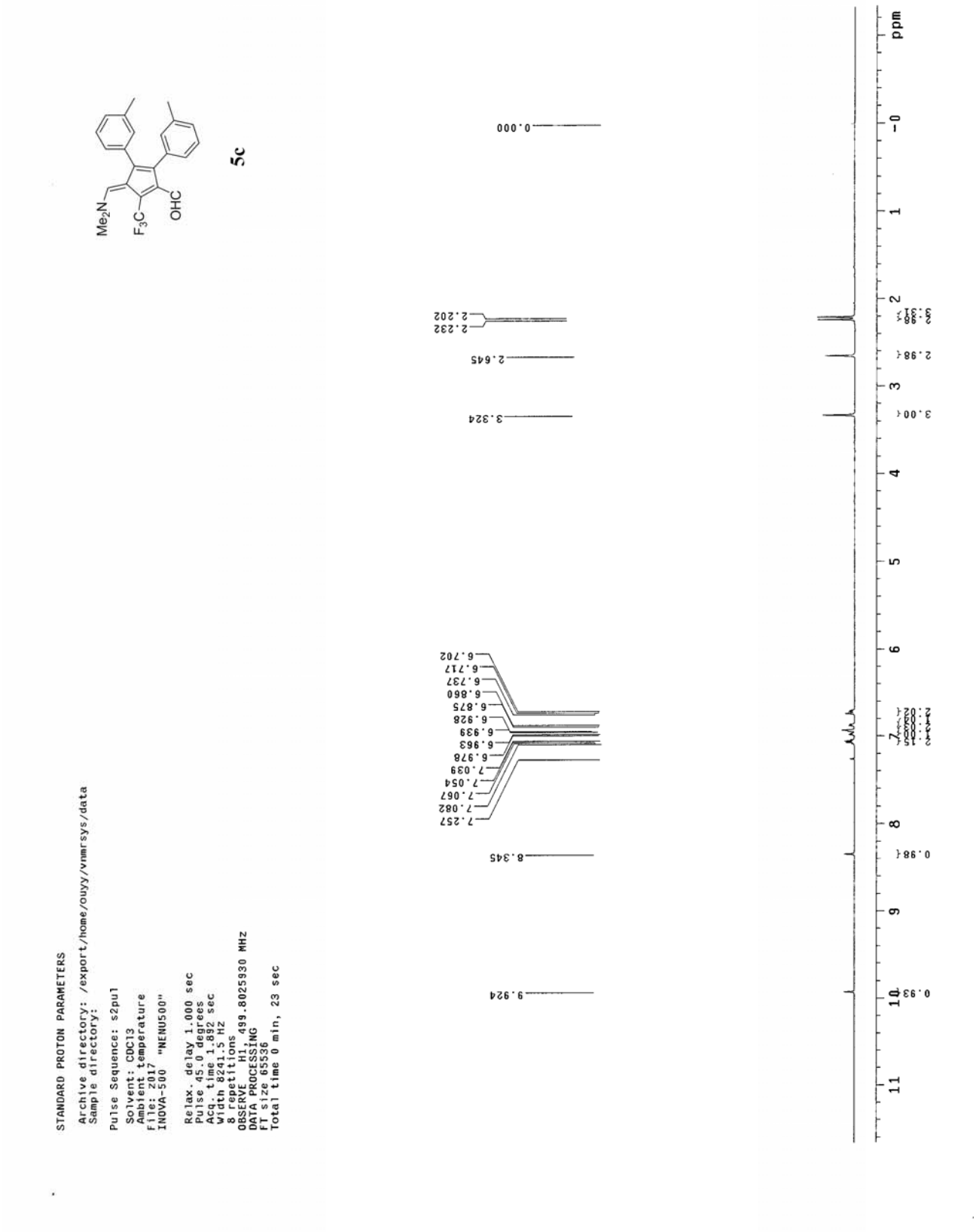
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: b040 "NENUS00"
INOVA-500

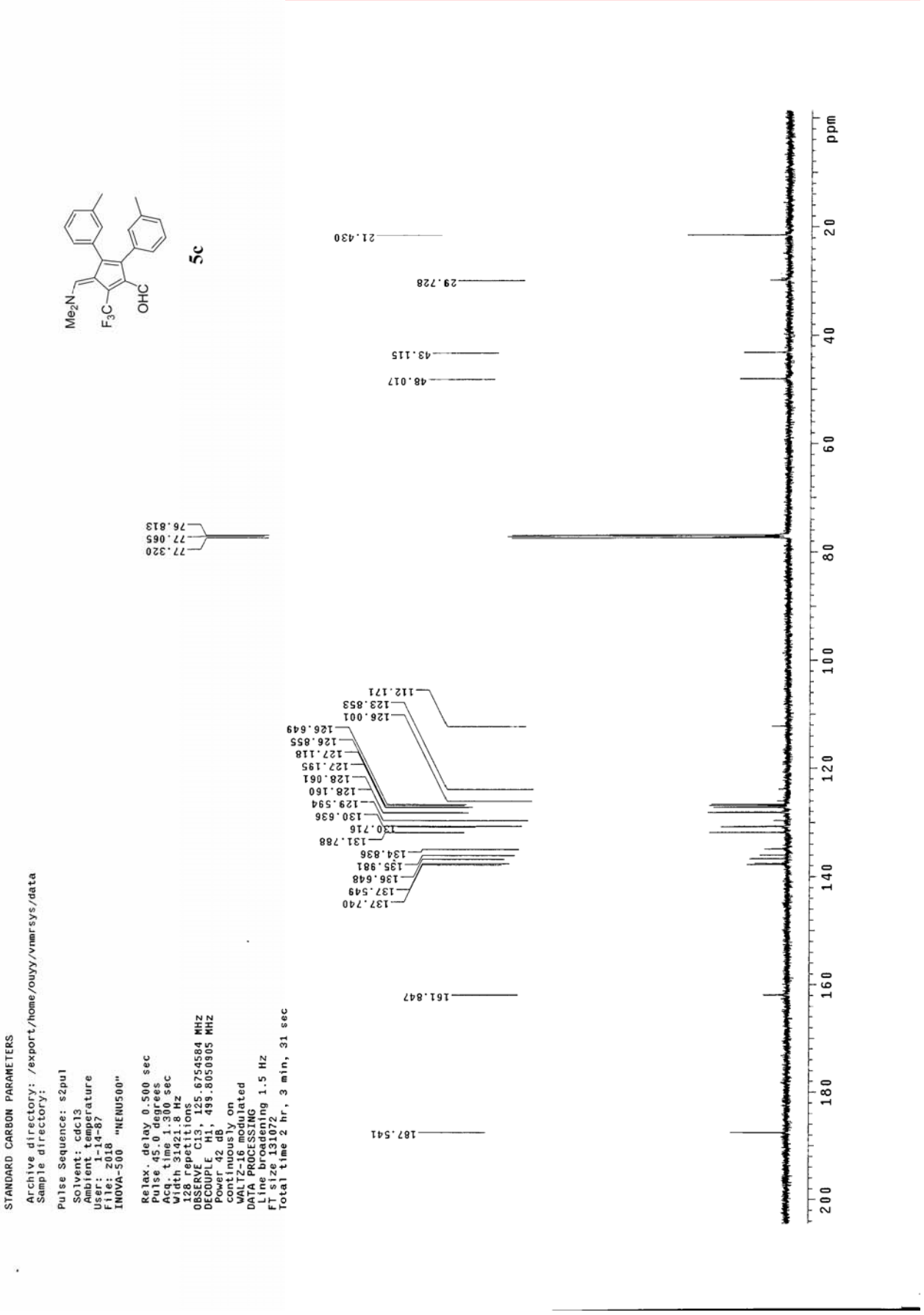
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
30000 repetitions
OBSERVE C13, 125.6754690 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 15 hr, 4 min, 41 sec

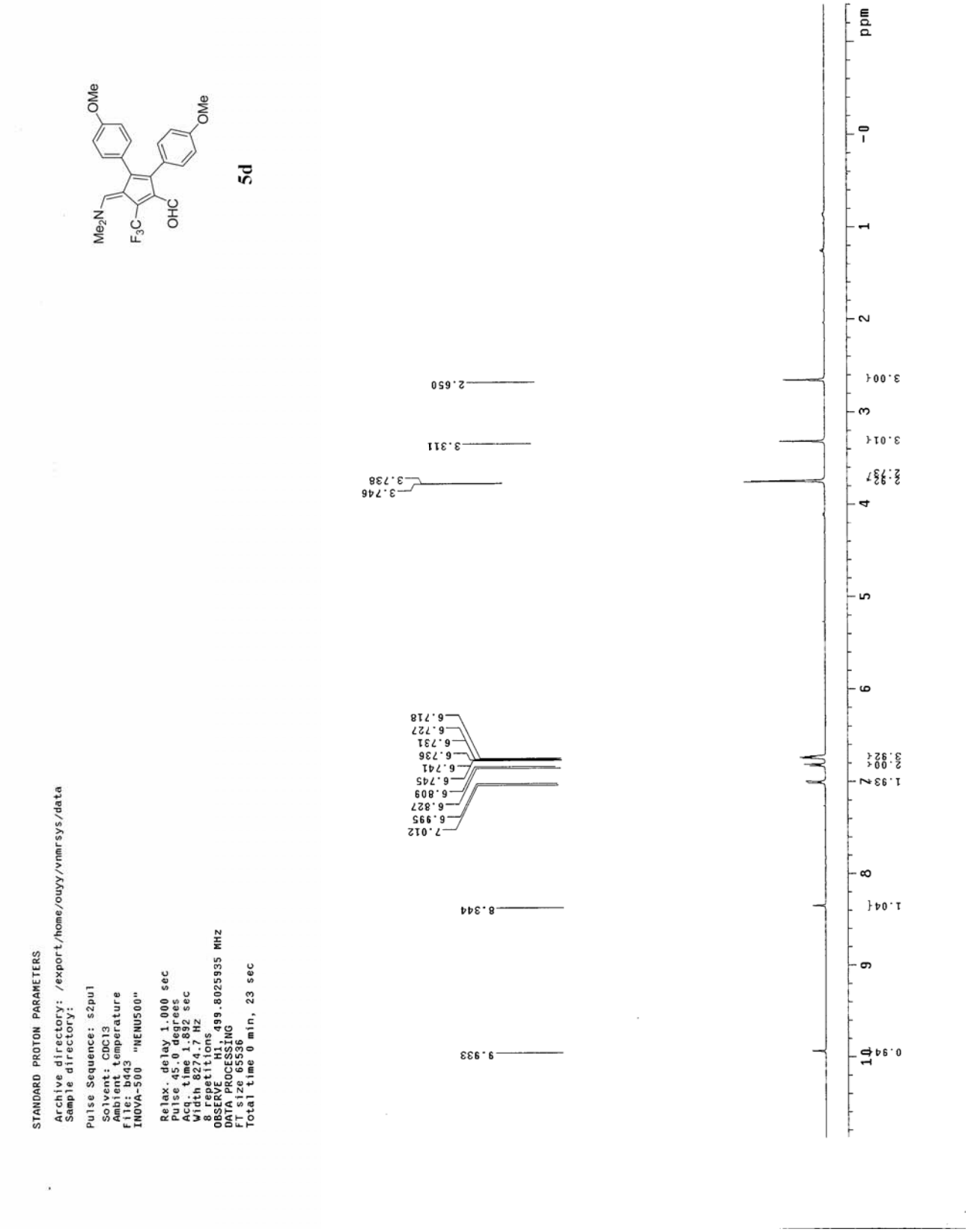

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: b047
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8476.4 Hz
8 repetitions
OBSERVE H1, 499.8025922 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
Me2N
F3C
OHC
5b
-0.000
2.627
3.340
6.909
6.923
7.083
7.095
7.099
7.126
7.164
7.179
7.194
7.260
8.348
9.975
ppm

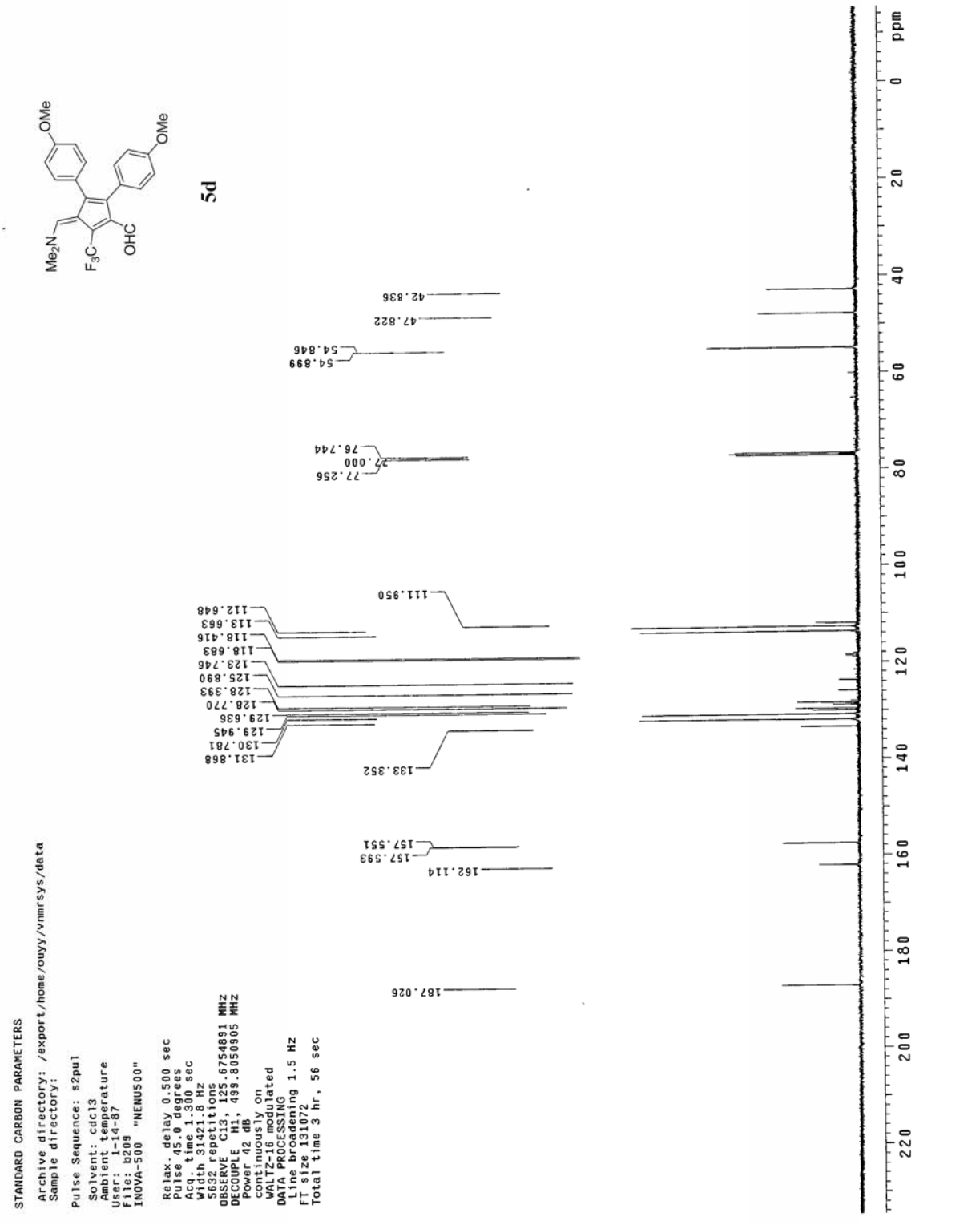


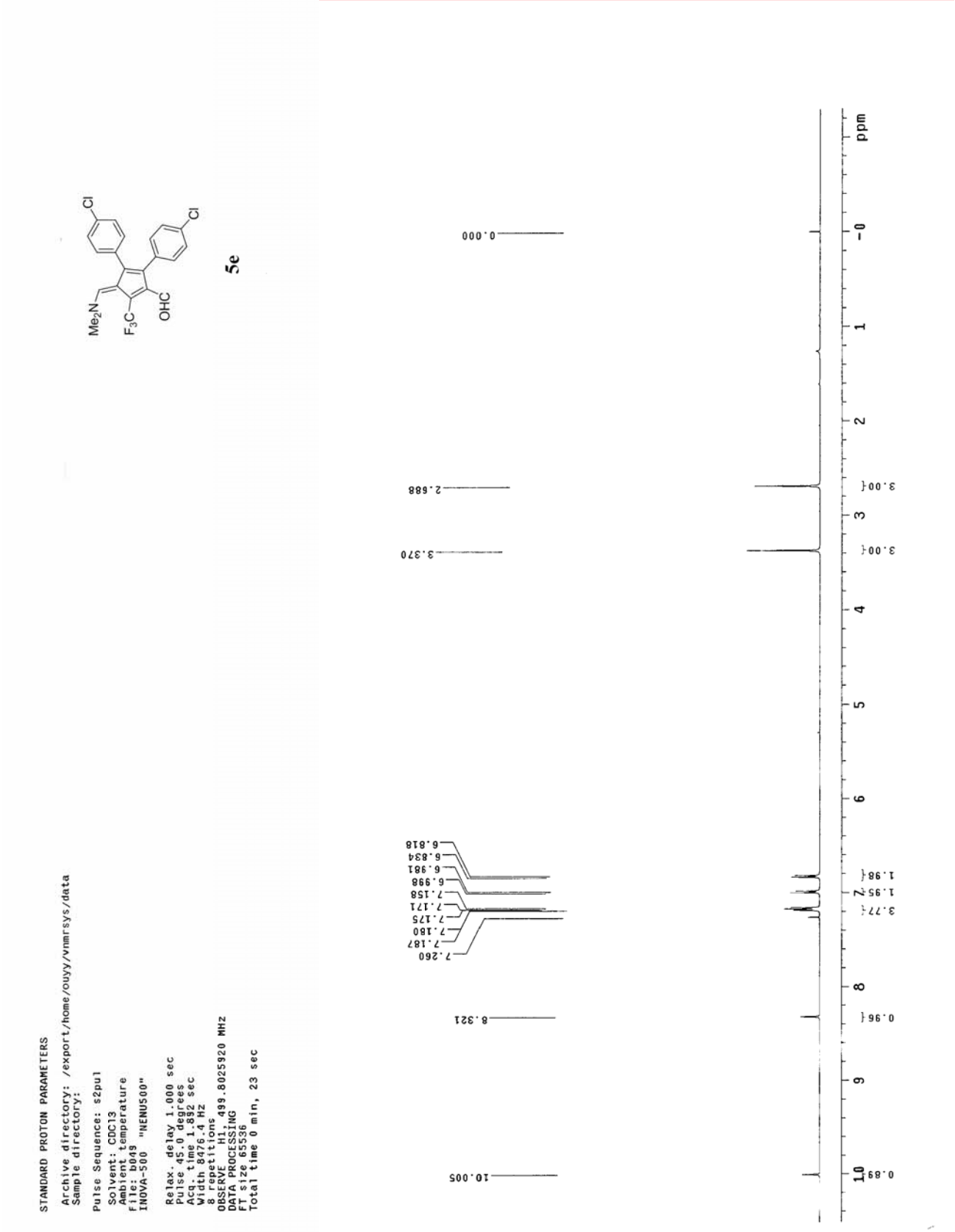

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
User: 1-14-87
File: u263
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 0.875 sec
Width 18868.4 Hz
180 repetitions
OBSERVE F19, 470.2852150 MHz
DECOUPLE H1, 499.8074646 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 524288
Total time 2 hr, 18 min, 22 sec
-50.506
Me2N
F3C
OHC
5b
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

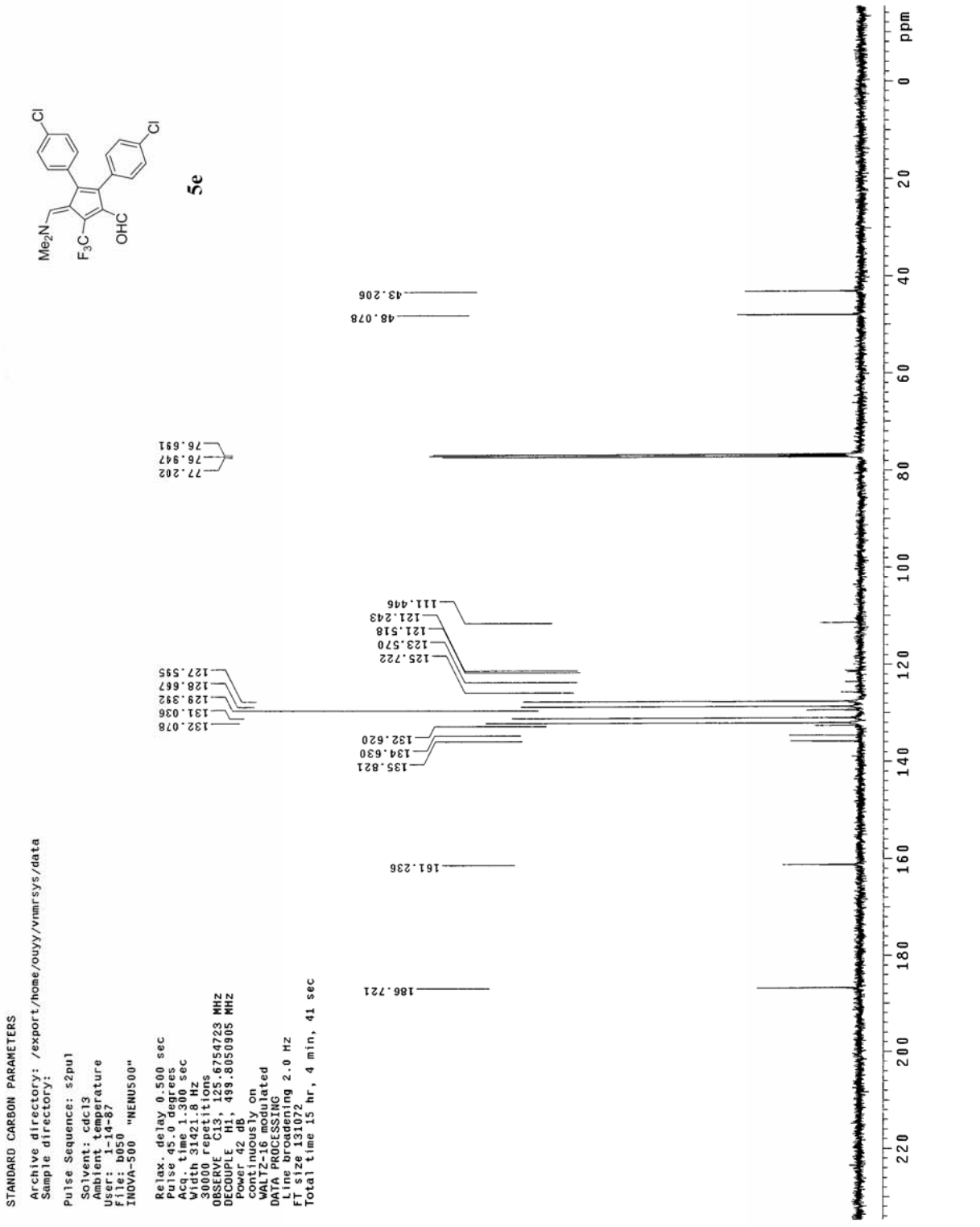

5c
Me2N
F3C
OHC
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 2017 "NENU500"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8241.5 Hz
8 repetitions
OBSERVE H1, 499.8025930 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
0.000
2.232
2.202
2.645
3.324
6.702
6.717
6.737
6.860
6.875
6.928
6.939
6.963
6.978
7.039
7.054
7.067
7.082
7.257
8.345
9.924
ppm

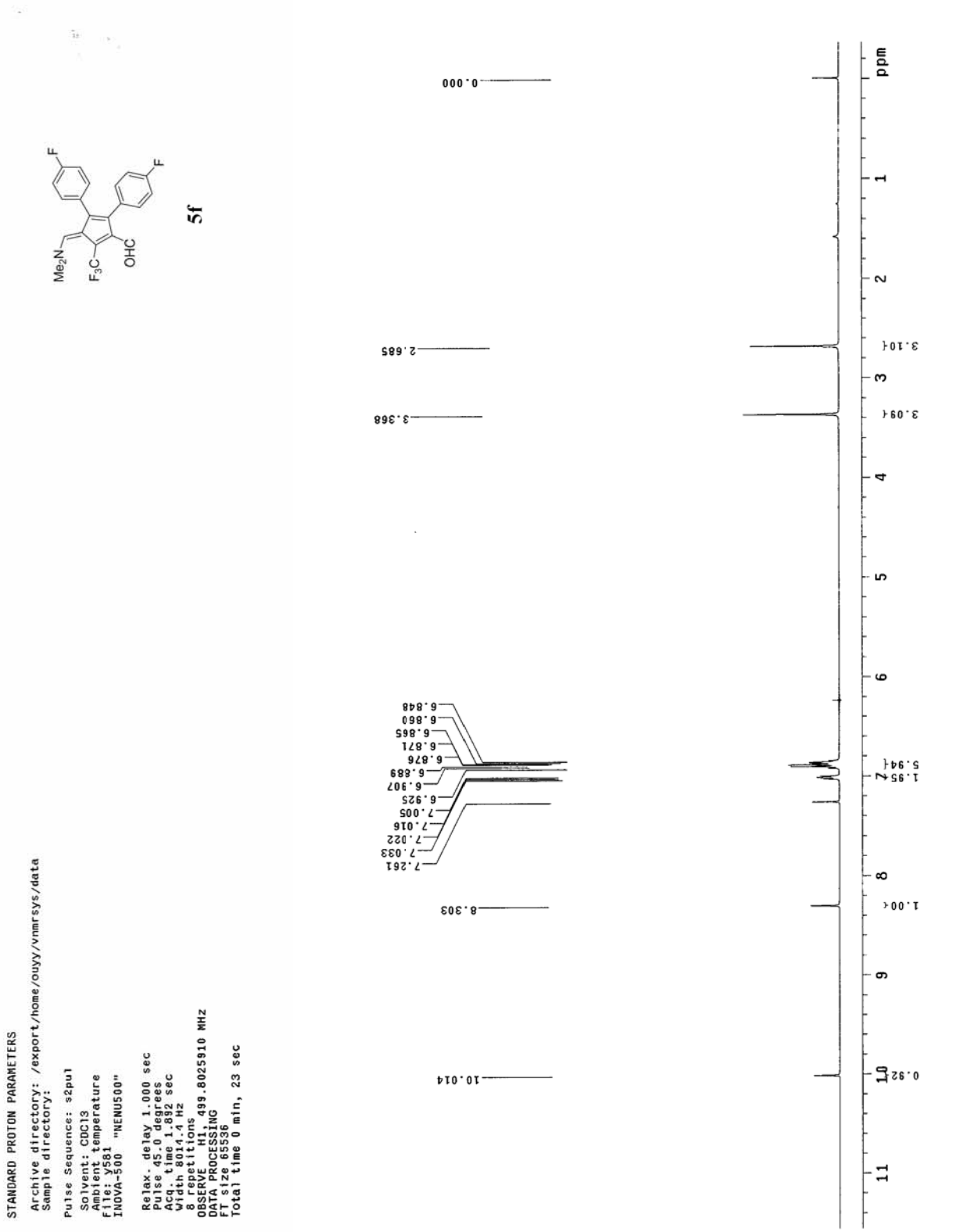


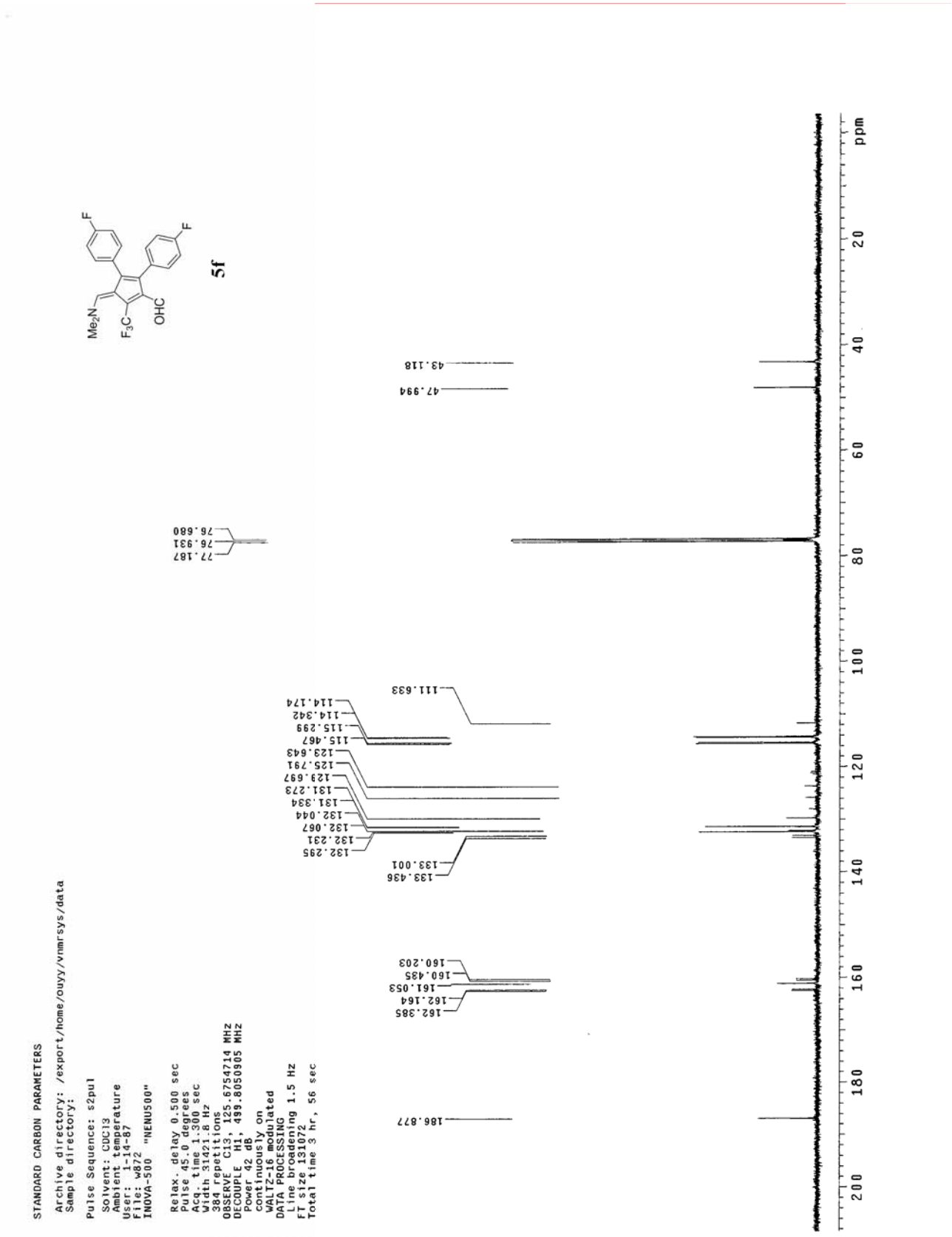


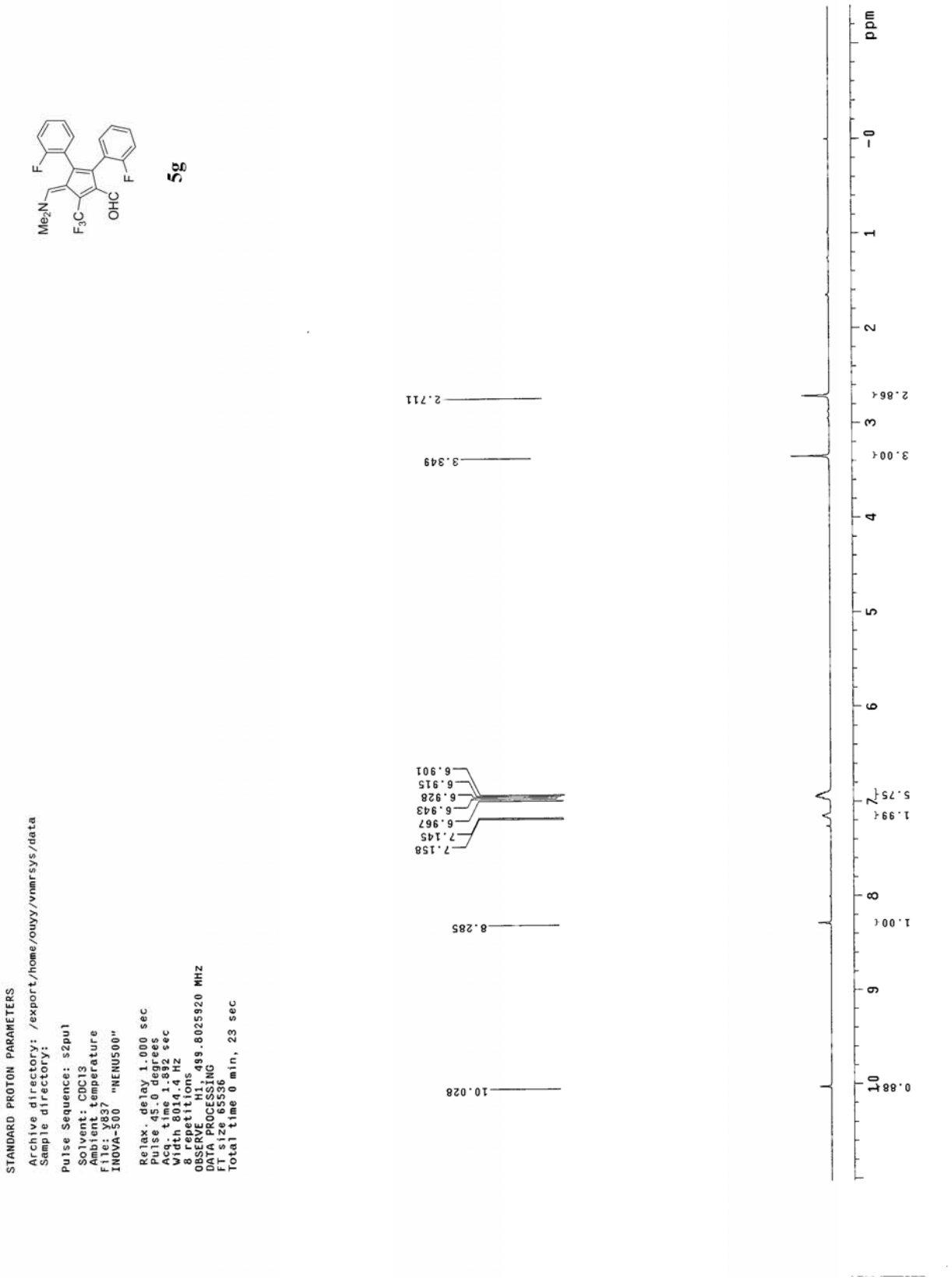

5d
OMe
OMe
Me2N
F3C
OHC
42.836
47.822
54.899
54.846
76.744
77.000
77.256
111.950
112.648
113.663
118.416
118.683
123.746
125.890
128.393
128.770
129.636
129.945
130.781
131.868
133.352
157.551
157.593
162.114
187.026
ppm
0
20
40
60
80
100
120
140
160
180
200
220
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: lzl-14-87
File: b209 "NENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
5632 repetitions
OBSERVE C13, 125.6754891 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

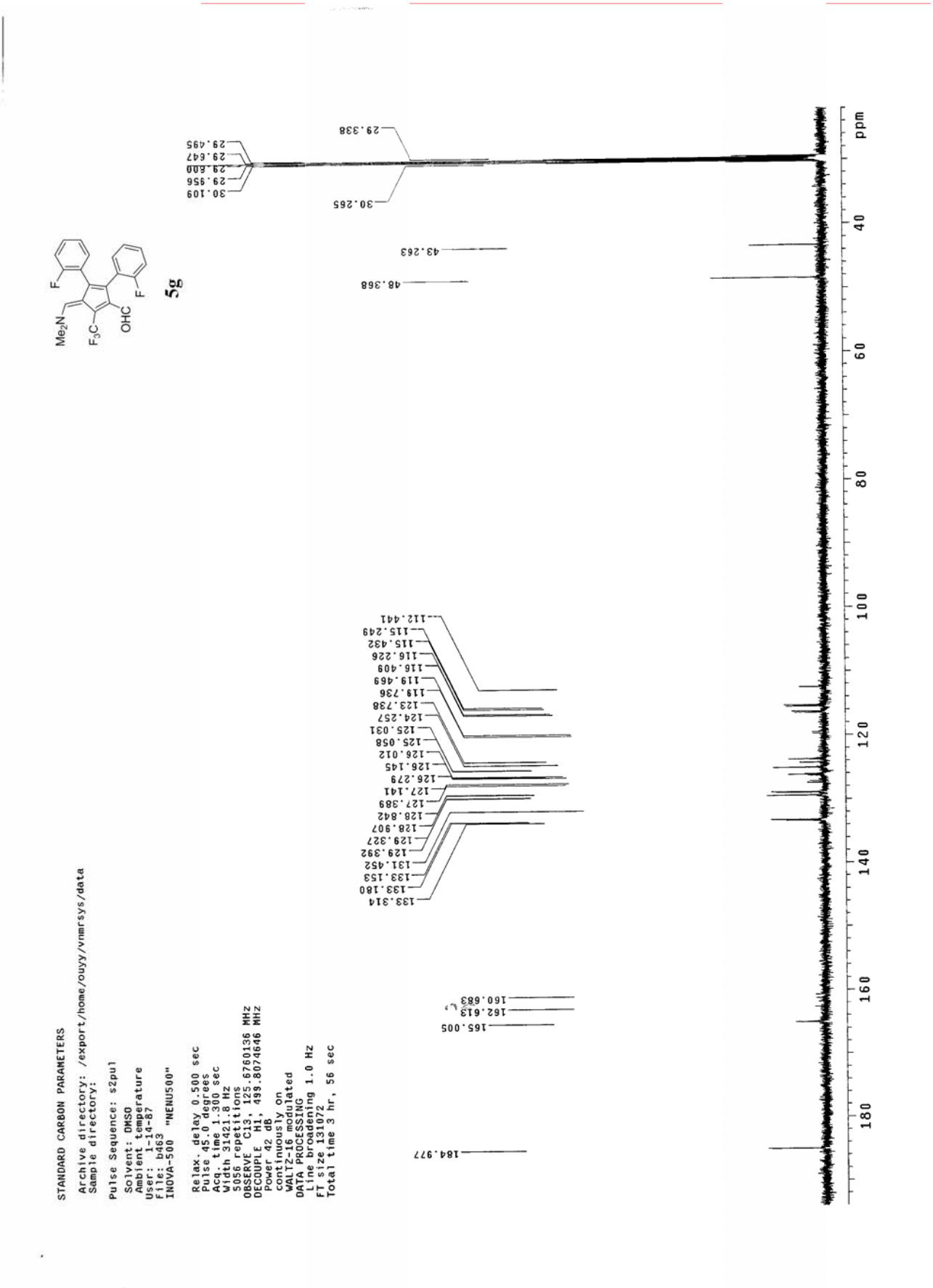

5e
Me2N
F3C
OHC
Cl
Cl
STANDARD PROTON PARAMETERS
Archive directory: /export1/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: b049
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 8476.4 Hz
8 repetitions
OBSERVE H1, 499.8025920 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
0.000
2.688
3.370
7.260
7.187
7.180
7.175
7.171
7.158
6.998
6.981
6.834
6.818
8.321
10.005
ppm

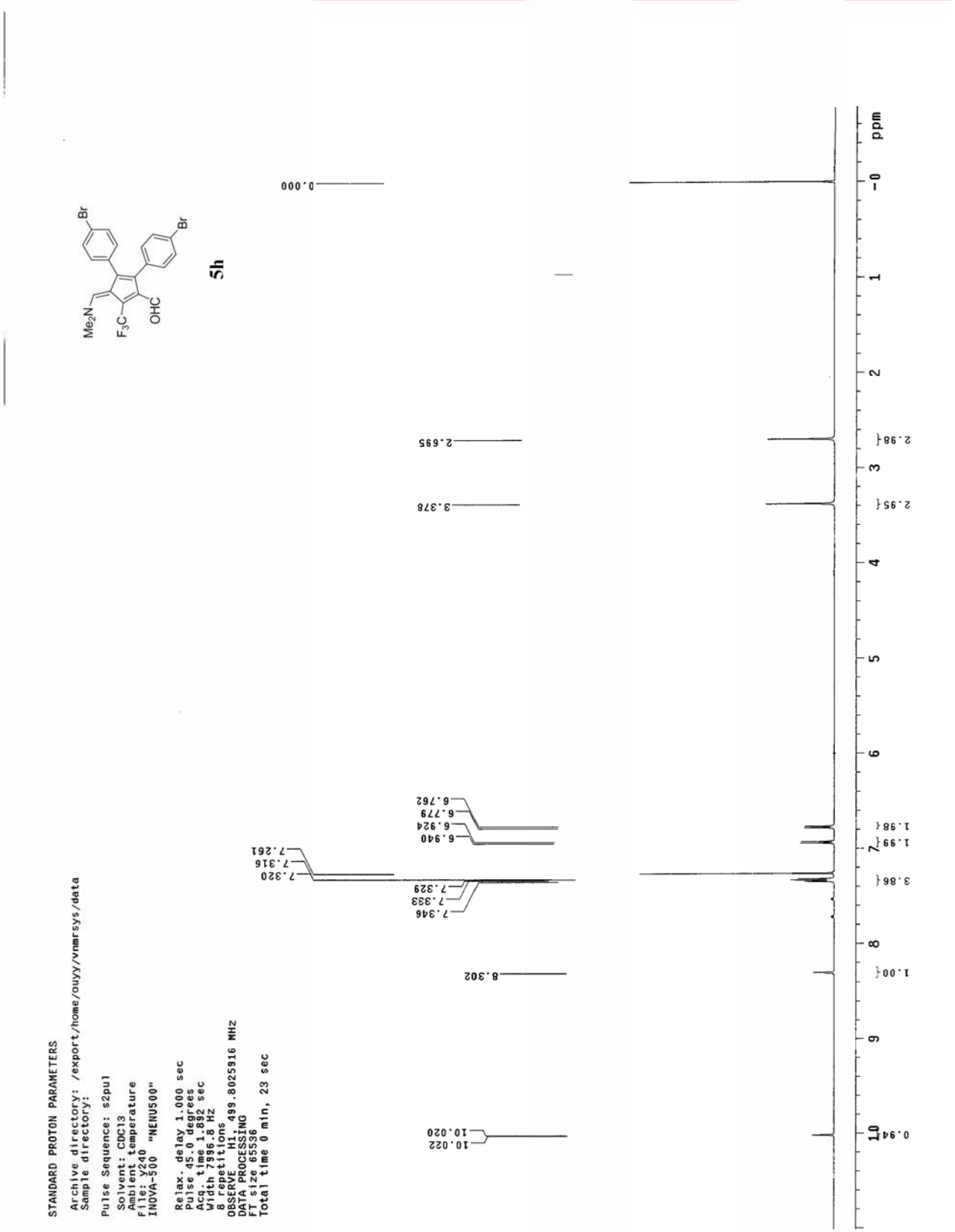


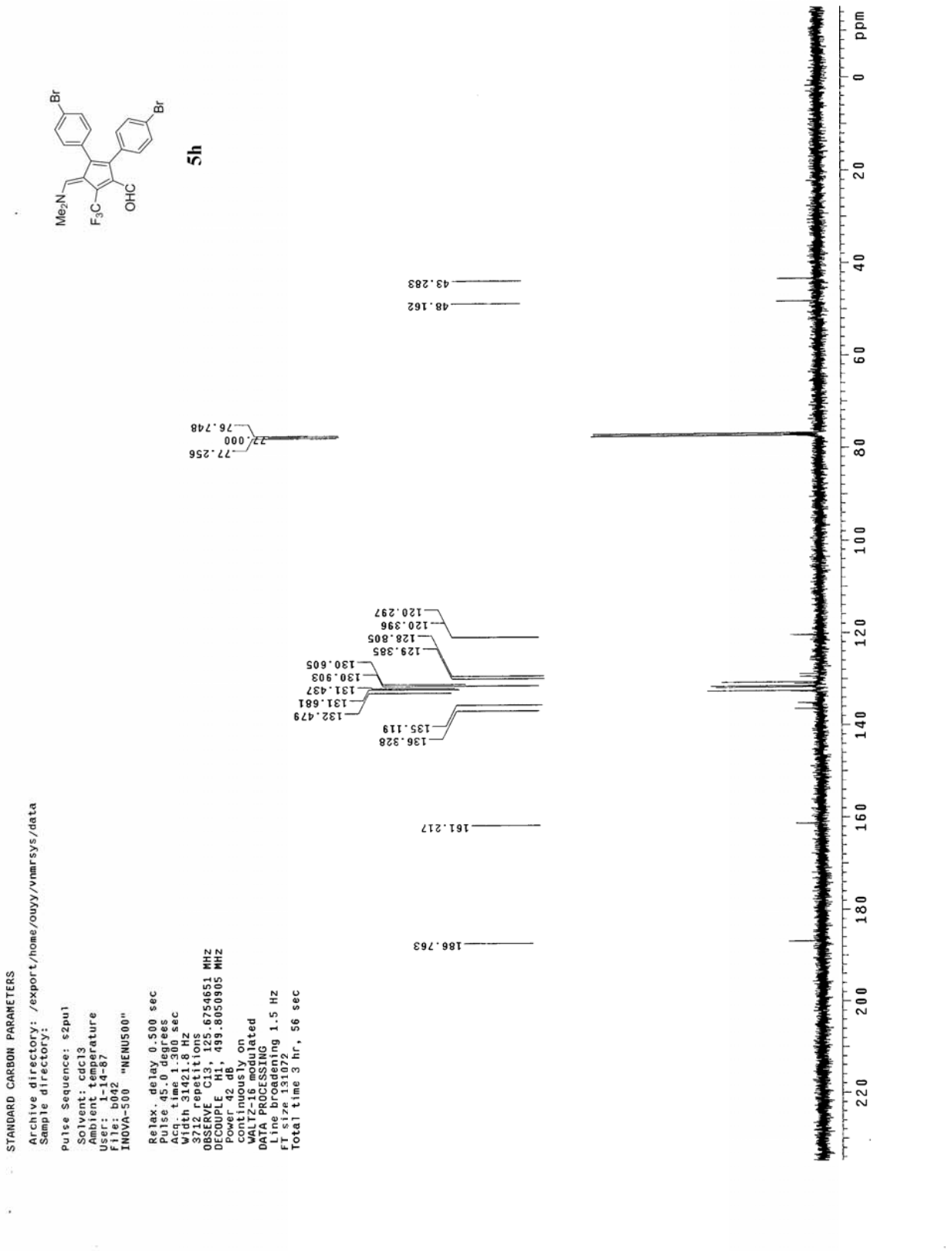



5f
F
F
Me2N
F3C
OHC
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: 1-14-87
File: w872 "NENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6754714 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec
186.877
162.385
162.164
161.053
160.485
160.203
133.436
133.001
132.295
132.231
132.067
132.044
131.334
131.273
129.697
125.791
123.643
115.467
115.299
114.342
114.174
111.633
77.187
76.931
76.680
47.994
43.118
ppm
200
180
160
140
120
100
80
60
40
20


5g
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: y837
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8014.4 Hz
8 repetitions
OBSERVE H1 499.8025920 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
10.028
8.285
7.158
7.145
6.967
6.943
6.928
6.915
6.901
3.349
2.711
ppm


5g
Me2N
F3C
OHC
F
F
29.338
30.265
43.263
48.368
112.441
115.249
115.432
116.226
116.409
119.469
119.736
123.738
124.257
125.031
125.058
126.012
126.145
126.279
127.141
127.389
128.842
128.907
129.327
129.392
131.452
133.153
133.180
133.314
160.683
162.613
165.005
184.977
ppm





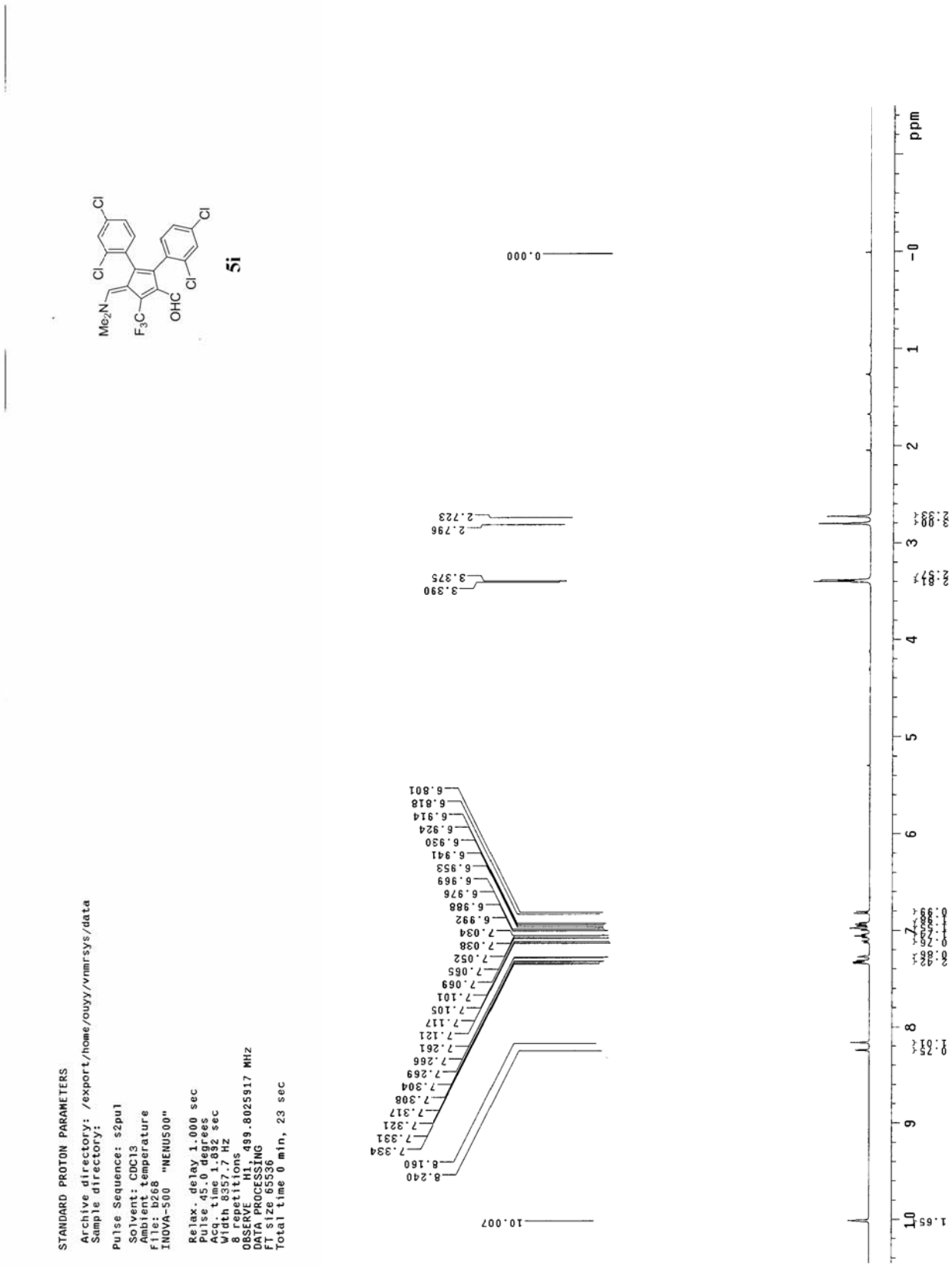
STANDARD CARBON PARAMETERS

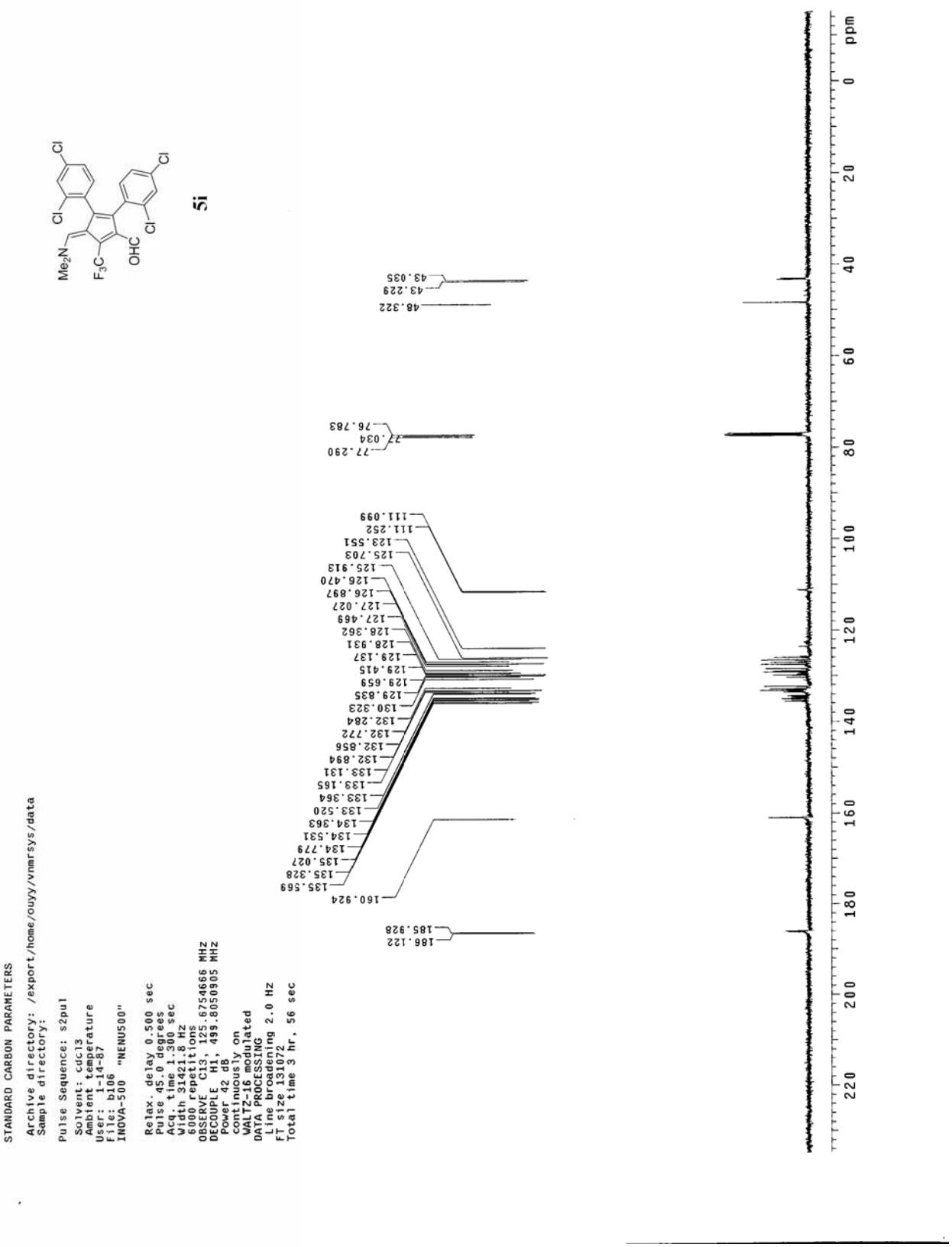
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:

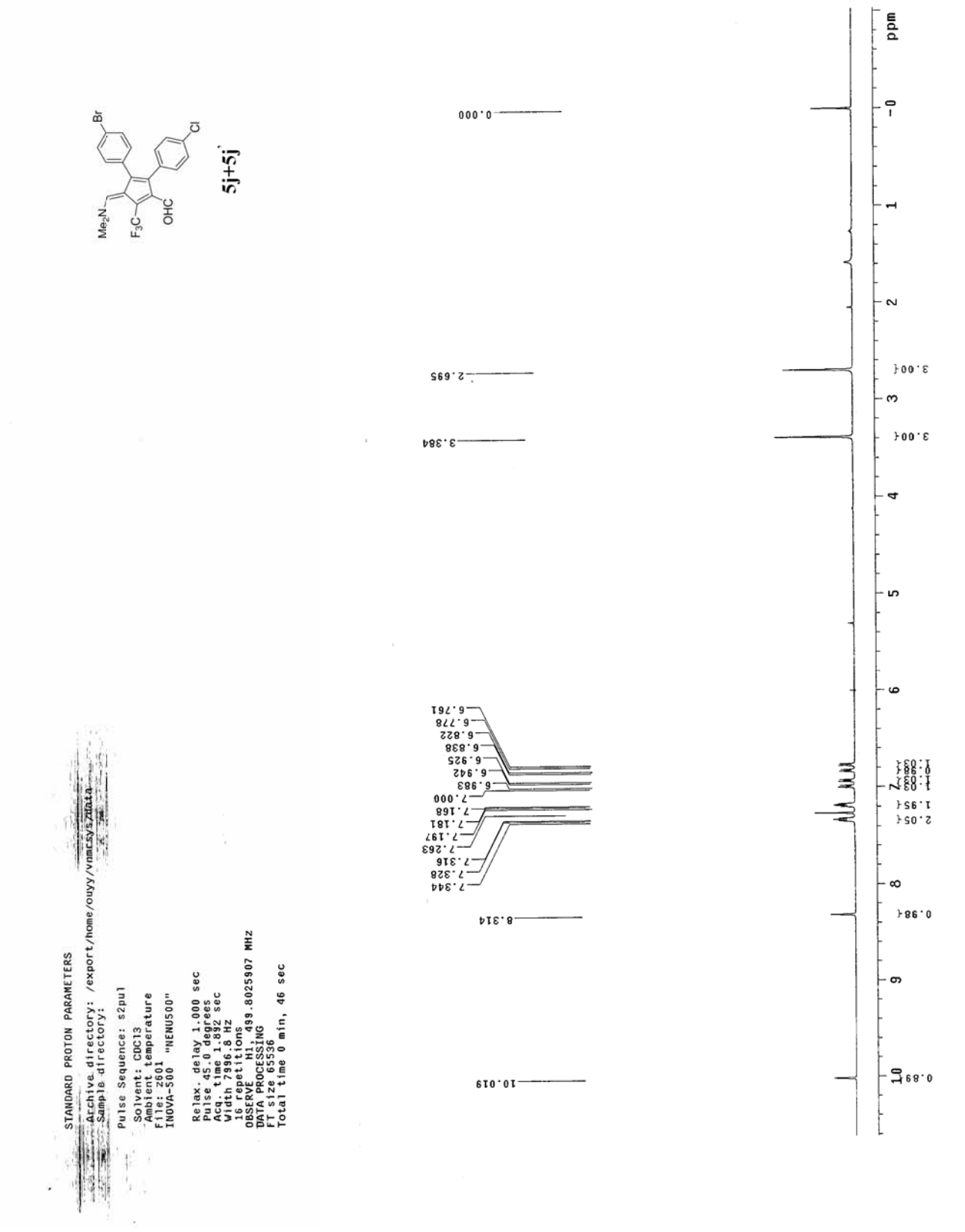
Pulse Sequence: s2pul

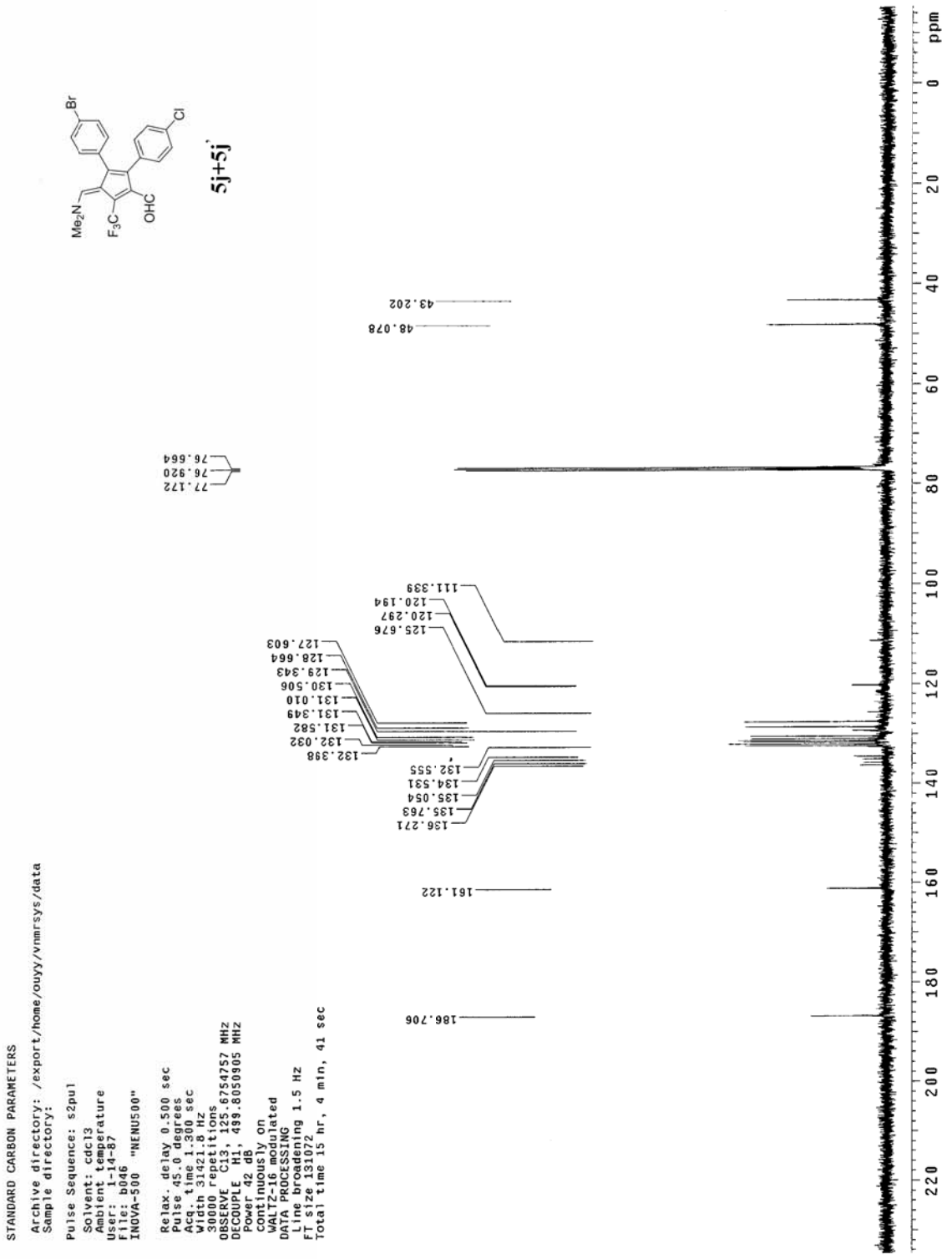
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: b042 "NENU500"
INOVA-500 "NENU500"

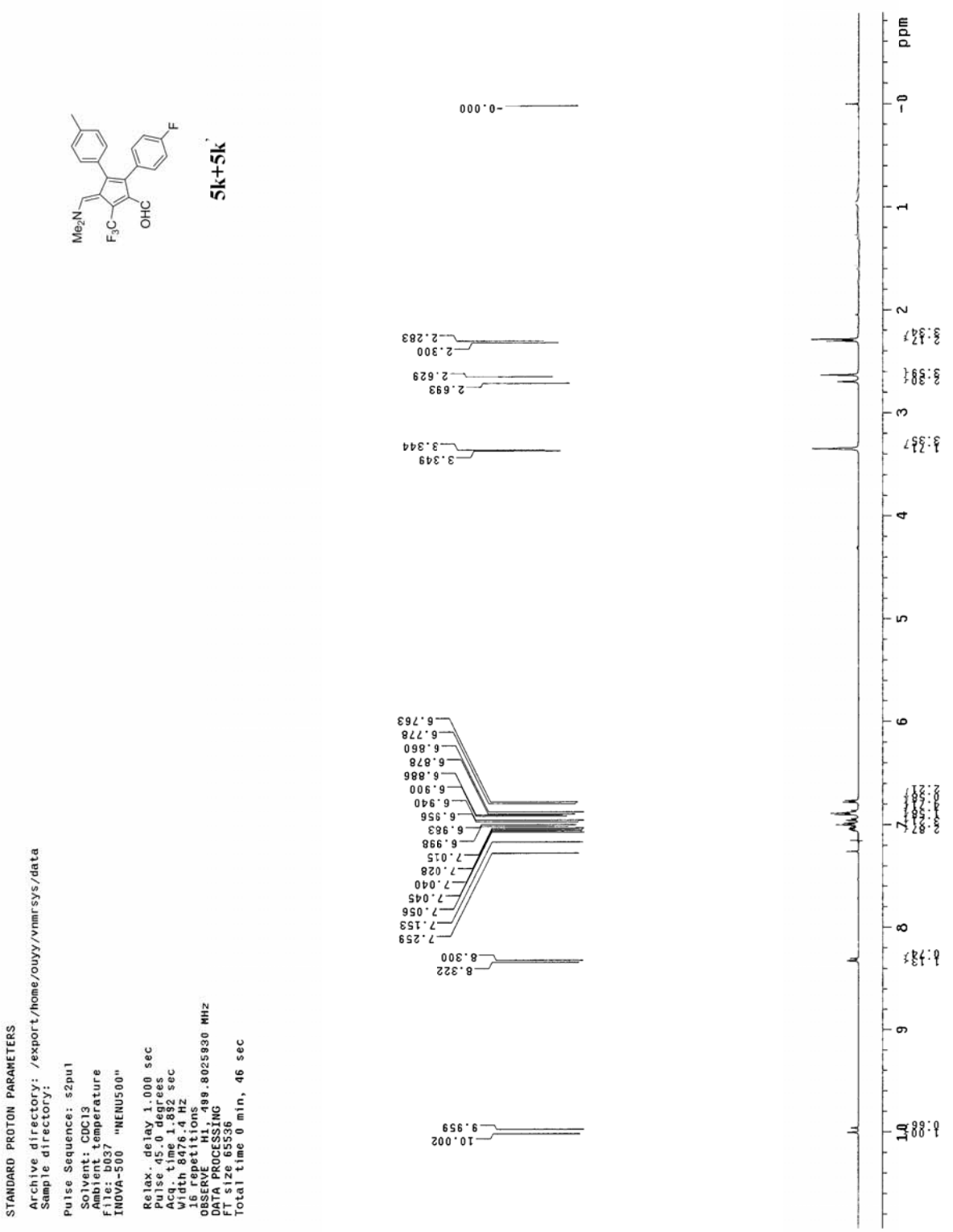
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
3712 repetitions
OBSERVE C13, 125.6754651 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec

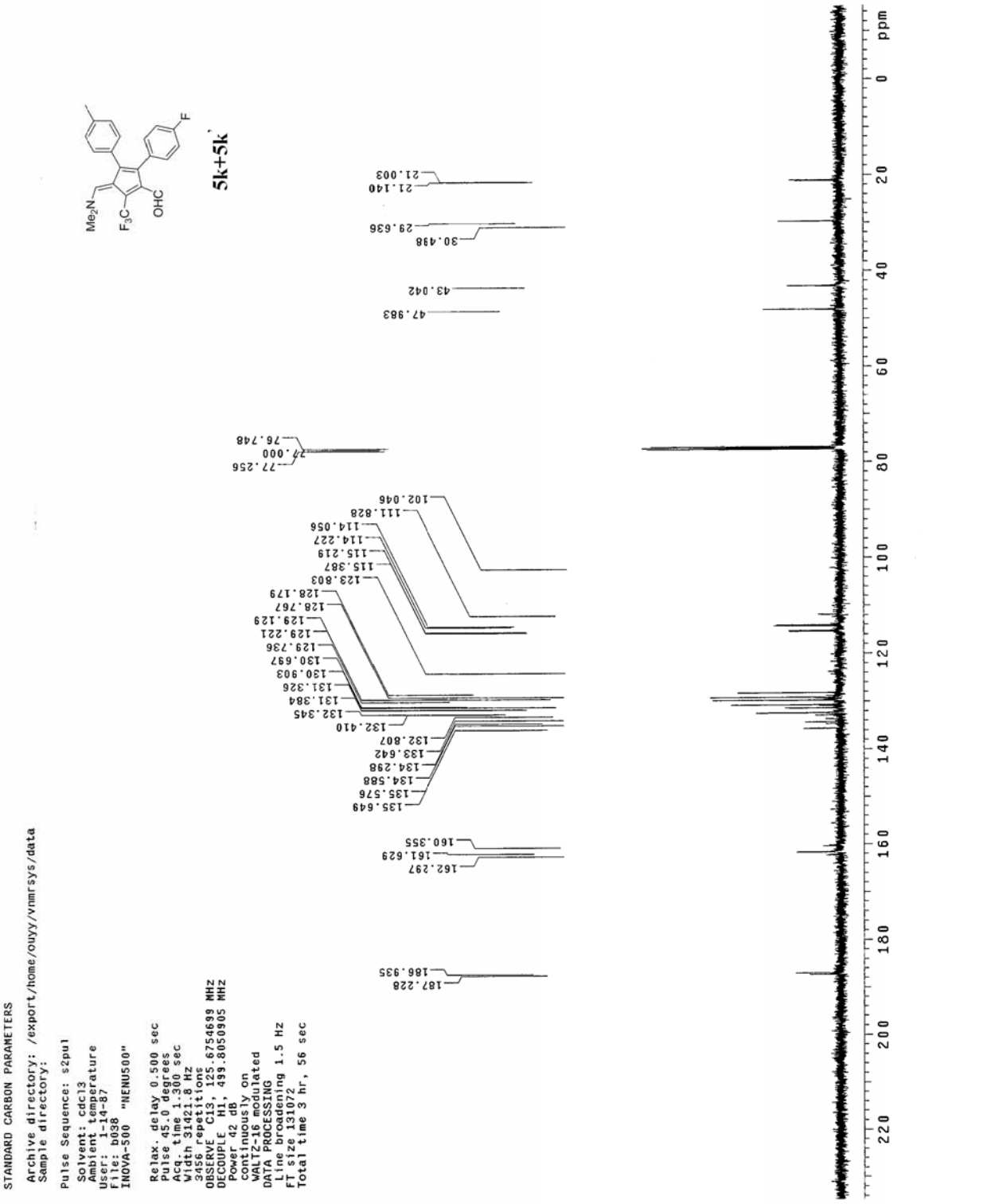

5i
Me2N
F3C
OHC
Cl
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: b268 "NENUS00"
INOVA-500
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.092 sec
Width 8357.7 Hz
8 repetitions
OBSERVE H1, 499.8025917 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
ppm

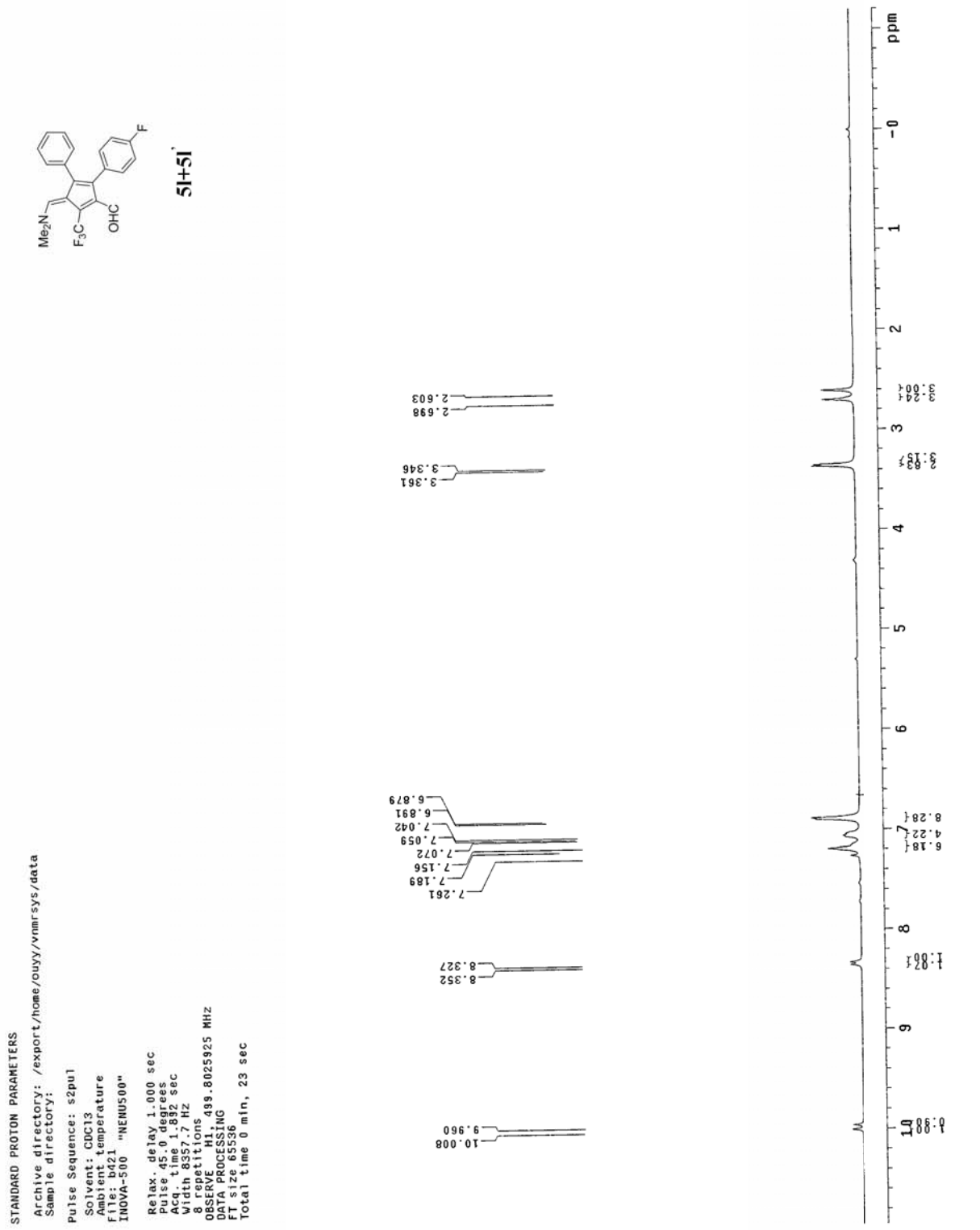


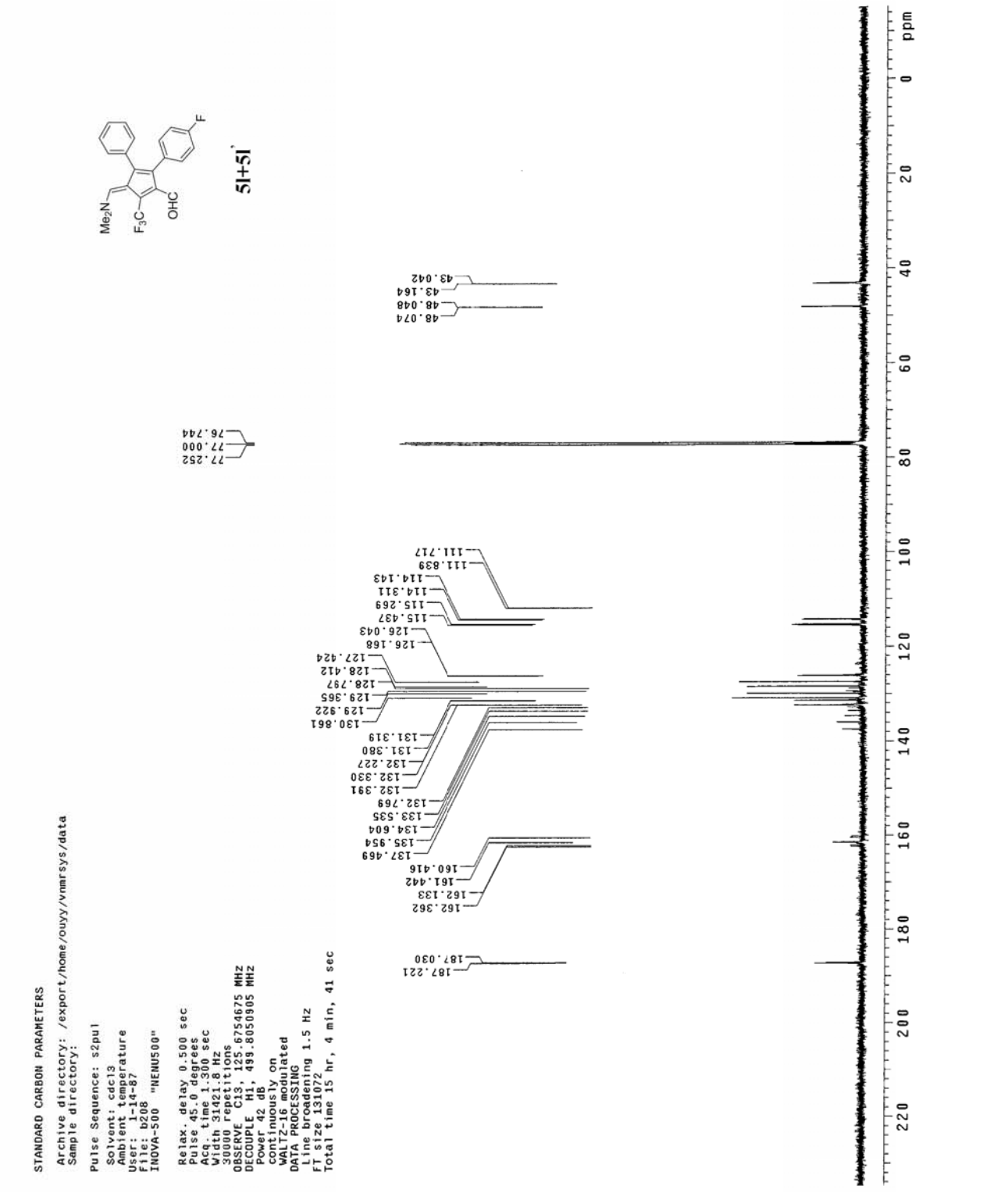


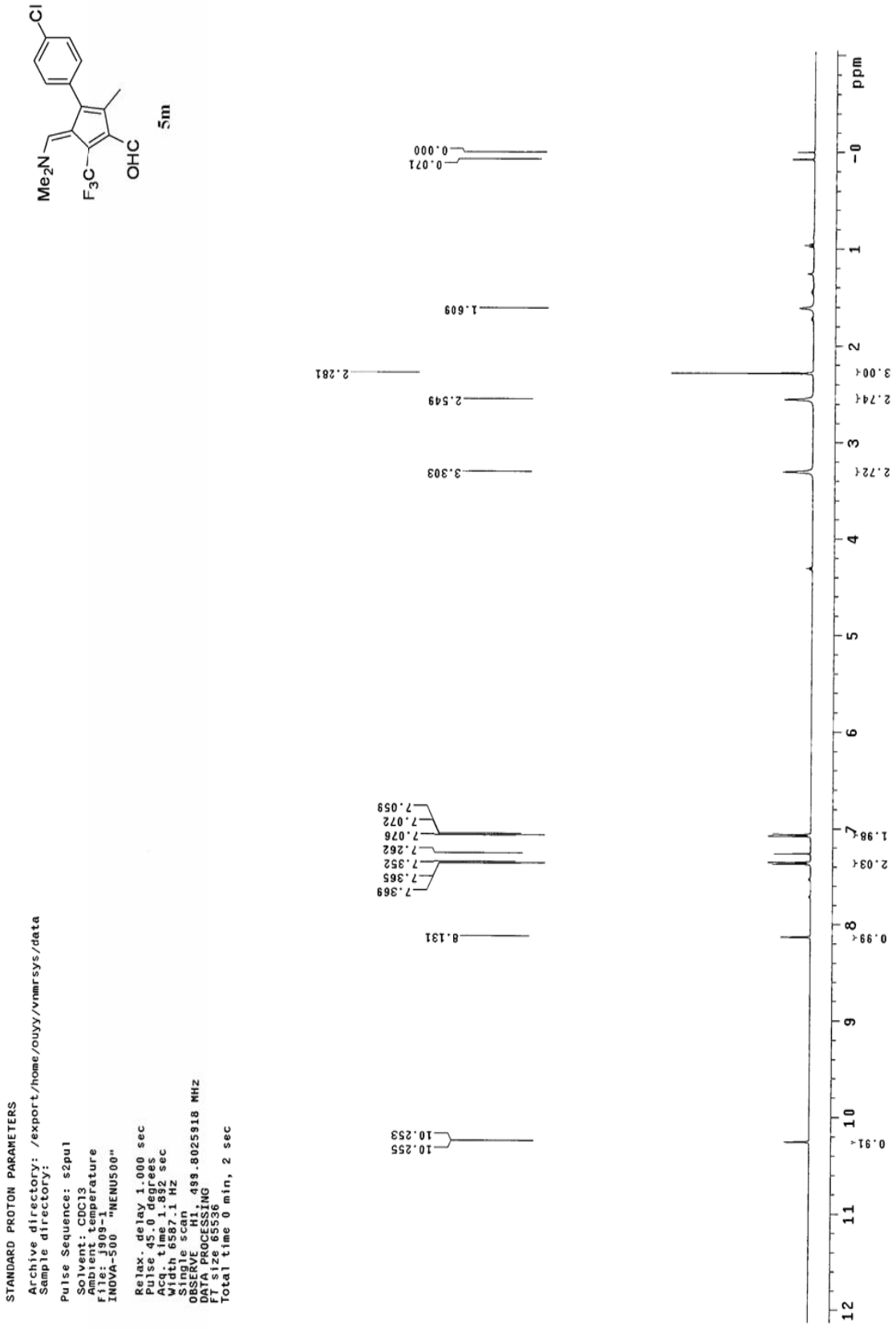

5j+5j'
Br
Cl
Me2N
F3C
OHC
STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: b046 "NENU500"
INOVA-500
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
30000 repetitions
OBSERVE C13, 125.6754757 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 15 hr, 4 min, 41 sec
186.706
161.122
136.271
135.763
135.054
134.531
132.555
132.398
132.032
131.582
131.349
131.010
130.506
129.343
128.664
127.603
125.676
120.297
120.194
111.339
77.172
76.920
76.664
48.078
43.202
ppm

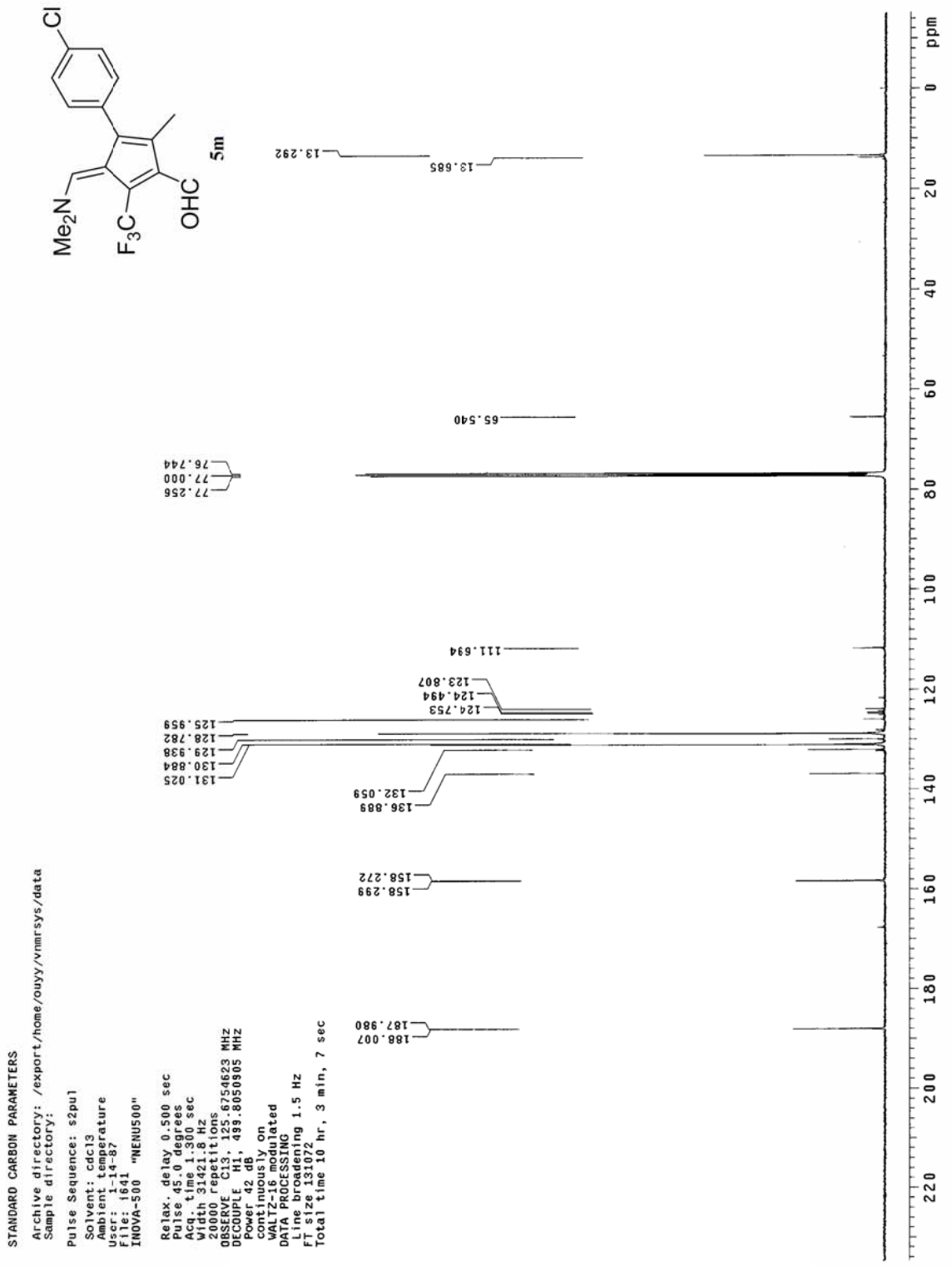

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: b037 "MENU500"
INOVA-500 "MENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 8476.4 Hz
16 repetitions
OBSERVE H1, 499.8025930 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 46 sec
Me2N
F3C
OHC
F
5k+5k'
10.002
9.959
8.322
8.300
7.259
7.153
7.056
7.045
7.040
7.028
7.015
6.998
6.963
6.956
6.940
6.900
6.886
6.878
6.860
6.778
6.763
3.349
3.344
2.693
2.629
2.300
2.283
0.000
ppm

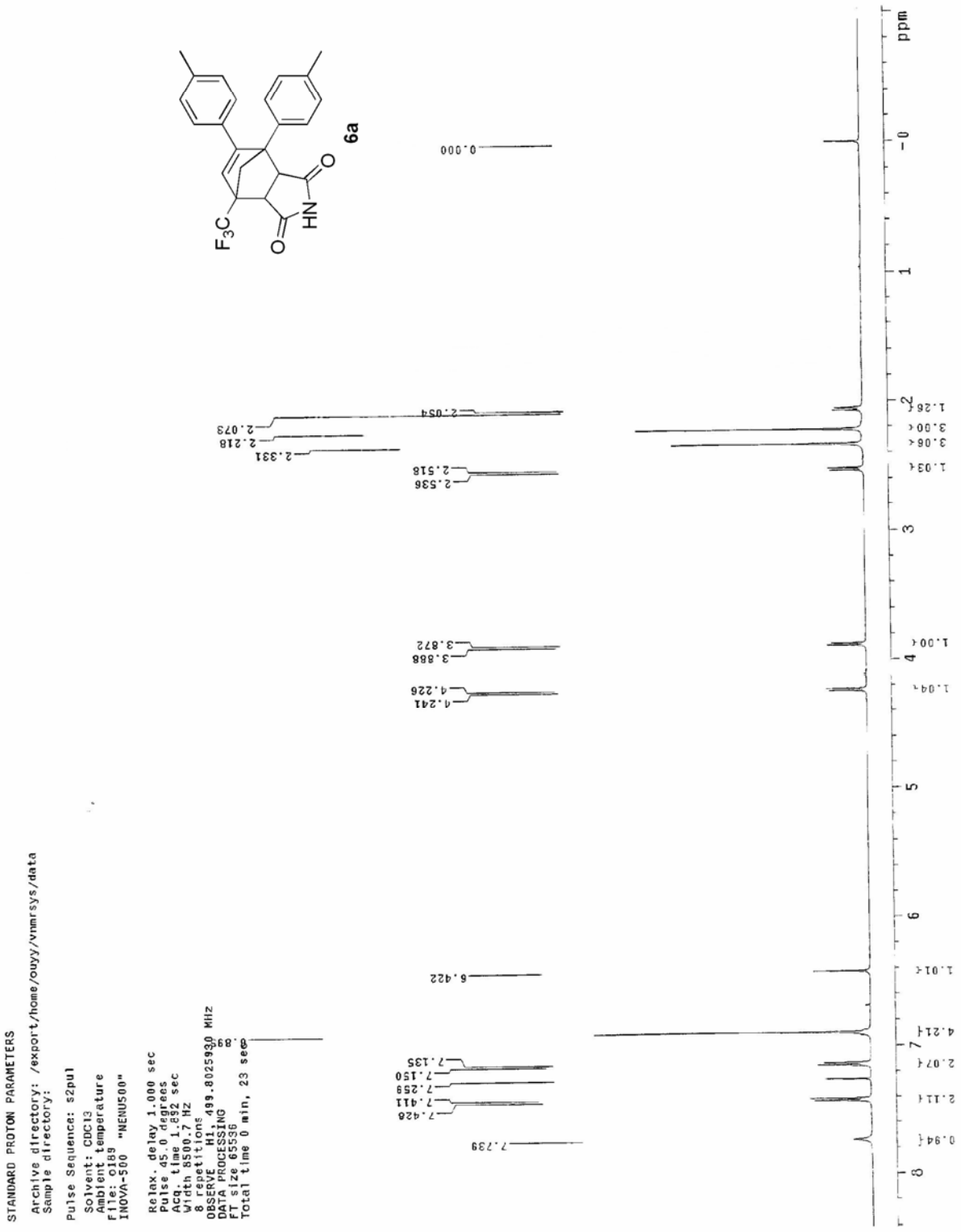


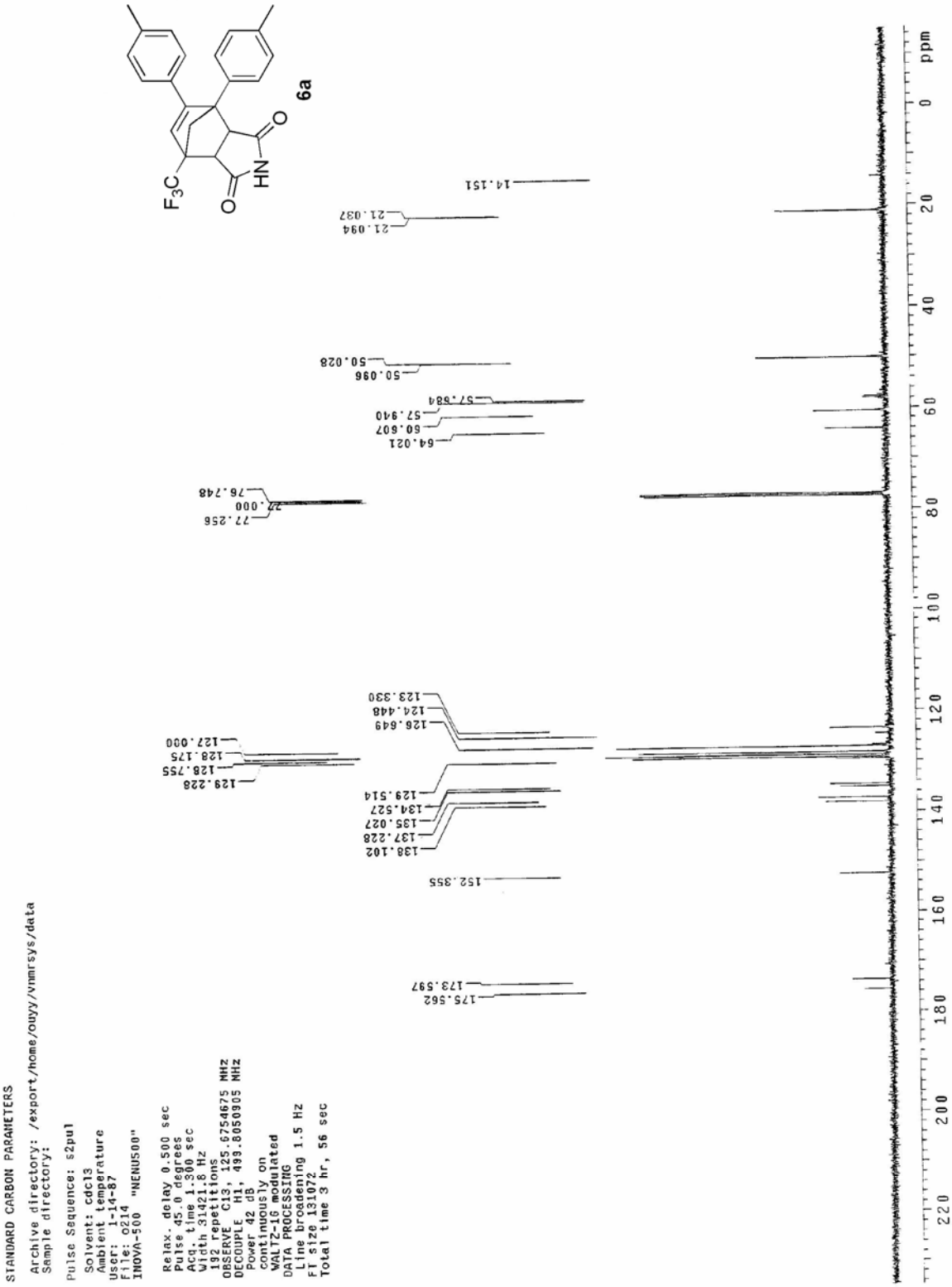

5l+5l'
Me2N
F3C
OHC
F
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: h421
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 8357.7 Hz
8 repetitions
OBSERVE H1, 499.8025925 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
10.008
9.960
8.352
8.327
7.261
7.189
7.156
7.072
7.059
7.042
6.891
6.879
3.361
3.346
2.698
2.603
ppm

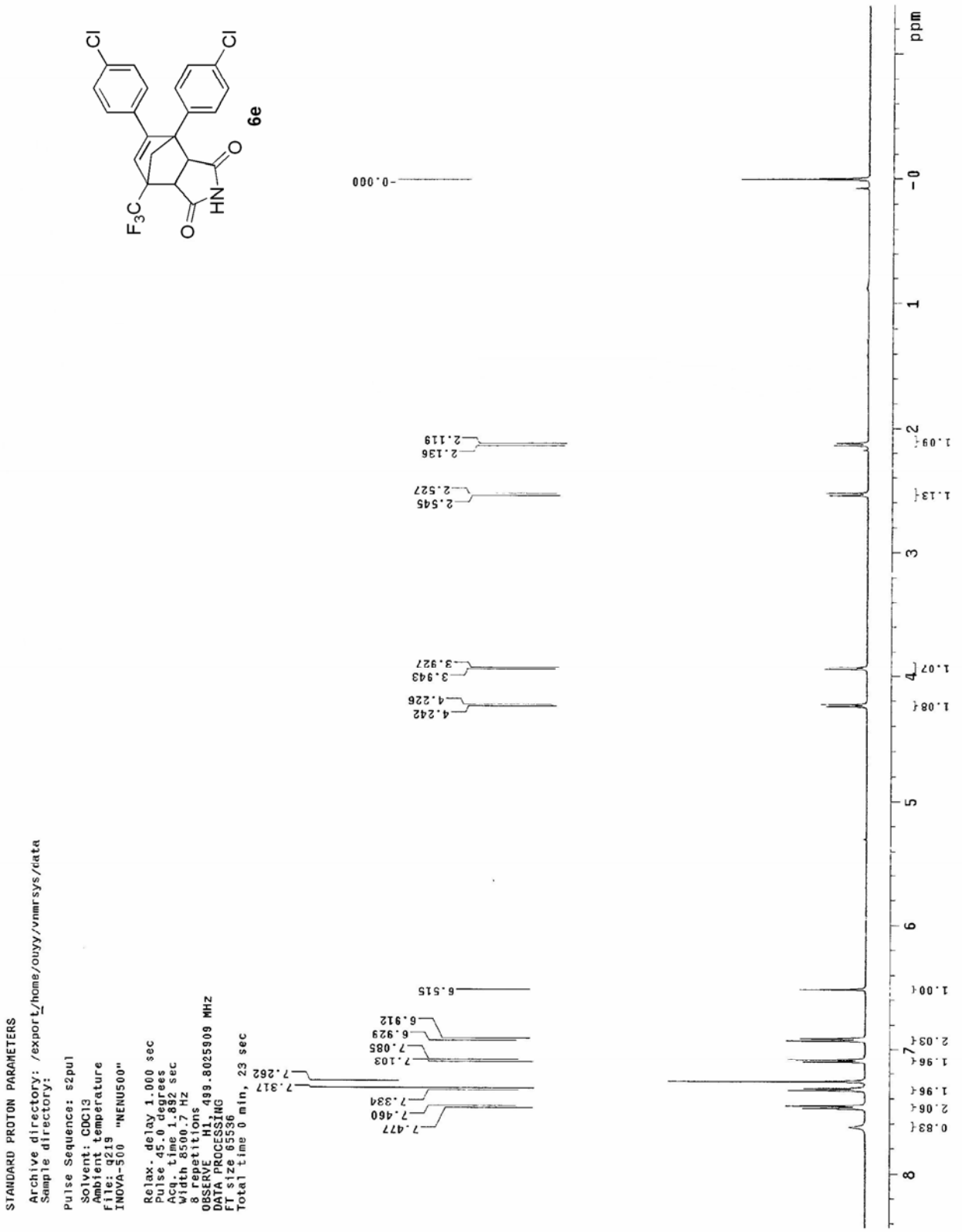


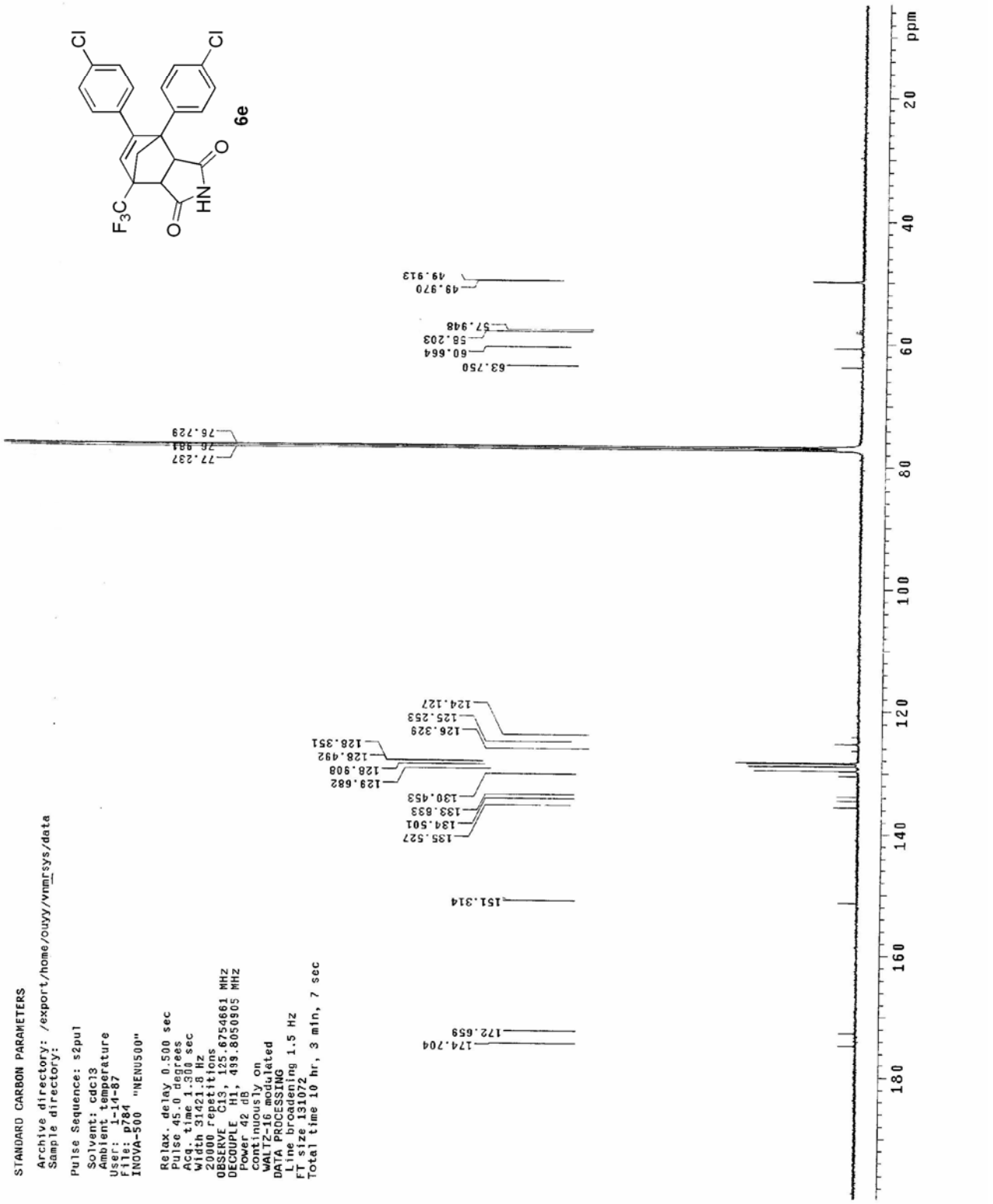

Cl
Me2N
F3C
OHC
5m
STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: j909-1
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 6587.1 Hz
Single scan
OBSERVE H1, 499.8025918 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 2 sec
0.000
0.071
1.609
2.281
2.549
3.303
7.059
7.072
7.076
7.262
7.352
7.365
7.369
8.131
10.253
10.255
ppm



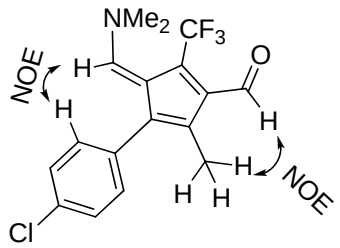




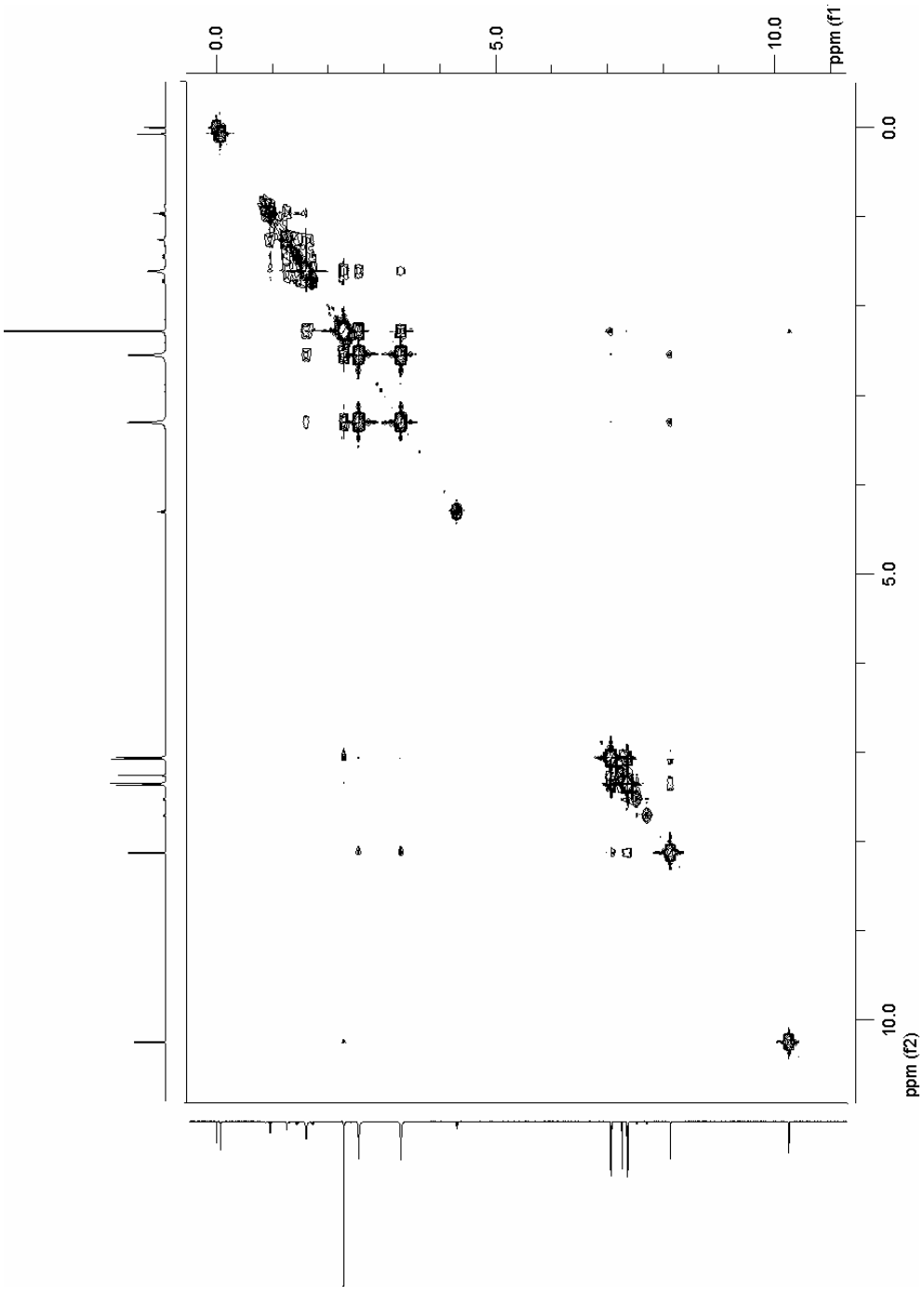




VIII. ^{1}H-^{1}H NOESY spectrum of **5m**.

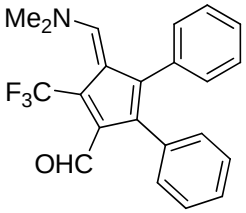


5m

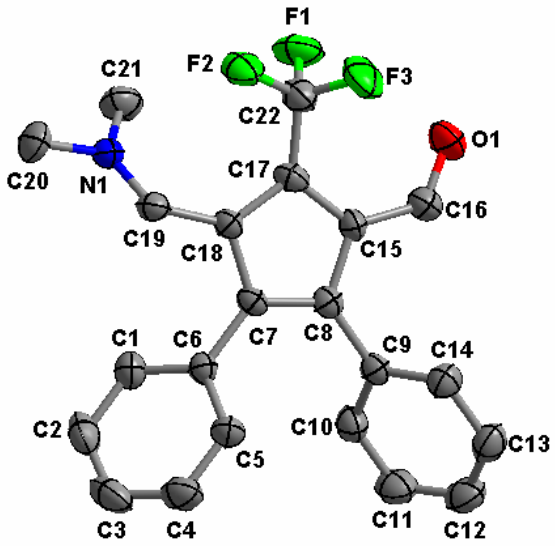


IX. Crystal data and OPTEP drawing of compound **5b**

1. ORTEP drawing of compound **5b**



5b



2. Crystal data

5b: $C_{22}H_{18}F_3NO$, colorless, Mr = 369.37, monoclinic, space group P2(1)/c, a = 17.229(3), b = 8.7040(9), c = 12.3240(12) Å, α=90.000, β= 103.236(2), γ= 90.000º, V = 1799.0(4) Å3, Z = 4, ρcalcd = 1.364, T = 293(2) K, 8807 reflections (3203 unique), 244 refined parameters, R1 = 0.0564 (I > 2σ(I)), wR2(F2) = 0.1370. The hydrogen atoms were refined as rigid groups. CCDC deposition number: 851500 (**5b**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).