**SUPPORTING INFORMATION**

# *trans-Hydroboration-Oxidation products in Δ⁵-steroids via a hydroboration-retro-hydroboration mechanism*

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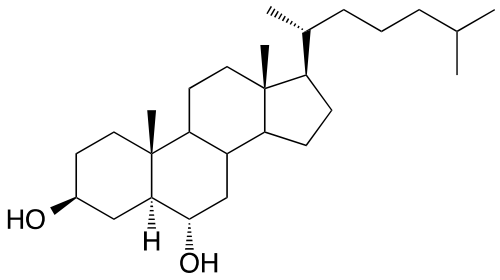
## I. Experimental section

### a. *General remarks*

Optical rotations were measured at 25 ºC in an Anton-Paar MCP500 polarimeter. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 500 and 125 MHz, respectively, on a Bruker Avance NMR instrument. The $^{1}H$ NMR spectra were referenced to residual protonated solvent (δ 7.26 ppm for $CDCl_3$ and 7.58 for Py-$d_5$) and the $^{13}C$ NMR spectra to the middle signal of $CDCl_3$ (77.0 ppm) or Py-$d_5$ (135.9). Processing of the spectra was performed using MestReNova software. High-resolution mass spectra were obtained by the electrospray ionization (ESI) technique, using an Agilent 6230 TOF LC/MS mass spectrometer. IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer (range: 4000-600 $cm^{-1}$). Column chromatography was carried out using a Teledyne Isco *Combiflash* apparatus and analytical thin-layer chromatography (TLC) on aluminum plates precoated with Silica Gel 60F-254.

### b. *Characterization data*

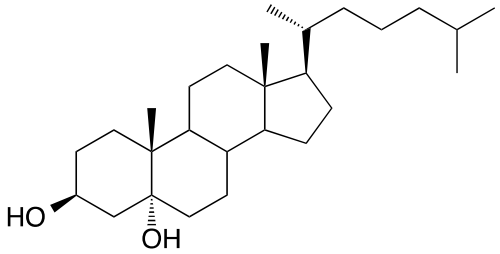
*5α-Cholestane-3β,6α-diol (**1a**)*




The purification of **1a** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 6:4 hexane/ethyl acetate for 30 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 219 – 221 °C. $R_f$ 0.283 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +38 (*c* 1.0, $CHCl_3$). IR: 3265 (OH), 2929 (CH, aliphatic). $^{1}H$ NMR (500 MHz, $CDCl_3$ δ): 3.58 (1H, m, H-3), 3.41 (1H, ddd, $J_{6,5}$ = $J_{6,7ax}$ = 10.7 Hz, $J_{6,7eq}$ = 4.1 Hz, H-6), 2.18 (1H, m, H-4), 1.98 (1H, m, H-12), 1.98 (1H, ddd, $J_{7\text{-}6}$ = $J_{7,8}$ = 4.7 Hz, $J_{gem}$ = 11.1 Hz, H-7), 0.89 (3H, d, $J_{21,20}$ = 6.6 Hz, $CH_3$-21), 0.86 (3H, d, $J_{26,25}$ = 2.5 Hz, $CH_3$-26), 0.85 (3H, d, $J_{27,25}$ = 2.5 Hz, $CH_3$-27), 0.81 (3H, s, $CH_3$-19), 0.64

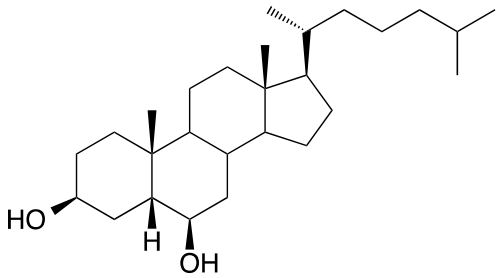
(3H, s, $CH_3$-18). $^{13}C$ NMR (125 MHz, $CDCl_3$ δ): 37.4 (C-1), 31.2 (C-2), 71.4 (C-3), 32.4 (C-4), 51.8 (C-5), 69.7 (C-6), 41.8 (C-7), 34.4 (C-8), 53.9 (C-9), 36.4 (C-10), 21.3 (C-11), 39.9 (C-12), 42.7 (C-13), 56.3 (C-14), 24.3 (C-15), 28.3 (C-16), 56.3 (C-17), 12.2 (C-18), 13.6 (C-19), 35.9 (C-20), 18.8 (C-21), 36.3 (C-22), 23.9 (C-23), 39.6 (C-24), 28.2 (C-25), 22.7 (C-26), 23.0 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{48}O_2$ Calcd: 404.3654. Found: 427.3543 $[M+Na]^+$.

*5α-Cholestane-3β,5-diol (**1b**)*



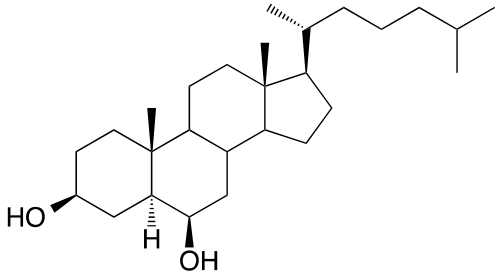

The purification of **1b** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 85:15 hexane/ethyl acetate for 30 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 223 – 224 °C. $R_f$ 0.380 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +19 (*c* 1.0, $CHCl_3$). IR: 3421, 3309 (OH), 2933 (CH, aliphatic). $^1H$ NMR (500 MHz, $CDCl_3$ δ): 4.09 (1H, m, H-3), 1.98 (1H, m, H-12*eq*), 0.99 (3H, s, $CH_3$-19), 0.89 (3H, d, $J_{21,20}$ = 6.5 Hz, $CH_3$-21), 0.86 (3H, d, $J_{26,25}$ = 2.4 Hz, $CH_3$-26), 0.85 (3H, d, $J_{27,25}$ = 2.4 Hz, $CH_3$-27), 0.65 (3H, s, $CH_3$-18). $^{13}C$ NMR (125 MHz, $CDCl_3$ δ): 31.0 (C-1), 30.9 (C-2), 67.5 (C-3), 44.0 (C-4), 75.5 (C-5), 34.5 (C-6), 26.1 (C-7), 34.8 (C-8), 46.1 (C-9), 38.9 (C-10), 21.5 (C-11), 40.2 (C-12), 42.8 (C-13), 56.3 (C-14), 24.2 (C-15), 28.4 (C-16), 56.4 (C-17), 12.3 (C-18), 16.4 (C-19), 36.0 (C-20), 18.8 (C-21), 36.3 (C-22), 24.0 (C-23), 39.6 (C-24), 28.2 (C-25), 22.7 (C-26), 23.0 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{48}O_2$ Calcd: 404.3654. Found: 427.3551 $[M+Na]^+$.

*5β-Cholestane-3β,6β-diol (**1c**)*




The purification of **1c** was achieved from an enriched fraction mixed with **1e** employing *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 85:15 hexane/ethyl acetate for 60 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 194 – 196 °C. $R_f$ 0.348 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +38 (*c* 1.0, $CHCl_3$:MeOH). IR: 3377 (OH), 2928, 2867 (CH, aliphatic). $^1$H NMR (500 MHz, $CDCl_{30,}$ δ): 4.09 (1H, $m_{br}$, H-3), 3.70 (1H, $m_{br}$, H-6), 2.00 (1H, ddd, $J_{gem}$ = 12.8 Hz, $J_{4eq,5}$ = 4.2 Hz, $J_{4eq,3}$ = 3.1 Hz, H-1*eq*), 1.82 (1H, ddd, $J_{7\text{-}6} = J_{7,8}$ = 4.0 Hz, $J_{gem}$ = 8.0 Hz, H-7), 1.77 (1H, m, H-5), 1.14 (3H, s, $CH_3$-19), 0.90 (3H, d, $J_{21,20}$ = 6.7 Hz, $CH_3$-21), 0.87 (3H, d, $J_{26,25}$ = 2.3 Hz, $CH_3$-26), 0.85 (3H, d, $J_{27,25}$ = 2.3 Hz, $CH_3$-27), 0.68 (3H, s, $CH_3$-18). $^{13}$C NMR (125 MHz, $CDCl_3$ δ): 40.1 (C-1), 34.4 (C-2), 66.2 (C-3), 33.6 (C-4), 43.7 (C-5), 73.4 (C-6), 28.3 (C-7), 24.2 (C-8), 30.6 (C-9), 34.8 (C-10), 20.9 (C-11), 40.1 (C-12), 42.7 (C-13), 56.5 (C-14), 30.1 (C-15), 27.5 (C-16), 56.3 (C-17), 12.1 (C-18), 26.2 (C-19), 35.8 (C-20), 18.7 (C-21), 36.1 (C-22), 23.8 (C-23), 39.5 (C-24), 28.0 (C-25), 22.6 (C-26), 22.6 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{48}O_2$ Calcd: 404.3654. Found: 427.3552 $[M+Na]^+$.

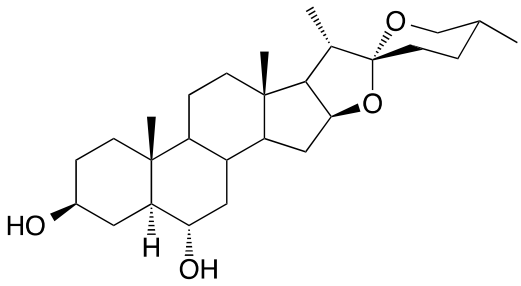
*5α-Cholestane-3β,6β-diol (**1e**)*




The purification of **1e** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 6:4 hexane/ethyl acetate for 30 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 192-193 °C. $R_f$ 0.348 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +11 (*c* 1.0, $CHCl_3$). IR: 3402 (OH),

2932 (CH, aliphatic). $^{1}$H NMR (500 MHz, $CDCl_3$ δ): 3.79 (1H, ddd, $J_{6,5} = J_{6,7ax} = 2.8$ Hz, $J_{6,7eq} = 2.4$ Hz, H-6), 3.63 (1H, m, H-3), 1.99 (1H, ddd, $J_{gem} = 12.4$ Hz, $J_{12,11} = 3.2$ and 3.6 Hz, H-12), 1.03 (3H, s, $CH_3$-19), 0.95 (3H, d, $J_{21,20} = 6.4$ Hz, $CH_3$-21), 0.87 (3H, d, $J_{26,25} = 1.6$ Hz, $CH_3$-26), 0.85 (3H, d, $J_{27,25} = 1.6$ Hz, $CH_3$-27), 0.69 (3H, s, $CH_3$-18). $^{13}$C NMR (125 MHz, $CDCl_3$ δ): 38.6 (C-1), 31.6 (C-2), 71.7 (C-3), 35.5 (C-4), 47.4 (C-5), 72.1 (C-6), 39.7 (C-7), 30.5 (C-8), 54.3 (C-9), 35.5 (C-10), 21.2 (C-11), 40.0 (C-12), 42.6 (C-13), 56.2 (C-14), 24.3 (C-15), 28.3 (C-16), 56.3 (C-17), 12.2 (C-18), 15.9 (C-19), 35.9 (C-20), 18.8 (C-21), 36.2 (C-22), 24.0 (C-23), 39.6 (C-24), 28.1 (C-25), 22.7 (C-26), 22.9 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{48}O_2$ Calcd: 404.3654. Found: 427.3552 $[M+Na]^+$.

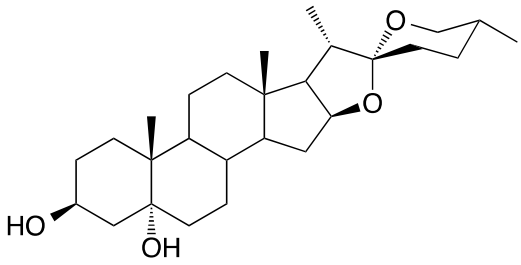
*(25R)-5α-Spirostane-3β,6α-diol (**2a**): α-chlorogenin*




The purification of **2a** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 1:1 hexane/ethyl acetate for 45 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 275-276 °C. $R_f$ 0.270 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ –64 (*c* 1.0, $CHCl_3$). IR: 3245 (OH), 2926 (CH, aliphatic), 980, 898 (O-C-O spiroketal). NMR experiments were acquired on Py-$d_5$ since **2a** showed low solubility on $CDCl_3$. $^{1}$H NMR (500 MHz, Py-$d_5$ δ): 6.04 (1H, s, OH-3), 5.81 (1H, d, $J_{OH,6} = 4.8$ Hz, OH-6), 4.54 (1H, m, H-16), 3.92 (1H, m, H-3), 3.66 (1H, m, H-6), 3.58 (1H, dd, $J_{26eq,25}$ =4.0 Hz, $J_{26eq,26ax} = 11.2$ Hz, H-26*eq*), 3.48 (1H, dd, $J_{26ax,25} = J_{26eq,26ax} = 11.2$ Hz, H-26*ax*), 3.01 (1H, m, H-4*eq*), 2.25 (1H, m, H-7*eq*), 2.09 (2H, m, H-15α and H-2*eq*), 1.97 (1H, dq, $J_{17,20} = 8$ Hz, $J_{20,21} = 7.2$ Hz, H-20), 1.84 (1H, dd, $J_{17,20} = 8.0$ Hz, $J_{17,16} = 6.4$ Hz, H-17), 1.15 (3H, d, $J_{21,20} = 7.2$ Hz , $CH_3$-21), 0.89 (3H, s, $CH_3$-19), 0.86 (3H, s, $CH_3$-18), 0.70 (1H, m, H-9), 0.69 (3H, d, $J_{27,25} = 6.0$ Hz, $CH_3$-27). $^{13}$C NMR (125 MHz, Py-$d_5$ δ): 37.6 (C-1), 31.8 (C-2), 70.5 (C-3), 33.4 (C-4), 52.3 (C-5), 68.0 (C-6), 42.4 (C-7), 33.9 (C-8), 53.8 (C-9), 36.2 (C-10), 21.0 (C-11), 39.7 (C-12), 40.4 (C-13), 55.9 (C-14), 32.0 (C-

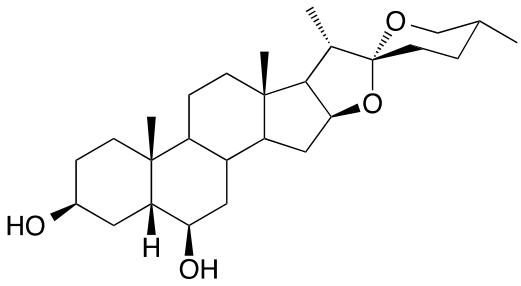
15), 80.6 (C-16), 62.5 (C-17), 16.3 (C-18), 13.4 (C-19), 41.6 (C-20), 14.7 (C-21), 108.6 (C-22), 31.4 (C-23), 28.9 (C-24), 30.2 (C-25), 66.4 (C-26), 17.0 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{44}O_4$ Calcd: 432.3240. Found: 433.3319 $[M+H]^+$.

*(25R)-5α-Spirostan-3β,5-diol (**2b**)*



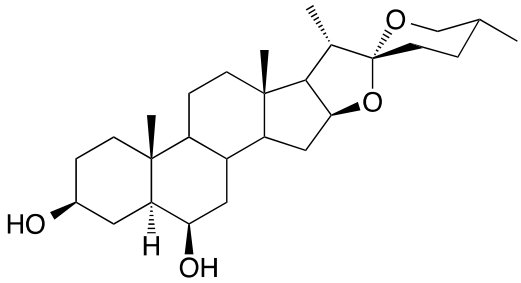

The purification of **2b** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 1:1 hexane/ethyl acetate for 45 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 254-255 °C. $R_f$ 0.337 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ –63 (*c* 1.0, $CHCl_3$). IR: 3265 (OH), 2929 (CH, aliphatic), 980, 897 (O-C-O spiroketal). $^1$H NMR (500 MHz, $CDCl_3$ δ): 4.38 (1H, ddd, $J_{16,17}$ = 8.4 Hz, $J_{16,15eq}$ = 6.8 Hz, $J_{16,15ax}$ = 7.2 Hz, H-16), 4.07 (1H, m, H-3), 3.46 (1H, ddd, $J_{26eq,26ax}$ = 10.8 Hz, $J_{26eq,25}$ = 4.8 Hz, $J_{26eq,24eq}$ = 1.2 Hz, H-26*eq*), 3.36 (1H, dd, $J_{26ax,26eq}$ = $J_{26ax,25}$ = 10.8 Hz, H-26*ax*), 1.98 (1H, m, H-15), 1.00 (3H, s, $CH_3$-19), 0.96 (3H, d, $J_{21,20}$ = 7.2 Hz, $CH_3$-21), 0.79 (3H, d, $J_{27,25}$ = 6.0 Hz, $CH_3$-27), 0.76 (3H, s, $CH_3$-18). $^{13}$C NMR (125 MHz, $CDCl_3$ δ): 30.9 (C-1), 30.9 (C-2), 67.3 (C-3), 44.0 (C-4), 75.3 (C-5), 34.4 (C-6), 26.2 (C-7), 30.4 (C-8), 45.9 (C-9), 39.0 (C-10), 21.3 (C-11), 40.1 (C-12), 40.7 (C-13), 56.0 (C-14), 31.8 (C-15), 80.8 (C-16), 62.1 (C-17), 16.7 (C-18), 16.4 (C-19), 41.7 (C-20), 14.6 (C-21), 109.2 (C-22), 31.4 (C-23), 28.9 (C-24), 34.4 (C-25), 66.8 (C-26), 17.3 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{44}O_4$ Calcd: 432.3240. Found: 433.3320 $[M+H]^+$.

*(25R)-5β-Spirostane-3β,6β-diol (**2c**)*




The purification of **2c** was achieved from an enriched fraction mixed with **2e** employing *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% $CH_2Cl_2$ to 9:1 $CH_2Cl_2$/MeOH for 60 min. Yields vary in dependence of temperature, see Table 1. Colorless solid mp 282-284 °C. $R_f$ 0.304 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +60 (*c* 1.0, $CHCl_3$:MeOH 1:1). IR: 3395 (OH), 2939 (CH, aliphatic), 982, 899 (O-C-O spiroketal). $^1$H NMR (500 MHz, $CDCl_3$ δ): 4.40 (1H, ddd, $J_{16,17}$ = 8.3 Hz, $J_{16,15eq}$ = 7.6 Hz, $J_{16,15ax}$ = 7.6 Hz, H-16), 4.10 (1H, m, H-3), 3.71 (1H, m, H-6), 3.47 (1H, ddd, $J_{26eq,26ax}$ = 10.9 Hz, $J_{26eq,25}$ = 4.1 Hz, $J_{26eq,24eq}$ = 2.1 Hz, H-26*eq*), 3.37 (1H, dd, $J_{26ax,26eq}$ = 10.9 Hz, $J_{26ax,25}$ = 11.9 Hz, H-26*ax*), 1.16 (3H, s, $CH_3$-19), 0.96 (3H, d, $J_{21,20}$ = 7.3 Hz, $CH_3$-21), 0.79 (3H, s, $CH_3$-18), 0.79 (3H, d, $J_{27,25}$ = 6.3 Hz, $CH_3$-27). $^{13}$C NMR (125 MHz, $CDCl_3$ δ): 30.1 (C-1), 33.6 (C-2), 66.1 (C-3), 34.6 (C-4), 40.2 (C-5), 73.2 (C-6), 27.4 (C-7), 30.2 (C-8), 43.7 (C-9), 35.0 (C-10), 20.7 (C-11), 40.2 (C-12), 40.7 (C-13), 56.3 (C-14), 31.8 (C-15), 80.8 (C-16), 62.2 (C-17), 16.5 (C-18), 26.1 (C-19), 41.6 (C-20), 14.5 (C-21), 109.3 (C-22), 31.3 (C-23), 28.7 (C-24), 30.3 (C-25), 66.9 (C-26), 17.1 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{44}O_4$ Calcd: 432.3240. Found: 433.3319 $[M+H]^+$.

*(25R)-5α-Spirostane-3β,6β-diol (**2e**): β-chlorogenin*




The purification of **2e** from the crude was performed by *flash* chromatography on a *Combiflash* apparatus by a gradient elution starting from 100% hexane to 1:1 hexane/ethyl acetate for 45 min. Yields vary in dependence of temperature, see Table 1. Colorless solid

mp 231-233 °C. $R_f$ 0.304 (93:7 $CH_2Cl_2$/MeOH). $[\alpha]_D$ +62 (*c* 1.0, $CHCl_3$:MeOH 1:1). IR: 3379 (OH), 2948 (CH, aliphatic), 982, 899 (O-C-O spiroketal). $^1$H NMR (500 MHz, $CDCl_3$ δ): 4.38 (1H, ddd, $J_{16,17}$ = 8.0 Hz, $J_{16,15eq}$ = 6.8 Hz, $J_{16,15ax}$ = 7.6 Hz, H-16), 3.80 (1H, ddd, $J_{6,7ax} = J_{6,5}$ = 2.8 Hz, $J_{6\text{-}7eq}$ = 2.4 Hz, H-6), 3.64 (1H, m, H-3), 3.46 (1H, ddd, $J_{26eq,26ax}$ = 10.4 Hz, $J_{26ee,25}$ = 2.4 Hz, $J_{26eq,24eq}$ = 0.8 Hz, H-26*eq*), 3.36 (1H, dd, $J_{26ax,26eq}$ = 10.4 Hz, $J_{26ax,25}$ = 11.2 Hz, H-26*ax*), 1.04 (3H, s, $CH_3$-19), 0.96 (3H, d, $J_{21,20}$ = 6.8 Hz, $CH_3$-21), 0.80 (3H, s, $CH_3$-18), 0.79 (3H, d, $J_{27,25}$ = 7.2 Hz, $CH_3$-27), 0.69 (1H, ddd, $J_{9,8} = J_{9,11ax}$ = 12.4 Hz, $J_{9,11eq}$ = 2.4 Hz, H-9). $^{13}$C NMR (125 MHz, $CDCl_3$ δ): 38.6 (C-1), 31.6 (C-2), 71.6 (C-3), 35.5 (C-4), 47.4 (C-5), 71.9 (C-6), 39.8 (C-7), 30.4 (C-8), 54.3 (C-9), 35.6 (C-10), 21.0 (C-11), 40.1 (C-12), 40.7 (C-13), 56.1 (C-14), 31.9 (C-15), 80.8 (C-16), 62.2 (C-17), 16.1 (C-18), 15.9 (C-19), 41.7 (C-20), 14.6 (C-21), 109.2 (C-22), 31.4 (C-23), 28.9 (C-24), 30.1 (C-25), 66.9 (C-26), 17.3 (C-27). HRMS (ESI-TOF) m/z for $C_{27}H_{44}O_4$ Calcd: 432.3240. Found: 433.3319 $[M+H]^+$.

## II. Details of X-ray collection, solution, and refinement of 2b, 1c, 2c, and 1e

Suitable single crystals for compounds **2b**, **1c**, **2c** and **1e** were obtained by slow evaporation of MeOH:$CH_2Cl_2$ solutions, at room temperature. Diffraction data were collected at 295 K on a STOE-Stadivari diffractometer [1] equipped with an AXO micro-focus source (Ag Kα radiation, λ = 0.56083 Å; 65 kV @ 0.55 mA) and a DECTRIS Pilatus-100K detector. Structures were solved and refined using SHELX programs [2]. Compounds synthesized starting from cholesterol, **1c** and **1e**, display disordered lateral chains bonded to the D ring, a common feature in cholestane derivatives. Compound **2b** crystallized as an hemihydrate, with Z' = 2. In all cases, H atoms bonded to C atoms were placed in calculated positions, and refined as riding to their carrier atom, while hydroxyl H atoms (H3 and H6) were found in difference maps, and refined with free coordinates, without geometric restraints. All H atoms were refined isotropically, with Uiso = 1.2 Ueq(carrier atom) (methine and methylene groups) or Uiso = 1.5 Ueq(carrier atom) (methyl and OH groups).

| Compound / CCDC | **2b / 1921283** | **1c / 1921284** | **2c / 1921285** | **1e / 1921286** |
|---|---|---|---|---|
| Formula | $C_{27}H_{44}O_4 \cdot (H_2O)_{0.5}$ | $C_{27}H_{47}D_1O_2$ | $C_{27}H_{44}O_4$ | $C_{27}H_{48}O_2$ |
| fw | 441.63 | 405.66 | 432.62 | 404.65 |
| Crystal size ($mm^3$) | 0.60×0.39×0.04 | 0.60×0.33×0.12 | 0.30×0.20×0.20 | 0.59×0.15×0.09 |
| Space group | $P2_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |
| *a* (Å) | 11.3797(10) | 8.1858(3) | 8.2099(2) | 8.3599(3) |
| *b* (Å) | 8.0820(4) | 10.4115(6) | 9.1989(3) | 10.7489(4) |
| *c* (Å) | 28.058(2) | 30.9258(12) | 32.4182(14) | 28.4769(14) |
| β (°) | 99.811(6) | - | - | - |
| *V* ($Å^3$) | 2542.7(3) | 2635.7(2) | 2448.29(15) | 2558.93(18) |
| *Z*, *Z*' | 4, 2 | 4, 1 | 4, 1 | 4, 1 |
| Diffractometer | Stadivari | Stadivari | Stadivari | Stadivari |
| Radiation | Ag *K*α | Ag *K*α | Ag *K*α | Ag *K*α |
| *T* (K) | 295 | 295 | 295 | 295 |
| Calc. density ($Mg/m^3$) | 1.154 | 1.022 | 1.174 | 1.050 |
| Transmission fact. | 0.2935 - 1 | 0.3630 - 1 | 0.5416 - 1 | 0.4766 - 1 |
| Refl. collected | 42679 | 45768 | 37982 | 55190 |
| Senθ/λ ($Å^{-1}$) | 0.62 | 0.68 | 0.65 | 0.65 |
| $R_{int}$ (%) | 15.44 | 8.16 | 6.48 | 11.43 |
| Completeness (%) | 99.3 | 99.2 | 98.0 | 99.8 |
| Data/parameters | 9025 / 594 | 6932 / 284 | 5592 / 290 | 5952 / 312 |
| Restraints | 1 | 0 | 0 | 158 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 4.10, 5.71 | 4.93, 11.81 | 3.91, 7.68 | 4.30, 8.62 |
| $R_1$, $wR_2$ [all data] | 13.76, 6.98 | 12.41, 13.81 | 6.81, 8.30 | 9.87, 9.77 |
| GOF on $F^2$ | 0.602 | 0.811 | 0.863 | 0.767 |

## checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1c, 1e, 2b, 2c

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: 2b

---

```
Bond precision:  C-C = 0.0062 A          Wavelength=0.56083

Cell:            a=11.3797(10)     b=8.0820(4)        c=28.058(2)
                 alpha=90          beta=99.811(6)     gamma=90
Temperature:     295 K

                Calculated                Reported
Volume          2542.8(3)                 2542.7(3)
Space group     P 21                      P 21
Hall group      P 2yb                     P 2yb
Moiety formula  2(C27 H44 O4), H2 O       C27 H44 O4, 0.5(H2 O)
Sum formula     C54 H90 O9                C27 H45 O4.50
Mr              883.26                    441.63
Dx,g cm-3       1.154                     1.154
Z               2                         4
Mu (mm-1)       0.049                     0.049
F000            972.0                     972.0
F000'           972.16
h,k,lmax        14,10,35                  14,10,35
Nref            10381[ 5577]              9025
Tmin,Tmax       0.977,0.998               0.294,1.000
Tmin'           0.971

Correction method= # Reported T Limits: Tmin=0.294 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.62/0.87      Theta(max)= 20.499

R(reflections)= 0.0410( 3338)     wR2(reflections)= 0.0698( 9025)

S = 0.602                 Npar= 594
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

## Alert level B

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 37% Check

## Alert level C

GOODF01_ALERT_2_C The least squares goodness of fit parameter lies
outside the range 0.80 <> 2.00
Goodness of fit given = 0.602
RINTA01_ALERT_3_C The value of Rint is greater than 0.12
Rint given 0.154
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.1 Ratio
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C25A Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00617 Ang.
PLAT417_ALERT_2_C Short Inter D-H..H-D H3B ..H6B . 2.13 Ang.
1-x,1/2+y,1-z = 2_656 Check
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 39 Ang**3
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 10 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 25 Report
PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage 73 %
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

## Alert level G

PLAT020_ALERT_3_G The Value of Rint is Greater Than 0.12 ..... 0.154 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ... 0.50 Check
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O16A 106.3 Degree
PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O16B 106.0 Degree
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 26 Note
PLAT791_ALERT_4_G Model has Chirality at C3A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C3B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C5A (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C5B (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C8A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C8B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C9A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C9B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C10A (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C10B (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C13A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C13B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C14A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C14B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C16A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C16B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C17A (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C17B (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C20A (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C20B (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C22A (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C22B (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C25A (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C25B (Chiral SPGR) R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 4 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
31 **ALERT level G** = General information/check it is not something unexpected

```
  2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  8 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
 26 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
```

---

## Datablock: 1c

---

```
Bond precision:  C-C = 0.0046 A          Wavelength=0.56083

Cell:            a=8.1858(3)     b=10.4115(6)     c=30.9258(12)
                 alpha=90        beta=90          gamma=90
Temperature:     295 K
```

| | Calculated | Reported |
|---|---|---|
| Volume | 2635.7(2) | 2635.7(2) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C27 H47 D O2 | C27 H47 D O2 |
| Sum formula | C27 H47 D O2 | C27 H47 D O2 |
| Mr | 405.66 | 405.66 |
| Dx,g cm-3 | 1.022 | 1.022 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.041 | 0.041 |
| F000 | 904.0 | 904.0 |
| F000' | 904.11 | |
| h,k,lmax | 11,14,42 | 11,14,42 |
| Nref | 6999[ 3966] | 6932 |
| Tmin,Tmax | 0.984,0.995 | 0.363,1.000 |
| Tmin' | 0.976 | |

```
Correction method= # Reported T Limits: Tmin=0.363 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.99       Theta(max)= 22.499

R(reflections)= 0.0493( 3034)      wR2(reflections)= 0.1381( 6932)

S = 0.811                  Npar= 284
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

**Alert level B**

PLAT230_ALERT_2_B Hirshfeld Test Diff for C2 --C3 . 9.3 s.u.

---

**Alert level C**

```
ABSMU01_ALERT_1_C  The ratio of given/expected absorption coefficient lies
               outside the range 0.99 <> 1.01
            Calculated value of mu =     0.041
            Value of mu given      =     0.041
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low ..        44% Check
PLAT220_ALERT_2_C Non-Solvent  Resd 1  C   Ueq(max)/Ueq(min) Range        4.4 Ratio
PLAT222_ALERT_3_C Non-Solv.  Resd 1  H   Uiso(max)/Uiso(min) Range        5.6 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C25      --C27B     .       0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C25      --C27A     .       0.24 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C23 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C20 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of        C24 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00462 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C24      - C25      .       1.41 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H24A     ..H25B     .       1.92 Ang.
                                                     x,y,z  =     1_555 Check
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of .         35 Ang**3
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1 Note
            C27 H47 D O2
PLAT905_ALERT_3_C Negative K value in the Analysis of Variance ...     -0.120 Report
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600        18 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.          0 Info
```

---

**Alert level G**

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          1 Report
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )         3% Note
PLAT791_ALERT_4_G Model has Chirality at C3          (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C5          (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C6          (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C8          (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C9          (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C10         (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C13         (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C14         (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C17         (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C20         (Chiral SPGR)          R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          6 Note
```

---

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
  17 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  14 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   7 ALERT type 3 Indicator that the structure quality may be low
  14 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

---

# Datablock: 2c

---

```
Bond precision:  C-C = 0.0032 A          Wavelength=0.56083
```

| | | | |
|---|---|---|---|
| Cell: | a=8.2099(2) | b=9.1989(3) | c=32.4182(14) |
| | alpha=90 | beta=90 | gamma=90 |
| Temperature: | 295 K | | |

| | Calculated | Reported |
|---|---|---|
| Volume | 2448.29(15) | 2448.29(15) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C27 H44 O4 | C27 H44 O4 |
| Sum formula | C27 H44 O4 | C27 H44 O4 |
| Mr | 432.62 | 432.62 |
| Dx,g cm-3 | 1.174 | 1.174 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.049 | 0.049 |
| F000 | 952.0 | 952.0 |
| F000' | 952.15 | |
| h,k,lmax | 10,12,42 | 10,12,42 |
| Nref | 5720[ 3273] | 5592 |
| Tmin,Tmax | 0.988,0.990 | 0.542,1.000 |
| Tmin' | 0.985 | |

Correction method= # Reported T Limits: Tmin=0.542 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.98 Theta(max)= 21.498

R(reflections)= 0.0391( 3643) wR2(reflections)= 0.0830( 5592)

S = 0.863 Npar= 290

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

**Alert level C**

PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 6 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 44 Report

---

**Alert level G**

PLAT398_ALERT_2_G Deviating C-O-C Angle From 120 for O16 106.5 Degree
PLAT791_ALERT_4_G Model has Chirality at C3 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C5 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C6 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C8 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C9 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C10 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C13 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C14 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C16 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C17 (Chiral SPGR) R Verify

```
PLAT791_ALERT_4_G Model has Chirality at C20         (Chiral SPGR)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C22         (Chiral SPGR)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C25         (Chiral SPGR)          R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         16 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

---

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  16 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
  14 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

---

# Datablock: 1e

---

```
Bond precision:  C-C = 0.0039 A          Wavelength=0.56083

Cell:            a=8.3599(3)     b=10.7489(4)     c=28.4769(14)
                 alpha=90        beta=90          gamma=90
Temperature:     295 K

                Calculated                Reported
Volume          2558.93(18)               2558.93(18)
Space group     P 21 21 21                P 21 21 21
Hall group      P 2ac 2ab                 P 2ac 2ab
Moiety formula  C27 H48 O2                C27 H48 O2
Sum formula     C27 H48 O2                C27 H48 O2
Mr              404.65                    404.65
Dx,g cm-3       1.050                     1.050
Z               4                         4
Mu (mm-1)       0.042                     0.042
F000            904.0                     904.0
F000'           904.11
h,k,lmax        10,14,37                  10,14,37
Nref            5966[ 3391]               5952
Tmin,Tmax       0.992,0.996               0.477,1.000
Tmin'           0.975

Correction method= # Reported T Limits: Tmin=0.477 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.76/1.00      Theta(max)= 21.499

R(reflections)= 0.0430( 2864)     wR2(reflections)= 0.0977( 5952)
```

S = 0.767 Npar= 312

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level.**
Click on the hyperlinks for more details of the test.

---

### Alert level B

PLAT220_ALERT_2_B Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 6.3 Ratio

---

### Alert level C

GOODF01_ALERT_2_C The least squares goodness of fit parameter lies
outside the range 0.80 <> 2.00
Goodness of fit given = 0.767
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low .. 48% Check
PLAT213_ALERT_2_C Atom C25B has ADP max/min Ratio ..... 3.3 oblate
PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 7.8 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C23 --C24B . 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C25A --C27A . 0.18 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C23 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C20 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C22 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 7 Report
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

---

### Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 9 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 8 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 5 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records 1 Report
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1 ) 14% Note
PLAT791_ALERT_4_G Model has Chirality at C3 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C5 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C6 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C8 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C9 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C10 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C13 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C14 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C17 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C20 (Chiral SPGR) R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 158 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min). 4 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
18 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
9 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
15 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

---

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

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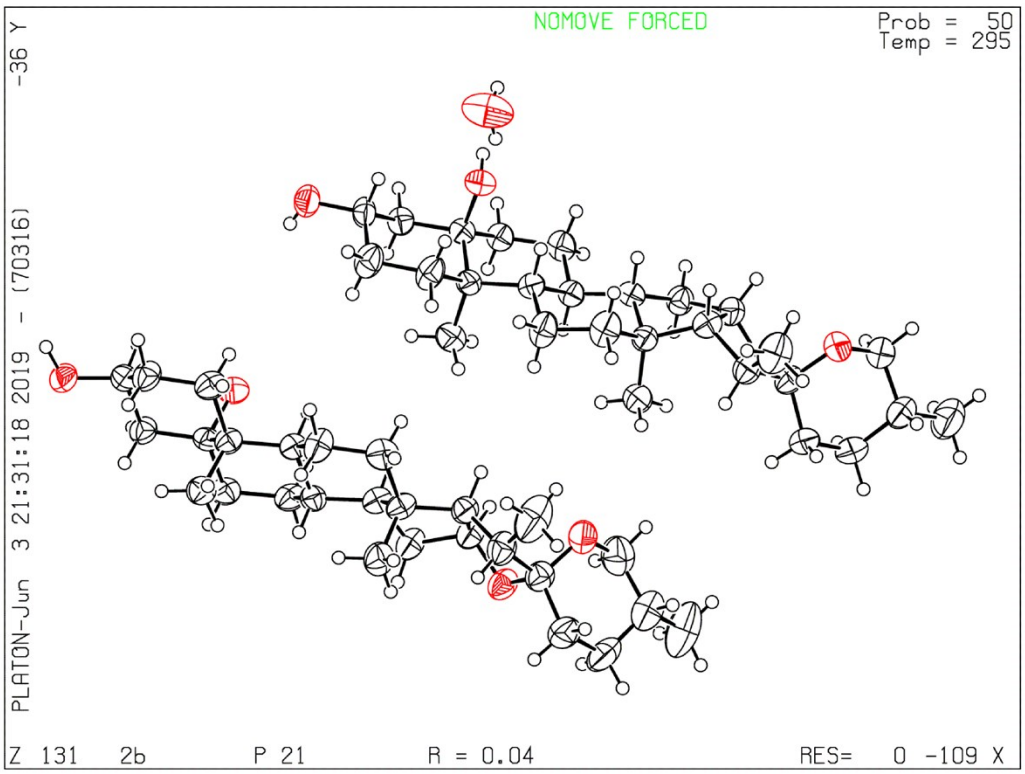
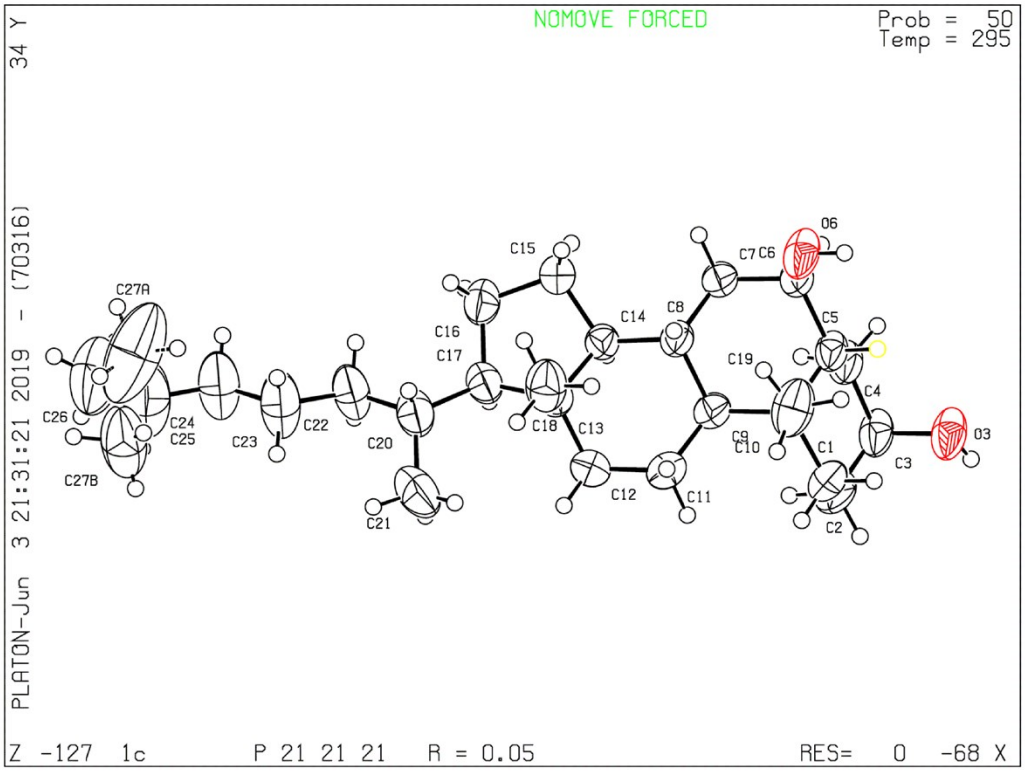
**PLATON version of 03/05/2019; check.def file version of 29/04/2019**

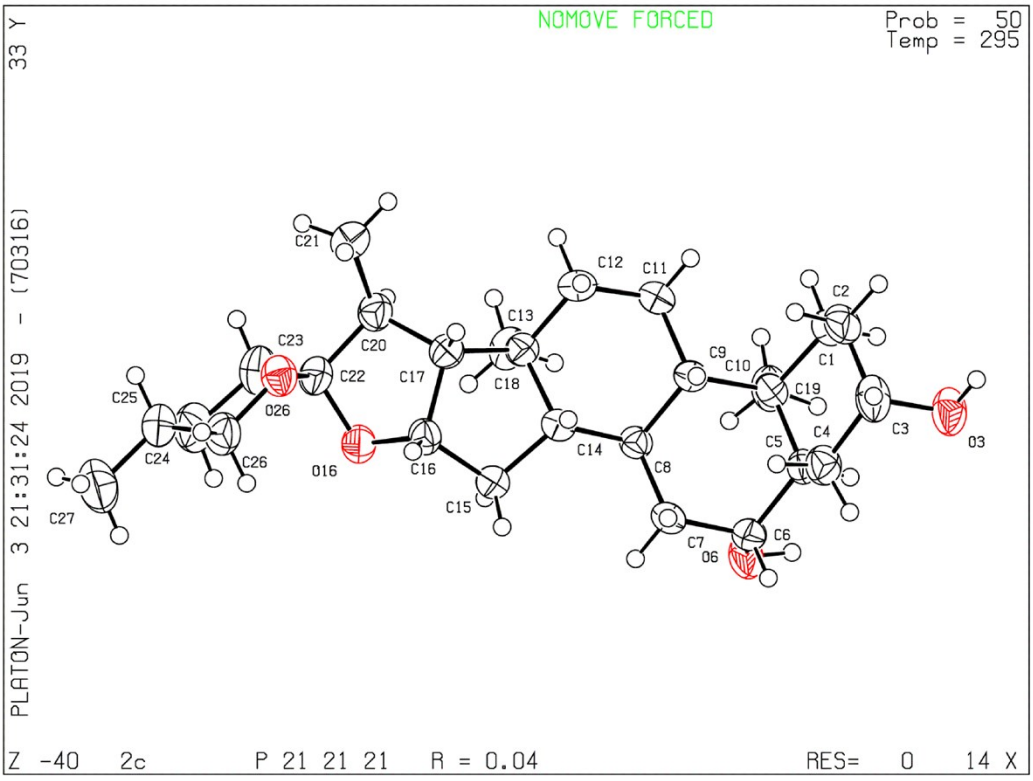
**Datablock 2b** - ellipsoid plot



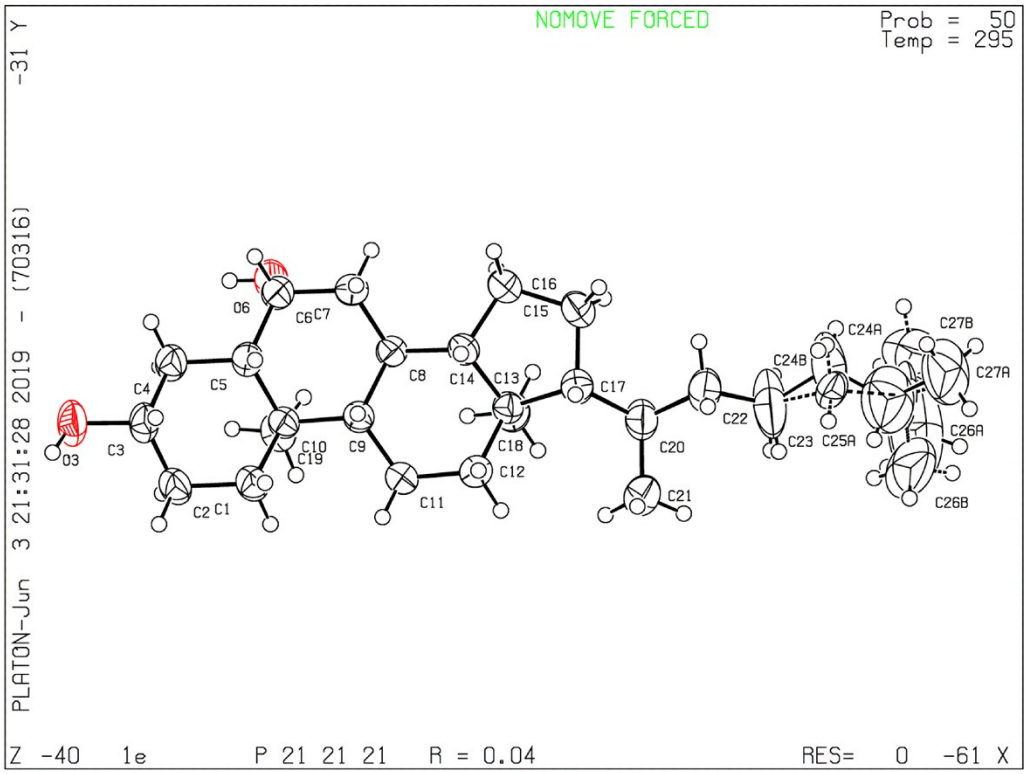
**Datablock 1c** - ellipsoid plot




**Datablock 2c** - ellipsoid plot

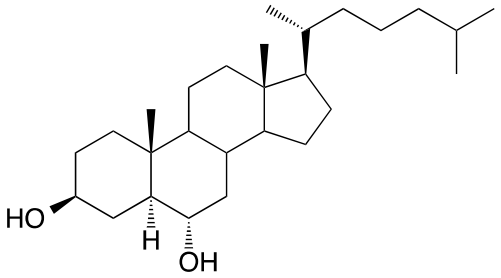


**Datablock 1e** - ellipsoid plot



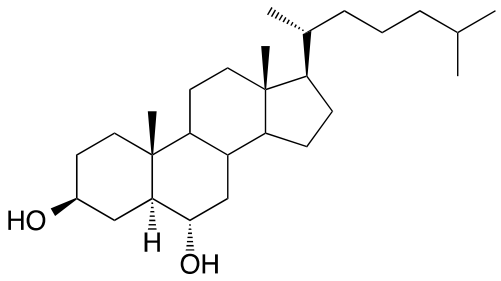

[1] Stoe & Cie (2019). *X-AREA* and *X-RED32*, Stoe & Cie, Darmstadt, Germany.
[2] Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst*. C71, 2005, 3-8.

## III. Copies of NMR spectra



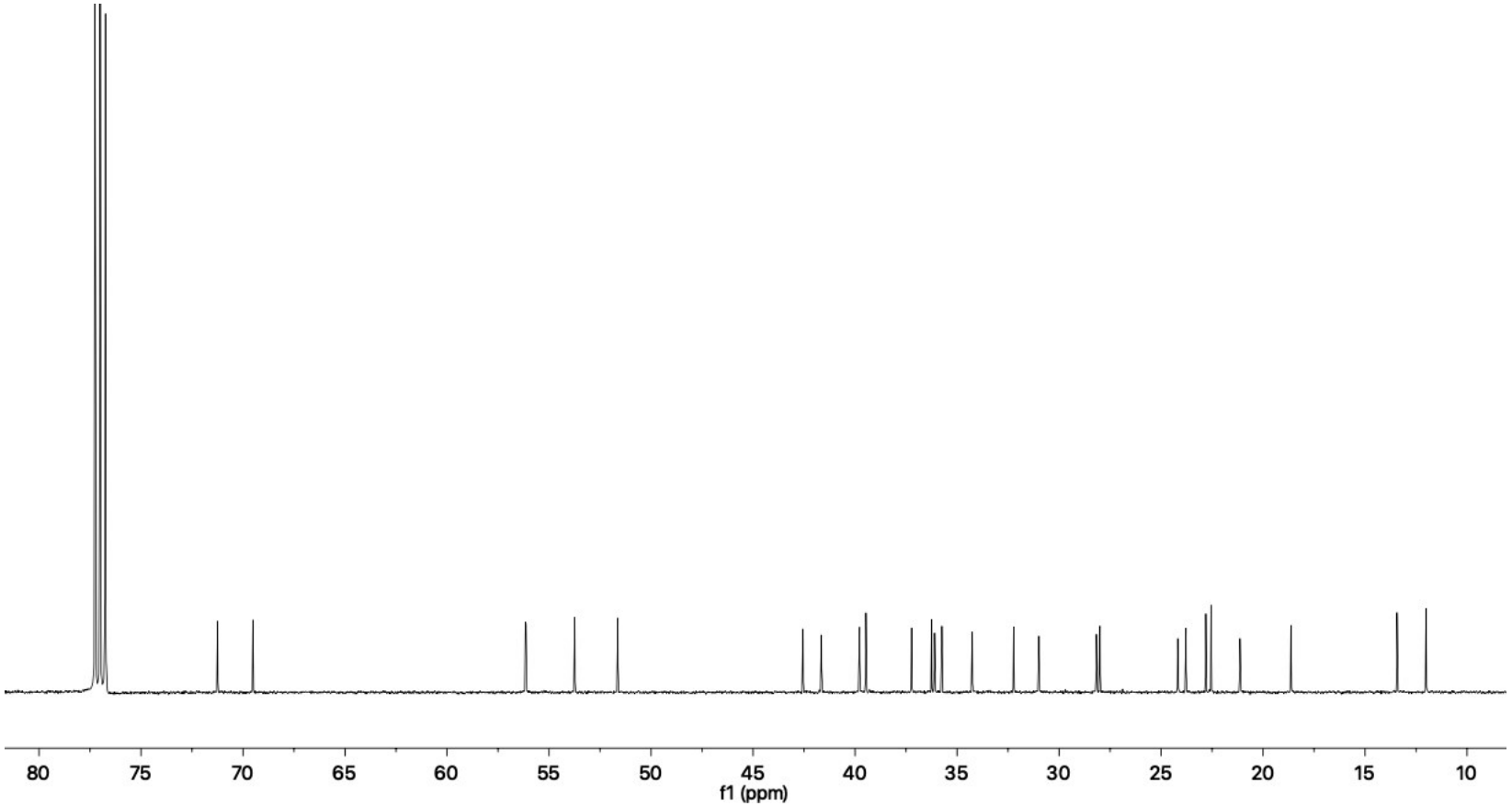

**1a**

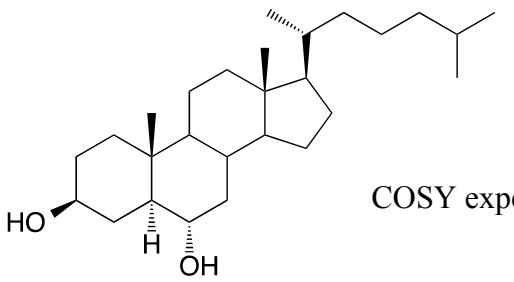
$^1$H NMR (500 MHz, $CDCl_3$)




**1a**

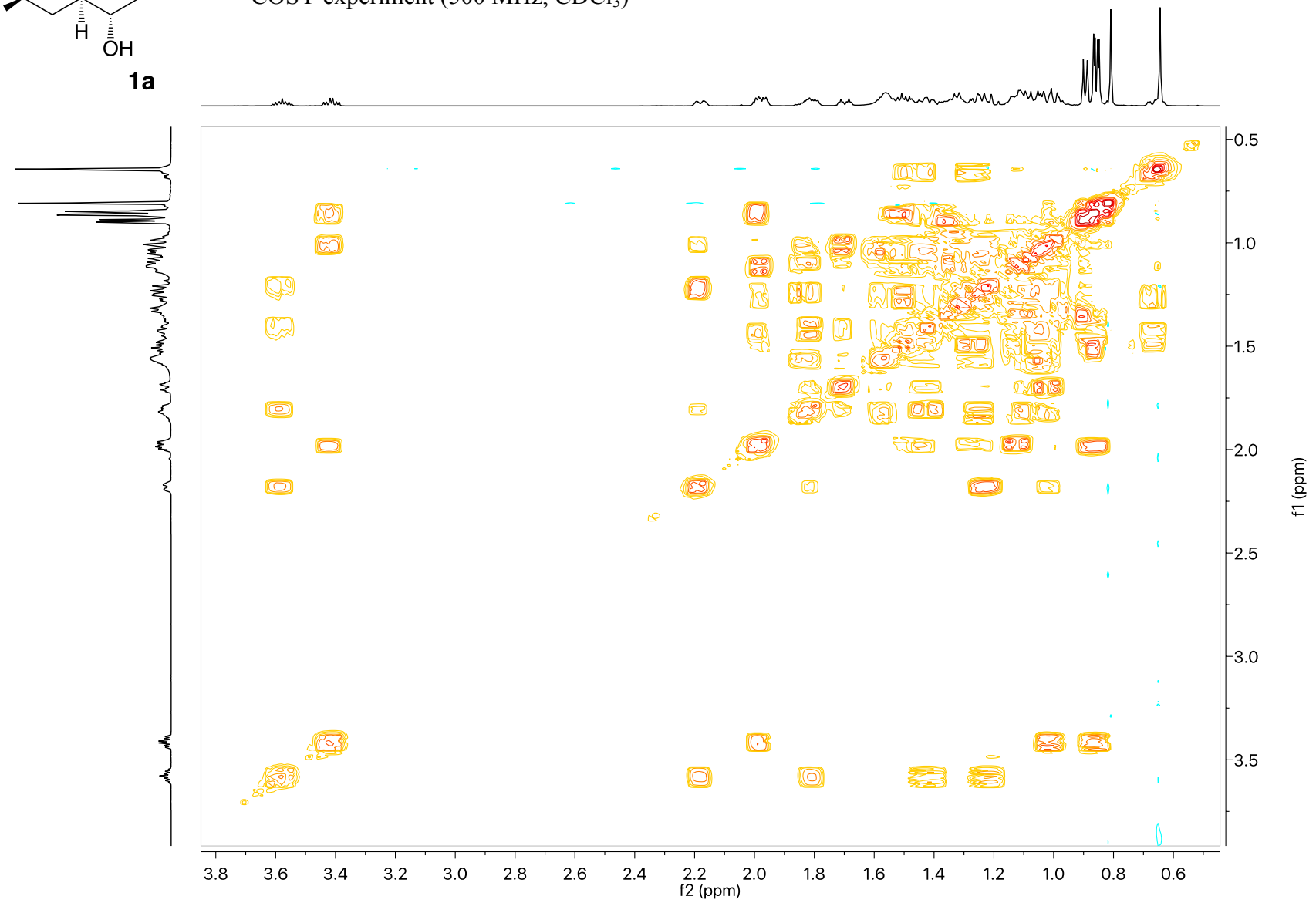
$^{13}C$ NMR (125 MHz, $CDCl_3$)

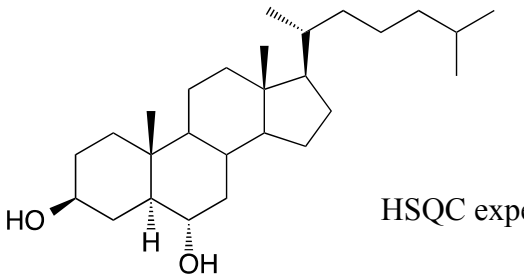





**1a**

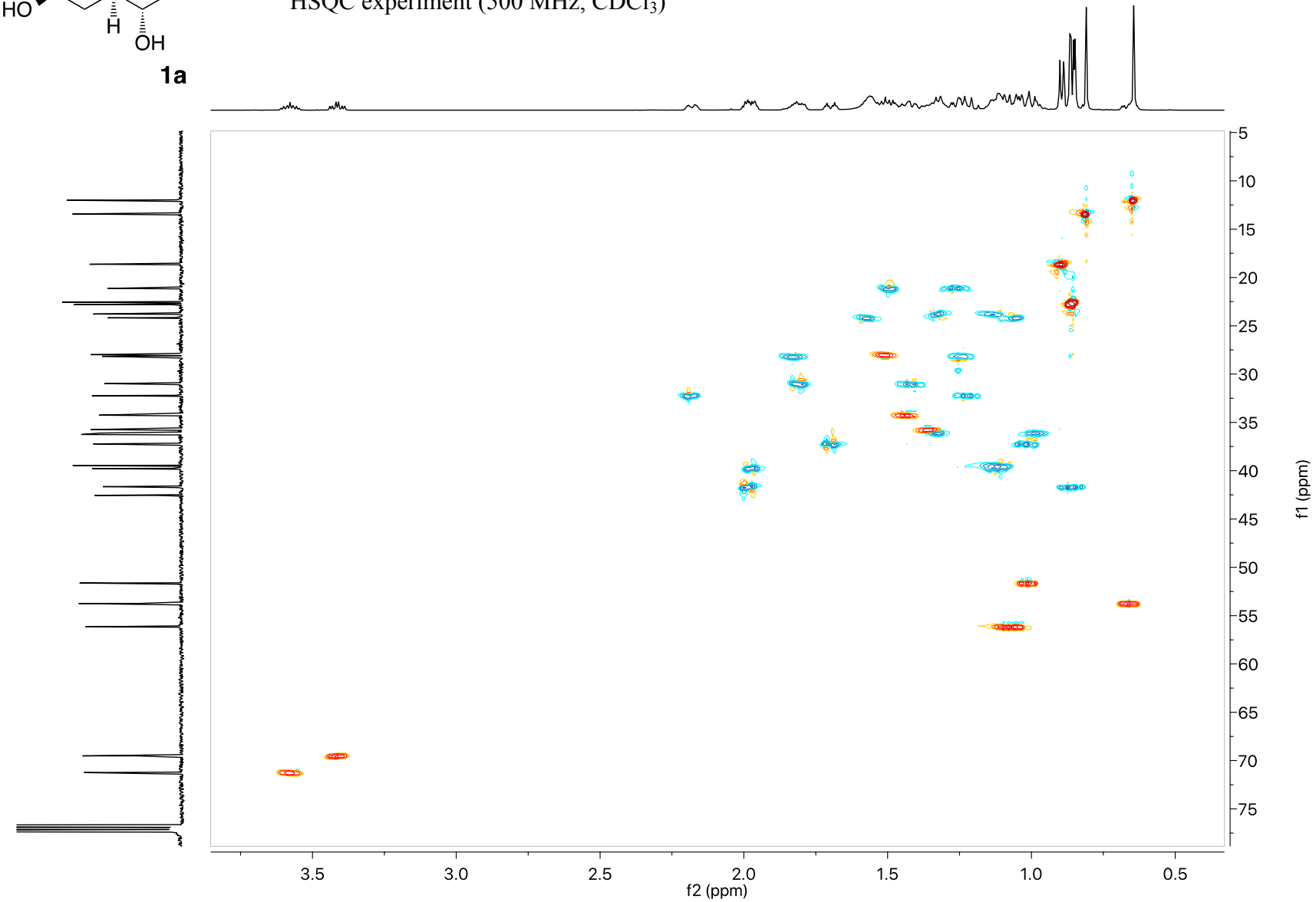
COSY experiment (500 MHz, $CDCl_3$)

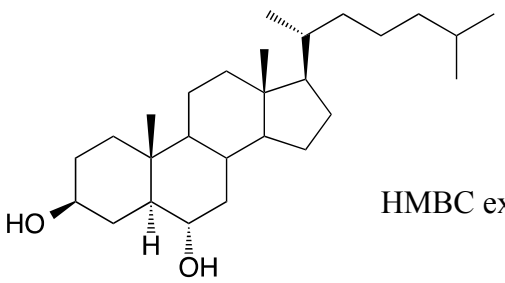





**1a**

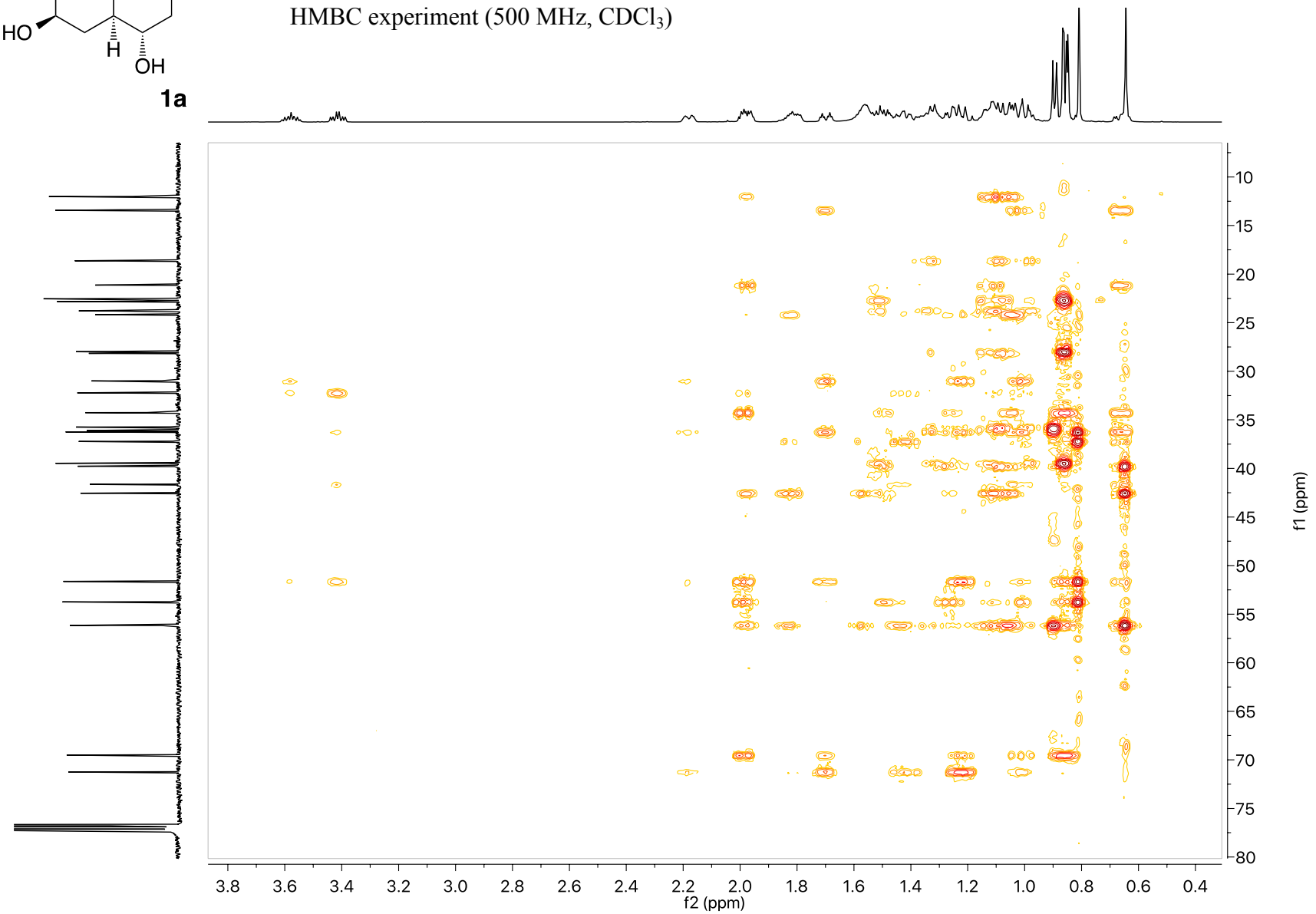
HSQC experiment (500 MHz, $CDCl_3$)

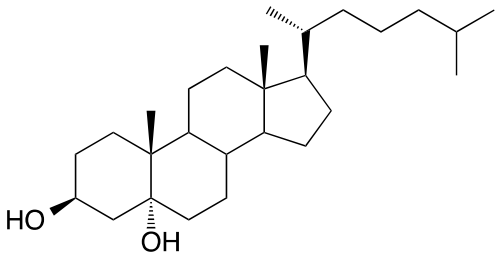





**1a**

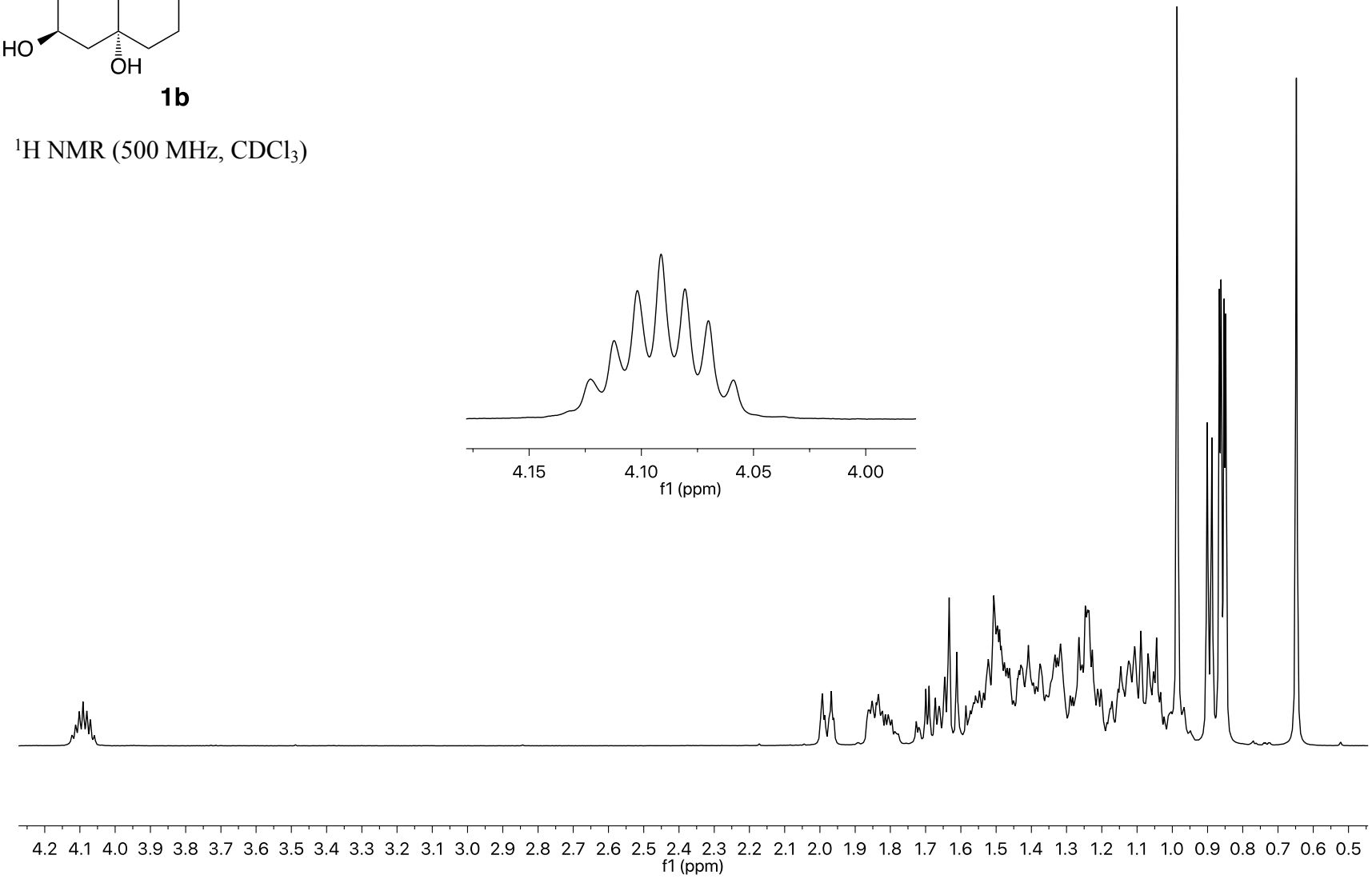
HMBC experiment (500 MHz, $CDCl_3$)

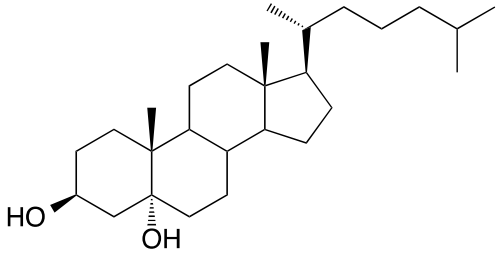





**1b**

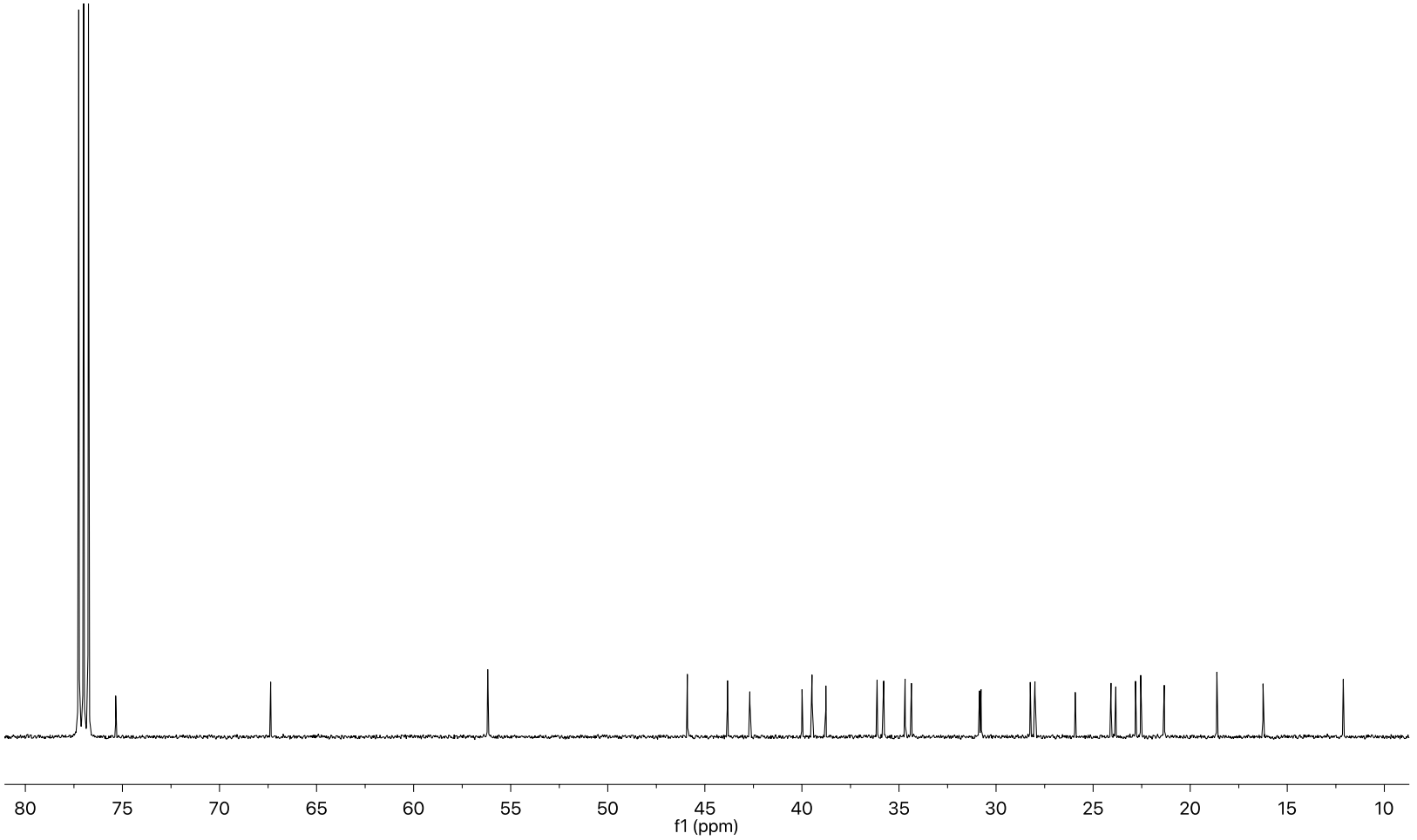
$^{1}$H NMR (500 MHz, $CDCl_3$)

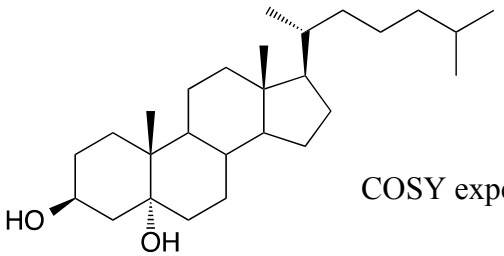





**1b**

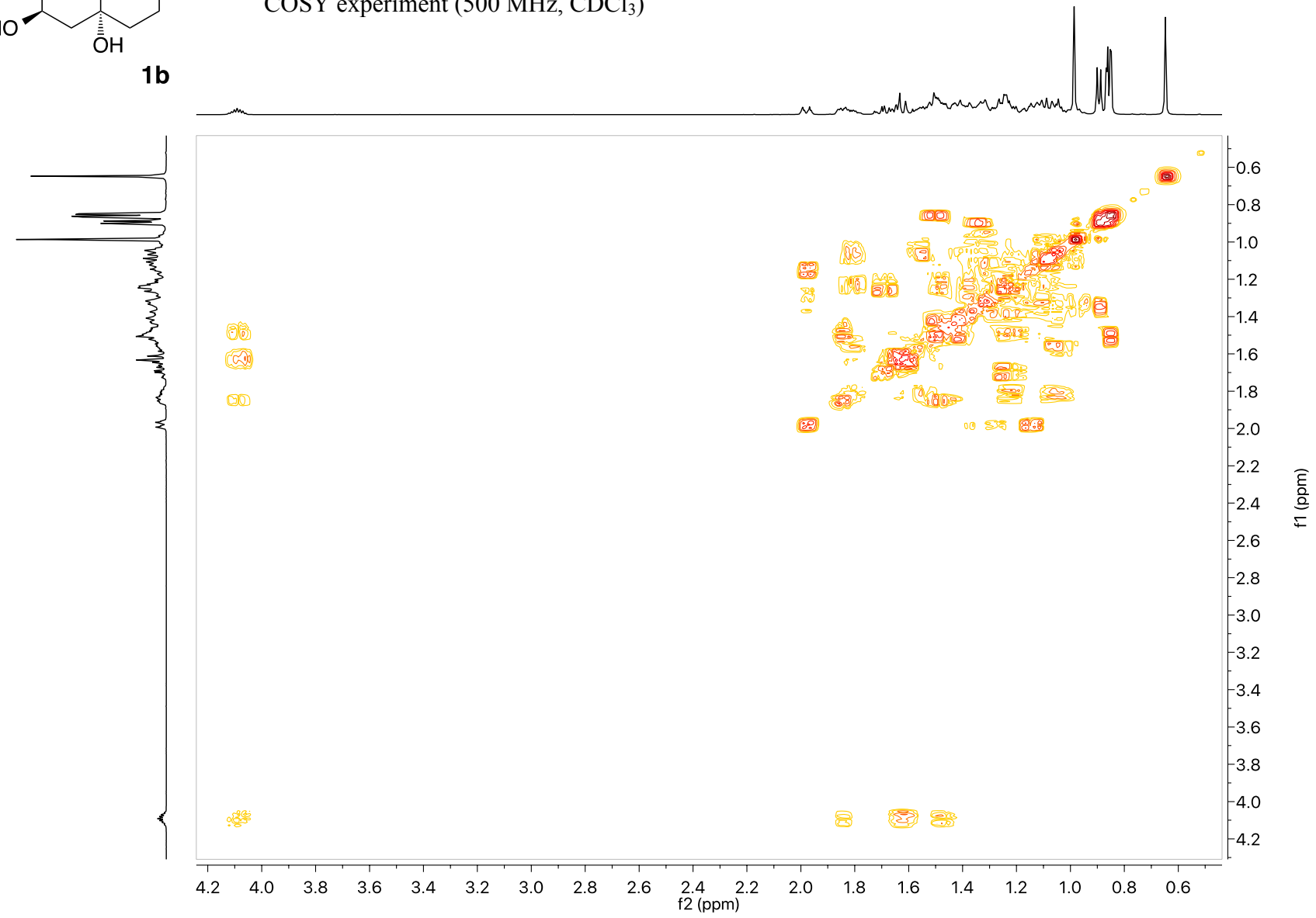
$^{13}C$ NMR (125 MHz, $CDCl_3$)

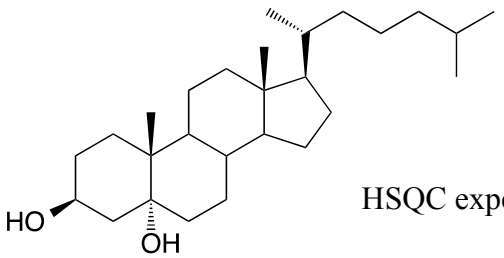





**1b**

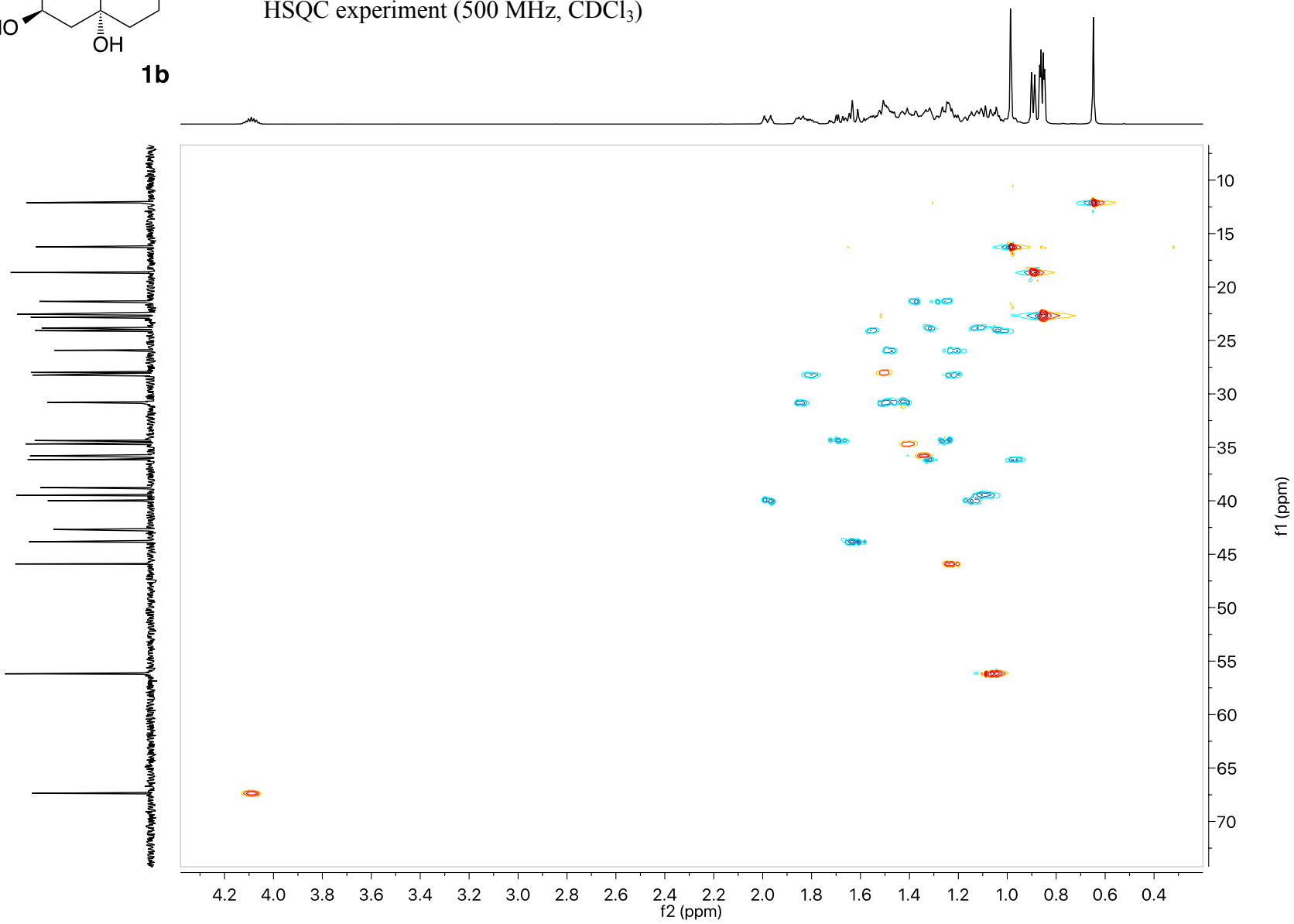
COSY experiment (500 MHz, $CDCl_3$)

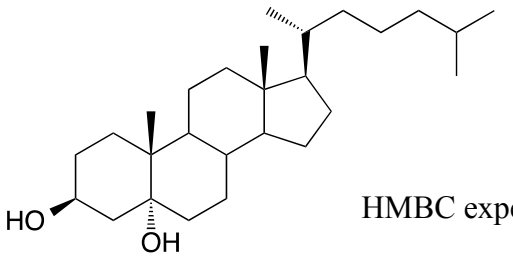





**1b**

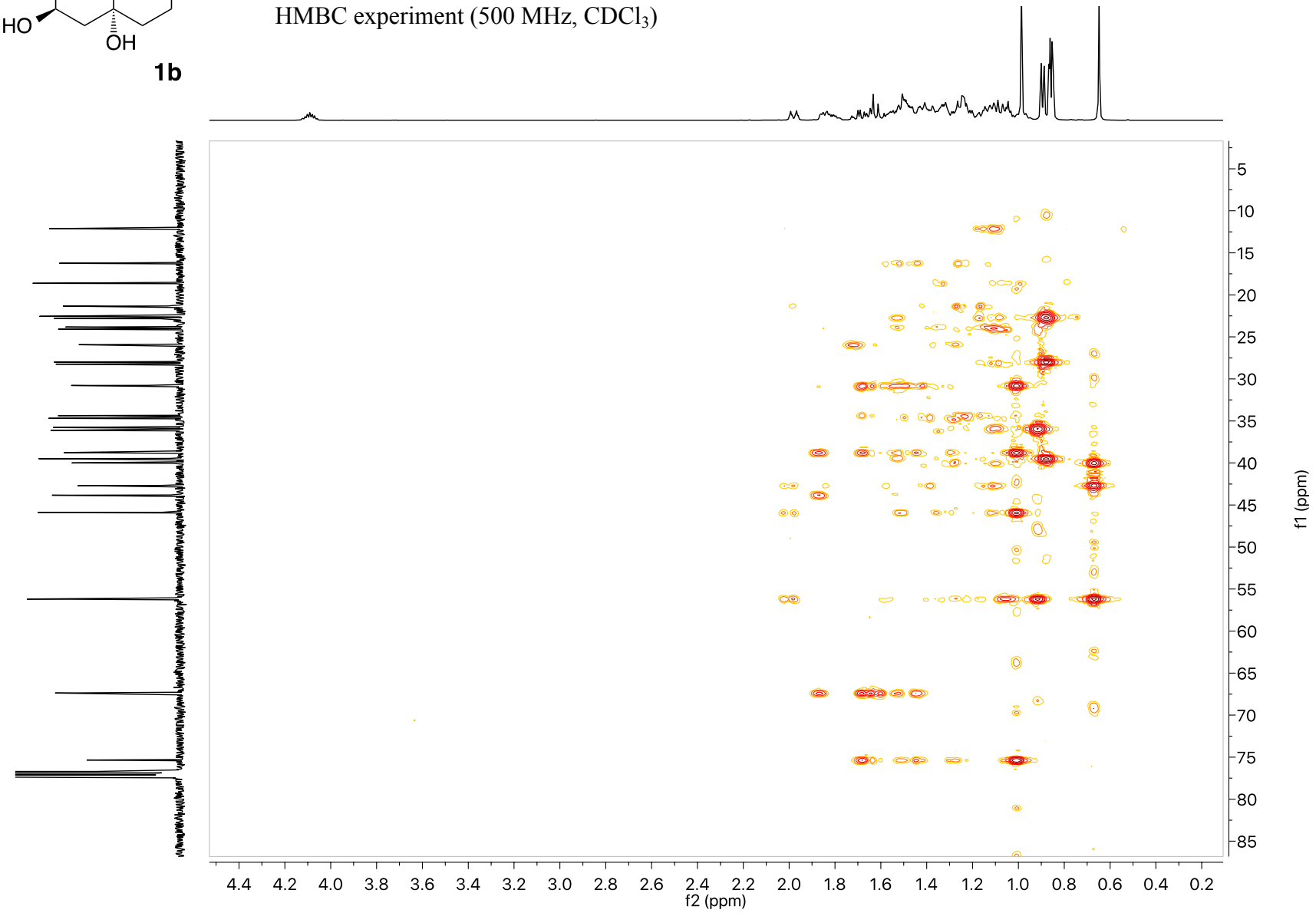
HSQC experiment (500 MHz, $CDCl_3$)

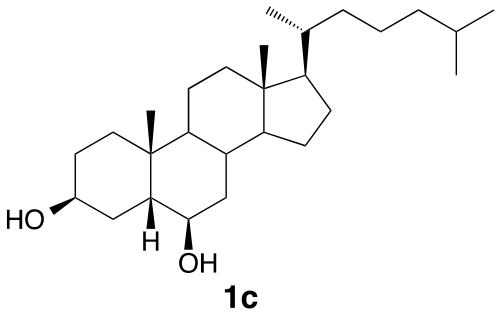





**1b**

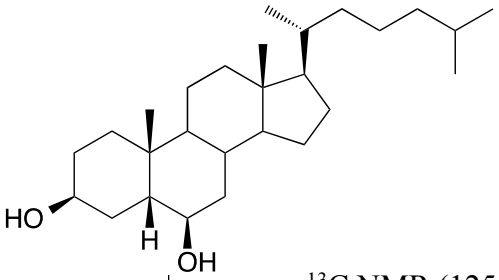
HMBC experiment (500 MHz, $CDCl_3$)





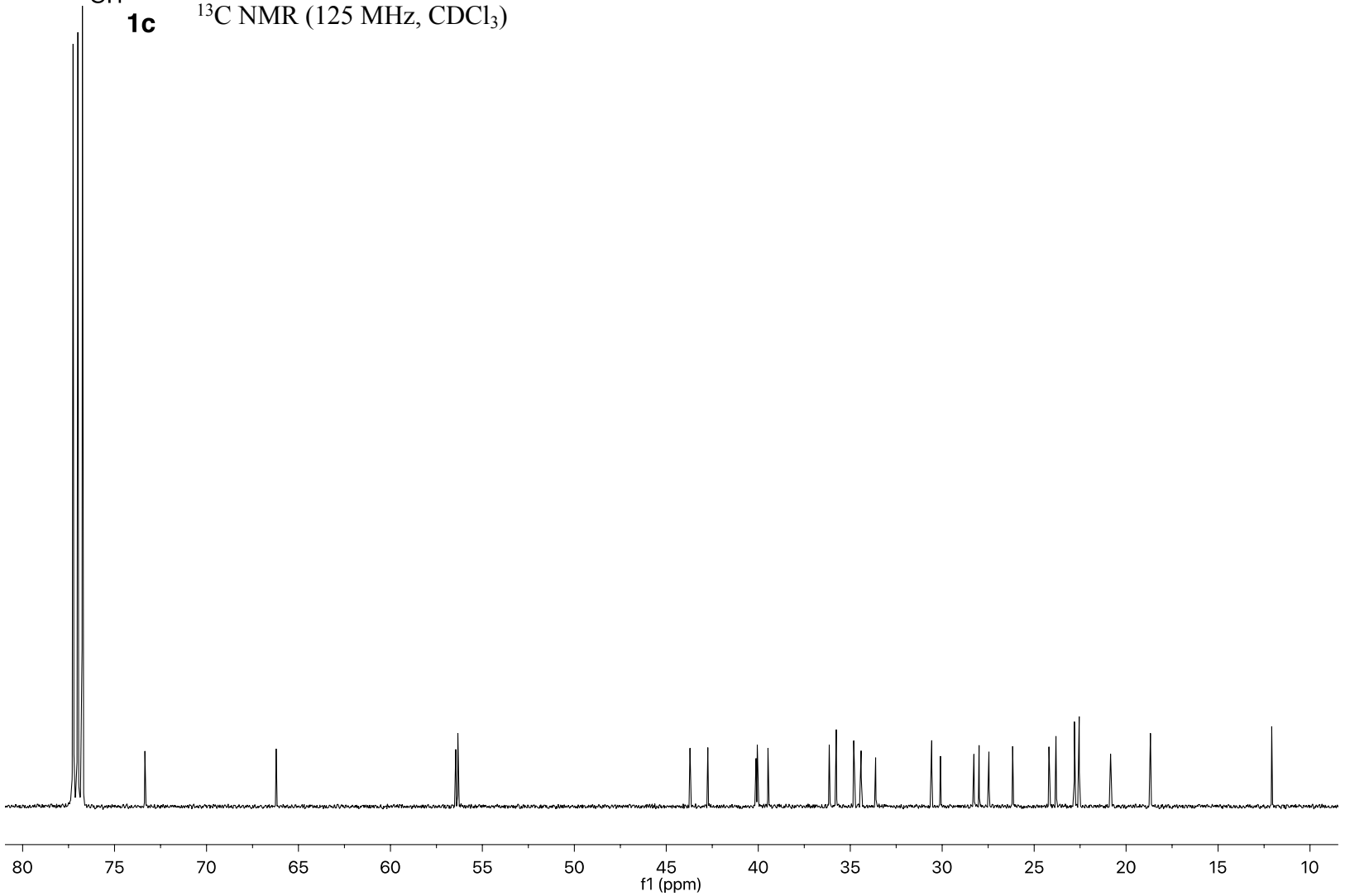

**1c**

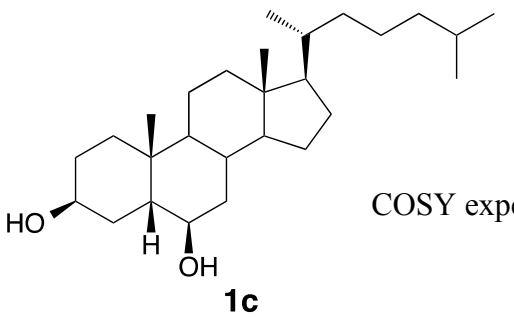
$^1$H NMR (500 MHz, $CDCl_3$)




**1c**

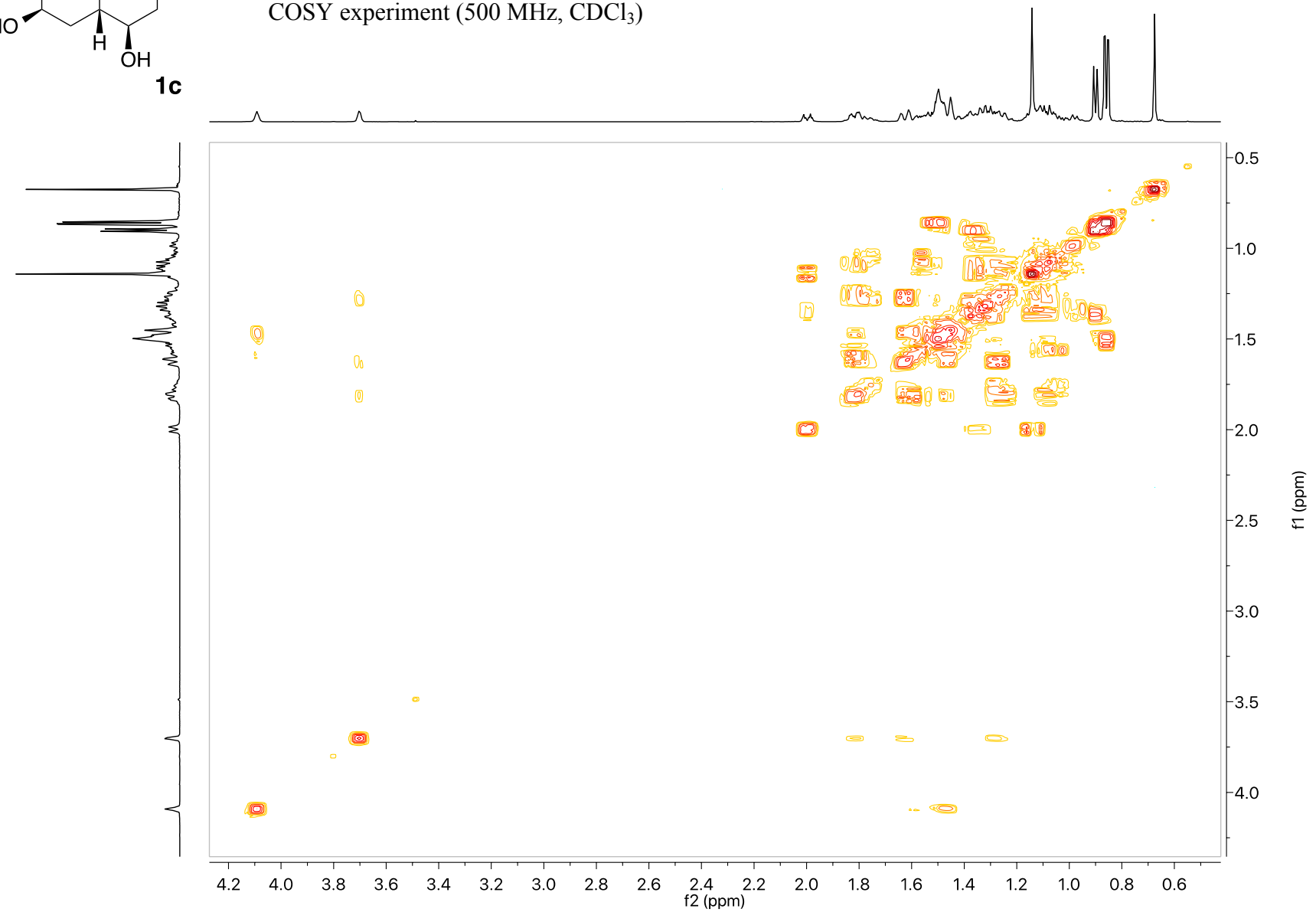
$^{13}$C NMR (125 MHz, $CDCl_3$)

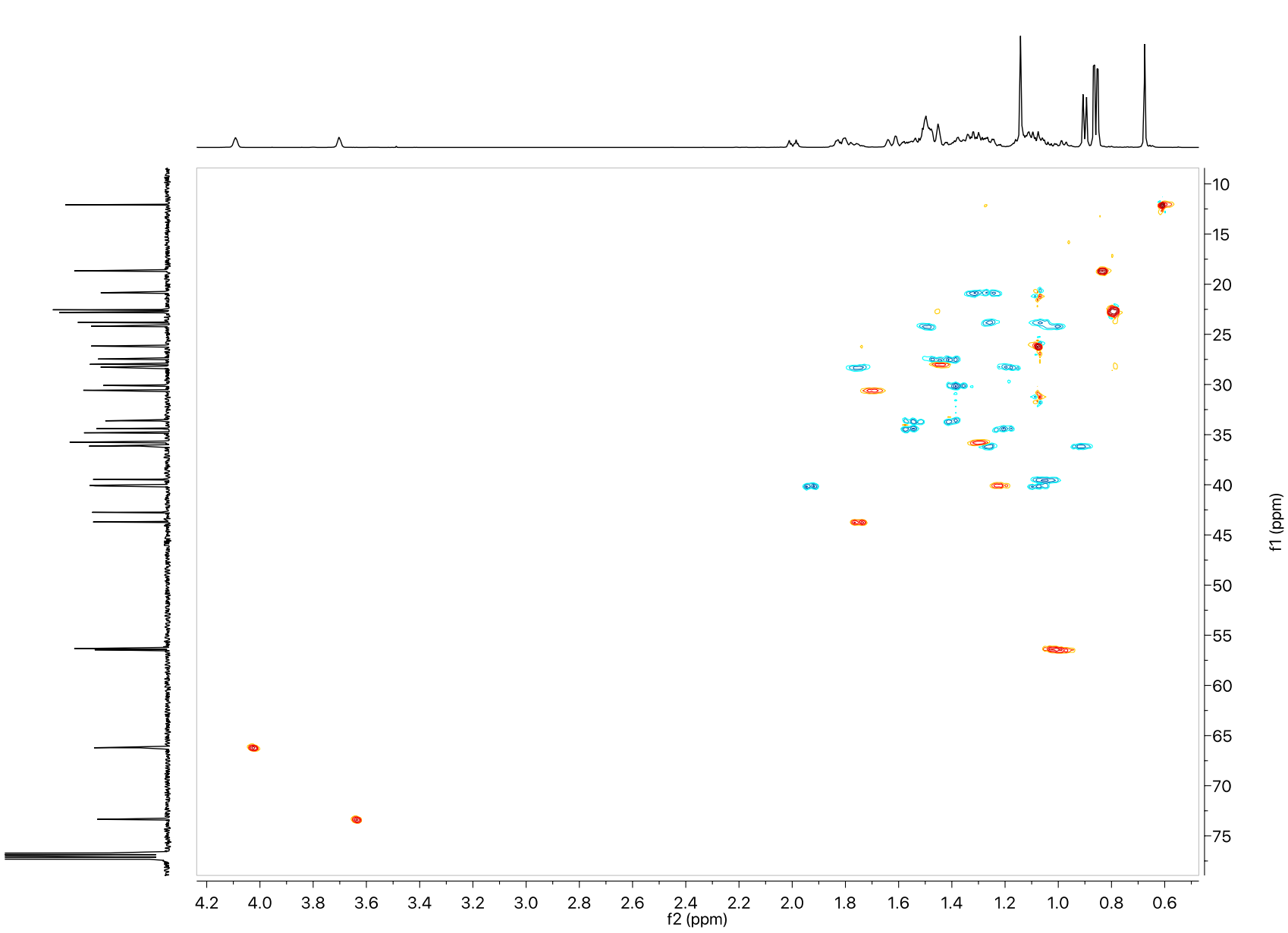


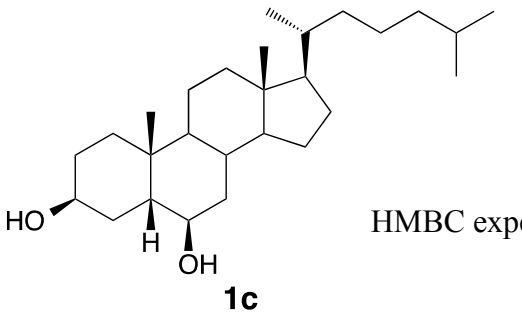



**1c**

COSY experiment (500 MHz, $CDCl_3$)

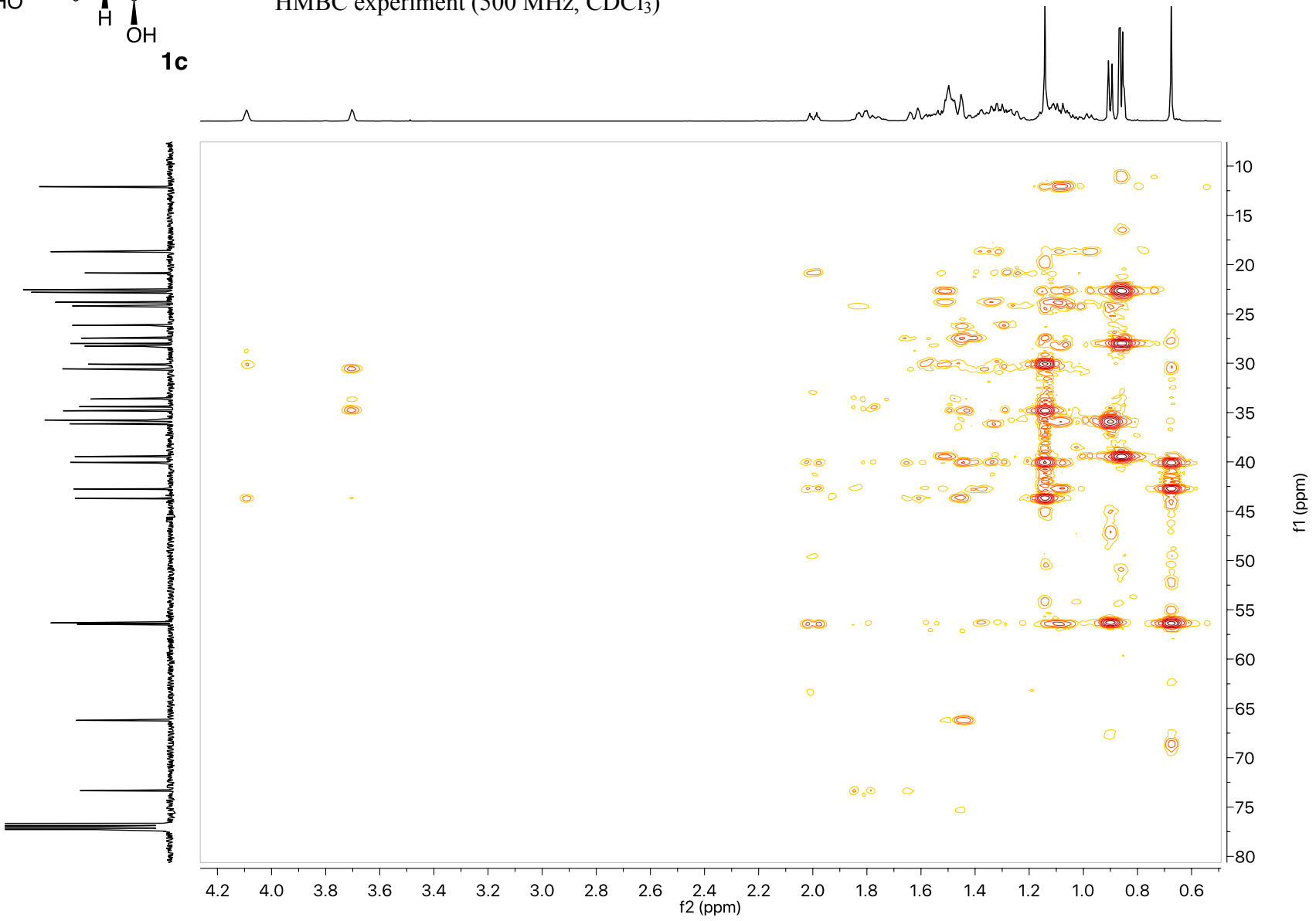


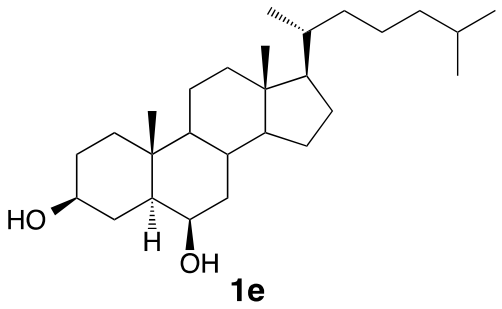

HO
H
f1 (ppm)
f2 (ppm)
10
15
20
25
30
35
40
45
50
55
60
65
70
75
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6




**1c**

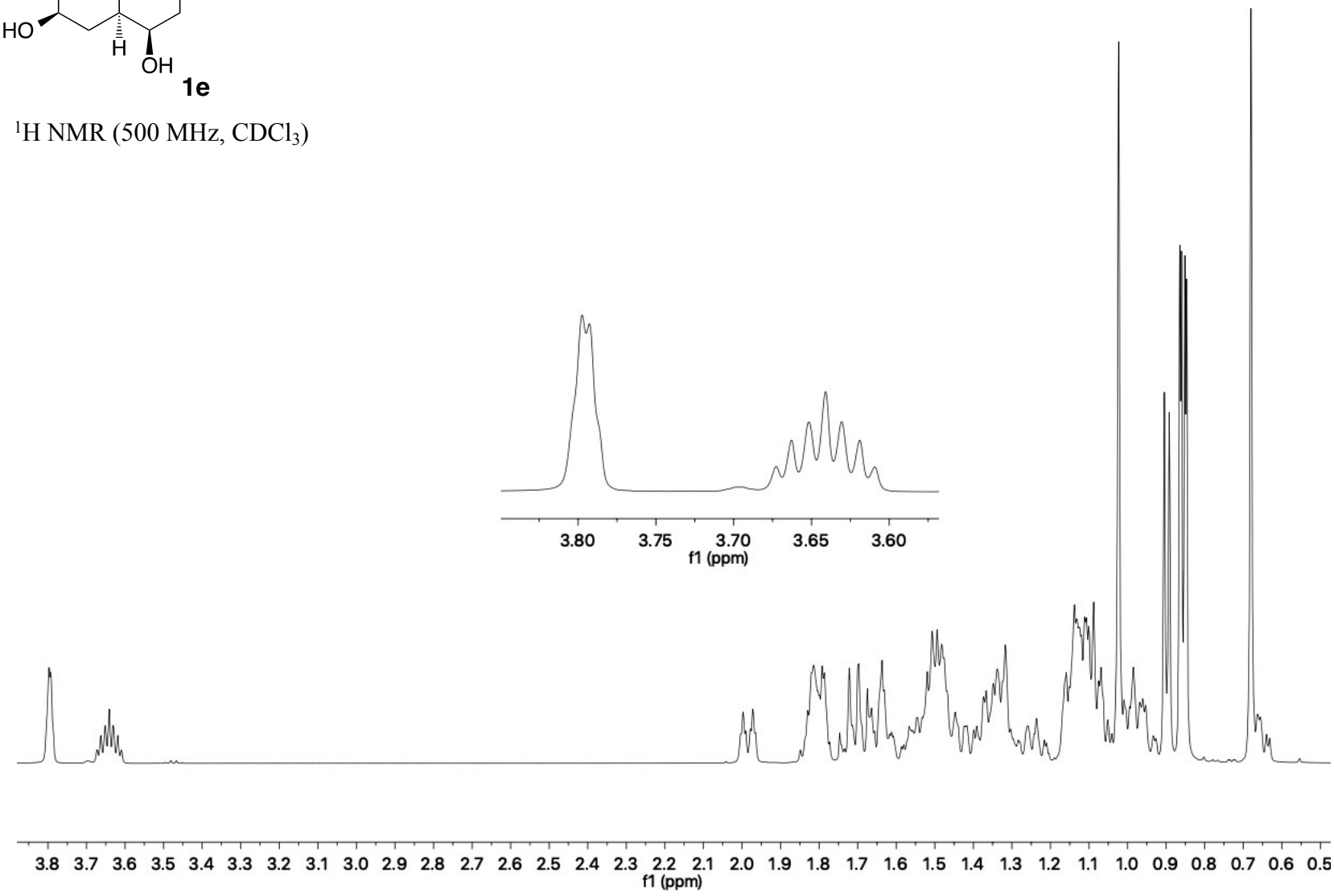
HMBC experiment (500 MHz, $CDCl_3$)

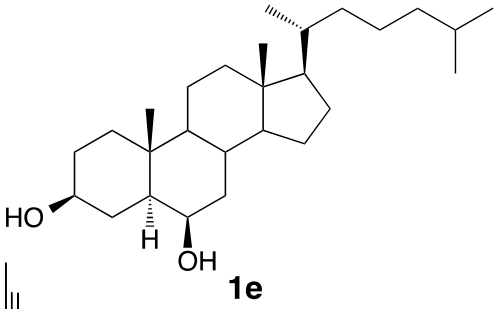





**1e**

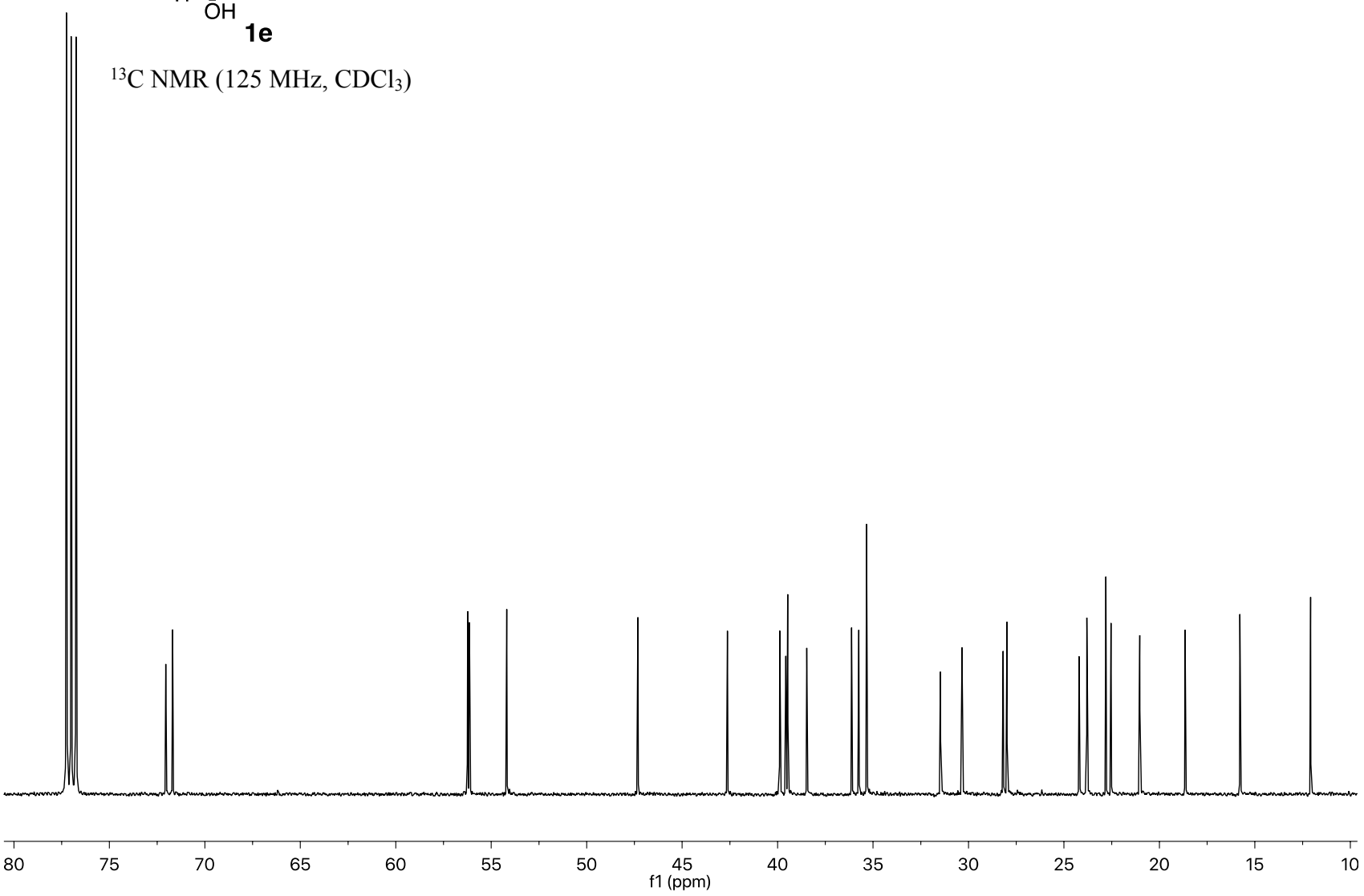
$^1$H NMR (500 MHz, $CDCl_3$)

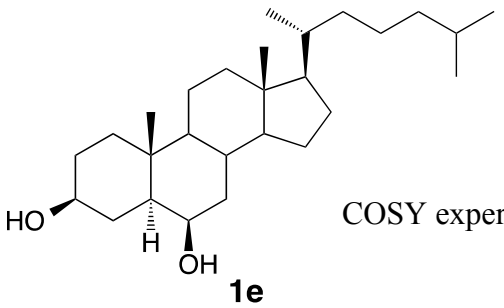





**1e**

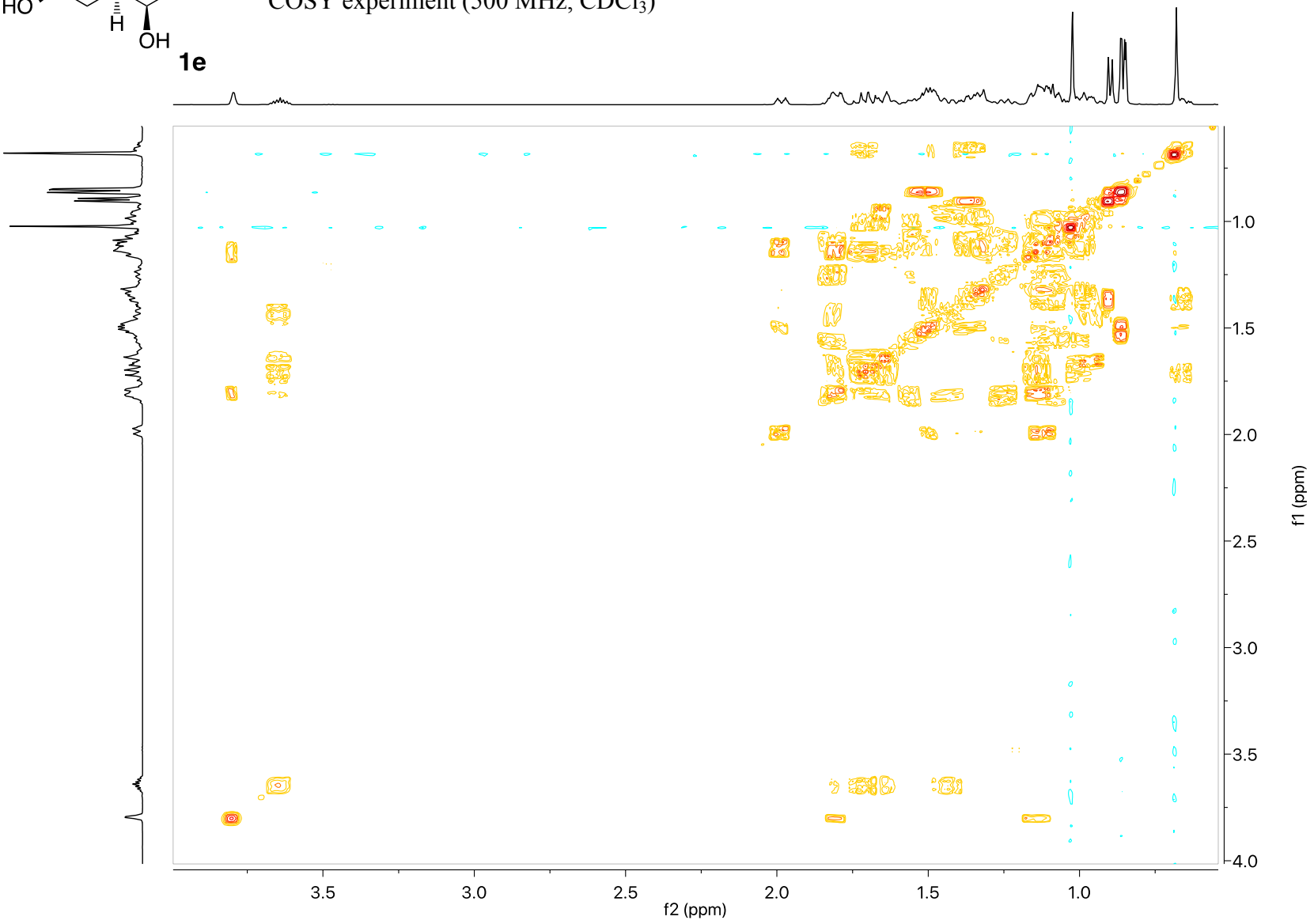
$^{13}C$ NMR (125 MHz, $CDCl_3$)

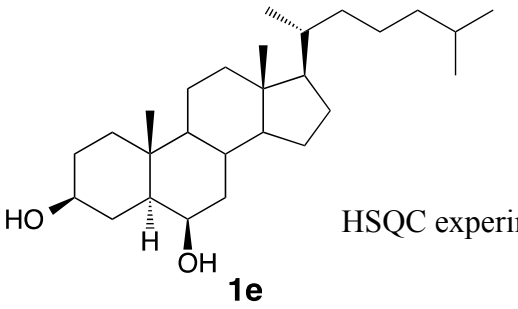





**1e**

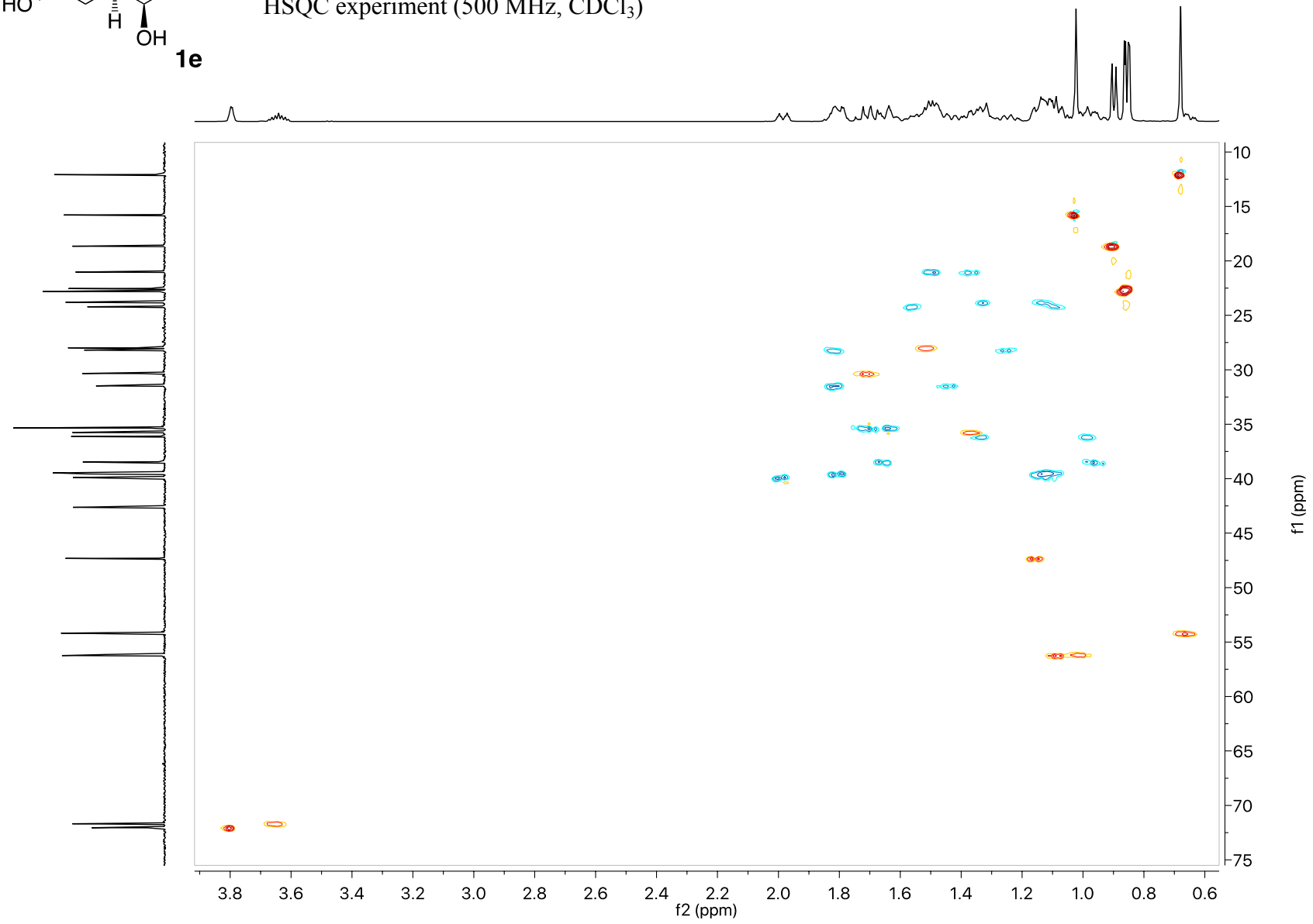
COSY experiment (500 MHz, $CDCl_3$)

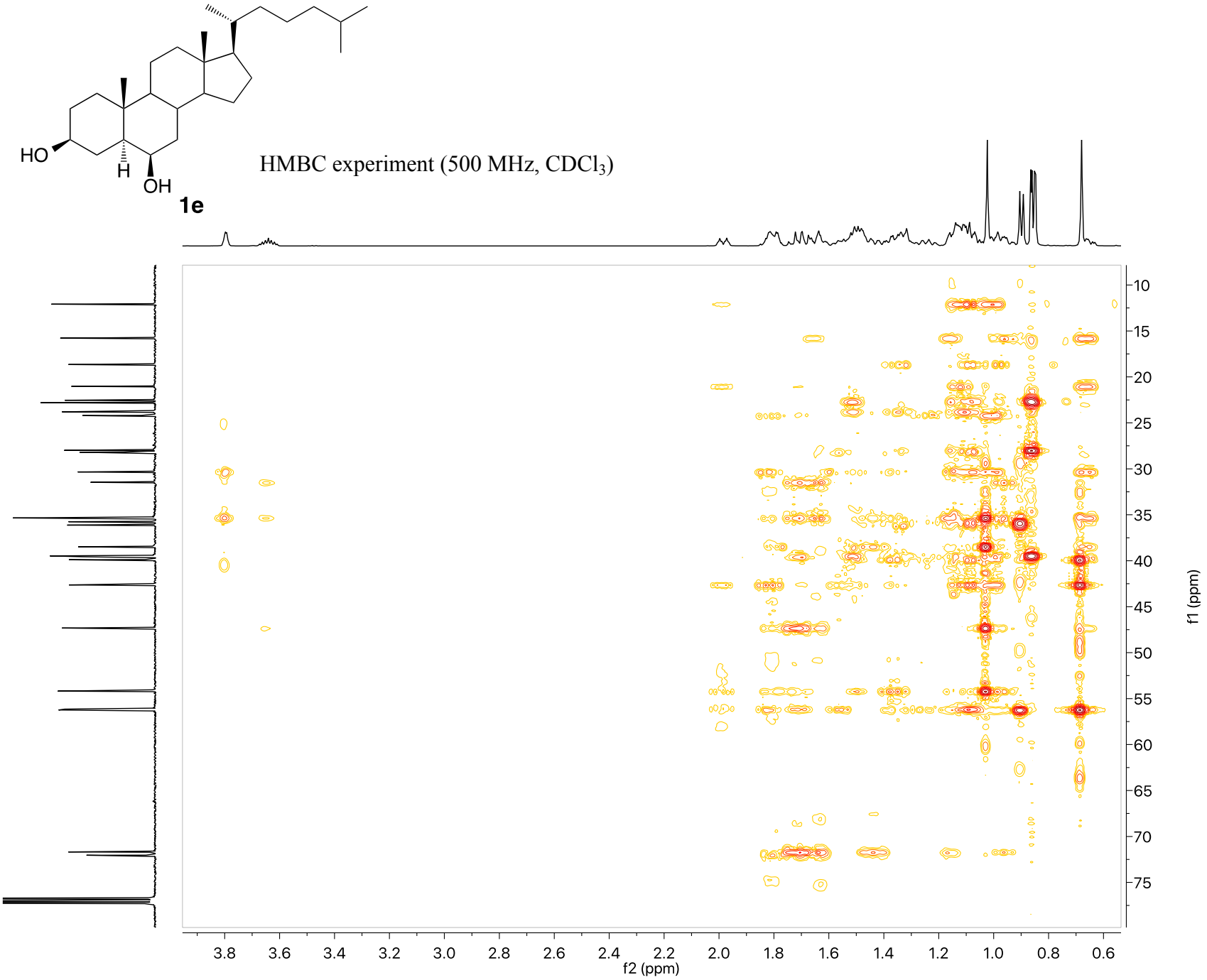


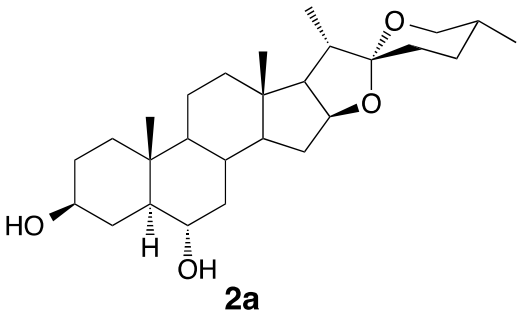



**1e**

HSQC experiment (500 MHz, $CDCl_3$)

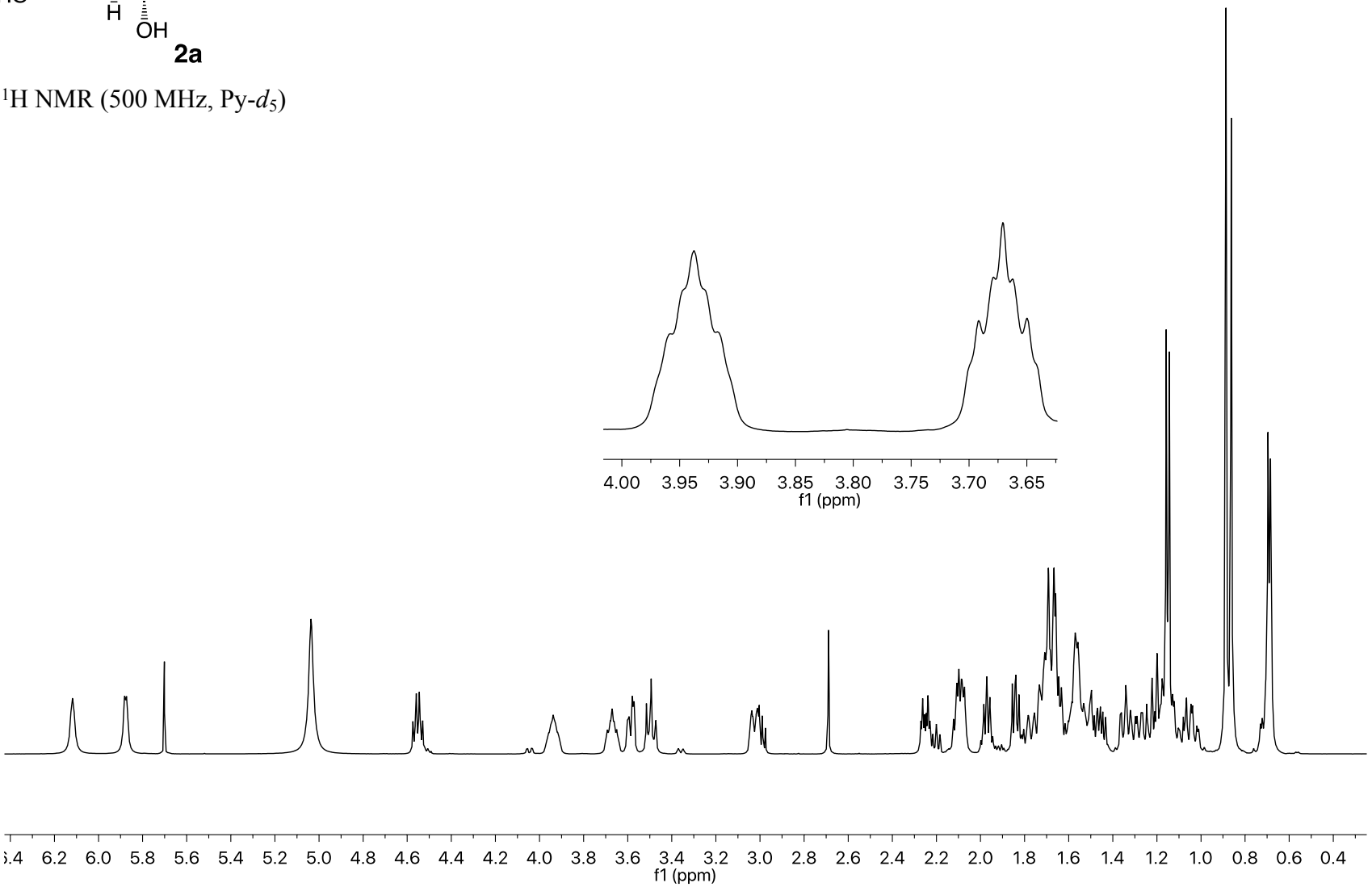


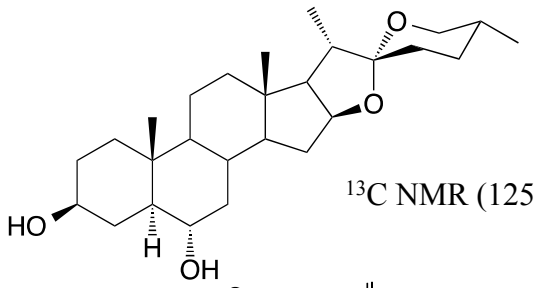

HO
H
OH
1e
HMBC experiment (500 MHz, CDCl3)
f2 (ppm)
f1 (ppm)




**2a**

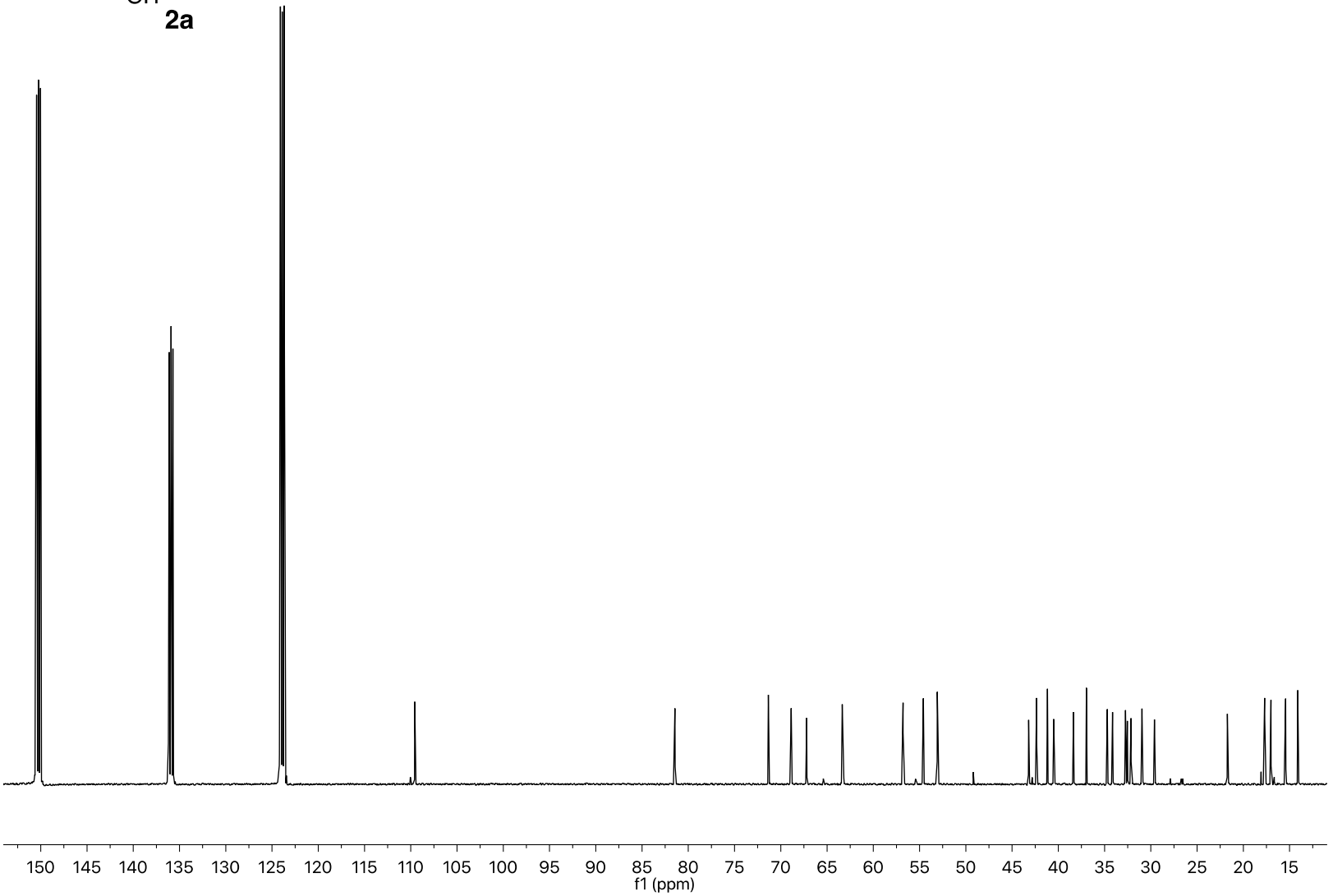
$^1$H NMR (500 MHz, Py-$d_5$)

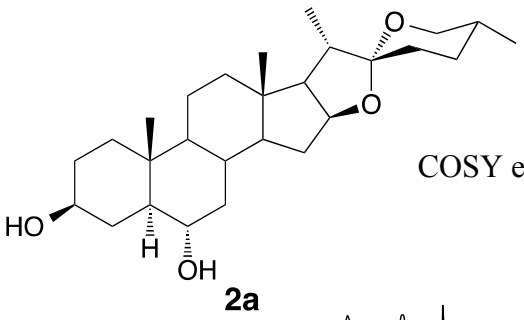





**2a**

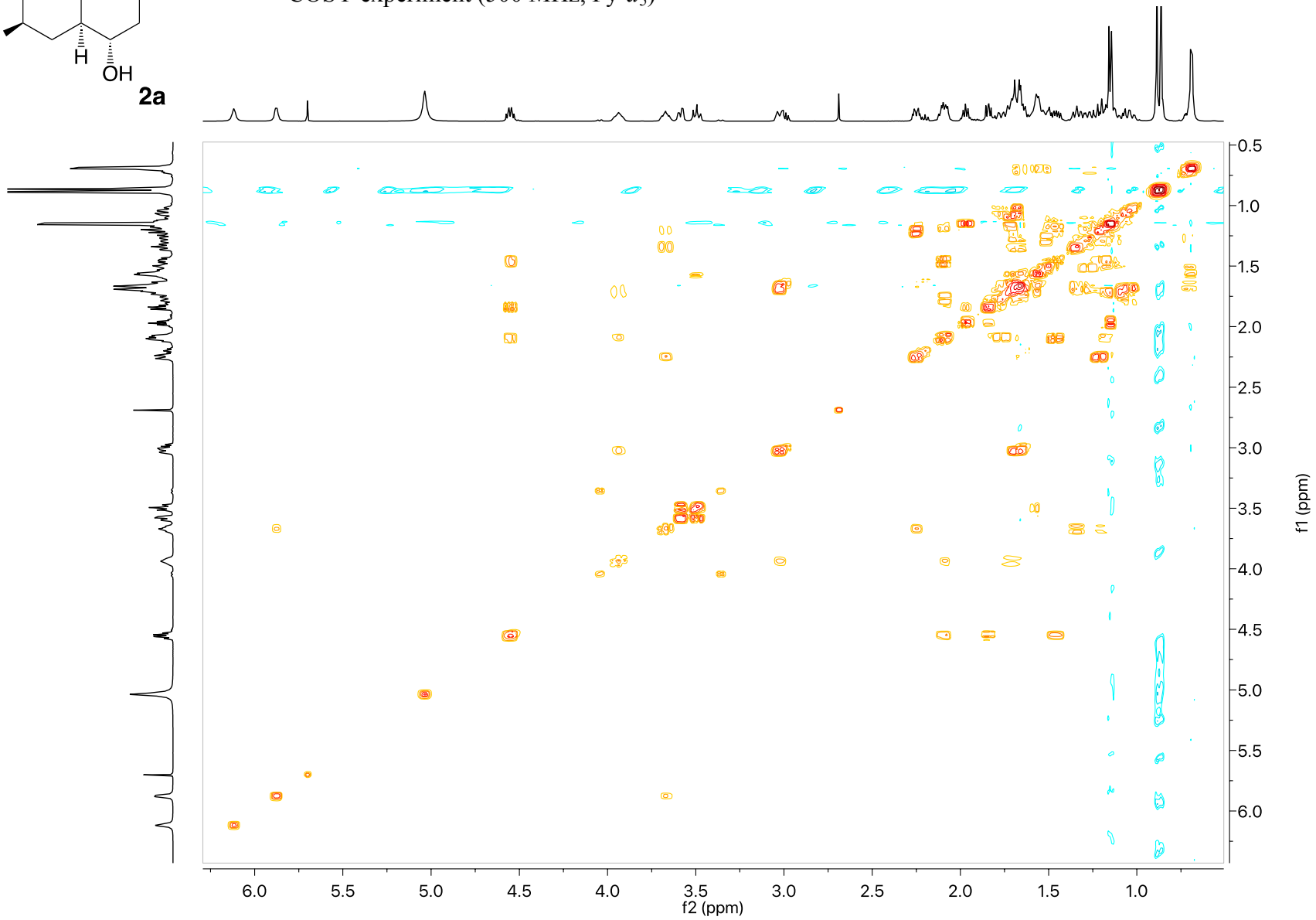
$^{13}$C NMR (125 MHz, Py-$d_5$)

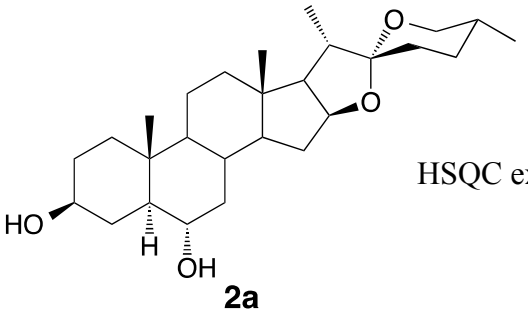





**2a**

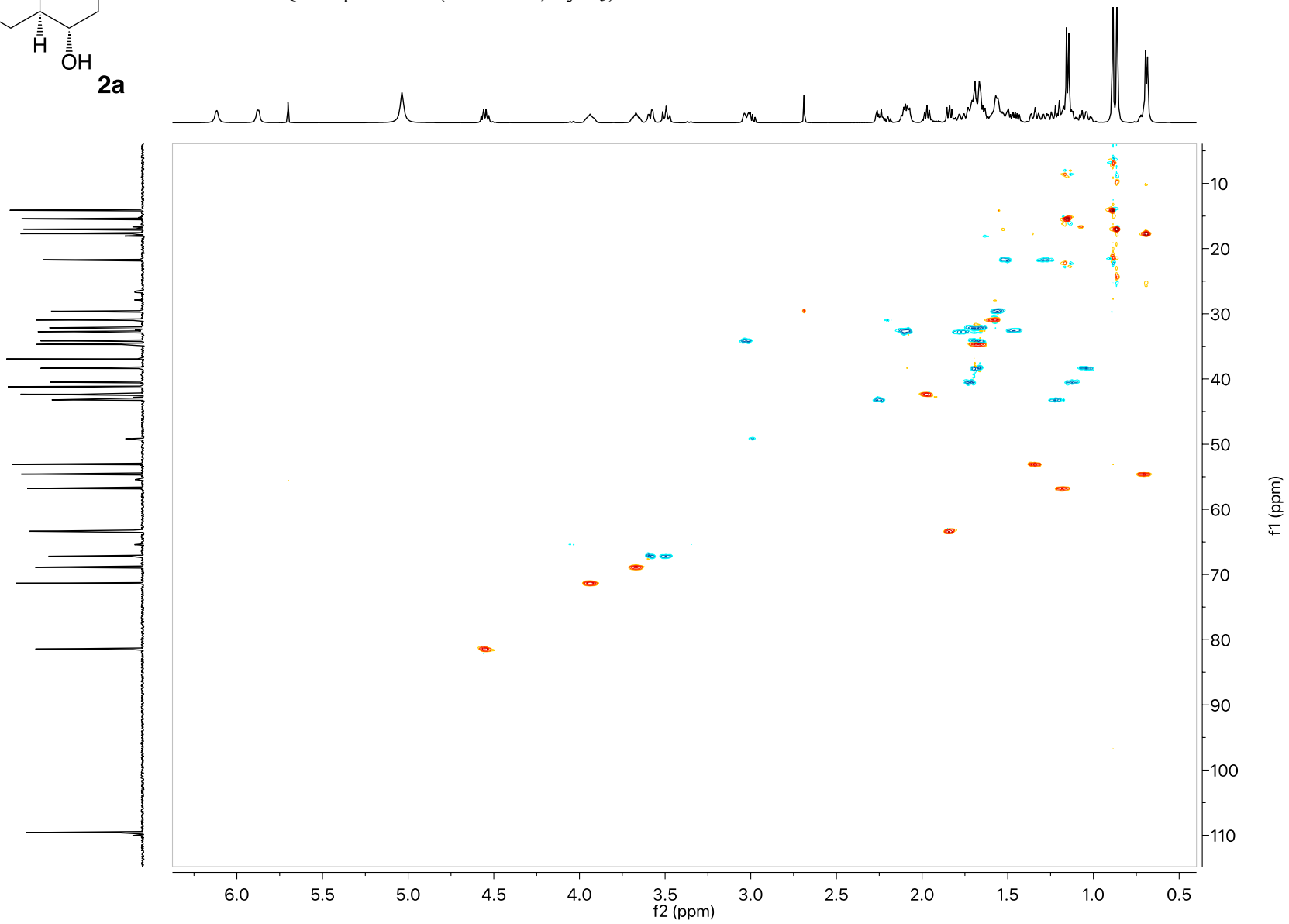
COSY experiment (500 MHz, Py-$d_5$)

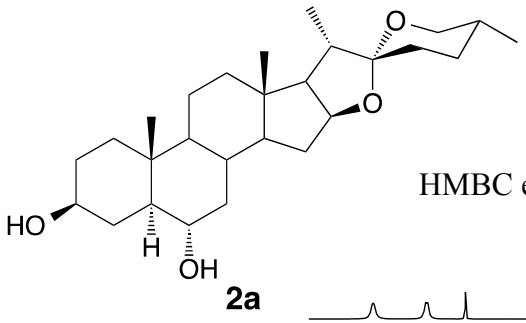





**2a**

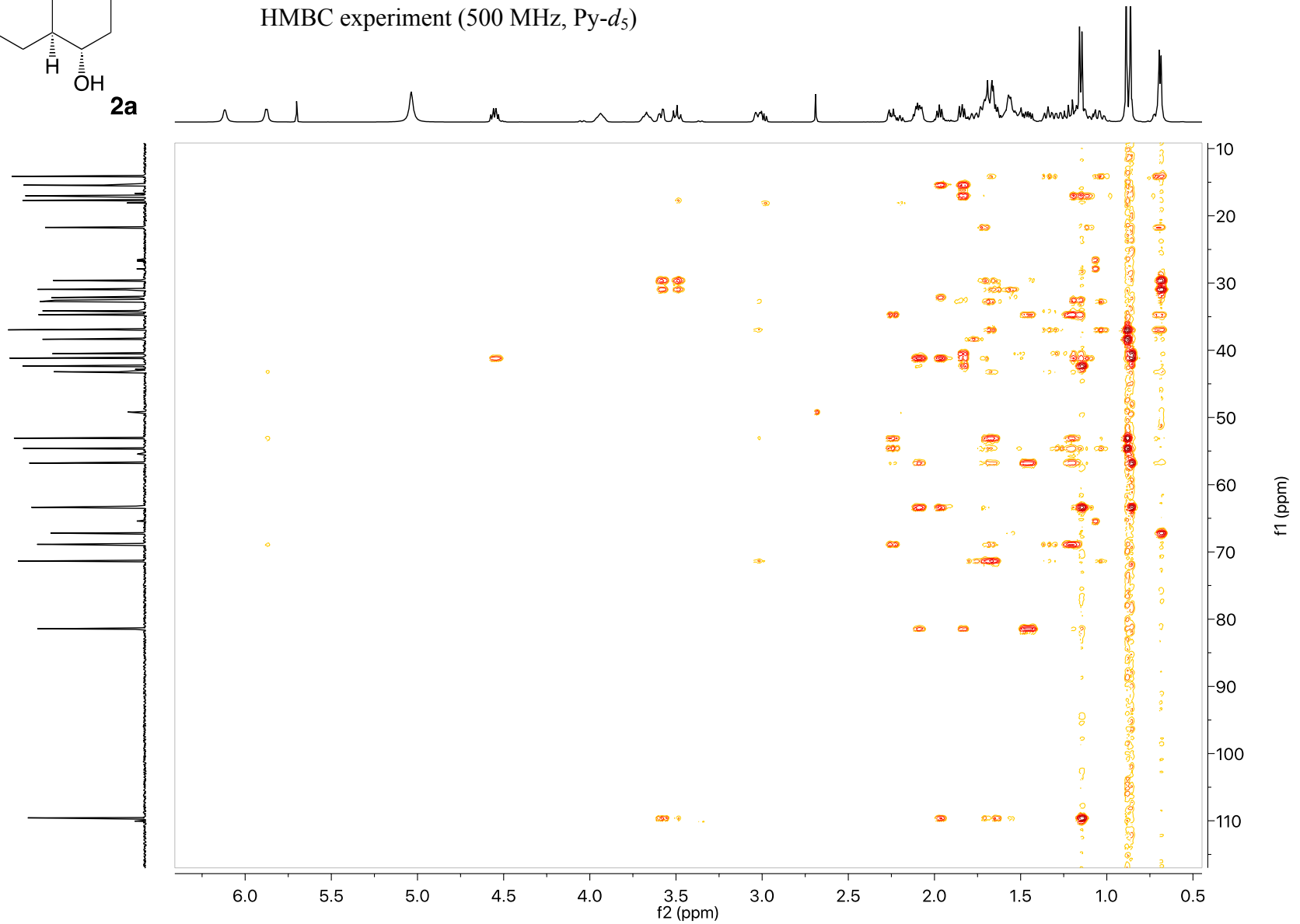
HSQC experiment (500 MHz, Py-$d_5$)

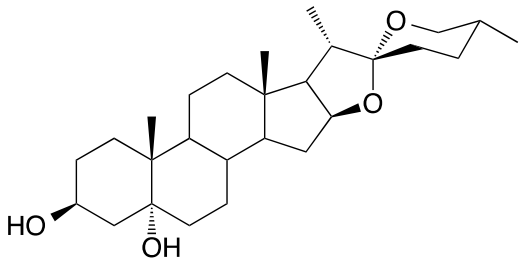





**2a**

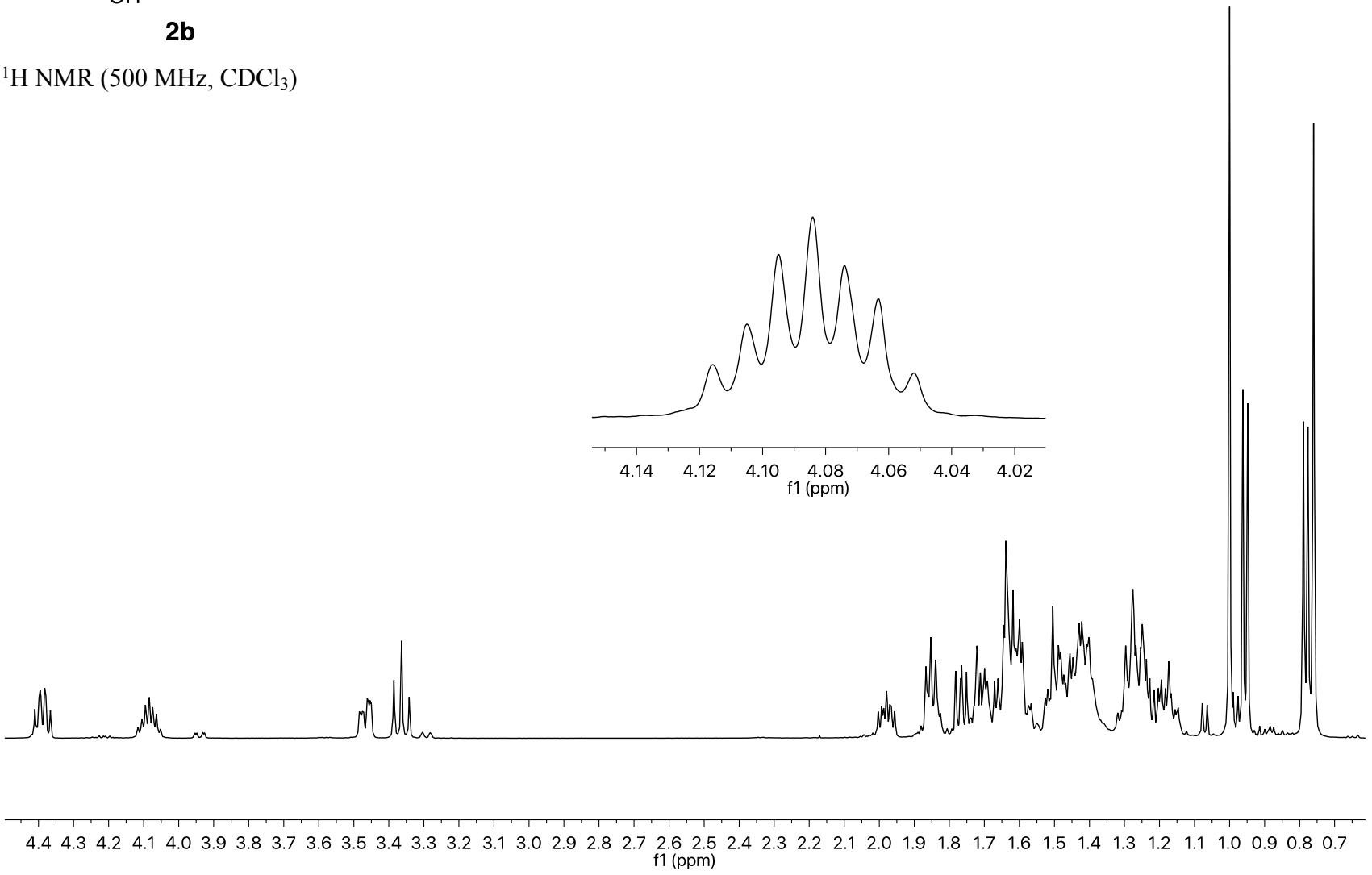
HMBC experiment (500 MHz, Py-$d_5$)

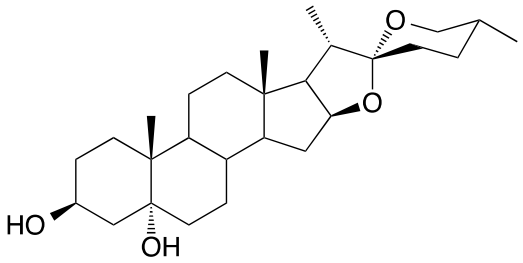





**2b**

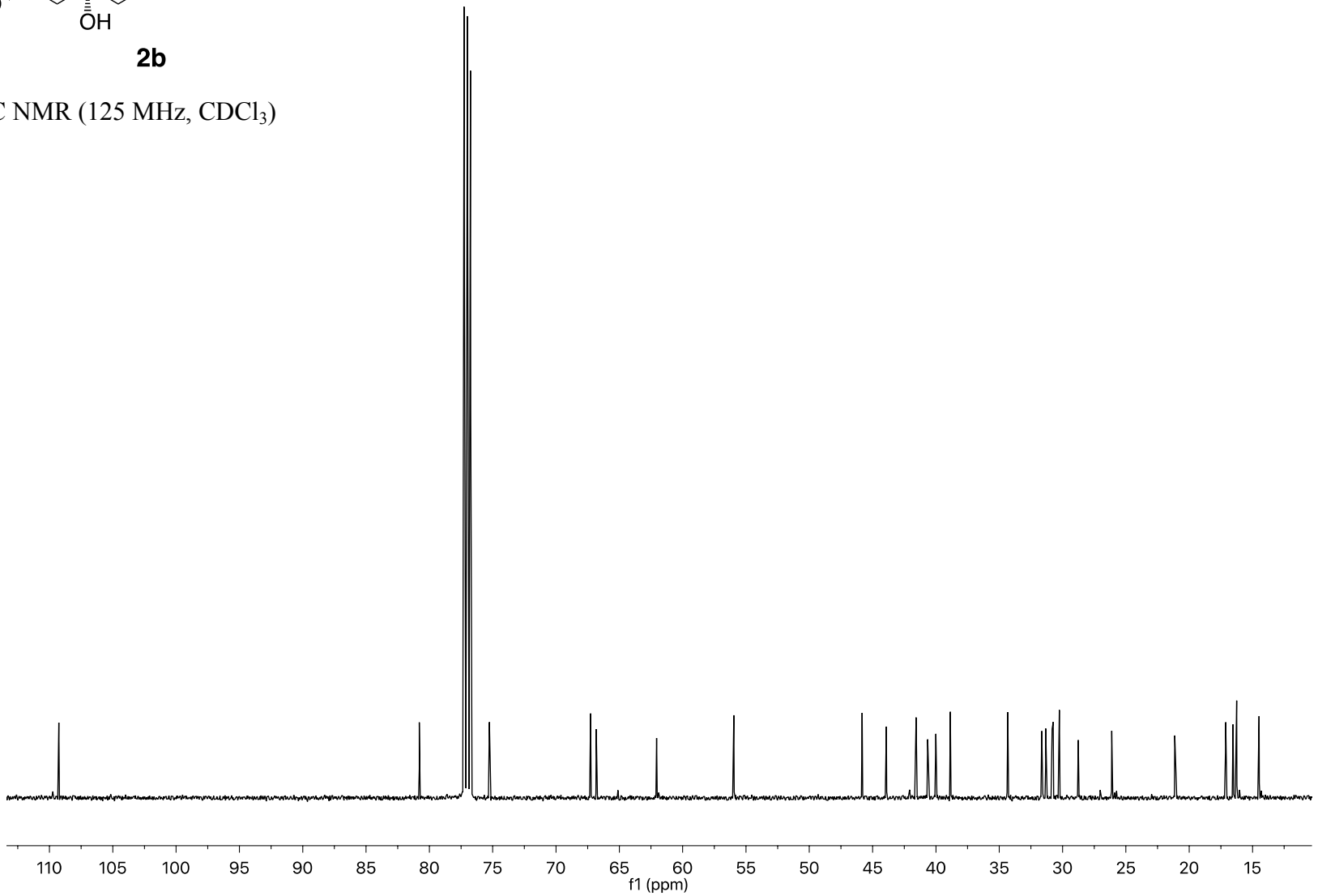
$^1$H NMR (500 MHz, $CDCl_3$)

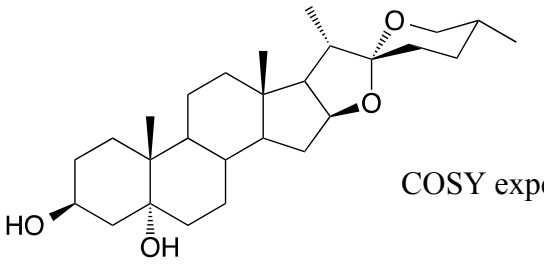





**2b**

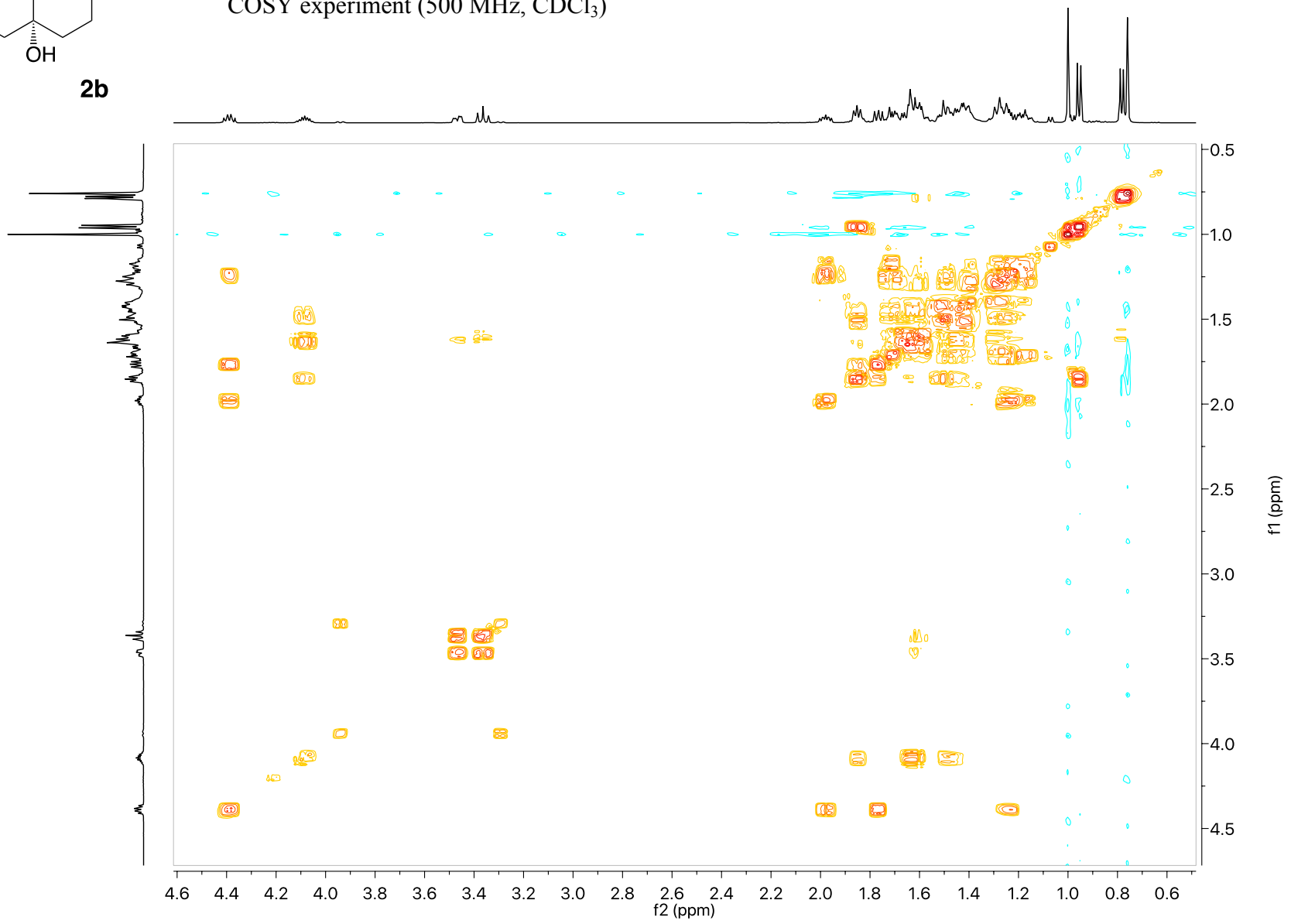
$^{13}C$ NMR (125 MHz, $CDCl_3$)

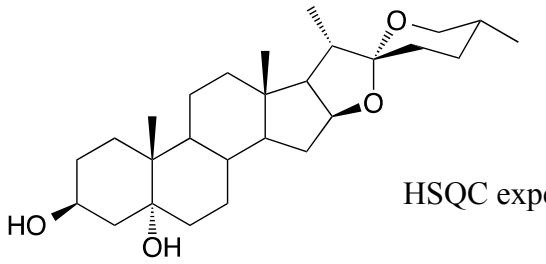





**2b**

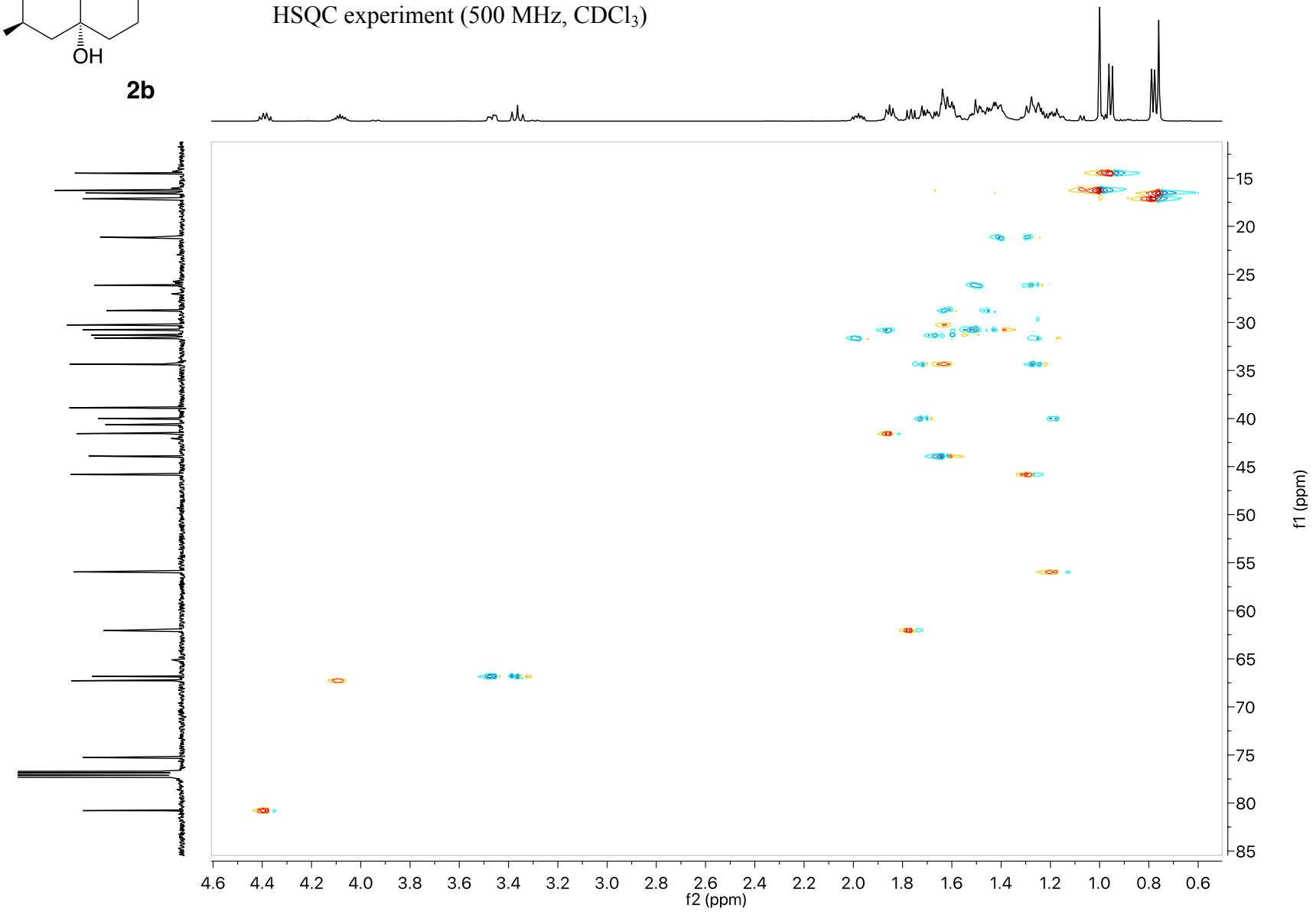
COSY experiment (500 MHz, $CDCl_3$)

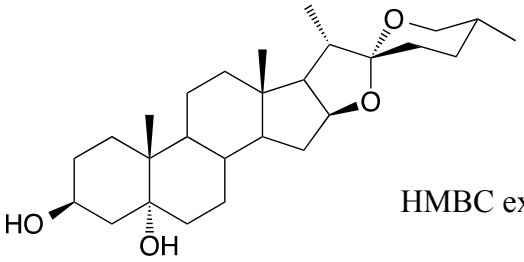





**2b**

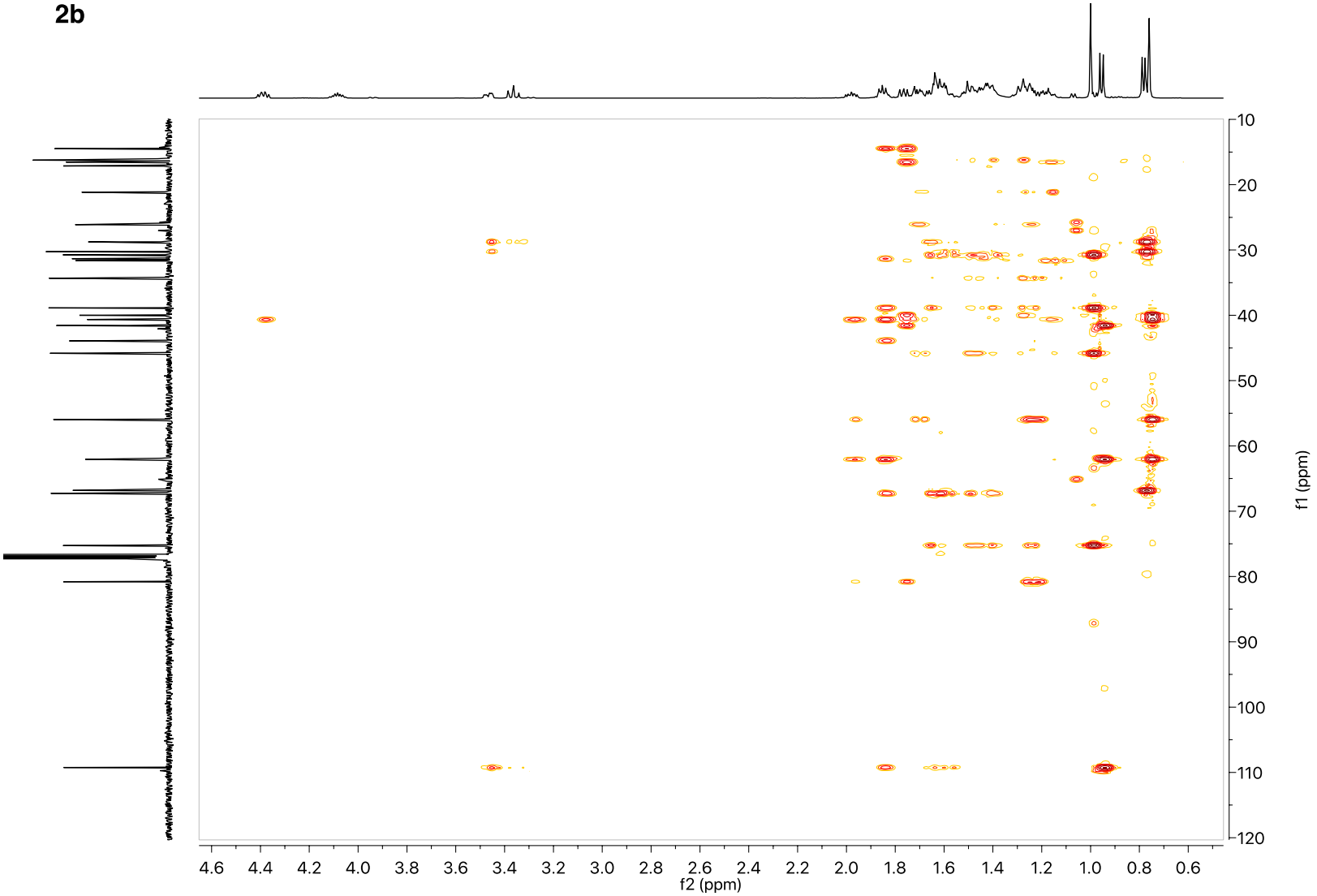
HSQC experiment (500 MHz, $CDCl_3$)

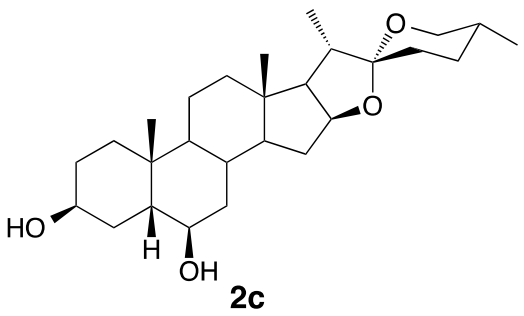





**2b**

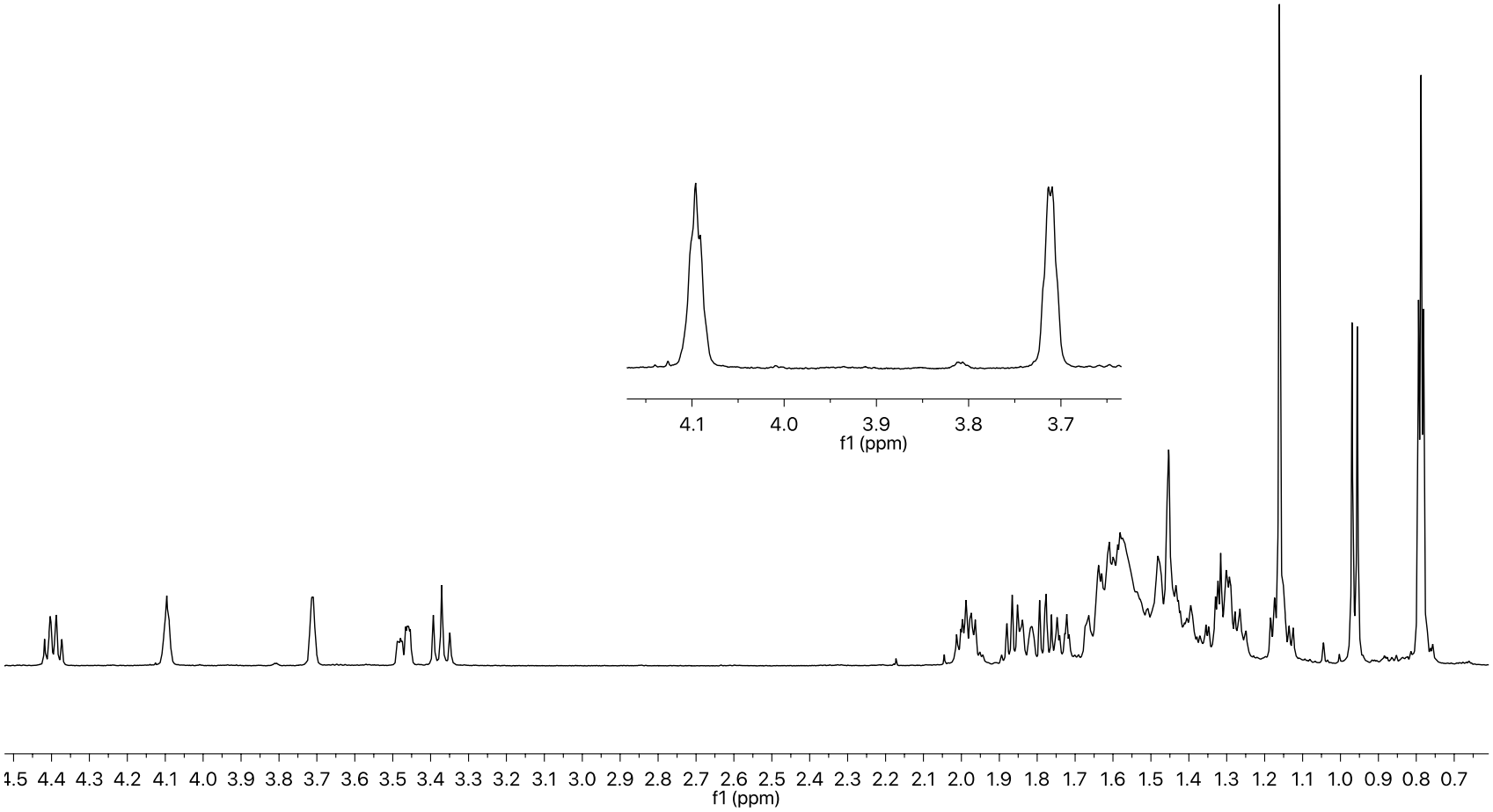
HMBC experiment (500 MHz, $CDCl_3$)

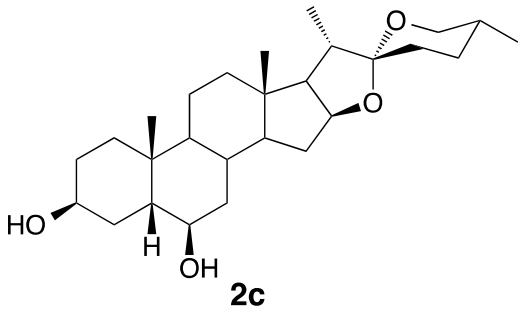





**2c**

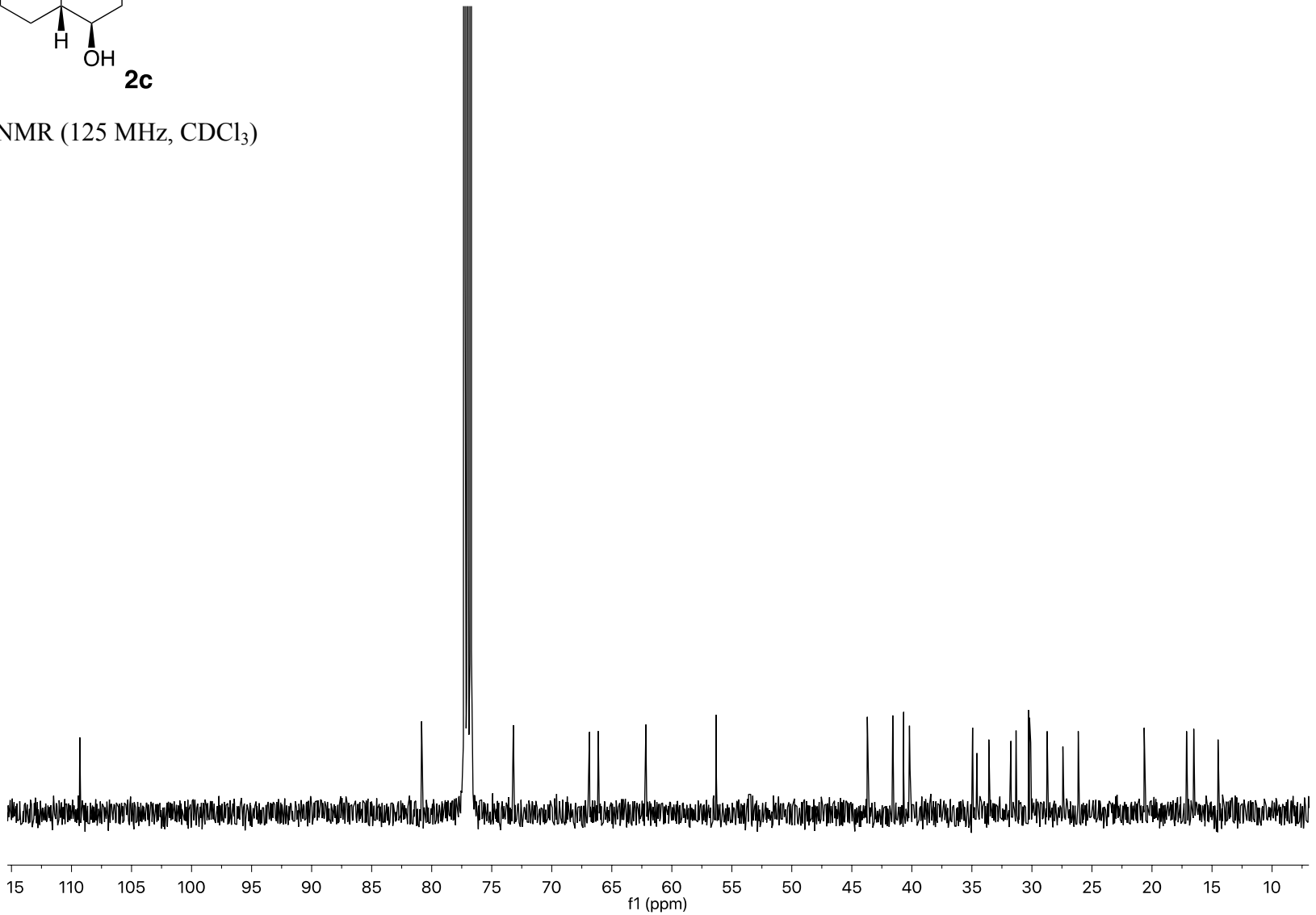
$^1$H NMR (500 MHz, $CDCl_3$)

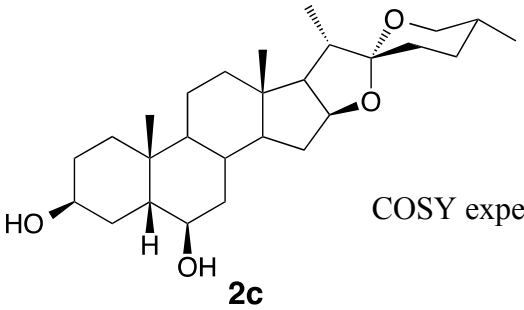





**2c**

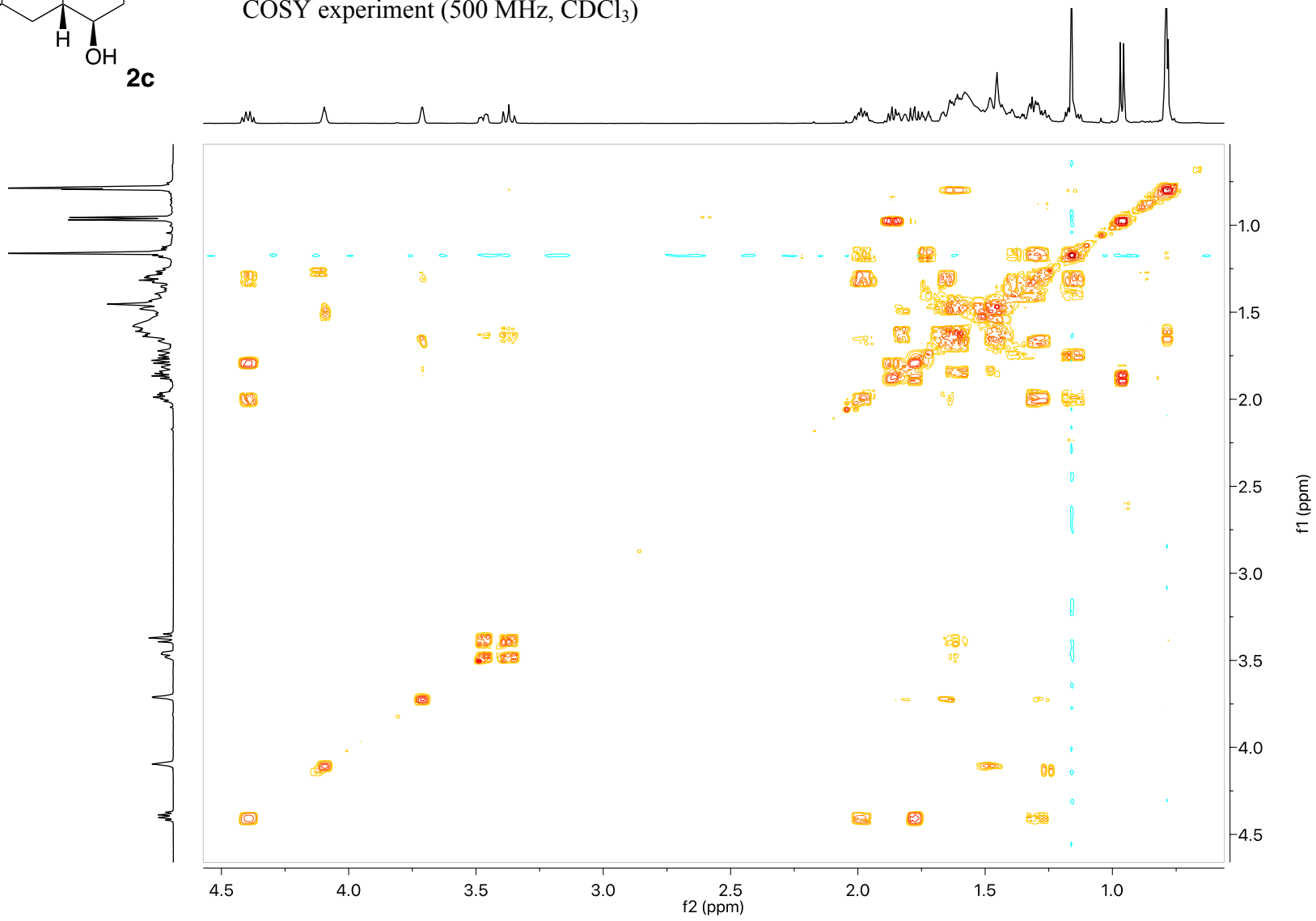
$^{13}C$ NMR (125 MHz, $CDCl_3$)

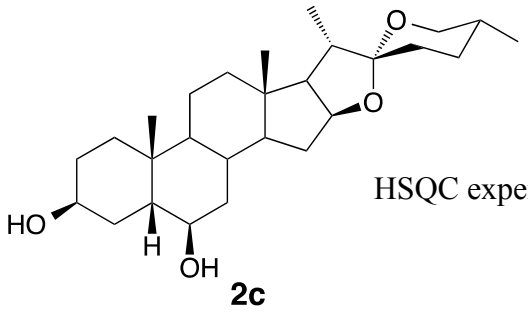





**2c**

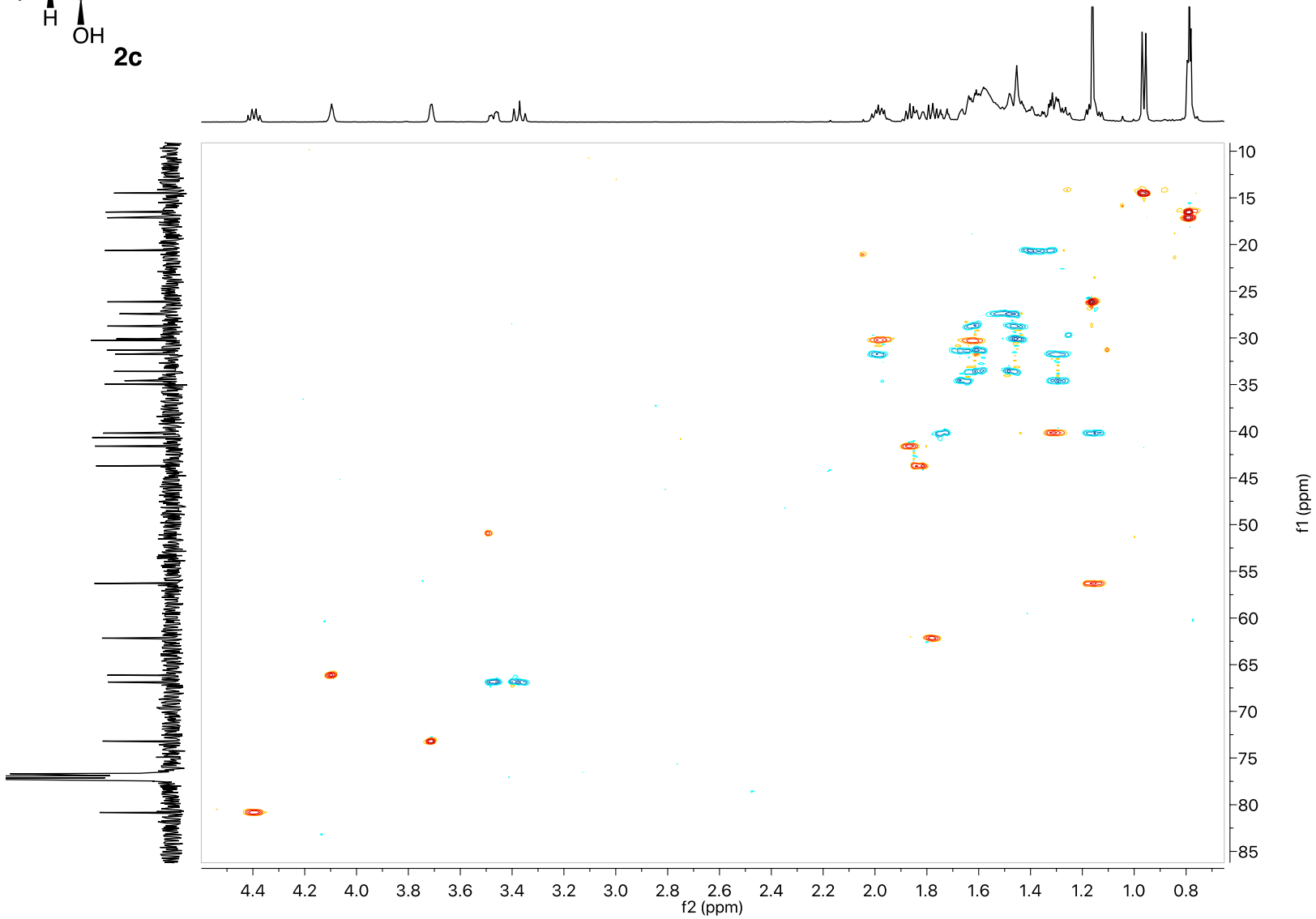
COSY experiment (500 MHz, $CDCl_3$)

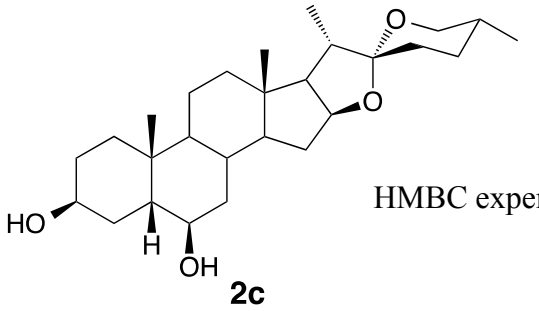





**2c**

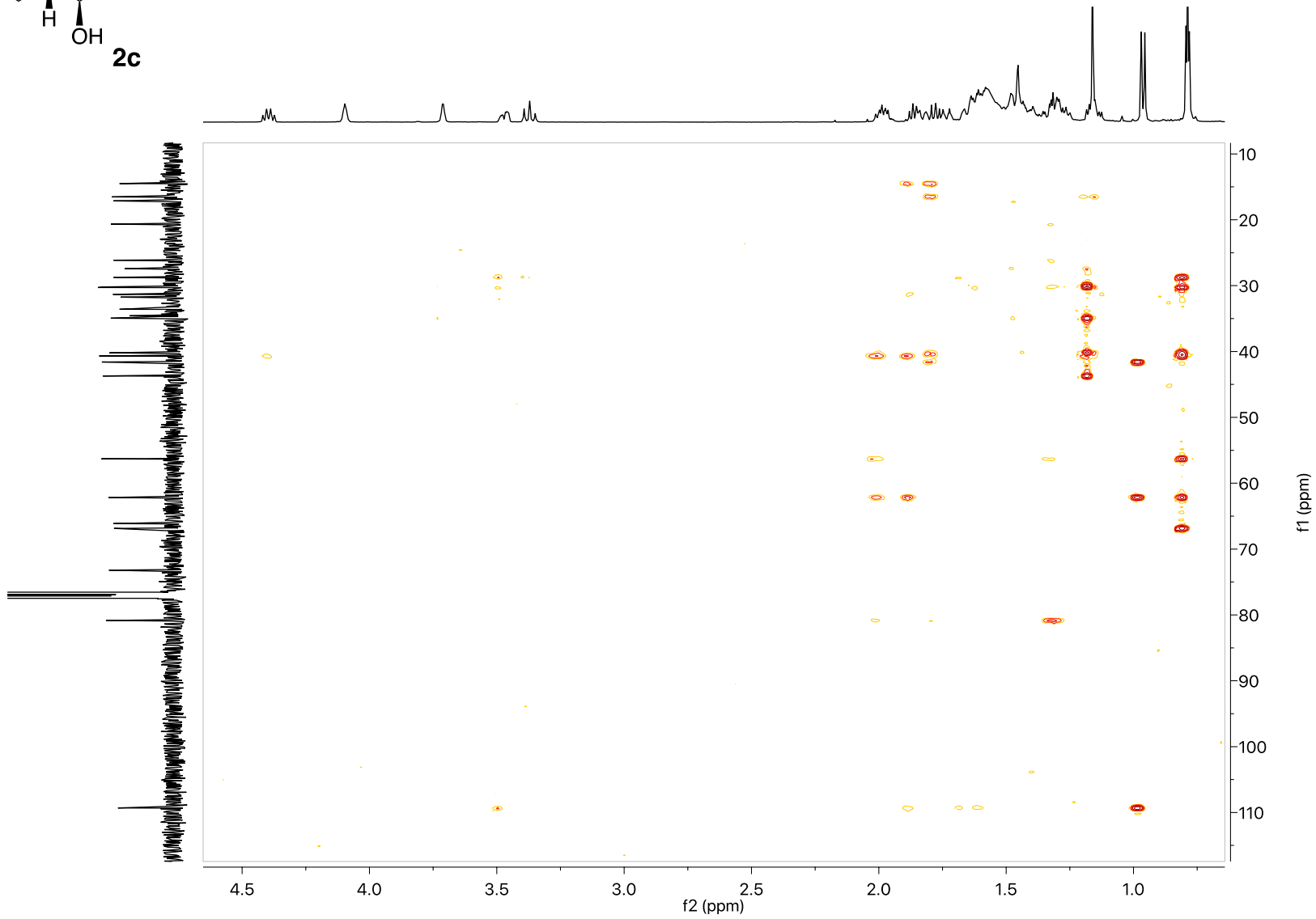
HSQC experiment (500 MHz, $CDCl_3$)

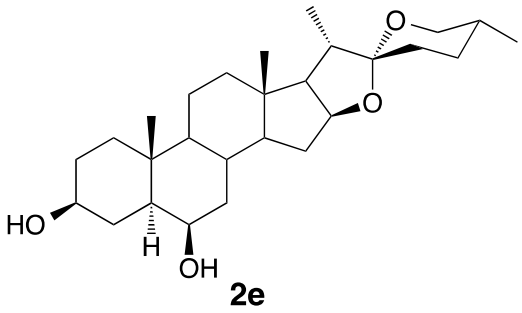





**2c**

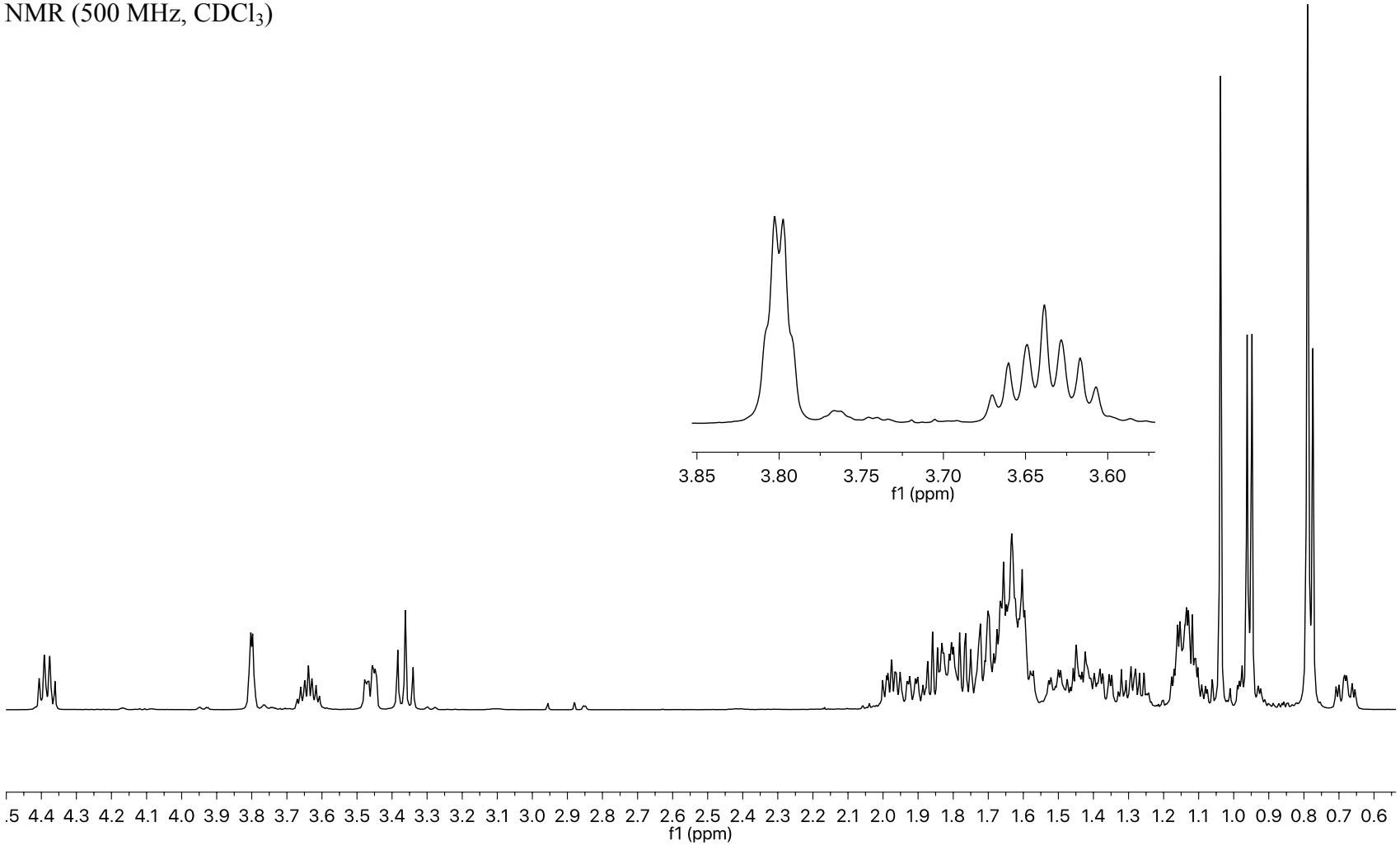
HMBC experiment (500 MHz, $CDCl_3$)

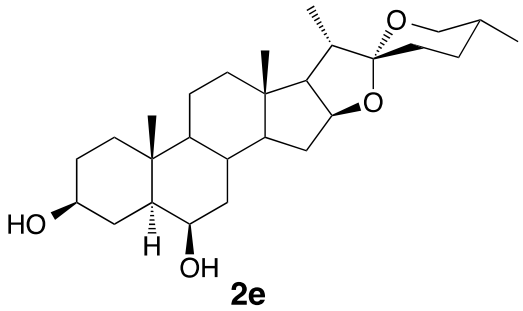





**2e**

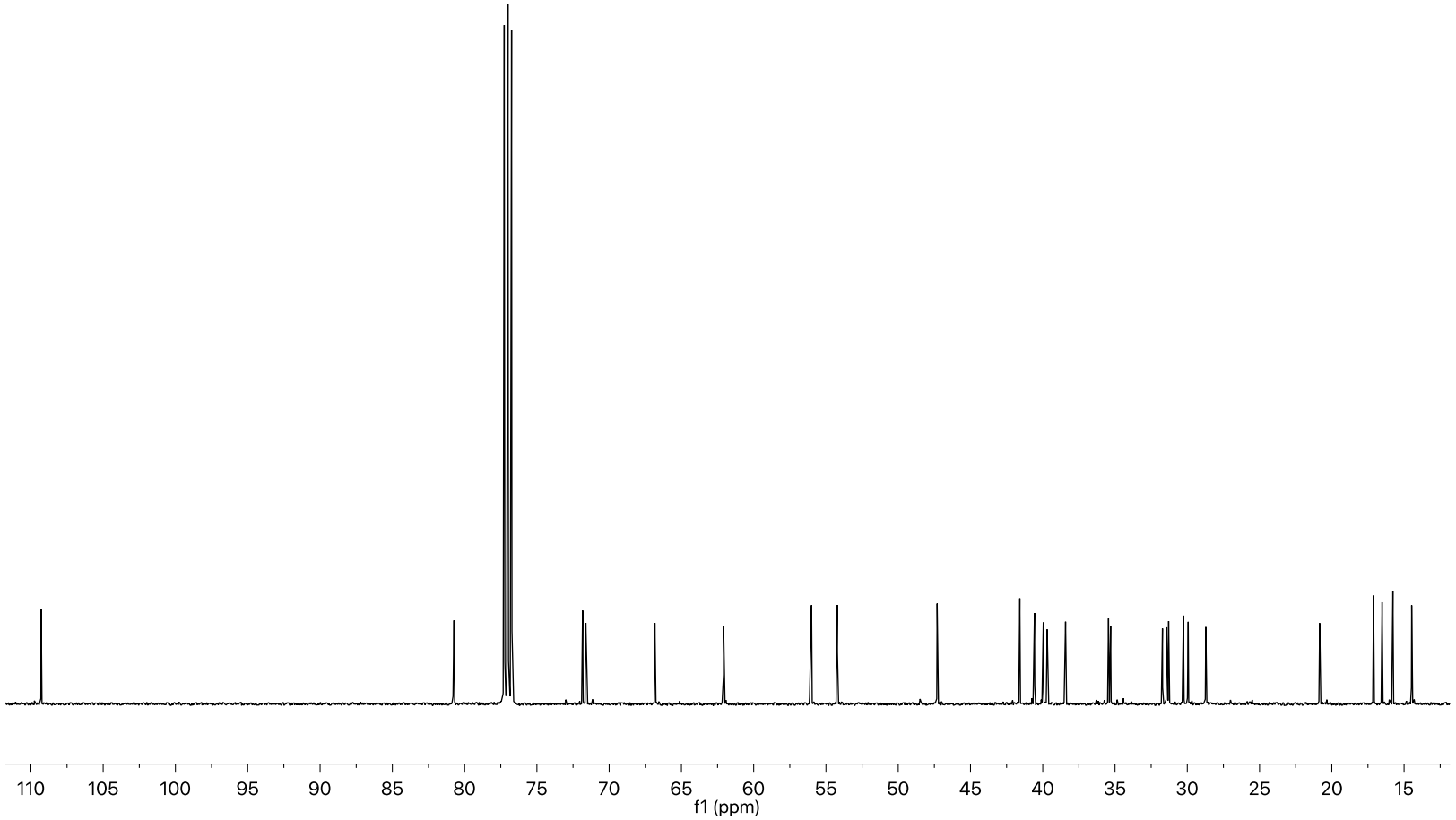
$^1$H NMR (500 MHz, $CDCl_3$)

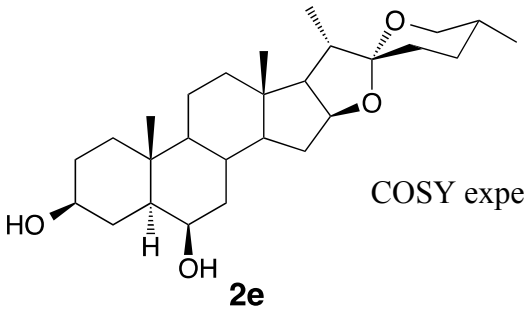





**2e**

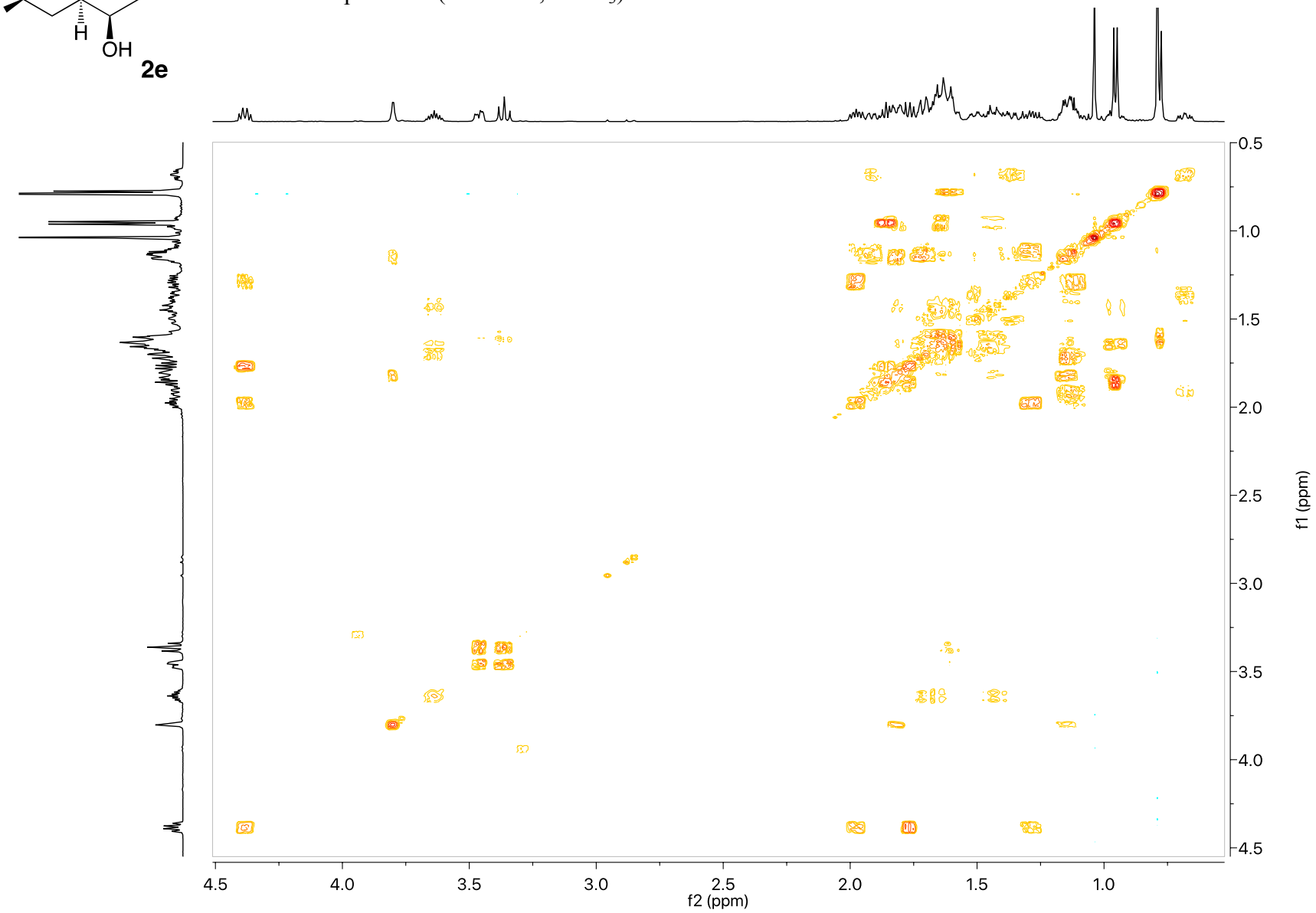
$^{13}C$ NMR (125 MHz, $CDCl_3$)

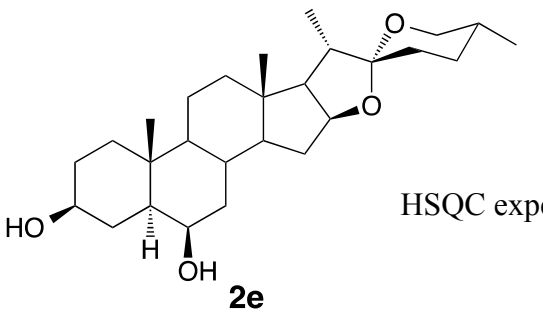





**2e**

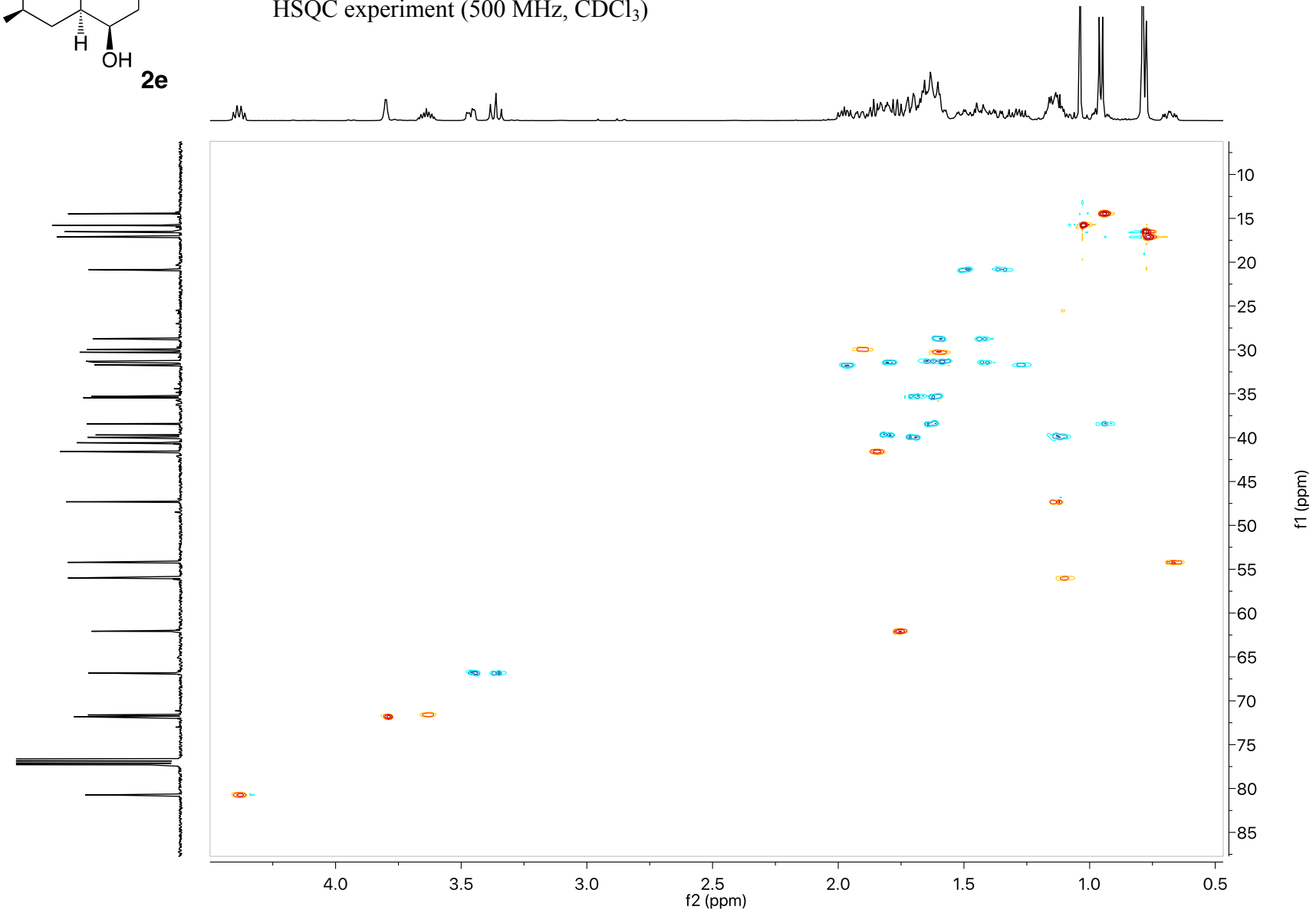
COSY experiment (500 MHz, $CDCl_3$)

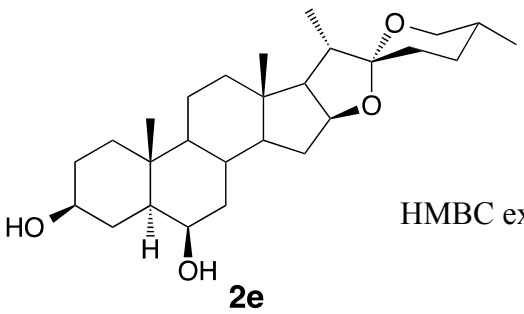





**2e**

HSQC experiment (500 MHz, $CDCl_3$)






**2e**

HMBC experiment (500 MHz, $CDCl_3$)