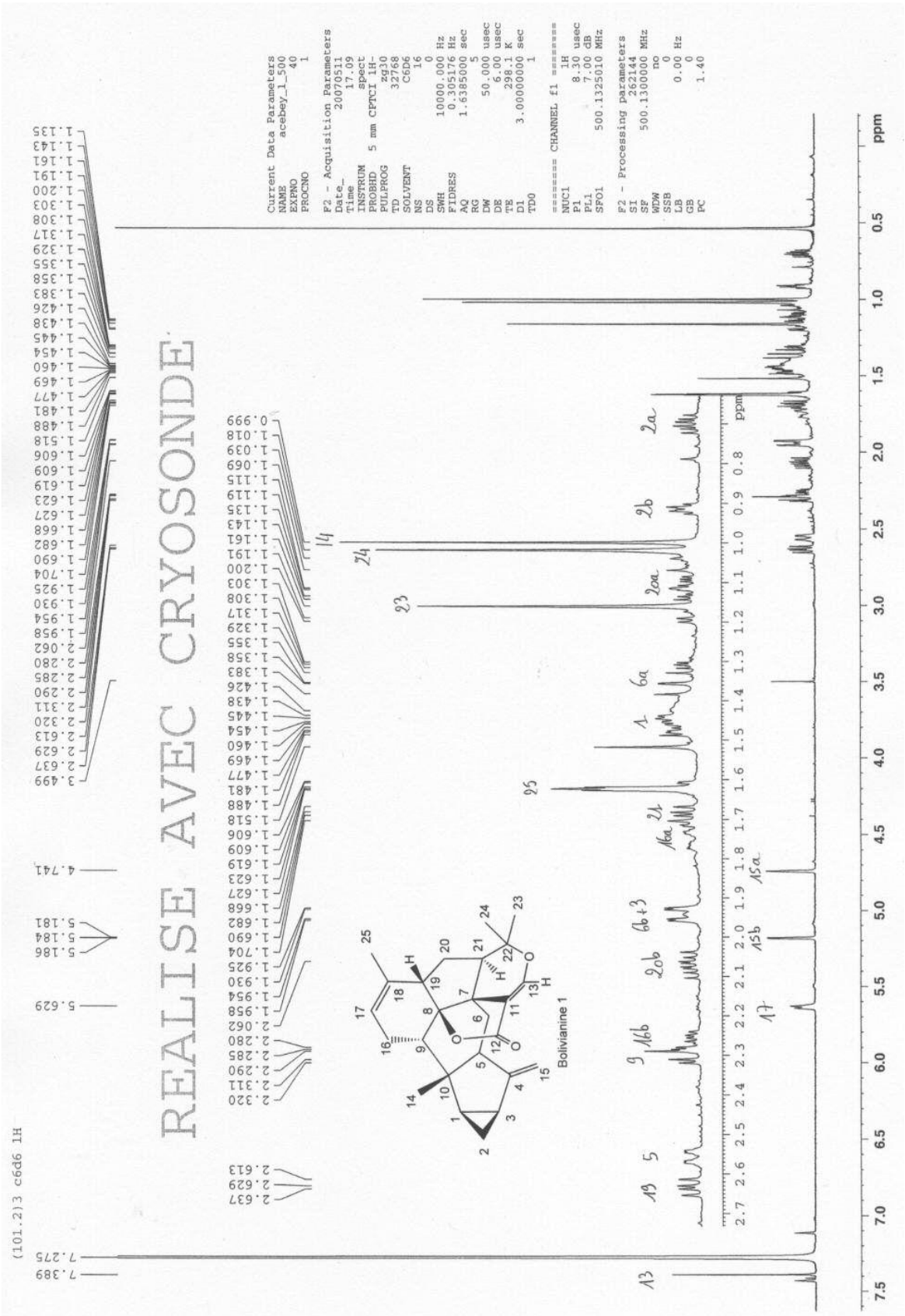
**Manuscript of Valérie Jullian**
**Title**: Bolivianine, a new sesterpene with an unusual skeleton from *Hedyosmum angustifolium,* and its isomer, isobolivianine

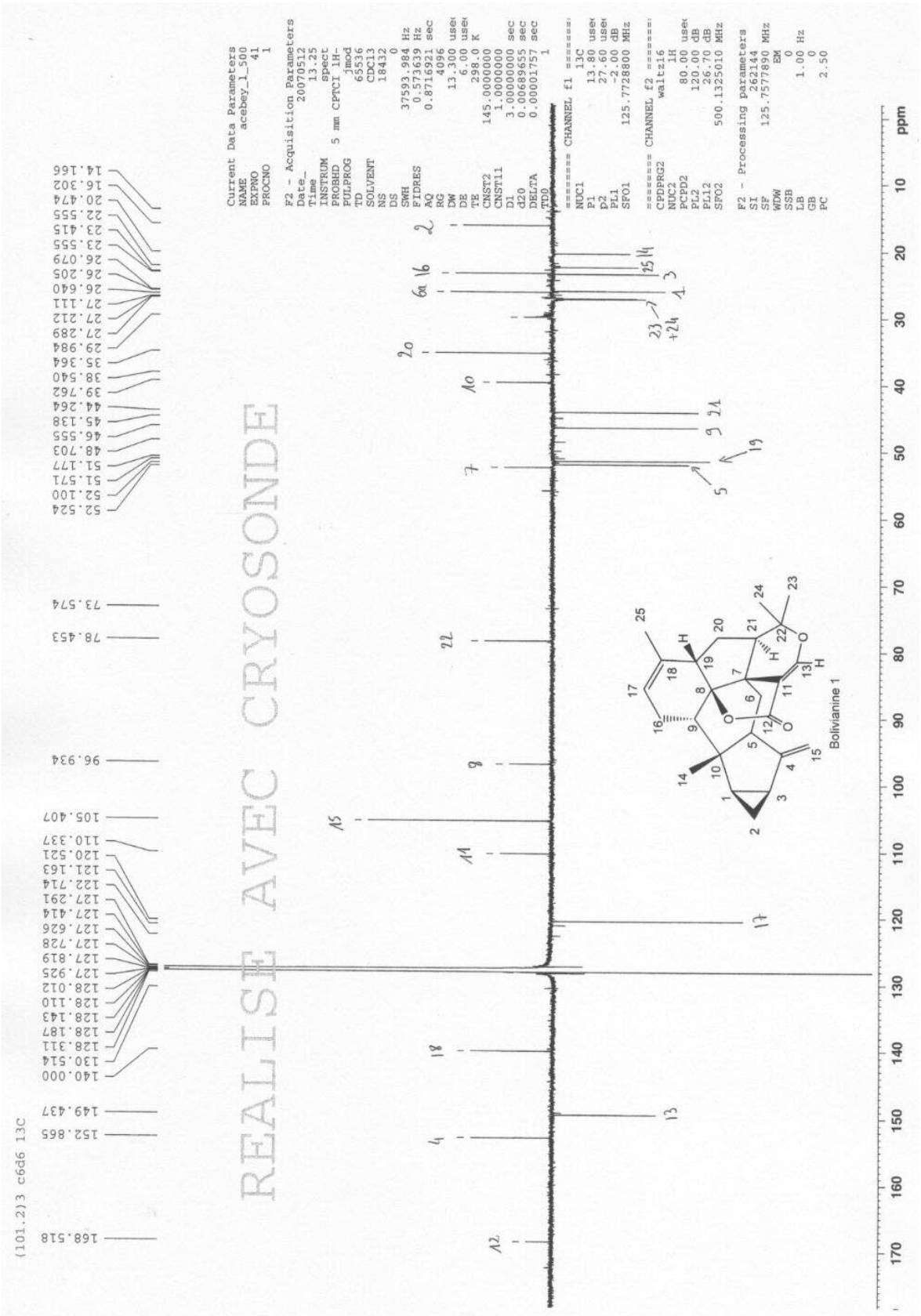
**Supporting informations**:

**Spectra:**

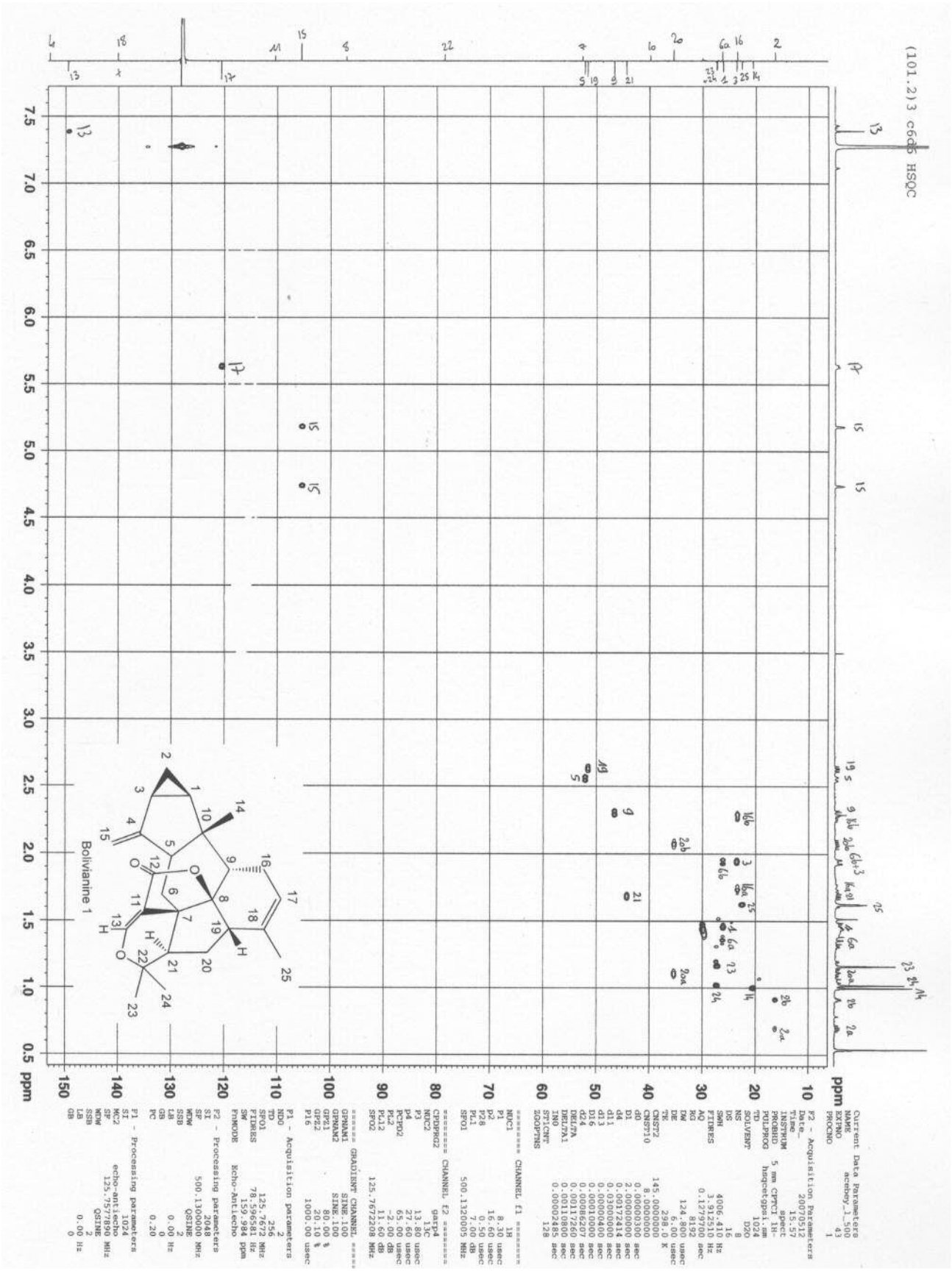

**Obtention of Bolivianine and Isobolivianine :**



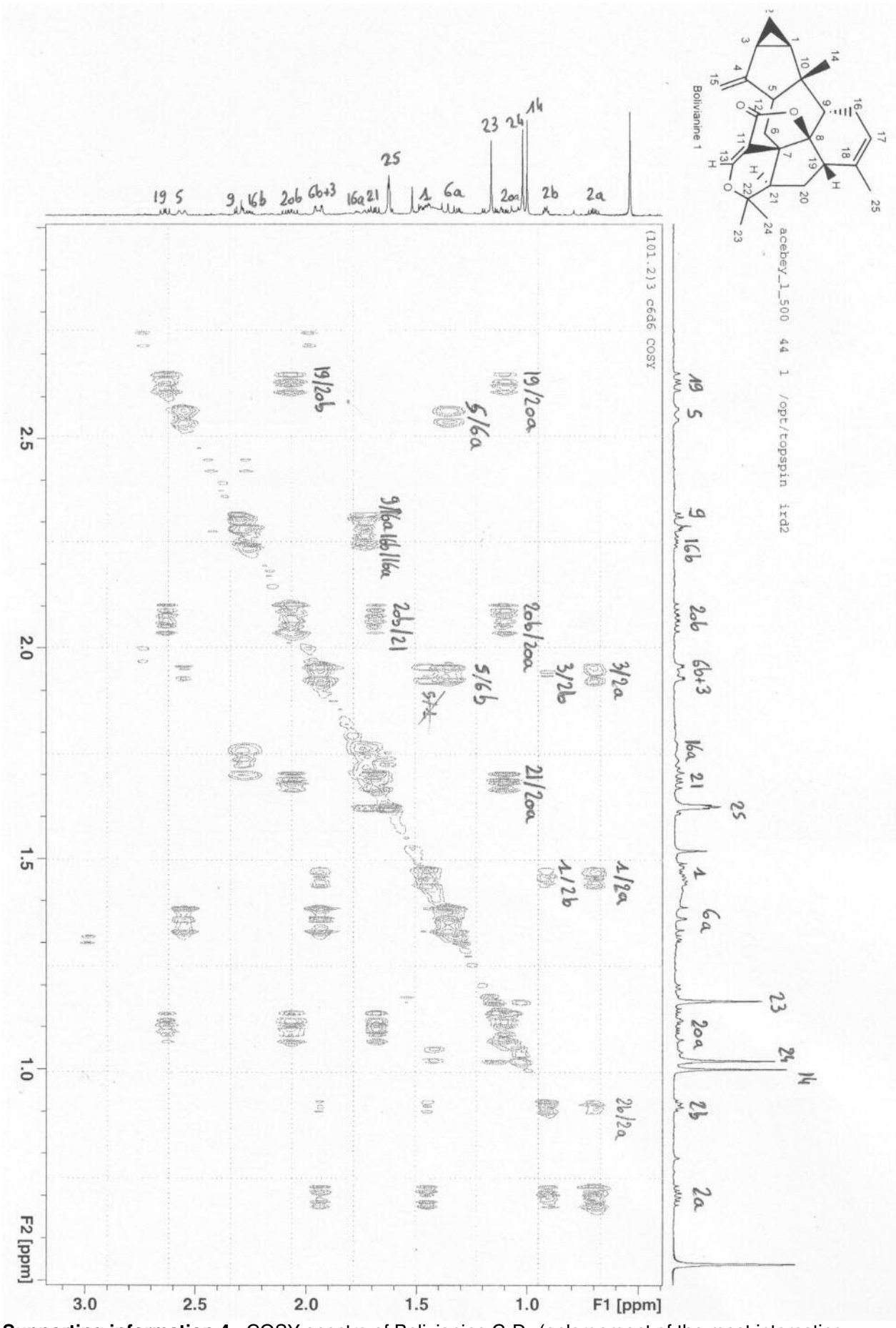

**Supporting information 1**: $^{1}H$ Bolivianine 500 MHz, $C_6D_6$



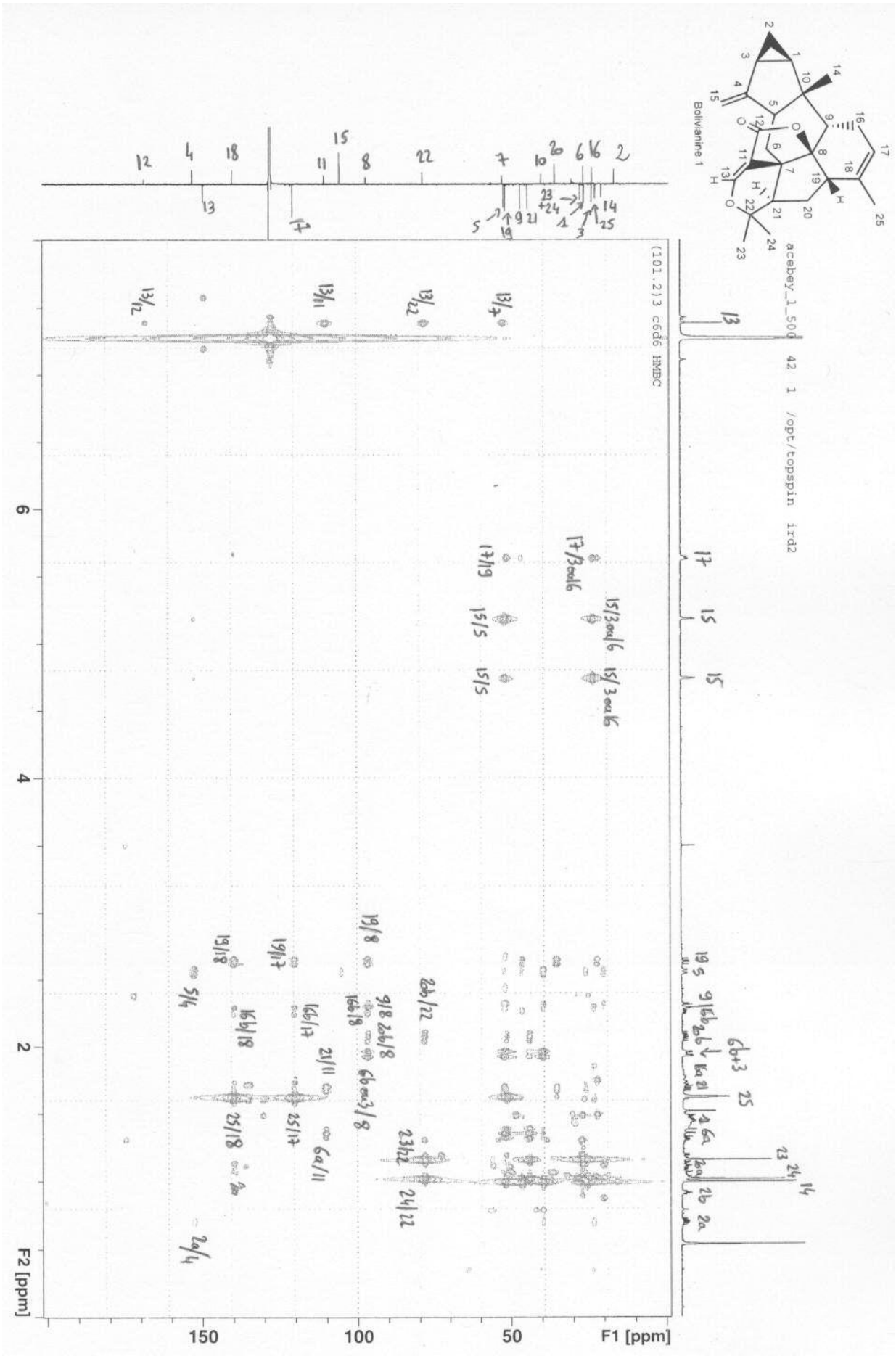

**Supporting information 2**: $^{13}C$ spectra of Bolivianine, 125 MHz, $C_6D_6$



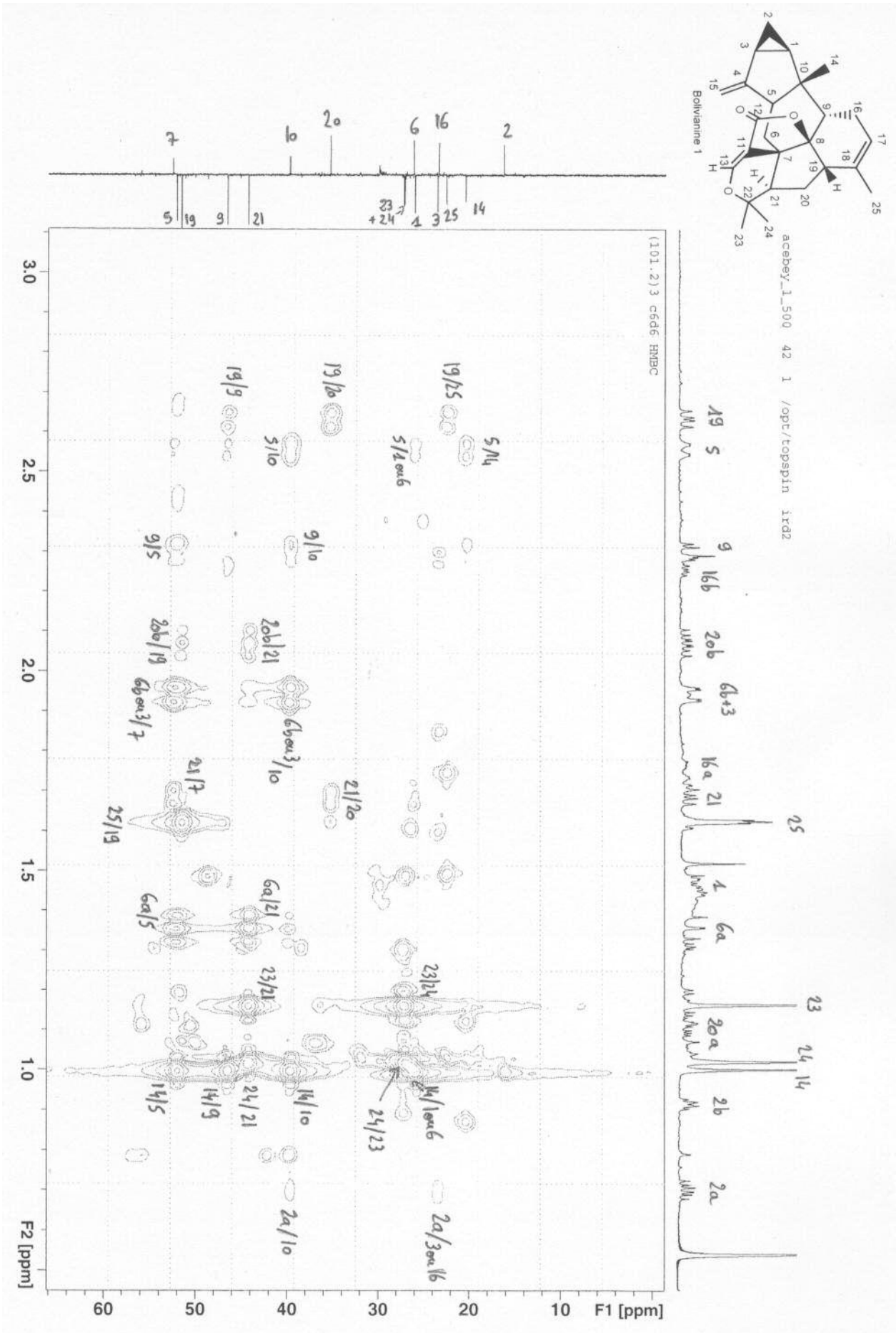

**Supporting information 3**: HSQC spectra of Bolivianine $C_6D_6$



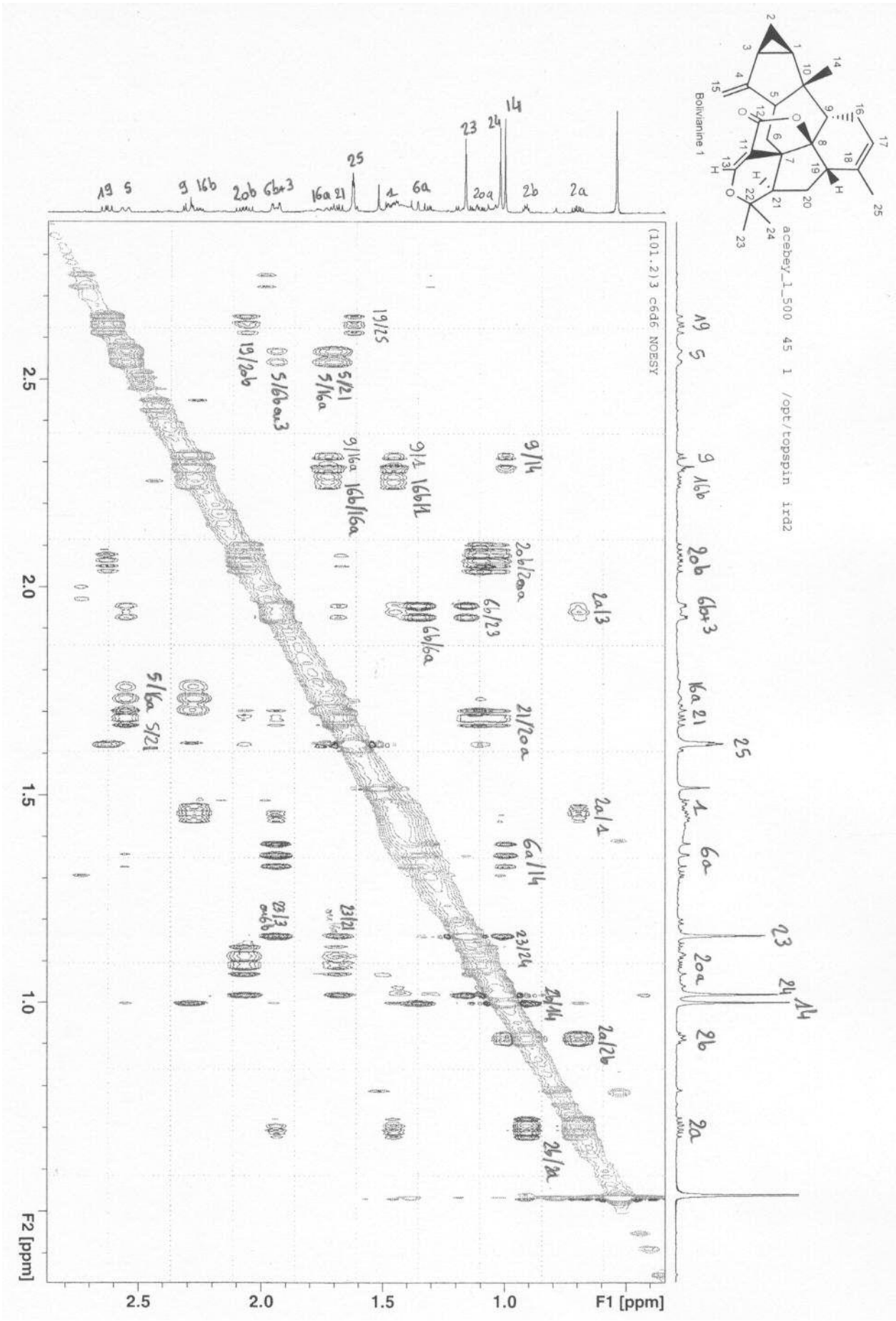

**Supporting information 4**: COSY spectra of Bolivianine $C_6D_6$ (enlargement of the most interesting part)



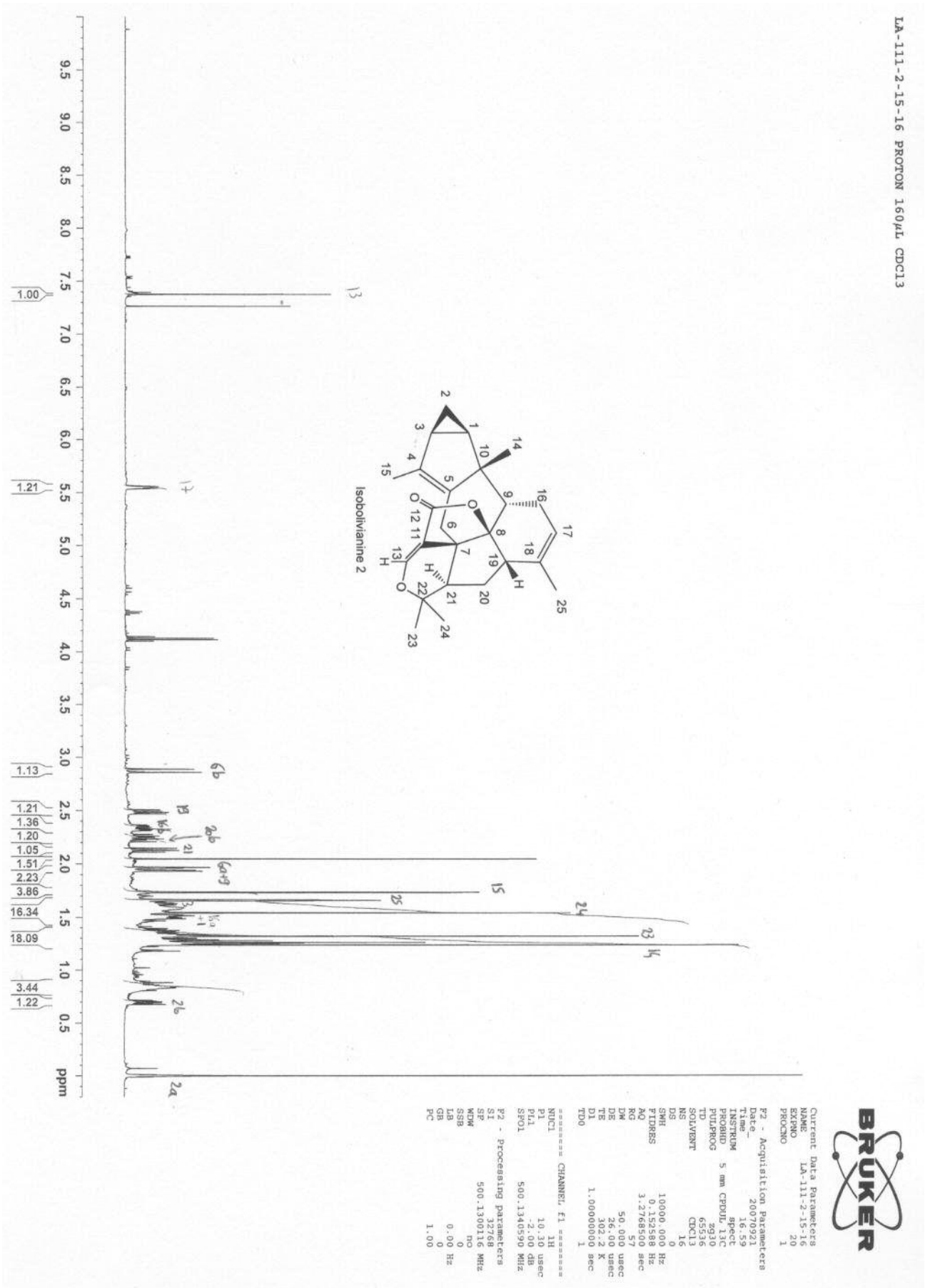

**Supporting information 5**: HMBC spectra of Bolivianine $C_6D_6$



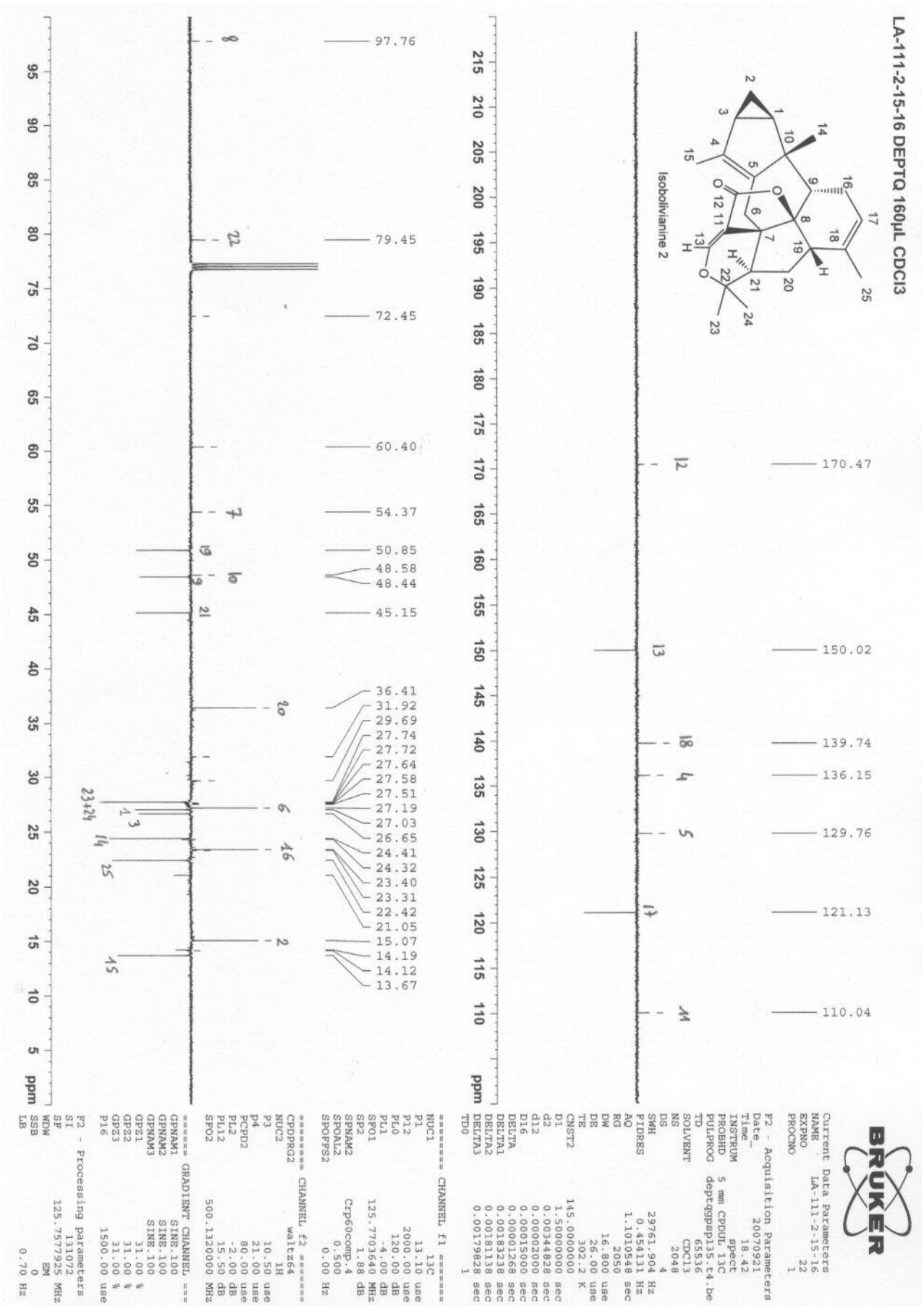

**Supporting information 6**: HMBC spectra of Bolivianine $C_6D_6$ (enlargement)



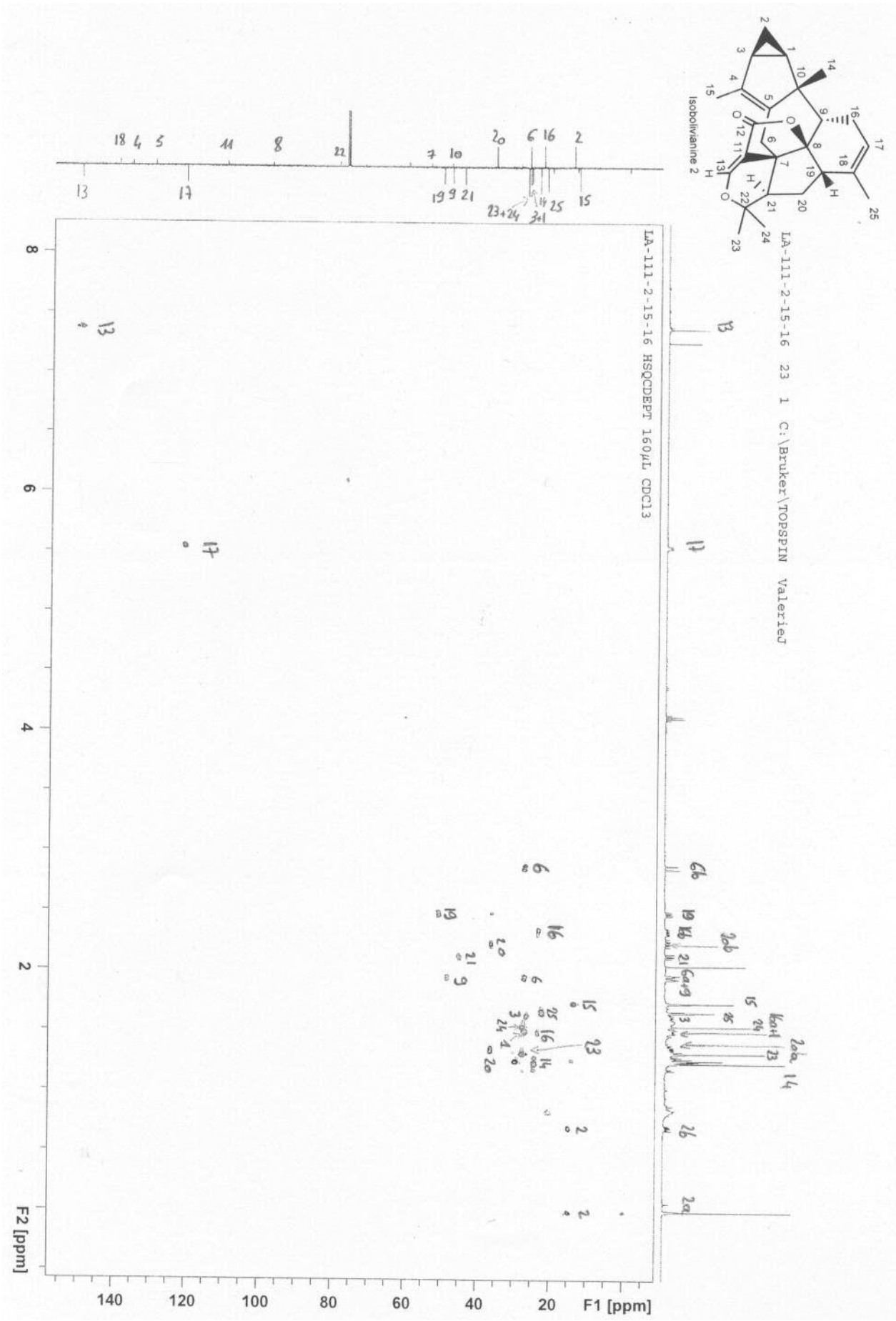

**Supporting information 7**: NOESY spectra of Bolivianine $C_6D_6$ (enlargement of the most interesting part)



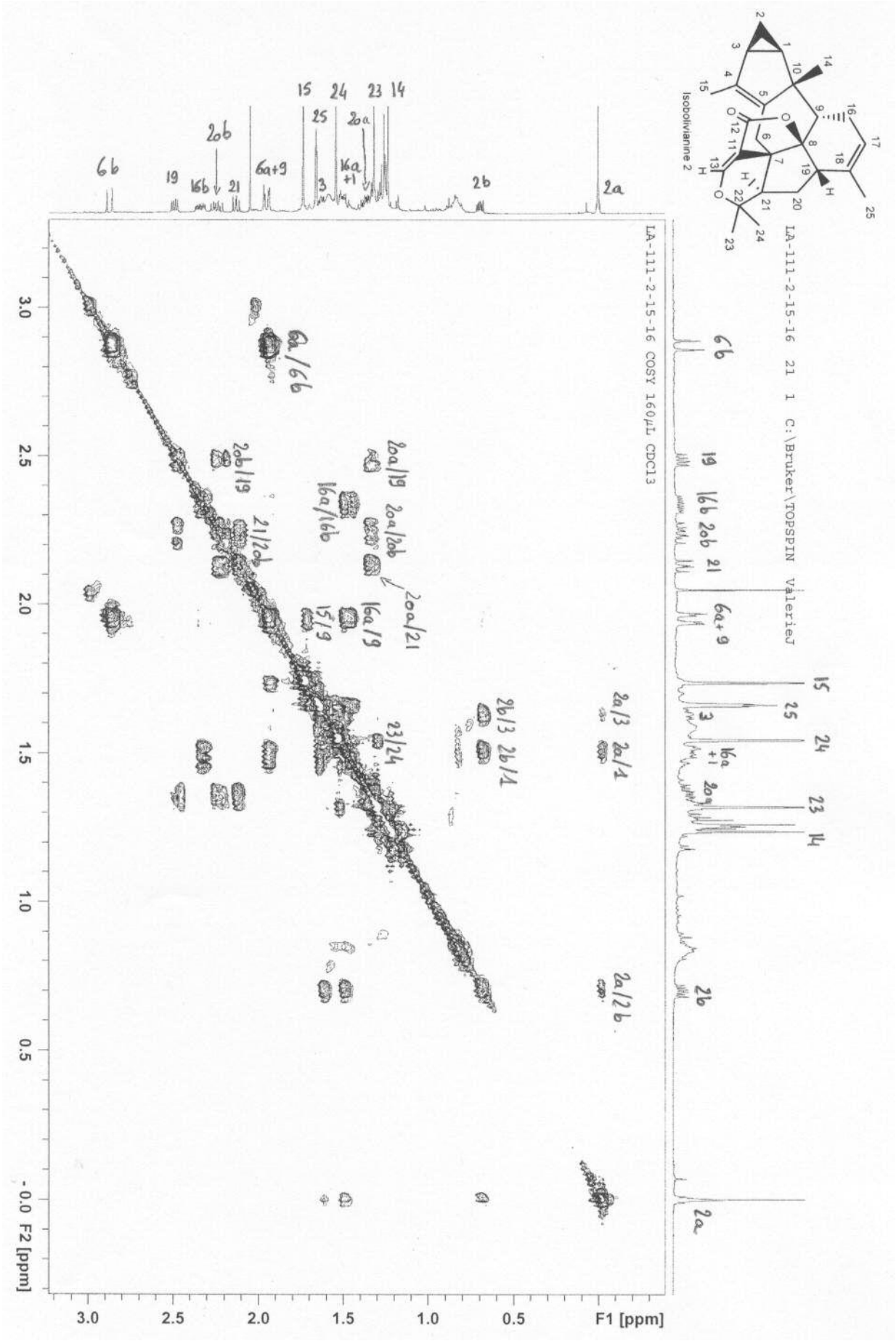

**Supporting information 8**: $^{1}H$ spectra of Isobolivianine 500 MHz, $CDCl_3$ + TMS



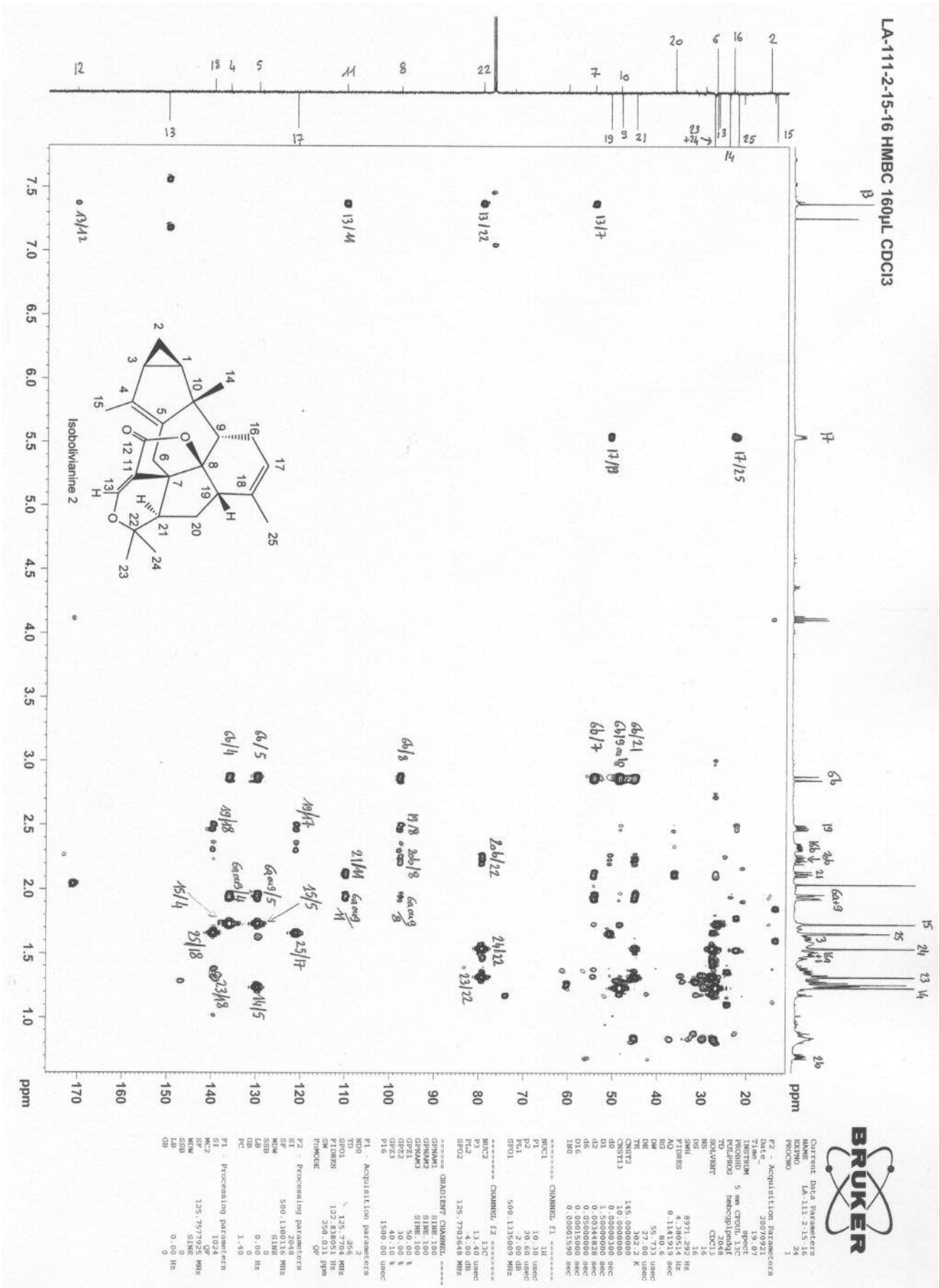

**Supporting information 9**: $^{13}C$ spectra of Isobolivianine, 125 MHz, $CDCl_3$ + TMS



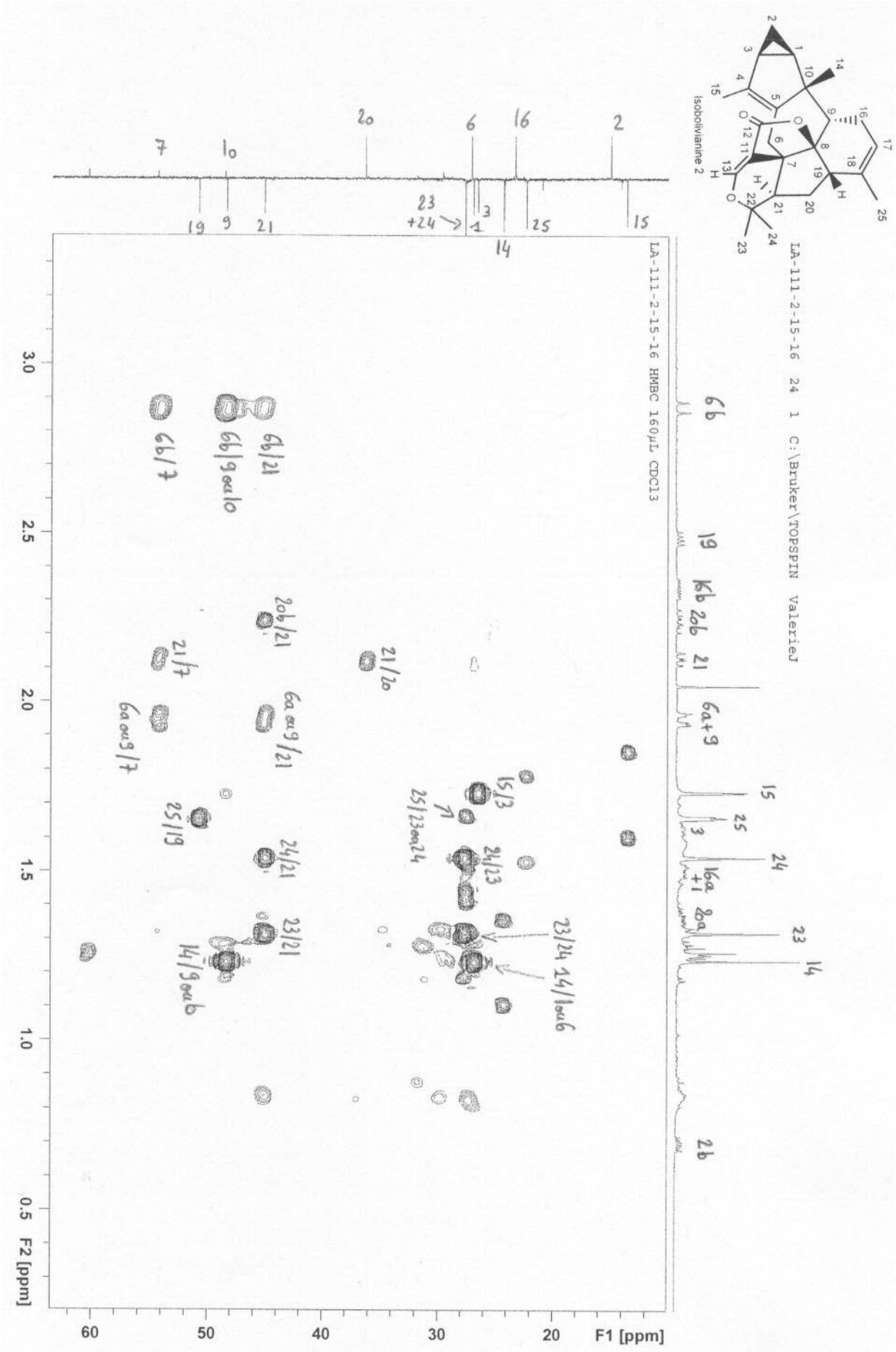

**Supporting information 10**: HSQC spectra of Isobolivianine $CDCl_3$ + TMS



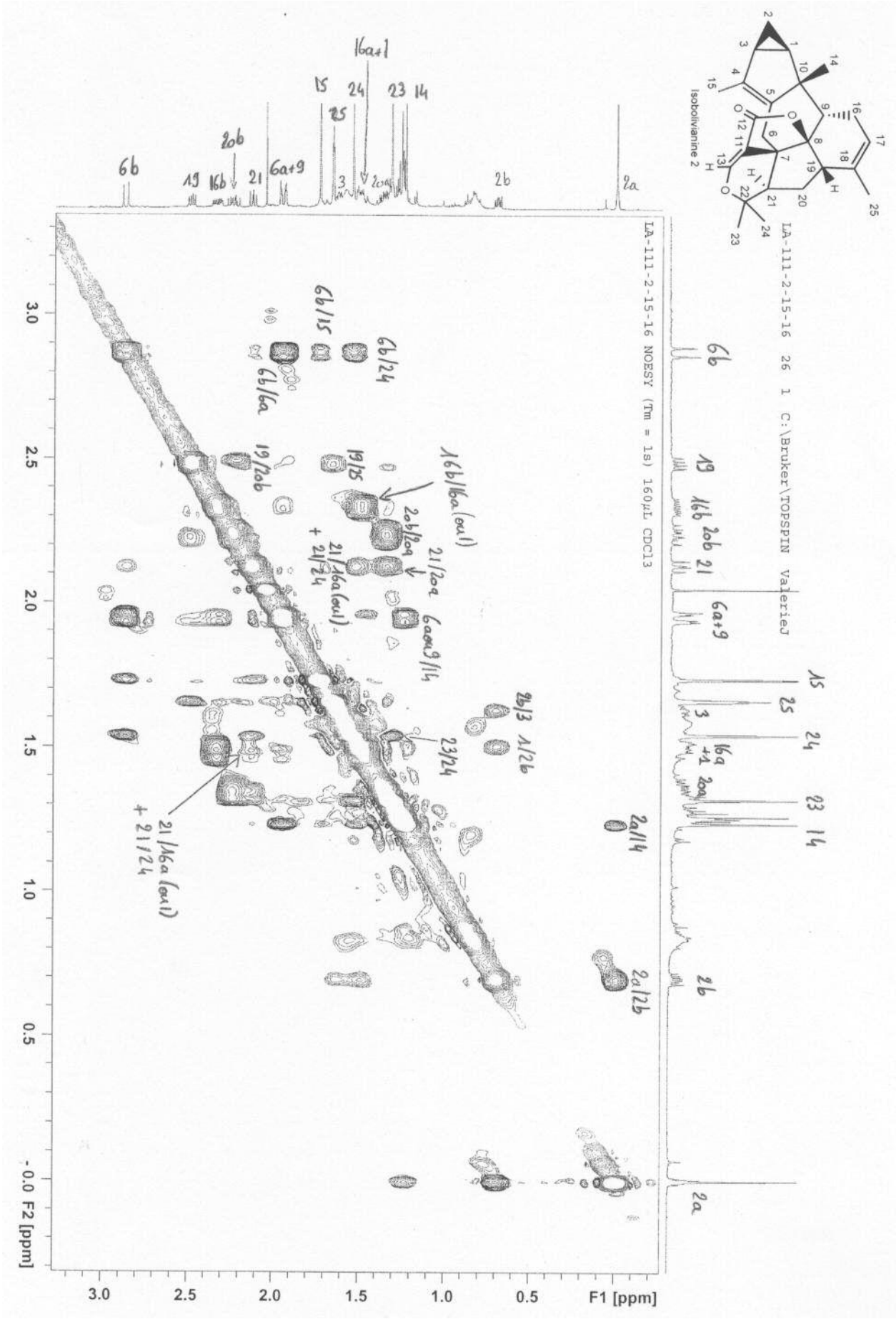

**Supporting information 11**: COSY spectra of Isobolivianine $CDCl_3$ + TMS (enlargement of the most interesting part)



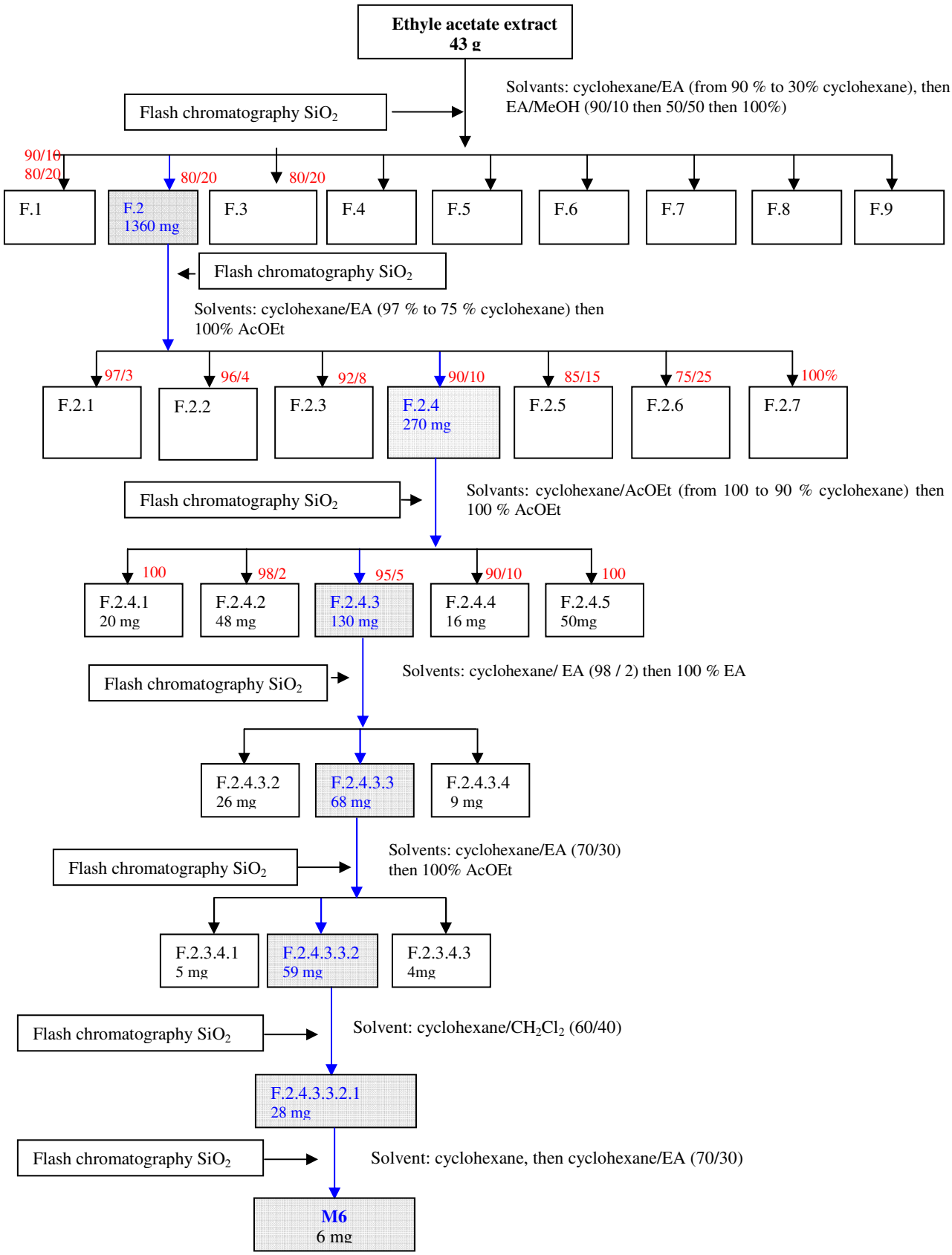

**Supporting information 12**: HMBC spectra of Isobolivianine $CDCl_3$ + TMS




**Supporting information 13**: HMBC spectra of Isobolivianine $CDCl_3$ + TMS(enlargement)




**Supporting information 14**: NOESY spectra of Isobolivianine $CDCl_3$ + TMS (enlargement of the most interesting part)




**Supporting information 15**: Purification scheme for Bolivianine, from 1Kg of *H. Angustifolium* trunk bark

**Supporting information 16**: Experimental procedure for the isomerization of bolivianine into isobolivianine

Bolivianine (2 mg) was dissolved in 600 μL of deuterated chloroform. Then, the solvent was removed under reduced pressure at 40°C. After 18 hours, a mixture of 80% Isobolivianine and 20% Bolivianine was obtained. After 72 hours at 40°C, without solvent, under atmospheric pressure, the isomerization was complete. Isomerization rate was determined by $^{1}$H NMR. After flash column chromatography (1g of silica gel, eluted with cyclohexane, then cyclohexane/ ethyl acetate 40/60) 0.6 mg of isobolivianine were obtained.

**Supporting information 17:** Biological evaluation for bolivianine **(1)** and isobolivianine **(2)**

The biological evaluations were performed on *Plasmodium falciparum* culture in vitro, and on MCF7, a mammalian tumoral cell line, following previously published procedure[1], and the results are summarized in the table T1

**Table T1**: Biological activities ($IC_{50}$, μM) of the sesterpenes **(1)** and **(2)**

| | *P. falciparum* (FCB1) | MCF7 Cell line |
|---|---|---|
| **1** | >60 | 37 |
| **2** | >60 | 108 |
| CQ[a] | 0.145 | |
| Dox[b] | | 0.4 |

[a] : CQ, chloroquine, positive control for *P. falciparum* inhibition
[b] : Dox, doxorubicine, positive control for MCF7 inhibition

(1) Jullian, V.; Bonduelle, C.; Valentin, A.; Acebey, L.; Duigou, A.-G.; Prevost, M.-F.; Sauvain, M. *Bioorganic & Medicinal Chemistry Letters* **2005**, *15*, 5065-5070, and ref. cited.