

Supplementary Information

Figure S1. ^1H NMR spectrum of violapyrone H (**1**) in CD_3OD (500 MHz).

Figure S2. ^{13}C NMR spectrum of violapyrone H (**1**) in CD_3OD (125 MHz).

Figure S3. HSQC spectrum of violapyrone H (**1**) in CD_3OD .

Figure S4. COSY spectrum of violapyrone H (**1**) in CD_3OD .

Figure S5. HMBC spectrum of violapyrone H (**1**) in CD_3OD .

Figure S6. HR-ESIMS data of violapyrone H (**1**).

Figure S7. ^1H NMR spectrum of violapyrone I (**2**) in CD_3OD (500 MHz).

Figure S8. ^{13}C NMR spectrum of violapyrone I (**2**) in CD_3OD (125 MHz).

Figure S9. HSQC spectrum of violapyrone I (**2**) in CD_3OD .

Figure S10. COSY spectrum of violapyrone I (**2**) in CD_3OD .

Figure S11. HMBC spectrum of violapyrone I (**2**) in CD_3OD .

Figure S12. HR-ESIMS data of violapyrone I (**2**).

Figure S13. ^1H NMR spectrum of violapyrone B (**3**) in CD_3OD (500 MHz).

Figure S14. ^{13}C NMR spectrum of violapyrone B (**3**) in CD_3OD (125 MHz).

Figure S15. ^1H NMR spectrum of natural (*S*)-violapyrone C (**4**) in CD_3OD (500 MHz).

Figure S16. ^1H NMR spectrum of synthetic (*S*)-violapyrone C in CD_3OD (500 MHz).

Figure S17. ^{13}C NMR spectrum of natural (*S*)-violapyrone C (**4**) in CD_3OD (125 MHz).

Figure S18. ^{13}C NMR spectrum of synthetic (*S*)-violapyrone C in CD_3OD (125 MHz).

Figure S1. ^1H NMR spectrum of violapyrone H (1) in CD_3OD (500 MHz).

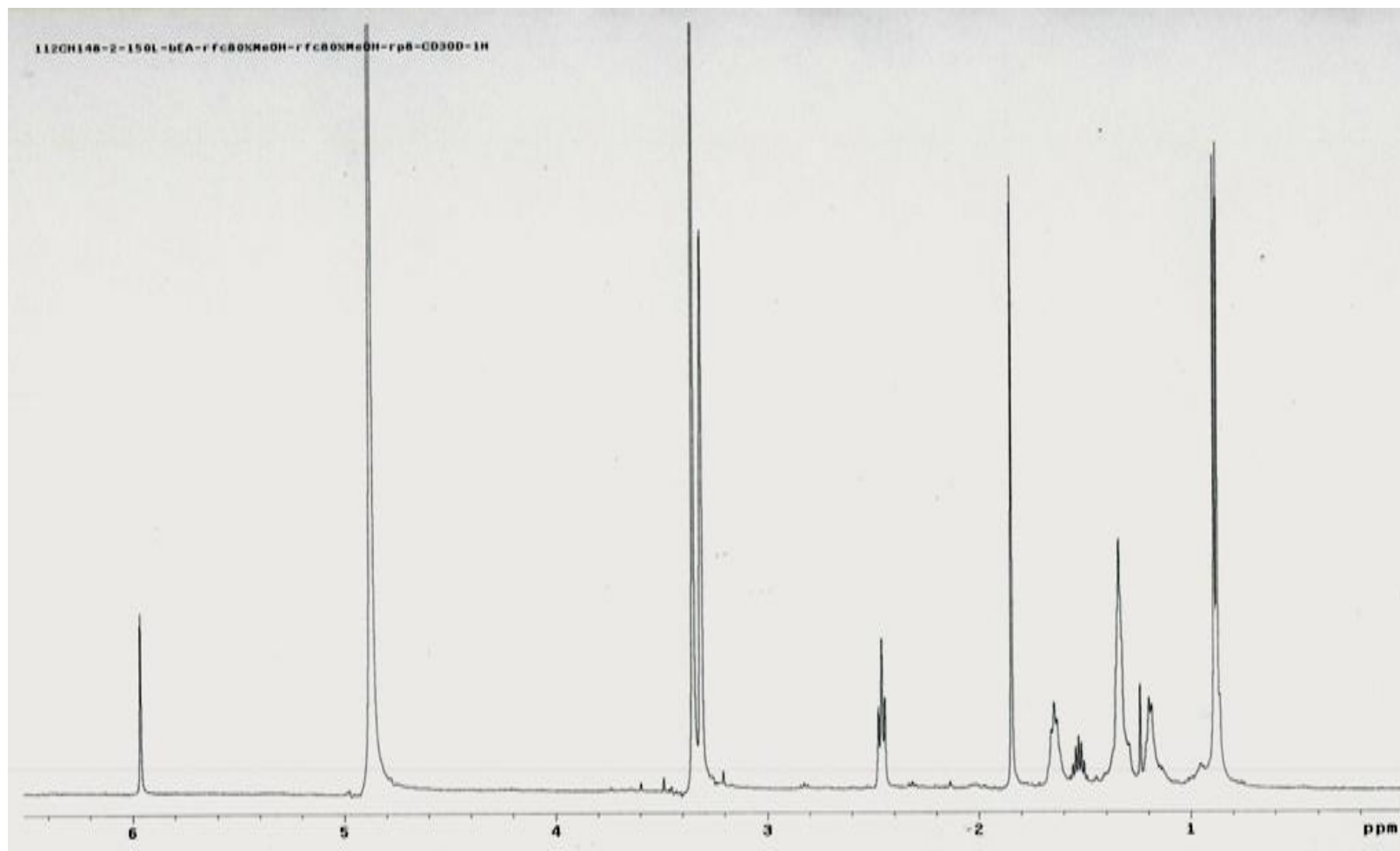


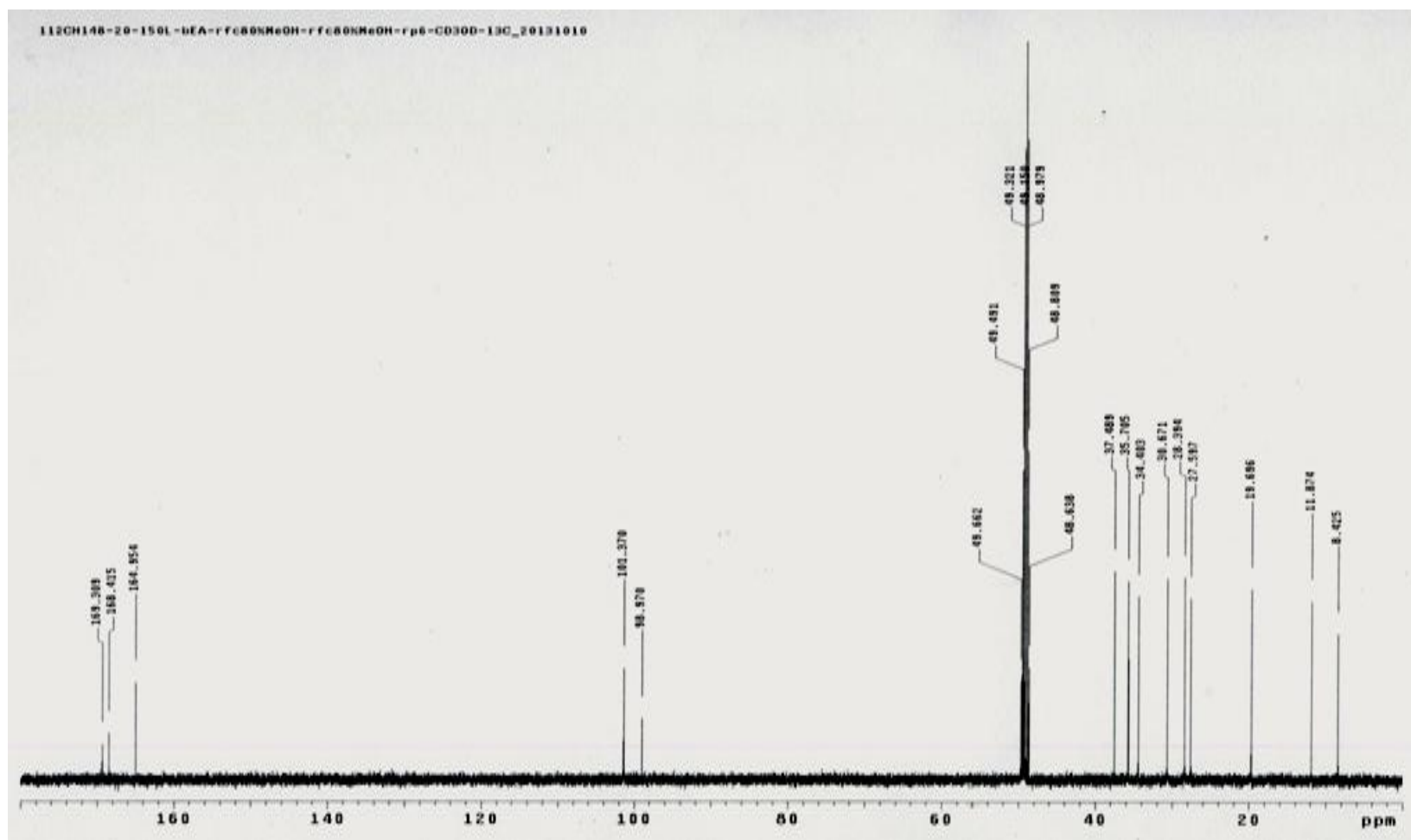
Figure S2. ^{13}C NMR spectrum of violapyrone H (1) in CD_3OD (125 MHz).

Figure S3. HSQC spectrum of violapyrone H (1) in CD₃OD.

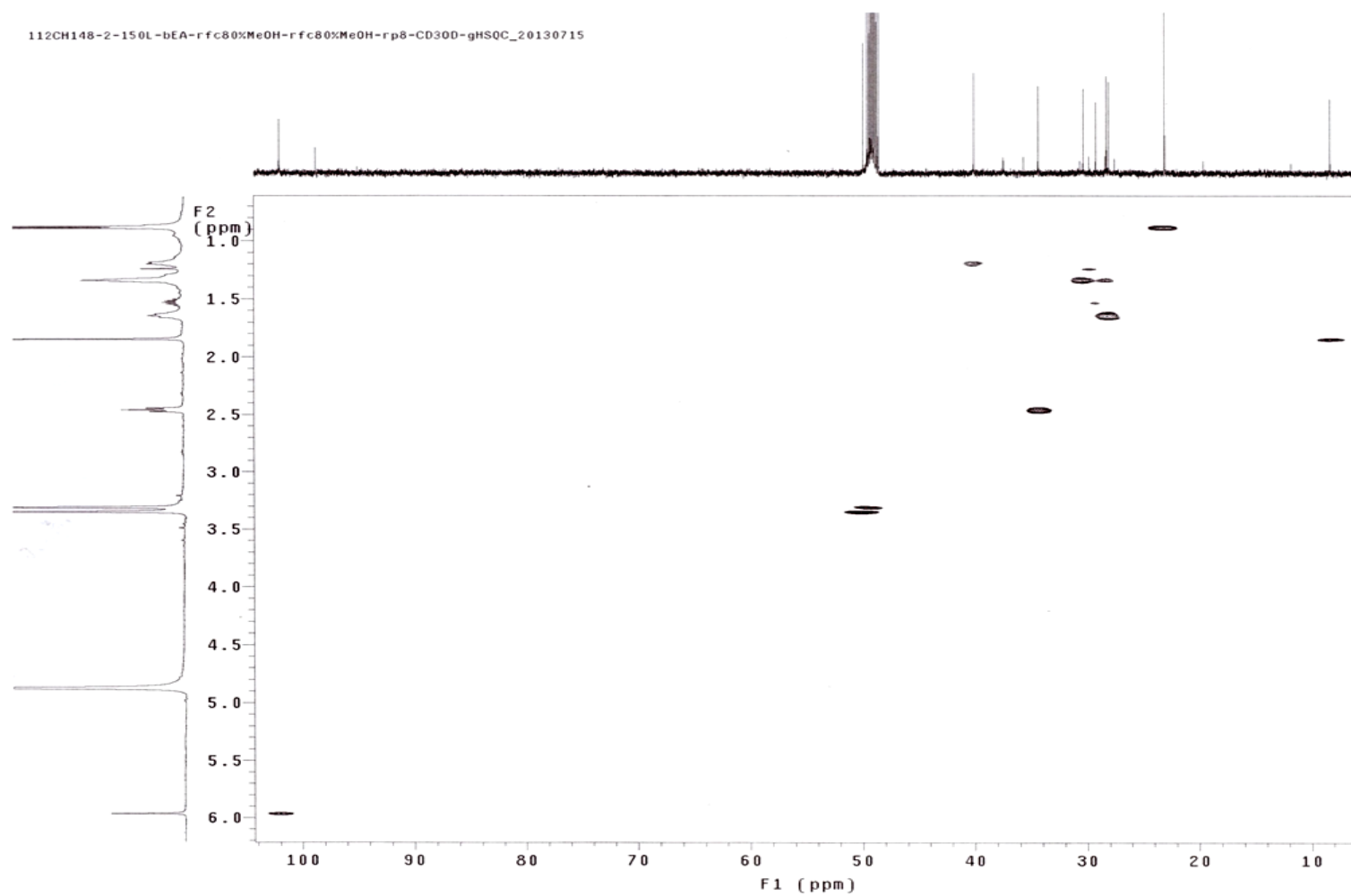


Figure S4. COSY spectrum of violapyrone H (1) in CD3OD.

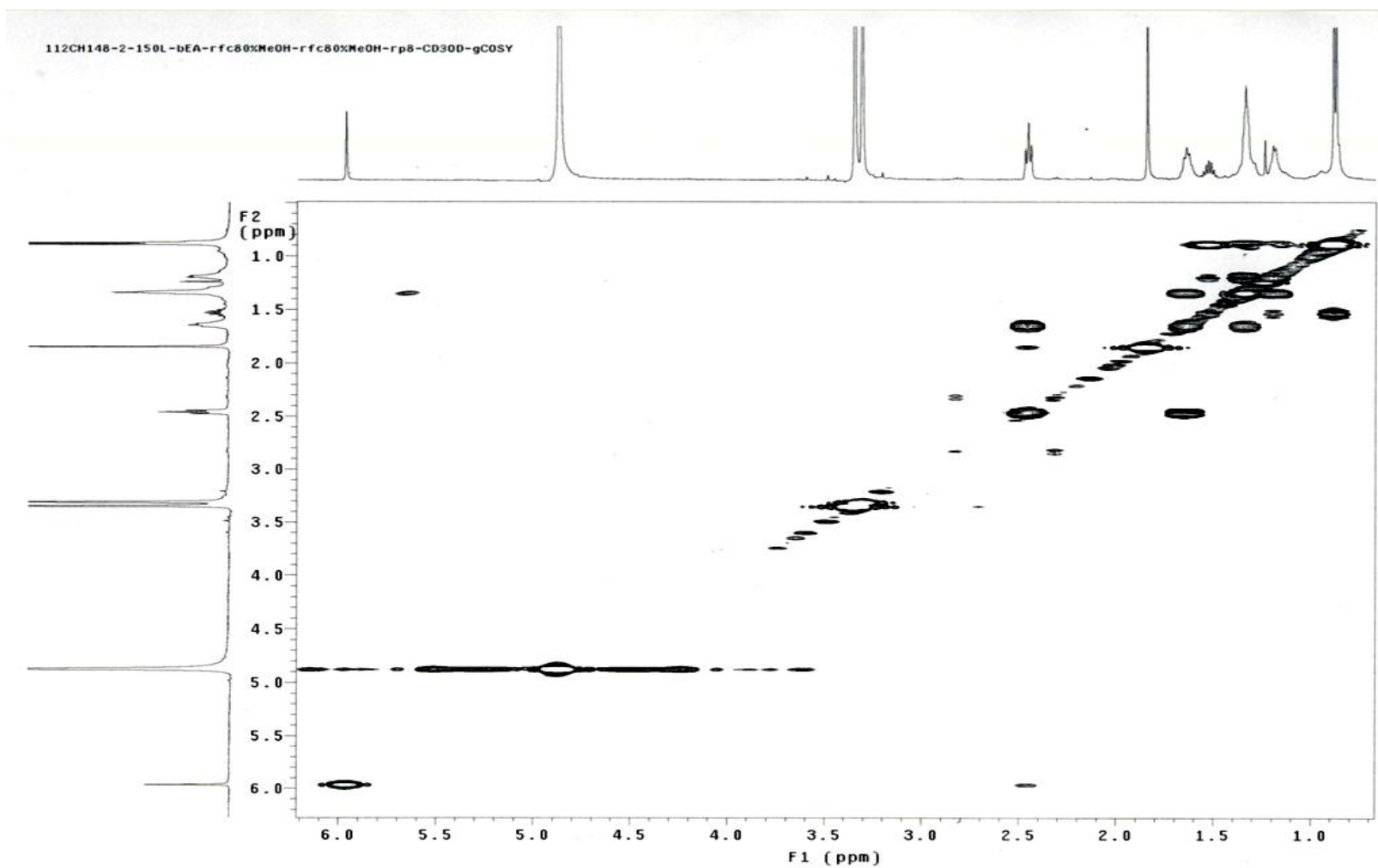


Figure S5. HMBC spectrum of violapyrone H (1) in CD₃OD.

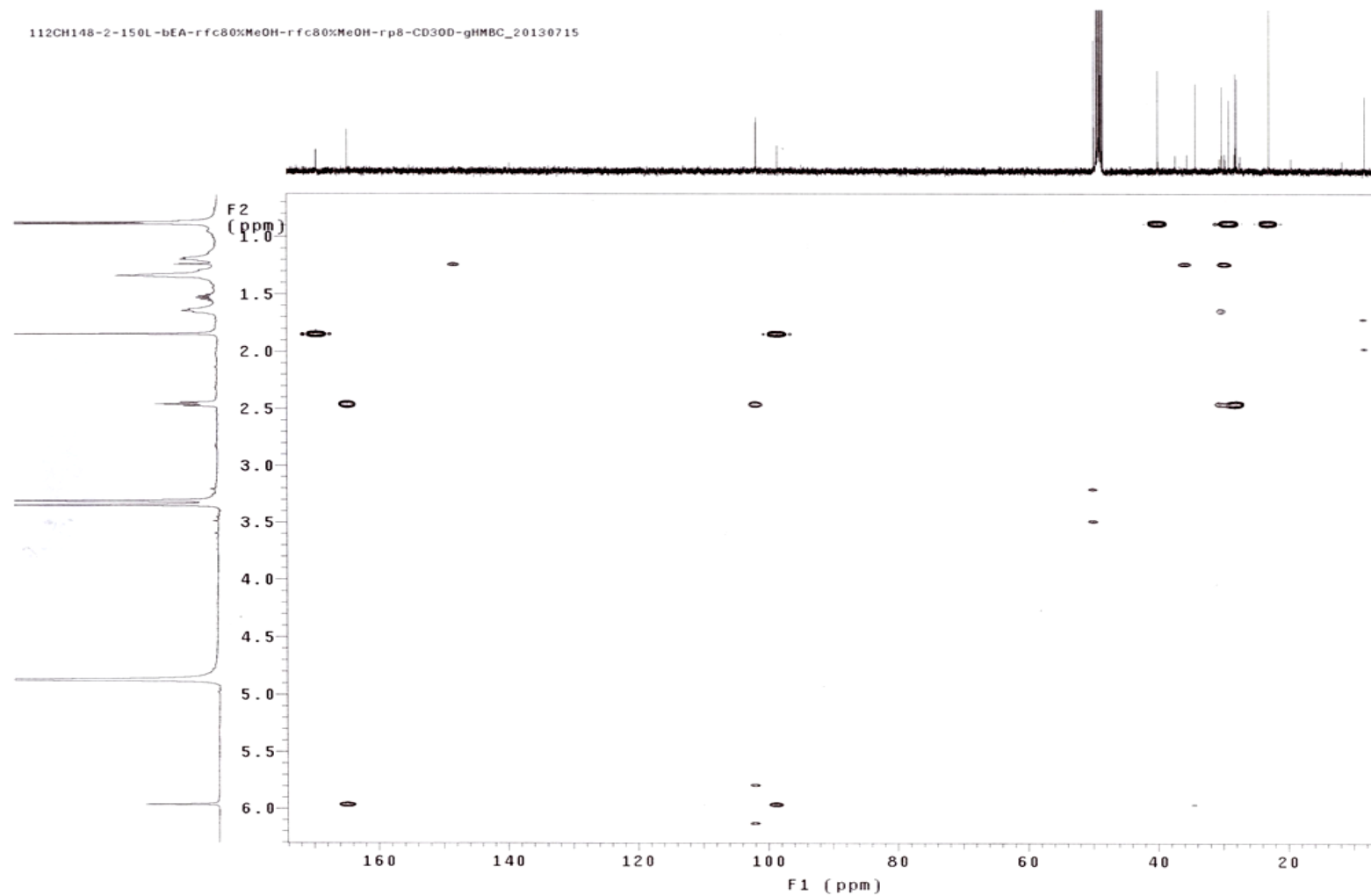


Figure S6. HR-ESIMS data of violapyrone H (1).

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 1-500 H: 1-1000 O: 1-100 Na: 1-1

Minimum:

Maximum: 5.0 10.0 -1.5

Mass Calc. Mass mDa PPM DBE i-FIT Norm Conf(%) Formula

261.1466 261.1467 -0.1 -0.4 3.5 900.0 n/a n/a C₁₄H₂₂O₃Na

131119_KIOST_5_HP

131119_KIOST_5_HP 39 (0.739) AM2 (Ar,30000,0,0,0,0,0); ABS; Cm (2:51)

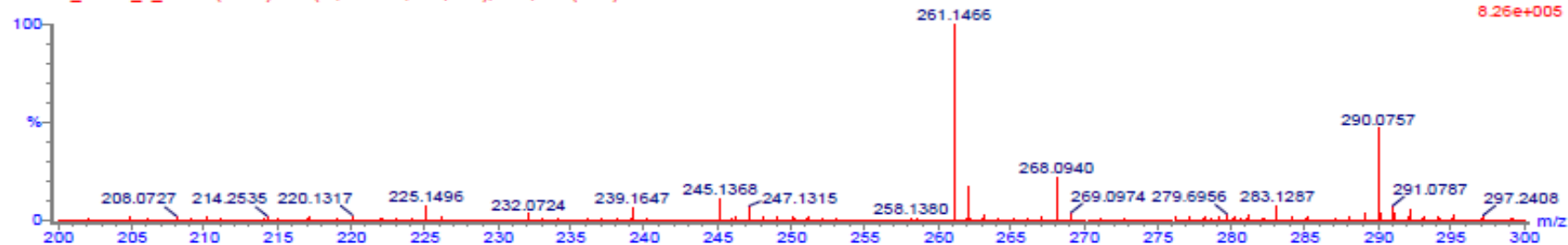
1: TOF MS ES+
8.26e+005

Figure S7. ^1H NMR spectrum of violapyrone I (**2**) in CD_3OD (500 MHz).

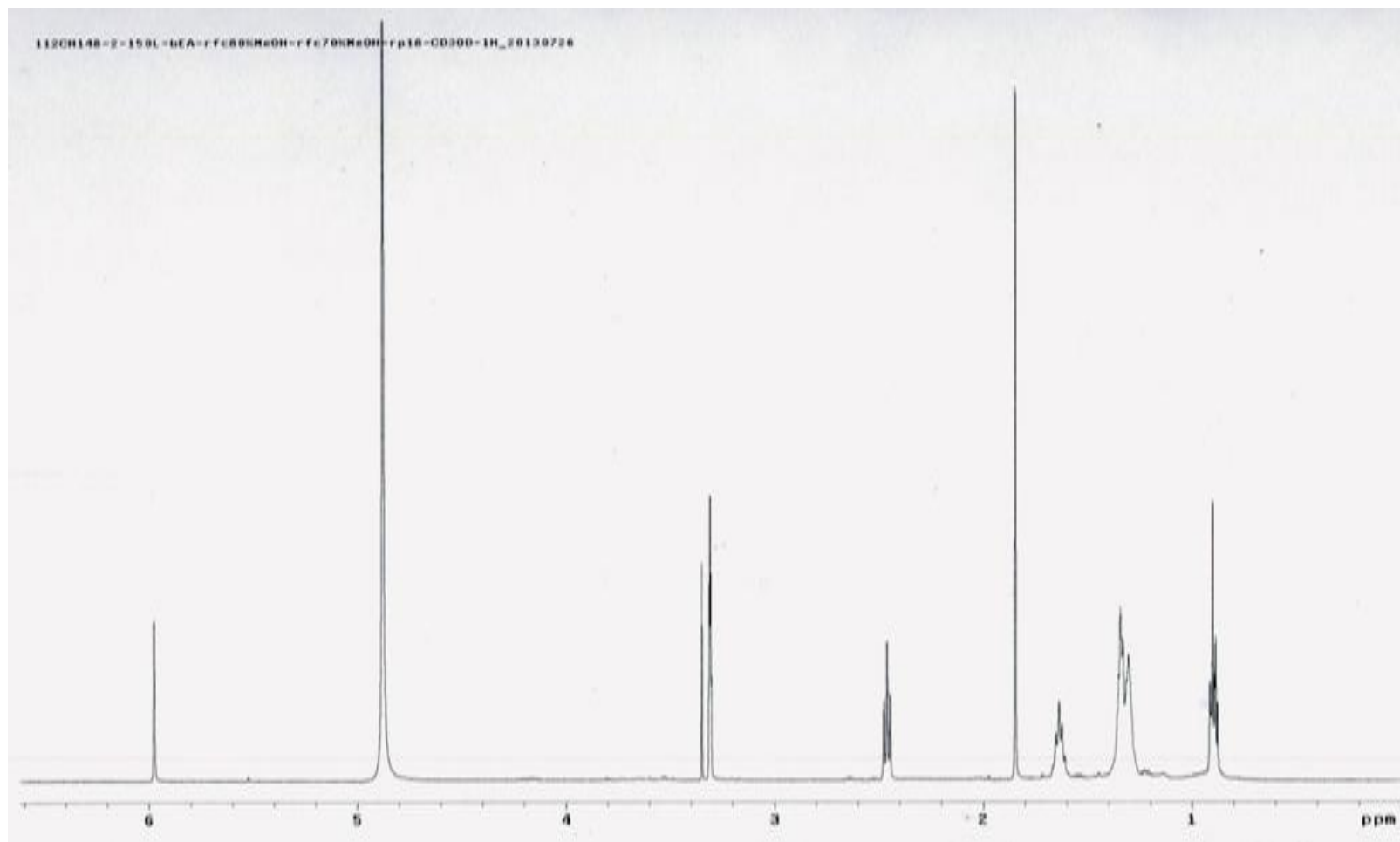


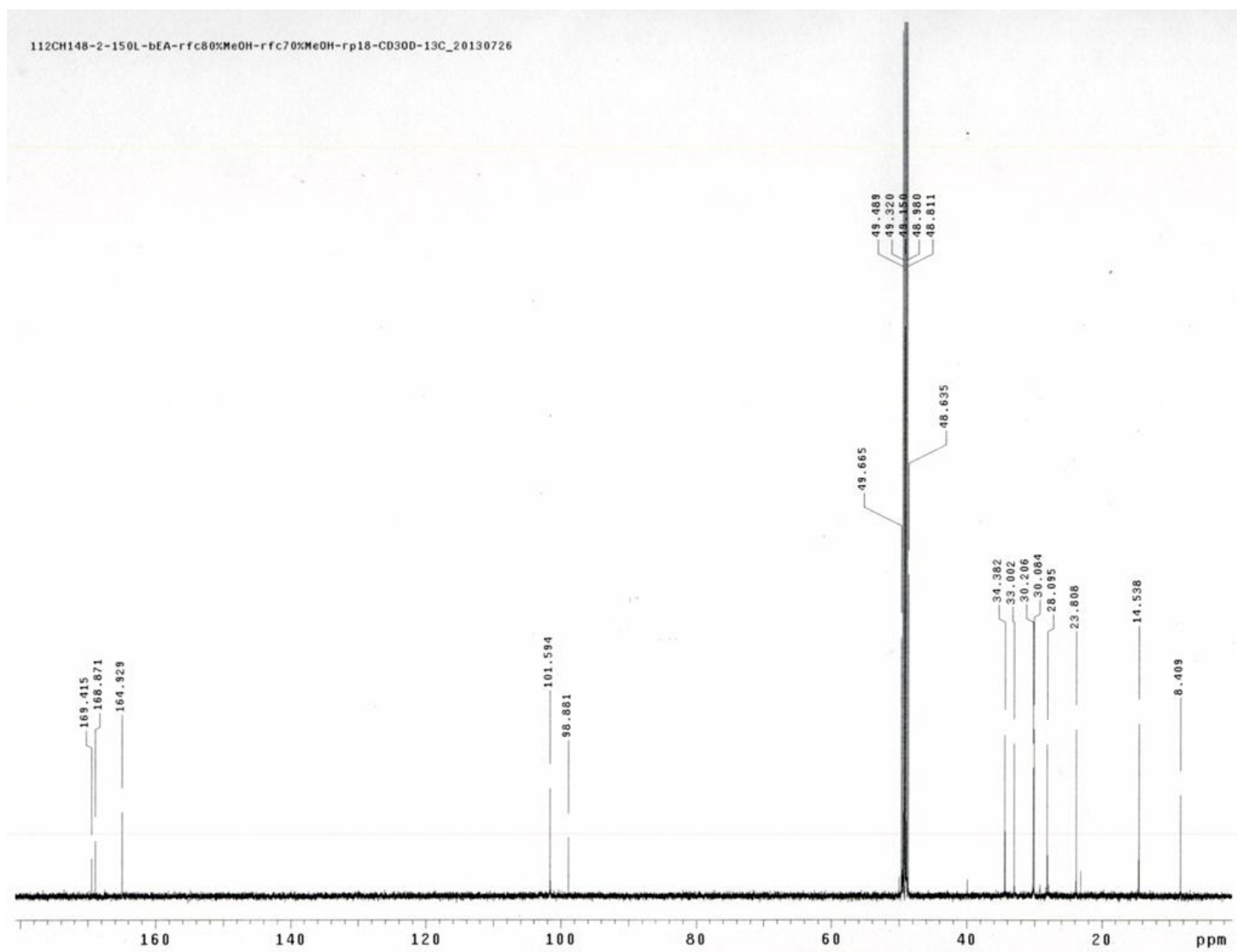
Figure S8. ^{13}C NMR spectrum of violapyrone I (**2**) in CD_3OD (125 MHz).

Figure S9. HSQC spectrum of violapyrone I (2) in CD₃OD.

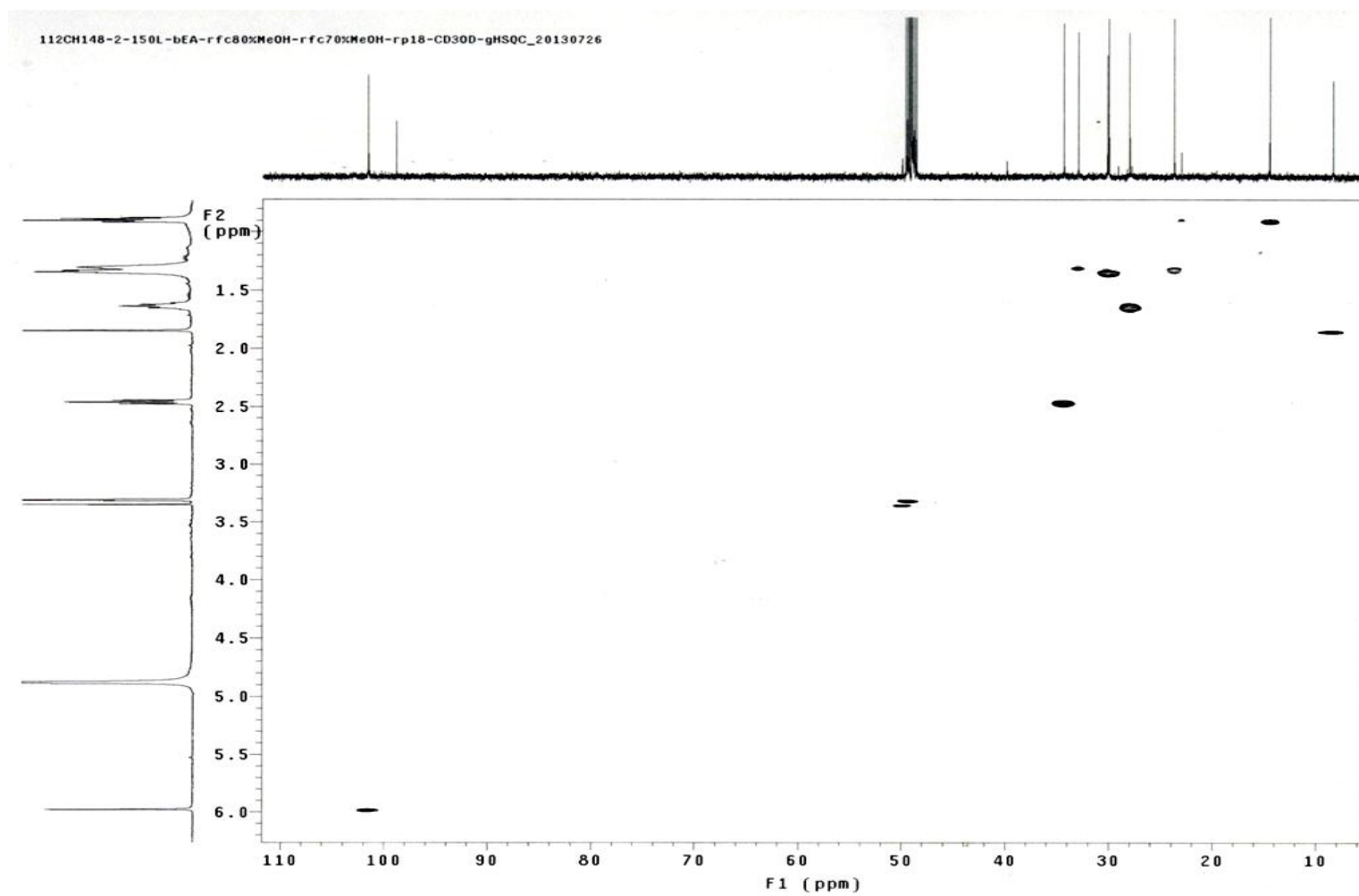


Figure S10. COSY spectrum of violapyrone I (2) in CD₃OD.

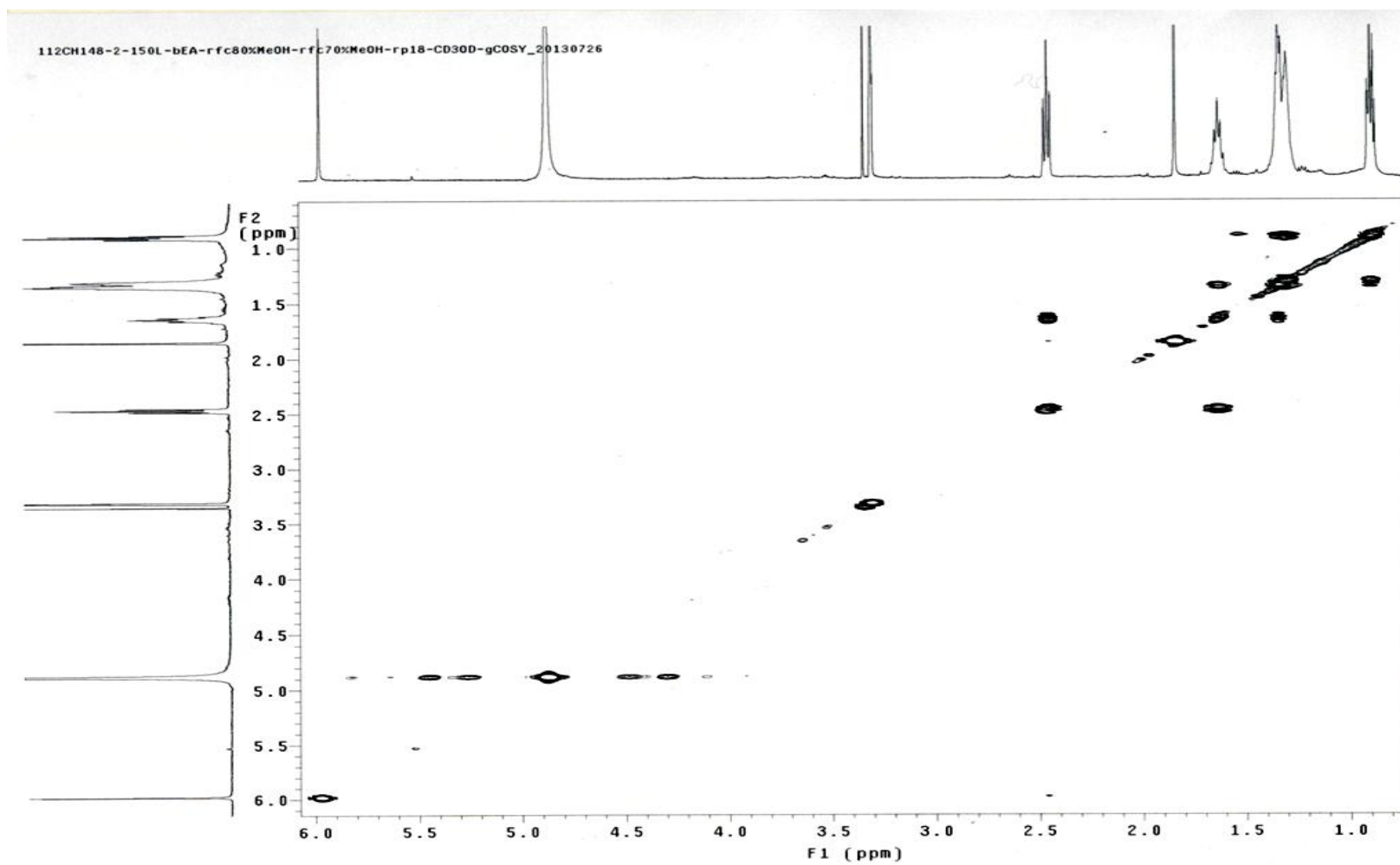


Figure S11. HMBC spectrum of violapyrone I (2) in CD₃OD.

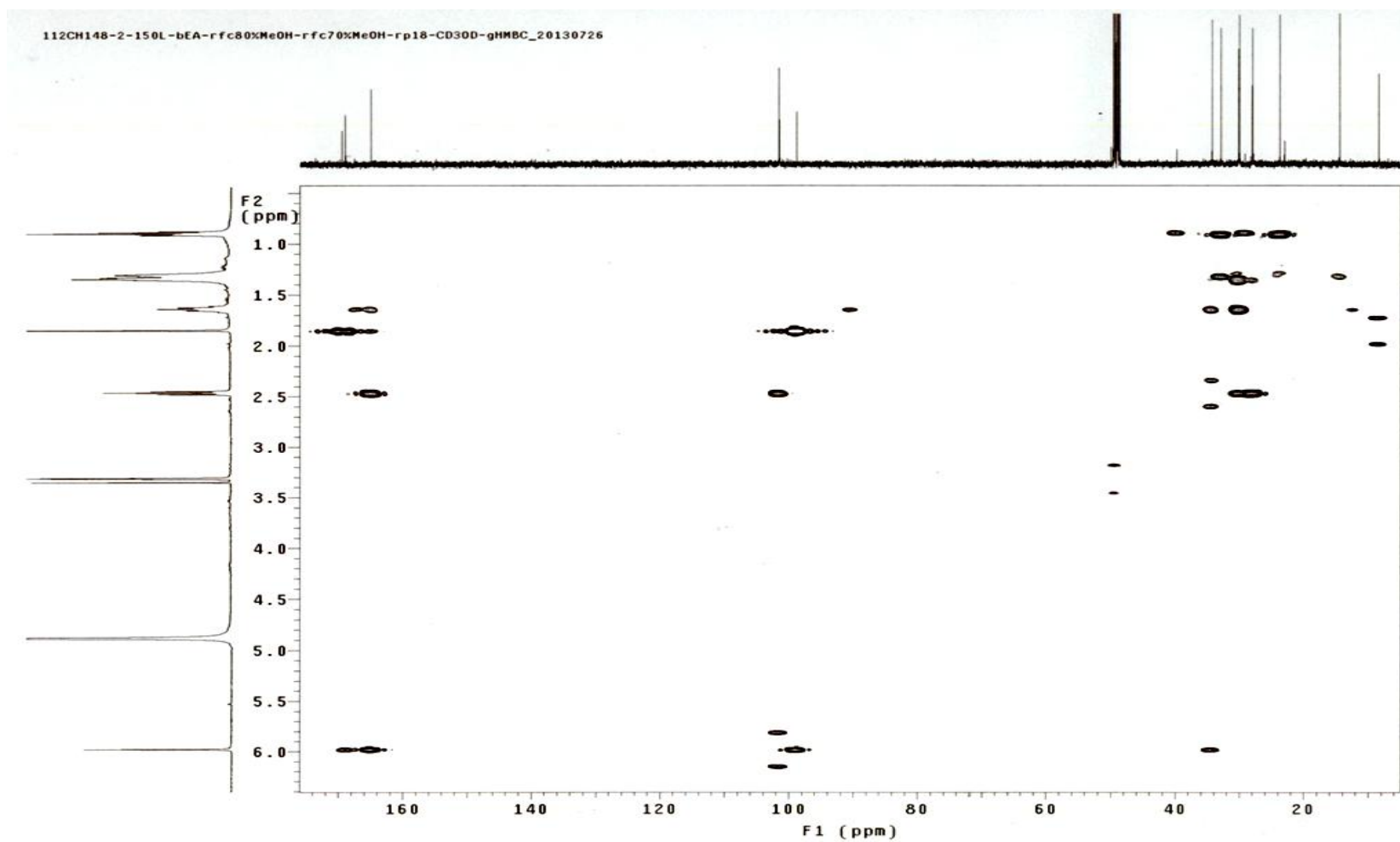


Figure S12. HR-ESIMS data of violapyrone I (2).

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
247.1313	247.1310	0.3	1.2	3.5	1028.8	n/a	n/a	C ₁₃ H ₂₀ O ₃ Na

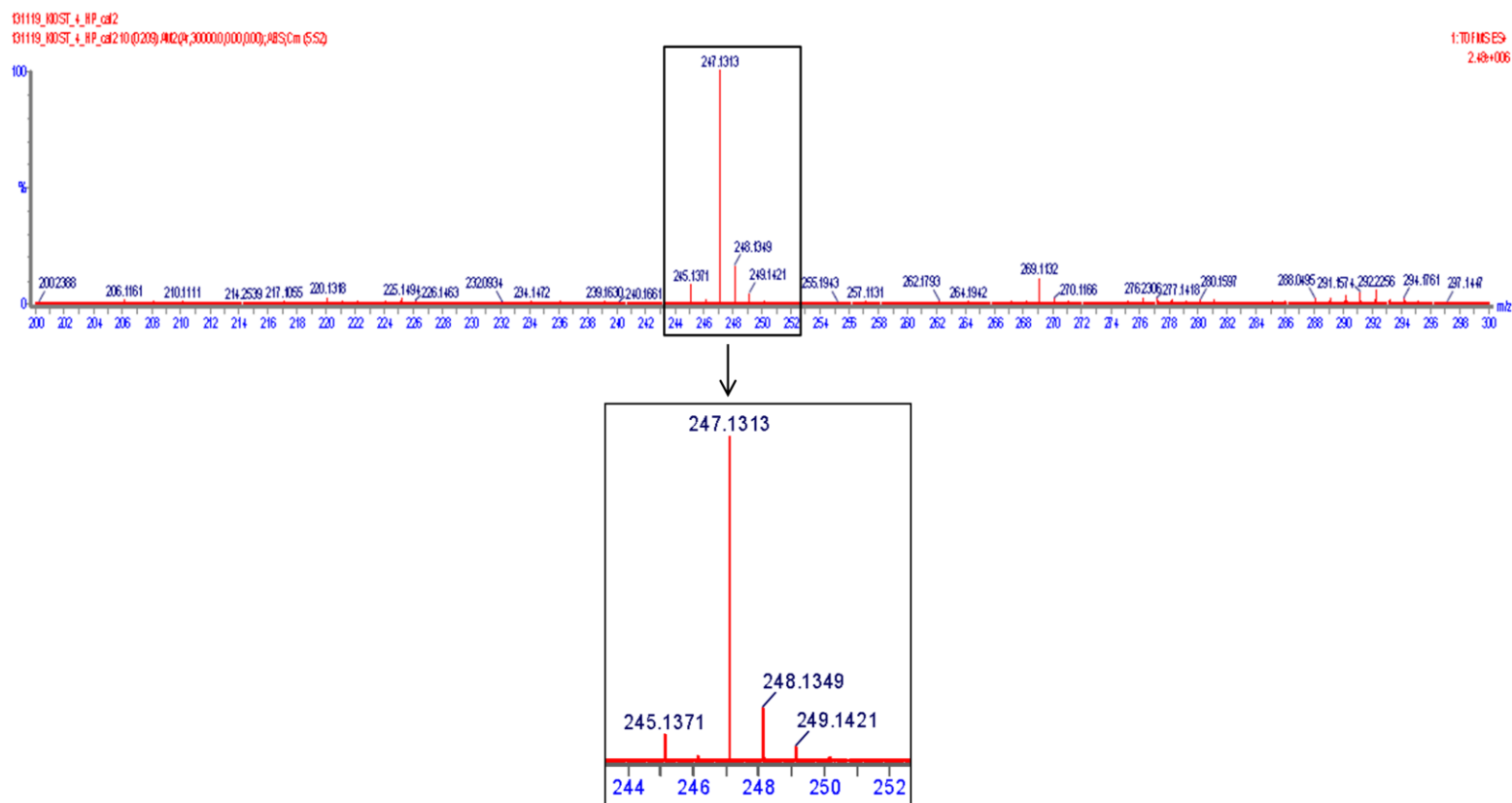


Figure S13. ^1H NMR spectrum of violapyrone B (**3**) in CD_3OD (500 MHz).

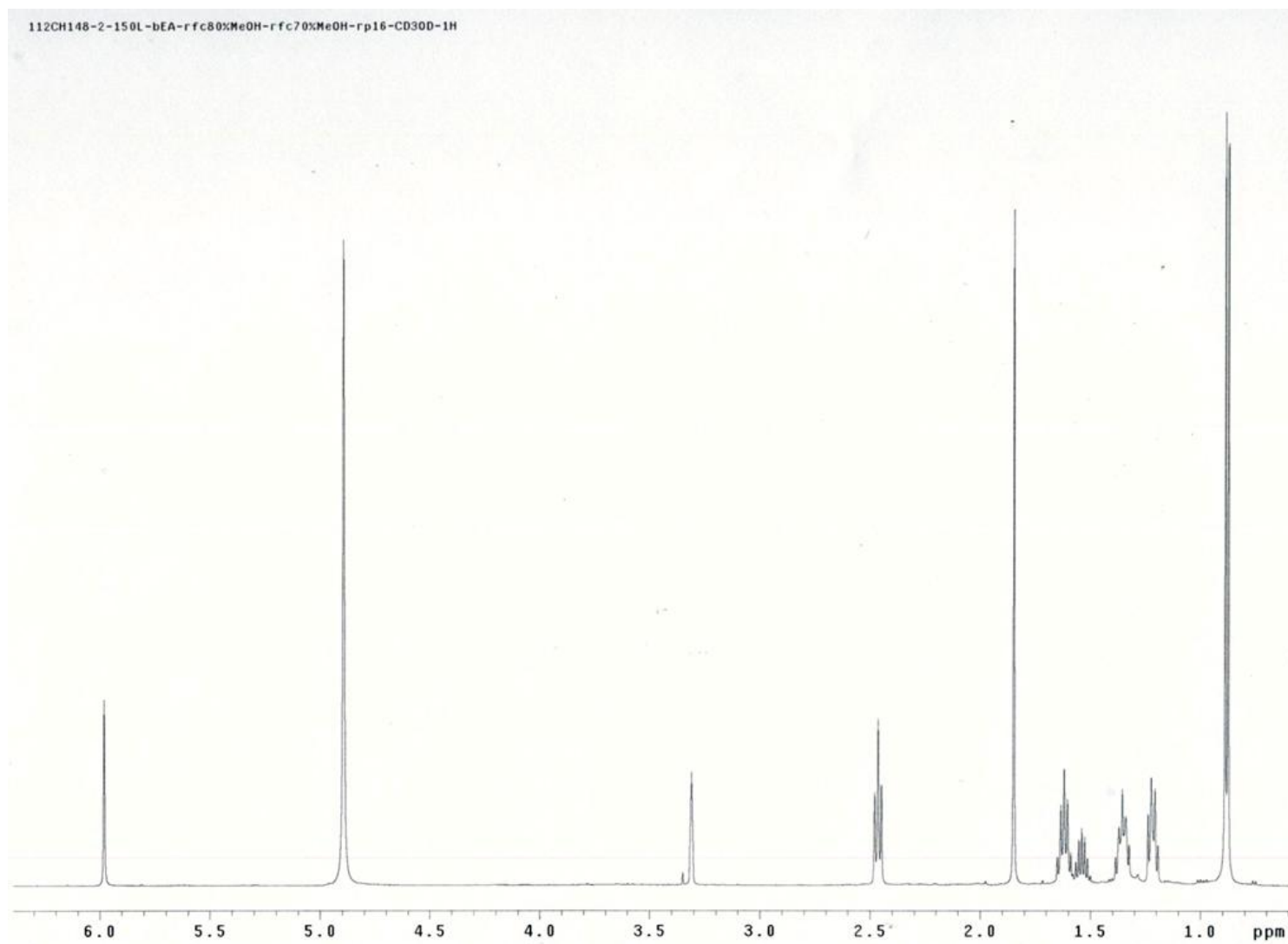


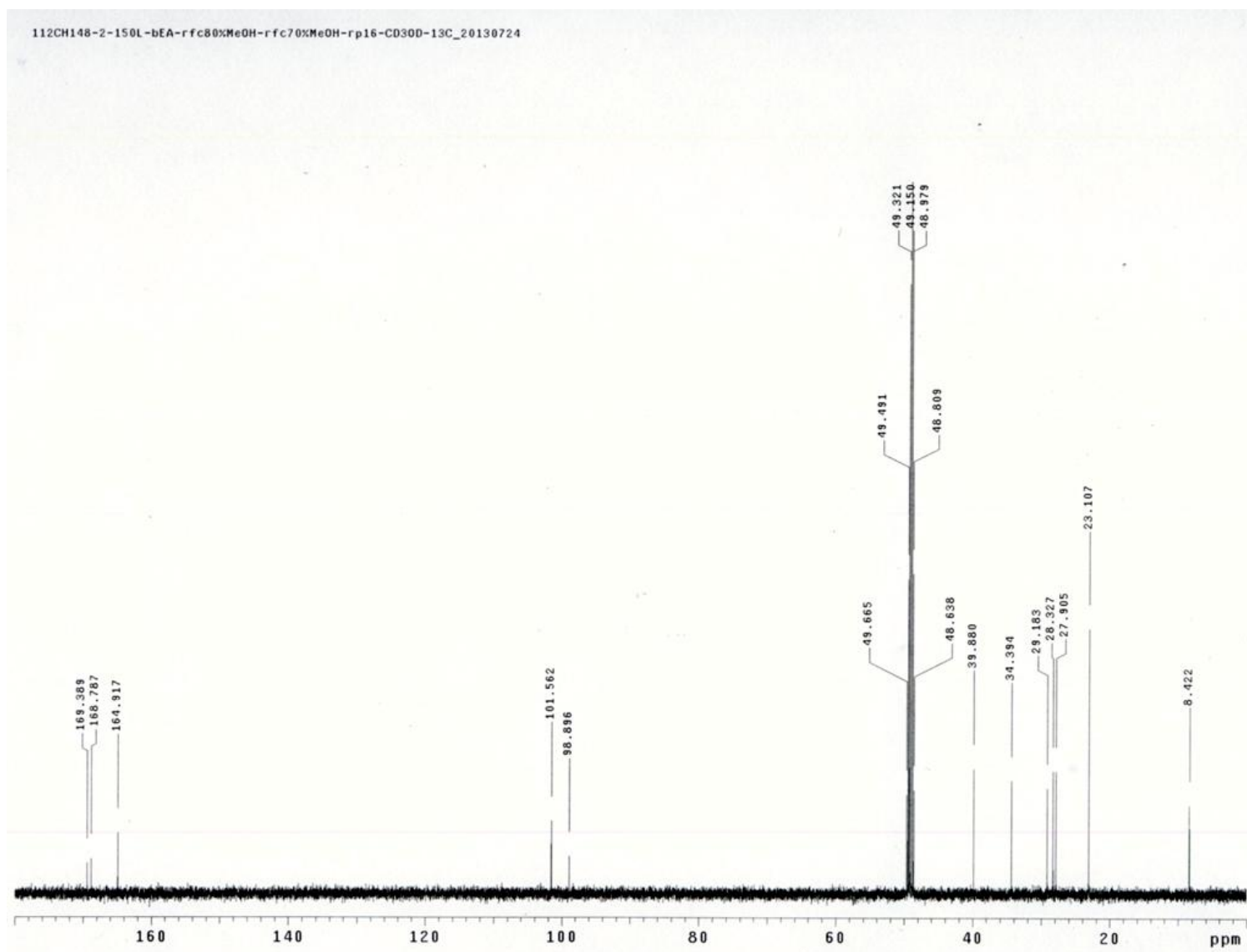
Figure S14. ^{13}C NMR spectrum of violapyrone B (**3**) in CD_3OD (125 MHz).

Figure S15. ^1H NMR spectrum of natural (*S*)-violapyrone C (**4**) in CD_3OD (500 MHz).

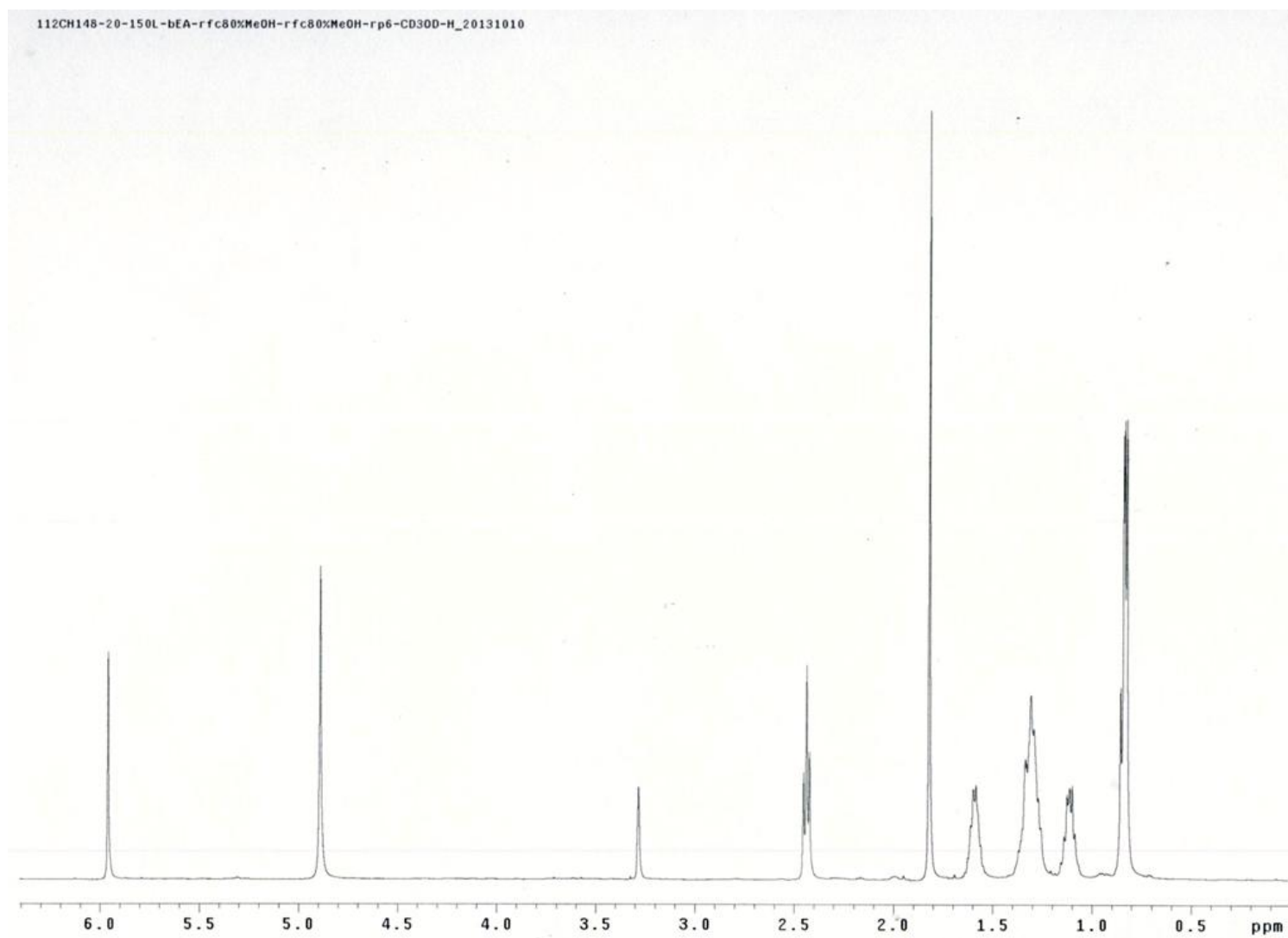


Figure S16. ^1H NMR spectrum of synthetic (*S*)-violapyrone C in CD_3OD (500 MHz).

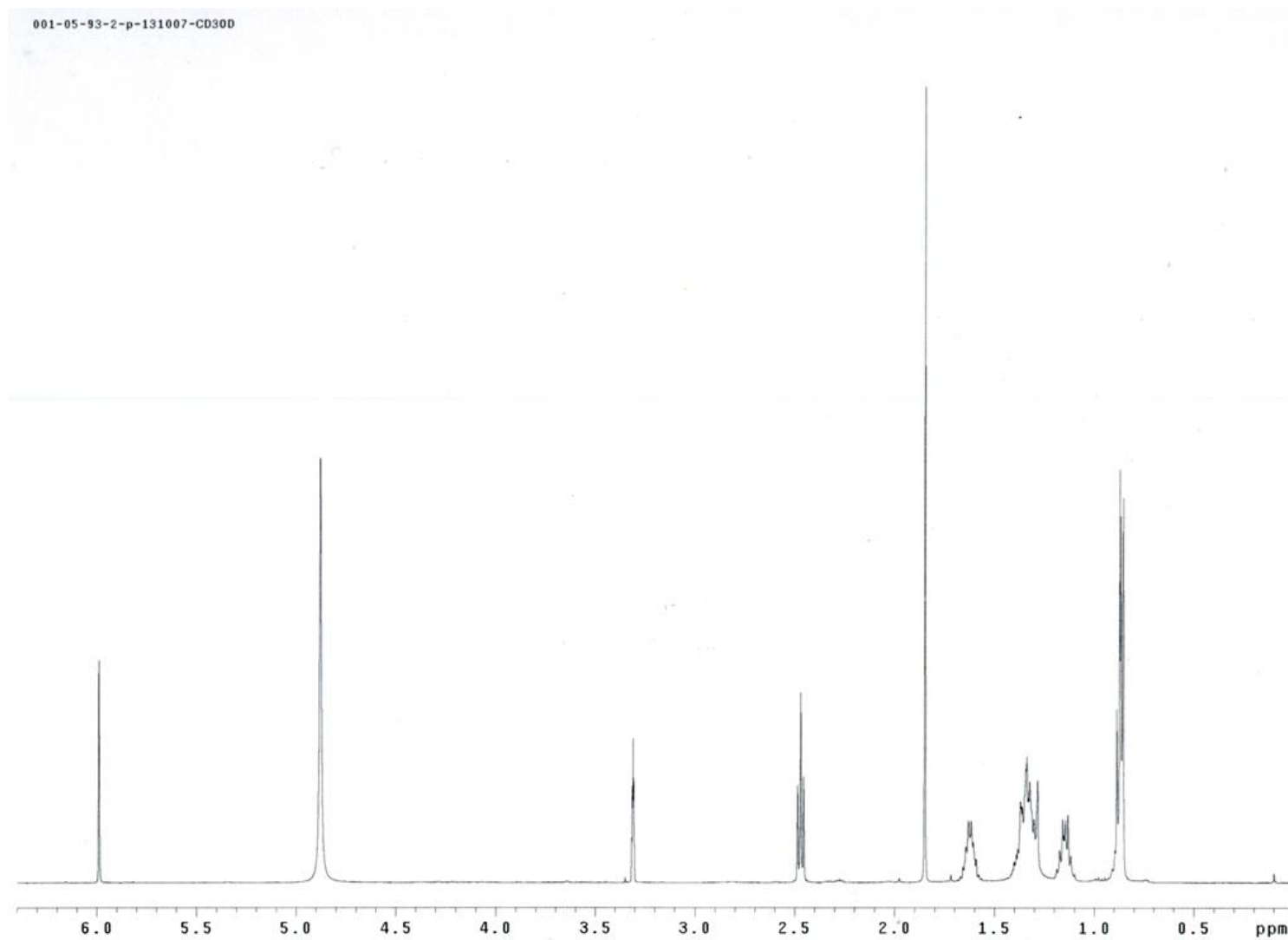


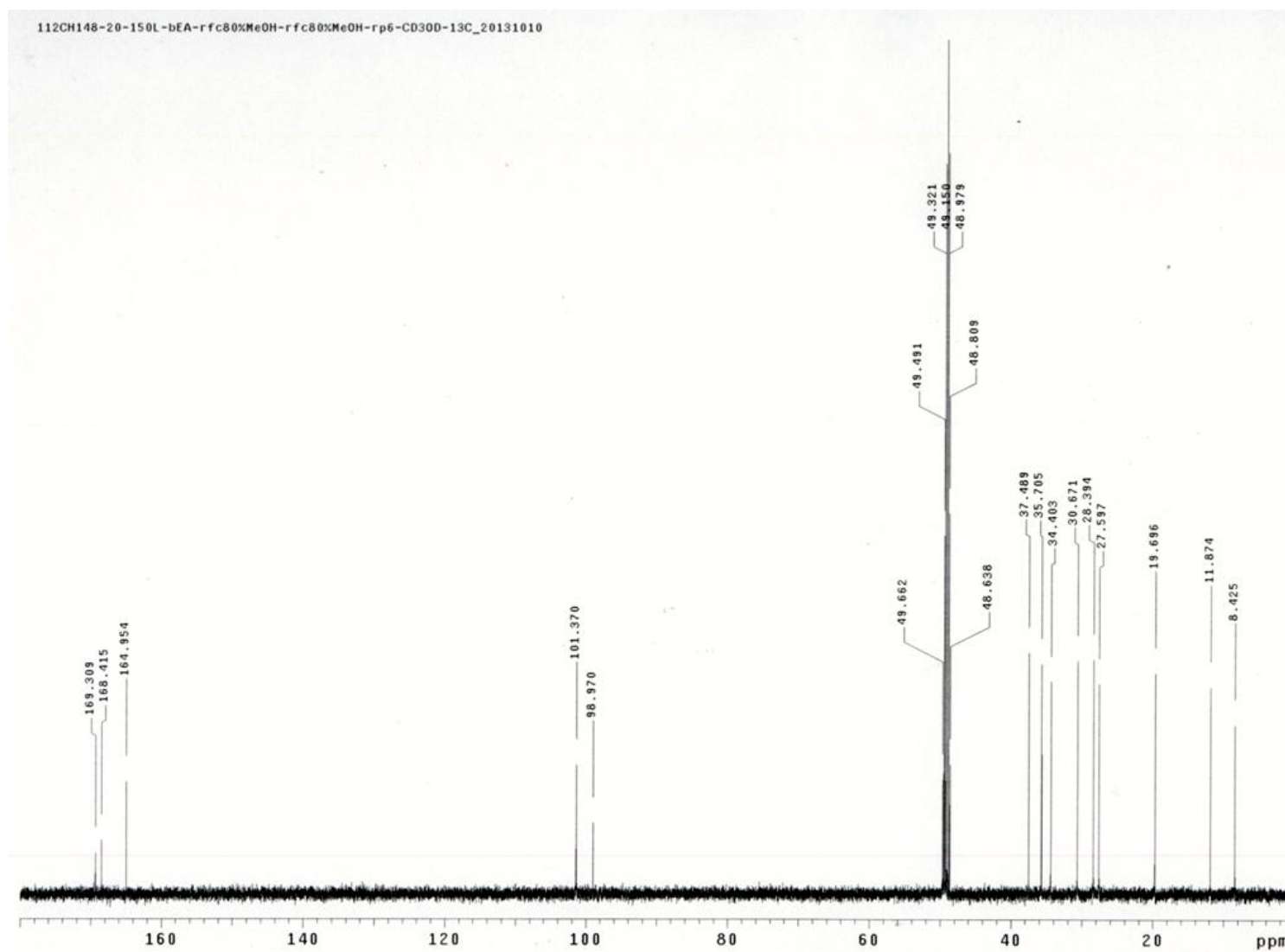
Figure S17. ^{13}C NMR spectrum of natural (*S*)-violapyrone C (**4**) in CD_3OD (125 MHz).

Figure S18. ^{13}C NMR spectrum of synthetic (*S*)-violapyrone C in CD_3OD (125 MHz).