Supporting Information

***Rec. Nat. Prod*. 20:3 (2026):e25123763**

An experimental and *in silico* study on the antifungal activity of guaianolides isolated from *Centaurea polypodiifolia* Boiss. against resistant *Candida* strains

Selin Tufan[1], Faika Başoğlu[2,3], Abdulilah Ece[4], Dilek Şatana[5], Mahmut Miski[1] and Nur Tan[1,*]

[1]Department of Pharmacognosy, Faculty of Pharmacy, İstanbul University, İstanbul, Fatih 34116, Türkiye
[2]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Near East University, Lefkoşa, Turkish Republic of Northern Cyprus
[3]DESAM Institute, Near East University, Lefkoşa, Turkish Republic of Northern Cyprus
[4]Department of Medical Biochemistry, Faculty of Medicine, Biruni University, İstanbul, Küçükçekmece 34295, Türkiye
[5]Department of Medical Microbiology, Faculty of Medicine, İstanbul University, İstanbul, Çapa 34093, Türkiye

*Corresponding author: E-Mail: nurtan@istanbul.edu.tr; Phone: 90 212-4400000-13400 Fax: 90 212-4400252

Table of Contents	Page

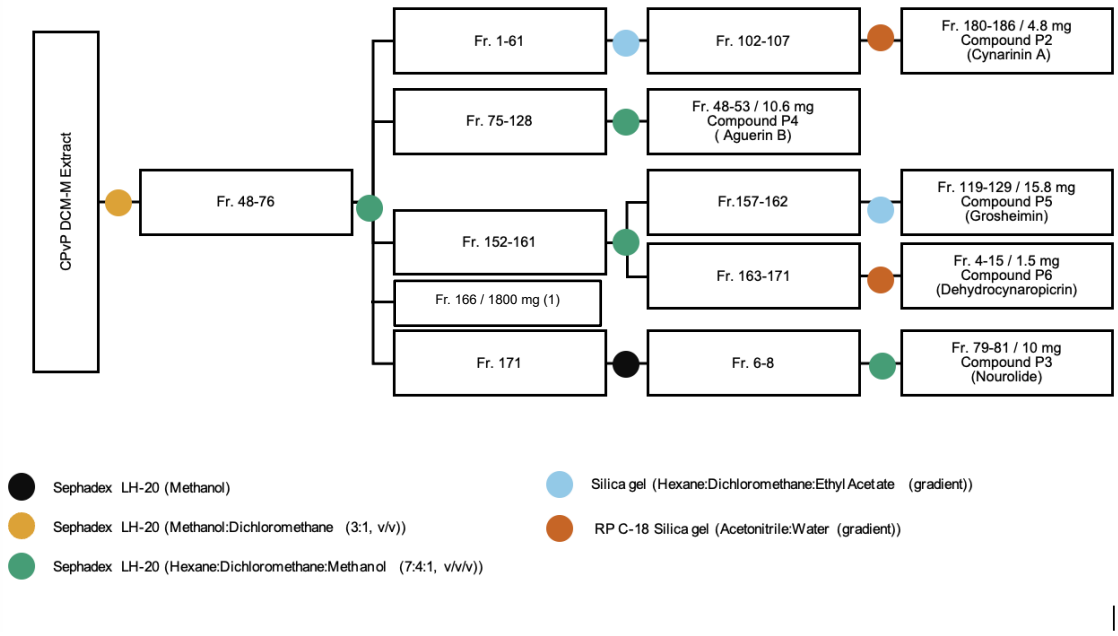
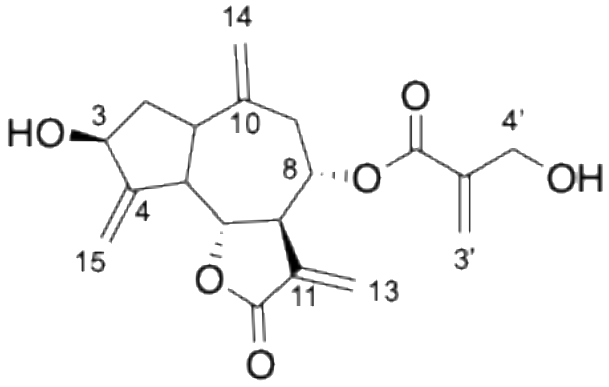


Figure S1: Isolation schema of DCM-M Extract

1. 1 (Cynaropicrin)



^{1}H NMR (500 MHz, $CDCl_3$); δ 6.34 (q, *J* = 0.9 Hz, 1H, 4'a), 6.23 (d, *J* = 3.4 Hz, 1H, 13a), 5.96 (q, *J* = 1.3 Hz, 1H, 4'b), 5.62 (d, *J* = 3.1 Hz, 1H, 13b), 5.50 (t, *J* = 1.9 Hz, 1H, 15a), 5.37 (t, *J* = 1.8 Hz, 1H, 15b), 5.15 (m, 2H, 8, 14a), 4.95 (d, *J* = 1.6 Hz, 1H, 14b), 4.57 (t, *J* = 7.5 Hz, 1H, 3), 4.39 (d, *J* = 4.6 Hz, 2H, 3'), 4.26 (dd, *J* = 10.6, 9.0 Hz, 1H, 6), 3.20 (tt, *J* = 9.4, 3.3 Hz, 1H, 7), 2.99 (dt, *J* = 10.8, 8.0 Hz, 1H, 1), 2.86 (ddt, *J* = 10.5, 8.8, 1.7 Hz, 1H, 5), 2.71 (dd, *J* = 14.6, 5.1 Hz, 1H, 9a), 2.40 (dd, *J* = 14.6, 3.8 Hz, 1H, 9b), 2.25 (m, 1H, 2a), 1.74 (ddd, *J* = 13.3, 11.0, 7.5 Hz, 1H, 2b).

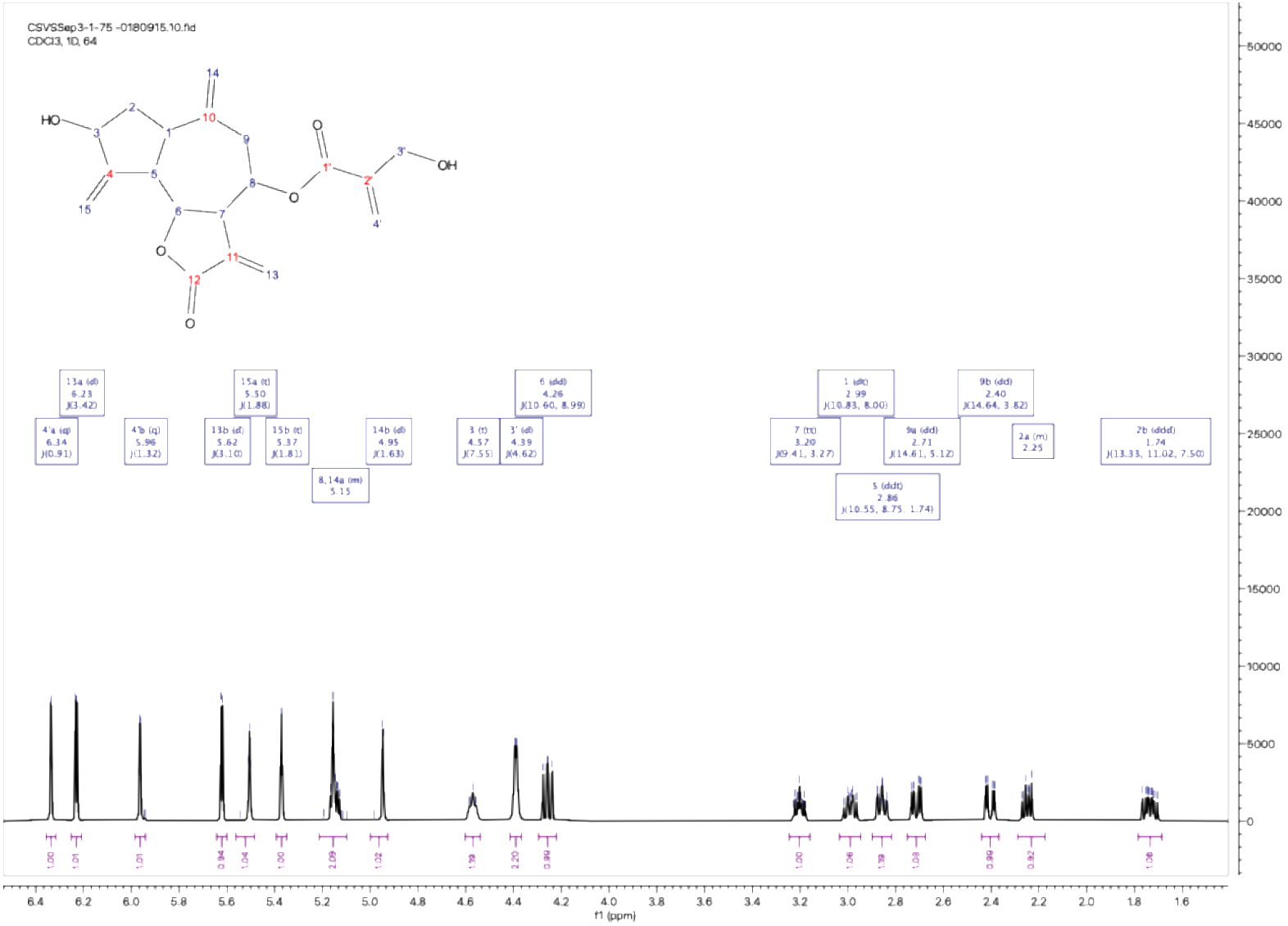


Figure S2: 1 (Cynaropicrin) 1D-^{1}H Proton NMR Spectrum

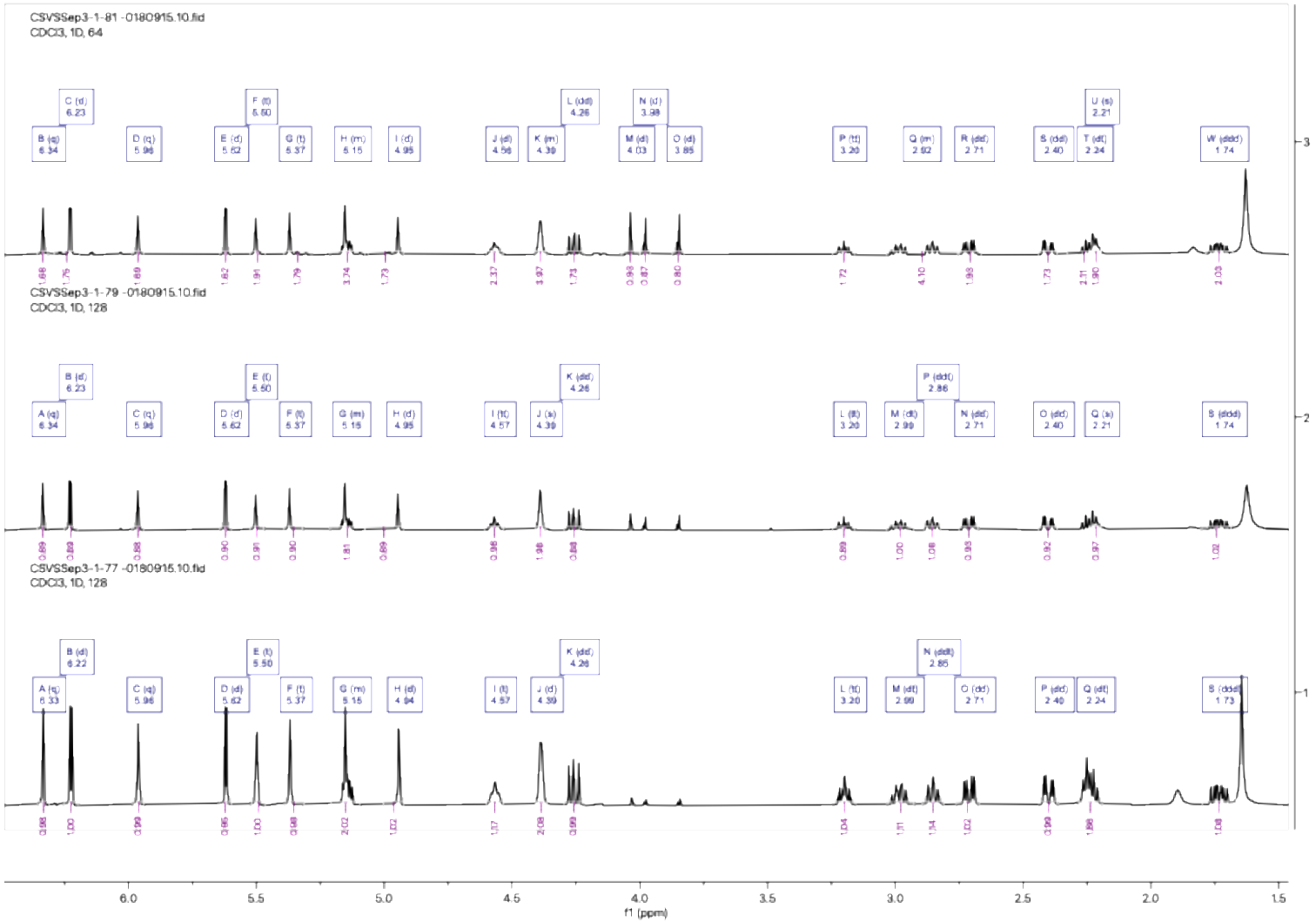
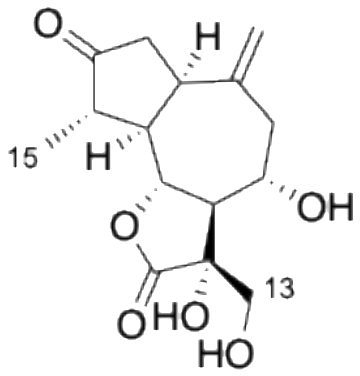


Figure S3: 1 (Cynaropicrin) stacked ^{1}H NMR Spectra of different fractions

2. 2 (Cynarinin A)



^{1}H NMR (500 MHz, $CDCl_3$); δ 5.08 (s, 1H, 14b), 4.81 (m, 1H, 14a), 4.61 (d, *J* = 11.5 Hz, 1H, 13a), 4.40 (dd, *J* = 11.5, 1.7 Hz, 1H, 13b), 4.08 (dd, *J* = 10.1, 8.4 Hz, 1H, 6), 3.91 (td, *J* = 10.3, 5.5 Hz, 1H, 8), 3.13 (td, *J* = 8.1, 4.2 Hz, 1H, 1), 2.88 (dd, *J* = 12.3, 5.5 Hz, 1H, 9β), 2.73 (t, *J* = 10.4 Hz, 1H, 7), 2.57 (m, 1H, 2α), 2.49 (m, 1H, 2β), 2.32 (m, 4H, 4, 5), 2.24 (dd, *J* = 12.3, 10.1 Hz, 1H, 9α).

^{1}H NMR (500 MHz, $CDCl_3$ + CD_3OD (95:5)); δ 5.02 (s, 1H, 14a), 4.74 (s, 1H, 14b), 4.57 (d, *J* = 11.1 Hz, 1H, 13a), 4.32 (dd, *J* = 11.2, 2.0 Hz, 1H, 13b), 4.02 (dd, *J* = 10.1, 8.5 Hz, 1H, 6), 3.80 (td, *J* = 10.3, 5.6 Hz, 1H, 8), 3.10 (td, *J* = 8.2, 4.0 Hz, 1H, 1), 2.81 (dd, *J* = 12.4, 5.6 Hz, 1H, 9β), 2.64 (t, *J* = 10.4 Hz, 1H, 7), 2.49 (m, 2H, 2), 2.27 (tt, *J* = 7.7, 3.6 Hz, 4H, 4, 5), 2.17 (dd, *J* = 12.3, 10.0 Hz, 1H, 9α).

^{13}C NMR (126 MHz, $CDCl_3$); δ 218.05 (3), 174.87, 173.22 (12), 143.30 (10), 130.21, 129.82, 115.52 (14), 81.37 (6), 76.51 (11), 70.44 (8), 64.25 (13), 56.04, 51.46 (5), 48.37 (9), 47.40 (4), 43.39 (2), 39.78 (1), 34.17, 32.07, 24.88, 22.84, 14.73 (15).

^{13}C NMR (126 MHz, $CDCl_3$ + CD_3OD (95:5)); δ 218.95 (3), 173.12 (12), 143.76 (10), 114.91 (14), 81.70 (6), 76.28 (11), 69.92 (8), 64.39 (13), 55.90 (7), 51.44 (5), 48.34 (9), 47.38 (4), 43.38 (2), 39.67 (1), 14.61 (15).

Table S1: 2 (Cynarinin A) HMBC, COSY, NOESY correlations *(in $CDCl_3$)*

No	HMBC	COSY	NOESY
1	-	H5(2.32), H2β(2.49), H2α(2.57), H14a(4.81)	H5(2.32), H2α(2.57)
2α	C3(218.0), C5(51.5), C1(39.8), C10(143.3)	H1(3.13)	H1(3.13)
2β	-	H1(3.13)	-
3	H2α(2.57), H15(1.25)	-	-
4	C5(51.5)	H6(4.08), H15(1.25)	-
5	C4(47.4)	H1(3.13), H6(4.08)	H1(3.13), H15(1.25)
6	C4(47.4)	H4(2.32), H5(2.32), H7(2.73)	H8(3.91)
7	C5(51.5), C6(81.4), C8(70.4), C11(76.5), C13b(64.2)	H6(4.08), H8(3.91)	-
8	-	H7(2.73), H9β(2.88), H9α(2.24)	H6(4.08), H9β(2.88), H13b(4.40), H13a(4.61)
9α	C8(70.4), C14b(115.5)	H8(3.91), H9β(2.88), H14b(5.08)	-
9β	C1(39.8), C7(56.0), C8(70.4), C10(143.3), C14b(115.5)	H8(3.91), H9α(2.24), H14b(5.08)	H8(3.91), H14b(5.08)
10	H2α(2.57), H9β(2.88)	-	-
11	H7(2.73), H13b(4.40)	-	-
12	H13b(4.40), H13a(4.61)	-	-
13a	C12(173.2)	-	H8(3.91)
13b	C12(173.2), C11(76.5)	-	H8(3.91)
14a	C1(39.8), C9β(48.4)	H1(3.13)	-
14b	C1(39.8), C9β(48.4)	H9β(2.88), H9α(2.24)	H9β(2.88)
15	C3(218.0)	H4(2.32)	H5(2.32)

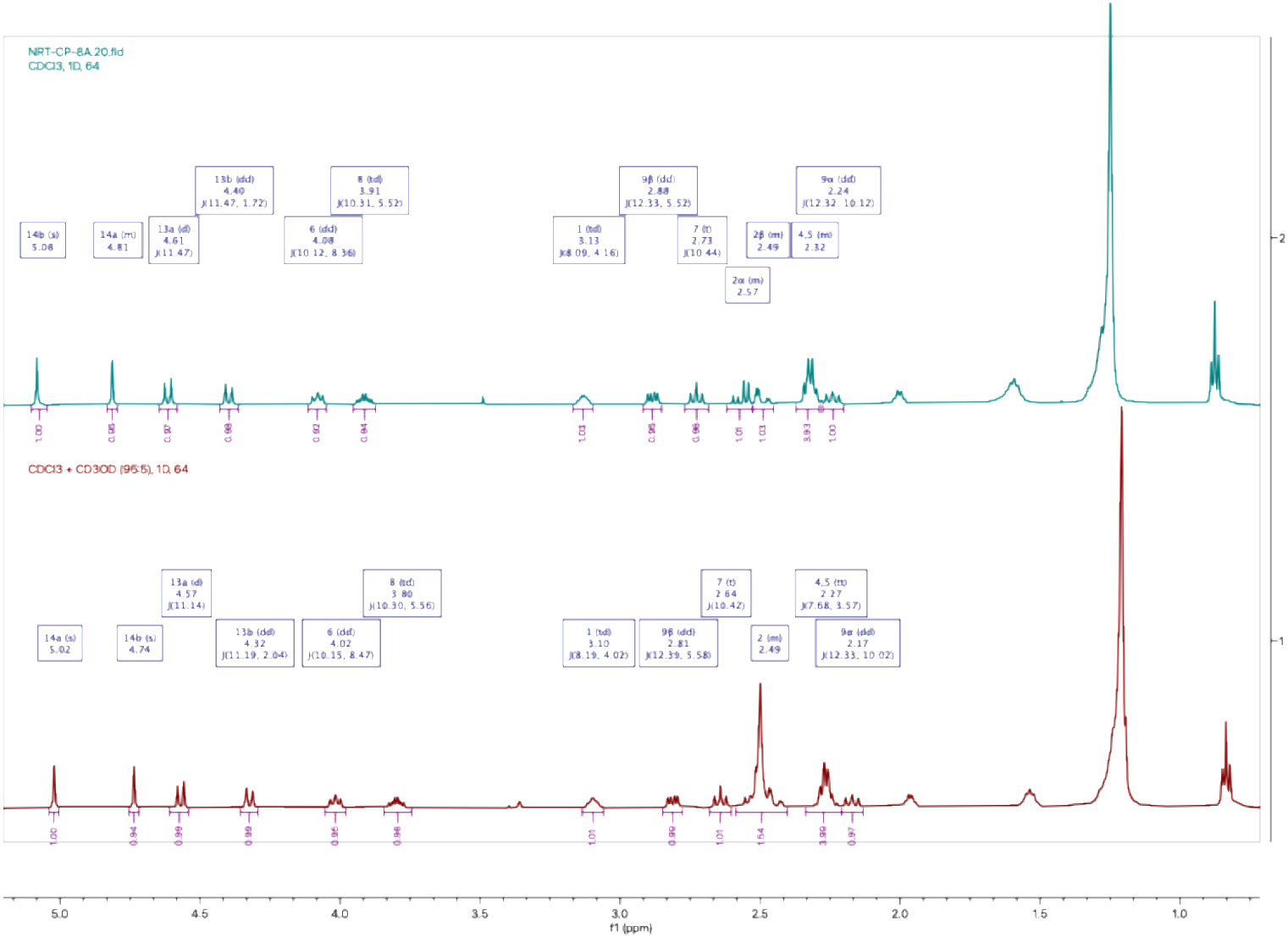


Figure S4: 2 (Cynarinin A) 1D-^{1}H Proton NMR Stacked Spectra in Different Solvents

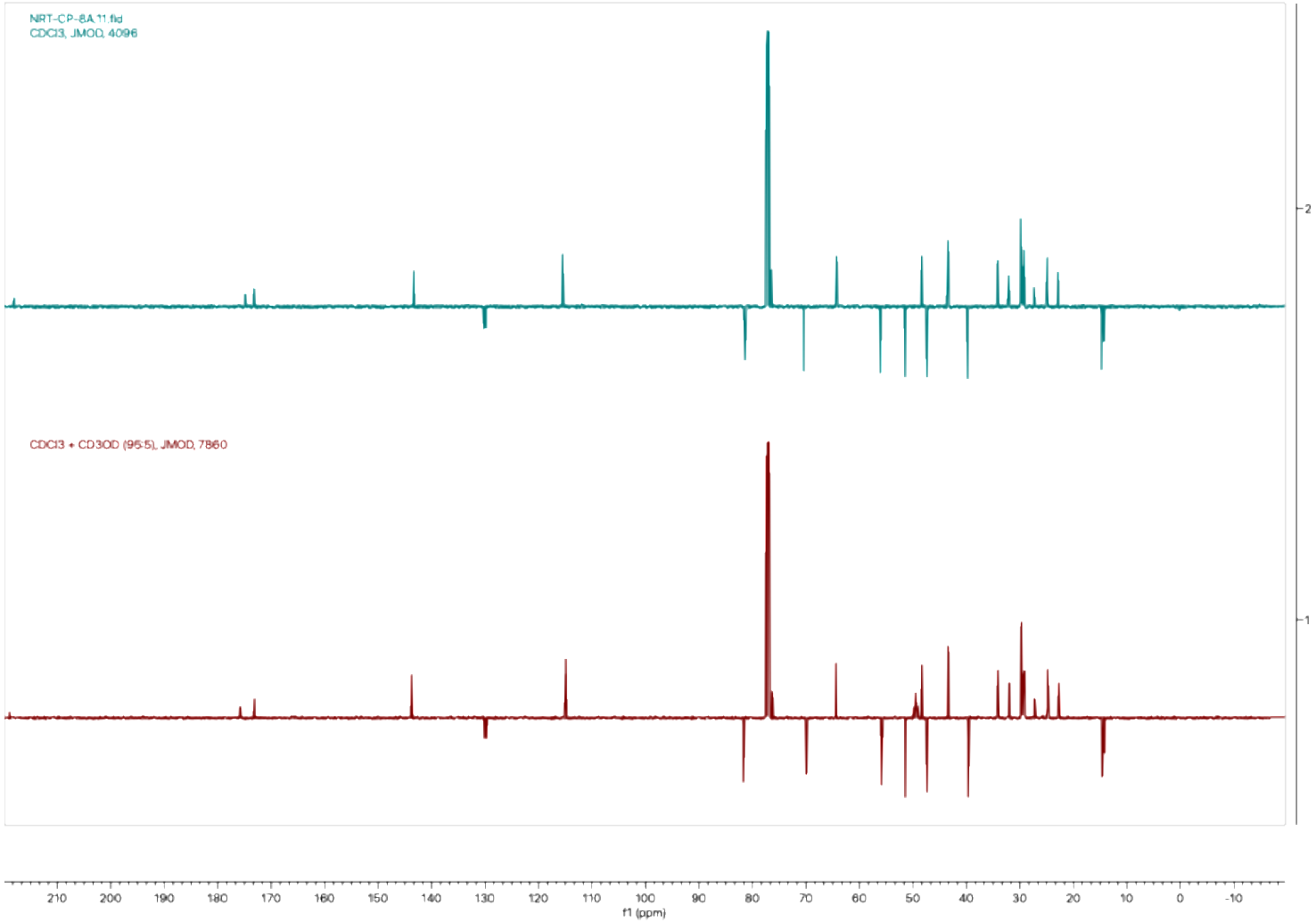


Figure S5: 2 (Cynarinin A) ^{13}C (APT) 1D- NMR Stacked Spectra

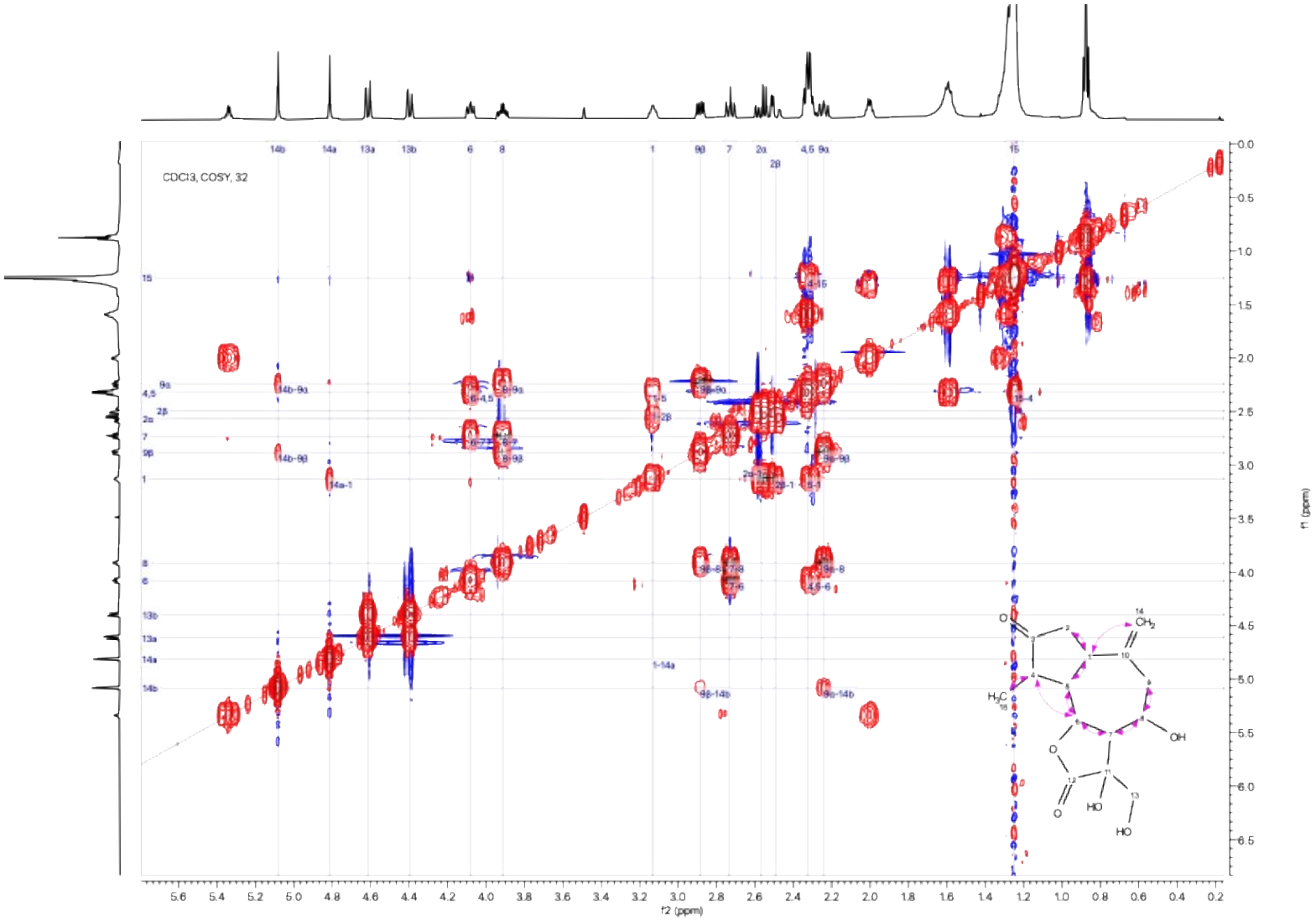


Figure S6: 2 (Cynarinin A) COSY 2D-NMR Spectrum

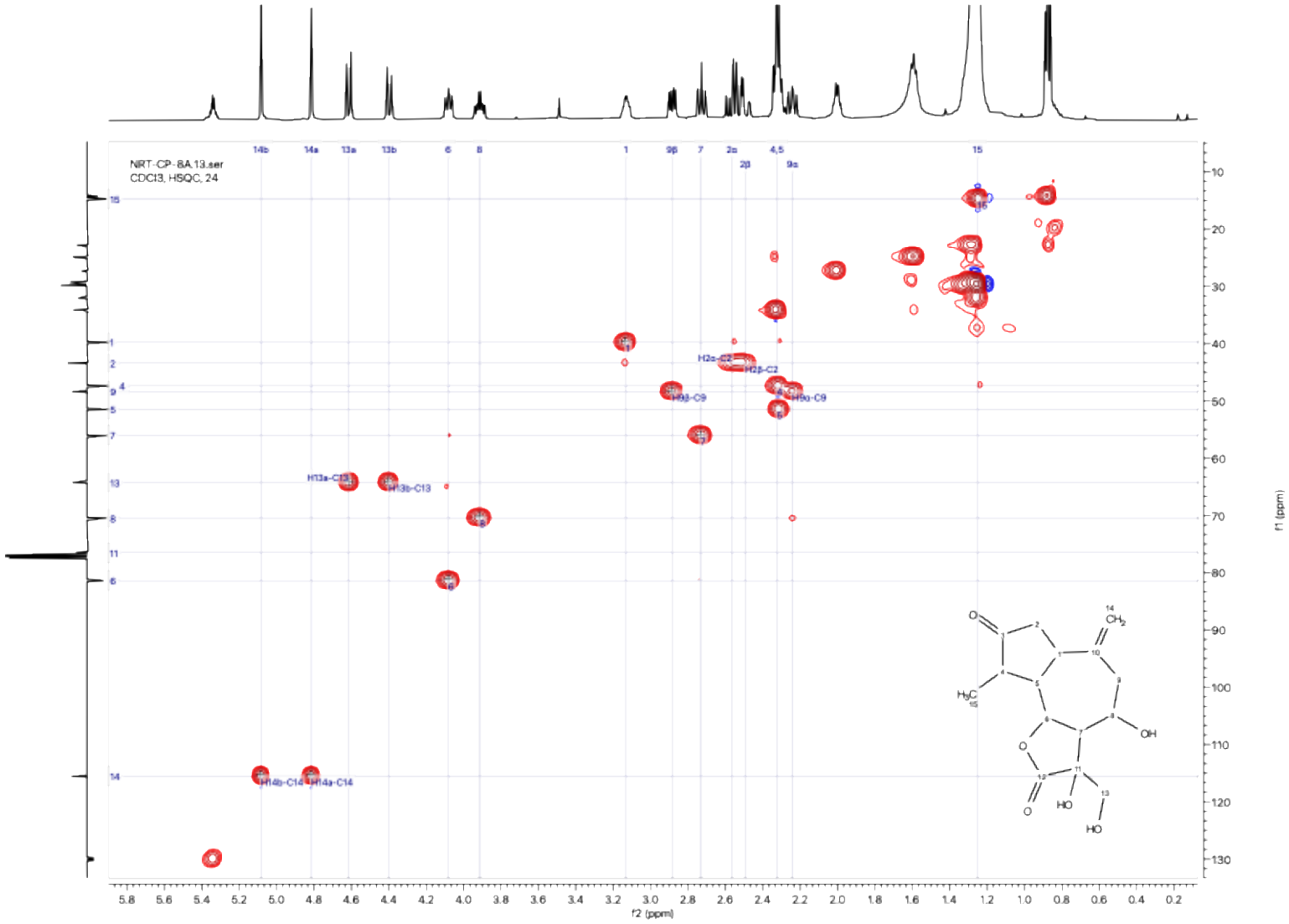


Figure S7: 2 (Cynarinin A) HSQC 2D-NMR Spectrum

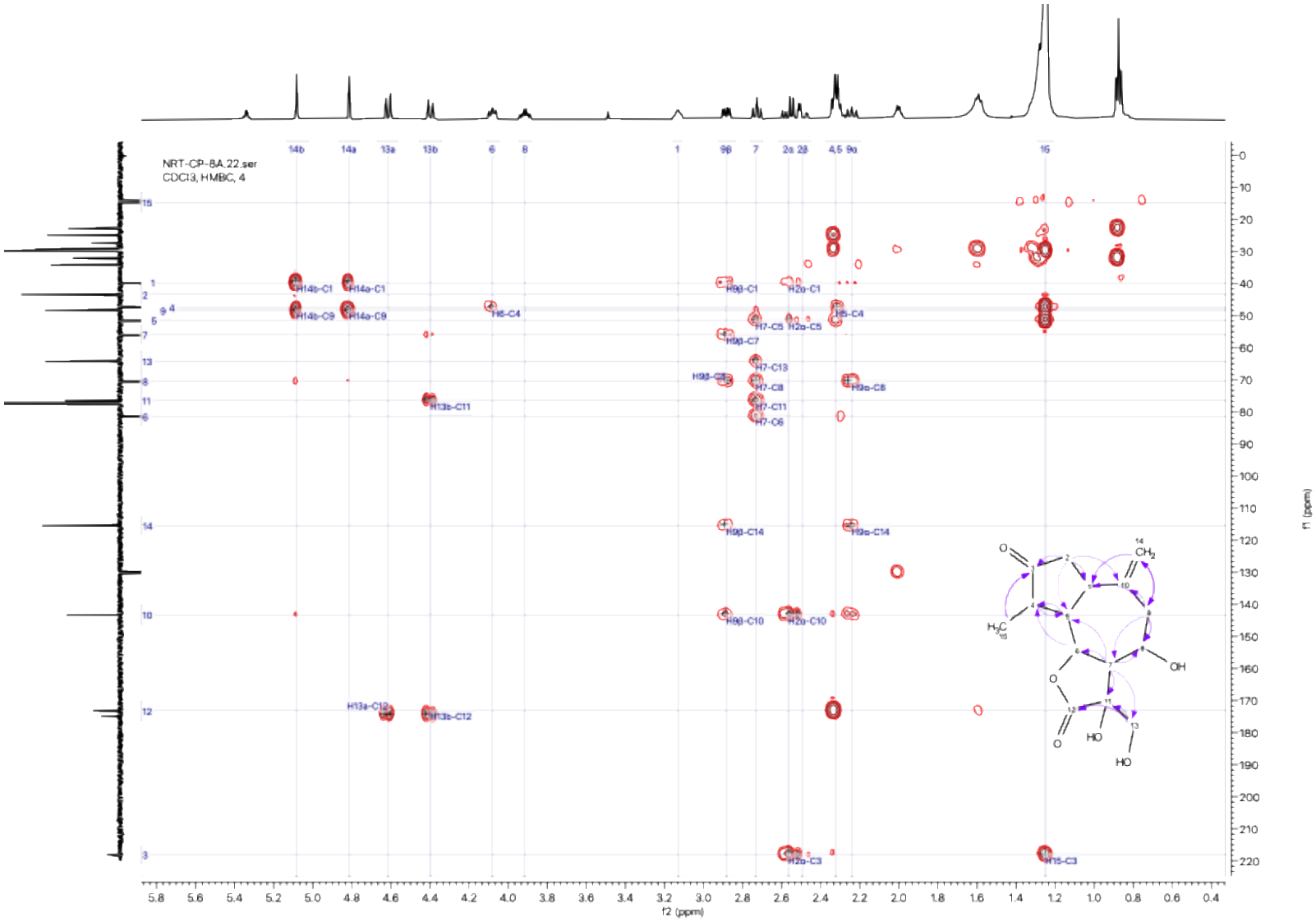


Figure S8: 2 (Cynarinin A) HMBC 2D-NMR Spectrum

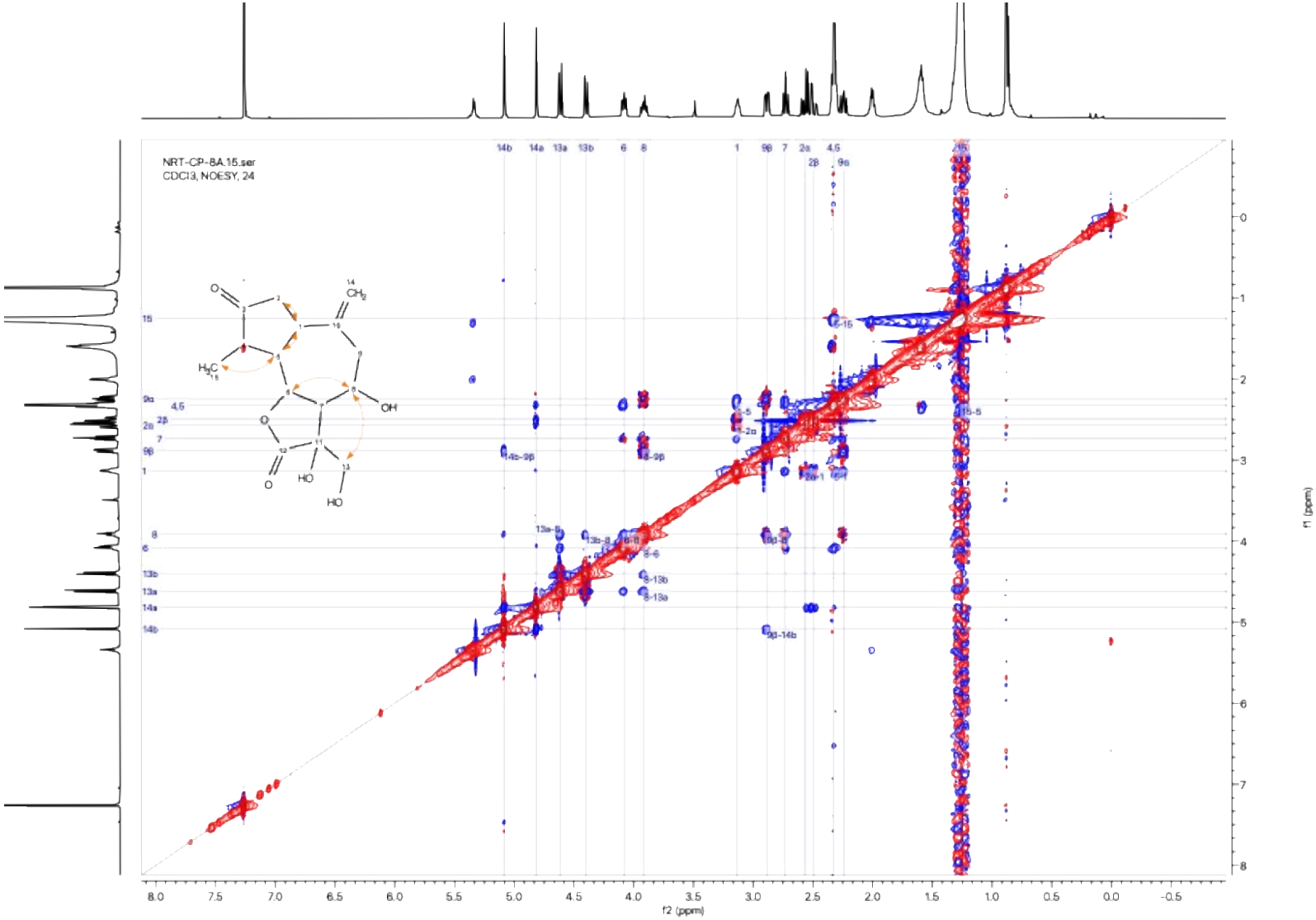


Figure S9: 2 (Cynarinin A) NOESY 2D-NMR Spectrum

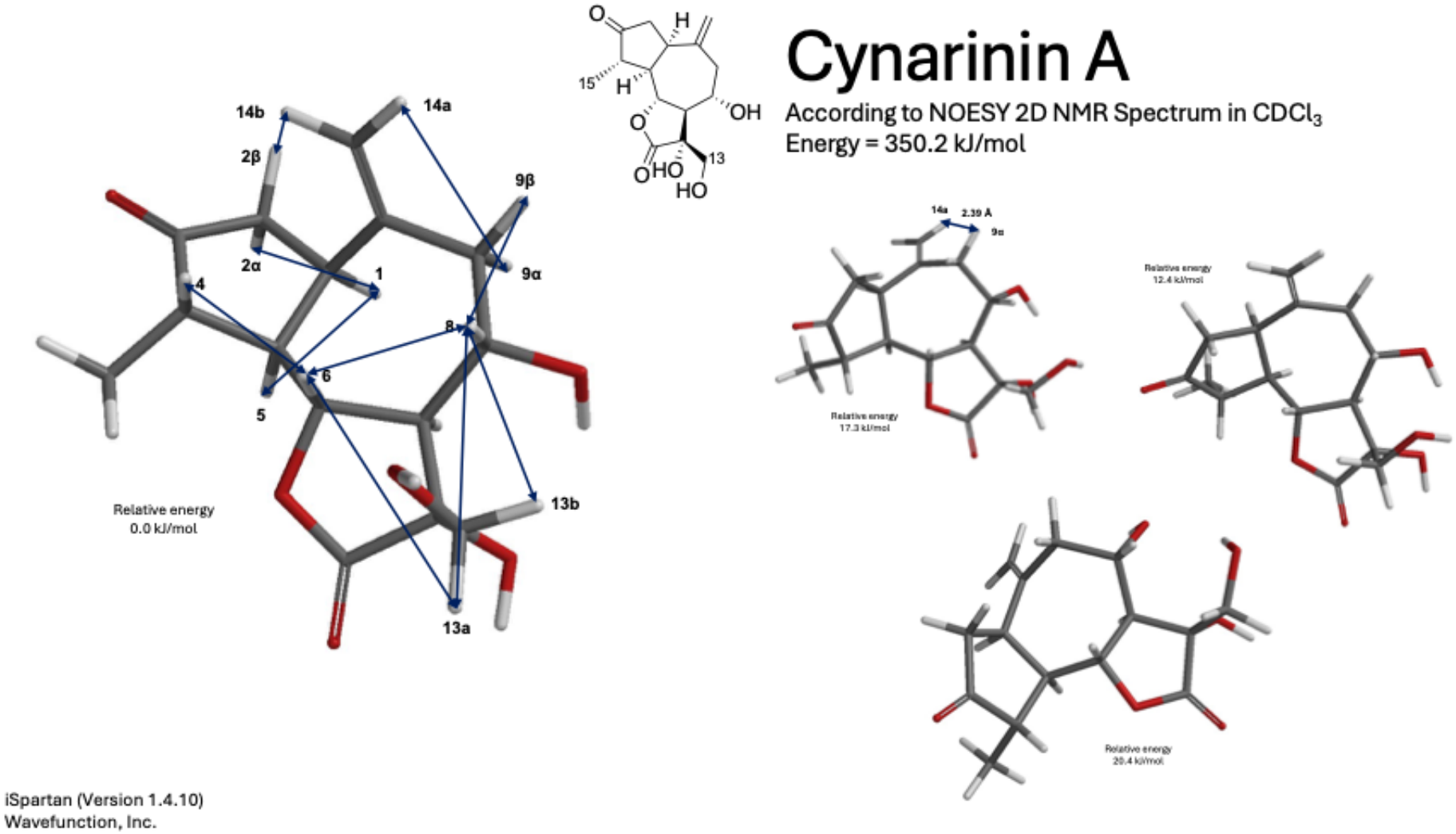


Figure S10: NOESY Correlations of 2 (Cynarinin A) (according to NOESY 2D-NMR spectrum in $CDCl_3$)

Table S2: 2 (Cynarinin A) NOESY correlation *(in $CDCl_3$:CD_3OD (95:5))*

No	NOESY
1	H7(2.64)
2	H14b(4.74)
4	H6(4.02)
5	H7(2.64)
6	H4(2.27), H8(3.80), H13a(4.57)
7	H5(2.27), H1(3.10)
8	H6(4.02), H8(3.80), H13b(4.32), H13a(4.57)
13a	H6(4.02), H8(3.80)
13b	H8(3.80)
14b	H2(2.49)

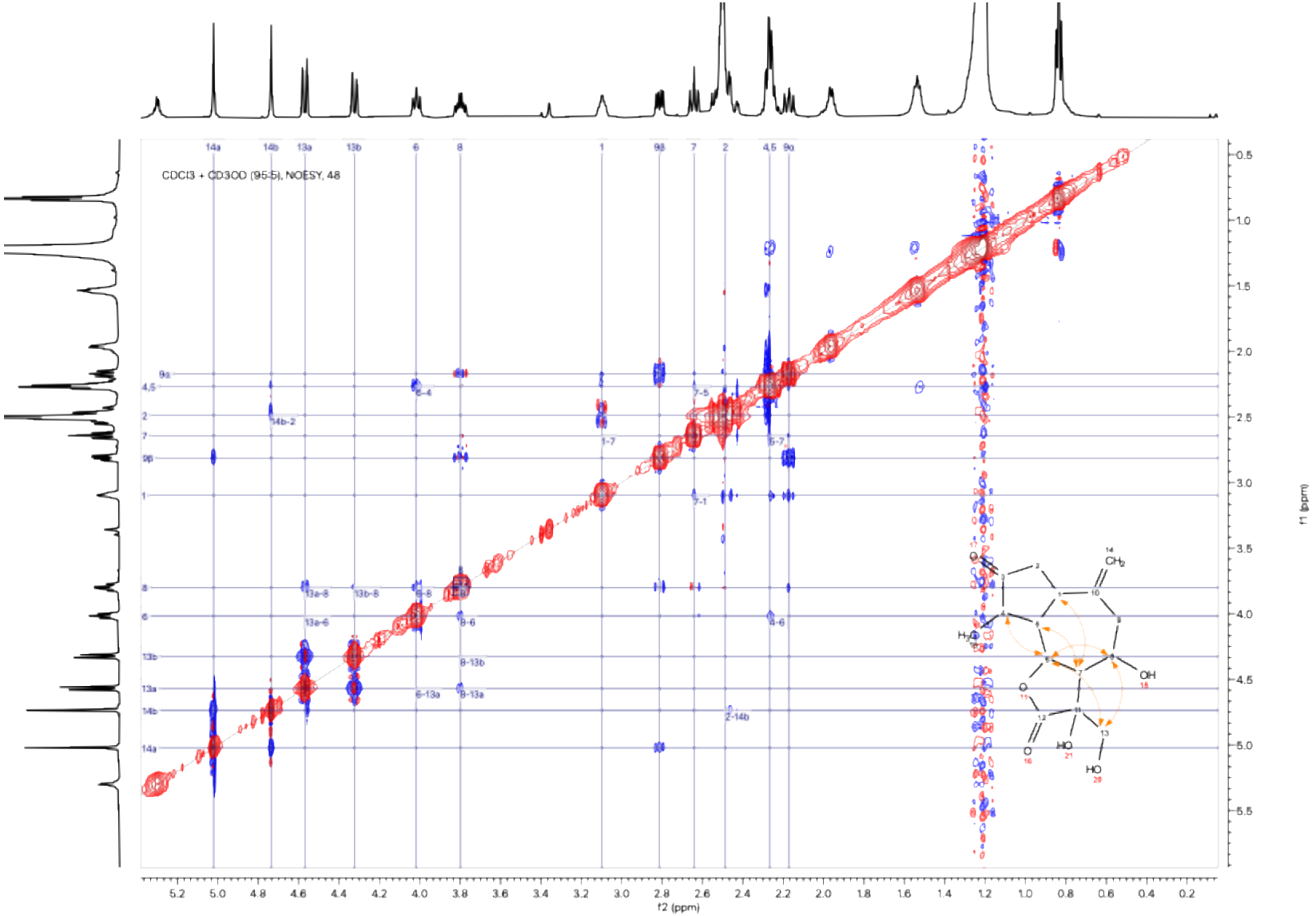


Figure S11: 2 (Cynarinin A) NOESY 2D-NMR Spectrum

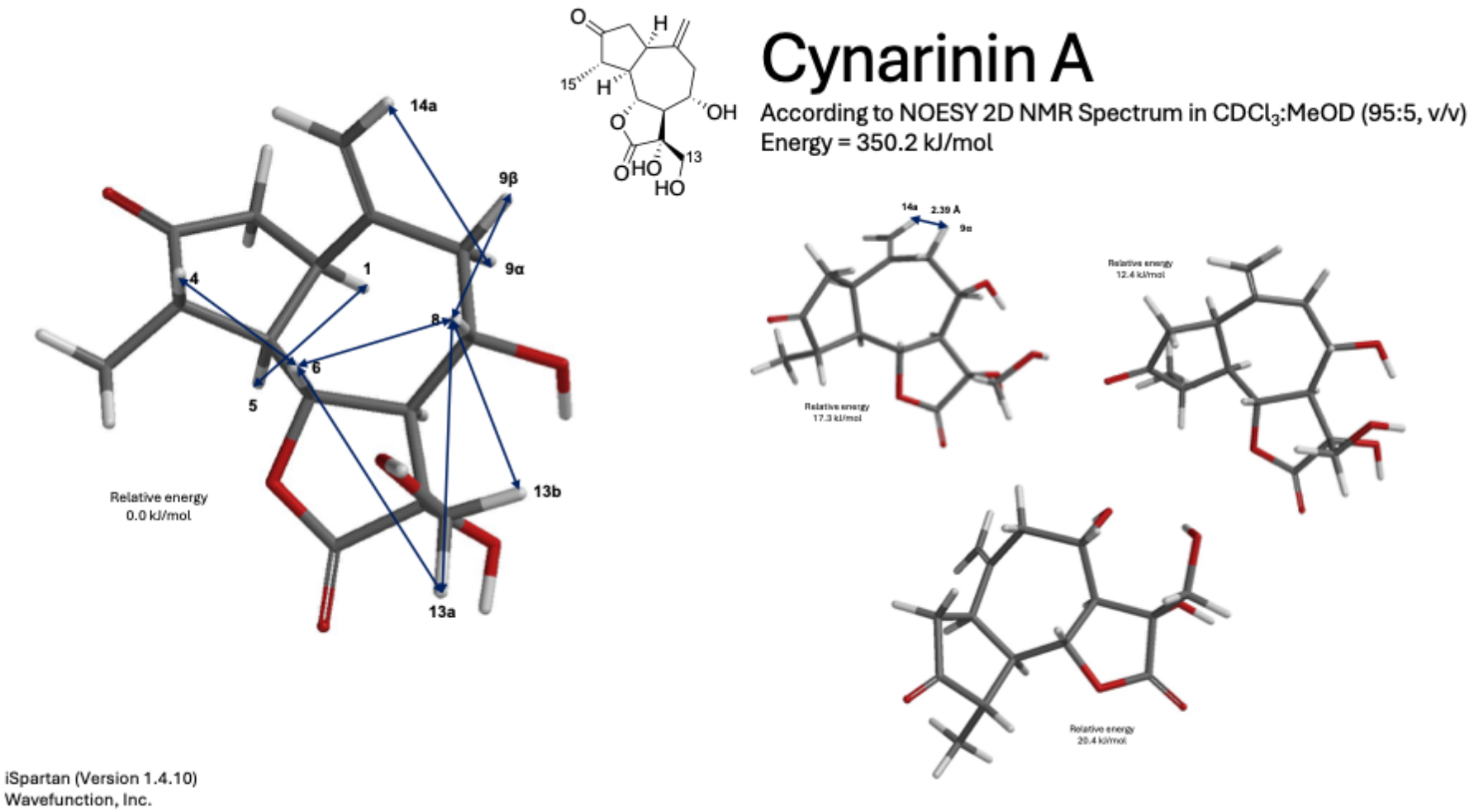
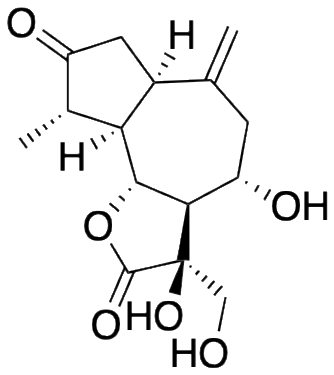


Figure S12: NOESY Correlations of 2 (Cynarinin A) (according to NOESY 2D-NMR spectrum in $CDCl_3$:MeOD (95:5, v/v))

3. 3 (Nourolide)



^{1}H NMR (500 MHz, CD_3OD_SPE); δ 5.06 (s, 1H, 14a), 4.75 (s, 1H, 14b), 4.20 (m, 1H, 6), 4.17 (m, 1H, 8), 4.13 (m, 1H, 13b), 3.76 (d, *J* = 10.4 Hz, 1H, 13a), 3.21 (td, *J* = 8.8, 3.4 Hz, 1H, 1), 2.84 (dd, *J* = 12.4, 5.7 Hz, 1H, 9α), 2.61 (m, 1H, 7), 2.58 (m, 1H, 2α, 7), 2.45 (ddd, *J* = 19.0, 4.0, 1.2 Hz, 1H, 2β), 2.30 (m, 2H, 4, 5), 2.23 (ddd, *J* = 12.4, 9.8, 1.0 Hz, 1H, 9β), 1.20 (m, 3H, 15).

^{1}H NMR (500 MHz, $CDCl_3$ + CD_3OD (95:5)); δ 5.04 (s, 1H, 14'), 4.73 (d, *J* = 2.7 Hz, 1H, 14''), 4.03 (m, 2H, 6, 8), 3.83 (m, 2H, 13', 13''), 3.10 (td, *J* = 8.4, 4.3 Hz, 1H, 1), 2.83 (dd, *J* = 12.5, 5.5 Hz, 1H, 9α), 2.63 (t, *J* = 10.3 Hz, 1H, 7), 2.50 (m, 2H, 2', 2''), 2.26 (m, 3H, 4, 5), 2.19 (dd, *J* = 12.5, 10.1 Hz, 1H, 9β), 1.19 (d, *J* = 6.7 Hz, 3H, 15).

^{13}C NMR (126 MHz, CD_3OD_SPE); δ 180.19 (12), 146.25 (10), 114.44 (14), 83.38, 79.60 (11), 70.79, 64.64 (13), 57.14 (7), 52.89 (5), 48.44 (4), 44.23 (2), 40.88 (1), 14.88 (15).

^{13}C NMR (126 MHz, $CDCl_3$ + CD_3OD (95:5)); δ 177.26 (12), 143.93 (10), 114.93 (14), 81.97, 78.44 (11), 70.28, 62.71, 56.14, 51.57 (4), 47.66 (9), 47.34 (5), 43.54, 39.63, 14.48 (15).

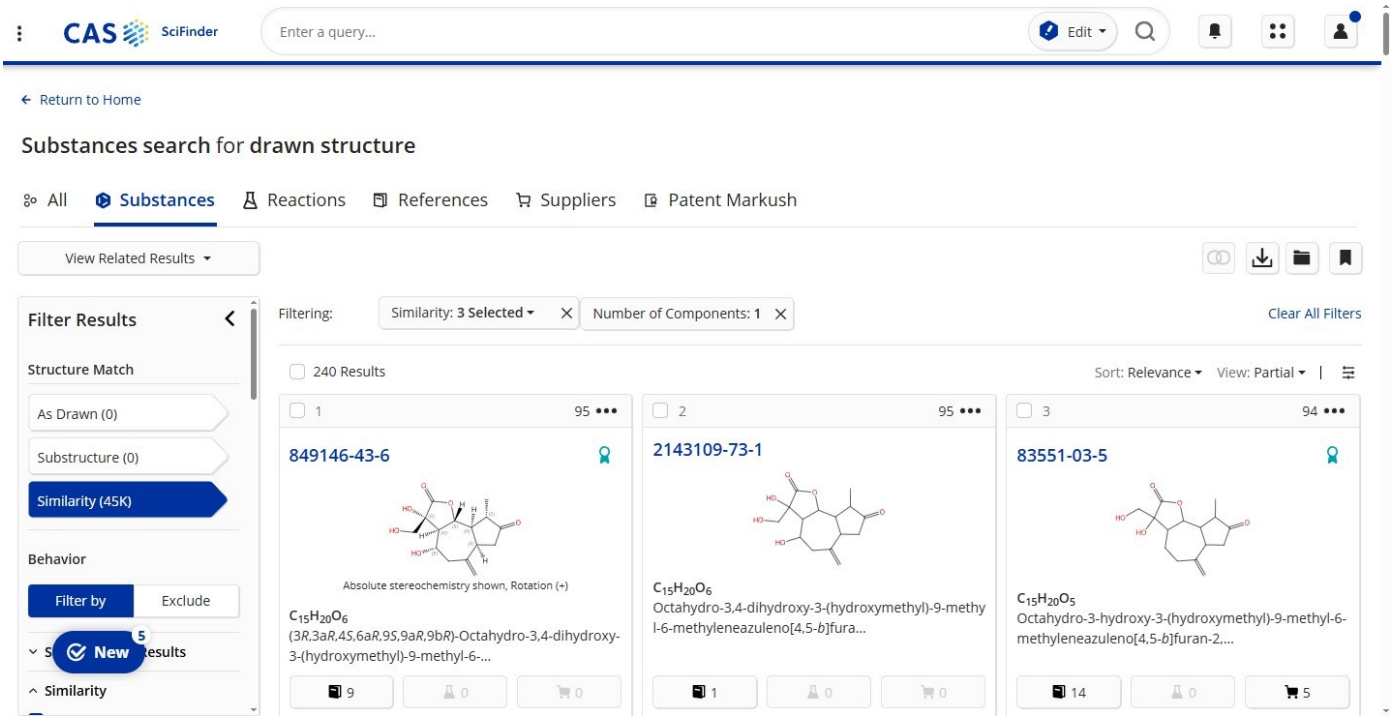


Figure S13: 3 novel compound, SciFinder ® report

Table S3: 3 (Nourolide) HMBC, COSY, NOESY correlations *(in $CDCl_3$:CD_3OD (95:5))*

No	δ_H	δ_C	HMBC	COSY	NOESY
1	3.10 (td, *J*=8.4,4.3 Hz, 1H)	39.4	-	2.26(4), 2.26(5), 2.50(2b), 2.50(2a)	2.26(5), 2.63(7)
2a	2.50 (m, 1H)	43.4	51.6(4), 143.9(10),219.8(3)	3.10(1)	-
2b			51.6(4), 143.9(10),219.8(3)	3.10(1)	-
3	-	219.8	1.19(15),2.50(2b), 2.50(2a)	-	-
4	2.26 (m, 1H)	51.6	-	1.19(15),3.10(1), 4.04(6)	4.04(6)
5	2.26 (m, 1H)	47.3	-	1.19(15),3.10(1), 4.04(6)	1.19(15),3.10(1)
6	4.03 (m, 1H)	81.8	70.2(8)	2.26(4), 2.26(5), 2.63(7)	2.26(4)
7	2.63 (t, *J*=10.3 Hz, 1H)	56.0	47.7(9β), 62.6(13b),70.2(8)	4.02(8),4.04(6)	3.10(1)
8	4.03 (m, 1H)	70.2	-	2.63(7), 2.83(9α)	2.19(9beta)
9α	2.83 (dd, 12.5,5.5 Hz, 1H)	47.7	39.4(1), 56.0(7), 70.2(8), 114.9(14b), 143.9(10)	2.19(9β),4.02(8)	5.04(14a)
9β	2.19 (dd, 12.5,10.1 Hz, 1H)	47.7	39.4(1), 70.2(8), 114.9(14b)	2.83(9α)	4.02(8)
10	-	143.9	2.50(2b), 2.50(2a), 2.83(9α), 4.73(14b), 5.04(14a)	-	-
11	-	78.4	3.83(13b), 3.83(13a)	-	-
12	-	177.3	3.83(13b), 3.83(13a)	-	-
13a	3.83 (m, 1H)	62.6	56.0(7), 78.4(11), 177.3(12)	-	-
13b			56.0(7), 78.4(11), 177.3(12)	-	-
14a	5.04 (s, 1H)	114.9	39.4(1), 47.7(9β), 70.2(8), 143.9(10)	-	-
14b	4.73 (d, *J*=2.7 Hz, 1H)		39.4(1),47.3(5), 47.7(9β), 70.2(8), 143.9(10)	-	2.83(9alpha)
15	1.19 (d, *J*=6.7 Hz, 3H)	14.5	81.8(6),219.8(3)	2.26(4), 2.26(5)	2.65 (5)

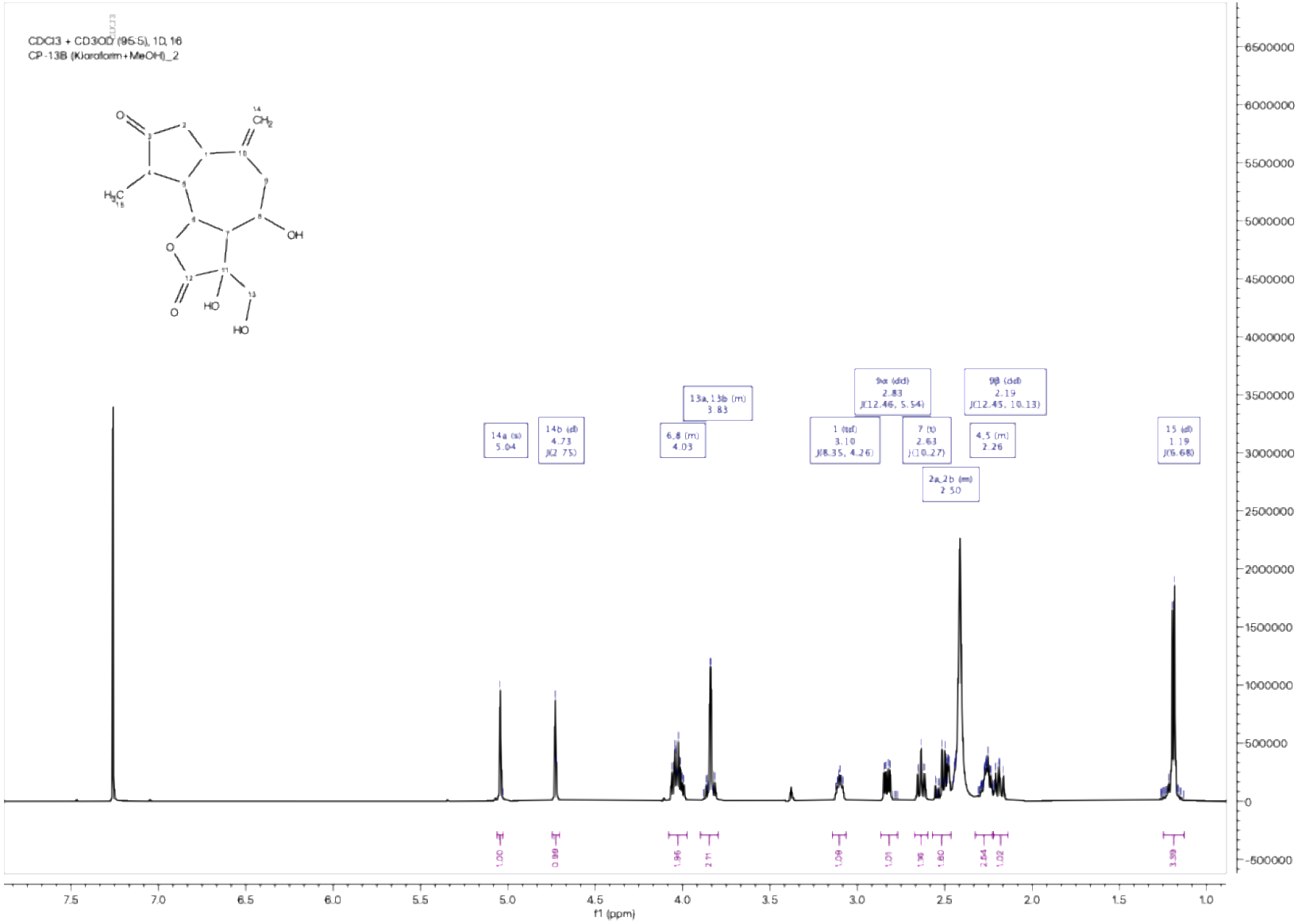


Figure S14: 3 (Nourolide) 1D-^{1}H Proton NMR Spectrum

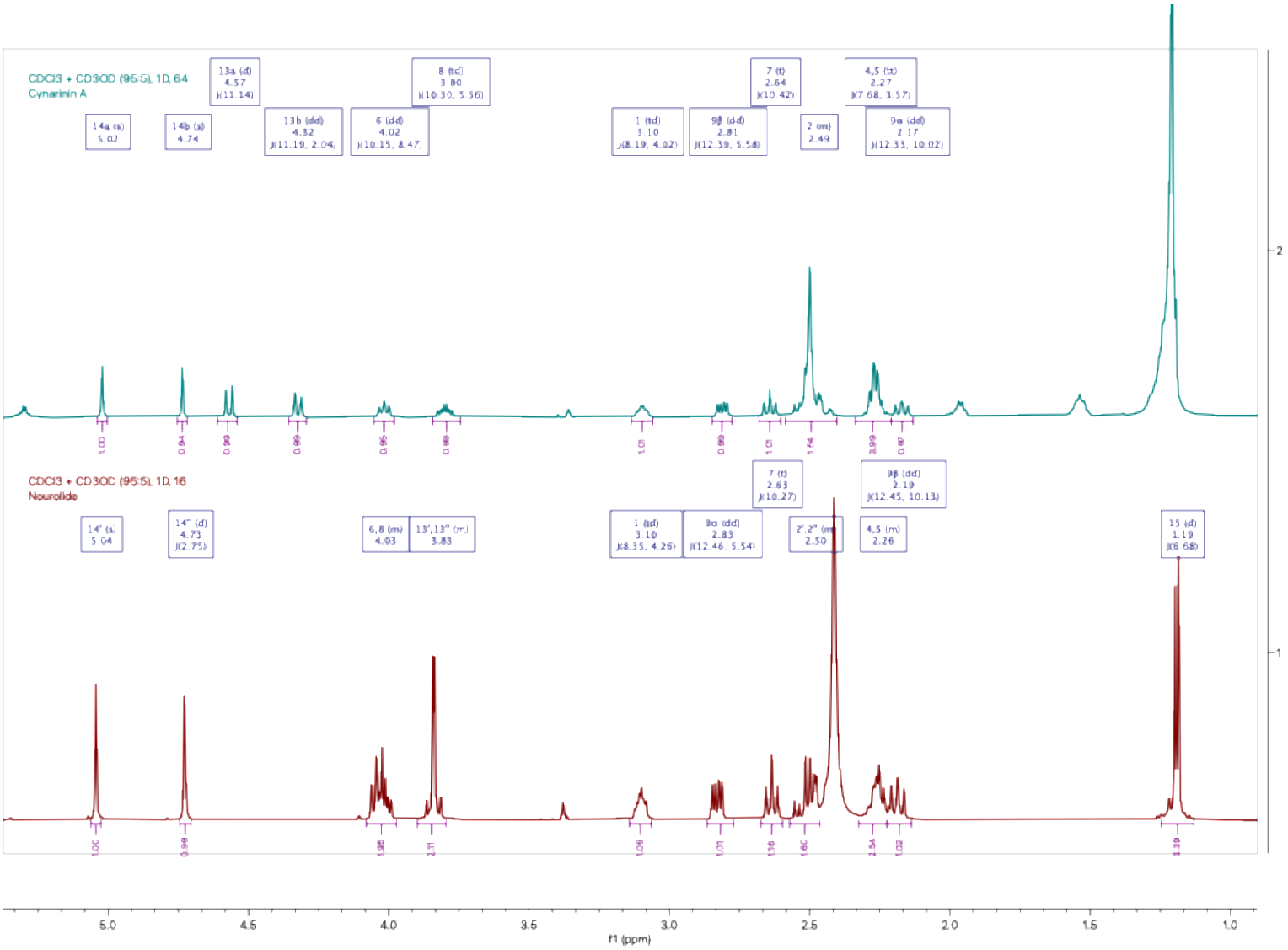


Figure S15: 2 (Cynarinin A) and 3 (Nourolide 5) 1D-^{1}H Proton NMR Stacked Spectra

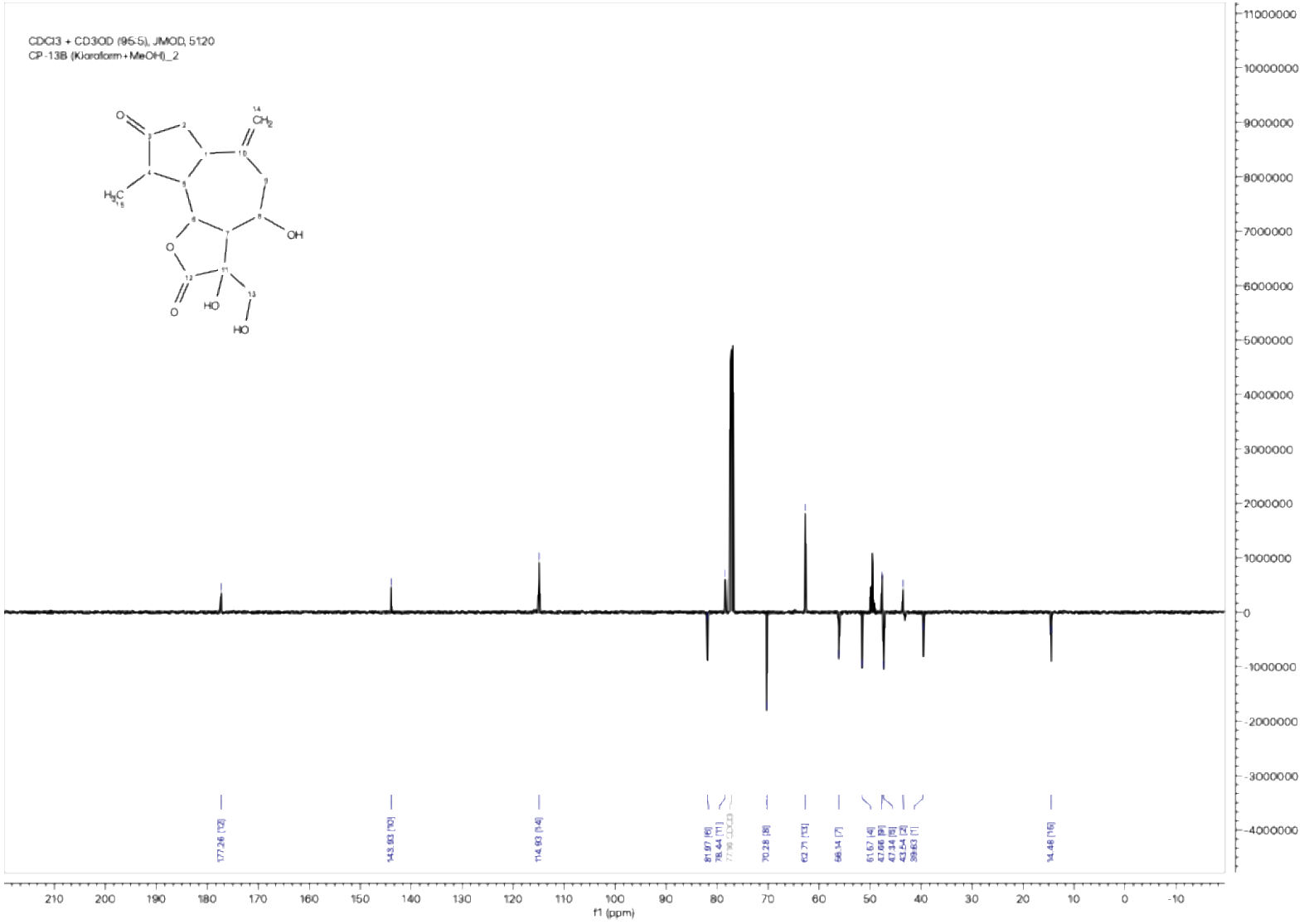


Figure S16: 3 (Nourolide) ^{13}C (APT) 1D-NMR Spectrum

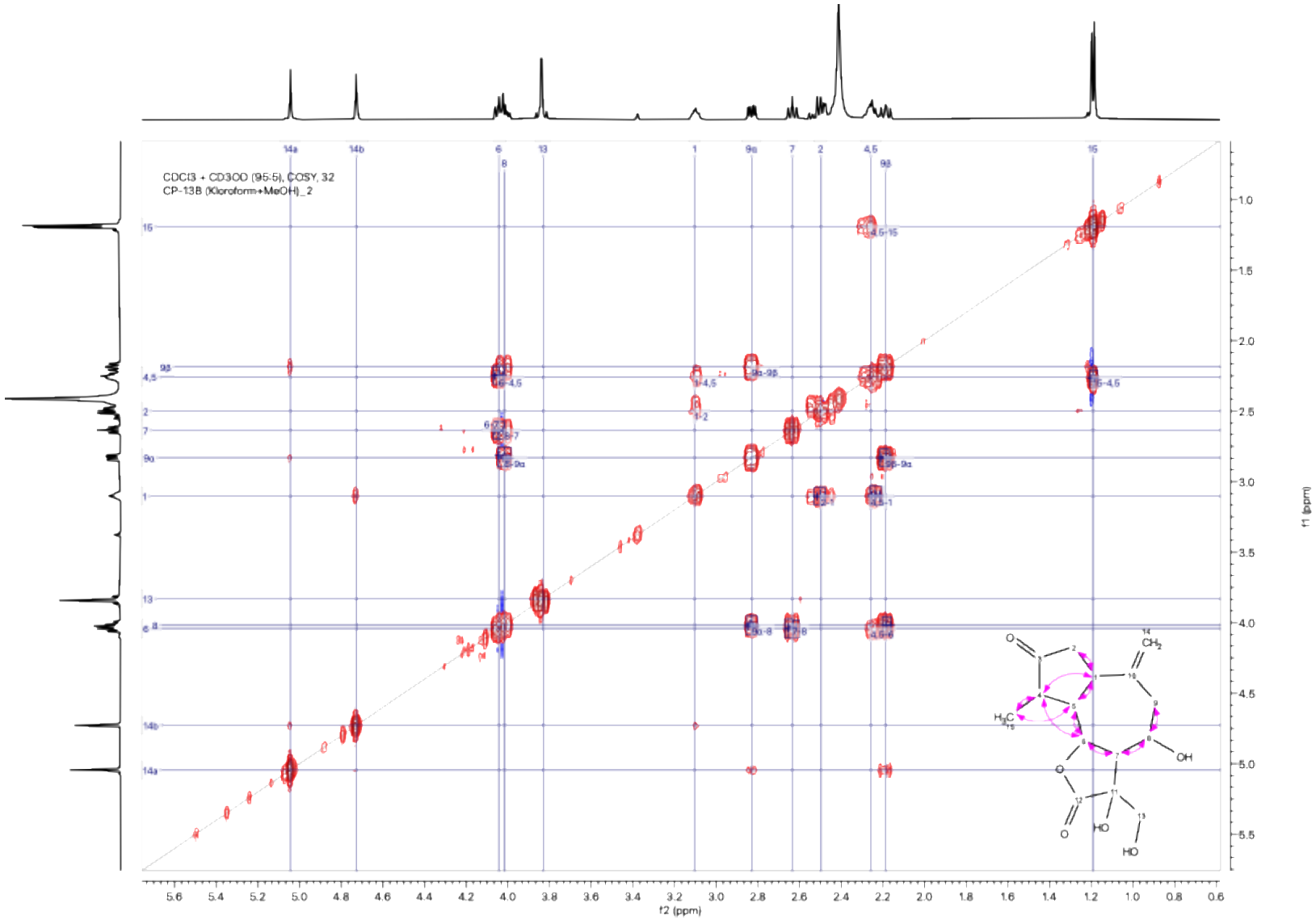
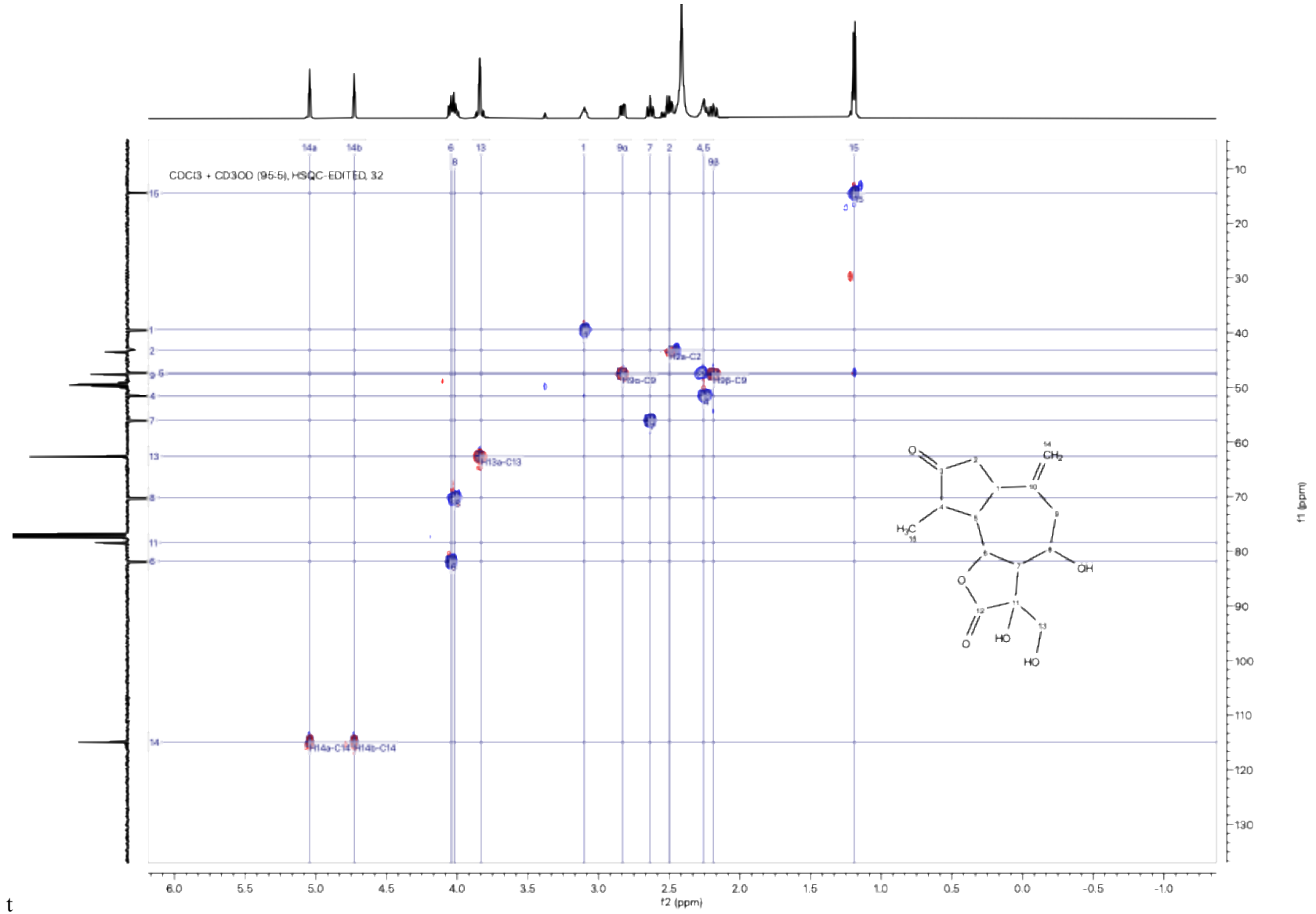


Figure S17: 3 (Nourolide) COSY 2D-NMR Spectrum



t

Figure S18: 3 (Nourolide) HSQC 2D-NMR Spectrum

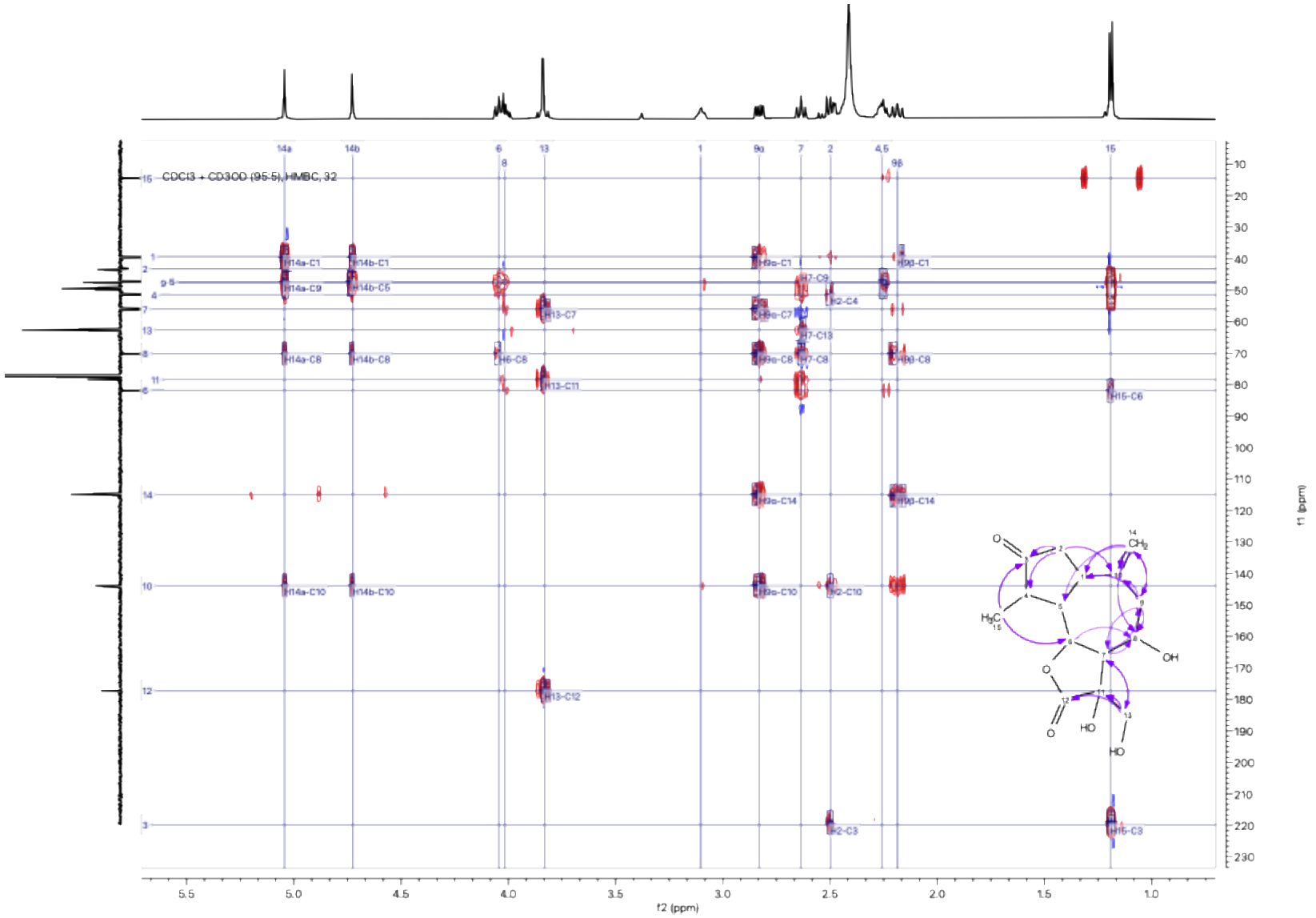


Figure S19: 3 (Nourolide) HMBC 2D-NMR Spectrum

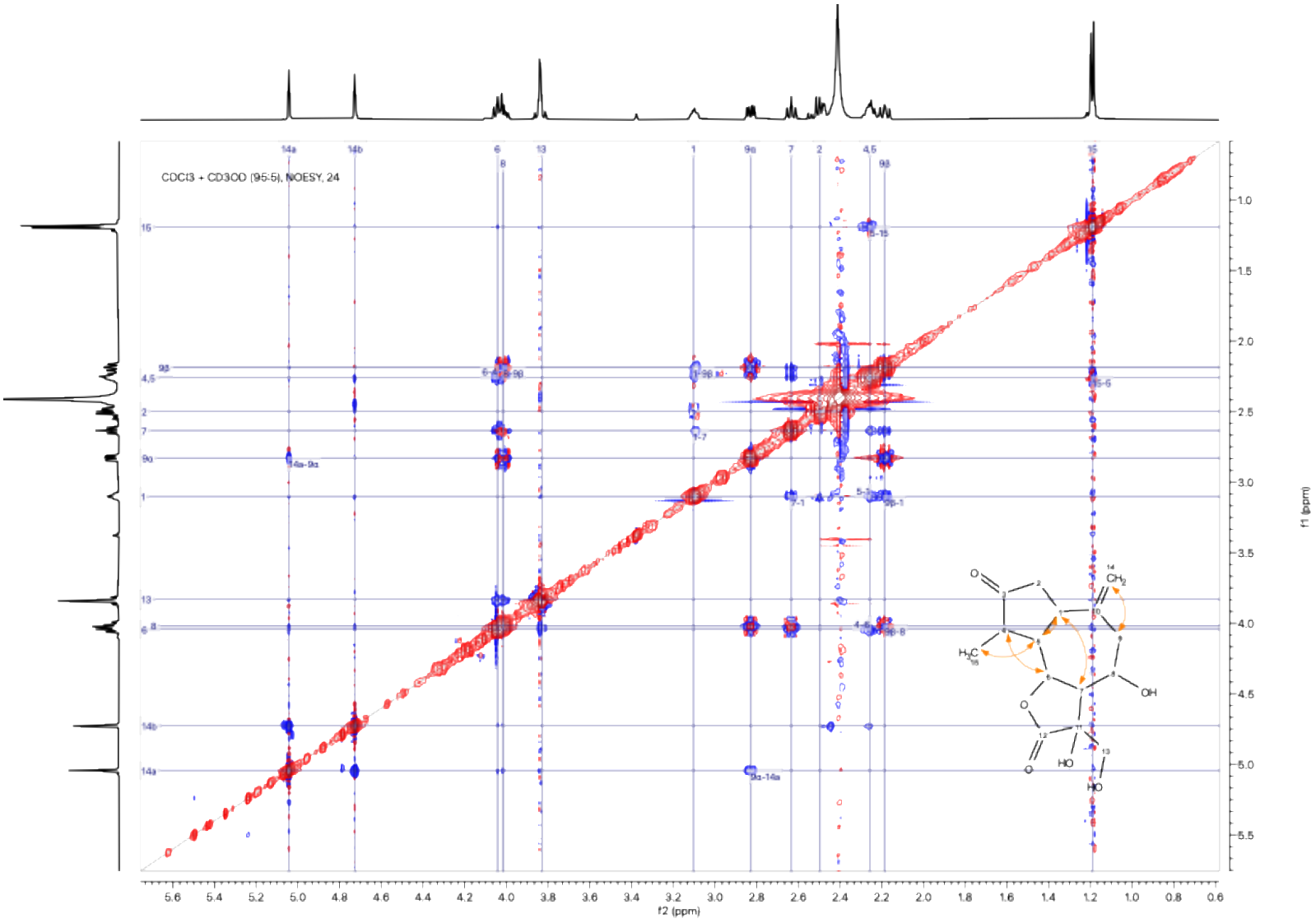


Figure S20: 3 (Nourolide) NOESY 2D-NMR Spectrum

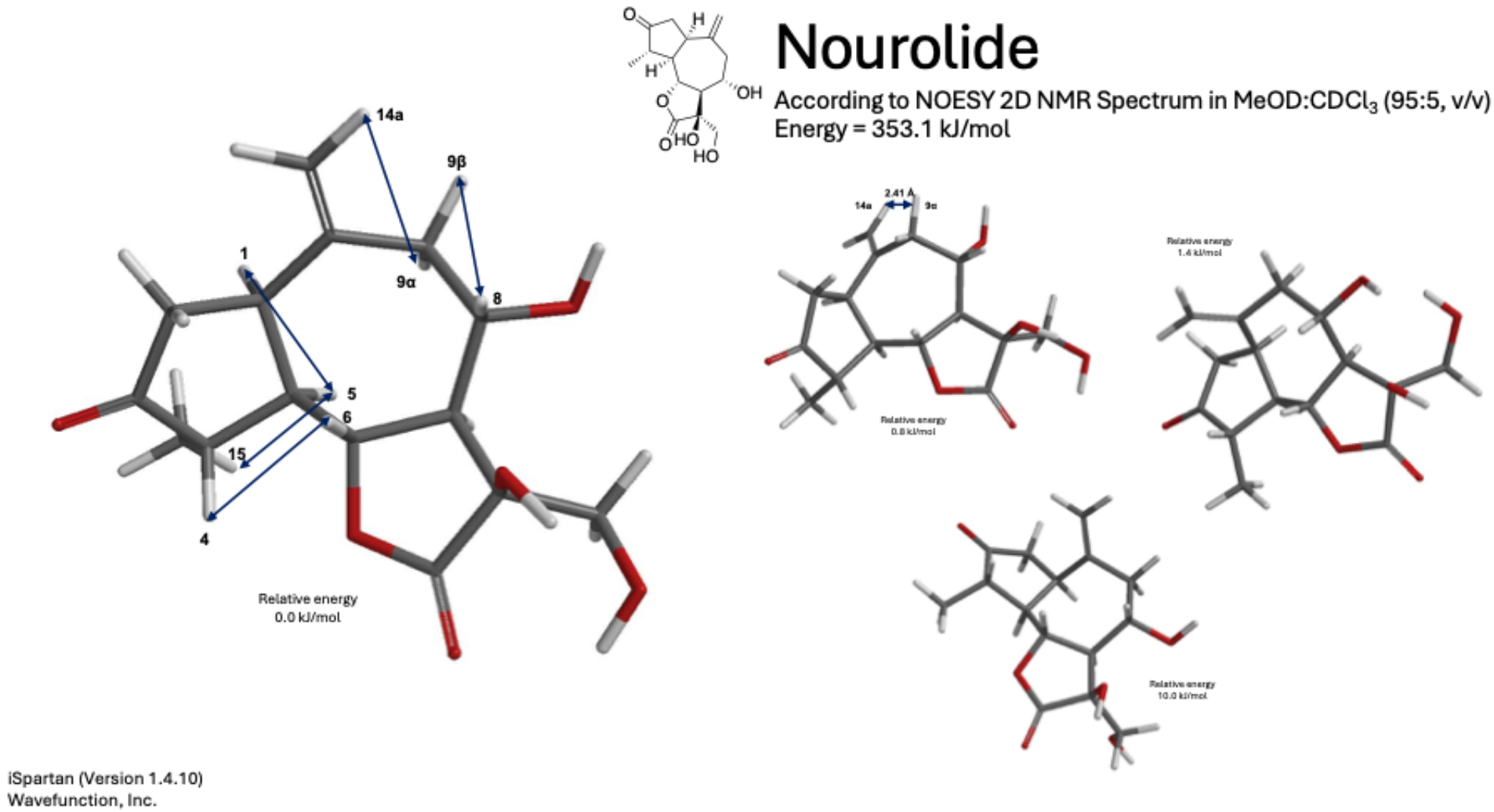


Figure S21: NOESY Correlations of 3 (Nourolide) (according to NOESY 2D-NMR spectrum in $CDCl_3$:MeOD (95:5, v/v))

Table S4: 3 (Nourolide) HMBC, COSY, NOESY correlations *(in CD_3OD)*

No	HMBC	COSY	NOESY
1	-	H4(2.30), H5(2.30), H2β(2.45), H14b(4.75)	H5(2.30)
2α	C6(83.2)	-	-
2β	C10(146.2)	H1(3.21)	H14b(4.75)
4	-	H1(3.21), H6(4.19), H15(1.20)	-
5	-	H1(3.21), H6(4.19), H15(1.20)	H1(3.21), H15(1.20)
6	C4(48.4), C8(70.6)	H4(2.30), H5(2.30), H7(2.61), H8(4.17)	-
7	C6(83.2), C8(70.6), C11(79.6)	H6(4.19), H8(4.17)	-
8	-	H6(4.19), H7(2.61), H9β(2.23), H9α(2.84)	H9β(2.23)
9α	C1(40.9), C7(57.1), C8(70.6), C10(146.2), C11(79.6), C14b(114.4)	H8(4.17), H9β(2.23), H14a(5.06)	H14a(5.06)
9β	C1(40.9), C8(70.6), C10(146.2), C14b(114.4)	H8(4.17), H9α(2.84), H14a(5.06)	H1(3.21), H8(4.17)
10	H2β(2.45), H9β(2.23), H9α(2.84), H14b(4.75), H14a(5.06)	-	-
11	H7(2.61), H9α(2.84), H13b(4.13), H13a(3.76)	-	-
12	H13b(4.13), H13a(3.76)	-	-
13a	C7(57.1), C12(180.2), C11(79.6)	-	-
13b	C7(57.1), C12(180.2), C11(79.6)	-	-
14a	C1(40.9), C8(70.6), C9β(49.2), C10(146.2)	H9β(2.23), H9α(2.84)	H9α(2.84), H14b(4.75)
14b	C1(40.9), C8(70.6), C9β(49.2), C10(146.2)	H1(3.21)	H2β(2.45), H14a(5.06)
15	C4(48.4), C5(52.9), C6(83.2)	H4(2.30), H5(2.30)	H5(2.30)

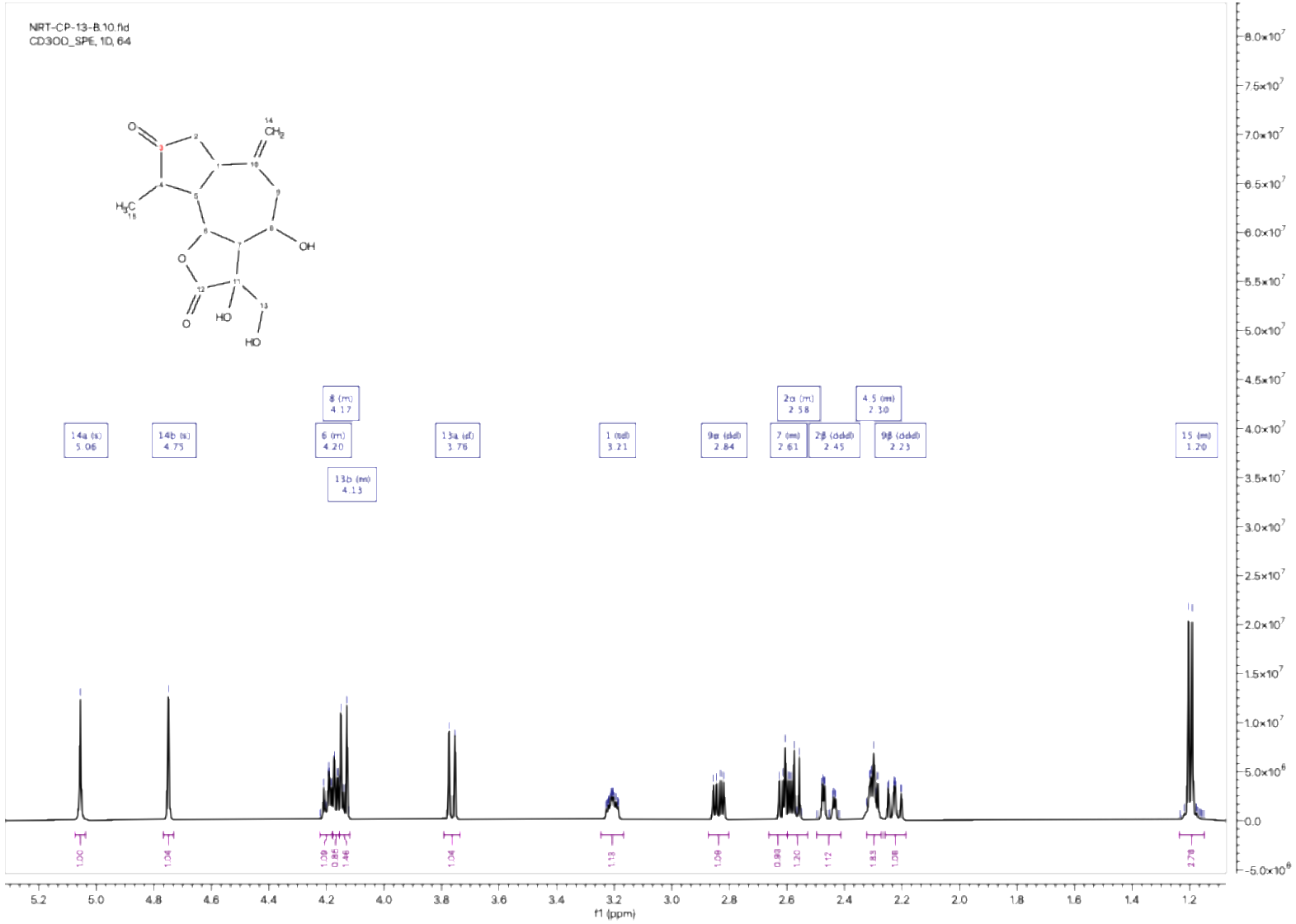


Figure S22: 3 (Nourolide) 1D-^{1}H Proton NMR Spectrum

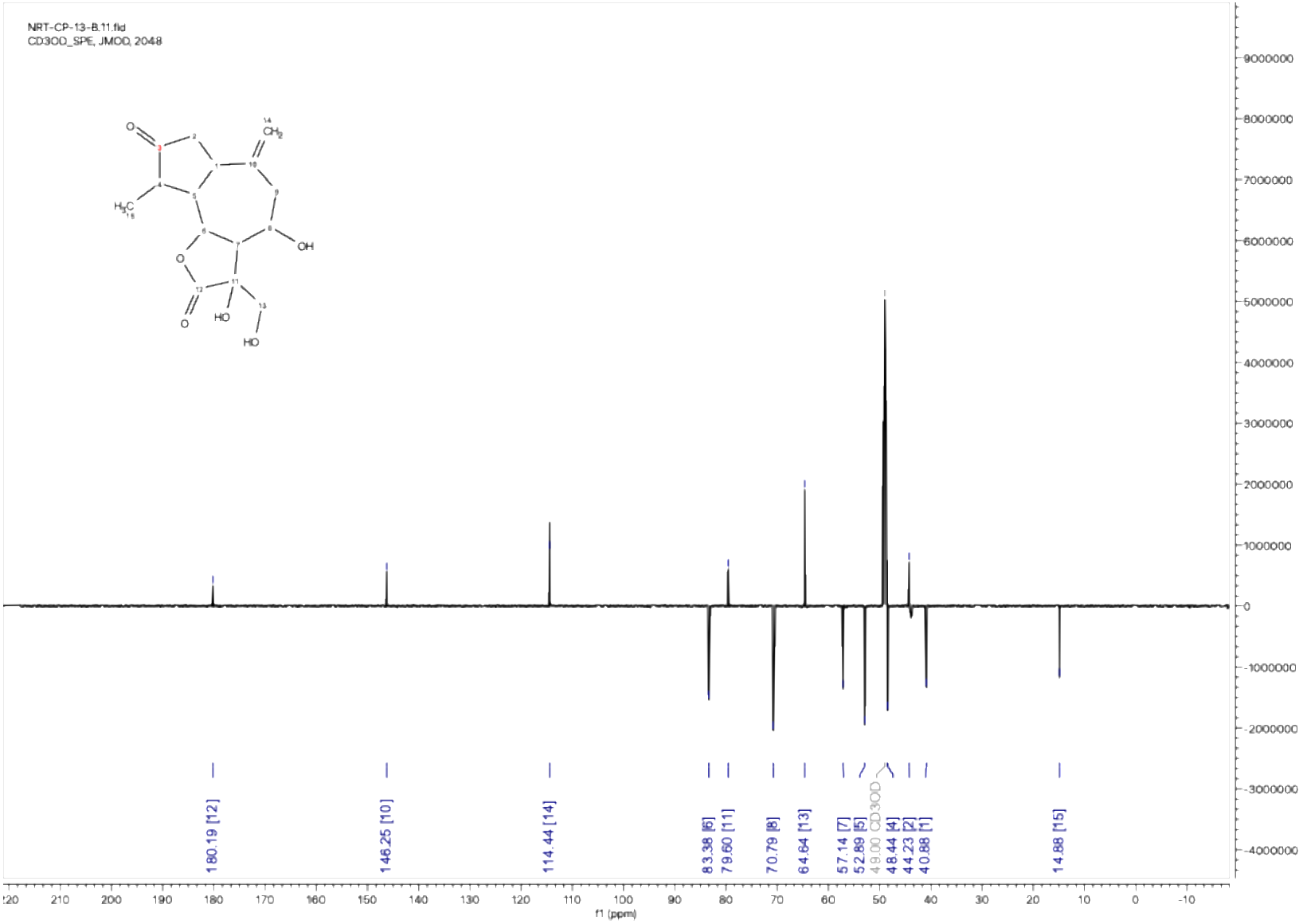


Figure S23: 3 (Nourolide) ^{13}C (APT) 1D-NMR Spectrum

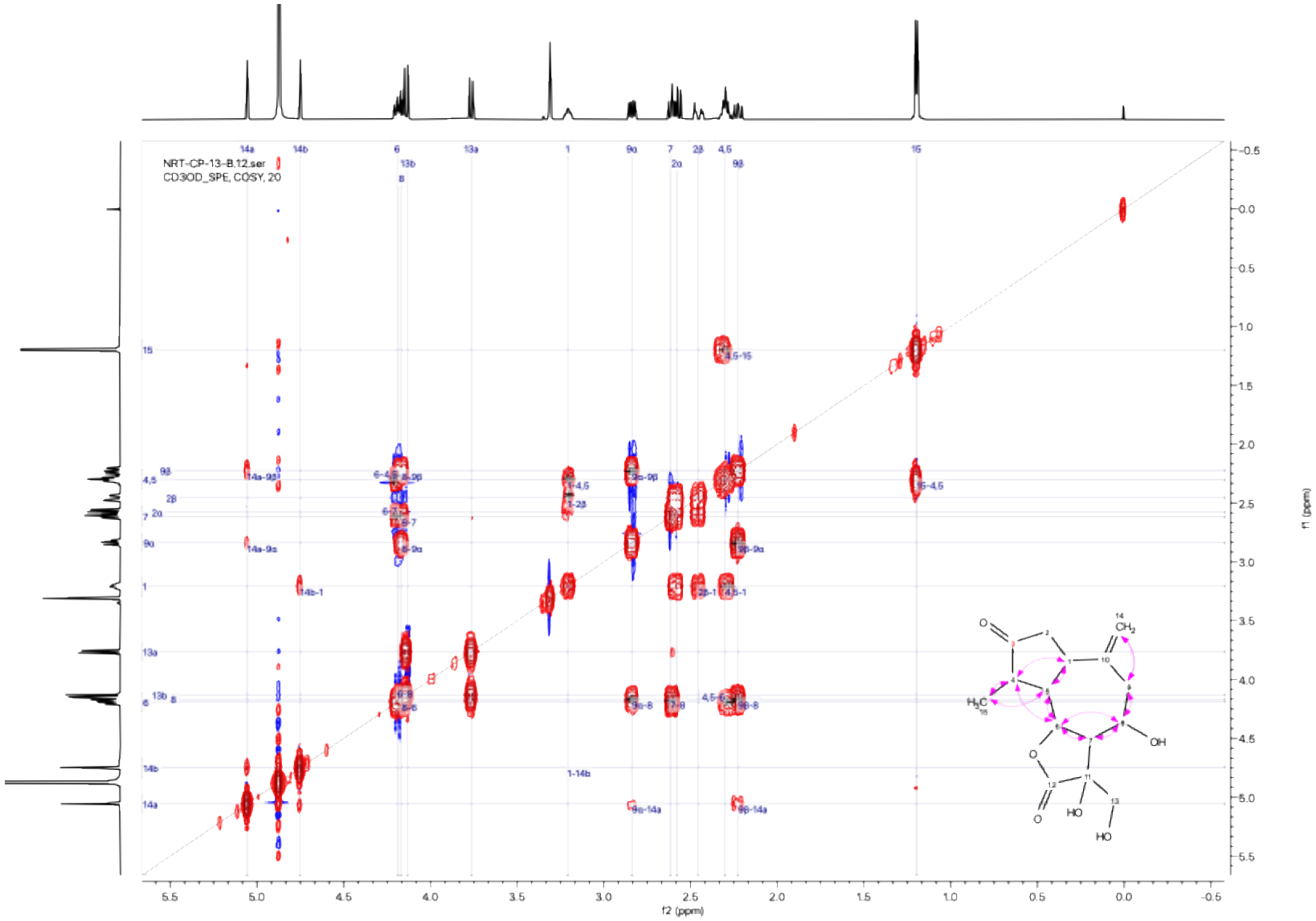


Figure S24: 3 (Nourolide) COSY 2D-NMR Spectrum

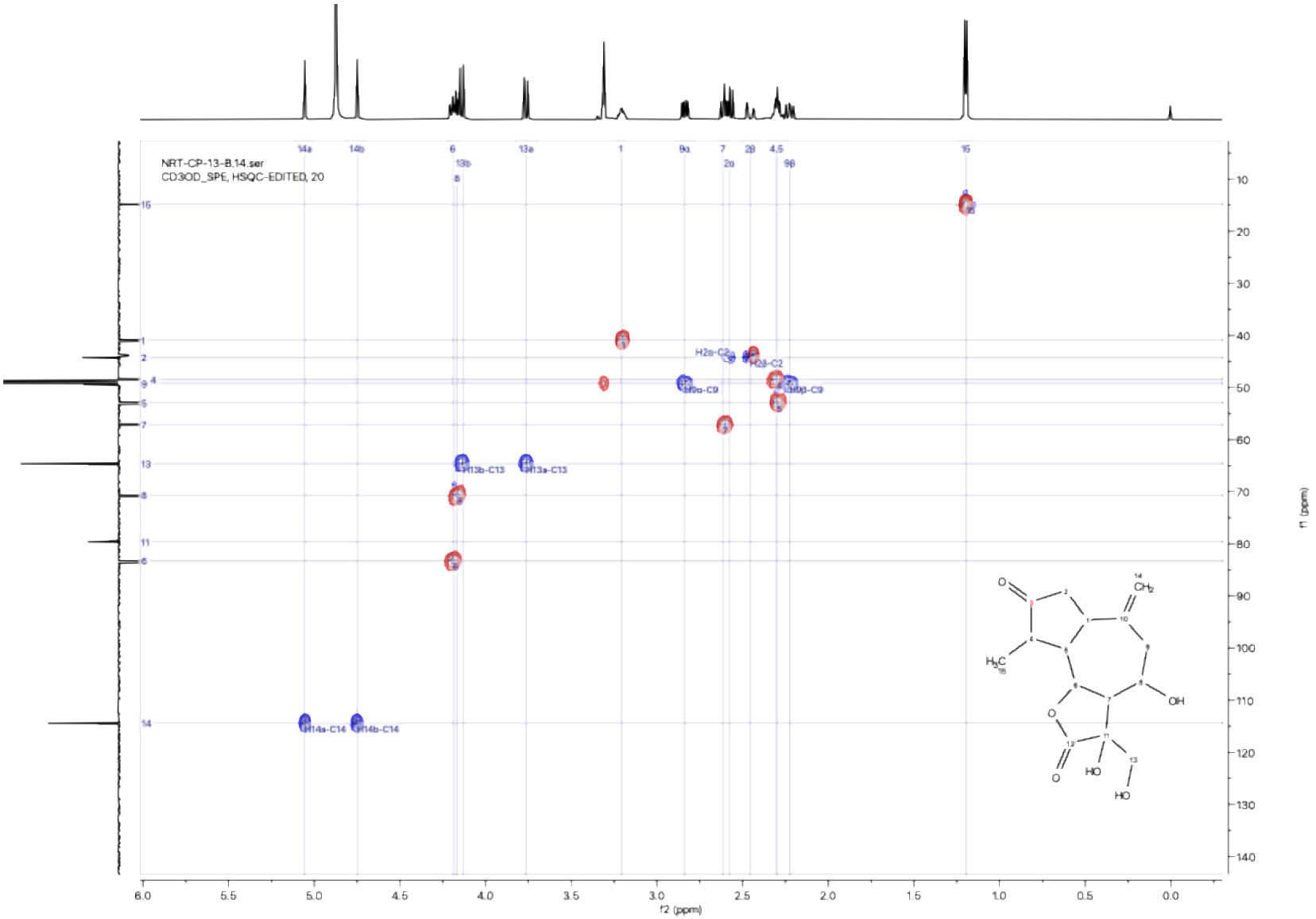


Figure S25: 3 (Nourolide) HSQC 2D-NMR Spectrum

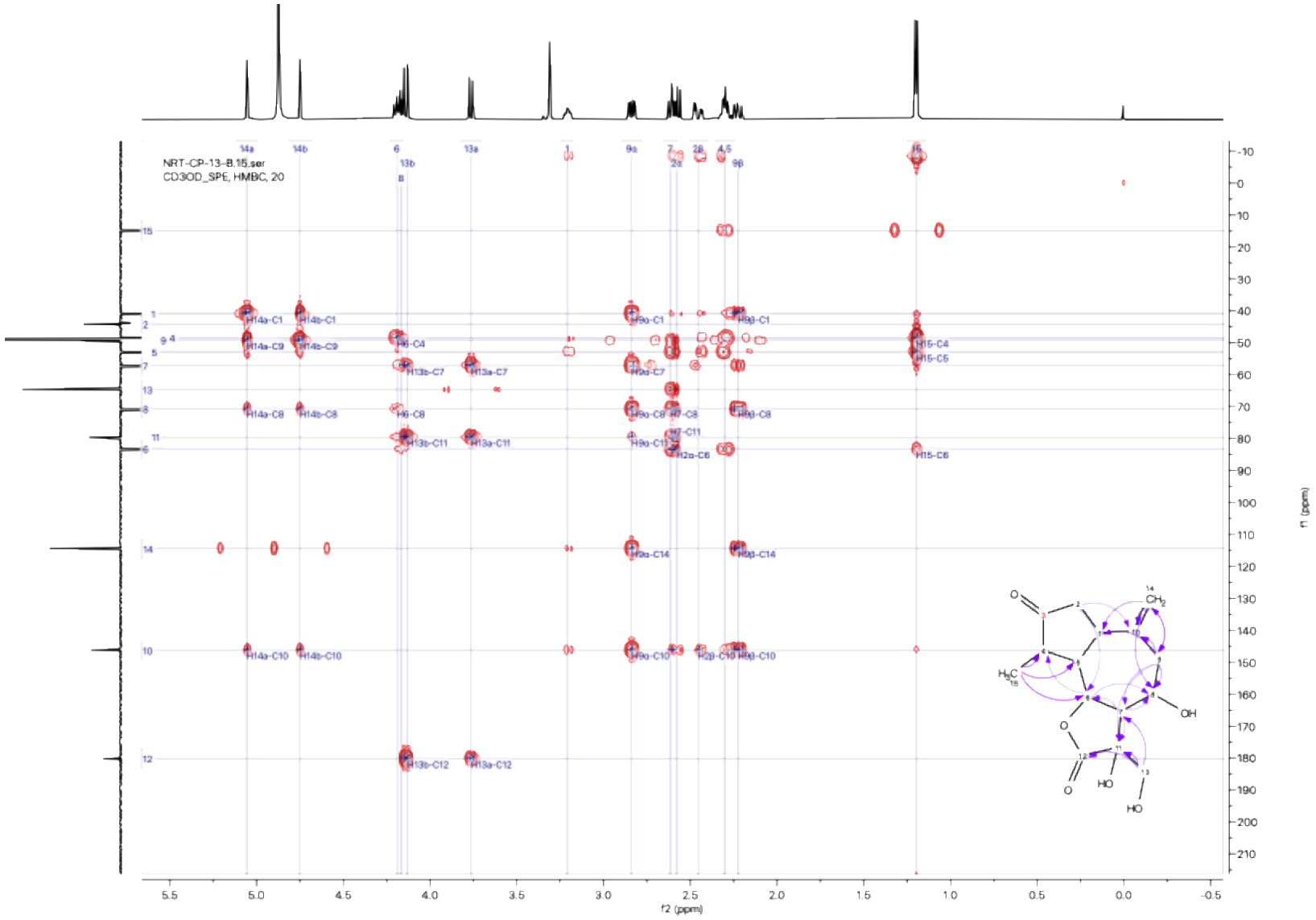


Figure S26: 3 (Nourolide) HMBC 2D-NMR Spectrum

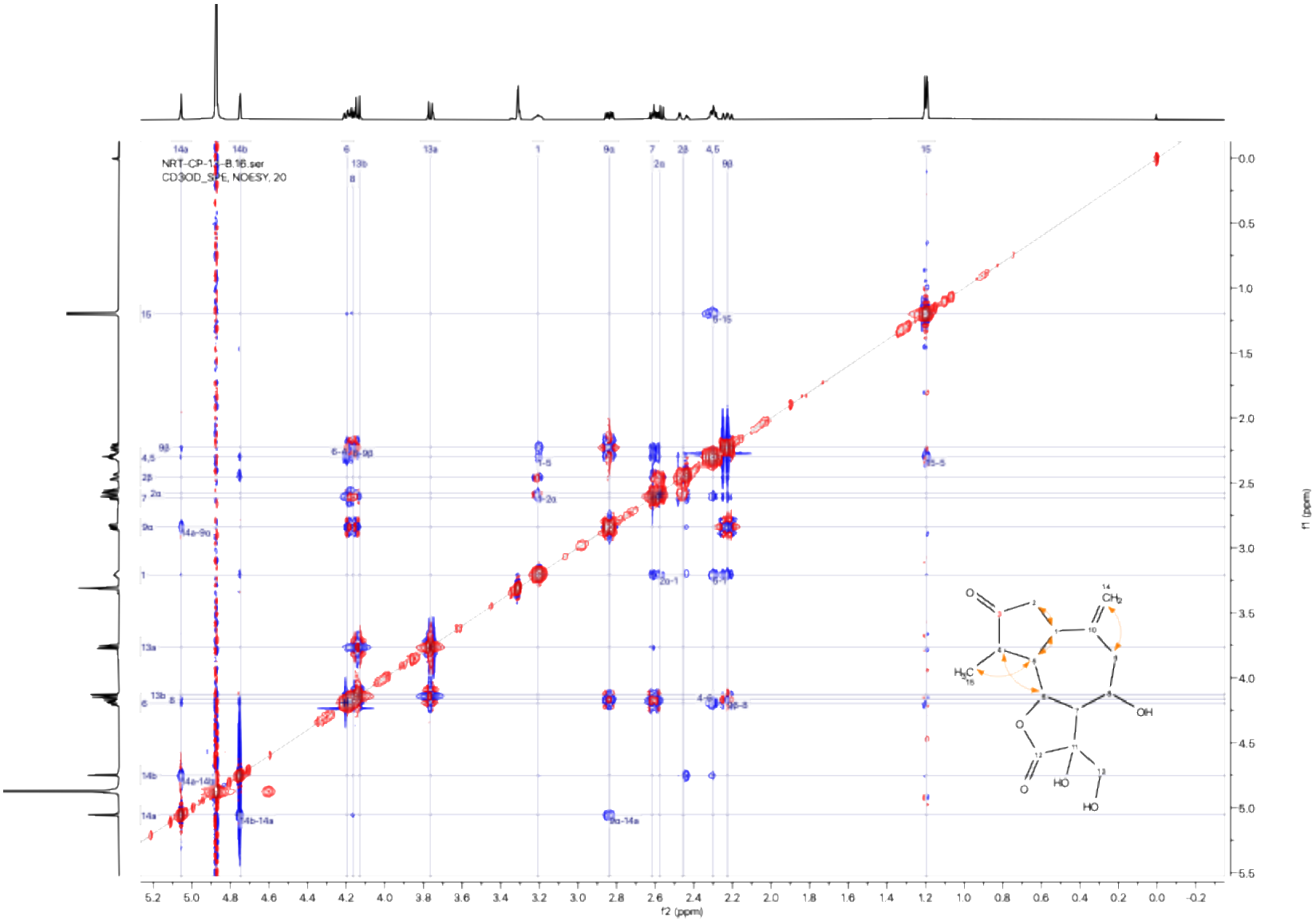


Figure S27: 3 (Nourolide) NOESY 2D-NMR Spectrum

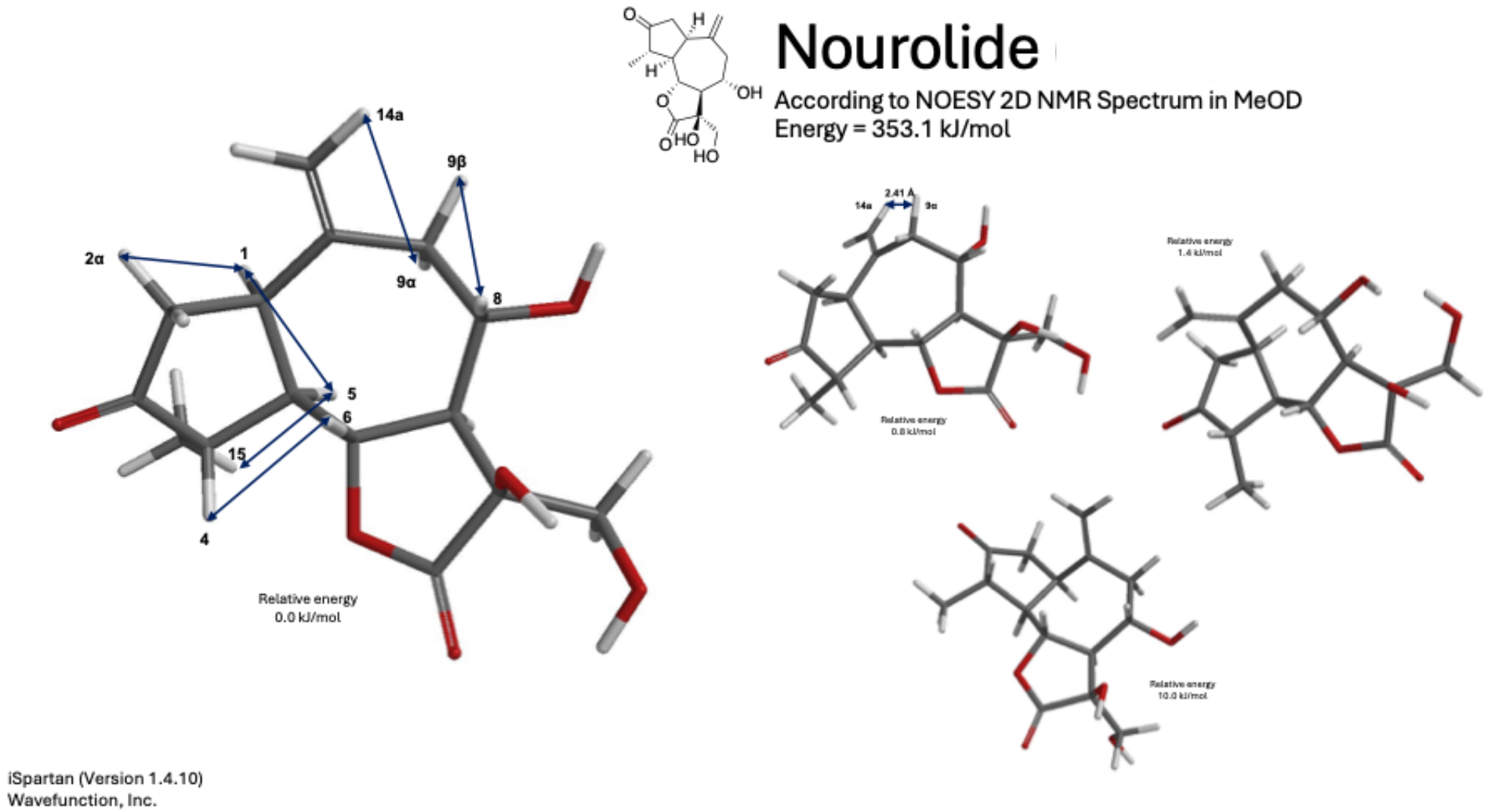


Figure S28: NOESY Correlations of 3 (Nourolide) (according to NOESY 2D-NMR spectrum in MeOD)

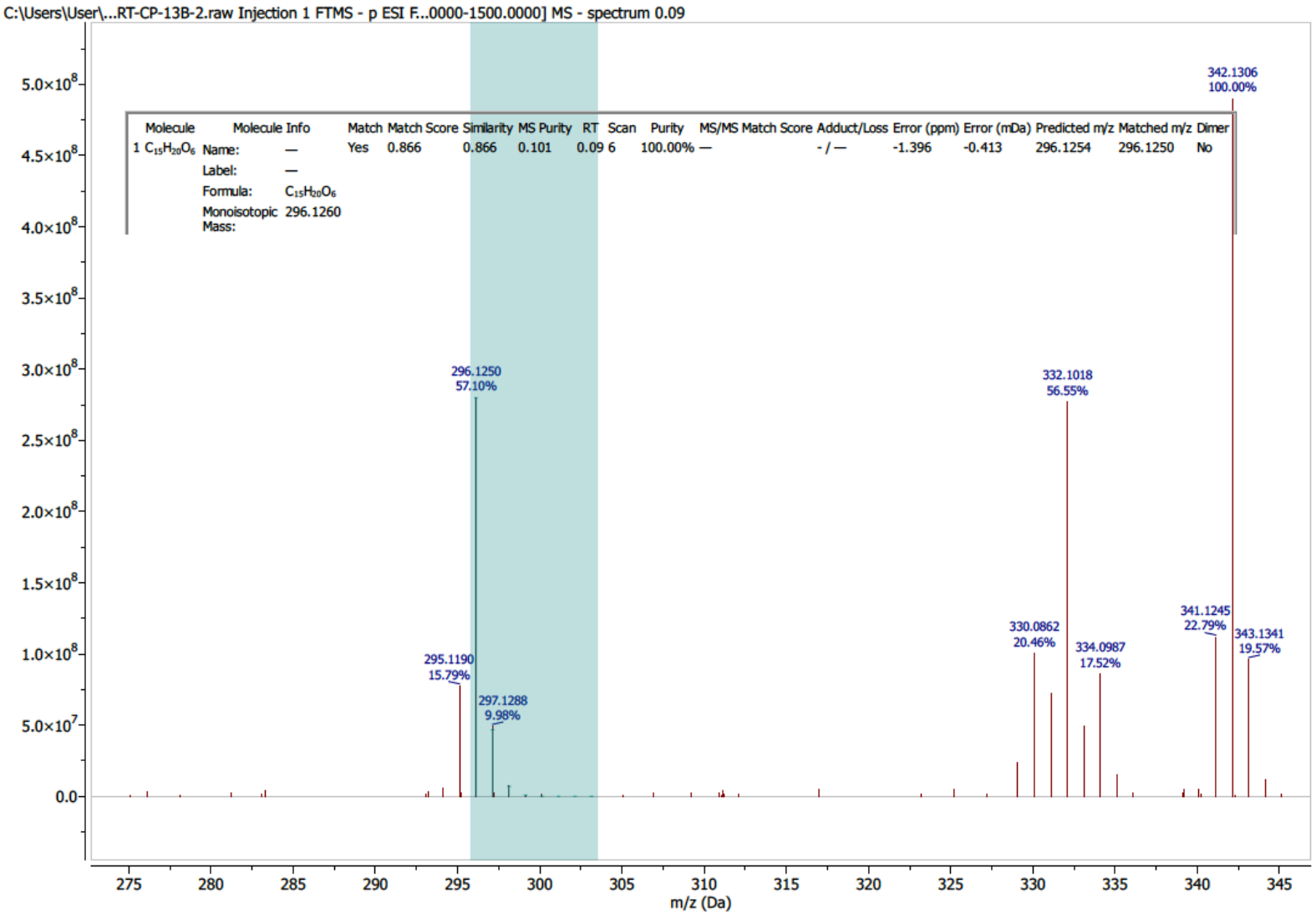


Figure S29: MS (-) Spectrum of 3 (Nourolide)

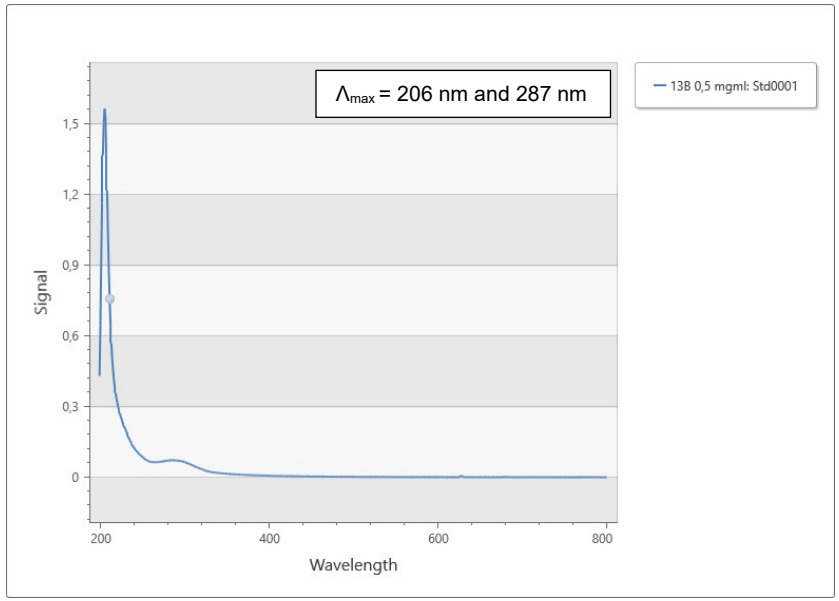


Figure S30: UV Absorbance Spectrum of 3 (Nourolide)

Figure S31: Polarimeter measurement at 19.8 ºC (0.5 mg/ml concentration)

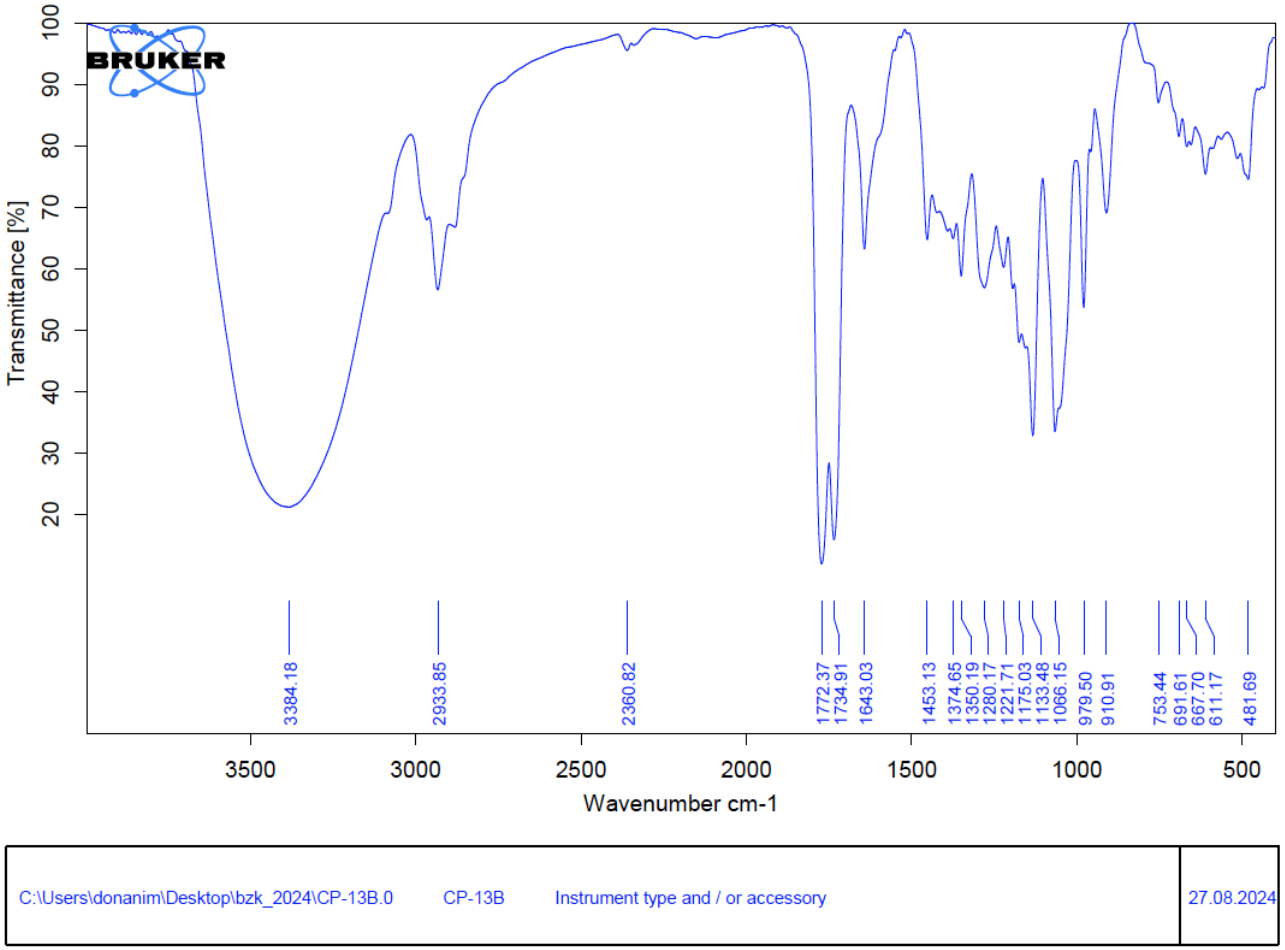
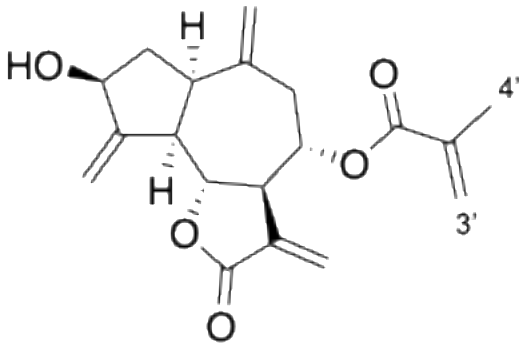


Figure S32: IR Spectrum of 3 (Nourolide)

4. 4 (Aguerin B)



^{1}H NMR (500 MHz, $CDCl_3$); δ 6.21 (1H, d, J = 3.4 Hz, 3'b, 13b), 6.18 (1H, s, 3'b), 5.67 (1H, m, 3'a), 5.61 (1H, d, J = 3.1 Hz, 13a), 5.50 (1H, t, J = 1.9 Hz, 15b), 5.36 (1H, t, J = 1.8 Hz, 15a), 5.14 (1H, d, J = 1.6 Hz, 14a), 5.09 (1H, ddd, J = 9.5, 5.1, 3.9 Hz, H-8), 4.94 (1H, d, J = 1.6 Hz, 14b), 4.56 (1H, td, J = 7.1, 2.0 Hz, H-3), 4.24 (1H, dd, J = 10.6, 9.0 Hz, H-6), 3.19 (1H, tt, J = 9.3, 3.3 Hz, H-7), 2.98 (1H, dt, J = 10.8, 8.0 Hz, H-1), 2.86 (1H, m, H-5), 2.70 (1H, dd, J = 14.5, 5.2 Hz, 9β), 2.38 (1H, dd, J = 14.5, 3.9 Hz, 9α), 2.23 (1H, dt, J = 13.2, 7.4 Hz, 2β), 1.99 (3H, s, 4'), 1.73 (1H, ddd, J = 13.2, 11.0, 7.6 Hz, 2α)

^{13}C NMR (126 MHz, $CDCl_3$); δ 169.28 (12), 166.50 (1'), 152.44 (4), 141.96 (10), 137.54 (11), 136.13 (2'), 126.72 (3'), 122.75, 118.21, 113.62 (15), 78.71 (6), 74.23 (8), 73.92 (3), 51.46 (5), 47.82 (7), 45.43 (1), 39.24 (2), 37.28 (9), 18.39 (4').

Table S5: 4 (Aguerin B) HMBC, COSY, NOESY correlations

No	HMBC	COSY	NOESY
1	51.5(5), 78.7(6), 118.2(14b), 142.0(10)	1.73(2α),2.23(2β)	1.73(2α), 2.86(5), 4.56(3)
2α	45.4(1), 51.5(5), 73.9(3), 142.0(10)	2.23(2β), 2.98(1), 4.56(3)	2.23(2β), 2.98(1), 4.56(3)
2β	51.5(5), 152.4(4)	1.73(2α), 2.98(1), 4.56(3)	1.73(2α)
3	113.6(15b),152.4(4)	1.73(2α),2.23(2β)	1.73(2α), 2.98(1)
4	2.23(2β), 2.86(5), 4.56(3), 5.36(15a), 5.49(15b)	-	-
5	39.2(2β), 45.4(1), 78.7(6), 113.6(15b), 152.4(4)	4.24(6)	2.98(1), 3.19(7), 5.49(15b)
6	-	2.86(5), 3.19(7)	2.70(9β), 5.09(8)
7	51.5(5), 74.2(8), 78.7(6), 137.5(11)	4.24(6),5.09(8), 5.61(13a), 6.21(13b)	2.86(5), 5.61(13a)
8	-	2.38(9α),2.70(9β), 3.19(7)	4.24(6)
9α	118.2(14b),142.0(10)	5.09(8)	2.70(9β)
9β	45.4(1), 118.2(14b), 142.0(10)	5.09(8)	2.38(9α), 4.24(6)
10	1.73(2α), 2.38(9α), 2.70(9β), 2.98(1), 5.14(14a)	-	-
11	3.19(7)	-	-
12	5.61(13a),6.21(13b)	-	-
13a	47.8(7), 169.3(12)	3.19(7)	3.19(7), 6.18(3'b), 6.21(13b)
13b	47.8(7), 169.3(12)	3.19(7)	5.61(13a)
14a	37.3(9β),45.4(1), 142.0(10)	-	-
14b	37.3(9β),45.4(1)	-	-
15a	51.5(5), 73.9(3), 152.4(4)	-	-
15b	51.5(5), 73.9(3), 152.4(4)	-	2.86(5)
1'	1.99(4'), 5.67(3'a),6.18(3'b)	-	-
2'	1.99(4'),6.18(3'b)	-	-
3'a	18.4(4'),166.5(1')	1.99(4')	1.99(4')
3'b	18.4(4'), 136.1(2'),166.5(1')	1.99(4')	5.61(13a)
4'	126.7(3'b), 136.1(2'),166.5(1')	5.67(3'a),6.18(3'b)	5.67(3'a)

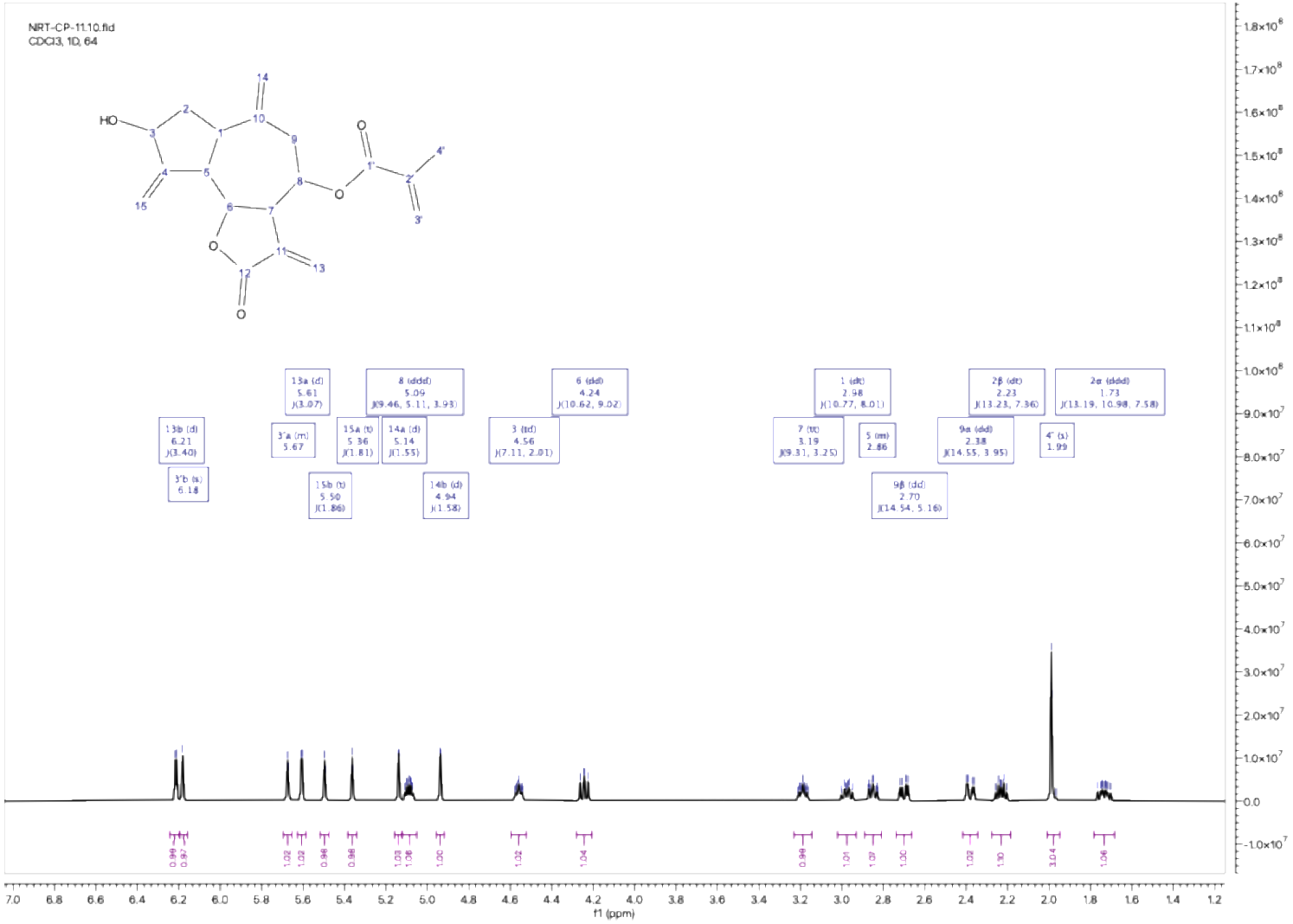


Figure S33: 4 (Aguerin B) 1D-^{1}H Proton NMR Spectrum

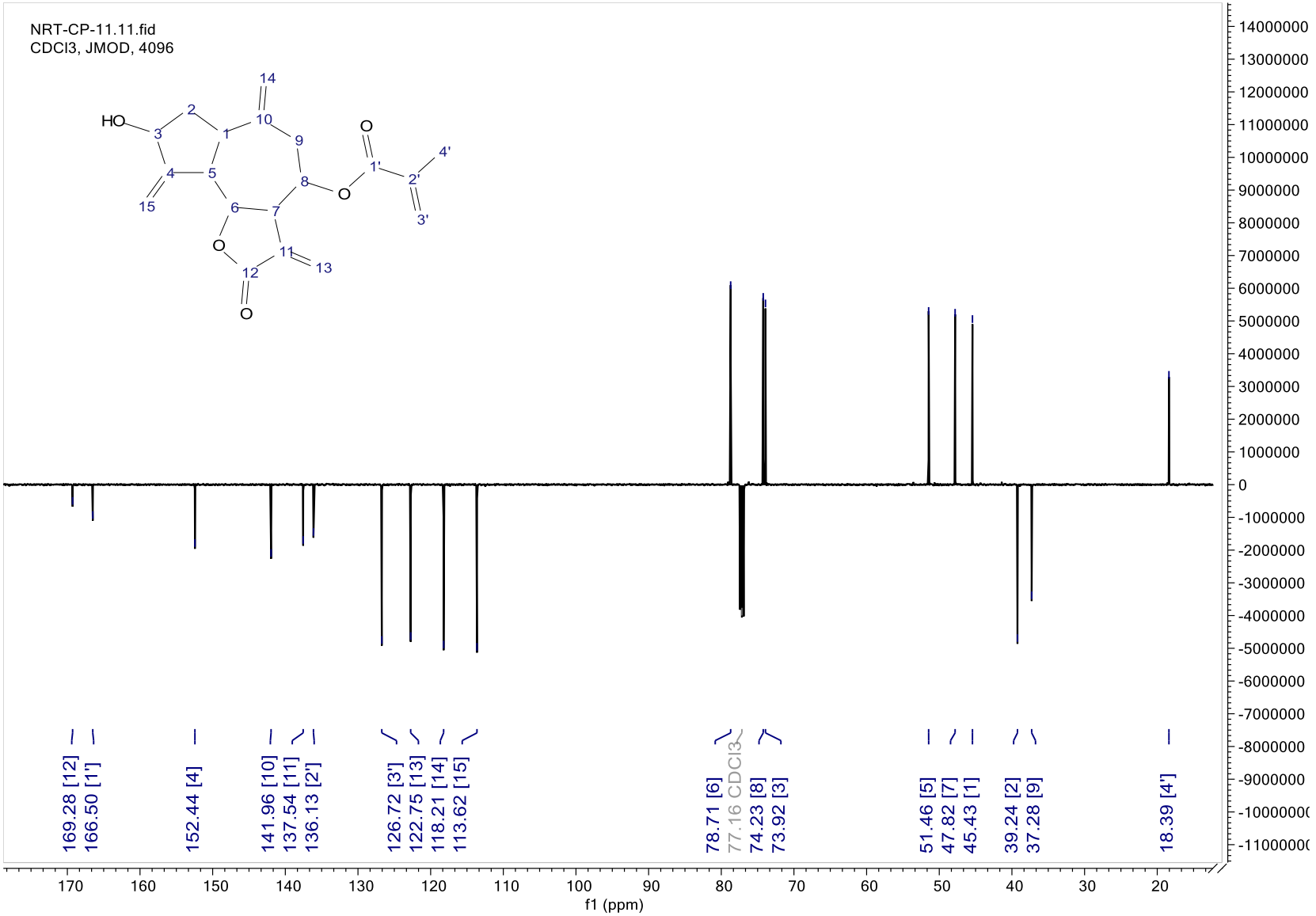


Figure S34: 4 (Aguerin B) ^{13}C (APT) 1D-NMR Spectrum

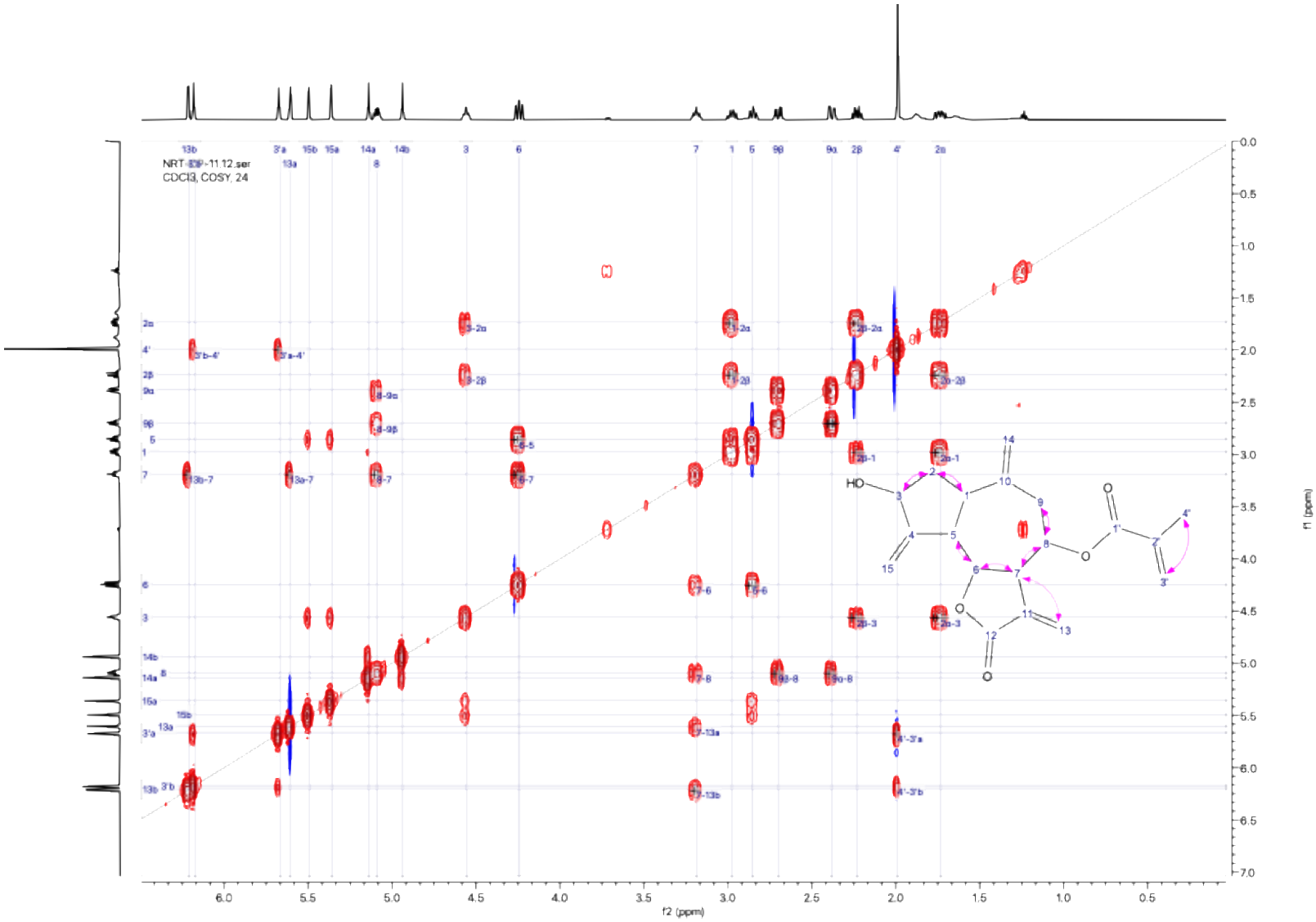


Figure S35: 4 (Aguerin B) COSY 2D-NMR Spectrum

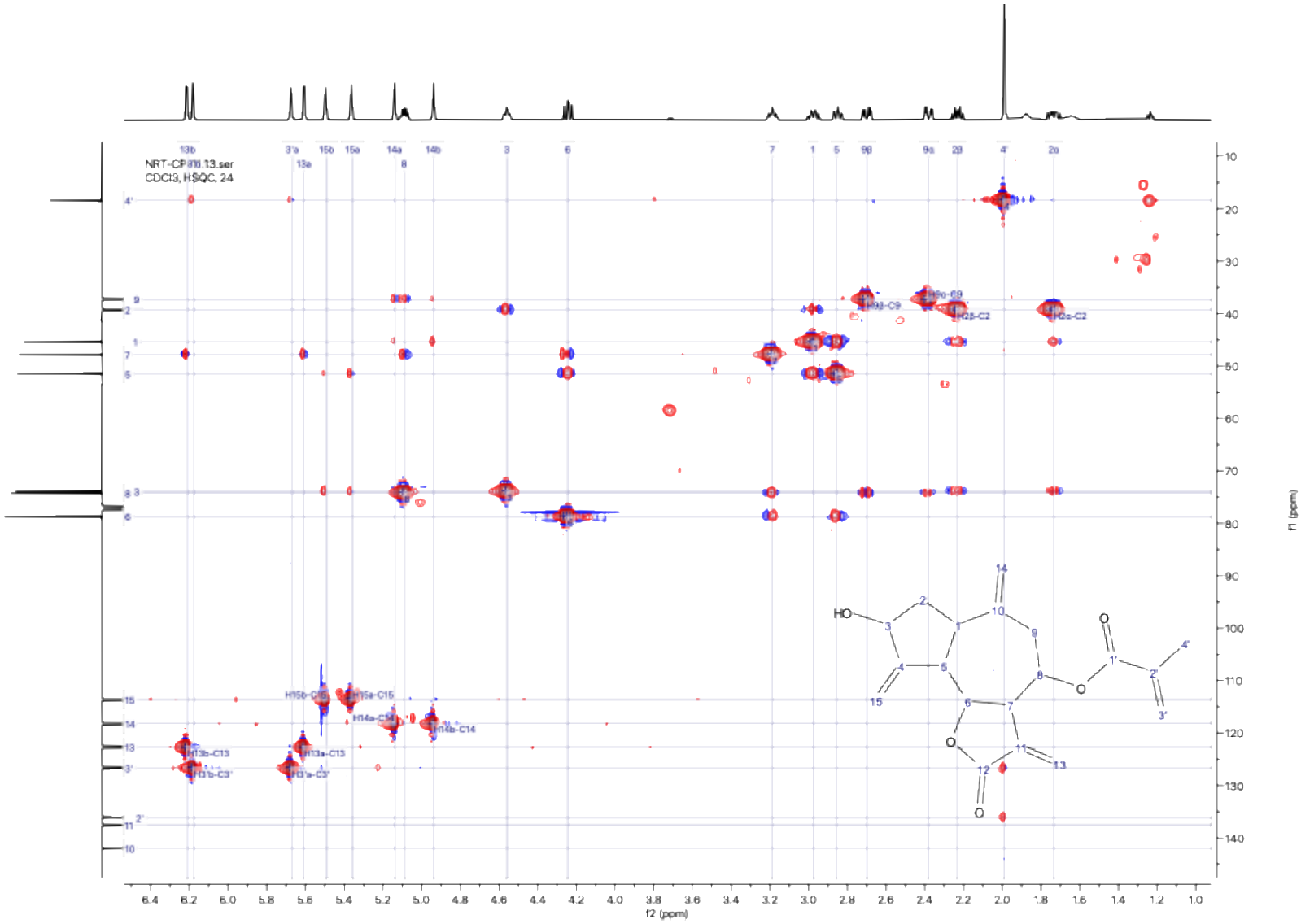


Figure S36: 4 (Aguerin B) HSQC 2D-NMR Spectrum

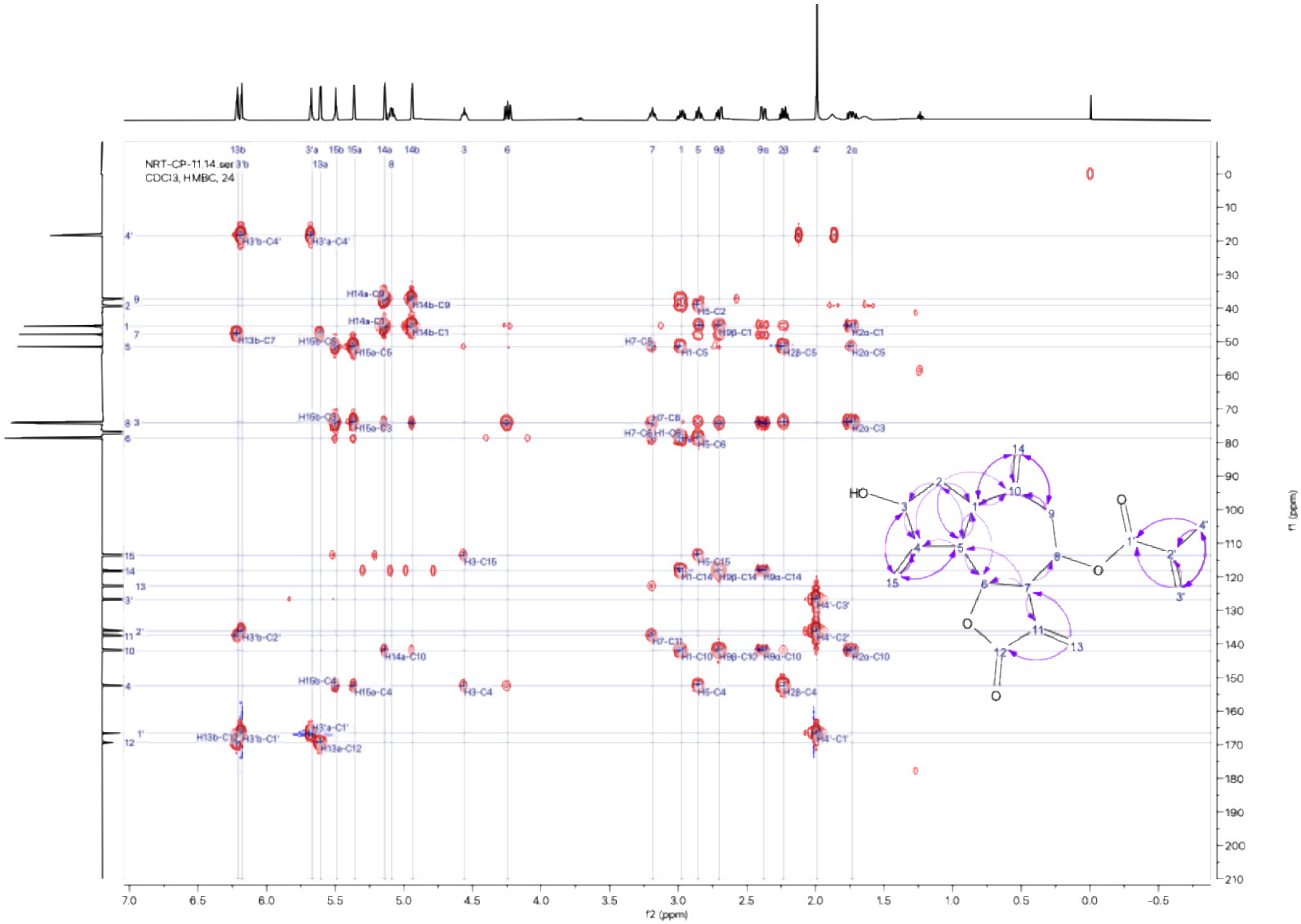


Figure S37: 4 (Aguerin B) HMBC 2D-NMR Spectrum

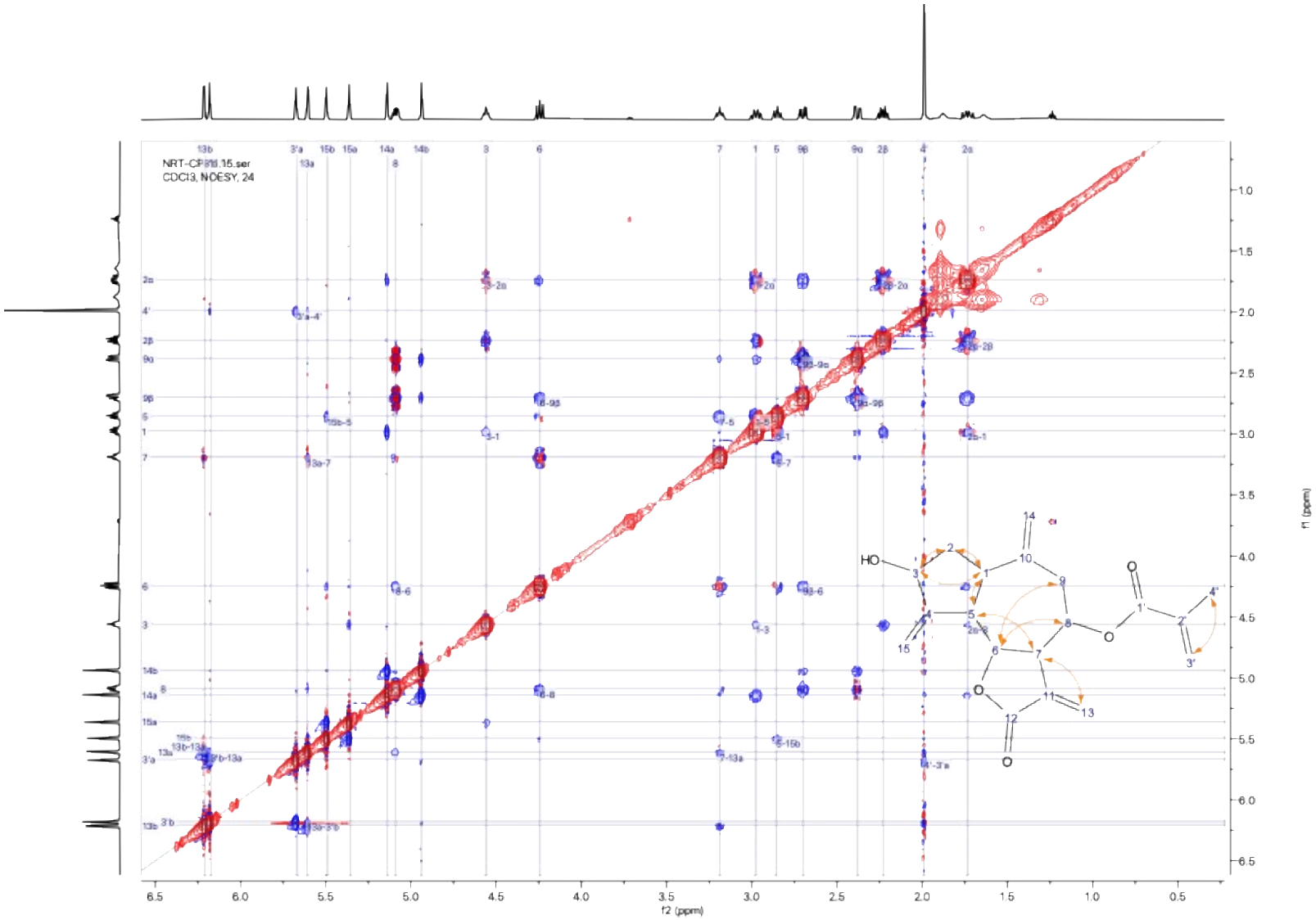
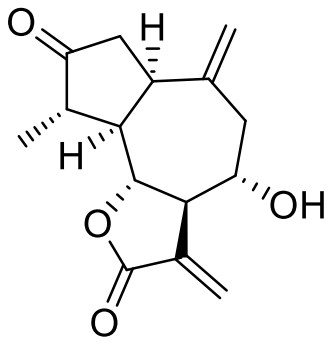


Figure S38: 4 (Aguerin B) NOESY 2D-NMR Spectrum

5. 5 (Grosheimin)



^{1}H NMR (500 MHz, $CDCl_3$); δ 6.36 (d, *J* = 3.3 Hz, 1H, 13b), 6.31 (d, *J* = 2.9 Hz, 1H, 13a), 5.08 (s, 1H, 14b), 4.83 (s, 1H, 14a), 3.98 (t, *J* = 9.1 Hz, 1H, 6), 3.90 (tt, *J* = 9.5, 5.5 Hz, 1H, 8), 3.17 (td, *J* = 8.1, 4.4 Hz, 1H, 1), 3.07 (tt, *J* = 9.2, 3.2 Hz, 1H, 7), 2.85 (dd, *J* = 12.9, 5.8 Hz, 1H, 9β), 2.55 (dd, *J* = 19.3, 8.6 Hz, 1H, 2α), 2.48 (dd, *J* = 19.4, 4.4 Hz, 1H, 2β), 2.39 – 2.24 (m, 3H, 4, 5, 9α), 2.03 (d, *J* = 5.5 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 3H, 15).

^{13}C NMR (126 MHz, $CDCl_3$); δ 219.00 (3), 169.93 (12), 143.31 (10), 136.58 (11), 125.83 (13), 115.85 (14), 82.34 (6), 77.41, 77.16, 76.91, 73.34 (8), 51.34, 49.40 (7), 48.03 (9), 47.12 (5), 43.32 (2), 40.35 (1), 15.08 (15).

Table S6: 5 (Grosheimin) HMBC, COSY, NOESY corelations

No	HMBC	COSY	NOESY
1	51.2(4), 115.8(14b), 143.3(10),219.0(3)	2.30(4), 2.30(5), 2.31(9α), 2.53(2α), 4.83(14a)	2.30(5), 4.83(14a)
2α	40.3(1), 51.2(4), 143.3(10),219.0(3)	3.17(1)	-
2β	51.2(4)	-	4.83(14a)
3	1.26(15), 2.53(2α),3.17(1)	-	-
4	15.1(15),40.3(1), 82.3(6)	1.26(15),3.17(1), 3.96(6)	-
5	15.1(15), 40.3(1),51.2(4), 73.3(8), 82.3(6), 115.8(14b)	1.26(15),3.17(1), 3.96(6)	1.26(15),3.17(1)
6	47.1(5), 73.3(8)	2.30(4), 2.30(5), 3.07(7)	3.90(8)
7	-	3.90(8),3.96(6), 6.31(13a), 6.36(13b)	2.31(9α), 6.31(13a)
8	-	2.31(9α), 2.85(9β),3.07(7)	2.85(9β),3.96(6)
9α	40.3(1), 73.3(8), 82.3(6), 115.8(14b)	2.85(9β),3.17(1), 3.90(8), 5.08(14b)	3.07(7)
9β	40.3(1), 49.4(7), 73.3(8), 115.8(14b), 143.3(10)	2.31(9α),3.90(8)	3.90(8), 5.08(14b)
10	2.53(2α), 2.85(9β),3.17(1), 4.83(14a), 5.08(14b)	-	-
12	6.31(13a),6.36(13b)	-	-
13a	49.4(7), 169.9(12)	3.07(7)	3.07(7)
13b	49.4(7), 169.9(12)	3.07(7)	-
14a	40.3(1), 48.0(9β), 143.3(10)	3.17(1)	2.48(2β),3.17(1), 5.08(14b)
14b	40.3(1), 48.0(9β), 143.3(10)	2.31(9α)	2.85(9β), 4.83(14a)
15	47.1(5), 51.2(4),219.0(3)	2.30(4), 2.30(5)	2.30(5)

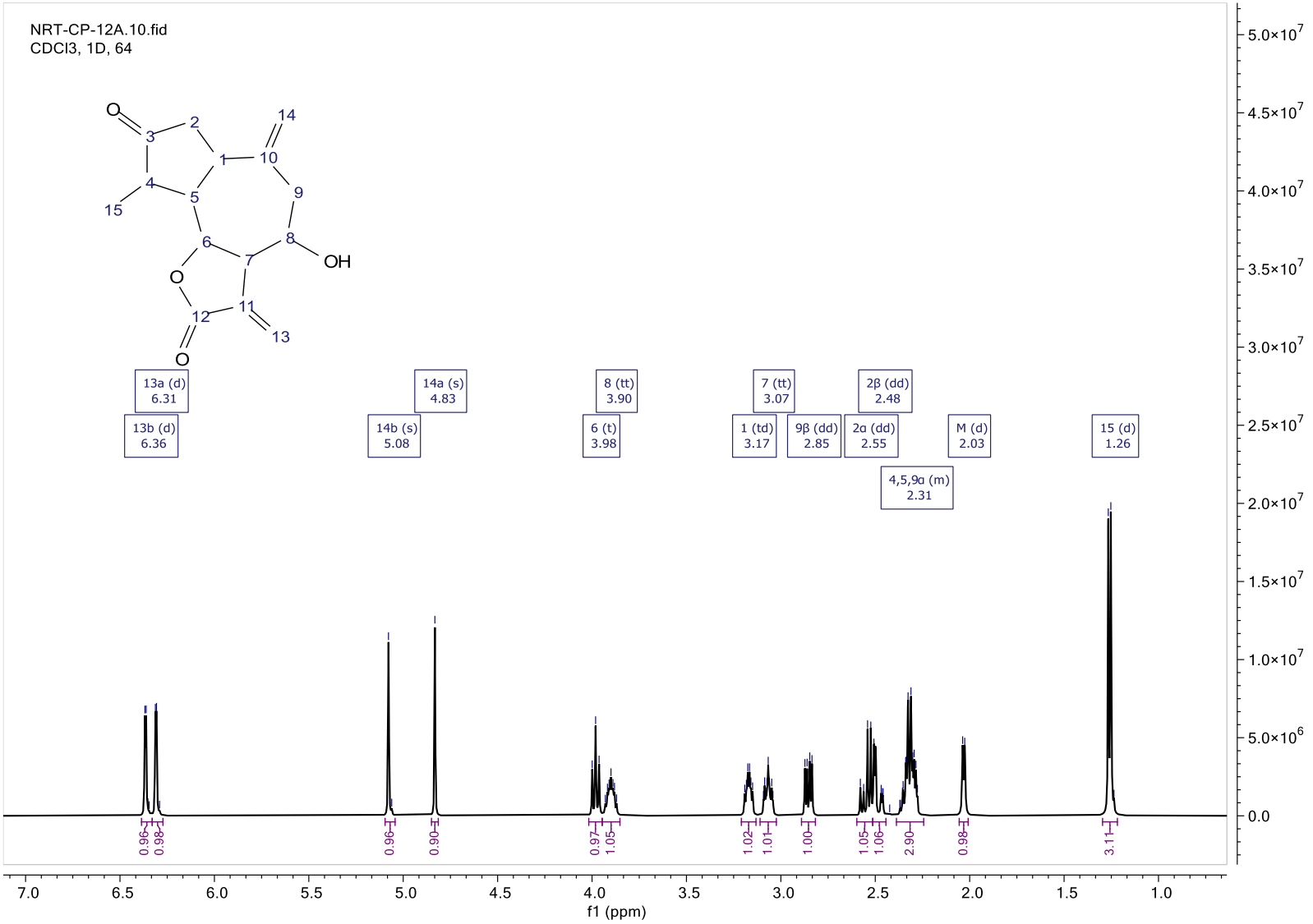


Figure S39: 5 (Grosheimin) 1D-^{1}H Proton NMR Spectrum

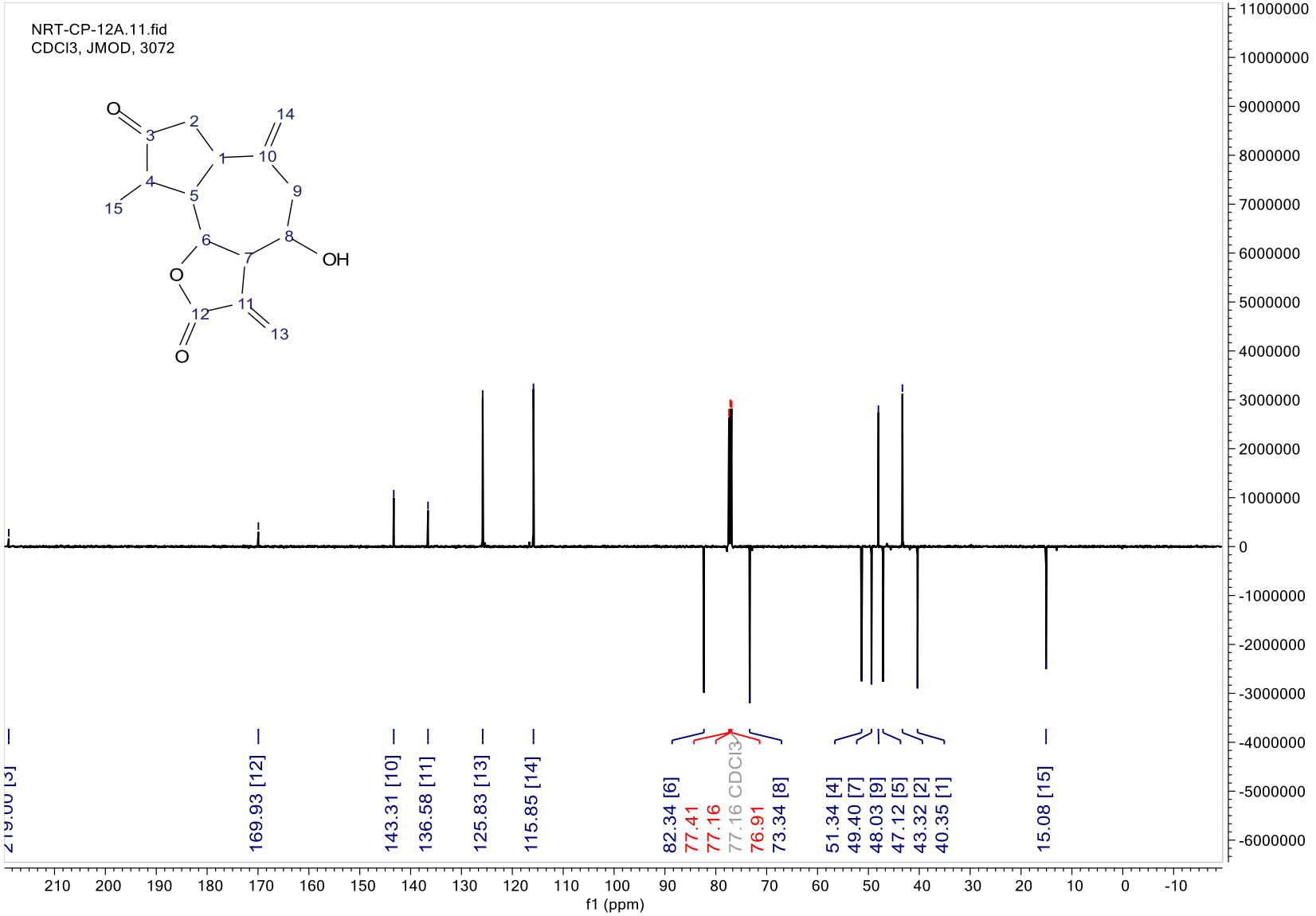


Figure S40: 5 (Grosheimin) ^{13}C (APT) 1D-NMR Spectrum

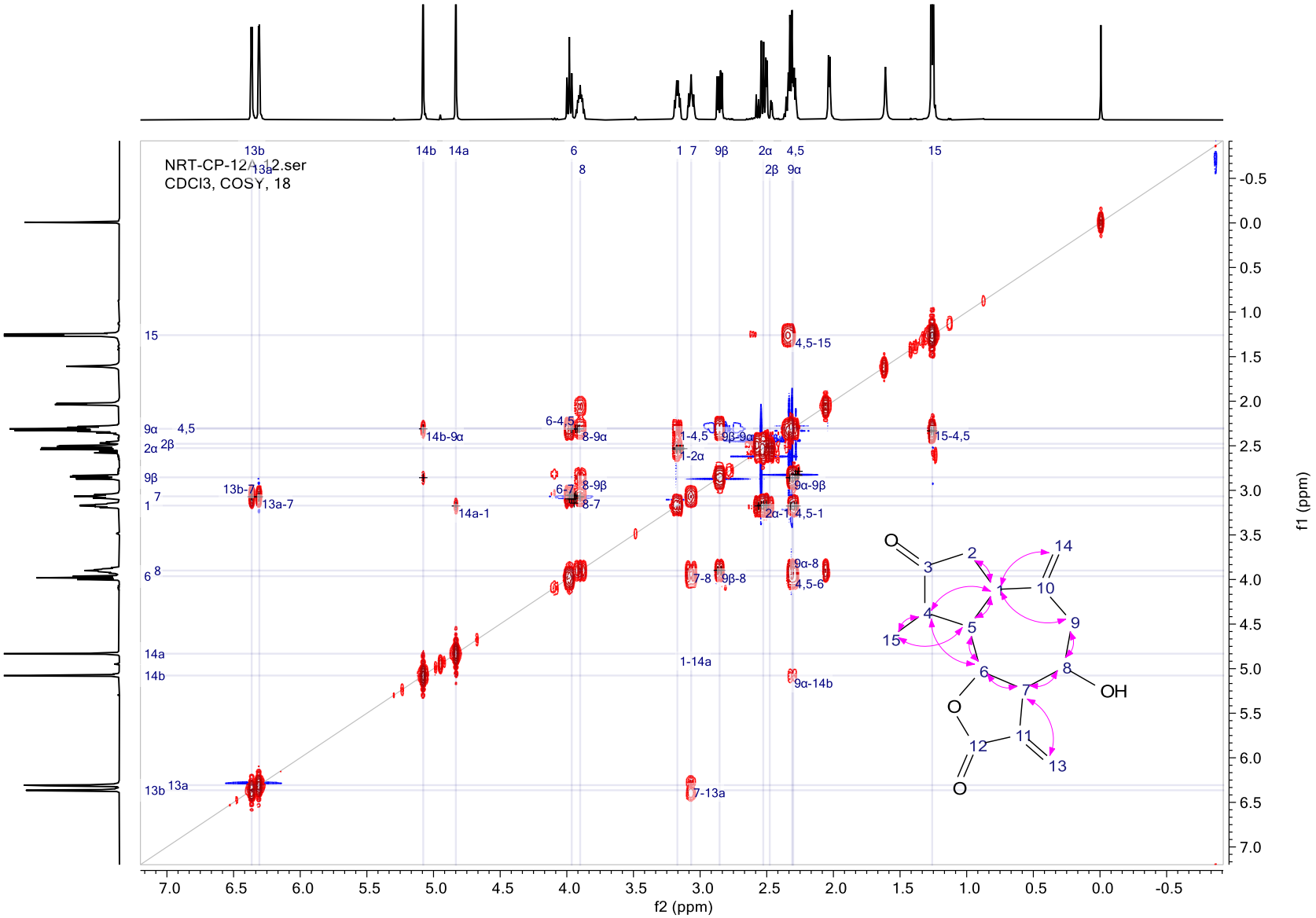


Figure S41: 5 (Grosheimin) COSY 2D-NMR Spectrum

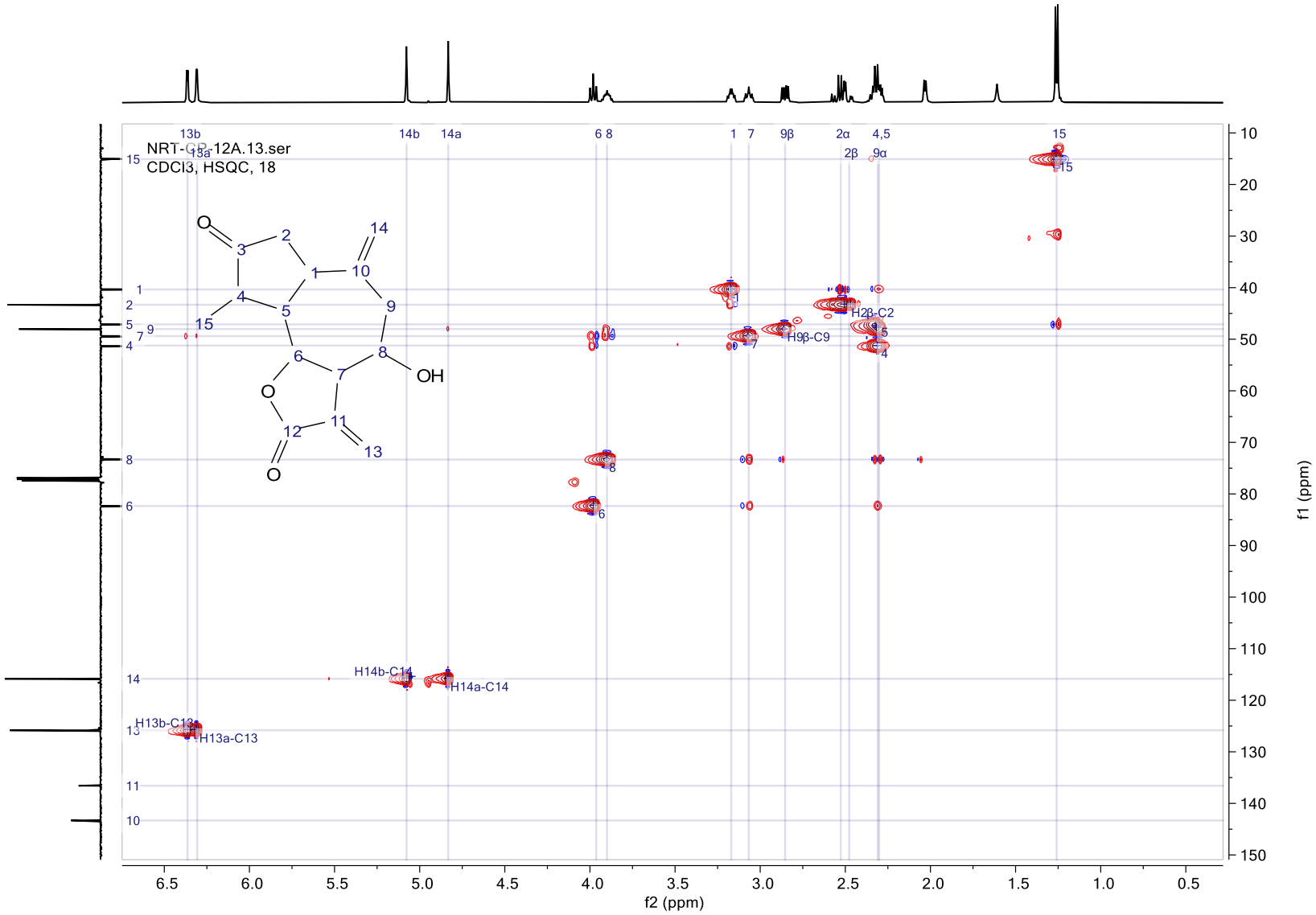


Figure S42: 5 (Grosheimin) HSQC 2D-NMR Spectrum

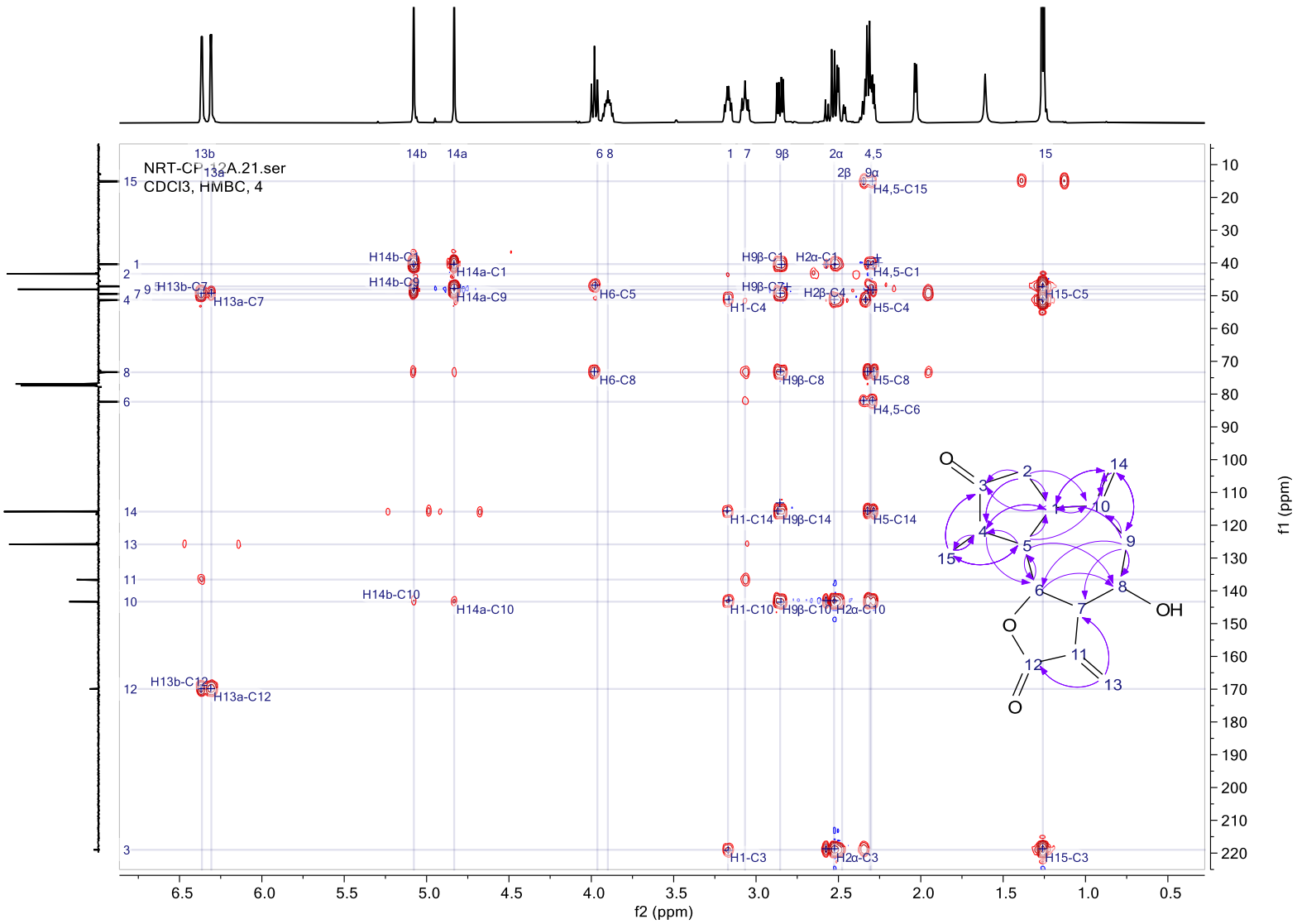


Figure S43: 5 (Grosheimin) HMBC 2D-NMR Spectrum

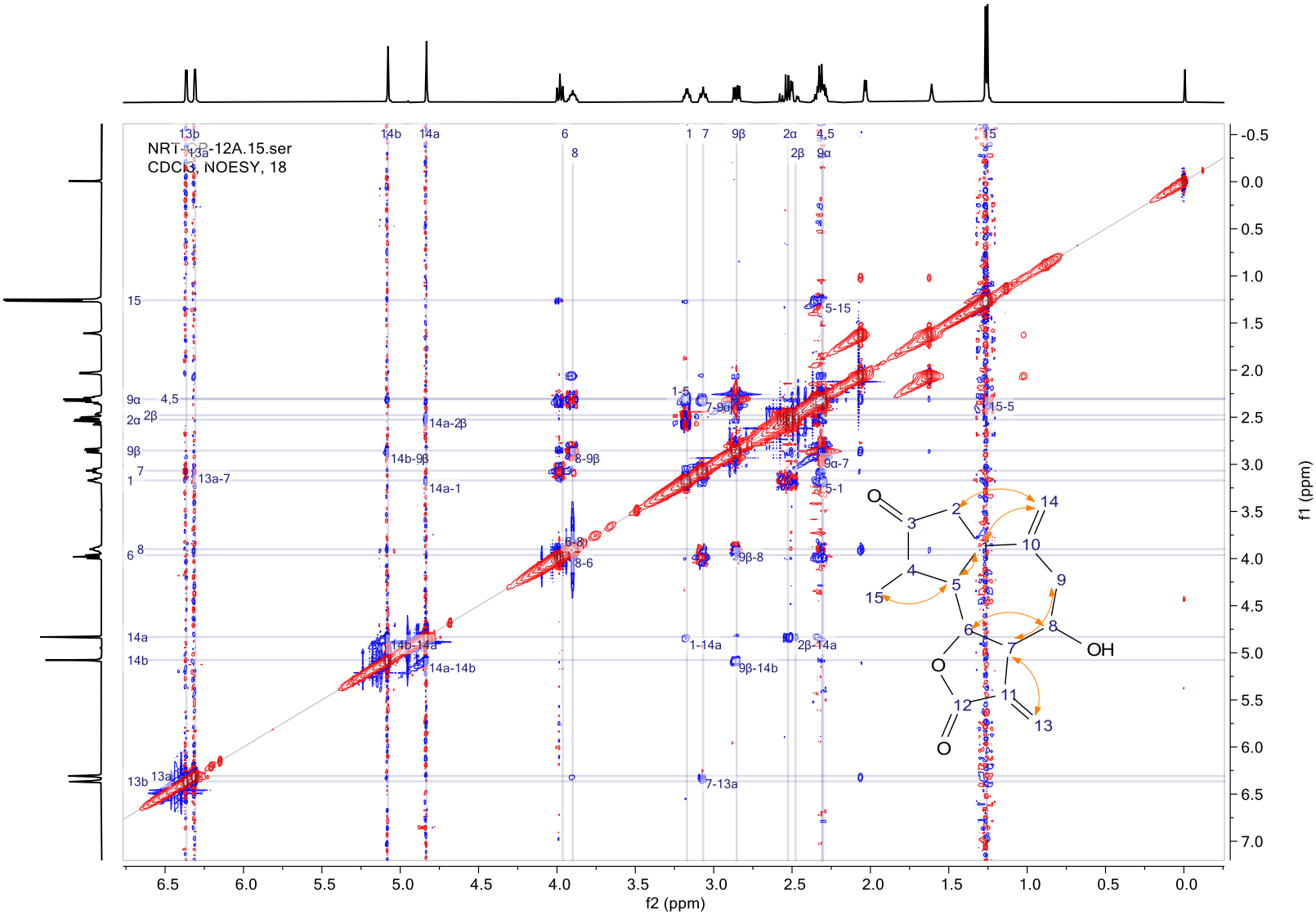
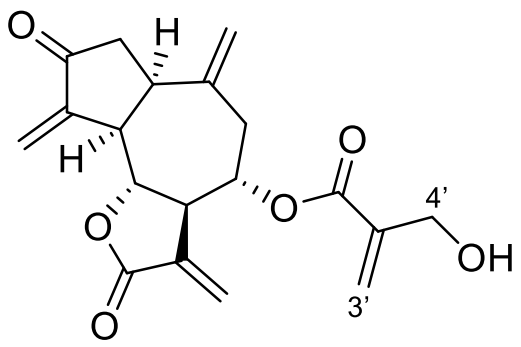


Figure S44: 5 (Grosheimin) NOESY 2D-NMR Spectrum

6. 6 (Dehydrocynaropicrin)



^{1}H NMR (500 MHz, $CDCl_3$); δ 6.35 (m, 1H, 3'b), 6.33 (d, *J* = 3.3 Hz, 1H, 13a), 6.30 (d, *J* = 2.4 Hz, 1H, 15b), 6.00 (q, *J* = 1.3 Hz, 1H, 3'a), 5.90 (dd, *J* = 2.4, 0.8 Hz, 1H, 15a), 5.86 – 5.77 (m, 1H, 13b), 5.13 (ddd, *J* = 10.3, 5.2, 2.3 Hz, 1H, 8), 5.09 (d, *J* = 4.2 Hz, 1H, 14a), 4.90 (s, 1H, 14b), 4.40 (s, 3H, 4'), 4.20 – 4.05 (m, 1H, 6), 3.43 (ddt, *J* = 12.2, 8.9, 3.1 Hz, 1H, 7), 3.33 – 3.25 (m, 1H, 5), 3.22 (td, *J* = 8.2, 5.1 Hz, 1H, 1), 2.92 (dd, *J* = 13.5, 5.8 Hz, 1H, 9β), 2.68 – 2.58 (m, 1H, 2α), 2.57 – 2.49 (m, 1H, 2β), 2.33 (dt, *J* = 13.4, 6.6 Hz, 1H, 9α).

^{13}C NMR (126 MHz, $CDCl_3$); δ 143.66 (4), 141.49 (10), 139.27 (2'), 127.00 (3'), 125.05 (13), 123.72 (15), 118.06 (14), 79.87 (6), 74.54 (8), 62.49 (4'), 49.14 (5), 46.78 (7), 43.49 (2), 41.79 (9), 40.60 (1).

Table S7: 6 (Dehydrocynaropicrin) HMBC, COSY, NOESY correlations

No	HMBC	COSY	NOESY
1	49.1(5), 118.1(14b), 141.5(10),203.6(3)	2.54(2β), 2.63(2α)	4.90(14b)
2α	203.6(3)	3.22(1)	-
2β	203.6(3)	3.22(1)	4.90(14b)
3	2.54(2β), 2.63(2α),3.22(1), 5.90(15a), 6.30(15b)	-	-
4	-	-	-
5	-	4.11(6), 5.90(15a), 6.30(15b)	-
6	74.5(8)	3.29(5), 3.43(7)	5.13(8)
7	-	4.11(6), 5.13(8), 5.80(13b), 6.33(13a)	-
8	-	2.33(9α), 2.92(9β),3.43(7)	4.11(6)
9α	74.5(8), 118.1(14b)	2.92(9β),5.13(8)	-
9β	46.8(7), 118.1(14b)	2.33(9α),5.13(8)	-
10	3.22(1)	-	-
12	5.80(13b), 6.33(13a)	-	-
13a	24.0(12),46.8(7)	3.43(7)	5.80(13b)
13b	24.0(12)	3.43(7)	6.33(13a)
14a	40.9(1)	-	-
14b	40.9(1)	-	2.54(2β),3.22(1)
15a	49.1(5),203.6(3)	3.29(5), 6.30(15b)	6.30(15b)
15b	49.1(5),203.6(3)	3.29(5), 5.90(15a)	5.90(15a)
1'	6.00(3'a)	-	-
2'	4.40(4'), 6.35(3'b)	-	-
3'a	62.5(4'),165.0(1')	4.40(4'), 6.35(3'b)	4.40(4'), 6.35(3'b)
3'b	62.5(4'),139.3(2')	4.40(4'), 6.00(3'a)	6.00(3'a)
4'	139.3(2')	6.00(3'a),6.35(3'b)	6.00(3'a)

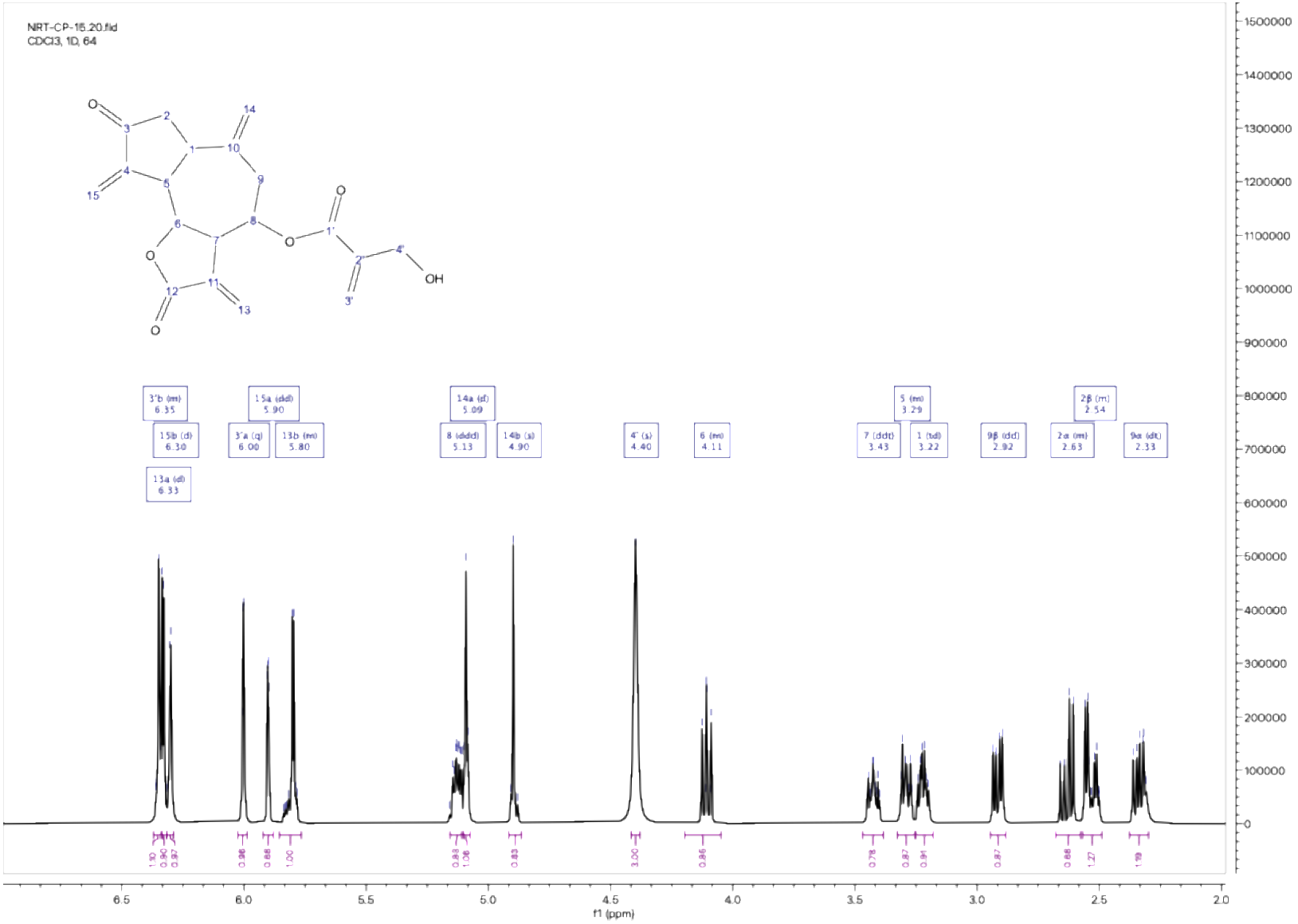


Figure S45: 6 (Dehydrocynaropicrin) 1D-^{1}H Proton NMR Spectrum

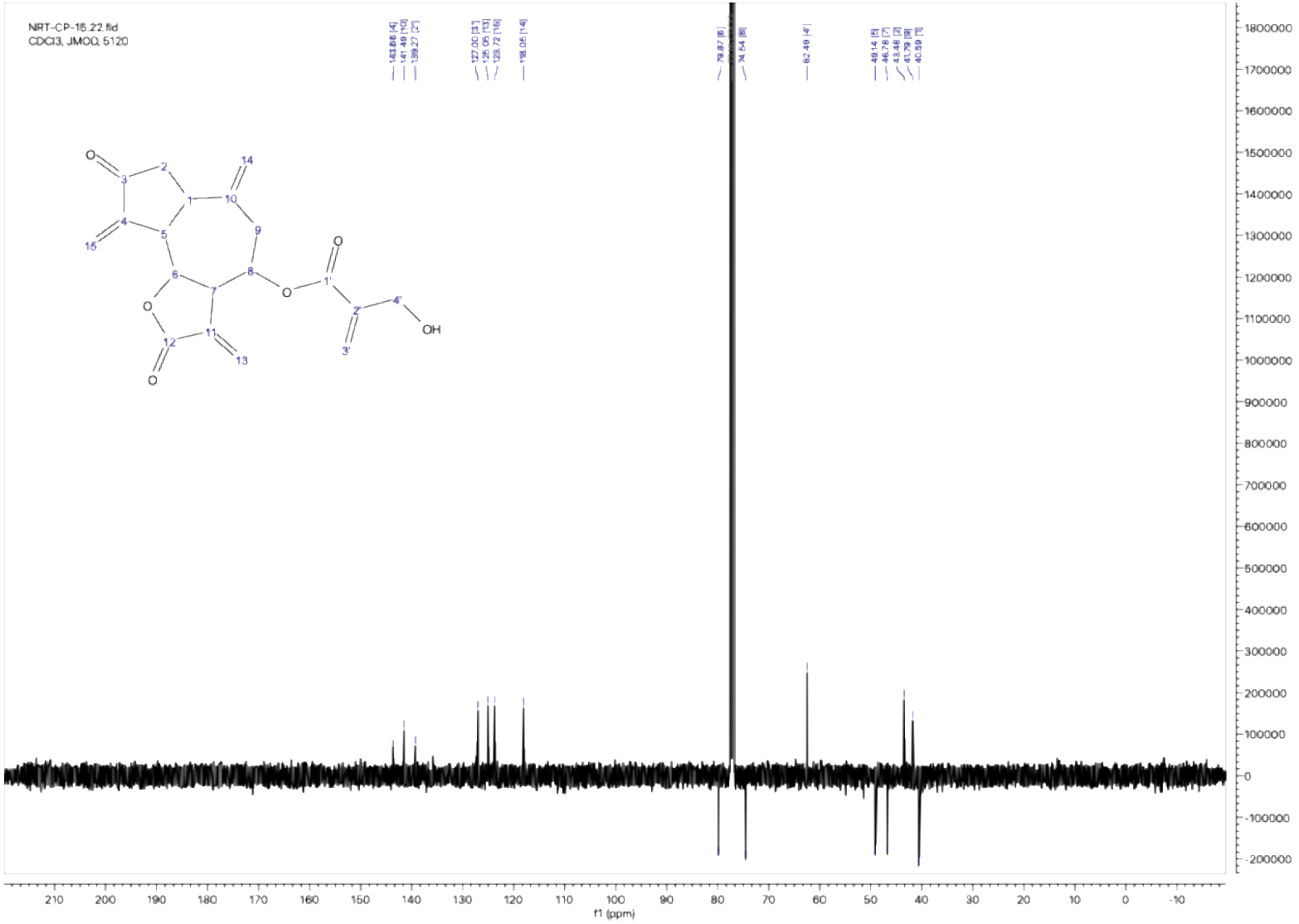


Figure S46: 6 (Dehydrocynaropicrin) ^{13}C (APT) 1D-NMR Spectrum

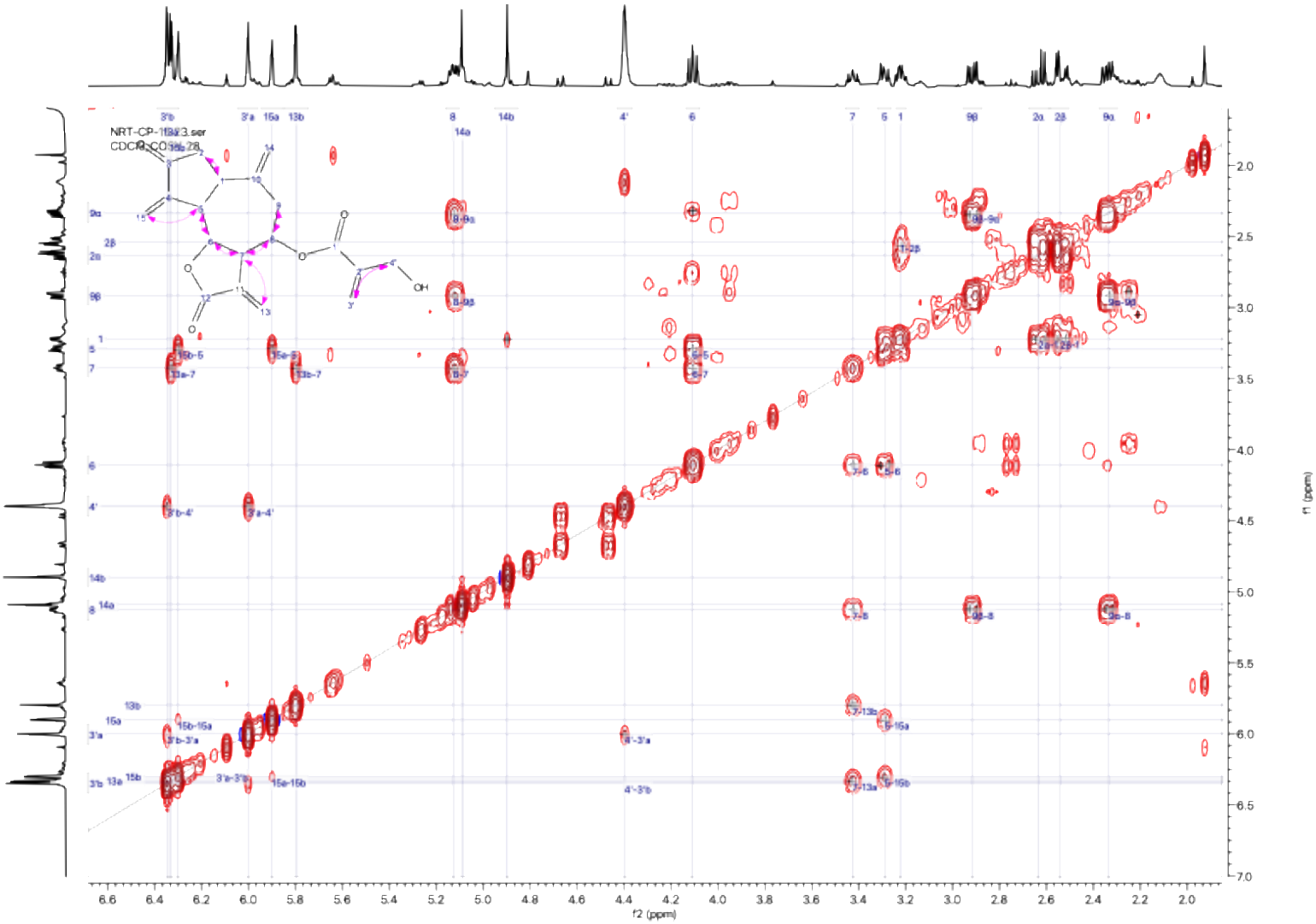


Figure S47: 6 (Dehydrocynaropicrin) COSY 2D-NMR Spectrum

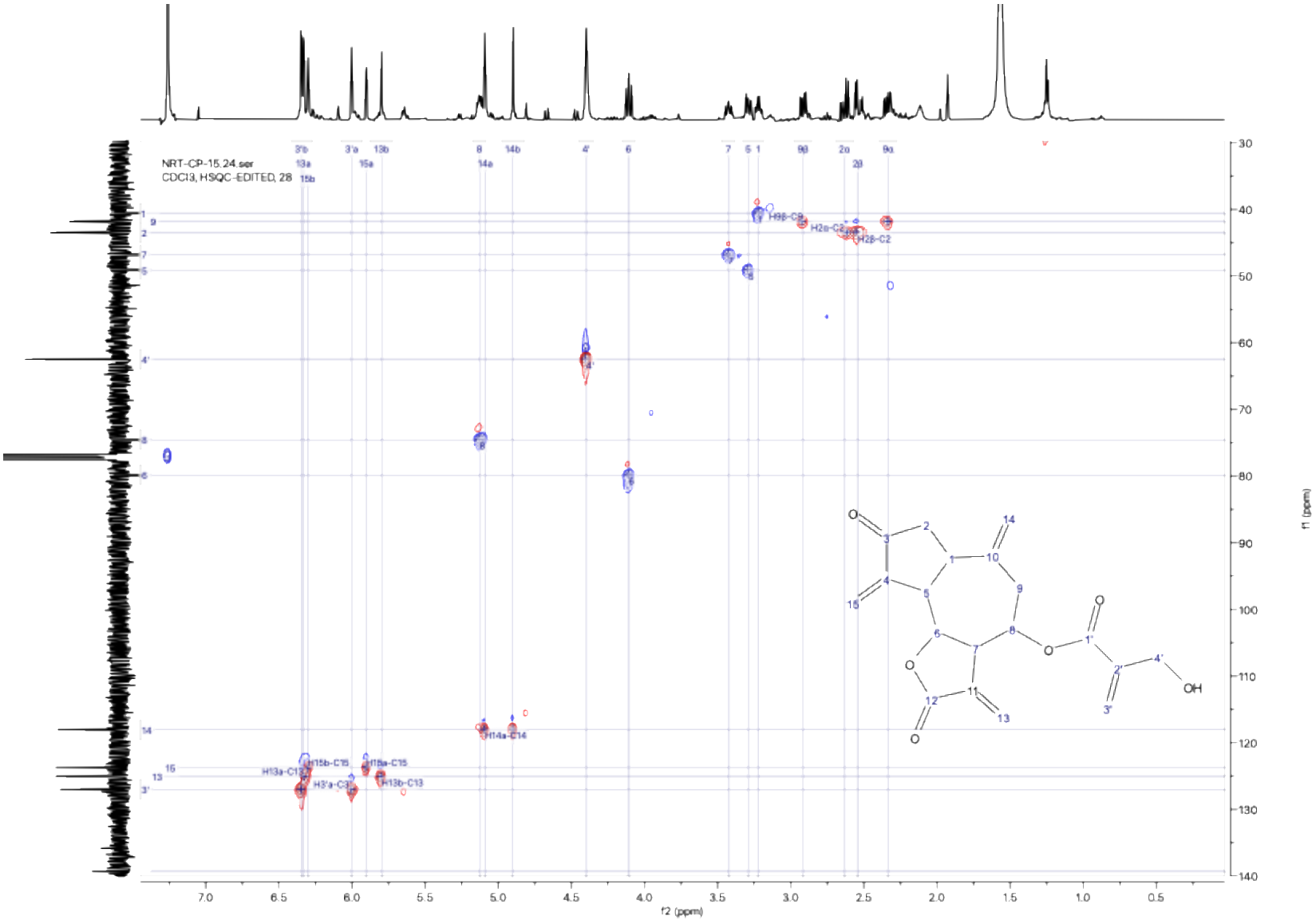


Figure S48: 6 (Dehydrocynaropicrin) HSQC 2D-NMR Spectrum

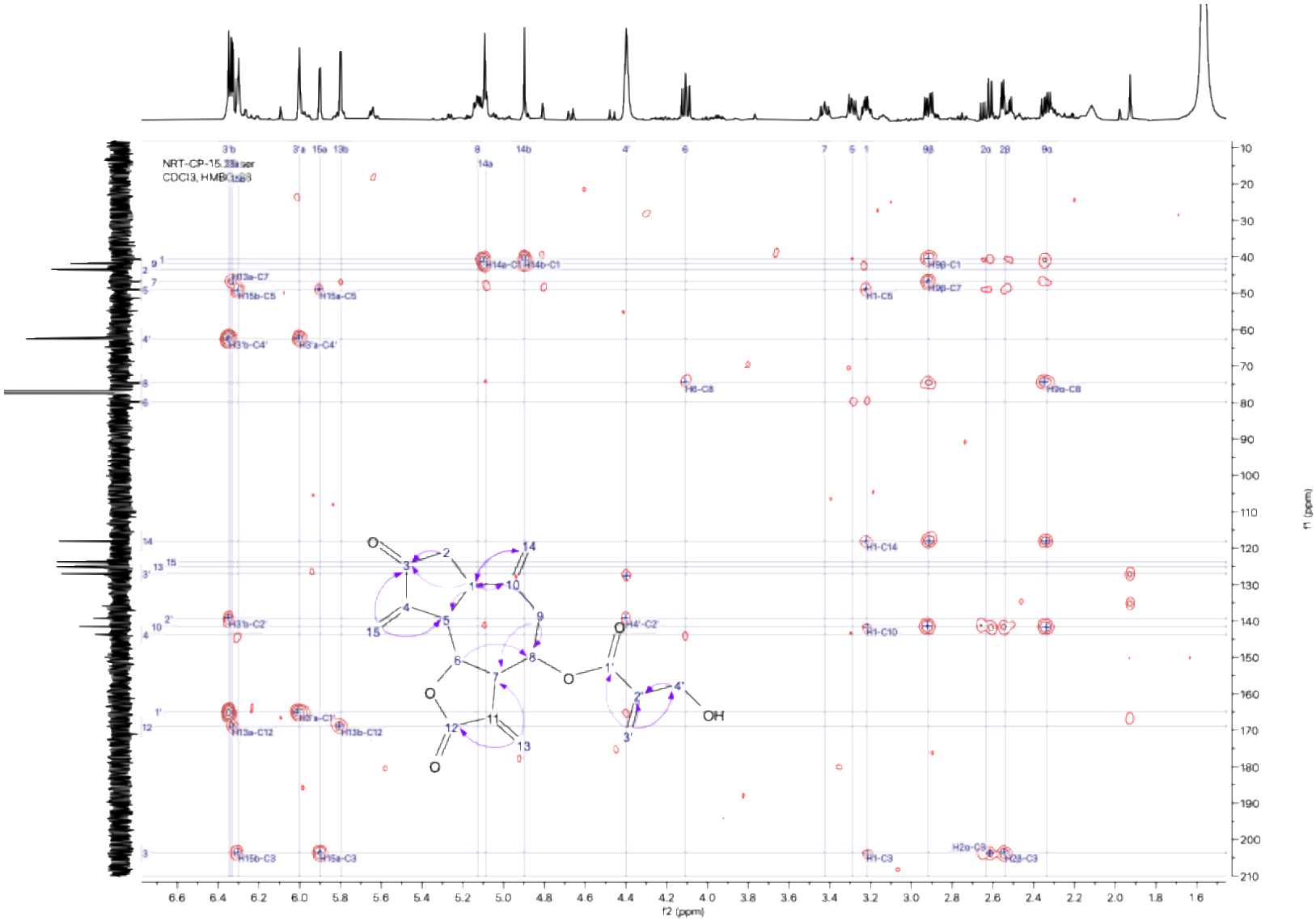


Figure 49: 6 (Dehydrocynaropicrin) HMBC 2D-NMR Spectrum

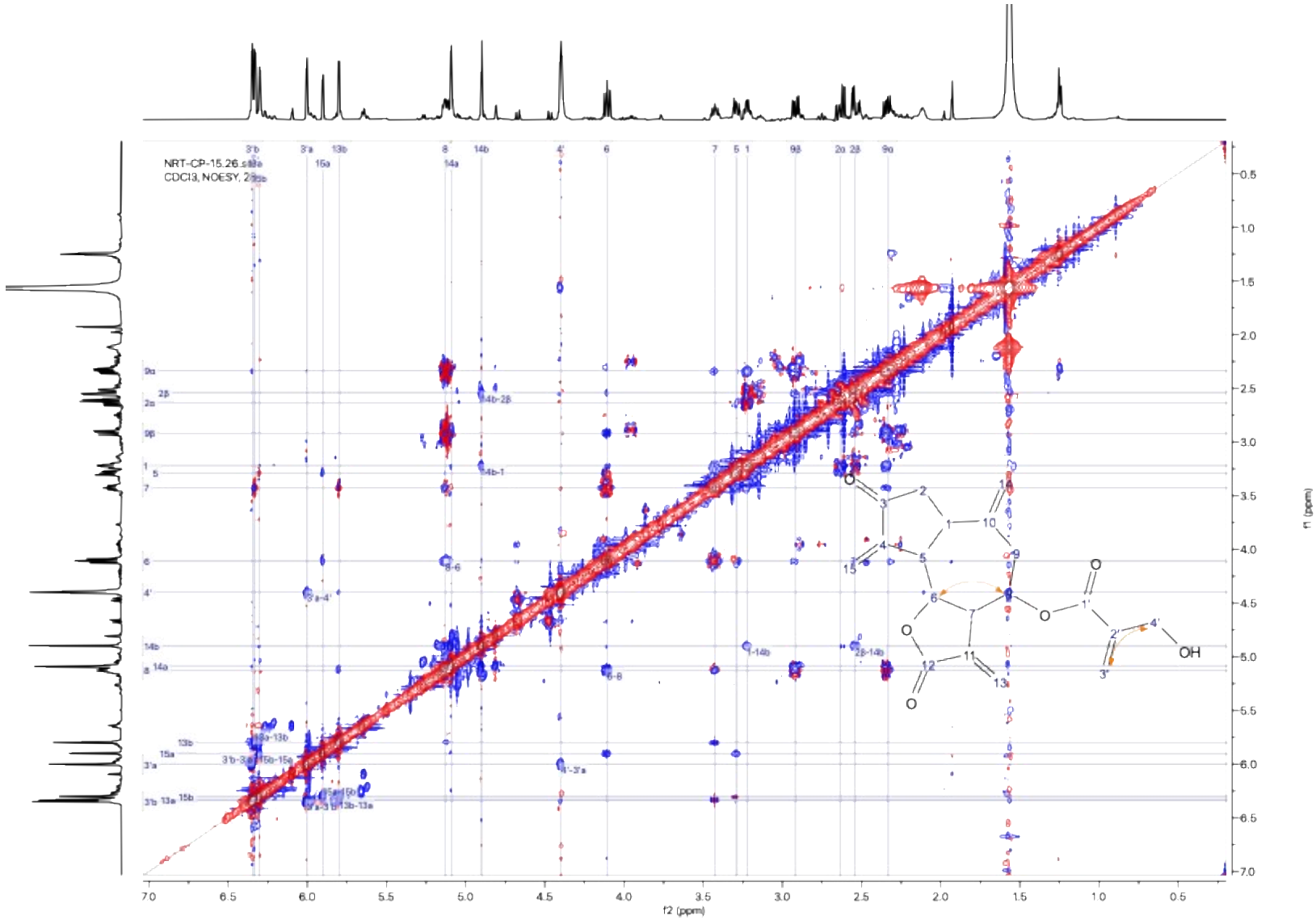
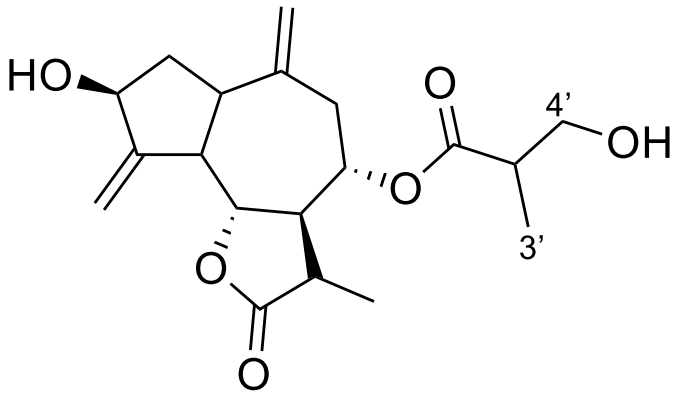


Figure S50: 6 (Dehydrocynaropicrin) NOESY 2D-NMR Spectrum

7. 1A (11,13, 2', 3'-tetrahydrocynaropicrin)



^{1}H NMR (500 MHz, $CDCl_3$); δ 5.42 (t, *J* = 2.0 Hz, 1H, 15b), 5.33 (t, *J* = 2.0 Hz, 1H, 15a), 5.16 – 5.11 (m, 1H, 14b), 5.03 (s, 1H, 14a), 4.97 (dtd, *J* = 10.3, 5.2, 2.7 Hz, 1H, 8), 4.55 (tt, *J* = 7.1, 2.0 Hz, 1H, 3), 4.13 (td, *J* = 9.9, 2.7 Hz, 1H, 6), 3.81 – 3.68 (m, 2H, 4'), 2.97 – 2.88 (m, 1H, 1), 2.82 (td, *J* = 9.4, 2.0 Hz, 1H, 5), 2.70 (dddt, *J* = 14.8, 9.9, 7.4, 3.8 Hz, 2H, 9α), 2.57 – 2.46 (m, 1H, 11), 2.33 – 2.27 (m, 1H, 2β), 2.26 – 2.23 (m, 1H, 7), 2.23 – 2.18 (m, 1H, 9β), 1.74 (dddd, *J* = 13.6, 9.4, 7.0, 2.4 Hz, 1H, 2α), 1.30 (dd, *J* = 7.0, 2.1 Hz, 3H), 1.21 (d, *J* = 7.3 Hz, 3H, 3', 13).

^{13}C NMR (126 MHz, $CDCl_3$); δ 177.88 (12), 175.01 (1'), 152.83 (4), 142.18 (10), 117.54 (14), 112.65 (15), 79.00 (6), 76.16 (8), 73.73 (3), 64.47 (4'), 53.19, 50.85 (5), 44.42 (1), 42.17 (2'), 41.48 (11), 40.39 (9), 38.94 (2), 15.66 (13), 13.64 (3').

Table S8: 1A HMBC, COSY, NOESY correlations

No	HMBC	COSY	NOESY
1	38.9(2β), 50.8(5), 79.0(6), 117.5(14b), 142.2(10)	2.82(5),2.92(1), 5.14(14b)	4.55(3), 5.14(14b)
2α	44.4(1), 73.7(3), 142.2(10)	4.55(3)	-
2β	152.8(4)	-	-
3	-	1.74(2α), 5.42(15b)	2.82(5),2.92(1), 5.33(15a)
4	2.29(2β), 2.82(5), 5.42(15b)	-	-
5	38.9(2β), 44.4(1), 79.0(6), 112.6(15b), 152.8(4)	2.92(1), 4.13(6), 5.33(15a), 5.42(15b)	4.55(3)
6	76.2(8)	2.26(7),2.82(5)	2.51(11),4.97(8), 5.42(15b)
7	15.7(13)	2.21(9β), 2.72(9α), 4.13(6), 4.97(8)	1.26(13),2.72(9α)
8	142.2(10), 175.0(1')	2.26(7),2.72(9α)	2.51(11),4.13(6)
9α	53.3(7)	2.21(9β), 2.26(7), 4.97(8)	2.21(9β), 2.26(7)
9β	76.2(8), 117.5(14b),142.2(10)	2.26(7),2.72(9α)	2.72(9α)
10	1.74(2α), 2.21(9β), 2.92(1), 4.97(8)	-	-
11	15.7(13), 53.3(7),76.2(8), 177.9(12)	-	4.13(6),4.97(8)
12	2.51(11)	-	-
13	-	-	2.26(7)
14a	40.4(9β)	-	-
14b	40.4(9β)	2.92(1)	2.92(1)
15a	50.8(5)	2.82(5)	4.55(3)
15b	50.8(5), 73.7(3), 152.8(4)	2.82(5), 4.55(3)	4.13(6)
1'	1.21(3'), 3.76(4'),4.97(8)	-	-
2'	-	-	-
3'	64.5(4'),175.0(1')	-	3.76(4')
4'	175.0(1')	-	1.21(3')

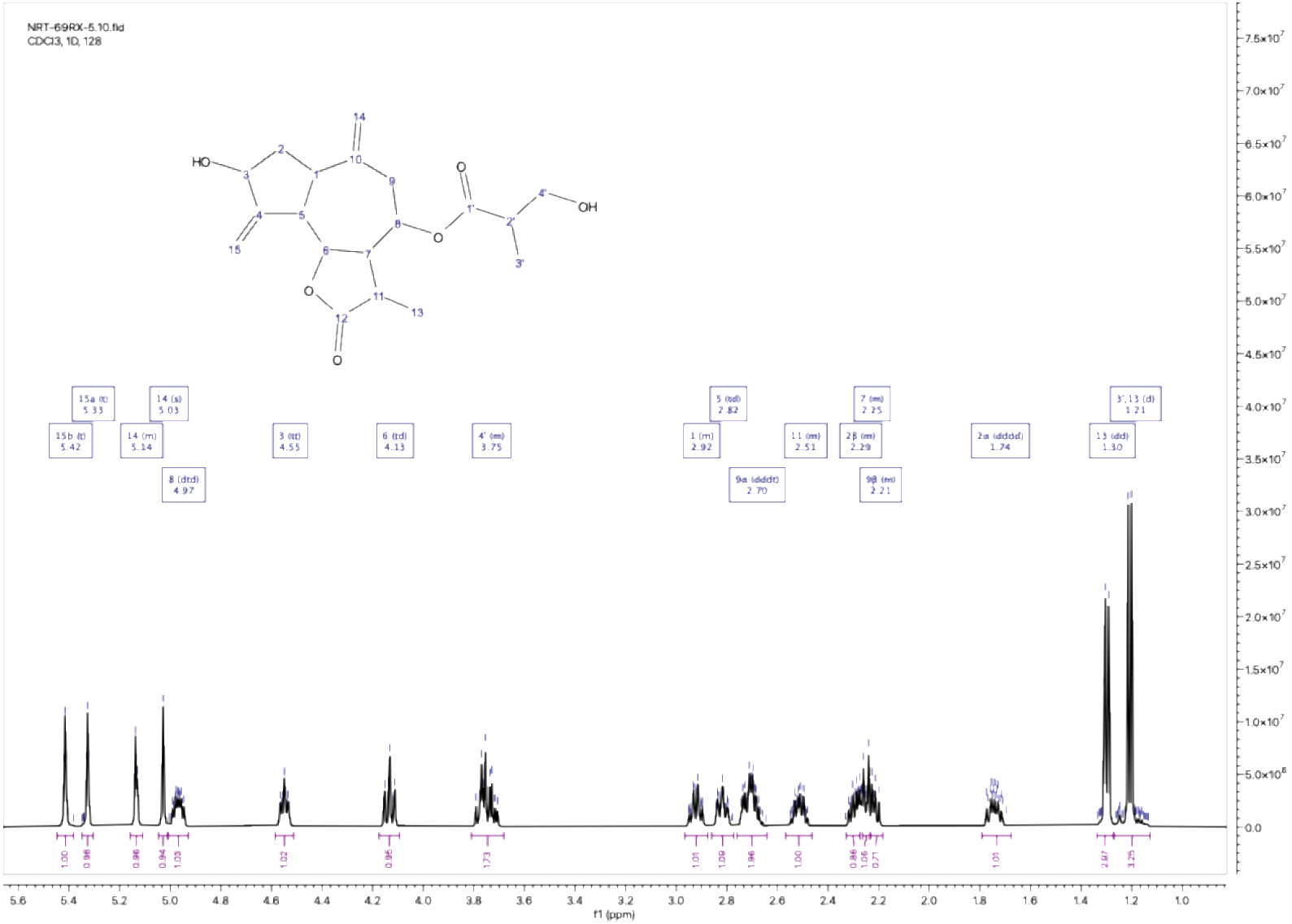


Figure S51: 1A 1D-^{1}H Proton NMR Spectrum

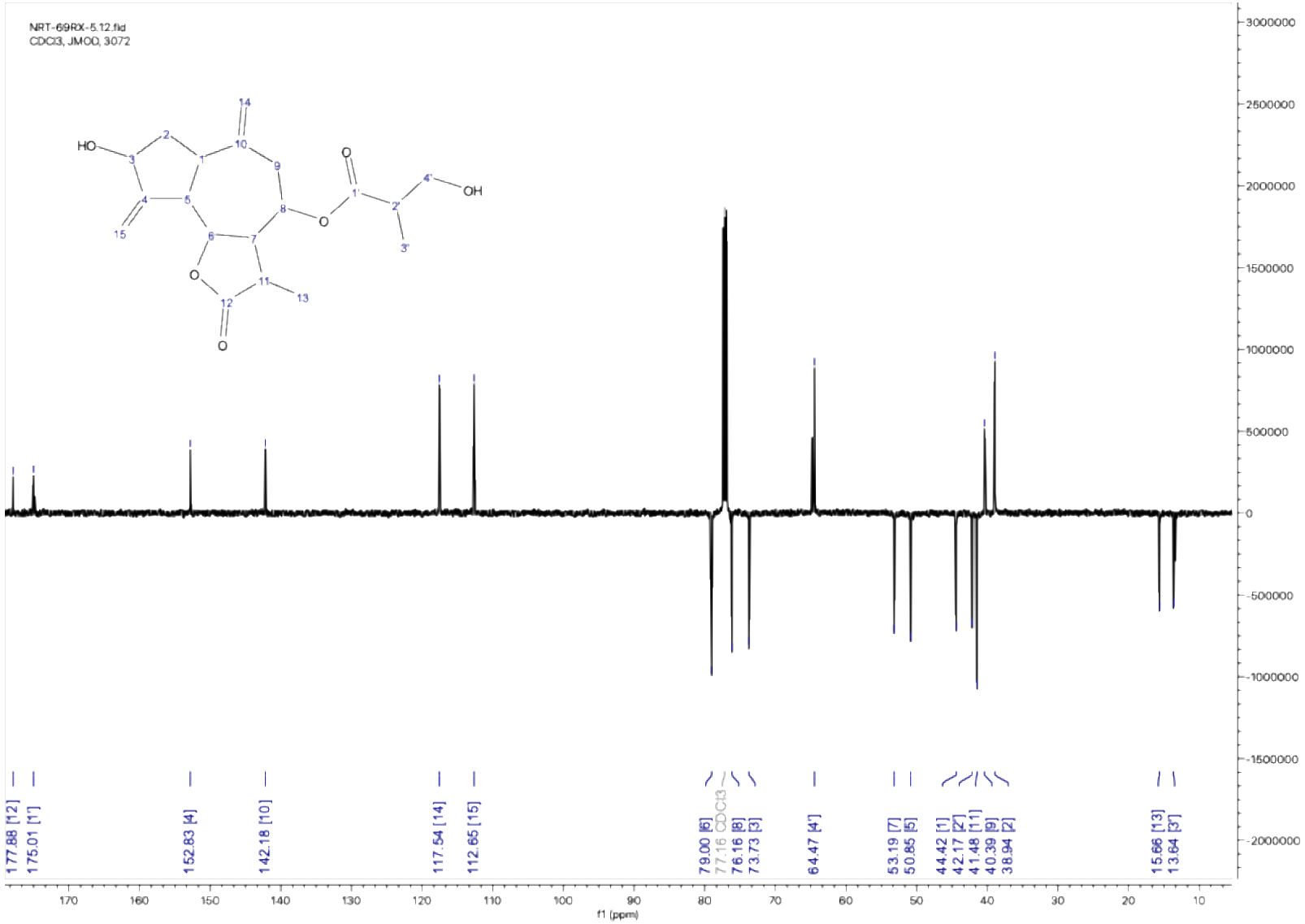


Figure S52: 1A ^{13}C (APT) 1D-NMR Spectrum

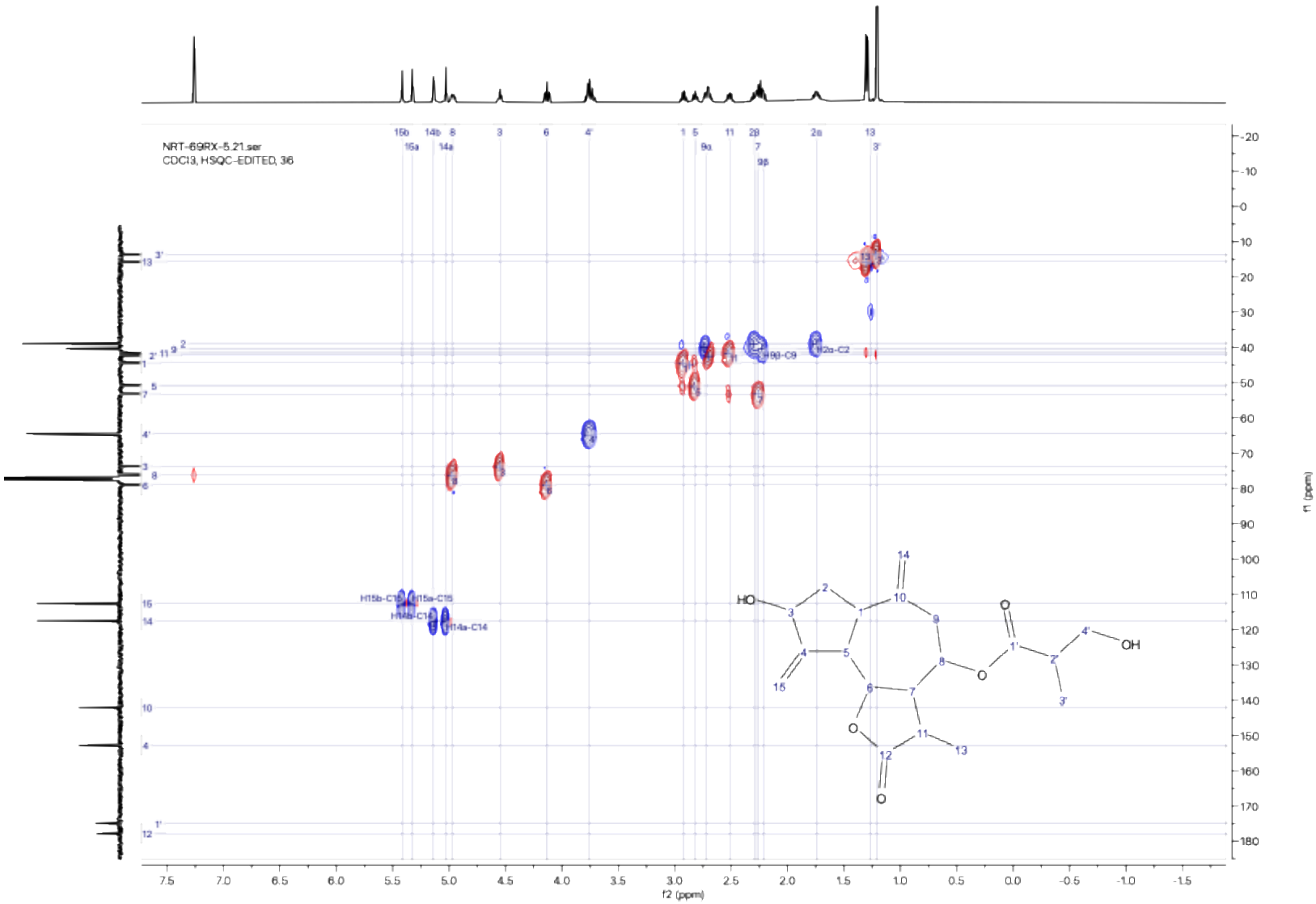


Figure S53: 1A HSQC 2D-NMR Spectrum

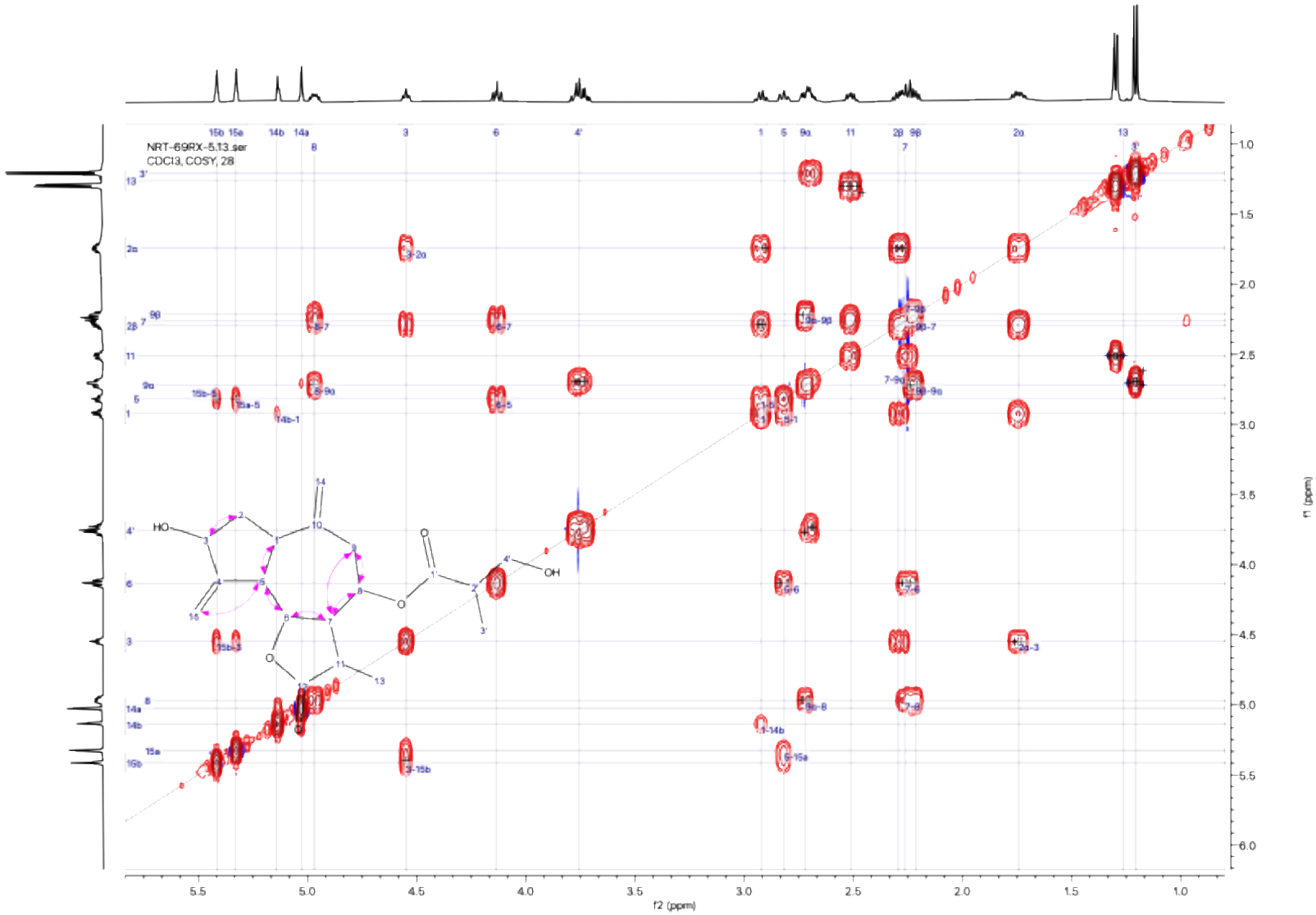


Figure S54: 1A COSY 2D-NMR Spectrum

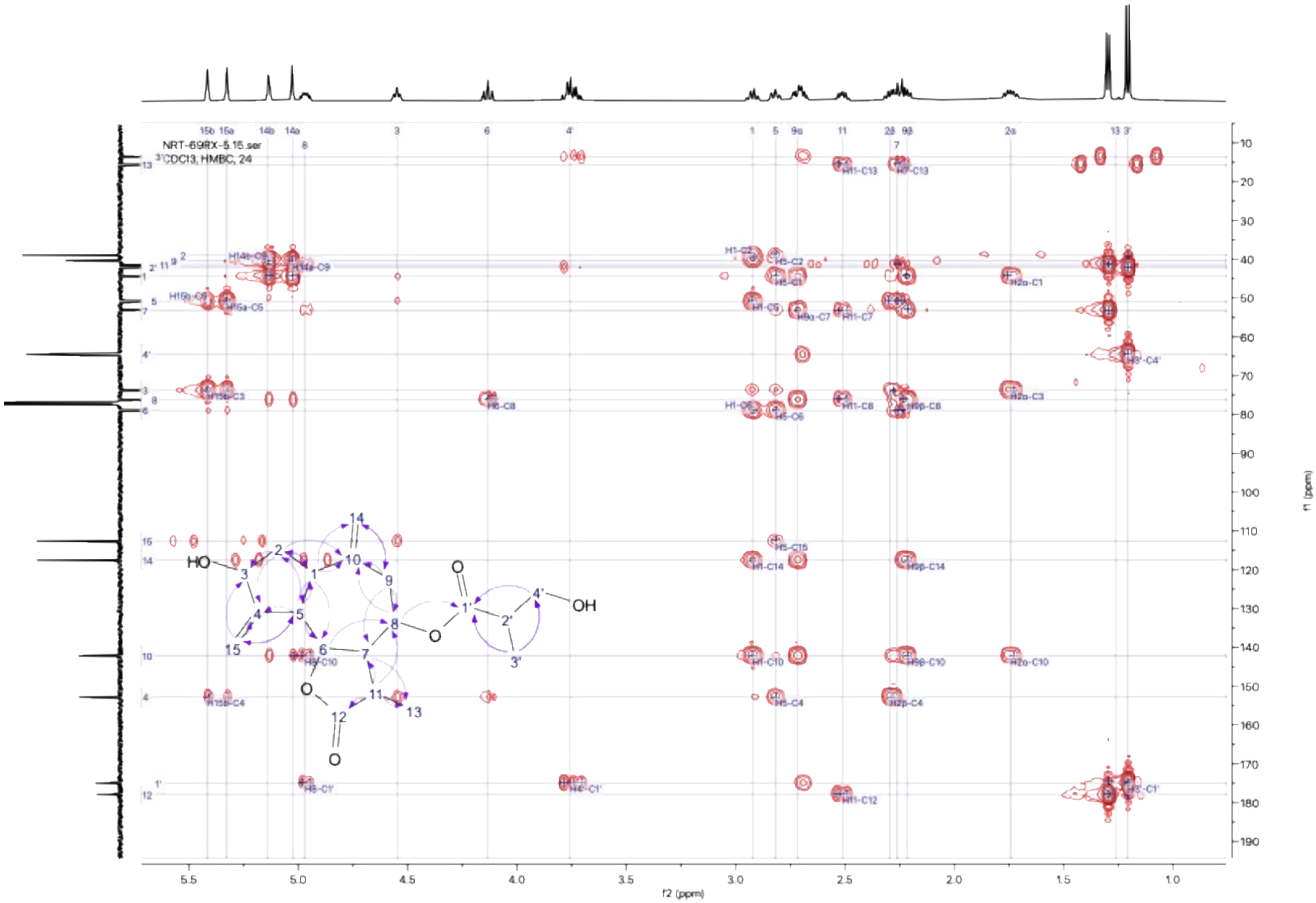


Figure S55: 1A HMBC 2D-NMR Spectrum

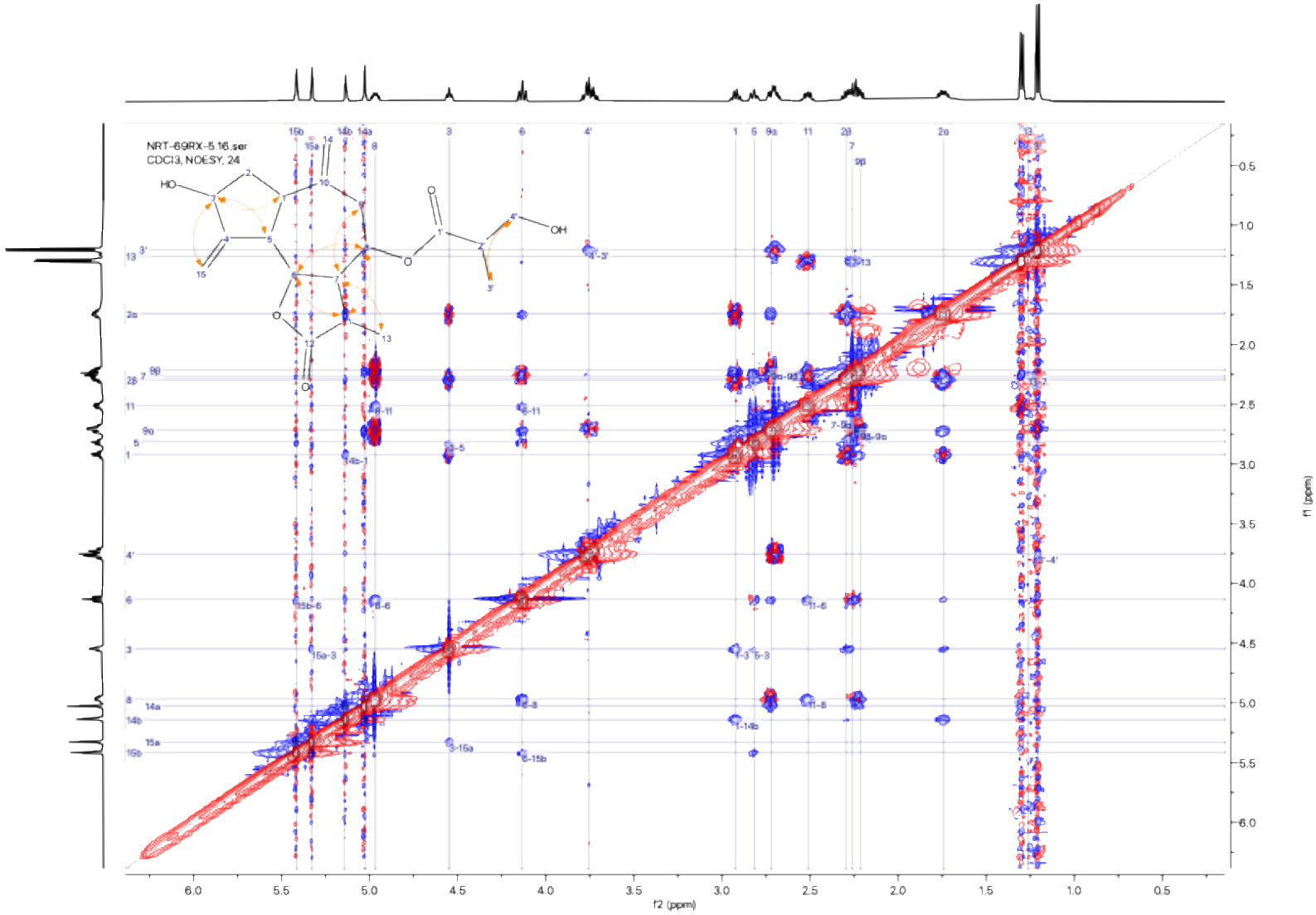
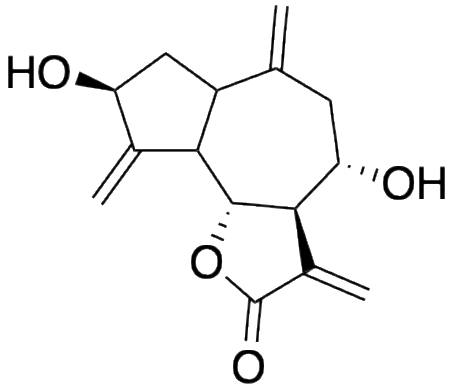


Figure S56: 1A NOESY 2D-NMR Spectrum

8. 1B (Deacylcynaropicrin)



^{1}H NMR (500 MHz, $CDCl_3$) δ; 6.27 (dd, *J* = 3.4, 0.9 Hz, 1H, 13b), 6.15 (dd, *J* = 3.2, 0.9 Hz, 1H, 13a), 5.50 (t, *J* = 1.8 Hz, 1H, 15a), 5.35 (t, *J* = 1.8 Hz, 1H, 15b), 5.14 (s, 1H, 14a), 4.98 (s, 1H, 14b), 4.56 (s, 1H, 3), 4.16 (dd, *J* = 10.6, 8.9 Hz, 1H, 6), 3.97 (m, 1H, 8), 2.98 (dt, *J* = 10.9, 8.2 Hz, 1H, 1), 2.80 (m, 2H, 5, 7), 2.71 (dd, *J* = 14.1, 5.1 Hz, 1H, 9a), 2.30 (dd, *J* = 14.1, 3.9 Hz, 1H, 9b), 2.24 (dt, *J* = 13.1, 7.4 Hz, 1H, 2a), 1.74 (m, 1H, 2b).

^{13}C NMR (126 MHz, $CDCl_3$) δ; 152.69 (4), 142.92 (10), 138.19, 123.28 (13), 117.34 (14), 113.44 (15), 78.83, 73.97, 72.19, 51.61 (7), 51.25 (5), 45.52, 41.37 (9), 39.55 (2).

Table S9: 1B HMBC and COSY correlations

No	HMBC	COSY
1	-	1.74(2b), 2.24(2a)
2a	74.1(3), 152.7(4)	1.74(2b), 2.97(1),4.56(3)
2b	-	2.24(2a), 2.97(1),4.56(3)
3	-	1.74(2b), 2.24(2a), 5.35(15b), 5.50(15a)
4	2.24(2a)	-
5	-	5.35(15b)
6	-	2.80(7)
7	-	3.97(8),4.16(6), 6.15(13a), 6.27(13b)
8	-	2.30(9b), 2.71(9a),2.80(7)
9a	45.6(1), 117.3(14b)	2.30(9b),3.97(8), 4.98(14b), 5.14(14a)
9b	72.3(8)	2.71(9a),3.97(8), 4.98(14b)
10	-	-
11	6.27(13b)	-
12	6.15(13a),6.27(13b)	-
13a	51.6(7), 169.6(12)	2.80(7)
13b	51.6(7), 138.2(11), 169.6(12)	2.80(7)
14a	41.4(9b),45.6(1)	2.71(9a)
14b	41.4(9b),45.6(1)	2.30(9b), 2.71(9a)
15a	-	4.56(3)
15b	-	2.80(5),4.56(3)

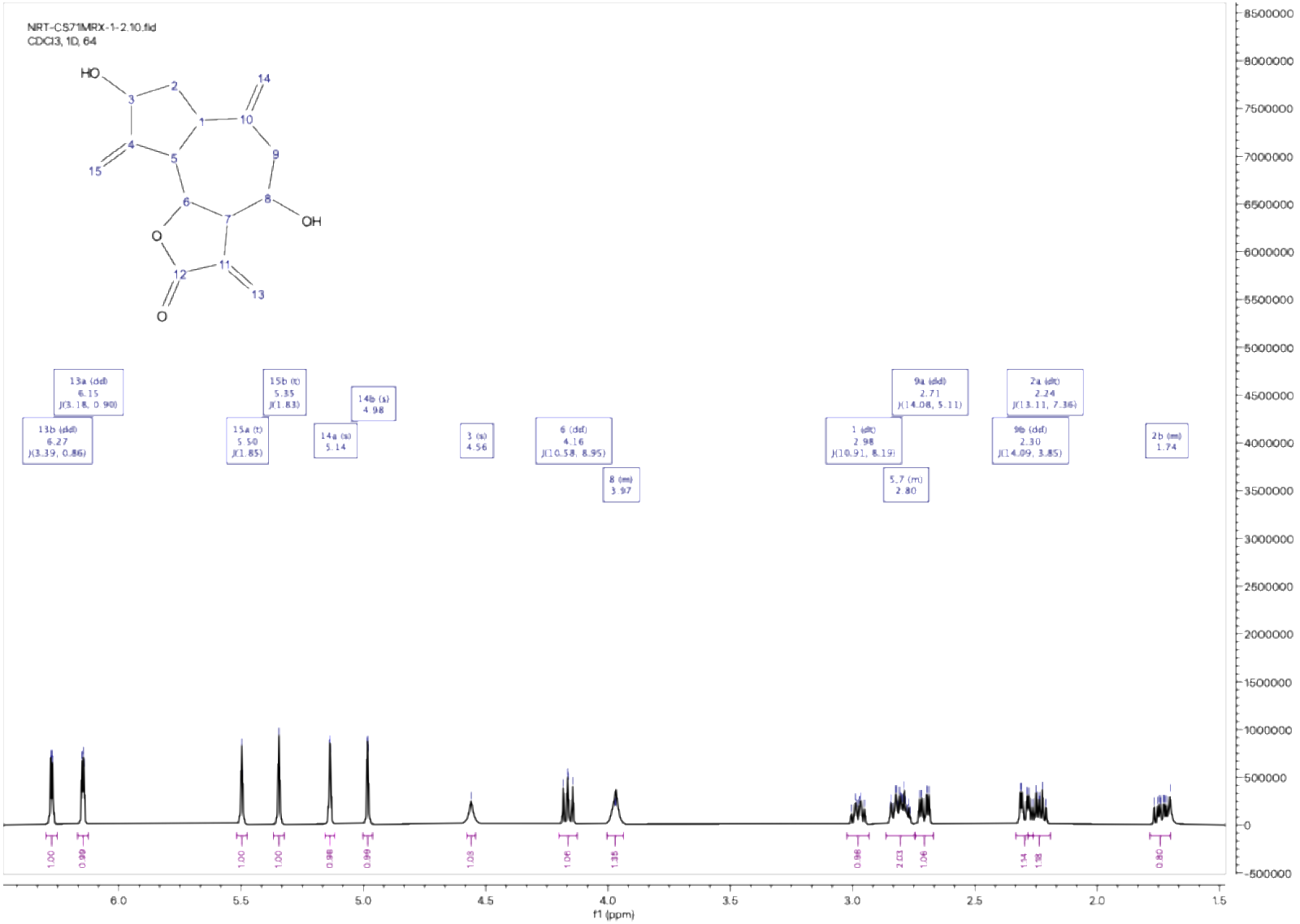


Figure S57: 1B 1D-^{1}H Proton NMR Spectrum

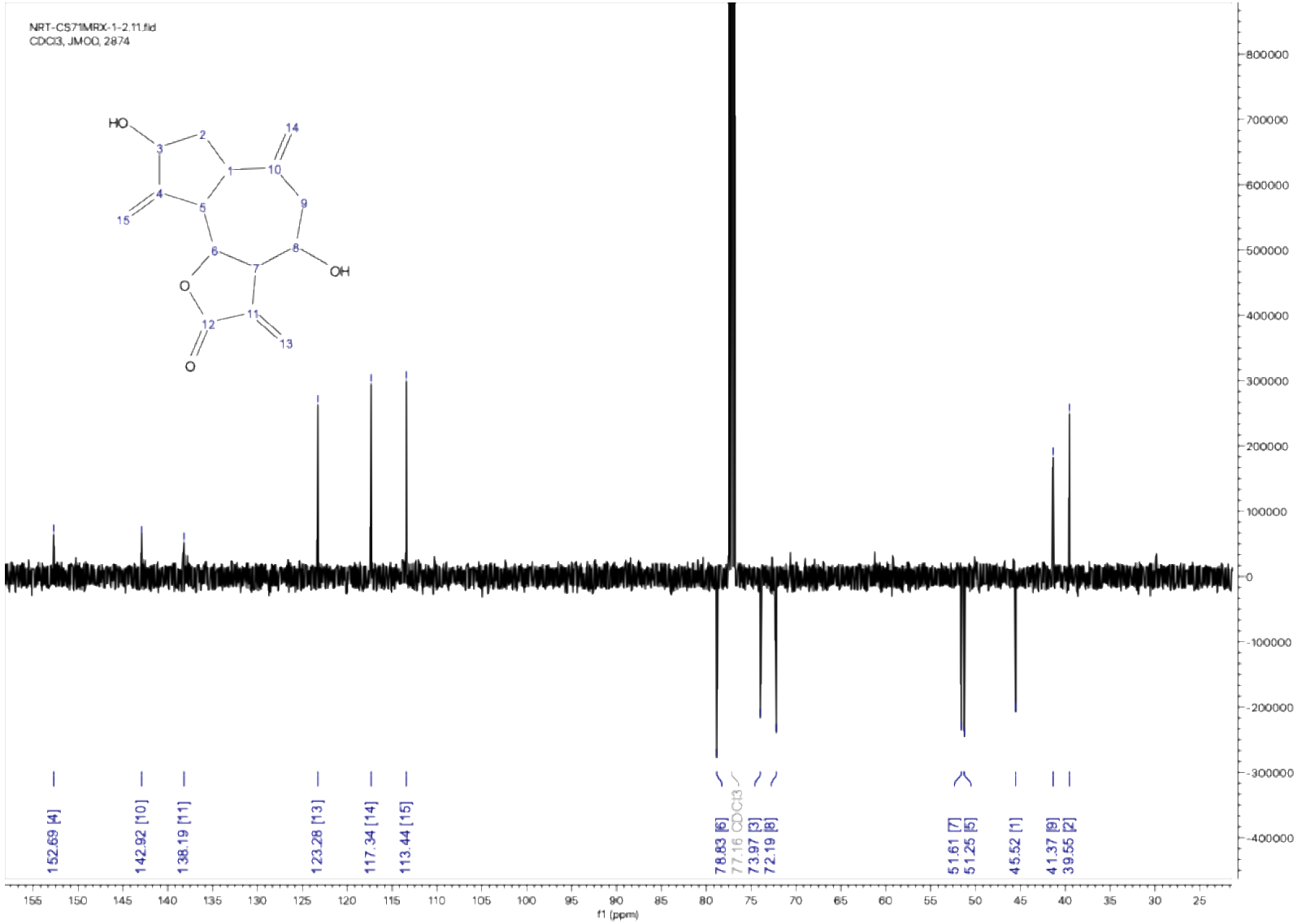


Figure S58: 1B ^{13}C (APT) 1D-NMR Spectrum

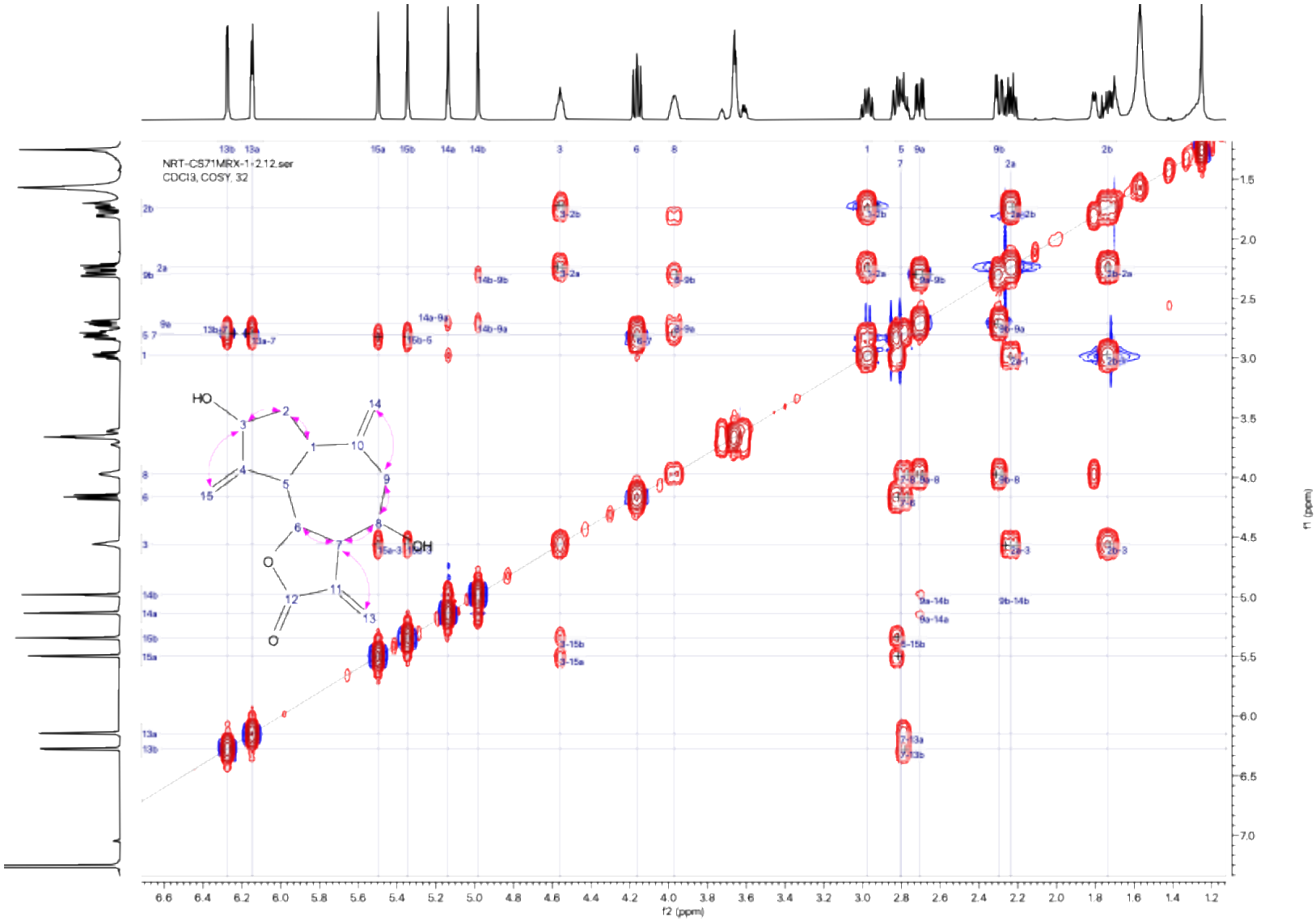


Figure S59: 1B COSY 2D-NMR Spectrum

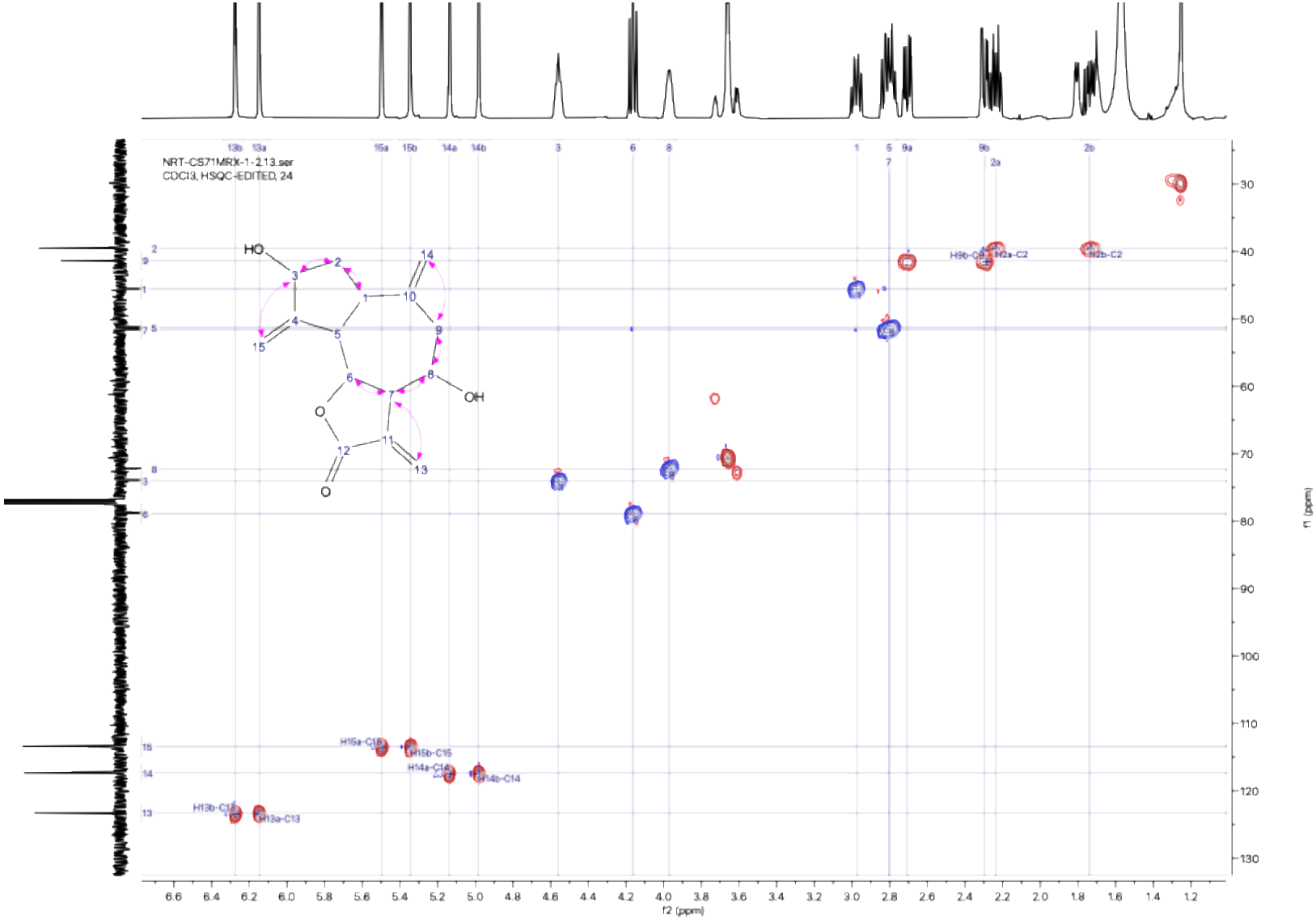


Figure S60: 1B HSQC 2D-NMR Spectrum

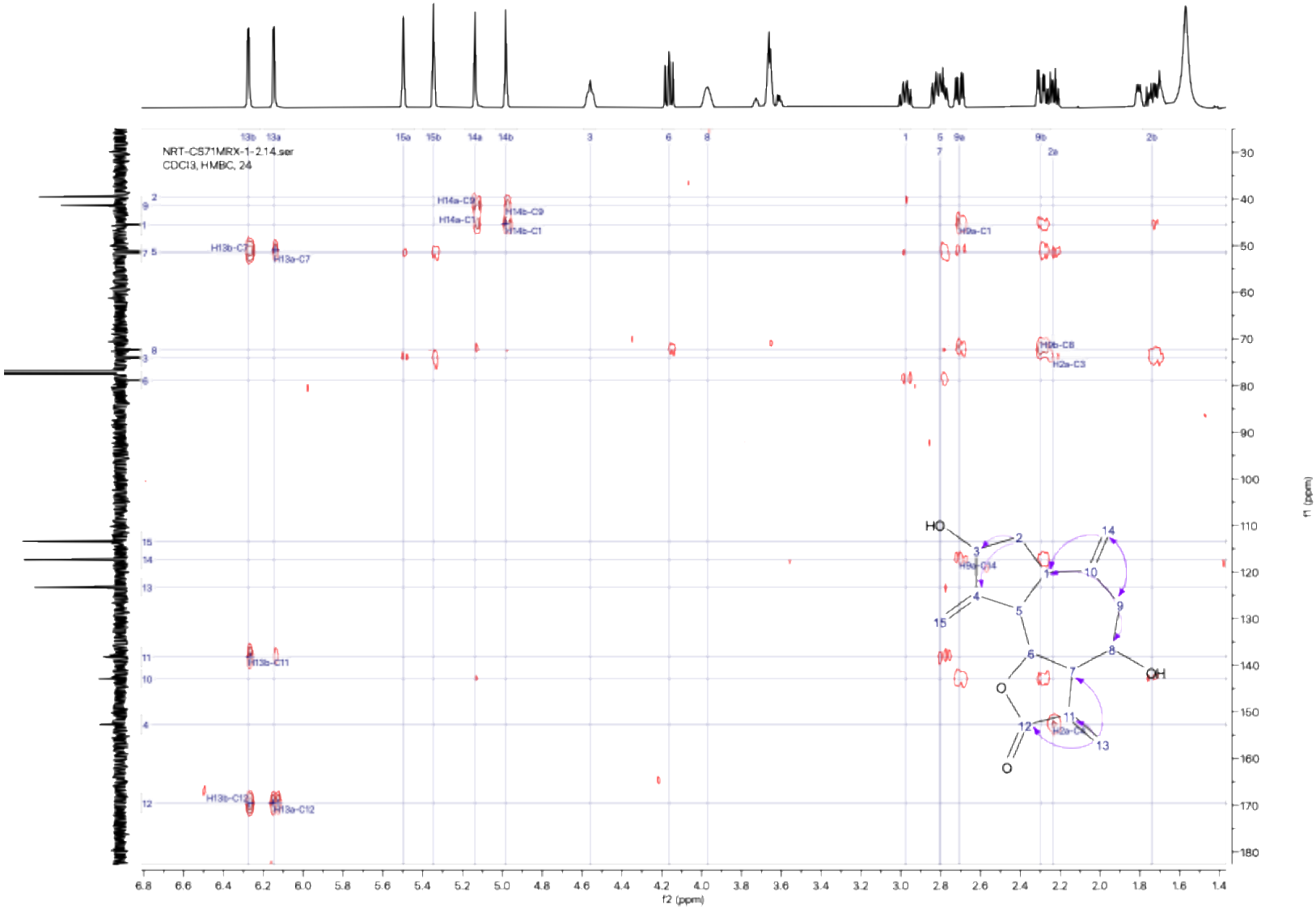


Figure S61: 1B HMBC 2D-NMR Spectrum