

Supporting Information

Molecular Networking-Guided Isolation of New Etzionin-Type Diketopiperazine Hydroxamates from the Persian Gulf Sponge *Cliona celata*

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Table S1. Putative identification of the compounds (cluster A and B) in the global molecular network of the crude extract of *Cliona celata*.

No.	<i>t_R</i> (min)	Parent mass <i>m/z</i>	Cluster	Molecular formula of the <i>m/z</i> [M + H] ⁺	Δ ppm	Key MS ² fragments	LoA*
1	5.43	459.332	A	C ₂₆ H ₄₃ N ₄ O ₃	0.0	205.097; 238.217; 343.238; 385.249; 441.297	3
2	4.97	473.293	A	C ₂₆ H ₄₁ N ₄ O ₄	0.4	221.093; 236.202; 357.213; 399.229; 456.887	3
3	5.42	475.315	A	C ₂₆ H ₄₃ N ₄ O ₄	0.1	221.093; 252.233; 359.233; 401.244; 458.302	5
4	5.44	489.332	A	C ₂₇ H ₄₅ N ₄ O ₄	0.2	221.093; 259.233; 359.233; 401.224; 471.333	5
5	6.03	491.305	A	C ₂₆ H ₄₃ N ₄ O ₅	0.4	214.181; 238.218; 375.228; 417.240; 474.229	3
6	5.54	503.359	A	C ₂₈ H ₄₇ N ₄ O ₄	0.4	221.093; 266.248; 359.233; 401.243; 485.347	3
7	5.86	503.359	A	C ₂₈ H ₄₇ N ₄ O ₄	1.2	221.093; 266.249; 373.249; 415.259; 485.347	3
8	5.35	505.338	A	C ₂₇ H ₄₅ N ₄ O ₅	-0.1	221.090; 238.216; 359.233; 401.240; 487.332	3
9	6.04	505.339	A	C ₂₇ H ₄₅ N ₄ O ₅	0.6	214.180; 252.232; 375.229; 417.246; 487.237	3
10	5.28	637.373	A	C ₃₂ H ₅₃ N ₄ O ₉	0.8	221.093; 238.277; 359.232; 401.245; 553.339	3
11	7.04	419.231	B	C ₂₃ H ₃₅ N ₂ O ₅	0.6	181.159; 196.170; 221.093; 359.233; 401.244	5
12	7.15	403.235	B	C ₂₃ H ₃₃ N ₂ O ₄	0.6	181.159; 205.096; 315.242; 343.237; 385.247	3

*: LoA (Level of Assignment); 1: Accurate mass matched to database-Tentative assignment, 2: Accurate mass matched to database and tandem MS spectrum matched to *in silico* fragmentation pattern, 3: Tandem MS spectrum matched to database or literature, 4: RT matched to standard compound, 5: MS/MS spectrum matched to standard compound.

Manual dereplication was performed considering the parent mass, biological source, retention time, elemental composition analysis, and predicated fragmentation patterns.

The MS² fragmentation pattern of a molecule was predicated on the Competitive Fragmentation Modeling for Metabolite Identification (CFM-ID) platform (<http://cfmid.wishartlab.com>) and compared with our experimental data.

Figure S1. Global molecular network of the crude extract of *Cliona celata*.

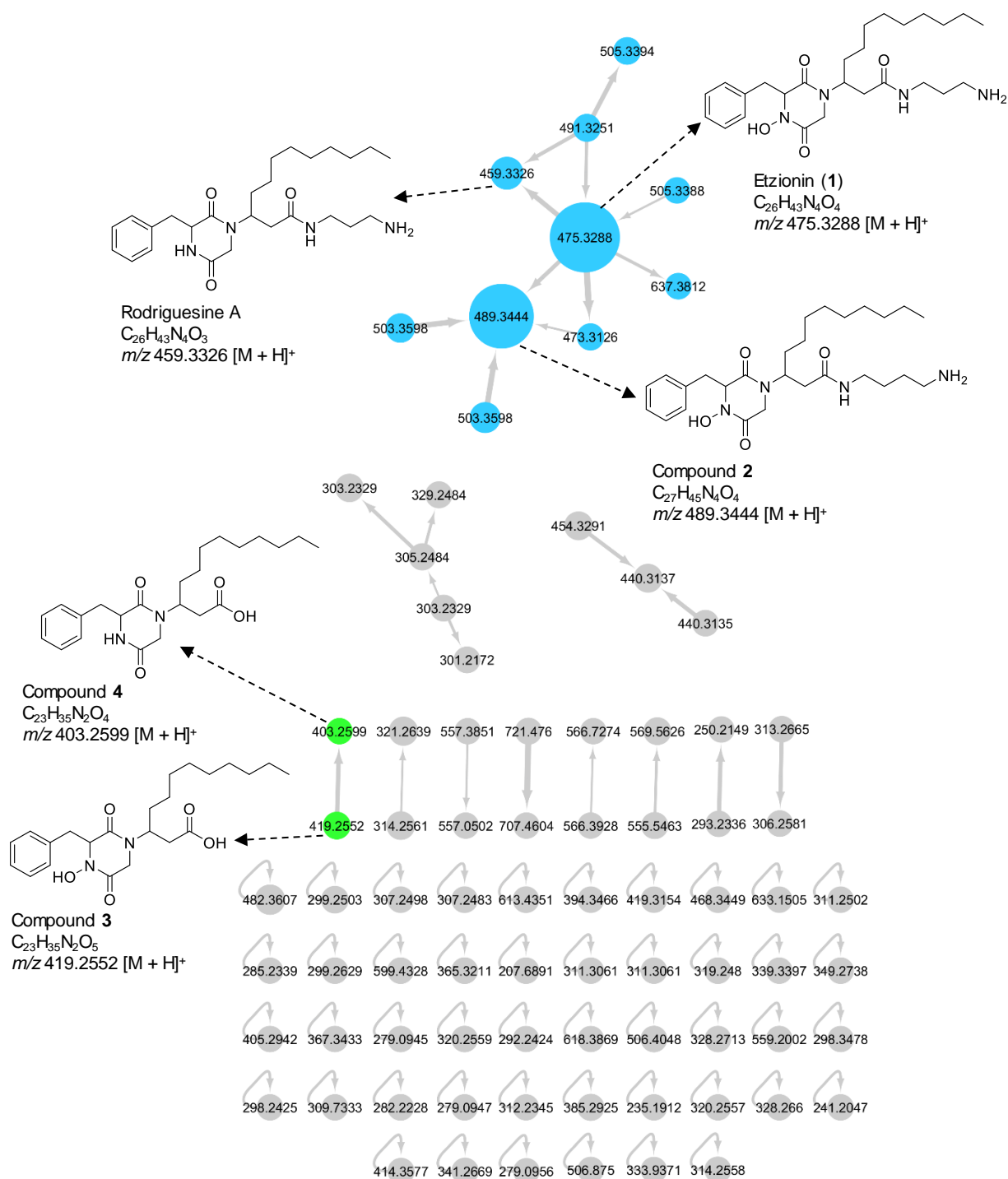


Figure S2. UPLC-HRMS chromatogram of the crude extract from *Cliona celata*.

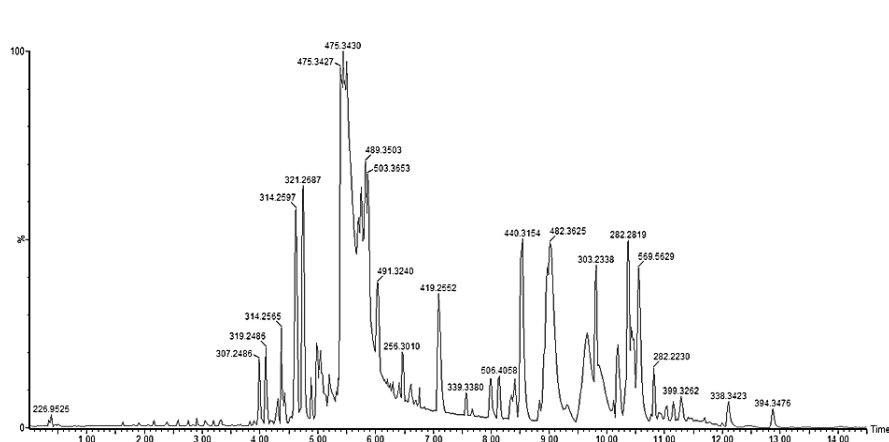


Figure S3. ^1H NMR spectrum of the fraction F3 from *Cliona celata* (600 MHz, CD_3OD)

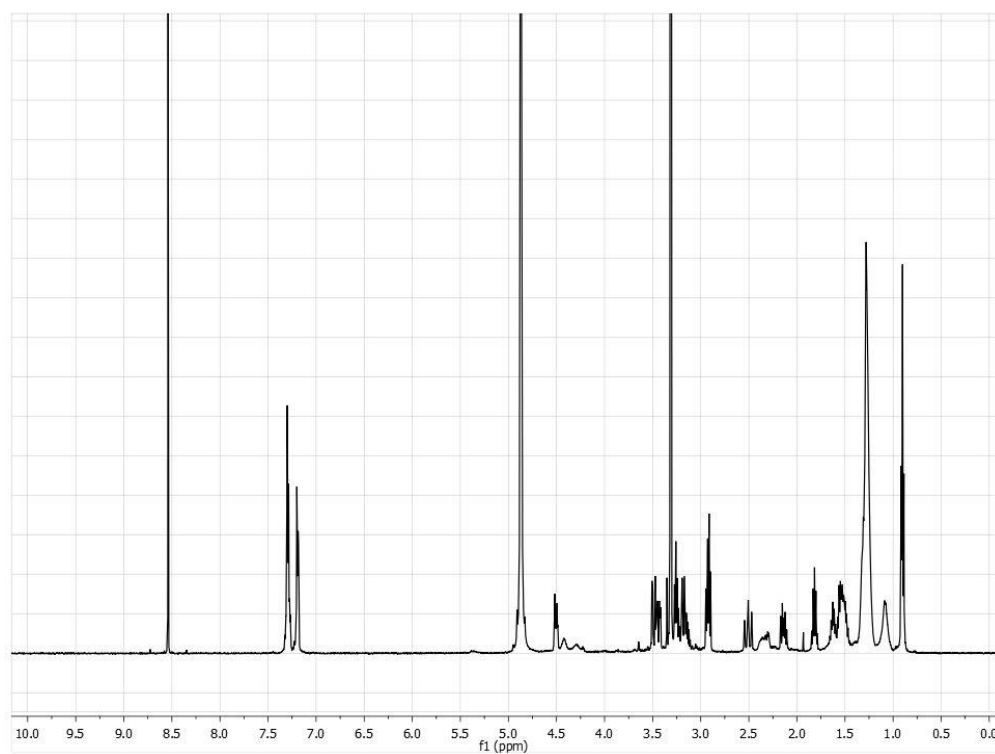


Figure S4. ^1H NMR spectrum of compound **1** (TFA salt, 600 MHz, CD_3OD).

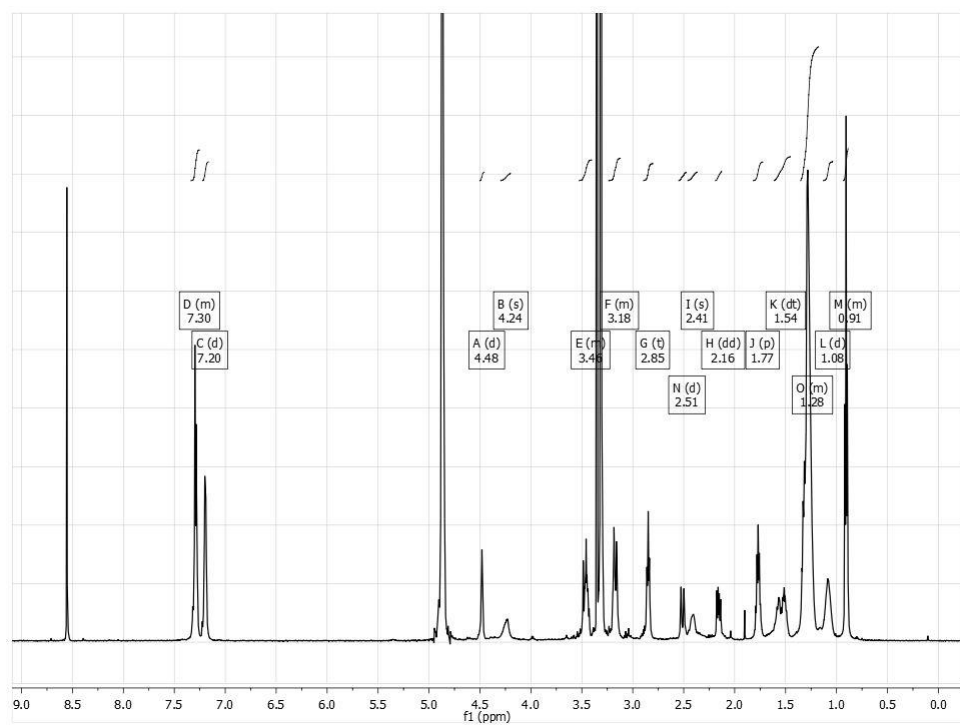


Figure S5. ^{13}C NMR spectrum of compound **1** (TFA salt, 150 MHz, CD_3OD).

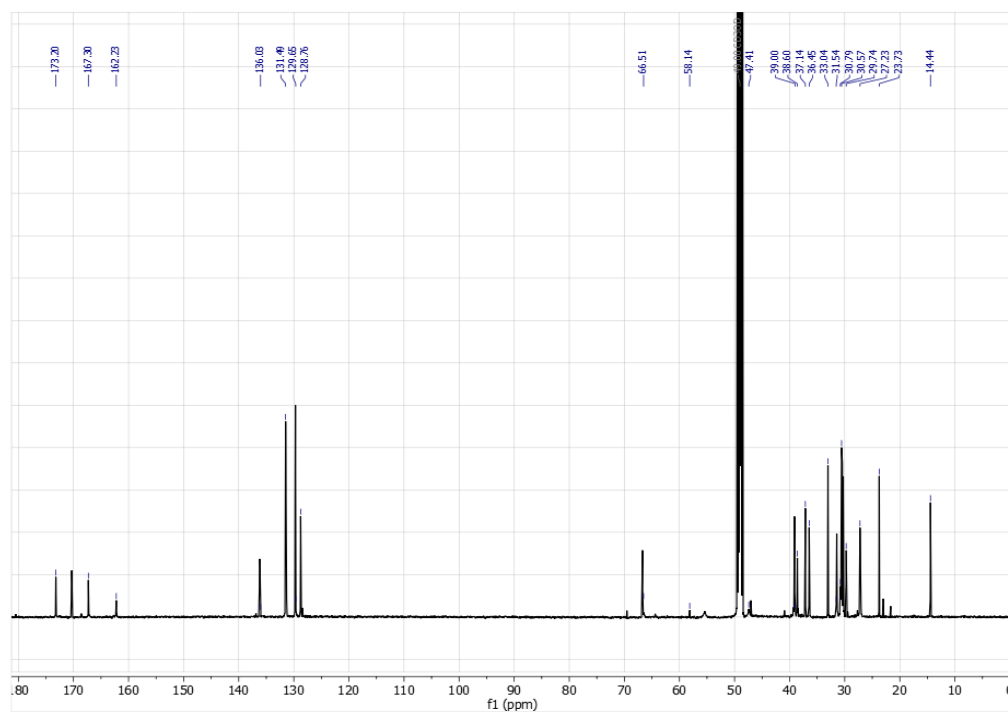


Figure S6. HSQC spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD, non-uniform sampling).

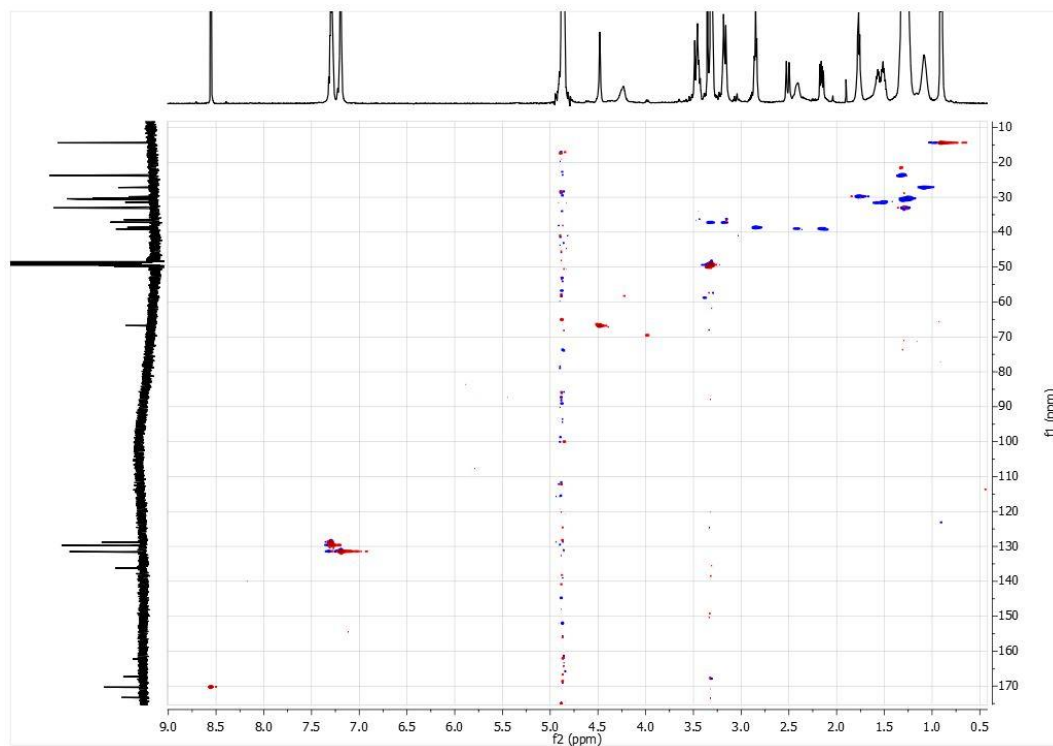


Figure S7. HSQC spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD, traditional planes).

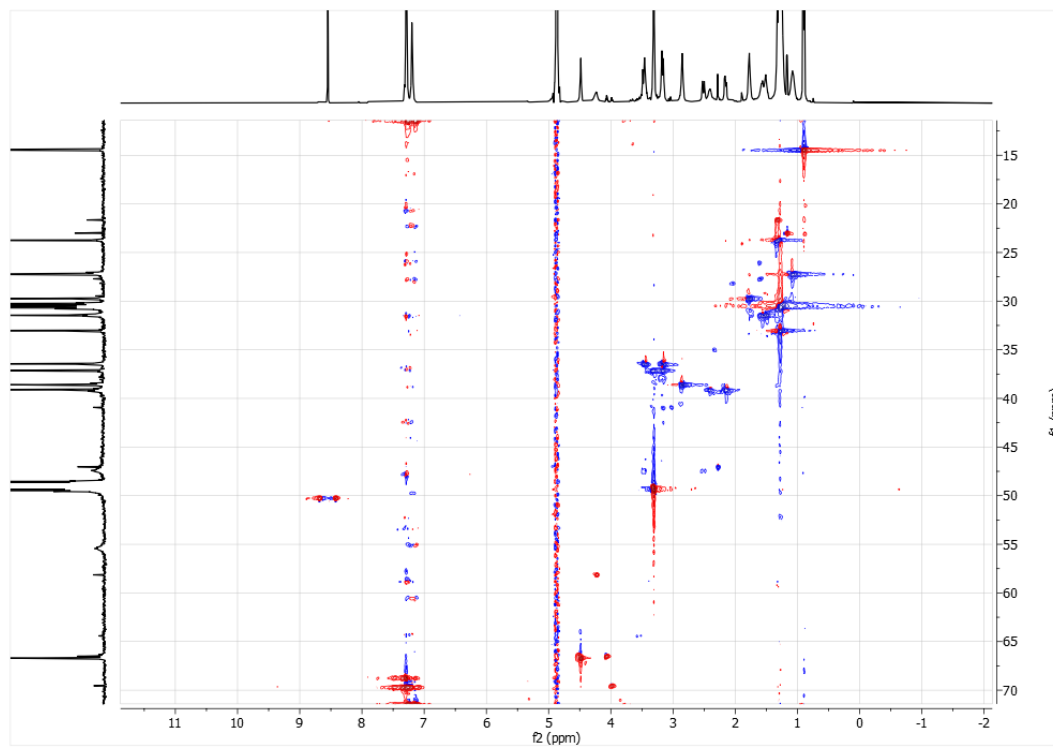


Figure S8. HMBC spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD, non-uniform sampling).

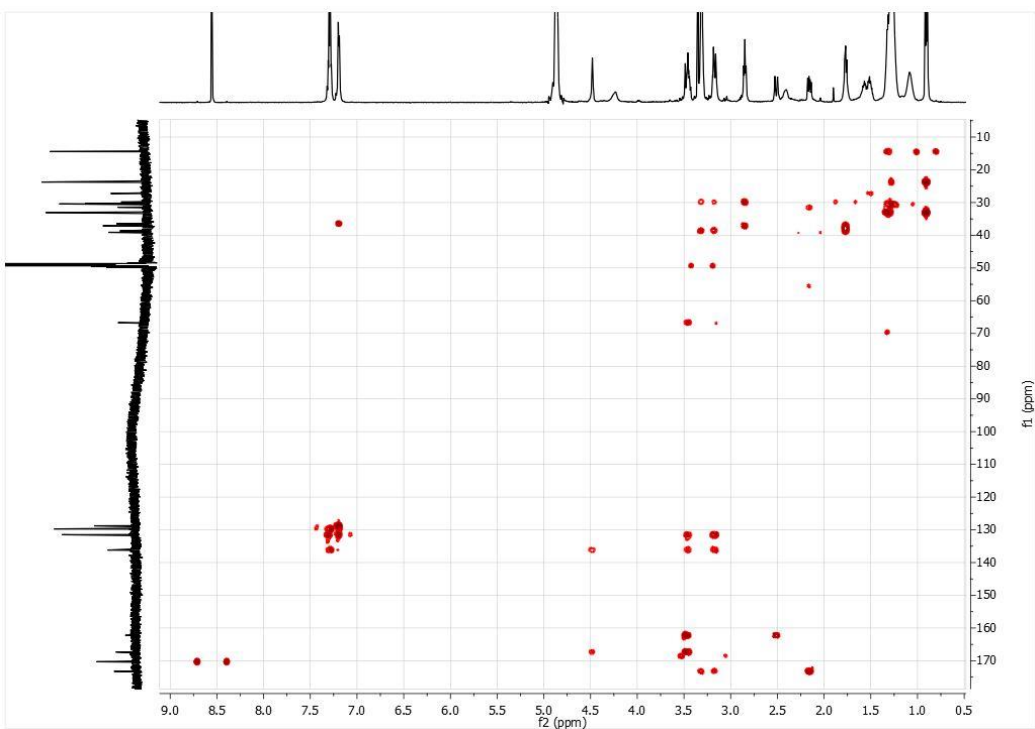


Figure S9. HMBC spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD, traditional planes).

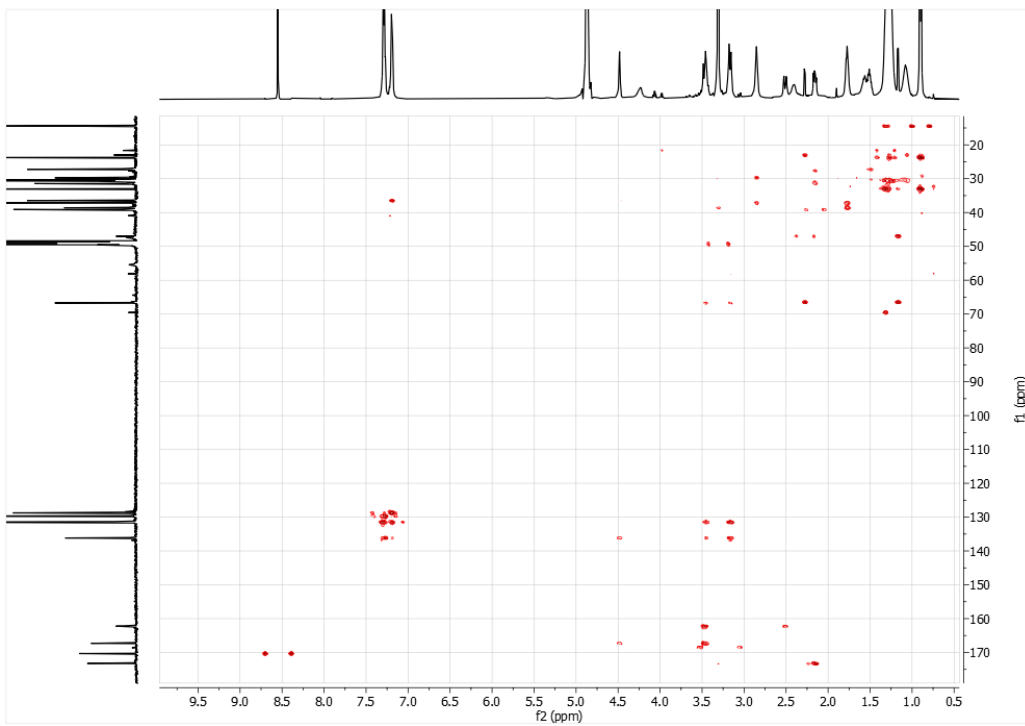


Figure S10. COSY spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD).

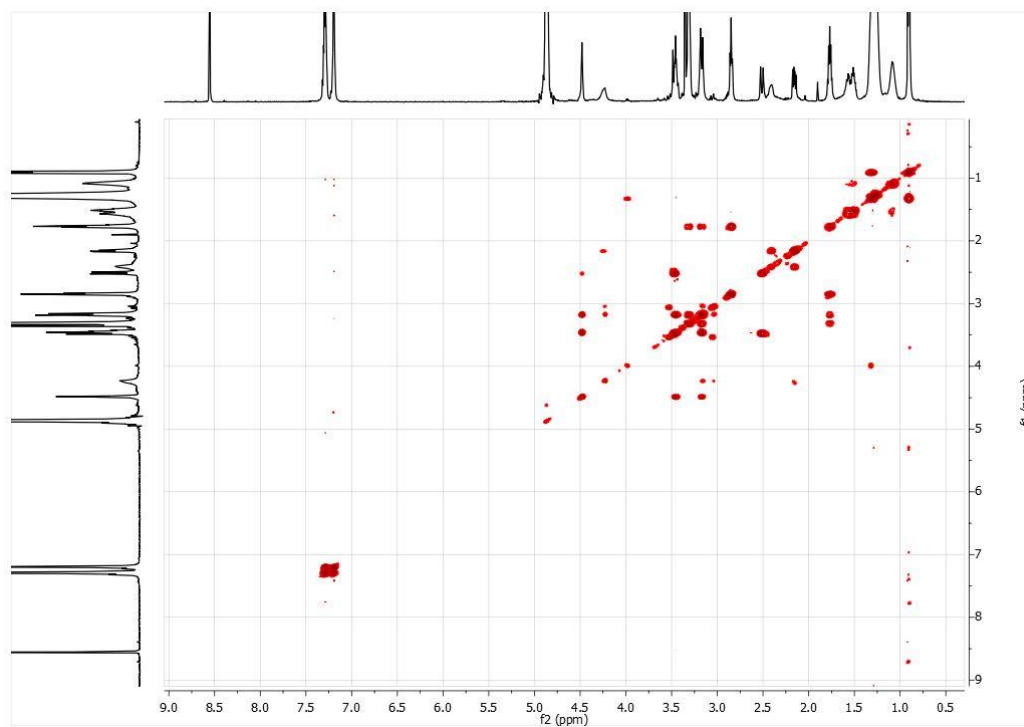


Figure S11. NOESY spectrum of compound **1** (TFA salt, 600 MHz, CD₃OD).

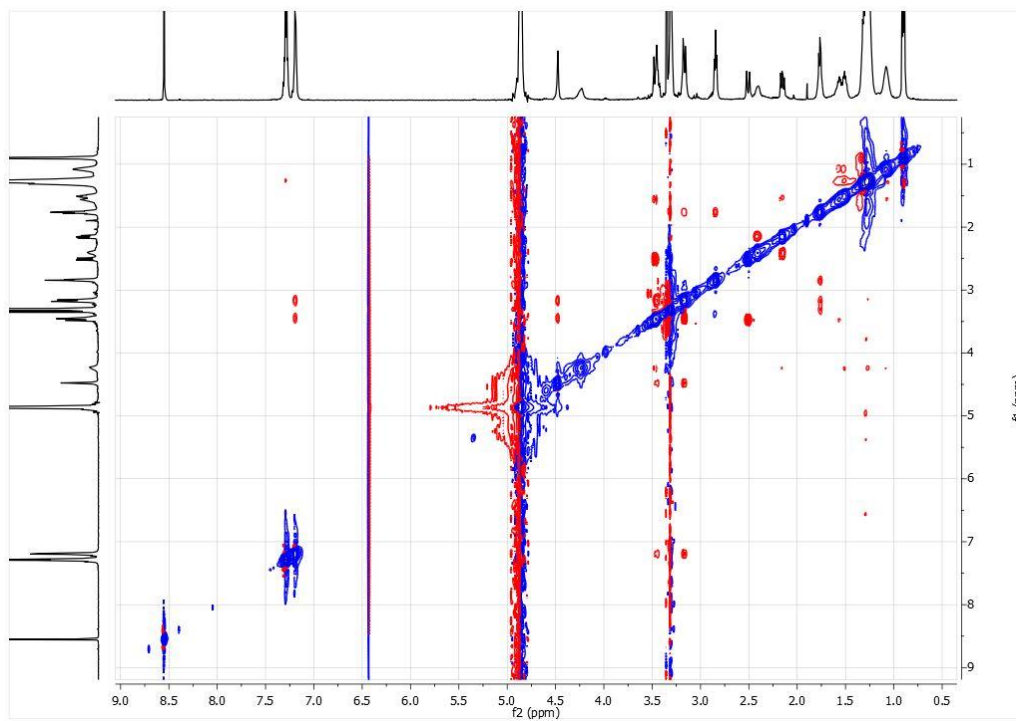


Figure S12. HR-ESIMS spectrum of compound **1**.

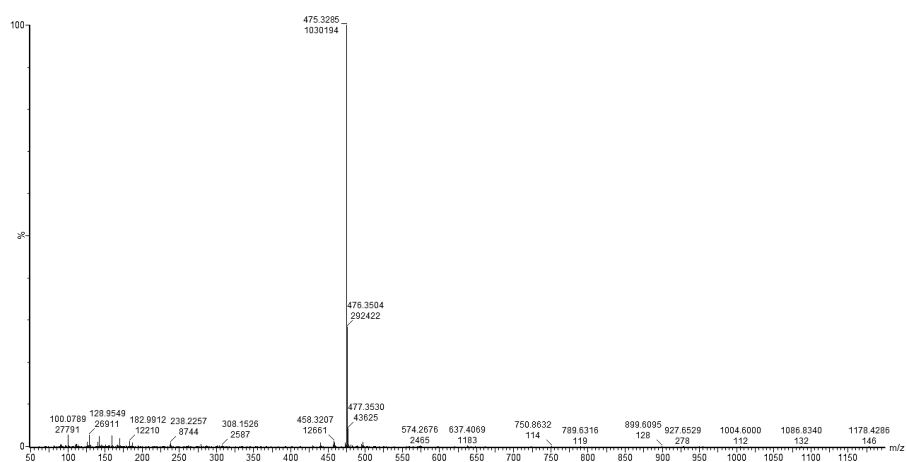


Figure S13. ^1H NMR spectrum of compound **2** (TFA salt, 600 MHz, CD_3OD).

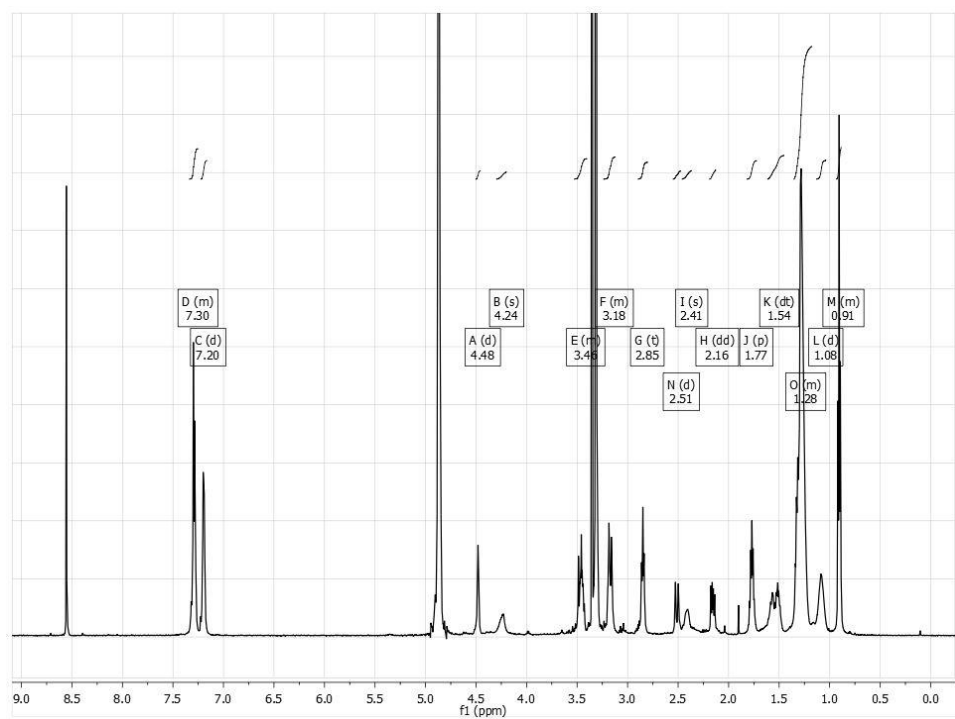


Figure S14. ^{13}C NMR spectrum of compound **2** (TFA salt, 150 MHz, CD_3OD).

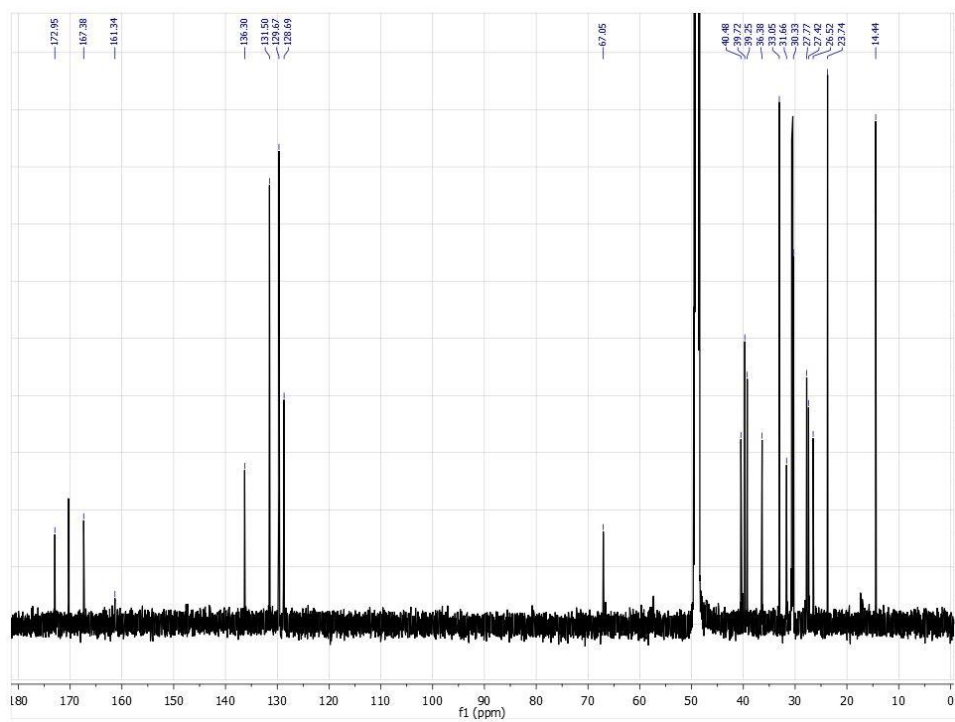


Figure S15. HSQC spectrum of compound **2** (TFA salt, 600 MHz, CD₃OD).

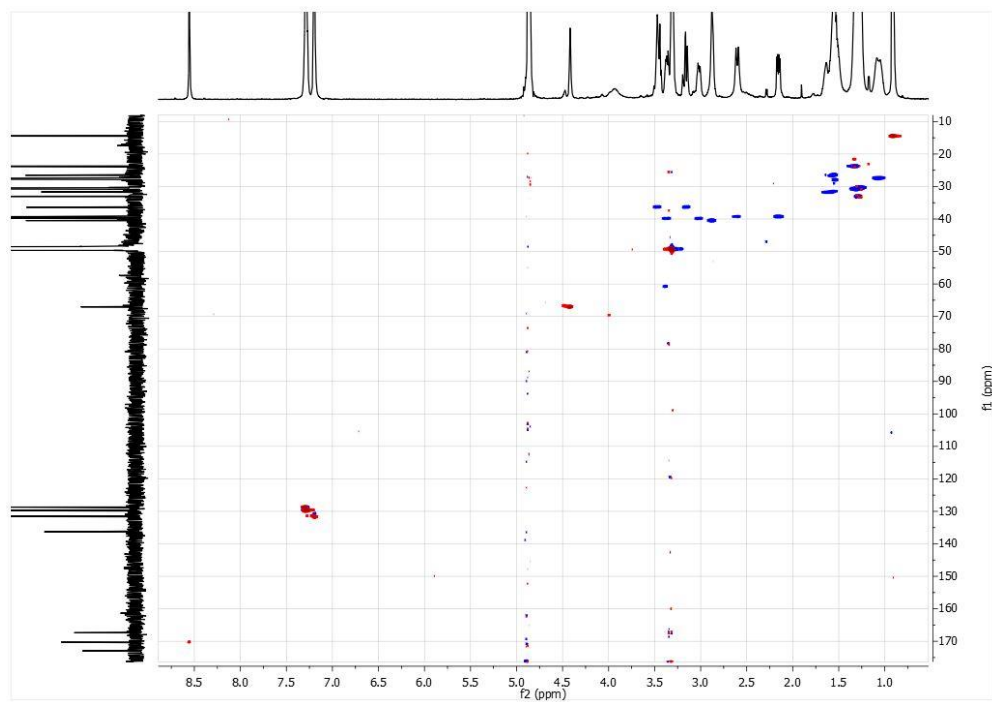


Figure S16. HMBC spectrum of compound **2** (TFA salt, 600 MHz, CD₃OD).

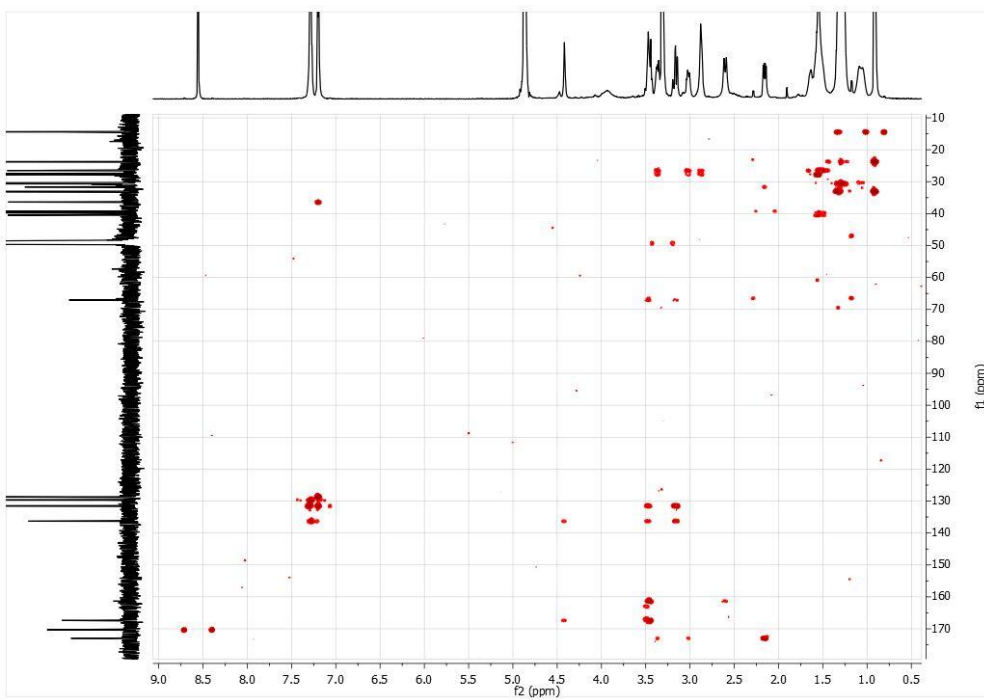


Figure S17. COSY spectrum of compound **2** (TFA salt, 600 MHz, CD₃OD).

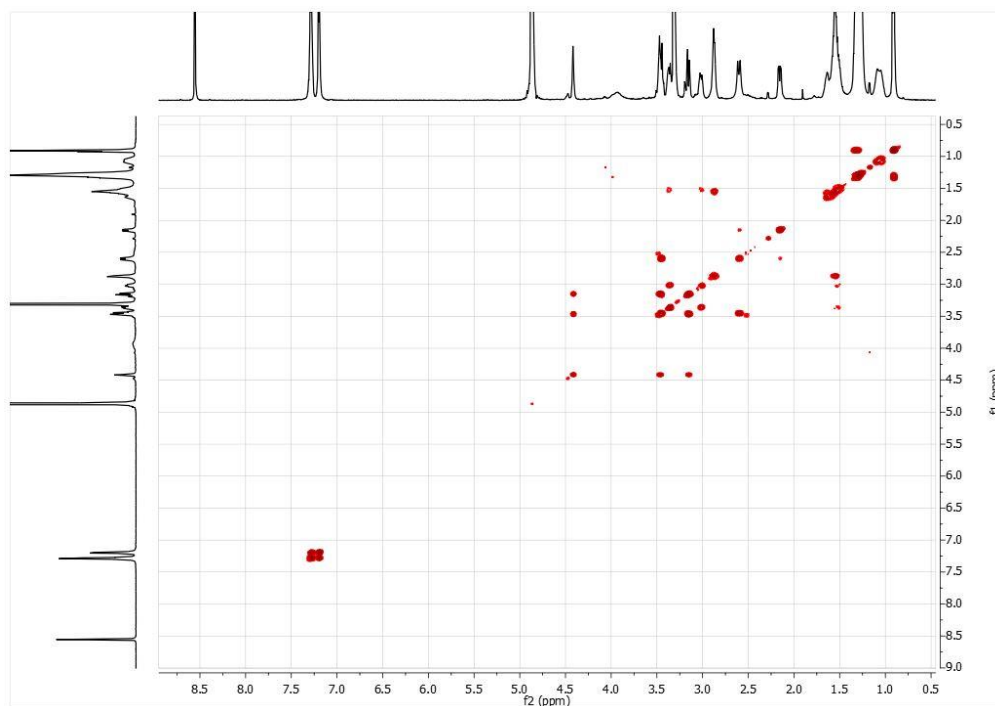


Figure S18. NOESY spectrum of compound **2** (TFA salt, 600 MHz, CD₃OD).

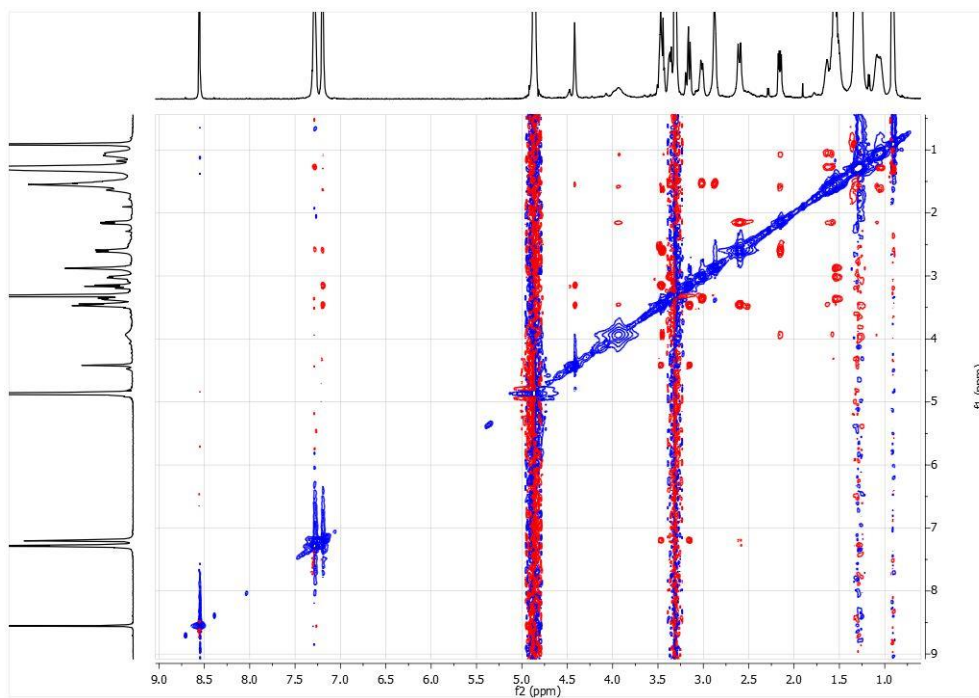


Figure S19. HR-ESIMS spectrum of compound **2**.

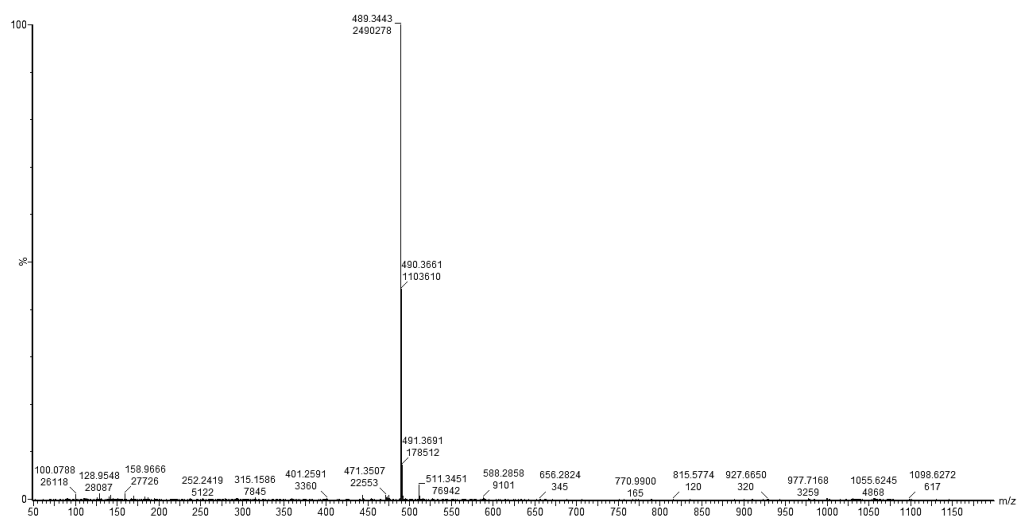


Figure S20. ^1H NMR spectrum of compound **3** (TFA salt, 600 MHz, CD_3OD).

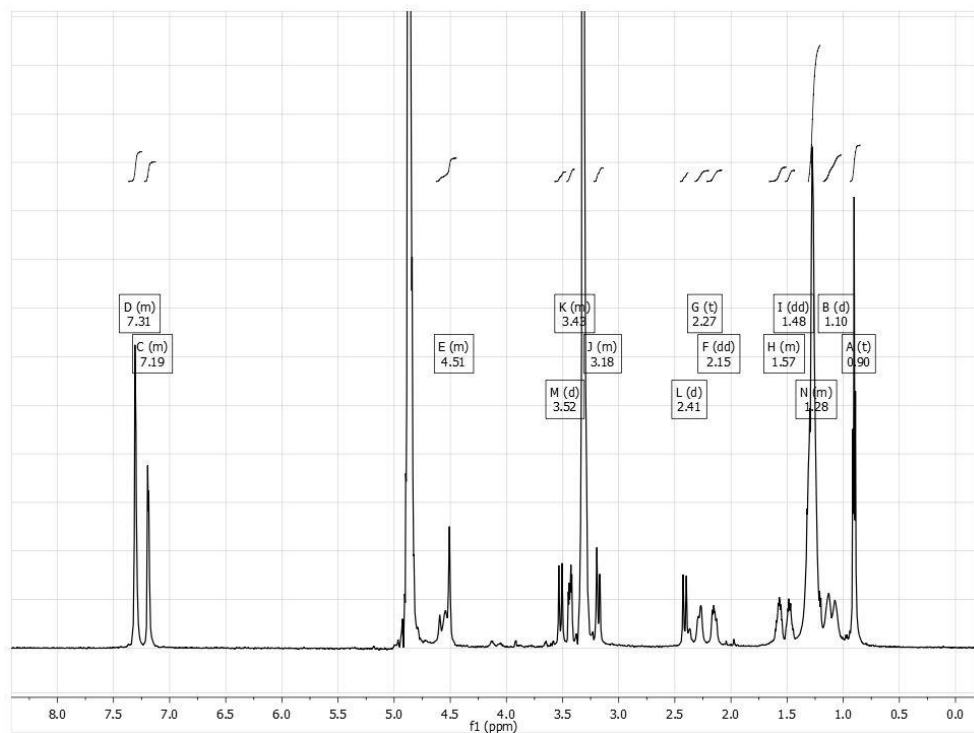


Figure S21. ^{13}C NMR spectrum of compound **3** (TFA salt, 150 MHz, CD_3OD).

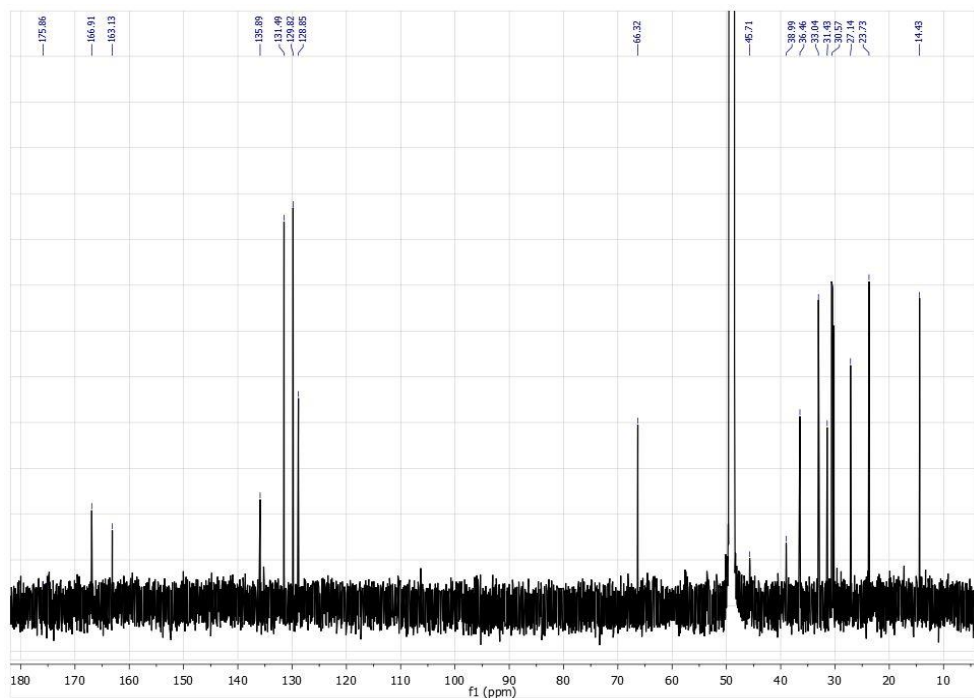


Figure S22. HSQC spectrum of compound **3** (TFA salt, 600 MHz, CD₃OD).

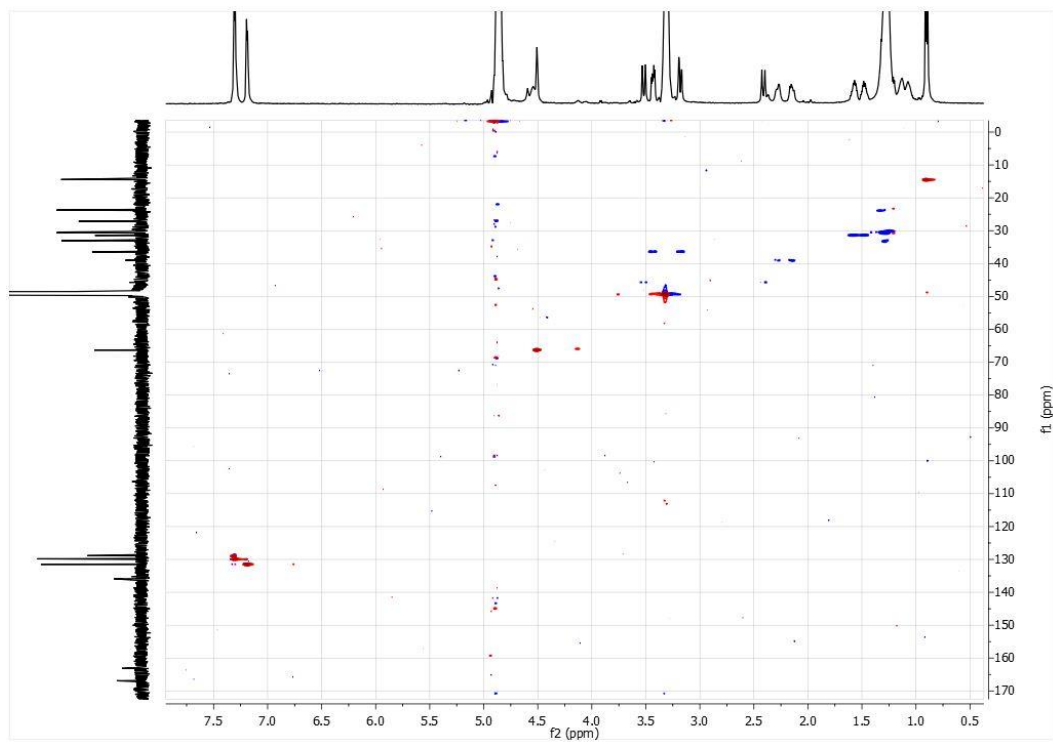


Figure S23. HMBC spectrum of compound **3** (TFA salt, 600 MHz, CD₃OD).

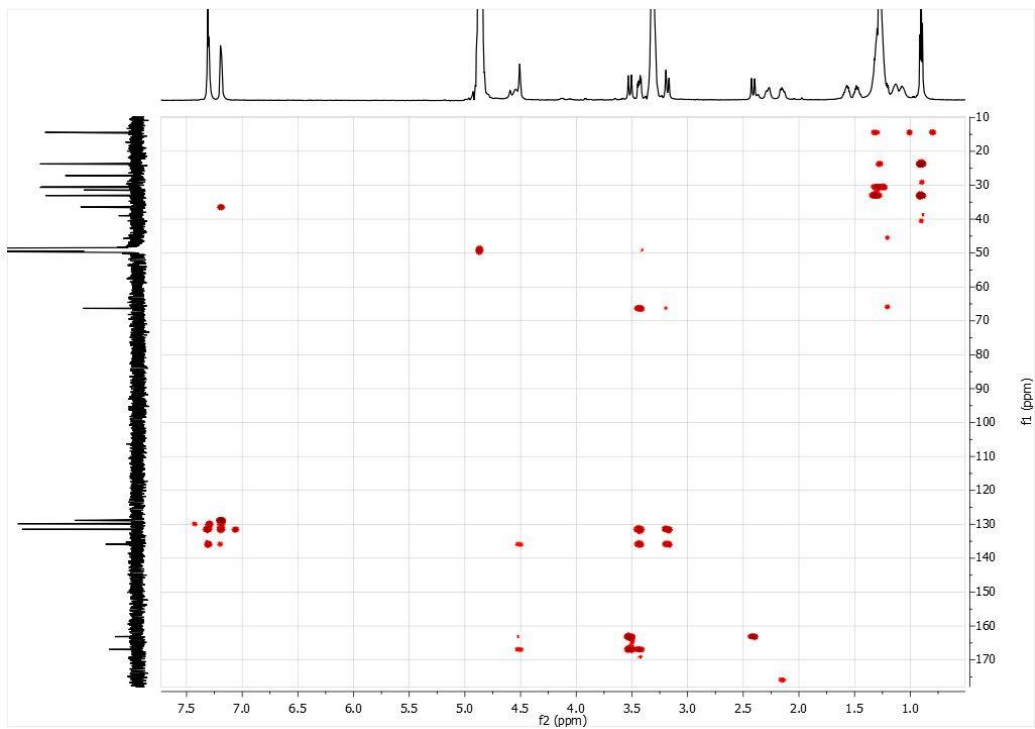


Figure S24. COSY spectrum of compound **3** (TFA salt, 600 MHz, CD₃OD).

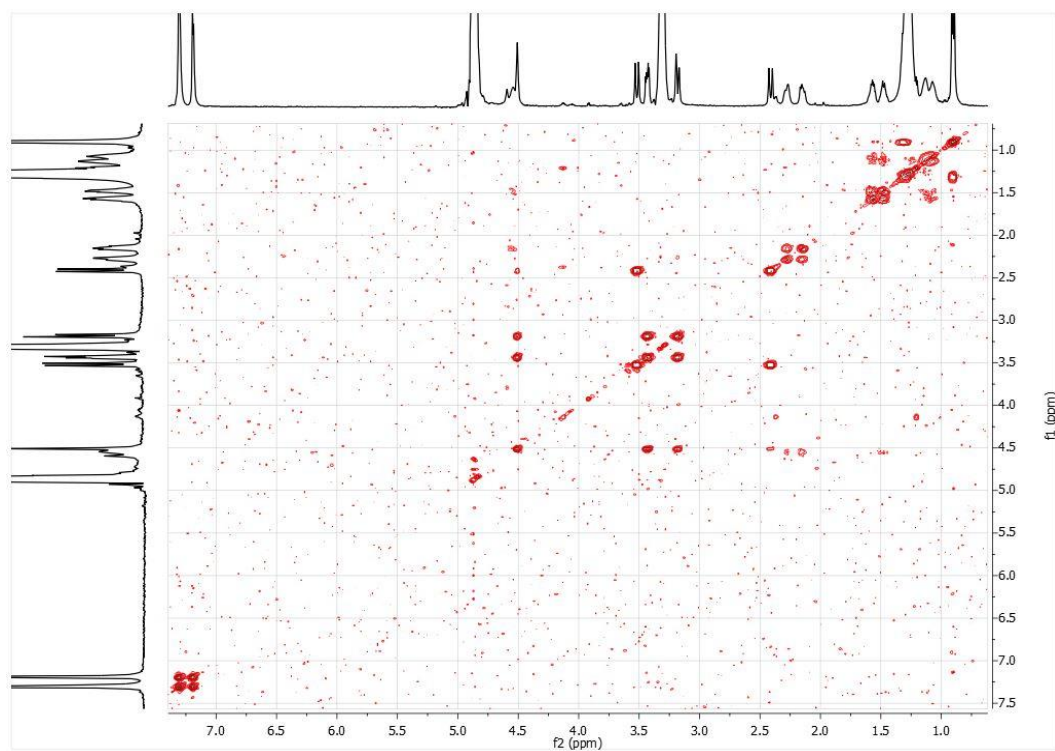


Figure S25. NOESY spectrum of compound **3** (TFA salt, 600 MHz, CD₃OD).

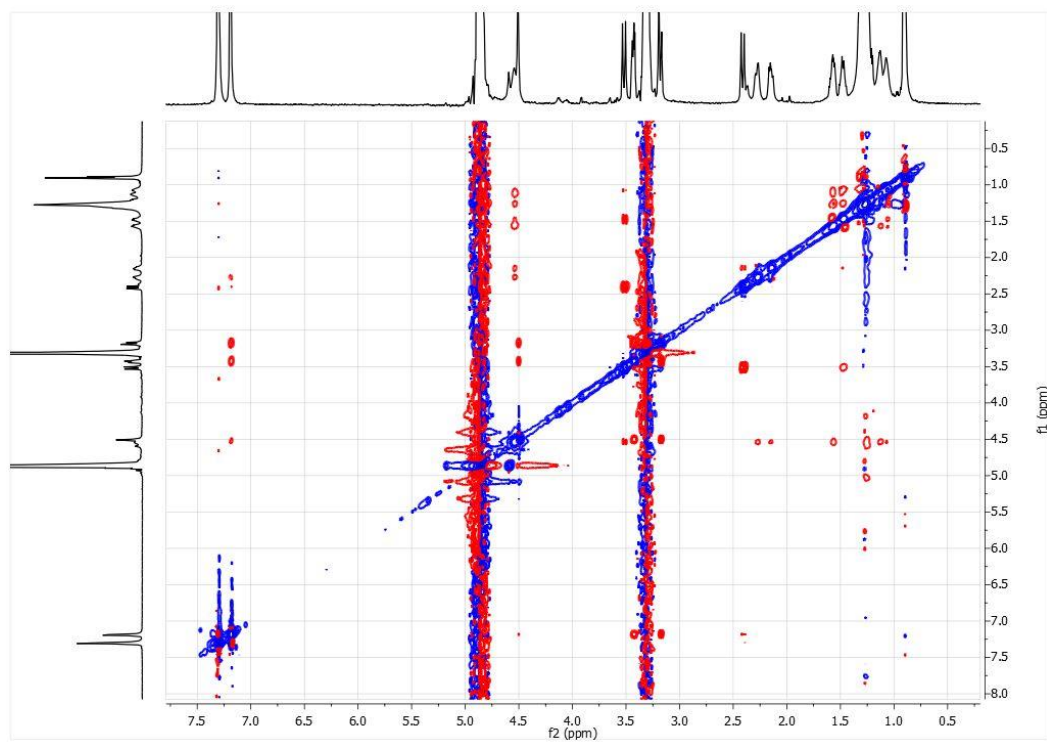


Figure S26. HR-ESIMS spectrum of compound **3**.

