Supporting Information

Hydroxy-*neo*-Clerodanes and 5,10-*seco*-*neo*-Clerodanes from *Salvia decora*

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Supporting Information

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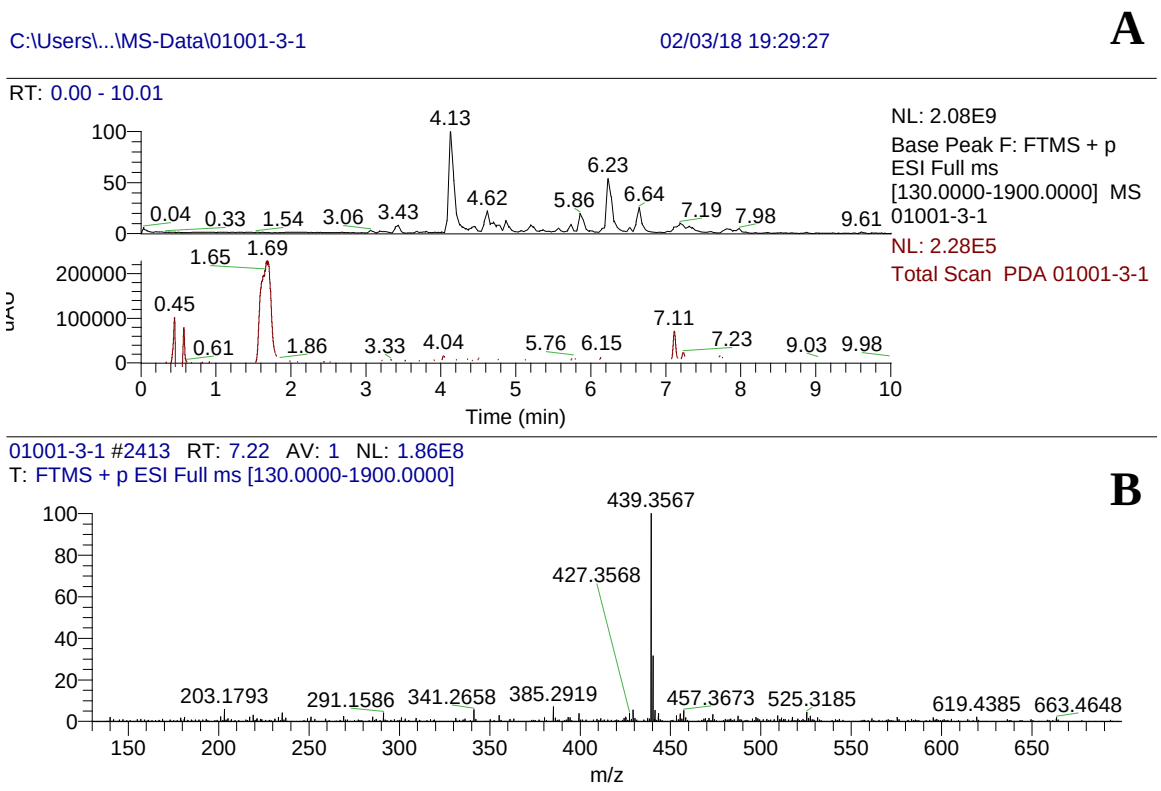


Figure S1. UPLC−PDA−HRMS−MS/MS data for primary fraction 1. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peak at 7.22 min.

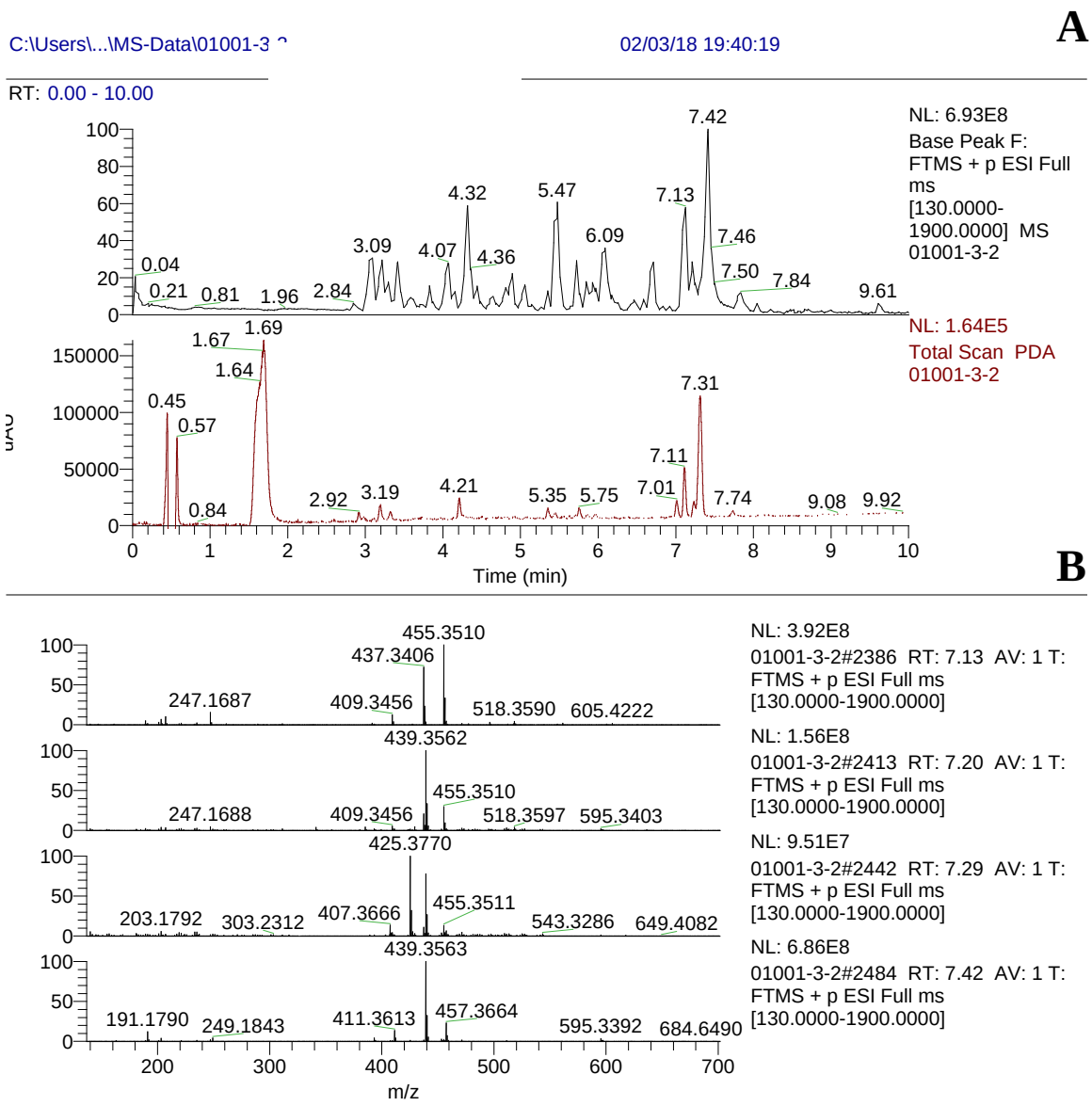


Figure S2. UPLC−PDA−HRMS−MS/MS data for primary fraction 2. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 7.13, 7.20, 7.29 and 7.42 min.

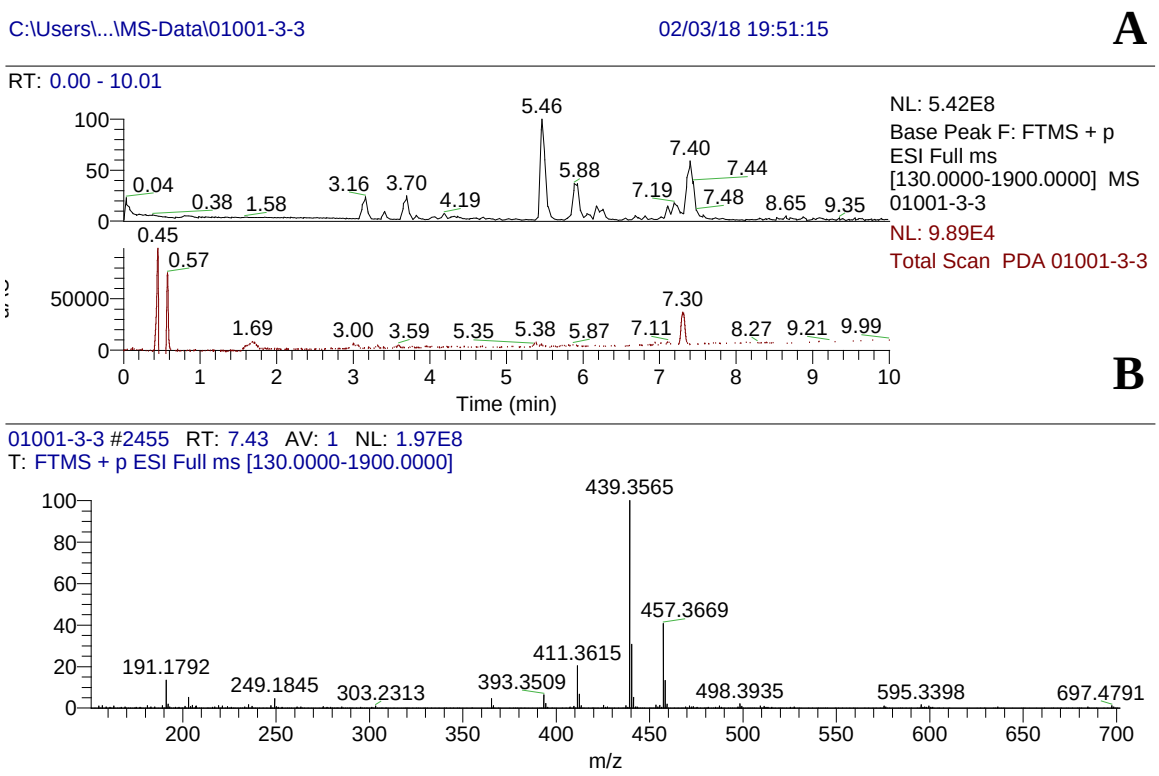


Figure S3. UPLC−PDA−HRMS−MS/MS data for primary fraction 3. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peak at 7.43 min.

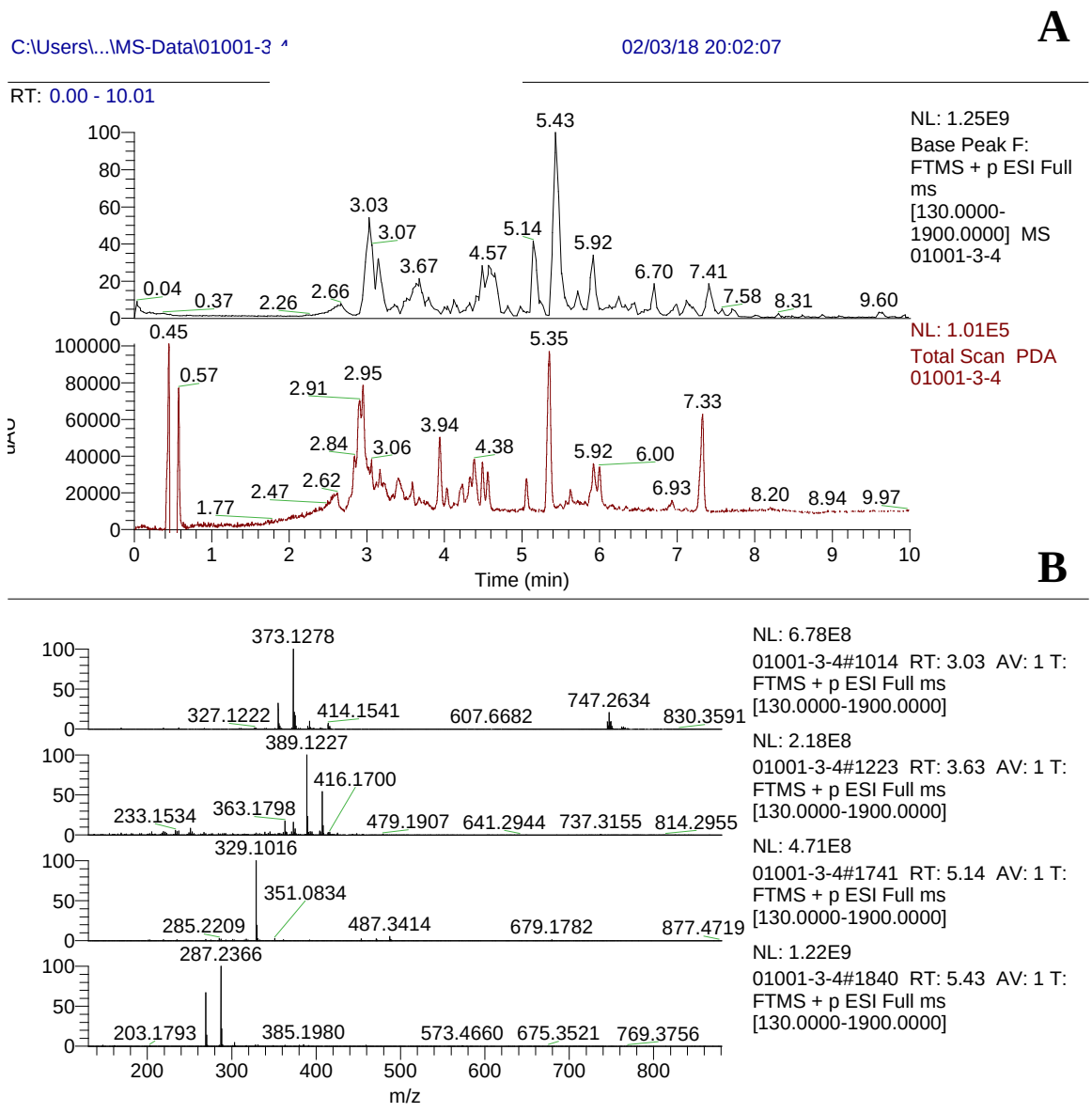


Figure S4. UPLC−PDA−HRMS−MS/MS data for primary fraction 4. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.03, 3.63, 5.14 and 5.43 min.

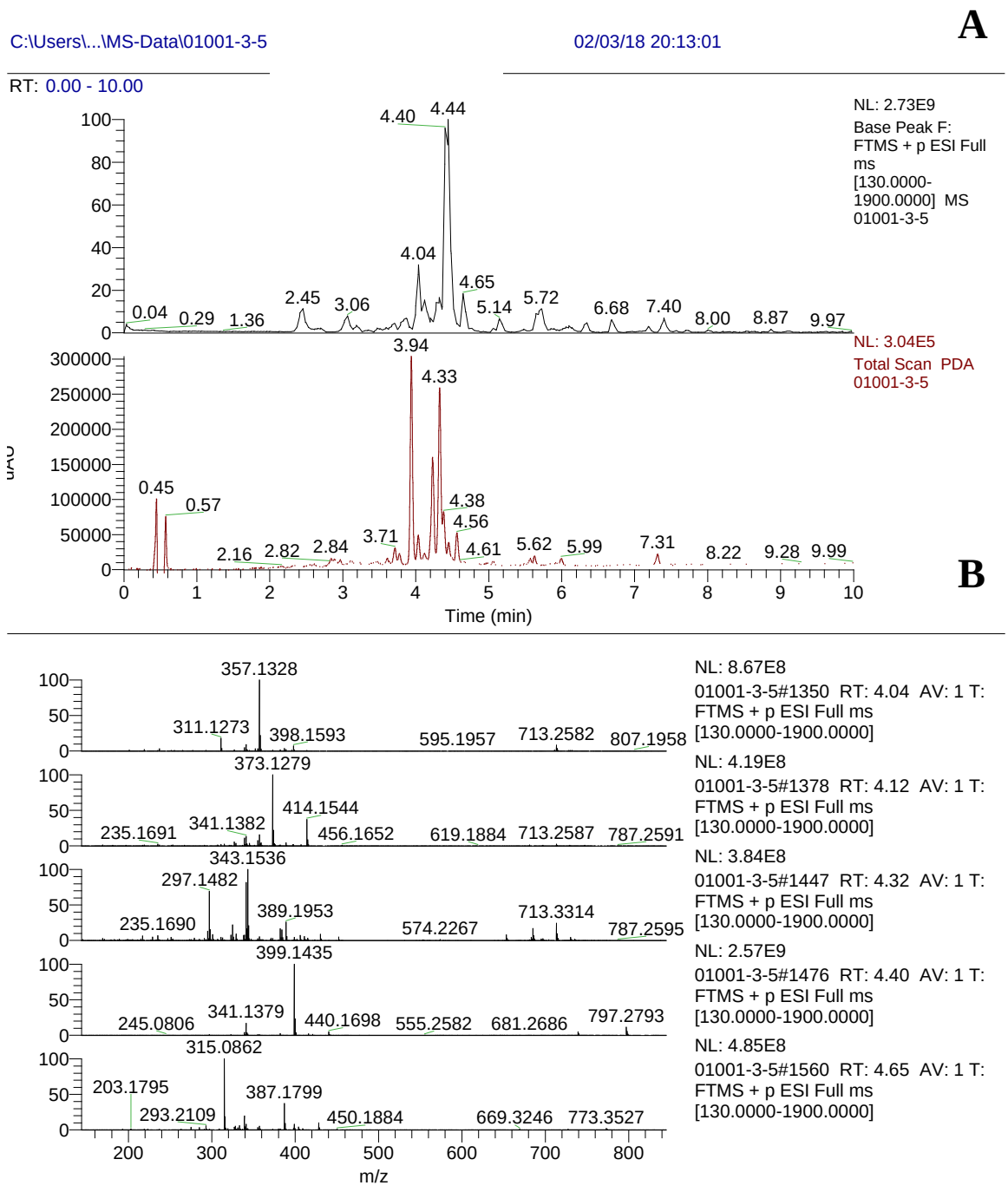


Figure S5. UPLC−PDA−HRMS−MS/MS data for primary fraction 5. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 4.04, 4.12, 4.32, 4.40 and 4.65 min.

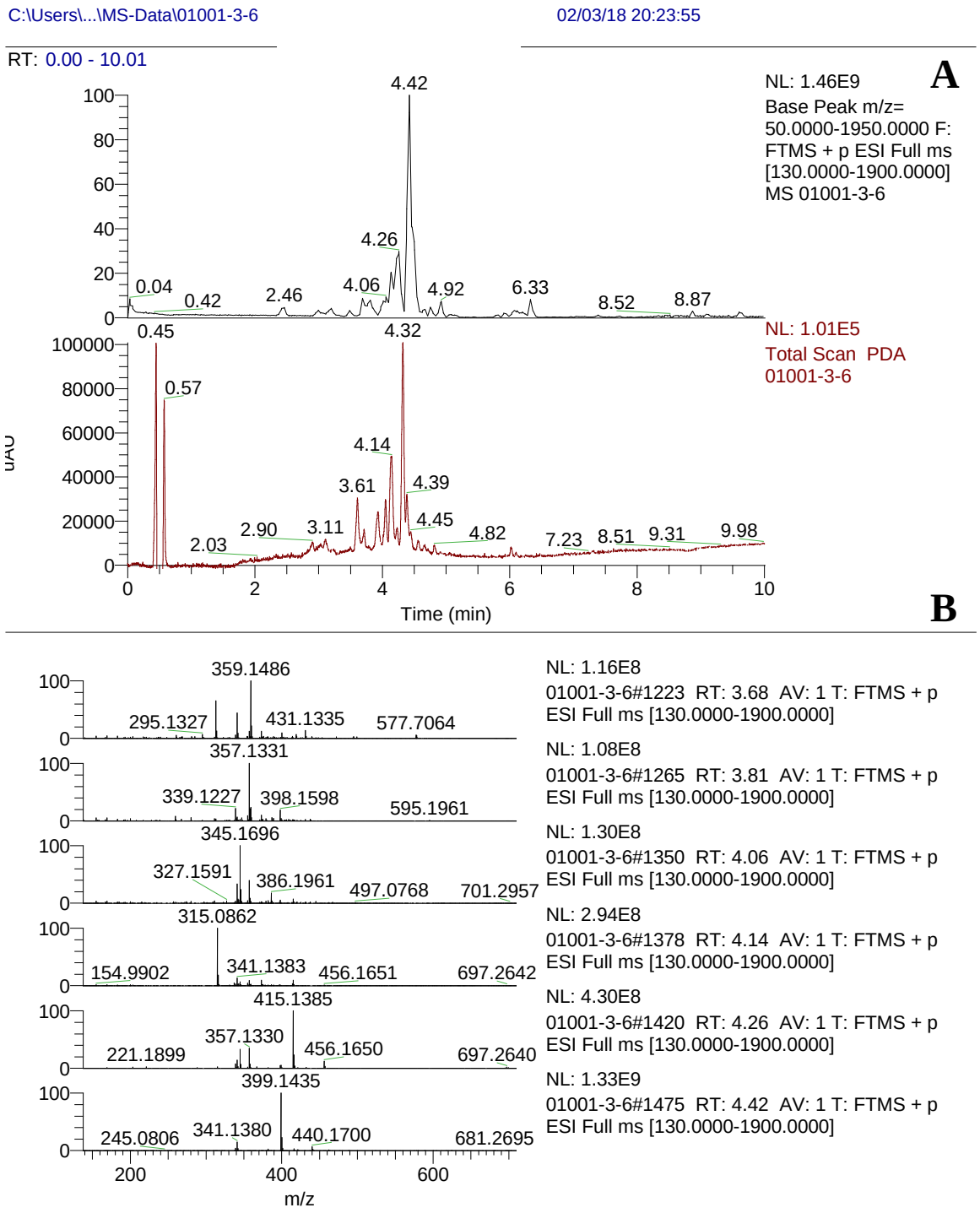


Figure S6. UPLC−PDA−HRMS−MS/MS data for primary fraction 6. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.68, 3.81, 4.06, 4.14, 4.26 and 4.42 min.

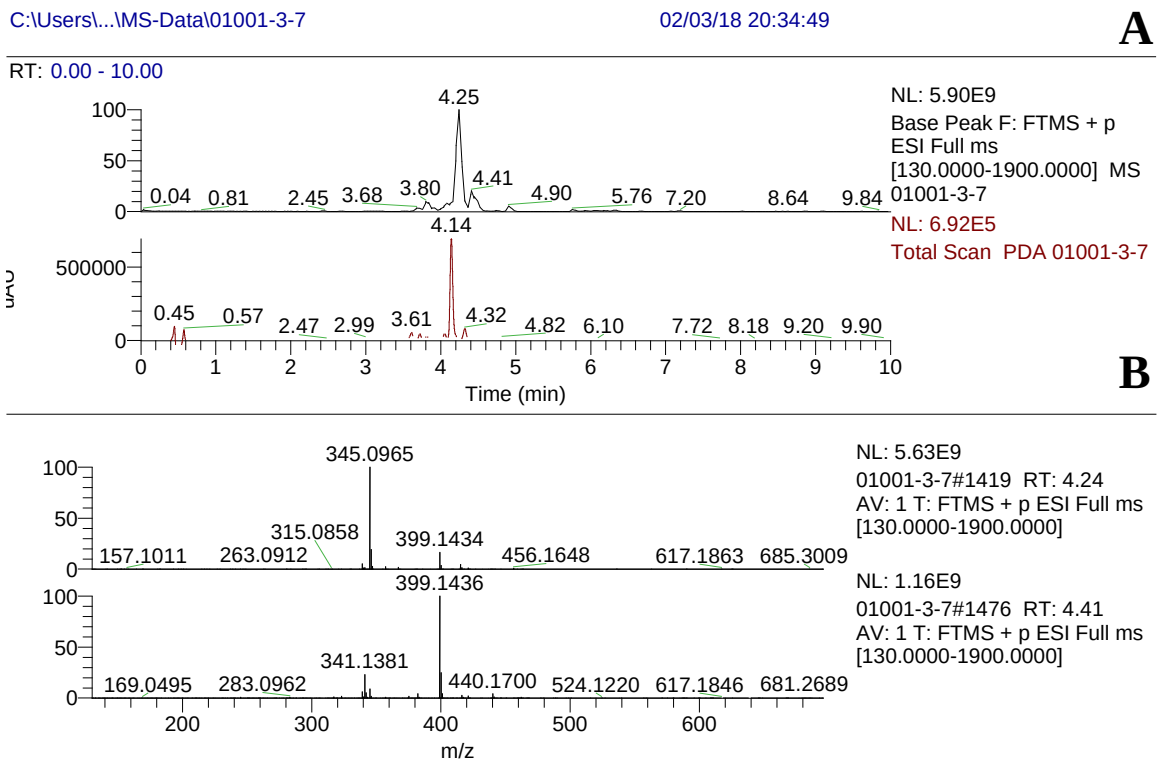


Figure S7. UPLC−PDA−HRMS−MS/MS data for primary fraction 7. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 4.24 and 4.41 min.

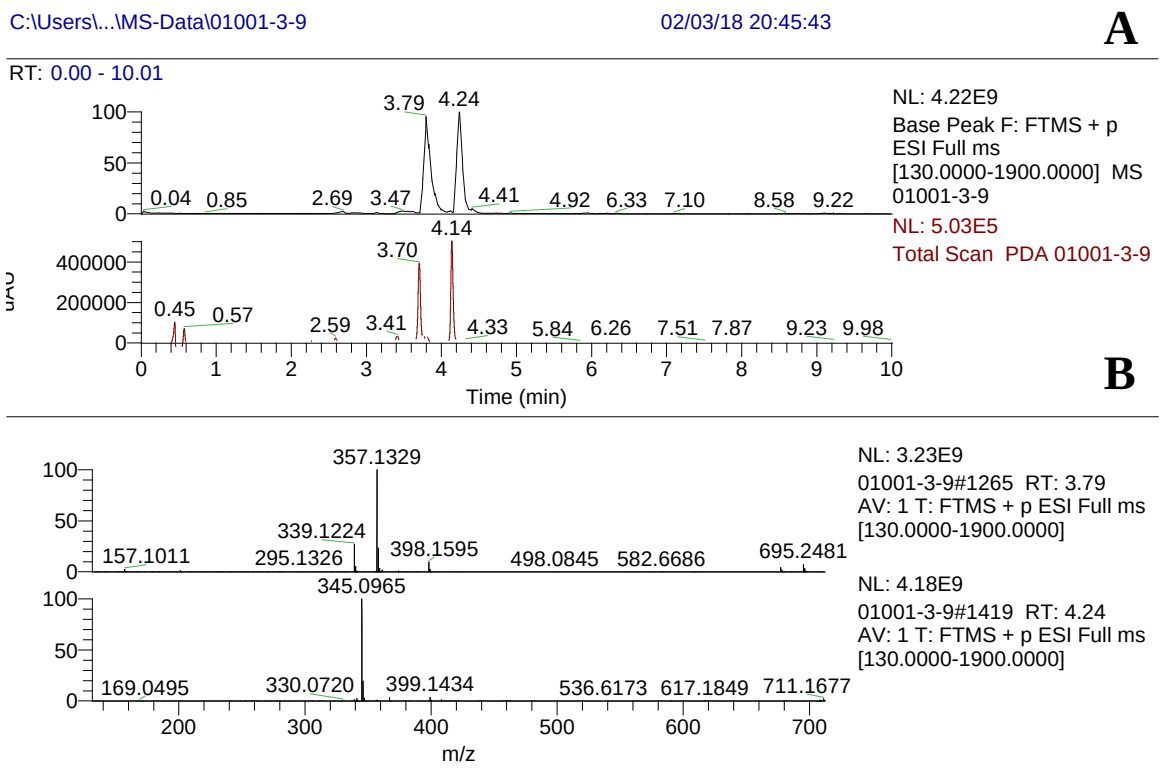


Figure S8. UPLC−PDA−HRMS−MS/MS data for primary fraction 9. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.79 and 4.24 min.

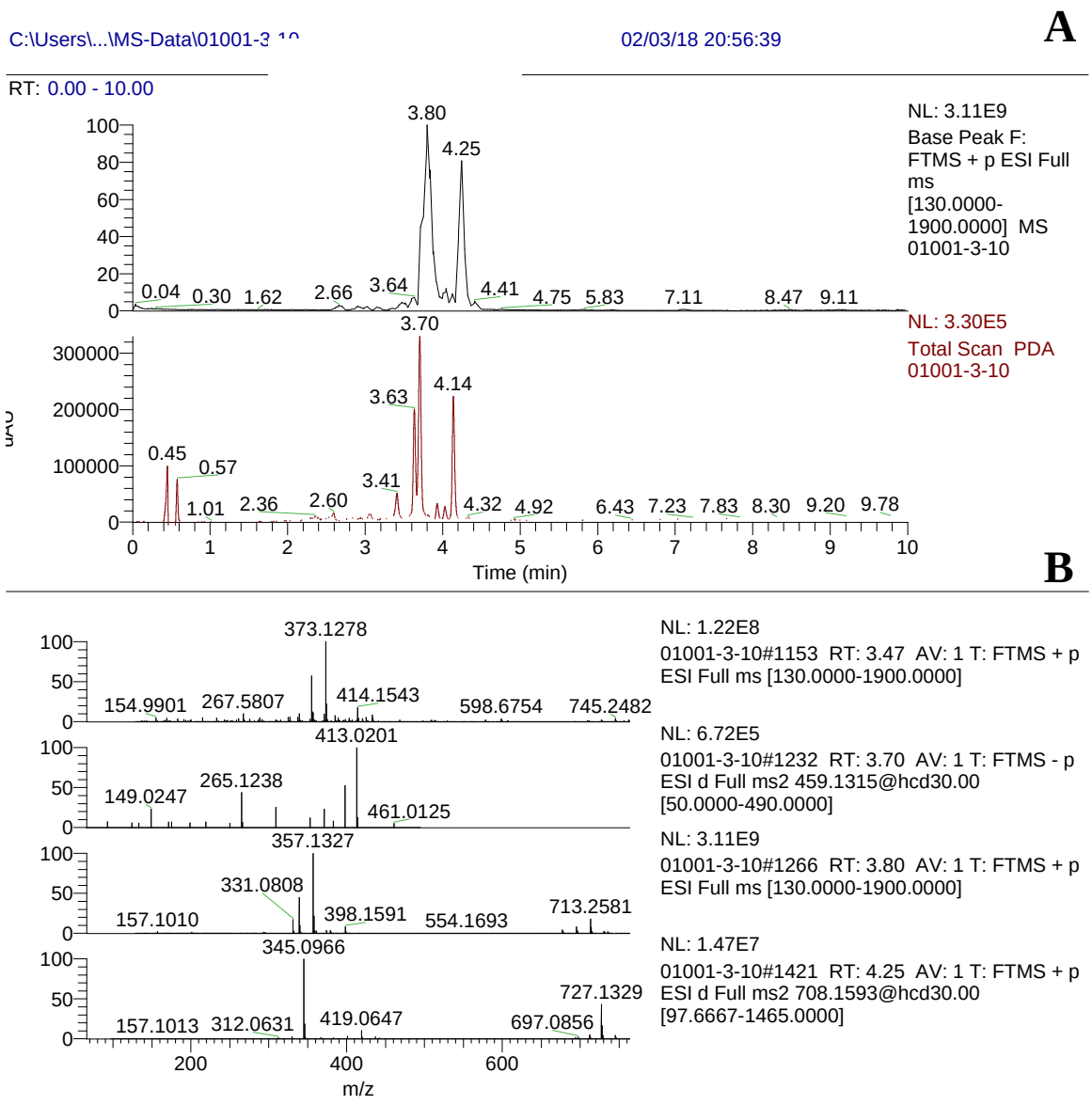


Figure S9. UPLC−PDA−HRMS−MS/MS data for primary fraction 10. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.47, 3.70, 3.80 and 4.25 min.

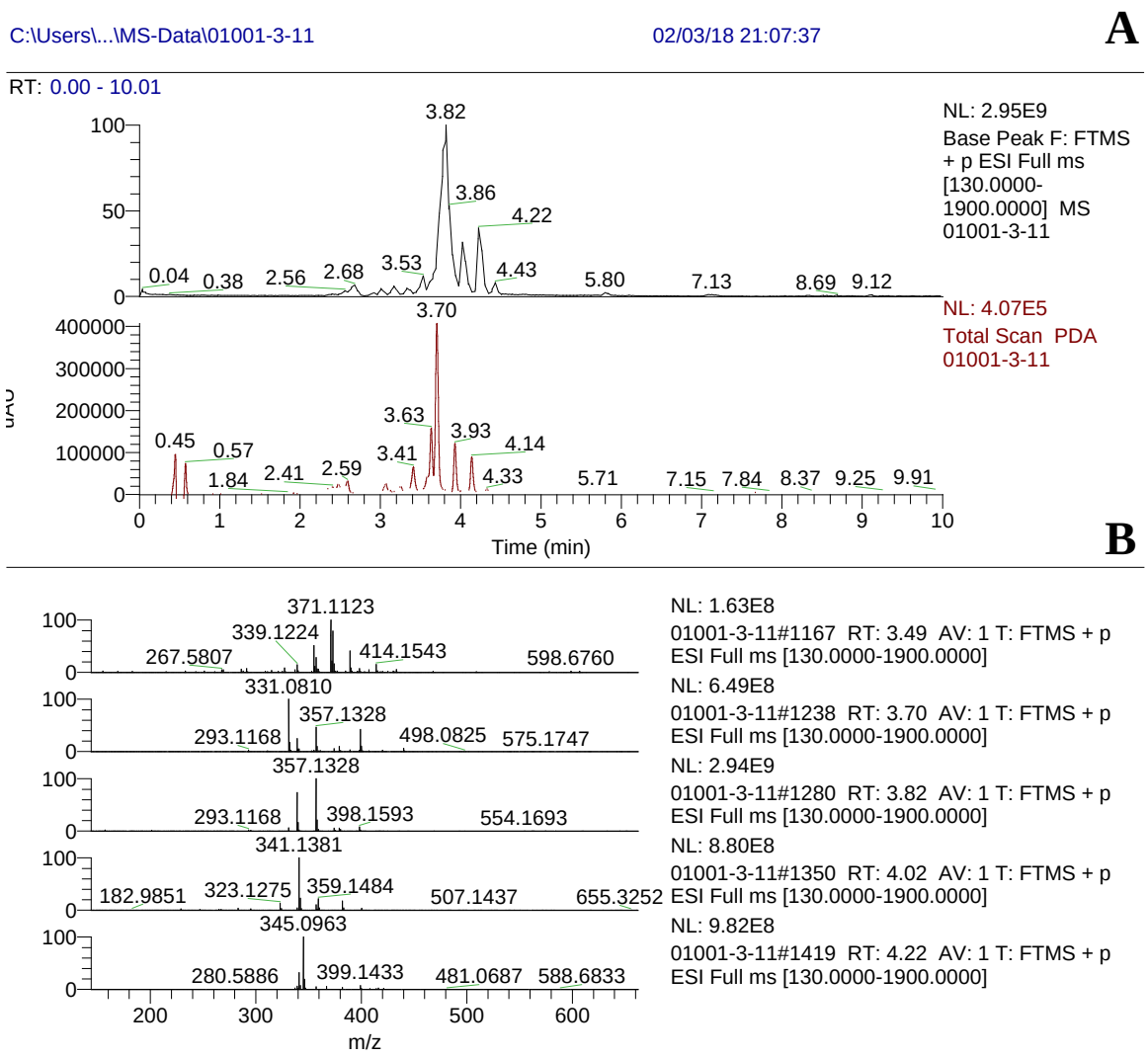


Figure S10. UPLC−PDA−HRMS−MS/MS data for primary fraction 11. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.49, 3.70, 3.82, 4.02 and 4.22 min.

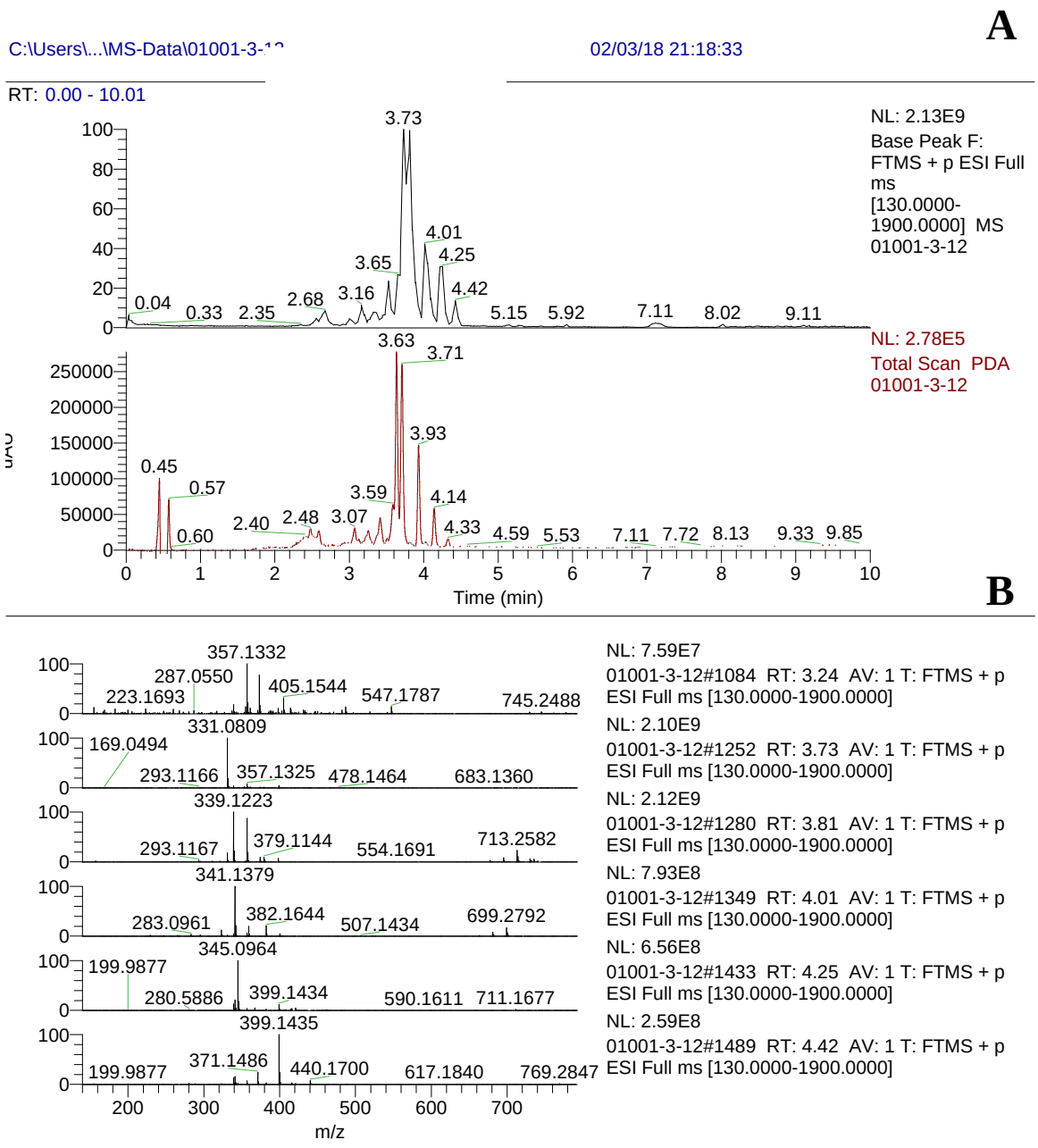


Figure S11. UPLC−PDA−HRMS−MS/MS data for primary fraction 12. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.24, 3.73, 3.81, 4.01, 4.25 and 4.42 min.

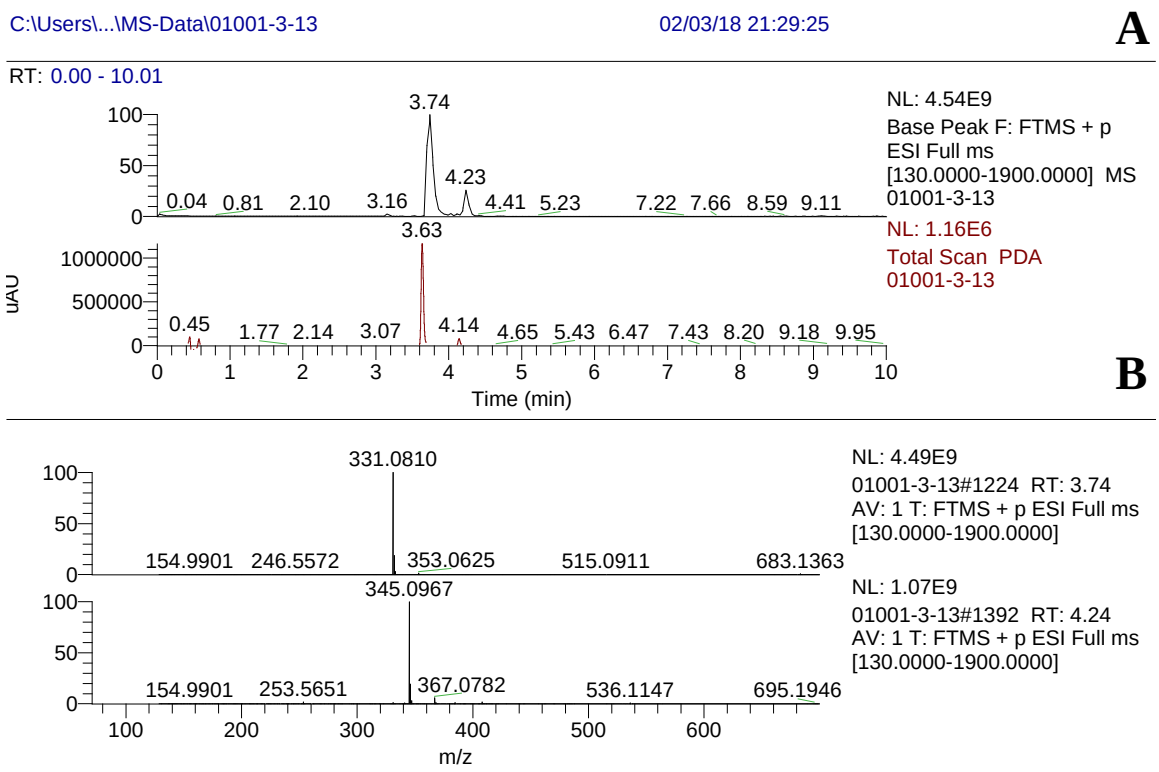


Figure S12. UPLC−PDA−HRMS−MS/MS data for primary fraction 13. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.74 and 4.24 min.

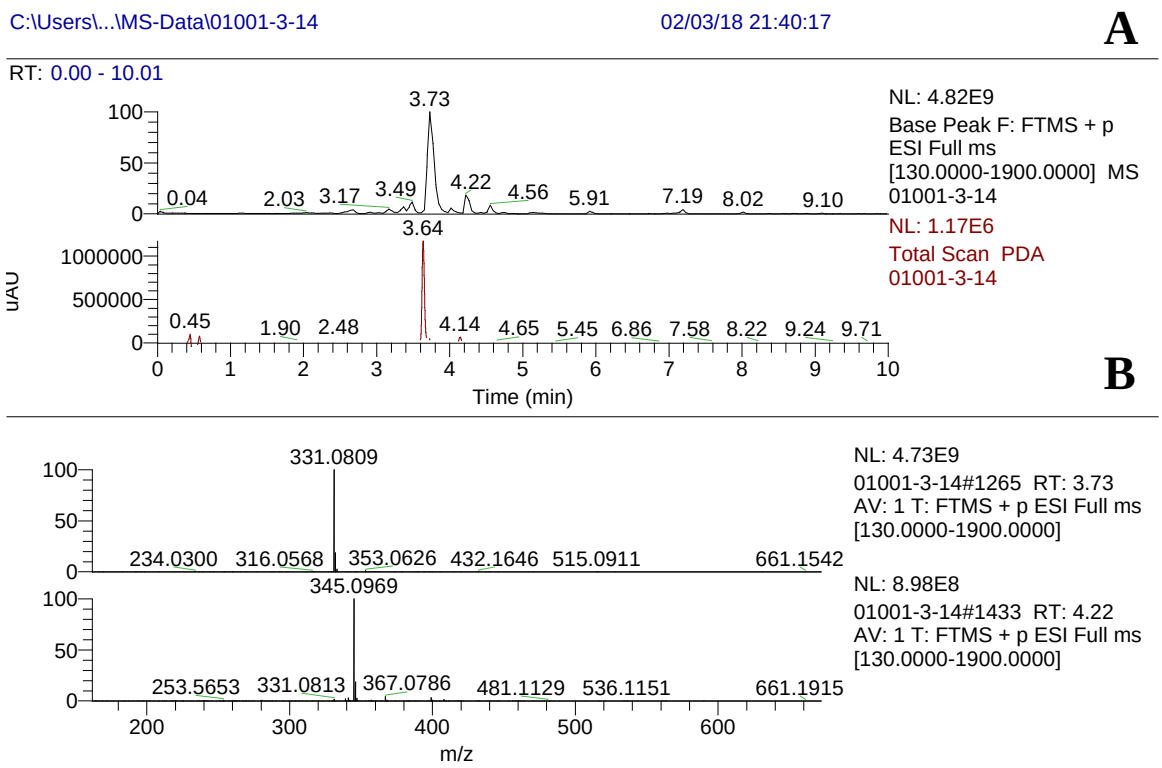


Figure S13. UPLC−PDA−HRMS−MS/MS data for primary fraction 14. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.73 and 4.22 min.

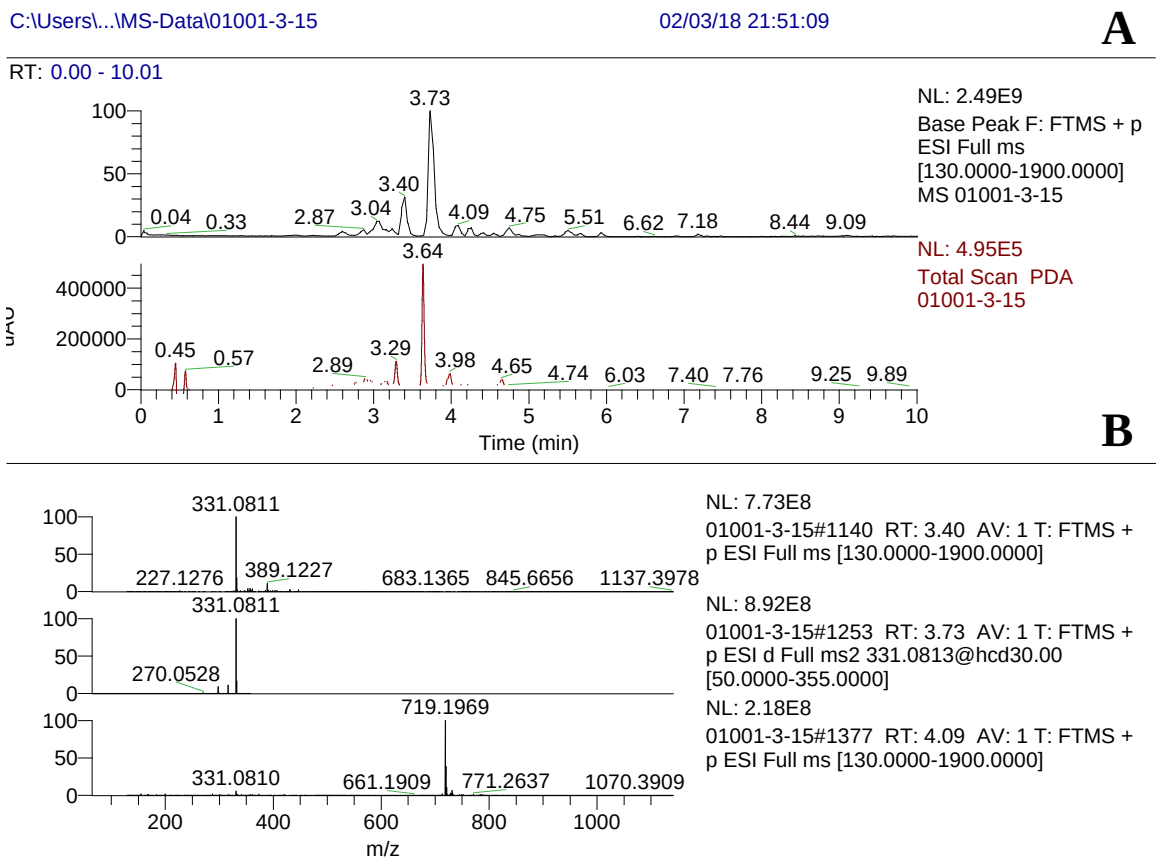


Figure S14. UPLC−PDA−HRMS−MS/MS data for primary fraction 15. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 3.40, 3.73 and 4.09 min.

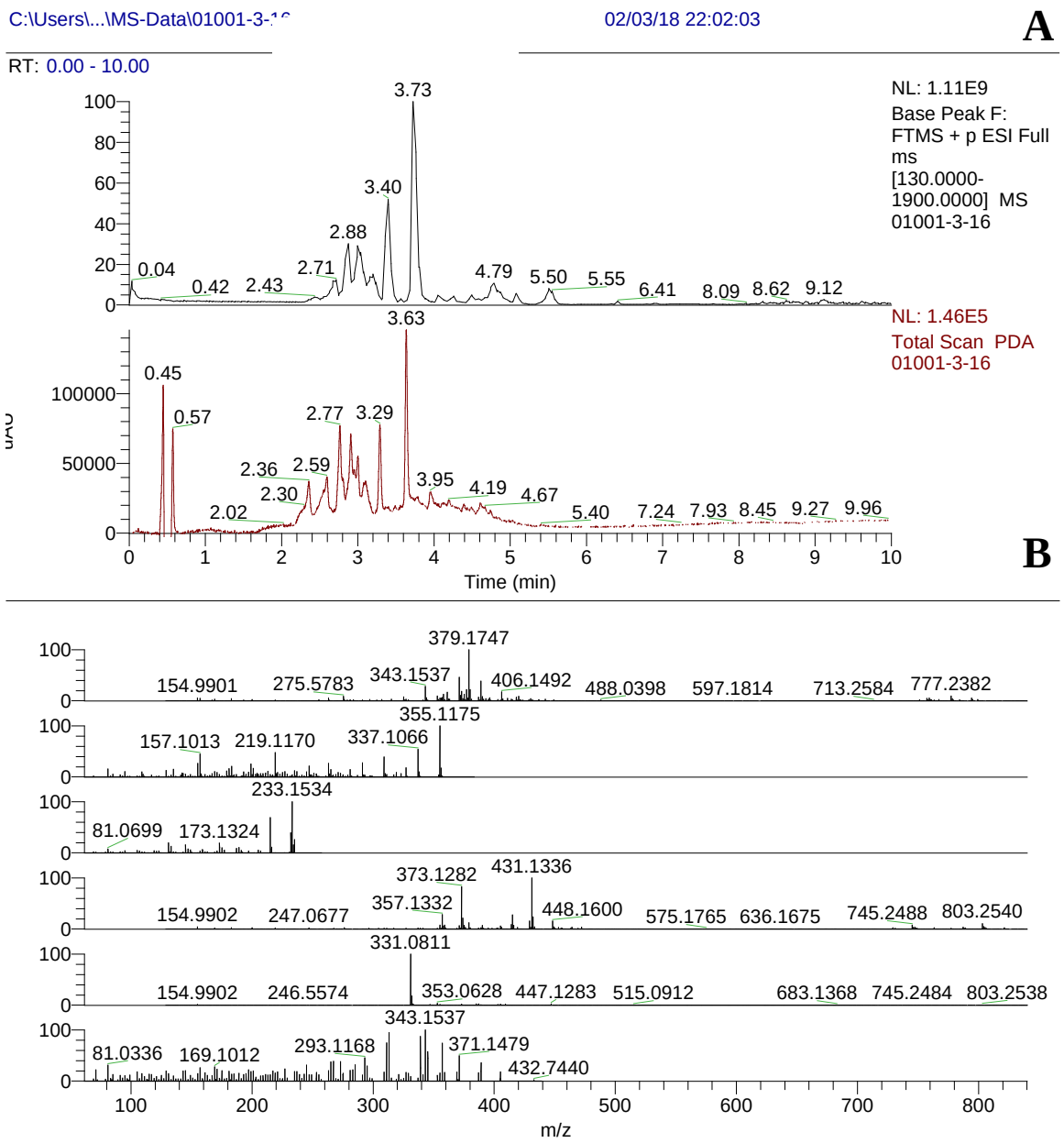


Figure S15. UPLC−PDA−HRMS−MS/MS data for primary fraction 16. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 2.71, 2.88, 3.01, 3.40, 3.73 and 4.79 min.

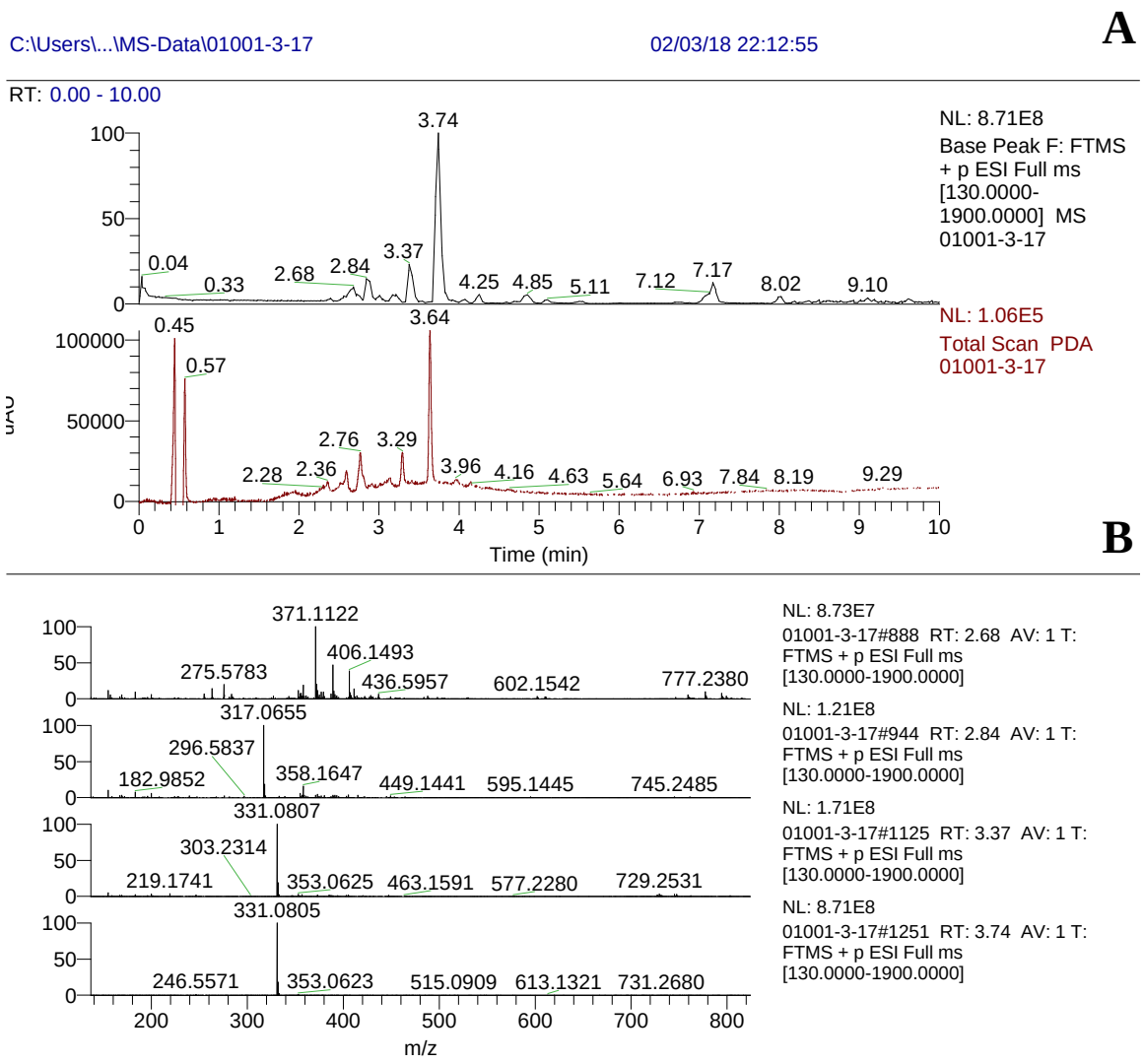


Figure S16. UPLC−PDA−HRMS−MS/MS data for primary fraction 17. A) Base peak chromatogram (top) and UV/vis (190−500 nm) chromatogram (bottom). B) HRMS spectrum of peaks at 2.68, 2.84, 3.37 and 3.74 min.

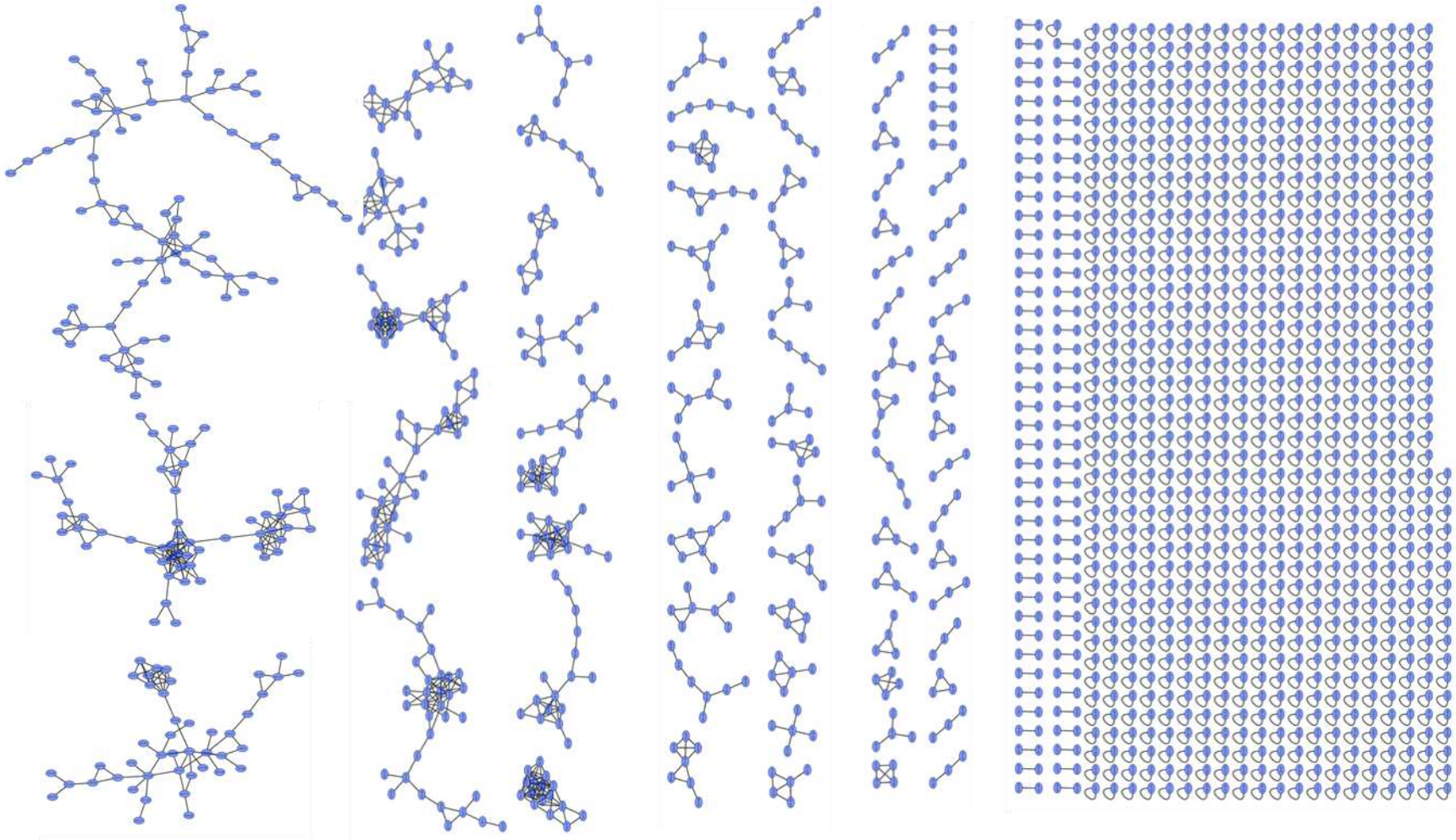


Figure S17. Molecular network of 17 primary fractions from *S. decora*, generated from analysis of MS^2 data via the Global Natural Products Social Molecular Networking (GNPS; http://gnps.ucsd.edu) tool.

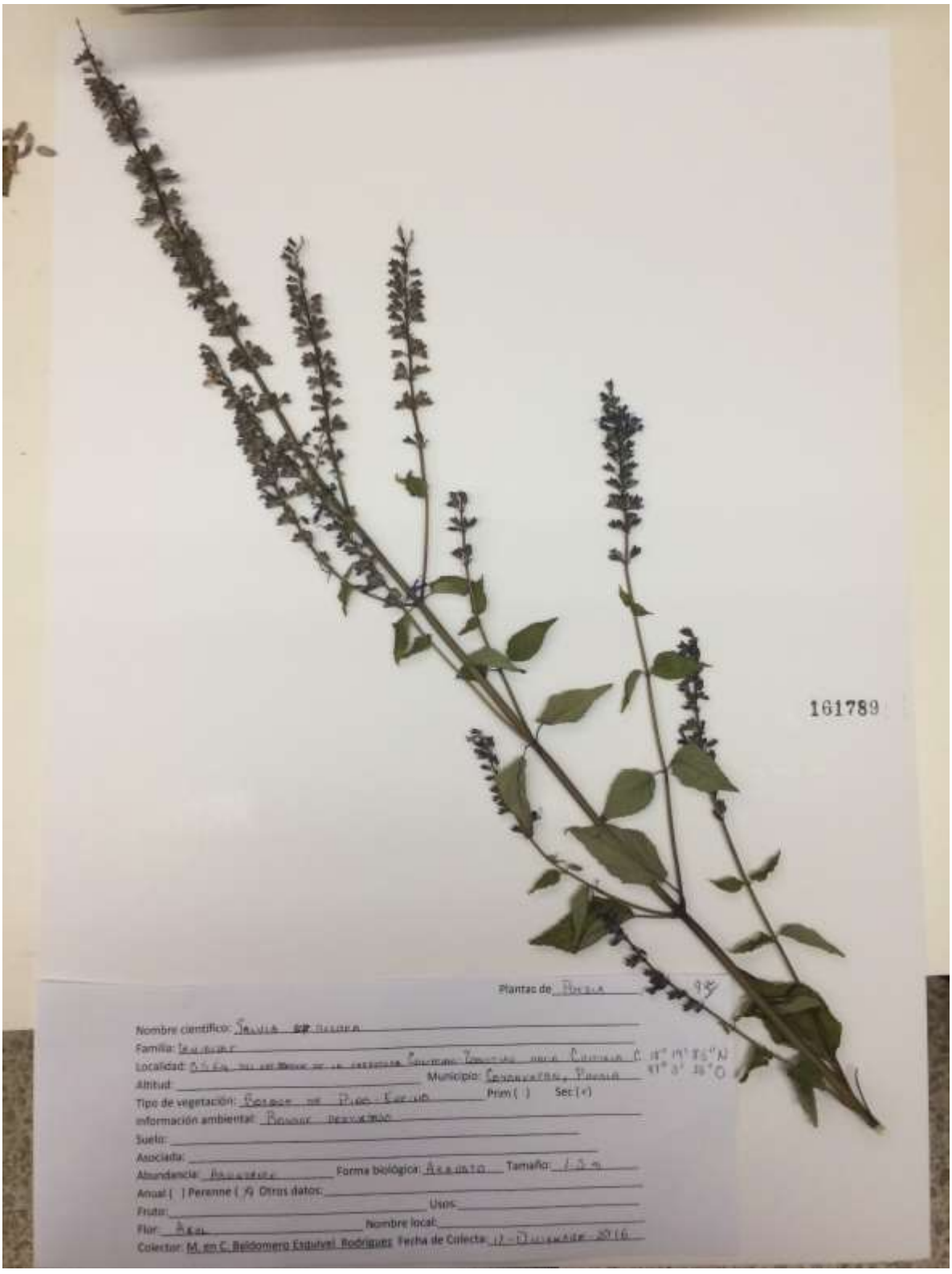


Figure S18. Herbarium specimen of *Salvia decora* collected by Dr. Baldomero Esquivel-Rodríguez from Coyomeapan, Puebla, Mexico, 18°19′85″ N, 97°3′26″ W, in December 2016.

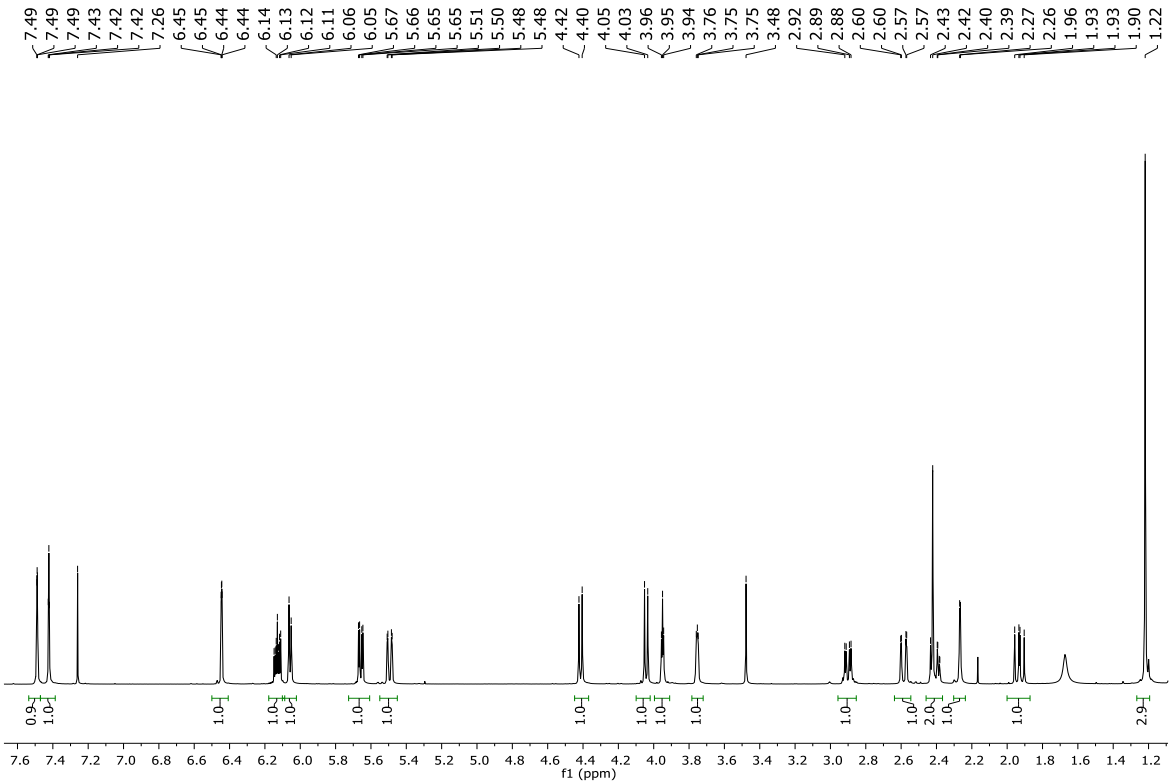


Figure S19. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **1**

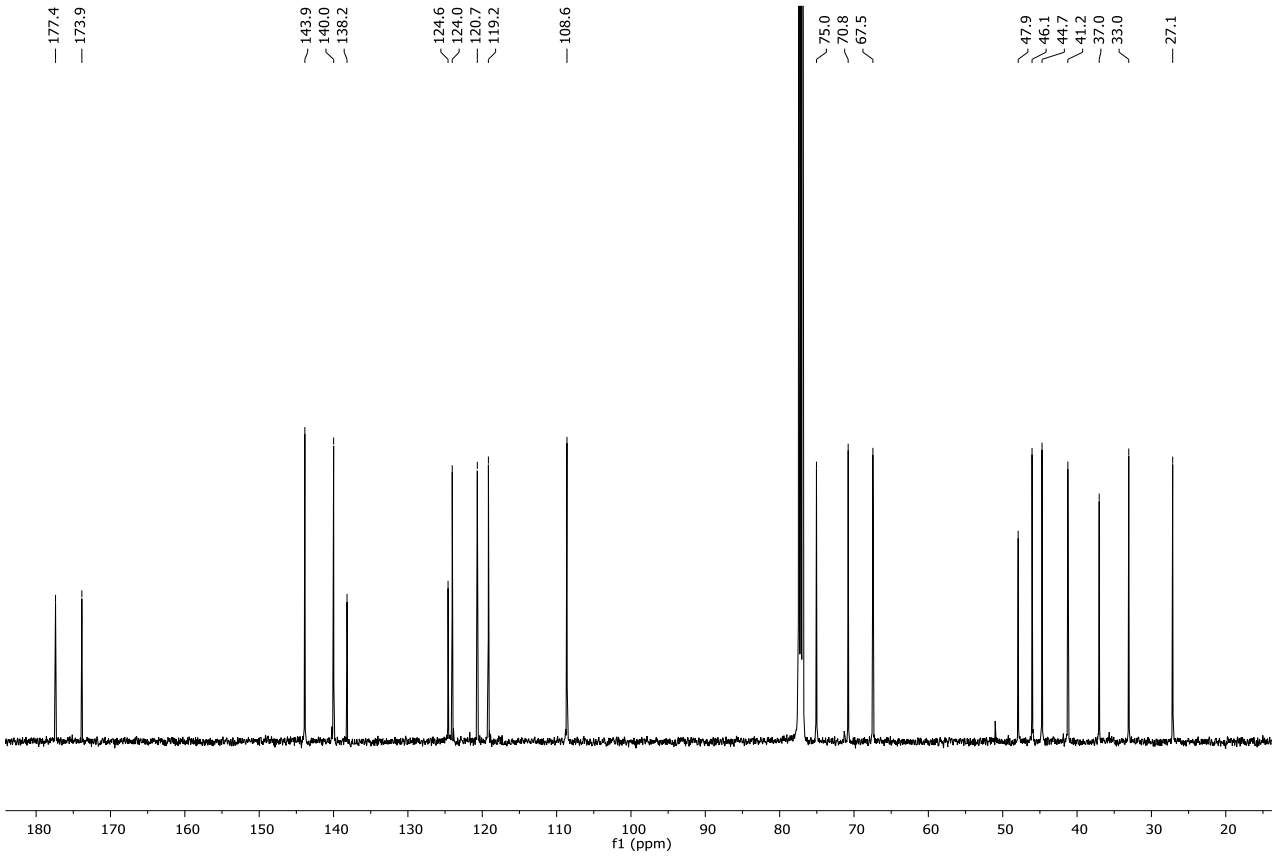


Figure S20. ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of **1**

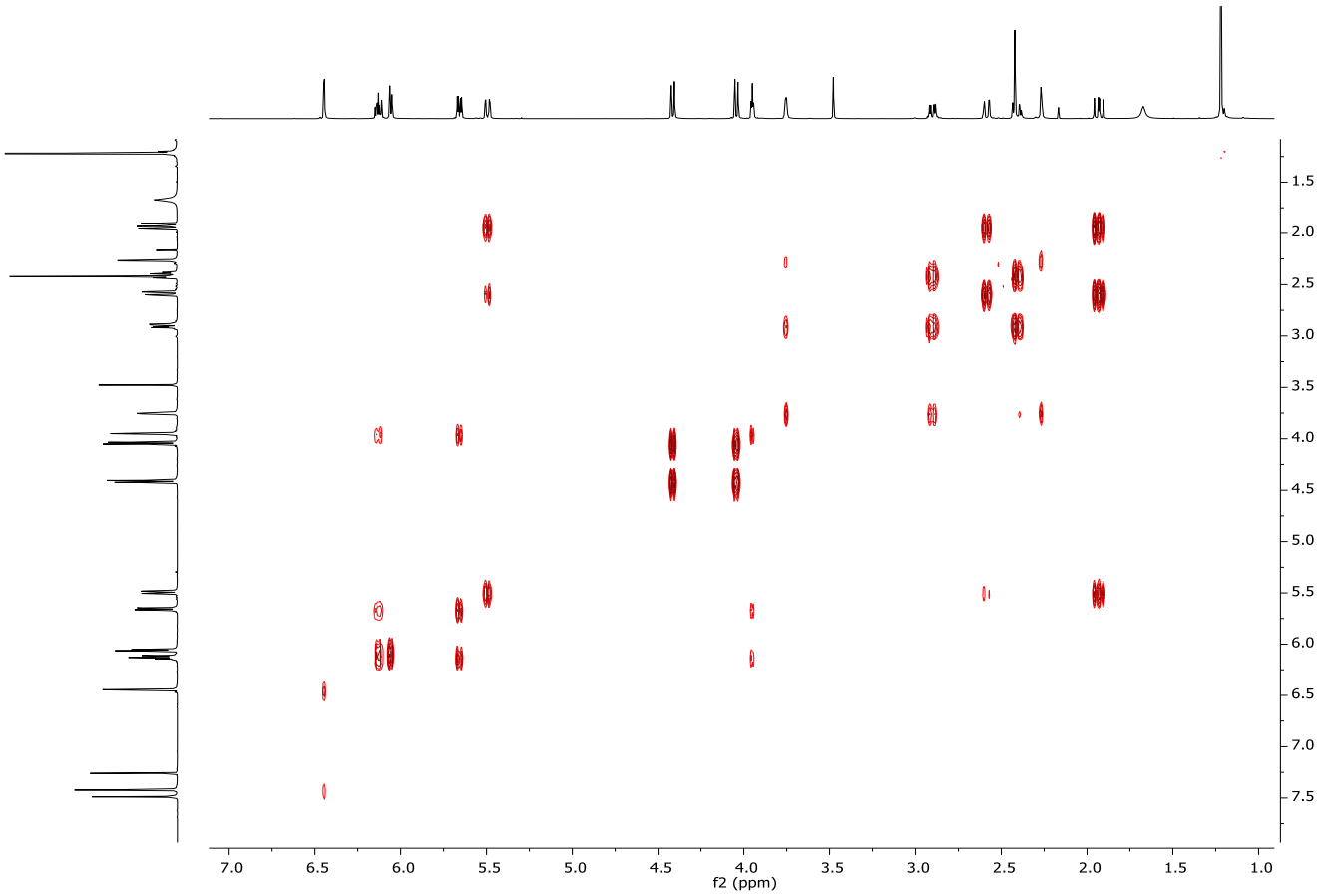


Figure S21. COSY NMR ($CDCl_3$, 500 MHz) spectrum of **1**

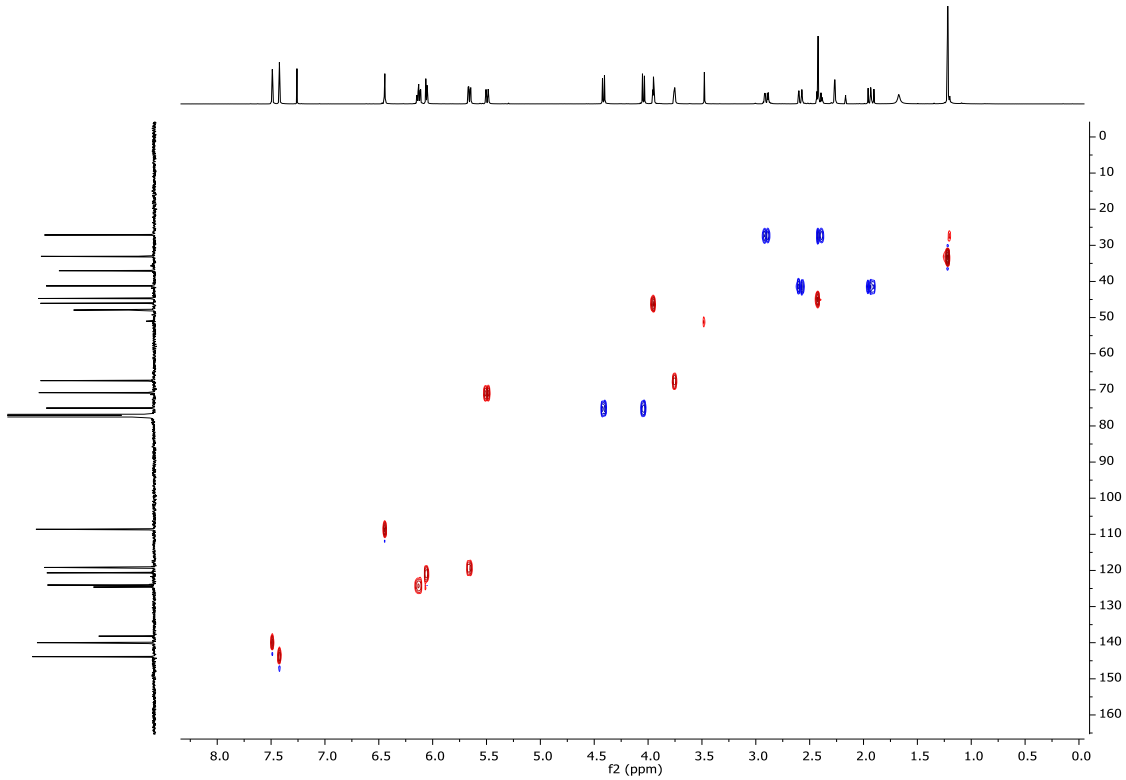


Figure S22. HSQC NMR ($CDCl_3$, 500 MHz) spectrum of **1**

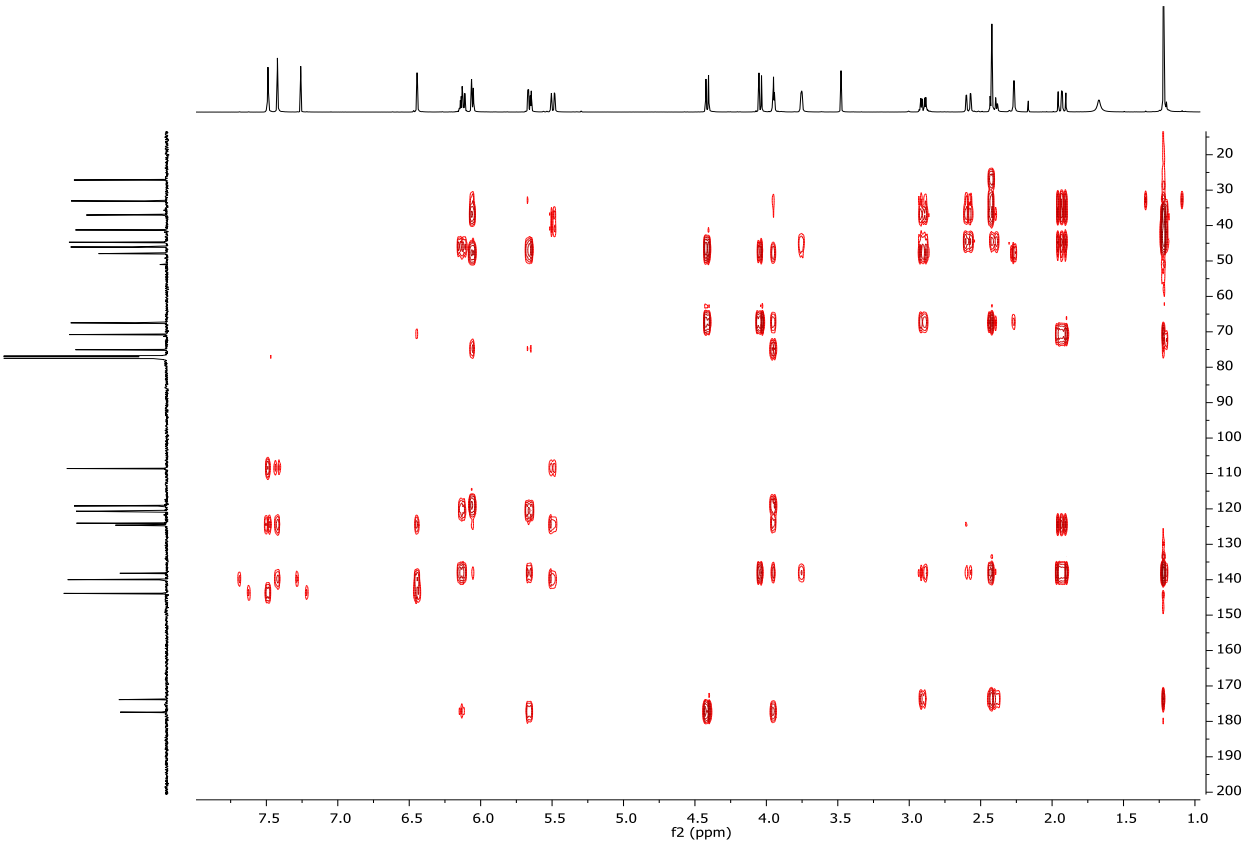


Figure S23. HMBC NMR ($CDCl_3$, 500 MHz) spectrum of **1**

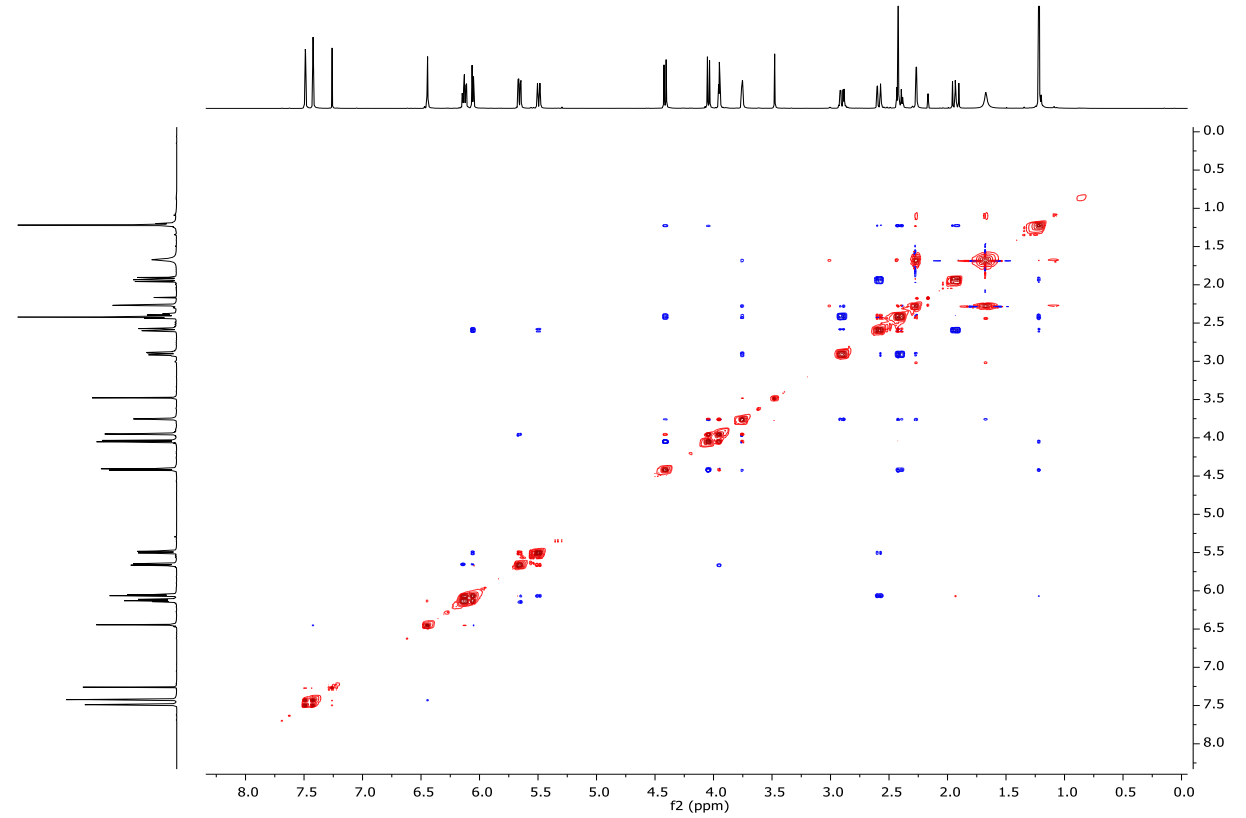


Figure S24. NOESY NMR ($CDCl_3$, 500 MHz) spectrum of **1**

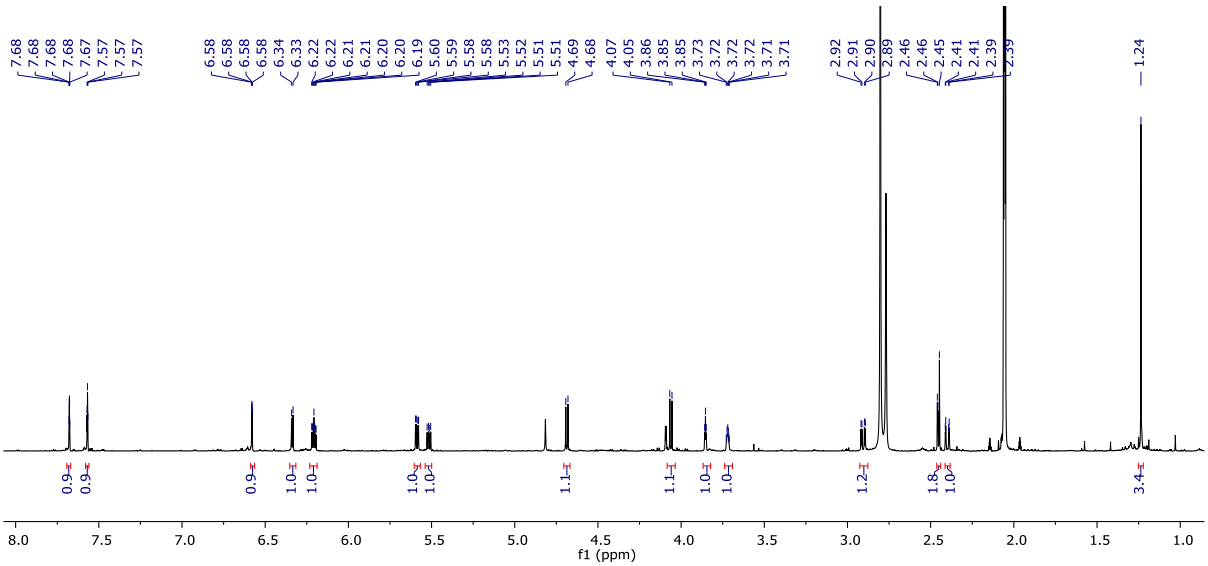


Figure S25. ^{1}H NMR (acetone-d_6, 700 MHz) spectrum of **2**

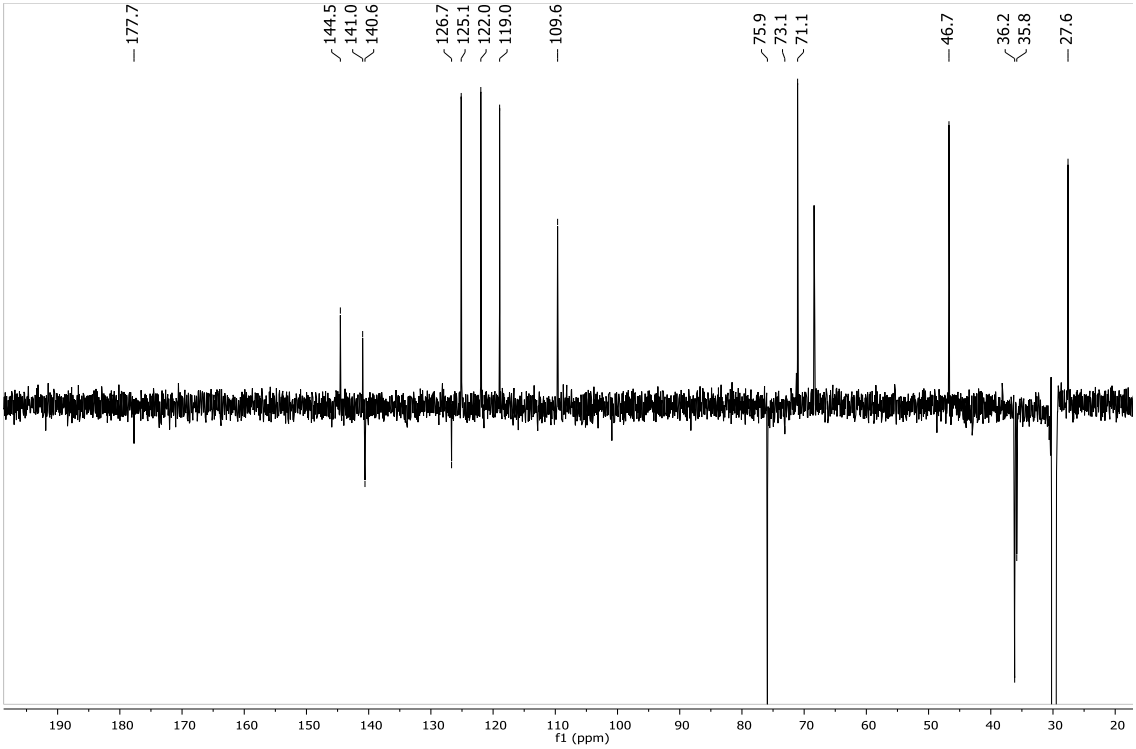


Figure S26. APT NMR (acetone-d_6, 175 MHz) spectrum of **2**

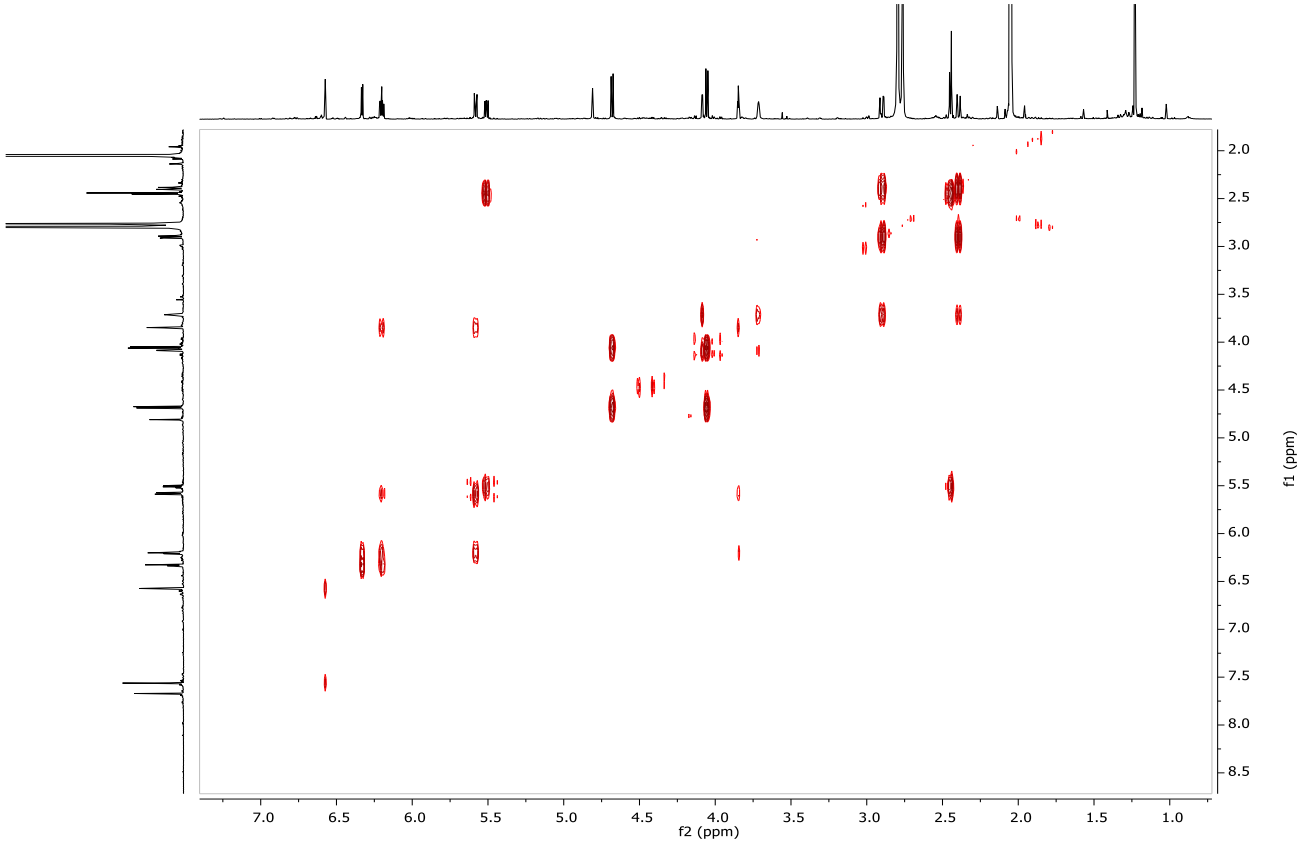


Figure S27. COSY NMR (acetone-d_6, 700 MHz) spectrum of **2**

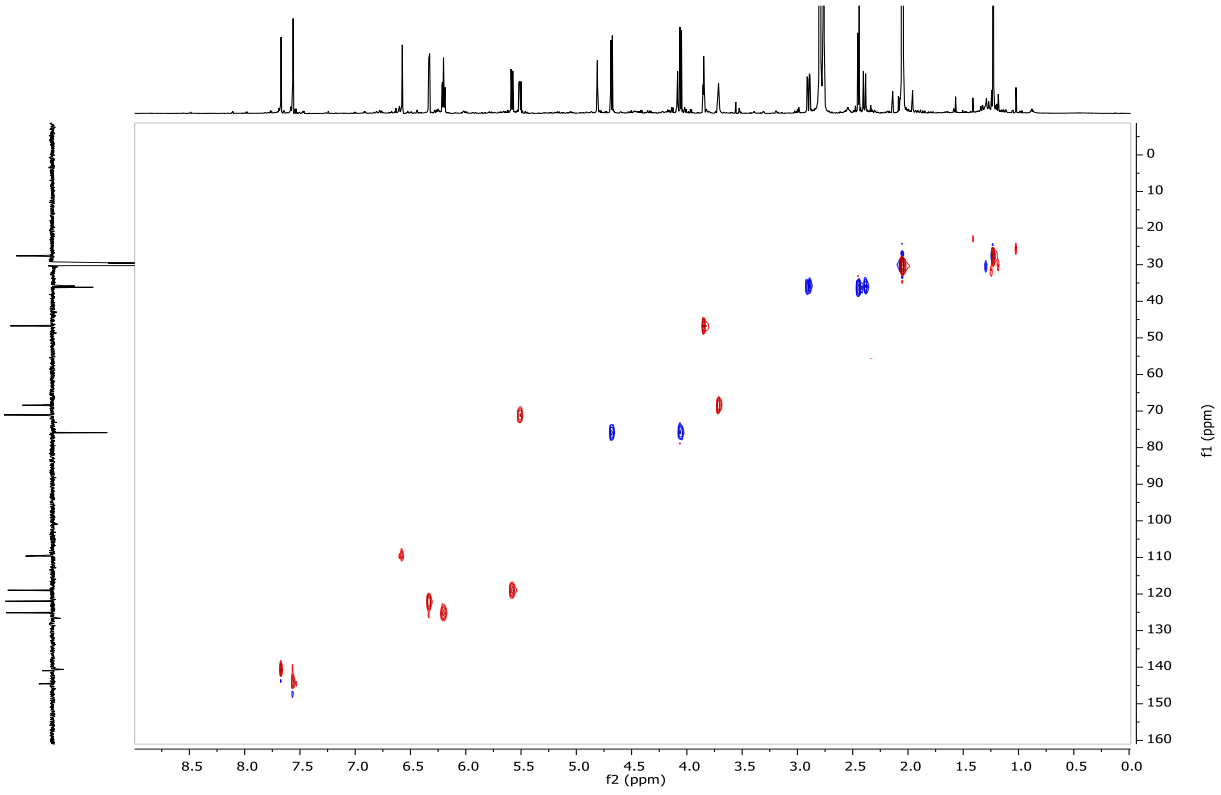


Figure S28. HSQC NMR (acetone-d_6, 700 MHz) spectrum of **2**

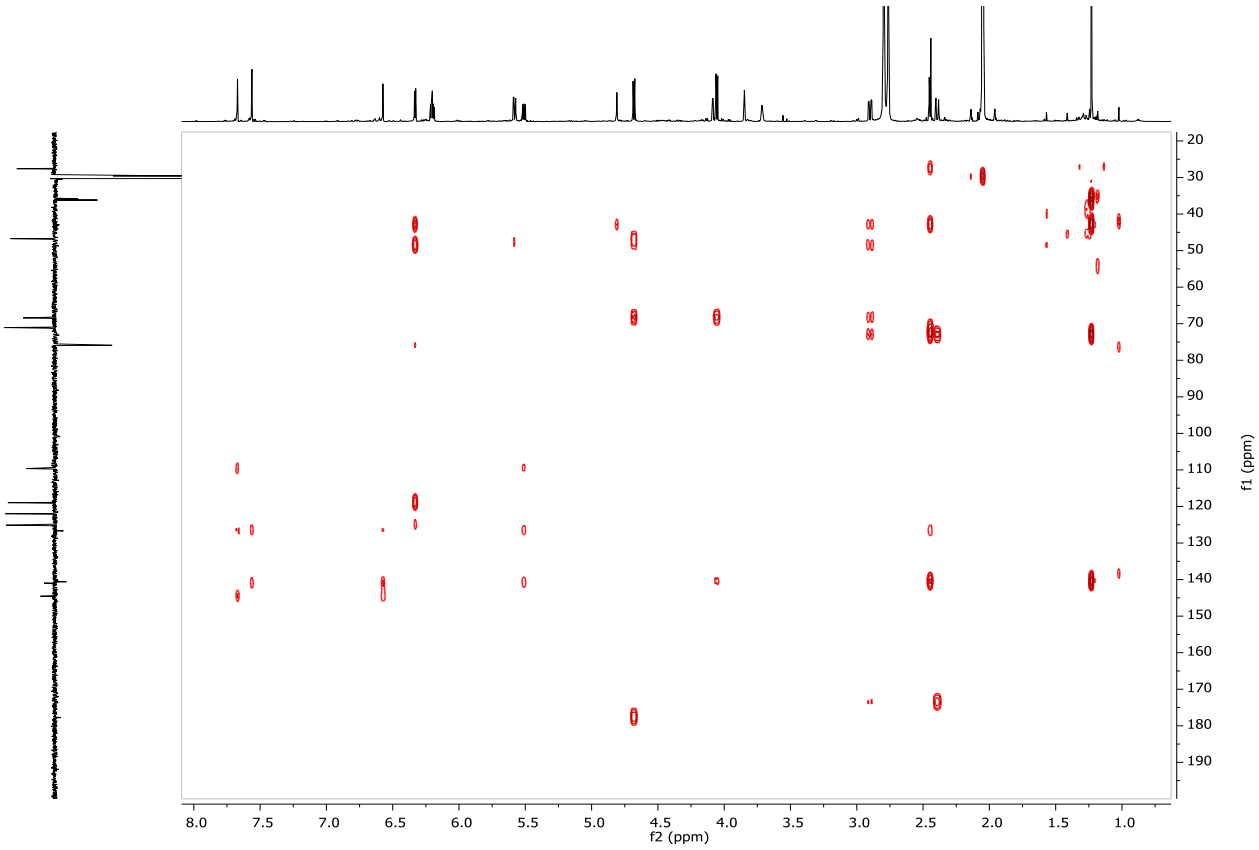


Figure S29. HMBC NMR (acetone-d_6, 700 MHz) spectrum of **2**

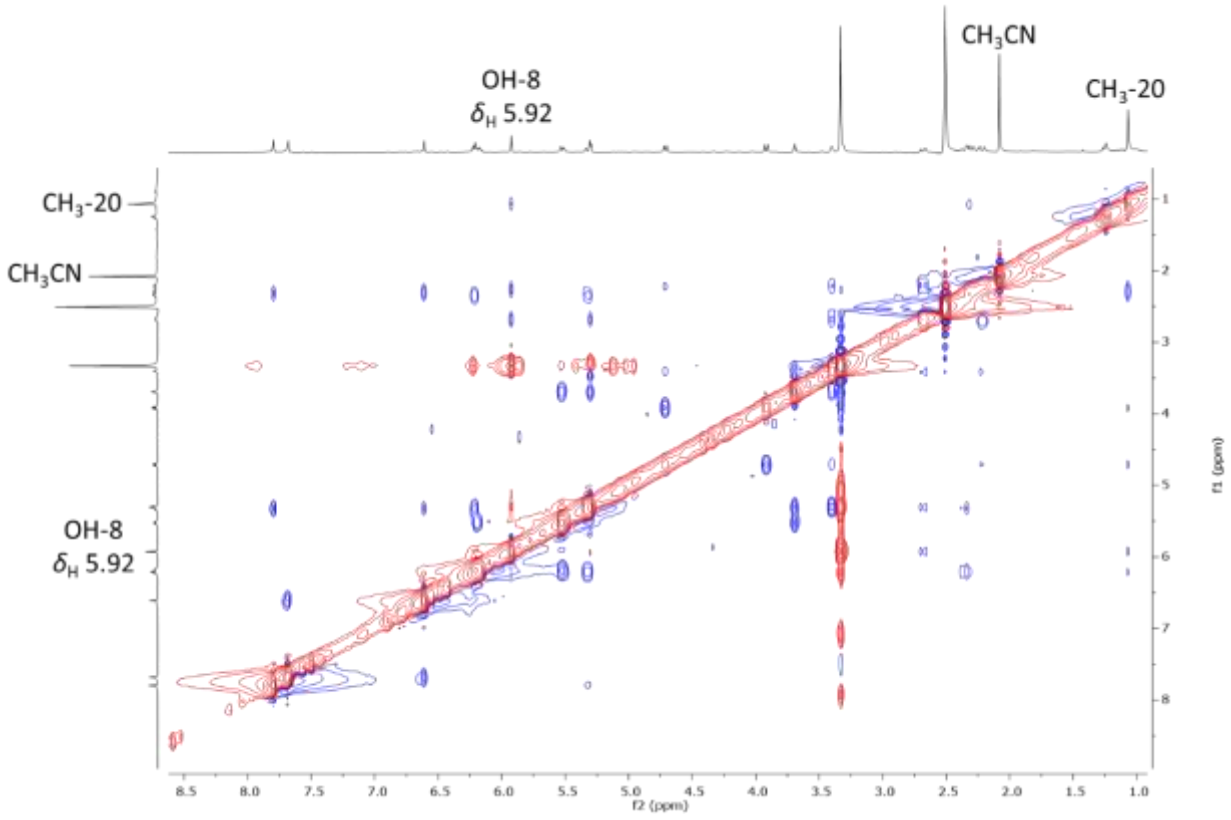


Figure S30. NOESY NMR (DMSO-d_6, 400 MHz) spectrum of **2**

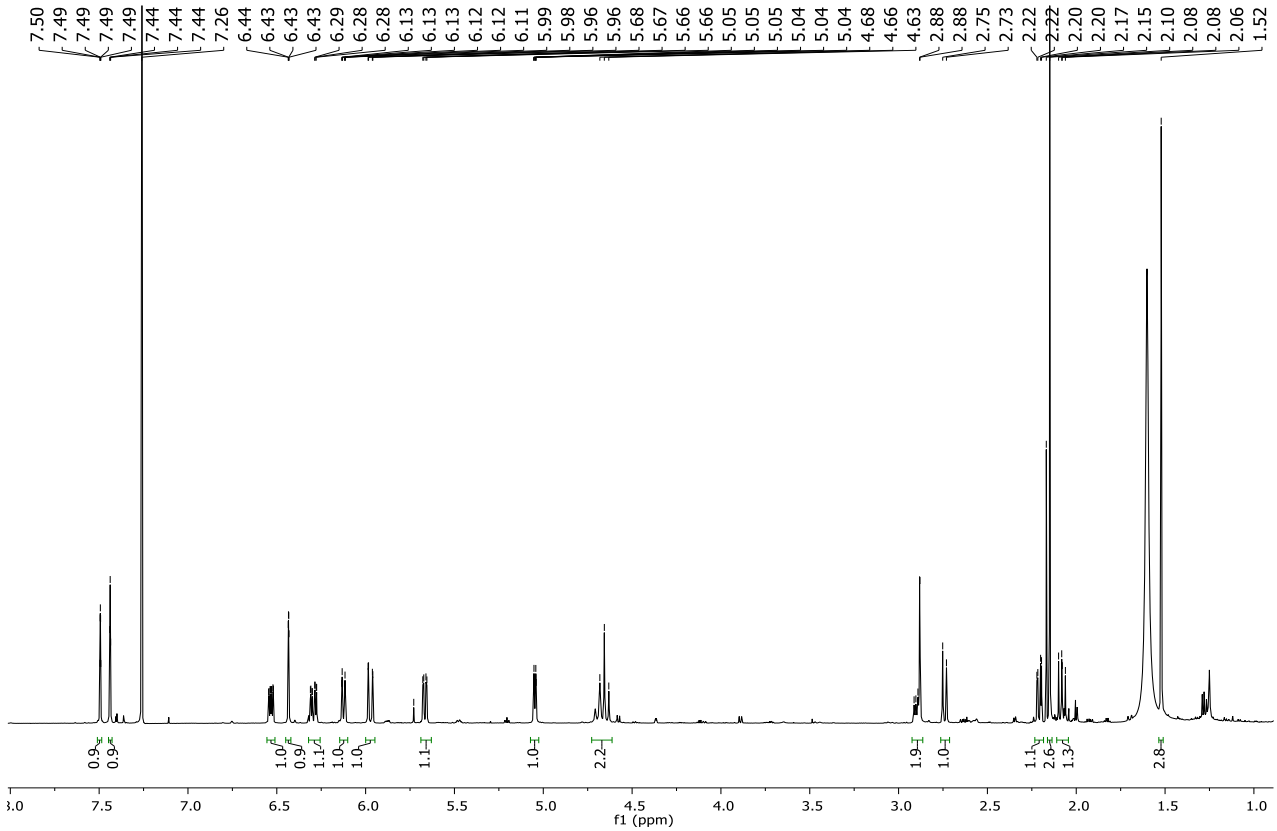


Figure S31. ^{1}H NMR ($CDCl_3$, 700 MHz) spectrum of **3**

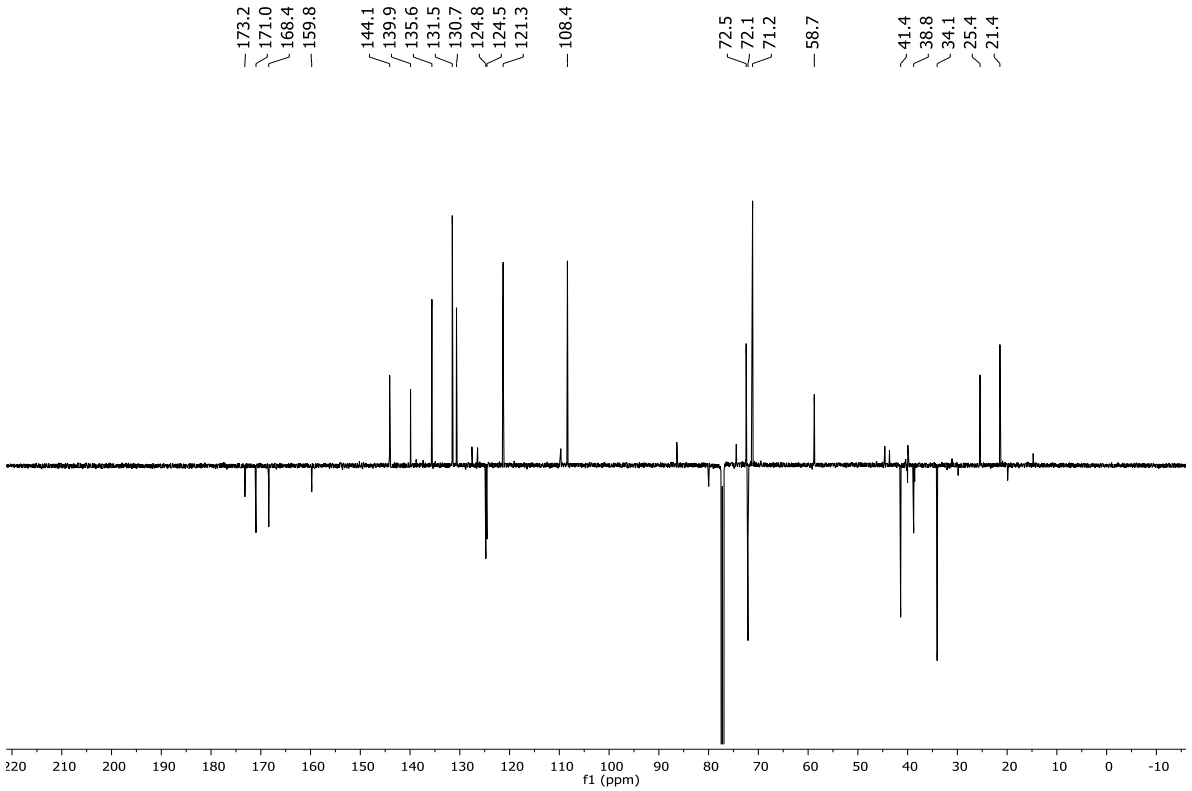


Figure S32. APT ($CDCl_3$, 175 MHz) spectrum of **3**

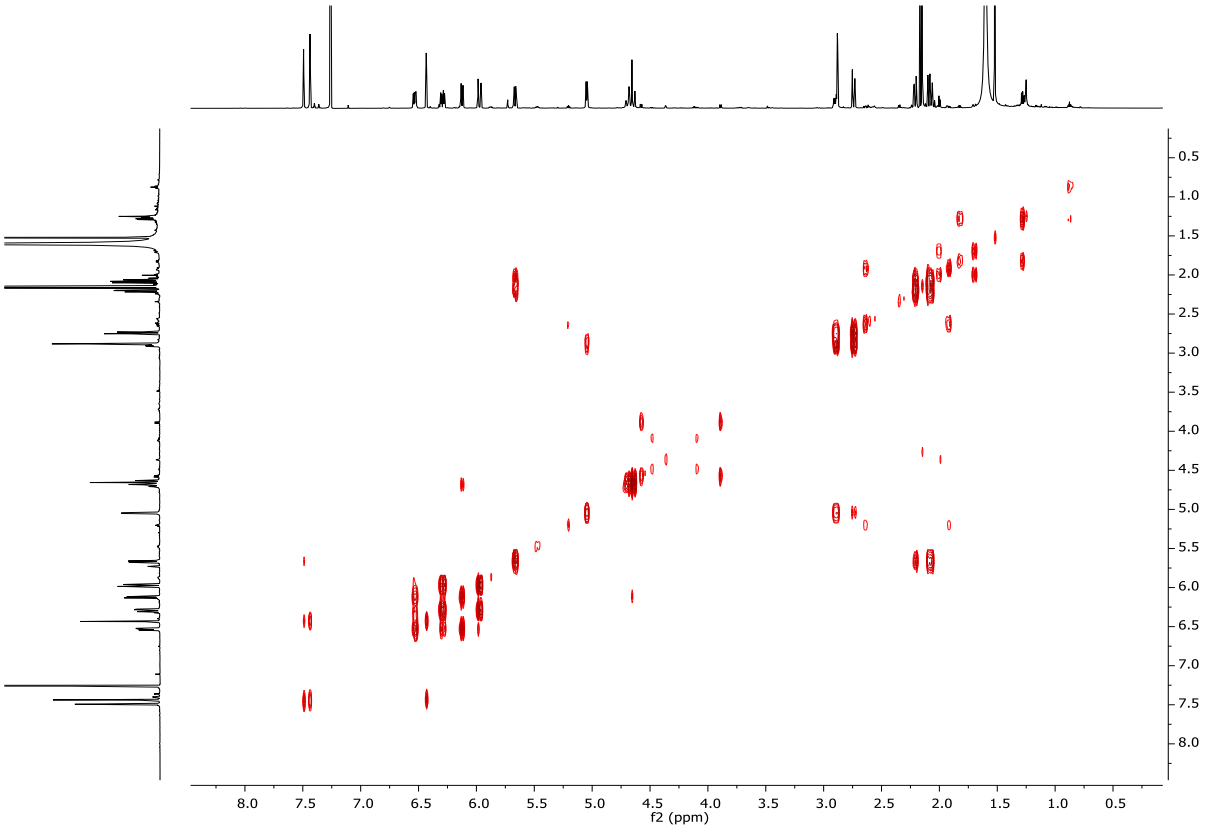


Figure S33. COSY NMR ($CDCl_3$, 700 MHz) spectrum of **3**

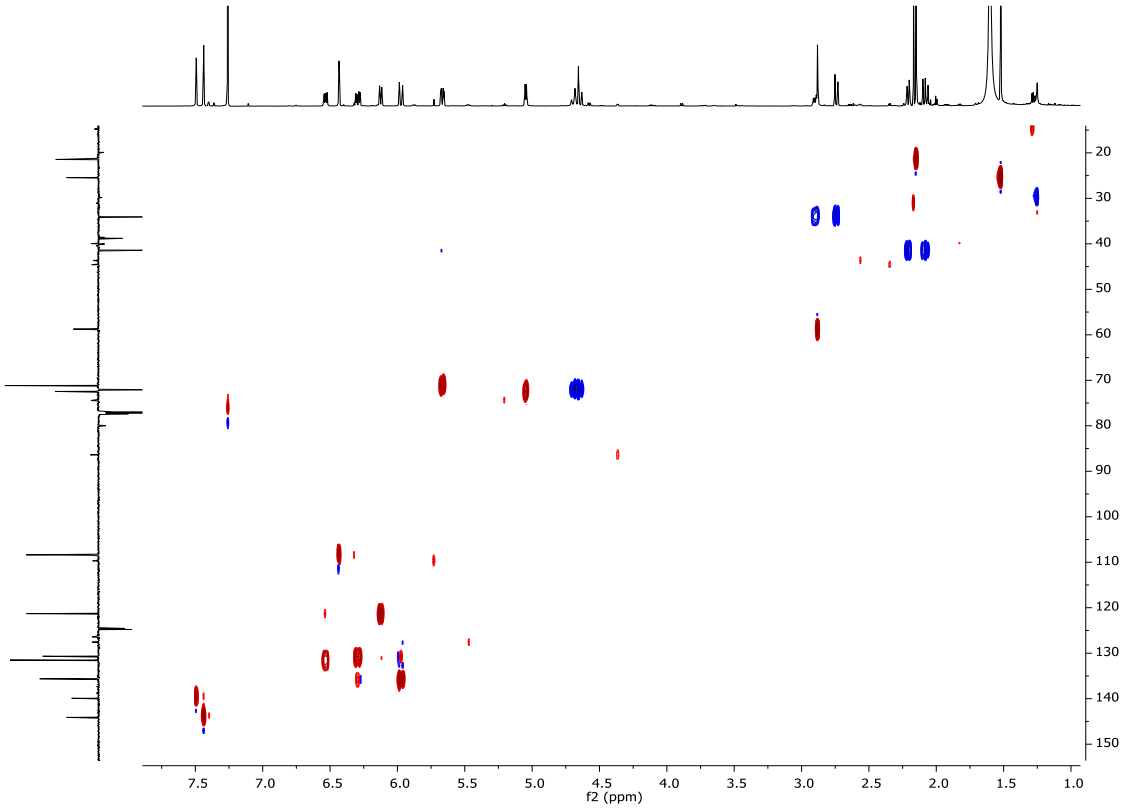


Figure S34. HSQC NMR ($CDCl_3$, 700 MHz) spectrum of **3**

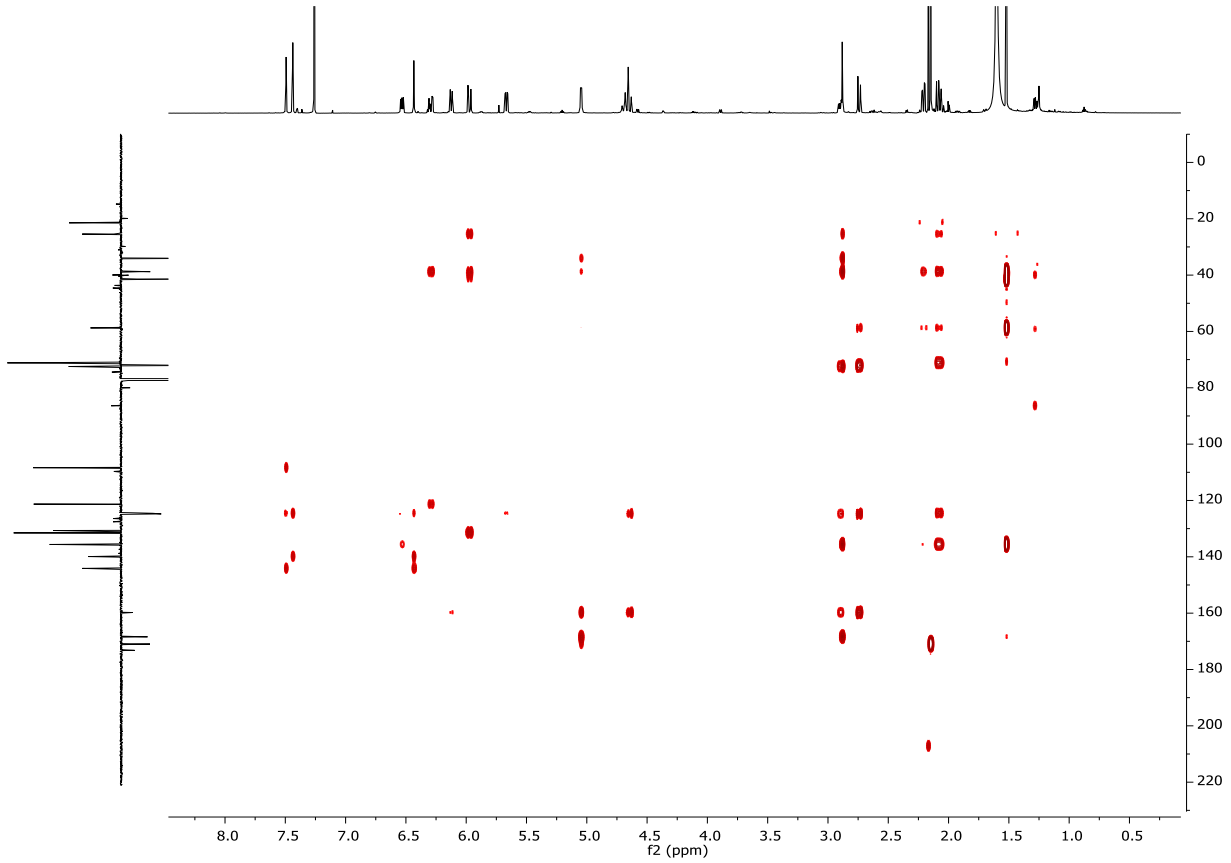


Figure S35. HMBC NMR ($CDCl_3$, 700 MHz) spectrum of **3**

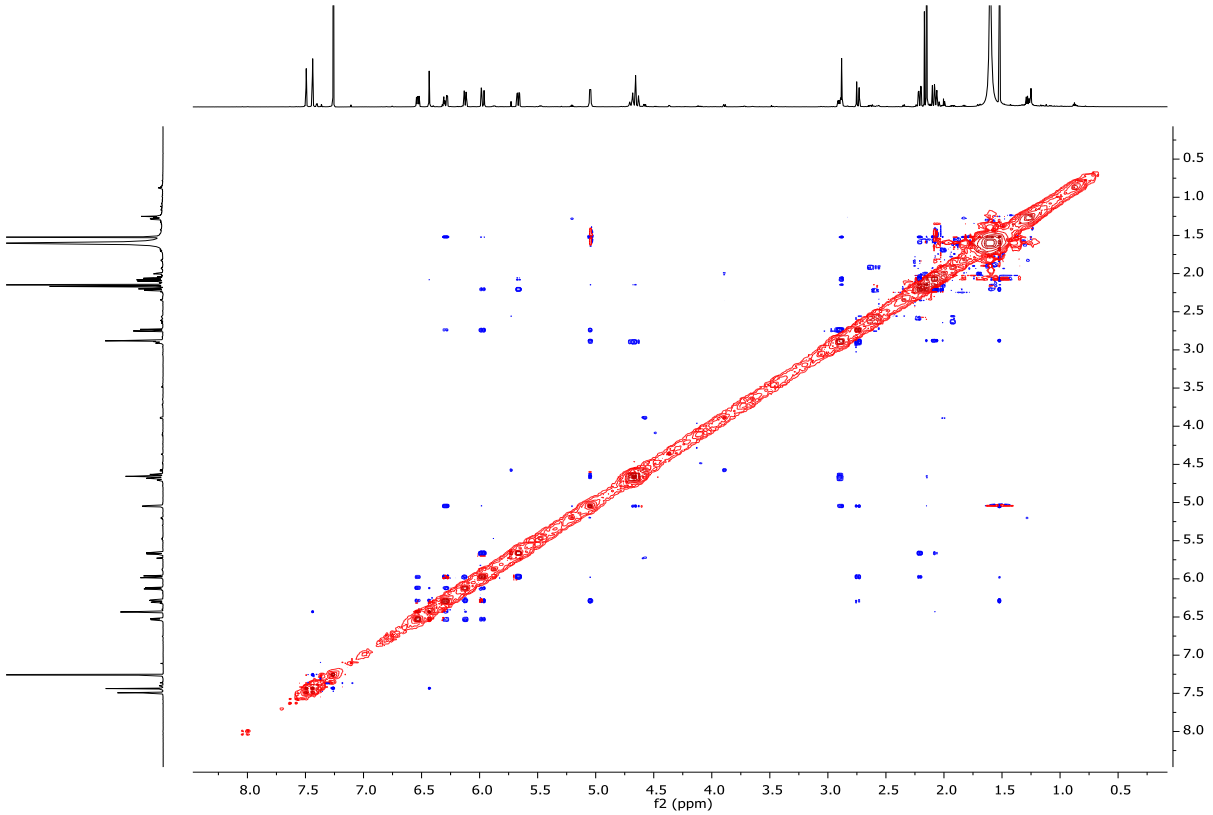


Figure S36. NOESY NMR ($CDCl_3$, 700 MHz) spectrum of **3**

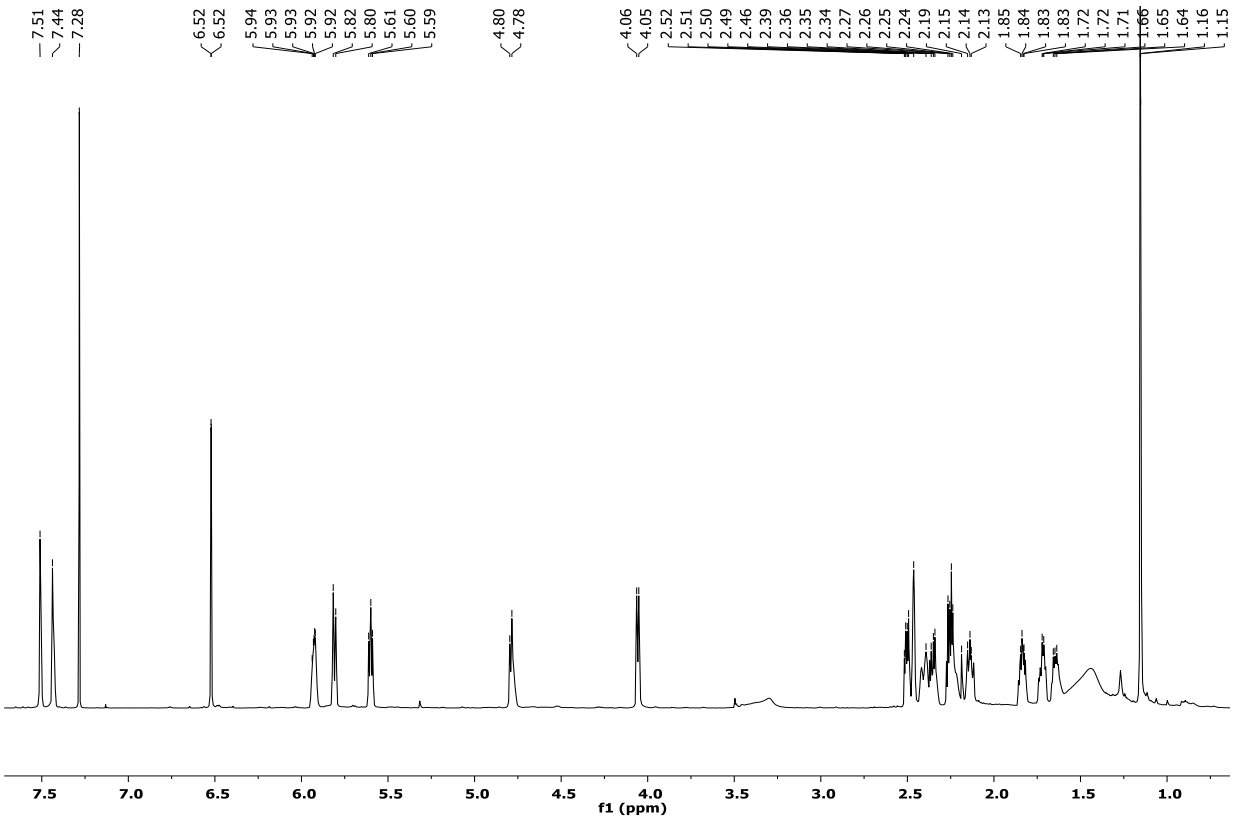


Figure S37. ^{1}H NMR ($CDCl_3$, 700 MHz) spectrum of **4**

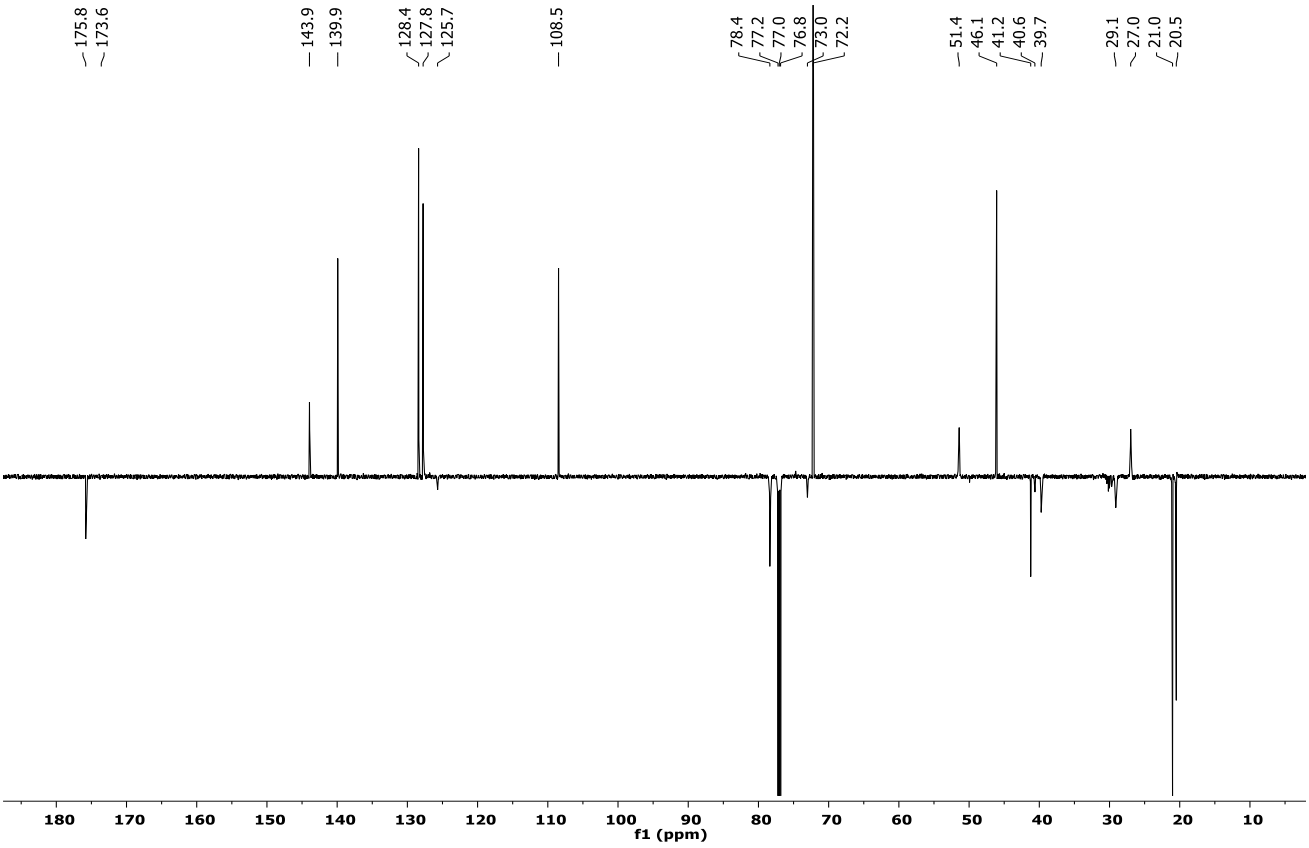


Figure S38. APT ($CDCl_3$, 175 MHz) spectrum of **4**

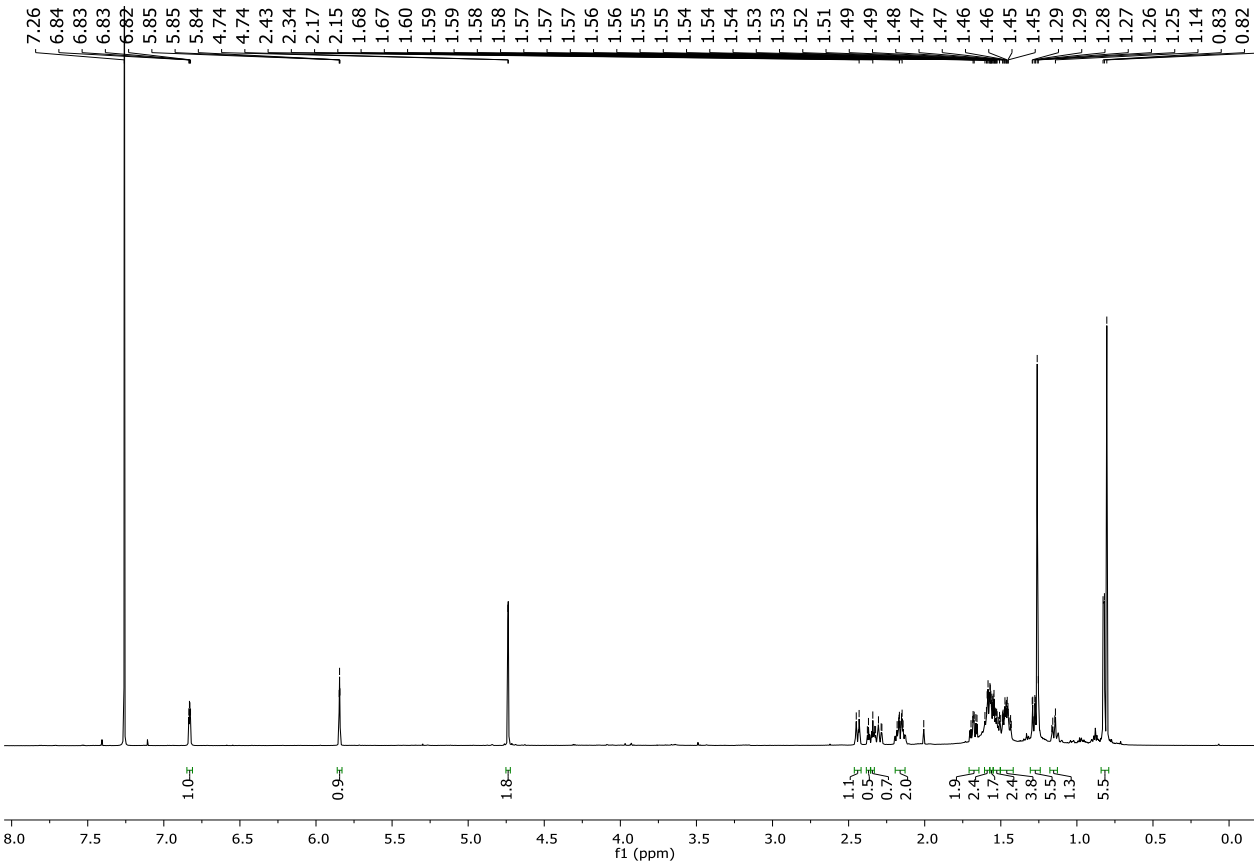


Figure S39. ^{1}H NMR ($CDCl_3$, 700 MHz) spectrum of **5**

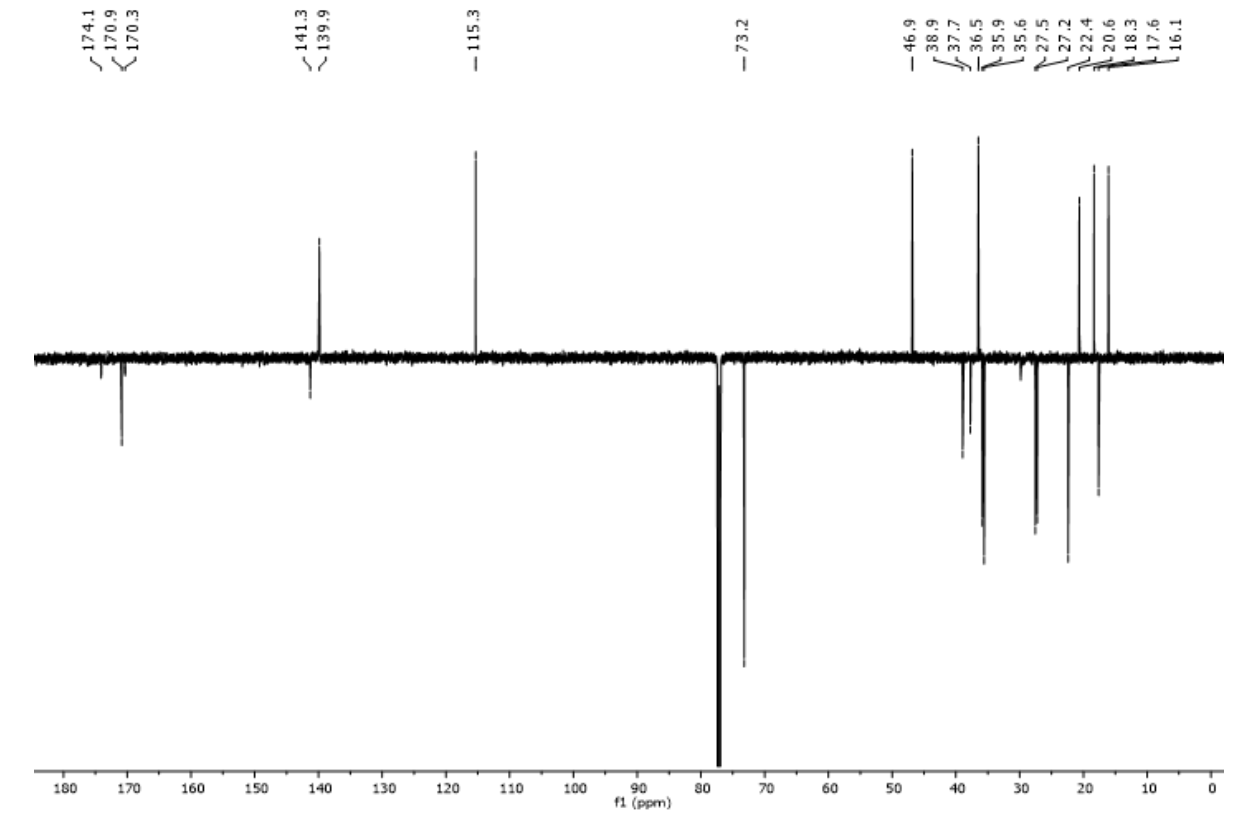


Figure S40. APT ($CDCl_3$, 175 MHz) spectrum of **5**

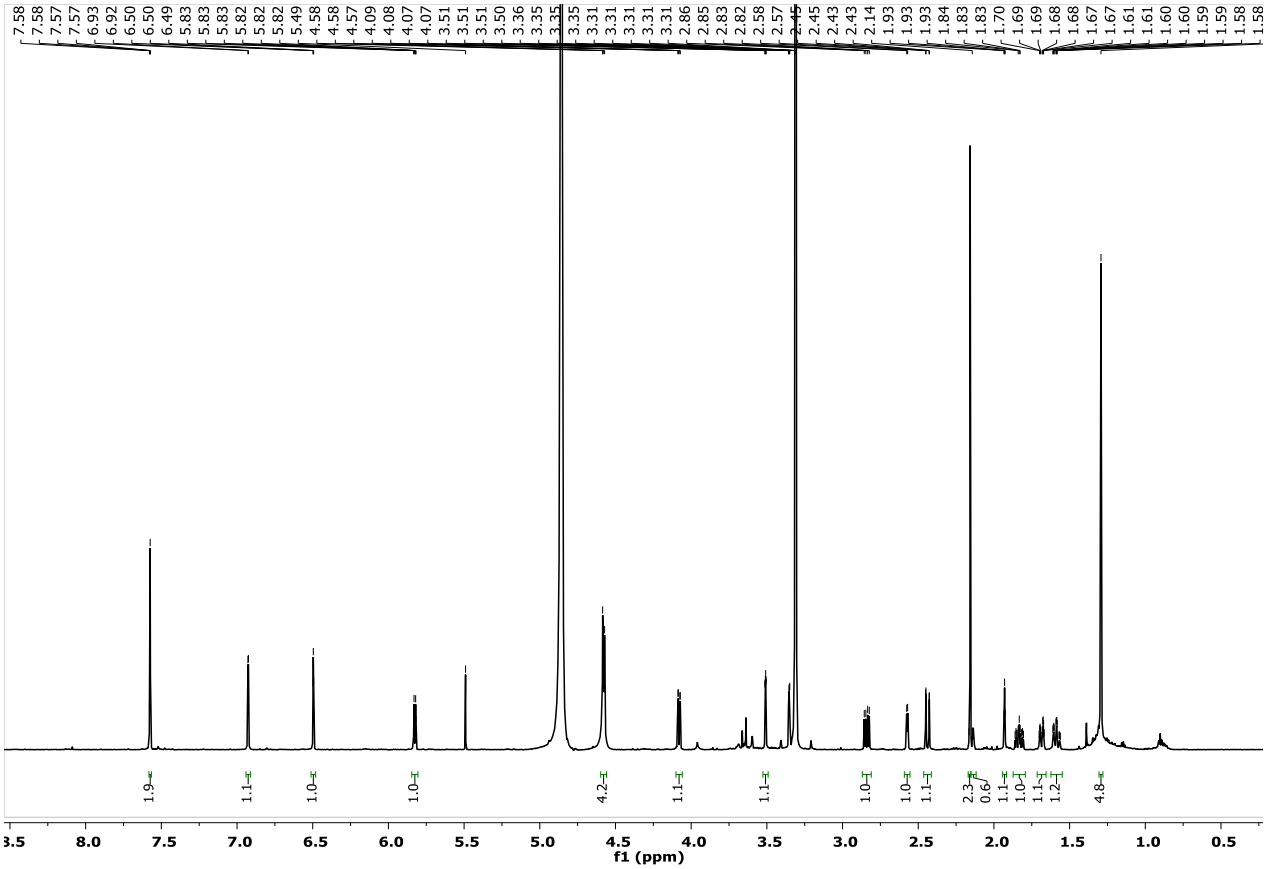


Figure S41. ^{1}H NMR (CD_3OD, 700 MHz) spectrum of **6**

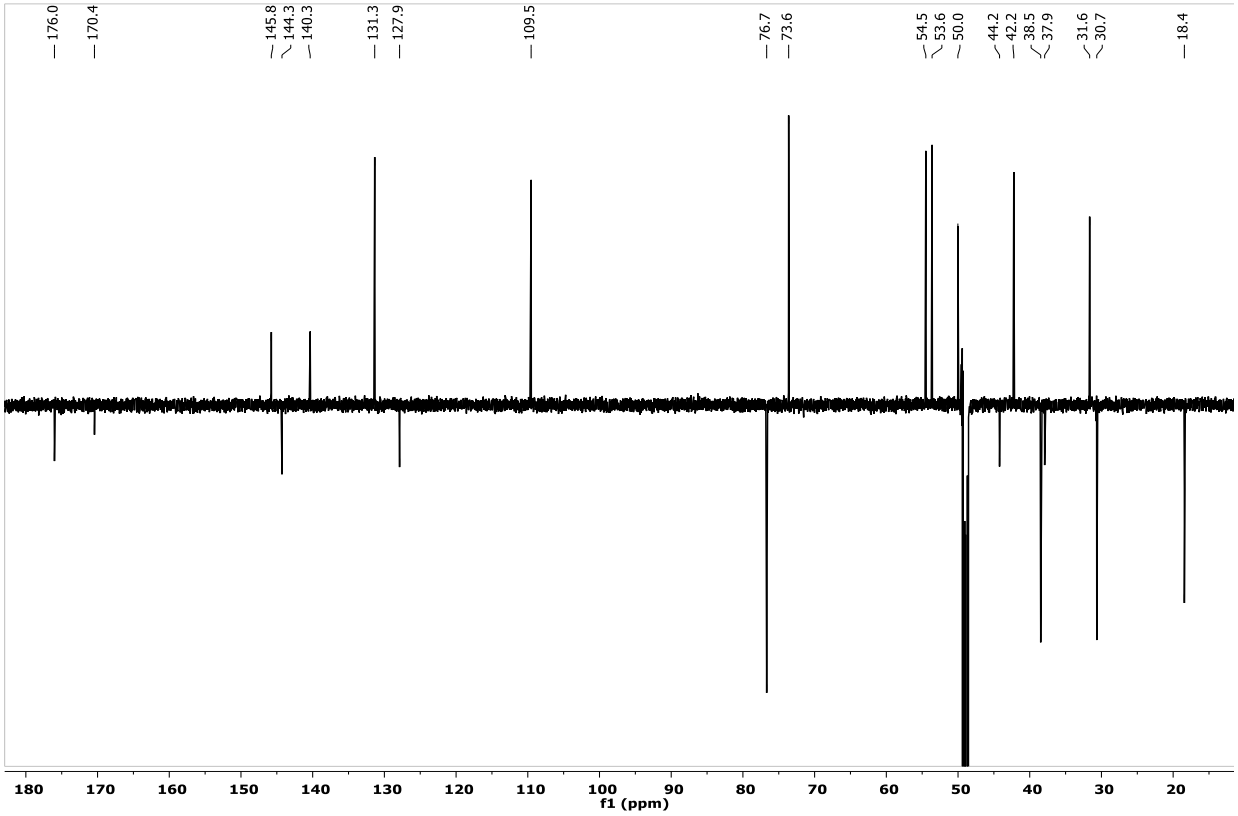


Figure S42. APT (CD_3OD, 175 MHz) spectrum of **6**

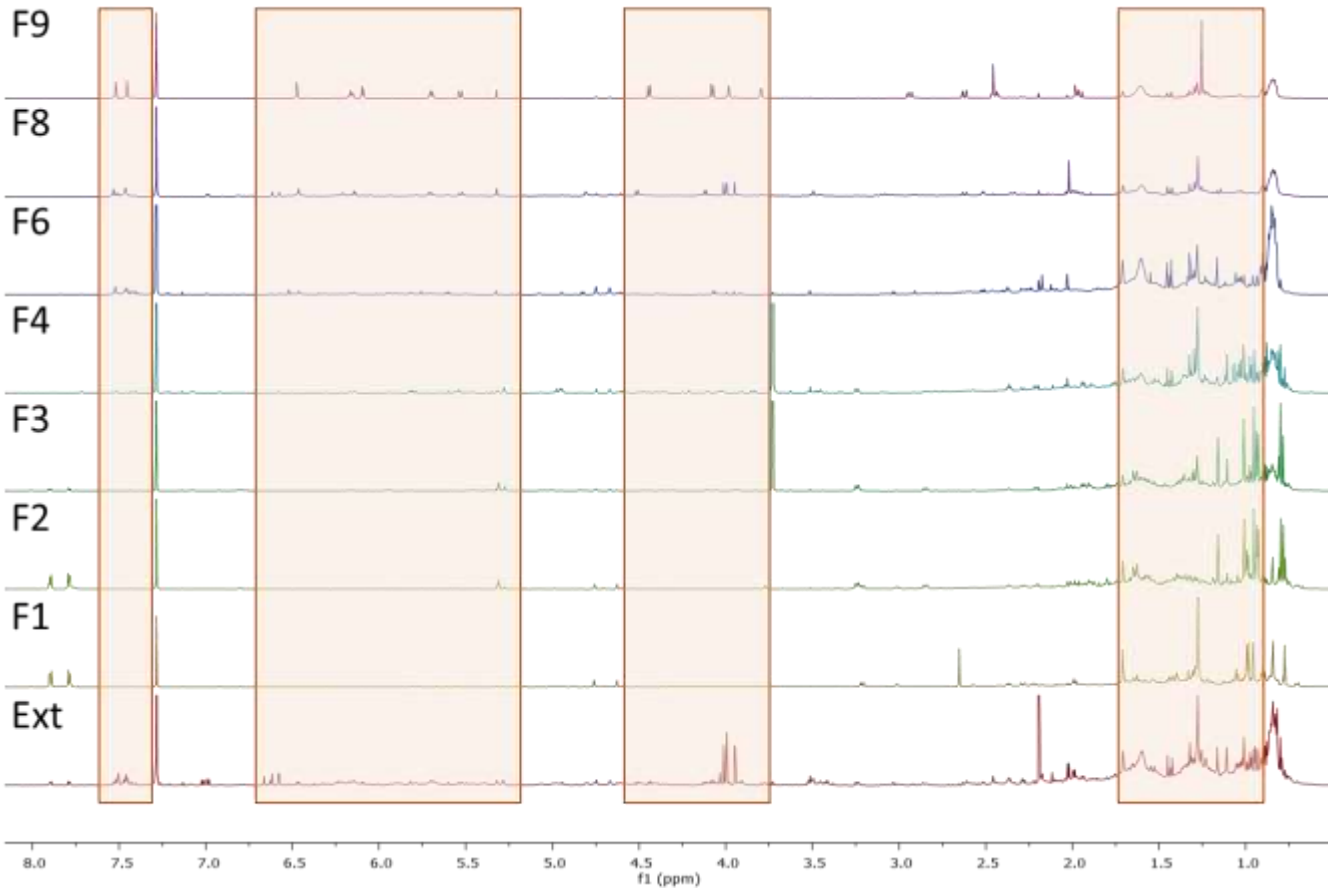


Figure S43. ^{1}H NMR spectrum of the acetone extract and fractions F1-F4, F6, F8, F9-F11 and F14-17. The orange boxes highlight signals attributed to clerodane type diterpenoids.

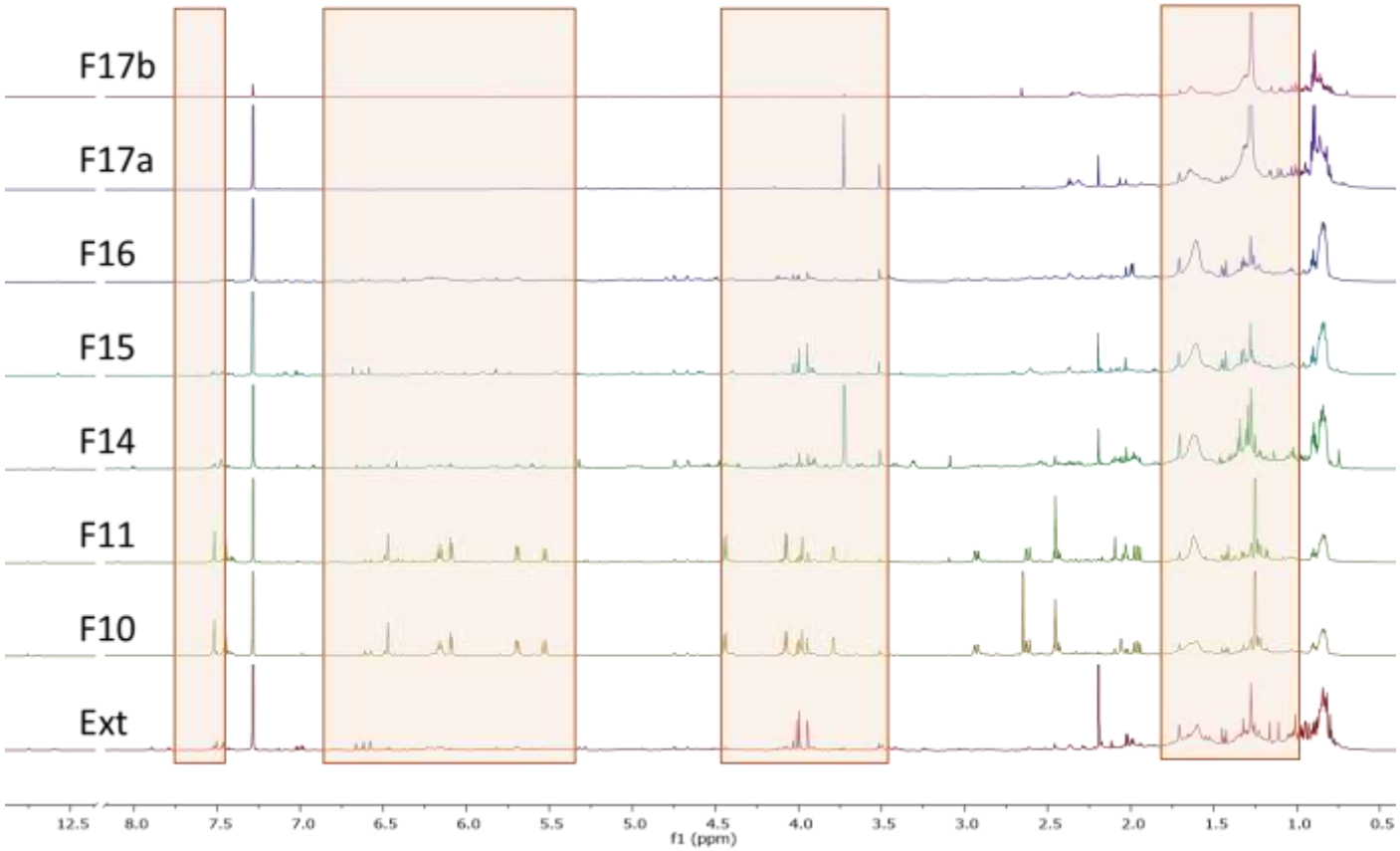
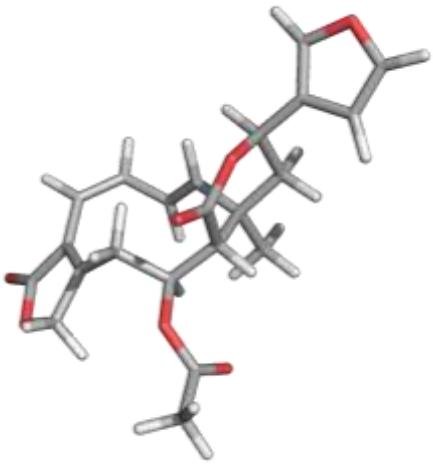
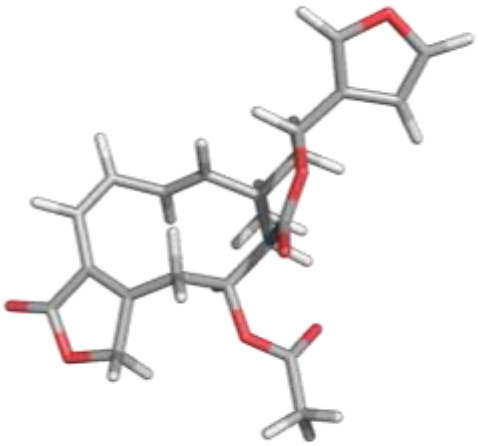


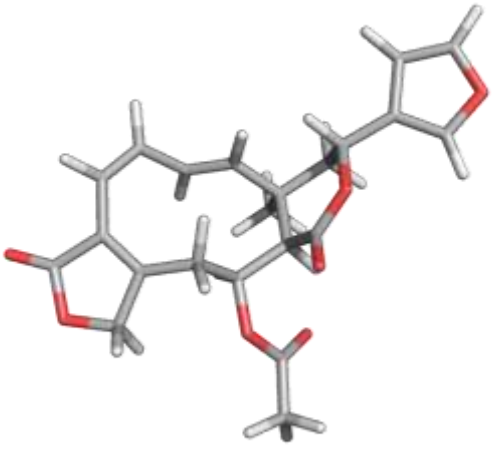
Figure S43 (continued). ^{1}H NMR spectrum of the acetone extract and fractions F1-F4, F6, F8, F9-F11 and F14-17. The orange boxes highlight signals attributed to clerodane type diterpenoids.



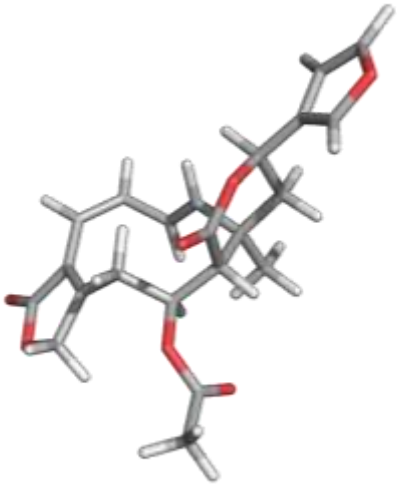
3a (*P* = 36.66 %)



3b (*P* = 36.47 %)



3c (*P* = 13.48 %)



3d (*P* = 13.39 %)

Figure S44. DFT B3LYP/DGDZVP geometry optimized conformers **3a**-**3d** at 298 K and 1 atm.

Table S1. Crystal data and structure refinement for **1**, co-crystal **1**-**2**, and **4**.

compound	**1**, 0.869(ketone), 0.131(water) (34ERB19)	**4** (285ERB18)
Empirical formula	$C_{22.6}H_{25.48}O_7$	$C_{20}H_{22}O_6$
Formula weight	409.19	358.37
Temperature (K)	100(2)	100(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a (Å)	12.3816(4)	9.1387(10)
b (Å)	7.6040(3)	24.286(3)
c (Å)	21.7468(7)	38.773(4)
α (°)	90	90
β (°)	101.7694(12)	90
γ (°)	90	90
Volume (Å^3)	2004.41(12)	8605.5(16)
Z	4	20
Dcalc (Mg/m^3)	1.356	1.383
Absorption coefficient (mm^{-1})	0.834	0.845
F(000)	868	3800
Crystal size (mm^3)	0.452 × 0.273 × 0.128	0.185 × 0.154 × 0.153
Theta range for data collection (°)	2.075 to 70.060	2.146 to 69.123
Index ranges	-15<=h<=15, -9<=k<=8, -26<=l<=26	-11<=h<=11, -28<=k<=29, -46<=l<=46
Total Reflections collected	35743	90876
Independent reflections	7010 [R_{int} = 0.0303]	16015 [R_{int} = 0.0386]
Completeness to theta = 67.679°	100.0 %	99.9%
Data / restraints / parameters	7010 / 56 / 569	16015 / 5841 / 2137
Goodness-of-fit on F^2	1.047	1.094
Final R indices [$I>2\sigma(I)$]	$R_1{}^a$ = 0.0353, $wR_2{}^b$ = 0.1006	$R_1{}^a$ = 0.0583, $wR_2{}^b$ = 0.1399
R indices (all data)	$R_1{}^a$ = 0.0356, $wR_2{}^b$ = 0.1010	$R_1{}^a$ = 0.0600, $wR_2{}^b$ = 0.1413
Largest diff. peak and hole (e.Å^{-3})	0.648 and -0.222	0.335 and -0.310
Absolute structure parameter, Parsons-Flack parameter	0.01(5)	0.07(3)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$