Meroterpene-like compounds derived from *β*-caryophyllene as potent *α*-glucosidase inhibitors

Shuang-Jiang Ma,[a†] Jie Yu,[a†] Da-Wei Yan,[a] Da-Cheng Wang, [a] Jin-Ming Gao*[,a] and Qiang Zhang*[,a,b]

a Shaanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry & Pharmacy, Northwest A&F University, Yangling 712100, PR China. E-mail: zhangq@nwsuaf.edu.cn; jinminggao@nwsuaf.edu.cn.

b State Key Laboratory of Medicinal Chemical Biology, Nankai University, Tianjin 300071, People's Republic of China.

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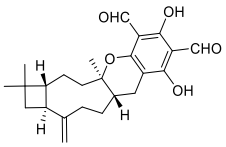
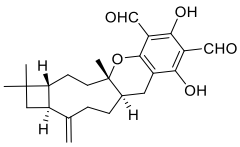
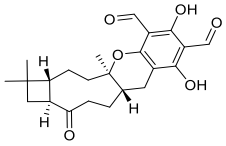
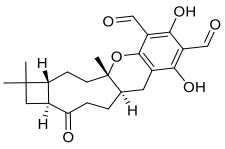
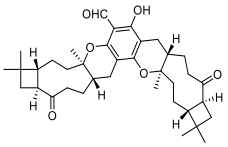
Table S1 Structure sheet of the synthesized natural-like library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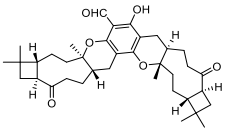	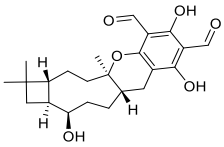	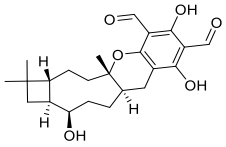	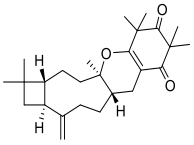	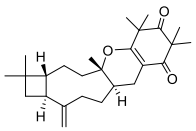
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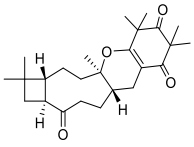	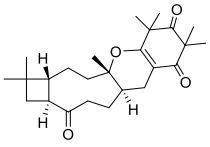	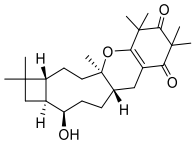	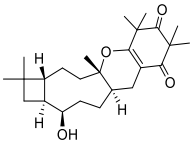	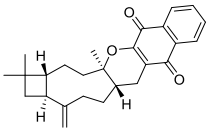
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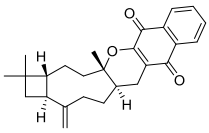	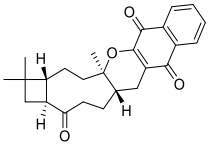	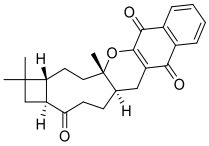	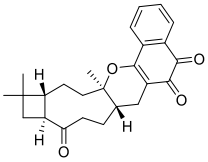	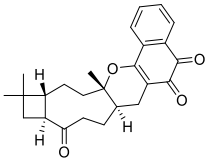
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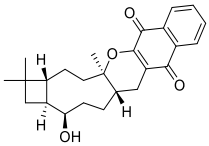
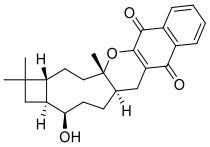
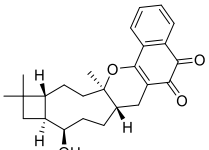
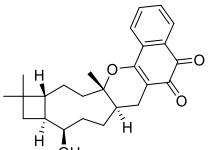
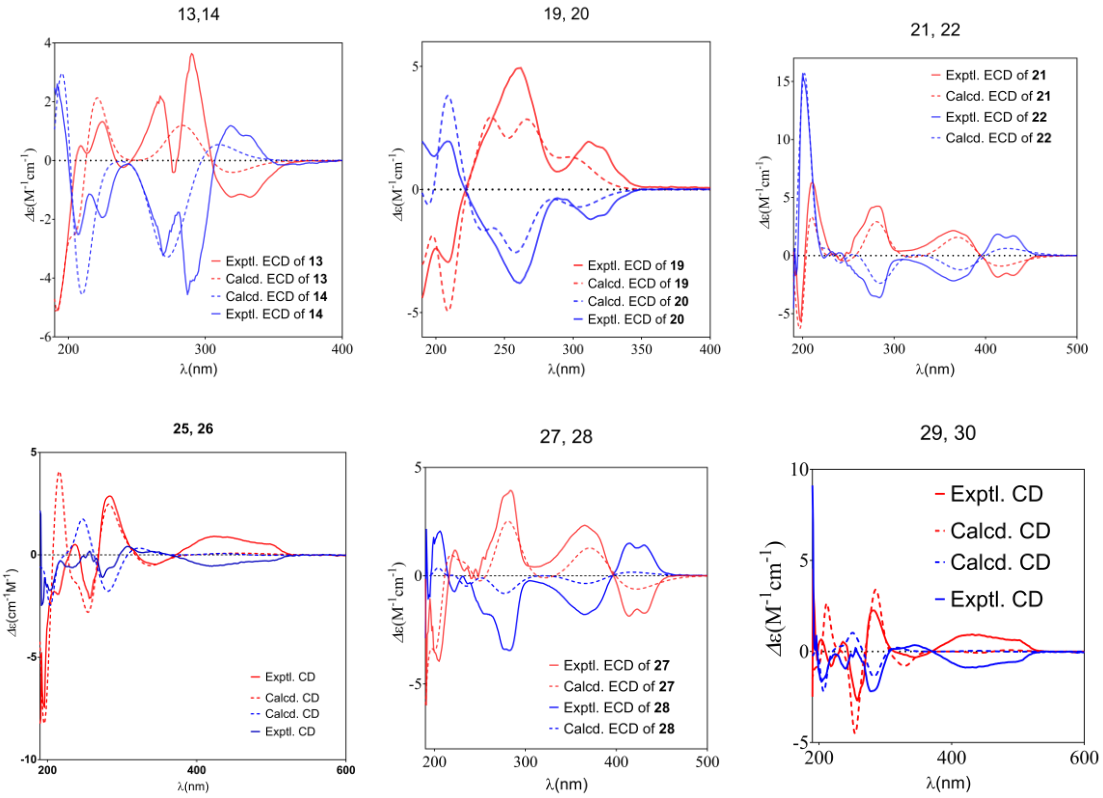
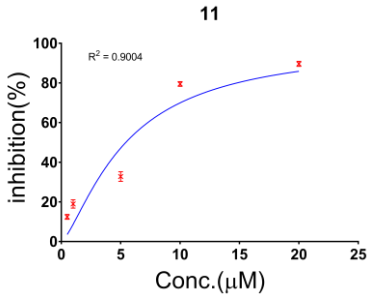
				
27	**28**	**29**	**30**	

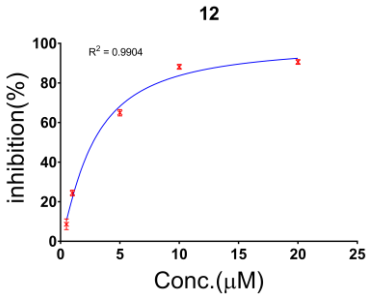
Figure S1. Experimental and calculated ECD spectra

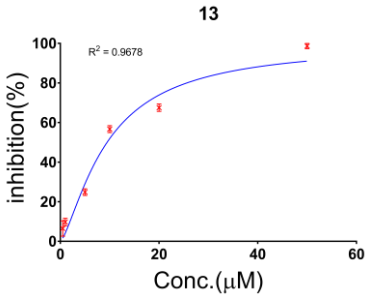


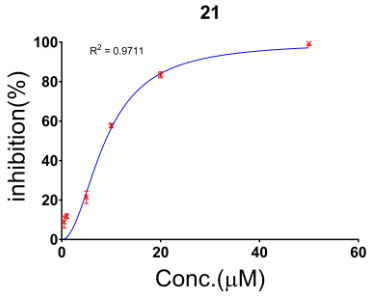
Note: the theoretical ECD spectra of compounds 25, 26, 29 30 were calculated by pbe0-1/3 at TZVP level, other compounds were calculated by cam-B3LYP/TZVP method.

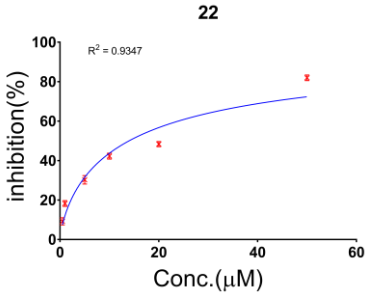
IC_{50} graphs of listed compounds in Table 1

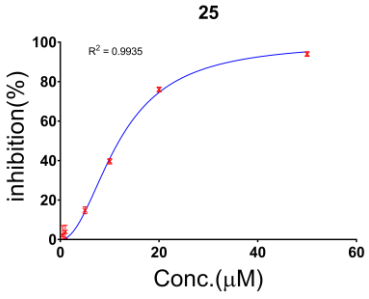


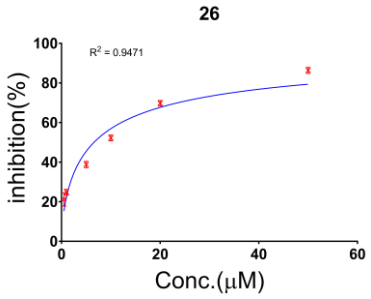


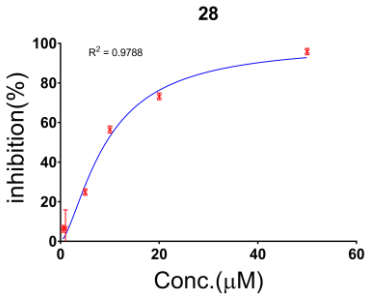


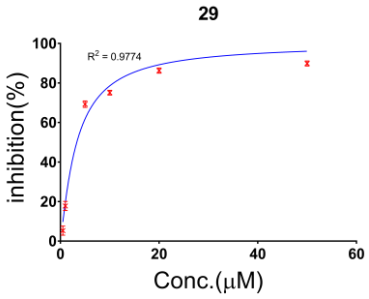












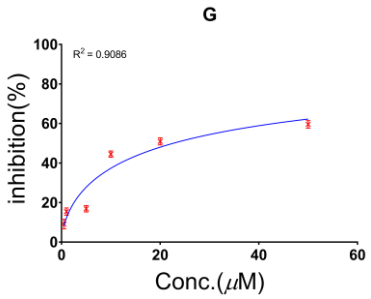
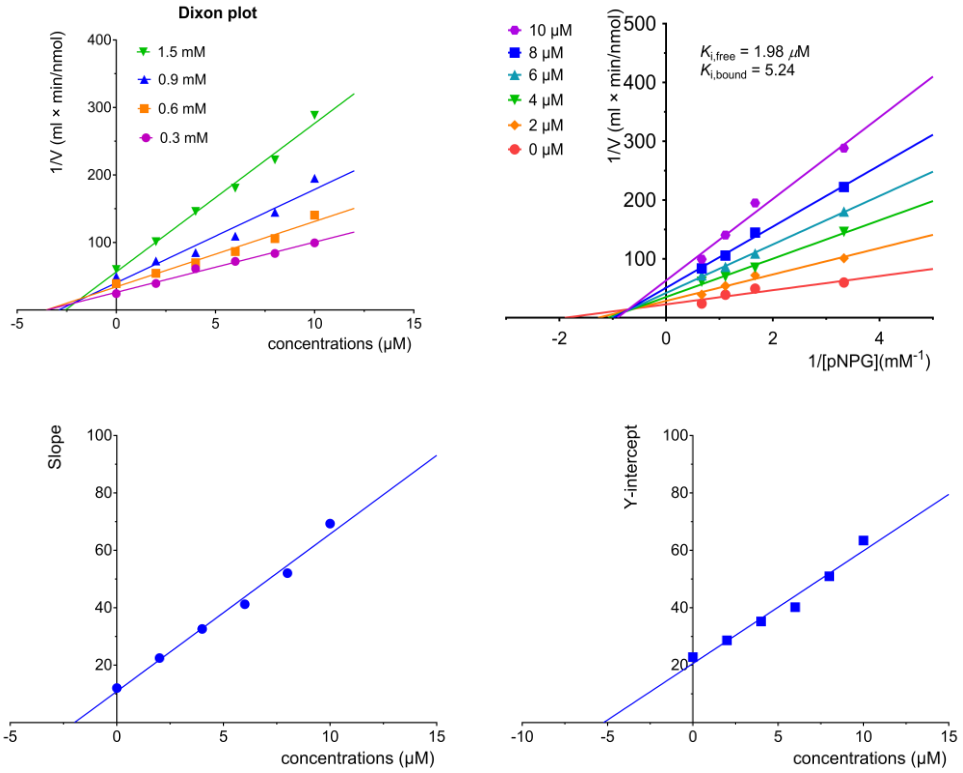


Figure S2 K_i related plots

Compound 12



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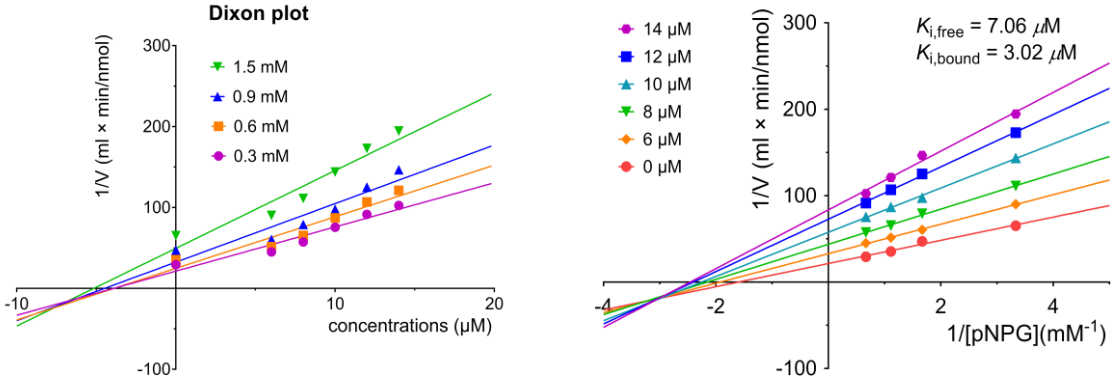

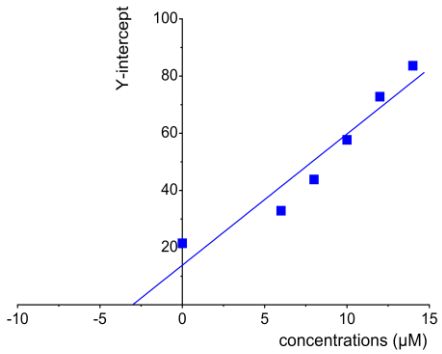
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-5
0
5
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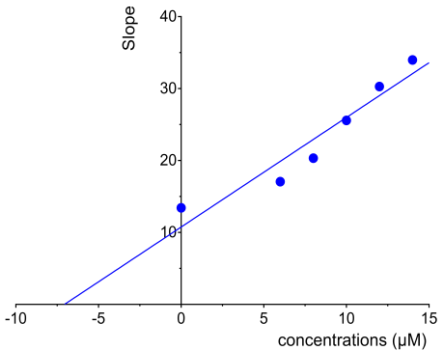
15
concentrations (μM)


Slope
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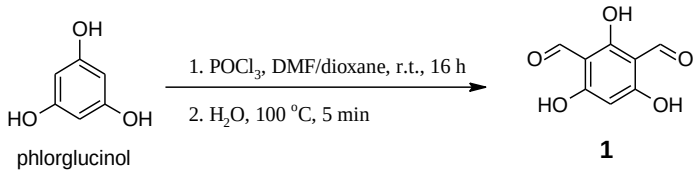
concentrations (μM)

Full citation of Gaussian 09

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Experimental

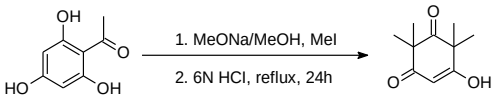
Preparation of pre-QMs 1



phlorglucinol **1**

The quinone methide (QM) donator 1 was prepared according to a previously reported method.[1] In a reaction tube with argon atmosphere was added DMF (0.65 ml), $POCl_3$ (0.8 ml) as added dropwise under 0-5 ℃ with an ice bath. The resulting mixture was stirred at ambient temperature for 30 min to afford Vilsmeier reagent. Phloroglucinol (513 mg) was dissolved in anhydrous 1,4-dioxane (2.5 ml), and the Vilsmeier reagent was added dropwise at 0 ℃. The reaction mixture was then stirred at ambient temperature for 12 h. Then the reaction mixture was added with ice water, and stirred for 4 h. The resulting mixture was filtered and the filtered residue was dissolved in water (7.5 ml) and refluxed for 10 min, then cooled down to 0 ℃, filtered. The filtered residue was dried in vacuo at 90 ℃ and then purified by column chromatography (silica gel, petroleum ether (PE) EtOAc 20:1) to afford the title compound **1** as an orange solid (544 mg, 75%).

2.2 Preparation of pre-QM 2

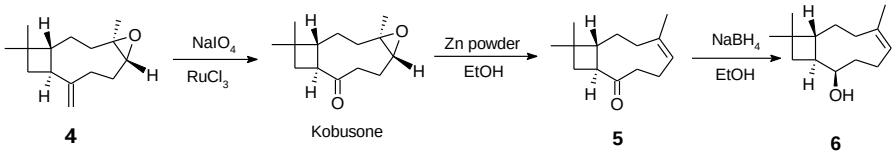


2',4',6'-trihydroxyacetophenone **2**

The QM precursor **2** was prepared according to a reported method.[2] The compound 2',4',6'-trihydroxyacetophenone (1.1 g), anhydrous MeOH (5 ml, slowly added) and MeONa (2.6 g) was mixed under room

temperature and was kept being stirred for 10 min. Then MeI (2.6 ml) was added dropwise at 0 ℃ and was stirred at 0 °C for 30 min, then at room temperature for a further 24 h. The reaction was quenched with 2N HCl, and the aqueous layer was extracted with EtOAc (3×50 ml). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, PE-EtOAc 50:1) to afford compound 4-acetyl-5-hydroxy-2,2,6,6-tetramethylcyclohex-4-ene-1,3-dione (630mg, 43%). The product was refluxed with 6N HCl (10 ml) at 100 ℃ for 24 h and extracted with EtOAc (3×30 ml), dried over Na_2SO_4 to yield the crude product **2**, which was purified by column chromatography (silica gel, PE-EtOAc 20:1) to afford compound **2** as a pale yellow solid (240 mg, 47%).

Preparation of caryophyllene derivates



4 Kobusone **5** **6**

The product kobusone was prepared according to our previously reported procedure.[3] (-)-β-caryophyllene epoxide (5.0 g), $NaIO_4$ (36.4 g) was added to a mixed solvent (25 ml MeCN, 25 ml EtOAc and 37.5 H_2O) and $RuCl_3$ (2.2% mol) in a 250 ml round-bottom flask equipped with a stir bar. After being stirred for 6 h, the reaction mixture was filtered. The filtrate was extracted with EtOAc (3×100ml). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE-EtOAc 20:1) to give the compound kobusone as a white solid (3.1 g, 61%).

To a solution of compound kobusone (2.00 g) in anhydrous EtOH (90 ml), activated zinc powder (100 g) was added. The reaction mixture was refluxed for 48 h. Then the reaction mixture was cooled to ambient temperature and filtered. The residue was washed with water and then extracted with EtOAc (3×120 ml). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, PE-EtOAc 50:1) to give the compound **5** as a colorless oil (1.00 g, 54%). Its structure was verified by comprising the ^{1}H and ^{13}C NMR data with the literature[4].

In an oven-dried flask were added anhydrous ethanol (35 ml) and compound **5** (1g). $NaBH_4$ (1.4g) was added portion-wise at 0 ℃. The reaction mixture was stirred at this temperature for 30 min, followed by warming up to ambient temperature for 12 h. After completion of the reaction, water (10 ml) was added slowly, and the aqueous layer was extracted with CH_2Cl_2 (3×15 ml). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE-EtOAc 100:1) to give the pure compound **6** as a colorless oil (0.9 g, 89%).

The structures of compounds 3 and 4 were verified on the basis of comparison NMR data with reported data in literatures.[4,5]

Preparation of meroterpenoid-like products 7-30

To a solution of 1.1 mmol pre-QM in 1,4- dioxane (3.0 ml) was added paraformaldehyde (774 mg) and 3 eq. *β*-caryophyllene (or its derivate). After being stirred under reflux for 24 h, the reaction mixture was removed solvent under vacuum. The crude products were separated on a silica gel column (PE-EtOAc from 50:1 to 10:1) and semi-HPLC C_{18} (gradient MECN 80~100%) repeatedly to yield pure products. The spectra data of compounds **7**, **11**, **17**, **21** and **25** were selected as representative examples listed as below. For the full list of all the synthetic products, please find them in the ESI.

Compound 7: yellow oil (mixed with compound **8**, **7**/**8** = 3:1, 209mg, 48% in total); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm 10.23 (m, 1H), 9.92 (m, 1H), 4.90 (m, 1H), 4.83 (m, 1H), 2.77 (m, 1H), 2.4 (m, 1H), 2.35 (m, 1H), 2.08 (s, 1H), 1.99 (m, 1H), 1.89 (m, 1H), 1.70 (m, 1H), 1.62 (m, 1H), 1.45 (s, 1H), 1.42 (s, 1H), 1.38 (m, 1H), 1.37 (m, 1H), 1.31 (m, 1H), 1.13 (m, 1H), 1.06 (m, 1H), 0.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* ppm 21.2, 22.2, 22.5, 24.0, 30.2, 30.4, 33.8, 35.2, 35.3, 36.4, 38.0, 41.7, 53.4, 84.8, 100.8, 103.6, 104.0, 110.6, 151.9, 163.1, 168.1, 168.4, 191.6, 191.9; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{24}H_{31}O_5$ 399.2171, found 399.2175.

Compound 8: yellow oil (mixed with compound **8**, **7**/**8** = 3:1, 209mg, 48% in total); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 10.23 (m, 1H), 9.92 (m, 1H), 4.90 (m, 1H), 4.83 (m, 1H), 2.77 (m, 1H), 2.4 (m, 1H), 2.35 (m, 1H), 2.08 (s, 1H), 1.99 (m, 1H), 1.89 (m, 1H), 1.70 (m, 1H), 1.62 (m, 1H), 1.45 (s, 1H), 1.42 (s, 1H), 1.38 (m, 1H), 1.37 (m, 1H), 1.31 (m, 1H), 1.13 (m, 1H), 1.06 (m, 1H), 0.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* ppm 20.2, 22.6, 22.7, 23.2, 29.7, 30.2, 33.4, 33.7, 34.2, 36.5, 38.6, 42.5, 56.2, 84.8, 100.2, 100.6, 103.4, 104.0, 154.6, 163.4, 168.2, 168.4, 191.6, 192.0.

Compound 9: colorless oil (53mg, 12%); $[\alpha]_D^{20}$ = −47.0 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 277 (4.51), 344 (3.43); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* ppm 1.00 (s, 3 H), 1.02 (s, 3 H), 1.24 (s, 3 H), 1.45 (dd, *J*=10.96, 7.43 Hz, 1 H), 1.55 − 1.66 (m, 1 H), 1.73 − 1.95 (m, 4 H), 2.01 − 2.24 (m, 4 H), 2.25 − 2.34 (m, 1 H), 2.46 (dt, *J*=13.69, 5.67 Hz, 1 H), 2.72 (dd, *J*=16.63, 4.89 Hz, 1 H), 2.77 − 2.86 (m, 1 H), 3.08 − 3.18 (m, 1 H), 10.00 (s, 1 H), 10.14 (s, 1 H), 13.23 (s, 1 H), 13.39 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 21.2, 21.9, 22.7, 23.6, 29.6, 29.6, 31.6, 34.6, 35.0, 37.3, 41.3, 46.0, 50.7, 83.9, 100.2, 103.7, 103.9, 162.6, 168.1, 168.4, 191.6, 191.6, 212.7; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{23}H_{29}O_6$ 401.1964, found 401.1968.

Compound 10: colorless oil (26 mg, 6%); $[\alpha]_D^{20}$ = −87.0 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 277 (4.52), 342 (3.47); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* ppm 0.99 (s, 3 H), 1.01 − 1.04 (s, 3 H), 1.13 − 1.18 (s, 3 H), 1.45 − 1.61 (m, 4 H), 1.61 − 1.73 (m, 1 H), 1.73 − 1.82 (m, 1 H), 1.90 (td, *J*=9.59, 3.13 Hz, 1 H), 2.03 − 2.16 (m, 2 H), 2.17 − 2.29 (m, 2 H), 2.45 − 2.63 (m, 2 H), 3.02 − 3.16 (m, 2 H), 10.02 (s, 1 H), 10.16 (s, 1 H), 13.31 (s, 1 H), 13.46 (br. s., 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 20.0, 22.5, 22.6, 22.8, 28.9, 28.9, 33.1, 34.4, 35.1,38.7, 42.7, 47.8, 55.1, 83.7, 100.2, 103.7, 104.0, 163.1, 168.2, 168.5, 191.6, 191.9, 213.0; HRESIMS *m/z* $[M+H]^+$ calcd for $C_{23}H_{29}O_6$ 401.1964, found 401.1961.

Compound 11: colorless oil (78mg, 12%); $[\alpha]_D^{20}$ = −78.0 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε)

304(4.31); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.99 (s, 3 H), 1.01 (s, 3 H), 1.05 (s, 6 H), 1.15 (s, 6 H), 1.44 (dt, *J*=11.0, 8.2 Hz, 2 H), 1.50 − 1.63 (m, 2 H), 1.63 − 1.75 (m, 2 H), 1.76 − 1.93 (m, 5 H), 1.93 − 2.00 (m, 1 H), 2.00 − 2.10 (m, 3 H), 2.10 − 2.17 (m, 2 H), 2.17 − 2.30 (m, 4 H), 2.38 − 2.49 (m, 2 H), 2.53 (dd, *J*=16.6, 5.3 Hz, 1 H), 2.72 − 2.80 (m, 2 H), 2.83 − 2.92 (m, 1 H), 3.04 − 3.20 (m, 2 H), 12.46 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.8, 21.3, 21.7, 22.1, 22.7, 22.8, 24.0, 25.2, 29.7, 29.7, 29.8, 30.2, 31.5, 31.8, 34.5, 34.7, 35.2, 35.4, 37.4, 37.4, 41.3, 41.3, 45.4, 46.7, 50.7, 50.7, 80.6, 81.9, 100.0, 100.0, 100.1, 154.7, 159.0, 160.6, 191.4, 213.1, 213.4; HRESIMS *m/z* $[M+H]^+$ calcd for $C_{37}H_{51}O_6$ 591.3686, found 591.3689.

Compound 12: colorless oil (13mg, 2%) ; $[\alpha]_D^{20}$ = −199.2 (*c* 0.01 CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 303 (4.47); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.82 − 0.93 (m, 1 H), 1.00 (s, 6 H), 1.02 (s, 3 H), 1.03 (s, 3 H), 1.09 (s, 3 H), 1.20 (s, 3 H), 1.42 − 1.53 (m, 4 H), 1.55 − 1.63 (m, 4 H), 1.69 − 1.82 (m, 4 H), 1.83 − 1.96 (m, 4 H), 2.03 − 2.11 (m, 2 H), 2.12 − 2.20 (m, 2 H), 2.20 − 2.31 (m, 2 H), 2.41 − 2.50 (m, 1 H), 2.50 − 2.56 (m, 1 H), 2.56 − 2.65 (m, 1 H), 2.80 − 2.90 (m, 1 H), 3.04 − 3.08 (m, 1 H), 3.08 − 3.12 (m, 1 H), 3.12 − 3.18 (m, 1 H), 10.06 (s, 1 H), 12.55 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.2, 20.2, 21.0, 22.0, 22.7, 22.9, 23.1, 25.0, 29.0, 29.0, 29.7, 29.9, 31.7, 33.0, 34.3, 34.6, 35.2, 35.5, 37.2, 39.0, 41.5, 42.9, 46.3, 47.7, 50.8, 55.2, 80.0, 81.6, 100.1, 100.3, 104.8, 154.9, 159.5, 160.8, 191.5, 213.4, 213.5; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{37}H_{51}O_6$ 591.3686, found 591.3681.

Compound 13: white solid (150mg, 34%); $[\alpha]_D^{20}$ = −46.4 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 278(4.55), 343 (3.53); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.97 (s, 3 H), 0.99 (s, 3 H), 1.20 (s, 3 H), 1.34 − 1.47 (m, 2 H), 1.48 − 1.64 (m, 2 H), 1.65 − 1.86 (m, 3 H), 2.00 (dd, *J*=9.78, 3.91 Hz, 2 H), 2.03 − 2.12 (m, 2 H), 2.20 − 2.36 (m, 2 H), 2.73 (dd, *J*=16.63, 5.28 Hz, 1 H), 3.88 (d, *J*=8.61 Hz, 1 H), 10.02 (s, 1 H), 10.14 (s, 3 H), 13.21 (s, 1 H) 13.41 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.6, 21.7, 22.5, 23.7, 28.0, 29.7, 32.4, 33.2, 34.2, 34.5, 38.3, 41.2, 42.6, 69.1, 84.6, 100.5, 103.2, 103.6, 162.9, 167.8, 168.0, 191.2, 191.6; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{23}H_{31}O_6$ 403.2121, found 403.2122.

Compound 14: colorless oil (70mg, 16%) ; $[\alpha]_D^{20}$ = −120.2 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 278 (4.54), 342 (3.53); ^{1}H NMR (400 MHz, CDCl3) δ ppm 0.96 (s, 3 H), 0.99 (s, 3 H), 1.13 (s, 3 H) 1.34 − 1.45 (m, 2 H), 1.46 − 1.53 (m, 2 H), 1.59 − 1.65 (m, 1 H), 1.71 − 1.83 (m, 2 H), 1.83 − 1.91 (m, 2 H), 1.91 − 1.96 (m, 1 H), 1.96 − 2.03 (m, 1 H), 2.03 − 2.10 (m, 1 H), 2.10 − 2.16 (m, 1 H), 2.21 − 2.28 (m, 1 H), 2.95 (dd, *J*=16.6, 5.3 Hz, 1 H), 3.61 − 3.68 (m, 1 H), 3.72 (br. s., 1 H), 10.01 (s, 1 H), 10.16 (s, 1 H), 13.27 (s, 1 H), 13.46 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.2, 22.4, 23.1, 23.2, 24.1, 29.4, 34.6, 34.7, 36.0, 36.5, 40.0, 42.2, 46.2, 70.8, 85.2, 101.0, 103.9, 104.3, 164.0, 168.5, 168.8, 191.9, 192.4; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{23}H_{31}O_6$ 403.2121, found 403.2112.

Compounds 15/16: 2:1 diastereomeric mixture, yellow oil (122mg, 28%), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.86 (s, 1H), 4.82 (s, 1H), 2.67 (m, 1H), 1.99 (m,1H), 1.87(s, 1H), 1.66 (m, 1H), 1.65 (m, 1H), 1.60 (m, 1H),1.41(m, 1H), 1.40 (m, 1H), 1.39 (m, 3H), 1.38 (m, 1H), 1.37 (m,6H), 1.36 (m, 1H), 1.13 (m, 1H), 1.06 (m, 1H), 0.97 (m, 3H), 0.97 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm **15**:20.8, 22.0, 22.7, 23.1, 24.6, 25.3, 25.7, 26.1, 30.1, 33.2, 33.6, 33.7, 36.3, 37.5, 38.7, 42.2, 47.5, 53.0, 54.8, 83.8, 106.9, 110.4, 151.7, 170.3, 197.7, 213.8; **16**: 19.7, 22.3, 22.5, 23.3,

24.6, 24.6, 25.3, 25.9, 29.6, 33.3, 33.8, 34.5, 35.2, 36.6, 38.7, 42.5, 47.5, 54.8, 56.1, 84.0, 106.8, 110.0, 154.8, 170.6, 197.6, 213.8; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{26}H_{38}O_3$ 399.2899, found 399.2897.

Compounds 17: white solid (228mg, 52%), $[\alpha]_D^{20}$ = +27.4 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 261(4.12); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.99 (s, 3 H), 1.01 (s, 3 H), 1.14 (s, 3 H), 1.31 (s, 3 H), 1.32 (s, 3 H), 1.34 (s, 3 H), 1.36 (s, 3 H), 1.44 (dd, *J*=11.0, 7.4 Hz, 1 H), 1.51 − 1.62 (m, 1 H), 1.62 − 1.70 (m, 1 H), 1.74 (dtd, *J*=11.7, 5.9, 5.9, 3.1 Hz, 2 H), 1.78 − 1.89 (m, 2 H), 2.00 − 2.08 (m, 1 H), 2.09 − 2.16 (m, 1 H), 2.17 − 2.28 (m, 2 H), 2.43 (dt, *J*=13.7, 5.9 Hz, 1 H), 2.54 (dd, *J*=17.0, 5.3 Hz, 1 H), 2.72 − 2.83 (m, 1 H), 3.08 − 3.19 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ ppm 20.7, 21.9, 22.5, 23.8, 24.6, 25.2, 25.3, 25.4, 29.1, 29.4, 31.8, 34.6, 35.5, 36.9, 41.4, 46.1, 47.4, 50.7, 54.8, 83.0, 106.7, 169.8, 197.4, 212.9, 213.5; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{37}O_4$ 401.2692, found 401.2696.

Compounds 18: white solid (110mg, 25%), $[\alpha]_D^{20}$ = −134.2 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 261 (4.16); ^{1}H NMR (400 MHz, CDCl3) δ ppm 0.98 (s, 3 H), 1.01 (s, 3 H), 1.06 (s, 3 H), 1.36 (s, 6 H), 1.36 (br. s., 3 H), 1.41 (s, 3 H), 1.44 − 1.54 (m, 3 H), 1.57 (dd, *J*=10.2, 6.3 Hz, 2 H), 1.70 (dd, *J*=15.7, 7.8 Hz, 1 H), 1.76 − 1.92 (m, 2 H), 2.05 − 2.20 (m, 3 H), 2.45 − 2.55 (m, 2 H), 2.91 (dd, *J*=16.8, 5.5 Hz, 1 H), 3.04 − 3.15 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.9, 22.7, 22.9, 23.5, 24.2, 24.9, 25.7, 26.3, 29.1, 29.2, 33.5, 34.6, 35.7, 38.6, 43.2, 47.9, 48.1, 55.2, 55.4, 83.3, 107.1, 170.9, 197.9, 213.7, 213.7; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{37}O_4$ 401.2692, found 401.2694.

Compounds 19: white solid (314mg, 71%), $[\alpha]_D^{20}$ = +27.8 (*c* 0.05 in CH_3CN); λ_{max}(MeCN)/nm (log ε) 263 (4.14); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.96 (s, 3 H), 0.97 − 0.99 (m, 3 H), 1.11 (s, 3 H), 1.32 (s, 3 H), 1.33 (s, 3 H), 1.35 (s, 3 H), 1.38 (s, 3 H), 1.47 − 1.55 (m, 1 H), 1.55 − 1.63 (m, 1 H), 1.67 (d, *J*=4.3 Hz, 1 H), 1.68 − 1.73 (m, 2 H), 1.73 − 1.76 (m, 1 H), 1.76 − 1.83 (m, 2 H), 1.90 − 1.96 (m, 2 H), 1.97 − 2.02 (m, 1 H), 2.02 − 2.10 (m, 1 H), 2.13 − 2.30 (m, 2 H), 2.55 (dd, *J*=17.0, 5.3 Hz, 1 H), 3.87 (d, *J*=8.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.1, 21.7, 22.5, 23.3, 24.3, 25.0, 25.3, 27.7, 29.5, 32.4, 33.1, 34.2, 34.9, 37.9, 41.4, 42.7, 47.1, 54.4, 69.1, 83.6, 106.6, 169.9, 197.3, 213.6, 213.6; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{39}O_4$ 403.2848, found 403.2849.

Compounds 20: colorless oil (79mg, 18%), $[\alpha]_D^{20}$ = −97.8 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 263 (3.97); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.94 (s, 3 H), 0.98 (s, 3 H), 1.04 (s, 3 H), 1.34 (br. s., 3 H), 1.34 (s, 3 H), 1.35 − 1.35 (m, 3 H), 1.38 (s, 3 H) 1.44 − 1.53 (m, 2 H), 1.56 (d, *J*=9.0 Hz, 2 H), 1.58 − 1.65 (m, 2 H), 1.68 − 1.77 (m, 2 H), 1.81 (dd, *J*=15.3, 9.4 Hz, 1 H), 1.86 − 1.94 (m, 1 H), 1.99 (t, *J*=9.8 Hz, 1 H), 2.05 − 2.13 (m, 2 H), 2.24 (q, *J*=9.0 Hz, 1 H), 2.78 (dd, *J*=16.4, 4.7 Hz, 1 H), 3.69 (br. s., 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.4, 22.6, 22.6, 23.3, 23.6, 24.6, 25.4, 26.0, 29.0, 34.3, 34.4, 35.9, 36.1, 39.4, 41.8, 45.8, 47.5, 54.8, 70.6, 84.1, 107.0, 171.0, 197.8, 213.8, 213.8; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{39}O_4$ 403.2848, found 403.2829.

Compound 21: yellow solid (116mg, 27%); $[\alpha]_D^{20}$ = −25.0 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251(4.41), 277(4.06), 329 (3.34); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.98 (s, 3 H), 0.99 − 1.01 (m, 3 H), 1.21 (s, 3 H), 1.42 − 1.51 (m, 1 H), 1.57 − 1.62 (m, 1 H), 1.62 − 1.65 (m, 1 H), 1.68 (d, *J*=10.1 Hz, 1 H), 1.71 − 1.78 (m, 1 H), 1.81 − 1.86 (m, 1 H), 1.84 − 1.85 (m, 1 H), 1.87 − 1.91 (m, 1 H), 2.00 − 2.05 (m, 1 H), 2.07 (d, *J*=17.3 Hz, 1 H), 2.08

− 2.12 (m, 1 H), 2.15 − 2.18 (m, 1 H), 2.19 − 2.23 (m, 1 H), 2.41 − 2.44 (m, 1 H), 2.45 − 2.49 (m, 1 H), 2.74 (dd, *J*=17.7, 4.10 Hz, 1 H), 4.87 (s, 1 H), 4.91 (s, 1 H), 7.66 (dtd, *J*=19.5, 7.4, 7.4, 1.3 Hz, 2 H), 8.07 (ddd, *J*=7.6, 4.6, 1.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.9, 22.2, 22.3, 25.4, 30.3, 33.4, 33.5, 33.9, 35.3, 36.5, 37.7, 41.4, 53.8, 84.4, 110.5, 120.0, 125.9, 126.2, 131.3, 132.2, 132.8, 133.8, 152.1, 154.3, 179.8, 184.1; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{26}H_{31}O_3$ 391.2273, found 391.2258..

Compound 22: yellow solid (47mg, 11%); $[\alpha]_D^{20}$ = −9.8 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251 (4.46), 277 (4.10), 329(3.41); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.96 (s, 3 H), 0.99 (s, 3 H), 1.14 (s, 3 H), 1.38 − 1.47 (m, 1 H), 1.48 − 1.56 (m, 1 H), 1.59 (d, *J*=10.7 Hz, 2 H), 1.61 − 1.64 (m, 1 H), 1.68 (d, *J*=10.4 Hz, 1 H), 1.75 (dd, *J*=10.7, 8.2 Hz, 1 H), 1.81 (dd, *J*=15.8, 8.2 Hz, 1 H), 2.01 (d, *J*=11.7 Hz, 1 H), 2.05 (s, 1 H), 2.12 (ddd, *J*=13.6, 8.6, 2.4 Hz, 1 H), 2.4 (dd, *J*=15.5, 10.4 Hz, 1 H), 2.5 (dd, *J*=9.5, 2.2 Hz, 1 H), 2.6 (q, *J*=9.3 Hz, 1 H), 2.9 (d, *J*=13.6 Hz, 1 H), 4.8 (s, 1 H), 4.8 (s, 1 H) 7.7 (td, *J*=7.4, 1.4 Hz, 2 H), 8.1 (ddd, *J*=7.3, 5.4, 1.6 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 19.9, 22.6, 23.0, 24.7, 29.7, 33.4, 33.7, 34.4, 36.6, 38.5, 38.6, 42.6, 56.4, 84.5, 110.1, 120.1, 125.9, 126.3, 131.3, 132.1, 132.8, 133.8, 154.6, 154.7, 179.8, 184.1; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{26}H_{31}O_3$ 391.2273, found 391.2271.

Compound 23: yellow solid (60mg, 14 %), $[\alpha]_D^{20}$ = −57.2 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251(4.41), 277 (4.07), 329 (3.35); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.99 (s, 3 H), 1.01 (s, 3 H), 1.20 − 1.26 (m, 3 H), 1.44 (dd, *J*=11.2, 7.6 Hz, 1 H), 1.55 − 1.67 (m, 1 H), 1.72 − 1.84 (m, 2 H), 1.86 − 2.00 (m, 2 H), 2.04 − 2.23 (m, 3 H), 2.24 − 2.30 (m, 2 H), 2.46 (dt, *J*=13.5, 5.8 Hz, 1 H), 2.74 − 2.88 (m, 2 H), 3.09 − 3.19 (m, 1 H), 7.60 − 7.75 (m, 2 H), 8.01 − 8.14 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 20.9, 21.8, 22.7, 25.1, 29.5, 29.7, 31.6, 34.6, 35.0, 36.9, 41.3, 45.9, 51.0, 83.5, 119.7, 126.0, 126.2, 131.2, 132.1, 132.9, 133.9, 154.0, 179.7, 183.8, 212.9; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{29}O_4$ 393.2066, found 393.2054.

Compound 24: rufous solid (26mg, 6%), $[\alpha]_D^{20}$ = −82.8 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251 (4.41), 277 (4.06), 332 (3.35); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.98 (s, 3 H), 1.01 (s, 3 H), 1.14 (s, 3 H), 1.49 (dd, *J*=11.0, 7.8 Hz, 1 H), 1.55 (td, *J*=7.7, 2.2 Hz, 1 H), 1.59 − 1.68 (m, 2 H), 1.68 − 1.79 (m, 2 H), 1.85 − 1.93 (m, 1 H), 2.03 − 2.11 (m, 1 H), 2.12 − 2.18 (m, 1 H), 2.22 (dt, *J*=11.6, 5.7 Hz, 1 H), 2.39 (dd, *J*=15.5, 8.8 Hz, 1 H), 2.47 − 2.52 (m, 1 H), 2.57 (d, *J*=1.6 Hz, 1 H), 3.03 − 3.10 (m, 1 H), 3.15 (dd, *J*=18.4, 5.1 Hz, 1 H), 7.65 − 7.74 (m, 2 H), 8.07 − 8.11 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 19.8, 22.7, 23.0, 23.9, 28.8, 28.9, 33.0, 34.4, 35.2, 38.2, 42.7, 47.9, 55.3, 83.5, 119.8, 126.0, 126.4, 131.2, 132.0, 133.0, 134.0, 154.6, 179.7, 184.0, 213.1; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{29}O_4$ 393.2066, found 393.2055.

Compound 25: rufous solid (21mg, 5 %), $[\alpha]_D^{20}$ = −44.6 (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 257(4.30); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.99 (s, 3 H), 1.04 (s, 3 H), 1.28 (s, 3 H), 1.46 (dd, *J*=11.0, 7.6 Hz, 1 H), 1.62 − 1.71 (m, 1 H), 1.75 − 1.97 (m, 4 H), 2.06 (dd, *J*=17.3, 11.0 Hz, 1 H), 2.15 (t, *J*=10.2 Hz, 1 H), 2.19 − 2.27 (m, 2 H), 2.31 − 2.40 (m, 1 H), 2.43 − 2.51 (m, 1 H), 2.71 − 2.85 (m, 2 H), 3.12 − 3.20 (m, 1 H), 7.52 (t, *J*=7.6 Hz, 1 H), 7.65 (td, *J*=7.7, 1.3 Hz, 1 H), 7.76 (d, *J*=7.9 Hz, 1 H), 8.04 − 8.09 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.3, 21.8, 22.7, 24.6, 29.4, 29.6, 31.7, 34.7, 35.3, 37.3, 41.2, 45.8, 50.7, 84.9, 112.6, 123.8, 128.7, 130.2, 130.8, 132.2,

134.8, 161.4, 178.0, 179.7, 212.6; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{29}O_4$ 393.2066, found 393.2065.

Compound 26: rufous solid (13mg, 3 %), $[\alpha]_D^{20} = -53.1$ (*c* 0.04 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 256 (4.18); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.99 (s, 3 H), 1.04 (s, 3 H), 1.20 (s, 3 H), 1.23 − 1.29 (m, 1 H), 1.47 − 1.61 (m, 2 H), 1.61 − 1.71 (m, 2 H), 1.79 − 1.86 (m, 1 H), 1.88 − 1.95 (m, 1 H), 2.02 − 2.10 (m, 1 H), 2.13 − 2.20 (m, 1 H), 2.25 − 2.39 (m, 2 H), 2.54 (td, *J*=7.0, 2.7 Hz, 1 H), 3.06 − 3.16 (m, 1 H), 4.13 (q, *J*=7.3 Hz, 1 H), 7.51 − 7.57 (m, 1 H), 7.67 (t, *J*=7.6 Hz, 1 H), 7.69 − 7.69 (m, 1 H), 7.79 (d, *J*=7.6 Hz, 1 H), 8.09 (d, *J*=7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.2, 22.7, 22.9, 23.5, 28.8, 29.0, 33.1, 34.4, 35.4, 38.6, 42.8,47.8,55.2, 84.8, 112.8, 124.1, 128.8, 130.2, 130.9, 132.2, 134.9, 162.1, 178.2, 179.7, 213.2; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{29}O_4$ 393.2066, found 393.2058.

Compound 27: yellow solid (117mg, 27%), $[\alpha]_D^{20} = -37.0$ (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251 (4.31), 277 (3.96), 329 (3.25); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.94 (d, *J*=1.6 Hz, 3 H), 0.96 (d, *J*=2.2 Hz, 3 H), 1.18 (d, *J*=1.6 Hz, 3 H), 1.34 − 1.45 (m, 2 H), 1.46 − 1.52 (m, 1 H), 1.53 − 1.60 (m, 1 H), 1.64 − 1.76 (m, 2 H), 1.77 − 1.88 (m, 3 H), 1.94 − 2.15 (m, 5 H), 2.19 − 2.32 (m, 2 H), 2.78 (ddd, *J*=18.6, 4.9, 2.0 Hz, 1 H), 3.86 (d, *J*=8.2 Hz, 1 H), 7.56 − 7.71 (m, 2 H), 7.97 − 8.11 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.6, 21.9, 22.9, 25.5, 28.1, 30.0, 32.7, 33.5, 34.5, 34.8, 38.2, 41.3, 43.0, 69.5, 84.6, 120.0, 125.9, 126.1, 131.2, 132.1, 132.7, 133.7, 154.3, 179.9, 184.1; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}O_4$ 395.2222, found 395.2227.

Compound 28: yellow solid (69mg, 16%), $[\alpha]_D^{20} = -46.4$ (*c* 0.04 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 251 (4.11), 277 (3.78), 327 (3.09); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.94 (s, 3 H), 0.98 (s, 3 H), 1.11 (s, 3 H), 1.23 − 1.29 (m, 2 H), 1.33 − 1.43 (m, 2 H), 1.51 − 1.64 (m, 4 H), 1.67 − 1.78 (m, 2 H), 1.78 − 1.89 (m, 2 H), 1.92 − 2.08 (m, 2 H), 2.22 (q, *J*=9.1 Hz, 1 H), 2.33 (dd, *J*=15.8, 10.1 Hz, 1 H), 3.02 (dd, *J*=18.3, 5.0 Hz, 1 H), 3.71 (br. s., 1 H) 7.59 − 7.75 (m, 1 H) 8.03 − 8.13 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 19.6, 22.8, 23.0, 23.6, 23.7, 29.1, 34.3, 34.4, 35.8, 36.2, 39.1, 41.9, 46.0, 70.5, 84.6, 120.3, 125.9, 126.3, 131.3, 132.1, 132.9, 133.8, 154.9, 179.9, 184.2; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}O_4$ 395.2222, found 395.2228.

Compound 29: rufous solid (134mg, 31%), $[\alpha]_D^{20} = +54.7$ (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 258 (4.25); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.97 (s, 3 H), 0.97 (s, 3 H), 1.23 − 1.25 (m, 3 H), 1.37 − 1.49 (m, 2 H), 1.49 − 1.55 (m, 1 H), 1.56 − 1.62 (m, 1 H), 1.64 − 1.73 (m, 1 H), 1.74 − 1.88 (m, 4 H), 1.94 − 2.15 (m, 4 H), 2.23 − 2.39 (m, 2 H), 2.76 (dd, *J*=17.5, 5.2 Hz, 1 H), 3.88 (d, *J*=8.5 Hz, 1 H), 7.46 − 7.55 (m, 1 H), 7.59 − 7.67 (m, 1 H), 7.78 (d, *J*=7.9 Hz, 1 H), 8.05 (d, *J*=7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.0, 22.1, 22.9, 25.0, 28.1, 29.9, 32.7, 33.6, 34.6, 35.1, 38.7, 41.4, 43.0, 69.4, 86.0, 113.0, 123.9, 128.5, 130.2, 130.6, 132.5, 134.7, 161.8, 178.1, 180.0; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}O_4$ 395.2222, found 395.2229.

Compound 30: rufous solid (56mg, 13%), $[\alpha]_D^{20} = -173.4$ (*c* 0.05 in CH_3CN); UV λ_{max}(MeCN)/nm (log ε) 257 (4.29); ^{1}H NMR (500 MHz, $CDCl^3$) δ ppm 0.95 (s, 3 H), 1.00 (s, 3 H), 1.10 (dt, *J*=14.3, 8.7 Hz, 1 H), 1.17 (s, 3 H), 1.34 − 1.44 (m, 1 H), 1.53 − 1.64 (m, 4 H), 1.67 (br. m, 2 H), 1.75 − 1.85 (m, 2 H), 1.89 − 2.00 (m, 2 H), 2.05 (t, *J*=10.1 Hz, 1 H), 2.20 − 2.33 (m, 2 H), 2.98 (dd, *J*=17.3, 5.0 Hz, 1 H), 3.72 (br. s., 1 H), 7.49 − 7.55 (m, 1 H), 7.65 (t, *J*=7.7 Hz, 1 H), 7.79 (d, *J*=7.9 Hz, 1 H), 8.07 (d, *J*=7.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.0, 22.8,

22.9, 23.2, 23.7, 29.1, 34.3, 34.4, 36.0, 36.1, 39.6, 41.9, 45.9, 70.4, 85.9, 113.2, 124.1, 128.6, 130.2, 130.7, 132.5, 134.8, 162.4, 178.2, 180.0; HRESIMS *m/z* $[M + H]^+$ calcd for $C_{25}H_{31}O_4$ 395.2222, found 395.2226.

Reference

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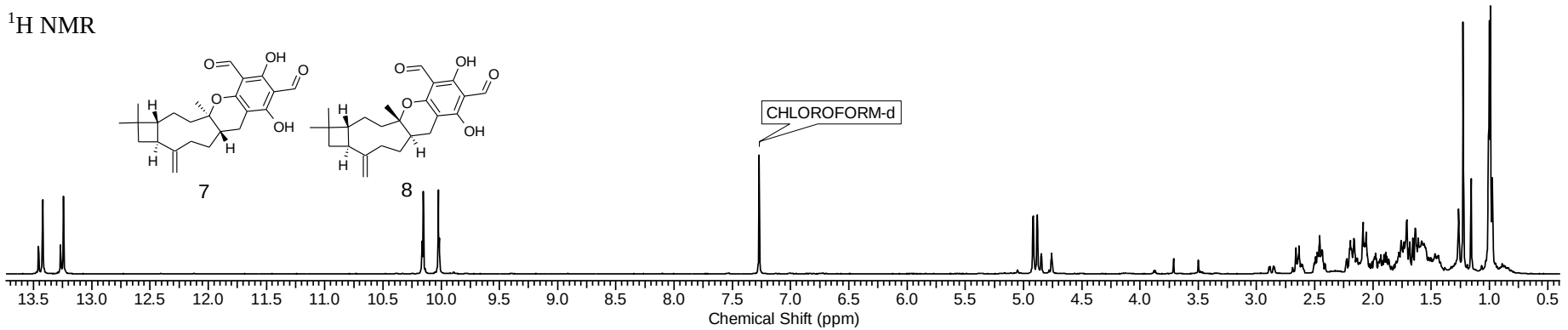
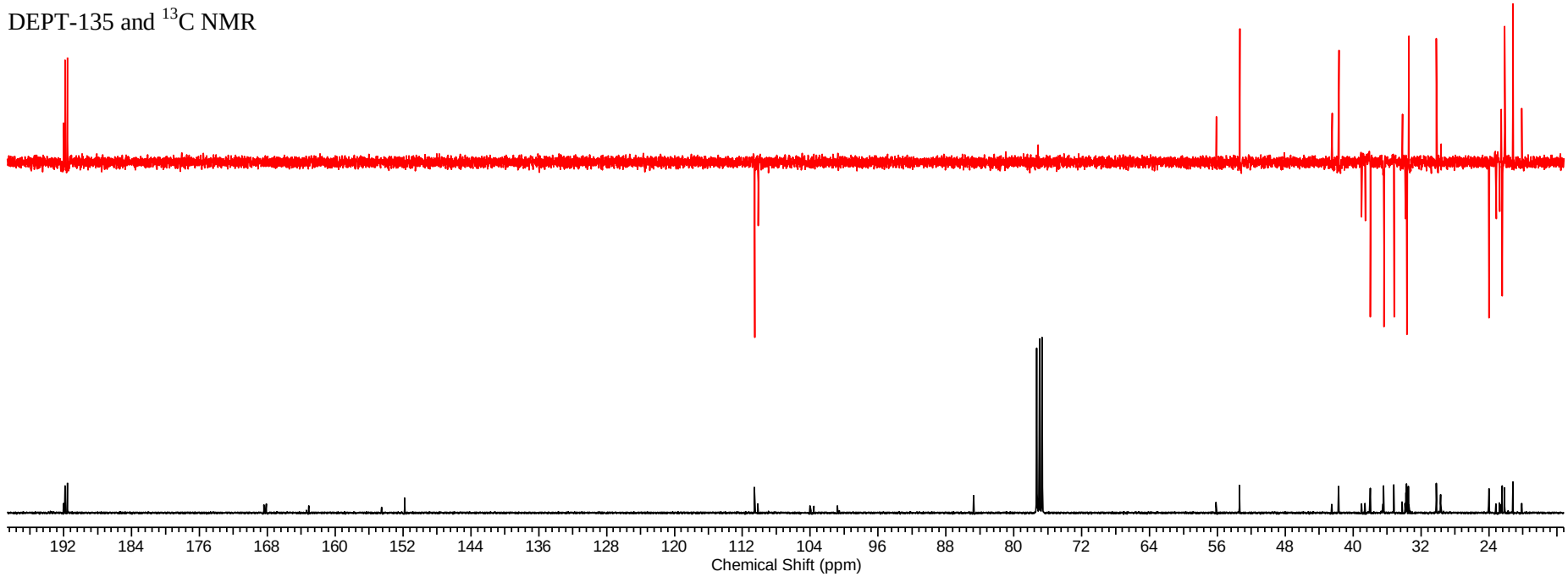
NMR and HR-MS spectra

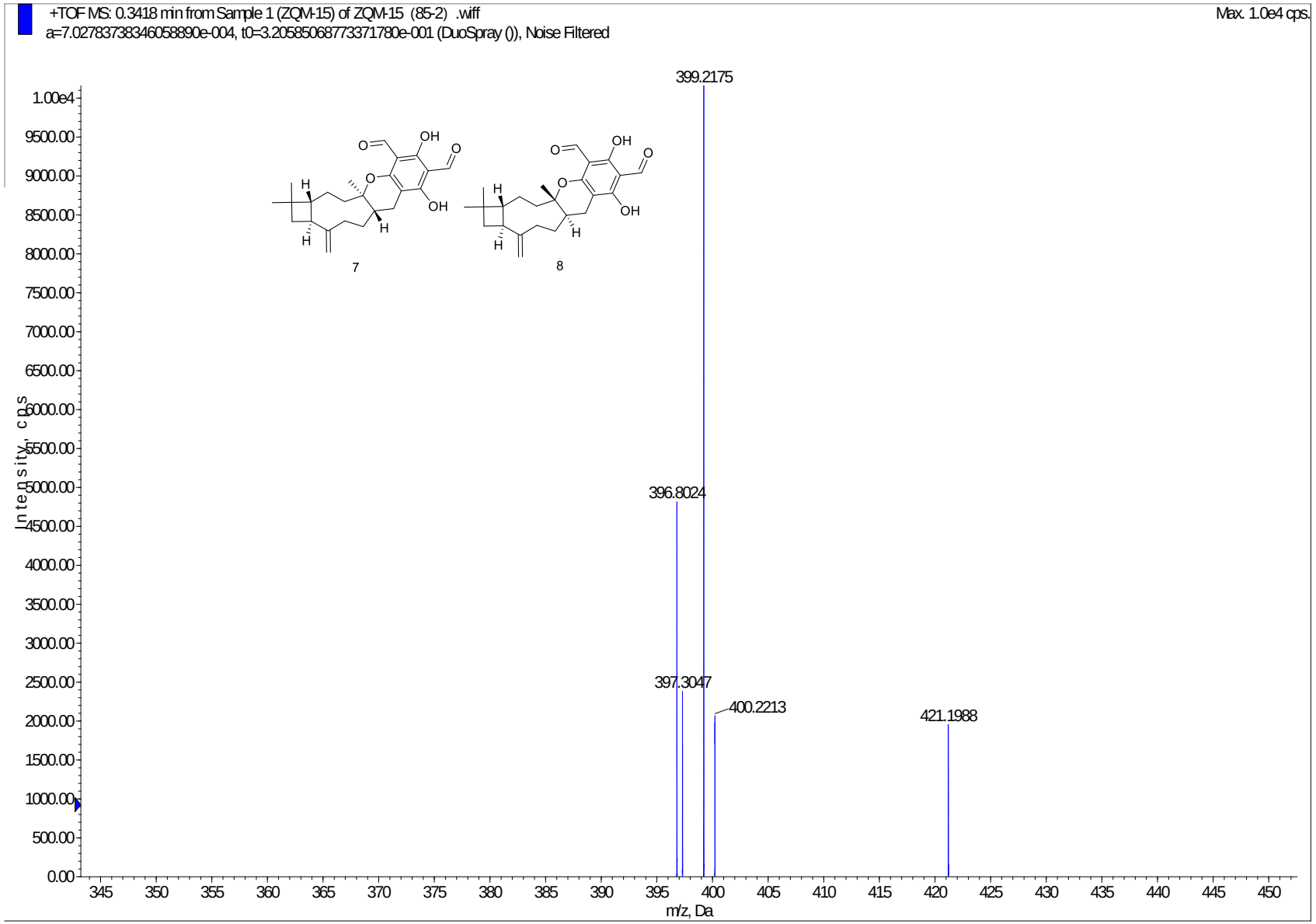
^{1}H NMR



7 8

DEPT-135 and ^{13}C NMR

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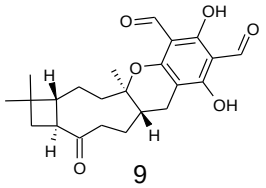
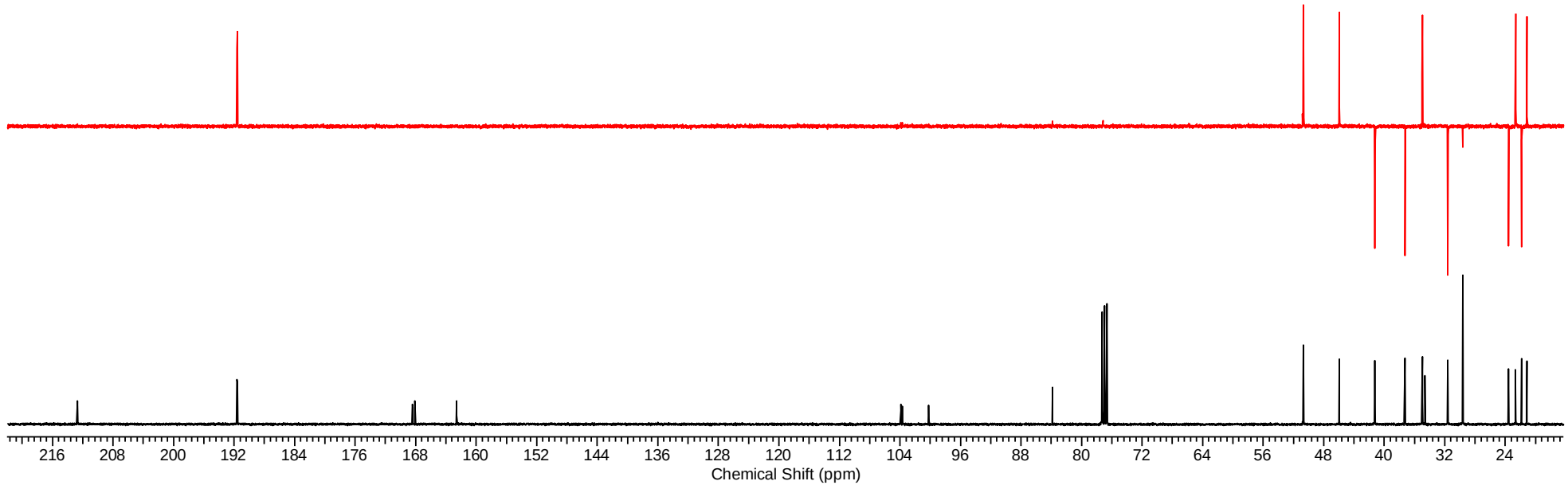
399.2175
396.8024
397.3047
400.2213
421.1988
7
8
Intensity, cps
m/z, Da

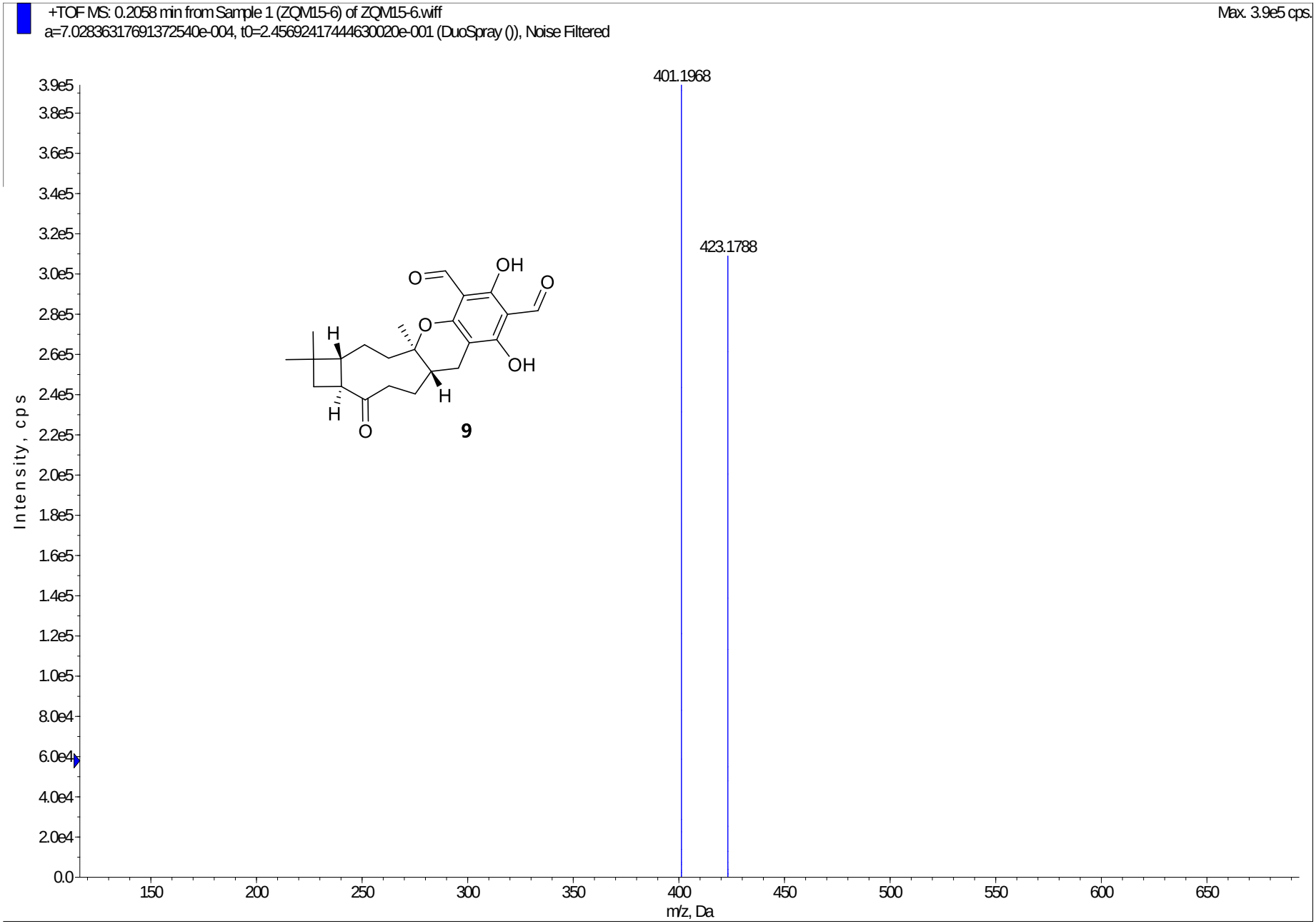
^{1}H NMR



9

DEPT-135 and ^{13}C NMR

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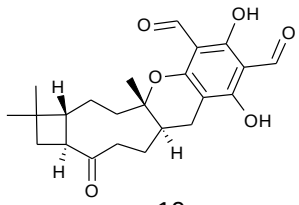
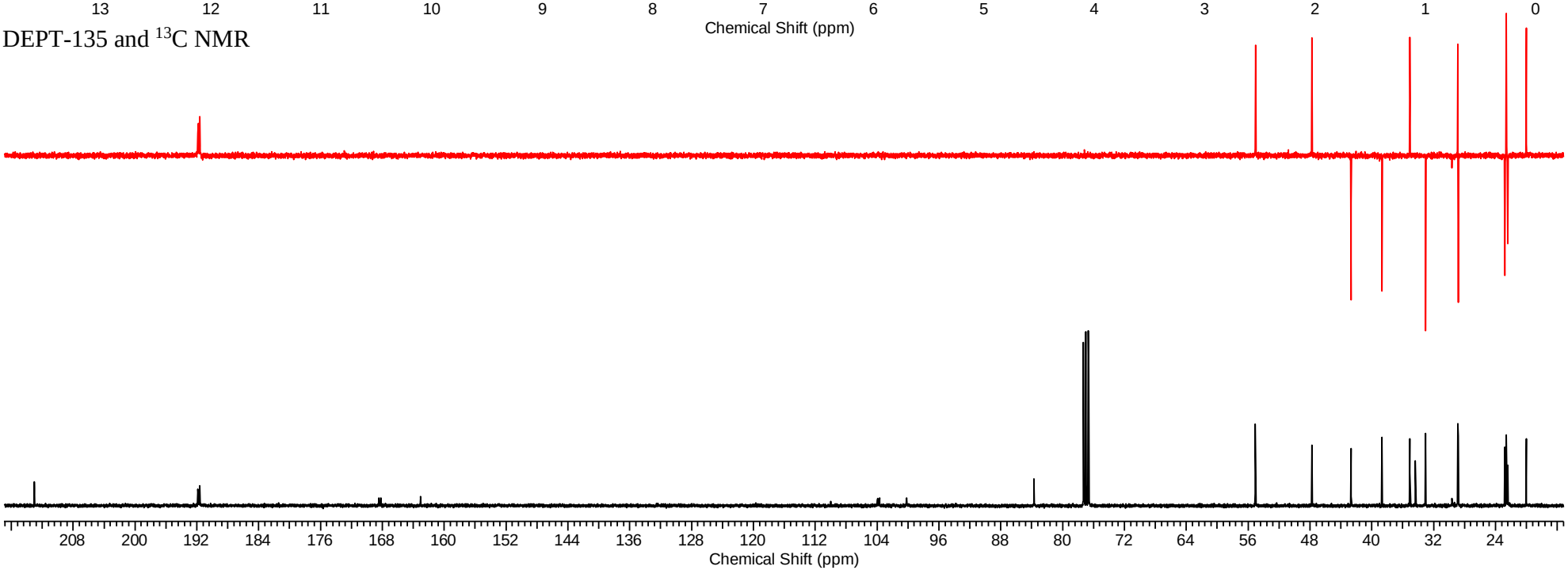
401.1968
423.1788
Intensity, cps
m/z, Da
9

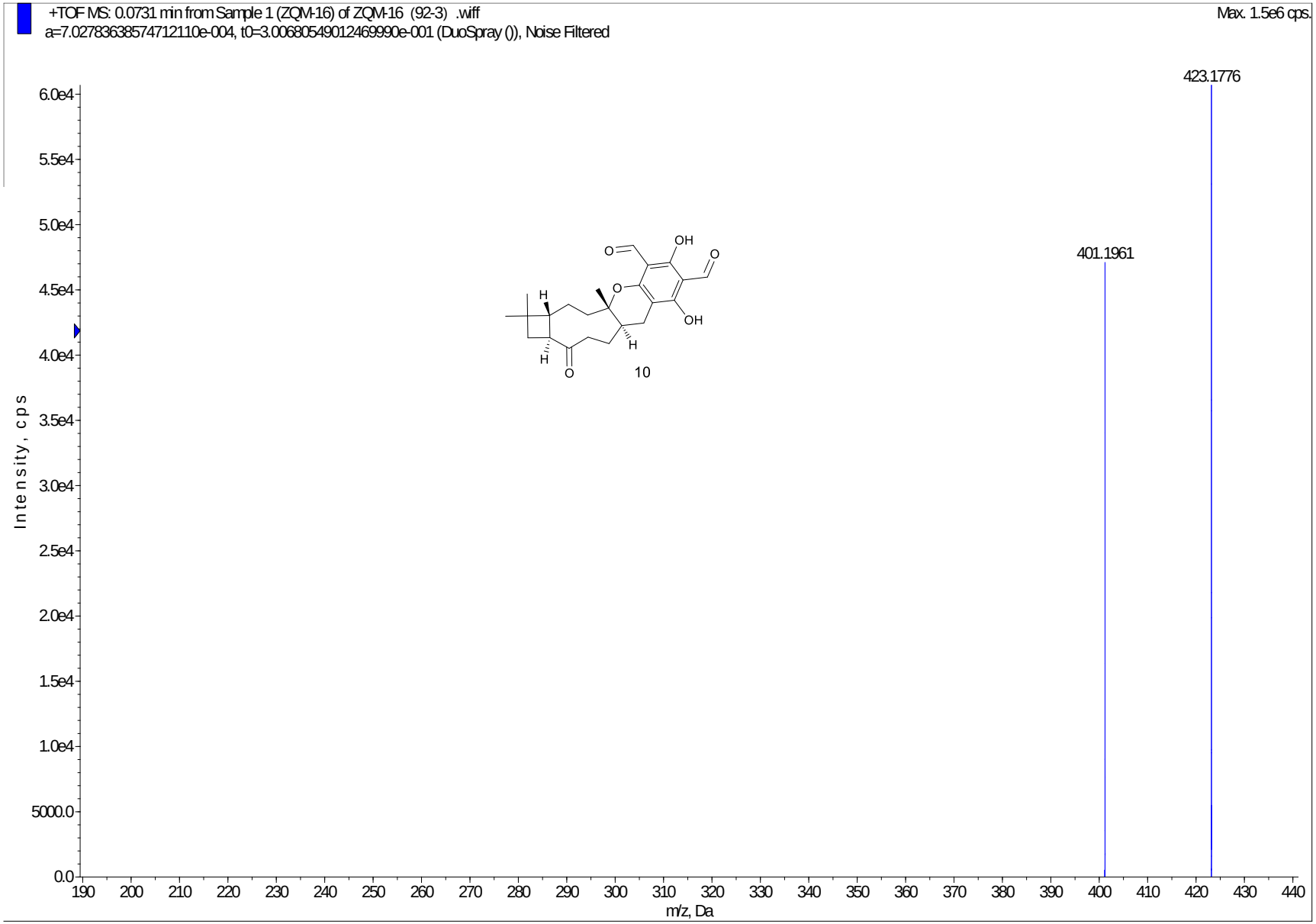
^{1}H NMR



10

DEPT-135 and ^{13}C NMR

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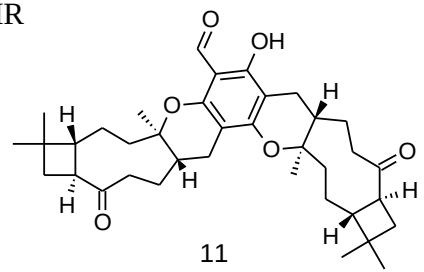
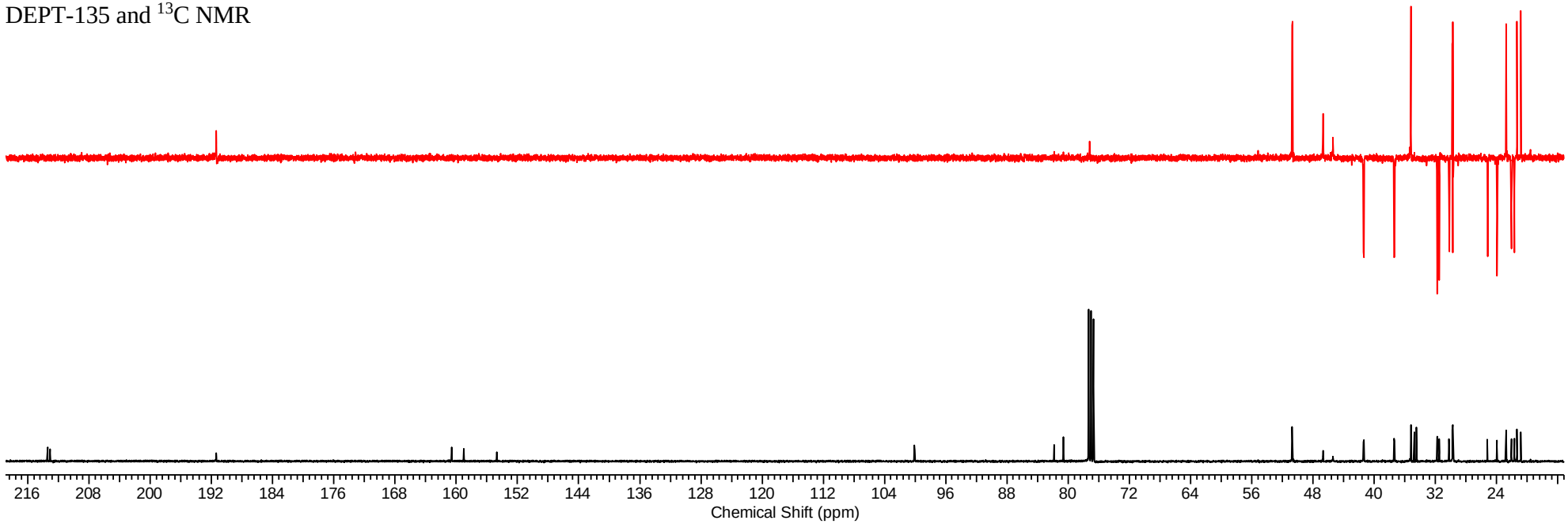
401.1961
Intensity, cps
m/z, Da
10

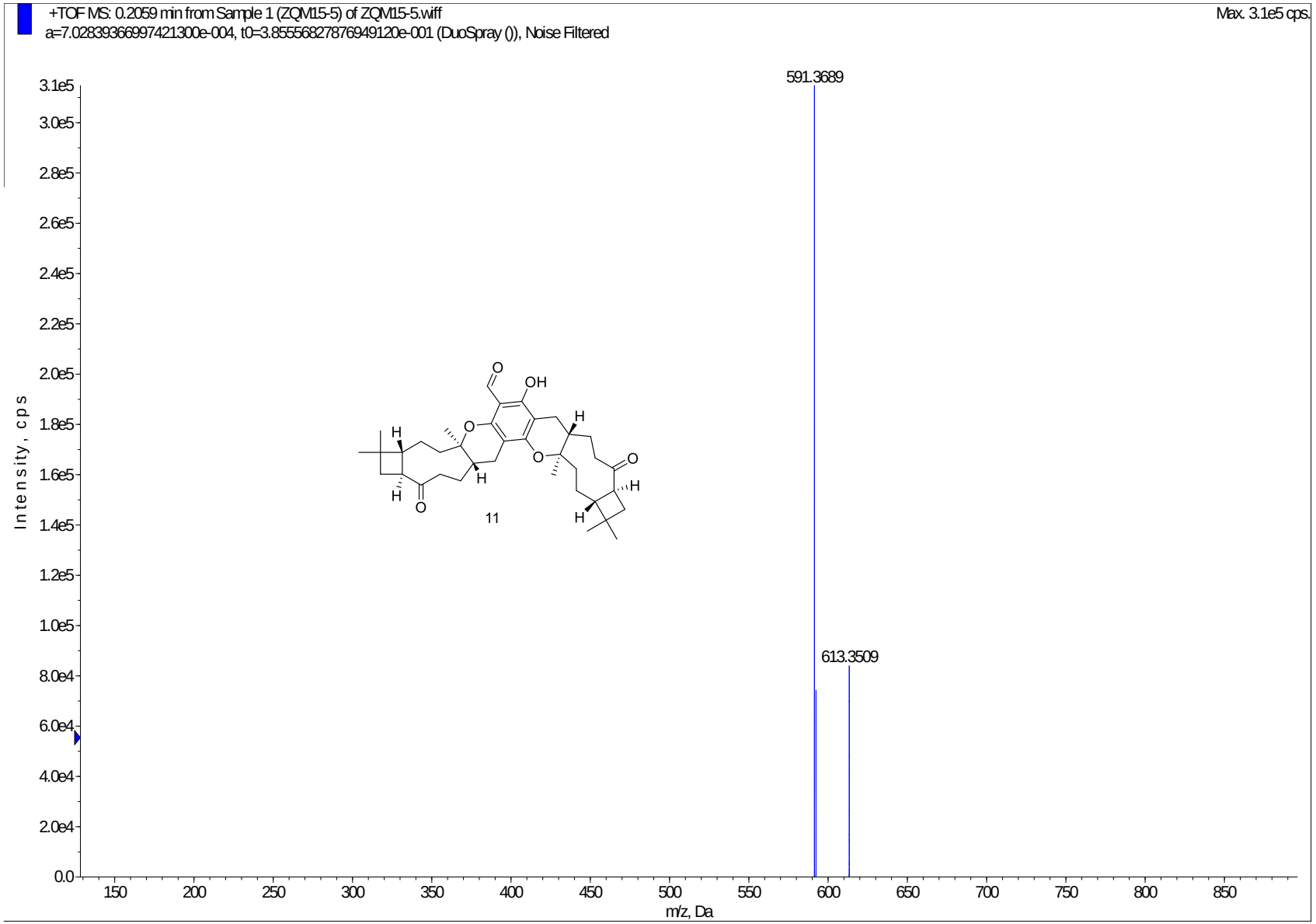
^{1}H NMR



11

DEPT-135 and ^{13}C NMR

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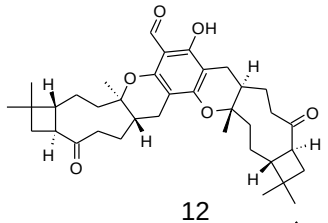
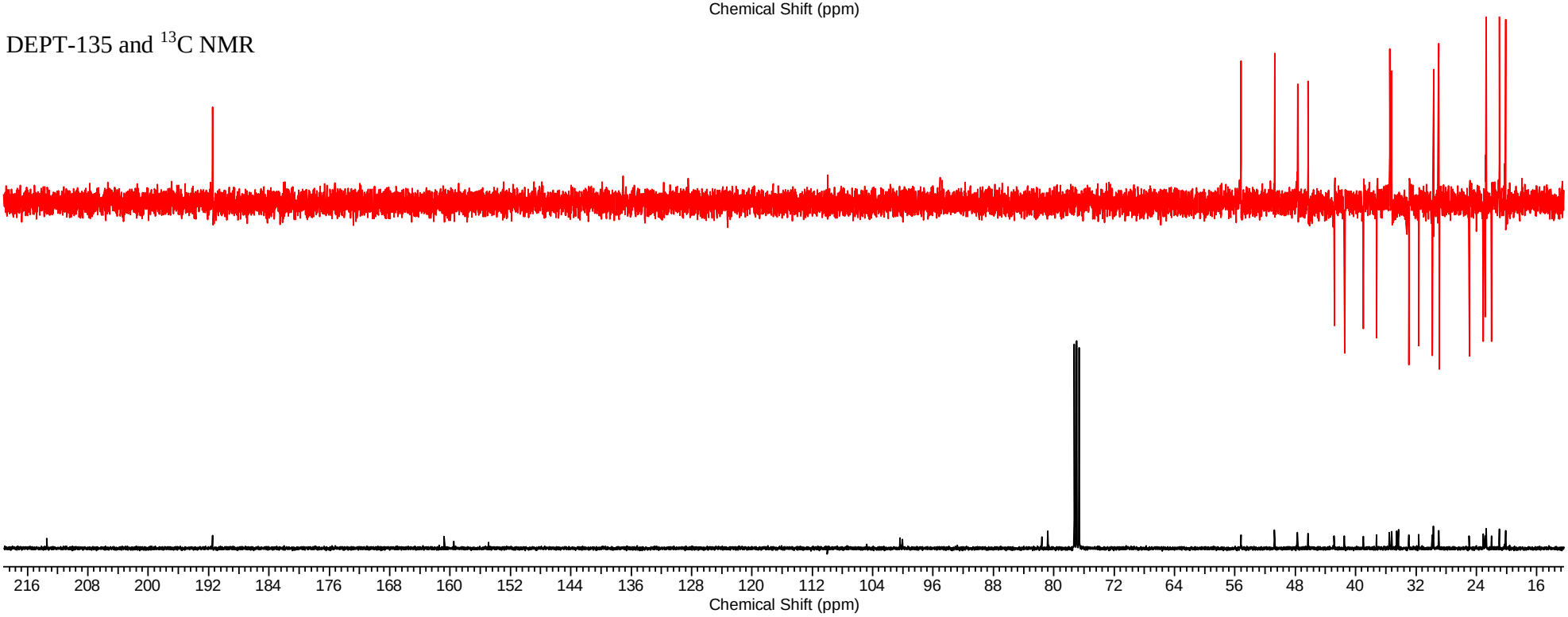
591.3689
613.3509
Intensity, cps
m/z, Da
11

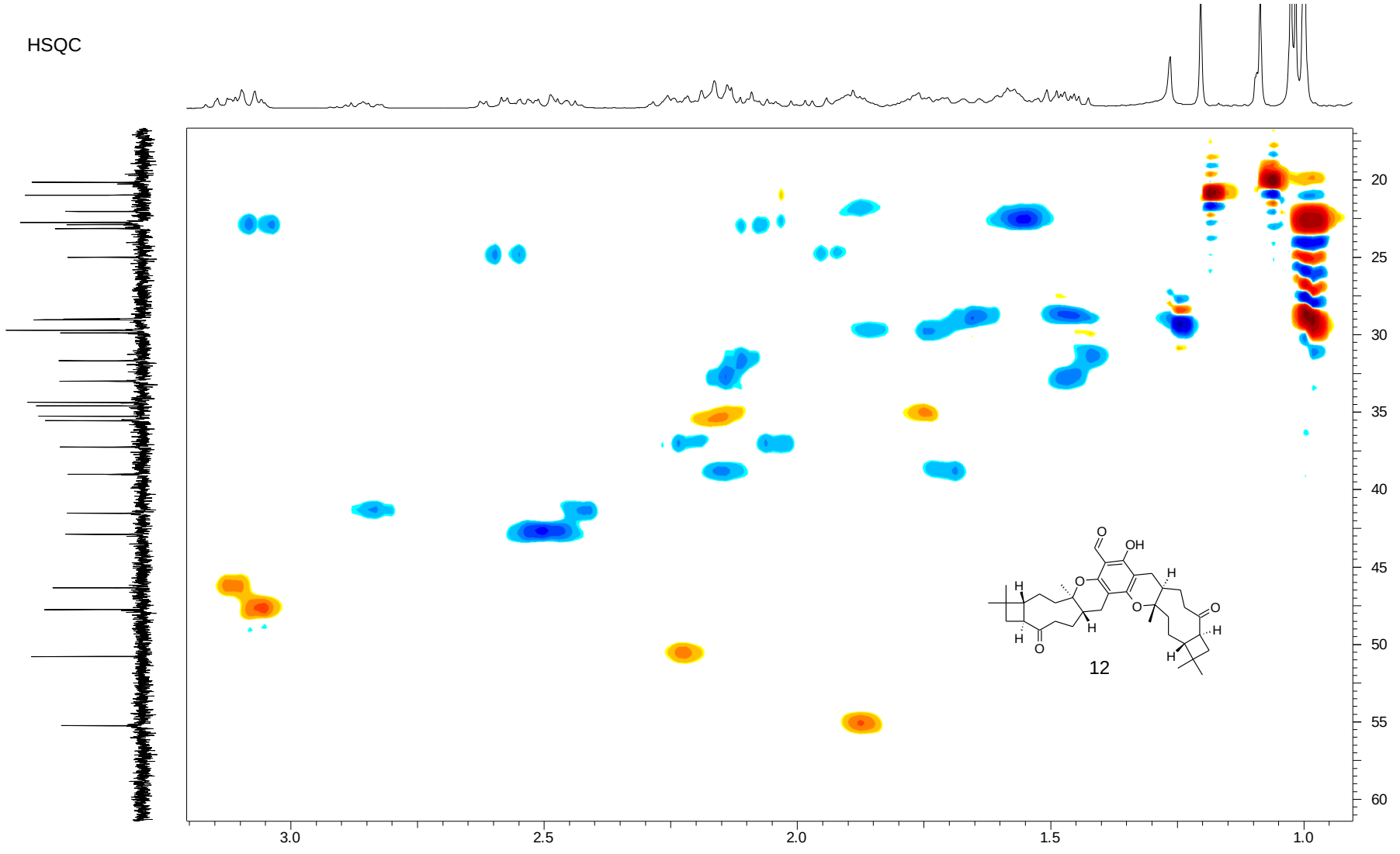
^{1}H NMR



12

DEPT-135 and ^{13}C NMR

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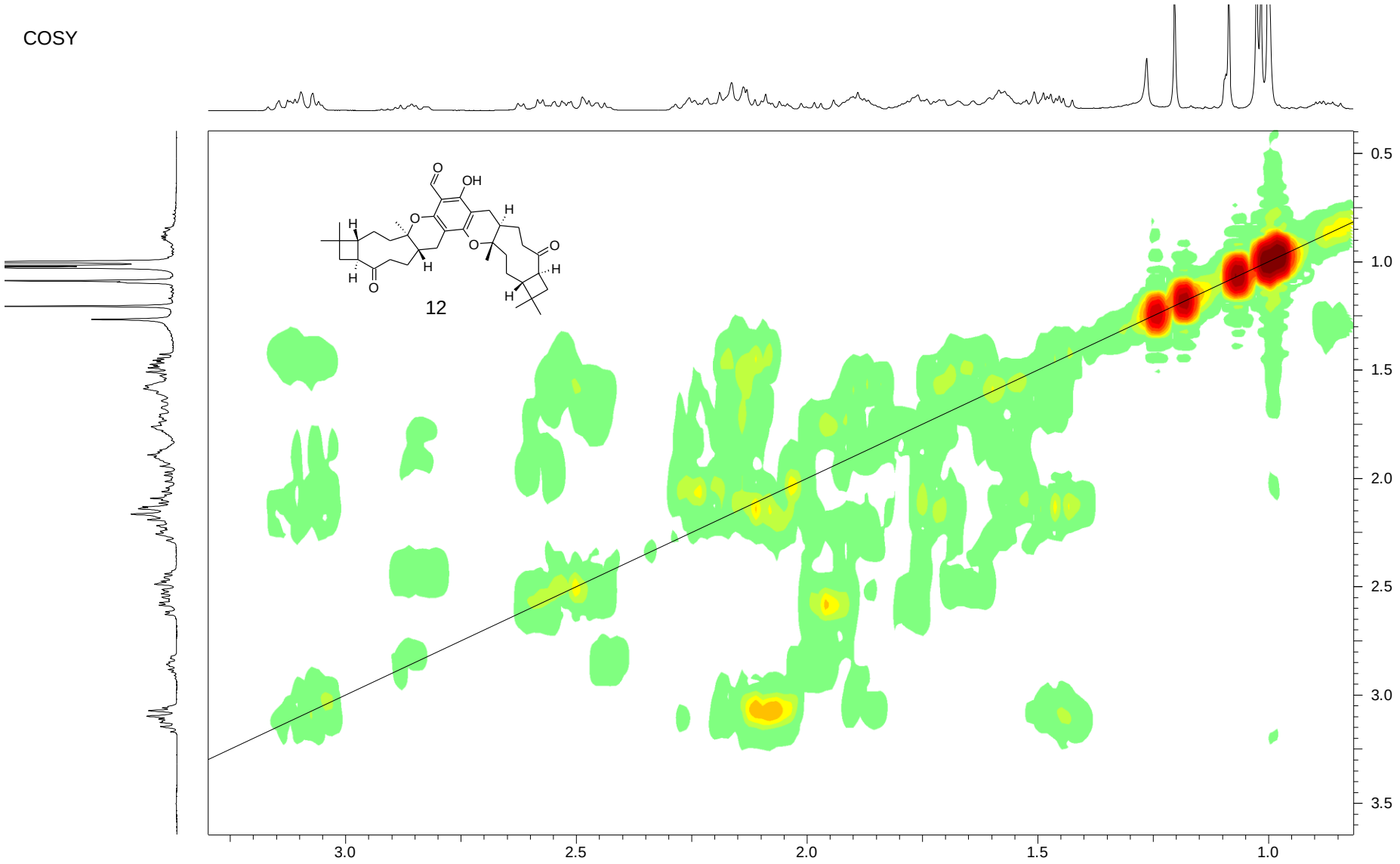
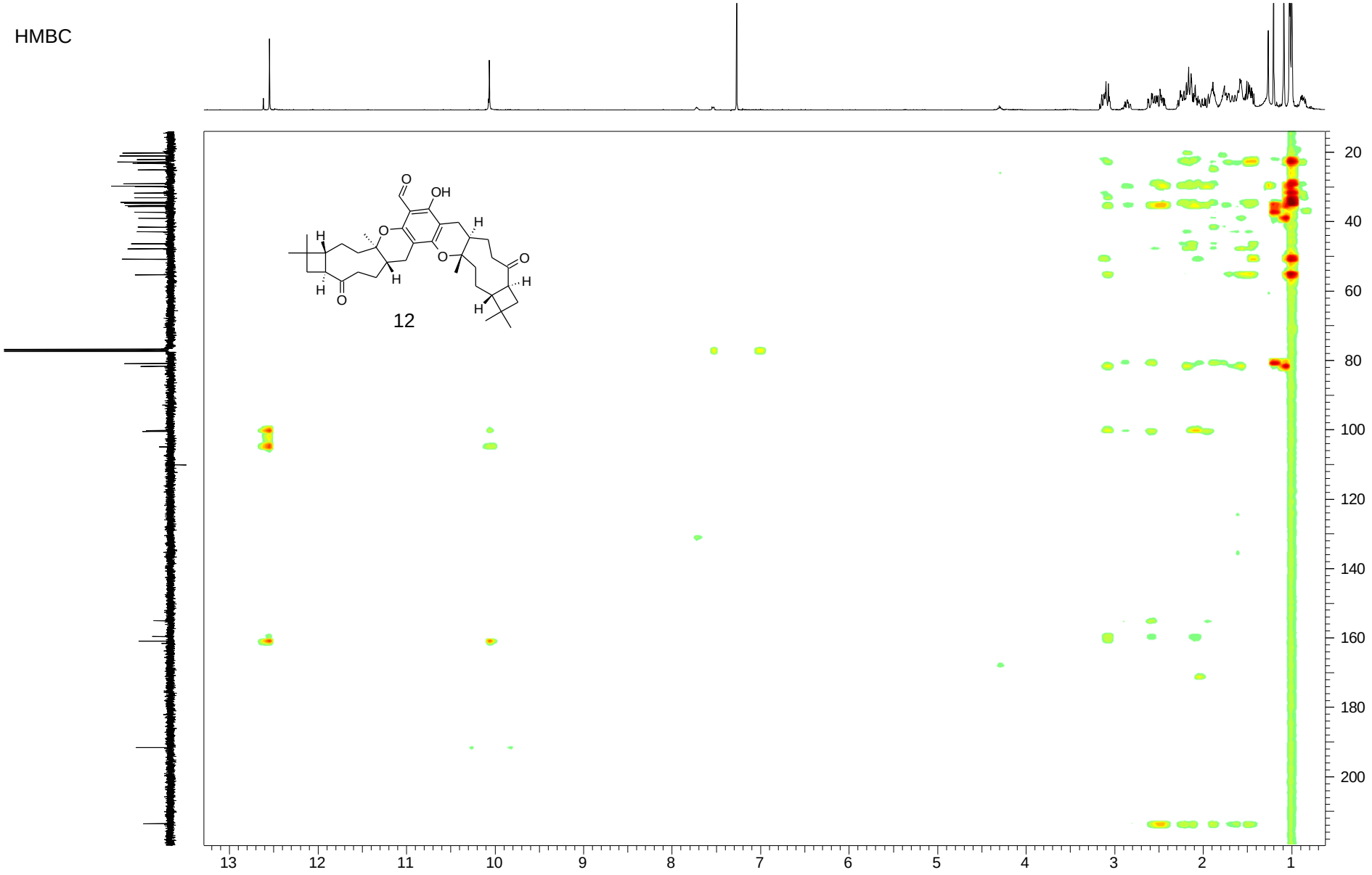
2.0
1.5
1.0
20
25
30
35
40
45
50
55
60
OH
O
H
12

COSY



HMBC


O
OH
H
O
H
O
H
O
H
H
O
H
12
20
40
60
80
100
120
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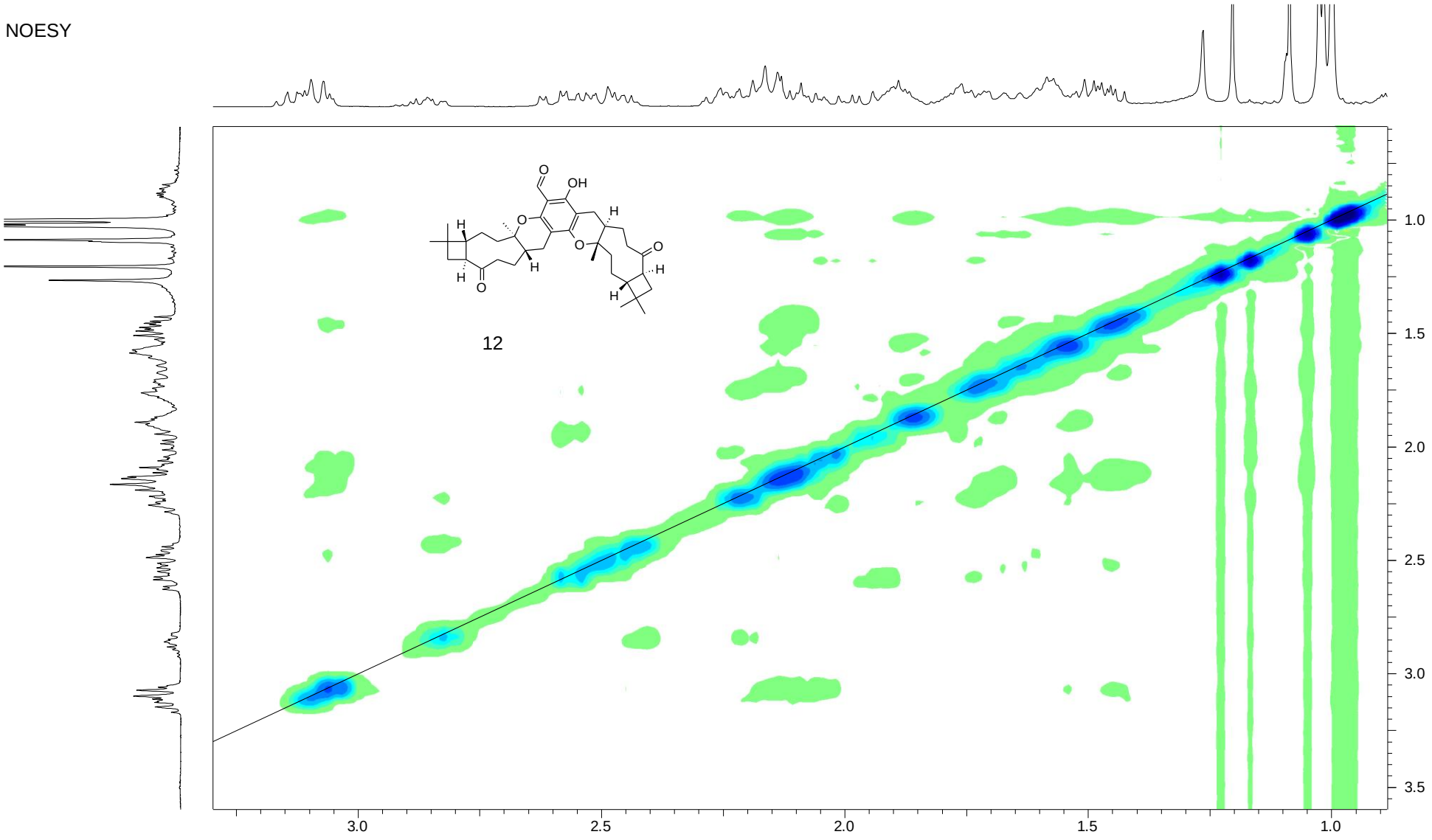
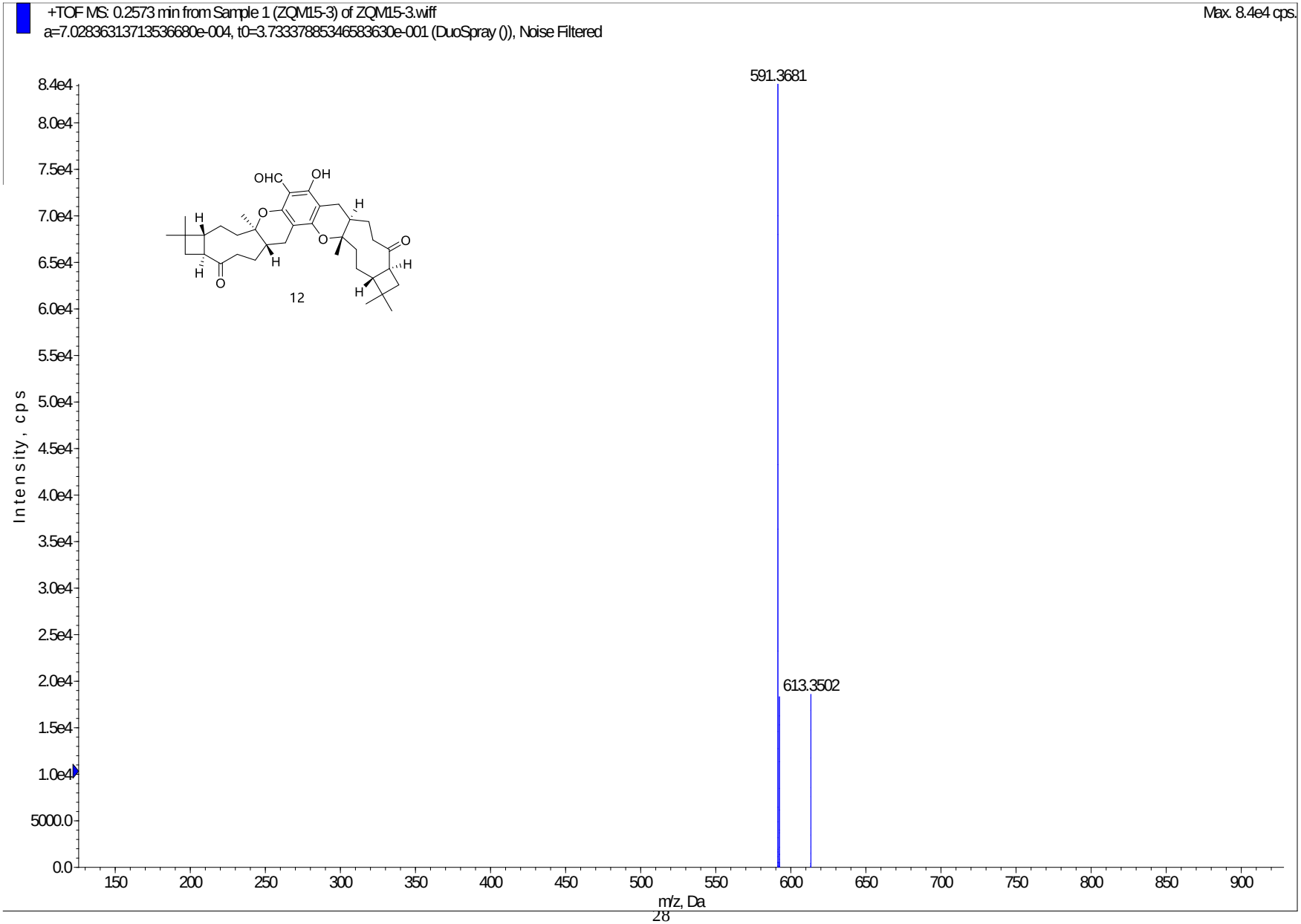
8
7
6
5
4
3
2
1

NOESY

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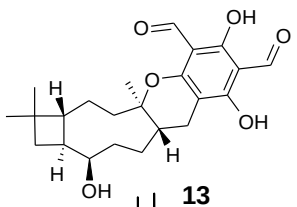
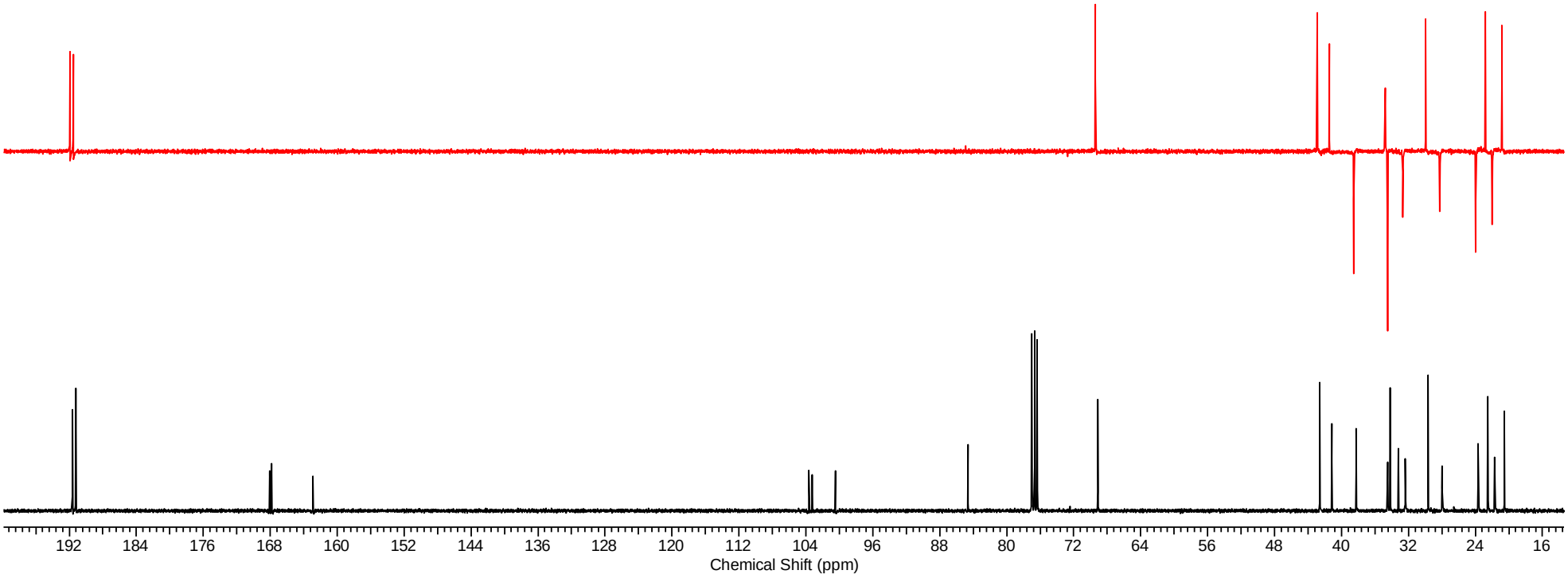
Max. 8.4e4 cps.
591.3681
613.3502
Intensity, cps
m/z, Da
12

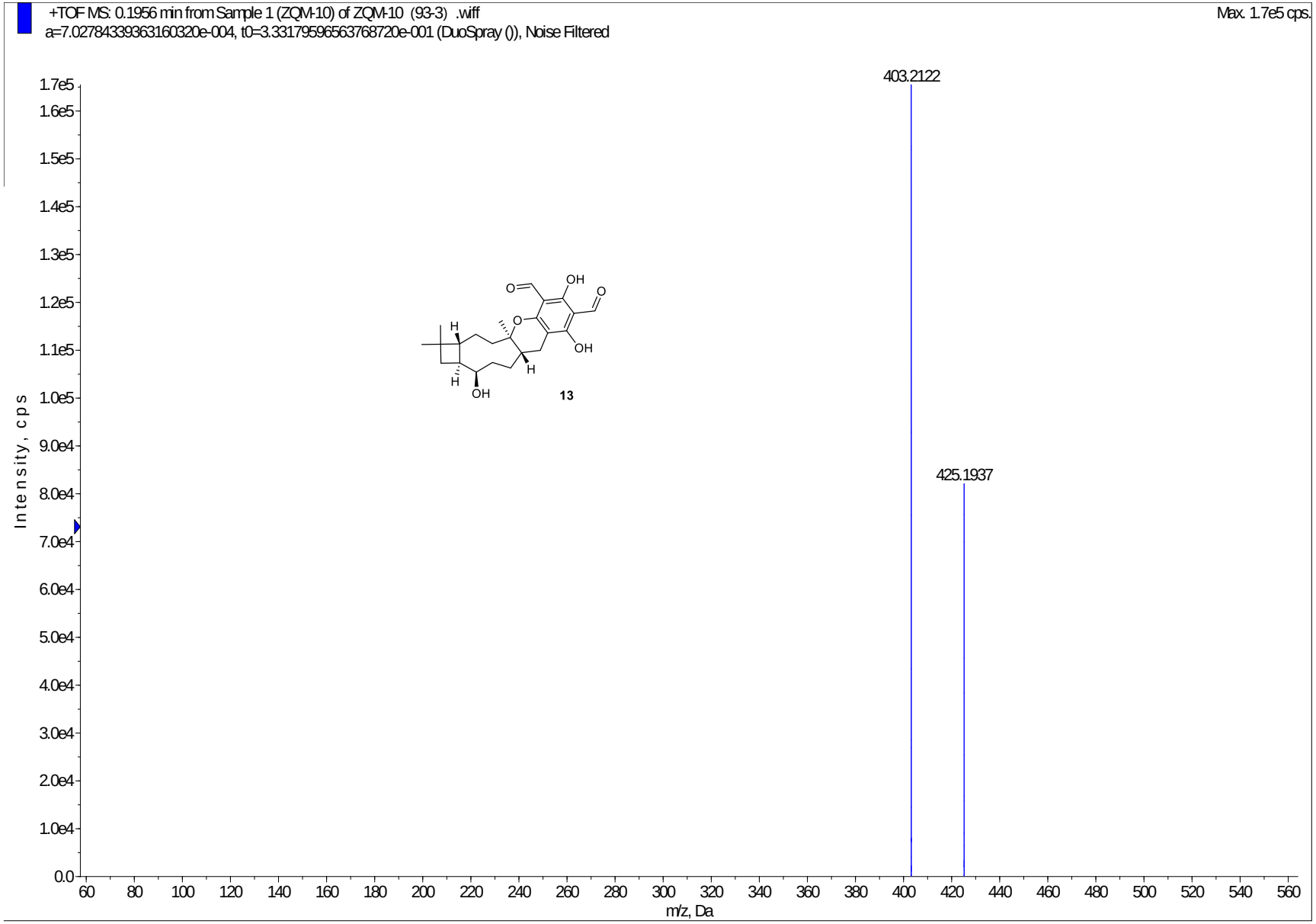
^{1}H NMR



13

DEPT-135 and ^{13}C NMR

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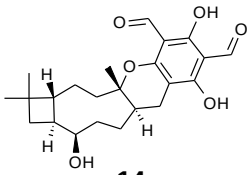
403.2122
425.1937
Intensity, cps
m/z, Da
13

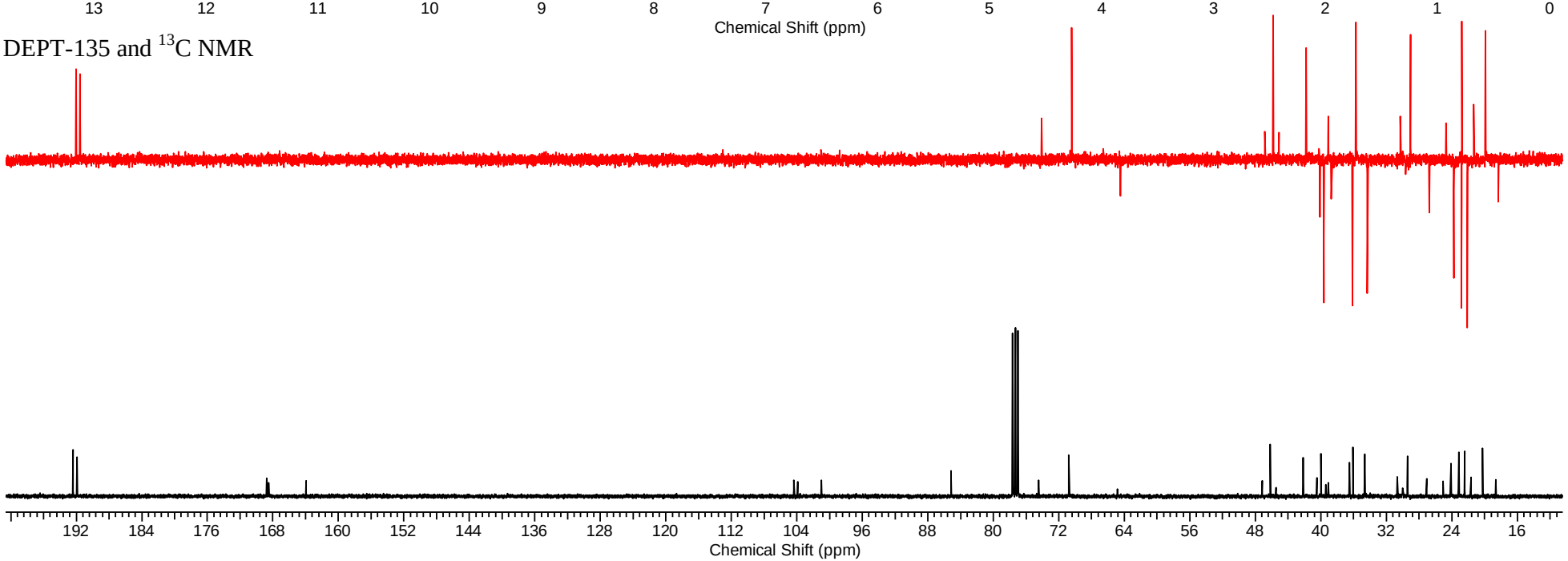
4

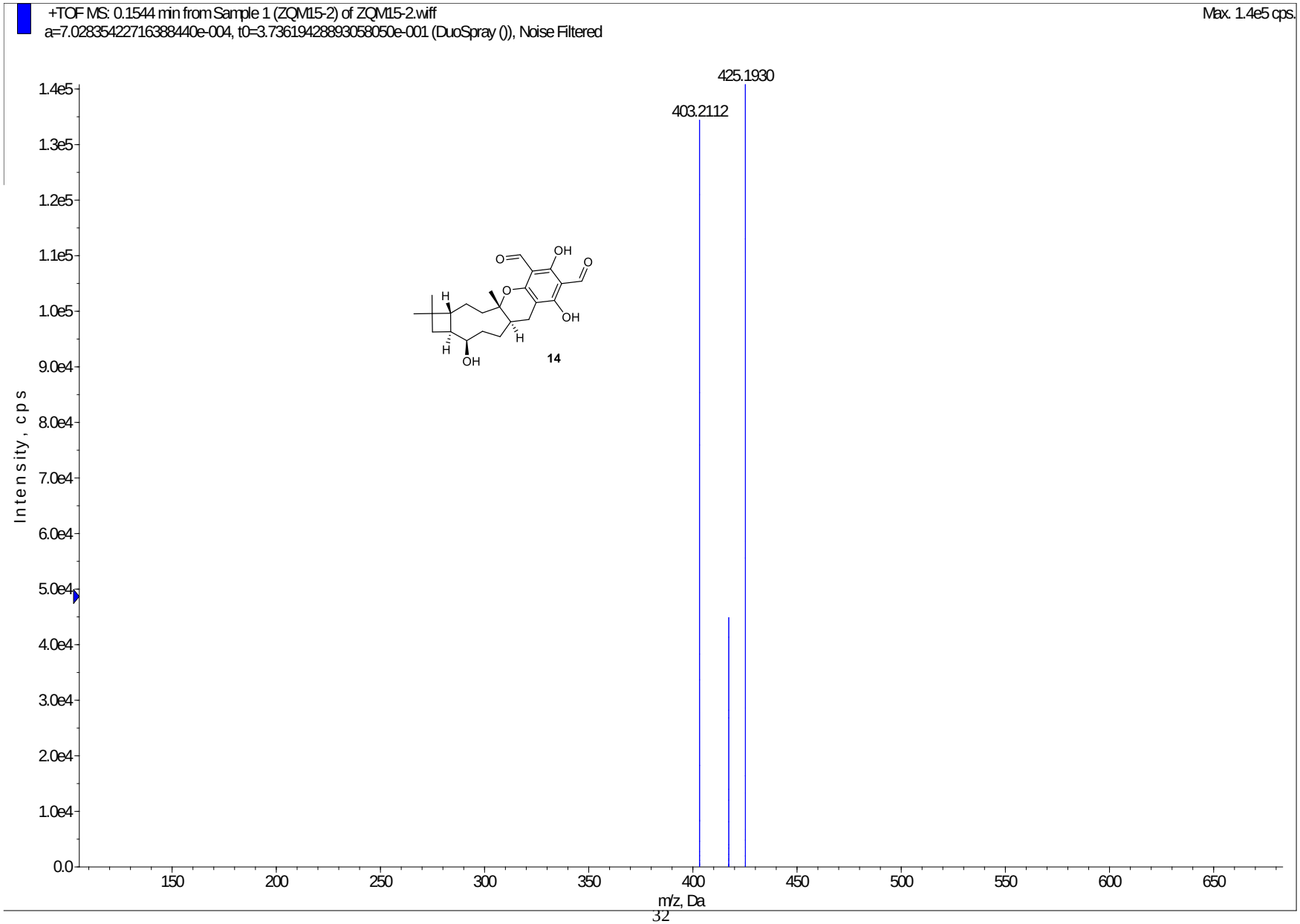
^{1}H NMR



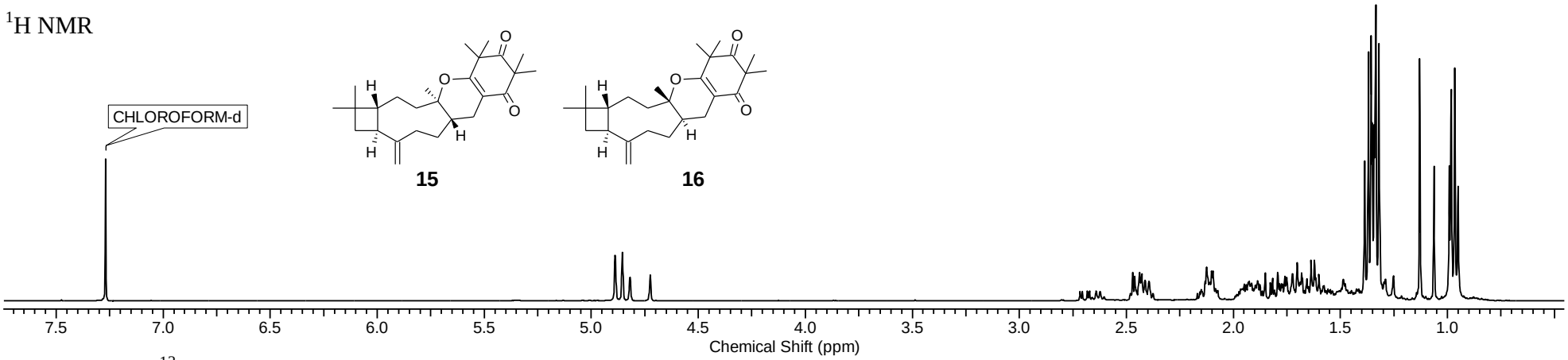
14

DEPT-135 and ^{13}C NMR

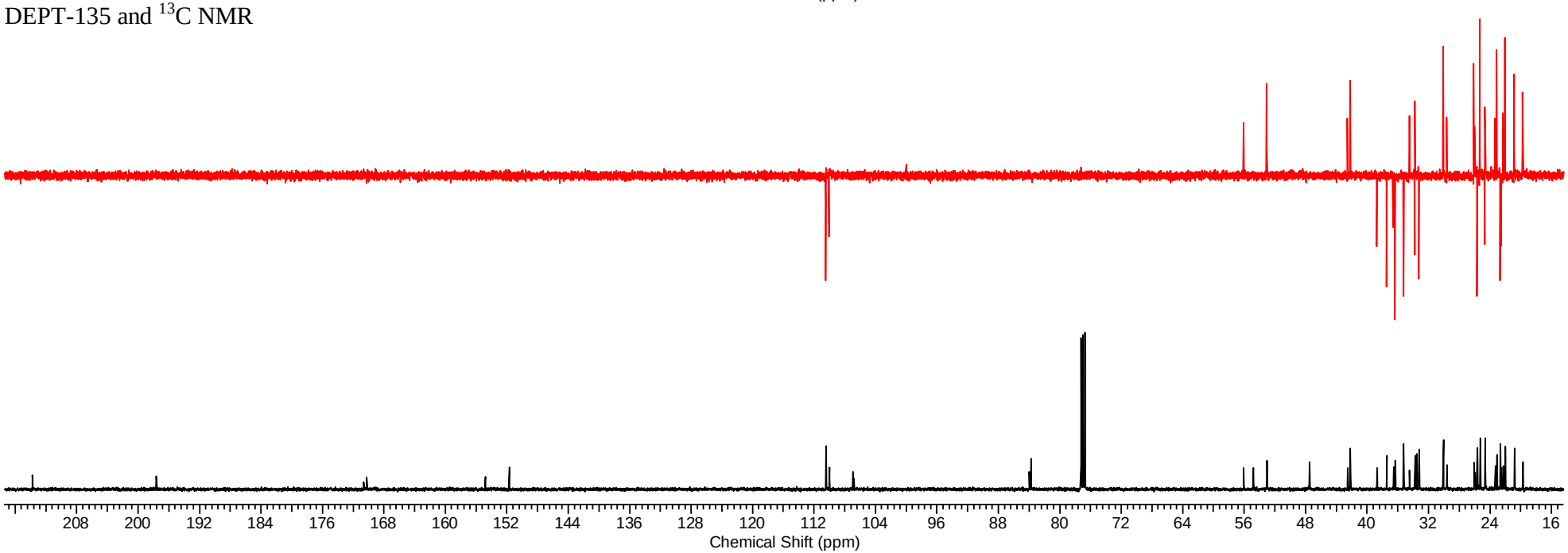


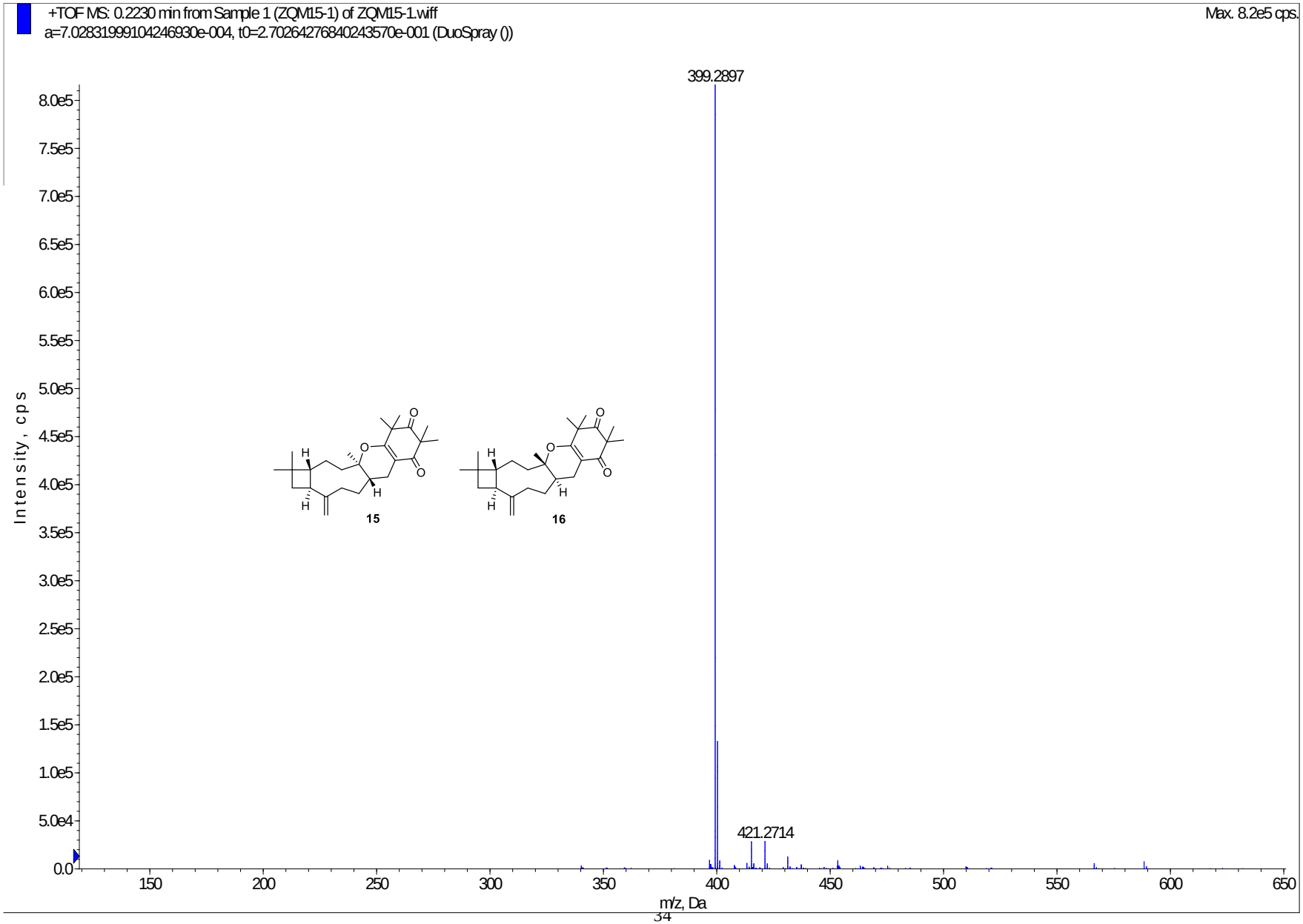

+TOF MS: 0.1544 min from Sample 1 (ZQM15-2) of ZQM15-2.wiff
a=7.02835422716388440e-004, t0=3.73619428893058050e-001 (DuoSpray ()), Noise Filtered
Max. 1.4e5 cps.
425.1930
403.2112
Intensity, cps
m/z, Da
14

^{1}H NMR

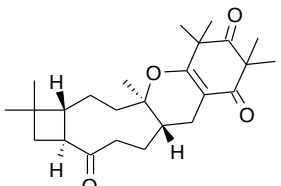


DEPT-135 and ^{13}C NMR



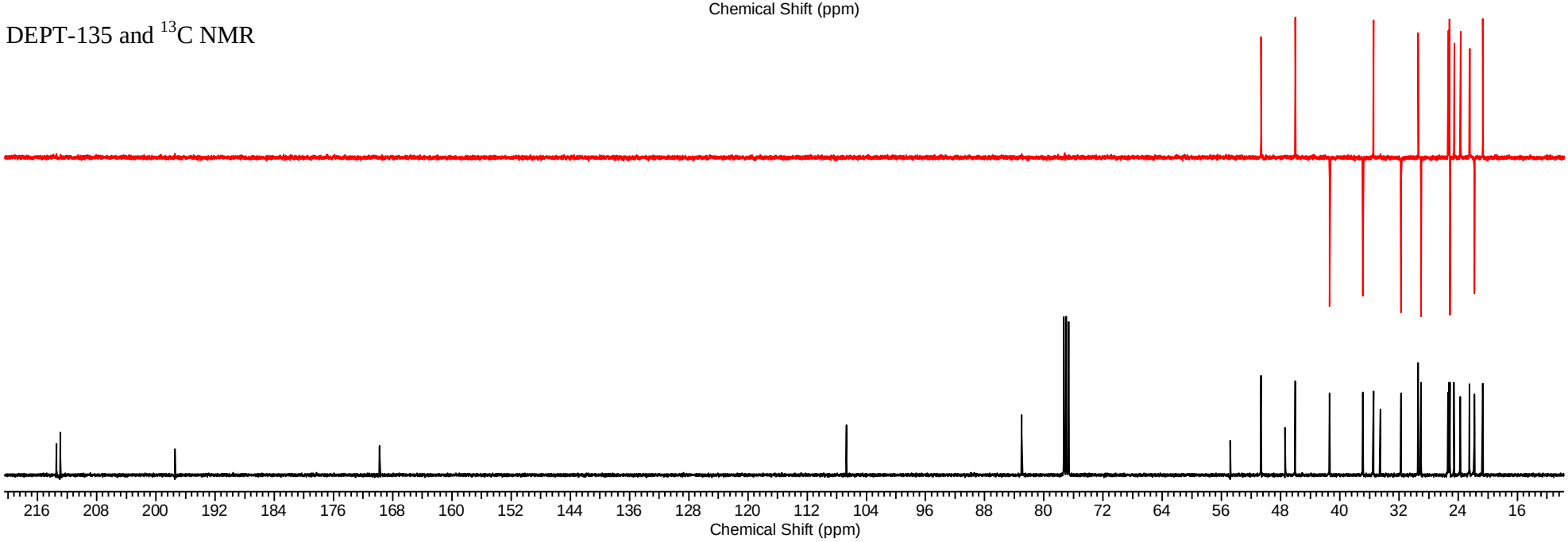

+TOF MS: 0.2230 min from Sample 1 (ZQM15-1) of ZQM15-1.wiff
a=7.02831999104246930e-004, t0=2.70264276840243570e-001 (DuoSpray ())
Max. 8.2e5 cps.
399.2897
421.2714
Intensity, cps
m/z, Da
8.0e5
7.5e5
7.0e5
6.5e5
6.0e5
5.5e5
5.0e5
4.5e5
4.0e5
3.5e5
3.0e5
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
0.0
150
200
250
300
350
400
450
500
550
600
650
15
16

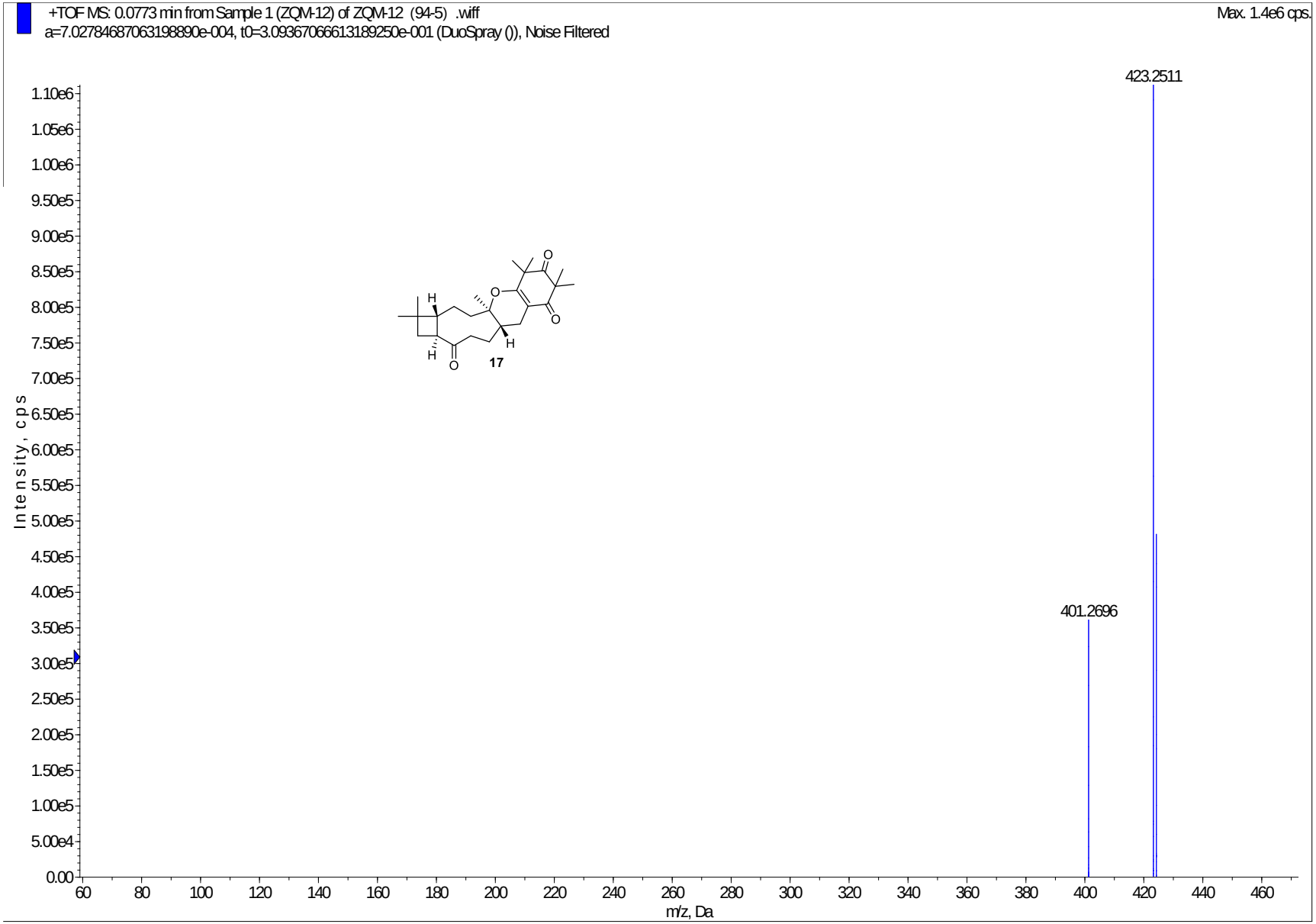
^{1}H NMR



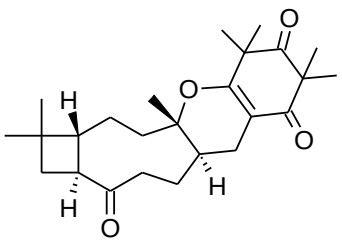
17

DEPT-135 and ^{13}C NMR



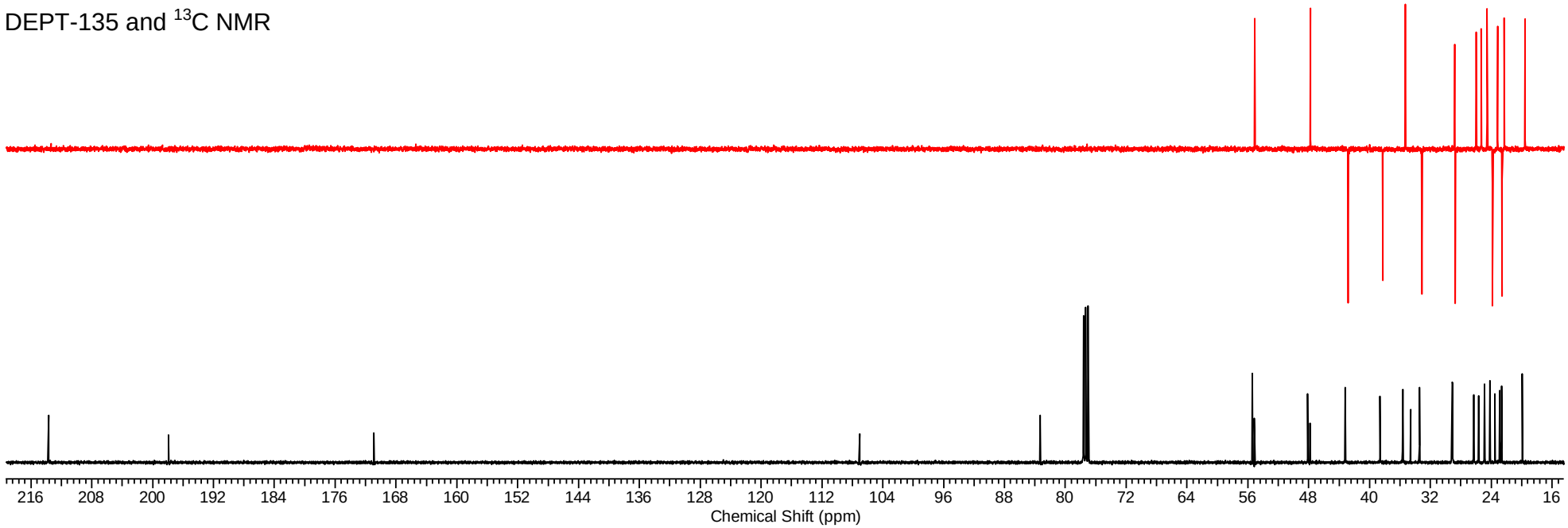

+TOF MS: 0.0773 min from Sample 1 (ZQM-12) of ZQM-12 (94-5) .wiff
a=7.027846870631988890e-004, t0=3.093670666131892500e-001 (DuoSpray ()), Noise Filtered
Max. 1.4e6 cps.
423.2511
401.2696
17
Intensity, cps
m/z, Da

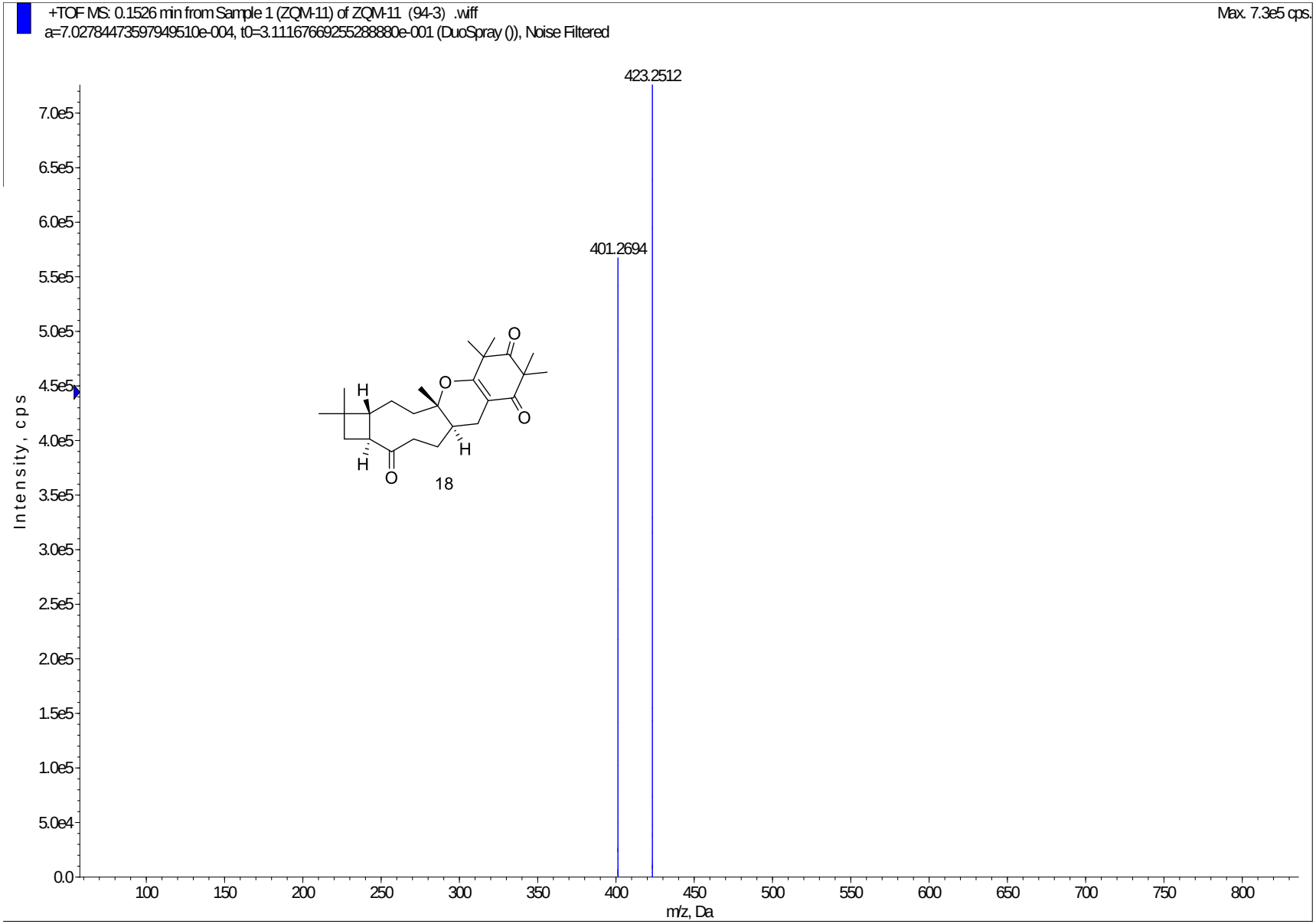
^{1}H NMR



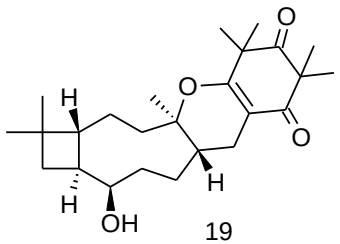
18

DEPT-135 and ^{13}C NMR



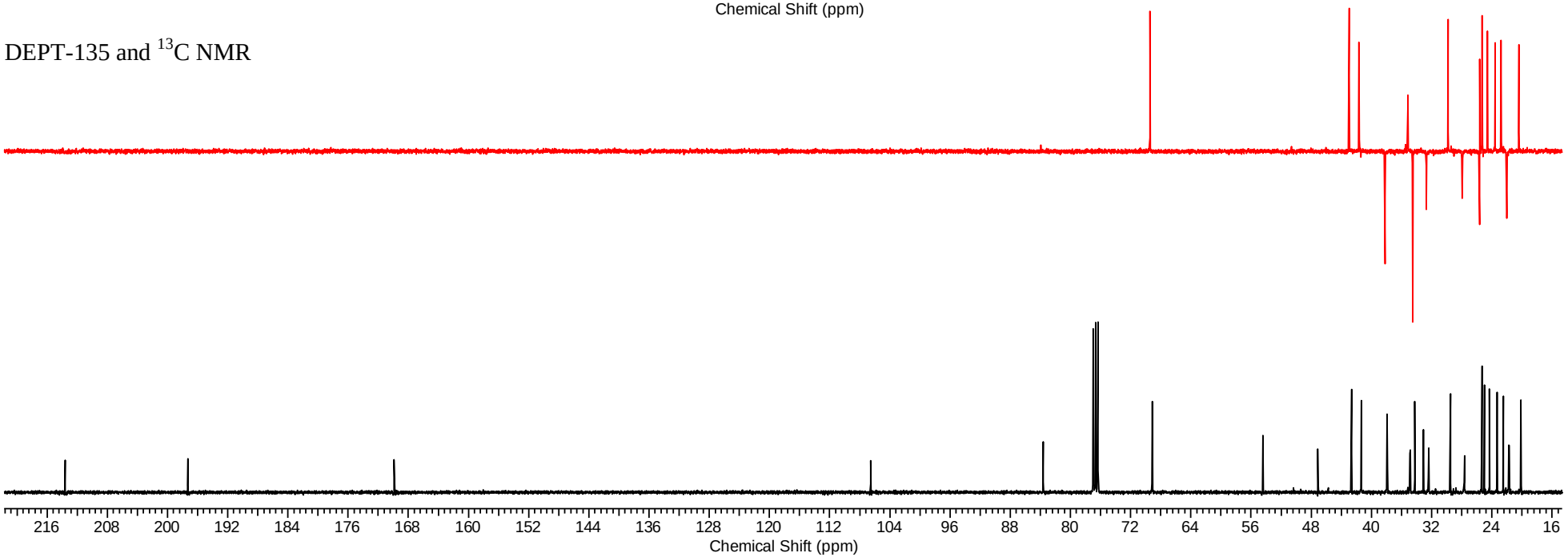

+TOF MS: 0.1526 min from Sample 1 (ZQM-11) of ZQM-11 (94-3) .wiff
a=7.02784473597949510e-004, t0=3.11167669255288880e-001 (DuoSpray ()), Noise Filtered
Max. 7.3e5 cps.
423.2512
401.2694
Intensity, cps
7.0e5
6.5e5
6.0e5
5.5e5
5.0e5
4.5e5
4.0e5
3.5e5
3.0e5
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
0.0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
m/z, Da
O
O
O
H
H
H
O
18

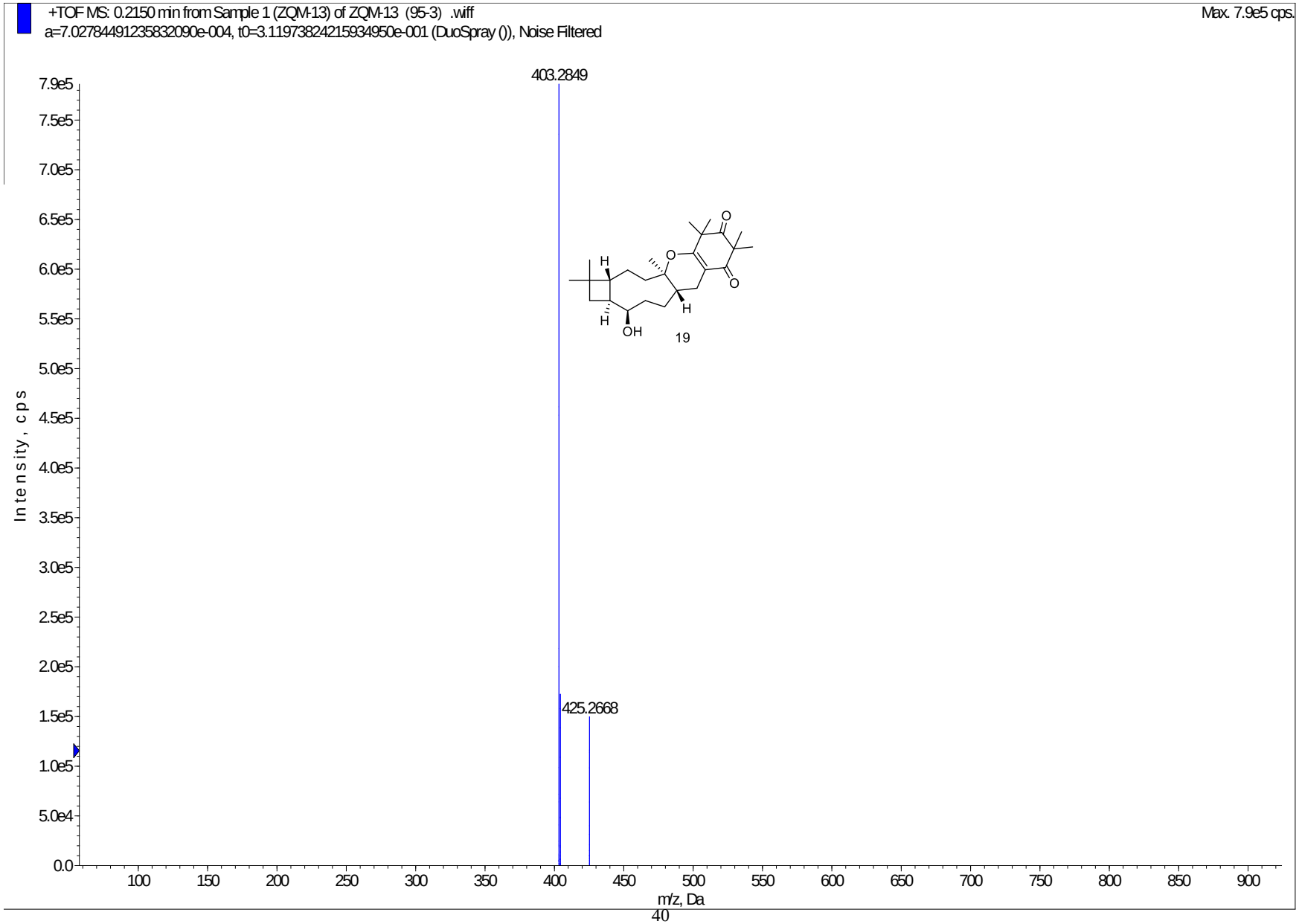
^{1}H-NMR



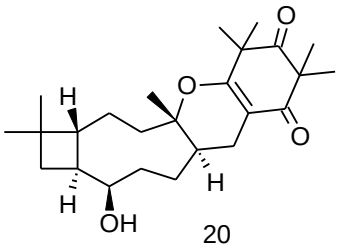
19

DEPT-135 and ^{13}C NMR

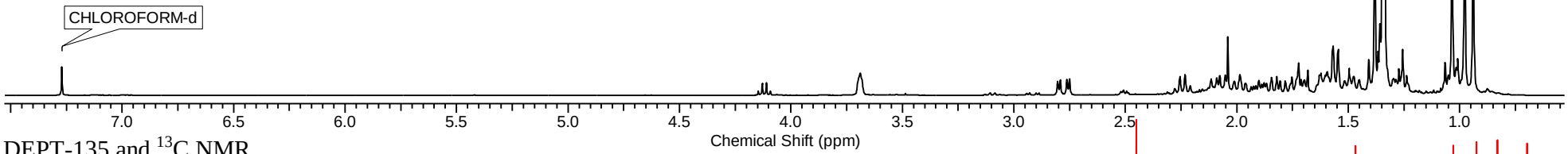



+TOF MS: 0.2150 min from Sample 1 (ZQM-13) of ZQM-13 (95-3) .wiff
a=7.02784491235832090e-004, t0=3.11973824215934950e-001 (DuoSpray ()), Noise Filtered
Max. 7.9e5 cps.
403.2849
425.2668
Intensity, cps
m/z, Da
19

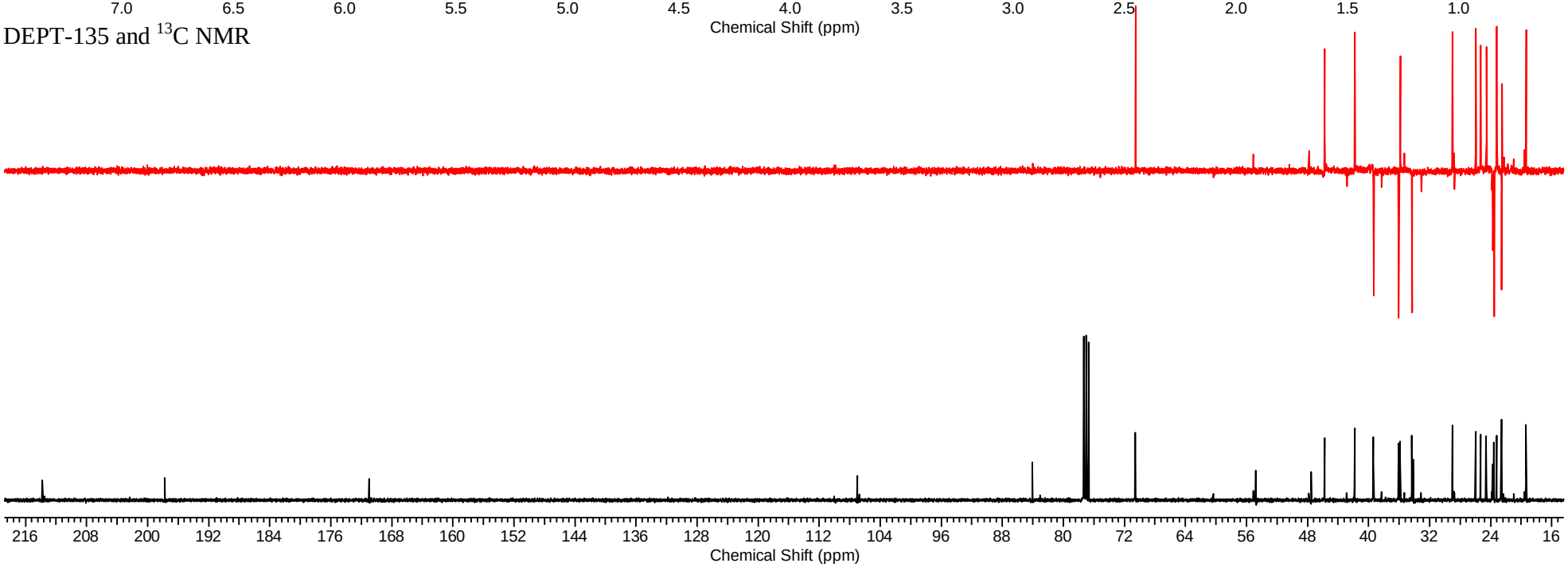
^{1}H-NMR

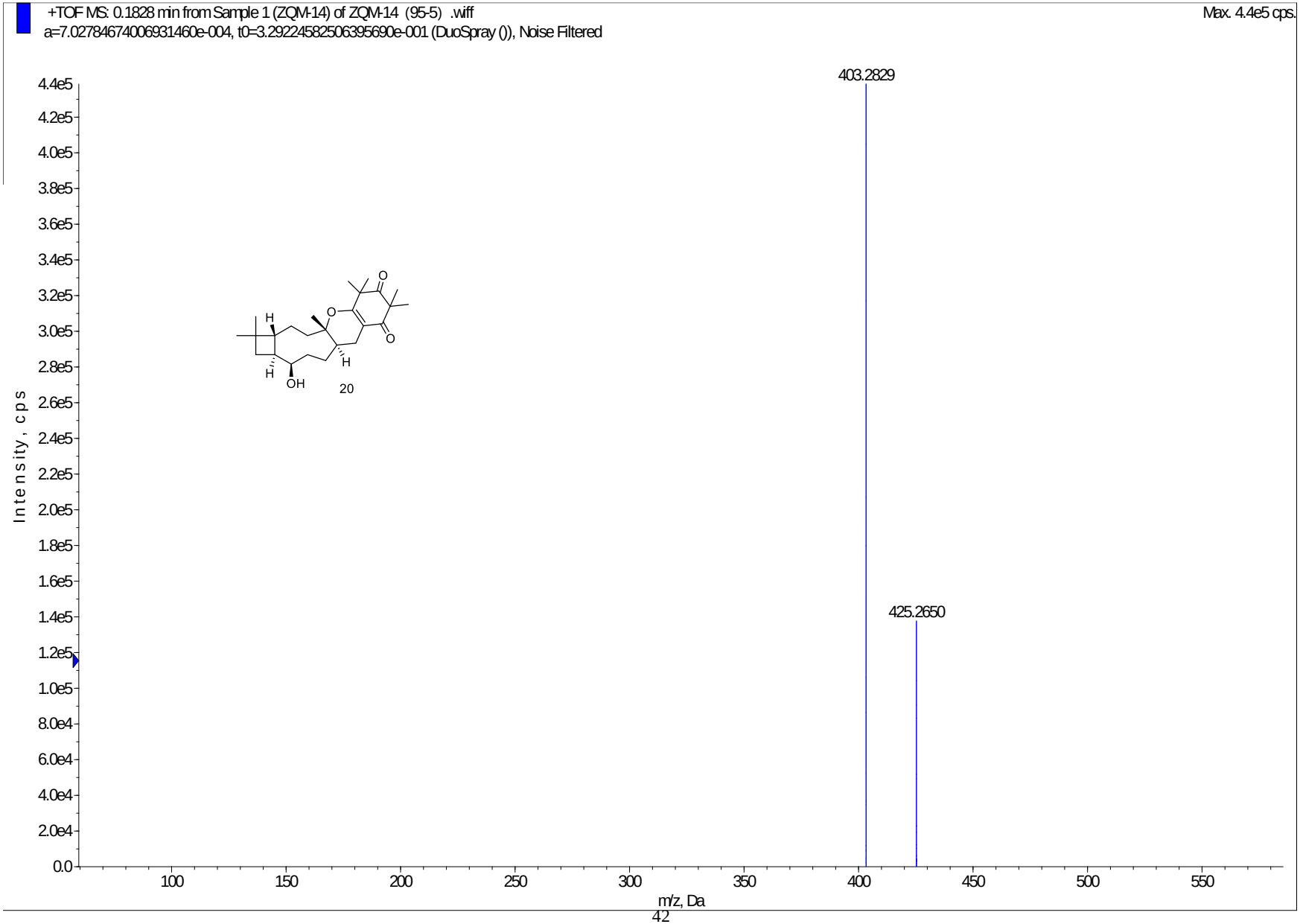


20

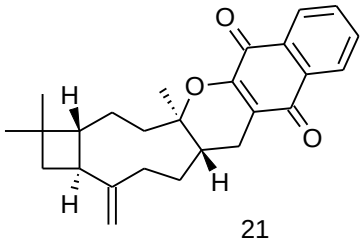


DEPT-135 and ^{13}C NMR



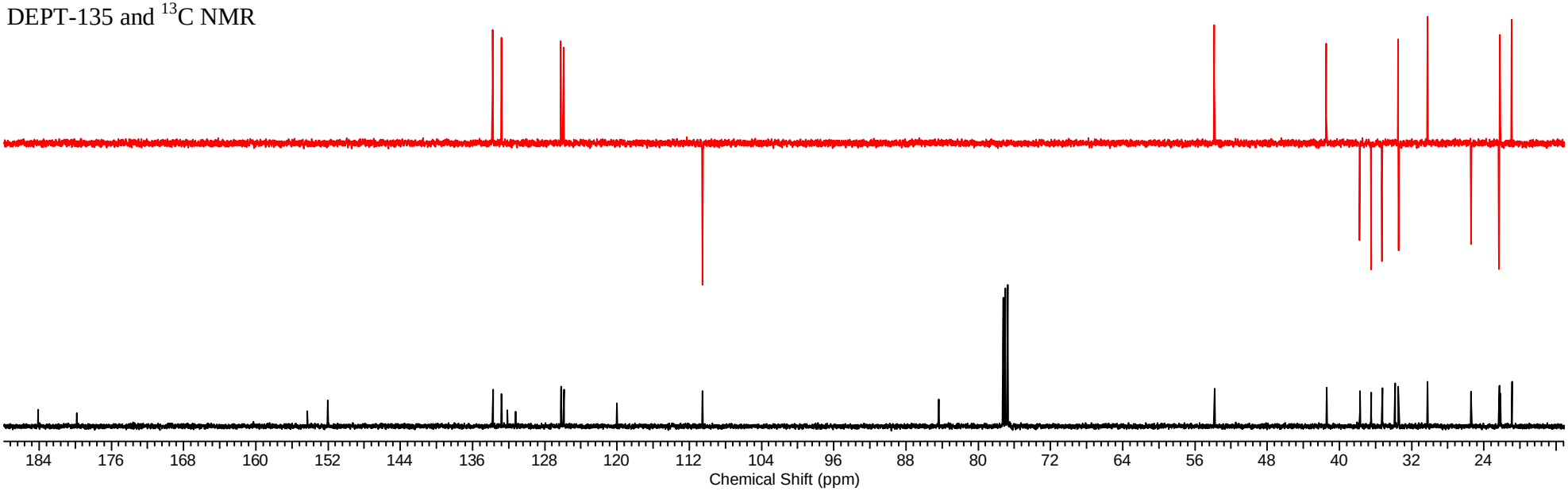

+TOF MS: 0.1828 min from Sample 1 (ZQM-14) of ZQM-14 (95-5) .wiff
a=7.027846740069314 60e-004, t0=3.2922458250639569 0e-001 (DuoSpray ()), Noise Filtered
Max. 4.4e5 cps.
403.2829
425.2650
Intensity, cps
m/z, Da
20

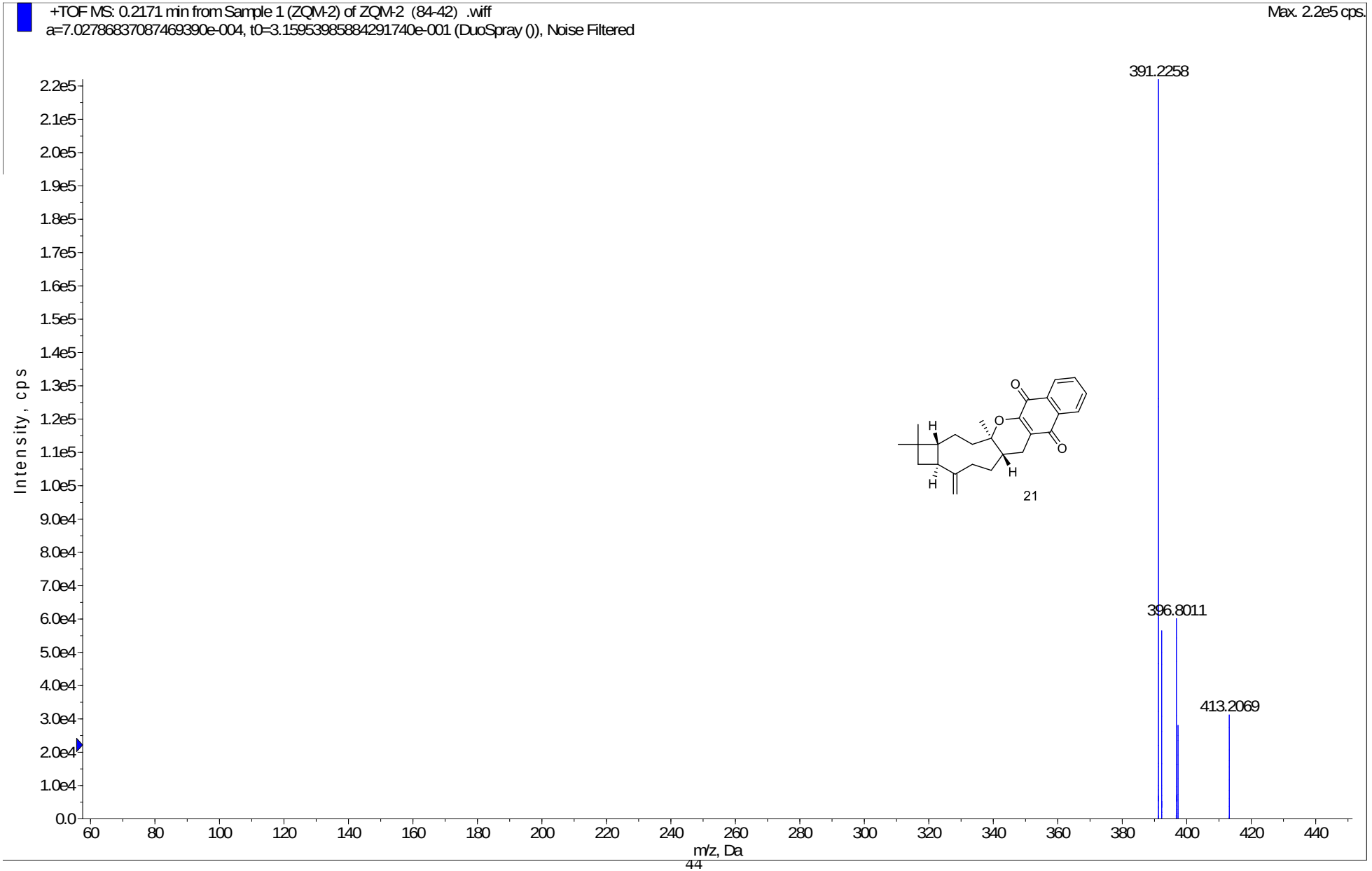
^{1}H NMR



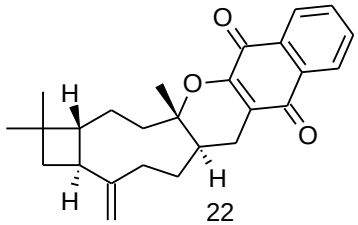
21

DEPT-135 and ^{13}C NMR



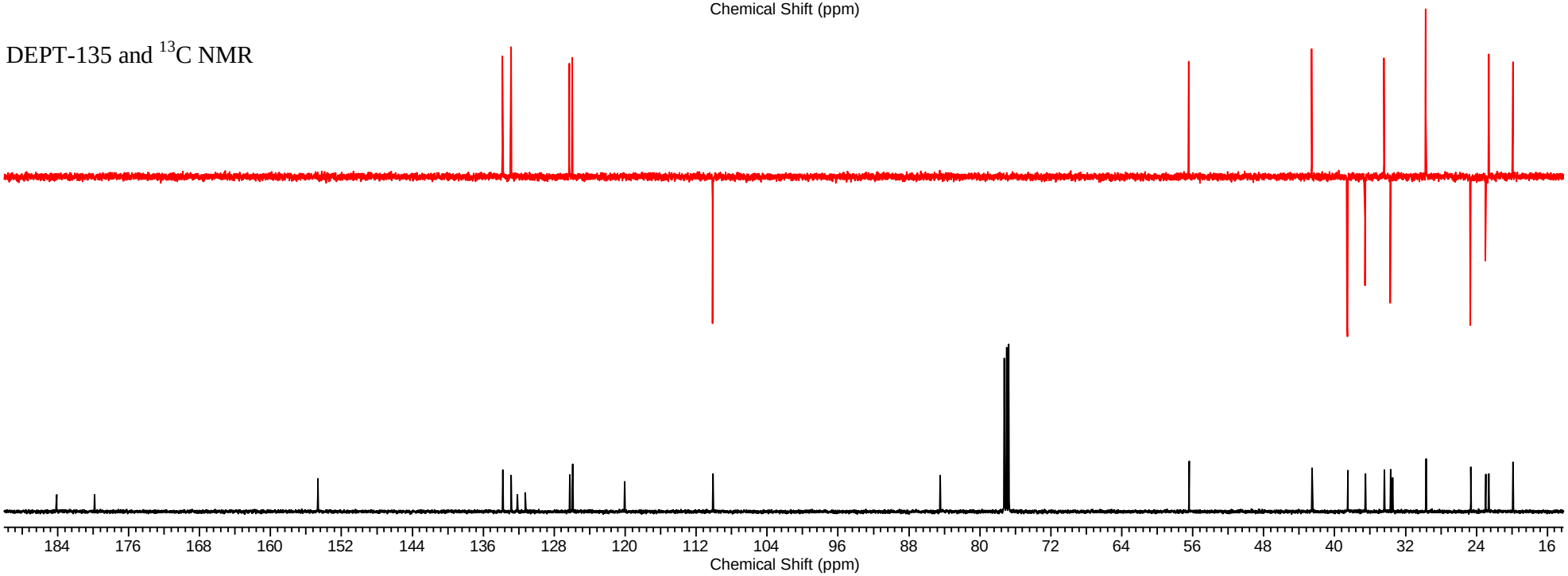

+TOF MS: 0.2171 min from Sample 1 (ZQM-2) of ZQM-2 (84-42) .wiff
a=7.027868370874693 90e-004, t0=3.159539858842917 40e-001 (DuoSpray ()), Noise Filtered
Max. 2.2e5 cps.
391.2258
396.8011
413.2069
21
Intensity, cps
m/z, Da
2.2e5
2.1e5
2.0e5
1.9e5
1.8e5
1.7e5
1.6e5
1.5e5
1.4e5
1.3e5
1.2e5
1.1e5
1.0e5
9.0e4
8.0e4
7.0e4
6.0e4
5.0e4
4.0e4
3.0e4
2.0e4
1.0e4
0.0
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440

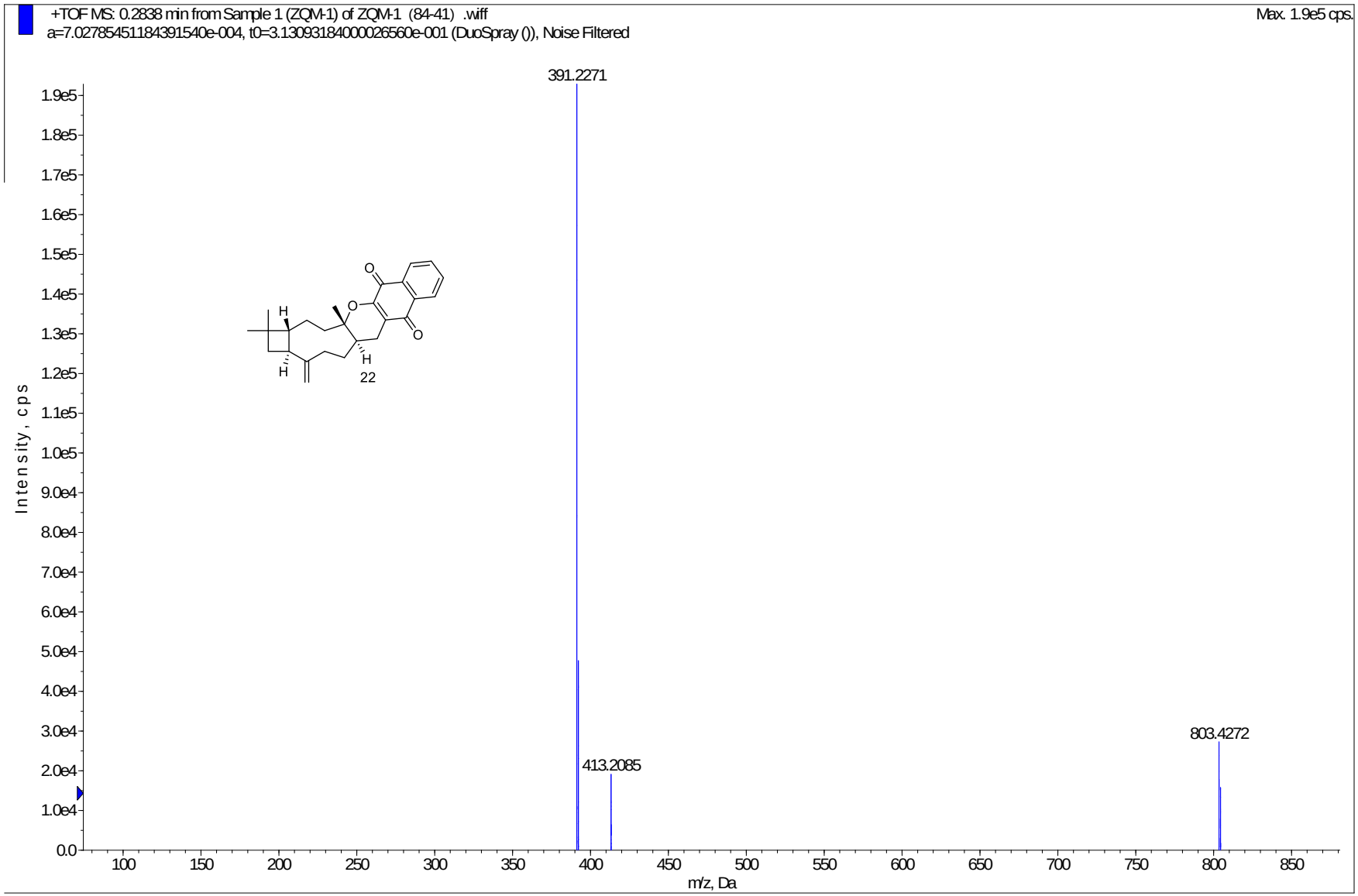
^{1}H NMR



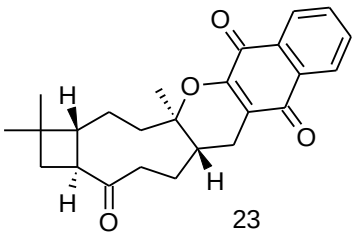
22

DEPT-135 and ^{13}C NMR



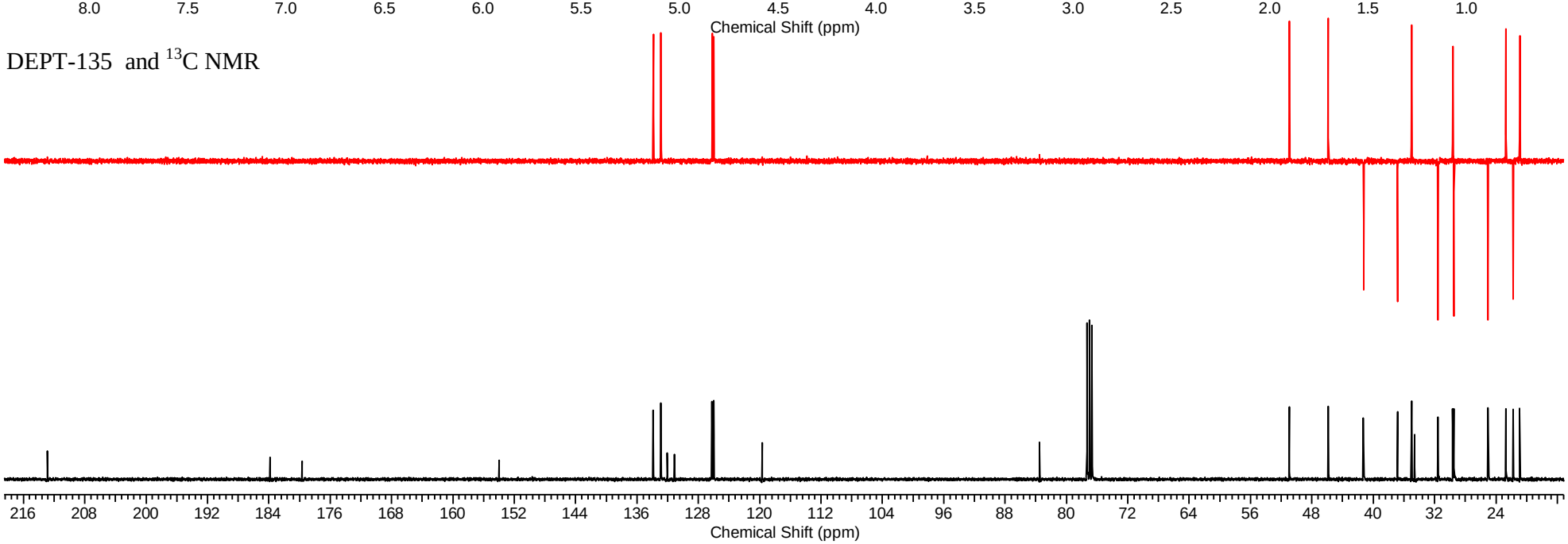

+TOF MS: 0.2838 min from Sample 1 (ZQM-1) of ZQM-1 (84-41) .wiff
a=7.027854511843915 40e-004, t0=3.13093184000026560e-001 (DuoSpray ()), Noise Filtered
Max. 1.9e5 cps.
391.2271
413.2085
803.4272
22
Intensity, cps
m/z, Da

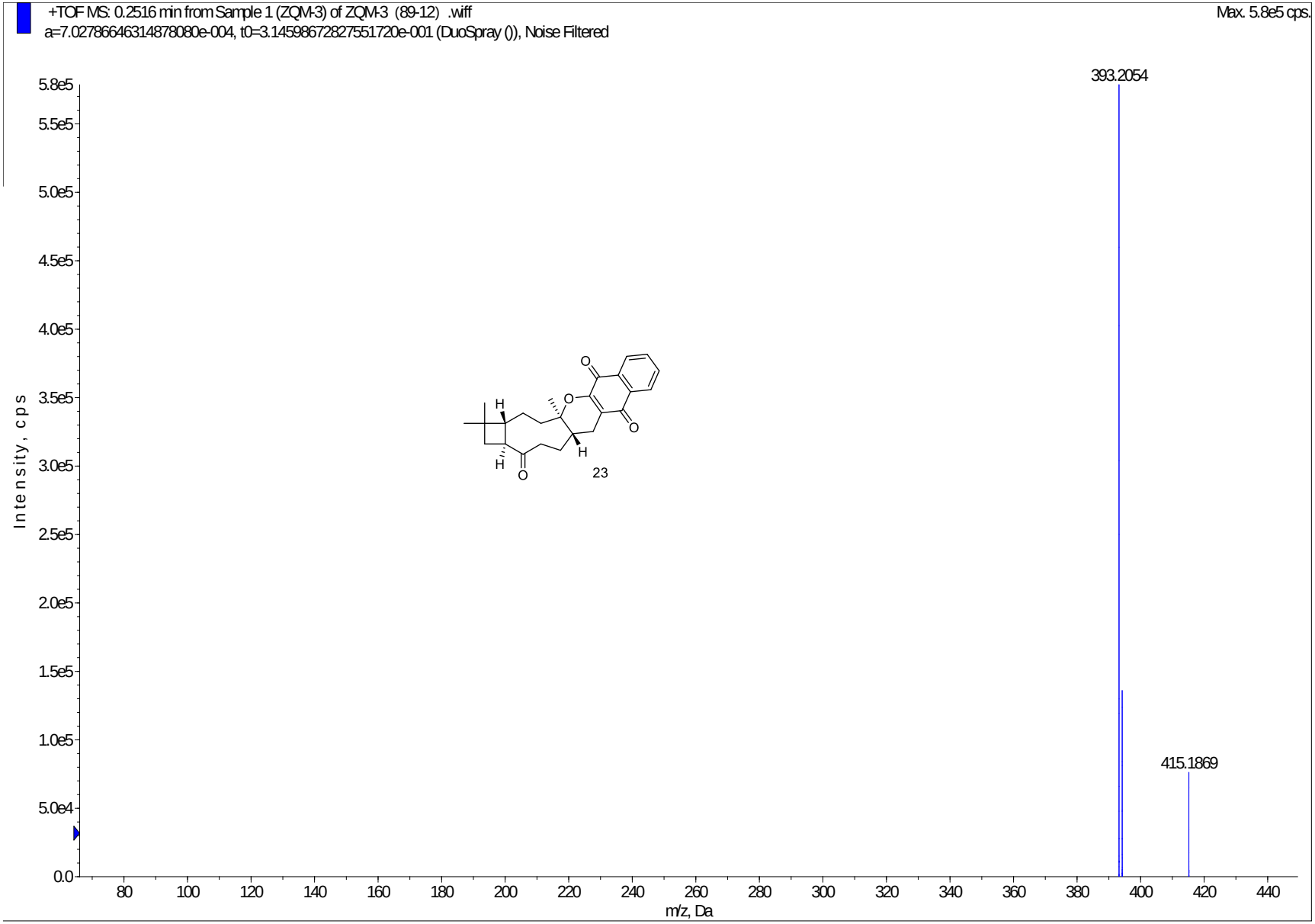
^{1}H NMR



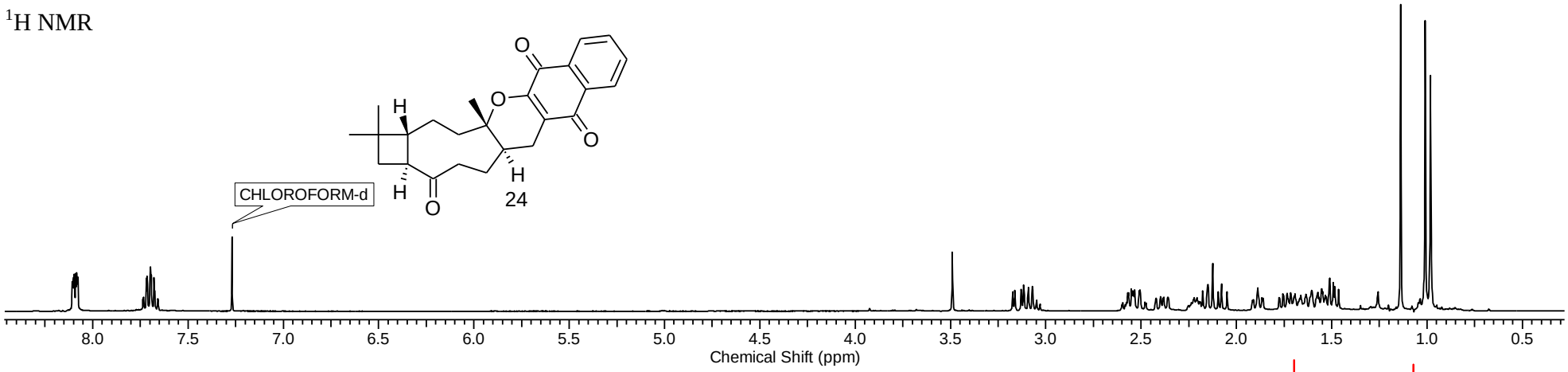
23

DEPT-135 and ^{13}C NMR

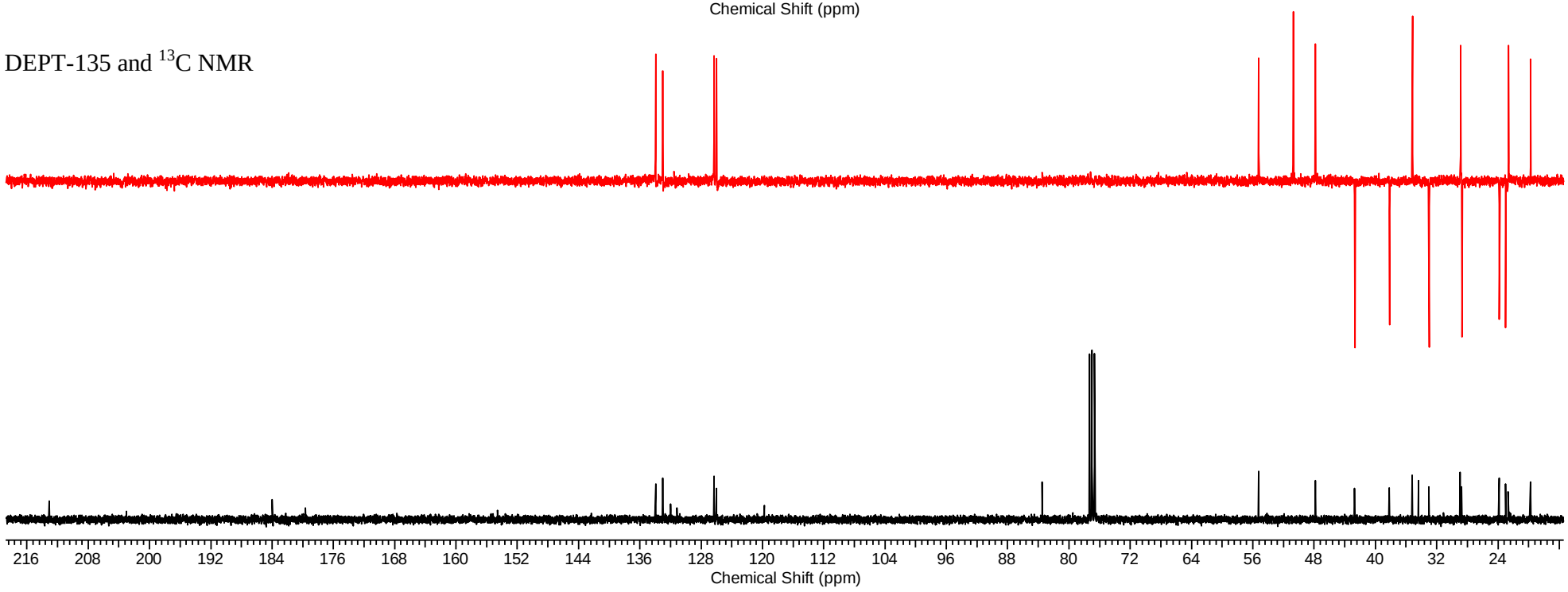


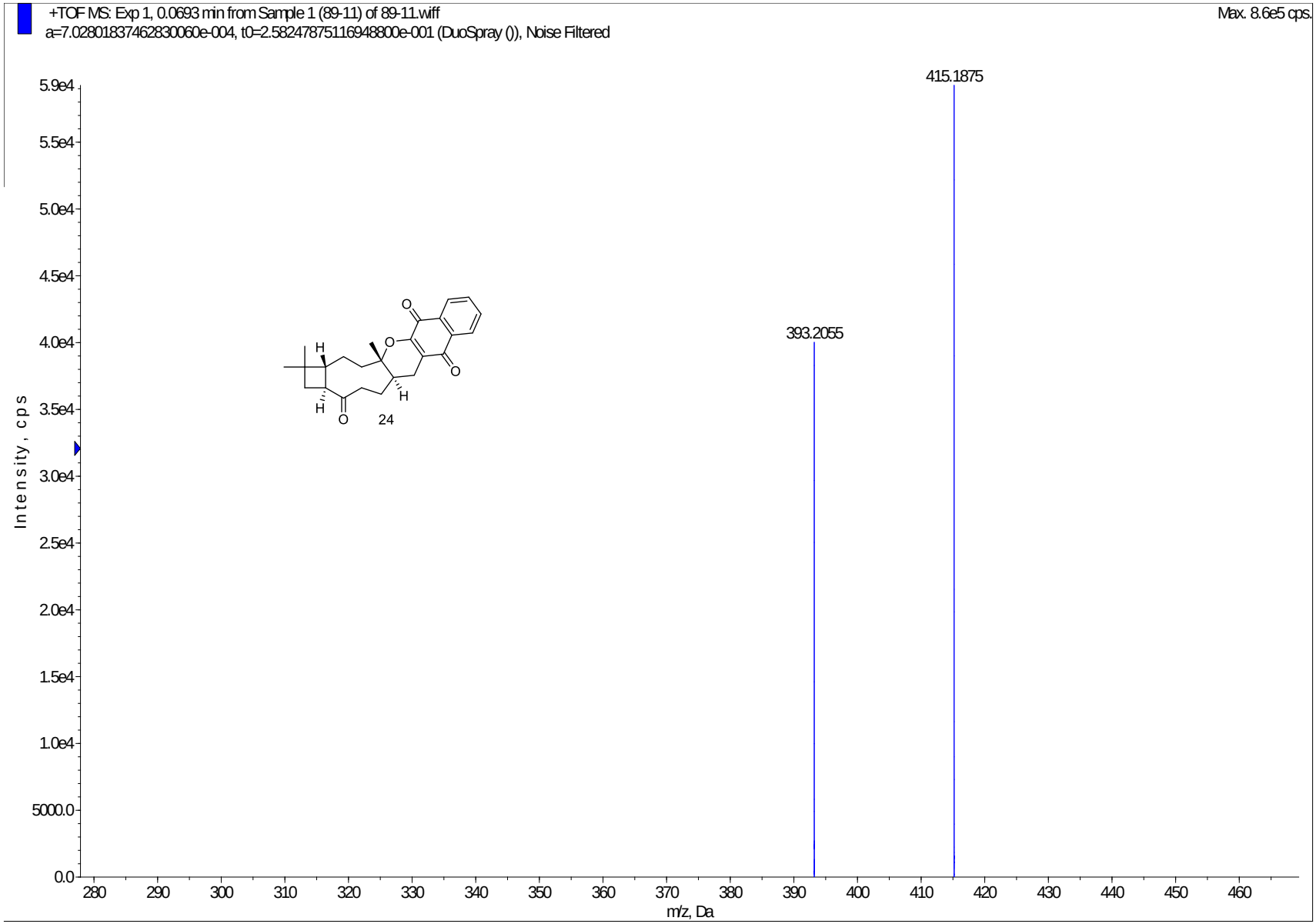

+TOF MS: 0.2516 min from Sample 1 (ZQM-3) of ZQM-3 (89-12) .wiff
a=7.0278664631487808 0e-004, t0=3.1459867282755172 0e-001 (DuoSpray ()), Noise Filtered
Max. 5.8e5 cps.
393.2054
415.1869
Intensity, cps
m/z, Da
23

^{1}H NMR

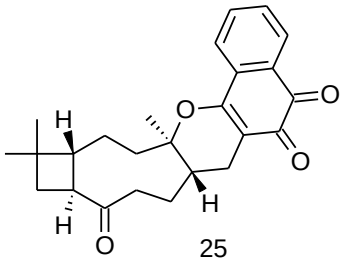


DEPT-135 and ^{13}C NMR



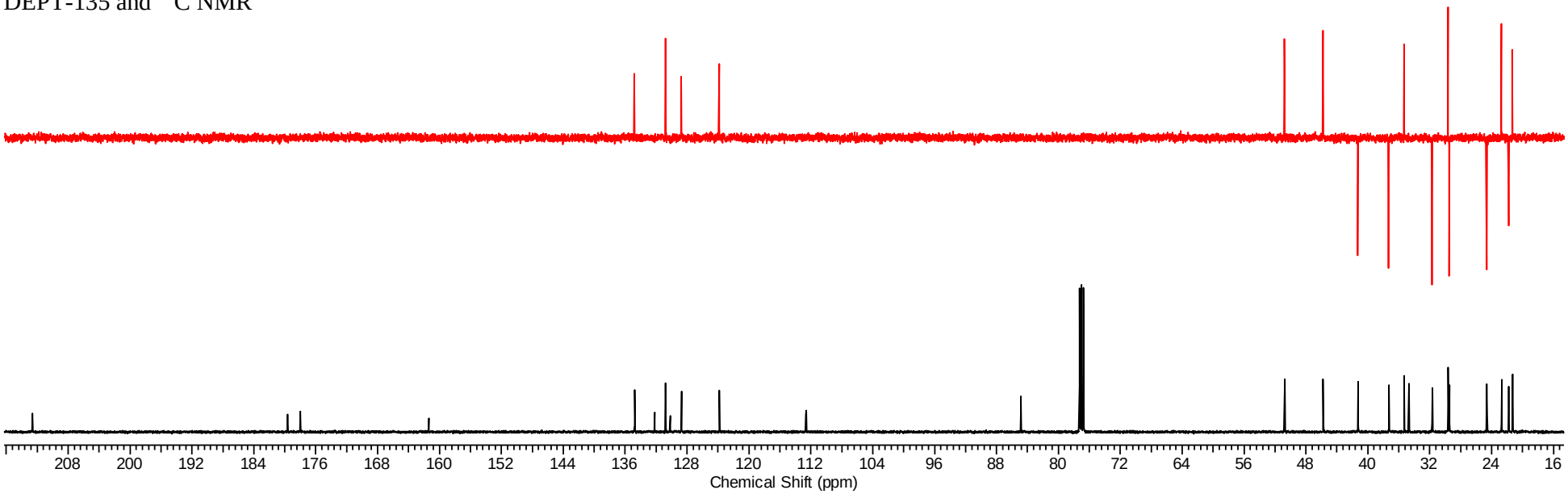

+TOF MS: Exp 1, 0.0693 min from Sample 1 (89-11) of 89-11.wiff
a=7.028018374628300 60e-004, t0=2.582478751169488 00e-001 (DuoSpray ()), Noise Filtered
Max. 8.6e5 cps.
415.1875
393.2055
24
Intensity, cps
m/z, Da
5.9e4
5.5e4
5.0e4
4.5e4
4.0e4
3.5e4
3.0e4
2.5e4
2.0e4
1.5e4
1.0e4
5000.0
0.0
280
290
300
310
320
330
340
350
360
370
380
390
400
410
420
430
440
450
460

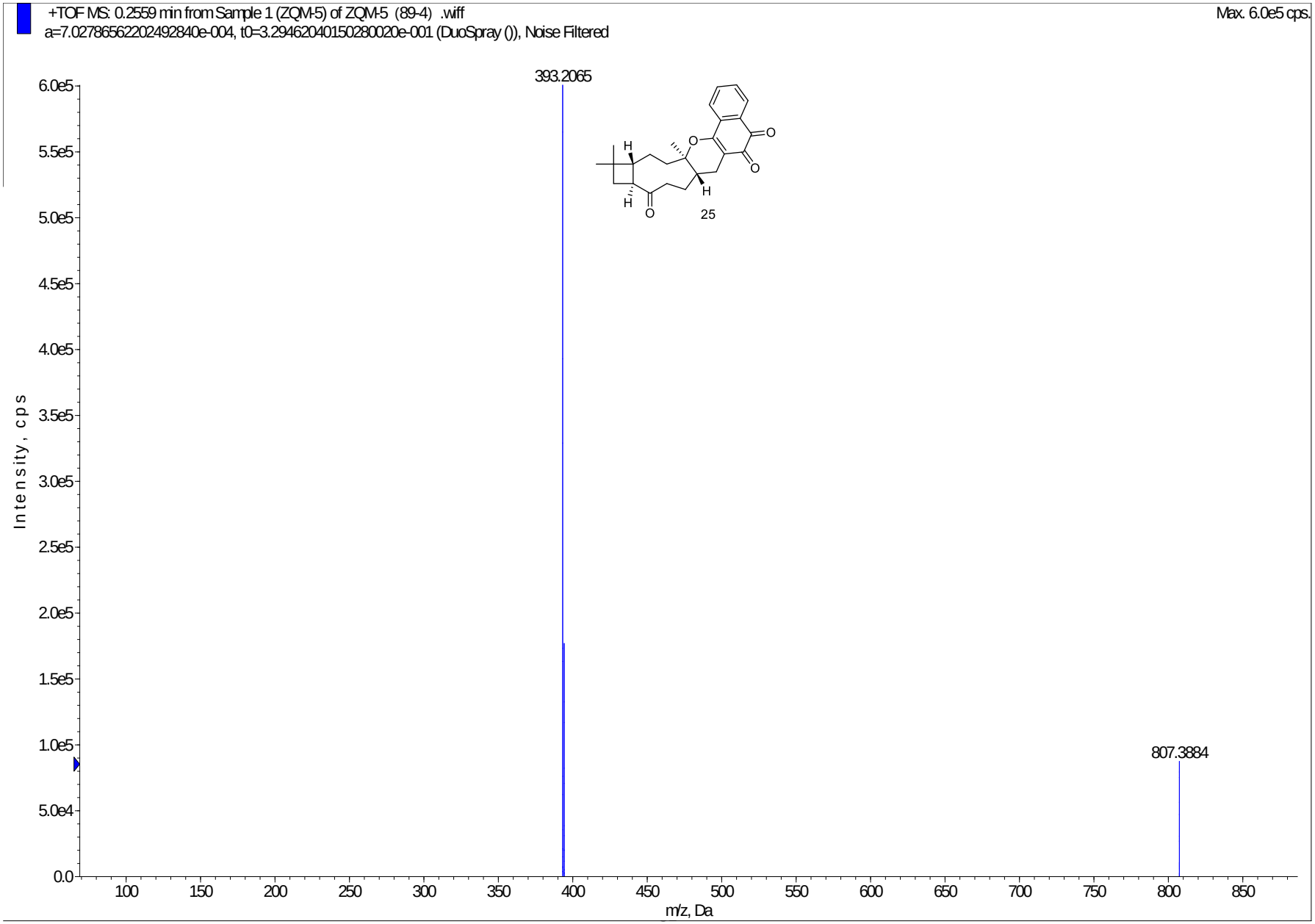
^{1}H NMR



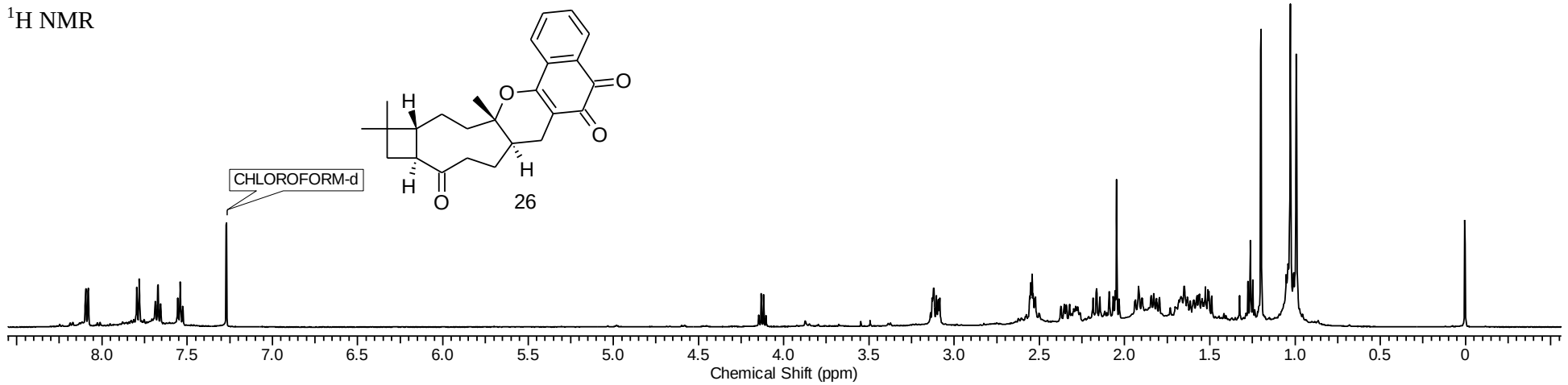
25

DEPT-135 and ^{13}C NMR

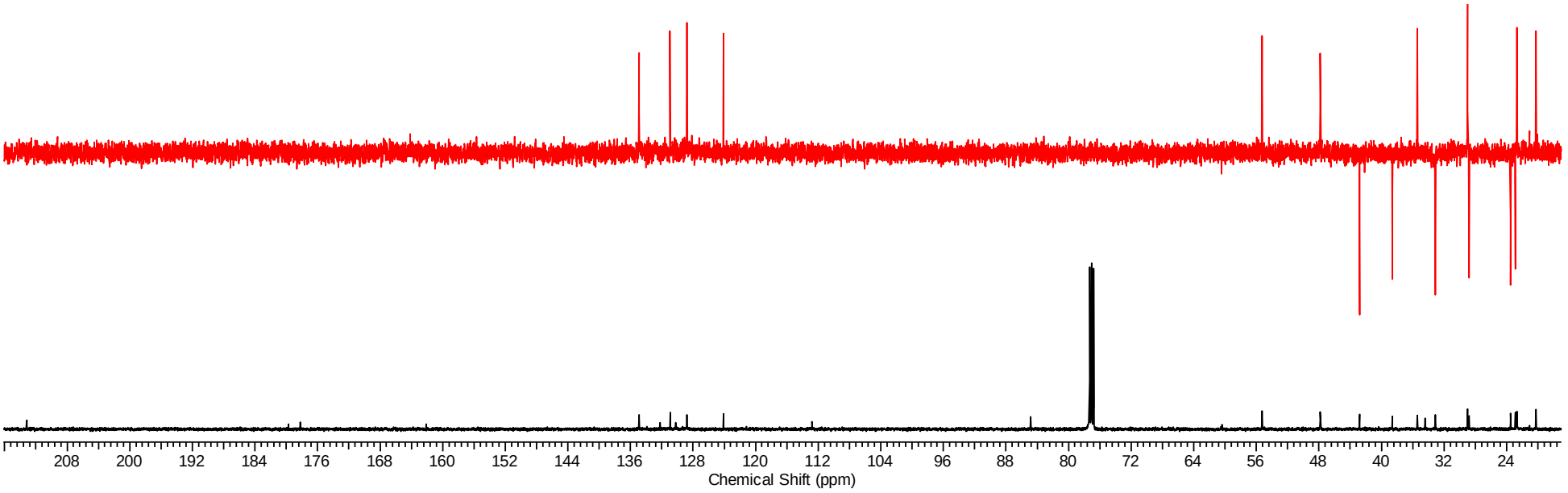


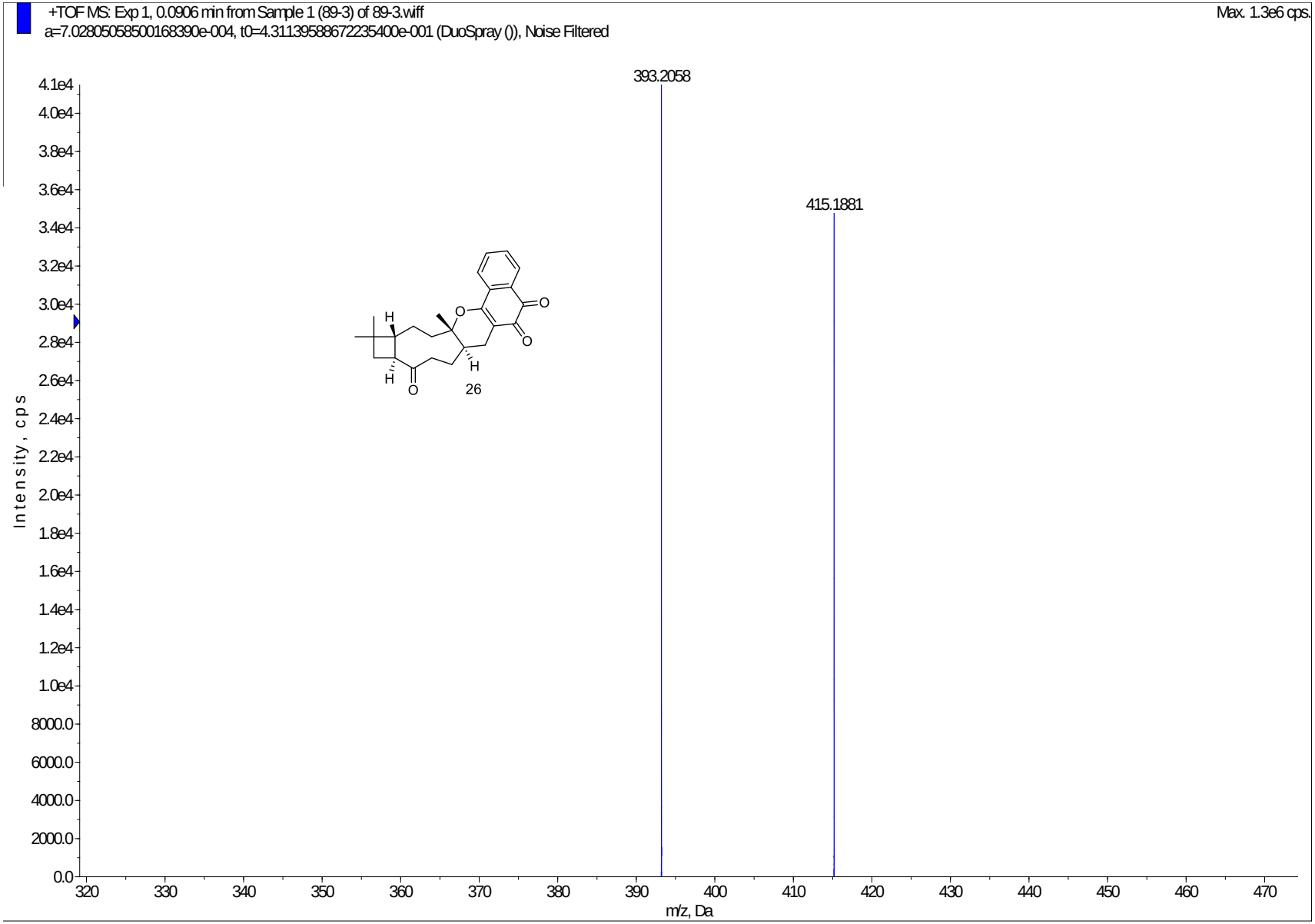

+TOF MS: 0.2559 min from Sample 1 (ZQM-5) of ZQM-5 (89-4) .wiff
a=7.02786562202492840e-004, t0=3.29462040150280020e-001 (DuoSpray ()), Noise Filtered
Max. 6.0e5 cps.
393.2065
807.3884
25
Intensity, cps
m/z, Da
6.0e5
5.5e5
5.0e5
4.5e5
4.0e5
3.5e5
3.0e5
2.5e5
2.0e5
1.5e5
1.0e5
5.0e4
0.0
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850

^{1}H NMR

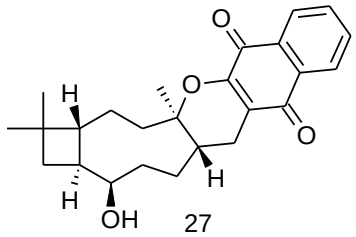


DEPT-135 and ^{13}C NMR



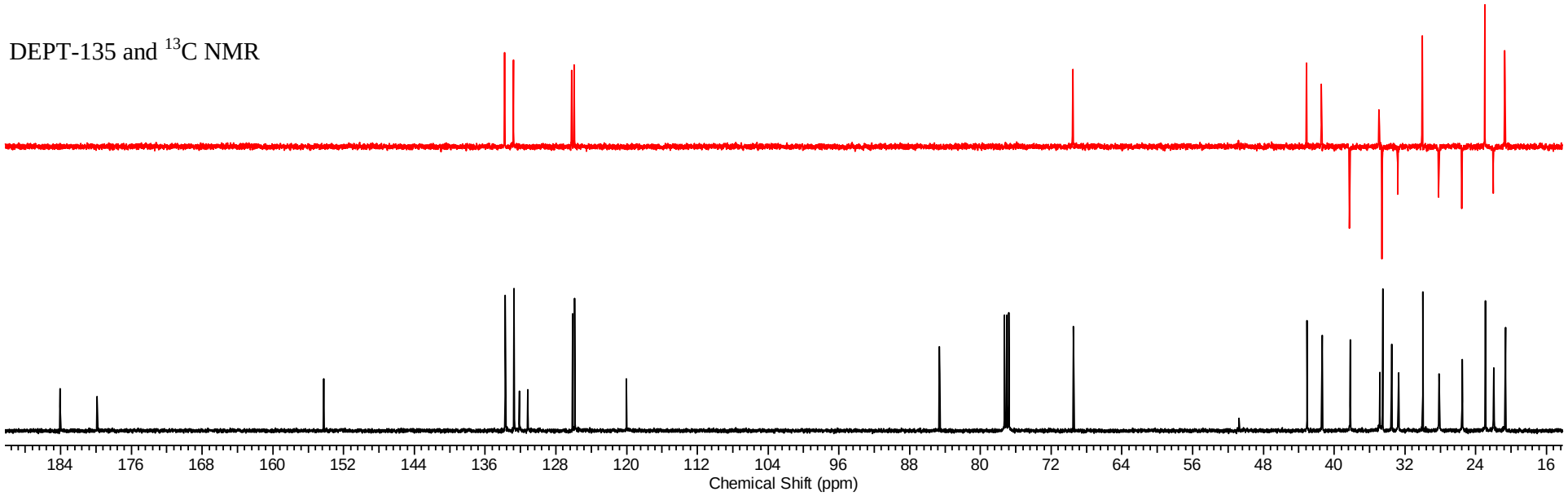

+TOF MS: Exp 1, 0.0906 min from Sample 1 (89-3) of 89-3.wiff
a=7.028050585001683 90e-004, t0=4.311395886722354 00e-001 (DuoSpray ()), Noise Filtered
Max. 1.3e6 cps.
393.2058
415.1881
Intensity, cps
m/z, Da
26

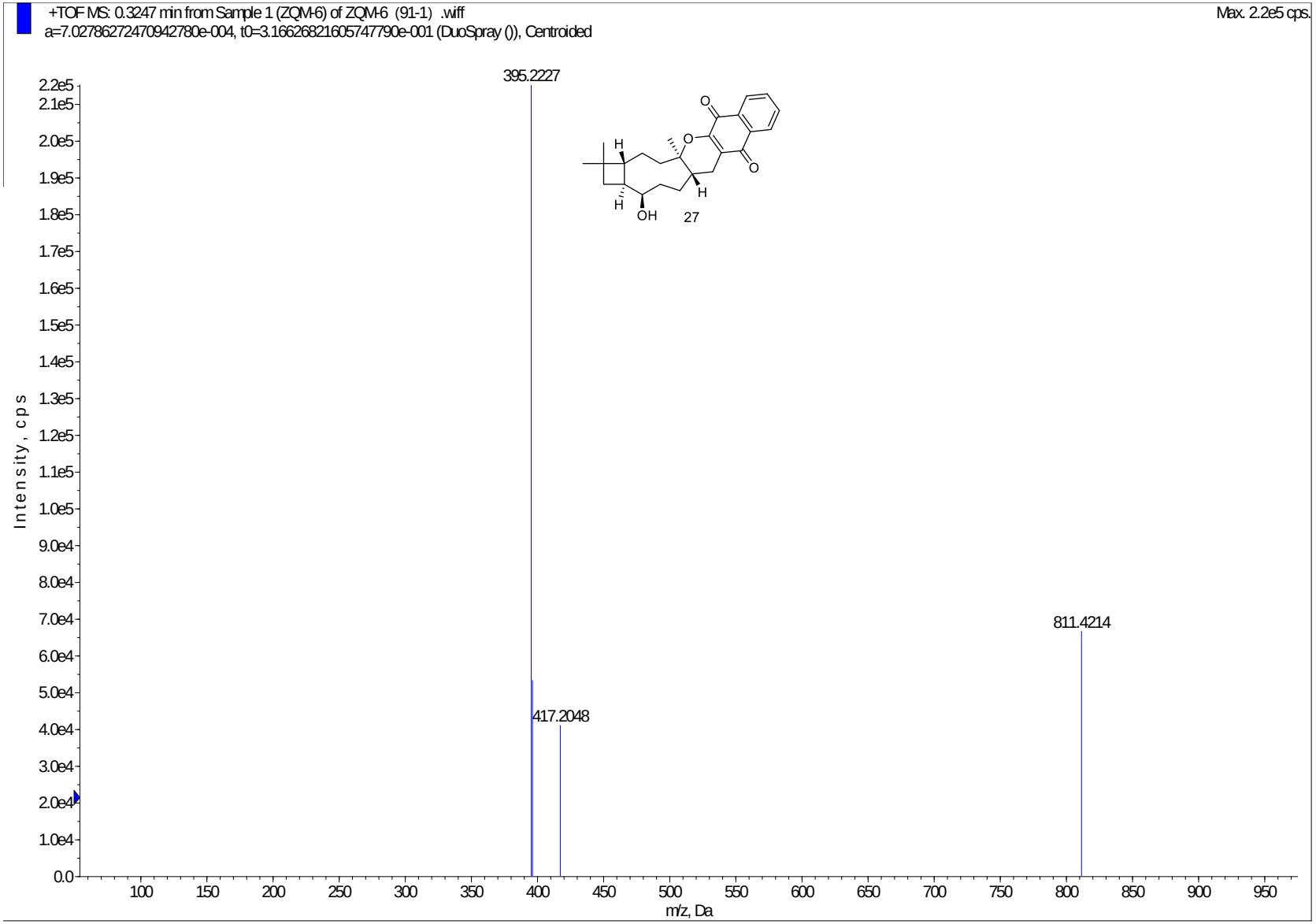
^{1}H NMR



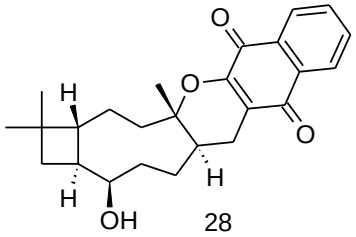
27

DEPT-135 and ^{13}C NMR




+TOF MS: 0.3247 min from Sample 1 (ZQM-6) of ZQM-6 (91-1) .wiff
a=7.0278627247094278e-004, t0=3.1662682160574779e-001 (DuoSpray ()), Centroided
Max. 2.2e5 cps.
395.2227
417.2048
811.4214
27
Intensity, cps
m/z, Da

^{1}H NMR



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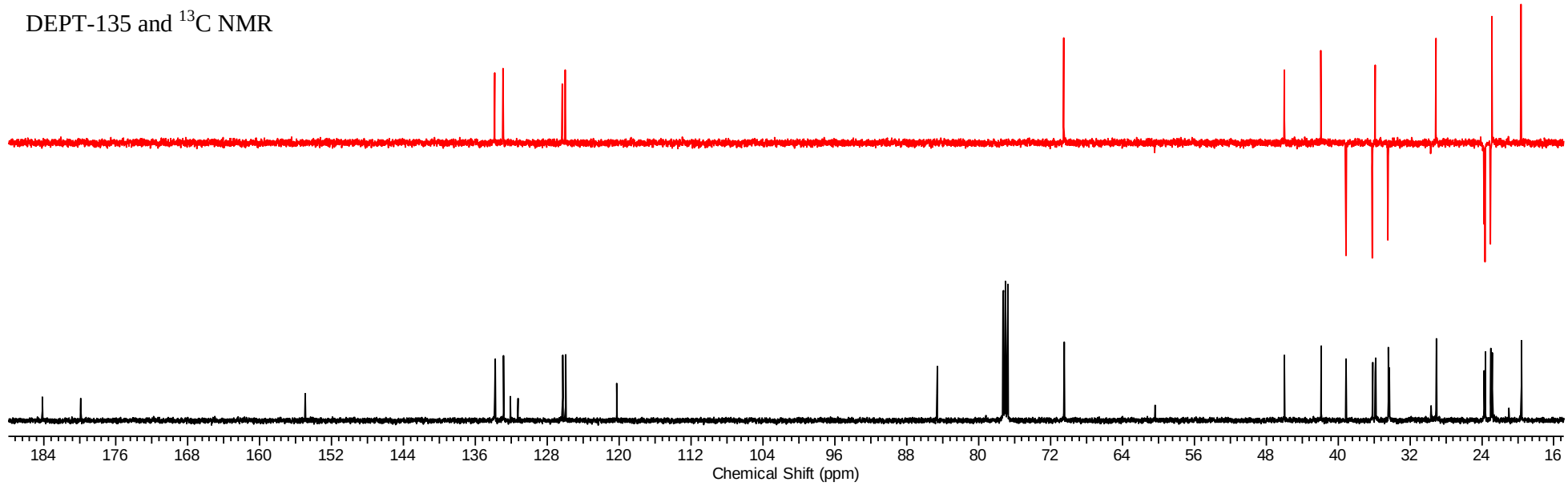
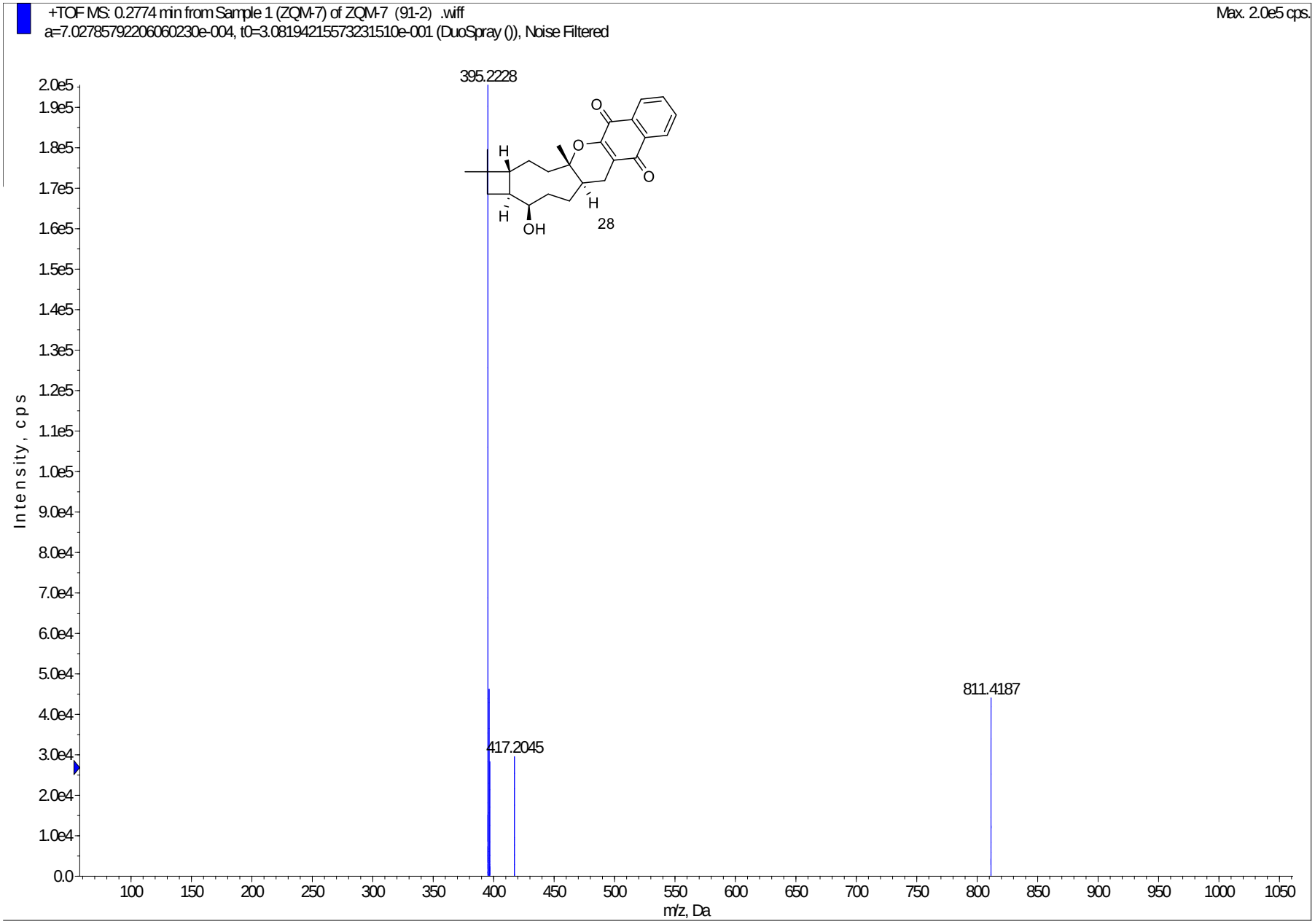
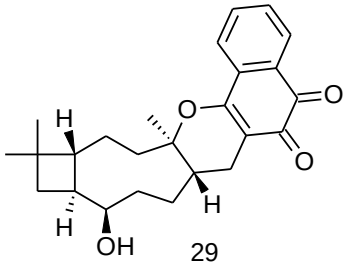
DEPT-135 and ^{13}C NMR



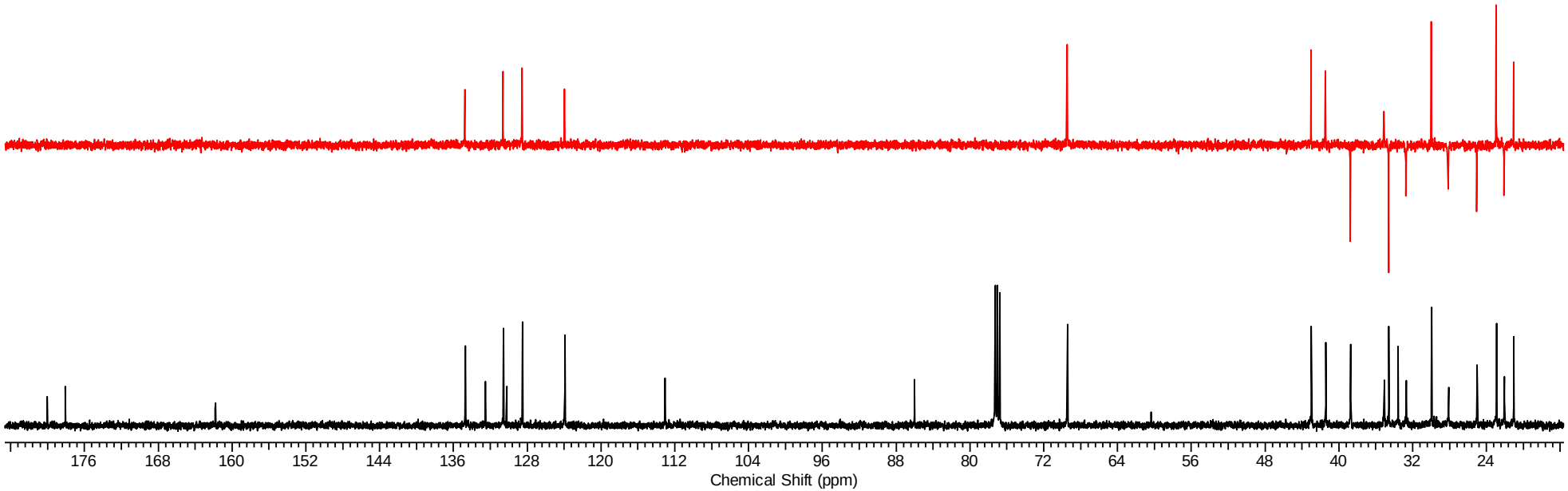

+TOF MS: 0.2774 min from Sample 1 (ZQM-7) of ZQM-7 (91-2) .wiff
a=7.02785792206060230e-004, t0=3.08194215573231510e-001 (DuoSpray ()), Noise Filtered
Max. 2.0e5 cps.
395.2228
811.4187
417.2045
28
Intensity, cps
m/z, Da

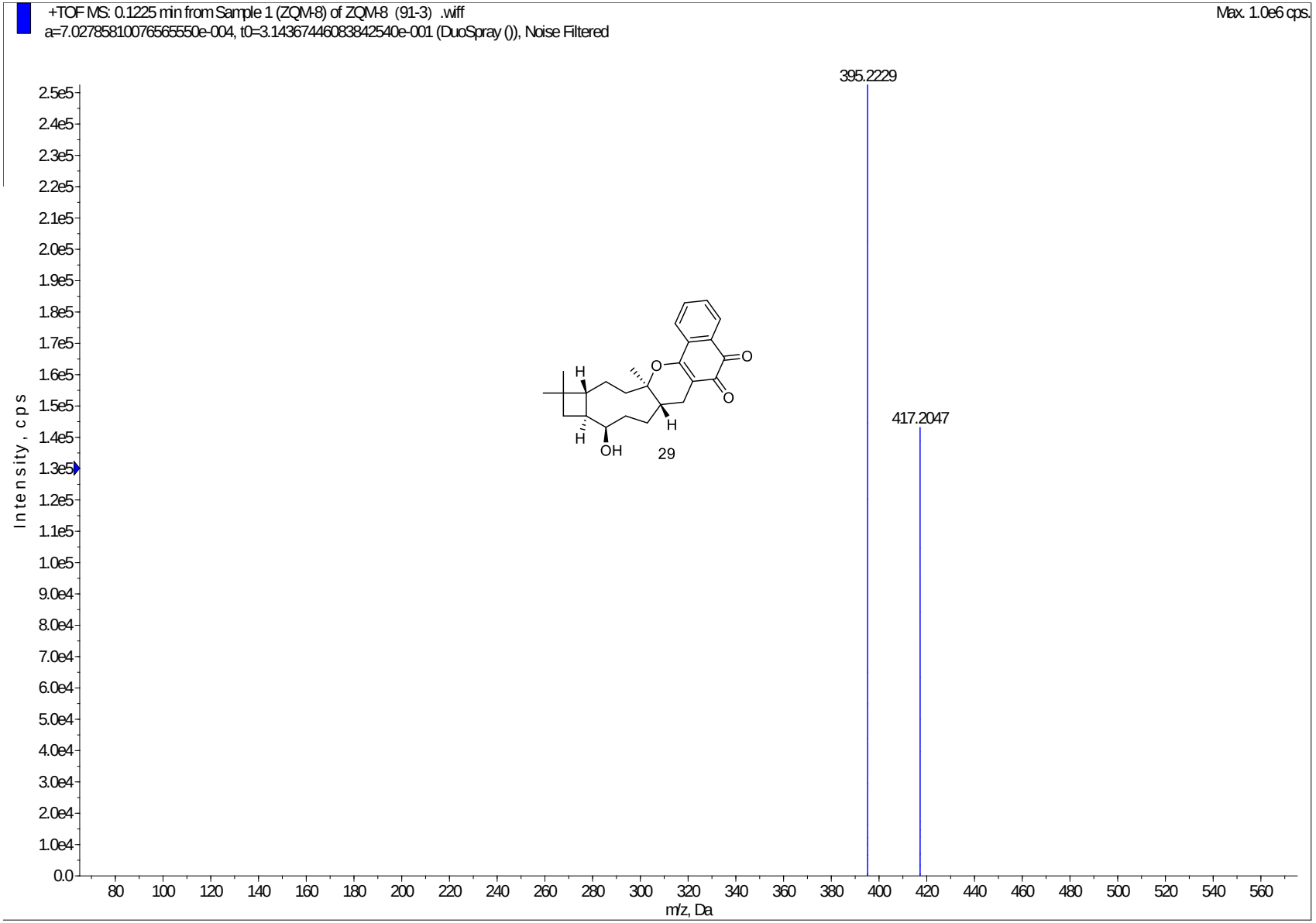
^{1}H NMR



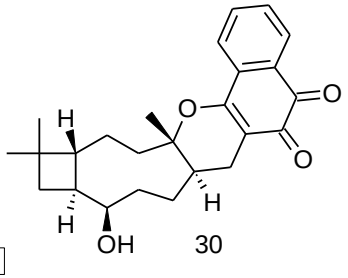
29

DEPT-135 and ^{13}C NMR



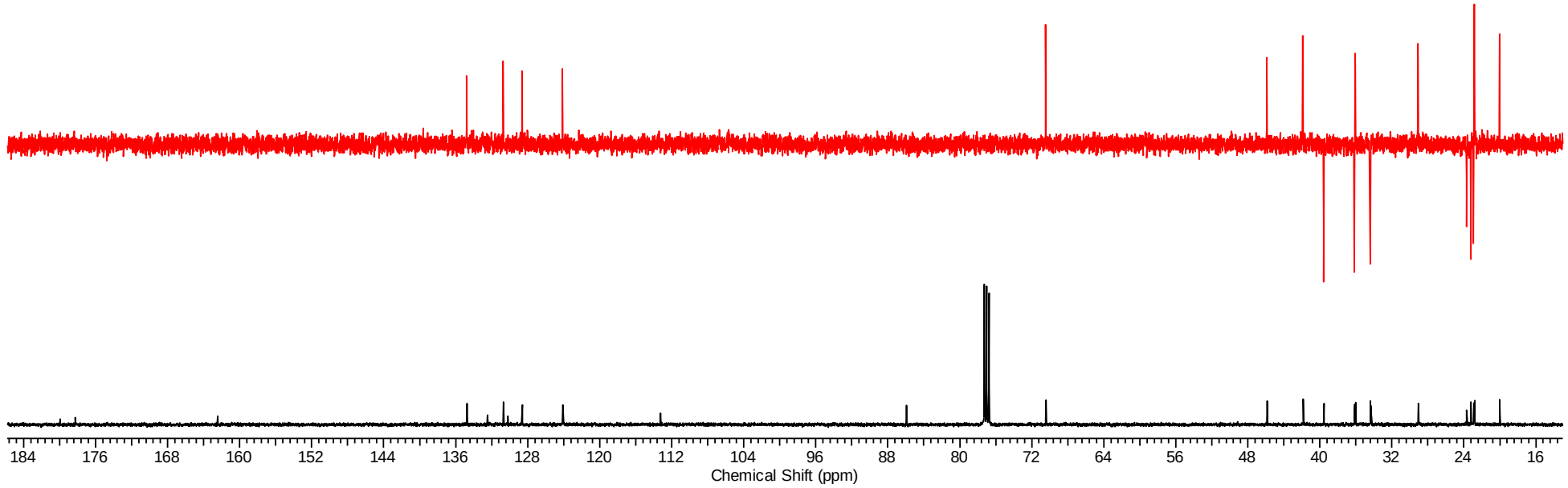

+TOF MS: 0.1225 min from Sample 1 (ZQM-8) of ZQM-8 (91-3) .wiff
a=7.0278581007656555 0e-004, t0=3.1436744608384254 0e-001 (DuoSpray ()), Noise Filtered
Max. 1.0e6 cps.
395.2229
417.2047
Intensity, cps
m/z, Da
29

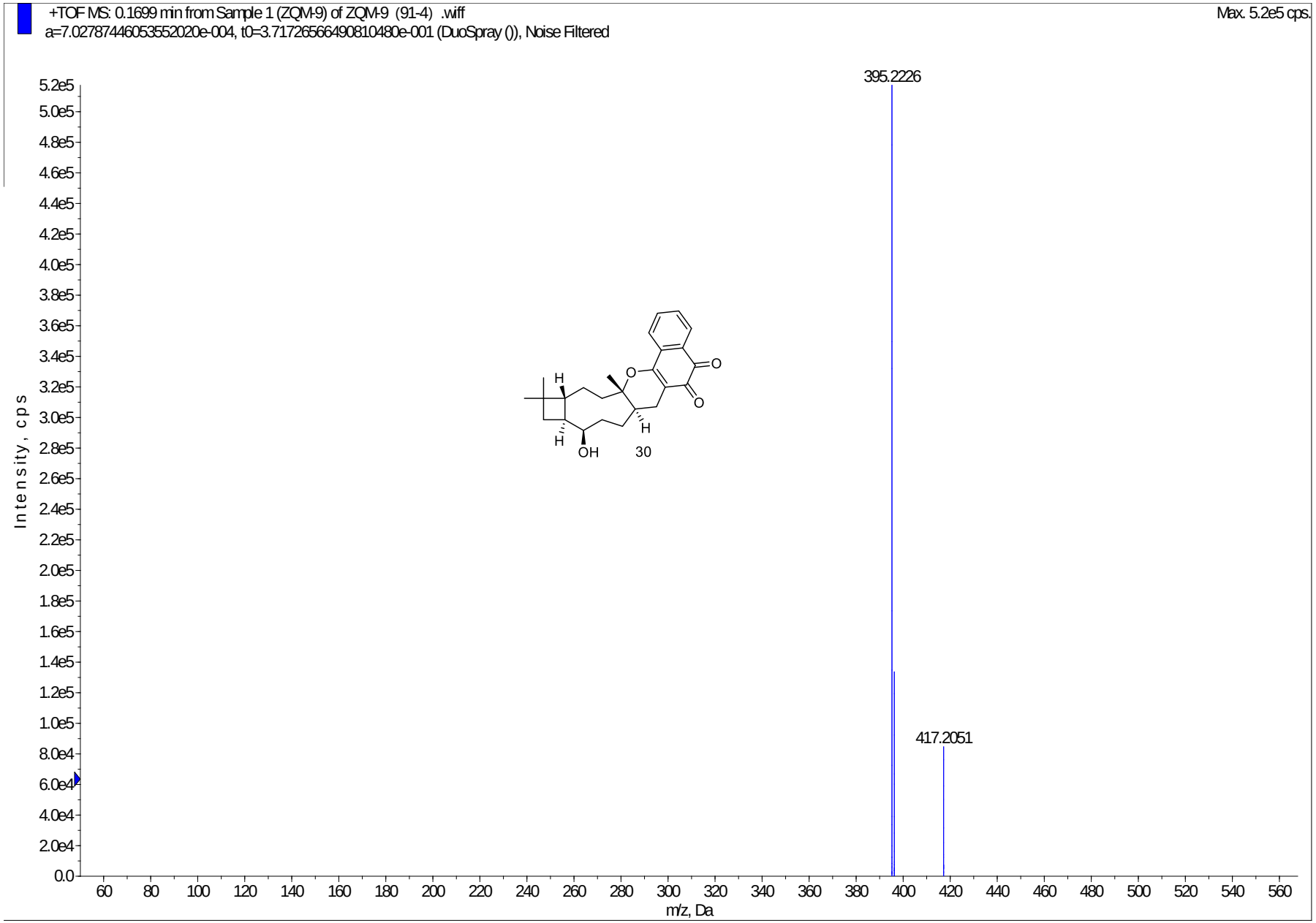
^{1}H NMR



30

DEPT-135 and ^{13}C NMR




+TOF MS: 0.1699 min from Sample 1 (ZQM-9) of ZQM-9 (91-4) .wiff
a=7.0278744605355202 0e-004, t0=3.7172656649081048 0e-001 (DuoSpray ()), Noise Filtered
Max. 5.2e5 cps.
395.2226
417.2051
Intensity, cps
m/z, Da
30