Supporting Information for:

Biosynthesis of lycosantalonol, a *cis*-prenyl derived diterpenoid

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Content

Detailed materials and methods

General. Unless otherwise noted, chemicals were purchased from Fisher Scientific and molecular biology reagents from Invitrogen. Sequence analyses were carried out with the CLC Main Workbench 6.9 software package (CLCbio). Flash chromatography was carried out with a Reveleris iES system (Grace). HPLC separations were carried out with an Agilent 1100 series instrument equipped with fraction collector and diode array detector. Gas chromatography with mass spectrometric detection (GC-MS) analyses were performed using a Varian (Palo Alto, CA, USA) 3900 instrument with HP-5ms column and Saturn 2100 ion trap mass spectrometer in electron ionization (70 eV) mode. Samples (generally 1 μL) were injected in splitless mode at 50 °C and, after a 3 min. hold, the temperature raised at 14 °C/min. to 300 °C, where it was held for 3 min. MS data was collected from *m/z* from 90 to 600, starting 12 min. after the injection until the end of the run. High resolution MS spectra were acquired on a Waters Micromass GCT Premier Mass Spectrometer, employing the same GC conditions as above. 1D and 2D NMR spectra were recorded at 25 °C on a Bruker Avance 700 spectrometer equipped with a 5-mm HCN cryogenic probe. Structural analysis was carried out using standard proton, triple quantum filtered-COSY, HSQC, HMBC, ^{13}C, and NOESY experiments. Optical rotation was measured at room temperature with a JASCO P-2000 digital polarimeter.

Cloning. To remove the plastid targeting leader peptide sequence, 52 and 44 amino acid residues were deleted from the N-termini of SlCPT2 and SlTPS21, respectively. A synthetic gene, with optimized codon usage for expression in *E. coli*, encoding CYP71D51 was obtained from Genscript. Each of these genes was cloned by directional topoisomerization into pENTR/SD/D-TOPO vectors, and the resulting constructs verified by full gene sequencing. This enabled facile transfer via direction recombination into a variety of DEST cassette containing expression vectors, both the commercially available pET-based pDEST constructs, and the previously described series of Duet vectors (Novagen) wherein the first multiple cloning site has been replaced by a DEST cassette.[1] However, initial expression studies with SlCPT2 indicated that only the originally reported pEXP5-CT-TOPO based expression construct exhibited robust flux to **1**. Accordingly, pEXP5/SlCPT2 constructs were used throughout these studies. For co-expression with SlCPT2, SlTPS21 was sub-cloned into pACYC-Duet/DEST, creating pACYC-Duet/DEST::SlTPS21. To enable co-expression of CYP71D51 with SlCPT2 and SlTPS21, NdeI and KpnI restriction sites were introduced following the truncated SlCPT2 open reading frame by PCR amplification, and this extended gene fragment was re-cloned into pEXP5-CT-TOPO.

The synthetic CYP71D51 gene was extended by PCR amplification to introduce a preceding NdeI restriction site and optimally spaced ribosome binding site, a KpnI restriction site following the open reading frame, and this cloned into pZeroBlunt. Both constructs were verified by complete sequencing of these extended gene fragments, then the CYP71D51 extended gene cloned into the extended pEXP5/SlCPT2 construct using the NdeI/KpnI restriction sites, creating a bicistronic pEXP5/SlCPT2-CYP71D51 dual expression vector. A non-extended version of CYP71D51 was sub-cloned into pET-Duet/DEST, creating pET-Duet/DEST::CYP71D51 expression vector for the production of CYP71D51 alone – i.e., for in vitro assays.

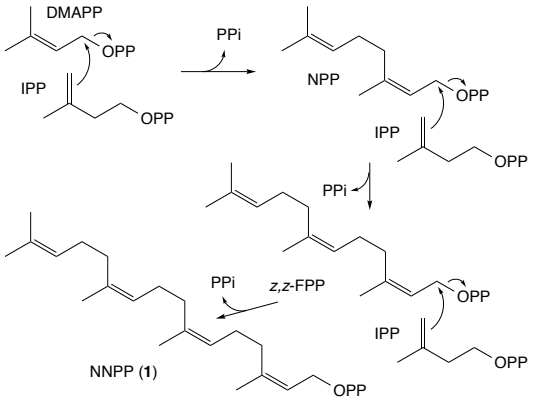
Metabolic engineering. All metabolic engineering was carried out using the C41 OverExpress strain of *E. coli* (Lucigen). For production of the dephosphorylated derivative of **1**, (*Z,Z,Z*)-nerylnerol (NNOH), pEXP5/SlCPT2 was co-transformed with pIRS, which overexpresses key enzymes from the endogenous isoprenoid precursor supply pathway, leading to increased flux to terpenoids.[1] For comparative purposes, a strain for production of the dephosphorylated derivative of (*E,E,E*)-geranylgeranyl diphosphate (GGPP), (*E,E,E*)-geranylgeraniol (GGOH), was constructed by co-transformation of pIRS with pGG, which expresses a plant GGPP synthase.[2] For the production of **2**, pEXP5/SlCPT2 was co-transformed with not only pIRS, but also pACYC-Duet/DEST::SlTPW21. GC-MS analysis demonstrated that the resulting olefin exhibited identical retention time and mass spectra to the previously reported product from in vitro reactions with recombinant SlCPT2 and SlTPS21,[3] indicating the expected equivalence. Finally, for the production of **3** and **4**, pEXP5/SlCPS2-CYP71D51 was co-transformed with pACYC-Duet/DEST::SlTPW21 and pCDF-Duet/DEST::AtCPR1, which expresses a CYP reductase from *Arabidopsis thaliana*.[4] These recombinant strains were grown at 37 °C in TB (terrific broth) with the appropriate antibiotics to an OD_{600} of 0.4–0.6, when the temperature was lowered to 16 °C, and after one hr of equilibration the cultures induced with 1 mM IPTG (isopropyl β-D-thiogalacto-pyranoside), then fermented for an additional 72 hrs at 16 °C.

Compound isolation. Following fermentation, the diterpenes were extracted with an equal volume of hexanes, which was dried under vacuum, and the residue was redissolved in 10 mL hexanes and subjected to flash chromatography over a 4-g. silica column. After loading, the column was washed with 24 mL hexanes and eluted with 48 mL of 9:1 hexanes-acetone (v/v) then 48 mL of 8:2 hexanes-acetone. The diterpene containing fractions, as ascertained by GC-MS analysis, were further subjected to HPLC separation carried out with a Supelcosil LC-18 column (4.6 x 250 mm, 5 mm) using a 0.5 mL/min flow rate. For isolation of NNOH, GGOH and **2**, after loading the column was washed with 50% acetonitrile/water (0 to 5 min) and eluted with 100% acetonitrile (5 to 30 min). For isolation of **3** and **4**, after loading the column was sequentially eluted with 82% acetonitrile/water (0 to 10 min), 87% acetonitrile (10 to 20 min) and 93% acetonitrile (20 to 30 min). For each compound the fractions containing the relevant diterpene, as determined by GC-MS analysis, were pooled, dried under a gentle stream of N_2, and resuspended in deuterated chloroform, with this evaporation-resuspension process repeated twice to completely remove protonated solvent. Initial analysis of **2** demonstrated that it was unstable in $CDCl_3$, necessitating the use of deuterated pyridine as the solvent. NMR data is presented below. The measured optical rotation values are **2**: $[\alpha]^{23}_D$ +7.9 (*c* 0.1, $CHCl_3$) and **4**: $[\alpha]^{23}_D$ +13.8 (*c* 0.2, $CHCl_3$).

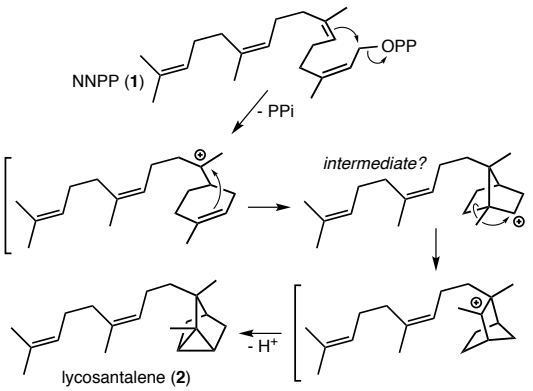
Analysis of CYP71D51. For in vitro assays, CYP71D51 was co-expressed with AtCPR1 in the C43 OverExpress strain of *E. coli* (Lucigen) using pET-Duet/DEST::CYP71D51 and pCDF-Duet/DEST::AtCPR1. This recombinant strain was grown, spheroblasts or microsomes prepared,

and reactions carried out, as previously described.[5] Briefly, the cultures were grown as above, with the cells collected by centrifugation (10 min. at 5,000 x *g*) and resuspended in lysis buffer (10 mM Tris-HCl, pH 7.2, 0.5 mM EDTA, 1 mM DTT, 20% glycerol). Lysis was carried by initial lysosome treatment (0.1 mg/mL for 10 min.), followed by brief, mild sonication (3 x 3 sec. bursts at 30% output). Spheroblasts were prepared by centrifugation (10 min. at 10,000 x *g*) to remove cellular debris. Microsomes were prepared by ultracentrifugation (30 min. at 76,000 x *g*), with resuspension of the ensuing pellet in lysis buffer. All preparative steps were carried out at 4 °C. Reactions were carried out using 400 μL of assay buffer (100 mM Tris/HCl, pH 7.8, 0.5 mM EDTA, 20% glycerol) and 100 μL of cell-free extract or microsomal preparations, which were initiated by the addition of 80 μM substrate (**2** or **3**). After 3 hrs, the resulting solutions were extracted twice with 1 mL hexanes and the extracts dried under N_2, with the residue resuspended in 150 μL hexanes for GC analysis. Given that α-hydroxy ketones are of some interest based on the presence of such a moiety in a number of natural products of pharmaceutical interest,[6-12] and that the production of an α-hydroxy ketone from an olefin, as shown to be catalyzed by CYP71D51 here, has drawn some interest from synthetic chemists as well,[13-19] we carried out further investigation of the catalyzed transformations. For $^{18}O_2$ labeling, assay buffer was bubbled with nitrogen for 10 min. and reactions carried out in 1 mL reaction vials (Thermo Scientific™ Reacti-Vial™) with laminated discs and open-top screw caps, which were evacuated, flushed with nitrogen and re-evacuated. After the addition of 400 μL degassed assay buffer and 100 μL fresh microsomes each vial was re-evacuated and pressurized by saturation with $^{18}O_2$. Reactions were then initiated by the addition of substrate and 0.4 mM NADPH via syringe. To verify assignment of the keto group in **4**, the ability of this oxygen to undergo exchange with water via a geminal dihydroxy form was investigated. Given the stability of keto groups in neutral aqueous solutions,[20] this was carried out by incubation of ~10 μg of **4** in 50 μL of ^{18}O-labeled water (97%; Cambridge Isotope Laboratories) acidified with 10 mM HCl at room temperature (~22 °C). Equivalent incubations were extracted after 4, 17 and 22 hours, twice with 100 μL hexanes, which were combined, dried under N_2, resuspended in 100 μL hexanes, and 5 μL injected for GC-MS analysis. Comparison of the resulting mass spectra to that from a control incubation in unlabeled water (also with 10 mM HCl) revealed the incorporation of a single atom of ^{18}O, present in increasing amounts with increased incubation time, reaching >25% of **4** after 22 hours (Figure S34), consistent with the presence of a keto group.

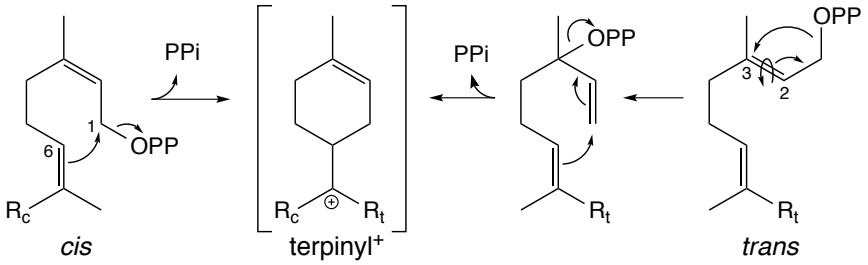
QCC analysis. Calculations were performed with GAUSSIAN09.[21] Geometries were optimized using the B3LYP method with the basis set of 6-31+G(d,p) in the absence and 6-31G(d) in the presence of PPi.[22] All stationary points were characterized as minima or transition state structures using frequency calculations at the same level. All reported energies include zero-point energy corrections (unscaled) from the frequency calculations at the same level. Intrinsic reaction coordinate (IRC) calculations were used for further characterization of transition state structures.[23] mPW1PW91[24] and MPWB1K[25] energies are also shown, since it is known that B3LYP underestimates the relative energies of cyclic structures versus acyclic isomers.[24] These energies include zero-point energy corrections (unscaled) from the frequency calculations using the B3LYP method at the same level. The validity of this computational approach for examining terpene-forming carbocation rearrangements is well-established.[26] Structural images were created with *Ball&Stick*.[27]



Scheme S1. Reactions catalyzed by SlCPT2. Condensation of dimethylallyl diphosphate (DMAPP) with isopentenyl diphosphate (IPP) to NPP, which is condensed with another molecule of IPP to *z,z*-FPP, which further is condensed with yet another molecule of IPP to yield the final product NNPP (**1**), with loss of pyrophosphate at each step.



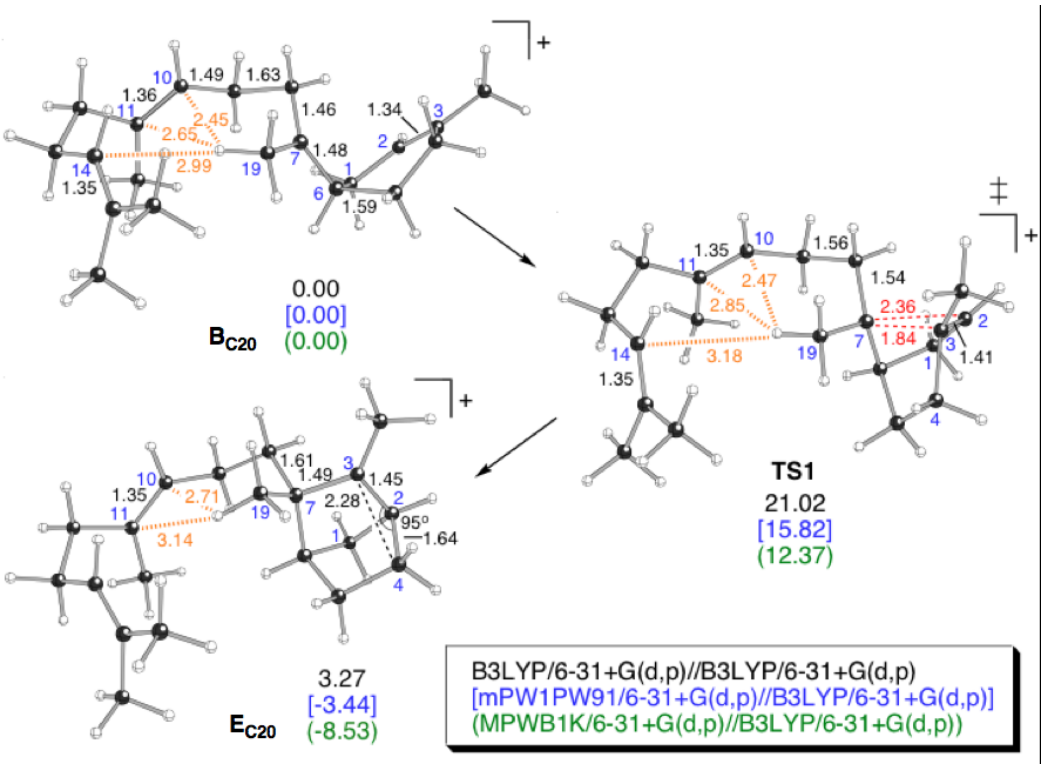
Scheme S2. Reaction catalyzed by SlTPS21 with **1**.



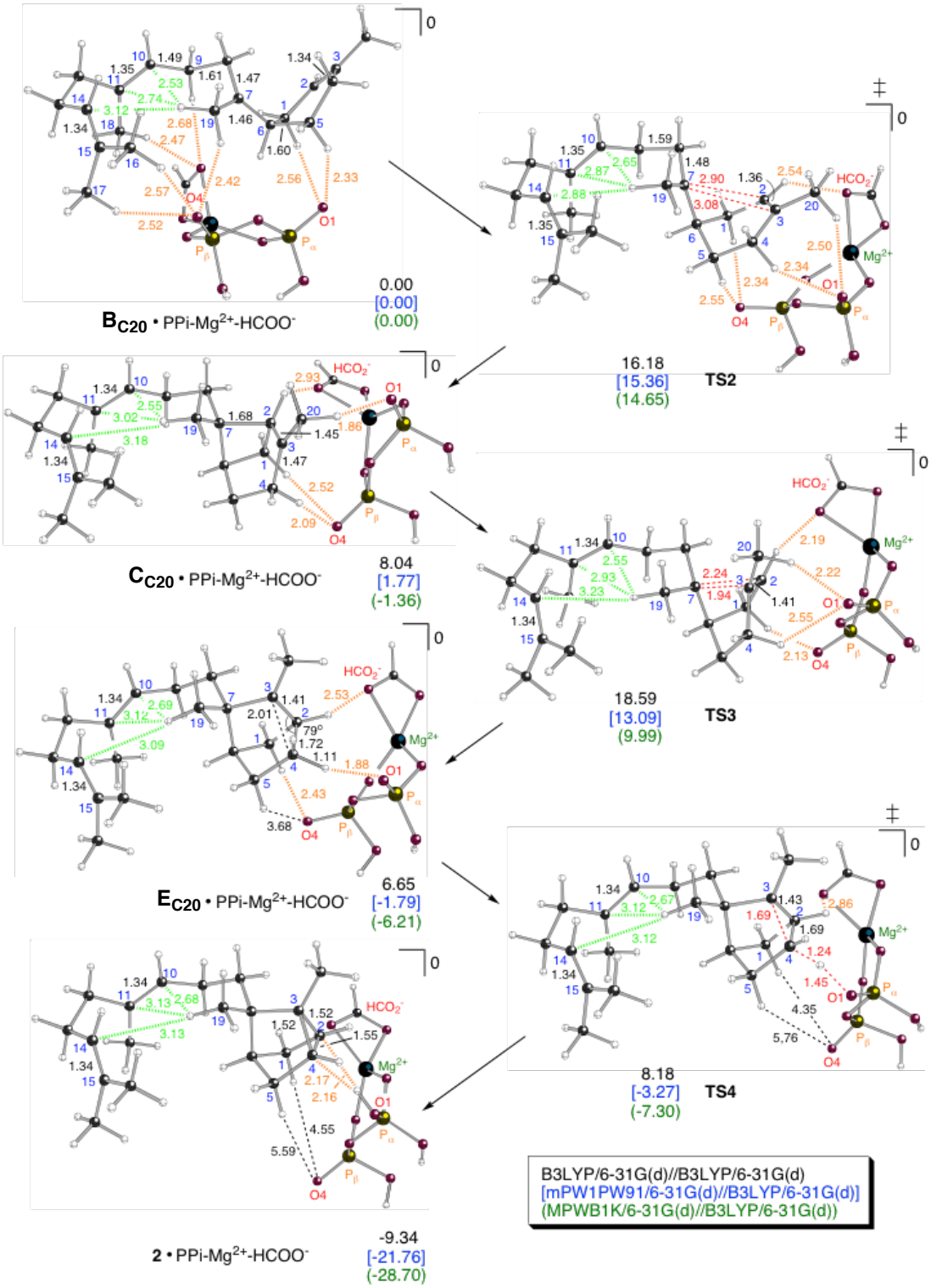
Scheme S3. C1-C6 cyclization requires isomerization of *transoid*, but not *cisoid*, prenyl diphosphate precursors.

Detailed results and discussion of QCC analysis

Rearrangements of cation **B** (*10e configuration*) were examined using quantum chemical calculations. The computed carbocation intermediates and transition state structures and computed energies involved in the *10e*-**B** conversion are shown in Scheme S4 (in the absence of PPi) and Scheme S5 (in the presence of PPi).



Scheme S4. Computed geometries (distances in Å) and energies (kcal/mol; all energies include zero-point energy corrections from the B3LYP frequency calculations) involved in the **B→E** conversion in the absence of PPi.



Scheme S5. **B→E** conversion in the presence of PPi. Computed complexes (selected distances in Å) and energies (kcal/mol; all energies include zero-point energy corrections from the B3LYP frequency calculations).

Based on our results, at least 12 kcal/mol barrier from the MPWB1K method is predicted for the **B→C** reaction (overall highest barrier) in the absence of PPi. Slightly higher barrier (approximately 15 kcal/mol from the MPWB1K method) is predicted for the reaction in the presence of PPi than in the absence of PPi. Variations in individual interactions between carbocations and PPi are also observed upon cationic center shifts one atom to another. It is notable that substantial PPi shift toward cationic center C7 is observed in the **B**-PPi complex compared to other complexes. This shift is believed in large to be owed to simple attraction of anionic PPi to cations due to lack of physical restriction in the absence of large part of the enzyme. Thus, the actual barrier for the **B→C** reaction could be less when physical constrain of PPi in the active site restricts migration of PPi. Note also that harnessing interactions between carbocation intermediates and PPi persist in large *in gas phase* throughout rearrangements of cation **B**. The complex of cation **E** and PPi is favorable for direct proton transfer (Scheme S5; **E→2** is predicted a barrierless process) enabling the ultimate cyclopropane product to form.

Coordinates and Energies, as well as *IRC Plots*, can be found at the end of this document.

Figure S1. The structures and numbering of NNOH and compounds **2**-**4**

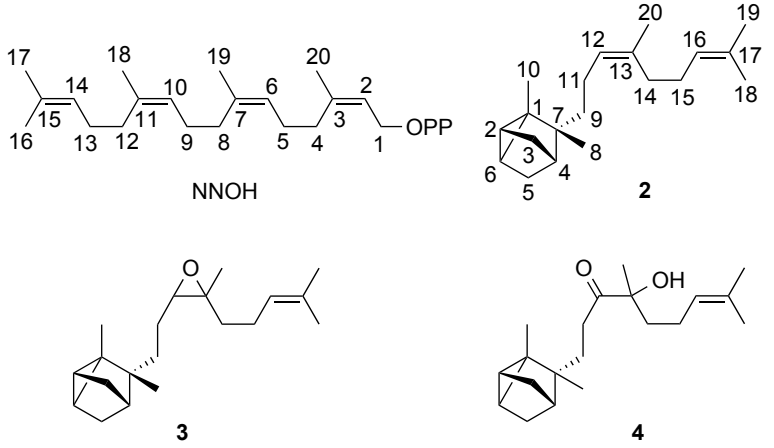


Figure S2. Selective NOESY correlations for NNOH and ^{1}H-^{1}H COSY and HMBC correlations for **2**-**4**

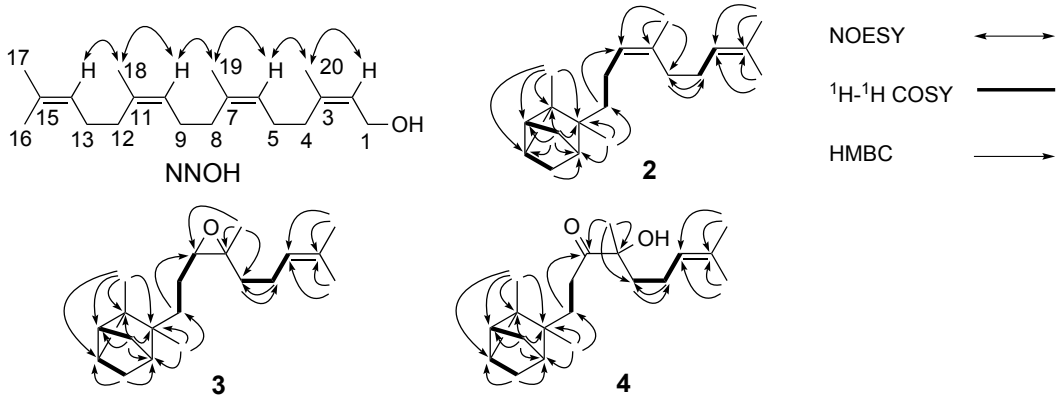


Table S1. NMR data for NNOH and GGOH ($CDCl_3$, 700 MHz)

Position	NNOH		GGOH	
	δ_H	δ_C	δ_H	δ_C
1	4.09 (2H, m)	59.6	4.15 (2H, d, J = 6.7 Hz)	60.0
2	5.44 (1H, t, J = 7.1 Hz)	124.9	5.42 (1H, t, J = 6.7 Hz)	123.9
3		140.5		140.5
4	2.10 (2H, m)	32.8	2.04 (2H, m)	40.2
5	2.09 (2H, m)	26.9	2.12 (2H, m)	26.9
6	5.13 (1H, m)	125.4	5.10 (1H, m)	125.0
7		136.7		136.0
8	2.04 (2H, m)	32.8	1.98 (2H, m)	40.31
9	2.05 (2H, m)	27.3	2.07 (2H, m)	27.2
10	5.12 (1H, m)	125.1	5.12 (1H, m)	124.4
11		136.0		135.6
12	2.04 (2H, m)	32.5	1.98 (2H, m)	40.28
13	2.05 (2H, m)	27.0	2.06 (2H, m)	27.4
14	5.11 (1H, m)	125.0	5.09 (1H, m)	124.8
15		132.1		131.9
16	1.61 (3H, s)	18.2	1.68 (3H, s)	26.3
17	1.68 (3H, s)	26.3	1.60 (3H, s)	18.3
18	1.69 (3H, s)	23.99	1.60 (3H, s)	16.61
19	1.69 (3H, s)	23.96	1.60 (3H, s)	16.60
20	1.75 (3H, s)	24.04	1.68 (3H, s)	16.9

Table S2. NMR data of **2** (pyridine-d_5, 700 MHz)

Position	δ_H	δ_C
1		28.0
2	0.72 (1H, m)	20.20
3 a	1.50 (1H, m)	31.6
b	0.91 (1H, d, J = 10.7 Hz)	
4	1.45 (1H, m)	38.8
5 a	1.47 (1H, m)	32.1
b	0.93 (1H, d, J = 10.7 Hz)	
6	0.73 (1H, m)	20.18
7		46.5
8	0.70 (3H, s)	17.9
9 a	1.15 (1H, dt, J = 5.5, 12.5 Hz)	35.5
b	1.06 (1H, dt, J = 5.5, 12.5 Hz)	
10	0.88 (3H, s)	11.1
11	1.87 (2H, m)	23.78
12	5.10 (1H, m)	127.0
13		134.8
14	2.02 (2H, m)	32.4
15	2.03 (2H, m)	27.3
16	5.11 (1H, m)	125.2
17		131.8
18	1.49 (3H, s)	18.0
19	1.56 (3H, s)	26.2
20	1.62 (3H, s)	23.84

Table S3. NMR data of **3** ($CDCl_3$, 700 MHz)

Position	δ_H	δ_C
1		28.0
2	0.77 (1H, m)	20.2
3 a	1.45 (1H, m)	31.6
b	0.95 (1H, d, J = 10.4 Hz)	
4	1.44 (1H, m)	38.8
5 a	1.52 (1H, d, J = 10.2 Hz)	32.1
b	0.98 (1H, d, J = 9.6 Hz)	
6	0.77 (1H, m)	20.1
7		46.3
8	0.74 (3H, s)	18.0
9	1.22 (2H, m)	31.4
10	0.93 (1H, s)	11.2
11	1.39 (m)	24.5
	1.35 (m)	
12	2.58 (1H, t, J = 6.2 Hz)	66.1
13		61.6
14	1.49 (1H, m)	33.4
	1.40 (1H, m)	
15	2.02 (2H, m)	24.7
16	5.03 (1H, t, *J = 6.6 Hz*)	124.4
17		132.6
18	1.54 (3H, s)	18.2
19	1.61 (3H, s)	26.3
20	1.21 (3H, s)	22.9

Table S4. NMR data of **4** ($CDCl_3$, 700 MHz)

Position	δ_H	δ_C
1		27.9
2	0.79 (1H, m)	20.2
3 a	1.45 (1H, m)	31.5
b	0.98 (1H, d, J = 10.7 Hz)	
4	1.42 (1H, m)	38.7
5 a	1.53 (1H, d, J = 10.2 Hz)	32.1
b	1.01 (1H, d, J = 10.3 Hz)	
6	0.79 (1H, m)	20.0
7		46.0
8	0.74 (3H, s)	17.9
9 a	1.46 (1H, m)	29.0
b	1.36 (1H, m)	
10	0.94 (1H, s)	11.1
11	2.33 (2H, m)	31.9
12		215.6
13		79.3
14	1.66 (2H, m)	40.2
15 a	1.98 (1H, m)	22.9
b	1.68 (1H, m)	
16	4.96 (1H, m)	124.0
17		133.1
18	1.49 (3H, s)	18.2
19	1.58 (3H, s)	26.30
20	1.27 (3H, s)	26.33

Synthetic gene sequence of CYP71D51

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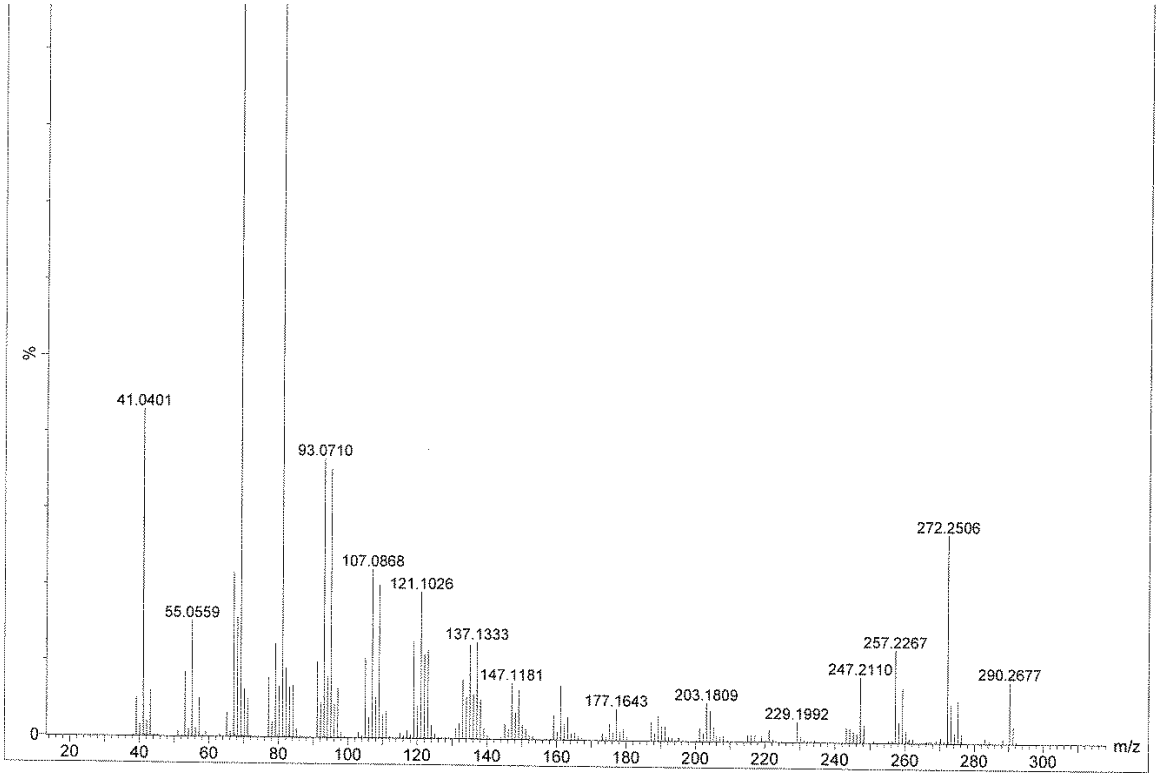
GATTAA

Figure S3. *A*



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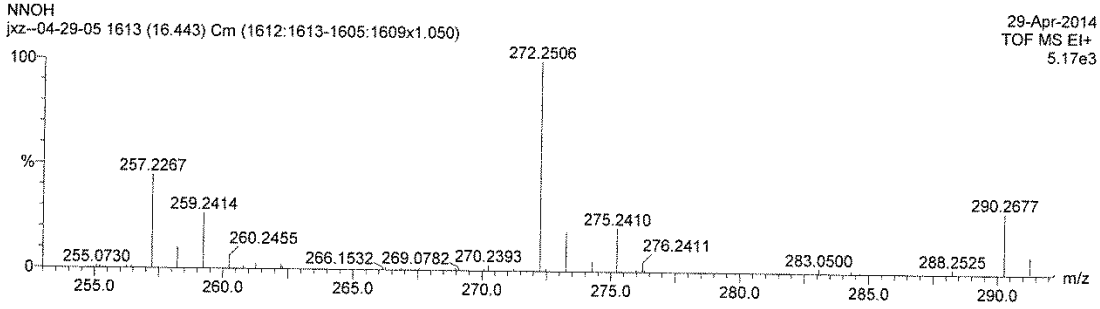
Multiple Mass Analysis: 6 mass(es) processed
Tolerance = 40.0 PPM / DBE: min = 0.0, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
72 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)



Minimum:	10.00				0.0		
Maximum:	100.00		3.0	40.0	50.0		
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259.2414	26.31	259.2426	-1.2	-4.5	4.5	1	C19 H31
272.2506	100.00	272.2504	0.2	0.7	5.0	1	C20 H32
273.2584	18.50	273.2582	0.2	0.6	4.5	1	C20 H33
275.2410	20.56	275.2375	3.5	12.7	4.5	1	C19 H31 O
290.2677	29.19	290.2610	6.7	23.2	4.0	1	C20 H34 O

Figure S4. ^{1}H NMR spectrum of NNOH.

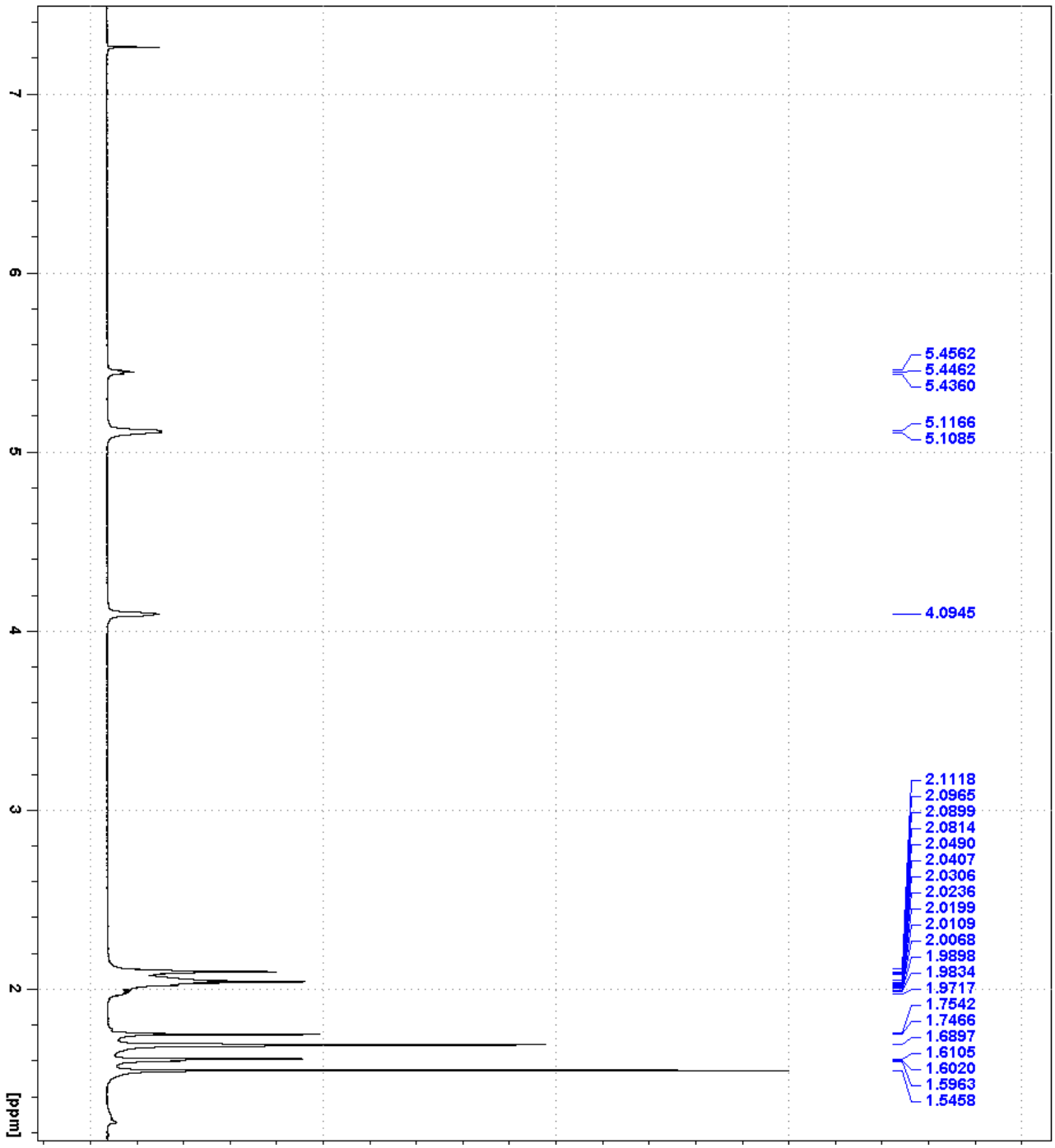


Figure S5. ^{13}C NMR spectrum of NNOH.

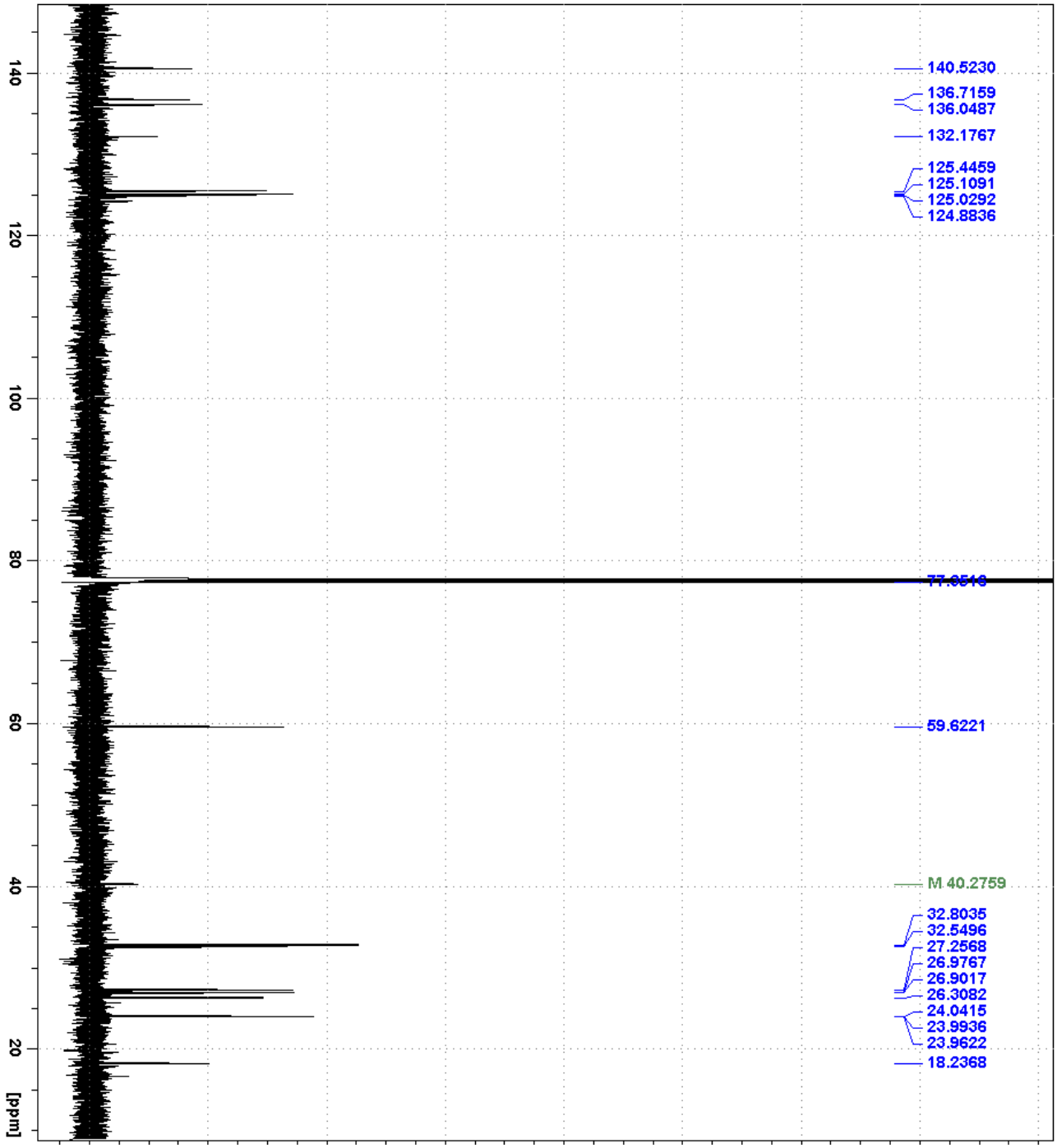


Figure S6. HSQC spectrum of NNOH.

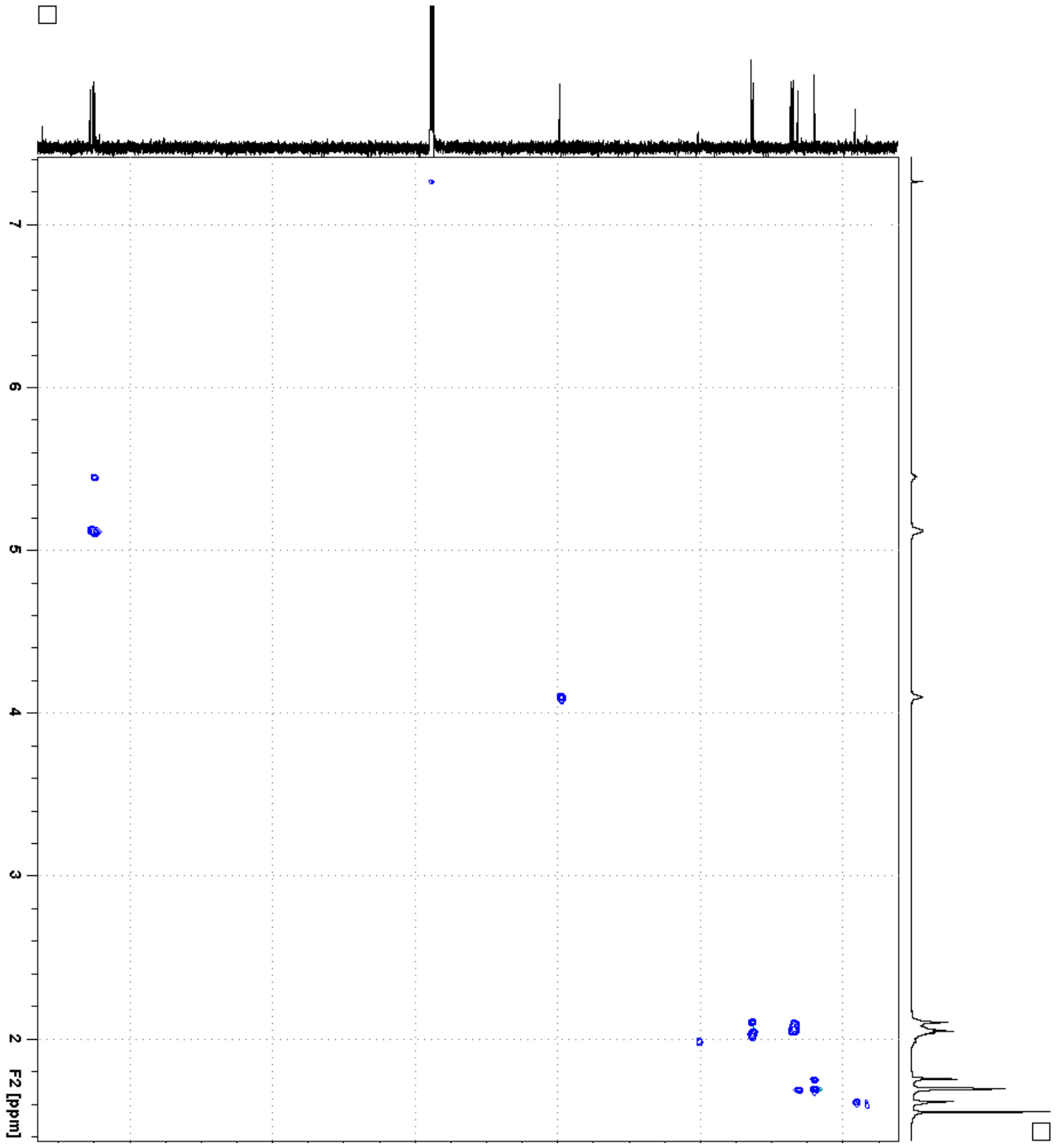


Figure S7. HMBC of NNOH.

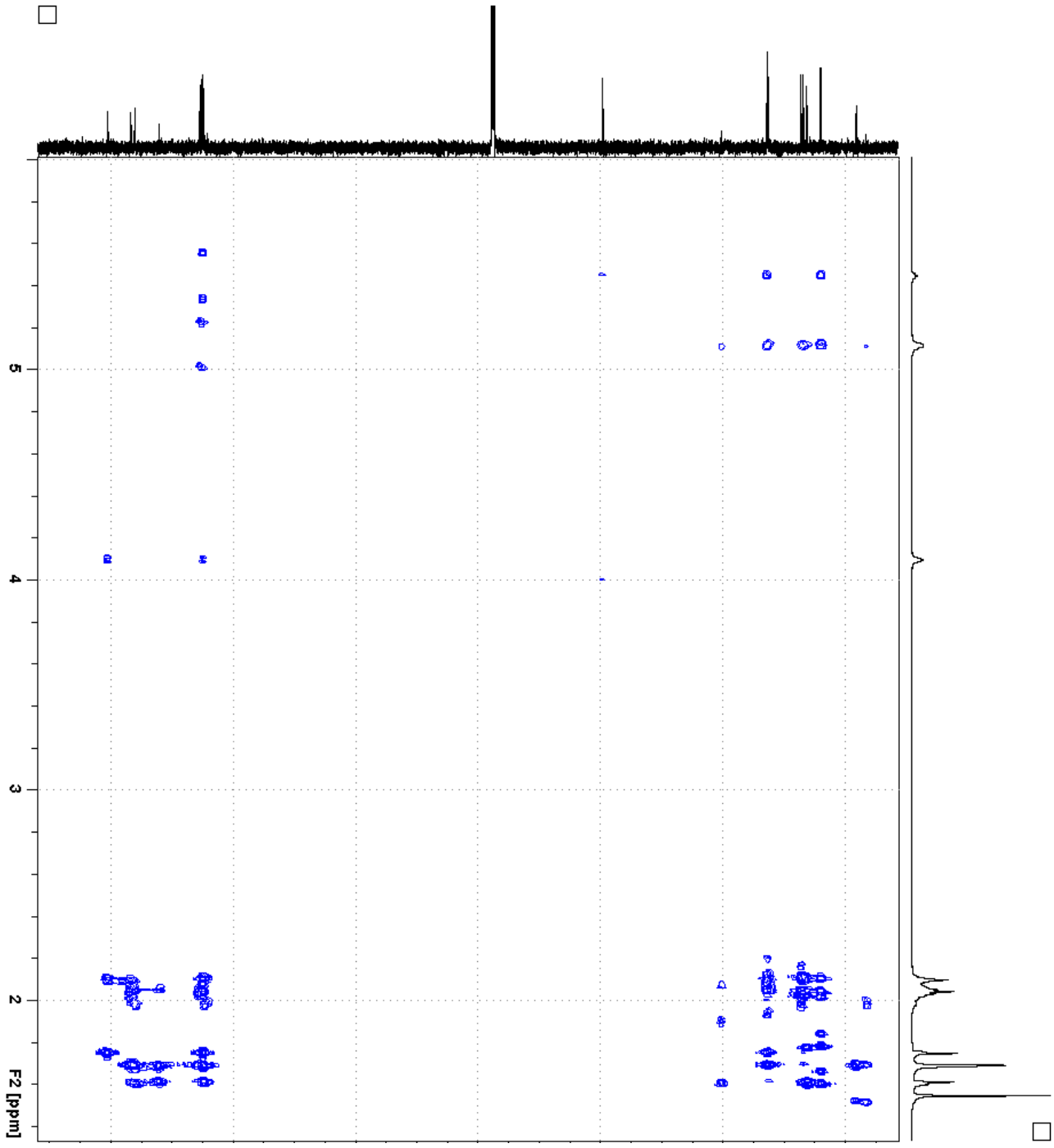


Figure S8. NOESY spectrum of NNOH.

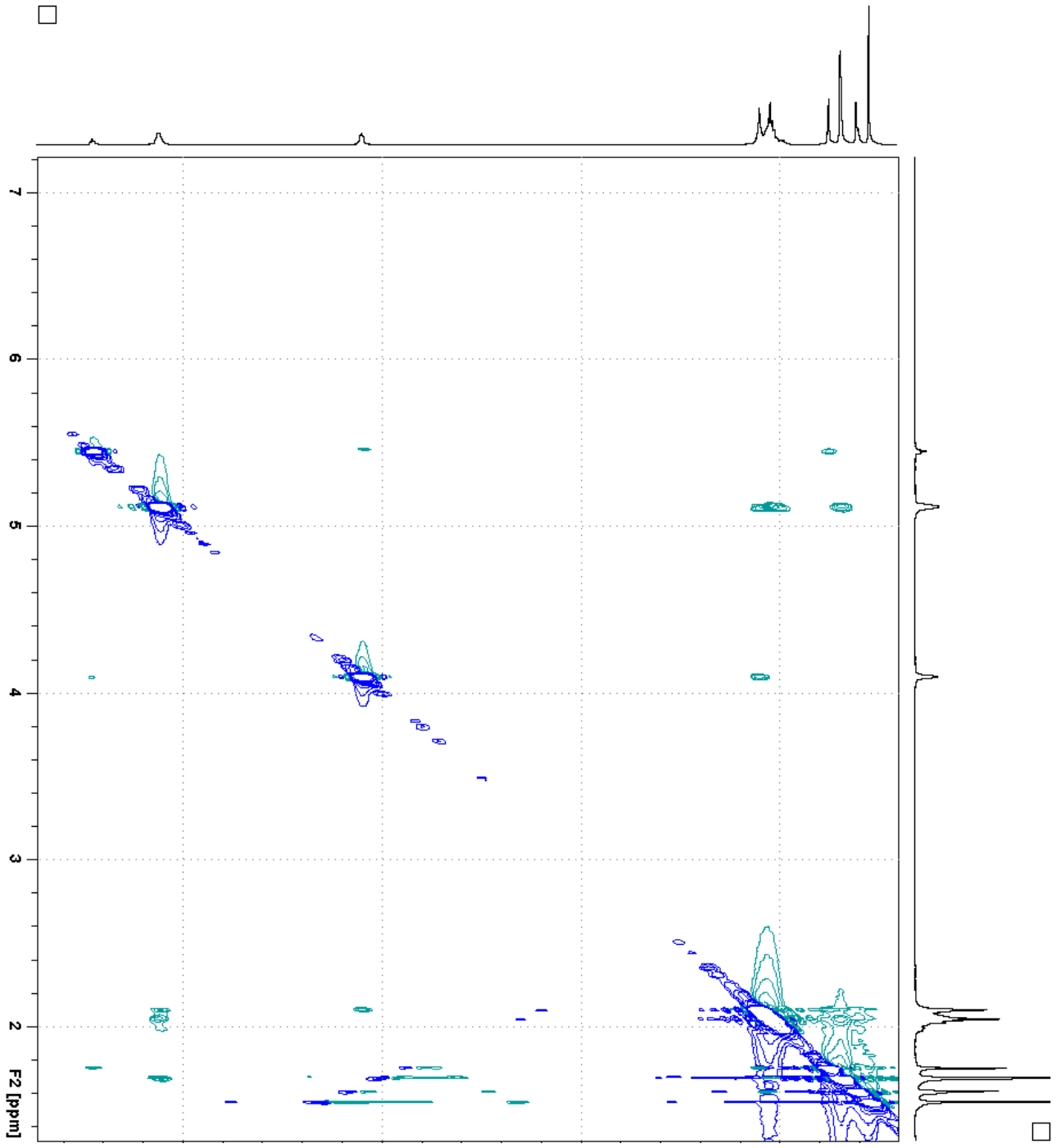


Figure S9. ^{1}H NMR spectrum of GGOH.

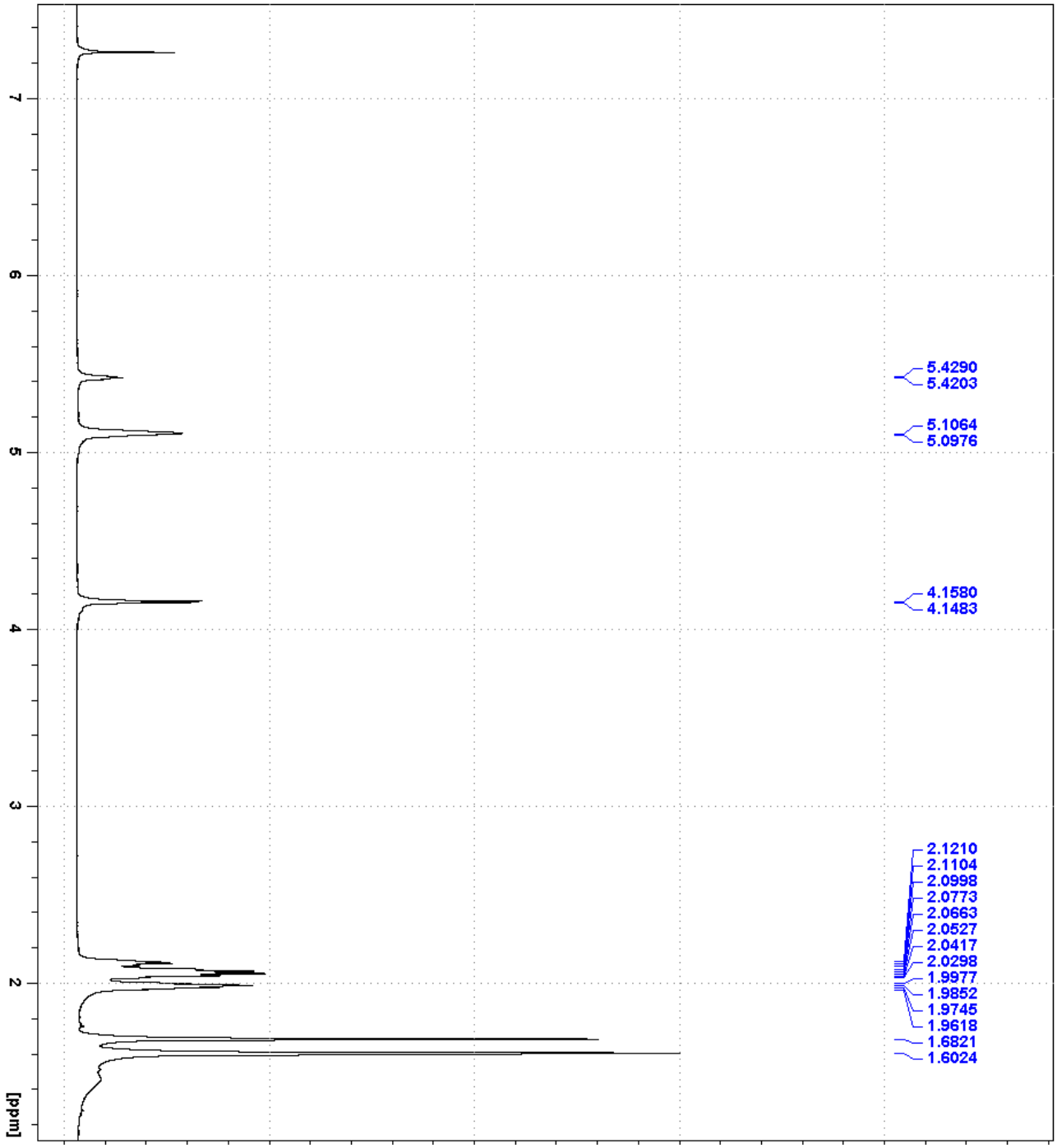


Figure S10. ^{13}C NMR spectrum of GGOH.

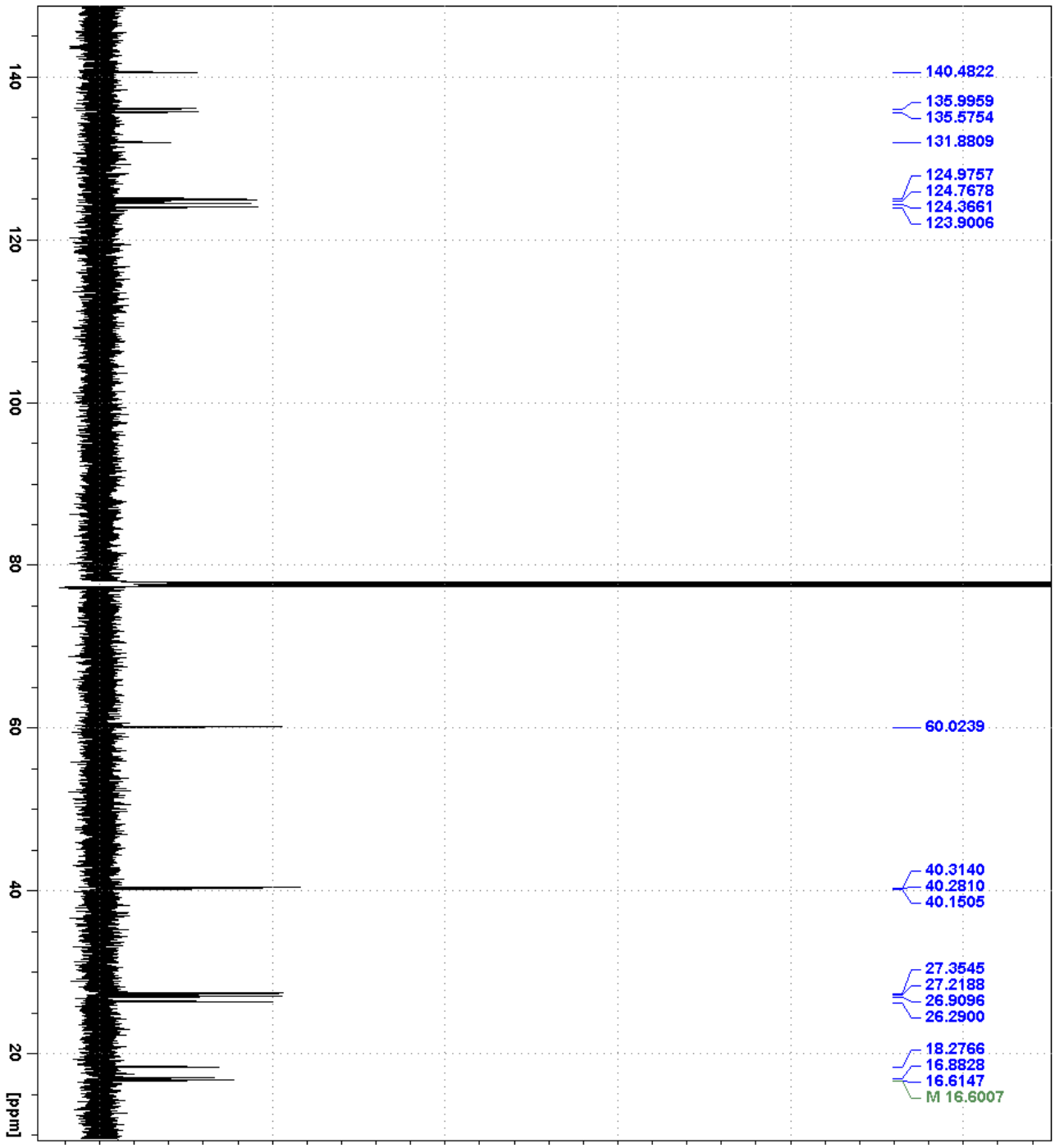


Figure S11. NOESY spectrum of GGOH.

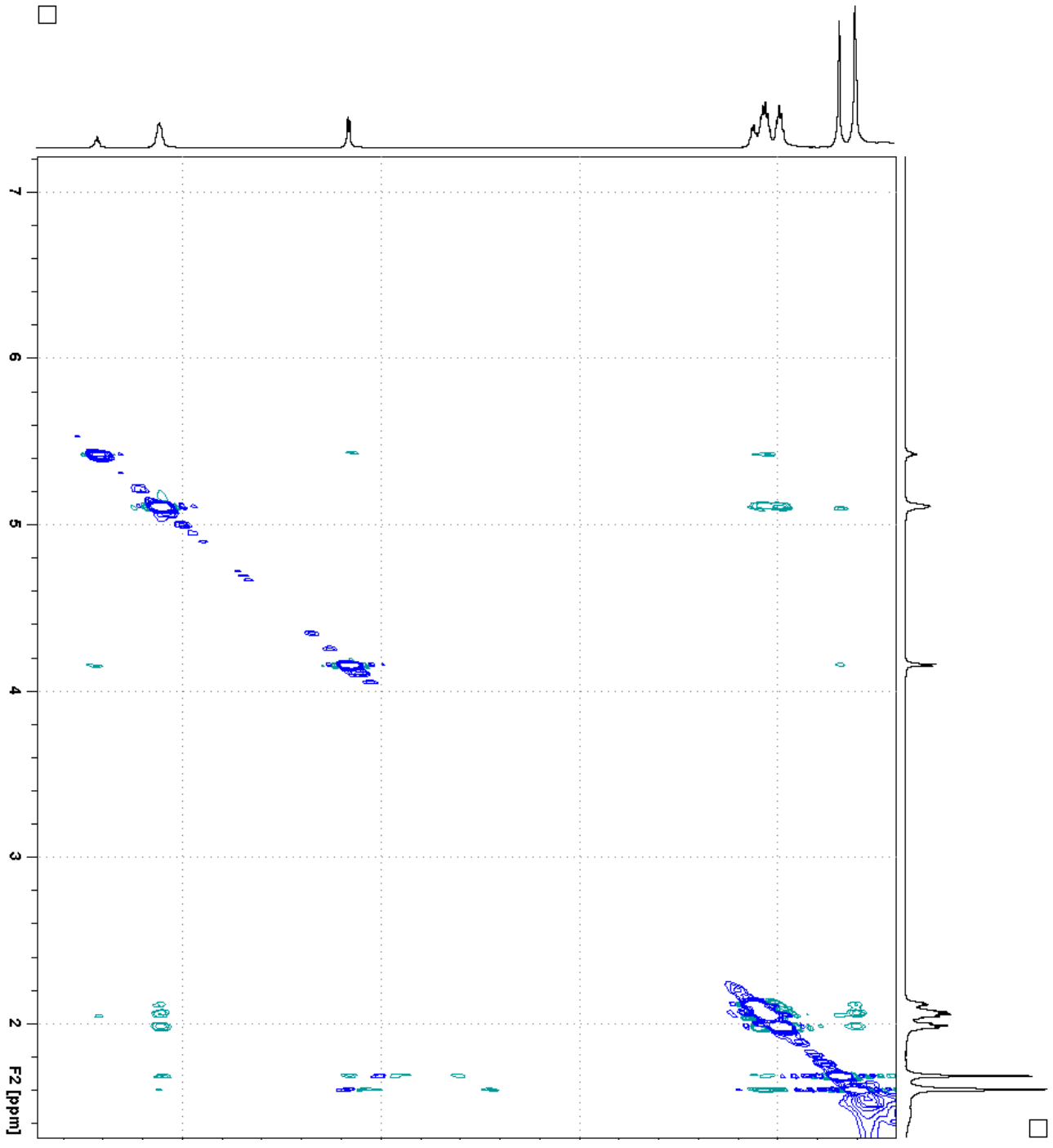
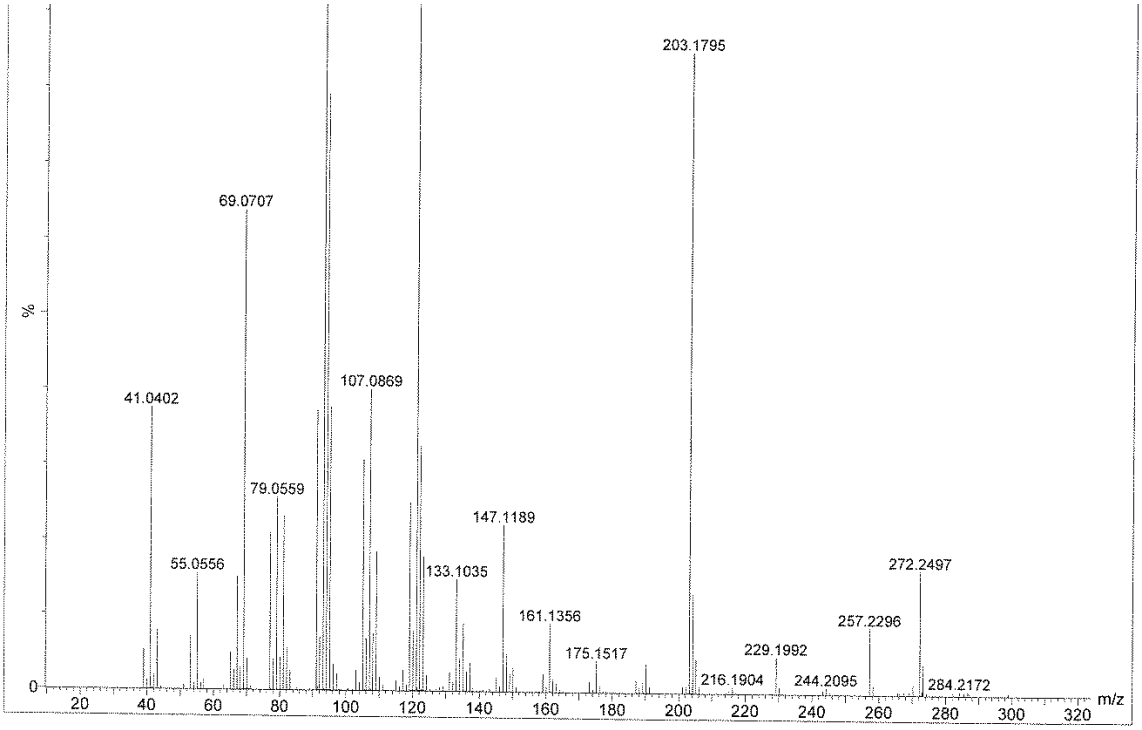
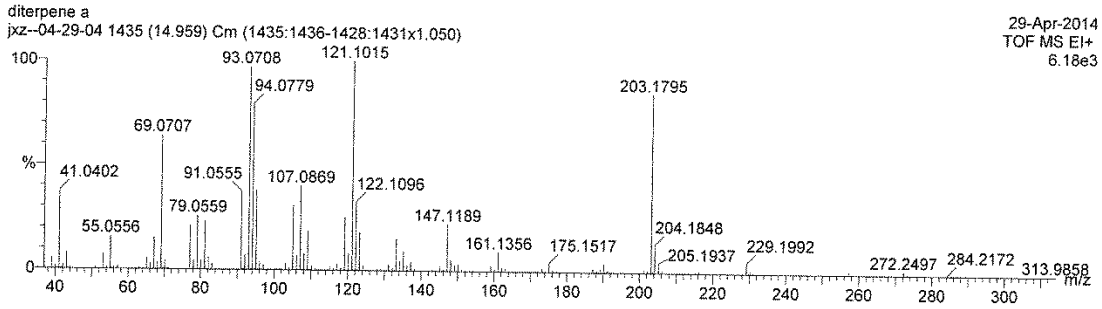


Figure S12. Accurate EIMS of lycosantalene (**2**).



Single Mass Analysis
Tolerance = 40.0 PPM / DBE: min = 0.0, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
12 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)



Minimum:				0.0		
Maximum:		3.0	40.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
272.2497	272.2504	-0.7	-2.6	5.0	1	C20 H32

Figure S13. ^{1}H NMR spectrum of **2**.

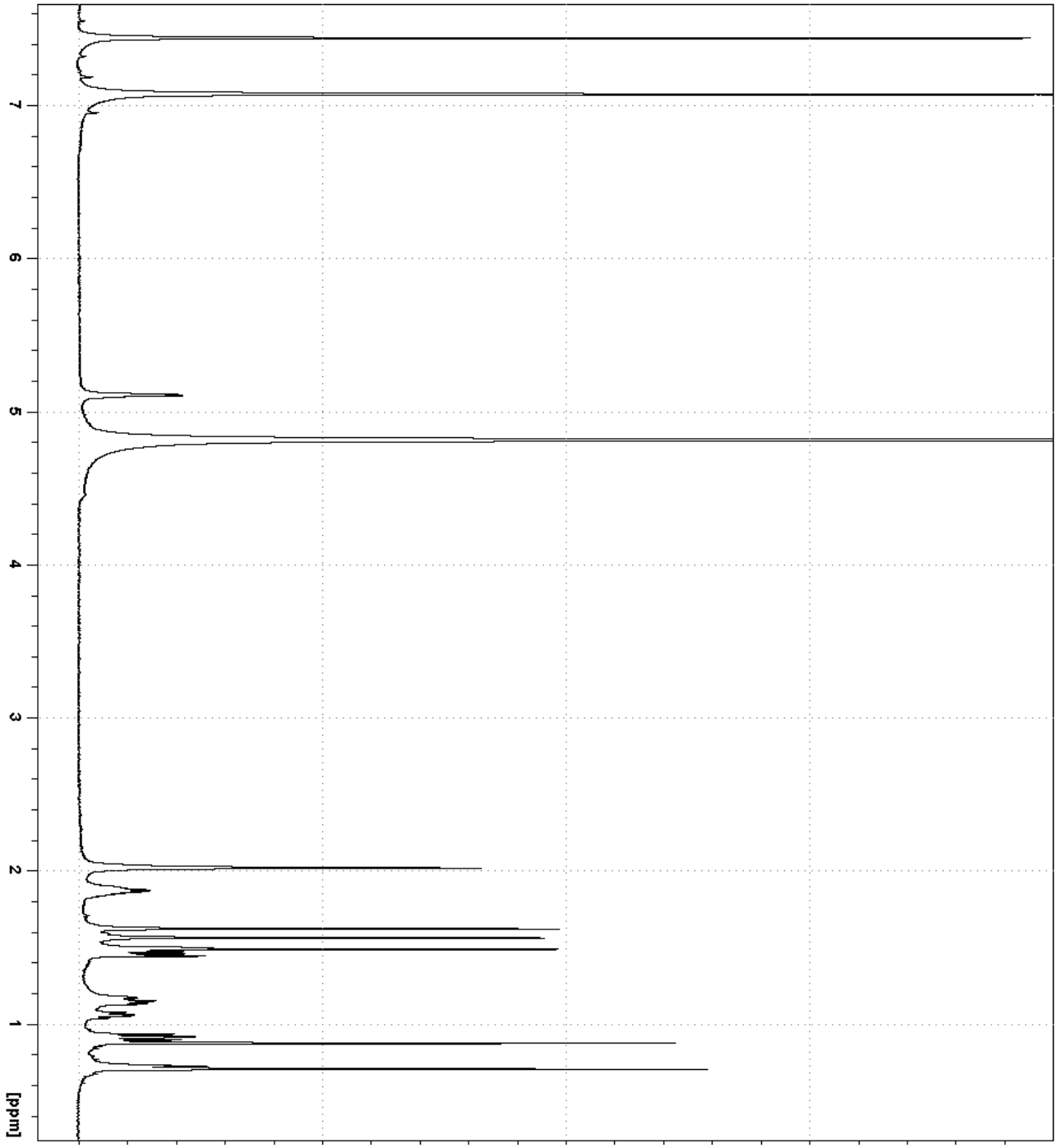


Figure S14. ^{13}C NMR spectrum of **2**.

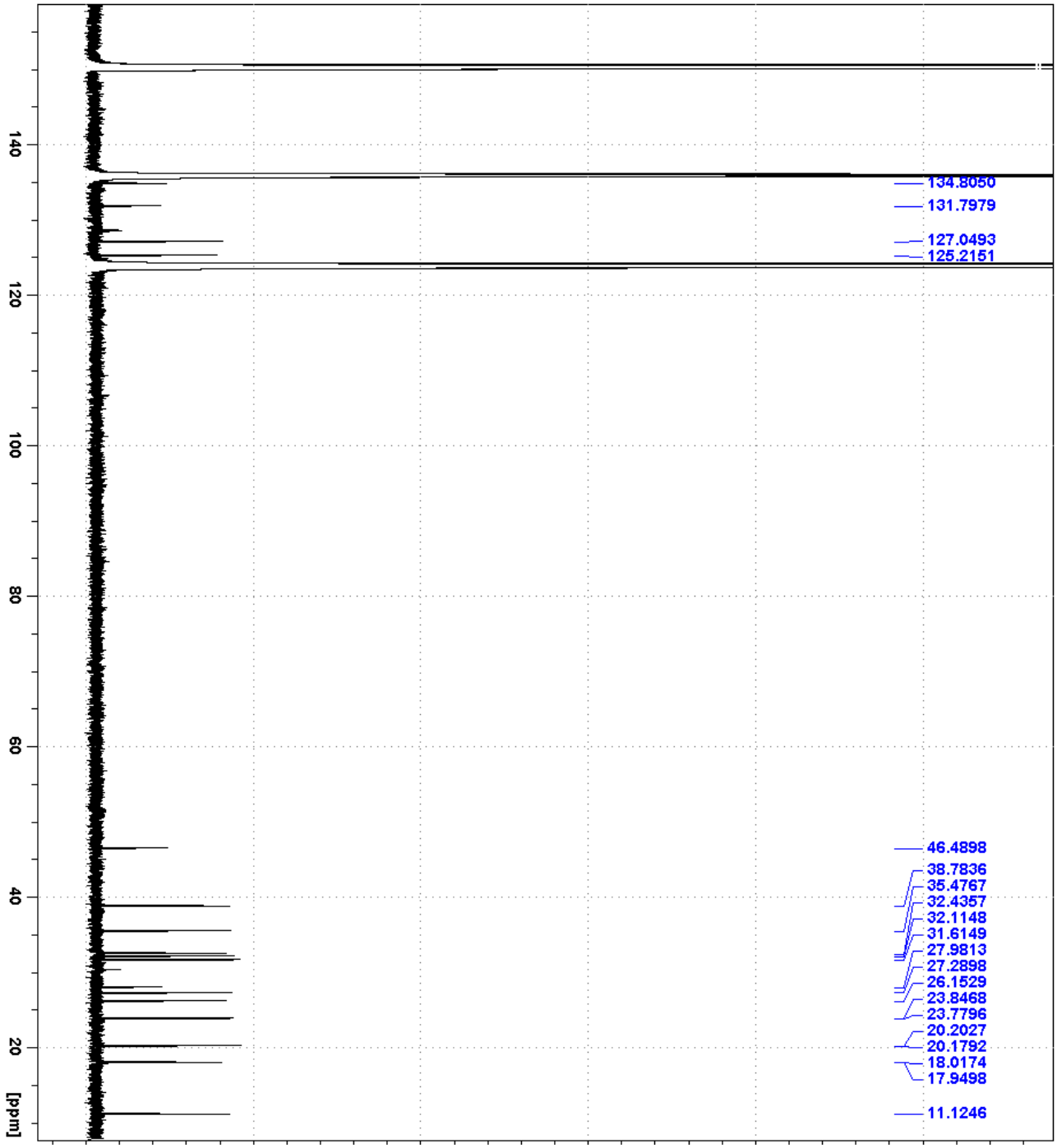


Figure S15. ^{1}H-^{1}H COSY spectrum of **2**.

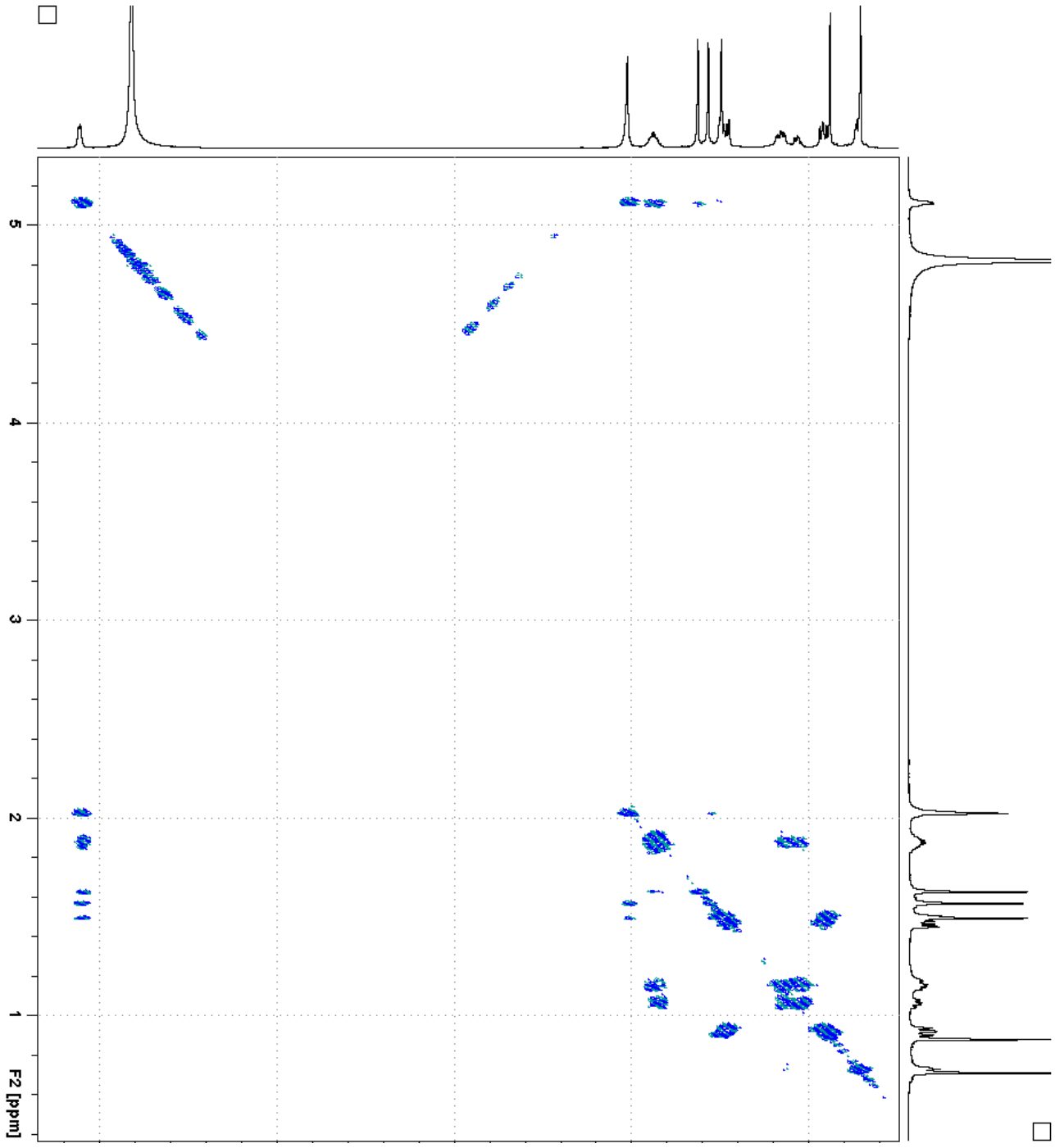


Figure S16. HSQC spectrum of **2**.

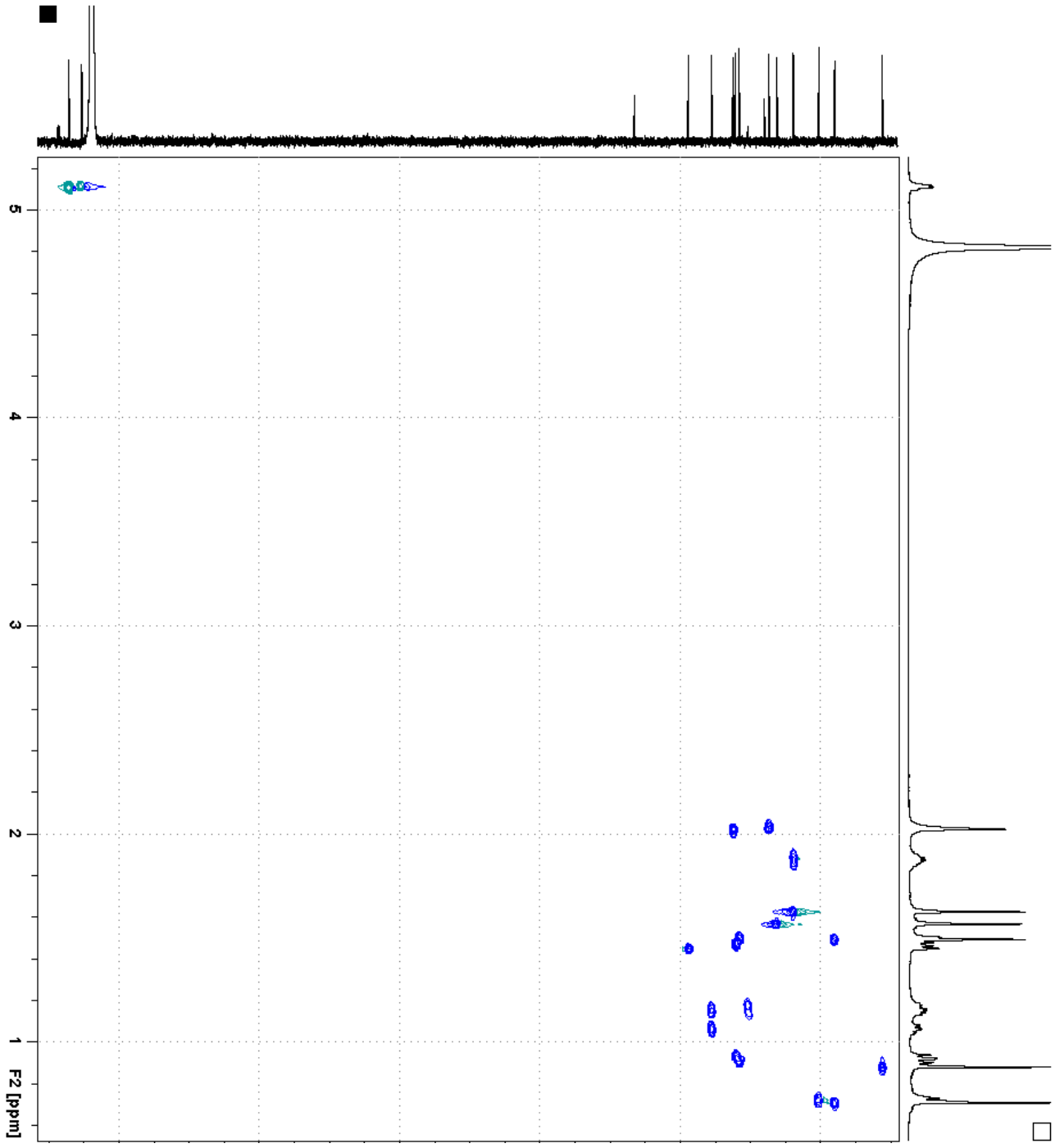


Figure S17. HMBC spectrum of **2**.

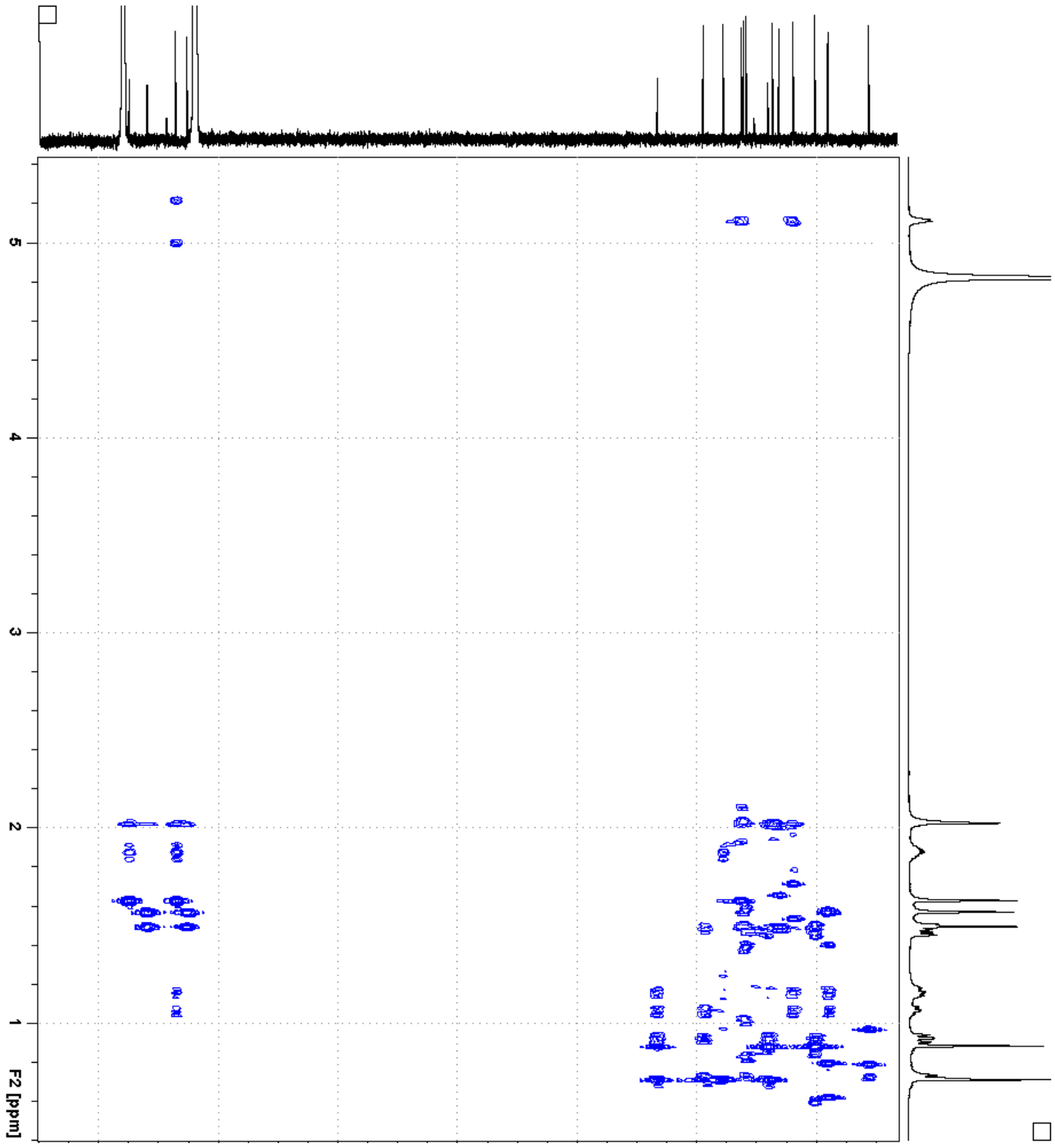
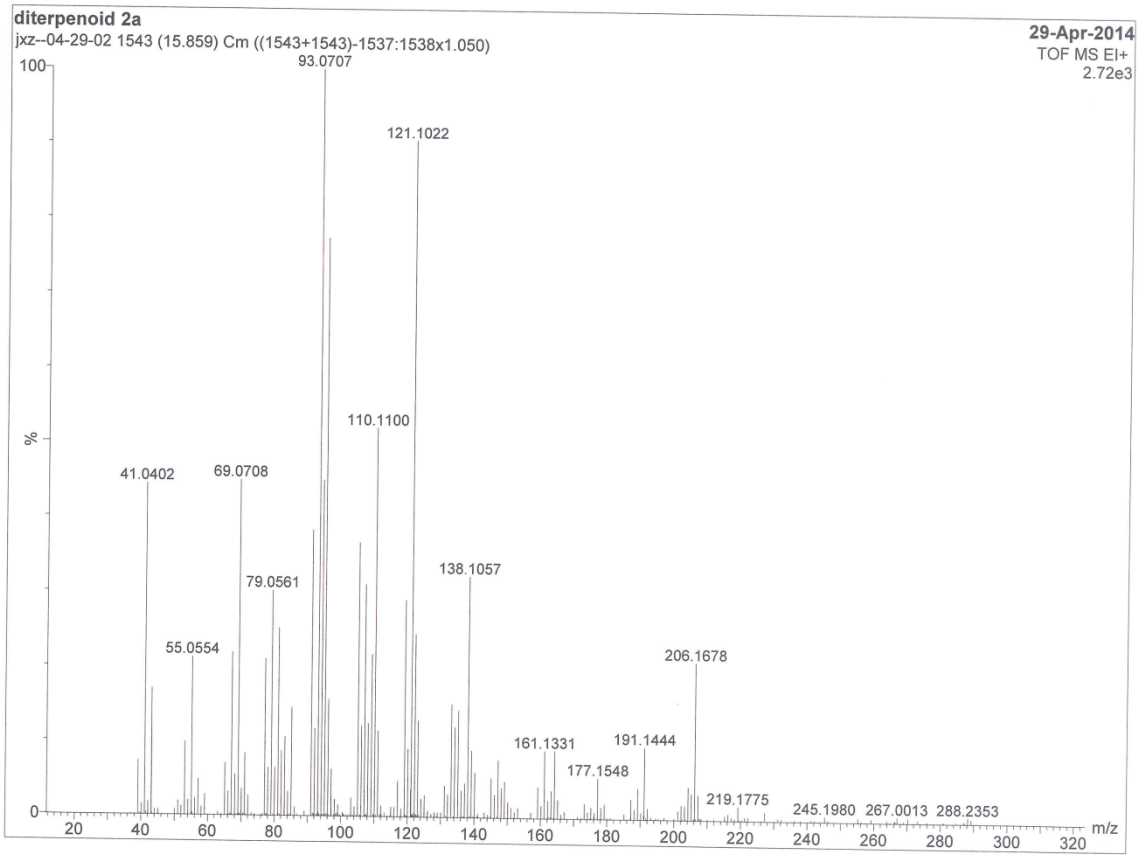
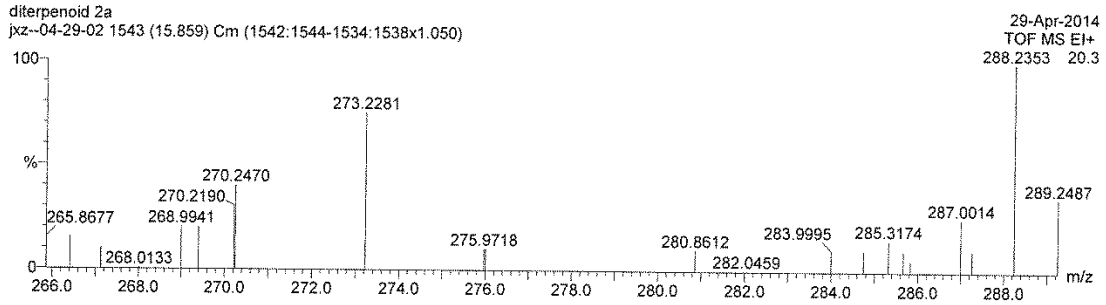


Figure S18 Accurate EIMS of **3**.





Minimum:				0.0		
Maximum:		3.0	100.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
288.2353	288.2453	-10.0	-34.7	5.0	1	C20 H32 O

Figure S19. ^{1}H NMR spectrum of **3**.

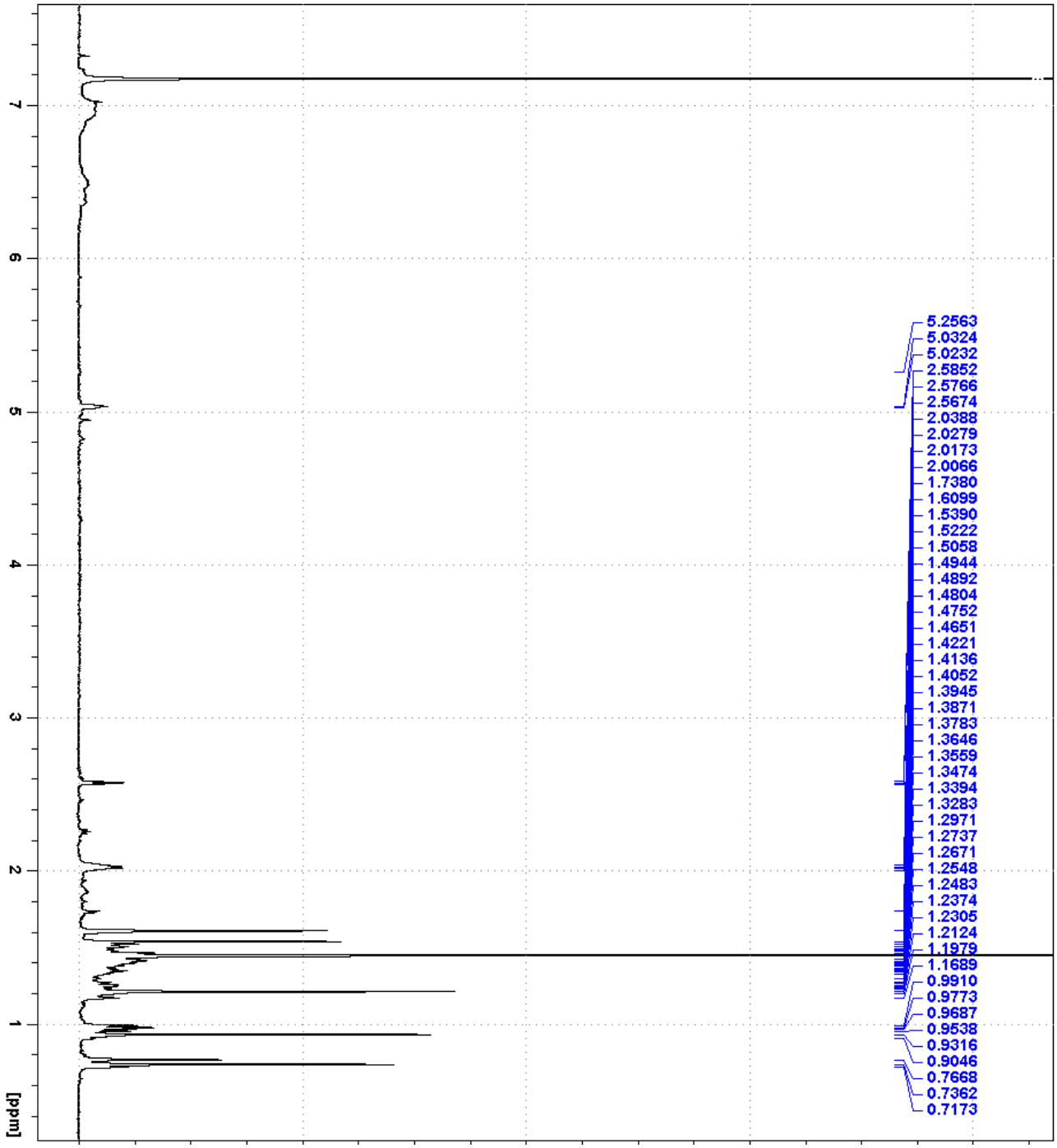


Figure S20. ^{13}C NMR spectrum of **3**.

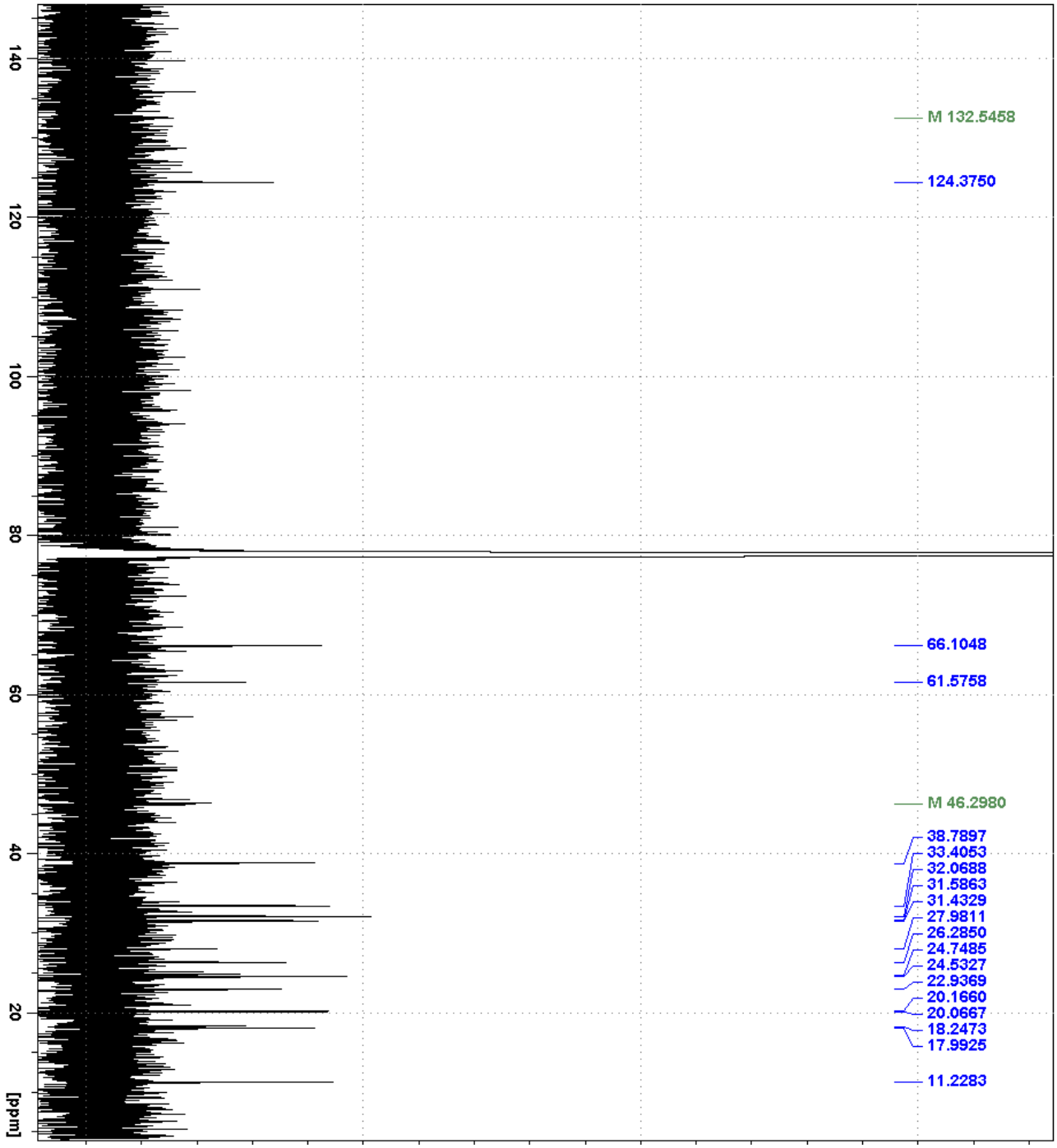


Figure S21. ^{1}H-^{1}H COSY spectrum of **3**.

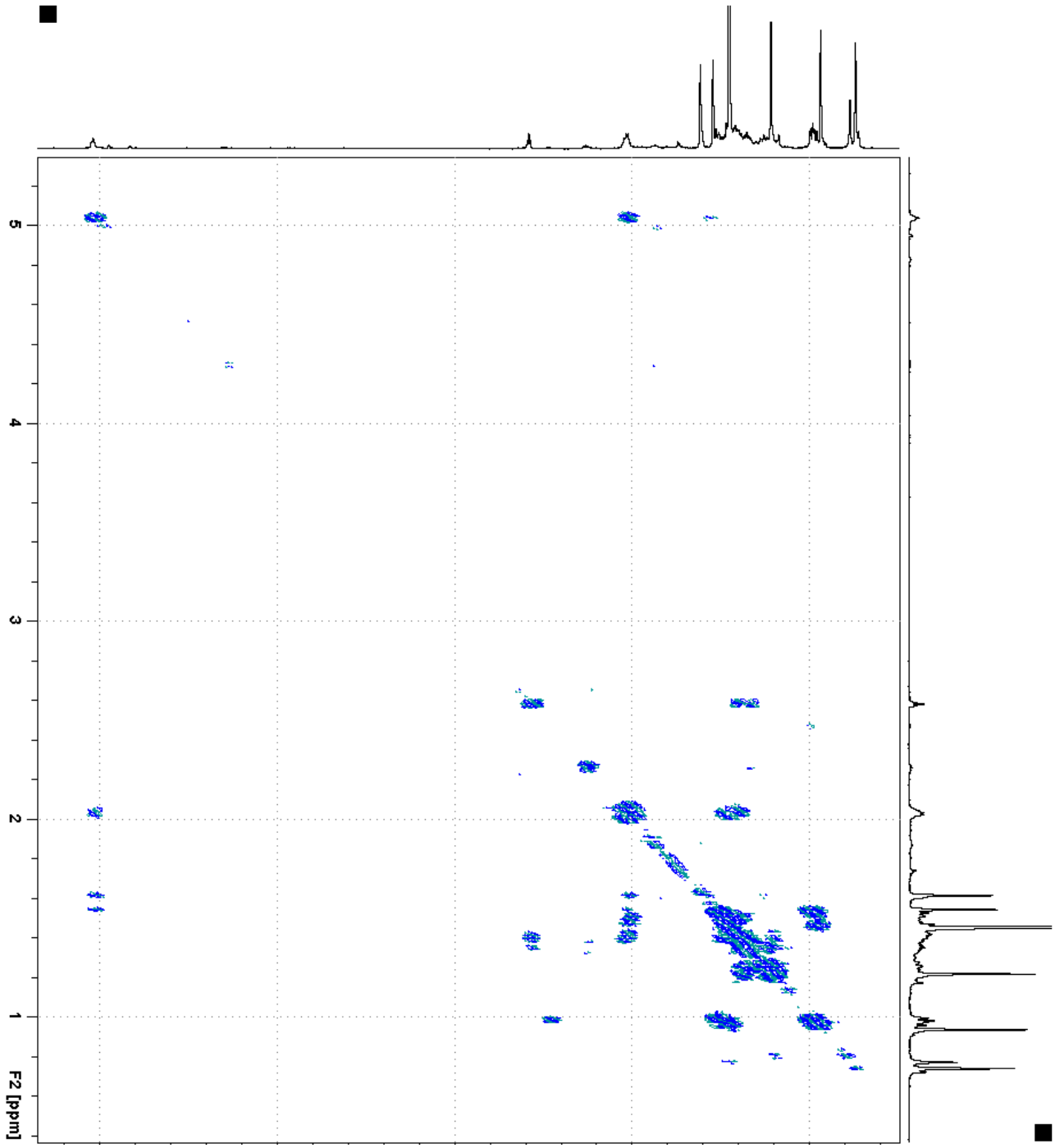


Figure S22. HSQC spectrum of **3**.

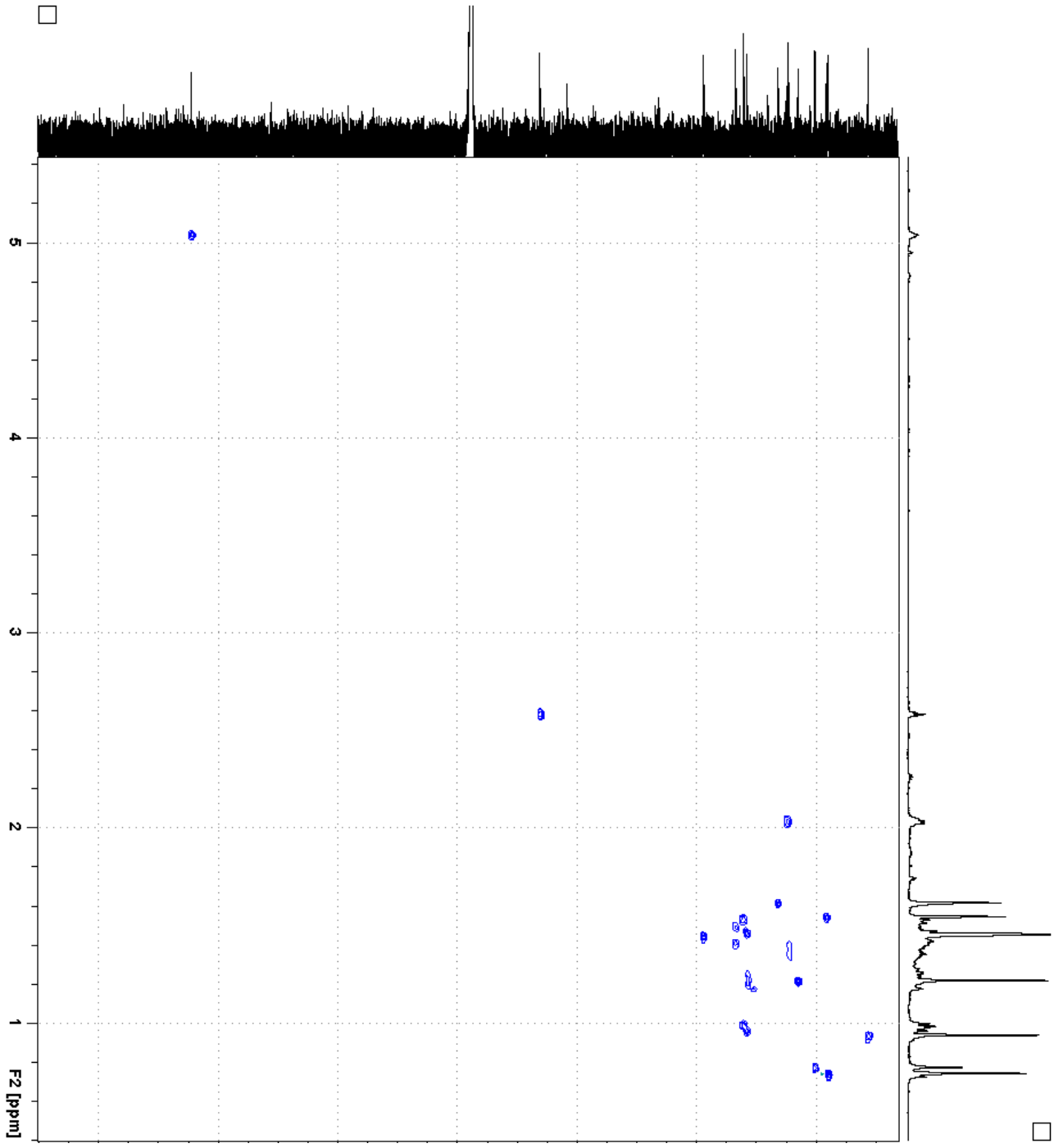


Figure S23. HMBC spectrum of **3**.

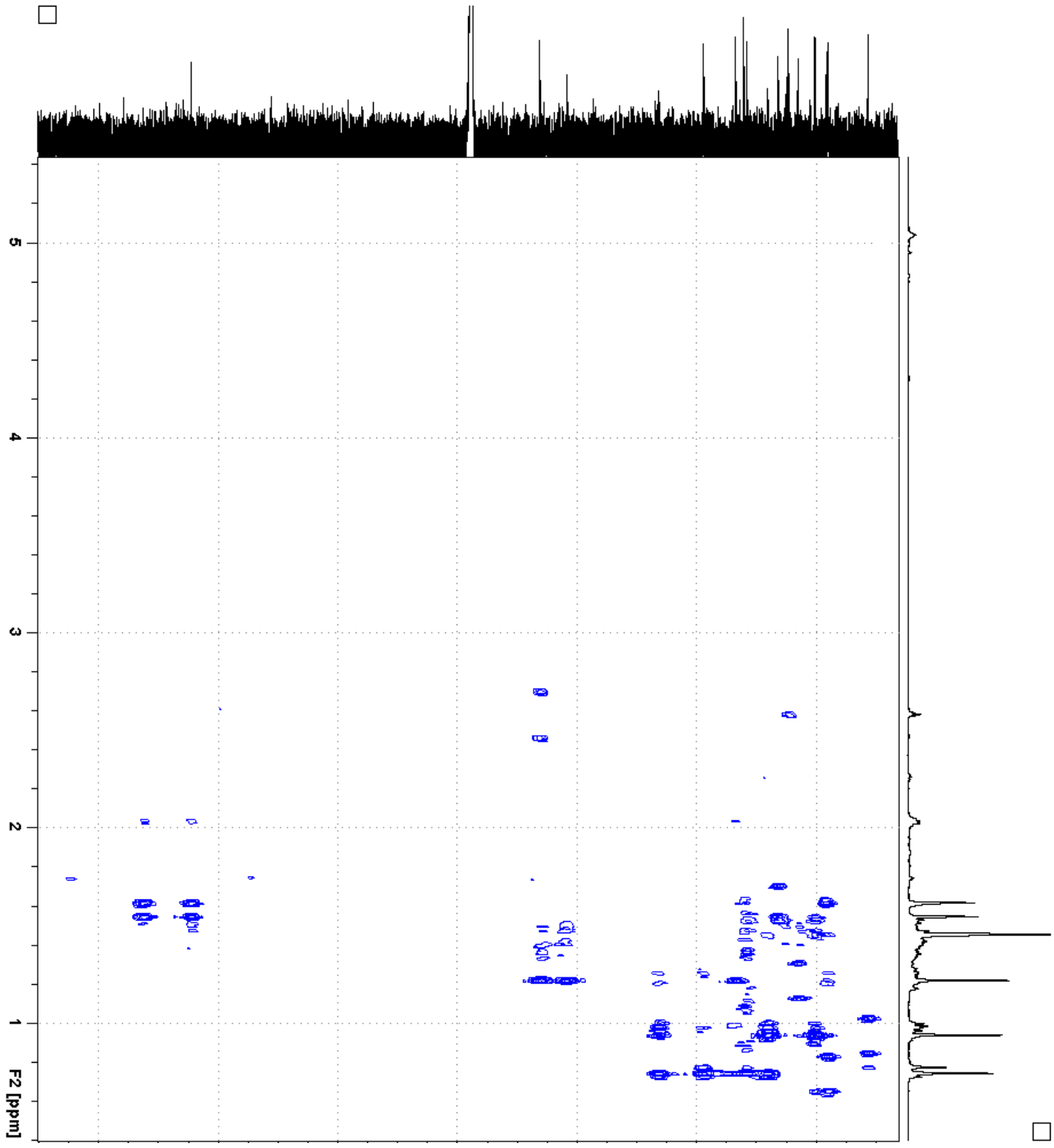
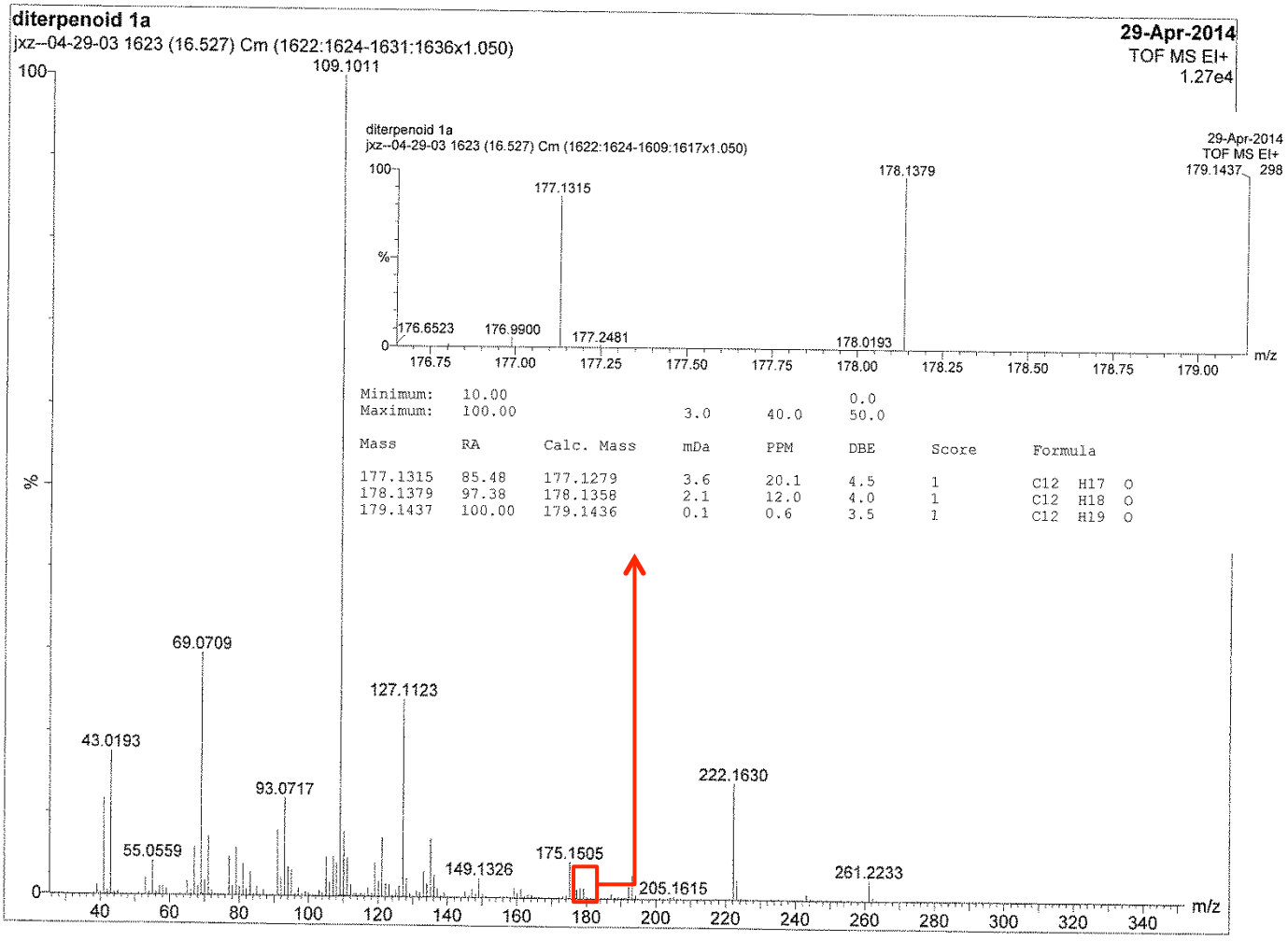
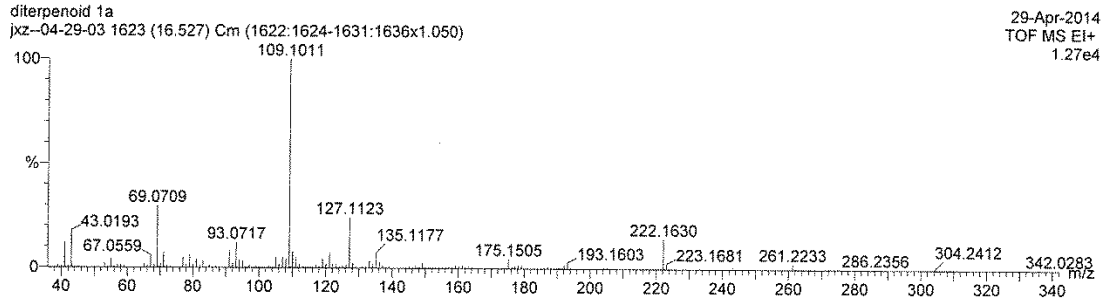


Figure S24 Accurate EIMS of **4**.



Minimum:	10.00			0.0	
Maximum:	100.00	3.0	40.0	50.0	

Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
177.1315	85.48	177.1279	3.6	20.1	4.5	1	C12 H17 O
178.1379	97.38	178.1358	2.1	12.0	4.0	1	C12 H18 O
179.1437	100.00	179.1436	0.1	0.6	3.5	1	C12 H19 O



Minimum:	10.00			0.0	
Maximum:	100.00	3.0	20.0	50.0	

Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
41.0405	11.67	---					
43.0193	17.55	---					
69.0709	29.54	69.0704	0.5	6.9	1.5	1	C5 H9
93.0717	11.95	93.0704	1.3	13.7	3.5	1	C7 H9
109.1011	100.00	109.1017	-0.6	-5.7	2.5	1	C8 H13
127.1123	24.14	127.1123	0.0	0.1	1.5	1	C8 H15 O
222.1630	14.24	222.1620	1.0	4.6	4.0	1	C14 H22 O2

Figure S25. ^{1}H NMR spectrum of **4**.

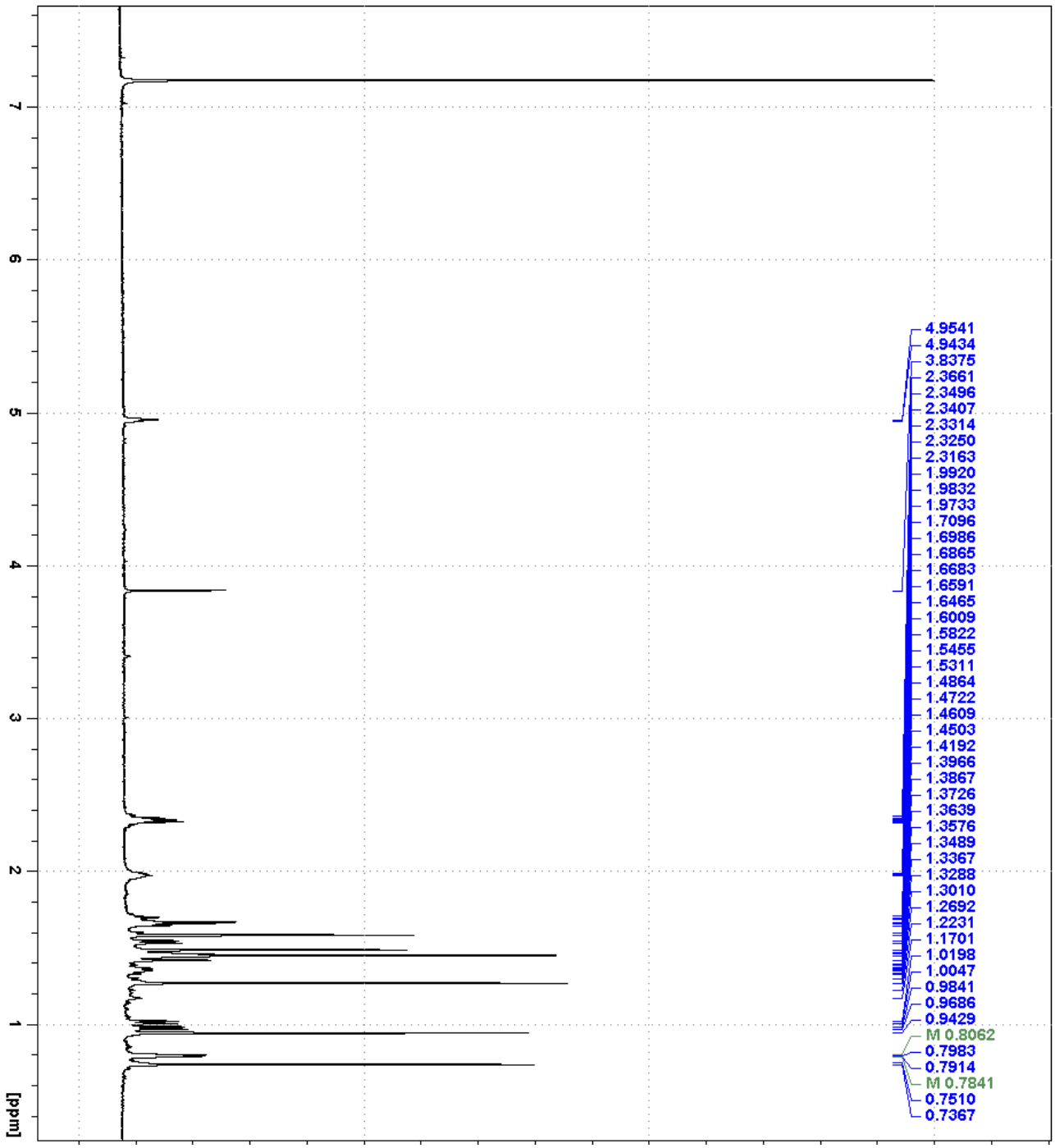


Figure S26. ^{13}C NMR spectrum of **4**.

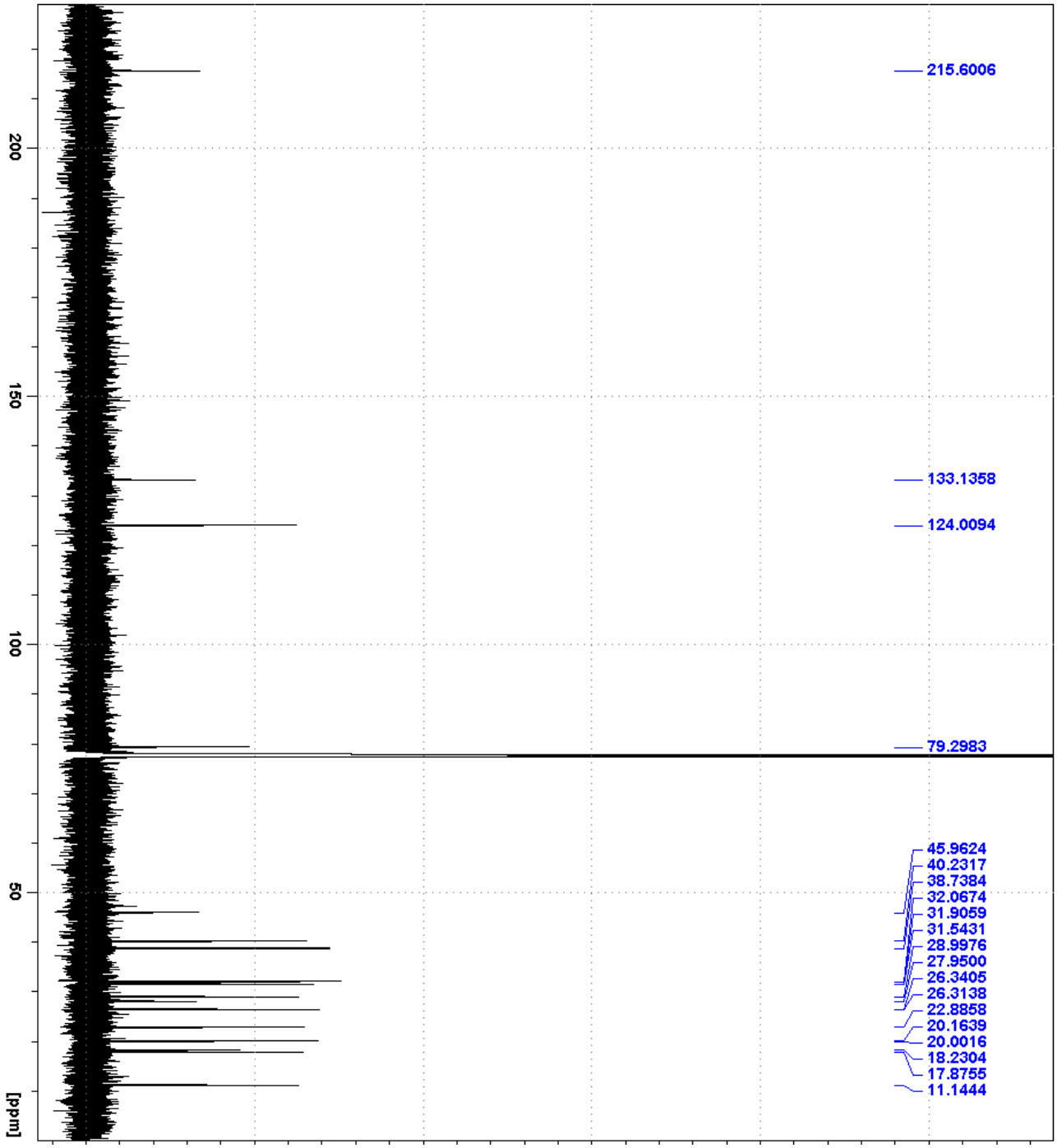


Figure S27. ^{1}H-^{1}H COSY spectrum of **4**.

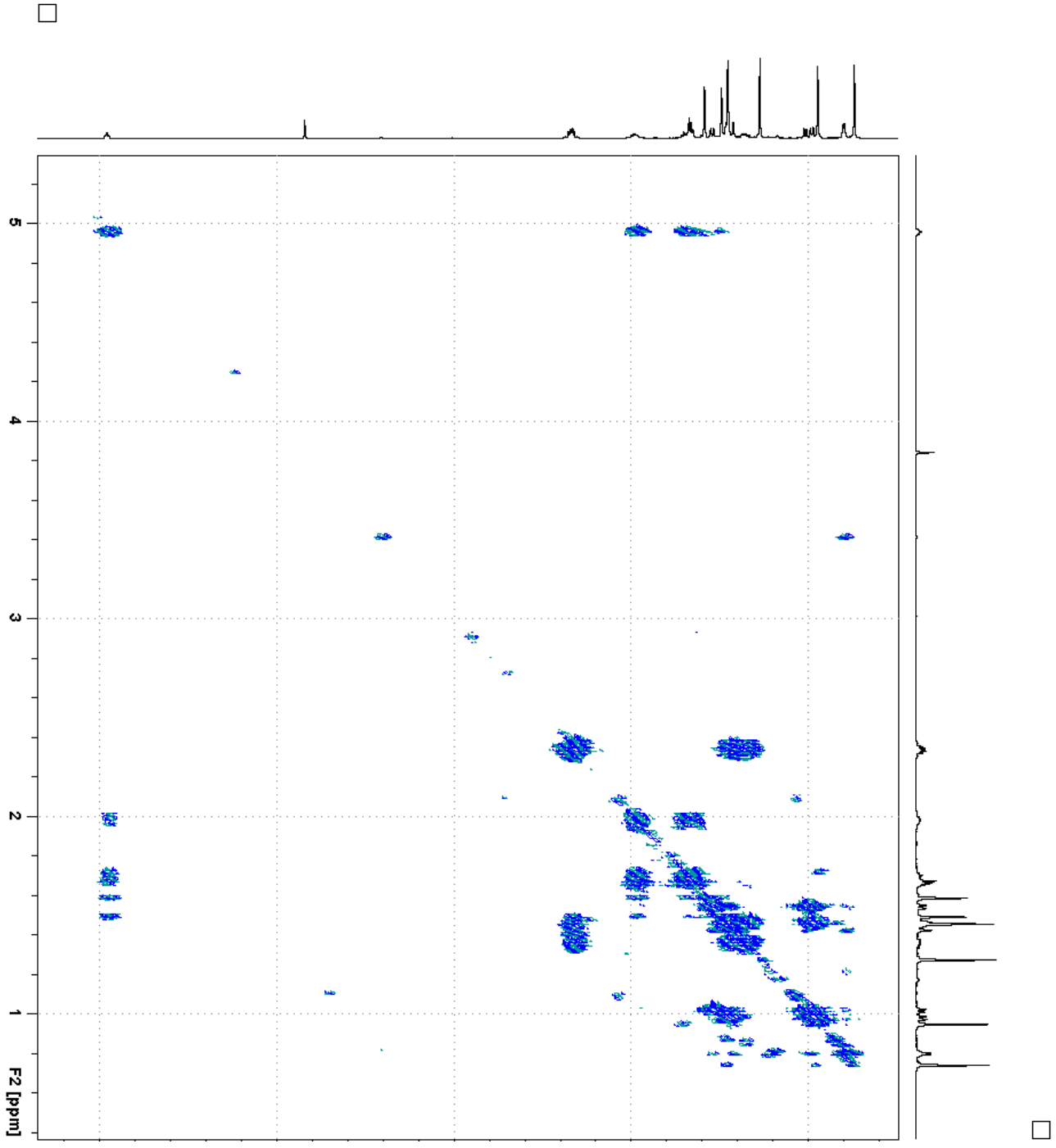


Figure S28. HSQC spectrum of **4**.

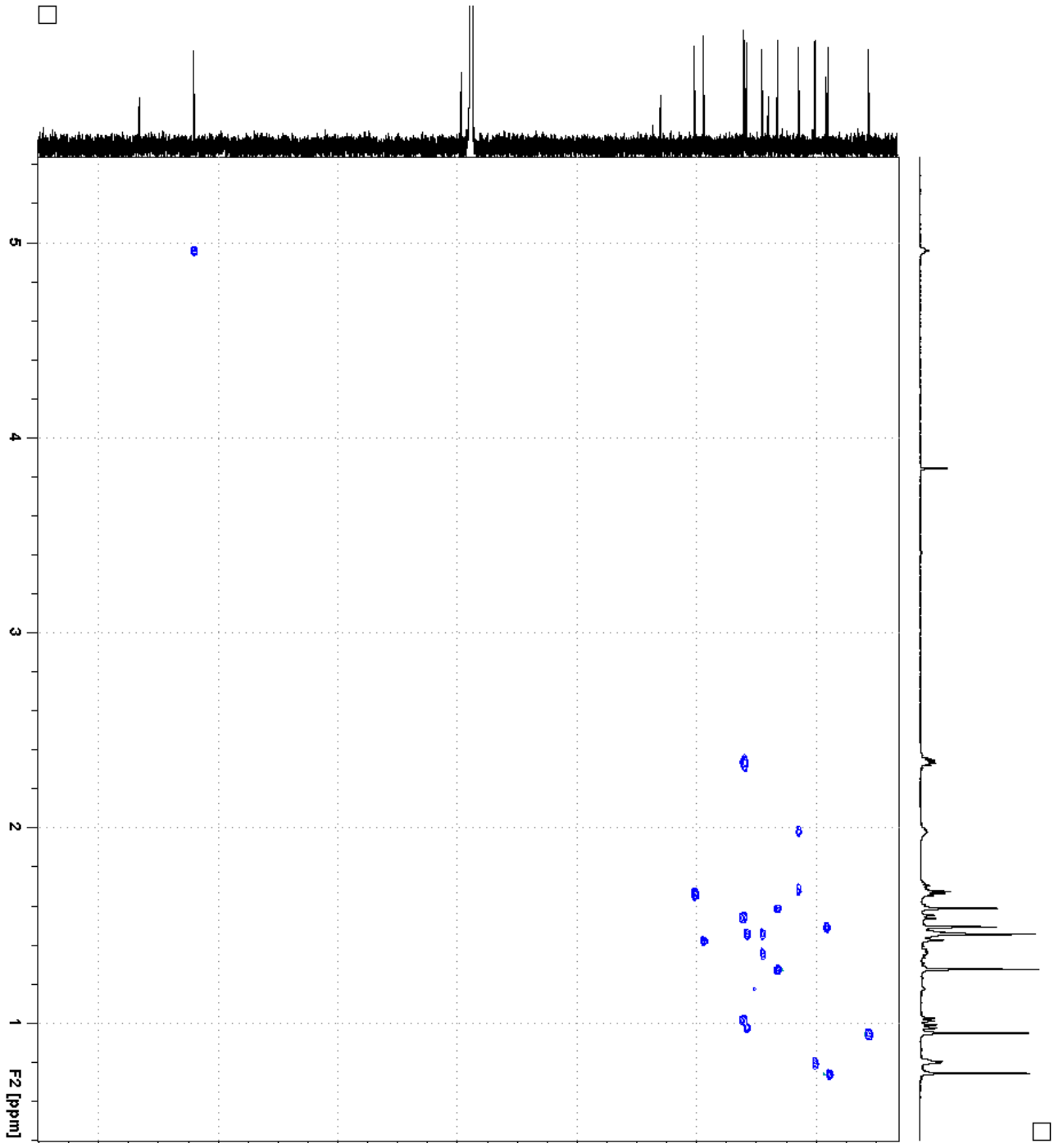


Figure S29. HMBC spectrum of **4**.

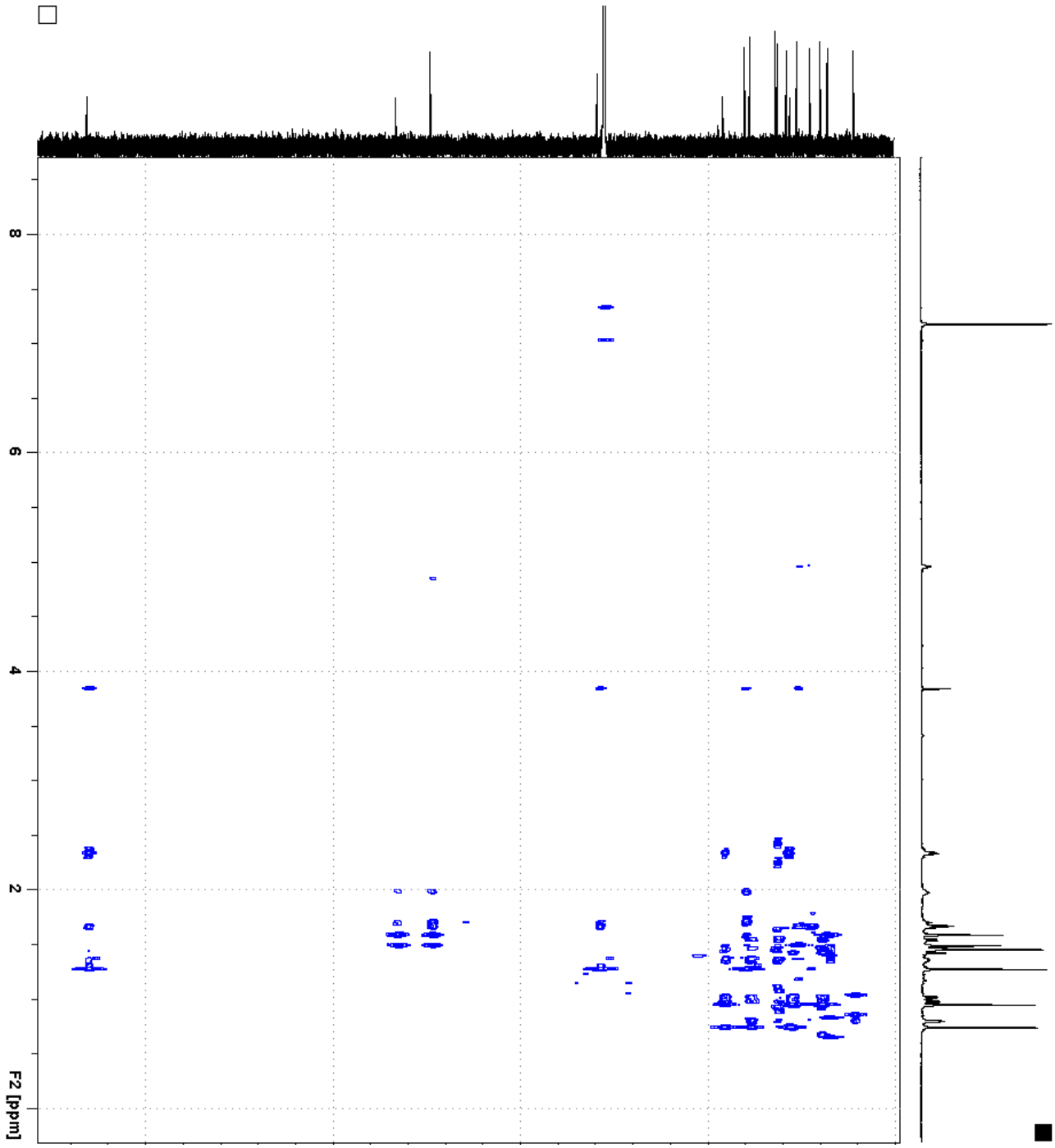


Figure S30. GC-MS chromatogram (extracted ions, *m/z* = 138 + 203 + 222) demonstrating the production of lycosantalonol (**4**), along with **3** from lycosantalene (**2**), in *E. coli* engineered to express SlCPT2, SlTPS21 and CYP71D51 (along with a plant CYP reductase). Mass spectra for NNOH and **2** - **4** can be found in Figures S3, S12, S18 & S24, respectively.

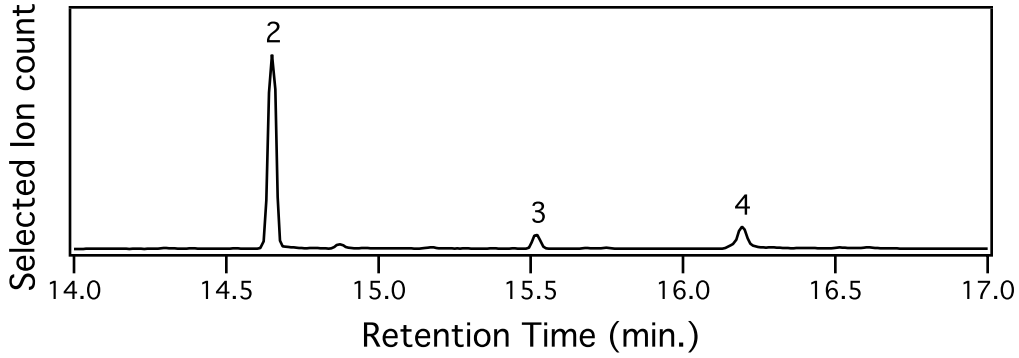


Figure S31. GC-MS chromatograms of in vitro assays of CYP71D51 with either A) purified **2** or B) **3**.

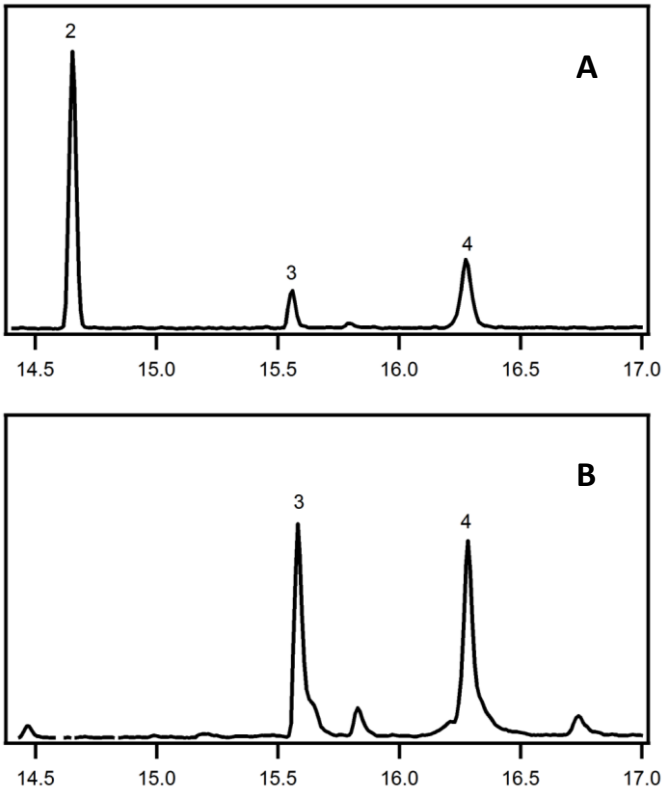


Figure S32. EIMS fragmentation of **4**. Accurate mass measurements for each fragment (A, B, C or D) can be found in Figure S24.

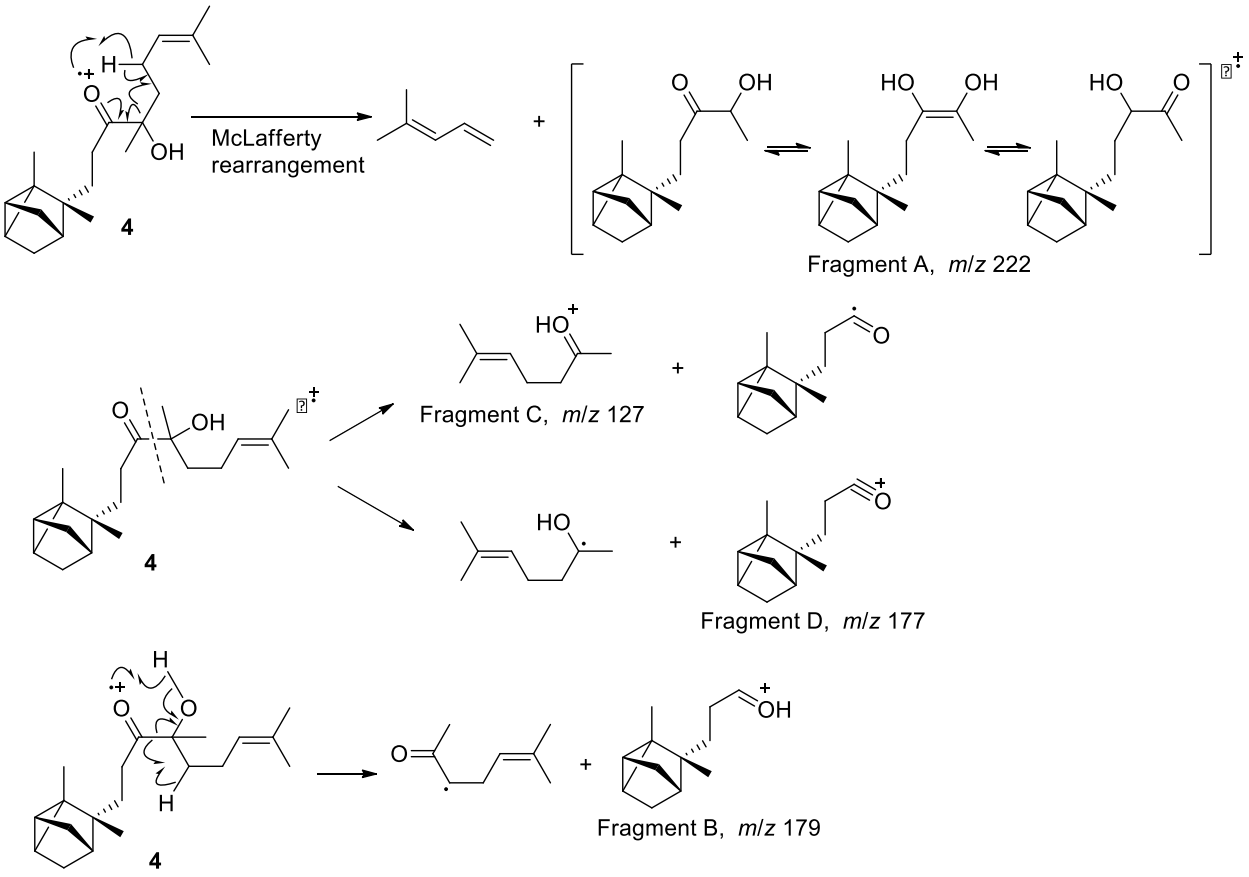


Figure S33. Comparison of the MS spectrum profiles of non-labeled, mono-^{18}O labeled and di-^{18}O labeled **4**. A) The MS spectrum of non-labeled **4**; and the MS spectra of 4 obtained from in vitro reaction of CYP71D51 with either B) **3** or C) **2**, respectively, under $^{18}O_2$.

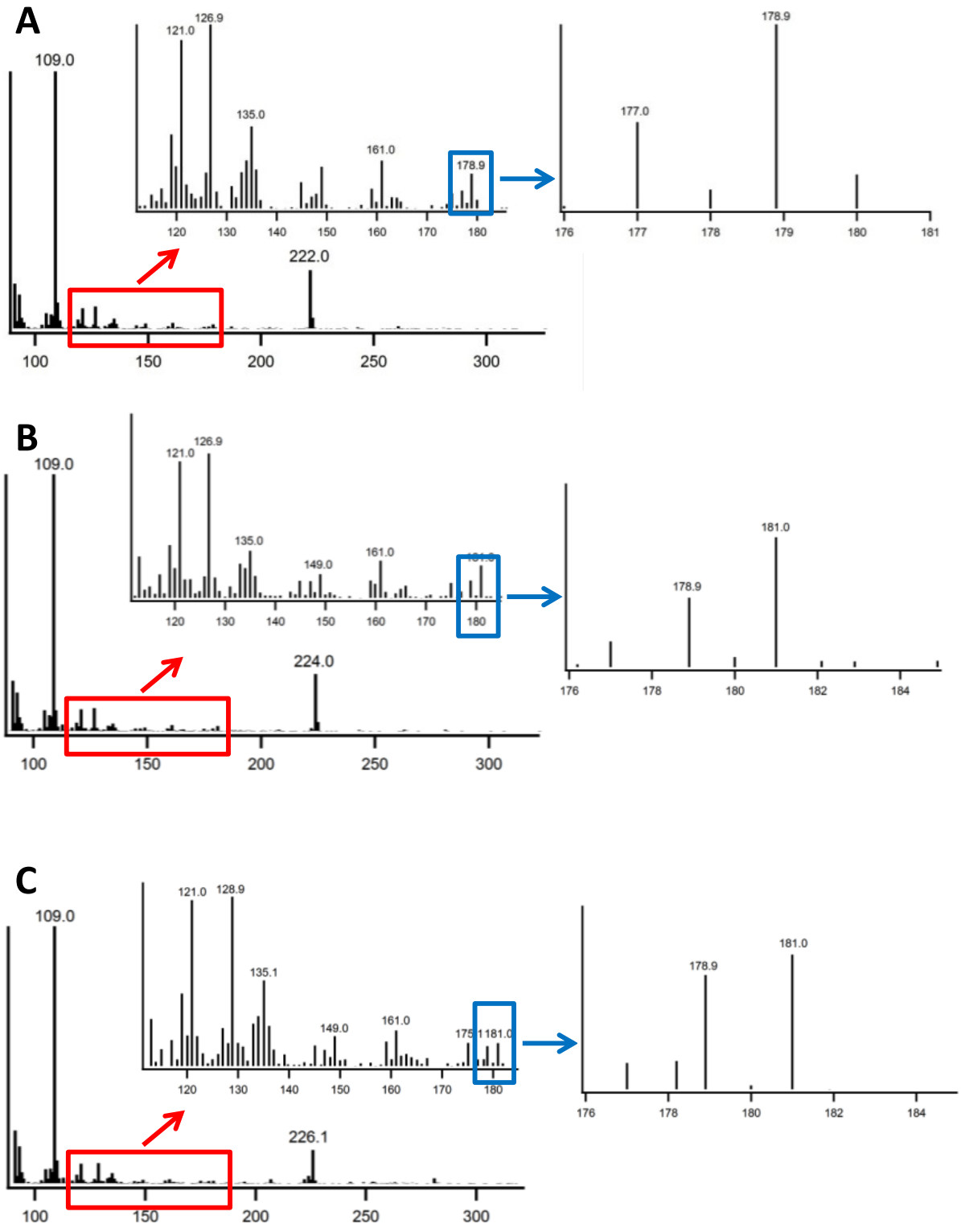
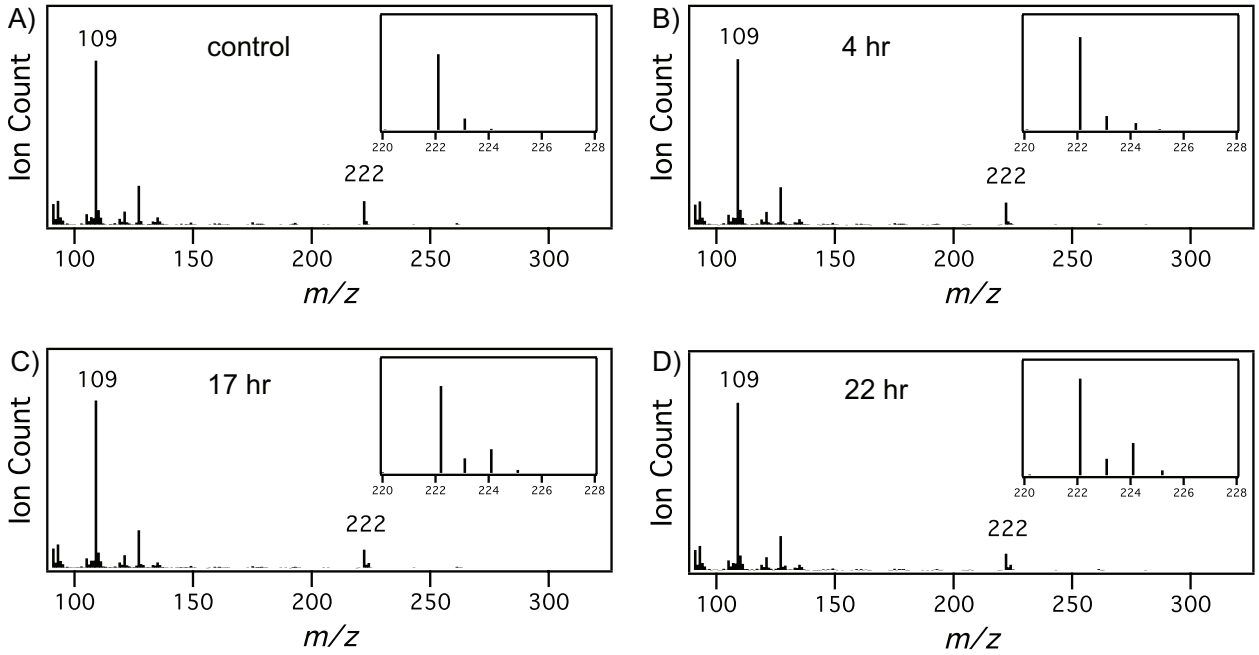


Figure S34. Comparison of MS for **4** after incubation in unlabeled or ^{18}O-labeled water (with 10 mM HCl). A) Control incubation of **4** in unlabeled water. B) 4, C) 17, D) 22 hour incubation of **4** in ^{18}O-labeled water.



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Coordinates and Energies

For Scheme S4

B

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.7724262 hartrees (-490570.015164762 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.481737 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.5875346 hartrees (-490453.993836846 kcal/mol)
MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.301688 hartrees (-490274.62223688 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.206650	-0.628832	0.804398
2	6	4.692417	0.219695	-0.115530
3	6	3.936598	1.473089	-0.504924
4	6	2.826107	1.849536	0.479274
5	6	1.958746	0.600963	0.935150
6	6	2.898467	-0.460331	1.540783
7	1	4.638811	2.314702	-0.563219
8	1	4.790180	-1.506334	1.076428
9	1	3.264452	2.231430	1.407150
10	1	2.185841	2.638526	0.075301
11	1	3.097305	-0.163499	2.580098
12	1	2.387805	-1.427498	1.619785
13	1	3.541537	1.362170	-1.526850
14	6	6.006096	-0.008524	-0.815743
15	1	6.712378	0.801160	-0.594016
16	1	6.466424	-0.953332	-0.516223
17	1	5.876299	-0.021458	-1.905659
18	1	1.281879	0.997885	1.704961
19	6	1.107843	0.208025	-0.210247
20	6	-0.074445	1.015070	-0.519279
21	1	-0.960516	0.351688	-0.366405
22	1	-0.185371	1.907895	0.096196
23	1	-0.132931	1.263198	-1.585400
24	6	1.337526	-0.994798	-1.001568
25	1	1.058698	-0.858039	-2.049740
26	1	2.364817	-1.350247	-0.920825
27	6	0.374867	-2.179331	-0.434388
28	1	0.814138	-3.062150	-0.911747

29	1	0.527051	-2.286268	0.639943
30	6	-1.057217	-2.053233	-0.814577
31	6	-2.132901	-1.992911	0.008930
32	6	-3.527213	-2.007819	-0.577965
33	1	-4.030221	-2.922173	-0.233510
34	1	-3.463527	-2.079297	-1.669386
35	6	-2.055572	-1.975496	1.513770
36	1	-2.537191	-1.076800	1.915022
37	1	-2.604273	-2.830624	1.927053
38	1	-1.037901	-2.016050	1.905452
39	1	-1.249048	-2.077139	-1.887454
40	6	-4.428185	-0.801969	-0.199761
41	1	-5.413944	-1.003386	-0.641806
42	1	-4.589516	-0.775028	0.881264
43	6	-3.924287	0.517824	-0.719951
44	6	-3.851195	1.699903	-0.077443
45	1	-3.649908	0.509859	-1.777189
46	6	-3.412727	2.947832	-0.808693
47	1	-2.561777	3.428520	-0.306532
48	1	-3.134950	2.741311	-1.846433
49	1	-4.218215	3.693111	-0.819734
50	6	-4.244922	1.926963	1.362401
51	1	-3.448203	2.449456	1.907425
52	1	-5.128312	2.576237	1.415665
53	1	-4.481735	1.008235	1.902565

TS1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.7387942 hartrees (-490548.910748442 kcal/mol)
Imaginary Frequencies: 1 (-301.6723 1/cm)
Zero-point correction = 0.481595 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.562181 hartrees (-490438.08419931 kcal/mol)
MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.2818263 hartrees (-490262.158821513 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	4.099576	-0.344620	0.095824
2	6	3.335739	0.604475	-0.612146
3	6	3.119277	1.894427	0.278869

4	6	2.377444	1.466375	1.567158
5	6	2.143588	-0.042894	1.364817
6	6	3.522914	-0.726748	1.406875
7	1	4.092240	2.351616	0.474325
8	1	4.954744	-0.871129	-0.332255
9	1	2.970039	1.654565	2.466144
10	1	1.437737	2.008635	1.688905
11	1	4.172081	-0.433628	2.246881
12	1	3.470779	-1.822720	1.466094
13	1	2.548988	2.599490	-0.330186
14	6	3.623901	0.860902	-2.076927
15	1	4.513600	1.490182	-2.189187
16	1	3.792424	-0.066119	-2.631795
17	1	2.792744	1.394841	-2.545428
18	1	1.419911	-0.472772	2.060442
19	6	1.754939	-0.196462	-0.138242
20	6	0.621701	0.661570	-0.658953
21	1	-0.319356	0.209995	-0.308321
22	1	0.631165	1.699079	-0.330130
23	1	0.576542	0.636811	-1.751144
24	6	1.634722	-1.626490	-0.692317
25	1	1.520709	-1.570620	-1.781255
26	1	2.550709	-2.198715	-0.520161
27	6	0.457830	-2.464683	-0.108643
28	1	0.702219	-3.507394	-0.359848
29	1	0.472434	-2.413287	0.984243
30	6	-0.909512	-2.163743	-0.662451
31	6	-2.071485	-2.013352	0.004610
32	6	-3.364056	-1.814307	-0.762022
33	1	-4.022044	-2.670732	-0.556863
34	1	-3.156000	-1.834016	-1.838257
35	6	-2.209194	-2.070692	1.506598
36	1	-2.553087	-1.108898	1.905608
37	1	-2.965309	-2.813265	1.789555
38	1	-1.282981	-2.335300	2.020277
39	1	-0.952596	-2.130462	-1.752421
40	6	-4.151963	-0.523909	-0.423154
41	1	-5.088198	-0.564920	-0.998168
42	1	-4.451526	-0.531698	0.628667
43	6	-3.420043	0.743306	-0.779045
44	6	-3.307482	1.877256	-0.062120
45	1	-2.975097	0.740609	-1.776577
46	6	-2.600692	3.085619	-0.632510
47	1	-1.785419	3.418132	0.025316
48	1	-2.188065	2.888702	-1.626589
49	1	-3.289180	3.936342	-0.717820

50	6	-3.896511	2.093205	1.311449
51	1	-3.134305	2.464969	2.008749
52	1	-4.679024	2.862260	1.273305
53	1	-4.341039	1.194038	1.741889

E

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.7690635 hartrees (-490567.905036885 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.483589 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.5948642 hartrees (-490458.593234142 kcal/mol)
MPWB1K/6-31+G(d,p)//B3LYP/6-31+G(d,p):
HF = -781.3171383 hartrees (-490284.317454633 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.801664	0.383860	0.639640
2	6	3.178567	0.128820	-0.645939
3	6	3.236286	1.916593	0.765833
4	6	1.765016	1.718274	1.201890
5	6	1.577598	0.186211	1.073982
6	6	2.903057	-0.315297	1.680621
7	1	3.878131	2.366840	1.528550
8	1	4.887939	0.332965	0.703167
9	1	1.625076	2.021989	2.242593
10	1	1.065428	2.294713	0.595338
11	1	3.084469	0.059549	2.690808
12	1	3.029269	-1.399725	1.686270
13	1	3.359949	2.507180	-0.146153
14	6	3.856464	0.239558	-1.948729
15	1	4.842307	0.702298	-1.875438
16	1	4.001335	-0.788702	-2.320070
17	1	3.239364	0.744665	-2.697939
18	1	0.657407	-0.191718	1.516715
19	6	1.742209	-0.196345	-0.438835
20	6	0.767170	0.483545	-1.418738
21	1	-0.260839	0.304941	-1.099069
22	1	0.924042	1.564570	-1.465480
23	1	0.876829	0.084052	-2.430431
24	6	1.735639	-1.786615	-0.657307

25	1	1.700645	-1.943076	-1.740754
26	1	2.676937	-2.231704	-0.315100
27	6	0.584348	-2.561869	0.028334
28	1	0.821990	-3.618813	-0.168253
29	1	0.648424	-2.444483	1.112365
30	6	-0.799914	-2.279735	-0.488270
31	6	-1.916652	-2.016827	0.217738
32	6	-3.250848	-1.886502	-0.492620
33	1	-3.896794	-2.711054	-0.158503
34	1	-3.105165	-2.026325	-1.570267
35	6	-1.970563	-1.888032	1.721183
36	1	-2.241168	-0.866637	2.015542
37	1	-2.746295	-2.545565	2.131843
38	1	-1.031746	-2.143587	2.216869
39	1	-0.904048	-2.372106	-1.570577
40	6	-4.015699	-0.562105	-0.253000
41	1	-4.994288	-0.667171	-0.743174
42	1	-4.231836	-0.440305	0.812350
43	6	-3.320472	0.649971	-0.817105
44	6	-3.160291	1.862556	-0.255931
45	1	-2.956566	0.523061	-1.839343
46	6	-2.505516	2.989979	-1.021473
47	1	-1.640853	3.392968	-0.475427
48	1	-2.173468	2.673760	-2.014889
49	1	-3.201241	3.828946	-1.152023
50	6	-3.644500	2.246564	1.122026
51	1	-2.834728	2.700057	1.708756
52	1	-4.434241	3.005804	1.050610
53	1	-4.047647	1.406987	1.691318

For Scheme S5

B-PPi

B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0388979 hartrees (-1494753.22882123 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.565298 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6552753 hartrees (-1494512.5018035 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.3649083 hartrees (-1494330.29360733 kcal/mol)

Coordinates (from last standard orientation):

Center	Atomic	Coordinates (Angstroms)		

Number	Number	X	Y	Z
1	8	-3.391111	-3.324621	-1.145190
2	15	-2.938782	-2.016036	-0.314045
3	8	-3.829082	-0.854804	-0.563853
4	8	-1.445861	-1.658905	-1.008154
5	8	-2.605851	-2.425796	1.136110
6	15	-0.047023	-2.524615	-0.976895
7	8	0.907257	-1.904405	-1.938039
8	8	-0.549373	-4.012305	-1.477508
9	8	0.330923	-2.702275	0.500325
10	1	-2.664473	-3.977666	-1.164208
11	1	-0.366418	-4.097723	-2.428138
12	12	-0.872435	-2.196906	1.926401
13	8	-0.487914	-2.280373	3.932522
14	6	-0.324823	-1.024227	3.914257
15	1	-0.088142	-0.504877	4.855824
16	8	-0.425230	-0.350661	2.841038
17	6	-3.115085	3.198928	0.565843
18	6	-3.274236	3.793536	-0.625207
19	6	-2.689383	3.197313	-1.888776
20	6	-2.230401	1.746961	-1.734162
21	6	-1.457577	1.488000	-0.361378
22	6	-2.370679	1.908295	0.801111
23	1	-3.446757	3.227758	-2.685349
24	1	-3.577070	3.648342	1.444571
25	1	-3.078414	1.058208	-1.654448
26	1	-1.620960	1.423037	-2.582277
27	1	-3.092104	1.089393	0.927829
28	1	-1.804530	1.952527	1.739583
29	1	-1.869541	3.839609	-2.252171
30	6	-4.045967	5.076665	-0.792237
31	1	-3.434174	5.852354	-1.274444
32	1	-4.923131	4.926752	-1.436512
33	1	-4.394811	5.468071	0.168453
34	1	-1.318733	0.400847	-0.385192
35	6	-0.136282	2.098088	-0.486339
36	6	0.871605	1.466516	-1.355866
37	1	1.816411	1.370479	-0.786827
38	1	0.586003	0.490142	-1.753463
39	1	1.133175	2.157070	-2.172356
40	6	0.253598	3.300451	0.259322
41	1	0.896168	3.956557	-0.336604
42	1	-0.619635	3.851396	0.608965
43	6	1.118353	2.833250	1.533992
44	1	0.960511	3.649511	2.250071

45	1	0.683618	1.935299	1.981112
46	6	2.575466	2.698533	1.231167
47	6	3.387182	1.639937	1.436582
48	6	4.868291	1.773169	1.144604
49	1	5.413987	1.728653	2.099738
50	1	5.068988	2.764496	0.719093
51	6	2.943167	0.310579	1.988445
52	1	3.066936	-0.477385	1.235409
53	1	3.571369	0.027555	2.844037
54	1	1.901355	0.292170	2.311348
55	1	3.029612	3.603998	0.823863
56	6	5.463529	0.687921	0.211474
57	1	6.536597	0.912935	0.113657
58	1	5.407067	-0.288961	0.700576
59	6	4.829660	0.652245	-1.153994
60	6	4.354423	-0.412441	-1.823575
61	1	4.781618	1.622634	-1.654590
62	6	3.765018	-0.261921	-3.206342
63	1	2.741308	-0.656019	-3.225290
64	1	3.756951	0.782010	-3.539755
65	1	4.339957	-0.844225	-3.940429
66	6	4.349228	-1.832242	-1.312416
67	1	3.323234	-2.219668	-1.309688
68	1	4.932271	-2.478379	-1.983769
69	1	4.767469	-1.938466	-0.308358

TS2

B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0125236 hartrees (-1494736.67868424 kcal/mol)
Imaginary Frequencies: 1 (-12.0927 1/cm)
Zero-point correction = 0.564711 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6302036 hartrees (-1494496.76906104 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.3409745 hartrees (-1494315.27490849 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-4.606665	-3.065347	0.058408
2	15	-3.832250	-1.854949	-0.689916
3	8	-3.092790	-2.328617	-1.887113

4	8	-2.707242	-1.409958	0.469161
5	8	-4.788710	-0.650215	-0.815069
6	15	-2.941662	-0.725661	1.939516
7	8	-1.636055	-0.693459	2.658386
8	8	-4.002229	-1.779935	2.642373
9	8	-3.743015	0.564600	1.724818
10	1	-4.817810	-2.807632	0.977210
11	1	-3.501547	-2.378955	3.220318
12	12	-4.627428	1.041271	0.072971
13	8	-5.982691	2.579711	-0.067848
14	6	-5.087775	3.233635	-0.682865
15	1	-5.317451	4.254086	-1.029270
16	8	-3.937843	2.748388	-0.910551
17	6	-0.808315	1.418442	-0.801618
18	6	-0.764072	0.413894	-1.714457
19	6	-0.103834	-0.912593	-1.426899
20	6	0.628609	-0.944006	-0.073722
21	6	1.143221	0.465616	0.300748
22	6	-0.072316	1.377860	0.517360
23	1	-0.896517	-1.672513	-1.438940
24	1	-1.448925	2.276519	-0.996991
25	1	-0.066374	-1.232804	0.719394
26	1	1.436166	-1.685118	-0.075104
27	1	-0.691126	0.980578	1.332724
28	1	0.225029	2.386087	0.828453
29	1	0.559285	-1.174021	-2.266714
30	6	-1.495410	0.506410	-3.025448
31	1	-0.806514	0.369413	-3.871322
32	1	-2.233617	-0.304388	-3.081357
33	1	-2.008203	1.465542	-3.141037
34	1	1.744262	0.382267	1.229153
35	6	2.071788	1.068272	-0.708277
36	6	2.969470	0.221166	-1.505910
37	1	3.915917	0.159357	-0.919440
38	1	2.613523	-0.795309	-1.661211
39	1	3.249442	0.690100	-2.453967
40	6	2.360117	2.519306	-0.735478
41	1	2.807497	2.810733	-1.690180
42	1	1.462638	3.113434	-0.568067
43	6	3.382551	2.904065	0.425383
44	1	3.401702	4.000990	0.395176
45	1	2.943768	2.621117	1.384729
46	6	4.773780	2.380305	0.246447
47	6	5.465205	1.553915	1.056223
48	6	6.909252	1.220777	0.738909
49	1	7.541729	1.618553	1.546427

50	1	7.212572	1.741271	-0.177826
51	6	4.925072	0.950539	2.329937
52	1	4.858828	-0.141668	2.249188
53	1	5.602274	1.159404	3.168154
54	1	3.935377	1.321723	2.604945
55	1	5.287323	2.760365	-0.638187
56	6	7.229666	-0.288640	0.593151
57	1	8.319596	-0.368843	0.465457
58	1	7.001404	-0.810891	1.527085
59	6	6.557876	-0.941927	-0.585255
60	6	5.885489	-2.106246	-0.631149
61	1	6.696086	-0.410127	-1.529671
62	6	5.363866	-2.645039	-1.942967
63	1	4.283574	-2.841340	-1.895829
64	1	5.555205	-1.960835	-2.775854
65	1	5.836509	-3.607290	-2.183153
66	6	5.626163	-3.003504	0.554883
67	1	4.554227	-3.223560	0.649906
68	1	6.126396	-3.971981	0.418373
69	1	5.971068	-2.585202	1.503272

C-PPi
B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.026676 hartrees (-1494745.55945676 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.565883 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6530376 hartrees (-1494511.09762438 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.3676604 hartrees (-1494332.0205776 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-5.550677	-1.955738	-1.113976
2	15	-4.296853	-0.972462	-1.371230
3	8	-3.521969	-1.386436	-2.574619
4	8	-3.318930	-1.275704	-0.045091
5	8	-4.748311	0.490604	-1.218991
6	15	-3.627804	-0.975398	1.546102
7	8	-2.536644	-1.614432	2.338076
8	8	-5.076217	-1.720109	1.771215

9	8	-3.918596	0.522833	1.666122
10	1	-5.889947	-1.847881	-0.204243
11	1	-4.925097	-2.598418	2.158733
12	12	-4.115106	1.700426	0.138997
13	8	-4.495855	3.701904	0.268021
14	6	-3.284522	3.900390	-0.053741
15	1	-2.920286	4.935930	-0.138961
16	8	-2.484892	2.940938	-0.278705
17	6	-0.226294	0.276496	-0.546516
18	6	-0.306531	-1.155643	-0.724326
19	6	0.004417	-1.975305	0.462259
20	6	1.069539	-1.302353	1.393375
21	6	1.156716	0.204138	1.113854
22	6	-0.287884	0.726198	0.935526
23	1	-0.953181	-2.011542	1.028834
24	1	-0.700284	0.869164	-1.330728
25	1	0.775790	-1.464426	2.434502
26	1	2.041123	-1.786442	1.244848
27	1	-1.051717	0.260554	1.559820
28	1	-0.386569	1.808626	0.998758
29	1	0.256552	-3.005022	0.194173
30	6	-0.626440	-1.734722	-2.021548
31	1	-1.749873	-1.709674	-2.131745
32	1	-0.285597	-1.101646	-2.848761
33	1	-0.292184	-2.767910	-2.138157
34	1	1.810269	0.701208	1.837191
35	6	1.437333	0.491943	-0.394201
36	6	2.392880	-0.413904	-1.170021
37	1	3.423415	-0.178046	-0.885088
38	1	2.237985	-1.481603	-0.990770
39	1	2.302911	-0.240751	-2.249056
40	6	1.701626	1.978056	-0.739978
41	1	1.797451	2.057605	-1.831253
42	1	0.833508	2.586356	-0.472430
43	6	2.940998	2.630971	-0.074351
44	1	2.832172	3.711959	-0.254188
45	1	2.882146	2.507860	1.011469
46	6	4.284008	2.205465	-0.609698
47	6	5.400731	1.892338	0.068976
48	6	6.687053	1.595341	-0.678672
49	1	7.421811	2.380543	-0.441982
50	1	6.503769	1.660768	-1.758669
51	6	5.505460	1.862334	1.575174
52	1	5.726240	0.849811	1.936850
53	1	6.330302	2.502898	1.916165
54	1	4.596712	2.201790	2.077022

55	1	4.349266	2.212042	-1.700007
56	6	7.349268	0.230310	-0.363722
57	1	8.293531	0.193830	-0.928202
58	1	7.632968	0.189250	0.692566
59	6	6.502019	-0.952019	-0.751947
60	6	6.176992	-2.031540	-0.021994
61	1	6.129822	-0.916410	-1.778354
62	6	5.335825	-3.139006	-0.613052
63	1	4.421314	-3.301197	-0.023995
64	1	5.043191	-2.925059	-1.645909
65	1	5.878369	-4.094836	-0.605740
66	6	6.611025	-2.277330	1.403135
67	1	5.739930	-2.441346	2.052827
68	1	7.219344	-3.190164	1.468927
69	1	7.197373	-1.458841	1.826909

TS3

B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0101636 hartrees (-1494735.19776064 kcal/mol)
Imaginary Frequencies: 1 (-213.2701 1/cm)
Zero-point correction = 0.566190 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6353108 hartrees (-1494499.97388011 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.3498872 hartrees (-1494320.86771687 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-4.959442	-2.625601	-0.683828
2	15	-3.937010	-1.442221	-1.083140
3	8	-2.852865	-1.931580	-1.971500
4	8	-3.232797	-1.059207	0.401920
5	8	-4.734956	-0.177833	-1.464090
6	15	-3.969348	-0.503867	1.774529
7	8	-2.994093	-0.609725	2.894128
8	8	-5.221101	-1.562083	1.955111
9	8	-4.624246	0.830541	1.397673
10	1	-5.465967	-2.383562	0.117577
11	1	-4.969293	-2.230220	2.614376
12	12	-4.592295	1.441975	-0.438322
13	8	-5.044771	3.329387	-1.073970

14	6	-3.799907	3.546431	-1.175245
15	1	-3.458646	4.532038	-1.527765
16	8	-2.939626	2.660252	-0.882265
17	6	-0.711533	0.453962	-0.089270
18	6	-0.057284	-0.455082	-0.935987
19	6	0.092153	-1.880680	-0.377095
20	6	0.763716	-1.805979	1.020345
21	6	1.003640	-0.308388	1.265252
22	6	-0.372019	0.382750	1.360939
23	1	-0.915601	-2.301981	-0.349147
24	1	-1.273436	1.295585	-0.498831
25	1	0.122392	-2.220189	1.802798
26	1	1.703422	-2.367053	1.040494
27	1	-1.136915	-0.154488	1.947997
28	1	-0.329567	1.391708	1.784784
29	1	0.665795	-2.483515	-1.086306
30	6	-0.177630	-0.309466	-2.431352
31	1	-1.077573	-0.852851	-2.745268
32	1	-0.273529	0.737402	-2.737267
33	1	0.686424	-0.750519	-2.939636
34	1	1.665938	-0.116833	2.115450
35	6	1.519227	0.279401	-0.082759
36	6	2.648558	-0.429810	-0.805004
37	1	3.582901	-0.212914	-0.269807
38	1	2.537582	-1.511834	-0.860774
39	1	2.774698	-0.038034	-1.818843
40	6	1.706540	1.806169	-0.159679
41	1	1.827099	2.092855	-1.212033
42	1	0.820132	2.333125	0.197277
43	6	2.911062	2.359871	0.656973
44	1	2.702901	3.432880	0.786376
45	1	2.896216	1.935006	1.665865
46	6	4.266570	2.223680	0.012845
47	6	5.437852	1.889601	0.580364
48	6	6.711508	1.908197	-0.243230
49	1	7.386409	2.675836	0.165454
50	1	6.476242	2.218522	-1.269072
51	6	5.610867	1.526921	2.035889
52	1	5.958334	0.491794	2.146808
53	1	6.374668	2.164389	2.501497
54	1	4.693858	1.633602	2.619736
55	1	4.283201	2.488103	-1.046546
56	6	7.495836	0.573000	-0.290914
57	1	8.410245	0.758809	-0.874826
58	1	7.835686	0.304039	0.714157
59	6	6.725392	-0.551122	-0.931214

60	6	6.552036	-1.809310	-0.494045
61	1	6.277698	-0.293393	-1.893711
62	6	5.772963	-2.812230	-1.313184
63	1	4.918363	-3.209968	-0.747238
64	1	5.394297	-2.377396	-2.243740
65	1	6.396943	-3.678200	-1.574875
66	6	7.112603	-2.363404	0.793854
67	1	6.314044	-2.796555	1.411925
68	1	7.817709	-3.180271	0.586308
69	1	7.638509	-1.618583	1.395505

E-PPi
B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0296908 hartrees (-1494747.45127391 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.566684 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6595214 hartrees (-1494515.16627371 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.37619 hartrees (-1494337.3729869 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.631921	0.924151	0.808840
2	6	-0.435821	1.407698	1.595303
3	6	0.167273	-0.510225	1.644023
4	6	-0.848980	-1.133225	0.685299
5	6	-1.273197	0.092766	-0.155069
6	6	0.107754	0.620836	-0.592922
7	1	1.186930	-0.941320	1.743696
8	1	1.662998	1.192941	1.016678
9	1	-0.362136	-1.876444	0.048348
10	1	-1.675503	-1.616914	1.210953
11	1	0.705506	-0.114060	-1.135502
12	1	0.070574	1.539205	-1.187553
13	1	-0.183816	-0.418015	2.677625
14	6	-0.287990	2.146029	2.881847
15	1	-1.047327	1.866557	3.617833
16	1	0.710375	2.024128	3.309206
17	1	-0.426873	3.213534	2.659276
18	1	-1.986086	-0.123508	-0.950723

19	6	-1.754047	1.186509	0.860365
20	6	-2.913630	0.761279	1.777138
21	1	-3.774858	0.451476	1.179989
22	1	-2.641926	-0.071342	2.433328
23	1	-3.233760	1.592483	2.415036
24	6	-2.073832	2.562969	0.169117
25	1	-2.515957	3.218555	0.930452
26	1	-1.141297	3.050590	-0.138267
27	8	4.520450	-2.886467	0.965455
28	15	3.831536	-1.438510	1.148603
29	8	2.913584	-1.409922	2.324177
30	8	2.871988	-1.315532	-0.211469
31	8	4.897756	-0.335970	1.002135
32	15	3.324919	-1.239757	-1.802019
33	8	2.109278	-1.411386	-2.637443
34	8	4.341465	-2.537554	-1.913175
35	8	4.230178	-0.007397	-1.928588
36	1	4.856320	-2.979121	0.050865
37	1	3.860283	-3.264414	-2.342388
38	12	4.758297	1.007330	-0.372815
39	8	5.699198	2.817584	-0.368145
40	6	4.592801	3.335762	-0.023876
41	1	4.546421	4.424264	0.138312
42	8	3.545000	2.640025	0.137096
43	6	-2.996918	2.531042	-1.071530
44	1	-2.985636	3.557760	-1.469721
45	1	-2.543862	1.909839	-1.848974
46	6	-4.429644	2.143434	-0.812220
47	6	-5.195538	1.262876	-1.478375
48	6	-6.659852	1.101572	-1.115129
49	1	-7.270145	1.438731	-1.967162
50	1	-6.904012	1.768082	-0.278166
51	6	-4.721569	0.424695	-2.642051
52	1	-4.720756	-0.642997	-2.387350
53	1	-5.397623	0.540214	-3.499873
54	1	-3.716121	0.684126	-2.980739
55	1	-4.902672	2.702617	-0.001929
56	6	-7.112342	-0.336828	-0.760350
57	1	-8.203028	-0.302914	-0.615652
58	1	-6.947157	-1.000512	-1.614763
59	6	-6.473696	-0.879457	0.490426
60	6	-5.871838	-2.064840	0.683009
61	1	-6.548968	-0.214130	1.353753
62	6	-5.335357	-2.447321	2.042854
63	1	-4.262395	-2.683413	1.996452
64	1	-5.479118	-1.651111	2.780197

65	1	-5.830954	-3.352307	2.421336
66	6	-5.692519	-3.127519	-0.374350
67	1	-4.632923	-3.399229	-0.477535
68	1	-6.219119	-4.048501	-0.087978
69	1	-6.060798	-2.829067	-1.358487

TS4

B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0240166 hartrees (-1494743.89065667 kcal/mol)
Imaginary Frequencies: 1 (-433.4371 1/cm)
Zero-point correction = 0.563458 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6586524 hartrees (-1494514.62096752 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.3747049 hartrees (-1494336.4410718 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.557569	0.808258	1.221433
2	6	-0.618690	1.116102	1.971489
3	6	-0.060842	-0.474742	2.121068
4	6	-0.958376	-1.268673	1.164196
5	6	-1.265176	-0.146061	0.150674
6	6	0.158982	0.372529	-0.179986
7	1	1.087900	-0.892219	1.945026
8	1	1.561414	1.118799	1.489115
9	1	-0.410538	-2.099848	0.710332
10	1	-1.846993	-1.670493	1.653245
11	1	0.820056	-0.398327	-0.585893
12	1	0.182747	1.233492	-0.853195
13	1	-0.054890	-0.610432	3.201634
14	6	-0.613576	1.947663	3.228449
15	1	-1.414679	1.650421	3.912597
16	1	0.341972	1.872870	3.756809
17	1	-0.768091	3.001679	2.969515
18	1	-1.872085	-0.441088	-0.705616
19	6	-1.847752	1.002656	1.036586
20	6	-3.138194	0.638783	1.792048
21	1	-3.923939	0.340228	1.093076
22	1	-2.994164	-0.173243	2.510446
23	1	-3.509224	1.503524	2.354015

24	6	-2.028047	2.352277	0.275669
25	1	-2.525182	3.060543	0.952144
26	1	-1.045205	2.789361	0.064995
27	8	4.768381	-2.119498	1.570876
28	15	3.512664	-1.258200	1.072092
29	8	2.269702	-1.713994	1.803323
30	8	3.353368	-1.650491	-0.509363
31	8	3.809534	0.251328	1.143812
32	15	4.457498	-1.378454	-1.735329
33	8	4.045380	-2.107509	-2.950716
34	8	5.808752	-2.048959	-1.041057
35	8	4.716535	0.133342	-1.723985
36	1	5.429383	-2.195267	0.846522
37	1	5.998645	-2.884651	-1.499864
38	12	4.164545	1.391630	-0.386614
39	8	4.717363	3.350281	-0.209073
40	6	3.501281	3.654555	-0.405627
41	1	3.212373	4.716930	-0.408456
42	8	2.612061	2.768957	-0.596723
43	6	-2.805158	2.312614	-1.061563
44	1	-2.692027	3.314250	-1.505547
45	1	-2.305604	1.627831	-1.753675
46	6	-4.278364	2.011095	-0.957225
47	6	-5.020542	1.177819	-1.705444
48	6	-6.521607	1.099388	-1.499062
49	1	-7.021449	1.479167	-2.403794
50	1	-6.813207	1.770615	-0.681277
51	6	-4.476175	0.315151	-2.819785
52	1	-4.572597	-0.751749	-2.579862
53	1	-5.044166	0.479210	-3.745739
54	1	-3.424797	0.510584	-3.042174
55	1	-4.800274	2.597487	-0.197702
56	6	-7.087472	-0.314631	-1.216040
57	1	-8.183195	-0.219651	-1.169411
58	1	-6.882168	-0.972986	-2.065985
59	6	-6.594631	-0.912346	0.074790
60	6	-6.070800	-2.129528	0.294144
61	1	-6.710600	-0.258004	0.941844
62	6	-5.667603	-2.558393	1.685903
63	1	-4.601529	-2.825168	1.726209
64	1	-5.850907	-1.773293	2.426252
65	1	-6.220409	-3.455439	1.998499
66	6	-5.851340	-3.182413	-0.765620
67	1	-4.800386	-3.502634	-0.784629
68	1	-6.442554	-4.081831	-0.543739
69	1	-6.120124	-2.850694	-1.771126

2-PPi
B3LYP/6-31G(d)//B3LYP/6-31G(d):
HF = -2382.0556793 hartrees (-1494763.75931754 kcal/mol)
Imaginary Frequencies: none found
Zero-point correction = 0.567198 (Hartree/Particle)

mPW1PW91/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.6918518 hartrees (-1494535.45392302 kcal/mol)
MPWB1K/6-31G(d)//B3LYP/6-31G(d):
HF = -2381.4125429 hartrees (-1494360.18479518 kcal/mol)

Coordinates (from last standard orientation):

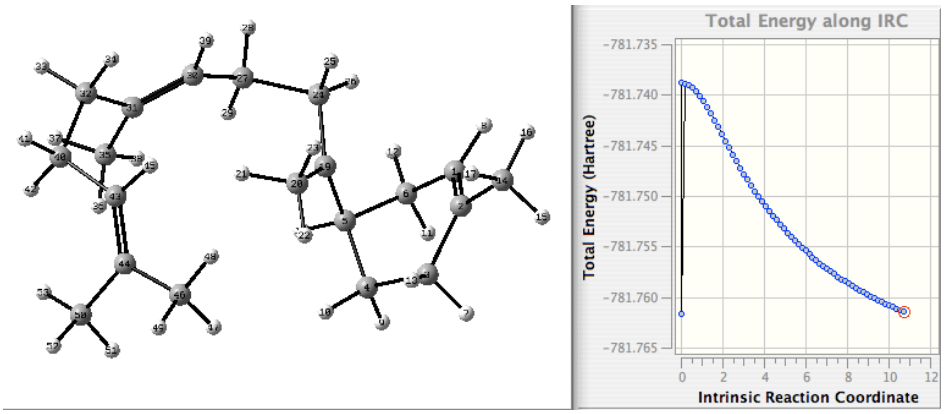
Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.394759	0.760122	1.731236
2	6	-0.930629	1.007284	2.428338
3	6	-0.324478	-0.380729	2.496734
4	6	-0.993204	-1.241281	1.426117
5	6	-1.305143	-0.092681	0.434181
6	6	0.106711	0.518230	0.248032
7	1	1.751591	-0.873469	2.121494
8	1	1.303531	1.237971	2.087528
9	1	-0.314601	-1.985886	0.991528
10	1	-1.880833	-1.767098	1.787300
11	1	0.795680	-0.196800	-0.219793
12	1	0.126864	1.436325	-0.344980
13	1	0.038094	-0.780648	3.440662
14	6	-1.035735	1.891153	3.647304
15	1	-1.923879	1.646776	4.242625
16	1	-0.161090	1.774209	4.297667
17	1	-1.099280	2.950166	3.369686
18	1	-1.829060	-0.386193	-0.476916
19	6	-2.028266	0.968394	1.332576
20	6	-3.379666	0.485554	1.891646
21	1	-4.074946	0.232060	1.085750
22	1	-3.272251	-0.389597	2.539295
23	1	-3.847280	1.273900	2.493783
24	6	-2.189004	2.359116	0.660482
25	1	-1.209957	2.849641	0.611160
26	8	4.949522	-1.792162	1.680103
27	15	3.668967	-1.051333	1.108333
28	8	2.529150	-1.483929	2.104757

29	8	3.341858	-1.729381	-0.303461
30	8	3.808869	0.452880	0.975154
31	15	4.360632	-1.619827	-1.667200
32	8	3.822308	-2.470581	-2.740663
33	8	5.724028	-2.257746	-0.974810
34	8	4.639860	-0.126514	-1.806542
35	1	5.521235	-2.099160	0.937218
36	1	5.880790	-3.140443	-1.352219
37	12	4.167870	1.399893	-0.721670
38	8	5.028411	3.245891	-0.760470
39	6	3.888171	3.686727	-1.108065
40	1	3.762822	4.764172	-1.289286
41	8	2.892026	2.912352	-1.250213
42	6	-2.795764	2.404094	-0.761984
43	1	-2.667315	3.438658	-1.118633
44	1	-2.194926	1.785004	-1.435663
45	6	-4.260366	2.060274	-0.859657
46	6	-4.884929	1.270041	-1.748639
47	6	-6.396958	1.143591	-1.726854
48	1	-6.800332	1.572078	-2.657946
49	1	-6.801024	1.751779	-0.907409
50	6	-4.187682	0.504993	-2.848753
51	1	-4.276478	-0.578664	-2.696727
52	1	-4.647117	0.722633	-3.822911
53	1	-3.124084	0.740740	-2.926500
54	1	-4.886320	2.569435	-0.123283
55	6	-6.955574	-0.296178	-1.602377
56	1	-8.050981	-0.224285	-1.689394
57	1	-6.629075	-0.897978	-2.456507
58	6	-6.613452	-0.963395	-0.296912
59	6	-6.111620	-2.190484	-0.082947
60	1	-6.829587	-0.355419	0.584425
61	6	-5.868840	-2.692181	1.321516
62	1	-4.815116	-2.969903	1.467122
63	1	-6.129084	-1.942162	2.074942
64	1	-6.457638	-3.597964	1.525485
65	6	-5.763085	-3.184772	-1.164399
66	1	-4.712937	-3.497432	-1.080693
67	1	-6.365471	-4.098011	-1.058158
68	1	-5.920083	-2.801164	-2.175191
69	1	-2.798019	2.991710	1.321304

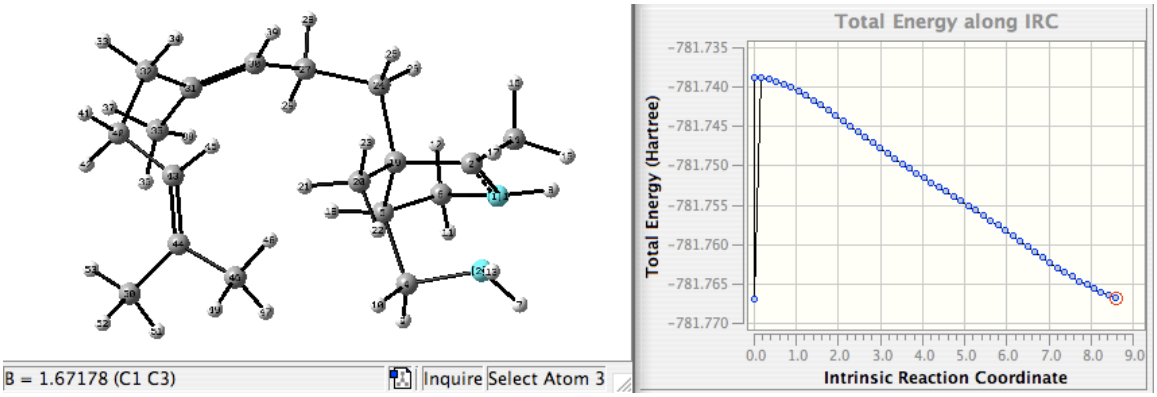
IRC Plots

For Scheme S4

TS1→B



TS1→E

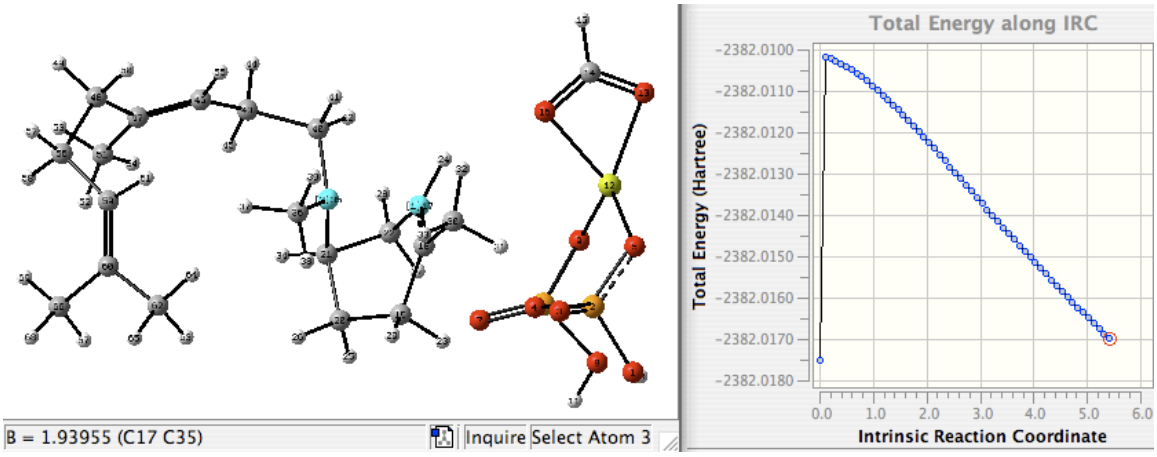


For Scheme S5

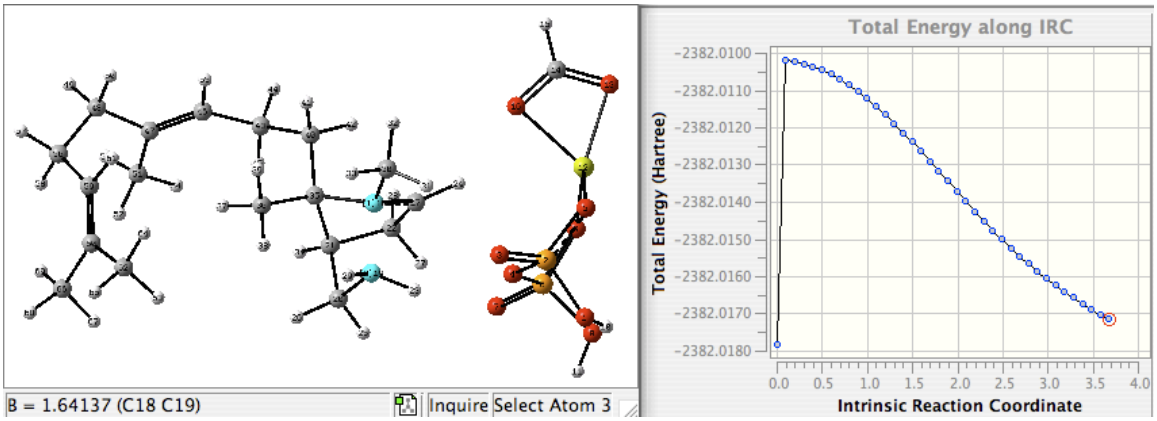
TS2→B-PPi: unsuccessful

TS2→A-PPi: unsuccessful

TS3→A-PPi



TS3→E-PPi



TS4→E-PPi: unsuccessful
TS4→2-PPi: unsuccessful