SUPPORTING INFORMATION

Unveiling sequential late-stage methyltransferase reactions in the meleagrin/oxaline biosynthetic pathway

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Figure S1.

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OxaG   1    MTRATNFTELYAGKGILETYMIAEKITRYFTRDLIELSGLLESELSPLKLLDLACGTGVV  60
            MTRATNFTELYAGKGIL+TYM+AEKITRY+T+DLI+LSGL ES L+PL +LDLACGTGVV
RoqN   1    MTRATNFTELYAGKGILDTYMVAEKITRYYTQDLIQLSGLSESSLTPLVILDLACGTGVV  60

OxaG   61   SERLHEMLASKAPASWELICGDISAELTGHVKRKIIEEGWTNSSARVMDAQNTELATAEL  120
            S+ LH+ML  +   +WEL CGDIS ELTGHVK+KI+E GW NS A+V+DAQNTEL T
RoqN   61   SDALHDMLNFQPKGNWELTCGDISTELTGHVKQKILERGWENSIAKVVDAQNTELPTGHY  120

OxaG   121  THVFAALAWTSFPDTYAALKDSLRILRPGGTLTISTWQKTEWLGVLEAAVKTIPTRLPFP  180
            THVFAALA+TSFPDTYAA+K+ +RIL+PGGTLTISTWQ+TEWL V+EAAV  IP  LPFP
RoqN   121  THVFAALAFTSFPDTYAAMKEVMRILQPGGTLTISTWQRTEWLAVVEAAVAIIPADLPFP  180

OxaG   181  TTKEFMSCMNPGWDDENYVRGRLEEAGFVHVYSTTISKEFQISTADLYKIAAPVIPIIVS  240
            TTKEFMSCMNPGWD E+YV  R EEAGF  V  TTISK+F+ S  DLYKIA PVIPIIVS
RoqN   181  TTKEFMSCMNPGWDSEDYVHSRFEEAGFHSVQVTTISKQFETSVEDLYKIAQPVIPIIVS  240

OxaG   241  KWWTTEQKEAHEHEILPALAKHLEATYGETGLVPQKWTAVFAKGEK  286
            KWW  EQ++ +E++ILPAL +HL  TYGE GLVPQ+WTAVFA G+K
RoqN   241  KWWNQEQRDKYENDILPALQRHLNETYGENGLVPQEWTAVFATGQK  286
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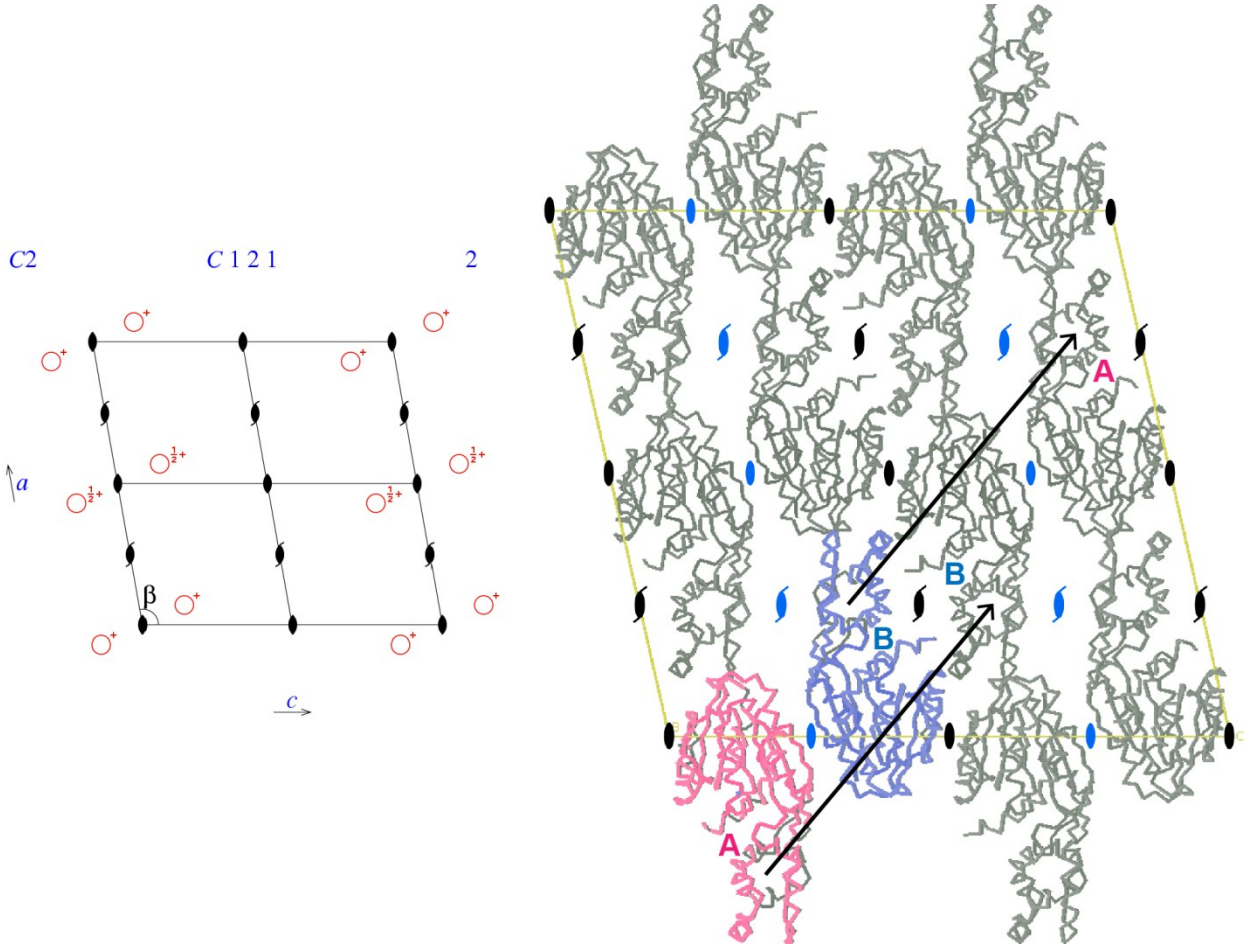
Figure S2.



A space-group diagram for *C* 2 (left). The crystallographic symmetry operators are shown in black. Notice in the OxaG unit cell (right) a parallel twofold (colored blue) relates the two subunits of the asymmetric unit. As a result, subunits A and B are also related by pseudotranslational symmetry (black arrows).

Figure S3.

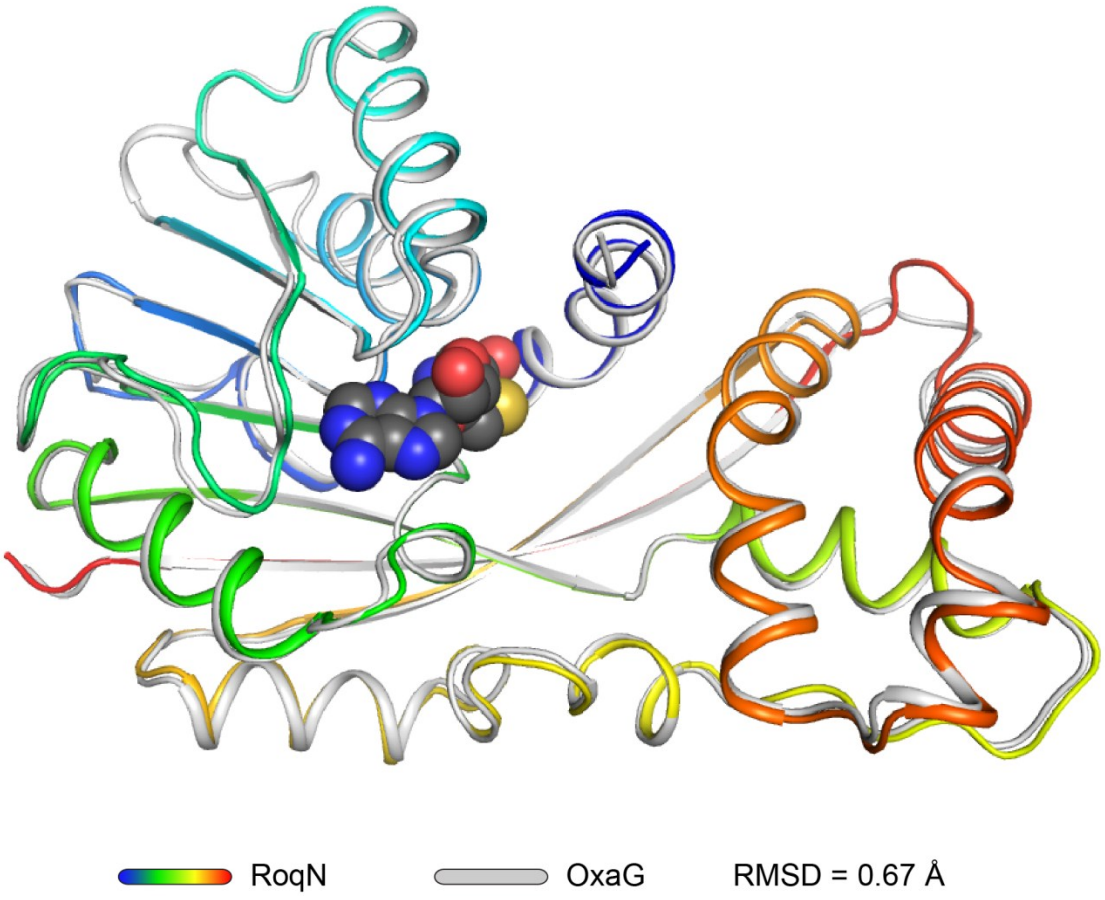


Figure S4.

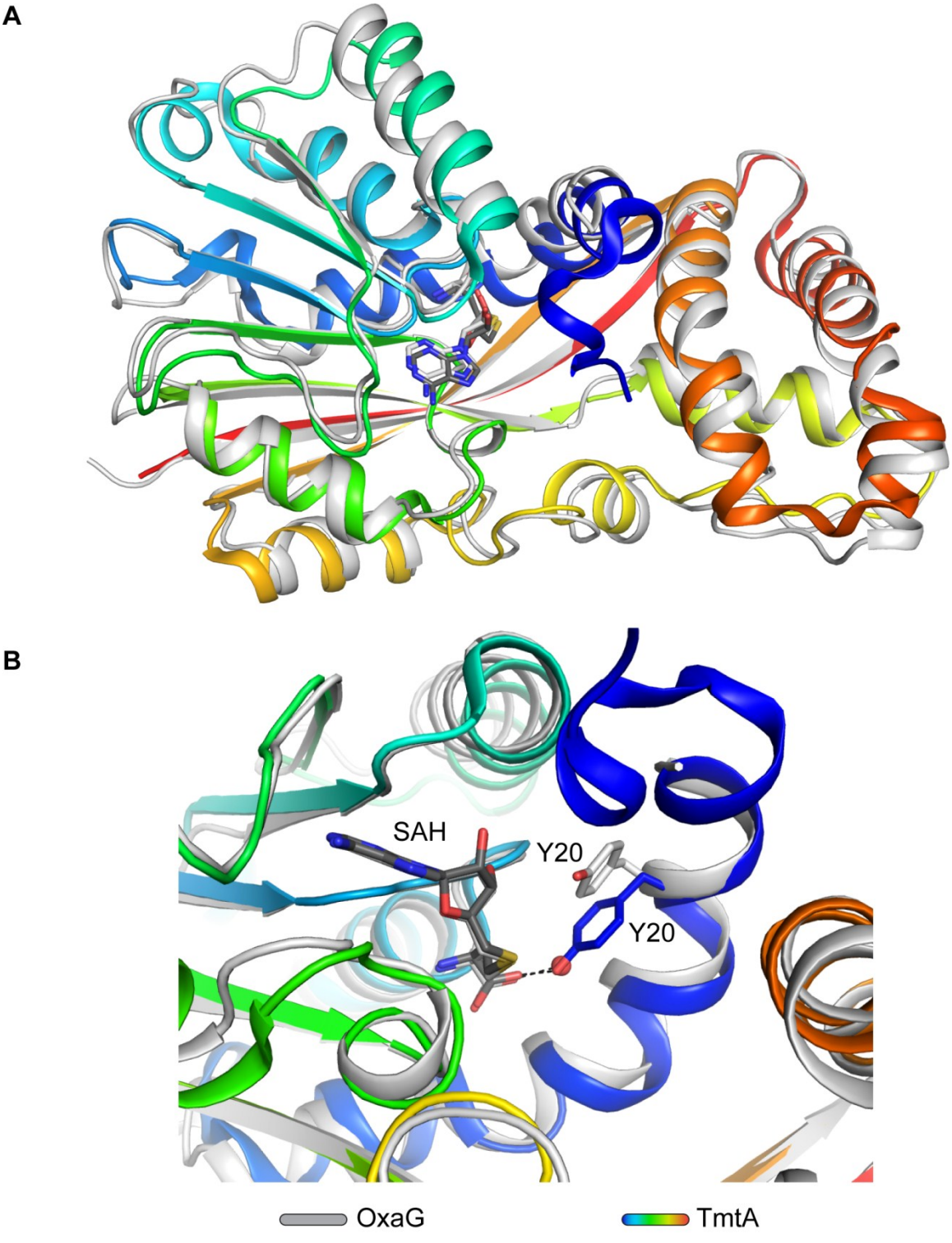


Figure S5.

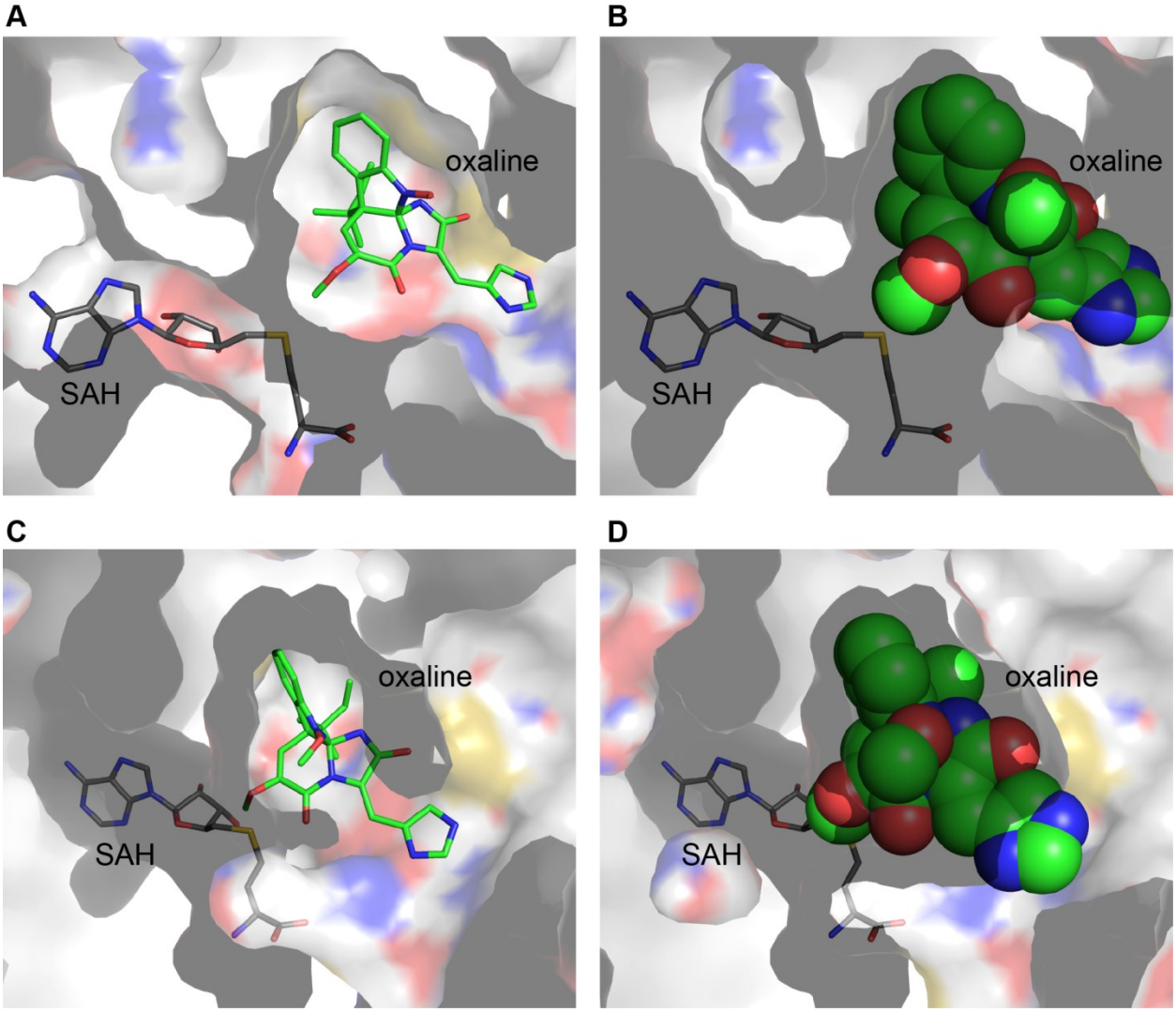
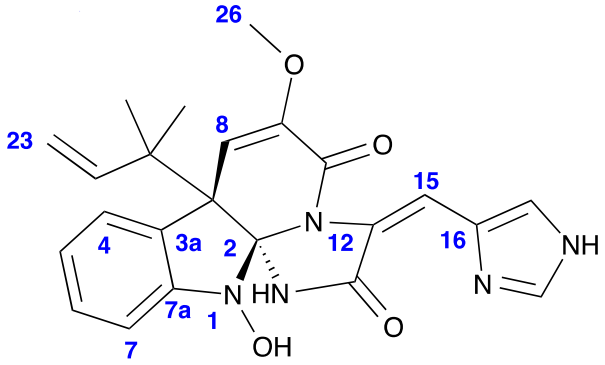


Table S1.

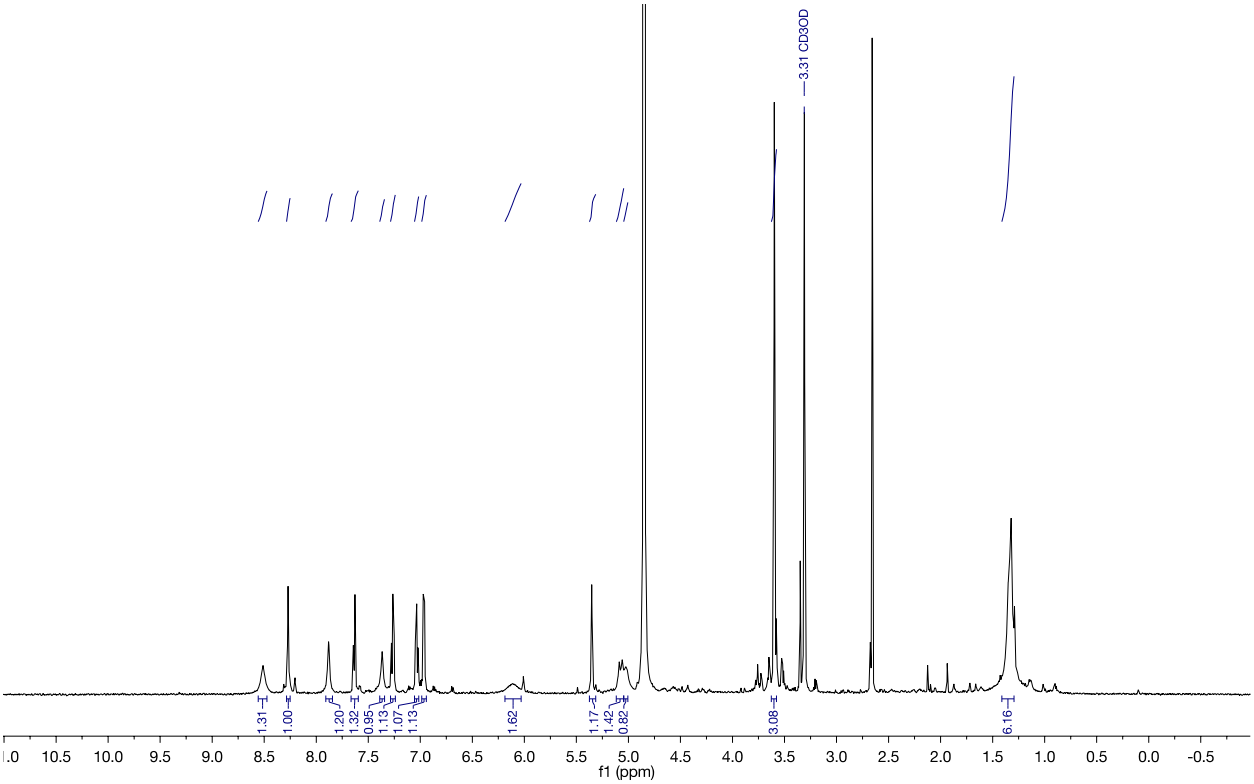
*oxaC*_for	5'– gagaatctctacttccaaggcgctagcATGACATTTTCAAACGCTGATGCGC –3'
*oxaC*_rev	5'– ggctttgttagcagccggatctcagTTATTTCAACCTGGCCTCGATGATGCC –3'
*oxaG*_for	5'– gagaatctctacttccaaggcgctagcATGACCCGCGCCACCAACTTTAC –3'
*oxaG*_rev	5'– ggctttgttagcagccggatctcagTCACTTCTCCTTCTCTCCCTTGGCAAATAC –3'
*roqN*_for	5'– ctgagaatctctacttccaaggcGCTAGCATGACTCGCGCCACCAACTTTACCG –3'
*roqN*_rev	5'– cctttcgggctttgttagcagccggatcCTAAGATCCCTTCTGACCAGTTGC –3'
*oxaG*_Y20F	5' – GCAAGGGCATCCTGGAGACGTTTATGATCGCCGAGAA GATTACGCGATATTTC –3'
*oxaG*_Y20A	5'- GCAAGGGCATCCTGGAGACGGCGATGATCGCCGAGAAGA TTACGCGATATTTC –3'
*oxaC*_D314A	5'– GATTTACTACTTCCGCCGCGTCTTTCACGCGTGGCCT GATTTGCCTGAAGGTAAAAAG –3'

Table 2. NMR SPECTRA

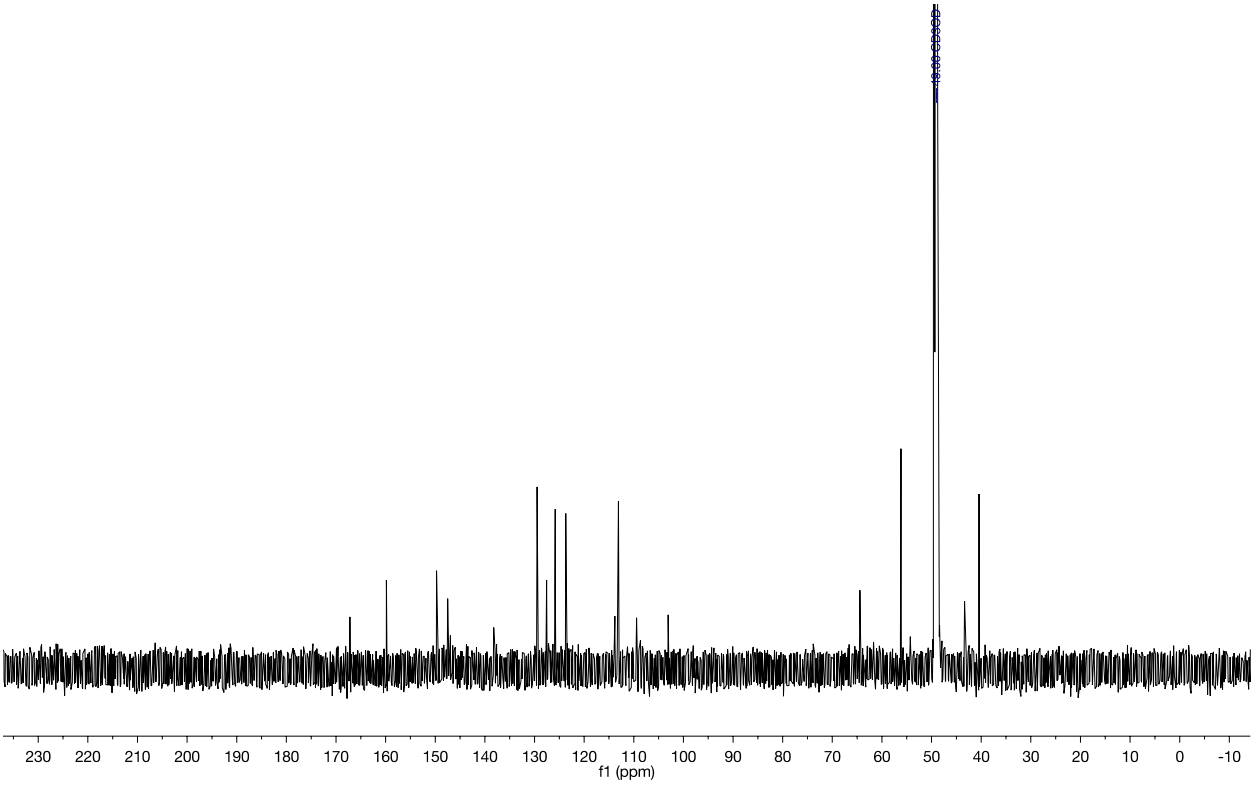


Position	Carbon	Hydrogen *J* Hz	HMBC correlations
2	103.10		
3	54.37		
3a	127.53		
4	125.84	7.63 (d, J = 7.7 Hz, 1H)	C3, C6, C7a
5	123.77	7.04 (t, J = 7.6 Hz, 1H)	C3a, C7
6	129.49	7.26 (t, *J* = 7.7 Hz, 1H)	C4, C7a
7	113.09	6.96 (d, *J* = 7.8 Hz, 1H)	C3a, C5
7a	149.76		
8	109.46	5.35 (s, 1H)	C2, C3a, C9, C10
9	147.51		
10	159.83		
12	127.17		
13	165.74		
15	108.80	8.27 (s, 1H)	C13, C12,(C16) C20
16	127.10		
18	138.31	7.88 (s, 1H)	
20	132.27	7.37 (s, 1H)	
21	41.69		
22	n.d	6.11 (s, 1H)	
23a (Trans)	113.85	5.08 (d, J = 17.0 hz, 1H)	
23b (Cis)	113.85	5.02 (bs, 1H)	
24	n.d	1.29 (s, 3H)	
25	n.d	1.32 (s, 3H)	
26	56.19	3.60 (s, 3H)	C8, C9, C10

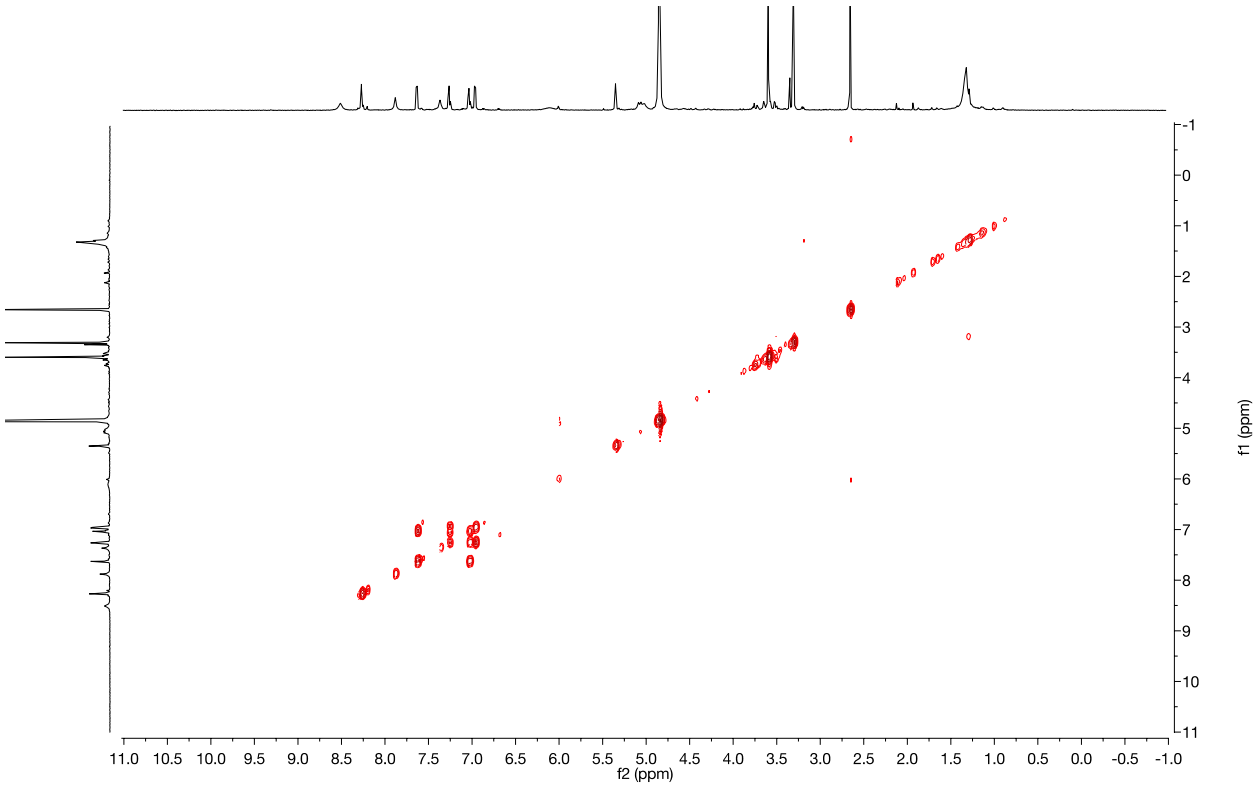
^{1}H NMR spectrum of glandicoline C in MeOH-d_4 at 600 MHz



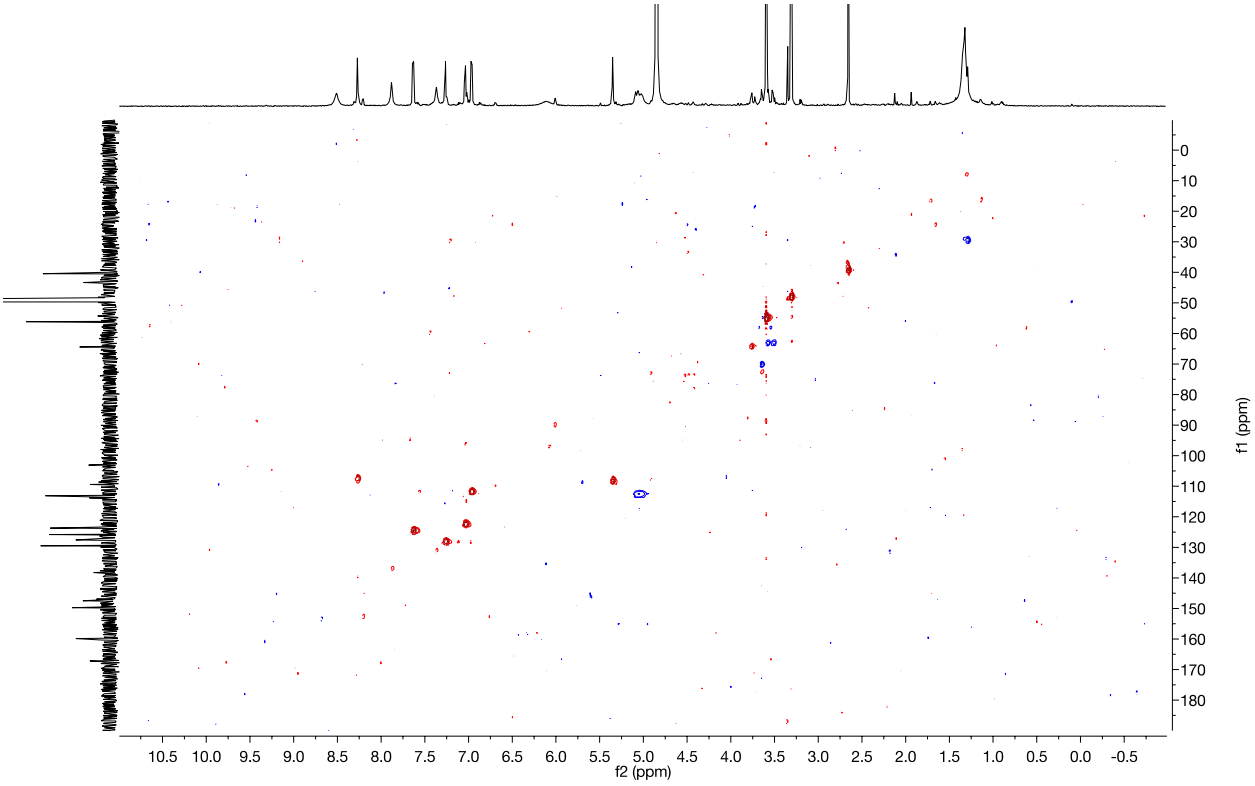
^{13}C NMR spectrum of glandicoline C in MeOH-d_4 at 125 MHz



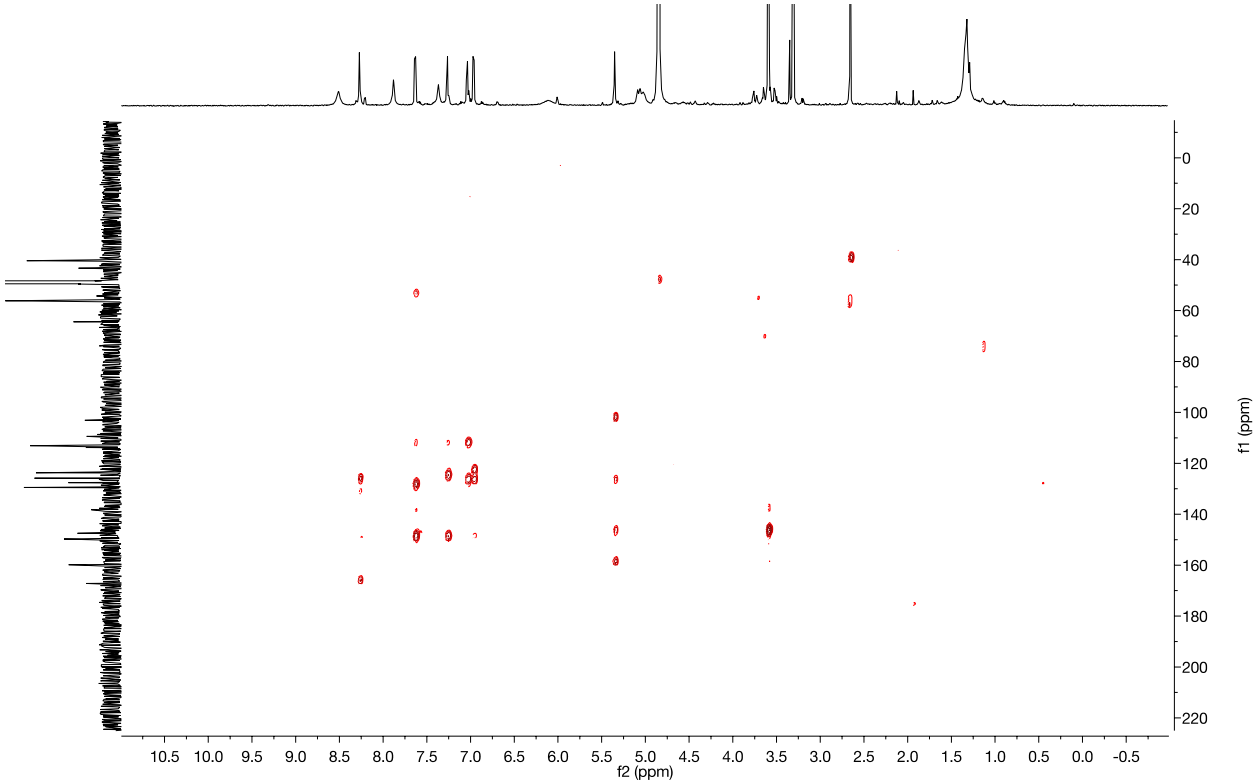
COSY NMR spectrum of glandicoline C in MeOH-d_4



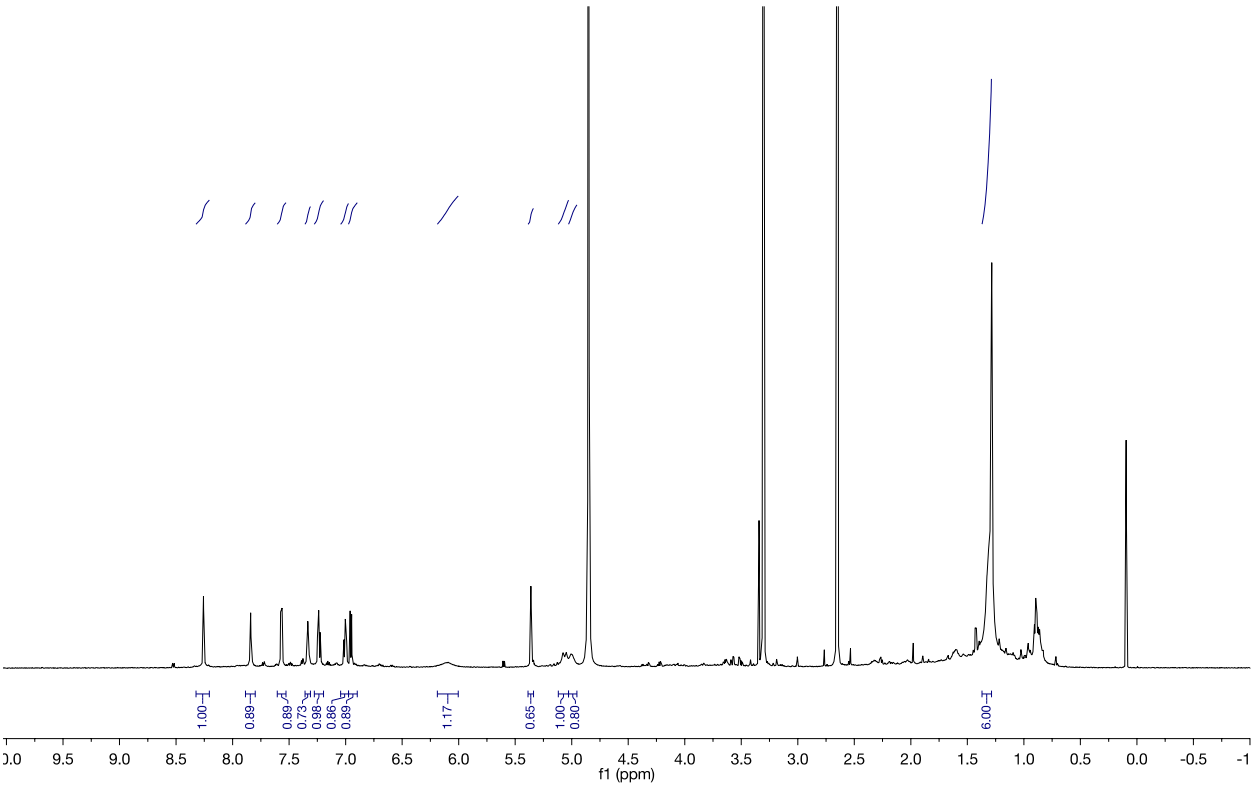
HSQC NMR spectrum of glandicoline C in MeOH-d_4



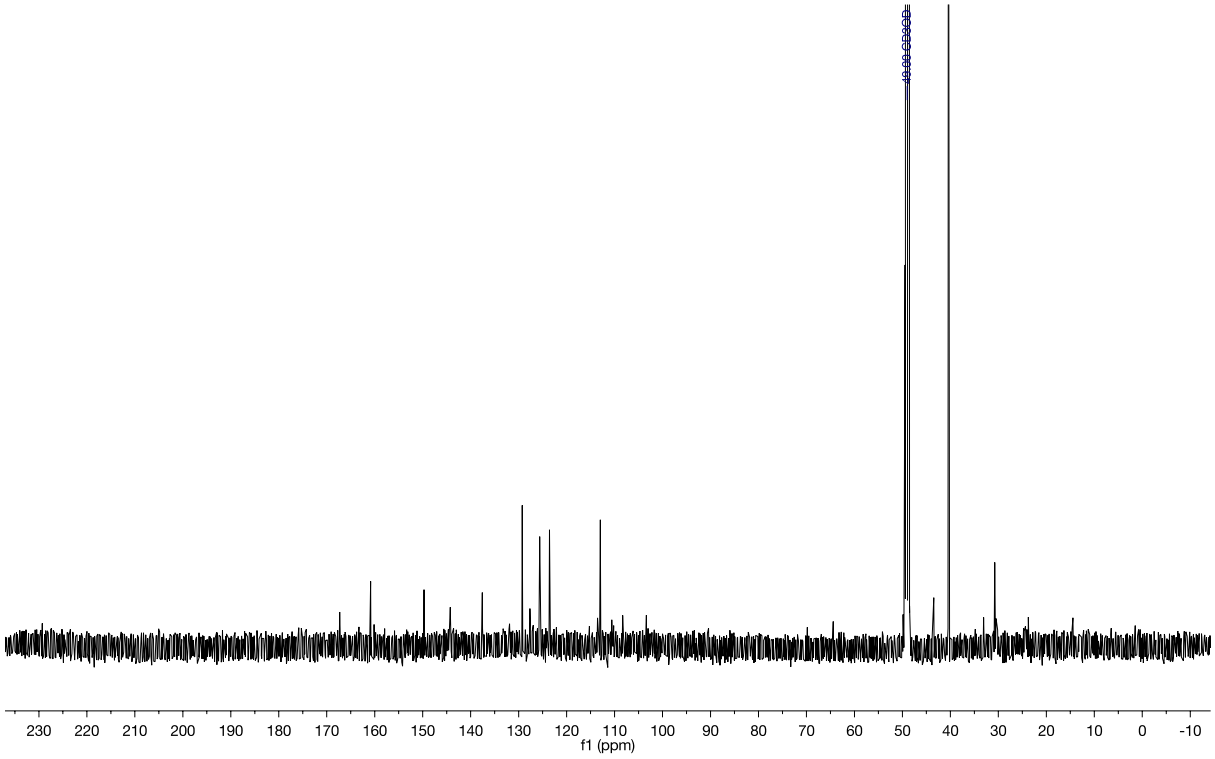
HMBC spectrum of glandicoline C in MeOH-d_4



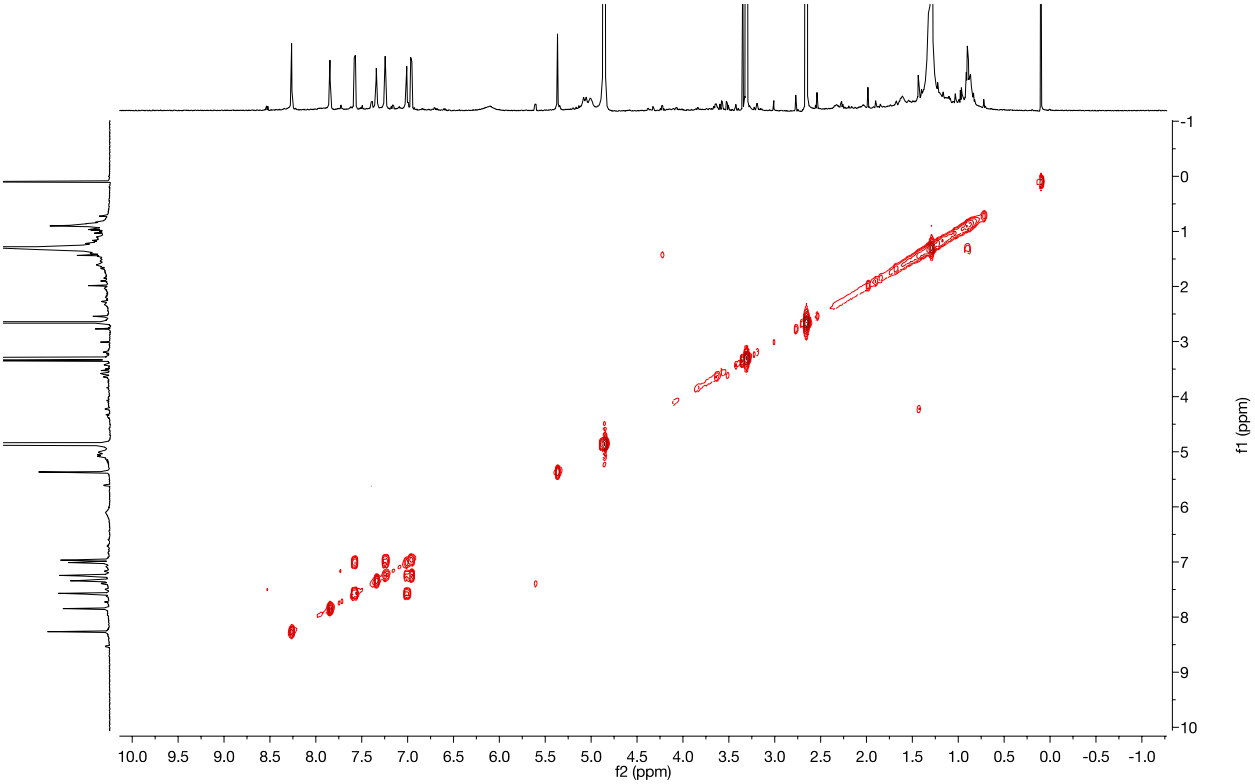
^{1}H NMR spectrum of glandicoline B in MeOH-d_4 at 600 MHz



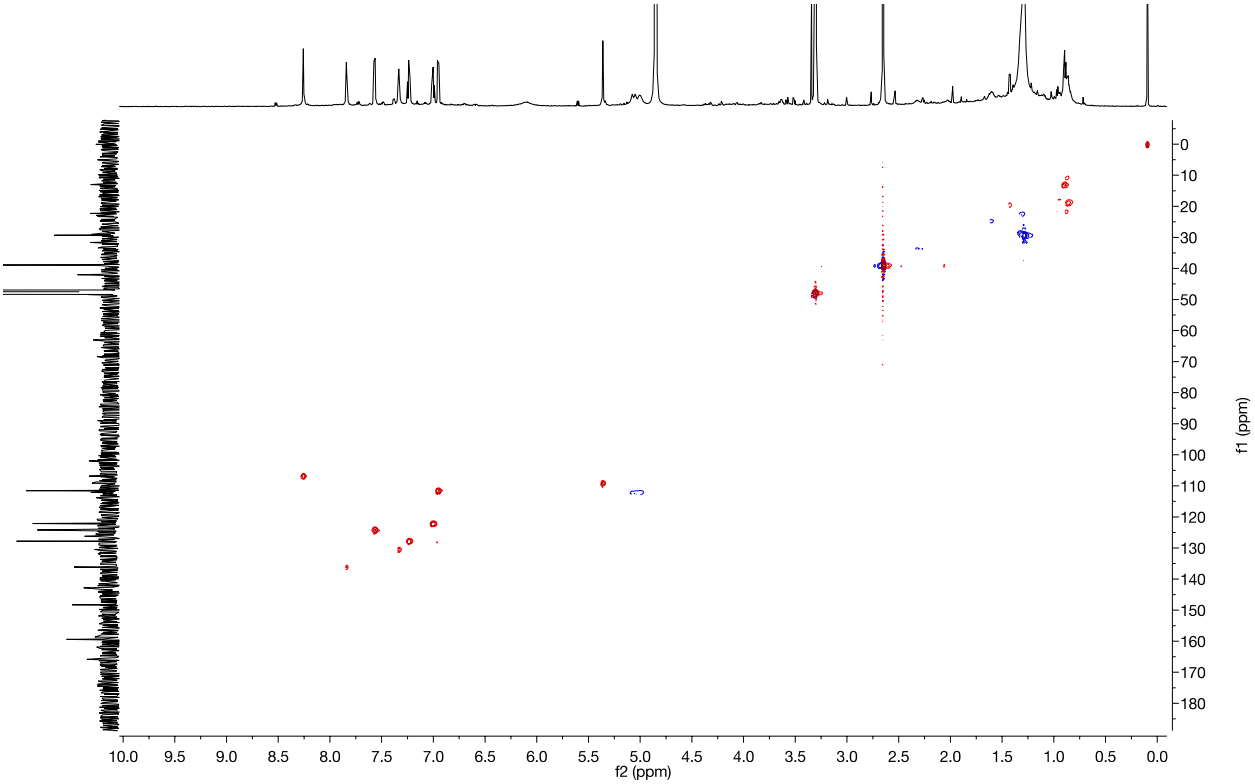
^{13}C NMR spectrum of glandicoline B in MeOH-d_4 at 125 MHz



COSY NMR spectrum of glandicoline B in MeOH-d_4



HSQC NMR spectrum of glandicoline B in MeOH-d_4



HMBC spectrum of glandicoline B in MeOH-d_4