Supporting Online Material for

Structural revision of glabramycins B and C, antibiotics from the fungus *Neosartorya glabra* by DFT calculations of NMR chemical shifts and coupling constants

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Table of Contents

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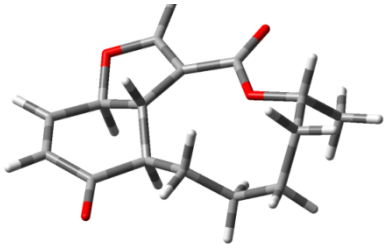
A. Cartesian coordinates for geometry-optimized structures

Glabramycin C (11*R*,20*R*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=chloroform)
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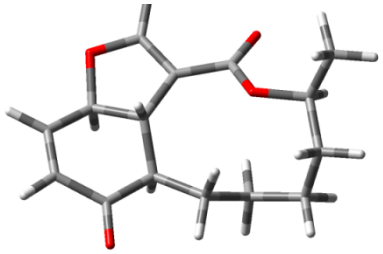
E = -1304.13968559 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	1.595216	3.589531	-0.081386
C	2.904341	3.857146	-0.200035
C	3.951634	2.828576	0.030075
C	3.542793	1.344526	0.287841
C	2.110598	1.139125	-0.278333
C	1.209280	2.214633	0.335920
C	4.656172	0.392431	-0.220812
O	2.761134	-1.689791	-0.305388
C	1.435570	-1.491180	-0.236258
C	1.155832	-0.056705	-0.115466
C	5.072482	-0.684701	0.802305
C	5.669423	-1.975229	0.203764
C	4.794893	-2.756904	-0.805009
C	3.342537	-3.020444	-0.390164
O	5.128533	3.165963	0.039244
O	0.611589	-2.398593	-0.264540
O	-0.137303	1.830994	-0.012061
C	-0.115596	0.462105	-0.069583
C	-1.393234	-0.203487	-0.091490
C	-2.576964	0.456952	-0.011650
C	-3.850944	-0.208167	-0.042286
C	-5.042663	0.441468	0.034468
C	-6.311374	-0.235607	0.005279
C	-7.510024	0.385758	0.075971
C	-8.761184	-0.385568	0.038586
O	-8.855956	-1.599108	-0.052212

Atom	Coordinates (Å)		
	X	Y	Z
O	-9.848536	0.421615	0.118375
C	3.176267	-3.785006	0.920355
H	0.828841	4.347880	-0.216270
H	3.271932	4.849292	-0.442568
H	3.488337	1.271101	1.386799
H	2.183815	1.333543	-1.361579
H	1.273296	2.137068	1.435597
H	4.314069	-0.069880	-1.148408
H	5.531662	0.998123	-0.466958
H	5.816187	-0.252580	1.485006
H	4.212707	-0.947512	1.423871
H	5.937330	-2.638009	1.035975
H	6.615454	-1.739724	-0.301127
H	4.769539	-2.228984	-1.764993
H	5.270095	-3.725063	-1.004254
H	2.820044	-3.558067	-1.189228
H	-1.352942	-1.282690	-0.180132
H	-2.577306	1.540545	0.080199
H	-3.845699	-1.293822	-0.131475
H	-5.052490	1.527009	0.121973
H	-6.305908	-1.321118	-0.079334
H	-7.589755	1.464932	0.161125
H	-10.628294	-0.158432	0.086676
H	2.118702	-3.938095	1.141175
H	3.655864	-4.765089	0.831076
H	3.638500	-3.254592	1.756961

Glabramycin C (11*R*,20*S*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=chloroform)
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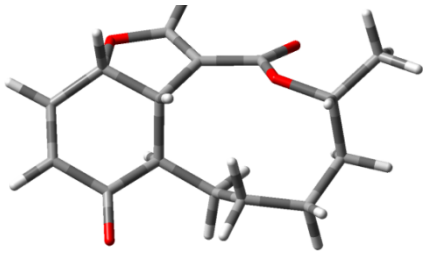
E = -1304.14555555 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	1.707017	3.580085	-0.474492
C	3.029220	3.793636	-0.575358
C	4.040501	2.792950	-0.135332
C	3.554727	1.418238	0.410699
C	2.181070	1.134333	-0.251611
C	1.265105	2.298392	0.141916
C	4.648850	0.345330	0.273540
O	2.689081	-1.722925	-0.509508
C	1.492230	-1.453768	0.054278
C	1.216546	-0.014829	0.034140
C	4.590462	-0.726408	1.377500
C	5.289013	-2.055617	1.035788
C	4.791405	-2.805228	-0.218046
C	3.282694	-3.041264	-0.300213
O	5.230141	3.076609	-0.183885
O	0.756143	-2.316260	0.517849
O	-0.072816	1.867269	-0.181221
C	-0.053280	0.505750	-0.017556
C	-1.327744	-0.164090	0.025191
C	-2.515388	0.492225	-0.012460
C	-3.787407	-0.176199	0.028989
C	-4.980593	0.474619	0.005060
C	-6.248757	-0.202617	0.051763
C	-7.447685	0.421928	0.035601
C	-8.699036	-0.348294	0.088200
O	-8.793908	-1.563817	0.146047

Atom	Coordinates (Å)		
	X	Y	Z
O	-9.786180	0.462670	0.063846
C	2.868874	-3.963943	-1.440329
H	0.972092	4.324487	-0.768201
H	3.433972	4.721897	-0.966405
H	3.378753	1.597447	1.485685
H	2.346488	1.164025	-1.341030
H	1.288637	2.400441	1.240740
H	4.564232	-0.109643	-0.716406
H	5.618532	0.849795	0.307805
H	5.056246	-0.319930	2.285132
H	3.551265	-0.928817	1.653054
H	5.191881	-2.721527	1.903257
H	6.365491	-1.878334	0.912472
H	5.101101	-2.282099	-1.130946
H	5.284070	-3.784553	-0.250328
H	2.893425	-3.428019	0.647285
H	-1.284835	-1.244361	0.106176
H	-2.519713	1.578105	-0.071533
H	-3.779336	-1.264047	0.085079
H	-4.992264	1.562273	-0.050040
H	-6.242566	-1.290121	0.104663
H	-7.527491	1.503265	-0.015275
H	-10.566217	-0.116655	0.101261
H	1.781344	-4.062611	-1.472644
H	3.301402	-4.958982	-1.297057
H	3.216865	-3.571782	-2.401375

Glabramycin C (11*S*,20*R*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=chloroform)
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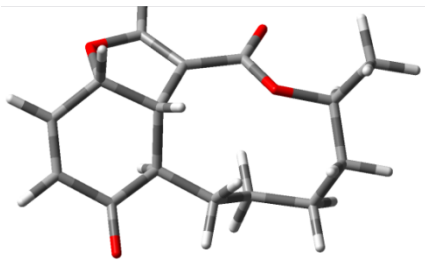
E = -1304.14931241 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	-1.741910	-3.552366	-0.888752
C	-2.801218	-3.846531	-0.121226
C	-3.590336	-2.796072	0.575635
C	-2.902138	-1.440687	0.684360
C	-2.302346	-1.044580	-0.701462
C	-1.381802	-2.143009	-1.252598
C	-3.725353	-0.352103	1.391674
O	-2.910076	1.712448	-0.941913
C	-1.673572	1.506142	-0.427196
C	-1.310567	0.094553	-0.582022
C	-4.937791	0.220947	0.634278
C	-5.306606	1.655337	1.063574
C	-4.242925	2.752315	0.836226
C	-3.726319	2.880911	-0.602711
O	-4.670043	-3.050257	1.092854
O	-0.974112	2.373781	0.079179
O	-0.043165	-1.791820	-0.756465
C	-0.053438	-0.441326	-0.535042
C	1.211261	0.205499	-0.298022
C	2.403472	-0.442664	-0.327333
C	3.659645	0.208802	-0.074577
C	4.859470	-0.429712	-0.098648
C	6.108906	0.236276	0.154915
C	7.316273	-0.371950	0.140565
C	8.545420	0.387746	0.412295
O	8.613913	1.580075	0.664445

Atom	Coordinates (Å)		
	X	Y	Z
O	9.645587	-0.403802	0.352998
C	-3.046440	4.212150	-0.913683
H	-1.151076	-4.343137	-1.344788
H	-3.119166	-4.872728	0.040717
H	-2.033924	-1.646572	1.330033
H	-3.105003	-0.836032	-1.411402
H	-1.321795	-2.061680	-2.346877
H	-4.060957	-0.759814	2.351421
H	-3.027947	0.453621	1.642444
H	-4.753556	0.215353	-0.443246
H	-5.802602	-0.430442	0.799042
H	-5.567917	1.657908	2.130119
H	-6.220718	1.947249	0.529846
H	-3.383137	2.623818	1.503367
H	-4.688797	3.715780	1.112205
H	-4.568147	2.756818	-1.292679
H	1.151618	1.265414	-0.074524
H	2.423188	-1.507215	-0.549043
H	3.633550	1.275042	0.147264
H	4.890648	-1.495945	-0.318425
H	6.079440	1.302573	0.373381
H	7.419558	-1.431938	-0.069290
H	10.409215	0.167267	0.543142
H	-2.268996	4.451719	-0.188860
H	-2.597250	4.187939	-1.910737
H	-3.803194	5.003512	-0.903392

Glabramycin C (11*S*,20*S*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=chloroform)
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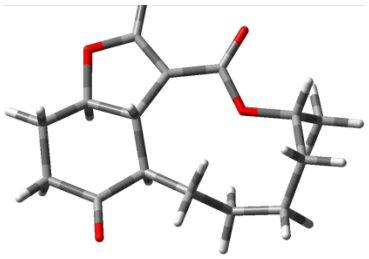
Atom	Coordinates (Å)		
	X	Y	Z
C	1.607475	3.580868	-0.855545
C	2.662649	3.920352	-0.106804
C	3.583232	2.916925	0.474288
C	3.090802	1.461107	0.536556
C	2.306272	1.079107	-0.764951
C	1.331473	2.169675	-1.262212
C	4.239354	0.491343	0.887641
O	2.973624	-1.698633	-0.733758
C	1.656891	-1.492995	-0.493878
C	1.321551	-0.076297	-0.613249
C	3.846519	-0.660089	1.833872
C	4.760760	-1.898365	1.754735
C	4.886885	-2.595149	0.382736
C	3.569882	-2.960587	-0.304893
O	4.649103	3.276819	0.957390
O	0.880292	-2.396458	-0.204282
O	0.008139	1.777778	-0.768664
C	0.050696	0.432713	-0.561694
C	-1.205117	-0.233632	-0.322897
C	-2.401196	0.408205	-0.335549
C	-3.652586	-0.253588	-0.085308
C	-4.854368	0.381509	-0.092799
C	-6.101268	-0.290548	0.157843
C	-7.308889	0.317090	0.159298
C	-8.536576	-0.446906	0.426563
O	-8.603251	-1.642725	0.661607

Atom	Coordinates (Å)		
	X	Y	Z
O	-9.637031	0.345053	0.383548
C	3.742685	-3.857193	-1.524784
H	0.933709	4.339749	-1.246259
H	2.899262	4.958579	0.107742
H	2.364387	1.476301	1.364970
H	3.044613	0.877891	-1.547008
H	1.264600	2.118665	-2.357886
H	4.645930	0.094636	-0.046496
H	5.040356	1.074483	1.350138
H	3.866733	-0.289298	2.867038
H	2.810360	-0.965798	1.663569
H	4.399894	-2.632217	2.487119
H	5.771789	-1.620904	2.080808
H	5.458517	-3.520854	0.522147
H	5.472542	-1.981840	-0.312723
H	2.876657	-3.428008	0.400571
H	-1.134819	-1.296474	-0.122392
H	-2.429542	1.475602	-0.542012
H	-3.620858	-1.322908	0.120029
H	-4.889366	1.450871	-0.296275
H	-6.069369	-1.359963	0.359953
H	-7.413593	1.380047	-0.034254
H	-10.399784	-0.228784	0.568939
H	4.177720	-4.817426	-1.230792
H	2.775546	-4.048732	-1.996919
H	4.404967	-3.389563	-2.260557

Glabramycin B (11*R*,20*R*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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E = -1305.37683163 Hartree

Atom	Coordinates (Å)		
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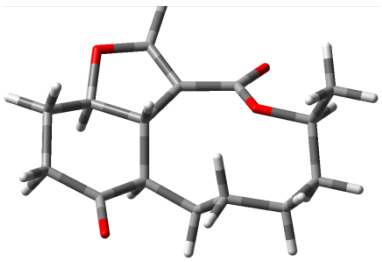
C	1.542080	3.597615	-0.172234
C	2.967721	3.867359	0.341818
C	3.971282	2.748007	0.064825
C	3.529890	1.262934	0.243194
C	2.084508	1.115232	-0.319113
C	1.186817	2.203416	0.281242
C	4.601631	0.303312	-0.334467
O	2.724434	-1.742350	-0.154831
C	1.402435	-1.521267	-0.207660
C	1.128435	-0.082969	-0.142987
C	5.131936	-0.727190	0.685586
C	5.664233	-2.047084	0.089393
C	4.699307	-2.855582	-0.808615
C	3.281177	-3.080661	-0.271138
O	-0.162968	1.801448	-0.056665
C	-0.142699	0.437004	-0.101402
C	-1.422260	-0.228001	-0.108571
C	-2.604188	0.436518	-0.034831
C	-3.879803	-0.226338	-0.052459
C	-5.069752	0.427906	0.016483
C	-6.339008	-0.248312	-0.000581
C	-7.537485	0.375237	0.062173
C	-8.789726	-0.393397	0.038057
O	-8.887307	-1.609293	-0.034722
O	-9.874675	0.416033	0.107334
O	5.119545	3.038593	-0.224866
H	2.162001	1.290999	-1.406085

Atom	Coordinates (Å)		
	X	Y	Z
H	3.477707	1.134111	1.336484
O	0.573080	-2.423500	-0.285116
C	3.197411	-3.811459	1.065421
H	1.502352	3.660908	-1.265247
H	0.846856	4.338946	0.232806
H	2.935920	3.985464	1.434821
H	3.383075	4.791146	-0.066036
H	1.255602	2.146339	1.379651
H	4.179644	-0.202357	-1.203485
H	5.436993	0.907650	-0.696371
H	5.942636	-0.267855	1.266973
H	4.343795	-0.961341	1.406025
H	5.997506	-2.679574	0.921730
H	6.564815	-1.843902	-0.504894
H	4.602597	-2.367012	-1.784764
H	5.144243	-3.838530	-1.005617
H	2.686543	-3.621514	-1.014715
H	-1.386975	-1.308154	-0.183913
H	-2.602314	1.521312	0.040322
H	-3.877656	-1.313262	-0.124979
H	-5.077343	1.514505	0.087342
H	-6.332644	-1.334982	-0.068814
H	-7.614826	1.455675	0.131091
H	-10.658553	-0.159299	0.085627
H	2.155074	-3.915925	1.374785
H	3.627679	-4.812887	0.963915
H	3.744747	-3.281587	1.849462

Glabramycin B (11*R*,20*S*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=methanol)
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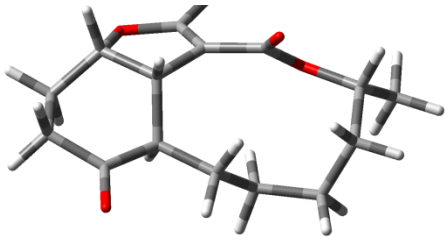
E = -1305.37987451 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	-1.701764	3.420867	0.743064
C	-3.128831	3.767946	0.255945
C	-4.054871	2.582632	-0.057437
C	-3.439574	1.327039	-0.710886
C	-2.126622	1.028282	0.064364
C	-1.225669	2.261114	-0.102068
C	-4.456392	0.192140	-0.922069
O	-2.544623	-1.783593	0.252786
C	-1.397180	-1.501222	-0.397480
C	-1.129257	-0.061682	-0.303534
C	-5.036664	-0.483717	0.335671
C	-5.520800	-1.932881	0.102603
C	-4.517154	-2.922253	-0.530493
C	-3.163853	-3.100289	0.171992
O	0.119416	1.795946	0.170179
C	0.127030	0.467895	-0.156164
C	1.409933	-0.184482	-0.235901
C	2.589209	0.463424	-0.058162
C	3.867576	-0.190250	-0.133373
C	5.052544	0.451675	0.046167
C	6.325381	-0.213523	-0.031183
C	7.518748	0.398606	0.142977
C	8.775090	-0.357419	0.046447
O	8.880466	-1.552495	-0.185922
O	9.854012	0.437456	0.249678
O	-5.253839	2.677639	0.144494
H	-2.383416	0.904526	1.128987

Atom	Coordinates (Å)		
	X	Y	Z
H	-3.135526	1.659726	-1.716809
O	-0.691379	-2.339644	-0.944020
C	-3.241948	-3.661061	1.586904
H	-1.713713	3.131444	1.799294
H	-1.050183	4.293686	0.641088
H	-3.052754	4.327074	-0.688102
H	-3.649339	4.417656	0.962794
H	-1.226310	2.556594	-1.162368
H	-5.277121	0.597163	-1.525001
H	-3.960360	-0.550682	-1.551182
H	-4.294096	-0.483432	1.136418
H	-5.882652	0.107407	0.701243
H	-6.402887	-1.915198	-0.551341
H	-5.872904	-2.334276	1.060987
H	-4.989568	-3.911263	-0.582417
H	-4.317718	-2.636129	-1.569355
H	-2.516300	-3.732657	-0.441060
H	1.381918	-1.245399	-0.459804
H	2.581583	1.530522	0.151079
H	3.871770	-1.258623	-0.346136
H	5.053114	1.519480	0.259659
H	6.326479	-1.281257	-0.244453
H	7.588678	1.460198	0.357967
H	10.641084	-0.128362	0.170698
H	-2.240141	-3.769340	2.011894
H	-3.715543	-4.647473	1.569806
H	-3.826094	-3.010904	2.244234

Glabramycin B (11*S*,20*R*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

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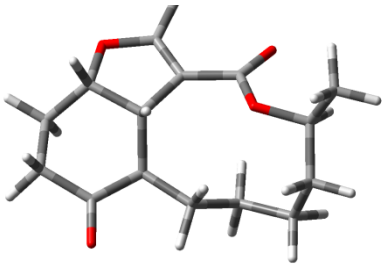
# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=methanol)
```

E = -1305.38013316 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	2.154489	-3.597423	-0.206503
C	3.687047	-3.669032	-0.258419
C	4.341313	-2.336053	-0.618005
C	3.424767	-1.115370	-0.531149
C	2.586927	-1.250137	0.785994
C	1.707670	-2.524659	0.786992
C	4.136200	0.239760	-0.722098
O	1.353160	2.133158	0.490162
C	1.906513	1.201732	1.293423
C	1.532195	-0.175791	0.930930
C	3.331603	1.217941	-1.612352
C	3.673860	2.714440	-1.458424
C	3.432078	3.365285	-0.078459
C	1.987337	3.457421	0.450555
O	0.359748	-2.064546	0.448180
C	0.314339	-0.711568	0.653513
C	-0.975007	-0.070262	0.579526
C	-2.134599	-0.736455	0.350521
C	-3.414007	-0.086951	0.259670
C	-4.580821	-0.745596	0.028540
C	-5.852201	-0.079807	-0.059835
C	-7.029780	-0.704240	-0.290953
C	-8.284046	0.056334	-0.367005
O	-8.403007	1.265898	-0.237806
O	-9.346057	-0.752003	-0.605905
O	5.513684	-2.276899	-0.948907
H	3.276193	-1.250637	1.636616

Atom	Coordinates (Å)		
	X	Y	Z
H	2.715893	-1.250859	-1.363702
O	2.710518	1.456918	2.177644
C	1.055335	4.321218	-0.385260
H	1.733487	-4.569521	0.063797
H	1.759617	-3.345006	-1.196125
H	4.032456	-4.422809	-0.972137
H	4.090320	-3.968972	0.719120
H	1.649612	-2.934047	1.802125
H	4.338634	0.676958	0.260661
H	5.115183	0.054183	-1.174606
H	3.501381	0.939529	-2.660622
H	2.261188	1.082033	-1.440668
H	3.119878	3.269319	-2.225766
H	4.735588	2.862355	-1.696688
H	4.039366	2.865979	0.680347
H	3.800166	4.398285	-0.119821
H	2.024364	3.832797	1.478069
H	-0.974141	1.008259	0.703338
H	-2.107248	-1.816231	0.225345
H	-3.435321	0.995151	0.384806
H	-4.566305	-1.827052	-0.098127
H	-5.865921	1.001497	0.067724
H	-7.087465	-1.779501	-0.427431
H	-10.132681	-0.181296	-0.642849
H	0.055415	4.345762	0.056589
H	1.438173	5.344929	-0.425955
H	0.970537	3.943964	-1.408191

Glabramycin B (11*S*,20*S*) isomer



(conjugated olefin sidechain not shown)

Gaussian keywords:

```
# opt b3lyp/6-31g(d,p) scrf=(iefpcm,solvent=methanol)
```

E = -1305.38985208 Hartree

Atom	Coordinates (Å)		
	X	Y	Z
C	1.564700	3.543985	-0.197347
C	3.053270	3.877014	-0.255677
C	3.930664	2.746725	0.263992
C	3.249333	1.388540	0.526145
C	2.266773	1.076235	-0.662609
C	1.299085	2.263399	-0.976541
C	4.301450	0.302231	0.815845
O	2.831824	-1.755226	-0.734524
C	1.550199	-1.487286	-0.392797
C	1.262182	-0.056888	-0.468817
C	3.859023	-0.802445	1.792138
C	4.675154	-2.106093	1.685015
C	4.734764	-2.786009	0.300490
C	3.386889	-3.057891	-0.370405
O	-0.045408	1.800008	-0.649436
C	-0.005835	0.462594	-0.443703
C	-1.273696	-0.198903	-0.245036
C	-2.463887	0.453213	-0.271955
C	-3.724362	-0.206522	-0.062956
C	-4.922922	0.434691	-0.083897
C	-6.175914	-0.239375	0.127647
C	-7.383135	0.369864	0.114420
C	-8.616887	-0.395919	0.341376
O	-8.690263	-1.596850	0.554543
O	-9.714505	0.397354	0.288493
O	5.118449	2.938061	0.466593
H	2.892345	0.880247	-1.540524

Atom	Coordinates (Å)		
	X	Y	Z
H	2.636290	1.553225	1.427266
O	0.756357	-2.362351	-0.057722
C	3.491677	-3.907390	-1.630783
H	0.963023	4.362258	-0.602813
H	1.249484	3.399110	0.841724
H	3.293843	4.780873	0.312179
H	3.365680	4.075881	-1.290348
H	1.299208	2.467850	-2.052902
H	4.606730	-0.130705	-0.139901
H	5.188432	0.797504	1.220642
H	3.954198	-0.425321	2.818941
H	2.796334	-1.029097	1.672410
H	4.269959	-2.822679	2.411224
H	5.708246	-1.909653	2.000735
H	5.350286	-2.200834	-0.393246
H	5.245876	-3.749618	0.416230
H	2.691544	-3.524290	0.332730
H	-1.219657	-1.264977	-0.060633
H	-2.481735	1.524711	-0.456475
H	-3.702340	-1.279866	0.121648
H	-4.950534	1.507703	-0.267345
H	-6.148000	-1.312300	0.310978
H	-7.481652	1.436233	-0.062399
H	-10.484768	-0.174893	0.446990
H	2.506376	-4.040063	-2.085873
H	3.893850	-4.895686	-1.388129
H	4.154226	-3.436217	-2.36396

The energies of the eight structures calculated above are summarized below:

Glabramycin C

	Energy / Hartree	Relative Energy / Hartree	Relative Energy / kcal mol^{-1}
(11*R*,20*R*)	-1304.13968559	0.01545280	9.69678
(11*R*,20*S*)	-1304.14555555	0.00958284	6.01332
(11*S*,20*R*)	-1304.14931241	0.00582598	3.65586
(11*S*,20*S*)	-1304.15513839	0.00000000	0.00000

Glabramycin B

	Energy / Hartree	Relative Energy / Hartree	Relative Energy / kcal mol^{-1}
(11*R*,20*R*)	-1305.37683163	0.01302045	8.17046
(11*R*,20*S*)	-1305.37987451	0.00997757	6.26102
(11*S*,20*R*)	-1305.38013316	0.00971892	6.09871
(11*S*,20*S*)	-1305.38985208	0.00000000	0.00000

B. Calculation of ^{13}C chemical shifts

Glabramycin C

Configuration	*a*	*b*	r^2
(11*R*,20*R*)	-4.29145	1.03285	0.99082
(11*R*,20S)	-5.30962	1.03941	0.99275
(11*S*,20*R*)	-2.20775	1.02481	0.99716
(11*S*,20*S*)	-3.85632	1.03802	0.99768

Table S1. Scaling constants a and b determined by least-squares linear regression between the calculated chemical shifts δ_{calcd} and the experimental ones δ_{exp}, and correlation coefficient r^2. All carbon atoms were included in the linear regression calculation. The NMR peak assignments were unchanged from the original report.[2]

Carbon Atom	Exp Shift	Predicted Chemical shift δ_{scaled}			
		(11*R*,20*R*)	(11*R*,20S)	(11*S*,20*R*)	(11*S*,20*S*)
1	170.8	163.1	163.2	163.9	164.4
2	122.2	119.1	119.0	120.1	120.4
3	145.5	145.1	145.0	146.0	146.2
4	134.5	134.0	133.9	134.8	135.4
5	140.0	140.3	139.9	141.2	141.3
6	135.9	135.6	135.2	136.1	137.5
7	122.9	123.5	122.4	123.5	124.3
8	163.1	166.1	165.9	162.9	165.5
9	112.0	112.8	112.9	115.1	113.0
10	44.0	53.1	52.5	44.8	48.1
11	77.5	81.9	82.4	79.2	77.7
12	137.6	147.5	147.9	138.3	139.1
13	132.5	126.3	126.4	132.2	130.9
14	198.7	199.3	198.6	199.7	198.6
15	48.3	56.5	56.0	49.8	49.8
16	22.9	23.7	20.0	19.4	21.7
17	23.6	27.7	23.5	19.8	25.0
18	32.4	20.6	23.1	27.2	25.1
19	24.8	26.7	27.3	28.7	28.6
20	73.2	71.6	71.9	80.3	71.7
22	164.9	160.2	163.2	163.3	164.2
23	20.6	13.2	17.7	21.4	19.4

Table S2. Experimental chemical shifts, and chemical shifts predicted for all of the suspected stereoisomers. Predicted shifts were scaled using the scaling constants in Table S1, $\delta_{\text{scaled}} = a + b \cdot \delta_{\text{calcd}}$. NMR peak assignments were unchanged from the original report.[2] $\Delta\delta$ values derived from this table are plotted in Figure 2 in the main text.

[2] H. Jayasuriya, D. Zink, A. Basilio, F. Vicente, J. Collado, G. Bills, M. L. Goldman, M. Motyl, J. Huber and G. Dezeny, *J. Antibiot.*, 2009, **62**, 265-269.

Glabramycin C, with reassignments of C18 and C19

Configuration	*a*	*b*	r^2
(11*R*,20*R*)	-3.93163	1.02561	0.99258
(11*R*,20S)	-4.92265	1.03194	0.99421
(11*S*,20*R*)	-1.84625	1.01786	0.99812
(11*S*,20*S*)	-3.52952	1.03166	0.99906

Table S3. Scaling constants a and b determined by least-squares linear regression between the calculated chemical shifts δ_{calcd} and the experimental ones δ_{exp}, and correlation coefficient r^2. The carboxylate C1 atom was excluded from the linear regression calculation. The assignments for the C18 and C19 NMR peaks were exchanged.

Carbon Atom	Exp Shift	Predicted Chemical shift δ_{scaled}			
		(11*R*,20*R*)	(11*R*,20S)	(11*S*,20*R*)	(11*S*,20*S*)
1	170.8	162.3	162.3	163.2	163.7
2	122.2	118.6	118.5	119.7	120.0
3	145.5	144.4	144.3	145.4	145.7
4	134.5	133.4	133.3	134.2	134.9
5	140.0	139.7	139.3	140.6	140.8
6	135.9	135.0	134.5	135.5	136.9
7	122.9	123.0	121.8	123.0	123.8
8	163.1	165.3	165.1	162.1	164.8
9	112.0	112.4	112.5	114.6	112.6
10	44.0	53.1	52.5	44.8	48.1
11	77.5	81.6	82.2	79.0	77.5
12	137.6	146.8	147.2	137.7	138.5
13	132.5	125.8	125.8	131.7	130.4
14	198.7	198.3	197.5	198.6	197.7
15	48.3	56.4	55.9	49.8	49.8
16	22.9	23.9	20.2	19.6	21.8
17	23.6	27.8	23.7	20.0	25.2
18	24.8	20.8	23.3	27.4	25.3
19	32.4	26.8	27.4	28.9	28.7
20	73.2	71.4	71.8	80.1	71.6
22	164.9	159.4	162.4	162.6	163.5
23	20.6	13.4	18.0	21.6	19.6

Table S4. Experimental chemical shifts, and chemical shifts predicted for all of the suspected stereoisomers. Predicted shifts were scaled using the scaling constants in Table S3, $\delta_{\text{scaled}} = a + b \cdot \delta_{\text{calcd}}$. The assignments for the C18 and C19 NMR peaks were exchanged. $\Delta\delta$ values derived from this table are plotted in Figure 3 in the main text.

Glabramycin B

Configuration	*a*	*b*	r^2
(11*R*,20*R*)	-3.30180	1.03367	0.99282
(11*R*,20S)	-1.92713	1.02606	0.99396
(11*S*,20*R*)	-0.73100	1.02416	0.99331
(11*S*,20*S*)	-1.58349	1.02256	0.99651

Table S5. Scaling constants a and b determined by least-squares linear regression between the calculated chemical shifts δ_{calcd} and the experimental ones δ_{exp}, and correlation coefficient r^2. The carboxylate C1 atom was excluded from the linear regression calculation. The NMR peak assignments were unchanged from the original report.

Carbon Atom	Exp Shift	Predicted Chemical shift δ_{scaled}			
		(11*R*,20*R*)	(11*R*,20S)	(11*S*,20*R*)	(11*S*,20*S*)
1	170.1	165.0	165.2	166.1	165.0
2	124.5	120.0	120.4	120.5	120.6
3	145.2	146.8	147.1	148.1	146.9
4	136.2	135.2	135.3	134.9	135.6
5	140.3	142.2	142.2	143.3	142.3
6	137.3	136.9	136.3	135.4	137.9
7	123.3	125.2	124.1	125.0	125.3
8	164.5	167.8	166.2	156.4	165.9
9	110.9	114.3	115.1	117.3	111.2
10	49.4	54.4	51.2	52.3	48.6
11	82.0	84.3	86.1	83.5	82.6
12	35.9	26.4	28.3	26.3	25.9
13	26.0	37.5	38.6	36.2	34.9
14	213.3	211.6	212.1	213.8	213.7
15	50.6	57.9	58.1	55.4	52.6
16	23.7	22.6	23.3	20.9	23.3
17	25.2	29.0	22.4	29.8	25.8
18	24.9	21.6	22.6	23.5	27.1
19	32.9	27.7	28.7	25.7	30.5
20	74.1	72.0	70.9	76.4	73.0
22	170.1	162.0	163.6	167.6	165.4
23	20.3	15.2	17.9	18.3	21.4

Table S6. Experimental chemical shifts, and chemical shifts predicted for all of the suspected stereoisomers. Predicted shifts were scaled using the scaling constants in Table S5, $\delta_{\text{scaled}} = a + b \cdot \delta_{\text{calcd}}$. The NMR peak assignments were unchanged from the original report.[2]

Glabramycin B, with reassignments of C12 and C13

Configuration	*a*	*b*	r^2
(11*R*,20*R*)	-3.44801	1.03527	0.99591
(11*R*,20S)	-2.06047	1.02753	0.99681
(11*S*,20*R*)	-0.85830	1.02558	0.99607
(11*S*,20*S*)	-1.69922	1.02383	0.99900

Table S7. Scaling constants a and b determined by least-squares linear regression between the calculated chemical shifts δ_{calcd} and the experimental ones δ_{exp}, and correlation coefficient r^2. The carboxylate C1 atom was excluded from the linear regression calculation. The assignments for the C12 and C13 NMR peaks were exchanged.

Carbon Atom	Exp Shift	Predicted Chemical shift δ_{scaled}			
		(11*R*,20*R*)	(11*R*,20S)	(11*S*,20*R*)	(11*S*,20*S*)
1	170.1	165.2	165.3	166.2	165.1
2	124.5	120.1	120.4	120.6	120.6
3	145.2	146.9	147.1	148.2	147.0
4	136.2	135.2	135.4	135.0	135.7
5	140.3	142.3	142.3	143.3	142.4
6	137.3	137.0	136.4	135.5	138.0
7	123.3	125.3	124.2	125.0	125.3
8	164.5	167.9	166.4	156.5	166.0
9	110.9	114.3	115.2	117.4	111.3
10	49.4	54.4	51.1	52.2	48.5
11	82.0	84.3	86.1	83.5	82.6
12	26.0	26.3	28.2	26.2	25.8
13	35.9	37.4	38.5	36.1	34.8
14	213.3	211.8	212.3	214.0	213.9
15	50.6	57.8	58.1	55.3	52.6
16	23.7	22.5	23.2	20.8	23.3
17	25.2	28.9	22.3	29.7	25.7
18	24.9	21.5	22.5	23.4	27.0
19	32.9	27.6	28.7	25.6	30.4
20	74.1	72.0	70.8	76.4	73.0
22	170.1	162.1	163.7	167.7	165.5
23	20.3	15.0	17.8	18.2	21.4

Table S8. Experimental chemical shifts, and chemical shifts predicted for all of the suspected stereoisomers. Predicted shifts were scaled using the scaling constants in Table S7, $\delta_{\text{scaled}} = a + b \cdot \delta_{\text{calcd}}$. The assignments for the C12 and C13 NMR peaks were exchanged. $\Delta\delta$ values derived from this table are plotted in Figure 4 in the main text.

C. Sample Gaussian input file for the calculation of coupling constants

The following is a template Gaussian input file used the calculation of proton-proton coupling constants. The core basis functions for hydrogen atoms are augmented and decontracted, while unmodified 6-31G(d,p) basis set is used for carbon and oxygen atoms. The Gaussian program is instructed to calculate the Fermi contact term only for spin-spin coupling constants, and calculate the coupling constants for hydrogen atoms only. The file was constructed from the work of Bally and Rablen.[3]

```
%nprocshared=4
%chk=path_to_checkfile.chk
# nmr=(giao,fconly,readatoms) b3lyp/gen geom=connectivity int=nobasistransform

Title: coupling constant calculation

0 1
 atom coordinates section

 atom connectivity section

C 0
6-31G(d,p)
****
O 0
6-31G(d,p)
****
H 0
S   1 1.00       0.000000000000
0.1873113696D+02  0.1000000000D+01
S   1 1.00       0.000000000000
0.2825394365D+01  0.1000000000D+01
S   1 1.00       0.000000000000
0.6401216923D+00  0.1000000000D+01
S   1 1.00       0.000000000000
0.1612777588D+00  0.1000000000D+01
S   1 1.00       0.000000000000
0.5619341088D+02  0.1000000000D+01
S   1 1.00       0.000000000000
0.1685802326D+03  0.1000000000D+01
S   1 1.00       0.000000000000
0.5057406979D+03  0.1000000000D+01
S   1 1.00       0.000000000000
0.1517222094D+04  0.1000000000D+01
P   1 1.00       0.000000000000
0.1100000000D+01  0.1000000000D+01
****

atoms=H
```

[3] T. Bally and P. R. Rablen, *J. Org. Chem.*, 2011, **76**, 4818-4830.