Skeleton Reassignment of Type C Polycyclic Polyprenylated Acylphloroglucinols

Xing-Wei Yang, Jing Yang, and Gang Xu

Supporting Information

Table of contents

SI-1. Computational Details of 3 and 3a

All computations were performed using Gaussian 09[1] and figured using GaussView 5.0.[2] Conformation search using molecular mechanics calculations was performed in Discovery Studio 3.5 Client with MMFF force field with 10 kcal mol^{-1} upper energy limit.[3]

For the calculations of ^{13}C NMR chemical shifts, mPW1PW91/6-31G(d,p) method was used to optimize the selected conformations. For all optimized structures, vibrational spectra were calculated to ensure that no imaginary frequencies for energy minimum were obtained. NMR calculations were performed at the levels of mPW1PW91/6-31G(d,p) with the gauge-independent atomic orbital (GIAO) method.[4] The solvent effect was considered by using chloroform for **3** and **3a** in the calculations to resemble the experimental condition. The polarized continuum model (PCM) of Tomasiet al. was used.[5] The calculated ^{13}C NMR chemical shifts were analyzed by subtracting the isotopic shifts for TMS calculated with the same methods.[4] Different conformers for structures **3** and **3a** were considered. The ^{13}C NMR chemical shifts in each compound were considered as the average values of the same atoms in the different conformers. The average values were obtained by the Boltzmann distributions, using the relative Gibbs free energies as weighting factors.[6] The differences $\Delta\delta$ were determined by subtracting the experimental chemical shifts δ_{exptl} from the calculated chemical shifts δ_{calcd}.

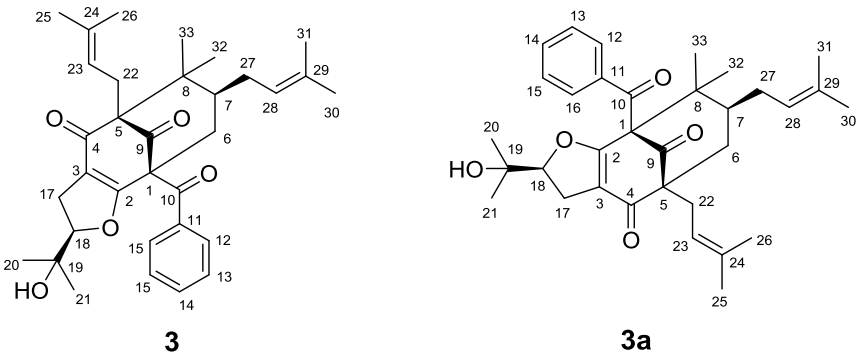

Figure S1. The proposed structures of **3** and **3a**.

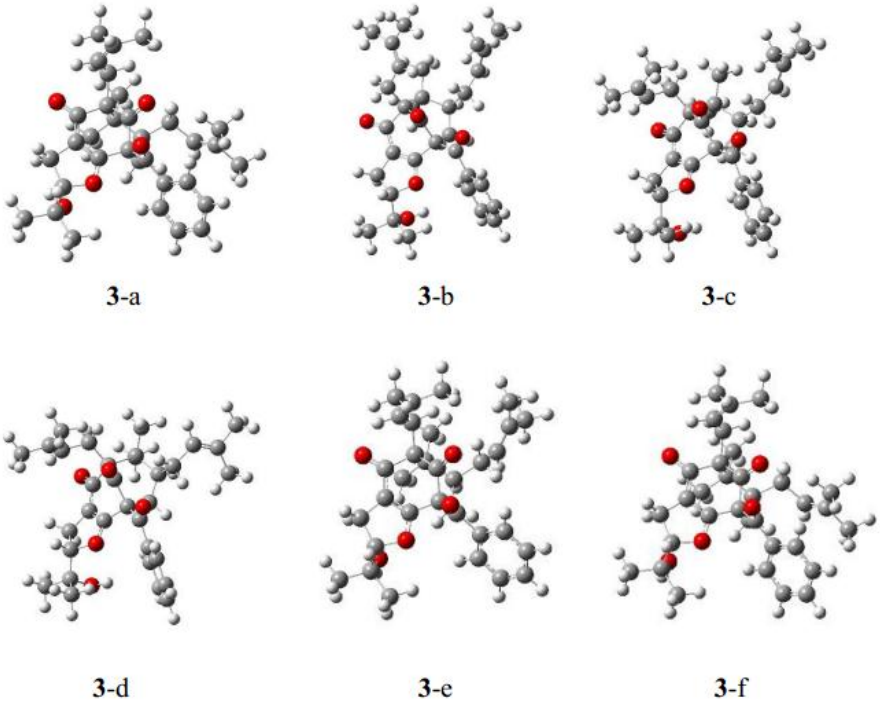

Figure S2. Optimized geometries of predominant conformers for compound **3** at the mPW1PW91/6-31G(d,p) level in the gas phase.

Table S1. Important Thermodynamic Parameters (a.u.) and Boltzmann Distributions of the Optimized 3 at mPW1PW91/6-31G(d,p) Level in Gas Phase

Conformations	E+ZPE[a]	G[b]	%[c]
3-a	-1657.861019	-1657.932260	3.0
3-b	-1657.852380	-1657.923888	2.6
3-c	-1657.856103	-1657.927987	42.3
3-d	-1657.854100	-1657.924669	1.4
3-e	-1657.857189	-1657.929604	50.1
3-f	-1657.860818	-1657.932101	0.6
3-g	-1657.850908	-1657.922761	0.0
3-h	-1657.850341	-1657.921765	0.0
3-i	-1657.858723	-1657.929445	0.0
3-j	-1657.857072	-1657.928873	0.0

[a] E+ZPE: total energy with zero point energy (ZPE). [b] G: Gibbs free energy in the gas phase at mPW1PW91/6-31G(d,p) level. [c] %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S2. Optimized Z-Matrixes of 3 in Gas Phase (Å) at mPW1PW91/6-31G(d,p) Level

3-a				**3**-b			
C	-2.45284	1.265565	0.267577	C	0.14746	-2.41729	0.366834
C	-1.34142	2.011151	-0.2613	C	-1.21718	-1.97861	0.183273

C	-0.12258	1.465071	-0.42758	C	-1.55803	-0.70486	-0.1156
C	0.251325	0.031002	-0.24552	C	-0.57719	0.433318	-0.14267
C	-1.07184	-0.76458	-0.29221	C	0.601215	-0.32877	-0.83099
C	-2.1697	-0.21328	0.618864	C	1.279205	-1.37031	0.072346
C	0.823233	-0.2263	1.186242	C	-0.1627	0.871991	1.304454
C	-0.15909	-0.9069	2.167585	C	1.340568	0.750821	1.55467
C	-1.59237	-0.2856	2.141587	C	1.808778	-0.72931	1.444492
O	-1.17387	-1.80592	-0.8917	O	0.824551	-0.22908	-2.01046
O	-3.54486	1.770898	0.487033	O	0.42408	-3.57069	0.653817
C	-2.52923	-1.0893	3.054398	C	3.334747	-0.78964	1.56261
C	-1.49618	1.107866	2.797385	C	1.275668	-1.50174	2.667062
C	-0.10762	-2.45277	2.065738	C	2.124098	1.773919	0.697583
C	-3.46985	-1.01847	0.392488	C	2.314603	-2.17932	-0.75595
C	-1.25445	3.481025	-0.53512	C	-2.46449	-2.8141	0.204228
C	0.253055	3.66452	-0.82881	C	-3.45349	-1.88312	-0.50988
O	0.831865	2.324299	-0.79618	O	-2.85049	-0.54345	-0.42855
C	1.019357	4.536007	0.182974	C	-4.86371	-1.78626	0.083196
C	2.515577	4.488052	-0.09929	C	-5.71755	-0.81043	-0.72713
C	0.514678	5.976396	0.115859	C	-5.50684	-3.16563	0.118698
O	0.855716	4.00449	1.492575	O	-4.76917	-1.35387	1.431486
C	1.140752	-0.35243	-1.4612	C	-1.01688	1.69661	-0.91199
C	1.270225	-2.99713	2.295646	C	3.346494	2.332602	1.370556
C	2.005561	-3.76424	1.478465	C	4.486495	2.745189	0.802653
C	3.364509	-4.24933	1.900415	C	5.591631	3.330902	1.63612
C	1.57327	-4.224	0.114952	C	4.775026	2.685466	-0.6694
O	0.605014	-0.45573	-2.54284	O	-0.26806	2.221383	-1.70659
C	2.613363	-0.57225	-1.33839	C	-2.32433	2.363757	-0.59057
C	-4.07691	-0.85045	-0.97132	C	3.452456	-1.45457	-1.41415
C	-4.2863	-1.78814	-1.90403	C	4.727823	-1.85887	-1.49521
C	-4.95483	-1.42887	-3.20211	C	5.730059	-1.0705	-2.29168
C	-3.89761	-3.23267	-1.78837	C	5.288325	-3.08857	-0.84037
C	3.192788	-1.49562	-2.21602	C	-2.78613	3.307206	-1.51442
C	4.564114	-1.71102	-2.20369	C	-3.96346	4.006077	-1.28421
C	5.375413	-0.98217	-1.336	C	-4.68265	3.792273	-0.11104
C	4.810209	-0.03871	-0.48319	C	-4.2208	2.872561	0.826922
C	3.433839	0.161274	-0.4766	C	-3.05431	2.155681	0.584705
H	1.697744	-0.87442	1.103991	H	-0.46115	1.911209	1.468633
H	1.168299	0.723296	1.60335	H	-0.7148	0.272634	2.032184
H	0.231601	-0.6762	3.16794	H	1.490664	1.037518	2.60435
H	-2.05737	-1.20245	4.035787	H	3.635221	-0.31654	2.502348
H	-2.76341	-2.0862	2.6829	H	3.852852	-0.28189	0.753164
H	-3.47102	-0.55788	3.207239	H	3.681148	-1.82525	1.589114
H	-0.7617	1.75996	2.32205	H	0.185976	-1.49818	2.748962
H	-2.46257	1.614956	2.784452	H	1.58943	-2.54617	2.633715

H	-1.19755	0.984097	3.842549	H	1.679161	-1.0531	3.57943
H	-0.51507	-2.80747	1.11948	H	1.449046	2.611747	0.478641
H	-0.757	-2.86017	2.84789	H	2.374143	1.356011	-0.28153
H	-3.27035	-2.06987	0.597204	H	2.656031	-3.00067	-0.12626
H	-4.19837	-0.66481	1.126589	H	1.737915	-2.65513	-1.55911
H	-1.87779	3.783041	-1.38071	H	-2.34307	-3.76684	-0.31333
H	-1.59608	4.068012	0.32471	H	-2.78767	-3.01856	1.230838
H	0.429675	4.040948	-1.83952	H	-3.50937	-2.11381	-1.57949
H	3.04379	5.102459	0.632148	H	-6.70327	-0.72314	-0.26539
H	2.884722	3.465384	-0.02832	H	-5.25855	0.180767	-0.75891
H	2.735103	4.867247	-1.10017	H	-5.84695	-1.15504	-1.75663
H	1.057966	6.584103	0.842525	H	-6.51408	-3.0836	0.531502
H	-0.5531	6.047968	0.344802	H	-4.93731	-3.84769	0.752493
H	0.670762	6.407509	-0.87631	H	-5.57763	-3.59252	-0.88464
H	-0.02076	4.243483	1.810483	H	-4.40334	-0.46251	1.402751
H	1.707061	-2.73975	3.261914	H	3.258527	2.453254	2.450902
H	3.623069	-3.91676	2.907864	H	5.332764	3.359344	2.696621
H	3.413561	-5.34433	1.880658	H	6.515459	2.750802	1.526508
H	4.137479	-3.89049	1.211261	H	5.827615	4.35267	1.316389
H	0.669761	-3.73241	-0.24595	H	3.982623	2.207726	-1.24526
H	2.367622	-4.03769	-0.61537	H	4.914367	3.695244	-1.07268
H	1.39616	-5.30607	0.113301	H	5.708573	2.144011	-0.85888
H	-4.42043	0.157362	-1.19017	H	3.175025	-0.56022	-1.96479
H	-5.22038	-0.37065	-3.24431	H	5.280247	-0.18989	-2.75429
H	-4.29956	-1.65037	-4.0527	H	6.563262	-0.73824	-1.66032
H	-5.86864	-2.01618	-3.35208	H	6.170754	-1.68337	-3.08699
H	-3.4299	-3.47919	-0.83682	H	4.555606	-3.63636	-0.24803
H	-4.77346	-3.87806	-1.92375	H	5.687851	-3.77775	-1.59343
H	-3.18528	-3.49484	-2.57811	H	6.127179	-2.82697	-0.18463
H	2.546968	-2.03112	-2.90244	H	-2.1996	3.475199	-2.41007
H	5.003445	-2.43916	-2.87698	H	-4.31744	4.723504	-2.01648
H	6.448125	-1.14409	-1.33085	H	-5.59726	4.344744	0.075777
H	5.441793	0.544317	0.178274	H	-4.7682	2.716887	1.750506
H	3.003316	0.909898	0.177295	H	-2.70863	1.446964	1.327703

	3-c				**3**-d		
C	0.088206	1.984362	-1.41566	C	0.019735	1.950678	-1.45276
C	-1.18677	1.468203	-0.97294	C	-1.20912	1.275335	-1.10348
C	-1.27856	0.343426	-0.23372	C	-1.2259	0.237257	-0.24216
C	-0.10192	-0.54483	0.035398	C	0.026376	-0.39992	0.279122
C	0.909032	0.556867	0.497604	C	0.772093	0.903476	0.719438
C	1.349672	1.451368	-0.66386	C	1.227819	1.73293	-0.48531
C	0.471878	-1.16168	-1.29304	C	0.875055	-1.03952	-0.8791
C	1.981726	-0.95473	-1.43755	C	2.33877	-0.59313	-0.86097
C	2.322738	0.570948	-1.58198	C	2.451961	0.94508	-1.15002

O	1.277137	0.700384	1.633433	O	0.946914	1.227755	1.863972
O	0.183323	2.905646	-2.21256	O	0.083543	2.778891	-2.34874
C	3.789843	0.813937	-1.21117	C	3.791807	1.476053	-0.62878
C	2.166088	0.951756	-3.06203	C	2.4612	1.137921	-2.67411
C	2.731704	-1.76323	-0.34998	C	3.04659	-1.14829	0.407638
C	2.036555	2.726654	-0.10529	C	1.612312	3.162538	-0.01787
C	-2.56746	2.033266	-1.14553	C	-2.62353	1.56918	-1.51438
C	-3.32482	1.281607	-0.03892	C	-3.40099	0.820882	-0.41936
O	-2.49594	0.106793	0.271071	O	-2.4492	-0.15099	0.138791
C	-4.72682	0.765468	-0.38404	C	-4.64067	0.034227	-0.8617
C	-5.33917	0.047728	0.819296	C	-5.29261	-0.64723	0.342002
C	-5.61089	1.921231	-0.83104	C	-5.6253	0.964295	-1.55615
O	-4.63395	-0.12007	-1.48843	O	-4.255	-0.93463	-1.82354
C	-0.36572	-1.67019	1.051751	C	-0.20591	-1.44381	1.386131
C	4.109745	-2.21654	-0.73517	C	4.533199	-1.36184	0.292148
C	5.198558	-2.30606	0.039295	C	5.146223	-2.38936	-0.31156
C	6.488425	-2.84909	-0.50916	C	6.6452	-2.489	-0.34162
C	5.256005	-1.89632	1.482821	C	4.427122	-3.51517	-0.99874
O	0.355739	-1.83687	2.010164	O	0.373348	-1.38092	2.447554
C	-1.48911	-2.6392	0.796329	C	-1.10828	-2.6163	1.104458
C	1.127411	3.671472	0.628275	C	0.467056	4.007557	0.464045
C	1.175641	4.026714	1.919228	C	0.266389	4.500386	1.693703
C	0.209356	5.043673	2.461321	C	-0.91538	5.388857	1.968939
C	2.149709	3.496937	2.930432	C	1.148603	4.256528	2.882814
C	-1.79033	-3.52985	1.831483	C	-1.41794	-3.43936	2.191866
C	-2.79954	-4.47244	1.685141	C	-2.2318	-4.5529	2.030088
C	-3.51168	-4.55133	0.491377	C	-2.7346	-4.87198	0.771654
C	-3.21047	-3.68133	-0.55387	C	-2.42111	-4.06968	-0.32304
C	-2.21038	-2.7273	-0.40066	C	-1.61895	-2.94588	-0.15728
H	0.259687	-2.23372	-1.32114	H	0.837938	-2.12951	-0.80214
H	-0.05263	-0.71416	-2.14131	H	0.415854	-0.77525	-1.83529
H	2.255138	-1.41243	-2.39754	H	2.818639	-1.09184	-1.71127
H	4.42699	0.147259	-1.79592	H	4.601013	0.867008	-1.03745
H	4.000318	0.618287	-0.15803	H	3.8662	1.443392	0.460324
H	4.089769	1.838538	-1.43849	H	3.961971	2.505192	-0.94945
H	1.19371	0.662783	-3.46868	H	1.61821	0.644706	-3.16453
H	2.264564	2.027547	-3.21223	H	2.411327	2.193174	-2.946
H	2.939206	0.443428	-3.64586	H	3.382903	0.712842	-3.08232
H	2.135893	-2.66952	-0.17078	H	2.576959	-2.11141	0.63508
H	2.734577	-1.2402	0.607828	H	2.835256	-0.52464	1.279527
H	2.864152	2.422276	0.532451	H	2.375865	3.082824	0.753595
H	2.453114	3.261732	-0.9645	H	2.058455	3.665647	-0.88172
H	-2.60676	3.115131	-1.00871	H	-2.85252	2.635989	-1.52556
H	-2.97602	1.794755	-2.13366	H	-2.84556	1.157012	-2.50482

H	-3.35498	1.872903	0.883156	H	-3.65449	1.493908	0.407408
H	-6.31596	-0.35461	0.542727	H	-6.14807	-1.23677	0.005759
H	-4.7029	-0.77754	1.148658	H	-4.58582	-1.31304	0.843818
H	-5.47186	0.728694	1.664272	H	-5.64266	0.085932	1.073545
H	-6.61062	1.544975	-1.05603	H	-6.51265	0.399032	-1.84732
H	-5.21585	2.38916	-1.7345	H	-5.18796	1.393403	-2.45951
H	-5.69397	2.679423	-0.04849	H	-5.93403	1.776864	-0.89382
H	-4.14244	-0.88936	-1.17683	H	-3.70484	-1.57473	-1.35641
H	4.203061	-2.56372	-1.76538	H	5.168769	-0.61577	0.763003
H	6.397079	-3.13846	-1.55814	H	7.119327	-1.64485	0.16293
H	7.292473	-2.10803	-0.42878	H	6.987693	-3.41112	0.142414
H	6.818842	-3.72715	0.057955	H	7.018284	-2.52294	-1.37203
H	4.32424	-1.46703	1.851108	H	3.343417	-3.46476	-0.88488
H	5.494838	-2.75859	2.116065	H	4.651445	-3.52342	-2.07184
H	6.056005	-1.1645	1.643773	H	4.761772	-4.48199	-0.60609
H	0.377646	4.157169	0.007488	H	-0.24805	4.289285	-0.30578
H	-0.46843	5.415425	1.689947	H	-1.51888	5.55528	1.07413
H	-0.3931	4.617627	3.27233	H	-1.56014	4.955324	2.742599
H	0.740146	5.902328	2.889253	H	-0.59317	6.366016	2.347769
H	2.783662	2.703752	2.539894	H	1.9406	3.536318	2.688699
H	2.785593	4.305332	3.310541	H	1.598071	5.195932	3.226191
H	1.613226	3.087025	3.792866	H	0.557178	3.867627	3.71867
H	-1.21441	-3.45978	2.746873	H	-1.00572	-3.18002	3.160088
H	-3.02896	-5.1491	2.501066	H	-2.47149	-5.17511	2.885475
H	-4.29573	-5.29137	0.372044	H	-3.36468	-5.74526	0.641379
H	-3.75098	-3.75057	-1.49206	H	-2.79691	-4.32343	-1.30873
H	-1.99071	-2.06191	-1.22763	H	-1.38896	-2.33646	-1.02373

3-e				**3**-f			
C	0.041234	-2.50381	-0.39043	C	-2.15002	1.728456	0.300048
C	1.35496	-1.98362	-0.11196	C	-0.90203	2.241615	-0.20328
C	1.563063	-0.69503	0.209513	C	0.174829	1.456054	-0.38056
C	0.523771	0.356897	0.408536	C	0.24493	-0.02712	-0.22367
C	-0.79149	-0.39922	0.721213	C	-1.21115	-0.53521	-0.28974
C	-1.13372	-1.50093	-0.28251	C	-2.18105	0.216289	0.622658
C	0.263042	1.102604	-0.94088	C	0.737673	-0.41771	1.207955
C	-1.09091	0.765927	-1.59929	C	-0.37181	-0.90011	2.170951
C	-1.33769	-0.77133	-1.72538	C	-1.64716	0.001961	2.148543
O	-1.5305	-0.05686	1.609479	O	-1.51727	-1.52765	-0.90337
O	-0.15165	-3.65952	-0.73949	O	-3.12003	2.439476	0.519456
C	-2.74426	-1.01403	-2.28727	C	-2.73702	-0.61214	3.038501
C	-0.36985	-1.32043	-2.79184	C	-1.27606	1.334002	2.833338
C	-2.25786	1.574712	-0.9633	C	-0.63812	-2.42181	2.041399
C	-2.37263	-2.28068	0.215063	C	-3.61649	-0.29919	0.372649
C	2.679817	-2.65493	-0.31067	C	-0.50284	3.670501	-0.41212

C	3.667342	-1.49788	-0.03228	C	0.992774	3.531982	-0.77893
O	2.848708	-0.33835	0.311086	O	1.293758	2.104008	-0.72717
C	4.56711	-1.11768	-1.213	C	1.959989	4.26533	0.155555
C	5.367766	0.145502	-0.90074	C	3.408535	3.91266	-0.17773
C	5.507489	-2.27908	-1.5356	C	1.736138	5.773313	0.038262
O	3.675517	-0.88063	-2.29672	O	1.630172	3.811231	1.462895
C	0.939157	1.1974	1.643654	C	1.051458	-0.56653	-1.43689
C	-3.21436	2.141839	-1.97189	C	0.598879	-3.24381	2.245098
C	-4.55124	2.198339	-1.91193	C	1.151038	-4.13226	1.406755
C	-5.34264	2.850911	-3.01078	C	2.383579	-4.89668	1.802518
C	-5.38197	1.648736	-0.78807	C	0.619457	-4.46936	0.042257
O	0.915738	0.661015	2.729068	O	0.517326	-0.55504	-2.52413
C	1.359272	2.627389	1.53224	C	2.452571	-1.07062	-1.30519
C	-2.15162	-3.05436	1.483615	C	-4.16224	0.012552	-0.99228
C	-2.76649	-2.90325	2.663463	C	-4.54166	-0.84672	-1.94668
C	-2.43268	-3.81315	3.813155	C	-5.11241	-0.33686	-3.24118
C	-3.80208	-1.86432	2.978113	C	-4.44632	-2.34155	-1.85992
C	0.950223	3.497464	2.547746	C	2.850929	-2.0784	-2.1906
C	1.360348	4.823976	2.540659	C	4.152795	-2.56002	-2.16745
C	2.210532	5.285151	1.538065	C	5.080455	-2.01733	-1.28037
C	2.647183	4.416368	0.541882	C	4.700596	-0.99168	-0.41975
C	2.216118	3.094114	0.531078	C	3.390659	-0.52423	-0.42482
H	0.290746	2.178992	-0.76557	H	1.463753	-1.22831	1.121381
H	1.082713	0.877003	-1.62871	H	1.26127	0.436778	1.644118
H	-1.00102	1.128408	-2.63161	H	0.05017	-0.7712	3.177183
H	-2.85973	-0.43939	-3.21034	H	-2.30775	-0.83725	4.020258
H	-3.54528	-0.70436	-1.61729	H	-3.16546	-1.53341	2.645183
H	-2.89019	-2.06778	-2.5334	H	-3.55195	0.097319	3.197333
H	0.682473	-1.14312	-2.5625	H	-0.42815	1.844783	2.3745
H	-0.50511	-2.39511	-2.92465	H	-2.12116	2.024616	2.83564
H	-0.58763	-0.83454	-3.74771	H	-1.01274	1.126895	3.874999
H	-1.82111	2.415306	-0.40688	H	-1.11741	-2.66592	1.093943
H	-2.7863	0.985578	-0.2139	H	-1.35216	-2.70107	2.82357
H	-3.20499	-1.5869	0.32648	H	-3.64358	-1.37217	0.559921
H	-2.63494	-2.99632	-0.56842	H	-4.26395	0.186372	1.107114
H	2.82891	-3.49677	0.370033	H	-1.07857	4.154335	-1.20483
H	2.774692	-3.02753	-1.33375	H	-0.63868	4.248729	0.505585
H	4.295328	-1.69057	0.841176	H	1.195051	3.841992	-1.80754
H	5.989915	0.416862	-1.75943	H	4.087502	4.429308	0.507937
H	4.698648	0.976115	-0.67748	H	3.570077	2.838744	-0.08723
H	6.032151	-0.00463	-0.04568	H	3.669506	4.21844	-1.1943
H	6.147615	-2.01432	-2.38282	H	2.416843	6.304053	0.711063
H	4.951281	-3.17952	-1.80238	H	0.714441	6.045937	0.309077
H	6.162239	-2.50995	-0.69107	H	1.935964	6.128869	-0.97608

H	4.202477	-0.66999	-3.07331	H	2.19195	4.277555	2.089022
H	-2.73954	2.595557	-2.84318	H	1.089163	-3.10058	3.20943
H	-4.69884	3.239834	-3.80239	H	2.715588	-4.64555	2.8121
H	-6.04755	2.142487	-3.46179	H	2.204048	-5.97744	1.762525
H	-5.94383	3.681783	-2.62333	H	3.207668	-4.69209	1.109426
H	-4.79412	1.145784	-0.02003	H	-0.1546	-3.78623	-0.30773
H	-5.94424	2.452388	-0.29864	H	1.43135	-4.45618	-0.69243
H	-6.12564	0.938912	-1.16819	H	0.207365	-5.48548	0.031273
H	-1.42644	-3.85984	1.398848	H	-4.29703	1.072527	-1.19198
H	-1.67772	-4.55313	3.540118	H	-5.16923	0.753355	-3.26011
H	-2.05465	-3.23957	4.667653	H	-4.50151	-0.66162	-4.0917
H	-3.32261	-4.34773	4.166457	H	-6.12012	-0.73404	-3.41258
H	-4.03379	-1.21701	2.134043	H	-4.02619	-2.69263	-0.91919
H	-4.73034	-2.33755	3.319503	H	-5.43374	-2.79869	-1.99481
H	-3.45515	-1.22136	3.794307	H	-3.80743	-2.72451	-2.66308
H	0.310541	3.113559	3.334233	H	2.121653	-2.46728	-2.89205
H	1.025096	5.497542	3.32187	H	4.448706	-3.35154	-2.84752
H	2.537659	6.319474	1.53688	H	6.099913	-2.38806	-1.26615
H	3.324898	4.768733	-0.22827	H	5.425811	-0.55379	0.257652
H	2.569259	2.415747	-0.23746	H	3.106626	0.286062	0.235529

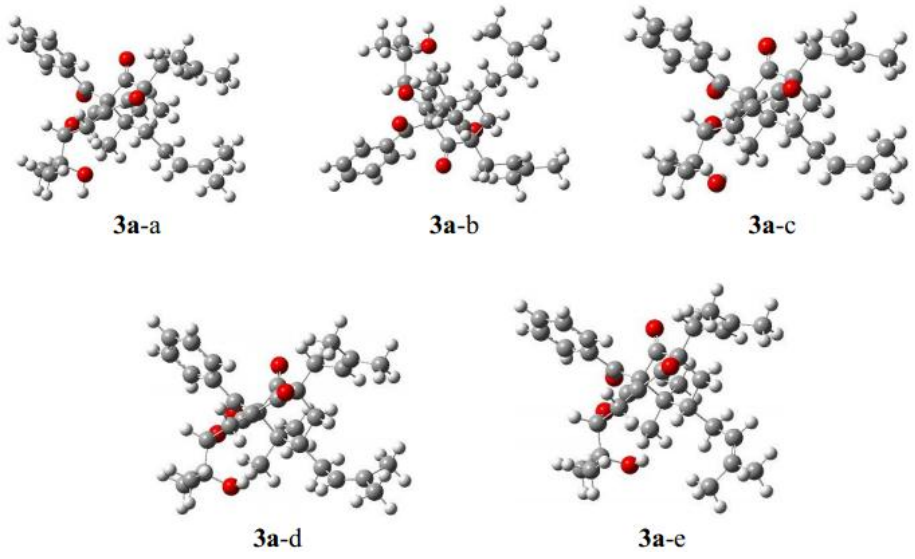

Figure S3. Optimized geometries of predominant conformers for compound **3a** at the mPW1PW91/6-31G(d,p) level in the gas phase.

Table S3. Important Thermodynamic Parameters (a.u.) and Boltzmann Distributions of the Optimized 3a at mPW1PW91/6-31G(d,p) Level in Gas Phase

Conformations	E+ZPE[a]	G[b]	%[c]
3a-a	-1657.884451	-1657.956997	20.4
3a-b	-1657.882945	-1657.954339	1.2

3a-c	-1657.885476	-1657.958133	68.0
3a-d	-1657.883598	-1657.956234	9.1
3a-e	-1657.882198	-1657.954411	1.3

[a] E+ZPE: total energy with zero point energy (ZPE). [b] G: Gibbs free energy in the gas phase at mPW1PW91/6-31G(d,p) level. [c] %: Boltzmann distributions, using the relative Gibbs free energies as weighting factors.

Table S4. Optimized Z-Matrixes of 3a in Gas Phase (Å) at mPW1PW91/6-31G(d,p) Level

3a-a				**3a**-b			
C	1.192032	0.387904	0.29832	C	-0.99185	0.341206	-0.27184
C	0.453333	0.113254	1.39223	C	-0.16255	0.064344	-1.29839
C	-0.6723	-0.78969	1.363762	C	0.87809	-0.93202	-1.21006
C	-1.04895	-1.35487	-0.02389	C	1.057054	-1.59998	0.172008
C	0.18313	-1.46193	-0.91486	C	-0.2715	-1.65443	0.915726
C	0.980911	-0.15654	-1.07673	C	-0.97811	-0.29827	1.078576
C	-1.95182	-0.31866	-0.75182	C	1.955072	-0.67889	1.04722
C	-1.28666	1.00855	-1.12682	C	1.351539	0.673781	1.437404
C	0.042147	0.831778	-1.92686	C	-0.06317	0.553548	2.08724
O	0.477426	-2.45155	-1.54648	O	-0.71345	-2.65197	1.439888
C	0.733562	2.193804	-2.0784	C	-0.66492	1.954391	2.267205
C	-0.2329	0.236356	-3.31551	C	0.017439	-0.15192	3.448969
C	-2.32966	1.894965	-1.84112	C	2.369707	1.448477	2.305232
C	2.356967	-0.47006	-1.73284	C	-2.43824	-0.53118	1.563696
O	2.65002	-0.00382	-2.81477	O	-2.80926	-0.11321	2.641438
C	-1.74414	-2.72833	0.109495	C	1.653276	-3.0178	0.029595
C	3.357062	-1.33264	-1.02115	C	-3.42243	-1.24973	0.688377
C	-3.42015	2.338602	-0.91187	C	3.654172	1.745829	1.579295
C	-4.74062	2.134635	-1.00986	C	3.909531	2.804006	0.798265
C	-5.6786	2.673559	0.034226	C	5.23942	2.960889	0.117171
C	-5.41579	1.38298	-2.12116	C	2.924113	3.902835	0.518804
C	-3.2138	-2.69874	0.407022	C	3.142976	-3.09995	-0.11997
C	-3.84988	-3.12509	1.505339	C	3.850437	-3.53357	-1.17076
C	-5.35016	-3.06771	1.5861	C	5.350343	-3.60829	-1.10038
C	-3.18183	-3.67867	2.728521	C	3.266266	-3.97197	-2.48055
O	2.215553	1.22201	0.509101	O	-1.91163	1.276439	-0.53189
C	2.200242	1.617886	1.913542	C	-1.71447	1.742571	-1.9005
C	0.99331	0.89291	2.553082	C	-0.50144	0.958557	-2.45291
O	-1.29963	-1.09183	2.366974	O	1.586642	-1.23071	-2.15862
C	2.154706	3.147026	1.986164	C	-1.55249	3.265299	-1.87737
C	2.273156	3.591269	3.444924	C	-1.47745	3.790526	-3.31151
C	3.270758	3.761107	1.143769	C	-2.70776	3.91911	-1.12244
O	0.881403	3.507995	1.462869	O	-0.32238	3.501378	-1.20092
C	3.124385	-2.01518	0.17731	C	-4.74998	-1.26127	1.135054

C	4.12507	-2.78849	0.754222	C	-5.74119	-1.89583	0.401445
C	5.370784	-2.89225	0.143538	C	-5.42069	-2.53546	-0.79381
C	5.613045	-2.21918	-1.05179	C	-4.10497	-2.53523	-1.24608
C	4.614322	-1.44818	-1.62763	C	-3.11182	-1.89743	-0.5117
H	-2.33104	-0.80209	-1.66091	H	2.211348	-1.23921	1.95501
H	-2.82057	-0.12145	-0.11857	H	2.889413	-0.51716	0.503614
H	-1.02472	1.534662	-0.20134	H	1.231594	1.268943	0.52619
H	1.728232	2.077839	-2.50626	H	-1.70459	1.891138	2.584642
H	0.161166	2.828521	-2.75921	H	-0.12213	2.496256	3.045465
H	0.813536	2.709183	-1.11819	H	-0.60788	2.533502	1.342072
H	-0.70744	-0.74651	-3.27156	H	0.430274	-1.16088	3.382811
H	-0.89724	0.904141	-3.86916	H	0.656757	0.427022	4.119306
H	0.690863	0.136955	-3.88103	H	-0.96804	-0.22305	3.903628
H	-2.74097	1.364974	-2.70406	H	2.602972	0.868955	3.204861
H	-1.83307	2.789024	-2.23457	H	1.916319	2.380691	2.650093
H	-1.59219	-3.24414	-0.8447	H	1.363383	-3.56409	0.933565
H	-1.20469	-3.31386	0.856424	H	1.148332	-3.51963	-0.79798
H	-3.06917	2.901696	-0.04637	H	4.449021	1.010787	1.692332
H	-5.14647	3.211155	0.82143	H	5.91201	2.130685	0.341483
H	-6.41233	3.35645	-0.41	H	5.11964	3.016427	-0.971
H	-6.25098	1.864421	0.502441	H	5.731113	3.891499	0.424204
H	-4.72109	0.988793	-2.86266	H	2.007418	3.81208	1.102139
H	-5.99273	0.54208	-1.71956	H	3.368958	4.882688	0.72658
H	-6.13182	2.028479	-2.64259	H	2.640423	3.901349	-0.53996
H	-3.83901	-2.32622	-0.40346	H	3.710456	-2.82014	0.766759
H	-5.79427	-2.66328	0.673837	H	5.731963	-3.28162	-0.13055
H	-5.77531	-4.06366	1.758424	H	5.703146	-4.63143	-1.27667
H	-5.67223	-2.44359	2.428008	H	5.809899	-2.9842	-1.87579
H	-2.09575	-3.6602	2.667623	H	2.184139	-3.86716	-2.52277
H	-3.46478	-3.09125	3.608558	H	3.680337	-3.36892	-3.29563
H	-3.50994	-4.70821	2.914793	H	3.530129	-5.01524	-2.69086
H	3.152487	1.276574	2.328739	H	-2.63816	1.497928	-2.43249
H	1.289272	0.249271	3.385208	H	-0.74852	0.397009	-3.35719
H	0.252204	1.60457	2.925972	H	0.33235	1.625065	-2.68893
H	2.225998	4.682608	3.505643	H	-1.34558	4.876426	-3.30275
H	1.459281	3.186253	4.049479	H	-0.63278	3.354003	-3.8478
H	3.224765	3.278214	3.882878	H	-2.39439	3.574555	-3.86644
H	3.222711	4.853612	1.196088	H	-2.57714	5.006013	-1.1047
H	3.17592	3.454612	0.102135	H	-2.7494	3.552701	-0.09672
H	4.255813	3.458201	1.508373	H	-3.66579	3.711718	-1.60628
H	0.845669	4.467498	1.405905	H	-0.23512	4.449492	-1.06516
H	2.16426	-1.95698	0.672623	H	-4.97762	-0.76325	2.069817
H	3.92668	-3.31649	1.680545	H	-6.76433	-1.89455	0.761525
H	6.148947	-3.49824	0.595547	H	-6.19294	-3.03559	-1.36877

H	6.580929	-2.29798	-1.53499	H	-3.84664	-3.03944	-2.17086
H	4.780989	-0.92033	-2.55885	H	-2.09634	-1.91974	-0.88406
	3a-c				**3a**-d		
C	1.135871	0.380666	0.214121	C	1.199099	0.389602	0.30152
C	0.446782	0.101023	1.338969	C	0.452632	0.107104	1.389814
C	-0.71527	-0.7589	1.344158	C	-0.67603	-0.79039	1.353055
C	-1.17576	-1.27807	-0.0364	C	-1.04007	-1.35715	-0.03613
C	0.01623	-1.41778	-0.97592	C	0.202765	-1.46633	-0.91326
C	0.847642	-0.13481	-1.15991	C	1.000873	-0.16041	-1.07347
C	-2.07081	-0.19428	-0.70105	C	-1.93546	-0.3232	-0.77625
C	-1.37426	1.107544	-1.10802	C	-1.26672	1.001699	-1.15266
C	-0.09318	0.879863	-1.96992	C	0.069105	0.82125	-1.93943
O	0.259713	-2.41275	-1.61968	O	0.50495	-2.45888	-1.53599
C	0.639749	2.212361	-2.16992	C	0.76025	2.182663	-2.09539
C	-0.45805	0.289992	-3.34016	C	-0.19478	0.214558	-3.3255
C	-2.41573	2.035573	-1.7699	C	-2.30384	1.884872	-1.8806
C	2.188186	-0.48549	-1.86997	C	2.384139	-0.47623	-1.71525
O	2.443664	-0.0362	-2.96859	O	2.681848	-0.02433	-2.80153
C	-1.9189	-2.62612	0.10036	C	-1.73619	-2.7306	0.093327
C	3.20357	-1.35293	-1.18757	C	3.383486	-1.32174	-0.98292
C	-3.45296	2.506672	-0.79421	C	-3.38732	2.359207	-0.95847
C	-4.7806	2.331103	-0.83306	C	-4.70272	2.110139	-1.00997
C	-5.65931	2.895932	0.248013	C	-5.63491	2.696127	0.013521
C	-5.52055	1.589475	-1.90923	C	-5.37698	1.259139	-2.04768
C	-3.36695	-2.54503	0.48225	C	-3.20839	-2.70054	0.378
C	-3.95783	-2.98085	1.601845	C	-3.85386	-3.1254	1.471414
C	-5.44723	-2.86444	1.770675	C	-5.3548	-3.06851	1.539047
C	-3.24644	-3.60184	2.766708	C	-3.19643	-3.67728	2.701086
O	2.19993	1.178068	0.399789	O	2.216306	1.224588	0.523872
C	2.382881	1.337546	1.847579	C	2.175681	1.63944	1.922953
C	1.0744	0.838155	2.485378	C	1.002357	0.860397	2.562484
O	-1.30547	-1.06103	2.368369	O	-1.31476	-1.08291	2.352472
C	2.748408	2.801395	2.120334	C	2.05302	3.173103	1.966023
C	2.94113	3.010258	3.616256	C	2.117997	3.654712	3.414911
C	4.010868	3.191056	1.351753	C	3.158208	3.817422	1.139268
O	1.663906	3.634645	1.742312	O	0.833772	3.578637	1.358056
C	2.985296	-2.07837	-0.01131	C	3.13656	-2.0113	0.208634
C	4.001212	-2.85193	0.538412	C	4.137735	-2.76847	0.805719
C	5.247708	-2.91214	-0.07664	C	5.398446	-2.84795	0.222734
C	5.475044	-2.1974	-1.25047	C	5.655012	-2.1677	-0.9655
C	4.460871	-1.42765	-1.80054	C	4.655493	-1.41377	-1.56213
H	-2.52659	-0.65056	-1.58847	H	-2.30517	-0.81069	-1.68692
H	-2.89137	0.035065	-0.01669	H	-2.81037	-0.12277	-0.15254
H	-1.05012	1.617843	-0.19257	H	-1.01132	1.533196	-0.22825

H	1.602009	2.060411	-2.65533	H	1.763024	2.063922	-2.50295
H	0.051706	2.877691	-2.80559	H	0.200495	2.806261	-2.79651
H	0.802845	2.721298	-1.21627	H	0.819517	2.714409	-1.14279
H	-0.98618	-0.66271	-3.26317	H	-0.66437	-0.77058	-3.27899
H	-1.10589	0.989196	-3.87395	H	-0.8591	0.875853	-3.88684
H	0.434474	0.132296	-3.94145	H	0.732916	0.116878	-3.88471
H	-2.8796	1.527676	-2.61941	H	-2.72223	1.341475	-2.7318
H	-1.90736	2.916747	-2.17713	H	-1.80062	2.766199	-2.29252
H	-1.84168	-3.12028	-0.87411	H	-1.57571	-3.24755	-0.85882
H	-1.36298	-3.25408	0.799157	H	-1.2031	-3.31524	0.845517
H	-3.05284	3.067191	0.051316	H	-3.0361	2.99402	-0.14411
H	-5.08174	3.425768	1.007832	H	-5.10391	3.305933	0.747099
H	-6.39636	3.592588	-0.16809	H	-6.39727	3.323725	-0.4627
H	-6.22831	2.101841	0.745125	H	-6.17343	1.907398	0.55153
H	-4.86899	1.172494	-2.67708	H	-4.68597	0.832474	-2.77458
H	-6.10054	0.766164	-1.477	H	-5.91684	0.432255	-1.57219
H	-6.24202	2.249499	-2.4041	H	-6.12539	1.841551	-2.59713
H	-4.02005	-2.12131	-0.27954	H	-3.8265	-2.32982	-0.43867
H	-5.9238	-2.40817	0.900196	H	-5.79122	-2.66513	0.622606
H	-5.90447	-3.84785	1.931859	H	-5.78092	-4.06449	1.708386
H	-5.69434	-2.25972	2.651091	H	-5.68456	-2.44401	2.377685
H	-2.1672	-3.64482	2.635887	H	-2.10983	-3.66263	2.648322
H	-3.43838	-3.02189	3.675672	H	-3.48435	-3.08677	3.57744
H	-3.62112	-4.6156	2.950908	H	-3.52885	-4.70531	2.887634
H	3.225407	0.686966	2.106383	H	3.138713	1.343889	2.347708
H	1.253717	0.19819	3.351227	H	1.335009	0.194367	3.36296
H	0.446879	1.676997	2.80488	H	0.247678	1.518737	3.008129
H	3.205602	4.052592	3.80383	H	2.021164	4.742028	3.437797
H	2.022316	2.792475	4.163887	H	1.313468	3.230424	4.023858
H	3.741517	2.374269	4.002033	H	3.067933	3.384515	3.883252
H	4.234322	4.244638	1.531432	H	3.051637	4.903221	1.173444
H	3.877832	3.03931	0.277827	H	3.094634	3.492529	0.100992
H	4.870492	2.594745	1.668792	H	4.14282	3.549577	1.530017
H	1.581407	3.569959	0.784558	H	0.10739	3.353371	1.948068
H	2.024291	-2.05868	0.484428	H	2.164108	-1.97394	0.681338
H	3.813666	-3.41508	1.446061	H	3.928233	-3.30325	1.725681
H	6.037957	-3.5173	0.354929	H	6.177229	-3.44085	0.690696
H	6.443353	-2.24243	-1.73699	H	6.634715	-2.22756	-1.42703
H	4.616037	-0.86883	-2.71554	H	4.833276	-0.88126	-2.48864

3a-e

C	1.005813	0.371771	0.303956
C	0.2076	-0.00089	1.326503
C	-0.77731	-1.04768	1.209833
C	-0.93742	-1.66531	-0.19618

C	0.388645	-1.62177	-0.94689
C	1.018873	-0.22339	-1.06705
C	-1.89081	-0.75585	-1.024
C	-1.3594	0.636139	-1.38064
C	0.052736	0.605688	-2.04653
O	0.882331	-2.57622	-1.50322
C	0.578678	2.039992	-2.19616
C	-0.00668	-0.07039	-3.4243
C	-2.41988	1.38602	-2.21875
C	2.486928	-0.36209	-1.56712
O	2.82256	0.0936	-2.64068
C	-1.46109	-3.11607	-0.10698
C	3.517633	-1.03744	-0.712
C	-3.714	1.604191	-1.48486
C	-4.0861	2.697015	-0.80432
C	-5.43088	2.768875	-0.13717
C	-3.24229	3.930269	-0.64777
C	-2.94394	-3.2776	0.047312
C	-3.62206	-3.78485	1.084455
C	-5.11687	-3.93108	1.018158
C	-3.00865	-4.24417	2.373558
O	1.865918	1.350198	0.59579
C	1.62172	1.783935	1.968447
C	0.53449	0.834974	2.525473
O	-1.45663	-1.41907	2.154705
C	1.244567	3.2765	1.941375
C	1.083298	3.794189	3.370243
C	2.307264	4.078617	1.201557
O	0.043296	3.459926	1.203242
C	3.251101	-1.73984	0.467847
C	4.284844	-2.33198	1.184114
C	5.597448	-2.23023	0.734235
C	5.874267	-1.53524	-0.44087
C	4.842627	-0.9471	-1.15719
H	-2.13797	-1.2969	-1.94557
H	-2.82204	-0.65906	-0.46018
H	-1.25776	1.212133	-0.45467
H	1.622381	2.041086	-2.50601
H	0.014022	2.564904	-2.9703
H	0.479982	2.599822	-1.26297
H	-0.3706	-1.09925	-3.38065
H	-0.67874	0.494478	-4.0743
H	0.976942	-0.0824	-3.88822
H	-2.63197	0.817254	-3.13117

H	-2.01257	2.345172	-2.54325
H	-1.15105	-3.61149	-1.03329
H	-0.92577	-3.62416	0.697327
H	-4.42418	0.779678	-1.51896
H	-6.01131	1.856808	-0.28919
H	-5.32857	2.931082	0.942165
H	-6.015	3.612607	-0.52307
H	-2.23728	3.82659	-1.05633
H	-3.7212	4.790229	-1.13069
H	-3.1415	4.194289	0.411233
H	-3.53067	-2.99377	-0.82552
H	-5.52085	-3.5858	0.06397
H	-5.41727	-4.97668	1.155028
H	-5.6016	-3.36208	1.820156
H	-1.93276	-4.08793	2.415474
H	-3.44713	-3.69487	3.213507
H	-3.2197	-5.30654	2.54383
H	2.574216	1.663965	2.49113
H	0.899958	0.232899	3.361682
H	-0.34679	1.369512	2.898224
H	0.810894	4.85106	3.341201
H	0.299921	3.258201	3.914957
H	2.012136	3.693858	3.937723
H	2.018456	5.131026	1.179182
H	2.409379	3.722022	0.176808
H	3.275922	3.99223	1.699656
H	-0.68997	3.099533	1.712228
H	2.239333	-1.84166	0.837337
H	4.061452	-2.88044	2.092678
H	6.401645	-2.69434	1.295406
H	6.894983	-1.45441	-0.79864
H	5.035826	-0.40741	-2.07644

Table S5. The Computed ^{13}C NMR Data for 3

no.	**3**	δ_{exptl}	Chloroform	
			δ_{calcd}	$\Delta\delta$
1	4	190.3	185.8	-4.5
2	3	118.5	113.6	-4.9
3	2	171.9	173.4	1.5
4	1	70.3	62.4	-7.9
5	9	206.9	204.6	-2.3
6	5	65.3	66.9	1.6
7	6	41.7	34.9	-6.8
8	7	43.1	45.3	2.2

9	8	47.0	47.5	0.5
10	32	15.7	27.9	12.2
11	33	24.1	30.0	5.9
12	27	27.7	31.0	3.3
13	22	29.3	31.7	2.4
14	17	26.5	29.6	3.1
15	18	93.5	89.8	-3.7
16	19	70.6	71.9	1.3
17	20	26.4	26.7	0.3
18	21	23.7	26.2	2.5
19	10	192.6	196.2	3.6
20	28	122.3	122.8	0.5
21	29	133.5	133.9	0.4
22	30	26.0	26.4	0.4
23	31	17.9	18.8	0.9
24	11	137.1	134.2	-2.9
25	23	119.5	121.4	1.9
26	24	134.7	132.8	-1.9
27	25	25.9	27.2	1.3
28	26	18.2	20.3	2.1
29	12	128.5	127.9	-0.6
30	13	128.2	125.4	-2.8
31	14	132.8	129.0	-3.8
32	15	128.2	123.4	-4.8
33	16	128.5	125.3	-3.2

Table S6. The Computed ^{13}C NMR Data for 3a

no.	**3a**	δ_{exptl}	Chloroform	
			δ_{calcd}	$\Delta\delta$
1	2	171.9	170.4	-1.5
2	3	118.5	117.8	-0.7
3	4	190.3	185.3	-5.0
4	5	65.3	66.2	0.9
5	9	206.9	207.4	0.5
6	1	70.3	70.6	0.3
7	6	41.7	39.3	-2.4
8	7	43.1	42.7	-0.4
9	8	47	50.1	3.1
10	32	15.7	16.7	1.0
11	33	24.1	25.0	0.9
12	27	27.7	30.9	3.2
13	10	192.6	191.5	-1.1
14	22	29.3	30.0	0.7
15	11	137.1	132.1	-5.0
16	28	122.3	123.0	0.7
17	29	133.5	132.7	-0.8
18	30	26	26.9	0.9

19	31	17.9	18.8	0.9
20	23	119.5	118.8	-0.7
21	24	134.7	133.9	-0.8
22	25	25.9	27.4	1.5
23	26	18.2	20.0	1.8
24	18	93.5	92.5	-1.0
25	17	26.5	29.5	3.0
26	19	70.6	70.2	-0.4
27	20	26.4	27.4	1.0
28	21	23.7	25.0	1.3
29	12	128.5	126.2	-2.3
30	13	128.2	124.0	-4.2
31	14	132.8	130.2	-2.6
32	15	128.2	125.1	-3.1
33	16	128.5	127.6	-0.9

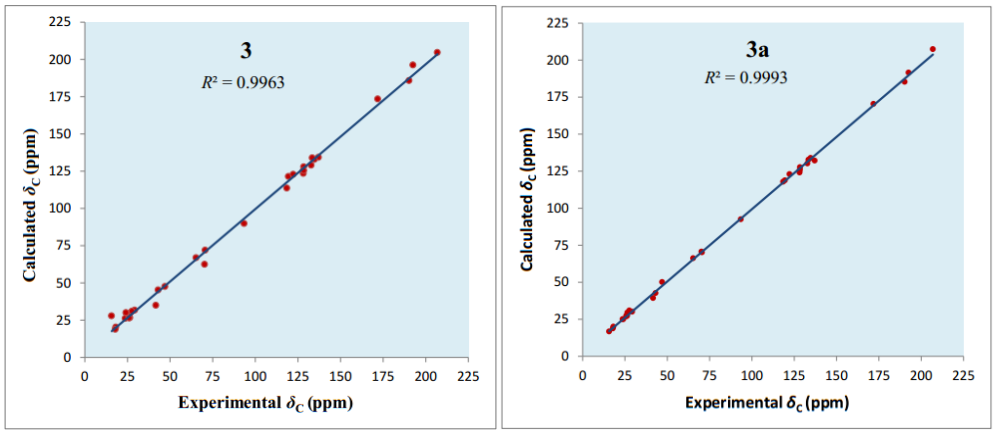

Figure S4. Linear correlations between the calculated and experimental ^{13}C NMR data for **3** and **3a**.

References

(1) Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A., et al. Gaussian, Inc., Wallingford CT, **2010**.

(2) GaussView, Version 5, Dennington, R.; Keith, T.; Millam, J. *Semichem Inc.*, Shawnee Mission, KS, **2009**.

(3) Smith, S. G.; Goodman, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 12946−12959.

(4) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Rohlfing, C. M.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9.(c) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(5) (a) Miertus, S.; Scrocc, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *J. Chem. Phys.* **1982**, *65*, 239. (c) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327.

(6) Tähtinen, P.; Bagno, A.; Klika, K. D.; Pihlaja, K. *J. Am. Chem. Soc.* **2003**, *125*, 4609−4618.

SI-2. Experimental Procedures

3.1 General Experimental Procedures: Melting points were obtained on an X-4 micro melting point apparatus. Optical rotations were measured on a Jasco P-1020 polarimeter. UV spectra were recorded on a Shmadzu UV-2401PC spectrometer. IR spectra were recorded on a Bruker FT-IR Tensor-27 infrared spectrophotometer with KBr disks. 1D and 2D NMR spectra were recorded on a Bruker DRX-600 spectrometer using TMS as an internal standard. Unless otherwise specified, chemical shifts (δ) are expressed in ppm with reference to the solvent signals. ESIMS and HREIMS data were acquired on Waters Xevo TQS and Waters AutoSpec Premier P776 mass spectrometers, respectively. X-ray data were generated using a Bruker Apex Duo instrument. Semi-preparative HPLC was performed on an Agilent 1100 HPLC with a Zorbarx SB-C_{18} (9.4 × 250 mm) column. Silica gel (100–200 and 200–300 mesh, Qingdao Marine Chemical Co., Ltd., Qingdao, People's Republic of China), and MCI gel (75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan) were used for column chromatography. Fractions were monitored by TLC (GF 254, Qingdao Marine Chemical Co., Ltd.), and spots were visualized by heating silica gel plates immersed in H_2SO_4 in ethanol.

3.2 Plant Material: The aerial parts of *Hypericum cohaerens* N. Robson were collected in Daguan Prefecture, Yunnan Province, People's Republic of China, in October 2009. The plant was identified by Dr. En-De Liu, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen was deposited at the Kunming Institute of Botany with identification number 200910H01.

SI-3. The Original NMR and MS Spectra of 8

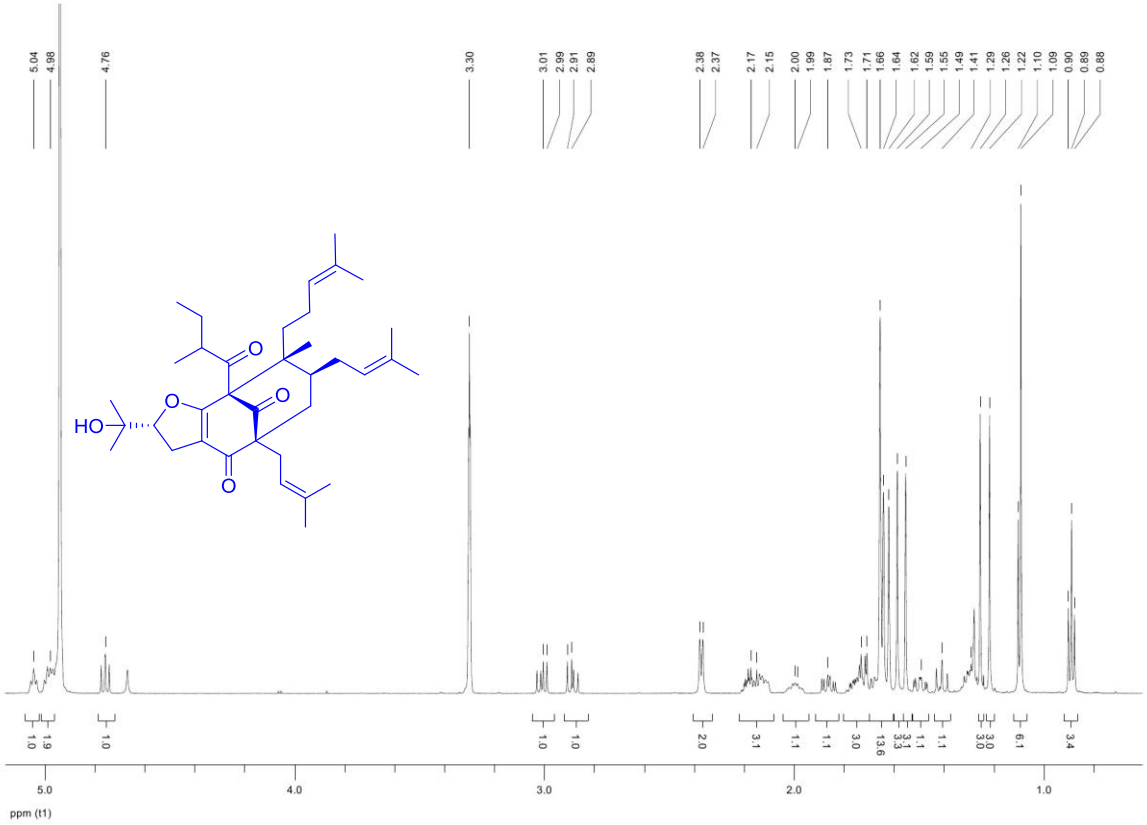

Figure S5. ^{1}H NMR (in methanol-d_4) spectrum of **8**.

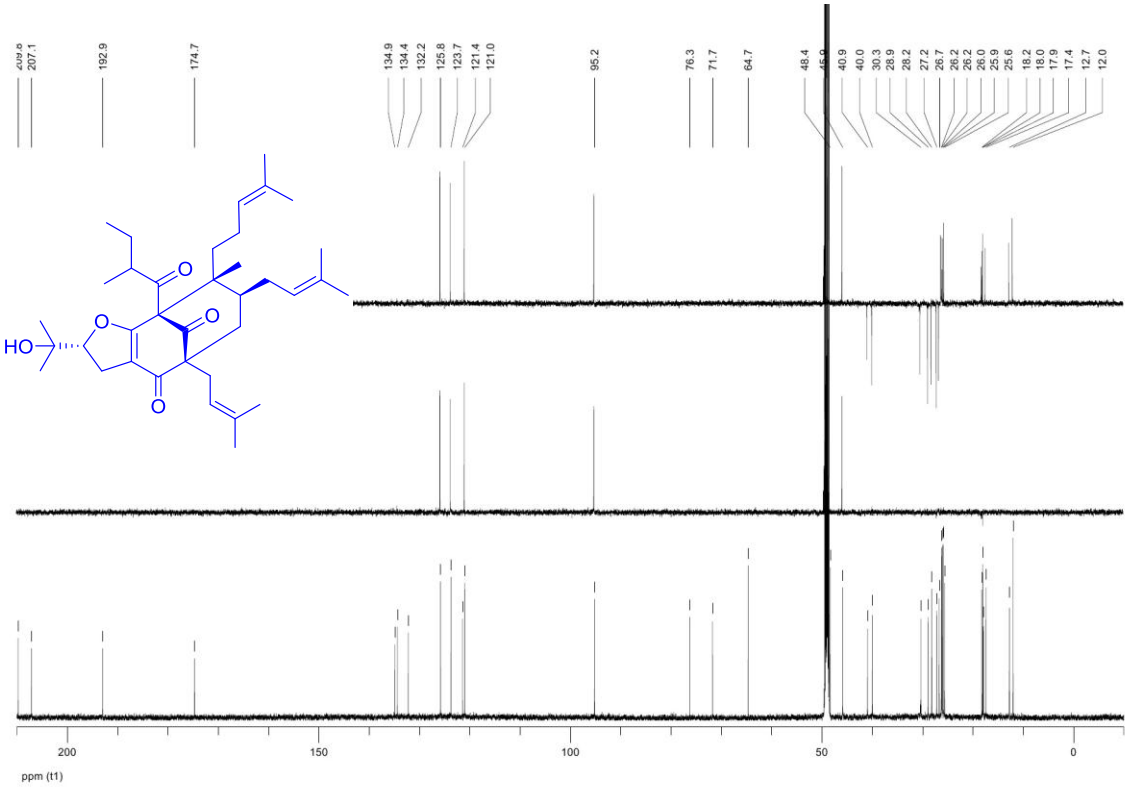

Figure S6. ^{13}C and DEPT NMR (in methanol-d_4) spectrum of **8**.

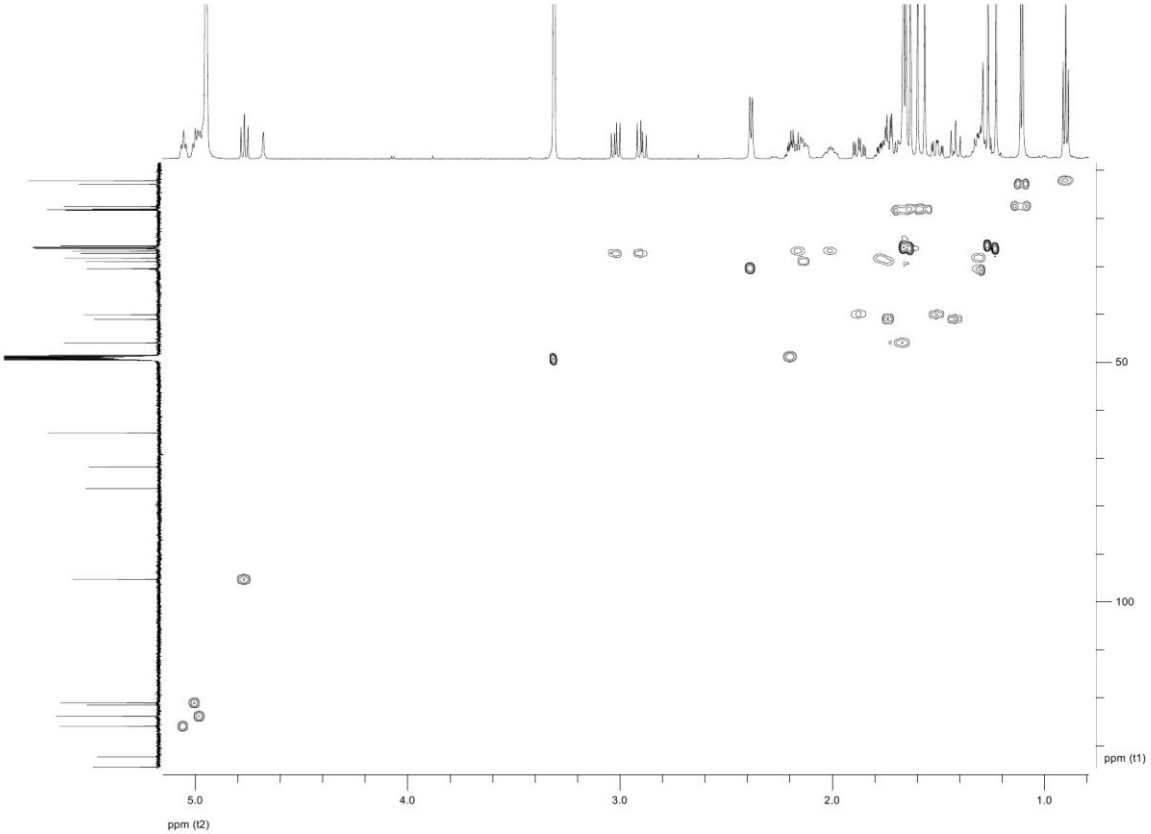

Figure S7. HSQC spectrum of **8**.

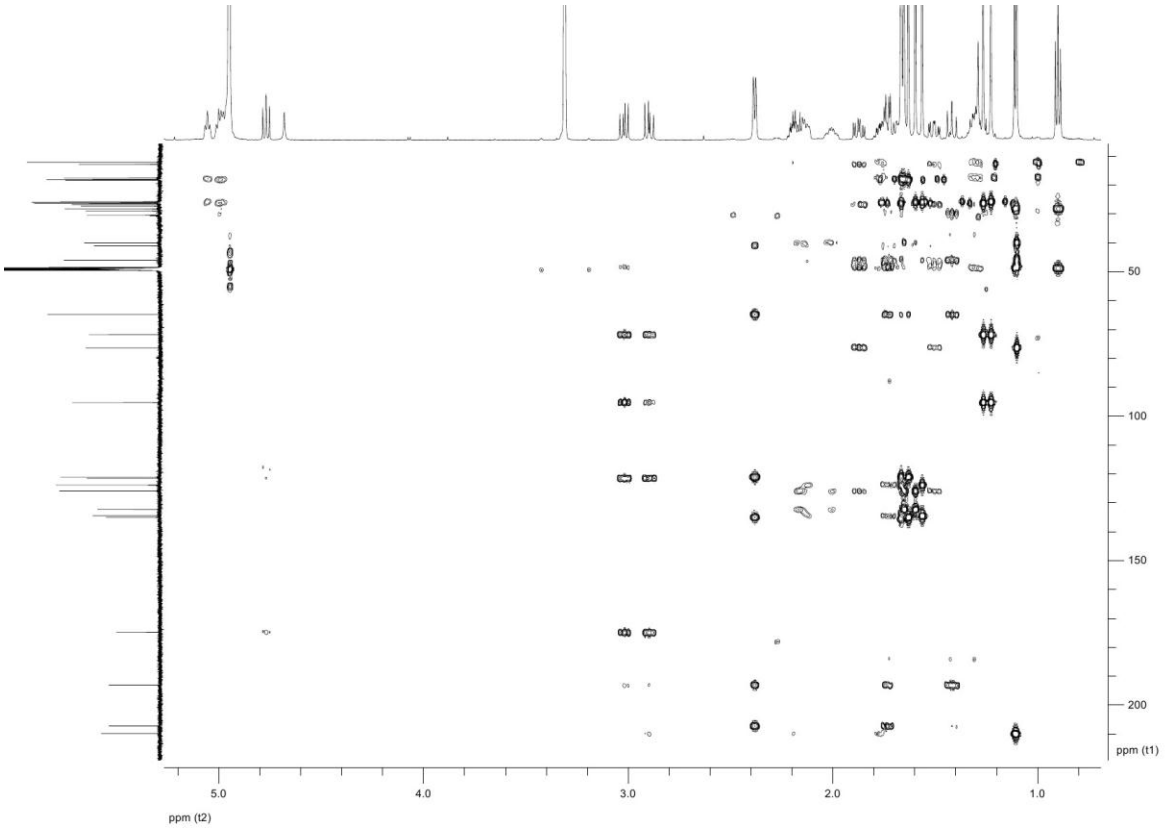

Figure S8. HMBC spectrum of **8**.

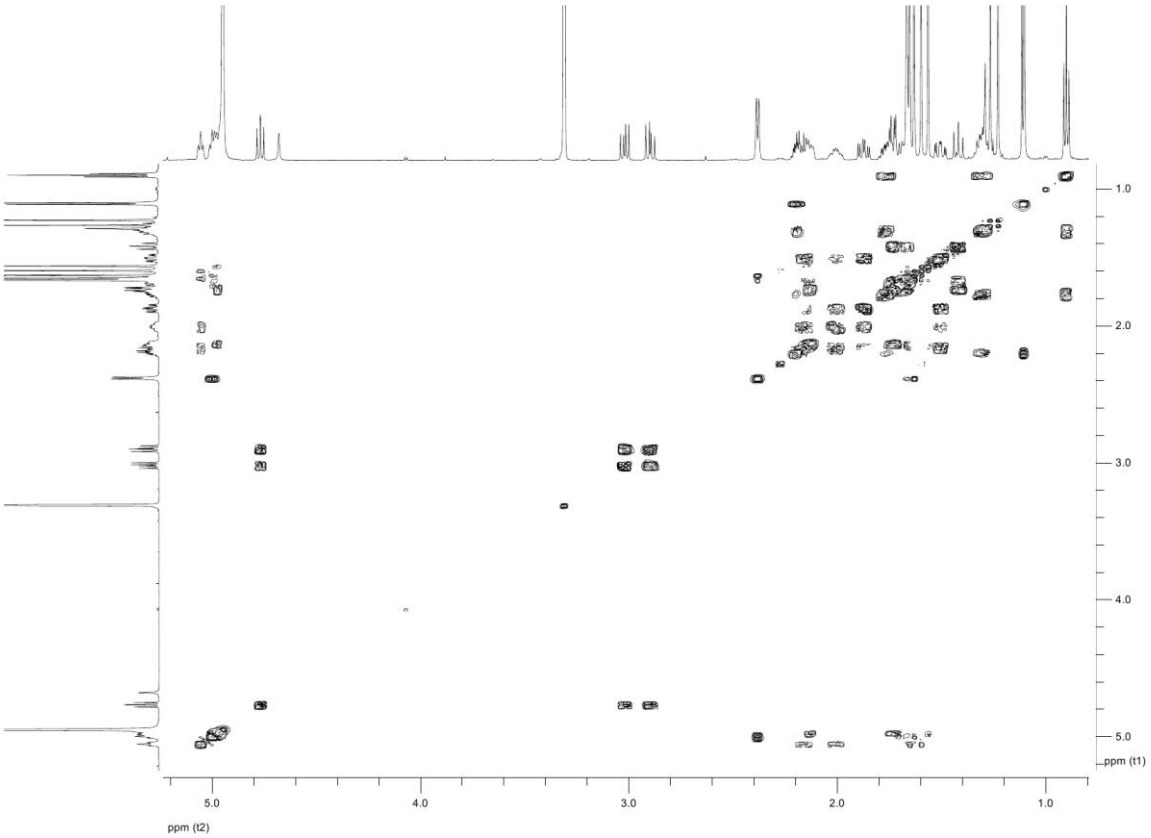

Figure S9. $^{1}H–^{1}H$ COSY spectrum of **8**.

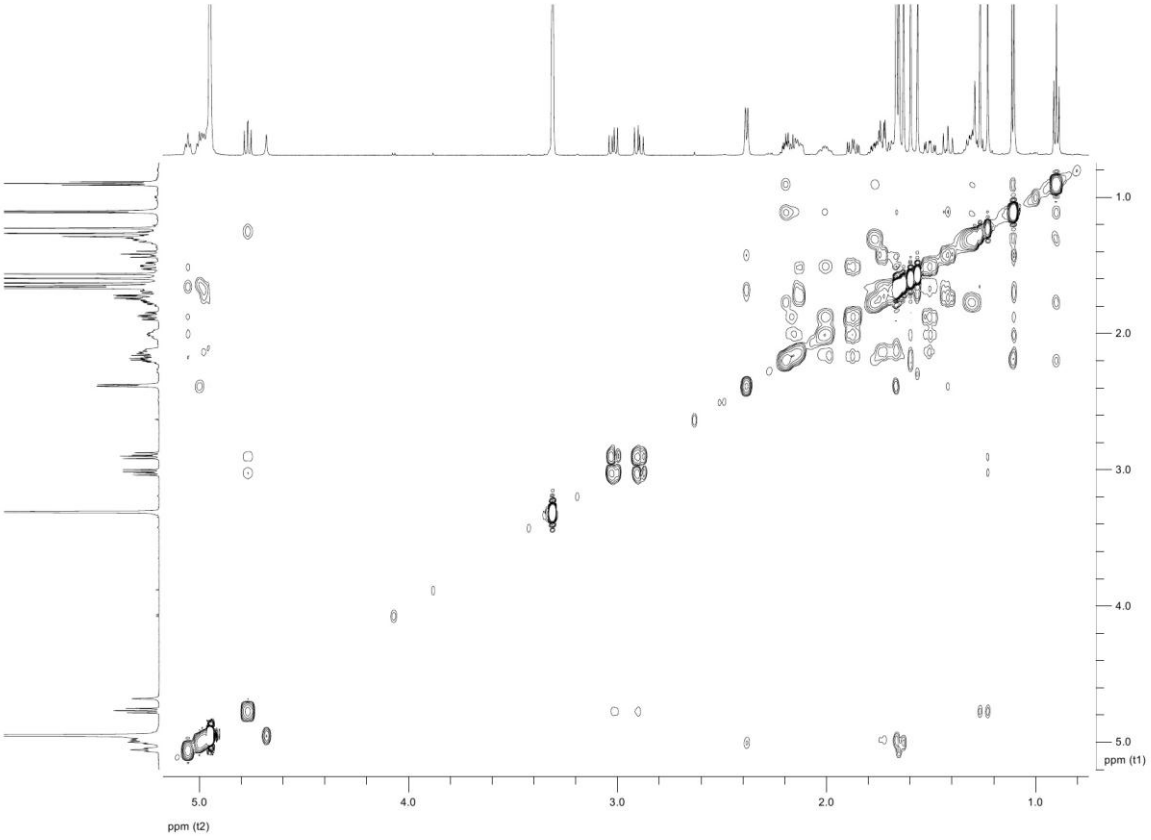

Figure S10. ROESY spectrum of **8**.

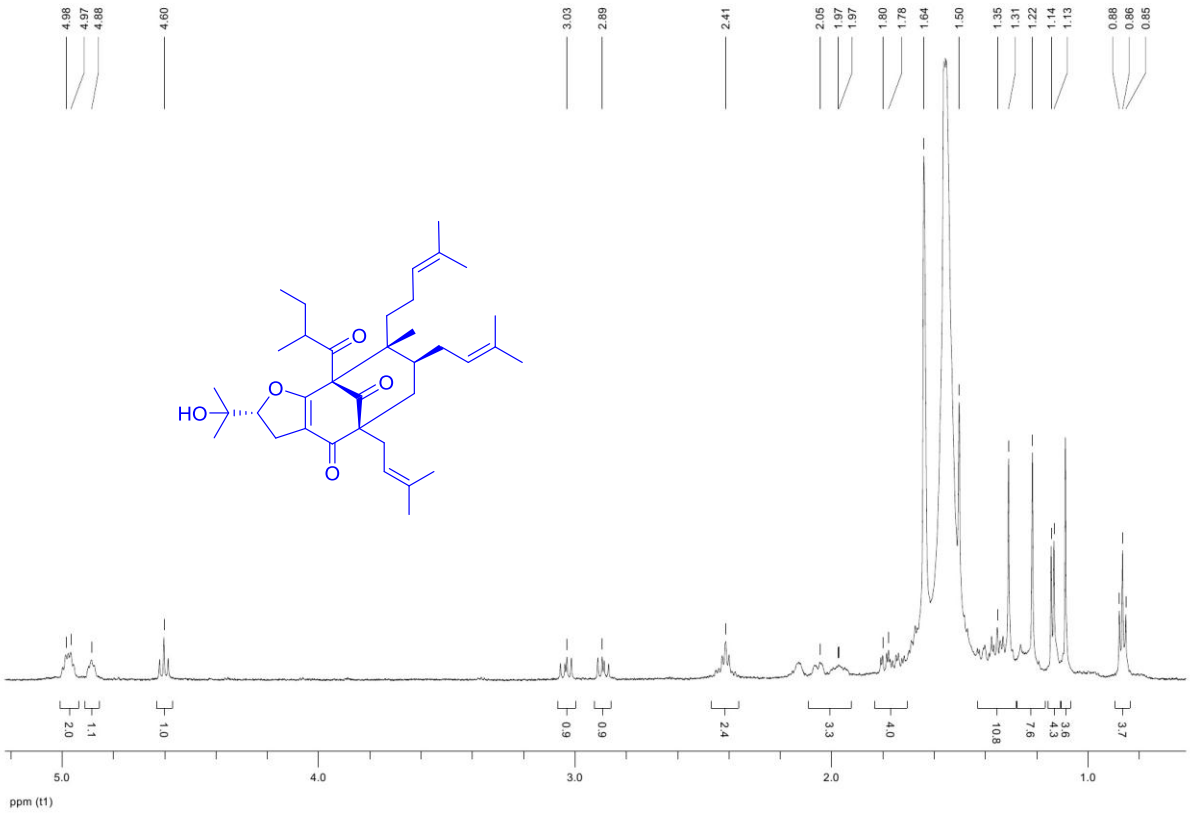

Figure S11. ^{1}H NMR (in $CDCl_3$) spectrum of **8**.

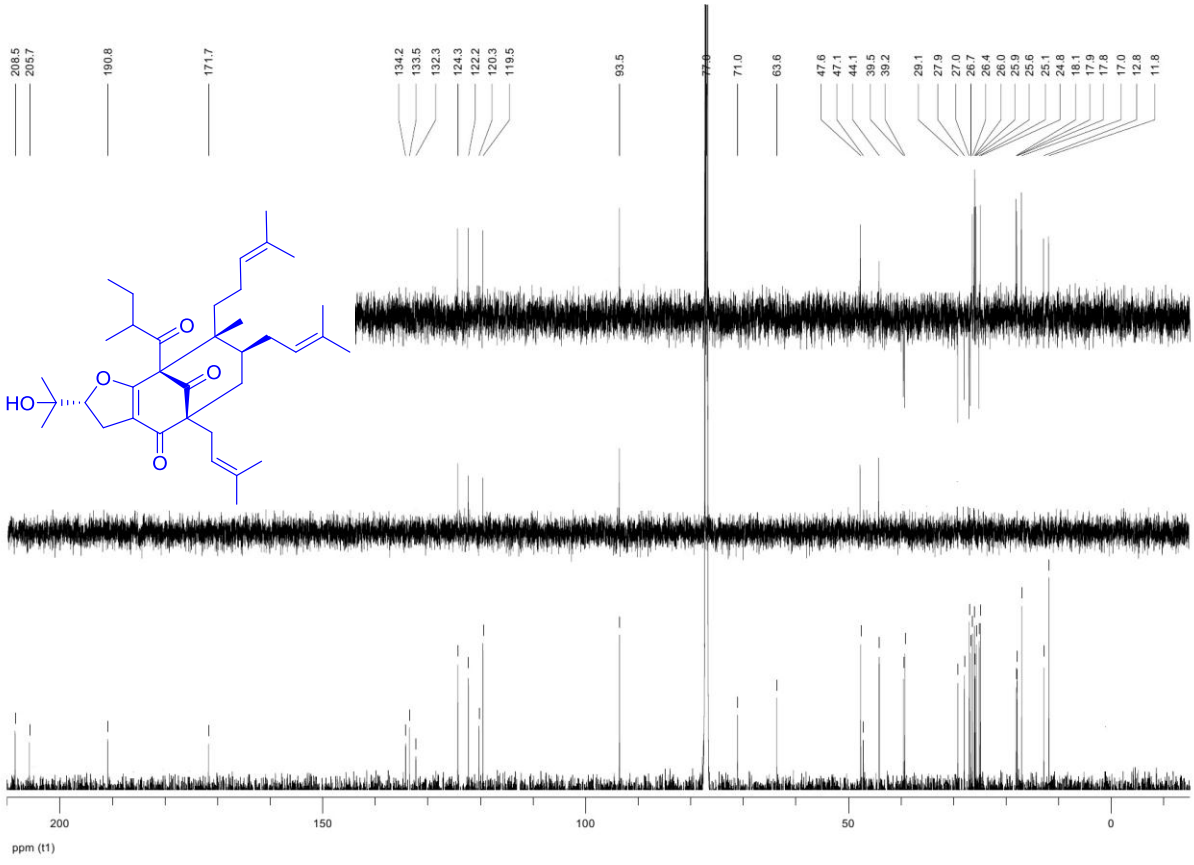

Figure S12. ^{13}C and DEPT NMR (in $CDCl_3$) spectrum of **8**.

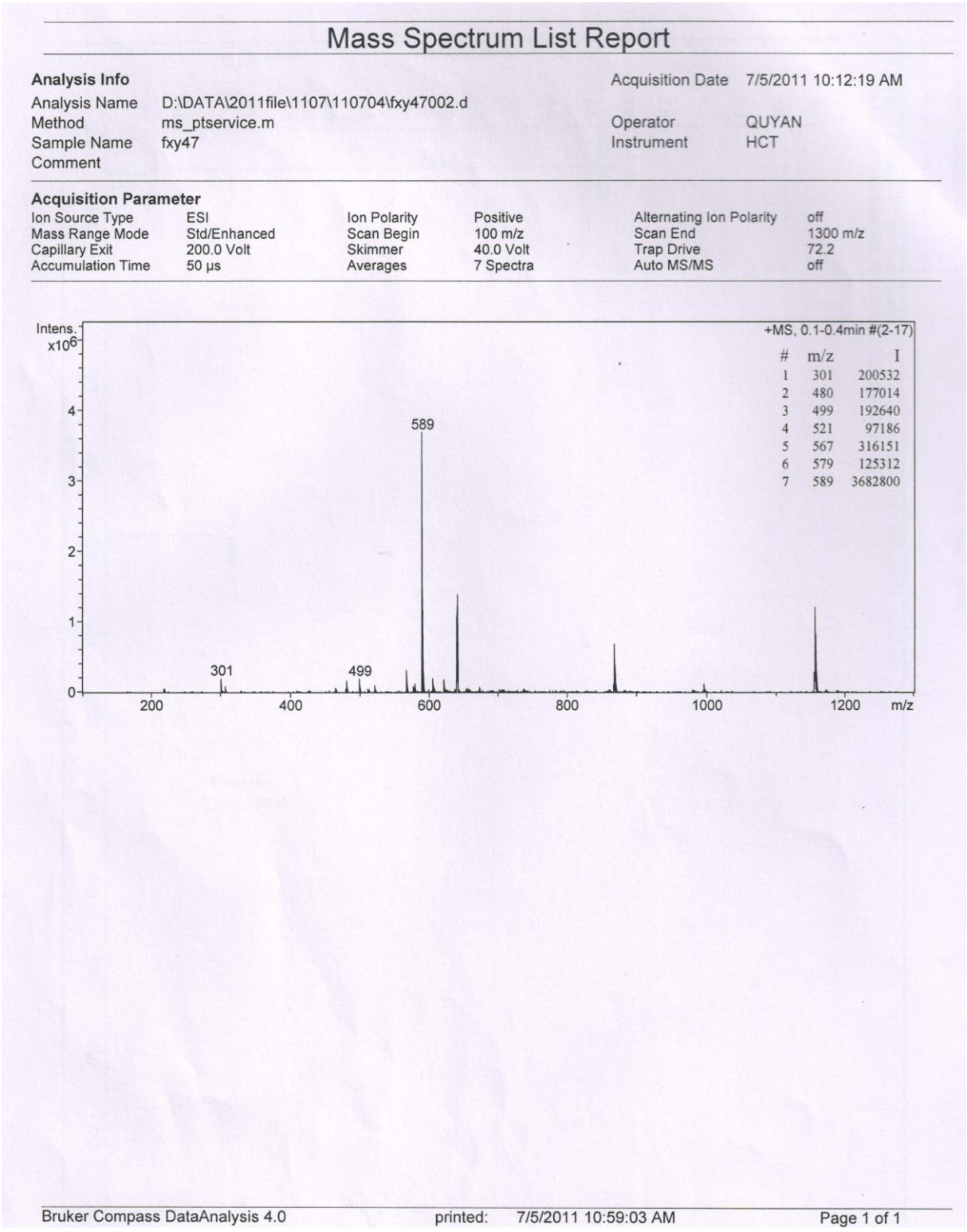

Figure S13. ESI-MS spectrum of **8**.

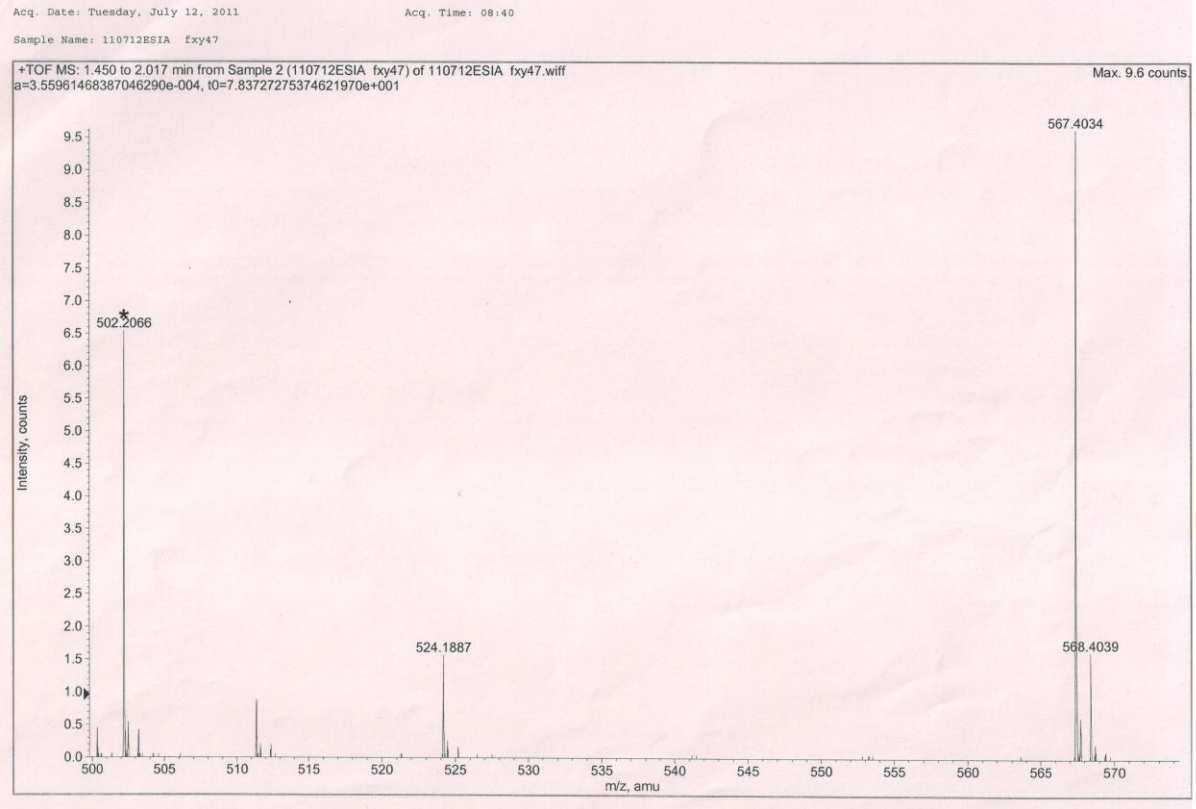

Figure S14. HR-TOFMS spectrum of **8**.