Supporting Information

Isolation of the Pyrrolizidine Alkaloid Intermedine-*N*-oxide from *Cerinthe glabra* and *ab initio* Calculation of its ^{13}C NMR Shifts

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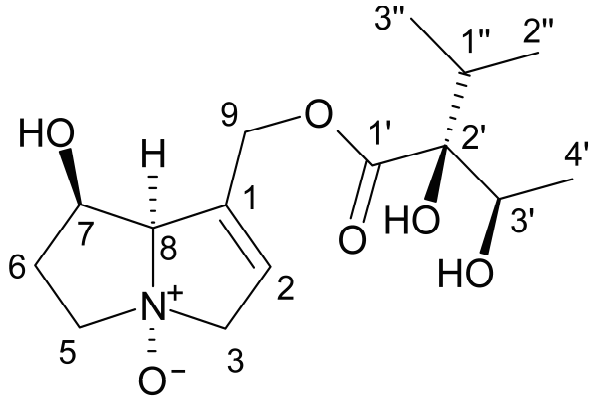


1 (7*R*, 2'*S*, 3'*R*)

General procedure for full-geometry optimization of intermedine-*N*-oxide (1)

The full-geometry optimization of **1** was calculated based on following defined six conditions [1] to [6]. Each condition was employed for both level of theories and all used basis sets 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p).

[1] All atomic coordinates (distances, angles and dihedral angles) were optimized without fixed values.

[2] The atomic coordinates of the bicyclic system were fixed using the optimized values from step 1.

[3] Each pair of methylene protons at positions 3, 5, 6 and 9 was defined with the same distance for geometry optimization.

[4] All atomic coordinates of the bicyclic system were fixed using the calculated values from the optimization step 3.

[5] All methyl and methylene protons of the molecule were fixed based on the calculated coordinates from optimization step 4.

[6] Finally, based on the fixed coordinates of methyl and methylene protons (step 5) the atomic coordinates of the bicyclic system were fixed.

Results from fully optimized structure of 1

Following Tables 1 to 8 present the calculated full-optimized coordinates of **1** from each performed optimization step [1] to [6] employing both levels of theory and the four basis sets as above and the resulting average values of distances, angles and dihedral angles. A overview of all average coordinates is given in Tables 9 and 10. All calculated standard free energy values are listed in tables 11 and 12.

Table 1. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* HF level using the 6-31G(d) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.31729	1.31729	1.31743	1.31743	1.31743	1.31743	1.31738
C(1)-C(9)	1.49880	1.49842	1.49876	1.49874	1.49876	1.49875	1.49871
C(2)-C(3)	1.49632	1.49632	1.49636	1.49636	1.49635	1.49635	1.49634
C(3)-N(4)	1.49456	1.49456	1.49298	1.49298	1.49298	1.49298	1.49351
N(4)-C(8)	1.51547	1.51547	1.51599	1.51599	1.51602	1.51602	1.51583
C(5)-C(6)	1.51883	1.51883	1.51738	1.51738	1.51736	1.51736	1.51786
C(6)-C(7)	1.52826	1.52826	1.52877	1.52877	1.52877	1.52877	1.52860
C(7)-C(8)	1.54341	1.54341	1.54519	1.54519	1.54522	1.54522	1.54461
C(7)-O	1.39778	1.39778	1.39782	1.39782	1.39779	1.39779	1.39780
C(9)-O	1.43189	1.43228	1.43176	1.43177	1.43176	1.43174	1.43187
O-C(1‘)	1.31186	1.31180	1.31204	1.31206	1.31206	1.31206	1.31198
C(1‘)-C(2‘)	1.53915	1.53940	1.53931	1.53933	1.53931	1.53936	1.53931
C(1‘)=O	1.19330	1.19323	1.19318	1.19317	1.19317	1.19318	1.19320
C(2‘)-C(3‘)	1.53930	1.53978	1.53982	1.53980	1.53982	1.53977	1.53972
C(2‘)-C(1‘‘)	1.56236	1.56347	1.56331	1.56333	1.56332	1.56330	1.56318
C(2‘)-O	1.40406	1.40401	1.40400	1.40400	1.40401	1.40399	1.40401
C(3‘)-C(4‘)	1.52371	1.52289	1.52290	1.52291	1.52290	1.52291	1.52304
C(3‘)-O	1.41596	1.41535	1.41530	1.41529	1.41528	1.41530	1.41541
C(1‘‘)-C(2‘‘)	1.53442	1.53443	1.53437	1.53438	1.53438	1.53439	1.53439
C(1‘‘)-C(3‘‘)	1.53482	1.53494	1.53492	1.53493	1.53492	1.53492	1.53491
N(4)-O	1.36991	1.37146	1.37007	1.37006	1.37006	1.37005	1.37027
Angles[b,d]							
C(8)-C(1)-C(9)	123.231	123.113	123.280	123.285	123.281	123.278	123.245
C(1)-C(2)-C(3)	112.595	112.595	112.641	112.641	112.641	112.641	112.626
C(2)-C(3)-N(4)	104.331	104.331	104.311	104.311	104.311	104.311	104.318

C(3)-N(4)-C(8)	107.808	107.808	107.883	107.883	107.885	107.885	107.858
C(5)-C(6)-C(7)	101.074	101.074	101.092	101.092	101.096	101.096	101.088
C(6)-C(7)-C(8)	101.902	101.902	101.969	101.969	101.968	101.968	101.946
C(8)-C(7)-O	112.707	112.707	112.926	112.926	112.938	112.938	112.857
N(4)-C(8)-C(7)	105.933	105.933	106.015	106.015	106.016	106.016	105.988
C(1)-C(9)-O	110.103	110.006	110.012	110.017	110.010	109.999	110.024
C(9)-O-C(1')	117.974	118.058	117.851	117.859	117.850	117.857	117.908
O-C(1')-C(2')	114.932	114.829	114.877	114.875	114.876	114.873	114.877
O-C(1')=O	124.182	124.196	124.114	124.116	124.112	124.112	124.138
C(1')-C(2')-C(3')	108.937	108.706	108.649	108.660	108.649	108.647	108.708
C(1')-C(2')-C(1'')	107.318	107.263	107.312	107.304	107.303	107.315	107.302
C(1')-C(2')-O	105.664	105.694	105.655	105.656	105.655	105.670	105.666
C(2')-C(3')-C(4')	115.784	115.438	115.430	115.430	115.431	115.439	115.492
C(2')-C(3')-O	106.909	106.926	106.917	106.914	106.918	106.909	106.916
C(2')-C(1'')-C(2'')	113.934	113.702	113.699	113.703	113.704	113.699	113.740
C(2')-C(1'')-C(3'')	113.966	113.799	113.783	113.781	113.778	113.786	113.815
O-N(4)-C(4)	109.572	109.367	109.606	109.606	109.607	109.607	109.561
Dihedral angles[b,d]							
(1)-(9)-O-(1')	200.258	200.694	198.442	198.500	198.395	198.379	199.111
(9)-O-(1')-(2')	183.522	184.046	183.427	183.476	183.428	183.442	183.557
(9)-O-(1')-O	1.632	1.982	1.458	1.502	1.460	1.482	1.586
O-(1')-(2')-(3')	317.729	316.860	317.074	317.120	317.105	317.097	317.164
O-(1')-(2')-(1'')	86.246	85.410	85.652	85.702	85.681	85.679	85.728
O-(1')-(2')-O	204.267	203.474	203.728	203.783	203.763	203.759	203.796
(1')-(2')-(1'')-(2'')	155.534	154.439	154.553	154.531	154.539	154.561	154.693
(1')-(2')-(1'')-(3'')	283.583	282.399	282.495	282.478	282.483	282.510	282.658
(4')-(3')-(2')-(1'')	63.252	300.499	64.147	64.153	64.174	64.164	103.398
O-(2')-(3')-O	61.656	62.104	62.411	62.407	62.428	62.437	62.240

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom. [d] Angles and dihedral angles in degree.

Table 2. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* HF level using the 6-311G(d) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.31670	1.31670	1.31652	1.31652	1.31652	1.31652	1.31658
C(1)-C(9)	1.49532	1.49516	1.49502	1.49501	1.49502	1.49501	1.49509
C(2)-C(3)	1.49633	1.49633	1.49654	1.49654	1.49655	1.49655	1.49647
C(3)-N(4)	1.49348	1.49348	1.49329	1.49329	1.49328	1.49328	1.49335
N(4)-C(8)	1.51430	1.51430	1.51393	1.51393	1.51393	1.51393	1.51405
C(5)-C(6)	1.51827	1.51827	1.51811	1.51811	1.51812	1.51812	1.51817
C(6)-C(7)	1.52319	1.52319	1.52320	1.52320	1.52320	1.52320	1.52320
C(7)-C(8)	1.54144	1.54144	1.53970	1.53970	1.53971	1.53971	1.54028
C(7)-O	1.40024	1.40024	1.40071	1.40071	1.40073	1.40073	1.40056
C(9)-O	1.43229	1.43215	1.43284	1.43283	1.43284	1.43283	1.43263
O-C(1‘)	1.32865	1.33009	1.32944	1.32948	1.32947	1.32947	1.32943
C(1‘)-C(2‘)	1.54076	1.54102	1.54115	1.54119	1.54117	1.54119	1.54108
C(1‘)=O	1.18081	1.18028	1.18047	1.18045	1.18045	1.18045	1.18048
C(2‘)-C(3‘)	1.54354	1.54276	1.54305	1.54305	1.54308	1.54306	1.54309
C(2‘)-C(1‘‘)	1.56264	1.56274	1.56371	1.56366	1.56371	1.56369	1.56336
C(2‘)-O	1.39319	1.39216	1.39203	1.39200	1.39202	1.39200	1.39223
C(3‘)-C(4‘)	1.52061	1.52059	1.52011	1.52011	1.52011	1.52011	1.52027
C(3‘)-O	1.41418	1.41398	1.41388	1.41392	1.41391	1.41391	1.41396
C(1‘‘)-C(2‘‘)	1.53409	1.53429	1.53462	1.53460	1.53461	1.53460	1.53447
C(1‘‘)-C(3‘‘)	1.53320	1.53313	1.53305	1.53305	1.53305	1.53305	1.53309
N(4)-O	1.36438	1.36432	1.36695	1.36696	1.36696	1.36696	1.36609
Angles[b,d]							
C(8)-C(1)-C(9)	123.147	123.076	122.984	122.983	122.983	122.982	123.026
C(1)-C(2)-C(3)	112.555	112.555	112.568	112.568	112.567	112.567	112.563
C(2)-C(3)-N(4)	104.468	104.468	104.458	104.458	104.458	104.458	104.461

C(3)-N(4)-C(8)	107.628	107.628	107.646	107.646	107.647	107.647	107.640
C(5)-C(6)-C(7)	101.291	101.291	101.302	101.302	101.301	101.301	101.298
C(6)-C(7)-C(8)	102.294	102.294	102.164	102.164	102.165	102.165	102.208
C(8)-C(7)-O	113.498	113.498	113.342	113.342	113.340	113.340	113.393
N(4)-C(8)-C(7)	106.125	106.125	106.178	106.178	106.177	106.177	106.160
C(1)-C(9)-O	110.109	110.172	109.980	109.978	109.981	109.979	110.033
C(9)-O-C(1')	116.312	116.170	116.272	116.271	116.269	116.269	116.261
O-C(1')-C(2')	114.733	114.704	114.731	114.727	114.729	114.729	114.725
O-C(1')=O	122.573	122.517	122.600	122.600	122.600	122.599	122.582
C(1')-C(2')-C(3')	107.521	107.685	107.668	107.672	107.666	107.672	107.647
C(1')-C(2')-C(1'')	108.628	108.633	108.397	108.396	108.390	108.395	108.473
C(1')-C(2')-O	106.726	106.575	106.536	106.541	106.536	106.536	106.575
C(2')-C(3')-C(4')	114.856	114.968	114.889	114.887	114.894	114.889	114.897
C(2')-C(3')-O	103.79	103.597	103.764	103.760	103.761	103.760	103.739
C(2')-C(1'')-C(2'')	113.147	113.209	113.030	113.025	113.033	113.028	113.079
C(2')-C(1'')-C(3'')	115.227	115.170	114.977	114.974	114.976	114.977	115.050
O-N(4)-C(4)	109.733	109.727	109.414	109.414	109.414	109.414	109.519
Dihedral angles[b,d]							
(1)-(9)-O-(1')	192.659	189.953	191.364	191.300	191.326	191.304	191.318
(9)-O-(1')-(2')	180.072	181.866	182.777	182.744	182.723	182.737	182.153
(9)-O-(1')-O	-0.761	0.827	1.540	1.509	1.514	1.514	1.024
O-(1')-(2')-(3')	304.181	304.188	303.816	303.863	303.857	303.857	303.960
O-(1')-(2')-(1'')	71.665	71.915	71.382	71.429	71.426	71.429	71.541
O-(1')-(2')-O	186.375	186.596	186.225	186.262	186.260	186.261	186.330
(1')-(2')-(1'')-(2'')	152.132	152.240	150.035	150.034	150.034	150.030	150.751
(1')-(2')-(1'')-(3'')	280.125	280.130	277.746	277.738	277.747	277.739	278.538
(4')-(3')-(2')-(1'')	69.801	68.392	69.306	69.276	69.286	69.282	69.224
O-(2')-(3')-O	68.901	67.331	68.134	68.114	68.110	68.113	68.117

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 3. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* HF level using the 6-31G(d,p) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.31813	1.32011	1.31767	1.31767	1.31762	1.31762	1.31814
C(1)-C(9)	1.49790	1.49720	1.49883	1.49883	1.49871	1.49870	1.49836
C(2)-C(3)	1.49652	1.50393	1.49583	1.49583	1.49590	1.49590	1.49732
C(3)-N(4)	1.49430	1.45469	1.49246	1.49246	1.49218	1.49218	1.48638
N(4)-C(8)	1.51360	1.46760	1.51479	1.51479	1.51531	1.51531	1.50690
C(5)-C(6)	1.51919	1.53162	1.51709	1.51709	1.51695	1.51695	1.51982
C(6)-C(7)	1.52462	1.52288	1.52681	1.52681	1.52894	1.52894	1.52650
C(7)-C(8)	1.53986	1.53539	1.54606	1.54606	1.54574	1.54574	1.54314
C(7)-O	1.40414	1.41628	1.39739	1.39739	1.39691	1.39691	1.40150
C(9)-O	1.43546	1.43118	1.43241	1.43241	1.43207	1.43207	1.43260
O-C(1‘)	1.33592	1.33594	1.31692	1.31692	1.31205	1.31205	1.32164
C(1‘)-C(2‘)	1.54176	1.54217	1.53800	1.53800	1.53852	1.53853	1.53950
C(1‘)=O	1.18532	1.18590	1.19147	1.19147	1.19327	1.19327	1.19012
C(2‘)-C(3‘)	1.54217	1.54795	1.54177	1.54177	1.54033	1.54031	1.54238
C(2‘)-C(1‘‘)	1.56401	1.56475	1.57091	1.57091	1.56466	1.56463	1.56664
C(2‘)-O	1.39265	1.39063	1.39411	1.39411	1.40233	1.40233	1.39602
C(3‘)-C(4‘)	1.52162	1.52090	1.52155	1.52155	1.52198	1.52197	1.52159
C(3‘)-O	1.41380	1.41299	1.41691	1.41691	1.41424	1.41425	1.41485
C(1‘‘)-C(2‘‘)	1.53489	1.53519	1.53384	1.53384	1.53382	1.53381	1.53423
C(1‘‘)-C(3‘‘)	1.53440	1.53519	1.53430	1.53430	1.53451	1.53450	1.53453
N(4)-O	1.36843	1.41506	1.36931	1.36931	1.37015	1.37015	1.37707
Angles[b,d]							
C(8)-C(1)-C(9)	122.989	123.641	123.411	123.411	123.393	123.391	123.373
C(1)-C(2)-C(3)	112.632	111.880	112.596	112.596	112.622	112.622	112.491
C(2)-C(3)-N(4)	104.391	103.720	104.304	104.304	104.305	104.305	104.222

C(3)-N(4)-C(8)	107.737	110.142	107.904	107.904	107.906	107.906	108.250
C(5)-C(6)-C(7)	101.317	102.492	101.336	101.336	101.120	101.120	101.453
C(6)-C(7)-C(8)	102.216	101.120	102.267	102.267	102.112	102.112	102.016
C(8)-C(7)-O	113.353	112.617	113.436	113.436	112.810	112.810	113.077
N(4)-C(8)-C(7)	106.031	105.207	106.033	106.033	105.968	105.968	105.873
C(1)-C(9)-O	110.022	111.874	109.533	109.533	110.148	110.145	110.209
C(9)-O-C(1')	117.730	119.156	117.232	117.232	117.910	117.915	117.862
O-C(1')-C(2')	114.164	113.223	114.727	114.727	114.689	114.684	114.369
O-C(1')=O	122.798	122.796	123.643	123.643	124.150	124.152	123.530
C(1')-C(2')-C(3')	108.096	107.400	108.904	108.904	108.491	108.486	108.380
C(1')-C(2')-C(1'')	107.841	108.178	106.631	106.631	107.174	107.178	107.272
C(1')-C(2')-O	106.733	106.694	106.425	106.425	105.803	105.809	106.315
C(2')-C(3')-C(4')	115.111	114.677	114.443	114.443	115.484	115.477	114.939
C(2')-C(3')-O	104.374	105.229	104.91	104.91	106.989	106.989	105.567
C(2')-C(1'')-C(2'')	113.351	113.028	113.137	113.137	113.336	113.331	113.220
C(2')-C(1'')-C(3'')	114.707	114.667	114.726	114.726	113.773	113.772	114.395
O-N(4)-C(4)	109.478	105.284	109.688	109.688	109.662	109.662	108.910
Dihedral angles[b,d]							
(1)-(9)-O-(1')	207.473	247.886	190.440	190.440	199.426	199.448	205.852
(9)-O-(1')-(2')	189.443	193.499	186.675	186.675	183.970	183.996	187.376
(9)-O-(1')-O	7.780	12.914	3.776	3.776	1.801	1.822	5.312
O-(1')-(2')-(3')	308.773	298.903	314.444	314.444	315.270	315.238	311.179
O-(1')-(2')-(1'')	75.949	66.946	81.017	81.017	83.543	83.500	78.662
O-(1')-(2')-O	190.580	181.927	197.930	197.930	201.832	201.796	195.333
(1')-(2')-(1'')-(2'')	151.237	148.474	151.703	151.703	151.489	151.503	151.018
(1')-(2')-(1'')-(3'')	278.980	276.051	279.885	279.885	279.572	279.576	278.992
(4')-(3')-(2')-(1'')	68.908	63.516	74.384	74.384	64.663	64.684	68.423
O-(2')-(3')-O	67.364	60.367	71.668	71.668	62.770	62.788	66.104

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 4. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* HF level using the 6-311G(d,p) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.31644	1.31644	1.31653	1.31653	1.31654	1.31654	1.31650
C(1)-C(9)	1.49486	1.49486	1.49497	1.49497	1.49497	1.49497	1.49493
C(2)-C(3)	1.49627	1.49627	1.49649	1.49649	1.49648	1.49648	1.49641
C(3)-N(4)	1.49470	1.49470	1.49364	1.49364	1.49363	1.49363	1.49399
N(4)-C(8)	1.51404	1.51404	1.51420	1.51420	1.51422	1.51422	1.51415
C(5)-C(6)	1.51926	1.51926	1.51847	1.51847	1.51847	1.51847	1.51873
C(6)-C(7)	1.52363	1.52363	1.52406	1.52406	1.52406	1.52406	1.52392
C(7)-C(8)	1.53912	1.53912	1.54004	1.54004	1.53999	1.53999	1.53972
C(7)-O	1.40121	1.40121	1.40122	1.40122	1.40119	1.40119	1.40121
C(9)-O	1.43416	1.43416	1.43419	1.43419	1.43419	1.43418	1.43418
O-C(1‘)	1.32370	1.32370	1.32377	1.32377	1.32380	1.32377	1.32375
C(1‘)-C(2‘)	1.53916	1.53916	1.53986	1.53985	1.53987	1.53985	1.53962
C(1‘)=O	1.18330	1.18330	1.18323	1.18323	1.18322	1.18322	1.18325
C(2‘)-C(3‘)	1.54358	1.54358	1.54399	1.54402	1.54400	1.54394	1.54385
C(2‘)-C(1‘‘)	1.56620	1.56620	1.56706	1.56715	1.56716	1.56719	1.56683
C(2‘)-O	1.39472	1.39472	1.39438	1.39439	1.39436	1.39437	1.39449
C(3‘)-C(4‘)	1.52119	1.52119	1.52081	1.52084	1.52083	1.52081	1.52095
C(3‘)-O	1.41270	1.41270	1.41309	1.41309	1.41308	1.41311	1.41296
C(1‘‘)-C(2‘‘)	1.53515	1.53515	1.53519	1.53521	1.53521	1.53519	1.53518
C(1‘‘)-C(3‘‘)	1.53413	1.53413	1.53399	1.53400	1.53400	1.53398	1.53404
N(4)-O	1.36538	1.36538	1.36700	1.36698	1.36701	1.36697	1.36645
Angles[b,d]							
C(8)-C(1)-C(9)	122.989	122.989	123.052	123.055	123.050	123.054	123.032
C(1)-C(2)-C(3)	112.544	112.544	112.538	112.538	112.538	112.538	112.540
C(2)-C(3)-N(4)	104.429	104.429	104.430	104.430	104.430	104.430	104.430

C(3)-N(4)-C(8)	107.661	107.661	107.705	107.705	107.704	107.704	107.690
C(5)-C(6)-C(7)	101.407	101.407	101.318	101.318	101.317	101.317	101.347
C(6)-C(7)-C(8)	101.992	101.992	102.051	102.051	102.050	102.050	102.031
C(8)-C(7)-O	113.360	113.360	113.353	113.353	113.348	113.348	113.354
N(4)-C(8)-C(7)	106.139	106.139	106.171	106.171	106.171	106.171	106.161
C(1)-C(9)-O	109.659	109.659	109.781	109.786	109.786	109.785	109.743
C(9)-O-C(1')	116.475	116.475	116.462	116.458	116.456	116.452	116.463
O-C(1')-C(2')	115.175	115.175	115.229	115.234	115.234	115.232	115.213
O-C(1')=O	122.748	122.748	122.734	122.733	122.730	122.731	122.737
C(1')-C(2')-C(3')	107.943	107.943	107.851	107.834	107.845	107.867	107.881
C(1')-C(2')-C(1'')	108.238	108.238	108.151	108.150	108.151	108.148	108.179
C(1')-C(2')-O	106.376	106.376	106.319	106.308	106.311	106.303	106.332
C(2')-C(3')-C(4')	114.597	114.597	114.488	114.505	114.494	114.473	114.526
C(2')-C(3')-O	104.493	104.493	104.426	104.419	104.420	104.433	104.447
C(2')-C(1'')-C(2'')	113.336	113.336	113.182	113.204	113.199	113.196	113.242
C(2')-C(1'')-C(3'')	115.588	115.588	115.336	115.349	115.346	115.335	115.424
O-N(4)-C(4)	109.452	109.452	109.375	109.376	109.376	109.376	109.401
Dihedral angles[b,d]							
(1)-(9)-O-(1')	190.314	190.314	190.490	190.447	190.467	190.354	190.398
(9)-O-(1')-(2')	180.936	180.936	181.085	181.066	181.098	181.099	181.037
(9)-O-(1')-O	-0.666	-0.666	-0.509	-0.549	-0.540	-0.568	-0.583
O-(1')-(2')-(3')	305.500	305.500	305.374	305.410	305.373	305.419	305.429
O-(1')-(2')-(1'')	72.833	72.833	72.796	72.858	72.815	72.864	72.833
O-(1')-(2')-O	188.522	188.522	188.467	188.520	188.480	188.536	188.508
(1')-(2')-(1'')-(2'')	153.783	153.783	153.352	153.386	153.330	153.298	153.489
(1')-(2')-(1'')-(3'')	281.755	281.755	281.208	281.278	281.213	281.154	281.394
(4')-(3')-(2')-(1'')	72.635	72.635	72.632	72.619	72.625	72.603	72.625
O-(2')-(3')-O	71.063	71.063	71.014	70.980	70.986	70.969	71.013

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 5. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-31G(d) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.33956	1.33956	1.33964	1.33964	1.33971	1.33971	1.33964
C(1)-C(9)	1.49759	1.49724	1.49728	1.49737	1.49750	1.49747	1.49741
C(2)-C(3)	1.49353	1.49353	1.49385	1.49385	1.49375	1.49375	1.49371
C(3)-N(4)	1.53220	1.53220	1.53108	1.53108	1.53173	1.53173	1.53167
N(4)-C(8)	1.56824	1.56824	1.56834	1.56834	1.56849	1.56849	1.56836
C(5)-C(6)	1.52210	1.52210	1.52148	1.52148	1.52157	1.52157	1.52172
C(6)-C(7)	1.53219	1.53219	1.53239	1.53239	1.53206	1.53206	1.53221
C(7)-C(8)	1.54241	1.54241	1.54282	1.54282	1.54264	1.54264	1.54262
C(7)-O	1.44100	1.44100	1.44112	1.44112	1.44162	1.44162	1.44125
C(9)-O	1.46272	1.46356	1.46336	1.46320	1.46326	1.46327	1.46323
O-C(1‘)	1.37862	1.37870	1.37901	1.37895	1.37818	1.37820	1.37861
C(1‘)-C(2‘)	1.55528	1.55590	1.55594	1.55587	1.55579	1.55580	1.55576
C(1‘)=O	1.20585	1.20575	1.20566	1.20566	1.20594	1.20593	1.20580
C(2‘)-C(3‘)	1.55943	1.56029	1.56028	1.56026	1.56081	1.56079	1.56031
C(2‘)-C(1‘‘)	1.57116	1.57166	1.57176	1.57179	1.57150	1.57150	1.57156
C(2‘)-O	1.41114	1.41087	1.41084	1.41087	1.41086	1.41085	1.41091
C(3‘)-C(4‘)	1.52615	1.52559	1.52559	1.52555	1.52509	1.52509	1.52551
C(3‘)-O	1.43652	1.43713	1.43714	1.43724	1.43699	1.43701	1.43700
C(1‘‘)-C(2‘‘)	1.53903	1.53902	1.53905	1.53909	1.53920	1.53920	1.53910
C(1‘‘)-C(3‘‘)	1.53801	1.53793	1.53797	1.53800	1.53793	1.53792	1.53796
N(4)-O	1.34503	1.34778	1.34692	1.34678	1.34669	1.34667	1.34664
Angles[b,d]							
C(8)-C(1)-C(9)	123.411	123.197	123.271	123.266	123.284	123.278	123.284
C(1)-C(2)-C(3)	113.262	113.262	113.230	113.230	113.231	113.231	113.241
C(2)-C(3)-N(4)	104.831	104.831	104.851	104.851	104.863	104.863	104.848

C(3)-N(4)-C(8)	106.050	106.050	106.052	106.052	106.014	106.014	106.039
C(5)-C(6)-C(7)	101.887	101.887	101.770	101.770	101.812	101.812	101.823
C(6)-C(7)-C(8)	103.237	103.237	103.202	103.202	103.181	103.181	103.207
C(8)-C(7)-O	112.925	112.925	112.915	112.915	112.892	112.892	112.911
N(4)-C(8)-C(7)	105.806	105.806	105.865	105.865	105.863	105.863	105.845
C(1)-C(9)-O	112.638	112.406	112.442	112.431	112.646	112.629	112.532
C(9)-O-C(1')	116.738	116.689	116.694	116.688	116.625	116.620	116.676
O-C(1')-C(2')	113.126	113.189	113.183	113.191	113.170	113.169	113.171
O-C(1')=O	122.277	122.283	122.270	122.258	122.245	122.247	122.264
C(1')-C(2')-C(3')	108.775	108.620	108.636	108.646	108.503	108.532	108.619
C(1')-C(2')-C(1'')	107.511	107.429	107.410	107.405	107.506	107.472	107.455
C(1')-C(2')-O	106.616	106.551	106.547	106.547	106.566	106.569	106.566
C(2')-C(3')-C(4')	114.713	114.592	114.590	114.593	114.564	114.558	114.602
C(2')-C(3')-O	105.436	105.327	105.332	105.346	105.370	105.366	105.363
C(2')-C(1'')-C(2'')	113.084	112.981	112.978	112.978	112.959	112.961	112.990
C(2')-C(1'')-C(3'')	114.097	113.956	113.958	113.966	114.046	114.037	114.010
O-N(4)-C(4)	110.892	110.545	110.717	110.715	110.740	110.740	110.725
Dihedral angles[b,d]							
(1)-(9)-O-(1')	250.159	249.093	249.119	249.107	251.117	250.980	249.929
(9)-O-(1')-(2')	193.811	193.922	193.911	193.946	194.08	194.046	193.953
(9)-O-(1')-O	12.049	12.293	12.263	12.304	12.49	12.428	12.305
O-(1')-(2')-(3')	303.213	303.059	303.166	303.191	302.48	302.577	302.948
O-(1')-(2')-(1'')	71.851	71.909	72.022	72.044	71.447	71.542	71.802
O-(1')-(2')-O	186.547	186.528	186.640	186.661	186.062	186.143	186.430
(1')-(2')-(1'')-(2'')	150.251	150.210	150.190	150.195	150.399	150.360	150.267
(1')-(2')-(1'')-(3'')	278.132	278.030	278.019	278.026	278.219	278.180	278.101
(4')-(3')-(2')-(1'')	59.290	59.441	59.460	59.446	59.286	59.319	59.374
O-(2')-(3')-O	55.576	55.828	55.825	55.806	55.550	55.568	55.692

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 6. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-311G(d) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.33581	1.33581	1.33591	1.33591	1.33591	1.33591	1.33587
C(1)-C(9)	1.49494	1.49493	1.49486	1.49483	1.49483	1.49439	1.49480
C(2)-C(3)	1.49183	1.49183	1.49206	1.49206	1.49207	1.49207	1.49199
C(3)-N(4)	1.52917	1.52917	1.52811	1.52811	1.52810	1.52810	1.52846
N(4)-C(8)	1.56252	1.56252	1.56390	1.56390	1.56391	1.56391	1.56344
C(5)-C(6)	1.52046	1.52046	1.51977	1.51977	1.51977	1.51977	1.52000
C(6)-C(7)	1.52907	1.52907	1.52925	1.52925	1.52924	1.52924	1.52919
C(7)-C(8)	1.54031	1.54031	1.54077	1.54077	1.54075	1.54075	1.54061
C(7)-O	1.43995	1.43995	1.43969	1.43969	1.43964	1.43964	1.43976
C(9)-O	1.46420	1.46416	1.46435	1.46437	1.46440	1.46317	1.46411
O-C(1‘)	1.37688	1.37687	1.37727	1.37722	1.37726	1.37810	1.37727
C(1‘)-C(2‘)	1.55384	1.55384	1.55471	1.55472	1.55476	1.55552	1.55456
C(1‘)=O	1.19841	1.19842	1.19814	1.19815	1.19814	1.19743	1.19812
C(2‘)-C(3‘)	1.55650	1.55658	1.55682	1.55676	1.55676	1.55307	1.55608
C(2‘)-C(1‘‘)	1.56896	1.56903	1.56971	1.56970	1.56968	1.56878	1.56931
C(2‘)-O	1.41029	1.41025	1.41002	1.41004	1.41004	1.41168	1.41039
C(3‘)-C(4‘)	1.52334	1.52334	1.52274	1.52274	1.52274	1.52279	1.52295
C(3‘)-O	1.43785	1.43783	1.43869	1.43868	1.43872	1.43937	1.43852
C(1‘‘)-C(2‘‘)	1.53686	1.53686	1.53692	1.53691	1.53690	1.53688	1.53689
C(1‘‘)-C(3‘‘)	1.53629	1.53630	1.53618	1.53617	1.53617	1.53572	1.53614
N(4)-O	1.34891	1.34889	1.35042	1.35038	1.35039	1.35045	1.34991
Angles[b,d]							
C(8)-C(1)-C(9)	123.100	123.091	123.073	123.067	123.063	123.481	123.146
C(1)-C(2)-C(3)	113.243	113.243	113.229	113.229	113.229	113.229	113.234
C(2)-C(3)-N(4)	104.844	104.844	104.871	104.871	104.872	104.872	104.862

C(3)-N(4)-C(8)	106.077	106.077	106.065	106.065	106.063	106.063	106.068
C(5)-C(6)-C(7)	102.060	102.060	101.983	101.983	101.984	101.984	102.009
C(6)-C(7)-C(8)	103.257	103.257	103.258	103.258	103.262	103.262	103.259
C(8)-C(7)-O	113.156	113.156	113.157	113.157	113.153	113.153	113.155
N(4)-C(8)-C(7)	105.940	105.940	105.974	105.974	105.976	105.976	105.963
C(1)-C(9)-O	112.022	112.038	111.999	111.980	111.982	111.429	111.908
C(9)-O-C(1')	117.111	117.124	117.123	117.119	117.118	117.104	117.117
O-C(1')-C(2')	113.069	113.060	113.097	113.104	113.104	113.186	113.103
O-C(1')=O	122.482	122.481	122.487	122.490	122.489	122.567	122.499
C(1')-C(2')-C(3')	108.756	108.768	108.648	108.642	108.656	108.899	108.728
C(1')-C(2')-C(1'')	107.647	107.648	107.497	107.503	107.490	107.133	107.486
C(1')-C(2')-O	106.734	106.729	106.683	106.679	106.681	106.727	106.706
C(2')-C(3')-C(4')	114.740	114.728	114.657	114.656	114.659	114.891	114.722
C(2')-C(3')-O	105.243	105.260	105.059	105.058	105.052	104.730	105.067
C(2')-C(1'')-C(2'')	113.187	113.183	113.096	113.095	113.097	113.192	113.142
C(2')-C(1'')-C(3'')	114.151	114.155	114.015	114.019	114.015	113.743	114.016
O-N(4)-C(4)	110.669	110.670	110.534	110.534	110.535	110.534	110.579
Dihedral angles[b,d]							
(1)-(9)-O-(1')	244.034	244.314	243.160	242.926	242.902	232.864	241.700
(9)-O-(1')-(2')	193.507	193.552	193.541	193.487	193.480	192.541	193.351
(9)-O-(1')-O	12.015	12.078	11.968	11.896	11.892	10.441	11.715
O-(1')-(2')-(3')	303.983	303.861	304.393	304.415	304.498	310.030	305.197
O-(1')-(2')-(1'')	72.345	72.225	72.959	72.980	73.068	78.422	73.666
O-(1')-(2')-O	187.044	186.932	187.551	187.570	187.652	192.718	188.245
(1')-(2')-(1'')-(2'')	150.131	150.097	150.069	150.081	150.088	151.053	150.253
(1')-(2')-(1'')-(3'')	278.117	278.080	278.039	278.051	278.061	278.991	278.223
(4')-(3')-(2')-(1'')	60.637	60.611	60.701	60.751	60.724	61.824	60.875
O-(2')-(3')-O	57.383	57.335	57.542	57.599	57.569	59.202	57.772

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 7. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-31G(d,p) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.33955	1.33955	1.33970	1.33970	1.33959	1.33960	1.33961
C(1)-C(9)	1.49683	1.49682	1.49686	1.49680	1.49702	1.49699	1.49689
C(2)-C(3)	1.49312	1.49312	1.49326	1.49326	1.49305	1.49291	1.49312
C(3)-N(4)	1.53159	1.53159	1.53076	1.53076	1.53208	1.53216	1.53149
N(4)-C(8)	1.56583	1.56583	1.56752	1.56752	1.56653	1.56605	1.56654
C(5)-C(6)	1.52196	1.52196	1.52112	1.52112	1.52211	1.52215	1.52174
C(6)-C(7)	1.53210	1.53210	1.53238	1.53238	1.53128	1.53132	1.53193
C(7)-C(8)	1.54200	1.54200	1.54235	1.54235	1.54128	1.54104	1.54184
C(7)-O	1.44062	1.44062	1.44068	1.44068	1.44101	1.44108	1.44078
C(9)-O	1.46342	1.46347	1.46335	1.46342	1.46294	1.46300	1.46327
O-C(1‘)	1.37787	1.37784	1.37795	1.37772	1.37710	1.37684	1.37756
C(1‘)-C(2‘)	1.55468	1.55471	1.55471	1.55525	1.55479	1.55451	1.55478
C(1‘)=O	1.20605	1.20606	1.20604	1.20601	1.20626	1.20638	1.20613
C(2‘)-C(3‘)	1.55926	1.55928	1.55919	1.56014	1.55990	1.56007	1.55964
C(2‘)-C(1‘‘)	1.57110	1.57115	1.57104	1.57208	1.57111	1.57121	1.57128
C(2‘)-O	1.41039	1.41037	1.41040	1.41020	1.41026	1.41025	1.41031
C(3‘)-C(4‘)	1.52566	1.52566	1.52559	1.53029	1.52525	1.52537	1.52630
C(3‘)-O	1.43553	1.43553	1.43524	1.43586	1.43545	1.43542	1.43550
C(1‘‘)-C(2‘‘)	1.53864	1.53864	1.53869	1.53361	1.53871	1.53868	1.53783
C(1‘‘)-C(3‘‘)	1.53763	1.53761	1.53753	1.53590	1.53753	1.53757	1.53729
N(4)-O	1.34643	1.34641	1.34739	1.34736	1.34634	1.34665	1.34676
Angles[b,d]							
C(8)-C(1)-C(9)	123.253	123.255	123.248	123.252	123.239	123.275	123.254
C(1)-C(2)-C(3)	113.230	113.230	113.221	113.221	113.223	113.257	113.230
C(2)-C(3)-N(4)	104.821	104.821	104.849	104.849	104.858	104.831	104.838

C(3)-N(4)-C(8)	106.104	106.104	106.083	106.083	106.046	106.065	106.081
C(5)-C(6)-C(7)	101.801	101.801	101.726	101.726	101.897	101.929	101.813
C(6)-C(7)-C(8)	103.124	103.124	103.161	103.161	103.038	103.037	103.107
C(8)-C(7)-O	112.945	112.945	112.942	112.942	112.930	112.923	112.938
N(4)-C(8)-C(7)	105.786	105.786	105.847	105.847	105.796	105.814	105.812
C(1)-C(9)-O	112.428	112.420	112.469	112.483	112.570	112.603	112.495
C(9)-O-C(1')	116.618	116.606	116.623	116.627	116.580	116.576	116.605
O-C(1')-C(2')	113.142	113.147	113.128	113.151	113.108	113.100	113.129
O-C(1')=O	122.315	122.311	122.310	122.312	122.287	122.294	122.305
C(1')-C(2')-C(3')	108.708	108.721	108.707	108.643	108.668	108.630	108.680
C(1')-C(2')-C(1'')	107.610	107.592	107.566	107.421	107.547	107.628	107.561
C(1')-C(2')-O	106.638	106.642	106.670	106.623	106.706	106.682	106.660
C(2')-C(3')-C(4')	114.554	114.555	114.631	114.476	114.584	114.532	114.556
C(2')-C(3')-O	105.494	105.503	105.566	105.431	105.516	105.579	105.515
C(2')-C(1'')-C(2'')	113.129	113.131	112.991	112.890	113.128	113.108	113.063
C(2')-C(1'')-C(3'')	114.114	114.113	114.135	114.041	114.199	114.204	114.134
O-N(4)-C(4)	110.796	110.795	110.668	110.666	110.755	110.725	110.734
Dihedral angles[b,d]							
(1)-(9)-O-(1')	249.232	249.272	249.333	249.576	251.093	251.564	250.012
(9)-O-(1')-(2')	193.668	193.647	193.644	193.898	193.838	193.892	193.765
(9)-O-(1')-O	12.063	12.047	11.995	12.269	12.210	12.323	12.151
O-(1')-(2')-(3')	302.903	302.991	302.740	302.658	303.119	302.510	302.820
O-(1')-(2')-(1'')	71.411	71.506	71.208	71.395	71.727	71.098	71.391
O-(1')-(2')-O	186.150	186.235	185.940	185.993	186.432	185.857	186.101
(1')-(2')-(1'')-(2'')	150.539	150.560	149.951	149.981	150.960	150.802	150.466
(1')-(2')-(1'')-(3'')	278.402	278.422	277.878	277.863	278.890	278.675	278.355
(4')-(3')-(2')-(1'')	59.741	59.717	59.791	59.691	59.054	59.263	59.543
O-(2')-(3')-O	56.145	56.118	56.244	56.182	55.292	55.490	55.912

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 8. Calculated distances, angles, and dihedral angles of the full-optimized structure of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-311G(d,p) basis set

	[1][a]	[2][a]	[3][a]	[4][a]	[5][a]	[6][a]	Average
Distances[b,c]							
C(1)-C(2)	1.33554	1.33553	1.33568	1.33568	1.33565	1.33565	1.33562
C(1)-C(9)	1.49396	1.49398	1.49389	1.49407	1.49363	1.49365	1.49386
C(2)-C(3)	1.49192	1.49194	1.49205	1.49205	1.49174	1.49174	1.49191
C(3)-N(4)	1.52923	1.52910	1.52809	1.52809	1.52836	1.52836	1.52854
N(4)-C(8)	1.56055	1.56035	1.56179	1.56179	1.56147	1.56147	1.56124
C(5)-C(6)	1.52136	1.52142	1.52053	1.52053	1.52060	1.52060	1.52084
C(6)-C(7)	1.53039	1.53034	1.53076	1.53076	1.53180	1.53180	1.53097
C(7)-C(8)	1.54108	1.54132	1.54171	1.54171	1.54274	1.54274	1.54189
C(7)-O	1.43663	1.43643	1.43631	1.43631	1.43639	1.43639	1.43641
C(9)-O	1.46614	1.46615	1.46626	1.46601	1.46625	1.46630	1.46618
O-C(1‘)	1.37705	1.37696	1.37666	1.37687	1.37650	1.37660	1.37677
C(1‘)-C(2‘)	1.55576	1.55580	1.55620	1.55620	1.55501	1.55500	1.55566
C(1‘)=O	1.19770	1.19771	1.19767	1.19762	1.19785	1.19784	1.19773
C(2‘)-C(3‘)	1.55216	1.55206	1.55249	1.55243	1.55322	1.55328	1.55261
C(2‘)-C(1‘‘)	1.56860	1.56870	1.56963	1.56947	1.57033	1.57021	1.56949
C(2‘)-O	1.41260	1.41263	1.41242	1.41248	1.41231	1.41230	1.41246
C(3‘)-C(4‘)	1.52491	1.52485	1.52423	1.52429	1.52364	1.52358	1.52425
C(3‘)-O	1.43962	1.43951	1.44012	1.44014	1.44006	1.43994	1.43990
C(1‘‘)-C(2‘‘)	1.53789	1.53791	1.53793	1.53798	1.53787	1.53786	1.53791
C(1‘‘)-C(3‘‘)	1.53632	1.53638	1.53637	1.53638	1.53649	1.53644	1.53639
N(4)-O	1.35035	1.35052	1.35184	1.35162	1.35161	1.35160	1.35126
Angles[b,d]							
C(8)-C(1)-C(9)	122.884	122.892	122.866	122.863	122.882	122.880	122.878
C(1)-C(2)-C(3)	113.227	113.212	113.209	113.209	113.204	113.204	113.211
C(2)-C(3)-N(4)	104.791	104.801	104.820	104.820	104.768	104.768	104.795

C(3)-N(4)-C(8)	106.156	106.158	106.163	106.163	106.237	106.237	106.186
C(5)-C(6)-C(7)	101.911	101.924	101.836	101.836	101.820	101.820	101.858
C(6)-C(7)-C(8)	103.040	103.055	103.079	103.079	103.104	103.104	103.077
C(8)-C(7)-O	113.165	113.150	113.189	113.189	113.251	113.251	113.199
N(4)-C(8)-C(7)	105.920	105.903	105.962	105.962	106.013	106.013	105.962
C(1)-C(9)-O	110.435	110.433	110.450	110.446	110.655	110.661	110.513
C(9)-O-C(1')	116.954	116.951	116.926	116.951	116.819	116.827	116.905
O-C(1')-C(2')	113.184	113.190	113.226	113.222	113.264	113.267	113.226
O-C(1')=O	122.603	122.599	122.617	122.607	122.651	122.652	122.621
C(1')-C(2')-C(3')	109.068	109.051	108.875	108.920	108.783	108.793	108.915
C(1')-C(2')-C(1'')	107.116	107.127	107.105	107.065	107.253	107.260	107.154
C(1')-C(2')-O	106.827	106.823	106.750	106.757	106.716	106.729	106.767
C(2')-C(3')-C(4')	115.097	115.099	114.941	114.945	114.787	114.767	114.939
C(2')-C(3')-O	104.849	104.866	104.750	104.755	104.766	104.790	104.796
C(2')-C(1'')-C(2'')	113.316	113.341	113.224	113.229	113.221	113.210	113.257
C(2')-C(1'')-C(3'')	113.999	114.008	113.819	113.818	113.810	113.795	113.875
O-N(4)-C(4)	110.589	110.582	110.451	110.449	110.484	110.483	110.506
Dihedral angles[b,d]							
(1)-(9)-O-(1')	223.822	223.660	223.091	223.208	225.114	225.158	224.009
(9)-O-(1')-(2')	190.998	190.972	190.860	191.031	191.107	191.131	191.016
(9)-O-(1')-O	8.779	8.716	8.630	8.816	9.025	9.111	8.846
O-(1')-(2')-(3')	311.404	311.387	310.905	311.184	309.559	309.542	310.663
O-(1')-(2')-(1'')	79.586	79.584	79.169	79.473	77.799	77.764	78.896
O-(1')-(2')-O	193.712	193.704	193.302	193.592	192.008	191.983	193.050
(1')-(2')-(1'')-(2'')	152.580	152.578	152.119	152.190	151.626	151.668	152.127
(1')-(2')-(1'')-(3'')	280.659	280.677	280.129	280.206	279.591	279.610	280.145
(4')-(3')-(2')-(1'')	61.750	61.828	62.314	62.162	62.712	62.704	62.245
O-(2')-(3')-O	59.397	59.511	60.053	59.870	60.394	60.376	59.933

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] Numbers of connected atoms in brackets; [c] Distances in Angstrom; [d] Angles and dihedral angles in degree.

Table 9. Average distances, angles and dihedral angles of the full-optimization of intermedine-*N*-oxide were calculated at *ab initio* HF level using the 6-31G(d), 6-311G(d), 6-31G(d.p) and 6-311G(d.p) basis sets

	6-31G(d)	6-311G(d)	6-31G(d,p)	6-311G(d,p)
Distances[a,b]				
C(1)-C(2)	1.31738	1.31658	1.31814	1.31650
C(1)-C(9)	1.49871	1.49509	1.49836	1.49493
C(2)-C(3)	1.49634	1.49647	1.49732	1.49641
C(3)-N(4)	1.49351	1.49335	1.48638	1.49399
N(4)-C(8)	1.51583	1.51405	1.50690	1.51415
C(5)-C(6)	1.51786	1.51817	1.51982	1.51873
C(6)-C(7)	1.52860	1.52320	1.52650	1.52392
C(7)-C(8)	1.54461	1.54028	1.54314	1.53972
C(7)-O	1.39780	1.40056	1.40150	1.40121
C(9)-O	1.43187	1.43263	1.43260	1.43418
O-C(1‘)	1.31198	1.32943	1.32164	1.32375
C(1‘)-C(2‘)	1.53931	1.54108	1.53950	1.53962
C(1‘)=O	1.19320	1.18048	1.19012	1.18325
C(2‘)-C(3‘)	1.53972	1.54309	1.54238	1.54385
C(2‘)-C(1‘‘)	1.56318	1.56336	1.56664	1.56683
C(2‘)-O	1.40401	1.39223	1.39602	1.39449
C(3‘)-C(4‘)	1.52304	1.52027	1.52159	1.52095
C(3‘)-O	1.41541	1.41396	1.41485	1.41296
C(1‘‘)-C(2‘‘)	1.53439	1.53447	1.53423	1.53518
C(1‘‘)-C(3‘‘)	1.53491	1.53309	1.53453	1.53404
Angles[a,c]				
C(8)-C(1)-C(9)	123.245	123.026	123.373	123.032
C(1)-C(2)-C(3)	112.626	112.563	112.491	112.540
C(2)-C(3)-N(4)	104.318	104.461	104.222	104.430

C(3)-N(4)-C(8)	107.858	107.640	108.250	107.690
C(5)-C(6)-C(7)	101.088	101.298	101.453	101.347
C(6)-C(7)-C(8)	101.946	102.208	102.016	102.031
C(8)-C(7)-O	112.857	113.393	113.077	113.354
N(4)-C(8)-C(7)	105.988	106.160	105.873	106.161
C(1)-C(9)-O	110.024	110.033	110.209	109.743
C(9)-O-C(1')	117.908	116.261	117.862	116.463
O-C(1')-C(2')	114.877	114.725	114.369	115.213
O-C(1')=O	124.138	122.582	123.530	122.737
C(1')-C(2')-C(3')	108.708	107.647	108.380	107.881
C(1')-C(2')-C(1'')	107.302	108.473	107.272	108.179
C(1')-C(2')-O	105.666	106.575	106.315	106.332
C(2')-C(3')-C(4')	115.492	114.897	114.939	114.526
C(2')-C(3')-O	106.916	103.739	105.567	104.447
C(2')-C(1'')-C(2'')	113.740	113.079	113.220	113.242
C(2')-C(1'')-C(3'')	113.815	115.050	114.395	115.424
Dihedral angles[a,c]				
(1)-(9)-O-(1')	199.111	191.318	205.852	190.398
(9)-O-(1')-(2')	183.557	182.153	187.376	181.037
(9)-O-(1')-O	1.586	1.024	5.312	-0.583
O-(1')-(2')-(3')	317.164	303.960	311.179	305.429
O-(1')-(2')-(1'')	85.728	71.541	78.662	72.833
O-(1')-(2')-O	203.796	186.330	195.333	188.508
(1')-(2')-(1'')-(2'')	154.693	150.751	151.018	153.489
(1')-(2')-(1'')-(3'')	282.658	278.538	278.992	281.394
(4')-(3')-(2')-(1'')	103.398	69.224	68.423	72.625
O-(2')-(3')-O	62.240	68.117	66.104	71.013

[a] Numbers of connected atoms in brackets; [b] Distances in Angstrom; [c] Angles and dihedral angles in degree.

Table 10. Average distances, angles, and dihedral angles of the full-optimization of intermedine-*N*-oxide were calculated at *ab initio* B3LYP level using the 6-31G(d), 6-311G(d), 6-31G(d.p) and 6-311G(d.p) basis sets

	6-31G(d)	6-311G(d)	6-31G(d,p)	6-311G(d,p)
Distances[a,b]				
C(1)-C(2)	1.33964	1.33587	1.33961	1.33562
C(1)-C(9)	1.49741	1.49480	1.49689	1.49386
C(2)-C(3)	1.49371	1.49199	1.49312	1.49191
C(3)-N(4)	1.53167	1.52846	1.53149	1.52854
N(4)-C(8)	1.56836	1.56344	1.56654	1.56124
C(5)-C(6)	1.52172	1.52000	1.52174	1.52084
C(6)-C(7)	1.53221	1.52919	1.53193	1.53097
C(7)-C(8)	1.54262	1.54061	1.54184	1.54189
C(7)-O	1.44125	1.43976	1.44078	1.43641
C(9)-O	1.46323	1.46411	1.46327	1.46618
O-C(1‘)	1.37861	1.37727	1.37756	1.37677
C(1‘)-C(2‘)	1.55576	1.55456	1.55478	1.55566
C(1‘)=O	1.20580	1.19812	1.20613	1.19773
C(2‘)-C(3‘)	1.56031	1.55608	1.55964	1.55261
C(2‘)-C(1‘‘)	1.57156	1.56931	1.57128	1.56949
C(2‘)-O	1.41091	1.41039	1.41031	1.41246
C(3‘)-C(4‘)	1.52551	1.52295	1.52630	1.52425
C(3‘)-O	1.43700	1.43852	1.43550	1.43990
C(1‘‘)-C(2‘‘)	1.53910	1.53689	1.53783	1.53791
C(1‘‘)-C(3‘‘)	1.53796	1.53614	1.53729	1.53639
Angles[a,c]				
C(8)-C(1)-C(9)	123.284	123.146	123.254	122.878
C(1)-C(2)-C(3)	113.241	113.234	113.230	113.211
C(2)-C(3)-N(4)	104.848	104.862	104.838	104.795

C(3)-N(4)-C(8)	106.039	106.068	106.081	106.186
C(5)-C(6)-C(7)	101.823	102.009	101.813	101.858
C(6)-C(7)-C(8)	103.207	103.259	103.107	103.077
C(8)-C(7)-O	112.911	113.155	112.938	113.199
N(4)-C(8)-C(7)	105.845	105.963	105.812	105.962
C(1)-C(9)-O	112.532	111.908	112.495	110.513
C(9)-O-C(1')	116.676	117.117	116.605	116.905
O-C(1')-C(2')	113.171	113.103	113.129	113.226
O-C(1')=O	122.264	122.499	122.305	122.621
C(1')-C(2')-C(3')	108.619	108.728	108.680	108.915
C(1')-C(2')-C(1'')	107.455	107.486	107.561	107.154
C(1')-C(2')-O	106.566	106.706	106.660	106.767
C(2')-C(3')-C(4')	114.602	114.722	114.556	114.939
C(2')-C(3')-O	105.363	105.067	105.515	104.796
C(2')-C(1'')-C(2'')	112.990	113.142	113.063	113.257
C(2')-C(1'')-C(3'')	114.010	114.016	114.134	113.875
Dihedral angles[a,c]				
(1)-(9)-O-(1')	249.929	241.700	250.012	224.009
(9)-O-(1')-(2')	193.953	193.351	193.765	191.016
(9)-O-(1')-O	12.305	11.715	12.151	8.846
O-(1')-(2')-(3')	302.948	305.197	302.820	310.663
O-(1')-(2')-(1'')	71.802	73.666	71.391	78.896
O-(1')-(2')-O	186.430	188.245	186.101	193.050
(1')-(2')-(1'')-(2'')	150.267	150.253	150.466	152.127
(1')-(2')-(1'')-(3'')	278.101	278.223	278.355	280.145
(4')-(3')-(2')-(1'')	59.374	60.875	59.543	62.245
O-(2')-(3')-O	55.692	57.772	55.912	59.933

[a] Numbers of connected atoms in brackets; [b] Distances in Angstrom; [c] Angles and dihedral angles in degree.

Table 11. : Free energy values of the full-optimized structure intermedine-*N*-oxide at HF level of theory for 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p) basis sets

	6-31G(d)[a]	6-311G(d)[a]	6-31G(d,p)[a]	6-311G(d,p)[a]
[1][b]	-1086.0829	-1086.3151	-1086.1314	-1086.3673
[2][b]	-1086.0802	-1086.3152	-1086.1199	-1086.3673
[3][b]	-1086.0814	-1086.3137	-1086.1303	-1086.3659
[4][b]	-1086.0814	-1086.3137	-1086.1303	-1086.3659
[5][b]	-1086.0814	-1086.3137	-1086.1358	-1086.3659
[6][b]	-1086.0814	-1086.3137	-1086.1358	-1086.3659
Average	-1086.0815	-1086.3142	-1086.1306	-1086.3663

[a] All free energy values are in [a.u.];. [b] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization).

Table 12. : Free energy values of the full-optimized structure intermedine-*N*-oxide at B3LYP level of theory for 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p) basis sets

	6-31G(d)[a]	6-311G(d)[a]	6-31G(d,p)[a]	6-311G(d,p)[a]
[1][b]	-1092.6219	-1092.8915	-1092.6692	-1092.9394
[2][b]	-1092.6187	-1092.8915	-1092.6692	-1092.9394
[3][b]	-1092.6203	-1092.8900	-1092.6681	-1092.9379
[4][b]	-1092.6203	-1092.8900	-1092.6667	-1092.9379
[5][b]	-1092.6203	-1092.8900	-1092.6692	-1092.9379
[6][b]	-1092.6203	-1092.8899	-1092.6692	-1092.9379
Average	-1092.6203	-1092.8904	-1092.6686	-1092.9384

[a] All free energy values are in [a.u.]; [b] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization).

General procedure for calculation of chemical shifts

The absolute chemical shielding values (σ) of all atoms were calculated from structure **1** and tetramethylsilane (TMS) at the *ab initio* HF and B3LYP levels using the implemented gauge including atomic orbitals (GIAO) methods and the same four basis sets 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p). In first calculations the geometry of the TMS molecule was optimized. The absolute chemical shieldings (σ) of TMS structure at HF and B3LYP levels are presented in Table 13. The ^{13}C chemical shift (δ) values of **1** were obtained by subtracting the calculated ^{13}C NMR isotropic magnetic shielding (IMS) values (σ_{atom}) of any given atom from the ^{13}C IMS of tetramethylsilane (TMS) using the equation $\delta = \sigma_{TMS} - \sigma_{atom}$.

Table 13. *Ab initio* calculation of absolute chemical shielding (σ) of TMS at the HF and B3LYP levels of theory

Theory	6-31G(d)[a]	6-311G(d)[a]	6-31G(d,p)[a]	6-311G(d,p)[a]
HF[b]	201.729	195.905	203.154	196.138
B3LYP[b]	189.762	184.529	191.867	184.665

[a] All values are in ppm; [b] Due to the high symmetry of TMS the value of only one carbon atom is listed here.

All calculated ^{13}C NMR chemical shift values relative to TMS, based on HF and B3LYP levels of theory, using the basis sets 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p) are presented in Tables 14 to 21.

Table 14. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* HF level using the 6-31G(d) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	129.96	129.56	130.20	130.21	130.20	130.20	130.06
2	128.11	128.65	128.13	128.13	128.13	128.13	128.21
3	68.54	67.28	67.65	67.65	67.65	67.65	67.74
5	61.19	62.10	61.12	61.12	61.12	61.12	61.29
6	32.18	32.25	32.37	32.37	32.36	32.36	32.31
7	61.24	60.85	60.95	60.94	60.95	60.95	60.98
8	88.98	89.34	89.16	89.16	89.16	89.16	89.16
9	55.94	55.87	55.90	55.90	55.90	55.89	55.90
1’	171.76	170.75	171.70	171.70	171.70	171.70	171.55
2’	72.81	72.75	72.79	72.79	72.80	72.80	72.79
3’	58.81	58.75	58.72	58.71	58.71	58.71	58.74
4’	18.59	18.36	18.33	18.33	18.33	18.33	18.38
1’’	29.94	29.36	29.35	29.35	29.34	29.34	29.45
2’’	16.90	16.72	16.72	16.72	16.72	16.72	16.75
3’’	16.16	16.12	16.12	16.12	16.13	16.12	16.13

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 15. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* HF level using the 6-311G(d) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	137.12	137.06	136.84	136.84	136.84	136.84	136.93
2	134.74	134.72	135.27	135.26	135.26	135.26	135.09
3	70.46	70.48	70.30	70.29	70.30	70.30	70.35
5	62.92	62.89	63.19	63.19	63.19	63.19	63.09
6	31.46	31.47	31.67	31.67	31.67	31.67	31.60
7	63.58	63.61	63.36	63.36	63.36	63.36	63.44
8	91.32	91.37	92.00	92.00	92.00	92.00	91.78
9	58.41	58.41	58.19	58.19	58.19	58.19	58.26
1’	177.48	177.28	177.35	177.34	177.34	177.34	177.35
2’	71.15	71.21	71.03	71.03	71.03	71.03	71.08
3’	61.74	61.86	61.81	61.81	61.81	61.81	61.81
4’	19.32	19.35	19.18	19.18	19.18	19.18	19.23
1’’	32.43	32.26	31.56	31.55	31.55	31.55	31.82
2’’	17.65	17.61	17.43	17.43	17.43	17.43	17.50
3’’	17.36	17.33	17.35	17.35	17.35	17.35	17.35

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 16. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* HF level using the 6-31G(d,p) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	130.00	130.76	131.86	131.86	132.17	132.17	131.47
2	130.46	132.16	129.11	129.11	128.75	128.75	129.73
3	68.91	66.15	67.90	67.90	67.90	67.89	67.78
5	62.06	58.99	61.61	61.61	61.54	61.54	61.23
6	31.26	32.62	32.15	32.15	33.03	33.03	32.37
7	62.83	64.09	61.99	61.99	61.58	61.58	62.34
8	89.36	85.66	89.80	89.80	90.05	90.05	89.12
9	55.34	54.53	56.39	56.39	56.31	56.30	55.88
1’	170.78	171.36	172.77	172.77	173.07	173.06	172.30
2’	74.36	74.45	72.53	72.53	74.00	74.00	73.65
3’	60.75	60.34	60.38	60.38	59.72	59.72	60.22
4’	19.61	19.46	19.27	19.27	18.52	18.52	19.11
1’’	30.05	28.94	31.02	31.02	30.15	30.14	30.22
2’’	17.20	17.12	17.62	17.62	17.08	17.09	17.29
3’’	17.22	17.01	17.17	17.17	16.24	16.25	16.84

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 17. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* HF level using the 6-311G(d,p) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	137.21	137.21	137.46	137.46	137.46	137.45	137.38
2	135.86	135.86	135.83	135.82	135.84	135.85	135.84
3	72.43	72.43	71.55	71.55	71.55	71.55	71.84
5	64.41	64.41	64.21	64.21	64.20	64.21	64.27
6	32.09	32.09	32.36	32.36	32.36	32.36	32.27
7	64.37	64.37	64.01	64.01	64.01	64.01	64.13
8	92.67	92.67	92.87	92.87	92.87	92.88	92.80
9	59.70	59.70	59.73	59.73	59.73	59.73	59.72
1’	179.00	179.00	178.96	178.98	178.97	178.98	178.98
2’	71.02	71.02	71.03	71.04	71.04	71.03	71.03
3’	61.68	61.68	61.65	61.65	61.66	61.65	61.66
4’	20.05	20.05	19.80	19.79	19.79	19.79	19.88
1’’	33.94	33.94	33.35	33.35	33.35	33.35	33.54
2’’	18.19	18.19	17.90	17.89	17.89	17.90	17.99
3’’	18.04	18.04	17.88	17.87	17.87	17.88	17.93

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure forfull-geometry optimization); [b] All values in ppm relative to TMS.

Table 18. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-31G(d) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	127.39	126.93	127.50	127.51	127.51	127.50	127.39
2	124.97	125.65	124.98	124.97	125.05	125.06	125.11
3	78.53	75.97	77.31	77.31	77.39	77.39	77.32
5	70.68	72.00	70.19	70.19	70.23	70.22	70.58
6	34.78	34.85	34.97	34.97	34.93	34.93	34.91
7	70.13	69.57	69.60	69.60	69.68	69.67	69.71
8	101.90	102.71	102.56	102.57	102.56	102.56	102.48
9	61.02	60.85	60.84	60.84	61.12	61.09	60.96
1’	170.66	170.61	170.59	170.59	170.82	170.80	170.68
2’	84.38	84.51	84.53	84.52	84.49	84.49	84.49
3’	67.92	67.93	67.92	67.92	67.98	67.96	67.94
4’	20.22	20.10	20.10	20.10	20.08	20.08	20.11
1’’	36.22	35.75	35.76	35.77	35.78	35.79	35.85
2’’	18.08	17.80	17.79	17.80	17.86	17.86	17.87
3’’	18.03	17.85	17.84	17.84	17.86	17.86	17.88

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 19. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-311G(d) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	140.06	140.06	140.26	140.25	140.26	140.18	140.18
2	136.62	136.59	136.48	136.50	136.49	136.97	136.61
3	85.54	85.55	84.15	84.16	84.16	84.21	84.63
5	75.64	75.65	74.94	74.93	74.94	74.94	75.17
6	37.49	37.49	37.78	37.78	37.77	37.83	37.69
7	76.15	76.15	75.53	75.53	75.52	75.46	75.72
8	110.88	110.88	111.62	111.63	111.63	111.58	111.37
9	64.94	64.95	64.84	64.80	64.80	64.10	64.74
1’	184.60	184.62	184.42	184.40	184.39	183.42	184.31
2’	90.11	90.10	90.30	90.30	90.31	90.75	90.31
3’	73.24	73.25	73.28	73.28	73.27	72.95	73.21
4’	21.07	21.07	20.94	20.94	20.94	20.99	20.99
1’’	40.44	40.44	39.95	39.95	39.96	40.13	40.15
2’’	18.92	18.93	18.63	18.63	18.63	18.44	18.70
3’’	18.80	18.80	18.62	18.63	18.62	18.62	18.68

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 20. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-31G(d,p) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average[b]
1	129.43	129.42	129.68	129.67	129.35	129.30	129.47
2	126.37	126.37	126.26	126.27	126.46	126.52	126.38
3	79.58	79.58	78.21	78.21	79.72	79.79	79.18
5	71.56	71.56	71.01	71.02	71.72	71.77	71.44
6	35.55	35.55	35.80	35.80	35.49	35.49	35.61
7	71.37	71.37	70.83	70.85	71.40	71.43	71.21
8	103.55	103.54	104.30	104.31	103.71	103.74	103.86
9	61.73	61.73	61.70	61.80	61.88	61.96	61.80
1’	172.83	172.84	172.80	172.86	173.02	173.08	172.91
2’	86.38	86.38	86.41	86.48	86.36	86.30	86.38
3’	69.07	69.05	69.05	69.81	69.07	69.12	69.19
4’	20.23	20.23	20.27	21.20	20.21	20.20	20.39
1’’	37.29	37.30	37.30	36.13	37.40	37.38	37.13
2’’	18.15	18.15	18.21	16.84	18.20	18.22	17.96
3’’	18.16	18.15	18.11	17.76	18.12	18.18	18.08

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure for full-geometry optimization); [b] All values in ppm relative to TMS.

Table 21. Calculated ^{13}C chemical shifts of intermedine-*N*-oxide at *ab initio* B3LYP level using the 6-311G(d,p) basis set

Position	[1][a,b]	[2][a,b]	[3][a,b]	[4][a,b]	[5][a,b]	[6][a,b]	Average [b]
1	139.81	139.83	140.01	140.04	140.13	140.13	139.99
2	138.48	138.50	138.39	138.32	138.24	138.25	138.36
3	87.10	87.08	85.62	85.61	85.66	85.66	86.12
5	76.35	76.34	75.71	75.71	75.57	75.57	75.87
6	38.18	38.20	38.55	38.56	38.64	38.64	38.46
7	76.42	76.42	75.84	75.84	75.93	75.93	76.06
8	112.33	112.30	113.11	113.10	113.07	113.07	112.83
9	64.61	64.61	64.63	64.63	64.69	64.68	64.64
1’	183.29	183.29	183.22	183.21	183.34	183.34	183.28
2’	90.81	90.81	90.90	90.90	90.81	90.81	90.84
3’	73.13	73.11	73.23	73.21	73.35	73.34	73.23
4’	21.63	21.59	21.42	21.44	21.34	21.35	21.46
1’’	41.15	41.14	40.66	40.66	40.63	40.61	40.81
2’’	18.83	18.82	18.59	18.60	18.64	18.64	18.68
3’’	19.03	19.04	18.93	18.92	19.02	19.02	18.99

[a] [1] to [6] define different full-optimization steps of intermedine-*N*-oxide (see general procedure forfull-geometry optimization); [b] All values in ppm relative to TMS.

Table 22 shows all differences between scaled theoretical and experimental chemical shift values for each atom based on both levels of theories and used basis sets, including both possible correlations of the ^{13}C chemical shift values 69.73 and 70.17 ppm to C-7 and C-3’.

Table 22. Differences between scaled theoretical and experimental ^{13}C NMR chemical shift values of each carbon atom.

Position	6-31G(d)[a,b]		6-311G(d)[a,b]		6-31G(d,p)[a,b]		6-311G(d,p)[a,b]	
1[c]	*-2,35*	**4,15**	*-4,19*	**2,42**	*-2,86*	**3,95**	*-3,68*	**2,91**
2[c]	*-10,40*	**-3,42**	*-12,32*	**-4,12**	*-11,02*	**-2,81**	*-12,11*	**-5,46**
3[c]	*5,75*	**0,95**	*5,64*	**0,10**	*6,39*	**0,32**	*5,01*	**-0,88**
5[c]	*3,54*	**-0,82**	*3,98*	**0,32**	*4,27*	**-0,51**	*3,64*	**0,12**
6[c]	*-2,23*	**0,90**	*-0,48*	**0,69**	*-1,74*	**0,90**	*-0,38*	**0,50**
7[c]	*4,14*	**0,36**	*3,92*	**0,08**	*3,43*	**0,00**	*4,06*	**0,22**
8[c]	*1,72*	**-7,37**	*2,43*	**-7,56**	*2,52*	**-7,18**	*2,29*	**-8,56**
9[c]	*0,84*	**0,94**	*0,52*	**2,02**	*1,50*	**1,14**	*-0,10*	**2,60**
1'[c]	*-2,09*	**1,70**	*-1,31*	**2,88**	*-1,79*	**1,90**	*-1,86*	**4,07**
2'[c]	*6,68*	**-0,40**	*10,96*	**0,76**	*6,52*	**-0,97**	*11,83*	**0,69**
3'[c]	*6,84*	**2,62**	*5,95*	**2,89**	*6,00*	**2,49**	*6,88*	**3,34**
4'[c]	*-5,97*	**-1,67**	*-6,27*	**-1,35**	*-6,20*	**-1,42**	*-6,18*	**-1,21**
1''[c]	*0,12*	**-0,61**	*-1,23*	**-2,17**	*-0,11*	**-1,18**	*-2,15*	**-2,25**
2''[c]	*-3,87*	**1,11**	*-4,13*	**1,28**	*-3,91*	**1,51**	*-3,90*	**1,88**
3''[c]	*-2,74*	**1,59**	*-3,48*	**1,79**	*-2,96*	**1,89**	*-3,33*	**2,08**
1[d]	*-2,31*	**4,19**	*-4,15*	**2,46**	*-2,83*	**3,98**	*-3,64*	**2,95**
2[d]	*-10,50*	**-3,52**	*-12,42*	**-4,23**	*-11,13*	**-2,92**	*-12,21*	**-5,56**
3[d]	*5,61*	**0,81**	*5,50*	**-0,04**	*6,25*	**0,18**	*4,87*	**-1,01**
5[d]	*3,56*	**-0,80**	*4,00*	**0,33**	*4,28*	**-0,49**	*3,65*	**0,13**
6[d]	*-2,22*	**0,91**	*-0,47*	**0,70**	*-1,73*	**0,91**	*-0,37*	**0,51**
7[d]	*4,60*	**0,82**	*4,38*	**0,54**	*3,88*	**0,46**	*4,51*	**0,67**
8[d]	*1,75*	**-7,34**	*2,45*	**-7,53**	*2,54*	**-7,15**	*2,32*	**-8,53**
9[d]	*0,86*	**0,96**	*0,54*	**2,04**	*1,52*	**1,16**	*-0,08*	**2,61**
1'[d]	*-2,04*	**1,75**	*-1,26*	**2,93**	*-1,75*	**1,95**	*-1,80*	**4,12**
2'[d]	*6,71*	**-0,37**	*10,98*	**0,79**	*6,54*	**-0,94**	*11,85*	**0,72**

3'[d]	*6,42*	**2,20**	*5,52*	**2,47**	*5,58*	**2,07**	*6,46*	**2,92**
4'[d]	*-5,96*	**-1,66**	*-6,26*	**-1,35**	*-6,20*	**-1,42**	*-6,17*	**-1,21**
1''[d]	*0,13*	**-0,60**	*-1,21*	**-2,16**	*-0,11*	**-1,17**	*-2,14*	**-2,24**
2''[d]	*-3,86*	**1,11**	*-4,12*	**1,28**	*-3,91*	**1,51**	*-3,89*	**1,88**
3''[d]	*-2,74*	**1,59**	*-3,48*	**1,80**	*-2,96*	**1,90**	*-3,33*	**2,09**

[a] Italic type defines calculated results using HF level of theory; [b] Bold type defines calculated results using B3LYP level of theory; [c] Values obtained using ^{13}C chemical shift values of 69.73 ppm for C-7 and 70.17 ppm for C-3'; [d] Values obtained using ^{13}C chemical shift values 70.17 ppm for C-7 and 69.73 ppm for C-3'.

Figure 1 shows the correlation plots of the ^{13}C chemical shift (CS) values, calculated for 6-31G(d), 6-311G(d), 6-31G(d,p) and 6-311G(d,p) basis sets at HF level (left column), and for 6-31G(d), 6-311G(d) and 6-311G(d,p) basis sets at B3LYP level (right column) versus reported correlation (solid line, ring symbols) and our new correlations (dotted line, filled box symbols) experimental data.

Figure 1: Correlation plots of theoretical versus reported and new correlations of ^{13}C NMR chemical shifts.

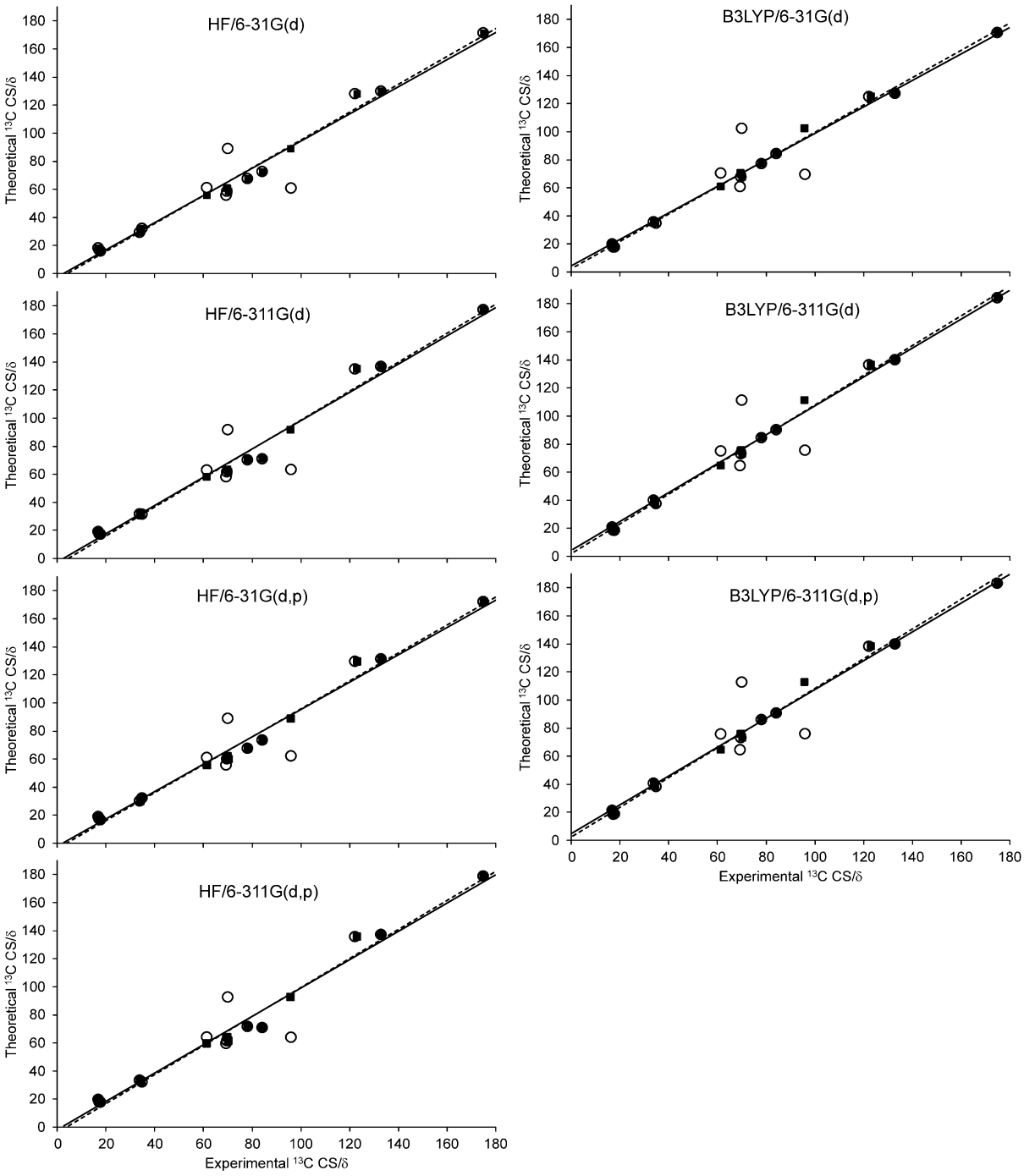
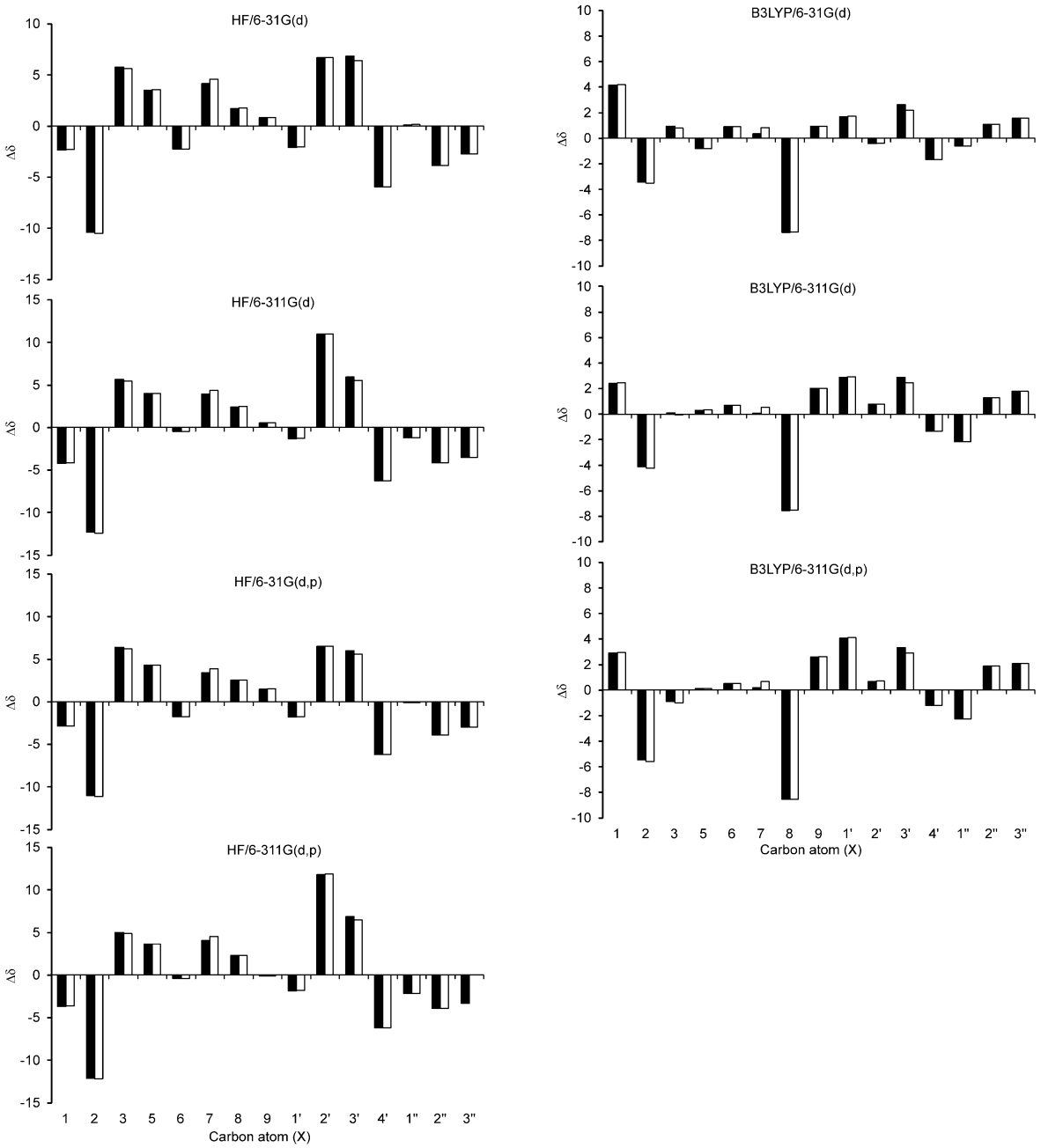


Figure 2 shows differences between scaled theoretical and experimental ^{13}C chemical shift values of any X carbon atom. Black columns define ^{13}C chemical shift values of 69.73 ppm for C-7 and 70.17 ppm for C-3', white column define the opposite allocation. The values were calculated at HF level of theory (left column), using 6-31G(d), 6-31G(d,p), 6-311G(d) and 6-311G(d,p) basis sets, and at B3LYP level of theory (right column), using 6-31G(d), 6-311G(d) and 6-311G(d,p).

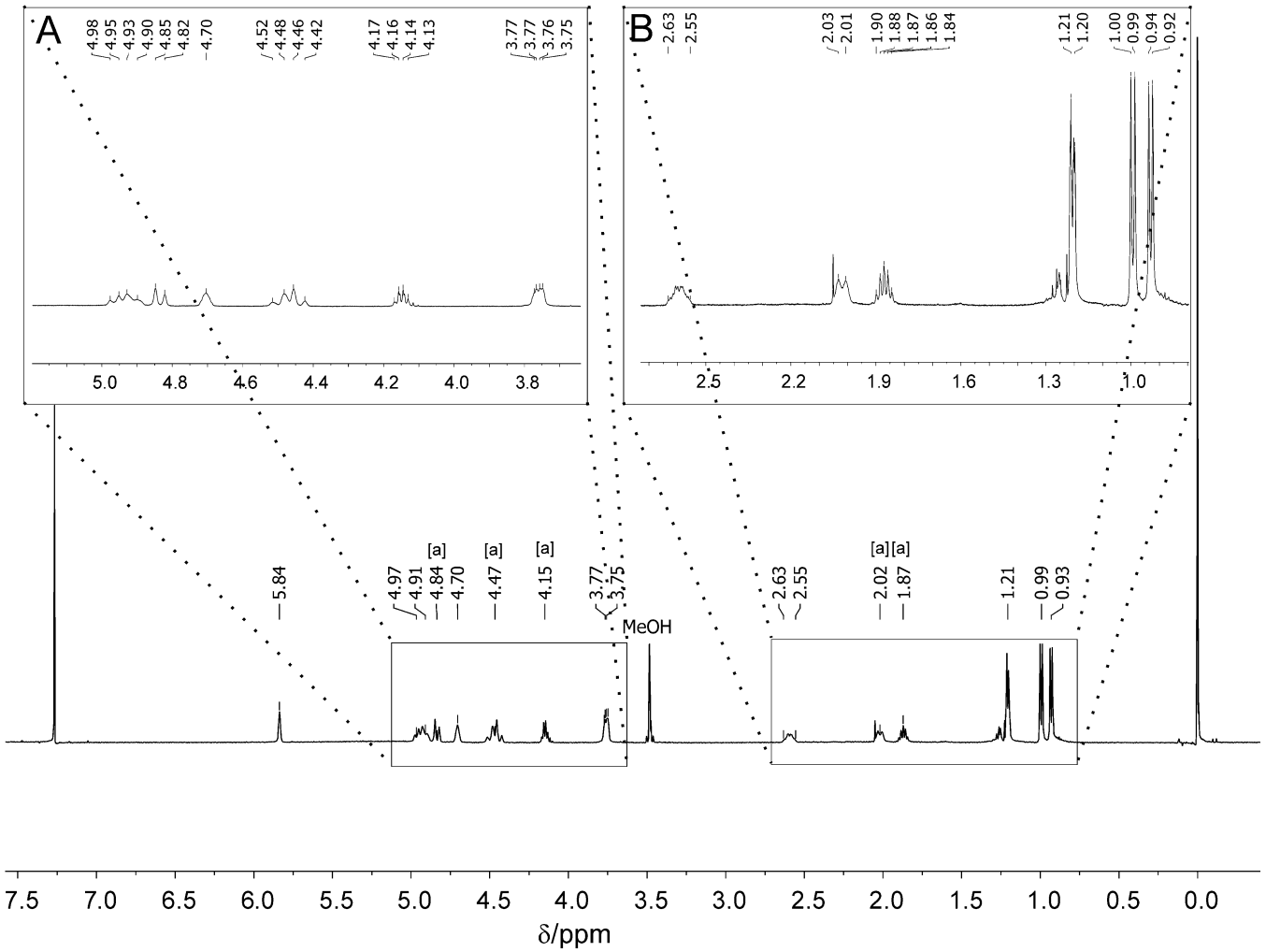
Figure 2: Differences between scaled theoretical and experimental ^{13}C NMR chemical shift values.



Figures 3 to 6 present the experimental ^{1}H, ^{13}C, HMQC and HMBC NMR spectra of **1.**

Figure 3 presents the experimental ^{1}H NMR spectrum of 1. Regions from 3.7 to 5.2 ppm and from 0.8 to 2.7 ppm are drawn to a larger scale in the boxes A and B.

Figure 3: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1**



[a] Average of ^{1}H chemical shift values

Figure 4 presents the experimental ^{13}C NMR spectrum of **1**. The regions from 60 to 75 ppm and from 15 to 40 ppm are drawn to a larger scale in the boxes on the top left and right of figure 4. All carbon atom correlations of **1** are indicated in round brackets above each ^{13}C chemical shift value.

Figure 4: ^{13}C NMR(125 MHz, $CDCl_3$) spectrum of **1**

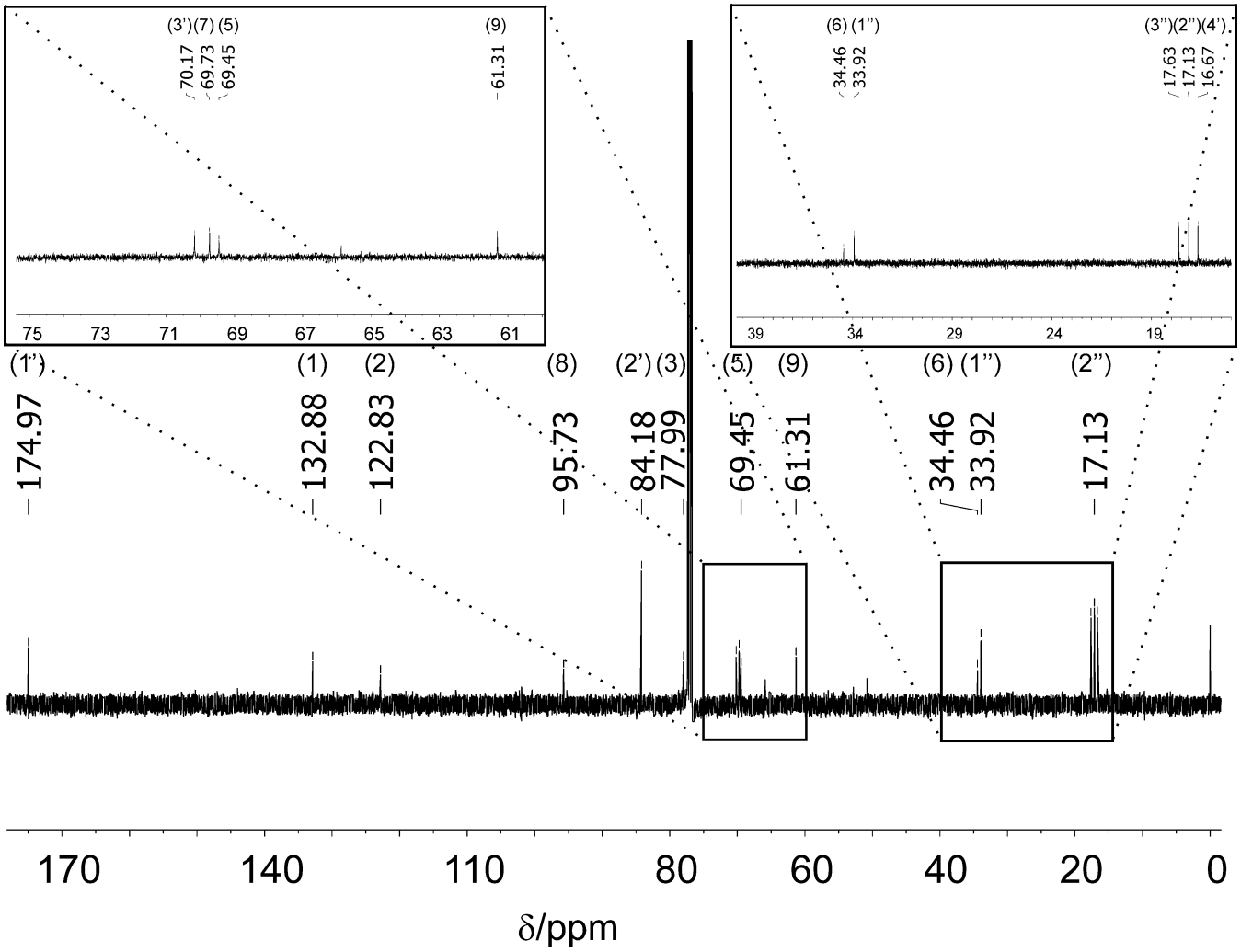
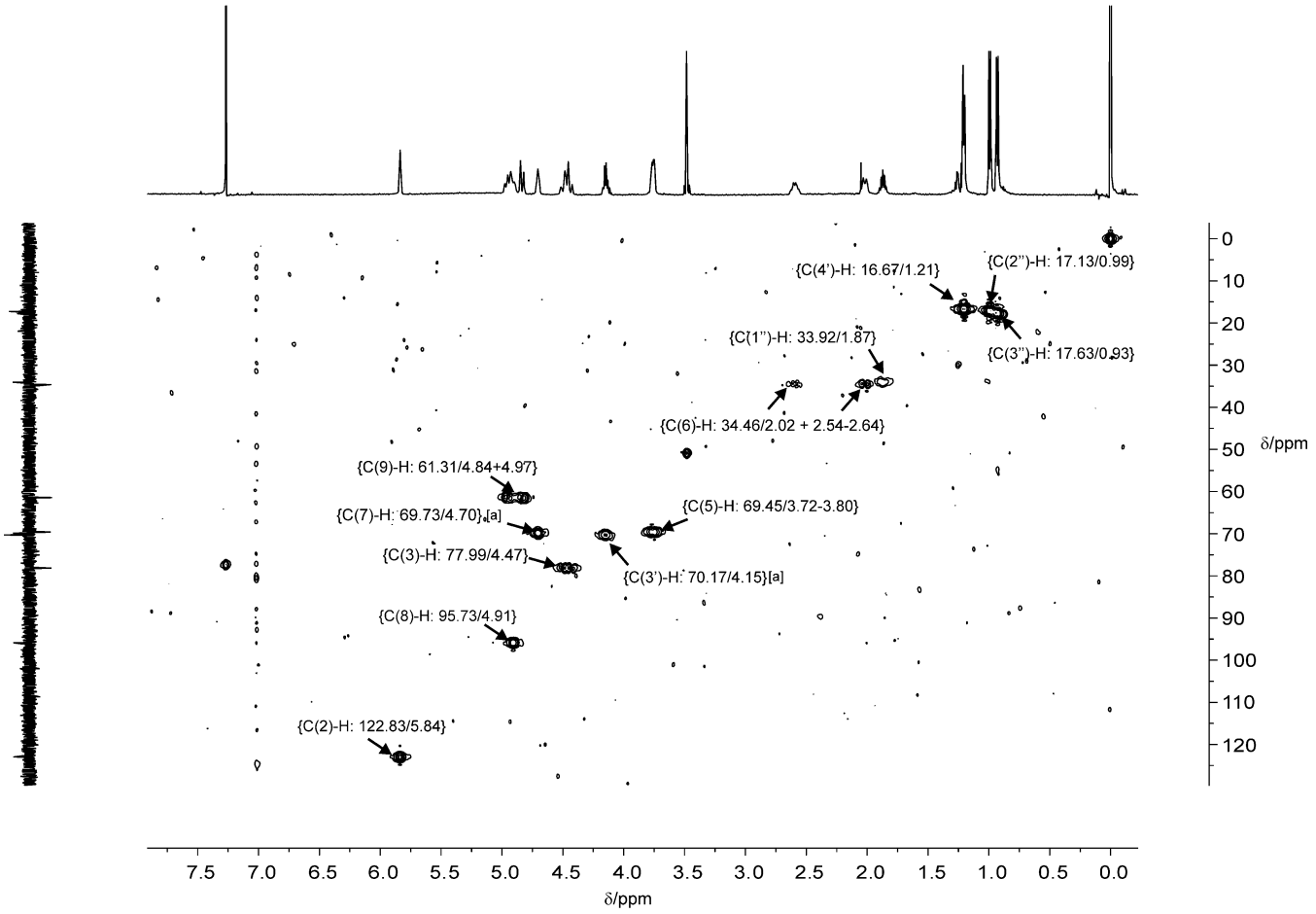


Figure 5 presents direct couplings between proton and carbon atoms of **1** in a HMQC spectrum. The correlations as well as the respective ^{1}H and ^{13}C NMR chemical shift values are indicated in curly brackets.

Figure 5: HMQC spectrum of **1**



[a] no exactly allocation of carbon atoms at position 7 and 3'

Figure 6 presents the experimental HMBC spectrum of **1**. Each coupling effects between proton and carbon atoms are described using ^{1}H and ^{13}C chemical shift values in curly brackets.

Figure 6: HMBC spectrum of **1**.