Supplementary Information

The Challenging Conformer Assignment of Proline Methyl Ester from Rotational Spectroscopy

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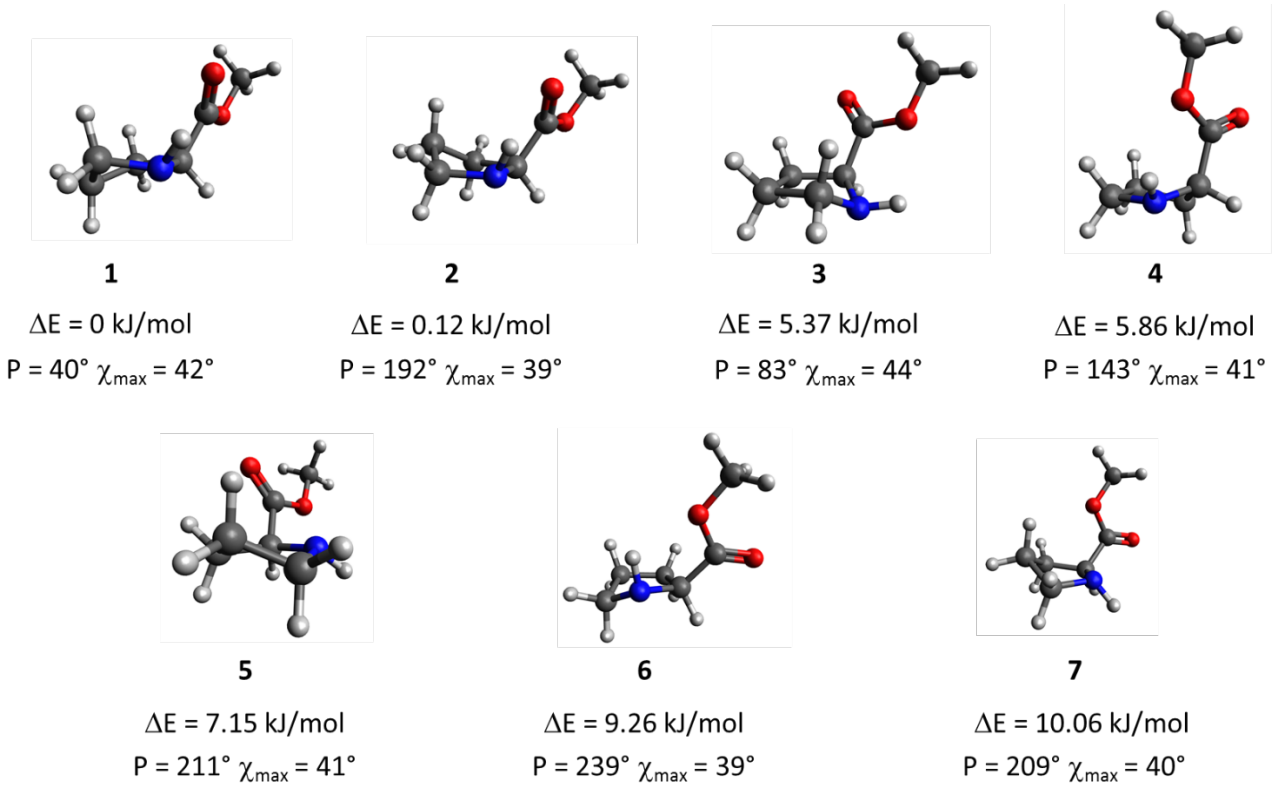

Figure S1. Optimized structures of the model conformers of PrOMe at the ωB97XD/6-311G++(d,p) level. The pseudorotational phase angle (P) and amplitude (χ_{max}) are described in the Discussion Section.

Table S1. Summary of the principal results for the model conformers of proline methyl ester at the ωB97XD/6-311++G(d,p) level of theory.

	1	**2**	**3**	**4**	**5**	**6**	**7**
ΔE^a / kJ mol^{-1}	0.00	0.12	5.37	5.86	7.15	9.26	10.06
H-bond Receptor	Carbonyl	Carbonyl	Ester	Ester	Ester	Ester	<none>
Pucker	C^{γ} exo / C^{δ} endo	C^{γ} endo	N exo	C^{α} exo / C^{β} endo	C^{γ} endo / C^{δ} exo	C^{δ} exo	C^{γ} endo / C^{δ} exo
P / °	40	192	83	143	211	239	209
χ_{max} / °	42	39	44	41	41	39	40
A / MHz	3761.186	3672.991	3115.340	2843.993	3694.479	3273.825	3005.344
B / MHz	1029.830	1044.732	1174.844	1245.648	1036.012	1046.507	1144.990
C / MHz	895.284	946.416	999.589	1070.610	920.162	968.698	1030.419
ΔI_{rms} / amu Å^2	17.11	2.06	39.73	63.87	8.09	12.76	40.99
P_{aa} / amu Å^2	460.432	440.070	386.765	350.032	450.124	425.130	381.841
P_{bb} / amu Å^2	104.058	93.923	118.821	122.0016	99.105	96.580	108.618
P_{cc} / amu Å^2	30.308	43.670	43.401	55.684	37.688	57.790	59.542
μ_a / D	0.77	0.86	-0.71	0.34	0.44	-0.77	-1.80
μ_b / D	-1.86	2.03	1.66	-1.91	-1.64	-1.69	-1.46
μ_c / D	-0.58	0.62	0.46	0.83	1.41	2.08	0.33
χ_{aa} / MHz	1.018	2.4440	-1.9223	-1.5823	0.9834	2.8221	-0.0983
χ_{bb} / MHz	2.4856	1.9160	2.8237	2.7926	2.6446	2.6300	0.7064
χ_{cc} / MHz	-3.5036	-4.3600	-0.9014	-1.2103	-3.6280	-5.4521	-0.6081
$\angle(i, a)$ / °	24.5	28.7	22.7	22.0	28.2	14.6	20.4
$\angle(i, b)$ / °	78.5	78.1	87.2	86.3	80.0	82.7	75.8
$\angle(i, c)$ / °	111.3	115.8	112.5	111.7	116.1	102.6	104.2

[a]Relative to conformer 1; includes zero-point energy correction.

Table S2. Summary of the principal results for the model conformers of proline methyl ester at the MP2/6-311++G(d,p) level of theory.

	1	**2**	**3**	**4**	**5**	**6**	**7**
ΔE^a / kJ mol^{-1}	0.00	0.16	4.85	5.10	6.23	7.54	9.21
H-bond Receptor	Carbonyl	Carbonyl	Ester	Ester	Ester	Ester	<none>
Pucker	C^{γ} exo / C^{δ} endo	C^{γ} endo	N exo	C^{α} exo / C^{β} endo	C^{γ} endo / C^{δ} exo	C^{δ} exo	C^{γ} endo / C^{δ} exo
P / °	46	205	98	142	212	243	211
χ_{max} / °	45	41	48	44	44	41	43
A / MHz	3685.038	3779.396	3091.868	2781.394	3682.824	3286.283	3001.448
B / MHz	1042.925	1018.287	1196.084	1279.708	1038.214	1034.736	1151.264
C / MHz	912.522	937.272	1045.596	1102.190	929.014	973.224	1031.914
ΔI_{rms} / amu Å^2	10.83	6.17	50.15	73.81	5.06	13.23	42.21
P_{aa} / amu Å^2	450.631	450.893	371.207	335.870	446.773	426.956	380.174
P_{bb} / amu Å^2	103.196	88.309	112.133	122.653	97.222	92.327	109.575
P_{cc} / amu Å^2	33.948	45.410	51.321	59.047	40.004	61.457	58.803
μ_a / D	-0.93	-0.76	1.09	-0.53	-0.44	-0.72	-1.66
μ_b / D	1.57	1.94	-1.21	-1.79	-1.42	1.61	1.31
μ_c / D	-0.69	-0.73	0.40	-0.89	-1.36	-2.05	-0.40
χ_{aa} / MHz	0.4395	2.6905	-2.2397	-2.0012	0.8920	2.6063	-0.0125
χ_{bb} / MHz	2.2466	1.4068	2.4019	2.5064	2.3553	2.3759	0.6817
χ_{cc} / MHz	-2.6861	-4.0973	-0.1622	-0.5052	-3.2473	-4.9822	-0.6692
$\angle(i, a)$ / °	26.9	29.1	27.2	22.2	30.3	13.5	20.4
$\angle(i, b)$ / °	77.1	78.8	82.1	85.8	78.5	82.4	77.2
$\angle(i, c)$ / °	113.1	116.5	115.8	111.7	117.6	101.0	105.6

[a]Relative to conformer 1; includes zero-point energy correction.

Table S3. Summary of the principal results for the model conformers of proline methyl ester at the ωB97XD/aug-cc-pVDZ level of theory.

	1	**2**	**3**	**5**	**6**	**7**
ΔE^a / kJ mol^{-1}	0.00	0.83	6.25	7.99	9.43	10.87
H-bond Receptor	Carbonyl	Carbonyl	Ester	Ester	Ester	<none>
Pucker	C^{γ} exo / C^{δ} endo	C^{γ} endo	N exo	C^{γ} endo / C^{δ} exo	C^{δ} exo	C^{γ} endo / C^{δ} exo
P / °	42	200	83	216	253	212
χ_{max} / °	42	38	45	41	38	40
A / MHz	3728.661	3731.363	3113.575	3693.649	3358.470	3028.742
B / MHz	1031.110	1026.436	1169.199	1030.293	1020.325	1127.208
C / MHz	895.682	931.582	995.012	907.976	948.211	1020.358
ΔI_{rms} / amu Å^2	16.87	5.30	38.19	12.49	9.02	36.36
P_{aa} / amu Å^2	459.416	449.709	388.921	455.148	438.907	388.390
P_{bb} / amu Å^2	104.824	92.787	118.992	101.452	94.074	106.905
P_{cc} / amu Å^2	30.715	42.654	43.323	35.372	56.405	59.956
μ_a / D	0.72	0.72	-0.62	0.47	-0.90	-1.84
μ_b / D	-1.87	2.09	-1.69	-1.71	-1.55	-1.42
μ_c / D	-0.51	0.50	-0.40	1.41	2.07	0.28
χ_{aa} / MHz	0.8216	2.4846	-1.7077	1.0297	2.4996	0.0298
χ_{bb} / MHz	2.3305	1.5128	2.6268	2.5152	2.2790	0.4244
χ_{cc} / MHz	-3.1521	-3.9974	-0.9191	-3.5448	-4.7786	-0.4541
$\angle(i, a)$ / °	24.8	27.7	22.7	27.3	12.6	19.2
$\angle(i, b)$ / °	78.0	78.8	86.6	80.0	84.9	76.2
$\angle(i, c)$ / °	111.3	115	112.4	115.2	101.5	103.0

[a]Relative to conformer 1; includes zero-point energy correction.

Table S4. Summary of the principal results for the model conformers of proline methyl ester at the MP2/aug-cc-pVDZ level of theory.

	1	**2**	**4**	**5**	**6**	**7**
ΔE^a / kJ mol^{-1}	0.00	-0.29	5.22	7.29	7.57	9.98
H-bond Receptor	Carbonyl	Carbonyl	Ester	Ester	Ester	<none>
Pucker	C^{γ} exo / C^{δ} endo	C^{γ} endo	C^{α} exo / C^{β} endo	C^{γ} endo / C^{δ} exo	C^{δ} exo	C^{γ} endo / C^{δ} exo
P / °	52	201	141	212	237	214
χ_{max} / °	46	41	44	44	41	44
A / MHz	3580.901	3711.213	2733.581	3650.192	3214.666	2999.827
B / MHz	1048.502	1017.340	1280.281	1029.363	1038.320	1131.629
C / MHz	918.755	936.800	1104.815	920.318	975.553	1017.167
ΔI_{rms} / amu Å^2	9.30	6.14	74.92	8.35	15.15	36.875
P_{aa} / amu Å^2	445.469	450.031	333.648	450.823	423.780	387.487
P_{bb} / amu Å^2	104.600	89.442	123.785	98.313	94.263	109.362
P_{cc} / amu Å^2	36.532	46.734	61.093	40.140	62.947	59.107
μ_a / D	0.94	0.77	0.37	0.46	-0.77	-1.71
μ_b / D	-1.56	1.94	-1.88	-1.47	-1.74	-1.32
μ_c / D	-0.60	0.66	0.80	1.38	1.94	0.36
χ_{aa} / MHz	0.0224	2.2799	-1.8988	0.7767	2.2971	0.1171
χ_{bb} / MHz	1.9374	1.3183	2.1104	2.1055	2.0671	0.4411
χ_{cc} / MHz	-1.9598	-3.5982	-0.2116	-2.8822	-4.3642	-0.5582
$\angle(i, a)$ / °	28.0	29.9	22.1	30.4	13.7	19.2
$\angle(i, b)$ / °	76.1	77.8	84.4	77.7	81.8	77.8
$\angle(i, c)$ / °	113.8	116.9	111.3	117.3	101.0	104.6

[a]Relative to conformer 1; includes zero-point energy correction.

Table S5. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 1.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.392379	-0.940846	0.644073
2	6	2.353249	-0.641567	-0.417732
3	6	0.397323	0.124215	0.681199
4	1	1.993206	-0.938857	-1.415597
5	1	3.300680	-1.152050	-0.230544
6	6	2.466587	0.875878	-0.337400
7	6	1.009136	1.299756	-0.128609
8	1	0.206129	0.432940	1.714721
9	6	-0.940764	-0.300345	0.102229
10	1	2.909856	1.319530	-1.230528
11	1	3.075652	1.154895	0.526624
12	1	0.506462	1.394109	-1.095468
13	1	0.899205	2.251712	0.390322
14	8	-1.164561	-1.357857	-0.429037
15	8	-1.860949	0.658387	0.259207
16	6	-3.161518	0.373097	-0.259049
17	1	-3.115456	0.203072	-1.336027
18	1	-3.579735	-0.511382	0.224074
19	1	-3.765078	1.250433	-0.037288
20	1	0.949653	-1.841998	0.514908

Rotational constants (MHZ):
3761.1855476 1029.8297906 895.2838996

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 1.0180 ba= -0.6971 ca= -3.9053
ab= -0.6971 bb= 2.4856 cb= -0.1096
ac= -3.9053 bc= -0.1096 cc= -3.5036

Dipole moment (Debye):
-0.7665026 1.8574782 -0.5824948 Tot= 2.0921404

Table S6. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 2.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.410598	-0.955076	0.662808
2	6	2.550015	-0.439704	-0.110024
3	6	0.404108	0.097870	0.773690
4	1	2.962782	-1.223916	-0.747724
5	1	3.345012	-0.119380	0.573913
6	6	2.014674	0.762255	-0.890601
7	6	1.019574	1.355629	0.107030
8	1	0.152988	0.309464	1.817663
9	6	-0.890935	-0.305024	0.087399
10	1	1.494827	0.425399	-1.793201
11	1	2.792982	1.468977	-1.185703
12	1	0.264365	2.002173	-0.341156
13	1	1.548589	1.938231	0.866035
14	8	-1.031759	-1.273921	-0.614930
15	8	-1.874534	0.558457	0.359118
16	6	-3.137988	0.283893	-0.248935
17	1	-3.511866	-0.689869	0.071215
18	1	-3.803124	1.076923	0.085459
19	1	-3.049056	0.292194	-1.336557
20	1	0.997321	-1.750597	0.191746

Rotational constants (MHZ):
3673.3975947 1044.6688490 946.4526395

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.4451 ba= 0.1162 ca= -2.7761
ab= 0.1162 bb= 1.9155 cb= 1.8238
ac= -2.7761 bc= 1.8238 cc= -4.3606

Dipole moment (Debye):
-0.8563107 2.0279921 -0.6202957 Tot= 2.2870913

Note: the values reported in the manuscript are averages of two nearly identical optimizations.

Table S7. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 3.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.059693	-1.049633	0.759001
2	6	1.653779	-1.151506	-0.571884
3	6	0.495531	0.287327	0.829273
4	1	0.892407	-1.257175	-1.363374
5	1	2.322022	-2.012837	-0.630867
6	6	2.384095	0.188056	-0.717219
7	6	1.559208	1.170658	0.148405
8	1	0.339067	0.579580	1.873519
9	6	-0.878075	0.457518	0.167096
10	1	2.449360	0.505018	-1.759246
11	1	3.400779	0.102373	-0.329454
12	1	1.085178	1.960035	-0.434319
13	1	2.185826	1.646493	0.902858
14	8	-1.325643	1.498800	-0.235940
15	8	-1.565800	-0.694327	0.139176
16	6	-2.883432	-0.623625	-0.408026
17	1	-2.847709	-0.284835	-1.444603
18	1	-3.281569	-1.634309	-0.350050
19	1	-3.500359	0.065567	0.170801
20	1	0.364483	-1.764044	0.931418

Rotational constants (MHZ):
3115.4445479 1174.8108556 999.5569834

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -1.9212 ba= -0.1740 ca= -4.1385
ab= -0.1740 bb= 2.8235 cb= 0.5459
ac= -4.1385 bc= 0.5459 cc= -0.9023

Dipole moment (Debye):
-0.7095661 -1.6645424 -0.4606668 Tot= 1.8671902

Note: the values reported in the manuscript are averages of four nearly identical optimizations.

Table S8. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 4.

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Principal axis orientation:
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 Center     Atomic                     Coordinates (Angstroms)
 Number     Number                        X           Y           Z
 ---------------------------------------------------------------------
      1          7                      1.176687   -0.796301    0.995718
      2          6                      1.858433   -1.171991   -0.255850
      3          6                      0.525976    0.486652    0.817589
      4          1                      1.337028   -1.980103   -0.780963
      5          1                      2.870103   -1.521537   -0.029485
      6          6                      1.878848    0.111656   -1.109257
      7          6                      1.483259    1.221061   -0.127635
      8          1                      0.429471    1.013674    1.772510
      9          6                     -0.885722    0.467218    0.225526
     10          1                      1.138176    0.046900   -1.911704
     11          1                      2.849263    0.288722   -1.574815
     12          1                      1.017984    2.084502   -0.602138
     13          1                      2.348063    1.559661    0.447191
     14          8                     -1.513406    1.457104   -0.047717
     15          8                     -1.365016   -0.774648    0.061405
     16          6                     -2.689688   -0.866432   -0.465906
     17          1                     -3.399144   -0.366243    0.195189
     18          1                     -2.739139   -0.406105   -1.453942
     19          1                     -2.909221   -1.930045   -0.528378
     20          1                      0.539782   -1.511275    1.315540
 ---------------------------------------------------------------------
 Rotational constants (MHZ):
   2843.7598479   1245.7687859   1070.6881487
 Nuclear quadrupole coupling constants [Chi] (MHz):
  1  N(14)
   aa=    -1.5869   ba=    -1.4373   ca=    -4.2964
   ab=    -1.4373   bb=     2.7922   cb=    -0.5589
   ac=    -4.2964   bc=    -0.5589   cc=    -1.2053
 Dipole moment (Debye):
     -0.3356284     -1.9111062     -0.8339898  Tot=      2.1119925
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Note: the values reported in the manuscript are averages of three nearly identical optimizations.

Table S9. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 5.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-0.937208	-1.198623	0.135510
2	6	-2.336491	-0.904079	0.440702
3	6	-0.394555	-0.135931	-0.727834
4	1	-2.617588	-1.344085	1.400546
5	1	-3.029895	-1.283569	-0.327037
6	6	-2.361117	0.619867	0.454207
7	6	-1.461829	0.969053	-0.735876
8	1	-0.180291	-0.495246	-1.740680
9	6	0.921950	0.316486	-0.110213
10	1	-1.917369	0.990877	1.381556
11	1	-3.368531	1.028764	0.361994
12	1	-1.019483	1.961786	-0.660088
13	1	-2.032518	0.913853	-1.666938
14	8	1.098224	1.323399	0.523863
15	8	1.881500	-0.590183	-0.339095
16	6	3.139055	-0.341318	0.288806
17	1	3.022512	-0.308830	1.373417
18	1	3.782465	-1.169634	-0.000261
19	1	3.558284	0.606324	-0.053644
20	1	-0.782500	-2.122928	-0.237966

Rotational constants (MHZ):
3694.4792890 1036.0120597 920.1624419

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.9834 ba= 0.0914 ca= -4.0291
ab= 0.0914 bb= 2.6446 cb= -0.9119
ac= -4.0291 bc= -0.9119 cc= -3.6280

Dipole moment (Debye):
-0.4433293 -1.6431199 -1.4115665 Tot= 2.2110866

Table S10. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 6.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.067450	0.716992	0.949982
2	6	-2.432545	0.668555	0.429009
3	6	-0.445422	-0.533151	0.515656
4	1	-2.872184	1.667342	0.416673
5	1	-3.043253	0.045799	1.092995
6	6	-2.322852	0.021069	-0.958219
7	6	-1.199483	-1.013057	-0.774860
8	1	-0.557962	-1.285984	1.298757
9	6	1.039477	-0.421392	0.262737
10	1	-2.028105	0.777410	-1.691566
11	1	-3.257358	-0.429602	-1.299215
12	1	-0.538823	-1.057798	-1.642889
13	1	-1.595899	-2.017605	-0.617622
14	8	1.825718	-1.317015	0.420645
15	8	1.381745	0.783186	-0.221327
16	6	2.764415	0.963806	-0.532904
17	1	3.077139	0.255784	-1.301968
18	1	2.853623	1.985789	-0.894621
19	1	3.377012	0.817610	0.357828
20	1	-0.572439	1.492140	0.523270

Rotational constants (MHZ):
3273.6364026 1046.5262067 968.7286587

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.8220 ba= -0.5703 ca= -0.0497
ab= -0.5703 bb= 2.6302 cb= -0.3292
ac= -0.0497 bc= -0.3292 cc= -5.4522

Dipole moment (Debye):
-0.7730424 1.6863265 -2.0758222 Tot= 2.7839414

Note: the values reported in the manuscript are averages of two nearly identical optimizations.

Table S11. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/6-311++G(d,p) optimization of PrOMe conformer 7.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.144928	-0.811412	0.864023
2	6	-2.344352	0.024469	0.799942
3	6	-0.453503	-0.788849	-0.433303
4	1	-2.571206	0.443685	1.783216
5	1	-3.229971	-0.531010	0.452989
6	6	-1.965695	1.089467	-0.223250
7	6	-1.192682	0.277029	-1.266354
8	1	-0.469916	-1.764442	-0.927680
9	6	1.017234	-0.487638	-0.180523
10	1	-1.309220	1.831334	0.236543
11	1	-2.834652	1.600279	-0.641447
12	1	-0.517103	0.883844	-1.869549
13	1	-1.890608	-0.224092	-1.942934
14	8	1.890417	-1.316798	-0.193249
15	8	1.232608	0.805345	0.091150
16	6	2.570029	1.156605	0.441727
17	1	2.554682	2.228657	0.626867
18	1	2.881462	0.618994	1.338981
19	1	3.256790	0.918678	-0.372507
20	1	-1.319982	-1.749308	1.191724

Rotational constants (MHZ):
3005.3440469 1144.9904970 1030.4186902

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -0.0983 ba= -2.5656 ca= -3.9342
ab= -2.5656 bb= 0.7064 cb= -2.3292
ac= -3.9342 bc= -2.3292 cc= -0.6081

Dipole moment (Debye):
-1.7995582 1.4581448 -0.3310521 Tot= 2.3396990

Table S12. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 1.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.413992	-0.909355	0.704812
2	6	2.283381	-0.660908	-0.453051
3	6	0.398756	0.146394	0.719207
4	1	1.817654	-0.952994	-1.408634
5	1	3.226681	-1.202319	-0.341130
6	6	2.442561	0.854993	-0.395786
7	6	1.002840	1.312175	-0.118232
8	1	0.198326	0.471161	1.746361
9	6	-0.923293	-0.296054	0.117967
10	1	2.847918	1.282130	-1.316836
11	1	3.098372	1.119841	0.439029
12	1	0.457175	1.417626	-1.062113
13	1	0.936800	2.265437	0.410348
14	8	-1.124624	-1.354783	-0.440985
15	8	-1.859953	0.662224	0.274922
16	6	-3.142532	0.341610	-0.290038
17	1	-3.057418	0.195581	-1.368441
18	1	-3.542094	-0.566084	0.165416
19	1	-3.777927	1.196417	-0.066433
20	1	0.966946	-1.820772	0.645143

Rotational constants (MHZ):
3685.0376141 1042.9250767 912.5221258

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.4395 ba= -0.9389 ca= -3.8188
ab= -0.9389 bb= 2.2466 cb= -0.4558
ac= -3.8188 bc= -0.4558 cc= -2.6861

Dipole moment (Debye):
-0.9263561 1.5706644 -0.6853505 Tot= 1.9480317

Table S13. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 2.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.377606	-0.967222	0.671620
2	6	2.589316	-0.421181	0.033945
3	6	0.393154	0.122645	0.739071
4	1	3.129624	-1.218104	-0.483953
5	1	3.250435	-0.007183	0.805309
6	6	2.094579	0.699682	-0.884701
7	6	1.015136	1.343140	-0.008666
8	1	0.165157	0.391043	1.775063
9	6	-0.903379	-0.285188	0.069391
10	1	1.647455	0.268087	-1.787352
11	1	2.877194	1.405363	-1.179124
12	1	0.267526	1.912896	-0.567015
13	1	1.476337	2.015084	0.722481
14	8	-1.026083	-1.200664	-0.719585
15	8	-1.909916	0.532068	0.434045
16	6	-3.166155	0.252821	-0.207743
17	1	-3.491815	-0.762795	0.022724
18	1	-3.864404	0.982684	0.197168
19	1	-3.073781	0.364963	-1.289580
20	1	0.988408	-1.685564	0.064631

Rotational constants (MHZ):
3779.4699901 1018.2605531 937.2373708

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.6909 ba= 0.0007 ca= -1.7510
ab= 0.0007 bb= 1.4063 cb= 2.2279
ac= -1.7510 bc= 2.2279 cc= -4.0972

Dipole moment (Debye):
-0.7581794 1.9403495 -0.7301098 Tot= 2.2074538

Note: the values reported in the manuscript are averages of two nearly identical optimizations.

Table S14. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 3.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.051502	-1.186472	-0.627058
2	6	-1.541760	-1.076268	0.754146
3	6	-0.505861	0.139006	-0.913529
4	1	-0.717743	-1.078888	1.487757
5	1	-2.210868	-1.907913	0.989448
6	6	-2.249145	0.294387	0.767255
7	6	-1.621376	1.068003	-0.422619
8	1	-0.307133	0.247088	-1.986460
9	6	0.813097	0.433360	-0.189226
10	1	-2.088917	0.811412	1.716589
11	1	-3.325672	0.175299	0.623991
12	1	-1.231262	2.046234	-0.138246
13	1	-2.350508	1.198096	-1.225262
14	8	1.124656	1.482164	0.333618
15	8	1.628098	-0.646971	-0.229281
16	6	2.907076	-0.448587	0.396239
17	1	2.779506	-0.214216	1.454617
18	1	3.439813	-1.389429	0.271274
19	1	3.444394	0.367757	-0.089583
20	1	-0.339035	-1.905912	-0.718108

Rotational constants (MHZ):
3092.1898112 1195.9414880 1045.4802644

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -2.2371 ba= -0.4463 ca= -3.7180
ab= -0.4463 bb= 2.4014 cb= -0.9755
ac= -3.7180 bc= -0.9755 cc= -0.1643

Dipole moment (Debye):
1.0916619 -1.2083132 0.4022157 Tot= 1.6773563

Note: the values reported in the manuscript are averages of four nearly identical optimizations.

Table S15. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 4.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.220591	-0.720679	1.051587
2	6	1.797358	-1.186511	-0.233008
3	6	0.545385	0.546780	0.813157
4	1	1.217822	-2.010373	-0.666169
5	1	2.818716	-1.540645	-0.060693
6	6	1.771623	0.050185	-1.158679
7	6	1.471863	1.218425	-0.207910
8	1	0.468193	1.130932	1.737164
9	6	-0.869018	0.477786	0.236938
10	1	0.963216	-0.041522	-1.891989
11	1	2.707183	0.179329	-1.708373
12	1	1.005194	2.076203	-0.696044
13	1	2.379598	1.544033	0.308446
14	8	-1.532841	1.451668	-0.050065
15	8	-1.303684	-0.794110	0.084157
16	6	-2.635663	-0.899842	-0.448604
17	1	-3.347270	-0.396463	0.207990
18	1	-2.683128	-0.449034	-1.441467
19	1	-2.843404	-1.967067	-0.498428
20	1	0.587655	-1.410553	1.441640

Rotational constants (MHZ):
2781.3764183 1279.7289745 1102.2182442

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -2.0026 ba= -1.6677 ca= -3.8119
ab= -1.6677 bb= 2.5060 cb= -0.6326
ac= -3.8119 bc= -0.6326 cc= -0.5034

Dipole moment (Debye):
-0.5267560 -1.7914509 -0.8865611 Tot= 2.0670653

Note: the values reported in the manuscript are averages of two nearly identical optimizations.

Table S16. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 5.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-0.934873	-1.202409	0.178415
2	6	-2.341088	-0.876425	0.460400
3	6	-0.391178	-0.169086	-0.738048
4	1	-2.636079	-1.298751	1.425147
5	1	-3.031252	-1.249186	-0.314009
6	6	-2.327507	0.649135	0.446350
7	6	-1.457025	0.937841	-0.783180
8	1	-0.175400	-0.573387	-1.734352
9	6	0.912728	0.303324	-0.118527
10	1	-1.837893	1.022353	1.350876
11	1	-3.327840	1.083836	0.374094
12	1	-1.010011	1.933568	-0.773832
13	1	-2.054966	0.826709	-1.693960
14	8	1.062711	1.307913	0.543442
15	8	1.895102	-0.590544	-0.364082
16	6	3.135293	-0.303453	0.301533
17	1	2.992293	-0.308028	1.383734
18	1	3.816691	-1.096971	0.000141
19	1	3.517523	0.671252	-0.006873
20	1	-0.810943	-2.135447	-0.199034

Rotational constants (MHZ):
3682.8241986 1038.2144108 929.0137216

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.8920 ba= 0.0334 ca= -3.7823
ab= 0.0334 bb= 2.3553 cb= -0.9713
ac= -3.7823 bc= -0.9713 cc= -3.2473

Dipole moment (Debye):
-0.4387922 -1.4228619 -1.3601933 Tot= 2.0167301

Table S17. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 6.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.072568	0.623071	1.014954
2	6	-2.451150	0.572254	0.511339
3	6	-0.444133	-0.577622	0.450248
4	1	-2.936709	1.544326	0.630494
5	1	-3.008349	-0.163983	1.103551
6	6	-2.336615	0.107566	-0.949687
7	6	-1.170176	-0.901139	-0.903824
8	1	-0.582628	-1.410325	1.145522
9	6	1.043975	-0.434902	0.245504
10	1	-2.074097	0.963899	-1.579844
11	1	-3.259409	-0.333260	-1.338486
12	1	-0.498948	-0.784621	-1.759631
13	1	-1.526599	-1.934854	-0.897135
14	8	1.856337	-1.320197	0.402757
15	8	1.360860	0.801181	-0.207885
16	6	2.759156	0.991554	-0.483007
17	1	3.090635	0.297425	-1.257276
18	1	2.849328	2.021370	-0.823399
19	1	3.347495	0.830079	0.421643
20	1	-0.612170	1.434856	0.607570

Rotational constants (MHZ):
3286.3852644 1034.6926270 973.2062008

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.6063 ba= -0.5288 ca= -0.3325
ab= -0.5288 bb= 2.3759 cb= 0.2793
ac= -0.3325 bc= 0.2793 cc= -4.9822

Dipole moment (Debye):
-0.7193285 1.6135350 -2.0523803 Tot= 2.7079870

Note: the values reported in the manuscript are averages of three nearly identical optimizations.

Table S18. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/6-311++G(d,p) optimization of PrOMe conformer 7.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.133475	-0.834144	0.850255
2	6	-2.353487	-0.014316	0.784865
3	6	-0.451178	-0.777876	-0.463515
4	1	-2.614358	0.349578	1.782684
5	1	-3.216170	-0.564017	0.374718
6	6	-1.950191	1.101134	-0.175365
7	6	-1.190175	0.320337	-1.255240
8	1	-0.477611	-1.741060	-0.985422
9	6	1.014379	-0.483817	-0.196679
10	1	-1.278183	1.800046	0.329581
11	1	-2.809282	1.648486	-0.572577
12	1	-0.511261	0.940709	-1.843911
13	1	-1.904345	-0.154052	-1.937164
14	8	1.894926	-1.319260	-0.191293
15	8	1.217729	0.821428	0.079719
16	6	2.563539	1.140542	0.465754
17	1	2.564504	2.212637	0.654622
18	1	2.837677	0.589691	1.367436
19	1	3.261238	0.888865	-0.335116
20	1	-1.318578	-1.792291	1.126063

Rotational constants (MHZ):
3001.4482193 1151.2643821 1031.9144573

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -0.0125 ba= -2.2822 ca= -3.7059
ab= -2.2822 bb= 0.6817 cb= -2.1249
ac= -3.7059 bc= -2.1249 cc= -0.6692

Dipole moment (Debye):
-1.6601156 1.3143904 -0.3955056 Tot= 2.1540730

Table S19. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 1.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.394587	0.941559	0.649041
2	6	-2.339697	0.647250	-0.430823
3	6	-0.399565	-0.125597	0.687858
4	1	-1.957858	0.942155	-1.426262
5	1	-3.289873	1.168516	-0.259018
6	6	-2.466182	-0.870377	-0.350798
7	6	-1.015443	-1.307825	-0.111109
8	1	-0.203527	-0.427746	1.727866
9	6	0.938859	0.297155	0.106316
10	1	-2.894877	-1.312961	-1.257604
11	1	-3.098158	-1.145403	0.503970
12	1	-0.496319	-1.428564	-1.071231
13	1	-0.926718	-2.255087	0.430529
14	8	1.166197	1.363835	-0.417660
15	8	1.859597	-0.667718	0.251952
16	6	3.158536	-0.369818	-0.268814
17	1	3.104589	-0.180273	-1.347510
18	1	3.577597	0.511902	0.230433
19	1	3.767246	-1.254184	-0.063468
20	1	-0.942719	1.840851	0.518401

Rotational constants (MHZ):
3728.6609663 1031.1098471 895.6818252

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.8216 ba= -0.6202 ca= 3.5935
ab= -0.6202 bb= 2.3305 cb= 0.0851
ac= 3.5935 bc= 0.0851 cc= -3.1521

Dipole moment (Debye):
0.7188801 -1.8736449 -0.5134956 Tot= 2.0714757

Table S20. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 2.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.385703	-0.971274	-0.646464
2	6	-2.576852	-0.443073	0.033740
3	6	-0.398873	0.105546	-0.743394
4	1	-3.054385	-1.231563	0.627651
5	1	-3.308760	-0.101799	-0.715480
6	6	-2.087873	0.744185	0.867620
7	6	-1.025843	1.350877	-0.052488
8	1	-0.160882	0.338167	-1.791097
9	6	0.905087	-0.293918	-0.075846
10	1	-1.628107	0.385957	1.799611
11	1	-2.882974	1.455363	1.123645
12	1	-0.279926	1.961608	0.468112
13	1	-1.500108	1.982332	-0.815080
14	8	1.050548	-1.252234	0.649192
15	8	1.893216	0.558249	-0.381183
16	6	3.159853	0.280763	0.224042
17	1	3.521764	-0.707254	-0.084190
18	1	3.832797	1.065514	-0.130889
19	1	3.076357	0.308375	1.317055
20	1	-0.976612	-1.717472	-0.091081

Rotational constants (MHZ):
3731.3630764 1026.4363655 931.5816169

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.4846 ba= -0.0935 ca= -1.9997
ab= -0.0935 bb= 1.5128 cb= -2.1156
ac= -1.9997 bc= -2.1156 cc= -3.9974

Dipole moment (Debye):
0.7129227 2.0941485 0.5038350 Tot= 2.2688249

Table S21. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 3.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	1.064542	-1.051676	0.756340
2	6	1.664887	-1.149078	-0.574045
3	6	0.494209	0.285075	0.827872
4	1	0.905102	-1.257673	-1.372794
5	1	2.339640	-2.011900	-0.629518
6	6	2.390675	0.195156	-0.713655
7	6	1.557882	1.173691	0.151119
8	1	0.334671	0.573273	1.877922
9	6	-0.880312	0.451921	0.167334
10	1	2.456939	0.516680	-1.759537
11	1	3.411270	0.112749	-0.321667
12	1	1.078911	1.963850	-0.435506
13	1	2.181044	1.654260	0.912533
14	8	-1.332043	1.498351	-0.234315
15	8	-1.569863	-0.702560	0.137568
16	6	-2.889411	-0.618426	-0.408092
17	1	-2.850917	-0.271439	-1.447443
18	1	-3.295681	-1.631889	-0.354806
19	1	-3.501920	0.075868	0.179177
20	1	0.367845	-1.769757	0.920631

Rotational constants (MHZ):
3113.5748068 1169.1987332 995.0115873

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -1.7077 ba= -0.0860 ca= -3.8157
ab= -0.0860 bb= 2.6268 cb= 0.4770
ac= -3.8157 bc= 0.4770 cc= -0.9191

Dipole moment (Debye):
-0.6247224 -1.6948991 -0.3979509 Tot= 1.8496827

Table S22. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 5.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.935822	-1.188901	-0.137015
2	6	2.351513	-0.925386	-0.395874
3	6	0.397586	-0.110337	0.712176
4	1	2.661962	-1.405216	-1.332964
5	1	3.012226	-1.289085	0.414186
6	6	2.396988	0.597719	-0.459155
7	6	1.461819	1.000376	0.688134
8	1	0.199311	-0.451245	1.740391
9	6	-0.933538	0.322687	0.110811
10	1	1.989977	0.942722	-1.418483
11	1	3.410689	0.998457	-0.343669
12	1	1.011237	1.987590	0.547747
13	1	2.009737	0.999217	1.639536
14	8	-1.140918	1.344633	-0.499494
15	8	-1.872404	-0.613533	0.325869
16	6	-3.142187	-0.365423	-0.282038
17	1	-3.035228	-0.293777	-1.371039
18	1	-3.770093	-1.218888	-0.012729
19	1	-3.574904	0.567547	0.098892
20	1	0.755802	-2.108608	0.243637

Rotational constants (MHZ):
3693.6489912 1030.2933263 907.9762995

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 1.0297 ba= -0.0732 ca= -3.5362
ab= -0.0732 bb= 2.5152 cb= 0.8394
ac= -3.5362 bc= 0.8394 cc= -3.5448

Dipole moment (Debye):
0.4673096 -1.7086328 1.4125098 Tot= 2.2656099

Table S23. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 6.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.056702	-0.799736	-0.869359
2	6	-2.451674	-0.673281	-0.444910
3	6	-0.445448	0.475592	-0.497460
4	1	-2.924475	-1.660483	-0.385051
5	1	-2.994665	-0.087855	-1.202555
6	6	-2.424101	0.082077	0.896642
7	6	-1.185124	0.995614	0.781312
8	1	-0.593446	1.190885	-1.316436
9	6	1.046562	0.400839	-0.276440
10	1	-2.297580	-0.631630	1.721648
11	1	-3.345939	0.646634	1.083400
12	1	-0.546669	0.920697	1.670115
13	1	-1.453118	2.051354	0.660724
14	8	1.816066	1.302738	-0.507272
15	8	1.422912	-0.769337	0.269953
16	6	2.819165	-0.896591	0.554270
17	1	3.134986	-0.126072	1.267503
18	1	2.942447	-1.894397	0.983331
19	1	3.405785	-0.796592	-0.366470
20	1	-0.608652	-1.541387	-0.337147

Rotational constants (MHZ):
3358.4701645 1020.3245484 948.2108205

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.4996 ba= 0.5006 ca= 0.5446
ab= 0.5006 bb= 2.2790 cb= -1.0090
ac= 0.5446 bc= -1.0090 cc= -4.7786

Dipole moment (Debye):
-0.8998979 -1.5530703 2.0697798 Tot= 2.7396774

Table S24. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the ωB97XD/aug-cc-pVDZ optimization of PrOMe conformer 7.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.141049	0.780329	-0.887984
2	6	-2.368587	-0.012279	-0.786691
3	6	-0.450658	0.784389	0.412226
4	1	-2.628584	-0.439555	-1.763810
5	1	-3.231747	0.580344	-0.429620
6	6	-2.003728	-1.073089	0.246873
7	6	-1.190179	-0.267717	1.266824
8	1	-0.471039	1.773033	0.890725
9	6	1.023218	0.482898	0.175301
10	1	-1.375493	-1.844726	-0.215014
11	1	-2.884167	-1.552985	0.689847
12	1	-0.507486	-0.886112	1.858952
13	1	-1.865205	0.249979	1.961065
14	8	1.901537	1.313814	0.215846
15	8	1.242518	-0.809112	-0.111753
16	6	2.591950	-1.149687	-0.434000
17	1	2.584732	-2.224392	-0.634863
18	1	2.923171	-0.594722	-1.320002
19	1	3.259197	-0.917923	0.405006
20	1	-1.295288	1.715608	-1.240719

Rotational constants (MHZ):
3028.7415644 1127.2076046 1020.3580632

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.0298 ba= 2.4407 ca= 3.4571
ab= 2.4407 bb= 0.4244 cb= -2.3276
ac= 3.4571 bc= -2.3276 cc= -0.4541

Dipole moment (Debye):
-1.8377200 -1.4226750 0.2813642 Tot= 2.3410222

Table S25. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 1.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.429615	0.896398	0.736861
2	6	-2.225414	0.683093	-0.489639
3	6	-0.406283	-0.160069	0.751569
4	1	-1.681761	0.978614	-1.410019
5	1	-3.165599	1.251999	-0.434939
6	6	-2.425807	-0.834071	-0.460690
7	6	-1.020301	-1.340841	-0.070722
8	1	-0.188593	-0.470998	1.786610
9	6	0.910063	0.288912	0.130587
10	1	-2.769290	-1.244338	-1.422040
11	1	-3.158800	-1.090424	0.319554
12	1	-0.416636	-1.527203	-0.972828
13	1	-1.039389	-2.272242	0.511935
14	8	1.105990	1.365156	-0.418839
15	8	1.859246	-0.674059	0.263219
16	6	3.139081	-0.325266	-0.321888
17	1	3.025921	-0.145119	-1.399805
18	1	3.541112	0.577278	0.158413
19	1	3.784783	-1.190098	-0.134276
20	1	-0.973699	1.811058	0.715449

Rotational constants (MHZ):
3580.9013863 1048.5016111 918.7545266

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.0224 ba= -0.9646 ca= 3.4045
ab= -0.9646 bb= 1.9374 cb= 0.4839
ac= 3.4045 bc= 0.4839 cc= -1.9598

Dipole moment (Debye):
0.9363660 -1.5562096 -0.6020890 Tot= 1.9133951

Table S26. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 2.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.392942	-0.960031	-0.698390
2	6	-2.587091	-0.427162	0.003362
3	6	-0.398208	0.132263	-0.758403
4	1	-3.097764	-1.239538	0.541726
5	1	-3.291367	-0.014730	-0.740282
6	6	-2.063671	0.697063	0.910085
7	6	-1.022100	1.354622	-0.009347
8	1	-0.160867	0.401369	-1.799675
9	6	0.896353	-0.281553	-0.079521
10	1	-1.573532	0.264797	1.798471
11	1	-2.845105	1.399212	1.240312
12	1	-0.263294	1.951708	0.517792
13	1	-1.523023	2.008476	-0.741343
14	8	1.016949	-1.216692	0.702485
15	8	1.914347	0.544117	-0.428142
16	6	3.170888	0.238834	0.228387
17	1	3.493563	-0.779029	-0.029552
18	1	3.879278	0.983304	-0.150841
19	1	3.058260	0.321261	1.318173
20	1	-0.984674	-1.692682	-0.112429

Rotational constants (MHZ):
3711.2134741 1017.3403250 936.7997108

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.2799 ba= 0.0161 ca= -1.7479
ab= 0.0161 bb= 1.3183 cb= -1.8128
ac= -1.7479 bc= -1.8128 cc= -3.5982

Dipole moment (Debye):
0.7674096 1.9413646 0.6597850 Tot= 2.1893219

Table S27. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 4.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.248190	-0.637821	-1.100702
2	6	-1.793286	-1.192556	0.171082
3	6	-0.550905	0.609870	-0.787246
4	1	-1.197031	-2.045102	0.537400
5	1	-2.823376	-1.542232	-0.001102
6	6	-1.748872	-0.015315	1.179229
7	6	-1.453278	1.218400	0.302629
8	1	-0.484961	1.259241	-1.675735
9	6	0.873225	0.487074	-0.239246
10	1	-0.927678	-0.160862	1.899524
11	1	-2.682844	0.083741	1.751337
12	1	-0.962319	2.040500	0.842000
13	1	-2.371690	1.592642	-0.175355
14	8	1.583459	1.442239	0.041677
15	8	1.264930	-0.809195	-0.087661
16	6	2.608922	-0.949796	0.439963
17	1	3.331942	-0.472459	-0.235435
18	1	2.675033	-0.482028	1.431941
19	1	2.781270	-2.030014	0.501563
20	1	-0.623550	-1.305617	-1.550388

Rotational constants (MHZ):
2733.5809157 1280.2812071 1104.8145552

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= -1.8988 ba= 1.7251 ca= -3.2258
ab= 1.7251 bb= 2.1104 cb= 0.7279
ac= -3.2258 bc= 0.7279 cc= -0.2116

Dipole moment (Debye):
0.3679559 -1.8819672 0.8009686 Tot= 2.0781585

Table S28. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 5.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.942534	-1.208387	-0.184254
2	6	2.356310	-0.874908	-0.459250
3	6	0.394324	-0.172569	0.739774
4	1	2.659416	-1.300489	-1.428004
5	1	3.048935	-1.246739	0.322991
6	6	2.334343	0.655619	-0.447785
7	6	1.458301	0.943948	0.785073
8	1	0.178684	-0.581588	1.741446
9	6	-0.914413	0.298632	0.120585
10	1	1.839381	1.028211	-1.358110
11	1	3.339009	1.098005	-0.375536
12	1	1.000637	1.942405	0.770929
13	1	2.058470	0.838752	1.703209
14	8	-1.071538	1.315402	-0.539714
15	8	-1.901382	-0.605220	0.361859
16	6	-3.151081	-0.297538	-0.303210
17	1	-2.999496	-0.268178	-1.391051
18	1	-3.832892	-1.108236	-0.023538
19	1	-3.534289	0.673936	0.038345
20	1	0.826087	-2.144081	0.200415

Rotational constants (MHZ):
3650.1920644 1029.3634502 920.3176928

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.7767 ba= -0.0618 ca= -3.3459
ab= -0.0618 bb= 2.1055 cb= 0.8378
ac= -3.3459 bc= 0.8378 cc= -2.8822

Dipole moment (Debye):
0.4601883 -1.4680824 1.3792860 Tot= 2.0662694

Table S29. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 6.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.091630	-0.556611	-1.070289
2	6	-2.456473	-0.565575	-0.503572
3	6	-0.447401	0.619741	-0.449499
4	1	-2.926450	-1.547837	-0.660265
5	1	-3.058384	0.193800	-1.032696
6	6	-2.284551	-0.177082	0.977396
7	6	-1.176565	0.899679	0.919896
8	1	-0.563350	1.487497	-1.115680
9	6	1.039760	0.443508	-0.234601
10	1	-1.936356	-1.055438	1.545225
11	1	-3.210129	0.192967	1.445432
12	1	-0.484696	0.835013	1.773281
13	1	-1.602494	1.914308	0.910735
14	8	1.873739	1.328906	-0.350323
15	8	1.339279	-0.821030	0.179493
16	6	2.748044	-1.026872	0.455101
17	1	3.078356	-0.350473	1.255262
18	1	2.828961	-2.074231	0.766096
19	1	3.340469	-0.837744	-0.450343
20	1	-0.605272	-1.387235	-0.723023

Rotational constants (MHZ):
3214.6659158 1038.3200336 975.5529295

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 2.2971 ba= 0.4950 ca= 0.0755
ab= 0.4950 bb= 2.0671 cb= 0.6172
ac= 0.0755 bc= 0.6172 cc= -4.3642

Dipole moment (Debye):
-0.7748138 -1.7367387 1.9427737 Tot= 2.7186334

Table S30. Principal-axis atomic coordinates and Pickett-format spectroscopic constants from the MP2/aug-cc-pVDZ optimization of PrOMe conformer 7.

Principal axis orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.136456	0.821823	-0.864751
2	6	-2.382362	0.031284	-0.771248
3	6	-0.451674	0.774233	0.456948
4	1	-2.675485	-0.325906	-1.770246
5	1	-3.227639	0.604800	-0.339339
6	6	-1.979992	-1.097354	0.181348
7	6	-1.188491	-0.329490	1.256418
8	1	-0.480915	1.744676	0.979008
9	6	1.018641	0.482279	0.195031
10	1	-1.322061	-1.808352	-0.340668
11	1	-2.845638	-1.638046	0.592368
12	1	-0.497594	-0.964501	1.828150
13	1	-1.887229	0.146974	1.963007
14	8	1.907936	1.323070	0.210256
15	8	1.226275	-0.827555	-0.099556
16	6	2.593348	-1.134698	-0.464954
17	1	2.599294	-2.209906	-0.676037
18	1	2.882960	-0.558069	-1.354384
19	1	3.273574	-0.892897	0.363505
20	1	-1.307516	1.784621	-1.150088

Rotational constants (MHZ):
2999.8270555 1131.6289529 1017.1674406

Nuclear quadrupole coupling constants [Chi] (MHz):
1 N(14)
aa= 0.1171 ba= 2.0469 ca= 3.2002
ab= 2.0469 bb= 0.4411 cb= -1.9819
ac= 3.2002 bc= -1.9819 cc= -0.5582

Dipole moment (Debye):
-1.7130555 -1.3155749 0.3591424 Tot= 2.1895844

Table S31. Assigned transition frequencies for PrOMe.

J'	K_a'	K_c'	F'	J''	K_a''	K_c''	F''	A obs (MHz)	A obs-calc (MHz)	E obs (MHz)	E obs-calc (MHz)
5	1	5	6	4	1	4	5			9665.038	0.002
			4				3			9665.111	0.005
			5				4			9665.129	0.009
6	0	6	6	5	1	5	5	9750.784	0.008	9751.057	0.008
			7				6	9751.366	0.010	9751.638	0.005
			5				4	9751.523	0.011	9751.797	0.006
5	0	5	6	4	0	4	5	9860.480	0.004	9860.444	0.002
			4				3	9860.515	0.000	9860.480	0.004
			5				4	9860.580	0.002	9860.547	0.008
5	2	4	4	4	2	3	3	9903.276	0.009	9905.910	0.002
			6				5	9903.297	0.006	9905.934	0.004
			5				4	9903.471	0.009	9906.118	0.002
5	1	4	4	4	1	3	3	10130.907	0.020	10130.877	0.008
			6				5	10130.958	0.006	10130.937	0.028
			5				4	10131.014	0.005	10130.977	0.010
4	1	4	3	3	0	3	2	10153.582	0.002	10153.228	0.004
			5				4	10153.708	0.002	10153.351	0.004
			4				3	10154.489	0.002	10154.130	0.002
4	1	3	4	3	0	3	3	11086.280	0.010	11086.068	0.004
			5				4	11087.370	0.007	11087.156	0.004
			3				2	11087.722	0.014	11087.513	0.003
6	1	6	7	5	1	5	6	11591.883	0.007	11591.861	0.001
			5				4	11591.932	0.006	11591.906	0.003

			6				5	11591.955	0.002	11591.932	0.008
6	0	6	7	5	0	5	6	11806.915	0.006	11806.871	0.000
			5				4	11806.938	0.001	11806.892	0.003
			6				5	11807.021	0.005	11806.983	0.008
6	2	5	5	5	2	4	4	11879.423	0.007	11880.575	0.007
			7				6	11879.423	0.009	11880.575	0.004
			6				5	11879.537	0.008	11880.692	0.004
7	0	7	7	6	1	6	6	11899.724	0.010	11899.963	0.008
			8				7	11900.256	0.012	11900.497	0.007
			6				5	11900.376	0.013	11900.618	0.008
5	1	5	4	4	0	4	3	11915.919	0.001	11915.578	0.004
			6				5	11916.031	0.002	11915.688	0.005
			5				4	11916.812	0.001	11916.469	0.004
2	2	1	1	1	1	0	0	11978.570	0.012	11963.879	0.002
			2				2	11979.180	0.003		
			3				2	11979.991	0.013	11965.202	0.006
			2				1	11980.340	0.012	11965.605	0.004
2	2	1	1	1	1	1	1	12073.480	0.001	12059.885	0.005
			3				2	12073.540	0.005	12059.946	0.007
2	2	0	1	1	1	1	1	12075.930	0.003	12088.984	0.006
			3				2	12075.980	0.003	12089.040	0.003
6	1	5	5	5	1	4	4	12149.701	0.009	12149.668	0.001
			7				6	12149.716	0.008	12149.687	0.004
			6				5	12149.767	0.005	12149.738	0.007
9	3	6	8	9	2	7	8	12931.872	0.001	12940.258	0.000
			10				10	12931.906	0.002	12940.293	0.002
			9				9	12932.189	0.000	12940.584	0.000

8	3	6	7	8	2	6	7	13084.128	0.011	13067.914	0.005
			9				9	13084.180	0.014	13067.943	0.003
			8				8	13084.386	0.000	13068.150	0.006
8	3	5	7	8	2	6	7	13102.288	0.001	13114.844	0.001
			9				9	13102.316	0.003	13114.871	0.003
			8				8	13102.500	0.002	13115.067	0.000
7	3	4	6	7	2	5	6	13229.658	0.002	13245.489	0.001
			8				8	13229.672	0.001	13245.503	0.001
			7				7	13229.749	0.003	13245.586	0.003
6	3	3	6	6	2	4	6	13318.756	0.008	13336.244	0.005
				7			7	13318.832	0.006	13336.308	0.008
5	3	2	5	5	2	3	5	13376.324	0.001	13393.691	0.002
			6				6	13376.554	0.004	13393.926	0.002
			4				4	13376.606	0.001	13393.978	0.001
4	3	1	4	4	2	2	4	13409.935	0.002	13425.060	0.000
			5				5	13410.415	0.001	13425.560	0.007
			3				3	13410.533	0.005	13425.673	0.007
4	3	2	4	4	2	3	4	13445.902	0.003	13428.033	0.000
			5				5	13446.528	0.002	13428.641	0.002
			3				3	13446.681	0.004	13428.793	0.002
5	3	3	5	5	2	4	5	13459.519	0.001	13439.404	0.003
			6				6	13459.973	0.002	13439.852	0.000
			4				4	13460.065	0.003	13439.960	0.016
6	3	4	6	6	2	5	6	13482.961	0.003	13462.729	0.002
			7				7	13483.334	0.004	13463.102	0.004
			5				5	13483.404	0.004	13463.177	0.007
6	3	3	6	6	2	5	6			13506.228	0.001

			7				7			13506.603	0.001
			5				5			13506.673	0.006
7	1	7	8	6	1	6	7	13515.687	0.001	13515.650	0.003
			6				5	13515.717	0.005	13515.679	0.003
			7				6	13515.737	0.004	13515.706	0.005
7	3	5	7	7	2	6	7	13519.844	0.003	13501.244	0.002
			8				8	13520.179	0.003	13501.583	0.003
			6				6	13520.231	0.002	13501.637	0.001
6	1	6	5	5	0	5	4	13647.342	0.001	13647.009	0.003
			7				6	13647.435	0.000	13647.103	0.005
			6				5	13648.186	0.001	13647.853	0.003
7	0	7	8	6	0	6	7	13740.774	0.007	13740.720	0.003
			6				5	13740.788	0.005	13740.733	0.005
			7				6			13740.831	0.001
7	2	6	8	6	2	5	7	13853.068	0.008	13853.581	0.006
			6				5	13853.068	0.011	13853.581	0.003
			7				6	13853.154	0.004	13853.666	0.008
3	2	2	2	2	1	1	1	13867.991	0.013	13857.353	0.006
			4				3	13868.273	0.016	13857.628	0.006
			3				2	13868.785	0.016	13858.112	0.003
3	2	1	2	2	1	1	1	13880.181	0.013	13888.791	0.003
			4				3	13880.436	0.015	13889.057	0.004
			3				2	13880.870	0.014	13889.511	0.002
7	3	5	6	6	3	4	5	13889.900	0.008	13892.048	0.004
			8				7	13889.914	0.006	13892.061	0.006
			7				6	13890.031	0.010	13892.178	0.005
7	3	4	6	6	3	3	5	13894.858	0.009	13892.666	0.006

			8				7	13894.871	0.007	13892.679	0.008
			7				6	13894.982	0.008	13892.794	0.008
7	2	5	7	6	2	4	6	13983.996	0.012	13983.448	0.005
			8				7	13984.023	0.010	13983.476	0.007
			6				5	13984.034	0.009	13983.488	0.008
8	0	8	8	7	1	7	7	14045.768	0.012	14045.971	0.011
			9				8	14046.237	0.012	14046.439	0.010
			7				6	14046.329	0.013	14046.532	0.010
3	2	2	3	2	1	2	2	14147.463	0.007	14137.171	0.008
			4				3	14148.718	0.003	14138.442	0.005
			2				1	14149.407	0.010	14139.147	0.006
3	2	1	3	2	1	2	2	14159.563	0.009	14168.568	0.005
			4				3	14160.889	0.005	14169.871	0.003
			2				1	14161.612	0.005	14170.584	0.002
7	1	6	6	6	1	5	5	14164.079	0.010	14164.020	0.005
			8				7	14164.095	0.016	14164.034	0.001
			7				6	14164.142	0.017	14164.079	0.003
7	1	7	6	6	0	6	5	15356.123	0.003	15355.809	0.009
			8				7	15356.201	0.001	15355.871	0.003
			7				6	15356.901	0.001	15356.578	0.002
4	2	3	3	3	1	2	2	15709.435	0.016	15703.462	0.010
			5				4	15709.631	0.017	15703.653	0.008
			4				3	15710.281	0.018	15704.284	0.004
4	2	2	3	3	1	2	2	15745.876	0.001	15.749.993	0.010
			5				4	15746.033	0.003	15750.153	0.006
			4				3	15746.539	0.004	15750.675	0.005
8	2	6	8	7	2	5	7	16015.226	0.012	16014.947	0.005

			9				8	16015.276	0.010	16015.000	0.009
			7				6	16015.289	0.008	16015.011	0.009
9	0	9	9	8	1	8	8	16179.839	0.011	16179.993	0.014
			10				9	16180.234	0.013	16180.384	0.009
			8				7	16180.320	0.002	16180.463	0.016
4	2	2	4	3	1	3	3	16305.231	0.023	16309.542	0.005
			5				4	16306.550	0.020	16310.847	0.004
			3				2	16307.028	0.019	16311.322	0.004
8	1	8	7	7	0	7	6	17051.560	0.003	17051.255	0.001
			9				8	17051.620	0.001	17051.315	0.003
			8				7	17052.255	0.003	17051.951	0.002
5	2	4	4	4	1	3	3	17504.105	0.001	17500.794	0.008
			6				5	17504.267	0.003	17500.954	0.005
			5				4	17505.005	0.004	17501.687	0.005
5	2	3	5	4	1	4	4	18521.101	0.010		
			6				5	18522.456	0.009	18524.094	0.003
			4				3	18522.824	0.004	18524.459	0.007
9	1	9	8	8	0	8	7	18743.205	0.005	18742.929	0.001
			10				9	18743.253	0.000	18742.976	0.004
			9				8	18743.813	0.004	18743.536	0.000

Table S32. Root-mean square differences between model and experimental second moments of inertia (amu Å^2).

Conformer	ωB97XD/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)	ωB97XD/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ
1	14.77	9.82	14.44	8.95
2	1.63	5.52	4.33	4.93
3	35.51	42.81	34.43	
4	56.34	64.46		66.02
5	6.99	4.46	10.35	6.34
6	12.76	13.22	7.15	15.14
7	37.19	38.14	33.46	34.20

Table S33. Root-mean square differences between model and experimental nuclear quadrupole coupling constants (MHz).

Conformer	ωB97XD/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)	ωB97XD/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ
1	0.931	1.336	1.047	1.737
2	0.338	0.275	0.130	0.233
3	3.072	3.426	2.944	
4	2.812	3.206		3.239
5	0.986	0.998	0.929	1.097
6	1.122	0.794	0.656	0.386
7	2.404	2.351	2.474	2.396

Table S34. Root-mean square differences between model and best-fit XIAM rotor-axis angles (degrees).

Conformer	wB97XD/ 6-311++G(d,p)	MP2/ 6-311++G(d,p)	wB97XD/ aug-cc-pVDZ	MP2/ aug-cc-pVDZ
1	3.12	1.22	2.89	0.45
2	1.28	1.88	1.48	1.87
3	7.14	3.46	6.84	
4	6.98	6.69		6.14
5	2.30	2.47	2.22	2.17
6	11.10	12.08	12.76	11.90
7	7.49	6.88	8.46	7.80