Supporting Information

O-Acetyl Side-chains in Monosaccharides: NMR *J*-Couplings and Statistical Models for Acetate Ester Conformational Analysis

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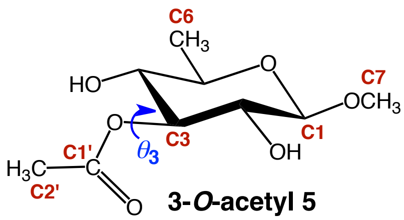
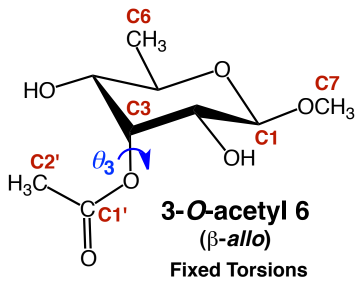
Scheme S1



3-*O*-acetyl 5
(β-*gluco*)

Fixed Torsions
C2-C1-O1-C7 = 180º
C3-C2-O2-H = 180º
C3-C4-O4-H = 180º
C3-O3-C1'-C2' = 180º

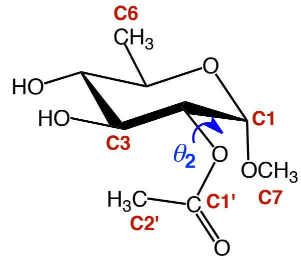
θ_3 (H3-C3-O3-C1') was rotated in 15º increments



3-*O*-acetyl 6
(β-*allo*)

Fixed Torsions
C2-C1-O1-C7 = 180º
C3-C2-O2-H = 180º
C3-C4-O4-H = 180º
C3-O3-C1'-C2' = 180º

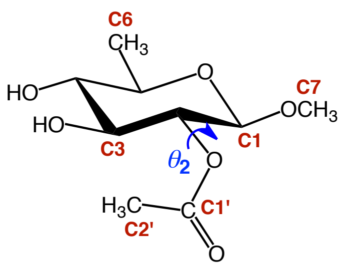
θ_3 (H3-C3-O3-C1') was rotated in 15º increments



2-*O*-acetyl 7
(α-*gluco*)

Fixed Torsions
C2-C1-O1-C7 = 180º
C2-C3-O3-H = 180º
C3-C4-O4-H = 180º
C2-O2-C1'-C2' = 180º

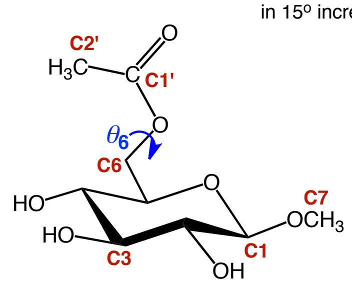
θ_2 (H2-C2-O2-C1') was rotated in 15º increments



2-*O*-acetyl 8
(β-*gluco*)

Fixed Torsions
C2-C1-O1-C7 = 180º
C2-C3-O3-H = 180º
C3-C4-O4-H = 180º
C2-O2-C1'-C2' = 180º

θ_2 (H2-C2-O2-C1') was rotated in 15º increments

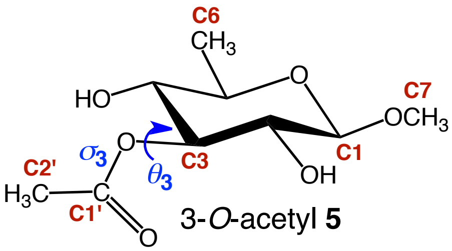


6-*O*-acetyl 9
(β-*gluco*)

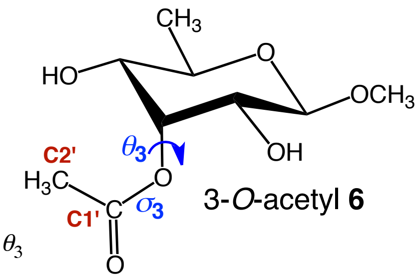
Fixed Torsions
C2-C1-O1-C7 = 180º
C3-C2-O2-H = 180º
C2-C3-O3-H = 180º
C3-C4-O4-H = 180º
C6-O6-C1'-C2' = 180º
C4-C5-C6-O6 = 180º

θ_6 (C5-C6-O6-C1') was rotated in 15º increments

Scheme S2



3-*O*-acetyl **5**



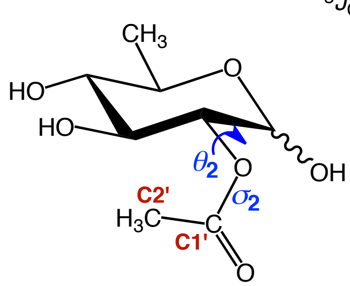
3-*O*-acetyl **6**

***J*-Couplings Sensitive to** θ_3

$^3J_{C1',H3}$
$^3J_{C1',C2}$
$^3J_{C1',C4}$
$^2J_{C1',C3}$

***J*-Couplings Sensitive to** σ_3

$^3J_{C2',C3}$



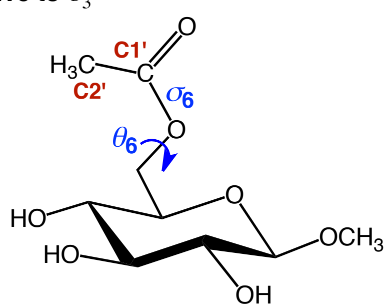
2-*O*-acetyl **7/8**

***J*-Couplings Sensitive to** θ_2

$^3J_{C1',H2}$
$^3J_{C1',C1}$
$^3J_{C1',C3}$
$^2J_{C1',C2}$

***J*-Couplings Sensitive to** σ_2

$^3J_{C2',C2}$



6-*O*-acetyl **9**

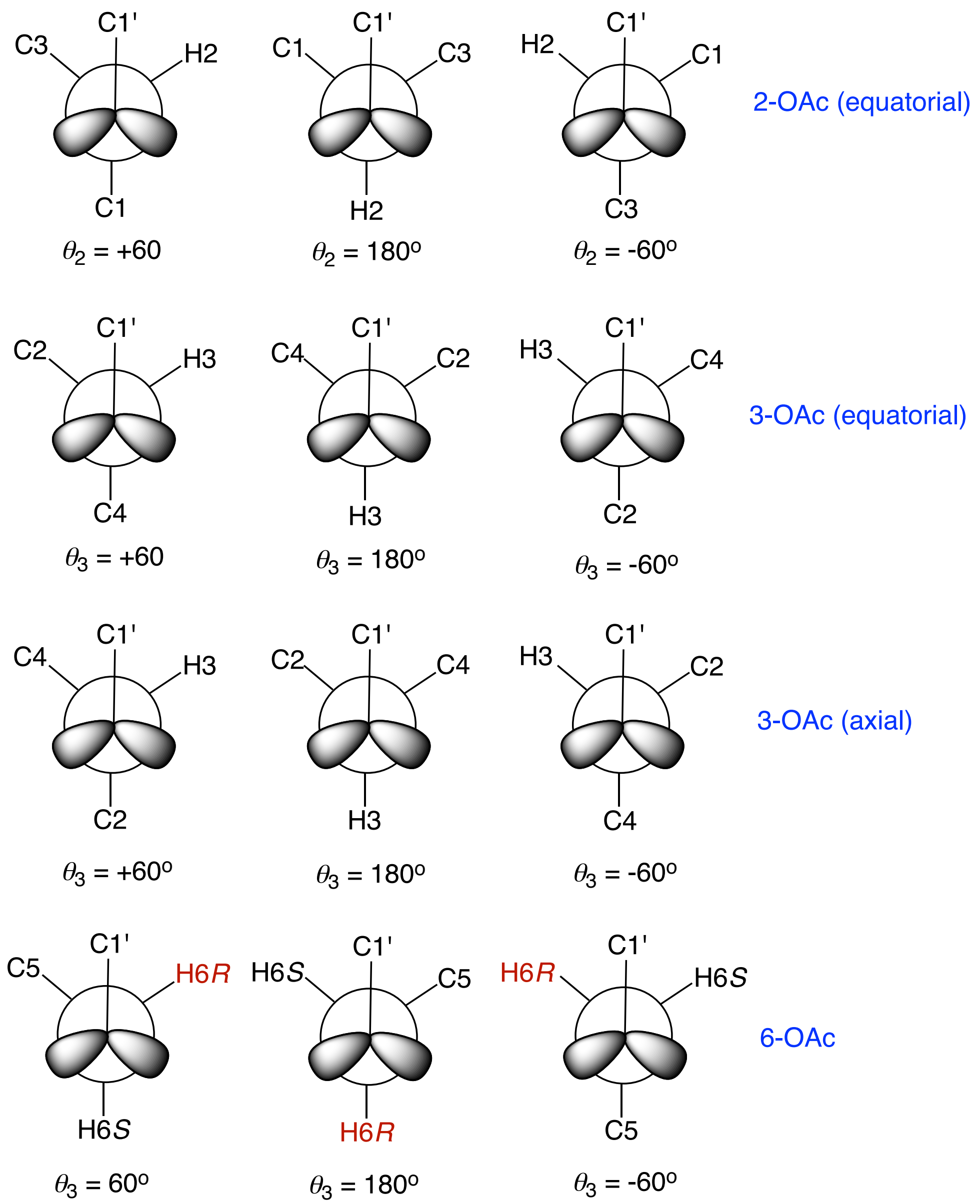
***J*-Couplings Sensitive to** θ_6

$^3J_{C1',H6R}$
$^3J_{C1',H6S}$
$^3J_{C1',C5}$
$^2J_{C1',C6}$

***J*-Couplings Sensitive to** σ_6

$^3J_{C2',C6}$

Scheme S3


C3
C1'
H2
C1
θ2 = +60
C1
C1'
C3
H2
θ2 = 180°
H2
C1'
C1
C3
θ2 = -60°
2-OAc (equatorial)
C2
C1'
H3
C4
θ3 = +60
C4
C1'
C2
H3
θ3 = 180°
H3
C1'
C4
C2
θ3 = -60°
3-OAc (equatorial)
C4
C1'
H3
C2
θ3 = +60°
C2
C1'
C4
H3
θ3 = 180°
H3
C1'
C2
C4
θ3 = -60°
3-OAc (axial)
C5
C1'
H6R
H6S
θ3 = 60°
H6S
C1'
C5
H6R
θ3 = 180°
H6R
C1'
H6S
C5
θ3 = -60°
6-OAc

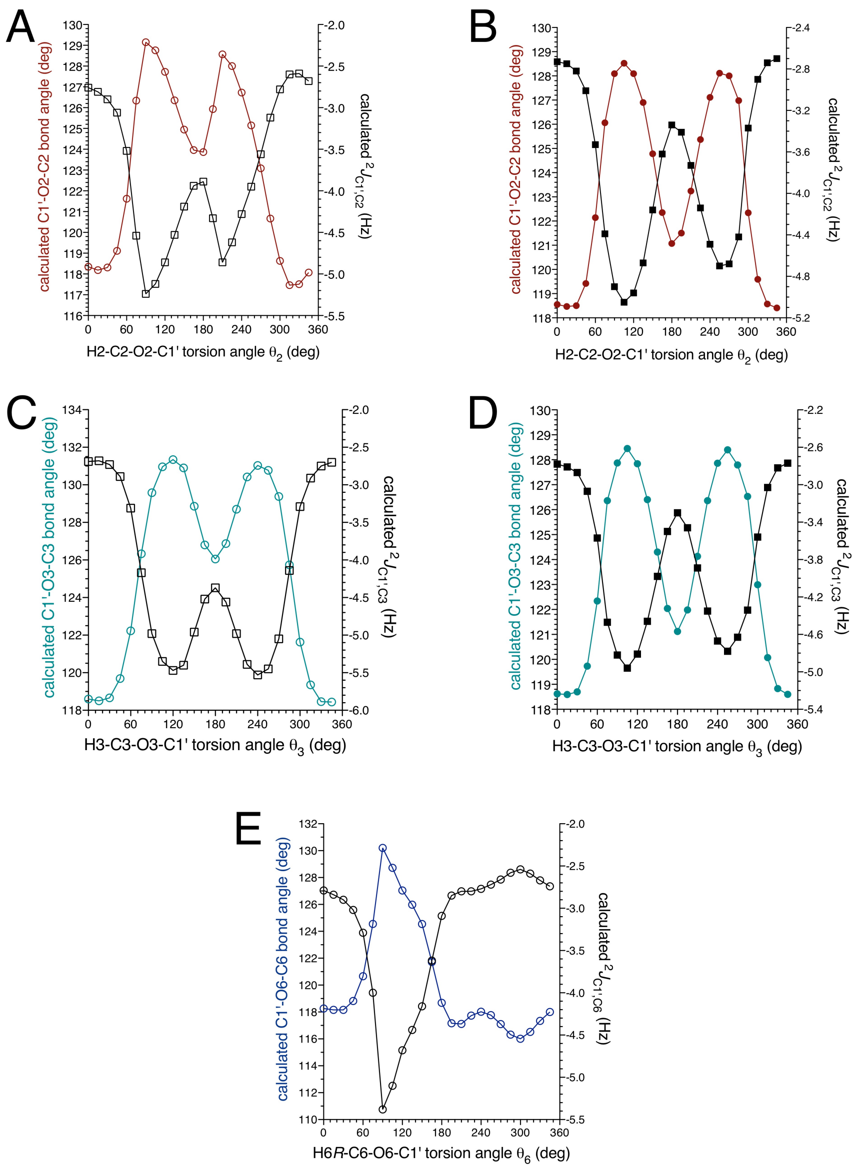


Figure S1: Plots showing correlations between $^2J_{C1',CX}$ and C1'-O$_X$-C$_X$ bond angle in **5-8** (x = 2 or 3). The calculated sign of $^2J_{C1',CX}$ is negative in all structures. (A) 2-*O*-acetyl in **7**. (B) 2-*O*-acetyl in **8**. (C) 3-*O*-acetyl in **6**. (D) 3-*O*-acetyl in **5**. (E) 6-*O*-acetyl in **9**.

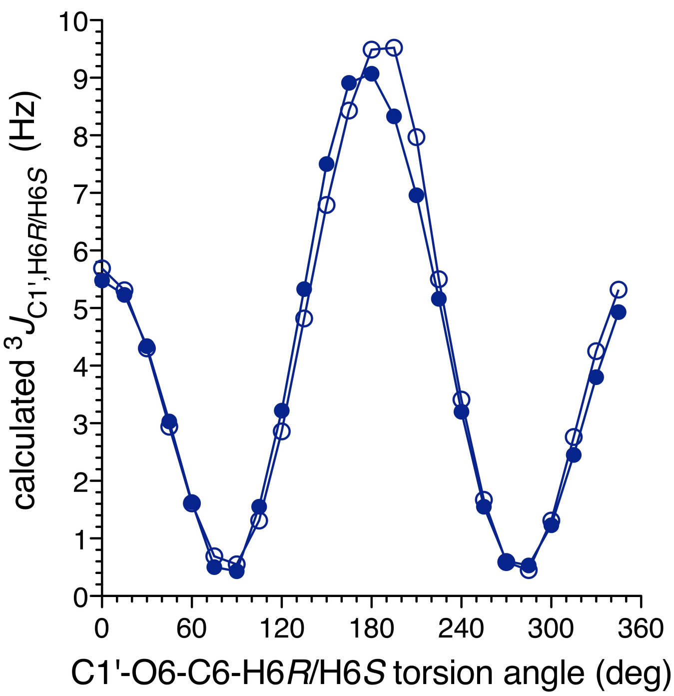


Figure S2. Plot of calculated $^3J_{C1',H6R}$ and $^3J_{C1',H6S}$ in **9** after shifting the latter curve shown in Figure 5 (see text) by 120°. Filled symbols, $^3J_{C1',H6R}$. Open symbols, $^3J_{C1',H6S}$.

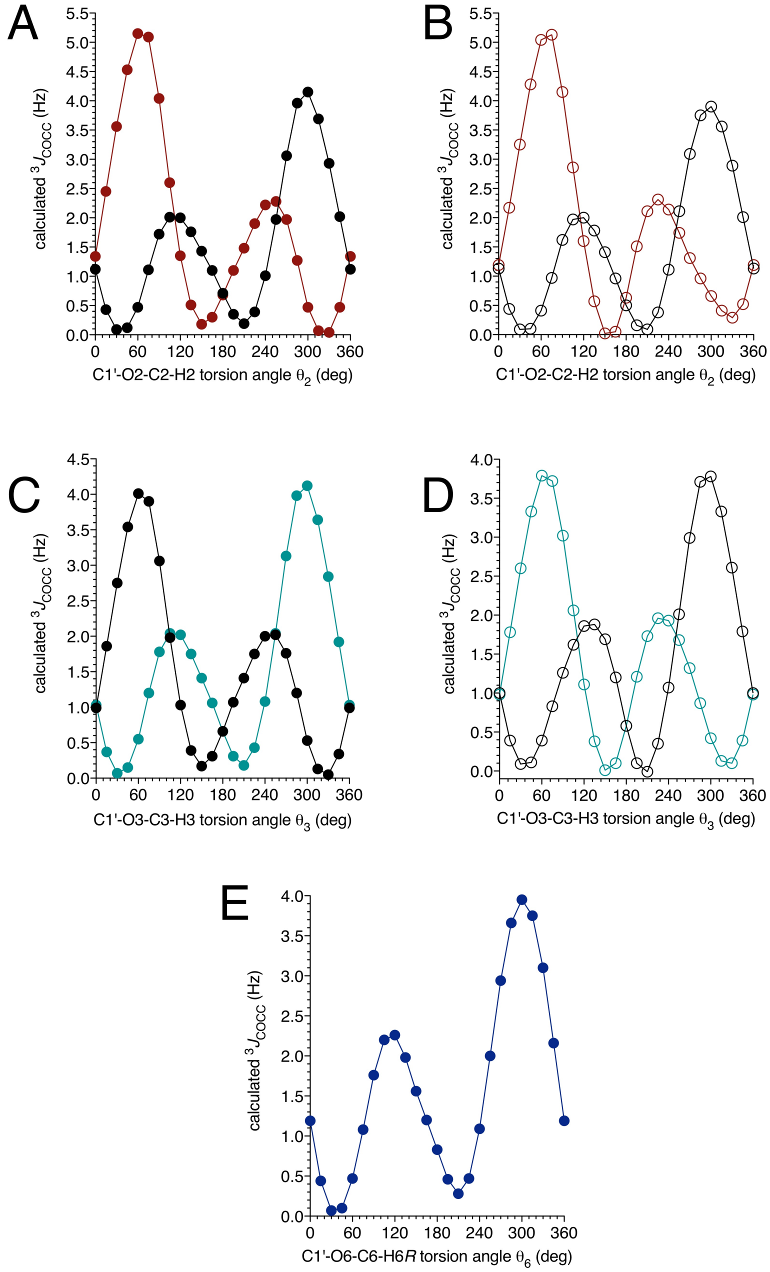


Figure S3. Plots of calculated $^3J_{C1',Cy}$ as a function of θ_x in **5-9**, where x = 2, 3 or 6 and y = x ± 1. (A) In **8**, $^3J_{C1',C1}$ (red) and $^3J_{C1',C3}$ (black). (B) In **7**, $^3J_{C1',C1}$ (red) and $^3J_{C1',C3}$ (black). (C) In **5**, $^3J_{C1',C2}$ (green) and $^3J_{C1',C4}$ (black). (D) In **6**, $^3J_{C1',C2}$ (green) and $^3J_{C1',C4}$ (black). (E) In **9**, $^3J_{C1',C5}$.

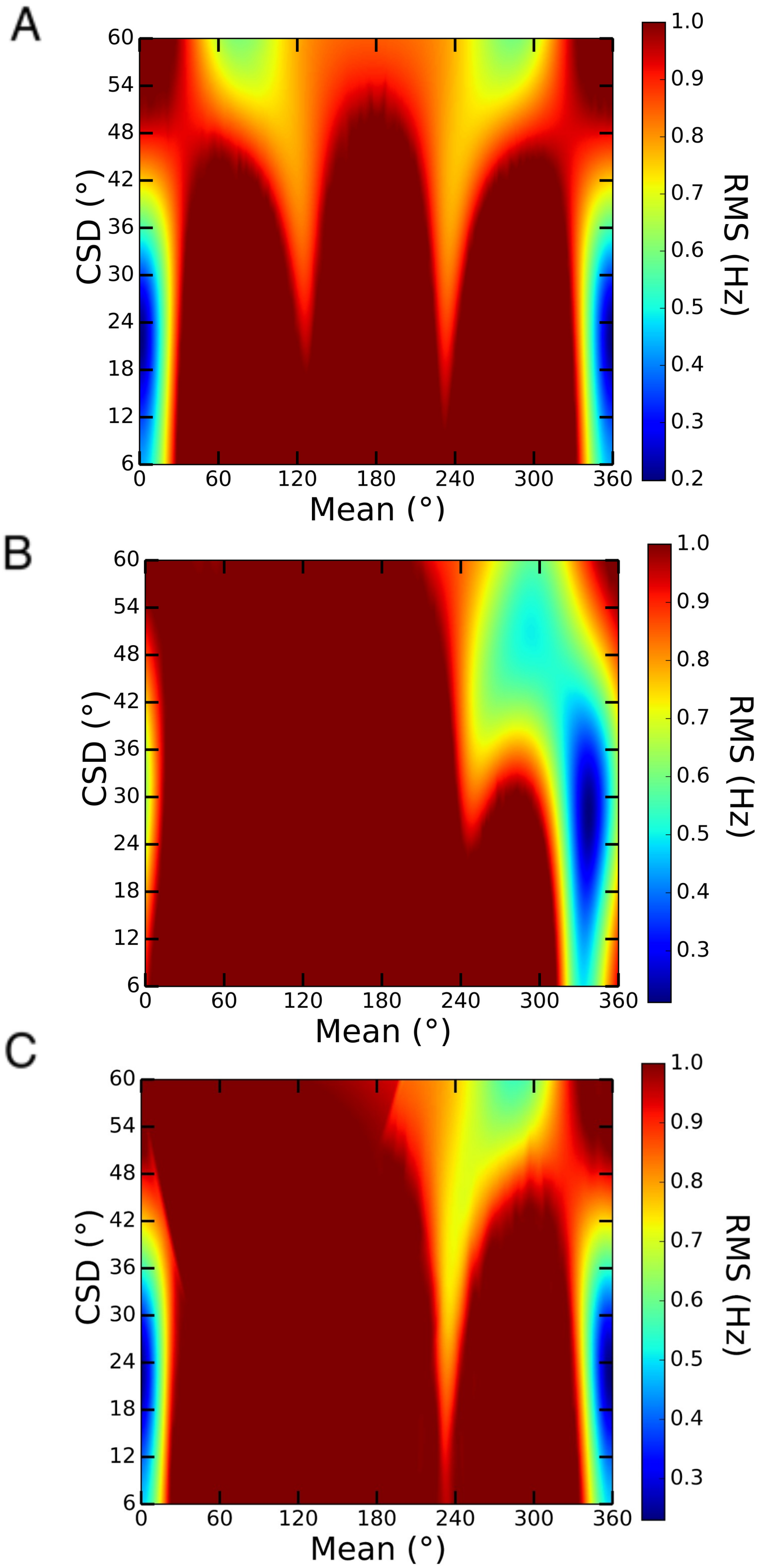


Figure S4. Parameter space for uniform models of θ in the 3-*O*-acetyl group of **1** (A) and the 2-*O*-acetyl groups of **2**α (B) and **2**β (C). Local minima are present in each parameter space, but are significantly different from the global minimum. These results indicate that the best-fitting model for each compound represents a unique solution.

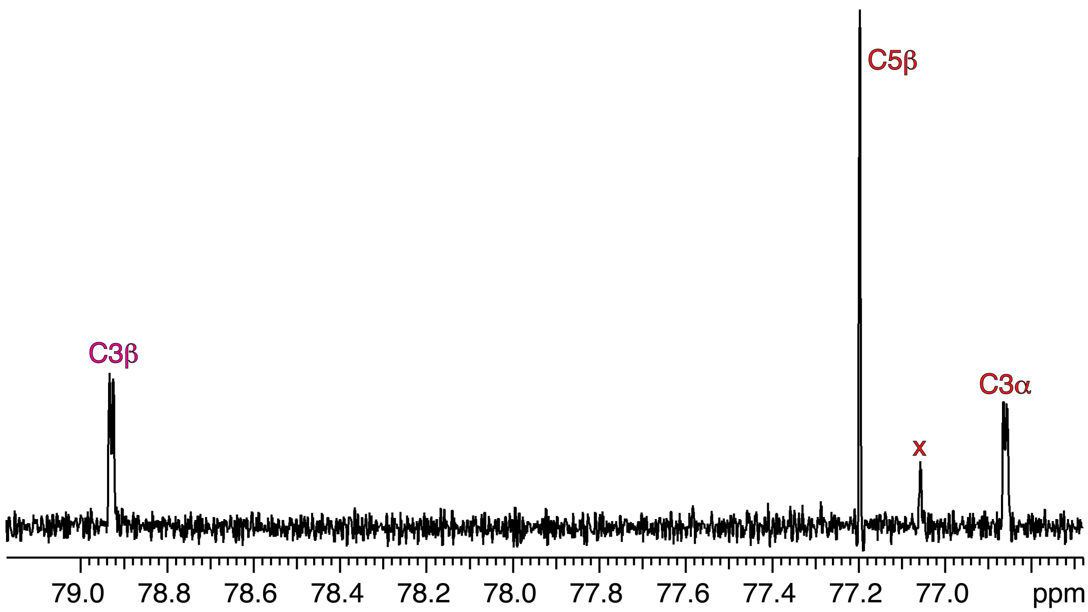


Figure S5. Partial $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) of **1**$^{2'}\alpha$ and **1**$^{2'}\beta$ showing signals aring from C3β, C5β and C3β. The C3β and C3α signals are split by the presence of ^{13}C enrichment (~99 atom-%) at C2' (CH_3), giving $^{3}J_{C2',C3}$ values of 1.3 Hz and 1.1 Hz, respectively (see Table 1 in text).

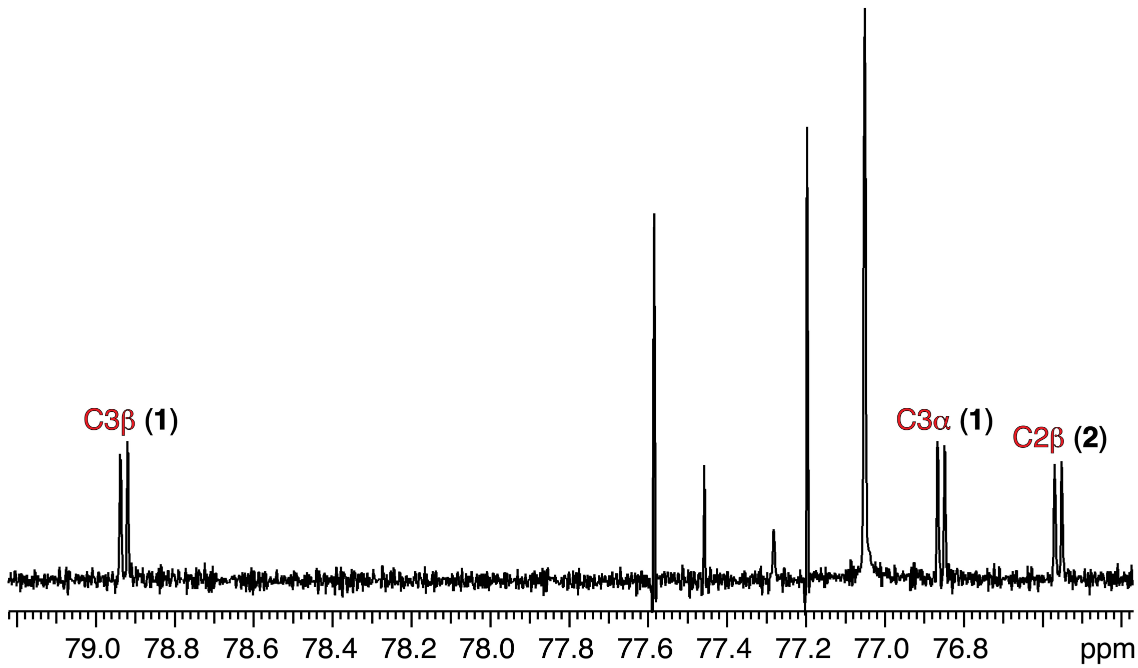


Figure S6. Partial $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) showing signals arising from C3 of $\mathbf{1}^{1'}\alpha$ and $\mathbf{1}^{1'}\beta$, and C2 of **2**β. The three signals are split by the presence of ^{13}C enrichment (~99 atom-%) at C1' (C=O), giving $^{2}J_{C1',C3}$ values of 2.8 Hz for C3α (**1**) and C3β (**1**), and 2.7 Hz for $^{2}J_{C1',C2}$ in C2β (**2**) (see Table 1 in text).

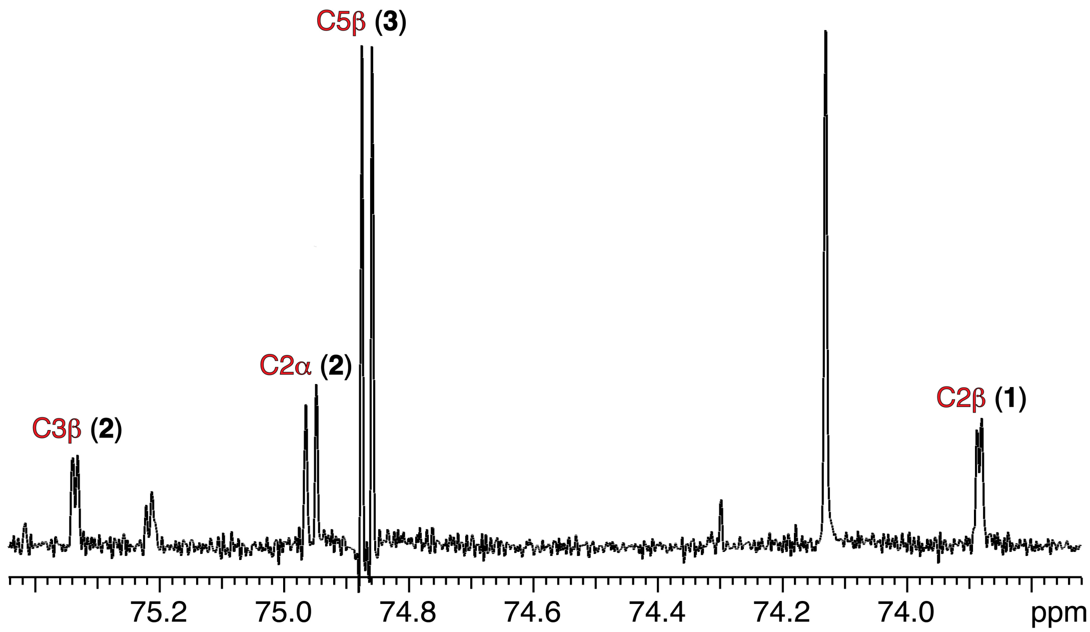


Figure S7. Partial $^{13}C\{^1H\}$ NMR spectrum (150 MHz) showing signals arising from C2 of $\mathbf{1}^{1'}\beta$, C2 of **2**α, C3 of **2**β, and C5 of **3**β. The four signals are split by the presence of ^{13}C enrichment (~99 atom-%) at C1' (C=O), giving a $^3J_{C1',C3}$ value of 1.1 Hz for C3β (**2**), a $^2J_{C1',C2}$ value of 2.6 Hz for C2α (**2**), a $^3J_{C1',C5}$ value of 2.5 Hz for C5β (**3**), and a $^2J_{C1',C2}$ value of 1.0 Hz for C2β (**1**) (see Table 1 in text).

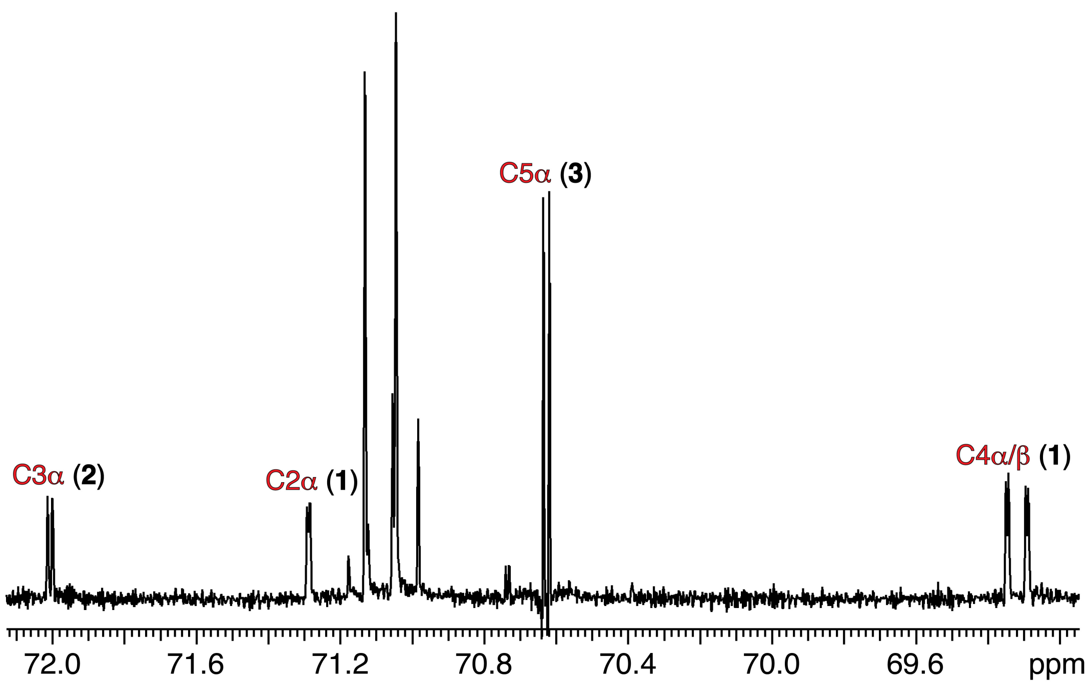


Figure S8. Partial $^{13}C\{^{1}H\}$ NMR spectrum (150 MHz) showing signals arising from C3 of **2**α, C2 of **1**$^{1'}$α, C5 of **3**α, and C4 of **1**$^{1'}$α/β. The four signals are split by the presence of ^{13}C enrichment (~99 atom-%) at C1' (C=O), giving a $^{3}J_{C1',C3}$ value of 2.0 Hz for C3α (**2**), a $^{3}J_{C1',C2}$ value of 1.0 Hz for C2α (**1**), a $^{3}J_{C1',C5}$ value of 2.5 Hz for C5α (**3**), and $^{3}J_{C1',C4}$ values of 1.0 Hz for C4α/β (**1**) (see Table 1 in text).

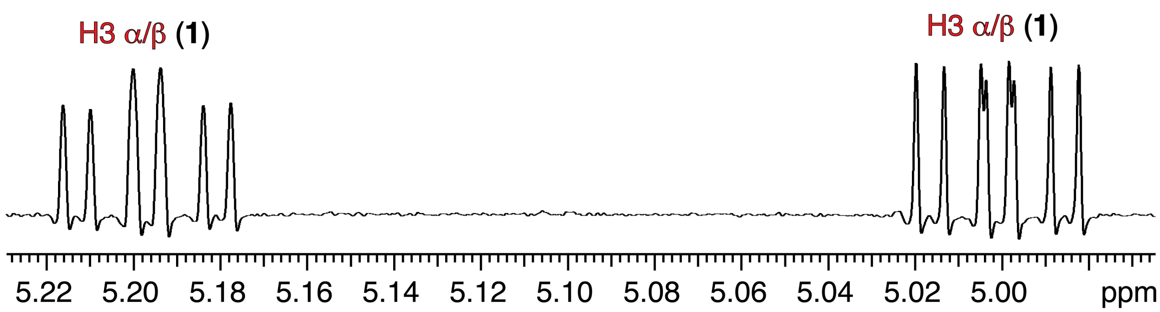


Figure S9. Partial ^{1}H NMR spectrum (600 MHz) showing signals arising from H3 of $\mathbf{1}^{1'}\alpha$ and $\mathbf{1}^{1'}\beta$. Each multiplet contains $^{3}J_{H2,H3}$, $^{3}J_{H3,H4}$ and $^{3}J_{C1',H3}$. $^{3}J_{HH}$ values of 9.0 and 9.6 Hz were extracted from the upfield multiplet, whereas the downfield gave corresponding values of ~9.8 Hz. Both multiplets yield a $^{3}J_{C1',H3}$ value of 3.9 Hz (see Table 1 in text).

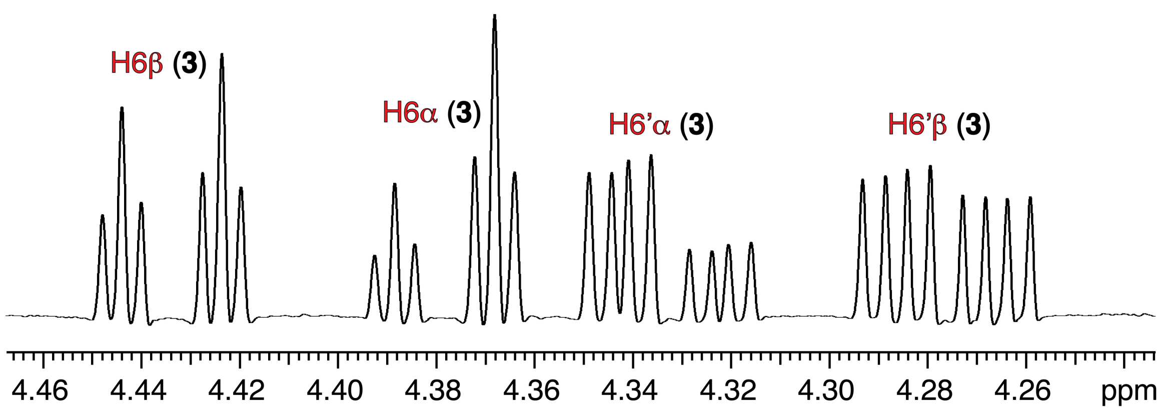


Figure S10. Partial ^{1}H NMR spectrum (600 MHz) showing signals arising from H6 and H6' of **3**α and **3**β. Each multiplet contains three *J*-values: $^{2}J_{H6,H6'}$, $^{3}J_{H5,H6(H6')}$, and $^{3}J_{C1',H6(H6')}$. The downfield signals for each anomer yield $^{3}J_{C1',H6}$ values of 2.4 Hz, and the upfield signals for each anomer yield $^{3}J_{C1',H6'}$ values of 2.8 Hz (see Table 1 in text).

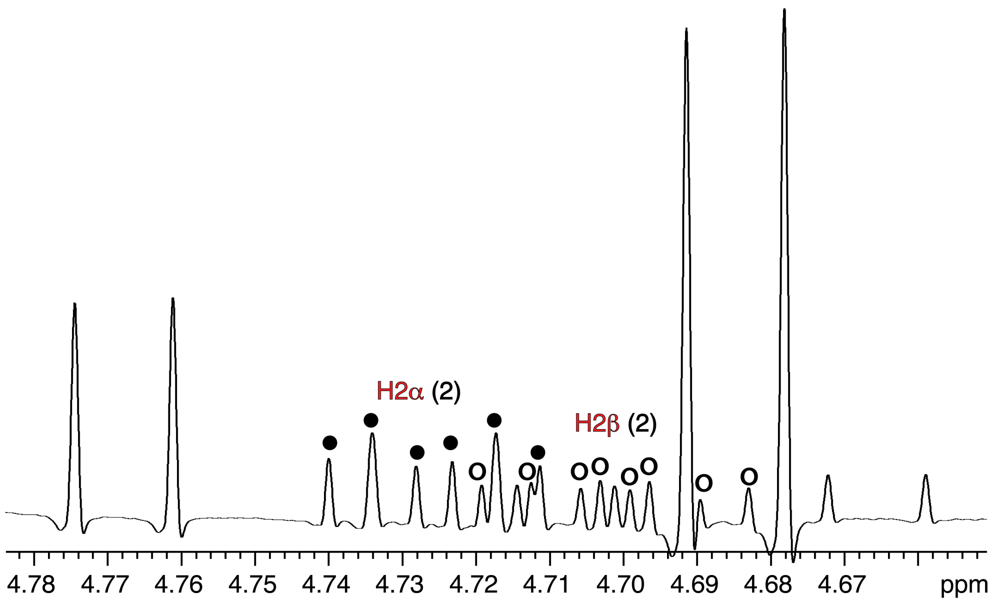


Figure S11. Partial ^{1}H NMR spectrum (600 MHz) showing signals arising from H2 of **2**α (filled circles) and **2**β (open circles). Each multiplet contains three *J*-values: $^{3}J_{H1,H2}$, $^{3}J_{H2,H3}$, and $^{3}J_{C1',H2}$. For H2α, these values are 3.6 Hz, 10.1 Hz and 3.6 Hz, respectively. For H2β, these values are 8.0 Hz, 9.6 Hz and 4.0 Hz, respectively (see Table 1 in text).

Cartesian Coordinates for B3LYP Optimized Rotamers of **5**.
Structure **5**: $\theta = 0°$

C	-1.714212	-0.687664	0.163560
C	-1.245530	1.635019	0.248945
C	0.198065	1.430712	-0.266850
C	0.681414	0.024996	0.091532
C	-0.312991	-1.046309	-0.341543
H	-1.735173	-0.709244	1.268703
H	0.193716	1.540299	-1.362194
H	0.855271	-0.039360	1.168610
H	-0.359317	-1.074183	-1.440477
H	-1.228884	1.557959	1.348411
O	-2.086383	0.606863	-0.289631
O	-2.590731	-1.630152	-0.363315
O	0.114847	-2.291992	0.185571
H	-0.538483	-2.948970	-0.108322
O	1.933651	-0.217347	-0.586786
O	1.116897	2.337069	0.331109
H	0.833112	3.240178	0.118883
C	-1.851406	2.969830	-0.160590
H	-2.884338	3.032778	0.194263
H	-1.298855	3.806698	0.279132
H	-1.849883	3.078963	-1.250719
C	-3.889845	-1.626245	0.233722
H	-4.406840	-0.679089	0.047995
H	-4.446448	-2.443423	-0.228758
H	-3.822294	-1.796914	1.316343
C	3.037146	-0.466095	0.157631
O	3.050975	-0.502971	1.371149
C	4.232395	-0.690994	-0.734496
H	5.115720	-0.881790	-0.124380
H	4.048860	-1.542509	-1.397637
H	4.399568	0.187332	-1.366084

Structure **5**: $\theta = 30°$

C	-1.613056	-0.771923	0.148631
C	-1.404035	1.584299	0.280633
C	0.062732	1.544918	-0.207345
C	0.696871	0.196447	0.149545
C	-0.171301	-0.960945	-0.337691
H	-1.651684	-0.823877	1.252214
H	0.070484	1.670474	-1.300807
H	0.846969	0.175060	1.232681
H	-0.196707	-0.933437	-1.437964
H	-1.398284	1.495354	1.379334

O	-2.122182	0.481128	-0.284222
O	-2.367904	-1.794276	-0.417469
O	0.357466	-2.191036	0.126118
H	-0.238315	-2.878583	-0.217458
O	1.988898	0.162974	-0.496583
O	0.857266	2.541098	0.425224
H	0.475968	3.407862	0.214491
C	-2.141093	2.852627	-0.125620
H	-3.178869	2.804195	0.217086
H	-1.684137	3.739105	0.326539
H	-2.138545	2.970668	-1.214768
C	-3.668975	-1.952626	0.153563
H	-4.288691	-1.067850	-0.025412
H	-4.118831	-2.819103	-0.334609
H	-3.601026	-2.136373	1.234028
C	3.010552	-0.475360	0.124158
O	2.934295	-0.982050	1.223684
C	4.263354	-0.393525	-0.713742
H	5.062532	-0.961126	-0.236042
H	4.078639	-0.782120	-1.719869
H	4.567478	0.653589	-0.816245

Structure **5**: $\theta = 60°$

C	1.599044	-0.773891	-0.148149
C	1.464853	1.573635	-0.272261
C	-0.028042	1.560582	0.116046
C	-0.704277	0.237923	-0.304504
C	0.112767	-0.951958	0.208106
H	1.725249	-0.818292	-1.245497
H	-0.103353	1.664337	1.209025
H	-0.788972	0.304329	-1.394825
H	0.044718	-0.947047	1.307458
H	1.536726	1.488872	-1.369096
O	2.112177	0.453069	0.337636
O	2.275424	-1.825605	0.465481
O	-0.334094	-2.186326	-0.322522
H	0.253892	-2.854228	0.071386
O	-2.026176	0.352618	0.278923
O	-0.747554	2.595529	-0.544493
H	-0.344981	3.443371	-0.299403
C	2.199499	2.823988	0.191167
H	3.259720	2.746089	-0.066966
H	1.805707	3.720959	-0.298022
H	2.113160	2.945862	1.276507
C	3.613569	-2.017380	0.000093
H	4.239684	-1.149897	0.232908
H	3.999225	-2.896940	0.518764

H	3.628013	-2.196061	-1.083211
C	-3.021598	-0.521884	-0.004017
O	-2.957239	-1.405665	-0.829607
C	-4.270868	-0.136577	0.755513
H	-5.028176	-0.911784	0.632279
H	-4.057279	0.015594	1.817287
H	-4.653318	0.809259	0.356104

Structure **5**: $\theta = 90°$

C	-1.591823	-0.743329	0.147599
C	-1.462886	1.590928	0.156331
C	0.071671	1.579708	0.025382
C	0.705746	0.265488	0.519849
C	-0.073278	-0.988618	0.095808
H	-1.905716	-0.678630	1.205361
H	0.315537	1.681736	-1.042958
H	0.750721	0.284413	1.614544
H	0.186455	-1.255390	-0.937182
H	-1.727848	1.539167	1.224998
O	-1.978785	0.441974	-0.521750
O	-2.184779	-1.842000	-0.470045
O	0.206473	-2.044319	1.005051
H	-0.308673	-2.806688	0.691013
O	2.075847	0.389116	0.034944
O	0.677063	2.619248	0.787146
H	0.297072	3.463731	0.498002
C	-2.109618	2.818378	-0.470462
H	-3.198263	2.742035	-0.394615
H	-1.806375	3.735632	0.045190
H	-1.838316	2.902286	-1.528545
C	-3.588166	-1.965555	-0.226053
H	-4.137575	-1.114834	-0.642212
H	-3.909164	-2.884952	-0.719199
H	-3.792033	-2.037949	0.850541
C	2.955869	-0.602533	-0.226604
O	2.751332	-1.791128	-0.116588
C	4.255904	0.005357	-0.709575
H	4.976463	-0.788262	-0.910602
H	4.081647	0.585453	-1.621521
H	4.658332	0.690186	0.043477

Structure **5**: $\theta = 120°$

C	-1.596859	-0.714251	0.213165
C	-1.407568	1.629512	0.100860
C	0.131460	1.564742	-0.022635

C	0.680650	0.259442	0.566125
C	-0.089050	-0.973819	0.084612
H	-1.868922	-0.604172	1.279111
H	0.393486	1.596092	-1.091666
H	0.582486	0.265975	1.658072
H	0.123628	-1.182714	-0.967984
H	-1.661984	1.662398	1.173058
O	-1.977639	0.457963	-0.489775
O	-2.238169	-1.816139	-0.344776
O	0.265731	-2.064967	0.921570
H	-0.236108	-2.829623	0.593031
O	2.117824	0.285704	0.340704
O	0.757422	2.627252	0.687344
H	0.422922	3.464528	0.329386
C	-2.016988	2.831922	-0.606685
H	-3.106800	2.800686	-0.516585
H	-1.675530	3.772010	-0.161034
H	-1.754621	2.829680	-1.670285
C	-3.631958	-1.902714	-0.038818
H	-4.181138	-1.051508	-0.454486
H	-3.992615	-2.827475	-0.493024
H	-3.791523	-1.942633	1.046915
C	2.872214	-0.629072	-0.307767
O	2.472531	-1.627197	-0.868810
C	4.317324	-0.178977	-0.292539
H	4.941505	-0.941438	-0.759980
H	4.413116	0.762087	-0.844356
H	4.655149	0.004461	0.731872

Structure **5**: $\theta = 150°$

C	1.628505	-0.681566	-0.244759
C	1.294529	1.663214	-0.117609
C	-0.242099	1.503839	-0.005941
C	-0.668660	0.176609	-0.635442
C	0.138278	-1.000967	-0.082064
H	1.888108	-0.569947	-1.313819
H	-0.519450	1.500144	1.059264
H	-0.470439	0.189257	-1.713119
H	-0.050290	-1.138687	0.984875
H	1.543135	1.736656	-1.189211
O	1.945269	0.519792	0.446782
O	2.333357	-1.736880	0.323964
O	-0.219579	-2.157493	-0.824677
H	0.304419	-2.887666	-0.455129
O	-2.111614	0.034659	-0.594054
O	-0.926768	2.534104	-0.707917
H	-0.667274	3.384947	-0.320726

C	1.827113	2.885216	0.617443
H	2.916577	2.926228	0.527044
H	1.424735	3.810864	0.193245
H	1.566616	2.841532	1.680652
C	3.727927	-1.750792	0.010148
H	4.232183	-0.865804	0.412069
H	4.141510	-2.648809	0.472832
H	3.883237	-1.795083	-1.076050
C	-2.786889	-0.585923	0.396664
O	-2.293642	-1.059237	1.400868
C	-4.269877	-0.542811	0.107909
H	-4.807420	-1.107769	0.870203
H	-4.611840	0.497598	0.113417
H	-4.482960	-0.953935	-0.883360

Structure **5**: $\theta = 180°$

C	1.692892	-0.617896	-0.213838
C	1.129091	1.684992	-0.198875
C	-0.385701	1.387452	-0.091087
C	-0.666028	0.012731	-0.708083
C	0.232541	-1.075250	-0.120479
H	1.993106	-0.522136	-1.273822
H	-0.663895	1.384968	0.969128
H	-0.462761	0.079581	-1.782101
H	0.002058	-1.221188	0.940748
H	1.395116	1.723586	-1.268192
O	1.863652	0.632747	0.439012
O	2.462689	-1.581411	0.429015
O	0.026673	-2.268832	-0.862140
H	0.610488	-2.935820	-0.463603
O	-2.070696	-0.346274	-0.691482
O	-1.168068	2.324875	-0.823851
H	-1.006722	3.205507	-0.450206
C	1.534824	2.987381	0.476330
H	2.617992	3.122383	0.402964
H	1.059753	3.847662	-0.006739
H	1.255006	2.978134	1.535507
C	3.867602	-1.469136	0.189436
H	4.262246	-0.529421	0.589573
H	4.338076	-2.310791	0.701101
H	4.086347	-1.526440	-0.885213
C	-2.730066	-0.530864	0.472051
O	-2.231959	-0.417350	1.575690
C	-4.170610	-0.895104	0.205944
H	-4.691294	-1.045352	1.152136
H	-4.659079	-0.098255	-0.364065
H	-4.222029	-1.808294	-0.395555

Structure **5**: θ = 210°

C	1.780208	-0.578762	-0.170132
C	1.052189	1.671971	-0.291916
C	-0.431380	1.280804	-0.090057
C	-0.633528	-0.134871	-0.650665
C	0.352971	-1.126450	-0.042201
H	2.065938	-0.537681	-1.237512
H	-0.651929	1.312350	0.979605
H	-0.472851	-0.041562	-1.730422
H	0.136031	-1.237607	1.030635
H	1.280245	1.647324	-1.370517
O	1.877571	0.720462	0.393523
O	2.612116	-1.448608	0.527006
O	0.234999	-2.366389	-0.721169
H	0.878310	-2.962496	-0.301860
O	-1.980948	-0.669543	-0.589053
O	-1.314733	2.124670	-0.821674
H	-1.209763	3.029889	-0.488991
C	1.390458	3.045686	0.268780
H	2.459101	3.244592	0.144899
H	0.842662	3.832441	-0.260104
H	1.146921	3.100545	1.335576
C	4.006349	-1.263790	0.269874
H	4.344992	-0.282329	0.617556
H	4.529990	-2.047534	0.820354
H	4.222182	-1.363573	-0.802216
C	-2.842429	-0.437271	0.423813
O	-2.595523	0.195955	1.430721
C	-4.148992	-1.148512	0.156676
H	-4.869616	-0.894178	0.934674
H	-4.545224	-0.874759	-0.825631
H	-3.979915	-2.230629	0.154097

Structure **5**: θ = 240°

C	-1.840063	-0.536862	0.146541
C	-1.019426	1.666717	0.251586
C	0.461267	1.233541	0.093820
C	0.622901	-0.216423	0.575869
C	-0.444174	-1.147355	0.001867
H	-2.111312	-0.461064	1.215539
H	0.746434	1.327843	-0.958409
H	0.548391	-0.168464	1.668553
H	-0.255640	-1.271227	-1.075447
H	-1.264010	1.652503	1.326481
O	-1.875957	0.753110	-0.441639
O	-2.720247	-1.380358	-0.523954

O	-0.374825	-2.390852	0.681767
H	-1.066724	-2.947968	0.286685
O	1.899160	-0.874696	0.338328
O	1.295369	2.023476	0.935235
H	1.215674	2.948795	0.655681
C	-1.293191	3.053111	-0.315642
H	-2.354916	3.293930	-0.208105
H	-0.723892	3.821234	0.217791
H	-1.031591	3.094695	-1.378711
C	-4.100890	-1.128498	-0.250976
H	-4.399305	-0.137516	-0.608489
H	-4.667303	-1.895114	-0.782888
H	-4.305931	-1.203328	0.825208
C	2.969416	-0.392070	-0.330471
O	3.041291	0.672923	-0.906190
C	4.069546	-1.431757	-0.320882
H	4.959488	-1.024667	-0.802320
H	4.305004	-1.738301	0.702687
H	3.734992	-2.322594	-0.862905

Structure **5**: $\theta = 270°$

C	-1.859289	-0.499763	0.162719
C	-1.012013	1.682958	0.109012
C	0.479726	1.238768	0.095765
C	0.644124	-0.234761	0.519986
C	-0.485379	-1.149959	0.032628
H	-2.113644	-0.322710	1.223799
H	0.884957	1.373894	-0.915742
H	0.679422	-0.261493	1.614856
H	-0.330700	-1.336498	-1.040460
H	-1.307980	1.768811	1.167026
O	-1.859339	0.732642	-0.537623
O	-2.772903	-1.372074	-0.421324
O	-0.424747	-2.356826	0.777913
H	-1.151089	-2.910729	0.444707
O	1.830263	-0.936806	0.040221
O	1.180977	2.026857	1.053785
H	1.088201	2.959080	0.802252
C	-1.229302	3.017360	-0.593878
H	-2.285614	3.296768	-0.539891
H	-0.650497	3.820125	-0.125458
H	-0.939311	2.947322	-1.647803
C	-4.141488	-1.058456	-0.151953
H	-4.415259	-0.088338	-0.579626
H	-4.737728	-1.845023	-0.618030
H	-4.333496	-1.046276	0.929129
C	3.048606	-0.416972	-0.227142

O	3.369783	0.746835	-0.130144
C	3.965888	-1.524651	-0.700750
H	4.955338	-1.114564	-0.906340
H	4.039433	-2.309115	0.058974
H	3.560461	-1.983409	-1.608341

Structure **5**: $\theta = 300°$

C	1.844164	-0.553021	-0.200974
C	1.070282	1.669106	-0.159817
C	-0.384675	1.253106	0.188945
C	-0.660941	-0.177910	-0.301095
C	0.469123	-1.119550	0.150671
H	1.959738	-0.478602	-1.298006
H	-0.486591	1.250868	1.285876
H	-0.701485	-0.281273	-1.391232
H	0.430018	-1.221650	1.245303
H	1.158959	1.685553	-1.258461
O	2.003081	0.730209	0.379734
O	2.789617	-1.423922	0.332492
O	0.272931	-2.371310	-0.488857
H	0.999051	-2.941873	-0.184920
O	-1.833817	-0.807768	0.275623
O	-1.299597	2.160906	-0.405429
H	-1.087376	3.045687	-0.068041
C	1.450105	3.034251	0.400969
H	2.501263	3.239160	0.178167
H	0.857082	3.835053	-0.051813
H	1.313844	3.061089	1.487849
C	4.121010	-1.208647	-0.141894
H	4.490108	-0.221219	0.154125
H	4.741705	-1.982704	0.313065
H	4.165372	-1.300347	-1.235257
C	-3.098547	-0.417283	-0.013846
O	-3.401831	0.409153	-0.845182
C	-4.081629	-1.275265	0.750744
H	-5.089404	-0.877112	0.626486
H	-4.045246	-2.296366	0.355195
H	-3.823455	-1.323136	1.812384

Structure **5**: $\theta = 330°$

C	-1.802199	-0.595093	0.189772
C	-1.093272	1.664336	0.208302
C	0.324710	1.290607	-0.287803
C	0.663404	-0.140099	0.141155
C	-0.438927	-1.110128	-0.282703

H	-1.838898	-0.582254	1.294661
H	0.320417	1.325336	-1.388610
H	0.792022	-0.225125	1.223968
H	-0.472181	-1.165921	-1.381000
H	-1.093651	1.625534	1.309965
O	-2.036071	0.715586	-0.304433
O	-2.763742	-1.459635	-0.323002
O	-0.156036	-2.378089	0.287366
H	-0.872807	-2.968194	-0.000582
O	1.872398	-0.597362	-0.504746
O	1.318792	2.157534	0.239436
H	1.098654	3.061706	-0.035669
C	-1.550142	3.040879	-0.253452
H	-2.577281	3.218909	0.078228
H	-0.923607	3.830499	0.173901
H	-1.519065	3.115076	-1.346120
C	-4.063829	-1.301474	0.250434
H	-4.476869	-0.313112	0.023923
H	-4.695231	-2.072726	-0.194509
H	-4.029828	-1.440285	1.339187
C	3.055120	-0.446367	0.139921
O	3.172412	-0.002700	1.262644
C	4.182518	-0.986888	-0.705858
H	5.135786	-0.799107	-0.210770
H	4.048681	-2.064795	-0.846510
H	4.177541	-0.522851	-1.696796

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Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian*09, Revision E.01**,** Gaussian, Inc., Wallingford CT, 2009.

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Case, D. A.; Babin, V.; Berryman, J. T.; Betz, R. M.; Cai, Q.; Cerutti, D. S.; Cheatham, T. E. I.; Darden, T. A.; Duke, R. E.; Gohlke, H.; Goetz, A. W.; Gusarov, S.; Homeyer, N.; Janowski, P.; Kaus, J.; Kolossváry, I.; Kovalenko, A.; Lee, T. S.; LeGrand, S.; Luchko, T.; Luo, R.; Madej, B.; Merz, K. M.; Paesani, F.; Roe, D. R.; Roitberg, A.; Sagui, C.; Salomon-Ferrer, R.; Seabra, G.; Simmerling, C. L.; Smith, W.; Swails, J.; Walker, R. C.; Wang, J.; Wolf, R. M.; Wu, X.; Kollman, P. A. **2014**, AMBER 14, University of California, San Francisco.