Supporting Information

Gem-dimethyl Peptide Nucleic Acid (α/β/γ–*gdm*-PNA) Monomers: Synthesis and the Role of *gdm*-Substituents in Preferential Stabilisation of Z/E-Rotamers

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Figure S1. ^{1}H NMR (200 MHz, $CDCl_3$) of Compound 2

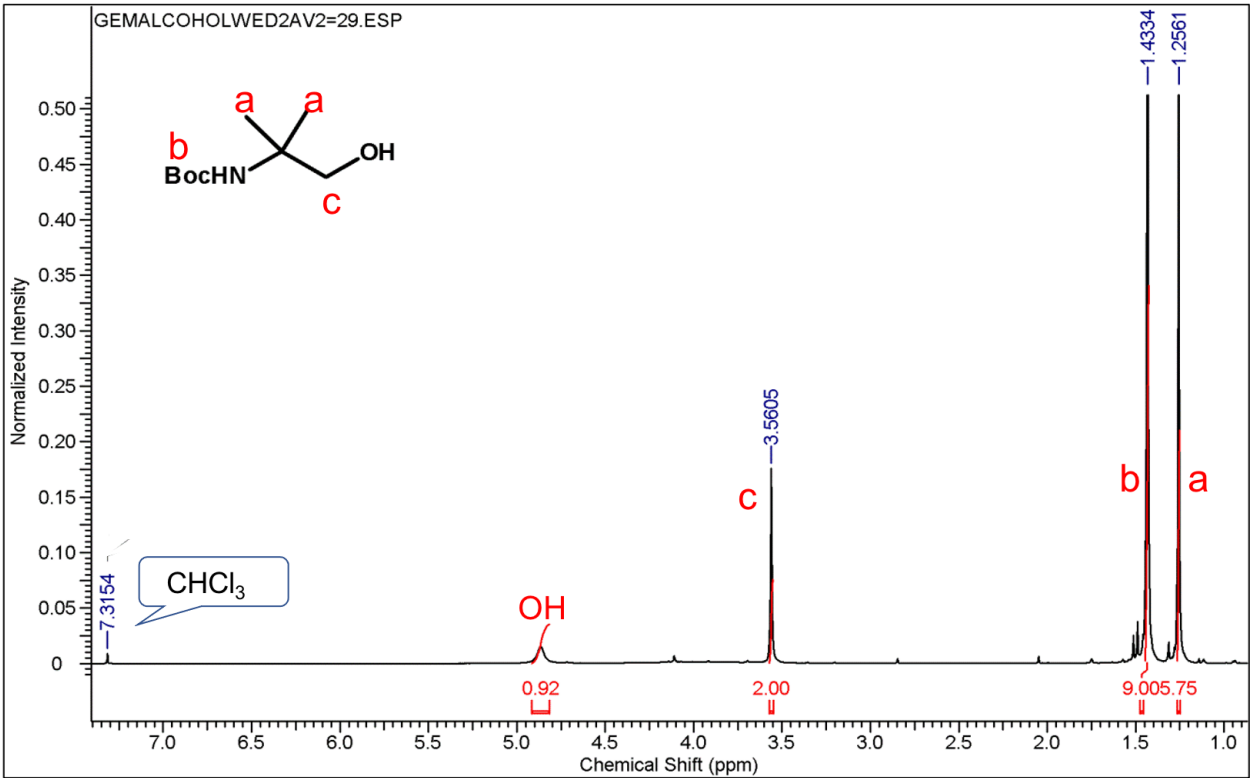
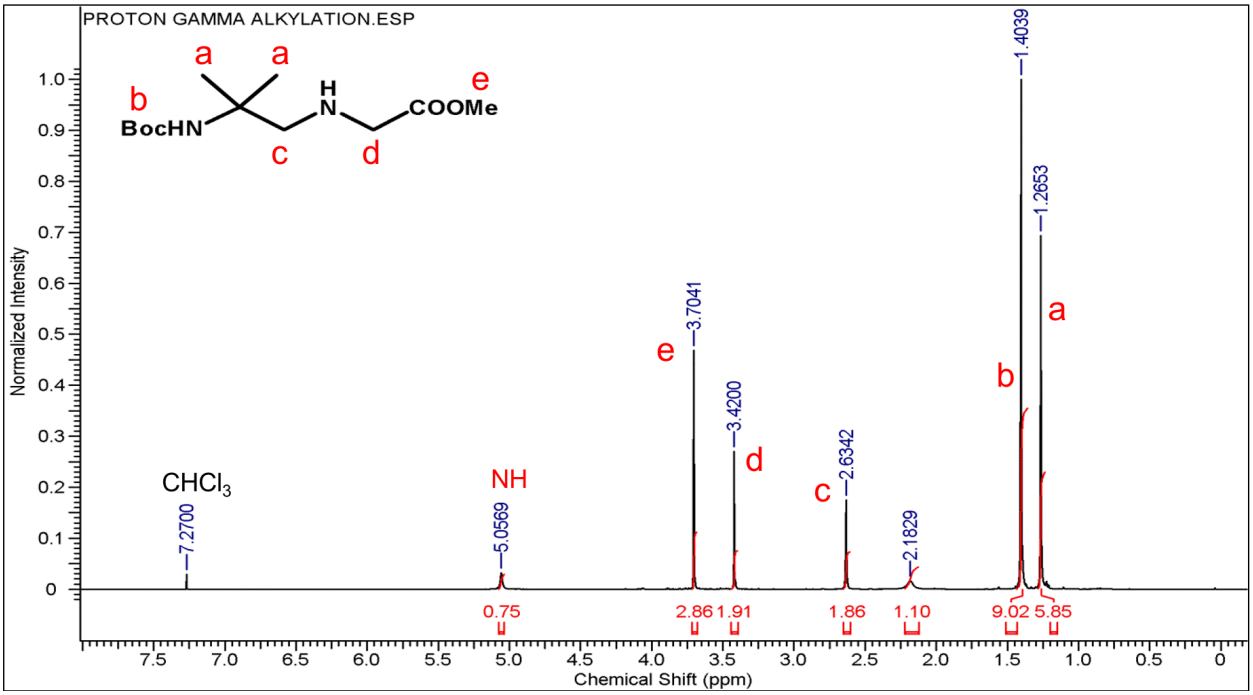


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound 4



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of compound 4:

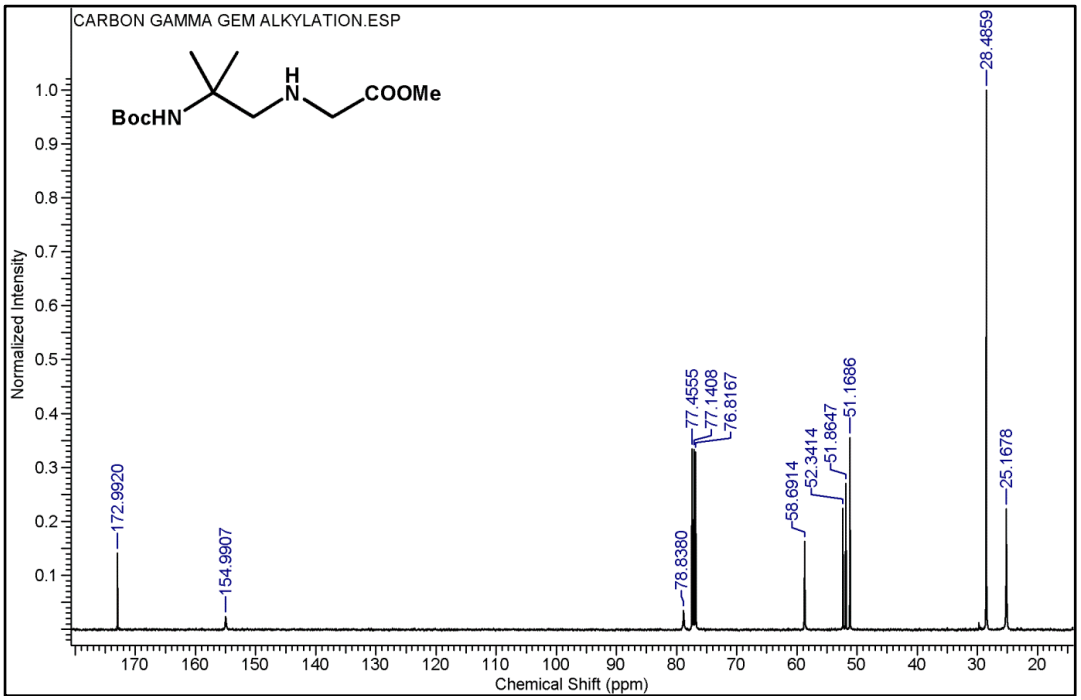
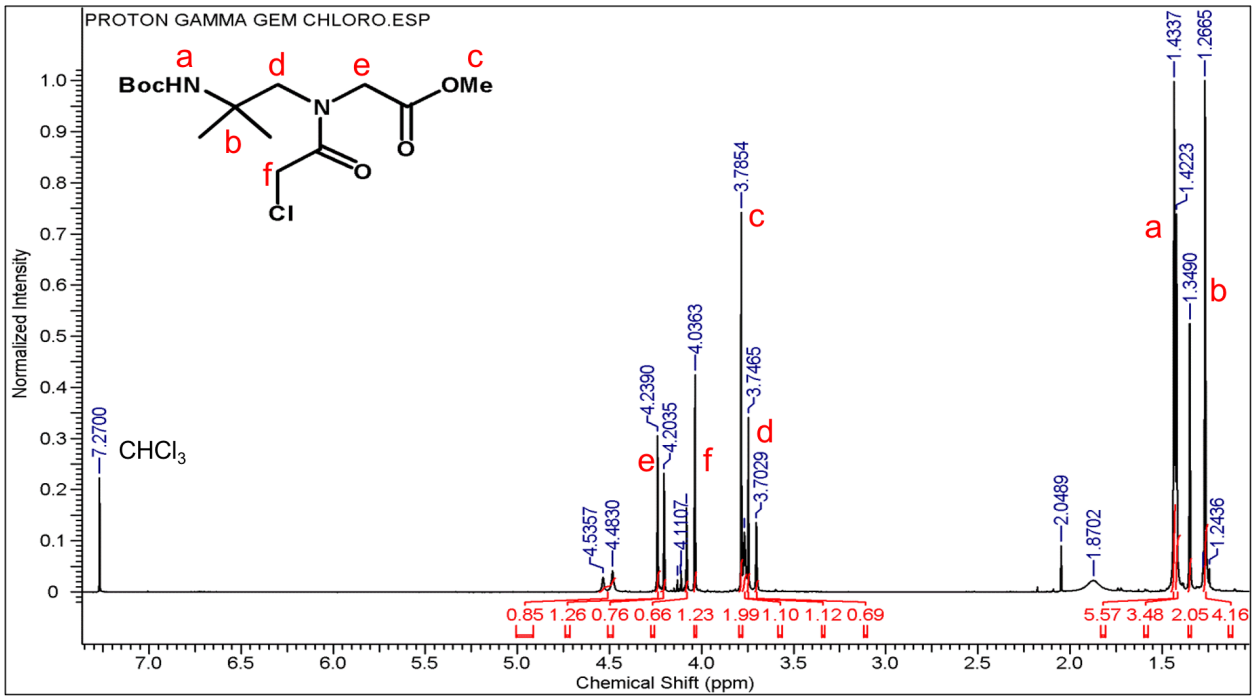


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound 5



^{13}C{^{1}H} NMR (100 MHz) of Compound 5:

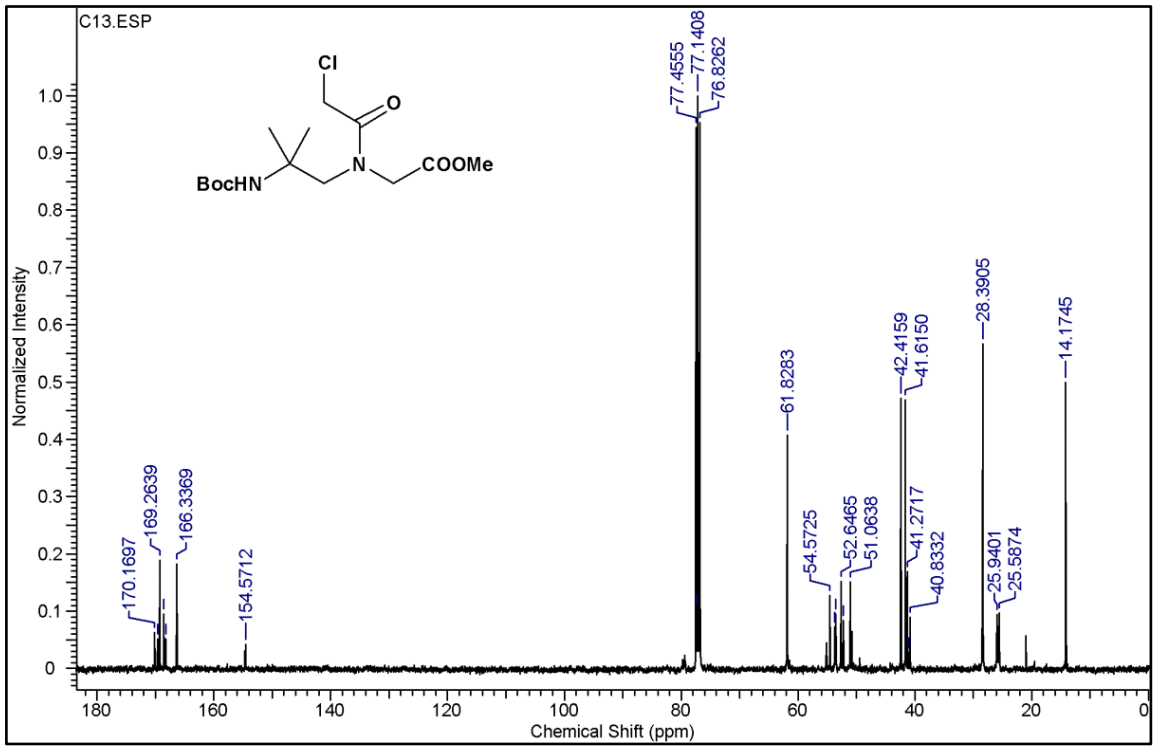
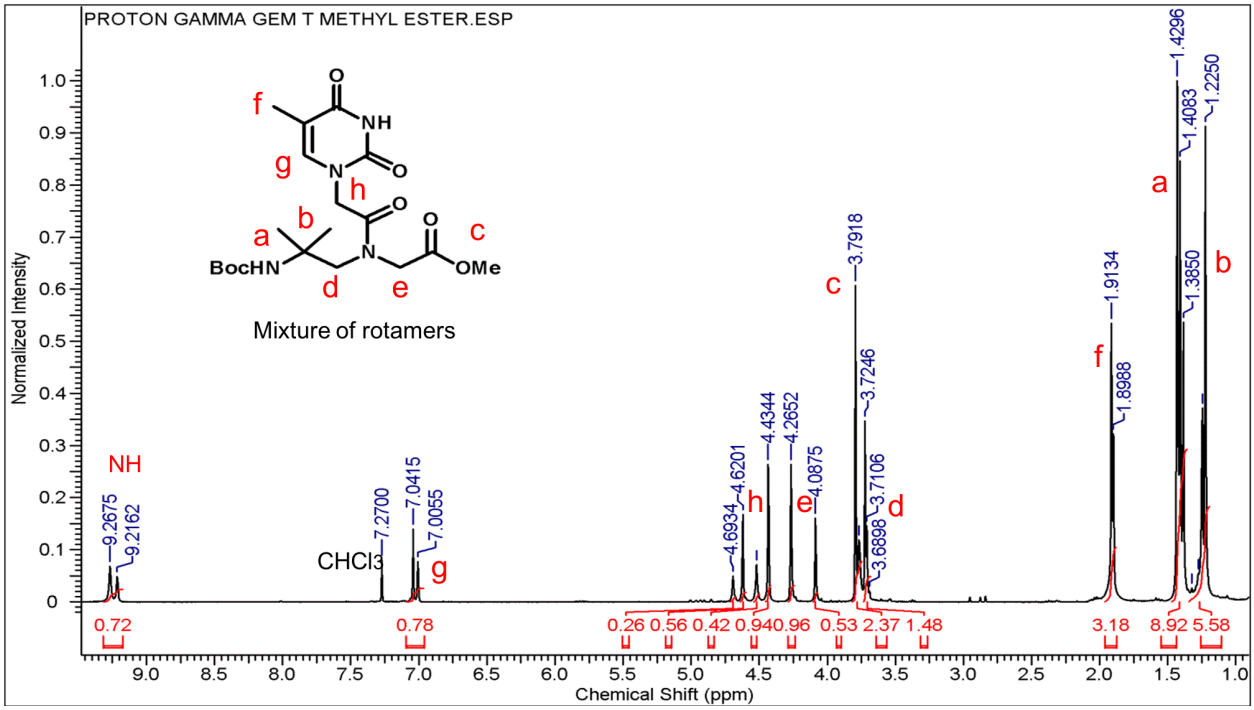


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound 6



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of Compound 6

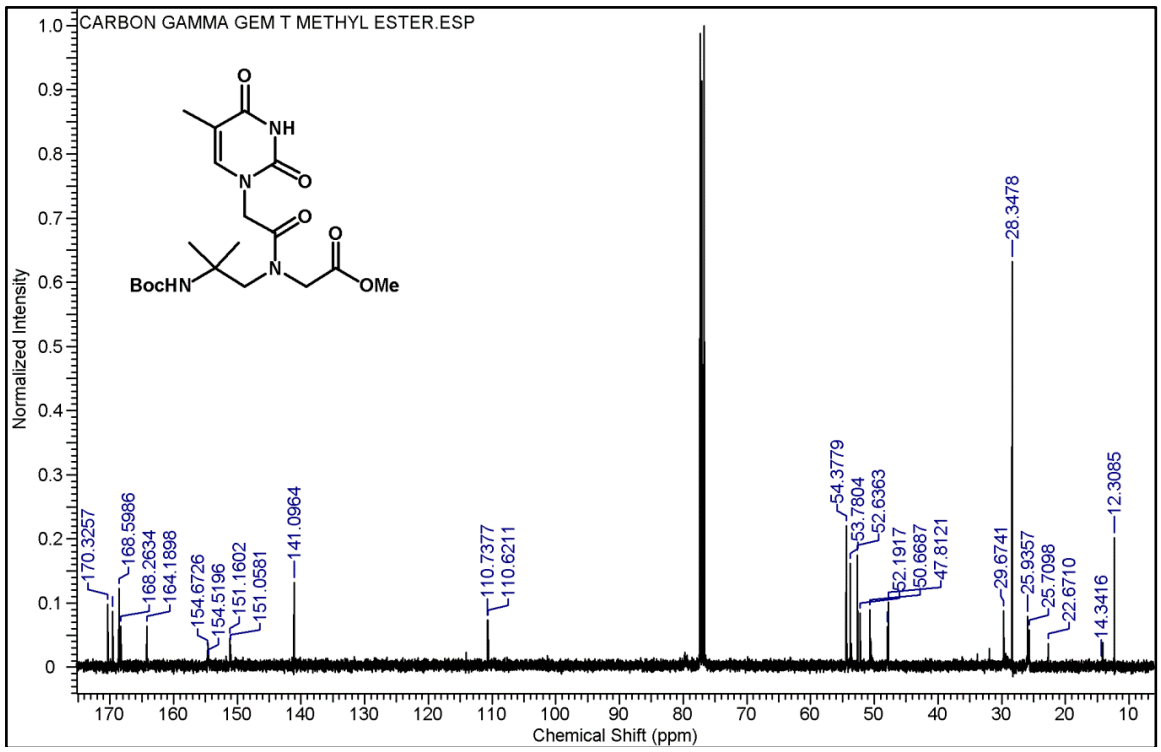
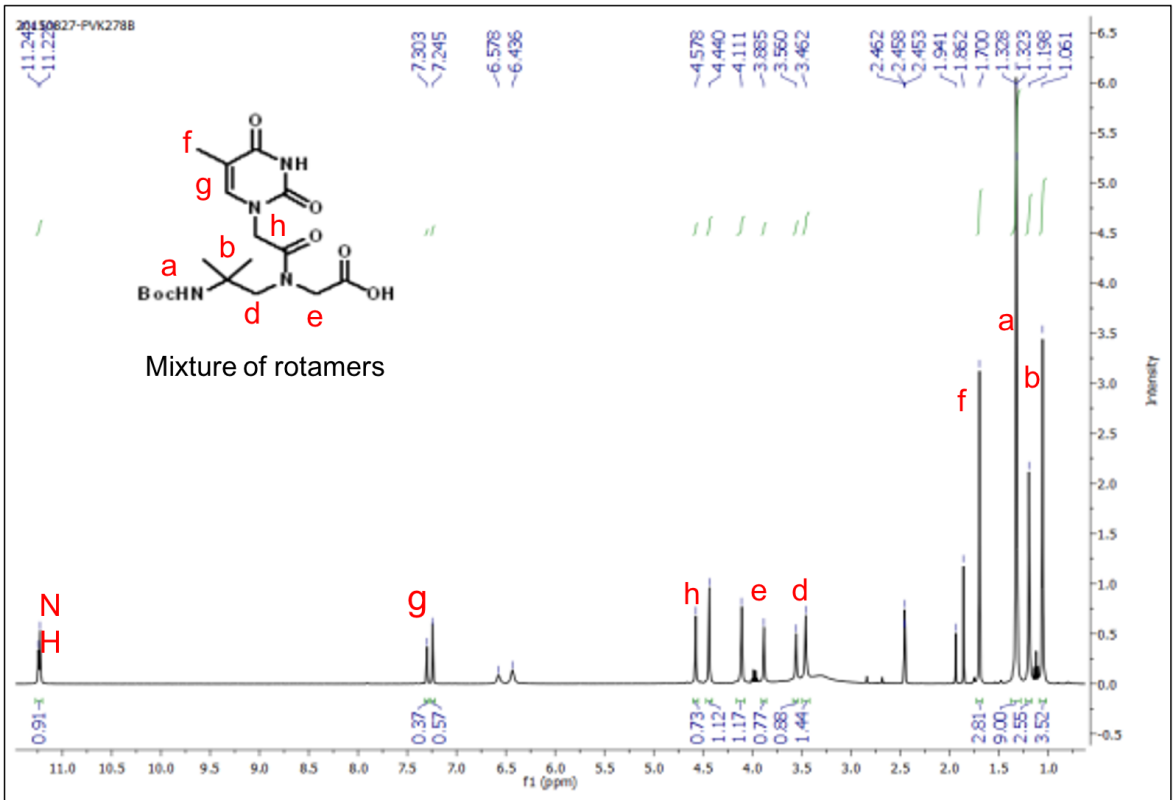


Figure S5. ^{1}H NMR (400 MHz, DMSO-d$_6$) of Compound 7



^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$) of Compound 7:

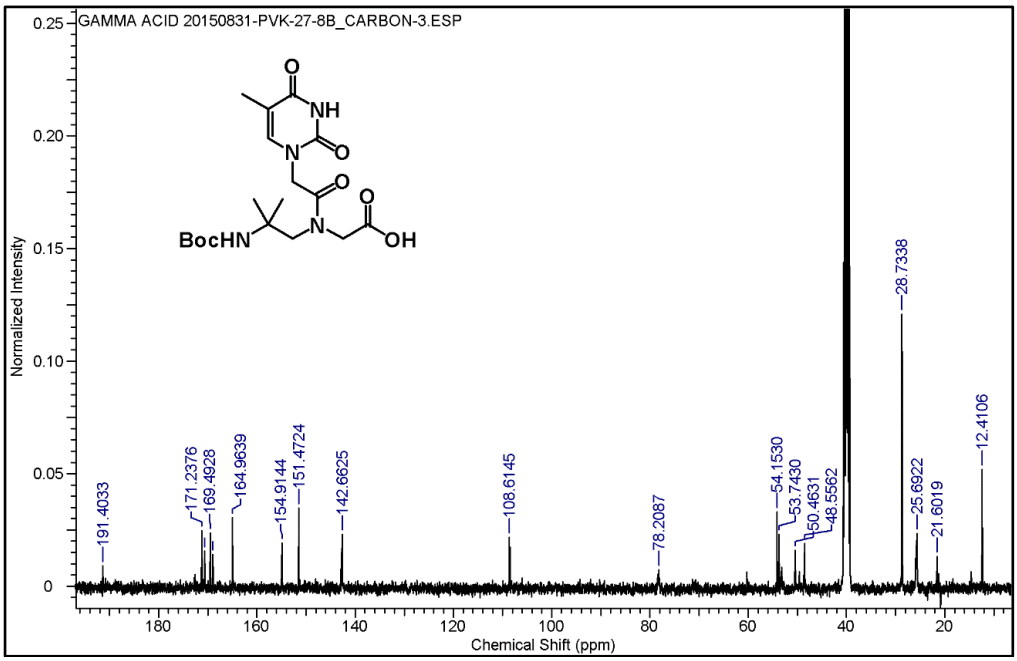
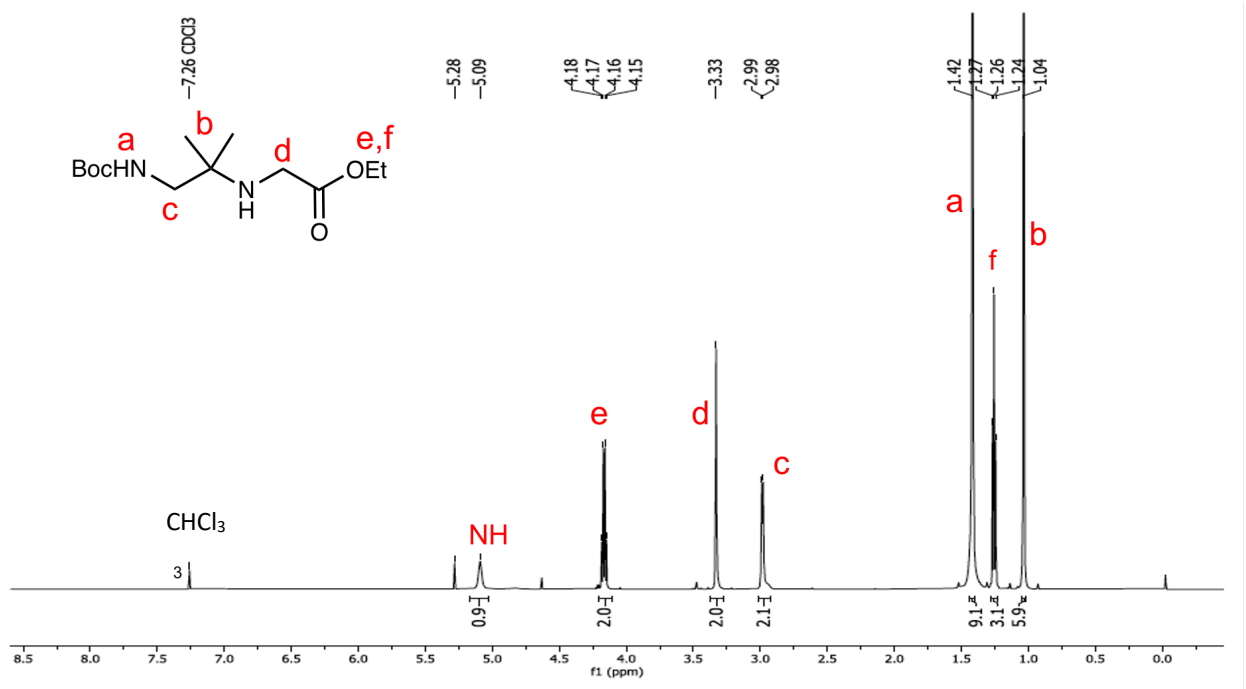


Figure S6. ^{1}H NMR (600 MHz, $CDCl_3$) of Compound 10:



$^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of Compound 10

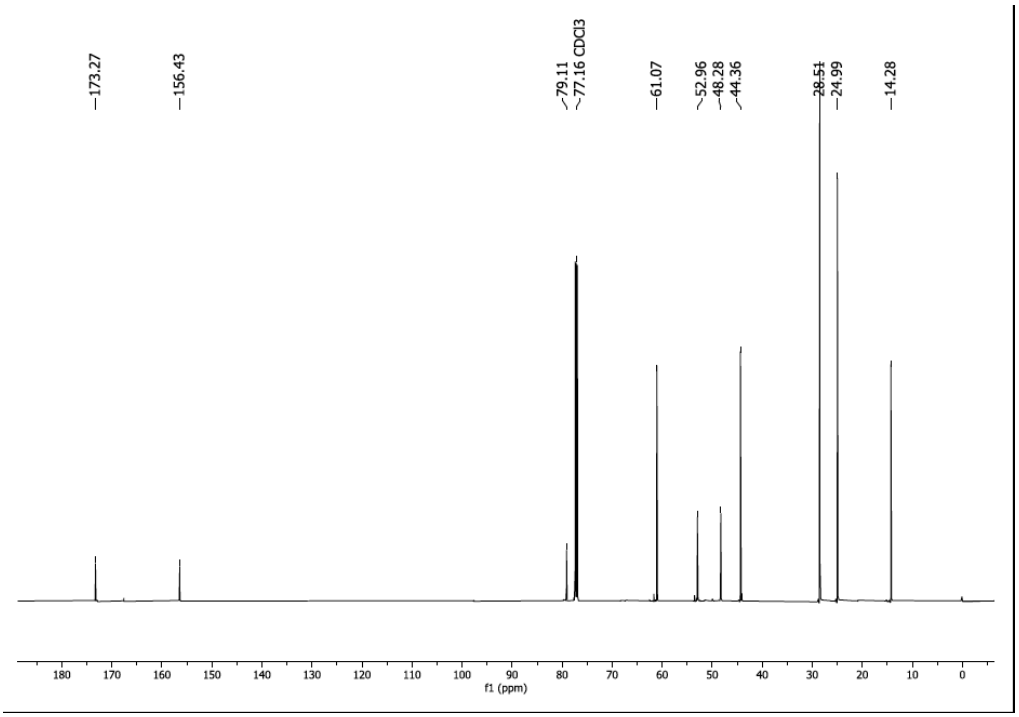
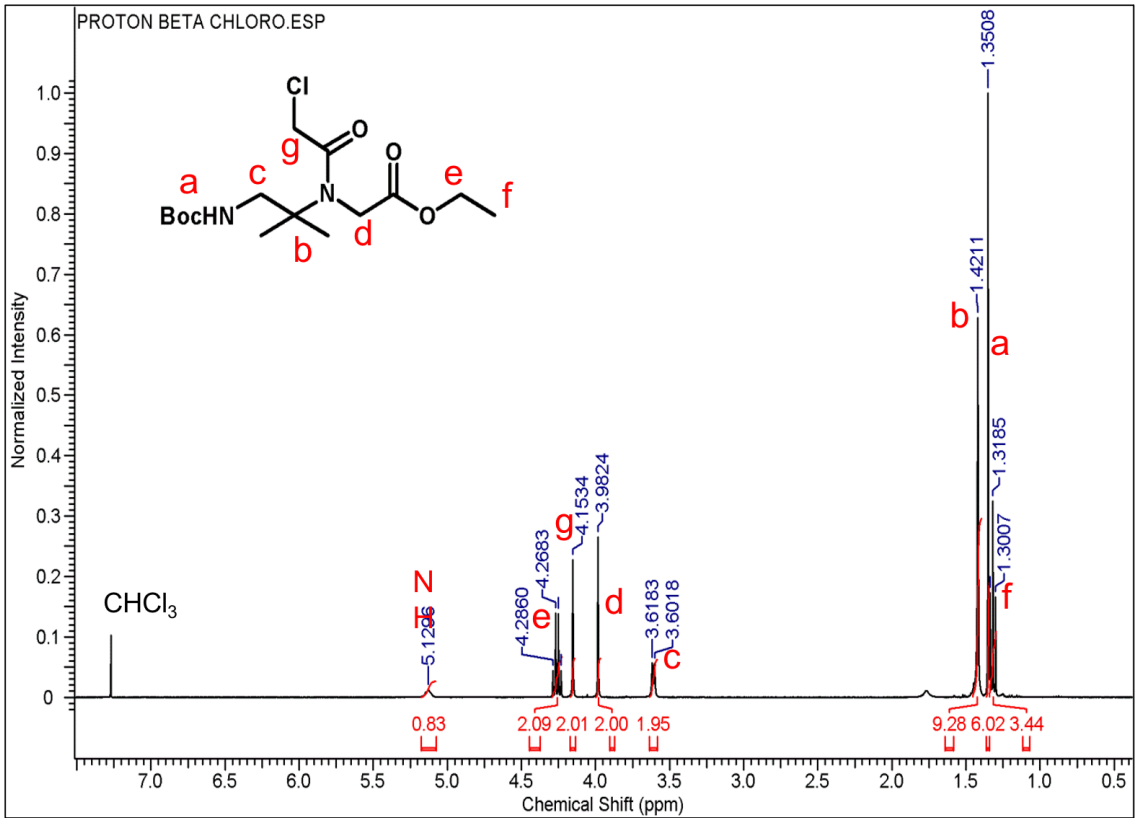


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound 11



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of Compound 11:

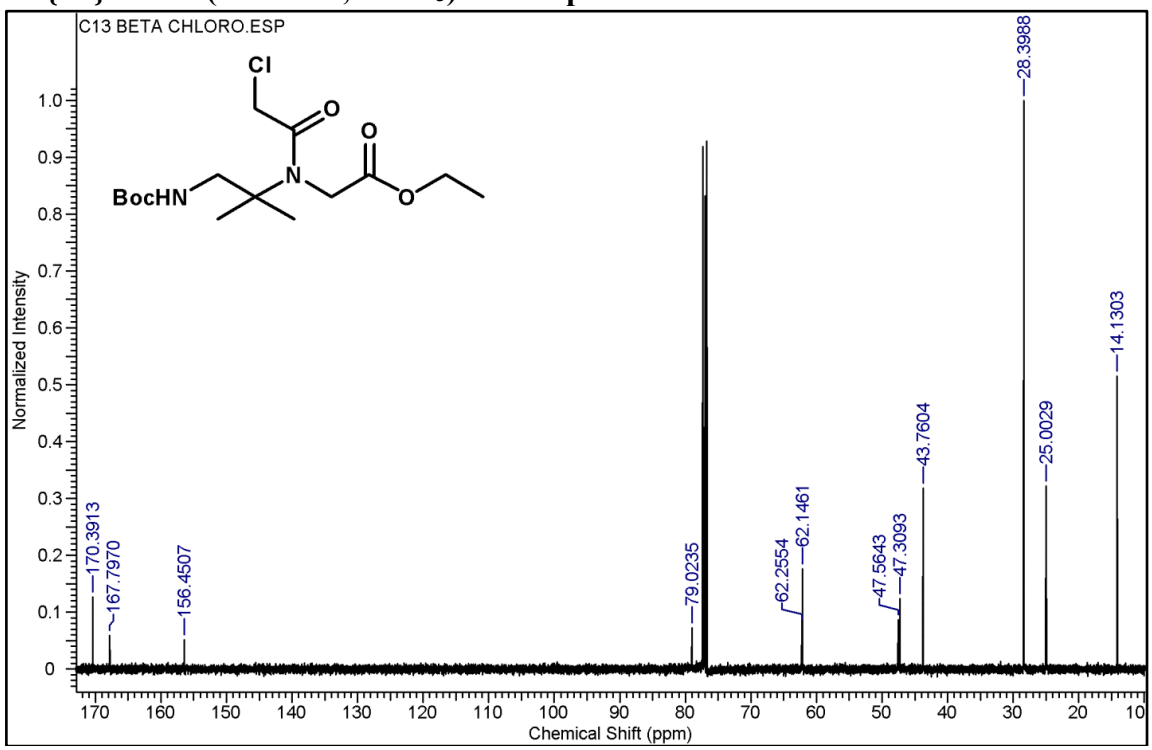
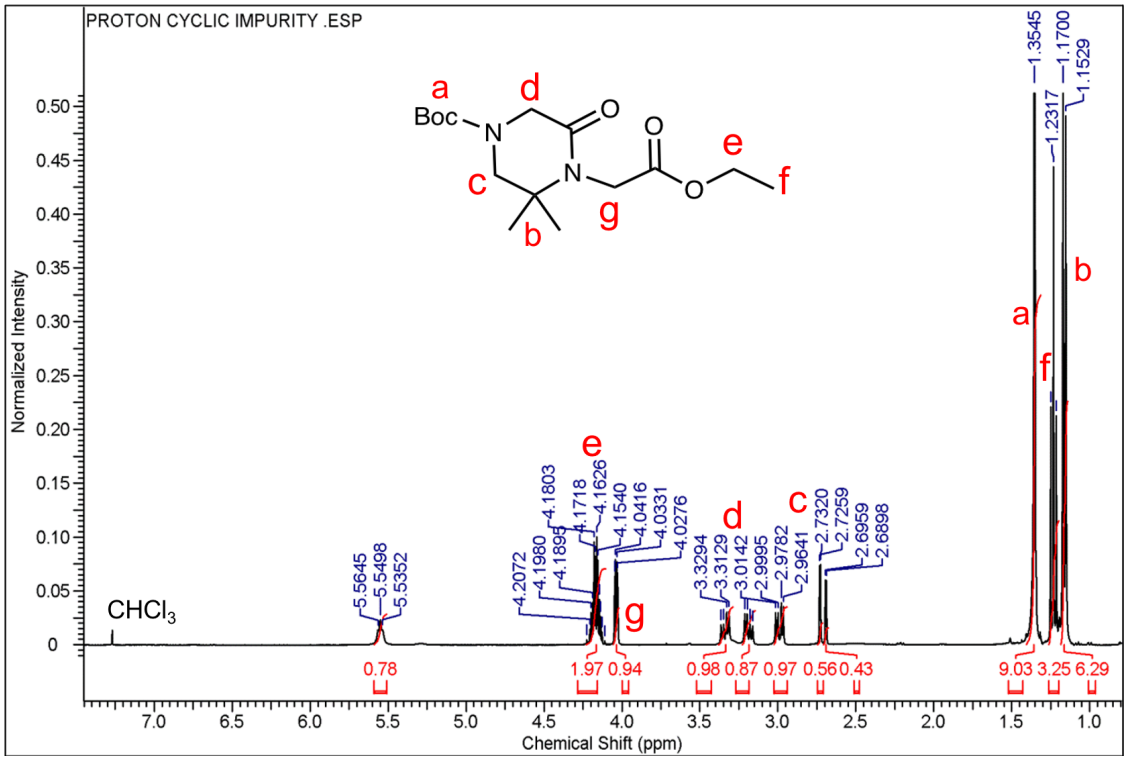


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of Compound 12



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of Compound 12

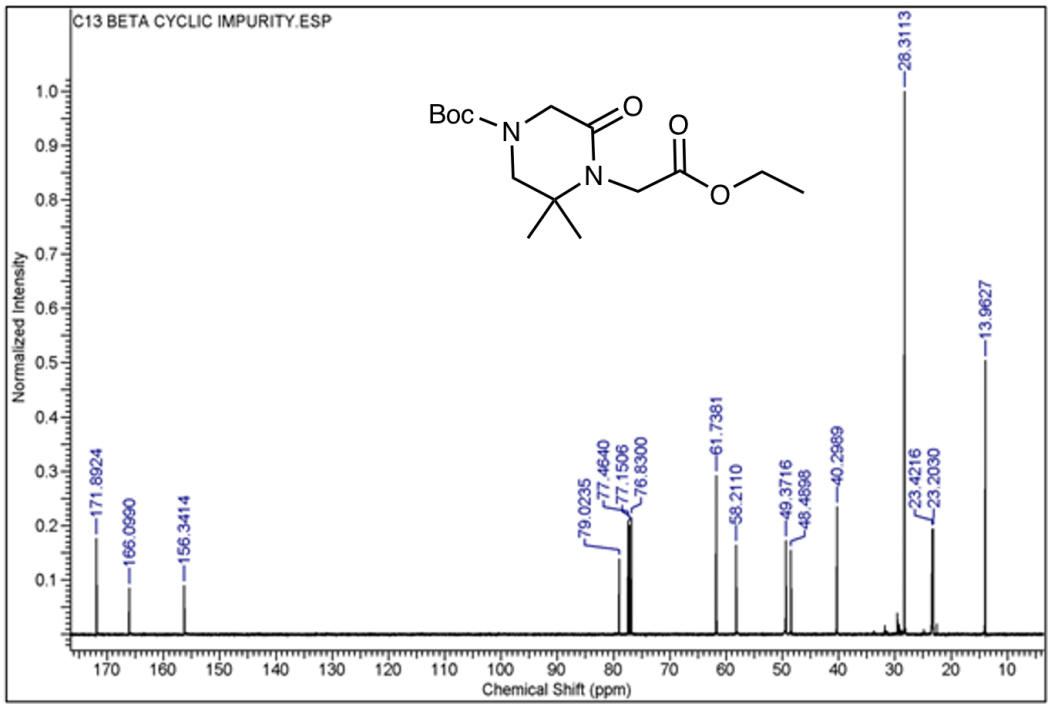
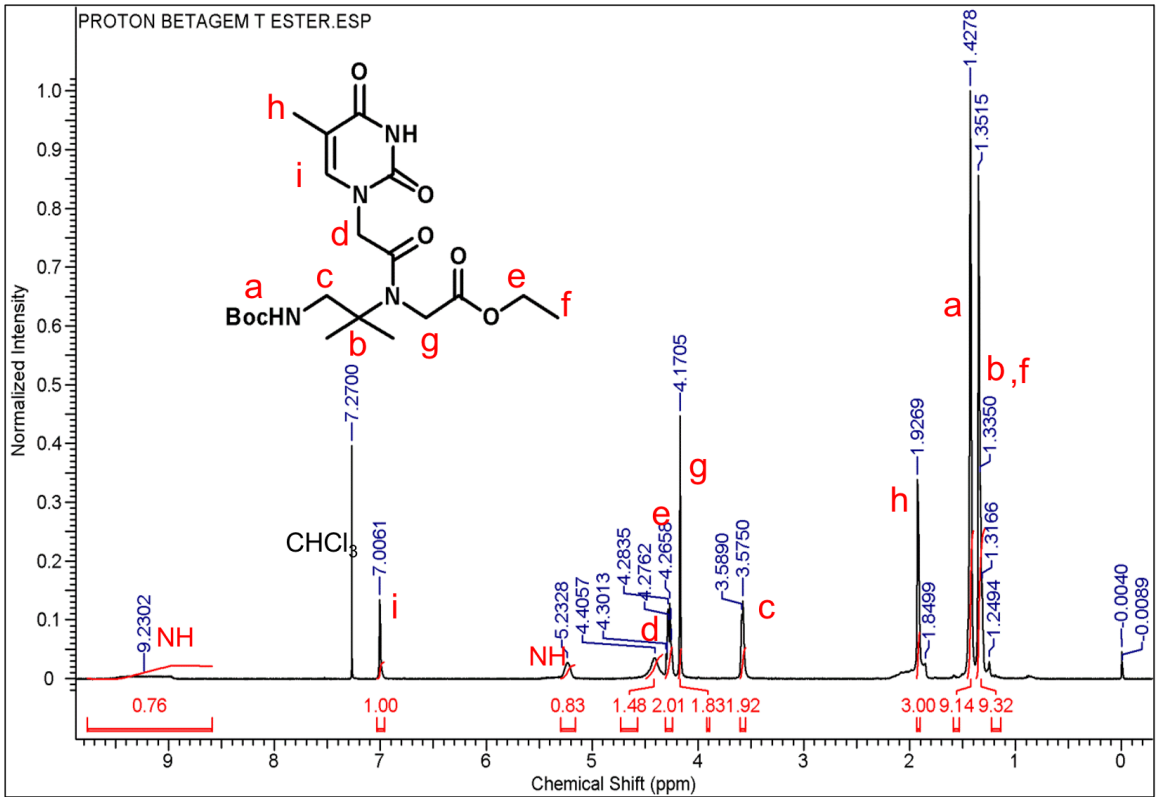


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$)) of Compound 13



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of Compound 13

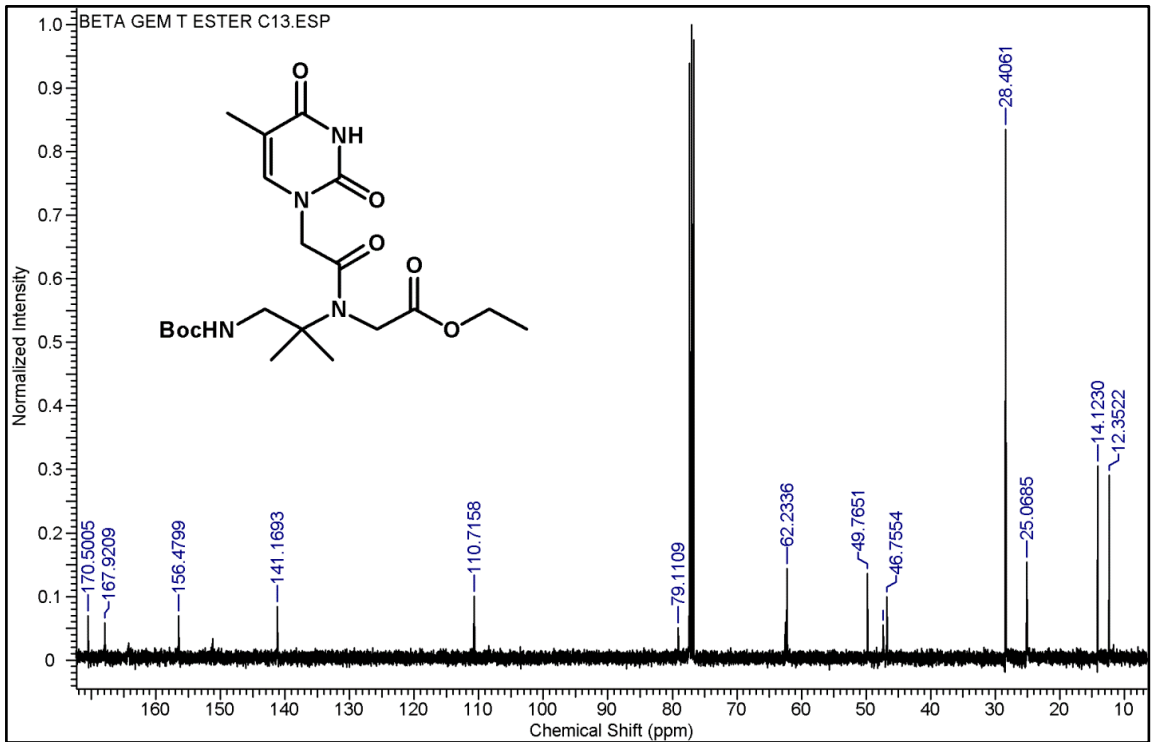
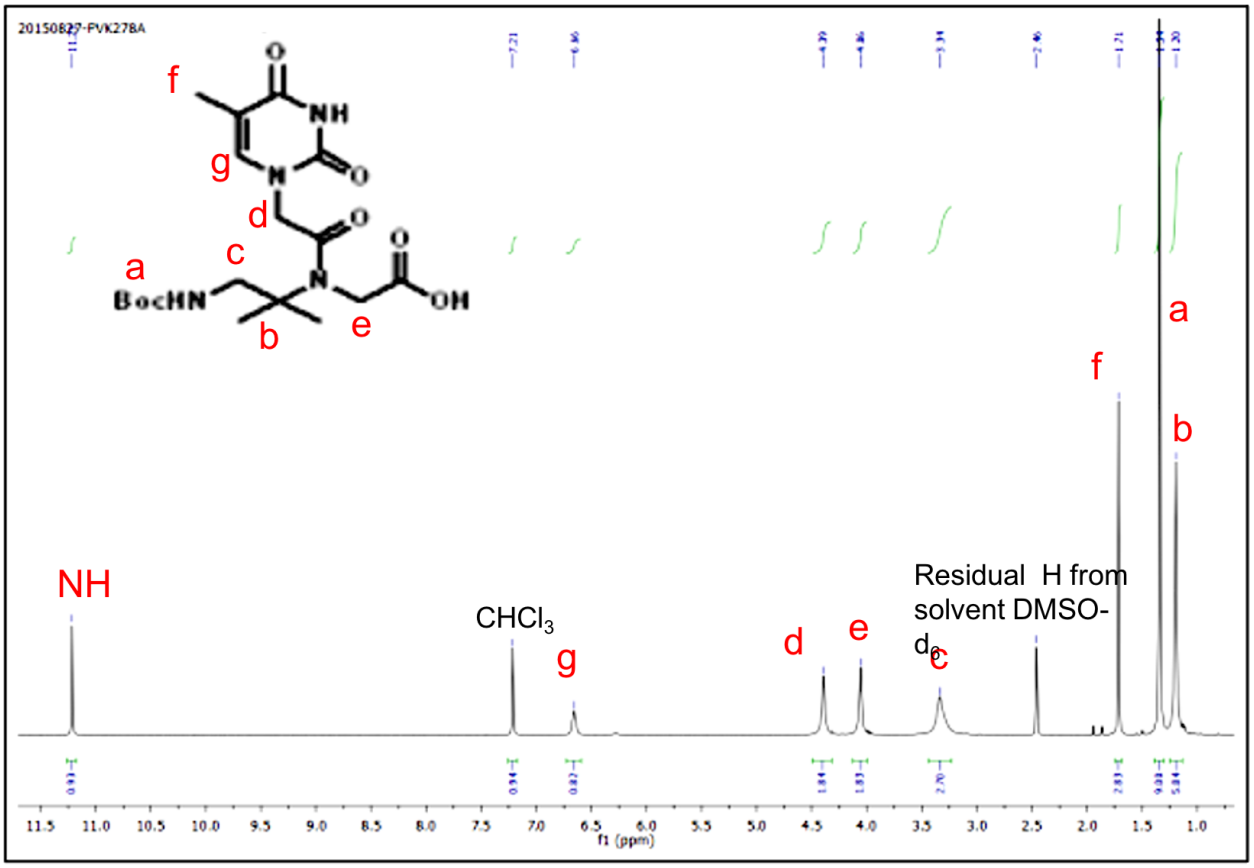


Figure S10. ^{1}H NMR (400 MHz, DMSO-d$_6$) of Compound 14



^{13}C{^{1}H} NMR (400 MHz, DMSO-d$_6$) of Compound 14

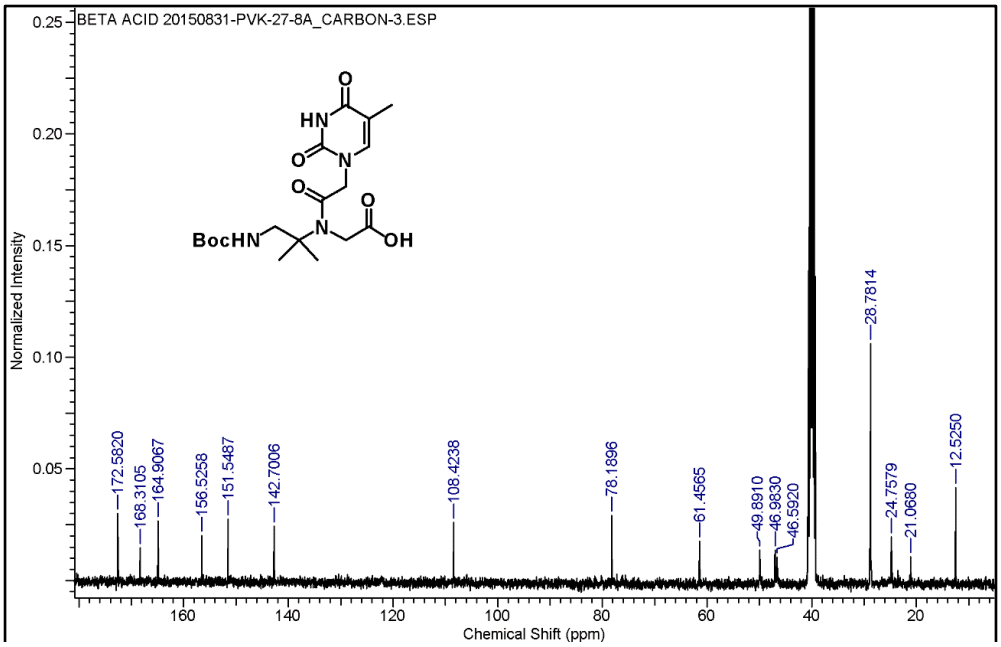


Figure S11. Full ^{1}H-^{1}H NOE Spectra of a-*gdm*-PNA monomer (400 MHz)

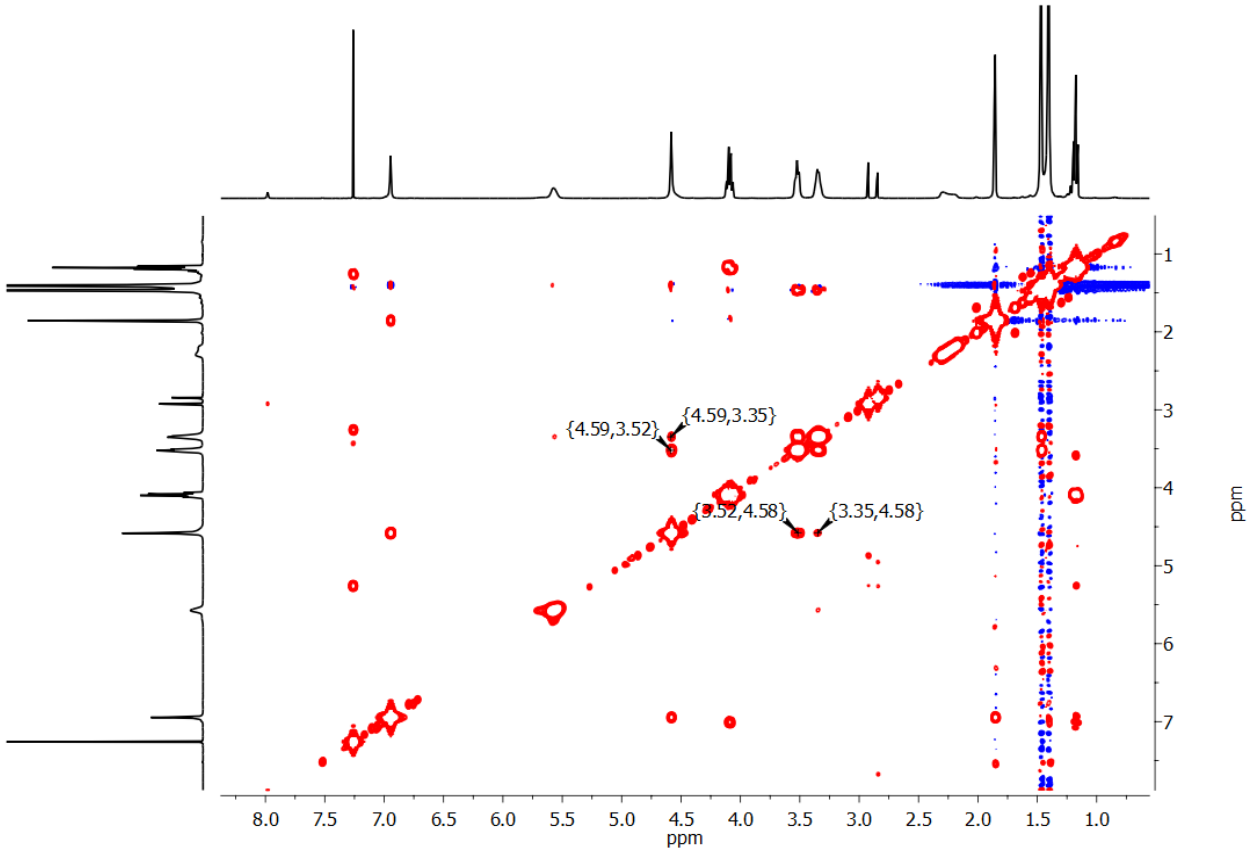
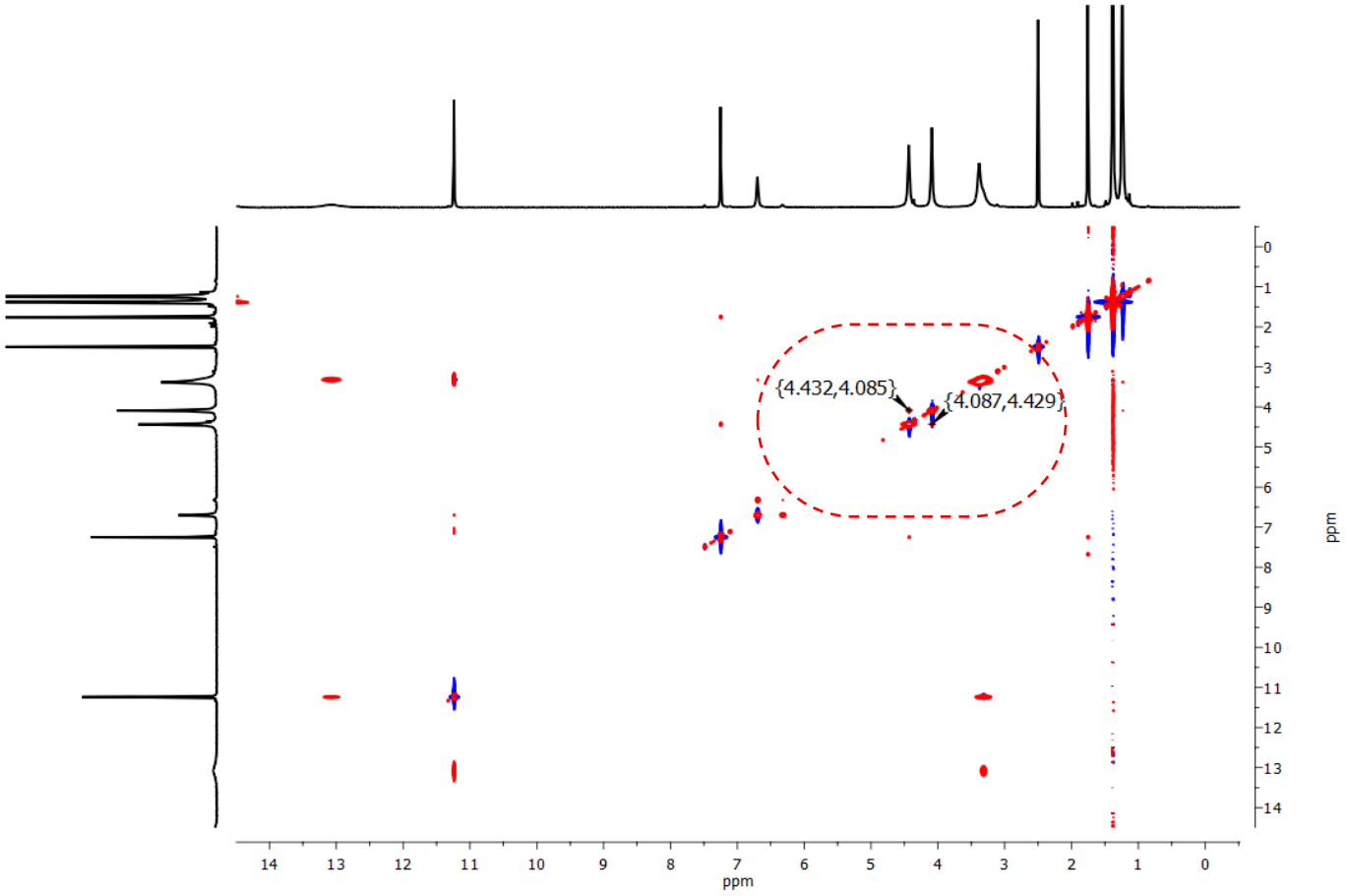
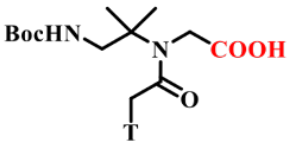


Figure S12. Full ^{1}H-^{1}H NOESY of b-*gdm* monomer acid (14) in 600 MHz





14

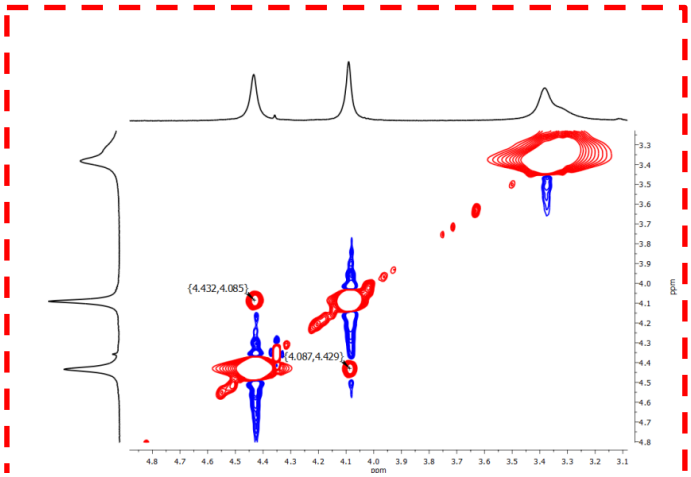
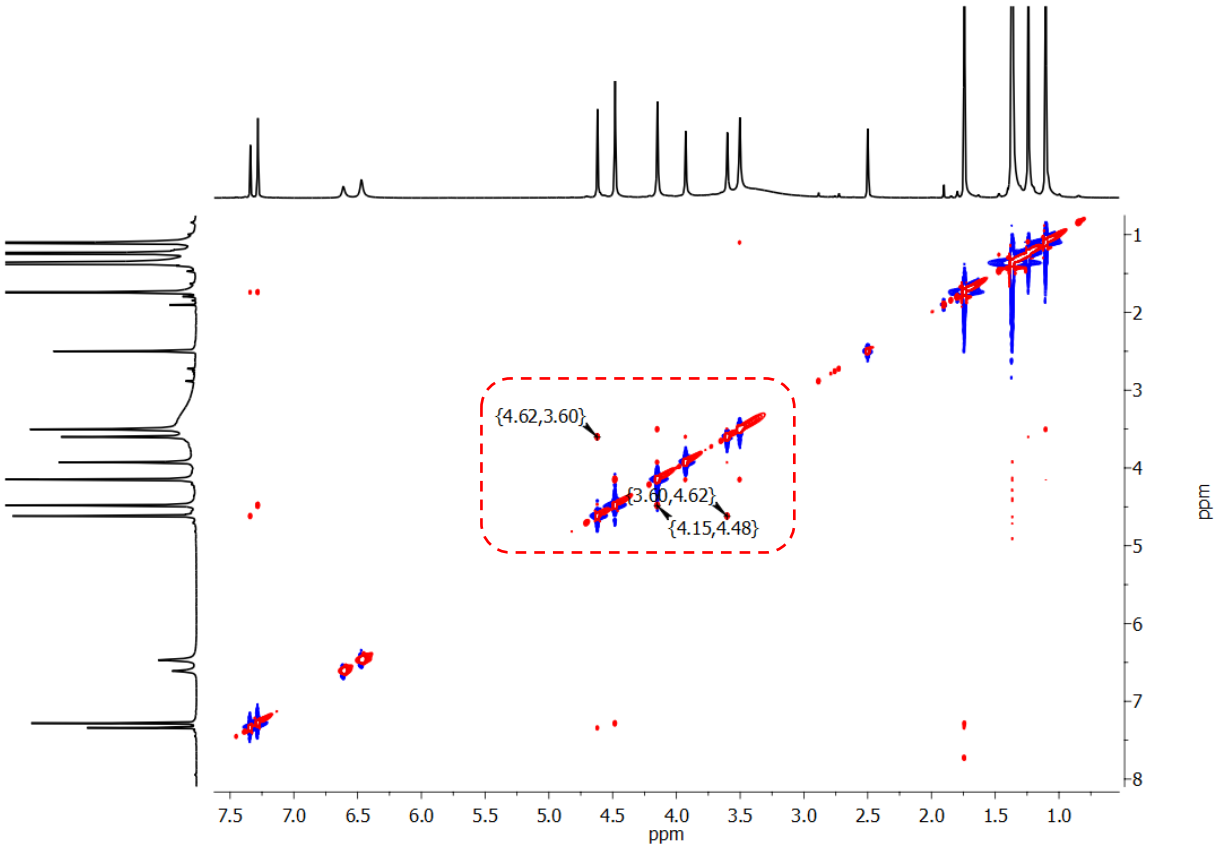
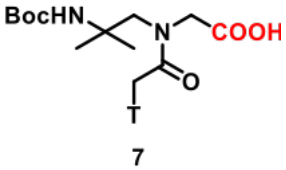


Figure S13. Full ^{1}H-^{1}H NOESY of γ-*gdm*-monomer acid (7) in 600 MHz





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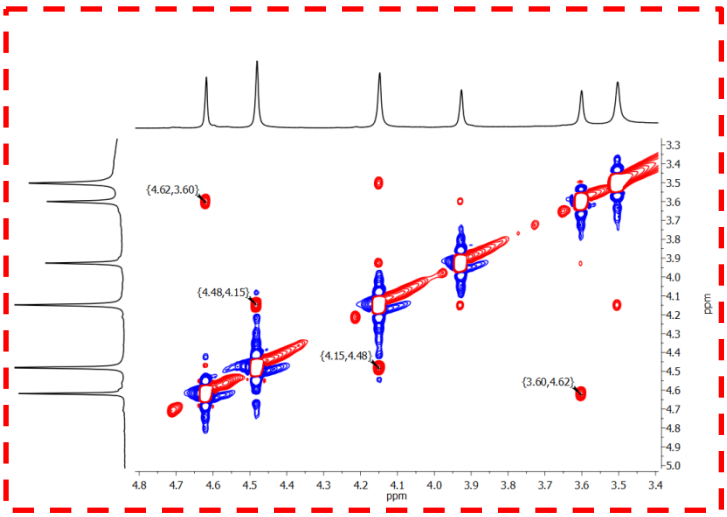

Figure S14. MALDI-TOF of Compound 4: Calcd for $C_{12}H_{24}N_2O_4Na$ 283.1634; Found 284.2077

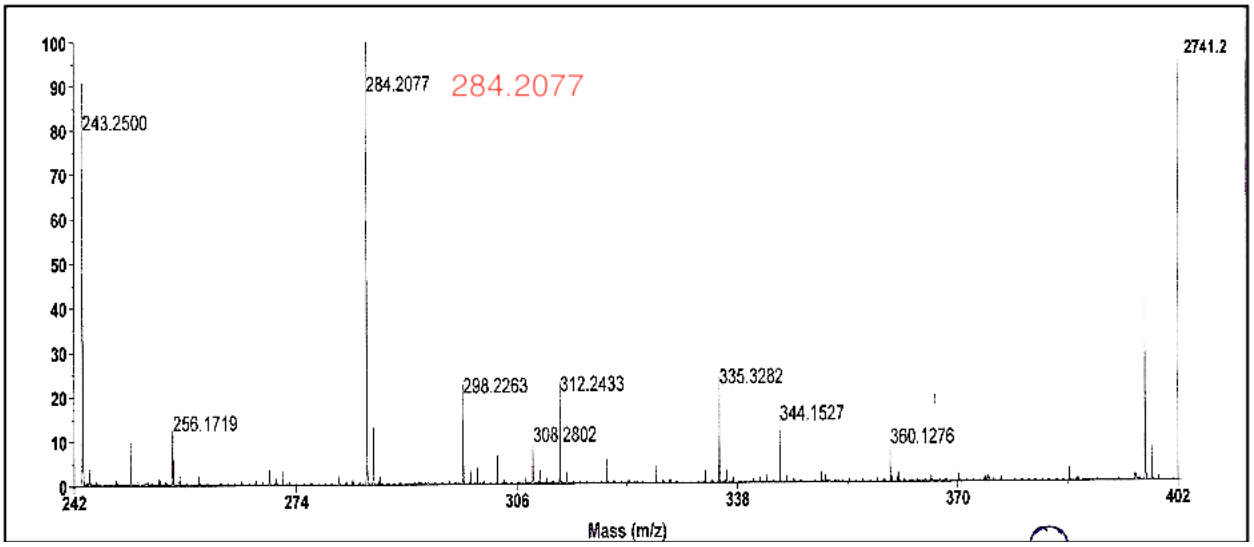

Figure S15. HRMS of Compound 5: Calcd for $C_{14}H_{25}ClN_2O_5Na$ 359.1342; Found: 359.1353

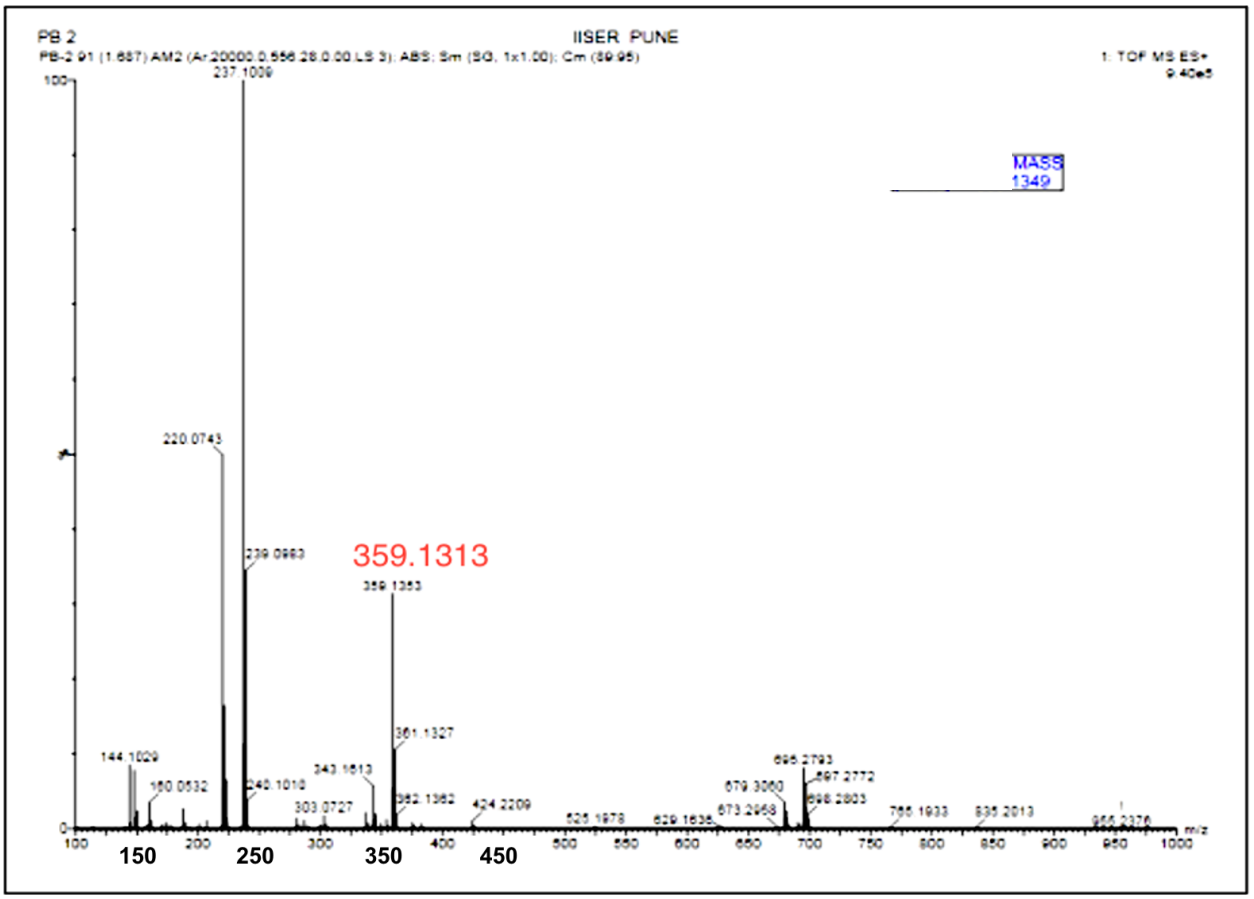

Figure S16. MALDI-TOF of Compound 6: Calcd for $C_{19}H_{30}N_4O_7K$ 465.1751; Found 465.1560

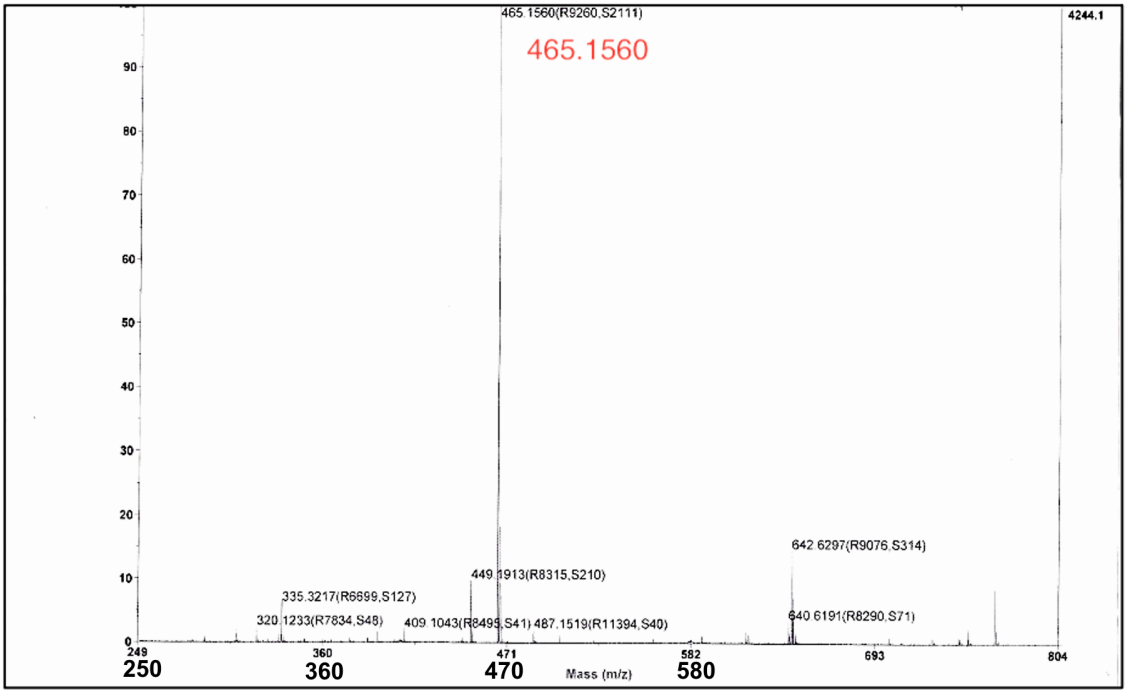

Figure S17. HRMS of Compound 7: m/z: Calcd for $C_{18}H_{28}N_4O_7Na$ 435.1855; Found 435.1855.

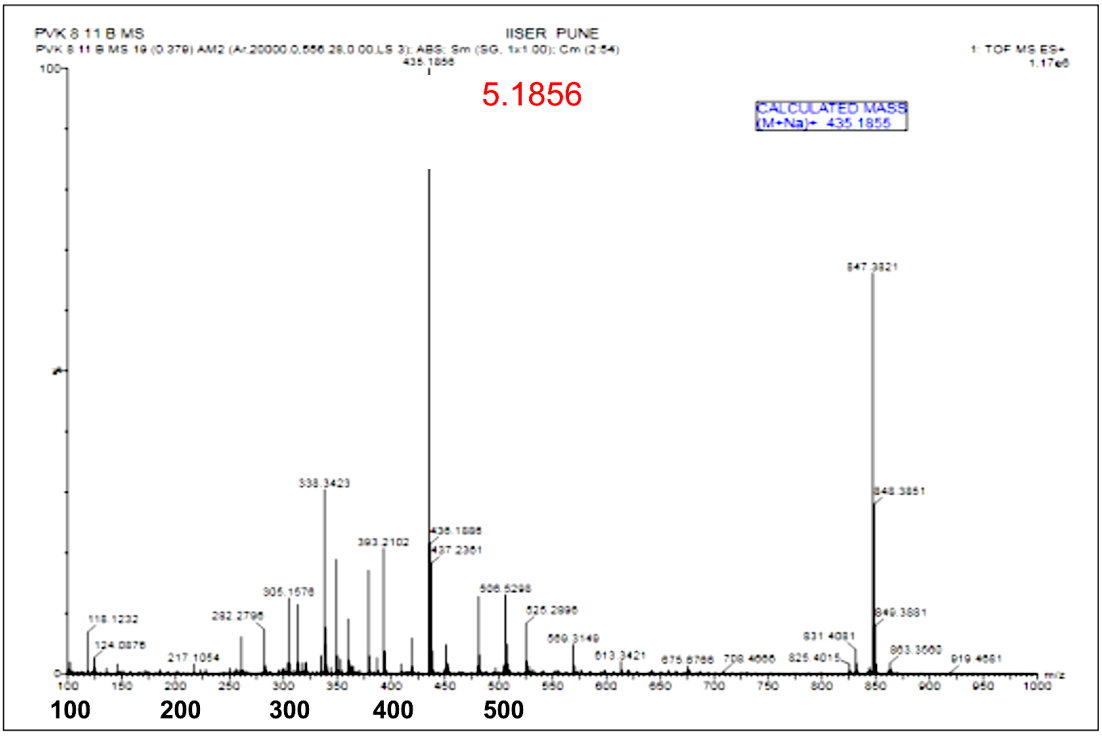

Figure S18. HRMS of Compound 10: m/z: Calcd for $C_{13}H_{23}N_2O_4$ 275.1971; Found 275.1977.

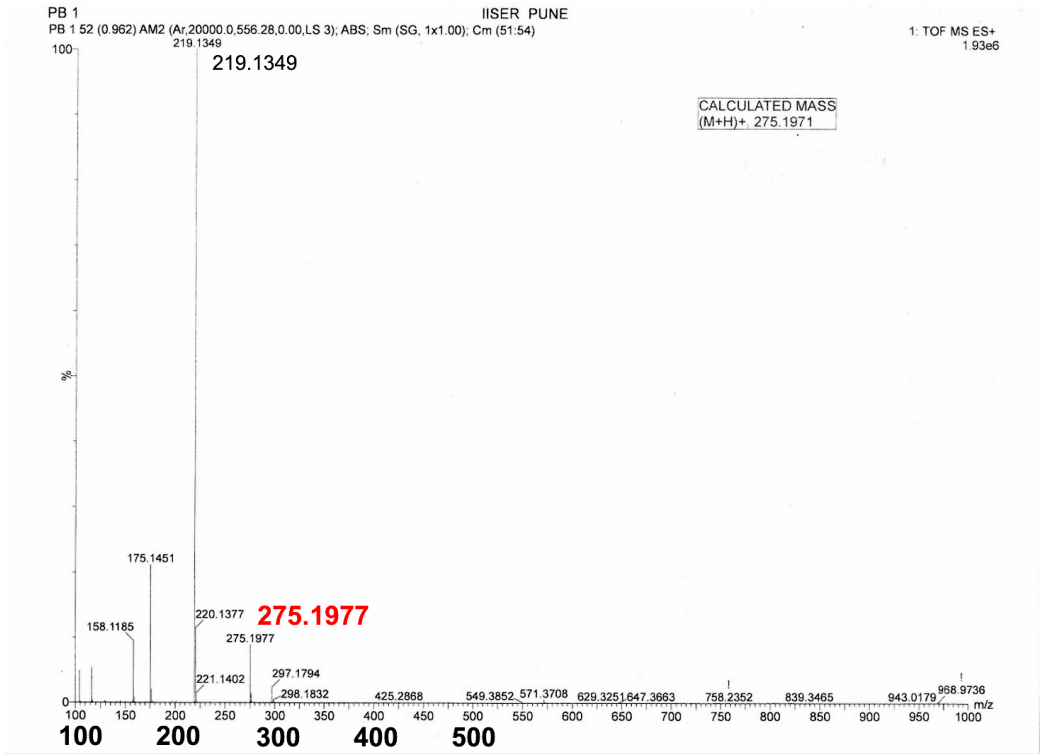

Figure S19. MALDI-TOF of Compound 11: m/z: Calcd for $C_{15}H_{27}ClN_2O_5K$ 389.1246; Found 389.0901

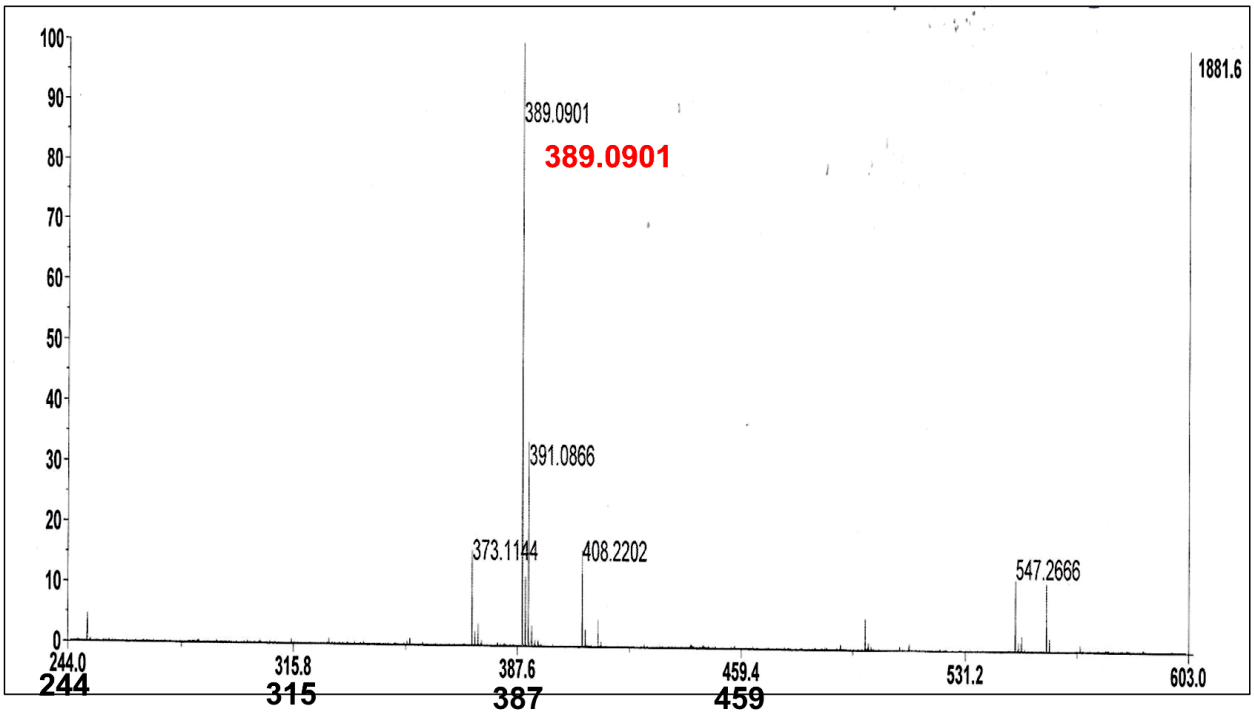

Figure S20. HRMS of Compound 12: m/z: Calcd for $C_{15}H_{26}N_5O_5Na$ 337.1739; Found 337.1741

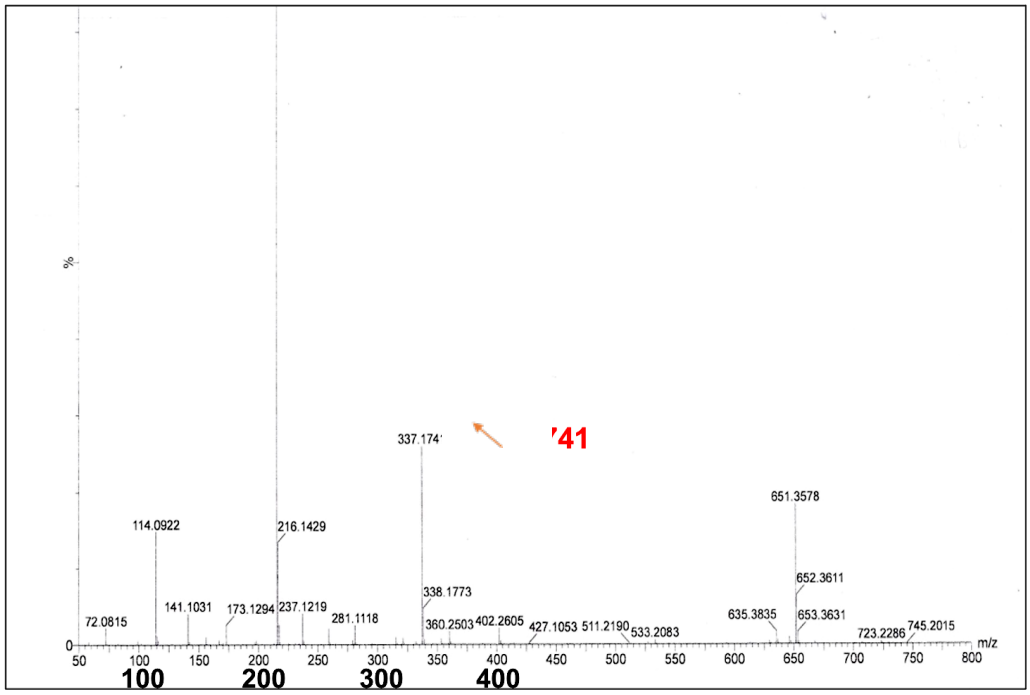

Figure S21. HRMS of Compound 13: m/z: Calcd for $C_{15}H_{26}N_5O_5Na$ 463.2168; Found 463.2182.

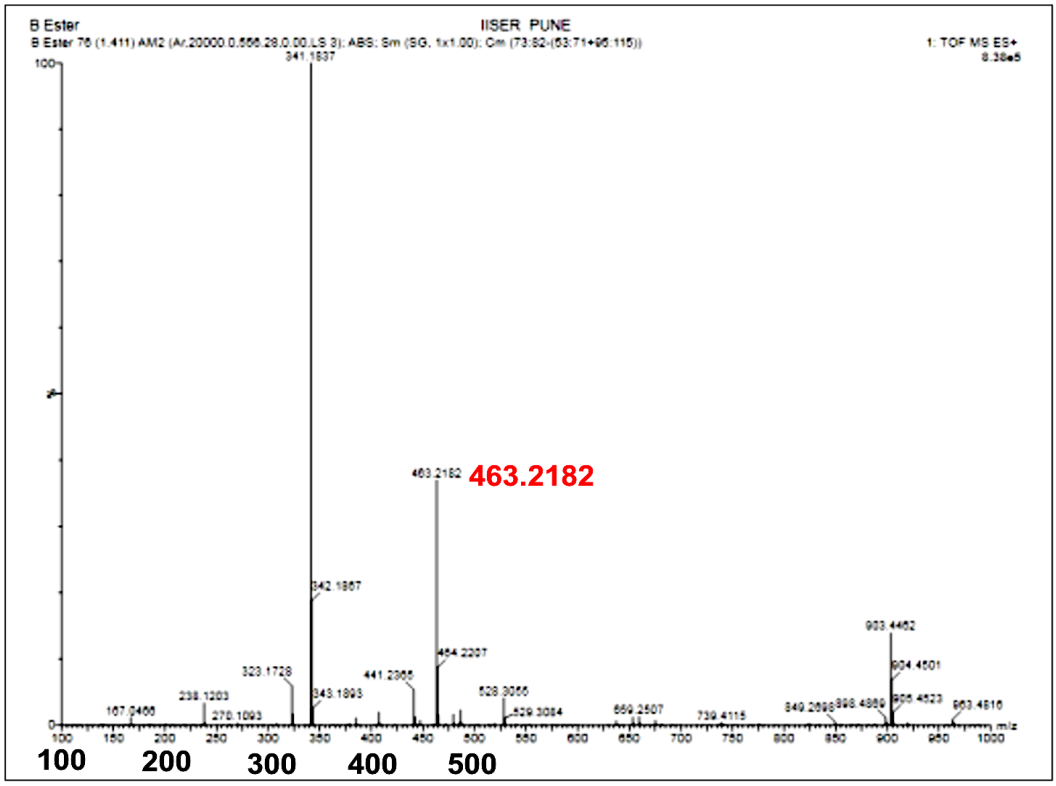

Figure S22. HRMS of Compound 14: HRMS (ESI-MS) m/z: Calcd for $C_{18}H_{28}N_4O_7Na$ 435.1855; Found 435.1864

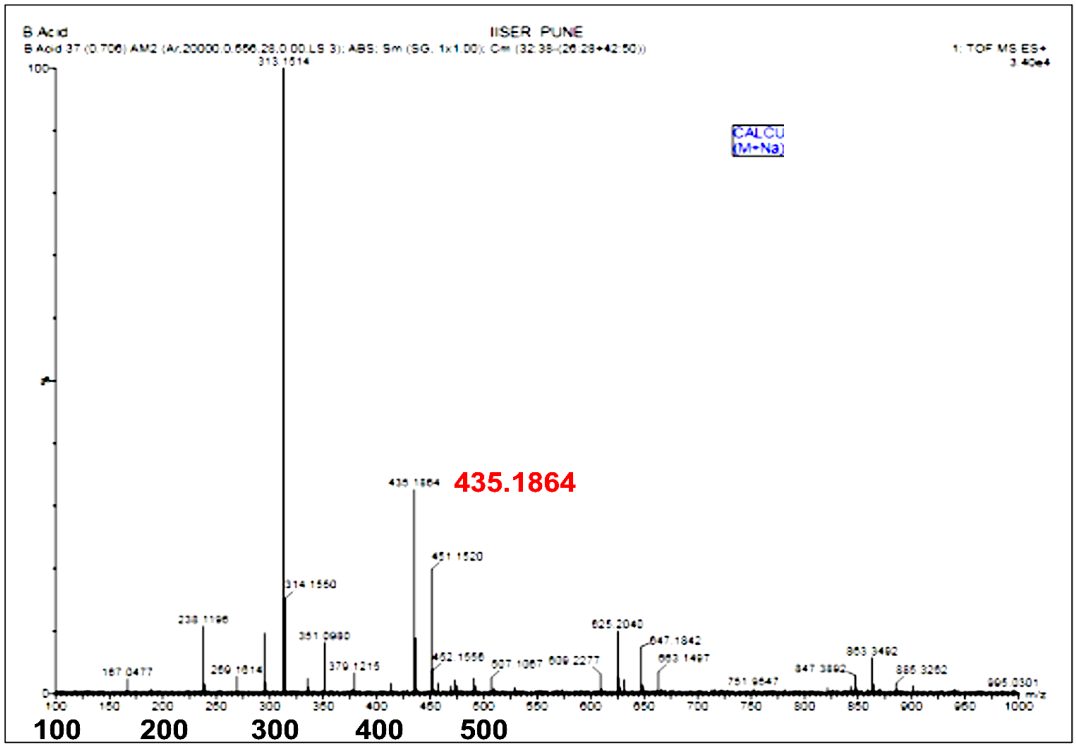

Figure S23. Validation for level of theory used – Results from M06-2X and ωB97X-D Computations

To ensure that the results presented in the main-text using B3-LYP(D3-BJ) are not artefacts of the level of theory employed, we used M06-2X and ωB97X-D density functionals. We found the exact same trend as was noticed with B3-LYP(D3-BJ) in the main-text, *viz.*

(i) the α Z gdm isomer being significantly more stable than the α E gdm isomer (by > 4kcal/mol at 25^0c)

(ii) the β E gdm isomer being significantly more stable than the β Z gdm isomer (by at least 3kcal/mol at 25^0c)

(iii) the free-energy difference the γ E gdm and γ Z gdm isomers being small (< 2 kcal/mol at 25^0c)

Table SI 1 and SI 2 summarize these results:

Table SI: Relative free-energies (kcal/mol) between E and Z isomers at 25^0c (M06-2X (SMD-DMSO)/6-31+G(d,p))

	Z	E
Relative free-energies for α gdm isomer	0.0	+6.3
Relative free-energies for β gdm isomer	+3.0	0.0
Relative free-energies for γ gdm isomer	0.0	+1.2

Table S2: Relative free-energies (kcal/mol) between E and Z isomers 25 °C (ωB97X-D (SMD-DMSO)/6-31+G(d,p))

	Z	E
Relative free-energies for α gdm isomer	0.0	+4.4
Relative free-energies for β gdm isomer	+3.8	0.0
Relative free-energies for γ gdm isomer	0.0	+ 0.6

Table S3 – Relative free-energies (kcal/mol) between E and Z isomers at 25 °C (B3-LYP(D3-BJ)(SMD-Water)/6-31+G(d,p)

	Z	E
Relative free energies of α gdm isomer	0.0	+ 3.1
Relative free energies of β gdm isomer	+3.1	0.0
Relative free energies of γ gdm isomer	0.0	+0.7

Note that the error-bar in density functional theory is within 2 kcal/mol. Hence, with the γ gdm isomers we cannot quantify the relative populations of the E and Z isomers using the DFT calculations. Only a qualitative assessment that both the E and Z isomers shall be observed experimentally, may be made.

Figure S24. Cartesian Co-ordinates, number of imaginary frequencies, and obtained energies and thermal correction to freeenergies of the minimum energy structures presented in the main-text

Legend:

The coordinates of all the minimum energy structures given in the main-text, are provided here. Followed by giving the name of the structure, the charge and spin multiplicities are provided. Then, the atomic number or atomic symbol of the atoms involved, and the X, Y and Z coordinates of all the atoms are provided.

level of theory used: B3-LYP(D3-BJ, SMD-DMSO)/6-311++G(3df,2p)//B3-LYP(D3-BJ, SMD-DMSO)/6-31+G(d,p).

Followed by the co-ordinates, the number of imaginary frequencies for all of these optimized geometries (0 in all cases), the single point energy (B3-LYP(D3-BJ, SMD-DMSO)/6-311++G(3df,2p)), and the thermal correction to the free-energy (B3-LYP(D3-BJ, SMD-DMSO)/6-31+G(d,p)) at 25 ^{O}C are presented, for each of the molecule.

α-*gdm*-E-isomer

0 1

7	-0.035217	-0.629631	-0.355799
6	0.100494	-1.923732	0.372433
6	1.110987	-2.817362	-0.377658

8	1.160838	-2.902321	-1.591431
8	1.868455	-3.535662	0.455082
6	2.803690	-4.480788	-0.147900
1	3.467218	-3.924794	-0.815526
1	2.229756	-5.197964	-0.740745
6	1.014210	0.201982	-0.628959
8	0.848583	1.347412	-1.062470
6	2.453095	-0.313388	-0.467583
1	2.730557	-0.837579	-1.382247
1	2.587887	-0.989815	0.373744
6	-1.366155	-0.077327	-0.646352
6	-1.945930	0.726447	0.528311
1	-1.248941	1.517702	0.813942
1	-2.106897	0.080009	1.392074
7	-3.217111	1.336108	0.178970
1	-3.211926	2.160645	-0.407370
7	3.376645	0.798593	-0.296470
6	3.394837	1.473570	0.905703
6	4.150387	1.203077	-1.370316
1	2.731236	1.064946	1.660075
6	4.170887	2.556978	1.152804
7	4.943675	2.302172	-1.106933
8	4.153464	0.636059	-2.462393
6	4.184274	3.271058	2.471333
6	5.027129	3.037685	0.078394
1	5.528020	2.612788	-1.877219
1	5.185944	3.260137	2.915697
1	3.896645	4.321814	2.353171
1	3.490021	2.799104	3.171618
8	5.787004	4.007859	0.148810
6	3.560327	-5.148801	0.977354
1	2.881535	-5.692138	1.642454
1	4.272021	-5.864888	0.553361
1	4.120880	-4.415505	1.566067
6	-4.398342	0.673233	0.316641
8	-4.525366	-0.402217	0.897351
8	-5.394409	1.386779	-0.256209
6	-6.803760	0.945454	-0.187830
6	-7.263222	0.890170	1.268620
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1	-8.341452	0.701839	1.297684
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1	-8.036898	-0.634297	-0.969188
1	-6.573578	-0.332964	-1.924045
1	-6.461788	-1.198209	-0.373001
6	-7.536889	2.053145	-0.940926
1	-7.181239	2.120716	-1.973947

1	-8.609690	1.839035	-0.956861
1	-7.383622	3.021099	-0.453293
1	-1.264102	0.579539	-1.510405
1	-2.044008	-0.883545	-0.917246
6	0.442452	-1.677715	1.852216
1	1.374957	-1.126859	1.987860
1	-0.363145	-1.091114	2.299909
1	0.520940	-2.623432	2.391417
6	-1.206221	-2.746146	0.313267
1	-2.011336	-2.238381	0.847607
1	-1.517349	-2.944584	-0.714229
1	-1.028219	-3.704063	0.809563

Number of imaginary frequency- 0
Single point energy - -1527.78642012 H
Thermal correction to Gibbs' free-energy - 0.458212 H

α-*gdm*-Z-isomer

0 1

7	-0.054837	0.803096	-0.090726
6	-0.063846	2.231049	0.334189
6	-1.144428	2.948859	-0.502153
8	-1.264758	2.803622	-1.706063
8	-1.833114	3.844358	0.212957
6	-2.816947	4.637574	-0.506445
1	-3.537864	3.955424	-0.965635
1	-2.305381	5.188706	-1.300645
6	-1.245666	0.149917	-0.068466
8	-2.306719	0.711898	0.224365
6	-1.250167	-1.333635	-0.468850
1	-0.509281	-1.900684	0.091796
1	-1.023545	-1.428099	-1.533676
6	1.201809	0.105808	-0.378490
6	1.899510	-0.423890	0.886226
7	3.091794	-1.182686	0.555066
1	2.983569	-2.134682	0.230163
7	-2.556108	-1.926612	-0.225576
6	-3.536820	-1.863290	-1.191191
6	-2.815194	-2.426550	1.038979
1	-3.221018	-1.415854	-2.126531
6	-4.800194	-2.324390	-1.015395
7	-4.096468	-2.911891	1.204055
8	-1.976648	-2.449197	1.939607
6	-5.848640	-2.260316	-2.086044
6	-5.140728	-2.904797	0.274121
1	-4.302699	-3.298255	2.120549

1	-6.212142	-3.261657	-2.343381
1	-6.716226	-1.678970	-1.754074
1	-5.446935	-1.795521	-2.990264
8	-6.242539	-3.368947	0.582513
6	-3.473983	5.565269	0.491304
1	-2.740778	6.238704	0.947125
1	-4.224865	6.173695	-0.023863
1	-3.974842	5.001000	1.284651
6	4.296458	-0.581939	0.348487
8	4.525066	0.603963	0.573908
8	5.188242	-1.488531	-0.111060
6	6.588373	-1.118005	-0.409560
6	7.288854	-0.648081	0.864660
1	6.881172	0.299639	1.219419
1	7.186590	-1.398549	1.655615
1	8.355836	-0.514431	0.658246
6	6.626032	-0.068070	-1.519252
1	7.664932	0.091265	-1.826043
1	6.062656	-0.414277	-2.392210
1	6.211334	0.883316	-1.183132
6	7.185730	-2.436126	-0.896257
1	6.658993	-2.795516	-1.785920
1	8.239177	-2.289378	-1.152385
1	7.121778	-3.202258	-0.117117
1	1.871174	0.779227	-0.911542
1	1.004072	-0.723604	-1.057989
1	2.187112	0.403219	1.536521
1	1.220036	-1.073541	1.443879
6	1.252033	2.942763	-0.029123
1	2.093928	2.523985	0.526519
1	1.462328	2.891405	-1.099678
1	1.159313	3.995898	0.251160
6	-0.292486	2.327441	1.849636
1	-1.246836	1.882793	2.133863
1	0.514766	1.798639	2.362894
1	-0.281450	3.370139	2.173868

Number of imaginary frequency- 0
Single point energy - -1527.79355108 H
Thermal correction to Gibbs' free-energy - 0.458179 H

β-*gdm*-E-isomer

0 1

7	-0.230554	-0.715334	-0.168591
6	-0.405278	-1.968996	-0.886001
6	-0.833689	-3.130266	0.003439

1	-1.142274	-1.865993	-1.683016
1	0.516435	-2.245690	-1.394045
8	-1.105427	-3.048375	1.186026
8	-0.878549	-4.261330	-0.710807
6	-1.286936	-5.473537	-0.007921
1	-2.287762	-5.311013	0.401086
1	-0.592253	-5.638360	0.820044
6	-1.292464	0.126981	-0.009245
8	-1.234171	1.209937	0.578579
6	-2.634746	-0.313978	-0.628749
1	-2.946987	-1.280117	-0.233136
1	-2.548572	-0.393582	-1.714321
6	1.094285	-0.403808	0.490438
6	1.635616	0.888261	-0.183839
1	0.917035	1.694457	-0.040735
1	1.751846	0.703579	-1.253381
7	2.919605	1.315591	0.338923
1	2.955968	1.728630	1.260848
6	2.100742	-1.541493	0.272702
1	2.366699	-1.679618	-0.777256
1	3.016201	-1.283725	0.809437
1	1.742206	-2.488435	0.684897
6	0.902267	-0.229842	2.006166
1	1.875108	-0.067800	2.479923
1	0.253510	0.613911	2.240202
1	0.465165	-1.139364	2.427112
7	-3.675889	0.659614	-0.339413
6	-3.818298	1.765915	-1.149229
6	-4.410583	0.515929	0.825097
1	-3.165775	1.778796	-2.014902
6	-4.701243	2.768085	-0.914399
7	-5.320905	1.530026	1.046060
8	-4.281138	-0.434869	1.594652
6	-4.846435	3.955328	-1.819528
6	-5.537643	2.673057	0.271780
1	-5.880885	1.438600	1.888165
1	-5.866551	4.030595	-2.212704
1	-4.639079	4.888152	-1.283004
1	-4.155064	3.881362	-2.663287
8	-6.387188	3.499037	0.619238
6	-1.259979	-6.610482	-1.003928
1	-0.254428	-6.754818	-1.412007
1	-1.561249	-7.534303	-0.498922
1	-1.954480	-6.429125	-1.830567
6	4.102340	1.086875	-0.289714
8	4.217875	0.584216	-1.404886
8	5.121819	1.509762	0.496027
6	6.528934	1.421078	0.055103

6	6.742133	2.273794	-1.195114
1	6.218324	1.857681	-2.056910
1	6.390135	3.296630	-1.024083
1	7.812429	2.315701	-1.422384
6	6.918558	-0.040953	-0.160740
1	7.995347	-0.101680	-0.349875
1	6.696256	-0.631134	0.734613
1	6.388635	-0.472907	-1.010693
6	7.288234	2.009288	1.242233
1	7.101721	1.425521	2.149204
1	8.362567	1.995395	1.035823
1	6.983319	3.044932	1.423083

Number of imaginary frequency- 0
Single point energy - -1527.78978339 H
Thermal correction to Gibbs' free-energy - 0.456038 H

β-*gdm*-Z-isomer

0 1

7	0.297993	0.721873	0.144027
6	0.106924	1.942238	-0.630683
6	0.359359	3.213934	0.164098
1	0.795150	1.944322	-1.477324
1	-0.900823	1.978931	-1.041410
8	0.644147	3.275850	1.344549
8	0.220217	4.281868	-0.635577
6	0.424465	5.593007	-0.032459
1	1.438819	5.630206	0.374308
1	-0.286237	5.707643	0.790645
6	1.590149	0.271879	0.128259
8	2.495566	0.957821	-0.361991
6	1.958585	-1.110331	0.690891
1	1.272875	-1.877660	0.341131
1	1.946679	-1.091200	1.779645
6	-0.928921	0.065222	0.722117
6	-1.510146	-0.840240	-0.396874
1	-0.760679	-1.587982	-0.671072
1	-1.727845	-0.234786	-1.278142
7	-2.732714	-1.520341	-0.017537
1	-2.688317	-2.248359	0.682799
6	-1.946525	1.145142	1.139371
1	-2.308412	1.753791	0.310408
1	-2.814916	0.648428	1.577124
1	-1.511538	1.798848	1.899071
6	-0.636328	-0.746031	1.996113
1	-1.584084	-0.944337	2.502300
1	-0.173994	-1.713104	1.803179

1	-0.008133	-0.173575	2.684446
7	3.303351	-1.480778	0.270848
6	4.390079	-1.138392	1.044645
6	3.456289	-2.051391	-0.980242
1	4.141713	-0.661752	1.986099
6	5.676980	-1.376071	0.687195
7	4.766283	-2.309709	-1.328133
8	2.509236	-2.317780	-1.719873
6	6.845051	-1.010655	1.554290
6	5.920445	-2.014483	-0.596668
1	4.900645	-2.743782	-2.236457
1	7.435946	-1.896000	1.815199
1	7.517542	-0.316059	1.038381
1	6.504056	-0.538111	2.479260
8	7.030082	-2.298141	-1.058342
6	0.211073	6.631223	-1.111091
1	-0.805032	6.578136	-1.515214
1	0.358294	7.628254	-0.682559
1	0.924636	6.501647	-1.931257
6	-3.967806	-1.092395	-0.395730
8	-4.177469	-0.189951	-1.202043
8	-4.914738	-1.822868	0.238101
6	-6.355831	-1.603058	-0.006994
6	-6.688362	-1.897160	-1.469218
1	-6.234085	-1.163873	-2.137132
1	-6.338258	-2.896978	-1.746959
1	-7.774648	-1.867508	-1.603347
6	-6.746924	-0.185572	0.408960
1	-7.835951	-0.084424	0.357572
1	-6.434642	0.008569	1.440464
1	-6.294571	0.561181	-0.244896
6	-7.011078	-2.632012	0.911328
1	-6.741857	-2.446685	1.956053
1	-8.099235	-2.568319	0.817557
1	-6.698696	-3.646285	0.643257

Number of imaginary frequency- 0
Single point energy - -1527.78724596 H
Thermal correction to Gibbs' free-energy - 0.458616 H

γ-*gdm*-E-isomer

0 1

N	-0.369975	0.856070	0.282114
C	-0.671689	2.147436	0.875623
C	-1.191732	3.154718	-0.145906
H	-1.391379	2.058735	1.691578

H	0.236043	2.560023	1.317803
O	-1.311513	2.938372	-1.337132
O	-1.490475	4.311622	0.453614
C	-1.990421	5.389478	-0.395981
H	-2.888241	5.032674	-0.907512
H	-1.226367	5.615427	-1.144569
C	-1.357574	-0.029542	-0.042600
O	-1.163214	-1.031997	-0.730466
C	-2.750249	0.262172	0.537226
H	-3.146939	1.194641	0.134870
H	-2.696732	0.350243	1.624905
C	0.960590	0.673306	-0.296143
C	1.978354	-0.011444	0.653289
N	3.213614	-0.065736	-0.154289
H	3.149933	0.180157	-1.133929
N	-3.681100	-0.805248	0.208354
C	-3.641214	-1.982971	0.924374
C	-4.501944	-0.655385	-0.896673
H	-2.940676	-1.984171	1.752002
C	-4.410936	-3.063805	0.645981
N	-5.289789	-1.756254	-1.165934
O	-4.542430	0.368196	-1.578067
C	-4.360748	-4.329025	1.449598
C	-5.320648	-2.977323	-0.486159
H	-5.906173	-1.666961	-1.968044
H	-5.338748	-4.558318	1.887685
H	-4.080569	-5.183390	0.823204
H	-3.631469	-4.239879	2.259109
O	-6.082594	-3.871947	-0.864347
C	-2.279968	6.576183	0.494437
H	-1.374849	6.916059	1.007885
H	-2.655426	7.400384	-0.121150
H	-3.041060	6.332605	1.242636
C	4.394732	-0.609087	0.240939
O	4.639873	-1.044307	1.363031
O	5.266780	-0.585342	-0.799488
C	6.653732	-1.072273	-0.661038
C	6.657736	-2.563229	-0.324050
H	6.263970	-2.748329	0.676275
H	6.057718	-3.119959	-1.051649
H	7.685249	-2.938637	-0.371160
C	7.402533	-0.237024	0.377098
H	8.460268	-0.519973	0.370272
H	7.333556	0.828202	0.132255
H	7.004967	-0.397040	1.380319
C	7.230714	-0.837455	-2.055491
H	7.192305	0.224755	-2.317109
H	8.274742	-1.163688	-2.081788

H	6.671408	-1.403759	-2.807008
H	0.857552	0.070361	-1.200402
H	1.347458	1.657022	-0.577480
C	2.208224	0.830366	1.916079
H	2.992647	0.381077	2.527926
H	2.509419	1.850223	1.654441
H	1.293283	0.874334	2.514170
C	1.515342	-1.425271	1.031054
H	0.568255	-1.380868	1.575959
H	1.370731	-2.037077	0.136768
H	2.259449	-1.902398	1.672907

Number of imaginary frequency- 0
Single point energy - -1527.79518994 H
Thermal correction to Gibbs' free-energy - 0.455231 H

γ-*gdm*-Z-isomer

0 1

N	0.394856	1.012647	-0.341609
C	0.574749	2.398618	-0.746736
C	1.421569	3.175744	0.254052
H	1.029498	2.463174	-1.736039
H	-0.399024	2.886801	-0.793888
O	1.598401	2.856911	1.415076
O	1.901754	4.291989	-0.307008
C	2.673828	5.184028	0.550609
H	3.532079	4.627969	0.937483
H	2.043181	5.483682	1.392222
C	1.526347	0.252639	-0.344289
O	2.586954	0.678070	-0.810745
C	1.457736	-1.142342	0.288307
H	0.715684	-1.762416	-0.209835
H	1.185828	-1.059058	1.342823
C	-0.867470	0.628785	0.286038
C	-1.997158	0.207378	-0.696444
N	-3.137014	-0.063553	0.203467
H	-3.083703	0.290156	1.150725
N	2.747454	-1.809537	0.207831
C	3.706147	-1.559259	1.166352
C	3.018001	-2.589802	-0.902748
H	3.382024	-0.905934	1.968514
C	4.956641	-2.082900	1.138024
N	4.286107	-3.134909	-0.913860
O	2.201488	-2.796004	-1.799869
C	5.980844	-1.810001	2.198983

C	5.307553	-2.947632	0.021962
H	4.503078	-3.721314	-1.714354
H	6.303620	-2.737917	2.684571
H	6.875453	-1.342616	1.772272
H	5.574341	-1.142869	2.963741
O	6.399638	-3.500055	-0.140214
C	3.099268	6.369113	-0.286585
H	2.230838	6.910934	-0.675004
H	3.681957	7.056170	0.336131
H	3.724885	6.054645	-1.128104
C	-4.369505	-0.481346	-0.193106
O	-4.672450	-0.828294	-1.331101
O	-5.208186	-0.468456	0.873712
C	-6.610000	-0.920780	0.764155
C	-6.658052	-2.391713	0.350979
H	-6.311792	-2.532169	-0.673938
H	-6.039148	-2.996735	1.022029
H	-7.689941	-2.750511	0.423529
C	-7.378911	-0.017692	-0.199703
H	-8.441172	-0.281632	-0.168783
H	-7.279980	1.031379	0.098701
H	-7.020613	-0.130733	-1.223845
C	-7.128361	-0.748433	2.190161
H	-7.054032	0.297019	2.506017
H	-8.178446	-1.051724	2.239613
H	-6.555555	-1.367061	2.888341
H	-1.216806	1.483208	0.874954
H	-0.696617	-0.192018	0.983040
C	-1.607319	-1.061861	-1.462379
H	-0.681332	-0.892581	-2.019666
H	-1.458834	-1.899243	-0.773441
H	-2.391385	-1.333171	-2.170682
C	-2.349342	1.334119	-1.678314
H	-2.588247	2.259307	-1.143536
H	-1.518744	1.525539	-2.363853
H	-3.217095	1.043902	-2.275235

Number of imaginary frequency- 0
Single point energy - -1527.79553382 H
Thermal correction to Gibbs' free-energy - 0.456522 H

Unsubsituted PNA monomer (E isomer) ***aeg*-E-isomer**

0 1

N	-0.15294119	-0.36470588	0.00000000
C	0.03240481	0.91237812	0.66005500
C	0.06260181	2.08327412	-0.31747700
O	-0.06714119	1.99301612	-1.52345100

O	0.25741781	3.22873212	0.34543700
C	0.32051381	4.45342712	-0.44666300
H	-0.61762019	4.55232012	-0.99916400
H	1.14090681	4.35521412	-1.16267300
C	-1.36674619	-0.93568488	-0.21850400
O	-1.50191319	-2.00967288	-0.81137700
C	-2.58848719	-0.19006388	0.34007100
H	-2.63696319	0.82618512	-0.05098400
H	-2.52519019	-0.13702188	1.42960800
C	1.04979781	-1.02323988	-0.51354400
C	1.66963481	-1.94575388	0.54590200
H	0.96210781	-2.73667488	0.80583000
H	1.89355081	-1.37575388	1.45059700
N	2.89443081	-2.56887688	0.07632100
H	2.82349781	-3.38621288	-0.51546900
N	-3.82243019	-0.87626888	-0.00800800
C	-4.25274319	-1.93715388	0.76007600
C	-4.47247219	-0.51699088	-1.17654300
H	-3.64371119	-2.13719188	1.63438600
C	-5.35055719	-2.68057888	0.47624400
N	-5.59840719	-1.26763688	-1.44845600
O	-4.09482519	0.39751012	-1.90799800
C	-5.80699319	-3.82152588	1.33622500
C	-6.10940619	-2.34482088	-0.71835500
H	-6.10026419	-1.01239588	-2.29370700
H	-6.82353019	-3.65291988	1.70923100
H	-5.82367519	-4.75989088	0.77039500
H	-5.14026219	-3.94670988	2.19348100
O	-7.12818219	-2.92341988	-1.10762100
C	0.53811081	5.60442012	0.50911500
H	1.47664681	5.48863612	1.06061400
H	0.58830581	6.53754112	-0.06181000
H	-0.28579919	5.68452712	1.22553200
C	4.09199881	-1.92188188	0.11392900
O	4.27884181	-0.84771888	0.68072500
O	5.02783581	-2.64935188	-0.53679500
C	6.43166881	-2.19649388	-0.64038500
C	7.05507081	-2.09577088	0.75095600
H	6.60504181	-1.29033088	1.33300900
H	6.93304981	-3.03915988	1.29360200
H	8.12711681	-1.89793888	0.64919300
C	6.49924081	-0.87752788	-1.40938700
H	7.54785381	-0.62875488	-1.60252500
H	5.98865281	-0.97105288	-2.37370200
H	6.04513781	-0.06168388	-0.84515100
C	7.08561781	-3.31947188	-1.44217100
H	6.61287481	-3.42138388	-2.42415400
H	8.14643081	-3.09606988	-1.58962400

H	7.00271081	-4.27368388	-0.91223100
H	0.78287081	-1.59716488	-1.40168900
H	1.76700881	-0.25102388	-0.80124300
H	-0.73730519	1.10146112	1.40976400
H	0.98274881	0.89751612	1.20136900

Number of imaginary frequency- 0
Single point energy - -1449.13169582 H
Thermal correction to Gibbs' free-energy - 0.401347 H

Unsubsituted PNA monomer (Z isomer) *aeg*-Z-isomer

0 1

N	0.57647063	0.15294117	0.00000000
C	0.27487063	1.44896517	-0.57489800
C	0.46793063	2.58118317	0.42627000
O	0.63416263	2.43899217	1.62307300
O	0.40424963	3.76531717	-0.19530500
C	0.52613963	4.95799917	0.63607900
H	1.47909063	4.90819517	1.16956600
H	-0.28585937	4.94949617	1.36844400
C	1.88164163	-0.20906883	0.08347900
O	2.79655663	0.51088817	-0.32968500
C	2.18251063	-1.56063283	0.74433500
H	1.56842163	-2.35398483	0.32151100
H	1.97241163	-1.49618983	1.81496000
C	-0.54084237	-0.64721283	0.50596300
C	-1.16795537	-1.50646083	-0.60315700
N	-2.33223837	-2.23376383	-0.13194400
H	-2.19338837	-3.10485983	0.36306600
N	3.58052563	-1.92249083	0.57062400
C	4.53033863	-1.46236883	1.45717600
C	3.93292963	-2.61674783	-0.57413600
H	4.13210663	-0.90036183	2.29439100
C	5.86079163	-1.68984583	1.32256300
N	5.28504263	-2.86381383	-0.69159800
O	3.11490763	-2.99282683	-1.41346500
C	6.87721863	-1.19511183	2.30812700
C	6.30879063	-2.44982283	0.16581300
H	5.56486863	-3.38538183	-1.51679300
H	7.43781863	-2.02738083	2.74868200
H	7.60713763	-0.53599283	1.82479700
H	6.39142963	-0.64006883	3.11497100
O	7.48103463	-2.73825283	-0.09298100
C	0.45174263	6.16137417	-0.27634800
H	-0.50262637	6.19404617	-0.81170700
H	0.53875563	7.07215217	0.32550400

H	1.26693163	6.15392717	-1.00704700
C	-3.56120337	-1.65204783	-0.05592500
O	-3.82768037	-0.54264383	-0.51206300
O	-4.42665437	-2.48275083	0.56753400
C	-5.84684737	-2.11864583	0.76348400
C	-6.53208037	-1.93660283	-0.59004700
H	-6.14843137	-1.06190983	-1.11700900
H	-6.38401437	-2.82343283	-1.21518900
H	-7.60772837	-1.80690683	-0.43201800
C	-5.94964537	-0.87412683	1.64438900
H	-7.00062237	-0.69956983	1.89692100
H	-5.39491937	-1.02007783	2.57728900
H	-5.56191337	0.00921517	1.13490400
C	-6.40717037	-3.33931283	1.48968800
H	-5.88745137	-3.49878283	2.43978000
H	-7.47037537	-3.18688283	1.69793500
H	-6.29967837	-4.23911383	0.87570400
H	-1.29065237	0.03776217	0.90966300
H	-0.20891437	-1.27879183	1.33129700
H	-1.46707337	-0.86885183	-1.43815200
H	-0.43684437	-2.23010083	-0.97233000
H	-0.76750937	1.46091517	-0.90475400
H	0.90269363	1.63753317	-1.44741000

Number of imaginary frequency- 0
Single point energy - -1449.13289033 H
Thermal correction to Gibbs' free-energy - 0.402857 H

Figure S25. Optimiseed geometries from theoretical calculations

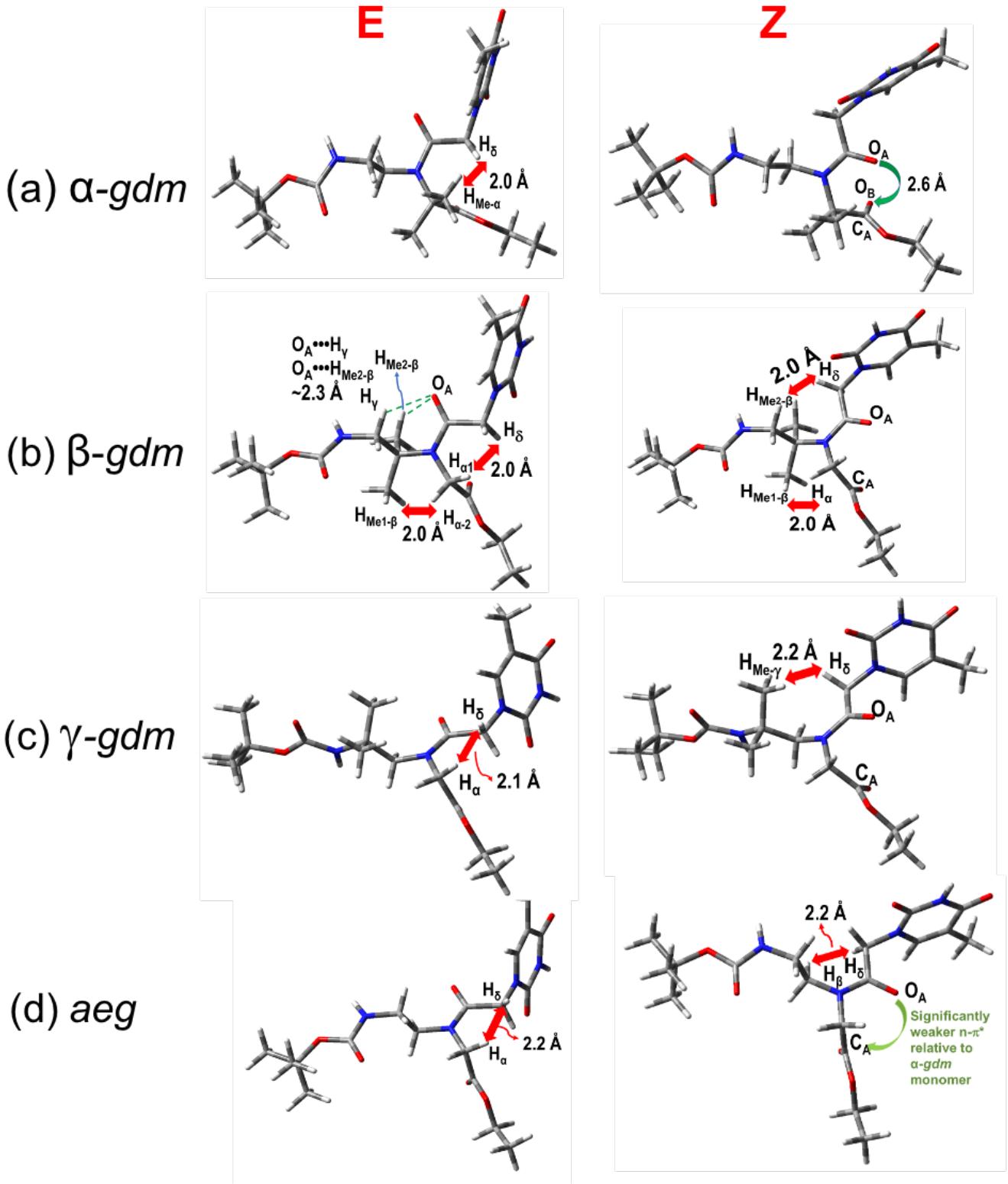

Figure S26. ORTEP diagram of compound 6; H-atoms are omitted for clarity. Four molecules are found in the asymmetric unit. Ellipsoids are drawn at 50% probability (CCDC **2054596**)