

## SUPPORTING INFORMATION

### **Elucidation of the role of betaine hydrochloride in glycerol esterification: towards bio-based ionic building blocks**

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## 1. Theoretical Calculations

All structures were studied using the B3LYP method<sup>1</sup> of the density functional theory. The structures were fully optimized using the 6-31+G(d,p) basis sets (B3LYP/6-31+G(d,p)).

Enthalpies and Gibbs free energies were computed at 298.15 K without scaling vibrational frequencies.

All calculations were performed with the Gaussian 09 package.<sup>2</sup>

## 2. Computed energies

**Table S1.** Total electronic energies ( $E_e$ ), zero-point corrected electronic energies ( $E_{ZPE}$ ), enthalpies ( $H_{298}$ ) and Gibbs free energies ( $G_{298}$ ) for gas phase compounds at 298.15K.

Compounds	Structures	$E_e^a$	$E_{ZPE}$	$H_{298}$	$G_{298}$	$\Delta G^b$
<b>GB</b> glycine betaine (zwitterion)		-402.35053	-402.18528	-402.17550	-402.21831	
<b>HCl</b>		-460.80321	-460.79649	-460.79319	-460.81438	
<b>GB1</b> (Betaine hydrochloride)	<b>GB1-1</b>	-863.19000	-863.01086	-862.99922	-863.04716	0.0
	<b>GB1-2</b>	-863.18380	-863.00640	-862.99537	-863.04190	3.3
	<b>GB1-3</b>	-863.18171	-863.00280	-862.99093	-863.03941	4.9
	<b>GB1-4</b>	-863.17620	-862.99734	-862.98542	-863.03422	8.1
	<b>GB1-5 (HCl)<sup>c</sup></b>	-863.17472	-863.00035	-862.98801	-863.03962	4.7
	<b>GB1-6 (HCl)</b>	-863.17463	-863.00014	-862.98784	-863.03915	5.0
	<b>GB1-7</b>	-863.17422	-862.99511	-862.98315	-863.03227	9.3
	<b>GB1-8</b>	-863.17098	-862.99195	-862.98082	-863.02748	12.4
	<b>GB1-9</b>	-863.16201	-862.98345	-862.97138	-863.02057	16.7
<b>GB1</b> dimer	<b>(GB1)<sub>2</sub>-1</b>	-1726,41572	-1726,05774	-1726,03322	-1726,11343	0.0
	<b>(GB1)<sub>2</sub>-2</b>	-1726,41652	-1726,05842	-1726,03408	-1726,11220	0.8
	<b>(GB1)<sub>2</sub>-3 (HCl)</b>	-1726.40878	-1726.05421	-1726.02931	-1726.11096	1.6
	<b>(GB1)<sub>2</sub>-4 (HCl)</b>	-1726.40626	-1726.05017	-1726.02547	-1726.10612	4.6
	<b>(GB1)<sub>2</sub>-5</b>	-1726,40807	-1726,04756	-1726,02255	-1726,10315	6.5

<sup>a</sup> Electronic structure calculations at the B3LYP/6-31+G(d,p) level. All values are in atomic units (1a.u. = 627.51kcal/mol).

<sup>b</sup> Relative Gibbs free energies in kcal/mol.

<sup>c</sup> This structure contains non-dissociated HCl unit.

**Table S2.** Total electronic energies ( $E_e$ ), zero-point corrected electronic energies ( $E_{ZPE}$ ), enthalpies ( $H_{298}$ ) and Gibbs free energies ( $G_{298}$ ) for gas phase structures involved in the reaction profiles.

Reaction profile for **GB1** + HCl + secondary hydroxyl glycerol

Structures	$E_e^a$	$E_{ZPE}$	$H_{298}$	$G_{298}$	$\Delta G^b$
<b>R</b>	-1668.83662	-1668.5291	-1668.50539	-1668.58461	0.0
<b>TS1</b>	-1668.80057	-1668.49019	-1668.46933	-1668.53911	28.6
<b>TI1</b>	-1668.8131	-1668.50227	-1668.48027	-1668.55359	19.5
<b>TI2</b>	-1668.81489	-1668.50438	-1668.48239	-1668.5559	18.0
<b>TS2</b>	-1668.79453	-1668.4858	-1668.46469	-1668.535	31.1
<b>P</b>	-1668.82971	-1668.52207	-1668.49809	-1668.57754	4.4

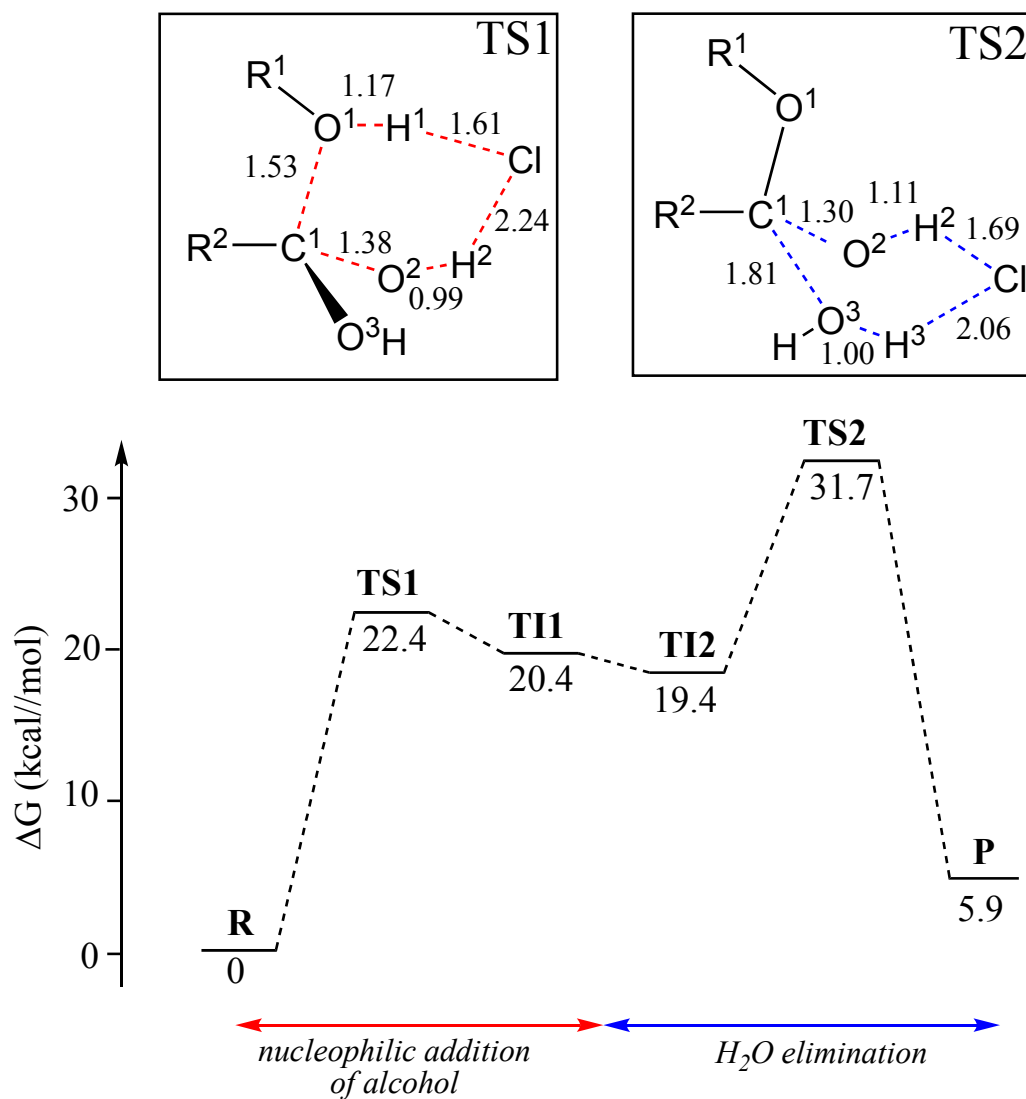
Reaction profile for **GB1** + HCl + primary hydroxyl glycerol

Structures	$E_e^a$	$E_{ZPE}$	$H_{298}$	$G_{298}$	$\Delta G^b$
<b>R</b>	-1668.83662	-1668.5291	-1668.50539	-1668.58461	0.0
<b>TS1</b>	-1668.81004	-1668.50029	-1668.47959	-1668.54893	22.4
<b>TI1</b>	-1668.81171	-1668.50168	-1668.47977	-1668.55209	20.4
<b>TI2</b>	-1668.81173	-1668.50204	-1668.48002	-1668.55376	19.4
<b>TS2</b>	-1668.79398	-1668.48577	-1668.46498	-1668.53416	31.7
<b>P</b>	-1668.82606	-1668.51899	-1668.49485	-1668.57519	5.9

<sup>a</sup> Electronic structure calculations at the B3LYP/6-31+G(d,p) level. All values are in atomic units (1 a.u. = 627.51 kcal/mol).

<sup>b</sup> Relative energies in kcal/mol.

### 3. Energetic profile (primary hydroxyl)



**Figure S1.** Computed B3LYP/6-31+G(d,p) Gibbs free energy profiles for the C-O bond formation step (primary hydroxyl) and H<sub>2</sub>O elimination step in the esterification reaction and calculated transition state structures. The Gibbs free energy are given in kcal.mol<sup>-1</sup> and distances are in angstroms.

## 4. Optimized structures

- Betaine (zwitterion) **GB**
  - gas phase HCl
  - Betaine hydrochloride **GB1** (nine structures, GB1-1 to GB1-9)
  - Betaine dimers: (**GB1**)<sub>2</sub> (five structures)
  - Equilibrium structures (**R**, **TI1**, **TI2**, **P**) and transition structures (**TS1**, **TS2**) for HCl-catalyzed esterification reaction profiles:
    - **GB1** + HCl + sec-glycerol
    - **GB1** + HCl + prim-glycerol
- R**: Reactant structure, i.e., (**GB** + HCl + glycerol) van der Waals complexe  
**TS1**: HCl-catalyzed nucleophilic addition transition structure  
**TI1**: tetrahedral intermediate resulting from nucleophilic addition  
**TI2**: rearranged tetrahedral intermediate  
**TS2**: HCl-catalyzed H<sub>2</sub>O elimination transition structure  
**P**: Product structure, i.e., (ester + HCl + H<sub>2</sub>O) Van der Waals complexe

## Cartesian Coordinates in Å

### Glycine Betaine (zwitterion) **GB**

Charge = 0 Multiplicity = 1

```
N,0,-2.7004742949,-1.2431285656,-1.1489255413
C,0,-1.5662412874,-0.3065789007,-0.6933491562
C,0,-4.0197578626,-0.6237428076,-0.8040200343
C,0,-2.6196236484,-1.4511643732,-2.6398663157
O,0,0.0631911641,-1.8948643736,-1.5407258912
C,0,-0.0843227435,-0.7852108802,-0.9695667859
O,0,0.7247643909,0.057239983,-0.5553539636
C,0,-2.5734660259,-2.5725567874,-0.4495006512
H,0,-1.7354169464,0.6463322847,-1.2000191914
H,0,-1.7021175063,-0.1630823688,0.3810516101
H,0,-4.8257465266,-1.2869562454,-1.126580171
H,0,-4.105441102,0.3381532259,-1.3113583217
H,0,-4.0720015194,-0.4741582603,0.275273423
H,0,-3.4338556465,-2.1116303331,-2.9448459937
H,0,-1.6402208221,-1.8840797498,-2.8478441999
H,0,-2.7215387908,-0.4797534315,-3.1267190976
H,0,-1.5950449853,-2.9774811568,-0.7114955665
H,0,-3.3880349097,-3.2201544715,-0.7800945354
H,0,-2.6427939371,-2.4010987883,0.6260673837
```

### HCl

Charge = 0 Multiplicity = 1

```
H,0,0.,0.,0.0068373448
Cl,0,0.,0.,1.2931626552
```

### GB1-1

Charge = 0 Multiplicity = 1

C,0,-0.7148845627,0.8047038037,-0.132909962  
C,0,-0.9267951171,-0.707577974,-0.3304551241  
O,0,-0.6809526561,1.5509964968,-1.0977623895  
O,0,-0.574950813,1.2081692451,1.1110441841  
N,0,0.3157226689,-1.3792542379,-0.9183063078  
C,0,0.1915183644,-2.8580091096,-0.6520141226  
C,0,0.3936426375,-1.1187777682,-2.398411301  
C,0,1.5826794514,-0.8816019358,-0.2518871946  
H,0,-1.7380589391,-0.8651068105,-1.04314484  
H,0,-1.1218594061,-1.2008638395,0.6239512159  
H,0,-0.4778230141,0.4330998492,1.7767275249  
H,0,1.035645887,-3.3690025784,-1.1180339741  
H,0,-0.7457303712,-3.2130722825,-1.0830310954  
H,0,0.1943505089,-3.0049880402,0.4302116556  
H,0,1.3175479306,-1.5557450465,-2.7804936552  
H,0,0.370722835,-0.0410666558,-2.5598320466  
H,0,-0.4677677735,-1.5830663384,-2.8810520649  
H,0,2.4138562177,-1.4752400332,-0.6351683908  
H,0,1.4675829882,-1.0082156568,0.8290890855  
H,0,1.7232589795,0.1676951455,-0.5103135362  
Cl,0,-0.0955237716,-1.215042109,2.7526884346

### GB1-2

Charge = 0 Multiplicity = 1

C,0,-0.5982403273,0.9125524809,-0.1507024871  
C,0,-0.6523082624,-0.6239033298,-0.0524319471  
O,0,0.2557762555,1.4843338535,-0.8200422979  
O,0,-1.5256941487,1.5164093666,0.530575004  
N,0,0.422556449,-1.3612962982,-0.8406871362  
C,0,0.1979204362,-2.8337497921,-0.6153036049  
C,0,0.3090527894,-1.0716780512,-2.3177704083  
C,0,1.802918067,-0.9982668553,-0.3494057437  
H,0,-1.624014853,-0.9863874876,-0.3940192643  
H,0,-0.5726861361,-0.9347773712,0.9912656664  
H,0,-2.1704188913,0.8511349155,1.0445554744  
H,0,0.9538442953,-3.3933175666,-1.168368629  
H,0,-0.8000355535,-3.0983186641,-0.9655193717  
H,0,0.2756263005,-3.0455564415,0.4513097806  
H,0,1.0487923985,-1.6763362851,-2.8450257407  
H,0,0.4856701048,-0.0091812852,-2.4703340537  
H,0,-0.6964094394,-1.3426159979,-2.642972285  
H,0,2.5315038512,-1.6033320041,-0.8915157953  
H,0,1.8544682822,-1.2174488993,0.7180300127  
H,0,1.9591496081,0.0632771162,-0.5285323203  
Cl,0,-3.1277844691,-0.4806265794,1.8206226015

### GB1-3

Charge = 0 Multiplicity = 1

C,0,-0.6421010713,0.8713686717,-0.1536552484  
C,0,-0.6595038051,-0.6267123266,-0.0117595771  
O,0,0.2182457643,1.553433803,-0.6775072642  
O,0,-1.7422430779,1.3865251686,0.4246678448  
N,0,0.3944279846,-1.3623827429,-0.8156976222

C,0,0.14974591,-2.8418829886,-0.5978481817  
C,0,0.2976568584,-1.0516728068,-2.2820778091  
C,0,1.7857125198,-1.0349708214,-0.3003135649  
H,0,-1.6387158845,-1.0141957992,-0.3013560618  
H,0,-0.4761465296,-0.9165964439,1.0582801895  
H,0,-1.6718530938,2.3560886644,0.3889605646  
H,0,0.9258124426,-3.39298272,-1.1307112141  
H,0,-0.8333146911,-3.0928503625,-1.0001068327  
H,0,0.1968990727,-3.0270347867,0.4823127302  
H,0,1.0238584953,-1.6694798642,-2.8125768168  
H,0,0.5141227771,0.0036592243,-2.4363979338  
H,0,-0.710574399,-1.290786481,-2.6256531623  
H,0,2.4937386769,-1.6541759803,-0.8533911895  
H,0,1.7964477845,-1.2774612258,0.7682276453  
H,0,1.9754814524,0.0214595596,-0.4755821479  
Cl,0,0.4032341291,-2.0015640953,2.6877804305

#### GB1-4

Charge = 0 Multiplicity = 1

C,0,-0.7045403322,0.9113327085,-0.3315615696  
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O,0,-1.7426015245,1.5145000408,-0.1817209107  
O,0,0.4560603977,1.5265909919,-0.6756061013  
N,0,0.4306998193,-1.3841642753,-0.8411716875  
C,0,0.1338818839,-2.8407381127,-0.5379265474  
C,0,0.3210282774,-1.1505571884,-2.3185472322  
C,0,1.8430247587,-1.0945286327,-0.3640999773  
H,0,-1.5818946179,-0.9997358058,-0.2927051325  
H,0,-0.3776748528,-0.7575581882,1.0102926985  
H,0,0.2686547506,2.4808045299,-0.7205966208  
H,0,0.8833638173,-3.4497876862,-1.0451334789  
H,0,-0.8623479493,-3.0773053241,-0.9150027083  
H,0,0.1891929197,-2.9634166491,0.5508968656  
H,0,1.011509128,-1.8233887376,-2.8295540861  
H,0,0.5813794872,-0.115897464,-2.5376637637  
H,0,-0.7022649356,-1.359425637,-2.6355299198  
H,0,2.5112944497,-1.779984343,-0.8877141033  
H,0,1.8574039243,-1.27274695,0.7176992524  
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Cl,0,0.520497153,-1.8062160681,2.6779150176

#### GB1-5

Charge = 0 Multiplicity = 1

C,0,-0.8272019714,0.8560659494,-0.0770935548  
C,0,-0.7534859288,-0.7086768153,-0.0574479433  
O,0,-1.7757744016,1.2885944266,0.5744411907  
O,0,0.0783239606,1.4504645269,-0.74548297  
N,0,0.3890649192,-1.3809058664,-0.8333296204  
C,0,0.2645290081,-2.8678441544,-0.6763939851  
C,0,0.3011635829,-1.0295528854,-2.2984115145  
C,0,1.7230411545,-0.9361260103,-0.2853396175  
H,0,-1.6830190218,-1.107659182,-0.4695456298  
H,0,-0.6605947871,-1.0413475949,0.9787504336  
H,0,0.2021059222,3.0053403006,-0.9049630677

H,0,1.0729737585,-3.3548732795,-1.2251589203  
H,0,-0.6991116258,-3.1892671523,-1.0734658737  
H,0,0.3296719271,-3.1217904154,0.3823053812  
H,0,1.1099569267,-1.5388697585,-2.8253748049  
H,0,0.3845822951,0.0531872169,-2.3827408593  
H,0,-0.6647025695,-1.3701458301,-2.6750949515  
H,0,2.5123909564,-1.4470045817,-0.8395697302  
H,0,1.7684313747,-1.2098832361,0.770018026  
H,0,1.7833398248,0.1450168264,-0.4031602871  
Cl,0,0.5103525385,4.3019417785,-1.182962718

### GB1-6

Charge = 0 Multiplicity = 1

C,0,-0.3528107913,0.976817547,-0.2854741888  
C,0,-0.5369357894,-0.5657110095,-0.0852197389  
O,0,0.5429266855,1.3817892806,-1.048617992  
O,0,-1.1991577412,1.5967749016,0.4057378149  
N,0,0.4226930519,-1.4725875387,-0.8634389741  
C,0,0.0965491418,-2.9023902368,-0.5475803632  
C,0,0.2642771466,-1.2434696138,-2.3469831729  
C,0,1.8486099361,-1.1876807274,-0.4583462044  
H,0,-1.548025836,-0.8480659798,-0.3867922439  
H,0,-0.4079504857,-0.8077153129,0.9720275576  
H,0,-1.2745578562,3.1793208594,0.4202387775  
H,0,0.776669722,-3.5547048311,-1.0989062789  
H,0,-0.9337755334,-3.1067110969,-0.841493675  
H,0,0.2122654057,-3.0663493489,0.5245339671  
H,0,0.9392562736,-1.9188872404,-2.8756091159  
H,0,0.5020386287,-0.1983941439,-2.5429350181  
H,0,-0.7704811717,-1.4587751451,-2.6181794235  
H,0,2.5062198894,-1.8635162448,-1.0079118236  
H,0,1.941471786,-1.3635836755,0.6145308893  
H,0,2.052405363,-0.1437043487,-0.6943303165  
Cl,0,-1.4563768755,4.5207628272,0.5311291994

### GB1-7

Charge = 0 Multiplicity = 1

C,0,-0.6256075126,0.9037549555,-0.1742037806  
C,0,-0.6666491195,-0.6165726545,-0.0855502808  
O,0,0.1595759598,1.5866982414,-0.7879108258  
O,0,-1.638192261,1.4002721276,0.5648200872  
N,0,0.387348675,-1.3619030298,-0.845868553  
C,0,0.1576996234,-2.8449916005,-0.6171767549  
C,0,0.300654153,-1.0980904655,-2.3389310257  
C,0,1.7843853025,-1.0224808245,-0.3565849075  
H,0,-1.6450754668,-0.9519017825,-0.4415631557  
H,0,-0.5897889948,-0.8980714362,0.9686542985  
H,0,-1.6080565575,2.3714288975,0.5051744462  
H,0,0.9403741783,-3.3761050719,-1.1813816964  
H,0,-0.8386408842,-3.0997867081,-0.9830567764  
H,0,0.2340905842,-3.0443760078,0.4532975422  
H,0,1.0540410742,-1.7448268211,-2.8095643399  
H,0,0.5066030153,-0.0450936122,-2.5174425001  
H,0,-0.7064251381,-1.3610080769,-2.6694537977



H,0,2.4717427991,-1.6731070193,-0.9146835203  
H,0,1.8261244467,-1.2313108369,0.7145067332  
H,0,1.9755408475,0.0295629321,-0.5559371201  
Cl,0,2.7997076933,-3.3805907339,-2.5759884552

### GB1-8

Charge = 0 Multiplicity = 1

C,0,-0.6087992768,0.9426077205,-0.1730904738  
C,0,-0.6307388389,-0.5837376654,-0.1705906762  
O,0,-1.3474049221,1.5573377526,0.5591875281  
O,0,0.2387683269,1.5243646296,-1.0420159074  
N,0,0.4337646481,-1.3756134287,-0.8789328968  
C,0,0.1727408678,-2.8454349728,-0.593251395  
C,0,0.3914561665,-1.1876530877,-2.3848007134  
C,0,1.8218260429,-1.04299362,-0.3649738751  
H,0,-1.5974861844,-0.8824932554,-0.5871543079  
H,0,-0.6230698754,-0.8827344661,0.8798154462  
H,0,0.1388802723,2.48939096,-0.9514361308  
H,0,0.9564290098,-3.411801195,-1.1191835755  
H,0,-0.8214170273,-3.0975019935,-0.9664716507  
H,0,0.2269005626,-3.0021114566,0.4853383065  
H,0,1.1527962,-1.8629619781,-2.7994770308  
H,0,0.6096541203,-0.1482748225,-2.6161552368  
H,0,-0.6081260465,-1.4589877332,-2.7302403322  
H,0,2.5125046104,-1.7282642038,-0.8768121569  
H,0,1.8308116438,-1.2046232794,0.7148138298  
H,0,2.0433256213,-0.0049065177,-0.6031552506  
Cl,0,2.8820144692,-3.4800206443,-2.4508731697

### GB1-9

Charge = 0 Multiplicity = 1

C,0,-0.6389021468,0.9583587742,-0.0940716652  
C,0,-0.6872981037,-0.5713486119,-0.0126859524  
O,0,0.1502918632,1.6074755753,-0.7273685881  
O,0,-1.6011071044,1.5669068855,0.6384625336  
N,0,0.3458520907,-1.3220249798,-0.7990290289  
C,0,0.1099414864,-2.8048886104,-0.5726684341  
C,0,0.2296851638,-1.0501315546,-2.2895329128  
C,0,1.7561806813,-0.9951662577,-0.3370514271  
H,0,-1.6694131962,-0.9112095521,-0.359220513  
H,0,-0.5789834325,-0.8708844717,1.0355666783  
H,0,-2.1781389502,0.9437203143,1.1059515765  
H,0,0.8777096651,-3.3381226426,-1.1571008375  
H,0,-0.8952348994,-3.0516226755,-0.919947854  
H,0,0.2090636522,-3.0112625021,0.4947788164  
H,0,0.9681927182,-1.7016956066,-2.7767489947  
H,0,0.4387398741,0.0021250181,-2.4671901285  
H,0,-0.7855246452,-1.3058201611,-2.6005667642  
H,0,2.424755138,-1.6495920674,-0.9131848086  
H,0,1.8192320476,-1.2115560687,0.7315843849  
H,0,1.9505061117,0.0564198074,-0.5341517009  
Cl,0,2.6906635418,-3.3712024833,-2.5755331936

**(GB1)<sub>2</sub>-1**

Charge = 0 Multiplicity = 1  
N,0,-0.0305258907,-0.2936801756,-1.5998437894  
C,0,1.3562788709,0.2988739108,-1.7758811179  
C,0,-0.924213882,0.814150495,-1.0932247017  
C,0,-0.5701780136,-0.8155782463,-2.9035113242  
O,0,2.2274725599,-1.8476799652,-2.5290741869  
C,0,2.4204358544,-0.6639328633,-2.3063410352  
O,0,3.5420214352,0.0017570353,-2.4661712839  
C,0,-0.0143622865,-1.3997126232,-0.5621188094  
H,0,1.2651513398,1.1457613135,-2.4606357319  
H,0,1.6531679967,0.6801976811,-0.7898251817  
H,0,-1.9230073785,0.4027318002,-0.9395372914  
H,0,-0.9572122501,1.6063404044,-1.8430145945  
H,0,-0.5057337107,1.1829295398,-0.1524386064  
H,0,-1.5905438245,-1.1642218866,-2.7369024881  
H,0,0.067486979,-1.6292621022,-3.2429298093  
H,0,-0.5717163732,-0.0015920482,-3.6308038603  
H,0,4.353516777,-0.5814150098,-2.7215614034  
H,0,0.6295016881,-2.1972864466,-0.9254362601  
H,0,-1.0404311998,-1.7504234326,-0.4385184933  
H,0,0.3617593203,-0.9693490582,0.3698153583  
Cl,0,1.2913899914,1.0630239079,1.6405980673  
N,0,7.4184424088,0.0236954826,0.3199869217  
C,0,6.0310729727,-0.5679253188,0.4948788796  
C,0,8.311626827,-1.0844959611,-0.1866523661  
C,0,7.4037065081,1.1303612902,-0.7171101173  
O,0,5.1609924373,1.5787965474,1.2488946652  
C,0,4.967327536,0.3953147075,1.0253767248  
O,0,3.8452174698,-0.2696957191,1.1843593366  
C,0,7.9576850119,0.5444866374,1.6242663244  
H,0,5.7344999076,-0.94831071,-0.4916309434  
H,0,6.1211984304,-1.4153574252,1.1790921589  
H,0,9.3107078546,-0.6736423861,-0.3399838241  
H,0,7.8932596658,-1.4528614771,-1.1276340907  
H,0,8.3440203591,-1.8768778087,0.5629627025  
H,0,8.4301014885,1.4804294627,-0.8398246481  
H,0,6.760177646,1.9281617484,-0.3536958032  
H,0,7.0278209278,0.7008195632,-1.649518317  
H,0,3.0340428008,0.3139653858,1.4397089397  
H,0,7.3205259359,1.3585864559,1.963636958  
H,0,8.9784823434,0.8922827352,1.4585121234  
H,0,7.957976713,-0.2698349316,2.3511881338  
Cl,0,6.0966067523,-1.3294825088,-2.9216642153

**(GB1)<sub>2</sub>-2**

Charge = 0 Multiplicity = 1  
N,0,-1.4886275739,-0.3394294231,-0.8567586246  
C,0,-0.5776228588,-1.3919153186,-0.2507682664  
C,0,-2.6921770958,-0.225883403,0.0494024706  
C,0,-0.8061798719,1.0158311739,-0.9044598842  
O,0,1.0836996298,-1.0473709757,-2.0001775383  
C,0,0.7048548622,-1.6874820233,-1.029336052  
O,0,1.3137182163,-2.7018791229,-0.4648468968

C,0,-1.9328961882,-0.7410556879,-2.2357338554  
H,0,-0.324184098,-1.0357500169,0.7575377064  
H,0,-1.1592602622,-2.3117381708,-0.1535559227  
H,0,-3.3577067537,0.5353316193,-0.3605669419  
H,0,-2.3396025087,0.0616003097,1.0438685937  
H,0,-3.2006683405,-1.1909956366,0.0789074087  
H,0,-1.5318521591,1.7324884825,-1.2932267074  
H,0,0.0589007017,0.9394929566,-1.5576376794  
H,0,-0.5116661168,1.2752952,0.1152982767  
H,0,2.2670856862,-2.8761003815,-0.8257714308  
H,0,-1.0584766507,-0.7923282054,-2.8816660645  
H,0,-2.6389887249,0.0061626228,-2.6010616302  
H,0,-2.4222456175,-1.7149676995,-2.1763944348  
Cl,0,-0.379224401,0.6585843767,2.5783705303  
N,0,5.1778389349,0.3322495849,-0.3361104566  
C,0,4.2971199188,-0.23832112,0.7610163182  
C,0,6.3962991834,-0.556303963,-0.4277979563  
C,0,4.4709364104,0.3015508092,-1.6792897141  
O,0,2.596664647,1.4612961759,0.3627403136  
C,0,3.0056700283,0.5304754019,1.0425161246  
O,0,2.426321536,0.0058740097,2.0949108454  
C,0,5.6026503513,1.7369551031,-0.0098521825  
H,0,4.0562420604,-1.2670220194,0.4583826592  
H,0,4.8967151355,-0.2806371686,1.6734308599  
H,0,7.0401536102,-0.1722718773,-1.2205171504  
H,0,6.0577057792,-1.5699709651,-0.6595734409  
H,0,6.9223865401,-0.5290033238,0.5279070379  
H,0,5.1763832588,0.6681543581,-2.4271404162  
H,0,3.5950275663,0.9418155172,-1.6185710468  
H,0,4.1914643205,-0.7348295969,-1.8836837657  
H,0,1.4696172485,0.3577273861,2.2694347829  
H,0,4.7171461919,2.3686739726,0.0260359986  
H,0,6.2885852146,2.0782791936,-0.7866253842  
H,0,6.1098636696,1.7340902561,0.9566956597  
Cl,0,4.1159335196,-3.1660604107,-1.1452741433

**(GB1)<sub>2</sub>-3**

Charge = 0 Multiplicity = 1

N,0,-1.5703403444,-1.2127977476,-1.4054195547  
C,0,-0.3909387265,-2.1355664173,-1.1121766392  
C,0,-1.4298255657,0.0000360798,-0.5252480281  
C,0,-1.5373880137,-0.7608974988,-2.8492006668  
O,0,-1.1835950046,-3.7321095293,-2.7618598269  
C,0,-0.2650155754,-3.3962311754,-2.0024517509  
O,0,0.867927759,-3.9543249226,-1.8195350458  
C,0,-2.8740522981,-1.9035128508,-1.1133821874  
H,0,0.50468873,-1.5263099985,-1.2430239255  
H,0,-0.4708404973,-2.4309844613,-0.062609544  
H,0,-2.2821509563,0.6590096869,-0.7008856758  
H,0,-0.4981017374,0.5074735401,-0.7762723714  
H,0,-1.4088459399,-0.3180679853,0.5176424763  
H,0,-2.3415512284,-0.0366869199,-2.9925781407  
H,0,-1.6791835479,-1.6375282689,-3.4777800643  
H,0,-0.564899189,-0.2996143467,-3.034100182  
H,0,1.5771178596,-4.5780487891,-2.9209564895

H,0,-2.9282100506,-2.7906657623,-1.7429326746  
H,0,-3.6897671505,-1.2109338496,-1.3288437338  
H,0,-2.8900924287,-2.1795725437,-0.0574045194  
Cl,0,2.0153372007,0.2023814114,-2.4501968699  
Cl,0,2.3290107153,0.5613149607,0.8031450903  
H,0,2.2144387628,0.4778237704,-0.5584327862  
N,0,4.895410802,-2.4794631807,-2.6798594767  
C,0,3.5609132608,-3.2086271988,-2.6460284996  
C,0,4.9555786168,-1.5978032617,-1.4545011781  
C,0,6.0551416616,-3.4398872076,-2.6453119389  
O,0,4.1615701725,-4.4027886764,-4.6687243562  
C,0,3.3387611387,-4.2299097469,-3.7795628484  
O,0,2.2157197912,-4.8912004262,-3.6940995953  
C,0,4.9795049376,-1.5953986448,-3.9050990953  
H,0,3.4887112452,-3.71206662,-1.6795967919  
H,0,2.7867846741,-2.4366323951,-2.6660515991  
H,0,5.9038986229,-1.0584598492,-1.4675616106  
H,0,4.8935812222,-2.2255528446,-0.5649351218  
H,0,4.1187713525,-0.8988417621,-1.4903252513  
H,0,6.9760528731,-2.8582747095,-2.5817354953  
H,0,6.0329166622,-4.0457748478,-3.5479355338  
H,0,5.9540395203,-4.0696278871,-1.7595662348  
H,0,4.9252185903,-2.2307140546,-4.7863799103  
H,0,5.9293531659,-1.0594298597,-3.8675246065  
H,0,4.146400917,-0.8906612091,-3.864515746

**(GB1)<sub>2</sub>-4**

Charge = 0 Multiplicity = 1

N,0,-1.5142752229,-1.1516791081,-1.458326179  
C,0,-0.4267945128,-2.1748353627,-1.1446968697  
C,0,-1.2619863116,0.047319398,-0.5801840444  
C,0,-1.4153577859,-0.7069425168,-2.9024557178  
O,0,-1.3581176663,-3.7192390402,-2.7551026556  
C,0,-0.3681359114,-3.4270546381,-2.0433748589  
O,0,0.7320296818,-4.0370926722,-1.9393721211  
C,0,-2.8847751104,-1.7050737974,-1.1808043763  
H,0,0.5201286134,-1.6342556759,-1.231973103  
H,0,-0.574709297,-2.4868080771,-0.1065173715  
H,0,-2.0327198897,0.7933216972,-0.7822139725  
H,0,-0.2696027353,0.4399780363,-0.8163222171  
H,0,-1.3127645101,-0.266710347,0.4637329942  
H,0,-2.1487033203,0.086264254,-3.0588536645  
H,0,-1.6302009836,-1.5643825767,-3.5366265902  
H,0,-0.4013465035,-0.3328039184,-3.0648431188  
H,0,1.5207209144,-4.5451875908,-3.163342652  
H,0,-3.0305138457,-2.5814466775,-1.8096742028  
H,0,-3.6213579944,-0.9306894088,-1.4023616778  
H,0,-2.9405007209,-1.9790471814,-0.1255920603  
Cl,0,2.0341409892,0.0698254254,-2.1571338368  
N,0,4.8214543201,-2.4656519466,-2.6627436662  
C,0,3.4791499533,-3.1782802609,-2.7201179571  
C,0,4.8868872644,-1.7467536292,-1.3345782142  
C,0,5.9721124786,-3.4326130559,-2.7510659899  
O,0,4.0647824357,-4.1167702465,-4.877279119  
C,0,3.2577751909,-4.0539165684,-3.9636662732

O,0,2.1352278977,-4.7361113291,-3.9568710748  
C,0,4.9142274638,-1.4313603884,-3.7658828947  
H,0,3.3951336154,-3.791226636,-1.8198453673  
H,0,2.7171717583,-2.3927069117,-2.6560184116  
H,0,5.8337214085,-1.2063435554,-1.2891404843  
H,0,4.8424777581,-2.4889847108,-0.5358650919  
H,0,4.0415383924,-1.0534716843,-1.2774960053  
H,0,6.8973873818,-2.8733640898,-2.6044674734  
H,0,5.9544278769,-3.9112276787,-3.7271840045  
H,0,5.8603906196,-4.1759103023,-1.9595121135  
H,0,4.8527576694,-1.9482299303,-4.7210490871  
H,0,5.8719800091,-0.9185452456,-3.6622773178  
H,0,4.0874601517,-0.7295793522,-3.6287354426  
H,0,-1.6869008512,-5.2404162177,-3.3655483149  
Cl,0,-2.154818161,-6.4143216523,-3.798844715

**(GB1)<sub>2</sub>-5**

Charge = 0 Multiplicity = 1

N,0,-2.7190525476,-1.4448205596,-0.8549882169  
C,0,-1.4171664458,-2.2175548574,-0.8290848385  
C,0,-3.3317045227,-1.5629219781,0.5271978677  
C,0,-2.470551607,0.0151131402,-1.1398364902  
O,0,-0.9529403603,-1.6798210608,-3.1729397044  
C,0,-0.651020222,-2.2194689348,-2.1250590046  
O,0,0.4789881173,-2.9362738384,-1.9715589721  
C,0,-3.6788626145,-2.0448158112,-1.8515390895  
H,0,-0.7985125322,-1.7737635413,-0.0300759379  
H,0,-1.6671126997,-3.2534292893,-0.5418237888  
H,0,-4.2713681039,-1.0080981854,0.5200292483  
H,0,-2.627409411,-1.1330936146,1.243158462  
H,0,-3.50330931,-2.6230264444,0.7274449912  
H,0,-3.4229925113,0.5419640818,-1.0619817859  
H,0,-2.0603026211,0.1148268618,-2.1425700301  
H,0,-1.7699624189,0.3849842913,-0.3880364027  
H,0,0.9530084322,-2.9208421738,-2.8206190505  
H,0,-3.2646548629,-1.9349686213,-2.8515556309  
H,0,-4.6280130085,-1.5126338744,-1.7698329903  
H,0,-3.810830115,-3.0975175675,-1.5921182075  
Cl,0,-0.1482855274,-0.7022606791,1.9708905317  
N,0,-0.1740036579,-4.3710783308,3.2643065451  
C,0,-1.4750702548,-3.5969826863,3.2390427328  
C,0,0.4391419899,-4.2524319469,1.8824037142  
C,0,0.786421243,-3.7731468788,4.261550392  
O,0,-1.9399821096,-4.1359429583,5.5825372189  
C,0,-2.2412991313,-3.5953552118,4.5349847052  
O,0,-3.370753468,-2.8775403664,4.3817955212  
C,0,-0.4241874842,-5.8310209443,3.5478314353  
H,0,-1.2243401133,-2.5611146779,2.9523491681  
H,0,-2.0942616254,-4.0398037794,2.4399438849  
H,0,1.3786302065,-4.8075565327,1.8896637674  
H,0,0.6111203679,-3.1922809573,1.6826984666  
H,0,-0.2649510758,-4.681779841,1.165966189  
H,0,1.7343842749,-4.3075551503,4.1806550519  
H,0,0.3711987765,-3.8820131601,5.2612725751  
H,0,0.9209359724,-2.720758055,4.0022418611

H,0,-3.8447678356,-2.8929632803,5.2308480216  
H,0,-0.834519319,-5.9311512791,4.5504930898  
H,0,0.5276591478,-6.3588727495,3.4694940626  
H,0,-1.1252059776,-6.199357732,2.7956654079  
Cl,0,-2.7440480343,-5.1124938255,0.438823229

**R (Esterification of GB1 + HCl + secondary glycerol)**

Charge = 0 Multiplicity = 1

N,0,-2.9907949665,-0.0455965002,-0.4120913621  
C,0,-1.4684880389,0.0828166157,-0.4461460836  
C,0,-3.521322799,1.179100262,0.2893876307  
C,0,-3.5417430802,-0.1157378962,-1.8117299084  
O,0,-0.7316957926,-1.5946155208,-1.9917829002  
C,0,-0.7769124363,-1.2348935789,-0.8185049276  
O,0,-0.2655912247,-1.9395990436,0.1586458386  
C,0,-3.4218357351,-1.2685806877,0.3685327942  
H,0,-1.2150759964,0.831203429,-1.1953597078  
H,0,-1.1660336788,0.4024879181,0.5512429732  
H,0,-4.611867398,1.1499406381,0.2687317869  
H,0,-3.1594950093,2.066301315,-0.2317618236  
H,0,-3.1550943237,1.1692644739,1.317108207  
H,0,-4.6216953769,-0.2593888585,-1.7533378663  
H,0,-3.0642783636,-0.9436147356,-2.3348857289  
H,0,-3.3134127754,0.8199623641,-2.3235268681  
H,0,-0.4010358568,-1.5164950403,1.0882948084  
H,0,-3.1205181939,-2.1609181655,-0.1800941379  
H,0,-4.5080819421,-1.2405246329,0.4644914866  
H,0,-2.937584379,-1.2402602297,1.3483660317  
Cl,0,-0.8293234622,-0.6084701984,2.7190873761  
C,0,2.6153322405,2.5845804879,0.357781692  
O,0,1.9295600813,3.5883041236,-0.3847222644  
C,0,1.7741536543,1.3220385492,0.5119753514  
C,0,2.4588792115,0.2337406609,1.3560793063  
O,0,1.3788565355,0.8394218552,-0.7941527688  
O,0,2.3651651512,0.5159404853,2.7418052224  
H,0,3.5739426353,2.3315044815,-0.1260062245  
H,0,2.8323592618,3.004880953,1.3432421796  
H,0,1.6356657141,3.1691543731,-1.206480295  
H,0,0.8325122721,1.5901055746,1.0021117294  
H,0,3.5284989958,0.1786391206,1.1145539507  
H,0,2.0112642392,-0.737861991,1.1126831166  
H,0,2.0999240674,0.3369112247,-1.2055485124  
H,0,1.4733819409,0.2510871808,3.0328132604  
Cl,0,2.2331205185,-1.8062761723,-3.0178339257  
H,0,0.98626131,-1.9279218345,-2.6359694368

**TS1 (Esterification of GB1 + HCl + secondary glycerol)**

Charge = 0 Multiplicity = 1

N,0,-5.2559197723,-3.5847468313,-2.1985183407  
C,0,-3.796005995,-3.1309268339,-2.1237612086  
C,0,-6.0651040396,-2.5344039182,-1.4761210863  
C,0,-5.7066533175,-3.6700725639,-3.6353282404  
O,0,-2.8278158972,-4.6855972951,-3.6619762493

C,0,-2.7703855417,-4.2308716715,-2.4146482075  
O,0,-2.5510399425,-5.1271952854,-1.4772077488  
C,0,-5.5013683202,-4.9169245849,-1.5175095105  
H,0,-3.6777603368,-2.3246309608,-2.8456515258  
H,0,-3.6413874256,-2.7749492512,-1.1044477775  
H,0,-7.1229072515,-2.7817236819,-1.574920891  
H,0,-5.8640578665,-1.5619887216,-1.9277598772  
H,0,-5.766903891,-2.5350647836,-0.4265227589  
H,0,-6.747097815,-3.9972001517,-3.6508591007  
H,0,-5.0670048362,-4.3774530335,-4.1597647735  
H,0,-5.6184704732,-2.6820073886,-4.0888008683  
H,0,-2.7360229842,-4.7632591857,-0.5268519627  
H,0,-4.9779883105,-5.6977613868,-2.0655992797  
H,0,-6.5774340163,-5.0949901213,-1.5341696383  
H,0,-5.1295752401,-4.856157271,-0.492666896  
Cl,0,-3.2601178481,-3.9299078134,1.0784509131  
C,0,0.0332470289,-1.3932253072,-1.6870707637  
O,0,-0.7927342366,-0.4205512042,-2.319374474  
C,0,-0.7418599513,-2.6378554313,-1.2670306576  
C,0,0.1137795001,-3.6481722097,-0.4769011587  
O,0,-1.3435767127,-3.1964407372,-2.4896643313  
O,0,0.152212077,-3.2664817189,0.8892878397  
H,0,0.8746383498,-1.6774968696,-2.3345282799  
H,0,0.4385711206,-0.9308398211,-0.7830763512  
H,0,-0.9977359442,-0.7424295394,-3.2069412614  
H,0,-1.5837857478,-2.3380420432,-0.6397989532  
H,0,1.1478802991,-3.6427100062,-0.8361842199  
H,0,-0.2762411955,-4.6613831564,-0.6116872295  
H,0,-0.676342555,-3.7966962456,-3.0535193702  
H,0,-0.7191781032,-3.459036261,1.2791587767  
Cl,0,0.0059881089,-5.0643611662,-4.1458987378  
H,0,-1.9358569174,-5.1146425473,-3.9263497994

### THI (Esterification of GBI + HCl + secondary glycerol)

Charge = 0 Multiplicity = 1

N,0,-2.8371091427,0.0724582654,-0.4036206313  
C,0,-1.3790349306,0.536319752,-0.3183508879  
C,0,-3.6455557491,1.084175139,0.3732377633  
C,0,-3.303864943,0.0553110024,-1.8354321059  
O,0,-0.4957716686,-1.0337893641,-1.8855388289  
C,0,-0.27376088,-0.5053382667,-0.6148750424  
O,0,-0.2087401639,-1.5305247874,0.2928416425  
C,0,-3.0822236633,-1.2877738213,0.2170500319  
H,0,-1.28186557,1.3707504847,-1.0129252457  
H,0,-1.2454862209,0.8755287951,0.708542511  
H,0,-4.7034700033,0.8379479204,0.2706667316  
H,0,-3.4512925772,2.077889453,-0.0327860139  
H,0,-3.3377529962,1.0338827341,1.4191665671  
H,0,-4.3486554977,-0.2583373612,-1.8542626257  
H,0,-2.6774356379,-0.6357905604,-2.3949290346  
H,0,-3.2103854455,1.0614806572,-2.2468455409  
H,0,-0.374561387,-1.2038718035,1.2335618544  
H,0,-2.5386019508,-2.0377670058,-0.3511487121  
H,0,-4.1577931975,-1.4693095924,0.1763374531  
H,0,-2.7259840546,-1.2640123109,1.2486021296

Cl,0,-0.9617002675,-0.3039500919,2.9144565065  
C,0,2.2598661704,2.100853899,-0.0060641372  
O,0,1.4286457283,3.005209889,-0.729919767  
C,0,1.5006004966,0.8783737972,0.4939156345  
C,0,2.3765512174,-0.0549623546,1.3554148031  
O,0,0.967133113,0.2259438819,-0.7059586054  
O,0,2.3975010299,0.4031849508,2.6976396574  
H,0,3.1163162518,1.7838619122,-0.619025918  
H,0,2.6446396568,2.6439151865,0.8606223983  
H,0,1.20295116,2.5775644256,-1.5665983631  
H,0,0.6678091372,1.2132459855,1.1156965887  
H,0,3.4141487634,-0.0439922231,1.0026931187  
H,0,2.0076223787,-1.0822013001,1.2789920161  
H,0,2.1825147365,-0.5254252502,-1.8258997338  
H,0,1.5206303394,0.2218158668,3.0844032144  
Cl,0,2.9658855053,-1.1507902259,-2.6777772803  
H,0,0.1177462629,-1.7760226783,-2.0114771479

## TI2 (Esterification of GB1 + HCl + secondary glycerol)

Charge = 0 Multiplicity = 1

N,0,-2.7958207657,0.0398574589,-0.393978544  
C,0,-1.3512261012,0.5373292268,-0.2743925836  
C,0,-3.6424853072,1.0147502764,0.3891650195  
C,0,-3.2384293732,0.0407961136,-1.8338298906  
O,0,-0.4245214447,-1.00988544,-1.8381525304  
C,0,-0.2080683913,-0.4626240384,-0.5743593205  
O,0,-0.1527366976,-1.4944275172,0.3618460198  
C,0,-3.0183956574,-1.3395309022,0.1917840355  
H,0,-1.2629849838,1.3881531655,-0.9504451557  
H,0,-1.2424220547,0.8604703911,0.7608380157  
H,0,-4.692104447,0.7445385933,0.2638961714  
H,0,-3.4667106575,2.0211324727,0.0065781345  
H,0,-3.3512898449,0.9514973742,1.4391168454  
H,0,-4.2751866718,-0.2961879927,-1.8761151925  
H,0,-2.5873366178,-0.6256588854,-2.3949265496  
H,0,-3.1613265114,1.0568240296,-2.2237702915  
H,0,-0.3301784795,-1.1643072907,1.3077463293  
H,0,-2.453143619,-2.0638546721,-0.3886133822  
H,0,-4.089104083,-1.5431422903,0.1331885422  
H,0,-2.6770923253,-1.3336716328,1.2280823575  
Cl,0,-0.9335930003,-0.3156063717,2.9547775252  
C,0,2.2667414034,2.1613468617,-0.0359486523  
O,0,1.4407209555,3.0067943364,-0.8335080532  
C,0,1.5099394474,0.9590307235,0.515918072  
C,0,2.3925066225,0.0754561248,1.4217829373  
O,0,1.0045533613,0.2552024174,-0.657496063  
O,0,2.3920276453,0.576943665,2.748941905  
H,0,3.1354669688,1.8126791828,-0.6134111872  
H,0,2.6286356975,2.7632464418,0.8011317664  
H,0,1.2035694641,2.4978013471,-1.6205163947  
H,0,0.6732854527,1.3190911147,1.1201289835  
H,0,3.4328746437,0.0942183185,1.0777852137  
H,0,2.047479659,-0.961579099,1.3784114237  
H,0,0.6568393787,-3.0387731122,-0.1177308207  
H,0,1.5219435757,0.3737755944,3.138736397



Cl,0,1.1819478334,-4.020581704,-0.8168366221  
H,0,0.3165330746,-1.6051710148,-2.041028447

**TS2 (Esterification of GB1 + HCl + sec-glycerol)**

Charge = 0 Multiplicity = 1

N,0,-2.7524886343,0.0522115553,-0.4285322617  
C,0,-1.3140536751,0.4448756087,-0.1251368709  
C,0,-3.6143288228,1.0047860963,0.3669705654  
C,0,-3.0703166045,0.2094811086,-1.8953454177  
O,0,-0.4606614587,-1.1754771495,-1.7105021825  
C,0,-0.2120431816,-0.4906474294,-0.6334377854  
O,0,-0.3015096876,-1.7552585171,0.6396847636  
C,0,-3.0848887984,-1.3584438832,0.0138101265  
H,0,-1.1510358871,1.4293742871,-0.5719936679  
H,0,-1.2452113967,0.5202117671,0.9659122135  
H,0,-4.6608244077,0.7879765815,0.1498615355  
H,0,-3.3754475386,2.0279084248,0.0740051792  
H,0,-3.4050563989,0.8597020904,1.4276885271  
H,0,-4.1230778856,-0.0345885238,-2.0446406854  
H,0,-2.4291605986,-0.4615497675,-2.4621410106  
H,0,-2.8842045726,1.2457909223,-2.1813089474  
H,0,-0.2293333539,-1.4103399299,1.6014544561  
H,0,-2.4995104576,-2.0596004405,-0.5745294829  
H,0,-4.1537162816,-1.5049471582,-0.1493956307  
H,0,-2.8349111035,-1.4574843103,1.0692650636  
Cl,0,-0.642864723,-0.315963772,3.1297592316  
C,0,2.0744284451,2.1063060965,-0.1467541477  
O,0,1.1120308235,2.7857573579,-0.9612228624  
C,0,1.4789981021,0.8778062794,0.5242578206  
C,0,2.4704799181,0.1342930906,1.4378113745  
O,0,1.0329634178,-0.0039134383,-0.5620758011  
O,0,2.5262589443,0.7685679213,2.7014928364  
H,0,2.952815128,1.821407745,-0.7392970676  
H,0,2.3953941275,2.8012027159,0.6337579261  
H,0,1.1552223828,2.4072002026,-1.8482287033  
H,0,0.6277582876,1.1715935997,1.1375274706  
H,0,3.4805703101,0.1608254207,1.0157556197  
H,0,2.1738636888,-0.9171273263,1.5175630152  
H,0,0.3426960288,-2.4619945666,0.3568482346  
H,0,1.7031682889,0.5436484049,3.1751039359  
Cl,0,1.1344456409,-3.4285095892,-1.3829388963  
H,0,0.2344609341,-2.049151475,-1.7662534744

**P (Esterification of GB1 + HCl + secondary glycerol)**

Charge = 0 Multiplicity = 1

N,0,-2.5318700276,0.1156345726,-0.5589508695  
C,0,-1.1170728931,0.6302035559,-0.3781730179  
C,0,-3.3908809134,0.8821398264,0.4261974486  
C,0,-3.0478450743,0.3651920116,-1.9529901535  
O,0,-0.3168072537,-0.8391842156,-2.1291590491  
C,0,-0.0538102211,-0.0781527703,-1.2031861735  
O,0,-1.0283158554,-1.8121241718,2.4755015666  
C,0,-2.6234709435,-1.3616972832,-0.2304659374

H,0,-1.1253113037,1.6891251517,-0.6565915729  
H,0,-0.9005623259,0.5956637802,0.7027107678  
H,0,-4.4079421139,0.49466291,0.3592189091  
H,0,-3.3713726617,1.9386469442,0.1554515596  
H,0,-2.9772732783,0.7606234704,1.4299681229  
H,0,-4.0901370072,0.0454912657,-1.9909904327  
H,0,-2.4431247388,-0.2008853863,-2.6572764897  
H,0,-2.9807992939,1.433738655,-2.1636473181  
H,0,-0.9231672255,-0.8895193977,2.8130460196  
H,0,-2.0626146777,-1.9145583805,-0.9807235118  
H,0,-3.6782612635,-1.6386111226,-0.2622789223  
H,0,-2.2079427837,-1.5349480607,0.7663569435  
Cl,0,-0.8231255303,1.231164792,2.9185021007  
C,0,2.7195301566,1.9991472258,-0.6271607853  
O,0,2.171527826,2.6993373328,-1.7384848112  
C,0,1.6705924451,1.158874394,0.087611714  
C,0,2.1916361758,0.3947945244,1.3156554679  
O,0,1.2085810415,0.180097521,-0.9177166232  
O,0,2.3615306665,1.2801608661,2.4003954159  
H,0,3.5593331633,1.3611913754,-0.9330904103  
H,0,3.0924249973,2.7424772513,0.0822636236  
H,0,2.1559688595,2.1037532625,-2.5019105038  
H,0,0.8407244463,1.7983319627,0.3911037876  
H,0,3.1665540608,-0.0531642295,1.0916374254  
H,0,1.4914602592,-0.4158480042,1.5545329513  
H,0,-0.899552445,-2.3940196908,3.2336572883  
H,0,1.476082441,1.4196643502,2.7977492079  
Cl,0,1.7741371565,-0.004761235,-4.3702739288  
H,0,1.0099631357,-0.5767020538,-3.4751298091

**R (Esterification of GB1 + HCl + primary glycerol)**

Charge = 0 Multiplicity = 1

C,0,-1.735603934,0.1982074548,2.0863178067  
C,0,-1.2496477543,0.1826552697,0.6276692126  
O,0,-1.2544240891,-0.7024352849,2.8989062431  
O,0,-2.5486426694,1.0427727969,2.4614468696  
N,0,-2.2620267428,-0.4360228789,-0.3322776296  
C,0,-1.6222435577,-0.4435020614,-1.7037579466  
C,0,-2.5764952826,-1.8567691587,0.0739072719  
C,0,-3.5376732515,0.3628415672,-0.392324072  
H,0,-0.3348094031,-0.3963015441,0.516992444  
H,0,-1.0739834155,1.2046197598,0.2916962538  
H,0,-2.7316852716,2.618115323,1.729672004  
H,0,-2.3244208909,-0.9031007122,-2.4008243747  
H,0,-0.6809707397,-0.9937997649,-1.6536269739  
H,0,-1.4088147213,0.5862480128,-1.9887488235  
H,0,-3.1971336518,-2.301877417,-0.7047157585  
H,0,-3.1215452688,-1.8420350009,1.0182236513  
H,0,-1.6410795295,-2.4065244182,0.1998776396  
H,0,-4.1940495775,-0.1068419415,-1.1263627091  
H,0,-3.3030958919,1.3847232941,-0.6898675072  
H,0,-4.0069896967,0.3701152068,0.5897063743  
Cl,0,-2.8122859897,3.7419615737,1.0363269026  
O,0,1.0583989919,1.5546489837,-1.2836732946  
H,0,1.1650293501,2.4788848878,-1.5394848751

C,0,2.2662674512,0.8457156104,-1.6234914683  
H,0,2.2235637156,0.5178389031,-2.6719553392  
H,0,3.1418468117,1.4894384715,-1.4875007795  
C,0,2.4242623491,-0.3710723941,-0.7281831523  
H,0,-0.5898869996,-1.3676523742,2.4721863773  
Cl,0,0.5486944773,-2.6193417796,1.6218193088  
H,0,2.307629852,-0.0499298188,0.3190998677  
O,0,1.4175734057,-1.3247516956,-1.05916448  
C,0,3.8151558213,-1.0066427213,-0.8975289202  
H,0,1.2738442466,-1.9041730667,-0.2756611691  
H,0,3.8315172216,-1.9627276733,-0.3598280417  
H,0,4.0016273336,-1.2155415697,-1.9560307403  
O,0,4.8699748682,-0.1447354342,-0.4661712944  
H,0,4.913082433,-0.160888405,0.4986861226

**TS1 (Esterification of GB1 + HCl + primary glycerol)**

Charge = 0 Multiplicity = 1

C,0,-1.2981084102,0.0153155923,0.4478942851  
C,0,-0.5485304322,-1.2976968069,0.1026549147  
O,0,-2.1046015823,0.484734251,-0.5145371783  
O,0,-0.5040637196,1.0529984525,0.8832084132  
N,0,0.5228192654,-1.202294629,-0.98191386  
C,0,0.8551600293,-2.6250239314,-1.3610912094  
C,0,0.0490944022,-0.4847935725,-2.2287476089  
C,0,1.7648859073,-0.5264109965,-0.459250643  
H,0,-1.2943121659,-2.009133617,-0.2575120618  
H,0,-0.0484144859,-1.6773765777,0.9950701295  
H,0,-0.1148876547,0.8107896431,1.7551693062  
H,0,1.6609378104,-2.6101156517,-2.0962895831  
H,0,-0.0390610481,-3.0852255218,-1.7831874857  
H,0,1.1728195941,-3.1637843372,-0.4675562777  
H,0,0.8398643573,-0.5731937295,-2.9754948611  
H,0,-0.1388961466,0.5587659798,-1.9872776093  
H,0,-0.871987193,-0.9602884099,-2.5717977877  
H,0,2.5248997139,-0.5531193052,-1.2415392011  
H,0,2.1129690937,-1.0622714192,0.4248872826  
H,0,1.5172732418,0.4999589944,-0.1968449488  
Cl,0,-0.1166757332,-0.5635174367,3.5241907864  
O,0,-2.1174030023,-0.508373417,1.6264243478  
H,0,-1.3769355204,-0.6034773919,2.527729907  
C,0,-3.3595228088,0.1852916832,2.008523012  
H,0,-3.4687095812,-0.0687985638,3.0655089537  
H,0,-3.2143875172,1.260834014,1.9007389059  
C,0,-4.5642688915,-0.3246307003,1.2051345722  
H,0,-2.5586215026,-0.2837735556,-1.0059000755  
Cl,0,-3.2185112498,-1.929450425,-1.80191037  
H,0,-4.5089092898,0.065297363,0.1822586983  
O,0,-4.6146535271,-1.7382187983,1.1889995627  
C,0,-5.8606131962,0.1818872327,1.8541922106  
H,0,-4.2703754752,-2.045799833,0.3281649  
H,0,-6.7097108365,-0.2110157645,1.2823144064  
H,0,-5.9374397143,-0.2053232704,2.8751589236  
O,0,-5.9029904959,1.6060952461,1.9634312769  
H,0,-6.071954235,1.9839642096,1.0905919669

**TI1 (Esterification of GB1 + HCl + primary glycerol)**

Charge = 0 Multiplicity = 1  
C,0,-0.4204698545,0.411677937,0.8057824236  
C,0,-1.0760429548,-0.0378018573,-0.5187430359  
O,0,0.0210341628,-0.601647834,1.6146464706  
O,0,-1.3466309544,1.1995518889,1.5089636592  
N,0,-2.5065105923,-0.5905071163,-0.4510701375  
C,0,-2.6751394604,-1.491521224,-1.6510538952  
C,0,-2.8047599548,-1.409410992,0.7891940972  
C,0,-3.4927896709,0.5465267712,-0.5343548891  
H,0,-0.4437248423,-0.8037370487,-0.9643778285  
H,0,-1.126193422,0.8206171352,-1.1897944844  
H,0,-0.9562752002,1.3753923309,2.3795355505  
H,0,-3.7133777398,-1.8248155759,-1.6921006776  
H,0,-2.0001606545,-2.3416209121,-1.5313115076  
H,0,-2.4272617621,-0.9273513455,-2.5514409796  
H,0,-3.8249466343,-1.7832248917,0.6859401391  
H,0,-2.7164239773,-0.7646281128,1.6594259953  
H,0,-2.0934069587,-2.2357915559,0.8367817141  
H,0,-4.5011569776,0.1325216291,-0.4910829421  
H,0,-3.3448333723,1.0723889843,-1.4784429221  
H,0,-3.3127581279,1.2209271772,0.3002207256  
Cl,0,-0.5772610548,3.8846705542,-0.7376589717  
O,0,0.6421477188,1.3340440506,0.510164155  
H,0,-0.0639482358,2.8671270334,-0.0681211338  
C,0,1.7981383255,1.041166637,-0.3317218188  
H,0,1.5334880398,1.2580951316,-1.3745449753  
H,0,2.5343894609,1.7718857133,0.0080521078  
C,0,2.4106402305,-0.3576353026,-0.2863377765  
H,0,0.0631985392,-1.5053846935,1.1770802453  
Cl,0,0.0536910801,-3.2932031044,0.2607516268  
H,0,2.3470837437,-0.7650820967,0.7298299343  
O,0,1.735084388,-1.1966410383,-1.2194425589  
C,0,3.891540508,-0.2824380586,-0.7021485837  
H,0,1.4408695006,-2.0320177242,-0.7911863503  
H,0,4.271255651,-1.3068373465,-0.8007232811  
H,0,3.9784548518,0.1990678811,-1.6816184726  
O,0,4.685911289,0.4938820729,0.1938598133  
H,0,4.8101249122,-0.0002660969,1.0147025643

**TI2 (Esterification of GB1 + HCl + primary glycerol)**

Charge = 0 Multiplicity = 1  
C,0,-0.2941880056,0.4349106476,0.7773119663  
C,0,-0.9986406001,-0.0321725986,-0.5147982854  
O,0,0.1340171706,-0.6268795157,1.5777917799  
O,0,-1.2054891707,1.2185636012,1.5028688899  
N,0,-2.4280152187,-0.5811718853,-0.3851978953  
C,0,-2.6440357642,-1.5030624719,-1.5617053515  
C,0,-2.6860296644,-1.3767671043,0.8812124191  
C,0,-3.4155976752,0.5547008211,-0.4498958046  
H,0,-0.3872251463,-0.8036148954,-0.9798170476  
H,0,-1.0708113018,0.8228195926,-1.1884037613  
H,0,-0.7129223025,1.6557643499,2.2163498438  
H,0,-3.683233879,-1.8359315126,-1.5561844919

H,0,-1.9649817904,-2.3515576996,-1.4530904339  
H,0,-2.4312260131,-0.9554004294,-2.4811812752  
H,0,-3.7146664475,-1.7369457324,0.8244795697  
H,0,-2.5507094099,-0.7210857381,1.7373712098  
H,0,-1.986574351,-2.2133609631,0.910730056  
H,0,-4.4222809004,0.1437263891,-0.3623868132  
H,0,-3.3049519679,1.0629041376,-1.4090501763  
H,0,-3.2038952672,1.2400312024,0.3683207388  
H,0,0.3253706255,-0.3751511425,3.3420212661  
O,0,0.766875205,1.307045927,0.4853330805  
Cl,0,0.3558461992,0.0553719342,4.5851368599  
C,0,1.8390534142,1.0318750294,-0.449087821  
H,0,1.489304534,1.2378589385,-1.4701302184  
H,0,2.5881232131,1.7781342698,-0.1784177816  
C,0,2.4822935324,-0.3561215283,-0.4469033883  
H,0,0.169677947,-1.530028694,1.1270552898  
Cl,0,0.1335651195,-3.2894981978,0.2191143123  
H,0,2.4812986204,-0.7644120764,0.5714960125  
O,0,1.7706579471,-1.2098615761,-1.3412985106  
C,0,3.9346874109,-0.2602985865,-0.9476951335  
H,0,1.4969727802,-2.0402191065,-0.8922902231  
H,0,4.3296146566,-1.2782570683,-1.0544190493  
H,0,3.95345732,0.2072397149,-1.9376820098  
O,0,4.7655921245,0.5458314963,-0.1136947688  
H,0,4.9341192907,0.0765627202,0.7139524407

**TS2 (Esterification of GB1 + HCl + primary glycerol)**

Charge = 0 Multiplicity = 1

C,0,-0.2969284334,0.5991882108,0.7513259888  
C,0,-0.9231230957,-0.0799612581,-0.4712389975  
O,0,0.3682167707,-0.8128178895,1.6676935503  
O,0,-1.1385593526,1.1694947441,1.5650746078  
N,0,-2.374615222,-0.5346000403,-0.3338188802  
C,0,-2.6335921127,-1.4465546456,-1.5117639109  
C,0,-2.6690720454,-1.3277288361,0.9294572098  
C,0,-3.3076798448,0.6484142089,-0.4027535059  
H,0,-0.3286309106,-0.9400861169,-0.7744792988  
H,0,-0.9196861626,0.6448139663,-1.2903841959  
H,0,-0.8913228966,1.0824644043,2.6412008401  
H,0,-3.685616489,-1.7337757897,-1.4985385198  
H,0,-1.9924408561,-2.3243789064,-1.4075721759  
H,0,-2.4044637733,-0.9091999398,-2.4333338921  
H,0,-3.7108489382,-1.6455940122,0.865234303  
H,0,-2.518799958,-0.6894311335,1.7959644553  
H,0,-2.0072691239,-2.1949849723,0.9479637418  
H,0,-4.332299193,0.2797851526,-0.342824278  
H,0,-3.1537986964,1.161364597,-1.3536221742  
H,0,-3.0866532533,1.3116602714,0.4306186015  
H,0,0.1316131989,-0.6916794389,2.6329006425  
O,0,0.8219316485,1.2976308324,0.5438693133  
Cl,0,-0.6150891632,0.4472052784,4.1812138423  
C,0,1.8293318602,1.0241522542,-0.4782178145  
H,0,1.3834221705,1.1729880493,-1.4688370159  
H,0,2.5592747603,1.8114189941,-0.2905091789  
C,0,2.5195883418,-0.3403267235,-0.4406035446  
H,0,0.2161121298,-1.7646071603,1.3263937075

Cl,0,0.0856199846,-3.3809931951,0.298177273  
H,0,2.5913550243,-0.6802105612,0.5987625097  
O,0,1.7910931193,-1.2679949759,-1.240366449  
C,0,3.9331920001,-0.2170808985,-1.0405118829  
H,0,1.5541266892,-2.0798972166,-0.7422310548  
H,0,4.3745572268,-1.2201285264,-1.0843387025  
H,0,3.8654338071,0.1580883031,-2.0669636122  
O,0,4.7630875632,0.7014900525,-0.3344511309  
H,0,5.0475852257,0.3034169174,0.4987226287

**P (Esterification of GB1+ HCl + primary glycerol)**

Charge = 0 Multiplicity = 1

C,0,-0.542674407,1.1760323584,0.2202476863  
C,0,-0.9921106141,0.256786776,-0.9007589364  
O,0,0.5352158122,-1.4890729678,1.4900459121  
O,0,-1.2775500205,1.4906239253,1.147547413  
N,0,-2.4492638477,-0.1678870474,-0.8553738143  
C,0,-2.6864511864,-1.0072814066,-2.0937059905  
C,0,-2.7147777216,-1.0385804291,0.3578948404  
C,0,-3.3885185219,1.0082032768,-0.8722356635  
H,0,-0.4168009271,-0.6761526061,-0.8819830224  
H,0,-0.8146068522,0.7195233699,-1.8741591521  
H,0,-0.8684692869,2.7681403528,2.4377343621  
H,0,-3.7135992823,-1.3728095419,-2.0615621858  
H,0,-1.9740684279,-1.8376694732,-2.0863277714  
H,0,-2.5392496129,-0.3798793077,-2.9740752214  
H,0,-3.7583411455,-1.3539552884,0.3135816202  
H,0,-2.518654711,-0.4549915712,1.2535021191  
H,0,-2.0457210142,-1.8979369583,0.300957528  
H,0,-4.4077474438,0.6277247191,-0.9524650704  
H,0,-3.1564023981,1.6258061566,-1.7417692543  
H,0,-3.2607195669,1.5773563943,0.0452182546  
H,0,0.7907164768,-1.928458018,2.309549469  
O,0,0.6890427406,1.6561611855,0.1762606926  
Cl,0,-0.7996097761,3.72063439,3.3332956564  
C,0,1.663565518,1.5204106767,-0.9126134561  
H,0,1.222793341,1.9049718524,-1.8382164532  
H,0,2.4555043543,2.1893649994,-0.5772810828  
C,0,2.2227927683,0.1126804019,-1.1453891688  
H,0,0.4875856542,-2.1869255376,0.7973048532  
Cl,0,0.0899163398,-3.0174996153,-1.1608016741  
H,0,2.0853591502,-0.4763563038,-0.2280469528  
O,0,1.5569486862,-0.4893316771,-2.2493129868  
C,0,3.7245910797,0.1938395581,-1.4777242304  
H,0,1.2803762478,-1.4067801818,-2.0205034966  
H,0,4.0798462604,-0.8179837242,-1.7080973793  
H,0,3.8705520733,0.8078123829,-2.3723361459  
O,0,4.4935405432,0.8062122952,-0.4452418515  
H,0,4.5430277184,0.2082145844,0.3122315538

## 5. Thermodynamic modelling

Considering that the esterification reaction takes place from an initial ‘pre-reactional complex’ and evolves through a rearrangement of this system, a first order rate law can be written:

$$d[\text{product}] / dt = k [\text{‘pre-reactional complex’}]$$

In the context of the transition state theory, the rate constant  $k$  is given by the Eyring equation:

$$k = k_B T / h \exp(-\Delta G^\ddagger / RT)$$

The initial rate  $d[\text{product}] / dt$  is determined from the experimental data (initial concentration: 4.88 M and a yield of 10% after 50 mn), giving  $1.63 \cdot 10^{-4} \text{ M}\cdot\text{s}^{-1}$ .

The critical point is the initial concentration of the ‘pre-reactional complex’ since the amount of non-dissociated HCl molecules in the reactive medium is unknown.

At this point we suggest two hypotheses:

**1<sup>st</sup> hypothesis:** The amount of non-dissociated HCl is 1% of the betaine hydrochloride initial amount, i.e., 0.0488 M in our experimental conditions.

Using the Eyring equation (150°C), we deduce:  $\Delta G^\ddagger = 29.9 \text{ kcal}\cdot\text{mol}^{-1}$ .

**2<sup>nd</sup> hypothesis:** The amount of non-dissociated HCl is 0.1% of the betaine hydrochloride initial amount, i.e., 0.00488 M in our experimental conditions.

Using the Eyring equation as above we deduce:  $\Delta G^\ddagger = 27.9 \text{ kcal}\cdot\text{mol}^{-1}$ .

Even though it is difficult to choose the more reasonable hypothesis (additive experimental results could help to this end), note that the estimated  $\Delta G^\ddagger$  are in reasonable agreement with the theoretical energetic profile values (31-32 kcal/mol).

## 6. Synthesis and characterization of acidified betaine

**6.1. General procedure for the synthesis of GB2-5:** Except for **GB1** which is commercially available (purchased to Sigma-Aldrich), all other acidified glycine betaine derivatives **GB2-5** were prepared as follow: **GB** (1mol) was mixed with 1.4 eq of acid and stirred for 20 min at room temperature (exothermic reaction). Then, the as-obtained paste was washed twice with 50 mL of absolute ethanol to remove the excess of acid. After washing, the corresponding **GB2-5** were obtained as a white solid in a nearly quantitative yield (95%). Next, **GB2-5** were dried at 80°C in an oven for one hour to remove potential trace of ethanol.

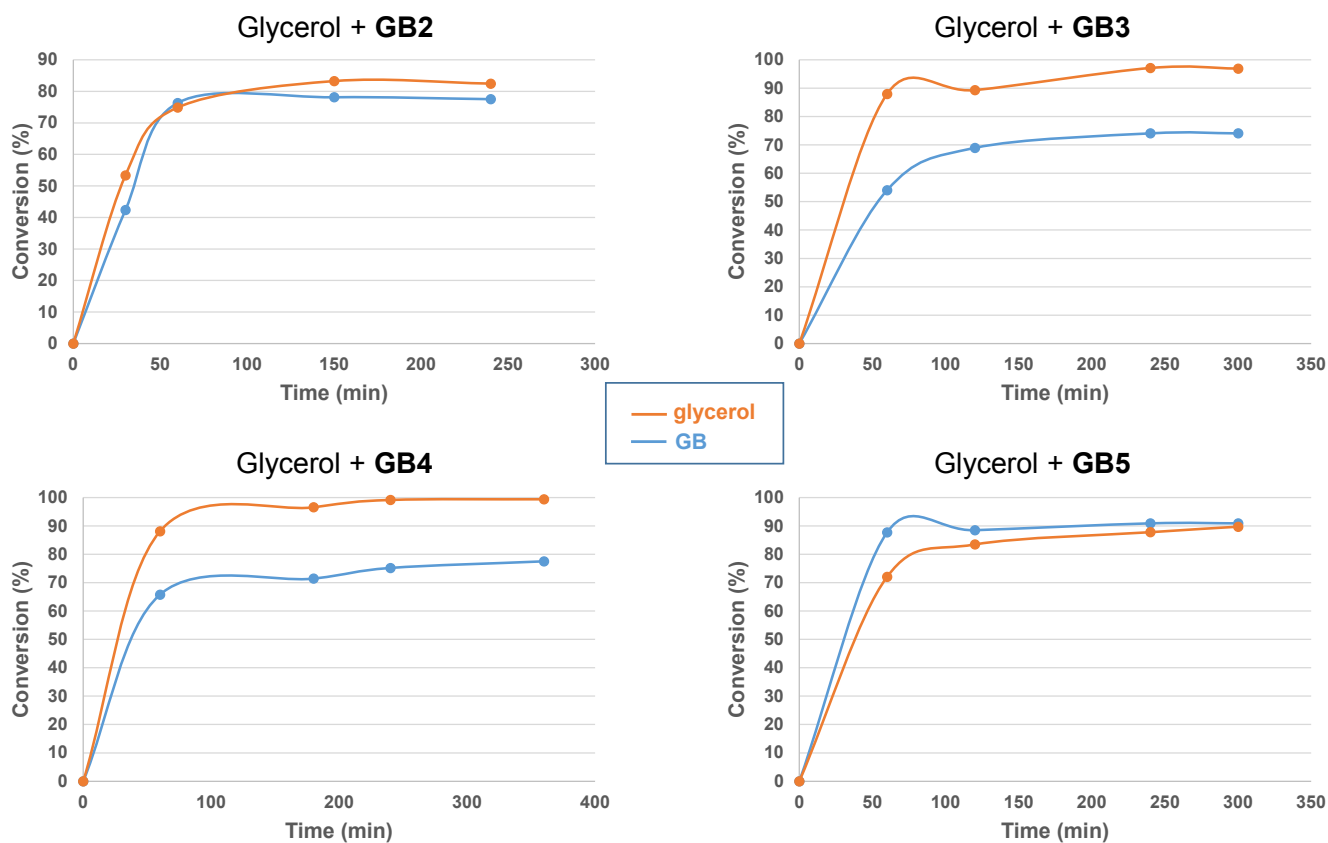
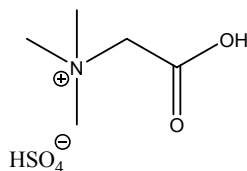


Figure S2. Typical kinetic profiles collected at 150°C

## 6.2. Characterizations of GB2-5



1-carboxy-*N,N,N*-trimethylmethanaminium hydrogenosulfate (**GB3**)

**Isolated yield :** 95%

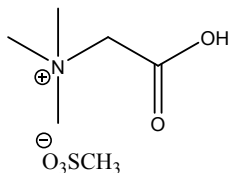
**FT-IR :**  $\nu$  ( $\text{cm}^{-1}$ ) : 1738  $\text{cm}^{-1}$  (C=O), 2895-2980 ( $-\text{CH}_2$ ,  $-\text{CH}_3$ ).

**NMR  $^1\text{H}$**  (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  (ppm): 3.23 (s, 9H,  $\text{N}^+(\text{CH}_3)_3$ ), 4.13 (s, 2H,  $-\text{CH}_2$ ).

**RMN  $^{13}\text{C}$**  (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  (ppm): 53.71 ( $-\text{N}^+(\text{CH}_3)_3$ ), 63.18 ( $-\text{CH}_2$ ), 166.64 ( $-\text{C}=\text{O}$ ).

**HRMS (ESI $^+$ ) :** [ $\text{C}_5\text{H}_{12}\text{NO}_6\text{S}$ ]:  $m/z$  = 118.0866 [ $\text{M}^+$ ]





1-carboxy-*N,N,N*-trimethylmethanaminium methanesulfonate (**GB2**)

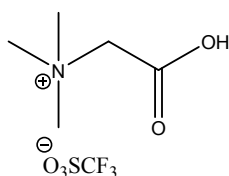
**Isolated yield** : 95%

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 1733 cm<sup>-1</sup> (C=O), 2851-2944 (-CH<sub>2</sub>, -CH<sub>3</sub>).

**NMR <sup>1</sup>H** (400 MHz, D<sub>2</sub>O) :  $\delta$  (ppm): 2.71 (s, 1H, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 3.24 (s, 9H, N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 4,13 (s, 2H, -CH<sub>2</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O) :  $\delta$  (ppm): 38.39 (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 53.72 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 63.40 (-CH<sub>2</sub>), 166.83 (-C=O).

**HRMS (ESI<sup>+</sup>)** : [C<sub>6</sub>H<sub>14</sub>NO<sub>5</sub>S]: m/z = 118.0868 [M<sup>+</sup>]



1-carboxy-*N,N,N*-trimethylmethanaminium trifluoromethanesulfonate (**GB4**)

**Isolated yield** : 95%

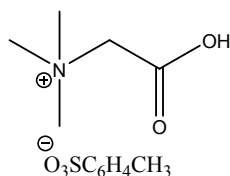
**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 1743 cm<sup>-1</sup> (C=O), 2962-2998 (-CH<sub>2</sub>, -CH<sub>3</sub>).

**NMR <sup>1</sup>H** (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm): 3.27 (s, 9H, N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 4.20 (s, 2H, -CH<sub>2</sub>).

**NMR <sup>19</sup>F** (376 MHz, D<sub>2</sub>O):  $\delta$  (ppm): -78.9 ppm (-CF<sub>3</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O):  $\delta$  (ppm): 53.79 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 63.26 (-CH<sub>2</sub>), 114.97-124.44 (q, <sup>1</sup>J<sub>CF</sub> = 315 Hz, CF<sub>3</sub>), 166.52 (-C=O).

**HRMS (ESI<sup>+</sup>)** : [C<sub>6</sub>H<sub>11</sub>NO<sub>5</sub>SF<sub>3</sub>]: m/z = 118.0866 [M<sup>+</sup>]



1-carboxy-*N,N,N*-trimethylmethanaminium *p*-toluenesulfonate (**GB5**)

**Isolated yield** : 95%

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 1734 cm<sup>-1</sup> (C=O), 2873-2949 (-CH<sub>2</sub>, -CH<sub>3</sub>).

**NMR** <sup>1</sup>H (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm) : 1.98 (s, 3H, -CH<sub>3</sub>), 2.88 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.85 (s, 2H, -CH<sub>2</sub>), 6.95 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8 Hz, =CH), 7.40 (d, 2H, <sup>3</sup>J<sub>HH</sub>=8Hz, =CH).

**RMN** <sup>13</sup>C (100 MHz, D<sub>2</sub>O):  $\delta$  (ppm) : 20.38 (-CH<sub>3</sub>), 53.56 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 62.97 (CH<sub>2</sub>), 129.24 (Ar), 129.28 (Ar), 139.98 (Ar), 141.89 (Ar), 166.27 (-C=O).

**HRMS** (ESI<sup>+</sup>) : [C<sub>12</sub>H<sub>18</sub>NO<sub>5</sub>S]: m/z = 118.0866 [M<sup>+</sup>]

## 7. Synthesis and characterization of glyceryl betaine ester (GlyGB)

**7.1. General procedure for the synthesis of GB derivatives:** **GB1-5** (1mol) was mixed with 1 eq. of glycerol and heated at 150°C in an opened round bottom flask equipped with a magnetic stirring bar (stirring rate = 1000 rpm). The reaction progress was monitored by GC and HPLC analysis.

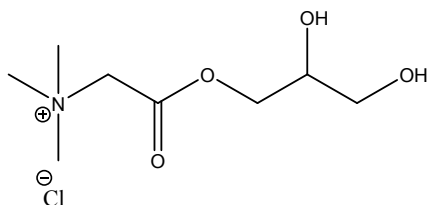
For the characterization of glyceryl betaine esters, the reaction media was washed with 50 mL of 2-propanol at the end of the reaction. This washing removed unreacted glycerol and/or trace of *in situ* produced polyglycerol. The residue was composed of (poly)glyceryl betaine ester and, in some cases, of unreacted **GB1-5**.

**GC Analysis:** Products were silylated before analysis according to the procedure described by Lee and *al.*<sup>3</sup> The GC Varian 3900 was equipped with a capillary column BP5 (L = 30m,  $\varnothing$  = 0.32 $\mu$ m, thickness = 1  $\mu$ m) and an ionisation flame detector. The temperature of the injector was fixed at 250°C. The program used is as follow : 90°C to 120°C (10°C/min) and then 120°C to 290°C (20°C/min), final temperature was holden during 20 minutes.

**HLPC Analysis :** Conversion of acidified betaine was determined by external calibration at 70°C using a HPLC Shimadzu apparatus composed of a Zorbax NH<sub>2</sub>-column (250  $\times$  4.6 mm), a Shimadzu LC-20AD pump, a Shimadzu Waters 2014 detector and using a mixture acetonitrile/water (20:80) as mobile phase (0.4 mL min<sup>-1</sup>).

## 7.2. Characterization of glyceryl betaine ester (GlyGB)

For the sake of clarity, all the following data correspond the esterification of glycerol on the primary hydroxyl group. Note that esterification on the secondary position also occurs but in a much lower extent.



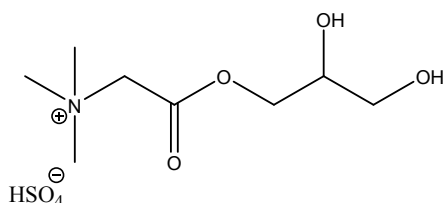
2-(2,3-dihydroxypropoxy)-*N,N,N*-trimethyl-2-oxoethan-1-ammonium chloride (**GlyGB1**)

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 3323 (O-H), 2966-2882 cm<sup>-1</sup> (CH<sub>2</sub>,CH<sub>3</sub>), 1749 cm<sup>-1</sup> (C=O).

**NMR <sup>1</sup>H** (400MHz, D<sub>2</sub>O):  $\delta$  (ppm) : 3.32 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.52 (m, 1H, -CH<sub>2</sub>OH), 3.62 (m, 1H, -CH<sub>2</sub>OH), 3.76 (m, -CHOH, 1H), 4.25 (m, 1H, -CH<sub>2</sub>OH), 4.36 (m, 1H, -CH<sub>2</sub>OH), 4.37 (s, 2H, -CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O) :  $\delta$  (ppm) :  $\delta$  (ppm) : 54.04 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 61.95 (-CH<sub>2</sub>OH), 63.04 (-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 66.75 (-CHOH), 69.05 (-OCH<sub>2</sub>-), 164,99 (-C=O).

**HRMS (ESI<sup>+</sup>)** : [C<sub>8</sub>H<sub>18</sub>NO<sub>4</sub>Cl]: m/z = 192.1232 [M<sup>+</sup>H]



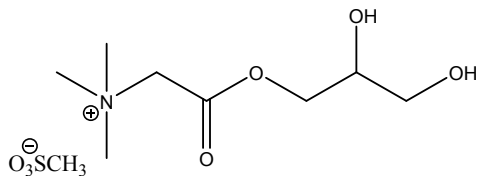
2-(2,3-dihydroxypropoxy)-*N,N,N*-trimethyl-2-oxoethan-1-ammonium hydrogenosulfate (**GlyGB2**)

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 3408 (O-H), 2988-2886 cm<sup>-1</sup> (CH<sub>2</sub>,CH<sub>3</sub>), 1747 cm<sup>-1</sup> (C=O)

**NMR <sup>1</sup>H** (400 MHz, D<sub>2</sub>O) :  $\delta$  (ppm) : 3.30 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.51 (m, 1H, -CH<sub>2</sub>OH), 3.61 (m 1H, -CH<sub>2</sub>OH), 3.76 (m, -CHOH, 1H), 4.24 (m, 1H, -CH<sub>2</sub>OH), 4.34 (m, 1H, -CH<sub>2</sub>OH), 4.36 (s, 2H, -CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O) :  $\delta$  (ppm) : 54.07 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 62.08 (-CH<sub>2</sub>OH), 63.35 (-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 66.79 (-CHOH), 69.10 (-OCH<sub>2</sub>-), 165,02 (-C=O).

**HRMS** : [C<sub>8</sub>H<sub>19</sub>NO<sub>8</sub>S]: m/z = 192.1230 [M<sup>+</sup>H]



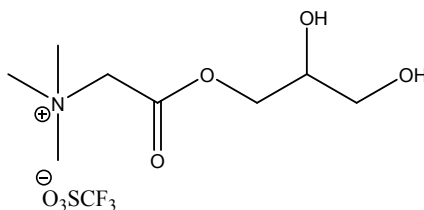
2-(2,3-dihydroxypropoxy)-*N,N,N*-trimethyl-2-oxoethan-1-ammonium methanesulfonate  
(**GlyGB3**)

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 3367 (O-H), 2944-2878 cm<sup>-1</sup> (CH<sub>2</sub>,CH<sub>3</sub>), 1751 cm<sup>-1</sup> (C=O)

**NMR <sup>1</sup>H** (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm): 2.77 (s, 1H, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 3.32 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.53 (m, 1H, -CH<sub>2</sub>OH), 3.62 (m, 1H, -CH<sub>2</sub>OH), 3.76 (m, -CHOH, 1H), 4.26 (m, 1H, -CH<sub>2</sub>OH), 4.36 (m, 1H, -CH<sub>2</sub>OH), 4.37 (s, 2H, -CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O):  $\delta$  (ppm): 38.48 (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>), 54.06 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 62.00 (-CH<sub>2</sub>OH), 66.22 (-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 66.80 (-CHOH), 69.09 (-OCH<sub>2</sub>-), 165.02 (-C=O).

**HRMS** : [C<sub>9</sub>H<sub>21</sub>NO<sub>7</sub>S]: m/z = 192.1232 [M<sup>+</sup>H]



2-(2,3-dihydroxypropoxy)-*N,N,N*-trimethyl-2-oxoethan-1-ammonium trifluoromethanesulfonate (**GlyGB4**)

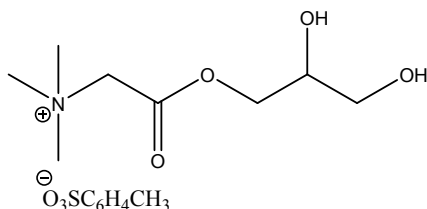
**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 3497 (O-H), 2988-2881 cm<sup>-1</sup> (CH<sub>2</sub>,CH<sub>3</sub>), 1751 cm<sup>-1</sup> (C=O)

**NMR <sup>1</sup>H** (400 MHz, D<sub>2</sub>O) :  $\delta$  (ppm) : 3.35 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.56 (m, 1H, -CH<sub>2</sub>OH), 3.66 (m, 1H, -CH<sub>2</sub>OH), 3.78 (m, -CHOH, 1H), 4.29 (m, 1H, -CH<sub>2</sub>OH), 4.38 (m, 1H, -CH<sub>2</sub>OH), 4.39 (s, 2H, -CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>).

**NMR <sup>19</sup>F** (376 MHz, D<sub>2</sub>O) :  $\delta$  (ppm) : -78,7 ppm (CF<sub>3</sub>).

**NMR <sup>13</sup>C** (100 MHz, D<sub>2</sub>O) : 54.06 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 61.98 (-CH<sub>2</sub>OH), 66.14 (-CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 66.77 (-CHOH), 69.07 (-OCH<sub>2</sub>-), 114.92-124.42 (q, <sup>1</sup>J<sub>CF</sub> = 315 Hz, CF<sub>3</sub>), 164.97 (-C=O).

**HRMS** : [C<sub>9</sub>H<sub>18</sub>NO<sub>7</sub>F<sub>3</sub>S]: m/z = 174.1125 [M<sup>+</sup>H-H<sub>2</sub>O]



2-(2,3-dihydroxypropoxy)-*N,N,N*-trimethyl-2-oxoethan-1-ammonium *p*-toluene sulfonate (**GlyGB5**)

**FT-IR** :  $\nu$  (cm<sup>-1</sup>) : 3385 (O-H), 2966-2882 cm<sup>-1</sup> (CH<sub>2</sub>,CH<sub>3</sub>), 1749 cm<sup>-1</sup> (C=O)

**NMR** <sup>1</sup>H (400 MHz, D<sub>2</sub>O):  $\delta$  (ppm): 2.32 (s, 3H, -CH<sub>3</sub>), 3.23 (s, 9H, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 3.52 (m, 1H, -CH<sub>2</sub>OH), 3.58 (m, 1H, -CH<sub>2</sub>OH), 3.68 (m, -CHOH, 1H), 4.23 (m, 1H, -CH<sub>2</sub>OH), 4.28 (s, 2H, CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 4.29 (m, 1H, -COOCH<sub>2</sub>-), 7.29 (dd, 2H, <sup>3</sup>J<sub>HH</sub>=8,0 Hz, =CH-), 7.64 (dd, 2H, <sup>3</sup>J<sub>HH</sub>=8,0 Hz, =CH-).

**NMR** <sup>13</sup>C (100 MHz, D<sub>2</sub>O)  $\delta$  (ppm): 20.45 (CH<sub>3</sub>), 53.95 (-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 61.94 (-CH<sub>2</sub>OH), 66.17 (CH<sub>2</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 66.73 (-CHOH), 69.03 (-OCH<sub>2</sub>-), 125.32 (Ar), 129.42 (Ar), 139.55 (Ar), 142.36 (Ar), 164.91 (C=O).

**HRMS** : [C<sub>15</sub>H<sub>25</sub>NO<sub>7</sub>S] m/z = 192.1232 [M<sup>+</sup>H]

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