

SUPPLEMENTARY INFORMATION for

**DFT investigation of the reaction mechanism for the guanidine catalysed ring-opening of cyclic carbonates by aromatic and alkyl-amines**

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# ESI1 - Racemic aminolysis of propylene carbonate by methylamine

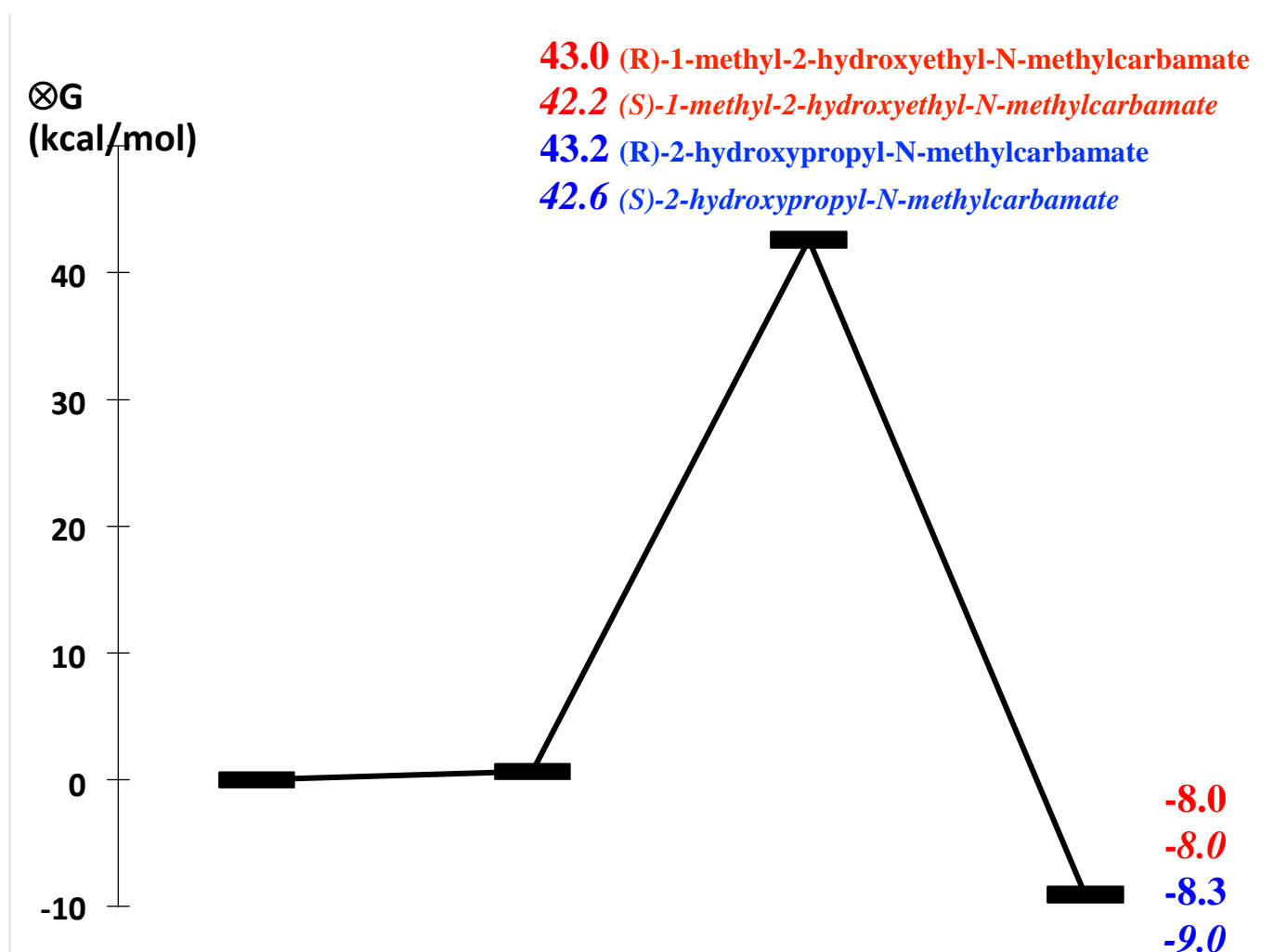


Figure S1: Gibbs free energy profile (M06-2X/6-311G(d,p)) for the racemic aminolysis of propylene carbonate by methylamine.

## ESI2 – Nucleophilic reaction pathway for the TBD catalysed methylamine – propylene carbonate coupling

The nucleophilic activation mechanism by TBD displays a two-step pathway (Figure S2 left), ie the nucleophilic attack of the carbonate by TBD ( $\Delta G= 22.6$  kcal/mol) and the subsequent addition of the amine on the activated carbonate ( $\Delta G= 23.4$  kcal/mol). The molecular structures of the corresponding intermediates and transition states are displayed in Figure S3. At a first glance we observe two transition states higher in energy about 7 – 8 kcal/mol than the ones involved in the proton shuttle mechanism (see Figure S2 right) that is fully discussed in the body of the paper.

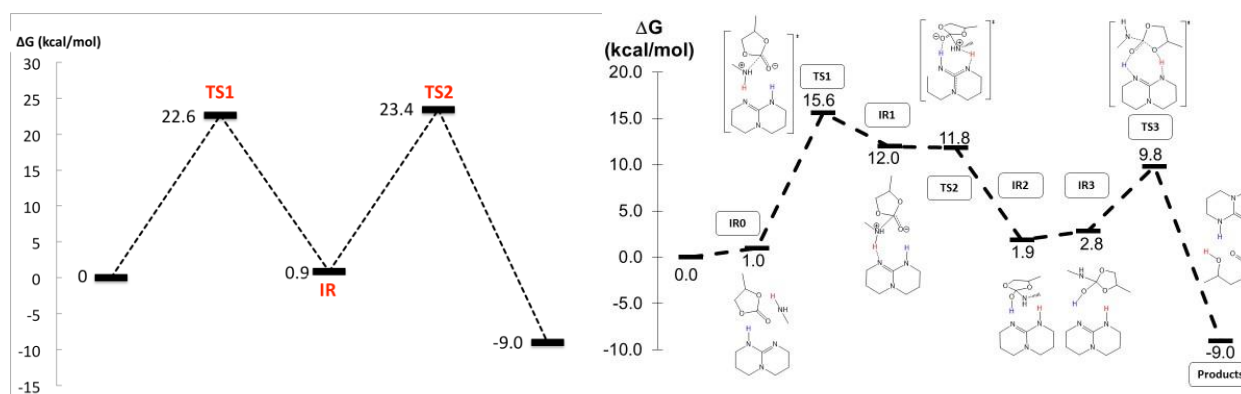
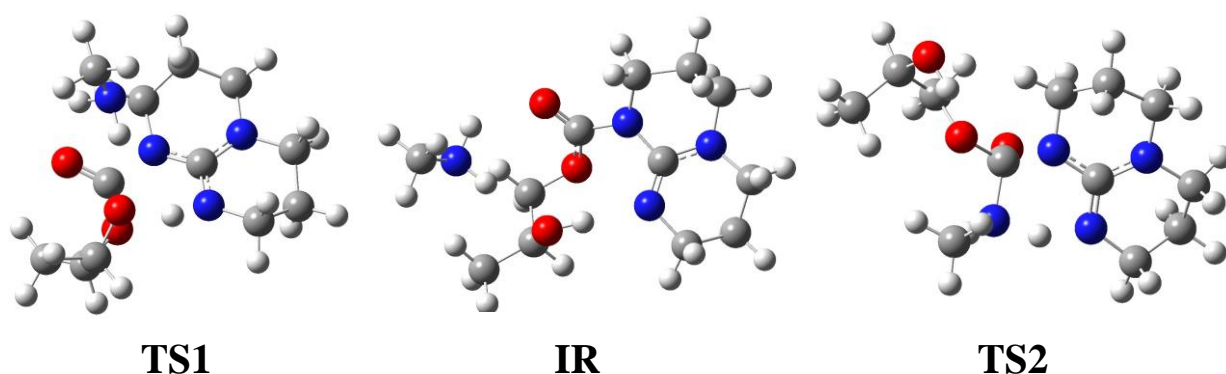


Figure S2: Gibbs free energy profile (M06-2X/6-311G(d,p)) for the reaction of propylene carbonate and methylamine with TBD acting as a nucleophilic catalyst (left) and TBD acting as a base (right). The molecular structures TS1, IR and TS2 of the nucleophilic pathway are depicted below.



ESI3: Aminolysis of propylene carbonate by cyclohexylamine catalyzed by TBD.

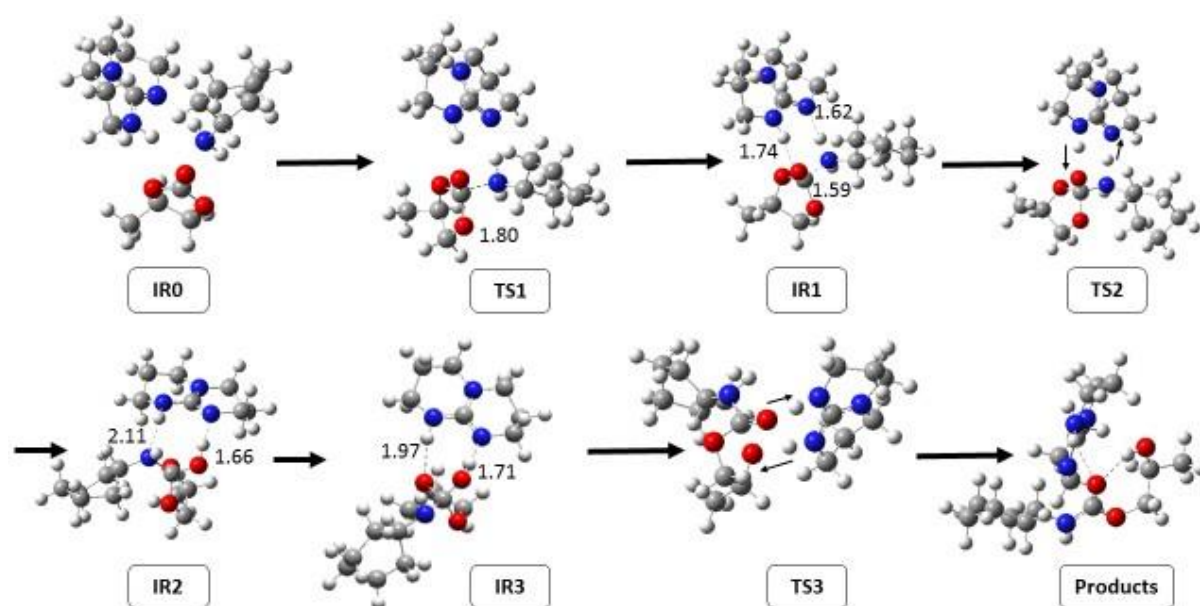


Figure S3: Optimized geometries of the structures (M06-2X/6-311G(d,p)) of the propylene carbonate/cyclohexylamine coupling in the presence of TBD as catalyst. The dashed lines depict hydrogen bond interactions, the arrows represent the concerted proton transfer and intermolecular distances are given in angstrom

ESI4 - Optimized Cartesian coordinates (Å) from M06-2X/6-311G(d) calculations

1- CYCLIC CARBONATE – AMINE COUPLING WITHOUT CATALYST

*TS - Propylene carbonate-methylamine coupling without catalyst*

C	-1.61256000	-0.41609100	-0.38389400
H	-1.73362000	-0.66884900	-1.45058100
C	-1.41122000	1.10687400	-0.28324800
H	-1.59641100	1.45816800	0.73739100
O	-0.03166600	1.30489800	-0.60475800
C	0.74426700	0.54952200	0.22683600
O	1.10578600	0.82397400	1.32922400
N	1.62807500	-0.32710200	-0.67737100
H	1.79818800	0.14737000	-1.56016300
C	2.83813400	-0.82930500	-0.01343900
H	2.52493100	-1.37514100	0.87373700
H	3.37543400	-1.48949400	-0.69195100
H	3.46648800	0.00521100	0.29349100
C	-2.83657700	-0.87842700	0.39049300
H	-2.69537200	-0.65493200	1.45005800
H	-3.74586400	-0.38280000	0.03751300
H	-2.96317200	-1.95612200	0.28238400
H	-1.99545100	1.68741600	-0.99515700
O	-0.43782400	-0.95935600	0.12917700
H	0.74568400	-1.03268500	-0.68475500

*TS - Propylene carbonate-cyclohexylamine coupling without catalyst*

C	3.14297200	0.72476300	-0.12895200
H	3.23386300	1.27651800	-1.07994700
C	3.26563000	-0.77666700	-0.44793100
H	3.49301900	-1.35084700	0.45640100

O	1.96897900	-1.14580500	-0.92631500
C	1.02539100	-0.82160700	0.00599300
O	0.71746500	-1.45279600	0.97106500
N	0.00486000	0.07857500	-0.70226900
H	-0.02822300	-0.14365600	-1.69603500
C	4.22537100	1.19018800	0.83253900
H	4.11519300	0.65987500	1.78082600
H	5.22659500	1.00538300	0.43173100
H	4.11891400	2.25831800	1.02462000
H	3.97889400	-1.01310800	-1.23582700
O	1.87023600	0.86655000	0.41361100
H	0.71351500	0.92102500	-0.44246700
C	-1.32770700	0.15010200	-0.07201600
C	-2.06497500	1.40683800	-0.55856100
C	-2.15097500	-1.10426400	-0.34033900
H	-1.12349400	0.21297400	0.99938200
C	-3.58965600	1.26115000	-0.38416400
H	-1.83003700	1.57878600	-1.61451100
H	-1.69442300	2.27431900	-0.00618000
C	-3.41936700	-1.08301000	0.53546200
H	-2.42005700	-1.12306700	-1.40407500
H	-1.55484800	-1.99271100	-0.12881800
C	-3.91021700	0.35347500	0.80480200
H	-4.02673900	0.82472100	-1.28795200
H	-4.04459400	2.24546700	-0.26090500
H	-3.21285100	-1.58463100	1.48332600
H	-4.20612900	-1.65555800	0.03850200
H	-3.42279300	0.75554500	1.69900600
H	-4.98207000	0.35123000	1.01092900

*TS - Propylene carbonate-aniline coupling without catalyst*

C	2.89806300	0.38220000	-0.63273500
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H	3.05421500	0.05024300	-1.67156300
C	3.08409900	-0.83839600	0.28906600
H	3.28204300	-0.52459600	1.31935300
O	1.82779500	-1.52012000	0.23982100
C	0.83286000	-0.64845700	0.57877000
O	0.47044500	-0.33881300	1.66574700
N	-0.18497900	-0.71154500	-0.62296200
H	-0.14140000	-1.62874000	-1.05943800
C	3.87351000	1.49908500	-0.30096100
H	3.68672400	1.84969400	0.71623100
H	4.91038500	1.15883000	-0.37723300
H	3.73107100	2.33645400	-0.98452000
H	3.84549800	-1.54049000	-0.04570400
O	1.57313700	0.77129900	-0.43317000
H	0.50879300	0.06003200	-1.07737500
C	-1.52128400	-0.25219100	-0.36055600
C	-2.60755700	-1.08791300	-0.57300200
C	-1.68687800	1.04498300	0.11211800
C	-3.88981800	-0.61269500	-0.32123000
H	-2.45592500	-2.10013100	-0.93223300
C	-2.97095200	1.50618100	0.36432800
H	-0.81210800	1.66245400	0.28208700
C	-4.07210400	0.68271300	0.14718000
H	-4.74271000	-1.25858300	-0.48904000
H	-3.11122100	2.51331800	0.73676500
H	-5.07115800	1.05033500	0.34635300

## 2- CYCLIC CARBONATE – ANILINE COUPLING WITH TBD AND MTBD CATALYST

*Propylene carbonate/Aniline coupling catalysed by TBD*

TS1-2

C	3.13121300	2.35768300	0.81102000
C	1.82120300	3.11890200	1.01193800
H	3.40699700	1.79429700	1.71446700
H	3.96807800	2.99147900	0.51582400
H	1.68529700	3.44507100	2.04565600
O	0.86604500	2.10415900	0.74166000
O	2.82002100	1.49034800	-0.25582100
C	1.43691400	1.18578100	-0.21237800
O	0.86232700	1.03491700	-1.30809400
C	1.66039600	4.27837900	0.04104000
H	0.64266400	4.66701000	0.09479000
H	2.36034000	5.08484600	0.27416300
H	1.84305300	3.92586600	-0.97647800
N	1.33401600	-0.18740900	0.66963900
H	1.69572100	0.00451600	1.60055300
C	1.99518400	-1.30856700	0.07731500
C	1.42679800	-1.89726200	-1.05039500
C	3.18354000	-1.80241300	0.60568000
C	2.05507100	-2.98766100	-1.63759700
C	3.80015200	-2.89909000	0.01599900
C	3.23706900	-3.49471800	-1.10701000
H	0.51533100	-1.48029000	-1.45722400
H	3.62525700	-1.32372800	1.47358100
H	1.61737000	-3.44369000	-2.51751800
H	4.72486600	-3.28268700	0.43049400
H	3.71964700	-4.34729700	-1.56923000
H	0.16880000	-0.39287300	0.70413400
C	-2.13888200	-0.19543900	0.00637400



C	-3.99517500	0.60393600	-1.95710300
H	-4.77534300	1.17006300	-2.46909100
H	-3.69938300	-0.23347200	-2.59365200
C	-4.53000000	0.08749600	-0.63177700
H	-5.26683400	-0.70635000	-0.79548800
H	-5.03985700	0.89761500	-0.09223100
C	-2.77383000	1.46520500	-1.67547600
H	-3.06576900	2.34932600	-1.09199700
H	-2.31189100	1.81600800	-2.59844500
C	-1.56330000	-1.79331100	1.66291500
H	-0.73499400	-1.92257200	2.36478100
H	-1.70865300	-2.76129900	1.16228300
C	-2.84005900	-1.40022300	2.39439100
H	-2.66775800	-0.45934400	2.92326000
H	-3.14322500	-2.15554800	3.12224000
C	-3.93840400	-1.22049200	1.35955200
H	-4.79351800	-0.68896600	1.79218700
H	-4.30168200	-2.19818000	1.01715800
N	-1.19078600	-0.76680200	0.71132600
N	-1.79930500	0.66346400	-0.97170900
N	-3.46910300	-0.45557700	0.20874400
H	-0.78274600	0.84983100	-1.10910200

TS3

C	0.90025900	-2.39681200	1.36748500
H	-0.00075800	-2.93728900	1.06213400
C	0.57009100	-0.94460400	1.79507800
O	0.68624800	-0.20253000	0.61632800
C	1.15753200	-1.38653300	-0.64315900
O	0.10095800	-1.73681900	-1.22051700
N	2.10248200	-0.70757700	-1.42954800
H	-0.52836100	0.51060500	0.37623800

H	-0.46429500	-0.90823200	2.17529700
O	1.76382600	-2.24417300	0.26132000
H	1.64703600	-0.34995800	-2.25583300
C	-2.54057800	0.29303500	-0.12626500
C	-4.10571100	2.13005300	0.37853400
C	-2.87192100	3.01673700	0.32027800
C	-1.71373700	2.28323000	0.97849000
H	-4.50288400	2.09156700	1.40074000
H	-3.07756100	3.96275600	0.82326300
H	-0.78421900	2.84708100	0.89565300
C	-4.96666400	-0.02509100	-0.47739900
H	-5.77018800	0.17864900	0.23689400
H	-5.31046500	0.30802800	-1.46472100
C	-4.63920000	-1.50973800	-0.50159300
H	-4.52247100	-1.88167100	0.51924400
H	-5.45642000	-2.05516200	-0.97588000
C	-3.33521200	-1.70925800	-1.25664800
H	-3.45936100	-1.41806300	-2.30764800
H	-3.01463700	-2.75083600	-1.23811100
N	-3.80986800	0.77285200	-0.07602500
N	-1.51758700	1.01010600	0.31578100
N	-2.29930900	-0.92213800	-0.61856600
H	-1.29233000	-1.21020200	-0.79286600
H	-4.89462700	2.52775200	-0.26694300
H	-2.61634200	3.22844400	-0.72093600
H	-1.92069400	2.14044400	2.04753700
H	1.43478200	-2.95995100	2.13211800
C	1.52371600	-0.42096200	2.86066000
H	1.32111400	0.63355400	3.05864900
H	1.42367100	-0.98005300	3.79564600
H	2.55196700	-0.50206000	2.50216700
C	3.18244600	0.05623300	-0.97775700

C	3.98870100	-0.32769900	0.09919200
C	3.50443400	1.22876700	-1.67072800
C	5.06345700	0.46553400	0.47901000
H	3.77246500	-1.25217900	0.61279100
C	4.59191700	2.00379400	-1.29418600
H	2.88717300	1.53146000	-2.51060900
C	5.37725600	1.63356600	-0.20832200
H	5.67432900	0.15376400	1.31901700
H	4.82067500	2.90607600	-1.84984600
H	6.22339200	2.23943900	0.09143300

*Propylene carbonate/Aniline coupling catalysed by MTBD*

TS1

C	2.34787400	1.16947900	-1.10249100
H	2.09179300	1.76753200	-1.98016100
C	3.31583500	0.03435900	-1.45334600
H	4.35434200	0.27111700	-1.22042600
O	2.88366200	-1.01976200	-0.61701800
C	1.48445100	-0.90111200	-0.48423800
O	0.73048700	-1.77397800	-0.84937800
N	1.40886600	-0.93963900	1.37444800
H	1.97757900	-0.21453100	1.80267500
C	1.80373200	-2.27527600	1.82993800
H	1.23863100	-2.99850000	1.24223700
H	2.86482900	-2.41884400	1.62850000
H	1.59894000	-2.42412100	2.89163100
C	2.86324400	2.06600900	0.01122200
H	3.18649100	1.46831900	0.86806400
H	3.72299500	2.64212800	-0.33929700
H	2.09219100	2.76480200	0.33840900
H	3.22931100	-0.25825600	-2.50472400
O	1.17548100	0.45811500	-0.71571600

H	0.41440100	-0.75148000	1.58768600
C	-1.77229800	-0.00783400	0.52298200
C	-1.09421700	2.36060500	0.32001600
C	-0.42924500	2.12655600	1.66660300
C	-1.29446000	1.16785200	2.47519700
H	-1.81643400	3.18312900	0.38803000
H	-0.27537500	3.08123600	2.17603900
H	-0.84785700	0.97431100	3.45355400
C	-1.97408300	1.22785400	-1.62635100
H	-2.42209500	2.19607400	-1.87379800
H	-0.98482700	1.17747900	-2.10554800
C	-2.83975300	0.08608800	-2.11554700
H	-3.86209000	0.20492500	-1.74740500
H	-2.86072300	0.07924300	-3.20703900
C	-2.25045900	-1.20589800	-1.58297000
H	-1.25140300	-1.38724500	-1.99605700
H	-2.88778800	-2.05433200	-1.84305400
N	-1.79827300	1.17986100	-0.18138200
N	-1.44951100	-0.09467700	1.78059500
N	-2.19249700	-1.13984300	-0.13083400
H	-0.33974100	2.64542600	-0.42538200
H	0.54515000	1.66055900	1.51078100
H	-2.27532500	1.63125100	2.65929200
C	-2.06972000	-2.41357800	0.55399000
H	-2.25128700	-2.26745200	1.61518700
H	-2.81326800	-3.09986200	0.14284200
H	-1.07097600	-2.83844800	0.40503200

TS2

C	-1.77221800	-1.52379500	-1.10546000
H	-1.26264200	-1.83439300	-2.02471700
C	-3.01833800	-0.66968100	-1.41950600

H	-3.94412700	-1.24601700	-1.39333500
O	-3.01916700	0.26138600	-0.36699400
C	-1.63175800	0.68768500	-0.29477000
O	-1.24807300	1.54821500	-1.10961300
N	-1.44850500	1.05869600	1.17401200
H	-1.94644900	0.34965100	1.70894400
C	-2.00915500	2.38517900	1.46163200
H	-1.53148200	3.10192800	0.79723300
H	-3.08376700	2.39883400	1.26971900
H	-1.80979200	2.65091400	2.50094300
C	-2.11236600	-2.73509600	-0.25002200
H	-2.68698000	-2.41012700	0.62205900
H	-2.71078700	-3.45599700	-0.81317600
H	-1.20674000	-3.23785000	0.09766800
H	-2.91855300	-0.15718400	-2.38169200
O	-0.93929400	-0.63752800	-0.37609500
H	-0.15188200	0.95641100	1.44879900
C	1.56698000	0.34996400	0.44826700
C	1.62825900	-2.07001600	0.91756100
C	0.72752700	-1.74207700	2.09663200
C	1.15244600	-0.39421600	2.66343000
H	2.55382000	-2.54739400	1.25939000
H	0.79745900	-2.53809700	2.84105200
H	0.51337500	-0.09700900	3.49773600
C	2.37435400	-1.25660300	-1.24277400
H	3.16680400	-2.00913600	-1.18498300
H	1.49862100	-1.72272700	-1.71393200
C	2.80930800	-0.05691900	-2.05992100
H	3.78711600	0.29899200	-1.72580900
H	2.88766800	-0.34411400	-3.10996200
C	1.77860600	1.04105100	-1.87145100
H	0.78250000	0.76117100	-2.23307000

H	2.08306100	1.95577600	-2.38156000
N	2.00257100	-0.89412800	0.12238200
N	1.05370000	0.63827600	1.64334100
N	1.68632500	1.34627300	-0.44919400
H	1.12366100	-2.77227900	0.24492700
H	-0.30472400	-1.66802200	1.75109600
H	2.17842000	-0.44756700	3.04712100
C	1.33864200	2.72163900	-0.11433700
H	1.36419100	2.84837100	0.96476700
H	2.07907200	3.38149200	-0.57329100
H	0.34207600	2.94127000	-0.50378800

TS3

C	-2.74540300	-0.90239800	0.39228000
H	-2.55640000	-1.98060400	0.52426000
C	-2.91868600	-0.59788200	-1.11561200
H	-3.95715100	-0.65017300	-1.44458800
O	-2.49064400	0.73687300	-1.23716200
C	-1.19807600	0.86048500	-0.71173000
O	-0.24416100	0.33124100	-1.28324700
N	-1.03389300	2.13645300	-0.08548500
H	-1.89094700	2.34233400	0.41567300
C	-0.75585600	3.18010300	-1.07488100
H	0.10539100	2.87275300	-1.66987300
H	-1.59254000	3.35774100	-1.76151100
H	-0.51184300	4.11259700	-0.56234200
C	-3.98905000	-0.50158500	1.17842900
H	-4.22807600	0.54138400	0.95349500
H	-4.85102700	-1.12314100	0.91852400
H	-3.79933200	-0.58919200	2.24940600
H	-2.30215100	-1.25232900	-1.74093200
O	-1.64555600	-0.14347200	0.79532200

H	-0.45108200	-0.94975400	1.16928300
C	1.41323900	-0.55583900	0.66958500
C	1.78847200	-1.91925500	-1.33813700
C	0.54357700	-2.67831000	-0.90890100
C	0.54177700	-2.77577600	0.60875100
H	2.63979600	-2.59695600	-1.46148200
H	0.53059300	-3.66170800	-1.38273300
H	-0.33894400	-3.29718500	0.98269100
C	3.05951500	0.12118200	-1.00590200
H	3.92845400	-0.39771900	-1.42029300
H	2.49420800	0.56929900	-1.83267700
C	3.47133200	1.20215100	-0.02748400
H	4.14719700	0.79840600	0.73068000
H	3.99124800	1.99857400	-0.56255000
C	2.21455300	1.73516700	0.63688700
H	1.54314000	2.20306000	-0.08781700
H	2.45716200	2.46697400	1.40814900
N	2.19987300	-0.87882300	-0.37751000
N	0.53490800	-1.43694400	1.17831100
N	1.52324000	0.62865600	1.28568400
H	1.59892900	-1.41748300	-2.29126800
H	-0.33597900	-2.11378800	-1.21959200
H	1.42538300	-3.31861300	0.96263600
C	0.71559500	0.92394100	2.46774200
H	0.64857400	0.03125800	3.08735400
H	1.21968600	1.71494300	3.02323300
H	-0.28623100	1.24488100	2.17981100

### 3- CYCLIC CARBONATE – METHYLAMINE COUPLING WITH TBD AND MTBD CATALYST

*Propylene carbonate/Methylamine coupling catalysed by TBD*

TS1

C	3.79180800	0.18367100	-0.55439600
H	4.28816000	1.08578800	-0.17742300
C	2.47869900	0.53755900	-1.25407100
O	1.53485700	0.44436400	-0.19404100
C	2.06829600	-0.30489900	0.87096300
O	1.75314200	-0.05136600	2.01679600
N	1.29095400	-1.96853900	0.54386400
H	0.28331400	-1.84600000	0.76984300
C	1.41463200	-2.54309300	-0.79158100
H	1.02221800	-3.56204300	-0.84487100
H	0.84131800	-1.91689500	-1.47679000
H	2.46477300	-2.54824300	-1.09091500
O	3.38740100	-0.63307200	0.52593000
H	1.73392100	-2.54428200	1.25402800
C	-1.69400900	-0.11669300	0.56727400
C	-3.64451400	-0.08288100	-0.94867400
C	-3.73735700	-1.54375400	-0.53591900
C	-2.32225500	-2.11073400	-0.46314700
H	-3.48815500	-0.00086300	-2.03243600
H	-4.36173900	-2.09029700	-1.24589900
H	-2.34735800	-3.16964600	-0.19557700
C	-2.54481100	2.03304200	-0.29275800
H	-2.85480500	2.33626500	-1.29811800
H	-3.27558300	2.44861500	0.41719800
C	-1.14905400	2.54588100	0.02226100
H	-0.44773900	2.15585000	-0.72030200



H	-1.12767100	3.63687200	-0.00550900
C	-0.74620600	2.03543200	1.39470400
H	-1.30444600	2.57484900	2.16926800
H	0.32067500	2.18825500	1.57241000
N	-2.54814600	0.58135900	-0.25446100
N	-1.52594000	-1.40398600	0.52181500
N	-1.00108800	0.60532800	1.49807400
H	-0.23042400	0.09303700	1.91492300
H	-4.57653100	0.44539100	-0.71328500
H	-4.19267500	-1.62427200	0.45473200
H	-1.86673000	-2.04431600	-1.46547100
H	4.48074600	-0.37340000	-1.19013800
C	2.44572300	1.92693400	-1.85267300
H	3.23122900	2.03484700	-2.60496900
H	1.48485900	2.12035100	-2.33131800
H	2.60211600	2.66957400	-1.06773200
H	2.24114600	-0.21078300	-2.01806900

TS2

C	4.11371600	-0.07102500	0.72131700
C	3.06081500	0.80195600	1.40576100
H	4.32830500	-0.96851500	1.31677100
H	5.04716800	0.45823600	0.51903700
H	3.09804800	0.71569700	2.49385600
O	1.86522800	0.17845200	0.96755400
O	3.50124100	-0.41413800	-0.50385800
C	2.07796000	-0.21330800	-0.40657800
O	1.57932900	0.51839400	-1.31144000
C	3.12188700	2.25845700	0.96669200
H	2.24386800	2.79144200	1.33550000
H	4.02035600	2.74266100	1.35792600
H	3.12339500	2.31025900	-0.12366200

N	1.44251200	-1.61572200	-0.41553800
H	1.84707700	-2.15754400	0.34404500
C	1.62080800	-2.27908500	-1.71300600
H	0.25186400	-1.41437200	-0.24711600
C	-1.65657600	-0.03535300	-0.19509300
C	-2.90920400	2.37411600	-0.93581800
H	-3.32951000	3.37931200	-0.86970800
H	-3.03067300	2.01315000	-1.95986900
C	-3.63830100	1.45608000	0.03125400
H	-4.65406700	1.24959900	-0.32375000
H	-3.72988100	1.94113600	1.01280600
C	-1.43014100	2.36093600	-0.58145200
H	-1.28271700	2.78069100	0.42348400
H	-0.84596600	2.96202500	-1.27852800
C	-1.89650500	-2.35781200	0.26832800
H	-1.22003200	-3.15451700	0.59091200
H	-2.47926300	-2.75530300	-0.57548700
C	-2.84332900	-1.96502900	1.39530300
H	-2.25276200	-1.62179900	2.24863900
H	-3.46249200	-2.80471700	1.71746000
C	-3.72997700	-0.84005200	0.89049000
H	-4.25027000	-0.35437200	1.72346200
H	-4.49791400	-1.23640200	0.21304800
N	-1.09241600	-1.22438100	-0.13878400
N	-0.94893800	1.00143800	-0.66349200
N	-2.95316800	0.17820700	0.19317900
H	0.05423300	0.82244100	-0.94405100
H	2.67904200	-2.45530000	-1.90687800
H	1.06679800	-3.21866800	-1.72749900
H	1.22616400	-1.60287000	-2.46919900

TS3

C	-3.17986000	0.10641500	-1.59262800
H	-2.55907800	-0.25242800	-2.41769700
C	-2.48639200	1.25313400	-0.82000000
O	-1.72368300	0.60256000	0.15537900
C	-2.08613200	-1.11083200	-0.03544700
O	-1.15592500	-1.58491000	-0.75941900
N	-2.23796000	-1.60750900	1.25985000
H	-0.23521600	0.80641700	0.00272200
C	-3.10981300	-0.89700400	2.17974000
H	-3.17093200	-1.45774400	3.11355100
H	-2.76680800	0.12369500	2.37837600
H	-4.10775800	-0.84935900	1.74545800
H	-1.84038800	1.82065200	-1.50814400
O	-3.32352600	-0.90959800	-0.62342700
H	-1.33257600	-1.84325600	1.64064900
C	1.69134500	0.02267400	-0.03211400
C	3.55278400	1.61915500	0.27822200
C	2.47860100	2.55683700	0.80478100
C	1.24134500	2.41186000	-0.06913400
H	3.96872300	2.00542100	-0.66121200
H	2.85242200	3.58189000	0.79691400
H	0.40955900	3.00366400	0.31620700
C	4.02639300	-0.77646800	-0.09226800
H	4.83391700	-0.38037700	-0.71632600
H	4.45425800	-1.00956500	0.89119600
C	3.42866700	-2.02566200	-0.71978100
H	3.21261000	-1.84492100	-1.77570500
H	4.14350600	-2.84716800	-0.64994900
C	2.13026700	-2.35563500	0.00357300
H	2.34534300	-2.62335900	1.04626600
H	1.62059400	-3.20281800	-0.45653800
N	3.02475200	0.27622700	0.05623300

N	0.81905200	1.02714700	-0.08048600
N	1.23285300	-1.22028100	-0.06424300
H	0.15951300	-1.38067400	-0.34753500
H	4.37722600	1.53691400	0.99361800
H	2.22338800	2.29037700	1.83348700
H	1.45842600	2.76514800	-1.08551200
H	-4.17490800	0.36910800	-1.95137800
C	-3.49835700	2.18776000	-0.16801600
H	-2.98950600	2.90103100	0.48380500
H	-4.07336000	2.74227600	-0.91530800
H	-4.18784600	1.59817800	0.44175500

*Propylene carbonate/Methylamine coupling catalysed by MTBD*

TS1

C	2.34787400	1.16947900	-1.10249100
H	2.09179300	1.76753200	-1.98016100
C	3.31583500	0.03435900	-1.45334600
H	4.35434200	0.27111700	-1.22042600
O	2.88366200	-1.01976200	-0.61701800
C	1.48445100	-0.90111200	-0.48423800
O	0.73048700	-1.77397800	-0.84937800
N	1.40886600	-0.93963900	1.37444800
H	1.97757900	-0.21453100	1.80267500
C	1.80373200	-2.27527600	1.82993800
H	1.23863100	-2.99850000	1.24223700
H	2.86482900	-2.41884400	1.62850000
H	1.59894000	-2.42412100	2.89163100
C	2.86324400	2.06600900	0.01122200
H	3.18649100	1.46831900	0.86806400
H	3.72299500	2.64212800	-0.33929700
H	2.09219100	2.76480200	0.33840900
H	3.22931100	-0.25825600	-2.50472400

O	1.17548100	0.45811500	-0.71571600
H	0.41440100	-0.75148000	1.58768600
C	-1.77229800	-0.00783400	0.52298200
C	-1.09421700	2.36060500	0.32001600
C	-0.42924500	2.12655600	1.66660300
C	-1.29446000	1.16785200	2.47519700
H	-1.81643400	3.18312900	0.38803000
H	-0.27537500	3.08123600	2.17603900
H	-0.84785700	0.97431100	3.45355400
C	-1.97408300	1.22785400	-1.62635100
H	-2.42209500	2.19607400	-1.87379800
H	-0.98482700	1.17747900	-2.10554800
C	-2.83975300	0.08608800	-2.11554700
H	-3.86209000	0.20492500	-1.74740500
H	-2.86072300	0.07924300	-3.20703900
C	-2.25045900	-1.20589800	-1.58297000
H	-1.25140300	-1.38724500	-1.99605700
H	-2.88778800	-2.05433200	-1.84305400
N	-1.79827300	1.17986100	-0.18138200
N	-1.44951100	-0.09467700	1.78059500
N	-2.19249700	-1.13984300	-0.13083400
H	-0.33974100	2.64542600	-0.42538200
H	0.54515000	1.66055900	1.51078100
H	-2.27532500	1.63125100	2.65929200
C	-2.06972000	-2.41357800	0.55399000
H	-2.25128700	-2.26745200	1.61518700
H	-2.81326800	-3.09986200	0.14284200
H	-1.07097600	-2.83844800	0.40503200

TS2

C	-1.77221800	-1.52379500	-1.10546000
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H	-1.26264200	-1.83439300	-2.02471700
C	-3.01833800	-0.66968100	-1.41950600
H	-3.94412700	-1.24601700	-1.39333500
O	-3.01916700	0.26138600	-0.36699400
C	-1.63175800	0.68768500	-0.29477000
O	-1.24807300	1.54821500	-1.10961300
N	-1.44850500	1.05869600	1.17401200
H	-1.94644900	0.34965100	1.70894400
C	-2.00915500	2.38517900	1.46163200
H	-1.53148200	3.10192800	0.79723300
H	-3.08376700	2.39883400	1.26971900
H	-1.80979200	2.65091400	2.50094300
C	-2.11236600	-2.73509600	-0.25002200
H	-2.68698000	-2.41012700	0.62205900
H	-2.71078700	-3.45599700	-0.81317600
H	-1.20674000	-3.23785000	0.09766800
H	-2.91855300	-0.15718400	-2.38169200
O	-0.93929400	-0.63752800	-0.37609500
H	-0.15188200	0.95641100	1.44879900
C	1.56698000	0.34996400	0.44826700
C	1.62825900	-2.07001600	0.91756100
C	0.72752700	-1.74207700	2.09663200
C	1.15244600	-0.39421600	2.66343000
H	2.55382000	-2.54739400	1.25939000
H	0.79745900	-2.53809700	2.84105200
H	0.51337500	-0.09700900	3.49773600
C	2.37435400	-1.25660300	-1.24277400
H	3.16680400	-2.00913600	-1.18498300
H	1.49862100	-1.72272700	-1.71393200
C	2.80930800	-0.05691900	-2.05992100
H	3.78711600	0.29899200	-1.72580900
H	2.88766800	-0.34411400	-3.10996200

C	1.77860600	1.04105100	-1.87145100
H	0.78250000	0.76117100	-2.23307000
H	2.08306100	1.95577600	-2.38156000
N	2.00257100	-0.89412800	0.12238200
N	1.05370000	0.63827600	1.64334100
N	1.68632500	1.34627300	-0.44919400
H	1.12366100	-2.77227900	0.24492700
H	-0.30472400	-1.66802200	1.75109600
H	2.17842000	-0.44756700	3.04712100
C	1.33864200	2.72163900	-0.11433700
H	1.36419100	2.84837100	0.96476700
H	2.07907200	3.38149200	-0.57329100
H	0.34207600	2.94127000	-0.50378800

### TS3

C	-2.74540300	-0.90239800	0.39228000
H	-2.55640000	-1.98060400	0.52426000
C	-2.91868600	-0.59788200	-1.11561200
H	-3.95715100	-0.65017300	-1.44458800
O	-2.49064400	0.73687300	-1.23716200
C	-1.19807600	0.86048500	-0.71173000
O	-0.24416100	0.33124100	-1.28324700
N	-1.03389300	2.13645300	-0.08548500
H	-1.89094700	2.34233400	0.41567300
C	-0.75585600	3.18010300	-1.07488100
H	0.10539100	2.87275300	-1.66987300
H	-1.59254000	3.35774100	-1.76151100
H	-0.51184300	4.11259700	-0.56234200
C	-3.98905000	-0.50158500	1.17842900
H	-4.22807600	0.54138400	0.95349500
H	-4.85102700	-1.12314100	0.91852400
H	-3.79933200	-0.58919200	2.24940600

H	-2.30215100	-1.25232900	-1.74093200
O	-1.64555600	-0.14347200	0.79532200
H	-0.45108200	-0.94975400	1.16928300
C	1.41323900	-0.55583900	0.66958500
C	1.78847200	-1.91925500	-1.33813700
C	0.54357700	-2.67831000	-0.90890100
C	0.54177700	-2.77577600	0.60875100
H	2.63979600	-2.59695600	-1.46148200
H	0.53059300	-3.66170800	-1.38273300
H	-0.33894400	-3.29718500	0.98269100
C	3.05951500	0.12118200	-1.00590200
H	3.92845400	-0.39771900	-1.42029300
H	2.49420800	0.56929900	-1.83267700
C	3.47133200	1.20215100	-0.02748400
H	4.14719700	0.79840600	0.73068000
H	3.99124800	1.99857400	-0.56255000
C	2.21455300	1.73516700	0.63688700
H	1.54314000	2.20306000	-0.08781700
H	2.45716200	2.46697400	1.40814900
N	2.19987300	-0.87882300	-0.37751000
N	0.53490800	-1.43694400	1.17831100
N	1.52324000	0.62865600	1.28568400
H	1.59892900	-1.41748300	-2.29126800
H	-0.33597900	-2.11378800	-1.21959200
H	1.42538300	-3.31861300	0.96263600
C	0.71559500	0.92394100	2.46774200
H	0.64857400	0.03125800	3.08735400
H	1.21968600	1.71494300	3.02323300
H	-0.28623100	1.24488100	2.17981100



#### 4- CYCLIC CARBONATE – CYCLOHEXYLAMINE COUPLING WITH TBD CATALYST

TS1

C	2.41621200	3.32324800	0.16745800
C	1.06160000	3.21350800	0.87893500
H	3.25982100	3.35354200	0.86008000
H	2.44470600	4.20978600	-0.47523300
H	1.17613500	2.71452100	1.85198600
O	0.32884100	2.37973600	0.00223900
O	2.48707400	2.15965900	-0.63294400
C	1.22054500	1.54941300	-0.69204100
O	0.85556800	0.99890100	-1.72104900
C	0.34049700	4.52999000	1.06218800
H	-0.63124300	4.37204700	1.53103300
H	0.92813600	5.20111800	1.69329700
H	0.18704600	5.00003200	0.08921100
N	1.44903600	0.24912000	0.54386200
H	1.80011700	0.64239600	1.41415000
H	0.48460100	-0.13804100	0.70447400
C	-2.12117500	-0.53527600	-0.01579900
C	-3.96469100	-0.35324100	-2.17658300
H	-4.75692200	0.03967500	-2.81664400
H	-3.60852900	-1.29478200	-2.60108400
C	-4.51121400	-0.58095800	-0.77651300
H	-5.17998900	-1.44925200	-0.76035400
H	-5.10642400	0.28957400	-0.46511600
C	-2.79258000	0.60987100	-2.07891900
H	-3.13517600	1.58173300	-1.69439200
H	-2.33357800	0.78172300	-3.05269300
C	-1.54523700	-1.50290700	2.04395400

H	-0.75501300	-1.35715200	2.78622500
H	-1.60848400	-2.58665600	1.86125800
C	-2.88311600	-1.01053000	2.58346700
H	-2.80126700	0.05711400	2.80464600
H	-3.17319600	-1.53157700	3.49849500
C	-3.93433200	-1.23510000	1.50953800
H	-4.84541200	-0.66960300	1.73742700
H	-4.21381500	-2.29649000	1.46727800
N	-1.17484700	-0.79465300	0.83585200
N	-1.79710100	0.00779800	-1.22173500
N	-3.45436300	-0.80794900	0.20146700
H	-0.82972000	0.31558000	-1.34035400
C	2.37038300	-0.78866100	0.04019200
C	3.16574000	-1.43394800	1.18877500
C	1.62627400	-1.87074400	-0.73730700
H	3.05795700	-0.27965000	-0.64398000
C	3.72895100	-2.81273600	0.78928900
H	2.50186500	-1.54678900	2.05344800
H	3.97685900	-0.76191500	1.48879800
C	2.64768500	-2.74563500	-1.48824000
H	1.04052800	-2.46752700	-0.02906500
H	0.92213400	-1.41306300	-1.43170400
C	3.97811900	-2.87546800	-0.71878700
H	3.01028600	-3.59434000	1.05577800
H	4.64295200	-3.02415700	1.34820200
H	2.83664200	-2.31487000	-2.47471300
H	2.21809400	-3.73743900	-1.65262300
H	4.65448500	-2.06156900	-0.99976400
H	4.48350100	-3.80550200	-0.98780400

## TS2

C	-3.05904900	2.48176100	-0.74310100
C	-1.75369600	3.22330800	-1.02684400
H	-3.46696100	2.03977000	-1.66385200
H	-3.82216500	3.10353100	-0.27142100
H	-1.74135200	3.67139100	-2.02311300
O	-0.82870000	2.15010700	-1.02575800
O	-2.65833300	1.47893900	0.16498700
C	-1.25015000	1.21533900	0.00146000
O	-0.60221400	1.21911500	1.08865500
C	-1.41158700	4.24909800	0.04446700
H	-0.39310700	4.61083400	-0.10438600
H	-2.09875900	5.09828100	0.00377100
H	-1.46910000	3.77849200	1.02782400
N	-1.10262600	-0.11857000	-0.76317000
H	-1.38480900	0.05166200	-1.72700000
C	-1.81738600	-1.30772900	-0.23735200
C	-1.75572400	-1.41875400	1.28420600
C	-3.27277700	-1.38034000	-0.74617500
C	-2.23946100	-2.81743500	1.71082800
C	-4.16113200	-2.20726600	0.19729200
C	-3.36174000	-3.36180900	0.80110500
H	-0.73979100	-1.23297700	1.63301800
H	-3.66769100	-0.36718100	-0.82612300
H	-1.39668100	-3.51490600	1.70803800
H	-4.52695400	-1.56696500	1.00598100
H	-2.93228900	-3.95516700	-0.01434800
H	0.10945100	-0.39041600	-0.73180300
C	2.31264000	-0.22951800	0.00453100
C	4.10454300	0.61369200	1.99460000
H	4.88013500	1.18067700	2.51257000

H	3.75086600	-0.17751000	2.66006600
C	4.68093500	0.00853600	0.72540500
H	5.37870200	-0.80108600	0.96523800
H	5.24369000	0.76985500	0.16806100
C	2.92819200	1.49824300	1.61049700
H	3.27890300	2.34112300	0.99889400
H	2.43693300	1.91275000	2.49106900
C	1.74516100	-1.88371100	-1.61808700
H	0.94774300	-1.98976500	-2.35907100
H	1.82516000	-2.84712100	-1.09356100
C	3.07091800	-1.56572600	-2.29644000
H	2.96482600	-0.63741900	-2.86362000
H	3.37586000	-2.35828700	-2.98258200
C	4.12340400	-1.39343300	-1.21445500
H	5.02753200	-0.93147000	-1.62605200
H	4.41345300	-2.37055500	-0.80600000
N	1.37291900	-0.82095900	-0.70753900
N	1.95702200	0.69844200	0.90014500
N	3.63848400	-0.54241100	-0.13395100
H	0.92113000	0.93202500	0.97500600
H	-3.27732100	-1.82662000	-1.74719700
H	-5.03947200	-2.57261500	-0.33947700
H	-4.01154800	-4.03535200	1.36418300
H	-2.59635300	-2.76429900	2.74248000
H	-2.37116600	-0.62831000	1.71925500
H	-1.26402900	-2.16870300	-0.63895000

### TS3

C	-1.74599100	3.20849300	0.21790800
H	-0.96283000	3.87650000	-0.14873000
C	-1.23840100	2.32984200	1.38939500

O	-0.74569900	1.17903100	0.77076500
C	-1.00600700	1.43207800	-0.96771500
O	0.07238300	1.92991400	-1.41426800
N	-1.41857500	0.19611300	-1.46480400
H	0.69229600	0.74084300	0.91424100
H	-0.44181600	2.86393100	1.92791500
O	-2.08739800	2.27563300	-0.78623400
H	-0.62974500	-0.33109700	-1.81604900
C	2.43362500	-0.00415600	0.03997600
C	3.88967100	-1.37590100	1.48943500
C	2.66222400	-1.48820500	2.37899600
C	1.97894300	-0.13026400	2.42763700
H	4.67813300	-0.80542000	1.99689400
H	2.96126600	-1.81851100	3.37487200
H	1.04070300	-0.17378300	2.98340500
C	4.54653200	-0.92388300	-0.84881000
H	5.54255600	-0.80612300	-0.41023200
H	4.47208900	-1.95134100	-1.22719900
C	4.33637700	0.07193100	-1.97813600
H	4.63362400	1.07216500	-1.65359700
H	4.95242700	-0.21004500	-2.83348800
C	2.85822100	0.08632300	-2.34000800
H	2.56595500	-0.89190800	-2.74420100
H	2.63982100	0.83580100	-3.10136900
N	3.56754900	-0.73304300	0.21857500
N	1.66078800	0.29740500	1.08120800
N	2.07693700	0.41682300	-1.16544000
H	1.19409300	1.09840200	-1.26501400
H	4.29513100	-2.36744800	1.26453000
H	1.96736000	-2.22302700	1.96421400
H	2.62970800	0.59850300	2.92759900
H	-2.64414100	3.77479900	0.46374700

C	-2.36125300	1.96928100	2.35588900
H	-2.00727300	1.24156000	3.08966900
H	-2.73424000	2.84998400	2.88679700
H	-3.18824300	1.51952800	1.79925800
C	-2.40565100	-0.59798400	-0.75075800
C	-3.37248400	-1.26625200	-1.74441700
C	-1.79290400	-1.66352900	0.16164300
H	-2.95671700	0.10732100	-0.12607000
C	-4.10649600	-2.47001400	-1.11987900
H	-2.79868500	-1.58864400	-2.61917300
H	-4.08269400	-0.51477400	-2.09895800
C	-2.87881700	-2.26466000	1.07504900
H	-1.34960000	-2.44567900	-0.46960300
H	-0.99420100	-1.21148500	0.75094900
C	-4.26091900	-2.27938500	0.39042800
H	-3.53737000	-3.38927600	-1.29743700
H	-5.07926600	-2.61132600	-1.59629800
H	-2.93594300	-1.68219400	1.99910500
H	-2.59851400	-3.28310100	1.35985500
H	-4.77713600	-1.33100000	0.57376900
H	-4.88795500	-3.06313500	0.82191800

5- CYCLIC CARBONATE – METHYLAMINE COUPLING WITH TBD  
ACTING AS A NUCLEOPHILE (SEE ESI2)

TS1

C	-2.49826900	-1.74811600	-1.15827300
H	-3.27567200	-1.22423600	-1.72227600
C	-2.62557400	-1.44857300	0.36967300
H	-2.43007300	-2.37881100	0.92512600
O	-1.63226900	-0.51005400	0.66343200
C	-1.13182500	0.03403200	-1.03875800
O	-1.88419000	0.91777200	-1.39444100
O	-1.22316600	-1.25568200	-1.52459000
C	1.16587000	-0.34478300	-0.13097000
C	3.00512700	1.18014300	-0.76418200
C	1.89874600	2.21213800	-0.84135300
C	0.71855100	1.59725700	-1.55954100
H	3.42645400	0.97622300	-1.75603600
H	2.24799900	3.09508300	-1.37870600
H	-0.13851800	2.26407800	-1.56266500
C	3.47106900	-0.87163600	0.53287800
H	4.36351400	-0.92950400	-0.09660800
H	3.75480000	-0.36654700	1.46529700
C	2.92709300	-2.25846100	0.82406400
H	2.81475000	-2.81604200	-0.10911200
H	3.62110300	-2.79991800	1.46836700
C	1.56769700	-2.10967400	1.48717000
H	1.68026000	-1.63304600	2.46936600
H	1.09832400	-3.08200400	1.64217900
N	2.48997300	-0.05787400	-0.18106100
N	0.29410800	0.37971000	-0.86353300
N	0.70422700	-1.32469300	0.62962200
H	-0.37334100	-1.17065100	0.80091000

H	3.81878000	1.52398100	-0.11906600
H	1.56664400	2.50584900	0.15833100
H	0.97051200	1.35200700	-2.59816100
H	-2.51654200	-2.81113600	-1.39254500
C	-4.00721600	-0.92133000	0.72223000
H	-4.78943900	-1.63324900	0.44105600
H	-4.07858100	-0.72981900	1.79414600
H	-4.16843700	0.01652200	0.18618500
C	-1.31958100	3.35568400	2.14080100
H	-0.72762600	3.21053700	3.04750200
H	-2.37995600	3.29639600	2.42081700
H	-1.12422300	4.37154500	1.78945500
N	-0.90006500	2.39432100	1.12341400
H	-1.12126400	1.44622300	1.42183600
H	-1.47030100	2.49989800	0.28787000

## TS2

C	-2.85079200	-0.08464700	0.93266500
H	-2.38533300	-0.80596300	1.61013400
C	-4.05573700	-0.70665500	0.24084200
O	-3.62434800	-1.77754700	-0.58807600
C	-0.65447300	0.72162300	0.34301700
O	-0.51465400	0.96283300	1.55181300
H	-4.70097500	-1.15670400	0.99994700
O	-1.95294400	0.26617300	-0.10888200
C	1.65438800	-0.02510000	-0.25166000
C	2.31524800	-2.41211500	0.07918500
C	0.89589500	-2.72003100	-0.34967800
C	-0.02295200	-1.68563200	0.26907000
H	2.47210800	-2.71338900	1.12291500



H	0.62067400	-3.72541000	-0.02735600
H	-1.05971600	-1.88730900	0.00643200
C	4.01444100	-0.64246300	0.05102700
H	4.45348000	-1.29461100	0.81221600
H	4.51955400	-0.86003600	-0.89942800
C	4.19394600	0.81702000	0.42786100
H	3.84267400	0.97766900	1.45029000
H	5.24990600	1.08820300	0.37525700
C	3.35421400	1.65525300	-0.52412500
H	3.75870100	1.57183800	-1.54222000
H	3.39102700	2.71105500	-0.24888000
N	2.59988100	-0.98810300	-0.05149500
N	0.32162400	-0.36046400	-0.24021400
N	1.97274200	1.22558100	-0.48760200
H	-2.93330300	-1.39804700	-1.14286700
H	3.04134800	-2.95713700	-0.53387200
H	0.80945900	-2.67239100	-1.43829500
H	0.05877700	-1.70150600	1.36485400
C	-1.02263700	3.13937400	-0.06066800
H	-0.63744600	3.28618400	0.94606800
H	-0.77475000	3.99291900	-0.69180900
H	-2.10718000	3.01810700	-0.00943900
N	-0.39912400	1.92640700	-0.59615600
H	-0.77951800	1.68272400	-1.50786900
H	0.83057300	1.86678800	-0.61550100
H	-3.12946200	0.79543900	1.52041400
C	-4.84702600	0.31633800	-0.56613100
H	-5.66110000	-0.17787200	-1.09781100
H	-5.26564100	1.08875500	0.08381200
H	-4.19125100	0.79728800	-1.29599800