

Transamidation vitrimers enabled by neighbouring fluorine atom activation

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Supporting information

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NMR spectra of isolated compounds

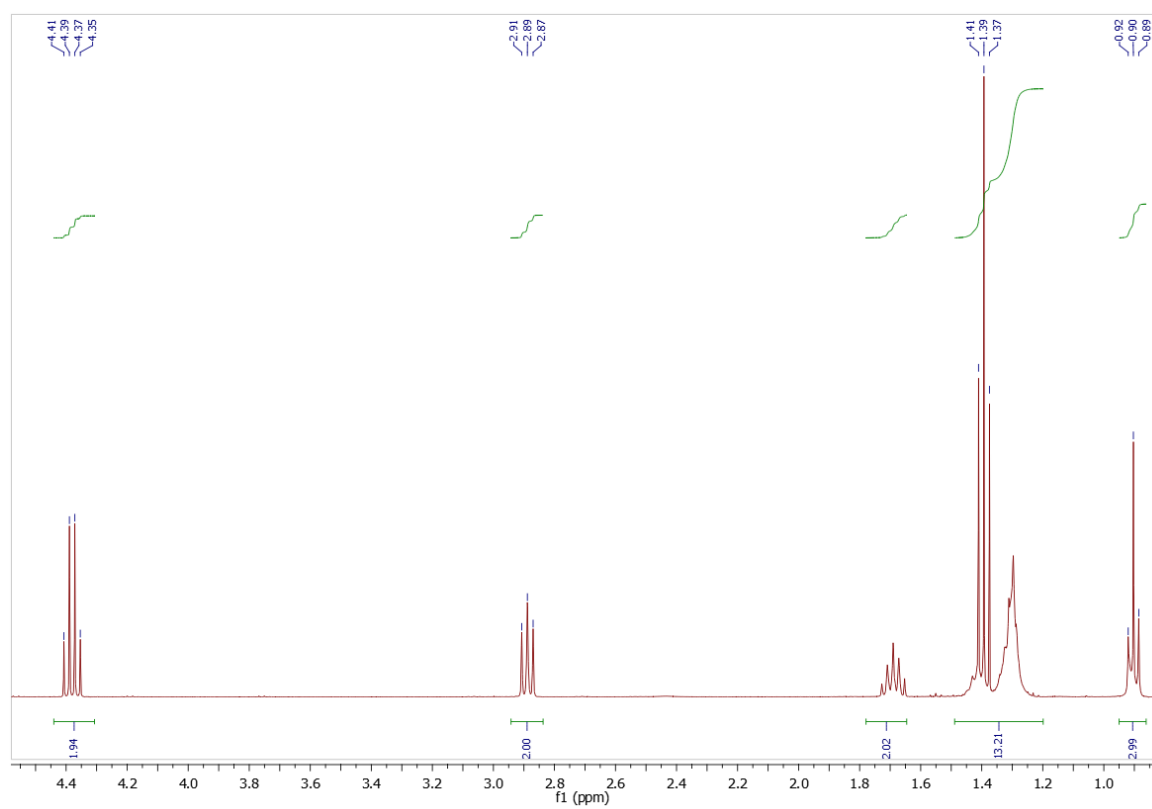


Figure S1. ¹H-NMR of **1**

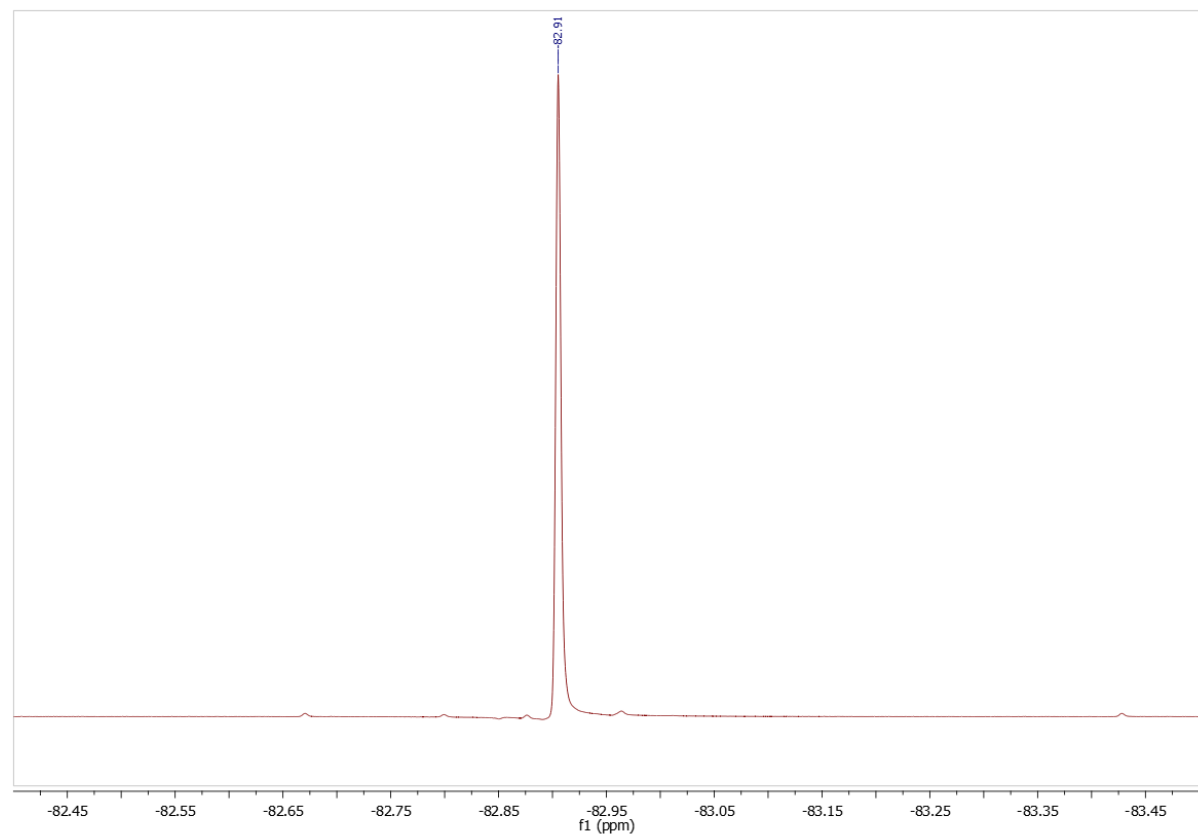


Figure S2. ¹⁹F-NMR of **1**

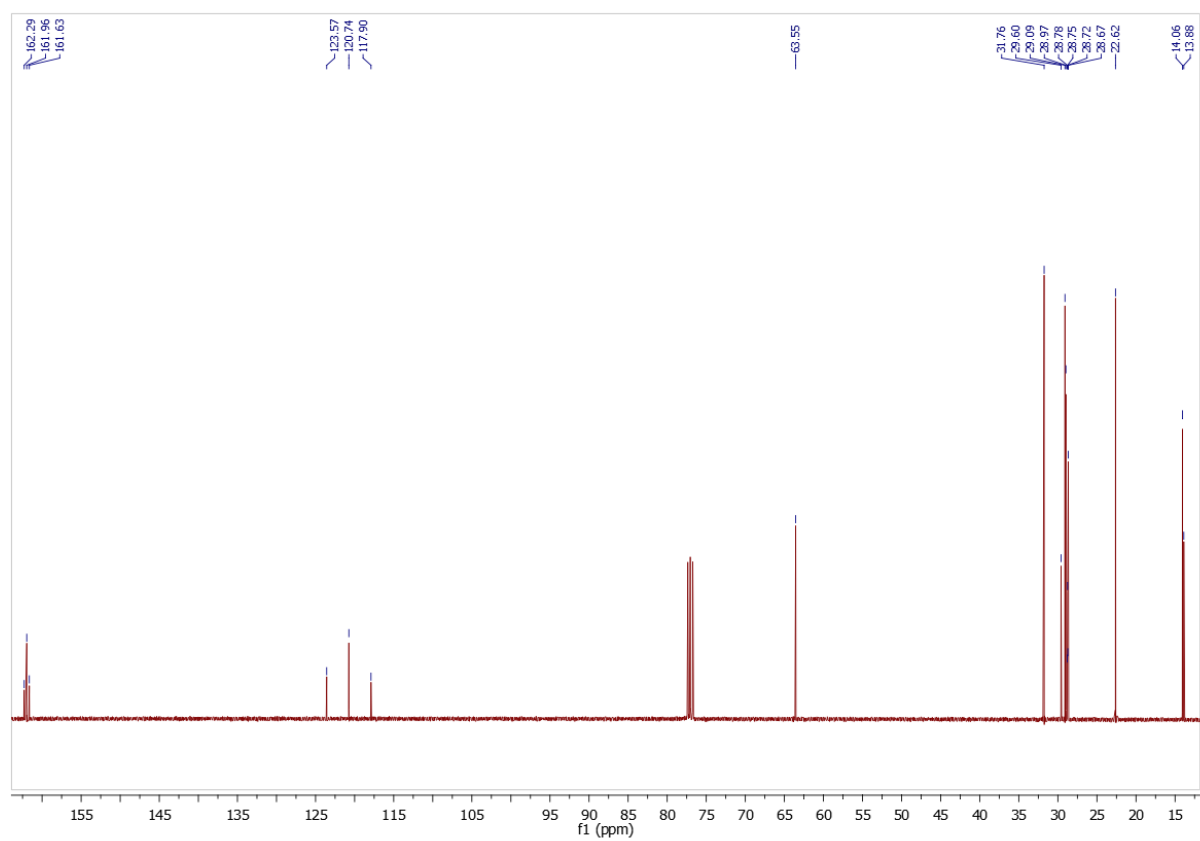


Figure S3. ^{13}C -NMR of **1**

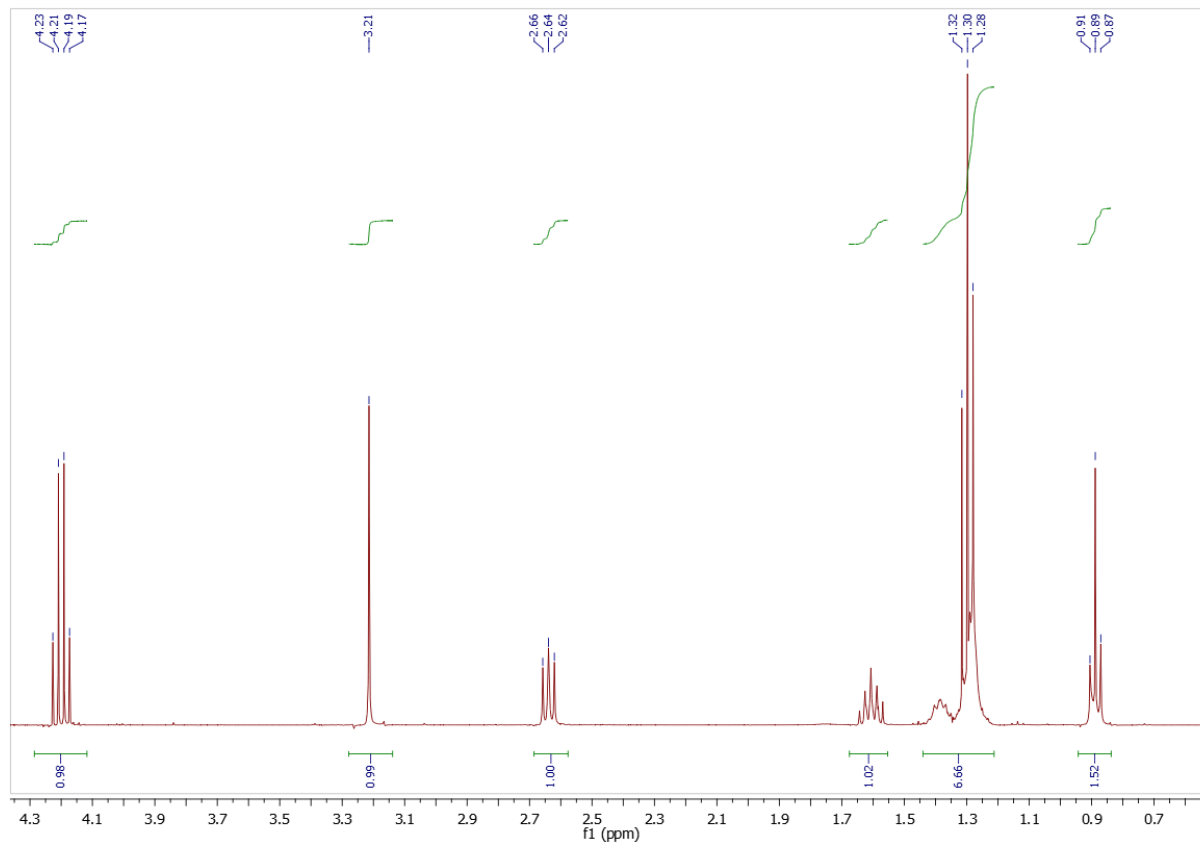


Figure S4. ^1H -NMR of **2**

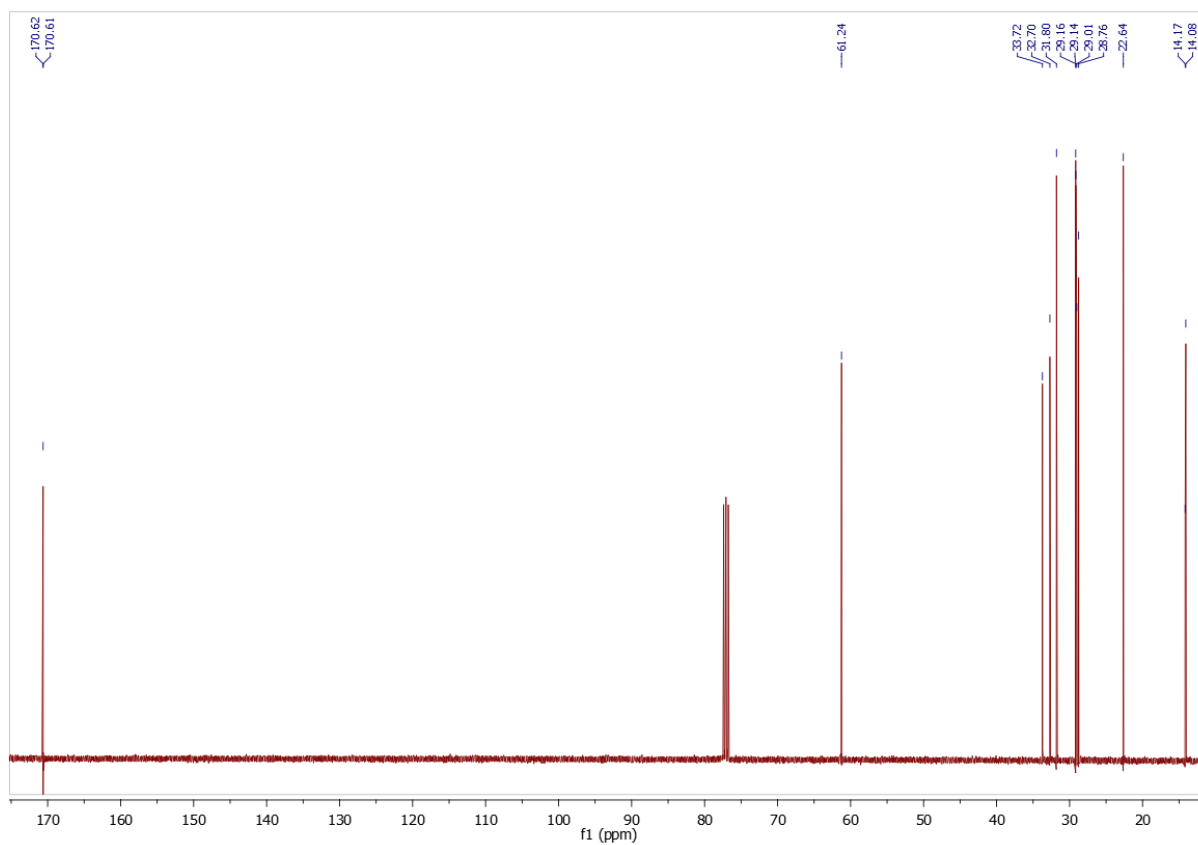


Figure S5. $^{13}\text{C-NMR}$ of **2**

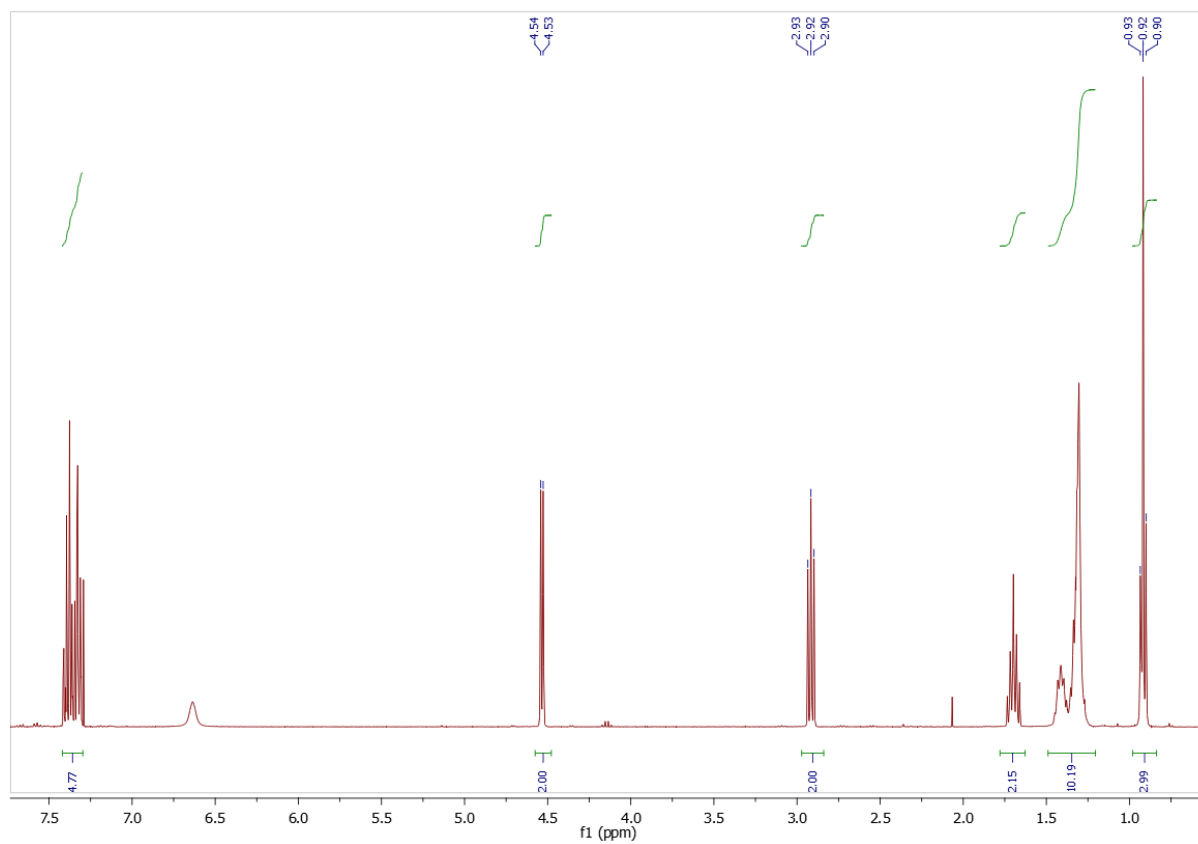


Figure S6. $^1\text{H-NMR}$ of **3**

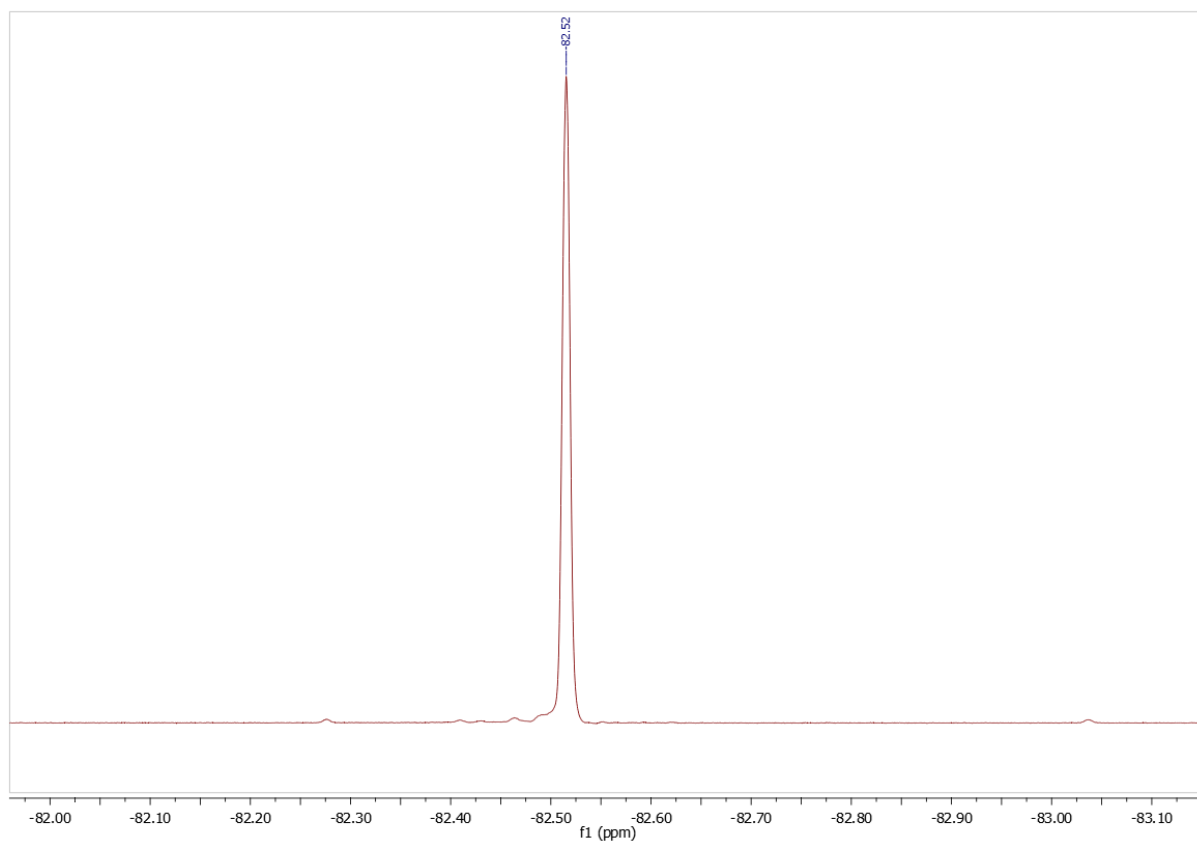


Figure S7. ^{19}F -NMR of **3**

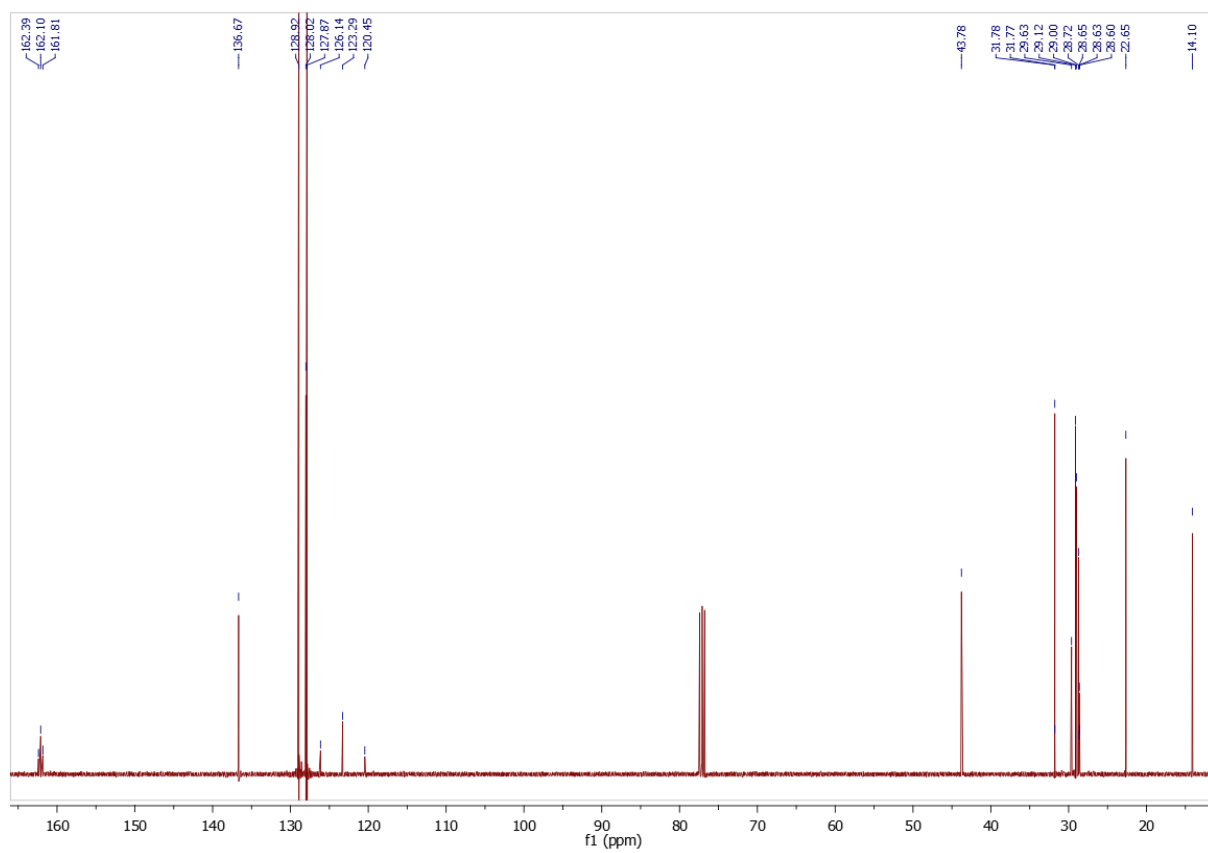


Figure S8. ^{13}C -NMR of **3**

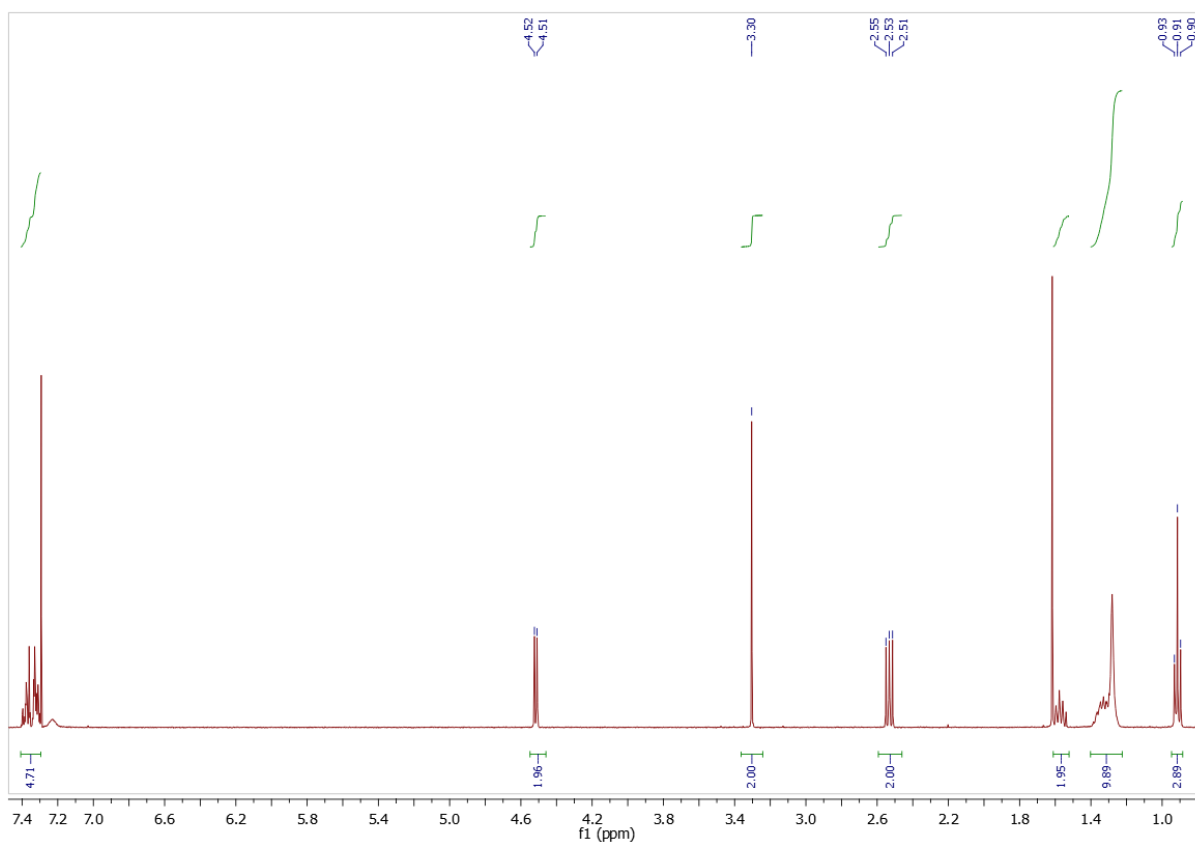


Figure S9. $^1\text{H-NMR}$ of **4**

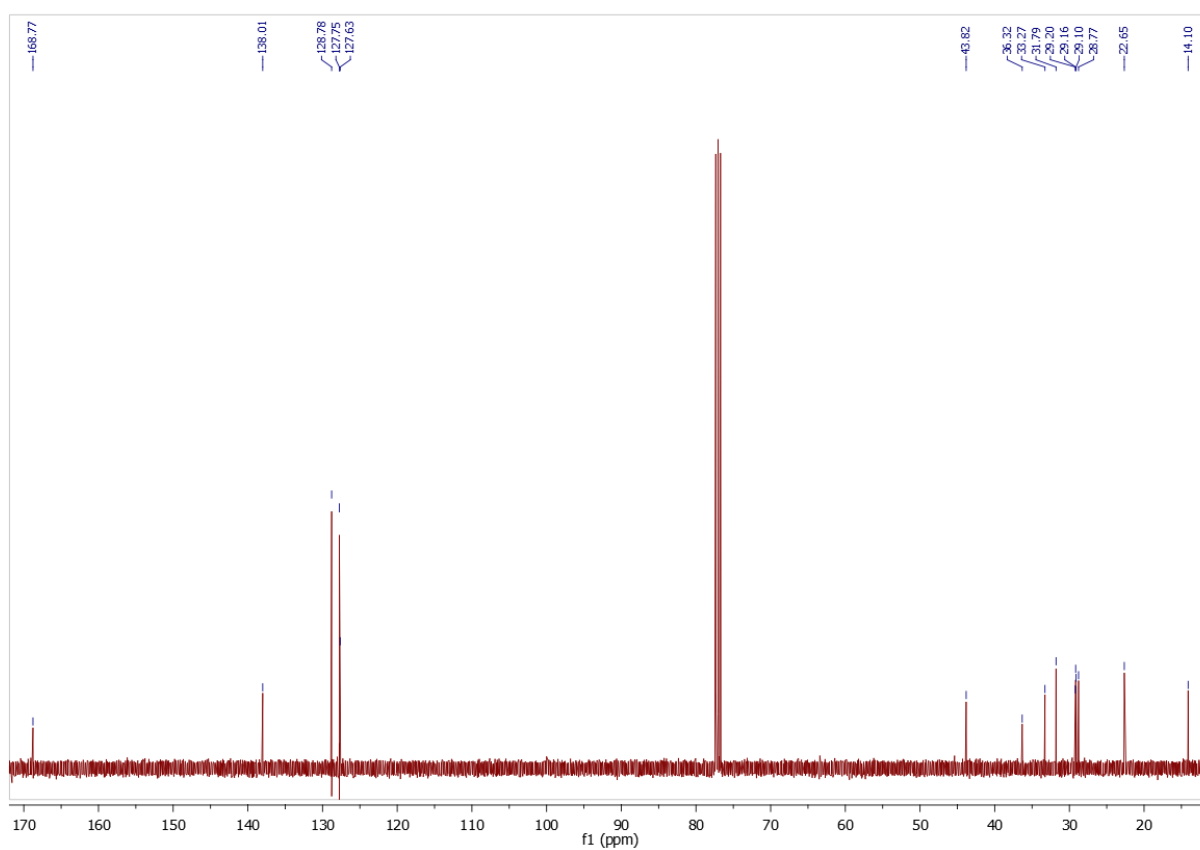
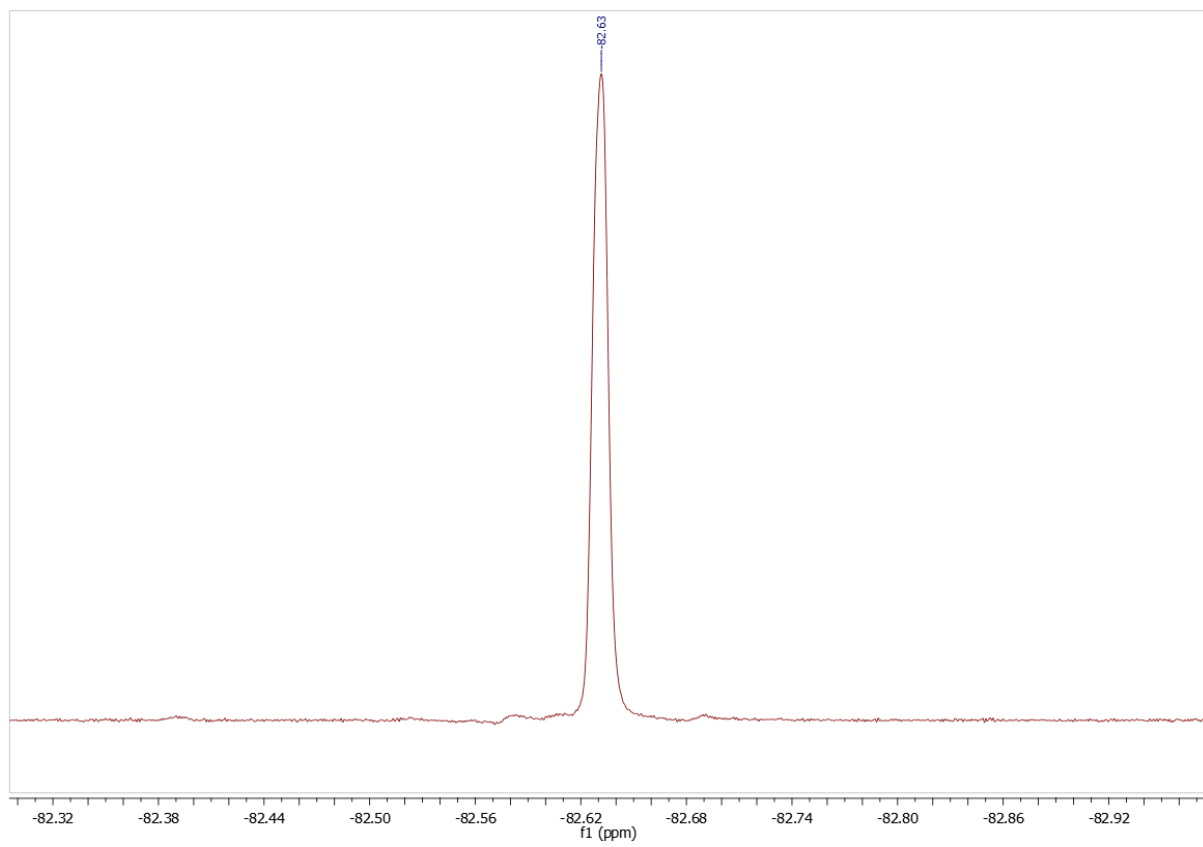
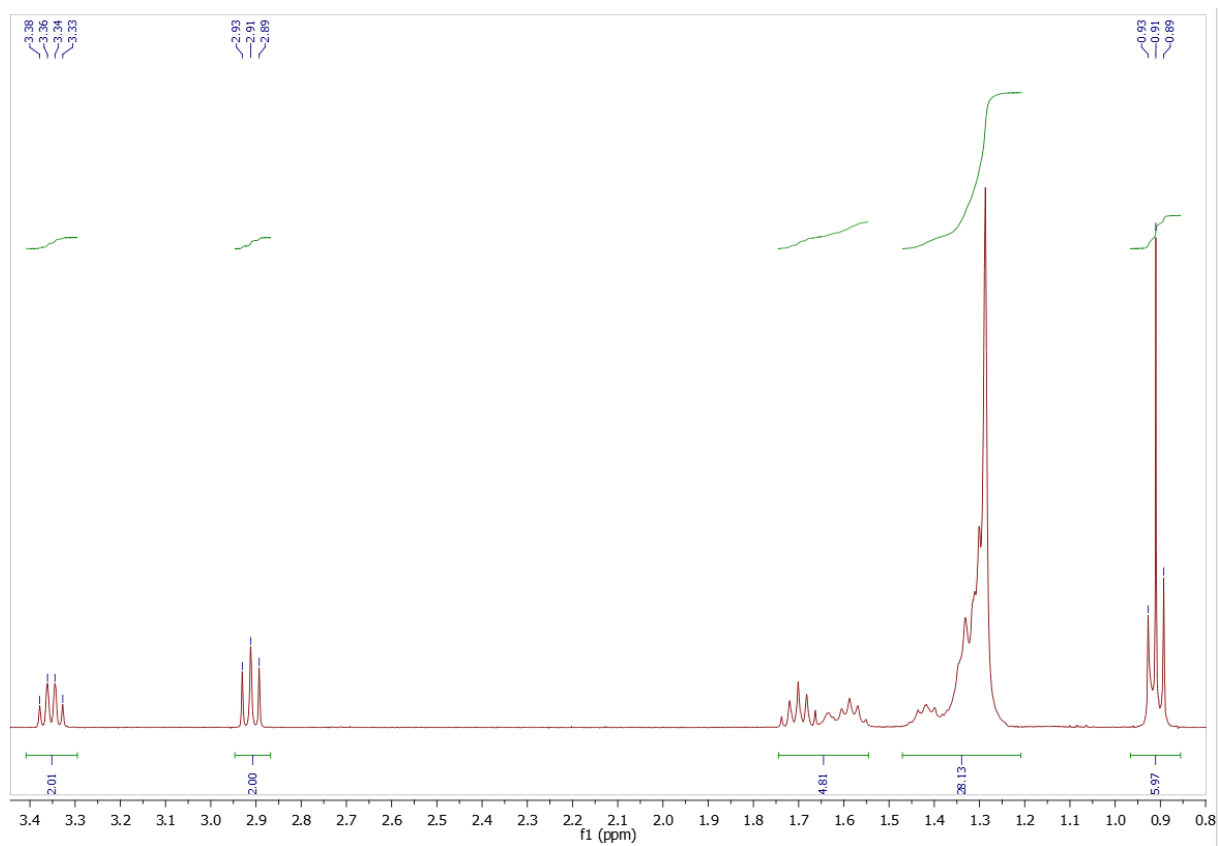


Figure S10. $^{13}\text{C-NMR}$ of **4**



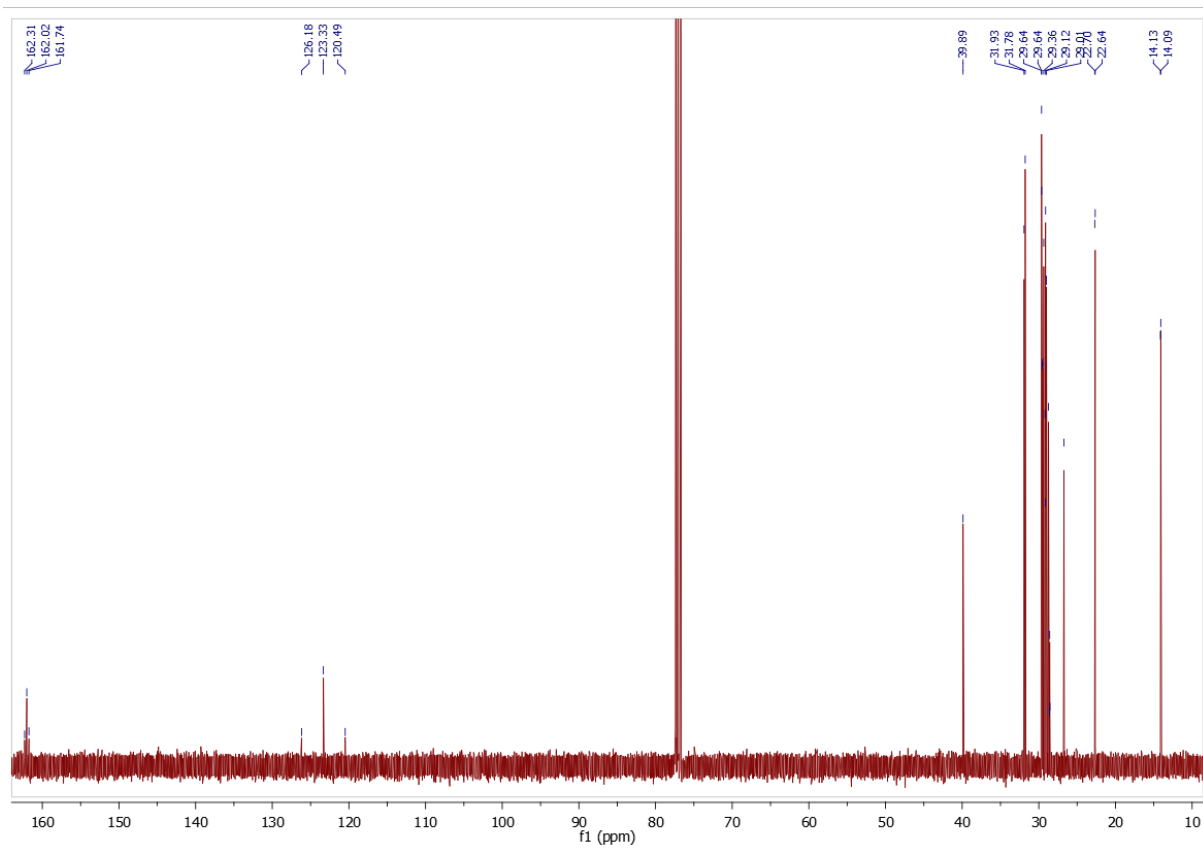


Figure S13. ^{13}C -NMR of **9**

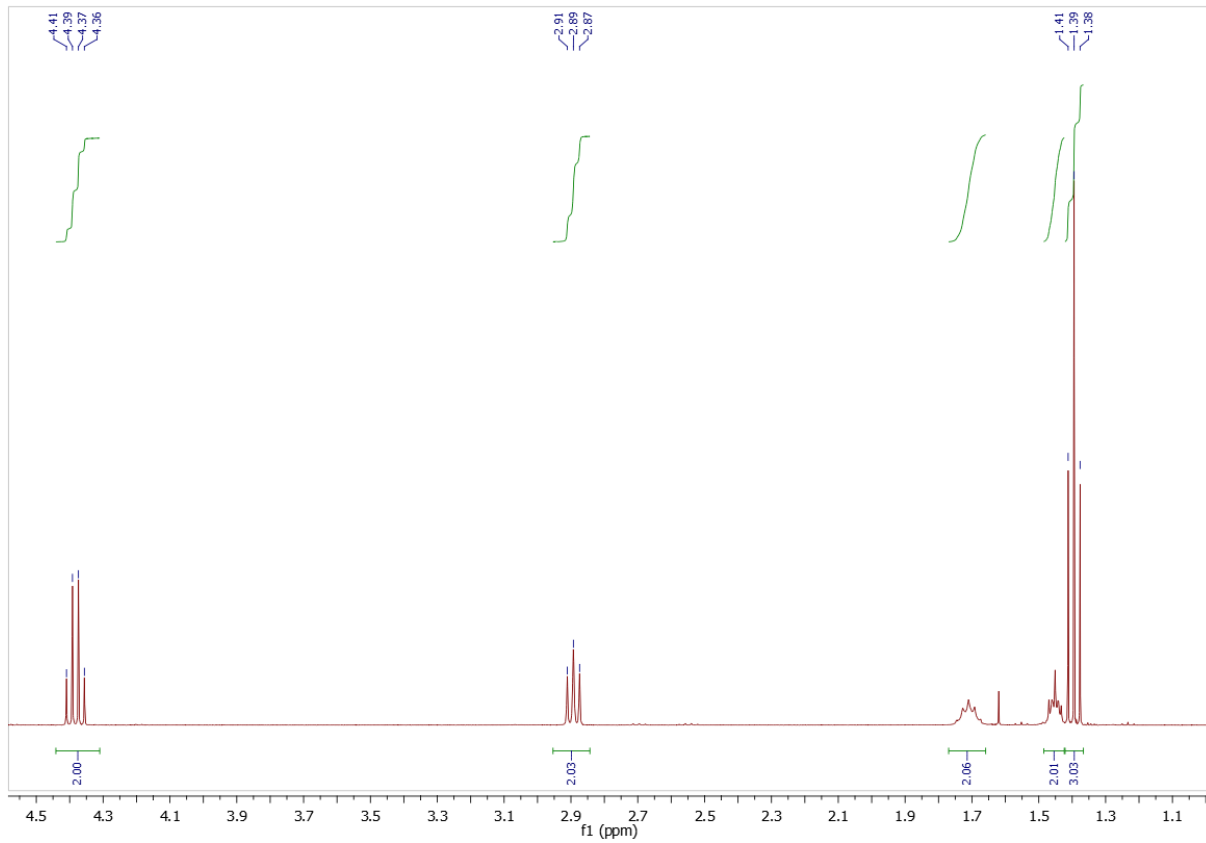


Figure S14. ^1H -NMR of **10**

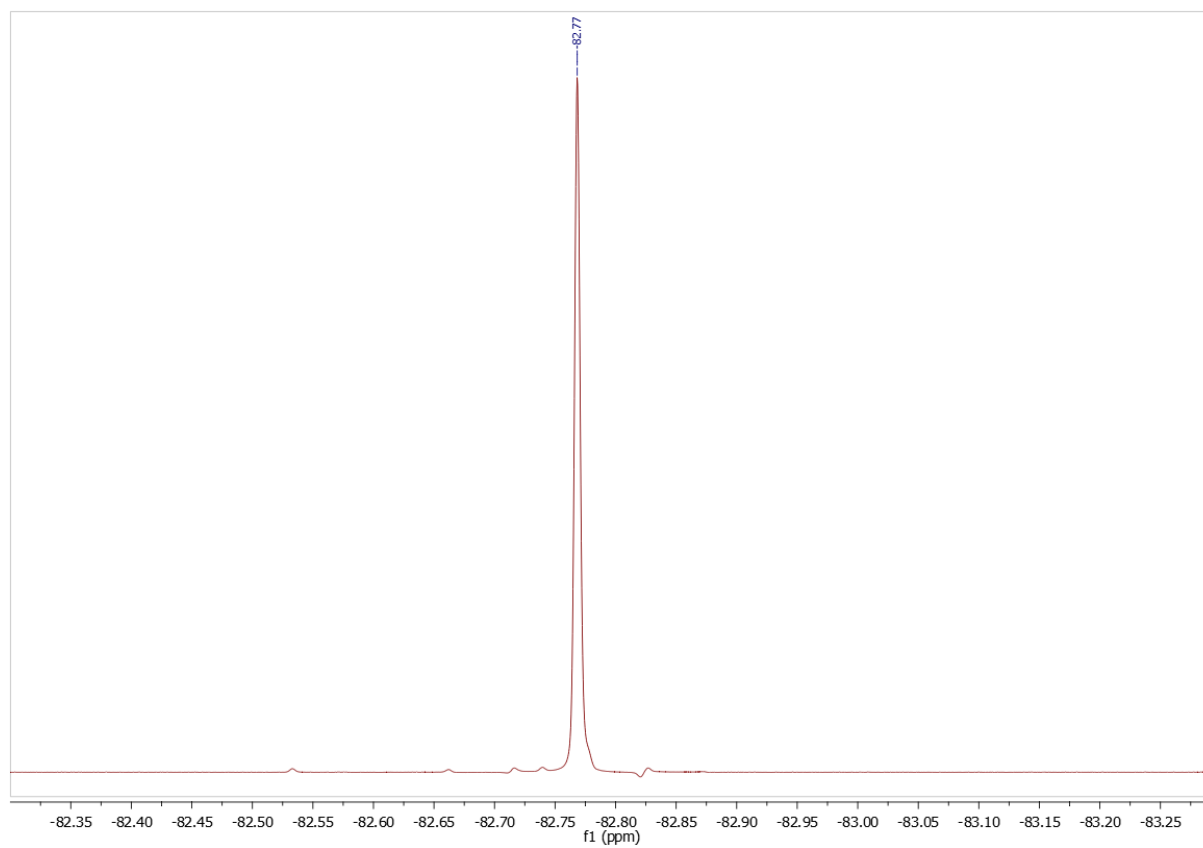


Figure S15. ^{19}F -NMR of **10**

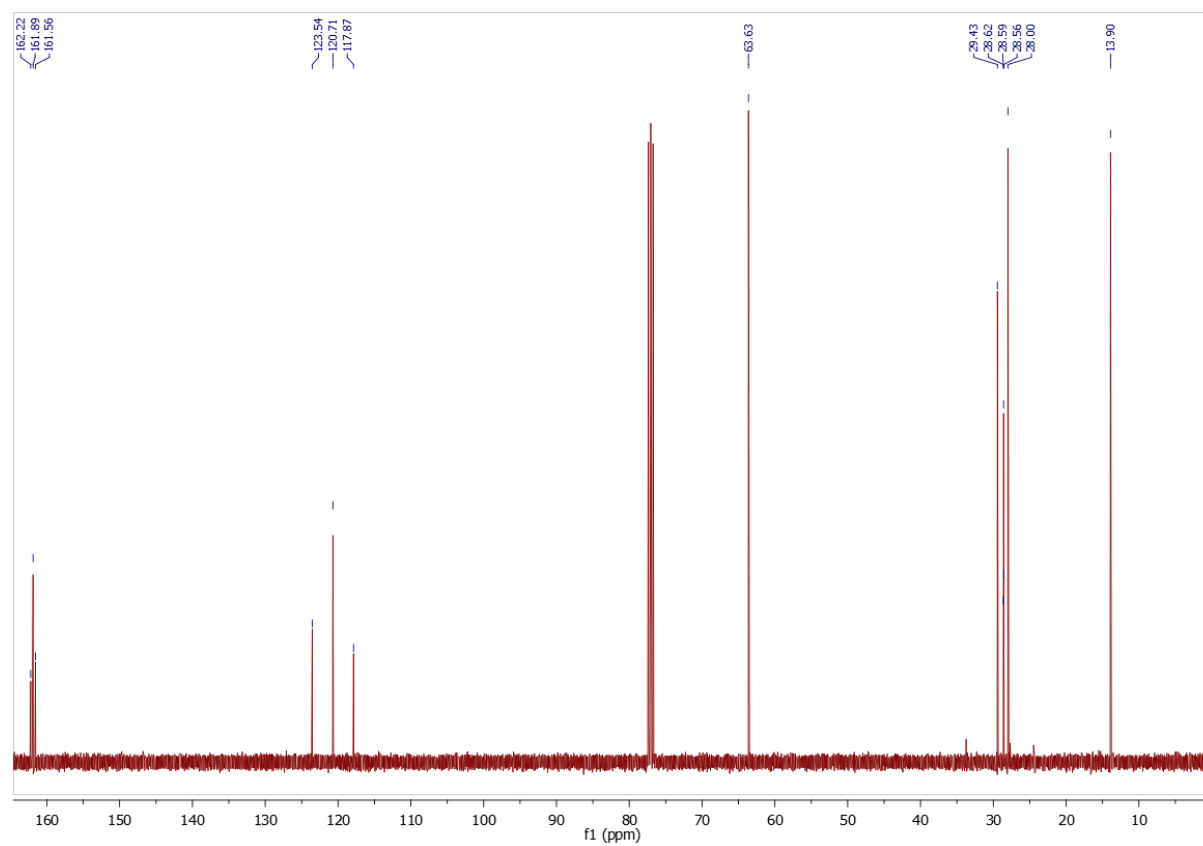


Figure S16. ^{13}C -NMR of **10**

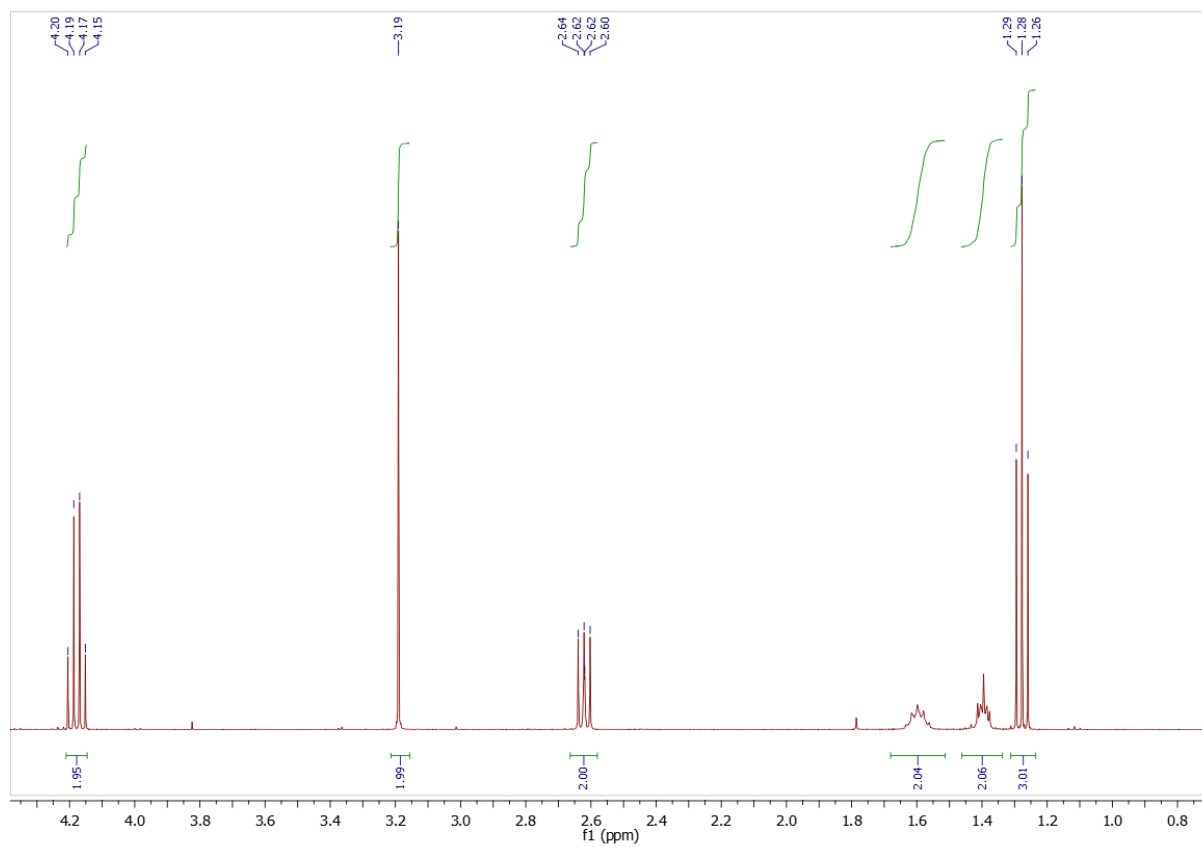


Figure S17. $^1\text{H-NMR}$ of **11**

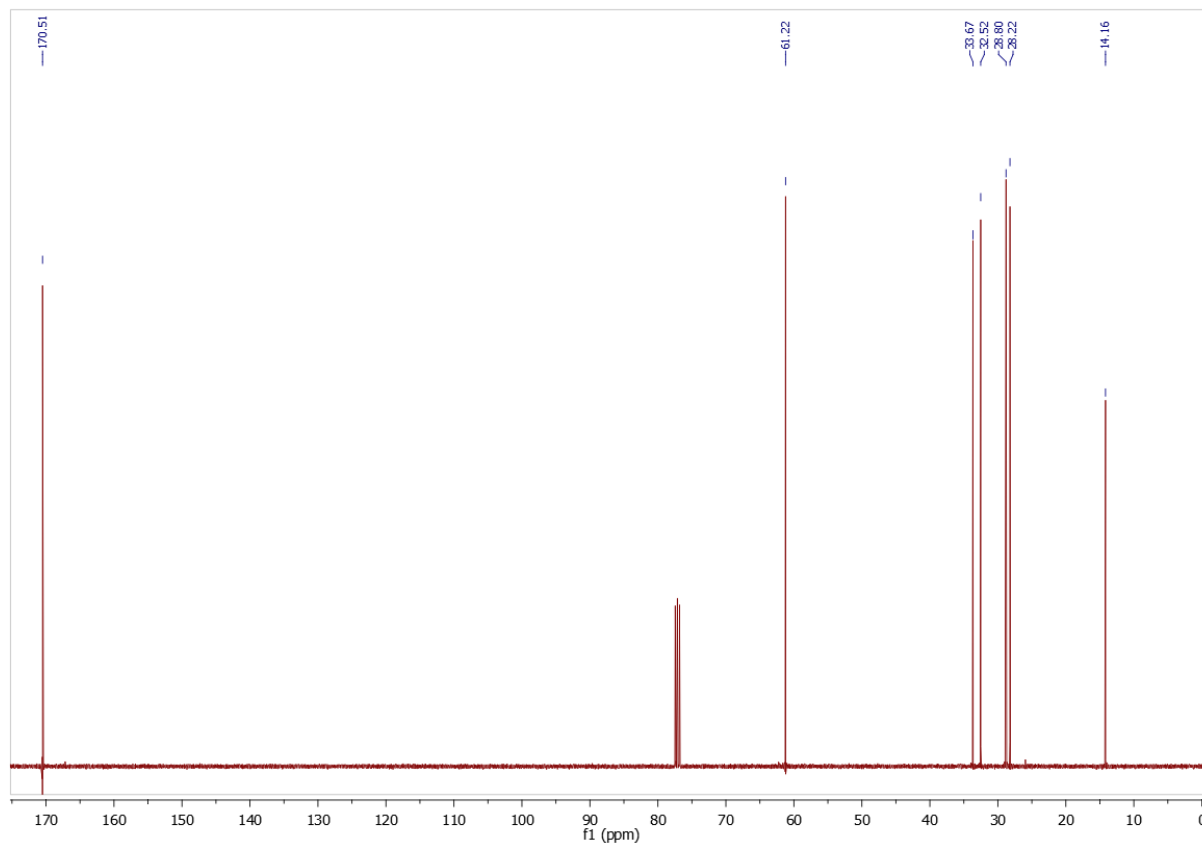


Figure S18. $^{13}\text{C-NMR}$ of **11**

DFT study

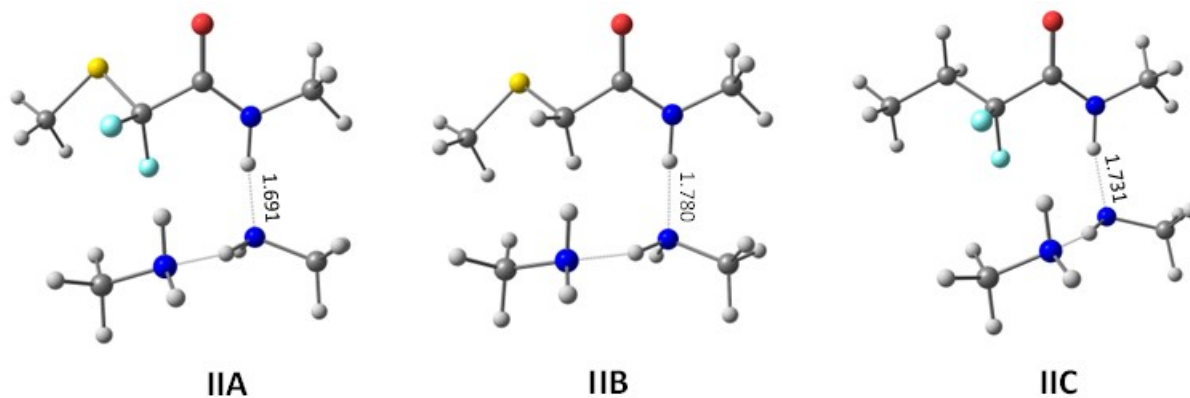


Figure S19. View of the optimized geometries of intermediates II (Figure 1)

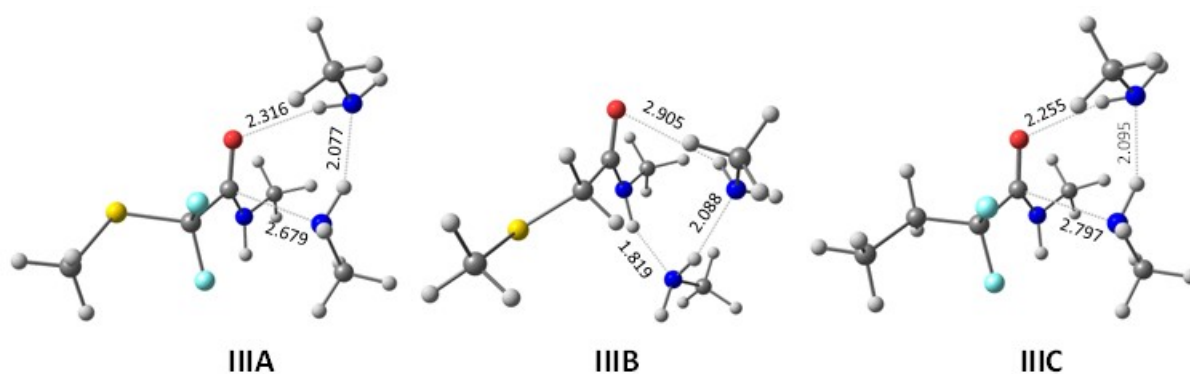


Figure S20. View of the optimized geometries of intermediates III (Figure 1)

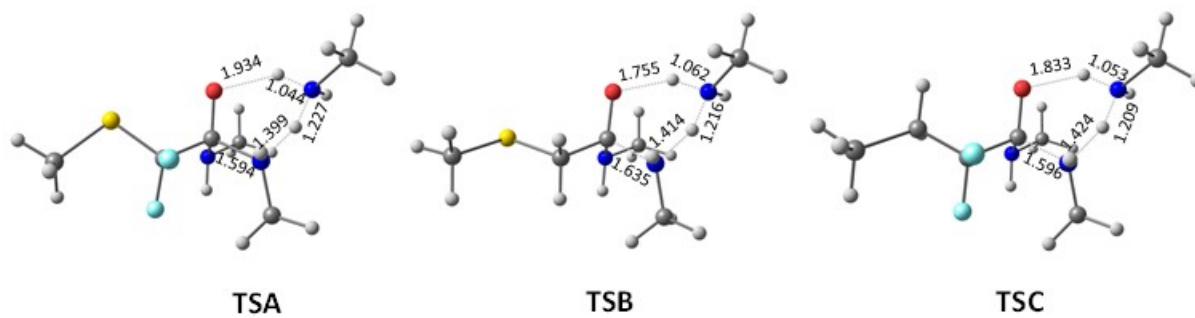


Figure S21. View of the optimized geometries of the transition states TS (Figure 1)

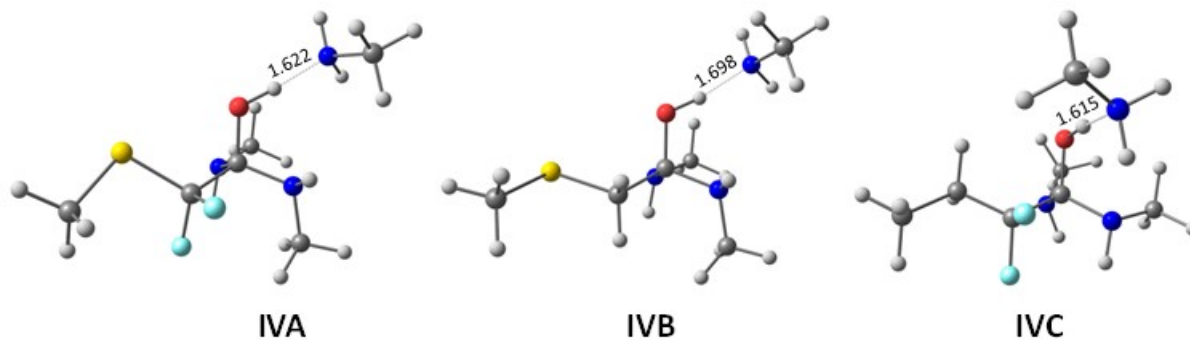


Figure S22. View of the optimized geometries of the tetrahedral intermediates IV (Figure 1)

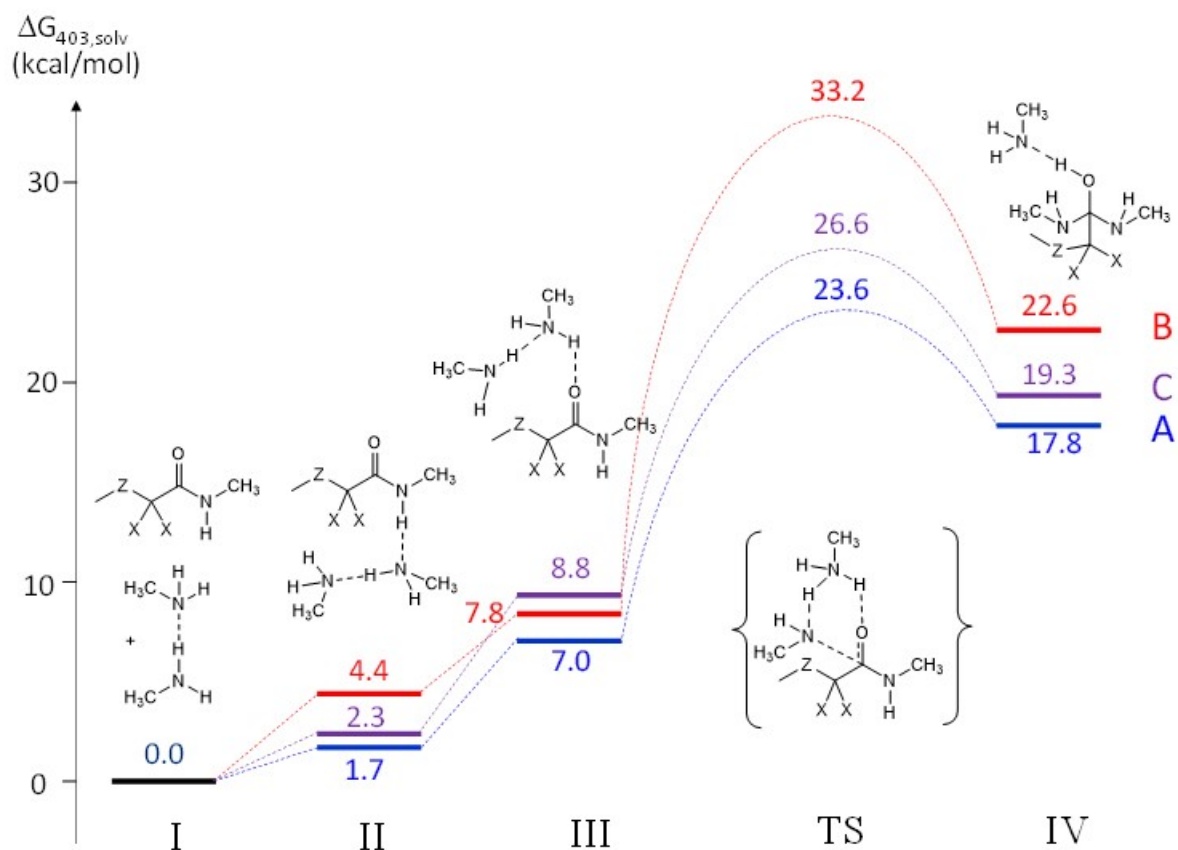


Figure S23. Gibbs energy profile ($T = 403$ K) for the transamidation process of the model molecules defined in Scheme 4.

Table S1. Cartesian coordinates (\AA) and energies (hartrees) of all optimized geometries

Amine reagent	7	-1.342135000	-0.668341000	-0.156406000
	1	-1.345804000	-1.312315000	0.643402000
MeNH₂	1	-0.446251000	-0.148599000	-0.079205000
E = -95.8928955381	6	-2.441746000	0.297157000	0.033932000
G ₂₉₈ = -95.850563	1	-3.416484000	-0.217177000	-0.023804000
G ₄₀₃ = -95.862423	1	-2.421766000	0.861792000	0.991601000
	1	-2.424929000	1.041109000	-0.780497000
	7	0.761074000	-0.000033000	-0.134362000
	1	1.134526000	-0.811805000	0.370759000
	1	1.134156000	0.811927000	0.370767000
	6	-0.709175000	-0.000026000	0.017321000
	1	-1.131554000	-0.885776000	-0.485116000
	1	-1.078679000	-0.000633000	1.064152000
	1	-1.130917000	0.886675000	-0.483956000
MeNH₂...MeNH₂				
E = -191.793084642				
G ₂₉₈ = -191.695455				
G ₄₀₃ = -191.713528				
	7	1.402238000	0.739805000	0.005794000
	1	1.626002000	1.312083000	-0.815233000
	1	1.628179000	1.320878000	0.819777000
	6	2.265869000	-0.458498000	0.009835000
	1	2.030800000	-1.082180000	-0.867708000
	1	3.353845000	-0.246171000	-0.003567000
	1	2.050952000	-1.061628000	0.906914000
	7	-1.342135000	-0.668341000	-0.156406000
	1	-1.345804000	-1.312315000	0.643402000
	1	-0.446251000	-0.148599000	-0.079205000
	6	-2.441746000	0.297157000	0.033932000
	1	-3.416484000	-0.217177000	-0.023804000
	1	-2.421766000	0.861792000	0.991601000
	1	-2.424929000	1.041109000	-0.780497000
A. Systems with X = F, Z = S				
IA				
E = -884.713410395				
G ₂₉₈ = -884.636394				
G ₄₀₃ = -884.658613				
	6	3.007870000	-0.217613000	-0.440583000
	1	2.872550000	-1.107312000	-1.069246000
	1	3.841944000	0.383906000	-0.830235000
	1	3.221787000	-0.499912000	0.599417000
	16	1.528159000	0.866007000	-0.514605000
	6	0.347552000	-0.261598000	0.299791000
	6	-1.083383000	0.313166000	0.173542000
	8	-1.300201000	1.472362000	0.554572000
	7	-1.996776000	-0.517862000	-0.357027000
	1	-1.720376000	-1.465545000	-0.609100000
	6	-3.391622000	-0.109565000	-0.514892000
	1	-3.928546000	-0.146931000	0.447453000

1	-3.434454000	0.919767000	-0.900253000
1	-3.879001000	-0.786719000	-1.227865000
9	0.635150000	-0.417217000	1.650158000
9	0.439526000	-1.544291000	-0.230271000

IIA

E = -1076.52932423

G₂₉₈ = -1076.337140

G₄₀₃ = -1076.369362

7	0.806173000	-1.667293000	0.007852000
8	-1.117199000	-2.298305000	-1.093750000
6	-0.439648000	-1.482417000	-0.435745000
6	-1.085437000	-0.118609000	-0.099300000
6	1.495307000	-2.913896000	-0.317644000
1	1.716224000	-2.982820000	-1.396783000
1	2.438544000	-2.947850000	0.243955000
1	0.879907000	-3.784416000	-0.039204000
7	2.544088000	0.203262000	1.053511000
1	1.168843000	1.466917000	-1.573310000
6	3.940244000	-0.256160000	0.920039000
1	4.693249000	0.536041000	1.102724000
1	4.140791000	-1.080585000	1.623280000
1	4.099761000	-0.639946000	-0.100930000
7	1.786957000	2.134680000	-1.100726000
1	2.367999000	0.985053000	0.383960000
6	0.975010000	3.271340000	-0.621248000
1	0.388160000	3.780388000	-1.411501000
1	0.271822000	2.917082000	0.147147000
1	1.633024000	4.020479000	-0.151737000
16	-2.819627000	-0.376107000	0.404978000
1	1.386897000	-0.896994000	0.498264000
6	-3.153811000	1.313421000	1.039773000
1	-2.948798000	2.062831000	0.262706000
1	-4.225571000	1.336396000	1.285447000
1	-2.567180000	1.519301000	1.944598000
1	2.448052000	2.462172000	-1.812346000
1	2.380704000	0.567916000	1.997254000
9	-0.385246000	0.583738000	0.866853000
9	-1.011566000	0.694659000	-1.241618000

IIIA

E = -1076.52032869

G₂₉₈ = -1076.328372

G₄₀₃ = -1076.361013

7	0.169278000	1.513142000	1.058224000
8	0.603054000	-0.730958000	1.315119000
6	0.022522000	0.203754000	0.743722000
6	-1.167209000	-0.109545000	-0.198904000
6	1.293590000	1.932141000	1.890984000
1	2.259929000	1.772609000	1.381532000
1	1.181633000	2.998448000	2.127373000
1	1.296008000	1.355494000	2.827597000
7	1.513110000	0.473591000	-1.466433000
1	2.910587000	-0.733844000	1.116060000
6	1.643846000	1.874405000	-1.874806000
1	2.454728000	2.080123000	-2.606767000
1	0.697678000	2.225870000	-2.319887000
1	1.842067000	2.501907000	-0.989144000
7	3.481818000	-1.022871000	0.313278000
1	2.378508000	0.125624000	-1.020640000
6	2.994166000	-2.342170000	-0.139286000
1	3.053343000	-3.142674000	0.625312000

1	1.939283000	-2.251812000	-0.439743000
1	3.569765000	-2.670221000	-1.020629000
16	-2.650482000	-0.465954000	0.826529000
1	-0.217683000	2.192763000	0.404896000
6	-3.879231000	-0.629289000	-0.526568000
1	-3.558397000	-1.398225000	-1.242797000
1	-4.817237000	-0.949300000	-0.049947000
1	-4.034783000	0.333977000	-1.030267000
1	4.444593000	-1.112836000	0.653355000
1	1.318107000	-0.121267000	-2.275407000
9	-0.871244000	-1.190380000	-0.998829000
9	-1.432132000	0.942991000	-1.067021000

TSA

E = -1076.50080001

G₂₉₈ = -1076.305193

G₄₀₃ = -1076.334484

Imaginary frequency = 615.8i cm⁻¹

7	0.162778000	1.426139000	1.001491000
8	0.583586000	-0.897653000	0.978701000
6	0.215893000	0.154023000	0.263853000
6	-1.226185000	-0.065974000	-0.337875000
6	1.400126000	1.764114000	1.708225000
1	2.275651000	1.964052000	1.053762000
1	1.232171000	2.663742000	2.320962000
1	1.656607000	0.938939000	2.389512000
7	1.212352000	0.285207000	-0.972962000
1	2.515768000	-0.891110000	1.059605000
6	1.173098000	1.506024000	-1.803339000
1	1.942628000	1.436141000	-2.589409000
1	0.195060000	1.665418000	-2.286594000
1	1.407324000	2.385045000	-1.183936000
7	3.240369000	-0.602792000	0.364800000
1	2.430233000	-0.045653000	-0.369362000
6	3.870394000	-1.781103000	-0.273644000
1	4.456706000	-2.367097000	0.450365000
1	3.073051000	-2.417847000	-0.683630000
1	4.527000000	-1.454933000	-1.093108000
16	-2.348150000	-0.758634000	0.926972000
1	-0.121821000	2.193162000	0.385963000
6	-3.920203000	-0.562055000	-0.002937000
1	-3.860700000	-1.067885000	-0.977349000
1	-4.698404000	-1.049005000	0.603180000
1	-4.176173000	0.497905000	-0.136907000
1	3.924718000	0.023265000	0.801262000
1	1.009753000	-0.532026000	-1.561454000
9	-1.158794000	-0.937336000	-1.434569000
9	-1.760660000	1.107026000	-0.890211000

IVA

E = -1076.51479123

G₂₉₈ = -1076.314450

G₄₀₃ = -1076.343711

7	0.186220000	1.131187000	1.375981000
8	0.767604000	-0.982314000	0.466084000
6	0.260214000	0.292249000	0.180026000
6	-1.224649000	0.041835000	-0.288078000
6	1.494882000	1.487897000	1.943237000
1	2.155999000	2.059653000	1.263490000

1	1.330111000	2.086466000	2.852399000
1	2.021284000	0.569752000	2.244555000
7	1.086012000	0.870754000	-0.890165000
1	1.807112000	-0.958810000	0.498381000
6	0.718913000	2.195915000	-1.412519000
1	1.506255000	2.528109000	-2.107961000
1	-0.248747000	2.232865000	-1.947651000
1	0.682264000	2.927766000	-0.590223000
7	3.416329000	-1.152574000	0.425872000
1	3.888030000	-0.258788000	0.597428000
6	3.711217000	-1.625317000	-0.944624000
1	3.173407000	-2.569050000	-1.124810000
1	3.339831000	-0.882520000	-1.666472000
1	4.786988000	-1.791987000	-1.137059000
16	-2.171476000	-1.100412000	0.780699000
1	-0.346977000	1.979142000	1.164000000
6	-3.790785000	-0.954905000	-0.074336000
1	-3.690852000	-1.213765000	-1.137587000
1	-4.459356000	-1.681752000	0.410048000
1	-4.209281000	0.054345000	0.039494000
1	3.787032000	-1.816105000	1.114235000
1	1.122116000	0.187692000	-1.652405000
9	-1.203980000	-0.439752000	-1.595410000
9	-1.893920000	1.266472000	-0.387231000

B. Systems with X = H, Z = S

IB

E = -686.1786817

G₂₉₈ = -686.083489

G₄₀₃ = -686.104030

6	3.177009000	-0.127558000	0.265607000
1	3.198252000	-0.674443000	1.220928000
1	3.951397000	-0.541880000	-0.397920000
1	3.387720000	0.939306000	0.436597000
16	1.570514000	-0.348635000	-0.585453000
6	0.478425000	0.426330000	0.693168000
1	0.549517000	-0.154644000	1.626956000
1	0.813758000	1.457719000	0.872704000
6	-0.956426000	0.492640000	0.176241000
8	-1.409190000	1.515201000	-0.370396000
7	-1.694038000	-0.634303000	0.335807000
1	-1.285652000	-1.433953000	0.815600000
6	-3.080659000	-0.708246000	-0.116517000
1	-3.737536000	-0.071388000	0.500207000
1	-3.161410000	-0.374095000	-1.162439000
1	-3.422577000	-1.748943000	-0.043858000

IIB

E = -877.991588286

G₂₉₈ = -877.780115

G₄₀₃ = -877.810508

7	0.953009000	-1.598906000	0.007430000
8	-0.886559000	-2.502375000	-1.014258000
6	-0.314135000	-1.545180000	-0.446671000
6	-1.017378000	-0.207722000	-0.238391000
6	1.751360000	-2.803902000	-0.188949000
1	1.957294000	-2.985677000	-1.258518000
1	2.706415000	-2.685488000	0.341079000
1	1.230043000	-3.691553000	0.206191000
7	2.264189000	0.703758000	1.016789000

1	0.728530000	1.647793000	-1.692227000
6	3.709482000	0.479549000	0.808122000
1	4.326546000	1.394396000	0.909440000
1	4.087044000	-0.264112000	1.528510000
1	3.872128000	0.076294000	-0.204927000
7	1.114535000	2.437841000	-1.163674000
1	1.931641000	1.425876000	0.342552000
6	0.007050000	3.275859000	-0.661207000
1	-0.722479000	3.589905000	-1.433570000
1	-0.543445000	2.733941000	0.123509000
1	0.420366000	4.185789000	-0.197287000
16	-2.700851000	-0.488196000	0.462320000
1	1.398337000	-0.749851000	0.462519000
6	-3.122065000	1.259137000	0.816301000
1	-3.101969000	1.865411000	-0.102673000
1	-4.147484000	1.265547000	1.216978000
1	-2.446229000	1.691478000	1.570159000
1	1.668791000	2.976651000	-1.837177000
1	2.104258000	1.072334000	1.959751000
1	-0.448570000	0.444315000	0.440092000
1	-1.123140000	0.291776000	-1.216503000

IIIB

E = -877.989850082

G₂₉₈ = -877.776874

G₄₀₃ = -877.805093

7	-0.416008000	-0.530221000	1.324001000
8	0.069331000	1.665493000	1.800280000
6	0.237957000	0.637489000	1.110192000
6	1.226927000	0.628623000	-0.054101000
6	-1.477772000	-0.581203000	2.325173000
1	-2.384238000	-0.035346000	2.001852000
1	-1.746639000	-1.631101000	2.508580000
1	-1.132015000	-0.130040000	3.266868000
7	-1.246767000	-1.638148000	-1.127142000
1	-2.184314000	1.314643000	0.001767000
6	-2.497617000	-2.388738000	-0.916049000
1	-3.162441000	-2.429366000	-1.802518000
1	-2.270181000	-3.424906000	-0.616298000
1	-3.066599000	-1.923381000	-0.094630000
7	-2.142849000	1.297116000	-1.023804000
1	-1.473453000	-0.651922000	-1.361328000
6	-1.505022000	2.546206000	-1.489048000
1	-2.055325000	3.468762000	-1.215708000
1	-0.494457000	2.626592000	-1.060790000
1	-1.402651000	2.523924000	-2.586550000
16	2.526712000	-0.671091000	0.152558000
1	-0.535816000	-1.146796000	0.473838000
6	3.600669000	-0.184459000	-1.250678000
1	4.013363000	0.825769000	-1.102617000
1	4.430448000	-0.906266000	-1.290900000
1	3.047223000	-0.227023000	-2.201765000
1	-3.120110000	1.282641000	-1.334523000
1	-0.715635000	-2.040560000	-1.904586000
1	1.710625000	1.614613000	-0.087199000
1	0.688689000	0.454536000	-1.000982000

TSB

E = -877.95261438

G₂₉₈ = -877.737920

G₄₀₃ = -877.764691

Imaginary frequency = 670.0i cm⁻¹

7	0.107788000	1.509658000	-0.580715000
---	-------------	-------------	--------------

8	-0.409262000	-0.747670000	-1.010508000
6	0.006513000	0.120850000	-0.093181000
6	1.359775000	-0.263860000	0.571525000
6	-1.089799000	2.020330000	-1.249435000
1	-1.998961000	2.084357000	-0.611848000
1	-0.886711000	3.031530000	-1.637056000
1	-1.320270000	1.372752000	-2.108886000
7	-1.066487000	0.080455000	1.139853000
1	-2.152191000	-0.688001000	-1.083599000
6	-1.037839000	1.171386000	2.129505000
1	-1.739500000	0.945976000	2.950053000
1	-0.038795000	1.332188000	2.575797000
1	-1.364629000	2.112155000	1.660486000
7	-2.992552000	-0.570522000	-0.444227000
1	-2.275336000	-0.145685000	0.441527000
6	-3.599393000	-1.876099000	-0.107673000
1	-4.097394000	-2.327449000	-0.979717000
1	-2.797521000	-2.551135000	0.226196000
1	-4.331480000	-1.759438000	0.705299000
16	2.762620000	-0.170682000	-0.623466000
1	0.395389000	2.137956000	0.175712000
6	4.038548000	-0.985381000	0.411768000
1	3.763619000	-2.026934000	0.644416000
1	4.975588000	-0.990727000	-0.166728000
1	4.209557000	-0.432164000	1.349395000
1	-3.668056000	0.099367000	-0.824390000
1	-0.882499000	-0.812315000	1.614716000
1	1.272717000	-1.308706000	0.911829000
1	1.600586000	0.378051000	1.436892000

IVB

E = -877.970478445

G₂₉₈ = -877.753444

G₄₀₃ = -877.781603

7	-0.107736000	1.118922000	1.164455000
8	0.533694000	-0.967648000	0.227299000
6	-0.005779000	0.303962000	-0.053353000
6	-1.426813000	0.079192000	-0.615856000
6	1.171897000	1.500326000	1.776277000
1	1.851003000	2.076998000	1.117299000
1	0.967666000	2.103067000	2.675175000
1	1.702810000	0.592960000	2.102039000
7	0.886055000	0.926172000	-1.070484000
1	1.539734000	-0.894932000	0.395158000
6	0.525248000	2.270194000	-1.539614000
1	1.280386000	2.605122000	-2.268730000
1	-0.468922000	2.353645000	-2.026584000
1	0.547609000	2.984478000	-0.700683000
7	3.219382000	-1.113202000	0.514991000
1	3.708800000	-0.217053000	0.603301000
6	3.592823000	-1.768704000	-0.757119000
1	3.039259000	-2.716067000	-0.850872000
1	3.294028000	-1.121635000	-1.596024000
1	4.673895000	-1.983678000	-0.852554000
16	-2.618329000	-0.592513000	0.628063000
1	-0.661853000	1.955911000	0.958822000
6	-3.934530000	-1.107726000	-0.540873000
1	-3.561593000	-1.863212000	-1.251049000
1	-4.744718000	-1.554741000	0.055586000
1	-4.341432000	-0.247999000	-1.097043000
1	3.521580000	-1.689099000	1.307545000

1	0.933499000	0.280182000	-1.865225000
1	-1.342290000	-0.649833000	-1.437550000
1	-1.836737000	1.020574000	-1.015507000

C. Systems with X = F, Z = CH₂

IC

E = -525.807941984

G₂₉₈ = -525.701605

G₄₀₃ = -525.722772

6	3.008308000	0.078945000	-0.549944000
1	3.121392000	-1.007739000	-0.687400000
1	3.671411000	0.583895000	-1.269158000
1	3.347889000	0.335826000	0.465153000
6	1.558177000	0.520175000	-0.772498000
6	0.586118000	-0.132264000	0.189158000
6	-0.867845000	0.377839000	0.039020000
8	-1.083822000	1.596678000	0.126861000
7	-1.807151000	-0.557213000	-0.194034000
1	-1.532661000	-1.538163000	-0.201523000
6	-3.218934000	-0.203102000	-0.323999000
1	-3.678909000	-0.028634000	0.663191000
1	-3.316075000	0.715791000	-0.920431000
1	-3.747379000	-1.022572000	-0.828288000
9	0.964340000	0.121512000	1.508889000
9	0.635858000	-1.526298000	0.054355000
1	1.215289000	0.273960000	-1.792082000
1	1.442949000	1.608211000	-0.645737000

IIC

E = -717.622834539

G₂₉₈ = -717.401274

G₄₀₃ = -717.432624

7	0.652746000	1.648728000	-0.057605000
8	-1.279686000	2.343628000	0.981215000
6	-0.620906000	1.506696000	0.328681000
6	-1.323625000	0.186762000	-0.071514000
6	1.389727000	2.850040000	0.326246000
1	1.638494000	2.848589000	1.402000000
1	2.321078000	2.892313000	-0.254457000
1	0.794599000	3.752702000	0.116579000
7	2.427930000	-0.297573000	-0.955597000
1	0.724620000	-1.528936000	1.518782000
6	3.799972000	0.139175000	-0.631215000
1	4.556910000	-0.668647000	-0.685168000
1	4.116053000	0.944073000	-1.314538000
1	3.817819000	0.543540000	0.394333000
7	1.383425000	-2.202773000	1.115037000
1	2.151111000	-1.064802000	-0.305220000
6	0.615561000	-3.273537000	0.447385000
1	-0.119620000	-3.786687000	1.098583000
1	0.069953000	-2.848283000	-0.407965000
1	1.311530000	-4.032853000	0.055000000
1	1.217727000	0.858615000	-0.513814000
1	1.906998000	-2.597519000	1.902679000
1	2.395167000	-0.678254000	-1.906509000
9	-0.579655000	-0.511470000	-1.023073000
9	-1.311420000	-0.637379000	1.074142000
6	-2.749609000	0.364811000	-0.549128000
1	-3.277534000	0.925315000	0.237872000
1	-2.710382000	1.016925000	-1.438170000

6	-3.446816000	-0.962213000	-0.864469000
1	-4.474594000	-0.775581000	-1.212244000
1	-2.915357000	-1.515279000	-1.654530000
1	-3.501934000	-1.603697000	0.028678000

IIIc

E = -717.613337869

G₂₉₈ = -717.391015

G₄₀₃ = -717.422219

7	-0.003194000	1.487633000	-1.106451000
8	-0.347632000	-0.767683000	-1.385601000
6	0.217544000	0.182470000	-0.820603000
6	1.431525000	-0.110666000	0.091771000
6	-1.187324000	1.866063000	-1.874350000
1	-2.116392000	1.625408000	-1.328761000
1	-1.153434000	2.945243000	-2.073848000
1	-1.199357000	1.325257000	-2.831793000
7	-1.364123000	0.533176000	1.459199000
1	-2.582713000	-0.891605000	-1.115770000
6	-1.542287000	1.939497000	1.831742000
1	-2.401439000	2.149987000	2.506109000
1	-0.633300000	2.315409000	2.331918000
1	-1.688769000	2.550646000	0.924245000
7	-3.156010000	-1.180209000	-0.314002000
1	-2.202449000	0.157686000	0.986409000
6	-2.558816000	-2.412065000	0.242705000
1	-2.513332000	-3.262535000	-0.467261000
1	-1.529268000	-2.196139000	0.565408000
1	-3.130136000	-2.738022000	1.127685000
1	0.358119000	2.162344000	-0.433170000
1	-4.090849000	-1.388781000	-0.679224000
1	-1.205103000	-0.039061000	2.292215000
9	1.100308000	-1.144057000	0.956178000
9	1.716475000	0.996369000	0.902721000
6	2.671143000	-0.494602000	-0.702340000
1	2.381380000	-1.341409000	-1.346575000
1	2.911540000	0.353658000	-1.364836000
6	3.863939000	-0.854312000	0.189682000
1	3.632878000	-1.717618000	0.832396000
1	4.736632000	-1.113779000	-0.429857000
1	4.144938000	-0.008547000	0.836567000

TSC

E = -717.592135817

G₂₉₈ = -717.366160

G₄₀₃ = -717.393952

Imaginary frequency = 528.1i cm⁻¹

7	0.072555000	1.622896000	-0.686966000
8	-0.481601000	-0.612712000	-1.229959000
6	-0.018509000	0.203258000	-0.286948000
6	1.432667000	-0.221293000	0.141074000
6	-1.178838000	2.167760000	-1.223219000
1	-2.027692000	2.183743000	-0.505946000
1	-1.008904000	3.201917000	-1.561999000
1	-1.481544000	1.572907000	-2.097912000
7	-0.954347000	0.065008000	0.998199000
1	-2.313748000	-0.585225000	-1.176623000
6	-0.884995000	1.080518000	2.068228000
1	-1.591171000	0.805403000	2.869338000

1	0.120085000	1.177779000	2.509187000
1	-1.195935000	2.060573000	1.676062000
7	-3.042753000	-0.494432000	-0.422854000
1	-2.227580000	-0.127518000	0.390740000
6	-3.625536000	-1.807523000	-0.067839000
1	-4.234010000	-2.214623000	-0.889338000
1	-2.799641000	-2.503061000	0.141106000
1	-4.248576000	-1.709415000	0.833025000
1	0.395735000	2.190226000	0.102671000
1	-3.750532000	0.203117000	-0.673696000
1	-0.720275000	-0.854166000	1.392199000
9	1.341280000	-1.429740000	0.857329000
9	1.962385000	0.697302000	1.078482000
6	2.418163000	-0.400558000	-0.996137000
1	1.972178000	-1.142951000	-1.675211000
1	2.454791000	0.554938000	-1.542331000
6	3.812612000	-0.830441000	-0.527962000
1	3.770482000	-1.784629000	0.020445000
1	4.482339000	-0.964945000	-1.392094000
1	4.262255000	-0.075073000	0.135922000

IVc

E = -717.603515841

G₂₉₈ = -717.376579

G₄₀₃ = -717.405609

7	1.791046000	-1.107104000	-0.427262000
8	0.510903000	0.703464000	-1.127135000
6	0.782259000	-0.105575000	-0.016234000
6	-0.503866000	-0.917338000	0.371282000
6	2.726294000	-0.715338000	-1.494235000
1	3.245569000	0.250567000	-1.344582000
1	3.490552000	-1.505251000	-1.574633000
1	2.199181000	-0.662826000	-2.458433000
7	1.121488000	0.722990000	1.158766000
1	-0.080588000	1.499930000	-0.812627000
6	2.412717000	1.418888000	1.052238000
1	2.542525000	2.067396000	1.933088000
1	3.294539000	0.749200000	0.991519000
1	2.403993000	2.062324000	0.159389000
7	-1.000325000	2.673874000	-0.193783000
1	-0.901138000	2.357999000	0.777853000
6	-2.418716000	2.640293000	-0.604828000
1	-2.505690000	2.988611000	-1.645924000
1	-2.778091000	1.601770000	-0.562424000
1	-3.079093000	3.264086000	0.026377000
1	2.308542000	-1.388152000	0.409046000
1	-0.638052000	3.631665000	-0.234468000
1	1.126114000	0.116856000	1.985724000
9	-1.470836000	-0.033266000	0.875117000
9	-0.182856000	-1.744248000	1.467824000
6	-1.129411000	-1.746377000	-0.732454000
1	-1.313566000	-1.063531000	-1.576748000
1	-0.371957000	-2.472112000	-1.061030000
6	-2.417679000	-2.450224000	-0.291939000
1	-3.194302000	-1.724995000	-0.003689000
1	-2.816244000	-3.065909000	-1.113459000
1	-2.231344000	-3.112002000	0.568594000

Kinetic data and graphs

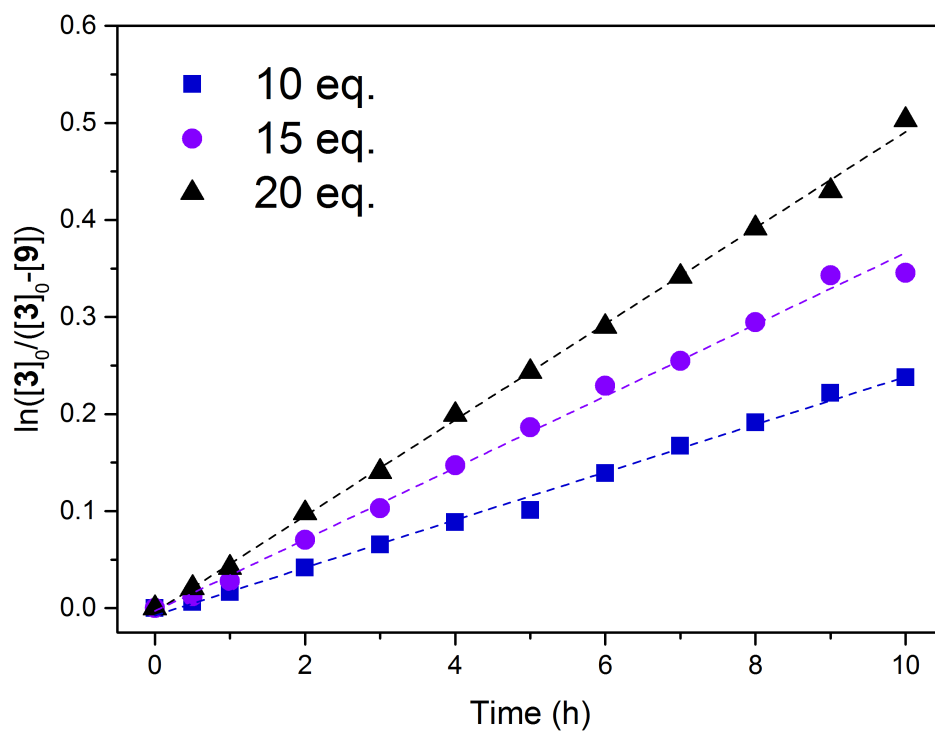


Figure S24. Transamidation of **3** with **8** monitoring in MST at 130 °C in presence of 10, 15 and 20 eq. of **8**

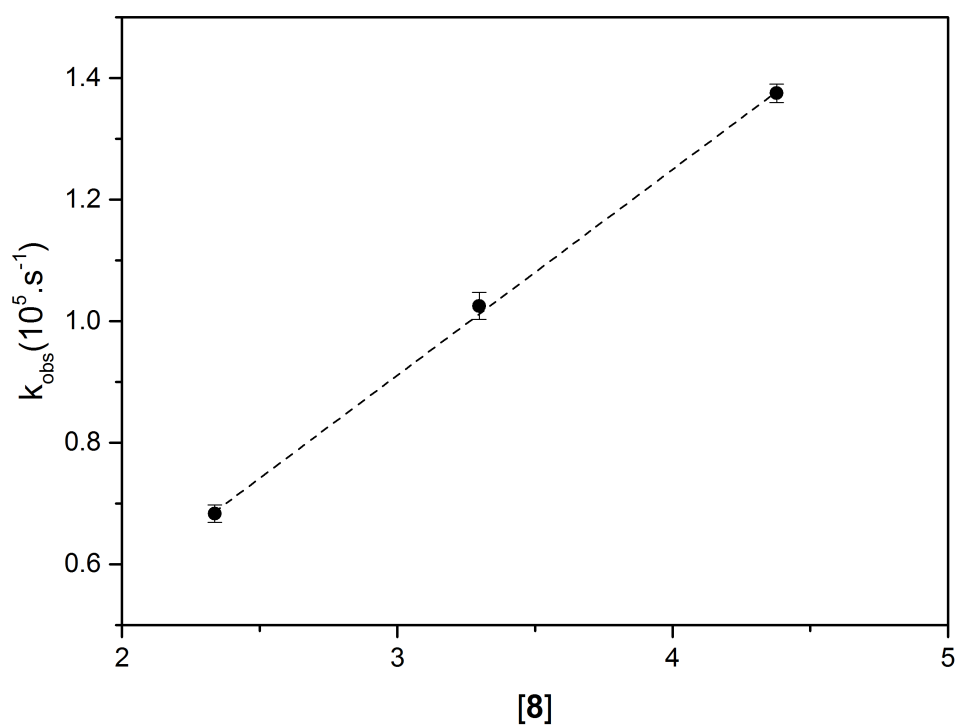


Figure S25. Plot of k_{obs} as a function of $[8]_0$ at 25 °C

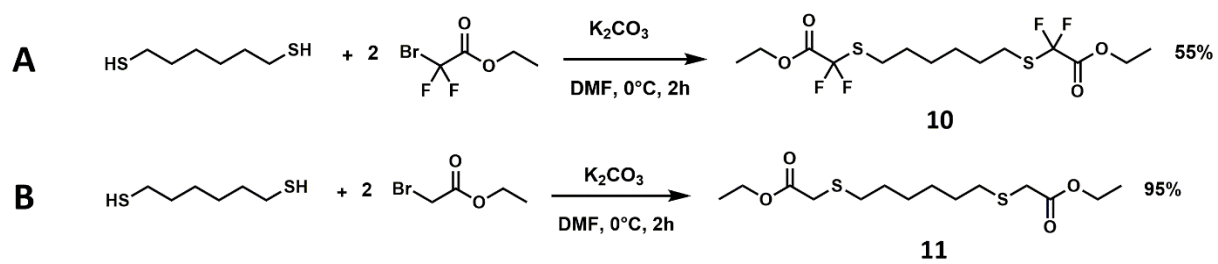
Table S2. Pseudo-first order rate constants from the least-squares linear fits of the data in Figure S24

$[3]_0$	$[8]_0$	$k_{\text{obs}} (\text{s}^{-1})$
0.25	2.4	$(0.68 \pm 0.01) \cdot 10^{-5}$
0.22	3.3	$(1.03 \pm 0.02) \cdot 10^{-5}$
0.21	4.4	$(1.38 \pm 0.02) \cdot 10^{-5}$

Table S3. Summary of the variable-temperature kinetic data for the transamidation of **3** with **8** in MST.

T (°C)	1000/T (K ⁻¹)	k (M ⁻¹ s ⁻¹)	ln(kh/Tk _B)
110	2.61	$(1.26 \pm 0.05) \cdot 10^{-6}$	-43.29 ± 0.04
120	2.54	$(1.71 \pm 0.07) \cdot 10^{-6}$	-43.01 ± 0.04
130	2.48	$(2.08 \pm 0.06) \cdot 10^{-6}$	-42.84 ± 0.03
140	2.42	$(2.93 \pm 0.09) \cdot 10^{-6}$	-42.52 ± 0.03

Material characterizations



Scheme S1. Syntheses of A) fluorinated and B) non-fluorinated diesters

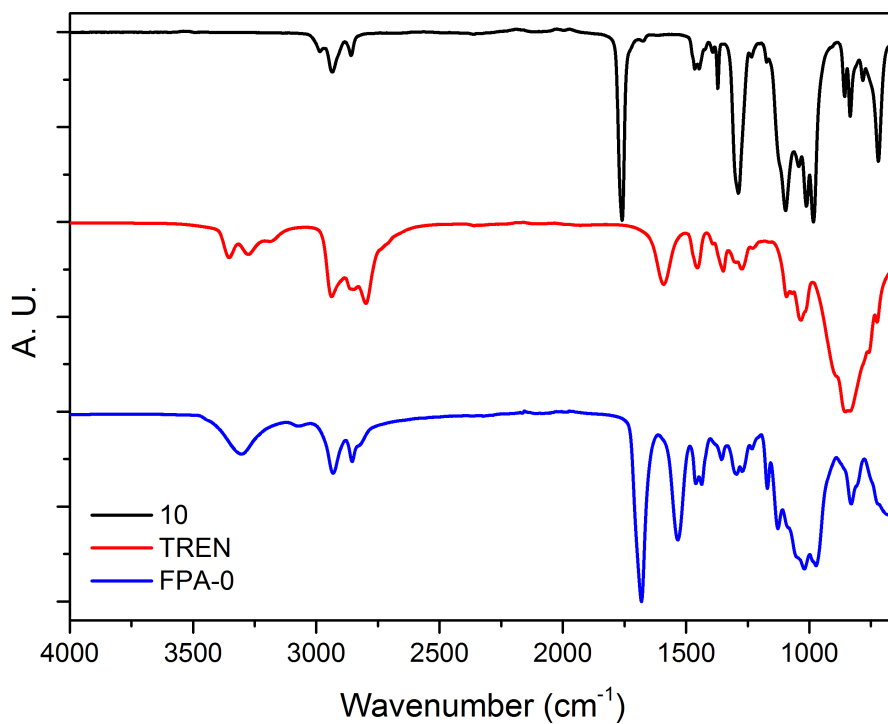


Figure S26. FTIR spectra of **10** (top black curve), **TREN** (middle red curve) and **FPA-0** (bottom blue curve)

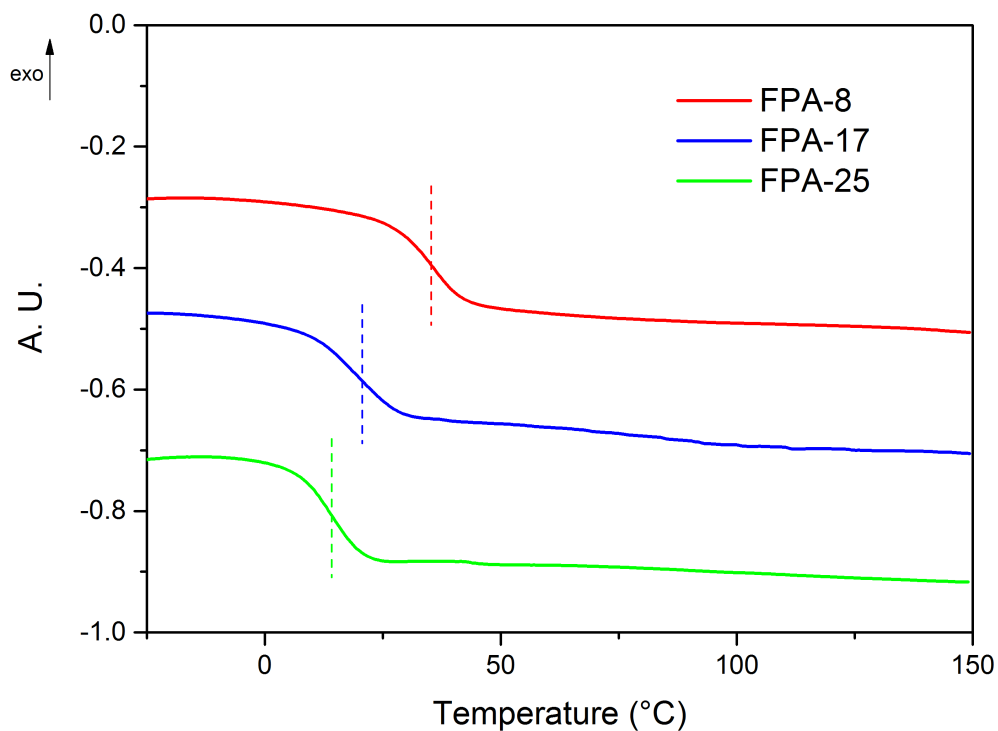


Figure S27. DSC curves (2nd heating ramp) of **FPA-8** (top red curve), **FPA-17** (blue middle curve) and **FPA-25** (green bottom curve)

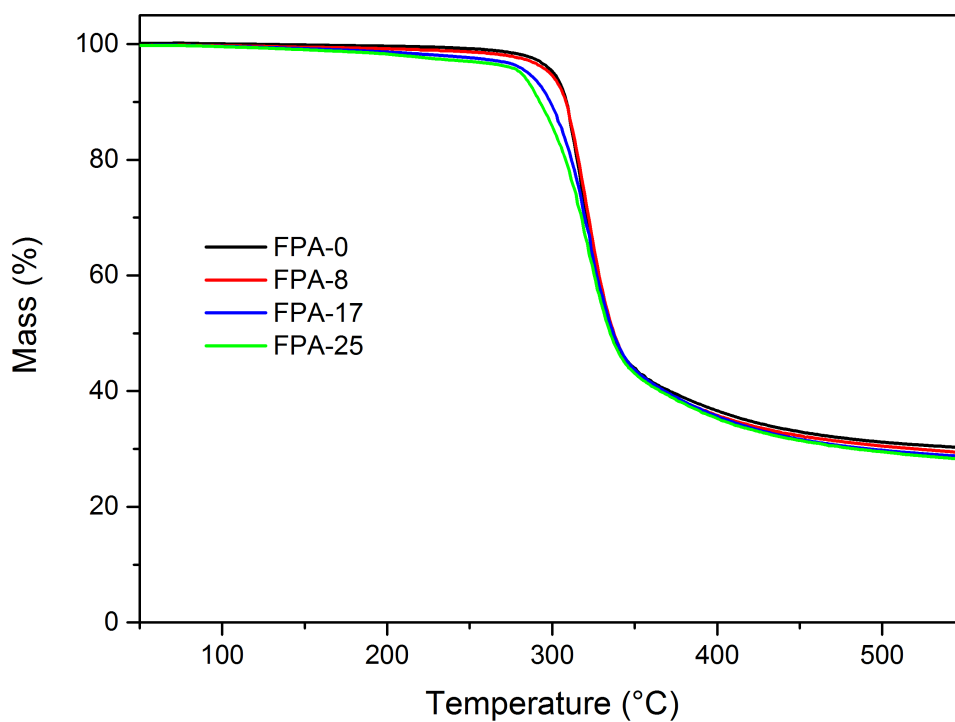


Figure S28. TGA of **FPA-0** (red curve), **FPA-8** (red curve), **FPA-17** (blue curve) and **FPA-25** (green curve)

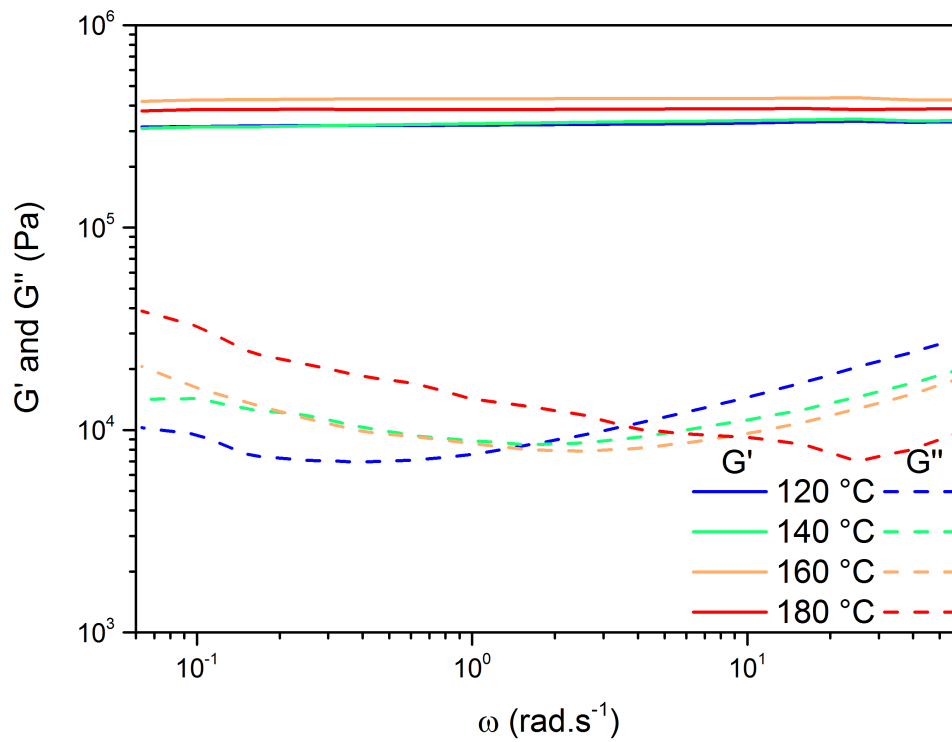


Figure S29. Frequency sweep measurements from 50 to 0.5 $\text{rad}\cdot\text{s}^{-1}$ of FPA-25 for temperature going from 120 °C to 180 °C

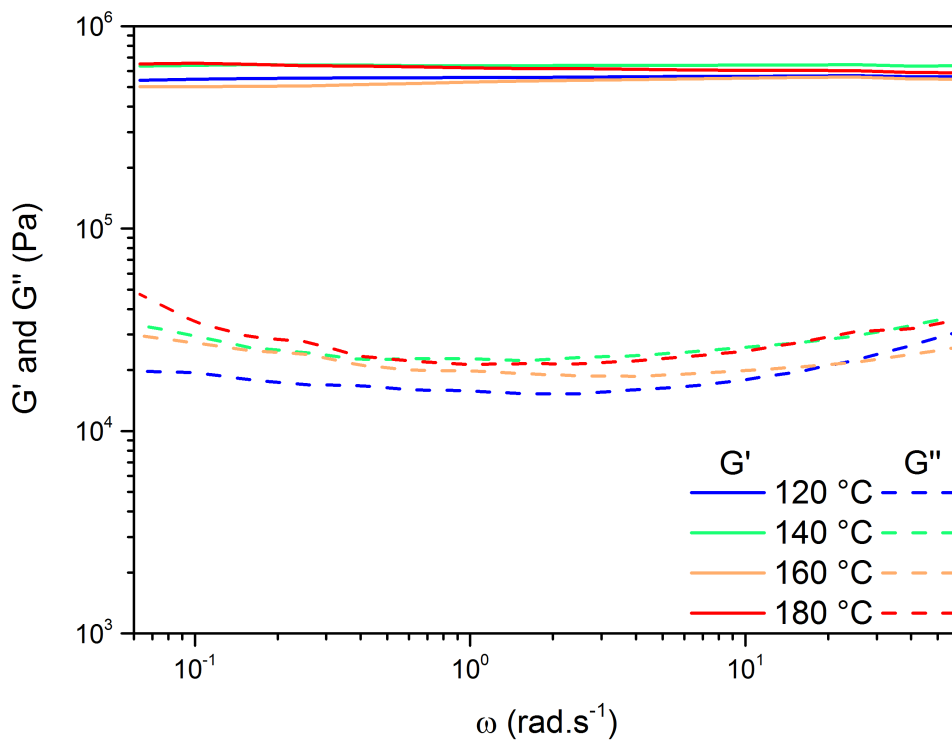


Figure S30. Frequency sweep measurements from 50 to 0.5 $\text{rad}\cdot\text{s}^{-1}$ of FPA-17 for temperature going from 120 °C to 180 °C

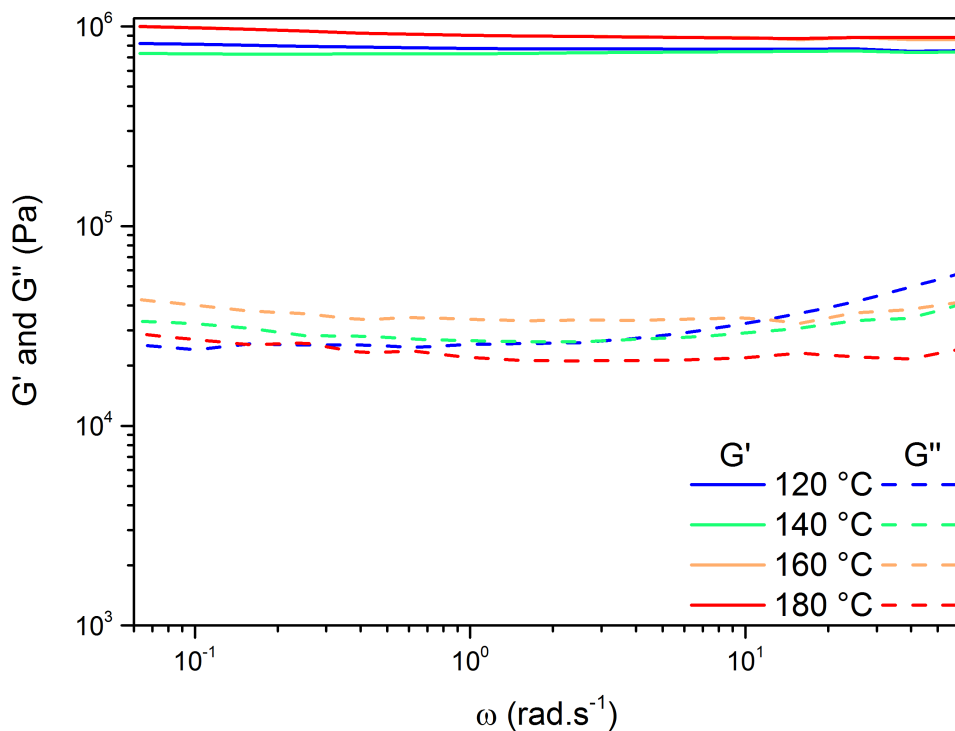


Figure S31. Frequency sweep measurements from 50 to 0.5 $\text{rad}\cdot\text{s}^{-1}$ of FPA-8 for temperature going from 120 °C to 180 °C

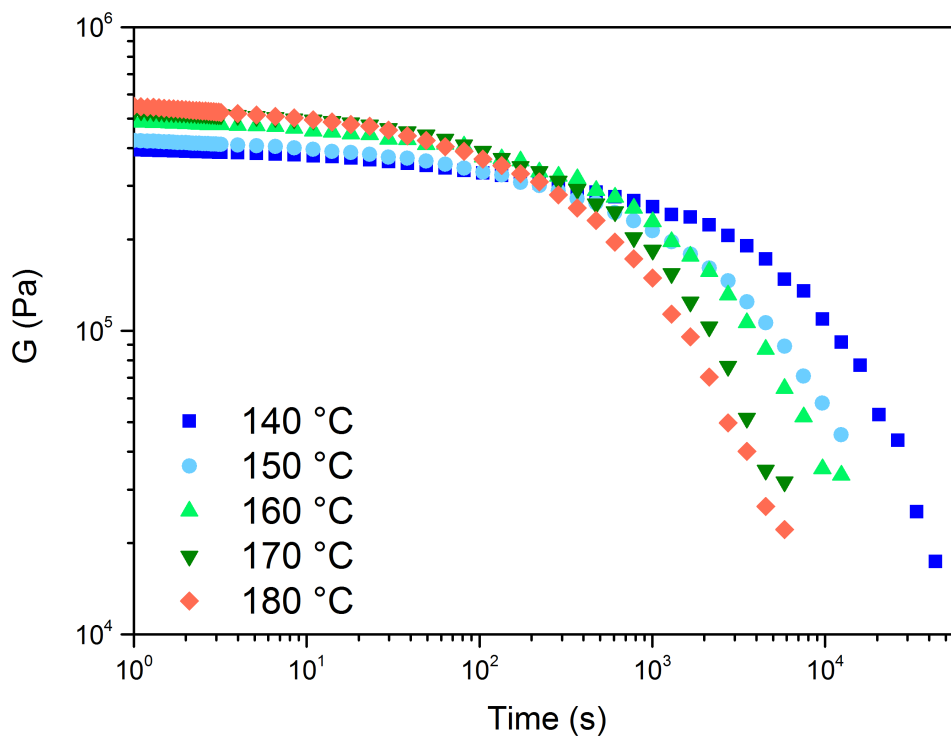


Figure S32. Non-Normalized stress relaxation for FPA-25.

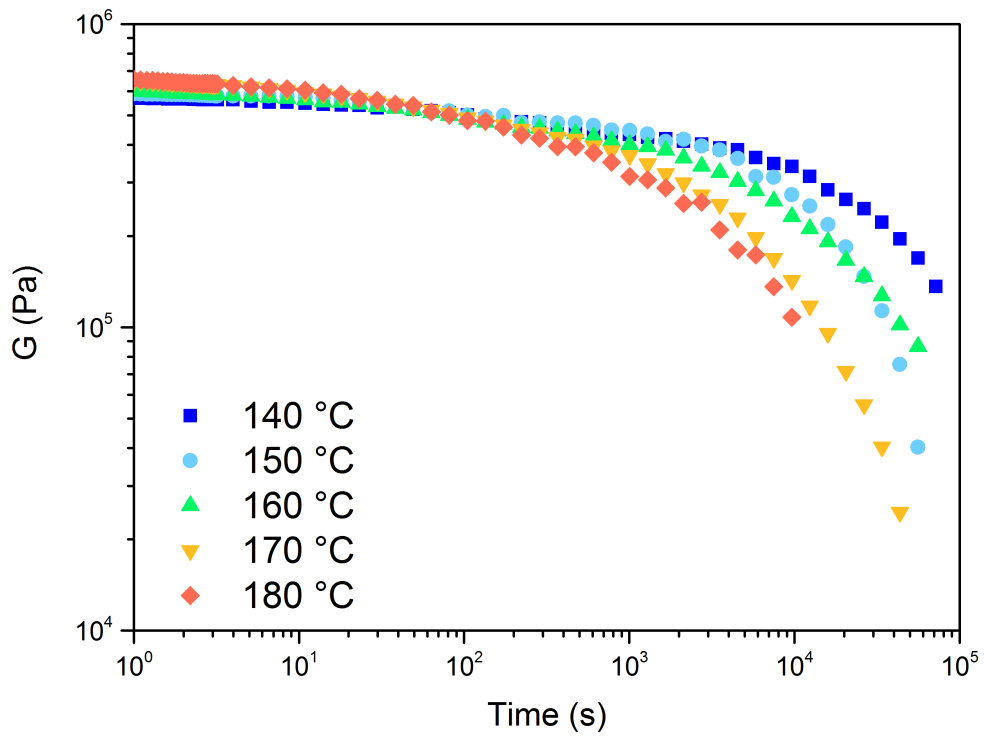


Figure 33. Non-Normalized stress relaxation for **FPA-17**.

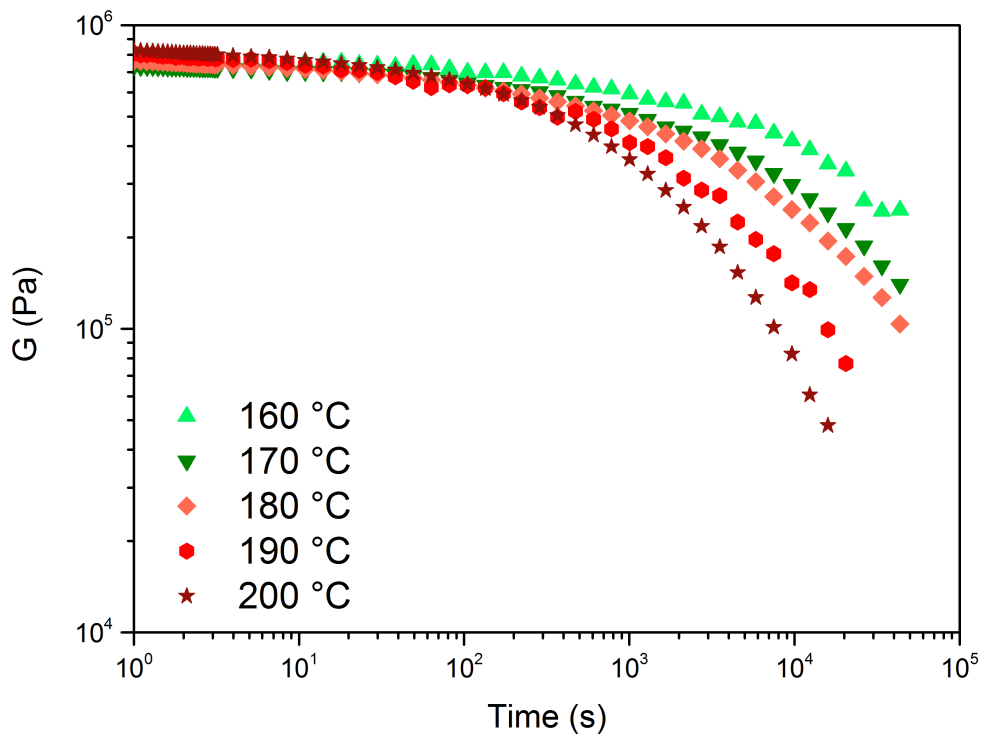


Figure S34. Non-Normalized stress relaxation for **FPA-8**.

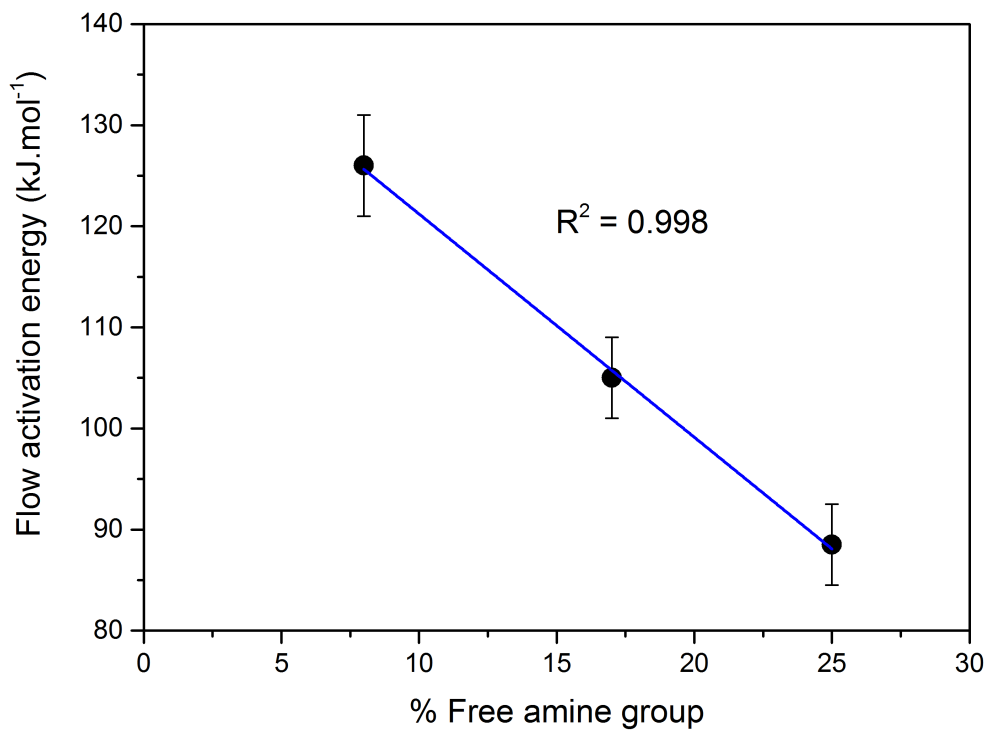


Figure 35. Plot of flow activation energy vs. percentage of free amine in FPA.

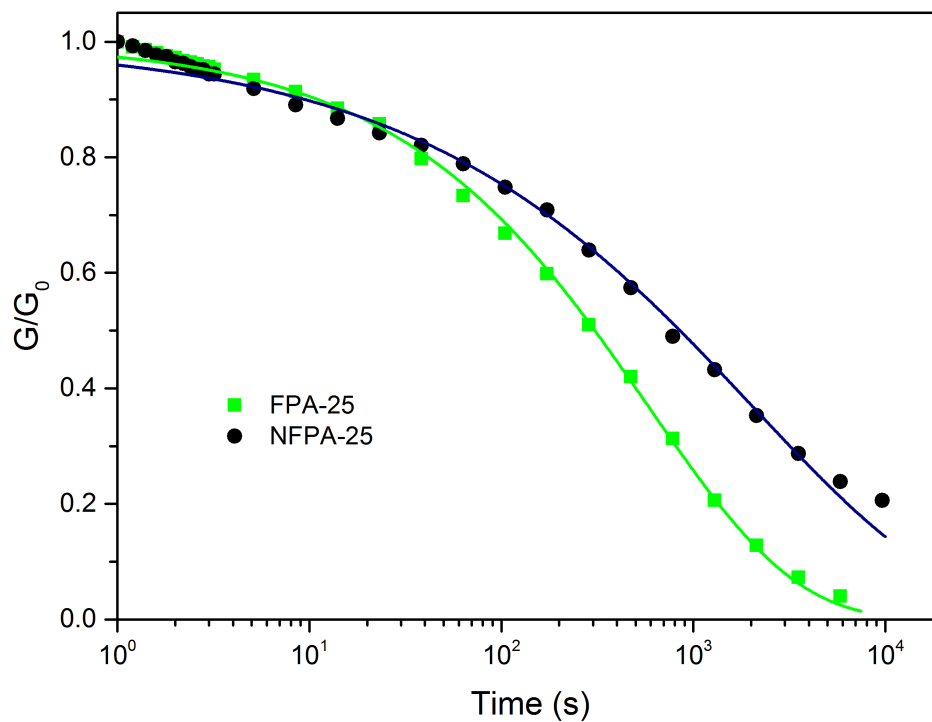


Figure S36. Normalized stress-relaxation of FPA-25 (green curve) and of NFPA-25 (black curve) at 180 °C.

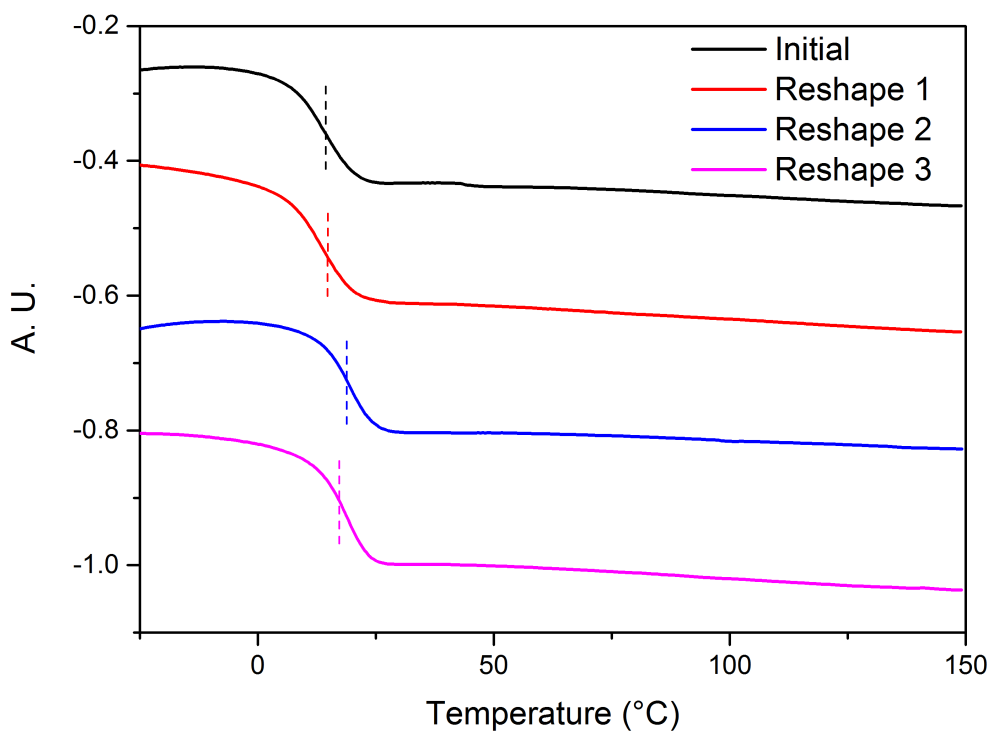


Figure S37. DSC curves of initial **FPA-25** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

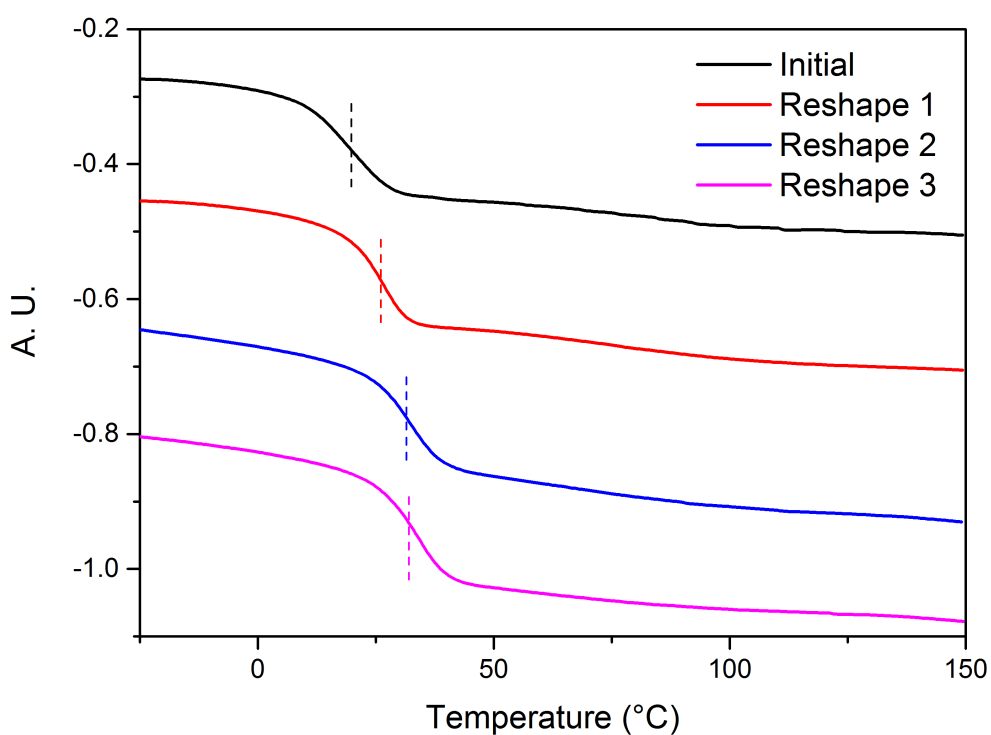


Figure S38. DSC curves of initial **FPA-17** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

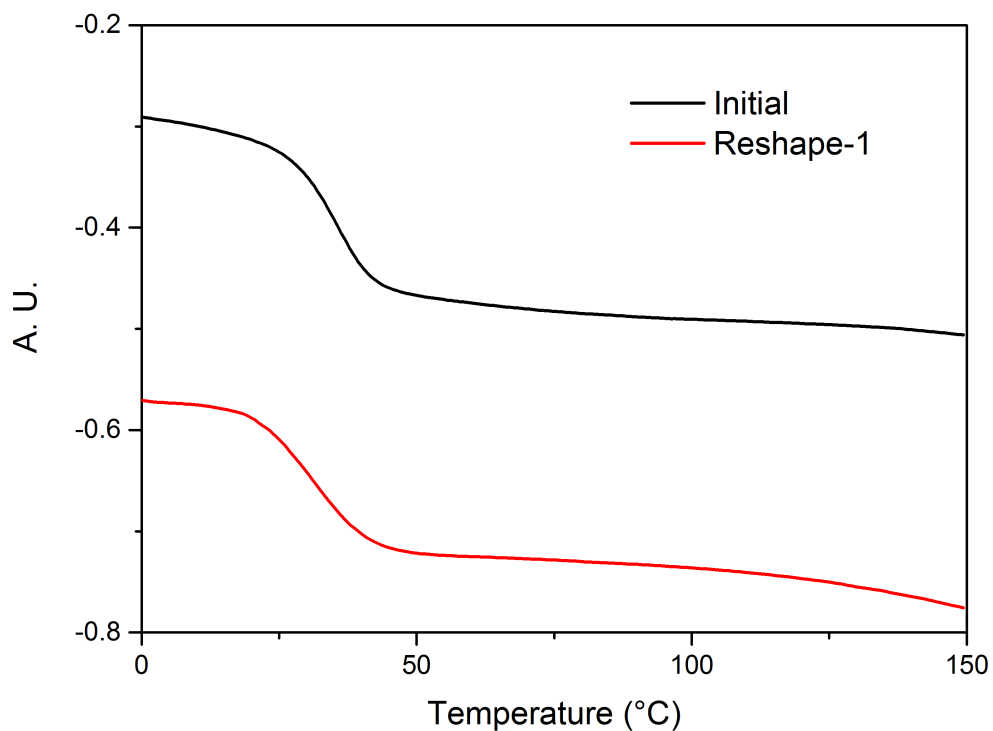


Figure S39. DSC curves of initial **FPA-8** (black curve) and after one reprocessing cycle (red curve)

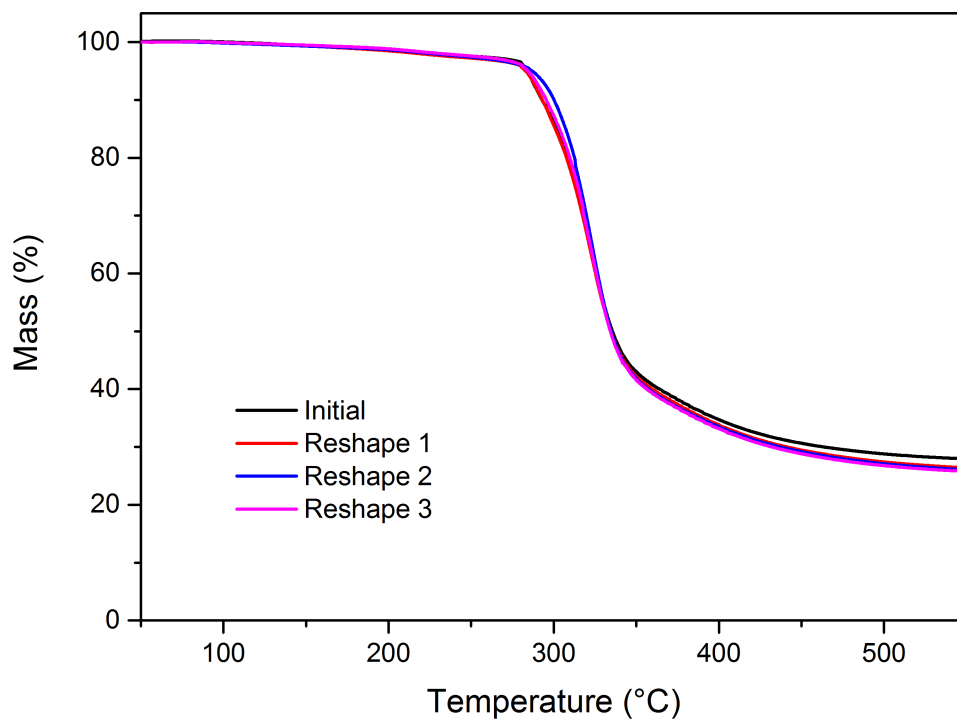


Figure S40. TGA of initial **FPA-25** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

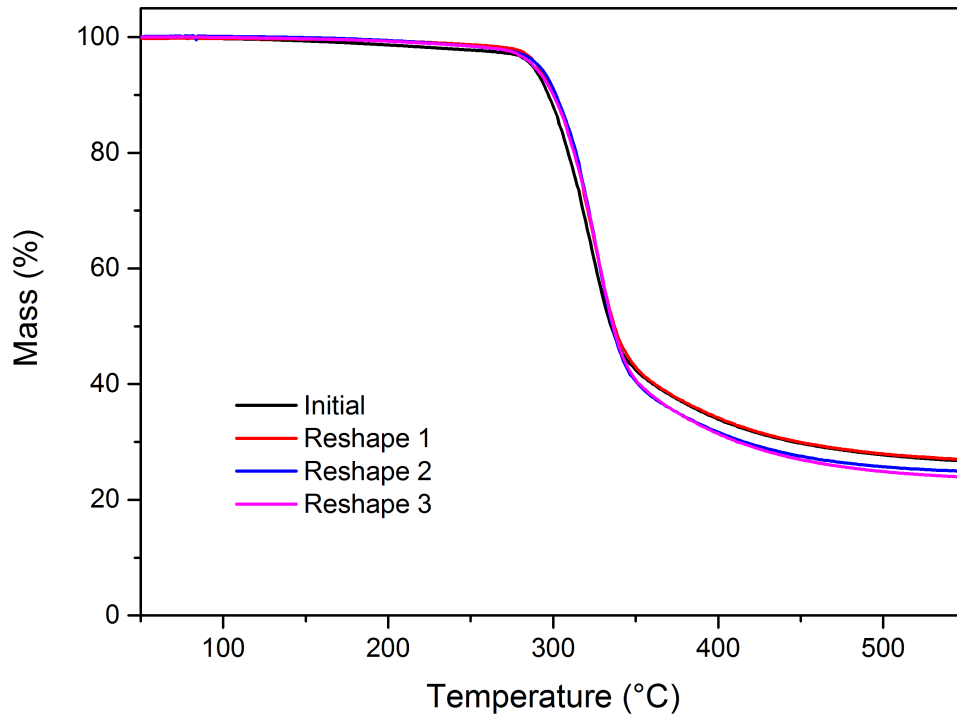


Figure S41. TGA of initial **FPA-17** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

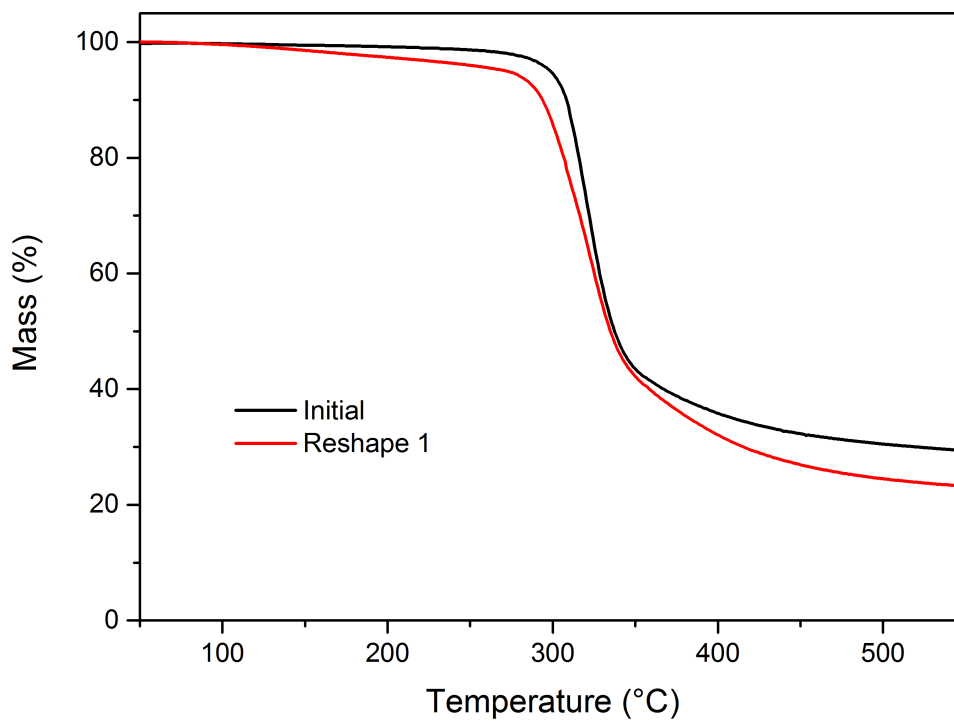


Figure 42. TGA curves of initial **FPA-8** (black curve) and after one reprocessing cycle (red curve)

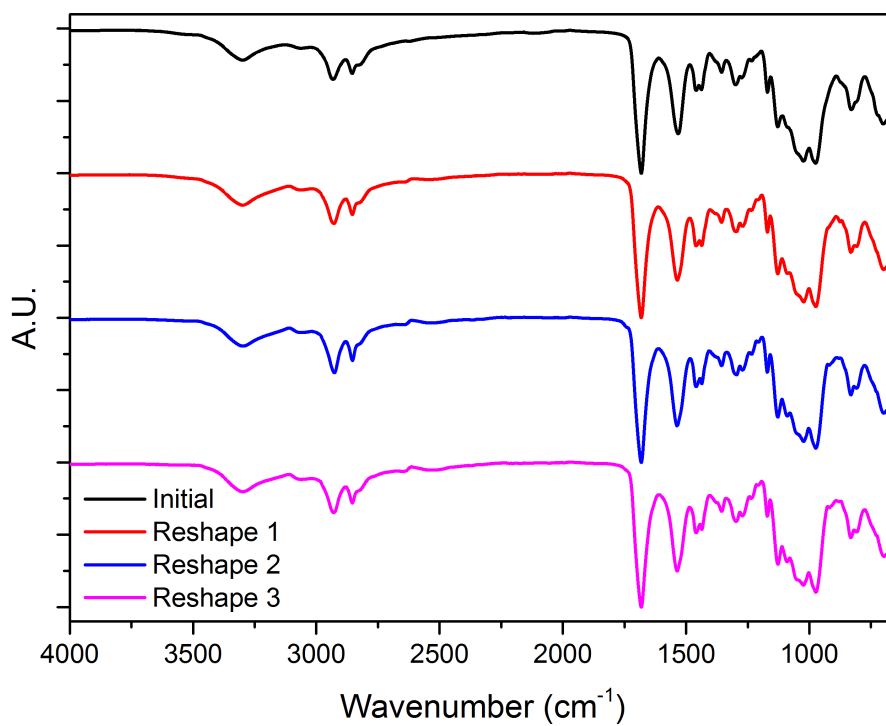


Figure S43. FTIR of initial **FPA-25** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

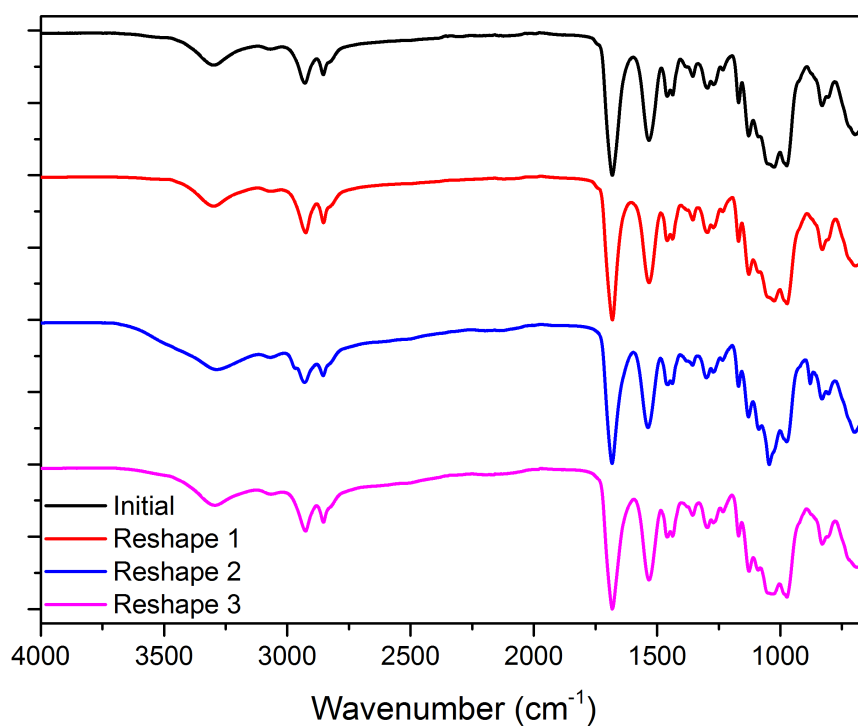


Figure S44. FTIR of initial **FPA-17** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

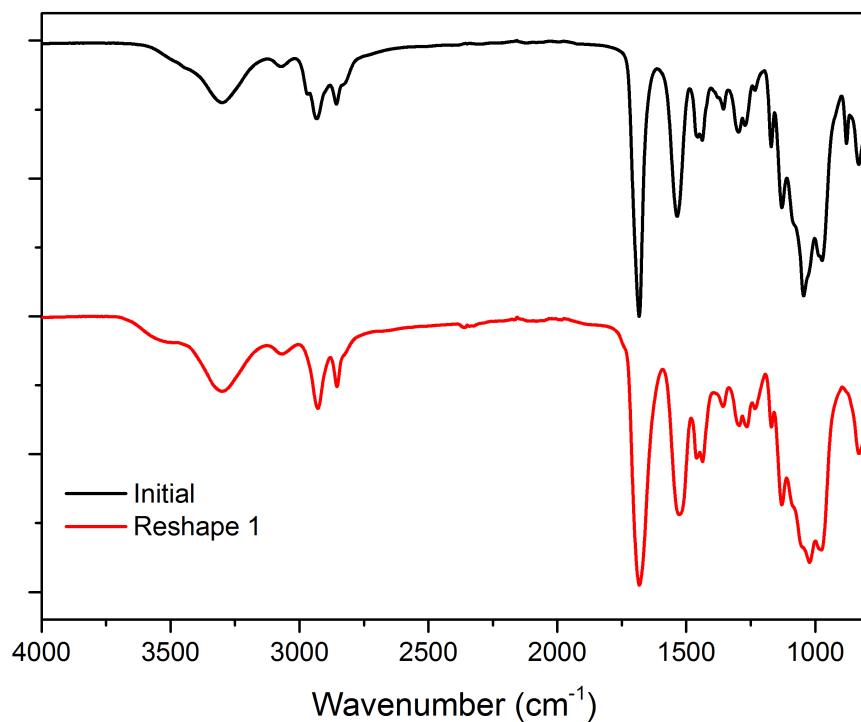


Figure 45. FTIR of initial **FPA-8** (black curve) and after one reprocessing cycle (red curve)

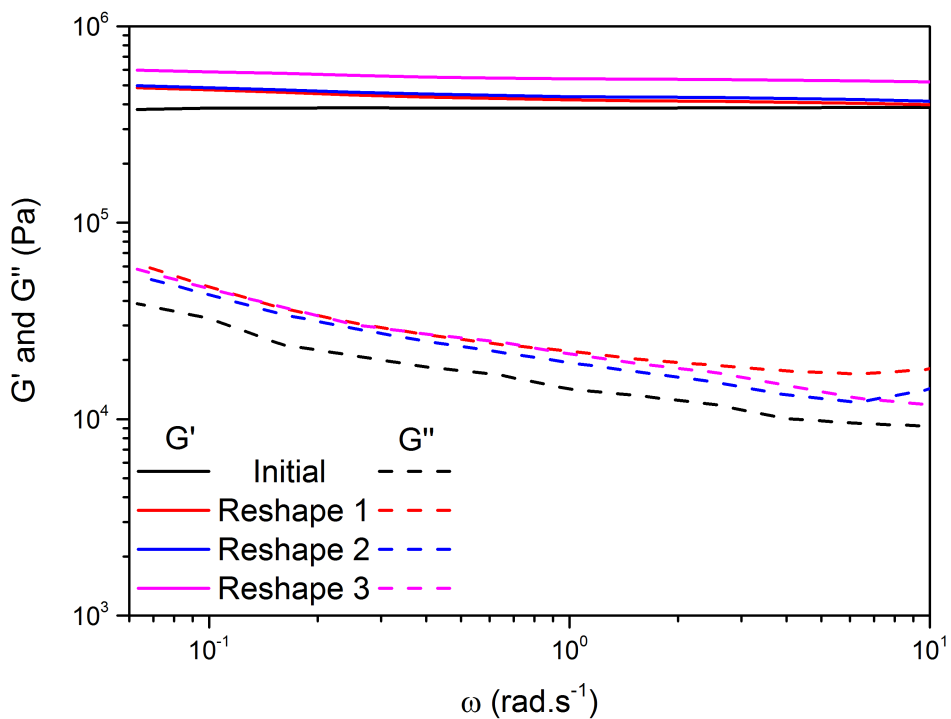


Figure S46. Frequency sweep measurements from 10 to 0.5 rad.s^{-1} at 180 °C of initial **FPA-25** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles

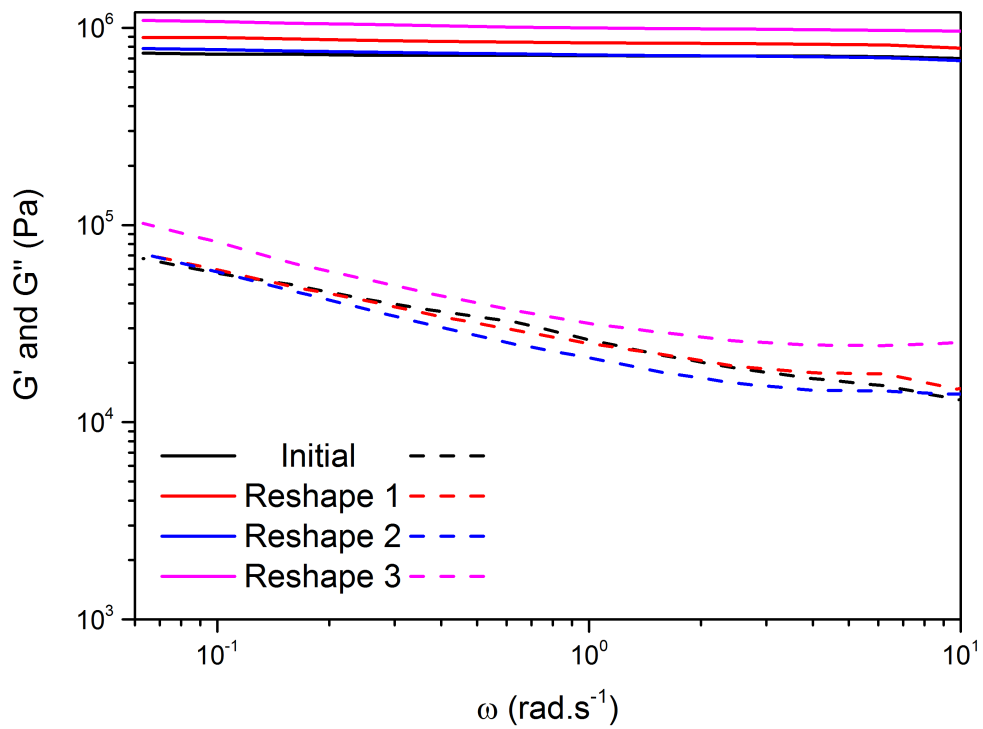


Figure S47. Frequency sweep measurements from 10 to 0.5 $\text{rad}\cdot\text{s}^{-1}$ at 180 °C of initial **FPA-17** (black curve) and after one (red curve), two (blue curve) and three (magenta curve) reprocessing cycles