

Supporting Information

Thiol-promoted catalytic synthesis of high-performance furan-containing lubricant base oils from biomass derived 2-alkylfurans and ketones

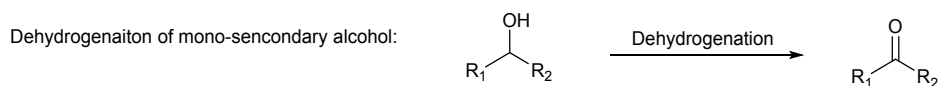
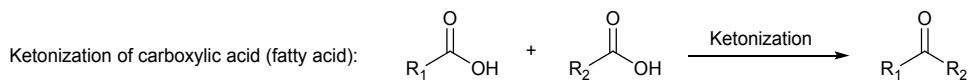
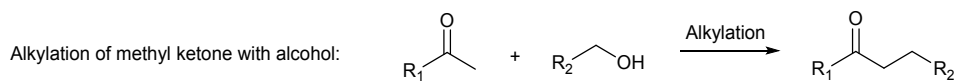
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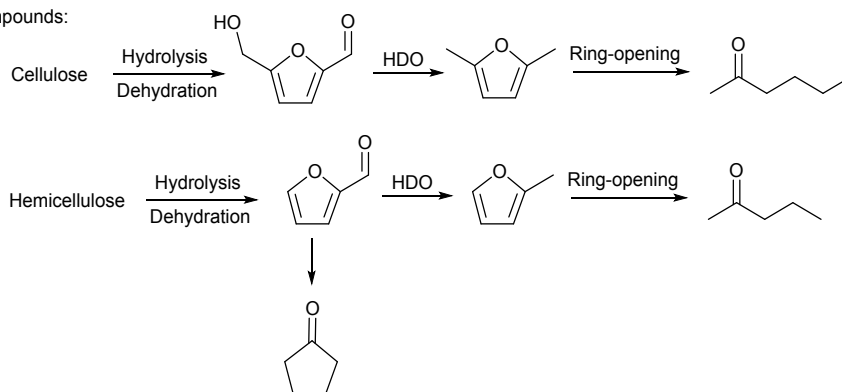
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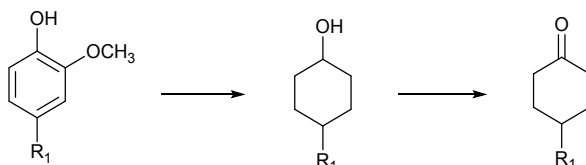
*Corresponding authors: vlachos@udel.edu, bsaha@udel.edu



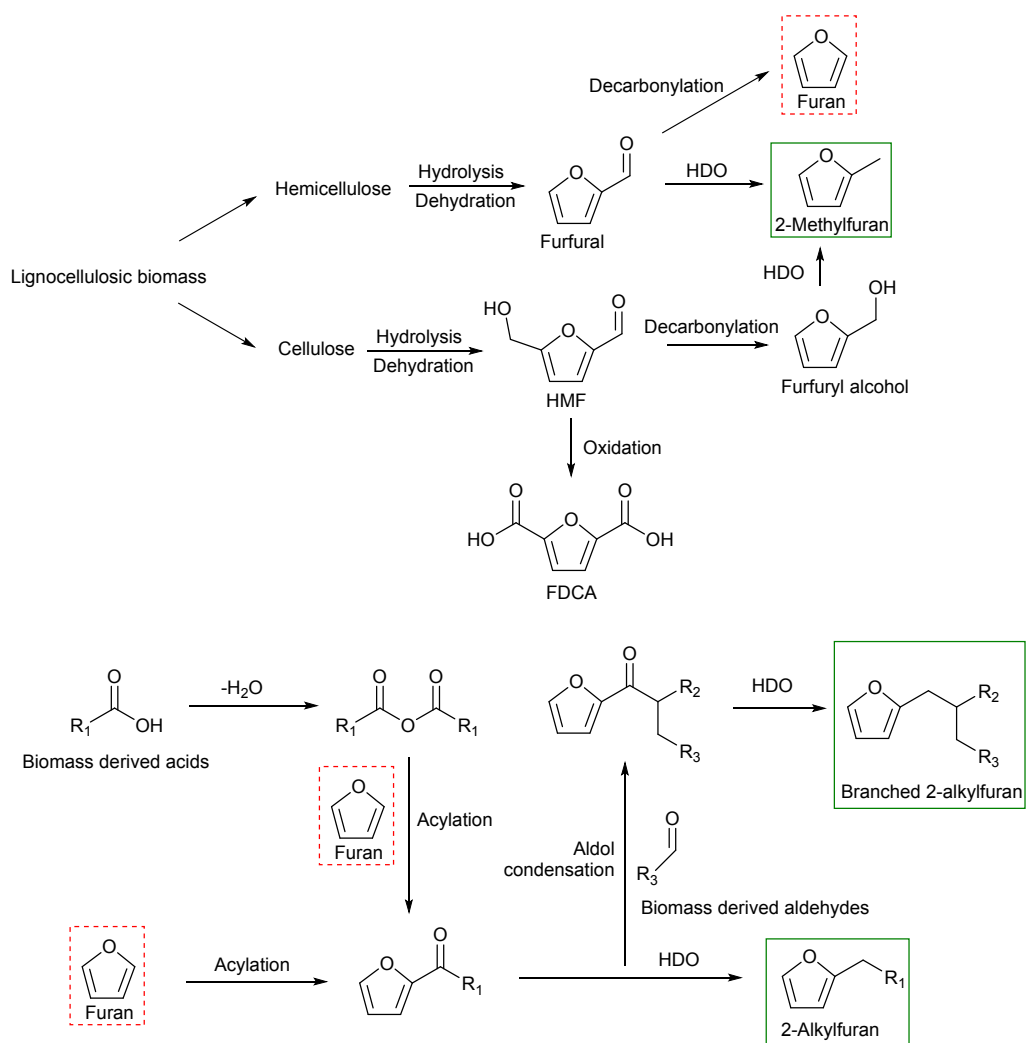
From fuanic compounds:



From lignin:



Scheme S1. Strategies for the synthesis of various ketones.



Scheme S2. Strategies for the synthesis of various furanic compounds.

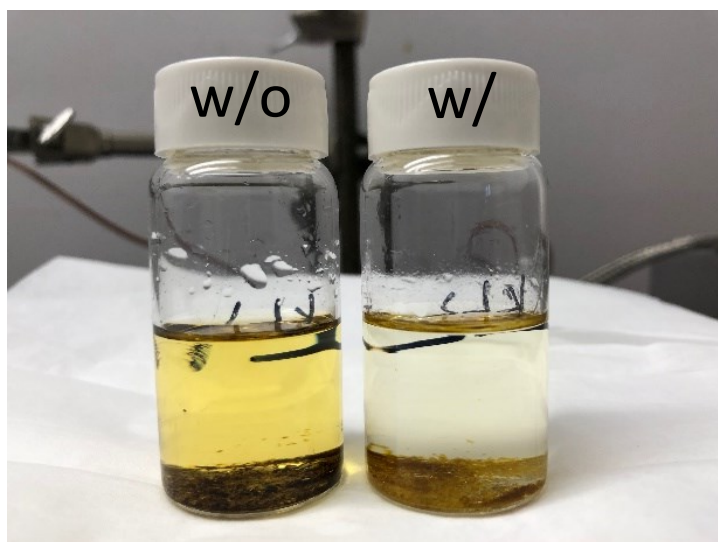


Figure S1. Solutions diluted by 10 ml cyclohexane and catalysts after the reaction without (left) and with (right) 1-propanethiol. Reaction conditions: 4 mmol 2-PF, 2 mmol 2-undecanone, 0.05 g Aquivion PW79S (0.063 mmol H⁺), SH/H⁺=1 (molar ratio), 65 °C, 4 h reaction time.

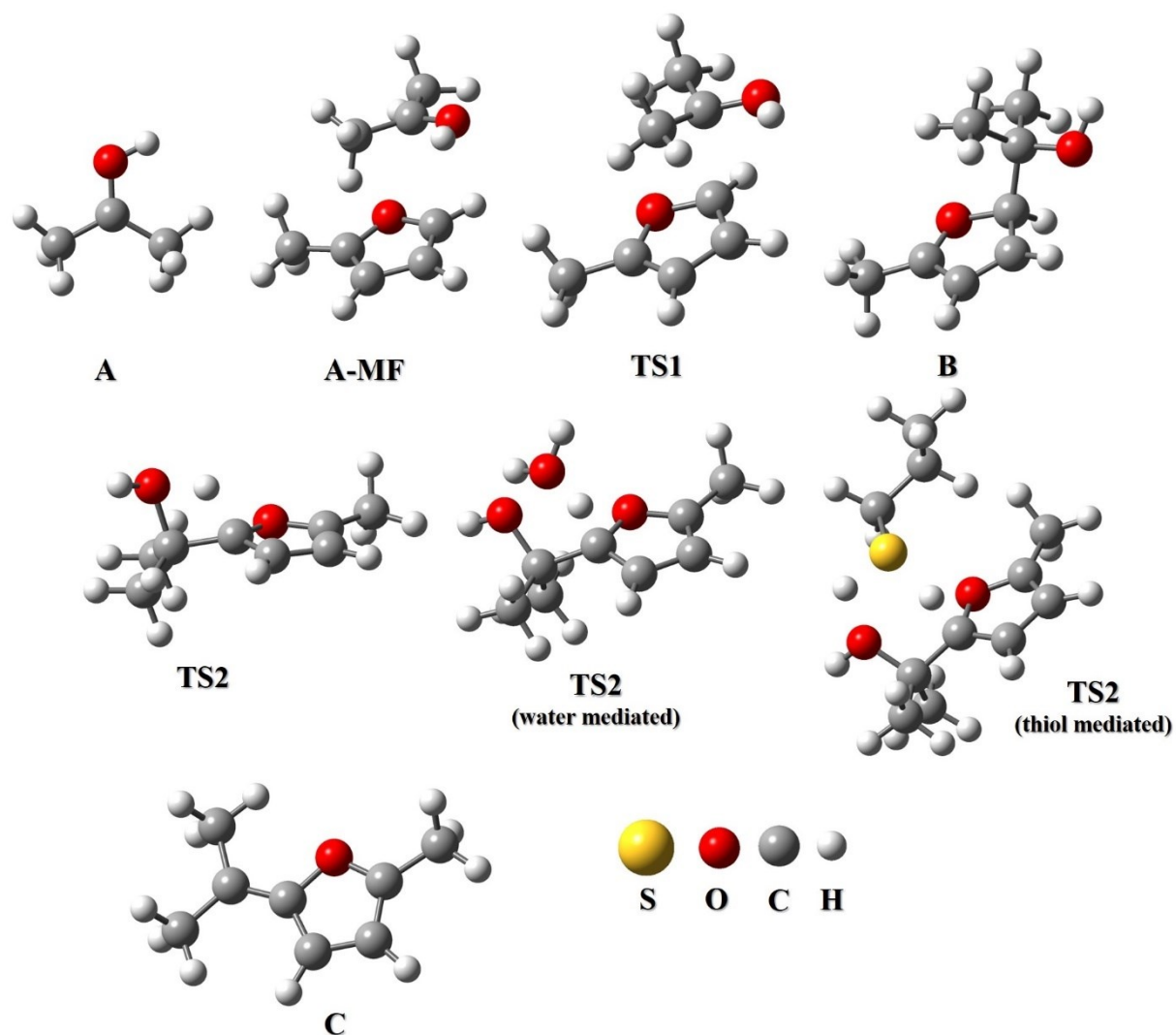
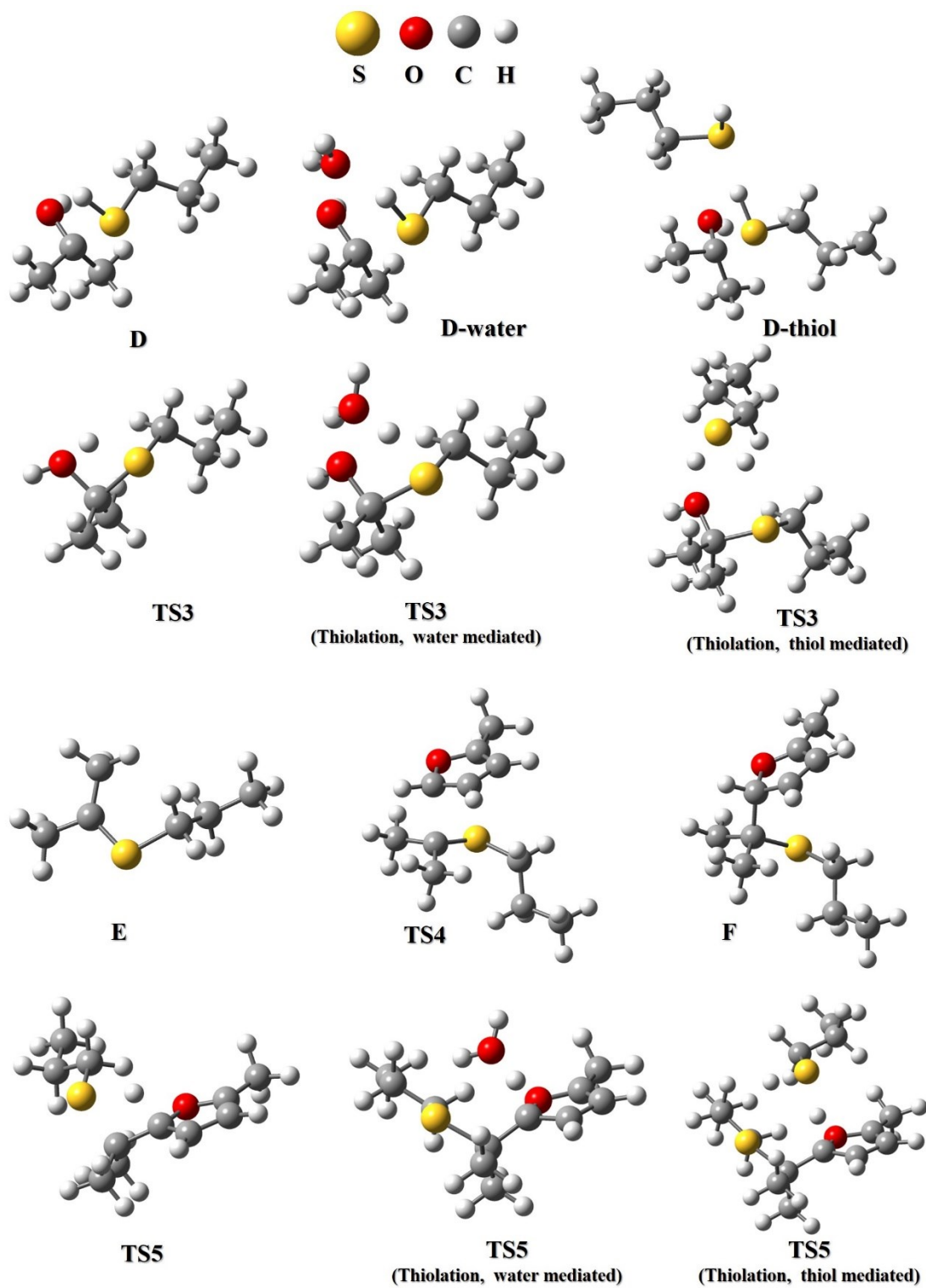


Figure S2: Optimized structures of intermediates and transition states shown in Figure 2a of the manuscript.



FigureS3: Optimized structures of intermediates and transition states shown in Figure 2b

of the manuscript.

Cartesian Coordinates:

A (Electronic energy: -193.4480054 Ha):

C	0.00530000	0.06452500	-0.00049300
C	1.34682500	-0.52480500	-0.00784800
H	1.36301800	-1.43145700	-0.61310400
H	2.10050000	0.19375800	-0.31856600
H	1.55271300	-0.83455200	1.02651000
C	-1.21274500	-0.75724400	0.00677200
H	-2.10342500	-0.20369600	0.29938400
H	-1.34282800	-1.13219400	-1.01745900
H	-1.07047300	-1.63383600	0.64002400
O	-0.04827200	1.33078500	-0.00482000
H	-0.94960200	1.70084000	0.03119200

A-MF (Electronic energy: -462.7861733 Ha):

C	1.85704200	-0.18224400	0.01159000
C	2.68161600	-1.40182300	0.17950500
O	0.96784100	-0.17513400	-1.01523400
C	1.79308200	1.00441600	0.67364100
C	0.34885600	1.03508100	-1.01642600
C	0.81403600	1.79851800	-0.00034200
H	2.05896900	-2.28787100	0.31602000
H	3.30213400	-1.56518600	-0.70250800
H	3.32989700	-1.29229400	1.04564400
H	2.39580200	1.28616500	1.52091500
H	0.53053500	2.81479200	0.21796200
H	-0.32756600	1.22363800	-1.83338000
C	-1.95123400	-0.30875700	0.24379600
C	-1.13663200	-0.82097300	1.34788400
H	-0.11508100	-0.42140800	1.21990000
H	-1.50617500	-0.49060600	2.31887100
H	-1.06977700	-1.90665700	1.30511000
C	-2.11620200	-1.04164700	-1.01792300

H	-2.54804300	-0.41537300	-1.79363500
H	-1.16568200	-1.47892900	-1.32280700
H	-2.80324600	-1.87138300	-0.80339300
O	-2.63067500	0.76341800	0.36019400
H	-2.52247700	1.20342000	1.22125700

TS1(Electronic energy: -462.7829104 Ha):

C	1.88314900	-0.06124400	-0.02877600
C	2.96877400	-0.98840400	0.35406700
O	0.93713500	-0.52633900	-0.85485800
C	1.61972900	1.24829000	0.30129100
C	0.01789000	0.46641900	-1.04833200
C	0.44308400	1.59467500	-0.37707900
H	2.56536400	-1.88333500	0.83047900
H	3.51561900	-1.30588800	-0.53533500
H	3.65641300	-0.49810000	1.03801200
H	2.21844100	1.86701900	0.94829700
H	-0.05548600	2.55200100	-0.38142000
H	-0.61349800	0.36297100	-1.91484900
C	-1.70878400	-0.19829600	0.23002400
C	-1.04364200	-0.29346700	1.55243700
H	-0.06275100	-0.76035100	1.46872400
H	-0.94461900	0.67397300	2.04163300
H	-1.66093200	-0.95118300	2.17413400
C	-1.97046500	-1.43931400	-0.54913800
H	-2.36461700	-1.20980300	-1.53613800
H	-1.08368500	-2.06347500	-0.61616500
H	-2.74278200	-1.98779700	0.00209800
O	-2.58174600	0.74729500	0.00708500
H	-2.52898300	1.46436600	0.65575800

B (Electronic energy: -462.8045912 Ha):

C	1.88857300	-0.10990500	-0.06945900
C	3.09406100	-0.90693900	0.18871400
O	0.84202600	-0.68704500	-0.54278600
C	1.68406500	1.28999900	0.12999700
C	-0.21014400	0.28608900	-0.70425100
C	0.41734100	1.54085600	-0.25242700
H	2.93122200	-1.95631000	-0.03832600

H	3.91283400	-0.51057800	-0.41824200
H	3.38763100	-0.78012900	1.23371100
H	2.42535800	1.97052100	0.51712700
H	-0.11638800	2.48043400	-0.23905200
H	-0.46067700	0.31548700	-1.76944700
C	-1.48156100	-0.13766800	0.08158100
C	-1.17966900	-0.34901300	1.55883800
H	-0.48318600	-1.17387900	1.71573100
H	-0.78473000	0.55868700	2.01483600
H	-2.10694700	-0.60335600	2.07315000
C	-2.08379800	-1.37757500	-0.55933900
H	-2.34501600	-1.18315300	-1.59961600
H	-1.39604500	-2.22229300	-0.51363500
H	-2.99065200	-1.65864500	-0.02112800
O	-2.28547500	1.00521200	-0.12030900
H	-3.19902000	0.80282300	0.10772300

TS2 (Electronic energy: -462.7488015 Ha):

C	-2.04137800	-0.05409800	-0.03458800
C	-3.26017600	-0.88577300	-0.02397800
O	-0.87683600	-0.66920900	0.08061200
C	-1.86505800	1.31839200	-0.11228600
C	0.12066400	0.29079400	0.13393300
C	-0.49792900	1.53743600	-0.04774800
H	-4.13304600	-0.27936400	-0.24953300
H	-3.17090800	-1.69022900	-0.75440100
H	-3.38677300	-1.34136900	0.96037900
H	-2.64984600	2.05055700	-0.19849100
H	0.00977900	2.48929400	-0.08657000
H	0.71125600	0.28619300	1.38143400
C	1.55492600	-0.17636800	-0.07510700
C	2.43385700	0.87935100	-0.70645600
H	2.15625800	1.01344900	-1.75126800
H	2.34667800	1.83957600	-0.19593200
H	3.47558300	0.55665300	-0.67165400
C	1.68445000	-1.54670300	-0.69100600
H	1.08705200	-2.27523100	-0.14768200
H	1.35368400	-1.51776800	-1.72918800
H	2.72949200	-1.85431700	-0.66457300

O	1.87625700	-0.28301300	1.39459500
H	2.69928000	0.16214600	1.64923500

TS2 (No thiolation, water mediated) (Electronic energy: -539.2228466 Ha):

C	2.12920800	-0.13579100	-0.02224800
C	3.35281500	-0.33849100	-0.82554400
O	0.96389900	-0.22894800	-0.64340300
C	1.94984800	0.18037200	1.31051000
C	-0.04854200	0.06962300	0.26460200
C	0.57424100	0.26925100	1.50299200
H	4.23318000	-0.29280700	-0.19036300
H	3.31370200	-1.30733900	-1.32456900
H	3.42732000	0.42947700	-1.59724000
H	2.73151900	0.33338200	2.03495100
H	0.05780500	0.50619900	2.42141500
H	-0.33648900	1.40627000	0.02623900
C	-1.40966600	-0.53464300	-0.04686700
C	-2.36860800	-0.25639100	1.10290300
H	-2.08084200	-0.80361900	2.00033100
H	-2.41574300	0.80975400	1.33237100
H	-3.36845800	-0.58407200	0.81749800
C	-1.27964600	-2.02387200	-0.33684300
H	-0.64245000	-2.18748400	-1.20408700
H	-0.85779100	-2.54656200	0.52173600
H	-2.26643900	-2.44685800	-0.53601100
O	-1.85914400	0.14808600	-1.23130000
H	-2.60547400	-0.32966700	-1.60860900
O	-0.93562100	2.41229700	-0.42890700
H	-0.40007800	3.04734000	-0.92286300
H	-1.54072400	1.93415600	-1.03894800

TS2 (No thiolation, thiol mediated) (Electronic energy: -539.2228466 Ha):

C	0.41165100	2.05536900	-0.22820000
C	1.51103100	2.84406900	0.36859600
O	-0.08767000	1.05105500	0.48748200
C	-0.24033400	2.15877500	-1.43783300
C	-1.07180700	0.42242800	-0.26425400
C	-1.21454800	1.15942100	-1.44142300
H	2.34176100	2.19710000	0.65340900
H	1.86225800	3.59211100	-0.33728300
H	1.15693900	3.34486800	1.27141600

H	-0.02668300	2.87716000	-2.21093400
H	-1.91420600	0.93226200	-2.23148300
H	-0.31778800	-0.62360200	-0.86371200
C	-2.10503000	-0.35690100	0.52670200
C	-3.13465000	-0.94844100	-0.42850100
H	-3.73951300	-0.17218100	-0.89718200
H	-2.65710300	-1.54556800	-1.20796000
H	-3.80261000	-1.60202700	0.13263200
C	-2.75745300	0.54823500	1.56628700
H	-2.01033100	0.91995400	2.26589200
H	-3.25288400	1.39415900	1.08965200
H	-3.51174300	-0.01471700	2.12031500
H	-0.22984000	-2.71775700	-0.51640300
C	1.75062000	-1.61856100	0.28633400
H	2.16063100	-2.58075700	0.59049600
H	1.12219000	-1.22246900	1.08321500
C	2.85226300	-0.65214500	-0.12153800
H	2.40645600	0.23925900	-0.57322800
H	3.47738400	-1.10947500	-0.89086200
C	3.69952400	-0.26674800	1.08604800
H	4.18528900	-1.14250000	1.51744400
H	4.48017700	0.43819600	0.80208000
H	3.08782700	0.19176400	1.86548800
S	0.66064900	-1.93412600	-1.14377800
O	-1.37429300	-1.39892600	1.17040300
H	-1.90050400	-1.73979500	1.90108000

C (Electronic energy: -386.3786327 Ha):

C	1.78897500	-0.05995800	0.00000000
C	3.02561200	-0.85675500	0.00006600
O	0.64262200	-0.69905000	0.00005400
C	1.58712000	1.32757800	-0.00008300
C	-0.37843500	0.23817200	0.00000300
C	0.22879400	1.51640700	-0.00008800
H	3.89850000	-0.21059500	-0.00026100
H	3.04521100	-1.50252500	0.88069300
H	3.04494900	-1.50312500	-0.88011800
H	2.36672100	2.07076700	-0.00013600
H	-0.29687800	2.45794100	-0.00015100

C	-1.67306300	-0.17391000	0.00002400
C	-2.78753300	0.80643700	0.00011200
H	-3.41721300	0.62693100	0.87559400
H	-2.46546200	1.84295200	-0.00083800
H	-3.41860500	0.62569000	-0.87409200
C	-2.02928700	-1.61401700	-0.00008700
H	-1.16673400	-2.27168100	0.00119300
H	-2.65359300	-1.82370000	0.87305000
H	-2.65097900	-1.82397900	-0.87505700

D (Electronic energy: -710.773199 Ha):

C	-1.50947800	0.31822300	0.06822800
C	-2.82624800	-0.31562600	-0.31920800
H	-2.82303100	-0.65167800	-1.35504000
H	-3.06901200	-1.14538900	0.34372500
H	-3.59928400	0.44465800	-0.19819100
C	-1.08990700	1.49311000	-0.78439900
H	-0.13068700	1.90111700	-0.45985800
H	-1.02742600	1.22581100	-1.83832900
H	-1.84875400	2.26988600	-0.67130200
C	1.32781600	-0.54568100	0.49337100
C	2.29155000	0.03546400	-0.53420400
C	3.55556200	0.53364100	0.15936000
S	-0.20698700	-1.11803800	-0.30016700
H	1.04257200	0.16545600	1.27055800
H	1.75173300	-1.42499100	0.97916800
H	1.81777000	0.85302400	-1.08192700
H	2.54067600	-0.73422700	-1.26677300
H	4.05747300	-0.27759000	0.68754200
H	4.25220900	0.93862600	-0.57207300
H	3.32878400	1.32040100	0.87990200
O	-1.48062000	0.55606100	1.40972900
H	-0.96261400	1.34173500	1.62006500
H	-0.66943100	-1.90149600	0.68849000

D-H₂O (Electronic energy: -787.2162875 Ha):

C	1.12686200	-0.85748600	0.14561500
C	2.46214700	-0.92237200	-0.56599000
H	2.35489400	-1.31366400	-1.57683400
H	2.92466900	0.06353500	-0.59635700
H	3.10794500	-1.59111700	0.00411500
C	0.40221200	-2.18164700	0.24248100
H	-0.54929500	-2.07896300	0.76852000
H	0.21694900	-2.60796400	-0.74236800
H	1.03440400	-2.87189400	0.80398400
C	-1.38777800	0.69439400	0.03132600
C	-2.60035400	-0.12464800	-0.39140600
C	-3.80013100	0.21886400	0.48499500
S	0.07603400	0.30637600	-0.97528400
H	-1.10936600	0.54310600	1.07561800
H	-1.56013800	1.76145000	-0.11400600
H	-2.37919300	-1.19199900	-0.32354000
H	-2.82553300	0.08422000	-1.43875800
H	-4.05282600	1.27669700	0.40490700
H	-4.67120500	-0.35737400	0.17889400
H	-3.60105900	-0.00422000	1.53407600
O	1.28784100	-0.23537600	1.36859600
H	0.69822000	-0.61680100	2.02847600
H	0.84380500	1.38855300	-0.64284400
O	2.01882000	2.30622800	0.28042600
H	2.48159200	3.14628000	0.21444800
H	2.19855900	1.93869000	1.15191400

D-Thiol (Electronic energy: -1228.0879181 Ha):

C	-0.76219300	-1.57527200	0.12189500
C	0.16600600	-2.41122000	-0.73480700
H	-0.35247700	-2.82128400	-1.60025800
H	1.02117400	-1.82141900	-1.06587300
H	0.53684300	-3.23250800	-0.12074000
C	-1.99138300	-2.31138600	0.60708700
H	-2.62408000	-1.66815000	1.22239400
H	-2.58134000	-2.69516300	-0.22413000
H	-1.66133200	-3.15439900	1.21681900
C	-2.23982600	0.97357100	0.00529500
C	-3.75000800	0.82331100	-0.12443800
C	-4.46040700	1.80523300	0.80104700
S	-1.33985400	-0.18145800	-1.07108000

H	-1.87970400	0.81583700	1.02370500
H	-1.91148100	1.96673000	-0.30635100
H	-4.04941200	-0.19994800	0.11214400
H	-4.03926400	1.00392800	-1.16126600
H	-4.20016500	1.62431900	1.84487100
H	-4.19376600	2.83452800	0.55863300
H	-5.53988300	1.70691500	0.70259900
O	-0.03545400	-0.99293700	1.13871600
H	-0.57374700	-0.87685300	1.92955800
H	-0.10462200	0.47100300	-0.99190100
H	2.06348300	2.21715200	-1.28428000
C	2.88117300	0.28047500	-0.11632700
H	2.96961100	-0.23167300	-1.07495100
H	2.50011100	-0.43140300	0.61791300
C	4.21856900	0.85747200	0.32324900
H	4.08673300	1.38075500	1.27191100
H	4.54772900	1.60232200	-0.40494600
C	5.26818400	-0.24004300	0.45921600
H	6.22289500	0.17776800	0.77487000
H	4.96651600	-0.98181000	1.20041700
H	5.42652800	-0.75441100	-0.48992600
S	1.56939000	1.54385900	-0.23606000

TS3 (Electronic energy: -710.7342954 Ha):

C	-1.41049700	0.30908100	-0.00571300
C	-2.61202600	0.17554900	-0.91185400
H	-2.34429700	0.46953000	-1.92563800
H	-2.99174700	-0.84694000	-0.93499400
H	-3.40323300	0.84345700	-0.56321800
C	-0.83203200	1.69429500	0.07706100
H	0.00593900	1.74808700	0.76850700
H	-0.51299400	2.02408900	-0.91075400
H	-1.61001600	2.37426300	0.42877800
C	1.33565000	-0.61855100	0.40327300
C	2.24060000	0.16172500	-0.53961000
C	3.57100800	0.46826000	0.14091700
S	-0.24853200	-1.09440600	-0.36850300
H	1.12570300	-0.08963200	1.33359500
H	1.78159300	-1.58088800	0.66409200
H	1.75452800	1.08969100	-0.84595800
H	2.40404100	-0.42588300	-1.44502000

H	3.42686000	1.07496600	1.03595200
H	4.08288600	-0.44980500	0.43139900
H	4.22481900	1.01690700	-0.53450700
O	-1.73876700	-0.18608800	1.35793000
H	-2.68668400	-0.15455600	1.56921100
H	-1.12697000	-1.23623000	0.97671600

TS3(Thiolation, thiol mediation) (Electronic energy: -1228.0773013 Ha):

C	-1.14826400	-1.44847300	0.55724400
C	-1.15505900	-2.92829600	0.20311200
H	-2.10530600	-3.21184200	-0.24711000
H	-0.35661200	-3.17623500	-0.49832900
H	-1.01254400	-3.51907700	1.10976300
C	-2.27279200	-1.09721800	1.51396400
H	-2.23128400	-0.04921900	1.80790500
H	-3.23964500	-1.30096700	1.05680700
H	-2.18882600	-1.71114900	2.41533400
C	-1.38208800	1.19832700	-0.47659000
C	-2.80950100	1.73053700	-0.45429200
C	-2.84420600	3.18532700	-0.00057100
S	-1.24919200	-0.53538500	-1.02366500
H	-0.90069100	1.27327500	0.50192400
H	-0.78342900	1.78104500	-1.17975500
H	-3.42479000	1.11418800	0.20304200
H	-3.23523900	1.63348500	-1.45472100
H	-2.44633100	3.29253500	1.01028500
H	-2.25259900	3.81817400	-0.66417900
H	-3.86412300	3.56669800	0.00046900
O	0.11304000	-1.09698400	1.16857200
H	0.08951300	-1.37450100	2.09329500
H	1.09684300	-1.04923800	-1.67365000
H	1.53654600	-1.46482200	0.14486700
C	2.43665800	0.61646000	-0.55430800
H	1.42731800	0.98629300	-0.37730600
H	2.85965200	1.08982700	-1.43992100
C	3.33135200	0.77346400	0.66595400
H	4.30107300	0.30658300	0.48059900
H	2.87473600	0.25774700	1.51423400
C	3.51506800	2.25291600	0.99040200
H	4.14337800	2.36995600	1.87137400
H	3.99386500	2.77898400	0.16422800

H	2.55697100	2.73274100	1.19342400
S	2.26357900	-1.15629400	-0.97950000

TS3(Thiolation, water mediation) (Electronic energy: -787.2104415 Ha):

C	1.11495600	-0.79137900	0.09223100
C	2.39885500	-1.06028200	-0.67477000
H	2.19105100	-1.56493300	-1.61749300
H	2.94006000	-0.13588600	-0.87993400
H	3.04006500	-1.70589100	-0.07241800
C	0.33362300	-2.05454800	0.39273800
H	-0.55520200	-1.84058700	0.98508700
H	0.04109400	-2.55756600	-0.52782400
H	0.97056200	-2.73764900	0.96065400
C	-1.37151900	0.65505100	0.05262800
C	-2.55751300	-0.17573800	-0.41946800
C	-3.77863600	0.09054200	0.45369800
S	0.12971400	0.38059800	-0.94895800
H	-1.10315600	0.45705800	1.09212500
H	-1.59445800	1.71949100	-0.03702200
H	-2.30274800	-1.23687100	-0.39823600
H	-2.77403100	0.07220300	-1.46020400
H	-4.06304900	1.14316700	0.42068400
H	-4.62935400	-0.49557900	0.11057500

H	-3.58548800	-0.17535800	1.49416200
O	1.39273500	-0.08246400	1.30526400
H	1.66226900	-0.71184200	1.98527600
H	1.08820600	1.65984100	-0.36985500
O	1.87530300	2.24114400	0.26281700
H	1.64125100	3.13800500	0.54111900
H	1.97460100	1.63150400	1.02964500

E (Electronic energy: -634.3391819 Ha):

C	1.50901900	0.23040600	-0.02277900
C	2.91985400	-0.00299100	0.38139400
H	3.17581200	0.68568600	1.19106200
H	3.11905500	-1.02687400	0.68720500
H	3.56426500	0.25602700	-0.46465700
C	1.10323100	1.61917800	-0.33207900
H	0.14887500	1.70973600	-0.84008600
H	1.04677500	2.16209900	0.61920100
H	1.89011800	2.10245100	-0.91441700
C	-1.11978400	-0.55836300	-0.56713900
C	-1.89134200	0.10121700	0.57287400
C	-3.30746300	0.44198400	0.12000300
S	0.54368600	-1.09200900	-0.07651100
H	-1.03424700	0.07250800	-1.45194100
H	-1.59284200	-1.49362400	-0.87272900
H	-1.37105300	1.00395500	0.89991700
H	-1.92039900	-0.57658700	1.42814700
H	-3.84803100	-0.45493500	-0.18325700
H	-3.86050300	0.90752000	0.93373100
H	-3.29788400	1.13560200	-0.72162900

TS4 (Electronic energy: -903.6728398 Ha):

C	2.11640600	-1.10707300	0.02962400
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C	2.71251600	-1.95490100	-1.02429000
O	2.37542300	0.20006200	-0.00674700
C	1.37367100	-1.41078900	1.15938000
C	1.69007400	0.78984700	1.01504700
C	1.14188500	-0.20454100	1.81351400
H	2.30136300	-2.96009800	-0.97718800
H	2.52908600	-1.52966100	-2.01032300
H	3.79342900	-2.01204400	-0.87886300
H	1.05330000	-2.39799800	1.44919000
H	0.60653400	-0.04363800	2.73615700
H	1.99426900	1.79301100	1.26329700
C	-0.04979600	1.42160200	-0.18263800
C	0.69503100	2.45201300	-0.99629600
H	1.17392400	3.18720300	-0.35137800
H	1.43898700	2.00336100	-1.65145900
H	-0.03549600	2.98067600	-1.61439000
C	-0.94235400	1.97163400	0.89047300
H	-1.42488900	1.20877300	1.49470900
H	-0.37686900	2.63878000	1.54121700
H	-1.71800300	2.57314600	0.40680500
C	-1.68739500	-0.86344500	-0.13833700
C	-3.10445200	-0.36783800	-0.40240600
C	-4.11704500	-1.19861000	0.37850000
S	-0.41779700	0.03063000	-1.07458700
H	-1.57216700	-1.89856900	-0.46613800
H	-1.42117000	-0.82787600	0.91904000
H	-3.30985500	-0.42829200	-1.47264300
H	-3.18814700	0.68478800	-0.12599300
H	-4.06274700	-2.25055800	0.09549100
H	-3.94161900	-1.12752900	1.45316900
H	-5.12981700	-0.85144300	0.18125300

F (Electronic energy: -903.6876057 Ha):

C	2.35924700	-0.97088900	0.02435800
C	3.21379000	-1.66712200	-0.94478900
O	2.27351900	0.30882400	-0.01743700
C	1.57686800	-1.51949500	1.08978100
C	1.26231500	0.74701900	0.90660800
C	0.94839200	-0.47761400	1.66313900
H	2.55866800	-2.18500000	-1.65291600

H	3.84452900	-0.96661100	-1.48475600
H	3.81116500	-2.42592900	-0.43846200
H	1.53799800	-2.56515300	1.34945200
H	0.28395800	-0.49962700	2.51509200
H	1.69459700	1.54806600	1.51139600
C	0.07391300	1.35651500	0.06216300
C	0.63978900	2.53724200	-0.73175000
H	1.09868200	3.26162400	-0.05560600
H	1.38444300	2.21792200	-1.45973400
H	-0.17088300	3.02968600	-1.26574200
C	-0.98996300	1.84254500	1.03892300
H	-1.46645100	1.03510200	1.59413100
H	-0.54706700	2.53904700	1.75552900
H	-1.76258400	2.37794300	0.48898900
C	-1.72230800	-0.88730500	-0.30147200
C	-3.16260600	-0.40199700	-0.41006300
C	-4.11871600	-1.36248000	0.28790200
S	-0.50776700	0.15003400	-1.17212400
H	-1.62395400	-1.87062500	-0.76619900
H	-1.42114600	-1.00738000	0.74210500
H	-3.42008500	-0.30983600	-1.46663600
H	-3.25313500	0.59747200	0.01800400
H	-4.05852000	-2.36139400	-0.14687300
H	-3.89021800	-1.44472900	1.35236900
H	-5.14819900	-1.02023000	0.19453200

TS5 (Electronic energy: -903.6436549 Ha):

C	-2.46142900	1.23396400	0.02054700
C	-2.74467500	2.66441400	0.25119300
O	-1.23208200	0.79755200	0.30213700
C	-3.23336100	0.21012300	-0.47960300
C	-1.15072100	-0.53591200	-0.05765200
C	-2.42493800	-0.92661400	-0.48806100
H	-3.79286300	2.87459600	0.05639600
H	-2.50586200	2.93342300	1.28078500
H	-2.13011700	3.28082300	-0.40774200
H	-4.25745100	0.29187800	-0.80184000
H	-2.69534500	-1.91942000	-0.81291400

H	-0.43391500	-0.56739400	-1.23030100
C	0.04678200	-1.32416800	0.45225300
C	-0.25030400	-2.81654500	0.41697200
H	-1.03520500	-3.04663800	1.13926200
H	-0.57692500	-3.14860600	-0.57025800
H	0.64642700	-3.37577000	0.68028100
C	0.57088800	-0.86161300	1.79660400
H	0.80248600	0.20191600	1.80873500
H	-0.19116900	-1.04969100	2.55562300
H	1.46466800	-1.42629300	2.06057300
C	1.89491300	0.63199700	-0.72859300
C	3.21313000	0.61262900	0.03689200
C	3.75187300	2.02906200	0.20748000
S	1.21426800	-1.03244600	-1.00195000
H	2.04230500	1.02821100	-1.73510000
H	1.13840100	1.24615600	-0.23796300
H	3.93124100	-0.00296700	-0.50761800
H	3.07288600	0.14438500	1.01255900
H	3.91745200	2.50449000	-0.76019000
H	3.05717100	2.64986900	0.77552800
H	4.70124700	2.01572600	0.74010500

TS5(Thiolation, Thiol mediation) (Electronic energy: -1420.978422 Ha):

C	1.96468400	0.48430800	1.52047300
C	2.37073900	-0.57406000	2.47135700
O	0.71619600	0.45133900	1.05720000
C	2.64005000	1.56883300	1.00873000
C	0.54173100	1.50821200	0.17133000
C	1.72613400	2.25133900	0.20264500
H	2.01681700	-1.55041200	2.14104200
H	3.45276400	-0.59302800	2.57654900
H	1.92979200	-0.37320900	3.45023300
H	3.66743300	1.82415500	1.20594300
H	1.90806200	3.14400200	-0.37612500
H	0.96827600	0.86109200	-1.01502500
C	-0.88301700	1.96390600	-0.07064000
C	-0.86450000	3.06937800	-1.12787000
H	-0.30346500	3.93294400	-0.76782700
H	-0.42121900	2.73167400	-2.06769200
H	-1.88422700	3.39020500	-1.33358200
C	-1.47598200	2.48801900	1.23811200

H	-1.45687700	1.73034600	2.02033500
H	-0.90123900	3.35013800	1.58307200
H	-2.50843700	2.79753600	1.07591200
H	0.10352600	0.04686900	-2.80980300
S	-1.92452100	0.62896500	-0.78947800
C	-2.33145100	-0.46022600	0.61049900
H	-2.97901700	0.08003800	1.30119800
H	-1.42241400	-0.75126400	1.13835900
C	-3.05441500	-1.68956400	0.07011500
H	-3.93303800	-1.37243800	-0.49601700
H	-2.40339600	-2.21681300	-0.63298200
C	-3.47052300	-2.62514900	1.19954100
H	-4.14621200	-2.12344600	1.89325800
H	-3.98483300	-3.50155900	0.80781800
H	-2.60288600	-2.96965200	1.76532200
C	0.79269000	-1.75220700	-1.37336700
H	0.34451300	-2.41068500	-2.11681600
H	0.03366000	-1.47212000	-0.64305400
C	2.00651300	-2.39619100	-0.72142900
H	2.53045000	-1.65561100	-0.10999400
H	2.71104800	-2.71624700	-1.49103600
C	1.58163800	-3.58536600	0.13319200
H	1.10876900	-4.35516700	-0.47755300
H	2.44164500	-4.03534300	0.62744600
H	0.86422300	-3.28455200	0.90021500
S	1.29145700	-0.23056200	-2.24820600

TS5(Thiolation, water mediation) (Electronic energy: -980.1019165 Ha):

C	2.19099300	1.61708700	-0.11359500
C	2.16795700	3.09313500	-0.18531100
O	1.02928100	0.98020900	-0.16978100
C	3.23003300	0.72408500	0.04228900
C	1.25678800	-0.38621500	-0.01257000
C	2.64945900	-0.54267900	0.06019100
H	3.18085100	3.48645500	-0.17955500
H	1.66038200	3.41307400	-1.09604300
H	1.61974000	3.50418200	0.66397900
H	4.27221900	0.97639100	0.14017400
H	3.15389700	-1.48992700	0.18040100
H	1.12538300	-0.58831200	1.33108900

C	0.21139900	-1.31456200	-0.61143600
C	0.65385600	-2.76071000	-0.37604400
H	1.58197300	-2.96304300	-0.91233500
H	0.80557600	-2.97676300	0.68377000
H	-0.10912700	-3.43883100	-0.75450400
C	0.06768000	-1.03141600	-2.10652300
H	-0.21141700	0.00353600	-2.29734100
H	1.01844900	-1.22693900	-2.60693300
H	-0.69205100	-1.68515700	-2.53475900
O	0.61323700	-0.87929600	2.47794800
H	0.71618400	-0.24114800	3.19597700
H	-0.33598000	-0.94586700	2.21845700
S	-1.41979300	-1.17716700	0.24618300
C	-2.14210900	0.39242200	-0.32593300
H	-2.31059200	0.31566200	-1.40003000
H	-1.45634300	1.21570900	-0.13154900
C	-3.46899000	0.60677900	0.39551700
H	-4.11627700	-0.25641000	0.22619300
H	-3.29562100	0.66531100	1.47275600
C	-4.15569100	1.87764100	-0.09233200
H	-4.36691500	1.82208200	-1.16092300
H	-5.10052300	2.02886800	0.42743800
H	-3.53152800	2.75509100	0.08396200

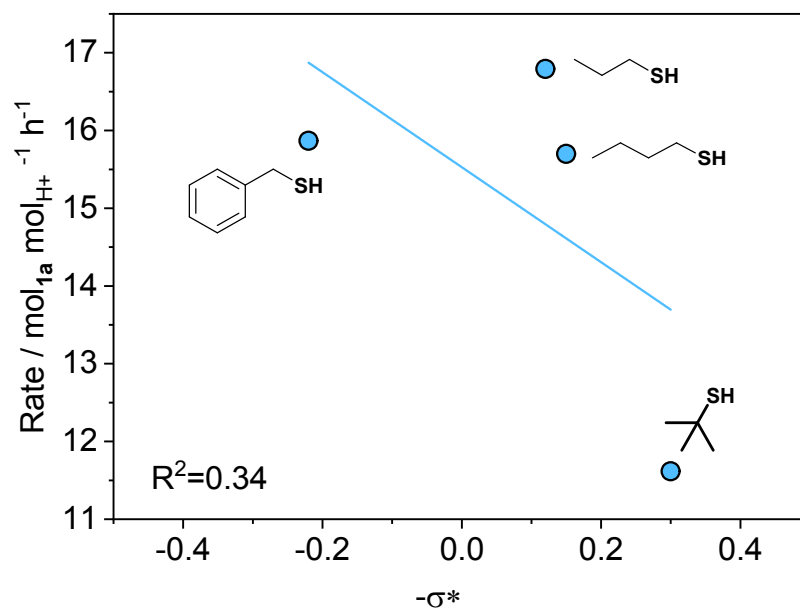


Figure S4. Formation rate of **1a** vs. electronic parameters. Reaction conditions: 4 mmol 2-PF, 2 mmol 2-undecanone, 0.05 g Aquivion PW79S (0.063 mmol H⁺), SH/H⁺=1 (molar ratio), 65 °C. The rates are calculated at low conversion of 2-pentylfuran <32%.

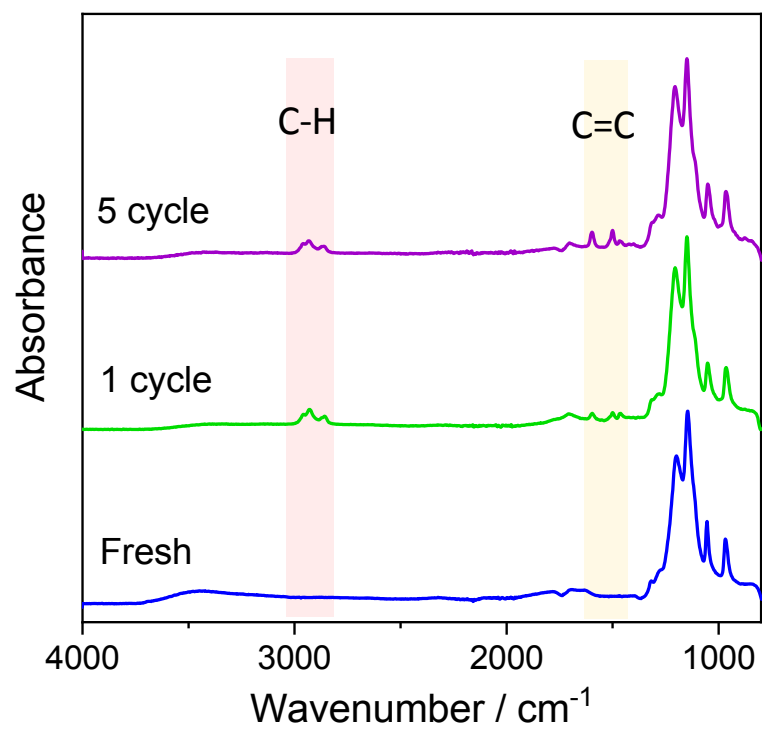


Figure S5. ATR-IR spectra of fresh and used Aquivion PW79S catalysts.

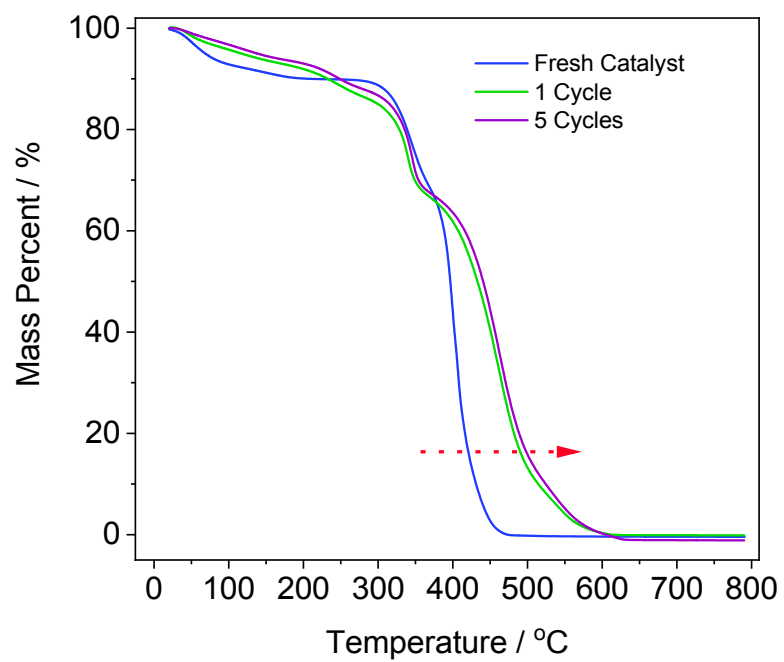
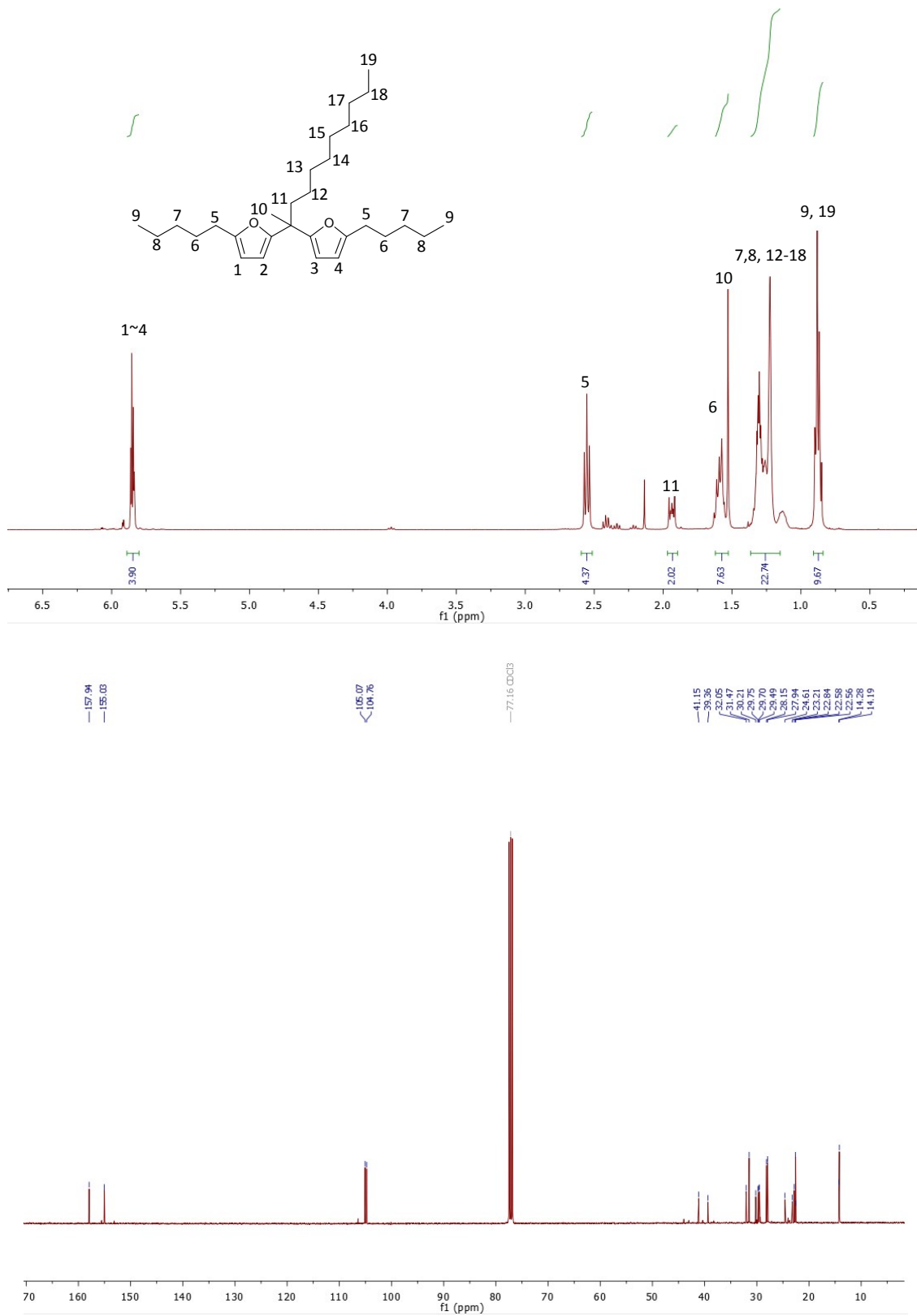
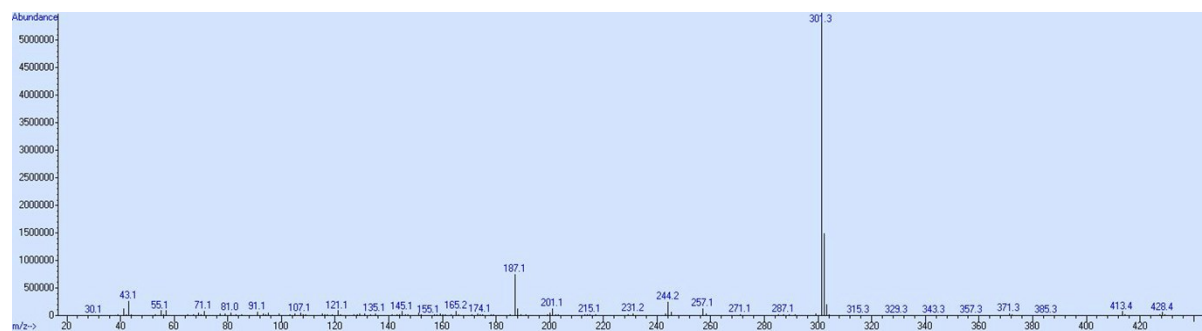


Figure S6. TGA of fresh and used Aquivion PW79S catalysts.

Identification of the synthesized compounds
C₂₉-FL1: HAA of 2-propylfuran + 2-undecanone
¹H and ¹³C-NMR Spectroscopy



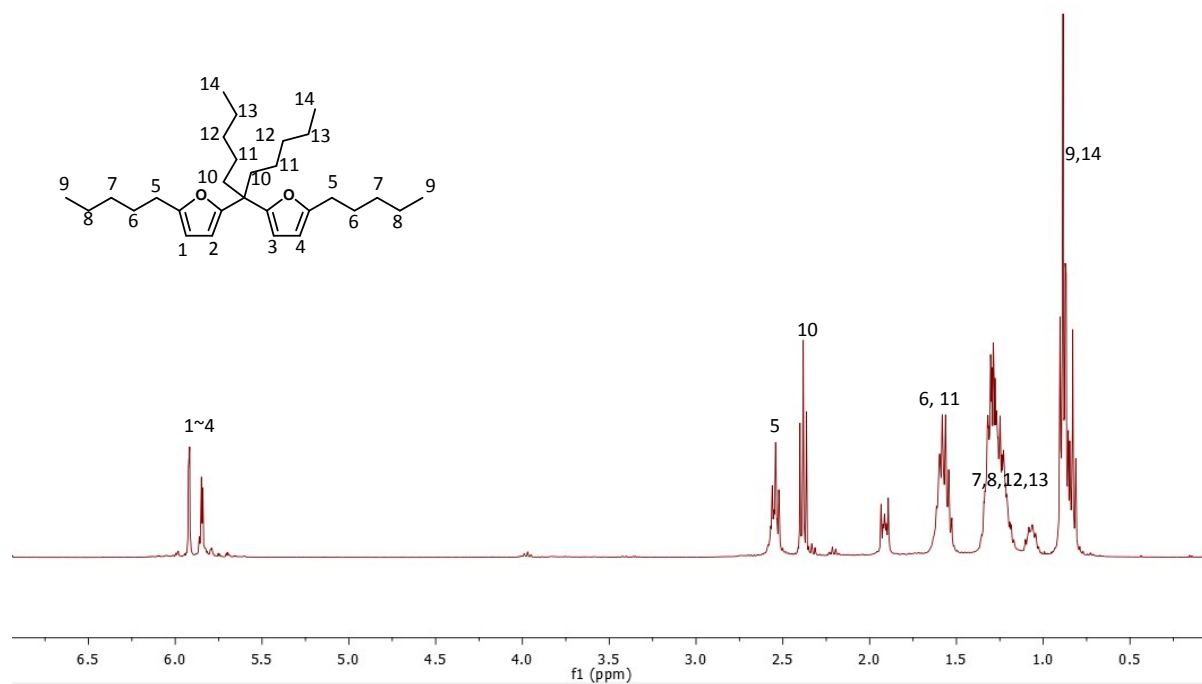
GC-MS (MS spectrum)



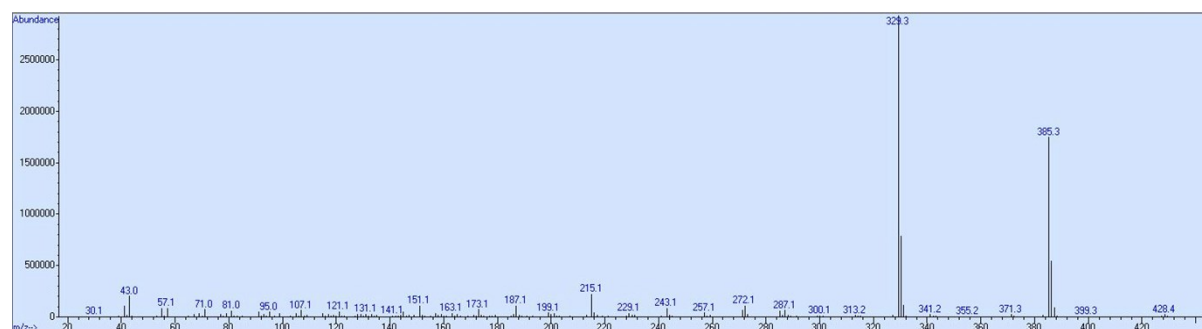
HR-MS-LIFDI: C₂₉H₄₈O₂ Calc. Mass 428.3654, found Mass 428.3669

C₂₉-FL2: HAA of 2-propylfuran + 4-undecanone

¹H and ¹³C-NMR Spectroscopy



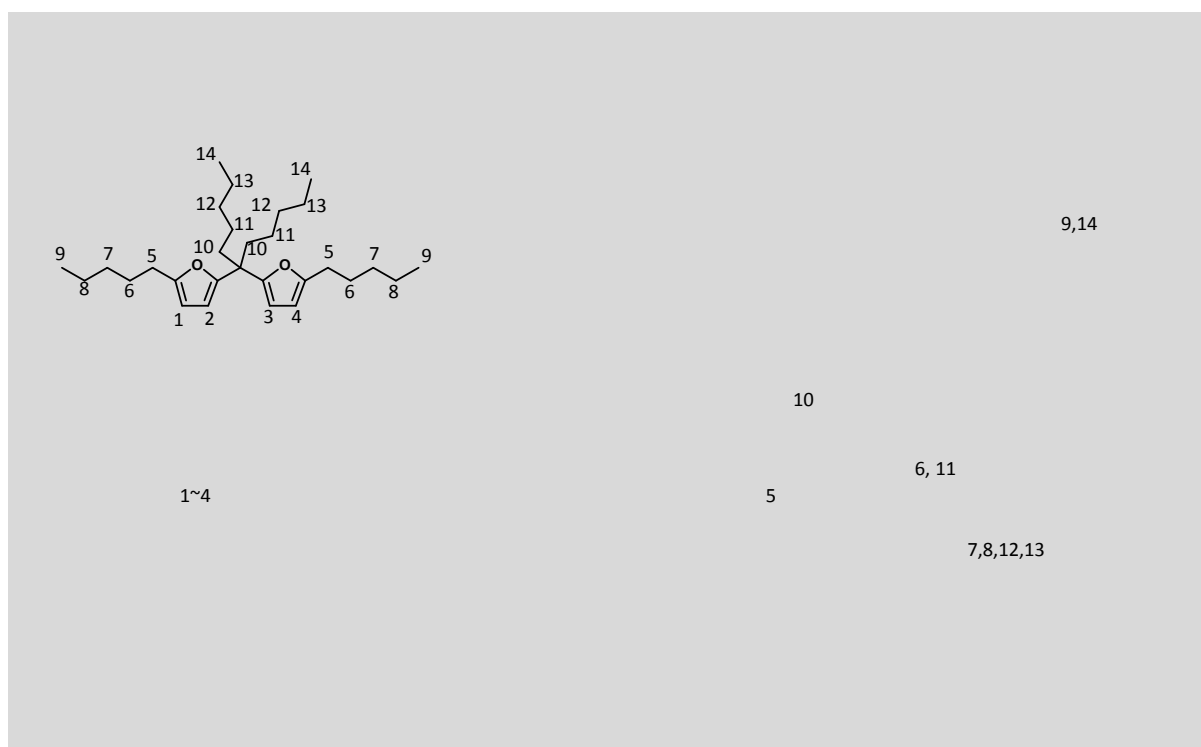
GC-MS (MS spectrum)



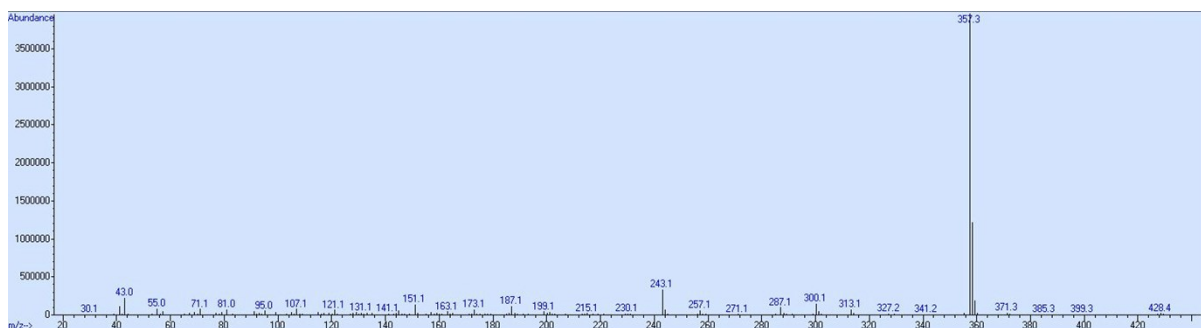
HR-MS-LIFDI: C₂₉H₄₈O₂ Calc. Mass 428.3654, found Mass 428.3652

C₂₉-FL3: HAA of 2-propylfuran + 6-undecanone

¹H and ¹³C-NMR Spectroscopy



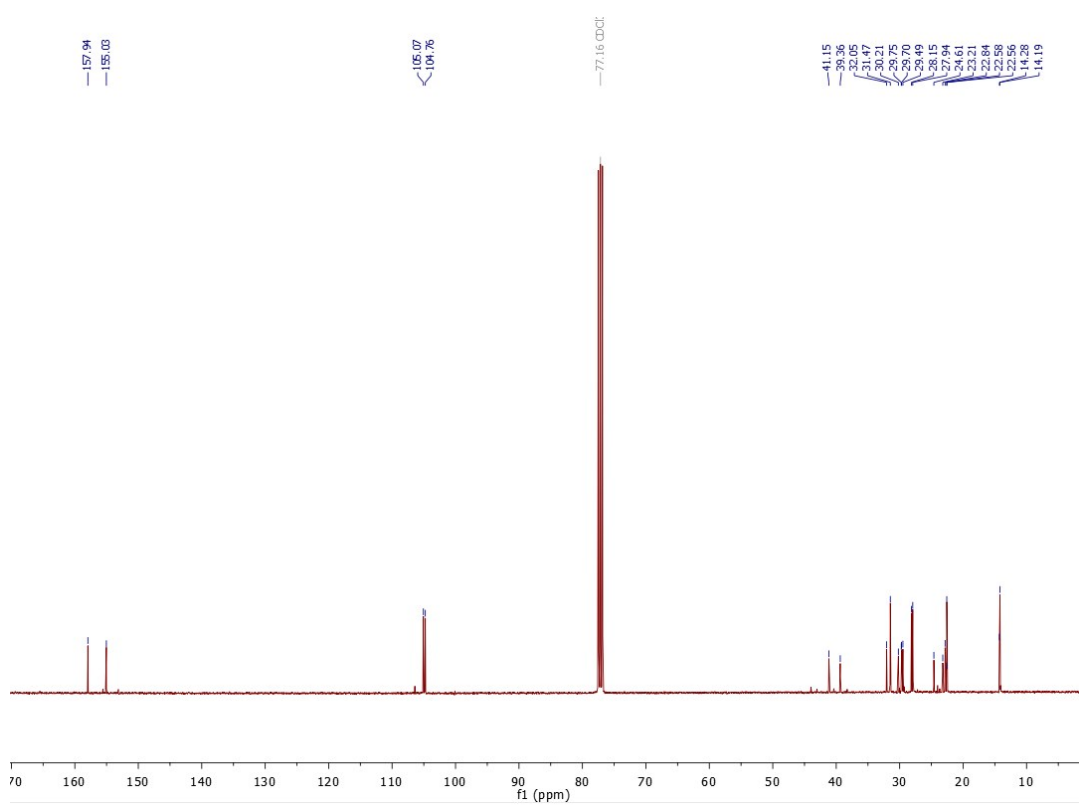
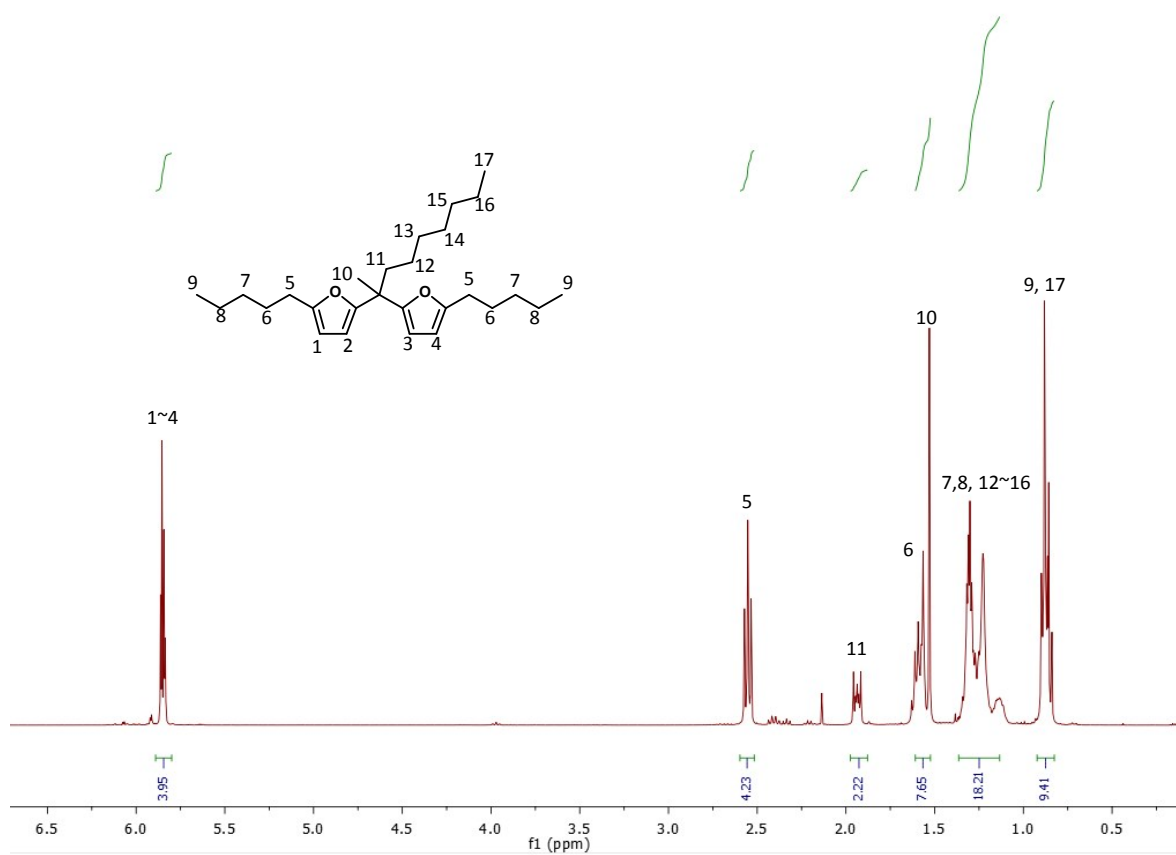
GC-MS (MS spectrum)



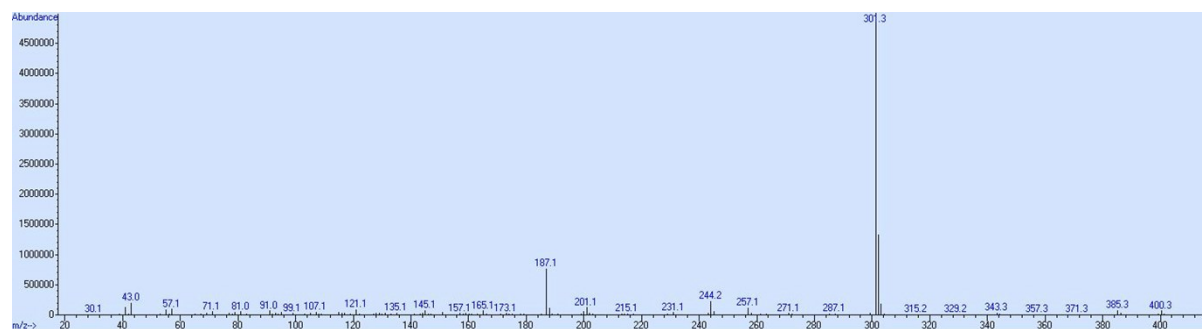
HR-MS-LIFDI: C₂₉H₄₈O₂ Calc. Mass 428.3654, found Mass 428.3656

C₂₇-FL1: CA-HAA of 2-pentylfuran + 2-nonanone

¹H and ¹³C-NMR Spectroscopy



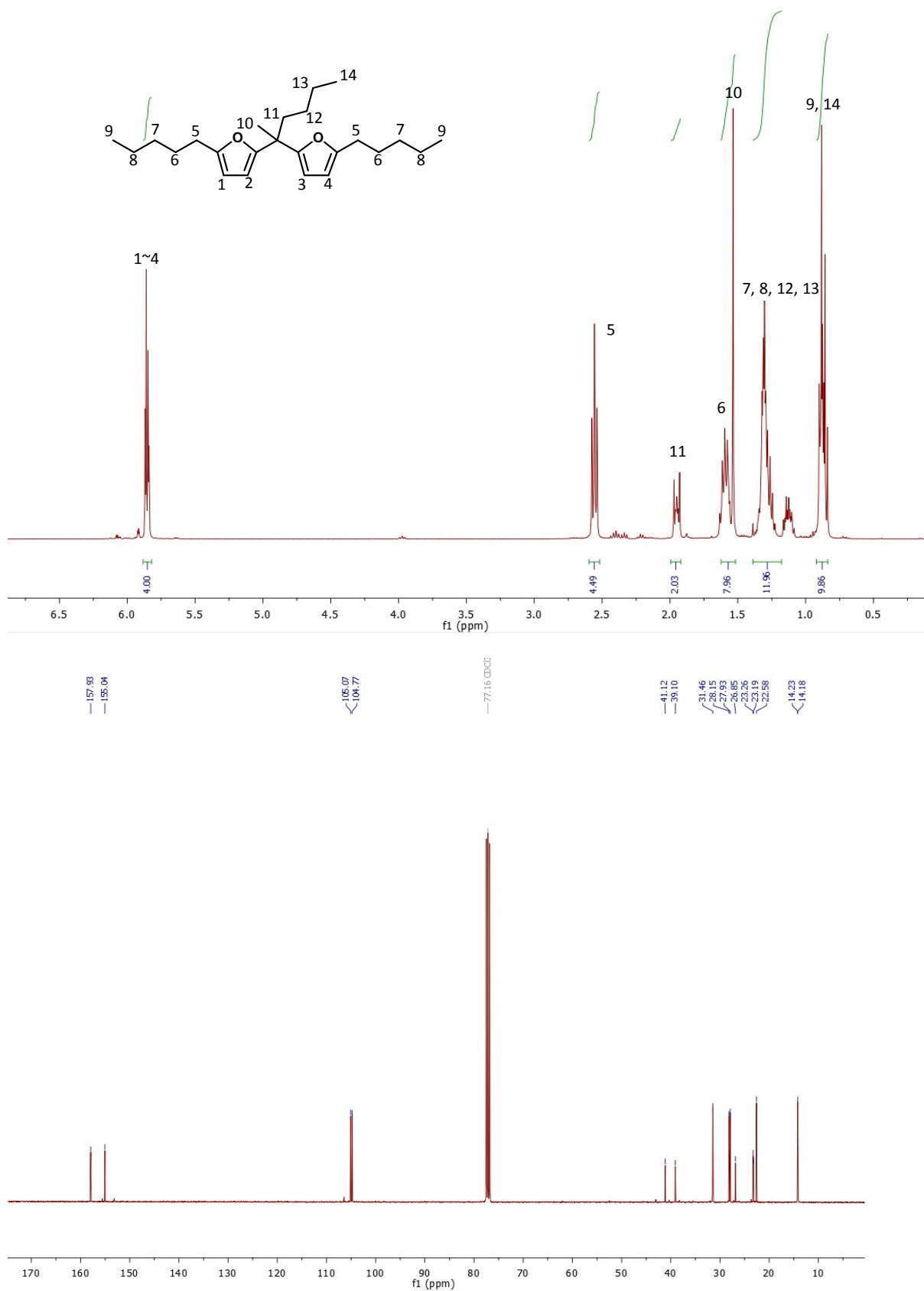
GC-MS (MS spectrum)



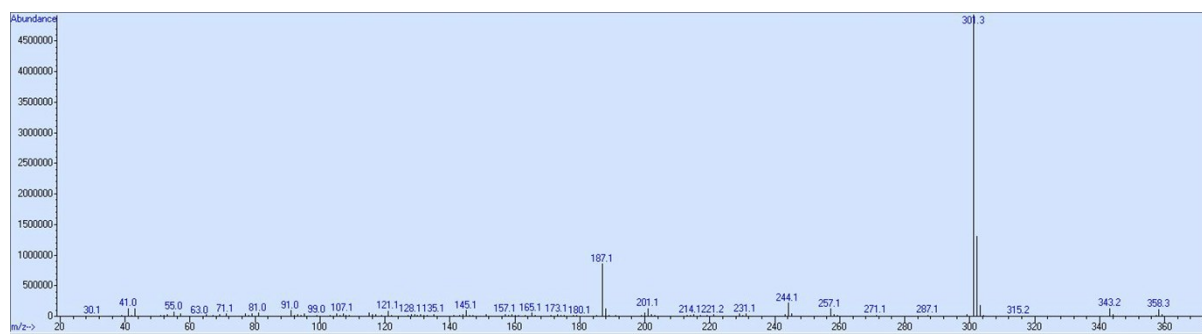
HR-MS-LIFDI: $C_{27}H_{44}O_2$ Calc. Mass 400.3341, found Mass 400.3346

C₂₄-FL: HAA of 2-pentylfuran + 2-hexanone

¹H and ¹³C-NMR Spectroscopy



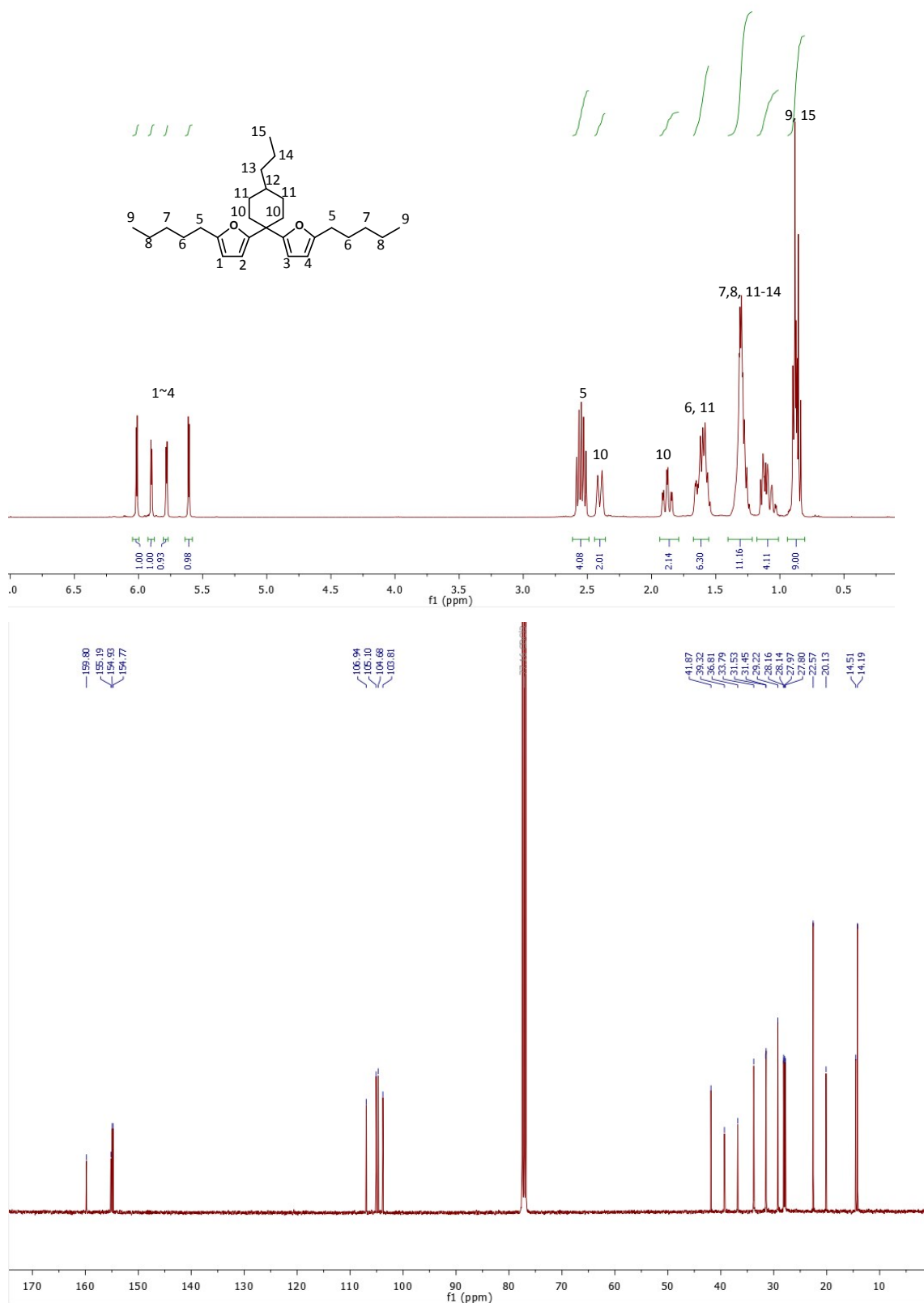
GC-MS (MS spectrum)



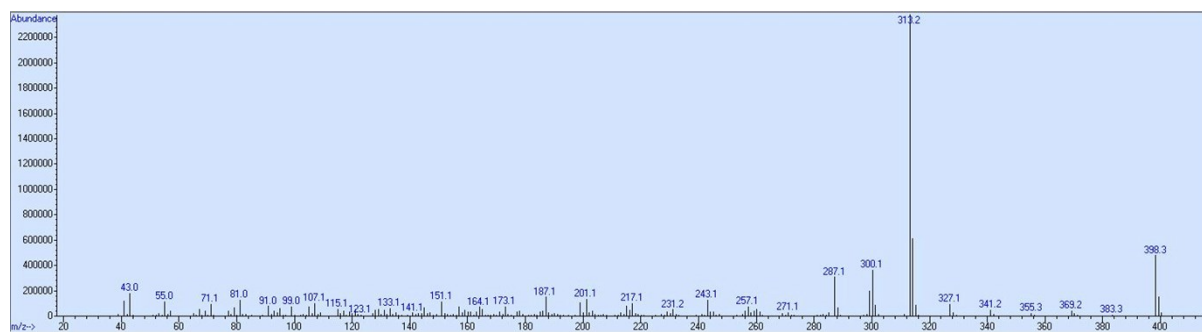
HR-MS-LIFDI: $C_{24}H_{38}O_2$ Calc. Mass 358.2872, found Mass 358.2889

C₂₇-FL2: HAA of 2-pentylfuran + 4-propylcyclohexanone

¹H and ¹³C-NMR Spectroscopy



GC-MS (MS spectrum)



HR-MS-LIFDI: $C_{27}H_{42}O_2$ Calc. Mass 398.3185, found Mass 398.3191