Electronic Supporting Information for:

Calix[4]arene with Acylguanidine Units as an Efficient Catalyst for the Phosphodiester Bond Cleavage in RNA and DNA Model Compounds

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S.1 Potentiometric titrations

The potentiometric titrations of compounds **2**·2HCl and **3**·HCl were carried out as described in the Experimental Section. The titration plot of **2**·2HCl is reported in the main text.

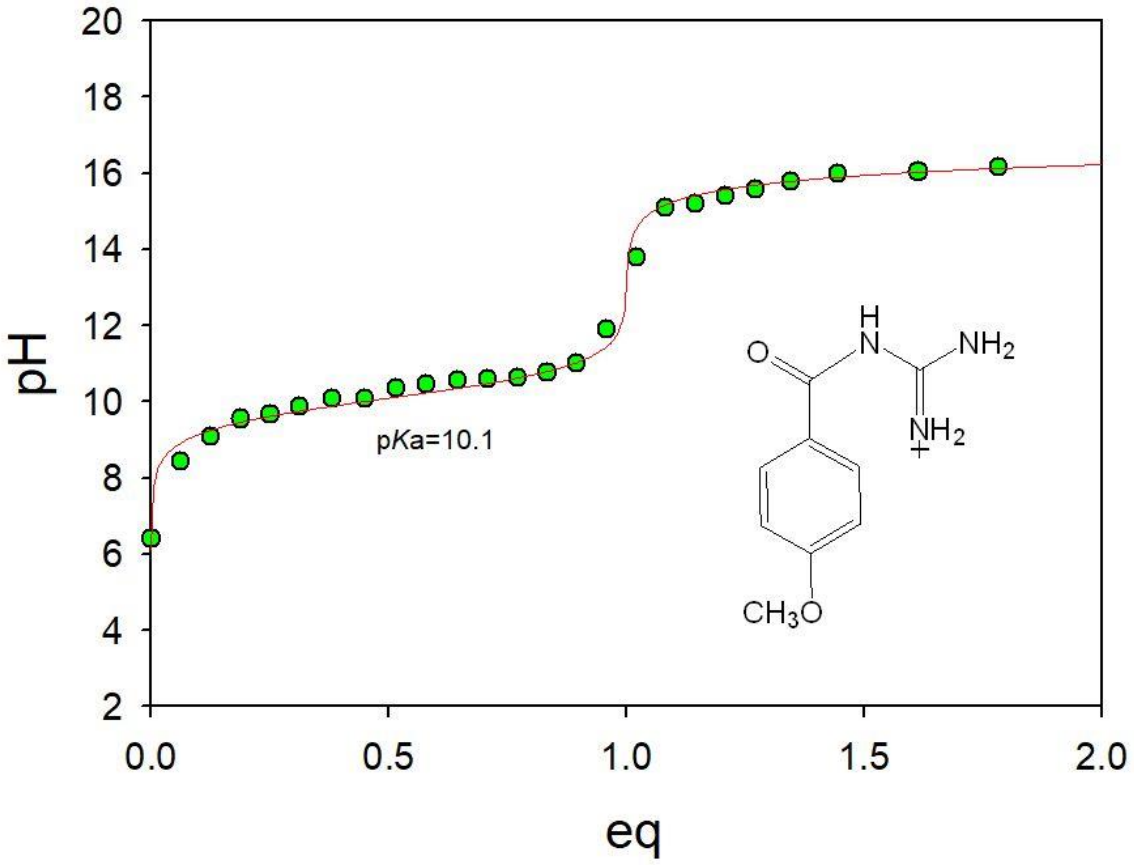
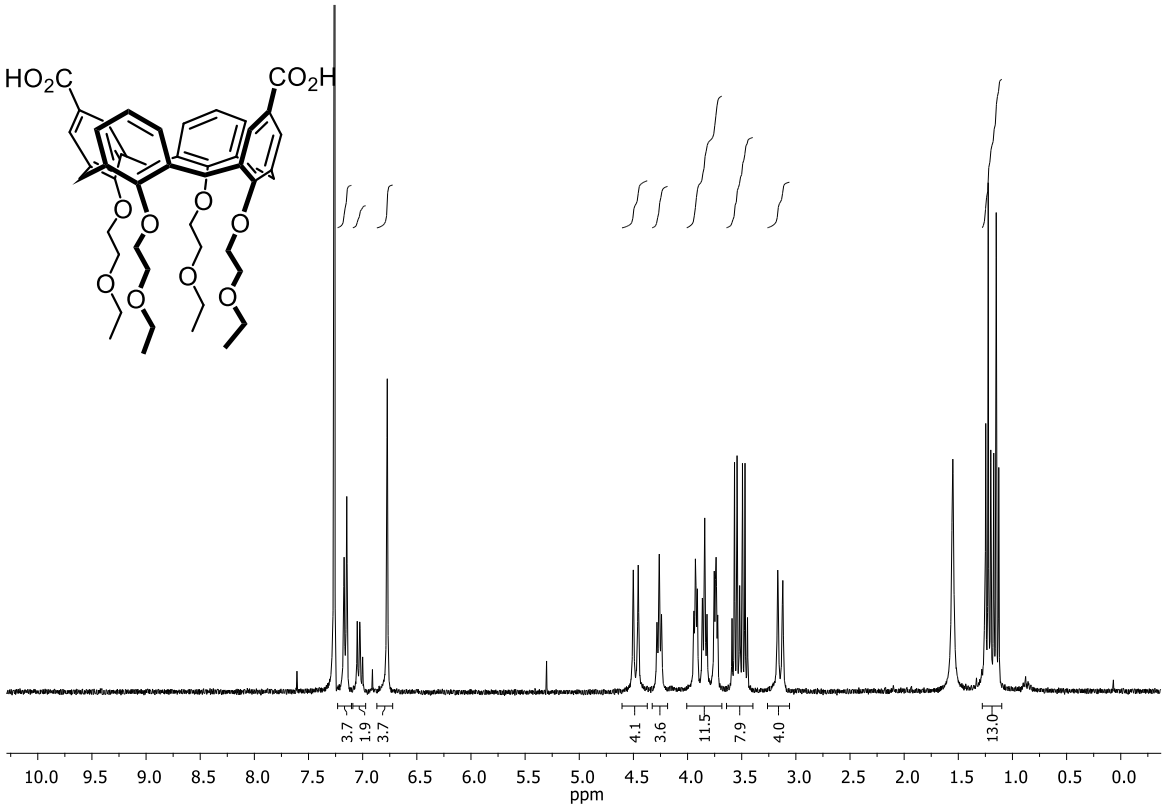


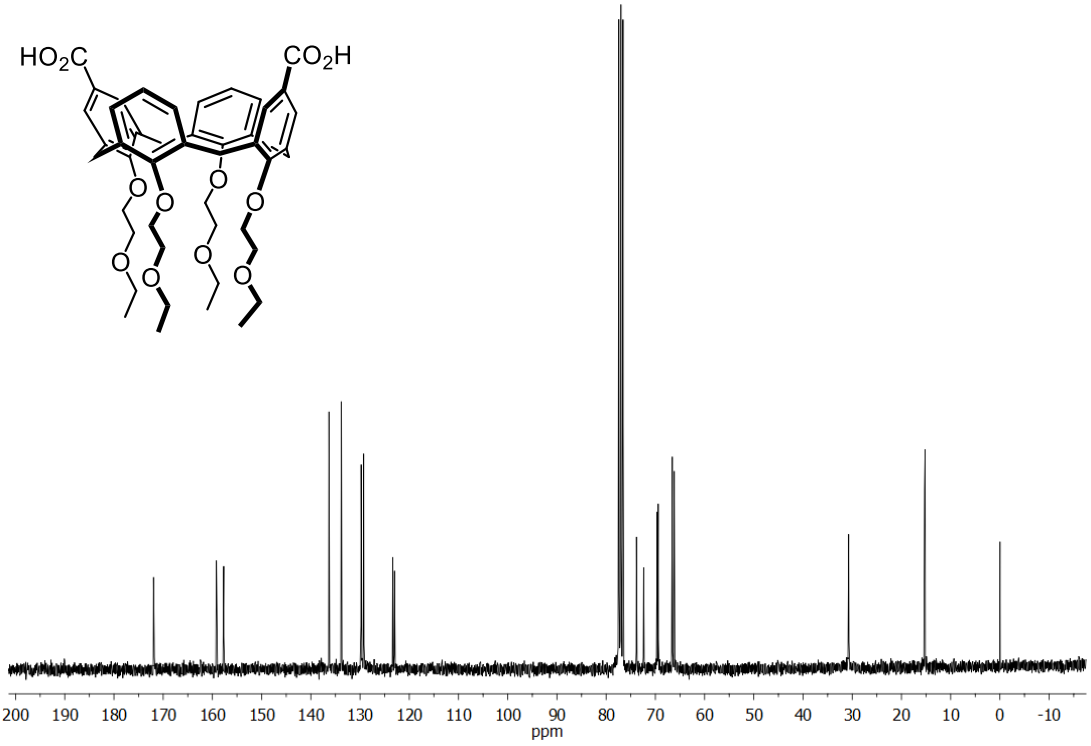
Fig. 1S Titration plot pf a 1.0 mM solution of **3**·HCl with Me_4NOH in 80% DMSO at 25 °C. The ionic strength was buffered with 10 mM of Me_4NClO_4. The acidity constant value determined by a non-linear least-square fitting procedure (see Experimental Section) is reported in the plot.

S.2 ^{1}H NMR and ^{13}C NMR of compounds 2-7

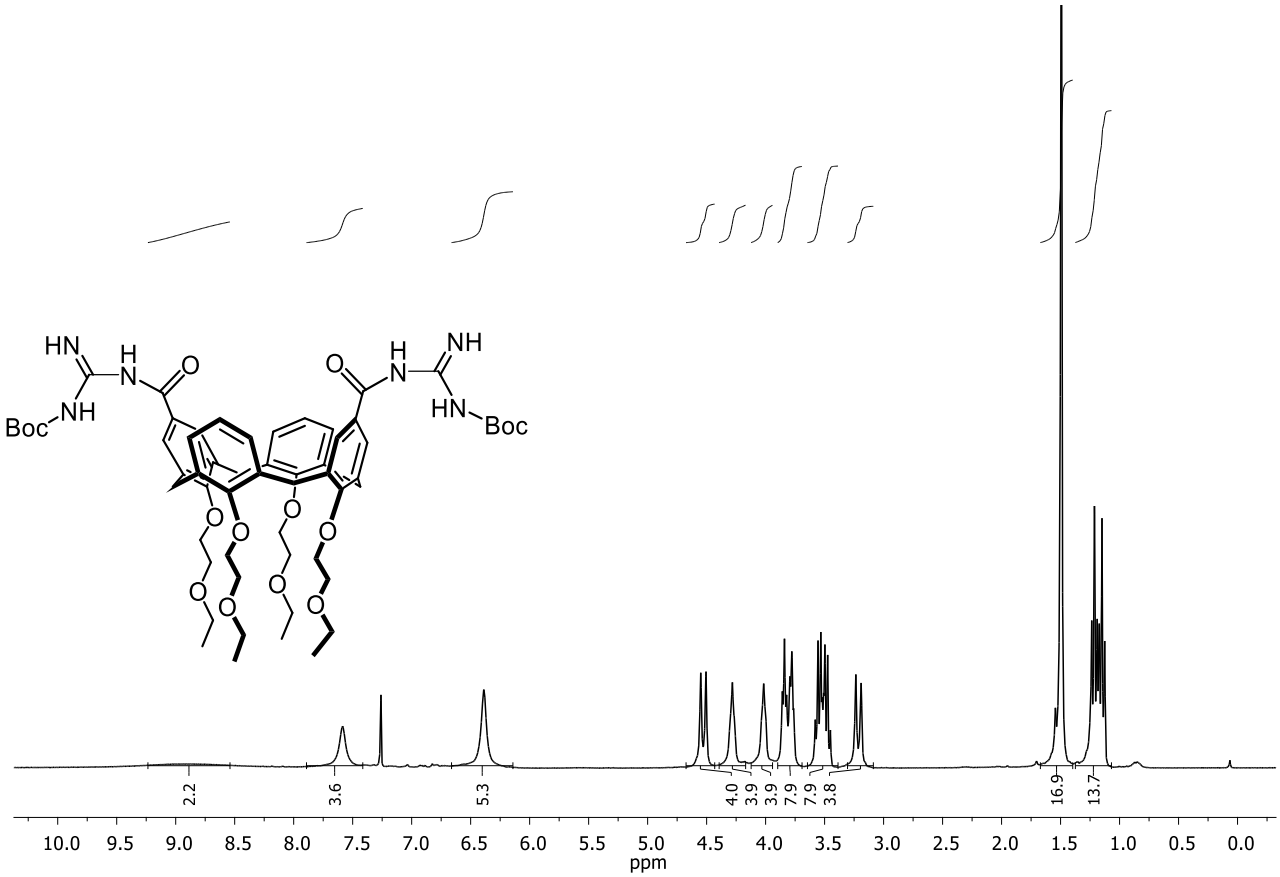
^{1}H NMR of **5** (300 MHz, $CDCl_3$)



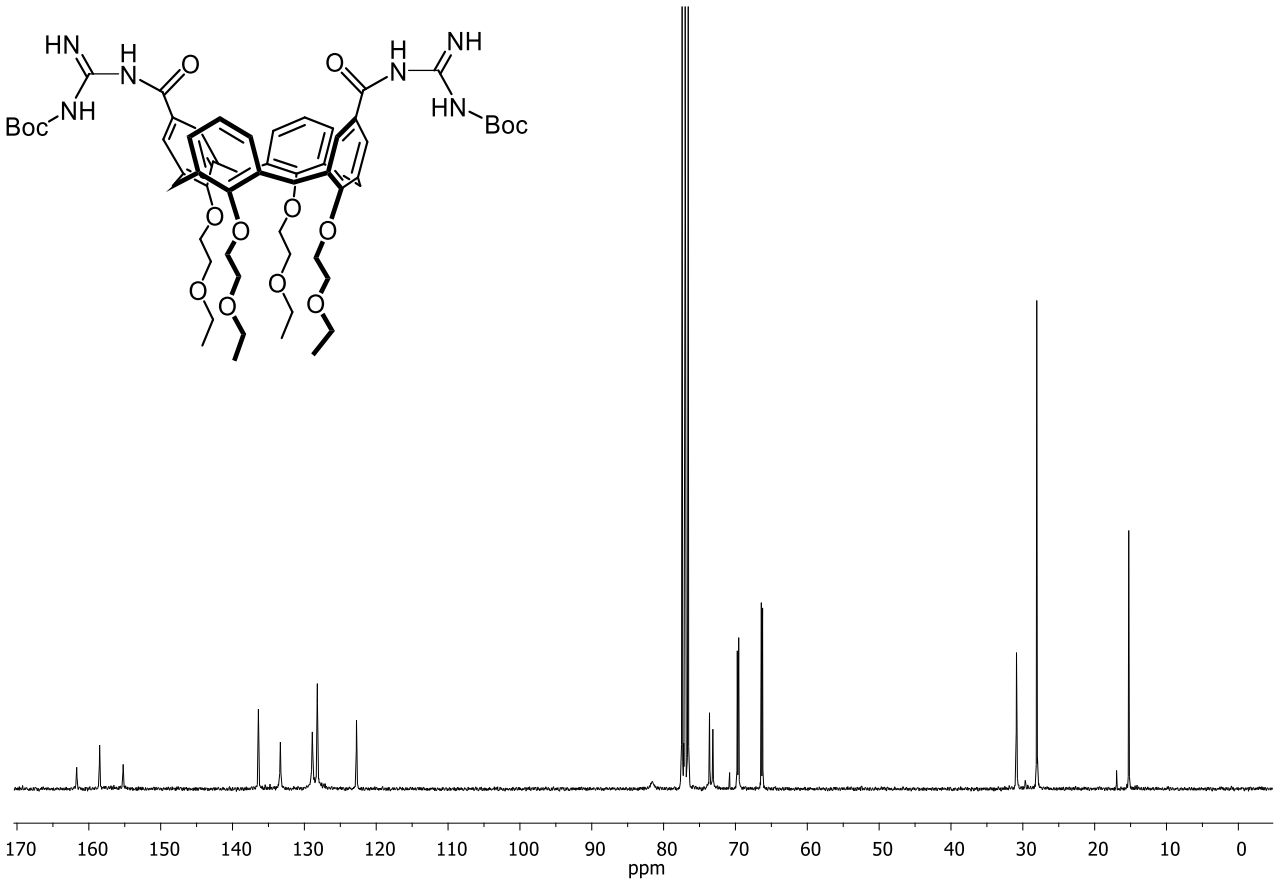
^{13}C NMR of **5** (75 MHz, $CDCl_3$)



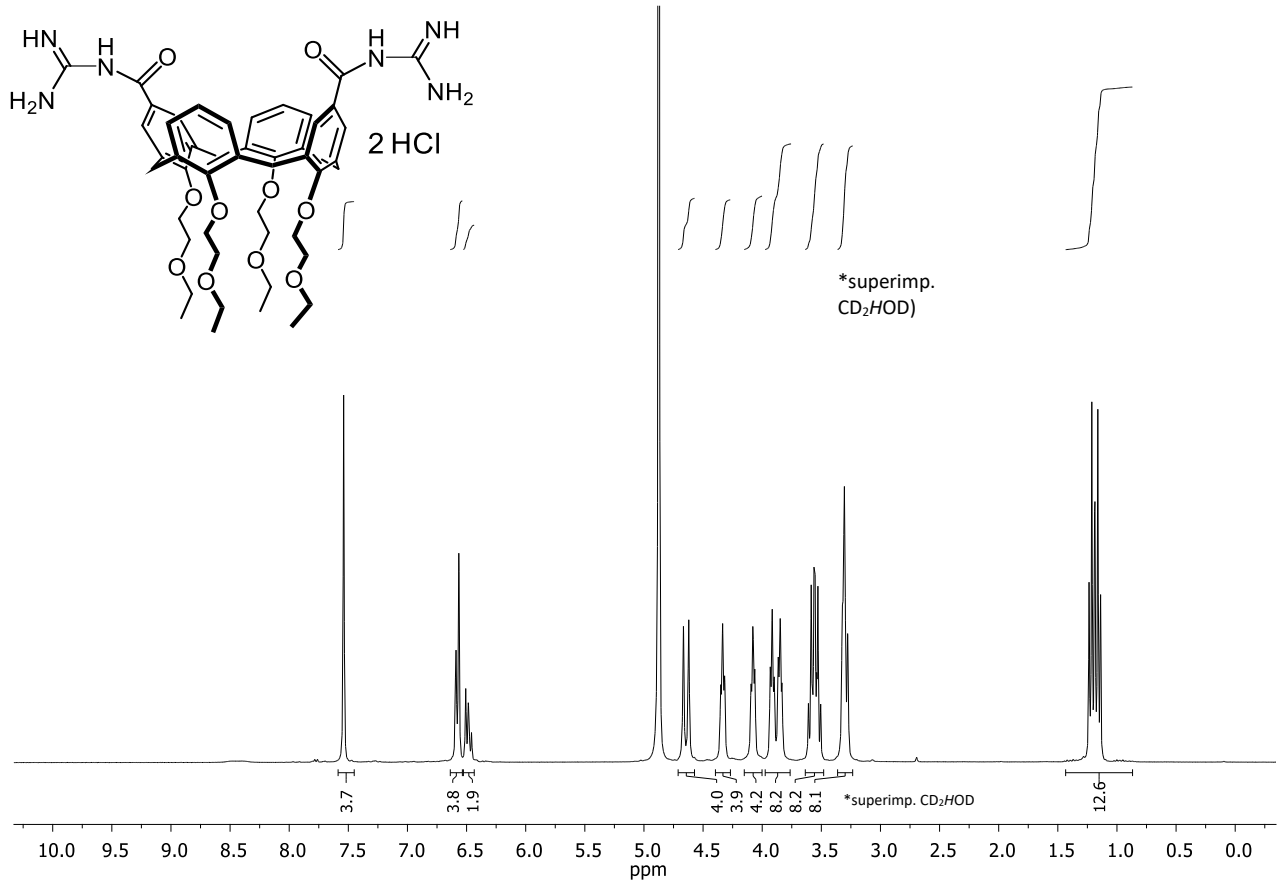
^{1}H NMR of **6** (300 MHz, $CDCl_3$)



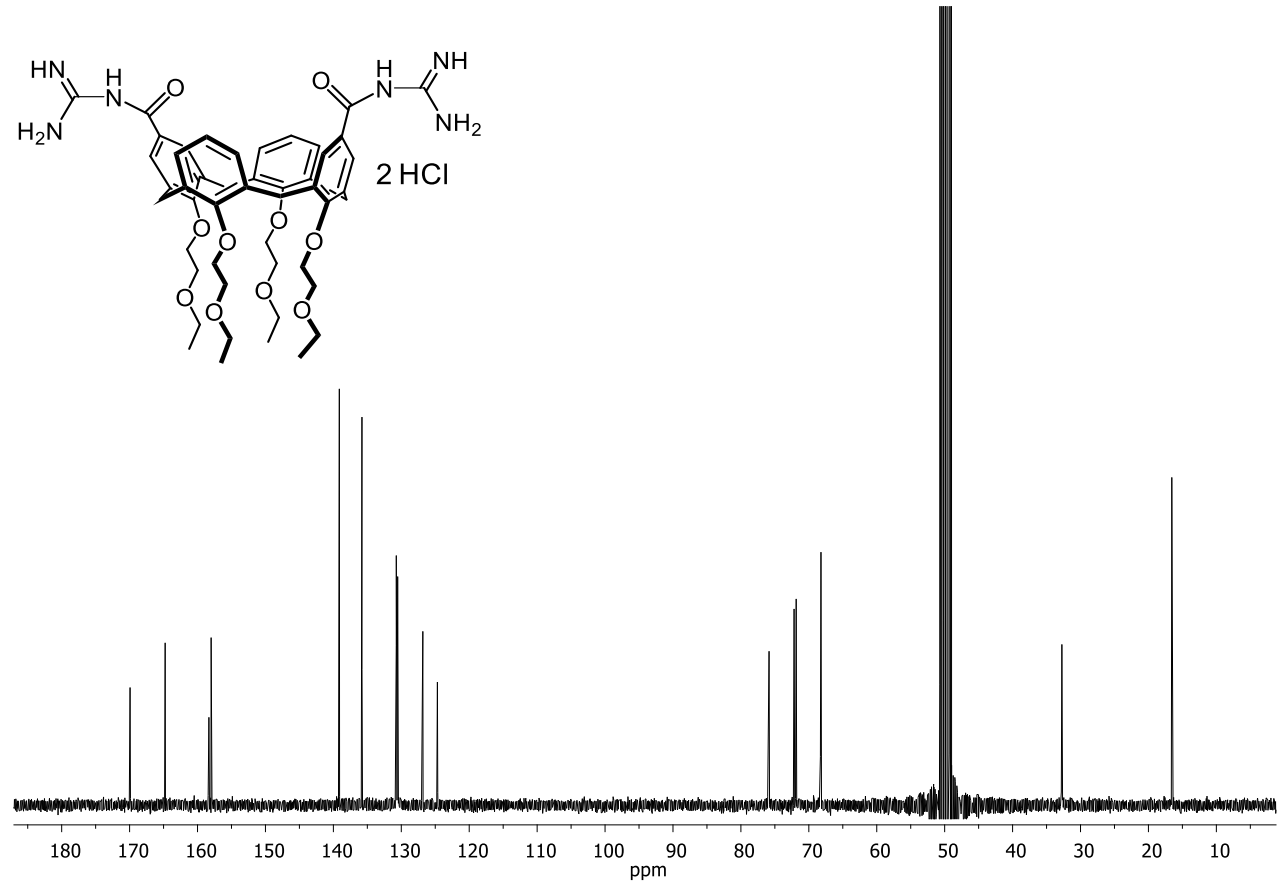
^{13}C NMR of **6** (75 MHz, $CDCL_3$)



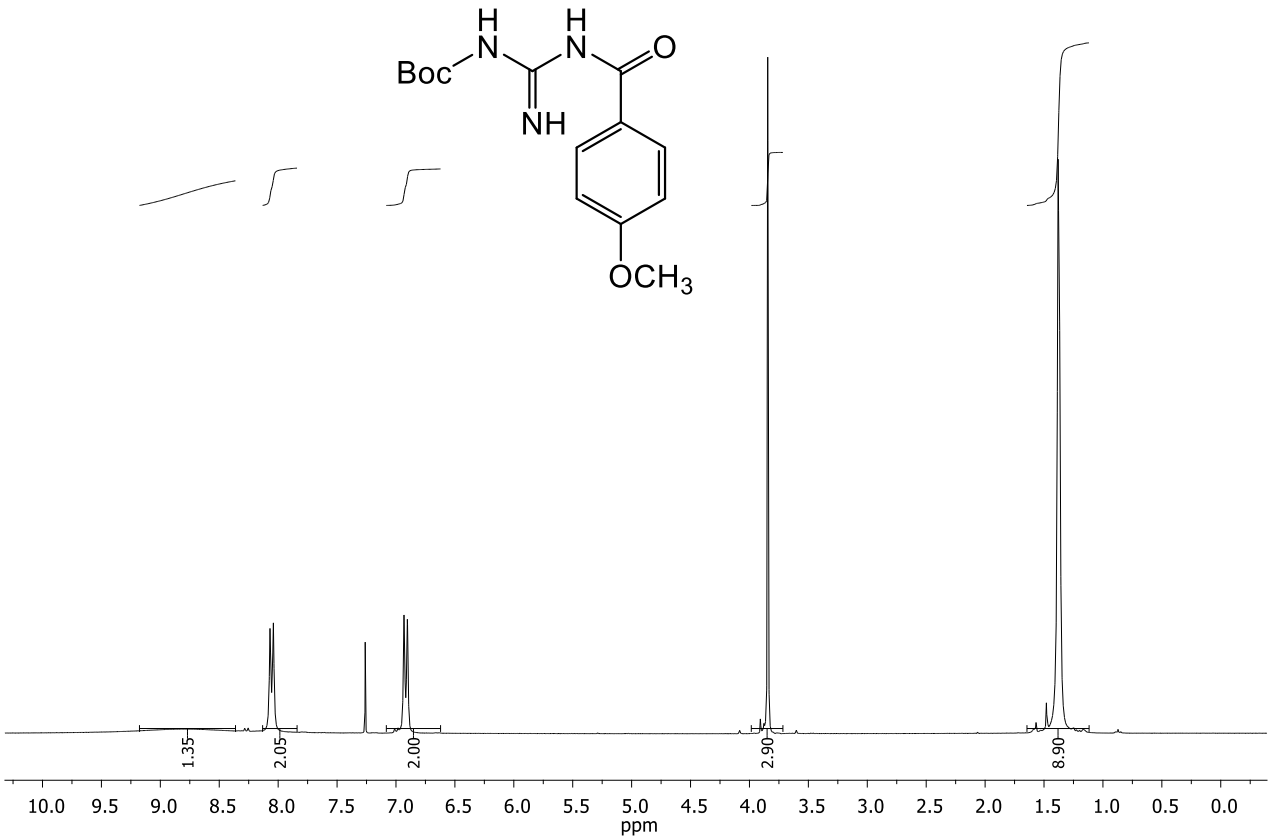
^{1}H NMR of **2**·2HCl (300 MHz, CD_3OD)



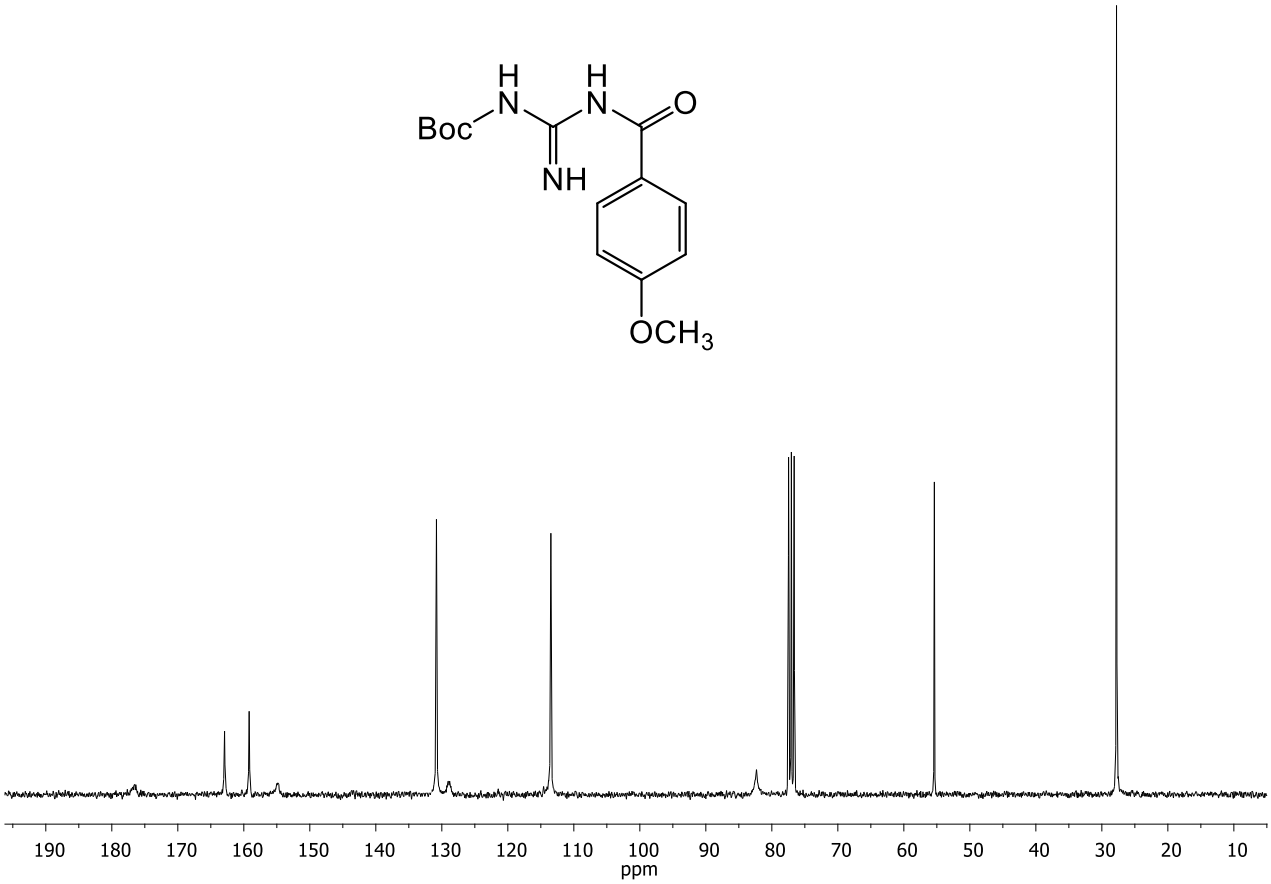
^{13}C NMR of **2**·2HCl (75 MHz, CD_3OD)



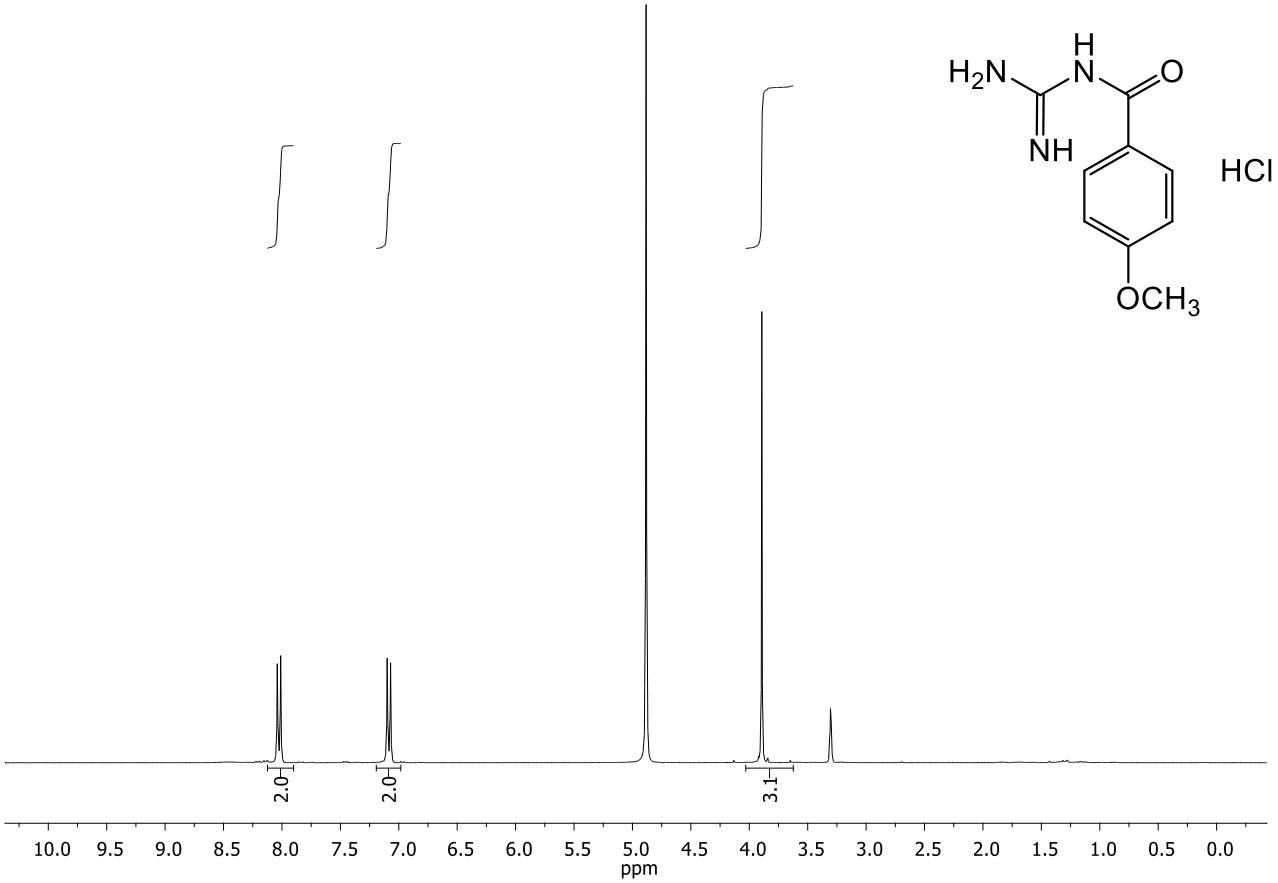
^{1}H NMR of **7** (300 MHz, CD_3Cl)



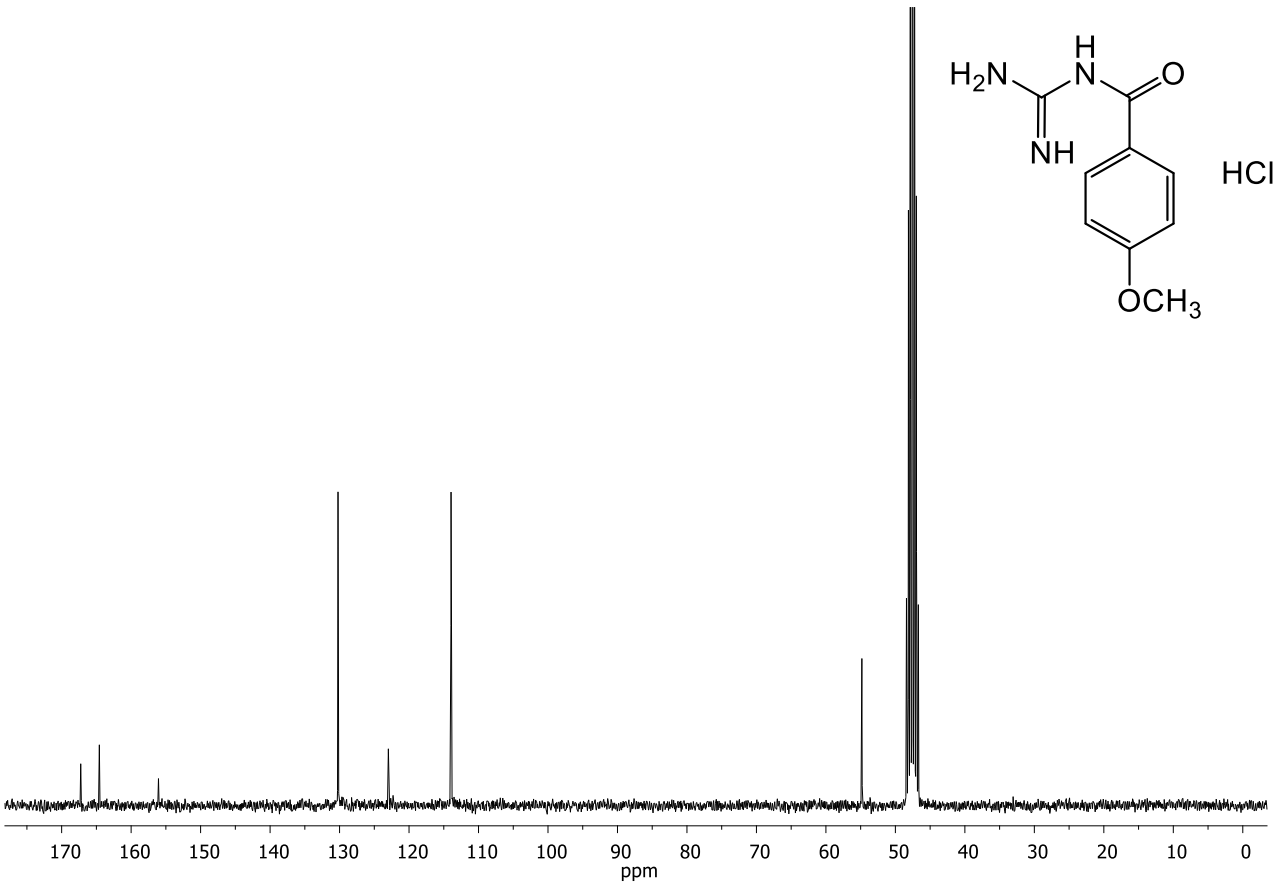
^{13}C NMR of **7**(75 MHz, CD_3Cl)



^{1}H NMR of **3**·HCl (300 MHz, CD_3OD)

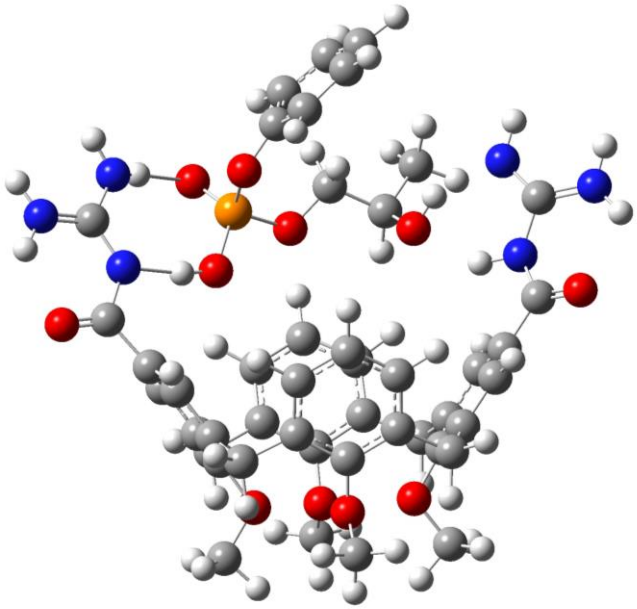


^{13}C NMR of **3**·HCl (75 MHz, CD_3OD)



S.3 Coordinates and energies of DFT calculations

S.3.1 Initial structure for the complex **2**H^+-HPNP obtained by MM, as described in the Experimental Section, and used as initial structure for the TS search.



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C	-0.38560000	-1.49150000	4.12450000
C	-1.65980000	-0.98110000	4.33410000
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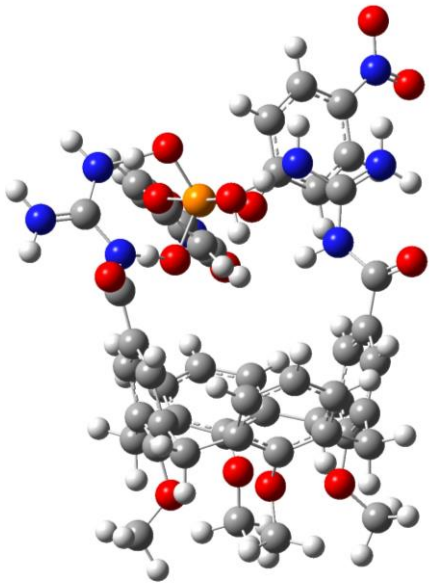
C	-6.88600000	-0.89950000	0.43320000
O	-8.03950000	-1.05390000	0.74890000

S.3.2 Initial structure for the complex **2**H^+-BNPP obtained by MM, as described in the Experimental Section, and used as initial structure for the TS search.



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C	1.48980000	2.08460000	-3.28630000
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C	2.26690000	4.28740000	-3.99360000
C	1.00540000	4.81330000	-3.65280000
C	-0.00260000	3.98830000	-3.12360000
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H	0.81190000	5.83930000	-3.77360000
N	3.29930000	5.13420000	-4.47950000
H	3.41720000	2.48140000	-4.07840000
O	4.34910000	4.70110000	-4.78840000
O	3.15760000	6.46440000	-4.47530000
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O	-0.61410000	1.76910000	-2.29840000
O	-2.89700000	1.79870000	-3.41600000
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C	-1.26180000	0.36150000	-4.53630000
C	-0.62620000	-0.00600000	-5.73200000
C	-1.08710000	0.48350000	-6.96680000
C	-2.18640000	1.36290000	-6.97780000
C	-2.78360000	1.77460000	-5.77510000
H	-0.92710000	-0.06500000	-3.63800000
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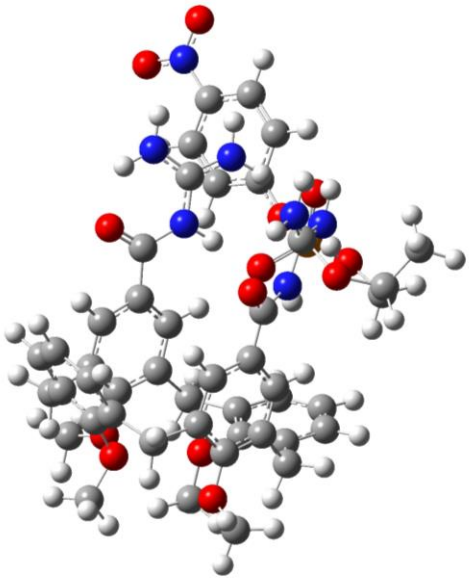
O	0.52960000	-0.81410000	-8.17320000
O	-0.81460000	0.62610000	-9.34630000
O	-2.94430000	0.46650000	-1.42210000
H	-1.72780000	1.48060000	0.28910000
H	-0.99270000	2.82760000	-0.06120000

S.3.3 Transition State Structure of the complex **2**H^+-HPNP determined by DFT calculations



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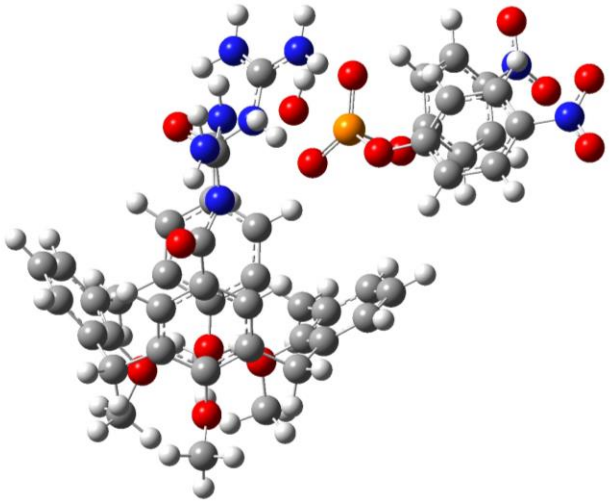
C	-6.14267000	8.37476200	-1.92995200
C	-5.36847300	8.60042200	-3.08635700
C	-4.60826000	7.58310700	-3.62403500
H	-5.40662900	5.09515800	-1.41250700
H	-6.75159800	6.94576400	-0.43343300
H	-5.38662500	9.58404600	-3.54180400
H	-4.00610600	7.75366700	-4.50885800
N	-6.91478600	9.43144900	-1.37138600
O	-6.90838200	10.54920200	-1.92707400
O	-7.57960100	9.21602000	-0.33651700
H	0.54801900	5.50713900	-4.55363300
P	-2.02851000	4.99965300	-4.04924300
O	-2.70532500	4.05967100	-5.20451300
C	-1.84909600	3.25904000	-6.03598200
C	-0.44032300	3.85431000	-6.03335900
C	-0.23137900	4.91132200	-7.11878900
O	-0.28144800	4.37927900	-4.68623500
H	-1.85474200	2.24009700	-5.64340600
H	-2.29032300	3.25648700	-7.03719800
H	-0.98161500	5.70600000	-7.05055400
H	0.76205200	5.36002000	-7.02900100
H	-0.30790100	4.44478100	-8.10807100
H	0.28583200	3.04459300	-6.16011100
C	2.79419000	3.90617000	4.14501000

C	2.31931300	2.69015700	3.63508100
C	3.18642700	1.93112000	2.83126200
C	4.44214100	2.41501000	2.42441500
C	4.87801100	3.63807500	2.94854000
C	4.07323500	4.36576000	3.82751700
C	5.23490700	1.67935800	1.35129400
C	4.57615400	1.84979300	-0.01542300
C	4.45557500	3.12310600	-0.56563400
C	4.01140300	0.76757300	-0.71955600
C	3.24344900	0.96688700	-1.88588400
C	3.12111700	2.26330700	-2.39027100
C	3.74790000	3.34382600	-1.75365600
C	2.52354100	-0.19289400	-2.56596800
C	1.01751900	0.01189800	-2.64844200
C	0.35470200	0.07669700	-3.87860000
C	-1.02036300	0.31292600	-3.93228400
C	-1.73285600	0.57678100	-2.76160100
C	-1.10568800	0.52079300	-1.51000800
C	0.25262600	0.16037700	-1.47698000
C	-1.87721900	0.82589200	-0.22921100
C	-1.26551400	1.93282900	0.62608100
C	-0.66993000	1.63140400	1.86856800
C	0.03202600	2.60627000	2.60339800
C	-0.01778200	3.91943900	2.14880600
C	-0.69381600	4.27498300	0.97182300
C	-1.27525000	3.26278700	0.18965100
C	0.87364400	2.25608300	3.83199200
H	2.15111400	4.49847500	4.79181800
O	2.77186200	0.69574600	2.37232700
H	5.85324500	4.02344400	2.66034200
H	4.43090100	5.30496400	4.24017100
H	6.25165800	2.08685700	1.32089000
H	5.31403500	0.61557900	1.57932500
H	4.89602600	3.97468200	-0.05807800
O	4.17687800	-0.51137700	-0.23711400
H	2.55058100	2.40548400	-3.30494200
C	3.72041500	4.74101600	-2.25484400
H	2.91039200	-0.31999100	-3.58398300
H	2.75700700	-1.11074600	-2.02191000
H	0.91677000	-0.07323800	-4.79706100
H	-1.53441100	0.30229100	-4.88843200
H	-2.79237200	0.81603800	-2.81424800
O	0.86615700	-0.02883800	-0.25677200
H	-2.89832500	1.10752300	-0.51014800
H	-1.95641800	-0.07723200	0.38230200
O	-0.75468800	0.34596200	2.36019500
H	0.47812000	4.70016300	2.71357900

H	-1.75125000	3.49655600	-0.75669800
H	0.46683100	2.76067700	4.71633400
H	0.81056200	1.18157800	4.00763500
C	3.17472800	-0.38375900	3.22162600
C	5.35070500	-1.17589400	-0.72706100
C	-1.81691900	0.16312200	3.30790300
C	0.81270200	-1.39063500	0.18716000
H	2.69327200	-0.31436800	4.20533700
H	4.26252000	-0.39793000	3.36046200
H	5.31943000	-1.28102700	-1.81835500
H	5.35663600	-2.16485800	-0.26490900
H	-1.69627500	0.82446800	4.17442700
H	-0.22347900	-1.73910400	0.26549700
H	1.27486100	-1.41129400	1.17192900
H	6.25988700	-0.63212400	-0.44395800
H	1.36302800	-2.05062000	-0.49411700
H	2.86359200	-1.30544400	2.72770100
H	-2.79329200	0.35405600	2.84552600
H	-1.76400700	-0.87732400	3.63422000
N	2.64592700	5.07865200	-3.07520200
C	2.37333000	6.31655900	-3.64076200
N	1.25252600	6.38757800	-4.33647300
N	3.24992500	7.30959100	-3.44111900
H	3.09182900	8.23358500	-3.81696600
H	4.04290800	7.13342600	-2.82689400
H	1.01587100	7.31515400	-4.68206300
H	1.90388200	4.40066300	-3.21043200
N	-1.13657000	6.21076100	-0.54458300
C	-1.30742500	7.54556900	-0.85148600
N	-1.24943800	8.47339400	0.10410700
N	-1.53769100	7.89699100	-2.10623200
H	-0.92107000	8.17564500	1.01979800
H	-1.27056600	9.45235900	-0.14538600
H	-1.74323800	8.86954900	-2.29491400
H	-1.63609500	7.25347300	-2.92798800
H	-1.34531400	5.53851700	-1.31910500
O	4.58511000	5.56121800	-1.94318700
C	-0.77008200	5.74390300	0.72059600
O	-0.50011500	6.52983500	1.63452400
O	-1.79830600	4.45750100	-2.65303100
O	-1.81230200	6.45767100	-4.41095400

S.3.4 Transition State Structure of the complex **2**H^+-HPNP determined by DFT calculations



C	-2.58216600	-2.24646400	4.93073600
C	-2.53980300	-3.33274700	4.04717900
C	-1.28096600	-3.85669800	3.70160300
C	-0.08233300	-3.27576000	4.15435800
C	-0.16834700	-2.19379600	5.04006200
C	-1.40740700	-1.69116500	5.43998200
C	1.26517600	-3.75145100	3.61860200
C	1.55665800	-3.11917600	2.26057600
C	1.80955400	-1.75007300	2.18519300
C	1.50439400	-3.85260500	1.05741900
C	1.53119500	-3.20963300	-0.19711900
C	1.69376600	-1.81968900	-0.22970000
C	1.88677800	-1.09766900	0.95257400
C	1.40319700	-3.99392100	-1.49860000
C	0.09158800	-3.78156400	-2.24560200
C	0.06538400	-3.16065100	-3.50107000
C	-1.13906300	-2.96560200	-4.17929000
C	-2.34221100	-3.36089500	-3.59200500
C	-2.35930800	-3.97904300	-2.33599100
C	-1.12878100	-4.21207400	-1.69625500
C	-3.67183300	-4.37117500	-1.66740700
C	-3.98717500	-3.55669600	-0.41717400
C	-3.90493300	-4.12681300	0.87091200
C	-4.08210900	-3.34562000	2.03360000
C	-4.51417600	-2.03255900	1.87596100
C	-4.70796900	-1.46862700	0.60589900
C	-4.38794800	-2.22212800	-0.53362900
C	-3.81695100	-3.89595100	3.43222800
H	-3.54563000	-1.83765000	5.22627700
O	-1.21948700	-4.93957400	2.84857600

H	0.74518300	-1.74246000	5.42013400
H	-1.45718000	-0.85920400	6.13712900
H	2.04810300	-3.46602400	4.33024600
H	1.27992100	-4.83716700	3.52608600
H	1.91229700	-1.17146300	3.09879000
O	1.40166300	-5.22628300	1.10800300
H	1.72237300	-1.31046600	-1.19019700
C	2.20466500	0.36275500	0.96688100
H	2.22207200	-3.70144400	-2.16565900
H	1.53681000	-5.05519000	-1.27834000
H	1.00000900	-2.83648400	-3.95289400
H	-1.14238200	-2.49483400	-5.15846700
H	-3.28148300	-3.18480000	-4.11078200
O	-1.12264900	-4.83321000	-0.46753800
H	-4.48009400	-4.23524600	-2.39448300
H	-3.65652100	-5.42997300	-1.40152900
O	-3.64223900	-5.47087000	0.99791000
H	-4.73486000	-1.42930400	2.75062600
H	-4.48879600	-1.79417400	-1.52582300
H	-4.65904400	-3.63213600	4.08175100
H	-3.76656200	-4.98366500	3.38550700
C	-1.21363300	-6.20429600	3.51209300
C	2.65448300	-5.90260000	1.26241800
C	-4.81499300	-6.29206300	1.08397300
C	-1.02363300	-6.25894000	-0.52318200
H	-2.12543600	-6.35079500	4.10487600
H	-0.34431100	-6.30511600	4.17426200
H	3.16190700	-5.60140800	2.18713400
H	3.31863200	-5.70738700	0.41102900
H	-4.45988300	-7.31950300	1.18568500
H	-0.09605000	-6.57237500	-1.01599100
H	-1.87678100	-6.69639300	-1.05491800
H	2.42220800	-6.96887000	1.30597600
H	-1.02122800	-6.59925400	0.50939000
H	-1.16436100	-6.96617500	2.73270700
H	-5.42511500	-6.02783000	1.95648000
H	-5.42831000	-6.20459400	0.17871200
N	1.25376900	1.16739300	0.37184100
C	1.17339800	2.57058700	0.42522700
N	0.00193400	3.07385400	0.19138500
N	2.32633000	3.22671800	0.68757800
H	2.30217900	4.22606700	0.82531900
H	3.11469800	2.69287200	1.03886900
H	0.02149500	4.09442400	0.22414600
H	0.38599800	0.72178200	0.09475600
N	-5.30119800	0.61444000	-0.59428500
C	-6.12889900	1.66873200	-0.90042500

N	-7.20896700	1.91128100	-0.16067100
N	-5.87502200	2.39214500	-1.98380400
H	-7.27242900	1.43849000	0.73791800
H	-7.75737000	2.74405200	-0.32812300
H	-6.47882100	3.17706700	-2.19369600
H	-4.97246100	2.37028500	-2.48972300
H	-4.49981100	0.43797800	-1.22641100
O	3.22257300	0.80312200	1.50467700
C	-5.41868800	-0.16746300	0.56744900
O	-6.13231300	0.19000100	1.50545100
C	-1.16777200	1.51834900	-5.39951900
C	-0.00606400	0.99816900	-5.98854000
C	0.28497300	1.28175500	-7.31741500
C	-0.59083600	2.09013200	-8.04862200
C	-1.74686300	2.61583300	-7.46883300
C	-2.03597700	2.33396300	-6.13875100
H	-2.92810600	2.74100500	-5.68244100
H	-2.41290200	3.23426200	-8.05879200
N	-0.28821100	2.40262300	-9.44269500
H	1.17526000	0.88510900	-7.78980800
O	0.70089800	1.87354900	-9.95972400
O	-1.03392800	3.18728100	-10.04399500
H	0.65316700	0.36902000	-5.40004500
O	-3.56115500	2.57577500	-3.46297400
P	-2.80294800	1.28742000	-3.28201500
O	-1.36564200	1.18100400	-4.08271400
O	-3.58747800	0.20305500	-4.67827500
O	-1.61000300	2.48831200	-1.79113900
C	-4.64696100	0.36845000	-5.43453200
C	-5.48711000	1.51987900	-5.43692200
C	-6.59256700	1.59369600	-6.26299500
C	-6.90110200	0.53230200	-7.12597500
C	-6.07893600	-0.60793800	-7.16738600
C	-4.97742000	-0.68494800	-6.34016100
H	-5.24188400	2.34862200	-4.78991800
H	-7.22738800	2.47228100	-6.25262400
N	-8.06008500	0.61248400	-7.96589200
H	-6.32024000	-1.41452700	-7.84982100
H	-4.33241400	-1.55852500	-6.36378600
O	-8.78535700	1.62083300	-7.89316500
O	-8.30683700	-0.32952700	-8.73934300
O	-2.97716500	0.26068200	-2.20535900
H	-1.61528200	3.39508900	-2.13825600
H	-0.89369578	2.56722187	-0.77260213

S4 - Appendix - Examples of kinetic profiles

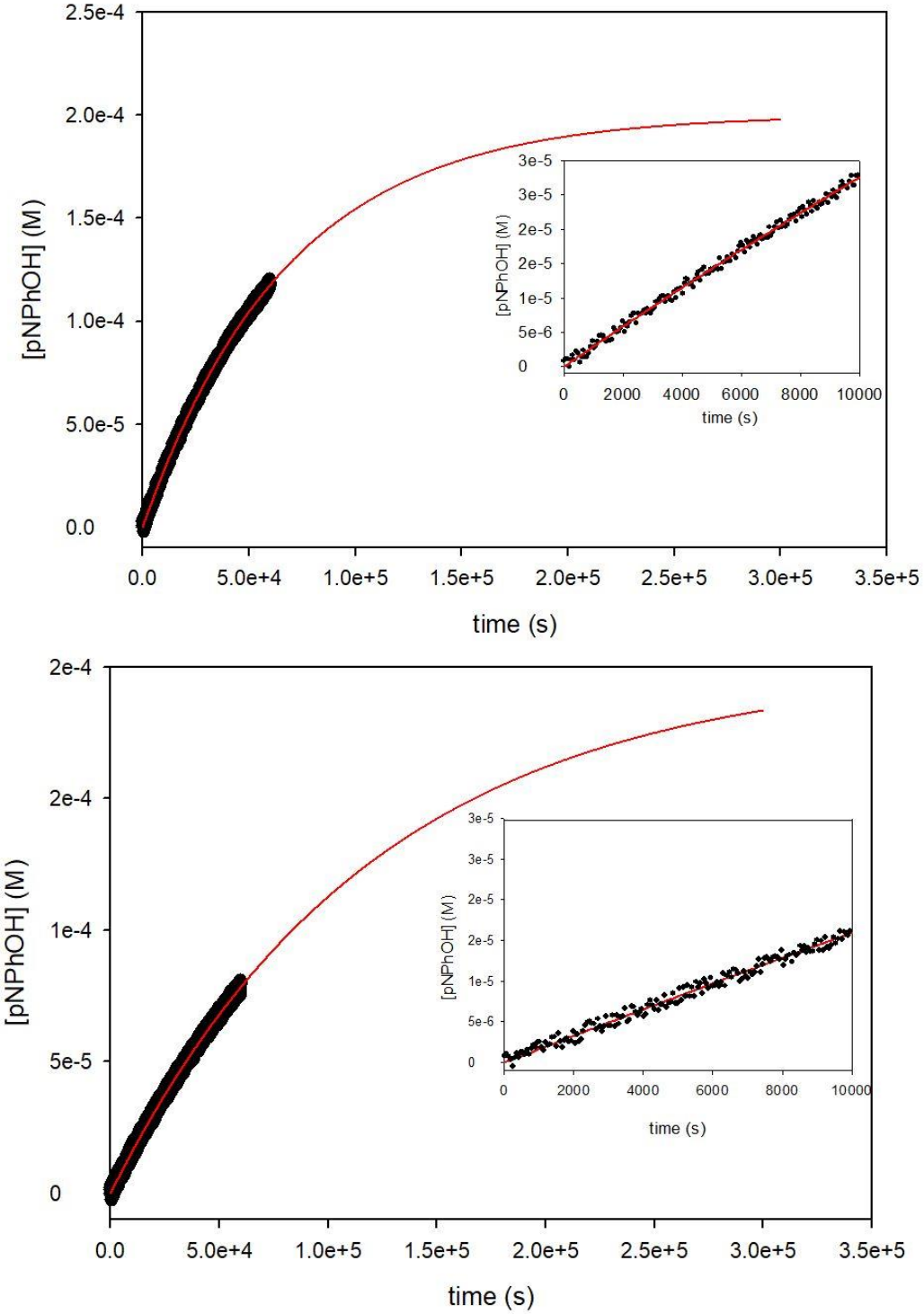


Figure 2S Plots of the product concentration versus time for the cleavage of HPNP promoted by **2**H^+ at pH 9.3 (top) and at pH 10.1 (bottom). The experiments correspond to entries 3 and 4 of Table 1. The solid red line is the fitting of the experimental data to a first order kinetic law. The good fitting of the experimental data to the first-order kinetic, especially in the first 10% of the reaction (see insets) indicates the absence of significant amount of a more reactive impurity in the HPNP sample used for the kinetic studies (see Experimental Section and references 36 and 37 in the main text).