Electronic Supplementary Material (ESI) for ChemComm.


*Supplementary information*

# Electrostatically-gated molecular rotors

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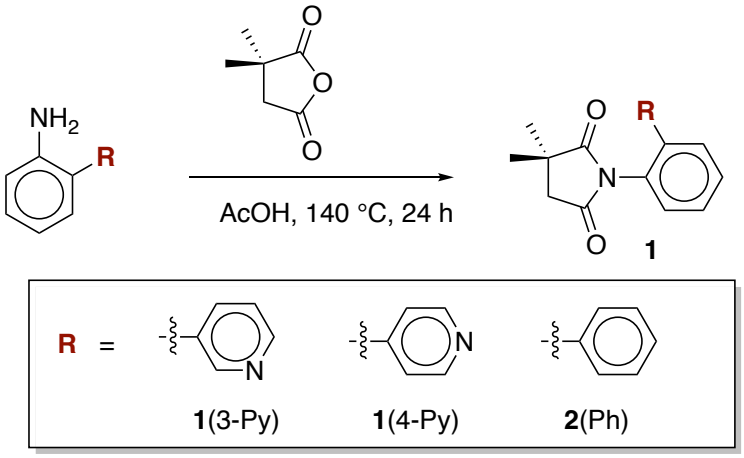
## 1. General experimental procedures

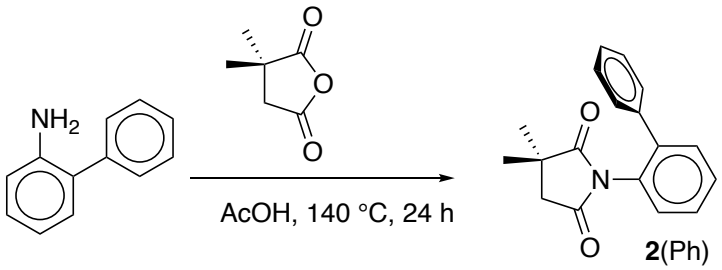
NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C. Chemical shifts are reported in ppm (δ) and were referenced to residual solvent peaks. Chemicals and solvents were purchased from commercial suppliers and used as received. Flash chromatography was performed using silica gel from Sorbent Technologies (60 Å, 200 – 400 mesh). HRMS were measured using a magnetic sector spectrometer (VG 70S) using EI sources.

## 2. Synthesis of the molecular rotors

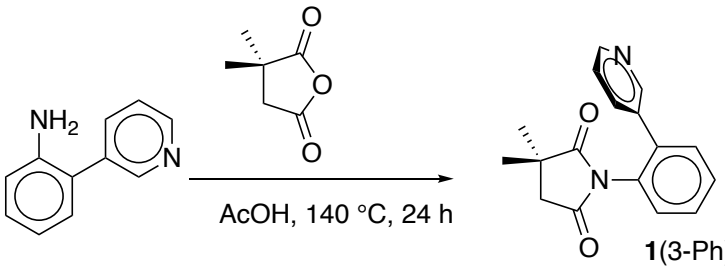
The rotors **1** and **2** were prepared via a thermal condensation between an *ortho*-substituted aniline and 2,2-dimethylsuccinic anhydride (**Scheme S1**).



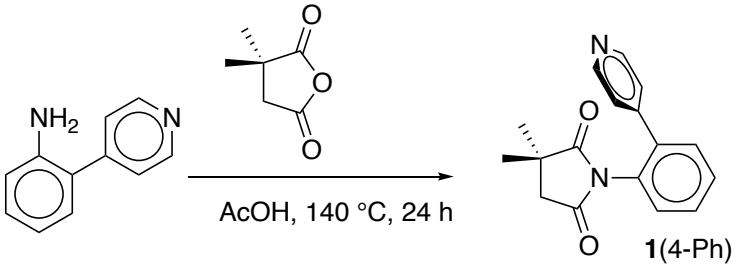

**Scheme S1.** General synthetic route to molecular rotors **1** and **2**.




Rotor **2**(Ph) (*1-([1,1'-biphenyl]-2-yl)-3,3-dimethylpyrrolidine-2,5-dione*): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and [1,1'-biphenyl]-2-amine (130 mg, 0.75 mmol) and 3 mL AcOH were added to a reaction tube. The tube was then sealed and heated to 140 °C for 24 hours. After letting the tube cool to room temperature, 50 mL EtOAc and 50 mL water was added to the reaction mixture. The organic layer was separated, and the solvent was removed under reduced pressure. The crude material was purified by column chromatography ($CH_2Cl_2$/MeOH = 200:1, v/v) to give **2**(Ph) as a colorless solid (130 mg, 92%). $^1$H NMR (400 MHz, chloroform-d) $\delta$ 7.55-7.45 (m, 3H), 7.40-7.32 (m, 3H), 7.28-7.22 (m, 3H), 2.59 (d, $J$ = 18.1 Hz, 1H), 2.38 (d, $J$ = 18.1 Hz, 1H), 1.34 (s, 3H), 0.94 (s, 3H). $^{13}$C NMR (100 MHz, chloroform-d) $\delta$ 182.3, 175.4, 141.4, 138.7, 130.9, 130.3, 129.7, 128.7, 128.65, 128.60, 128.3, 127.8, 43.9, 40.4, 25.45, 25.33. HRMS (EI) *m/z* calculated for $[C_{18}H_{17}NO_2]^+$ ($M^+$): calculated 279.1259; observed 279.1268.




Rotor **1**(3-Py) (*3,3-dimethyl-1-(2-(pyridin-3-yl)phenyl)pyrrolidine-2,5-dione*): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and 2-(pyridin-3-yl)aniline (102 mg, 0.6 mmol) were and 3 mL AcOH were added to a reaction tube. The tube was then sealed and heated to 140 °C in a silicon oil bath for 24 hours. After letting the tube cool to room temperature, using 50 mL EtOAc and 50 mL water to extract AcOH away. Collecting the organic layer and making second extraction with 50 mL $NaH_2CO_3$ solution, recollecting the organic layer and drying it under vacuum, the crude material was purified by column chromatography ($CH_2Cl_2$/MeOH = 200:1, v/v) to give **1**(3-Py) as a colorless solid (100 mg, 72%). $^1$H NMR (400 MHz, chloroform-d) $\delta$ 8.51 (d, $J$ = 4.34 Hz, 1H), 8.41 (s, 1H), 7.56-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.38-7.35 (m, 1H), 7.24 (dd, $J$ = 8.2 Hz, $J$ = 4.9 Hz, 1H), 7.20-7.16 (m, 1H), 2.60 (d, $J$ = 18.3 Hz, 1H), 2.42 (d, $J$ = 18.3 Hz, 1H), 1.33 (s, 3H), 0.97 (s, 3H). $^{13}$C NMR (100 MHz, chloroform-d) $\delta$ 182.2, 175.1, 149.0, 148.96, 137.6, 136.3, 134.5, 130.9, 130.4, 129.94, 129.59, 128.9, 123.3, 43.8, 40.4, 25.65, 25.23. HRMS (EI) *m/z* calculated for $[C_{17}H_{16}N_2O_2]^+$ ($M^+$): calculated 280.1212; observed 280.1213.




Rotor **1**(4-Py) (*3,3-dimethyl-1-(2-(pyridin-4-yl)phenyl)pyrrolidine-2,5-dione*): The reactants 3,3-dimethyldihydrofuran-2,5-dione (65 mg, 0.5 mmol) and 2-(pyridin-4-yl)aniline (130 mg, 0.75 mmol) and 3 mL AcOH were added to a reaction tube. The tube was then sealed and heated to 140 °C in a silicon oil bath for 24 hours. After letting the tube cool to room temperature, using 50 mL EtOAc and 50 mL water to extract AcOH away. Collecting the organic layer and making second extraction with 50 mL $NaH_2CO_3$ solution, recollecting the organic layer and drying it under vacuum, the crude material was purified by column chromatography ($CH_2Cl_2$/MeOH = 200:1, v/v) to give **1**(4-Py) as a colorless solid (100 mg, 72%). $^1$H NMR (400 MHz, chloroform-d) $\delta$ 8.61 (dd, $J$ = 4.6 Hz, $J$ = 1.6 Hz, 2H), 7.57-7.53 (m, 2H), 7.44-7.40 (m, 1H), 7.25-7.22 (m, 1H), 7.188 (dd, $J$ = 4.7 Hz, $J$ = 1.6 Hz, 2H), 2.61 (d, $J$ = 18.1 Hz, 1H), 2.41 (d, $J$ = 18.1 Hz, 1H), 1.33 (s, 3H), 0.99 (s, 3H). $^{13}$C NMR (100 MHz, chloroform-d) $\delta$ 182.2, 175.1, 149.9, 146.6, 138.7, 130.3, 130.0, 129.9, 129.0, 123.5, 43.9, 40.5, 25.46 (d, $J$ = 15.5 Hz). HRMS (EI) *m/z* calculated for $[C_{17}H_{16}N_2O_2]^+$ ($M^+$): calculated 280.1212; observed 280.1222.

## 3. $^{1}$H and $^{13}$C NMR spectra

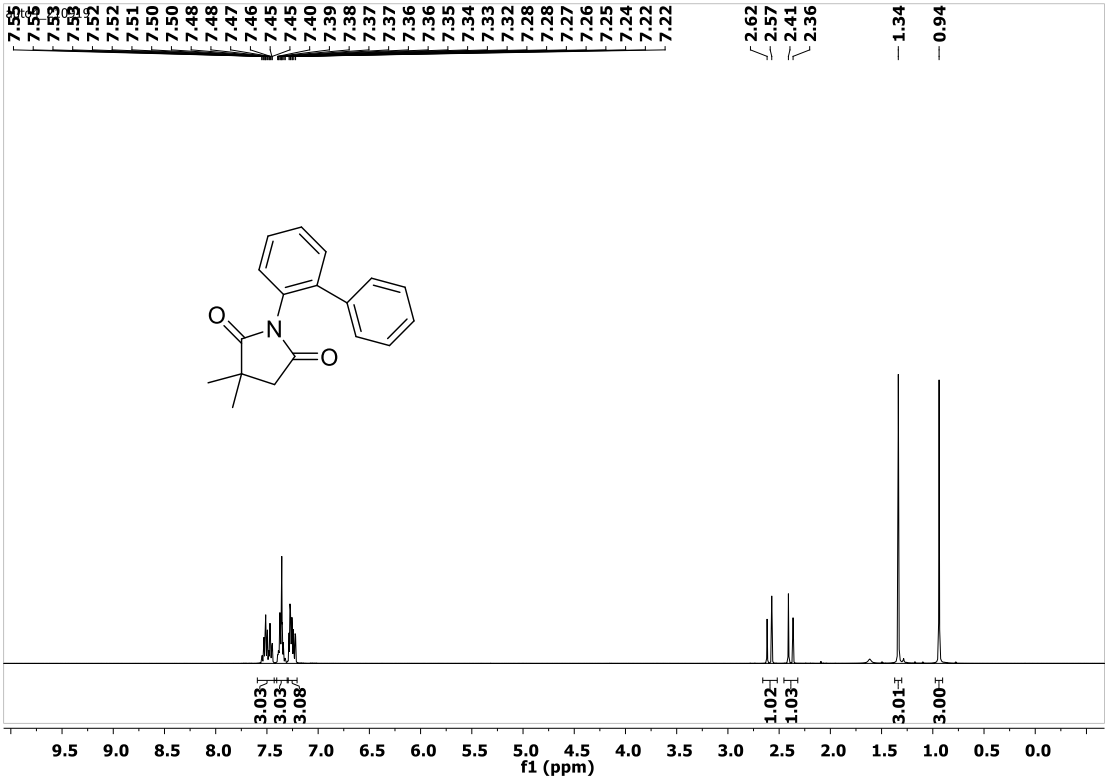



**Figure S1.** $^{1}$H NMR spectra (400 MHz) of rotor **2**(Ph) in $CDCl_3$.

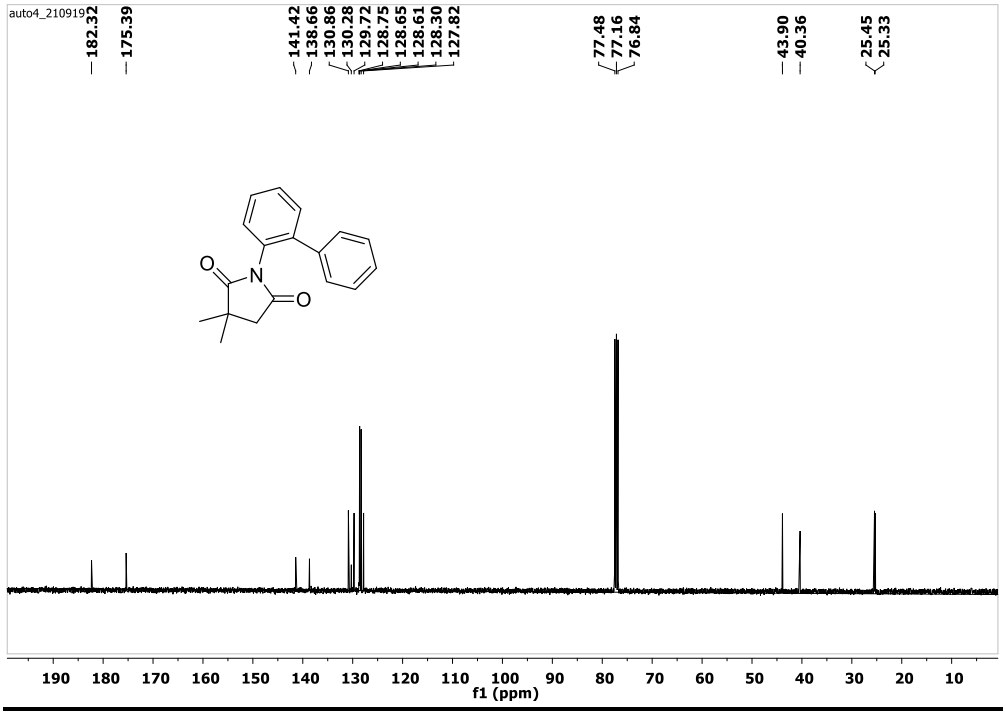



**Figure S2.** $^{13}$C NMR spectra (100 MHz) of rotor **2**(Ph) in $CDCl_3$.

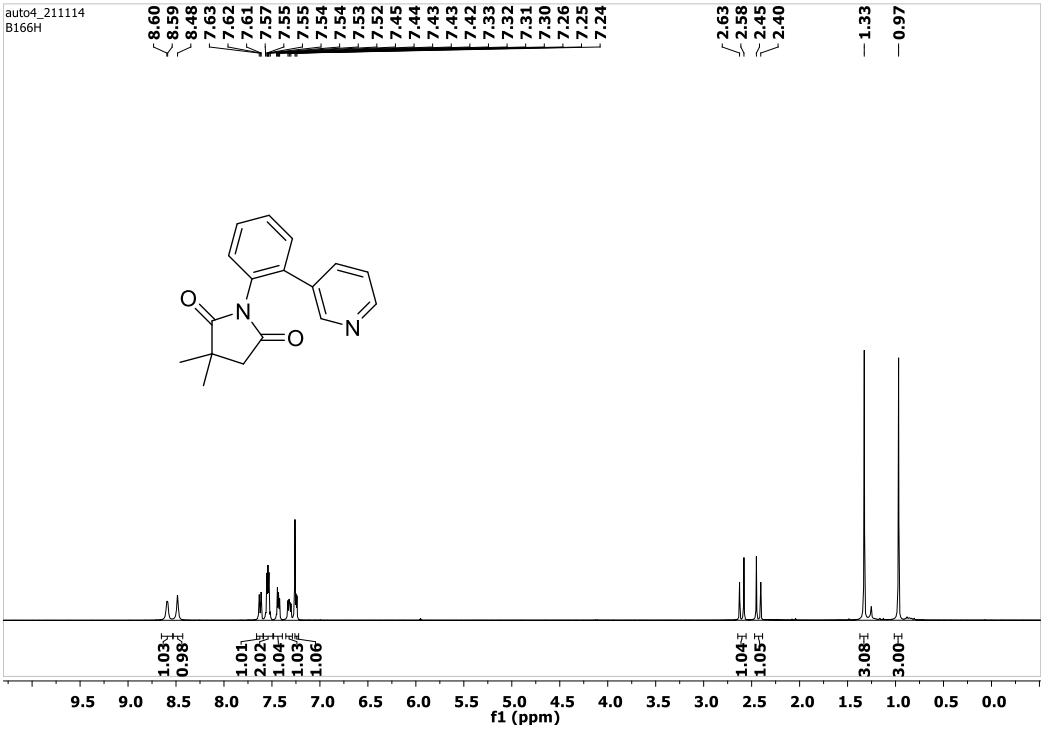



**Figure S3.** $^{1}$H NMR spectra (400 MHz) of rotor **1**(3-Py) in $CDCl_3$.

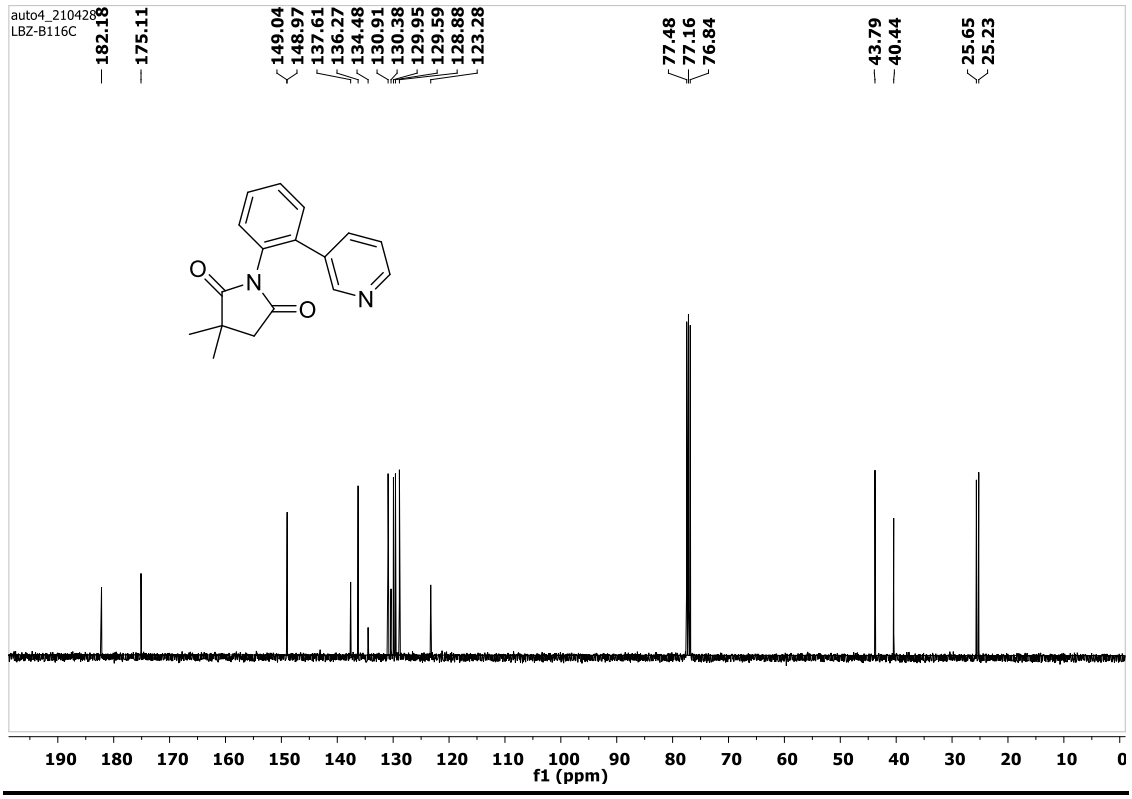



**Figure S4.** $^{13}$C NMR spectra (100 MHz) of rotor **1**(3-Py) in $CDCl_3$.

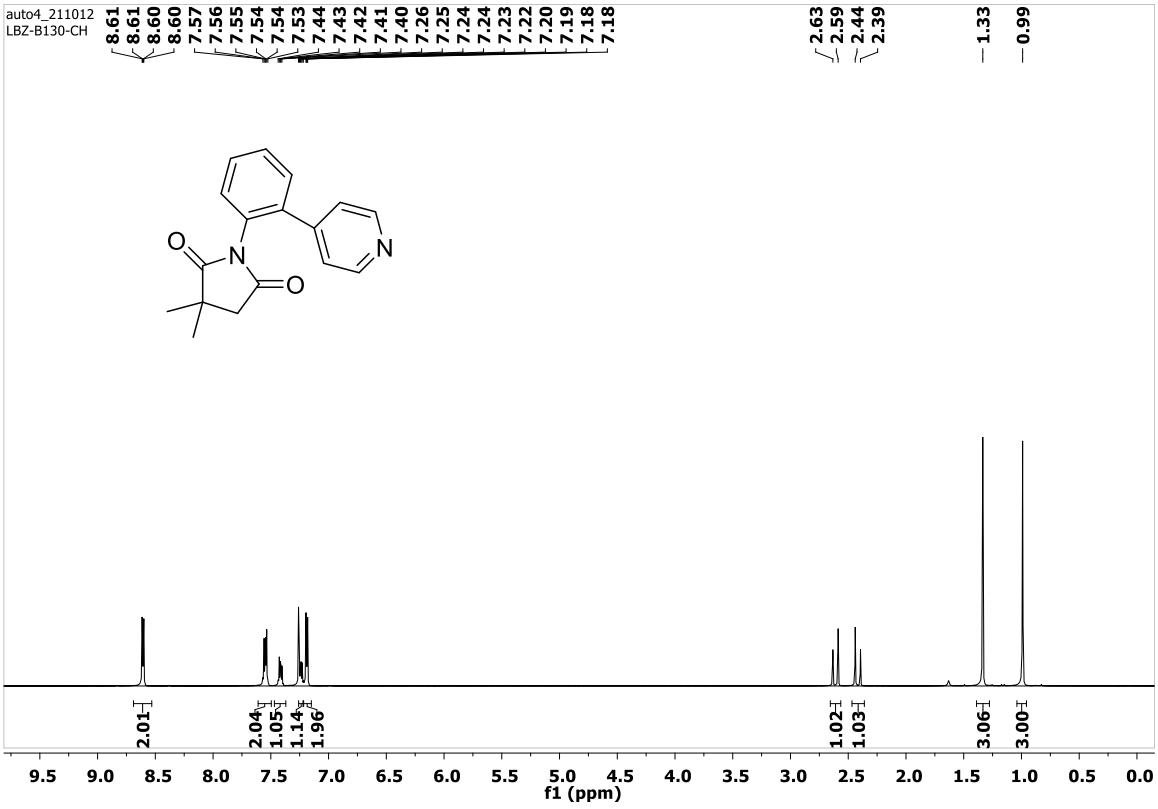



**Figure S5.** $^{1}$H NMR spectra (400 MHz) of rotor **1**(4-Py) in $CDCl_3$.

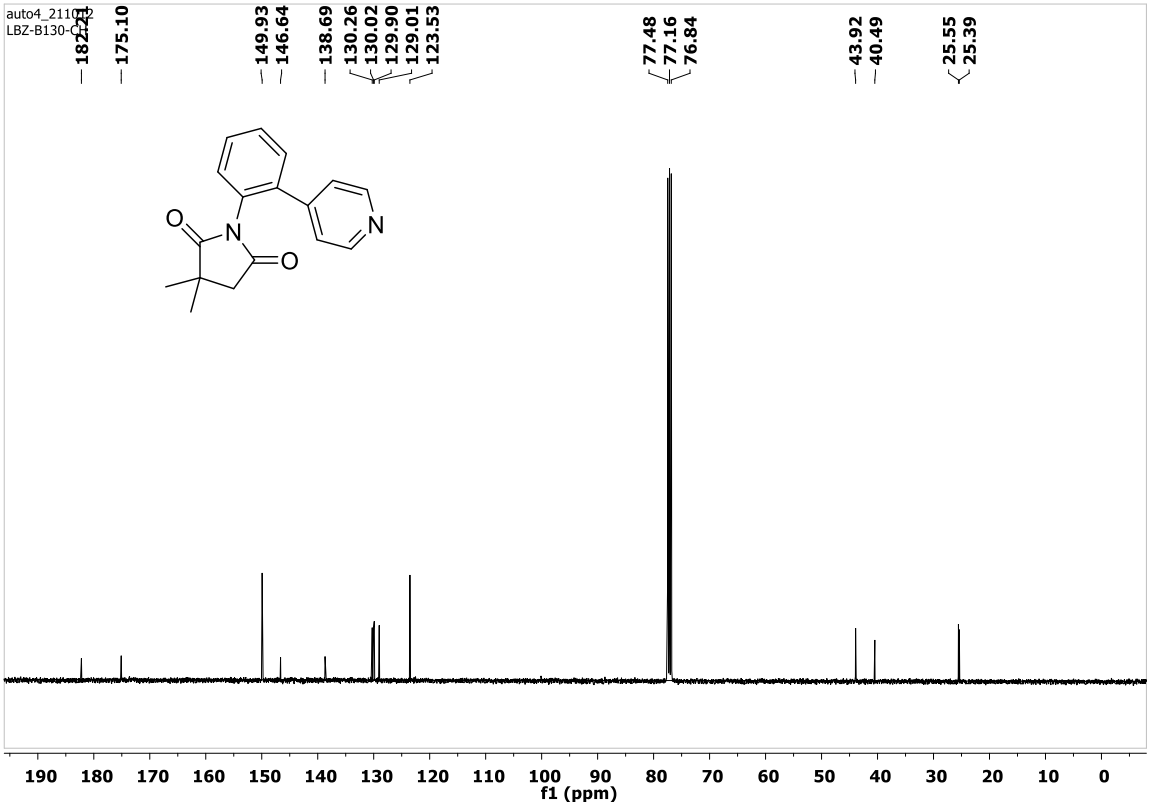



**Figure S6.** $^{13}$C NMR spectra (100 MHz) of rotor **1**(4-Py) in $CDCl_3$.

## 4. Experimental measurement of the rotor rotational barriers

The experimental rotational barriers of the rotors were determined via exchange spectroscopy (EXSY) NMR experiments in TCE-d2. An example of the 2D NOESY spectra is shown in Figure S7 and integration of the crosspeak and diagonal signals were performed using the Brucker Topspin software, and rate constants were calculated using EXSYCalc. The rotational barrier for each rotor were extrapolated to room temperature for consistency. The TS enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for rotor were obtained using Eyring plots (Figures S8 – S10).

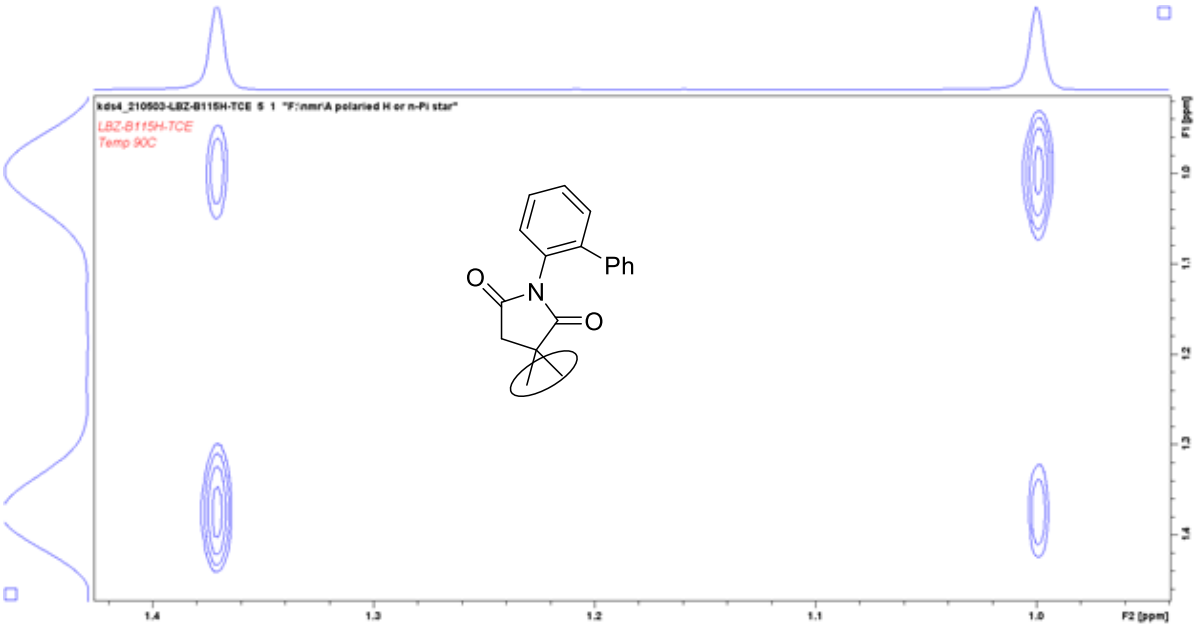



**Figure S7** 2D NMR of diastereotopic methyl groups of **2**(Ph) in TCE-d2 at 90 °C.

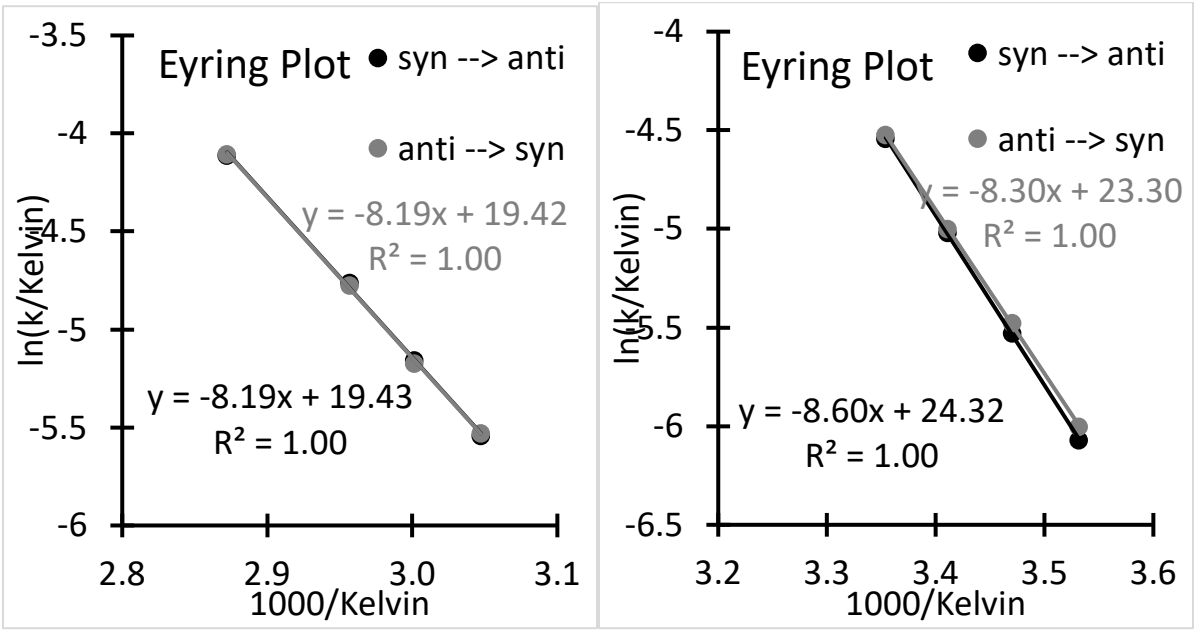



**Figure S8.** Eyring plots for (left) rotors **1**(3-Py) and (right) **1**(3-Py)•$H^+$ in 2.8 eq. MsOH.

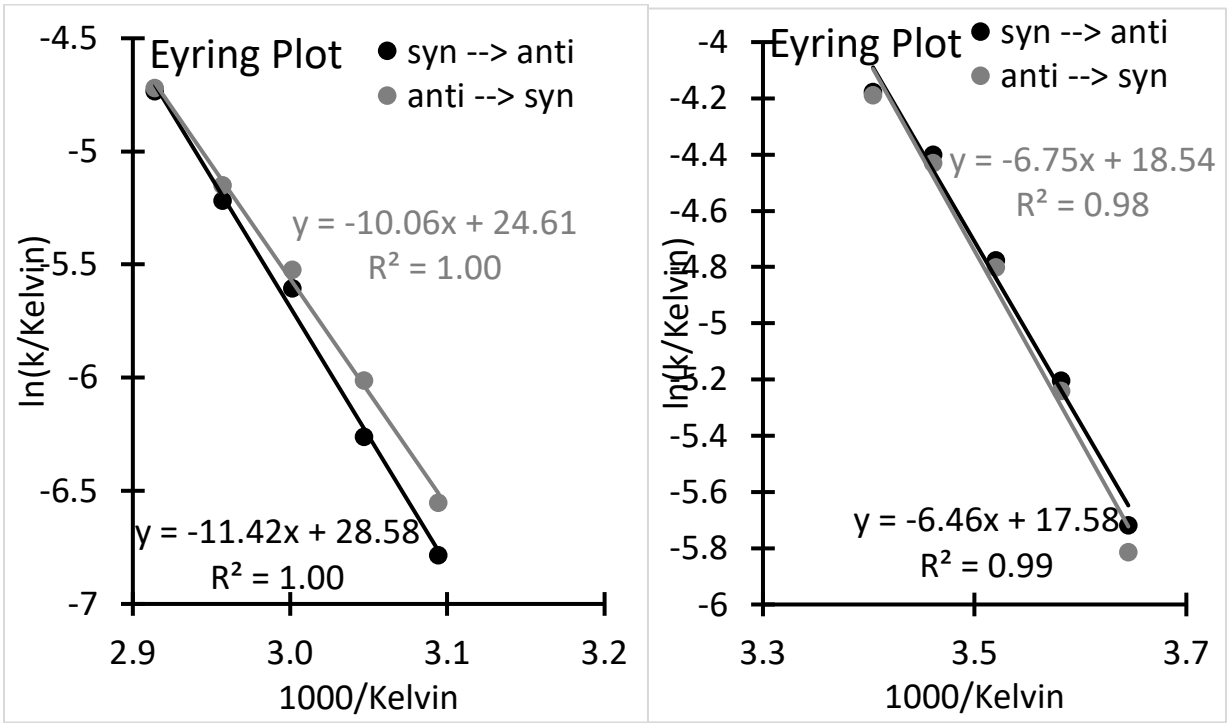



**Figure S9 .**Eyring plots for (left) rotor **1**(4-Py) and (right) rotor **1(**4-Py)•$H^+$ in 2.8 eq. MsOH.

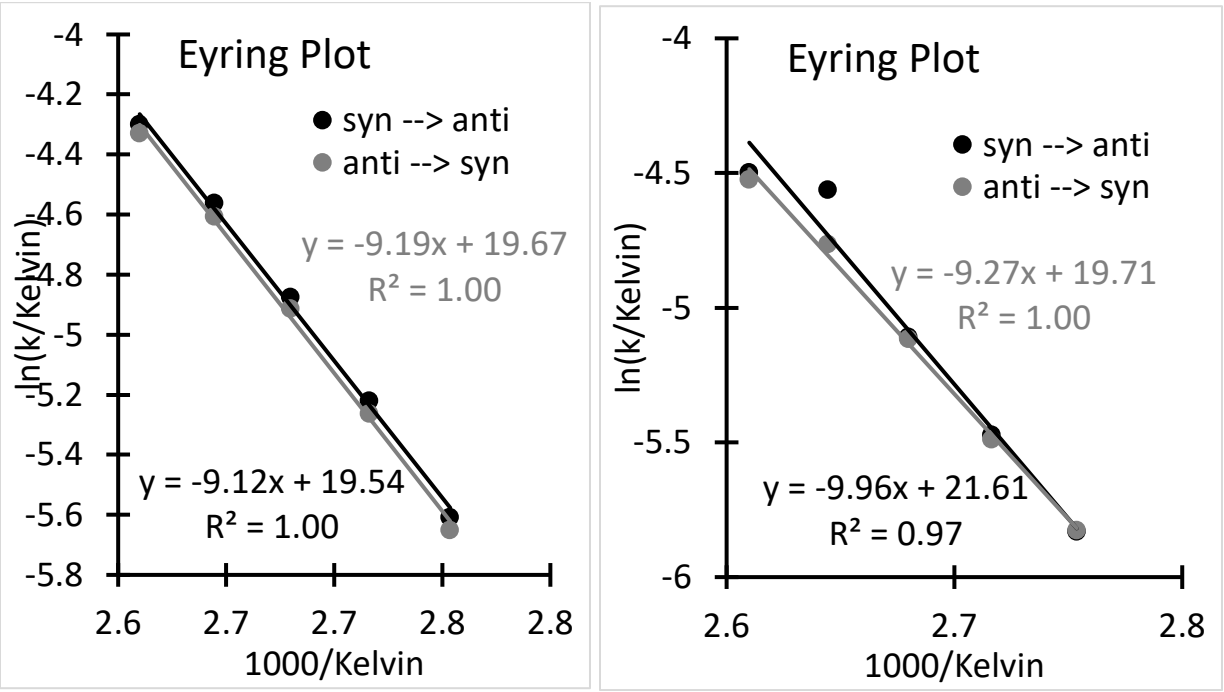



**Figure S10.** Eyring plots for (left) rotor **2**(Ph) and (right) rotor **2**(Ph) in 2.4 eq. MsOH.

## Experimental barriers in MsOH containing solutions.

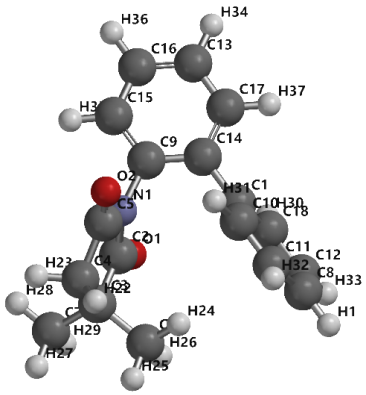
**Table S1.** The experimentally measured rotational barriers for rotors during titration with MsOH. The experimental barriers were measured by EXSY NMR in TCE-d2.

| MsOH/ (eq) | $\Delta G^{\ddagger}_{expt}$ **1**(3-Py) (kcal/mol) | MsOH (eq) | $\Delta G^{\ddagger}_{expt}$ **1**(4-Py) (kcal/mol) | MsOH (eq) | $\Delta G^{\ddagger}_{expt}$ **2**(Ph) (kcal/mol) |
|---|---|---|---|---|---|
| 0 | 18.83 | 0 | 19.65 | 0 | 20.63 |
| 0.15 | 17.80 | 0.14 | 17.45 | 0.6 | 20.93 |
| 0.3 | 17.45 | 0.31 | 17.0 | 1.3 | 20.94 |
| 0.62 | 17.0 | 0.64 | 16.72 | 2.4 | 21.07 |
| 1.02 | 16.80 | 0.99 | 16.5 | | |
| 1.2 | 16.78 | 1.2 | 16.5 | | |
| 2.8 | 16.75 | 2.8 | 16.49 | | |

### 5. Molecular Modeling Studies

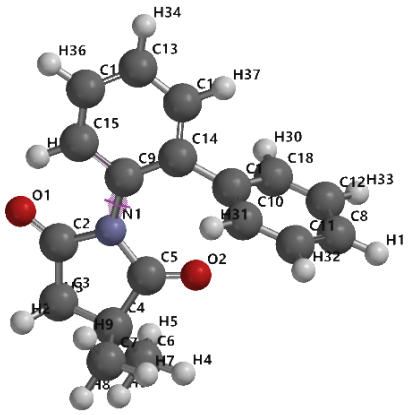
The optimized the ground state (GS) and transition state (TS) for the rotors were calculated (B3LYP-D3(0)/6-311G*) in Spartan '18.[1] Convergence criteria were $10^{-4}$ Hartree and $10^{-4}$ atomic units as the maximum norm of the cartesian gradient. Vibrational analyses were also carried out at the B3LYP-D3(0)/6-311G* level of theory. The free energies were calculated at 298.15 K using the calculated thermodynamic terms. Solvent calculations were performed using the C-PCM continuum solvent model with dielectric of 8.42 to match the dielectric of 1,1,2,2-tetrachloroethylene (TCE). The XYZ coordinates for the GS and TS structures are in Tables S2 – S6.

**Table S2.** The GS structure of rotor **2**(Ph) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



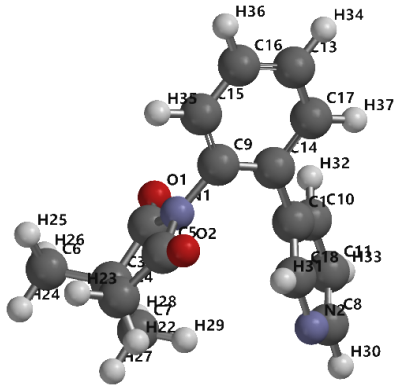

| | | | |
|---|---|---|---|
| N1 | 0.511393855 -0.882941210 0.741806000 | N1 | 0.488869277 -0.867428579 0.740306362 |
| C2 | 1.151406681 0.332079166 1.029756069 | C2 | 1.111251523 0.350425681 1.031875998 |
| C3 | 0.486528753 0.943530489 2.268594571 | C3 | 0.478383527 0.930899191 2.296462247 |
| C4 | -0.433734911 -0.182369035 2.777721420 | C4 | -0.414954275 -0.215971401 2.809812600 |
| C5 | -0.482574541 -1.216881421 1.668609451 | C5 | -0.448146571 -1.245897024 1.703815732 |
| C6 | -0.327500654 2.158349122 1.783025030 | C6 | -0.361315853 2.149348561 1.864556344 |
| C7 | 1.557092584 1.370554753 3.276091551 | C7 | 1.571924061 1.343633911 3.286628247 |
| O1 | 2.040438897 0.814034531 0.376111470 | O1 | 1.977857859 0.852781540 0.353786147 |
| O2 | -1.223178269 -2.162957828 1.572865005 | O2 | -1.141648332 -2.235202863 1.628465787 |
| C1 | -0.654282174 0.001691258 -1.730740305 | C1 | -0.655165365 0.015746048 -1.761984209 |
| C8 | -2.337170012 2.237558798 -1.849432365 | C8 | -2.325615336 2.262238860 -1.926845428 |
| C18 | -0.244169958 1.161491595 -2.394476760 | C18 | -0.262352583 1.139313703 -2.497643060 |
| C10 | -1.916374426 -0.027642431 -1.125051229 | C10 | -1.896610137 0.028232092 -1.112907916 |
| C11 | -2.753908905 1.083041478 -1.187803211 | C11 | -2.727573502 1.143107755 -1.197078243 |
| C12 | -1.080891356 2.273893031 -2.451288931 | C12 | -1.091712307 2.256780733 -2.577211227 |
| C9 | 0.762140583 -1.635316866 -0.450250416 | C9 | 0.746420859 -1.620282887 -0.451279135 |
| C13 | 1.325191840 -3.062270326 -2.762940366 | C13 | 1.332909042 -3.057780623 -2.752923527 |
| C14 | 0.231253980 -1.191433728 -1.668293093 | C14 | 0.225862888 -1.179553770 -1.676994408 |
| C15 | 1.547702910 -2.781132713 -0.382367732 | C15 | 1.533125312 -2.766349047 -0.369674098 |
| C16 | 1.825279951 -3.501725435 -1.539557508 | C16 | 1.821284133 -3.493034495 -1.521772280 |
| C17 | 0.536694341 -1.916907536 -2.823919569 | C17 | 0.545755759 -1.911240733 -2.826961612 |
| H22 | -1.448936268 0.143385565 3.010498943 | H22 | -1.434276132 0.092286104 3.047948540 |
| H23 | -0.039417236 -0.670543449 3.673956849 | H23 | -0.003376587 -0.697076857 3.701562275 |
| H24 | -1.095406510 1.863985100 1.063142143 | H24 | -1.141143024 1.862020934 1.154664280 |
| H25 | -0.819853622 2.642606955 2.631181439 | H25 | -0.839648638 2.595173412 2.740266989 |
| H26 | 0.326314216 2.884569470 1.297156945 | H26 | 0.272707317 2.901789731 1.391527415 |
| H27 | 1.095055819 1.841010984 4.148380068 | H27 | 1.119977369 1.769833329 4.185766184 |
| H28 | 2.142240905 0.513514139 3.621194831 | H28 | 2.181016753 0.485007720 3.581512580 |
| H29 | 2.244104303 2.083995253 2.818349070 | H29 | 2.226906950 2.093231413 2.838814682 |
| H30 | 0.741892708 1.192693612 -2.845211362 | H30 | 0.701198276 1.138574222 -2.996359544 |
| H31 | -2.236562183 -0.928178056 -0.611060755 | H31 | -2.214450140 -0.844857257 -0.552232405 |
| H32 | -3.733755819 1.043919234 -0.722324551 | H32 | -3.689250471 1.135379702 -0.694266298 |
| H33 | -0.749082039 3.171174057 -2.963659120 | H33 | -0.773561093 3.123548997 -3.147407922 |
| H34 | 1.540808837 -3.617457401 -3.670267680 | H34 | 1.557646122 -3.615975630 -3.655939938 |
| H35 | 1.939510312 -3.098371528 0.577397575 | H35 | 1.918964886 -3.076837969 0.594788730 |
| H36 | 2.432918302 -4.398753500 -1.486475947 | H36 | 2.428976701 -4.389198520 -1.458760362 |
| H37 | 0.128472911 -1.585650112 -3.773113036 | H37 | 0.151471764 -1.584348305 -3.783427606 |
| H1 | -2.989643803 3.103453983 -1.897604492 | H1 | 1 -2.971710034 3.131682323 -1.990891921 |

**Table S3.** The TS structure of rotor **2**(Ph) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



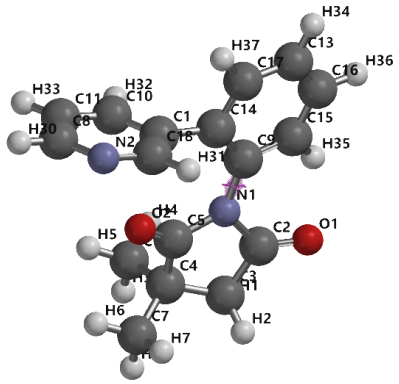

| | | | |
|---|---|---|---|
| N1 | -0.126171779 0.585344422 0.771863203 | N1 | -0.569494909 0.825259999 0.941146935 |
| C2 | -0.588320171 1.124783758 2.011998210 | C2 | -1.088593627 1.347420464 2.162603432 |
| C3 | -0.429720550 0.079975313 3.120266218 | C3 | -0.701161301 0.437521409 3.303021896 |
| C4 | 0.574535972 -0.888596986 2.514628222 | C4 | 0.205003433 -0.631693476 2.704478076 |
| C5 | 0.409489403 -0.717133786 1.022669441 | C5 | -0.032966846 -0.465690918 1.209316399 |
| C6 | -1.805076509 -0.597479103 3.298618581 | O1 | -1.773812115 2.334003237 2.299734554 |
| C7 | 0.022297877 0.739414898 4.422246927 | O2 | 0.195168713 -1.320832471 0.395193473 |
| O1 | -1.085681641 2.205802797 2.208537148 | C1 | 0.141693107 -0.402195423 -2.012838316 |
| O2 | 0.674654865 -1.556378543 0.210669101 | C8 | 1.399963292 -2.717657099 -2.975011716 |
| C1 | 0.540332610 -0.659703444 -2.184711130 | C18 | -0.614111105 -1.456640556 -2.531668066 |
| C8 | 1.692673829 -3.023739147 -3.150122088 | C10 | 1.537003442 -0.501015993 -2.020674850 |
| C18 | -0.264631117 -1.711052887 -2.627347962 | C11 | 2.161965865 -1.653506496 -2.491385713 |
| C10 | 1.928899576 -0.787301985 -2.271273748 | C12 | 0.009345664 -2.612266232 -2.998268014 |
| C11 | 2.501579628 -1.965025440 -2.741728336 | C9 | -0.722382917 1.478049217 -0.352406175 |
| C12 | 0.307063607 -2.890294441 -3.095839394 | C13 | -1.301425571 2.960273805 -2.711342828 |
| C9 | -0.296745870 1.239378875 -0.524054151 | C14 | -0.509249759 0.891990413 -1.632028896 |
| C13 | -0.872682717 2.713036807 -2.888417397 | C15 | -1.110785240 2.833240096 -0.319116389 |
| C14 | -0.069923132 0.653894360 -1.801704097 | C16 | -1.395579236 3.562390168 -1.464632160 |
| C15 | -0.735218863 2.578859611 -0.493606822 | C17 | -0.845306254 1.652981525 -2.768011224 |
| C16 | -1.018239547 3.302047538 -1.642480092 | H30 | -1.696534272 -1.378432995 -2.552258786 |
| C17 | -0.393736834 1.414872319 -2.940034155 | H31 | 2.133530343 0.324599383 -1.646256339 |
| H22 | 0.427124085 -1.936415744 2.777203092 | H32 | 3.245556263 -1.719908149 -2.483868153 |
| H23 | 1.604256870 -0.618843564 2.772645752 | H33 | -0.591823743 -3.429741723 -3.384628256 |
| H24 | -2.131287971 -1.093352696 2.379620489 | H34 | -1.541917577 3.499177006 -3.621500883 |
| H25 | -1.748619445 -1.353487353 4.086356871 | H35 | -1.218907396 3.329053618 0.627451453 |
| H26 | -2.562935876 0.137364732 3.575818549 | H36 | -1.696160835 4.600101634 -1.366192064 |
| H27 | 0.112455312 -0.010793314 5.212415214 | H37 | -0.699743074 1.184506260 -3.735262924 |
| H28 | 0.993185049 1.228067220 4.304844449 | H1 | 1.885914115 -3.616687571 -3.340752442 |
| H29 | -0.697089157 1.495406332 4.739375336 | H2 | -0.237284140 1.034634641 4.090289778 |
| H30 | -1.344467383 -1.609629601 -2.58411135 | H3 | -1.625052144 0.019697963 3.712353269 |
| H31 | 2.560653834 0.036633210 -1.955414320 | C6 | -0.144345596 -2.056197444 3.142999143 |
| H32 | 3.582251844 -2.055671282 -2.793703547 | H4 | 0.476948033 -2.782761846 2.616931885 |
| H33 | -0.331422335 -3.705981733 -3.421716142 | H5 | -1.192012388 -2.289758735 2.934889994 |
| H34 | -1.102553709 3.251596140 -3.801788904 | H6 | 0.024149853 -2.166306547 4.216895735 |
| H35 | -0.877998315 3.064300520 0.453327611 | C7 | 1.695753551 -0.332100509 2.960233282 |
| H36 | -1.357548321 4.328055635 -1.545095973 | H7 | 2.328469652 -1.038276252 2.417675756 |
| H37 | -0.229966129 0.945205946 -3.903617321 | H8 | 1.908553920 -0.424161037 4.028149438 |
| H1 | 2.138582955 -3.943159332 -3.516337382 | H9 | 1.959630746 0.680930635 2.644739696 |

**Table S4** The GS structure of rotor **1**(3-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



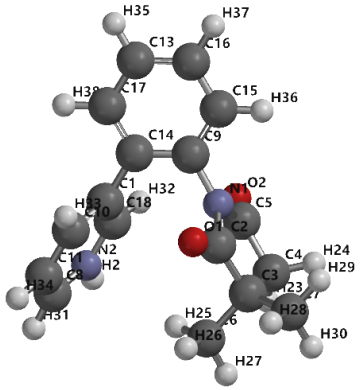

| | | | |
|---|---|---|---|
| N1 | -0.087138608 0.629438990 1.002136613 | N1 | 0.018464570 0.612306834 0.998265215 |
| C2 | -0.873065819 -0.510628201 1.226793414 | C2 | -0.648069449 -0.612224205 1.069115443 |
| C3 | 0.012150307 -1.594943932 1.843955588 | C3 | 0.180008255 -1.584515235 1.905516351 |
| C4 | 1.299946362 -0.832709198 2.212138645 | C4 | 1.364056312 -0.722731694 2.392556880 |
| C5 | 1.218982811 0.502360328 1.487865999 | C5 | 1.210457579 0.629943329 1.728356106 |
| C6 | -0.693231293 -2.248915379 3.034650198 | C6 | -0.682458642 -2.129314960 3.052380903 |
| C7 | 0.263781195 -2.632204536 0.729706829 | C7 | 0.633944724 -2.733078012 0.983653860 |
| O1 | -2.033582580 -0.613017617 0.922834467 | O1 | -1.702229132 -0.843257193 0.521546767 |
| O2 | 2.093780294 1.317948041 1.338484062 | O2 | 1.962024527 1.576262722 1.782620682 |
| C1 | 0.198957387 0.461301699 -1.831104694 | C1 | 0.171077185 0.458331375 -1.882414001 |
| C8 | 1.316935034 -1.722305556 -3.038239069 | C8 | 1.403888540 -1.663511370 -3.100553460 |
| C18 | -0.538626867 -0.490086881 -2.545137325 | C18 | 1.503400231 0.096870404 -1.644055813 |
| C10 | 1.579918101 0.269361356 -1.735364110 | C10 | -0.545870571 -0.306582553 -2.806549374 |
| C11 | 2.148462803 -0.841469930 -2.349139856 | C11 | 0.079795169 -1.382047584 -3.427414367 |
| N2 | -0.005291998 -1.560487284 -3.138570651 | N2 | 2.114728311 -0.939080621 -2.226092960 |
| C9 | -0.567559393 1.716272513 0.203932485 | C9 | -0.473935138 1.703188851 0.212439739 |
| C13 | -1.682641083 3.717026274 -1.360074289 | C13 | -1.593242711 3.754621089 -1.286443376 |
| C14 | -0.474819305 1.621064909 -1.190959253 | C14 | -0.446347652 1.614351188 -1.188104413 |
| C15 | -1.200456931 2.793703988 0.811596936 | C15 | -1.038198091 2.800623502 0.855613970 |
| C16 | -1.753133213 3.802576672 0.028147482 | C16 | -1.590525142 3.835357672 0.105442262 |
| C17 | -1.050018939 2.633218217 -1.963064558 | C17 | -1.029037408 2.652937361 -1.923785322 |
| H22 | 2.218286686 -1.344686463 1.920546785 | H22 | 2.338666145 -1.135182021 2.124281794 |
| H23 | 1.368531097 -0.631711629 3.285505498 | H23 | 1.362060723 -0.575700428 3.475419211 |
| H24 | -0.068917199 -3.040559079 3.457178294 | H24 | -0.103125432 -2.838493772 3.648683843 |
| H25 | -0.905845190 -1.522935997 3.824164558 | H25 | -1.024410969 -1.326123337 3.710355946 |
| H26 | -1.641113387 -2.687242713 2.717561879 | H26 | -1.559296655 -2.646340310 2.656823998 |
| H27 | 0.906742637 -3.433967545 1.103563177 | H27 | 1.232946680 -3.446286144 1.555006706 |
| H28 | -0.679919229 -3.069693970 0.398201762 | H28 | -0.231583720 -3.256889351 0.572234514 |
| H29 | 0.747459564 -2.182271637 -0.141140472 | H29 | 1.238652985 -2.365271159 0.151117434 |
| H30 | 1.727510668 -2.600428146 -3.530882435 | H30 | 1.917997131 -2.504654963 -3.557776215 |
| H31 | -1.618019759 -0.386004019 -2.621937786 | H31 | 2.106477673 0.680710920 -0.954507455 |
| H32 | 2.186038579 0.973694942 -1.178054157 | H32 | -1.583503298 -0.072068905 -3.019696139 |
| H33 | 3.216754926 -1.021852729 -2.297848585 | H33 | -0.450031844 -1.999104522 -4.144514887 |
| H34 | -2.120896396 4.495101574 -1.976263312 | H34 | -2.031469557 4.551497320 -1.877755769 |
| H35 | -1.271196707 2.823955997 1.892870687 | H35 | -1.055741664 2.826388549 1.939175449 |
| H36 | -2.247689592 4.644473264 0.500353343 | H36 | -2.028018225 4.691893446 0.606291165 |
| H37 | -0.991074962 2.566623672 -3.044408147 | H37 | -1.021551440 2.597173779 -3.007234690 |

**Table S5** The TS structure of rotor **1**(3-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



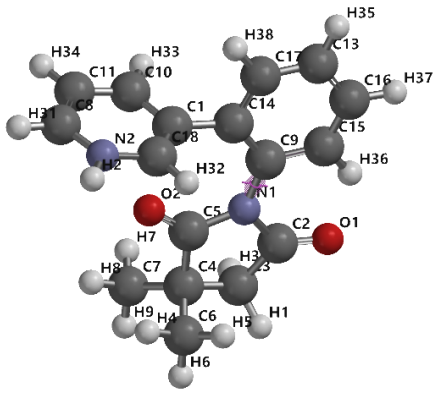

| | | | |
|---|---|---|---|
| N1 | 0.081937663 0.603139500 1.105314533 | N1 | -0.210453572 0.492686750 1.149928862 |
| C2 | 0.359390802 0.915983703 2.469643852 | C2 | -0.297662030 0.656742938 2.565385264 |
| C3 | 0.936226496 -0.311708198 3.147221073 | C3 | 0.193129823 -0.599241606 3.244794361 |
| C4 | 0.771997408 -1.454310693 2.150336438 | C4 | 0.731643751 -1.497536206 2.136817246 |
| C5 | 0.606865154 -0.695224874 0.836619364 | C5 | 0.137536793 -0.860864366 0.888385085 |
| O1 | 0.208489441 1.975542449 3.022251928 | O1 | -0.730999507 1.614729173 3.160971845 |
| O2 | 0.887556098 -1.144842609 -0.239123020 | O2 | -0.014302197 -1.442579927 -0.15402842 |
| C1 | -0.205304111 0.230467177 -2.111717223 | C1 | -0.489416197 0.168069005 -2.087484147 |
| C8 | 0.369396719 -1.808323114 -3.837220819 | C8 | -0.119949362 -1.851187580 -3.898263912 |
| C18 | -1.037221230 -0.876777730 -2.306973019 | C18 | -1.534421598 -0.594940107 -2.614054759 |
| C10 | 0.952607813 0.307519424 -2.881961946 | C10 | 0.799429010 -0.097772001 -2.551877607 |
| C11 | 1.251461510 -0.734585549 -3.752895369 | C11 | 0.989359226 -1.128279398 -3.465649699 |
| N2 | -0.767202505 -1.88189966 -3.13817394 | N2 | -1.368844781 -1.590426565 -3.490657768 |
| C9 | -0.575138922 1.509610070 0.174009382 | C9 | -0.556342055 1.526182322 0.184858508 |
| C13 | -1.899146797 3.471253629 -1.398807619 | C13 | -1.395233601 3.717237588 -1.424240013 |
| C14 | -0.650302648 1.358527235 -1.237815924 | C14 | -0.765395156 1.347624783 -1.211455799 |
| C15 | -1.228338531 2.619391437 0.746159882 | C15 | -0.677130980 2.835196426 0.693478893 |
| C16 | -1.873293059 3.580881614 -0.016669058 | C16 | -1.087533617 3.908325560 -0.084673504 |
| C17 | -1.301254081 2.363566009 -1.975640432 | C17 | -1.211425777 2.452654959 -1.960283210 |
| H30 | 0.574112327 -2.642502080 -4.504106940 | H30 | -0.006457707 -2.665327736 -4.609441864 |
| H31 | -1.969108558 -0.952456476 -1.750763433 | H31 | -2.556101228 -0.396843063 -2.299542930 |
| H32 | 1.614804645 1.161209795 -2.784342826 | H32 | 1.639339619 0.487694453 -2.193621137 |
| H33 | 2.151498341 -0.718139357 -4.358369337 | H33 | 1.978135810 -1.369083907 -3.840695339 |
| H34 | -2.388785140 4.216270221 -2.016763460 | H34 | -1.740604539 4.533896716 -2.048792676 |
| H35 | -1.211316997 2.751478706 1.812445619 | H35 | -0.467306379 3.019165542 1.730637585 |
| H36 | -2.351357537 4.415223621 0.485703357 | H36 | -1.167231555 4.888945811 0.372055427 |
| H37 | -1.346237706 2.232415672 -3.051312522 | H37 | -1.385922039 2.295818046 -3.019212132 |
| H1 | 1.988206304 -0.104057711 3.364698512 | H1 | 0.926816890 -0.328484789 4.006203616 |
| H2 | 0.430120957 -0.457604262 4.103445572 | H2 | -0.662591025 -1.046436428 3.758728311 |
| C6 | 1.961059366 -2.411460823 2.069494140 | C6 | 2.265882739 -1.398686375 2.009537701 |
| H3 | 2.067886213 -2.968829478 3.003934087 | H3 | 2.734158526 -1.827836967 2.898787399 |
| H4 | 2.894149539 -1.874403813 1.881152877 | H4 | 2.594386351 -0.360101433 1.918384236 |
| H5 | 1.818872096 -3.121848235 1.254151948 | H5 | 2.613049463 -1.950760888 1.133227124 |
| C7 | -0.537140773 -2.237205907 2.387024561 | C7 | 0.291410432 -2.959163483 2.251807778 |
| H6 | -0.703660802 -2.957195286 1.582647244 | H6 | 0.635256500 -3.533574912 1.389931839 |
| H7 | -1.405334605 -1.574282541 2.435003415 | H7 | -0.797397352 -3.040971120 2.304126570 |
| H8 | -0.476494890 -2.784821651 3.331399211 | H8 | 0.713187106 -3.404871161 3.155927316 |

**Table S6.** The GS structure of rotor **1**(3-Py)•$H^+$ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



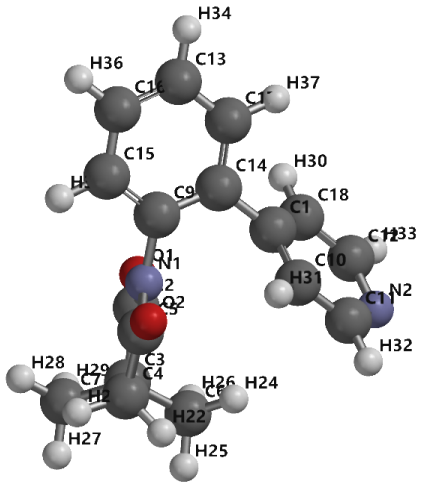

| | | | |
|---|---|---|---|
| N1 | 0.354477191 0.700232750 0.935541595 | N1 | 0.375230795 0.685665422 0.946897590 |
| C2 | -0.986011532 0.303785691 1.092435402 | C2 | -0.926376815 0.185431678 1.056778049 |
| C3 | -1.041380067 -0.826789169 2.121928076 | C3 | -0.958879693 -0.869927775 2.159930747 |
| C4 | 0.410782377 -0.912984439 2.639922816 | C4 | 0.429007539 -0.737654634 2.821040216 |
| C5 | 1.243947182 -0.119544604 1.652382820 | C5 | 1.244409132 0.161298380 1.916463428 |
| C6 | -1.446201770 -2.107698545 1.365615026 | C6 | -1.139067702 -2.244777572 1.485618255 |
| C7 | -2.077700474 -0.501314067 3.203389069 | C7 | -2.124266100 -0.587879579 3.115723739 |
| O1 | -1.899100950 0.743031167 0.441653936 | O1 | -1.842821892 0.522471212 0.342397929 |
| O2 | 2.430122702 -0.177193503 1.441952100 | O2 | 2.424019394 0.415007606 1.975697684 |
| C1 | 0.474759712 -0.005340334 -1.814161397 | C1 | 0.390378048 -0.014519891 -1.860012965 |
| C8 | 0.072128540 -2.657006539 -2.563918273 | C8 | -0.159847772 -2.600605056 -2.724427549 |
| C18 | 1.386447776 -0.999604546 -1.480799102 | C18 | 1.165142897 -1.094379468 -1.462143334 |
| C10 | -0.665560505 -0.378416410 -2.536688754 | C10 | -0.685298930 -0.266760044 -2.722104387 |
| C11 | -0.862830294 -1.706418895 -2.918729438 | C11 | -0.958348449 -1.560645450 -3.158694899 |
| N2 | 1.159020355 -2.274777184 -1.857448285 | N2 | 0.867957311 -2.333065209 -1.896698338 |
| C9 | 0.731700899 1.699032224 -0.016145335 | C9 | 0.742394097 1.669502649 -0.023140448 |
| C13 | 1.247767578 3.688271363 -1.892860593 | C13 | 1.306446699 3.645829498 -1.898964878 |
| C14 | 0.725774577 1.387854289 -1.381344115 | C14 | 0.707549900 1.354328914 -1.389306417 |
| C15 | 1.000623501 2.994067073 0.407013220 | C15 | 1.065226657 2.955096211 0.400358399 |
| C16 | 1.269658015 3.986592121 -0.532416730 | C16 | 1.358118659 3.941341499 -0.537574107 |
| C17 | 0.972111022 2.392115508 -2.318630074 | C17 | 0.977973352 2.361078680 -2.321122552 |
| H2 | 1.842707499 -2.978542679 -1.599878445 | H2 | 1.454058075 -3.102567120 -1.587740896 |
| H23 | 0.798007056 -1.929062431 2.724698376 | H23 | 0.945526350 -1.689226208 2.954731198 |
| H24 | 0.522187668 -0.445894722 3.623268335 | H24 | 0.372328731 -0.256059767 3.801137272 |
| H25 | -0.715118265 -2.369843098 0.591925221 | H25 | -0.307624451 -2.475353521 0.814305514 |
| H26 | -2.417234873 -1.977304530 0.885183432 | H26 | -2.066004950 -2.270878324 0.909019569 |
| H27 | -1.512802713 -2.949672188 2.057965788 | H27 | -1.182255852 -3.023815217 2.250303361 |
| H28 | -3.065613601 -0.373442231 2.757781399 | H28 | -3.073731956 -0.615788168 2.577276944 |
| H29 | -1.827394242 0.419626193 3.735525593 | H29 | -2.023980275 0.393030067 3.586744046 |
| H30 | -2.131187609 -1.311861930 3.934210858 | H30 | -2.151219493 -1.345755756 3.902308891 |
| H31 | -0.005116473 -3.706722071 -2.813029884 | H31 | -0.300505768 -3.635129462 -3.004393601 |
| H32 | 2.278423049 -0.806313545 -0.898002617 | H32 | 2.026071119 -1.009280836 -0.814077563 |
| H33 | -1.406467403 0.374746878 -2.777473986 | H33 | -1.316473075 0.554993522 -3.038536841 |
| H34 | -1.741537656 -2.006578073 -3.474906110 | H34 | -1.788497737 -1.767142524 -3.821089283 |
| H35 | 1.447879476 4.462791022 -2.624177989 | H35 | 1.524280222 4.413197842 -2.633309153 |
| H36 | 0.980283924 3.220424470 1.466467880 | H36 | 1.067907156 3.176770452 1.460975811 |
| H37 | 1.482498209 4.996233624 -0.201103158 | H37 | 1.612029352 4.941401126 -0.204918120 |
| H38 | 0.969950117 2.153521361 -3.377146659 | H38 | 0.949145425 2.124766824 -3.379453309 |

**Table S7.** The TS structure of rotor **1**(3-Py)•$H^+$ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



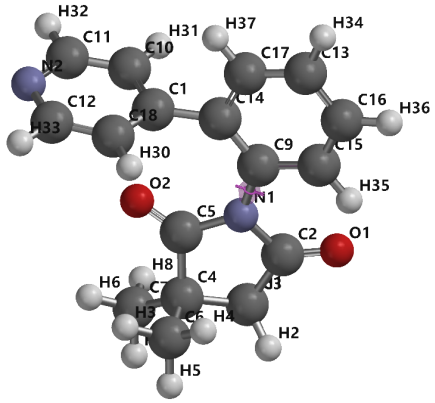

| | | | |
|---|---|---|---|
| N1 | 0.217425013 0.790065647 1.136475050 | N1 | 0.269789301 0.756025233 1.138079618 |
| C2 | 0.275476813 1.212860932 2.525047650 | C2 | 0.410053187 1.151327982 2.510298022 |
| C3 | 0.013832136 0.008658410 3.396696361 | C3 | 0.048705588 -0.014628327 3.395830304 |
| C4 | -0.579141379 -1.053746483 2.477455222 | C4 | -0.582449188 -1.057268057 2.480717246 |
| C5 | -0.194962434 -0.549361363 1.094325756 | C5 | -0.116115188 -0.603941699 1.107311666 |
| O1 | 0.508138246 2.315587622 2.929406638 | O1 | 0.789287365 2.219327548 2.922457830 |
| O2 | -0.278672189 -1.227866396 0.093565723 | O2 | -0.101369712 -1.317697460 0.133475528 |
| C1 | 0.237961910 -0.086479882 -1.997295183 | C1 | 0.286938202 -0.101612085 -2.006902665 |
| C8 | -0.427565050 -2.401151757 -3.404731629 | C8 | -0.413268687 -2.390873140 -3.422562505 |
| C18 | -1.062886260 -0.340423142 -2.409504684 | C18 | -1.032184760 -0.379805916 -2.332911694 |
| C10 | 1.225246395 -1.000660210 -2.387087907 | C10 | 1.270449961 -0.981416804 -2.469927102 |
| C11 | 0.891565361 -2.163641382 -3.076673851 | C11 | 0.919335844 -2.134596726 -3.167225672 |
| N2 | -1.353951515 -1.476260631 -3.072805321 | N2 | -1.337007440 -1.502150856 -3.007240909 |
| C9 | 0.551698336 1.627403801 -0.001946218 | C9 | 0.560388704 1.607664581 -0.003235309 |
| C13 | 1.315236441 3.463939862 -2.049141395 | C13 | 1.266217953 3.479343350 -2.037518447 |
| C14 | 0.580749866 1.224819508 -1.368201413 | C14 | 0.628222107 1.205123499 -1.367002399 |
| C15 | 0.896663357 2.965377339 0.268928332 | C15 | 0.792779495 2.970417926 0.266805083 |
| C16 | 1.267871705 3.862110493 -0.722823123 | C16 | 1.136151069 3.885876157 -0.718358860 |
| C17 | 0.969066156 2.156441459 -2.346828170 | C17 | 0.998831116 2.153162687 -2.336851760 |
| H2 | -2.318753241 -1.644748920 -3.334261999 | H2 | -2.313109777 -1.686032848 -3.216772561 |
| H31 | -0.777475930 -3.277686325 -3.932205969 | H31 | -0.778983327 -3.258799948 -3.952751888 |
| H32 | -1.887556190 0.326600092 -2.200201123 | H32 | -1.860985329 0.256598873 -2.057070695 |
| H33 | 2.257823002 -0.804056123 -2.124211939 | H33 | 2.313025127 -0.769443848 -2.265183240 |
| H34 | 1.646865596 -2.886461117 -3.357418728 | H34 | 1.670473894 -2.833256587 -3.511728176 |
| H35 | 1.609436507 4.147478980 -2.837013092 | H35 | 1.548721553 4.173205324 -2.821091544 |
| H36 | 0.877465202 3.315227552 1.284677658 | H36 | 0.719364897 3.324864445 1.277620196 |
| H37 | 1.522384752 4.876943411 -0.439187105 | H37 | 1.304036621 4.919327251 -0.435656603 |
| H38 | 0.989391433 1.827576033 -3.380707666 | H38 | 1.052272323 1.821474300 -3.368055015 |
| H1 | -0.620718174 0.303641995 4.232777652 | H1 | -0.595878075 0.333413441 4.204006350 |
| H3 | 0.976605507 -0.302220757 3.815254756 | H3 | 0.977846370 -0.376206040 3.846772597 |
| C6 | -2.121870896 -1.063988154 2.540376905 | C6 | -2.124063178 -0.962344165 2.487759205 |
| H4 | -2.531861869 -1.738832580 1.786335747 | H4 | -2.553386343 -1.633257298 1.740320854 |
| H5 | -2.541145461 -0.067096810 2.376897147 | H5 | -2.467579190 0.054453946 2.279062434 |
| H6 | -2.449194651 -1.409268270 3.523295484 | H6 | -2.499749271 -1.252387042 3.471727655 |
| C7 | -0.023924468 -2.464792611 2.697035606 | C7 | -0.129544649 -2.493141876 2.755059251 |
| H7 | 1.067053318 -2.482291922 2.633614832 | H7 | 0.958953998 -2.580254336 2.712628175 |
| H8 | -0.415881167 -3.151731142 1.945689433 | H8 | -0.555749704 -3.177640861 2.019508528 |
| H9 | -0.312396337 -2.831967161 3.684390456 | H9 | -0.460420962 -2.804850571 3.748606504 |

**Table S8.** The GS structure of rotor **1**(4-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



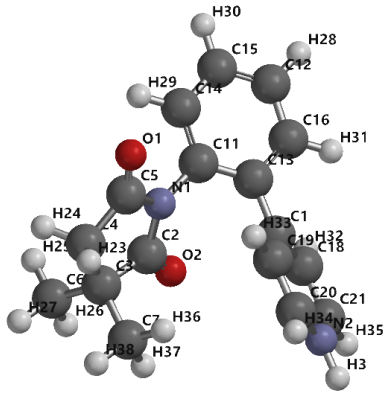

| | | | |
|---|---|---|---|
| N1 | -0.806206936 -0.396631993 0.686564976 | N1 | -0.786266308 -0.368711984 0.685929558 |
| C2 | 0.440982253 -0.990673368 0.928384371 | C2 | 0.460153510 -0.948648616 0.940403351 |
| C3 | 1.037469997 -0.378241010 2.197643534 | C3 | 1.019872916 -0.370745797 2.237421854 |
| C4 | -0.073022738 0.563390564 2.705767249 | C4 | -0.120498400 0.530207759 2.754549620 |
| C5 | -1.144919448 0.581046632 1.630734219 | C5 | -1.179469756 0.537149286 1.674872565 |
| C6 | 2.303409355 0.389550895 1.778802636 | C6 | 2.278104103 0.437915366 1.873929754 |
| C7 | 1.381519234 -1.501456498 3.183803195 | C7 | 1.363909732 -1.517878910 3.197005432 |
| O1 | 0.950635809 -1.823565858 0.223038036 | O1 | 0.992785091 -1.757815989 0.215841255 |
| O2 | -2.116559355 1.290444033 1.566180145 | O2 | -2.196209183 1.191741401 1.632644773 |
| C1 | 0.056523914 0.731938776 -1.795042620 | C1 | 0.080406043 0.727908007 -1.834590142 |
| N2 | 2.309554677 2.417039076 -1.881745168 | N2 | 2.343631985 2.395817296 -2.005769229 |
| C18 | 1.221295173 0.346596590 -2.459019189 | C18 | 1.193228407 0.361796391 -2.594677172 |
| C10 | 0.046668830 1.987064841 -1.178596343 | C10 | 0.127405968 1.957711194 -1.170461473 |
| C11 | 1.185984019 2.782676747 -1.255092577 | C11 | 1.267615421 2.746087193 -1.288445102 |
| C12 | 2.308794308 1.217361136 -2.469929801 | C12 | 2.288377296 1.219975781 -2.644478500 |
| C9 | -1.568463500 -0.666275077 -0.494160241 | C9 | -1.547011670 -0.645966756 -0.495111955 |
| C13 | -2.977476648 -1.304156725 -2.799712249 | C13 | -2.971670793 -1.303687643 -2.787464857 |
| C14 | -1.128318275 -0.160921486 -1.724448855 | C14 | -1.109189414 -0.155350686 -1.734055240 |
| C15 | -2.703125484 -1.466328844 -0.412282810 | C15 | -2.68487493 -1.442536725 -0.398142519 |
| C16 | -3.415927749 -1.778474696 -1.565834730 | C16 | -3.406139216 -1.763407306 -1.545218505 |
| C17 | -1.840478021 -0.504730209 -2.876818659 | C17 | -1.829928232 -0.511508451 -2.879610711 |
| H22 | 0.264300473 1.585518541 2.886530566 | H22 | 0.190672008 1.556961726 2.954810788 |
| H23 | -0.532516858 0.210967039 3.633566206 | H23 | -0.577095899 0.145762209 3.670476316 |
| H24 | 2.070555305 1.182517977 1.063610761 | H24 | 2.040349811 1.241331116 1.171879981 |
| H25 | 2.777056930 0.841942726 2.654162960 | H25 | 2.707343009 0.879704955 2.776340096 |
| H26 | 3.016584840 -0.287105987 1.305135658 | H26 | 3.025151204 -0.209917316 1.411192567 |
| H27 | 1.841056766 -1.088616174 4.085885833 | H27 | 1.779457986 -1.116090806 4.124318166 |
| H28 | 0.488176211 -2.058836344 3.480268565 | H28 | 0.475710167 -2.105846764 3.444574921 |
| H29 | 2.079872905 -2.205380031 2.727950179 | H29 | 2.101532222 -2.184111412 2.745495193 |
| H30 | 1.287388541 -0.628014796 -2.929318872 | H30 | 1.214307461 -0.585468192 -3.121617537 |
| H31 | -0.836373553 2.330742127 -0.650586963 | H31 | -0.715036769 2.300043158 -0.580074482 |
| H32 | 1.198200814 3.764207742 -0.787401785 | H32 | 1.319589794 3.705309605 -0.780540975 |
| H33 | 3.230564750 0.931656557 -2.970681514 | H33 | 3.166596994 0.946298215 -3.223274244 |
| H34 | -3.524744938 -1.551310839 -3.703568755 | H34 | -3.524252004 -1.557800487 -3.685890903 |
| H35 | -3.015857206 -1.845366452 0.554002563 | H35 | -2.991296694 -1.813683893 0.573261756 |
| H36 | -4.304721743 -2.397005117 -1.501982673 | H36 | -4.296363014 -2.378291390 -1.469659737 |
| H37 | -1.507882652 -0.121570497 -3.83580785 | H37 | -1.500898847 -0.144251536 -3.845864664 |

**Table S9.** The TS structure of rotor **1**(4-Py) in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



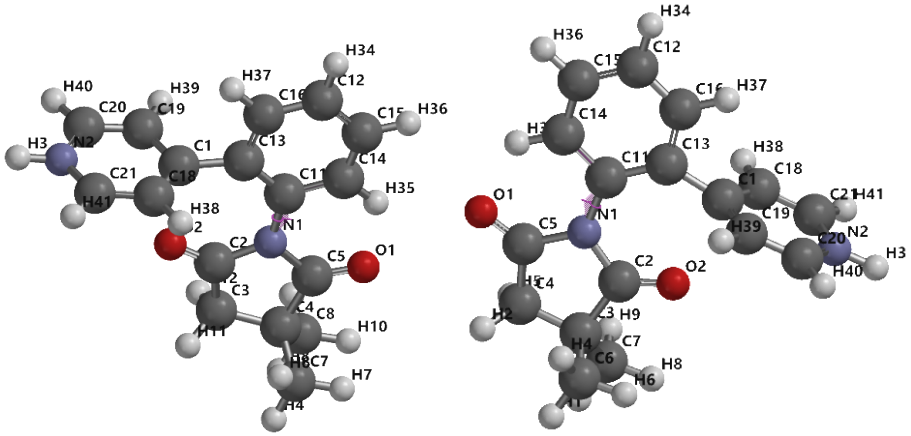

| | | | |
|---|---|---|---|
| N1 | -0.249635531 0.885262648 0.854937501 | N1 | -0.234519150 0.882771116 0.854652434 |
| C2 | -0.440221826 1.579167197 2.087186789 | C2 | -0.403650190 1.585652541 2.081373600 |
| C3 | 0.005256305 0.682054832 3.225839345 | C3 | -0.006461890 0.678160591 3.223971717 |
| C4 | 0.254462490 -0.687566522 2.602221378 | C4 | 0.251379585 -0.690982662 2.595706141 |
| C5 | 0.451575736 -0.323970490 1.133780316 | C5 | 0.485098724 -0.312474584 1.141226648 |
| O1 | -0.854143349 2.700144940 2.238605133 | O1 | -0.763231555 2.731873618 2.212948982 |
| O2 | 1.093487780 -0.970785604 0.354442671 | O2 | 1.174815541 -0.921260720 0.366511629 |
| C1 | 0.493096454 -0.360360212 -2.060990345 | C1 | 0.508305582 -0.350237310 -2.059648861 |
| N2 | 1.895877433 -2.615957713 -2.998023200 | N2 | 1.878950482 -2.624598586 -3.003657061 |
| C18 | -0.129143944 -1.603894651 -2.180663970 | C18 | -0.109268019 -1.602139007 -2.106537832 |
| C10 | 1.823984553 -0.267307293 -2.464166493 | C10 | 1.815485138 -0.259857640 -2.537930777 |
| C11 | 2.474649353 -1.414588187 -2.908492504 | C11 | 2.453143981 -1.414162322 -2.982115154 |
| C12 | 0.610938623 -2.688259050 -2.638633885 | C12 | 0.611791334 -2.695058912 -2.572737307 |
| C9 | -0.676634233 1.383530830 -0.442957556 | C9 | -0.670145248 1.375115389 -0.437358254 |
| C13 | -1.670507064 2.568776961 -2.826656847 | C13 | -1.650902323 2.585425444 -2.815537870 |
| C14 | -0.310415807 0.852636914 -1.708770419 | C14 | -0.283862550 0.868670711 -1.706723119 |
| C15 | -1.577340619 2.467544026 -0.427018230 | C15 | -1.606546419 2.428876440 -0.416404633 |
| C16 | -2.064573862 3.049839817 -1.586933820 | C16 | -2.087559206 3.024904482 -1.572899316 |
| C17 | -0.814822711 1.480819166 -2.861848568 | C17 | -0.774775187 1.512645444 -2.857722772 |
| H30 | -1.172800275 -1.726751993 -1.910181579 | H30 | -1.134594945 -1.727556088 -1.775713655 |
| H31 | 2.350518801 0.679315615 -2.416249029 | H31 | 2.335735575 0.691006898 -2.552098493 |
| H32 | 3.517459020 -1.366567064 -3.213817378 | H32 | 3.476973971 -1.364621274 -3.344481472 |
| H33 | 0.145661474 -3.667695785 -2.727892316 | H33 | 0.147400799 -3.677702187 -2.607466577 |
| H34 | -2.031861734 3.013754033 -3.747609019 | H34 | -2.001894876 3.044271312 -3.733372855 |
| H35 | -1.890007814 2.881188050 0.514359631 | H35 | -1.960756792 2.804787157 0.526602416 |
| H36 | -2.752532257 3.884835100 -1.505934487 | H36 | -2.804911831 3.834344591 -1.488585763 |
| H37 | -0.521745756 1.063206943 -3.818739071 | H37 | -0.464178018 1.118543834 -3.819220810 |
| H1 | 0.917501320 1.111787449 3.650394112 | H1 | 0.895644200 1.094346038 3.681398279 |
| H2 | -0.755491014 0.701000274 4.008772170 | H2 | -0.794918479 0.689689829 3.979106065 |
| C6 | -1.002264530 -1.581151763 2.677759656 | C6 | -1.013103884 -1.577912583 2.635337869 |
| H3 | -0.863396958 -2.494792521 2.095224988 | H3 | -0.863774551 -2.492544617 2.056499251 |
| H4 | -1.889279265 -1.067523209 2.296943439 | H4 | -1.886022777 -1.056690894 2.234098928 |
| H5 | -1.195069593 -1.863281443 3.716091042 | H5 | -1.227238172 -1.855725790 3.670181520 |
| C7 | 1.474872033 -1.428892556 3.145071335 | C7 | 1.452055438 -1.438609837 3.172070696 |
| H6 | 1.655166394 -2.340217120 2.572561431 | H6 | 1.629251881 -2.364150702 2.620512173 |
| H7 | 1.320685557 -1.700241836 4.192747383 | H7 | 1.266059940 -1.691710465 4.218591544 |
| H8 | 2.376694765 -0.815059731 3.078640399 | H8 | 2.360223889 -0.833089413 3.119422584 |

**Table S10.** The GS structure of rotor **1**(4-Py)•$H^+$ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).




| | | | |
|---|---|---|---|
| N1 | 1.215212548 -0.163959449 0.074382964 | N1 | 1.221352037 -0.105651867 0.068784530 |
| C2 | 0.532586709 0.695595662 0.951424338 | C2 | 0.668177857 0.840616170 0.942603360 |
| C3 | 0.863963972 0.302295813 2.390459504 | C3 | 0.873848214 0.360469273 2.378569041 |
| C4 | 1.911733112 -0.817641207 2.239350775 | C4 | 1.789905328 -0.870006589 2.222213443 |
| C5 | 2.031208515 -1.103941415 0.757217983 | C5 | 1.861047964 -1.159527621 0.741386647 |
| O1 | 2.676736619 -1.954084880 0.209604425 | O1 | 2.363850131 -2.108192893 0.187767289 |
| O2 | -0.231968976 1.561219717 0.598953553 | O2 | 0.090262032 1.839396115 0.581014726 |
| C6 | 1.395235008 1.534181973 3.136689250 | C6 | 1.501986874 1.482396103 3.212516144 |
| C11 | 1.185468588 -0.038603287 -1.344756356 | C11 | 1.189729878 0.019409229 -1.353784754 |
| C12 | 1.174975217 0.397748553 -4.108358947 | C12 | 1.171177880 0.398897937 -4.115389084 |
| C13 | -0.037740068 0.060131528 -2.034926725 | C13 | -0.034546885 0.037320610 -2.041677885 |
| C14 | 2.384966631 0.058922794 -2.045087008 | C14 | 2.388372318 0.175077394 -2.044185036 |
| C15 | 2.379412693 0.259107376 -3.422173899 | C15 | 2.381078766 0.349900546 -3.425500625 |
| C16 | -0.024119651 0.311395829 -3.414938001 | C16 | -0.027473773 0.254831446 -3.425356441 |
| C1 | -1.332259892 -0.145909774 -1.372180949 | C1 | -1.324115523 -0.204074635 -1.361259626 |
| N2 | -3.783975824 -0.570996036 -0.188864184 | N2 | -3.7429697 -0.680750555 -0.151753113 |
| C18 | -2.393667836 0.759850026 -1.553020534 | C18 | -2.394422709 0.689686478 -1.515016340 |
| C19 | -1.569448435 -1.285045843 -0.578316193 | C19 | -1.525139712 -1.352902100 -0.580490413 |
| C20 | -2.799189097 -1.478511087 0.003184611 | C20 | -2.746892197 -1.572328810 0.017416362 |
| C21 | -3.607333693 0.533192622 -0.951478952 | C21 | -3.599542125 0.432244512 -0.898456749 |
| H3 | -4.684338024 -0.724790438 0.249011379 | H3 | -4.635750696 -0.855493492 0.298408513 |
| C7 | -0.436882307 -0.203874508 3.040250438 | C7 | -0.508142744 -0.029552362 2.936687525 |
| H23 | 1.649538118 -1.740907683 2.759721375 | H23 | 1.431741016 -1.756720113 2.747850610 |
| H24 | 2.899632979 -0.524427794 2.603859995 | H24 | 2.808781298 -0.677996315 2.570324945 |
| H25 | 2.309142076 1.917068630 2.674995356 | H25 | 2.469093715 1.785221078 2.802703978 |
| H26 | 0.653953449 2.334627836 3.131693206 | H26 | 0.847502494 2.355677903 3.232713748 |
| H27 | 1.622162814 1.276864549 4.173742461 | H27 | 1.656591917 1.139365074 4.238082739 |
| H28 | 1.168784620 0.564807366 -5.179282466 | H28 | 1.158290884 0.545063384 -5.189756045 |
| H29 | 3.320648527 -0.023219053 -1.508392227 | H29 | 3.320708214 0.168582619 -1.492806184 |
| H30 | 3.320091240 0.321632594 -3.957029638 | H30 | 3.318477807 0.461179730 -3.958726070 |
| H31 | -0.963643760 0.387171306 -3.952929625 | H31 | -0.968399919 0.273550586 -3.964918586 |
| H32 | -2.251571700 1.661863450 -2.132930373 | H32 | -2.285218906 1.593261711 -2.099868382 |
| H33 | -0.797766757 -2.031366044 -0.443364438 | H33 | -0.742828617 -2.089545338 -0.456163392 |
| H34 | -3.044813255 -2.339518552 0.610473917 | H34 | -2.969995932 -2.438488649 0.624722658 |
| H35 | -4.451976304 1.203567371 -1.038279525 | H35 | -4.460433049 1.082511791 -0.968339586 |
| H36 | -0.829095633 -1.084472302 2.519733116 | H36 | -0.957887275 -0.837468434 2.353112390 |
| H37 | -1.201485136 0.575018415 3.021982155 | H37 | -1.185045494 0.826683585 2.918146274 |
| H38 | -0.254177088 -0.484994058 4.079579237 | H38 | -0.403171371 -0.372643501 3.968423390 |

**Table S11.** The TS structure of rotor **1**(4-Py)•$H^+$ in solvent and the XYZ coordinates in gas phase (left) and in solvent (right).



| | | | |
|---|---|---|---|
| N1 | 0.283850500 0.937747087 0.160057111 | N1 | 0.138365601 1.417996688 0.160136779 |
| C2 | 0.601981353 -0.056564251 1.084435364 | C2 | 0.467606107 0.426635313 1.101584002 |
| C3 | 1.305370774 0.538709881 2.273589552 | C3 | 1.232366278 1.014509399 2.274080835 |
| C4 | 1.121765973 2.049164466 2.145189609 | C4 | 1.007886985 2.512834405 2.102867840 |
| C5 | 0.676648202 2.226465279 0.697194905 | C5 | 0.480862512 2.701120087 0.703408808 |
| O1 | 0.633940414 3.275598402 0.120854345 | O1 | 0.356800893 3.772245216 0.164070707 |
| O2 | 0.370173502 -1.240546246 0.944585785 | O2 | 0.211610660 -0.750435315 0.989265169 |
| C11 | -0.323395172 0.715113654 -1.133866336 | C11 | -0.452391213 1.186073387 -1.144612025 |
| C12 | -1.492452424 0.511527313 -3.720331163 | C12 | -1.591571702 0.996980785 -3.750605240 |
| C13 | -0.704702834 -0.550200137 -1.656635537 | C13 | -0.846320181 -0.074739307 -1.670557853 |
| C14 | -0.553880419 1.840740382 -1.946189279 | C14 | -0.644222934 2.310439058 -1.971373327 |
| C15 | -1.124679143 1.745662575 -3.207344926 | C15 | -1.198568308 2.225160148 -3.240840502 |
| C16 | -1.276969234 -0.611973242 -2.939503114 | C16 | -1.406681774 -0.125462983 -2.959996702 |
| C1 | -0.620912752 -1.920629834 -1.063384944 | C1 | -0.773466747 -1.455941781 -1.096796101 |
| N2 | -0.666123967 -4.585838392 -0.366129765 | N2 | -0.808502648 -4.114862659 -0.413275136 |
| C18 | -1.740218285 -2.486103028 -0.420083680 | C18 | -1.897383499 -2.025045683 -0.477394118 |
| C19 | 0.436290207 -2.783366740 -1.415525655 | C19 | 0.306573585 -2.295109187 -1.414447629 |
| C20 | 0.403363887 -4.102464617 -1.041306984 | C20 | 0.273867355 -3.620687569 -1.050026210 |
| C21 | -1.734750745 -3.810246389 -0.064108604 | C21 | -1.888120773 -3.355565596 -0.130975942 |
| H3 | -0.678112098 -5.562324978 -0.099908007 | H3 | -0.819830321 -5.095852862 -0.156785110 |
| H34 | -1.937605244 0.416510241 -4.703975751 | H34 | -2.028740240 0.904564296 -4.738444063 |
| H35 | -0.271915257 2.813834199 -1.586593417 | H35 | -0.352673459 3.279856696 -1.612475674 |
| H36 | -1.274253863 2.651644988 -3.783598681 | H36 | -1.316557954 3.132611642 -3.822841951 |
| H37 | -1.562690566 -1.584771732 -3.326359722 | H37 | -1.702474593 -1.095506627 -3.344958879 |
| H38 | -2.601889407 -1.875736521 -0.185245857 | H38 | -2.769704170 -1.425181896 -0.255240855 |
| H39 | 1.289405164 -2.407654308 -1.964402631 | H39 | 1.174265856 -1.909208443 -1.932514282 |
| H40 | 1.194030391 -4.806665700 -1.263445075 | H40 | 1.075134764 -4.318454259 -1.250466126 |
| H41 | -2.555030795 -4.294798221 0.448771430 | H41 | -2.712900724 -3.853906930 0.359707800 |
| C7 | -0.037756764 2.550743480 3.031418831 | H2 | 1.902115113 3.123535222 2.232279591 |
| H4 | 0.236866318 2.456719487 4.084359399 | H5 | 0.245048792 2.895769478 2.787281045 |
| H6 | -0.951247259 1.971271038 2.866628290 | C6 | 2.714246615 0.629205204 2.080400641 |
| H7 | -0.255085706 3.599016650 2.822642710 | H1 | 3.306162631 1.044640469 2.898931260 |
| C8 | 2.397616295 2.856977642 2.401392855 | H4 | 3.110514909 1.017985291 1.138283890 |
| H1 | 3.220216986 2.516793018 1.766533019 | H6 | 2.828967516 -0.456618149 2.080828789 |
| H8 | 2.705794159 2.750493758 3.443830421 | C7 | 0.692701445 0.449613654 3.591926670 |
| H10 | 2.228734968 3.914040861 2.194988083 | H7 | 1.241260695 0.883090615 4.431272164 |
| H11 | 0.901123522 0.102765912 3.188431463 | H8 | 0.811729634 -0.634727890 3.622564541 |
| H12 | 2.356499373 0.238343810 2.213036009 | H9 | -0.367976760 0.682440136 3.715737245 |

## 6. Energy Decomposition Analyses I

The intramolecular interaction energies between the imide carbonyl groups (C=O) and the aromatic gates (phenyl, pyridyl, and pyridinium) for the optimized (B3LYP-D3/6-311G*) transition states were calculated by functional group interaction analysis method, FI-SAPT (SAPT(0), jun-cc-pVZT) as implemented in Psi4.[2]

**Table S12.** FI-SAPT total and component energies.

| Rotor | $E_{total}$ | $E_{exch}$ | $E_{elst}$ | $E_{ind}$ | $E_{disp}$ |
|---|---|---|---|---|---|
| phenyl | 13.57 | 20.86 | 0.74 | -4.09 | -3.94 |
| 3-pyridyl | 12.63 | 21.64 | -1.04 | -4.02 | -3.95 |
| 4-pyridyl | 11.60 | 20.51 | -0.67 | -4.23 | -4.01 |
| 3-pyridinium | -4.64 | 20.89 | -16.59 | -4.76 | -4.18 |
| 4-pyridinium | -8.04 | 20.97 | -18.06 | -6.50 | -4.44 |

## 7. Reversibility study

To test the reversibility of the rotors, a sample of rotor **1**(3-Py) was titrated with methanesulfonic acid in TCE-d2 and then neutralized with sodium bicarbonate through four cycles (Figure S11**)**. Changes in the rate of rotation were followed by rate of exchange of the succinimide methylene ($CH_2$) protons in the $^1$H NMR spectra at 25 °C (Figure S11). In the unprotonated pyridyl rotors (0 equiv MsOH), slow rotation was observed as seen by the separate diastereotopic methylene which were two doublets. When methanesulfonic acid (3.0 equiv) was added to form the pyridinium rotors, the rate of rotation increased dramatically and the methylene peaks coalesced into a singlet. The pyridinium rotors were neutralized by washing the solution with aqueous sodium bicarbonate powder. The methylene protons cleanly reverted to the slowly rotating diastereomeric pair of doublets. This process was repeated through 4 cycles and the spectra cleanly showed the transition from slowly rotating **1**(3-Py) to quickly rotating **1**(3-Py)$H^+$ without degradation and the appearance of additional peaks.

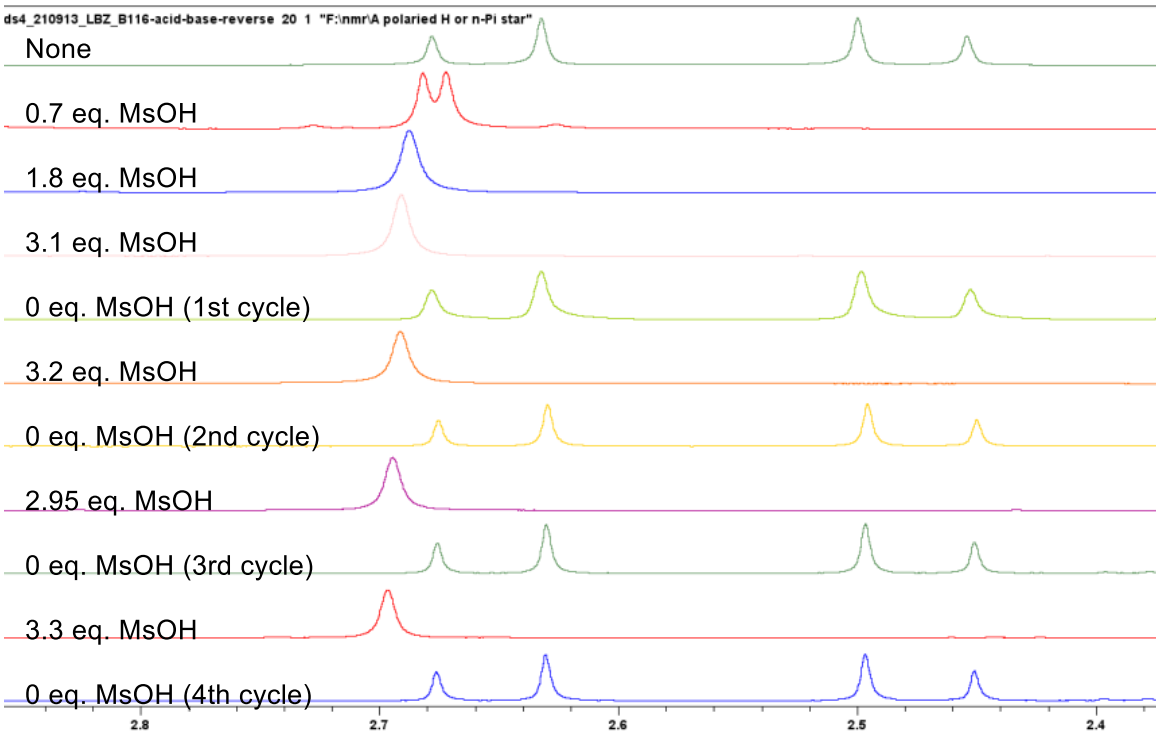
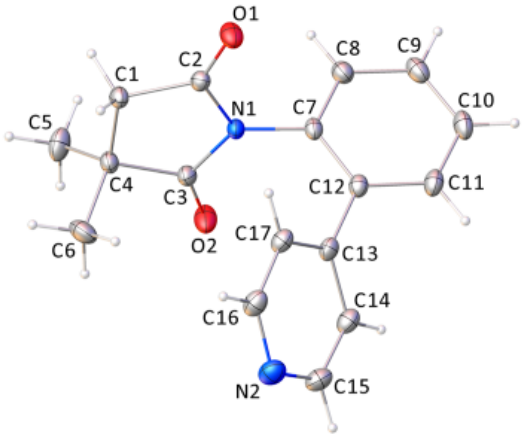



**Figure S11** $^{1}$H NMR spectra of rotor **1(3-Py)** with various equiv. of MsOH in TCE-d2 at 25 °C.

## 8. Crystallographic structures

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[3,4] The structure was solved with SHELXT.[5] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2018[4] using OLEX2.[5]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_1/n$, which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d$(C-H) = 0.95 Å and $U$iso(H) = 1.2$U$eq(C) for arene hydrogen atoms, $d$(C-H) = 0.99 Å and $U$iso(H) = 1.2$U$eq(C) for methylene hydrogen atoms, and $d$(C-H) = 0.98 Å and $U$iso(H) = 1.5$U$eq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is 0.36 $e^-$/Å$^3$, located 0.76 Å from C4.




**X-Ray Structure Determination of 1 (4-Py) ($C_{17}H_{16}N_2O_2$)**

X-ray intensity data from a colorless needle were collected at 100(2) K using a Bruker D8 QUEST diffractometer equipped with a PHOTON-II area detector and an Incoatec microfocus source (Mo Kα radiation, λ = 0.71073 Å). The raw area detector data frames were reduced, scaled and corrected for absorption effects using the Bruker APEX3, SAINT+ and SADABS programs.[3,4] The structure was solved with SHELXT.[5] Subsequent difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXL-2018[3] using OLEX2.[6]

The compound crystallizes in the monoclinic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $P2_1/n$, which was confirmed by structure solution. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were located in difference Fourier maps before being placed in geometrically idealized positions and included as riding atoms with $d$(C-H) = 0.95 Å and $U$iso(H) = 1.2$U$eq(C) for arene hydrogen atoms, $d$(C-H) = 0.99 Å and $U$iso(H) = 1.2$U$eq(C) for methylene hydrogen atoms, and $d$(C-H) = 0.98 Å and $U$iso(H) = 1.5$U$eq(C) for methyl hydrogens. The methyl hydrogens were allowed to rotate as a rigid group to the orientation of maximum observed electron density. The largest residual electron density peak in the final difference map is 0.36 $e^-/Å^3$, located 0.76 Å from C4.

**Table S13** Crystal data and structure refinement for rotor **1 (4-Py).**

| | |
|---|---|
| Identification code | lbz_b130 |
| Empirical formula | $C_{17}H_{16}N_2O_2$ |
| Formula weight | 280.32 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 5.8248(4) |
| b/Å | 28.7309(17) |
| c/Å | 8.8878(5) |
| α/° | 90 |
| β/° | 106.165(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 1428.58(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.303 |
| μ/mm$^{-1}$ | 0.087 |
| F(000) | 592.0 |
| Crystal size/mm$^3$ | 0.26 × 0.05 × 0.03 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.978 to 61.046 |
| Index ranges | $-8 \le h \le 8$, $-41 \le k \le 40$, $-11 \le l \le 12$ |
| Reflections collected | 72974 |
| Independent reflections | 4356 [$R_{int}$ = 0.0413, $R_{sigma}$ = 0.0160] |
| Data/restraints/parameters | 4356/0/193 |
| Goodness-of-fit on F$^2$ | 1.040 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0395, $wR_2$ = 0.0977 |
| Final R indexes [all data] | $R_1$ = 0.0470, $wR_2$ = 0.1024 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.21 |

**Table S14** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for lbz_b130. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O1 | 770.5(13) | 4097.2(2) | -294.8(9) | 23.23(16) |
| O2 | 7207.9(14) | 3289.1(3) | 2626.5(10) | 27.57(18) |
| N1 | 4222.3(14) | 3785.8(3) | 1335.1(9) | 14.27(15) |
| N2 | 3131.0(17) | 3549.4(3) | 6746.0(10) | 25.05(19) |
| C1 | 1353.4(17) | 3255.7(3) | -82.9(11) | 17.60(18) |
| C2 | 1962.3(16) | 3762.5(3) | 250.9(10) | 15.23(17) |
| C3 | 5221.7(17) | 3348.9(3) | 1763.4(11) | 16.50(17) |
| C4 | 3440.4(16) | 2974.8(3) | 965.9(11) | 16.43(17) |
| C5 | 4659.0(19) | 2656.6(4) | 42.5(14) | 27.1(2) |
| C6 | 2677(2) | 2702.0(4) | 2226.8(13) | 26.8(2) |
| C7 | 5435.1(16) | 4212.4(3) | 1910.0(11) | 15.41(17) |
| C8 | 6431.1(17) | 4464.7(3) | 917.9(11) | 19.19(19) |
| C9 | 7639.0(18) | 4878.6(3) | 1429.4(13) | 22.2(2) |
| C10 | 7846.4(18) | 5034.6(3) | 2937.1(13) | 22.7(2) |
| C11 | 6916.0(17) | 4773.8(3) | 3944.4(12) | 20.54(19) |
| C12 | 5675.7(16) | 4358.1(3) | 3454.0(11) | 16.12(17) |
| C13 | 4744.2(16) | 4085.0(3) | 4574.2(11) | 16.52(17) |
| C14 | 6217.8(17) | 3992.1(3) | 6078.7(11) | 20.04(19) |
| C15 | 5345.6(19) | 3727.3(4) | 7098.8(12) | 23.4(2) |
| C16 | 1705.4(18) | 3649.1(4) | 5314.1(12) | 21.6(2) |
| C17 | 2411.7(17) | 3912.7(3) | 4210.0(11) | 18.34(18) |

**Table S15** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for lbz_b130. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11+2hka^*b^*U12+\ldots]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O1 | 19.0(3) | 17.3(3) | 28.9(4) | 2.0(3) | -0.7(3) | 2.1(3) |
| O2 | 22.8(4) | 18.3(3) | 32.5(4) | -0.8(3) | -7.6(3) | 2.7(3) |
| N1 | 15.0(3) | 11.5(3) | 15.0(3) | -0.9(2) | 2.1(3) | -0.6(3) |
| N2 | 26.0(4) | 30.3(5) | 19.9(4) | -1.0(3) | 8.0(3) | -2.3(4) |
| C1 | 17.9(4) | 14.3(4) | 18.3(4) | 0.0(3) | 1.3(3) | -2.6(3) |
| C2 | 14.5(4) | 15.5(4) | 15.2(4) | -0.1(3) | 3.4(3) | -1.3(3) |
| C3 | 19.0(4) | 13.2(4) | 15.9(4) | -0.4(3) | 2.5(3) | 0.6(3) |
| C4 | 17.6(4) | 12.3(4) | 18.4(4) | -0.5(3) | 3.3(3) | -0.6(3) |
| C5 | 23.6(5) | 22.6(5) | 34.6(6) | -12.4(4) | 7.1(4) | 0.4(4) |
| C6 | 29.0(5) | 21.8(5) | 28.6(5) | 9.8(4) | 6.5(4) | -1.3(4) |
| C7 | 13.8(4) | 12.1(4) | 18.8(4) | -0.9(3) | 2.0(3) | -0.3(3) |
| C8 | 19.1(4) | 17.0(4) | 20.5(4) | 1.9(3) | 4.1(3) | -0.8(3) |
| C9 | 18.9(4) | 17.0(4) | 29.6(5) | 4.7(4) | 4.9(4) | -1.4(3) |
| C10 | 17.6(4) | 14.8(4) | 33.0(5) | -2.2(4) | 2.4(4) | -2.8(3) |
| C11 | 17.6(4) | 17.6(4) | 24.0(5) | -5.4(3) | 1.8(3) | -1.5(3) |
| C12 | 13.3(4) | 14.9(4) | 19.0(4) | -1.8(3) | 2.5(3) | -0.2(3) |
| C13 | 15.9(4) | 16.3(4) | 17.1(4) | -4.3(3) | 4.2(3) | 0.2(3) |
| C14 | 16.4(4) | 23.4(4) | 18.6(4) | -4.2(3) | 2.0(3) | -0.4(3) |
| C15 | 22.9(5) | 29.2(5) | 16.4(4) | -1.4(4) | 2.7(4) | 0.8(4) |
| C16 | 18.4(4) | 26.7(5) | 20.5(4) | -4.5(4) | 6.5(4) | -3.4(4) |
| C17 | 15.3(4) | 21.8(4) | 17.1(4) | -3.8(3) | 3.2(3) | -0.6(3) |

**Table S16** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for lbz_b130.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1A | 1165.29 | 3185.25 | -1201.11 | 21 |
| H1B | -157.9 | 3177.99 | 163.66 | 21 |
| H5A | 3546.79 | 2410.78 | -467.46 | 41 |
| H5B | 6081.07 | 2515.92 | 757.75 | 41 |
| H5C | 5130.11 | 2839.09 | -754.58 | 41 |
| H6A | 1876.03 | 2912.11 | 2787.65 | 40 |
| H6B | 4091.39 | 2566.68 | 2966.74 | 40 |
| H6C | 1576.78 | 2452.64 | 1732.8 | 40 |
| H8 | 6288.71 | 4354.79 | -112.23 | 23 |
| H9 | 8315.83 | 5052.73 | 750.46 | 27 |
| H10 | 8628.95 | 5321.22 | 3282.69 | 27 |
| H11 | 7124.31 | 4879.29 | 4986.89 | 25 |
| H14 | 7804.07 | 4109.75 | 6397.42 | 24 |
| H15 | 6380.91 | 3667.88 | 8112.9 | 28 |
| H16 | 116.99 | 3532.32 | 5039.18 | 26 |
| H17 | 1319.43 | 3975.09 | 3217.53 | 22 |

## 9. Variable Temperature NMR Spectra of the Rotors.

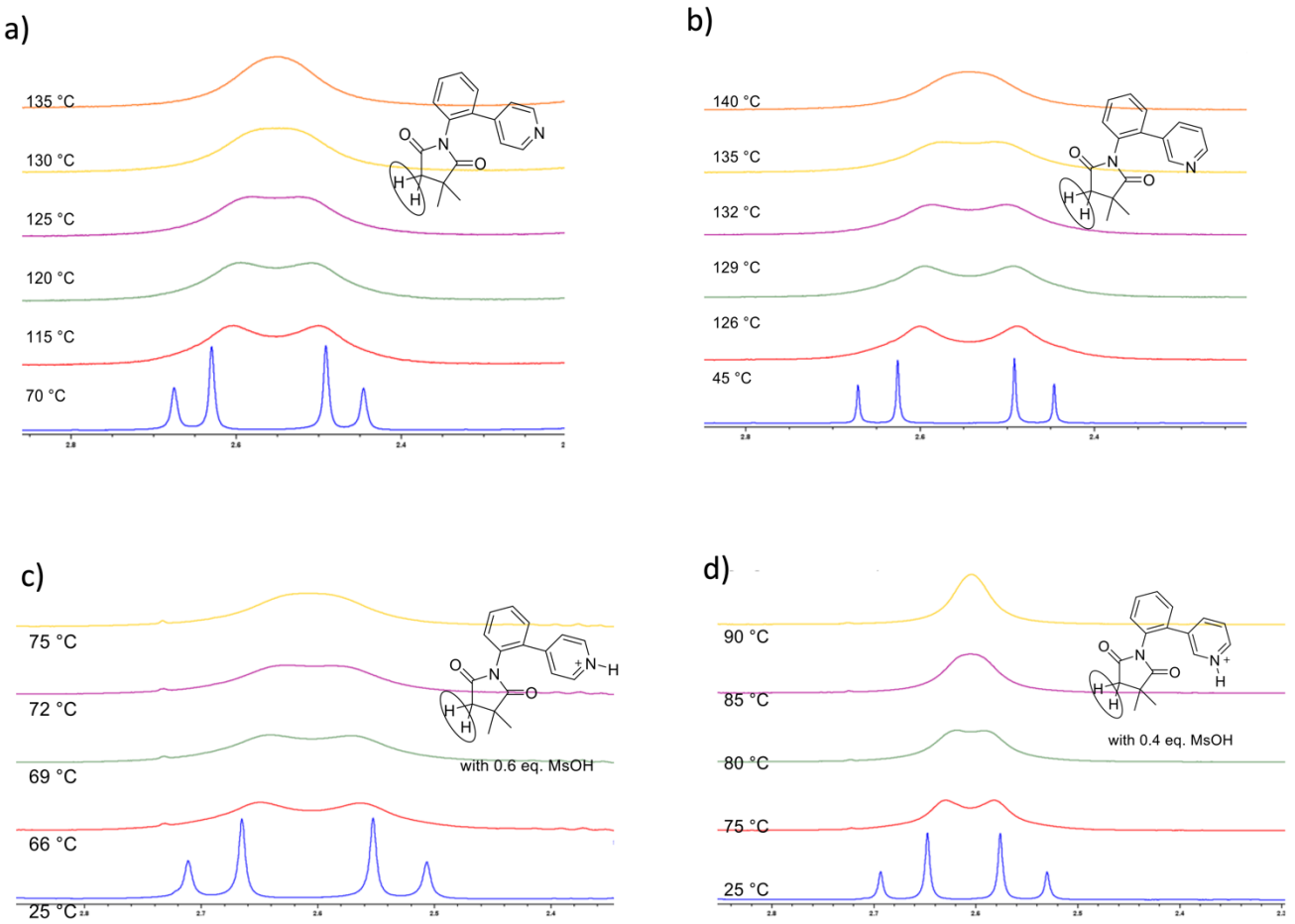



**Figure S12** Variable temperature $^{1}$H NMR spectra (400 MHz) of rotors a) **1**(4-Py), b) **1**(3-Py), c) **1**(4-Py)•$H^+$, and d) **1**(3-Py)•$H^+$ in TCE-d2 highlighting the differences in dynamic behavior when protonated or unprotonated. The following equation was used to calculate the rates at coalescence temperatures, $k_c = \pi\Delta\upsilon/\sqrt{2}$, where $k_c$ is the exchange rate at coalescence temperature and $\Delta\upsilon$ is the maximum peak separation (25 °C) in Hz: a) **1**(4-Py), 167 Hz at 130 °C; b) **1**(3-Py), 156 Hz at 135 °C; c) **1**(4-Py)•$H^+$, 144 Hz at 72 °C; and d) **1**(3-Py)•$H^+$, 112 Hz at 85 °C.

## 10. Energy Decomposition Analyses II

A more comprehensive FI-SAPT analysis of the effects of protonation on the intramolecular interaction energies in the rotors TS and GS structures were carried out to confirm the dominant role of the electrostatic term to the changes in barrier on protonation. To capture more of the intramolecular interactions of the pyridyl and pyridinium gates and also the weak interactions in the GS, the rotor fragment was expanded to include the entire dimethylsuccinimide rotor. Specifically, the intramolecular interaction between the pyridyl/pyridinium ($C_5NH_4$ or $C_5NH_5^+$) and dimethylsuccinimide ($C_4H_8NO_2$) fragments were calculated. The input structures for the FI-SAPT0(jun-cc-pVDZ) analyses in Psi4[2] were the solvent GS and TS structures of rotors **1**(3-Py), **1**(4-Py), **1**(3-Py)•$H^+$, and **1**(4-Py)•$H^+$ found using B3LYP-D3/6-311G* (solvent = TCE). The results are shown in Table S17.

**Table S17.** Intramolecular interaction energies (E, kcal/mol) between the pyridyl/pyridinium gates and the dimethylsuccinimide stators calculated using FI-SAPT0(jun-cc-pVDZ).

| rotor | GS / TS | $E_{total}$ | $E_{elst}$ | $E_{ind}$ | $E_{exch}$ | $E_{disp}$ |
|---|---|---|---|---|---|---|
| **1**(3-Py) | GS | 0.960213 | 1.709445 | -1.58873 | 7.057821 | -6.21832 |
| **1**(3-Py)•$H^+$ | GS | 2.504429 | 5.921008 | -3.66906 | 5.830294 | -5.57782 |
| **1**(4-Py) | GS | 1.523185 | 2.623817 | -1.52361 | 6.520781 | -6.09781 |
| **1**(4-Py)•$H^+$ | GS | 3.012289 | 6.516217 | -3.70031 | 5.631448 | -5.43506 |
| **1**(3-Py) | TS | 12.11141 | 3.095865 | -2.62218 | 17.03878 | -5.40105 |
| **1**(3-Py)•$H^+$ | TS | 5.887928 | -2.57875 | -5.23037 | 19.30853 | -5.61148 |
| **1**(4-Py) | TS | 11.30839 | 3.756733 | -2.67025 | 15.56096 | -5.33906 |
| **1**(4-Py)•$H^+$ | TS | 3.357543 | -3.39307 | -6.92164 | 19.39143 | -5.71917 |

To check the consistency of the FI-SAPT analysis with the structural and barrier modeling studies conducted using B3LYP-D3/6-311G*, the changes in barrier calculated by both methods were compared. FI-SAPT cannot directly calculate the rotational barriers of the rotors as the method only calculates the interaction energy between structural fragments. However, the relative changes in the rotational barriers can be estimated based on the assumption that the changes in the rotational barriers are due to the intramolecular interactions. Thus, the change in barrier of rotors **1**(3-Py) and **1**(4-Py) on protonation ($\Delta\Delta E^{‡}$) were calculated using equations 1 and 2 from the FI-SAPT values in Table S18.

$$\Delta\Delta E^{‡} \text{ for } \mathbf{1}\text{(3-Py)} \rightarrow \mathbf{1}\text{(3-Py)}\bullet H^+ = [E_{(TS\ 1(3\text{-Py}))} - E_{(GS\ 1(3\text{-Py}))}] - [E_{(TS\ 1(3\text{-Py})\bullet H+)} - E_{(GS\ 1(3\text{-Py})\ \bullet H+)}] \quad (1)$$

$$\Delta\Delta E^{‡} \text{ for } \mathbf{1}\text{(4-Py)} \rightarrow \mathbf{1}\text{(4-Py)}\bullet H^+ = [E_{(TS\ 1(4\text{-Py}))} - E_{(GS\ 1(4\text{-Py}))}] - [E_{(TS\ 1(4\text{-Py})\bullet H+)} - E_{(GS\ 1(4\text{-Py})\ \bullet H+)}] \quad (2)$$

**Table S18.** Comparison of the calculated $\Delta\Delta G^{‡}$ and $\Delta\Delta E^{‡}$ values for the rotational barriers of rotors **1**(3-Py) and **1**(4-Py) on protonation in the gas phase.

| rotor energy difference | $\Delta\Delta G^{‡}$ B3LYP-D3/6-311G* (kcal/mol) | $\Delta\Delta E^{‡}$ SAPT0 (MP2/jun-cc-pVDZ) (kcal/mol) |
|---|---|---|
| **1**(3-Py) - **1**(3-Py)•$H^+$ | -7.8 | -8.9 |
| **1**(4-Py) - **1**(4-Py)•$H^+$ | -9.4 | -7.8 |

The changes in barrier on protonation of the rotors were very similar despite the differences in the two energy calculation methods. The barrier calculation in Table 1 of the manuscript used B3LYP-D3/6-311G* and included frequency analysis to calculate $\Delta\Delta G^{\ddagger}$. The FI-SAPT0 analysis in Psi4 uses the equivalent of MP2/jun-cc-pVDZ to calculate $\Delta\Delta E^{\ddagger}$. The similarity of the $\Delta\Delta G^{\ddagger}$ and $\Delta\Delta E^{\ddagger}$ values suggest that the FI-SAPT is accurately capturing the key energy terms in the changes in the rotational barriers.

The advantage of this more comprehensive FI-SAPT analysis that it captures the energy terms in the GS and TS, whereas the previous SAPT analysis (Table 1) only captured the energy terms of the TS. The contributing energy terms to the changes in barrier ($\Delta\Delta E^{\ddagger}$) were examined (Figure S13). Comparison of the relative contributions of the electrostatic, induction, exchange, and dispersion terms showed that that the electrostatic term ($E_{elst}$) was the dominant component of $\Delta\Delta E^{\ddagger}$ ($E_{total}$). This was consistent with the TS only SAPT analysis in Section 6 of the SI. The steric exchange term ($E_{exch}$) was the second largest contributing term, but was much smaller than the electrostatic term.

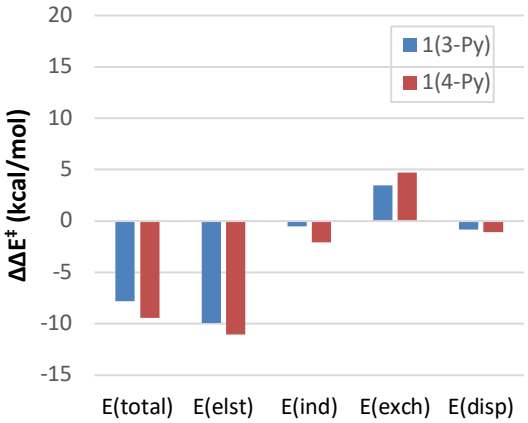



**Figure S13.** The FI-SAPT analysis of the changes in difference in the TS and GS energies of **1**(3-Py) and **1**(4-Py) on protonation.

Interestingly, the electrostatic ($E_{elst}$) and exchange ($E_{exch}$) terms have opposite signs. The electrostatic term is negative and stabilizing, which supports the hypothesis that protonation of the pyridyl gate lowers the barrier due to the formation of attractive electrostatic interactions between the positively charged pyridinium surface and the electrostatically negative oxygen of the succinimide carbonyl. The steric term, on the other hand, is positive and destabilizing. Comparison of the changes in the GS and TS of the FI-SAPT analysis (Table S17) reveals that the majority of the destabilizing exchange interactions are in the TS. We hypothesize that the formation of attractive electrostatic interactions in the TS brings the pyridinium gate and succinimide carbonyl closer together leading to the increase in the steric interactions. The overall changes in energy ($E_{total}$) as well as the component energy terms including exchange ($E_{exch}$) were much smaller for the GS. This confirms that the majority of the effects of protonation on the rotation barriers are due to changes in the TS energies.

## 11. Comparison of the molecular modeling and X-ray structures

The structures for rotor **1**(4-Py) from the crystal structure (SI, Section 8, page S22) and from GS molecular modeling (B3LYP-D3/6-311G*) of the GS of **1**(4-Py) were compared. The structures were very similar, which provided support for the ability of the molecular modeling to accurately simulate the geometry and rotational barriers. The 4-pyridyl group is tipped toward the dimethyl groups of the succinimide in both structures. The dihedral angles along the central atropisomeric C-N bond were almost identical. The C(succinimide)-N(succinimide)-C(phenyl)-C(phenyl) dihedrals were 70.67 ° and 71.22° for the calculated and crystal structure respectively.

## 12. References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