Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Fluorescence quenching of deprotonated phenylurea through twisting motion induced by electron-donating substituent group

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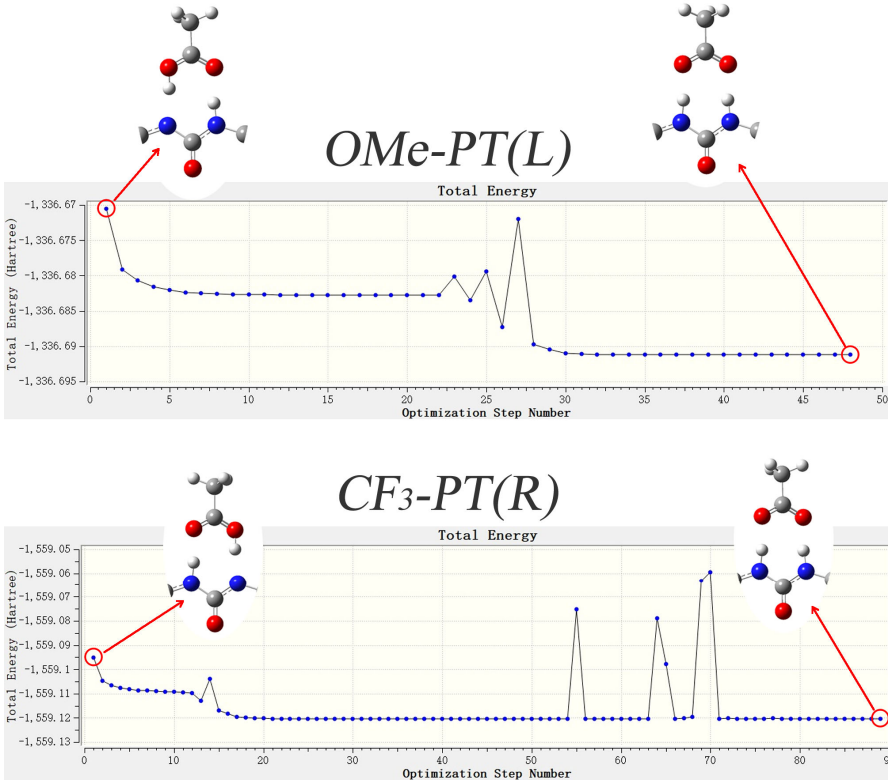

Figure S1. The plots of total energy changes in optimizations of OMe-PT(L) and CF_3-PT(R) structures in S_1 state.

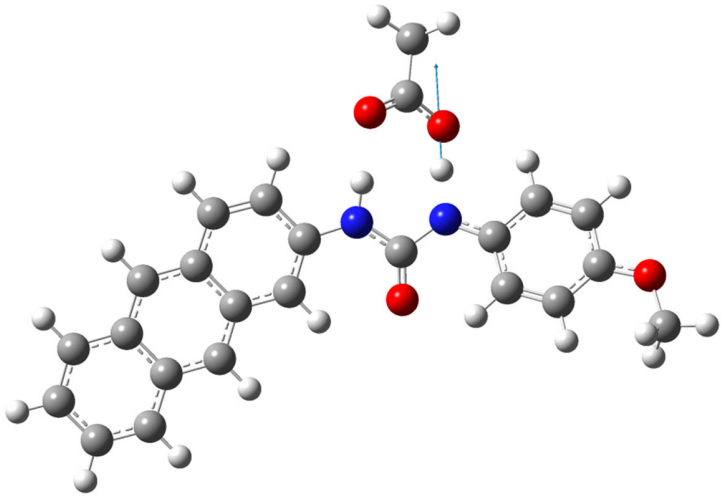

Figure S2. The structure and imaginary frequency of TS for the ESPT(R) in OMe-2PUA:AcO^-.

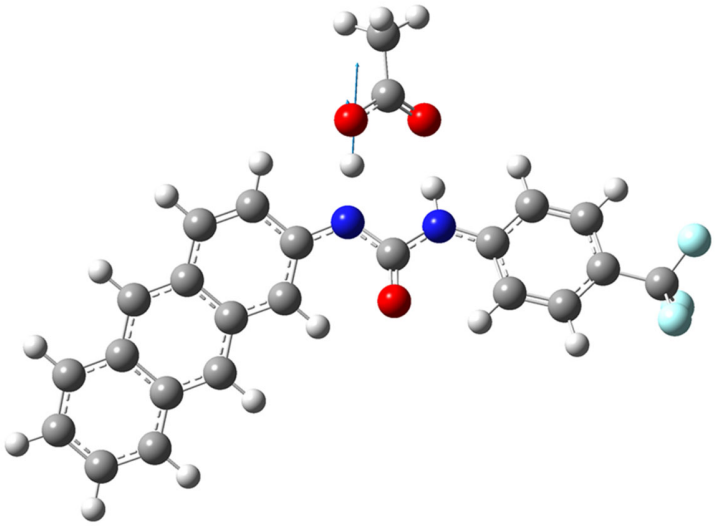

Figure S3. The structure and imaginary frequency of TS for the ESPT (L) in CF_3-2PUA:AcO^- .

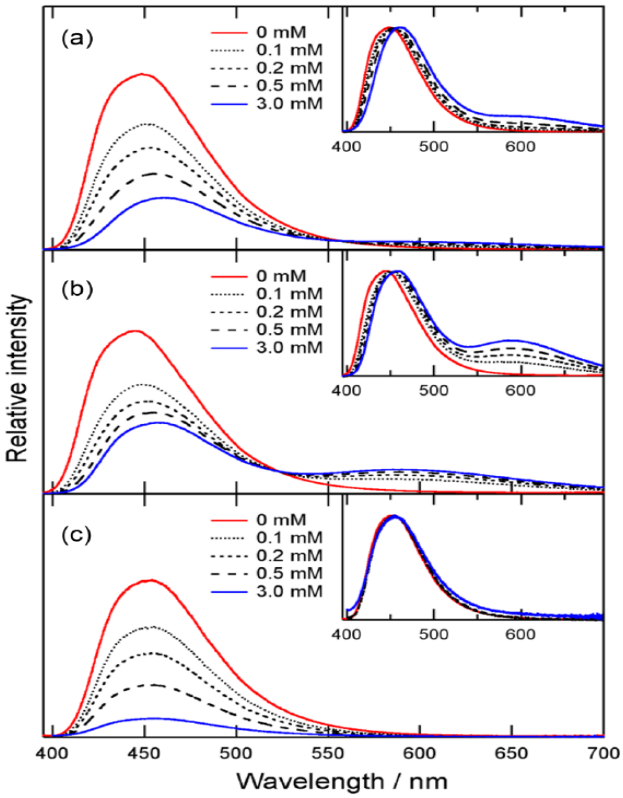

Figure S4. The experimental fluorescence spectra of (a) 2PUA, (b) CF3-2PUA, and (c) OMe-2PUA with addition of TBAAc from Ref. 30 (Photochem. Photobio. Sci., 2021, 20, 523–532).

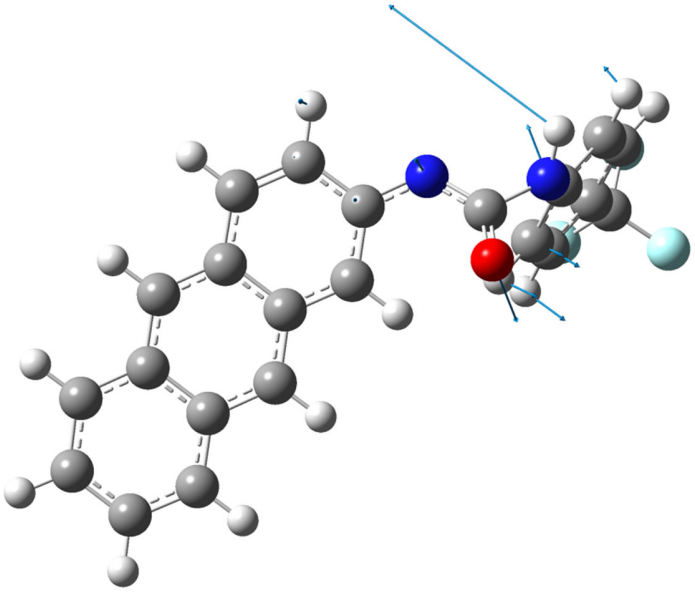

Figure S5. The structure and imaginary frequency of TS for twisting motion of CF_3-2PUA$^-$.

Table S1. Cartesian coordinates (in Å) for all optimized geometries of for both stable structures and transition states at the PBE0/TZVP level of theory.

1. OMe-2PUA in S_0 state.

Charge = 0 Multiplicity = 1

C	5.64354700	0.02252500	0.00051400
C	4.84532000	1.21315900	-0.07670600
C	5.50680200	2.47110500	-0.15728500
C	6.86767300	2.54696600	-0.16108100
C	7.65600400	1.36920700	-0.08451800
C	7.06073600	0.14546400	-0.00622600
C	3.45535200	1.10673500	-0.07114400
C	2.81672500	-0.13016000	0.00701300
C	3.61862100	-1.31692100	0.08359600
C	5.00564500	-1.21494100	0.07912300
C	2.94875500	-2.57021400	0.16196000
C	1.59405800	-2.64092000	0.16276000
C	0.79260800	-1.45943500	0.08632000
C	1.39888600	-0.23374000	0.01016800
N	-0.58479300	-1.67381500	0.09142400
C	-1.58683900	-0.73165900	0.04737200
N	-2.83470800	-1.29465000	0.01549900
C	-4.06667600	-0.62424900	-0.02581300
C	-5.18279100	-1.35138100	-0.45065200
C	-6.43524400	-0.77439300	-0.48279500
C	-6.60903000	0.55515100	-0.09956400
C	-5.50394500	1.28520700	0.32164600
C	-4.24359500	0.69790900	0.36639200
O	-7.87417200	1.04145900	-0.17096600
C	-8.08190200	2.38477600	0.22006800
O	-1.38183000	0.47182200	0.04342900
H	4.90364700	3.37128800	-0.21598200
H	7.35801300	3.51204200	-0.22299800
H	8.73707100	1.45041700	-0.08895000
H	7.65976500	-0.75751800	0.05223300
H	2.85546700	2.00984200	-0.12983000
H	5.60469400	-2.11881300	0.13762600
H	3.53968400	-3.47791400	0.22088400
H	1.10238800	-3.60685700	0.22239500
H	0.80288000	0.66463200	-0.04479400
H	-0.85978400	-2.64176900	0.14636800
H	-2.89482500	-2.29394900	-0.09912300
H	-5.06618500	-2.38508300	-0.75994100
H	-7.29553900	-1.34550800	-0.81168700
H	-5.60307700	2.31774700	0.62953700
H	-3.39567500	1.27825700	0.69723200
H	-9.14521500	2.57646900	0.09172600
H	-7.51224700	3.07647800	-0.40851900
H	-7.81079400	2.54211100	1.26878100

2. OMe-2PUA in S_1 state.

Charge = 0 Multiplicity = 1

C	5.64678500	0.03832900	0.01139700
C	4.84283600	1.22710000	-0.06519300
C	5.48207700	2.47545200	-0.13668400
C	6.87724700	2.57631900	-0.12688800
C	7.65039700	1.43026600	-0.05000900
C	7.03885900	0.17006600	0.02054500
C	3.44196900	1.09119100	-0.07887400
C	2.80144500	-0.16476800	-0.00185300
C	3.60615300	-1.35187200	0.07142100
C	4.99817700	-1.21939500	0.08655300
C	2.94779900	-2.59389900	0.14437900
C	1.56347400	-2.69546700	0.13213900
C	0.78086000	-1.53980500	0.05813000
C	1.40948600	-0.27344600	-0.01841800
N	-0.58919900	-1.69880800	0.03866200
C	-1.57672500	-0.72793300	0.03448800
N	-2.82609600	-1.27283900	-0.05967000
C	-4.05578700	-0.60311000	-0.05738400
C	-5.19654700	-1.36944100	-0.32445000
C	-6.44963700	-0.79776900	-0.32437300
C	-6.60360900	0.56392600	-0.05851100
C	-5.47508700	1.33160300	0.20663300
C	-4.21056200	0.75394500	0.21101500
O	-7.87161100	1.03942300	-0.08195200
C	-8.06330800	2.41540900	0.18867000
O	-1.35208900	0.46807400	0.11036900
H	4.87400600	3.37221500	-0.19744600
H	7.34750200	3.55130200	-0.18145600
H	8.73218800	1.50069000	-0.04204100
H	7.65151400	-0.72348800	0.08048100
H	2.82829900	1.98525300	-0.13913100
H	5.61072500	-2.11438200	0.14652800
H	3.54421900	-3.49821000	0.20465200
H	1.08800400	-3.66834000	0.18777700
H	0.79795000	0.61434900	-0.07471000
H	-0.89264300	-2.66118300	0.05649500
H	-2.89577700	-2.26997300	-0.19237200
H	-5.09617100	-2.42908500	-0.53588900
H	-7.32804300	-1.39729900	-0.53188300
H	-5.55864700	2.38946600	0.41762900
H	-3.34385100	1.36301700	0.41608300
H	-9.13529800	2.58916200	0.12432800
H	-7.55083900	3.04149300	-0.54819400
H	-7.71428400	2.67634800	1.19246100

3. OMe-2PUA:AcO^- in S_0 state.

Charge = -1 Multiplicity = 1

C	-6.02177000	-0.24095400	0.02599800
C	-5.32983300	-1.49075700	-0.11529100
C	-6.09941100	-2.68183200	-0.24142900
C	-7.46206200	-2.64072800	-0.22830700
C	-8.14485500	-1.40451700	-0.08801400
C	-7.44389400	-0.24143300	0.03524600
C	-3.93570200	-1.50399900	-0.12480000
C	-3.18907700	-0.33192400	-0.00106100
C	-3.88665700	0.91461500	0.13784200
C	-5.27674200	0.93202600	0.14921000
C	-3.10845200	2.10077300	0.26133700
C	-1.75293600	2.05676000	0.24836800
C	-1.04983100	0.81420200	0.11104400
C	-1.76842400	-0.34988400	-0.01262500
N	0.33188200	0.92244900	0.10493500
C	1.24121800	-0.10741200	0.05336000
N	2.52590100	0.34669900	-0.02572900
C	3.69073900	-0.42279400	-0.02853000
C	4.89473500	0.25274100	-0.27963800
C	6.10079500	-0.41612200	-0.28109800
C	6.15074100	-1.78783200	-0.03376600
C	4.96600700	-2.46761500	0.21598900
C	3.74768100	-1.79245300	0.22201000
O	7.38451400	-2.36223600	-0.05881100
C	7.46095100	-3.75013600	0.19447000
O	0.92702700	-1.29521800	0.07821900
H	-5.57716400	-3.62714800	-0.34859300
H	-8.03436400	-3.55663500	-0.32543700
H	-9.22892800	-1.39181700	-0.07964200
H	-7.96156800	0.70647700	0.14264500
H	-3.41737100	-2.45234300	-0.23152500
H	-5.79453600	1.88089100	0.25596400
H	-3.62026300	3.05184300	0.36702800
H	-1.16763300	2.96489400	0.34300900
H	-1.25316300	-1.29340900	-0.11100900
H	0.69698200	1.89142100	0.19643900
H	2.67814200	1.36357500	-0.17205900
H	4.86669800	1.31959000	-0.47207100
H	7.02433200	0.11733900	-0.47626500
H	4.96603600	-3.53196200	0.41291600
H	2.83535200	-2.33636700	0.41333500
H	8.51502700	-4.01345800	0.13120900
H	6.90089600	-4.32498900	-0.55035700
H	7.08745100	-3.99637200	1.19382700
C	2.26509700	3.85876400	-0.07888200
O	1.13303500	3.56296600	0.38550500
O	3.11376100	3.02255900	-0.47862400
C	2.61344500	5.33419100	-0.16157700

H	3.62882100	5.48831000	-0.52429000
H	2.50281700	5.79418400	0.82288000
H	1.91069100	5.83530200	-0.83189900

4. OMe-2PUA:AcO^- in S_1 state.

Charge = -1 Multiplicity = 1

C	-6.01556500	-0.25002700	0.02115000
C	-5.30889900	-1.49434700	-0.13372300
C	-6.04833100	-2.68243500	-0.27676800
C	-7.44446500	-2.67211800	-0.26621900
C	-8.12450900	-1.47217000	-0.11457300
C	-7.41673500	-0.27350500	0.02875400
C	-3.90172500	-1.46928600	-0.14349900
C	-3.16637800	-0.27442700	0.00522400
C	-3.87209200	0.96681300	0.15517200
C	-5.26916700	0.94606100	0.16639100
C	-3.10980400	2.14686900	0.29711000
C	-1.72766200	2.14350100	0.28882300
C	-1.03227200	0.92812600	0.14671900
C	-1.76852600	-0.27452000	-0.00627000
N	0.33465100	0.98261000	0.12725400
C	1.22277600	-0.07973800	0.10911500
N	2.50703500	0.35415100	-0.02551100
C	3.65655800	-0.42965200	-0.02598800
C	4.87316600	0.23622800	-0.25420600
C	6.06624300	-0.44979500	-0.25868800
C	6.09191600	-1.82861800	-0.03509100
C	4.89412800	-2.49822300	0.19075600
C	3.68801600	-1.80783000	0.19589700
O	7.31209200	-2.41739700	-0.05814200
C	7.37358300	-3.81262800	0.16943700
O	0.88890100	-1.25548200	0.20824000
H	-5.51230400	-3.61890400	-0.39510200
H	-7.99267500	-3.60087200	-0.37731400
H	-9.20892500	-1.45784600	-0.10539400
H	-7.95571600	0.66116400	0.14676200
H	-3.35940100	-2.40324100	-0.26033500
H	-5.80911200	1.88151700	0.28286000
H	-3.63598700	3.08955300	0.41240400
H	-1.16459300	3.06216300	0.39630000
H	-1.23042300	-1.20400200	-0.11658200
H	0.73334100	1.95334300	0.19949200
H	2.67651000	1.37056700	-0.20246600
H	4.86010300	1.30630700	-0.42774900
H	7.00031800	0.07097100	-0.43537800
H	4.87871900	-3.56589300	0.36644700
H	2.76519300	-2.33987000	0.36720600
H	8.42599700	-4.08231800	0.11165700

H	6.81631200	-4.36570700	-0.59293400
H	6.98763000	-4.07201300	1.16009200
C	2.32689200	3.82327100	-0.11049700
O	1.19460800	3.54671400	0.36633800
O	3.14862600	2.96824200	-0.52752600
C	2.70290200	5.28770700	-0.21405300
H	3.77994700	5.41503800	-0.31674400
H	2.33986500	5.84050700	0.65311900
H	2.21928300	5.71004400	-1.09965300

5. OMe-PT(R) in S_1 state.

Charge = -1 Multiplicity = 1

C	5.99659900	-0.19158300	-0.28437300
C	5.35716200	-1.34730600	0.29409600
C	6.16143200	-2.44365800	0.67153700
C	7.53805600	-2.43085100	0.49904000
C	8.15863700	-1.31040700	-0.06148500
C	7.40144800	-0.21480100	-0.44454700
C	3.95746100	-1.33415000	0.45870500
C	3.16422600	-0.24160200	0.07735200
C	3.80327100	0.91341100	-0.50103200
C	5.20123700	0.90413800	-0.66368300
C	2.98657500	1.99993900	-0.87632300
C	1.61155700	1.97765900	-0.70658400
C	0.99186500	0.84944200	-0.14605200
C	1.75836300	-0.24279800	0.24077600
N	-0.40491300	0.90860100	-0.01318700
C	-1.25691500	-0.03257100	0.45465000
N	-2.57380200	0.44370800	0.42613100
C	-3.60686800	-0.38186300	0.24065200
C	-4.91868300	0.15899700	0.41044600
C	-6.03250800	-0.59950900	0.20899000
C	-5.91224500	-1.94482000	-0.19070200
C	-4.63876600	-2.50163700	-0.38240400
C	-3.51488800	-1.74324900	-0.17275900
O	-7.05743800	-2.60408600	-0.36502000
C	-7.01172100	-3.96715600	-0.77241800
O	-0.92940800	-1.13053100	0.89483800
H	5.67687100	-3.31318500	1.10691800
H	8.13071800	-3.28863600	0.79899200
H	9.23521600	-1.29734700	-0.19752000
H	7.88581500	0.65460800	-0.88010700
H	3.47465400	-2.20475400	0.89464900
H	5.68338000	1.77509300	-1.09961500
H	3.45610100	2.87711200	-1.31152900
H	1.00581000	2.82751200	-1.00195500
H	1.27757300	-1.10762400	0.67334200
H	-0.83913200	1.77775600	-0.32768200

H	-2.87214700	1.97557000	0.71636400
H	-5.01334500	1.19348400	0.71588800
H	-7.02466800	-0.18775000	0.34657900
H	-4.53007100	-3.52862900	-0.70329400
H	-2.53897000	-2.18079700	-0.31925400
H	-8.04732100	-4.28890200	-0.84203800
H	-6.48691400	-4.57669400	-0.03367700
H	-6.53075100	-4.06552300	-1.74803700
C	-2.51181400	3.79963200	0.14150000
O	-1.63917500	3.45940100	-0.64395900
O	-3.15150600	2.95429000	0.91634100
C	-2.95586300	5.21876000	0.30959200
H	-4.00129400	5.30960100	0.00660500
H	-2.34055400	5.88153100	-0.29376800
H	-2.89544800	5.50471400	1.36108900

6. OMe-2PUA-Tw in S_1 state.

Charge = -1 Multiplicity = 1

C	5.33935300	0.06419800	0.57351700
C	4.76812600	0.92482000	-0.43086300
C	5.59384100	1.90288500	-1.02542700
C	6.92522900	2.04851700	-0.66631000
C	7.47976800	1.21322200	0.30852800
C	6.69948700	0.24156500	0.91388300
C	3.41187900	0.75583700	-0.77727900
C	2.59664800	-0.21805700	-0.18188800
C	3.17003800	-1.07916200	0.82423900
C	4.52180700	-0.91332300	1.17060500
C	2.33492700	-2.05259200	1.41292200
C	1.00468100	-2.19114500	1.04922500
C	0.45111300	-1.35169500	0.07402300
C	1.23411000	-0.37703700	-0.53092600
N	-0.91334400	-1.54571200	-0.21974900
C	-1.68965100	-0.96795000	-1.16437000
N	-2.99060500	-1.48019700	-1.17300900
C	-3.96531500	-0.72708100	-0.68322800
C	-5.30608000	-1.21389000	-0.77719500
C	-6.35423100	-0.50787000	-0.26870400
C	-6.13710900	0.73618000	0.35701200
C	-4.83552800	1.24611300	0.46463000
C	-3.77769700	0.53641500	-0.04666700
O	-7.22906300	1.35267200	0.81800700
C	-7.08253400	2.61202700	1.46236700
O	-1.31460900	-0.13834300	-1.98668000
H	5.16218400	2.55137500	-1.78283600
H	7.53491100	2.80985200	-1.14155400
H	8.52136200	1.32504100	0.59153000
H	7.13080400	-0.40730500	1.67108800

H	2.98259700	1.40598100	-1.53497000
H	4.95144100	-1.56338500	1.92824000
H	2.75244500	-2.70770500	2.17140800
H	0.38728500	-2.95046600	1.51923600
H	0.80360300	0.26643400	-1.28419400
H	-1.38331500	-2.23748600	0.34400800
H	-5.46263900	-2.17005300	-1.26082500
H	-7.36954000	-0.87864100	-0.33835300
H	-4.65434200	2.19852500	0.94371500
H	-2.77674200	0.94063700	0.03929700
H	-8.08598300	2.91705400	1.74740800
H	-6.65471200	3.35148800	0.78167800
H	-6.45952300	2.52352000	2.35525200

7. CF_3-2PUA in S_0 state.

Charge = 0 Multiplicity = 1

C	-6.36187800	-0.06246800	0.01188900
C	-5.55017400	-1.24638400	-0.00221100
C	-6.19685200	-2.51448600	-0.00853100
C	-7.55669800	-2.60605900	-0.00133800
C	-8.35843800	-1.43495800	0.01268100
C	-7.77758600	-0.20189700	0.01905500
C	-4.16153600	-1.12381700	-0.00918900
C	-3.53788600	0.12287900	-0.00285600
C	-4.35282900	1.30296600	0.01101400
C	-5.73861800	1.18482700	0.01809200
C	-3.69781100	2.56643500	0.01716400
C	-2.34402500	2.65281600	0.01029400
C	-1.53078000	1.47772800	-0.00340500
C	-2.12108800	0.24270700	-0.01002700
N	-0.15385100	1.70858700	-0.00916000
C	0.85450900	0.77965300	-0.01554500
N	2.10229500	1.36343900	-0.01694900
C	3.34255200	0.73537300	-0.02096900
C	4.47012800	1.56513500	-0.01390200
C	5.74082400	1.02896400	-0.01726500
C	5.91347100	-0.35097700	-0.03541000
C	4.79918200	-1.17900300	-0.03995300
C	3.51956900	-0.65094100	-0.03700800
C	7.28573000	-0.93706700	0.01395700
O	0.66936000	-0.42479800	-0.01998600
H	-5.58338100	-3.40949800	-0.01920900
H	-8.03597300	-3.57860700	-0.00626600
H	-9.43846800	-1.52878900	0.01826900
H	-8.38706500	0.69587300	0.02975700
H	-3.55113900	-2.02167200	-0.01977000
H	-6.34811400	2.08348300	0.02869000
H	-4.29914600	3.46906800	0.02761400

H	-1.86323800	3.62601000	0.01540000
H	-1.51553400	-0.65081200	-0.02038900
H	0.10726200	2.68173100	-0.00589100
H	2.14507400	2.37079800	-0.00969400
H	4.34442000	2.64248300	-0.00553000
H	6.59901700	1.68978400	-0.01433600
H	4.92201800	-2.25542500	-0.05478000
H	2.65938800	-1.30123700	-0.04616600
F	7.35708700	-2.12616400	-0.60786600
F	7.70738800	-1.14947900	1.28082300
F	8.20355800	-0.13853000	-0.55676500

8. CF_3-2PUA in S_1 state.

Charge = 0 Multiplicity = 1

C	-6.35765100	-0.09238900	0.02340400
C	-5.53402100	-1.26637200	-0.05872000
C	-6.15187900	-2.52493600	-0.12538000
C	-7.54606800	-2.64950900	-0.10395800
C	-8.33786000	-1.51797200	-0.02130800
C	-7.74637900	-0.24667400	0.04444700
C	-4.13595300	-1.10695000	-0.08497000
C	-3.51479000	0.15970100	-0.01221400
C	-4.33972500	1.33190900	0.06736900
C	-5.72972200	1.17571500	0.09412000
C	-3.70437100	2.58485500	0.13478500
C	-2.32045800	2.70917800	0.11250200
C	-1.51940300	1.56945200	0.03302200
C	-2.12573200	0.29203700	-0.04061900
N	-0.14976000	1.75450300	-0.00049300
C	0.84966000	0.80278400	0.01716600
N	2.09541600	1.36869900	-0.11009800
C	3.33167800	0.73173300	-0.07932900
C	4.45919200	1.53369600	-0.29247300
C	5.72539200	0.98818300	-0.27137700
C	5.89206800	-0.37389800	-0.04323500
C	4.77777500	-1.17317300	0.17267000
C	3.50227400	-0.63554600	0.15358500
C	7.26489100	-0.95735100	0.03052200
O	0.65170700	-0.39273600	0.13320700
H	-5.52975400	-3.41155200	-0.19068300
H	-7.99936900	-3.63259400	-0.15470700
H	-9.41806100	-1.60648700	-0.00436200
H	-8.37356700	0.63631100	0.10906200
H	-3.50834600	-1.99089300	-0.15023200
H	-6.35641800	2.06050000	0.15878400
H	-4.31516300	3.47899600	0.19973300
H	-1.86244400	3.69062900	0.16494200
H	-1.50079000	-0.58595300	-0.10279300

H	0.13588800	2.72243000	-0.00324800
H	2.14245800	2.36327100	-0.27005000
H	4.33708300	2.59553600	-0.47641200
H	6.58428500	1.62568000	-0.44200400
H	4.89670400	-2.23495500	0.35207300
H	2.64156100	-1.26534100	0.31283300
F	7.29002100	-2.25315400	-0.32224600
F	7.78084500	-0.89564500	1.27820500
F	8.13570800	-0.31486200	-0.76645900

9. CF_3-2PUA:AcO^- in S_0 state.

Charge = -1 Multiplicity = 1

C	-6.58787000	-0.45474700	0.02953000
C	-5.82870900	-1.66697500	-0.09228000
C	-6.53162900	-2.90017300	-0.20111800
C	-7.89445200	-2.93326300	-0.19010700
C	-8.64385300	-1.73412000	-0.06931800
C	-8.00796700	-0.53275800	0.03717800
C	-4.43591600	-1.60407400	-0.10082700
C	-3.75544300	-0.39100600	0.00487200
C	-4.51959700	0.81755100	0.12537500
C	-5.90869400	0.75898400	0.13575500
C	-3.80793100	2.04626200	0.23105600
C	-2.45197400	2.07642400	0.21716300
C	-1.68367100	0.87230800	0.09615100
C	-2.33549500	-0.33140800	-0.00687100
N	-0.30731300	1.05604800	0.08464600
C	0.65046300	0.07928200	0.03144500
N	1.91670300	0.60789000	-0.04649700
C	3.11253300	-0.08586600	-0.03585500
C	4.28254700	0.67483600	-0.20311700
C	5.52347800	0.07529400	-0.19404700
C	5.63591300	-1.30276400	-0.02556500
C	4.48597600	-2.06194800	0.14555600
C	3.23403300	-1.47098800	0.13827500
C	6.98185600	-1.93910500	0.03530600
O	0.40771800	-1.12267100	0.05026500
H	-5.95834800	-3.81702600	-0.29355700
H	-8.41579900	-3.88033700	-0.27403000
H	-9.72701100	-1.78054600	-0.06246400
H	-8.57694300	0.38683700	0.12953800
H	-3.86613400	-2.52393500	-0.19305300
H	-6.47784400	1.67947000	0.22794700
H	-4.37097600	2.96927000	0.32377800
H	-1.91726100	3.01630300	0.29817700
H	-1.76982400	-1.24690800	-0.09222200
H	0.00366500	2.04595300	0.16548300
H	2.01233300	1.63738700	-0.18377400

H	4.19349500	1.74643500	-0.33939600
H	6.41042700	0.68351600	-0.32837300
H	4.55928500	-3.13489600	0.27910100
H	2.34621300	-2.07121300	0.25952000
C	1.46604000	4.08466200	-0.09435000
O	0.33693300	3.73448900	0.33312000
O	2.36435200	3.28809700	-0.47244300
C	1.78847800	5.56640900	-0.14079100
H	2.27362500	5.81803000	-1.08532600
H	2.49578500	5.79932100	0.66006800
H	0.89527400	6.17539400	-0.00718100
F	6.95555200	-3.23801200	-0.30999800
F	7.52181300	-1.89301500	1.27631600
F	7.87192400	-1.33640200	-0.77513200

10. CF_3-2PUA:AcO^- in S_1 state.

Charge = -1 Multiplicity = 1

C	-6.57627400	-0.48133300	0.02756600
C	-5.79882200	-1.67810200	-0.15143700
C	-6.46713300	-2.90322500	-0.32006500
C	-7.86323600	-2.97368100	-0.30944000
C	-8.61063800	-1.82021800	-0.13388800
C	-7.97157900	-0.58404400	0.03526900
C	-4.39569500	-1.57098100	-0.16314700
C	-3.72885800	-0.33832700	0.01166900
C	-4.50631500	0.85559300	0.18538100
C	-5.89895600	0.75304400	0.19936400
C	-3.81614400	2.07498900	0.35060400
C	-2.43458800	2.15237600	0.33850800
C	-1.66991400	0.98594000	0.17332200
C	-2.33567800	-0.25664500	-0.00475800
N	-0.30848700	1.12196000	0.14935900
C	0.63759500	0.11312500	0.13388300
N	1.89579100	0.61954300	-0.04095700
C	3.08647700	-0.08656100	-0.02670200
C	4.25535900	0.65208900	-0.27718700
C	5.48988300	0.04021900	-0.27374300
C	5.59378700	-1.32693200	-0.02679300
C	4.44448500	-2.06342400	0.22562000
C	3.19825100	-1.46017500	0.22315600
C	6.93837900	-1.97003900	0.02365800
O	0.37657800	-1.07527600	0.26811800
H	-5.87863400	-3.80469500	-0.45775000
H	-8.35616400	-3.93027000	-0.44023600
H	-9.69388100	-1.86800300	-0.12454700
H	-8.56361800	0.31508600	0.17206200
H	-3.80072100	-2.46952600	-0.29916000
H	-6.49194500	1.65319000	0.33420700

H	-4.39583400	2.98282900	0.48555600
H	-1.92702500	3.10069900	0.46314800
H	-1.74501600	-1.15078500	-0.13671800
H	0.03469200	2.11465200	0.21470300
H	1.99568800	1.63885800	-0.25839200
H	4.17091800	1.71480500	-0.47261600
H	6.37777800	0.62906500	-0.47261100
H	4.51303000	-3.12719500	0.41933700
H	2.30962700	-2.04259200	0.40807900
C	1.50429800	4.05786400	-0.17891100
O	0.41549400	3.72706700	0.35935700
O	2.33986300	3.24298400	-0.64796200
C	1.84615800	5.53281000	-0.23317100
H	2.48341800	5.75491500	-1.08906000
H	2.39908700	5.79407600	0.67398900
H	0.94433700	6.14391700	-0.26480600
F	6.88412100	-3.29761700	-0.17282900
F	7.55142400	-1.78995200	1.21641800
F	7.77919000	-1.47064500	-0.90166100

11. CF_3-PT(L) in S_1 state.

Charge = -1 Multiplicity = 1

C	-6.46822900	-0.58976500	-0.03160600
C	-5.63097100	-1.74427800	-0.23373500
C	-6.23872200	-2.99289100	-0.46548700
C	-7.62647300	-3.12715700	-0.49925800
C	-8.43336800	-2.01300100	-0.30306100
C	-7.86117700	-0.75988900	-0.07104600
C	-4.23415200	-1.57275600	-0.19754700
C	-3.63552200	-0.31924900	0.04102700
C	-4.47024200	0.83155100	0.23885600
C	-5.85659000	0.66685800	0.20258900
C	-3.83603700	2.07700600	0.46294700
C	-2.46638700	2.22054200	0.49296500
C	-1.62422300	1.09286100	0.32125100
C	-2.24576200	-0.16969800	0.08019100
N	-0.28631700	1.28743600	0.31358500
C	0.61110800	0.25127800	0.42236100
N	1.85894700	0.64989900	-0.00506300
C	3.04026100	-0.06425300	0.00362700
C	4.17699100	0.58831000	-0.50221800
C	5.40076600	-0.04432000	-0.53076800
C	5.52372300	-1.35058000	-0.06295200
C	4.40554500	-2.00240600	0.44176700
C	3.17132700	-1.37748600	0.47438100
C	6.85794600	-2.01553900	-0.04520400
O	0.38715300	-0.87181500	0.87059000
H	-5.60384000	-3.86019800	-0.61832500

H	-8.07208800	-4.09926000	-0.67892900
H	-9.51331000	-2.11239000	-0.32842700
H	-8.49796600	0.10593200	0.08119400
H	-3.59305200	-2.43700000	-0.34731800
H	-6.49518200	1.53325700	0.35050500
H	-4.46432700	2.95019000	0.61374600
H	-2.01764200	3.19046500	0.66445600
H	-1.61737000	-1.03472800	-0.07710200
H	0.17030700	2.70612000	0.35072700
H	1.91765600	1.59471800	-0.39851700
H	4.08177200	1.60354600	-0.87070000
H	6.26305400	0.47833300	-0.92749900
H	4.48985500	-3.01881800	0.80800900
H	2.30375300	-1.89128400	0.85786300
C	1.40889200	4.11316200	-0.31791300
O	0.39507000	3.75736900	0.42011500
O	2.10007100	3.31826200	-0.94826500
C	1.66217100	5.58989200	-0.33660900
H	2.56720000	5.81407300	-0.89614500
H	1.75055200	5.96435900	0.68468200
H	0.81101700	6.09681300	-0.79672900
F	6.76714400	-3.35471800	-0.11795800
F	7.55396100	-1.74860600	1.08468800
F	7.64196100	-1.61946900	-1.06428700

12. CF_3-2PUA$^-$ in S_1 state.

Charge = -1 Multiplicity = 1

C	-6.27692500	-0.13103200	-0.06366000
C	-5.41851100	-1.28846200	-0.09605500
C	-6.00387600	-2.56826900	-0.15790300
C	-7.38776000	-2.73114000	-0.18628500
C	-8.21603400	-1.61381000	-0.15387200
C	-7.66889400	-0.33212300	-0.09336400
C	-4.02516500	-1.08828100	-0.06714700
C	-3.45091700	0.19587400	-0.00083700
C	-4.30536300	1.34875200	0.02715200
C	-5.69009500	1.15516300	-0.00175200
C	-3.69416700	2.62676400	0.08161300
C	-2.32996800	2.79503900	0.10310300
C	-1.46053600	1.66825900	0.10223900
C	-2.06153800	0.37428300	0.03374800
N	-0.13890900	1.90665500	0.09621100
C	0.78272200	0.92920800	0.31497200
N	2.03492800	1.39682300	-0.07062300
C	3.25698600	0.76106200	-0.05542300
C	4.36456900	1.47739600	-0.53769400
C	5.62062800	0.91129700	-0.55458500
C	5.80648600	-0.39149000	-0.09851600

C	4.71674500	-1.10705400	0.38278400
C	3.45132300	-0.54905500	0.40381800
C	7.17422800	-0.98327000	-0.06713000
O	0.63613500	-0.18863500	0.81451000
H	-5.35259600	-3.43674700	-0.18296700
H	-7.81560500	-3.72656800	-0.23338000
H	-9.29393100	-1.73600600	-0.17568000
H	-8.32174300	0.53495800	-0.06871800
H	-3.36788900	-1.95326700	-0.08884200
H	-6.34466000	2.02216800	0.01883100
H	-4.34071100	3.49987200	0.09991700
H	-1.88525600	3.78231800	0.13807500
H	-1.41592100	-0.49255700	0.00885300
H	2.01493100	2.33702300	-0.43514400
H	4.22767200	2.49005400	-0.90110500
H	6.45883200	1.48366000	-0.93378300
H	4.84958500	-2.12128800	0.74048000
H	2.60604600	-1.10852100	0.77365300
F	7.15662900	-2.32520700	-0.14143500
F	7.84351300	-0.68007300	1.06980200
F	7.94612600	-0.54416900	-1.07799100

13. CF_3-2PUA-Tw in S_1 state.

Charge = -1 Multiplicity = 1

C	-4.04980700	-0.86962700	-0.17183200
C	-5.30391300	-0.30971500	-0.38524500
C	-5.44556000	1.07450000	-0.35837900
C	-4.34866900	1.87738500	-0.12633700
C	-3.07907200	1.32162600	0.09350300
C	-2.94357300	-0.07142000	0.05453300
N	-2.03335200	2.20182300	0.30277700
C	-0.70860500	2.01614900	0.68816000
N	-0.40313400	0.77224400	1.11764000
C	0.84690700	0.28814300	1.06505900
C	1.15286200	-0.87012200	1.83020500
C	2.40979500	-1.42775800	1.77232900
C	3.43916600	-0.91089800	0.94754100
C	3.14744400	0.24544100	0.14754900
C	1.86821800	0.81343700	0.21839300
O	0.01801000	3.01767600	0.68822000
H	-6.41453600	1.52971100	-0.52459500
H	-4.46950100	2.95523600	-0.10669100
H	-1.97132900	-0.51139700	0.21859400
H	-2.24274400	3.17474600	0.13654100
H	0.37941000	-1.28550400	2.46469100
H	2.63346700	-2.30357900	2.37531500
H	1.64086700	1.67991000	-0.38906000
H	-3.92450400	-1.94575200	-0.19909700

C	-6.49541200	-1.18442800	-0.57755500
F	-7.45013000	-0.59643200	-1.32009900
F	-7.08667300	-1.51871100	0.59341500
F	-6.18842100	-2.34603600	-1.18183000
C	4.14347800	0.77643200	-0.69153000
C	5.43413300	0.21715800	-0.77416500
C	5.72935800	-0.94147500	0.03037500
C	4.72010900	-1.46890700	0.86912300
C	7.01865000	-1.49957400	-0.05346100
C	7.99200100	-0.95434700	-0.88980800
C	7.70686600	0.16416500	-1.66650600
C	6.43955000	0.74199600	-1.60795400
H	3.90961300	1.65229000	-1.29056900
H	4.95123300	-2.34489400	1.46893500
H	7.24931500	-2.37248700	0.54936600
H	8.97689700	-1.40771300	-0.93205800
H	8.46606400	0.58619600	-2.31573500
H	6.21053700	1.61500300	-2.21168300

14. Transition state (TS) of the ESPT reactions of OMe-2PUA:AcO^- along HB(R) in S_1 state.

Charge = -1 Multiplicity = 1

C	-6.03040900	-0.18748500	0.16144700
C	-5.35686400	-1.41138800	-0.19563200
C	-6.13487900	-2.56221600	-0.44263500
C	-7.51982800	-2.53781000	-0.34978800
C	-8.17259500	-1.35213400	-0.00429100
C	-7.44018000	-0.20063200	0.24613000
C	-3.95094800	-1.40720800	-0.28398300
C	-3.18424800	-0.25733400	-0.03477300
C	-3.85680500	0.96474700	0.32366700
C	-5.25967500	0.96413500	0.41025700
C	-3.06442600	2.10601800	0.57059600
C	-1.68389400	2.07703400	0.47745800
C	-1.03000700	0.88302600	0.12703800
C	-1.77459500	-0.26798800	-0.12391200
N	0.36443700	0.93801100	0.04885100
C	1.23556700	-0.06191600	-0.23626600
N	2.54477300	0.42287400	-0.22863500
C	3.62610400	-0.37309900	-0.13344400
C	4.90157600	0.24315500	-0.30097300
C	6.05587400	-0.47458200	-0.19144900
C	6.01188400	-1.84950700	0.10653400
C	4.77215800	-2.47802700	0.28994700
C	3.60652800	-1.76027400	0.17520100
O	7.19110100	-2.46511400	0.19451300
C	7.21975700	-3.85659700	0.49195000
O	0.92095800	-1.22001300	-0.49159900
H	-5.62444000	-3.48278100	-0.71118600

H	-8.09273200	-3.43802900	-0.54531200
H	-9.25502900	-1.32977100	0.06910900
H	-7.95073600	0.71971600	0.51483400
H	-3.44070100	-2.32797700	-0.55371300
H	-5.76878500	1.88550500	0.67996200
H	-3.56090400	3.03320600	0.84097200
H	-1.09679200	2.96799500	0.66934100
H	-1.26700900	-1.18338800	-0.38885000
H	0.77638800	1.85043600	0.28698400
H	2.77722000	1.69532400	-0.47863100
H	4.93909400	1.30105200	-0.52758000
H	7.02210600	-0.00420600	-0.32597000
H	4.71893500	-3.53117700	0.53004700
H	2.65601900	-2.25144000	0.31123400
H	8.27055400	-4.13303500	0.50887000
H	6.70172400	-4.43006300	-0.27990100
H	6.77235600	-4.05508700	1.46837500
C	2.44654900	3.71132300	-0.11858700
O	1.47120800	3.47940100	0.60116400
O	3.10131100	2.79552600	-0.75231100
C	2.96159000	5.10899100	-0.31613400
H	2.31928600	5.83125200	0.18296600
H	3.01794600	5.33511300	-1.38252900
H	3.97500100	5.18137200	0.08517300

15. The TS of the ESPT reactions of CF_3-2PUA:AcO^- along HB(L) in S_1 state.

Charge = -1 Multiplicity = 1

C	6.47075900	-0.58812100	0.03441400
C	5.63492400	-1.74420500	0.23174700
C	6.24403600	-2.99246400	0.46085600
C	7.63225400	-3.12459100	0.49622700
C	8.43749600	-2.00905000	0.30450900
C	7.86323100	-0.75568200	0.07514500
C	4.23804500	-1.57472200	0.19445200
C	3.63729900	-0.32108800	-0.04105400
C	4.47094700	0.83134200	-0.23405400
C	5.85712200	0.66853700	-0.19711300
C	3.83566300	2.07633400	-0.45518700
C	2.46523400	2.21797500	-0.48647300
C	1.62650900	1.08916300	-0.31761500
C	2.24792500	-0.17372600	-0.08000600
N	0.28654600	1.28126300	-0.31093300
C	-0.61764200	0.24888300	-0.41609900
N	-1.86597900	0.65870900	-0.00564000
C	-3.05180400	-0.04834300	-0.02857900
C	-4.18922100	0.61140800	0.46596300
C	-5.41798400	-0.01210500	0.47869300
C	-5.54851600	-1.30999300	-0.00966200

C	-4.42827100	-1.97129800	-0.49721200
C	-3.18918600	-1.35539000	-0.51433200
C	-6.86673200	-2.00369700	0.05363300
O	-0.39075500	-0.87980500	-0.84644500
H	5.61043000	-3.86123500	0.61031500
H	8.07895800	-4.09654300	0.67380800
H	9.51751700	-2.10659800	0.33110900
H	8.49890800	0.11151300	-0.07361100
H	3.59813000	-2.44037000	0.34092700
H	6.49458400	1.53632200	-0.34160300
H	4.46252400	2.95099600	-0.60277900
H	2.01462900	3.18747000	-0.65505200
H	1.62008400	-1.03978400	0.07298300
H	-0.14808200	2.61683800	-0.34649000
H	-1.92422100	1.60419600	0.39212300
H	-4.09013200	1.62475700	0.83855600
H	-6.28180900	0.51793700	0.86194800
H	-4.51833700	-2.98143700	-0.87912600
H	-2.32266800	-1.87289600	-0.89516800
C	-1.38596500	4.08243300	0.31888200
O	-0.38796400	3.71008900	-0.42107400
O	-2.09066300	3.30040500	0.95769300
C	-1.62247200	5.56394600	0.34370300
H	-2.52206200	5.79920600	0.90786500
H	-1.71073100	5.94270800	-0.67606200
H	-0.76311300	6.05926300	0.80133900
F	-7.06013300	-2.64017600	1.23244100
F	-7.00199300	-2.94057300	-0.90092600
F	-7.90069900	-1.15379700	-0.08168100

16. The TS of the CF_3-2PUA$^-$ twisting in S_1 state.

Charge = -1 Multiplicity = 1

C	5.31454800	0.59634700	-0.58405600
C	4.67189900	0.99919800	0.64076700
C	5.33056400	1.91103800	1.48728400
C	6.58536100	2.42437300	1.16148900
C	7.20537000	2.03467200	-0.02015500
C	6.57850600	1.13264500	-0.88175700
C	3.40565900	0.46100900	0.93971500
C	2.75624300	-0.45216000	0.08639200
C	3.39417100	-0.85070300	-1.13735300
C	4.65230500	-0.32055400	-1.43621500
C	2.70909500	-1.75903600	-1.98083900
C	1.46277700	-2.26078000	-1.67476500
C	0.82813000	-1.90323400	-0.46057100
C	1.49692500	-0.97725900	0.39503600
N	-0.40916200	-2.37989600	-0.21274900
C	-0.93244200	-2.41947100	1.01870700

N	-2.38277500	-2.51878100	1.00952600
C	-3.12889300	-1.43123800	0.61810600
C	-4.43777500	-1.60239200	0.14389900
C	-5.21102100	-0.51292000	-0.20020100
C	-4.69854600	0.77745400	-0.09314400
C	-3.40212500	0.95831900	0.37801600
C	-2.62382800	-0.12742200	0.72798600
C	-5.55278200	1.95298700	-0.41637300
O	-0.35568900	-2.45368100	2.10207300
H	4.84147500	2.21186800	2.40871000
H	7.07408400	3.12517700	1.82922600
H	8.18166700	2.43132600	-0.27797300
H	7.06912000	0.83354000	-1.80273100
H	2.91309800	0.75359800	1.86287800
H	5.14255400	-0.61426900	-2.36018700
H	3.19298600	-2.05865500	-2.90616500
H	0.95349900	-2.94756500	-2.33982900
H	1.01082700	-0.67404700	1.31357300
H	-2.71616000	-3.40293800	0.65135500
H	-4.84276500	-2.60374900	0.04522300
H	-6.21769500	-0.67013600	-0.56945700
H	-2.99011000	1.95662400	0.46703600
H	-1.61687000	0.03400200	1.09444800
F	-6.44987500	1.68734300	-1.38392500
F	-4.83563900	3.01406400	-0.82815700
F	-6.27354000	2.38305600	0.64742200