Supplementary Information

The halogen(I) complex of astatine: a theoretical perspective on structural and bonding properties

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S1 Benchmark Calculations

Table S1. Comparison between experimental and computational data for both bond lengths and bond angles of $[D\cdots I\cdots D]^+$ complexes.

donor	Experiment[1-3]		Our work		$\varepsilon(d_{avg(D\text{-}At)})$[b]
	$d_{avg(D\text{-}I)}$ (Å)	$\alpha_{D\text{-}I\text{-}D}$ (°)	$d_{avg(D\text{-}I)}$ (Å)	$\alpha_{D\text{-}I\text{-}D}$ (°)	
quinuclidine	2.294	180.0	2.351	179.9	2.5%
pyridine	2.256	177.7	2.298	180.0	1.9%
acetonitrile	2.198	180.0	2.219	180.0	1.0%

[a] $d_{avg(D\text{-}I)}$ represents the average bond length between I and the two donor atoms; $\alpha_{D\text{-}I\text{-}D}$ stands for the corresponding bond angle.

[b] Relative error between calculated values and experimental values, i.e., $|d_{avg(D\text{-}I)}$ (experiment) - $d_{avg(D\text{-}I)}$ (this work) | / $d_{avg(D\text{-}I)}$ (experiment).

[1-3] Experimental data were obtained from references 1-3 (see Section S7).

S2 Effect of the SOC.

Table S2. DFT/B3LYP-D3 optimized bond lengths and bond angles of the $[D\cdots At\cdots D]^+$ complexes at the SR and SO levels. [a]

donor	SR-DFT		SO-DFT		$\Delta SO(d_{avg(D\text{-}At)})$[b]
	$d_{avg(D\text{-}At)}$ (Å)	$\alpha_{D\text{-}At\text{-}D}$ (°)	$d_{avg(D\text{-}At)}$ (Å)	$\alpha_{D\text{-}At\text{-}D}$ (°)	(Å)
piperidine	2.455	180.0	2.514	179.9	0.059
quinuclidine	2.440	179.8	2.500	179.9	0.060
ammonia	2.431	180.0	2.492	179.9	0.061
pyridine	2.387	180.0	2.446	180.0	0.059
imidazole	2.364	180.0	2.423	180.0	0.059
acetonitrile	2.308	180.0	2.393	180.0	0.085
furan	2.337	179.5	2.469	179.9	0.132
acetone	2.326	180.0	2.410	179.9	0.084
methyl acetate	2.309	180.0	2.404	179.8	0.095
thiophene	2.776	179.0	2.876	178.2	0.100
thioacetone	2.751	180.0	2.822	180.0	0.071
thiane	2.761	179.1	2.838	179.4	0.077

[a] $d_{avg(D\text{-}At)}$ represents the average bond length between At and the two donor atoms; $\alpha_{D\text{-}At\text{-}D}$ stands for the corresponding bond angle.

[b]The increase of the bond length due to the influence of spin-orbit coupling, i.e., $d_{avg(D\text{-}At)}$ (SO-DFT) - $d_{avg(D\text{-}At)}$ (SR-DFT).

Table S3. DFT/B3LYP-D3 calculated interaction energies between D and $[D\cdots At]^+$ fragments at the SR and SO levels, respectively, based on the SO-DFT/B3LYP-D3 optimized structures of the $[D\cdots At\cdots D]^+$ complexes.

donor	ΔE_{int}(SR-DFT) (kcal·mol^{-1})	ΔE_{int}(SO-DFT) (kcal·mol^{-1})	ΔSO(ΔE_{int})[a] (kcal·mol^{-1})
piperidine	-40.71	-36.31	4.40
quinuclidine	-42.29	-37.44	4.85
ammonia	-42.58	-35.23	7.35
pyridine	-40.43	-35.13	5.30
imidazole	-42.76	-37.97	4.79
acetonitrile	-39.35	-32.62	6.73
furan	-29.09	-20.56	8.53
acetone	-37.76	-30.83	6.93
methyl acetate	-35.65	-27.90	7.75
thiophene	-25.50	-21.11	4.39
thioacetone	-30.50	-28.34	2.16
thiane	-32.26	-29.42	2.84

[a]The decrease of the interaction energy due to the influence of spin-orbit coupling, i.e., ΔE_{int} (SO-DFT) - ΔE_{int} (SR-DFT).

S3 Effect of Different Donors

Table S4. Key geometrical parameters of the $[D\cdots At\cdots D]^+$ complexes and Mulliken charges q(e) on At atom at the SO-DFT/B3LYP-D3 level.[a]

	$d_{1(D\text{-}At)}$ (Å)	$d_{2(D\text{-}At)}$ (Å)	$\alpha_{D\text{-}At\text{-}D}$ (°)	R_{XB}	q(e)
piperidine	2.514	2.514	179.9	0.70	0.34
quinuclidine	2.500	2.500	179.9	0.70	0.34
ammonia	2.492	2.493	179.9	0.70	0.40
pyridine	2.446	2.446	180.0	0.68	0.42
imidazole	2.423	2.423	180.0	0.68	0.45
acetonitrile	2.393	2.393	180.0	0.67	0.61
furan	2.469	2.469	179.9	0.70	0.62
acetone	2.409	2.410	179.9	0.68	0.44
methyl acetate	2.404	2.404	179.8	0.68	0.59
thiophene	2.876	2.877	178.2	0.75	0.23
thioacetone	2.823	2.822	180.0	0.74	0.12
thiane	2.838	2.838	179.4	0.74	0.11

[a] $d_{1(D\text{-}At)}$ and $d_{2(D\text{-}At)}$ represents the bond length between At and the two donor atoms, respectively; R_{XB} is the ratio between the bond length of the interaction atoms and the sum of their van der Waals radii, i.e., $R_{XB} = d_{XB}/(X_{vdW} + B_{vdW})$); see footnote a of Table S2 for $\alpha_{D\text{-}At\text{-}D}$.

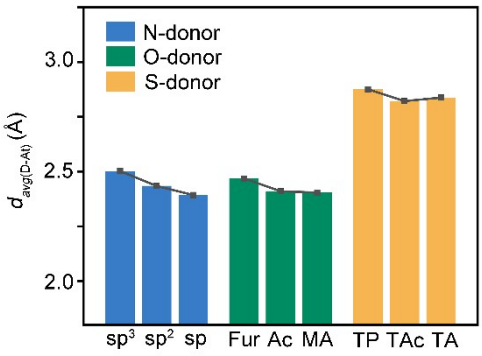

Figure S1. The bond lengths ($d_{avg(D-At)}$) of different $[D\cdots At\cdots D]^+$ complexes at the SO-DFT/B3LYP-D3 level. The horizontal axis represents different donors. The hybridization type of the nitrogen atom in N-donor groups are labelled by sp^3, sp^2 and sp, respectively.

Table S5. SO-CCSD(T) calculated interaction energies ΔE_{int}(SO-CC) in $[D\cdots At\cdots D]^+$ complexes and SR-DFT/B3LYP-D3 calculated the polarizability α of At atom in $[D\cdots At\cdots D]^+$ complexes, maximum electrostatic potential values $V_{s,\ max}$ and local electrophilicity indices ω_{cubic} (At) of the $[D\cdots At]^+$ cations.

donor	ΔE_{int}(SO-CC) (kcal·mol^{-1})	α(At) (a.u.)	$V_{s,\ max}$ (kcal·mol^{-1})	ω_{cubic}(At) (e • eV)
piperidine	-34.23	37.67	137	3.71
quinuclidine	-36.31	37.88	129	3.43
ammonia	-32.67	38.53	168	5.29
pyridine	-33.45	38.42	144	3.66
imidazole	-37.07	38.83	147	3.89
acetonitrile	-31.47	38.39	175	5.18
furan	-20.09	37.98	174	8.16
acetone	-28.48	39.35	159	5.17
methyl acetate	-26.11	39.15	167	5.55
thiophene	-17.41	40.27	138	3.70
thioacetone	-21.78	40.76	130	3.22
thiane	-24.50	39.89	127	3.27

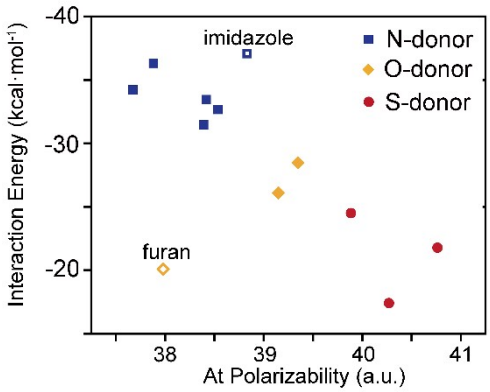

Figure S2. The interaction energy ΔE_{int}(SO-CC) and the polarizability α of At in $[D\cdots At\cdots D]^+$ complexes with different donor types. The $[IA\cdots At\cdots IA]^+$ and $[Fur\cdots At\cdots Fur]^+$ complexes are labeled using hollow patterns.

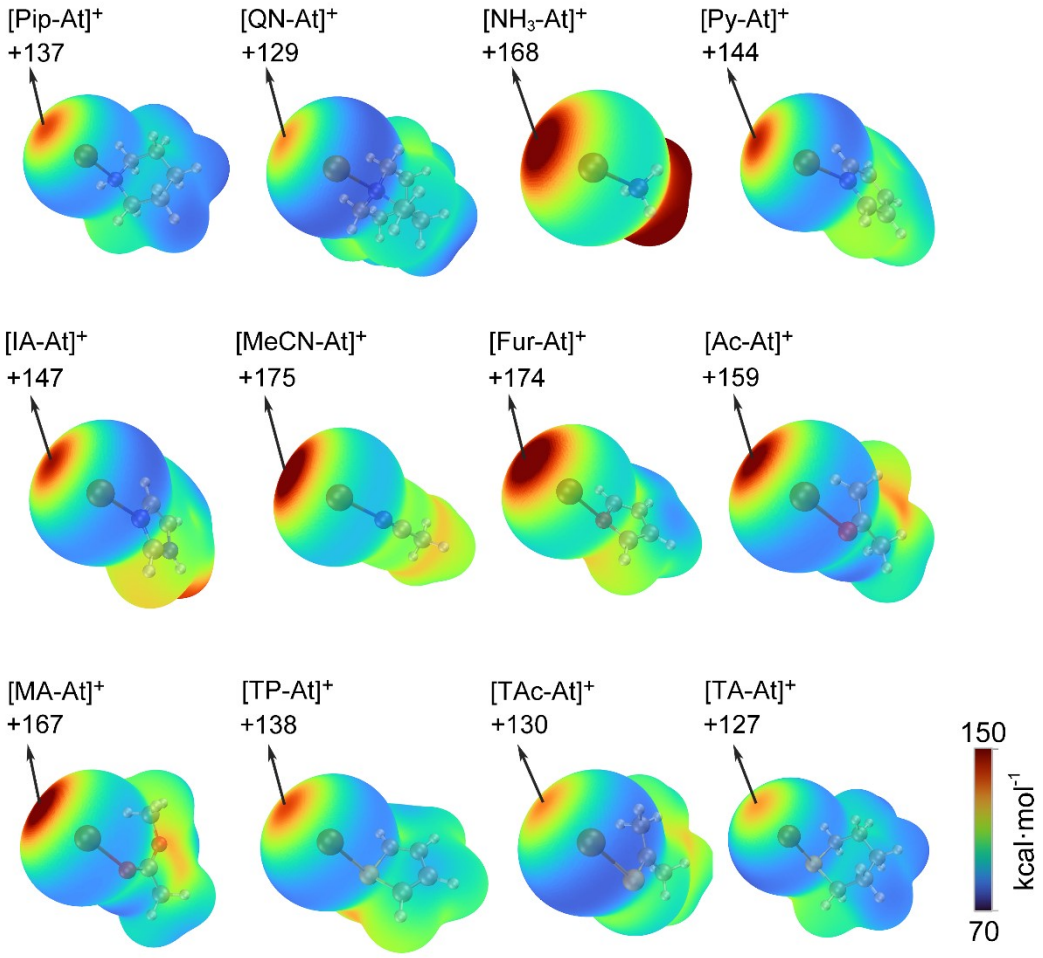

Figure S3. SR-DFT/B3LYP-D3 calculated MEP maps for $[D\cdots At]^+$ cations at the SO-DFT/B3LYP-D3 optimized geometries of $[D\cdots At]^+$ cations. Energies are given in kcal·mol^{-1}. Blue and red colors indicate the least and most positive MEP values, respectively.

Table S6. Energy decomposition analysis of the total bonding energy (in kcal·mol^{-1}) between D and [D···At]$^{+}$ fragments in halogen(I) complexes.

donor	Pauli	Electrostatic (elstat%)[a]	orbital interaction (orb%)[b]	Dispersion (disp%)[c]	Total bonding energy[d]
piperidine	67.97	-61.68 (52.26%)	-50.73 (42.98%)	-5.61 (4.75%)	-50.05
quinuclidine	71.48	-63.99 (52.61%)	-51.94 (42.70%)	-5.71 (4.69%)	-50.16
ammonia	56.59	-58.28 (56.01%)	-44.30 (42.58%)	-1.47 (1.41%)	-47.46
pyridine	69.32	-64.54 (54.77%)	-50.24 (42.64%)	-3.05 (2.59%)	-48.50
imidazole	70.91	-70.64 (57.44%)	-49.69 (40.40%)	-2.66 (2.16%)	-52.07
acetonitrile	52.64	-54.25 (54.76%)	-43.69 (44.10%)	-1.13 (1.14%)	-46.44
furan	32.74	-30.48 (44.99%)	-34.31 (50.64%)	-2.96 (4.37%)	-35.01
acetone	46.70	-47.41 (51.82%)	-41.69 (45.57%)	-2.39 (2.61%)	-44.79
methyl acetate	41.59	-44.09 (51.43%)	-38.59 (45.02%)	-3.04 (3.55%)	-44.13
thiophene	40.62	-25.82 (35.19%)	-44.56 (60.72%)	-3.00 (4.09%)	-32.76
thioacetone	62.13	-47.74 (46.43%)	-52.57 (51.12%)	-2.52 (2.45%)	-40.70
thiane	61.17	-47.22 (45.65%)	-51.64 (49.92%)	-4.59 (4.44%)	-42.29

[a]The values in parentheses represent the percentage of electrostatic interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[b]The values in parentheses represent the percentage of orbital interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[c]The values in parentheses represent the percentage of dispersion interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[d]Total bonding energy is the sum of Pauli, electrostatic, orbital, and dispersion interactions.

S4 Effect of Various R Substituents at Pyridine

Table S7. Key geometrical parameters and interaction energies of the [4-R-Py···At···4-R-Py]$^+$ complexes at the SO-DFT/B3LYP-D3 level.[a]

R	$d_{1(D\text{-}At)}$ (Å)	$d_{2(D\text{-}At)}$ (Å)	$\alpha_{D\text{-}At\text{-}D}$ (°)	σ
NH_2	2.431	2.431	180.0	−0.66
OH	2.438	2.438	180.0	−0.37
CH_3	2.440	2.440	180.0	−0.17
H	2.446	2.446	180.0	0
CFH_2	2.442	2.442	179.9	0.11
CF_2H	2.446	2.446	180.0	0.32
CF_3	2.449	2.449	180.0	0.54
NO_2	2.452	2.452	180.0	0.78

[a] See footnote a of Table S4 for $d_{1(D\text{-}At)}$, $d_{2(D\text{-}At)}$ and $\alpha_{D\text{-}At\text{-}D}$. σ is the Hammett constant of ssubstituents.

Table S8. SO-CCSD(T) calculated interaction energies ΔE_{int}(SO-CC) in [4-R-Py···At···4-R-Py]$^+$ complexes and SR-DFT/B3LYP-D3 calculated maximum electrostatic potential values $V_{s,\,max}$ and the local electrophilicity indices ω_{cubic} (At) of the [4-R-Py···At]$^+$ cations.

R	ΔE_{int}(SO-CC) (kcal·mol^{-1})	$V_{s,\,max}$ (kcal/mol)	ω_{cubic}(At) (e • eV)
NH_2	-35.81	135	3.62
OH	-34.49	142	3.80
CH_3	-34.95	141	3.51
H	-33.45	144	3.66
CFH_2	-33.36	144	3.79
CF_2H	-31.57	147	3.75
CF_3	-30.50	150	3.85
NO_2	-28.65	153	3.91

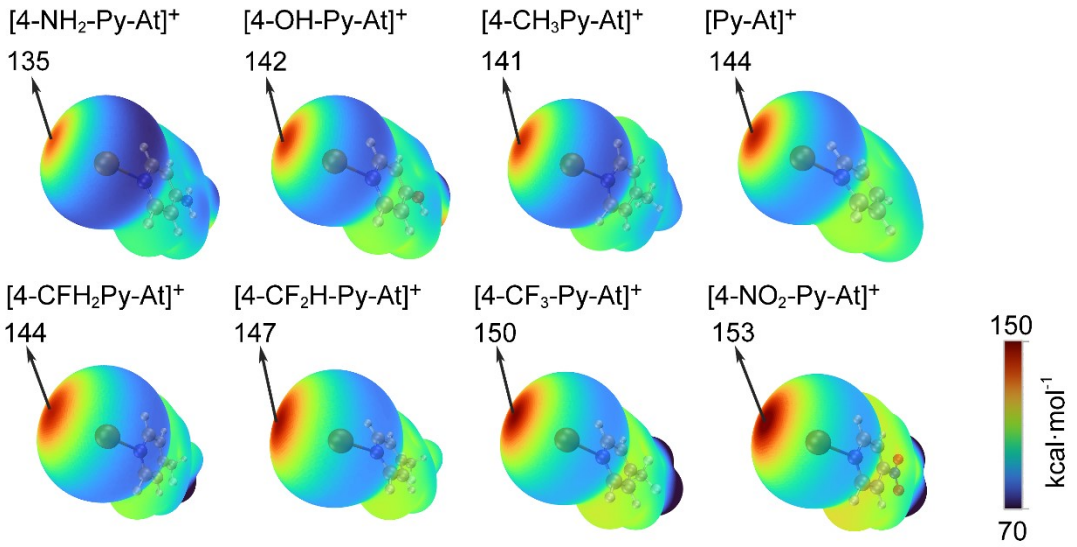

Figure S4. SR-DFT/B3LYP-D3 calculated MEP maps for [4-R-py···At]$^+$ cations at the SO-DFT/B3LYP-D3 optimized geometries of [4-R-py···At]$^+$ cations. Energies are given in kcal·mol^{-1}. Blue and red colors indicate the least and most positive MEP values, respectively.

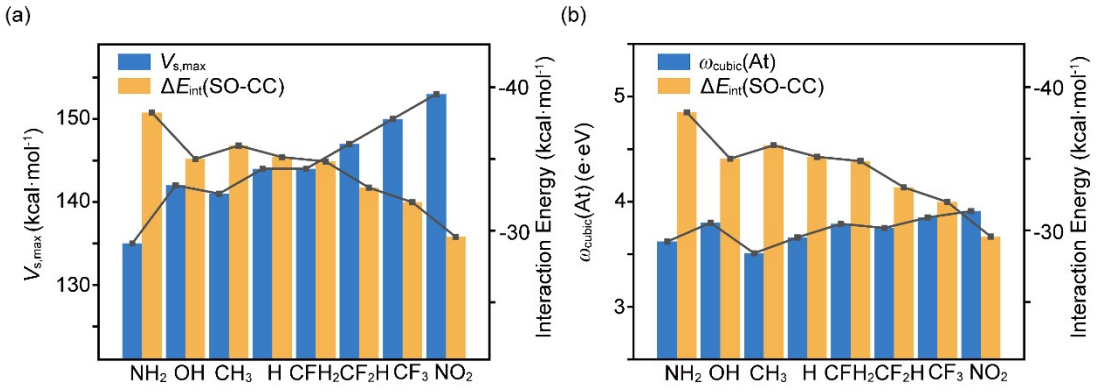

Figure S5. (a) The SR-DFT/B3LYP-D3 calculated $V_{s,max}$ values of [4-R-Py···At]$^+$ cations and SO-CCSD(T) calculated interaction energies (ΔE_{int}(SO-CC)) in different [4-R-Py···At···4-R-Py]$^+$ complexes. (b) The SR-DFT/B3LYP-D3 calculated ω_{cubic}(At) values and SO-CCSD(T) calculated interaction energies (ΔE_{int}(SO-CC)) in different [4-R-Py···At···4-R-Py]$^+$ complexes. The horizontal axis represents different R substituents.

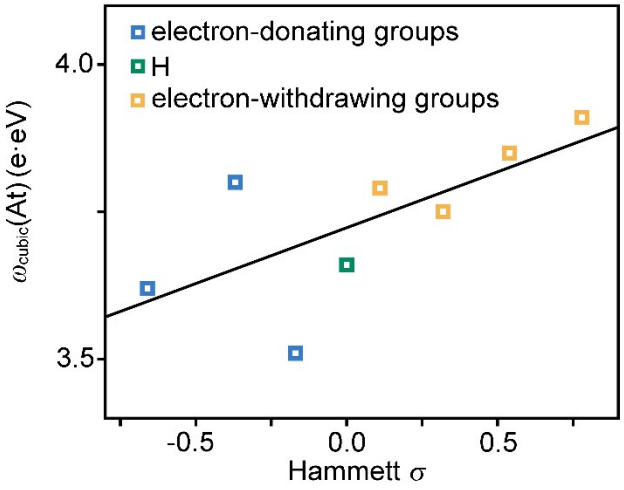

Figure S6. Dependence on the Hammett σ parameter of the local electrophilicity index ω_{cubic}(At) (ω_{cubic}(At) = 0.19·σ + 3.72, R^2 = 0.47).

Table S9. Energy decomposition analysis of the total bonding energy (in kcal·mol^{-1}) between 4-R-Py and [4-R-Py···At]$^+$ fragments in [4-R-Py···At···4-R-Py]$^+$ complexes.

R	Pauli	Electrostatic (elstat%)[a]	orbital interaction (orb%)[b]	Dispersion (disp%)[c]	Total bonding energy[d]
NH_2	74.32	-71.17 (56.35%)	-52.08 (41.23%)	-3.06 (2.42%)	-51.99
OH	71.27	-66.76 (55.27%)	-50.96 (42.19%)	-3.06 (2.53%)	-49.50
CH_3	71.14	-66.39 (55.10%)	-51.04 (42.36%)	-3.07 (2.55%)	-49.36
H	69.32	-64.54 (54.77%)	-50.24 (42.64%)	-3.05 (2.59%)	-48.50
CFH_2	69.86	-64.31 (54.49%)	-50.64 (42.91%)	-3.07 (2.60%)	-48.17
CF_2H	68.06	-61.23 (53.52%)	-50.10 (43.79%)	-3.07 (2.68%)	-46.34
CF_3	66.78	-59.02 (52.79%)	-49.72 (44.47%)	-3.07 (2.75%)	-45.03
NO_2	65.14	-55.50 (51.41%)	-49.38 (45.74%)	-3.07 (2.84%)	-42.81

[a]The values in parentheses represent the percentage of electrostatic interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[b]The values in parentheses represent the percentage of orbital interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[c]The values in parentheses represent the percentage of dispersion interactions in the total sum of electrostatic, orbital, and dispersion interactions.

[d]Total bonding energy is the sum of Pauli, electrostatic, orbital, and dispersion interactions.

S5 Effect of the Central Atom

Table S10. DFT/B3LYP-D3 calculated bond lengths, bond angles, R_{XB} and interaction energies of the $[Py\cdots I\cdots Py]^+$ complex at the SR and SO levels.

Relativistic Level	$d_{avg(D-X)}$ (Å)[a]	α_{D-X-D} (°)	R_{XB}	ΔE_{int} (kcal·mol^{-1})
SR	2.296	180.0	0.65	-37.01
SO	2.306 (0.4%)[b]	180.0	0.65	-36.36 (1.8%)[c]

[a] D refers to Py, and X represents for I. The $d_{avg(D-X)}$ refers to the average bond length between At and the two donor atoms in $[Py\cdots I\cdots Py]^+$ complex.

[b]The percentage increase in the bond length due to the influence of the SOC.

[c]The percentage increase in the interaction energy due to the influence of the SOC.

Table S11. The interaction energies (ΔE_{int}, in kcal·mol^{-1}) in the $[D\cdots I\cdots D]^+$ and $[D\cdots At\cdots D]^+$ complexes.

D	$[D\cdots I\cdots D]^+$	$[D\cdots At\cdots D]^+$	
	ΔE_{int}(SR-CC)	ΔE_{int}(SR-CC)	ΔE_{int}(SO-CC)
piperidine	-35.91	-38.55	-34.23
quinuclidine	-38.89	-40.01	-36.31
ammonia	-36.35	-39.08	-32.67
pyridine	-35.31	-38.03	-33.45
imidazole	-37.41	-41.00	-37.07
acetonitrile	-32.59	-36.46	-31.47
furan	-24.58	-26.63	-20.09
acetone	-31.84	-33.98	-28.48
methyl acetate	-27.76	-31.31	-26.11
thiophene	-17.71	-20.98	-17.41
thioacetone	-22.02	-25.39	-21.78

thiane	-24.89	-27.77	-24.50

Table S12. DFT/B3LYP-D3 calculated lowest unoccupied molecular orbital (LUMO) energy level of the $[Py\cdots At]^+$ cation at the SR and SO levels. [a]

Relativistic Level	LUMO energy level (eV)
SR	-8.31
SO	-8.08

[a] Molecular orbitals at the SR and SO levels were based on the SO-DFT/B3LYP-D3 optimized geometry of $[Py\cdots At]^+$ cation.

S6 Cartesian Coordinates (Å) of Optimized Structures

Table S13. SO-DFT/B3LYP-D3 optimized geometries of $[D\cdots At\cdots D]^+$ complexes.

D = piperidine				D = quinuclidine			
C	1.24190360	-3.05827876	-0.83477129	C	0.69717232	2.99473483	-1.21994580
C	1.24468324	-3.61080840	0.58408521	C	-1.41135003	2.99875783	0.00719724
C	-0.02327453	-4.41924792	0.87005900	C	0.00177601	5.07160093	0.00390609
C	-1.27645943	-3.59912062	0.55380001	C	0.70596312	2.99296198	1.21951391
C	-1.23426580	-3.04706141	-0.86459347	C	0.73716511	4.54325485	1.24282376
N	0.01042001	-2.26004639	-1.10113807	N	-0.00393790	2.50017058	0.00197307
H	2.10551790	-2.41982445	-1.02043384	C	-1.44077390	4.54920402	0.02161035
H	1.27437790	-3.88192608	-1.55727748	C	0.70616936	4.54517786	-1.25370661
H	1.33226390	-2.78589481	1.29776269	H	0.18395155	2.57499013	-2.08441877
H	2.13541907	-4.22818098	0.71189284	H	1.70681069	2.58560955	-1.20493009
H	-0.03722651	-4.74201755	1.91182576	H	-1.90481598	2.57771421	0.88245336
H	-0.02024412	-5.32948093	0.26185264	H	-1.90406529	2.59405103	-0.87619420
H	-1.37367381	-2.77334377	1.26521950	H	0.00433963	6.16137228	0.00475626
H	-2.17564573	-4.20829470	0.65994603	H	1.70962536	2.56940729	1.20722202
H	-2.08735586	-2.40103750	-1.07149483	H	0.18680398	2.58632871	2.08676805
H	-1.25644276	-3.87076039	-1.58744605	H	1.76811699	4.89945660	1.25023069
H	0.02342458	-1.96813879	-2.07451923	H	0.26392714	4.91584442	2.15214329
At	0.00871878	0.00021888	0.00021664	H	-1.96168354	4.90824081	0.91016663
C	1.24210838	3.05972945	0.83474772	H	-1.98972990	4.92318982	-0.84351936
C	1.24199466	3.61354109	-0.58359873	H	0.19953273	4.90588196	-2.14980503
C	-0.02708750	4.42132576	-0.86644808	H	1.73153602	4.91468768	-1.29563904
C	-1.27908179	3.60003577	-0.54854539	At	-0.00676866	0.00006355	0.00185738
C	-1.23399400	3.04640120	0.86915529	C	-0.37587367	-2.99701854	-1.35500819
N	0.01181204	2.26024803	1.10257996	C	1.36032572	-2.99315936	0.35813608
H	2.10660325	2.42192171	1.01850535	C	0.00095069	-5.07205881	0.00409987
H	1.27503761	3.88285331	1.55783845	C	-0.99224712	-2.99731805	1.00566663
H	1.32900415	2.78943555	-1.29828173	C	-1.00728363	-4.54780021	1.03523662
H	2.13199776	4.23179041	-0.71227582	N	-0.00369774	-2.50049383	0.00295086
H	-0.04334030	4.74489993	-1.90793362	C	1.39647615	-4.54357046	0.36211714
H	-0.02345971	5.33108421	-0.25754359	C	-0.38941601	-4.54740410	-1.38399017
H	-1.37691391	2.77484626	-1.26057595	H	0.34522871	-2.58662988	-2.06107502
H	-2.17893357	4.20858952	-0.65255981	H	-1.35213575	-2.58007466	-1.59987673
H	-2.08611275	2.39921153	1.07640876	H	1.61293807	-2.58072083	1.33437883
H	-1.25590819	3.86905795	1.59318392	H	2.05753900	-2.57538045	-0.36730049
H	0.02694313	1.96737751	2.07563131	H	0.00294957	-6.16183227	0.00435320
				H	-1.96535835	-2.58929515	0.73444078
				H	-0.71660892	-2.57786881	1.97262591
				H	-2.00765938	-4.91922319	0.80931856

			H	-0.74985595	-4.90826117	2.03203801
			H	1.69913030	-4.91067662	1.34361205
			H	2.13381524	-4.90516854	-0.35576068
			H	0.30735747	-4.91603106	-2.13786204
			H	-1.38022773	-4.91072489	-1.65980510
D = ammonia			**D = acetonitrile**		
N	0.00541888	-2.46958767	0.00188319	At	0.01392399	-0.01382124	0.00138222
At	0.00200917	0.02397914	-0.00058143	N	0.51996470	2.32518993	0.00098445
N	-0.00414228	2.51633696	0.00008633	C	0.76189470	3.44545341	0.00214716
H	0.87317895	2.87821258	0.36493081	C	1.06723428	4.85974190	0.00382174
H	0.36426991	-2.82718955	0.88349316	H	1.80556515	5.07406675	0.77775166
H	0.59110682	-2.82885951	-0.74768330	H	1.46890051	5.14893010	-0.96831687
H	-0.93506809	-2.83332237	-0.12888329	H	0.15906783	5.43021033	0.20339415
H	-0.12931548	2.87338282	-0.94356966	N	-0.49212766	-2.35277365	0.00220419
H	-0.76140082	2.87018185	0.57888332	C	-0.73384354	-3.47308336	0.00218657
				C	-1.03882290	-4.88745612	0.00204988
				H	-0.45684592	-5.38745526	-0.77341349
				H	-0.78913432	-5.31606113	0.97363613
				H	-2.10200272	-5.03290779	-0.19421990
D = pyridine			**D = imidazole**		
H	-2.06629207	2.53025760	0.00000000	At	0.02439347	0.00222836	0.00000000
H	0.00000000	6.28942913	0.00000000	C	1.14278305	3.23696104	0.00000000
H	-2.15090607	5.01091574	0.00000000	C	0.73552697	4.53602174	0.00000000
H	2.15090607	5.01091574	0.00000000	C	-1.03236968	3.21215483	0.00000000
H	2.06629207	2.53025760	0.00000000	H	2.14180756	2.83861207	0.00000000
C	1.15888496	3.11923079	0.00000000	H	1.28873949	5.45789288	0.00000000
C	1.19693734	4.50278131	0.00000000	H	-1.25355834	5.29677365	0.00000000
C	-1.15888496	3.11923079	0.00000000	H	-2.06080242	2.89400875	0.00000000
C	-1.19693734	4.50278131	0.00000000	C	1.08124624	-3.20824215	0.00000000
C	0.00000000	5.20758718	0.00000000	C	-0.68644893	-4.53230448	0.00000000
N	0.00000000	2.44583594	0.00000000	C	-1.09390190	-3.23330362	0.00000000
N	0.00000000	-2.44583594	0.00000000	H	2.10962188	-2.88989657	0.00000000
C	1.15888496	-3.11923079	0.00000000	H	1.30254332	-5.29303222	0.00000000
C	1.19693734	-4.50278131	0.00000000	H	-1.23941840	-5.45432940	0.00000000
C	0.00000000	-5.20758718	0.00000000	H	-2.09303426	-2.83525484	0.00000000
C	-1.19693734	-4.50278131	0.00000000	N	0.02915452	2.42514083	0.00000000
C	-1.15888496	-3.11923079	0.00000000	N	0.01970664	-2.42135206	0.00000000
H	2.15090607	-5.01091574	0.00000000	N	-0.63878030	4.49786776	0.00000000
H	2.06629207	-2.53025760	0.00000000	N	0.68781971	-4.49407660	0.00000000
H	-2.06629207	-2.53025760	0.00000000				
H	-2.15090607	-5.01091574	0.00000000				
H	0.00000000	-6.28942913	0.00000000				
At	0.00000000	0.00000000	0.00000000				
D = funan				**D = acetone**			

At	-0.03357088	-0.00028636	0.00068718
C	-1.14069580	-3.25453187	-0.06078569
C	-0.71448601	-4.49443056	0.22782877
C	0.72188936	-4.48527651	0.14946065
C	1.09896588	-3.24033168	-0.18294674
H	-2.10319538	-2.78351204	-0.14648978
H	-1.34273459	-5.33929146	0.45595273
H	1.38162599	-5.32222729	0.30663157
H	2.04051373	-2.75764141	-0.37363531
C	1.10656780	3.23764043	0.18845820
C	0.73319633	4.48269482	-0.14746941
C	-0.70286392	4.49441407	-0.23195336
C	-1.13269406	3.25581200	0.05677967
H	2.04644857	2.75351319	0.38352826
H	1.39520814	5.31799590	-0.30362565
H	-1.32856557	5.34005874	-0.46405438
H	-2.09659612	2.78686214	0.13929507
O	-0.03768348	-2.44598994	-0.33659072
O	-0.03220617	2.44575307	0.33855280

C	0.74754255	4.66398554	0.01035022
C	-1.48519827	3.39452402	-0.00694281
H	0.31749936	5.33500639	0.75737723
H	1.80735401	4.51043271	0.19370592
H	-1.82025075	3.46480012	1.03424679
H	-1.90708244	2.48946838	-0.44028586
C	0.00716265	3.36796064	-0.00461952
O	0.66074127	2.31842264	-0.00080960
At	0.00121892	0.00104850	-0.00317805
C	1.48653955	-3.39435081	-0.00183126
C	-0.74699888	-4.66229797	0.00048738
H	1.81521100	-3.47372042	-1.04440228
H	1.91188431	-2.48629940	0.42166601
H	-0.32091791	-5.33813072	-0.74447025
H	-1.80761694	-4.50925044	-0.17851408
C	-0.00578512	-3.36667376	0.00434484
O	-0.65870953	-2.31676077	-0.00166078
H	-1.86374890	4.27502292	-0.52433735
H	0.61100020	5.15050782	-0.96105380
H	-0.60577017	-5.14318660	0.97404579
H	1.86740176	-4.27111024	0.52026559

D = methyl acetate			
C	1.44159015	-4.55930247	-0.06291715
H	1.35697049	-5.19315329	0.82140654
H	1.28385957	-5.19618690	-0.93462211
C	0.38013459	-3.50665870	-0.01813587
O	0.67203345	-2.30460314	-0.00083472
O	-0.83136679	-3.99877695	0.00294893
C	-1.99462477	-3.14075282	0.06445207
H	-2.04830986	-2.51833266	-0.82665017
H	-1.96484489	-2.53317760	0.96668829
At	-0.00703160	0.00161542	0.00203871
C	-1.49037635	4.55116461	-0.06551106
H	-1.38107212	5.22701058	0.78384867
H	-1.37185583	5.14743788	-0.97204801
C	-0.41595745	3.51179372	-0.01649153
O	-0.69079531	2.30621023	-0.00069877
O	0.78953688	4.01907632	0.00579080
C	1.96208972	3.17323710	0.05780576
H	2.01356675	2.54947969	-0.83251659
H	1.94706758	2.56760277	0.96182956
H	2.42456601	-4.10102536	-0.10303772
H	-2.84106069	-3.81866609	0.09773475
H	-2.46884132	4.08177234	-0.05193641

D = thiophene			
At	0.35062082	0.00256160	0.00067771
C	-1.27236592	3.20890629	-0.91404090
C	-1.64753324	4.00244026	0.11304840
C	-0.59588732	4.23386327	1.07041022
C	0.56179218	3.61315456	0.75508192
H	-1.83646281	2.89197789	-1.77593432
H	-2.63558020	4.43193514	0.19861884
H	-0.71525927	4.85311251	1.94804888
H	1.50837086	3.62556686	1.27013781
C	-1.30459141	-3.20268564	0.87391344
C	-1.63931296	-4.01554138	-0.15187700
C	-0.55216731	-4.26043813	-1.06511338
C	0.59122768	-3.62986509	-0.71854367
H	-1.90153584	-2.87028631	1.70720767
H	-2.62241218	-4.44934492	-0.26680216
H	-0.63708903	-4.89638478	-1.93468762
H	1.55625152	-3.64869519	-1.19787850
S	0.37992462	-2.76653231	0.78038339
S	0.40895000	2.77447237	-0.76539861

H	2.80175308	3.85986271	0.08158627				
D = thioacetone				**D = thiane**			
C	0.20722685	5.23076348	0.01435927	C	-0.72778811	3.41800010	-1.40955756
C	-1.64947713	3.50252761	0.01169436	C	0.76212393	3.73712380	-1.39142210
H	-0.30845348	5.75224958	0.82630573	C	1.19695527	4.53932819	-0.16245724
H	1.28007884	5.37443851	0.10907772	C	0.93267214	3.81049570	1.15732324
H	-2.06066004	3.79628564	0.98442261	C	-0.54044980	3.49950321	1.39186735
H	-1.88454890	2.45724811	-0.16460224	H	-1.01217466	2.80128055	-2.26174700
C	-0.19101472	3.79108302	0.01193654	H	-1.33098884	4.32849110	-1.44304675
At	0.01784836	0.01139973	0.01278469	H	1.33732821	2.80914110	-1.45604472
C	1.68528027	-3.47979584	-0.00358145	H	0.98534142	4.30309792	-2.29943451
C	-0.17168582	-5.20774036	0.00227274	H	2.26208066	4.76255032	-0.24019135
H	2.09219396	-3.77911390	-0.97636285	H	0.68091170	5.50526421	-0.15578555
H	1.92153002	-2.43377104	0.16647618	H	1.51435030	2.88519732	1.19767611
H	0.33728427	-5.72734920	-0.81509534	H	1.27312186	4.42628630	1.99368792
H	-1.24529219	-5.35100052	-0.08422088	H	-0.70703638	2.93454782	2.30866039
C	0.22679055	-3.76807417	0.00479471	H	-1.13703439	4.41298575	1.45201388
H	-2.15249162	4.12658851	-0.73142437	At	-0.00010723	0.00001726	0.05230768
H	-0.13632357	5.69344678	-0.91699014	C	0.73480347	-3.41889866	-1.40576319
H	0.17924221	-5.67275739	0.92968398	C	-0.75539594	-3.73686067	-1.39498849
H	2.19127584	-4.10010479	0.74075685	C	-1.19683774	-4.53876146	-0.16819182
S	0.99901042	2.65813158	0.02098864	C	-0.93813942	-3.81074332	1.15317172
S	-0.96318207	-2.63506953	0.00590490	C	0.53381338	-3.49933564	1.39460643
				H	1.02411044	-2.80306688	-2.25693573
				H	1.33742495	-4.32991295	-1.43542419
				H	-1.32956897	-2.80843870	-1.46244191
				H	-0.97462552	-4.30269255	-2.30406042
				H	-2.26187596	-4.76060891	-0.25098043
				H	-0.68209938	-5.50537142	-0.15937220
				H	-1.52045903	-2.88579096	1.19201578
				H	-1.28178218	-4.42751220	1.98751808
				H	0.69559112	-2.93368124	2.31183420
				H	1.13027590	-4.41263731	1.45851542
				S	1.32597334	-2.50902801	0.07129182
				S	-1.32605451	2.50863430	0.06504465

Table S14. SO-DFT/B3LYP-D3 optimized geometries of [4-R-pyridine···At···4-R-pyridine]$^{+}$ complexes.

R = NH_2				R = OH			
H	-2.01962648	2.57450977	-0.16153171	H	-2.07194128	2.53785036	-0.00419621
H	-2.07200608	5.02856426	-0.18079553	H	-2.16365378	5.00344118	-0.00446671
H	2.23485953	4.95988928	0.13146114	H	2.14182153	5.02259891	0.00429818
H	2.10244068	2.50877981	0.13735709	H	2.06211901	2.54023043	0.00424159
C	1.20097670	3.10352246	0.06830102	C	1.15092616	3.12343919	0.00235254
C	1.27037488	4.47447693	0.06468073	C	1.19702702	4.49808115	0.00239581
C	-1.09922378	3.14020082	-0.09846584	C	-1.15984114	3.11997351	-0.00235363
C	-1.12385826	4.51265485	-0.10890291	C	-1.20645425	4.49805351	-0.00249475
C	0.08530830	5.23205981	-0.02589649	C	-0.00501619	5.21267637	-0.00007373
N	0.03959693	2.43063037	-0.01153608	N	-0.00579060	2.43809091	0.00002149
N	-0.03959693	-2.43063037	0.01153608	N	0.00579060	-2.43809091	0.00002149
C	1.09922378	-3.14020082	0.09846584	C	1.15984114	-3.11997351	-0.00235363
C	1.12385826	-4.51265485	0.10890291	C	1.20645425	-4.49805351	-0.00249475
C	-0.08530830	-5.23205981	0.02589649	C	0.00501619	-5.21267637	-0.00007373
C	-1.27037488	-4.47447693	-0.06468073	C	-1.19702702	-4.49808115	0.00239581
C	-1.20097670	-3.10352246	-0.06830102	C	-1.15092616	-3.12343919	0.00235254
H	2.07200608	-5.02856426	0.18079553	H	2.16365378	-5.00344118	-0.00446671
H	2.01962648	-2.57450977	0.16153171	H	2.07194128	-2.53785036	-0.00419621
H	-2.10244068	-2.50877981	-0.13735709	H	-2.06211901	-2.54023043	0.00424159
H	-2.23485953	-4.95988928	-0.13146114	H	-2.14182153	-5.02259891	0.00429818
At	0.00000000	0.00000000	0.00000000	At	0.00000000	0.00000000	0.00004002
N	-0.10730010	-6.57976002	0.03283513	O	0.06741508	6.54661418	0.00003163
H	0.74047103	-7.11483419	0.09762498	H	-0.80798581	6.95626309	-0.00175780
H	-0.97209433	-7.08752542	-0.02652030	O	-0.06741508	-6.54661418	0.00003163
N	0.10730010	6.57976002	-0.03283513	H	0.80798581	-6.95626309	-0.00175780
H	0.97209433	7.08752542	0.02652030				
H	-0.74047103	7.11483419	-0.09762498				
R = CH_3				R = CFH_2			
H	-2.05316172	2.53707665	-0.00528046	H	-1.90413227	-2.65344920	0.00172146
H	-2.13642646	5.00501136	-0.00546933	H	-1.83699896	-5.13462963	0.00746910
H	2.16018933	5.00568514	0.00546393	H	2.45300711	-4.86540528	0.00084286
H	2.07828119	2.53923599	0.00525385	H	2.22051283	-2.40678518	-0.00478667
C	1.16747816	3.12332828	0.00291873	C	1.34724535	-3.04533273	-0.00207622
C	1.20185740	4.50293818	0.00300890	C	1.46608469	-4.42061058	0.00110291
C	-1.14207967	3.12094302	-0.00296014	C	-0.96066099	-3.18315805	0.00150683
C	-1.17799623	4.50336837	-0.00304471	C	-0.91876414	-4.56598665	0.00477470
C	0.01024167	5.23427489	-0.00002692	C	0.31514483	-5.20899803	0.00465207
N	0.01179975	2.44191233	-0.00002730	N	0.15146425	-2.43766183	-0.00189212
N	0.01684245	-2.43772761	-0.00005606	N	-0.15146425	2.43766183	-0.00189212

C	1.17072806	-3.11674231	-0.00300974	C	0.96066099	3.18315805	0.00150683
C	1.20666577	-4.49916986	-0.00311903	C	0.91876414	4.56598665	0.00477470
C	0.01844037	-5.23009133	-0.00009498	C	-0.31514483	5.20899803	0.00465207
C	-1.17318771	-4.49876954	0.00294499	C	-1.46608469	4.42061058	0.00110291
C	-1.13882923	-3.11916170	0.00287938	C	-1.34724535	3.04533273	-0.00207622
H	2.16510565	-5.00079451	-0.00558384	H	1.83699896	5.13462963	0.00746910
H	2.08180542	-2.53286760	-0.00534253	H	1.90413227	2.65344920	0.00172146
H	-2.04963706	-2.53507684	0.00521002	H	-2.22051283	2.40678518	-0.00478667
H	-2.13151032	-5.00153440	0.00536812	H	-2.45300711	4.86540528	0.00084286
At	0.01431323	0.00210042	-0.00003742	At	0.00000000	0.00000000	-0.00408253
C	0.00908008	-6.72837282	-0.00000850	C	0.42045342	-6.70803992	0.00843843
H	-0.51390994	-7.10878017	0.88014173	C	-0.42045342	6.70803992	0.00843843
H	-0.52019848	-7.10891290	-0.87632012	F	-0.83148478	-7.28959125	0.00962351
H	1.01743593	-7.13780026	-0.00355215	F	0.83148478	7.28959125	0.00962351
C	0.01961759	6.73255577	-0.00008082	H	0.95741324	-7.05023049	0.89770968
H	0.54442281	7.11309621	0.87891800	H	-0.95789557	7.05477559	-0.87876247
H	0.54711946	7.11294732	-0.87754203	H	0.95789557	-7.05477559	-0.87876247
H	-0.98873520	7.14199985	-0.00169872	H	-0.95741324	7.05023049	0.89770968
R = CF_2H				**R = CF_3**			
H	-2.06516189	2.53344111	0.10985881	H	-2.06722205	2.53576345	0.01705069
H	-2.14608848	5.01185968	0.19935368	H	-2.15022562	5.01704732	0.03709596
H	2.15198948	5.00876085	0.21327576	H	2.15009381	5.01702629	0.03684177
H	2.06807069	2.53045867	0.12325220	H	2.06707539	2.53575404	0.01679244
C	1.15919261	3.11658173	0.14833366	C	1.15800161	3.12189517	0.01816424
C	1.19952237	4.49836020	0.20349947	C	1.19845619	4.50512953	0.02670758
C	-1.15561878	3.11824977	0.14083338	C	-1.15814211	3.12189648	0.01830857
C	-1.19431419	4.50008851	0.19574337	C	-1.19859663	4.50514514	0.02685379
C	0.00303125	5.20683738	0.22486714	C	-0.00007437	5.20718344	0.03088435
N	0.00138632	2.44364005	0.11781532	N	-0.00007813	2.44915435	0.01347512
N	-0.00138632	-2.44364005	-0.11781532	N	-0.00007958	-2.44915440	-0.01352718
C	1.15561878	-3.11824977	-0.14083338	C	1.15799924	-3.12189786	-0.01804958
C	1.19431419	-4.50008851	-0.19574337	C	1.19845193	-4.50513396	-0.02624300
C	-0.00303125	-5.20683738	-0.22486714	C	-0.00007965	-5.20718808	-0.03022759
C	-1.19952237	-4.49836020	-0.20349947	C	-1.19860040	-4.50514710	-0.02638945
C	-1.15919261	-3.11658173	-0.14833366	C	-1.15814373	-3.12189597	-0.01819432
H	2.14608848	-5.01185968	-0.19935368	H	2.15008936	-5.01703404	-0.03623751
H	2.06516189	-2.53344111	-0.10985881	H	2.06707358	-2.53575753	-0.01684159
H	-2.06807069	-2.53045867	-0.12325220	H	-2.06722290	-2.53576166	-0.01710063
H	-2.15198948	-5.00876085	-0.21327576	H	-2.15023021	-5.01705023	-0.03649170
At	0.00000000	0.00000000	0.00000000	At	-0.00008357	-0.00000038	-0.00012001
C	0.00387920	6.71871200	0.30308054	C	0.00004256	6.72533513	-0.00061597
C	-0.00387920	-6.71871200	-0.30308054	C	0.00004218	-6.72533343	0.00161243
F	-1.09624647	7.21461495	-0.32264236	F	1.08481940	7.22258062	0.60718622
F	1.10860839	7.21301206	-0.31576724	F	-1.08614750	7.22278838	0.60445239

F	-1.10860839	-7.21301206	0.31576724
F	1.09624647	-7.21461495	0.32264236
H	0.00093224	7.08493010	1.33404652
H	-0.00093224	-7.08493010	-1.33404652

F	0.00169948	7.15886977	-1.27204933
F	-1.08619208	-7.22292593	-0.60326043
F	0.00180159	-7.15858878	1.27314127
F	1.08477338	-7.22270956	-0.60616470

R = NO_2

H	-2.06854733	2.53469020	0.00000000
H	-2.14423775	5.04071808	0.00000000
H	2.14423775	5.04071808	0.00000000
H	2.06854733	2.53469020	0.00000000
C	1.16052280	3.12218371	0.00000000
C	1.20581388	4.50632126	0.00000000
C	-1.16052280	3.12218371	0.00000000
C	-1.20581388	4.50632126	0.00000000
C	0.00000000	5.18294060	0.00000000
N	0.00000000	2.45241421	0.00000000
N	0.00000000	-2.45241421	0.00000000
C	-1.16052280	-3.12218371	0.00000000
C	-1.20581388	-4.50632126	0.00000000
C	0.00000000	-5.18294060	0.00000000
C	1.20581388	-4.50632126	0.00000000
C	1.16052280	-3.12218371	0.00000000
H	-2.14423775	-5.04071808	0.00000000
H	-2.06854733	-2.53469020	0.00000000
H	2.06854733	-2.53469020	0.00000000
H	2.14423775	-5.04071808	0.00000000
At	0.00000000	0.00000000	0.00000000
N	0.00000000	-6.67520647	0.00000000
O	1.08597695	-7.21833206	0.00000000
O	-1.08597695	-7.21833206	0.00000000
N	0.00000000	6.67520647	0.00000000
O	1.08597695	7.21833206	0.00000000
O	-1.08597695	7.21833206	0.00000000

Table S15. SR-DFT/B3LYP-D3 optimized geometries of $[D\cdots At\cdots D]^{+}$ complexes.

D = piperidine				D = quinuclidine			
C	2.98156200	-1.23950000	0.86160100	At	-0.00010400	-0.00076800	0.00385500
C	3.51952000	-1.25970400	-0.56203500	C	2.94039100	1.07327600	0.91486100
C	4.33484700	-0.00004700	-0.86394100	C	2.94098100	-1.32962900	0.47090200
C	3.51954600	1.25963900	-0.56209000	C	5.01220000	0.00137700	-0.00563100
C	2.98158800	1.23950900	0.86154700	C	2.93569300	0.25631200	-1.38809600
N	2.18616700	0.00001800	1.11639800	C	4.48261300	0.34100700	-1.40487500
H	2.34032500	-2.09662300	1.06461800	N	2.44047800	-0.00036000	0.00039300
H	3.81041600	-1.25790500	1.57781300	C	4.48790500	-1.38180800	0.40140000
H	2.68541500	-1.34349000	-1.26465400	C	4.48769700	1.04398000	0.99021000
H	4.12750900	-2.15684800	-0.68809200	H	2.48278500	0.91211600	1.88974000
H	4.65691100	-0.00007300	-1.90580100	H	2.56858700	2.02112400	0.52792300
H	5.24393500	-0.00004300	-0.25398400	H	2.47991900	-2.09283400	-0.15417400
H	2.68544200	1.34341100	-1.26471300	H	2.57334800	-1.46812000	1.48679300
H	4.12755300	2.15676600	-0.68818700	H	6.10177700	0.00208500	-0.00815800
H	2.34036900	2.09665300	1.06452600	H	2.47405000	1.17966600	-1.73458900
H	3.81044200	1.25792800	1.57775800	H	2.56479100	-0.55392400	-2.01443300
H	1.89859100	0.00004300	2.09161700	H	4.80365000	1.34238800	-1.69456800
At	0.00000000	0.00001600	0.00000000	H	4.88655600	-0.35274600	-2.14279500
C	-2.98156200	-1.23950000	-0.86160100	H	4.80910200	-2.13232700	-0.32199900
C	-3.51952000	-1.25970400	0.56203400	H	4.89560200	-1.67288400	1.36992800
C	-4.33484700	-0.00004700	0.86394100	H	4.81266500	0.79385000	2.00095000
C	-3.51954600	1.25963900	0.56208900	H	4.89168900	2.02949300	0.75668400
C	-2.98158800	1.23950900	-0.86154700	C	-2.93735200	1.25638100	-0.64322500
N	-2.18616700	0.00001800	-1.11639800	C	-2.93768600	-1.18396100	-0.76759400
H	-2.34032500	-2.09662300	-1.06461800	C	-5.01203900	0.00080600	-0.00555400
H	-3.81041600	-1.25790500	-1.57781400	C	-2.94228900	-0.07140300	1.40810800
H	-2.68541500	-1.34349000	1.26465400	C	-4.48894300	0.01302700	1.43666400
H	-4.12750900	-2.15684900	0.68809100	N	-2.44020200	0.00013600	0.00025500
H	-4.65691100	-0.00007400	1.90580000	C	-4.48443200	-1.25346800	-0.71415200
H	-5.24393500	-0.00004300	0.25398300	C	-4.48380800	1.24264300	-0.73551500
H	-2.68544300	1.34341100	1.26471200	H	-2.47200800	1.32779200	-1.62511600
H	-4.12755300	2.15676600	0.68818600	H	-2.57196300	2.08861800	-0.04302200
H	-2.34036800	2.09665300	-1.06452600	H	-2.47567400	-2.07112800	-0.33722300
H	-3.81044200	1.25792800	-1.57775900	H	-2.56895900	-1.08091700	-1.78730900
H	-1.89859000	0.00004300	-2.09161700	H	-6.10160600	0.00102700	-0.00803100
				H	-2.48023000	0.74411900	1.96235800
				H	-2.57693900	-1.00663100	1.83030200
				H	-4.80917000	0.92408600	1.94384800
				H	-4.89832600	-0.82815400	1.99684200
				H	-4.80493600	-2.14865900	-0.17963600
				H	-4.89024000	-1.31885000	-1.72410600

			H	-4.80066500	1.22720200	-1.77914700
			H	-4.89246900	2.14925800	-0.28829900
D = ammonia			**D = acetonitrile**		
N	-2.43069700	-0.00001300	-0.00024500	At	-0.00000100	0.00020900	0.00000100
At	-0.00000800	0.00000100	0.00006200	N	2.30849800	0.00054500	-0.00042500
N	2.43076400	-0.00001100	-0.00026200	C	3.45409300	-0.00015300	-0.00016300
H	2.79020500	0.32434200	-0.89524400	C	4.90022600	-0.00102000	0.00019700
H	-2.78993500	-0.40922500	-0.85983200	H	5.26488500	-0.88999300	-0.51689100
H	-2.79007200	0.94898200	0.07500700	H	5.26598100	0.89102500	-0.51079100
H	-2.79033900	-0.53971600	0.78382900	H	5.26501900	-0.00476500	1.02856500
H	2.79013900	0.61292500	0.72812700	N	-2.30849400	-0.00036200	0.00043400
H	2.79021700	-0.93725200	0.16636100	C	-3.45408900	-0.00047500	0.00016500
				C	-4.90022200	-0.00059800	-0.00021000
				H	-5.26511300	0.62951100	-0.81289000
				H	-5.26517700	-1.01940500	-0.13973700
				H	-5.26558500	0.38802100	0.95169000
D= pyridine			**D = imidazole**		
H	-1.45495300	-1.46693500	2.46830700	At	0.00000000	0.00023800	0.00000000
H	0.00000000	0.00000000	6.22999100	C	3.18768900	1.08607800	0.00000000
H	-1.51499700	-1.52747900	4.95116100	C	4.48082900	0.66164700	0.00000000
H	1.51499700	1.52747900	4.95116100	C	3.13725700	-1.09303100	0.00000000
H	1.45495300	1.46693500	2.46830700	H	2.79551600	2.08719400	0.00000000
C	0.81752700	0.82426100	3.06002200	H	5.40946300	1.20332700	0.00000000
C	0.84308100	0.85003400	4.44327400	H	5.21774200	-1.33678700	0.00000000
C	-0.81752700	-0.82426100	3.06002200	H	2.80109300	-2.11537500	0.00000000
C	-0.84308100	-0.85003400	4.44327400	C	-3.13756300	1.09259300	0.00000000
C	0.00000000	0.00000000	5.14809500	C	-4.48062600	-0.66247300	0.00000000
N	0.00000000	0.00000000	2.38740100	C	-3.18736300	-1.08653000	0.00000000
N	0.00000000	0.00000000	-2.38740100	H	-2.80171500	2.11504200	0.00000000
C	0.81752700	-0.82426100	-3.06002200	H	-5.21811600	1.33575200	0.00000000
C	0.84308100	-0.85003400	-4.44327400	H	-5.40910200	-1.20442300	0.00000000
C	0.00000000	0.00000000	-5.14809500	H	-2.79488200	-2.08752500	0.00000000
C	-0.84308100	0.85003400	-4.44327400	N	2.36429700	-0.02006900	0.00000000
C	-0.81752700	0.82426100	-3.06002200	N	-2.36429200	0.01985400	0.00000000
H	1.51499700	-1.52747900	-4.95116100	N	4.42604200	-0.71283600	0.00000000
H	1.45495300	-1.46693500	-2.46830700	N	-4.42623800	0.71202700	0.00000000
H	-1.45495300	1.46693500	-2.46830700				
H	-1.51499700	1.52747900	-4.95116100				
H	0.00000000	0.00000000	-6.22999100				
At	0.00000000	0.00000000	0.00000000				
D = furan				**D = acetone**			
At	0.00000000	0.06870200	-0.00000100	C	4.55926300	-0.75056000	-0.00059900
C	-3.11077300	-0.83738500	-0.85014200	C	3.23925600	1.46180000	-0.00097800
C	-4.38658800	-0.71716300	-0.45554800	H	5.13779400	-0.43883700	0.87451600

C	-4.43794200	0.30021100	0.56166300
C	-3.19132900	0.75849400	0.74547000
O	-2.33349700	0.07804600	-0.12862600
H	-2.58076100	-1.43751800	-1.56731600
H	-5.21844800	-1.27955000	-0.84550900
H	-5.31568700	0.64711600	1.08085800
H	-2.72904900	1.50080000	1.37054100
C	3.19132900	0.75848600	-0.74547800
C	4.43794200	0.30020200	-0.56166800
C	4.38658700	-0.71716000	0.45555500
C	3.11077200	-0.83737200	0.85015400
O	2.33349800	0.07805000	0.12862800
H	2.72905100	1.50078500	-1.37055900
H	5.31568400	0.64710100	-1.08087100
H	5.21844400	-1.27954500	0.84552300
H	2.58076200	-1.43749600	1.56733700

H	4.41950700	-1.82784800	-0.00051800
H	2.68974600	1.81460100	0.87600300
H	2.69324700	1.81316900	-0.88079800
C	3.25887300	-0.02913700	-0.00011200
O	2.21693200	-0.70345200	0.00098800
At	0.00000500	-0.00003800	0.00029200
C	-3.23933700	-1.46170400	-0.00118900
C	-4.55923900	0.75072100	0.00023200
H	-2.69206600	-1.81341000	-0.88004200
H	-2.69111500	-1.81421100	0.87676300
H	-5.13806900	0.43912800	-0.87472000
H	-4.41942200	1.82800100	0.00031600
C	-3.25888700	0.02922500	-0.00063700
O	-2.21691000	0.70349000	-0.00049300
H	4.23966200	1.88583500	0.00044500
H	5.13708900	-0.43883400	-0.87618200
H	-5.13680600	0.43893400	0.87597700
H	-4.23975900	-1.88570200	-0.00083100

D = methyl acetate			
C	4.44976000	-1.44453300	0.00314600
H	5.34292800	-1.10952600	-0.51964800
H	4.71605400	-1.63230300	1.04687900
C	3.39853000	-0.38345400	-0.01835500
O	2.19848400	-0.70451400	-0.01566200
O	3.87502200	0.82746900	-0.01472400
C	3.01801400	1.99861800	0.01670400
H	2.41114500	1.99185000	0.91943600
H	2.39418700	2.02639300	-0.87389700
At	-0.00003100	-0.00016400	-0.00004500
C	-4.44862100	1.44574100	-0.01443700
H	-4.68551500	1.65366900	-1.06144400
H	-5.35553100	1.10391200	0.47903100
C	-3.39873900	0.38351700	0.01554000
O	-2.19851800	0.70398200	0.01461200
O	-3.87569800	-0.82720700	0.01686600
C	-3.01876500	-1.99865100	-0.00414200
H	-2.39610700	-2.01940400	0.88747900
H	-2.41063800	-1.99902400	-0.90604800
H	4.05992500	-2.36337000	-0.42610800
H	3.70162800	2.84085800	0.02627800
H	-4.06836700	2.35648100	0.44039400
H	-3.70243700	-2.84088200	-0.00800700

D = thiophene			
At	0.00020400	-0.23283800	0.00001500
C	3.17201600	1.36887400	-0.65513000
C	4.05888100	1.37906200	0.36101400
C	4.26104200	0.08135900	0.96126400
C	3.52462200	-0.89443400	0.39175000
H	2.84080200	2.17626500	-1.28753100
H	4.57492900	2.27098400	0.68668400
H	4.94233900	-0.09419100	1.78155100
H	3.48079400	-1.94659400	0.62114700
C	-3.17136700	1.36849200	0.65540600
C	-4.05924700	1.37953600	-0.35987000
C	-4.26224000	0.08223800	-0.96069300
C	-3.52554600	-0.89410100	-0.39235500
H	-2.83911500	2.17545100	1.28781000
H	-4.57524800	2.27179600	-0.68467100
H	-4.94435800	-0.09269200	-1.78043100
H	-3.48229700	-1.94614500	-0.62238400
S	-2.60526200	-0.25822000	0.95019800
S	2.60500200	-0.25739400	-0.95093200

D = thioacetone			
C	5.09352800	0.21622000	-0.00168500

D = thiane			
C	-3.24701500	-1.40922300	0.84629000

C	3.30294500	-1.59511800	-0.00466200
H	5.56868000	-0.23705500	-0.87866300
H	5.27497700	1.28784300	0.00132200
H	2.69131100	-1.83375400	-0.87865600
H	2.69559600	-1.83785300	0.87125900
C	3.64907000	-0.14547400	-0.00183800
At	-0.00000300	0.00007400	0.00110000
C	-3.30292000	1.59494400	-0.00465800
C	-5.09353900	-0.21637600	-0.00175400
H	-2.69546900	1.83759700	0.87119600
H	-2.69137900	1.83363500	-0.87872200
H	-5.56971000	0.24133400	0.87236200
H	-5.27500700	-1.28799900	0.00042500
C	-3.64907200	0.14530000	-0.00176300
H	4.19344700	-2.22028300	-0.00817100
H	5.56987800	-0.24224600	0.87192400
H	-5.56885200	0.23767200	-0.87822900
H	-4.19341200	2.22012300	-0.00802500
S	2.53604800	1.06596600	0.00145100
S	-2.53603800	-1.06611100	0.00146300

C	-3.53078000	-1.47842700	-0.64917800
C	-4.36655900	-0.30208600	-1.15958200
C	-3.68224500	1.05153200	-0.95438100
C	-3.41296300	1.37243100	0.51060400
H	-2.61108100	-2.22480100	1.18961200
H	-4.17036500	-1.43252400	1.43009200
H	-2.58692800	-1.53345200	-1.19798600
H	-4.05680000	-2.41748000	-0.83760100
H	-4.57113200	-0.44246700	-2.22181700
H	-5.33840700	-0.29954100	-0.65478500
H	-2.74410200	1.08614400	-1.51442700
H	-4.31257300	1.85067700	-1.35191800
H	-2.88123300	2.31455200	0.64139300
H	-4.34047600	1.42547700	1.08580200
At	0.00000500	0.10146700	0.00003500
C	3.24690900	-1.40855400	-0.84742900
C	3.53067300	-1.47899000	0.64797800
C	4.36652700	-0.30312100	1.15934700
C	3.68228100	1.05070400	0.95527400
C	3.41304600	1.37283900	-0.50944700
H	2.61088100	-2.22378300	-1.19140200
H	4.17025600	-1.43148600	-1.43124800
H	2.58682300	-1.53441000	1.19675100
H	4.05663200	-2.41823500	0.83561900
H	4.57110900	-0.44439600	2.22146200
H	5.33836700	-0.30020600	0.65453700
H	2.74413200	1.08489200	1.51533700
H	4.31263800	1.84948900	1.35348700
H	2.88137300	2.31509800	-0.63946600
H	4.34057900	1.42631200	-1.08457500
S	2.39181900	0.12318100	-1.37893300
S	-2.39178200	0.12199200	1.37901400

Table S16. SR-DFT/B3LYP-D3 optimized geometries of [pyridine···X···pyridine]$^+$ complexes.

X = Cl				X = Br			
H	-4.54735700	-1.51927300	-1.52537000	H	4.68150700	-1.51996700	-1.52381400
H	-2.04374000	-1.45366100	-1.45920300	H	2.18531100	-1.45637300	-1.46005400
H	-2.04398000	1.45350300	1.45945400	H	2.18530800	1.45636900	1.46005500
H	-4.54763200	1.51926500	1.52502800	H	4.68150400	1.51997200	1.52381300
H	-5.81995700	0.00005500	-0.00032400	H	5.95627700	0.00000500	-0.00000100
H	2.04373000	1.46006600	-1.45280600	H	-2.18531100	-1.46006600	1.45635900
H	5.81992500	-0.00012400	-0.00033500	H	-5.95627800	0.00000200	-0.00000100
H	4.54732800	1.52592500	-1.51869100	H	-4.68150700	-1.52382400	1.51995800
H	4.54756300	-1.52597700	1.51834500	H	-4.68150500	1.52382700	-1.51995800
H	2.04392000	-1.45987100	1.45308400	H	-2.18530900	1.46006600	-1.45635900
C	2.65268900	-0.82641200	0.82253500	C	-2.78815900	0.82449600	-0.82240300
C	4.03662000	-0.85080800	0.84655900	C	-4.17174900	0.84903300	-0.84687700
C	2.65256500	0.82652000	-0.82240400	C	-2.78816000	-0.82449600	0.82240300
C	4.03651600	0.85078700	-0.84677300	C	-4.17175000	-0.84903000	0.84687600
C	4.73805400	-0.00004400	-0.00020500	C	-4.87439800	0.00000200	0.00000000
N	2.00209000	0.00009700	0.00013800	N	-2.12992200	0.00000000	0.00000000
Cl	0.00008600	0.00002400	0.00015200	Br	0.00000100	-0.00000200	0.00000000
N	-2.00212700	-0.00007300	0.00012200	N	2.12992200	-0.00000200	0.00000100
C	-2.65258400	-0.82289600	-0.82602500	C	2.78816000	-0.82241000	-0.82448900
C	-4.03653600	-0.84709400	-0.85050000	C	4.17175000	-0.84688100	-0.84902500
C	-4.73808500	0.00000400	-0.00019700	C	4.87439800	0.00000300	-0.00000100
C	-4.03667400	0.84706400	0.85028200	C	4.17174800	0.84688400	0.84902500
C	-2.65273300	0.82279700	0.82613100	C	2.78815800	0.82240900	0.82449000

X = I			
H	-4.85573900	1.51770900	1.52523100
H	-2.36855000	1.45704100	1.46358200
H	-2.36846300	-1.45668000	-1.46376100
H	-4.85564200	-1.51812100	-1.52479500
H	-6.13313000	-0.00043100	0.00040000
H	2.36828300	-1.46397500	1.45656400
H	6.13312000	-0.00005000	0.00051100
H	4.85545700	-1.52528100	1.51801900
H	4.85590200	1.52509100	-1.51746400
H	2.36870900	1.46370200	-1.45682200
C	2.96409400	0.82384900	-0.81996700
C	4.34724800	0.84903200	-0.84478400
C	2.96385300	-0.82407900	0.81992600
C	4.34699800	-0.84922300	0.84518900
C	5.05123300	-0.00007600	0.00032500
N	2.29575400	-0.00011500	-0.00012200

I	0.00000800	0.00010500	-0.00014100
N	-2.29576400	0.00018400	-0.00008000
C	-2.96400900	0.82011900	0.82386200
C	-4.34716200	0.84494900	0.84919200
C	-5.05124300	-0.00024400	0.00025100
C	-4.34710400	-0.84521200	-0.84887500
C	-2.96395700	-0.81995300	-0.82388400

Table S17. SO-DFT/B3LYP-D3 optimized geometry of [pyridine···I···pyridine]$^{+}$ complex.

[pyridine···I···pyridine]$^{+}$			
H	2.15144359	4.86540076	-0.00657071
H	2.06521532	2.37916005	-0.00631759
H	-2.06521532	2.37916005	0.00631759
H	-2.15144359	4.86540076	0.00657071
H	0.00000000	6.14264805	0.00000000
H	2.06521532	-2.37916005	0.00631759
H	0.00000000	-6.14264805	0.00000000
H	2.15144359	-4.86540076	0.00657071
H	-2.15144359	-4.86540076	-0.00657071
H	-2.06521532	-2.37916005	-0.00631759
C	-1.16168371	-2.97358216	-0.00355055
C	-1.19770691	-4.35669761	-0.00363831
C	1.16168371	-2.97358216	0.00355055
C	1.19770691	-4.35669761	0.00363831
C	0.00000000	-5.06069812	0.00000000
N	0.00000000	-2.30596690	0.00000000
I	0.00000000	0.00000000	0.00000000
N	0.00000000	2.30596690	0.00000000
C	1.16168371	2.97358216	-0.00355055
C	1.19770691	4.35669761	-0.00363831
C	0.00000000	5.06069812	0.00000000
C	-1.19770691	4.35669761	0.00363831
C	-1.16168371	2.97358216	0.00355055

Table S18. SR-DFT/B3LYP-D3 optimized geometries of $[D\cdots I\cdots D]^+$ complexes.

D = piperidine				D = quinuclidine			
C	2.88561100	-1.24204600	0.85971300	I	-0.00001100	0.00064700	0.00255500
C	3.45114700	-1.25873100	-0.55335600	C	-2.84795200	0.49348400	1.32216400
C	4.27429200	0.00028000	-0.83555100	C	-2.84449500	0.89783400	-1.08825600
C	3.45100200	1.25909800	-0.55290600	C	-4.91874700	-0.00036100	-0.00316000
C	2.88546900	1.24184700	0.86015400	C	-2.84519600	-1.39194500	-0.23292300
N	2.09183100	-0.00019700	1.10631800	C	-4.39136700	-1.43459000	-0.14324000
H	2.23518500	-2.09583900	1.04679100	N	-2.35099000	-0.00030500	0.00098600
H	3.69904900	-1.26673600	1.59295600	C	-4.39012100	0.83867700	-1.17413900
H	2.63087800	-1.33875600	-1.27196800	C	-4.39375400	0.59499800	1.31004600
H	4.05989900	-2.15675200	-0.66890900	H	-2.37653800	1.45677900	1.51004100
H	4.62005500	0.00048600	-1.86975400	H	-2.48946700	-0.20379300	2.07812100
H	5.16911900	0.00022100	-0.20478000	H	-2.37153000	0.57906200	-2.01570400
H	2.63073200	1.33929100	-1.27149500	H	-2.48520400	1.90046800	-0.86079700
H	4.05965500	2.15722800	-0.66813600	H	-6.00826300	-0.00047300	-0.00476400
H	2.23493500	2.09548600	1.04754500	H	-2.37498100	-2.03579500	0.50857000
H	3.69890300	1.26636200	1.59340400	H	-2.48329200	-1.69765400	-1.21364300
H	1.78580100	-0.00040200	2.07601800	H	-4.70460800	-2.03412800	0.71245400
I	0.00000800	-0.00007500	0.00001100	H	-4.80335200	-1.90692900	-1.03545200
C	-2.88549200	-1.24193500	-0.85986500	H	-4.70024400	0.39662300	-2.12188900
C	-3.45107000	-1.25883800	0.55318400	H	-4.80402200	1.84676500	-1.13823900
C	-4.27432100	0.00007300	0.83551900	H	-4.70560000	1.63631600	1.40045700
C	-3.45112300	1.25898700	0.55305000	H	-4.80890000	0.05914600	2.16407900
C	-2.88557100	1.24194200	-0.86001400	C	2.84744400	-1.02931600	0.96600700
N	-2.09182400	0.00003700	-1.10631100	C	2.84413200	-0.32253800	-1.37354400
H	-2.23497100	-2.09563200	-1.04703700	C	4.91877000	-0.00011700	-0.00307900
H	-3.69891400	-1.26661600	-1.59312400	C	2.84662100	1.35061100	0.40816400
H	-2.63083400	-1.33890100	1.27182000	C	4.39234000	1.34623700	0.51152100
H	-4.05976300	-2.15692100	0.66858100	N	2.35078700	-0.00035300	0.00088700
H	-4.62011400	0.00011100	1.86971200	C	4.38950000	-0.22820400	-1.42521400
H	-5.16913200	0.00002200	0.20472400	C	4.39299300	-1.11847400	0.90652200
H	-2.63085400	1.33914100	1.27164700	H	2.37332800	-1.97521700	0.70932600
H	-4.05983800	2.15706000	0.66838200	H	2.49216100	-0.73780600	1.95338900
H	-2.23513400	2.09568600	-1.04728700	H	2.36899100	0.37263100	-2.06380800
H	-3.69900900	1.26648200	-1.59326500	H	2.48708900	-1.32314700	-1.61330000
H	-1.78576300	0.00001200	-2.07600100	H	6.00828500	-0.00016800	-0.00448300
				H	2.37491900	1.60113200	1.35694200
				H	2.48790100	2.05905000	-0.33725200
				H	4.70308300	1.49927500	1.54588000
				H	4.80715500	2.16713200	-0.07404500
				H	4.69755100	0.59165000	-2.07543400
				H	4.80459400	-1.14514400	-1.84438800

	H 4.70173300 -2.09098600 0.52092300 H 4.81022500 -1.02225400 1.90925800
D = ammonia	**D = acetonitrile**
N -2.34357500 0.00000100 0.00000800 I -0.00000700 -0.00000600 -0.00000600 N 2.34361500 0.00001600 0.00001000 H 2.69725200 0.82671300 0.47676400 H -2.69695500 0.92005600 -0.25377700 H -2.69747900 -0.24010400 0.92353400 H -2.69739300 -0.67970700 -0.66977200 H 2.69705000 -0.82627100 0.47762400 H 2.69763400 -0.00050700 -0.95417300	I -0.00000100 -0.00014900 0.00003200 N -2.18152000 -0.07298900 -0.40179200 C -3.30740500 -0.11009100 -0.60904200 C -4.72859300 -0.15701900 -0.87067900 H -4.99104800 0.61235300 -1.59863100 H -4.99410600 -1.13801500 -1.26802200 H -5.27618300 0.01908400 0.05661000 N 2.18152000 0.07279600 0.40183400 C 3.30740800 0.11036900 0.60898200 C 4.72859900 0.15781500 0.87050900 H 5.23440200 -0.60529000 0.27673900 H 5.11614300 1.14201300 0.60237800 H 4.91081000 -0.02737000 1.93033800
D = pyridine	**D = imidazole**
H -4.85573900 1.51770900 1.52523100 H -2.36855000 1.45704100 1.46358200 H -2.36846300 -1.45668000 -1.46376100 H -4.85564200 -1.51812100 -1.52479500 H -6.13313000 -0.00043100 0.00040000 H 2.36828300 -1.46397500 1.45656400 H 6.13312000 -0.00005000 0.00051100 H 4.85545700 -1.52528100 1.51801900 H 4.85590200 1.52509100 -1.51746400 H 2.36870900 1.46370200 -1.45682200 C 2.96409400 0.82384900 -0.81996700 C 4.34724800 0.84903200 -0.84478400 C 2.96385300 -0.82407900 0.81992600 C 4.34699800 -0.84922300 0.84518900 C 5.05123300 -0.00007600 0.00032500 N 2.29575400 -0.00011500 -0.00012200 I 0.00000800 0.00010500 -0.00014100 N -2.29576400 0.00018400 -0.00008000 C -2.96400900 0.82011900 0.82386200 C -4.34716200 0.84494900 0.84919200 C -5.05124300 -0.00024400 0.00025100 C -4.34710400 -0.84521200 -0.84887500 C -2.96395700 -0.81995300 -0.82388400	I 0.00003000 -0.00001200 0.00000000 C 1.10634300 -3.08923400 0.00000000 C 0.68751800 -4.38416700 0.00000000 C -1.07540100 -3.05029500 0.00000000 H 2.10466900 -2.69005700 0.00000000 H 1.23379000 -5.31012300 0.00000000 H -1.30720500 -5.13158100 0.00000000 H -2.09864800 -2.71703600 0.00000000 C 1.07533200 3.05026400 0.00000000 C -0.68752100 4.38421400 0.00000000 C -1.10640500 3.08929900 0.00000000 H 2.09856900 2.71697100 0.00000000 H 1.30723700 5.13154300 0.00000000 H -1.23374800 5.31019600 0.00000000 H -2.10474800 2.69016500 0.00000000 N -0.00495000 -2.27435700 0.00000000 N 0.00485200 2.27437300 0.00000000 N -0.68752100 -4.33641900 0.00000000 N 0.68751700 4.33641000 0.00000000
D = funan	**D = acetone**
C -2.99177100 -0.83413000 -0.87063500 C -4.25713600 -0.78348000 -0.43211300 C -4.33327000 0.23826300 0.58079700	C -4.46771100 -0.74256600 0.00020300 C -3.13737300 1.46289700 0.00023400 H -5.04386900 -0.42767200 -0.87540800

C -3.11137500 0.77072600 0.72027700	H -4.33366300 -1.82056700 0.00050900
O -2.24668300 0.13709900 -0.18502600	H -2.58672400 1.81332200 -0.87689200
H -2.45081200 -1.40577300 -1.60259800	H -2.58880900 1.81293500 0.87884800
H -5.06904300 -1.39309100 -0.79221400	C -3.16494300 -0.02669000 0.00011800
H -5.21307300 0.54006700 1.12426500	O -2.12805100 -0.71202800 -0.00022500
H -2.67065000 1.54454300 1.32210000	I 0.00000400 -0.00001900 -0.00014300
C 3.11125500 0.76958400 -0.72157600	C 3.13739300 -1.46286800 0.00029500
C 4.33317400 0.23731200 -0.58152500	C 4.46768700 0.74261500 0.00010200
C 4.25722600 -0.78278900 0.43305100	H 2.58795000 -1.81299200 0.87831300
C 2.99195600 -0.83264200 0.87195200	H 2.58764200 -1.81324500 -0.87742400
O 2.24676500 0.13750700 0.18497100	H 5.04405300 0.42737900 0.87544300
H 2.67044300 1.54241700 -1.32459800	H 4.33362000 1.82061400 0.00019000
H 5.21285900 0.53821200 -1.12568400	C 3.16493200 0.02671200 0.00011400
H 5.06917900 -1.39185600 0.79396900	O 2.12803200 0.71204700 -0.00001000
H 2.45116200 -1.40307400 1.60498200	H -4.13672300 1.88920900 -0.00075200
I -0.00002000 0.12329500 -0.00002200	H -5.04407200 -0.42712600 0.87547100
	H 5.04385700 0.42754300 -0.87543500
	H 4.13675700 -1.88914900 0.00020000
D = methyl acetate	**D = thiophene**
C 4.37037500 1.42099100 -0.01025400	C -3.08999600 1.31667100 0.65879900
H 5.24692700 1.08199100 0.53789000	C -3.98268300 1.33010300 -0.35157400
H 4.66086800 1.57618200 -1.05289200	C -4.19211900 0.03207900 -0.95218500
C 3.30134900 0.37768500 0.01728100	C -3.45544400 -0.94581200 -0.38769200
O 2.10718000 0.73175700 0.02037600	H -2.75139600 2.12257700 1.28914600
O 3.75613400 -0.83860600 0.01320000	H -4.49876000 2.22332300 -0.67368800
C 2.89511600 -2.00913900 -0.00894900	H -4.87925300 -0.14059900 -1.76823100
H 2.28745000 -2.00604900 -0.91066600	H -3.41464400 -1.99776600 -0.61852000
H 2.27350300 -2.02874300 0.88292700	C 3.08994900 1.31667300 -0.65881100
I 0.00000000 0.00000000 0.00002300	C 3.98263500 1.33011900 0.35155700
C -4.37037200 -1.42099100 0.01050700	C 4.19207000 0.03210300 0.95219400
H -4.66079800 -1.57605100 1.05318400	C 3.45539300 -0.94579500 0.38772200
H -5.24695900 -1.08206600 -0.53762700	H 2.75133700 2.12256500 -1.28917000
C -3.30135100 -0.37768600 -0.01722600	H 4.49870800 2.22334500 0.67366400
O -2.10718100 -0.73175700 -0.02030000	H 4.87919300 -0.14055600 1.76825200
O -3.75613600 0.83860500 -0.01332900	H 3.41458900 -1.99774400 0.61857600
C -2.89511800 2.00914100 0.00857700	S 2.52666800 -0.31169900 -0.94983500
H -2.27350900 2.02856400 -0.88330500	S -2.52668600 -0.31168100 0.94981900
H -2.28744800 2.00623400 0.91029200	I 0.00003200 -0.28750800 0.00000300
H 3.98986900 2.35675300 0.38922900	
H 3.57891900 -2.85124000 -0.01416000	
H -3.98988600 -2.35680300 -0.38887700	
H -3.57892000 2.85124400 0.01362100	
D = thioacetone	**D = thiane**
C 5.01339700 -0.22158300 0.00031600	C -3.15589200 -1.39021500 0.85551100

C	3.22615700	1.59387600	0.00271500
H	5.48947500	0.23184000	0.87670500
H	5.19311700	-1.29356100	-0.00168800
H	2.61520100	1.83438200	0.87650000
H	2.61846400	1.83703800	-0.87267000
C	3.56978600	0.14373500	0.00087800
I	-0.00004600	0.00017800	-0.00066000
C	-3.22566400	-1.59408500	0.00262700
C	-5.01336400	0.22091700	0.00049600
H	-2.61789400	-1.83709900	-0.87274100
H	-2.61466800	-1.83447700	0.87642500
H	-5.48963300	-0.23570700	-0.87412500
H	-5.19336300	1.29284900	-0.00117200
C	-3.56965800	-0.14402200	0.00078300
H	4.11868100	2.21603900	0.00518800
H	5.48974000	0.23520600	-0.87417400
H	-5.48927700	-0.23292000	0.87675600
H	-4.11804300	-2.21645800	0.00508300
S	2.45518700	-1.06566800	-0.00094800
S	-2.45539400	1.06569300	-0.00105100

C	-3.45911600	-1.46358400	-0.63622700
C	-4.30559200	-0.29125700	-1.13782500
C	-3.61825300	1.06321300	-0.94990400
C	-3.33049000	1.39331600	0.50980800
H	-2.50912800	-2.20033300	1.19172600
H	-4.07093000	-1.41959000	1.45223800
H	-2.52258100	-1.51611600	-1.19707500
H	-3.98430200	-2.40503600	-0.81451900
H	-4.52687500	-0.43654000	-2.19601700
H	-5.26922700	-0.28752400	-0.61746000
H	-2.68737400	1.09362000	-1.52158300
H	-4.25329000	1.86061500	-1.34332800
H	-2.79265400	2.33371700	0.62807200
H	-4.25077700	1.45489400	1.09590500
I	-0.00000600	0.12501400	-0.00001900
C	3.15595600	-1.39055400	-0.85495200
C	3.45914900	-1.46331000	0.63681900
C	4.30558800	-0.29075300	1.13795100
C	3.61823200	1.06363100	0.94946000
C	3.33045100	1.39311100	-0.51039000
H	2.50925800	-2.20085100	-1.19086200
H	4.07101400	-1.42010800	-1.45164200
H	2.52260000	-1.51563800	1.19766400
H	3.98435500	-2.40467600	0.81550000
H	4.52686200	-0.43559500	2.19620600
H	5.26923000	-0.28721500	0.61759700
H	2.68736300	1.09427700	1.52114100
H	4.25326600	1.86120800	1.34253300
H	2.79260600	2.33345800	-0.62904500
H	4.25073800	1.45446000	-1.09651200
S	2.30538900	0.14581600	-1.37682200
S	-2.30539200	0.14641200	1.37675700

Table S19. SO-DFT/B3LYP-D3 optimized geometries of $[D\cdots At]^+$ cations.

D = piperidine				D = quinuclidine			
C	-0.82173834	-1.81701234	1.25001115	At	0.00000000	-0.00000000	-1.54115422
C	0.58122831	-2.40243440	1.26262394	C	-0.00114553	1.42269284	1.30862833
C	0.86115038	-3.22155062	0.00000000	C	-1.23151537	-0.71233848	1.30862833
C	0.58122831	-2.40243440	-1.26262394	C	0.00000000	0.00000000	3.38103232
C	-0.82173834	-1.81701234	-1.25001115	C	1.23266090	-0.71035436	1.30862833
N	-1.07447230	-1.02177309	0.00000000	C	1.28508517	-0.65212021	2.85714062
H	-1.01347336	-1.17005266	2.10458075	N	0.00000000	0.00000000	0.81934480
H	-1.57256885	-2.61429409	1.25310854	C	-1.20729526	-0.78685629	2.85714062
H	1.31503359	-1.59707794	1.36573623	C	-0.07778991	1.43897651	2.85714062
H	0.67821265	-3.02013058	2.15675616	H	-0.85186808	1.92473803	0.85241205
H	1.89505364	-3.56666231	0.00000000	H	0.90906939	1.88949170	0.93667209
H	0.23400427	-4.11836018	0.00000000	H	-1.24093799	-1.70010842	0.85241205
H	1.31503359	-1.59707794	-1.36573623	H	-2.09088251	-0.15746867	0.93667209
H	0.67821265	-3.02013058	-2.15675616	H	0.00000000	0.00000000	4.47029523
H	-1.01347336	-1.17005266	-2.10458075	H	2.09280607	-0.22462961	0.85241205
H	-1.57256885	-2.61429409	-1.25310854	H	1.18181312	-1.73202304	0.93667209
H	-2.04342945	-0.70860034	0.00000000	H	2.15722903	-0.08104063	3.17630272
At	0.03325695	1.06748653	0.00000000	H	1.39530305	-1.66040681	3.25609575
				H	-1.14879776	-1.82769483	3.17630272
				H	-2.13560600	-0.37816448	3.25609575
				H	-1.00843127	1.90873546	3.17630272
				H	0.74030295	2.03857129	3.25609575
D = ammonia				**D = acetonitrile**			
N	0.00000000	-0.00000000	2.20474734	At	0.00000000	0.00000000	0.67121148
At	-0.00000000	0.00000000	-0.16958308	N	-0.00000000	0.00000000	-1.59360194
H	-0.45986447	0.84141342	2.55015037	C	0.00000000	-0.00000000	-2.74023915
H	0.95861763	-0.02245239	2.55015037	C	0.00000000	-0.00000000	-4.18313249
H	-0.49875316	-0.81896103	2.55015037	H	-0.29899159	0.98556726	-4.54555721
				H	1.00302208	-0.23384932	-4.54555721
				H	-0.70403049	-0.75171794	-4.54555721
D = pyridine				**D = imidazole**			
N	0.00000000	0.00000000	-1.17803683	At	0.00647736	0.92893304	0.00000000
C	0.00000000	1.17142406	-1.83742817	C	1.06801335	-2.11712313	0.00000000
C	0.00000000	1.19915161	-3.21885345	C	-0.71183539	-3.43331473	0.00000000
C	0.00000000	0.00000000	-3.92150728	C	-1.13199145	-2.14091182	0.00000000
C	0.00000000	-1.19915161	-3.21885345	H	2.09395094	-1.79111603	0.00000000
C	0.00000000	-1.17142406	-1.83742817	H	1.27875012	-4.19279231	0.00000000
H	0.00000000	2.15366710	-3.72622373	H	-1.26416841	-4.35628314	0.00000000
H	0.00000000	2.07513652	-1.24481694	H	-2.12934241	-1.73910161	0.00000000
H	0.00000000	-2.07513652	-1.24481694	N	-0.00768823	-1.33807030	0.00000000

H 0.00000000 -2.15366710 -3.72622373 H 0.00000000 0.00000000 -5.00348352 At 0.00000000 0.00000000 1.12016207	N 0.66356634 -3.39179827 0.00000000
D = funan	**D = acetone**
At 0.29118393 0.92606957 0.00000000 C -0.19203573 -2.18181949 -1.12703545 C 0.22972223 -3.38893487 -0.72111890 C 0.22972223 -3.38893487 0.72111890 C -0.19203573 -2.18181949 1.12703545 H -0.38890688 -1.72203924 -2.07907851 H 0.48018628 -4.21681095 -1.36406747 H 0.48018628 -4.21681095 1.36406747 H -0.38890688 -1.72203924 2.07907851 O -0.48718233 -1.39980589 0.00000000	C 0.76218011 3.69167208 0.00007380 C -1.47396143 2.42200251 -0.00146264 H 0.31679279 4.37914672 0.72304998 H 1.81883855 3.53991196 0.20165957 H -1.80174949 2.44181754 1.04569858 H -1.89485128 1.53462051 -0.47297599 C 0.01100146 2.40643001 -0.00282870 O 0.69015257 1.36143275 0.00910708 At 0.00622919 -0.85426857 0.00562743 H -1.85894999 3.32359317 -0.47488539 H 0.63902387 4.15198607 -0.98716365
D = methyl acetate	**D = thiophene**
C 1.47660510 -3.42906674 -0.00774434 H 1.35385433 -4.05599788 0.87777430 H 1.33305744 -4.06515597 -0.88318208 C 0.42159036 -2.37110288 0.00097863 O 0.77409163 -1.16945242 0.02336974 O -0.78797175 -2.82916268 -0.01246230 C -1.97545997 -1.99279217 0.00871803 H -2.01306112 -1.37992655 -0.88916122 H -1.98924761 -1.39040680 0.91431566 At 0.01146869 1.02049764 -0.00106702 H 2.46575207 -2.98305657 -0.01997976 H -2.80270823 -2.69446181 0.01526888	At -0.00083704 1.06058597 -0.00541795 C -1.26746256 -2.27164591 0.06918818 C -0.72437395 -3.17213834 -0.77026157 C 0.72738746 -3.17164512 -0.76833327 C 1.26762096 -2.27079982 0.07258696 H -2.30114243 -2.06602265 0.29591041 H -1.31432612 -3.84392663 -1.37835345 H 1.31942398 -3.84300623 -1.37487059 H 2.30056281 -2.06443466 0.30203461 S -0.00141058 -1.45672755 0.96820675
D = thioacetone	**D = thiane**
At 0.00216301 0.92042798 -0.18081886 C 1.66521240 -2.34721409 0.02055616 C -0.25090921 -4.03270873 0.04691475 H 2.00586940 -2.26265447 -1.02038915 H 1.91728418 -1.41237095 0.51908857 H 0.25979141 -4.59300400 -0.74362055 H -1.32720262 -4.14950775 -0.05607443 C 0.20983532 -2.61671726 0.00635873 H 0.07338685 -4.47283345 0.99683001 H 2.20859723 -3.17656837 0.47192847 S -0.98678523 -1.48070062 -0.07915411	At 0.00572197 1.19472512 -0.00240464 C 0.68678637 -2.04761196 -1.38100215 C -0.78544653 -2.42805051 -1.31396711 C -1.16061194 -3.20706855 -0.05128485 C -0.90159483 -2.42575615 1.23885497 C 0.55845157 -2.04485802 1.43860723 H 0.94003691 -1.44618625 -2.25347669 H 1.33780725 -2.92754106 -1.37998678 H -1.40176251 -1.52952194 -1.40519806 H -0.99420312 -3.03221079 -2.20019581 H -2.21737096 -3.47159643 -0.09912095 H -0.60923763 -4.15246035 -0.02534923 H -1.52372379 -1.52722452 1.27224777 H -1.18984255 -3.02845564 2.10352844 H 0.73130556 -1.44158829 2.32925277

	H 1.20690895 -2.92463344 1.49860632 S 1.30436357 -1.09055745 0.05889330

Table S20. SO-DFT/B3LYP-D3 optimized geometries of [4-R-pyridine···At]$^+$ cations.

R = NH_2				**R = OH**			
H	0.00000000	-2.07765855	0.93604238	H	-2.07773505	0.93489988	0.00000000
H	0.00000000	-2.16440485	3.38632318	H	-2.16685545	3.39860381	0.00000000
H	0.00000000	2.16440485	3.38632318	H	2.14679530	3.42242105	0.00000000
H	0.00000000	2.07765855	0.93604238	H	2.07545710	0.94026512	0.00000000
C	0.00000000	1.16862068	1.52049711	C	1.16785052	1.52674106	0.00000000
C	0.00000000	1.20505921	2.88695867	C	1.20212113	2.89725592	0.00000000
C	0.00000000	-1.16862068	1.52049711	C	-1.17025078	1.52184533	0.00000000
C	0.00000000	-1.20505921	2.88695867	C	-1.20851588	2.89574622	0.00000000
C	0.00000000	0.00000000	3.62696957	C	-0.00408572	3.61233322	0.00000000
N	0.00000000	0.00000000	0.84146238	N	-0.00224221	0.85277840	0.00000000
At	0.00000000	0.00000000	-1.43100477	At	0.00319864	-1.43321469	0.00000000
N	0.00000000	0.00000000	4.96588821	O	0.07200965	4.93666661	0.00000000
H	0.00000000	0.85859260	5.49027300	H	-0.79687626	5.36292592	0.00000000
H	0.00000000	-0.85859260	5.49027300				
R = CH_3				**R = CFH_2**			
H	-2.07666408	0.91622139	0.00000000	N	-0.10985791	0.52040130	-0.00113101
H	-2.15550070	3.38323164	0.00000000	C	1.00915750	1.26460611	-0.00080738
H	2.14729612	3.38680755	0.00000000	C	0.94430274	2.64317998	-0.00006386
H	2.07312774	0.92078950	0.00000000	C	-0.29786057	3.27439299	0.00038605
C	1.16587207	1.50793265	0.00000000	C	-1.44395266	2.47626461	-0.00004276
C	1.18868689	2.88475455	0.00000000	C	-1.32293076	1.10427003	-0.00077817
C	-1.16982681	1.50421313	0.00000000	H	1.85771979	3.22001105	0.00010825
C	-1.19605803	2.88373999	0.00000000	H	1.95416666	0.73984390	-0.00120681
C	-0.00578964	3.61536645	0.00000000	H	-2.18658303	0.45460475	-0.00119783
N	-0.00249038	0.83883718	0.00000000	H	-2.43531572	2.91076307	0.00015792
At	0.00147538	-1.44900928	0.00000000	At	0.04813315	-1.76684106	-0.00115072
C	0.00350377	5.11062831	0.00000000	C	-0.41108642	4.77220594	0.00140869
H	0.53321103	5.48797263	0.87782318	F	0.83647501	5.35490200	-0.00005659
H	0.53321103	5.48797263	-0.87782318	H	-0.95404973	5.11162122	-0.88586667
H	-1.00335560	5.52241856	0.00000000	H	-0.95138049	5.11049778	0.89075771
R = CF_2H				**R = CF_3**			
H	0.08713645	0.32008163	-2.07520464	H	0.01430470	0.07195814	-2.07544660
H	0.19219918	2.79907510	-2.15151130	H	0.03535378	2.55458136	-2.15255080
H	0.19219918	2.79907510	2.15151130	H	0.03535378	2.55458136	2.15255080
H	0.08713645	0.32008163	2.07520464	H	0.01430470	0.07195814	2.07544660
C	0.11942822	0.90908811	1.16973303	C	0.01587354	0.66165933	1.16983700
C	0.18323153	2.28840123	1.19881490	C	0.02486627	2.04310896	1.20029979
C	0.11942822	0.90908811	-1.16973303	C	0.01587354	0.66165933	-1.16983700
C	0.18323153	2.28840123	-1.19881490	C	0.02486627	2.04310896	-1.20029979
C	0.21332898	2.99451842	0.00000000	C	0.02901481	2.74359218	0.00000000

N	0.08922316	0.24846448	0.00000000
At	-0.03381225	-2.04692670	0.00000000
C	0.29545351	4.50918521	0.00000000
F	-0.32587951	4.99685581	-1.10284925
F	-0.32587951	4.99685581	1.10284925
H	1.32943639	4.86815141	0.00000000

N	0.01085590	0.00100429	0.00000000
At	-0.00224395	-2.30317245	0.00000000
C	-0.00114808	4.26616677	0.00000000
F	0.60560632	4.75567507	1.08554276
F	0.60560632	4.75567507	-1.08554276
F	-1.27295583	4.68969084	0.00000000

R = NO_2

N	0.00000000	0.00000000	-0.32509006
C	0.00000000	-1.17193126	-0.98387487
C	0.00000000	-1.20755464	-2.36603182
C	0.00000000	0.00000000	-3.04080847
C	0.00000000	1.20755464	-2.36603182
C	0.00000000	1.17193126	-0.98387487
H	0.00000000	-2.14633982	-2.90102341
H	0.00000000	-2.07663880	-0.39263988
H	0.00000000	2.07663880	-0.39263988
H	0.00000000	2.14633982	-2.90102341
At	0.00000000	0.00000000	1.98416936
N	0.00000000	0.00000000	-4.53639107
O	0.00000000	1.08694340	-5.07395463
O	0.00000000	-1.08694340	-5.07395463

Table S21. SR-DFT/B3LYP-D3 optimized geometries of $[D\cdots At]^+$ cations.

D = piperidine				**D = quinuclidine**			
At	1.05495400	-0.38914500	0.00000000	At	0.00000000	0.00000000	1.49502000
C	-1.84510400	-0.06572900	1.25336700	C	-1.42872900	-0.04282500	-1.26613100
C	-1.84510400	1.45279000	1.26246300	C	0.67727700	1.25872800	-1.26613100
C	-2.49629900	2.02313400	0.00000000	C	0.00000000	0.00000000	-3.33071400
C	-1.84510400	1.45279000	-1.26246300	C	0.75145200	-1.21590300	-1.26613100
C	-1.84510400	-0.06572900	-1.25336700	C	0.60968300	-1.30400500	-2.80368100
N	-1.19285300	-0.60961500	0.00000000	N	0.00000000	0.00000000	-0.76158400
H	-1.32841200	-0.49551000	2.10918100	C	0.82446000	1.18000300	-2.80368100
H	-2.86726400	-0.45600400	1.23242400	C	-1.43414300	0.12400100	-2.80368100
H	-0.81949800	1.81890000	1.36377700	H	-1.97720300	0.75049800	-0.76442000
H	-2.37716200	1.77760100	2.15784000	H	-1.84020300	-0.99869600	-0.94846500
H	-2.41879400	3.11007200	0.00000000	H	1.63855200	1.33705900	-0.76442000
H	-3.56437900	1.78492600	0.00000000	H	0.05520500	2.09301000	-0.94846500
H	-0.81949800	1.81890000	-1.36377700	H	0.00000000	0.00000000	-4.41949400
H	-2.37716200	1.77760100	-2.15784000	H	0.33865100	-2.08755700	-0.76442000
H	-1.32841200	-0.49551000	-2.10918100	H	1.78499700	-1.09431400	-0.94846500
H	-2.86726400	-0.45600400	-1.23242400	H	-0.02104300	-2.15160600	-3.07259300
H	-1.29299000	-1.62388200	0.00000000	H	1.59182100	-1.47715000	-3.24292400
				H	1.87386700	1.05757900	-3.07259300
				H	0.48333900	2.11713300	-3.24292400
				H	-1.85282400	1.09402700	-3.07259300
				H	-2.07516000	-0.63998200	-3.24292400
D = ammonia				**D = acetonitrile**			
N	-1.99881900	0.00000200	-0.00002200	At	-0.72548000	0.00001000	0.00000900
At	0.24746600	0.00000400	-0.00000200	N	1.38254900	-0.00018300	-0.00017100
H	-2.34827200	0.49643000	-0.82136300	C	2.52903700	-0.00009600	-0.00003800
H	-2.34760300	0.46311300	0.84082400	C	3.97000700	0.00009100	0.00006900
H	-2.34700900	-0.95990200	-0.01911900	H	4.33106200	0.80764500	0.64106000
				H	4.33135600	-0.95869200	0.37892300
				H	4.33128900	0.15149400	-1.01969800
D = pyridine				**D = imidazole**			
H	0.00000000	2.07889900	-1.08186500	At	0.00000000	1.00055500	0.00000000
H	0.00000000	0.00000000	-4.83971400	C	-1.07370700	-1.94087600	0.00000000
H	0.00000000	2.15379300	-3.56071300	C	0.70694400	-3.25916100	0.00000000
H	0.00000000	-2.15379300	-3.56071300	C	1.13550000	-1.97056700	0.00000000
H	0.00000000	-2.07889900	-1.08186500	H	-2.09608700	-1.60480700	0.00000000
C	0.00000000	-1.17594900	-1.67399300	H	-1.28645200	-4.01251800	0.00000000
C	0.00000000	-1.19870800	-3.05444000	H	1.25617000	-4.18390500	0.00000000
C	0.00000000	1.17594900	-1.67399300	H	2.13107700	-1.56509500	0.00000000
C	0.00000000	1.19870800	-3.05444000	N	0.00919300	-1.16654500	0.00000000

C	0.00000000	0.00000000	-3.75784400	N	-0.66878300	-3.21305600	0.00000000
N	0.00000000	0.00000000	-1.01278000				
At	0.00000000	0.00000000	1.18238300				
D = funan				**D = acetone**			
At	-0.97548600	0.00000000	-0.03028100	C	3.49250300	-0.76523500	-0.00000700
C	1.98942100	-1.14815000	0.15108600	C	2.20573500	1.46942500	-0.00000600
C	3.20360400	-0.72398800	-0.20105600	H	4.07479400	-0.45931000	0.87613000
C	3.20361000	0.72398300	-0.20104900	H	3.33265800	-1.83959200	0.00013300
C	1.98942400	1.14815100	0.15107800	H	1.65841800	1.82517400	0.87968000
O	1.18701300	0.00000400	0.42111700	H	1.65785100	1.82532200	-0.87926100
H	1.50415500	-2.09380800	0.31383400	C	2.22031700	-0.00814900	-0.00001900
H	4.04775900	-1.36079700	-0.41153800	O	1.17414700	-0.70872800	0.00002600
H	4.04777200	1.36078700	-0.41151400	At	-0.88132600	-0.01508300	-0.00000100
H	1.50416300	2.09381300	0.31381700	H	3.20984200	1.88360100	-0.00026400
				H	4.07464200	-0.45952300	-0.87632200
D = methyl acetate				**D = thiophene**			
C	3.25332100	-1.41174800	0.01974900	At	-1.09777300	0.00002200	-0.09111800
H	4.15767400	-1.03078800	-0.45011600	C	2.11205400	-1.27529000	0.12258700
H	3.46801000	-1.62092200	1.07232600	C	3.09606600	-0.72911100	-0.60609600
C	2.18254400	-0.37353100	-0.02015800	C	3.09585000	0.72978800	-0.60572500
O	0.99246700	-0.81089500	-0.05597300	C	2.11170500	1.27526900	0.12326500
O	2.59381900	0.83748900	0.00492200	H	1.87039500	-2.30687800	0.32277400
C	1.78360900	2.05872300	-0.00188000	H	3.83139200	-1.31631700	-1.13905400
H	1.17711800	2.09905700	0.89841300	H	3.83092600	1.31747300	-1.13849600
H	1.18085200	2.09150600	-0.90499700	H	1.86960100	2.30664100	0.32402000
At	-1.02848300	-0.04610800	0.00308600	S	1.21339700	-0.00042100	0.94822300
H	2.91147800	-2.32916200	-0.45211000				
H	2.51882200	2.85604400	-0.00368700				
D = thioacetone				**D = thiane**			
At	1.03832100	0.03433200	-0.00000100	At	1.23921800	0.00000000	-0.14131300
C	-2.14989600	1.61773400	0.00001500	C	-1.83058800	-1.40837800	0.70324600
C	-3.79150100	-0.34939100	0.00000400	C	-2.30691500	-1.27682400	-0.73572400
H	-1.55325100	1.89952900	0.87416700	C	-3.10894700	0.00000400	-0.99744200
H	-1.55410800	1.89938500	-0.87481000	C	-2.30691400	1.27683000	-0.73571500
H	-4.30557000	0.05946200	0.87726600	C	-1.83058600	1.40837400	0.70325600
H	-3.87532300	-1.43445600	0.00029200	H	-1.22006800	-2.29265900	0.88276900
C	-2.39423000	0.15968300	0.00011400	H	-2.66216700	-1.41423600	1.41547600
H	-4.30499700	0.05880100	-0.87793600	H	-1.44924900	-1.33575900	-1.41059100
H	-3.08318500	2.17581400	0.00032800	H	-2.92203400	-2.15565700	-0.94232100
S	-1.22294200	-1.00905600	-0.00000100	H	-3.44746600	0.00000800	-2.03366300
				H	-4.01126000	0.00000200	-0.37760400
				H	-1.44924900	1.33576800	-1.41058200
				H	-2.92203200	2.15566500	-0.94230700
				H	-1.22006600	2.29265300	0.88278500

	H -2.66216600 1.41422800 1.41548500 S -0.81650300 -0.00000600 1.30665100

Table S22. SO-DFT/B3LYP-D3 optimized geometries of [pyridine···I]$^+$ cations.

X = I			
H	2.15144359	4.86540076	-0.00657071
H	2.06521532	2.37916005	-0.00631759
H	-2.06521532	2.37916005	0.00631759
H	-2.15144359	4.86540076	0.00657071
H	0.00000000	6.14264805	0.00000000
H	2.06521532	-2.37916005	0.00631759
H	0.00000000	-6.14264805	0.00000000
H	2.15144359	-4.86540076	0.00657071
H	-2.15144359	-4.86540076	-0.00657071
H	-2.06521532	-2.37916005	-0.00631759
C	-1.16168371	-2.97358216	-0.00355055
C	-1.19770691	-4.35669761	-0.00363831
C	1.16168371	-2.97358216	0.00355055
C	1.19770691	-4.35669761	0.00363831
C	0.00000000	-5.06069812	0.00000000
N	0.00000000	-2.30596690	0.00000000
I	0.00000000	0.00000000	0.00000000
N	0.00000000	2.30596690	0.00000000
C	1.16168371	2.97358216	-0.00355055
C	1.19770691	4.35669761	-0.00363831
C	0.00000000	5.06069812	0.00000000
C	-1.19770691	4.35669761	0.00363831
C	-1.16168371	2.97358216	0.00355055

Table S23. SR-DFT/B3LYP-D3 optimized geometries of [pyridine···X]$^+$ cations.

X = Cl			
H	-2.05386100	-2.15567600	0.00000200
H	0.44710800	-2.07511700	-0.00000100
H	0.44711000	2.07511700	0.00000100
H	-2.05386100	2.15567600	0.00000100
H	-3.32780200	0.00000000	-0.00000100
Cl	2.18963800	0.00000000	0.00000000
N	0.47732700	-0.00000100	-0.00000200
C	-0.16706500	-1.18722600	0.00000000
C	-1.54528600	-1.20189900	0.00000000
C	-2.24593600	0.00000000	0.00000000
C	-1.54528500	1.20190000	0.00000000
C	-0.16706500	1.18722700	0.00000000

X = Br			
H	-0.15089600	-2.07737500	-0.00000100
H	-3.91951400	0.00000000	0.00000000
H	-2.64339600	-2.15521400	0.00000000
H	-2.64339600	2.15521400	0.00000000
H	-0.15089600	2.07737500	0.00000100
C	-0.75699100	1.18403100	0.00000000
C	-2.13597300	1.20075000	-0.00000100
C	-0.75699100	-1.18403100	0.00000000
C	-2.13597300	-1.20075000	0.00000100
C	-2.83764600	0.00000000	0.00000000
N	-0.10813800	0.00000000	0.00000000
Br	1.77161500	0.00000000	0.00000000

X = I			
H	-3.09967600	2.15417500	0.00004400
H	-0.61773700	2.07933100	0.00001700
H	-0.61774000	-2.07933200	-0.00001200
H	-3.09967900	-2.15417300	0.00001300
H	-4.37775900	0.00000200	0.00004300
I	1.53096600	0.00000000	-0.00001300
N	-0.55423400	-0.00000100	0.00000300
C	-1.21320500	1.17876500	0.00001800
C	-2.59293400	1.19936500	0.00003200
C	-3.29587900	0.00000100	0.00003100
C	-2.59293600	-1.19936300	0.00001500
C	-1.21320700	-1.17876500	0.00000100

Table S24. SR-DFT/B3LYP-D3 optimized geometries of $[D\cdots I]^+$ cations.

D = piperidine			**D = quinuclidine**		
I	1.42426600	0.00000000 -0.16393700	I	0.00000000	0.00000000 1.85239000
C	-1.20183300	1.25686900 0.83716500	C	-0.17079000	1.42256500 -0.80125500
C	-1.90741300	1.26227600 -0.50692300	C	1.31737200	-0.56337400 -0.80125500
C	-2.74998500	-0.00000200 -0.70646500	C	0.00000000	0.00000000 -2.86385700
C	-1.90741000	-1.26227800 -0.50692100	C	-1.14658200	-0.85919100 -0.80125500
C	-1.20183100	-1.25686700 0.83716700	C	-1.24688900	-0.71989200 -2.33702200
N	-0.36918300	0.00000200 1.01926900	N	0.00000000	0.00000000 -0.29536800
H	-0.54146800	2.11027400 0.97643900	C	1.24688900	-0.71989200 -2.33702200
H	-1.92219400	1.23297300 1.66004900	C	0.00000000	1.43978400 -2.33702200
H	-1.17017900	1.36306800 -1.30805300	H	0.56849600	2.03762900 -0.29462800
H	-2.52901800	2.15813200 -0.54634100	H	-1.16109300	1.74299900 -0.48459900
H	-3.18806800	-0.00000300 -1.70416200	H	1.48039100	-1.51114600 -0.29462800
H	-3.58375500	-0.00000200 0.00227000	H	2.09002800	0.13403600 -0.48459900
H	-1.17017800	-1.36307100 -1.30805200	H	0.00000000	0.00000000 -3.95252800
H	-2.52901500	-2.15813400 -0.54633600	H	-2.04888700	-0.52648300 -0.29462800
H	-0.54146400	-2.11027100 0.97644200	H	-0.92893500	-1.87703600 -0.48459900
H	-1.92219200	-1.23297300 1.66005000	H	-2.14542200	-0.16307300 -2.60355200
H	0.00653300	0.00000300 1.96734600	H	-1.33611300	-1.71204900 -2.77870200
			H	1.21393600	-1.77645300 -2.60355200
			H	2.15073500	-0.30108300 -2.77870200
			H	0.93148600	1.93952600 -2.60355200
			H	-0.81462200	2.01313300 -2.77870200
D = ammonia			**D = acetonitrile**		
N	-1.78024500	-0.00000600 -0.00005500	I	-0.99895100	0.00000500 -0.00000700
I	0.35564600	0.00002000 -0.00000900	N	0.98633000	-0.00006900 0.00006400
H	-2.13088000	0.50765700 -0.81573200	C	2.13313800	-0.00000100 0.00005700
H	-2.12922200	0.45266000 0.84804000	C	3.57308500	0.00002200 -0.00003900
H	-2.12742600	-0.96131300 -0.03145500	H	3.93432700	0.09936900 1.02651900
			H	3.93421800	-0.93869900 -0.42732800
			H	3.93418500	0.83940800 -0.59939500
D = pyridine			**D = imidazole**		
H	-3.09967600	2.15417500 0.00004400	I	0.01768400	-1.31494000 0.00000000
H	-0.61773700	2.07933100 0.00001700	C	-1.09648000	1.50031600 0.00000000
H	-0.61774000	-2.07933200 -0.00001200	C	0.66858700	2.84135400 0.00000000
H	-3.09967900	-2.15417300 0.00001300	C	1.11733000	1.56031600 0.00000000
H	-4.37775900	0.00000200 0.00004300	H	-2.11302400	1.14676200 0.00000000
I	1.53096600	0.00000000 -0.00001300	H	-1.33536400	3.56698500 0.00000000
N	-0.55423400	-0.00000100 0.00000300	H	1.20447900	3.77394400 0.00000000
C	-1.21320500	1.17876500 0.00001800	H	2.11732600	1.16571700 0.00000000
C	-2.59293400	1.19936500 0.00003200	N	0.00000000	0.74237000 0.00000000

C	-3.29587900	0.00000100	0.00003100	N	-0.70675500	2.77570300	0.00000000
C	-2.59293600	-1.19936300	0.00001500				
C	-1.21320700	-1.17876500	0.00000100				
D = funan				**D = acetone**			
C	1.57480100	-1.15488000	0.14258800	I	-1.17049000	-0.02500700	-0.00002600
C	2.79129100	-0.72478000	-0.18714700	C	1.80221100	1.47177200	-0.00001300
C	2.79129400	0.72476300	-0.18717400	C	3.08778000	-0.76421900	-0.00019500
C	1.57481700	1.15487900	0.14259900	H	1.25221700	1.82701700	-0.87871400
O	0.76641500	0.00001600	0.40480200	H	1.25237400	1.82737600	0.87862900
H	1.08198500	-2.09814000	0.29649000	H	3.67108300	-0.45887600	-0.87623100
H	3.64065200	-1.35955500	-0.38357800	H	2.92543500	-1.83827500	-0.00052900
H	3.64066200	1.35952800	-0.38361000	C	1.82131800	-0.00237100	0.00035700
H	1.08203000	2.09815700	0.29649100	O	0.77371600	-0.71124300	0.00019300
I	-1.28245000	0.00000000	-0.04772500	H	3.67120600	-0.45949200	0.87598100
				H	2.80608500	1.88646900	-0.00021800
D = methyl acetate				**D = thiophene**			
C	2.84955000	-1.38415400	0.01907500	C	1.69388800	-1.27788600	0.12106300
H	3.74541100	-0.98682500	-0.45359100	C	2.70735200	-0.73041200	-0.56258600
H	3.07026800	-1.58646700	1.07206100	C	2.70715700	0.73098900	-0.56228600
C	1.76249000	-0.36491800	-0.01996200	C	1.69359200	1.27787600	0.12164100
O	0.57933700	-0.84339100	-0.05533400	H	1.44185000	-2.30897700	0.31134300
O	2.14137600	0.85081400	0.00461600	H	3.46573300	-1.31656100	-1.06374000
C	1.33082800	2.07837600	-0.00249900	H	3.46530700	1.31753100	-1.06332700
H	0.72524100	2.11693300	0.89776100	H	1.44111600	2.30877100	0.31238700
H	0.72990000	2.10956300	-0.90622400	S	0.76557100	-0.00036800	0.91467600
I	-1.32622400	-0.08017000	0.00508400	I	-1.41273700	0.00003300	-0.14789600
H	2.52387300	-2.30917700	-0.44957100				
H	2.07225000	2.86977300	-0.00384000				
D = thioacetone				**D = thiane**			
I	1.34959500	0.05664100	0.00000800	I	1.54424400	0.00000000	-0.24003600
C	-1.75922400	1.61794200	-0.00004700	C	-1.38276400	-1.40958700	0.71085300
C	-3.36573000	-0.38110500	0.00005000	C	-1.93978600	-1.27651000	-0.69853900
H	-1.16729000	1.90915700	0.87446700	C	-2.75633500	0.00000000	-0.91287900
H	-1.16597800	1.90913800	-0.87365100	C	-1.93978400	1.27651000	-0.69854100
H	-3.88738000	0.01696900	0.87784800	C	-1.38276700	1.40958700	0.71085300
H	-3.42800400	-1.46789700	0.00018800	H	-0.76111100	-2.29245100	0.85649600
C	-1.98010500	0.15744000	-0.00003200	H	-2.17084500	-1.41360600	1.47125300
H	-3.88740900	0.01675200	-0.87782800	H	-1.12196900	-1.33512500	-1.42090500
H	-2.70178700	2.16007000	-0.00069200	H	-2.56487200	-2.15604800	-0.86922000
S	-0.79127100	-0.99448900	-0.00003700	H	-3.15398900	-0.00000100	-1.92779500
				H	-3.62137700	0.00000100	-0.24198700
				H	-1.12196500	1.33512000	-1.42090400
				H	-2.56486600	2.15604900	-0.86922800
				H	-0.76111800	2.29245400	0.85650200

	H	-2.17085000	1.41360000	1.47125000
	S	-0.33896100	0.00000100	1.25912400

Table S25. SR-DFT/B3LYP-D3 optimized geometries of donors (D).

D = piperidine				**D = quinuclidine**			
C	1.21322056	0.74731165	-0.21931344	C	-1.37867587	-0.80512465	0.07897996
C	1.26186396	-0.71127328	0.23271596	C	0.76454087	-0.79991549	1.15333711
C	0.00268209	-1.45854610	-0.21730571	C	-0.00577738	1.28853284	0.00466659
C	-1.25921542	-0.71588913	0.23261444	C	0.62368871	-0.79196979	-1.24021095
C	-1.21592623	0.74275960	-0.21946978	C	0.64985384	0.76638102	-1.28420849
N	-0.00256886	1.38141668	0.28612712	N	0.00527435	-1.28855719	-0.00450032
H	2.07727875	1.29370837	0.16518460	C	0.78561913	0.75795614	1.21121416
H	1.26950709	0.77772439	-1.32330486	C	-1.44447517	0.75252748	0.08050819
H	1.33464669	-0.73772173	1.32400392	H	-1.82371086	-1.21627134	0.98731676
H	2.15795347	-1.19286135	-0.16778922	H	-1.93215868	-1.21992624	-0.76584444
H	0.00451663	-2.48118493	0.16791030	H	1.77706867	-1.20293113	1.08594587
H	0.00276309	-1.53379474	-1.31113734	H	0.31172053	-1.21900611	2.05413833
H	-1.33196695	-0.74261836	1.32390040	H	-0.01059157	2.38013567	0.00859607
H	-2.15349135	-1.20081164	-0.16792480	H	0.06155489	-1.19780108	-2.08369388
H	-2.08204888	1.28596973	0.16489075	H	1.63365087	-1.20249812	-1.30006519
H	-1.27206782	0.77294864	-1.32346869	H	0.10977585	1.14280093	-2.15667532
H	-0.00440647	2.36889651	0.06467832	H	1.67470846	1.13906970	-1.35773771
				H	1.81023101	1.13713990	1.18004246
				H	0.33863534	1.12183888	2.13987450
				H	-1.93376833	1.12322711	0.98481612
				H	-2.02420507	1.12085844	-0.76972388
D = ammonia				**D = acetonitrile**			
N	0.00000000	0.00000000	0.11682146	N	0.00000000	-0.00000000	1.43649583
H	-0.45420650	-0.82636141	-0.25506381	C	0.00000000	0.00000000	0.28704880
H	0.94275322	0.01982634	-0.25506381	C	0.00000000	0.00000000	-1.16898388
H	-0.48854673	0.80653507	-0.25506381	H	-0.28388345	0.98385148	-1.54387330
				H	0.99398210	-0.24607546	-1.54387330
				H	-0.71009865	-0.73777602	-1.54387330
D = pyridine				**D = imidazole**			
N	0.00000000	0.00000000	1.41561282	C	0.76510377	-0.82609362	0.00000000
C	0.00000000	1.13926895	0.72266840	C	-1.09708684	0.35500285	0.00000000
C	0.00000000	1.19373947	-0.66740752	C	0.00085787	1.17033347	0.00000000
C	0.00000000	0.00000000	-1.37710841	H	1.40845330	-1.69151220	0.00000000
C	0.00000000	-1.19373947	-0.66740752	H	-1.13086209	-1.77527830	0.00000000
C	0.00000000	-1.13926895	0.72266840	H	-2.15348075	0.55801716	0.00000000
H	0.00000000	2.14925386	-1.17560001	H	0.02530749	2.24748416	0.00000000
H	0.00000000	2.05425872	1.30629250	N	1.15512261	0.42435165	0.00000000
H	0.00000000	-2.05425872	1.30629250	N	-0.59375410	-0.92555783	0.00000000
H	0.00000000	-2.14925386	-1.17560001				
H	0.00000000	0.00000000	-2.45998542				

D = funan				D = acetone			
C	0.35041751	1.09114157	-0.00301510	C	0.73749975	-1.20528140	0.05293751
C	-0.95336825	0.72147898	-0.00792922	C	0.46339123	1.35186985	-0.01721881
C	-0.96143600	-0.71069853	-0.00810543	H	1.38904205	-1.11251148	0.92536922
C	0.33810229	-1.09502625	-0.00328677	H	0.15950470	-2.12459534	0.11453539
H	0.84983054	2.04396931	-0.00112401	H	0.96102398	1.50140429	0.94491611
H	-1.80491924	1.38070709	-0.01086310	H	-0.28416537	2.12779170	-0.16605127
H	-1.82035932	-1.36029126	-0.01131459	C	-0.19040507	-0.01333552	-0.05010123
H	0.82674895	-2.05342069	-0.00180350	O	-1.38729446	-0.14463955	-0.15616862
O	1.15536251	-0.00651115	-0.00008349	H	1.23509633	1.42451578	-0.78788990
				H	1.38752514	-1.24137990	-0.82591091
D = methyl acetate				**D = thiophene**			
C	-0.69202270	-1.71606741	0.00224596	C	0.00496616	0.00546160	-1.23530787
H	-1.31623831	-1.75616742	0.89615283	C	-0.01466973	1.26592767	-0.71111884
H	-1.35733751	-1.73721377	-0.86183814	C	-0.01466973	1.26592767	0.71111884
C	0.11154752	-0.44390430	0.00005428	C	0.00496616	0.00546160	1.23530787
O	1.31355439	-0.37239832	0.00188519	H	0.00886724	-0.28290797	-2.27400815
O	-0.69712115	0.63692187	-0.00208426	H	-0.02852464	2.16132706	-1.31586755
C	-0.03487326	1.91236550	0.00365375	H	-0.02852464	2.16132706	1.31586755
H	0.57750570	2.02891446	-0.89065201	H	0.00886724	-0.28290797	2.27400815
H	0.60294950	2.00856986	0.88229024	S	0.02333594	-1.18950060	0.00000000
H	-0.02011587	-2.56927936	-0.02100450				
H	-0.82821539	2.65485385	0.02306724				
D = thioacetone				**D = thiane**			
C	1.19737096	-1.15776039	0.00243844	C	-0.28536674	0.42557684	-1.37582601
C	-1.32245390	-0.95277885	-0.02179337	C	0.26116127	-0.99750734	-1.27943489
H	1.19627167	-1.75438058	-0.91606075	C	-0.18123893	-1.71488156	0.00000000
H	2.13069691	-0.60533668	0.07011426	C	0.26116127	-0.99750734	1.27943489
H	-1.35908288	-1.64555145	-0.86878943	C	-0.28536674	0.42557684	1.37582601
H	-2.15316659	-0.25503609	-0.08568948	H	0.05773152	0.91948947	-2.28582329
C	0.00299822	-0.24685679	0.01486894	H	-1.37913540	0.41340267	-1.39820488
H	-1.43619305	-1.56369637	0.88043824	H	1.35363323	-0.96488426	-1.32451803
H	1.13359001	-1.87032669	0.83158831	H	-0.07960403	-1.56527866	-2.15155839
S	0.13434207	1.37313632	0.06913007	H	0.21151122	-2.73473649	0.00000000
				H	-1.27421207	-1.80346714	0.00000000
				H	1.35363323	-0.96488426	1.32451803
				H	-0.07960403	-1.56527866	2.15155839
				H	0.05773152	0.91948947	2.28582329
				H	-1.37913540	0.41340267	1.39820488
				S	0.26345741	1.49173092	0.00000000

Table S26. SR-DFT/B3LYP-D3 optimized geometries of 4-R-pyridine.

R = NH_2				**R = OH**			
H	0.01688915	-1.75675717	-2.05412226	H	-2.04150892	-1.75391203	0.00000000
H	-0.01345834	0.70576142	-2.15206975	H	-2.14753658	0.71967764	0.00000000
H	-0.01345834	0.70576142	2.15206975	H	2.14675354	0.75223879	0.00000000
H	0.01688915	-1.75675717	2.05412226	H	2.06744404	-1.73643084	0.00000000
C	0.00996755	-1.18274549	1.13269150	C	1.14668470	-1.16226926	0.00000000
C	-0.00947411	0.20120933	1.19318523	C	1.20386164	0.22292450	0.00000000
C	0.00996755	-1.18274549	-1.13269150	C	-1.12364847	-1.17467800	0.00000000
C	-0.00947411	0.20120933	-1.19318523	C	-1.18913641	0.21312926	0.00000000
C	-0.02048165	0.93415416	0.00000000	C	0.00475869	0.92992905	0.00000000
N	0.01947251	-1.88933140	0.00000000	N	0.01313360	-1.86919314	0.00000000
N	0.00767915	2.31230663	0.00000000	O	0.06185632	2.28577808	0.00000000
H	-0.27431216	2.78075252	0.84472999	H	-0.82905149	2.65523042	0.00000000
H	-0.27431216	2.78075252	-0.84472999				
R = CH_3				**R = CFH_2**			
H	0.00243906	1.79601678	2.05400935	N	0.38412564	-2.29122977	0.00000000
H	-0.01698341	-0.67557042	2.14521926	C	1.32047885	-1.34429107	0.00000000
H	-0.01698341	-0.67557042	-2.14521926	C	1.04497847	0.02003855	0.00000000
H	0.00243906	1.79601678	-2.05400935	C	-0.28115767	0.43132539	0.00000000
C	0.00161456	1.21786690	-1.13535618	C	-1.26860140	-0.55151276	0.00000000
C	-0.00854818	-0.17068730	-1.18657874	C	-0.88729827	-1.88586208	0.00000000
C	0.00161456	1.21786690	1.13535618	H	1.84574849	0.74559217	0.00000000
C	-0.00854818	-0.17068730	1.18657874	H	2.34974733	-1.68823058	0.00000000
C	-0.01151935	-0.90151062	0.00000000	H	-1.64031794	-2.66714342	0.00000000
N	0.00730206	1.91700618	0.00000000	H	-2.32013376	-0.28857225	0.00000000
C	0.00928366	-2.40440761	0.00000000	C	-0.66900737	1.88338908	0.00000000
H	1.03956996	-2.77126710	0.00000000	F	0.44711149	2.71177751	0.00000000
H	-0.48258503	-2.80968721	-0.88506963	H	-1.26060825	2.12373298	-0.88819026
H	-0.48258503	-2.80968721	0.88506963	H	-1.26060825	2.12373298	0.88819026
R = CF_2H				**R = CF_3**			
H	-0.13011957	-2.49793480	-2.05449091	H	-0.00569791	-2.73336149	-2.05481760
H	0.12647446	-0.02740127	-2.14597188	H	0.03069843	-0.24742255	-2.14695375
H	0.12647446	-0.02740127	2.14597188	H	0.03069843	-0.24742255	2.14695375
H	-0.13011957	-2.49793480	2.05449091	H	-0.00569791	-2.73336149	2.05481760
C	-0.06403639	-1.92056091	1.13849171	C	-0.00073864	-2.15138541	1.13965723
C	0.08350639	-0.53929135	1.19459103	C	0.01716328	-0.76236974	1.19670102
C	-0.06403639	-1.92056091	-1.13849171	C	-0.00073864	-2.15138541	-1.13965723
C	0.08350639	-0.53929135	-1.19459103	C	0.01716328	-0.76236974	-1.19670102
C	0.15731027	0.16678804	0.00000000	C	0.02669532	-0.05898686	0.00000000
N	-0.13558305	-2.60974604	0.00000000	N	-0.00996016	-2.84199013	0.00000000
C	0.36523065	1.65807005	0.00000000	C	0.00323234	1.44830253	0.00000000

F	-0.20847279	2.22693278	-1.10358190
F	-0.20847279	2.22693278	1.10358190
H	1.42285112	1.93979705	0.00000000
F	0.61188412	1.96195656	1.08603449
F	0.61188412	1.96195656	-1.08603449
F	-1.26497318	1.91552688	0.00000000

R = NO_2

N	0.00000000	0.00000000	2.52693611
C	-0.02717387	-1.14138132	1.83930017
C	-0.02865442	-1.20356683	0.44965165
C	0.00000000	0.00000000	-0.23185756
C	0.02865442	1.20356683	0.44965165
C	0.02717387	1.14138132	1.83930017
H	-0.05100869	-2.14250641	-0.08217934
H	-0.04892871	-2.05524037	2.42210330
H	0.04892871	2.05524037	2.42210330
H	0.05100869	2.14250641	-0.08217934
N	0.00000000	0.00000000	-1.71643035
O	0.02575969	1.08208939	-2.27687370
O	-0.02575969	-1.08208939	-2.27687370

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