Table S1: The B3LYP/6-311G(d,p) calculated and experimental ionization energies (IE in eV) for substituted benzenes, pyridine, pyrimidine and phosphabenzene.

System	X	Calc.	Expt.[a]
$X\text{-}C_6H_5$	H	8.99	9.24
	F	8.96	9.20
	Cl	8.85	9.07
	CH_3	8.55	8.83
	OCH_3	7.96	8.20
	NH_2	7.44	7.72
	$N(CH_3)_2$	6.82	7.12
	CF_3	9.46	9.68
	CN	9.40	9.73
	OH	8.23	8.49
	SH	8.09	8.30
Pyridine		8.97	9.26
Pyrimidime		9.07	9.33
Phosphabenzene		8.85	9.00

[a]Expt. IE values are taken from the NIST Chemistry web book, Number 69, Release June, 2005

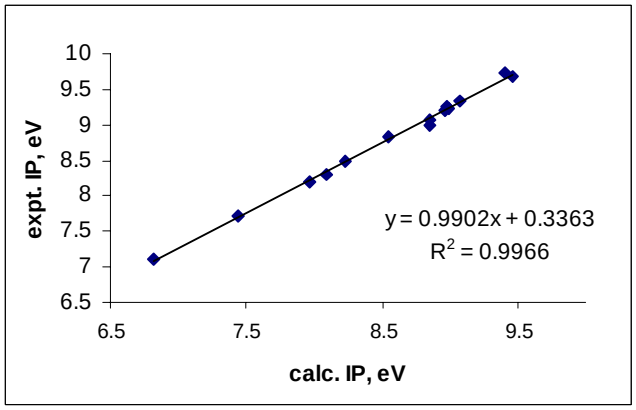

Figure-S1: The correlation between experimental and calculated IE values,
IEexpt. = IEcalc.× 0.9902 + 0.3363 (eV)

Table S2: The B3LYP/6-311G(d,p) calculated ionization energies (in eV) for 5- and 6- substituted (X) 3-pyridinethiols (X-C_5NH_3SH) compounds.

X	5X	6X
H	8.44	8.44
F	8.61	8.51
Cl	8.58	8.44
CH_3	8.25	8.32
OCH_3	8.05	7.78
NH_2	7.64	7.38
$N(CH_3)_2$	7.27	6.98
CF_3	8.82	8.83
CN	8.93	8.85
NO_2	9.02	9.01

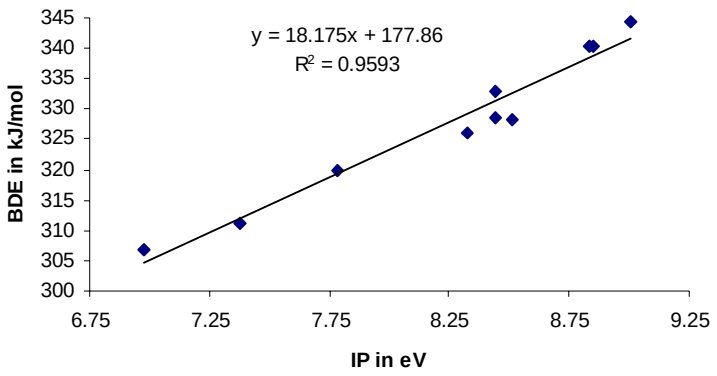

Figure-S2: The correlation between BDE(S-H) and IE values of 6X-C_5NH_3S-H.

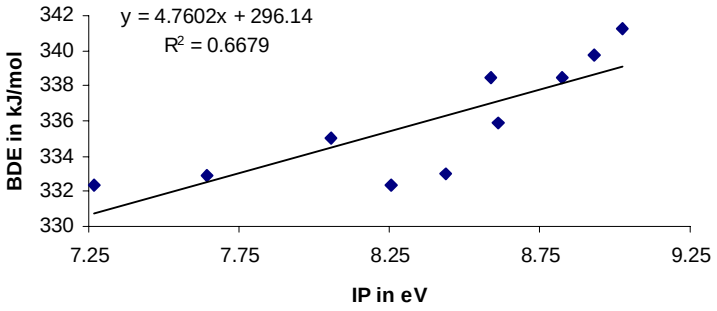

Figure-S3: The correlation between BDE(S-H) and IE values of 5X-C_5NH_3S-H.