Supporting Information

Does a Nitrogen Lone Pair Lead to Two Centered – Three Electron (2c-3e) Interactions in Pyridyl Radical Isomers?

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Table S1: Electronic and thermodynamic parameters of all the radical isomers and their respective parents at both (U)B3LYP/cc-pVTZ and (U)M06/cc-pVTZ levels of theory. Normal font indicates (U)B3LYP and italics represent (U)M06.

Species	Absolute energy (Hartrees)	ZPVE (Hartrees)	Lowest frequency	Spin Contamination		Point group	Electronic state	Absolute free energy (G) (Hartrees)	Absolute Enthalpy (H) (Hartrees)
				Before annhilation	After annhilation				
1	**–248.37319**	**0.088611**	**385.54**	**0.0000**	**0.0000**	C_{2v}	$^1A_1$	**–248.31131**	**–248.27937**
	–248.17229	*0.088222*	*376.68*	*0.0000*	*0.0000*			*–248.11081*	*–248.07883*
1a	**–247.69339**	**0.075746**	**386.75**	**0.7552**	**0.7500**	C_s	$^2A'$	**–247.64561**	**–247.61245**
	–247.49468	*0.075448*	*376.52*	*0.7584*	*0.7500*			*–247.44720*	*–247.41400*
1b	**–247.68336**	**0.075550**	**391.16**	**0.7570**	**0.7500**	C_s	$^2A'$	**–247.63577**	**–247.60262**
	–247.48606	*0.075325*	*381.60*	*0.7626*	*0.7501*			*–247.43870*	*–247.40552*
1c	**–247.68519**	**0.075321**	**380.29**	**0.7563**	**0.7500**	C_{2v}	$^2A_1$	**–247.63717**	**–247.60469**
	–247.48811	*0.075106*	*365.84*	*0.7618*	*0.7501*			*–247.44032*	*–247.40779*
2	**–248.74382**	**0.102891**	**393.19**	**0.0000**	**0.0000**	C_{2v}	$^1A_1$	**–248.66776**	**–248.63563**
	–248.54114	*0.102296*	*384.93*	*0.0000*	*0.0000*			*–248.46568*	*–248.43350*
2a	**–248.04299**	**0.089265**	**384.25**	**0.7573**	**0.7500**	C_s	$^2A'$	**–248.98179**	**–248.94844**
	–248.84509	*0.088901*	*373.64*	*0.7623*	*0.7501*			*–248.78426*	*–248.75087*
2b	**–248.04440**	**0.089526**	**379.22**	**0.7567**	**0.7500**	C_s	$^2A'$	**–248.98294**	**–248.94959**
	–247.84697	*0.089131*	*367.24*	*0.7618*	*0.7501*			*–247.78591*	*–247.75251*
2c	**–248.04825**	**0.089534**	**390.59**	**0.7564**	**0.7500**	C_{2v}	$^2A_1$	**–247.98611**	**–247.95345**
	–248.85048	*0.089123*	*380.58*	*0.7629*	*0.7501*			*–247.78876*	*–247.75605*
3	**–323.56750**	**0.092807**	**211.02**	**0.0000**	**0.0000**	C_{2v}	$^1A_1$	**–323.50274**	**–323.46870**
	–323.32992	*0.092503*	*211.25*	*0.0000*	*0.0000*			*–323.26546*	*–323.23141*
3a	**–322.86826**	**0.079324**	**198.66**	**0.7623**	**0.7501**	C_s	$^2A'$	**–322.81832**	**–322.78287**
	–322.63503	*0.079289*	*200.16*	*0.7677*	*0.7501*			*–322.58511*	*–322.54967*
3b	**–322.87665**	**0.079527**	**206.68**	**0.7581**	**0.7500**	C_s	$^2A'$	**–322.82642**	**–322.79113**
	–322.64360	*0.079458*	*206.75*	*0.7637*	*0.7501*			*–322.59343*	*–322.55814*
3c	**–322.87402**	**0.079597**	**218.88**	**0.7641**	**0.7501**	C_{2v}	$^2A_1$	**–322.82307**	**–322.78842**
	–322.64134	*0.079481*	*219.47*	*0.7723*	*0.7502*			*–322.59049*	*–322.55585*

Table S2: Energies of all the radicals at different electronic state and the corresponding energy difference at (U)B3LYP/cc-pVTZ level of theory.

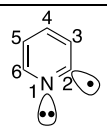
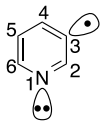
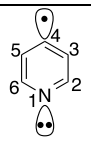
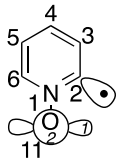
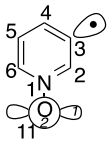
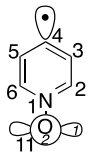
Species	Radical isomer	Ground Electronic state (GS)		Excited electronic state (ES)		ΔE (ES-GS) kcal/mol
		Energy (in Hartrees) (Electronic state)	Number of Imaginary frequencies	Energy (in Hartrees) (Electronic state)	Number of imaginary frequency	
Pyridyl radicals	**1a**	–247.61766 ($^2A'$)	0	–247.51217 ($^2A''$)	1	65.6
	1b	–247.60781 ($^2A'$)	0	–247.52383 ($^2A''$)	1	52.7
	1c	–247.60987 ($^2A_1$)	0	–247.51157 ($^2B_1$)	2	61.7
Pyridinyl radicals	**2a**	–247.95373 ($^2A'$)	0	–247.87470 ($^2A''$)	0	49.6
	2b	–247.95488 ($^2A'$)	0	–247.85437 ($^2A''$)	1	63.1
	2c	–247.95872 ($^2A_1$)	0	–247.83451 ($^2B_1$)	1	77.9
Pyridyl-N-oxide radicals	**3a**	–322.78894 ($^2A'$)	0	–322.76529 ($^2A''$)	0	14.8
	3b	–322.79713 ($^2A'$)	0	–322.74643 ($^2A''$)	0	31.8
	3c	–322.79443 ($^2A_1$)	0	–322.74903 ($^2B_1$)	0	28.5

Table S3. Relative stability order of isomeric pyridyl **1a-c**, pyridinyl **2a-c**, and pyridyl-N-oxide **3a-c** radicals at different levels of theory.

Level of theory	Relative energy[a] (kcal/mol)								
	Pyridyl radicals			Pyridinyl radicals			Pyridyl-N-oxide radicals		
	1a	**1b**	**1c**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**
(U)B3LYP/6-311++G(d,p)	0.0	6.0	4.7	3.1	2.3	0.0	5.0	0.0	1.5
(U)B3LYP/cc-pVDZ	0.0	6.0	4.8	3.0	2.3	0.0	5.3	0.0	1.9
(U)B3LYP/cc-pVTZ	0.0	6.2	4.9	3.1	2.4	0.0	5.1	0.0	1.7
(U)B3LYP/cc-pVQZ	0.0	6.2	4.9	3.1	2.4	0.0	5.0	0.0	1.6
(U)B3LYP/aug-cc-pVDZ	0.0	5.8	4.6	3.1	2.4	0.0	4.9	0.0	1.5
(U)B3LYP/aug-cc-pVTZ	0.0	6.1	4.8	3.1	2.4	0.0	4.9	0.0	1.5
(U)B3LYP/aug-cc-pVQZ	0.0	6.2	4.9	3.1	2.4	0.0	5.0	0.0	1.5
(U)BLYP/cc-pVTZ	0.0	5.7	4.9	2.9	2.1	0.0	5.8	0.0	2.8
(U)M06/cc-pVTZ	0.0	5.3	3.9	3.2	2.2	0.0	5.3	0.0	1.4
CBS-QB3	0.0	6.8	5.4	3.8	2.6	0.0	5.8	0.0	1.8
(U)CCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVTZ[b]	0.0	5.8	4.3	3.4	2.7	0.0	4.4	0.0	0.4

[a]Zero-point energy corrected; [b]Single point energy calculation performed at (U)CCSD(T)/cc-pVTZ using (U)B3LYP/cc-pVTZ optimized geometry

Table S4: The second order perturbation energy from the NBO analysis at different levels of theory

1a 			**1b** 			**1c** 		
Donor	Acceptor	$<E^2>^{a,b}$	Donor	Acceptor	$<E^2>^{a,b}$	Donor	Acceptor	$<E^2>^{a,b}$
$n_{(N1)}$	$n^*_{(C2)}$	**20.8** *20.6* 23.5	$n_{(N1)}$	$n^*_{(C3)}$	**0.7** *0.8* 0.7	$n_{(N1)}$	$n^*_{(C4)}$	-
$n_{(N1)}$	$\pi^*_{(C5-C6)}$	**5.0** *5.1* 6.6	$n_{(N1)}$	$\pi^*_{(C5-C6)}$	**5.1** *5.4* 5.2	$n_{(N1)}$	$\pi^*_{(C5-C6)}$	**6.2** *6.3* 5.8
$n_{(N1)}$	$\pi^*_{(C2-C3)}$	**3.3** *3.5* 5.5	$n_{(N1)}$	$\pi^*_{(C2-C3)}$	**5.8** *5.7* 6.2	$n_{(N1)}$	$\pi^*_{(C2-C3)}$	**6.2** *6.3* 5.8
$\pi^*_{(C5-C6)}$	$\pi^*_{(C2-N1)}$	**30.2** *29.7* 16.1	$\pi^*_{(C5-C6)}$	$\pi^*_{(C4-C3)}$	**38.6** *38.3* 51.6	$\pi^*_{(C2-N1)}$	$\pi^*_{(C4-C3)}$	**30.5** *31.1* 42.8
$\pi^*_{(C4-C3)}$	$\pi^*_{(C2-N1)}$	**41.7** *39.8* 18.3	$\pi^*_{(C2-N1)}$	$\pi^*_{(C4-C3)}$	**37.6** *39.8* 24.3	$\pi^*_{(C5-C6)}$	$\pi^*_{(C4-C3)}$	**39.8** *39.3* 71.6
3a 			**3b** 			**3c** 		
$n_{1(O11)}$	$n^*_{(C2)}$	**1.1** *0.7*	$n_{1(O11)}$	$n^*_{(C3)}$	-	$n_{1(O11)}$	$n^*_{(C4)}$	-
$n_{1(O11)}$	$\pi^*_{(C2-N1)}$	**5.7** *7.0*	$n_{1(O11)}$	$\pi^*_{(C2-C3)}$	**0.4** *0.4*	$n_{1(O11)}$	$\pi^*_{(C2-C3)}$	**0.4** *0.5*
$n_{1(O11)}$	$\pi^*_{(C5-C6)}$	**0.4** *0.5*	$n_{1(O11)}$	$\pi^*_{(C2-N1)}$	**7.4** *8.0*	$n_{1(O11)}$	$\pi^*_{(C2-N1)}$	**5.4** *6.2*
$n_{1(O11)}$	$\pi^*_{(C6-N1)}$	**5.0** *6.7*	$n_{1(O11)}$	$\pi^*_{(C5-C6)}$	**0.4** *0.4*	$n_{1(O11)}$	$\pi^*_{(C5-C6)}$	**0.4** *0.5*
$n_{2(O11)}$	$\pi^*_{(C2-C3)}$	**0.4** *0.4*	$n_{1(O11)}$	$\pi^*_{(C6-N1)}$	**4.5** *5.5*	$n_{1(O11)}$	$\pi^*_{(C6-N1)}$	**5.4** *6.2*
$n_{2(O11)}$	$\pi^*_{(C6-N1)}$	**26.9** *59.5*	$n_{2(O11)}$	$\pi^*_{(C6-N1)}$	**34.8** *39.6*	$n_{2(O11)}$	$\pi^*_{(C2-N1)}$	**26.7** *13.9*
$\pi^*_{(C6-N1)}$	$\pi^*_{(C2-C3)}$	**13.9** *23.7*	$\pi^*_{(C6-N1)}$	$\pi^*_{(C2-C3)}$	**10.7** *10.6*	$\pi^*_{(C2-N1)}$	$\pi^*_{(C4-C3)}$	**21.1** *0.85*

[a]Interaction energies expressed in kcal/mol [b]Bold = (U)B3LYP/cc-pVTZ; Italics = (U)M06/cc-pVTZ; Normal = (U)CCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVTZ.

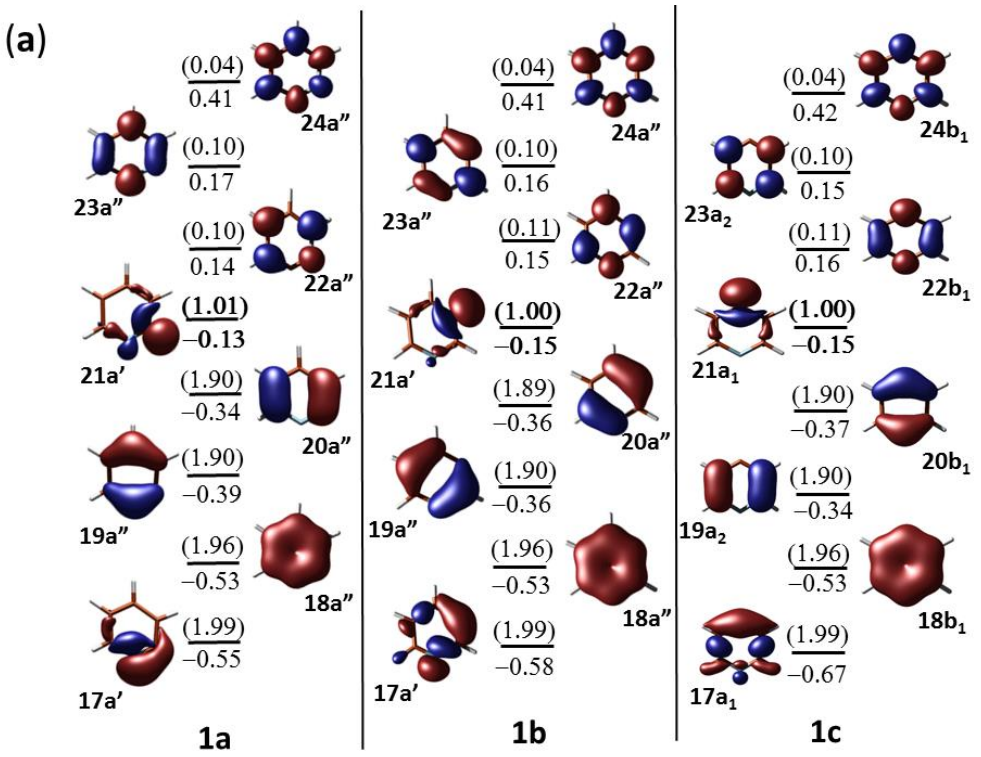
Table S5: VIE and VDE of all the radical isomers at (U)B3LYP/cc-pVTZ, (U)M06/ cc-pVTZ and CBS-QB3 levels of theory. The energy values are given in kcal/mol.

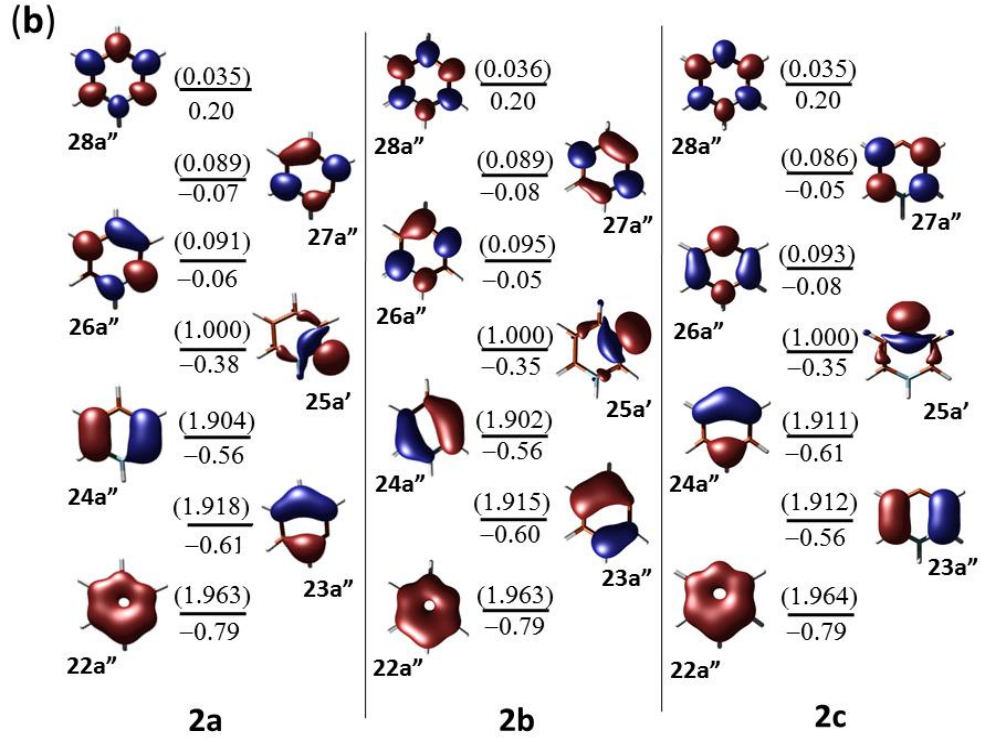
Species	(U)B3LYP/cc-pVTZ		(U)M06/cc-pVTZ		CBS-QB3	
	VIE	**VDE**	**VIE**	**VDE**	**VIE**	**VDE**
1a	178.5	12.8	172.7	12.8	176.7	21.8
1b	190.5	27.1	185.3	26.7	186.8	36.9
1c	193.7	27.9	189.5	27.6	193.5	37.2
2a	344.5	163.7	338.3	162.6	344.9	169.0
2b	335.3	148.9	330.8	147.4	336.0	153.1
2c	327.6	144.7	323.1	143.9	328.1	148.7
3a	213.1	43.6	210.1	42.5	206.2	55.7
3b	204.2	39.1	200.6	38.3	200.3	50.8
3c	207.1	38.4	203.9	37.4	200.8	–

Table S6: Computed frequency shifts in the selected normal modes of the isomeric pyridyl **1a-c**, pyridinyl **2a-c,** and pyridyl-N-oxide **3a-c** radicals**,** relative to the corresponding modes in pyridine

		Normal mode	Symmetry	(U)B3LYP/cc-pVTZ		(U)M06/cc-pVTZ	
				ν (cm^{-1})	**Δν^{a} (cm^{-1})**	**ν (cm^{-1})**	**Δν^{a} (cm^{-1})**
Pyridine		ν_{21}	B_2	**1620.3**	-	**1636.4**	-
	1	ν_{10}	A_1	**1012.3**	-	**1007.6**	-
		ν_3	A_1	**616.8**	-	**602.6**	-
Pyridyl radicals	**1a**	ν_{20}	A′	1663.9	43.6	1667.6	31.2
	1b	ν_9	A′	991.1	–21.2	979.6	–28.0
	1c	ν_3	A_1	619.0	2.2	600.7	–1.9
Pyridinyl radicals	**2a**	ν_{22}	A′	1654.6	34.3	1667.5	31.1
	2b	ν_{10}	A′	1014.7	2.4	1005.9	–1.7
	2c	ν_3	A_1	620.0	3.2	604.2	1.6
Pyridyl-N-oxide	**3a**	ν_{23}	A′	1629.3	9.0	1645.6	9.2
	3b	ν_{10}	A′	847.8	–164.5	852.8	–154.8
	3c	ν_5	A_1	555.7	–61.1	547.1	–55.5

[a]The difference in the frequency (in cm^{-1}), $\Delta\nu = \nu_{radical} - \nu_{pyridine}$ (A positive value indicates a blue shift and negative value indicating a red shift relative to the corresponding vibrational frequency in pyridine)


(a)
(0.04)
0.41
24a″
(0.10)
0.17
23a″
(0.10)
0.14
22a″
(1.01)
−0.13
21a′
(1.90)
−0.34
20a″
(1.90)
−0.39
19a″
(1.96)
−0.53
18a″
(1.99)
−0.55
17a′
1a
(0.04)
0.41
24a″
(0.10)
0.16
23a″
(0.11)
0.15
22a″
(1.00)
−0.15
21a′
(1.89)
−0.36
20a″
(1.90)
−0.36
19a″
(1.96)
−0.53
18a″
(1.99)
−0.58
17a′
1b
(0.04)
0.42
24b1
(0.10)
0.15
23a2
(0.11)
0.16
22b1
(1.00)
−0.15
21a1
(1.90)
−0.37
20b1
(1.90)
−0.34
19a2
(1.96)
−0.53
18b1
(1.99)
−0.67
17a1
1c


(b)
(0.035)
0.20
28a″
(0.089)
−0.07
27a″
(0.091)
−0.06
26a″
(1.000)
−0.38
25a′
(1.904)
−0.56
24a″
(1.918)
−0.61
23a″
(1.963)
−0.79
22a″
2a
(0.036)
0.20
28a″
(0.089)
−0.08
27a″
(0.095)
−0.05
26a″
(1.000)
−0.35
25a′
(1.902)
−0.56
24a″
(1.915)
−0.60
23a″
(1.963)
−0.79
22a″
2b
(0.035)
0.20
28a″
(0.086)
−0.05
27a″
(0.093)
−0.08
26a″
(1.000)
−0.35
25a′
(1.911)
−0.61
24a″
(1.912)
−0.56
23a″
(1.964)
−0.79
22a″
2c

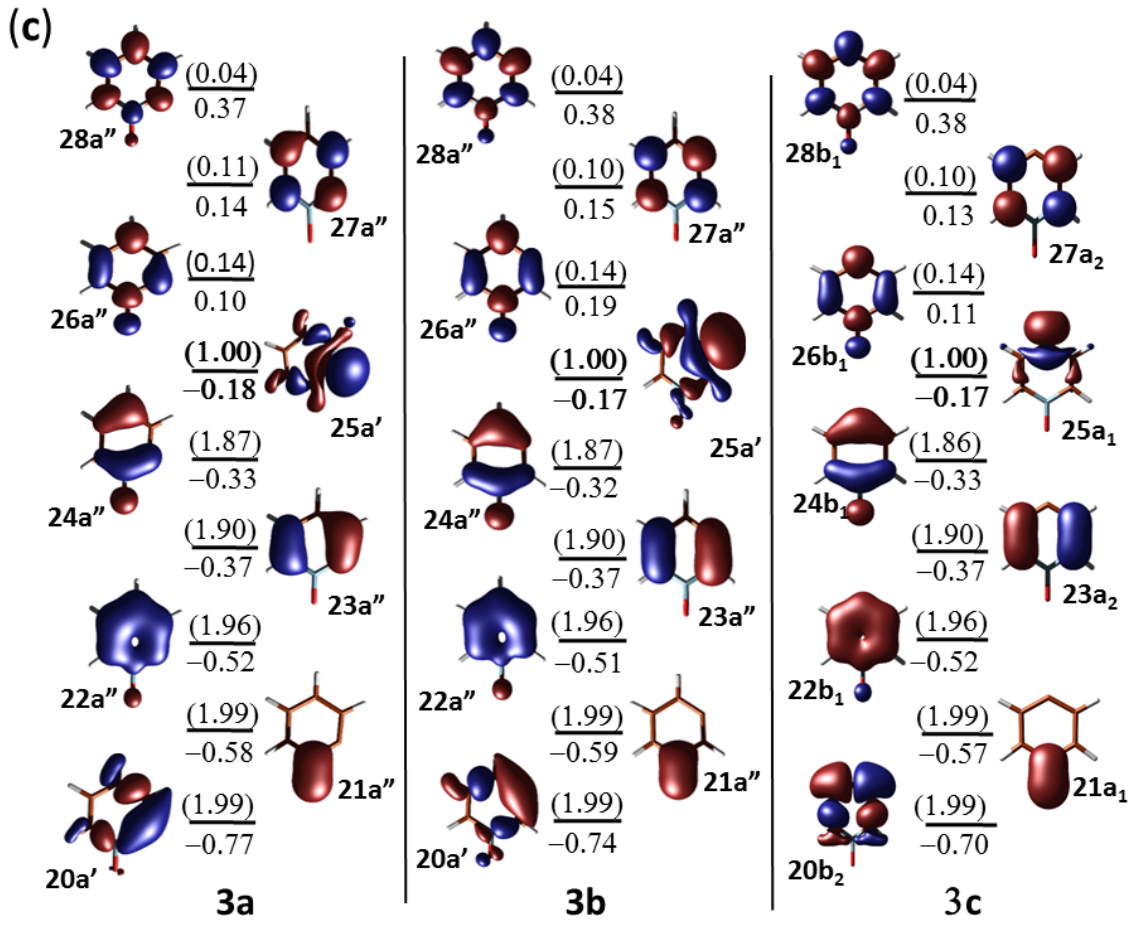


Figure S1: The complete active space molecular orbital diagrams of all the radicals at CASSCF/cc-pVTZ//(U)B3LYP/cc-pVTZ level of theory; (a) pyridyl radicals **1a-c** (b) pyridinyl radicals **2a-c** (c) pyridyl-N-oxide radicals **3a-c**. The values in normal font indicate orbital energies (hartree) and values in parenthesis represent the occupancies. Orbital number and their respective symmetry are designated in bold. All the orbitals are rendered at an isovalue 0.05.

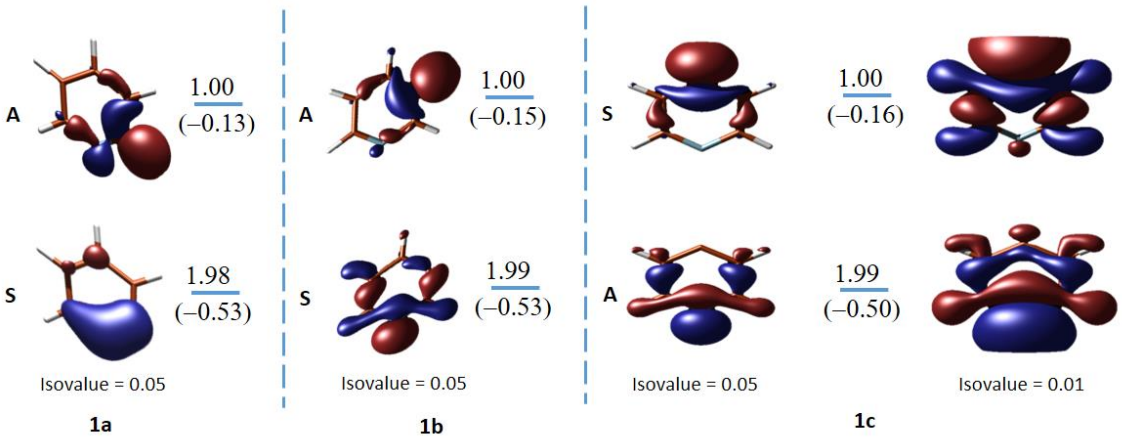


Figure S2: Molecular orbitals representing symmetric and antisymmetric combinations of lone pair and radical electron at CASSCF(3.,2)/cc-pVTZ//(U)B3LYP/cc-pVTZ level of theory for pyridyl radicals **1a-c**.The values in normal font indicate orbital occupancies and values in parenthesis represent the orbital energies (in hartree). (For **1a** and **1b**, the symmetric combination of orbital corresponding to nitrogen lone pair and radical electron is found to lower in energy as compared to the anti-symmetric combination (SOMO) of those orbitals; However, in case of **1c**, the anti-symmetric combination orbital is found to be low-lying relative to the symmetric combination (SOMO) orbital. All the orbitals are rendered at an isovalue 0.05. For clarity, the SOMO and SOMO-1 orbitals of **1c** were rendered at an isovalue 0.01. This supports the consequence of dominating through bond interaction in **1c**.

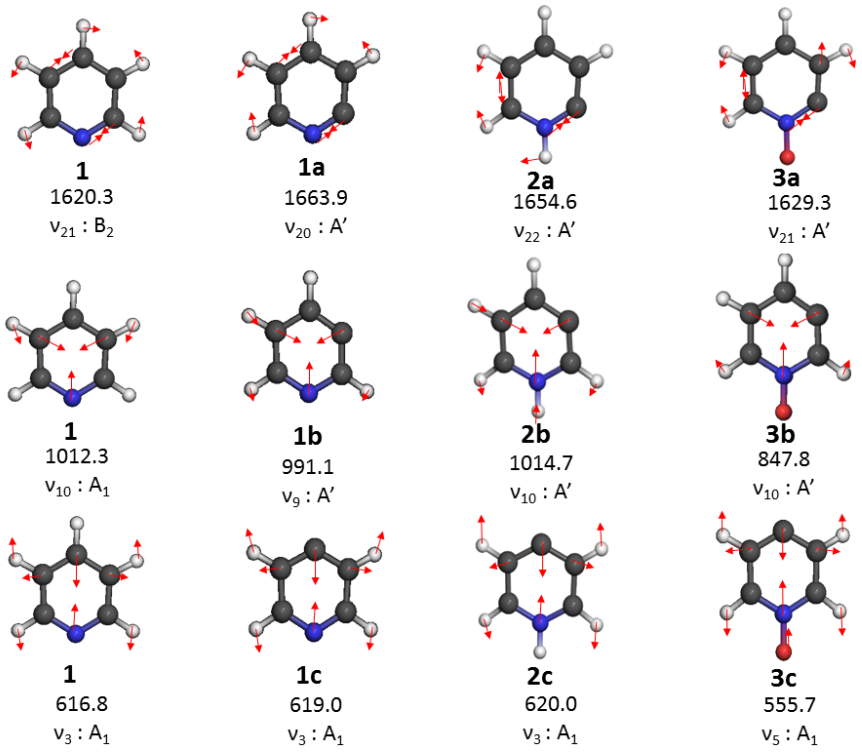
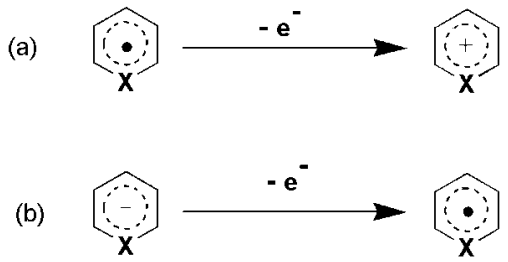


Figure S3: Selected vibrational normal modes of the pyridyl **1a-c**, pyridinyl **2a-c** and pyridyl-N-oxide **3a-c** radicals and their corresponding parent compound showing interactions between the radical center and the nitrogen atom. The frequencies (cm^{-1}), normal mode number and symmetry of each normal mode at (U)B3LYP/cc-pVTZ level of theory are indicated.



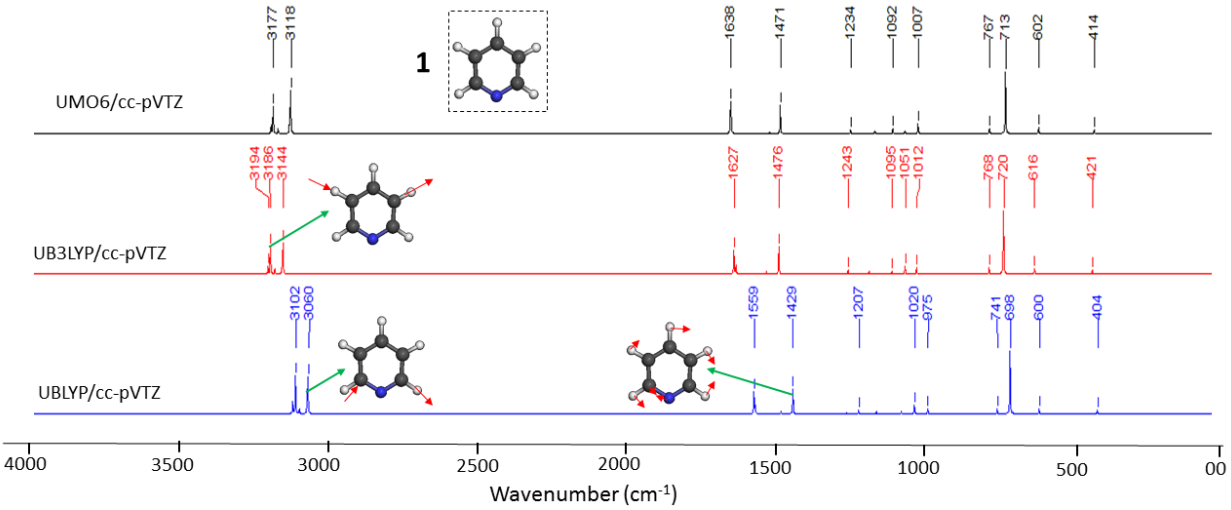
X = N, NH^+, N^+-O^-

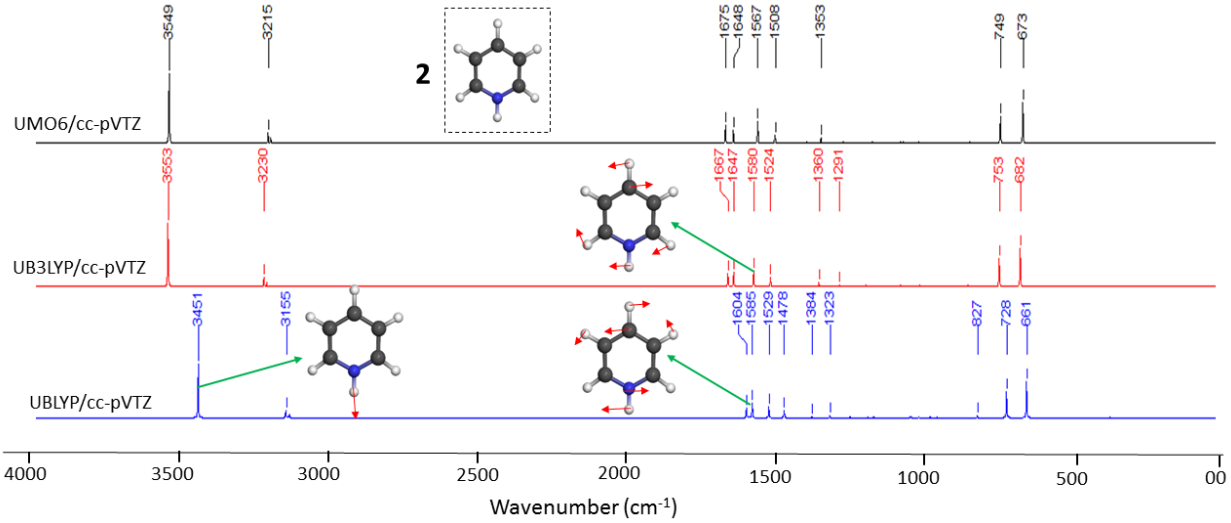
Scheme S1. (a) VIE and (b) VDE of radical isomers of pyridine **1a-c**, cationic pyridine **2a-c** and pyridine-N-oxide **3a-c**.

$(VIE)^{\Delta E} = E_{N-1}(G_N) - E_N(G_N)$

$(VDE)^{\Delta E} = E_N(G_{N+1}) - E_{N+1}(G_{N+1})$

Where $E_{N-1}(G_N)$ and $E_N(G_N)$ are the total energies of (N-1) and N electron systems calculated at the G_N geometry; on the other hand $E_N(G_{N+1})$ and $E_{N+1}(G_{N+1})$ are the total energies of N and (N+1) electron systems calculated at G_{N+1} geometry.


1
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
3177
3118
1638
1471
1234
1092
1007
767
713
602
414
3194
3186
3144
1627
1476
1243
1095
1051
1012
768
720
616
421
3102
3060
1559
1429
1207
1020
975
741
698
600
404
4000
3500
3000
2500
2000
1500
1000
500
00
Wavenumber (cm-1)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UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
3549
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1675
1648
1567
1508
1353
749
673
3553
3230
1667
1647
1580
1524
1360
1291
753
682
3451
3155
1604
1585
1529
1478
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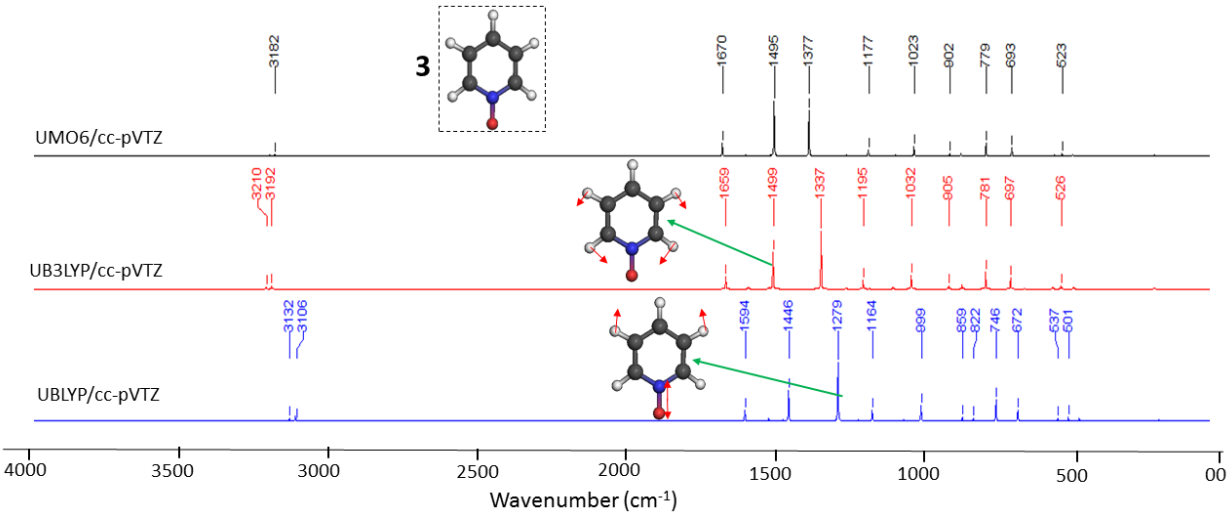
827
728
661
4000
3500
3000
2500
2000
1500
1000
500
00
Wavenumber (cm-1)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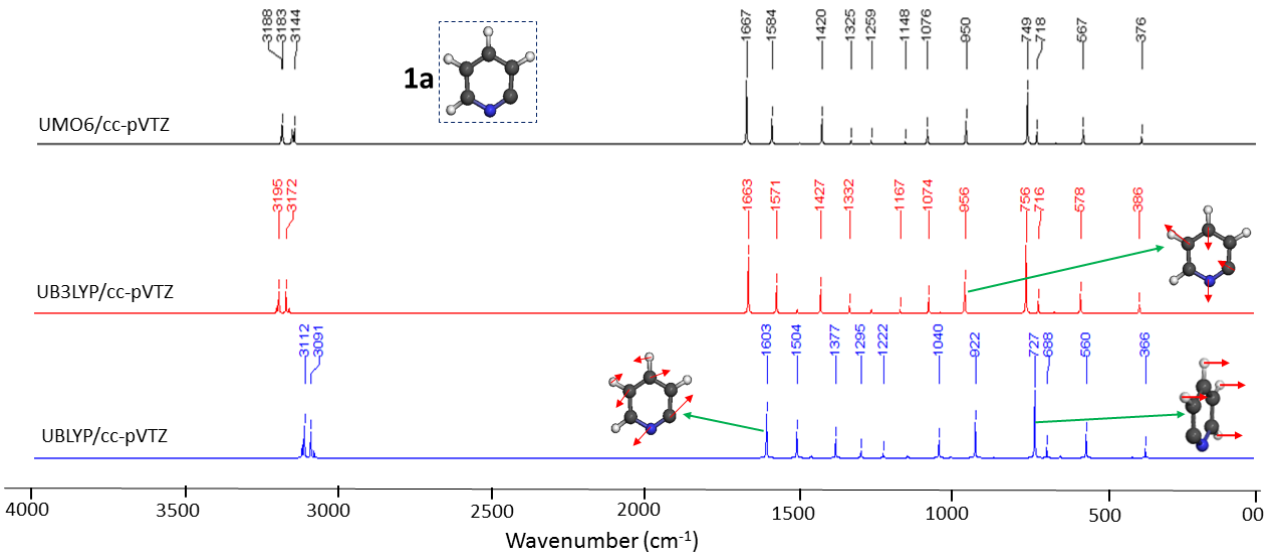
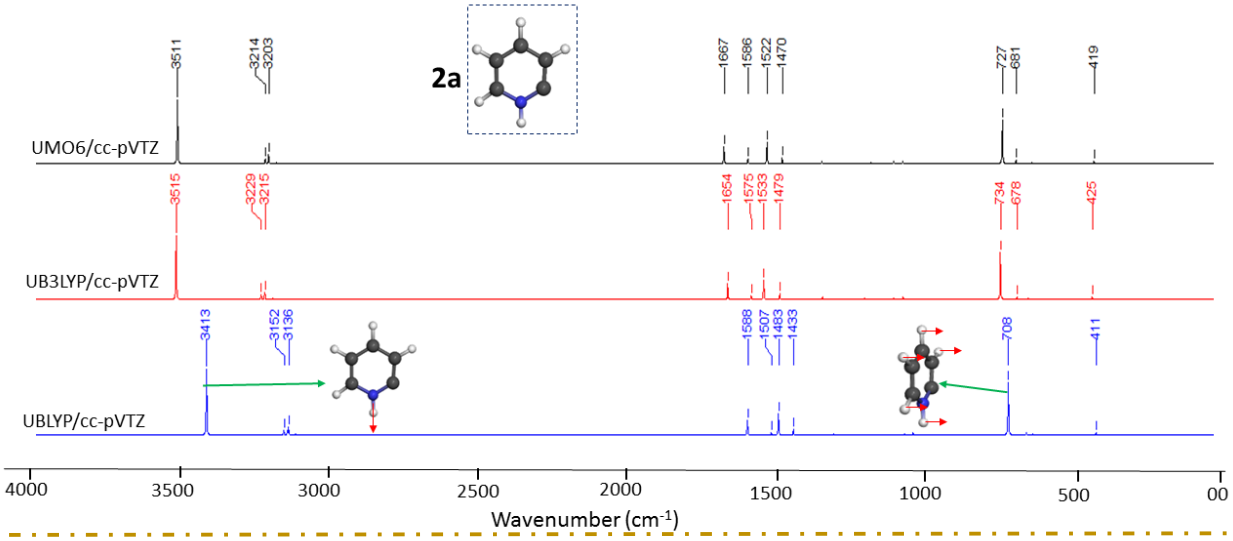
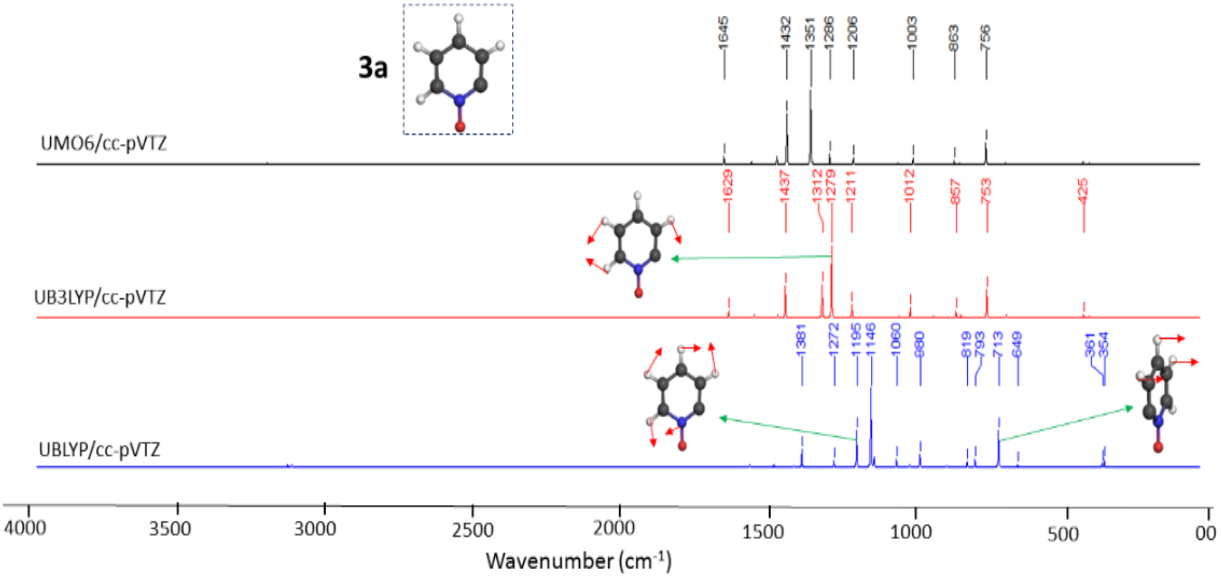
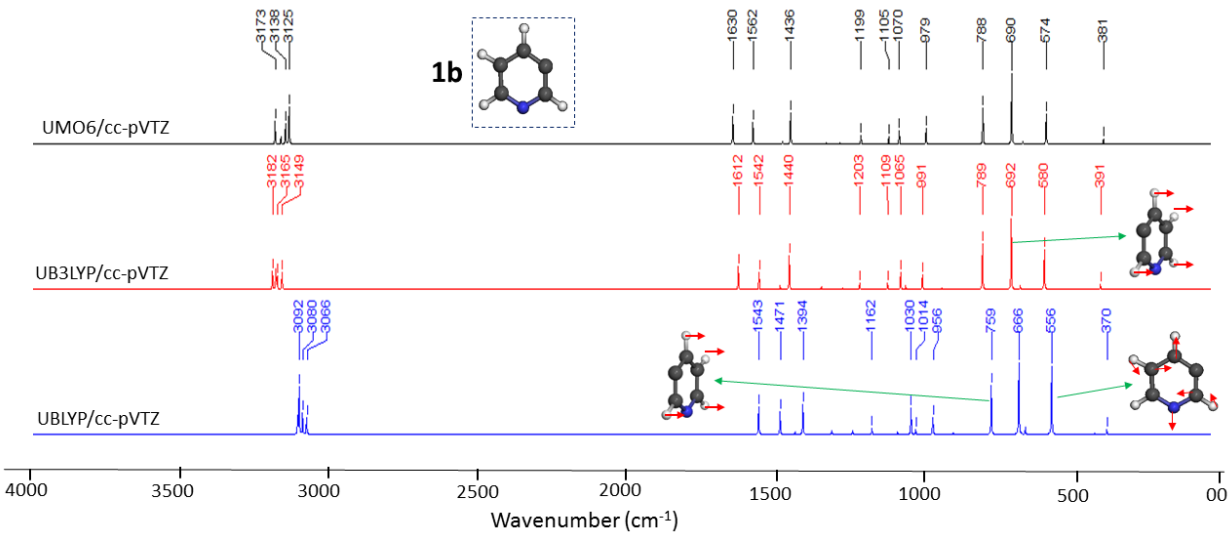
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
3182
1670
1495
1377
1177
1023
902
779
693
523
3210
3192
1659
1499
1337
1195
1032
905
781
697
626
3132
3106
1594
1446
1279
1164
999
859
822
746
672
637
601
4000
3500
3000
2500
2000
1500
1000
500
00
Wavenumber (cm-1)


1a
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


2a
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


3a
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)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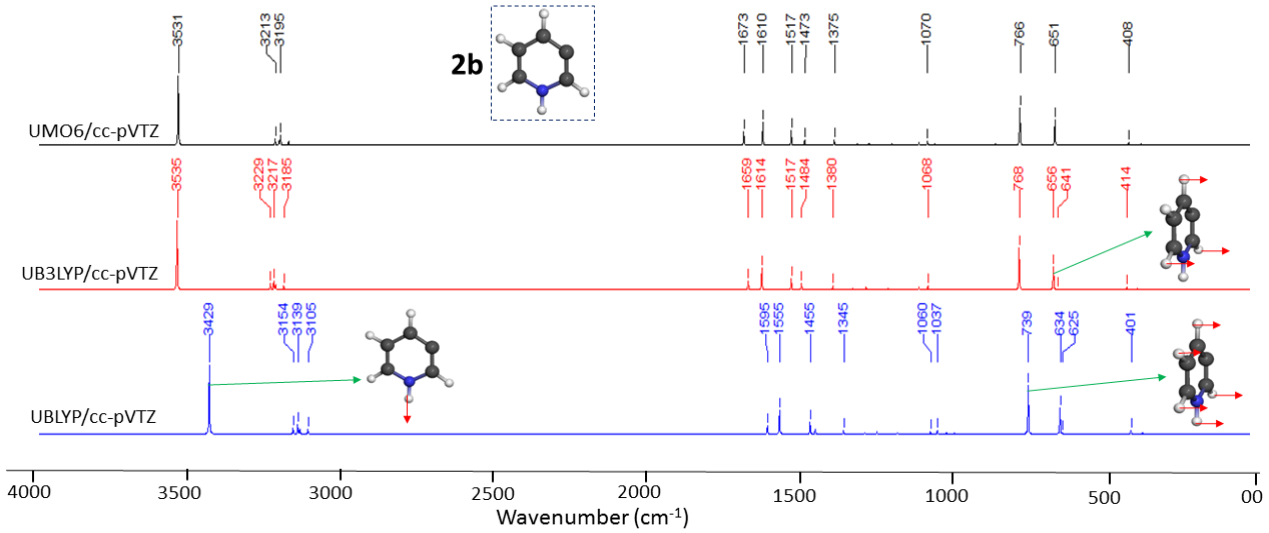
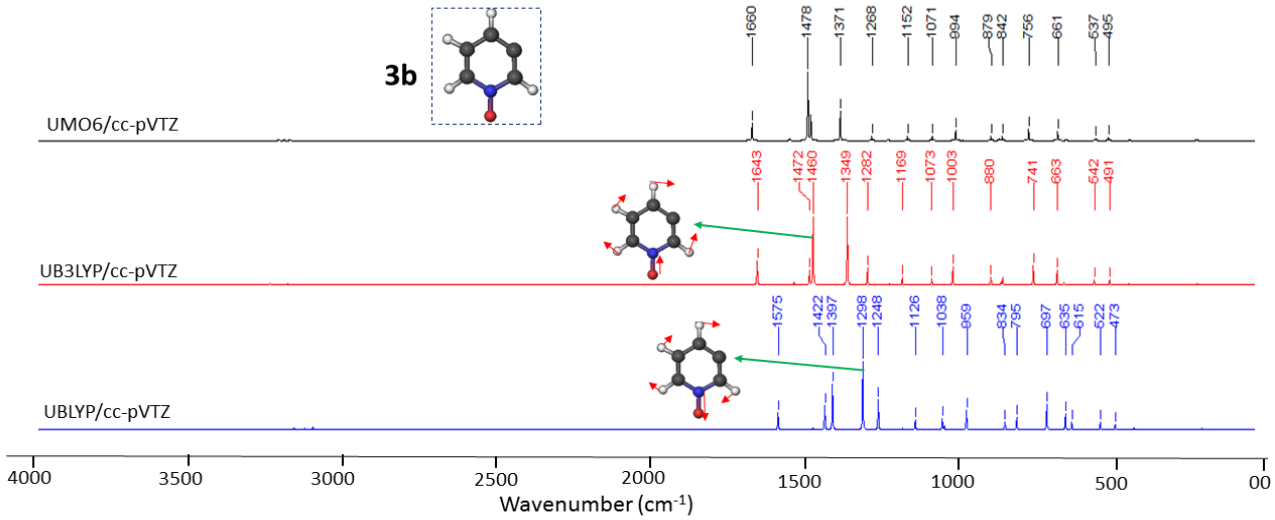
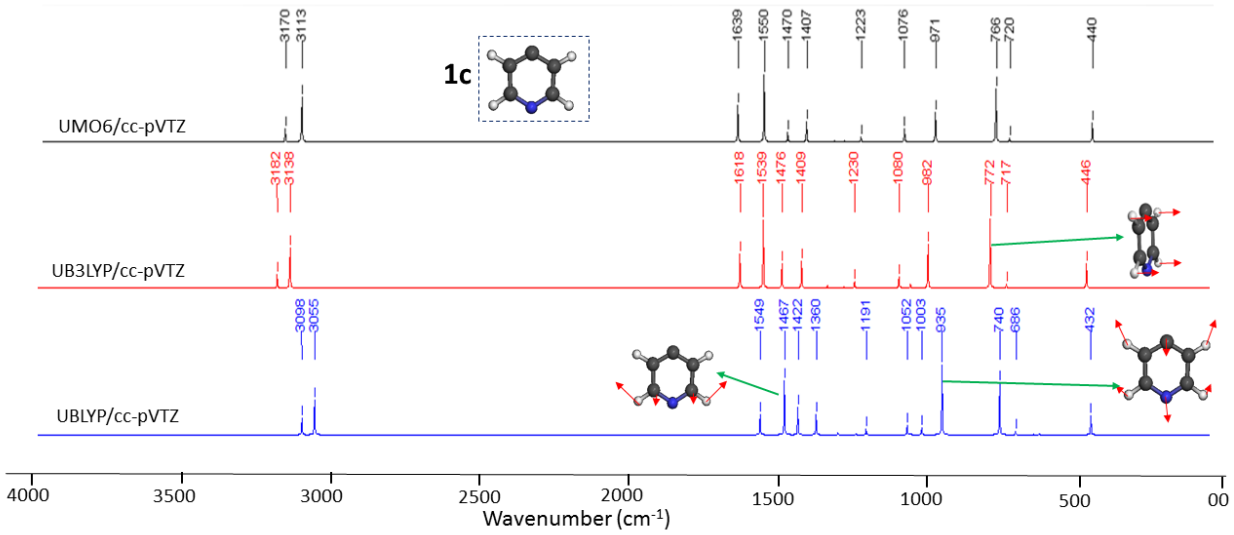
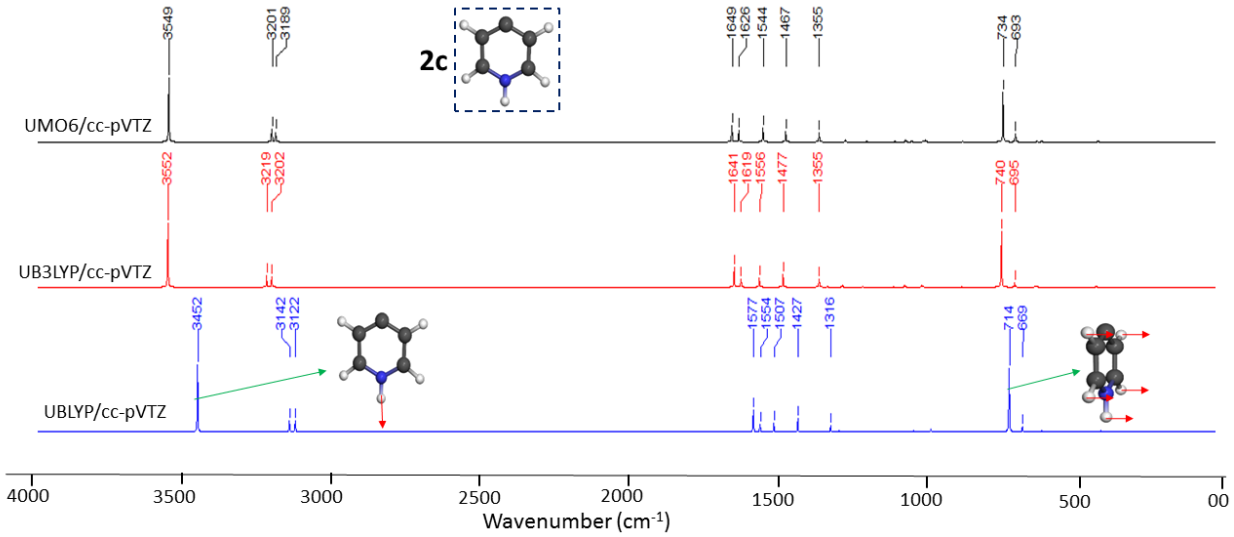
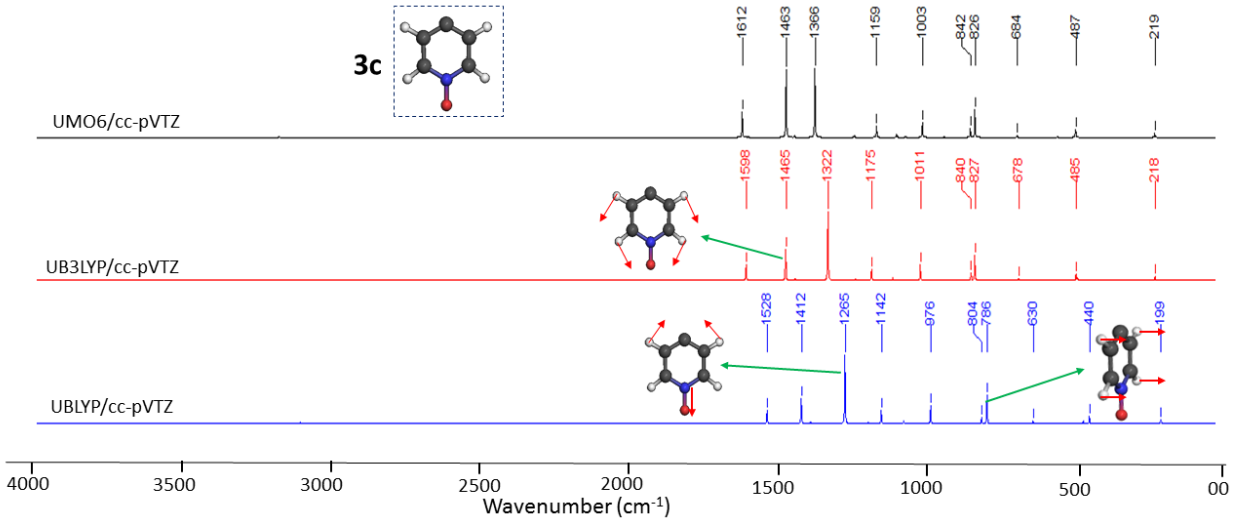
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


2b
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


3b
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


1c
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


2c
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)


3c
UMO6/cc-pVTZ
UB3LYP/cc-pVTZ
UBLYP/cc-pVTZ
Wavenumber (cm-1)

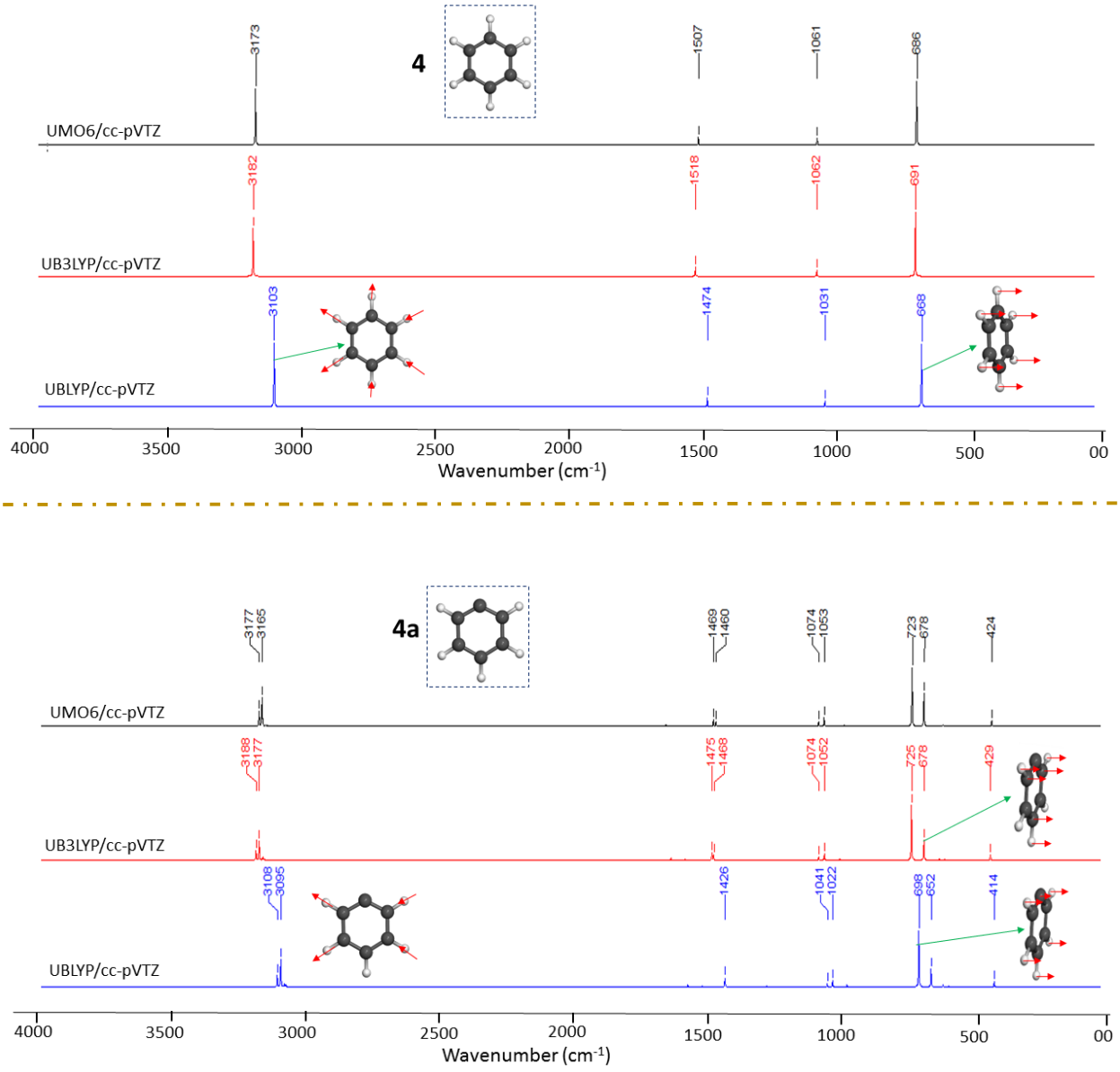


Figure S4: The computed vibrational spectra of all the radical isomers and their parent compounds at different levels of theory are indicated along with their structures. The frequency values are in cm^{-1} and all the spectra are unscaled.

Appendix S1: Cartesian coordinates of the optimized structures at different levels of theory.

Pyridine (1)

(U)B3LYP/cc-pVTZ			
C	0.00000000	-1.13906500	0.71943500
C	0.00000000	-1.19336700	-0.66978600
C	0.00000000	0.00000000	-1.37910100
C	0.00000000	1.19336700	-0.66978600
C	0.00000000	1.13906500	0.71943500
N	0.00000000	0.00000000	1.41286300
H	0.00000000	0.00000000	-2.46109800
H	0.00000000	-2.05338900	1.30255400
H	0.00000000	-2.14809200	-1.17761900
H	0.00000000	2.14809200	-1.17761900
H	0.00000000	2.05338900	1.30255400

(U)M06/cc-pVTZ			
C	0.00000000	1.13339700	0.71678400
C	0.00000000	1.18878000	-0.66686000
C	0.00000000	0.00000000	-1.37257900
C	0.00000000	-1.18878000	-0.66686000
C	0.00000000	-1.13339700	0.71678400
N	0.00000000	0.00000000	1.40654600
H	0.00000000	0.00000000	-2.45510900
H	0.00000000	2.05100500	1.29787200
H	0.00000000	2.14369000	-1.17503700
H	0.00000000	-2.14369000	-1.17503700
H	0.00000000	-2.05100500	1.29787200

2-Pyridyl radical (1a)

(U)B3LYP/cc-pVTZ			
C	-1.19791800	0.60815800	0.00000000
C	0.00000000	1.30262200	0.00000000
C	1.19833200	0.58653500	0.00000000
C	1.16899900	-0.80306400	0.00000000
C	-0.09891400	-1.36847500	0.00000000
N	-1.21210100	-0.73804800	0.00000000
H	2.14608200	1.11061200	0.00000000
H	-2.15440500	1.11490000	0.00000000
H	-0.00047600	2.38359600	0.00000000
H	2.07051800	-1.39742800	0.00000000

(U)M06/cc-pVTZ			
C	-1.19200400	0.60199000	0.00000000
C	0.00000000	1.29626400	0.00000000
C	1.19390600	0.58489200	0.00000000
C	1.16605500	-0.79871200	0.00000000
C	-0.09594800	-1.35914900	0.00000000
N	-1.21330000	-0.73756300	0.00000000
H	2.14112200	1.11117700	0.00000000
H	-2.14735000	1.11466000	0.00000000
H	-0.00175000	2.37762300	0.00000000
H	2.06902500	-1.39222400	0.00000000

3-Pyridyl radical (2b)

(U)B3LYP/cc-pVTZ			
C	0.00000000	1.27824300	0.00000000
C	1.20851100	0.58907700	0.00000000
C	1.17161600	-0.80671300	0.00000000
C	-0.07489500	-1.37342900	0.00000000
C	-1.24477900	-0.65350900	0.00000000
N	-1.19407500	0.68816500	0.00000000
H	2.08044100	-1.39475000	0.00000000
H	-0.00832100	2.36230200	0.00000000
H	2.14913500	1.12444000	0.00000000
H	-2.22544400	-1.11116100	0.00000000

(U)M06/cc-pVTZ			
C	0.00000000	1.27151400	0.00000000
C	1.20340800	0.58328400	0.00000000
C	1.16641500	-0.80525900	0.00000000
C	-0.07593700	-1.36870300	0.00000000
C	-1.23776300	-0.64614700	0.00000000
N	-1.19084300	0.68810200	0.00000000
H	2.07547100	-1.39432900	0.00000000
H	-0.00094000	2.35726900	0.00000000
H	2.14372300	1.11982000	0.00000000
H	-2.21908900	-1.10760700	0.00000000

4-Pyridyl radical (1c)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	0.00000000	1.14106200	0.65663800	C	0.00000000	1.13650200	0.65305300
C	0.00000000	1.20782400	-0.74336900	C	0.00000000	1.20415700	-0.73933700
C	0.00000000	0.00000000	-1.38484800	C	0.00000000	0.00000000	-1.37725600
C	0.00000000	-1.20782400	-0.74336900	C	0.00000000	-1.20415700	-0.73933700
C	0.00000000	-1.14106200	0.65663800	C	0.00000000	-1.13650200	0.65305300
N	0.00000000	0.00000000	1.33979200	N	0.00000000	0.00000000	1.33289200
H	0.00000000	2.05696600	1.23836900	H	0.00000000	2.05386600	1.23572800
H	0.00000000	2.16171800	-1.25271000	H	0.00000000	2.15736100	-1.25137600
H	0.00000000	-2.05696600	1.23836900	H	0.00000000	-2.05386600	1.23572800
H	0.00000000	-2.16171800	-1.25271000	H	0.00000000	-2.15736100	-1.25137600

Pyridinyl cation (2)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	0.00000000	1.18500600	0.66364600	C	0.00000000	1.18038900	0.66044400
C	0.00000000	1.20650700	-0.71366100	C	0.00000000	1.20213100	-0.71076400
C	0.00000000	0.00000000	-1.40908400	C	0.00000000	0.00000000	-1.40225300
C	0.00000000	-1.20650700	-0.71366100	C	0.00000000	-1.20213100	-0.71076400
C	0.00000000	-1.18500600	0.66364600	C	0.00000000	-1.18038900	0.66044400
N	0.00000000	0.00000000	1.30404900	N	0.00000000	0.00000000	1.29933300
H	0.00000000	0.00000000	-2.49034900	H	0.00000000	0.00000000	-2.48406900
H	0.00000000	2.07136100	1.27961100	H	0.00000000	2.06841300	1.27509500
H	0.00000000	2.15448400	-1.23004700	H	0.00000000	2.14989500	-1.22796200
H	0.00000000	-2.15448400	-1.23004700	H	0.00000000	-2.14989500	-1.22796200
H	0.00000000	-2.07136100	1.27961100	H	0.00000000	-2.06841300	1.27509500
H	0.00000000	0.00000000	2.31756100	H	0.00000000	0.00000000	2.31181600

2- Pyridinyl radical (2a)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	-1.18264900	0.63280200	0.00000000	C	-1.17730600	0.62960100	0.00000000
C	0.00000000	1.33291200	0.00000000	C	0.00000000	1.32731100	0.00000000
C	1.21586800	0.64492300	0.00000000	C	1.21088400	0.64179500	0.00000000
C	1.24490100	-0.75305700	0.00000000	C	1.23965300	-0.74912600	0.00000000
C	0.02509500	-1.36139500	0.00000000	C	0.02529200	-1.35638900	0.00000000
N	-1.13491700	-0.72718300	0.00000000	N	-1.13076900	-0.72481600	0.00000000
H	2.14879900	1.19364200	0.00000000	H	2.14289100	1.19303100	0.00000000
H	-2.16341700	1.08419700	0.00000000	H	-2.15730400	1.08406800	0.00000000
H	-0.02605900	2.41231300	0.00000000	H	-0.02632900	2.40690300	0.00000000
H	2.16609300	-1.31685200	0.00000000	H	2.16103100	-1.31325000	0.00000000
H	-2.00028600	-1.26012600	0.00000000	H	-1.99605300	-1.25618900	0.00000000

3- Pyridinyl radical (2b)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	1.14872400	0.57946700	0.00000000	C	1.14375800	0.57589400	0.00000000
C	1.11501600	-0.80090100	0.00000000	C	1.11076700	-0.79877800	0.00000000
C	-0.12048100	-1.45908900	0.00000000	C	-0.11945300	-1.45157200	0.00000000
C	-1.23620600	-0.66238400	0.00000000	C	-1.23283200	-0.65928600	0.00000000
C	-1.22208200	0.69786300	0.00000000	C	-1.21714000	0.69467300	0.00000000
N	0.00000000	1.28282800	0.00000000	N	0.00000000	1.27814600	0.00000000
H	-0.17847600	-2.54020100	0.00000000	H	-0.17814700	-2.53332400	0.00000000
H	2.06515700	1.14986700	0.00000000	H	2.06177900	1.14493300	0.00000000
H	2.04196700	-1.35588500	0.00000000	H	2.03876500	-1.35243000	0.00000000
H	0.05204300	2.29632300	0.00000000	H	0.05330600	2.29057300	0.00000000
H	-2.09051400	1.34035600	0.00000000	H	-2.08630300	1.33764000	0.00000000

4- Pyridinyl radical (2c)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	0.00000000	1.19165400	0.59766000	C	0.00000000	1.18757100	0.59439100
C	0.00000000	1.22526300	-0.78487700	C	0.00000000	1.22101500	-0.78133200
C	0.00000000	0.00000000	-1.40286700	C	0.00000000	0.00000000	-1.39599400
C	0.00000000	-1.22526300	-0.78487700	C	0.00000000	-1.22101500	-0.78133200
C	0.00000000	-1.19165400	0.59766000	C	0.00000000	-1.18757100	0.59439100
N	0.00000000	0.00000000	1.23033100	N	0.00000000	0.00000000	1.22490300
H	0.00000000	2.07459100	1.22013100	H	0.00000000	2.07079900	1.21760500
H	0.00000000	2.16645300	-1.31636800	H	0.00000000	2.16201900	-1.31390600
H	0.00000000	0.00000000	2.24395200	H	0.00000000	0.00000000	2.23754200
H	0.00000000	-2.07459100	1.22013100	H	0.00000000	-2.07079900	1.21760500
H	0.00000000	-2.16645300	-1.31636800	H	0.00000000	-2.16201900	-1.31390600

Pyridine-N-oxide (3)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	0.00000000	1.17566400	0.28219000	C	0.00000000	1.17080700	0.28166300
C	0.00000000	1.18930000	-1.09504800	C	0.00000000	1.18438500	-1.09012600
C	0.00000000	0.00000000	-1.81448100	C	0.00000000	0.00000000	-1.80630800
C	0.00000000	-1.18930000	-1.09504800	C	0.00000000	-1.18438500	-1.09012600
C	0.00000000	-1.17566400	0.28219000	C	0.00000000	-1.17080700	0.28166300
N	0.00000000	0.00000000	0.98316000	N	0.00000000	0.00000000	0.98209500
H	0.00000000	0.00000000	-2.89401800	H	0.00000000	0.00000000	-2.88631700
H	0.00000000	2.05367100	0.90678400	H	0.00000000	2.04797500	0.91000800
H	0.00000000	2.14625100	-1.59765800	H	0.00000000	2.14151700	-1.59327500
H	0.00000000	-2.14625100	-1.59765800	H	0.00000000	-2.14151700	-1.59327500
H	0.00000000	-2.05367100	0.90678400	H	0.00000000	-2.04797500	0.91000800
O	0.00000000	0.00000000	2.25435300	O	0.00000000	0.00000000	2.23969800

2-Pyridyl-N-oxide radical (3a)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	-1.15047700	0.25569300	0.00000000	C	1.14544200	0.25584900	0.00000000
C	-1.09772700	-1.12068800	0.00000000	C	1.09303200	-1.11497200	0.00000000
C	0.12051900	-1.79358200	0.00000000	C	-0.12033300	-1.78532600	0.00000000
C	1.29188600	-1.03114700	0.00000000	C	-1.28552900	-1.02668100	0.00000000
C	1.15552300	0.32464800	0.00000000	C	-1.15207300	0.32504300	0.00000000
N	0.00000000	1.01263300	0.00000000	N	0.00000000	1.01118400	0.00000000
H	-2.05381000	0.84500700	0.00000000	H	2.04821900	0.84865500	0.00000000
H	-2.03030500	-1.66677900	0.00000000	H	2.02607000	-1.66114300	0.00000000
H	2.27221400	-1.48612300	0.00000000	H	-2.26607400	-1.48281300	0.00000000
O	-0.03413500	2.28533300	0.00000000	O	0.03405000	2.26983100	0.00000000
H	0.16664100	-2.87274800	0.00000000	H	-0.16385400	-2.86511400	0.00000000

3- Pyridyl-N-oxide radical(3b)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	1.13428700	0.19036400	0.00000000	C	1.12878200	0.18802500	0.00000000
C	1.08143200	-1.18721100	0.00000000	C	1.07572800	-1.18436200	0.00000000
C	-0.13968900	-1.86737400	0.00000000	C	-0.14087000	-1.85870300	0.00000000
C	-1.23483300	-1.04306500	0.00000000	C	-1.23129100	-1.03657900	0.00000000
C	-1.22467900	0.31377900	0.00000000	C	-1.21893800	0.31520400	0.00000000
N	0.00000000	0.95982400	0.00000000	N	0.00000000	0.95864300	0.00000000
H	2.04591100	0.76413000	0.00000000	H	2.04009000	0.76519700	0.00000000
H	2.01482500	-1.73427800	0.00000000	H	2.01003400	-1.73080800	0.00000000
O	0.06434900	2.22316000	0.00000000	O	0.06740500	2.20886700	0.00000000
H	-0.19730900	-2.94542200	0.00000000	H	-0.20057000	-2.93736700	0.00000000
H	-2.07732300	0.97256900	0.00000000	H	-2.06925500	0.98004200	0.00000000

4- Pyridyl-N-oxide radical (3c)

(U)B3LYP/cc-pVTZ				(U)M06/cc-pVTZ			
C	0.00000000	1.18132500	0.21917500	C	0.00000000	1.17706500	0.21859400
C	0.00000000	1.20737900	-1.16455800	C	0.00000000	1.20238300	-1.15848400
C	0.00000000	0.00000000	-1.81425100	C	0.00000000	0.00000000	-1.80674400
C	0.00000000	-1.20737900	-1.16455800	C	0.00000000	-1.20238300	-1.15848400
C	0.00000000	-1.18132500	0.21917500	C	0.00000000	-1.17706500	0.21859400
N	0.00000000	0.00000000	0.91324800	N	0.00000000	0.00000000	0.91194500
H	0.00000000	2.05636700	0.84879900	H	0.00000000	2.04990300	0.85391100
H	0.00000000	2.15870000	-1.67811900	H	0.00000000	2.15414400	-1.67269900
H	0.00000000	-2.15870000	-1.67811900	H	0.00000000	-2.15414400	-1.67269900
H	0.00000000	-2.05636700	0.84879900	H	0.00000000	-2.04990300	0.85391100
O	0.00000000	0.00000000	2.18700100	O	0.00000000	0.00000000	2.17163800