10.1071/CH14149_AC

Australian Journal of Chemistry 2014, 67(8 & 9), 1324-1329

Supplementary Material

Pyridyl- and Pyridylperoxy Radicals – A Matrix Isolation Study

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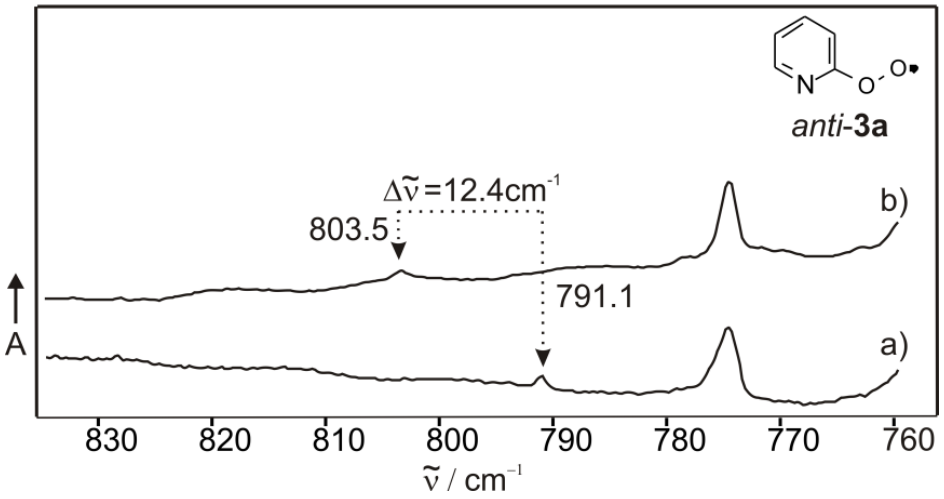


Figure S1. Spectrum measured after FVP of **2a** and deposition in an oxygen doped matrix. Labelled peaks show the shift of the O-O vibration due to $^{16}O_2$ and ^{18}O, respectively a) Matrix doped with $^{16}O_2$ b) Matrix doped with $^{18}O_2$.

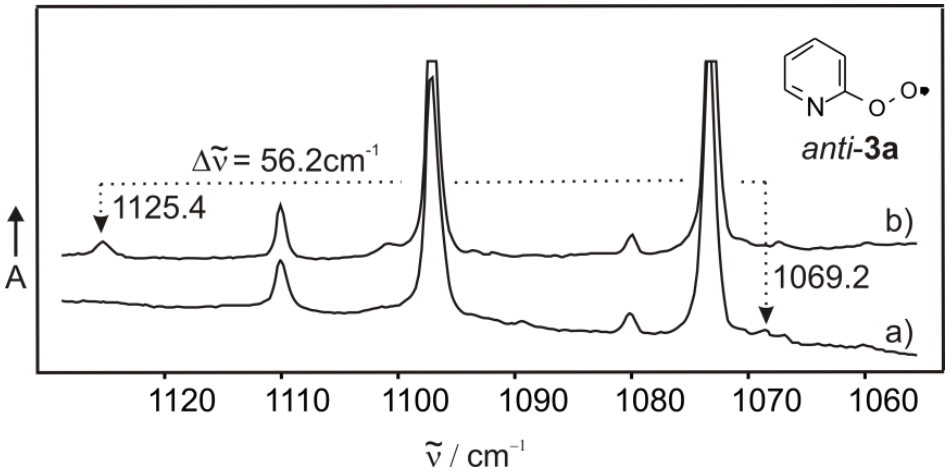


Figure S2. Spectrum measured after FVP of **2a** and deposition in an oxygen doped matrix. Labelled peaks show the shift of the C-O vibration due to $^{16}O_2$ and ^{18}O, respectively a) Matrix doped with $^{16}O_2$ b) Matrix doped with $^{18}O_2$.

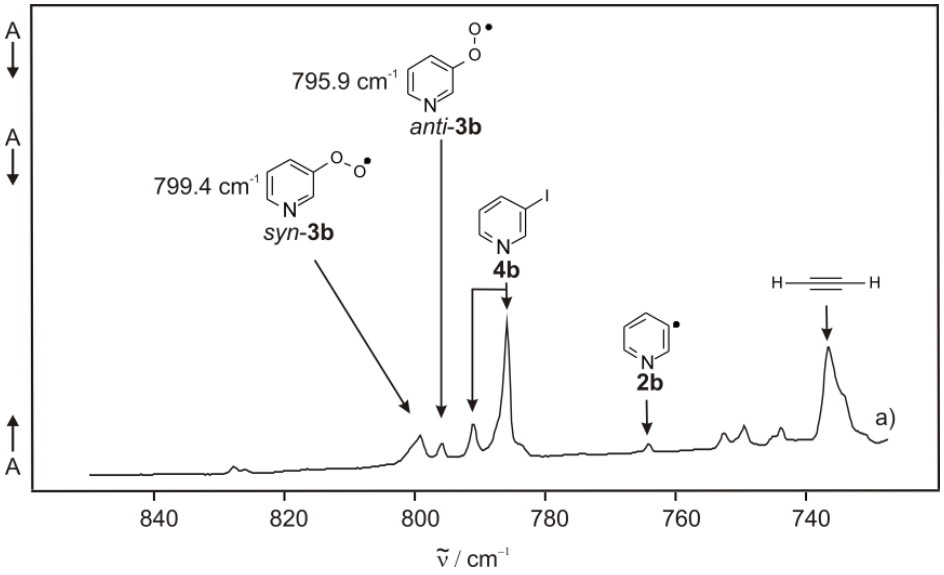


Figure S3. Matrix IR spectra showing the formation of the 3-pyridylperoxy radical **3b**. a) FVP of **4a** and deposition in argon containing 2% oxygen at 10 K. b) IR spectrum of *syn*-**3b** and c) of *anti*-**3b** calculated at the UB3LYP/cc-pVTZ level of theory.

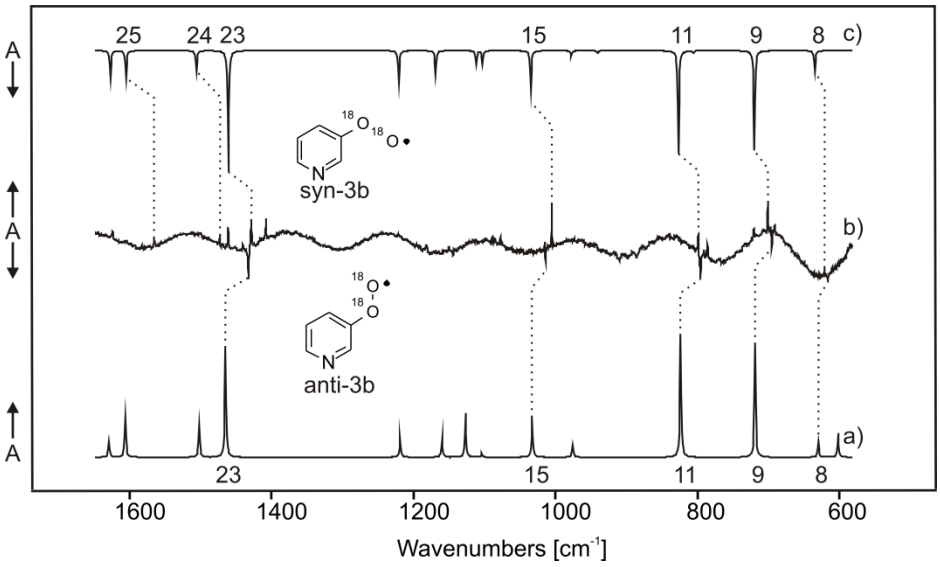


Figure S4. a) and c) Calculated spectra of the oxygen-18-isotopomers of **3b**. b) Difference spectrum after irradiation with visible light (λ > 550 nm).

2-Pyridyl radical 2a

Table S1. IR spectroscopic data of **2a**.

Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
12	A'	1044.3 (19)	1074 (20)	CH def.
11	A'	-	1037 (0)	ring stretch
10	A''	-	1012 (0)	out-of-plane
9	A''	-	975 (0)	CH def. out of plane
8	A'	940.9 (45)	956 (43)	ring def.
7	A''	-	893 (0)	CH def. out of plane
6	A''	735.1 (100)	755 (100)	CH def. out of plane
5	A''	-	716 (14)	CH def. out of plane
4	A'	-	663 (0)	ring def.
3	A'	564.5 (33)	578 (27)	ring def.

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S2. Z matrix (UB3LYP/cc-pVTZ) of **2a**.

Atom Type	X	Y	Z	Energy
C	-1.197868	0.608069	0.000000	-247.693397
C	-0.098890	-1.368472	0.000000	
C	1.168956	-0.802951	0.000000	
C	1.198365	0.586678	0.000000	
C	0.000000	1.302582	0.000000	
H	-2.154309	1.114914	0.000000	
H	2.070414	-1.397429	0.000000	
H	2.146156	1.110666	0.000000	
H	-0.000547	2.383574	0.000000	
N	-1.212156	-0.738165	0.000000	

2-Pyridyl radical 2b

Table S3. IR spectroscopic data of **2b**.

Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
19	A'	1499.9 (33)	1542 (24)	CH def. (in-plane)
18	A'	1426.0 (11)	1471 (6)	CH def. (in-plane)
17	A'	1405.1 (94)	1440 (48)	CH def. (in-plane)
16	A'	1306.1 (3)	1331 (4)	CH def. (in-plane)
15	A'	1209.1 (4)	1260 (3)	ring def.
14	A'	1181.2 (4)	1203 (9)	CH def. (in-plane)
13	A'	1084.9 (16)	1109 (9)	CH def. (in-plane)
12	A'	1035.9 (24)	1066 (24)	CH def. (in-plane)
11	A'	1023.7 (8)	1047 (5)	ring stretch
10	A''	-	998 (0)	CH def. (out-of-plane)
9	A'	972.9 (30)	991 (21)	ring stretch
8	A''	-	951 (0)	CH def. (out-of-plane)
7	A''	-	927 (2)	CH def. (out-of-plane)
6	A''	764.3 (60)	788 (65)	CH def. (out-of-plane)
5	A''	671.8 (100)	692 (100)	CH def. (out-of-plane)
4	A'	646.3 (9)	662 (6)	ring stretch
3	A'	569.5 (71)	580 (56)	ring def.

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S4. Z matrix (UB3LYP/cc-pVTZ) of **2b**.

Atom Type	X	Y	Z	Energy
C	0.000000	1.278239	0.000000	-247.683367
C	-1.244782	-0.653498	0.000000	
C	-0.074901	-1.373423	0.000000	
C	1.171618	-0.806721	0.000000	
C	1.208511	0.589063	0.000000	
H	-0.008316	2.362297	0.000000	
H	-2.225445	-1.111156	0.000000	
H	2.080418	-1.394796	0.000000	
H	2.149113	1.124466	0.000000	
N	-1.194063	0.688175	0.000000	

3-Pyridyl radical 2c

Table S5. IR spectroscopic data of **2c**.

Mode	Sym.	Argon[a]	DFT[b]	Argon[a]	DFT[b]	Assignment[c]
		C_5H_4N		C_5D_4N		
20	B_2	-	1618 (49)	1550.4 (38)	1599.7 (39)	CH def. (in-plane)
19	A_1	-	1539 (99)	1465.1 (100)	1500.6 (100)	CH def. (in-plane)
18	A_1	-	1476 (35)			CH def. (in-plane)
17	B_2	-	1409 (38)	1260.4 (26)	1301.8 (11)	CH def. (in-plane)
16	B_2	1570.9 (50)	1322 (3)			ring def.
15	B_2	1496.8 (25)	1266 (1)	1223.5 (13)	1233.9 (12)	CH def. (in-plane)
14	A_1	1439.9 (10)	1230 (9)	884.9 (17)	899.4 (16)	CH def. (in-plane)
13	A_1	1372.3 (12)	1080 (16)	809.4 (25)	819.7 (23)	CH def. (in-plane)
12	B_2	-	1080 (2)			ring stretch
11	A_1	-	1041 (6)	1001.7	1024.5 (4)	CH def. (out-of-plane)
10	A_2	-	990 (0)			ring stretch
9	A_1	1052.7 (10)	982 (64)	958.7 (13)	975.0 (12)	CH def. (out-of-plane)
8	B_1	1031.8 (<1)	968 (0)			CH def. (out-of-plane)
7	A_2	1017.4 (10)	831 (0)			CH def. (out-of-plane)
6	B_1	-	772 (100)	592.1 (30)	610.1 (22)	CH def. (out-of-plane)

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S6. Z matrix (UB3LYP/cc-pVTZ) of **2c**.

Atom Type	X	Y	Z	Energy
C	0.000000	1.141060	0.656640	-247.685195
C	0.000000	-1.141060	0.656640	
C	0.000000	-1.207833	-0.743369	
C	0.000000	0.000000	-1.384850	
C	0.000000	1.207833	-0.743369	
H	0.000000	2.056962	1.238373	
H	0.000000	-2.056962	1.238373	
H	0.000000	-2.161733	-1.252700	
H	0.000000	2.161733	-1.252700	
N	0.000000	0.000000	1.339787	

2-Pyridylperoxy radical 3a

Table S7. IR spectroscopic data of pyridylperoxy radical *anti*-**3a** and its oxygen-18 isotopomer.

$C_5H_4NO_2$ / $C_5H_4N^{18}O_2$ **3a**				
Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
26	A'	1598.7 (27)	1637 (62)	ring str.
		1596.3 (59)	*1636 (63)*	
25	A'	1573.2 (5)	1613 (36)	ring str.
		1571.6 (17)	*1613 (36)*	
24	A'	1464.7 (10)	1500 (18)	CH def. (in plane)
		1465.6 (37)	*1500 (19)*	
23	A'	1428.6 (84)	1464 (90)	CH def. (in plane)
		1429.5 (44)	*1463 (89)*	
22	A'	1310.2 (5)	1340 (3)	CH def. (in plane)
		1308.9 (<5)	*1339 (3)*	
21	A'	1260.3 (5)	1312 (3)	CH def. (in plane)
		1262.1 (<5)	*1311 (2)*	
20	A'	1176.4 (41)	1200 (18)	O-O str./CH def.
		1171.4 (32)	*1191 (28)*	
19	A'	-	1182 (8)	O-O str./CH def.
		-	*1168 (9)*	
18	A'	1125.5 (40)	1158 (34)	O-O str./CH def.
		1069.2 (17)	*1111 (13)*	
17	A'	-	1113 (4)	CH def. (in plane)
		-	*1112 (0)*	
16	A'	1038.8 (15)	1061 (11)	CH def. (in plane)
		1036.3 (12)	*1060 (12)*	
14	A'	986.4 (5)	1010 (11)	ring str.
		985.8 (<5)	*1009 (14)*	
13	A''	-	993 (1)	CH def. (out-of-plane)
		-	*993 (1)*	
12	A''	-	911 (2)	CH def. (out-of-plane)
		-	*911 (2)*	
11	A'	803.5 (8)	817 (12)	C-O str./ring str.
		791.1 (22)	*804 (14)*	
10	A''	774.5 (100)	799 (100)	CH def. (out-of-plane)
		775.2 (100)	*799 (100)*	
9	A''	726.5 (<5)	753 (6)	CH def. (out-of-plane)
		728.6 (7)	*753 (6)*	
8	A'	-	646 (3)	ring str.
		-	*638 (3)*	
7	A'	-	610 (11)	ring def.
		-	*597 (9)*	

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S8. IR spectroscopic data of *syn*-**3a** and its oxygen-18 isotopomer.

$C_5H_4NO_2$ / $C_5H_4N^{18}O_2$ **3a**				
Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
26	A'	1593.3 (28)	1637 (57)	ring str.
		1593 (32)	*1636 (57)*	
25	A'	1575.0 (9)	1615 (43)	ring str.
		1573.7 (31)	*1614 (43)*	
24	A'	1467.8 (27)	1504 (24)	ring str./C C-H def.
		1467.8 (23)	*1503 (25)*	
23	A'	1427.6 (48)	1463 (88)	CH def.(in plane)
		1428.5 (70)	*1462 (89)*	
22	A'	1313.1 (7)	1342 (5)	CH def.(in plane)
		1312.5 (<5)	*1342 (4)*	
21	A'	-	1311 (1)	CH def.(in plane)
		-	*1310 (1)*	
20	A'	1166.2 (75)	1186 (52)	CH def./C-O str
		1161.4 (54)	*1182 (37)*	
19	A'	1143.9 (7)	1170 (21)	O-O str /C-H def.
		1073.5 (30)	*1123 (6)*	
18	A'	1121.3 (14)	1167 (18)	CH def.
		-	*1167 (30)*	
17	A'	-	1116 (4)	CH def.(in plane)
		1097.5 (21)	*1123 (6)*	
16	A'	1040.9 (7)	1063 (7)	CH def.(in plane)
		-	*1061 (4)*	
14	A'	985.0 (<5)	1009 (9)	Ring str.
		983.5 (6)	*1009 (8)*	
13	A''	961.1 (<5)	991 (1)	CH def.(out of plane)
		-	*991 (1)*	
12	A''	-	901 (1)	CH def.(out of plane).
		-	*900 (2)*	
11	A'	807.9 (5)	822 (15)	C-O str./ring str.
		792.7 (10)	*806 (17)*	
10	A''	771.4 (100)	794 (100)	CH def.(out of plane)
		771.5 (100)	*794 (100)*	
9	A''	-	751 (7)	CH def.(out-of- plane)
		-	*751 (7)*	
8	A'	648.6 (9)	660 (5)	COO def./ring str.
		628.1 (<5)	*641 (2)*	
7	A'	614.3 (9)	629 (5)	ring def.
		613.5 (7)	*628 (6)*	

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S9. Z matrix (UB3LYP/cc-pVTZ) of *anti*-**3a**

Atom Type	X	Y	Z	Energy
C	1.6733960	-0.9849530	0.0000000	-398.1429979
C	0.0000000	0.5284810	0.0000000	
C	-1.0042820	-0.4303650	0.0000000	
C	-0.5879590	-1.7519210	0.0000000	
C	0.7732080	-2.0418570	0.0000000	
H	2.7417450	-1.1630500	0.0000000	
H	-1.3197820	-2.5482540	0.0000000	
H	1.1291130	-3.0620070	0.0000000	
N	1.2913420	0.2932050	0.0000000	
H	-2.0422900	-0.1420150	0.0000000	
O	-0.2753230	1.9081970	0.0000000	
O	-1.5589710	2.2101260	0.0000000	

Table S10. Z matrix (UB3LYP/cc-pVTZ) of *syn*-**3a**

Atom Type	X	Y	Z	Energy
C	1.1710690	-1.3227230	0.0000010	-398.1397861
C	-0.4752410	0.2110030	0.0000000	
C	0.4020010	1.2910120	0.0000000	
C	1.7539010	0.9935190	0.0000000	
C	2.1521260	-0.3404610	0.0000000	
H	1.4383010	-2.3726360	0.0000010	
H	2.4863180	1.7890900	0.0000000	
H	3.1974750	-0.6135750	0.0000000	
N	-0.1367850	-1.0522630	0.0000000	
H	0.0267860	2.3036470	0.0000000	
O	-1.8320460	0.5780060	0.0000000	
O	-2.6947690	-0.4198540	-0.0000010	

2-pyridylperoxy radical 3b

Table S111. IR spectroscopic data of *anti*-**3b** and its oxygen-18 isotopomer.

$C_5H_4NO_2$ / $C_5H_4N^{18}O_2$ **3b**				
Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
26	A'	1594.6 (17)	1627 (24)	ring str.
		1592.6 (11)	*1627 (24)*	
25	A'	1565.5 (21)	1606 (25)	CH def. (in plane)
		1565.5 (25)	*1606 (25)*	
24	A'	1473.9 (25)	1507 (19)	CH def. (in plane)
		1473.3 (29)	*1507 (20)*	
23	A'	1429.4 (100)	1462(100)	CH def. (in plane)
		1428.8 (70)	*1461 (90)*	
22	A'	-	1356 (1)	CH def. (in plane)
		1319.8 (6)	*1355 (2)*	
21	A'	-	1293 (2)	ring str./ CH def.
		-	*1293 (2)*	
20	A'	1191.1 (26)	1223 (28)	CH def. (in plane)
		1190.1 (14)	*1221 (27)*	
19	A'	1155.7 (21)	1175 (31)	CH def./C-O str.
		1150.6 (16)	*1169 (22)*	
18	A'	-	1166 (2)	O-O str.
		1189.2 (18)	*1103 (14)*	
17	A'	-	1114 (16)	CH def. (in plane)
		1085.9 (9)	*1112 (13)*	
16	A'	-	1059 (1)	ring str.
		1077.7 (23)	*1059 (2)*	
15	A'	1016.5 (42)	1035 (35)	ring def.
		1015.4 (25)	*1035 (35)*	
14	A''	-	1014 (1)	CH def.(out of plane)
		-	*1014 (1)*	
13	A''	-	977 (8)	CH def.(out of plane)
		-	*977 (8)*	
12	A''	-	941 (5)	CH def.(out of plane)
		-	*941 (5)*	
11	A''	799.4 (72)	827 (86)	CH def.(out of plane)
		799.3 (51)	*827 (86)*	
10	A'	-	820 (5)	C-O str./ring str.
		-	*806 (4)*	
9	A''	701.6 (30)	720 (84)	ring def.
		701.9 (100)	*720 (83)*	
8	A'	646.4 (18)	623 (22)	C-O-O def./ring str.
		611.3 (21)	*636 (19)*	
7	A'	-	618 (5)	ring str.
		-	*609 (2)*	

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S122. IR spectroscopic data of *syn*-**3b** and its oxygen-18 isotopomer.

$C_5H_4NO_2$ / $C_5H_4N^{18}O_2$ **3b**				
Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
26	A'	1590.1 (7)	1629 (15)	ring str.
		-	1629 (15)	
25	A'	1569.5 (10)	1607 (34)	ring str.
		-	1606 (34)	
24	A'	1468.1 (39)	1502 (27)	C-H def. (in plane)
		-	1502 (28)	
23	A'	1434.3 (55)	1466 (93)	C-H def. (in plane)
		1432.7 (100)	1465 (93)	
22	A'	-	1355 (0)	C-H def. (in plane)
		-	1354 (0)	
21	A'	-	1288 (4)	ring str./C-H def.
		-	1287 (3)	
20	A'	1189.5 (22)	1189 (22)	C-H def. (in plane)
		-	1219 (19)	
19	A'	1151.2 (29)	1151 (30)	O-O str.
		-	1104 (4)	
18	A'	-	1163 (13)	C-H def./ C-O str.
		1144.4 (13)	1160 (17)	
17	A'	1119.0 (16)	1125 (22)	C-H def. (in plane)
		-	1127 (38)	
16	A'	-	1060 (0)	ring str.
		-	1059 (0)	
15	A'	1014.7 (42)	1014 (42)	ring def.
		1014.2 (42)	1033 (35)	
14	A''	-	1008 (0)	C-H def. (out-of-plane)
		-	1008 (0)	
13	A''	-	976 (13)	C-H def. (out-of-plane)
		-	976 (12)	
12	A''	-	945 (2)	C-H def. (out-of-plane)
		-	945 (2)	
11	A''	795.9 (100)	823 (100)	C-H def. (out-of-plane)
		796.4 (81)	823 (100)	
10	A'	-	818 (1)	C-O str./ring str.
		-	806 (2)	
9	A''	696.0 (45)	719 (96)	ring def.
		695.9 (60)	719 (96)	
8	A'	627.2 (17)	639 (18)	C-O-O def./ring str.
		616.8 (20)	630 (16)	
7	A'	599.2 (16)	613 (22)	C-O-O def.
		591.0 (10)	602 (21)	

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S133. Z matrix (UB3LYP/cc-pVTZ) of *anti*-**3b**.

Atom Type	X	Y	Z	Energy
C	0.6871830	-2.0576830	0.0000000	-398.051905
C	1.3285900	0.1304080	0.0000000	
C	0.0000000	0.5419190	0.0000000	
C	-1.0286080	-0.3847540	0.0000000	
C	-0.6638420	-1.7218820	0.0000000	
H	0.9938930	-3.0966730	0.0000000	
H	2.1238340	0.8665630	0.0000000	
H	-2.0566060	-0.0582000	0.0000000	
H	-1.4169910	-2.4973930	0.0000000	
N	1.6689210	-1.1540390	0.0000000	
O	-0.1972370	1.9213180	0.0000000	
O	-1.4610780	2.3056730	0.0000000	

Table S144. Z matrix (UB3LYP/cc-pVTZ) of *syn*-**3b**.

Atom Type	X	Y	Z	Energy
C	0.6077950	-2.0717190	0.0000000	-398.050839
C	-0.9871700	-0.4302490	0.0000000	
C	0.0000000	0.5488770	0.0000000	
C	1.3414350	0.2007530	0.0000000	
C	1.6496830	-1.1495760	0.0000000	
H	0.8164450	-3.1348440	0.0000000	
H	-2.0314170	-0.1540230	0.0000000	
H	2.1022310	0.9689350	0.0000000	
H	2.6776090	-1.4835250	0.0000000	
N	-0.6803460	-1.7252890	0.0000000	
O	-0.2642270	1.9184600	0.0000000	
O	-1.5448860	2.2430350	0.0000000	

4-pyridyl peroxy radical 3c

Table S155. IR spectroscopic data of **3c** and its oxygen-18 isotopomer.

$C_5H_4NO_2$ / $C_5H_4N^{18}O_2$ **3c**				
Mode	Sym.	Argon[a]	DFT[b]	Assignment[c]
26	A´	1600.0 (62)	1638 (53)	ring str.
		1699.8 (58)	*1635 (53)*	
25	A´	1572.3 (100)	1607(100)	ring str.
		1569.6 (51)	*1607(100)*	
24	A´	1484.3 (31)	1514 (29)	ring str./C C-H def.
		1484.3 (37)	*1514 (29)*	
23	A´	1405.8 (35)	1445 (42)	C-H def.(in plane)
		1411.2 (53)	*1445 (42)*	
22	A´	-	1360 (0)	C-H def.(in plane)
		-	*1359 (1)*	
21	A´	-	1285 (3)	Ring str.
		-	*1285 (3)*	
20	A´	1220.0 (1)	1243 (2)	C-H def. (in plane)
		1220.0 (2)	*1242 (2)*	
19	A´	1119.2 (31)	1172 (19)	O-O str.
		1061.5 (16)	*1108 (14)*	
18	A´	1149.5 (31)	1164 (10)	C-O str./ring str.
		1142.9 (16)	*1159 (9)*	
17	A´	-	1099 (0)	C-H def.(in plane)
		-	*1098 (3)*	
16	A´	-	1069 (1)	C-H def.(in plane)
		-	*1067 (1)*	
15	A´´	-	1014 (0)	CH def.(out of plane)
		-	*1013 (0)*	
14	A´	990.1 (14)	1010 (10)	Ring str.
		990.1 (9)	*1010 (10)*	
13	A´´	-	990 (2)	CH def.(out of plane).
		-	*990 (2)*	
12	A´´	-	874 (4)	CH def.(out of plane)
		-	*874 (4)*	
11	A´´	817.1 (80)	848 (92)	CH def.(out of plane)
		816.9 (100)	*847 (92)*	
10	A´	807.7 (46)	818 (35)	C-O str./ring str.
		791.5 (56)	*801 (39)*	
9	A´´	-	746 (1)	ring def.
		-	*746 (1)*	
8	A´	-	674 (1)	Ring str.
		-	*674 (0)*	
7	A´	-	622 (23)	COO def./ring str.
		-	*604 (18)*	
6	A´´	507.8(24)	525 (27)	ring def.

[a] Argon matrix at 10K. Wavenumbers in cm^{-1} and relative intensities in parenthesis. [b] Calculated at the UB3LYP/cc-pVTZ level of theory. [c] Approximate description.

Table S16. Z matrix (UB3LYP/cc-pVTZ) of **3c**.

Atom Type	X	Y	Z	Energy
C	-1.0080700	-0.3958060	0.0000000	-398.137355
C	-0.6109750	-1.7270480	0.0000000	
C	1.6036590	-1.1888220	0.0000000	
C	1.3327730	0.1733490	0.0000000	
C	0.0000000	0.5519400	0.0000000	
H	-2.0459990	-0.1054700	0.0000000	
H	-1.3610630	-2.5091960	0.0000000	
H	2.6305920	-1.5346190	0.0000000	
N	2.1200180	0.9131140	0.0000000	
H	0.6607380	-2.1312530	0.0000000	
O	-0.2308790	1.9285040	0.0000000	
O	-1.5032500	2.2806520	0.0000000	

Table S17. Z matrix (UB3LYP/cc-pVTZ) of the oxygen-18 isotopomer of *para*-pyridyl peroxy radical **3c**.

Atom Type	X	Y	Z	Energy
C	-0.0716480	1.0765450	0.0000110	-398.053584
C	1.3000010	1.2760800	0.0000040	
C	1.7451440	-0.9492740	-0.0000150	
C	0.4004200	-1.2784820	0.0000000	
C	-0.4985120	-0.2329980	0.0000110	
H	-0.7686080	1.8947140	0.0000210	
H	1.6902740	2.2833010	0.0000090	
H	2.4897880	-1.7315890	-0.0000160	
H	0.0597830	-2.3004460	0.0000000	
N	2.1996920	0.2987660	-0.0000060	
O	-1.8432520	-0.5996610	0.0000300	
O	-2.6719370	0.4010900	-0.0000340	

***ortho*-TS**

Table S18. Z matrix (UB3LYP/cc-pVTZ) of the TS for the isomerization of **3a**

Atom Type	X	Y	Z	Energy
C	-1.406689	-1.203939	0.055322	-398.13546
C	0.490848	-0.022615	-0.225087	
C	-0.143178	1.20553	-0.133088	
C	-1.515118	1.183303	0.070711	
C	-2.161697	-0.044201	0.165084	
H	-1.872202	-2.179329	0.125216	
H	-2.06982	2.108098	0.151644	
H	-3.229697	-0.102923	0.319055	
N	-0.084051	-1.195964	-0.137056	
H	0.417997	2.123698	-0.219861	
O	1.880743	-0.039746	-0.500889	
O	2.588892	0.003963	0.624101	

Table S19 Calculated IR spectrum of *ortho*-**TS**

ModeNr.	Symmetry	Wavenumber	Abs.Int.	Rel.Int.
1	A	-95.1	0.2	0
2	A	152.1	0.9	2
3	A	340	3.2	7
4	A	397.4	0.4	1
5	A	424.2	3.3	7
6	A	517.9	2.7	6
7	A	624.6	9	19
8	A	639.6	3.5	7
9	A	760.2	16.1	34
10	A	799.9	32.3	69
11	A	858	12.3	26
12	A	909.7	1.1	2
13	A	992.6	0.6	1
14	A	1014.8	7.7	16
15	A	1022.2	0	0
16	A	1065.6	6.2	13
17	A	1116.8	2.9	6
18	A	1137.2	32.3	69
19	A	1171.9	3	6
20	A	1201.5	41.1	88
21	A	1301.2	0.1	0
22	A	1326.7	3.6	8

23	A	1465.6	46.7	99
24	A	1499.9	27	57
25	A	1615.9	33.1	70
26	A	1633.6	42.8	91
27	A	3164.2	9.9	21
28	A	3182.8	5.6	12
29	A	3200.6	9.5	20
30	A	3212.4	0.7	1

meta-TS

Table S20. Z matrix (UB3LYP/cc-pVTZ) of the TS for the isomerization of **3b**

Atom Type	X	Y	Z	Energy
C	-2.143648	-0.101755	0.167278	-398.129260
C	-0.158979	-1.186509	-0.135989	
C	0.508717	0.023929	-0.231655	
C	-0.174586	1.220025	-0.132001	
C	-1.544922	1.150317	0.076383	
H	-3.211624	-0.186275	0.32957	
H	0.386447	-2.118544	-0.222851	
H	0.351485	2.160729	-0.213642	
H	-2.139156	2.048694	0.166872	
N	-1.473137	-1.249962	0.063749	
O	1.892711	0.028672	-0.497596	
O	2.607952	-0.002536	0.62631	

Table S21. Calculated IR spectrum of *meta*-**TS**

ModeNr.	Symmetry	Wavenumber	Abs.Int.	Rel.Int.
1	A	-96.3	0.7	2
2	A	159.1	1.3	4
3	A	340.4	2.4	7
4	A	370.2	5.3	16
5	A	419.7	2.6	8
6	A	502.4	2.2	6
7	A	624.5	4.3	13
8	A	651.9	3.6	11
9	A	725.5	34	100
10	A	809	9.9	29
11	A	855.6	10.7	32
12	A	946.3	1	3
13	A	980.7	1.9	6
14	A	1012.5	0	0

15	A	1041.4	16.5	48
16	A	1061.4	0.3	1
17	A	1123.9	14.9	44
18	A	1129.1	6.4	19
19	A	1187	20.5	60
20	A	1220	4.9	14
21	A	1280.3	0.5	2
22	A	1352	0.7	2
23	A	1457.1	28.7	84
24	A	1504.8	16.7	49
25	A	1614.5	4.6	13
26	A	1623.6	4.8	14
27	A	3158.2	14.7	43
28	A	3167.5	3.7	11
29	A	3189.5	6.6	19
30	A	3203.6	2.8	8

Para-TS

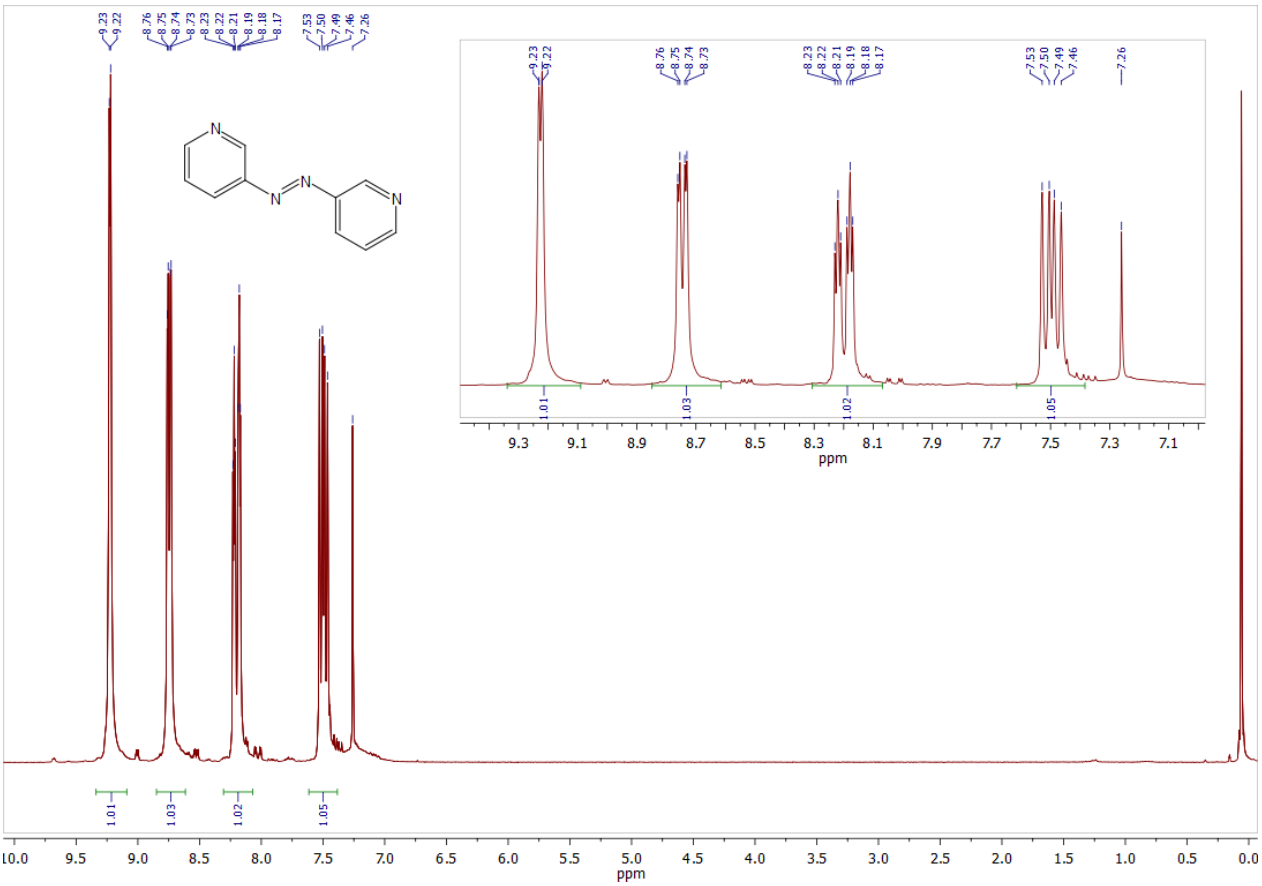
Table S22. Z matrix (UB3LYP/cc-pVTZ) of the TS for the isomerization of **3c.**

Atom Type	X	Y	Z	Energy
C	0.16387	-1.205941	-0.129703	-398.130050
C	1.537404	-1.135279	0.078574	
C	1.523593	1.145862	0.069838	
C	0.149306	1.198435	-0.138523	
C	-0.515208	-0.008212	-0.230853	
H	-0.354315	-2.150277	-0.208606	
H	2.118456	-2.045536	0.168869	
H	2.093838	2.063625	0.152682	
H	-0.380362	2.135796	-0.223936	
N	2.212249	0.009738	0.177109	
O	-1.901014	-0.019444	-0.500889	
O	-2.61363	0.014323	0.622792	

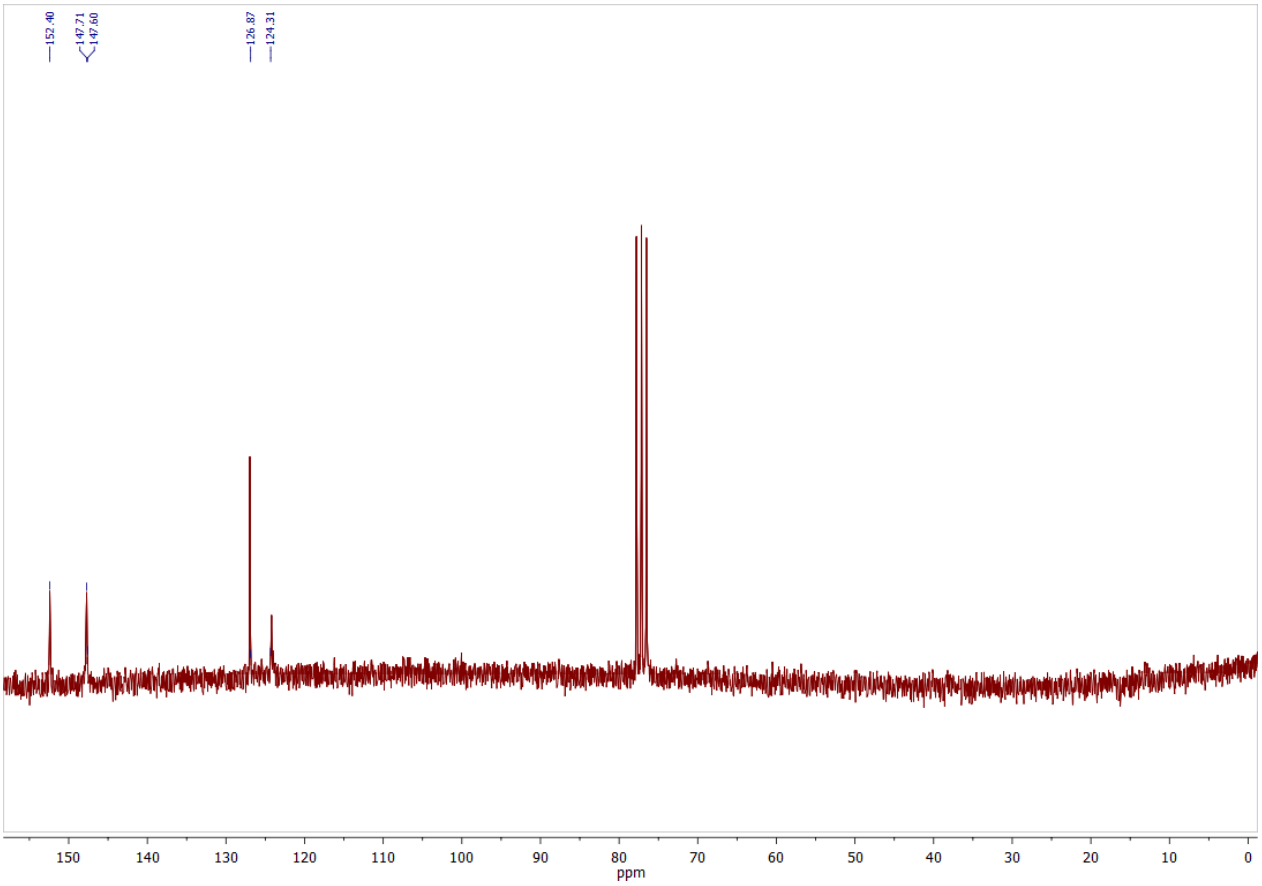
Table S23. Calculated IR spectrum of *para*-**TS**

ModeNr.	Symmetry	Wavenumber	Abs.Int.	Rel.Int.
1	A"	-653.8	2.6	1
2	A'	-477.5	2.1	1
3	A"	168.3	3.7	1
4	A'	284.5	5.3	2
5	A"	388.1	0	0
6	A'	441.6	3.2	1
7	A"	486	11.6	4
8	A'	672.3	0	0
9	A"	731.7	6	2
10	A'	738.9	80.8	30
11	A"	811.2	61.5	23
12	A"	834.5	0	0
13	A"	973.4	0.2	0
14	A"	1002.5	0	0
15	A'	1004.5	6.4	2
16	A'	1067.8	14.4	5
17	A'	1083.8	29.1	11
18	A'	1100.5	0.2	0
19	A'	1241.5	11.9	4
20	A'	1266.6	1.9	1
21	A'	1351.6	2.4	1
22	A'	1441.2	10.1	4
23	A'	1448	133.3	50
24	A'	1515.1	265.4	100
25	A'	1588.6	59.5	22
26	A'	1598.8	190	72
27	A'	3150.4	27	10
28	A'	3153.5	4.8	2
29	A'	3216.8	0.1	0
30	A'	3217.7	0.7	0

NMR spectra



FigureS5. ^{1}H-NMR spectrum of precursor 3,3'-azopyridine



FigureS6. ^{13}C-NMR spectrum of precursor 3,3'-azopyridine