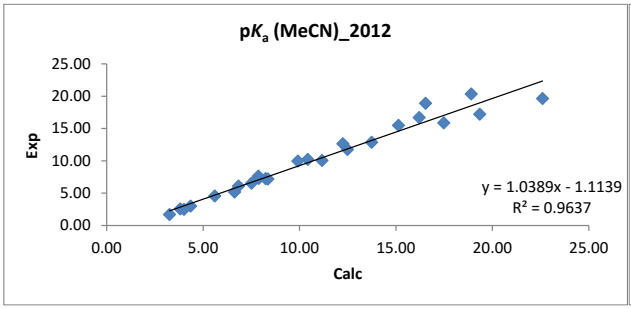
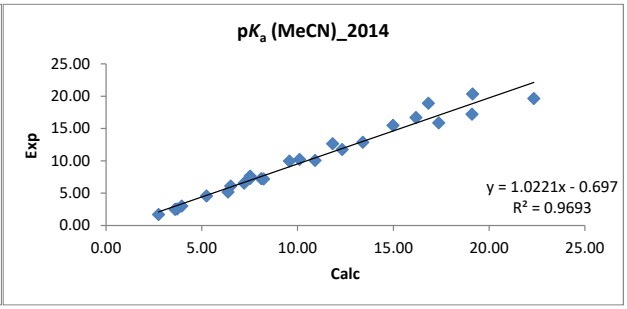
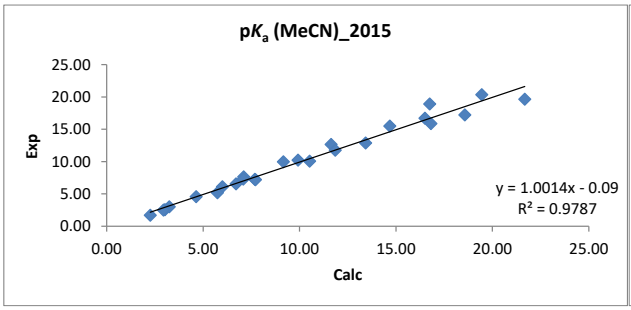
Contents

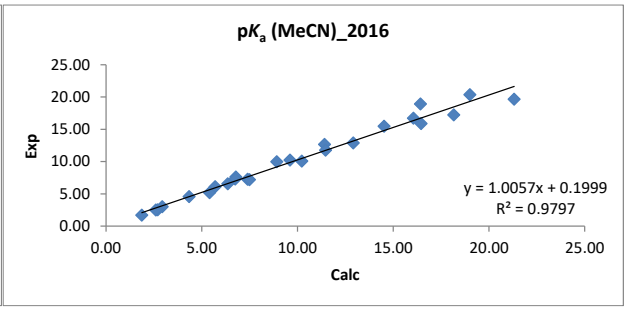
Additional correlations

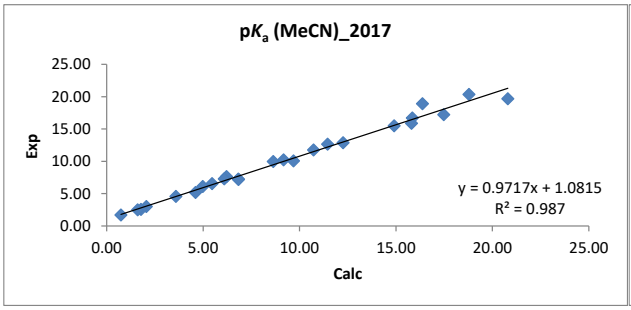
Parametrisation correlation plots and equations according to Table 2 in the main text.

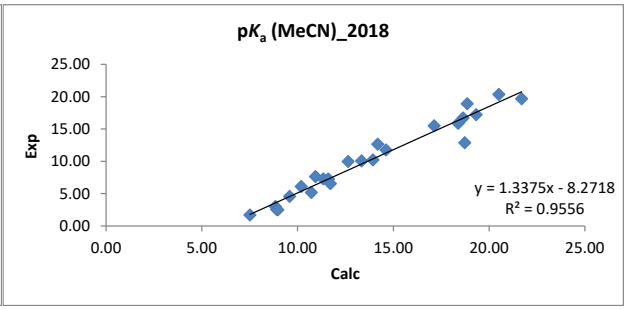


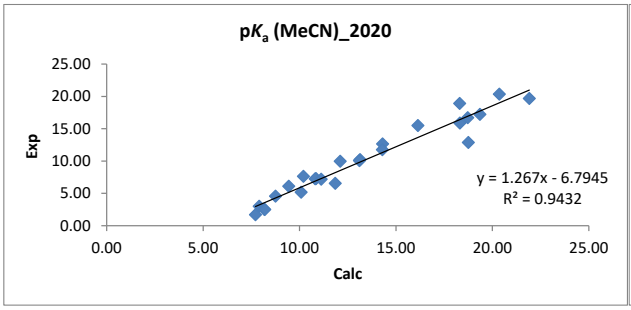


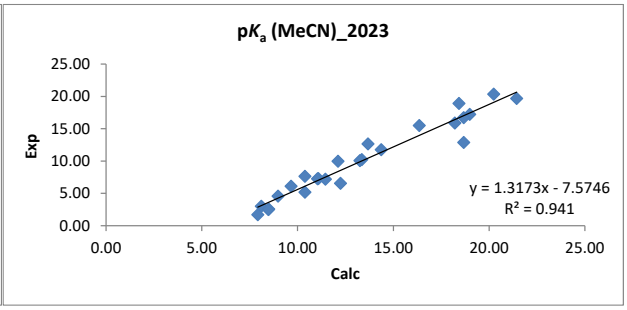








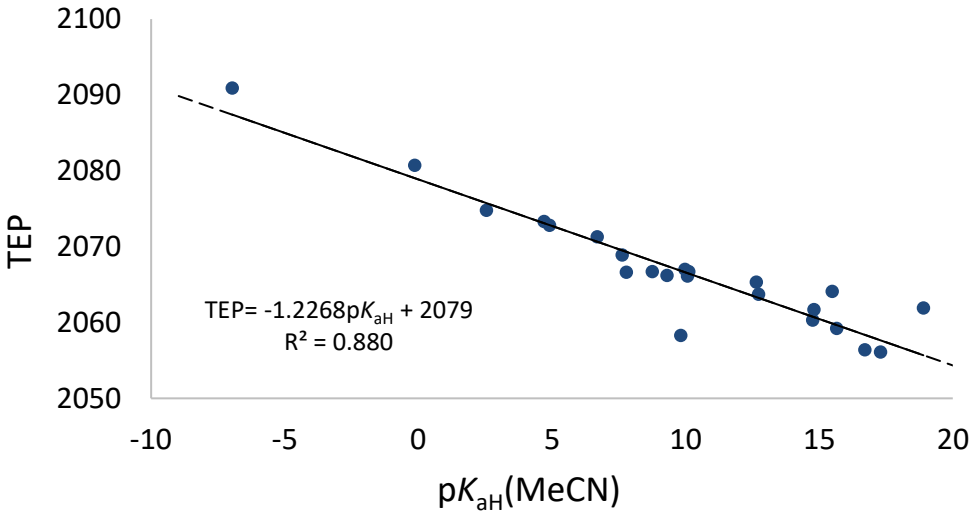




Correlation eq 5 in the main text without any excluded datapoints.

$$\mathrm{TEP} = -1.227(0.099) \cdot \mathrm{p}K_{\mathrm{aH}} + 2079(1.1) \quad \text{(S1)}$$

n = 23; R^2 = 0.880; S = 2.84



pK_a measurements

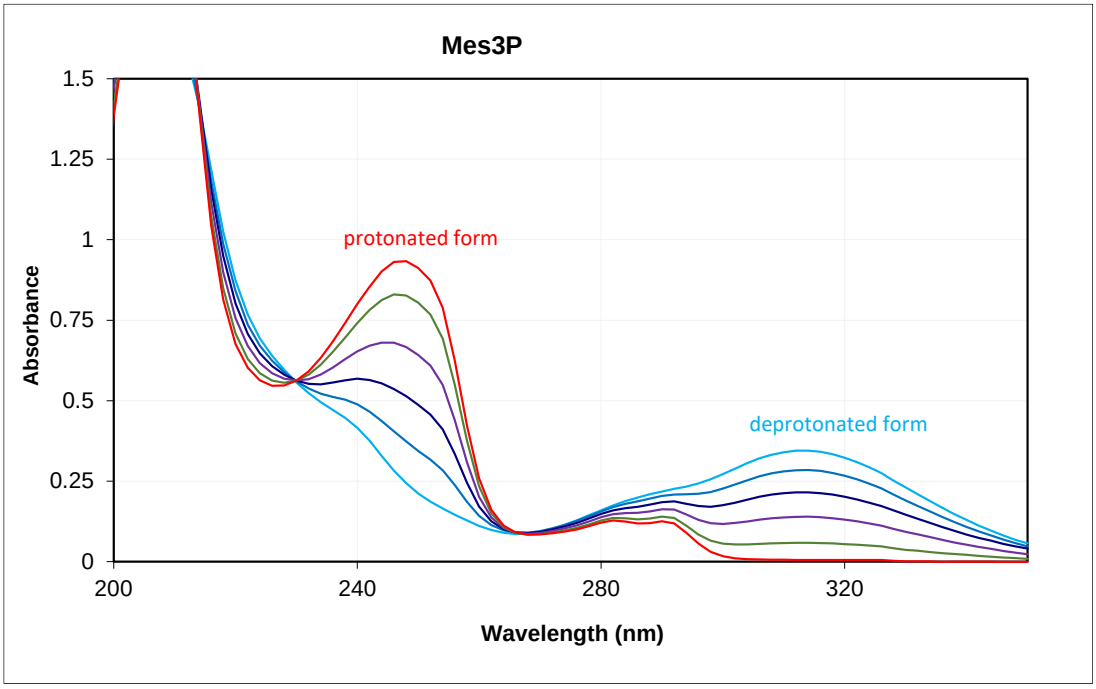
Table S1. Results of pK_{aH} measurements in MeCN.

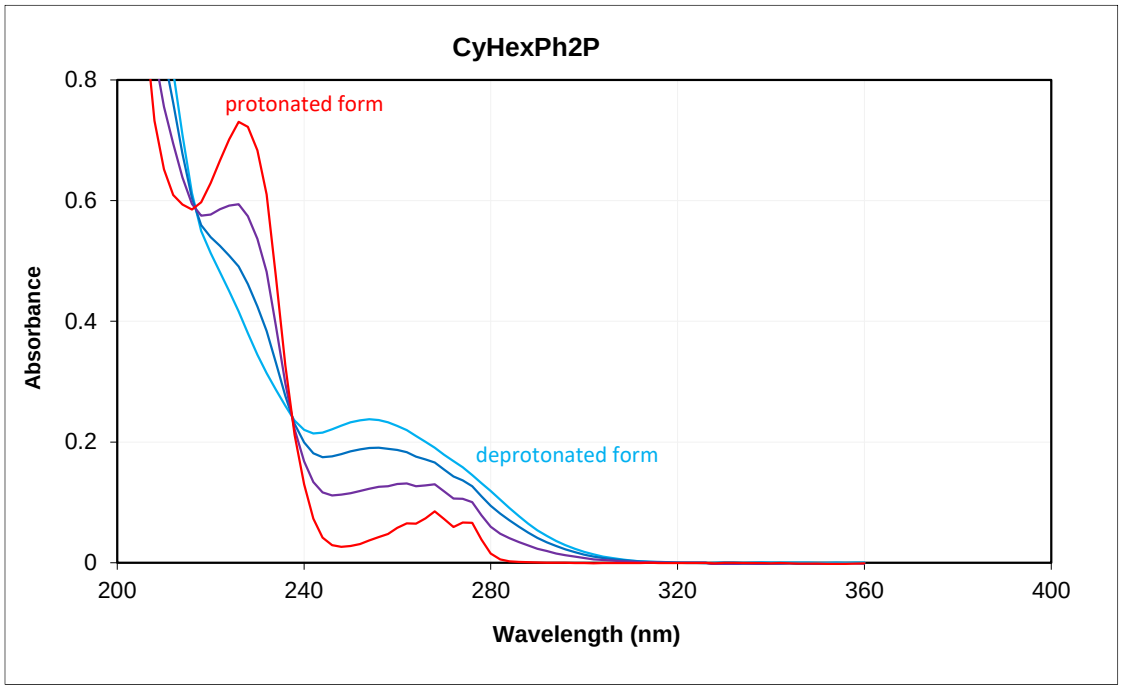
Base (B)	Reference Base (RB)	pK_{aH}(RB) [a]	ΔpK_{aH}	pK_{aH}(B)	Assigned pK_{aH}
$PMes_3$	Pyridine	12.53	-0.37	12.90	**12.87**
	2-Me-Pyridine	13.28	0.40	12.88	
	4-MeO-Aniline	11.87	-0.95	12.82	
	$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]Ph_2P$	11.76	-1.12	12.88	
$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]Ph_2P$	Pyridine	12.53	0.77	11.76	**11.76**
	$PMes_3$	12.87	1.12	11.75	
	4-MeO-Aniline	11.87	0.11	11.76	
$(3\text{-}MeO\text{-}C_6H_4)_3P$	$2,5\text{-}Cl_2$-Aniline	6.23	-1.03	7.26	**7.25**
	2-Cl-Pyridine	6.79	-0.46	7.25	
	$2,6\text{-}(MeO)_2$-Pyridine	7.65	0.41	7.24	
$[3,5\text{-}(MeO)_2\text{-}C_6H_3]_3P$	2,5-Cl2-Aniline	6.23	-0.97	7.20	**7.19**
	2-Cl-Pyridine	6.79	-0.41	7.20	
	$2,6\text{-}(MeO)_2$-Pyridine	7.65	0.44	7.21	
	$NaphtPh_2P$	7.29	0.14	7.15	
$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]_2PhP$	$2\text{-}NO_2\text{-}4\text{-}CF_3\text{-}C_6H_3\text{-}N{=}P_1$(pyrr)	16.54	0.65	15.89	**15.87**
	$2,3\text{-}(NH_2)_2$-Pyridine	15.26	-0.53	15.79	
	$2,4,6\text{-}Me_3$-Pyridine	15.00	-0.92	15.92	
	$[2,6\text{-}(MeO)_2\text{-}C_6H_3]_3P$	17.23	1.37	15.86	

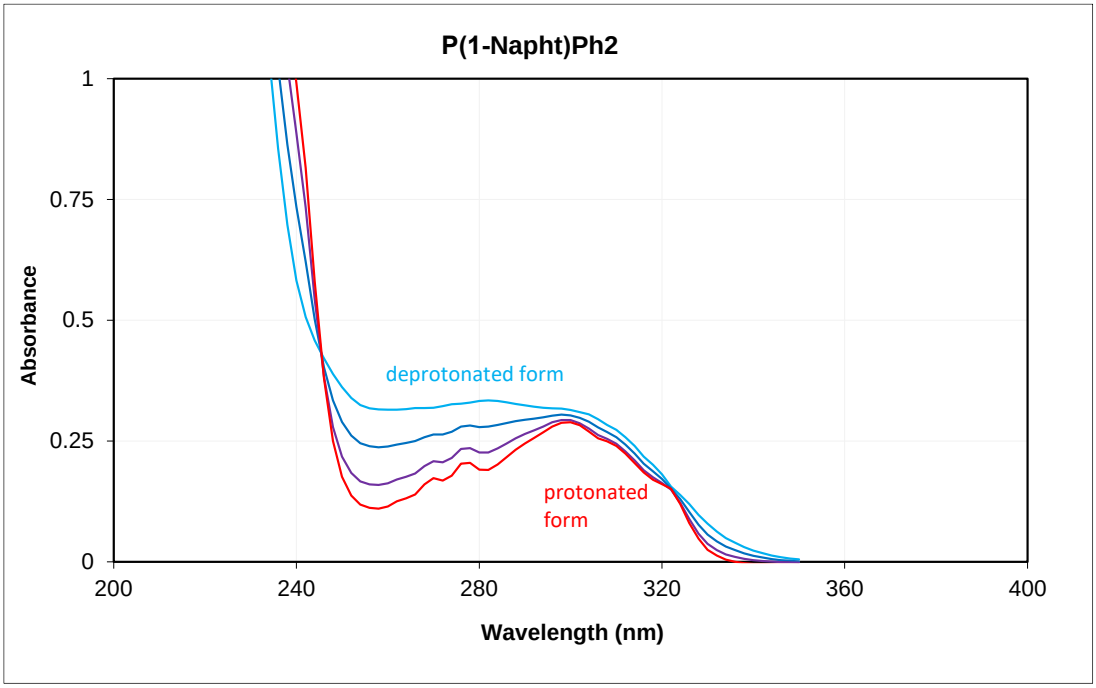
$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]_3P$	$4\text{-}CF_3\text{-}C_6H_4\text{-}N{=}P_1(pyrr)$	20.25	0.55	19.70	**19.66**
	$2\text{-}Cl\text{-}C_6H_4\text{-}N{=}P_1(pyrr)$	20.19	0.57	19.62	
	$2\text{-}Cl\text{-}C_6H_4\text{-}N{=}P_1(dma)$	19.10	-0.55	19.65	
$PCyPh_2$	2-Me-Aniline	10.49	0.27	10.22	**10.23**
	2-MeO-Pyridine	9.94	-0.30	10.24	
	1-Naphtylamine	9.78	-0.46	10.24	
$1\text{-}NaphtPh_2P$	$2,6\text{-}(MeO)_2$-Pyridine	7.65	0.39	7.26	**7.29**
	2-Cl-Pyridine	6.79	-0.48	7.27	
	$[3,5\text{-}(MeO)_2\text{-}C_6H_3]_3P$	7.20	-0.14	7.34	
$[2,6\text{-}(MeO)_2\text{-}C_6H_3]_3P$	$2\text{-}NO_2\text{-}4\text{-}CF_3\text{-}C_6H_3\text{-}N{=}P_1(pyrr)$	16.54	-0.68	17.22	**17.23**
	$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]_2PhP$	15.87	-1.37	17.24	
	$2\text{-}NO_2\text{-}5\text{-}Cl\text{-}C_6H_3\text{-}N{=}P_1(pyrr)$	17.28	0.05	17.23	
$P(dma)_3$	$2\text{-}Cl\text{-}C_6H_4\text{-}N{=}P_1(dma)$	19.10	-0.20	18.90	**18.9**
	$2,6\text{-}Cl_2\text{-}C_6H_3\text{-}N{=}P_1(pyrr)$	18.56	0.40	18.96	
	$4\text{-}(4\text{-}dma\text{-}C_6H_4\text{-}N{=}N)\text{-}C_6H_4P_1(pyrr)_2Ph$	19.04	-0.27	18.77	
$P(pyrr)_3$	$4\text{-}(Ph\text{-}N{=}N)\text{-}C_6H_4P_1(pyrr)_3$	20.27	0.02	20.29	**20.35**
	$Ph\text{-}N{=}P_1(dma)_3$	21.26	-0.93	20.33	
	$2\text{-}Cl\text{-}C_6H_4\text{-}N{=}P_1(pyrr)$	20.19	0.20	20.39	
	$[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]_3P$	19.66	0.74	20.40	
PCy_3	$2\text{-}NO_2\text{-}4\text{-}CF_3\text{-}C_6H_3\text{-}N{=}P_1(pyrr)_3$	16.54	0.18	16.72	**16.70**
	$2\text{-}NO_2\text{-}5\text{-}Cl\text{-}C_6H_3\text{-}N{=}P_1(pyrr)_3$	17.28	-0.58	16.70	
	$2\text{-}NO_2\text{-}4\text{-}Cl\text{-}C_6H_3\text{-}N{=}P_1(pyrr)_3$	17.70	-1.01	16.69	

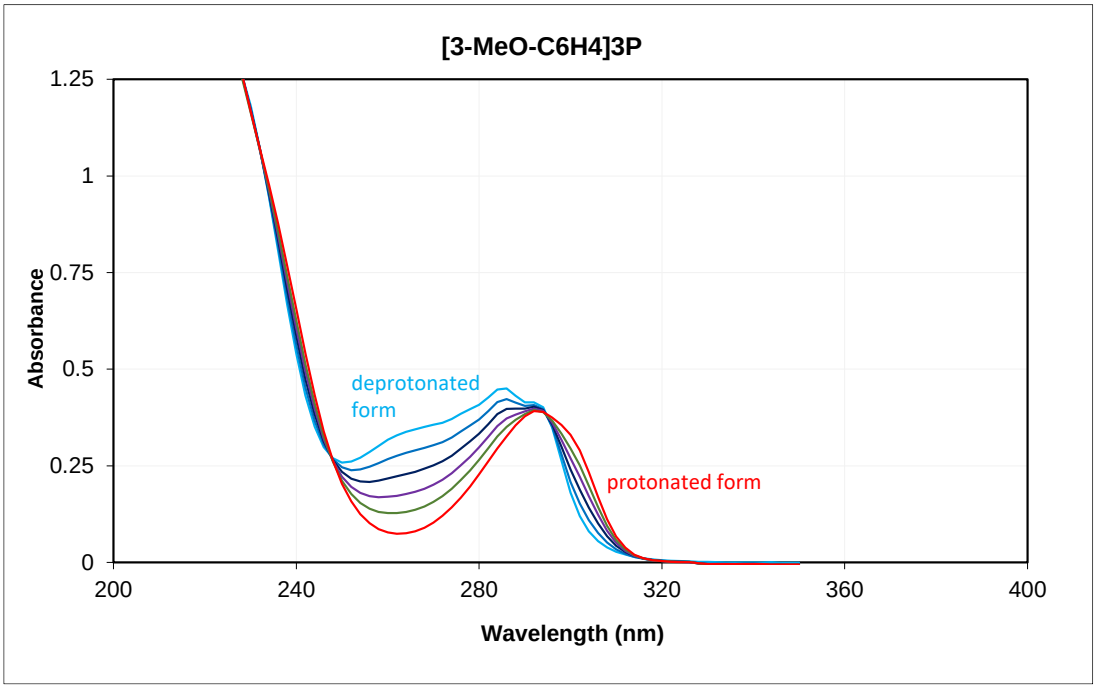
[a] The pK_{aH} values of reference bases are from ref 44.

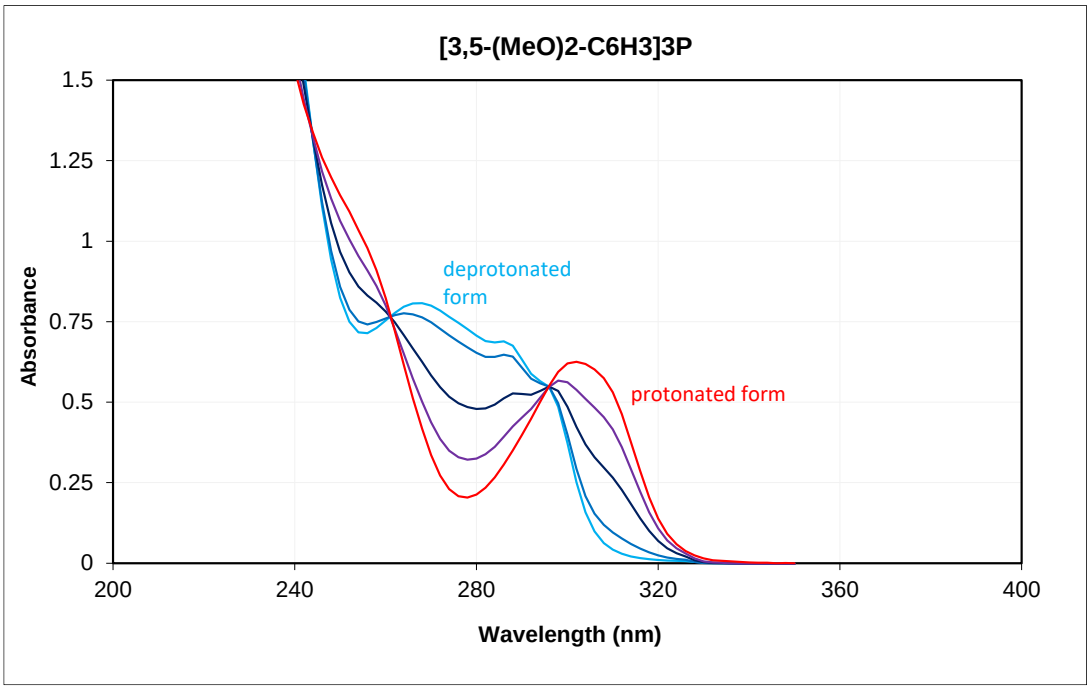
UV-Vis spectra

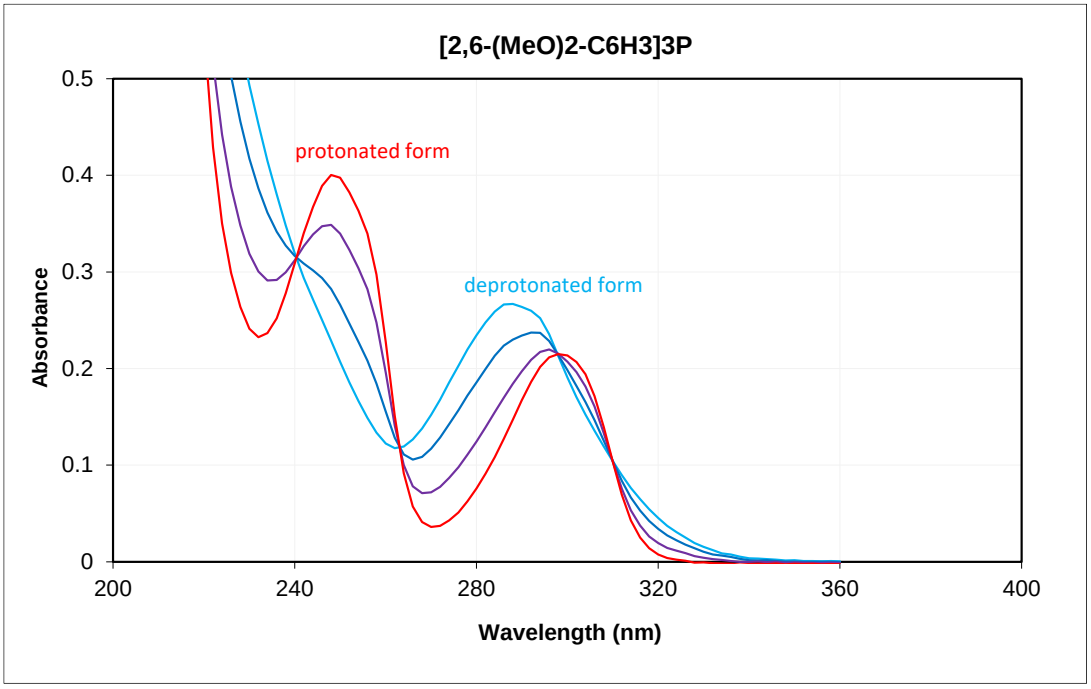


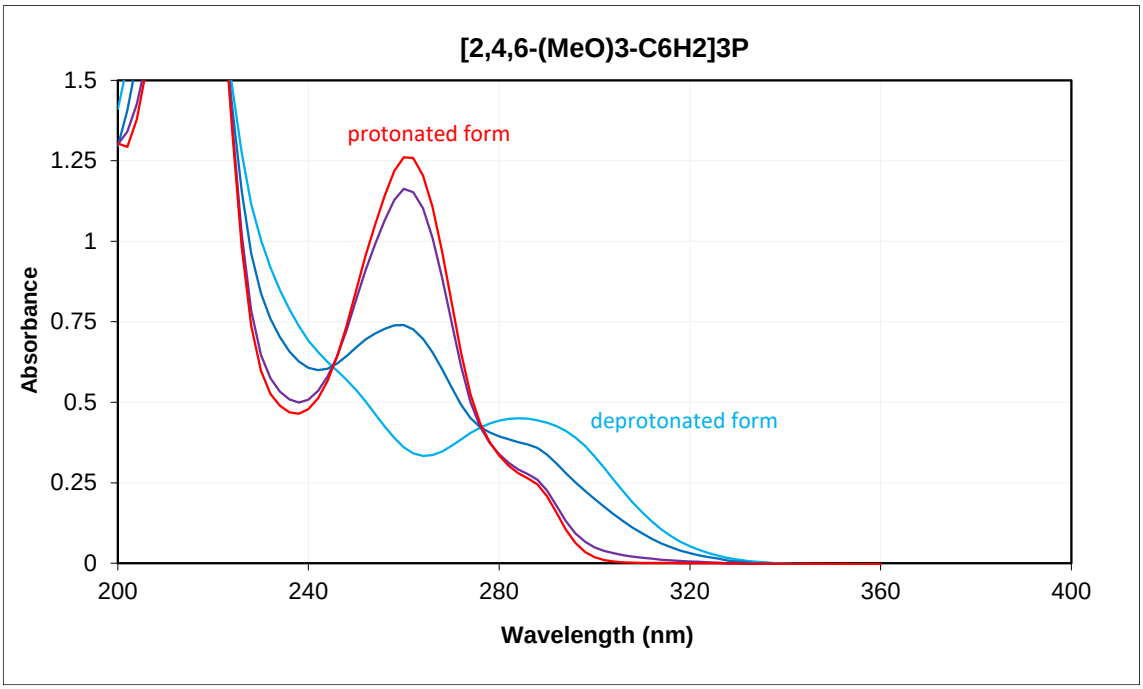


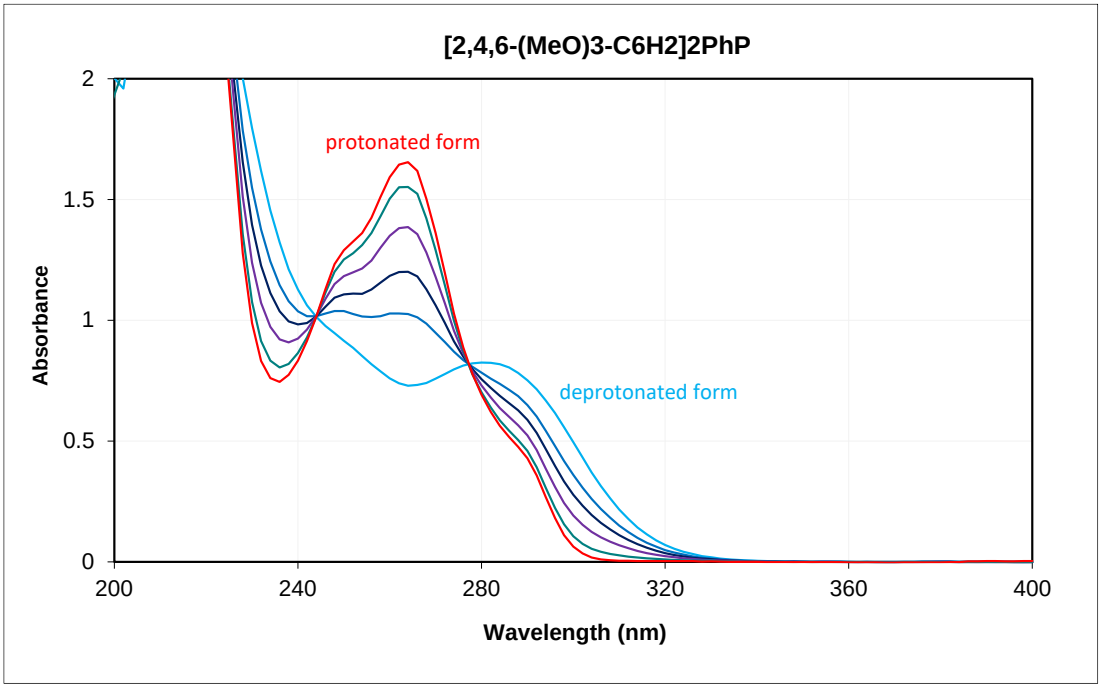

P(1-Napht)Ph2
Absorbance
1
0.75
0.5
0.25
0
200
240
280
320
360
400
Wavelength (nm)
deprotonated form
protonated form

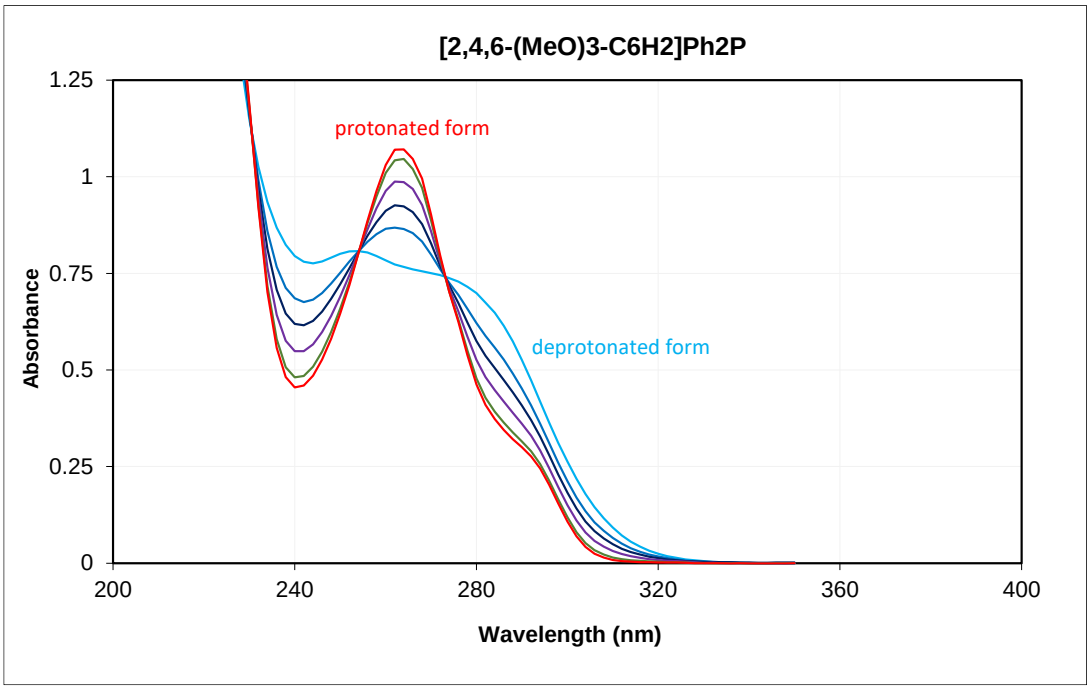

[3-MeO-C6H4]3P
Absorbance
1.25
1
0.75
0.5
0.25
0
200
240
280
320
360
400
Wavelength (nm)
deprotonated form
protonated form


[3,5-(MeO)2-C6H3]3P
Absorbance
Wavelength (nm)
deprotonated form
protonated form
1.5
1.25
1
0.75
0.5
0.25
0
200
240
280
320
360
400


[2,6-(MeO)2-C6H3]3P
Absorbance
Wavelength (nm)
protonated form
deprotonated form
0.5
0.4
0.3
0.2
0.1
0
200
240
280
320
360
400


[2,4,6-(MeO)3-C6H2]3P
protonated form
deprotonated form
Absorbance
Wavelength (nm)
1.5
1.25
1
0.75
0.5
0.25
0
200
240
280
320
360
400

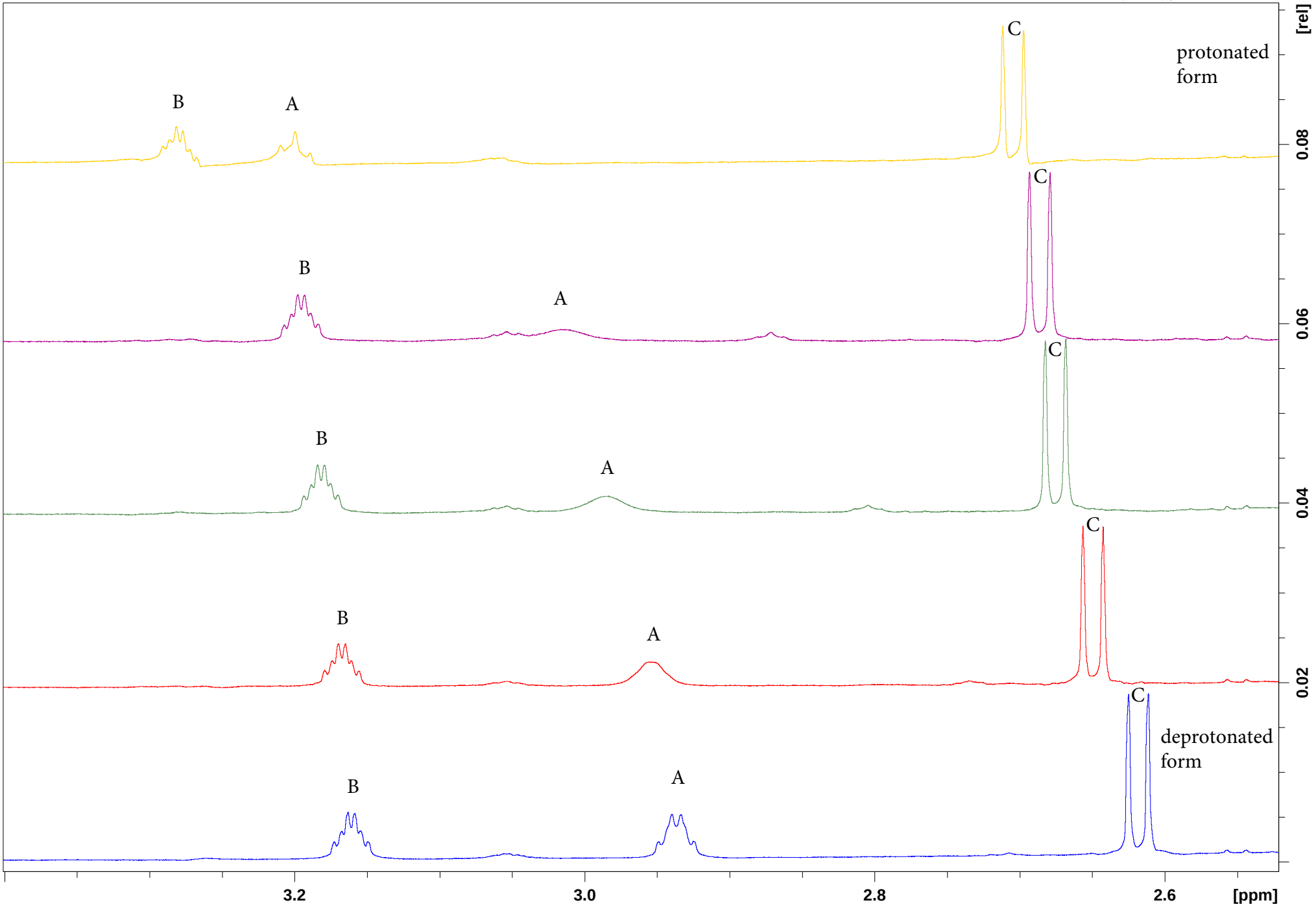

[2,4,6-(MeO)3-C6H2]2PhP
protonated form
deprotonated form
Absorbance
Wavelength (nm)
2
1.5
1
0.5
0
200
240
280
320
360
400

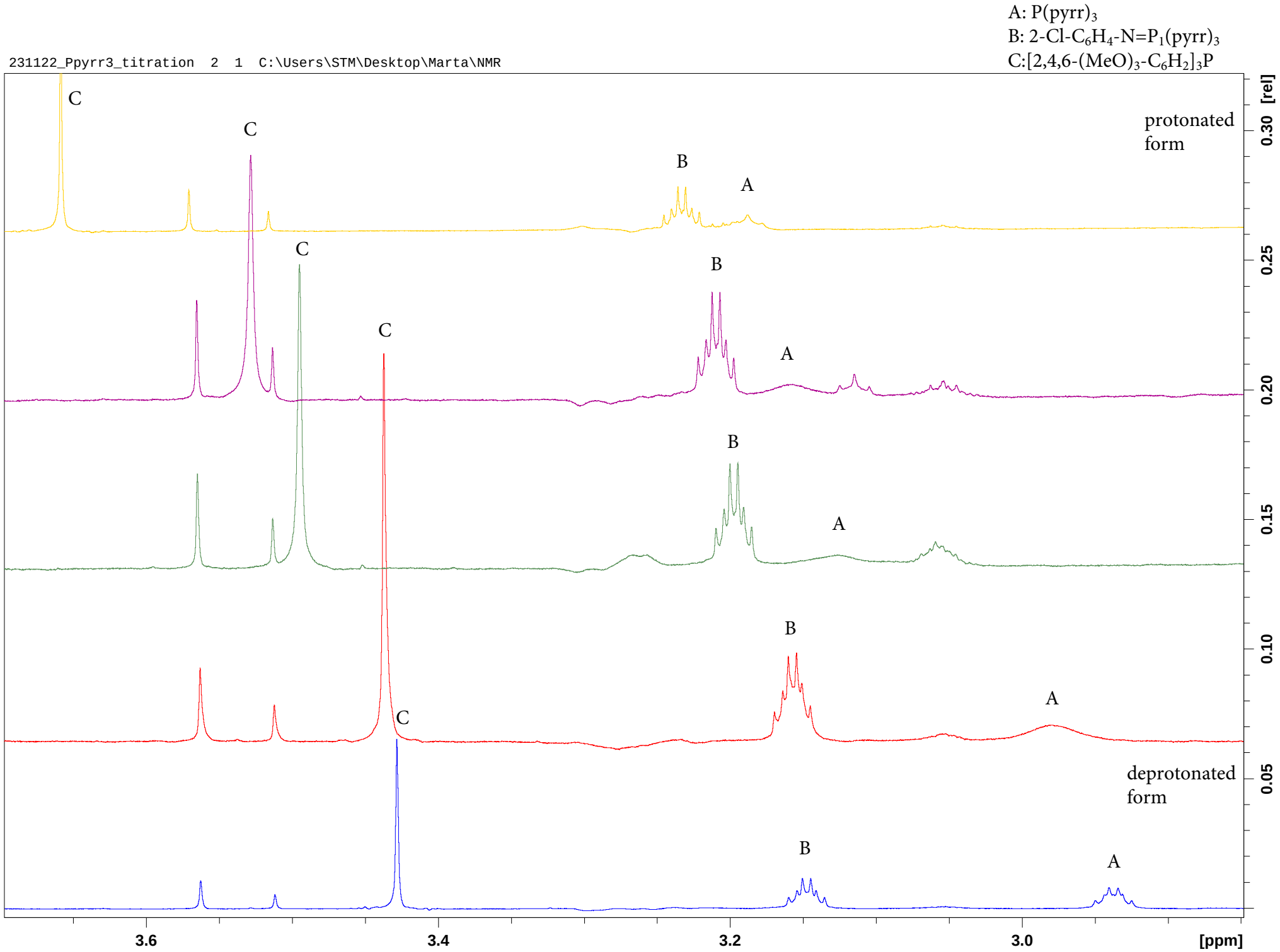

[2,4,6-(MeO)3-C6H2]Ph2P
protonated form
deprotonated form
Absorbance
Wavelength (nm)
1.25
1
0.75
0.5
0.25
0
200
240
280
320
360
400

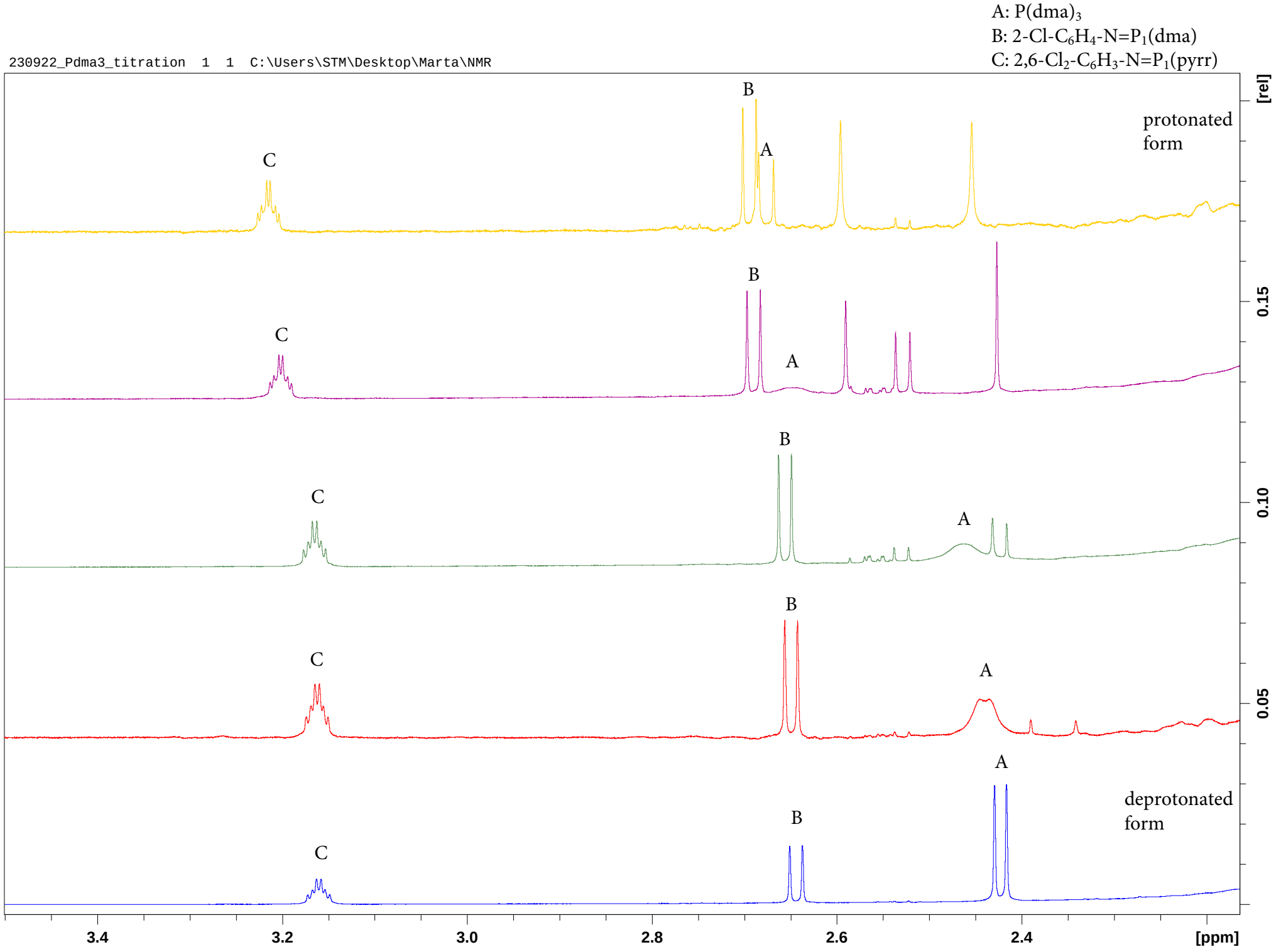
NMR spectra

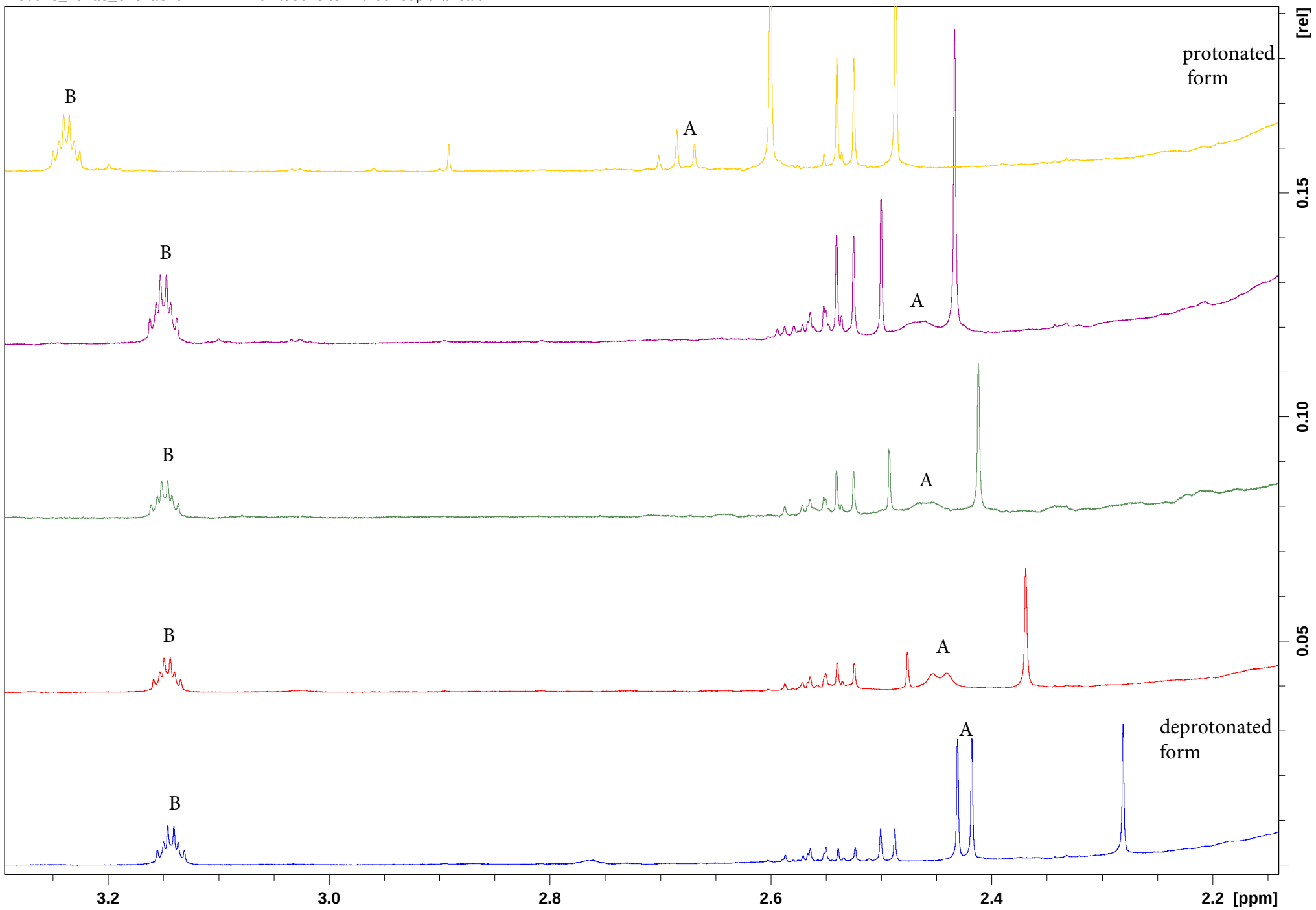
231018_Ppyrr3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR

A: $P(pyrr)_3$
B: 4-(Ph-N=N)-$C_6H_4P_1(pyrr)_3$
C: Ph-N=$P_1(dma)_3$



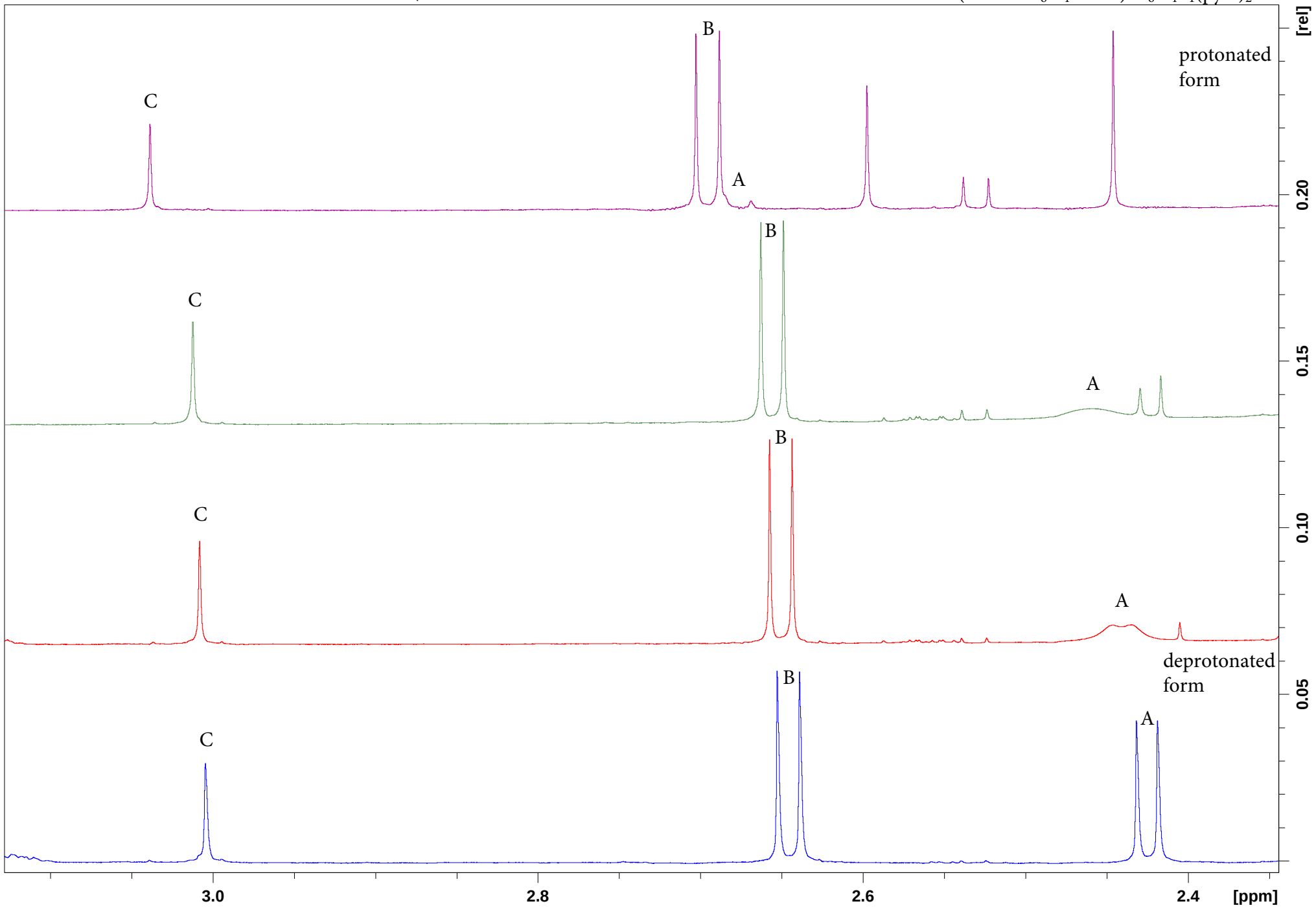

A: P(pyrr)3
B: 2-Cl-C6H4-N=P1(pyrr)3
C:[2,4,6-(MeO)3-C6H2]3P
231122_Ppyrr3_titration 2 1 C:\Users\STM\Desktop\Marta\NMR
protonated form
deprotonated form
C
B
A
0.30 [rel]
0.25
0.20
0.15
0.10
0.05
3.6
3.4
3.2
3.0
[ppm]

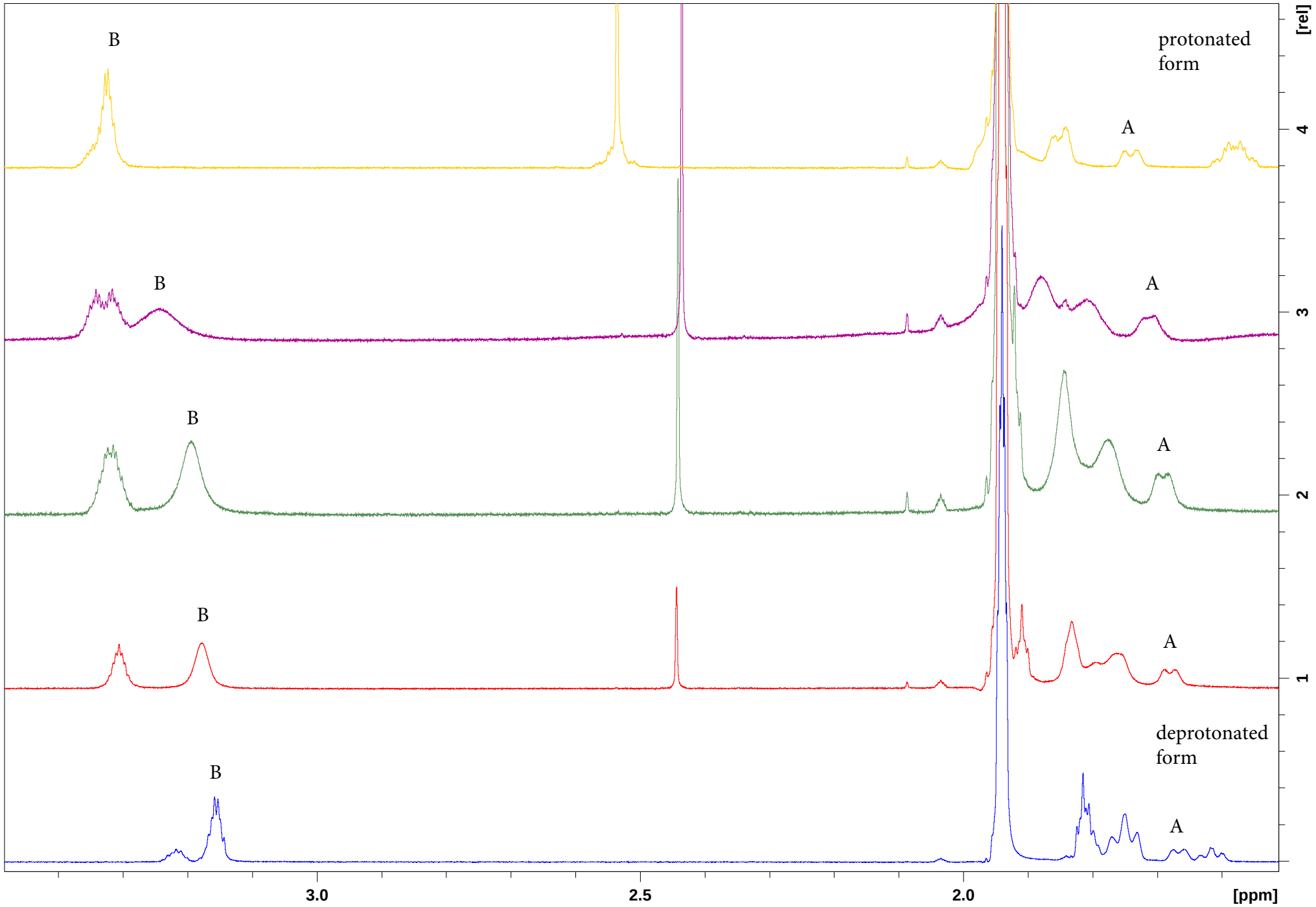

A: P(dma)3
B: 2-Cl-C6H4-N=P1(dma)
C: 2,6-Cl2-C6H3-N=P1(pyrr)
230922_Pdma3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR
protonated form
deprotonated form
[rel]
0.15
0.10
0.05
[ppm]
3.4
3.2
3.0
2.8
2.6
2.4
A
B
C

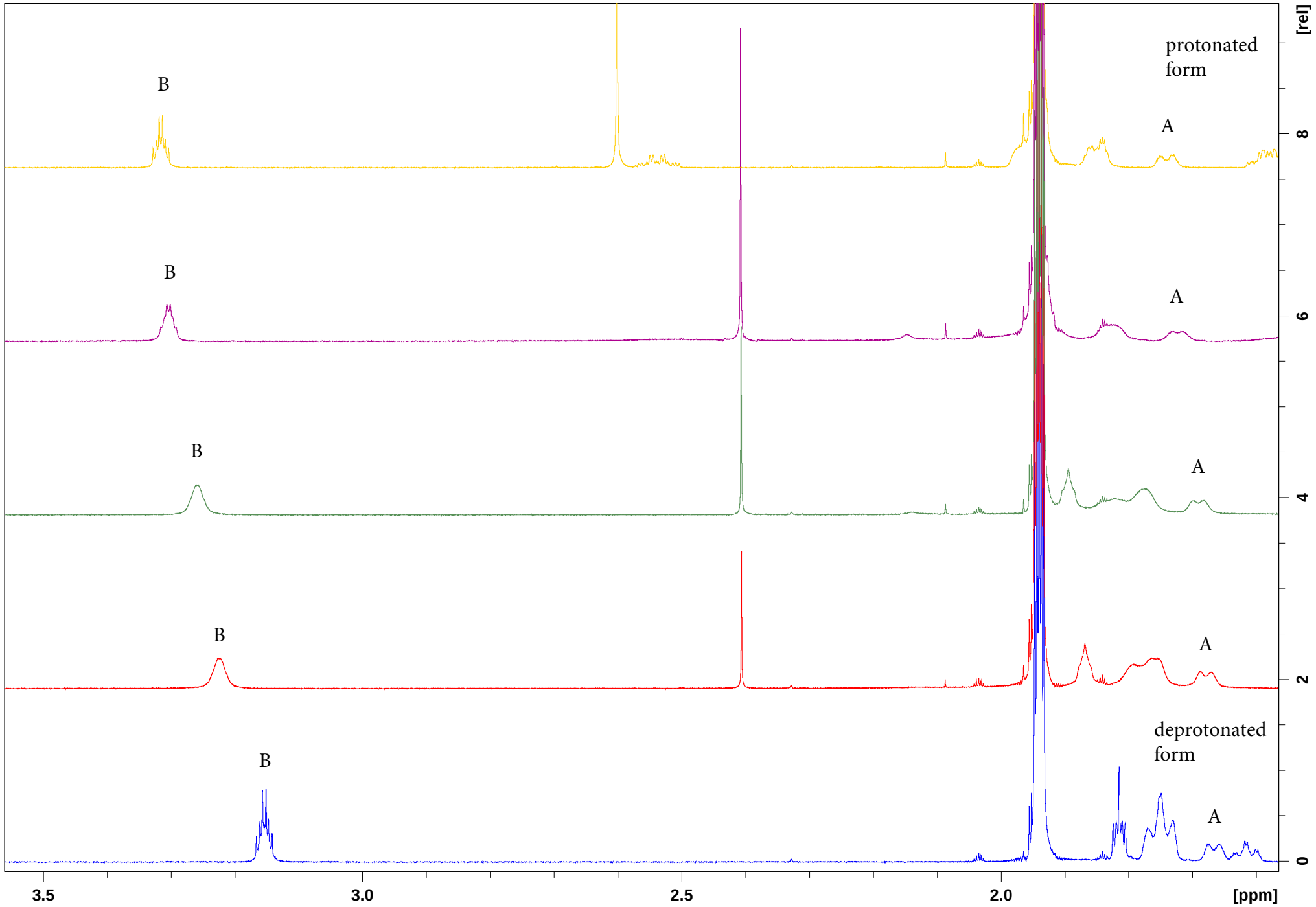

A: P(dma)3
B: 2,5-Cl2-PhP1(pyrr)
230925_Pdma3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR
protonated form
deprotonated form
B
A
[rel]
0.15
0.10
0.05
3.2
3.0
2.8
2.6
2.4
2.2 [ppm]

A: $P(dma)_3$
B: 2-Cl-C_6H_4-N=P_1(dma)
C: 4-(4-dma-C_6H_4-N=N)-$C_6H_4P_1(pyrr)_2Ph$

231215_Pdma3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR




A: PCy3
B: 2-NO2-4-CF3-C6H3-N=P1(pyrr)3
240221_PCy3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR
protonated form
deprotonated form
B
A
[rel]
4
3
2
1
3.0
2.5
2.0
[ppm]


A: PCy3
B: 2-NO2-5-Cl-C6H3-N=P1(pyrr)3
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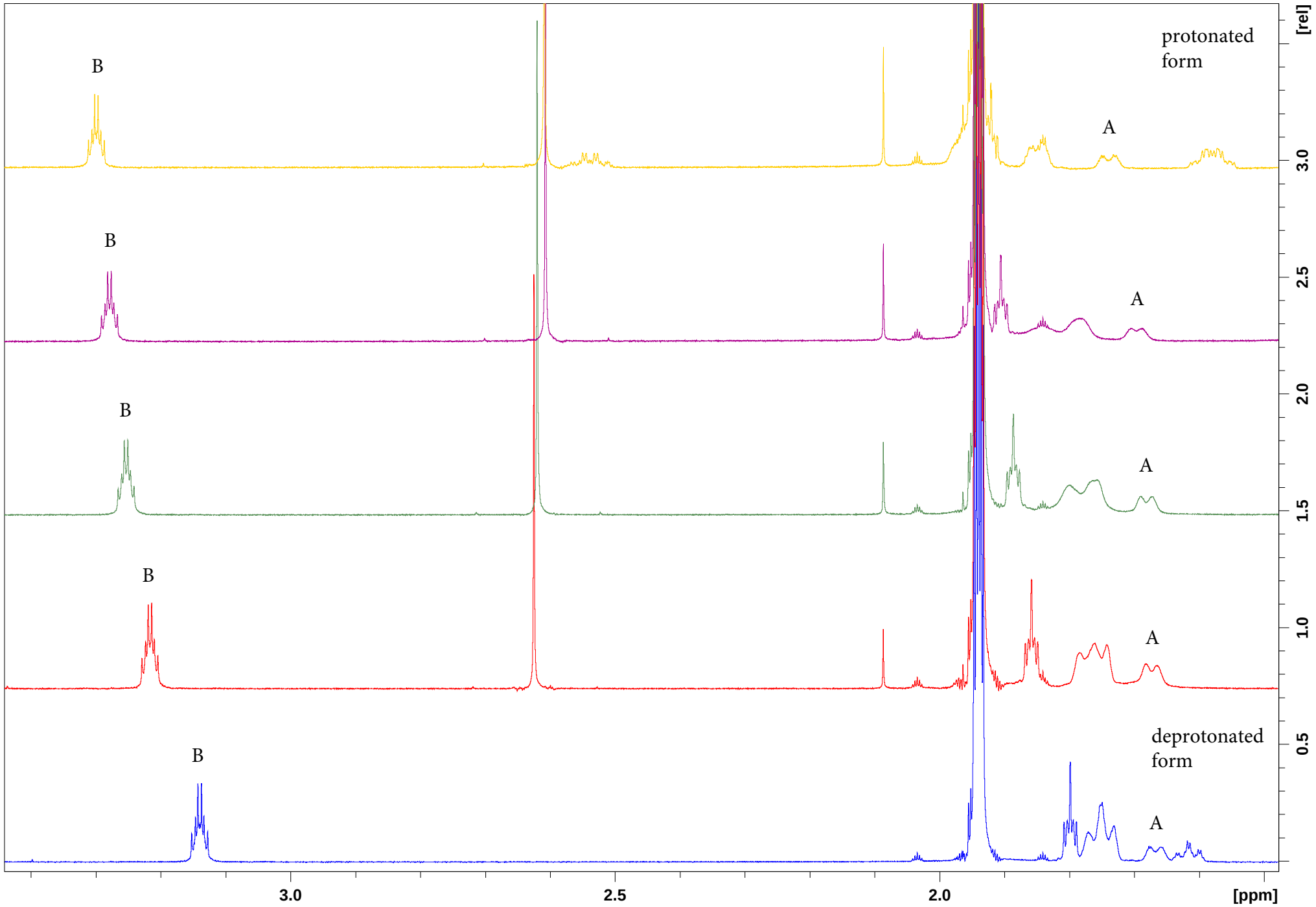
protonated form
deprotonated form
B
A
[rel]
8
6
4
2
0
3.5
3.0
2.5
2.0
[ppm]


A: PCy3
B: 2-NO2-4-Cl-C6H3-N=P1(pyrr)3
240229_PCy3_titration 1 1 C:\Users\STM\Desktop\Marta\NMR
protonated form
deprotonated form
B
A
[rel]
3.0
2.5
2.0
1.5
1.0
0.5
[ppm]

Computational methods

Proton Affinity (PA) and Gas-phase Basicity (GB) values in the gas phase

The geometries (.xyz files) for all the calculated species (both neutral and ionic forms) are available at DataDOI (https://doi.org/10.23673/re-461).[74]

No	Compound	Neutral/ Cation	SCF-Energy, AU	Enthalpy, AU	PA, kcal/mol	Chem. pot, AU	GB, kcal/mol
1	P(pyrr)3	Neutral Cation	-977.64583 -978.05552	0.36708 0.38010	250.4	0.29970 0.31405	241.8
2	[2,4,6-(MeO)3-C6H2]3P	Neutral Cation	-2067.79433 -2068.23621	0.58771 0.60047	270.8	0.46786 0.48301	261.5
3	P(dma)3	Neutral Cation	-745.29819 -745.69342	0.25675 0.26996	241.2	0.20059 0.21216	234.5
4	P(adamantyl)3	Neutral Cation	-1512.15264 -1512.56582	0.70624 0.71810	253.3	0.62949 0.64026	246.2
5	P(t-Bu)3	Neutral Cation	-815.09851 -815.49807	0.37662 0.38806	245.0	0.31543 0.32556	238.1
6	[2,6-(MeO)2-C6H3]3P	Neutral Cation	-1724.06200 -1724.49134	0.48564 0.49847	262.8	0.38527 0.39944	254.2
7	PCy3	Neutral Cation	-1047.47797 -1047.87868	0.48885 0.50008	245.9	0.41920 0.42699	240.3
8	[2,4,6-(MeO)3-C6H2]2PhP	Neutral Cation	-1724.07205 -1724.49745	0.48604 0.49837	260.7	0.38549 0.39835	252.6
9	P(i-Pr)3	Neutral Cation	-697.14408 -697.53537	0.29089 0.30220	239.9	0.23468 0.24456	233.1
10	PMe2Et	Neutral Cation	-500.52431 -500.90085	0.14617 0.15722	230.8	0.10521 0.11560	223.5
11	PMe3	Neutral Cation	-461.19924 -461.57260	0.11688 0.12797	228.8	0.07994 0.09055	221.4
12	P(i-Pr)2Me	Neutral Cation	-618.49898 -618.88426	0.23277 0.24405	236.2	0.18142 0.19235	228.6
13	PMeEt2	Neutral Cation	-539.84923 -540.22882	0.17549 0.18657	232.7	0.13095 0.14131	225.4
14	P(n-Pr)3	Neutral Cation	-697.15560 -697.54240	0.29145 0.30287	237.0	0.23109 0.24220	229.5
15	PEt3	Neutral Cation	-579.17393 -579.55611	0.20471 0.21592	234.3	0.15628 0.16702	226.8
16	P(n-Bu)3	Neutral Cation	-815.13709 -815.52617	0.37825 0.38969	238.4	0.30575 0.31830	230.0
17	P(t-Bu)2Ph	Neutral Cation	-888.94679 -889.34315	0.34465 0.35609	243.0	0.28125 0.29141	236.1
18	P(i-Bu)3	Neutral Cation	-815.13674 -815.52473	0.37680 0.38812	237.8	0.30769 0.31962	229.7
19	PCy2Ph	Neutral Cation	-1043.86228 -1044.25742	0.42023 0.43166	242.3	0.35220 0.36260	235.1
20	P(Mes)3	Neutral Cation	-1390.56884 -1390.97473	0.53758 0.54948	248.7	0.43855 0.45284	239.5
21	P(Np)3	Neutral Cation	-933.11173 -933.49981	0.46157 0.47260	238.1	0.38766 0.39709	231.3
22	PEt2Ph	Neutral Cation	-731.65712 -732.04087	0.23068 0.24171	235.4	0.17712 0.18720	228.2
23	P(n-Bu)2Ph	Neutral Cation	-888.96583 -889.35360	0.34662 0.35762	237.9	0.27838 0.28673	231.8
24	PMe2Ph	Neutral Cation	-653.00600 -653.38444	0.17210 0.18316	232.0	0.12509 0.13593	224.4
25	[2,4,6-(MeO)3-Ph]Ph2P	Neutral	-1380.34899	0.38420	248.9	0.30208	241.5

		Cation	-1380.75526	0.39621		0.31343	
26	P(t-Bu)Ph2	Neutral Cation	-962.78456 -963.17558	0.31369 0.32477	239.9	0.24934 0.25962	232.6
27	PCyPh2	Neutral Cation	-1040.24191 -1040.63113	0.35113 0.36252	238.6	0.28452 0.29512	231.3
28	PEtPh2	Neutral Cation	-884.13856 -884.52188	0.25655 0.26780	235.0	0.19733 0.20849	227.3
29	(4−MeO−C6H4)3P	Neutral Cation	-1380.35739 -1380.75909	0.38445 0.39584	246.4	0.30032 0.31042	239.5
30	PMePh2	Neutral Cation	-844.81368 -845.19523	0.22730 0.23848	233.9	0.17148 0.18201	226.5
31	(2-MeO-C6H4)3P	Neutral Cation	-1380.35295 -1380.75976	0.38429 0.39625	249.2	0.30282 0.31490	241.4
32	P(Bn)3	Neutral Cation	-1154.61220 -1154.99808	0.36807 0.37927	236.6	0.29265 0.30342	229.1
33	(4-Me-C6H4)3P	Neutral Cation	-1154.61556 -1155.00905	0.36768 0.37872	241.5	0.28833 0.29771	234.8
34	(2-Me-C6H4)3P	Neutral Cation	-1154.61170 -1155.00046	0.36756 0.37899	238.3	0.29380 0.30489	230.7
35	PPh3	Neutral Cation	-1036.62153 -1037.00600	0.28251 0.29369	235.7	0.21777 0.22801	228.6
36	1-NaphtPh2P	Neutral Cation	-1190.32184 -1190.70922	0.33061 0.34183	237.5	0.26049 0.27141	230.0
37	(3-MeO-C6H4)3P	Neutral Cation	-1380.35698 -1380.75028	0.38426 0.39549	241.2	0.30099 0.31037	234.6
38	[3,5-(MeO)2-C6H3]3P	Neutral Cation	-1724.09080 -1724.49103	0.48615 0.49723	245.7	0.38300 0.39410	237.9
39	(4-F-C6H4)3P	Neutral Cation	-1334.49046 -1334.86660	0.26108 0.27202	230.6	0.19066 0.19979	224.0
40	(1-Napht)3P	Neutral Cation	-1497.72251 -1498.11473	0.43467 0.42326	232.3	0.34001 0.35210	254.8
41	(2-F-C6H4)Ph2P	Neutral Cation	-1135.91074 -1136.29281	0.27541 0.28649	234.3	0.20940 0.21894	227.5
42	(2,6-F2-C6H3)Ph2P	Neutral Cation	-1235.19462 -1235.57667	0.26819 0.27962	234.0	0.19999 0.21146	226.3
43	(4-Cl-C6H4)3P	Neutral Cation	-2415.62482 -2415.99918	0.25829 0.26892	229.7	0.18344 0.19194	223.3
44	PPh2H	Neutral Cation	-805.47926 -805.84585	0.19758 0.20866	224.6	0.14469 0.15592	216.7
45	(2-F-C6H4)2PhP	Neutral Cation	-1235.19969 -1235.57953	0.26830 0.27945	232.8	0.20037 0.21116	225.3
46	(2-F-C6H4)3P	Neutral Cation	-1334.48825 -1334.86606	0.26112 0.27235	231.5	0.19163 0.20225	224.1
47	(C6F5)Ph2P	Neutral Cation	-1533.03064 -1533.40197	0.24737 0.25863	227.4	0.17286 0.18378	219.9
48	(2,6-F2-C6H3)2PhP	Neutral Cation	-1433.76794 -1434.14575	0.25385 0.26516	231.5	0.18287 0.19231	224.9
49	(2,6−Cl2−C6H3)3P	Neutral Cation	-3794.58897 -3794.96994	0.23304 0.24417	233.6	0.15186 0.16343	225.5
50	(2,6-F2-C6H3)3P	Neutral Cation	-1632.34173 -1632.71590	0.23955 0.25094	229.1	0.16478 0.17511	222.0
51	P[CH2CH(CF3)2]3	Neutral Cation	-2602.42079 -2602.76305	0.25348 0.26424	209.5	0.15325 0.16382	201.9
52	PPh2Cl	Neutral Cation	-1265.17634 -1265.53726	0.19182 0.20283	221.1	0.13516 0.14738	212.5
53	P(C6F5)2Ph	Neutral Cation	-2029.43871 -2029.79556	0.21208 0.22329	218.4	0.12743 0.13789	211.1
54	P[3,5-(CF3)2Ph]3	Neutral Cation [a]	-3059.89105 -3060.23299	0.32980 0.33928	210.1	0.20752 0.21993	200.5
55	P(CH2CF3)3	Neutral Cation	-1472.83350 -1473.16349	0.14269 0.15318	202.0	0.07782 0.08763	194.6
56	P(C6F5)3	Neutral Cation	-2525.84636 -2526.18925	0.17688 0.18816	209.6	0.08164 0.09294	201.8

[a] imaginary frequency of –5 cm^{-1} remained

HOMO-LUMO energies

No	Compound	gas phase (BP86/def2-TZVP)				gas phase SP (MP2/def2-TZVPP)				cosmo (BP86/def-TZVP)			
		HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
		neutral		cation		neutral		cation		neutral		cation	
1	P(pyrr)3	-0.1662	0.0017	-0.3378	-0.1384	-0.3100	0.1274	-0.5024	-0.0015	-0.1686	-0.0026	-0.2094	-0.0175
2	[2,4,6-(MeO)3-C6H2]3P	-0.1429	-0.0256	-0.2858	-0.1477	-0.2443	0.1301	-0.4007	0.0189	-0.1633	-0.0394	-0.2046	-0.0646
3	P(dma)3	-0.1701	0.0056	-0.3573	-0.1523	-0.3143	0.1262	-0.5208	-0.0118	-0.1729	-0.0008	-0.2160	-0.0128
4	P(adamantyl)3	-0.1734	-0.0093	-0.3496	-0.1624	-0.2970	0.1138	-0.4965	0.0003	-0.1796	-0.0047	-0.2438	-0.0492
5	P(t-Bu)3	-0.1804	0.0088	-0.4177	-0.1798	-0.3058	0.1332	-0.5673	-0.0116	-0.1845	0.0131	-0.2875	-0.0459
6	[2,6-(MeO)2-C6H3]3P	-0.1551	-0.0414	-0.3014	-0.1703	-0.2553	0.1217	-0.4129	-0.0059	-0.1723	-0.0507	-0.2093	-0.0772
7	PCy3	-0.1824	0.0059	-0.3820	-0.1554	-0.3103	0.1279	-0.5369	0.0009	-0.1904	0.0034	-0.2660	-0.0247
8	[2,4,6-(MeO)3-C6H2]2PhP	-0.1568	-0.0375	-0.3003	-0.1702	-0.2596	0.1275	-0.4178	-0.0054	-0.1748	-0.0523	-0.2102	-0.0795
9	P(i-Pr)3	-0.1864	0.0038	-0.4317	-0.1708	-0.3149	0.1336	-0.5899	-0.0138	-0.1916	0.0063	-0.2937	-0.0248
10	PMe2Et	-0.1950	0.0093	-0.4766	-0.1794	-0.3274	0.1362	-0.6438	-0.0351	-0.1999	0.0110	-0.3166	-0.0067
11	PMe3	-0.1961	0.0166	-0.5214	-0.1850	-0.3294	0.1346	-0.6886	-0.0424	-0.2006	0.0181	-0.3460	-0.0054
12	P(i-Pr)2Me	-0.1905	0.0064	-0.4434	-0.1711	-0.3207	0.1322	-0.6009	-0.0216	-0.1959	0.0087	-0.2985	-0.0156
13	PMeEt2	-0.1941	0.0079	-0.4649	-0.1744	-0.3255	0.1359	-0.6288	-0.0286	-0.1993	0.0086	-0.3096	-0.0123
14	P(n-Pr)3	-0.1928	0.0076	-0.4337	-0.1612	-0.3232	0.1374	-0.6002	-0.0126	-0.1987	0.0083	-0.2997	-0.0130
15	PEt3	-0.1934	0.0072	-0.4598	-0.1738	-0.3239	0.1416	-0.6238	-0.0262	-0.1988	0.0081	-0.3093	-0.0131
16	P(n-Bu)3	-0.1922	0.0097	-0.4073	-0.1613	-0.3225	0.1365	-0.5715	-0.0133	-0.1986	0.0099	-0.2881	-0.0125
17	P(t-Bu)2Ph	-0.1879	-0.0595	-0.3733	-0.2067	-0.3153	0.1058	-0.4732	-0.0411	-0.1936	-0.0591	-0.2544	-0.0846
18	P(i-Bu)3	-0.1912	0.0032	-0.4211	-0.1538	-0.3199	0.1342	-0.5860	-0.0100	-0.1912	0.0078	-0.2927	-0.0226
19	PCy2Ph	-0.1904	-0.0567	-0.3705	-0.2047	-0.3129	0.1067	-0.4713	-0.0406	-0.1977	-0.0577	-0.2548	-0.0856
20	PMes3	-0.1693	-0.0581	-0.3338	-0.1863	-0.2631	0.1022	-0.4348	-0.0247	-0.1751	-0.0593	-0.2357	-0.0857
21	P(Np)3	-0.1898	0.0022	-0.4106	-0.1576	-0.3165	0.1256	-0.5703	-0.0019	-0.1888	0.0071	-0.2904	-0.0254
22	PEt2Ph	-0.1985	-0.0604	-0.3822	-0.2190	-0.3322	0.1038	-0.4815	-0.0537	-0.2049	-0.0598	-0.2551	-0.0861
23	P(n-Bu)2Ph	-0.1978	-0.0598	-0.3770	-0.2125	-0.3315	0.1048	-0.4772	-0.0476	-0.2048	-0.0596	-0.2550	-0.0859
24	PMe2Ph	-0.1951	-0.0534	-0.3867	-0.2242	-0.3084	0.1090	-0.4856	-0.0587	-0.1997	-0.0547	-0.2544	-0.0839
25	[2,4,6-(MeO)3-Ph]Ph2P	-0.1751	-0.0506	-0.3165	-0.1935	-0.2777	0.1116	-0.4358	-0.0308	-0.1904	-0.0599	-0.2167	-0.0910
26	P(t-Bu)Ph2	-0.1920	-0.0664	-0.3700	-0.2142	-0.3061	0.0956	-0.4694	-0.0526	-0.2001	-0.0670	-0.2546	-0.0956
27	PCyPh2	-0.1960	-0.0632	-0.3677	-0.2098	-0.3084	0.0993	-0.4675	-0.0477	-0.2054	-0.0660	-0.2533	-0.0914

28	PEtPh2	-0.1958	-0.0626	-0.3738	-0.2182	-0.3058	0.1000	-0.4723	-0.0566	-0.2019	-0.0628	-0.2537	-0.0898
29	(4−MeO−C6H4)3P	-0.1762	-0.0535	-0.3189	-0.1854	-0.2802	0.1038	-0.4308	-0.0308	-0.1886	-0.0605	-0.2199	-0.0838
30	PMePh2	-0.1958	-0.0617	-0.3752	-0.2191	-0.3039	0.1016	-0.4735	-0.0567	-0.2032	-0.0629	-0.2536	-0.0888
31	(2-MeO-C6H4)3P	-0.1750	-0.0515	-0.3229	-0.1866	-0.2772	0.1111	-0.4322	-0.0227	-0.1919	-0.0616	-0.2224	-0.0850
32	P(Bn)3	-0.2039	-0.0520	-0.3430	-0.1824	-0.3146	0.1124	-0.4417	-0.0155	-0.2088	-0.0549	-0.2378	-0.0740
33	(4-Me-C6H4)3P	-0.1864	-0.0572	-0.3472	-0.1974	-0.2875	0.1048	-0.4473	-0.0384	-0.1974	-0.0620	-0.2418	-0.0888
34	(2-Me-C6H4)3P	-0.1893	-0.0619	-0.3537	-0.2018	-0.2916	0.1002	-0.4528	-0.0391	-0.1952	-0.0630	-0.2460	-0.0922
35	Ph3P	-0.1944	-0.0639	-0.3675	-0.2099	-0.2982	0.0990	-0.4662	-0.0498	-0.2034	-0.0663	-0.2545	-0.0916
36	1-NaphtPh2P	-0.1910	-0.0830	-0.3283	-0.2153	-0.2828	0.0735	-0.4135	-0.0598	-0.1994	-0.0873	-0.2256	-0.1082
37	(3-MeO-C6H4)3P	-0.1883	-0.0624	-0.3160	-0.1945	-0.2943	0.0956	-0.4264	-0.0389	-0.1999	-0.0663	-0.2202	-0.0907
38	[3,5-(MeO)2-C6H3]3P	-0.1831	-0.0511	-0.2956	-0.1774	-0.2955	0.1053	-0.4078	-0.0243	-0.1990	-0.0628	-0.2136	-0.0885
39	(4-F-C6H4)3P	-0.2021	-0.0739	-0.3652	-0.2165	-0.3111	0.0827	-0.4766	-0.0610	-0.2051	-0.0699	-0.2509	-0.0941
40	(1-Napht)3P	-0.2950	-0.0821	-0.5337	-0.2833	-0.4648	0.0859	-0.7467	-0.1052	-0.2923	-0.0804	-0.3868	-0.1287
41	(2-F-C6H4)Ph2P	-0.1973	-0.0676	-0.3633	-0.2118	-0.3024	0.0943	-0.4671	-0.0499	-0.2067	-0.0695	-0.2518	-0.0958
42	(2,6-F2-C6H3)Ph2P	-0.1964	-0.0769	-0.3642	-0.2226	-0.3012	0.0845	-0.4663	-0.0625	-0.2054	-0.0772	-0.2529	-0.1069
43	(4-Cl-C6H4)3P	-0.2055	-0.0792	-0.3532	-0.2176	-0.3112	0.0803	-0.4634	-0.0629	-0.2075	-0.0745	-0.2482	-0.1002
44	PPh2H	-0.2068	-0.0643	-0.3821	-0.2297	-0.3134	0.0982	-0.4799	-0.0666	-0.2159	-0.0673	-0.2545	-0.0916
45	(2-F-C6H4)2PhP	-0.2000	-0.0698	-0.3634	-0.2135	-0.3066	0.0912	-0.4700	-0.0512	-0.2095	-0.0720	-0.2530	-0.0982
46	(2-F-C6H4)3P	-0.2020	-0.0723	-0.3655	-0.2149	-0.3091	0.0896	-0.4742	-0.0520	-0.2121	-0.0741	-0.2544	-0.1006
47	(C6F5)Ph2P	-0.2069	-0.0858	-0.3648	-0.2316	-0.3145	0.0715	-0.4760	-0.0774	-0.2104	-0.0851	-0.2566	-0.1146
48	(2,6-F2-C6H3)2PhP	-0.2044	-0.0768	-0.3621	-0.2230	-0.3129	0.0852	-0.4681	-0.0629	-0.2105	-0.0807	-0.2529	-0.1101
49	(2,6−Cl2−C6H3)3P	-0.1987	-0.0868	-0.3511	-0.2210	-0.3054	0.0728	-0.4603	-0.0619	-0.2077	-0.0893	-0.2506	-0.1173
50	(2,6-F2-C6H3)3P	-0.2068	-0.0795	-0.3628	-0.2226	-0.3177	0.0830	-0.4782	-0.0615	-0.2173	-0.0819	-0.2555	-0.1123
51	P(CH2CH(CF3)2)3	-0.2412	-0.0363	-0.4706	-0.2105	-0.3843	0.1239	-0.6756	-0.0422	-0.2355	-0.0315	-0.3597	-0.0596
52	PPh2Cl	-0.2129	-0.0870	-0.3835	-0.2494	-0.3241	0.0781	-0.4819	-0.0833	-0.2215	-0.0987	-0.2597	-0.1259
53	P(C6F5)2Ph	-0.2249	-0.0952	-0.3691	-0.2401	-0.3415	0.0597	-0.4874	-0.0916	-0.2217	-0.0929	-0.2585	-0.1236
54	P((3,5-CF3)2C6H3)3	-0.2433	-0.1201	-0.4065	-0.2502	-0.3569	0.0329	-0.5219	-0.0978	-0.2321	-0.1080	-0.2888	-0.1264
55	P(CH2CF3)3	-0.2514	-0.0357	-0.5061	-0.2214	-0.3957	0.1132	-0.7191	-0.0565	-0.2431	-0.0246	-0.3668	-0.0604
56	P(C6F5)3	-0.2358	-0.1067	-0.3762	-0.2474	-0.3636	0.0444	-0.5154	-0.1012	-0.2342	-0.0994	-0.2630	-0.1311

Calculations with COSMOthermX

To calculate pK_{aH}(MeCN) values for bases with COSMOthermX program:

1. Make sure "TZVPD-FINE" has been chosen under "Level" and select your compounds from files under "Load compounds" (Figure S1)
2. All conformers have to be composed into a conformer set; if the names of the files are uniform, e.g. "compound_c0", "compound_c1", "compound_H_c0", and "compound_H_c1", then the program will do that itself and formed conformer sets will look like in Figure S1

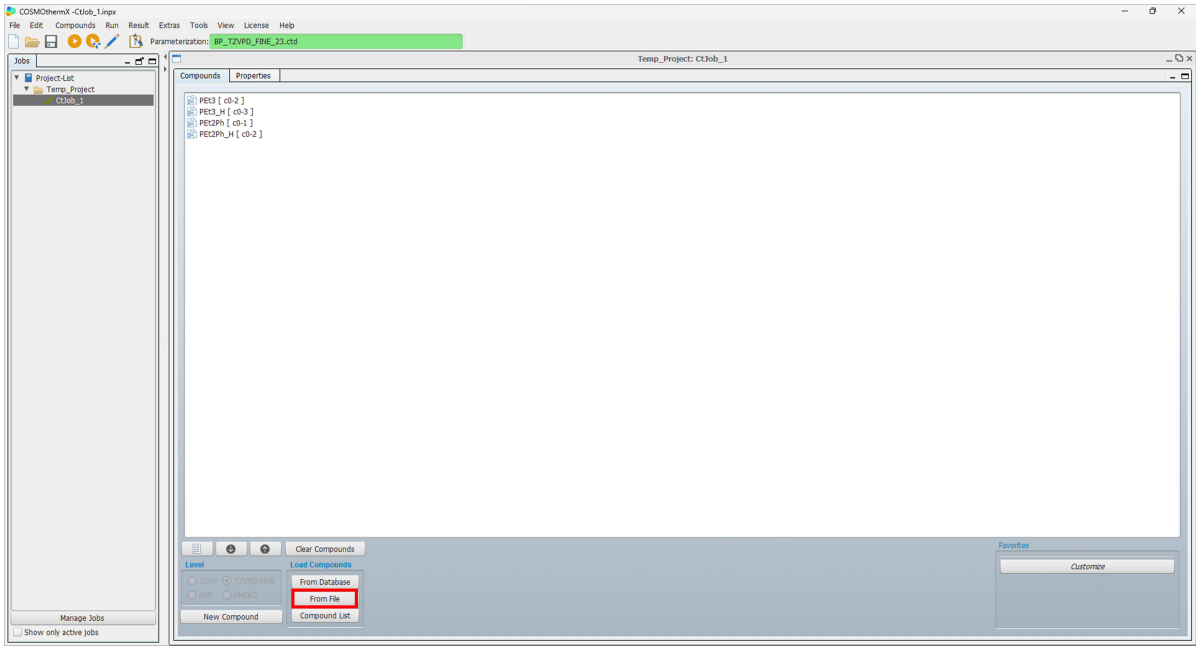


Figure S1. Choose the compounds from files.

3. Select "pKa" under "Properties" tab
4. Choose the job type
5. Select the neutral and ionic forms of a compound and click "Add"; this has to be done for all the compounds in the list (Figure S2)
6. In order to change the parameterization, click on the current parameterization and choose an alternative one under "OLDPARAM" (Figure S3)
7. Click "Run Job (local)"

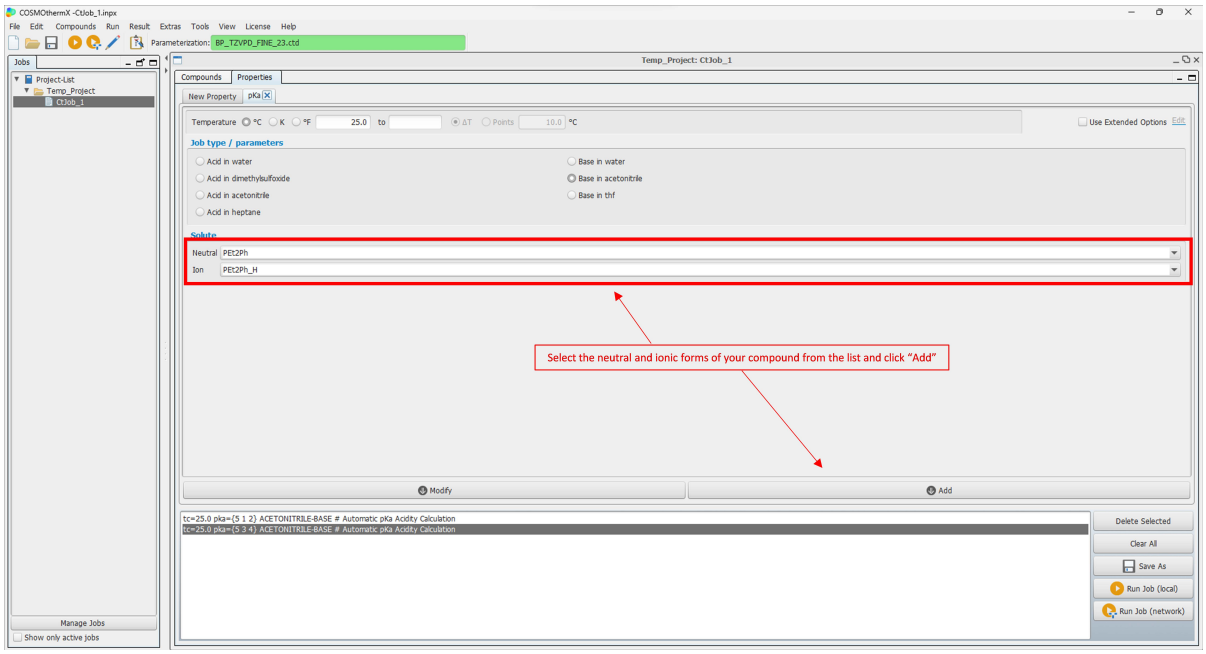


Figure S2. Choose the neutral and ionic form.

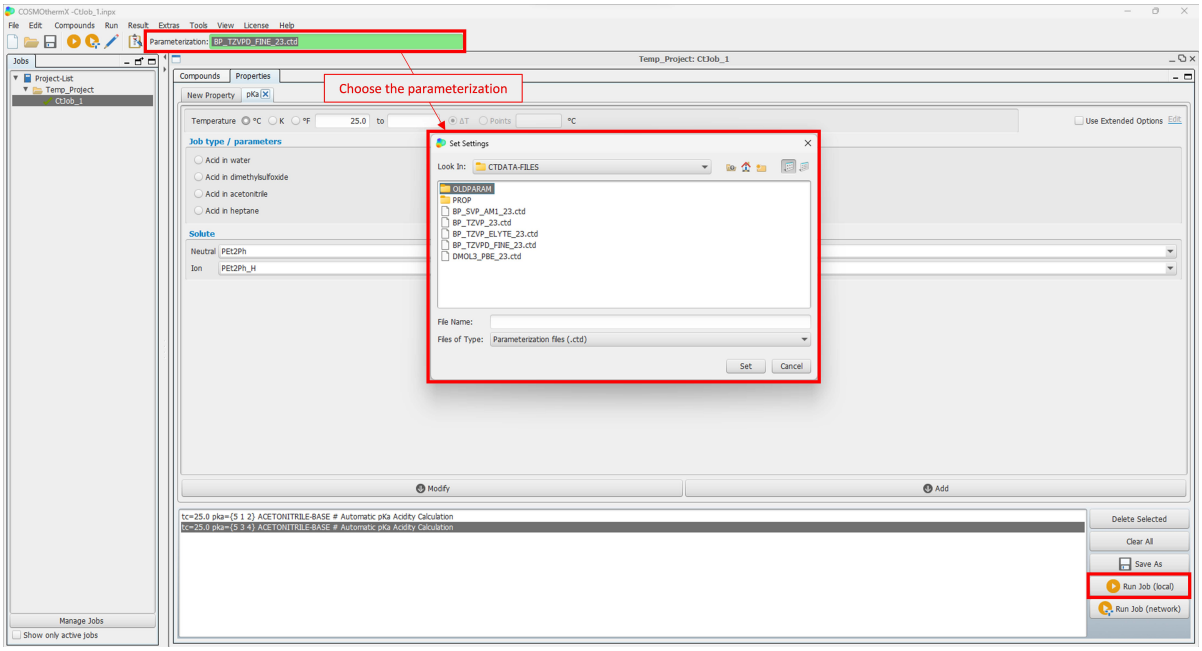


Figure S3. Choose the parameterisation.

8. Calculated pK_{aH} values will appear under ".tab file"; click on the tabs in the bottom row in order to toggle between compounds (Figure S4)

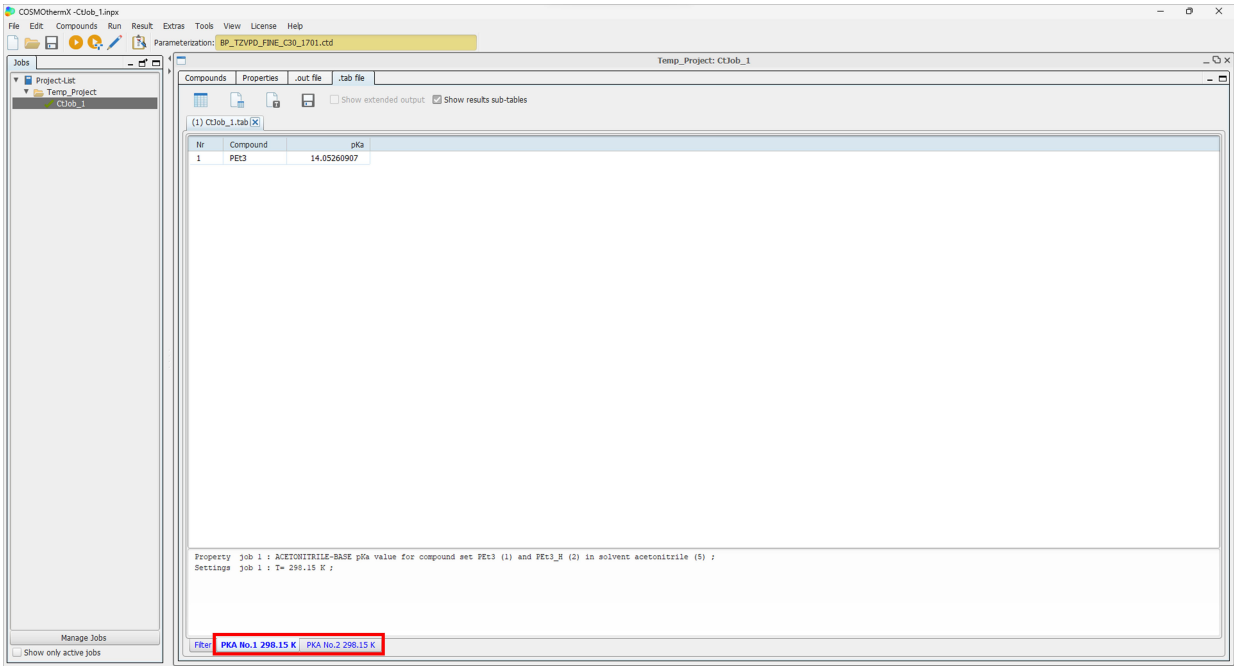


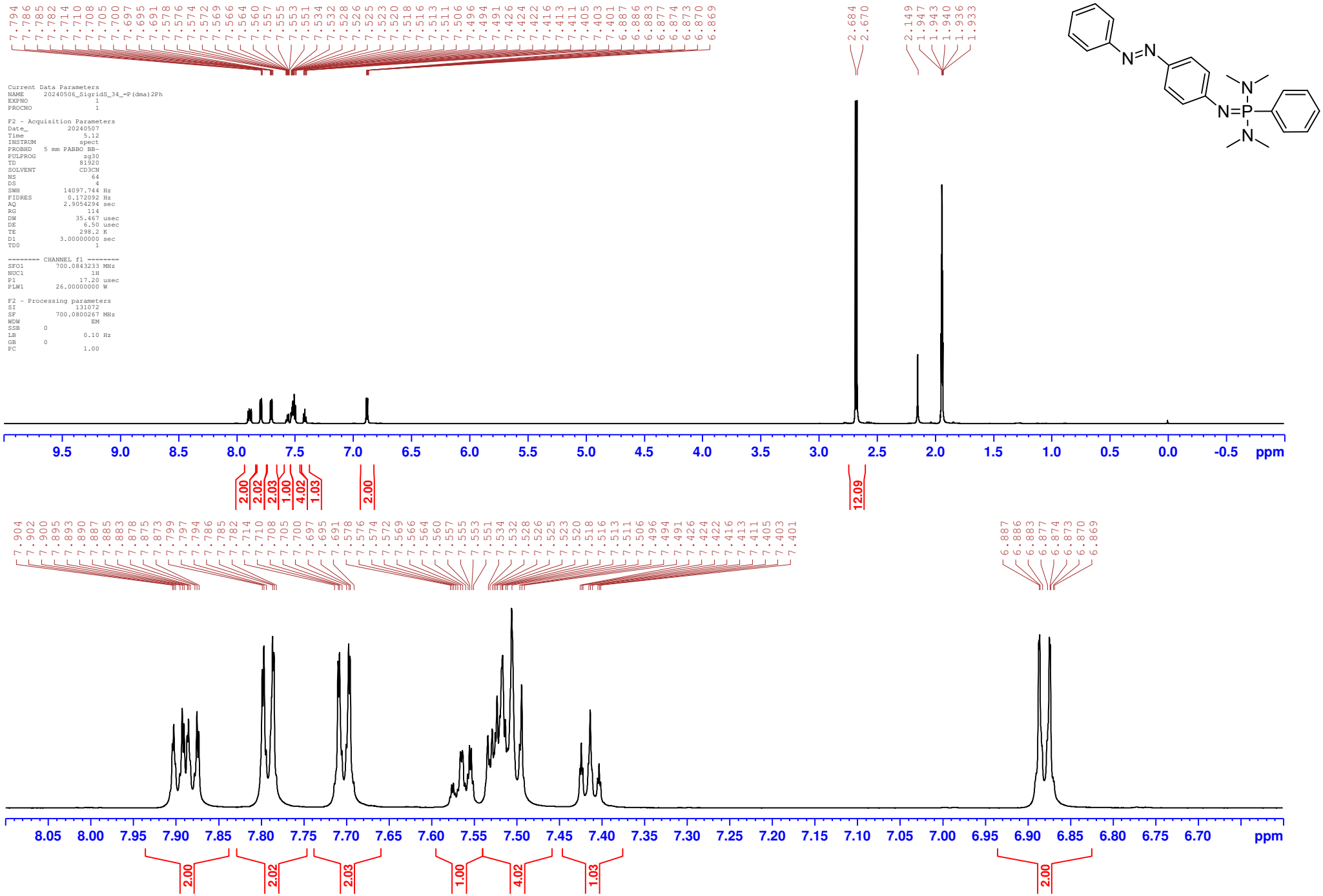
Figure S4. Results for different compounds.

4-(Ph-N=N)-C_6H_4-N=P1(dma)$_2$Ph

A solution of 4-azidoazobenzene (0.45 g, 2 mmol) in dry toluene (5 mL) was added drop-wise to a stirred solution of P(dma)$_2$Ph (0.39 g, 2 mmol) in dry toluene (5 mL) at 0-4 °C under argon atmosphere. The reaction mixture was stirred at 0-4 °C for 1 h and for 4 h at room temperature. After the completion of reaction, the reaction mixture was concentrated under reduced pressure to get the oily product. The crude compound was dissolved in ethylamine (10 mL), and 2 mL of distilled water was added. Crystals formed, and to obtain the pure compound (0.50 g, 1.28 mmol, 64%), the crystals were filtered and washed with a mixture of ethylamine and water.

Data for **4-(Ph-N=N)-C_6H_4-N=P1(dma)$_2$Ph**: 64%, ^{1}H NMR (700.1 MHz, CD_3CN, 25 °C): δ = 7.87-7.90 (m, 2H), 7.78-7.80 (m, 2H), 7.69-7.71 (m, 2H), 7.55-7.58 (m, 1H), 7.49-7.53 (m, 4H), 7.40-7.43 (m, 1H), 6.87-6.89 (m, 2H), 2.67-2.68 (m, 12H) ppm. ^{13}C{^{1}H} NMR (176.0 MHz, CD_3CN, 25 °C): δ = 157.8, 154.2, 145.2, 133.3 (d, J_{CP}=8.52 Hz), 132.4 (d, J_{CP}=2.78 Hz), 130.9, 130.4, 130.1, 129.4 (d, J_{CP}=13.17 Hz), 125.4 (d, J_{CP}=2.64 Hz), 124.2 (d, J_{CP}=18.28 Hz), 122.8, 37.6 (d, J_{CP}=3.18 Hz) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, CD_3CN, 25 °C): δ = 21.08 ppm. HRMS (ESI) m/z calcd for $C_{22}H_{26}N_5P$+H: 392.1999 [M + H]$^+$; found: 392.1990.

^{1}H CD_3CN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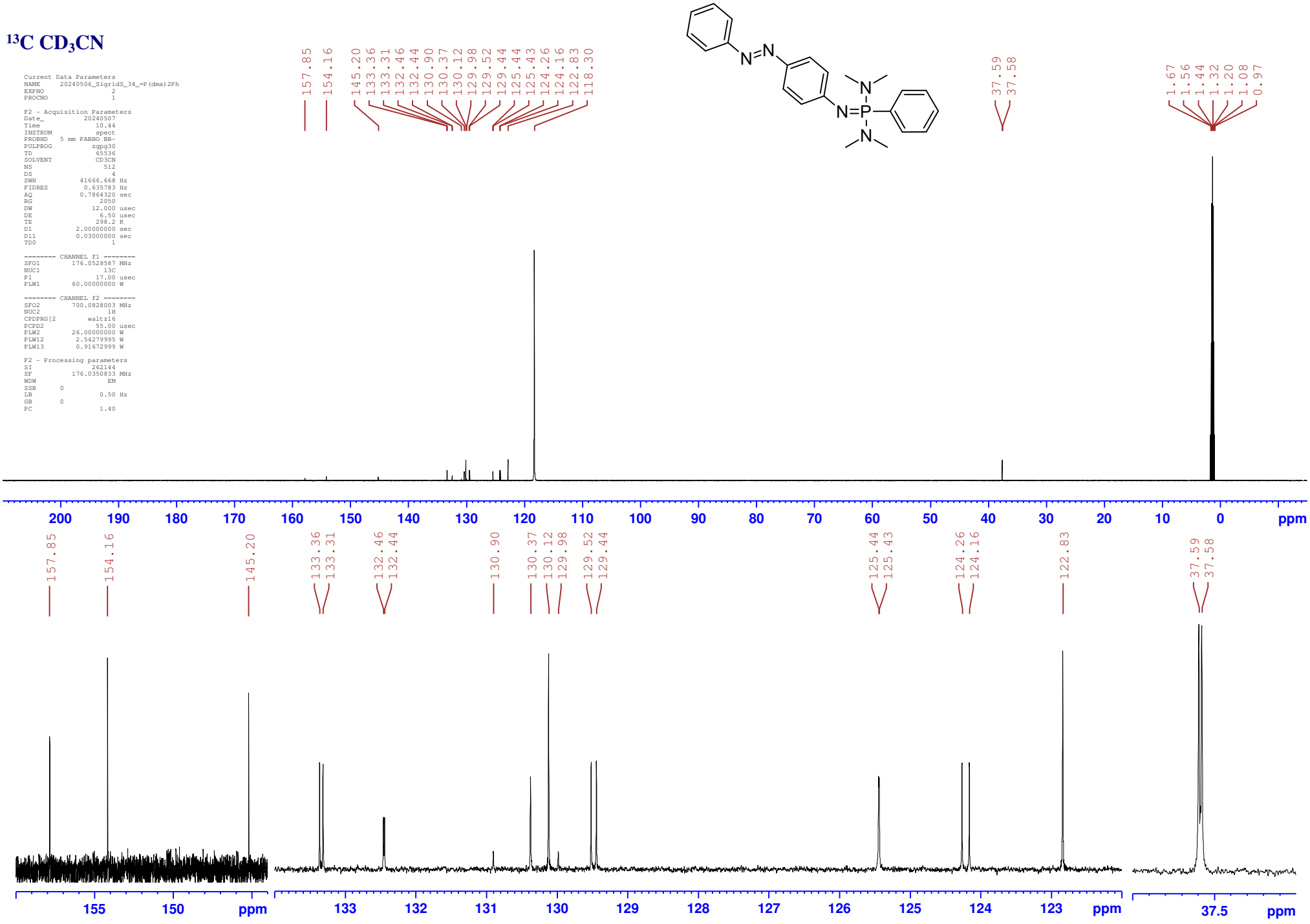
2.684 2.670
2.149 1.947 1.943 1.940 1.936 1.933
Current Data Parameters
NAME 20240506_SigridS_34_-P(dma)2Ph
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20240507
Time 5.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 81920
SOLVENT CD3CN
NS 64
DS 4
SWH 14097.744 Hz
FIDRES 0.172092 Hz
AQ 2.9054294 sec
RG 114
DW 35.467 usec
DE 6.50 usec
TE 298.2 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 700.0843233 MHz
NUC1 1H
P1 17.20 usec
PLW1 26.00000000 W
F2 - Processing parameters
SI 131072
SF 700.0800267 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
N=N
N=P
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.00 2.02 2.03 1.00 4.02 1.03 2.00
12.09
7.904 7.902 7.900 7.895 7.893 7.890 7.887 7.885 7.883 7.878 7.875 7.873 7.799 7.797 7.794 7.786 7.785 7.782 7.714 7.710 7.708 7.705 7.700 7.697 7.695 7.691 7.578 7.576 7.574 7.572 7.569 7.566 7.564 7.560 7.557 7.555 7.553 7.551 7.534 7.532 7.528 7.526 7.525 7.523 7.520 7.518 7.516 7.513 7.511 7.506 7.496 7.494 7.491 7.426 7.424 7.422 7.416 7.413 7.411 7.405 7.403 7.401
6.887 6.886 6.883 6.877 6.874 6.873 6.870 6.869
8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 ppm
2.00 2.02 2.03 1.00 4.02 1.03 2.00

^{13}C CD_3CN

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PROCNO                1

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Time              10.44
INSTRUM           spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  512
DS                    4
SWH           41666.668 Hz
FIDRES            0.635783 Hz
AQ            0.7864320 sec
RG                 2050
DW                12.000 usec
DE                 6.50 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         176.0528587 MHz
NUC1                13C
P1                 17.00 usec
PLW1         60.00000000 W

======== CHANNEL f2 ========
SFO2         700.0828003 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2              55.00 usec
PLW2         26.00000000 W
PLW12         2.54279995 W
PLW13         0.91672999 W

F2 - Processing parameters
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WDW                  EM
SSB       0
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GB        0
PC                 1.40
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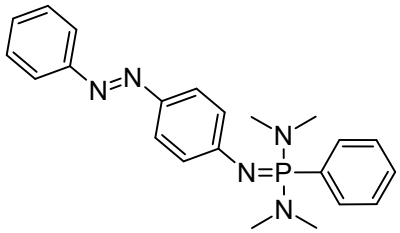
^{31}P CD_3CN

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EXPNO                  4
PROCNO                 1

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INSTRUM           spect
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PULPROG         zgpg30
TD                8500
SOLVENT           CD3CN
NS                 256
DS                   4
SWH           17006.803 Hz
FIDRES         2.000800 Hz
AQ             0.2499000 sec
RG                2050
DW               29.400 usec
DE                6.50 usec
TE               298.1 K
D1            0.25000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        283.4046639 MHz
NUC1               31P
P1                26.92 usec
PLW1        43.00000000 W

======== CHANNEL f2 ========
SFO2        700.0828003 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             55.00 usec
PLW2        26.00000000 W
PLW12        2.54279995 W
PLW13        0.91672999 W

F2 - Processing parameters
SI               131072
SF          283.3975723 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC        0
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