Phosphitylation and 31P NMR Analysis
Chemical shifts (δ ppm) of model compounds Relevant to Lignin/Pyrolysis Oils/Coal Related Aliphatic/Phenoxy/Carboxylic Acids

TMDP (2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane) is a very powerful reagent for tagging hydroxyl groups as the 31P–NMR active phosphite derivative (Figure 1). TMDP derivatization/31P–NMR spectroscopy has been effectively applied to analyze lignin, coal, biodiesel, and pyrolysis compounds.

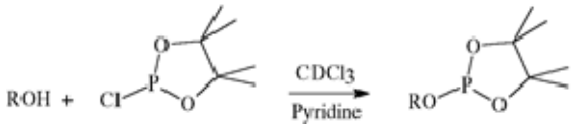


Figure 1. Phosphitylation of a hydroxyl group by TMDP.

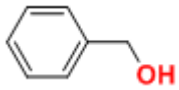
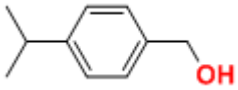
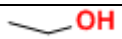
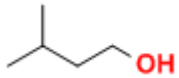
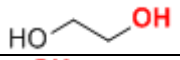
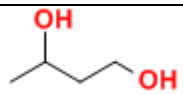
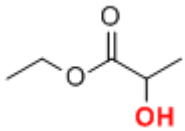
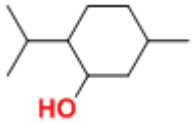
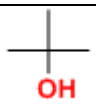
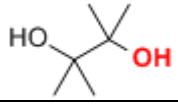
The chemical shift analysis is dependent on a data-base of model chemical shift studies. This artilces concisely summarizes these model compound studies.

Working with TMDP as derivatizing agent and using $CDCl_3$ as pure solvent Wroblewski et al in 1988 *(Wroblewski AE, Lensink C, Markuszewski R, Verkade JG. ^{31}P NMR Spectroscopic Analysis of Coal Pyrolysis Condensates and Extracts for Heteroatom Functionalities Possessing Labile Hydrogen. Energy Fuels 2, 765-774, 1988)*[26] measured the chemical shifts of different model compounds.
Jiang et al *(Jiang Z-H, Argyropoulos DS, Granata A, Correlation Analysis of 31P-NMR Chemical Shifts with Substituent Effects of Phenols, Magnetic Resonance in Chemistry 33, 375-382, 1995)*[27] used TMDP as derivatizing agent and pyridine:CDCl3 (1.6:1) as solvent, hence their results can be used directly. **Reference 27 is assigned as upper case 2 in the tables.**

The tables are separated into alcohols (148.93-141.33 ppm, **red**), phenols including model compounds[27] (143.73-137.83 ppm, **black**) and acids (136.18-134.63, **blue**). If a compound contains multiple of these functional groups then it can be found under the category according to the following priority: acids>phenols>alcohols. Under each category the molecules are ranked by their chemical shifts when derivatized with TMDP.

Comparing the chemical shifts of 15 compounds plus TMDP-anhydride that appeared in both references[26-27] showed that on average when using **only $CDCl_3$[26] as solvent the chemical shifts will show 0.64 ppm higher compared to the pyridinated[27] solvent with a 1.19% standard deviation**.

31P NMR Analysis of Phosphitylated Compounds

Structure:	Name:	δ [ppm]:
Alcohols:		
	Methyl	148.93[1]
	Benzyl	148.74[1]
	p-isopropylbenzyl	148.22[2]
	2,2-dimethylpropane-1,3-diol	148.03[1]
	ethyl	147.99[2]
	Isoamyl	147.76[1]
	Ethylene glycol	147.75[1]
	Butane-1,3-diol Butane-2,3-diol	1-147.58[1]; 2-146.39[1] 2-146.70[1]; 3-146.89[1]
	Ethyl-L-lactate	146.99[1]
	L-menthol	146.53[1]; 146.25[2]
	*tert*-butyl	142.83[1]
	*tert*-amyl	142.66[1]
	pinacol	141.33[1]

Structure:	Name:	δ [ppm]:
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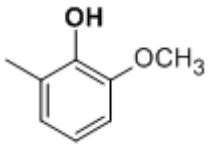
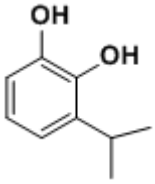
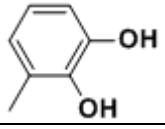
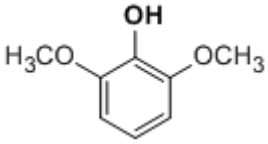
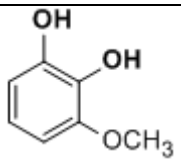
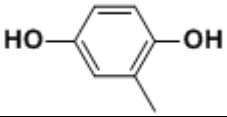
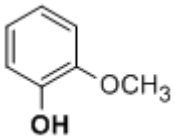
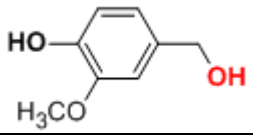
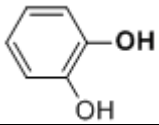
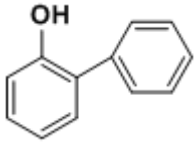
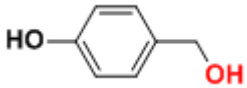
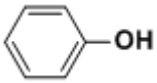
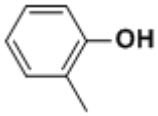
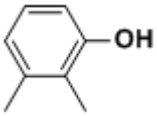
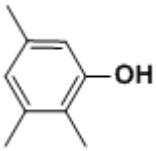
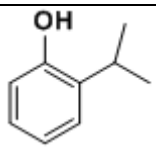
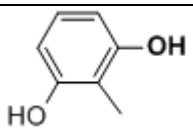
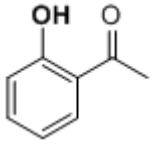
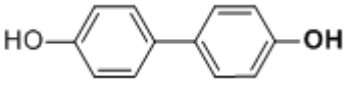
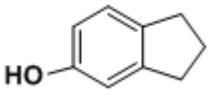
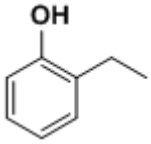
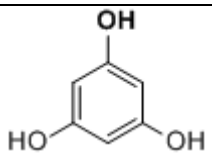
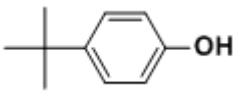
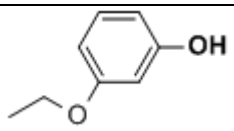
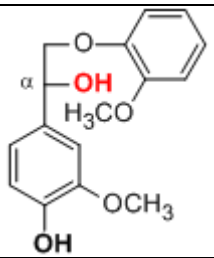
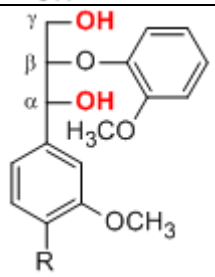
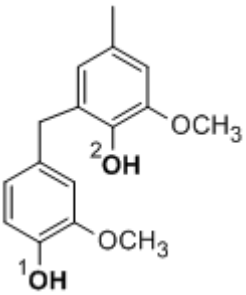
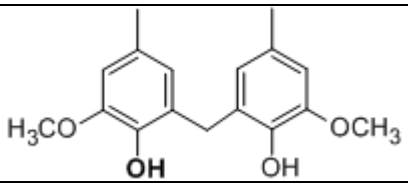
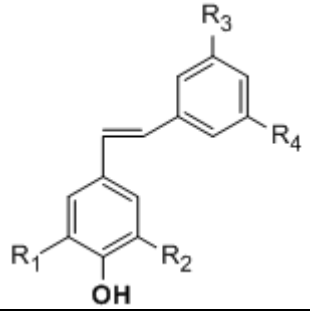
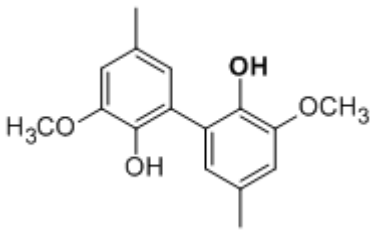
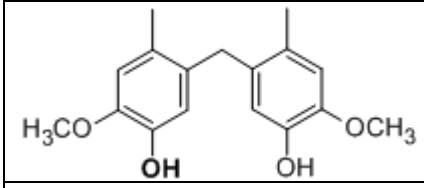
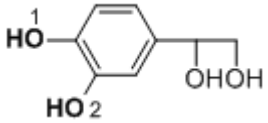
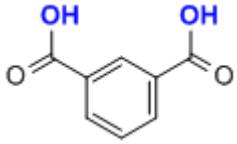
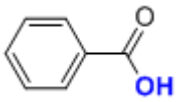
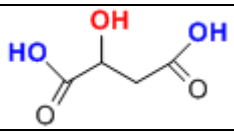
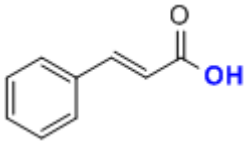
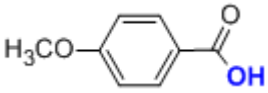
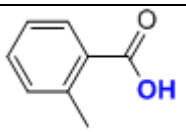
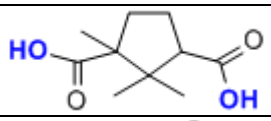
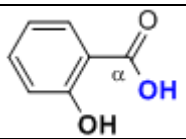
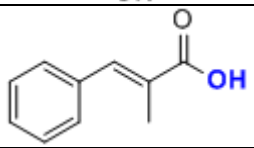
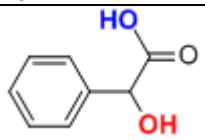
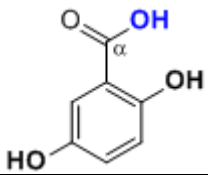
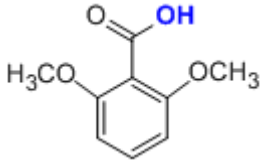
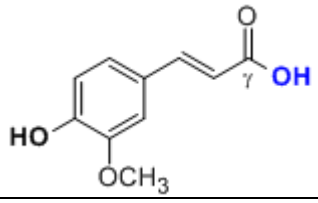
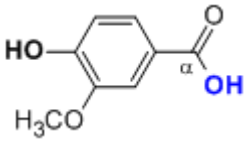
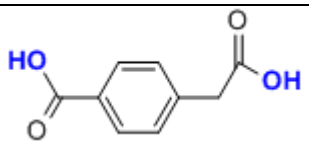
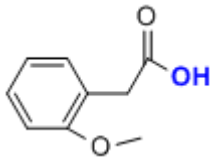
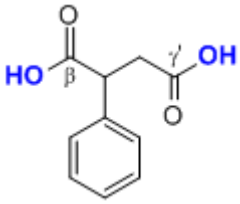
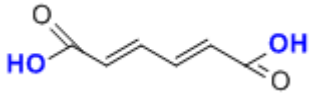
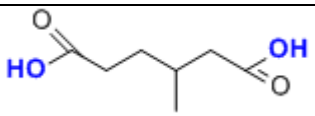
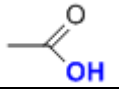
	2-methoxy-6-methylphenol	143.73[1]
	3-isopropylcatechol	1-143.06[1]; 2-143.14[1]
	3-methylcatechol 4-methylcatechol	1-142.89[1]; 2-142.96[1] 1-140.00[1]; 2-139.62[1]
	2,6-dimethoxyphenol 3,4-dimethoxyphenol	142.87[2] 138.29[2]
	3-methoxycatechol	2-142.72[2]; 3-138.60[2]
	methylhydroquinone	1-139.69[1]; 4-138.87[1]
	Guiacol (2-methoxyphenol) 3-methoxyphenol 4-methoxyphenol	140.55[1]; 139.78[2] 138.33[1]; 137.72[2] 139.08[1]; 138.72[2]
	4-hydroxy-3-methoxybenzyl alcohol phenyl group	148.40[2] 139.78[2]
	Catechol Resorcinol hydroquinone	139.71[1]; 138.92[2] 138.44[1] 139.00[1]
	*o*-phenylphenol	139.32[1]

	4-hydroxybenzyl alcohol phenyl-group	148.74[1] 138.69[1]
	phenol	138.68[1]; 138.02[2]
	*o*-cresol *m*-cresol *p*-cresol	139.29[1] 138.60[1]; 137.98[2] 138.83[1]; 138.15[2]
	2,3-xylenol 2,4-xylenol 2,5-xylenol 2,6-xylenol 3,4-xylenol 3,5-xylenol	139.29[1] 139.52[1] 139.21[1]; 138.66[2] 143.04[1] 138.72[1] 138.46[1]
	2,3,5-trimethylphenol 2,3,6-trimethylphenol 2,4,6-trimethylphenol 3,4,5-trimethylphenol	139.21[1] 143.58[1] 143.35[1] 138.58[1]
	*o*-isopropylphenol	139.18[1]
	2-methylresorcinol	139.14[1]
	2-hydroxyacetophenone 3-hydroxyacetophenone 4-hydroxyacetophenone	138.97[1] 138.53[2] 137.65[2]
	4,4'-dihydroxybiphenyl 2,2'-biphenol	138.68[1] 138.00[2]
	5-indanol	138.67[1]
	*o*-ethylphenol *p*-ethylphenol	138.56[1] 138.74[1]; 138.06[2]
	phloroglucinol	138.28[1]
	4-*tert*-butylphenol 3-*tert*-butylphenol 3,5-di-*tert*-butylphenol	138.11[2] 138.02[2] 137.92[2]

	3-ethoxyphenol	137.83[2]
Model compounds[2]		
	1.	139.60[2]; α-147.30[2]
	2. R=OH (α-erythro) 3. R=OH (α-threo) 4. R=OCH_3 (α-erythro) 5. R=OCH_3 (α-threo)	139.49[2]; α-148.23[2]; γ-147.47[2] 139.55[2]; α-147.87[2]; γ-147.47[2] α-148.20[2]; γ-147.50[2] α-147.80[2]; γ-147.50[2]
	6.	1-139.82[2]; 2-143.94[2]
	7.	143.71[2]
	8. R_1=R_2=OCH_3 R_3=R_4=H 9. R_1=R_2=R_3=R_4=OCH_3 10. R_1=OCH_3 R_2=R_3=R_4=H 11. R_1=R_3=R_4=OCH_3 R_2=H 12. R_1=R_2=R_3=R_4=H	142.82[2] 142.80[2] 139.73[2] 139.70[2] 137.98[2]
	13.	141.87[2]

	14.	139.80[2]
	15.	1-138.85[2]; 2-139.00[2]

Structure:	Name:	δ [ppm]:
Acids:		
	Isophthalic terephthalic	136.17[1] 136.18[1]
	benzoic	135.89[1]
	L-malic Aliphatic-OH	1-135.83[1]; 3-135.69[1] 1-134.98[2]; 3-134.79[2] 148.54[1]; 147.96[2]
	Cinnamic	135.80[1]
	*p*-methoxybenzoic	135.80[1]
	*o*-toluic *m*-toluic	135.79[1] 135.81[1]
	D-camphoric	1-135.72[1]; 3-135.35[1]
	Salicylic (*o*-hydroxybenz.) Phenyl group *m*-hydroxybenzoic	α-135.70[1]; α-135.13[2] 2-138.40[1]; 2-137.74[2] α-135.82[1]; 3-139.07[1]
	α-methylcinnamic	135.63[1]
	D-mandelic Benzyl-OH	135.41[1] 147.27[1]
	2,5-dihydroxybenzoic	2-138.91[1]; 5-139.24[1] α-135.62[1]
	2,6-dimethoxybenzoic 3,5-dimethoxybenzoic 2,4,6-trimethoxybenzoic	135.23[1] 135.06[2] 134.91[1]

	4-hydroxy-3-methoxycinnamic phenyl group	γ-135.15[2] 139.43[2]
	4-hydroxy-3-methoxybenzoic phenyl group	α-135.09[2] 139.14[2]
	(p-carboxyphenyl) acetic Benzyl COOH	134.84[1] 135.81[1]
	2-methoxyphenyl acetic	134.80[2]
	phenylsuccinic	β-134.79[2] γ'-134.69[2]
	muconic	134.78[2]
	3-methyladipic	1-134.73[2] 4-134.78[2]
	acetic	134.63[2]