Supplimentary Information for:

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A new method for rapid DS and purity determination of chloroform-soluble cellulose esters, using ^{31}P NMR

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Python Script for DS determination

```
#Python Script for DS Determination of Substituted Celluloses.
#Alistair W. T. King
#Variables:
#Molecular weight of the substituent, from point of attachment to the cellulose oxygen atom (g/mol)
#Molarity of the internal standard (mMol)
#Volume of the internal standard (microL)
#integration ratio of free OHs to IS, by 31P-NMR
#The sample weight for analysis (mg)

print("Determination of DS of native or artifact lignocellulosics from 31P NMR\n\n")

#  DSvalue      free OH per weight    based on the molecular weight of the monomer unit (3/162)
#
#         0                                        18.52
#         1                                        12.35
#         2                                        6.173
#         3                                        0

y = 0.01852

#y is mol hydroxyls per gram of unsubstituted sample

FragMW1 = input("\n\nPlease enter the molecular weight of the substituent fragment\nDo not include the attaching oxygen\nIf the fragment has extra labile protons, devide the Molecular weight by\nthe number of extra labile protons\nIf there is no substituent, enter '1': ")

FragMW = FragMW1 - 1

#FragMW = corrected value for substraction of a hydrogen atom from available hydroxyls

ISmMol = input('\n\nEnter the internal standard molarity, in mmol/L: ')

#ISmMol has to be a float or a zero division error is returned as of python v 2.3

ISmMol= float(ISmMol)
```

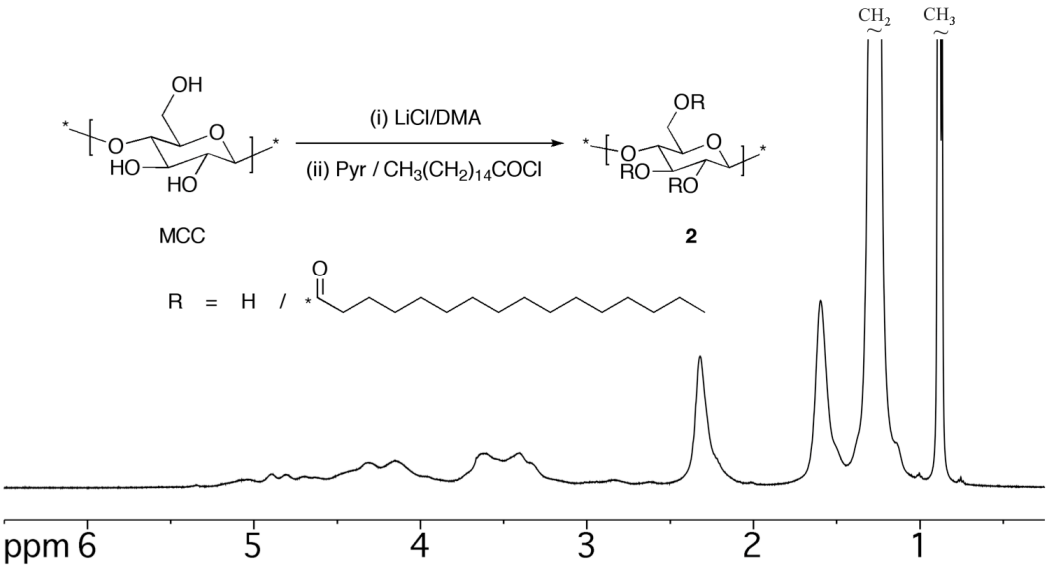
```
#float(x) is required to avoid a python error. If x is already a float, it is simply returned unaltered

ISvol = input('\n\nEnter the volume of IS in the NMR sample, in microL: ')

#ISvol = internal standard volume

OHrat = input('\n\nEnter the total integration ratio of free HO to \ninternal standard integrals: ')

ISmol = ISmMol * ISvol / 1000000000

#ISmol = mols of internal standard in solution

FOHmol = ISmol * OHrat

#FOHmol = mols of free OH groups in the solution

Swt = input('\n\nEnter the weight of the sample that was analysed, in mg: ')

FOHpg = 1000 * FOHmol / Swt

#FOHpg = mols per gram based upon the 31P integration

mFOHpg =str(round(1000 * FOHpg, 4))

#mFOHpg = mmols of hydroxyls per gram, from 31P integration values to 4 decimals

FOHth = ((y/FOHpg) - 1)/(FragMW + (1/FOHpg))

#FOHth = quantitiy of hydroxyls that are taken up by substituent, in mmol/g
#the more condensed FOHth = y + y/FOHpg*FragMW - FOHpg - 1/FragMW gives a zero integer
division error with python 2.3

DS = 3 * FOHth / y
psDS = 100 * FOHth / y

#DS = DS value
#psDS = % DS value

DS = str(round(DS, 3))

#value to 3 decimals

if FragMW1 == 1:
   totpsphos = str(round(100 - psDS, 2))
   # % of total theoretical (3/162) nuclei observed in solution to 2 decimals
   print("\n\n\nThe % phosphitylation is " + `totpsphos` + " % of the total theoretical value.\nThis can
be an indication of either insolubility\nof the phosphitylated product or incomplete
phosphitylation.\n\n")
   print("The integral region corresponds to a value of " + `mFOHpg` + " mmol/g\n\n")


else:
   print("\n\n\nThe degree of substitution is " + `DS` + "\n\n")
```

Java Script for DS Determination

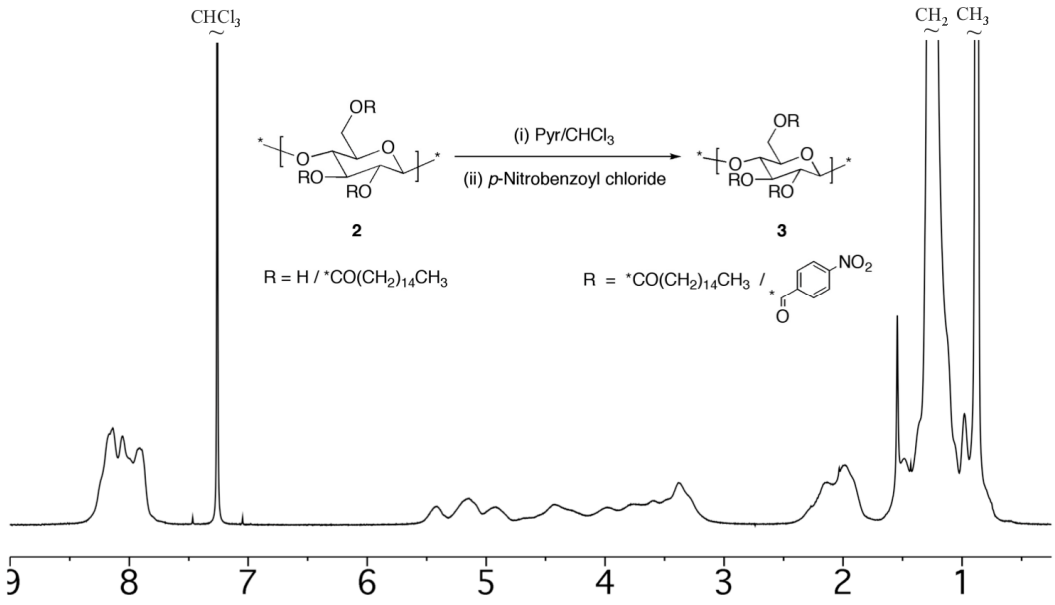
```
/**
* Java Script for DS Determination of Substituted Celluloses
* by Jarno Jalomäki and Alistair King
*/
import java.util.*;

import java.math.*;

public class PhosphorusCell {

	static Scanner keyboard= new Scanner(System.in);
	public static void main(String[] args){

		print("\n* Determination of DS of native or artifact lignocellulosics from 31P NMR
		*\n");
		print("\n\nPlease enter the molecular weight of the substituent fragment\n Do not
include the attaching oxygen\nIf the fragment has extra labile protons, devide the Molecular weight
by\nthe number of extra labile protons\nIf there is no substituent, enter '1': ");

		double FragMW1 = input();
		double FragMW = FragMW1 - 1;

		print("\n\nEnter the internal standard molarity, in mmol/L: ");
		double ISmMol = input();

		print("\n\nEnter the volume of IS in the NMR sample, in microL: ");
		double ISvol = input();

		double ISmol = ISmMol * ISvol / 1000000000;

		print("\n\nEnter the total integration ratio of free OH to \ninternal standard integrals:
		");
		double OHrat = input();

		double FOHmol = ISmol * Ohrat;
		print("\n\nEnter the weight of the sample that was analysed, in mg: ");
		double Swt = input();

		double y = 0.01852;

		double FOHpg = 1000 * FOHmol / Swt;

//round to four decimal points.
		double mFOHpg = roundThis((1000 * FOHpg), 4);
		double FOHth = ((y/FOHpg) - 1)/(FragMW + (1/FOHpg));

// round to two decimal points.
		double DS = roundThis((3 * FOHth / y), 2);

		double psDS = 100 * FOHth / y;

// round to two decimal points.
		if(FragMW1 == 1){
			double totpsphos = roundThis((100 -		psDS), 2);
```

```
                print("\n\n\nThe % phosphitylation is "+totpsphos+" % of the total theoretical
value.\nThis can be an indication of either insolubility\nof the phosphitylated product or incomplete
phosphitylation.\n\n");

                print("The integral region corresponds to a value of "+mFOHpg+" mmol/g\n\n");
                        }
                else print("\n\n\nThe degree of substitution is "+DS+"\n\n");
        }

/**
* method for reading input from keyboard
*/
        public static double input() {

                return keyboard.nextDouble();
        }

/**
* method for displaying messages
*/

        public static void print(String print) {

                System.out.println(print);
        }

/**
* method to round double numbers
*/
        public static double roundThis(double number, int decimals) {

                double factor = Math.pow(10,decimals);
                return (Math.round(number*factor)/factor);
        }
}
```

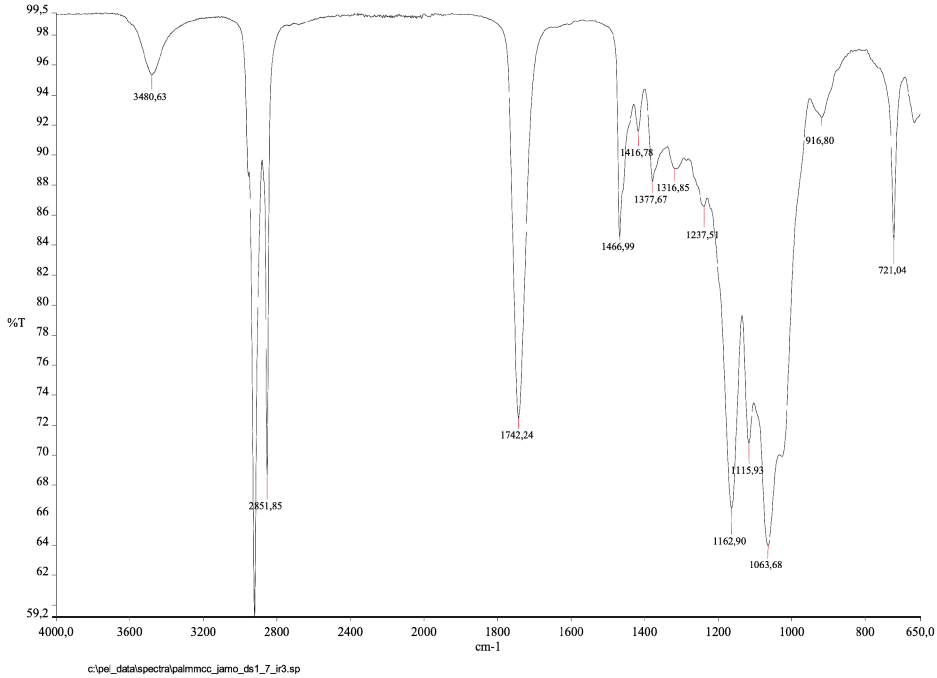
Experimental Data for the Cellulose Esters



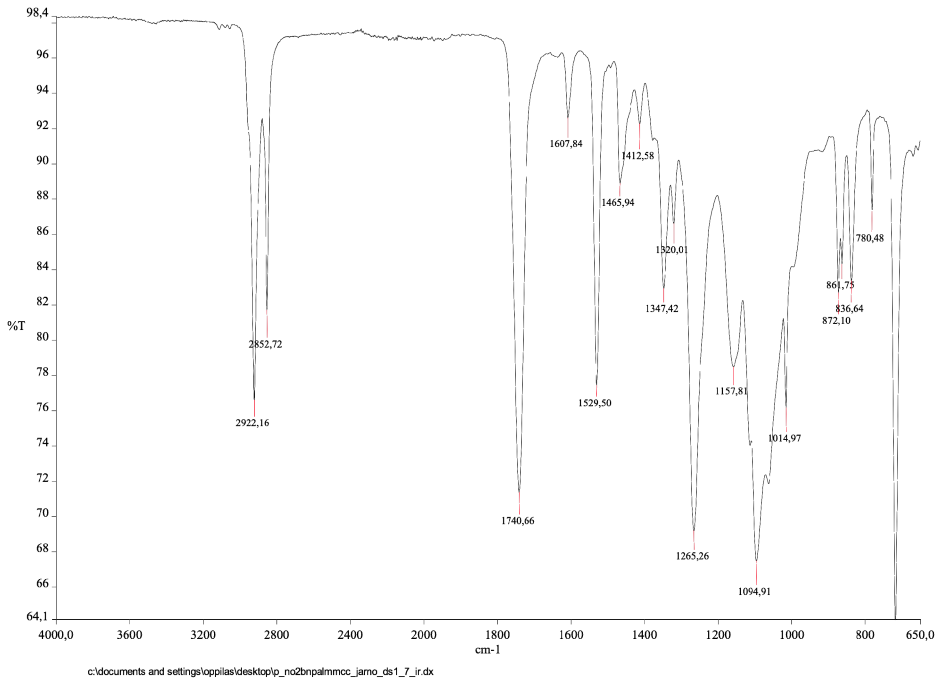
*Quantitative ^{1}H NMR of Palmitoyl cellulose **2**.*

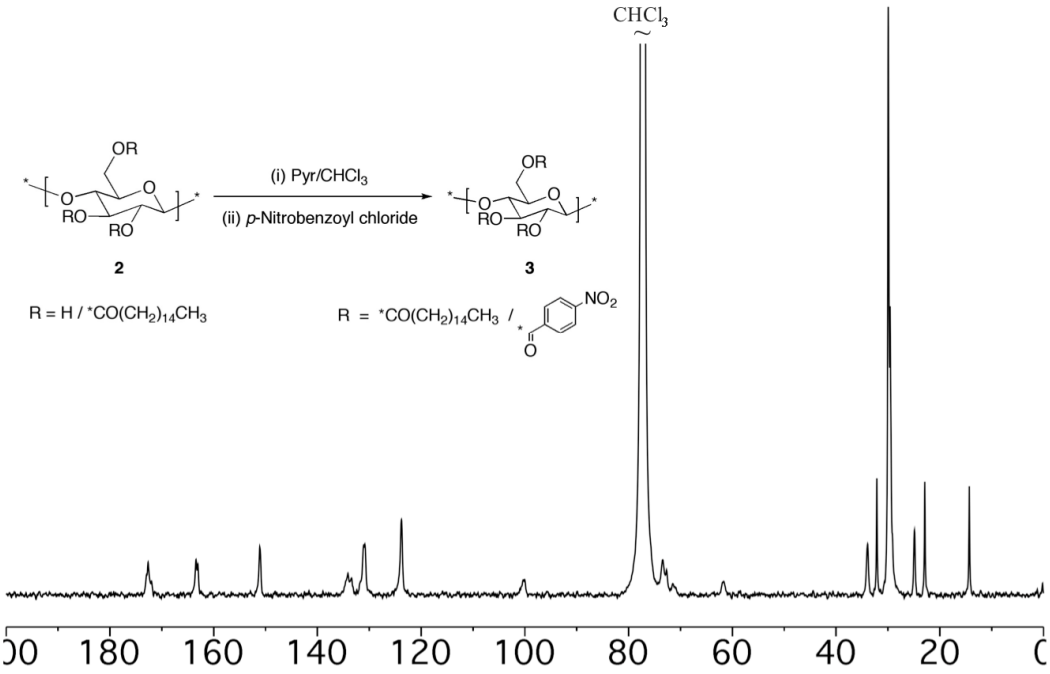


*Quantitative ^{1}H NMR of p-Nitrobenzoyl-Palmitoyl cellulose **3**.*



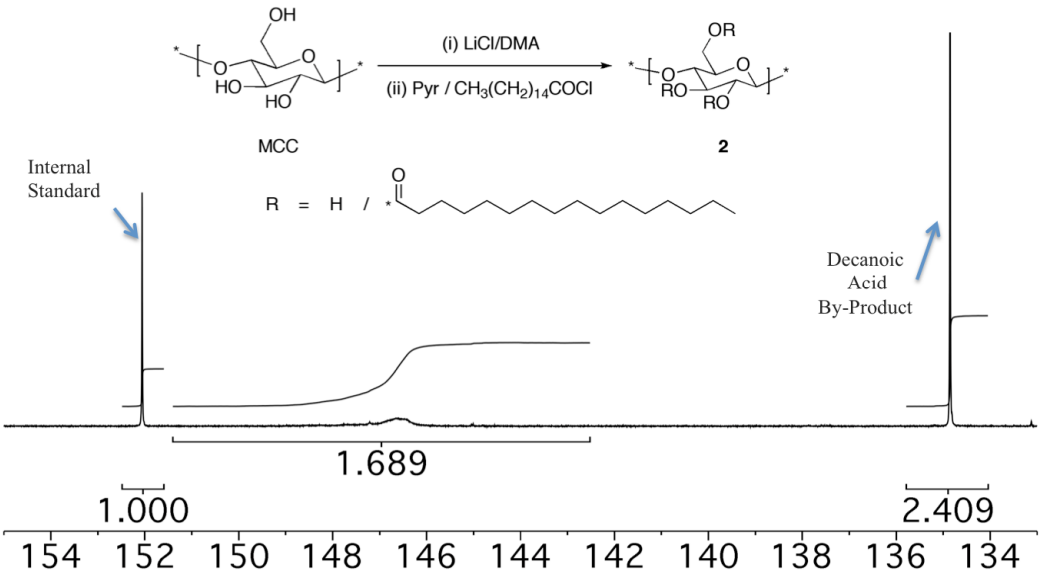
*ATR-IR of Palmitoyl cellulose **2**.*



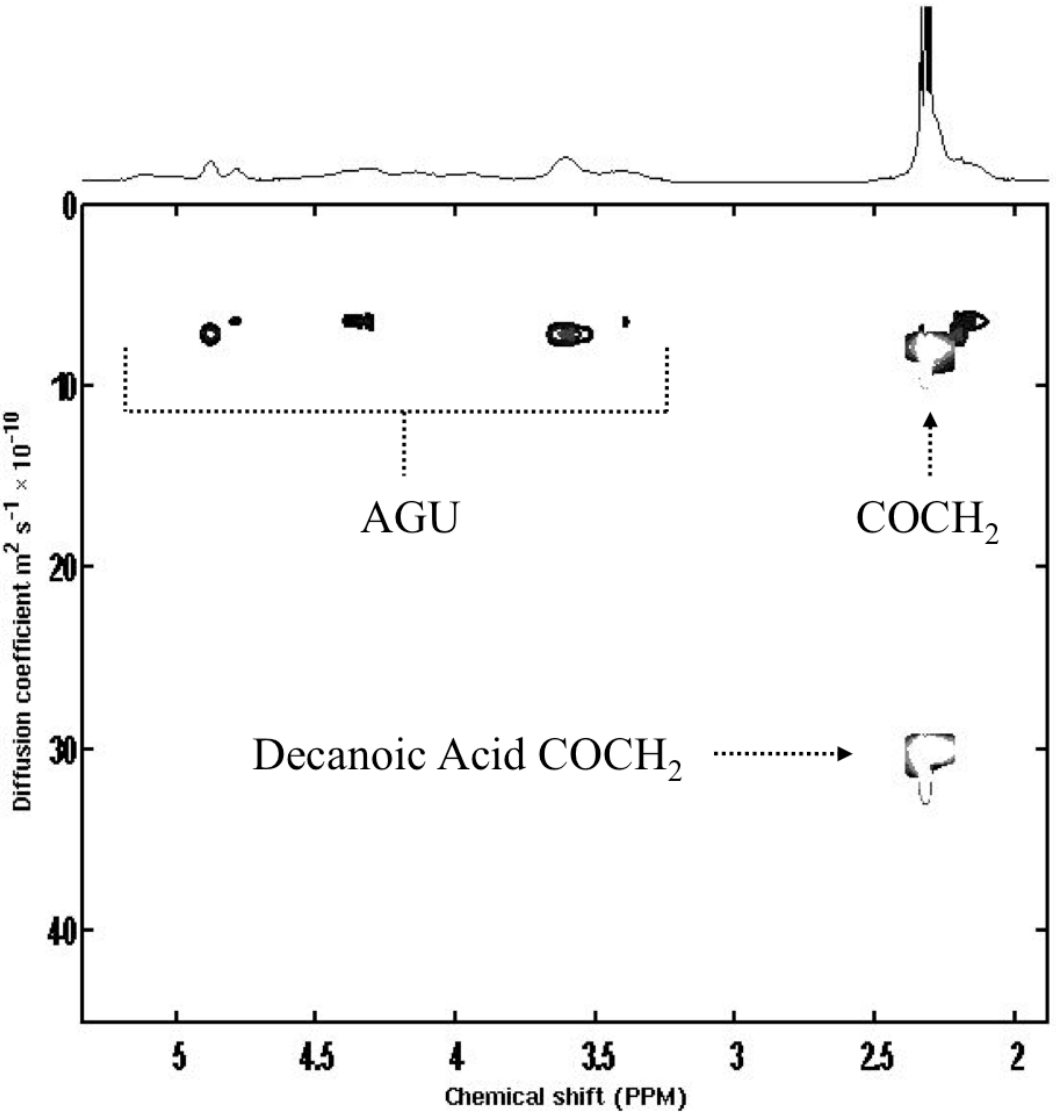


*ATR-IR of p-Nitrobenzoyl-Palmitoyl cellulose **3**.*

*Quantitative ^{13}C NMR of p-Nitrobenzoyl-Palmitoyl cellulose **3**.*



*Quantitative ^{31}P NMR of TMDP-phosphitylated Decanoyl cellulose **4**, containing Decanoic Acid impurity.*



*DOSY Spectra of Decanoyl cellulose **5**, containing Decanoic Acid impurity.*