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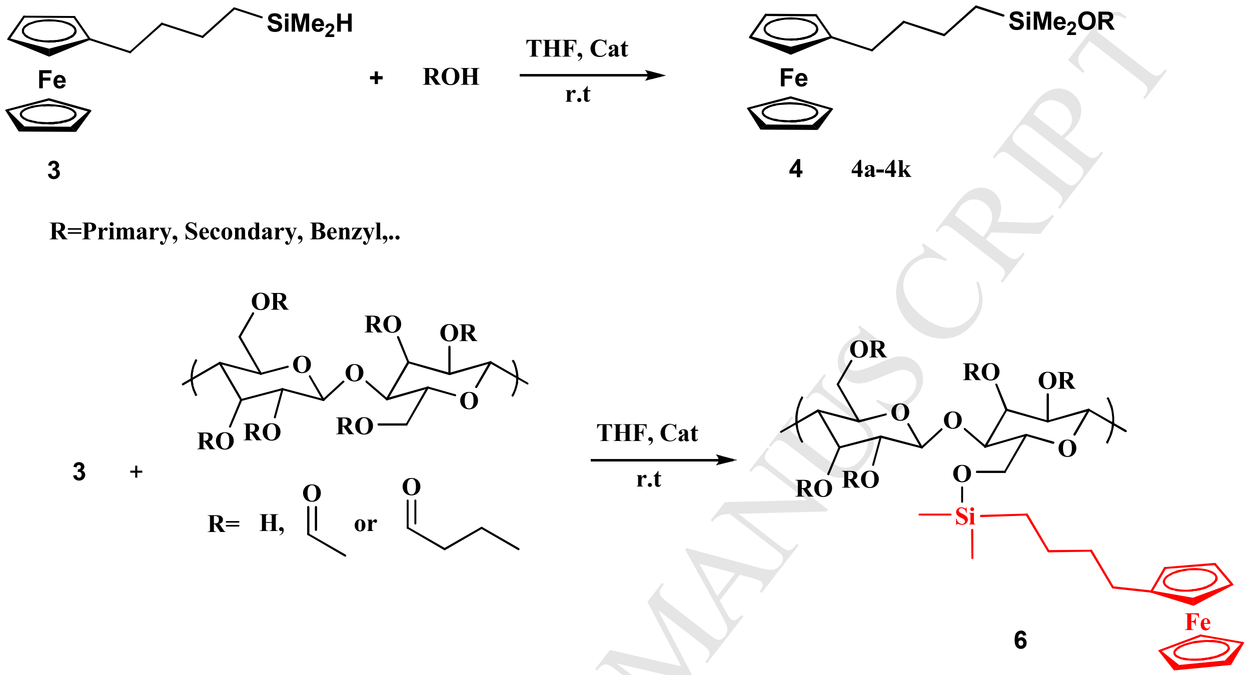
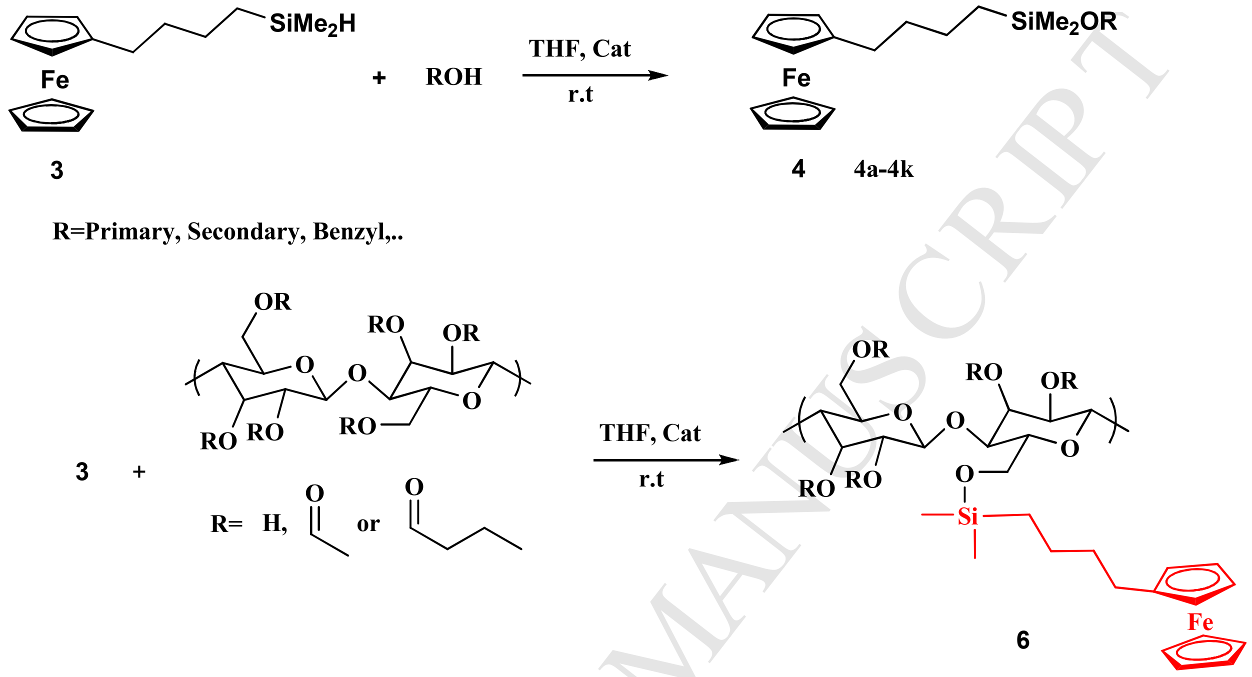
Graphical abstract



Graphical abstract



Synthesis of novel ferrocenyl silyl ethers via dehydrocoupling reactions under Karstedt catalyst

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Abstract

(4-Ferrocenylbutyl)dimethylsilane is prepared by a Grignard reaction from 4-chlorobutylferrocene and chlorodimethylsilane in THF. The Si-H group reacts with primary and secondary alcohols at room temperature to give good yields of (4-ferrocenylbutyl)dimethylsilyl ethers with Karstedt catalyst in THF. Ferrocenyl groups in pendant side chain are attchaed to cellulose acetate butyrate via alcoholysis at room temperature with Karstedt catalyst.

Keywords: Ferrocene, Silane, Silyl Ether, Alcoholysis, Dehydrocondensation, Cellulose acetate butyrate

1-Introduction

Derivatives of ferrocene continue to attract attention 60 years after its discovery [1-3]. The sustained interest is in part due to the rich chemistry of the iron (II) center and the variety of synthetic methods available for functionalizing the cyclopentadienyl-ligands [4-5]. The role of the ferrocene gropus as a three-dimensional metal-containing equivalent of benzene has prompted the synthesis of novel air-stable compounds.

Derivatives of ferrocene are widely used in catalysis and materials science [6]. They are starting materials in both organic and organometallic chemistry [7-8]. They have shown a broad variety of applications in materials [9-10], medicine [11-13], organic synthesis [14-15], organometallic polymers [16], dendritic macromolecules [17-18] and liquid crystals [19-20]. Ferrocene derivatives are a well-known class of one-electron donors which exhibit well established reversible redox couples. As a consequence, ferrocene derivatives, particularly those possessing functionalized tethers, have emerged as strong candidates for molecular electronic devices, electro-optical materials, multielectron redox catalysts and electrode surface modifiers [21-22]. Numerous ferrocene derivatives are used as catalyst for asymmetric synthesis of a large number of optically active organic compounds [3, 23].

Organosilicon reagents and compounds are valuable in organic synthesis, so methods to synthesize them have become of considerable importance. Examples are silyl ethers and silyl ketals [24]. A special feature of hydrosilanes is their ability to undergo alcoholysis leading to alkoxysilanes and gaseous hydrogen (dehydrocondensation). The rate of dehydrocondensation significantly depends on the extent of Si-H bond polarization in the silane, and the reaction occurrs in the presence of either nucleophilic or electrophilic catalysts [25-26].

Over the years, there have been significant developments in silyl ether synthesis and their applications to organic chemistry. Silyl ethers are important in organic synthesis due to their versatility, compatibility with a wide range of reaction conditions, safety, and the ease of usage. They are used in the areas of tethering reactants for stereospecific intramolecular reactions [27-28], protecting agents for many functional groups [29], anchoring reagents, substrates for solid support synthesis, organic synthesis [30] and multistep synthesis [31-32]. They have an important role in inorganic synthesis as precursor in the preparation of sol gel and other condensed siloxane materials [33] and in the preparation of prodrugs for drug delivery [34].

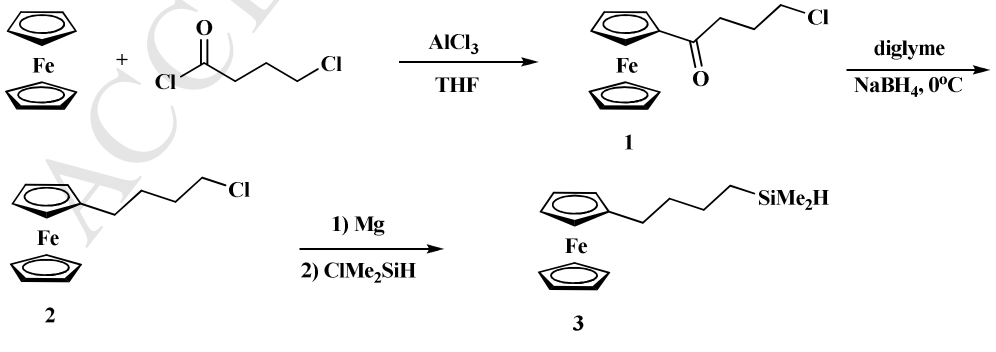
We recently reported formation of functionalized polymers with dehydrocoupling reactions with Karstedt catalyst [35]. The development of environmentally friendly polymers based on renewable materials is of great interest. Indeed, requirements for ecological safety constantly increase and renewable polymers show considerable economic promise for manufacture of industrially advanced polymers. The attraction of easily available functional cellulose derivatives provides strong motivation to validate synthetic methods with respect to their potential for the preparation of new polymers based on renewable raw materials. In particular, cellulose derivatives bearing ionic, electro- or photochromic, redox- or catalytically active side groups are of interest.

Among cellulose derivatives, ester-modified celluloses such as cellulose acetate butyrate are known as good film-forming materials with high scratch resistance, and are commercially available in different grades, at reasonable prices. Polymers using ferrocene in pendant side chains have been emphasized and their special properties have been illustrated. Functionalization of celluloses backbone with ferrocene derivatives has been recently reported in the literature [36-37]. The reported methods usually require severe conditions and multistep reactions. Here we report a very simple and one-pot reaction for the modification of cellulose acetate butyrate with ferrocenyl groups and formation of ferrocenyl silyl ethers with various alcohols under mild conditions by the use of the Karstedt catalyst at room temperature.

2-Results and discussion

We have recently reported the synthesis of silyl ether derivatives of Calixarenes and tris(alkoxydimethylsilyl)methanes via the reaction of tris(dimethylsilyl)methane and Calixarenes having Si-H group with various alcohols in the presence of the Karstedt catalyst under mild conditions [38-39]. In continues of our work on silyl ethers we extended the procedure to include coupling of alcohols with Si-H groups functionalized with ferrocenyl groups. A few articles reporting the synthesis of (4-ferrocenylbutyl)dimethylsilane are found in the literature [40-42]. Due to interesting properties of ferrocene derivatives we decided to use our methodology to attach the (4-ferrocenylbutyl)dimethylsilyl side chain to a polymer backbone.

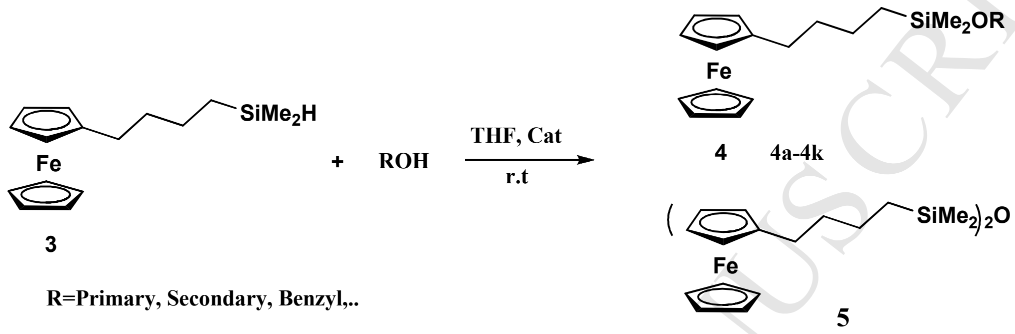
(4-Ferrocenylbutyl)dimethylsilane is synthesized from 4-chlorobutylferrocene via a Grignard reaction in THF [40-42]. 4-Chlorobutyroylferrocene was prepared by Friedel-Crafts acylation of ferrocene with 4-chlorobutyroyl chloride in dichloromethane in the presence of $AlCl_3$ as catalyst (Scheme 1) [43-44]. 4-Chlorobutyroylferrocene was reduced to 4-chlorobutylferrocene by $NaBH_4$ in diglyme [44]. We examined several ether solvents such as THF, 1, 4-dioxane, diethyl ether and diglyme for this reduction. The best result (85%) obtained in diglyme at 0^oC.



Scheme 1. Synthesis of (4-ferrocenylbutyl)dimethylsilane

As reported in literature [24], (4-ferrocenylbutyl)dimethylsilane is an air sensitive and unstable compound that decomposes on exposure to air, but we found that this compound is stable to air and moisture and does not decompose at room temperature.

For dehydrocoupling reaction of alcohols with Si-H group, we started with the reaction of compound **3** with a primary alcohol, methanol, at room temperature and THF as a solvent under Karstedt catalyst (Scheme 2).



Scheme 2. Reaction of ferrocene compound 3 with various alcohols

The reaction was tracked by FT-IR spectroscopy and stopped when the Si-H stretching bond frequency is disappeared in FT-IR spectrum after 2 h (Entry 1, Table 1).

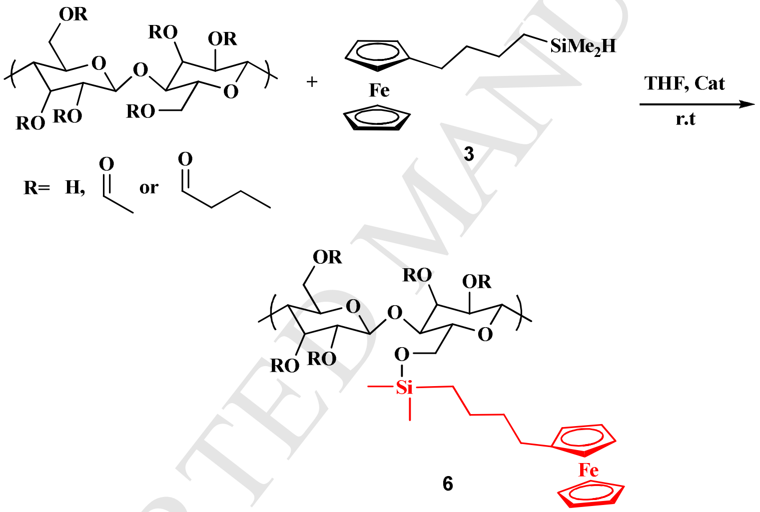
[Table 1]

Refluxing of the reaction decreased the yield of the desired silyl ether products and (4-ferrocenylbutyl)dimethylsiloxane **5** was formed as the main product.

Long chain primary alcohols show lower reactivity than methanol. As shown in Table 1 (4e and 4f) the yields decreased respectively to about 82% and 80% with increasing alcohol chain length. Secondary alcohols reacting with compound **3** to give desired silyl ethers in good yield (Table 1, 4g, 4h). Aromatic alcohols such as benzyl alcohol produced the desired silyl ether in high yields (4j, 93%) and showed higher reactivity than the aliphatic alcohols, but the phenolic silyl ether could not be obtained from the reaction of phenol with compound **3** (4k, Table 1).

Cellulose derivatives such as cellulose acetate butyrate (CAB) are commercially available in different grades. The hydroxyl groups on the cellulose acetate butyrate backbone are good candidates for dehydrocoupling reactions.

Our synthetic procedure was applied to cellulose acetate butyrate containing freely accessible hydroxyl functional side groups, statistically distributed along and among the individual cellulose acetate butyrate chains. The solubility of cellulose acetate butyrate in organic solvents such as THF is the main factor in the selection of this polymer for the current reaction (Scheme 3). CAB was reacted with compound **3** in THF in the presence of Karstedt catalyst at room temperature giving CAB **6** functionalized with ferrocene groups. The cellulose acetate butyrate that was used for this reaction had 36-40% butyryl and 12-15% acetyl groups (Scheme 3).



Scheme 3. Synthesis of cellulose acetate butyrate with ferrocenyl groups

The comparison of NMR spectra of cellulose acetate butyrate bearing ferrocenyl units (Fig 1, a) with pure cellulose acetate butyrate (Fig 1, b) indicates that ferrocenyl groups are attached to the polymer backbone via silyl ether bands. The singlet SiMe$_2$ peak at 0.13 ppm in the NMR spectra of the modified polymer confirmed the presence of the (4-ferrocenylbuyl)dimethylsilyl side chain in compound **6**. Also ferrocene peaks assigned to C-H bonds appeared at 4.03-4.08 ppm as sharp doublets.

[Fig. 1]

FT-IR spectra of polymer **6** (Fig. 2, b) in comparison with the FT-IR spectra of pure cellulose acetate butyrate (Fig. 2, a) showed the appearance of Si-C peak at 883 cm^{-1} and also Cp-H peak at 3094 cm^{-1}. Absence of Si-H peak at 2010 cm^{-1} showed the attachment of ferrocene groups to the polymer is via Si-O bonds.

[Fig. 2]

Other properties of cellulose acetate butyrate modified with ferrocene groups and electrochemical behavior of the obtained polymer and ferrocenyl silyl ethers are under investigation.

3-Conclusion

In summary, we report the synthesis of some silyl ethers containing ferrocenyl groups by reaction of (4-Ferrocenylbutyl)dimethylsilane with various primary and secondary alcohols, in the presence of the Karstedt catalyst at room temperature, in high yields (76-93%). In addition a simple method for attachment of ferrocenyl groups to cellulose acetate butyrate via dehydrocoupling under the same conditions was developed.

4-Experimental

4.1. Solvents and reagents

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka, Aldrich and Yantai Suny Chem. International Co., Ltd. Commercial products were used without purification

4.2. Spectra

The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as solvent. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrometer. The mass spectra were obtained with a GC-Mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. Elemental analyses were carried out with an Elementar vario EL III instrument.

4.3. General procedure for the synthesis of ferrocenyl silyl ether

A 25 ml round-bottomed two-neck flask with magnetic stirrer was charged with 0.20 g (0.66 mmol) silane **3**, 1 ml ROH, and 5 ml dry THF as a solvent. 20 µl of Karstedt catalyst ($[Pt]/[Si–H] = 3.1 \times 10^{-6}$) was added. To follow the reaction progress, several samples were taken at different times and were analyzed by FT-IR spectroscopy. The reaction mixture was stirred at room temperature until the complete disappearance of Si–H bond in FT-IR spectra. The alcohols and THF were evaporated under reduced pressure and the residue purified by column chromatography (n-hexane-ethylacetate, 10:1) to give the corresponding products.

4.3.1. 4-(Methoxydimethylsilyl)butylferrocene (4a)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2925 (C-H), 1634, 1459 (Cp), 1253, 831 (Si-C), 1094, 1005 (Cp), 1029 (Si-O); ^{1}H NMR (400MHz, $CDCl_3$, ppm): 0.15 (s, 6H, $SiMe_2$), 0.63-0.68 (t, 2H, CH_2-$SiMe_2$), 1.37-1.45 (m, 2H, *CH_2*-CH_2-$SiMe_2$), 1.52-1.59 (m, 2H, Cp-CH_2*CH_2*), 2.33-2.36 (t, 2H, Cp-*CH_2*), 3.46 (s, 3H, OMe,), 4.06-4.08 (d, 4H, Cp), 4.1 (s, 5H, Cp); ^{13}C NMR (100MHz, $CDCl_3$, ppm): -3.6 ($SiMe_2$), 16.6 (*CH_2*-$SiMe_2$), 22.0 (Cp-CH_2), 28.17 (*CH_2*-CH_2-$SiMe_2$), 33.69 (Cp-CH_2*CH_2*), 49.2 (OMe), 65.9, 66.9, 67.3 (Cp), 88.2 (C_1 Cp); m/z (EI): 330 (100%$[M]^+$), 199 (17% $[Fc\text{-}CH_2]^+$), 121 (11% $[Cp\text{-}Fe]^+$). Anal. Calc. for $C_{17}H_{26}FeOSi$: C, 61.81; H, 7.93. Found: 61.72, 7.85%.

4.3.2. 4-(Ethoxydimethylsilyl)butylferrocene (4b)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3093 (Cp-H), 2924 (C-H), 1628, 1449 (Cp), 1253, 821 (Si-C), 1107 (Cp), 1022 (Si-O); ^{1}H NMR (400MHz, $CDCl_3$, ppm): 0.10 (s, $SiMe_2$, 6H), 0.60-0.64 (t, 2H, *CH_2*-$SiMe_2$), 1.18-1.21 (t, 3H, CH_3), 1.34-1.42 (m, 2H, *CH_2*-CH_2-$SiMe_2$), 1.50-1.57 (m, 2H, Cp-CH_2*CH_2*), 2.30-2.34 (t, 2H, Cp-CH_2), 3.64-3.69 (q, 2H, OCH_2), 4.03-4.04 (d, 4H, Cp), 4.09 (s, 5H, Cp); ^{13}C NMR (100MHz, $CDCl_3$, ppm): -3.05 ($SiMe_2$), 15.2 (CH_3), 17.5 (*CH_2*-$SiMe_2$), 22.2 (Cp-*CH_2*), 28.2 (*CH_2*-CH_2-$SiMe_2$), 33.7 (Cp-CH_2*CH_2*), 57.2 (OCH_2), 65.9, 67.0, 67.4 (Cp), 88.4 (C_1 Cp), m/z (EI): 344 $[M]^+$, 199 ($[Fc\text{-}CH_2]^+$), 121 ($[Cp\text{-}Fe]^+$). Anal. Calc. for: $C_{18}H_{28}FeOSi$: C, 62.78; H, 8.20. Found: 62.63, 8.06%.

4.3.3. 4-(Propoxydimethylsilyl)butylferrocene (4c)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2925 (C-H), 1623, 1460 (C=C), 1252, 835 (Si-C), 1094 (Cp), 1007 (Si-O); ^{1}H NMR (400MHz, $CDCl_3$, ppm): 0.11 (s, 6H, $SiMe_2$), 0.60-0.65 (t, 2H, CH_2-SiMe$_2$), 0.89-0.92 (t, 3H, CH$_3$), 1.35-1.43 (m, 2H, CH_2-CH$_2$-SiMe$_2$), 1.5- 1.60 (m, 4H, -CH$_2$-), 2.31-2.35 (t, 2H, Cp-CH_2), 3.53-3.57 (t, 2H, OCH$_2$), 4.04-4.05 (d, 4H, Cp), 4.10 (s, 5H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm): −3.08 (SiMe$_2$), 9.28 (CH$_3$), 15.2 (CH_2-CH$_2$-SiMe$_2$), 22.1(CH_2-SiMe$_2$), 24.85 (CH_2-CH$_3$), 28.1 (Cp-CH_2), 33.7 (Cp-CH$_2$$CH_2$), 63.3 (OCH$_2$), 65.9, 66.9, 67.3 (Cp), 88.3 (C$_1$ Cp), m/z (EI): 358 (100% [M]$^+$), 199 (20% [Fc-CH$_2$]$^+$), 121 (11% [Cp-Fe]$^+$). Anal. Calc. for: C$_{19}$H$_{30}$FeOSi: C, 63.68; H, 8.44. Found: 63.54, 8.37%.

4.3.4. 4-(Butoxydimethylsilyl)butylferrocene (4d)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2954 (C-H), 1632, 1461 (C=C), 1253, 830 (Si-C), 1095 (Cp), 1006 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.11(s, 6H, SiMe$_2$), 0.60-0.65 (t, 2H, CH_2-SiMe$_2$), 0.91-0.95 (t, 3H, CH$_3$), 1.35-1.43 (m, 4H, -CH$_2$-), 1.49-1.58 (m, 4H, -CH$_2$-) , 2.31-2.35 (t, 2H, Cp-CH_2), 3.58-3.61 (t, 2H, OCH$_2$), 4.04-4.06 (d, 4H, Cp), 4.10 (s, 5 H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm) −3.11 (SiMe$_2$), 12.9 (CH$_3$), 15.1 (CH_2-CH$_3$), 17.9, 18.1 (-CH$_2$-), 22.1(CH_2-SiMe$_2$), 33.7 (Cp-CH$_2$$CH_2$), 33.8 (-CH$_2$-) , 61.4 (OCH$_2$), 65.9, 66.9, 67.3 (Cp), 88.3 (C$_1$ Cp), m/z (EI): 372(100% [M]$^+$), 199 (13% [Fc-CH$_2$]$^+$), 121 (6% [Cp-Fe]$^+$). Anal. Calc. for: C$_{20}$H$_{32}$FeOSi: C, 64.50; H, 8.66. Found: 64.41, 8.59%.

4.3.5. 4-(Pentoxydimethylsily)butylferrocene (4e)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2927 (C-H), 1632, 1461 (Cp), 1252, 833 (Si-C), 1096 (Cp), 1009 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.01(s, 6H, SiMe$_2$), 0.60-0.64 (t, 2H, CH_2-SiMe$_2$), 0.89-0.93 (t, 3H, CH$_3$), 1.28-1.42 (m, 6H, -CH$_2$-), 1.50-1.65 (m, 4H, -CH$_2$-), 2.30-2.34 (t, 2H, Cp-CH_2) 3.56-3.59 (t, 2H, OCH$_2$), 4.03-4.05 (d, 4H, Cp), 4.09 (s, 5H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm): -3.09 (SiMe$_2$), 13.10 (CH$_3$), 15.18 (CH_2CH$_3$), 21.4, 22.1, 26.97, 28.18 (-CH$_2$-), 28.67 (Cp-CH_2), 31.4 (-CH$_2$-), 33.7 (Cp-CH$_2$$CH_2$), 61.77 (OMe$_2$), 65.9, 66.9, 67.3 (Cp), 88.3 (C$_1$ Cp), m/z (EI): 386 (100% [M]$^+$), 199 (12% [Fc-CH$_2$]$^+$), 121 (8% [Cp-Fe]$^+$). Anal. Calc. for: C$_{21}$H$_{34}$FeOSi: C, 65.27; H, 8.87. Found: 65.19, 8.82%.

4.3.6. 4-(Hexoxydimethylsilyl)butylferrocene (4f)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2926 (C-H), 1633, 1461 (C=C), 1253, 835 (Si-C) 1096 (Cp), 1007 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.09 (s, 6H, SiMe$_2$), 0.59-0.63 (t, 2H, CH_2-SiMe$_2$), 0.88-0.91 (t, 3H, CH$_3$), 1.26-1.49 (m, 8H, -CH$_2$-), 1.49-1.57

(m, 4H, -CH$_2$-), 2.30-2.33 (t, 2H, Cp-*CH$_2$*), 3.55-3.59 (t, 2H, OCH$_2$), 4.03-4.09 (d, 4H, Cp), 4.14 (s, 5H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm): -3.0 (SiMe$_2$), 13.08 (CH$_3$), 15.1, 21.6, 22.2, 24.4, 28.1 (-CH$_2$-), 28.6 (Cp-*CH$_2$*), 30.6, 31.7 (-CH$_2$-), 33.7 (Cp-CH$_2$*CH$_2$*), 61.8 (OCH$_2$), 65.93, 66.96, 67.38 (Cp), 88.3 (C$_1$ Cp); m/z (EI): 400 (100% [M]$^+$), 199(10% [Fc-CH$_2$]$^+$), 121 (6% [Cp-Fe]$^+$). Anal. Calc. for: $C_{22}H_{36}FeOSi$: C, 65.98; H, 9.06. Found: 65.88, 8.98%.

4.3.7. 4-(iso-Propoxydimethylsilyl)butylferrocene (4g)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3095 (Cp-H), 2960 (C-H), 1631, 1460 (C=C), 1252, 879 (Si-C) 1096 (Cp), 1025 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.10 (s, 6H, SiMe$_2$), 0.59-0.63 (t, 2H, CH$_2$- SiMe$_2$), 1.15-1.16 (t, 6H, CH*(CH$_3$)$_2$*), 1.33-1.1.41 (m, 2H, *CH$_2$*-CH$_2$-SiMe$_2$), 1.50-1.57 (m, 2H, Cp-CH$_2$*CH$_2$*), 2.30-2.34 (t, 2H, Cp-CH$_2$), 3.95-4.01(m, 1H, OCH), 4.03-4.04 (m, 4H, Cp), 4.09 (s, 5H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm): -2.52 (SiMe$_2$), 15.6 (*CH$_2$*-CH$_2$- SiMe$_2$), 22.2 (*CH$_2$*- SiMe$_2$), 24.8 (CH*(CH$_3$)$_2$*), 28.1 (Cp-*CH$_2$*), 33.8 (Cp-CH$_2$*CH$_2$*), 63.7 (OCH), 65.9, 66.97, 67.4 (Cp), 88.4 (C$_1$ Cp), m/z (EI): 358 (100% [M]$^+$), 199(14% [Fc-CH$_2$]$^+$), 121 (7% [Cp-Fe]$^+$). Anal. Calc. for $C_{19}H_{30}FeOSi$: C, 63.68; H, 8.44 Found: 63.57, 8.39%.

4.3.8. 4-(sec-Butoxydimethylsilyl)butylferrocene (4h)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3092 (Cp-H), 2926 (C-H), 1634, 1457 (Cp), 1252, 828 (Si-C), 1049 (Cp), 1009 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.10(s, 6H, SiMe$_2$), 0.59-0.63 (t, 2H, CH$_2$- SiMe$_2$), 0.86-0.90 (t, 3H, CH$_2$*CH$_3$*), 1.12-1.14 (d, 3H, CH*CH$_3$*), 1.36-1.55 (m, 6H, -CH$_2$-), 2.30-2.34 (t, 2H, Cp-*CH$_2$*), 3.67-3.71 (m, 1H, O*CH*), 4.03-4.05 (d, 4H, Cp), 4.09 (s, 5H, Cp); ^{13}C NMR (100MHz, CDCl$_3$, ppm): -2.3 (SiMe$_2$), 9.3 (CH$_2$*CH$_3$*), 15.81 (*CH$_2$*-SiMe$_2$), 22.2 (*CH$_2$*- SiMe$_2$), 22.4, 28.1, 22.6, 31.3 (-CH$_2$-), 33.87 (Cp-CH$_2$*CH$_2$*), 65.9, 66.9, 67.3 (Cp), 68.8 (O*CH*), 88.4 (C$_1$ Cp), m/z (EI): 372(100% [M]$^+$), 199 (12% [Fc-CH$_2$]$^+$), 121 (7% [Cp-Fe]$^+$). Anal. Calc. for $C_{20}H_{32}FeOSi$: C, 64.50; H, 8.66. Found: 64.36, 8.59%.

4.3.9. 4-(iso Pentoxydimethylsily) butylferrocene (4i)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3091 (Cp), 2955 (C-H), 1631, 1462 (Cp), 1252, 818 (Si-C) 1093 (Cp), 1026 (Si-O); ^{1}H NMR (400MHz, CDCl$_3$, ppm): 0.99 (s, 6H, SiMe$_2$), 0.60-0.64 (t, 2H, *CH$_2$*-SiMe$_2$), 0.90-0.91 (d, 6H, CH*(CH$_3$)$_2$*), 1.35-1.46 (m, 4H), 1.51-1.58 (m, 2H), 1.66-1.73 (m, 1H, *CH*(CH$_3$)$_2$), 2.31-2.359 (t, 2H, *CH$_2$*-Cp), 3.60- 3.63 (t, 2H, O*CH$_2$*), 4.04-

4.05 (d, 4H, Cp), 4.10 (s, 5H, Cp); ^{13}C NMR (100MHz, $CDCl_3$, ppm): -3.09 ($SiMe_2$), 15.2 21.6, 22.1, 23.5, 28.1, 33.7, 40.6, 60.0 (O*CH_2*), 65.9, 66.7, 66.9, 67.3 (Cp), 88.3 (C_1 Cp), m/z (EI): 358 (100% $[M]^+$), 199(16% $[Fc\text{-}CH_2]^+$), 121 (14% $[Cp\text{-}Fe]^+$). Anal. Calc. for $C_{21}H_{34}FeOSi$: C, 65.27; H, 8.87. Found: 65.02, 8.85%.

4.3.10. 4-(Benzyloxydimethylsilyl)butylferrocene (4j)

A yellowish oil: FT-IR (KBr, cm^{-1}): 3090, 3031 (C-H), 2924 (C-H), 1634, 1493 (C=C), 1255, 838 (Si-C), 1099 (Cp), 1027 (Si-O); ^{1}H NMR (400MHz, $CDCl_3$, ppm): 0.07(s, 6H, $SiMe_2$), 0.56-0.61 (t, 2H, *CH_2*-$SiMe_2$), 1.30-1.36 (m, 2H, CH_2-*CH_2*-$SiMe_2$), 1.42-1.48 (m, 2H, *CH_2*-CH_2-$SiMe_2$), 2.21-2.25 (t, 2H, *CH_2*-Cp), 3.9 (d, 4H, Cp), 4.02 (s, 5H, Cp), 4.6 (s, 2H, O*CH_2*Ar), 7.18-7.27 (s, 5H, *Ar*); ^{13}C NMR (100MHz, $CDCl_3$, ppm): -3.0 ($SiMe_2$), 15.2 (*CH_2*-CH_2-$SiMe_2$), 22.1 (CH_2-$SiMe_2$), 28.1(*CH_2*-Cp), 33.6 (*CH_2*-CH_2-Cp), 63.63 (O*CH_2*-Ar), 65.9, 66.9, 67.3 (Cp), 88.3 (C_1 Cp), 125.4, 126.0, 127.2 (*Ar*), 140 (C_1 *Ar*); m/z (EI): 406 (100% $[M]^+$), 199(9% $[Fc\text{-}CH_2]^+$), 121 (6% $[Cp\text{-}Fe]^+$). Anal. Calc. for $C_{23}H_{30}FeOSi$: C, 67.97, H, 7.44. Found: C, 68.29, H, 7.40%.

4.4. Synthesis of ferrocenyl cellulose acetate butyrate (6)

A 25 ml round-bottomed two-neck flask with magnetic stirrer was charged with 0.20g cellulose acetate butyrate and silane **3** (0.6g) and 10 ml dry THF as a solvent. Then 40 µl of Karstedt catalyst ([Pt]/[Si–H] = 3.1 × 10-6) was added. The mixture was stirred at room temperature for 6h. After completion of the reaction, the mixture was poured into water (50 ml) and was extracted three times with dichloromethane. The combined organic layers were dried (Na_2SO_4) and filtered. The solvent was evaporated and the residue washed with *n*-hexane several times until all unreacted silane was removed, and the cellulose acetate butyrate appeared as a thin film.

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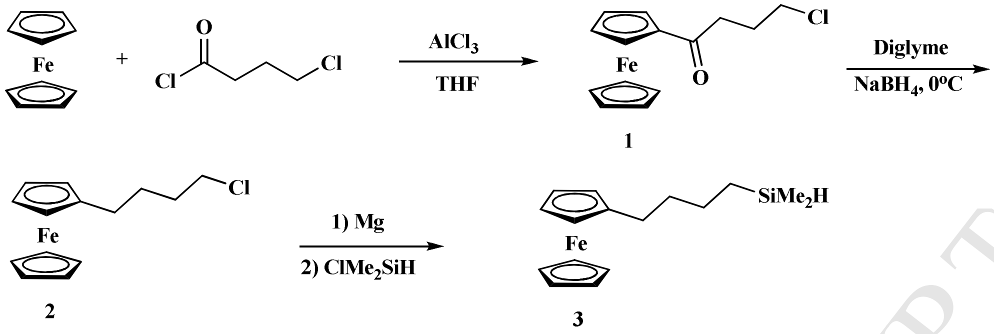
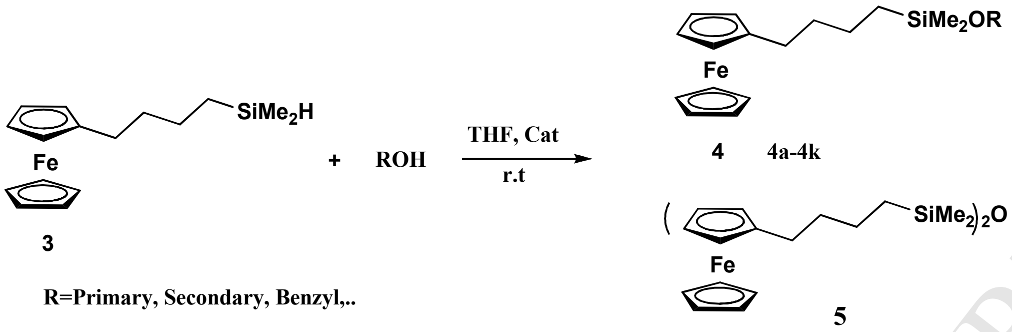


1

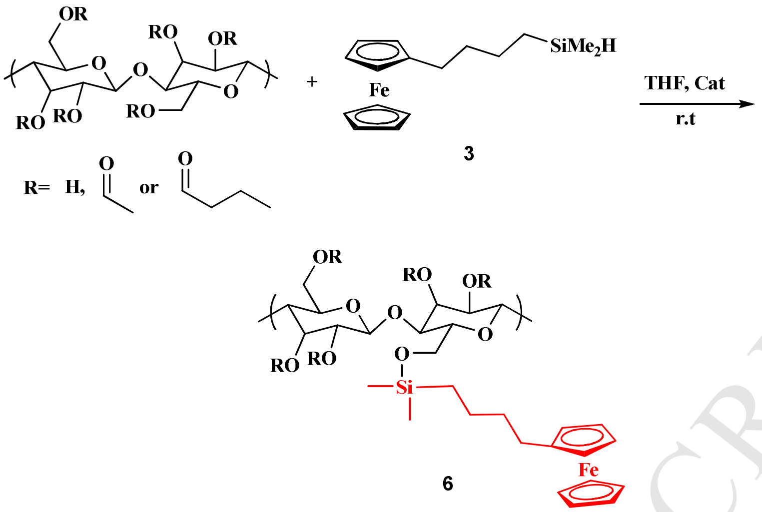
2

3

Scheme 1. Synthesis of (4-ferrocenylbutyl)dimethylsilane



Scheme 2. Reaction of ferrocene compound 3 with various alcohols



Scheme 3. Synthesis of cellulose acetate butyrate with ferrocene group

Table 1 Synthesis of ferrocenyl silyl ethers with various alcohols in the presence of Karstedt Catalyst

Entry	Alcohol	product	Yield (%)
1	CH_3OH	4a	89
2	CH_3CH_2OH	4b	86
3	$CH_3CH_2CH_2OH$	4c	85
4	$CH_3CH_2CH_2CH_2OH$	4d	82
5	$CH_3CH_2CH_2CH_2CH_2OH$	4e	82
6	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	4f	80
7	$(CH_3)_2CHOH$	4g	78
8	$(CH_3)CHOHCH_2CH_3$	4h	76
9	$(CH_3)_2CHCH_2CH_2OH$	4i	84
10	$PhCH_2OH$	4j	93
11	PhOH	4k	-

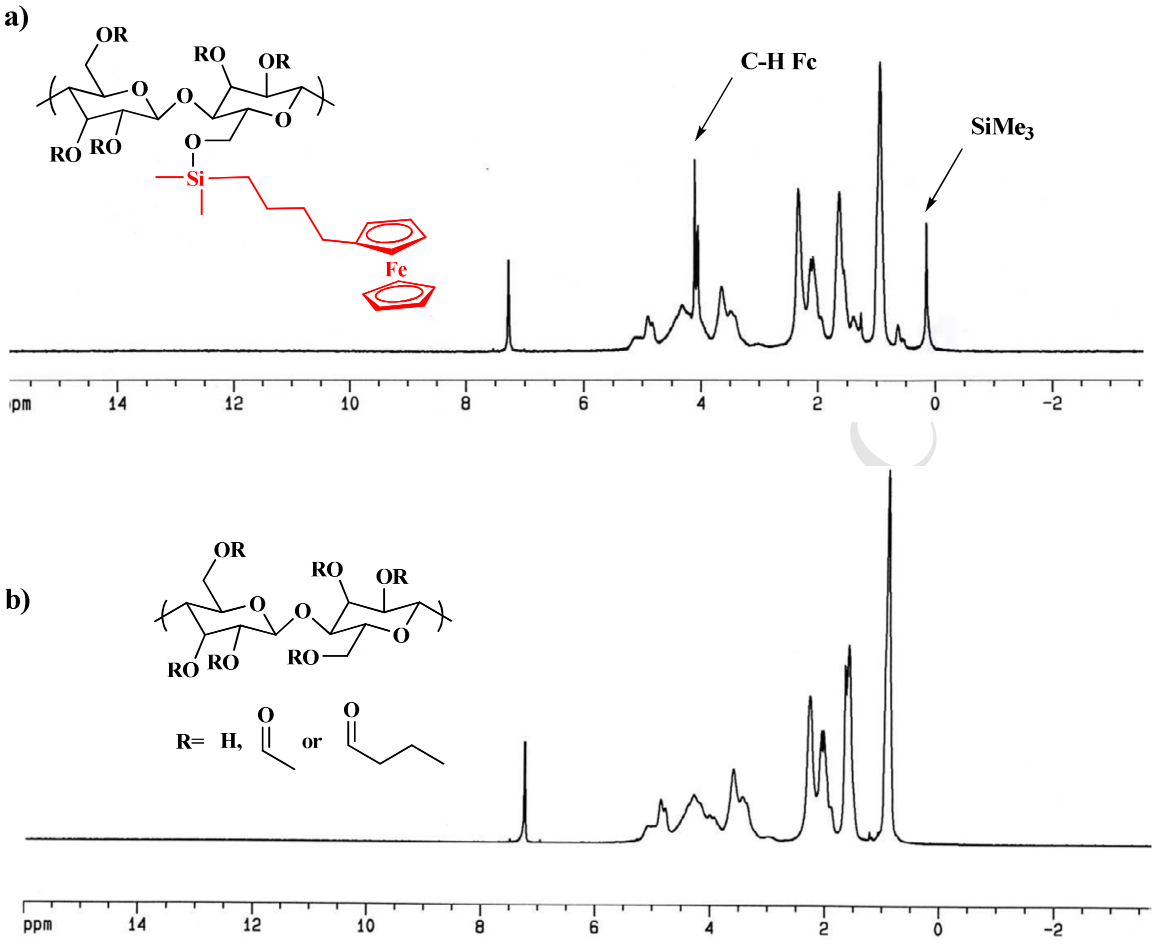


Fig 1. NMR spectra of a) cellulose acetate butyrate attached ferrocene groups b) pure cellulose acetate butyrate

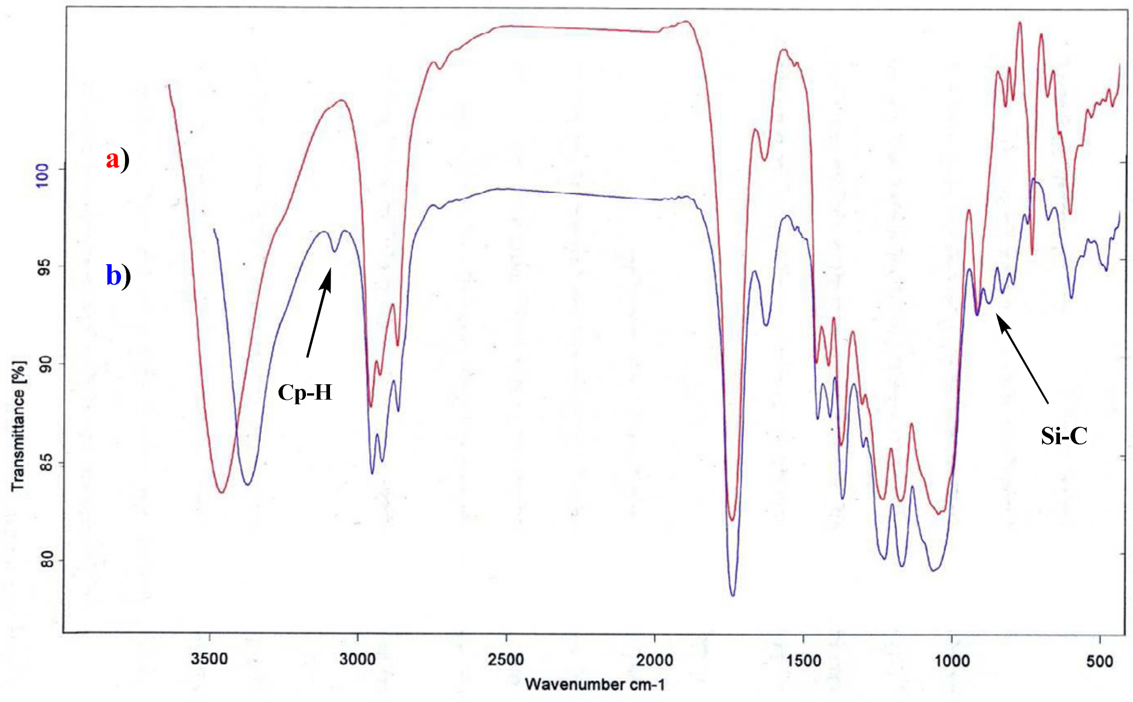


Fig 2. Comparing the FT-IR spectra of the a) pure cellulose acetate butyrate b) cellulose acetate butyrate attached ferrocene groups

Highlights

1) Novel ferrocenyl silyl ethers have been synthesized
2) Polymers attached with ferrocene groups have been synthesized.
3) A convenient method to attaching ferrocene on polymers have been developed

Table 1 Synthesis of ferrocenyl silyl ethers with various alcohols in the presence of Karstedt Catalyst

Entry	Alcohol	product	Yield (%)
1	CH_3OH	4a	89
2	CH_3CH_2OH	4b	86
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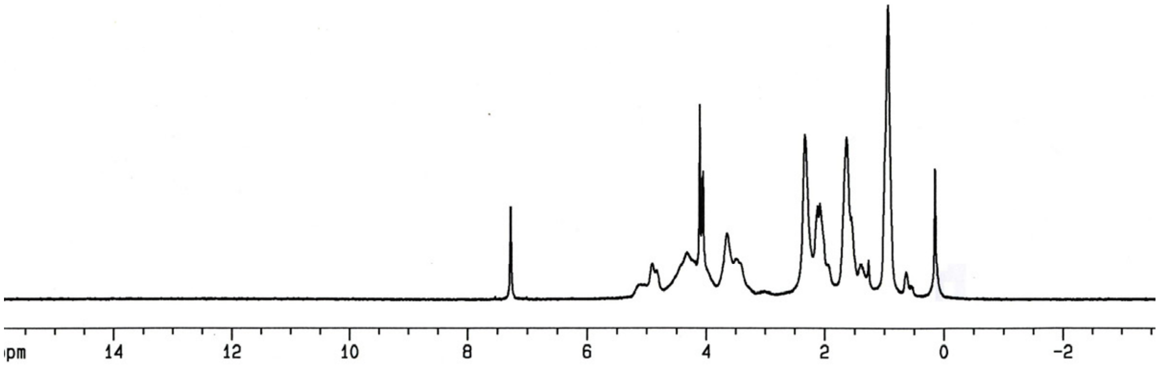
4	$CH_3CH_2CH_2CH_2OH$	4d	82
5	$CH_3CH_2CH_2CH_2CH_2OH$	4e	82
6	$CH_3CH_2CH_2CH_2CH_2CH_2OH$	4f	80
7	$(CH_3)_2CHOH$	4g	78
8	$(CH_3)CHOHCH_2CH_3$	4h	76
9	$(CH_3)_2CHCH_2CH_2OH$	4i	84
10	$PhCH_2OH$	4j	93
11	PhOH	4k	-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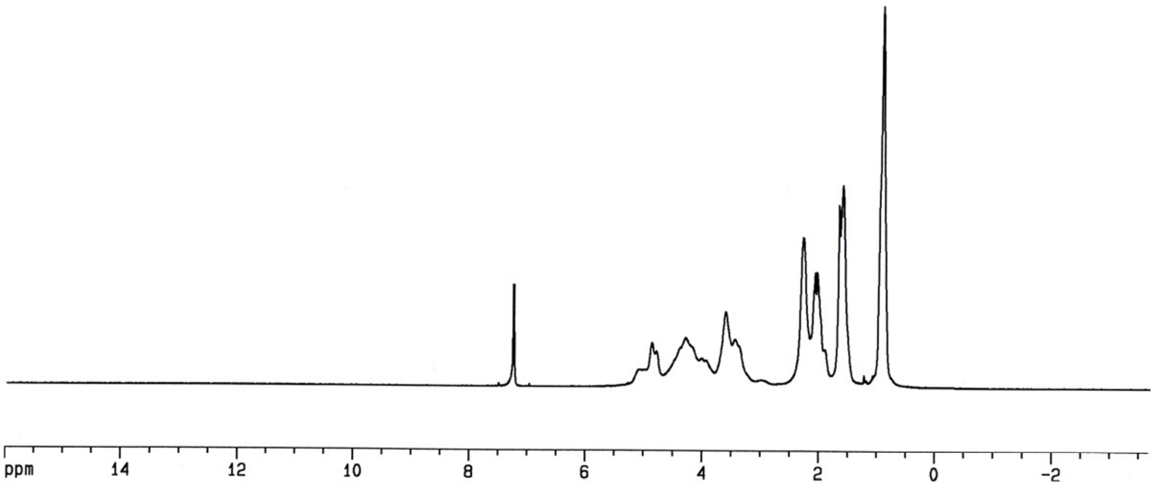
8
6
4
2
0
-2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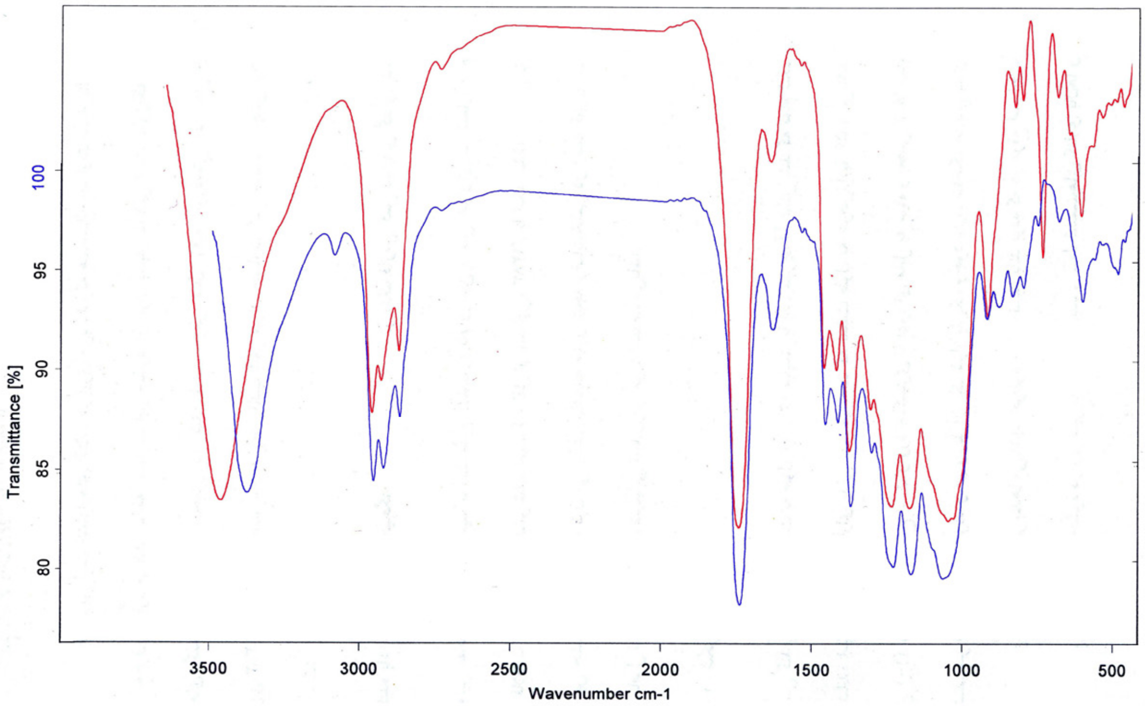
Transmittance [%]
100
95
90
85
80
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
500