# Supplementary Materials

## Pyrrole Compounds from the Two Steps One Pot Conversion of 2,5-Dimethylfuran for Elastomer Composites with Low Dissipation of Energy

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**S.1. Reaction mechanism for the functionalization of $sp^2$ carbon allotropes with pyrrole compounds**

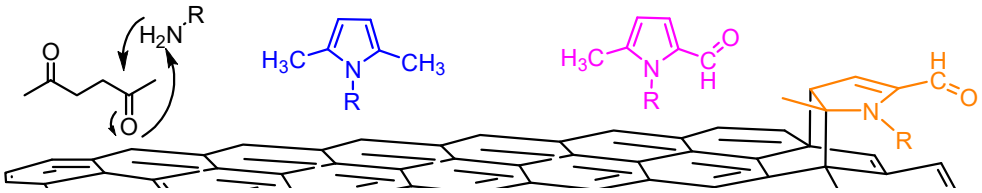



**Figure S.1**. Reaction mechanism for the functionalization of $sp^2$ carbon allotropes with a pyrrole compound with methyl groups in α positions. It is also shown the synthesis of the pyrrole compound.

**S.2. Kinetic studies for the ring opening reaction of DF to HD**

The kinetics of the ring opening reaction of DF to HD was studied collecting 5 aliquots of the reaction mixture at increasing times and analysing them by means of $^{1}$H-NMR spectroscopies.

Reaction parameters: molar ration DF / water = 1 / 1, 15 mol% of $H_2SO_4$, 50 °C. $^{1}$H-NMR spectra were collected in $CDCl_3$ after 2 hours, 3 hours and 30 minutes, 5 hours, 8 hours and 24 hours. They are shown in Figure S.2 a-e, respectively. The red arrows show the methyl group of DF. It is evident the decreasing of the concentration of DF as the reaction time increases.

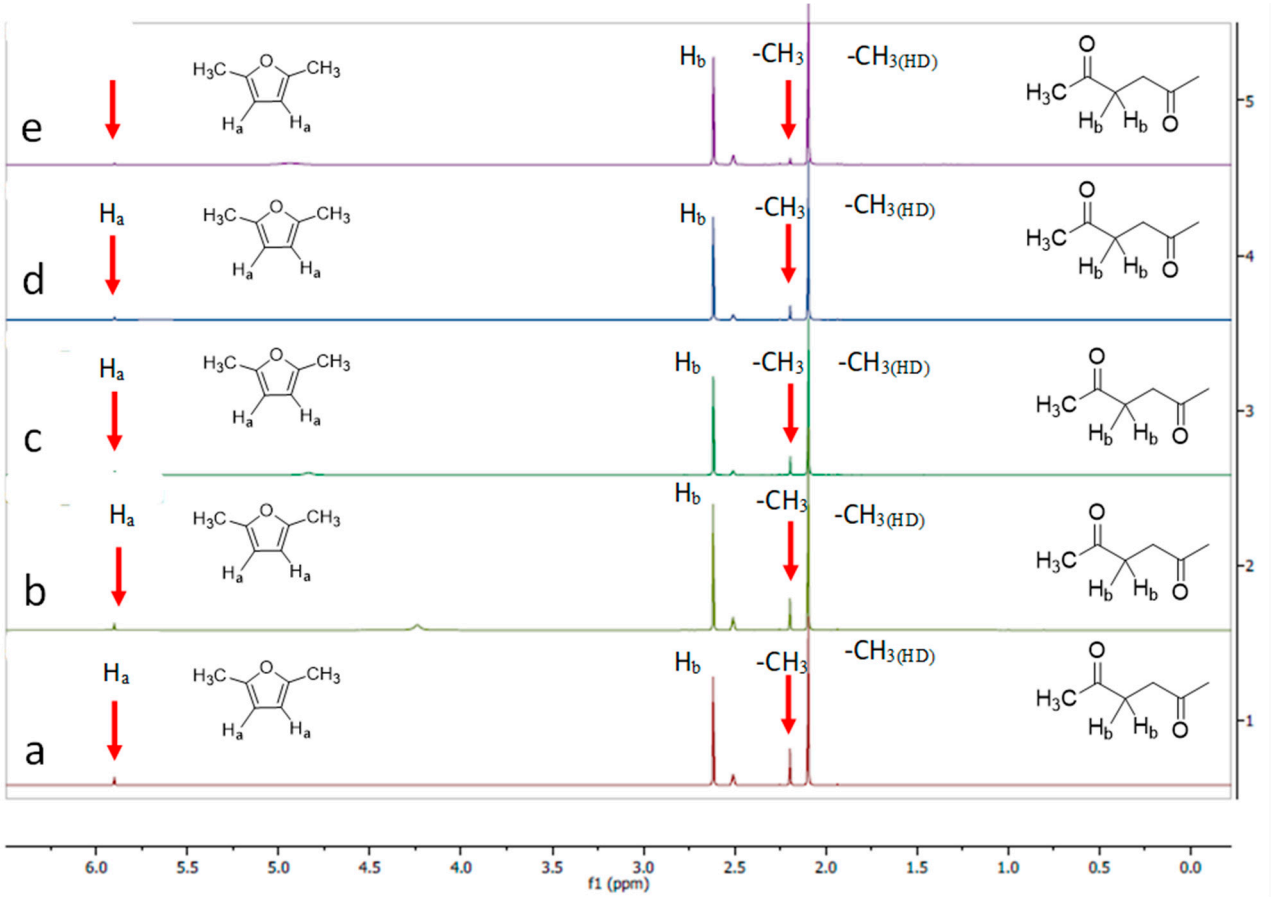



**Figure S.2.** $^{1}$H NMR spectra (400 MHz, DMSO-$d_6$) recorded on the ring opening reaction of 2,5-dimethylfuran to 2,5-hexanedione.

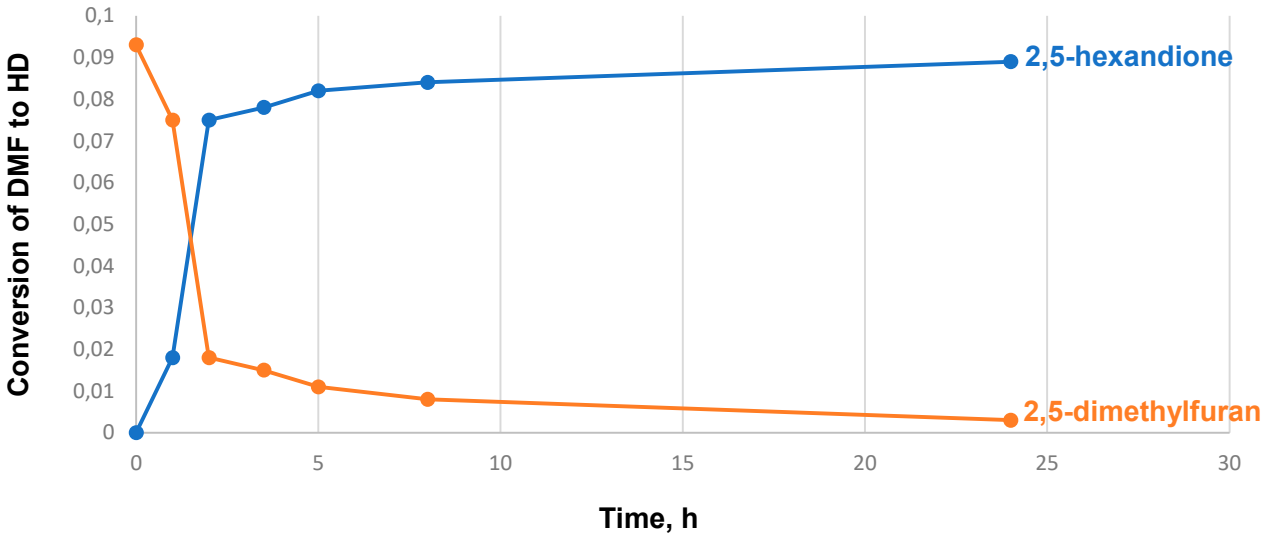



**Figure S.3.** Conversion of the ring opening reaction of DF to HD, at different reaction times. The graph shows the relative concentration of DF (orange line) and HD (blue line) vs time.

## S2. Screening of the amount of water

Different DF/$H_2O$ ratio were investigated. The reactions were followed by NMR spectroscopy.

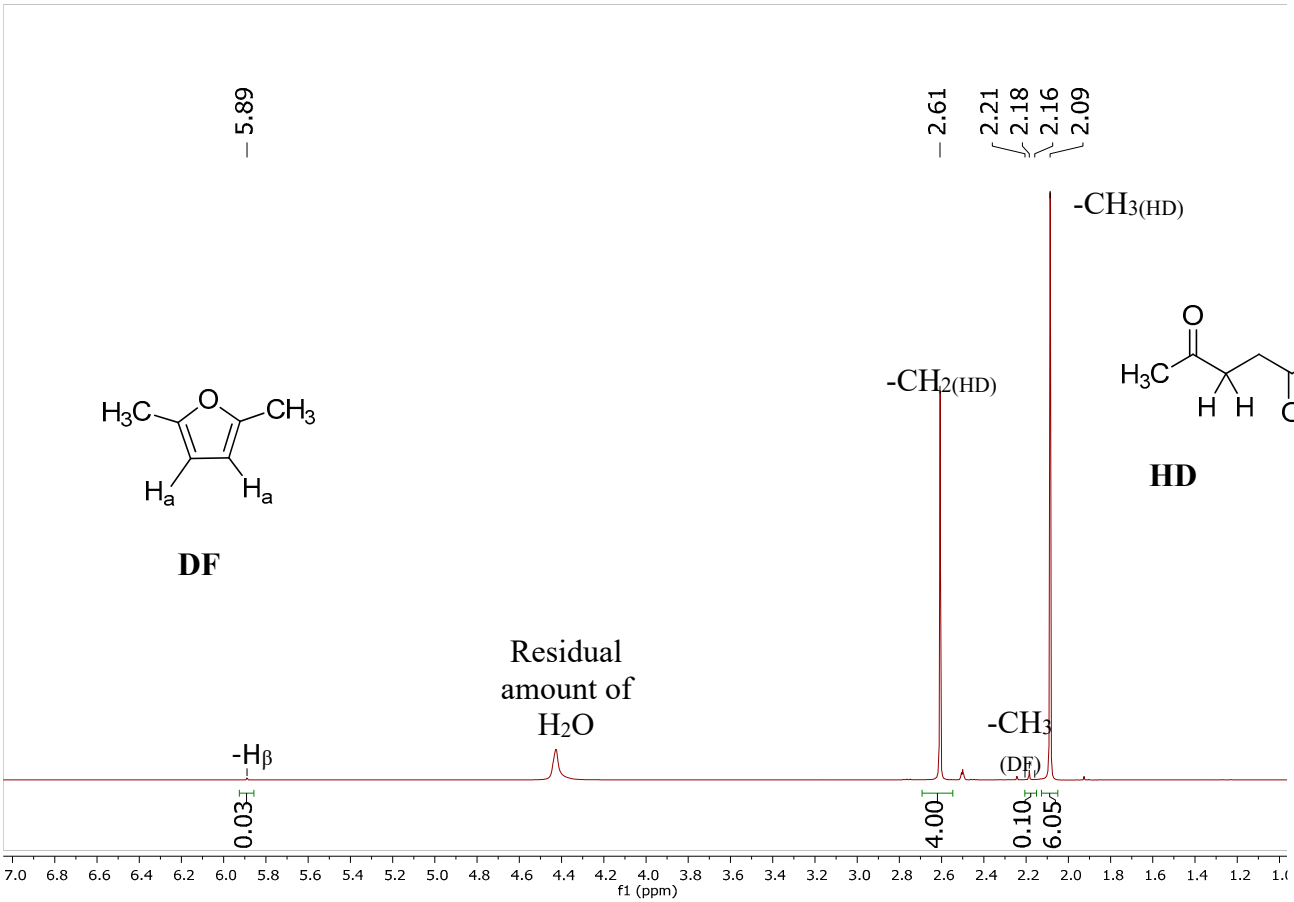



**Figure S.4.** $^1$H-NMR spectrum (400 MHz, DMSO-$d_6$) of the reaction between DF, water (ratio DF/$H_2O$ 1:3.0) and sulfuric acid 15 mol%. DF was converted by 95% in HD; residual amount of water was observed at 4.39 ppm.

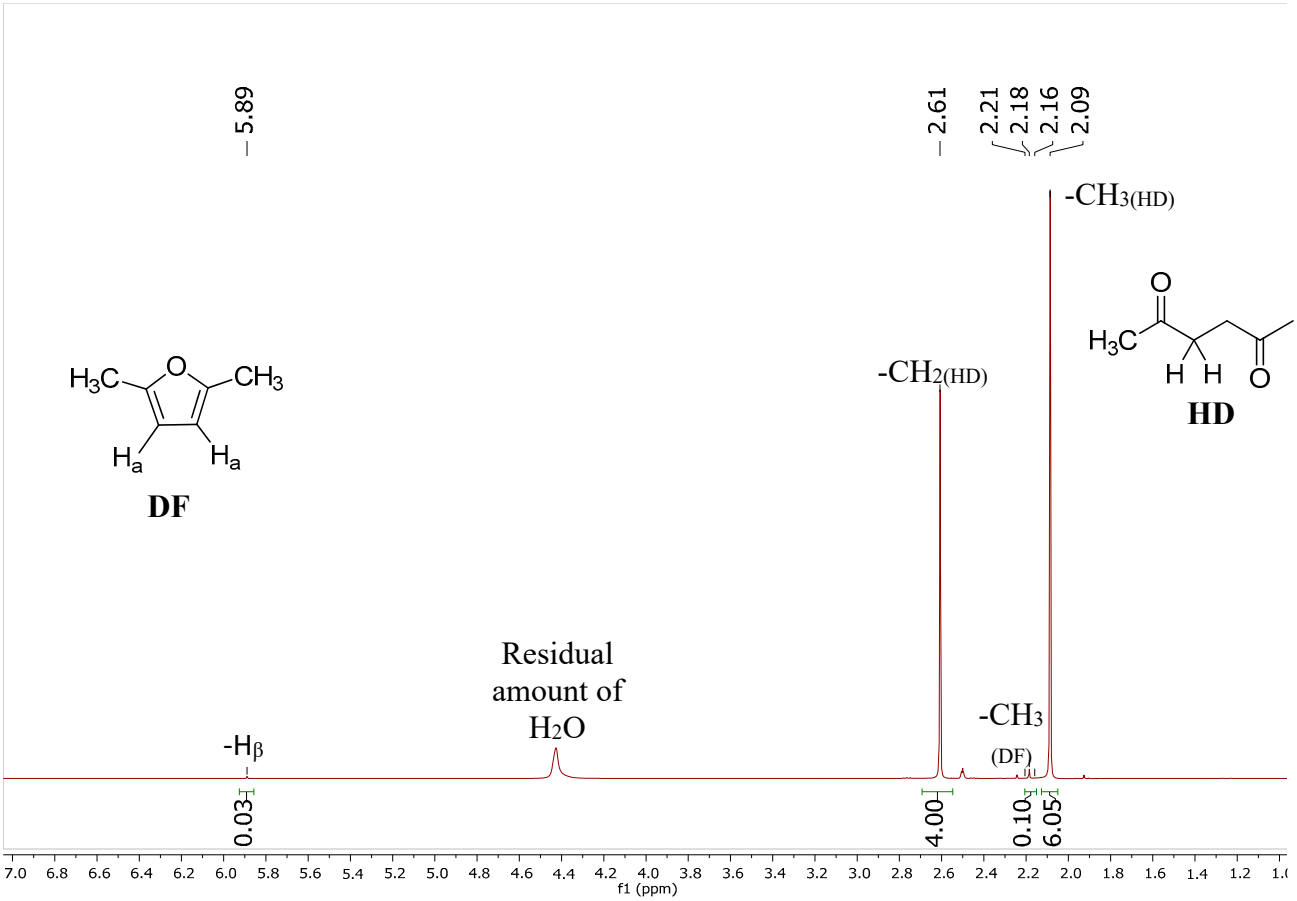



**Figure S.5.** $^{1}$H-NMR spectrum (400 MHz, DMSO-$d_6$) of the reaction between DF, water (ratio DF/$H_2O$ 1/2.0) and sulfuric acid 15 mol%. DF was converted by 95% in HD; residual amount of water was observed at 4.43 ppm.

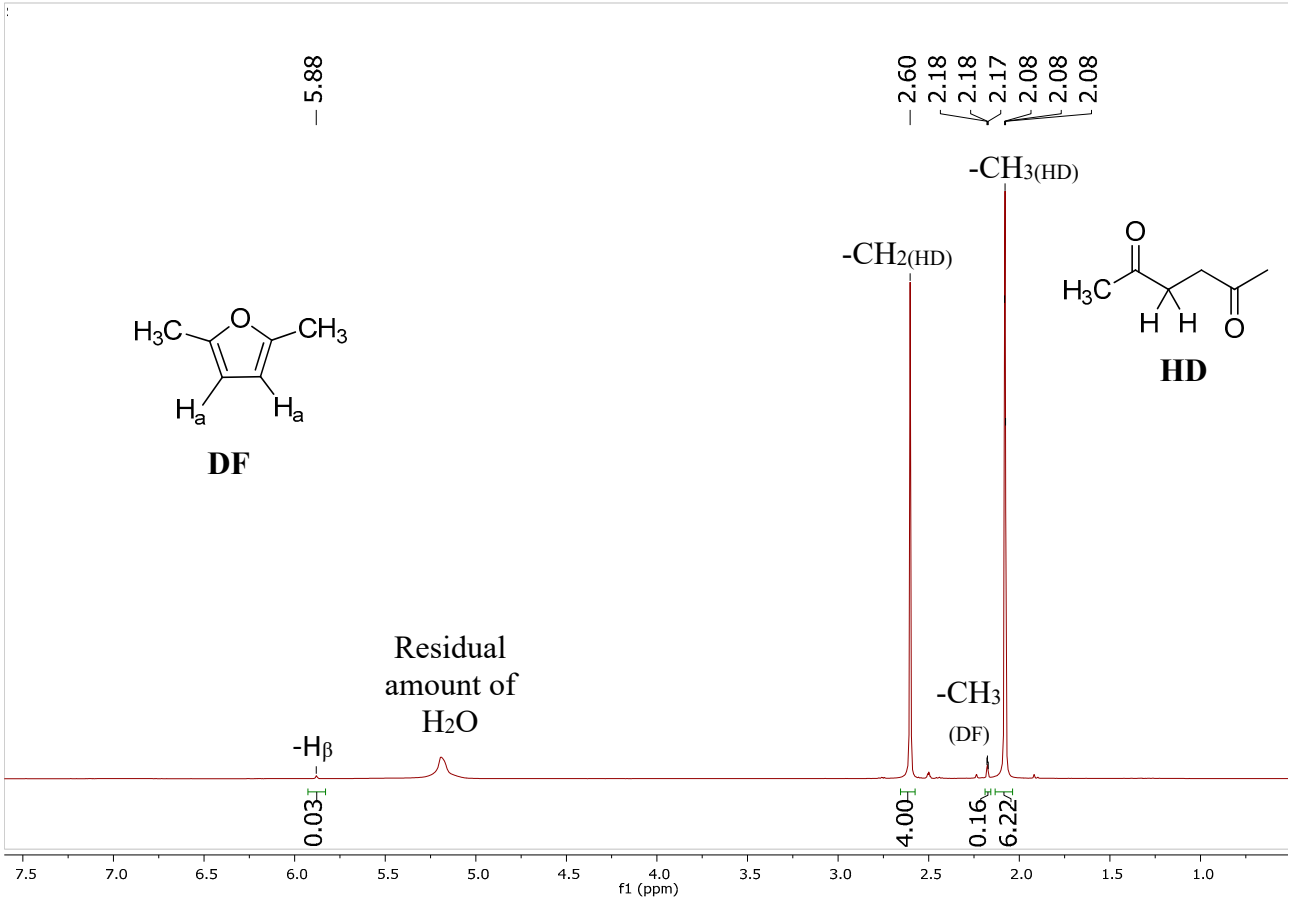



**Figure S.6.** $^{1}$H-NMR spectrum (400 MHz, DMSO-*d*$_6$) of the reaction between DF, water (ratio DF/$H_2O$ 1: 1.5) and sulfuric acid 15 mol%. DF was converted by 95% in HD; residual amount of water was observed at 5.19 ppm

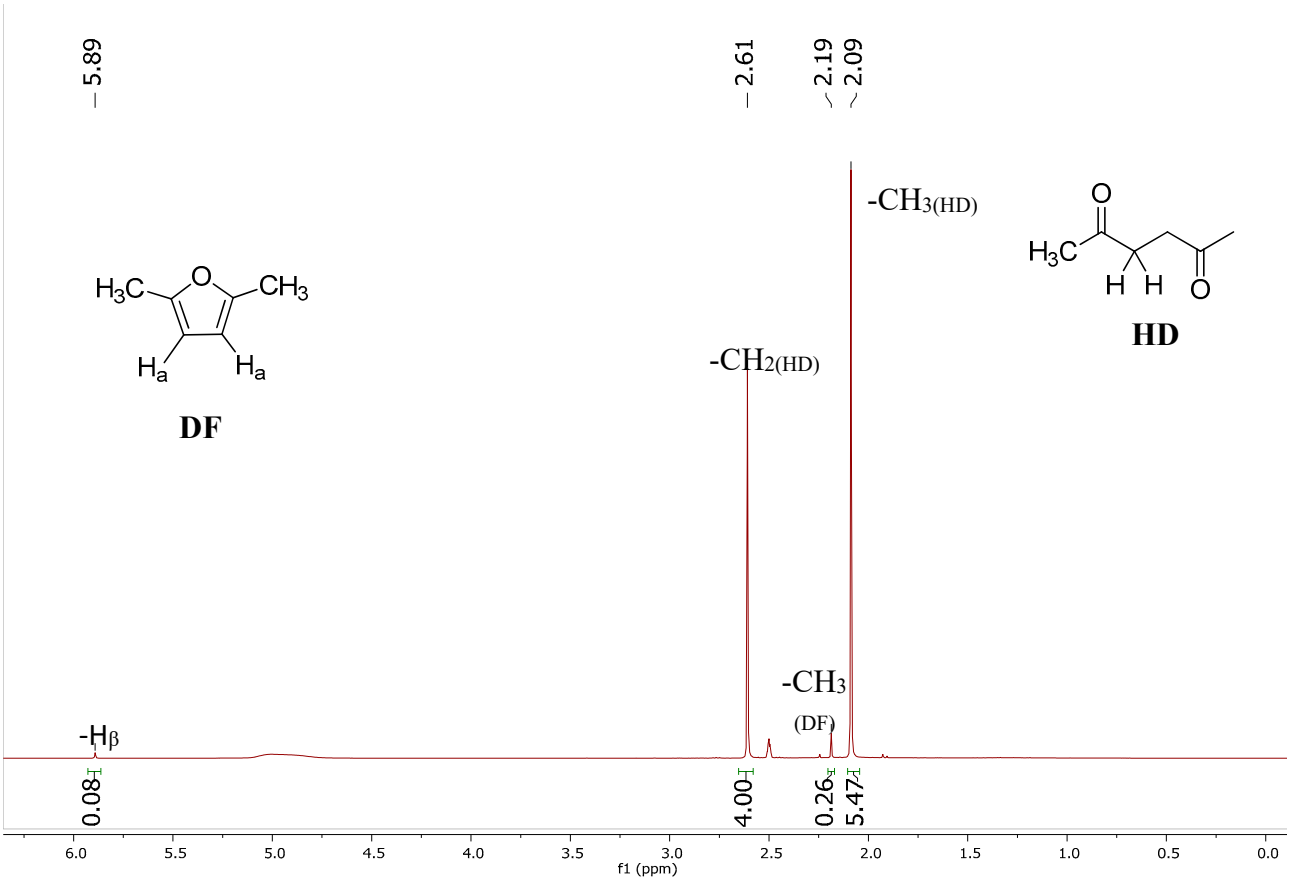



**Figure S.7**. $^{1}$H-NMR spectrum (400 MHz, DMSO-*d*$_6$) of the reaction between DF, water (ratio DF / $H_2O$ 1: 1) and sulfuric acid 15 mol%. DF was converted by 95% in HD

## S3. Screening of the amount of acid

The amount of sulfuric acid was investigated. The reactions were followed by NMR spectroscopy.

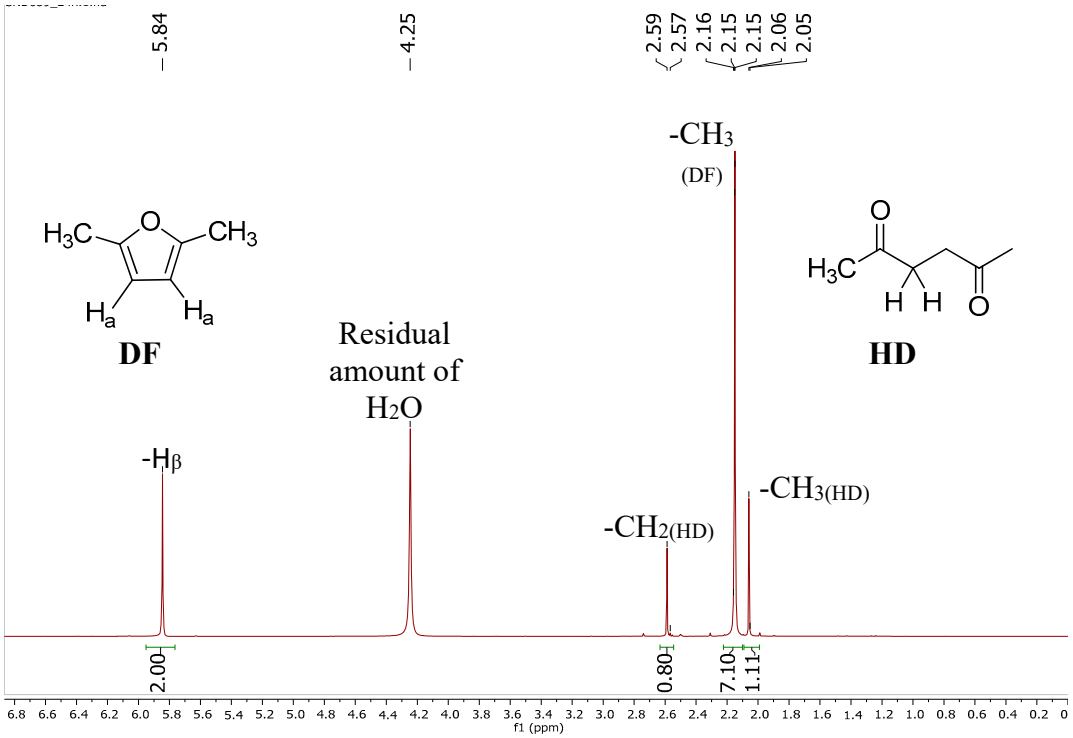



**Figure S.8.** $^{1}$H NMR spectrum (400 MHz, DMSO-$d_6$) of the reaction DF, water (ratio DF/$H_2O$ 1: 1) and 1.7 mol% of sulfuric acid. DF was converted by only 17% in HD.

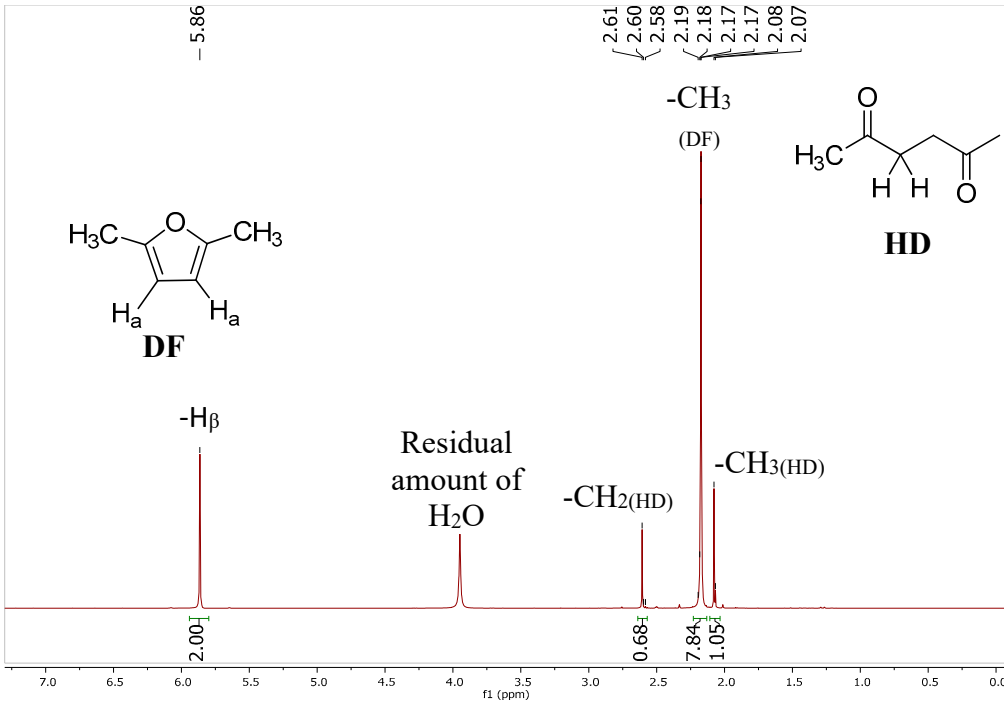



**Figure S.9.** $^{1}$H-NMR spectrum (400 MHz, DMSO-$d_6$) of the reaction between DF, water (molar ratio DF/$H_2O$ 1: 1) and catalitic amount of sulfuric acid. DF was converted by only 13% in HD.

**S4**. **Screening of the type of acids**

Different acids were investigated. The reactions were followed by NMR spectroscopy.

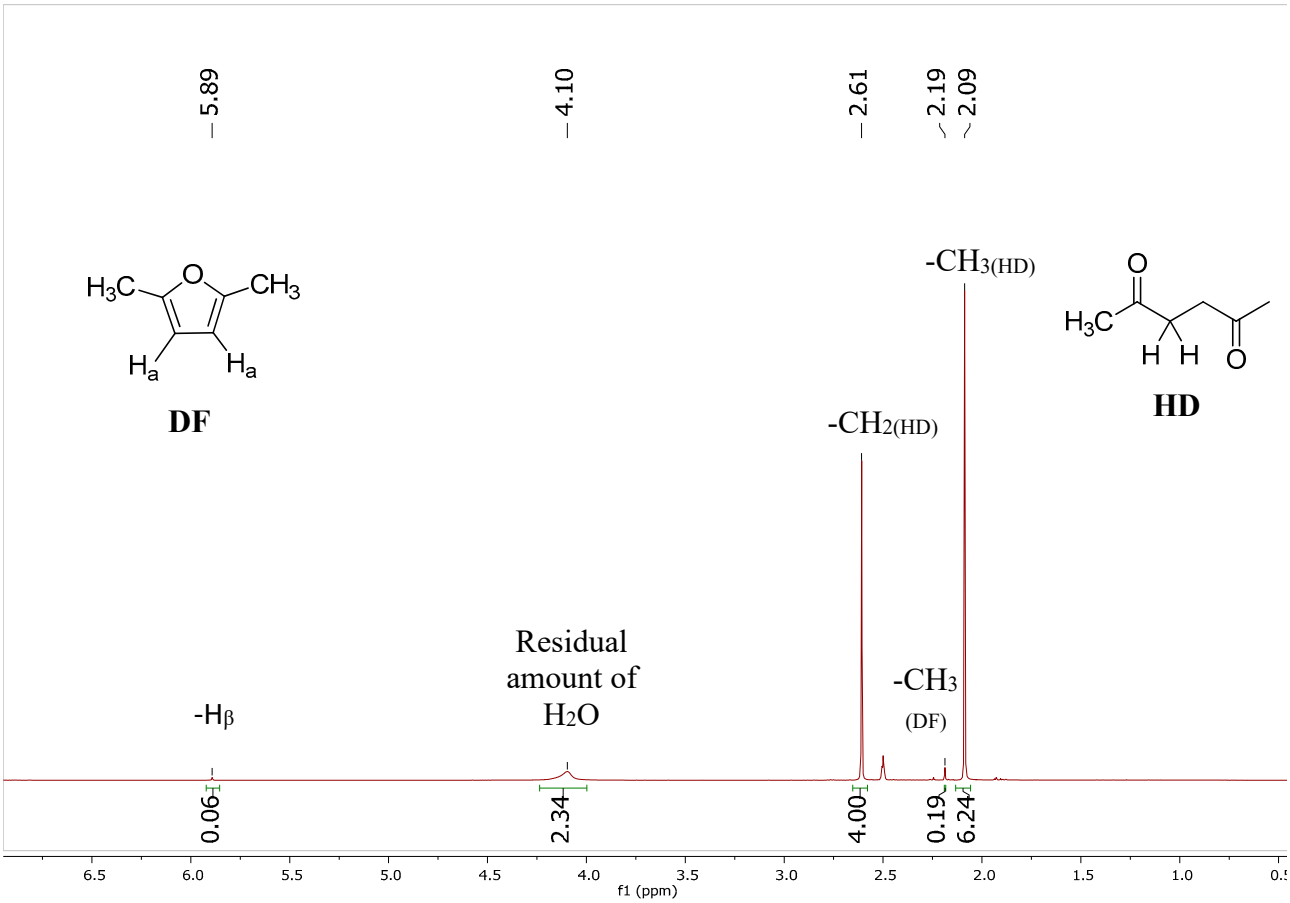



**Figure S.10.** $^{1}$H-NMR spectrum (400 MHz, DMSO-*d*$_6$) of the reaction between DF, water and 4 mol% of hydrochloridric acid. Residual water was observed at 4.10 ppm.

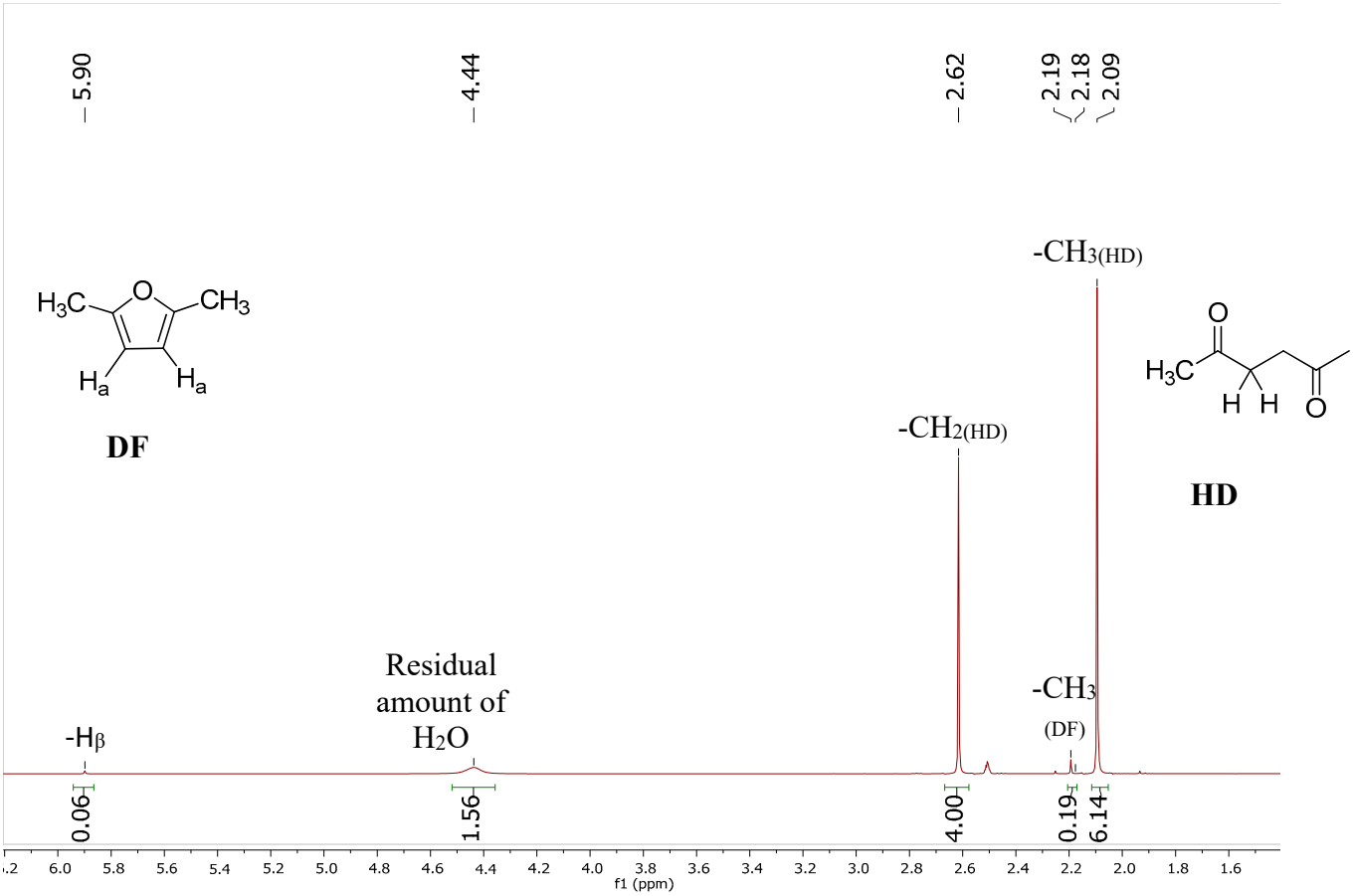



**Figure S.11.** $^{1}$H NMR spectrum (400 MHz, DMSO-*d*$_6$) of the reaction between DF, water and 4 mol% of hydrobromidric acid. Residual water was observed at 4.44 ppm.

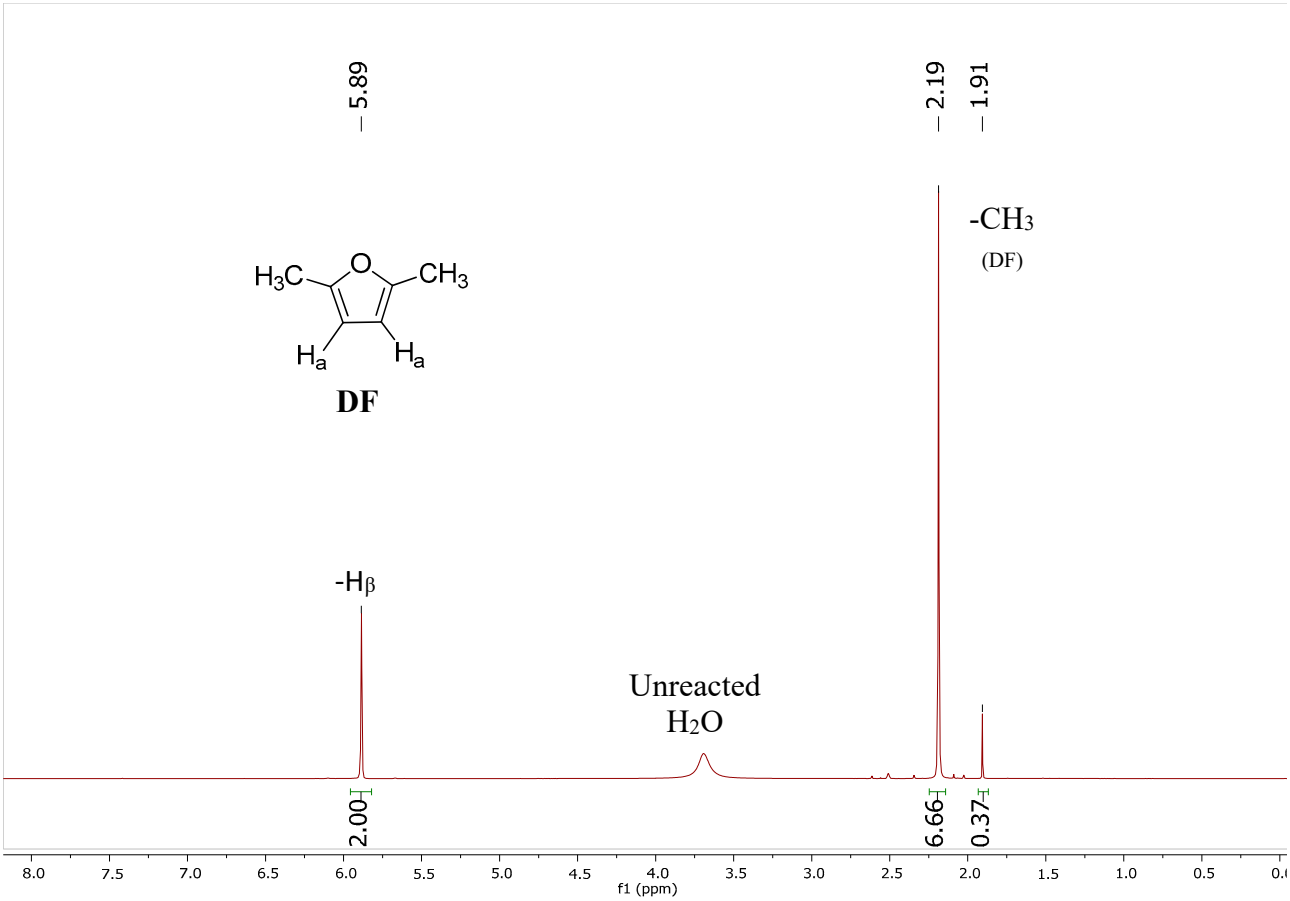
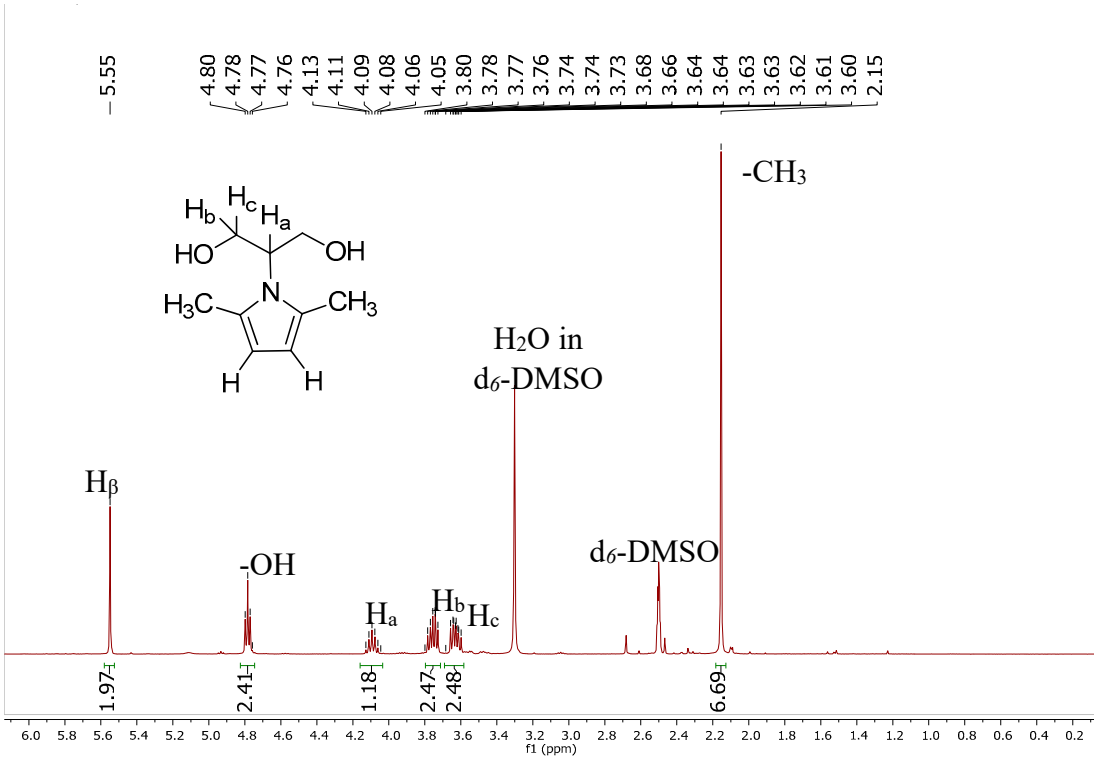



**Figure S.12.** $^{1}$H NMR spectrum (400 MHz, DMSO-*d*$_6$) of the reaction between DF, water and 4 mol% of acetic acid. DF was not converted in HD.

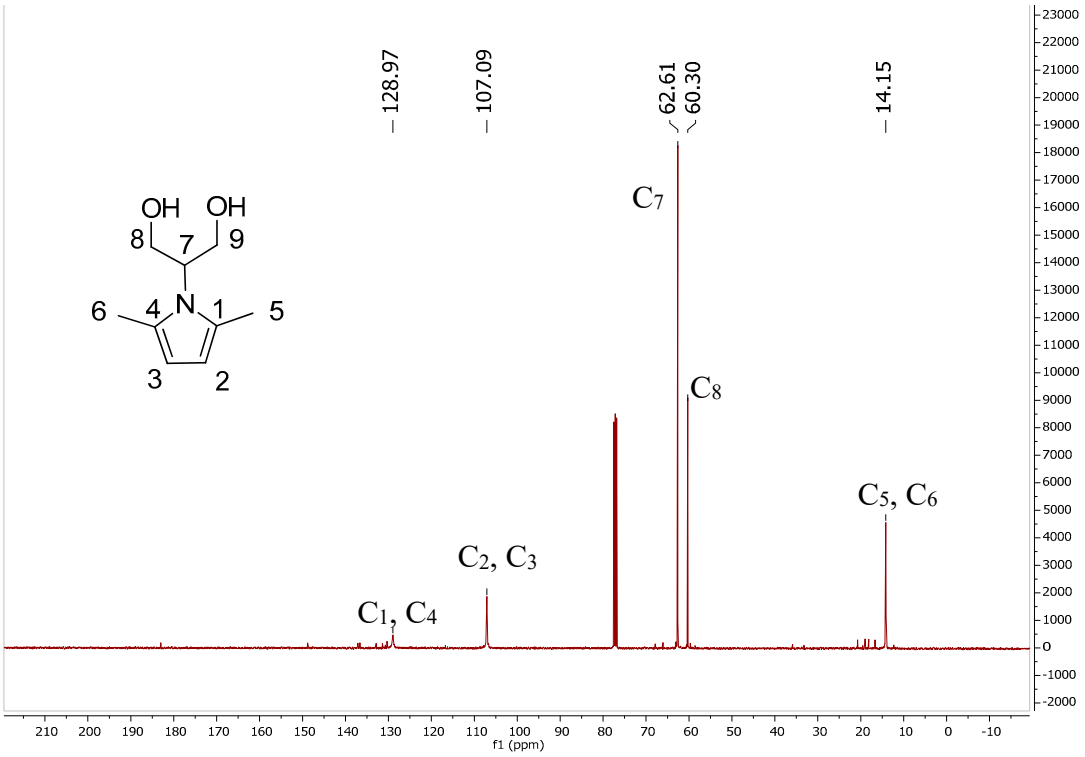
## S5. Characterization of bio-pyrroles

All pyrrole derivatives were characterized by NMR spectroscopy and further confirmed by Gas Chromatography Mass (GC-Mass) and Electrospray Ionization Mass (ESI-MS) spectrometries.

**3a)** ***2-(2,5-dimethyl-1H-pyrrol-1-yl)propane-1,3-diol*** **(**Serinol pyrrole, SP)




(A)




(B)

**Figure S.13** NMR spectra of (A) $^{1}$H (400 MHz, DMSO-*d*$_6$) and (B) $^{13}$C of 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)propane-1,3-diol (Serinol pyrrole, SP).

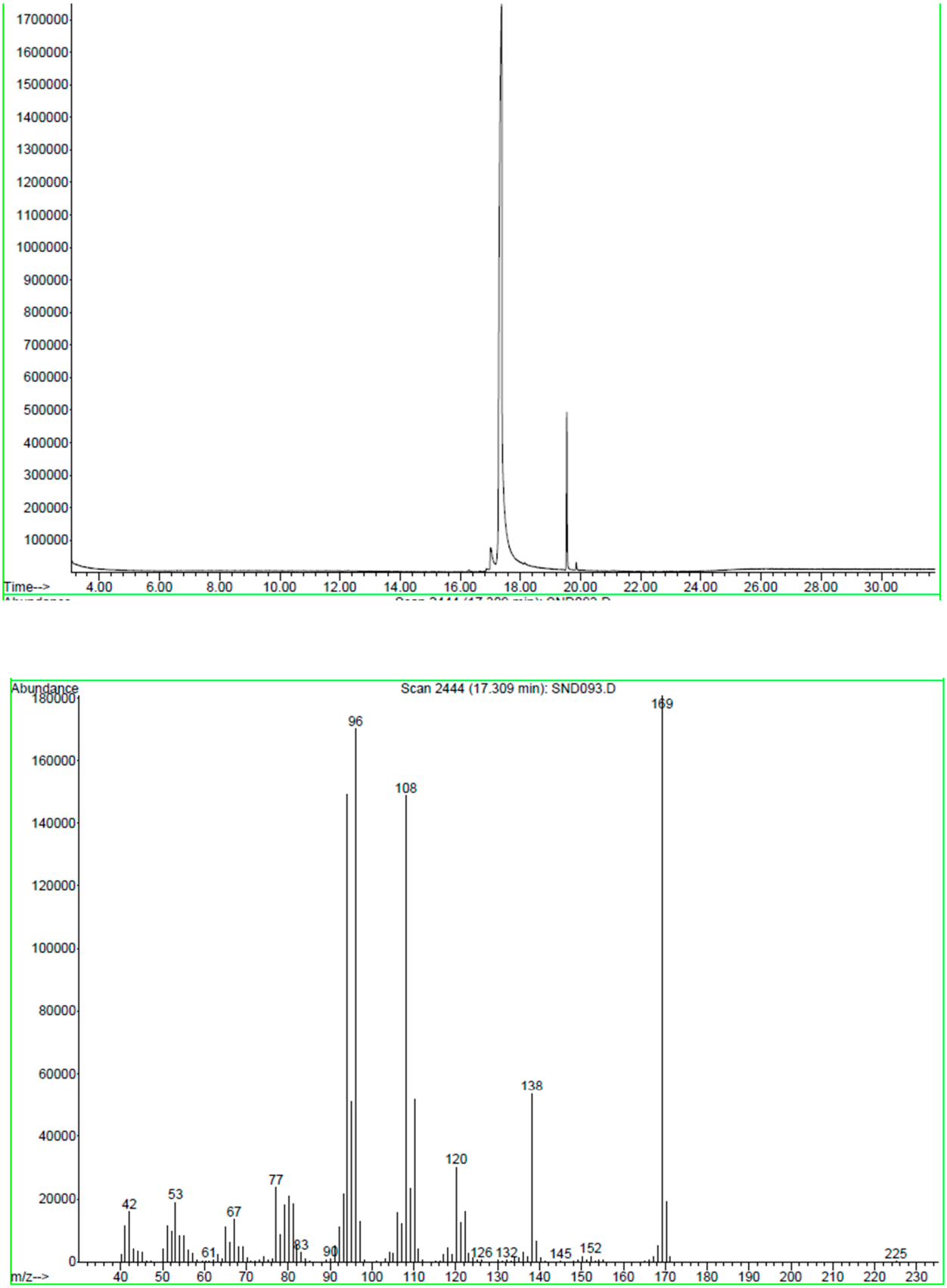



**Figure S.14:** GC-Mass chromatogram of Serinol pyrrole.

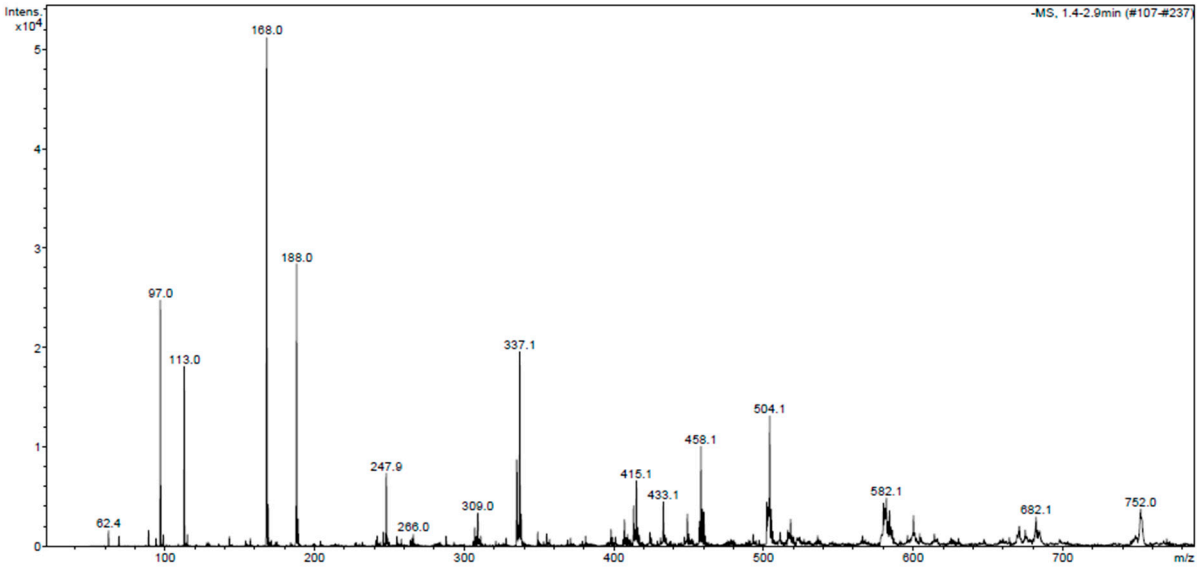
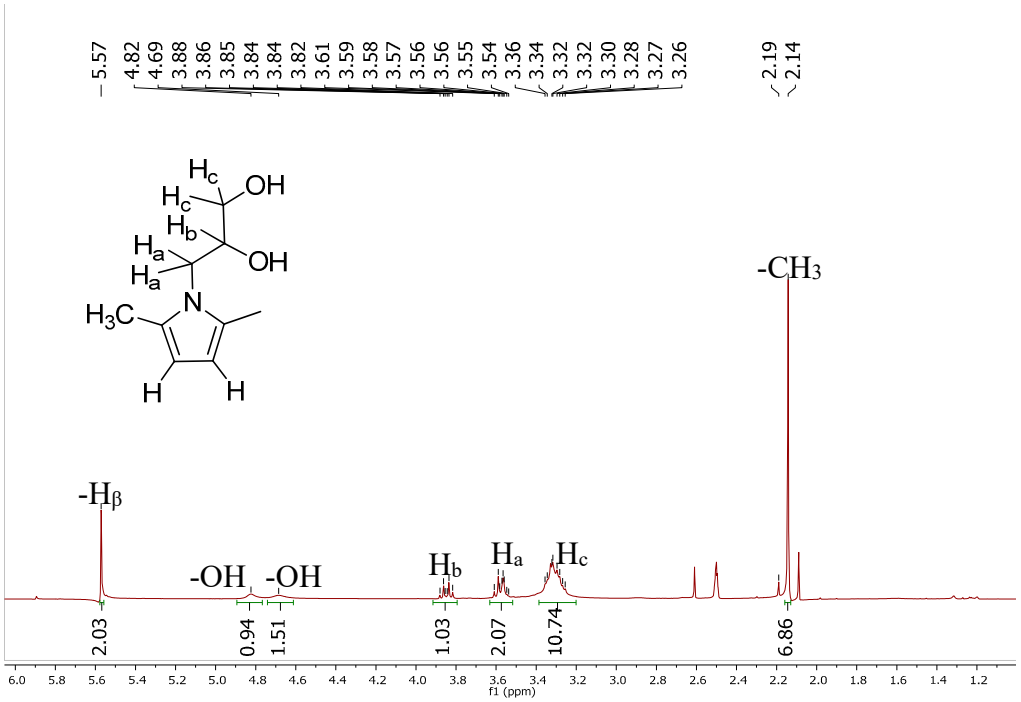
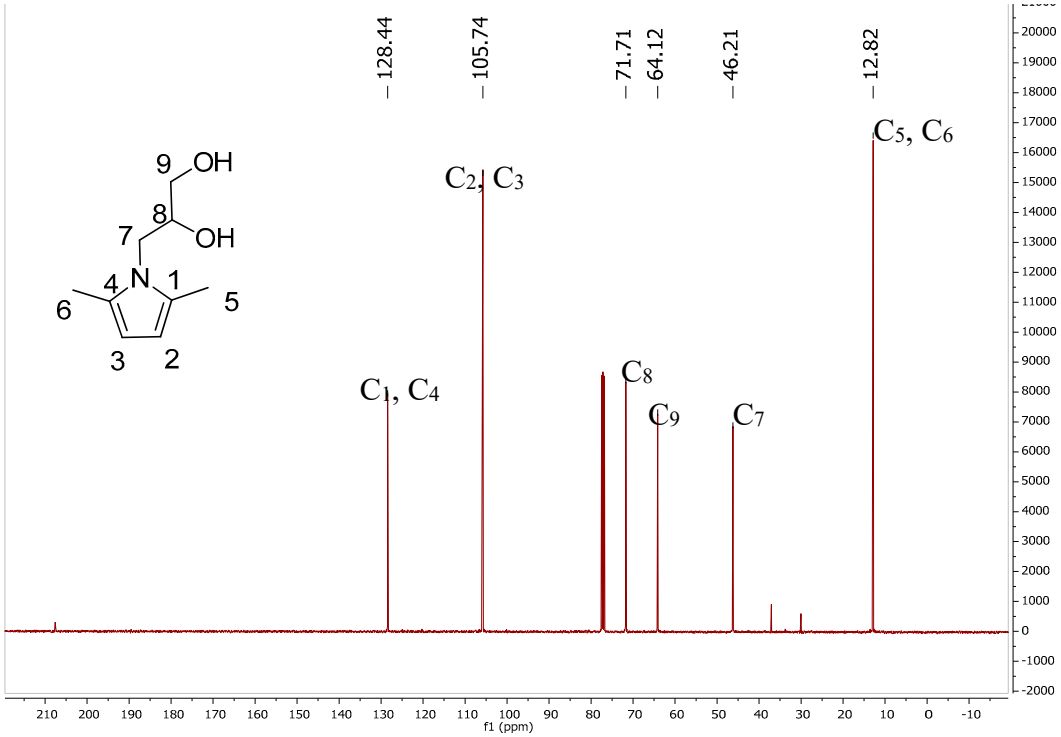



**Figure S.15.** Positive ESI-MS spectrum (1:100 MeOH) of Serinol pyrrole

**3b)** ***3-(2,5-dimethyl-1H-pyrrol-1-yl)propane-1,2-diol*** (iso-SP)




(A)




(B)

**Figure S.16.** NMR spectra of (A) $^{1}$H (400 MHz, DMSO-*d*$_6$) and (B) $^{13}$C of 3-(2,5-dimethyl-1*H*-pyrrol-1-yl)propane-1,2-diol (iso-Serinol Pyrrole).

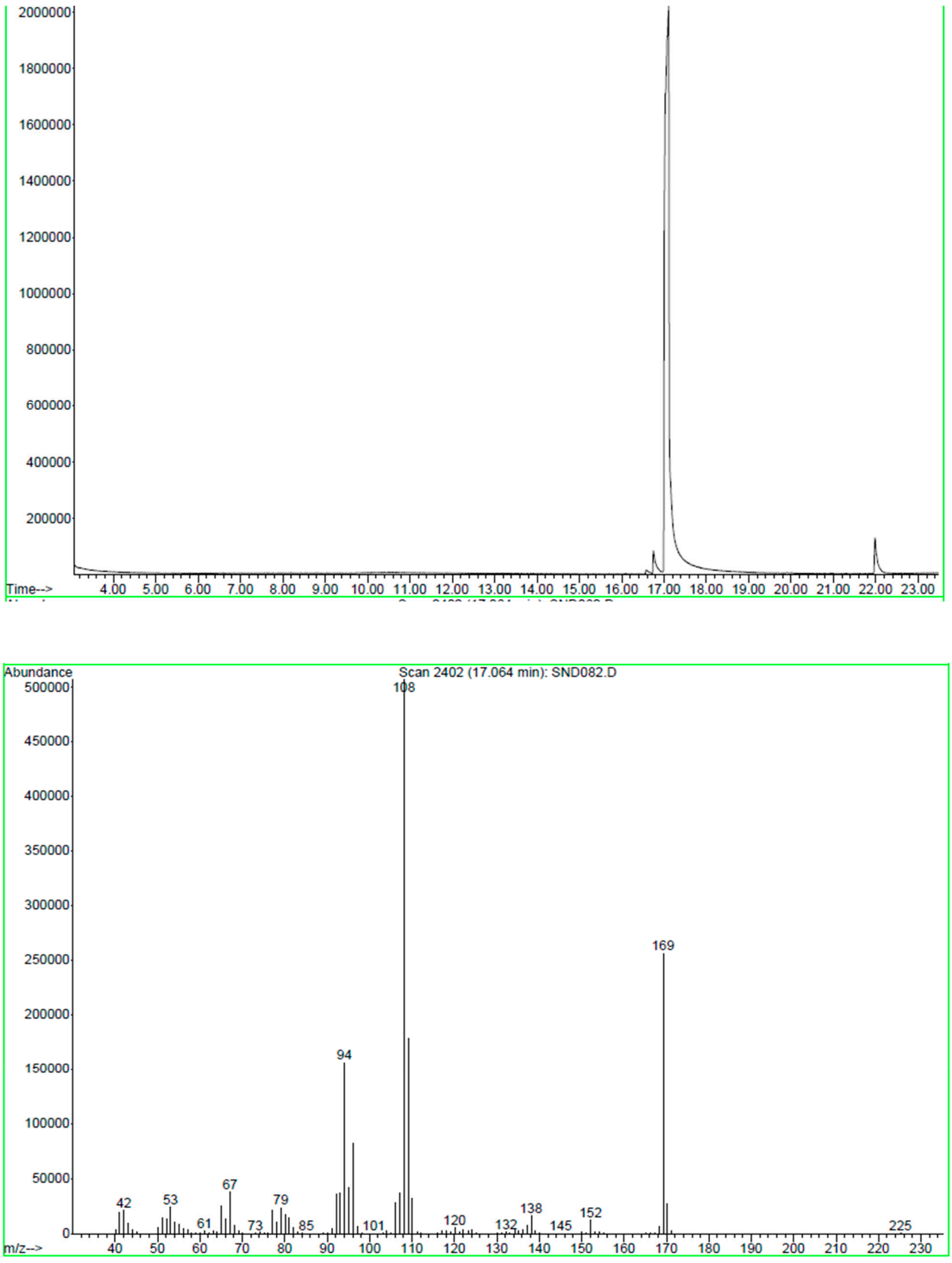



**Figure S.17:** GC-Mass chromatogram of 3-(2,5-dimethyl-1*H*-pyrrol-1-yl)propane-1,2-diol

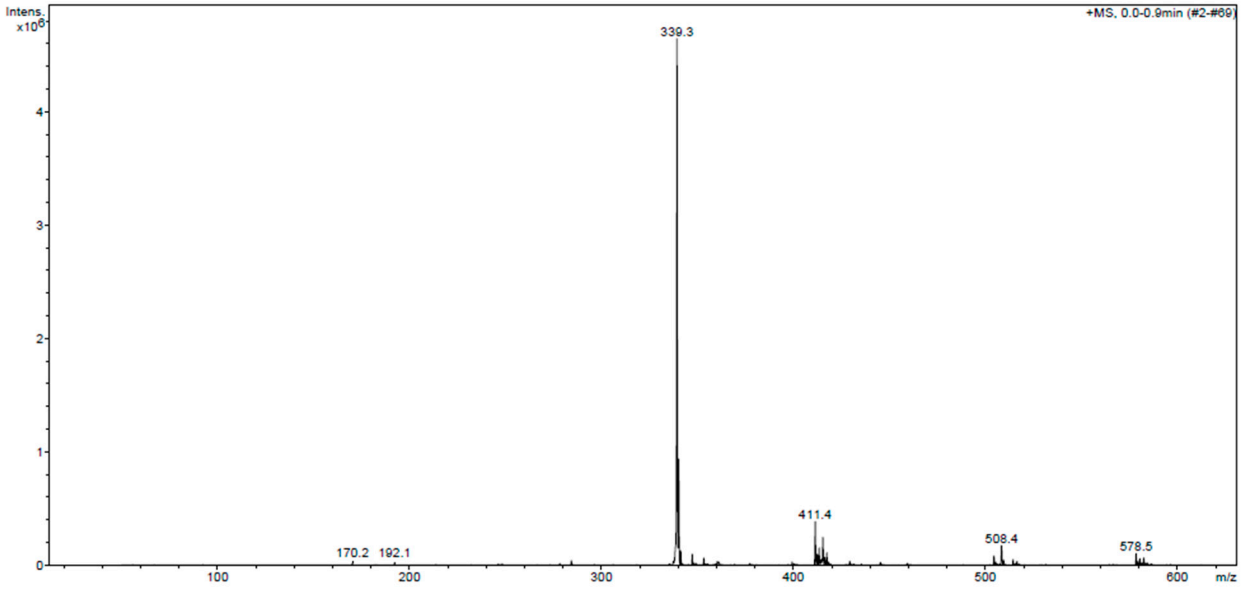
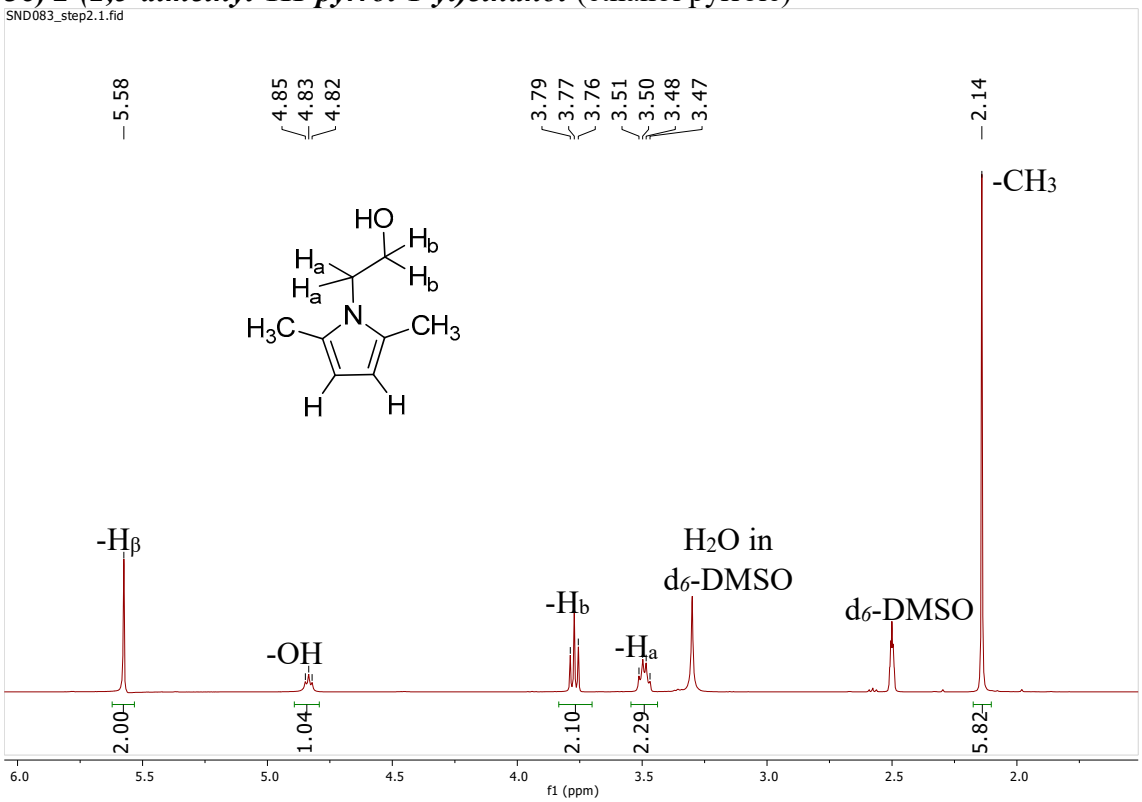
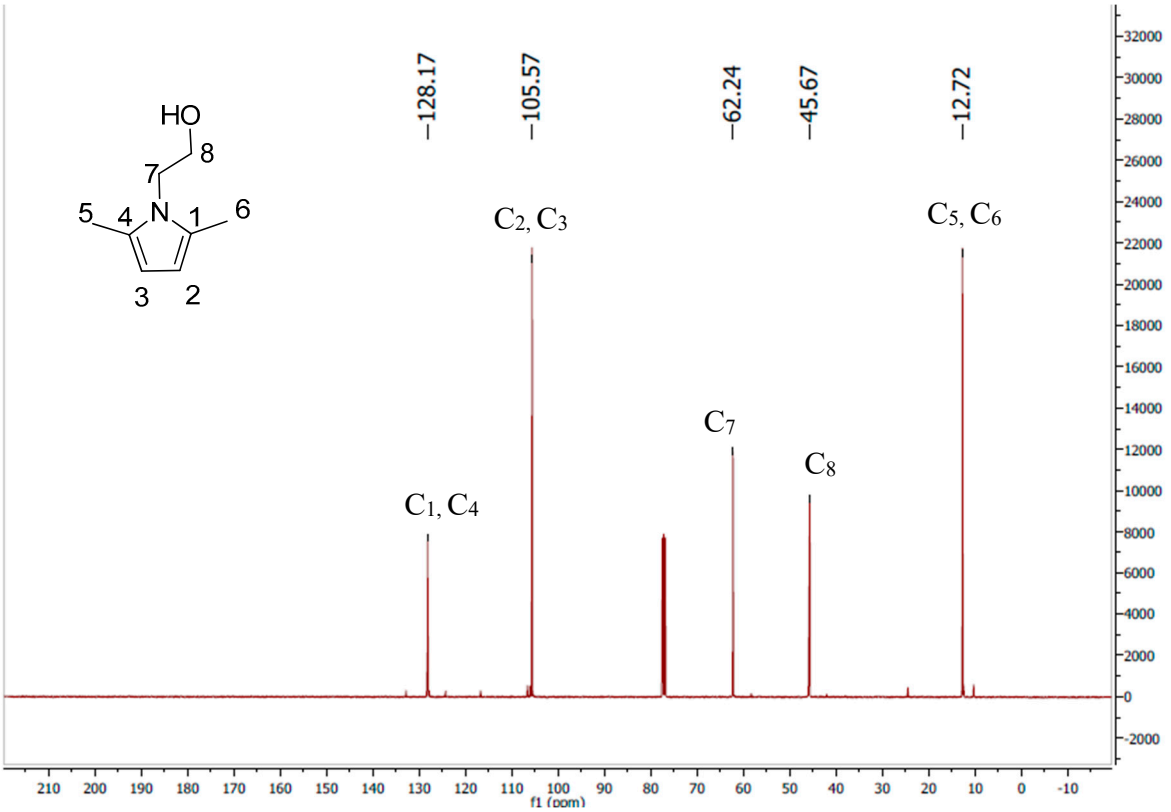



**Figure S.18**. Positive ESI-MS spectrum (1:100 MeOH) of 3-(2,5-dimethyl-1*H*-pyrrol-1-yl)propane-1,2-diol

**3c) 2-*(2,5-dimethyl-1H-pyrrol-1-yl)ethanol*** (ethanol pyrrole)




(A)




(B)

**Figure S.19.** NMR spectra of (A) $^{1}$H (400 MHz, DMSO-*d*$_6$) and (B) $^{13}$C of 2-(2,5-dimethyl-1*H*-pyrrol-1-yl)ethanol (ethanol pyrrole)

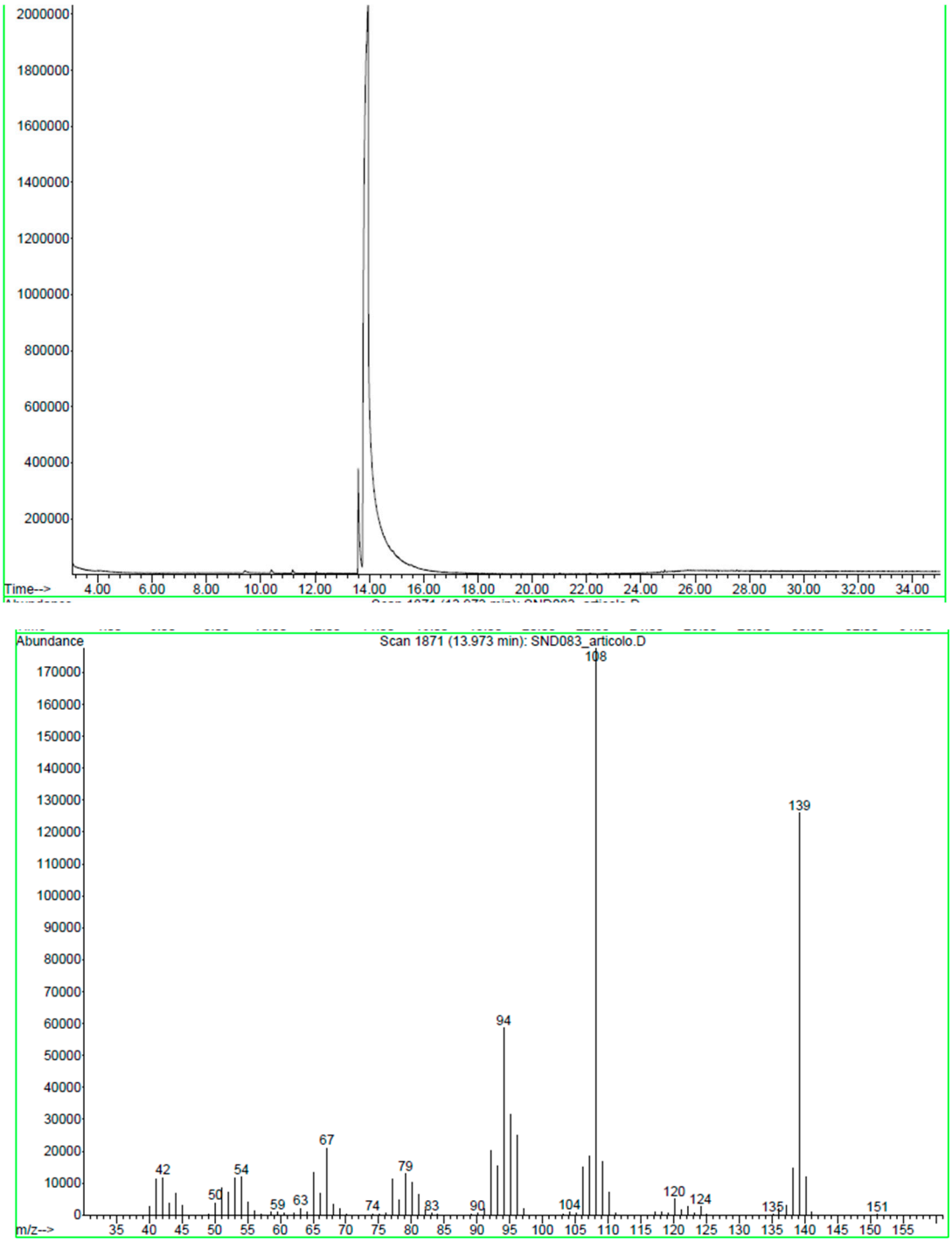



**Figure S.20.** GC-Mass chromatogram of -(2,5-dimethyl-1*H*-pyrrol-1-yl)ethanol (ethanol pyrrole)

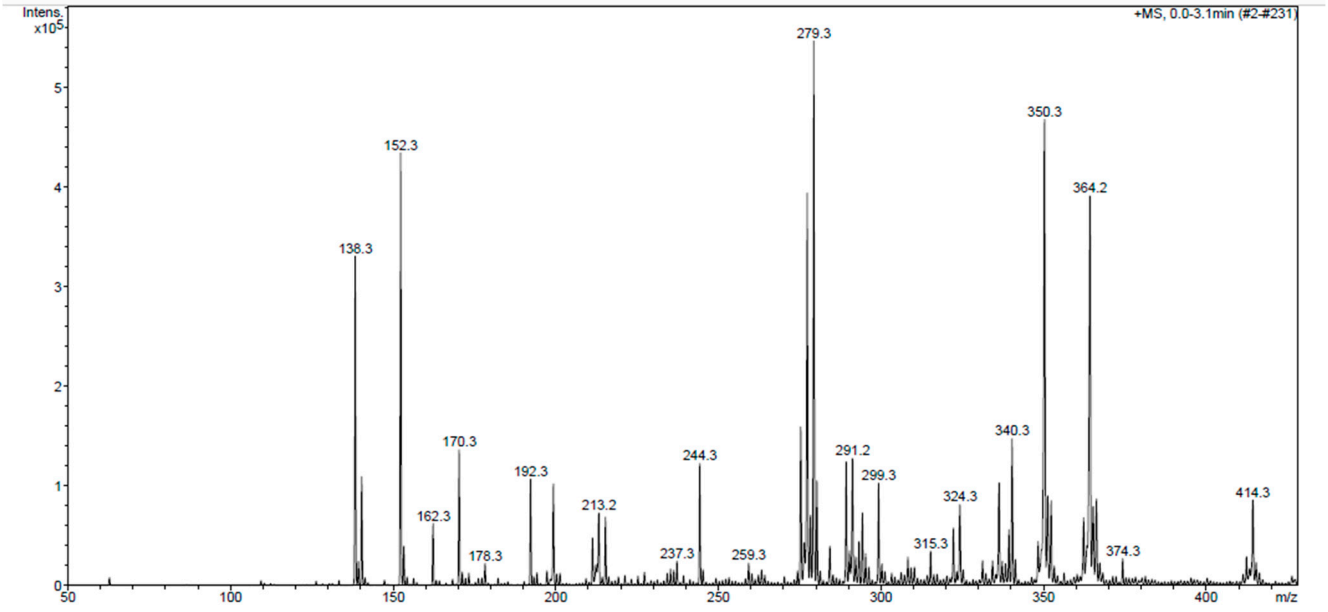



**Figure S.21.** Positive ESI-MS spectrum (1:100 MeOH) of ethanol pyrrole.

**3d) 1,2,5-*trimethyl-1H-pyrrole*** (trimethyl pyrrole)

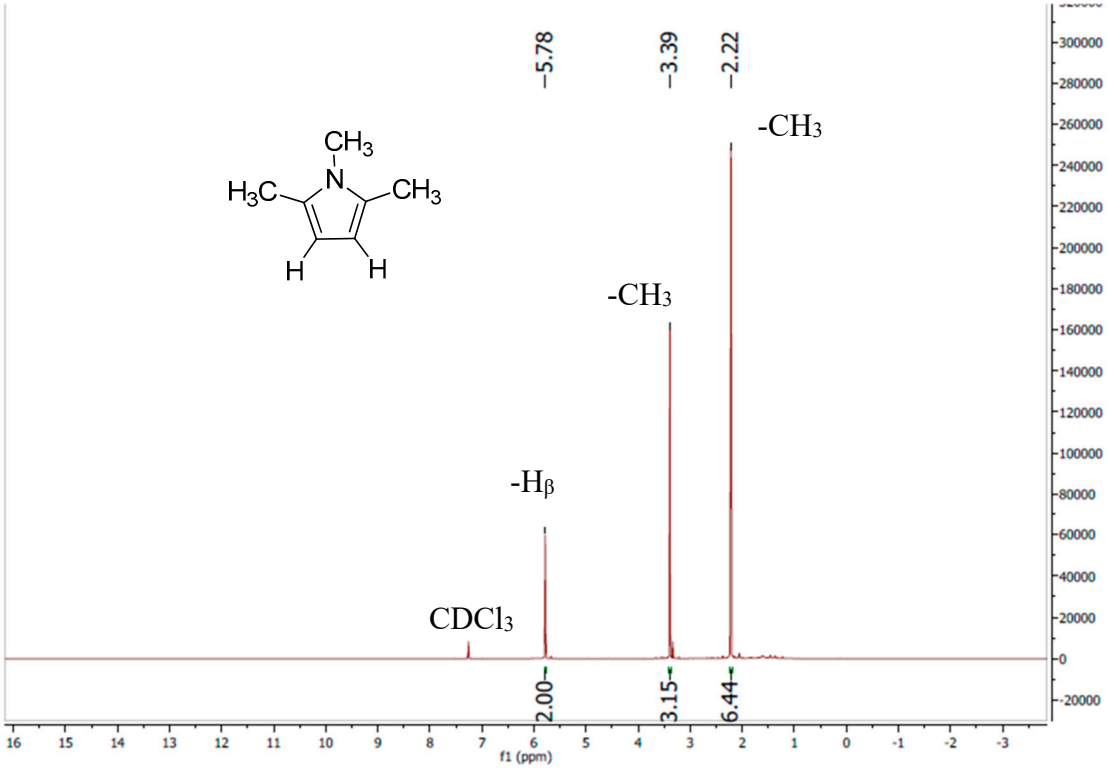
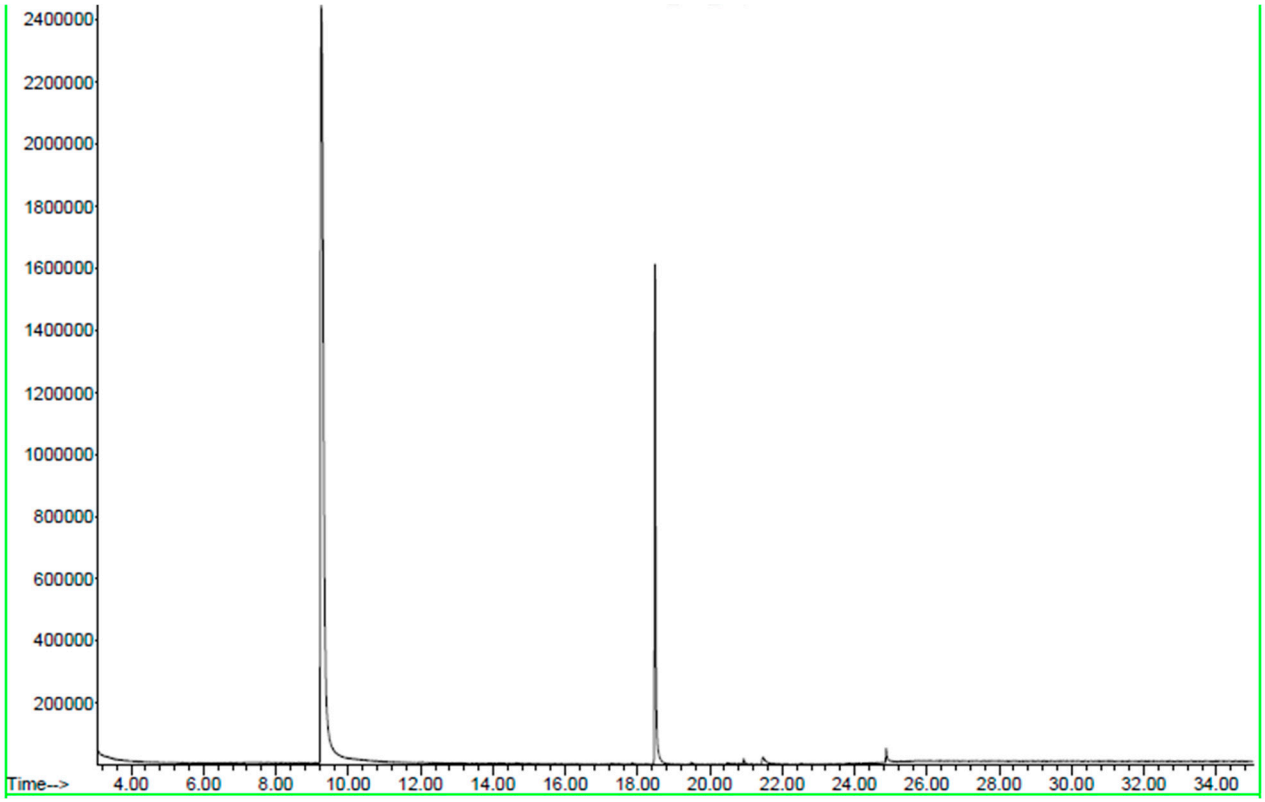



**Figure S.22.** NMR spectra of (A) $^{1}$H (400 MHz, $CDCl_3$) and (B) $^{13}$C of 1,2,5-trimethyl-1*H*-pyrrole (trimethyl pyrrole).



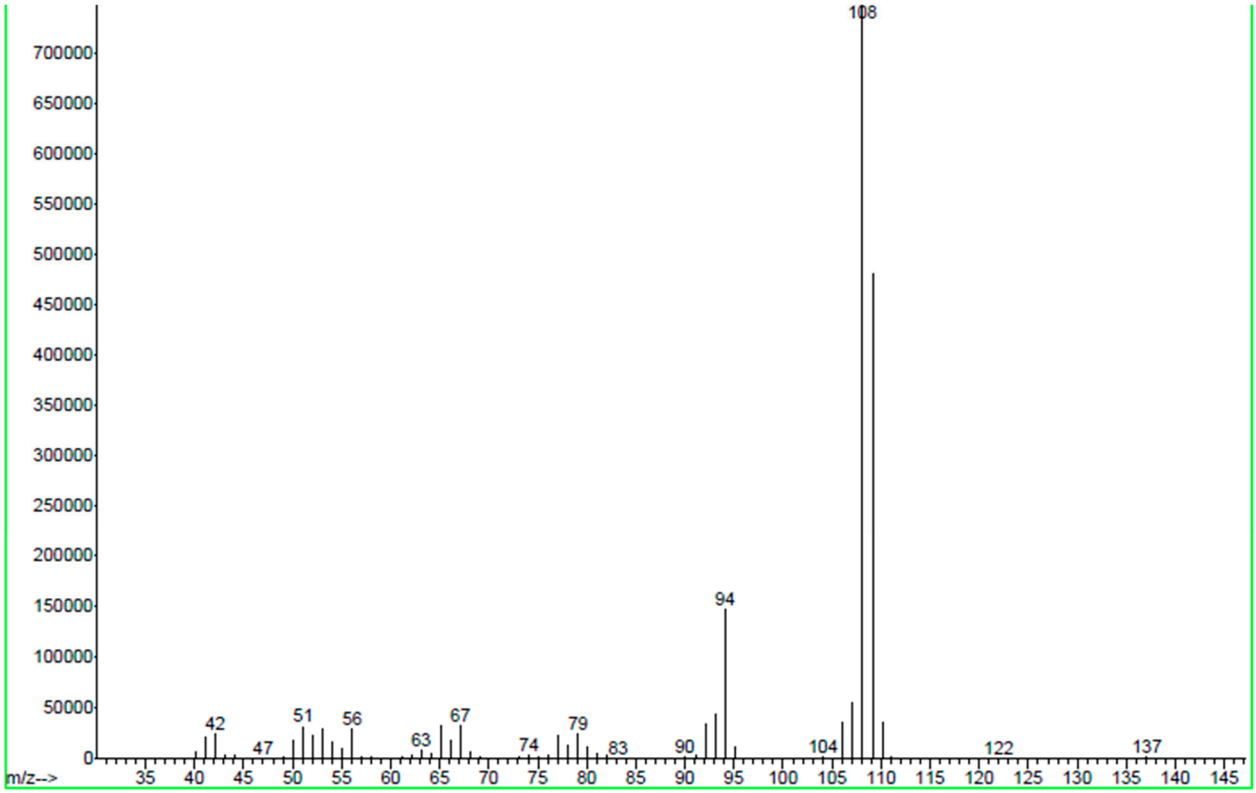




**Figure S.23:** GC-Mass chromatogram of trimethyl pyrrole.

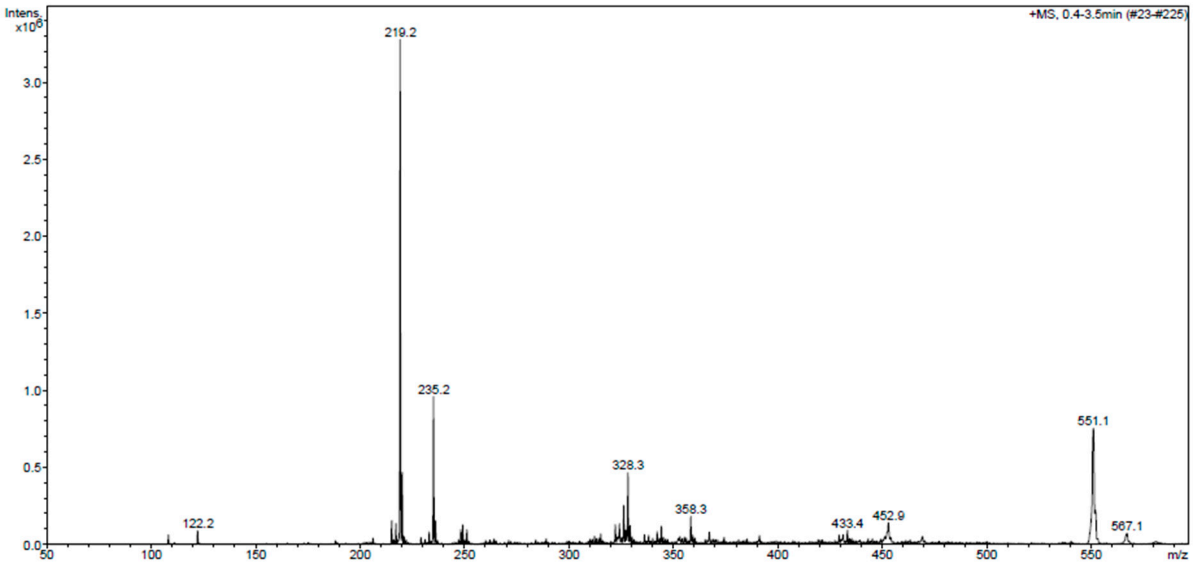
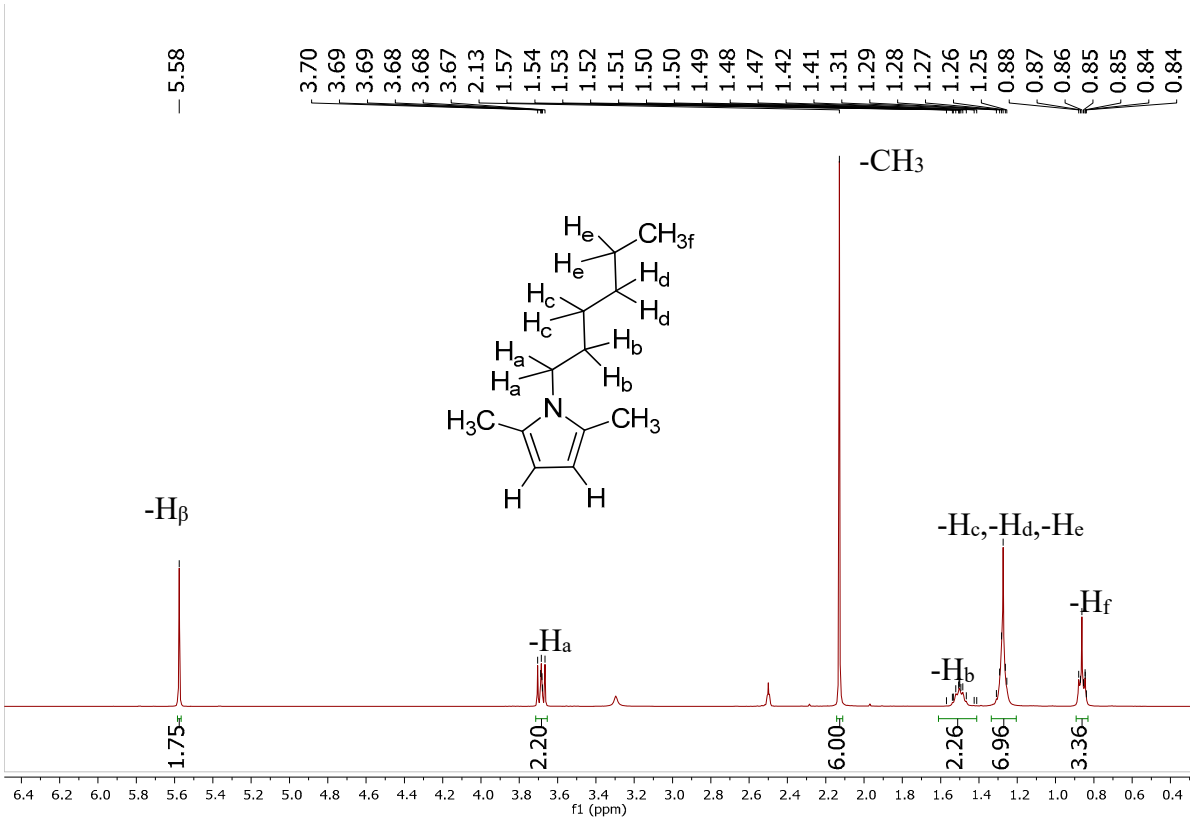
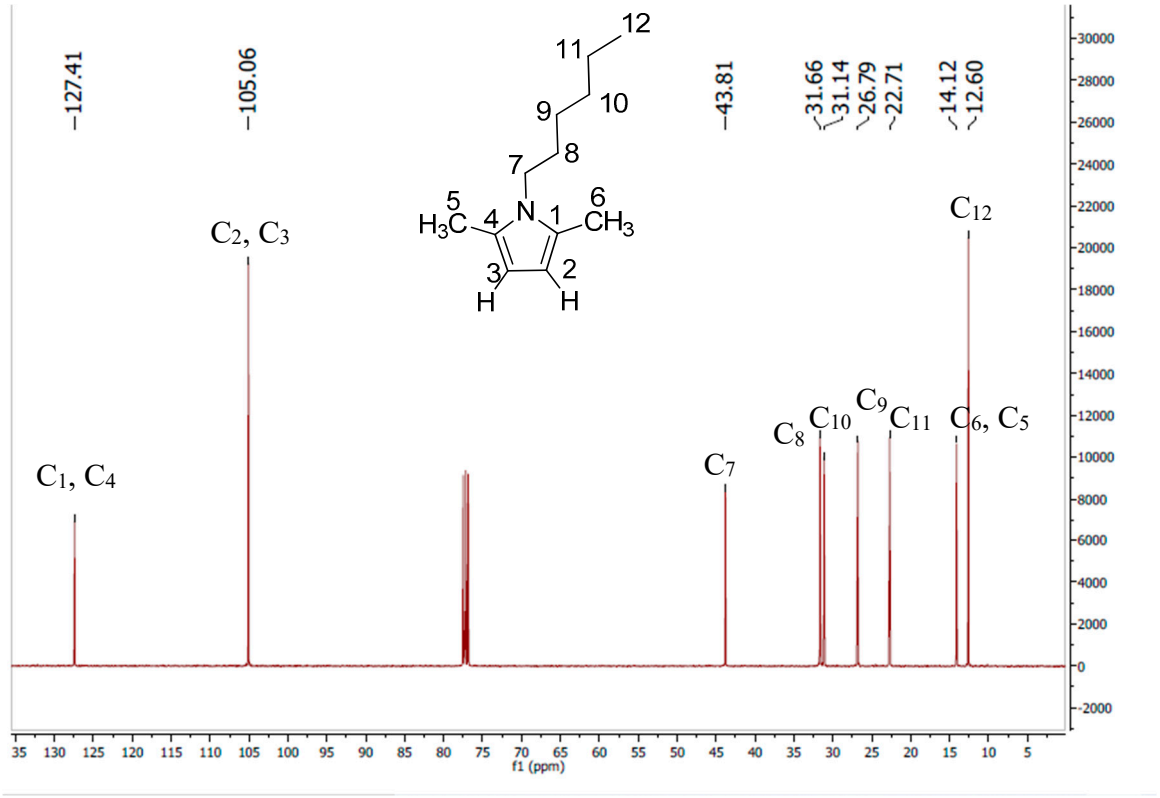



**Figure S.24.** Positive ESI-MS spectrum (1:100 MeOH) of trimethyl pyrrole

**3e)** ***1-hexyl-2,5-dimethyl-1H-pyrrole*** (hexylpyrrole).




(A)




(B)

**Figure S.25.** NMR spectra of (A) $^{1}$H (400 MHz, DMSO-*d*$_6$) and (B) $^{13}$C of 1-hexyl-2,5-dimethyl-1*H*-pyrrole (hexylpyrrole).

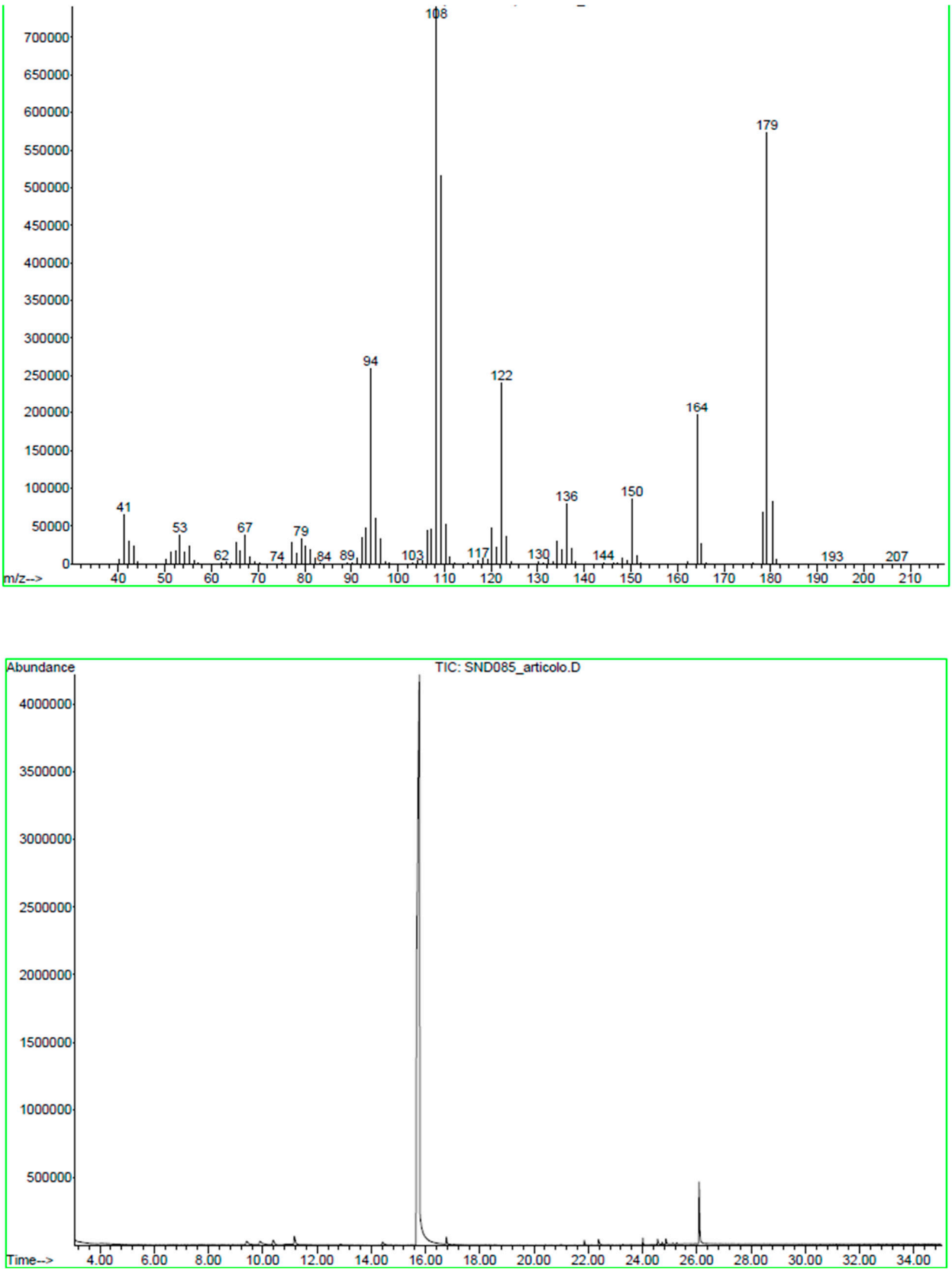



**Figure S.26.** GC-Mass chromatogram of 1-hexyl-2,5-dimethyl-1*H*-pyrrole

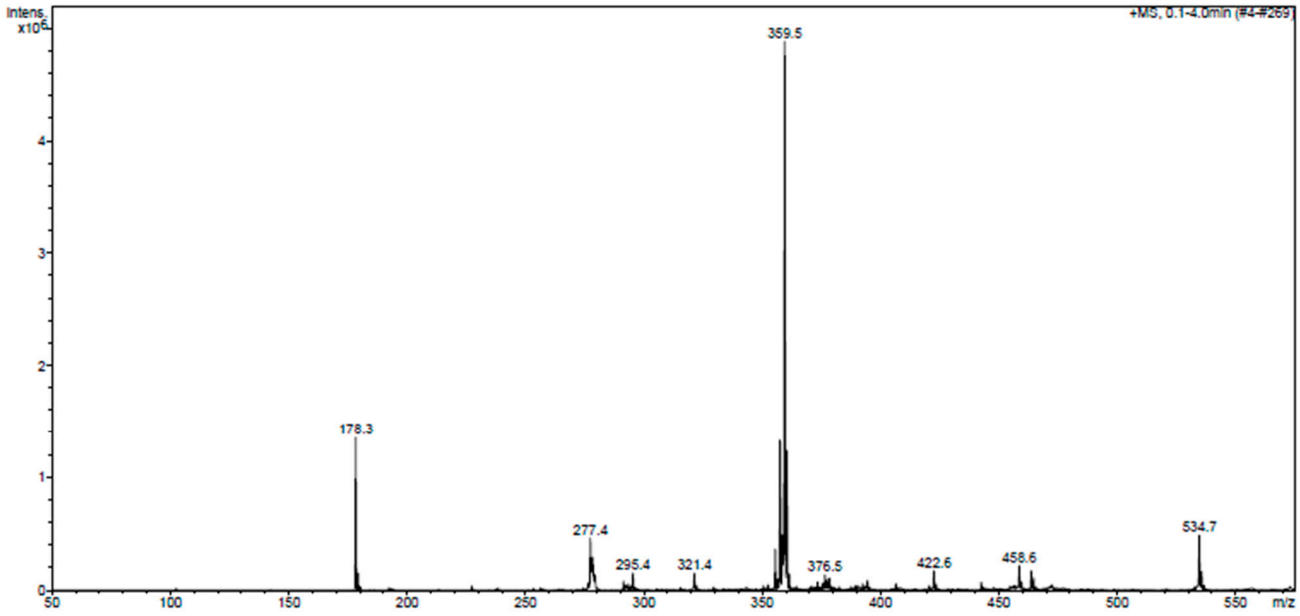
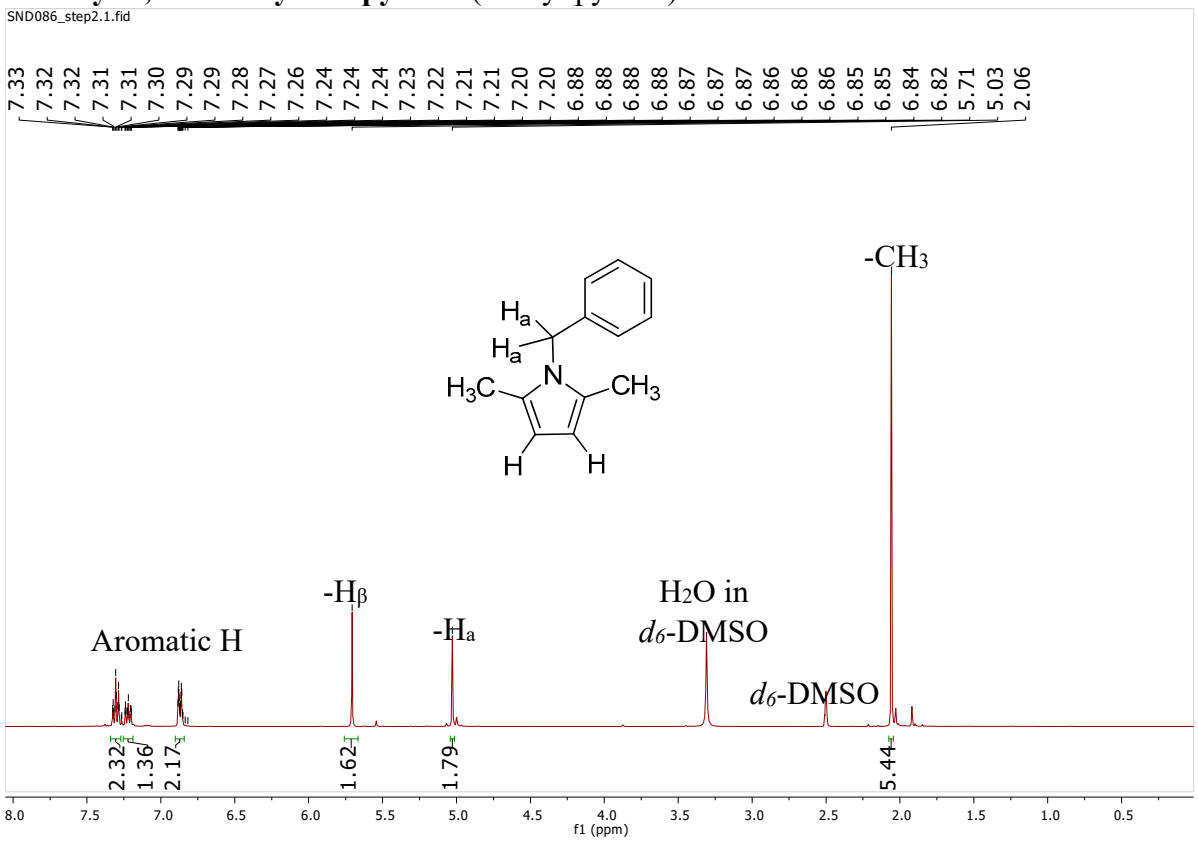
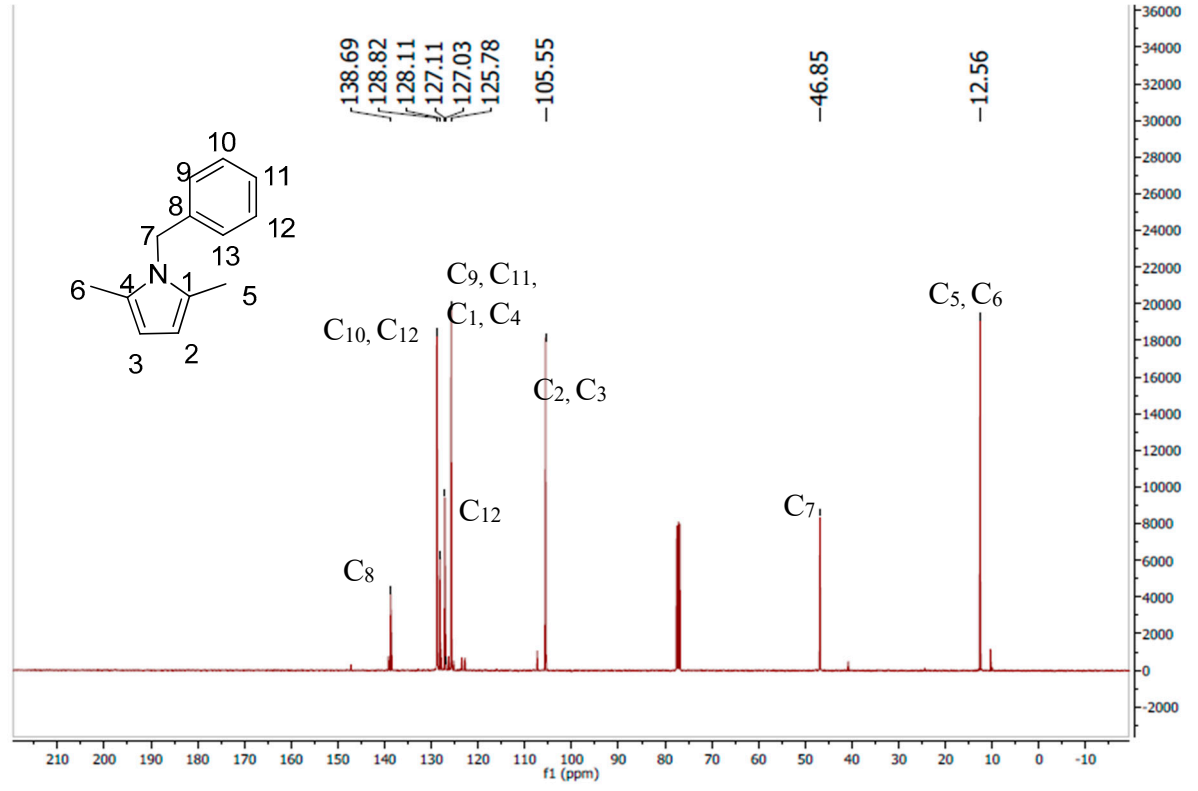



**Figure S.27** Positive ESI-MS spectrum (1:100 MeOH) of 1-hexyl-2,5-dimethyl-1*H*-pyrrole

**3f) 1-benzyl-2,5-dimethyl-1*H*-pyrrole** (benzyl pyrrole)




(A)




(B)

**Figure S.28.** NMR spectra of (A) $^{1}$H (400 MHz, DMSO-*d*$_6$) and (B) $^{13}$C of 1-benzy-l,2,5-dimethyl-1*H*-pyrrole (benzyl pyrrole)

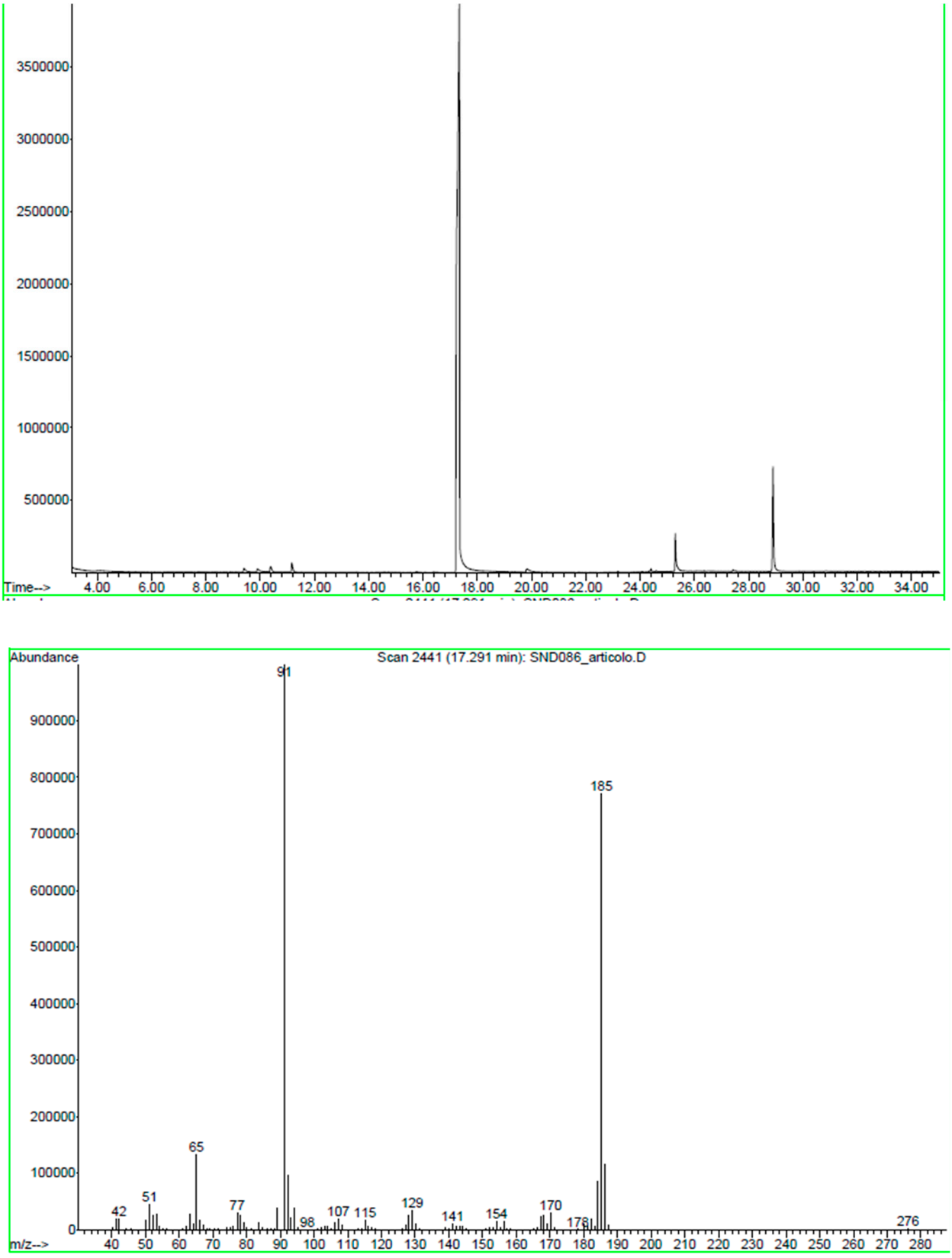



**Figure S.29.** GC-Mass chromatogram of 1-benzy-l,2,5-dimethyl-1*H*-pyrrole (benzyl pyrrole)

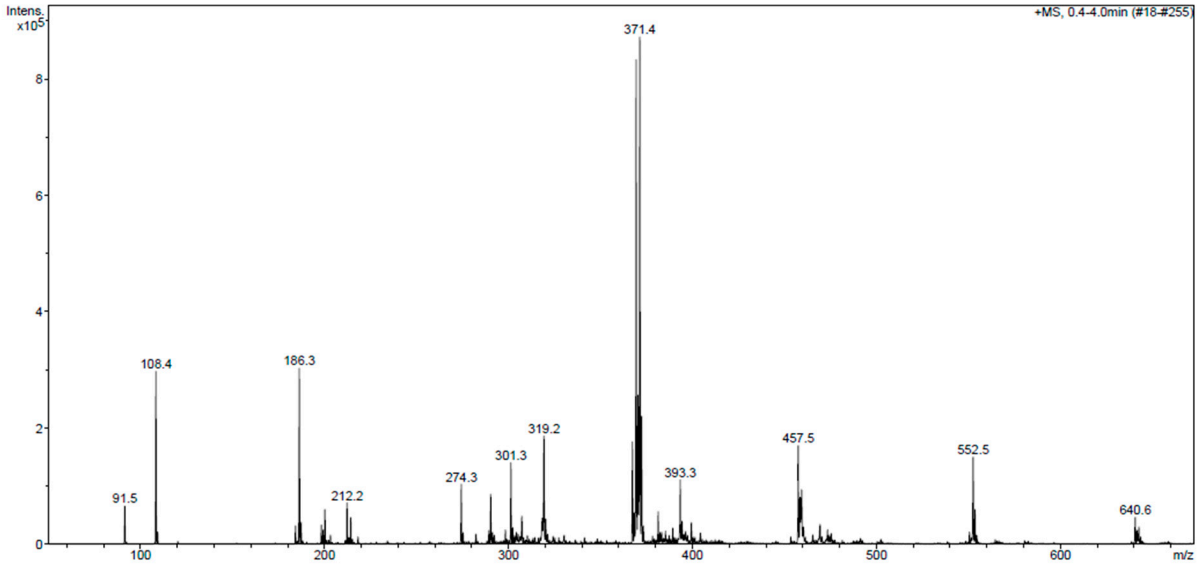
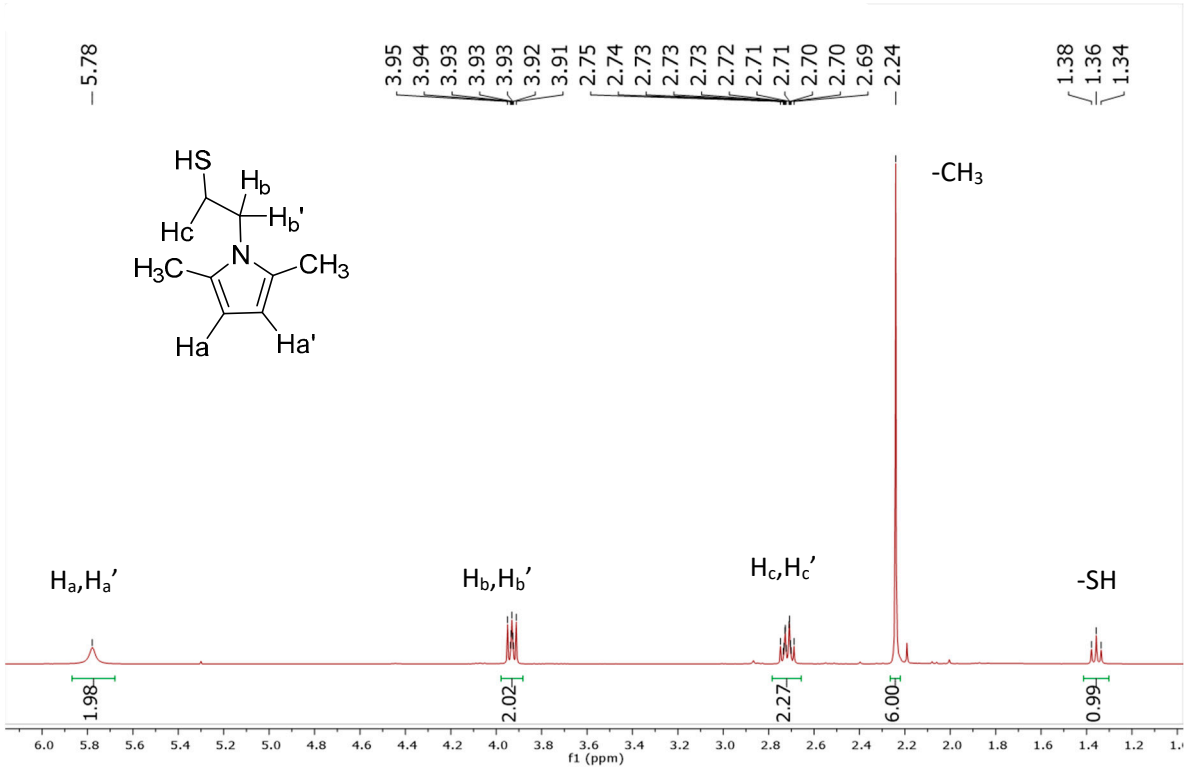
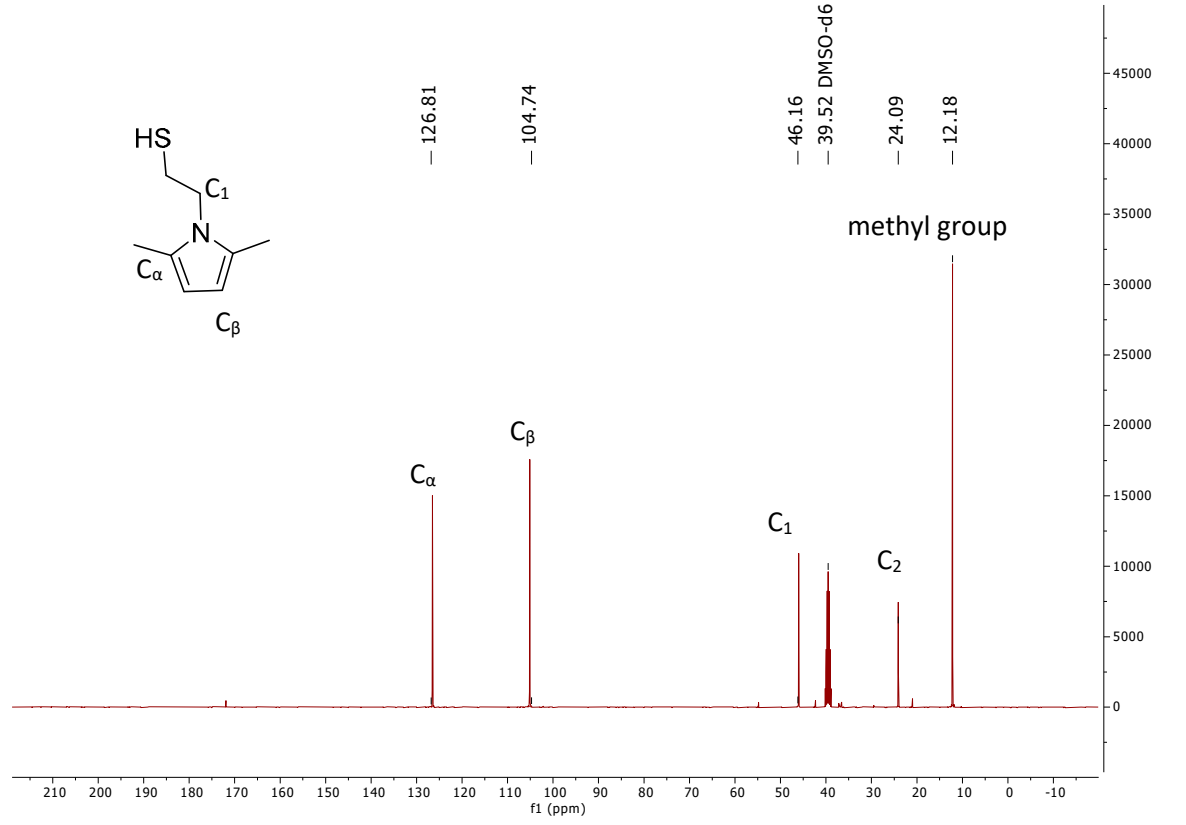



**Figure S.30.** Positive ESI-MS spectrum (1:100 MeOH) of 1-benzy-l,2,5-dimethyl-1*H*-pyrrole (benzyl pyrrole)

3g) **2-(2,5-dimethyl-1H-pyrrol-1-yl)ethane-1-thiol** *(SHP)*




(A)




(B)

**Figure S.31.** (A) $^{1}$H-NMR and (B) $^{13}$C-NMR spectra of SHP performed in *d*$_6$-DMSO

**GC-Mass analysis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)ethane-1-thiol** (SHP)

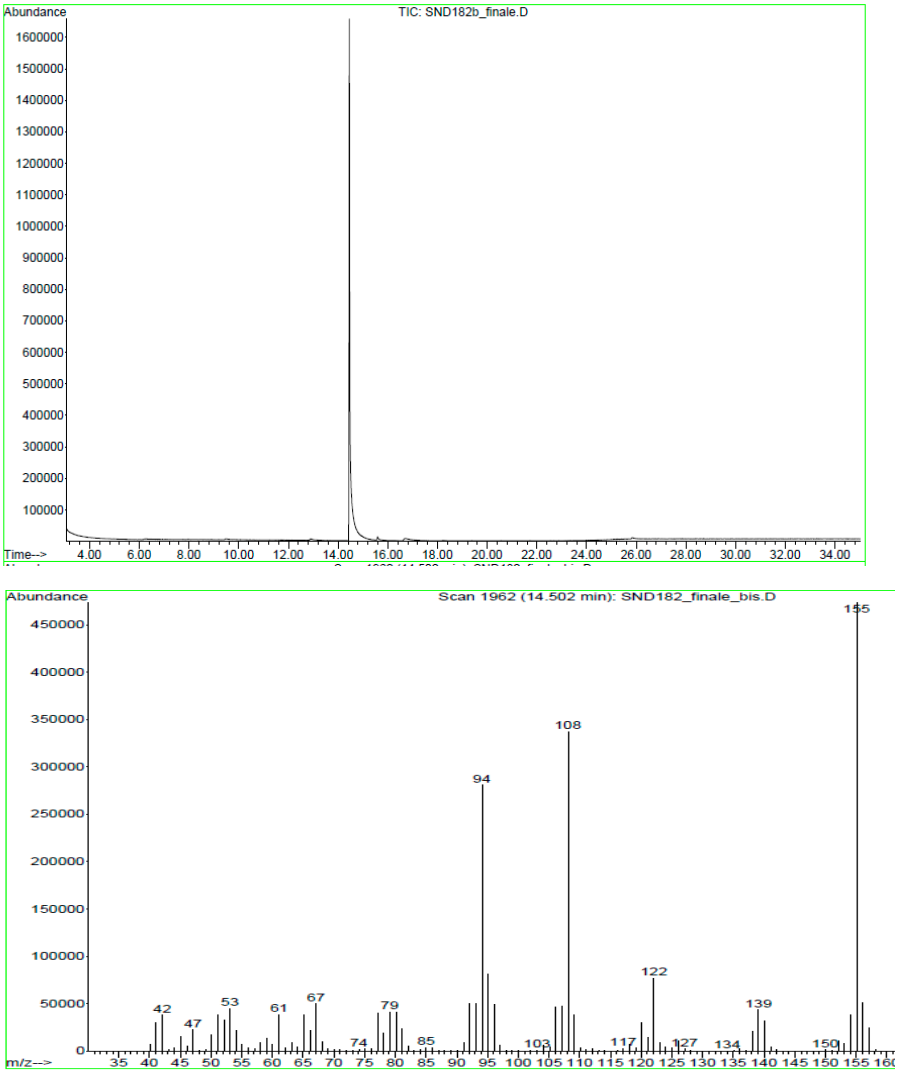
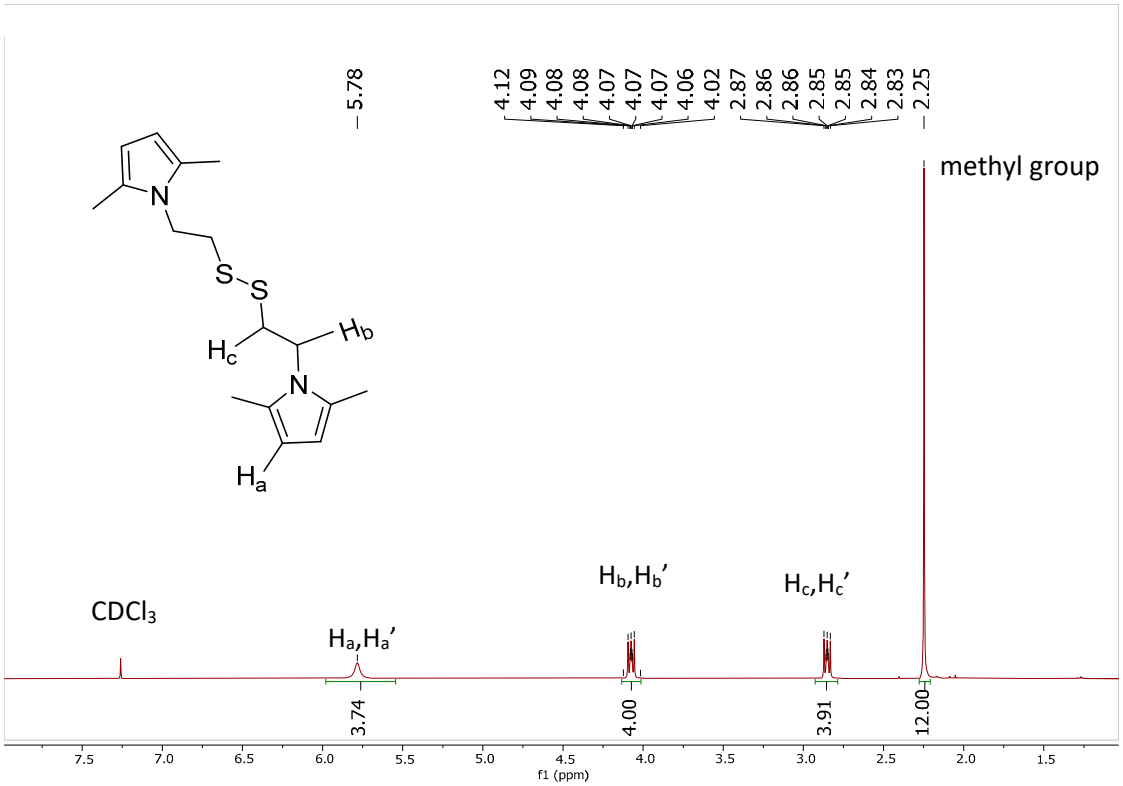



**Figure S.32:** GC-mass analysis of 2-(2,5-dimethyl-1H-pyrrol-1-yl)ethane-1-thiol (SHP)

3h) **1,2-bis(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl)disulfane** (SSP)




(A)

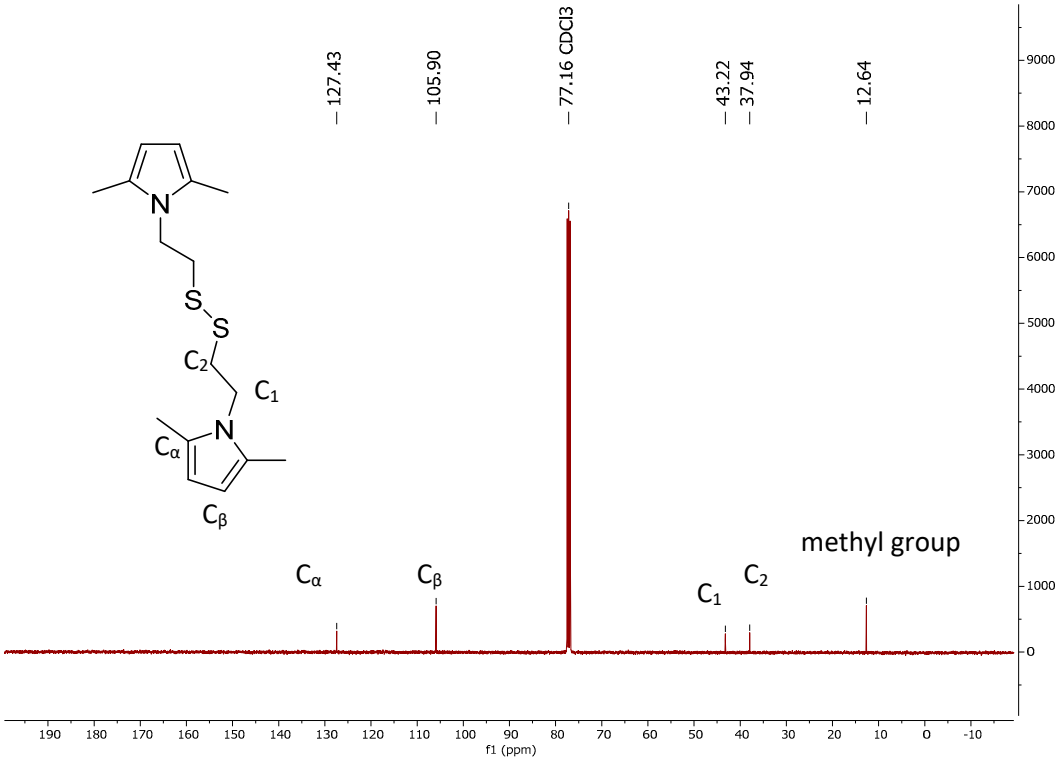



**Figure S.33.** (A) $^{1}$H-NMR and (B) $^{13}$C-NMR spectra of 1,2-bis(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl)disulfane (SSP) performed in $CDCl_3$

**GC-Mass analysis of 1,2-bis(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl)disulfane** (SSP)

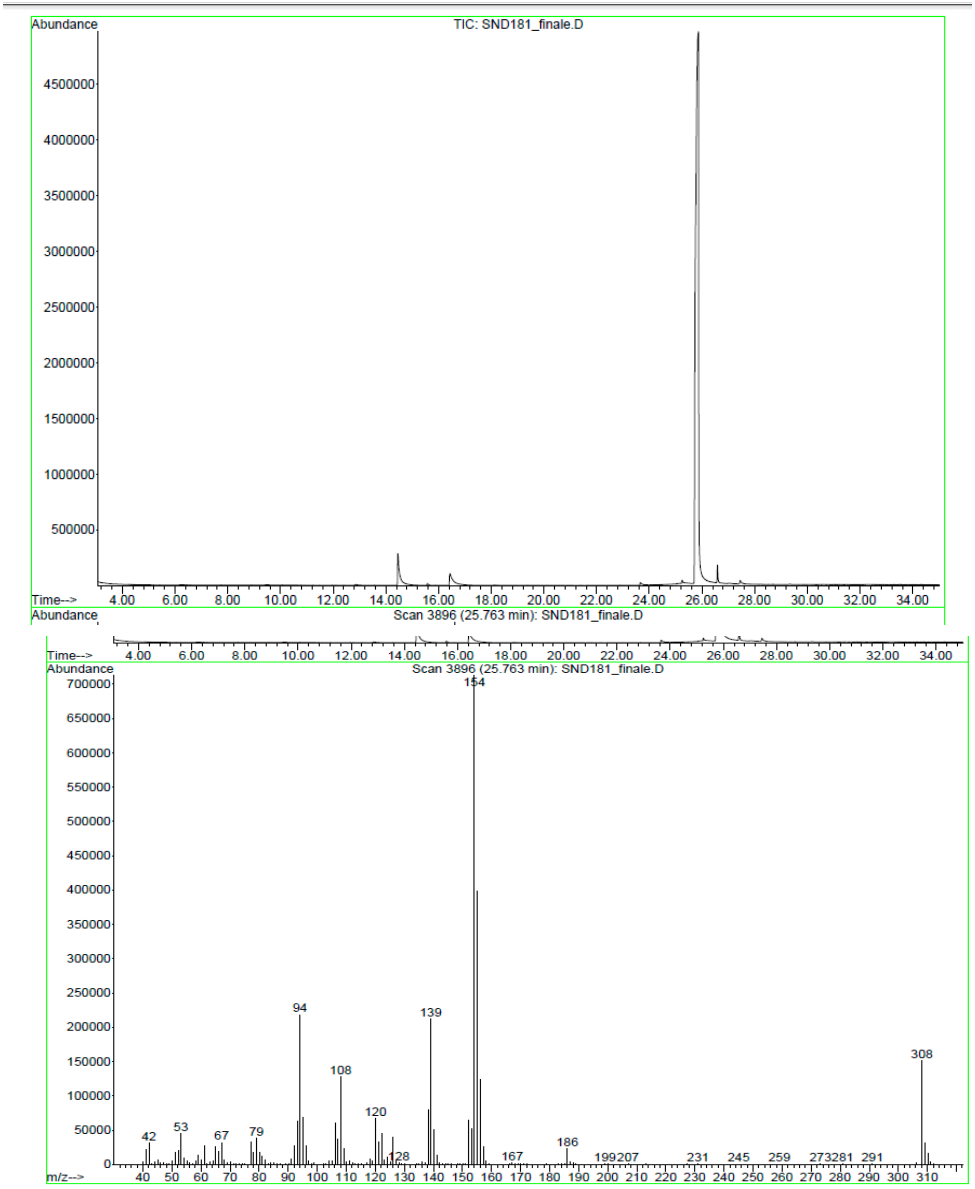



**Figure S.34.** GC-mass analysis of 1,2-bis(2-(2,5-dimethyl-1H-pyrrol-1-yl)ethyl)disulfane (SSP)

***S6 Synthesis and characterization of SHP and SSP from***

***Synthesis of SHP***

**STEP 1**: *2,5-hexanedione from 2,5-dimethylfuran*

In a round bottom flask, equipped with a magnetic stirrer, were introduced in order water (0.85 mL, 47.0 mmol), sulfuric acid (1.88 mmol, 4 mol%, 10 drops) and 2,5-dimethylfuran (5.0 ml, 47.0 mmol). The reaction mixture was heated at 50 °C and stirred for 24 hours, 400 rpm.

2,5-hexanedione was obtained, without any further purifications, as a dark brown liquid with a yield of 95%.

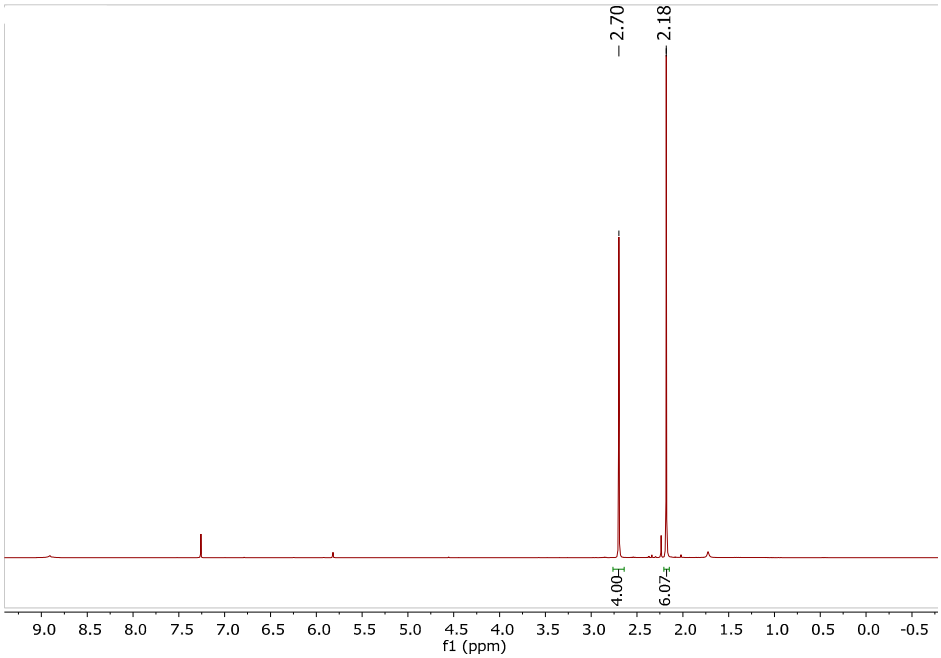



**Figure S.35:** $^{1}$H-NMR of 2,5-hexanedione starting from 2,5-dimethylfuran

***STEP 2: SHP from 2,5-hexanedione***

Bio-2,5-hexanedione obtained during the first step (44.65 mmol) was stirred with sodium acetate trihydrate (0.1 eq respect to 2,5-hexanedione, 4.46 mmol, 607.6 mg) at room temperature for 1 hour.

In a second bottom flask, equipped with magnetic stirrer, were introduced sodium acetate trihydrate (6,075 g, 44.65 mmol) and cisteamine hydrochloride (5,072 g, 44.65 mmol); the mixture was stirred at room temperature since an homogeneous solution was obtained.

Then, the solution of bio-2,5-hexanedione and sodium acetate trihydrate was added to the solution of cisteamine hydrochloride dropwise. The resulting solution was stirred at room temperature for 4 hours, 400 rpm.

*Neutralization:*

A satured solution of NaHCO3 was added to the mixture, under stirring, until the end of the effervescence.

*WORK-UP:*

Then, the organic phase was extracted with dicloromethane and anhydrified with Na2SO4. The solvent was removed under reducted pression to rotavapor.

SHP was obtained as a dark brown liquid.

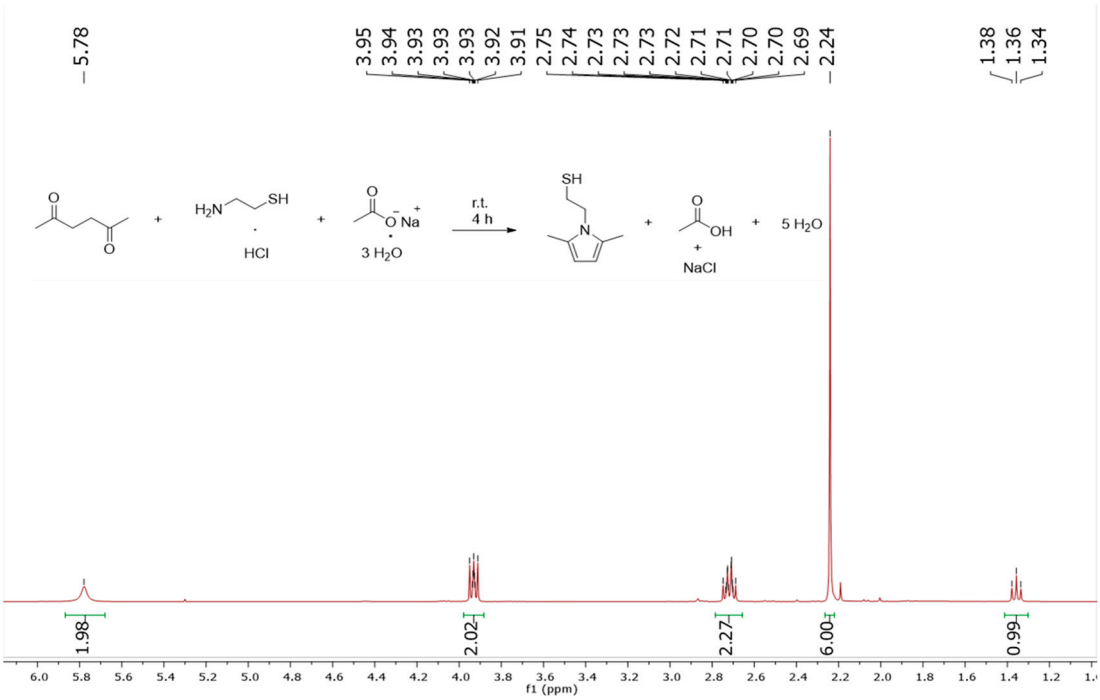



**Figure S.36:** $^{1}$H-NMR of SHP starting from obtained by using cysteamine hydrochloride as the hydrochloric salt

***Synthesis of SSP***

**STEP 1**: **2,5-hexanedione from 2,5-dimethylfuran**

In a round bottom flask, equipped with a magnetic stirrer, were introduced in order water (0.85 mL, 47.0 mmol), sulfuric acid (1.88 mmol, 4 mol%, 10 drops) and 2,5-dimethylfuran (5.0 mL, 47.0 mmol). The reaction mixture was heated at 50 °C and stirred for 24 hours, 400 rpm.

2,5-hexanedione was obtained, without any further purifications, as a dark brown liquid.

**STEP 2: SSP from 2,5-hexanedione**

Bio-2,5-hexanedione obtained during the first step was stirred with sodium acetate trihydrate (0.1 eq. respect to 2,5-hexanedione, 4.46 mmol, 607.6 mg) at 100 °C for 1 hour.

In a second bottom flask, equipped with magnetic stirrer, were introduced sodium acetate trihydrate (6,075 g, 44.65 mmol) and cistamine dihydrochloride (5,072 g, 22.32 mmol); the solution was stirred at 100 °C since an homogeneous solution was obtained.

Then, the solution of bio-2,5-hexanedione was added to the solution of cistamine dihydrochloride dropwise. The resulting solution was stirred at 100 °C for 2 hours, 400 rpm.

*NEUTRALIZATION*

A satured solution of NaHCO3 was added to the mixture, under stirring, until the end of the effervescence.

*WORK-UP:*

Then, the organic phase was extracted with ethyl acetate and anhydrified with Na2SO4; the solvent was removed under reducted pression.

SSP was obtained as a dark orange solid.

$^{1}$H-NMR confirmed the result.

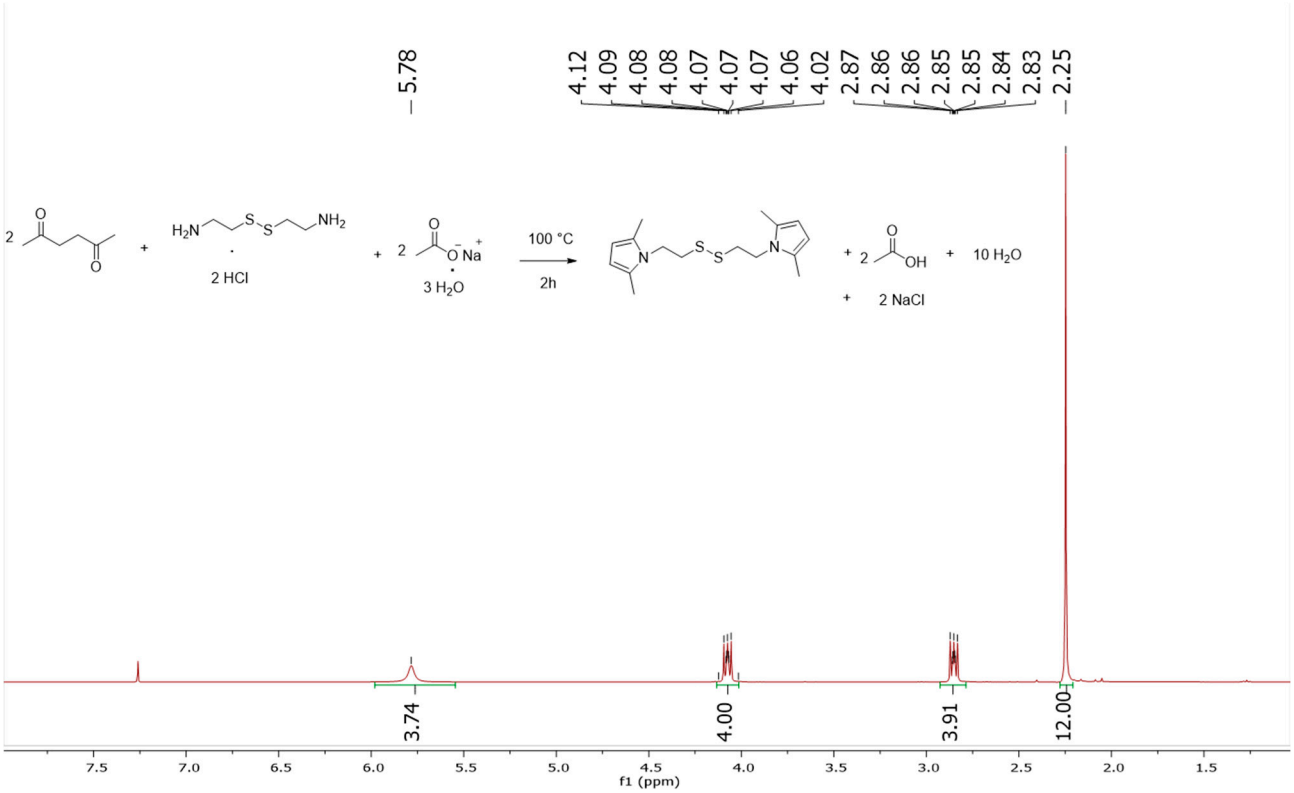



**Figure S.37:** $^{1}$H-NMR of SSP starting from obtained by using cistamine dihydrochloride ad the hydrochloric salt

***S7 Green metrics calculation for bio-pyrroles***

Green metrics parameters are implemented by using the definition reported in references 56 and 57.

Atom economy.

The atom economy gives the indication of the reagents' atoms which are converted into the desired product, without considering the yield of the reaction.

*Atom economy* is calculated through the Equation 1 below:

AEc (%) = (Molecular Mass of the product)/(∑〖Molecular Mass of all reagents〗)*100 Eq. 1

*Atom efficiency*. The atom efficiency considers the yield of the reaction and is calculated through Equation 2 below:

AEf (%) = AEc ∗ yield Eq. 2

*Carbon economy*

Carbon economy is calculated through the Equation 3 below:

CEc (%) = (Molar Mass of C atoms the product)/(∑〖Molar Mass of C in the all reagents)*100 Eq.3

*Carbon efficiency*

The Carbon Efficiency (CEf) was calculated through the Equation 4 below and indicates the actual amount of carbon in the product:

CEf (%) = CEc ∗ yield Eq. 4

*Reaction Mass efficiency*

The Reaction Mass Efficiency (RME) was calculated through the equation 5 below.

RME = (Mass of the product)/(∑〖Mass of the all reagents〗)*100……Eq. 5

*E factor*

The E-factor takes into account all the materials used to perform the chemical reactions, is defined as the ratio of the mass of waste per mass of product and was calculated through the Equation 6 below:

E-Factor = (Mass of Waste)/(Mass of Product) Eq. 6

*Reference for the Green metrics calculation are in the main text [49-51,66,67].*

### *S8. Rheometric data*

**Table S1:** Properties from the vulcanization of composites in Table 4.

| | **Composite based on** | | | |
|---|---|---|---|---|
| **Property** | **Silica** | **CB/SHP** | **CB + S** | **CB** |
| $M_L$ (dNm) | 4.33 | 3.83 | 2.56 | 2.60 |
| $M_H$ (dNm) | 24.44 | 19.00 | 18.68 | 16.46 |
| $M_H$-$M_L$ (dNm) | 20.11 | 15.17 | 16.12 | 13.86 |
| $t_{S1}$ (min) | 2.01 | 3.03 | 3.31 | 3.56 |
| $t_{90}$ (min) | 10.00 | 6.76 | 8.17 | 8.79 |
| ($M_H$-$M_L$) / ($t_{90}$-$t_{S1}$) (dNm/min) | 2.52 | 3.84 | 3.32 | 2.65 |

**Table S2:** G'$\gamma_{min}$, G'$\gamma_{max}$, $\Delta$G' , $\Delta$G'/G'$\gamma_{min}$, G''$_{max}$ and Tan $\delta_{max}$ from strain sweep tests on composites of Table 4.

| | **Composite based on** | | | |
|---|---|---|---|---|
| **Property** | **Silica** | **CB/SHP** | **CB + S** | **CB** |
| G'$\gamma_{min}$ (MPa) | 4.68 | 2.67 | 4.79 | 3.60 |
| G'$\gamma_{max}$ (MPa) | 1.53 | 1.33 | 1.18 | 1.08 |
| $\Delta$G' (MPa) | 3.15 | 1.34 | 3.61 | 2.52 |
| $\Delta$G' / G'$\gamma_{min}$ | 0.67 | 0.50 | 0.75 | 0.60 |
| G''$_{max}$ (MPa) | 0.40 | 0.28 | 0.55 | 0.52 |
| Tan $\delta_{max}$ | 0.18 | 0.16 | 0.27 | 0.28 |