### Supporting Information

# Ionic Liquids derived from proline: application as surfactants

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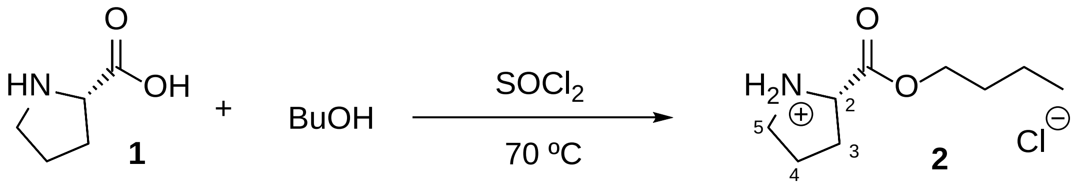
## Synthesis of ILs derived from prolinium

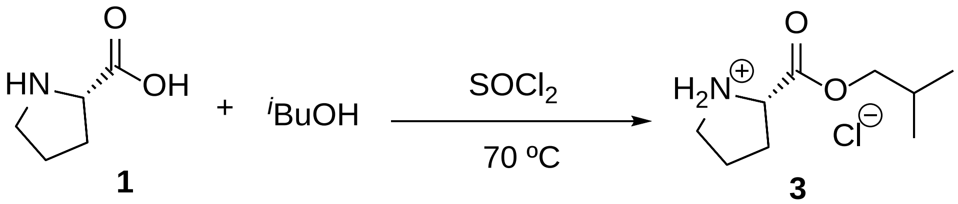
### Synthesis of (S)-2-(butoxycarbonyl)pyrrodilin-1-ium chloride [*ⁿ*C4Pro][Cl] (**2**)



Thionyl choride (0.824 mL, 11.5 mmol) was slowly added to *n*-butyl alcohol (5 mL, 38.5 mmol) at 0 ºC followed by slow addition of (L)-proline (**1**, 1 g, 7.7 mmol). The mixture was allowed to stir at 70 ºC for 4 h until the end of reaction, as indicated by t.l.c. (silica gel, MeOH:$CH_2Cl_2$ 5%). The excess of *n*-butyl alcohol was removed by heating under reduced pressure. $^t$BuOMe (20 mL) was then added and [$^n$C$_4$Pro][Cl] **2** was extracted with $H_2O$ (3 x 15 mL). The solvent was removed by heating under reduced pressure and the resulting IL was dried under high vacuum (2 x $10^{-1}$ Pa) to obtain [$^n$C$_4$Pro][Cl] (**2**) (1.50 g, 94 %) as a pale yellow liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ= 10.54 (s, 1H; $NH_2$), 9.07 (s, 1H; $NH_2$), 4.45 (m, 1H;H-2), 4.16 (m, 2H; $OCH_2$), 3.57 (m, 1H; H-5a), 3.47 (m, 1H; H-5b), 2.39 (m, 1H; H-3a), 2.13 (m, 1H; H-3b), 2.09 (m, 1H; H-4a), 1.97 (m, 1H; H-4b), 1.60 (m, 2H; $OCH_2C\underline{H}_2$), 1.32 (m, 2H; $O(CH_2)_2C\underline{H}_2$), 0.88 (t, $J_{H,H}$=7.4 Hz, 3H; $CH_3$); **$^{13}$C NMR (100 MHz, $CDCl_3$,):** δ=168.91 (C=O), 66.58 ($\underline{C}$-2), 59.30 ($O\underline{C}H_2$), 45.80 (C-5), 30.29 ($OCH_2\underline{C}H_2$), 28.50 (C-4), 23.60 (C-3), 19.93 ($O(CH_2)_2\underline{C}H_2$), 13.57 ($CH_3$); **HRMS (ESI):** *m/z* calcd for $[(C_9H_{18}NO_2)_2(Cl)]^+$: 379.2353 $[A_2B]^+$; found: 379.2358.

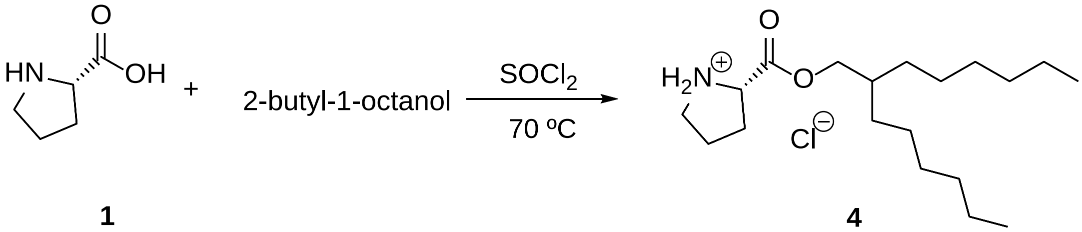
### Synthesis of (S)-2-(isobutoxycarbonyl)pyrrodilin-1-ium chloride [*ⁱ*C4Pro][Cl] (**3**)



Thionyl choride ($SOCl_2$, 0.82 mL, 11.5 mmol) was slowly added to *iso*-butyl alcohol (5 mL, 38.5 mmol) at 0 ºC followed by the addition of (L)-proline **1** (1 g, 7.7 mmol). The mixture was allowed to stir at 70 ºC for 4 h until the end of reaction as indicated by t.l.c. (silica gel, $CH_2Cl_2$:MeOH 5%). The excess of *iso*-butyl alcohol was removed by heating under reduced pressure. $^t$BuOMe (20 mL) was then added and [$^i$C$_4$Pro][Cl] (**3**) was extracted with $H_2O$ (3 x 15 mL). The solvent was removed by heating under reduced pressure and the resulting IL was dried under high vacuum (2 x $10^{-1}$ Pa) to obtain [$^{i}$C$_4$Pro][Cl] (**3**) as a pale yellow liquid (1.56 g, 97 %).[1]

**$^1$H NMR (400 MHz, CDCl$_3$):** δ= 10.53 (s, 1H; N$\underline{H}_2$), 9.06 (s, 1H; N$\underline{H}_2$), 4.44 (m, 1H; H-2), 3.96 (dd, $J_{H,H}$=10.5, 6.7 Hz, 1H; H-5a), 3.87 (dd, $J_{H,H}$=10.5, 6.6 Hz, 1H; H-5b), 3.51 (m, 2 H; OC$\underline{H}_2$), 2.38 (m, 1H; H-3a), 2.10-1.99 (m, 3H; H-3b, H-4), 1.92 (m, 1H; OCH$_2$C$\underline{H}$), 0.86 (d, $J_{H,H}$=6.7 Hz, 6H; CH$_3$); **$^{13}$C NMR (100 MHz, CDCl$_3$):** δ=169.80 (C=O), 72.45 (C-2), 59.19 (O$\underline{C}$H$_2$), 45.79 (C-5), 28.75 (C-4), 27.47 (OCH$_2\underline{C}$H), 23.47 (C-3), 18.86 (CH$_3$); **HRMS (ESI):** *m/z* calcd for $[(C_9H_{18}NO_2)_2(Cl)]^+$: 379.2353 $[A_2B]^+$; found: 379.2358.

### Synthesis of (2S)-2-(2'-butyloctyloxycarbonyl)pyrrolidin-1-ium chloride [C$_4$C$_8$Pro][Cl] (4)



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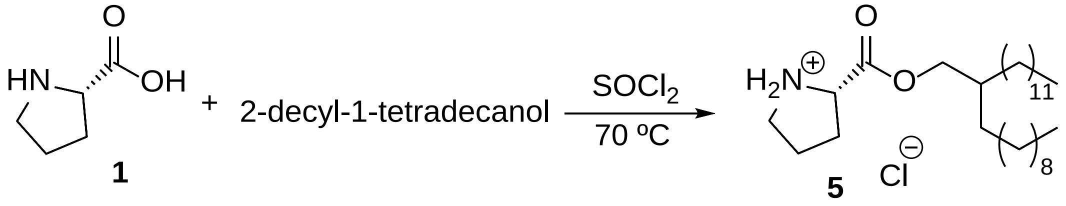
Thionyl chloride (SOCl$_2$, 0.47 mL, 6.4 mmol ) was slowly added to 2-butyl-1-octanol (4 mL, 17.2 mmol) at 0 °C followed by the addition of (L)-proline (**1**) (0.5 g, 4.3 mmol). The mixture was allowed to stir at 70 °C for 4 h until the end of reaction as indicated by t.l.c. (silica gel, CH$_2$Cl$_2$:MeOH 5%). $^t$BuOMe (20 mL) was then added and the product was extracted with H$_2$O (3 x 15 mL). The solvent was removed by heating under reduced pressure and the resulting IL was dried under high vacuum (2 x $10^{-1}$ Pa) to obtain [C$_4$C$_8$Pro][Cl] (**4**) (1.11 g, 80 %) as a pale yellow liquid.

**$^1$H NMR (400 MHz, CDCl$_3$):** δ= 10.91 (s, 1H; N$\underline{H}_2$), 8.98 (s, 1H; N$\underline{H}_2$), 4.47 (m, 1H; H-2), 4.20 (m, 1H; H-5a), 4.07 (m, 1H; H-5b), 3.58 (m, 2H; OC$\underline{H}_2$), 2.46 (m, 1H; H-3a), 2.16-2.06 (m, 3H; H-3b, H-4), 1.68 (m, 1H; OCH$_2$C$\underline{H}$), 1.28 (s, 16H; OCH$_2$CH(C$\underline{H}_2$)$_8$), 0.87 (t, $J_{H,H}$=6.7 Hz, 6H; CH$_3$). **$^{13}$C NMR (100 MHz, CDCl$_3$):** δ= 169.12 (C=O), 69.63 (C-2), 59.15 (O$\underline{C}$H$_2$), 45.94 (C-5), 37.15 (OCH$_2\underline{C}$H), 31.76, 31.07, 30.72, 29.54 (C-4), 28.96, 28.77, 26.57, 23.56 (C-3), 22.90, 22.61, 14.05; **HRMS (ESI):** *m/z* calcd for $[(C_{17}H_{34}NO_2)_2(Cl)]^+$: 603.4858 $[A_2B]^+$; found: 603.4862.

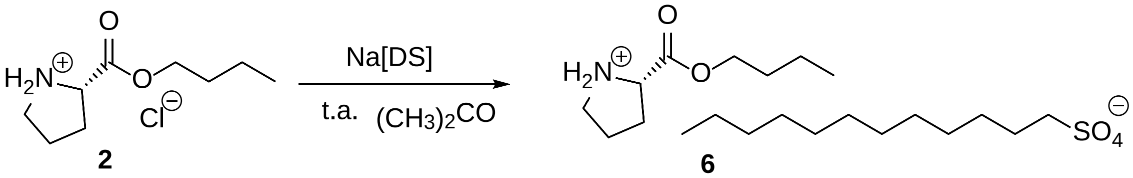
### Synthesis of (2S)-2-(2’-decyltetradecyloxycarbonyl)pyrrolidin-1-ium chloride [$C_{10}C_{14}$Pro][Cl] (<u>5</u>)



Thionyl choride ($SOCl_2$, 0.47 mL, 6.5 mmol) was slowly added to (L)-proline (<u>1</u>) (0.5 g, 4.3 mmol) at 0 ºC. The mixture was allowed to stir at 30 ºC for 2 h. Then, 2-decyl-1-tetradecanol (1.81 mL, 4.3 mmol) and $CH_2Cl_2$ (20 mL) were added and the solution was stirred at 40 ºC for 20 h. The solvent was removed by heating under reduced pressure and the reaction product was washed with hexane (3 x 10 mL) and dried under high vacuum (2 x $10^{-1}$ Pa) to obtain [$C_{10}C_{14}$Pro][Cl] (<u>5</u>) (2 g, 82 %) as a pale yellow liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=9.07 (s, 1H; N<u>H</u>$_2$), 8.21 (s, 1H; N<u>H</u>$_2$),4.10 (t, $J_{H,H}$=8.1 Hz,1H; H-2), 3.85 (m, 1H; H-5a), 3.72 (m, 1H; H-5b), 3.43 (m, 2H; OC<u>H</u>$_2$), 2.21 (m, 1H; H-3a), 2.13 (m, 1H; H-3b),1.93 (m, 1H; H-4a), 1.84 (m, 1H; H-4b), 1.57 (m, 1H; $OCH_2C$<u>H</u>),1.28 (s, 40H; O(C<u>H</u>$_2$)$_{20}$), 0.82 (t, $J_{H,H}$=6.8 Hz, 6H; (C<u>H</u>$_3$)$_2$); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=166.52 (C=O),69.41 (C-2),63.18 (O<u>C</u>H$_2$), 48.93 (C-5), 45.30 ($OCH_2$<u>C</u>H), 39.94, 31.92, 31.59, 29.83, 29.63, 27.68 (C-4), 26.58, 25.70, 23.31 (C-3), 22.68, 14.09 ($CH_3$); **HRMS (ESI):** *m/z* calcd for $[(C_{29}H_{58}NO_2)_2(Cl)]^+$: 939.8647 $[A_2B]^+$; found: 939.8641.

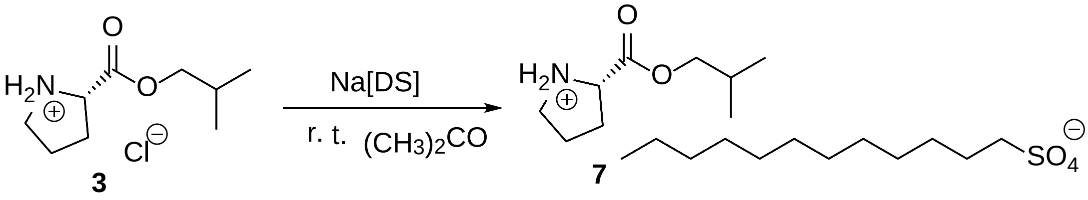
### Synthesis of (S)-2-(butoxycarbonyl)pyrrodilin-1-ium dodecylsulfate [$^n$C$_4$Pro][DS] (<u>6</u>)



[$^n$C$_4$Pro][Cl] (<u>2</u>) (0.71 g, 3.4 mmol) was dissolved in acetone (15 mL). Na[DS] (1.27 g, 4.4 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and $CH_2Cl_2$ was added to precipitate the formed NaCl and the excess of Na[DS], affording [$^n$C$_4$Pro][DS] (<u>6</u>) as a pale yellow liquid (1.10 g, 74 %).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ= 9.13 (s, 1H; NH$_2$), 8.37 (s, 1H; NH$_2$), 4.49 (t, $J_{H,H}$= 7.9 Hz, 1H; H-2), 4.16 (m, 2H; $OC\underline{H}_2$), 3.93 (t, $J_{H,H}$=6.8 Hz, 2H; $O_3SOC\underline{H}_2$), 3.57 (m, 1H; H-5a), 3.50 (m, 1H; H-5b), 2.41 (m, 1H; H-3a), 2.11 (m, 1H; H-3b), 2.06 (m, 1H; H-4a), 1.97 (m, 1H; H-4b), 1.60 (m, 4H; $OCH_2\underline{CH_2CH_2}$), 1.31 (m, 4H; $SOCH_2\underline{CH_2CH_2}$), 1.19 (m, 16H; $SO(CH_2)_3(C\underline{H_2})_8$), 0.89 (t, $J_{H,H}$=6.8 Hz, 3H; $O(CH_2)_3C\underline{H_3}$), 0.81 (t, $J_{H,H}$=6.9 Hz, 3H; $SO(CH_2)_{11}C\underline{H_3}$); **$^{13}$C NMR (100 MHz, CDCl$_3$):** δ=169.07 (C=O), 68.17 ($\underline{C}$-2), 66.43 ($O\underline{C}H_2$), 59.53 ($O_3SO\underline{C}H_2$), 46.57 (C-5), 31.79 ($O_3SOCH_2\underline{C}H_2$), 30.74 ($O_3SO(CH_2)_2\underline{C}H_2$), 30.24 ($OCH_2\underline{C}H_2$), 29.55 ($O_3SO(CH_2)_3\underline{C}H_2$), 29.51 ($O_3SO(CH_2)_4\underline{C}H_2\underline{C}H_2$), 29.26 ($O_3SO(CH_2)_6\underline{C}H_2$), 29.22 ($O_3SO(CH_2)_7\underline{C}H_2$), 28.62 (C-4), 25.71 ($O_3SO(CH_2)_8\underline{C}H_2$), 23.72 (C-3), 23.47 ($O_3SO(CH_2)_9\underline{C}H_2$), 22.54 ($O_3SO(CH_2)_{10}\underline{C}H_2$), 18.86 ($OCH_2CH_2\underline{C}H_2CH_3$), 13.96 ($O_3SO(CH_2)_{11}\underline{C}H_3$), 13.50 ($OCH_2CH_2CH_2\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_9H_{18}NO_2)_2(C_{12}H_{25}O_4S)]^+$: 609.4120 $[A_2B]^+$; found: 609.4135.

### Synthesis of (S)-2-(isobutoxycarbonyl)pyrrodilin-1-ium dodecylsulfate $[{}^iC_4Pro][DS]$ (7)

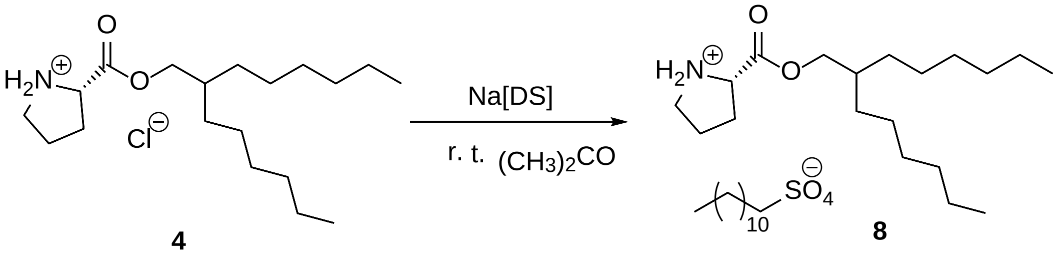


$[{}^iC_4Pro][Cl]$ (3) (0.90 g, 4.3 mmol) was dissolved in acetone (15 mL). Na[DS] (1.50 g, 5.2 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and $CH_2Cl_2$ was added to precipitate the formed NaCl and the excess of Na[DS], to afford $[{}^iC_4Pro][DS]$ (7) as a pale yellow liquid (1.45 g, 77 %).

**$^1$H NMR (400 MHz, CDCl$_3$):** δ= 9.15 (s, 1H; NH$_2$), 8.38 (s, 1H; NH$_2$), 4.53 (dd, $J_{H,H}$=8.5, 6.0 Hz, 1H; H-2), 3.97 (m, 2H; $O_3SO\underline{CH_2}$), 3.92 (m, 2H; $OC\underline{H_2}$), 3.56-3.52 (m, 2H; H-5), 2.47-2.12 (m, 2H; H-3), 2.10-1.94 (m, 3H; H-4, $OCH_2C\underline{H}$), 1.61 (m, 2H; $O_3SOCH_2C\underline{H_2}$), 1.21 (m, 18H; $O_3SO(CH_2)_2(C\underline{H_2})_9$), 0.90 (d, $J_{H,H}$=6.7 Hz, 6H; $OCH_2CH(C\underline{H_3)_2}$), 0.84 (t, $J_{H,H}$=6.7 Hz, 3H; $O_3SO(CH_2)_{11}C\underline{H_3}$); **$^{13}$C NMR (100 MHz, CDCl$_3$):** δ=169.11 (C=O), 72.53 (C-2), 68.33 ($O\underline{C}H_2$), 59.91 ($O_3SO\underline{C}H_2$), 46.61 (C-5), 31.85 ($O_3SOCH_2\underline{C}H_2$), 30.84 ($O_3SO(CH_2)_2\underline{C}H_2$), 29.61 ($O_3SO(CH_2)_3\underline{C}H_2$), 29.57 ($O_3SO(CH_2)_4\underline{C}H_2\underline{C}H_2$), 29.32 ($O_3SO(CH_2)_6\underline{C}H_2$), 29.28 ($O_3SO(CH_2)_7\underline{C}H_2$), 28.75 (C-4), 28.51 ($O_3SO(CH_2)_8\underline{C}H_2$), 27.51 ($OCH_2\underline{C}H$), 23.81 (C-3), 23.51 ($O_3SO(CH_2)_9\underline{C}H_2$), 22.61

($O_3SO(CH_2)_{10}\underline{C}H_2$), 18.87 ($OCH_2CH\underline{C}H_3$), 18.84 ($OCH_2CH\underline{C}H_3$), 14.03 ($O_3SO(CH_2)_{11}\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_9H_{18}NO_2)_2(C_{12}H_{25}O_4S)]^+$: 609.4120 $[A_2B]^+$; found: 609.4135.

### Synthesis of (2S)-2-(2'-butyloctyloxycarbonyl)pyrrolidin-1-ium dodecylsulfate [$C_4C_8$Pro][DS] (**8**)



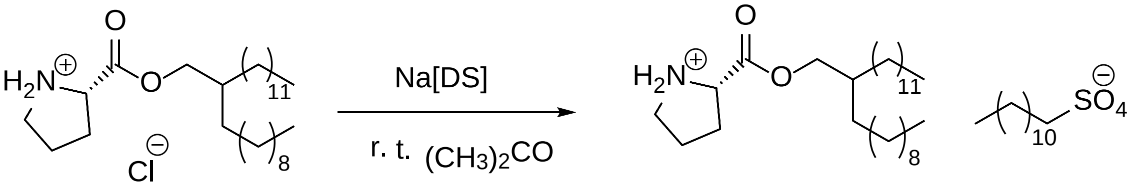
**4**

**8**

[$C_4C_8$Pro][Cl] (**4**) (0.96 g, 3 mmol) was dissolved in acetone (15 mL). Na[DS] (1.03 g, 3.6 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and $CH_2Cl_2$ was added to precipitate the formed NaCl and the excess of Na[DS], to afford [$C_4C_8$Pro][DS] (**8**) as a pale yellow liquid (1.25 g, 75 %).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=9.36 (s, 1H; $NH_2$), 8.43 (s, 1H; $NH_2$), 4.56 (dd, $J_{H,H}$=8.2, 6.0 H, 1H; H-2), 4.20 (m, 1H; H-5a), 4.04 (m, 1H; H-5b), 3.99 (m, 2H;$O_3SOC\underline{H}_2$), 3.58 (m, 2H; $OC\underline{H}_2$), 2.46 (m, 1 H; H-3a), 2.16 (m, 1H; H-3b), 2.10 (m, 1H; H-4a), 2.03 (m, 1H; H-4b), 1.68 (m, 3H; $OCH_2C\underline{H}$; $O_3SOCH_2C\underline{H}_2$), 1.28 (m, 34H; $OCH_2CH(C\underline{H}_2)_8$, $O_3SOCH_2CH_2(C\underline{H}_2)_9$), 0.88 (t, $J_{H,H}$=5.6 Hz,9H; $O(CH_2)_{10}C\underline{H}_3$, $O_3SO(CH_2)_{11}C\underline{H}_3$); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=169.24 (C=O), 69.67 (C-2), 68.45 ($O\underline{C}H_2$), 59.51 ($O_3SO\underline{C}H_2$), 46.68 (C-5), 37.18 ($OCH_2\underline{C}H$), 31.92 ($O_3SOCH_2\underline{C}H_2$), 31.80, 31.07, 30.73, 29.69 ($O_3SO(CH_2)_2\underline{C}H_2$), 29.65 ($O_3SO(CH_2)_3\underline{C}H_2$), 29.62 ($O_3SO(CH_2)_4\underline{C}H_2\underline{C}H_2$), 29.59 (C-4), 29.38 ($O_3SO(CH_2)_6\underline{C}H_2\underline{C}H_2$), 28.96, 28.77, 26.61 ($O_3SO(CH_2)_8\underline{C}H_2$), 26.58, 25.82 ($O_3SO(CH_2)_9\underline{C}H_2$), 23.58 (C-3), 22.93, 22.68, 22.64 ($O_3SO(CH_2)_{10}\underline{C}H_2$), 14.07, 14.01 ($O_3SO(CH_2)_{11}\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_{17}H_{34}NO_2)_2(C_{12}H_{25}O_4S)]^+$: 833.6617 $[A_2B]^+$; found: 833.6624.

### Synthesis of (2S)-2-(2’-decyltetradecyloxycarbonyl)pyrrolidin-1-ium dodecyl-sulfate [$C_{10}C_{14}$Pro][DS] (<u>9</u>)

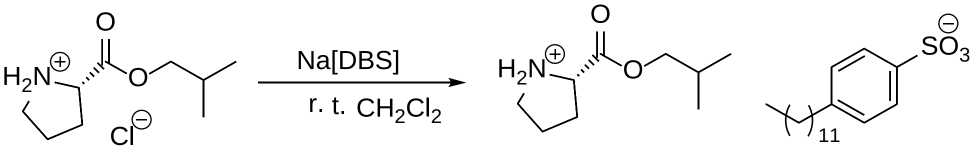


**5** **9**

[$C_{10}C_{14}$Pro][Cl] (<u>7</u>) ( 1 g, 2 mmol) was dissolved in acetone (15 mL). Na[DS] (0.70 g, 2.4 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and $CH_2Cl_2$ was added to precipitate the NaCl formed and the excess of Na[$C_{12}SO_4$], to afford [$C_{10}C_{14}$Pro][DS] (**<u>9</u>**) as a pale yellow liquid (1 g, 70 %).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=9.36 (s, 1H; $NH_2$), 8.43 (s, 1H; $NH_2$), 4.22 (t,$J_{H,H}$=7.9 Hz, 1H; H-2), 3.67 (t,$J_{H,H}$=6.6 Hz, 2H; $O_3SOC\underline{H_2}$), 3.56 (m, 4H; $OC\underline{H_2}$; H-5), 2.35 (m, 1H; H-3a), 2.19 (m, 1H; H-3b), 2.07 (m, 1 H; H-4a), 1.95 (m, 1H; H-4b), 1.68 (m, 1H; $OCH_2C\underline{H}$),1.60 (m, 2H; $O_3SOCH_2C\underline{H_2}$), 1.30 (m, 58H; $(C\underline{H}_2)_{29}$), 0.89 (t, $J_{H,H}$=6.6 Hz, 9H; $CH_3$); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=166.52 (C=O),69.41 (C-2),63.18 ($O\underline{C}H_2$), 60.59 ($O_3SO\underline{C}H_2$), 48.93 (C-5), 45.30 ($OCH_2\underline{C}H$), 39.94, 32.39 ($O_3SOCH_2\underline{C}H_2$), 31.92, 31.59, 29.83, 29.63, 29.35 ($O_3SO(CH_2)_4\underline{C}H_2\underline{C}H_2$), 27.68 (C-4), 26.58, 25.70, 23.31 (C-3), 22.68, 14.09; **HRMS (ESI):** *m/z* calcd for [$(C_{29}H_{58}NO_2)_2(C_{12}H_{25}O_4S)$]+: 1170.0415 [$A_2B$]$^+$; found: 1170.0423.

### Synthesis of (S)-2-(isobutoxycarbonyl)pyrrodilin-1-ium dodecylbenzensulfonate [$^i$$C_4$Pro][DBS] (<u>10</u>)



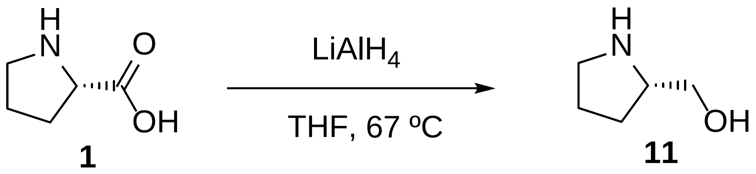
**3** **10**

[$^i$$C_4$Pro][Cl] (**<u>3</u>**) (1.80 g, 8.6 mmol) was dissolved in $CH_2Cl_2$ (15 mL). Na[DBS] (3.60 g, 10 mmol) was added and the reaction mixture was stirred for 8 days at room temperature. The solvent was removed under reduced pressure and acetone was added to precipitate the formed NaCl and the excess of Na[DBS], to afford [$^i$$C_4$Pro][DBS] (**<u>10</u>**) as a pale yellow liquid (3.40 g, 78 %).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=9.15 (s, 1H; $NH_2$), 8.38 (s, 1H; $NH_2$), 7.82 (dd, $J_{H,H}$=8.2, 1.7 Hz, 2H; Ar H-1), 7.12 (d, $J_{H,H}$=8.2 Hz, 2H; Ar H-2), 4.58 (dd, $J_{H,H}$=8.5, 5.9 Hz, 1H; H-2), 4.00-3.92 (m, 2H; H-5), 3.55 (m, 2H; $OC\underline{H_2}$), 2.44 (m, 1H; $OC\underline{H}$), 2.13-2.09 (m, 2H; H-3), 1.98-1.95 (m, 2H; H-4), 1.62-1.52 (m, 4H; $O_2SOC\underline{H_2CH_2}$), 1.29 (m, 18H; $O_2SOCH_2CH_2(C\underline{H_2})_9$), 0.83 (d,$J_{H,H}$=6.7 Hz, 6H; $OCH_2CH(C\underline{H_3)_2}$), 0.81 (m, 3H; $O_2SOCH_2(CH_2)_{10}C\underline{H_3}$). **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=169.08 (C=O), 127.56 (Ar C1), 125.90 (Ar C2), 72.52 (C-2), 59.39 ($O\underline{C}H_2$), 46.26 ($O_2SO\underline{C}H_2$), 36.85 (C-5), 31.86 ($O_2SOCH_2\underline{C}H_2$), 31.76 (C-4), 29.73 ($OCH_2\underline{C}H$), 29.39 ($O_2SO(CH_2)_2\underline{C}H_2$), 28.83 ($O_2SO(CH_2)_3(\underline{C}H_2)_2$), 27.50 ($O_2SO(CH_2)_5(\underline{C}H_2)_4$), 23.48 (C-3), 22.63 ($O_2SO(CH_2)_9\underline{C}H_2$), 18.89 ($OCH_2CH(\underline{C}H_3)_2$), 14.07 ($O_2SO(CH_2)_{11}\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_9H_{18}NO_2)_2(C_{18}H_{29}O_3S)]^+$: 669.4475 $[A_2B]^+$; found: 669.4485.

## Synthesis of ILs derived from prolinolium

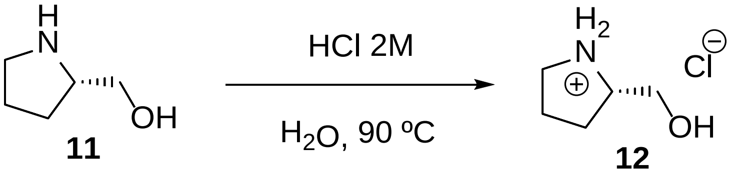
### Synthesis of L-Prolinol (**<u>11</u>**)



(L)-Proline (**<u>1</u>**) (0.50 g, 4.3 mmol) was added to a cooled suspension of $LiAlH_4$ (0.49 g, 12.9 mmol) in 40 mL of dry THF under a $N_2$ atmosphere. The reaction mixture was warmed to room temperature and then refluxed at 67 ºC for 24 h. The excess of $LiAlH_4$ was removed by slow addition of water (20 mL) and an aqueous solution of KOH 15% (5 mL). The mixture was stirred for 30 min and a white precipitate was separated by filtration. The aqueous phase was concentrated and the product was washed with $CH_2Cl_2$ and dried under high vacuum (2 x $10^{-1}$ Pa) to give (L)-prolinol (**<u>11</u>**) (0.20 g, 45%) as a yellow oil.[2]

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=3.45-3.26 (m, 2H; $C\underline{H_2}OH$), 3.10 (m, 1H; H-2), 2.79 (m, 2H; H-5), 1.70-1.31 (m, 4H; H-3, H-4); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=64.63 ($\underline{C}H_2OH$), 59.80 (C-2), 46.32 (C-5), 27.51 (C-3), 25.86 (C-4).

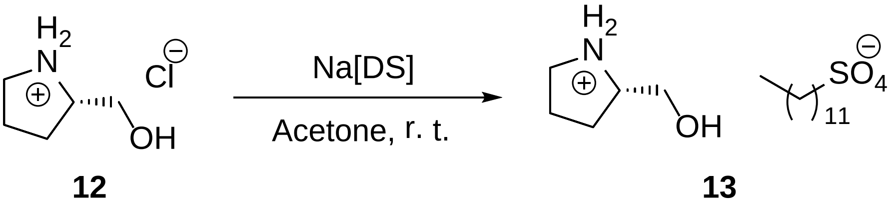
### Synthesis (S)-(+)-2-(Hydroxymethyl)pirrolidinium chloride [HOPro][Cl] (**12**)



HCl 2M ( 0.64 mL, 1.2 mmol) was added to a solution of (L)-prolinol (**11**) (0.13 g, 1.2 mmol) in $H_2O$ (5 mL). The reaction mixture was stirred and heated at 90 ºC for 16 h. Neutralization with NaOH 2 M was performed. The solution was washed with $CH_2Cl_2$ (3 x 10 mL) and the aqueous phase was concentrated and dried under high vacuum (2 x $10^{-1}$ Pa) to give [HOPro][Cl] (**12**) (0.12 g, 70%) as a brown liquid.

**$^{1}$H NMR (400 MHz, $D_2O$):** δ=3.84 (dd, $J_{H,H}$=11.9, 3.7 Hz, 1H; H-2), 3.71 (m, 1H; $\mathrm{C\underline{H}_2OH}$), 3.67 (m, 1H; $\mathrm{C\underline{H}_2OH}$), 3.29 (t, $J_{H,H}$=7.3 Hz, 2H; H-5), 2.12 – 1.97 (m, 3H; H-3, H-4a), 1.70 (m, 1H; H-4b); **$^{13}$C NMR (100 MHz, $D_2O$):** δ=61.34 (C-2), 60.30 ($\mathrm{\underline{C}H_2OH}$), 45.63 (C-5), 25.80 (C-3), 23.34 (C-4); **HRMS (ESI):** *m/z* calcd for $[(C_5H_{12}NO)_2(Cl)]^+$: 239.1562 $[A_2B]^+$; found: 239.1570.

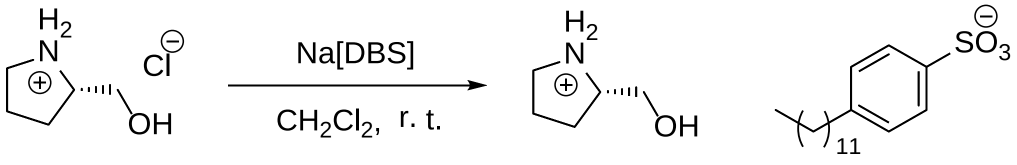
### Synthesis of (S)-(+)-2-(Hydroxymethyl)pirrolidinium dodecylsulfate [HOPro][DS] (**13**)



[HOPro][Cl] (**12**) ( 0.10 g, 0.7 mmol) was dissolved in acetone (7 mL). Na[DS] (0.20 g, 0.8 mmol) was added and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure and $CH_2Cl_2$ was added to precipitate the NaCl formed and the excess of Na[DS], to afford [HOPro][DS] (**13**) as a brown liquid (0.19 g, 73 %).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ=4.03 (t, $J_{H,H}$=6.8 Hz, 2H; $\mathrm{O_3SOC\underline{H_2}}$), 3.96 (dd, $J_{H,H}$=12.2, 3.2 Hz, 1H; $\mathrm{C\underline{H}_2OH}$), 3.91 – 3.83 (m, 1H; H-2), 3.75 (m, 1H; $\mathrm{C\underline{H}_2OH}$), 3.44 (m, 2H; H-5), 2.19 – 1.97 (m, 3 H; H-3, H-4a), 1.86 – 1.74 (m, 1 H; H-4b), 1.72 – 1.62 (m, 2H; $\mathrm{O_3SOCH_2C\underline{H_2}}$), 1.27 (s, 18H; $\mathrm{O_3SO(CH_2)_2(C\underline{H_2})_9}$), 0.89 (t, $J_{H,H}$=6.8 Hz, 3H; $\mathrm{O_3SO(CH_2)_{11}C\underline{H_3}}$); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=68.70 ($\mathrm{O_3SO\underline{C}H_2}$), 61.98 (C-2), 60.99 ($\underline{C}H_2OH$), 45.95 (C-5), 31.89 ($O_3SOCH_2\underline{C}H_2$), 29.65-29.31 ($O_3SO(CH_2)_2(\underline{C}H_2)_7$), 26.17 ($O_3SO(CH_2)_9\underline{C}H_2$), 25.77(C-3), 24.03 (C-4), 22.65 ($O_3SO(CH_2)_9CH_2\underline{C}H_2$),14.08 ($O_3SO$ $(CH_2)_{11}\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_5H_{12}NO)_2(C_{12}H_{25}O_4S)]^+$: 469.3295 $[A_2B]^+$; found: 469.3302.

### Synthesis of (S)-(+)-2-(Hydroxymethyl)pirrolidinium dodecylbenzenesulfonate [HOPro][DBS] (<u>14</u>)



**12** **14**

[HOPro][Cl] (**<u>12</u>**) (0.10 g, 0.7 mmol) was dissolved in $CH_2Cl_2$ (10 mL). Na[DBS] (0.30 g, 0.8 mmol) was added and the reaction mixture was stirred for 10 days at room temperature. The solvent was removed under reduced pressure and acetone was added to precipitate the formed NaCl and the excess of Na[DBS], to afford [HOPro][DBS] (**<u>14</u>**) as a yellow viscous liquid (0.26 g, 83 %).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ=8.85 (s, 1H; $NH_2$), 8.25 (s, 1H; $NH_2$), 7.70 (dd, $J_{H,H}$=8.1, 3.0 Hz, 2H; Ar H-1), 7.15 (d,$J_{H,H}$=8.2 Hz, 2H; Ar H-2), 3.87 (m, 1H; $C\underline{H}_2OH$), 3.80 (s, 1H; H-2), 3.66 (m, 1H; $C\underline{H}_2OH$), 3.20 (m, 2H; H-5), 2.51 (m, 1H; H-3a), 1.86 – 1.80 (m, 3H; H-3b, H-4), 1.64–1.48 (m, 6H; $O_2SOC\underline{H_2}C\underline{H_2}C\underline{H_2}$), 1.17 (m, 16H; $O_2SO(CH_2)_3(C\underline{H_2})_8CH_3$), 0.87-0.81 (m, 3H; $O_2SO(CH_2)_{11}C\underline{H_3}$); **$^{13}$C NMR (100 MHz, $CDCl_3$):** δ=149.28 (Ar C1), 149.21 (Ar C4), 127.65 (Ar C2), 126.01 (Ar C3), 61.78 (C-2), 60.88 ($\underline{C}H_2OH$), 45.88 (C-5), 45.56 ($O_2SO\underline{C}H_2$), 36.80 ($O_2SOCH_2\underline{C}H_2$), 31.93 ($O_2SO(CH_2)_2\underline{C}H_2$), 31.89 ($O_2SO(CH_2)_3\underline{C}H_2$), 31.76 ($O_2SO(CH_2)_4\underline{C}H_2$), 29.72 ($O_2SO(CH_2)_5\underline{C}H_2$), 29.37 ($O_2SO(CH_2)_6\underline{C}H_2$), 29.22 ($O_2SO(CH_2)_7\underline{C}H_2$), 27.58 ($O_2SO(CH_2)_8\underline{C}H_2$), 27.21 ($O_2SO(CH_2)_9\underline{C}H_2$), 26.04 (C-3), 23.78 (C-4), 22.60 ($O_2SO(CH_2)_{10}\underline{C}H_2$), 14.07 ($O_2SO(CH_2)_{11}\underline{C}H_3$); **HRMS (ESI):** *m/z* calcd for $[(C_5H_{12}NO)_2(C_{18}H_{29}O_3S)]^+$: 529.3656 $[A_2B]^+$; found: 529.3666.

## References

1.- T. J. Trivedi, K. S. Rao, T. Singh, S. K. Mandal, N. Sutradhar, A. B. Panda, A. Kumar, *ChemSusChem* **2011**, *4*, 604.

2.- T.Yu, T.Yamada, G.C. Gaviola, R.G. Weiss, *Chem. Mater* **2008**, *20*, 5337.

## $^1$H, $^{13}$C NMR Spectra

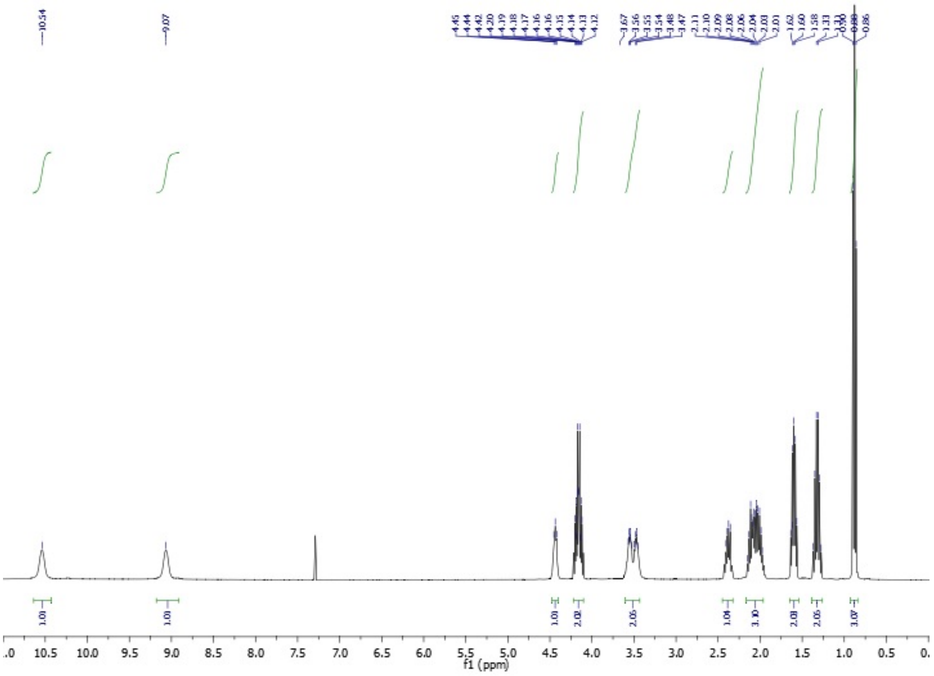


**Fig S1**. $^1$H NMR spectrum of [$^n$C$_4$Pro][Cl] (**2**)

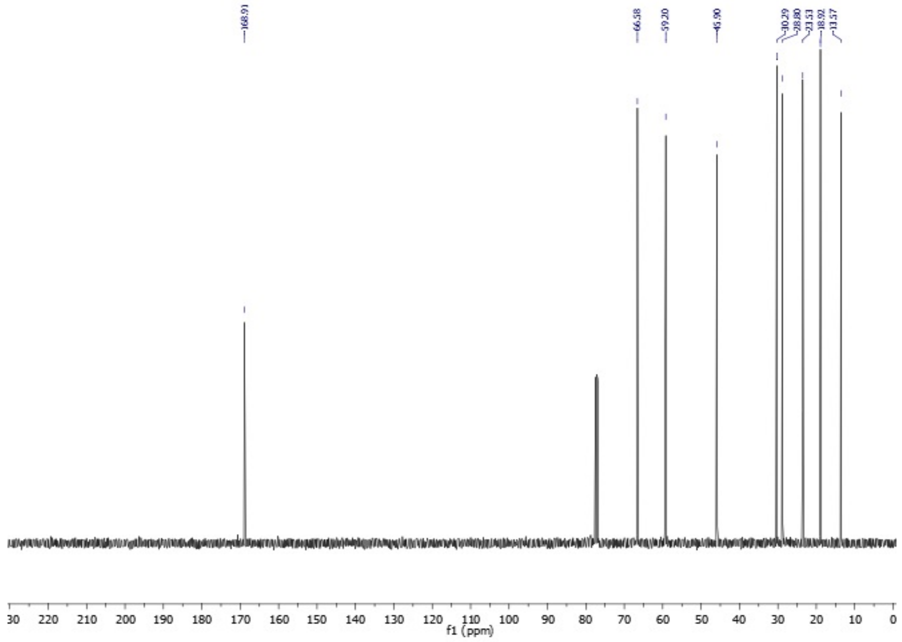


**Fig S2**. $^{13}$C NMR spectrum of [$^n$C$_4$Pro][Cl] (**2**)

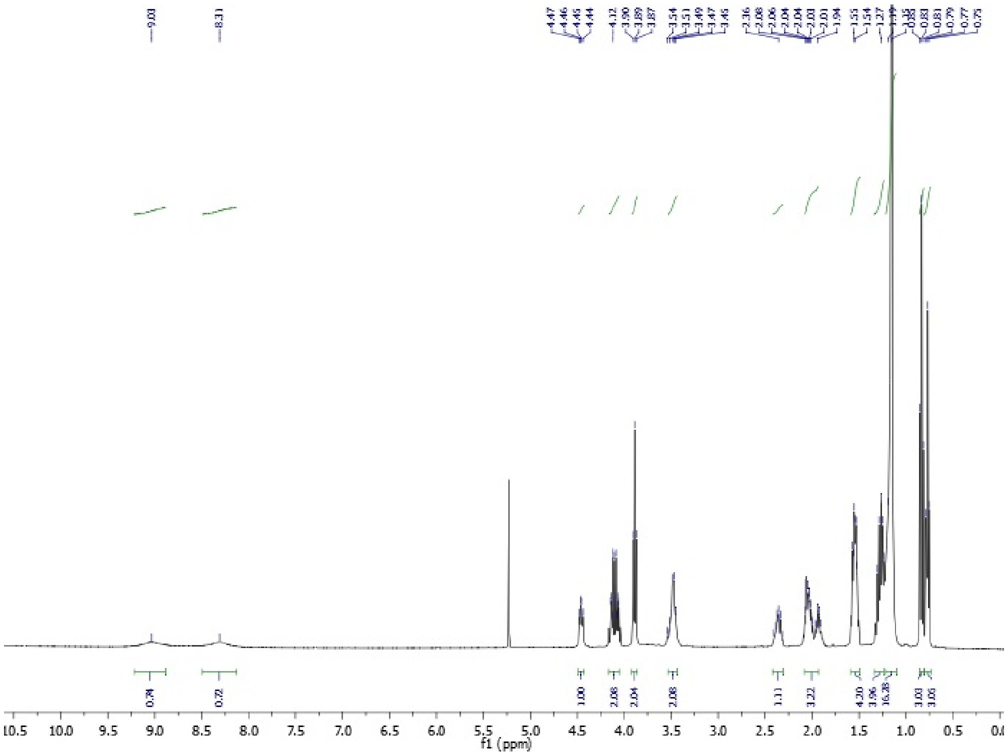


**Fig S3**. $^{1}$H NMR spectrum of [$^{n}$C$_4$Pro][DS] (**6**)

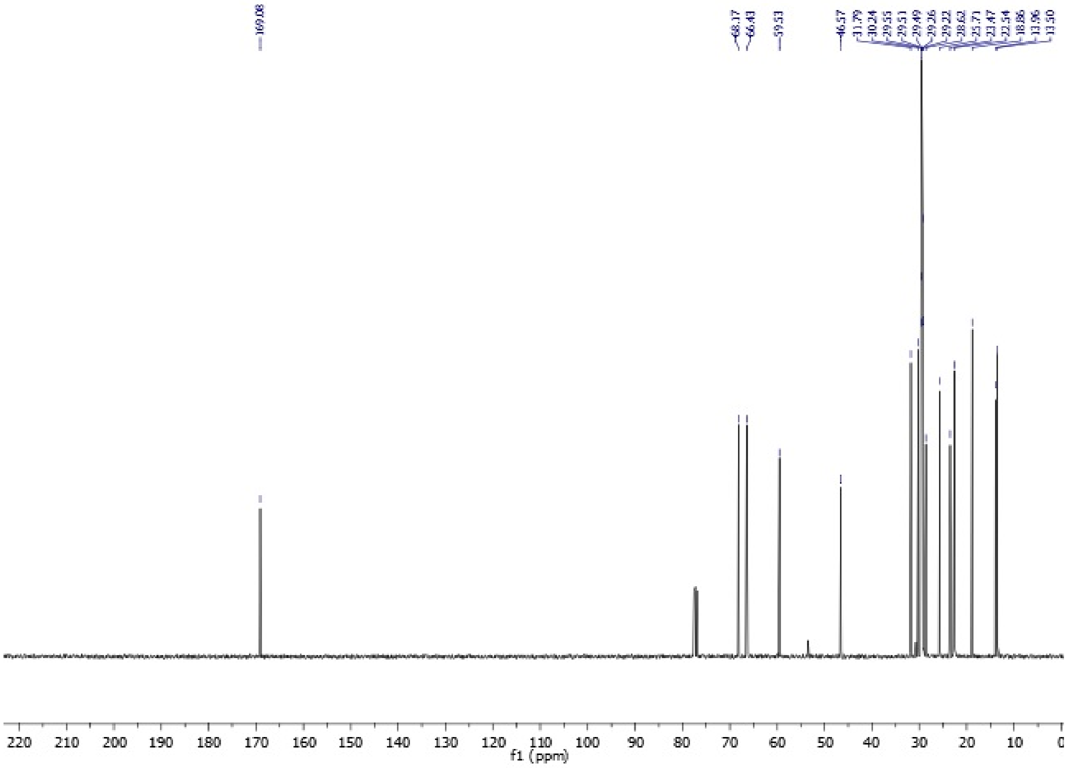


**Fig S4**. $^{13}$C NMR spectrum of [$^{n}$C$_4$Pro][DS] (**6**)

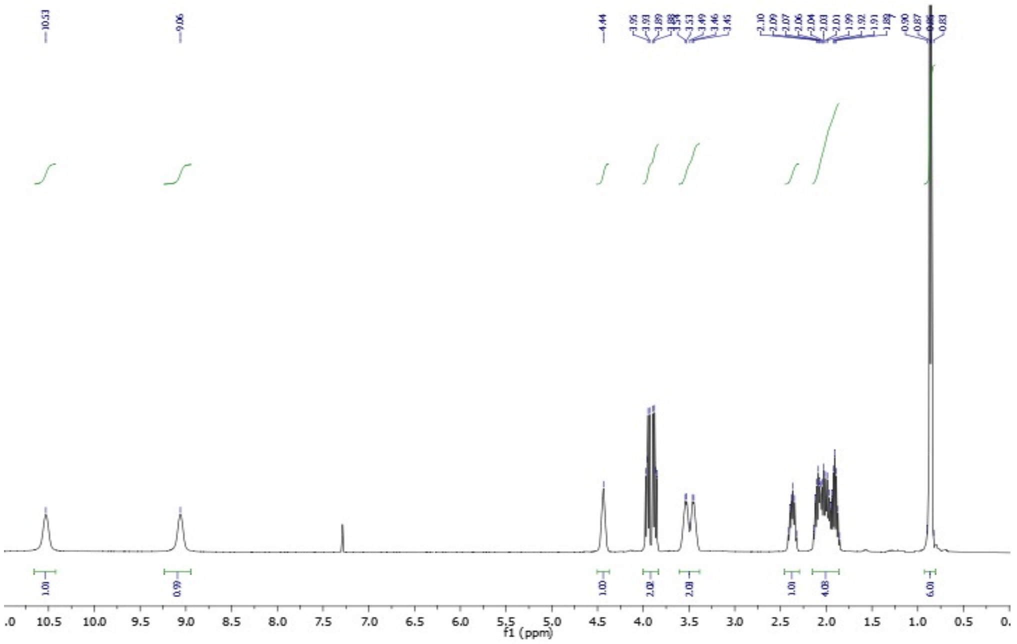


**Fig S5**. $^1$H NMR spectrum of [$^i$C$_4$Pro][Cl] (**3**)

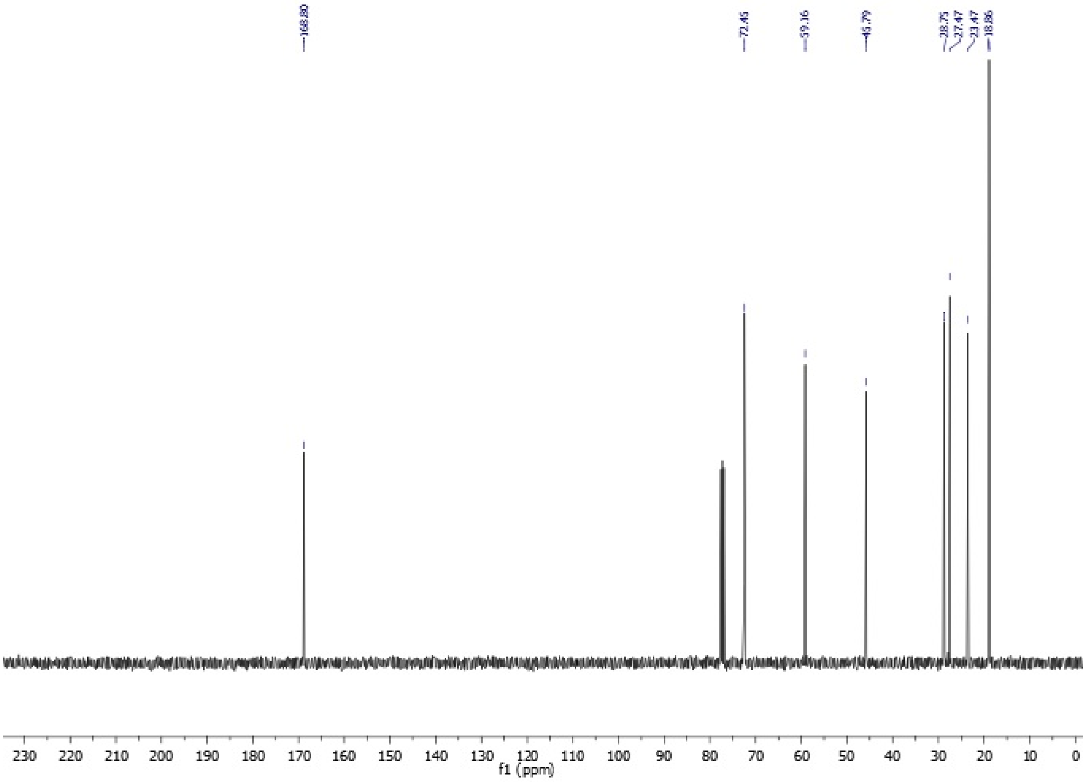


**Fig S6**. $^{13}$C NMR spectrum of [$^i$C$_4$Pro][Cl] (**3**)

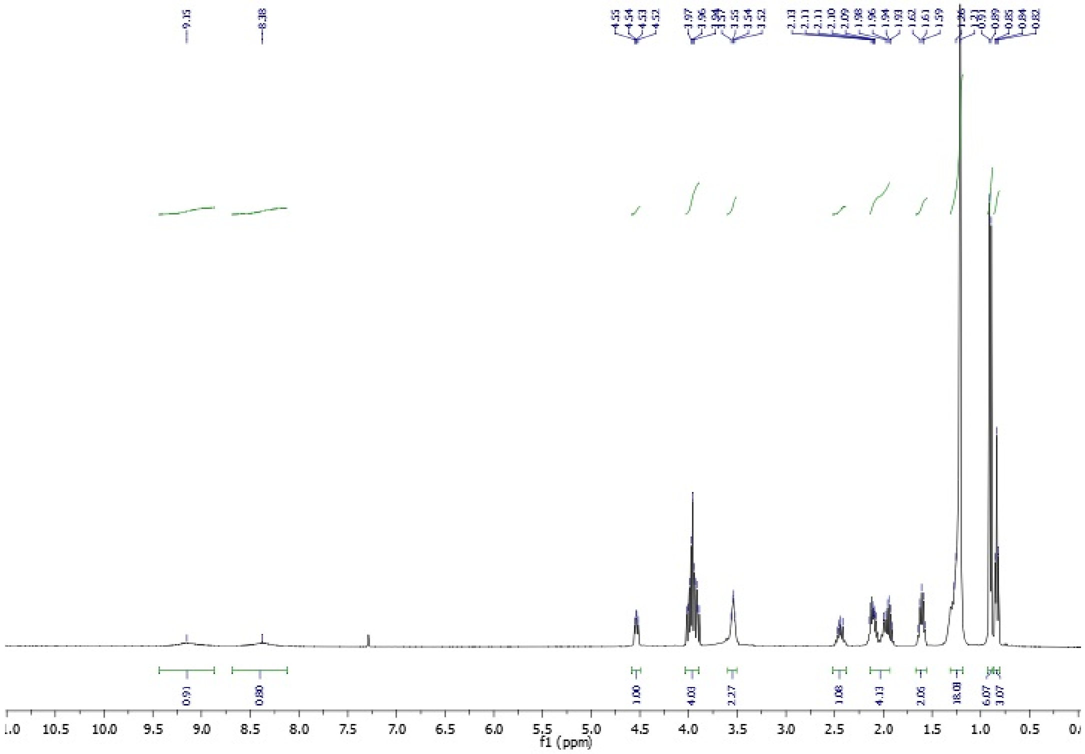


**Fig S7**. $^1$H NMR spectrum of [$^i$C$_4$Pro][DS] (**<u>7</u>**)

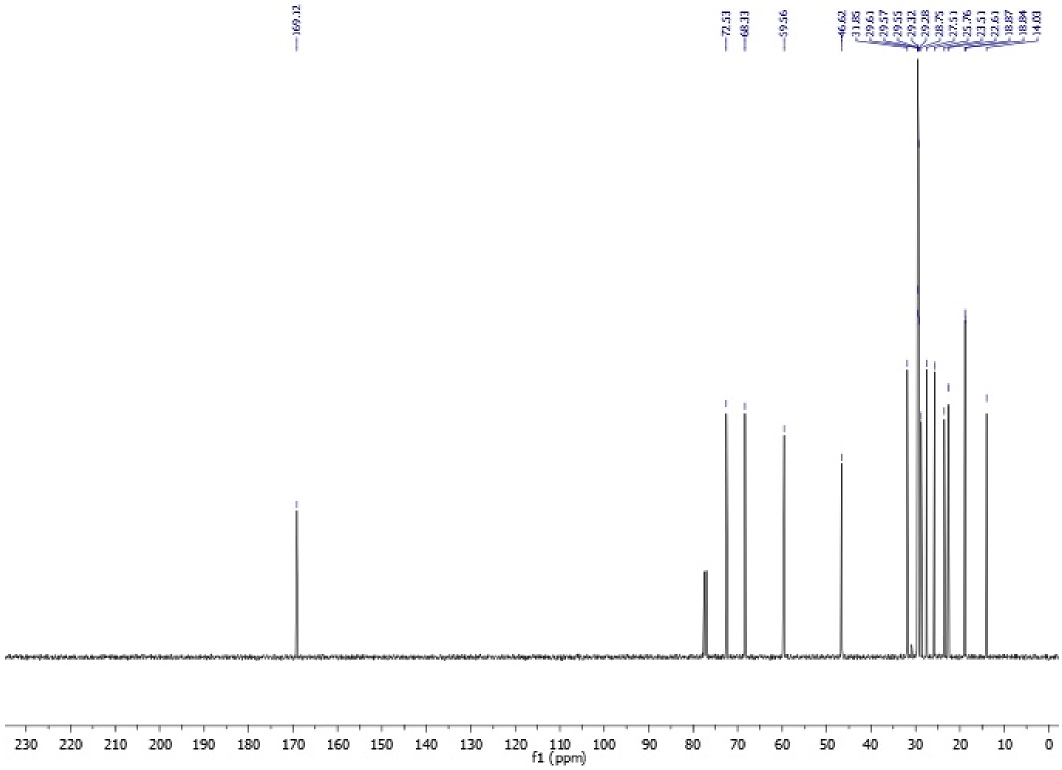


**Fig S8**. $^{13}$C NMR spectrum of [$^i$C$_4$Pro][DS] (**<u>7</u>**)

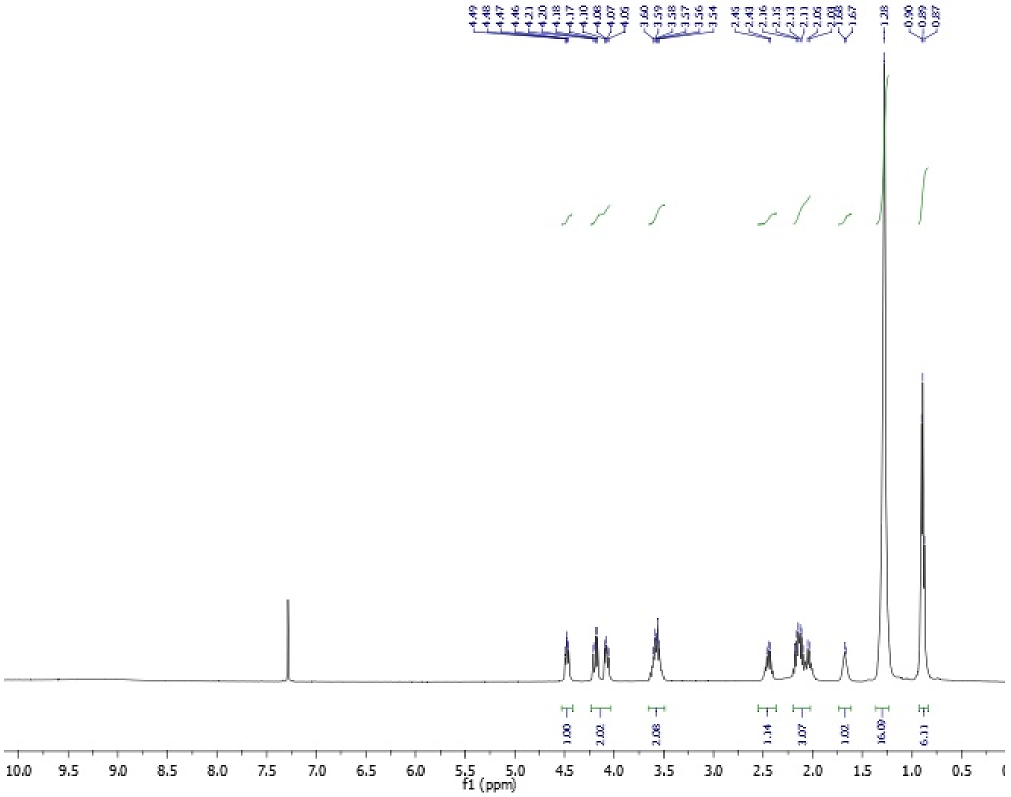


**Fig S9**. $^1$H NMR spectrum of [$C_4C_8$Pro][Cl] (**4**)

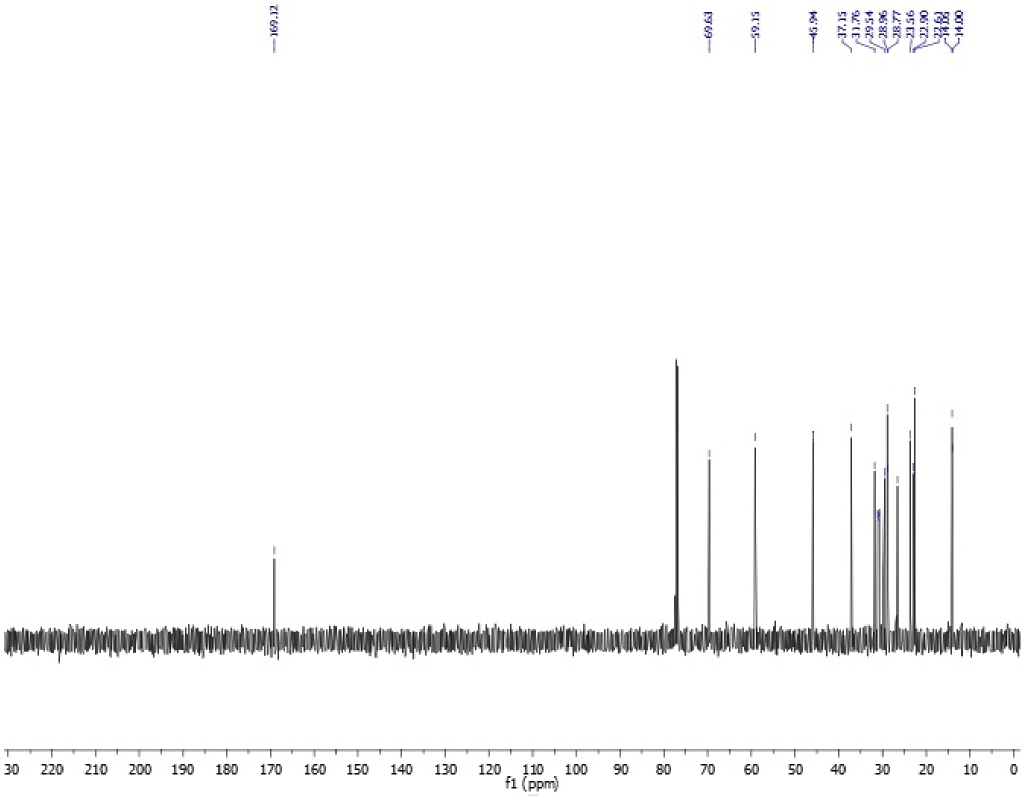


**Fig S10**. $^{13}$C NMR spectrum of [$C_4C_8$Pro][Cl] (**4**)

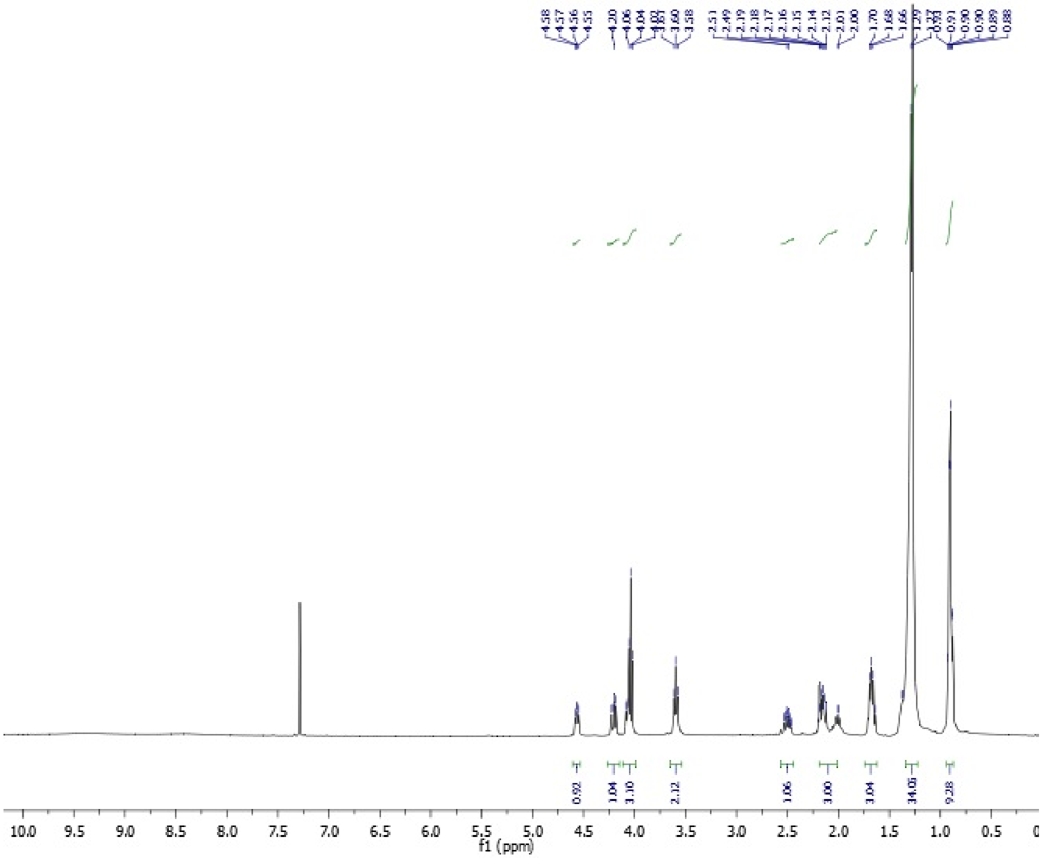


**Fig S11**. $^1$H NMR spectrum of [$C_4C_8$Pro][DS] (**8**)

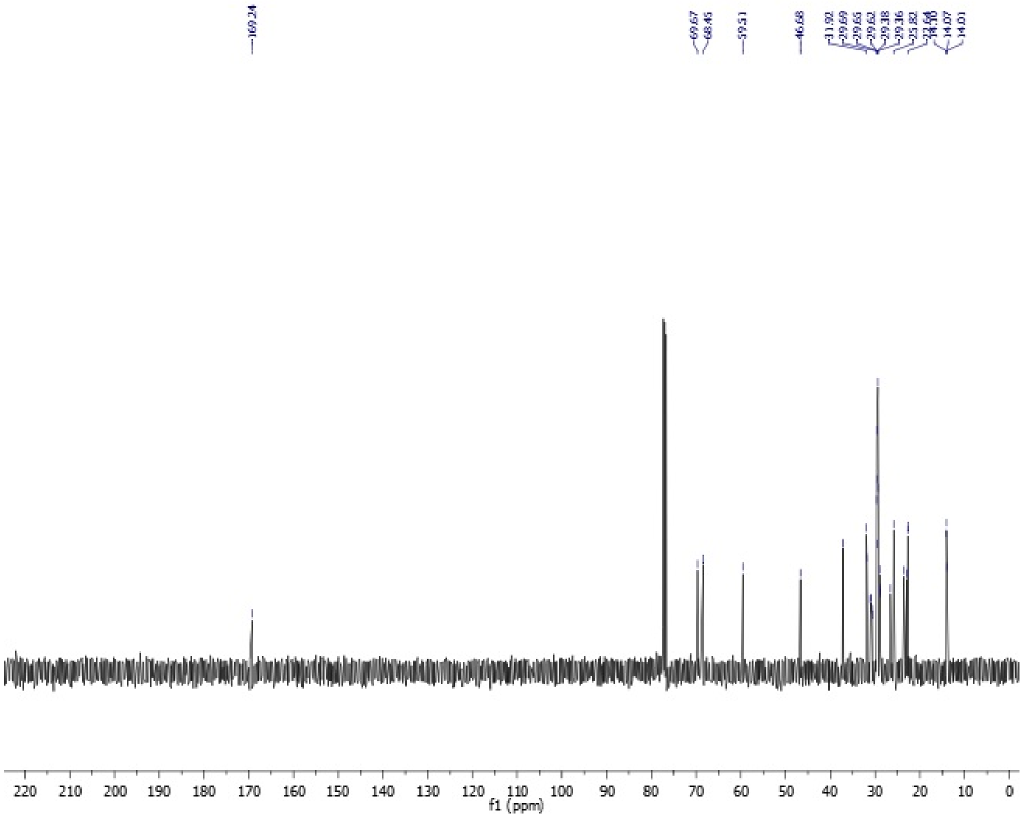


**Fig S12**. $^{13}$C NMR spectrum of [$C_4C_8$Pro][DS] (**8**)

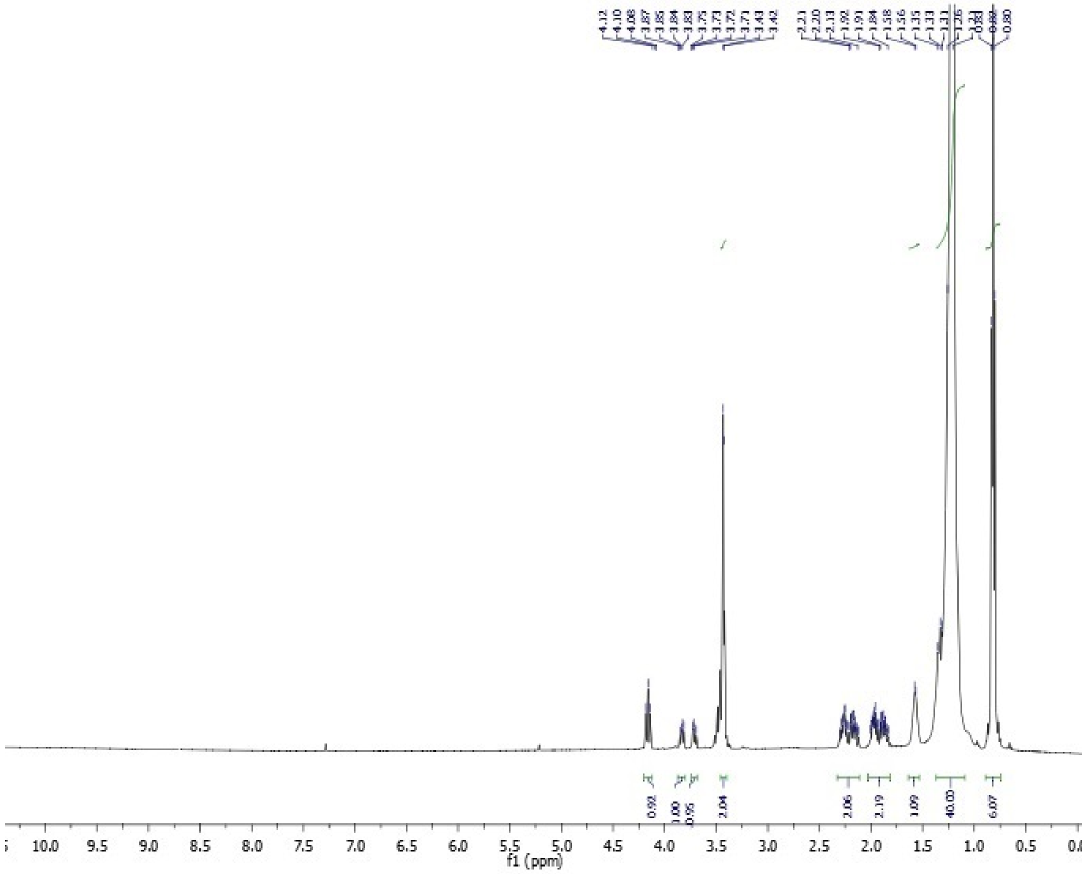


**Fig S13**. $^1$H NMR spectrum of [$C_{10}C_{14}$Pro][Cl] (**5**)

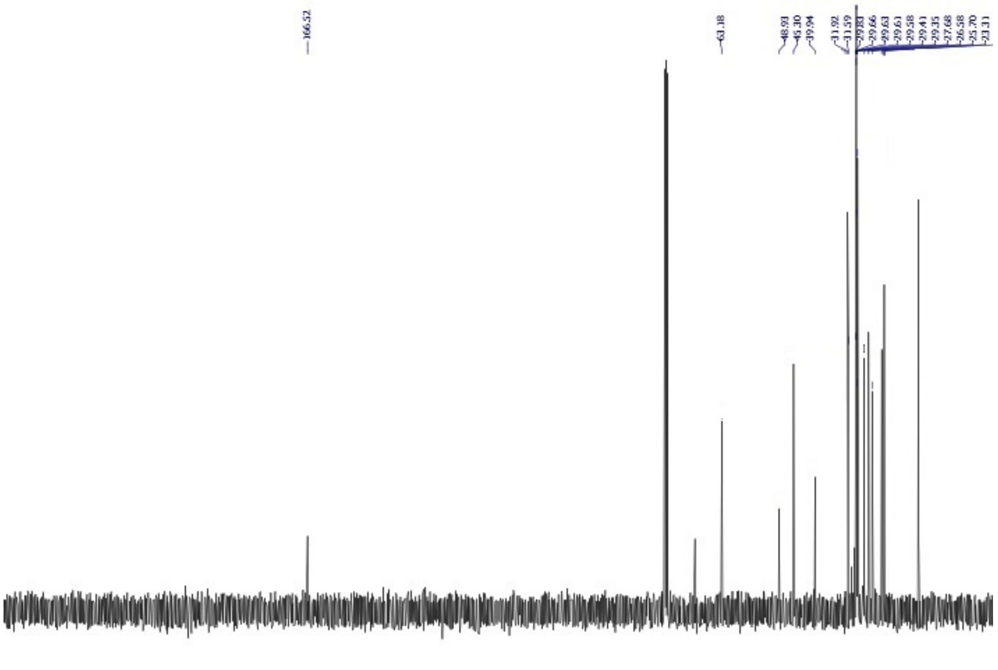


**Fig S14**. $^{13}$C NMR spectrum of [$C_{10}C_{14}$Pro][Cl] (**5**)

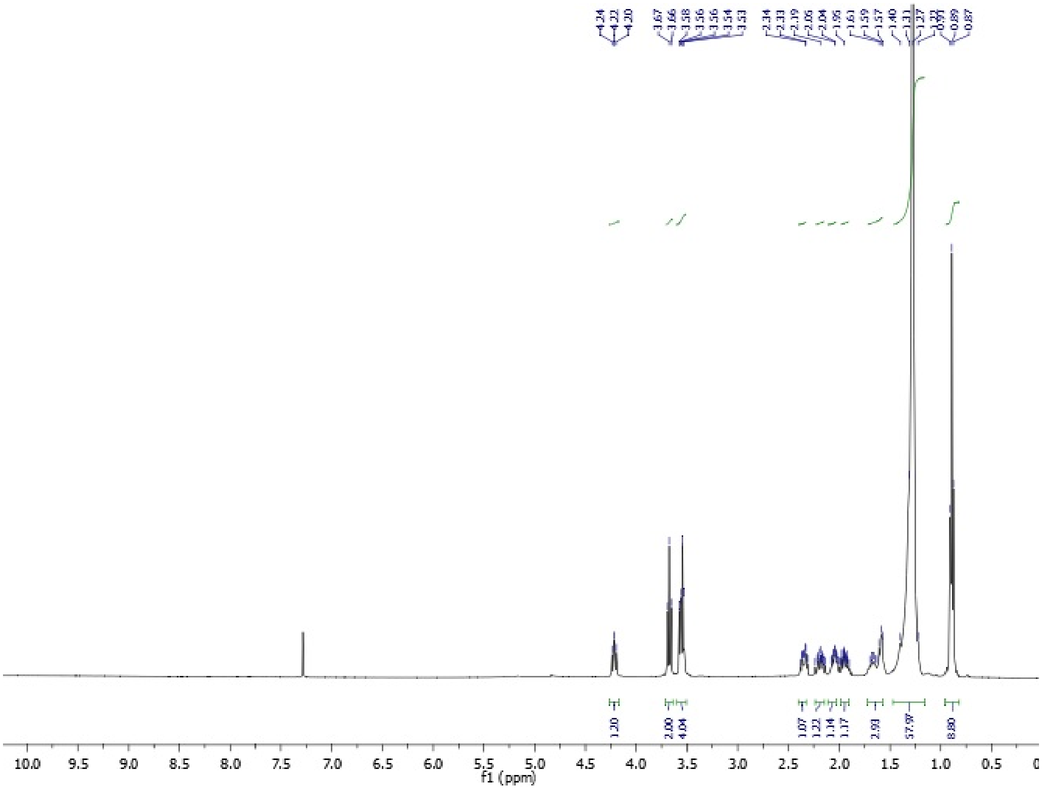


Fig S15. $^{1}H$ NMR spectrum of [$C_{10}C_{14}$Pro][DS] (**9**)

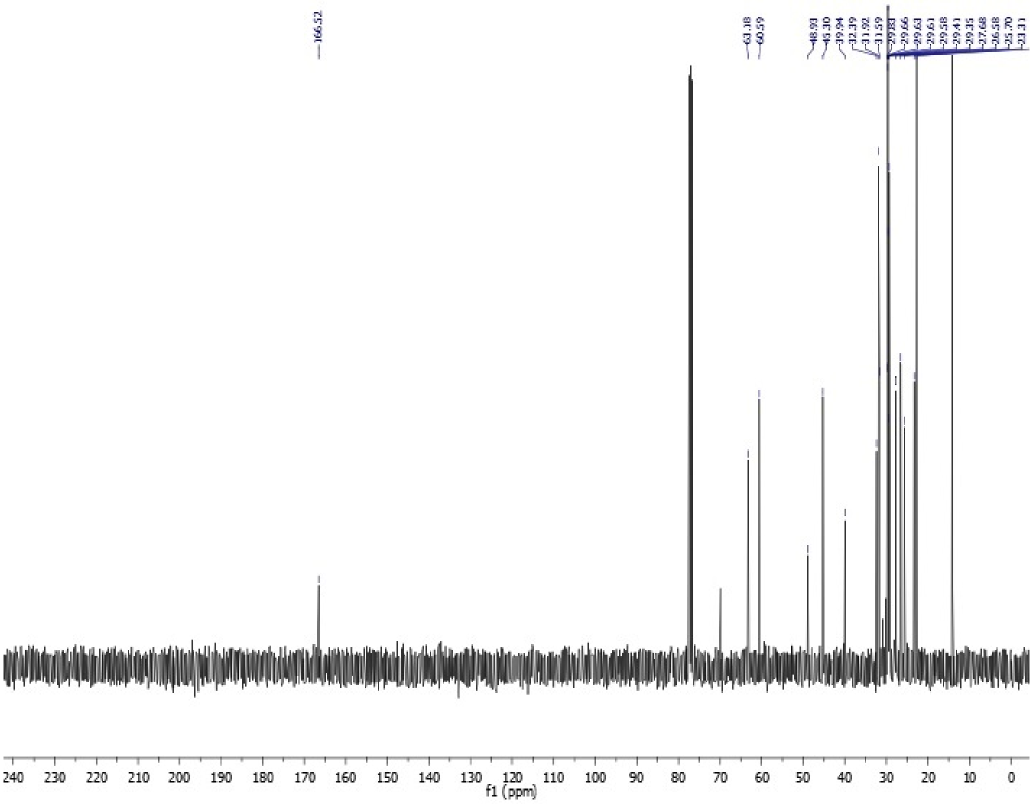


Fig S16. $^{13}C$ NMR spectrum of [$C_{10}C_{14}$Pro][DS] (**9**)

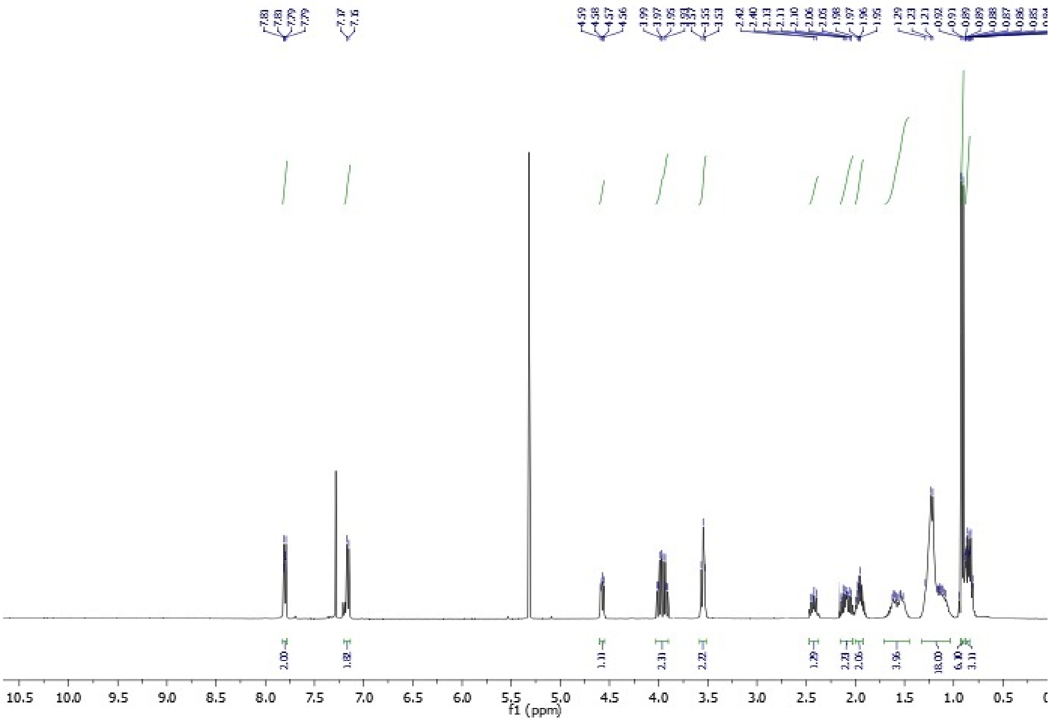


**Fig S17**. $^1$H NMR spectrum of [$^i$C$_4$Pro][DBS] (**10**)

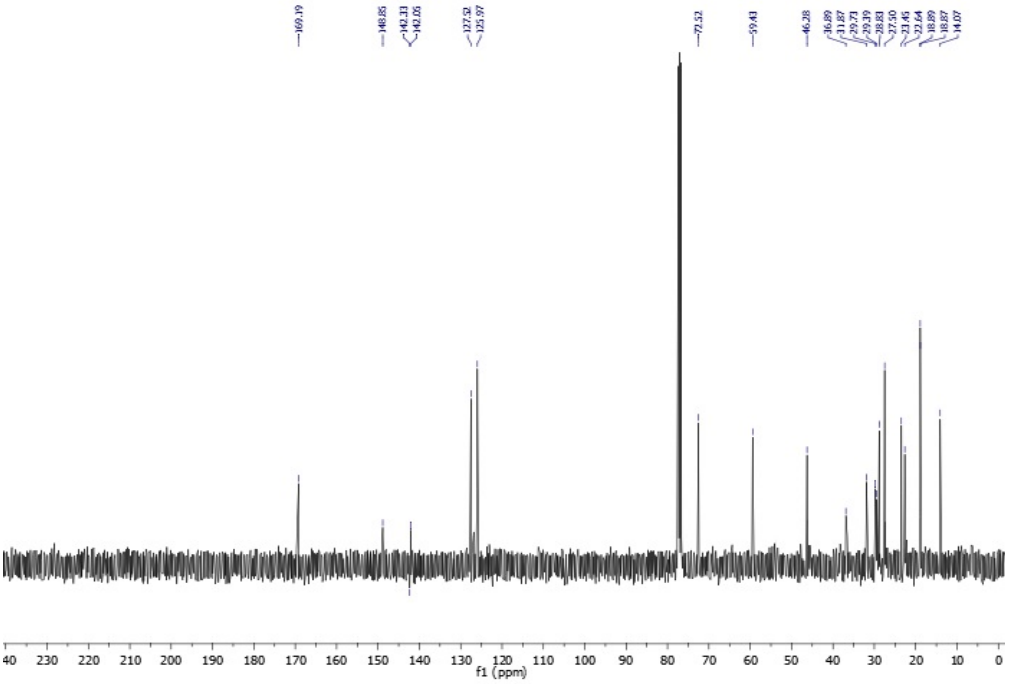


**Fig S18**. $^{13}$C NMR spectrum of [$^i$C$_4$Pro][DBS] (**10**)

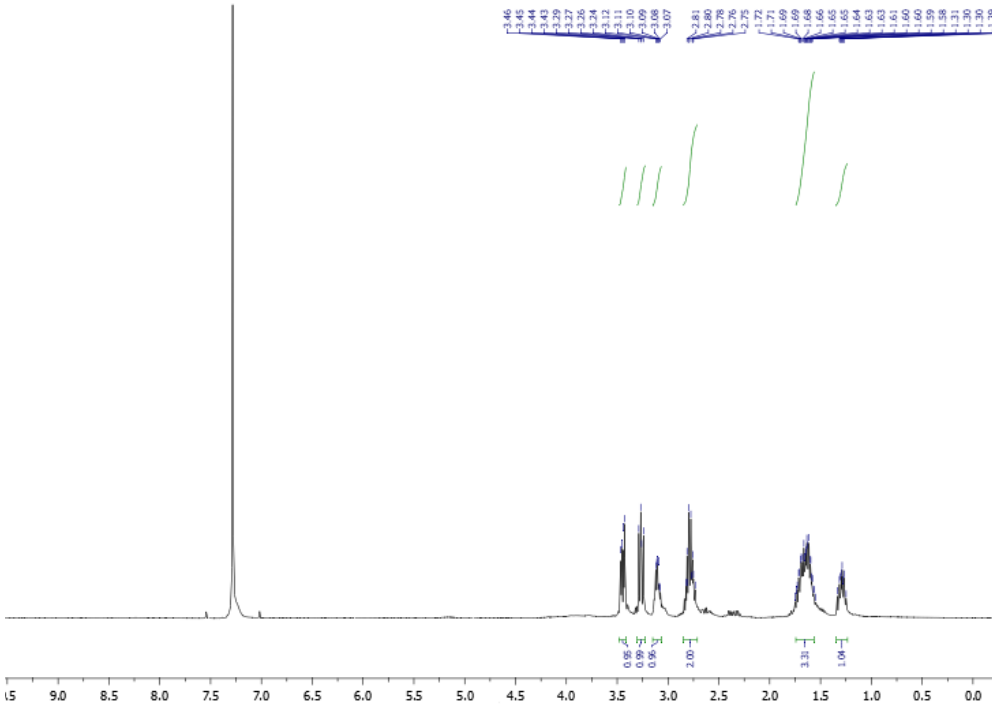


**Fig S19**. $^{1}$H NMR spectrum of (L)-Prolinol (**<u>11</u>**)

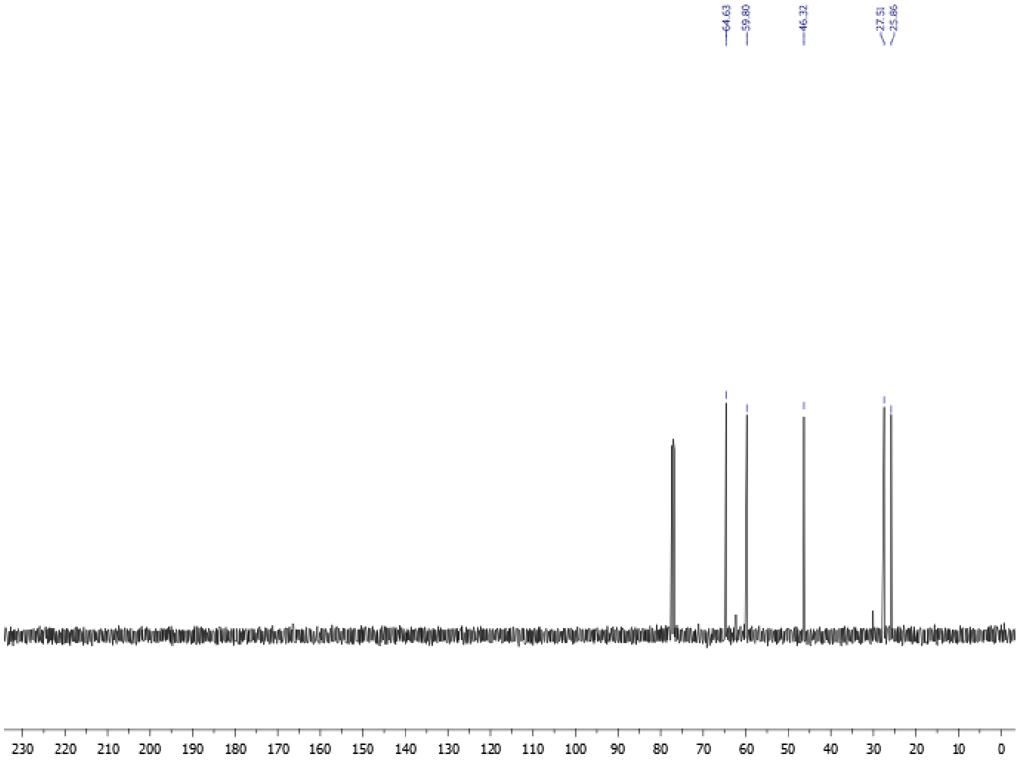


**Fig S20**. $^{13}$C NMR spectrum of (L)-Prolinol (**<u>11</u>**)

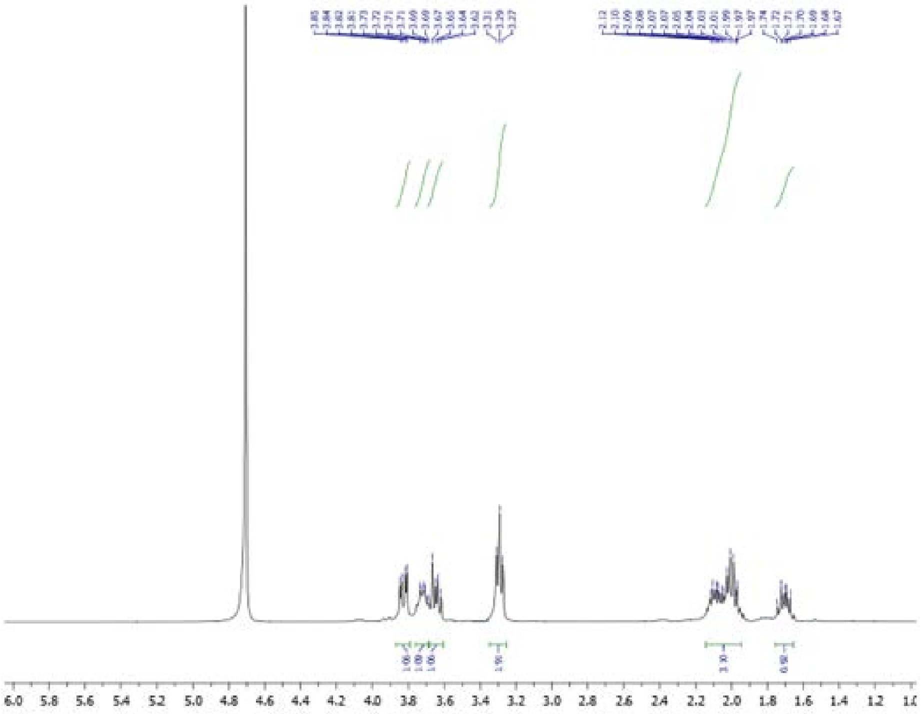


**Fig S21**. $^{1}$H NMR spectrum of [HOPro][Cl] (**<u>12</u>**)

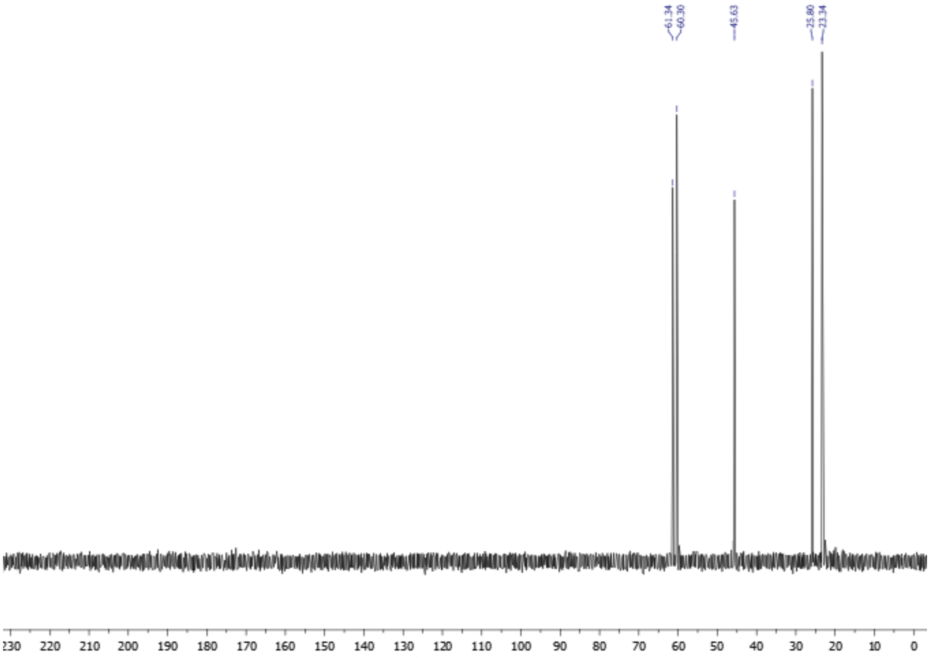


**Fig S22**. $^{13}$C NMR spectrum of [HOPro][Cl] (**<u>12</u>**)

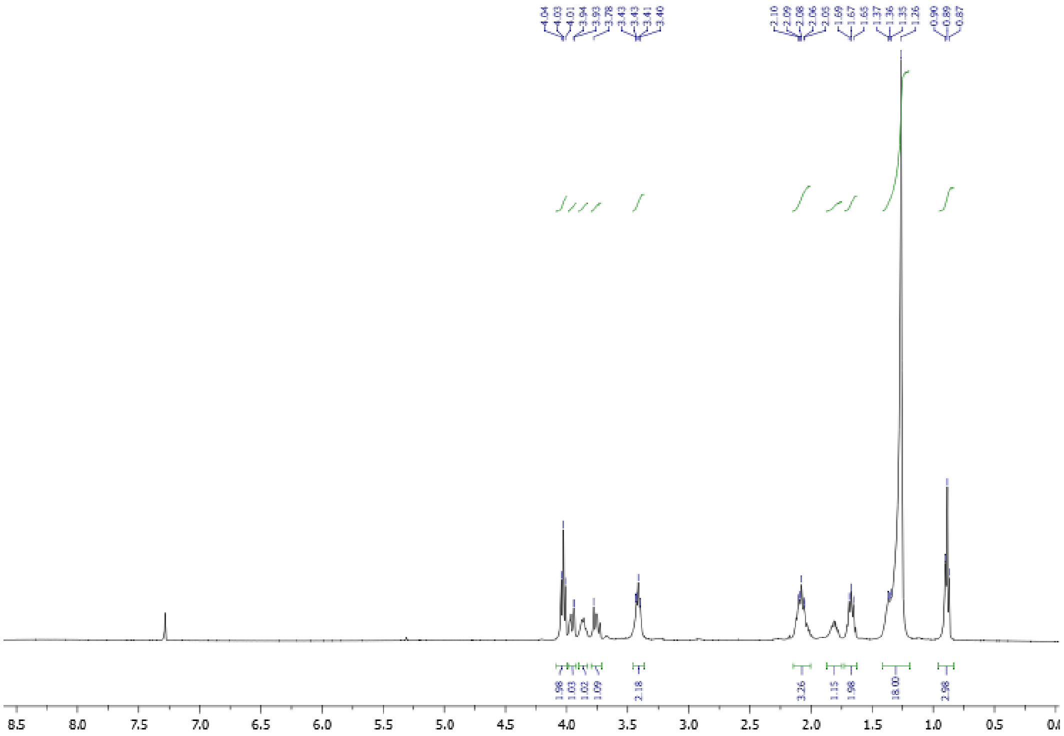


**Fig S23**. $^{1}$H NMR spectrum of [HOPro][DS] (**<u>13</u>**)

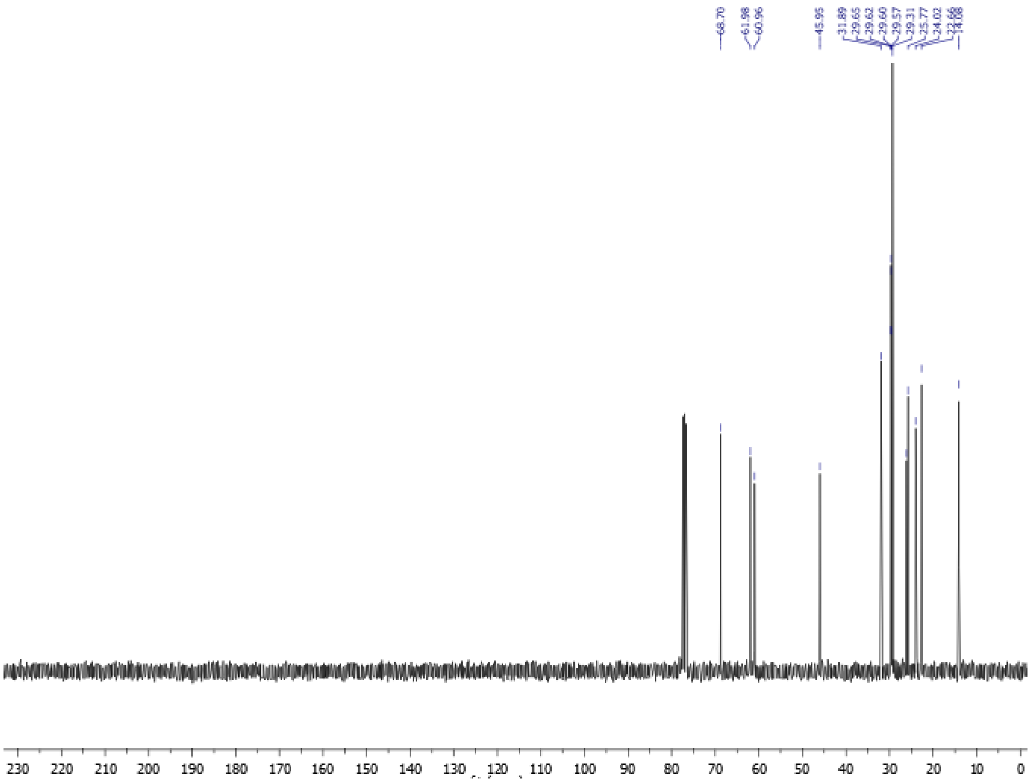


**Fig S24**. $^{13}$C NMR spectrum of [HOPro][DS] (**<u>13</u>**)

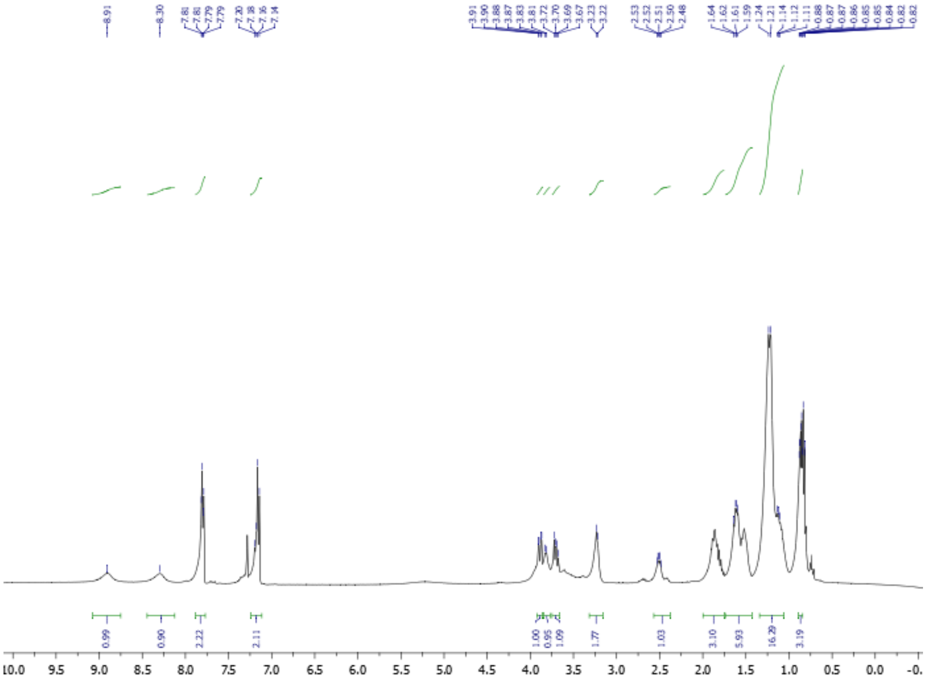


**Fig S25**. $^1$H NMR spectrum of [HOPro][DBS] (**14**)

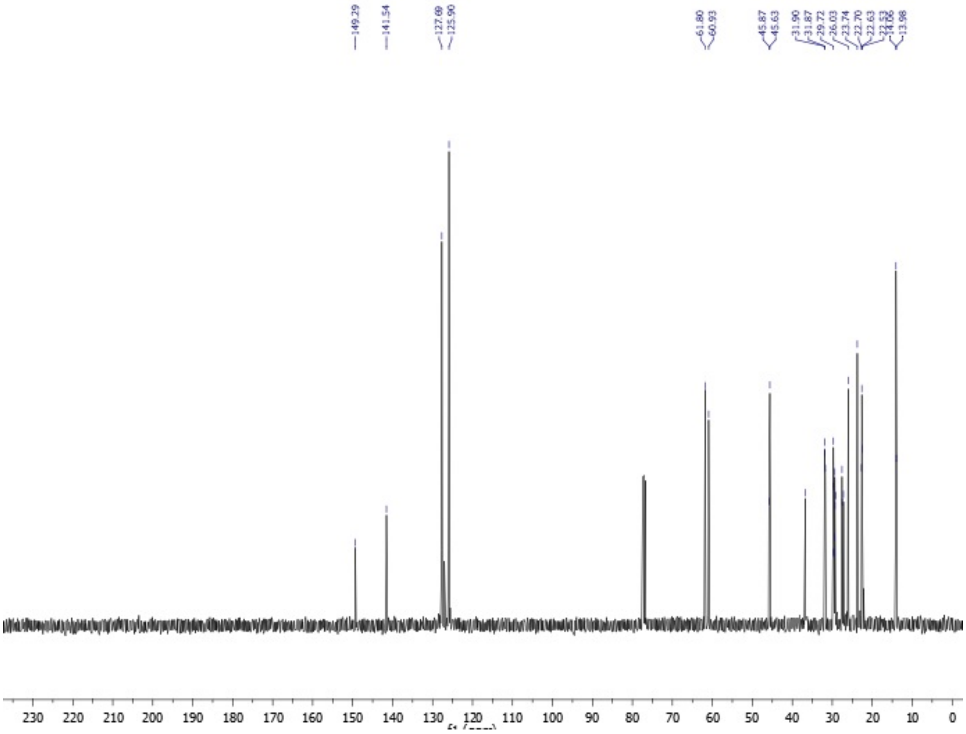


**Fig S26**. $^{13}$C NMR spectra of [HOPro][DBS] (**14**)

## Studies on hydrolytic degradation

### Studies on the hydrolytic degradation of [$^{i}C_4$Pro][DS] (**<u>7</u>**) and [$^{i}C_4$Pro][DBS] (**<u>10</u>**):

When [$^{i}C_4$Pro][DS] (**<u>7</u>**) was kept at r.t. in a vial occasionally open to the atmosphere (several ppm of water), a change in the color was observed after two months. With the aim of knowing the stability of the IL, [$^{i}C_4$Pro][DS] (**<u>7</u>**) (1 g) was dissolved in water (9 mL) and heated for some days at different temperatures as shown in table 1.

**Table 1**. Decomposition of [$^{i}C_4$Pro][DS] (**7**) and [$^{i}C_4$Pro][DBS] (**10**) when heating in water.

| IL | Temperature (K) | Days | Decomposition |
|---|---|---|---|
| [$^{i}C_4$Pro][DS] (**7**) | 313.15 | 1 | No |
| [$^{i}C_4$Pro][DS] (**7**) | 313.15 | 4 | Partial |
| [$^{i}C_4$Pro][DS] (**7**) | 373.15 | 1 | Partial |
| [$^{i}C_4$Pro][DS] (**7**) | 373.15 | 4 | Complete |
| [$^{i}C_4$Pro][DBS] (**10**) | 373.15 | 5 | Partial |

When heating at 313.15 K a partial decomposition (25 %) was observed in the $^{1}$H-NMR (Fig S27) after 4 days.

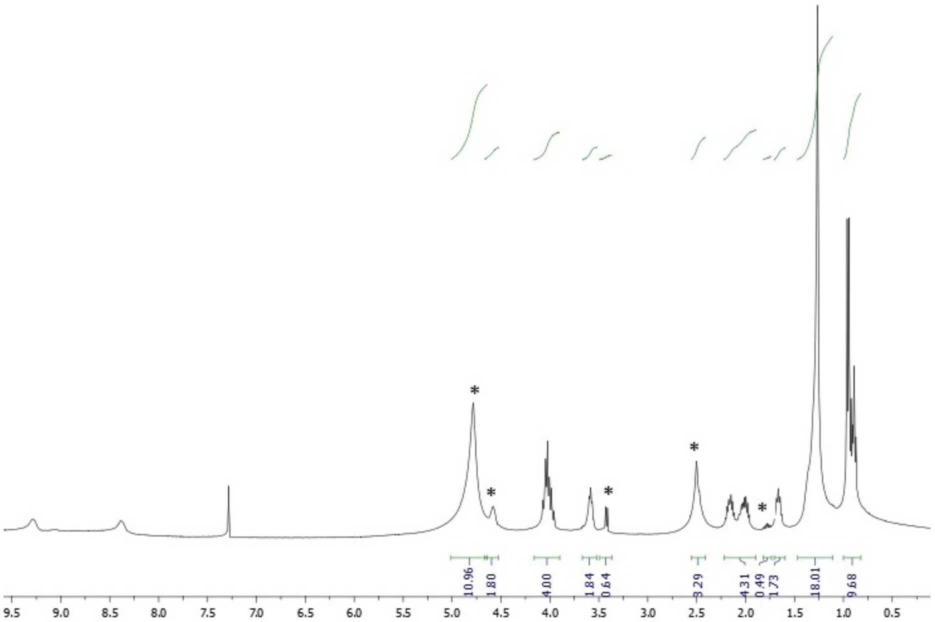
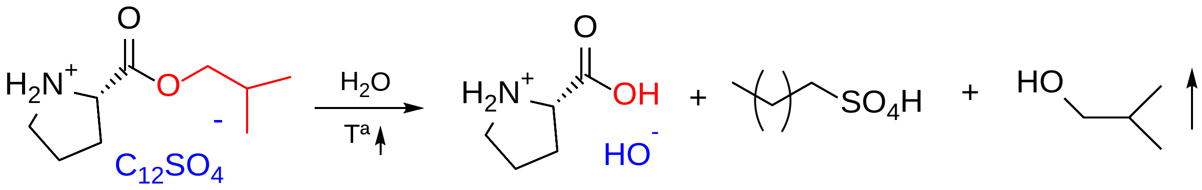


**Fig S27**. $^{1}$H NMR spectrum of [$^{i}C_4$Pro][DS] (**<u>7</u>**) after 4 days heating at 313.15 K (asterisks correspond to the decomposition compounds).

Taking into account the tendency of esther groups to hydrolyse, the following transformation was proposed (Scheme 1).



[$^i$C$_4$Pro][DS] (**7**)

**Scheme 1**. Hydrolysis decomposition of [$^i$C$_4$Pro][DS] (**7**) .

When the temperature was increased to 373.15 K, a partial decomposition (21%) was observed after only one day (Fig S28).

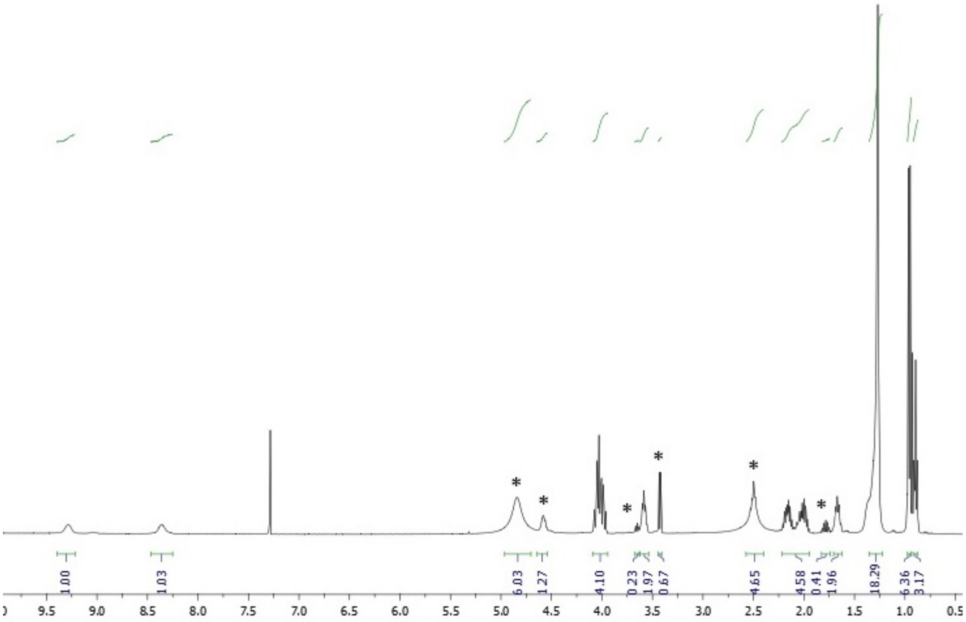


**Fig S28.** $^1$H NMR spectrum of [$^i$C$_4$Pro][DS] (**7**) after 1 day heating at 373.15 K

And finally, when the temperature was kept at 373.15 K for 4 days, the complete hydrolysis of the ester group was observed, to give the corresponding prolinium hydroxide, dodecylsulfonic acid and isobutyl alcohol. A liquid-liquid extraction of the crude reaction product with $CH_2Cl_2$ allowed the separation of dodecylsulfonic acid (organic phase) from the prolinium hydroxide (aqueous phase). The isobutyl alcohol was not isolated because it quickly evaporates when heated under low pressure to eliminate the water. The NMR spectra of the isolated compounds (Figs. S29, S30, S31, S32) as well as the MS data of prolinium hydroxyde confirmed their structures.

**Prolinium hydroxyde $^{1}$H NMR (400 MHz, MeOD):** δ= 5.36 (s, 4H, OH, $NH_2$), 4.46 (m, 1H; H-2), 3.46 (m, 2H; H-5), 2.48 (m, 1H; H-3), 2.14 (m, 2H; H-4); **$^{13}$C NMR (100 MHz, MeOD):** δ=170.37 (C=O), 59.49 (C-2), 46.11 (C-5), 28.21 (C-4), 23.28 (C-3); **MS (ESI):** *m/z* (%) $[C_5H_{10}NO_2]^+$: 116.07 $[A]^+$ (100%); $[A_2B]^+$: 249.14 (1.1).

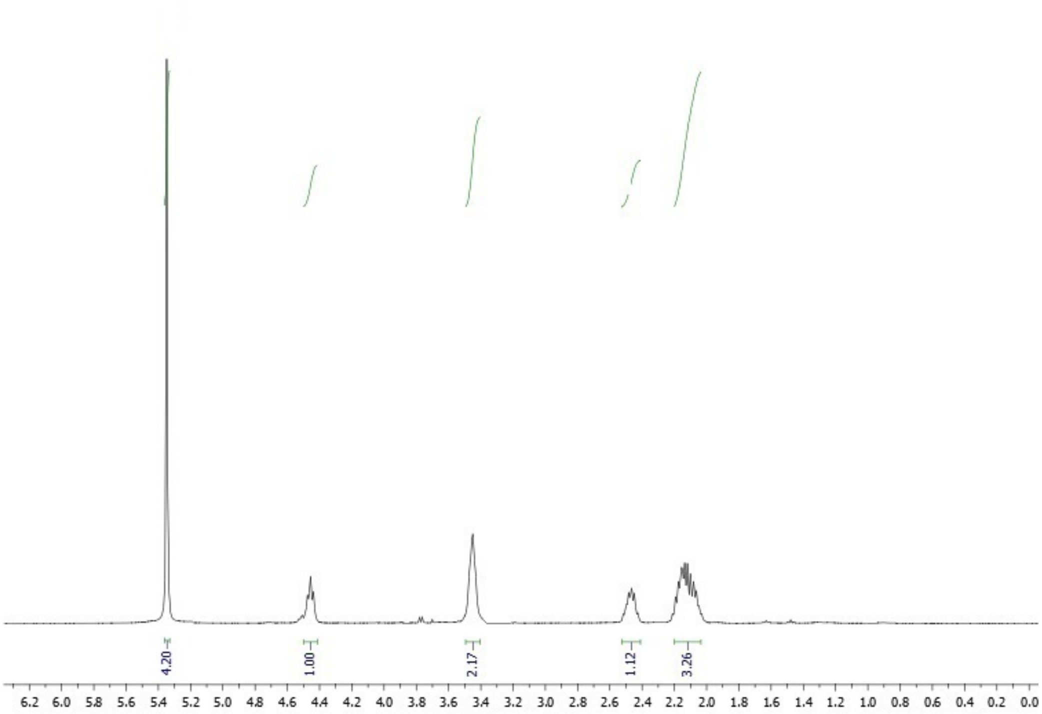


**Fig S29**. $^{1}$H NMR spectrum of prolinium hydroxide.

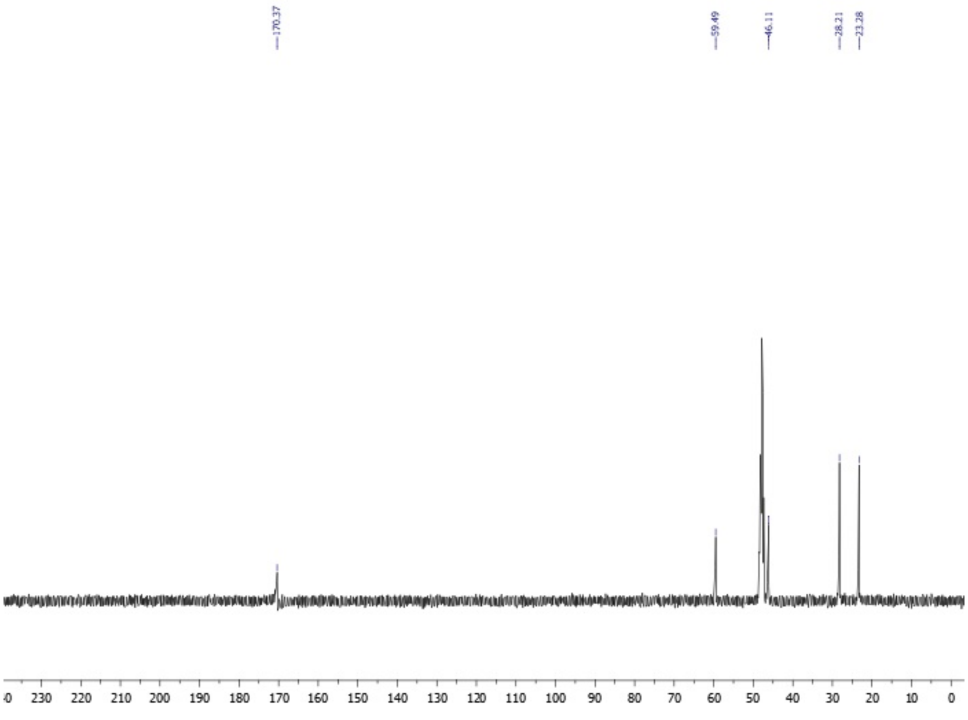


**Fig S30**. $^{13}$C NMR spectrum of prolinium hydroxide.

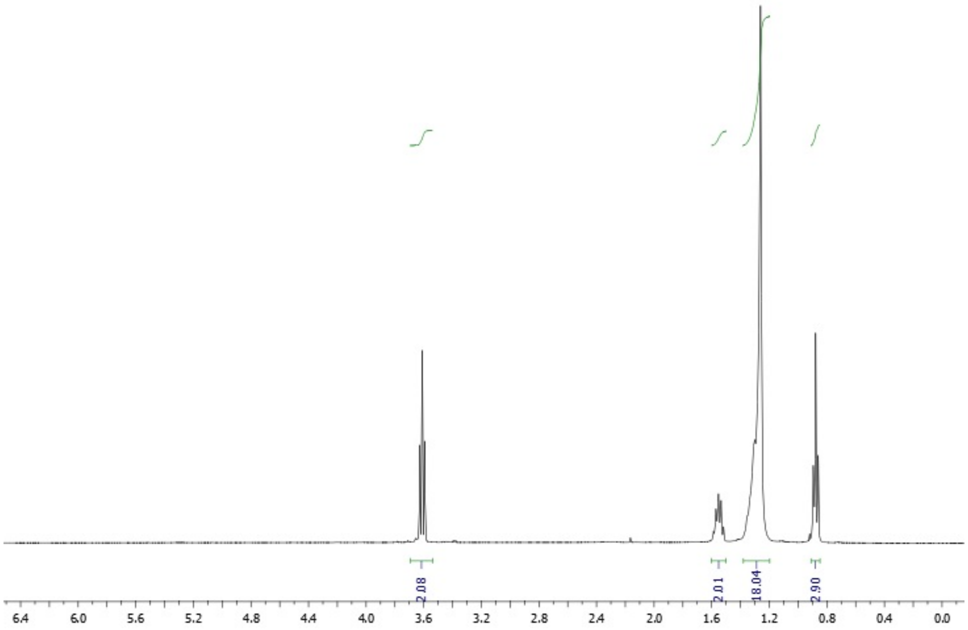


**Fig S31**. $^1$H NMR spectrum of dodecylsulfonic acid.

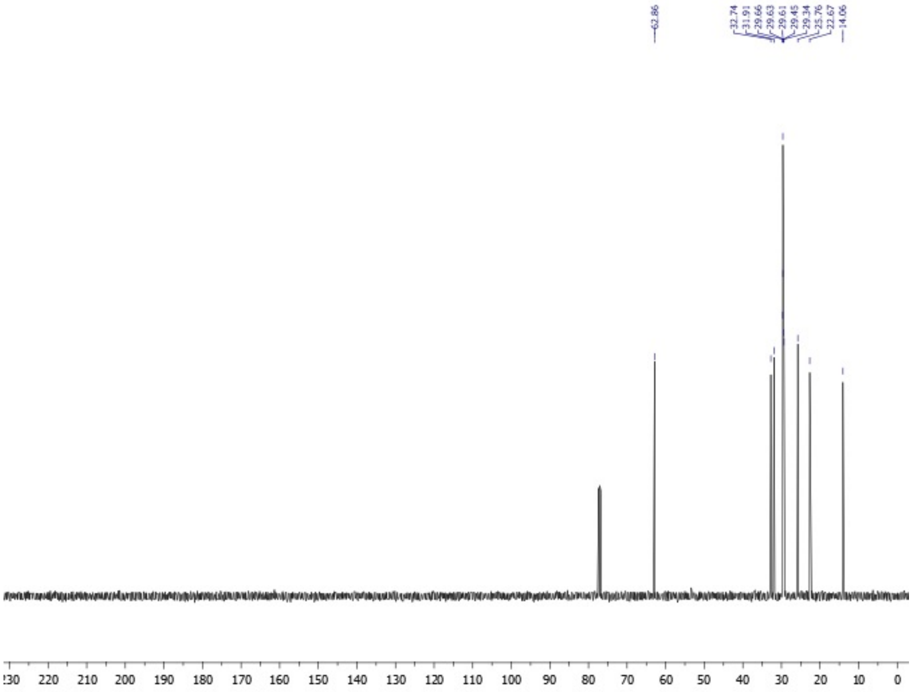


**Fig S32**. $^{13}$C NMR spectrum of dodecylsulfonic acid.

To know the thermal stability of [$^{i}C_4$Pro][DBS] (**<u>10</u>**), a solution in water using the same concentration as above, was heated at 373.15 K, but only a partial decomposition (10%) was observed in the $^1$H-NMR (Fig S33) after 5 days.

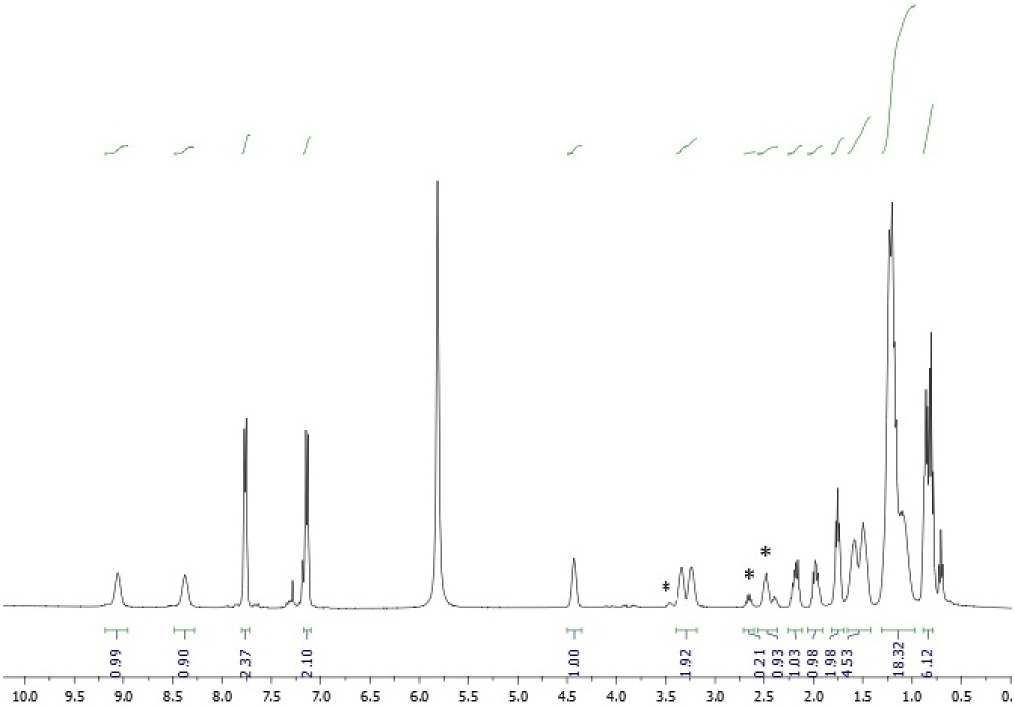


**Fig S33.** $^1$H NMR spectrum of [$^{i}C_4$Pro][DBS] (**<u>10</u>**) after 5 days heating at 373.15 K (asterisks correspond to the decomposition compounds).

## Studies on the hydrolytic degradation of [HOPro][DS] (<u>13</u>) and [HOPro][DBS] (<u>14</u>)

No decomposition of [HOPro][DS] (**<u>13</u>**) or [HOPro][DBS] (**<u>14</u>**) was observed when they were kept in the presence of water at r. t., even after several weeks. However, when [HOPro][DS] (**<u>13</u>**) (1 g) was dissolved in water (9 mL) and heated for 4 days at 373.15 K, a partial degradation was observed, as shown in table 2. It is due to the equilibrium that is produced between the [DS] anion and dodecylsulfonic acid (Fig S34). Due to the higher stability of [DBS] anion, [HOPro][DBS] (**<u>14</u>**) showed to be thermally and hydrolytically stable, even after heating at 373.15 K for 5 days. No signs of decomposition were found in the $^1$H NMR spectrum.

**Table 2**. Study on the thermal decomposition of [HOPro][DS] (**13**) and [HOPro][DBS] (**14**) when heating in water.

| IL | Temperature (K) | Days | Decomposition |
|---|---|---|---|
| [HOPro][DS] (**13**) | 313.15 | 4 | No |
| [HOPro][DS] (**13**) | 373.15 | 4 | Partial |
| [HOPro][DBS] (**14**) | 373.15 | 5 | No |

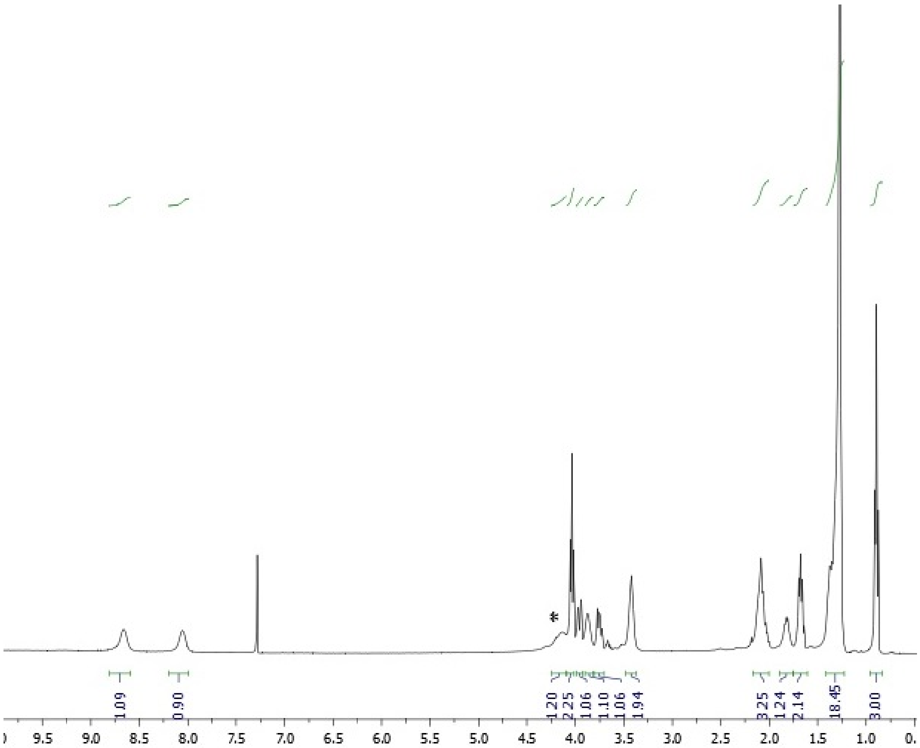


**Fig S34.** $^1$H NMR spectrum of [HOPro][DS] (<u>**13**</u>) after 5 days heating at 373.15 K (asterisk correspond to the decomposition compounds).