Electronic Supplementary Information

Effect of Residue Structure on the Thermal and Thermoresponsive Properties of γ-Substituted Poly(*N*-acryloyl-2-pyrrolidone)s

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Experimental Section

Single Crystal X-Ray Analysis. A suitable crystal of **StSNP** was selected and mounted on a Bruker-AXS SMART APEX II CCD diffractometer at 100(1)K. The cell dimensions and the intensities were collected with Cu-Ka radiation (l = 1.54178 Å). Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs.[1] The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2, using the SHELXTL V 6.14 program package.[2] All non-hydrogen atoms were refined anisotropically. All the H atoms in all of the structures were found in electron-density difference maps.

The methyl H atoms were put in ideally staggered positions with C---H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The methine, methylene, and pyrrolidone Hs were all placed in geometrically idealized positions and constrained to ride on their parent C atoms with C---H distances of 0.93, 0.97, and 0.98 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$.

5-Ethylthio-2-pyrrolidone. Method A. Yield, 70%. Analytical data consistent with reported data.[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (br, s, 1H), 4.83 (m, 1H), 2.64 (q, $^3J_{HH}$ = 7.40 Hz, 2H), 2.52 (m, 2H), 2.33 (m, 1H), 2.09 (m, 1H), 1.30 (t, $^3J_{HH}$ = 7.40 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$): δ 178.24, 58.89, 29.75, 28.58, 24.35, 14.79.

EthSNP. Yield, 25%. R_f = 0.54. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, $^3J_{HH}$ = 16.95 Hz, $^3J_{HH}$ = 10.47 Hz, 1H), 6.52 (d, $^3J_{HH}$ = 16.91 Hz, 1H), 5.87 (d, $^3J_{HH}$ = 10.27 Hz, 1H), 5.67 (d, $^3J_{HH}$ = 7.38 Hz, 1H), 2.88 (m, 2H), 2.73 (m, 1H), 2.55 (m, 1H), 2.45 (m, 1H), 2.14 (m, 1H), 1.30 (t, $^3J_{HH}$ = 7.31 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$): δ 174.79, 165.28, 131.33, 129.13, 61.34, 32.53, 27.54, 26.38, 14.88. GC/MS: m/z (%): 199 (6%) [M^+], 138 (90%), 84 (23%), 55 (100%), 28 (12%).

poly(EthSNP). Yield, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.66 (br, s, 1H), 3.69 (br, s, 1H), 2.83-2.52 (br, m, 4H), 2.01 – 1.51 (br, m, 4H), 1.27(s, 3H).

5-Butylthio-2-pyrrolidone. Method A. Yield, 40%. Analytical data consistent with reported data.[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.51 (s, 1H), 4.78 (dd, $^3J_{HH}$ = 7.16 Hz, $^3J_{HH}$ = 3.52 Hz, 1H), 2.52 (m, 4H), 2.30 (m, 1H), 2.09 (m, 1H), 1.57 (m, 2H), 1.39 (m, 2H), 0.90 (t, $^3J_{HH}$ = 7.32 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.24, 59.17, 31.69, 29.93, 29.75, 28.64, 22.02, 13.63. GC/MS: m/z (%): 128 (100%), 98 (49%), 90 (3%), 83 (9%), 68 (5%), 55 (9%), 45 (33%), 28 (24%).

BuSNP. Yield, 53%. R_f = 0.61. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, $^3J_{HH}$ = 16.96 Hz, $^3J_{HH}$ = 10.46 Hz, 1H), 6.55 – 6.48 (m, 1H), 5.90 – 5.83 (m, 1H), 5.63 (d, $^3J_{HH}$ = 7.46 Hz, 1H), 2.92 (m, 1H), 2.81 (m, 1H), 2.70 (m, 1H), 2.55 (m, 1H), 2.44 (m, 1H), 2.15 (m, 1H), 1.60 (m, 2H), 1.41 (m, 2H), 0.92 (t, $^3J_{HH}$ = 7.25 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.82, 165.25, 131.31, 129.15, 61.67, 32.52, 31.98, 31.94, 27.59, 21.99, 13.65.

poly(BuSNP). Yield, 25%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.49 (s, 1H), 3.63-3.47 (m, 1H), 3.01-2.60 (m, 4H), 1.97 (s, 3H), 1.56 (s, 3H), 1.38 (s, 2H), 0.89 (s, 3H).

5-Phenylthio-2-pyrrolidone. Method A. Yield, 86%. Analytical data consistent with reported data.[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.39 (m, 2H), 7.42 – 7.28 (m, 3H), 6.14 (s, 1H), 5.03 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.56 (m, 1H), 2.31 – 2.04 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.71, 134.54, 131.53, 129.39, 128.78, 62.27, 29.11, 28.22.

PhSNP. Yield, 21%. R_f = 0.38. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.55 (m, 2H), 7.47 (dd, $^{3}J_{HH}$ = 17.00 Hz, $^{3}J_{HH}$ = 10.45 Hz, 1H), 7.39 (m, 3H), 6.57 (dd, $^{3}J_{HH}$ = 17.00 Hz, $^{3}J_{HH}$ = 1.64 Hz, 1H), 5.91 (dd, $^{3}J_{HH}$ = 10.44 Hz, $^{3}J_{HH}$ = 1.64 Hz, 1H), 5.74 (d, $^{3}J_{HH}$ = 7.30 Hz, 1H), 2.86 – 1.72 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.75, 164.60, 135.58, 131.74, 131.06, 129.34, 129.23, 128.99, 64.07, 31.95, 26.35. GC/MS: m/z (%): 247 [M^+] (3%), 138 (98%), 109 (12%), 84 (10%), 55 (100%), 28 (20%).

poly(PhSNP). Yield, 35% ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 2H), 7.27 (s, 3H), 5.67 (s, 1H), 3.66 (s, 1H), 2.38 – 1.32 (br m, 6H).

5-Stearylthio-2-pyrrolidone. Method A. Yield, 74%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (br, s, 1H), 4.81 (dd, $^{3}J_{HH}$ = 7.37 Hz, $^{3}J_{HH}$ = 3.52 Hz, 1H), 2.59 (t, $^{3}J_{HH}$ = 7.42, 2H), 2.52 (m, 2H), 2.33 (m, 1H), 2.11 (m, 1H), 1.60 (m, 2H), 1.38 (m, 2H), 1.26 (s, 28H), 0.88 (t, $^{3}J_{HH}$ = 6.93Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.87, 165.28, 131.42, 129.12, 61.69, 32.55, 32.35, 31.93, 29.89, 29.71, 29.67, 29.60, 29.51, 29.38, 29.21, 28.92, 27.60, 22.71, 14.15.

StSNP. Yield, 22%, R_f = 0.67. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (dd, $^{3}J_{HH}$ = 16.96, 10.46 Hz, 1H), 6.52 (m, 1H), 5.86 (d, $^{3}J_{HH}$ = 10.41 Hz, 1H), 5.62 (d, $^{3}J_{HH}$ = 7.42 Hz, 1H), 2.91 (m, 1H), 2.80 (m, 1H), 2.68 (m, 1H), 2.54 (m, 1H), 2.43(m, 1H), 2.14 (m, 1H), 1.59 (m, 2H), 1.38 – 1.33 (m, 2H), 1.25 (s, 28H), 0.87 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.87, 165.28, 131.42, 129.12, 61.69, 32.55, 32.35, 31.93, 29.89, 29.71, 29.60, 29.51, 29.38, 29.21, 28.92, 27.60. GC/MS: m/z (%): 286 (14%), 252 (14%), 224 (5%), 196 (2%), 182 (2%), 168 (3%).

poly(StSNP). Yield, 44%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.60 (s, 1H), 3.51 (s, 1H), 2.71 (br d, 4H), 1.99 (s, 2H), 1.59 (s, 2H), 1.29 (s, 32H), 0.91 (t, $^{3}J_{HH}$ = 6.73 Hz, 3H).

5-Cyclohexylthio-2-pyrrolidone. Method A. Yield, 77% ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.50 (br s, 1H), 4.90 (dd, $^{3}J_{HH}$ = 7.36, $^{3}J_{HH}$ = 4.09 Hz, 1H), 2.79 (m, 1H), 2.53 (m, 2H), 2.33 (m, 1H), 2.09 (m, 1H), 1.97 (m, 2H), 1.79 (m, 2H), 1.64 (m, 1H), 1.46 – 1.21 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.42, 57.81, 43.40, 34.30, 34.20, 29.50, 29.43, 26.03, 25.91, 25.59.

CySNP. Yield, 36%, R_f = 0.38. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, $^{3}J_{HH}$ = 17.01, 10.45 Hz, 1H), 6.53 (d, $^{3}J_{HH}$ = 17.01 Hz, $^{3}J_{HH}$ = 1.76Hz, 1H), 5.88 (dd, $^{3}J_{HH}$ = 10.46 Hz, $^{3}J_{HH}$ = 1.76 Hz, 1H), 5.68 (d, $^{3}J_{HH}$ = 7.32 Hz, 1H), 2.80 (m, 1H), 2.63 – 2.46 (m, 2H), 2.33 (m, 1H), 2.22 – 2.08 (m, 1H), 1.96 (m, 2H), 1.78 (m, 2H), 1.69 – 1.59 (m, 1H), 1.37

(m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.87, 165.17, 131.21, 129.24, 60.50, 44.48, 34.68, 33.48, 32.49, 28.47, 25.70 ppm. GC/MS: m/z (%): 253 (9%) [M^+], 170 (4%), 138 (100%), 84 (18%), 55 (78%).

poly(CySNP). Yield, 74%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.55 (s, 1H), 3.52 (s, 1H), 3.21 – 2.28 (m, 6H), 1.97 (m, 4H), 1.76 – 1.29 (m, 7H).

5-Methoxyethanethio-2-pyrrolidone. Method A. Yield, 70%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (br s, 1H), 4.85 (dd, $^3J_{HH}$ = 7.52 Hz, $^3J_{HH}$ = 4.50 Hz, 1H), 3.68 (m, 1H), 3.60 (m, 1H), 3.41 (s, 3H), 2.83 (m, 2H), 2.53 (m, 2H), 2.36 (m, 1H), 2.02 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 176.79, 73.77, 60.69, 58.87, 32.50, 29.94, 28.48.

MeOEtSNP. Yield, 16%, R_f = 0.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, $^3J_{HH}$ = 17.00, 10.45 Hz, 1H), 6.53 (dd, $^3J_{HH}$ = 17.00, 1.71 Hz, 1H), 5.89 (dd, $^3J_{HH}$ = 10.45, 1.70 Hz, 1H), 5.71 (d, $^3J_{HH}$ = 7.51 Hz, 1H), 3.62 (m, 2H), 3.39 (s, 3H), 3.08 (m, 1H), 2.93 (m, 2H), 2.63 – 2.40 (m, 2H), 2.20 (m, 1H). ^{13}C NMR **(**126 MHz, $CDCl_3$**):** δ 174.78 , 165.42 , 131.44 , 129.12 , 72.20 , 62.16 , 58.80 , 32.46 , 32.14 , 27.64. GC/MS: m/z (%): 229 (2%) [M^+], 197 (13%), 170 (9%), 138 (100%), 84 (24%), 55 (80%).

poly(MeOEtSNP). Yield, 61% ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.59 (br,s, 1H) 3.64 (br, m, 3H), 3.39 (s, 3H), 3.04 - 2.05 (br m, 5H), 2. 04 – 1.25 (br m, 3H).

5-Tetrahydrofurfuryloxy-2-pyrrolidone. Method B. Yield, 22%**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (br, d, 1H), 4.99 (m, 1H), 3.99 (m, 1H), 3.86 (m, 1H), 3.76 (m, 1H), 3.62 - 3.54 (m, 1H), 3.41 (m, 1H), 2.49 (m, 1H), 2.24 (m, 2H), 2.05 (m, 1H), 1.90 (m, 4H), 1.58 – 1.47 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*): δ 177.48, 176.98, 85.30, 84.54, 77.62, 76.33, 76.01, 69.34, 68.01, 66.44, 66.39, 66.19, 62.79, 26.58, 26.49, 26.36, 26.26, 25.95, 25.24, 23.97, 23.61, 23.58.

FurONP: Yield, 13% R_f = 0.12. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, $^3J_{HH}$ = 17.00, 10.45 Hz, 1H), 6.51 (d, $^3J_{HH}$ = 17.01 Hz, 1H), 5.88 (m, 1H), 5.80 (d, $^3J_{HH}$ = 5.28 Hz, 1H), 4.00 (m, 1H), 3.86 (m, 1H), 3.80 (m, 1H), 3.66 (m, 2H), 2.91 (m, 1H), 2.48 (m, 1H), 2.11 (m, 2H), 1.99 – 1.78 (m, 3H), 1.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): 175.78, 175.74, 166.04, 166.02, 131.37, 129.27, 87.63, 87.35, 78.06, 77.73, 76.82, 73.08, 72.53, 68.46, 68.32, 31.51, 27.94, 27.78, 26.47, 26.42, 25.72, 25.55. GC/MS: m/z (%): 169 (11%), 138 (69%), 111 (6%), 84 (74%), 71 (100%), 55 (70%), 43 (22%), 27 (9%).

poly(FurONP). Yield, 34% ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (s, 1H); 4.01 (s, 2H), 3.87-3.60 (m, 4H); 2.78- 1.61 (br, m, 10H).

5-Cyclohexanoxy-2-pyrrolidone. Method B. Yield, 40%, ^{1}H NMR (500 MHz, $CDCl_3$): 6.87 (br, m, 1H), 5.12 (d, $^3J_{HH}$ = 6.10Hz, 1H), 3.37 (m, 1H), 2.55 (m, 1H), 2.33 (m, 1H), 2.23 (m, 1H), 2.05 (m, 1H), 1.87 (m, 2H), 1.76 (m, 2H), 1.56 (m, 1H), 1.37-1.21 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.88, 83.62, 75.44, 33.36, 32.36, 29.16, 28.35, 25.55, 24.15, 24.06.

CyONP. Yield, 26%**.** R_f = 0.62 ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, $^3J_{HH}$ = 17.00 Hz, $^3J_{HH}$ = 10.45 Hz, 1H); 6.55 (d, $^3J_{HH}$ 17.02 Hz, 1H); 5.88 (d, $^3J_{HH}$ 10.47 Hz, 1H), 5.85

(d, $^{3}J_{HH}$ 5.4 Hz, 1H), 3.70 (m, 1H), 2.93 (m, 1H), 2.48 (m, 1H) 2.15 (m, 1H); 2.03 (m, 1H); 1.96 (m, 1H) 1.88 (m, 1H) 1.74 (m, 2H); 1.55 (m, 1H); 1.3 (m, 5H**).** ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.75, 165.86, 131.14, 129.47, 85.13, 32.93, 32.72, 31.56, 27.20, 25.61, 24.14, 24.06 GC/MS: m/z (%): 207 (1%), 138 (100%), 111 (9)%), 84 (32%), 55 (100%), 28 (20%).

poly(CyONP). Yield, 65%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.70 (br, s, 1H), 3.65 (br, m, 2H), 2.77 (br, m, 3H), 2.17 (br m, 2H), 1.86 (br, m, 3H), 1.70 (br, s, 1H), 1.51 (br, s, 2H), 1.27 (br, m, 5H).

poly(PNP). Yield, 68% ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.74 (br, m, 3H), 2.48 (br, m, 2H), 1.97 (s, 2H), 1.71 - 1.38 (br, m, 2H).

Compound 3. Over a period of 30 min, *n*-butyllithium (1.6 M in hexanes, 13.76 mmol) was added drop-wise to a solution of 5-methoxyethoxy-2-pyrrolidone (12.5 mmol) in anhydrous THF (*ca*. 50 mL) at -78 °C. The reaction mixture was stirred at same temperature for 2.5 hr followed by the addition of acryloyl chloride (2.3mL, 16.5 mmol). The solution was allowed to warm up to room temperature overnight. The next morning the solution was quenched with saturated aqueous NH_4Cl (*ca*. 5 mL). The solvent was removed by reduced pressure and the residue extracted with ethyl acetate (3 x 50 mL). Tho organic phases were combined and washed with brine (*ca*. 10mL) and dried over anhydrous Na_2SO_4. After filtering the mixture, the solvent was removed under reduced pressure to afford a yellow opaque oil. The crude product was purified twice by column chromatography (silica followed by alumina, ethyl acetate/hexanes, 1:1) to afford the product. Yield, 70%, ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.78 (d, $^{3}J_{HH}$ = 4.78 Hz, 1H), 3.90 – 3.71 (m, 2H), 3.68 – 3.56 (m, 1H), 3.51 (t, $^{3}J_{HH}$ = 4.63 Hz, 2H), 3.37 (s, 3H), 2.91 (m, 1H), 2.47 (m ,1H), 2.09 (m, 2H), 1.71 (m, 2H), 1.62 – 1.39 (m, 2H), 0.92 (t, $^{3}J_{HH}$ = 7.43 Hz, 3H), 0.88 (t, $^{3}J_{HH}$ = 7.42 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 177.82, 175.30, 87.49, 72.00, 69.37, 58.97, 46.78, 31.83, 26.23, 24.54, 24.05, 11.62, 11.36. GC/MS: m/z (%): 228 (1%), 198 (3%), 182 (45%), 174 (3%), 153 (8%), 126 (1%), 115 (1%), 98 (58%), 84 (100%), 71 (48%), 59 (16%), 43 (8%).

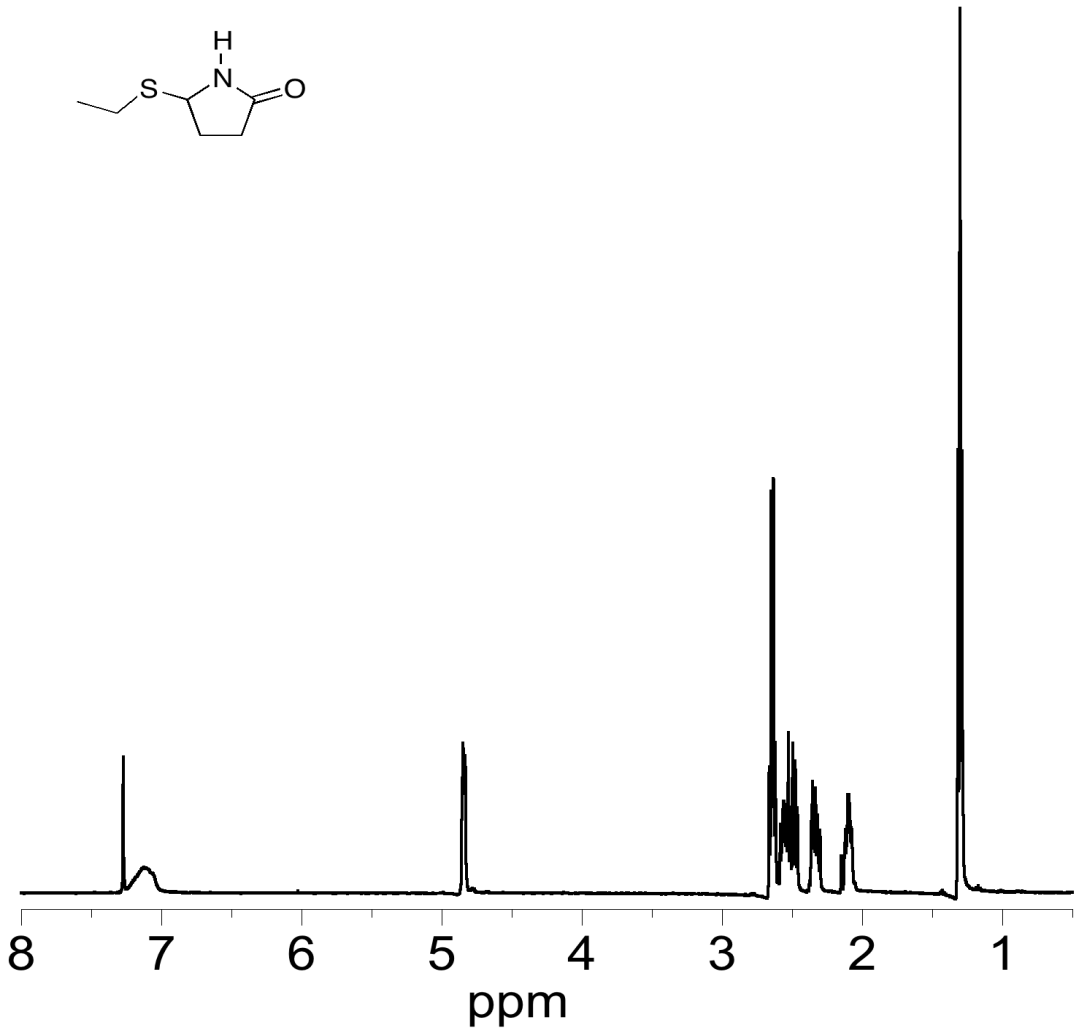

Figure S 1. ^{1}H NMR spectrum of 5-ethylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

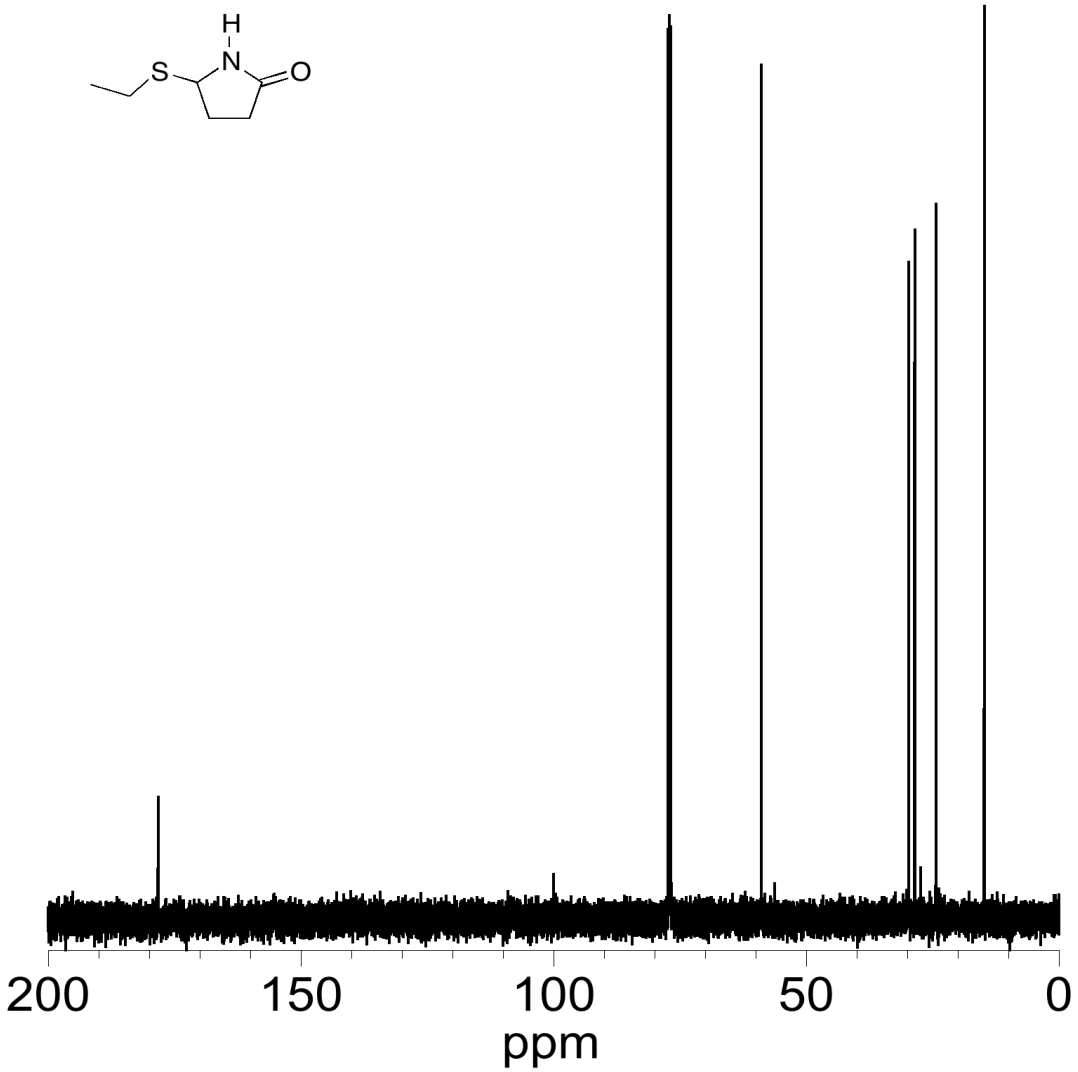

Figure S 2. ^{13}C NMR spectrum of 5-ethylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

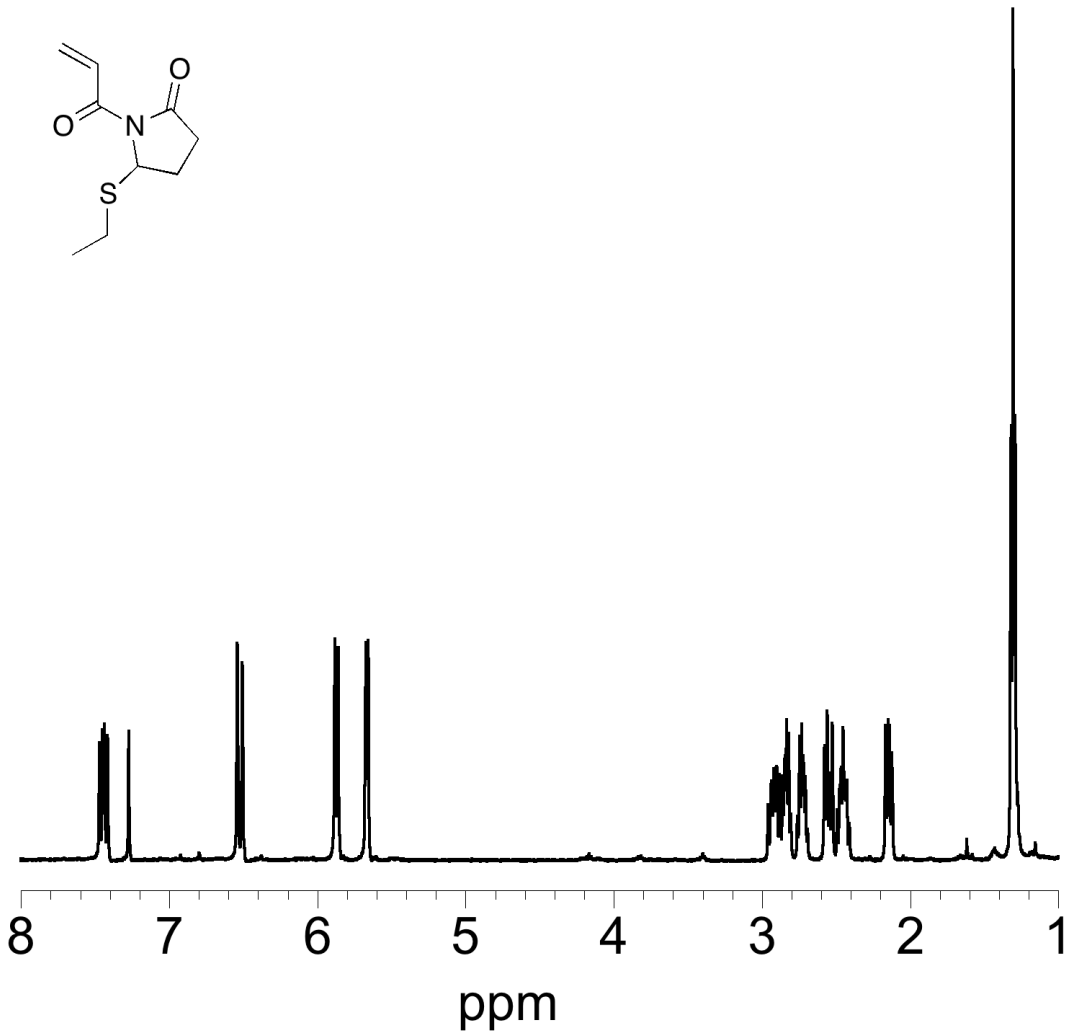

Figure S 3. ^{1}H NMR spectrum of **EthSNP** (500 MHz, $CDCl_3$).

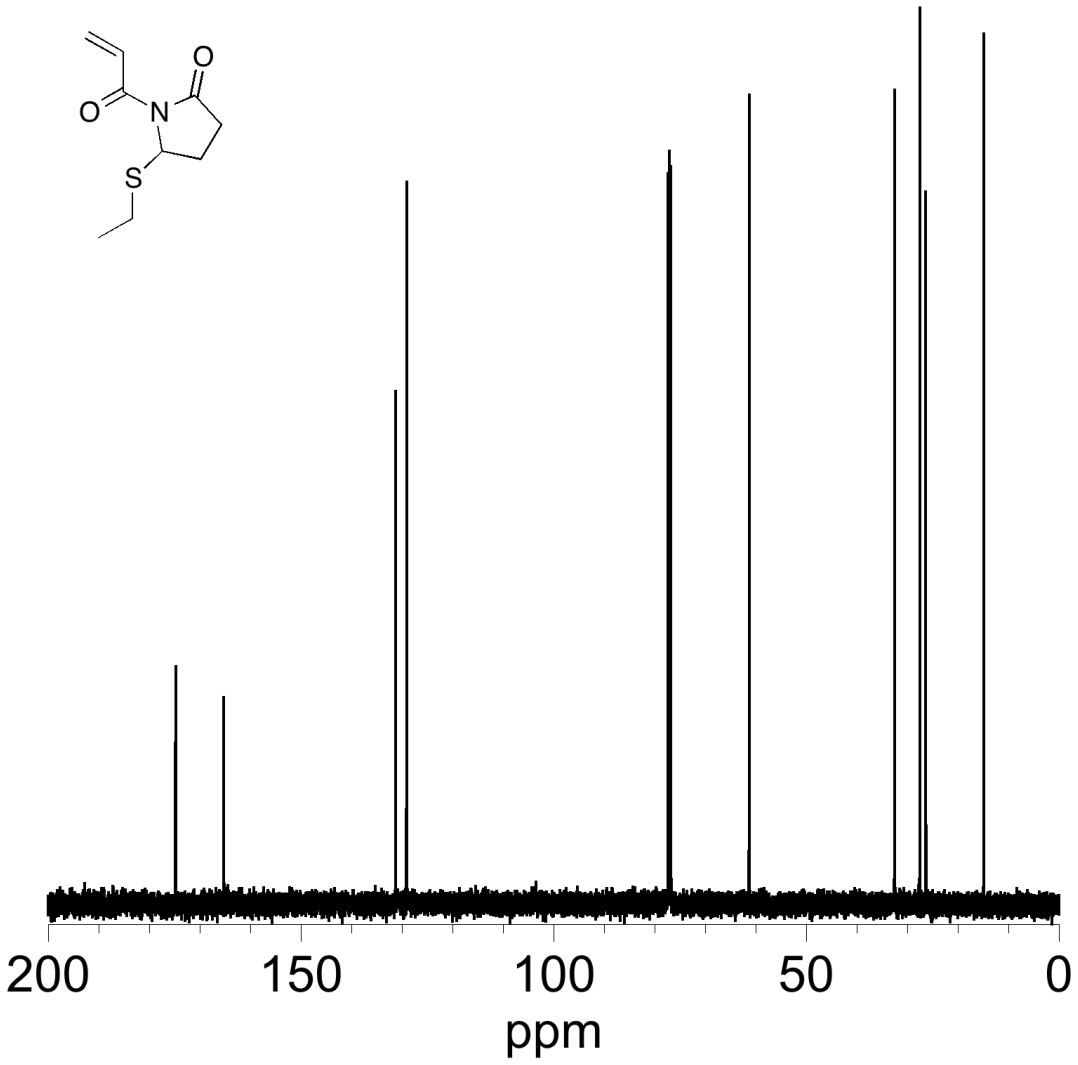

Figure S 4. ^{13}C NMR spectrum of **EthSNP** (126 MHz, $CDCl_3$).

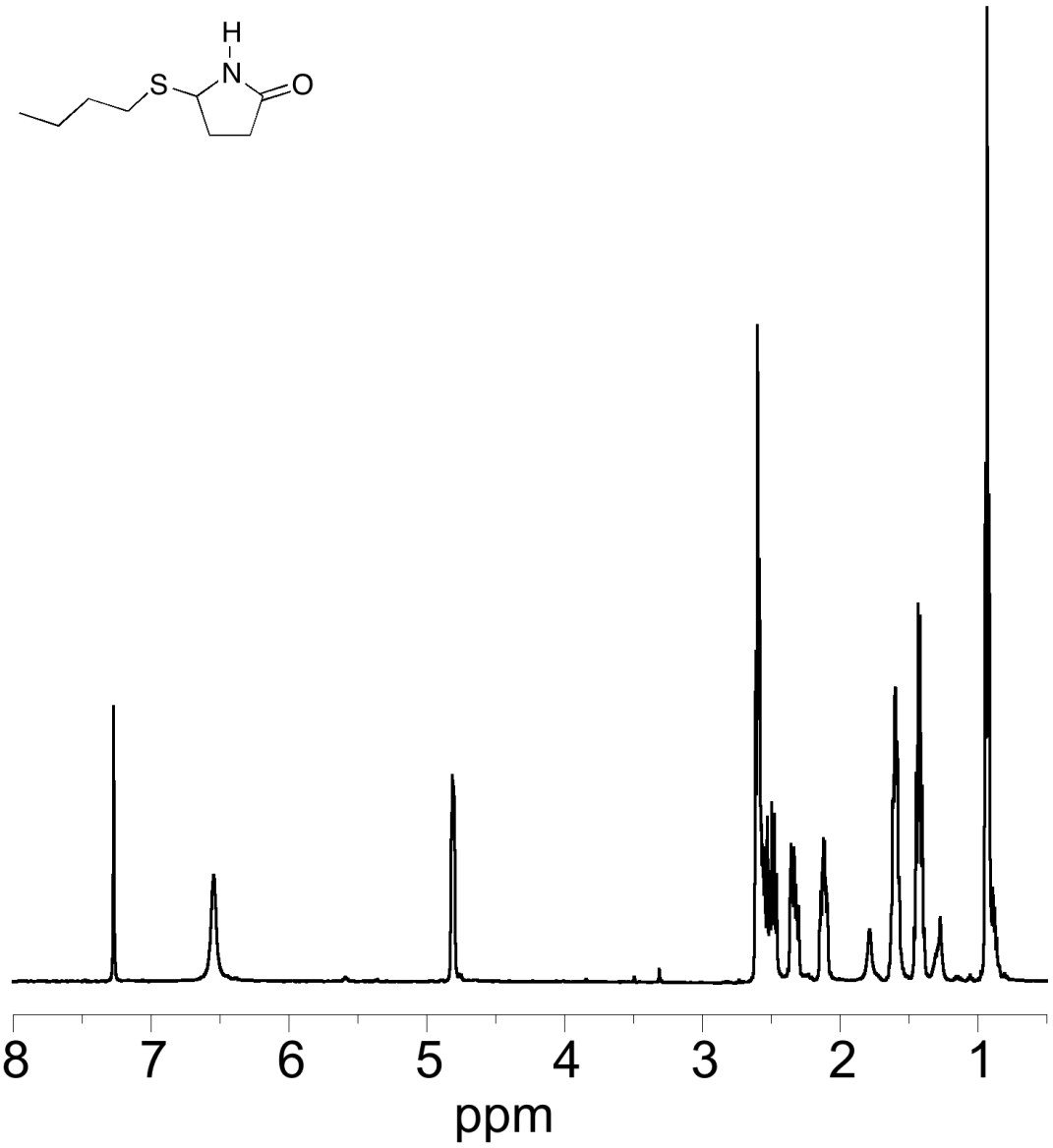

Figure S 5. ^{1}H NMR spectrum of 5-butylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

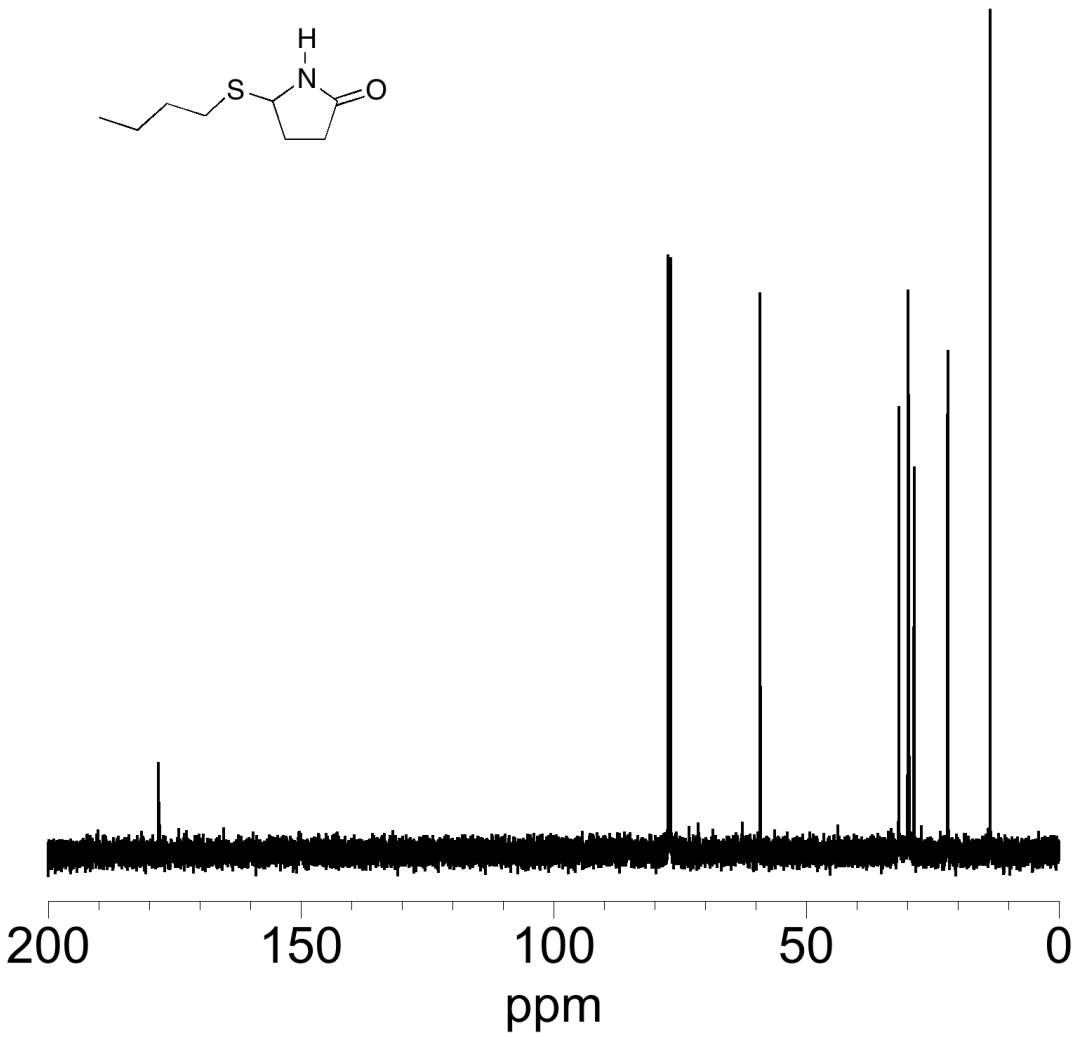

Figure S 6. ^{13}C NMR spectrum of 5-butylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

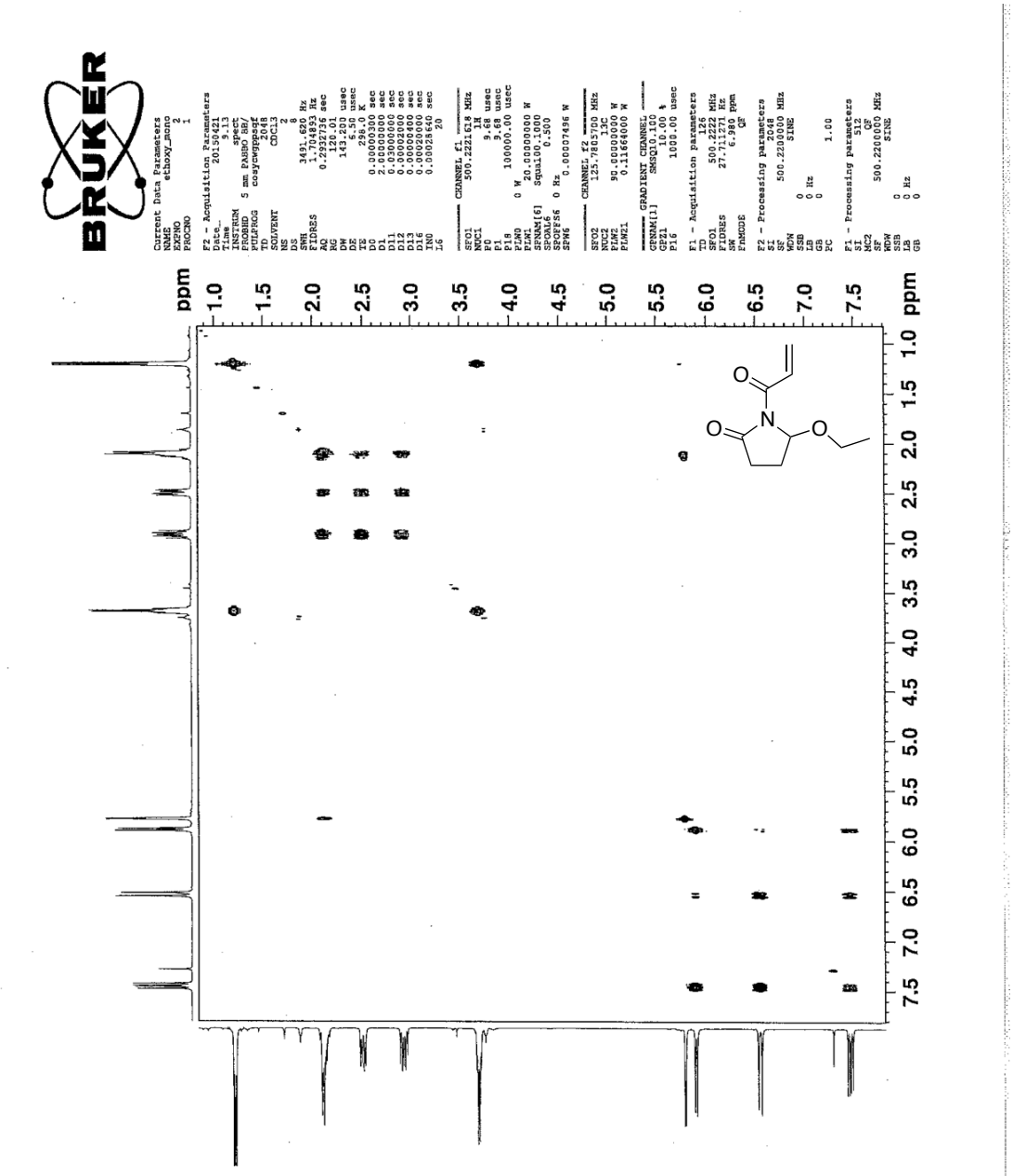

Figure S 7. 2D COSY NMR spectrum of **EthONP** (500 MHz, $CDCl_3$).

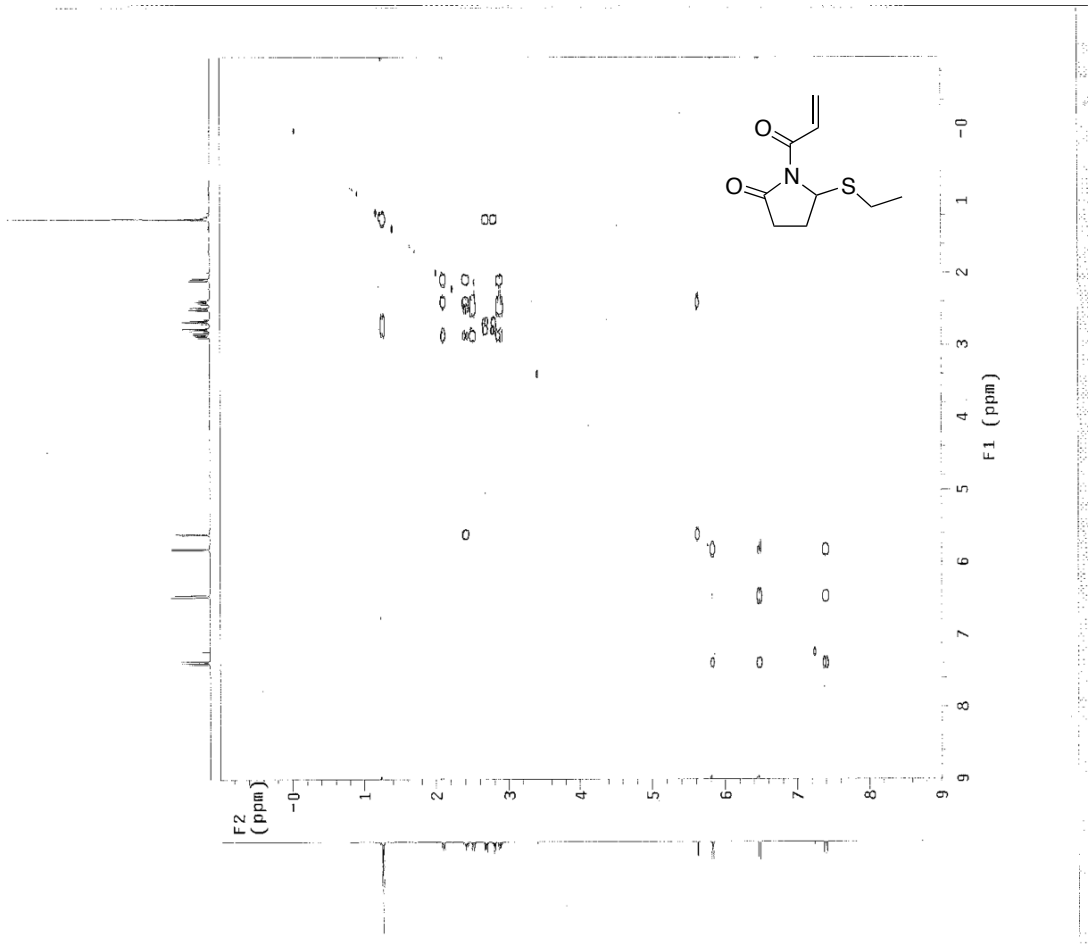

Figure S 8. 2D COSY NMR spectrum of **EthSNP** (500 MHz, $CDCl_3$).

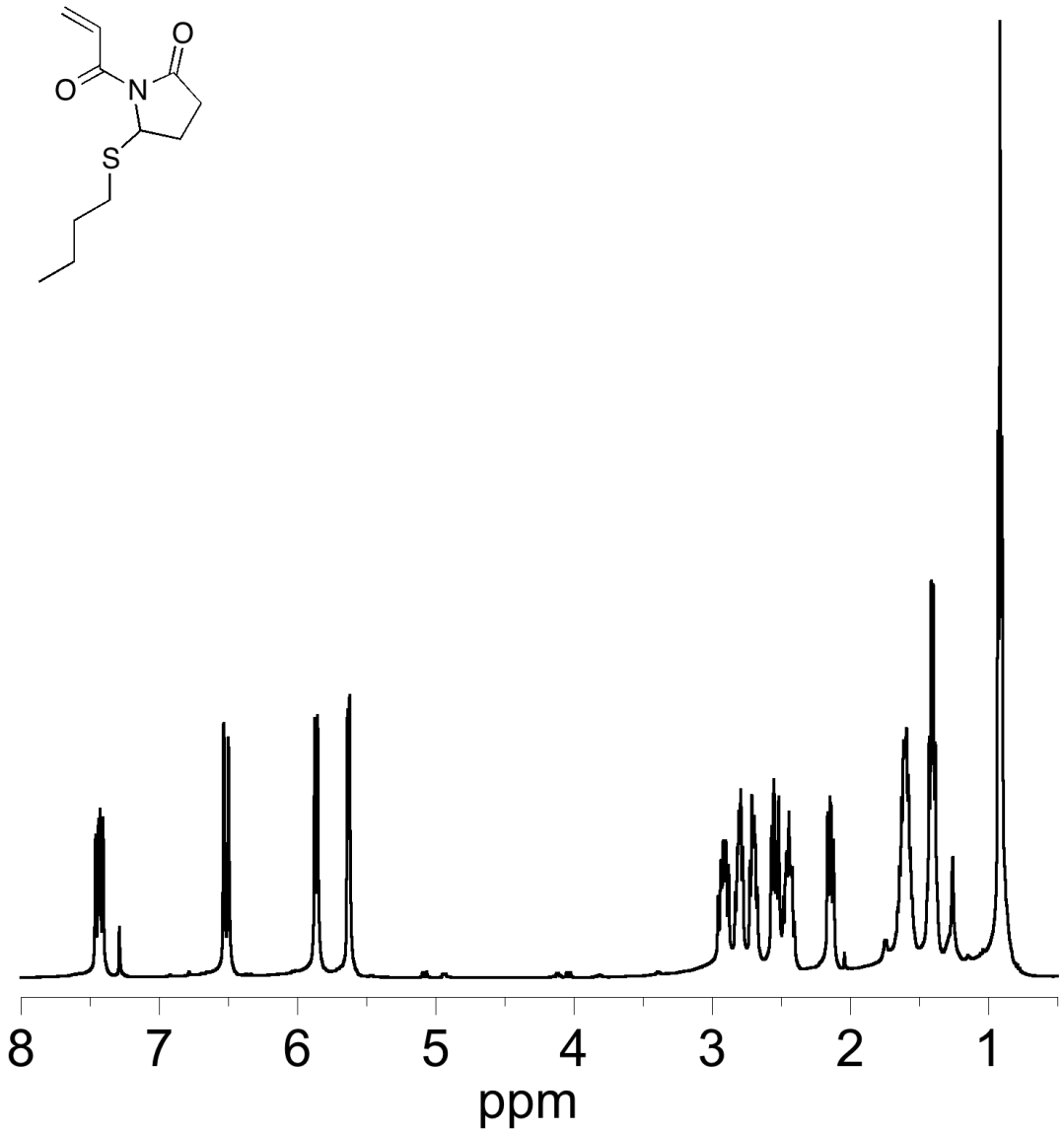

Figure S 9. ^{1}H NMR spectrum of **BuSNP** (500 MHz, $CDCl_3$).

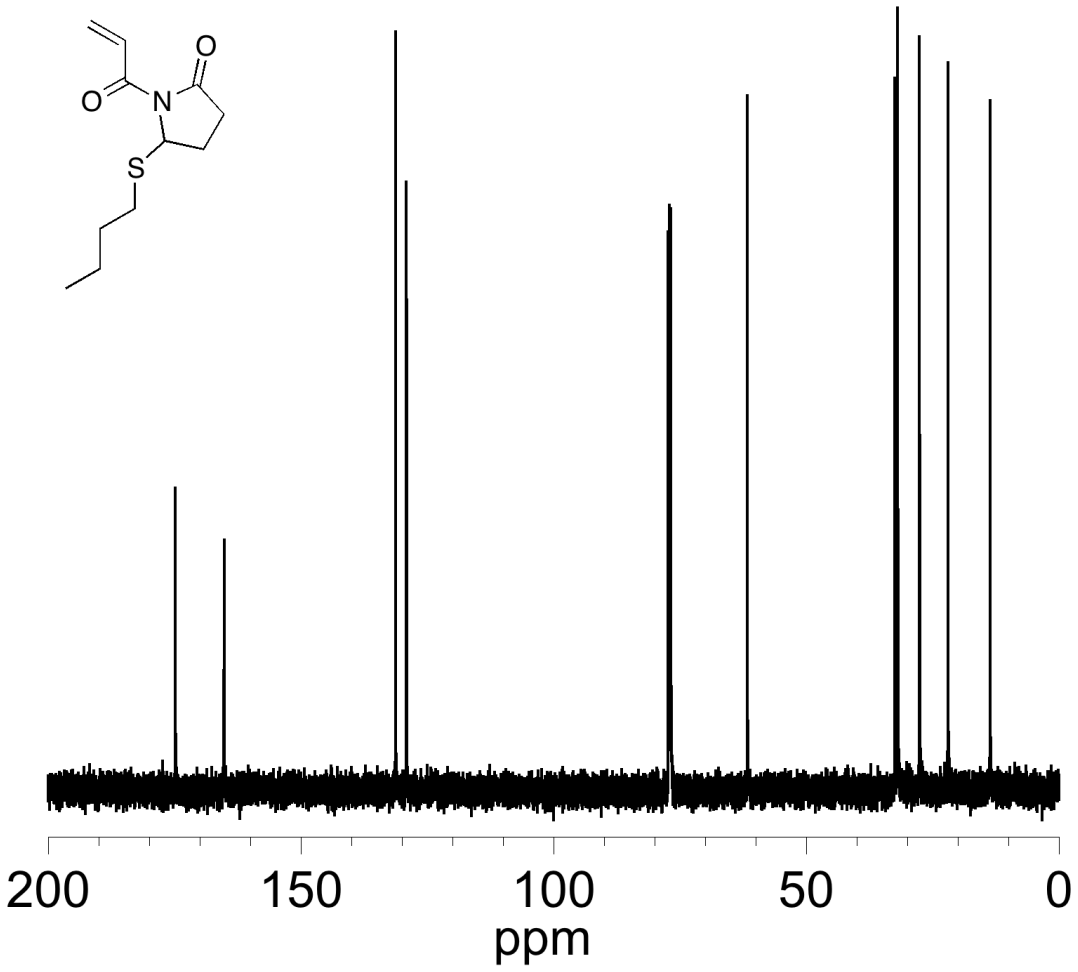

Figure S 10. ^{13}C NMR spectrum of **BuSNP** (126 MHz, $CDCl_3$).

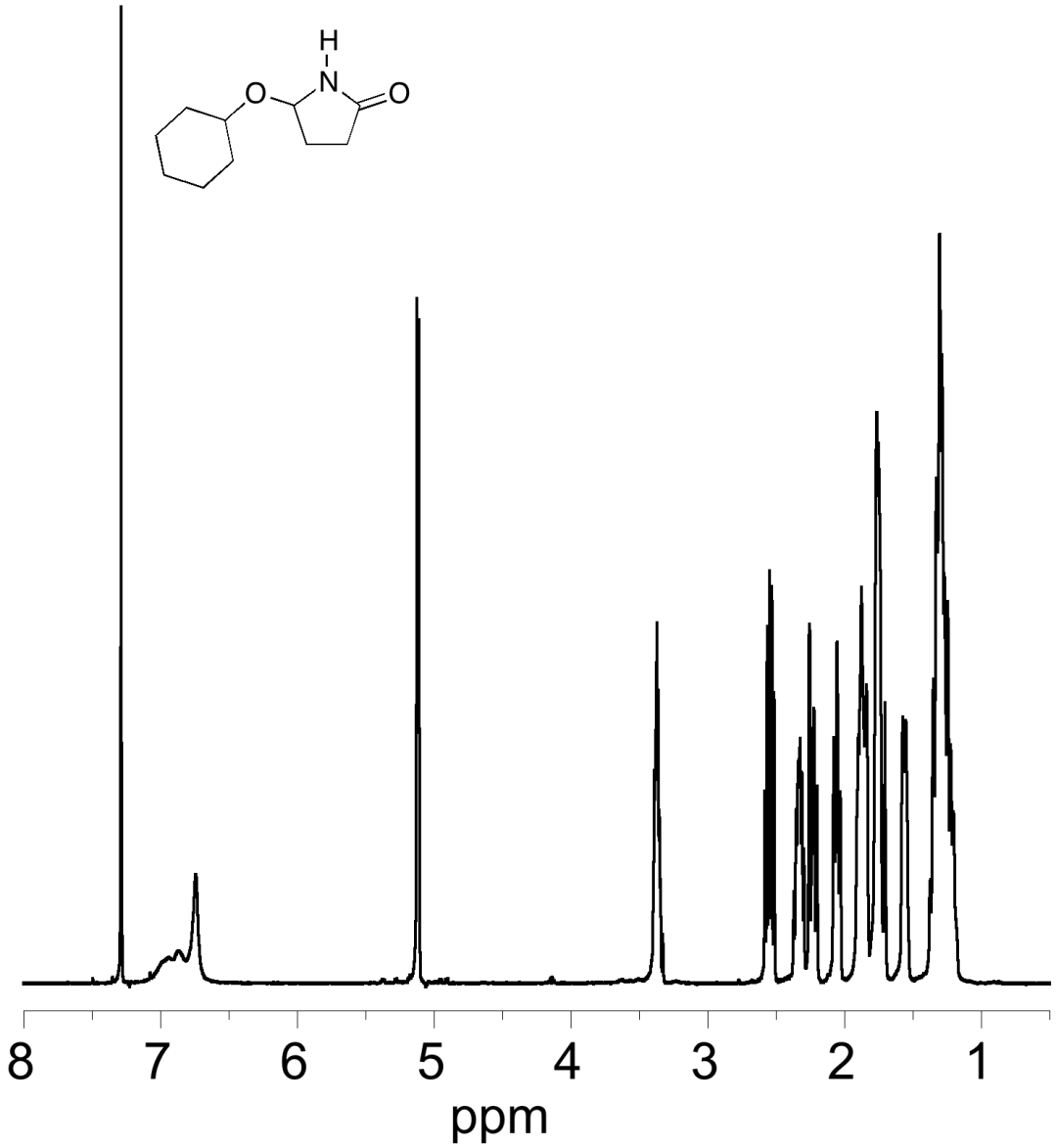

Figure S 11. ^{1}H NMR spectrum of 5-cyclohexyloxy-2-pyrrolidone (500 MHz, $CDCl_3$).

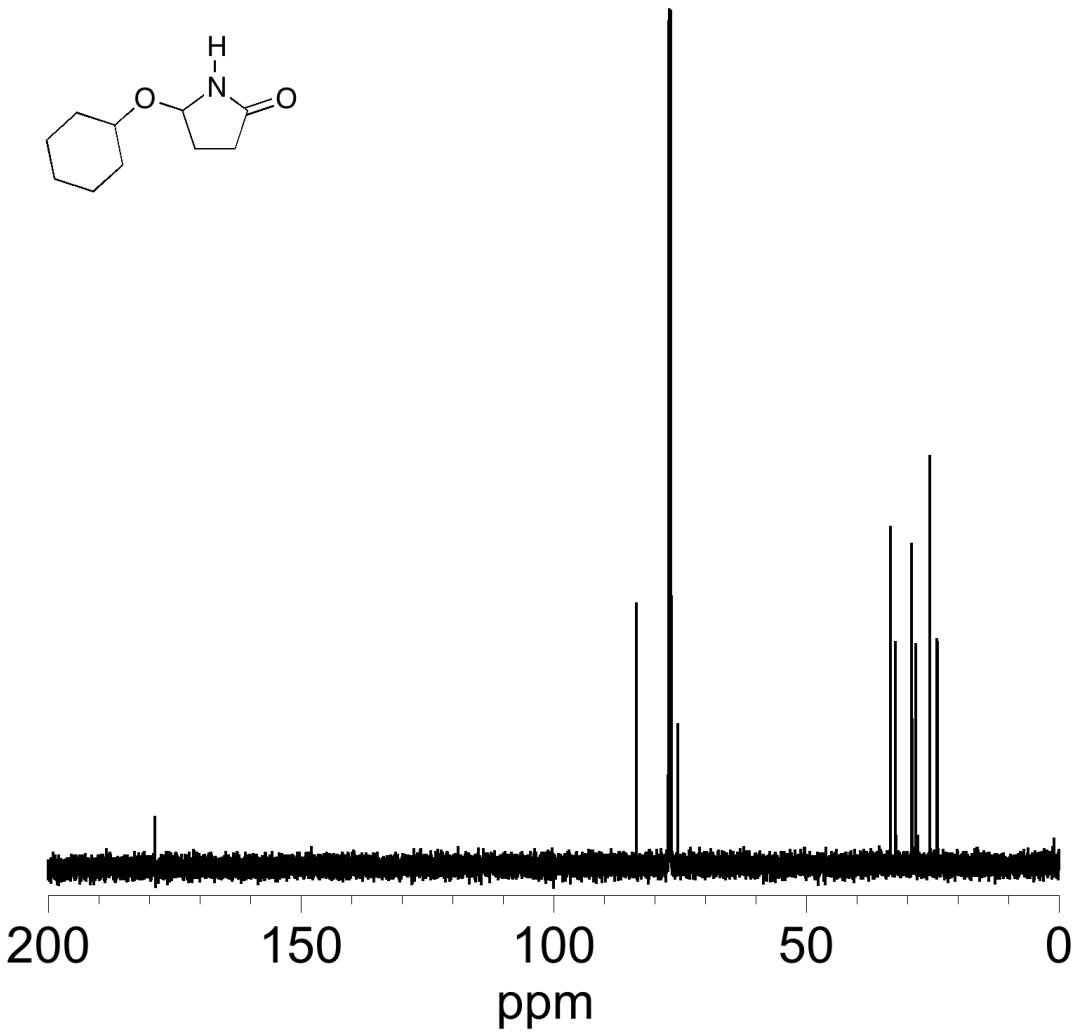

Figure S 12. ^{13}C NMR spectrum of 5-cyclohexyloxy-2-pyrrolidone (126 MHz, $CDCl_3$).

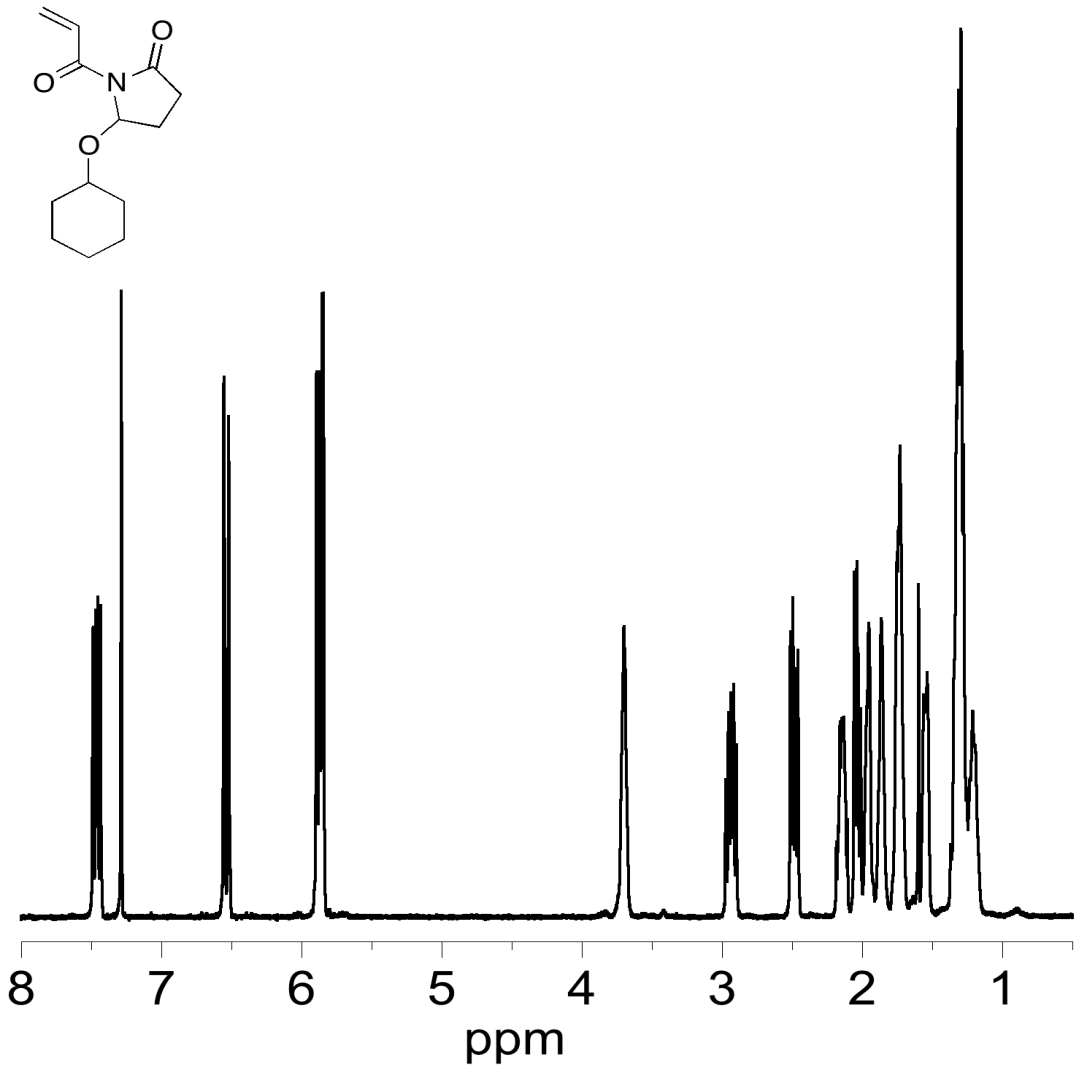

Figure S 13. ^{1}H NMR spectrum of **CyONP** (126 MHz, $CDCl_3$).

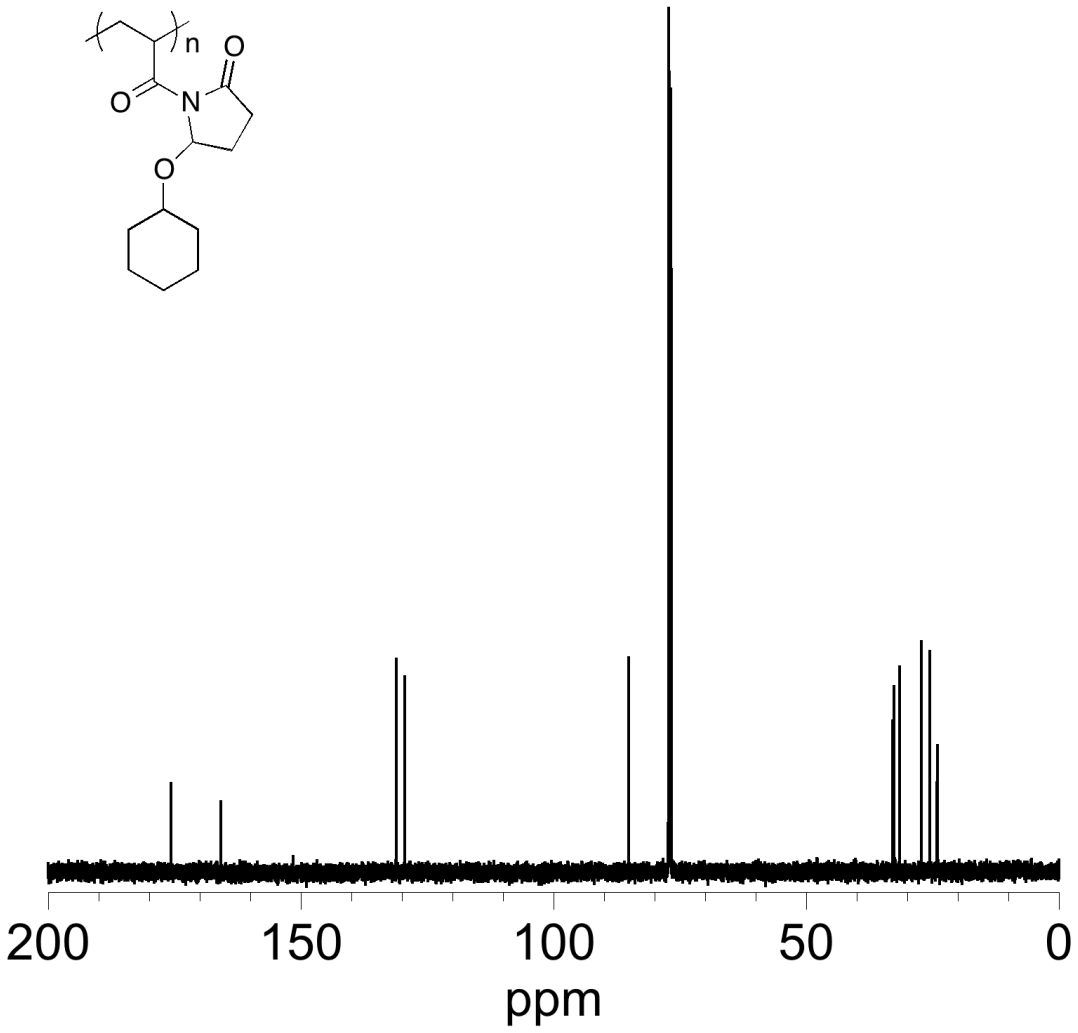

Figure S 14. ^{13}C NMR spectrum of **CyONP** (126 MHz, $CDCl_3$).

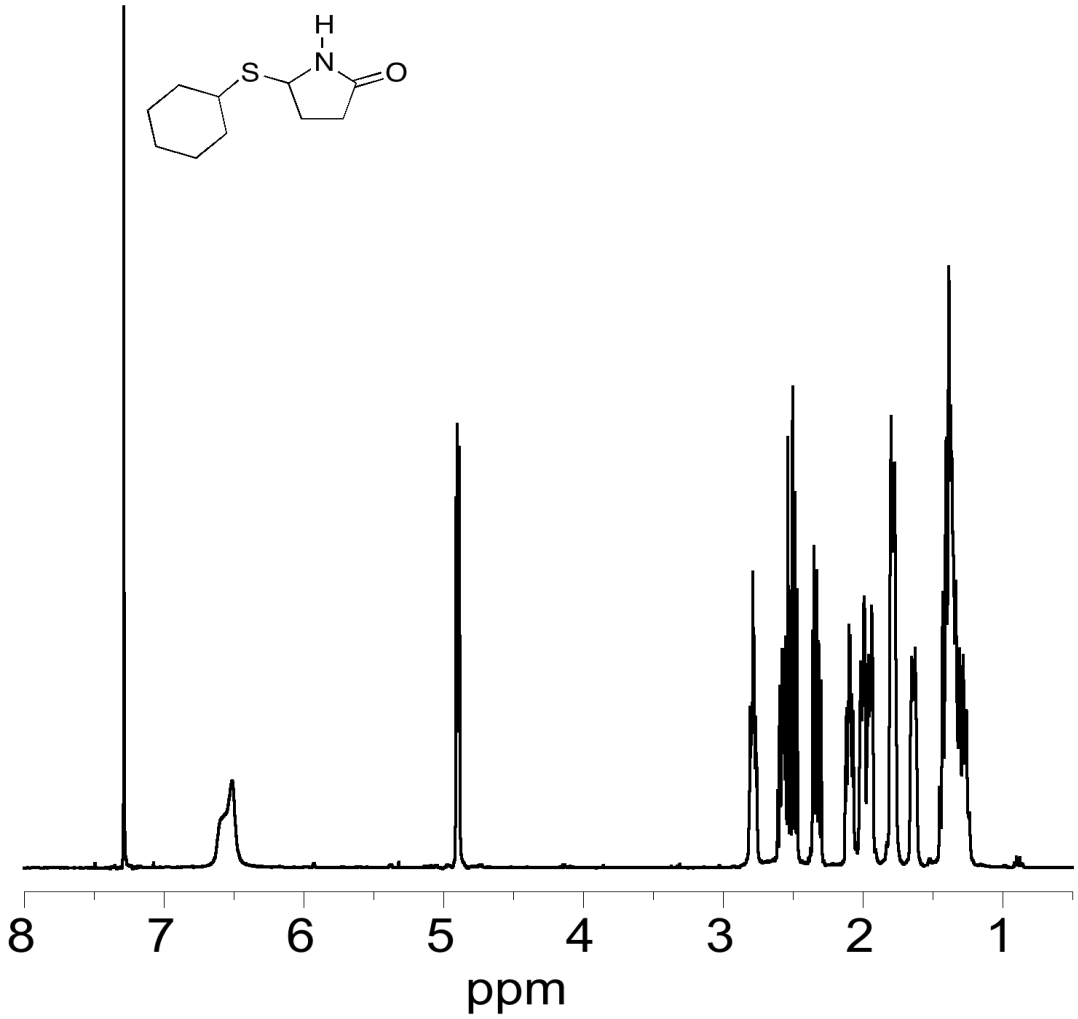

Figure S 15. ^{1}H NMR spectrum of 5-cyclohexylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

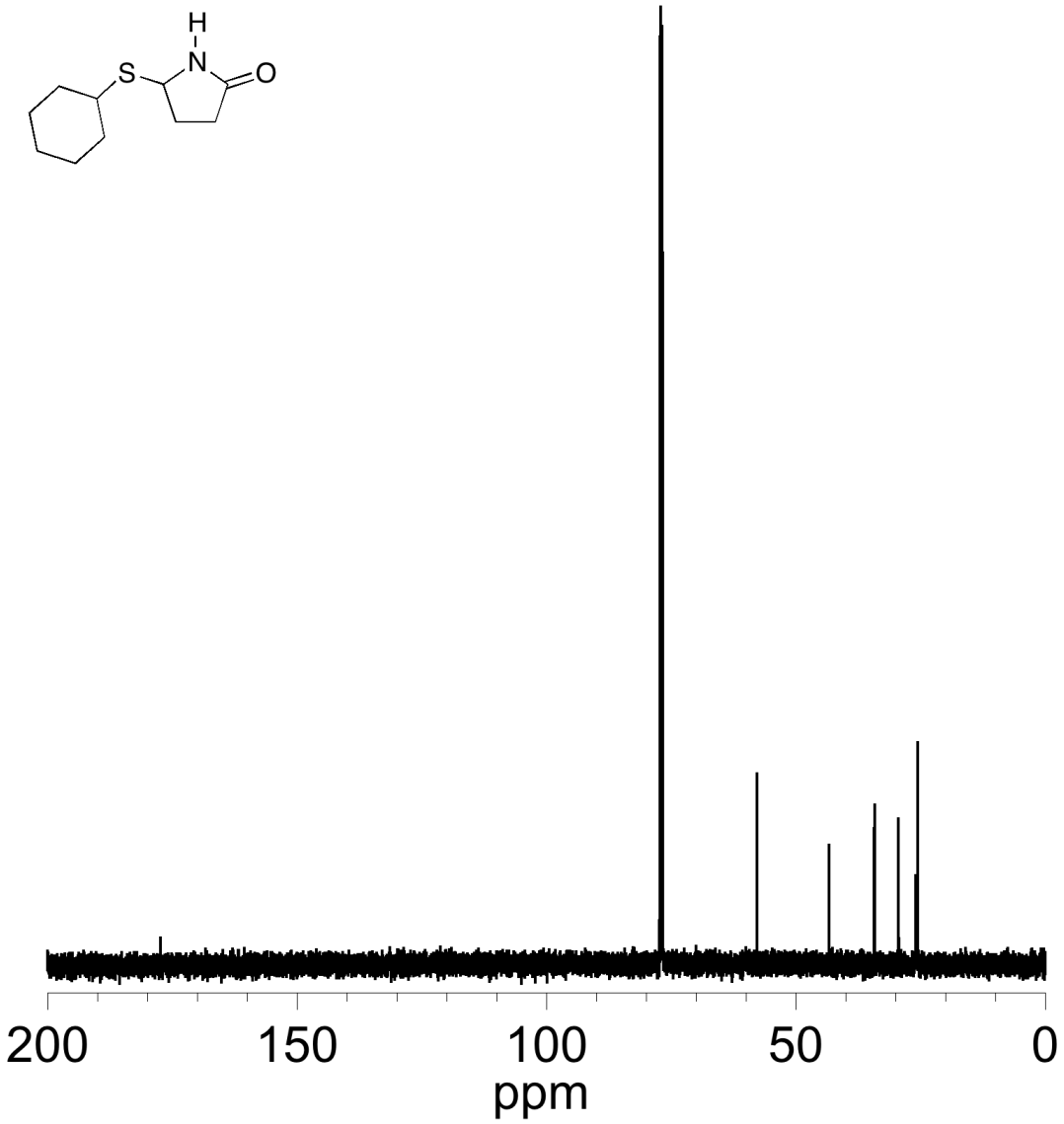

Figure S 16. ^{13}C NMR spectrum of 5-cyclohexylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

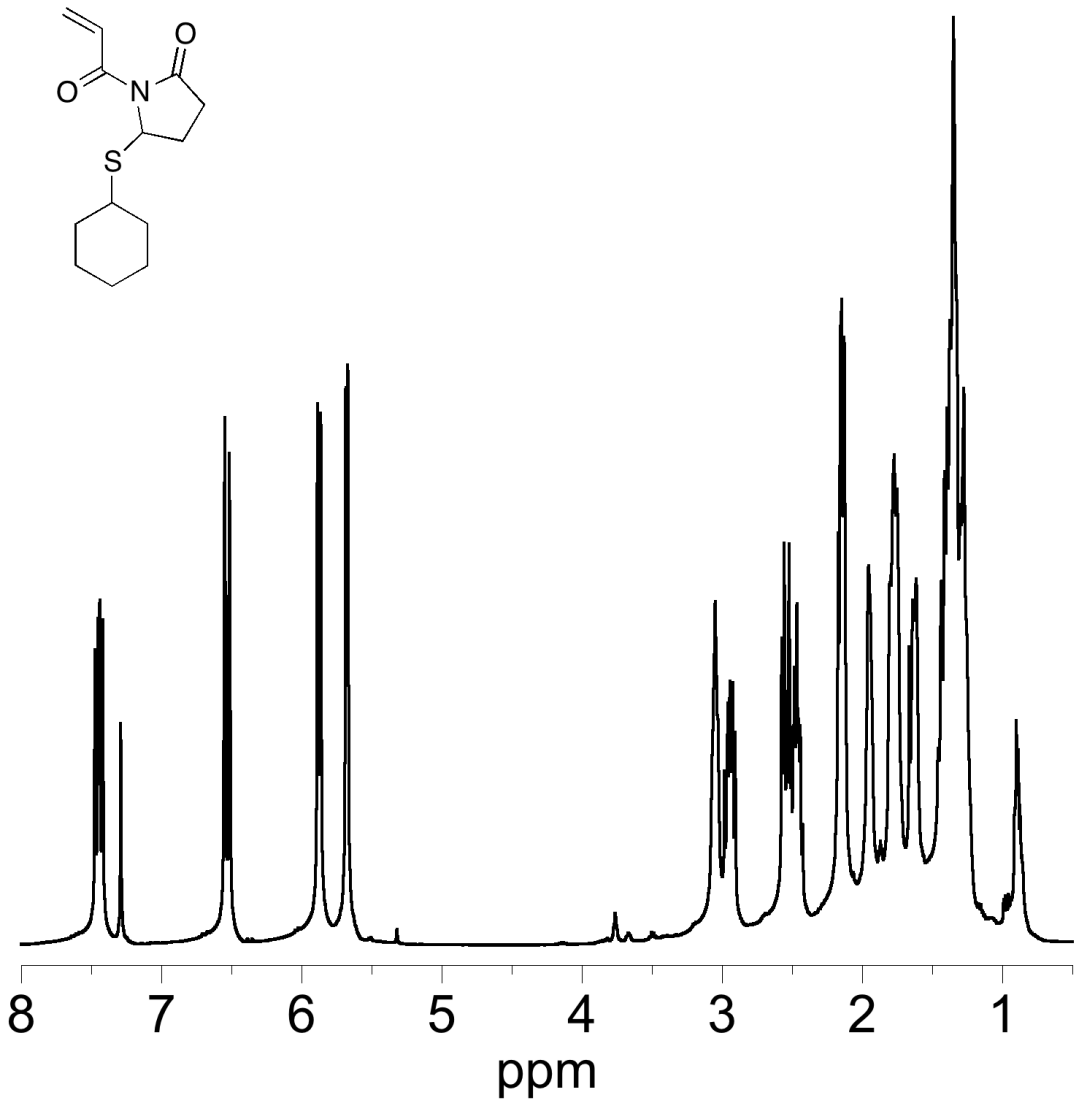

Figure S 17. ^{1}H NMR spectrum of **CySNP** (500 MHz, $CDCl_3$).

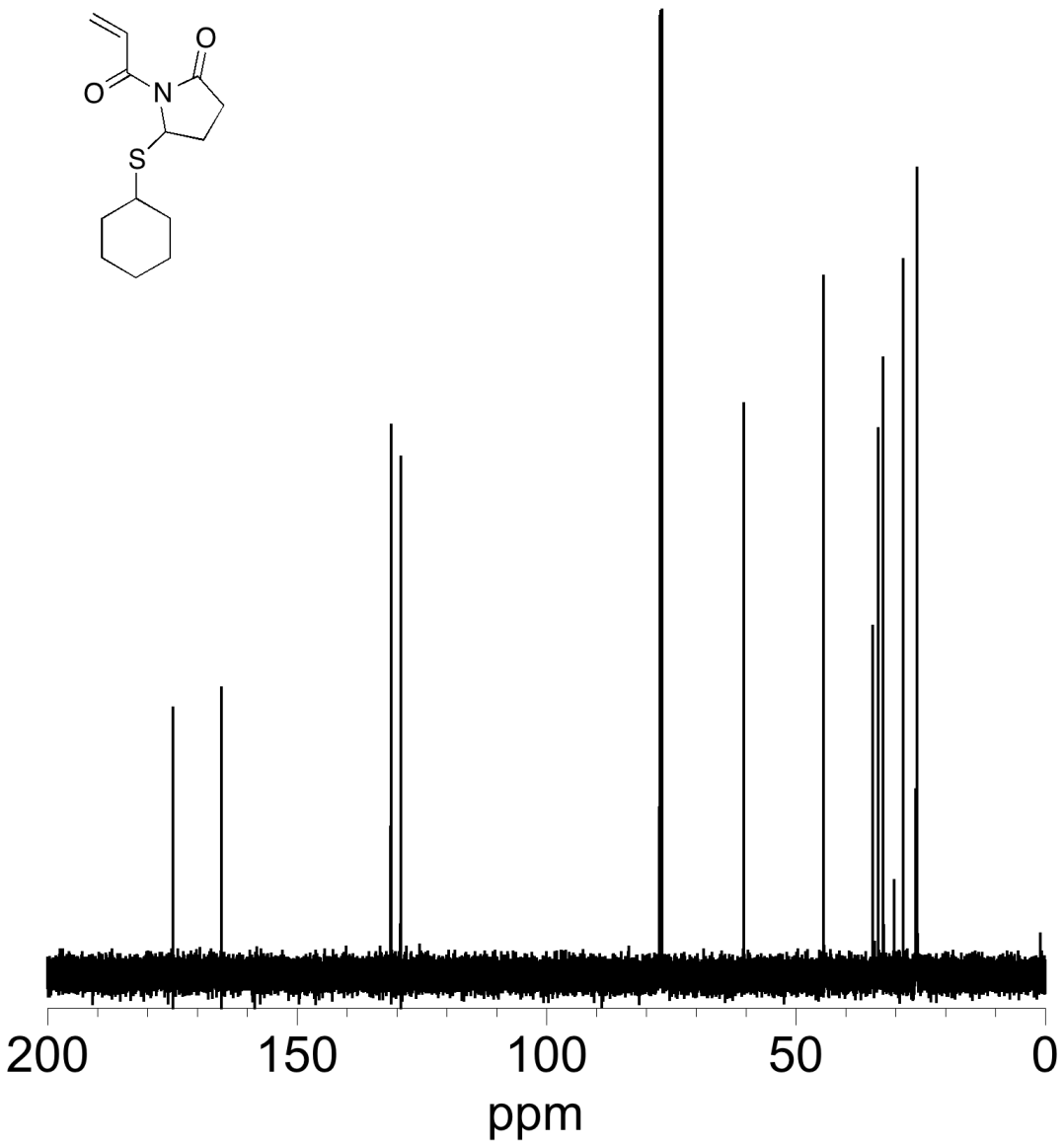

Figure S 18. ^{13}C NMR spectrum of **CySNP** (126 MHz, $CDCl_3$).

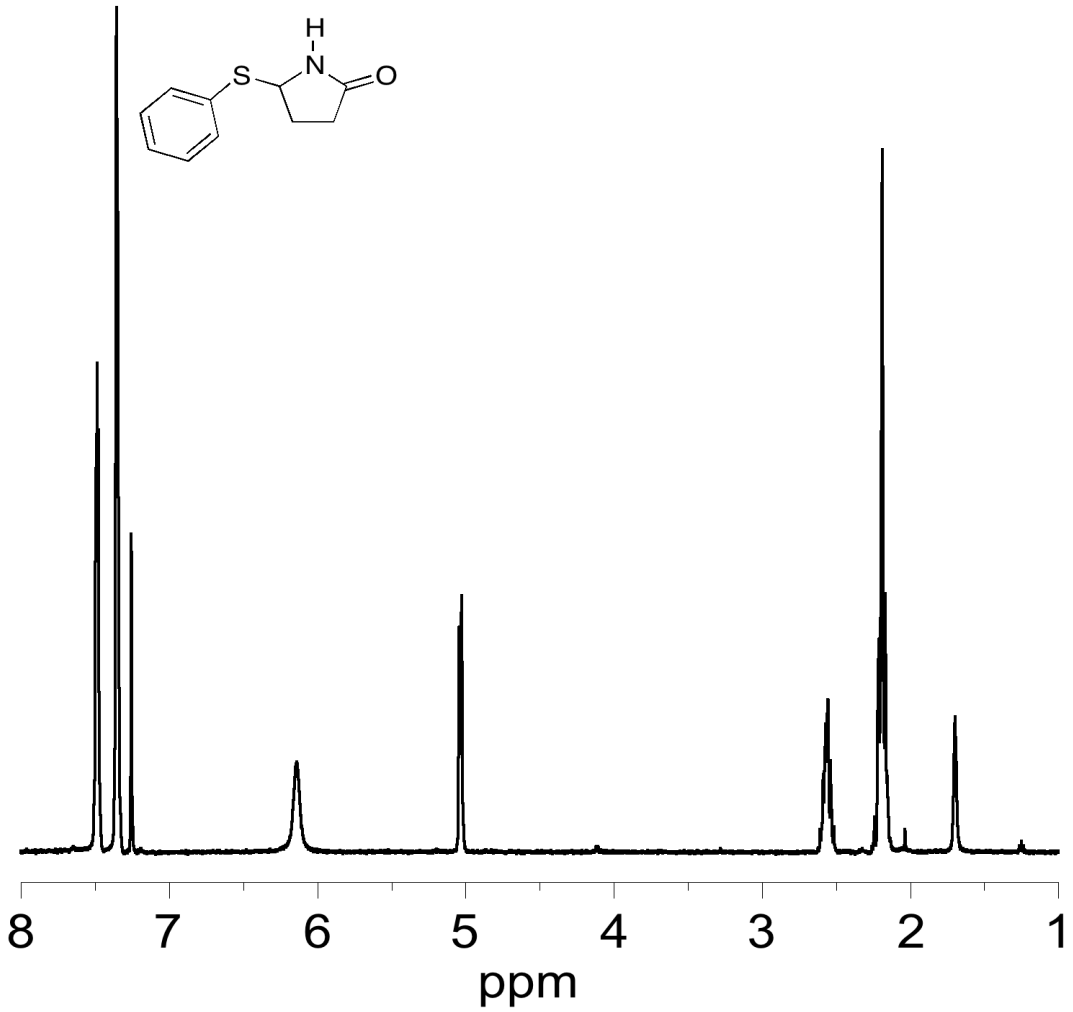

Figure S 19. ^{1}H NMR spectrum of 5-phenylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

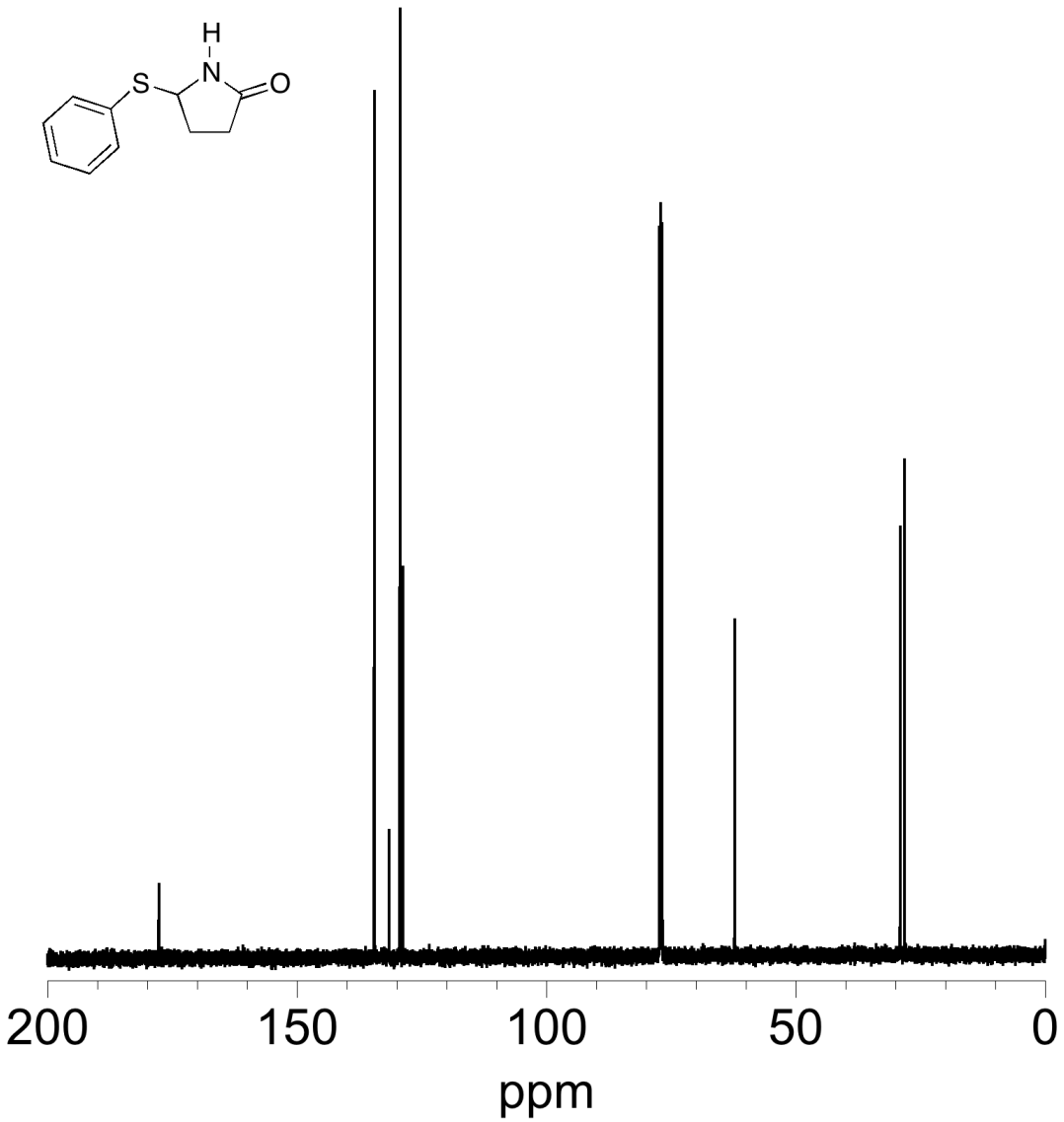

Figure S 20. ^{13}C NMR spectrum of 5-phenylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

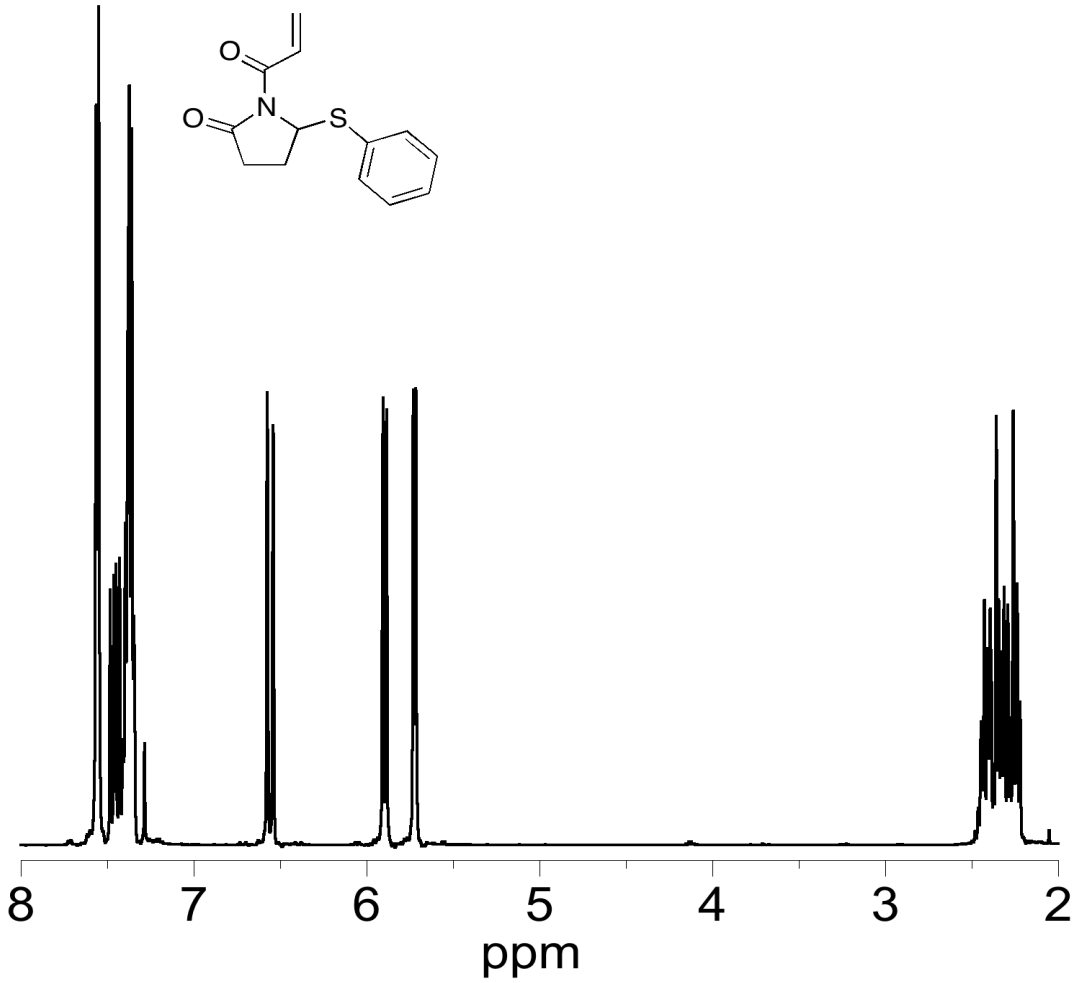

Figure S 21. ^{1}H NMR spectrum of **PhSNP** (500 MHz, $CDCl_3$).

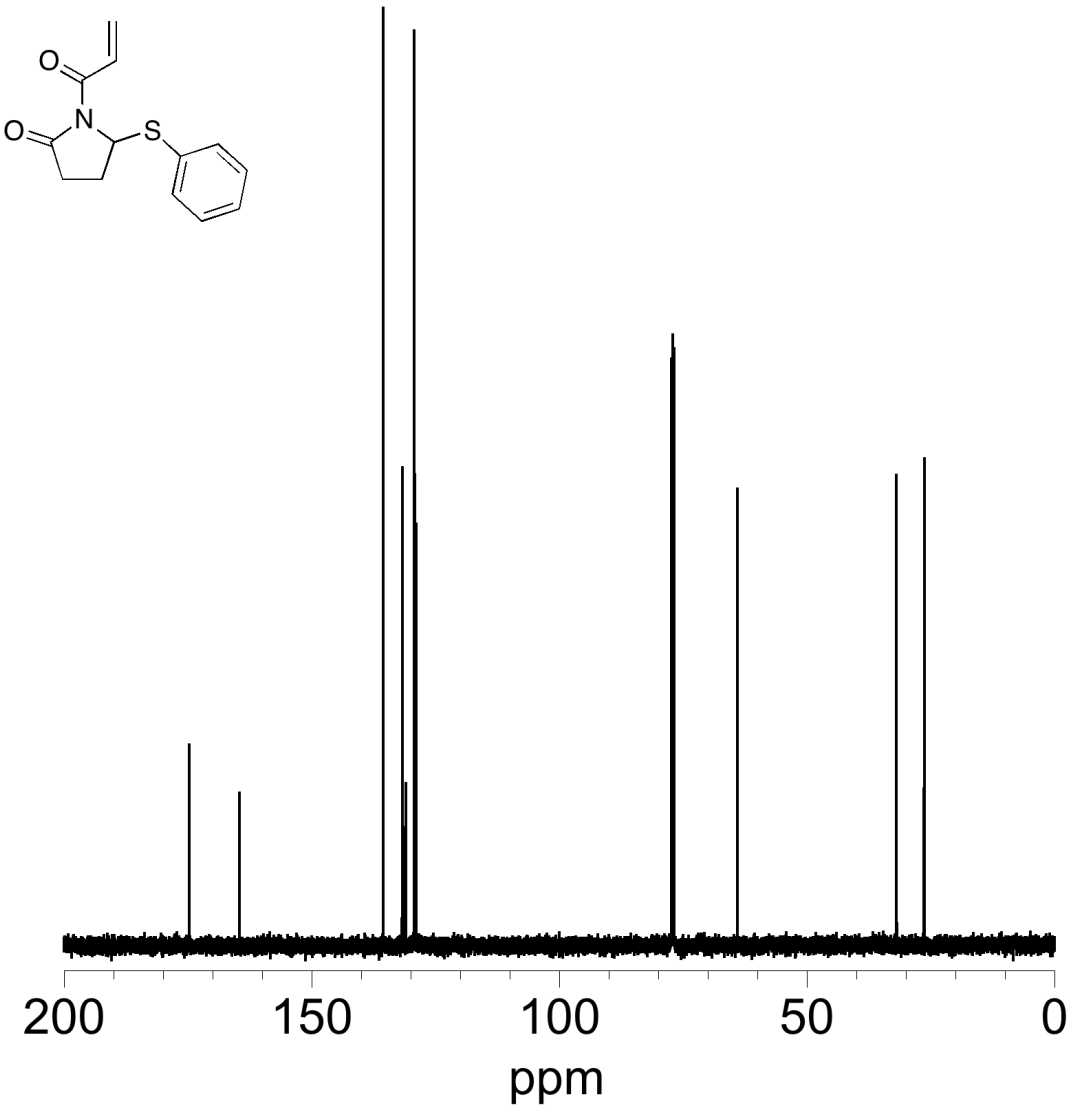

Figure S 22. ^{13}C NMR spectrum of **CySNP** (126 MHz, $CDCl_3$).

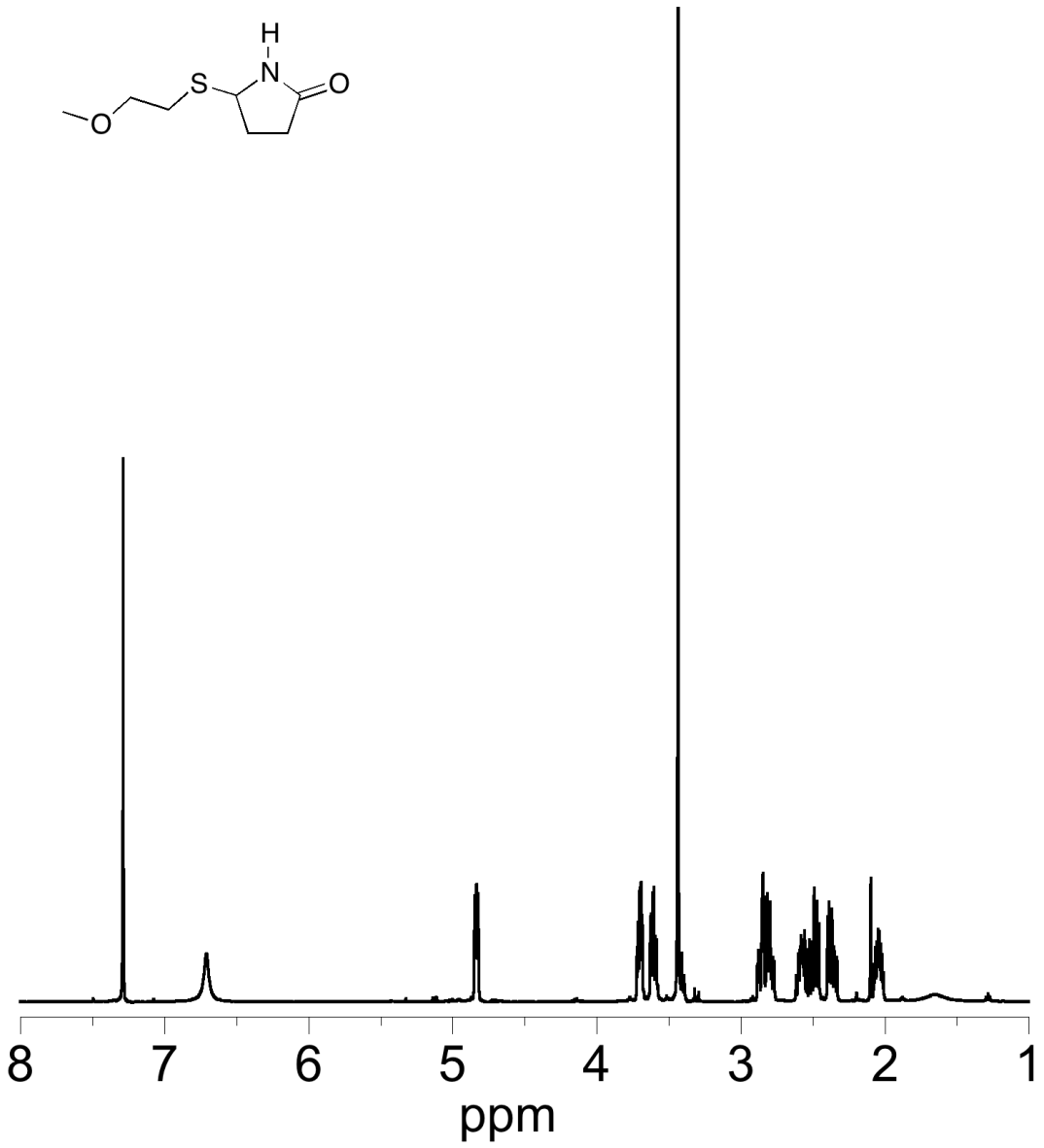

Figure S 23. ^{1}H NMR spectrum of 5-methoxyethylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

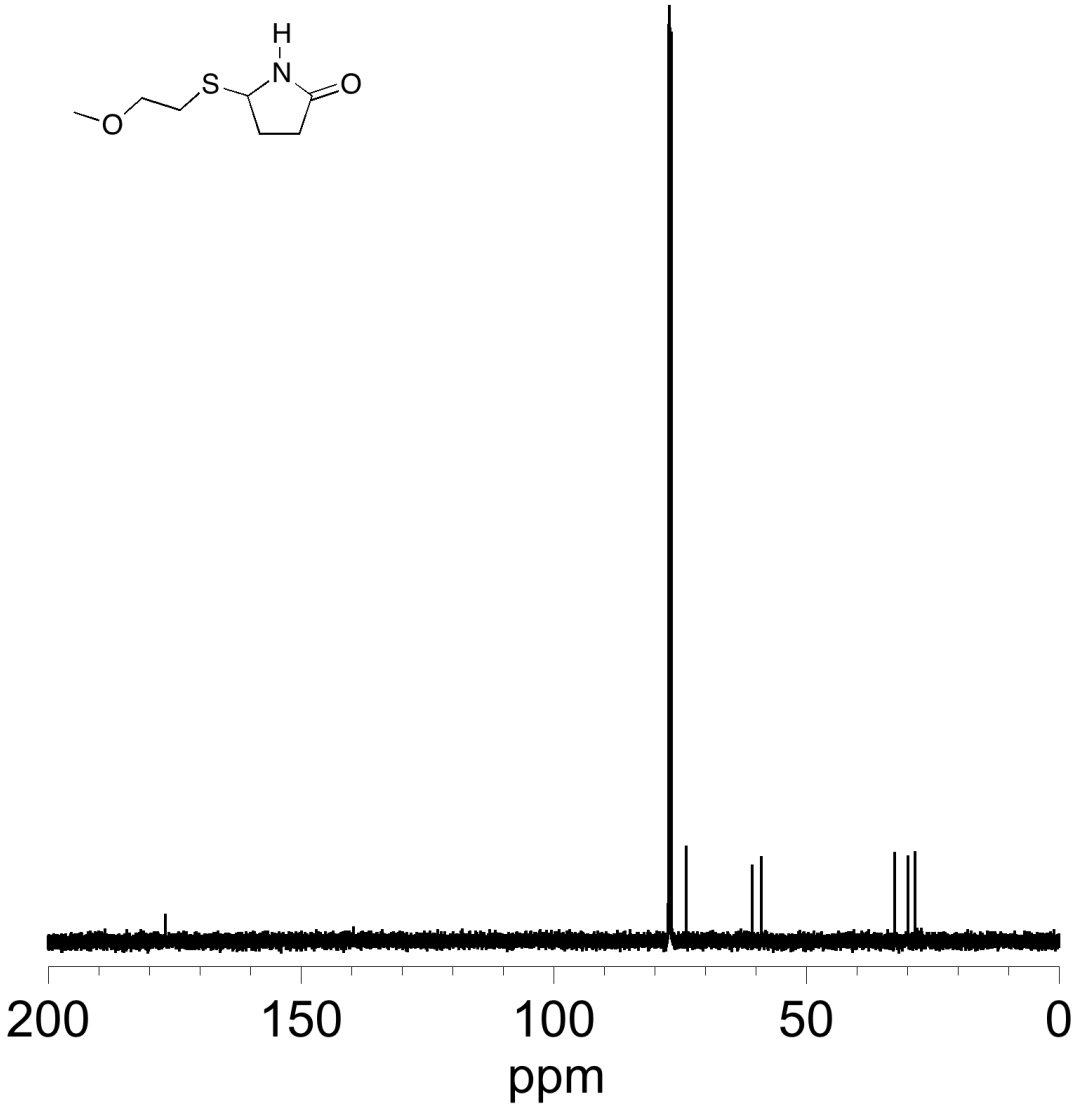

Figure S 24. ^{13}C NMR spectrum of 5-methoxyethylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

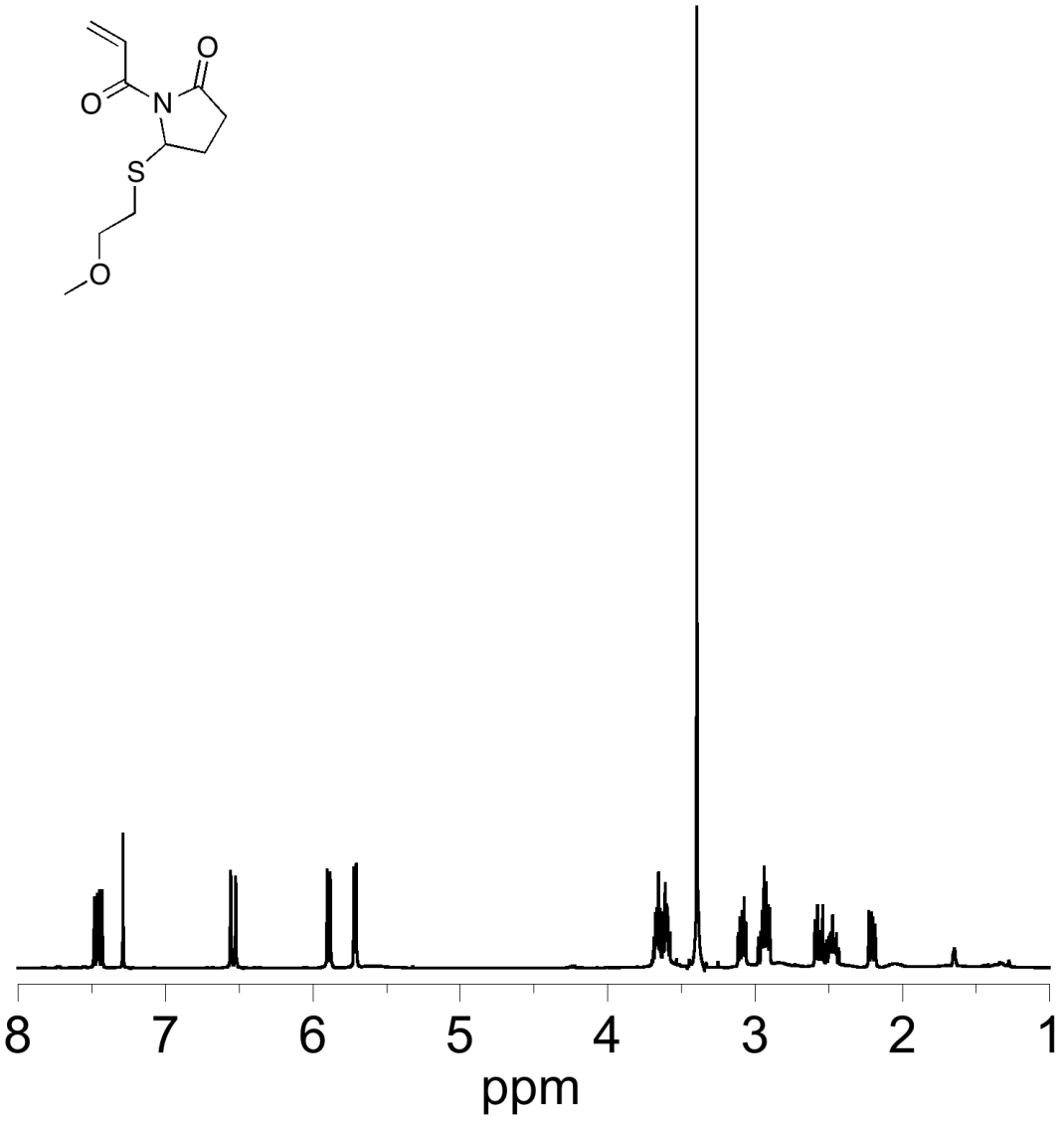

Figure S 25. ^{1}H NMR spectrum of **MeOEthSNP** (500 MHz, $CDCl_3$).

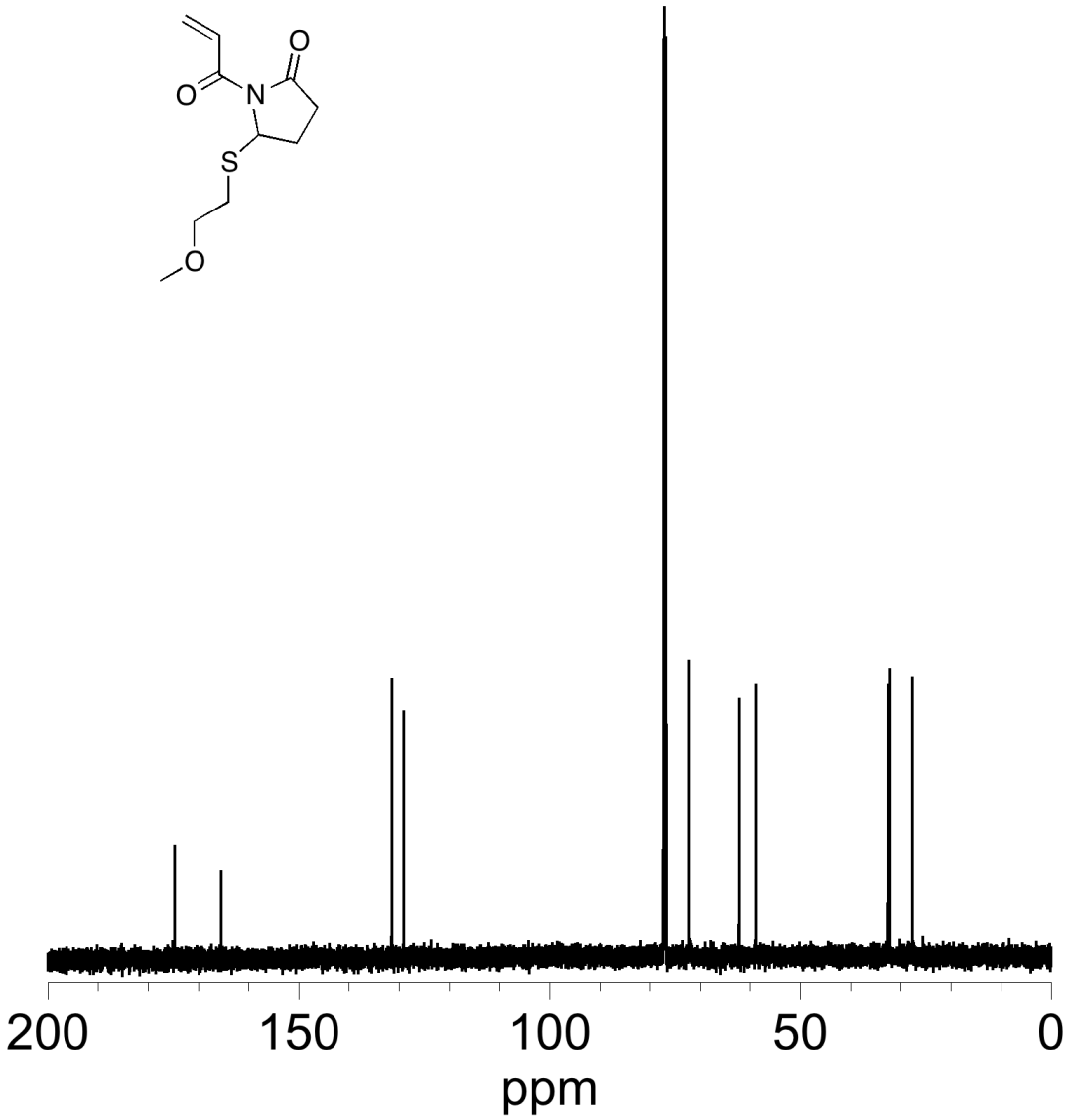

Figure S 26. ^{13}C NMR spectrum of **MeOEthSNP** (126 MHz, $CDCl_3$).

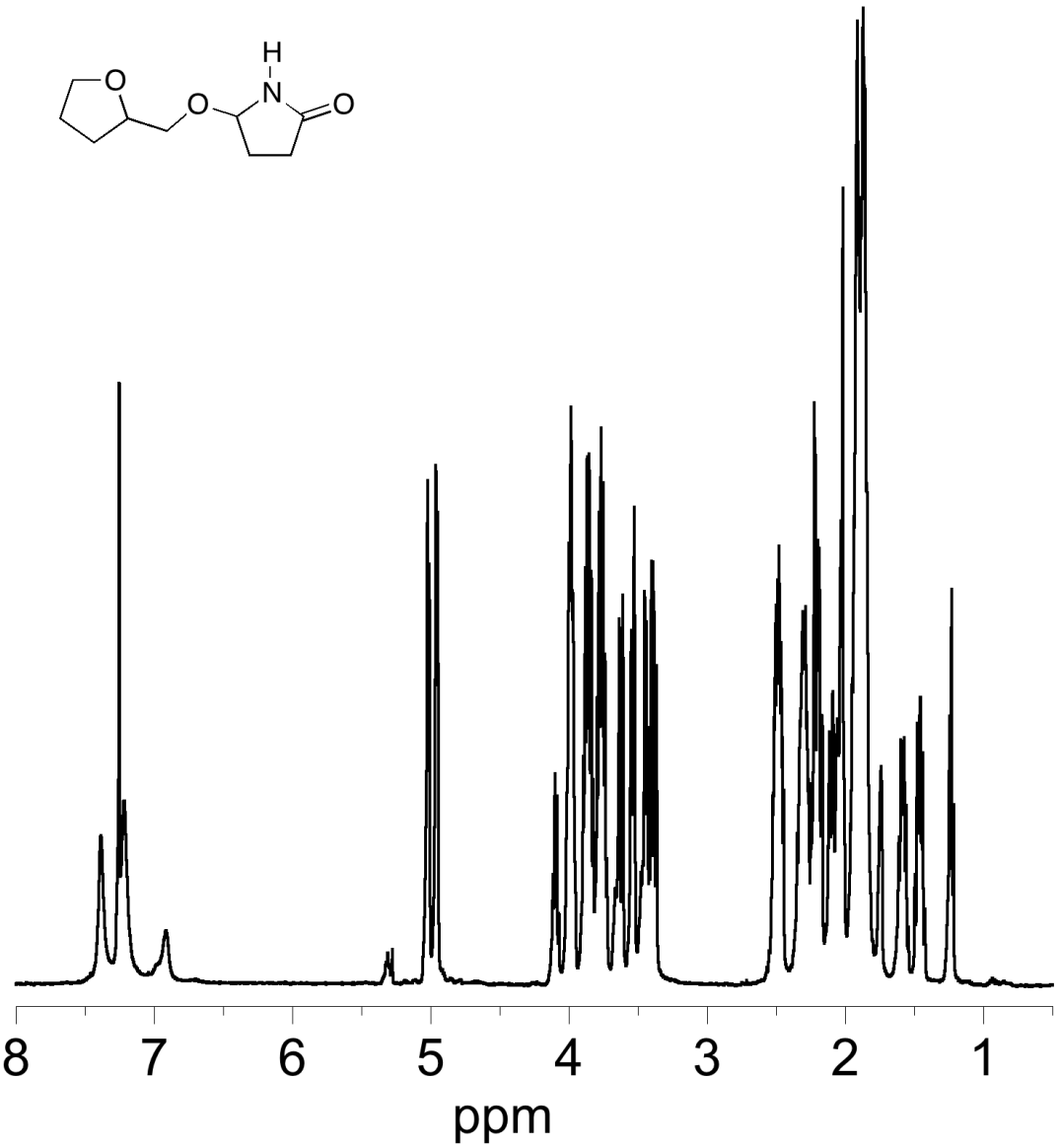

Figure S 27. ^{1}H NMR spectrum of 5-tetryhydrofurfuryloxy-2-pyrrolidone (500 MHz, $CDCl_3$). Note:

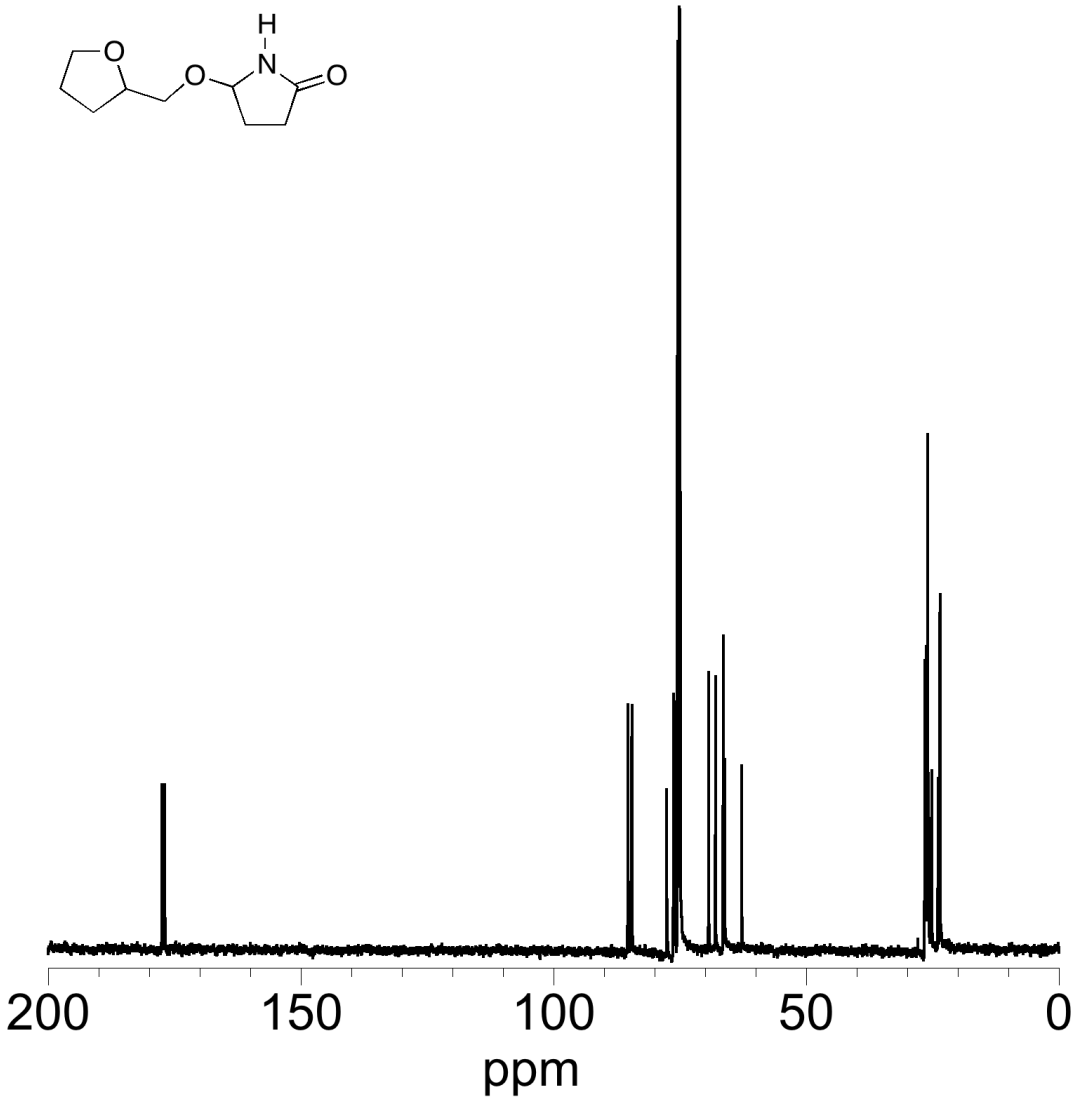

Figure S 28. ^{13}C NMR spectrum of 5-tetryhydrofurfuryloxy-2-pyrrolidone (126 MHz, $CDCl_3$).

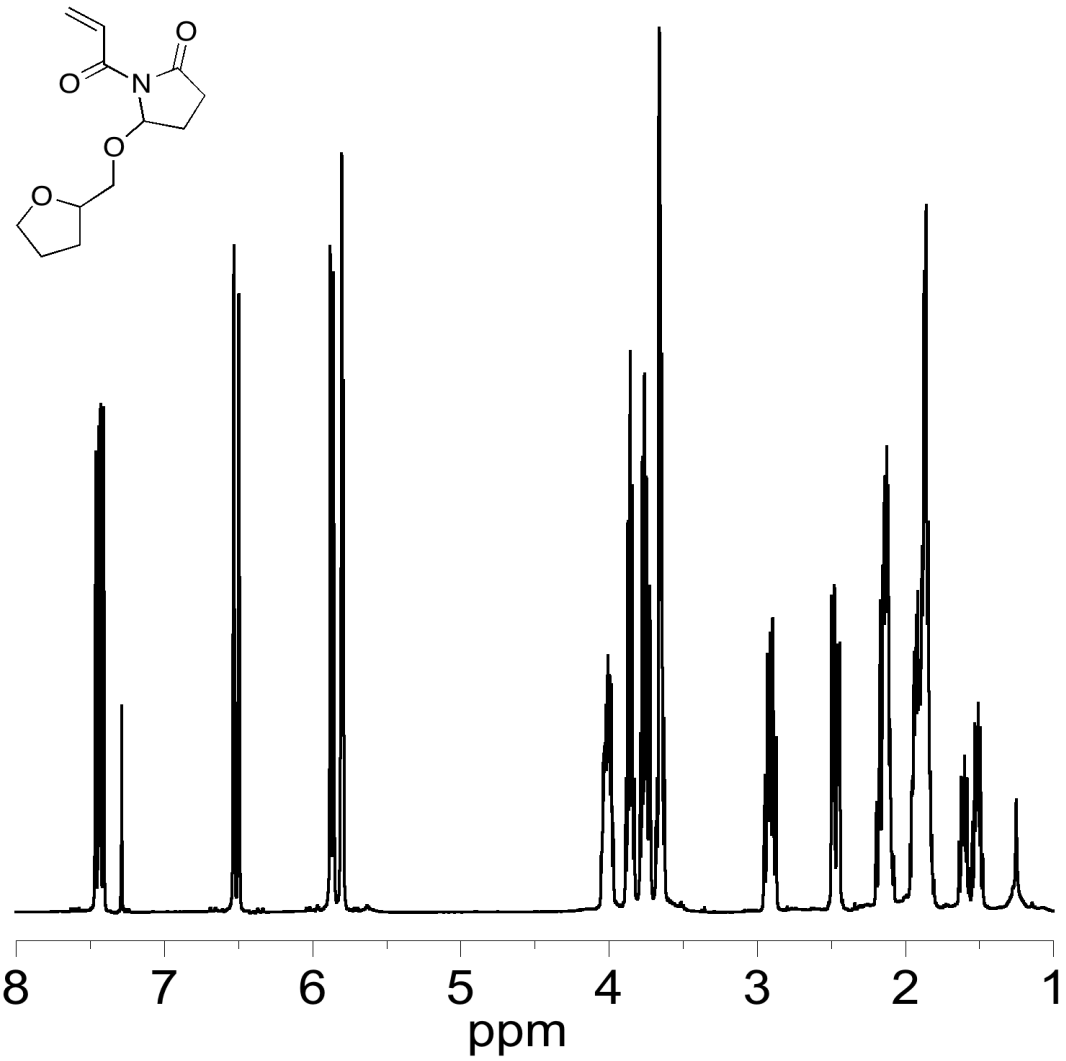

Figure S 29. ^{1}H NMR spectrum of **FurONP** (500 MHz, $CDCl_3$).

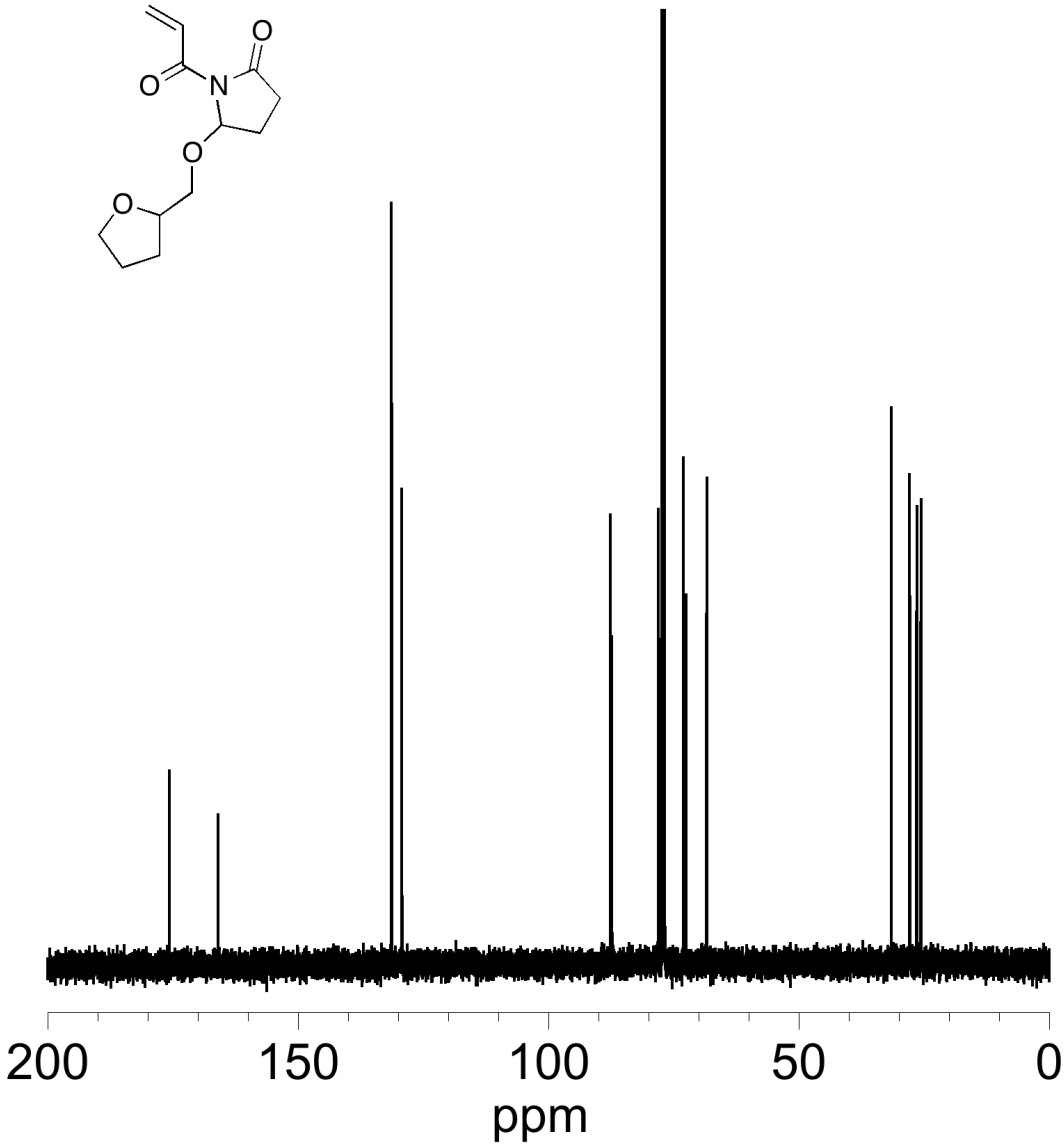

Figure S 30. ^{13}C NMR spectrum of **FurONP** (126 MHz, $CDCl_3$).

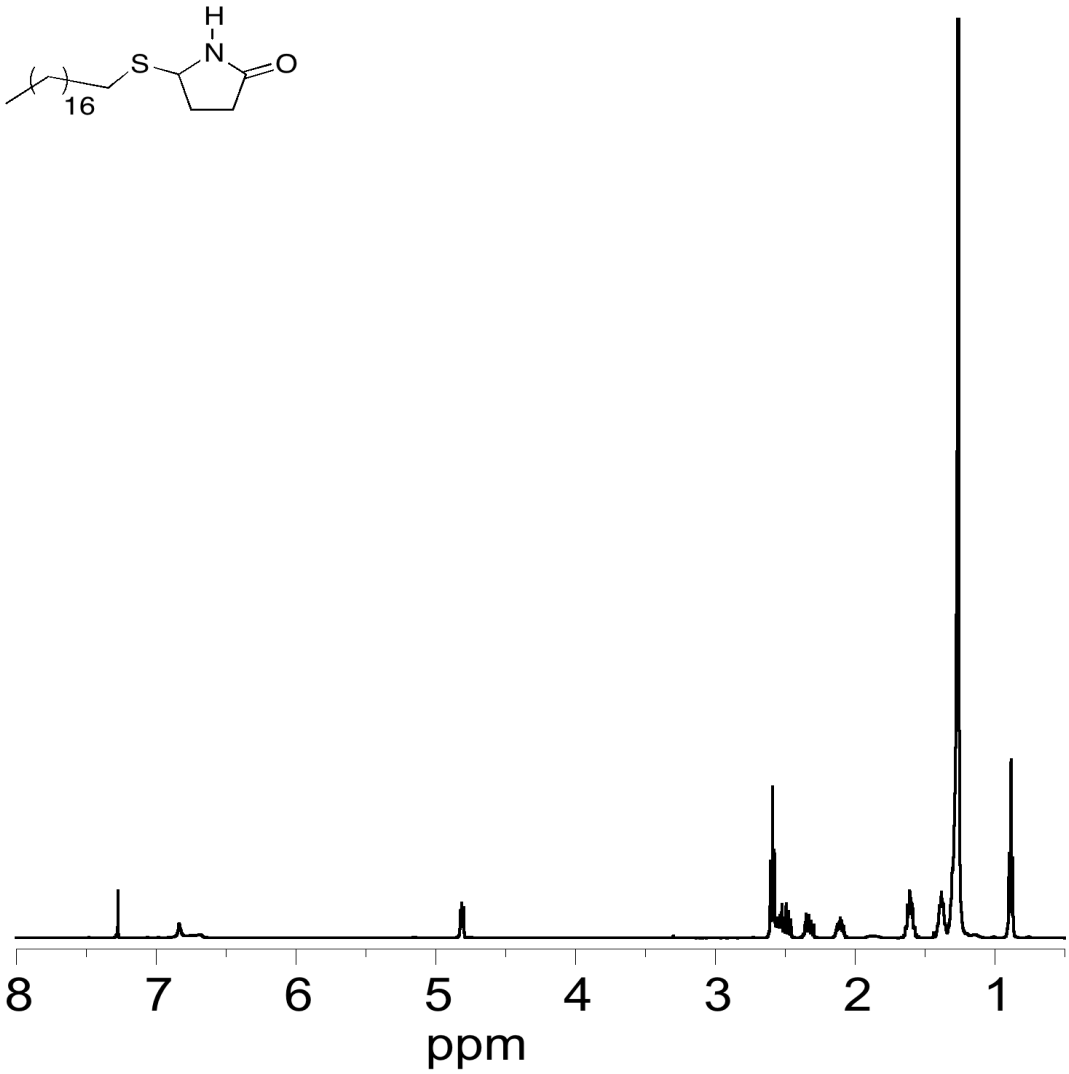

Figure S 31. ^{1}H NMR spectrum of 5-stearylthio-2-pyrrolidone (500 MHz, $CDCl_3$).

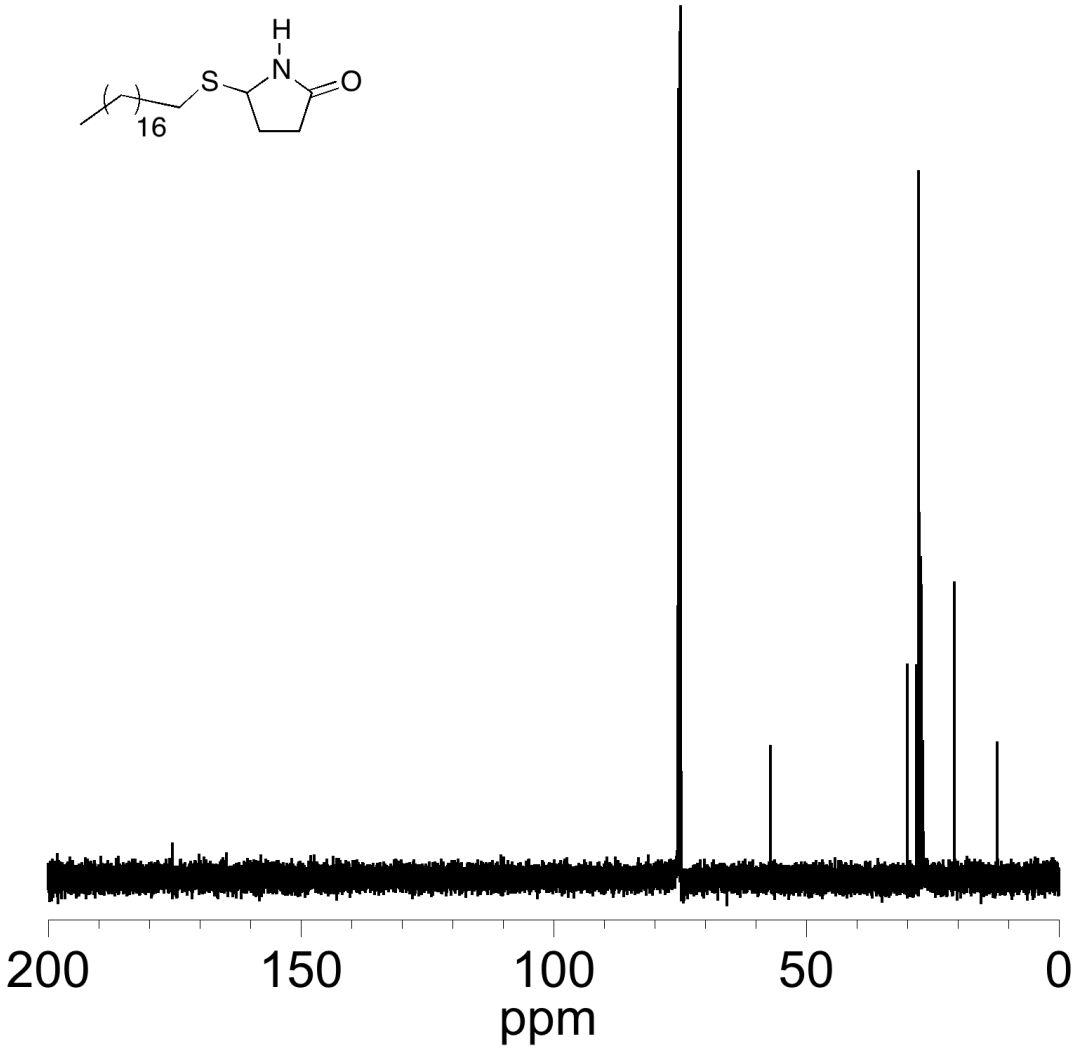

Figure S 32. ^{13}C NMR spectrum of 5-stearylthio-2-pyrrolidone (126 MHz, $CDCl_3$).

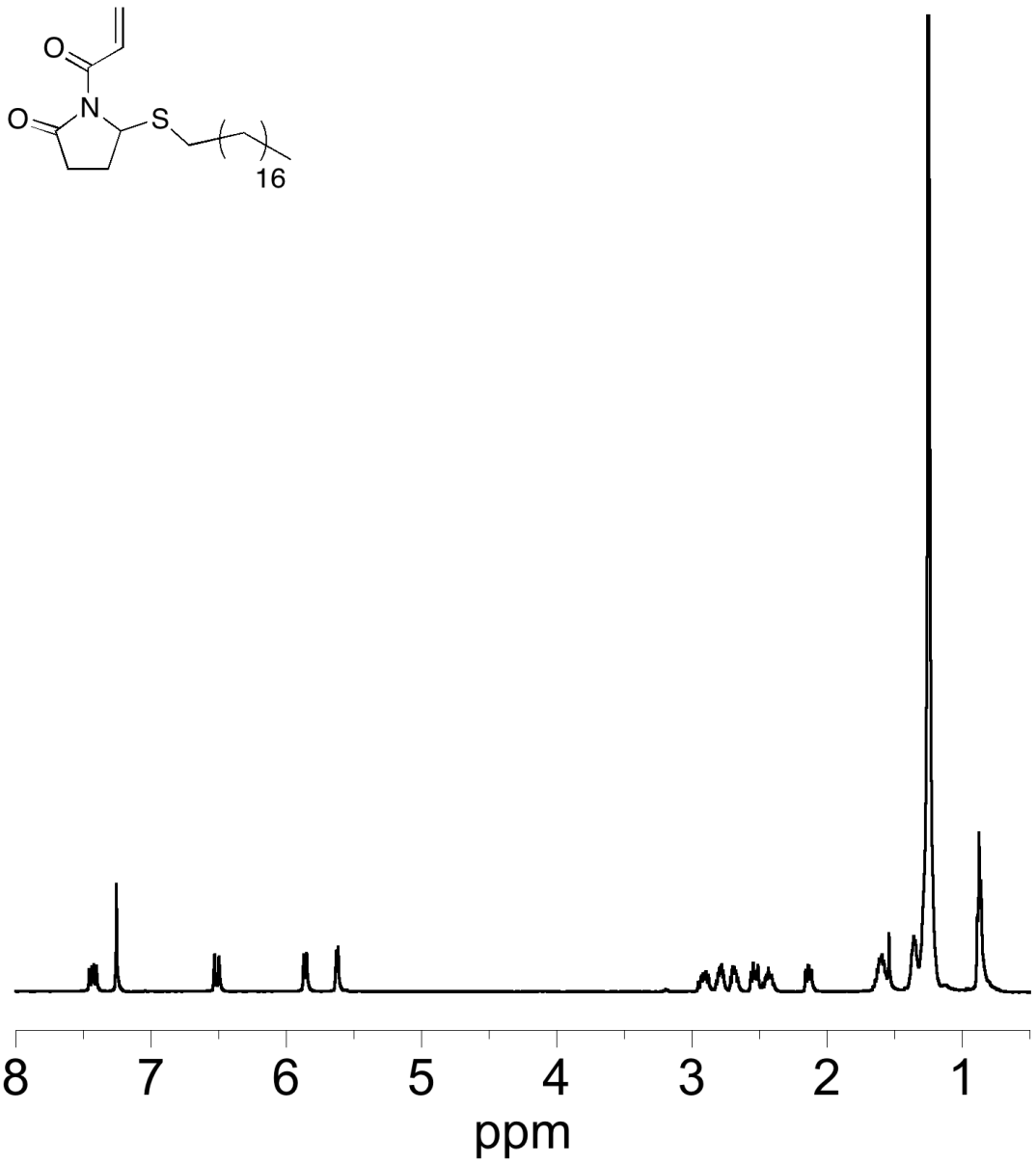

Figure S 33. ^{1}H NMR spectrum of **StNP** (500 MHz, $CDCl_3$).

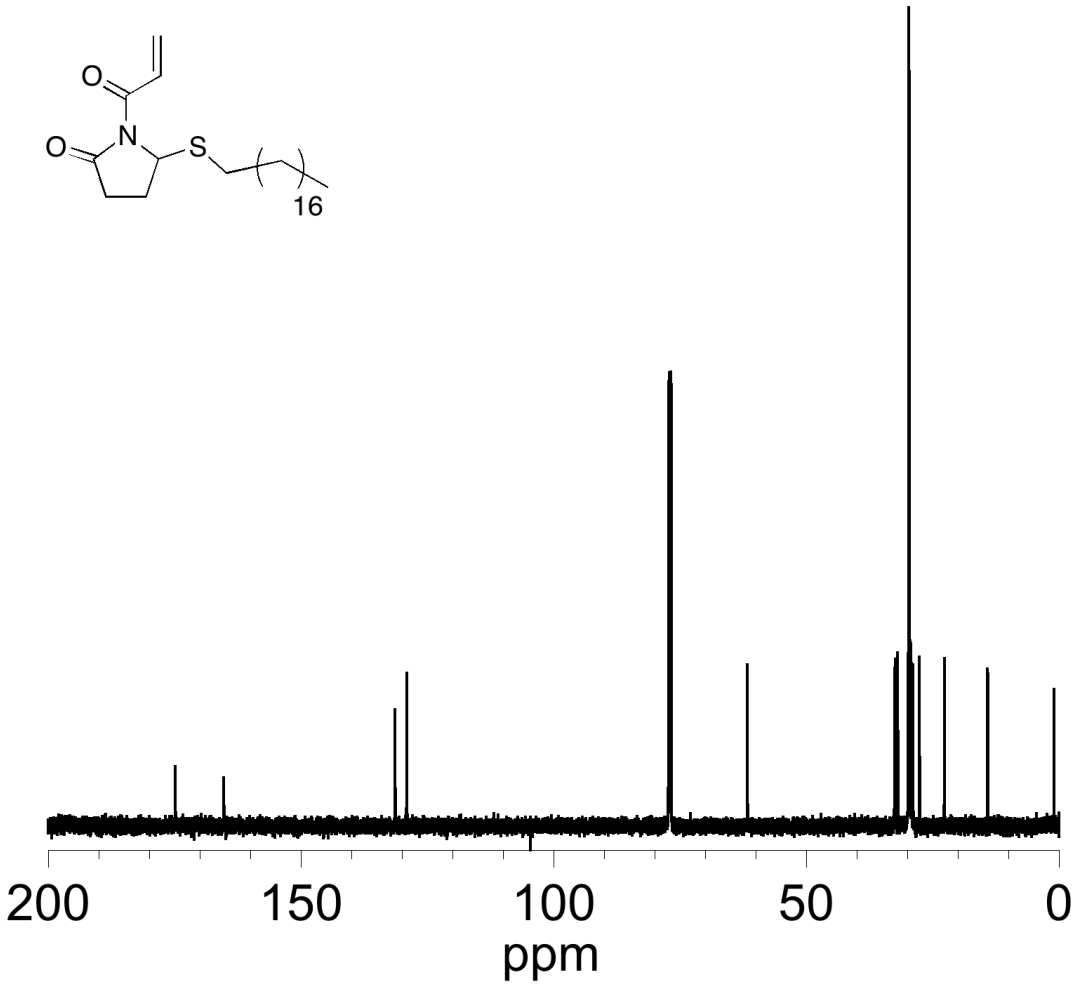

Figure S 34. ^{13}C NMR spectrum of **StSNP** (126 MHz, $CDCl_3$).

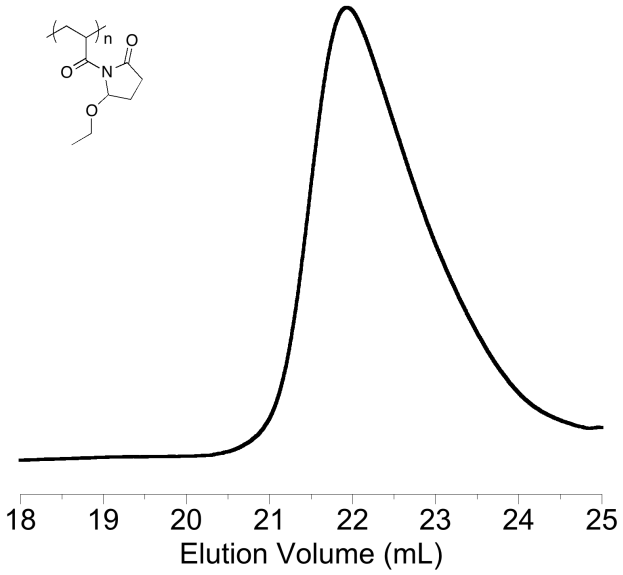

Figure S 35. GPC trace of **poly(EthONP)**.

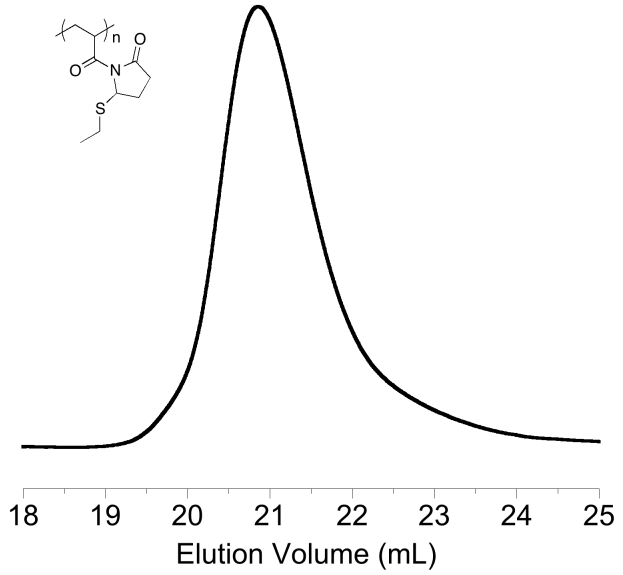

Figure S 36. GPC trace of **poly(EthSNP)**.

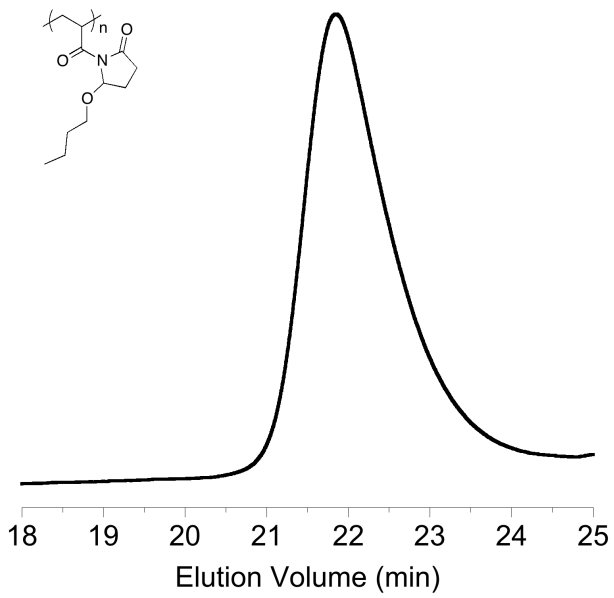

Figure S 37. GPC trace of **poly(BuONP)**.

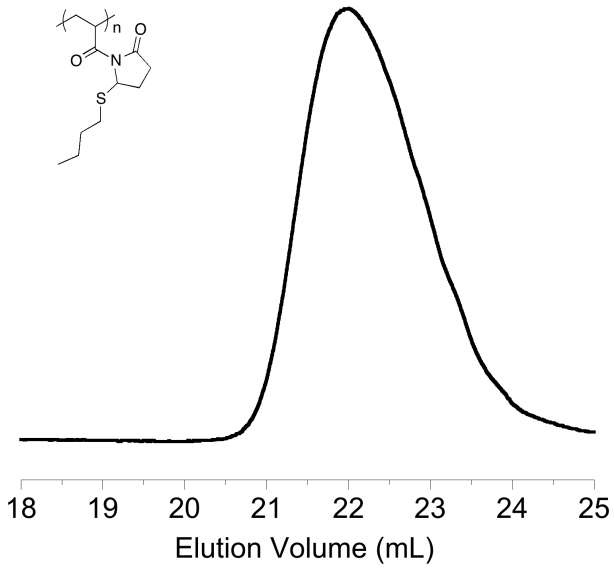

Figure S 38. GPC trace of **poly(BuSNP)**.

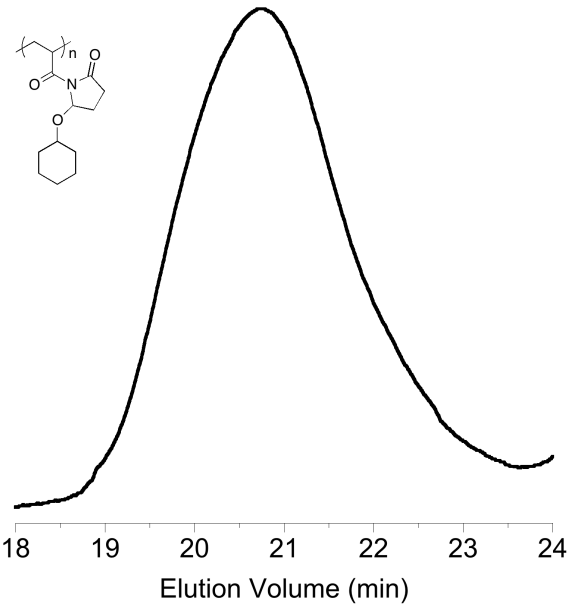

Figure S 39. GPC trace of **poly(CyONP)**.

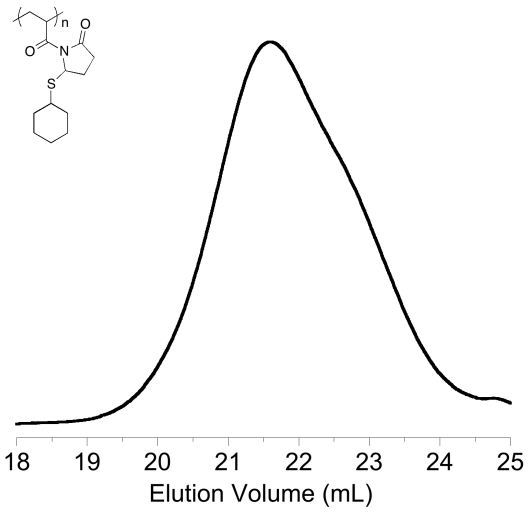

Figure S 40. GPC trace of **poly(CySNP)**.

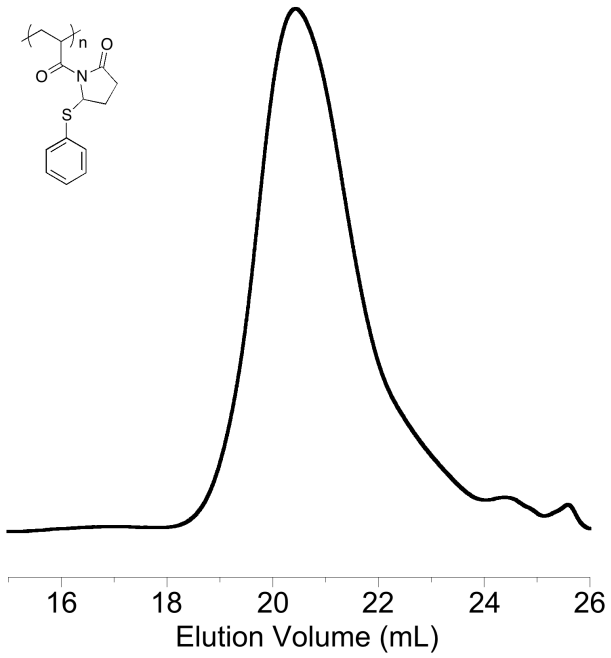

Figure S 41. GPC trace of **poly(PhSNP)**.

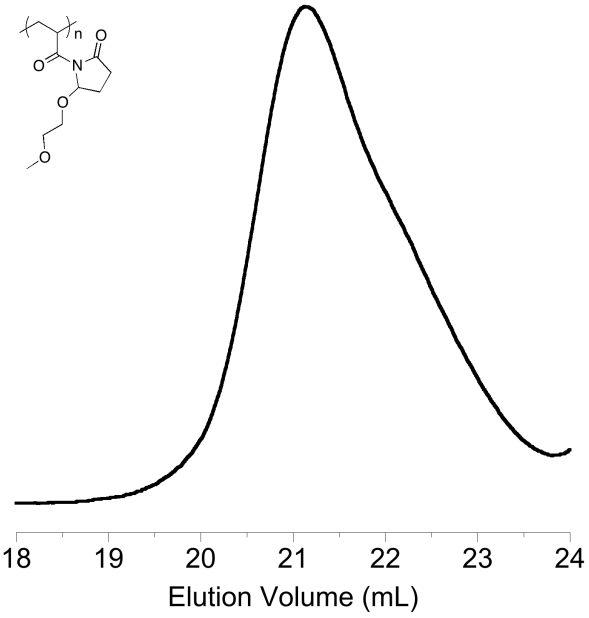

Figure S 42. GPC trace of **poly(MeOEthONP)**.

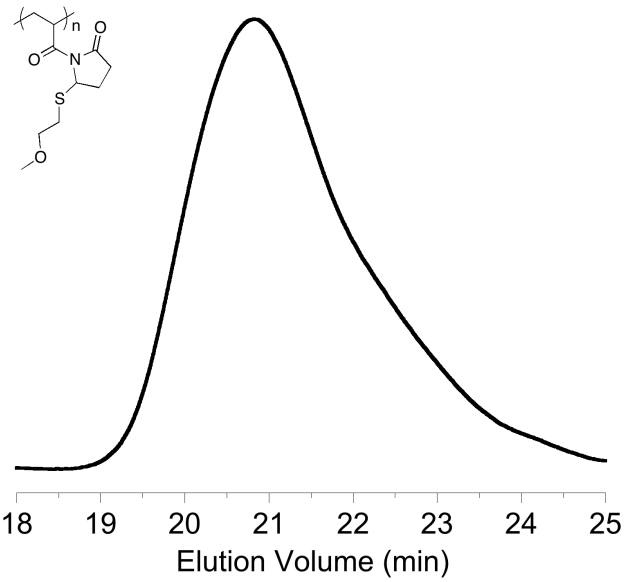

Figure S 43. GPC trace of **poly(MeOEthSNP)**.

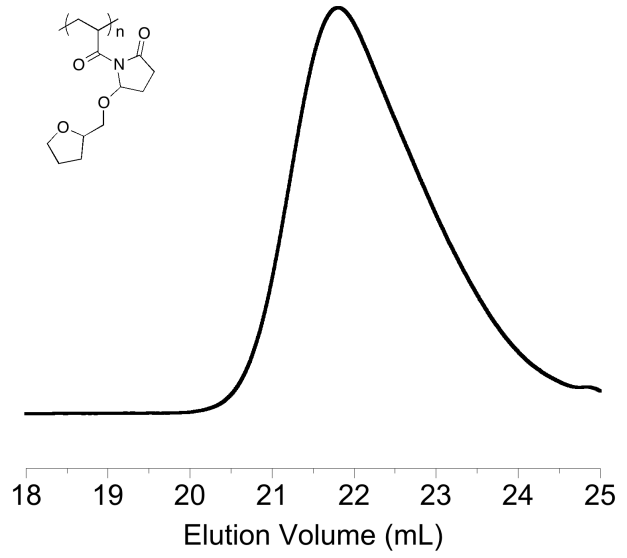

Figure S 44. GPC trace of **poly(FurONP)**.

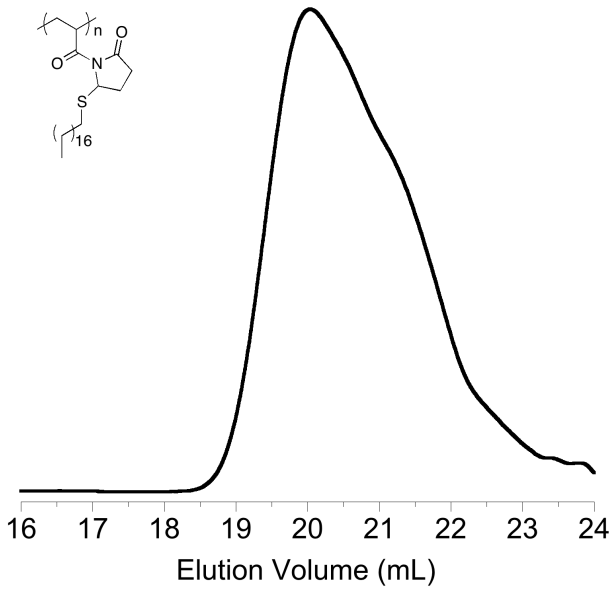

Figure S 45. GPC trace of **poly(StSNP)**.

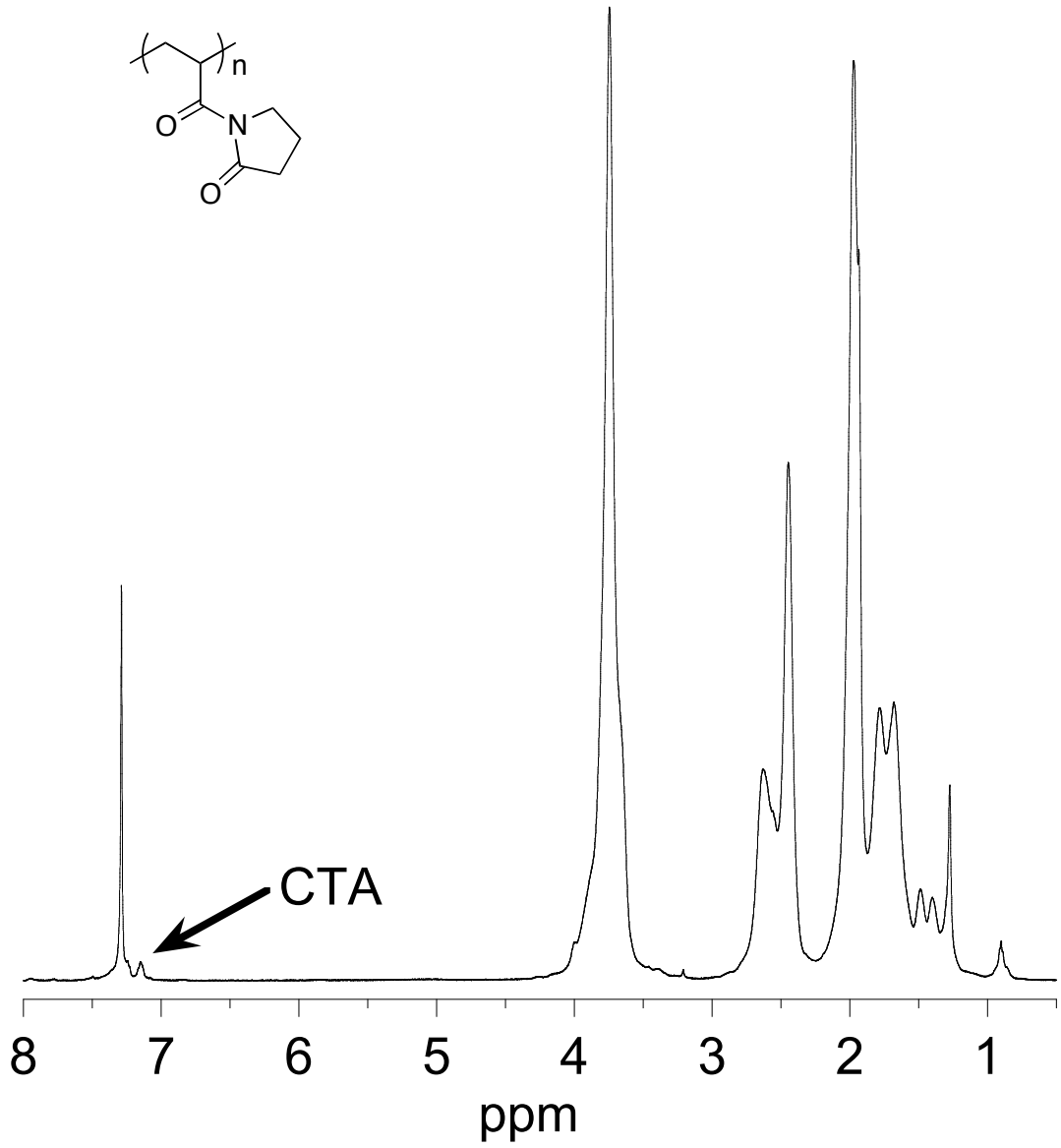

Figure S 46. ^{1}H NMR spectrum of **poly(NP)** (500 MHz, $CDCl_3$).

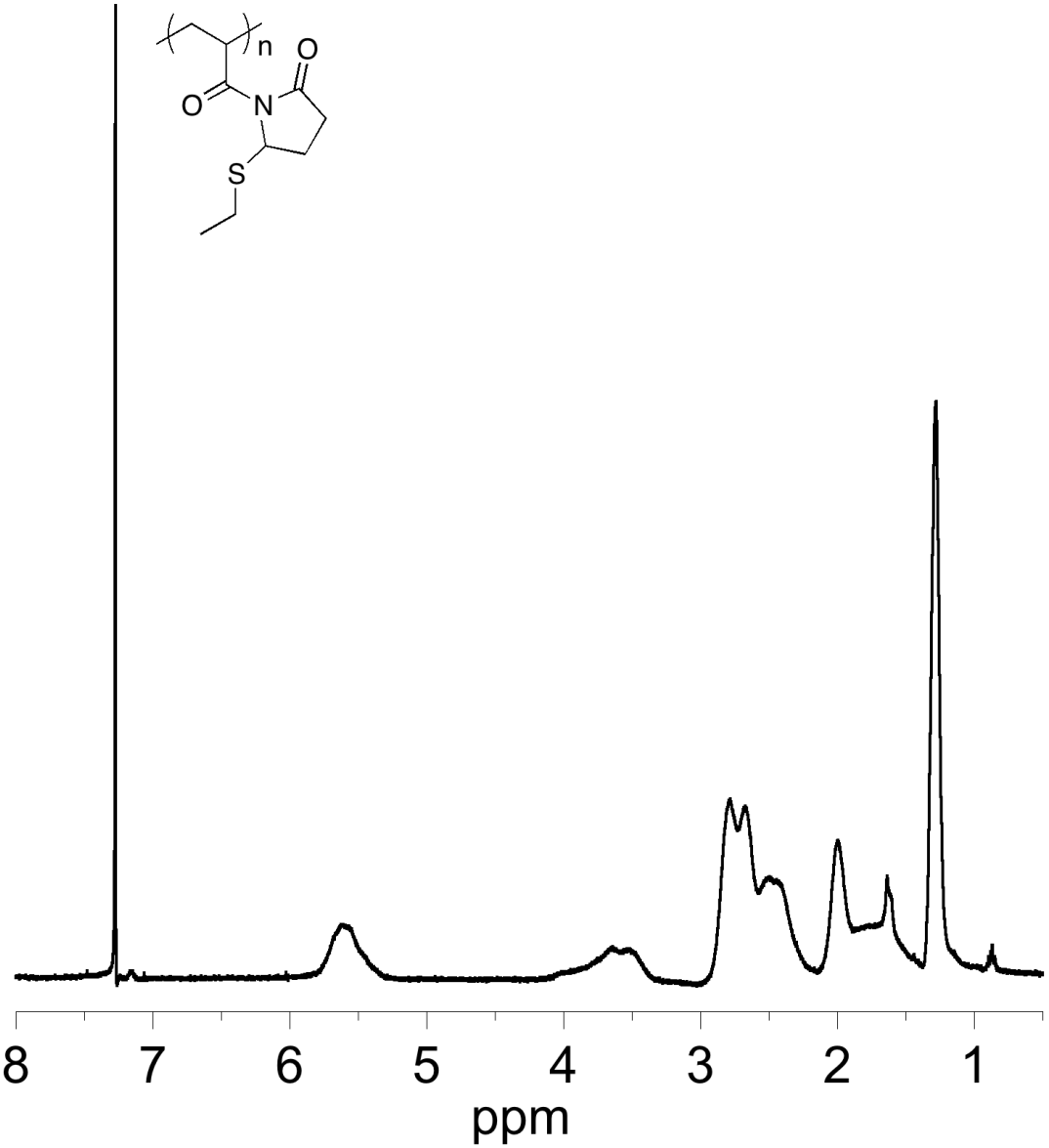

Figure S 47. ^{1}H NMR spectrum of **poly(EthSNP)** (500 MHz, $CDCl_3$).

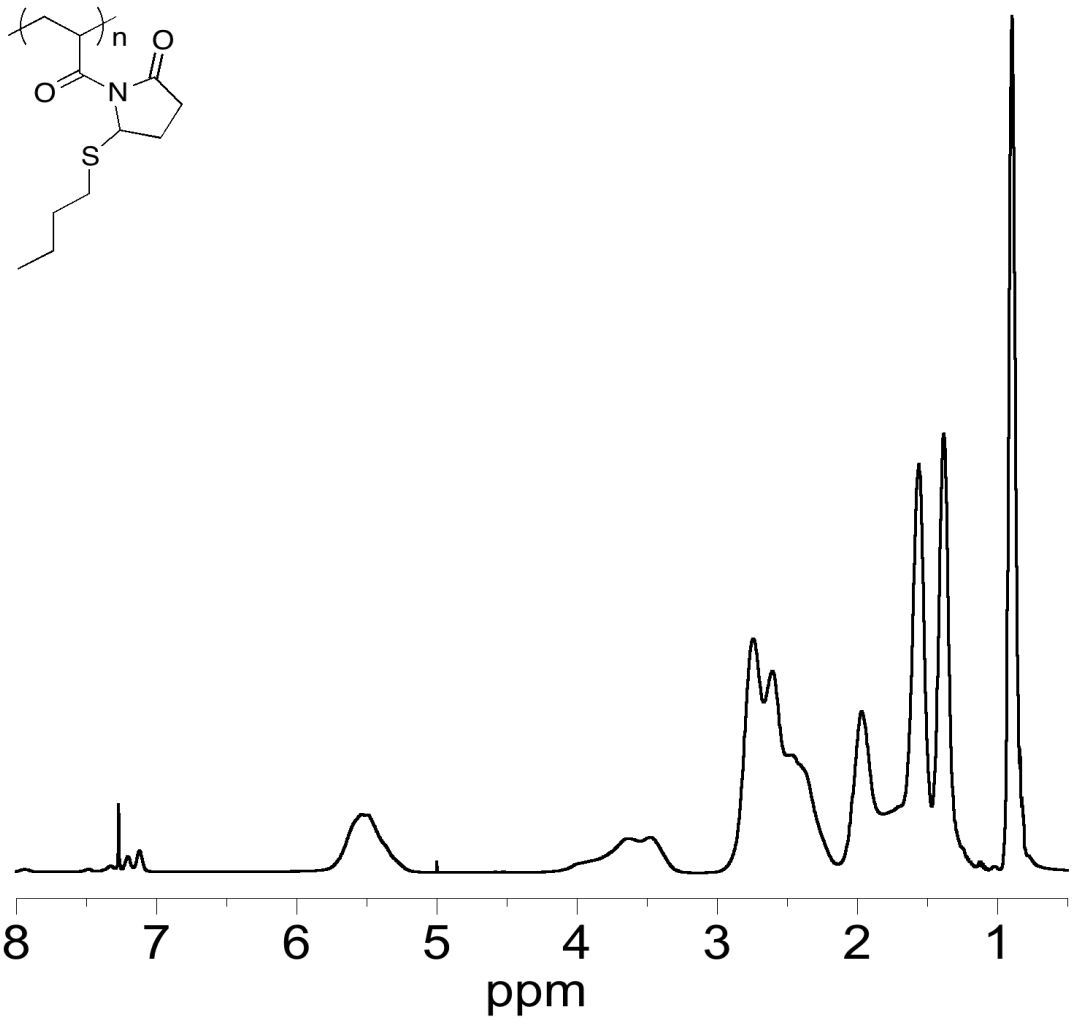

Figure S 48. ^{1}H NMR spectrum of **poly(BuSNP)** (500 MHz, $CDCl_3$).

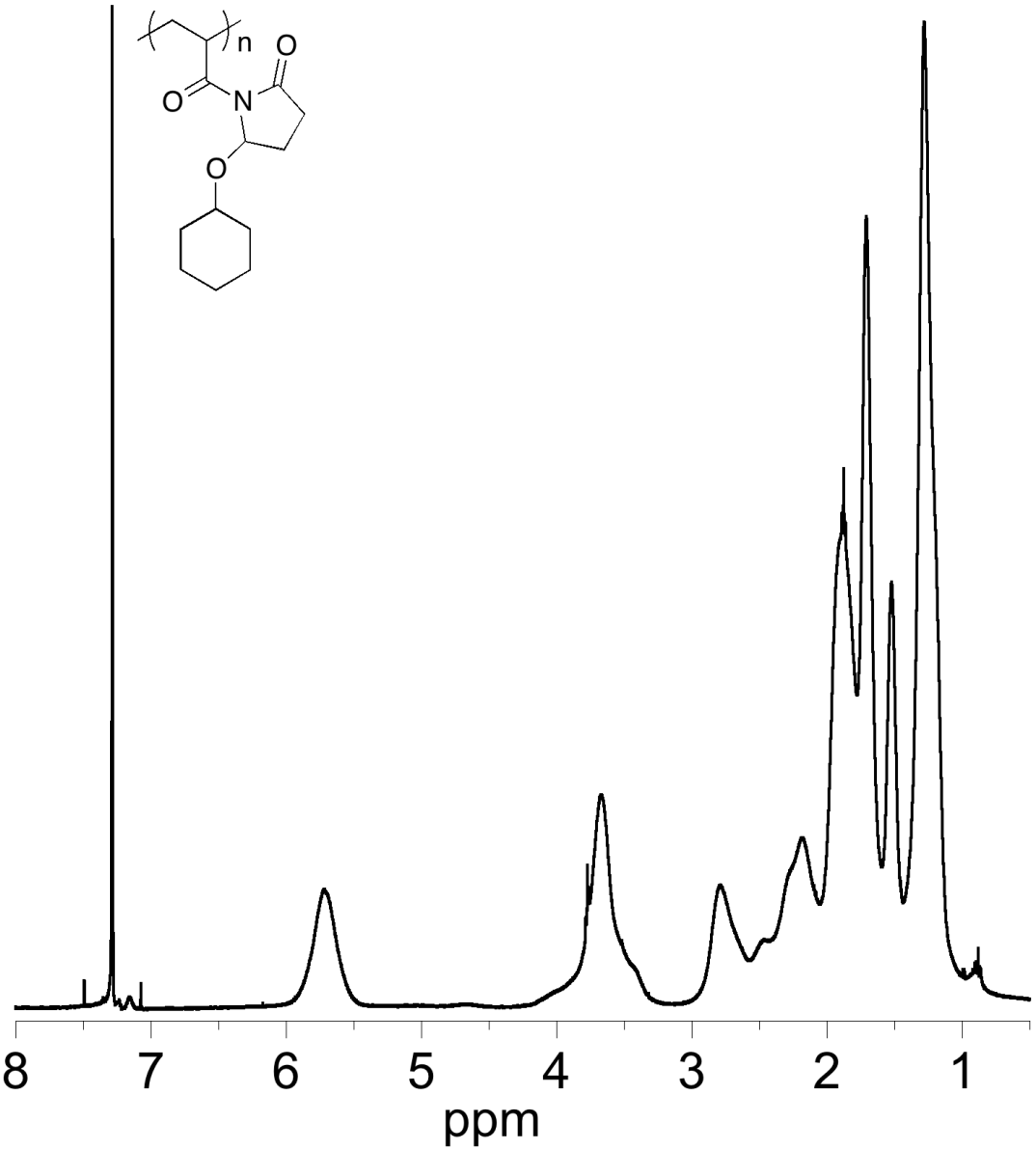

Figure S 49. ^{1}H NMR spectrum of **poly(CyONP)** (500 MHz, $CDCl_3$).

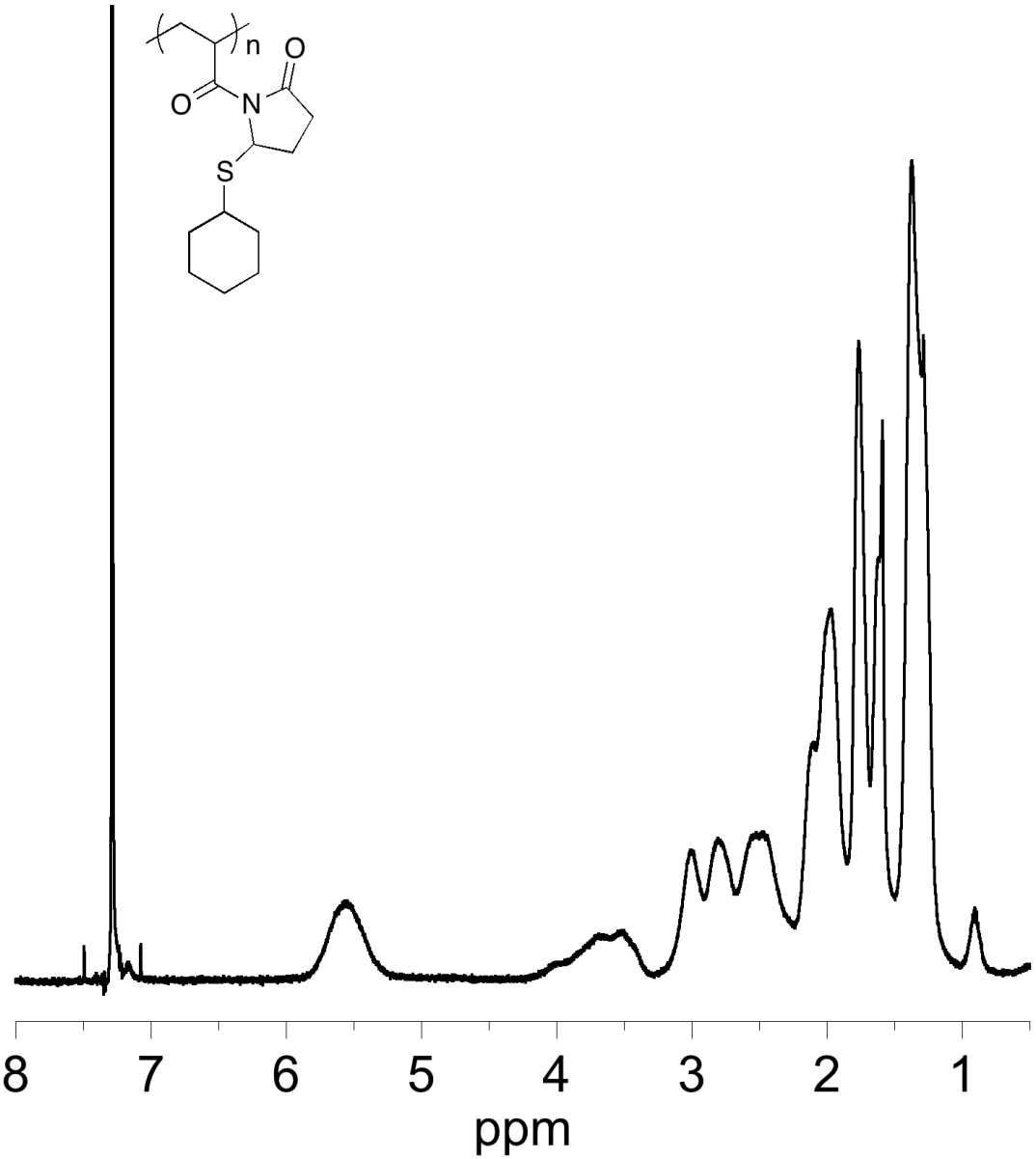

Figure S 50. ^{1}H NMR spectrum of **poly(CySNP)** (500 MHz, $CDCl_3$).

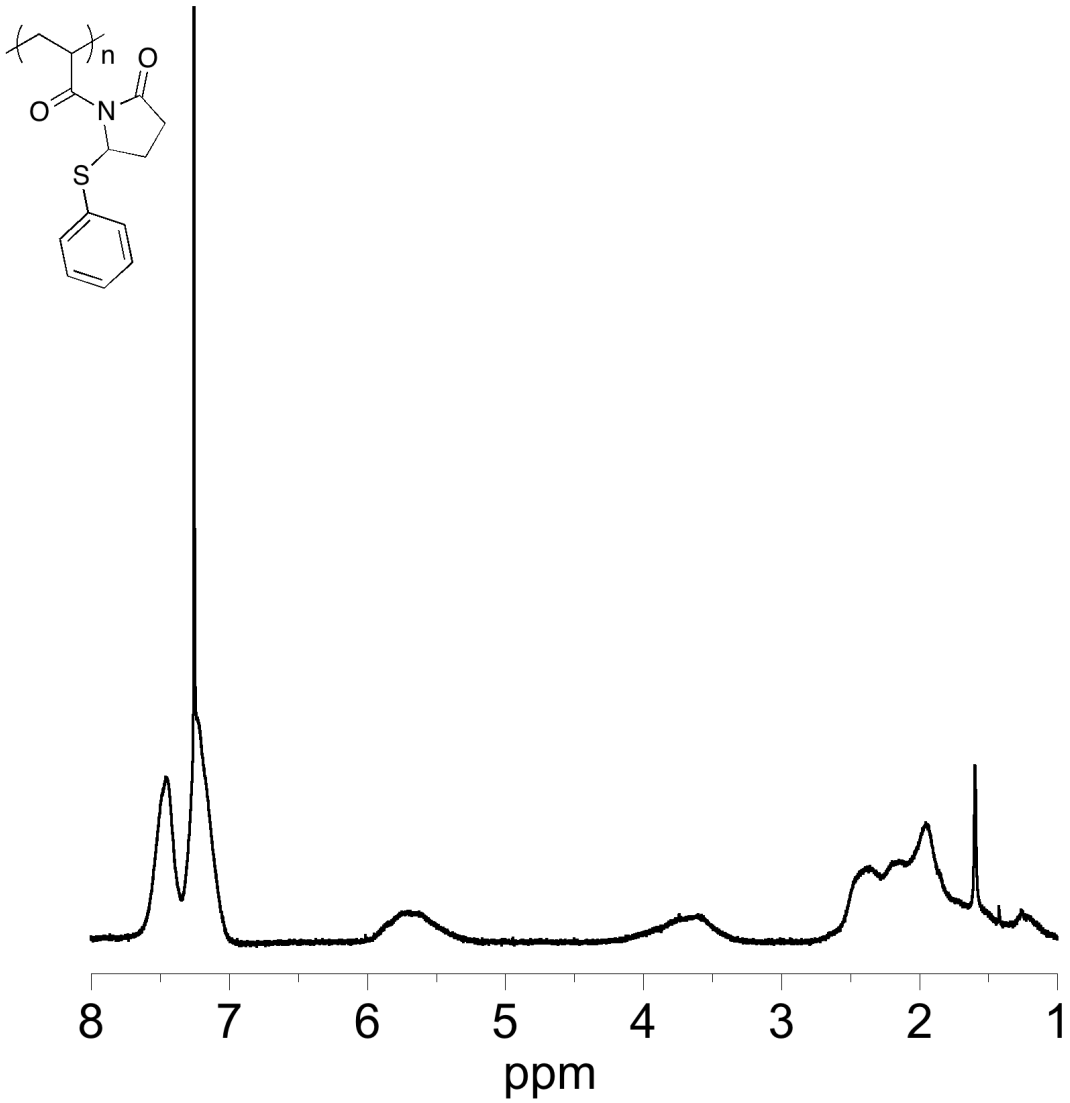

Figure S 51. ^{1}H NMR spectrum of **poly(PhSNP)** (500 MHz, $CDCl_3$).

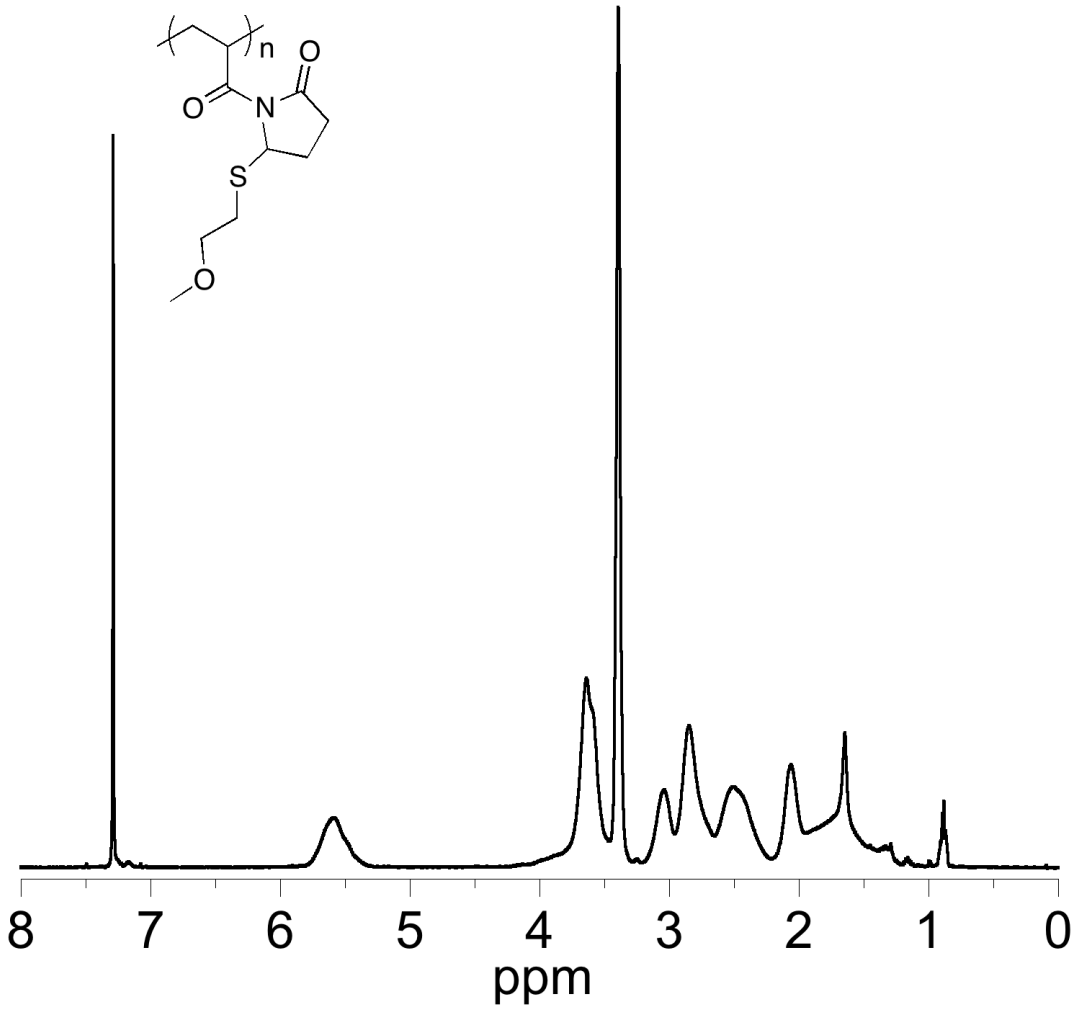

Figure S 52. ^{1}H NMR spectrum of **poly(MeOEthSNP)** (500 MHz, $CDCl_3$).

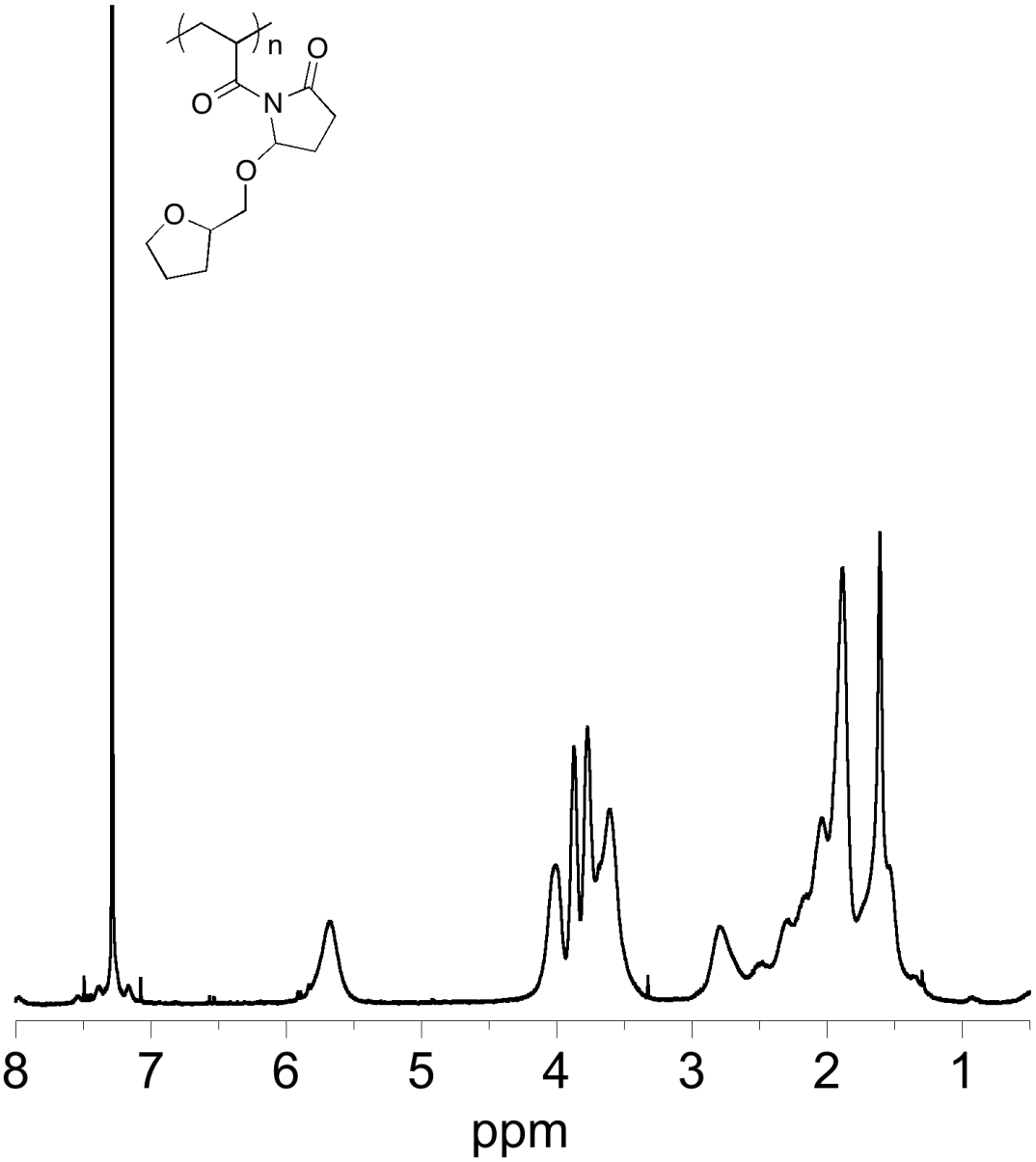

Figure S 53. ^{1}H NMR spectrum of **poly(FurONP)** (500 MHz, $CDCl_3$).

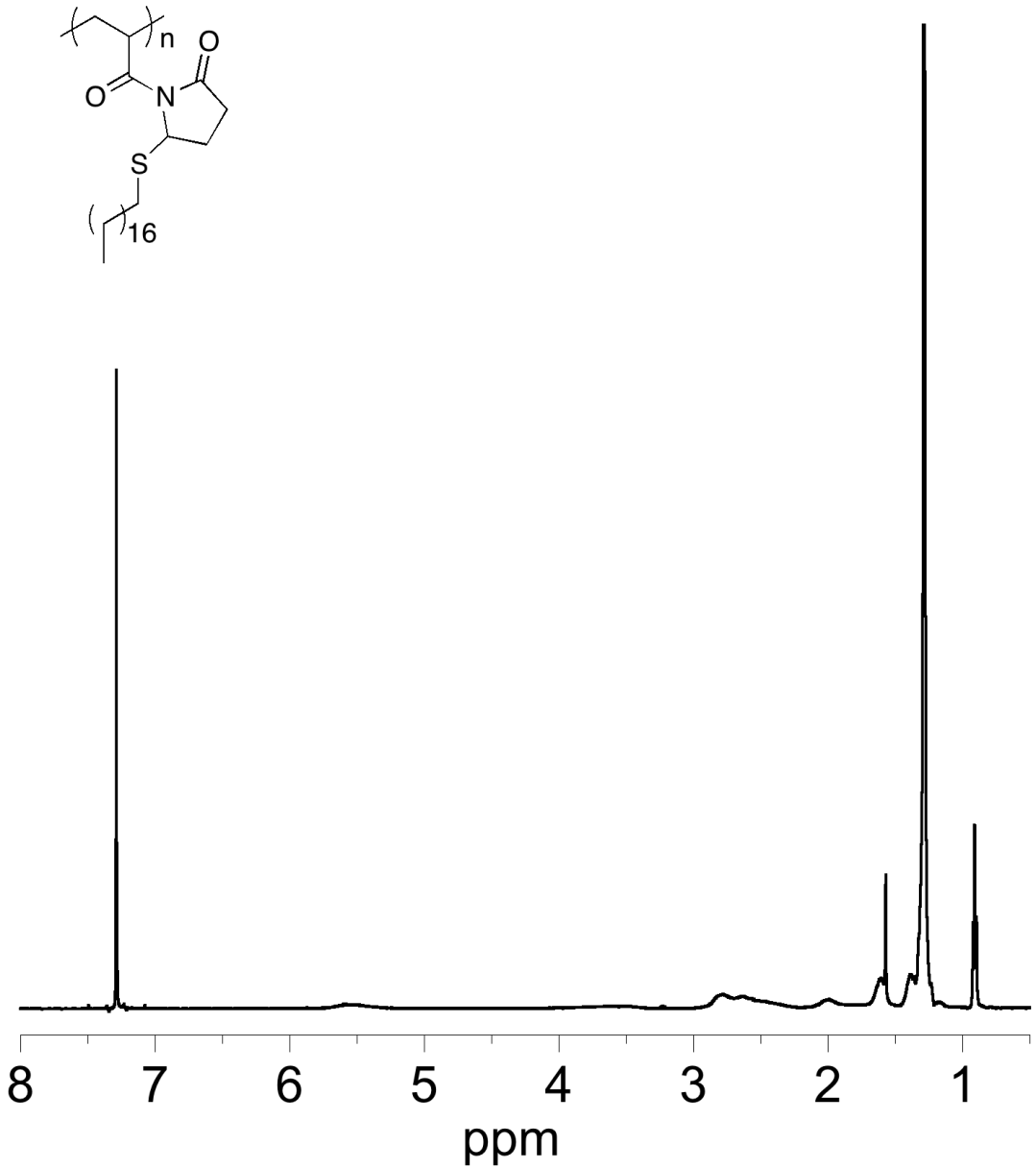

Figure S 54. ^{1}H NMR spectrum of **poly(StSNP)** (500 MHz, $CDCl_3$).

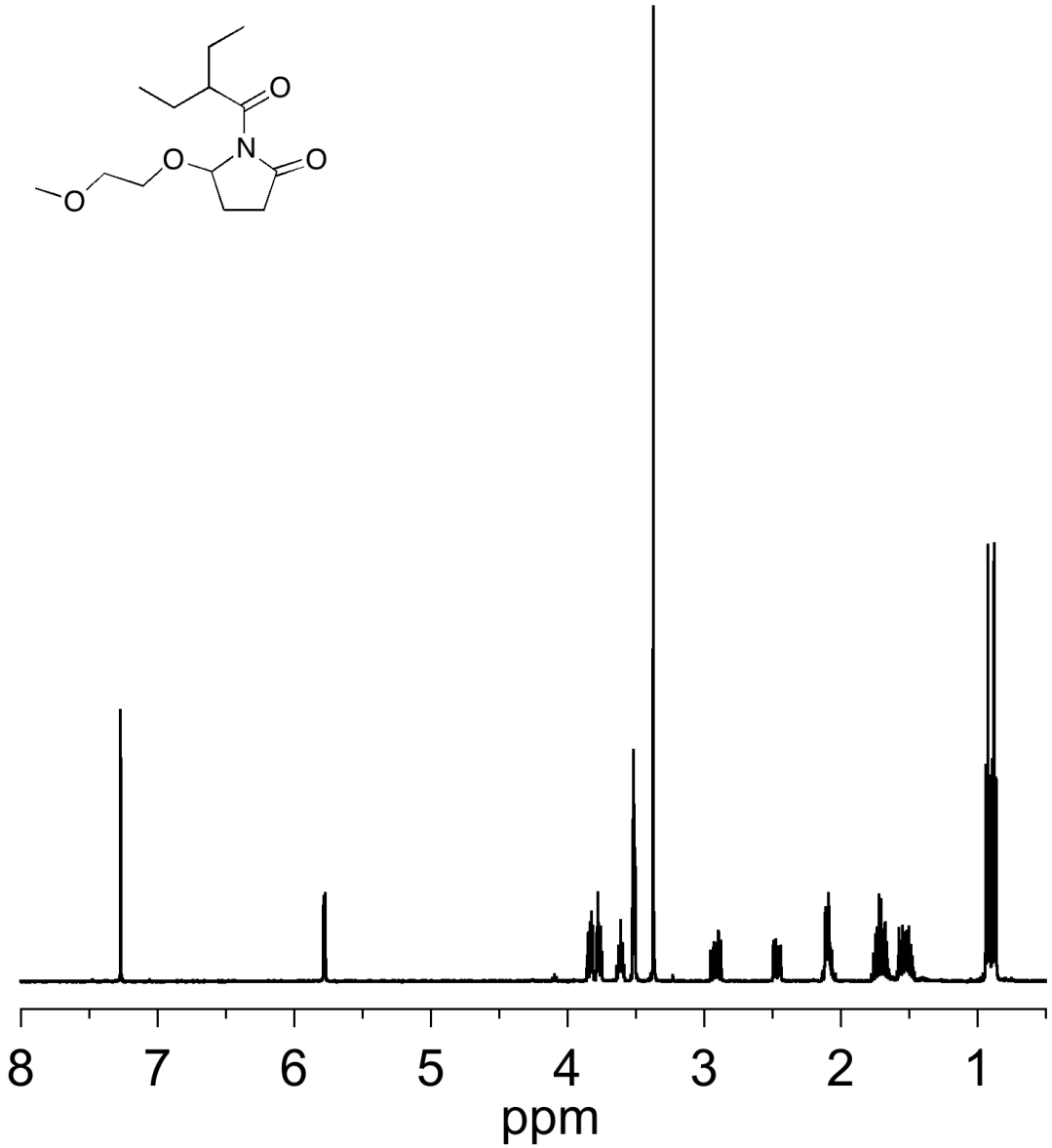

Figure S 55. ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$).

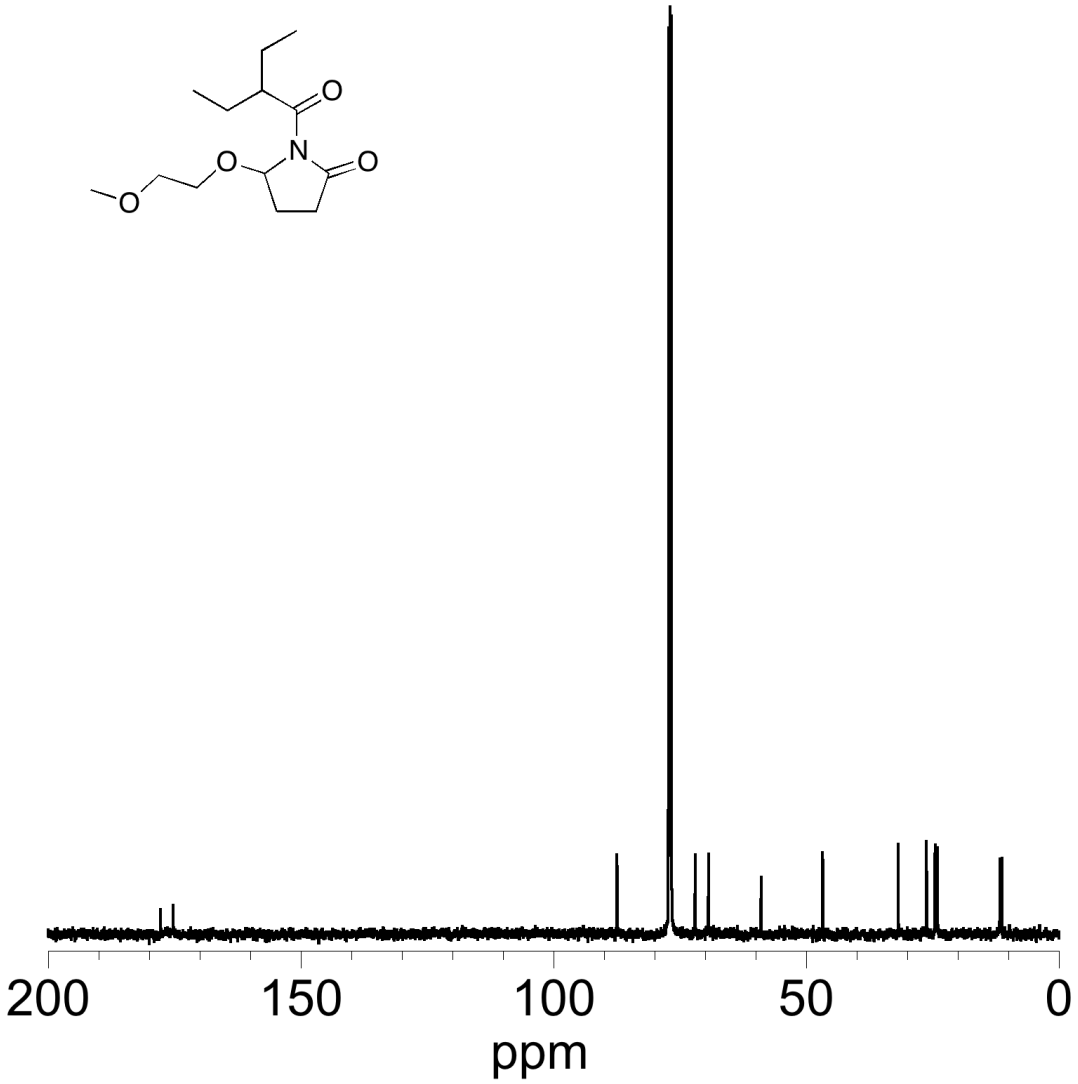

Figure S 56. ^{13}C NMR spectrum of **3** (500 MHz, $CDCl_3$).

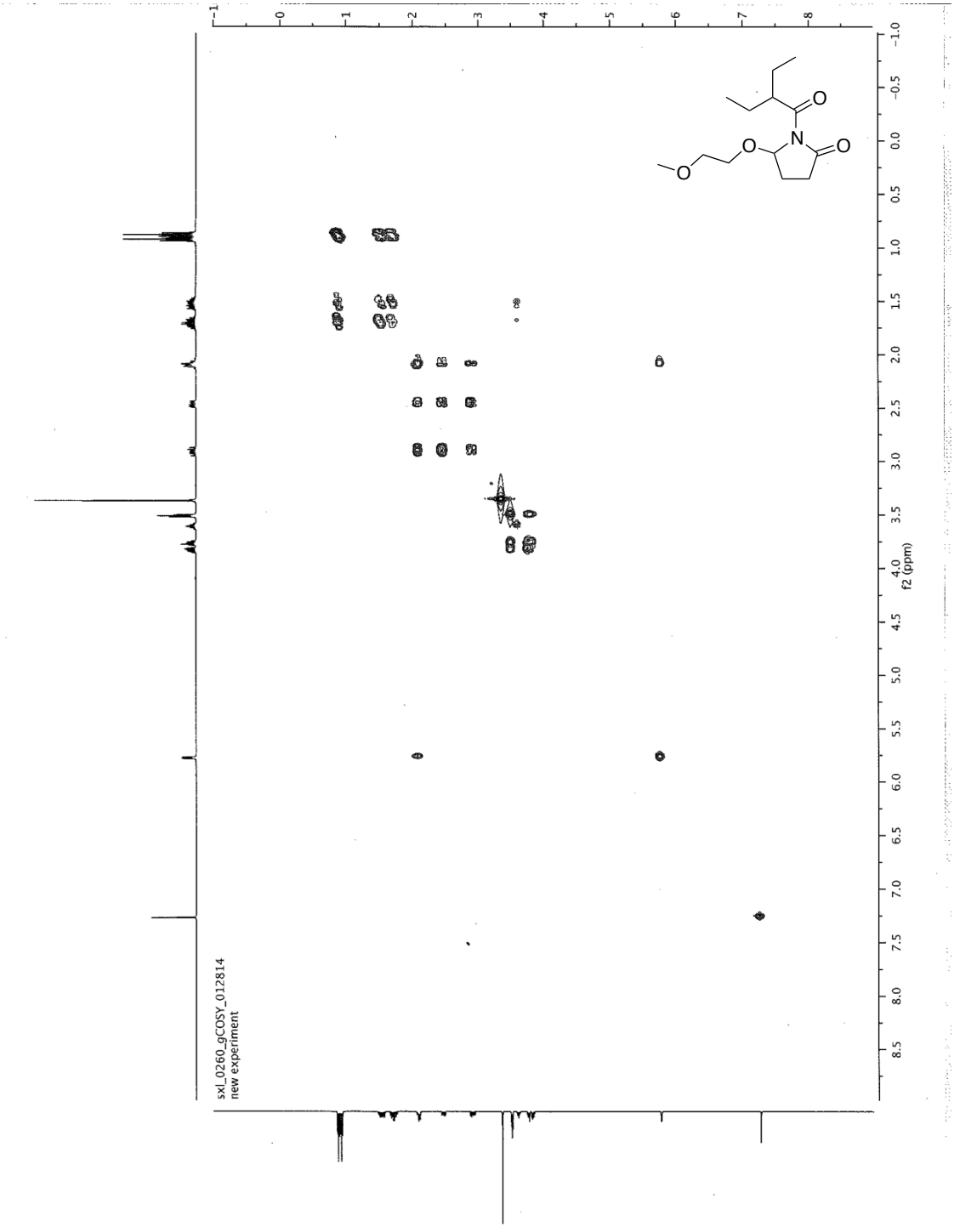

Figure S 57. 2D COSY NMR spectrum of **3** (500 MHz, $CDCl_3$).

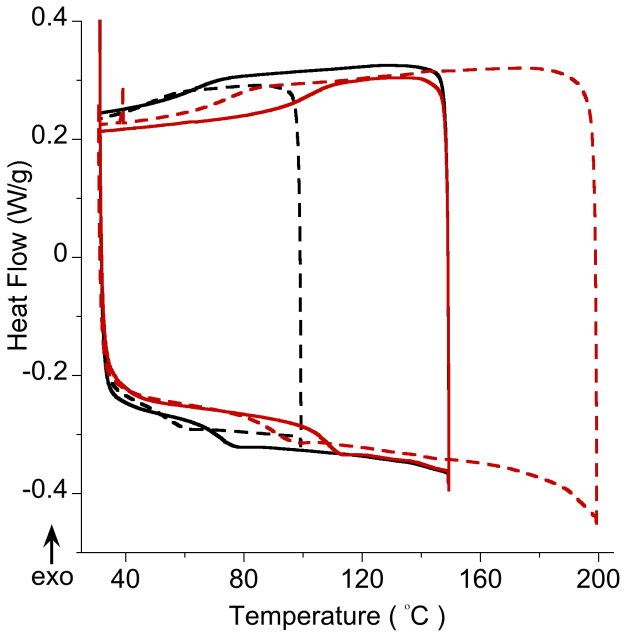

Figure S 58. DSC traces of **poly(EthONP)** (red, solid), **poly(EthSNP)** (red, dash), **poly(BuONP)** (black, solid), **poly(BuSNP)** (black, dash). Second scan, ramp rate: 10 °C/min.

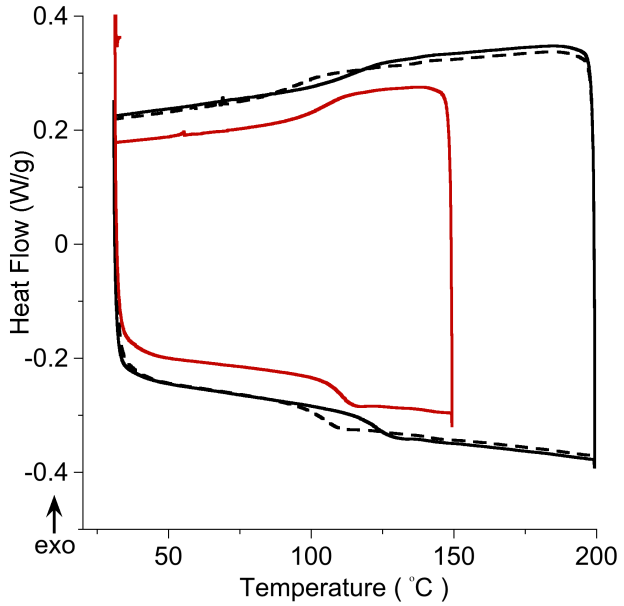

Figure S 59. DSC traces of **poly(CyONP)** (black, solid), **poly(CySNP)** (black, dash), **poly(PhSNP)** (red, solid). Second scan, ramp rate: 10 °C/min.

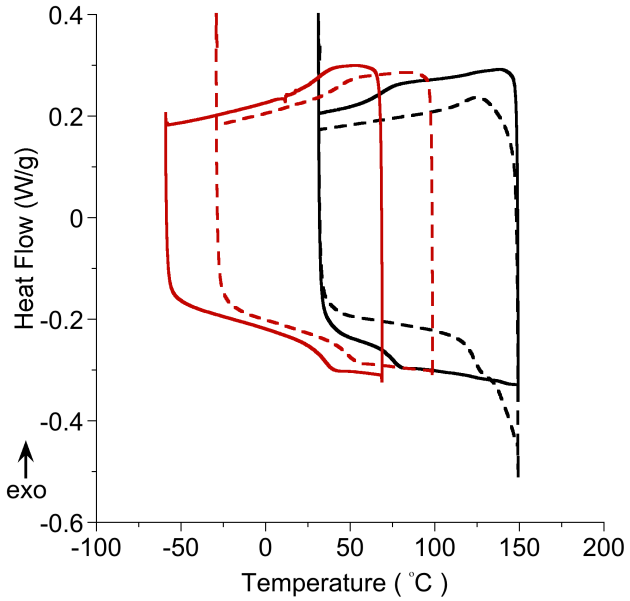

Figure S 60. DSC traces of **poly(FuONP)** (black, solid), **poly(NP)** (black, dash), **poly(MeOEthONP)** (red, solid) and **poly(MeOEthSNP)** (red,dash). Second scan, ramp rate: 10 °C/min.

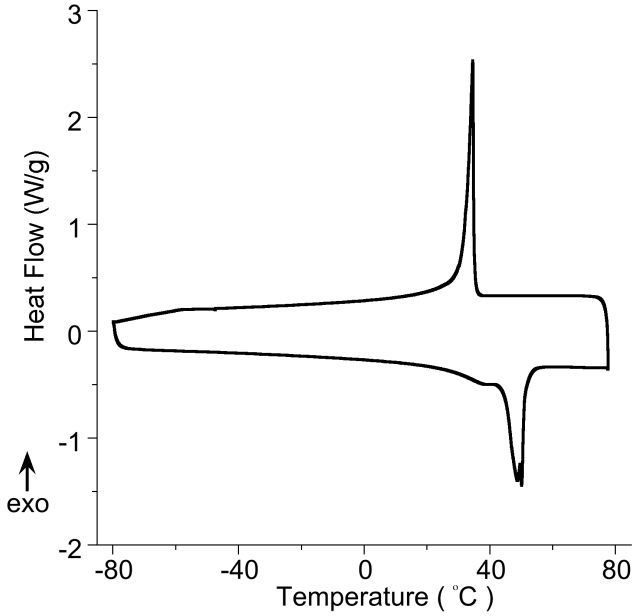

Figure S 61. DSC traces of **poly(StSNP)**. Second scan, ramp rate: 10 °C/min.

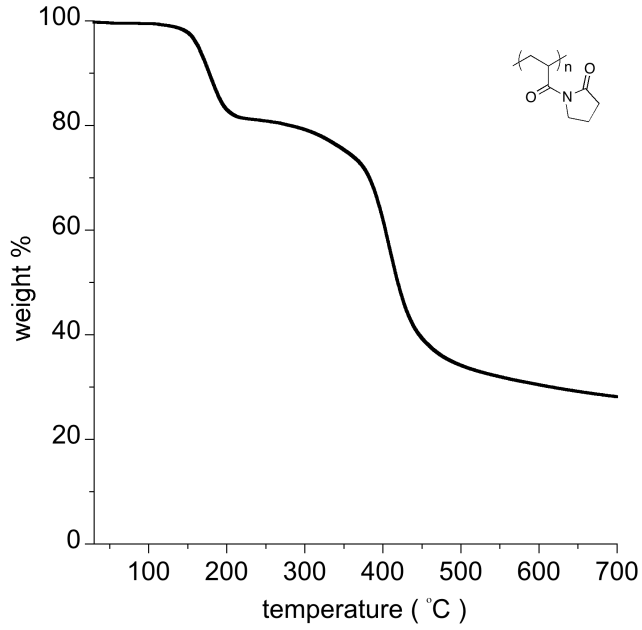

Figure S 62. TGA thermograms of **poly(NP)**.

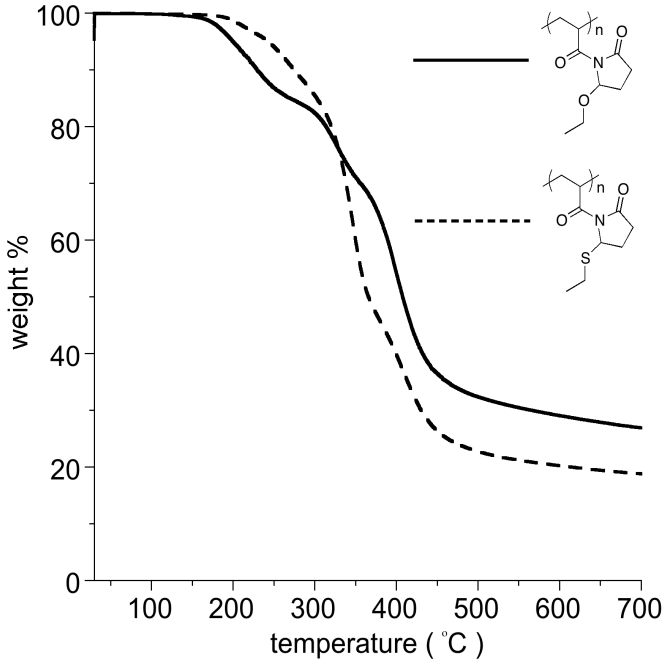

Figure S 63. TGA thermograms of **poly(EthONP)** and **poly(EthSNP)**.

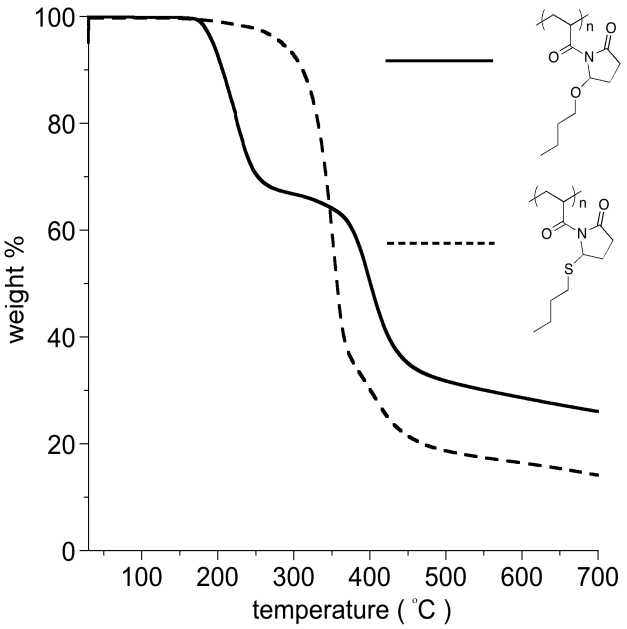

Figure S 64. TGA thermograms of **poly(BuONP)** and **poly(BuSNP)**.

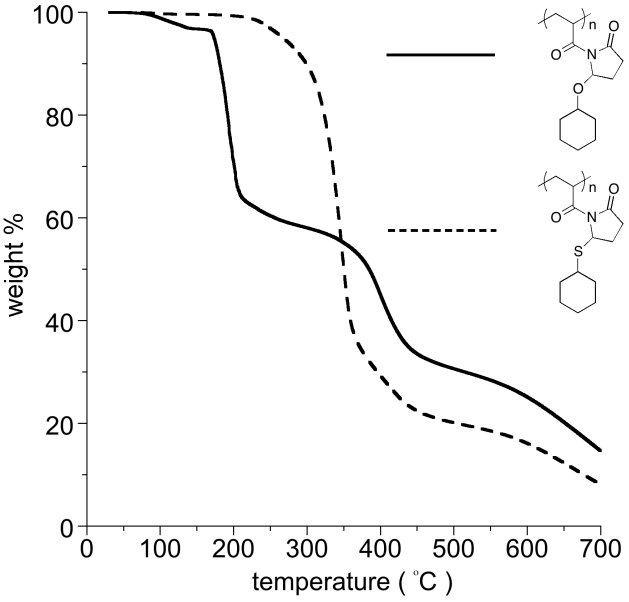

Figure S 65. TGA thermograms of **poly(CyONP)** and **poly(CySNP)**.

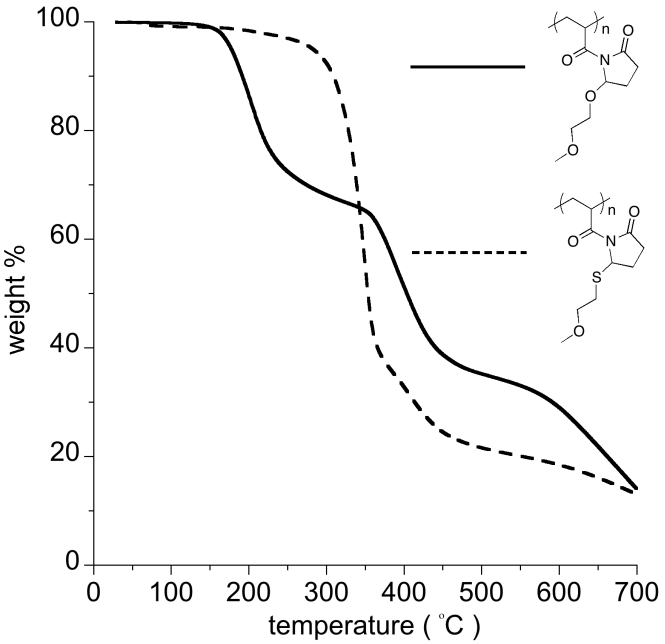

Figure S 66. TGA thermograms of **poly(MeOEthONP)** and **poly(MeOEthSNP)**.

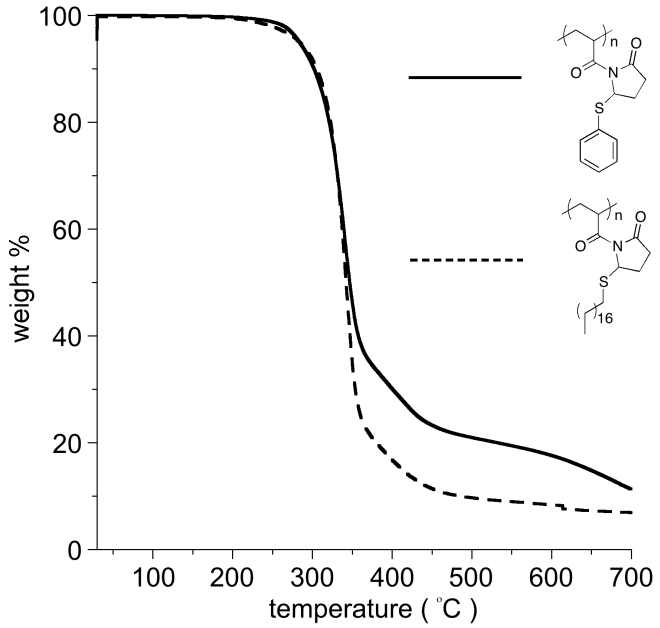

Figure S 67. TGA thermograms of **poly(PhSNP)** and **poly(StSNP)**.

Table S 1. Cloud point temperatures of **poly(MeOEthONP)** and **poly(FurONP)**.[a]

Polymer	Conc. (mg/mL)	Medium	CP (°C)
poly(MeOEthONP)	0.2	DI-water	47
poly(MeOEthONP)	0.4	DI-water	44
poly(MeOEthONP)	0.6	DI-water	40
poly(MeOEthONP)	0.8	DI-water	40
poly(MeOEthONP)	1.0	DI-water	37
poly(MeOEthONP)	0.2	PBS	45
poly(MeOEthONP)	0.4	PBS	40
poly(MeOEthONP)	0.6	PBS	39
poly(MeOEthONP)	0.8	PBS	38
poly(MeOEthONP)	1.0	PBS	36
poly(FurONP)	0.2	DI-water	15
poly(FurONP)	0.4	DI-water	13
poly(FurONP)	0.6	DI-water	10
poly(FurONP)	0.8	DI-water	10
poly(FurONP)	1.0	DI-water	9
poly(FurONP)	0.2	PBS	16
poly(FurONP)	0.4	PBS	17
poly(FurONP)	0.6	PBS	9
poly(FurONP)	0.8	PBS	7
poly(FurONP)	1.0	PBS	6

[a] Cloud points were measured by turbidimetry (λ = 500 nm) and taken as the temperature at which the solution lost 50% of its original optical transmission during the heating scan.

[1] a) Bruker (2005). *SAINT*, Version 7.23a. Bruker AXS Inc., Madison, Wisconsin, USA. b) Bruker (2006). *APEX 2*, Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA.

[2] a) Sheldrick, G. M. (2008a). *SADABS*. University of Göttingen, Germany. b) Sheldrick, G. M. (2008b). Acta Cryst. A, **64**, 112-122.

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