Full and Partial Amidation of Poly(methyl acrylate) as basis for functional polyacrylamide (co)polymers

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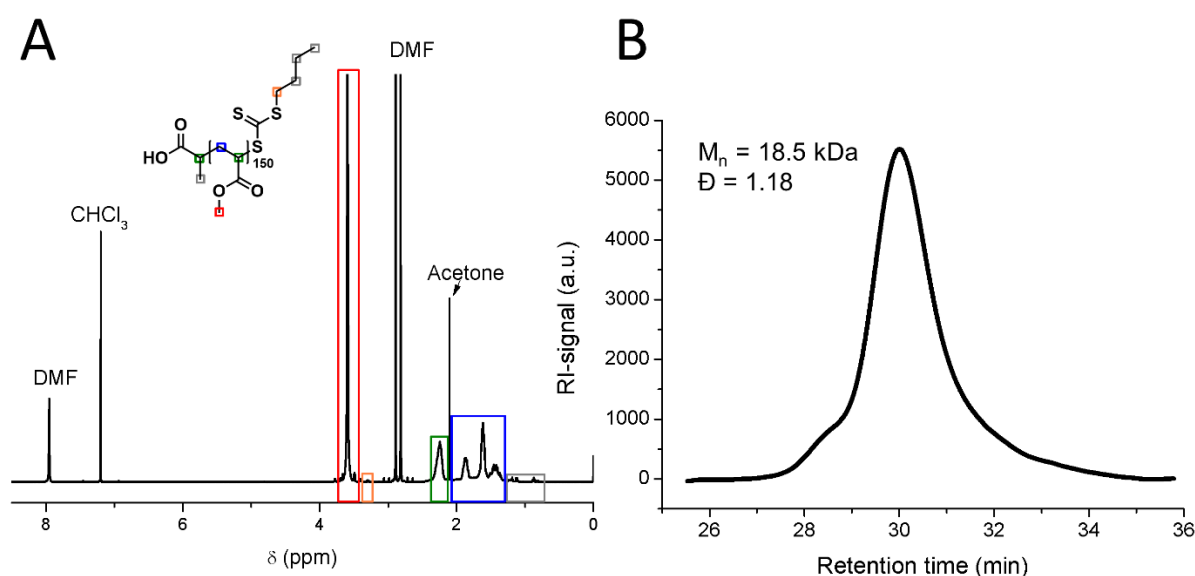
Experimental

Figure S1 A) ^{1}H NMR spectrum of PMA with the respective annotated proton annotations. B) Size-exclusion chromatogram (refractive index (RI)-trace) of PMA obtained with DMA with LiCl (50 mM) as eluent, number average molecular weight (Mn) and dispersity (Ð) are given relative to PMMA standards.

Calculation of conversion

The calculation of conversion was performed by utilizing the signals of the olefin groups of allylamine (signal at 6 ppm was utilized) and cyclohexenylethylamine (signals at 5.5 ppm), which integrate for 1 proton, as well as utilizing the signal of the ester present at 3.6 ppm, integrating for 3 protons of the methyl ester. The calculation was done as following:

$$\frac{Integral\ olefin}{(integral\ olefin + \frac{integral\ ester}{3})} = conversion$$

For benzyl amine, the CH2 protons of the benzyl group were utilized (sum of integrals of signals at 4.9 and 4.4 ppm) which integrate for 2 protons, and the signal of the ester present at 3.6 ppm, integrating for 3 protons of the methyl ester. The calculation was done as following:

$$\frac{\frac{integral\ benzylamide}{2}}{(\frac{integral\ benzylamide}{2} + \frac{integral\ ester}{3})} = conversion$$

For the equimolar mixture of primary amines, the relative amide content of the respective amines was determined in a similar manner, the total conversion could be determined by the sum of the individual conversions of each amine. Finally, for pyrrolidine and *N,N*-diethylamine, a different approach was utilized due to the lack of well resolved olefin protons. For this purpose, the CH signal from the ploymer backbone (2.8- 2.1 ppm) which remains constant during the modification reaction, was compared to the diminishing signal of the ester groups of the methyl acrylate groups (3.6 ppm). The calculation was done as following:

$$\frac{\frac{integral\ ester}{3}}{(integral\ CH\ backbone)} = conversion$$

Variation of equivalents of amine to ester

PMA (200 mg, 1 equivalent of ester groups, 2.3 mol), TBD (138 mg, 0.5 eq, 1.15 mol) and varying equivalents (0.5, 2, 4, 6 eq relative to ester groups) of allylamine were dissolved in an appropriate amount of ACN, so that the total volume of the mixture would be 10 mL. Next, the mixture was heated to 70°C and left to react, while 1 mL samples were taken at regular intervals. These samples were precipitated in 10 mL cold diethyl ether in a 15 mL centrifuge tube. The resulting opaque mixture was centrifuged at 7500 revolutions per minute (rpm), after which the solvent was decanted and the kinetic sample was dried overnight in a vacuum oven at 50°C. These samples were then subjected to ^{1}H NMR and SEC analysis. In ^{1}H NMR the conversion was determined by integrating the same interval corresponding to the methyl ester signal and the formed amide signal, dividing those integrals by the corresponding protons they represent and taking the ratio of those values.

Variation of equivalents of TBD to ester and temperature

PMA (200 mg, 1 equivalent of ester groups, 2.3 mol), TBD (276 mg, 1 eq, 2.3 mol) and (6 eq relative to ester groups) allylamine were dissolved in an appropriate amount of ACN, so that the total volume of the mixture would be 10 mL. Next, the mixture was heated to 70°C and left to react, while 1 mL samples were taken at regular intervals. These samples were precipitated in 10 mL cold diethyl ether in a 15 mL centrifuge tube. The resulting opaque mixture was centrifuged at 7500 revolutions per minute (rpm), after which the solvent was decanted and the kinetic sample was dried overnight in a vacuum oven at 50°C. These samples were then subjected to ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra the conversion was determined by integrating the same interval corresponding to the methyl ester signal and the formed amide signal, dividing those integrals by the corresponding protons they represent and taking the ratio of those values.

Variation of total concentration

PMA (200 mg, 1 equivalent of ester groups, 2.3 mol), TBD (138 mg, 0.5 eq, 2.3 mol) and (6 eq relative to ester groups) allylamine were dissolved in an appropriate amount of ACN, so that the total volume of the mixture would be 5 mL. Next, the mixture was heated to 70°C and left to react, while 1 mL samples were taken at regular intervals. These samples were precipitated in 10 mL cold diethyl ether in a 15 mL centrifuge tube. The resulting opaque mixture was centrifuged at 7500 revolutions per minute (rpm), after which the solvent was decanted and the kinetic sample was dried overnight in a vacuum oven at 50°C. These samples were then subjected to ^{1}H NMR spectroscopy. The conversion was determined by integrating the same interval corresponding to the methyl ester signal and the formed amide signal in the ^{1}H NMR spectra, dividing those integrals by the corresponding protons they represent and taking the ratio of those values.
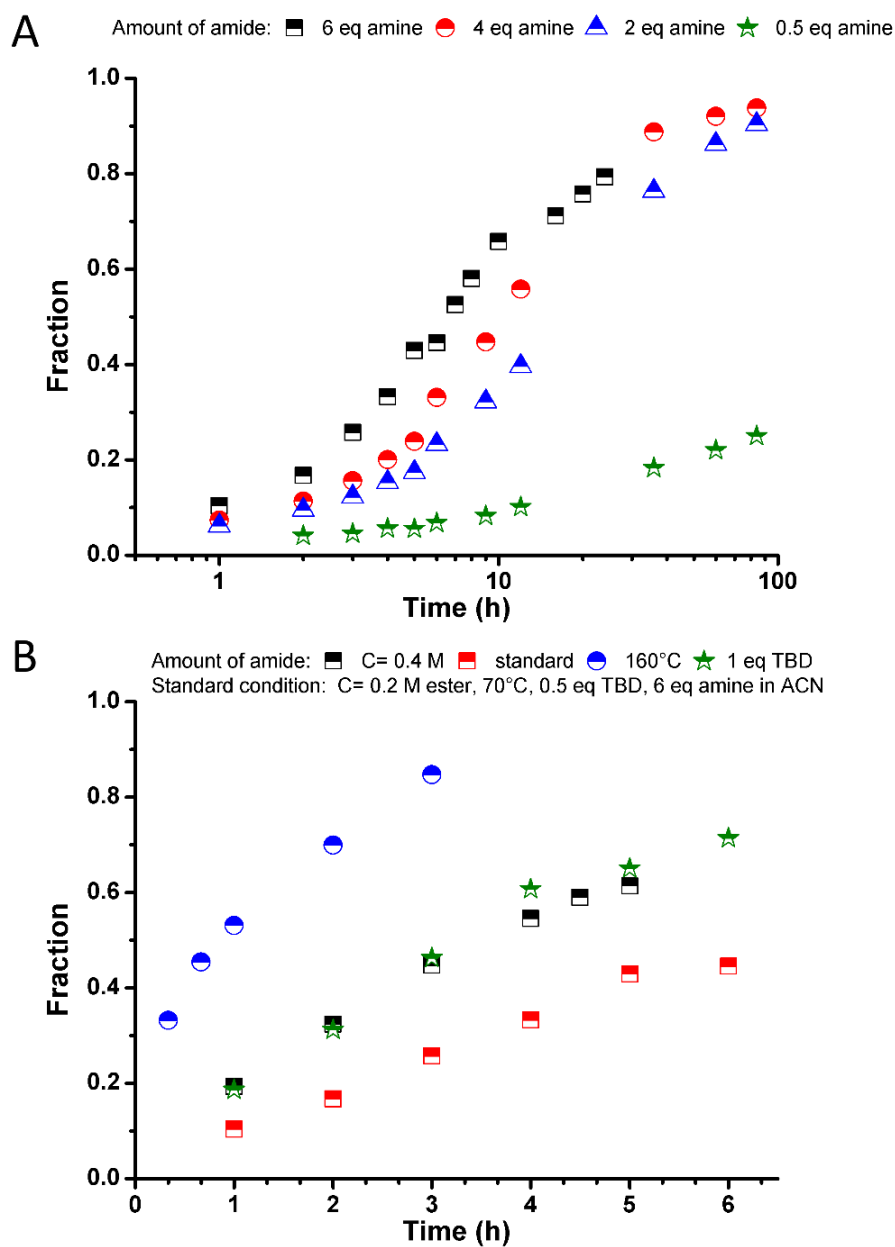
Figure S2: A) Kinetic investigation on different parameters of the amidation reaction with variation of equivalents of amine relative to ester with a logarithmic X-axis for graphical purposes and B) variation of ester concentration, temperature and equivalents of catalyst versus standard condition, only the specific variation versus the standard condition is listed in the legend.

Table 1: pKa values of the utilized amines for the kinetic investigation of the TBD-catalyzed amidation.

Amine	pKa of conjugate acid
Benzylamine[1]	9.33
Allylamine[2]	9.7
Cyclohexenylethyl amine (propylamine)[1]	Not reported (10.71)
N,N-diethylamine[1]	10.98
Pyrrolidine[1]	11.3

<u>Additional characterization data:</u>
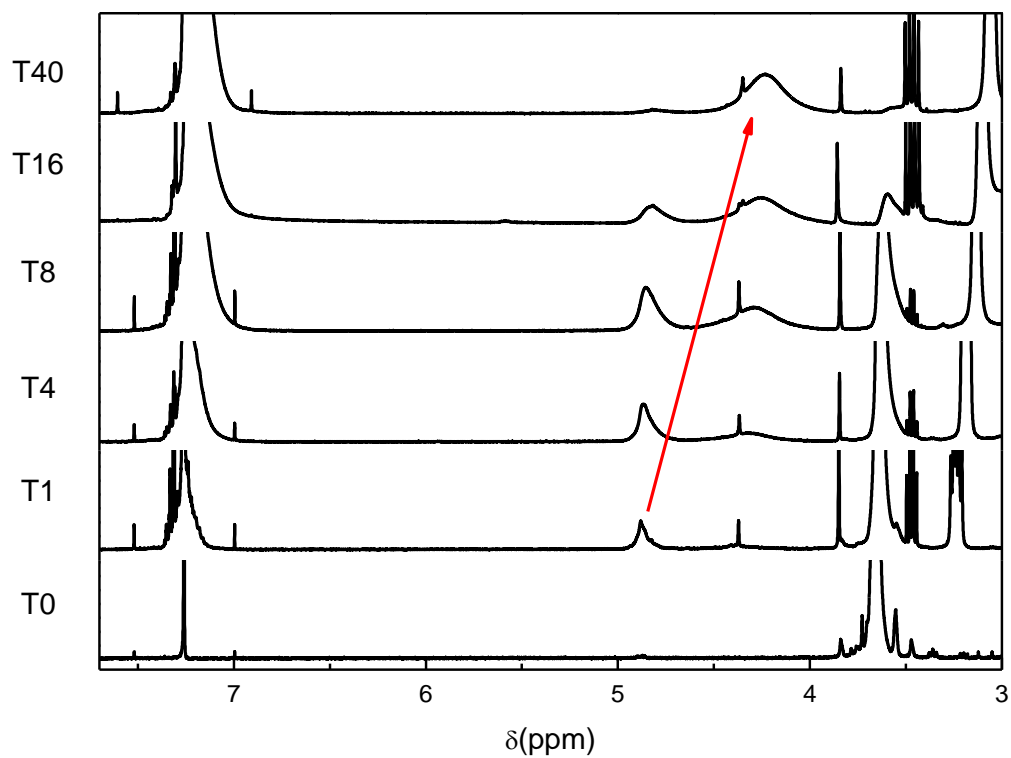
Figure S3: Stacked ¹H NMR spectra of different time points in the amidation of PMA with benzylamine. The arrow indicates a change in relative intensity between the two peaks.
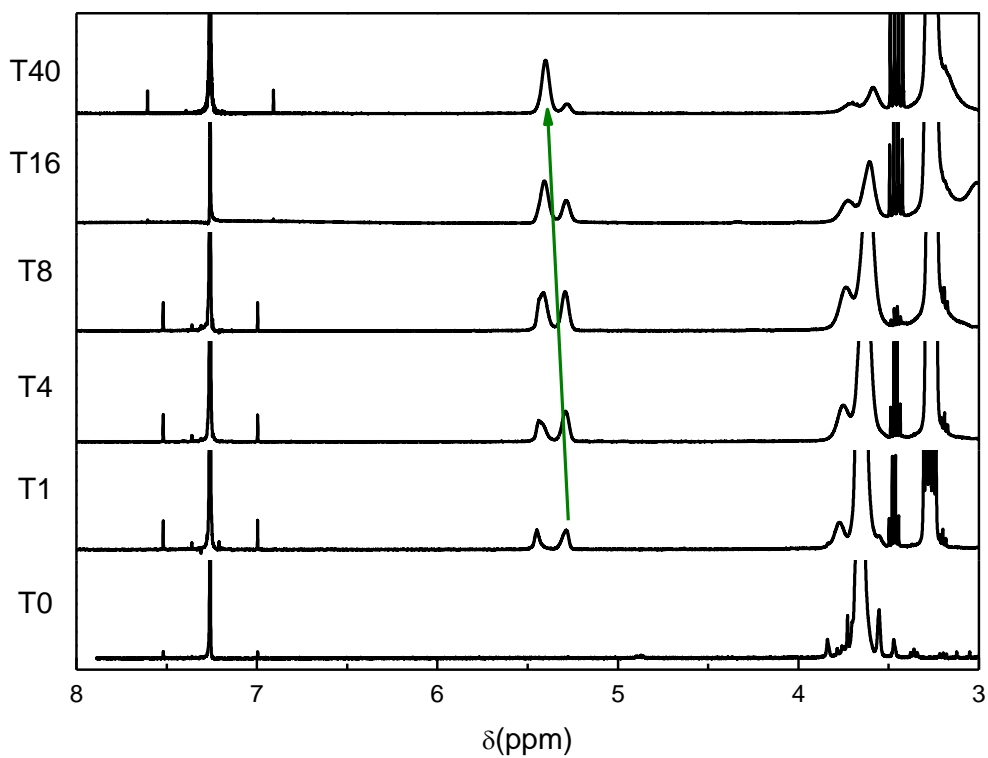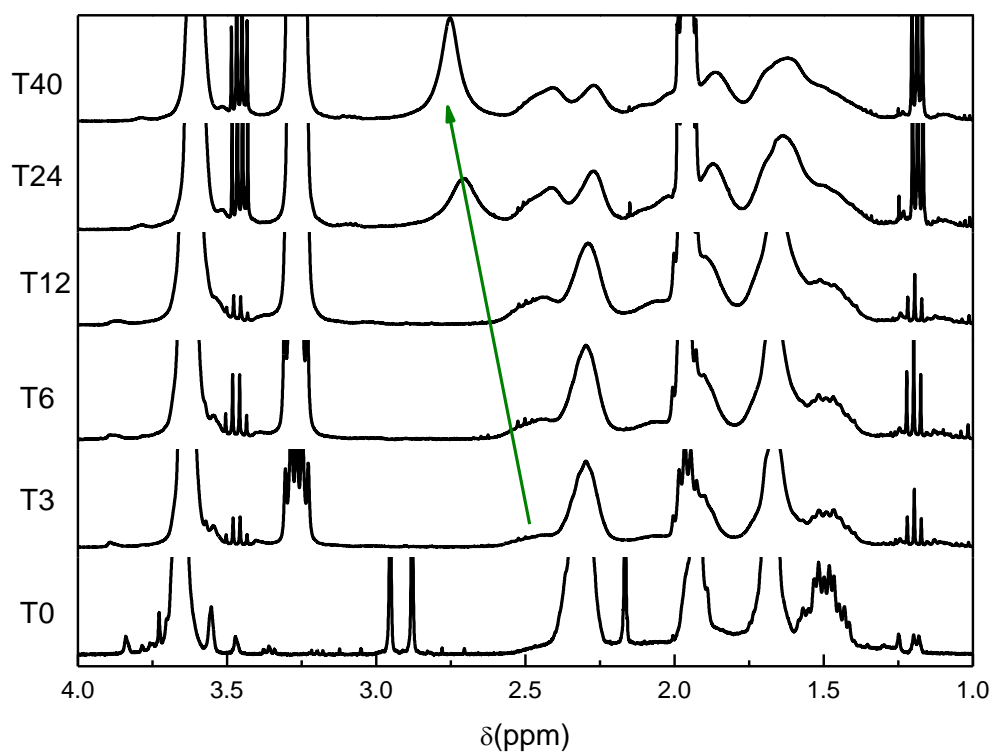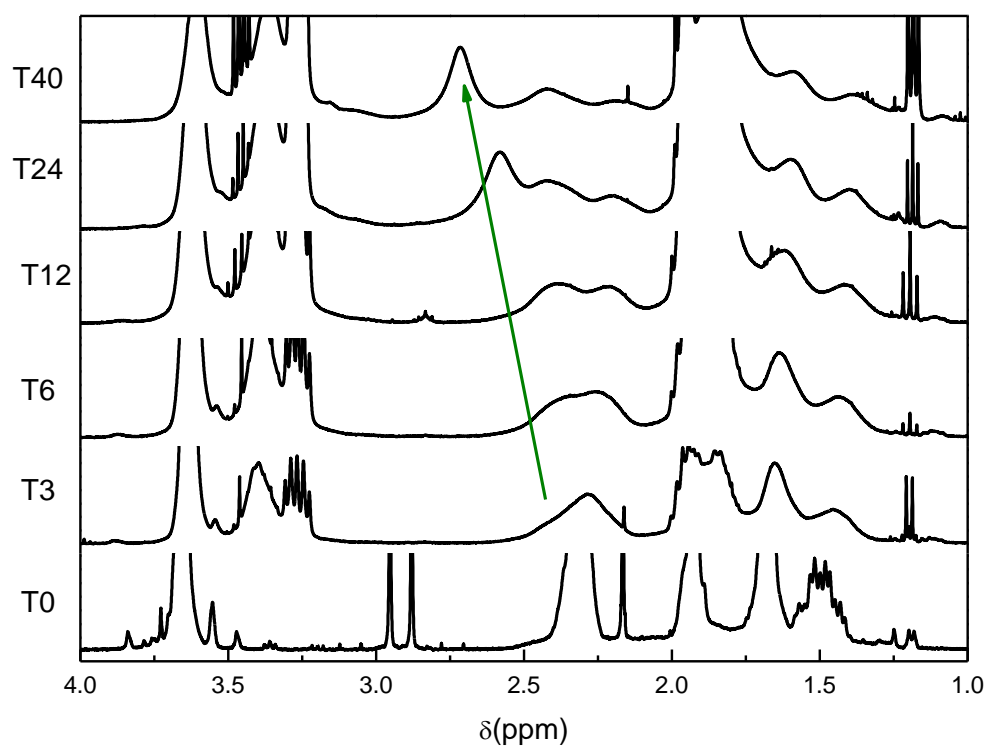

Figure S4: Stacked ¹H NMR spectra of different time points in the amidation of PMA with cyclohexenylethylamine. The arrow indicates change in relative intensity between the two peaks.
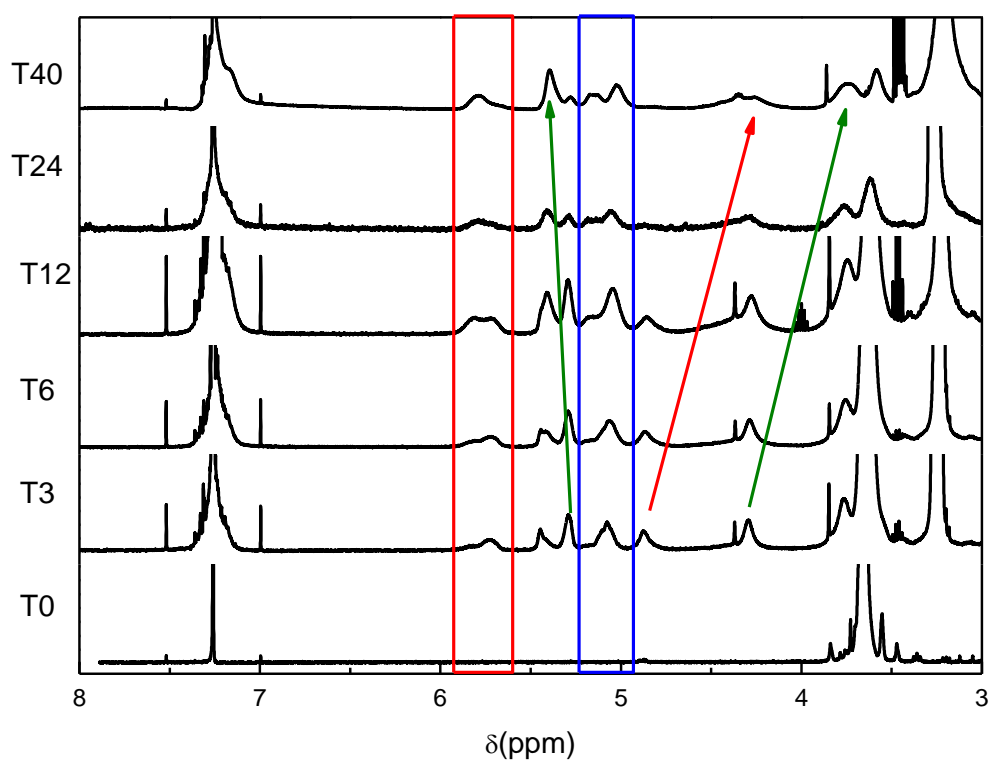
Figure S5: Stacked ¹H NMR spectra of different time points in the amidation of PMA with an equimolar mixture of allylamine, benzylamine and cyclohexenylethylamine. The arrow indicates change in relative intensity between the two peaks and frames indicate a change in peak shape.

Figure S6: Stacked ¹H NMR spectra of different time points in the amidation of PMA with N,N-diethylamine. The arrow indicates change in relative intensity between the two peaks.

Figure S7: Stacked ^{1}H NMR spectra of different time points in the amidation of PMA with pyrrolidine. The arrow indicates change in relative intensity between the two peaks.
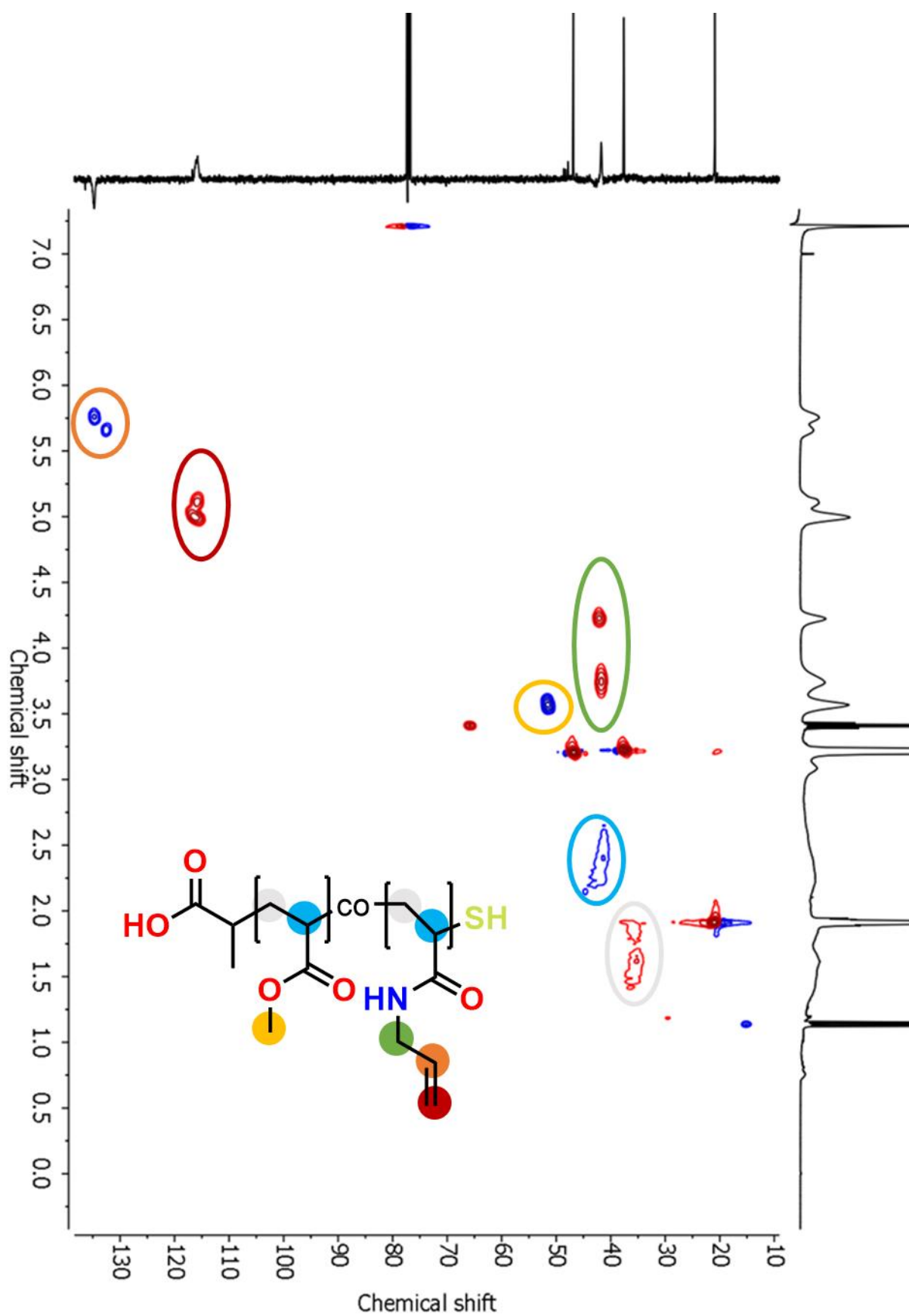
Figure S8: HSQC spectrum of P(MA-co-AllylAm) after 16 hours of reaction time.
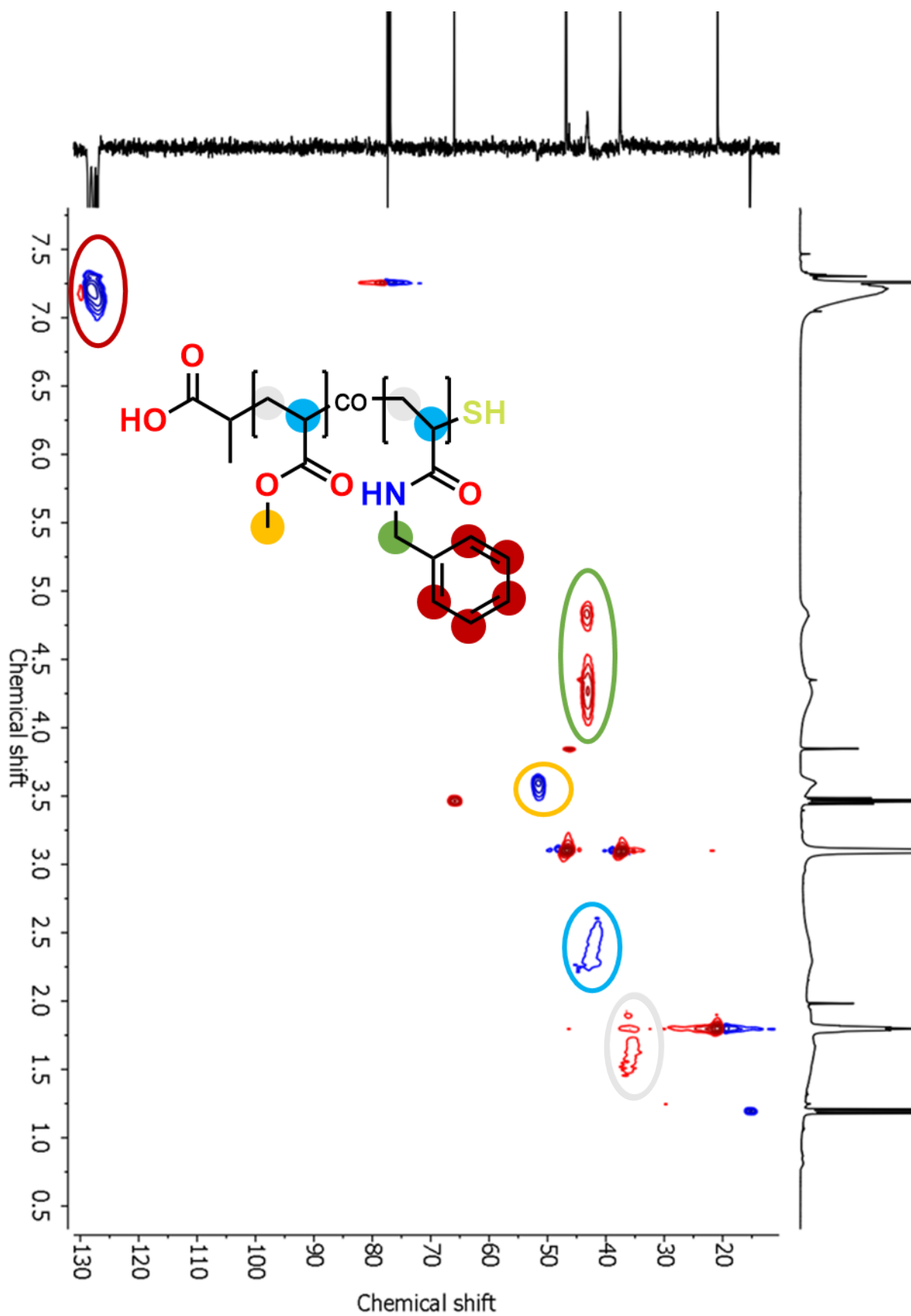
Figure S9: HSQC spectrum of P(MA-co-BzAm) after 16 hours of reaction time.
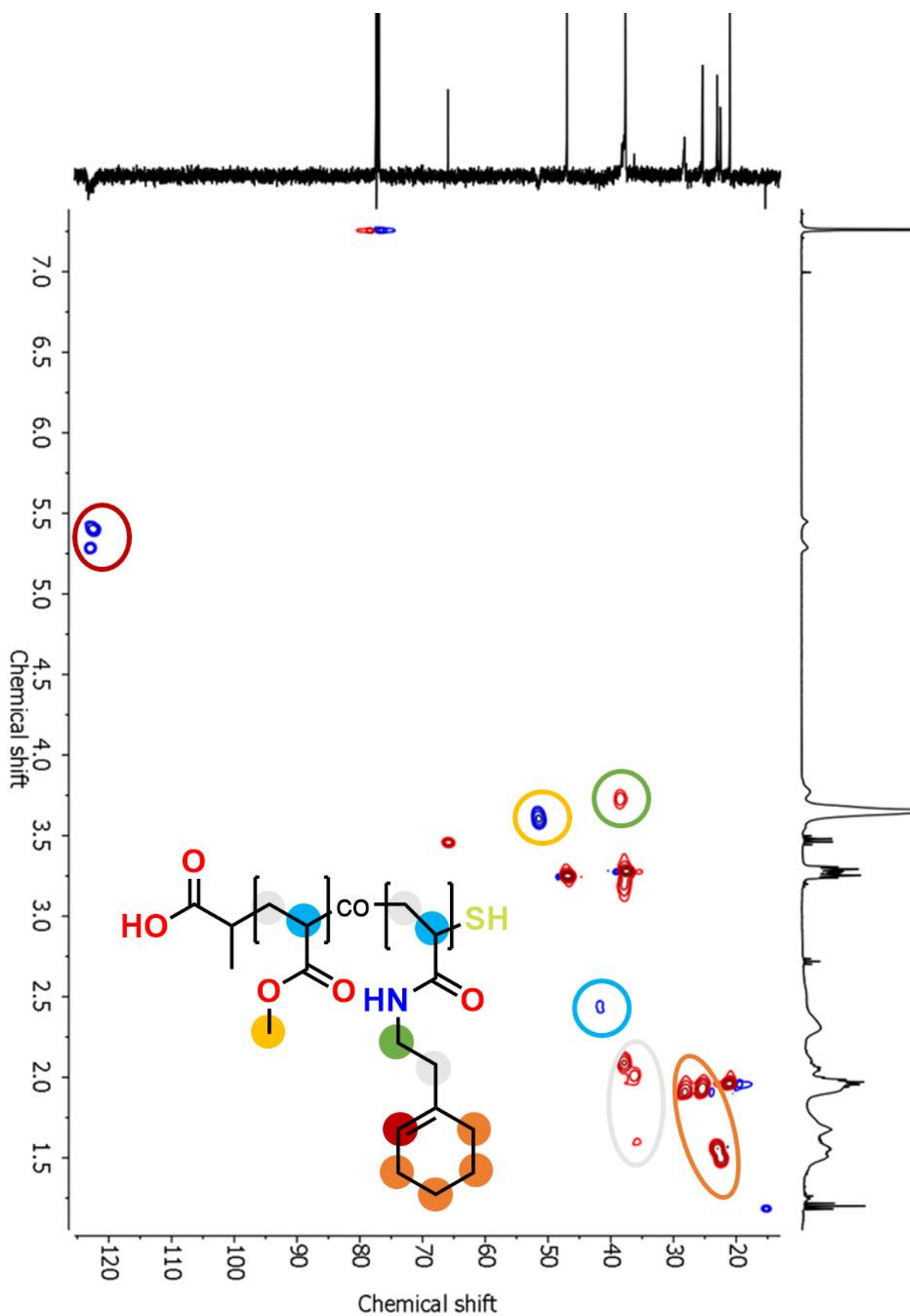
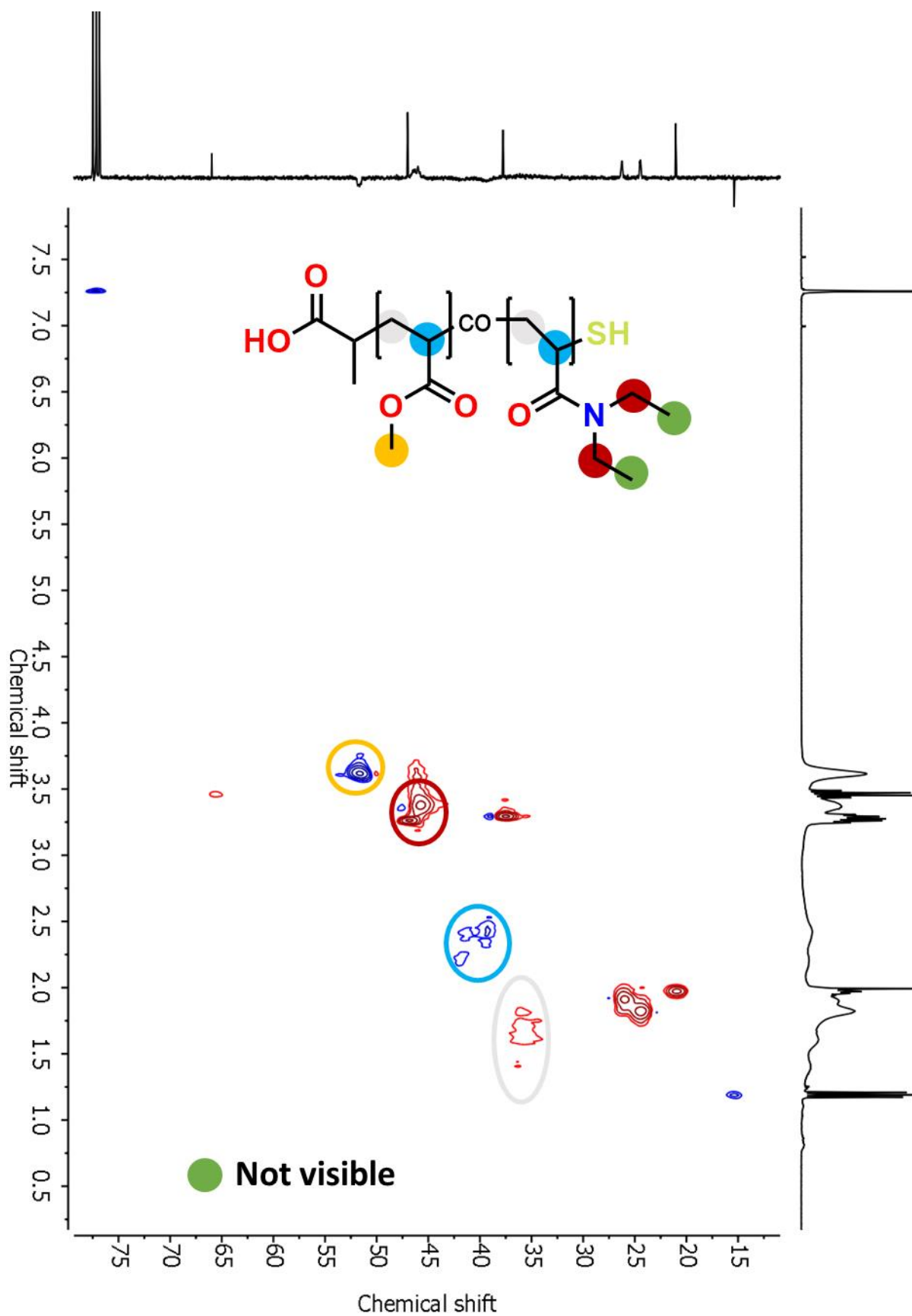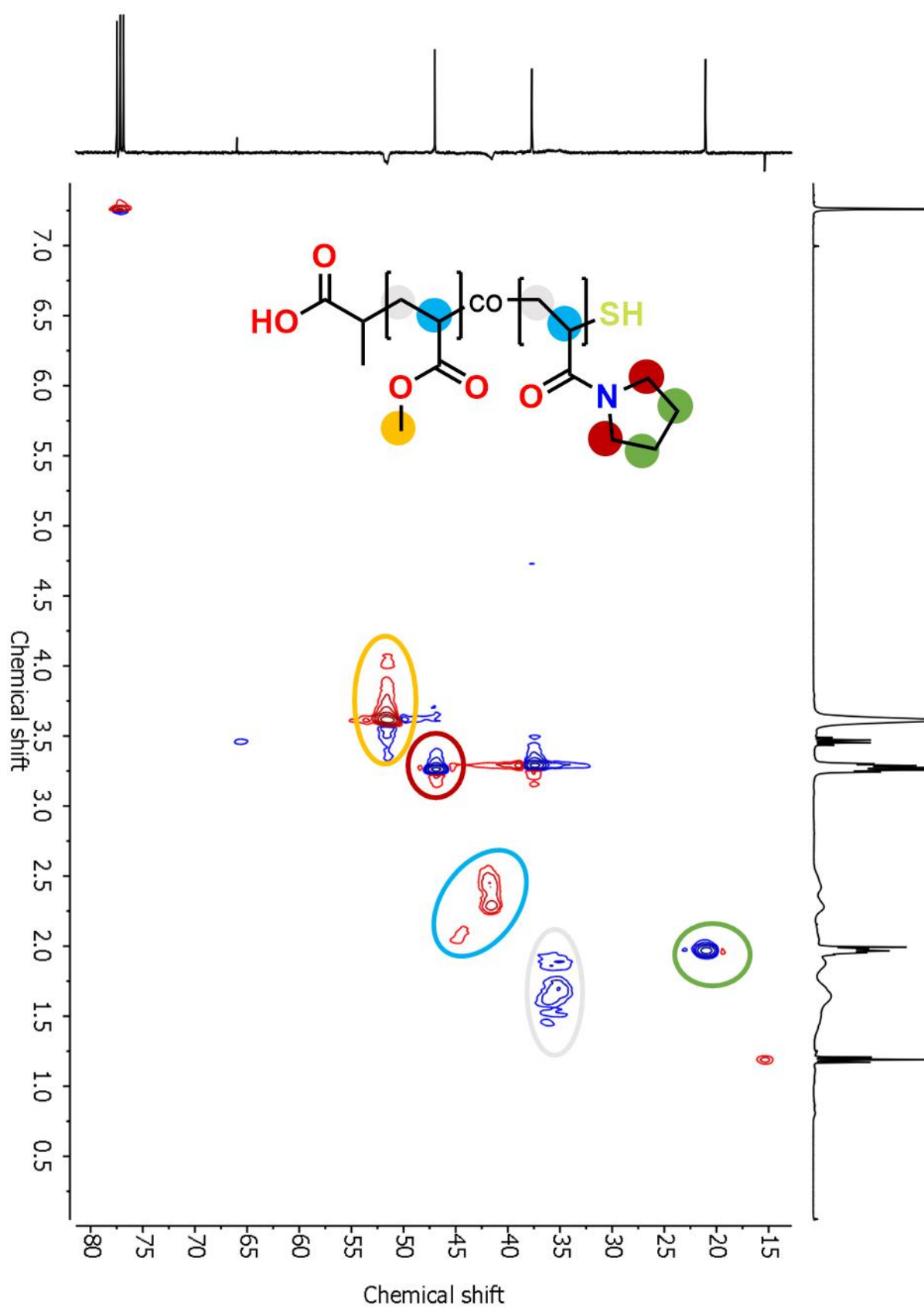*Figure S10: HSQC spectrum of P(MA-co-cyclohexenylethylAm) after 16 hours of reaction time.*

Figure S11: HSQC spectrum of P(MA-co-N,N-diethylAm) after 16 hours of reaction time.

Figure S12: HSQC spectrum of P(MA-co-pyrrolidineAm) after 16 hours of reaction time.
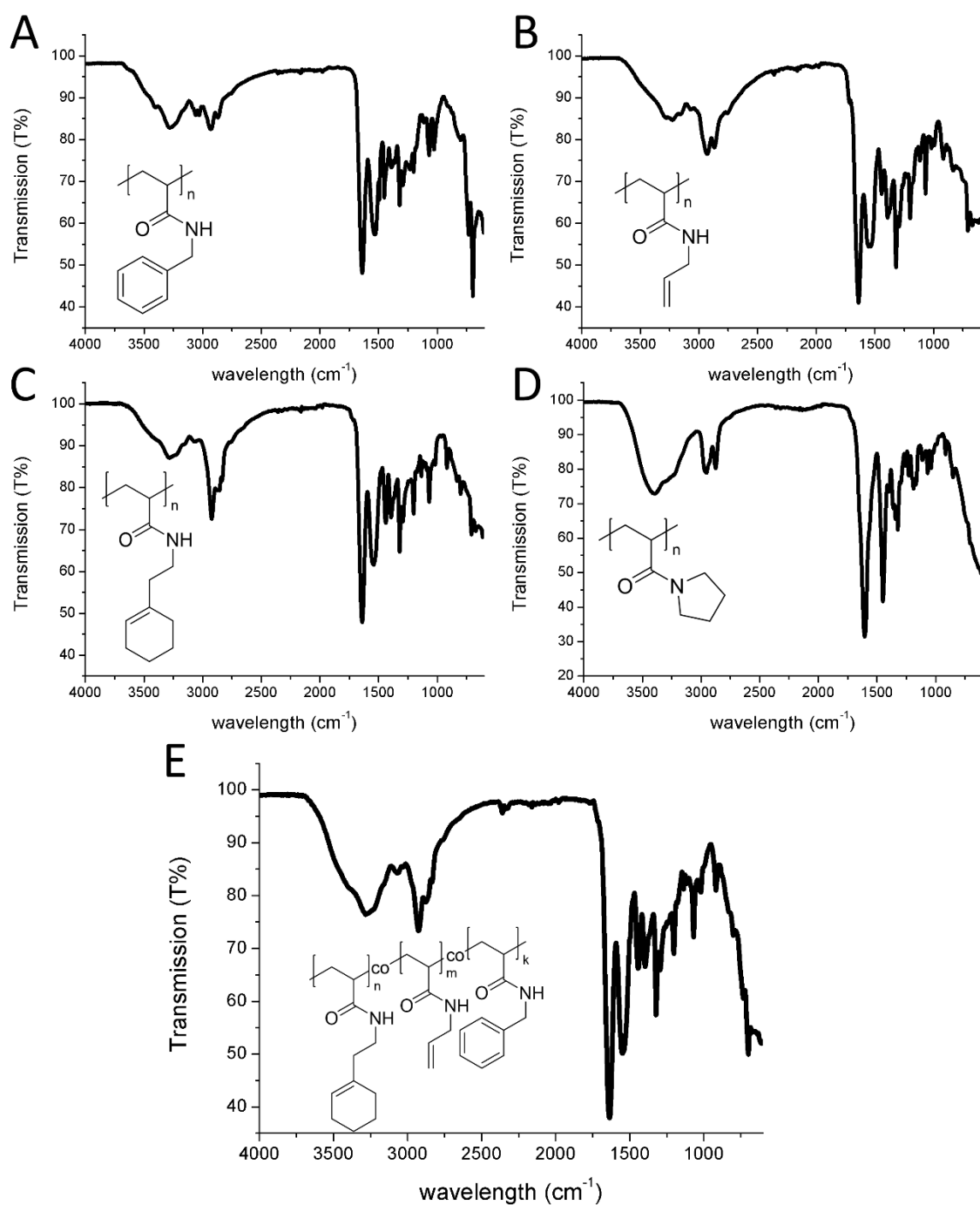
Figure S13: FT-IR-spectra of (quasi-)completely modified PMA with A) benzylamine, B) allylamine, C) cyclohexenylethylamine, D) pyrrolidine and E) the equimolar mixture of the aforementioned primary amines.
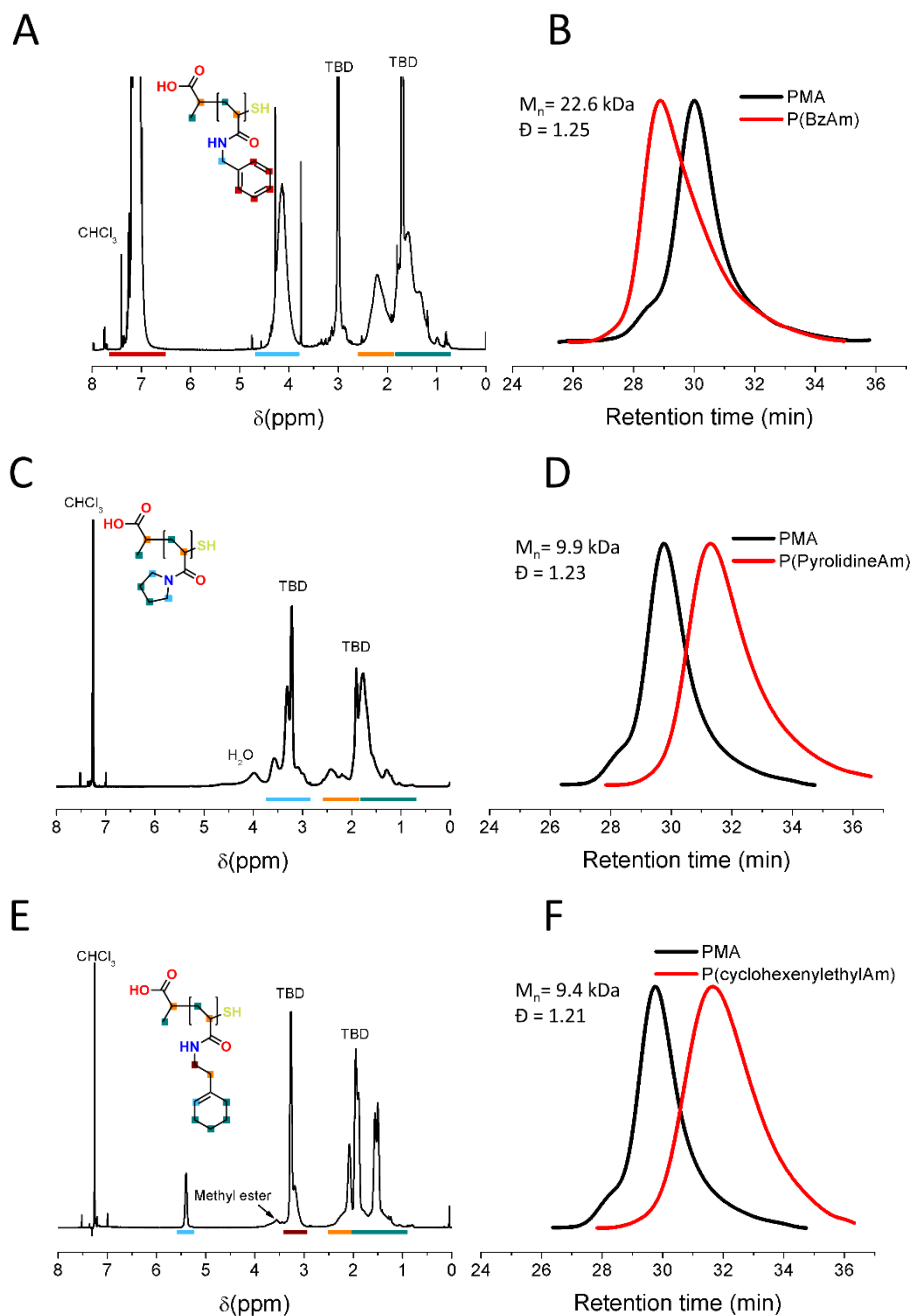
Figure S14: A) Annotated ¹H NMR spectrum of P(BzAm)), B) P(pyrrolidineAm) and C) P(cyclohexenylethylAm). B) The corresponding RI-trace in SEC, in red the final polymer and in black the starting material for P(BzAm) (top), D) P(pyrrolidineAm) and F) P(cyclohexenylethylAm). Mn and Đ are given for the resulting polymers.
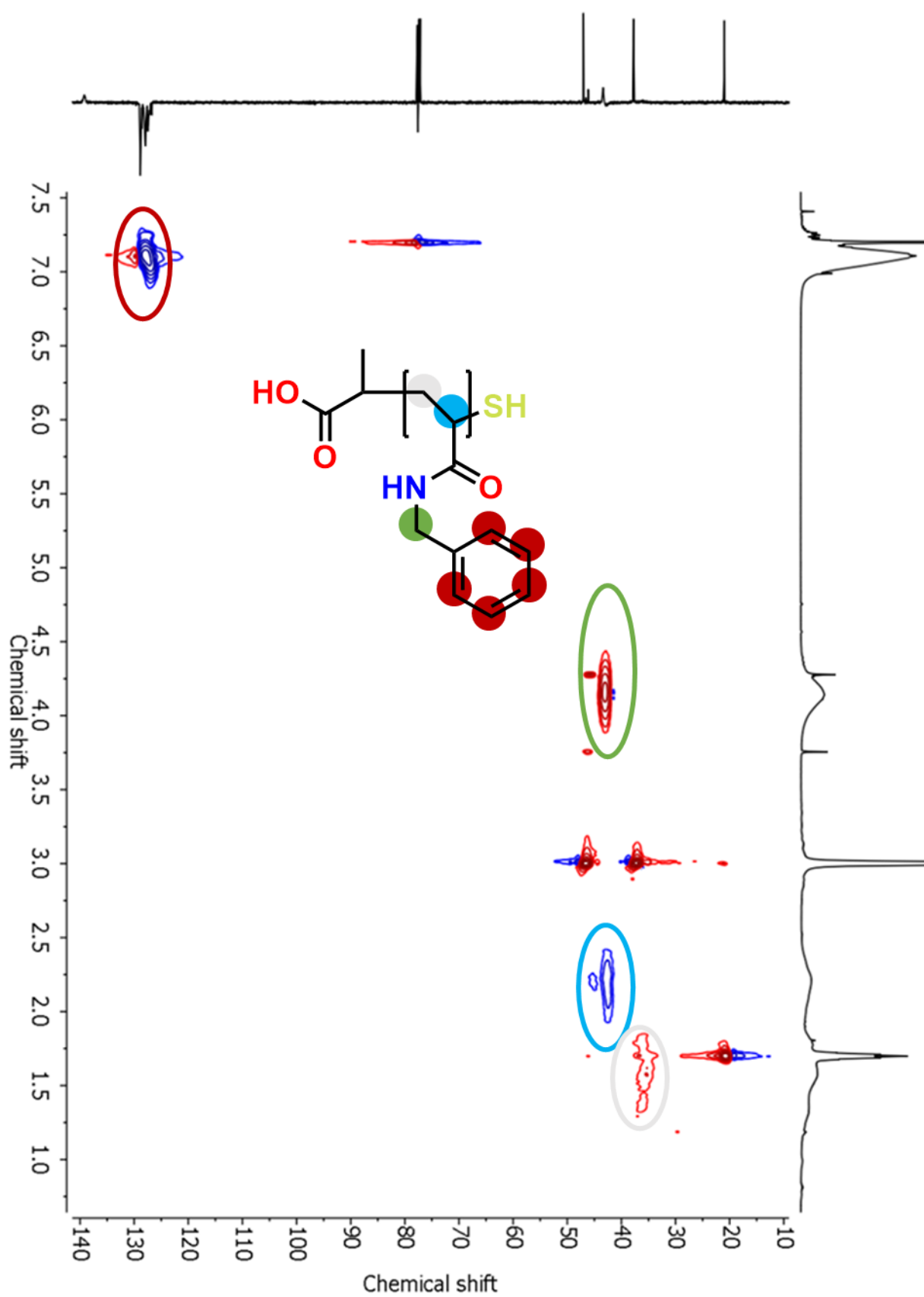
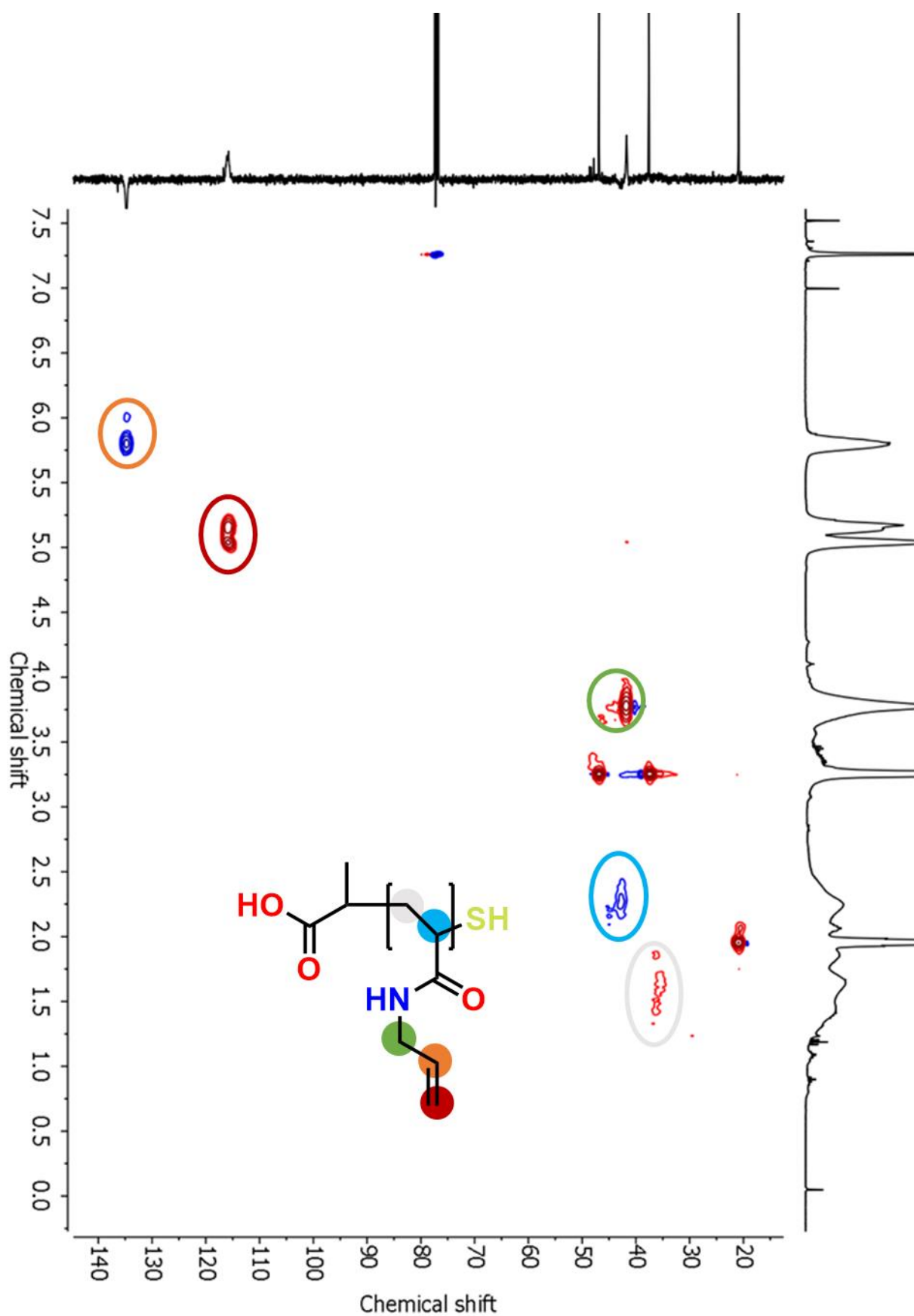*Figure S15: HSQC spectrum of P(BzAm) after full conversion.*

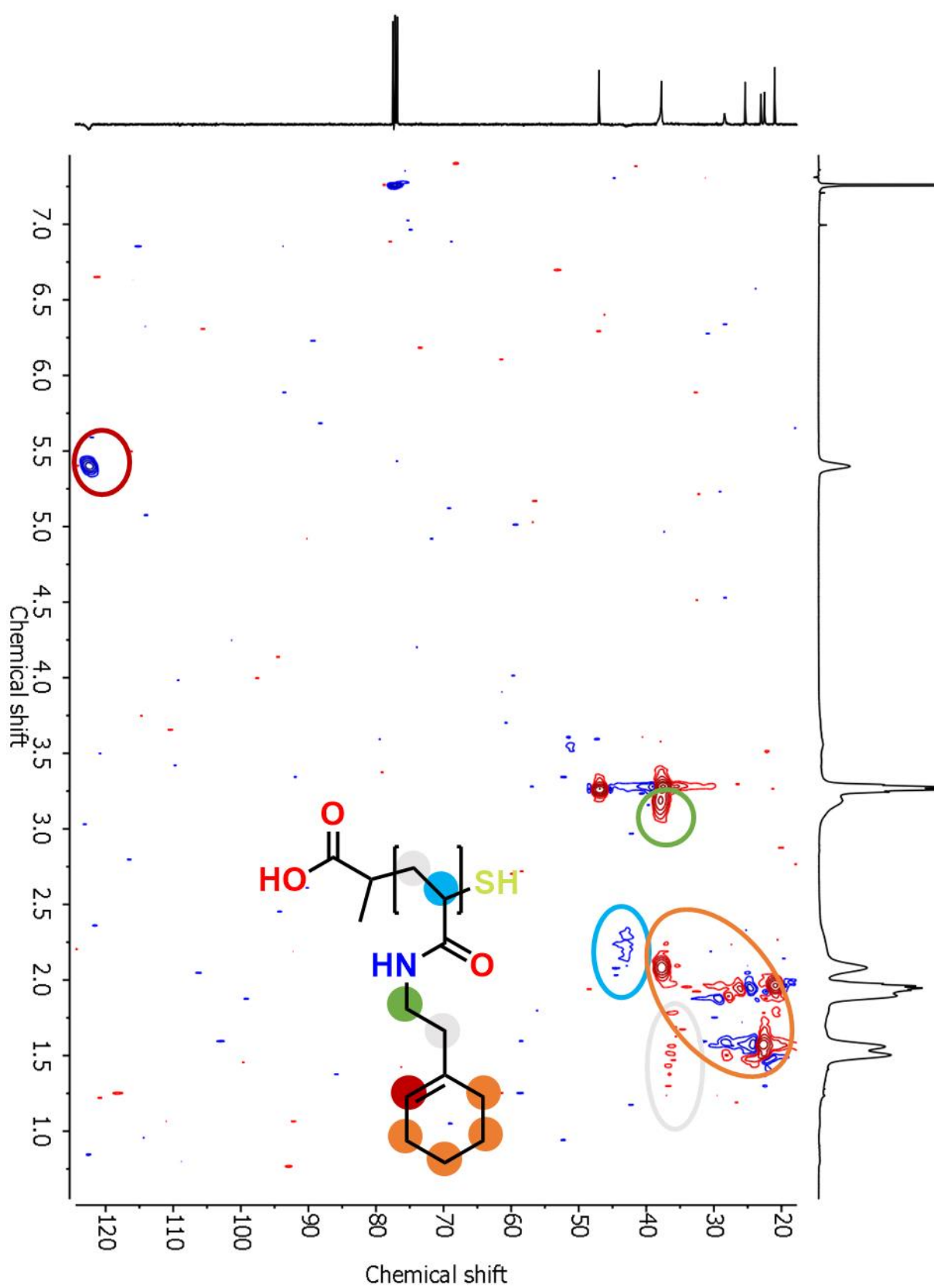*Figure S16: HSQC spectrum of P(AllylAm) after full conversion.*

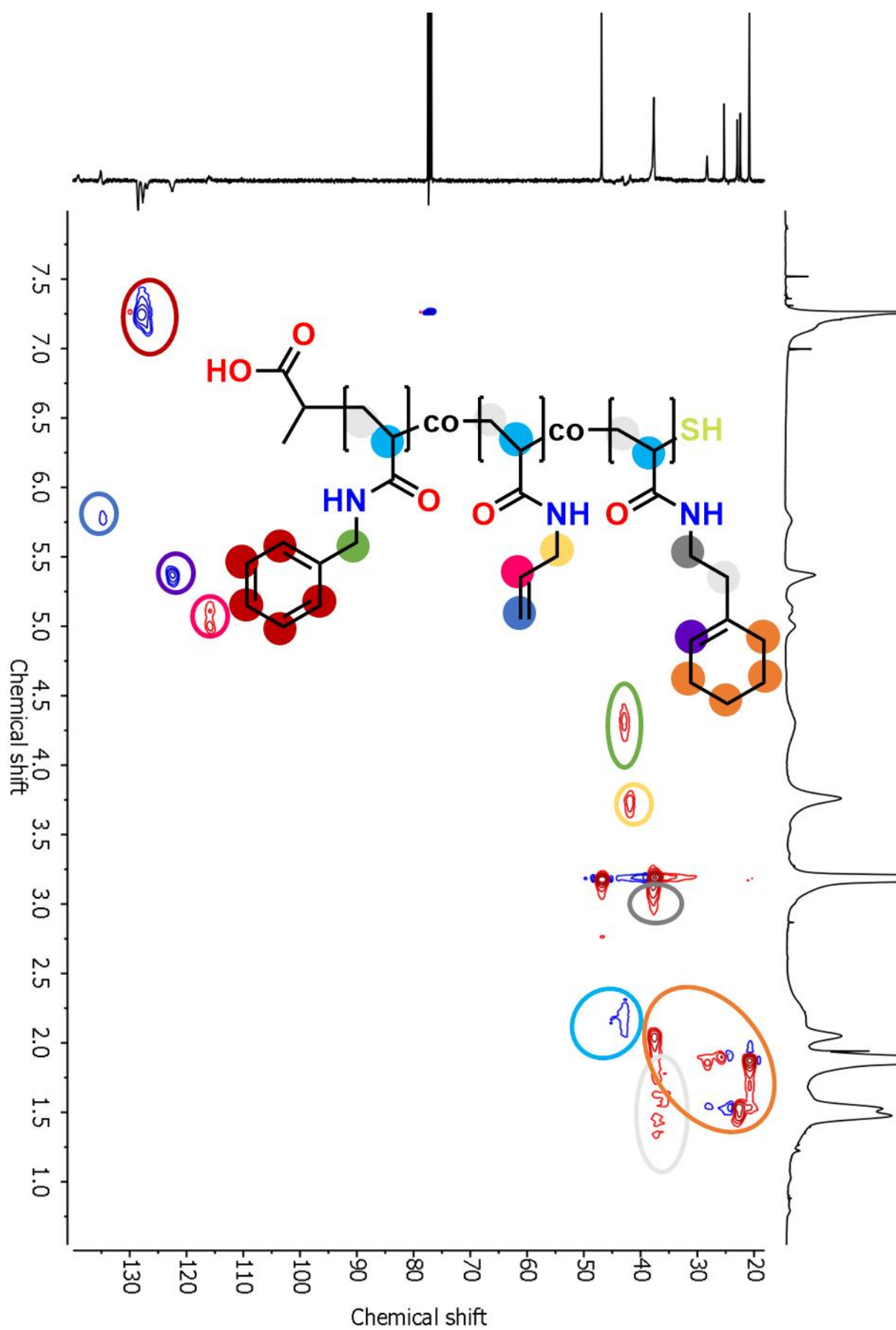Figure S17 HSQC spectrum of P(cyclohexenylethylAm) the final sample.

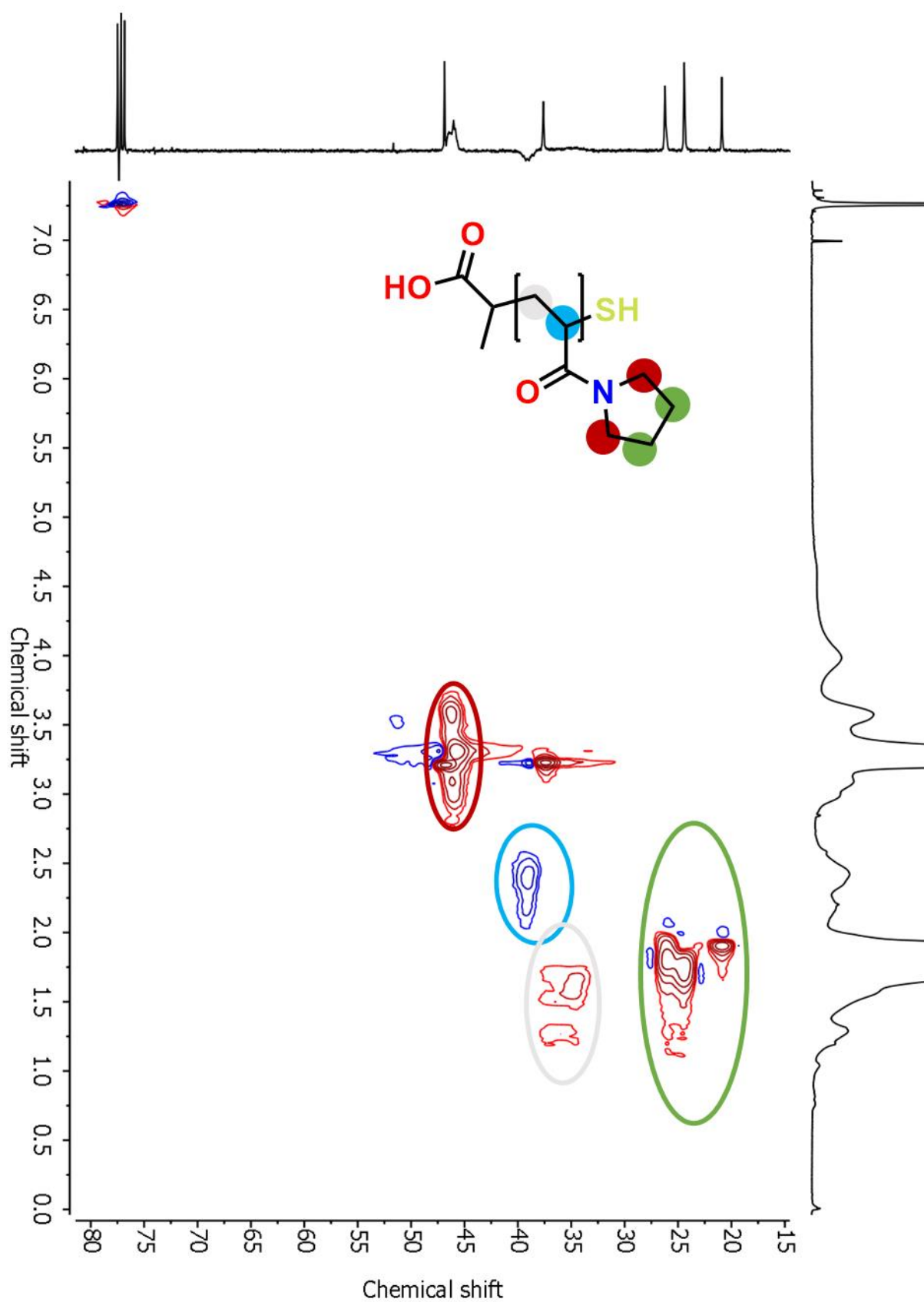*Figure S18: HSQC spectrum of P(BzAm-co-AllylAm-co-cyclohexenylethylAm) after full conversion.*

Figure S19: HSQC spectrum of P(pyrrolidineAm), the final sample.

References

(1)   Hall, H. K. Correlation of the Base Strengths of Amines. *J. Am. Chem. Soc.* , **1957**, *79,* 5441–5444

(2)   Braude, E. A. & Nachod, F. C. Determination of organic structures by physical methods. **Academic Press, New York, 1955**)