

Supplementary Materials: Synthesis and Mechanochemical Activity of Peptide-Based Cu(I) Bis(*N*-Heterocyclic Carbene) Complexes

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1. Materials

The following chemicals were purchased from Sigma-Aldrich: 1-methylimidazole (99%), copper(I) oxide (97%), lithium hydroxide monohydrate, 3-bromopropan-1-amine hydrobromide (98%), triethylamine (Et₃N) (99%), trifluoroacetic acid (99%), thionyl chloride (99%), *N,N'*-dicyclohexylcarbodiimide (DCC) (99%), pentafluorophenol (99%), *N,N*-diisopropylethylamine (DIPEA) (99%), and sodium azide (99.5%). 6-Bromohexanoic acid (98%) and 11-bromoundecanoic acid (99%) were purchased from Tokyo Chemical Industry Co., Ltd., and di-*tert*-butyl dicarbonate (99%) and *N'*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC-HCl) (98%) were obtained from Carbolution Chemicals GmbH. Sodium chloride, sodium sulfate, glycine (>99%) and L-valine (>99%) were purchased from Carl Roth GmbH & Co. KG. The following chemicals were purchased from Fluka: methanesulfonic acid (98%) and benzyl bromide (98%). Hydrochloric acid (37%) and sodium bicarbonate were obtained from Grüssing GmbH, and magnesium sulfate (99%) was purchased from Alfa Aesar. High performance liquid chromatography (HPLC) grade methanol was obtained from VWR, and HPLC grade dimethylformamide (DMF) was obtained from VWR BDH Prolabo. Ce(SO₄)·4 H₂O and (NH₄)₆Mo₇O₂₄·4 H₂O were obtained from VEB. Lithium(I) bis(trifluoromethanesulfonyl)imide (LiTf₂N) was purchased from J&K Chemicals Ltd. Deuterated chloroform (CDCl₃), deuterated dimethyl sulfoxide (DMSO-d₆) and deuterated tetrahydrofuran (THF-d₈) were purchased from Chemotrade GmbH.

2. Characterization of 11-bromoundecanoic acid methyl ester (1)

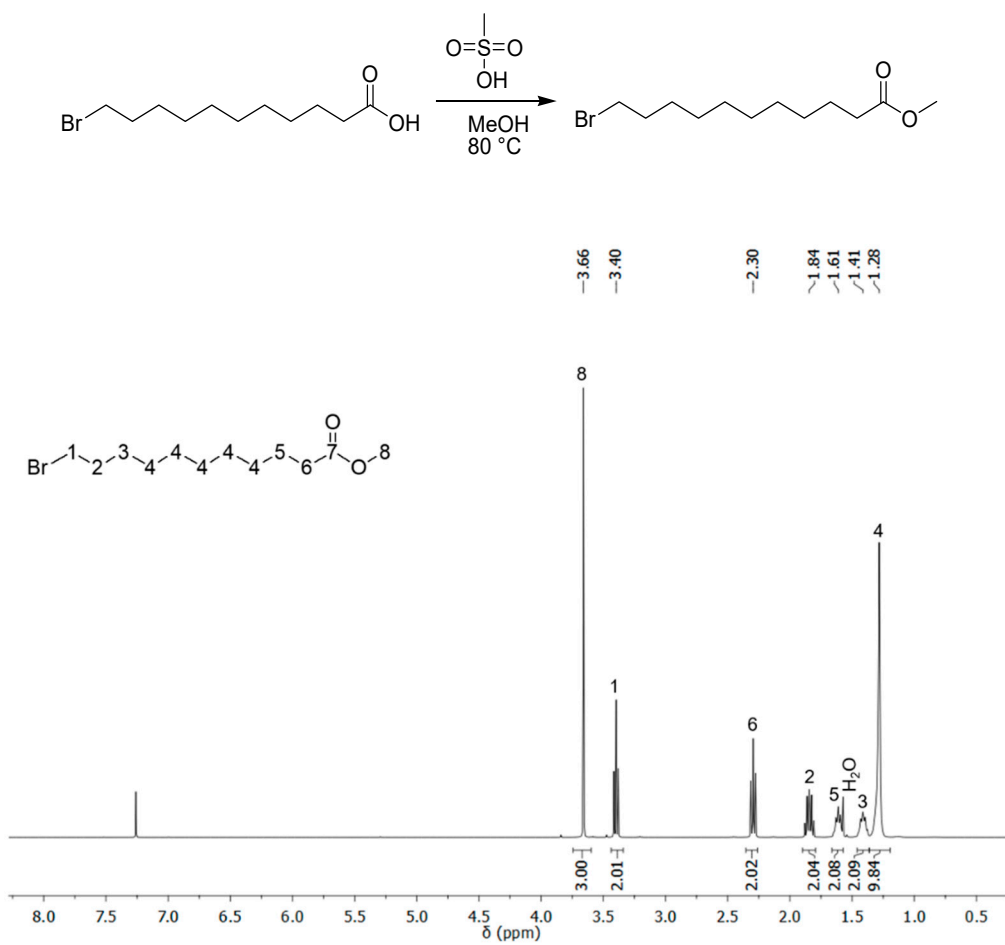


Figure S1. ¹H NMR spectrum of 11-bromoundecanoic acid methyl ester (1).

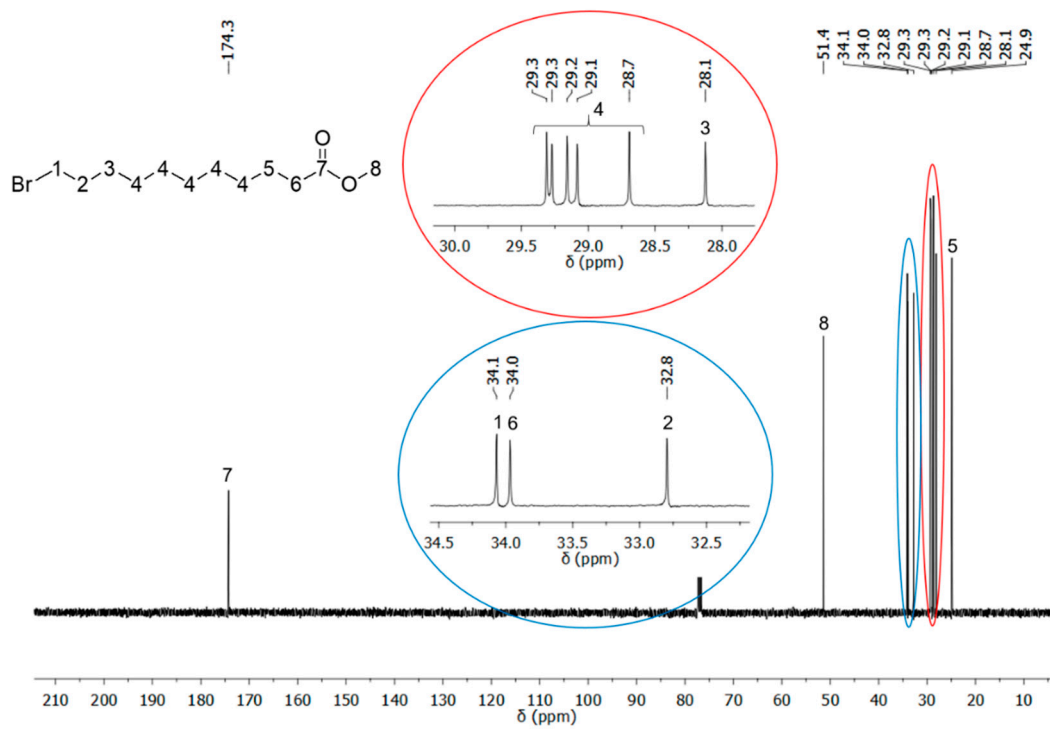


Figure S2. ^{13}C NMR spectrum of 11-bromoundecanoic acid methyl ester (1).

3. Characterization of 3-(11-methoxy-11-oxoundecyl)-1-methyl-1*H*-imidazolium bromide (2)

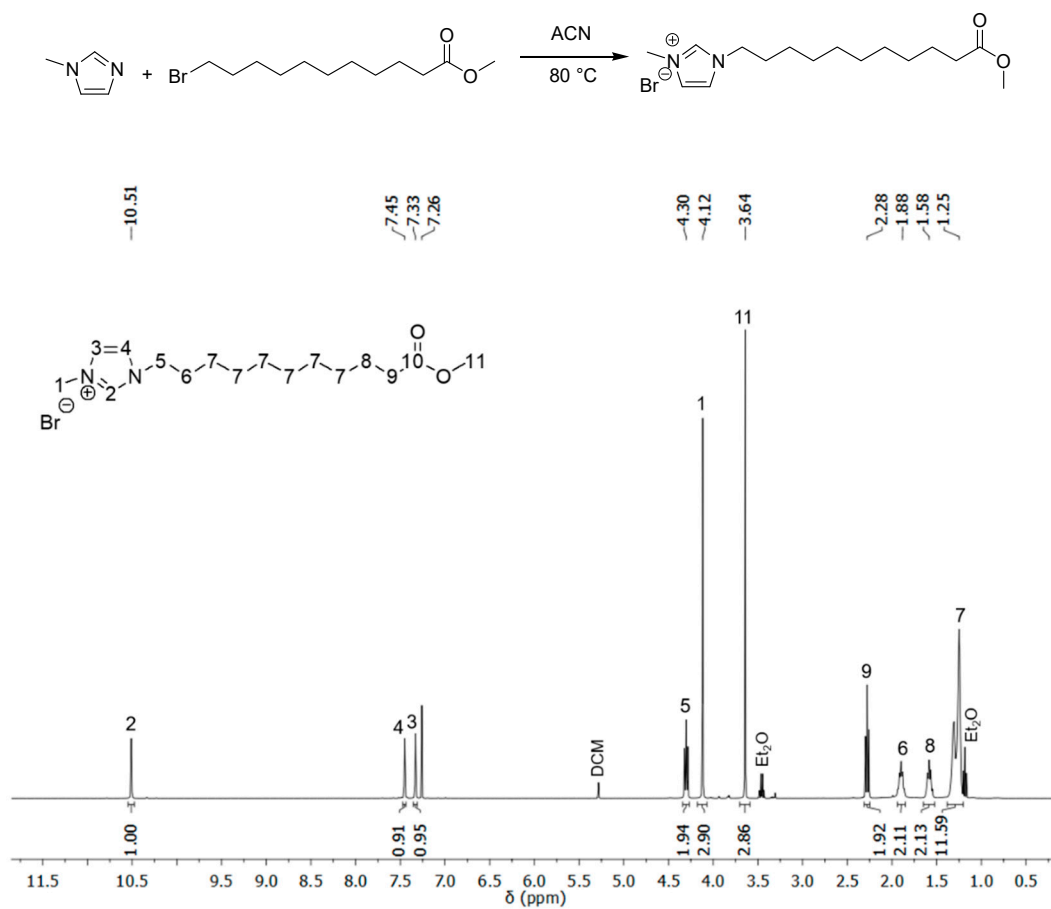


Figure S3. ¹H NMR spectrum of 3-(11-methoxy-11-oxoundecyl)-1-methyl-1*H*-imidazolium bromide (2).



Figure S4. ^{13}C NMR spectrum of 3-(11-methoxy-11-oxoundecyl)-1-methyl-1H-imidazolium bromide (2).

4. Characterization of $[\text{Cu}(\text{C}_{10}\text{COOMe-NHC})_2]\text{Br}$ (3) [1]

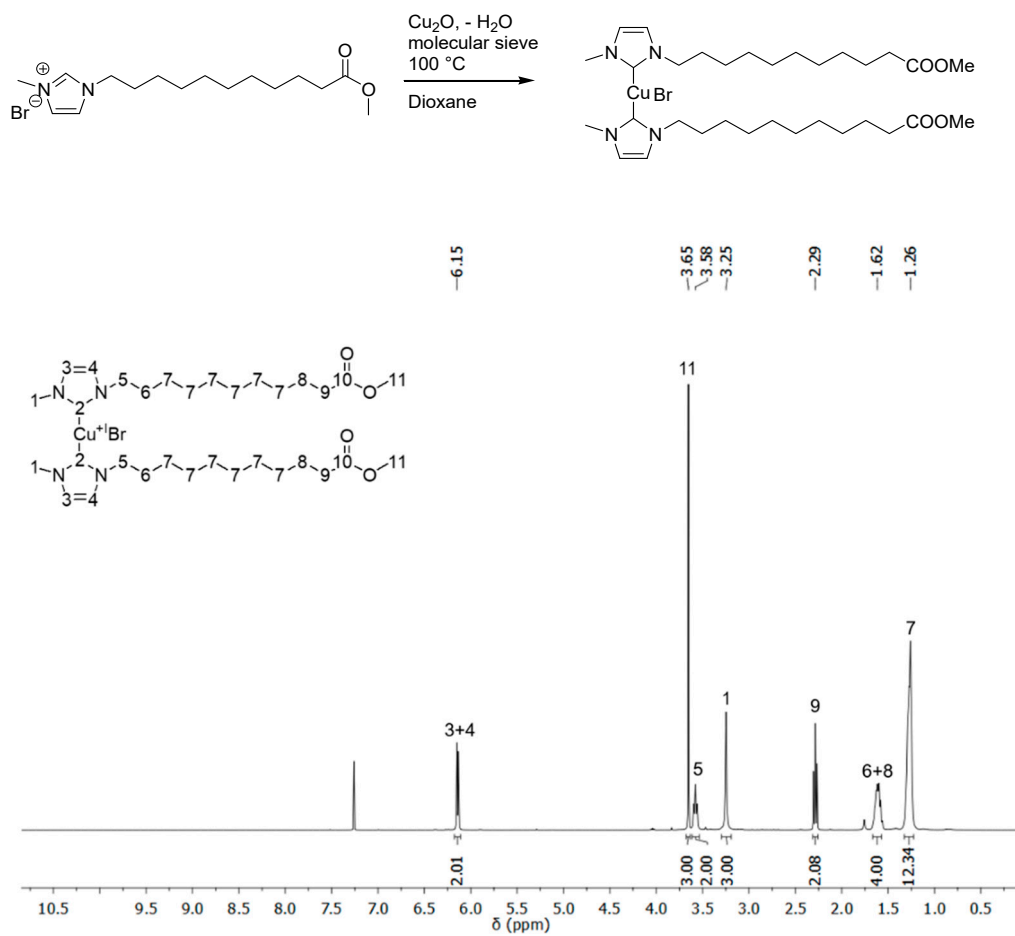


Figure S5. ^1H NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOMe-NHC})_2]\text{Br}$ (3).

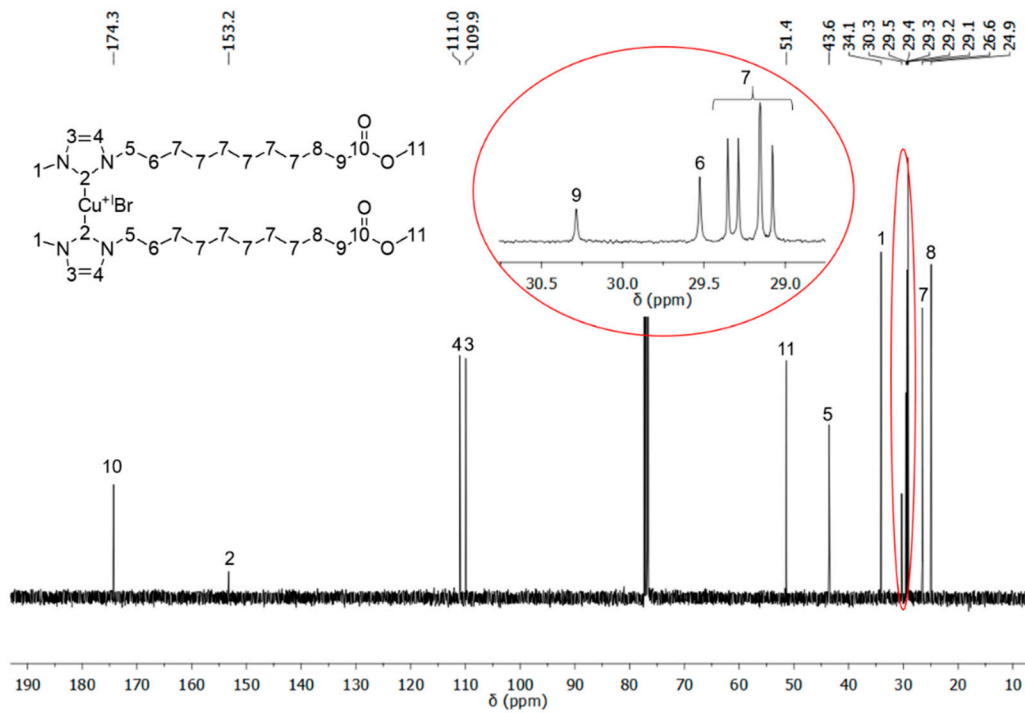


Figure S6. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOMe-NHC})_2]\text{Br}$ (3).

5. Characterization of $[\text{Cu}(\text{C}_{10}\text{COOH-NHC})_2]\text{Br}$ (4) [2]

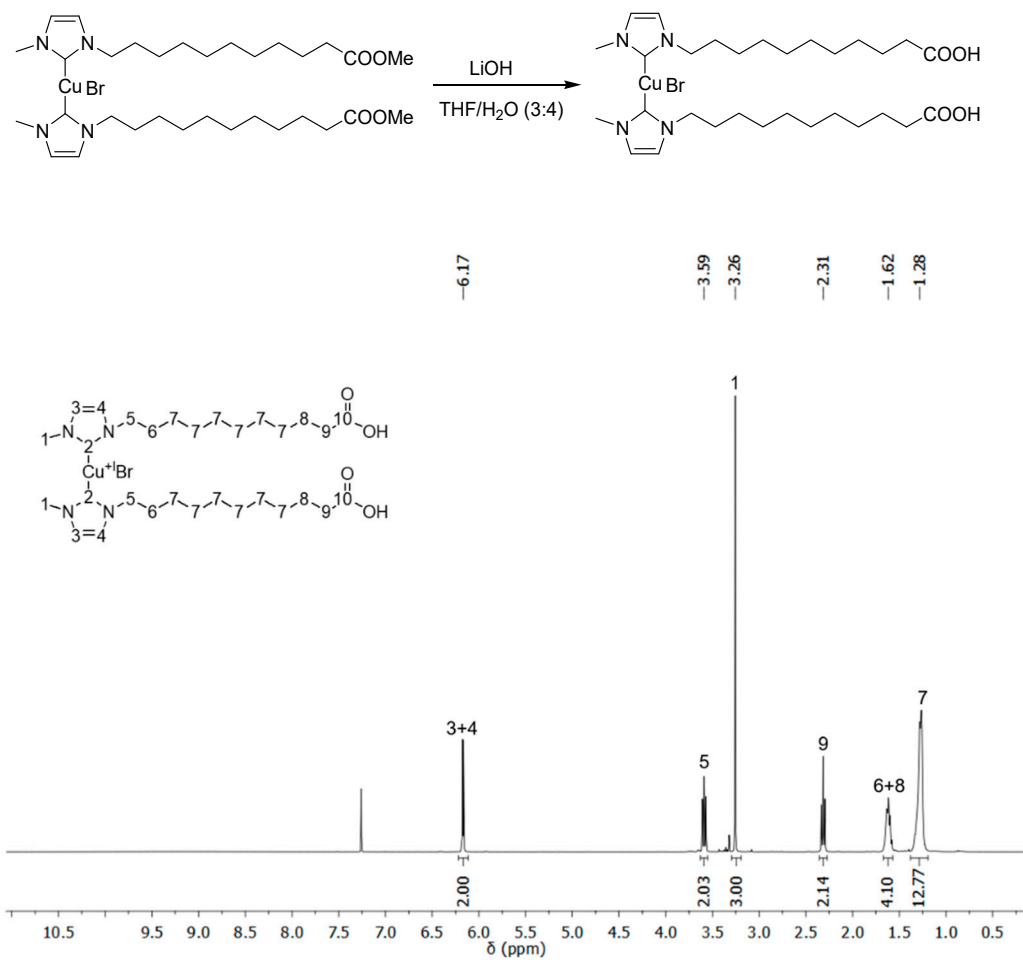


Figure S7. ^1H NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-NHC})_2]\text{Br}$ (4).

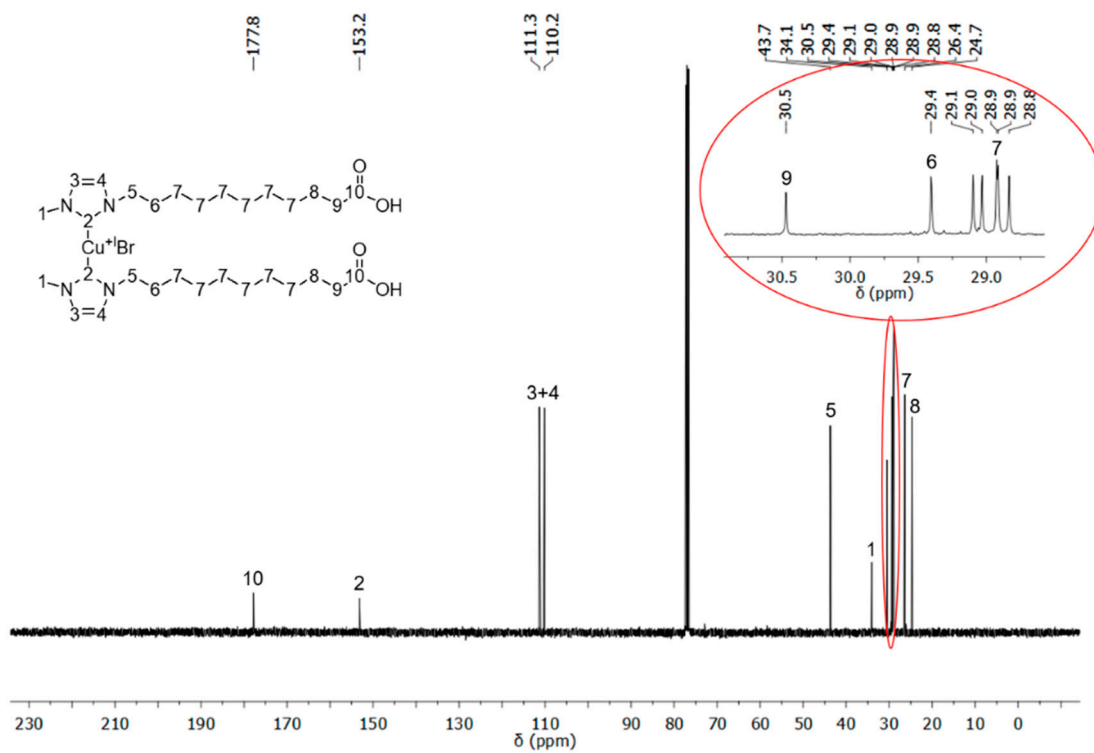


Figure S8. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-NHC})_2]\text{Br}$ (4).

6. Characterization of *N*-(*tert*-butoxycarbonyl)-3-bromopropylamine (5) [3]

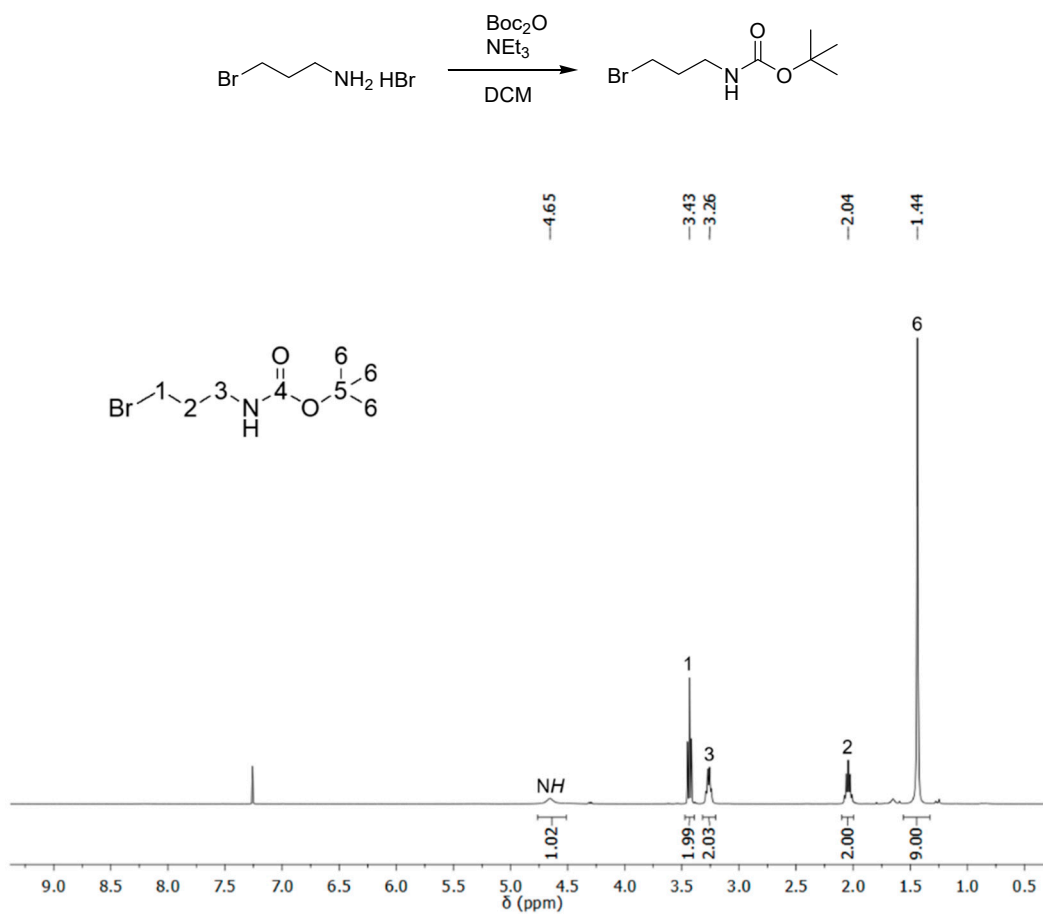


Figure S9. ¹H NMR spectrum of *N*-(*tert*-butoxycarbonyl)-3-bromopropylamine (5).

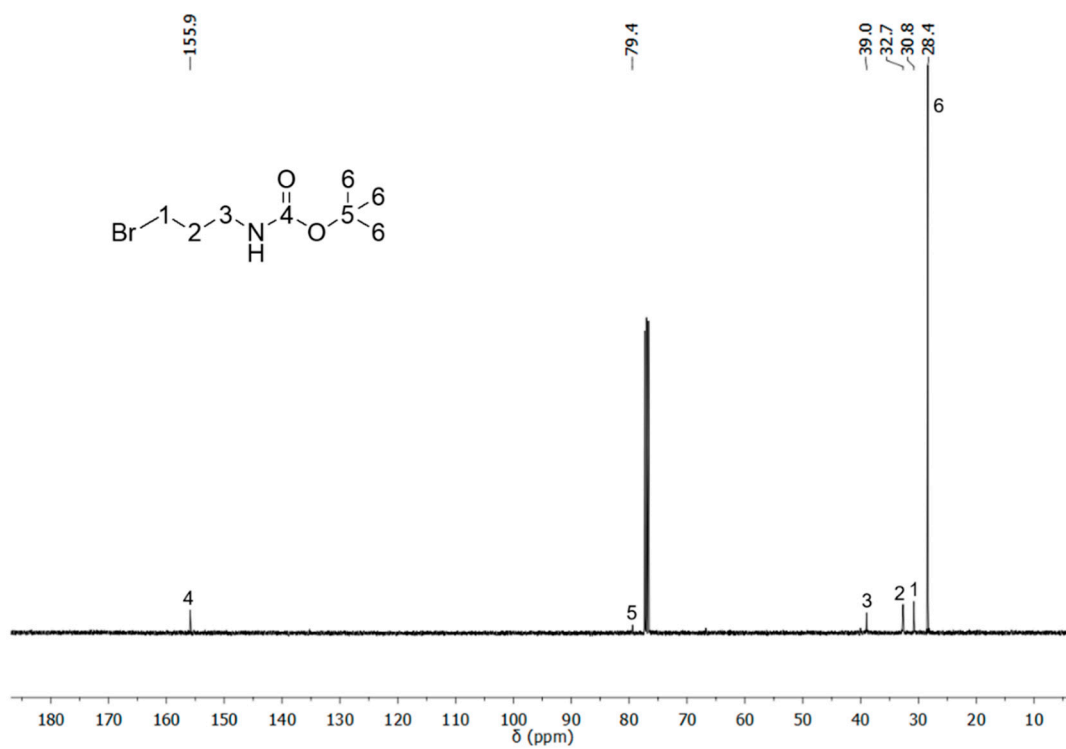


Figure S10. ^{13}C NMR spectrum of *N*-(*tert*-butoxycarbonyl)-3-bromopropylamine (5).

7. Characterization of 3-[3-[[1,1-dimethylethoxy)carbonyl]amino]propyl]-1-methyl-1*H*-imidazolium bromide (6)

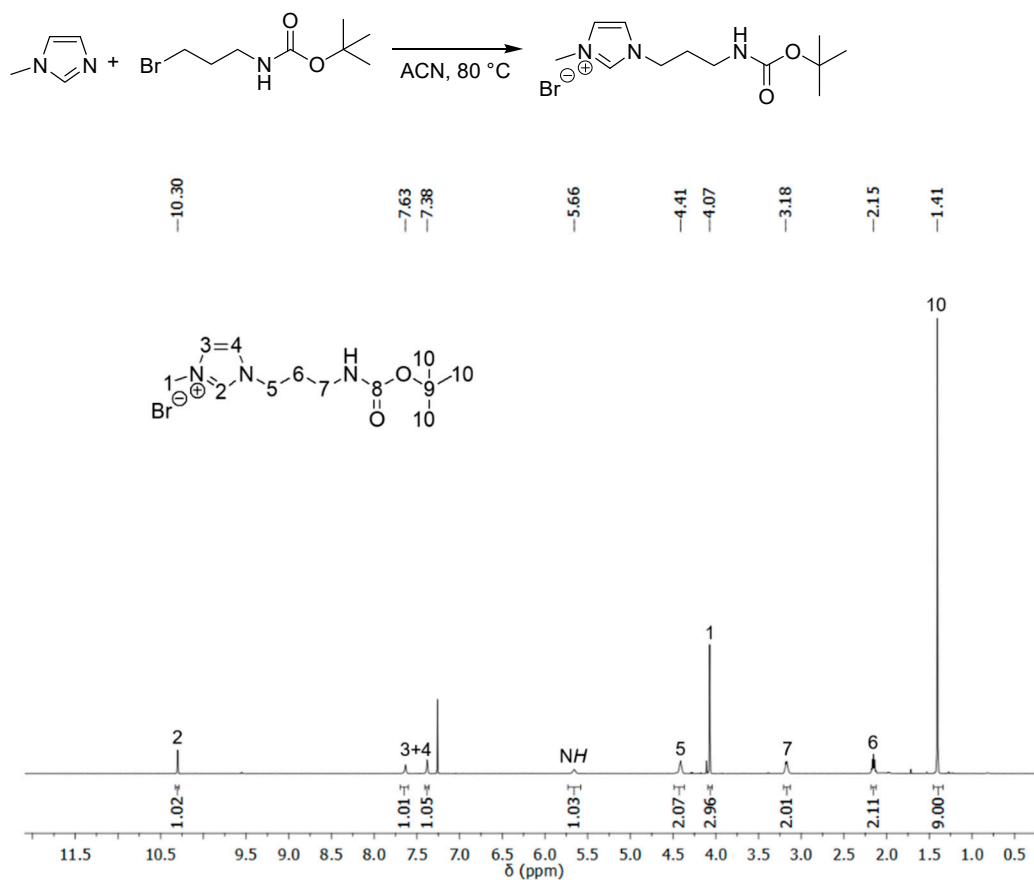


Figure S11. ¹H NMR spectrum of 3-[3-[[1,1-dimethylethoxy)carbonyl]amino]propyl]-1-methyl-1*H*-imidazolium bromide (6).

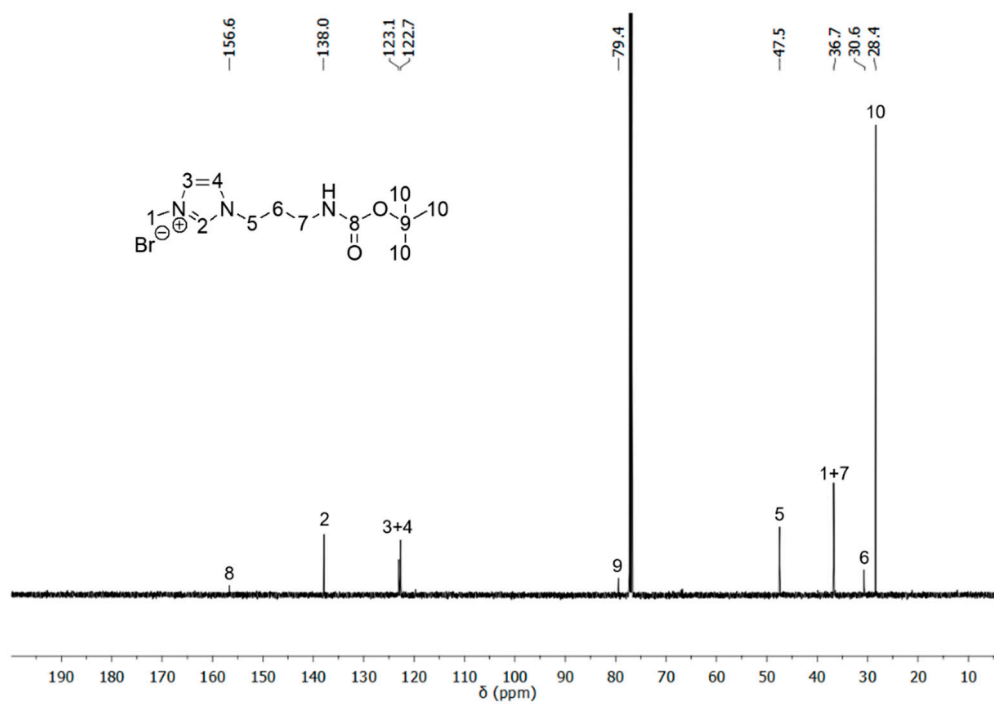


Figure S12. ¹³C NMR spectrum of 3-[3-[[[(1,1-dimethylethoxy)carbonyl]amino]propyl]-1-methyl-1H-imidazolium bromide (**6**).

8. Characterization of $[\text{Cu}(\text{C}_3\text{NHBoc-NHC})_2]\text{Br}$ (7) [1]

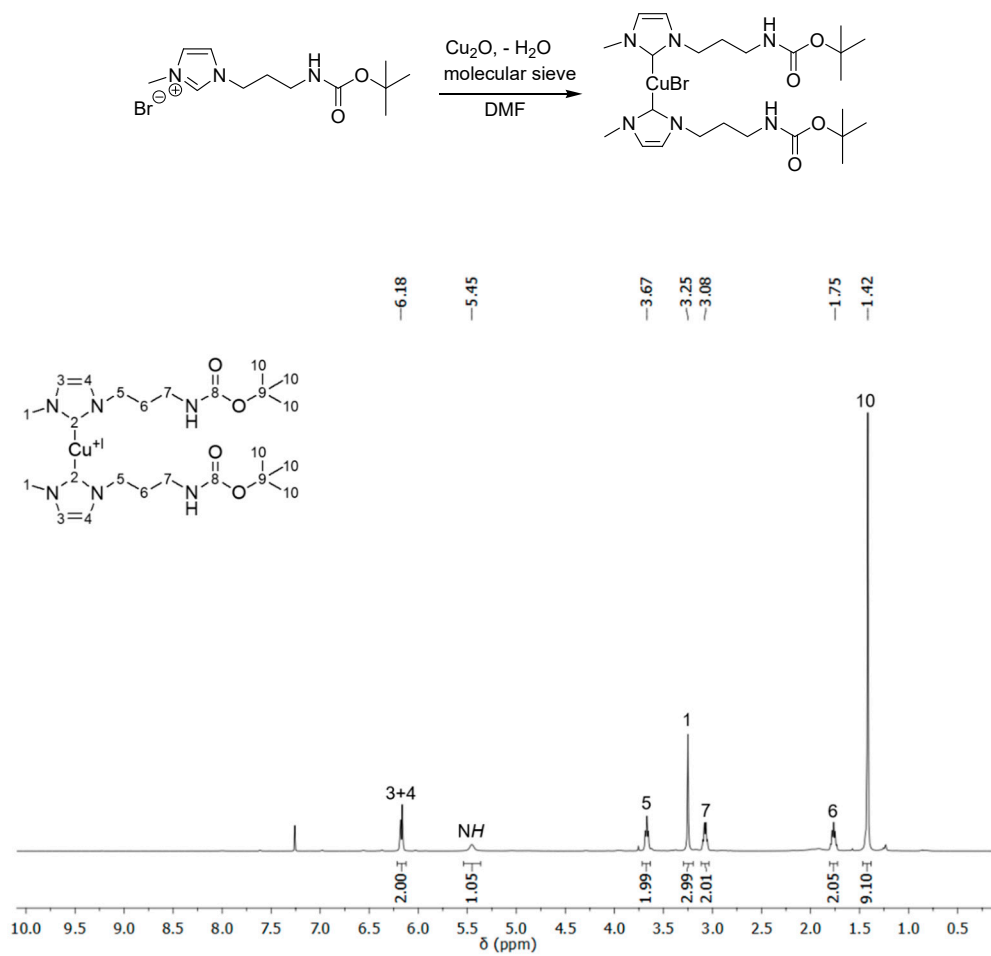


Figure S13. ^1H NMR spectrum of $[\text{Cu}(\text{C}_3\text{NHBoc-NHC})_2]\text{Br}$ (7).

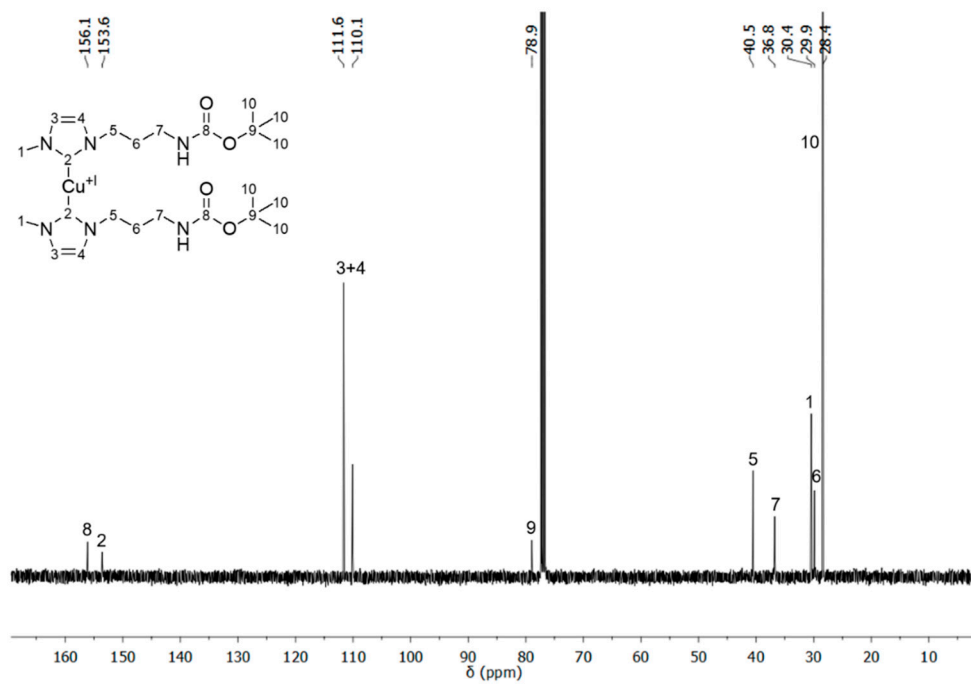


Figure S14. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_3\text{NHBoc-NHC})_2]\text{Br}$ (7).

9. Characterization of $[\text{Cu}(\text{C}_3\text{NH}_2\text{-NHC})_2]\text{Br}$ (8)

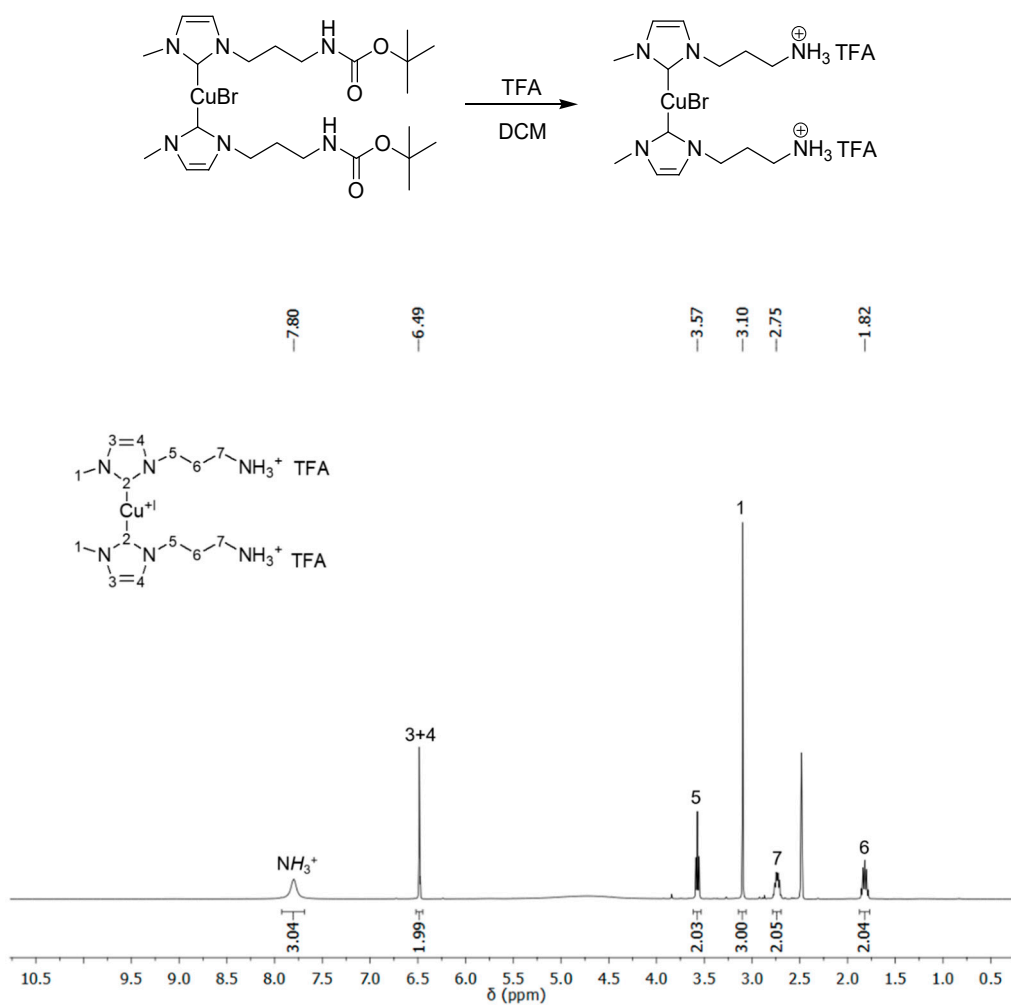


Figure S15. ^1H NMR spectrum of $[\text{Cu}(\text{C}_3\text{NH}_2\text{-NHC})_2]\text{Br}$ (8).

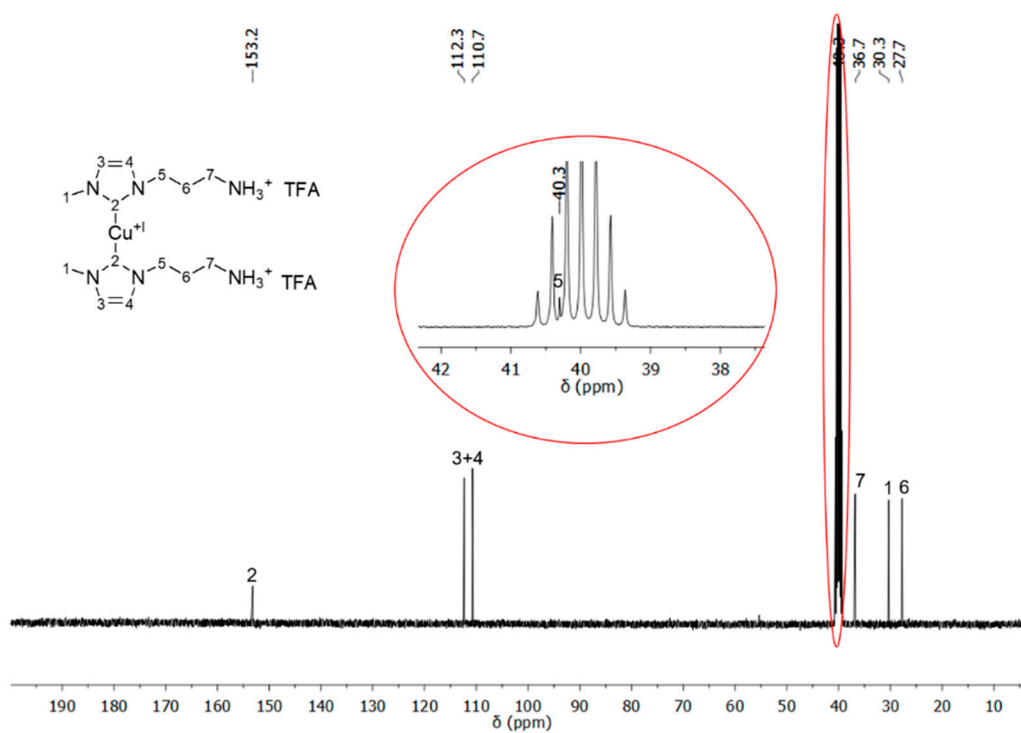
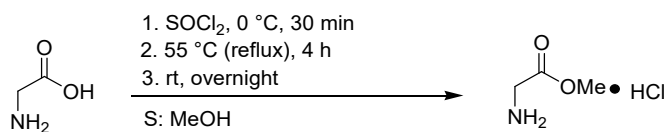


Figure S16. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_3\text{NH}_2\text{-NHC})_2]\text{Br}$ (8).

10. Synthesis and characterization of glycine methyl ester hydrochloride (9) [4]



Glycine (5.0 g, 66.6 mmol) was dissolved in MeOH (65.0 mL) and cooled down to 0 °C before SOCl₂ (8.70 g, 5.3 mL, 73.3 mmol) was slowly added. Subsequently the reaction mixture was heated to 55 °C for 4 h and then was cooled down to room temperature (rt). After stirring overnight, the solvent and the excess of SOCl₂ were removed under vacuum. Recrystallization from MeOH yielded the pure product as white crystalline needles. Yield: 6.58 g, 52.37 mmol, 79%.

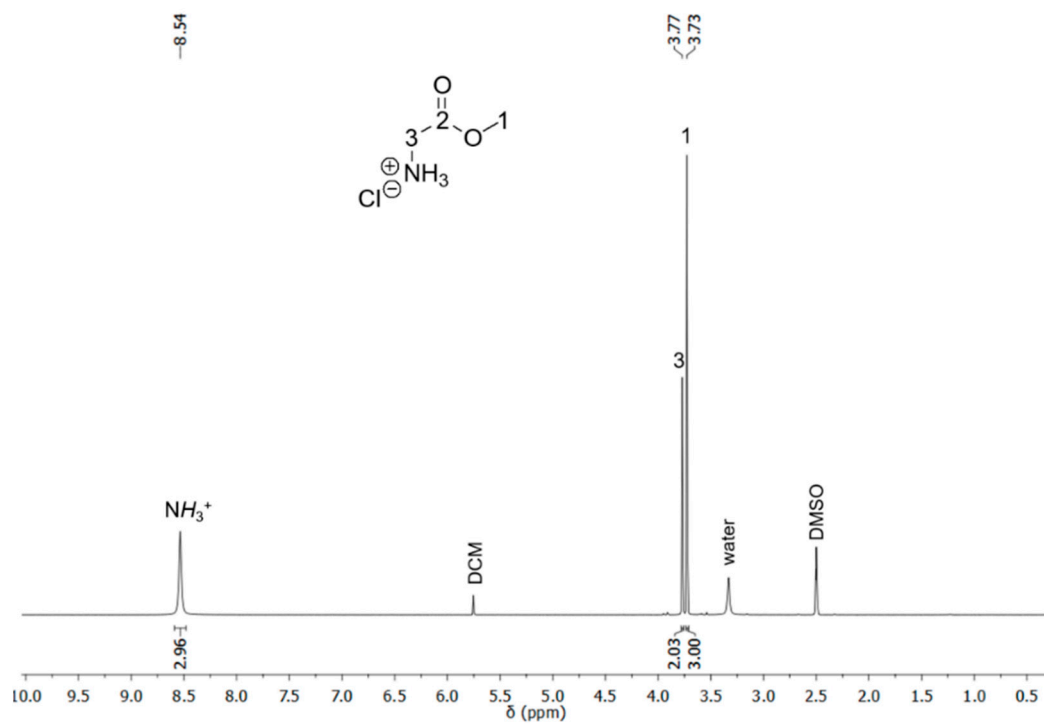


Figure S17. ^1H NMR spectrum of glycine methyl ester hydrochloride (9).

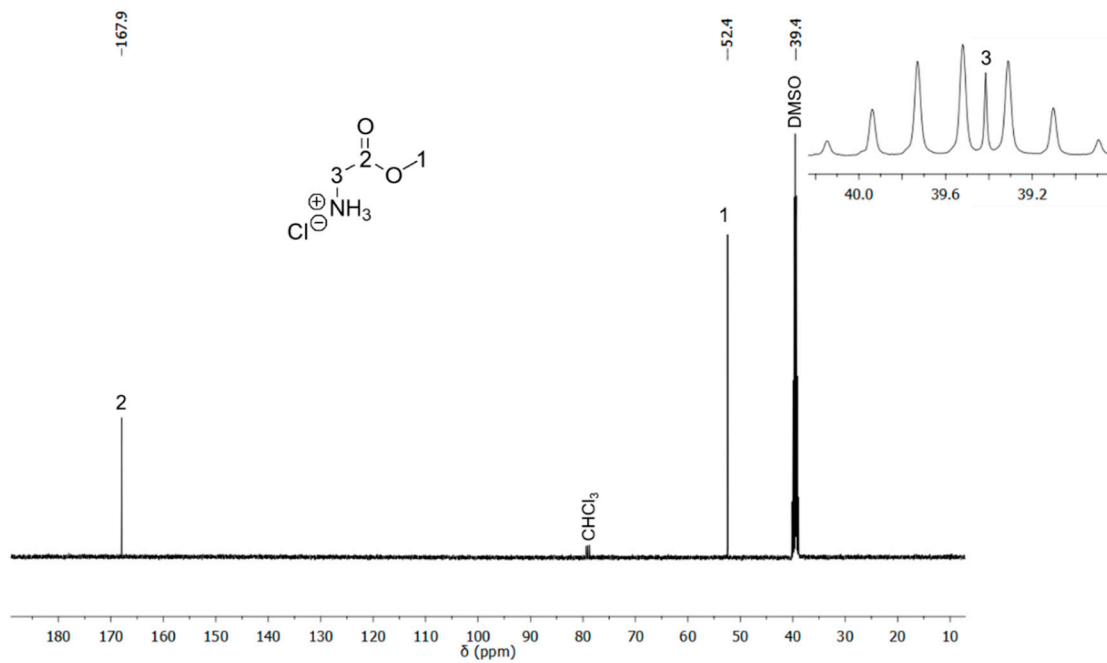
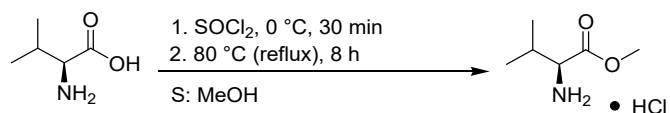


Figure S18. ^{13}C NMR spectrum of glycine methyl ester hydrochloride (9).

11. Synthesis and characterization of L-valine methyl ester hydrochloride (10) [5]



L-Valine (5.0 g, 42.67mmol) was dissolved in dry methanol (60.0 mL) and was cooled down to 0 °C. Freshly distilled thionyl chloride (7.6 g, 4.64 mL, 64.2 mmol) was slowly added and after stirring for 30 min the temperature was increased to 80 °C and the mixture was refluxed for another 8 h. After removal of the solvent and the excess of thionyl chloride, the product was recrystallized from methanol followed by filtration to obtain the pure product as a colorless powder. Yield: 6.21 g, 37.1 mmol, 87%.

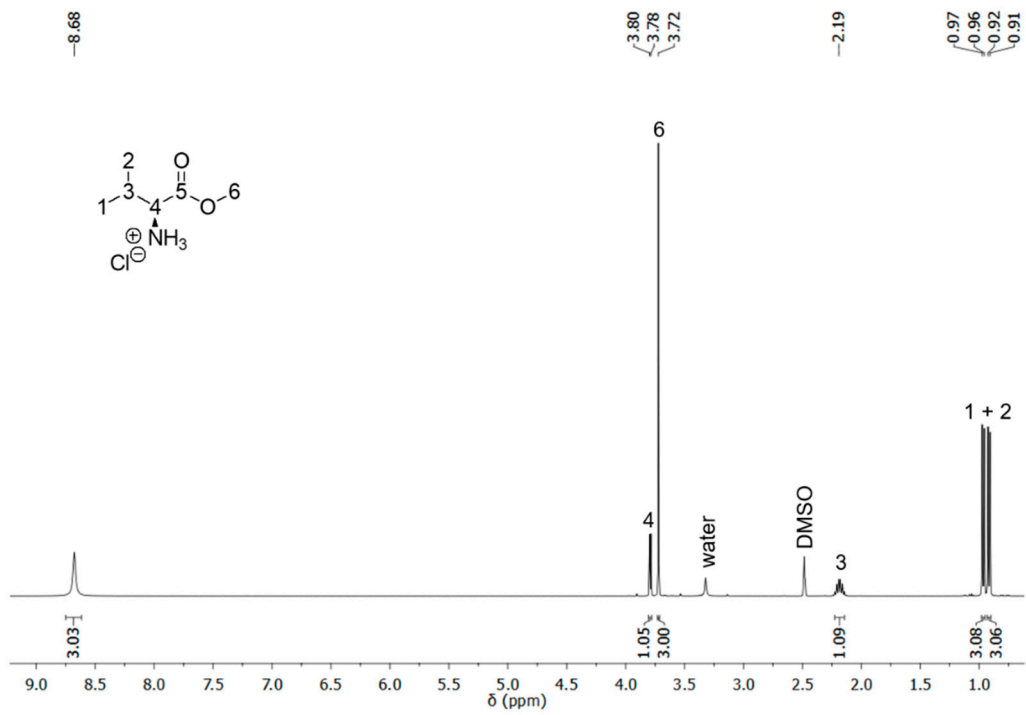


Figure S19. ¹H NMR spectrum of L-valine methyl ester hydrochloride (10).

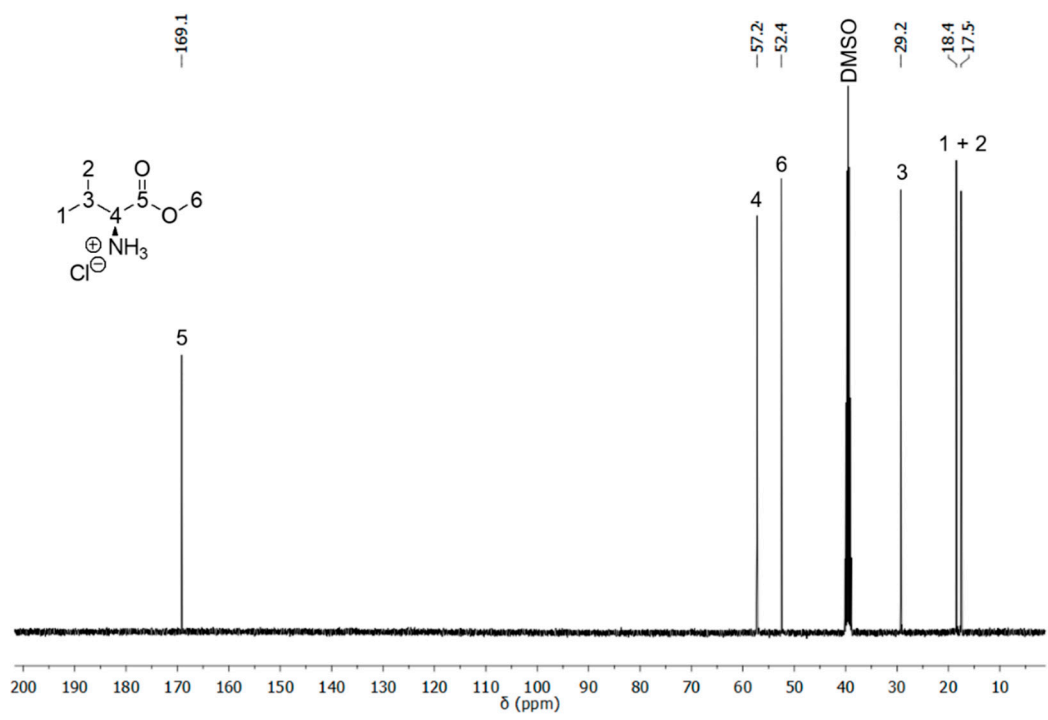


Figure S20. ^{13}C NMR spectrum of L-valine methyl ester hydrochloride (10).

12. Characterization of $[\text{Cu}(\text{C}_{10}\text{COOH-Gly-NHC})_2]\text{Br}$ (**11**) [6,7]

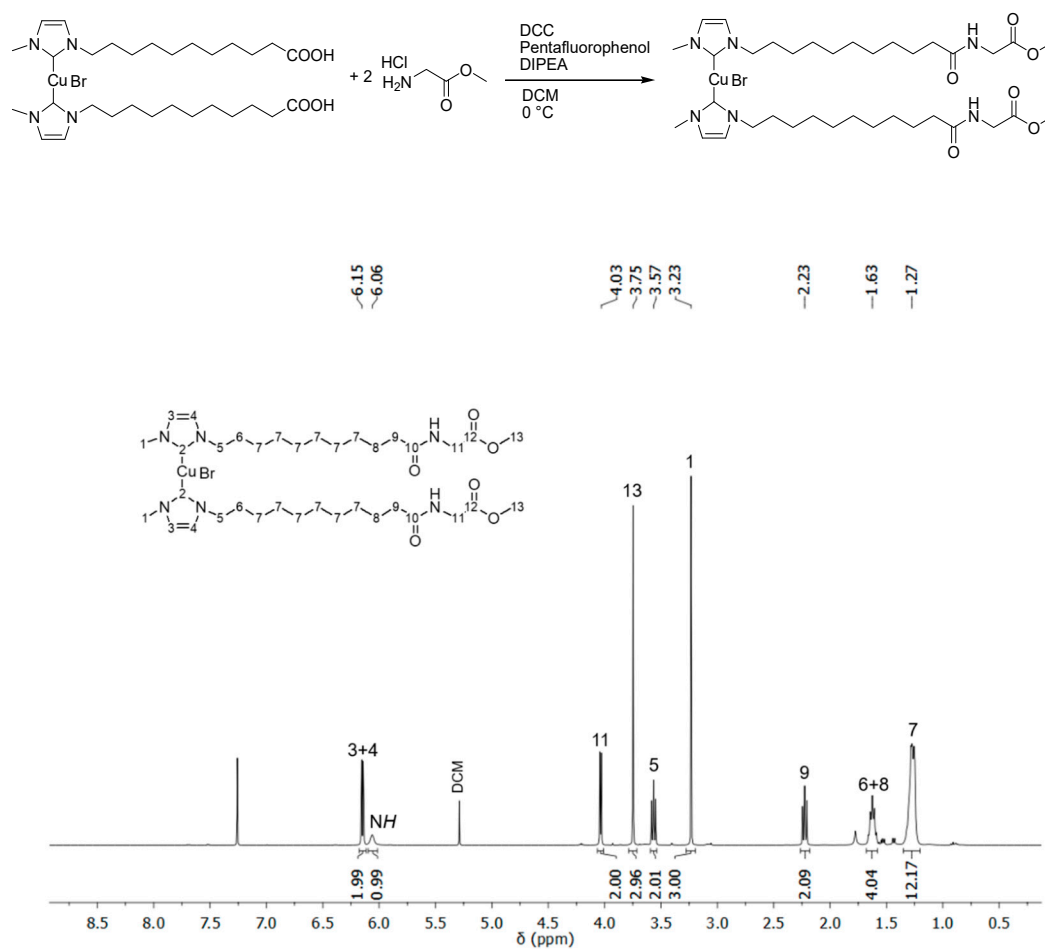


Figure S1. ^1H NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-Gly-NHC})_2]\text{Br}$ (**11**).

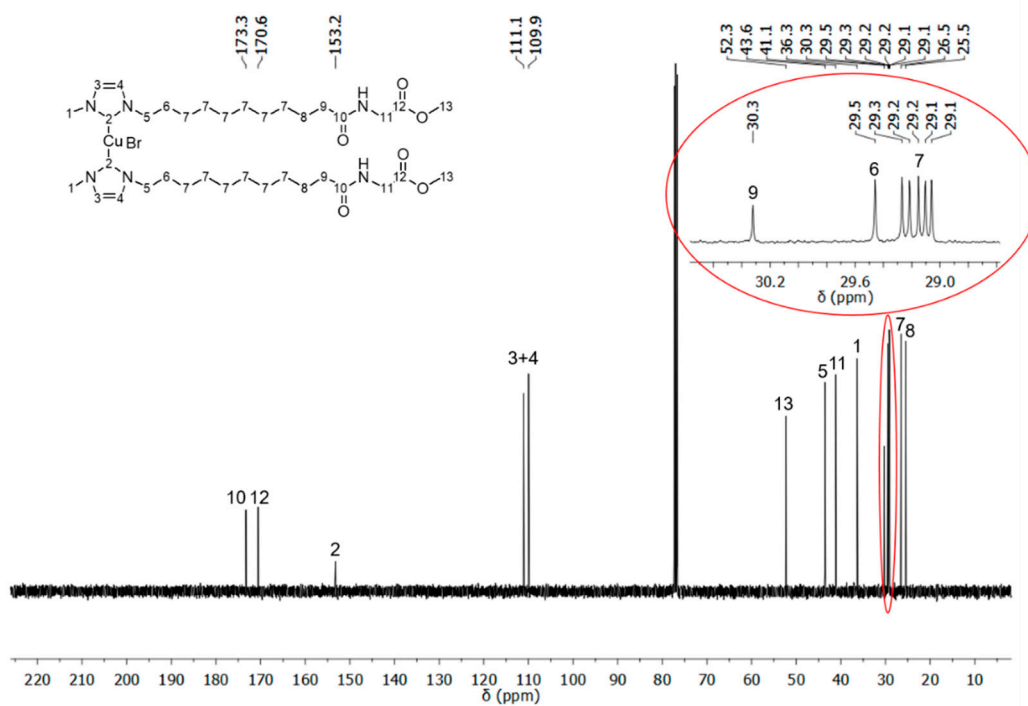


Figure S22. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-Gly-NHC})_2]\text{Br}$ (11).

13. Characterization of $[\text{Cu}(\text{C}_{10}\text{COOH-Val-NHC})_2]\text{Br}$ (**12**) [6,7]

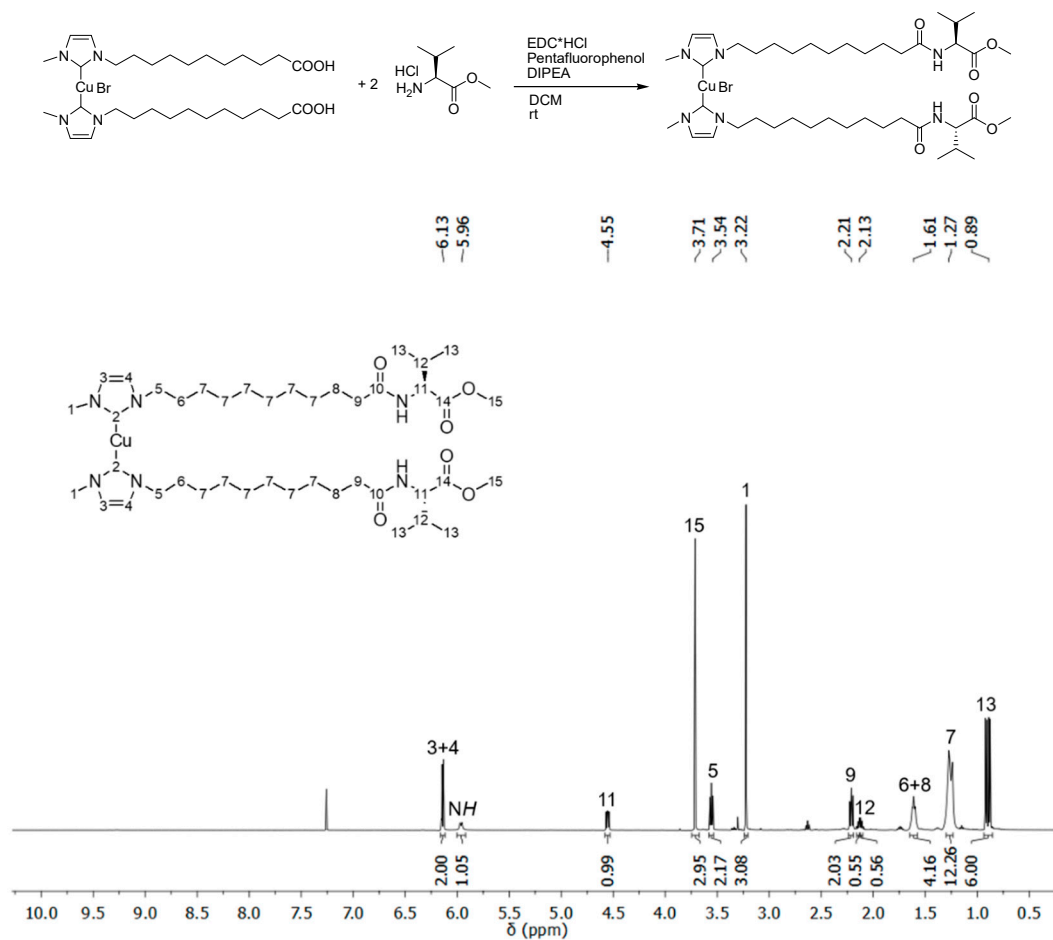


Figure S23. ¹H NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-Val-NHC})_2]\text{Br}$ (**12**).

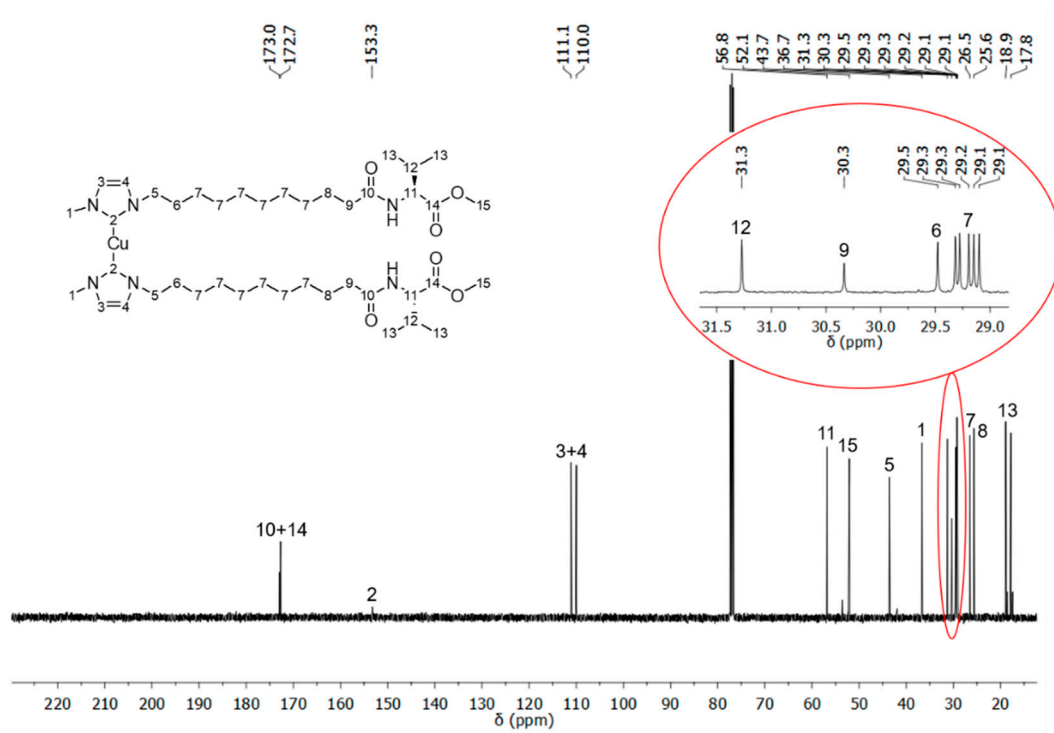


Figure S24. ^{13}C NMR spectrum of $[\text{Cu}(\text{C}_{10}\text{COOH-Val-NHC})_2]\text{Br}$ (12).

14. Characterization of the polymeric catalyst (13) [6,7]

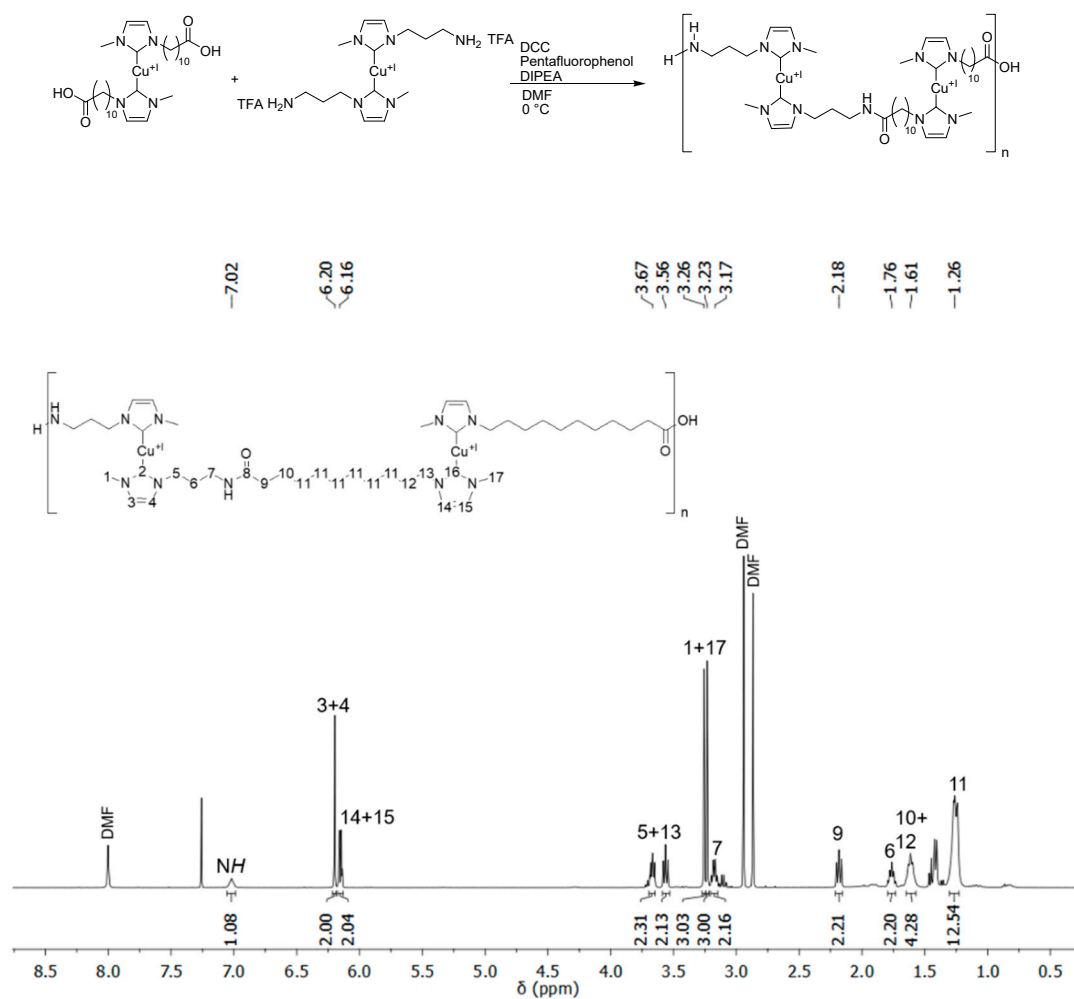


Figure S25. ^1H NMR spectrum of the polymeric catalyst 13.

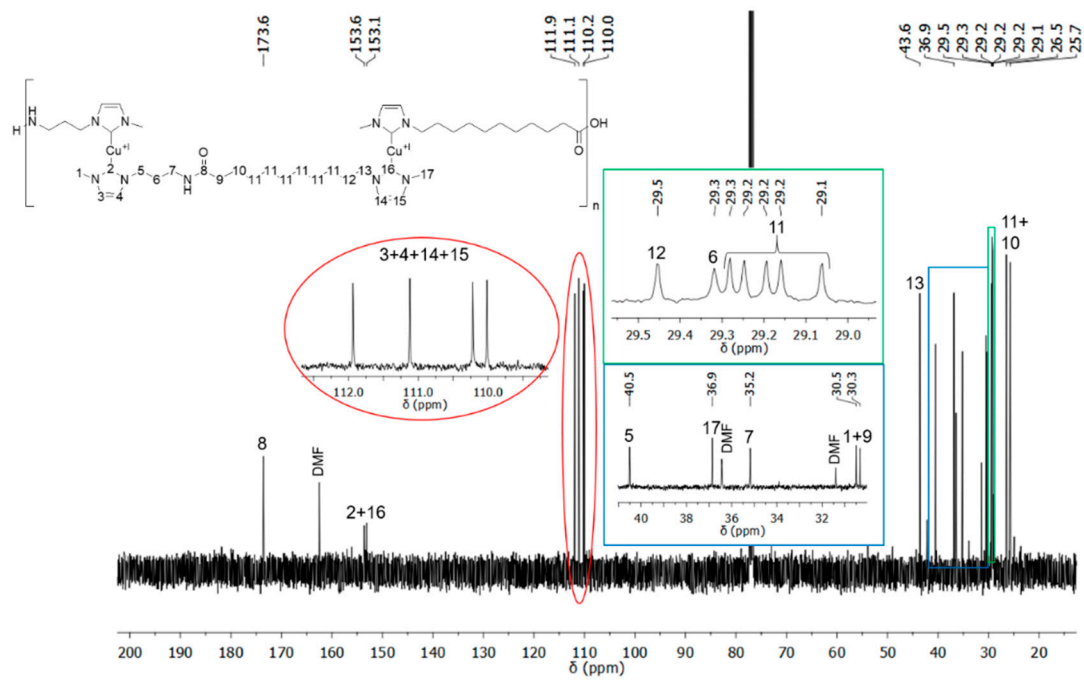
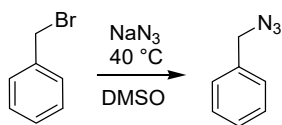


Figure S26. ^{13}C NMR spectrum of the polymeric catalyst 13.

15. Synthesis and characterization of benzyl azide (14) [8]



Sodium azide (5.5 g, 84.7 mmol) and benzyl bromide (**14**) (13.2 g, 9.17 mL, 77.0 mmol) were dissolved in DMSO (170.0 mL). The reaction mixture was stirred at 40 °C for 90 h. Afterward, water (50.0 mL) was added and the reaction was further stirred, until it was cooled down to room temperature. The mixture was extracted with Et₂O (3 × 30.0 mL) and the combined organic phases were washed with water (2 × 50.0 mL) and brine (50.0 mL). Subsequently the organic phase was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. Yield: 9.45 g, 71.0 mmol, 92%.

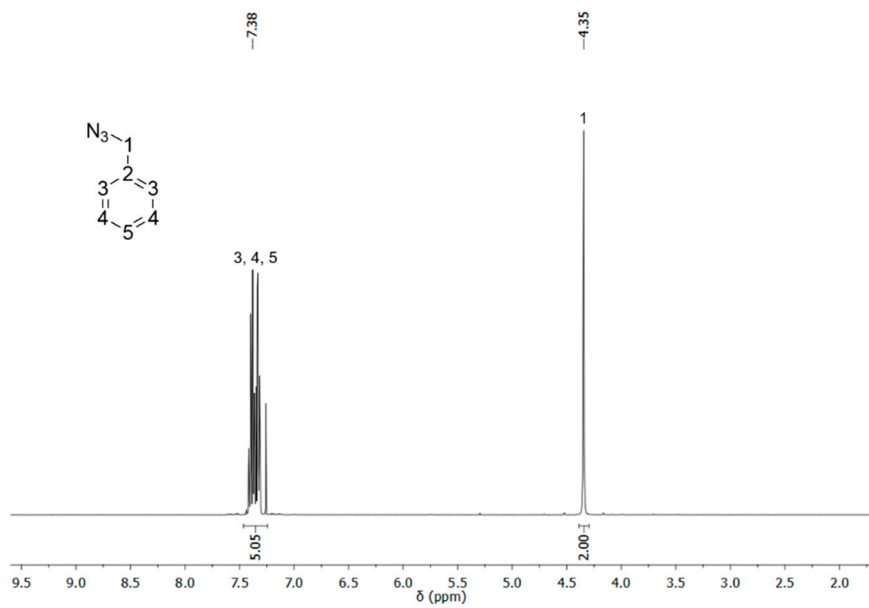


Figure S27. ¹H NMR spectrum of benzyl azide (14).

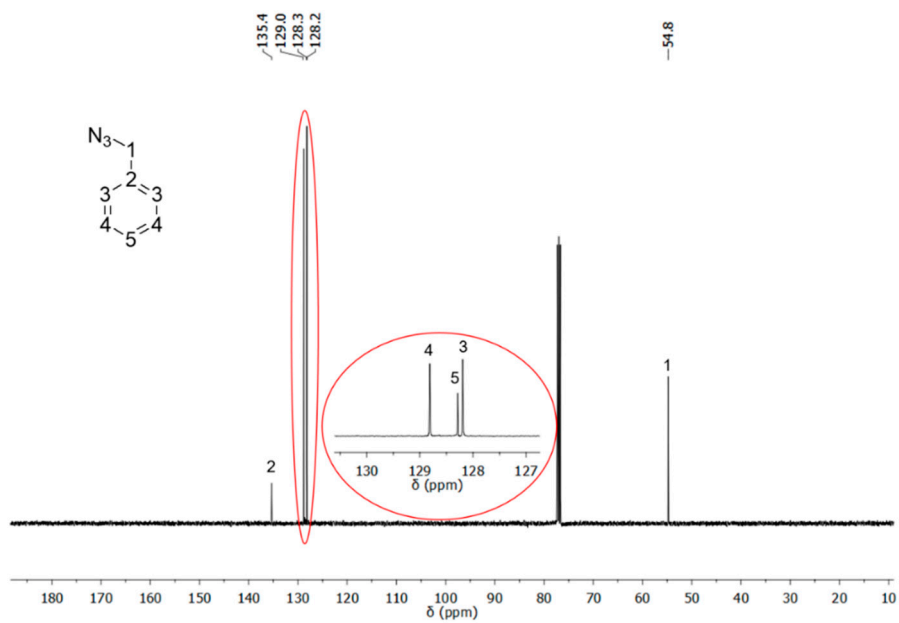
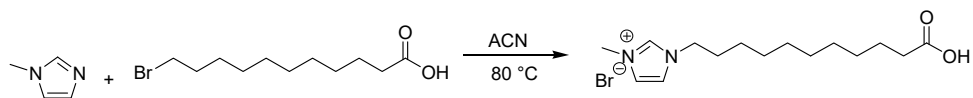


Figure S28. ^{13}C NMR spectrum of benzyl azide (14).

16. Synthesis and characterization of 3-(10-carboxydecyl)-1-methyl-1*H*-imidazolium bromide



11-Bromoundecanoic (10.0 g, 37.73 mmol) and 1-methylimidazole (3.27 g, 3.13 mL, 39.62 mmol) were dissolved in ACN (27.0 mL). The reaction mixture was stirred for 48 h at 80 °C. Afterward, the solvent was removed and the crude product was washed with Et₂O (2 × 20.0 mL) and cold ACN (4 × 10.0 mL). The pure product was obtained as a white, crystalline solid. Yield: 11.63 g, 33.49 mmol, 89%.

¹H NMR (400 MHz, DMSO-*d*₆, 27 °C): δ (ppm) = 11.94 (s, 1H), 9.13 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.14 (t, 2H), 3.83 (s, 3H), 2.16 (t, 2H), 1.75 (m, 2H), 1.46 (m, 2H), 1.22 (m, 12H); ¹³C NMR (100 MHz, DMSO-*d*₆, 27 °C): δ (ppm) = 174.9, 136.9, 124.0, 122.7, 49.2, 36.2, 34.1, 29.8, 29.2, 29.2, 29.1, 29.0, 28.8, 25.9, 25.0.

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