Supporting Information

Polystyrene-Bound $AlCl_3$ - a Catalyst for the Solvent-Free Synthesis of Aryl-Substituted Tetrazoles

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Contents

Determination of the Lewis Acid Strength

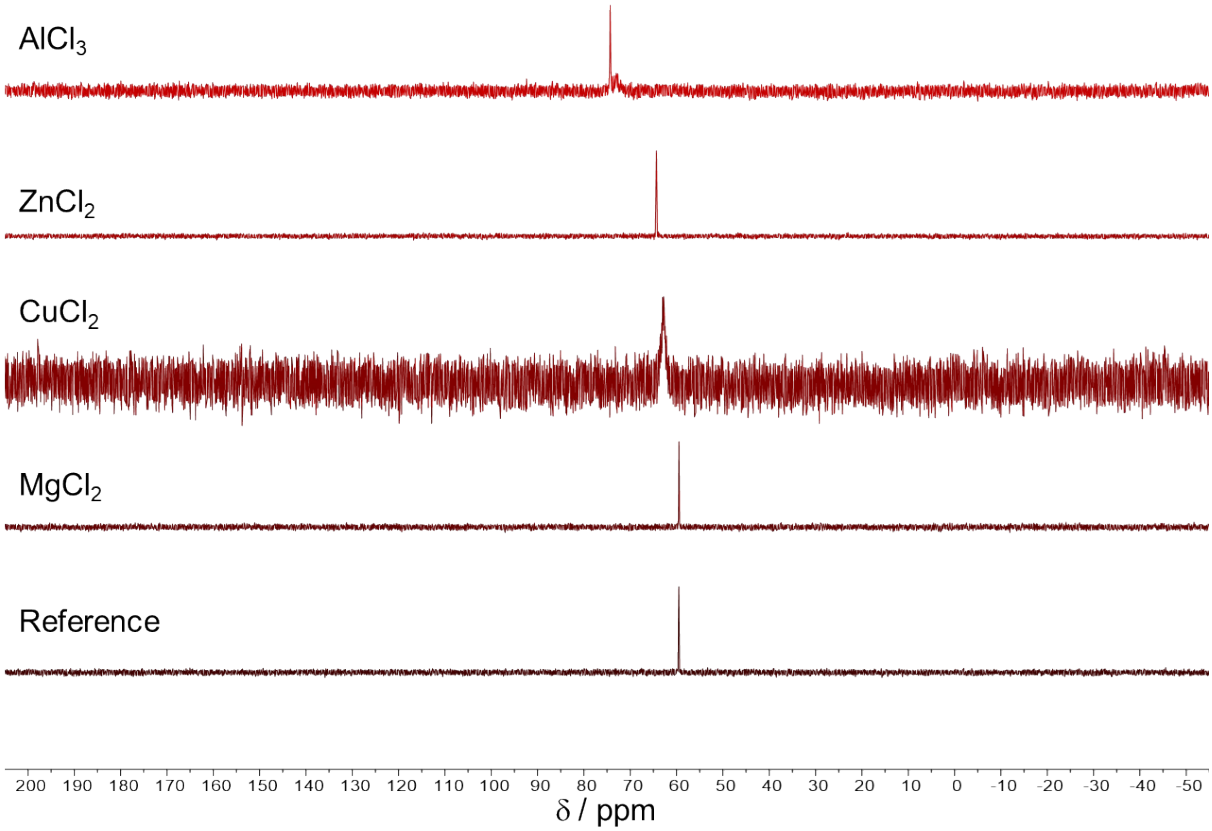


Figure S1. ^{31}P NMR spectra of TEPO in the presence of different LAs; spectra were recorded in MeOH-d_4.

The Lewis acid strength, as determined by the Gutmann-Beckett method, shows a clear correlation with the catalytic activity in the formation of tetrazoles. Lewis acids inducing a higher chemical shift in the ^{31}P NMR also lead to higher product formation when employed as catalysts.

^{1}H NMR Spectra

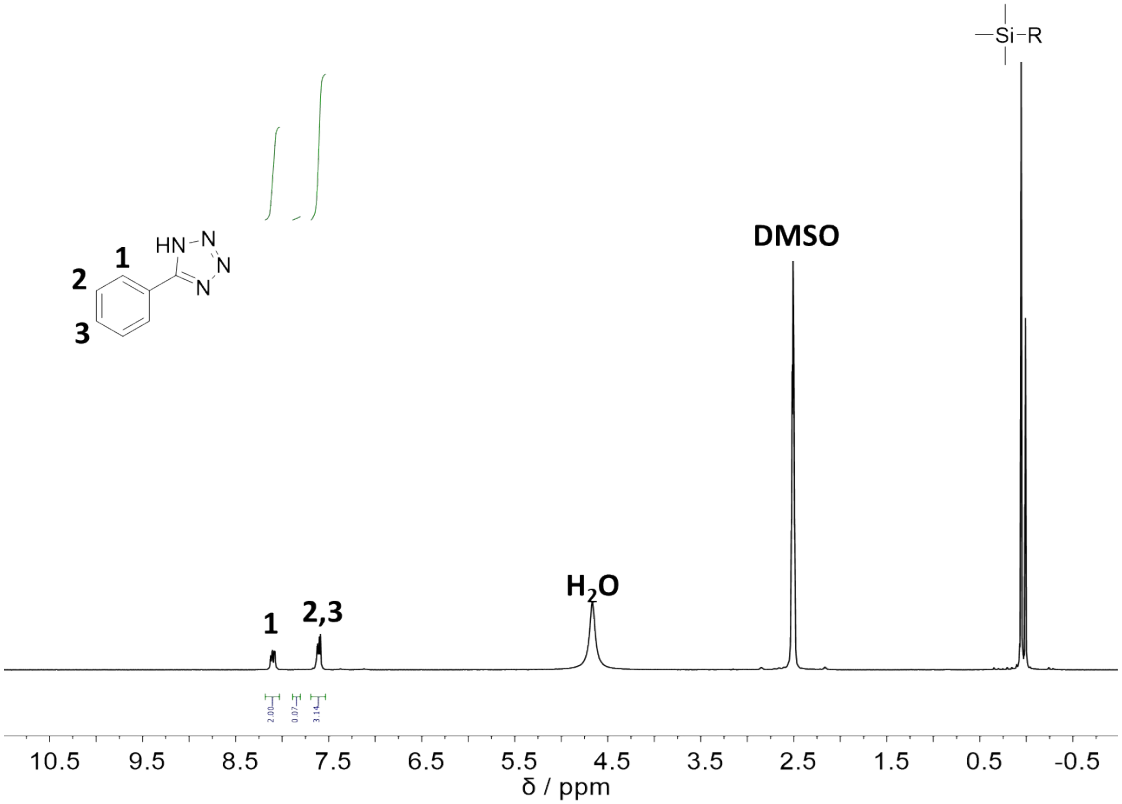


Figure S2 ^{1}H-NMR-spectrum of 5-phenyltetrazole formation reaction using $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6.

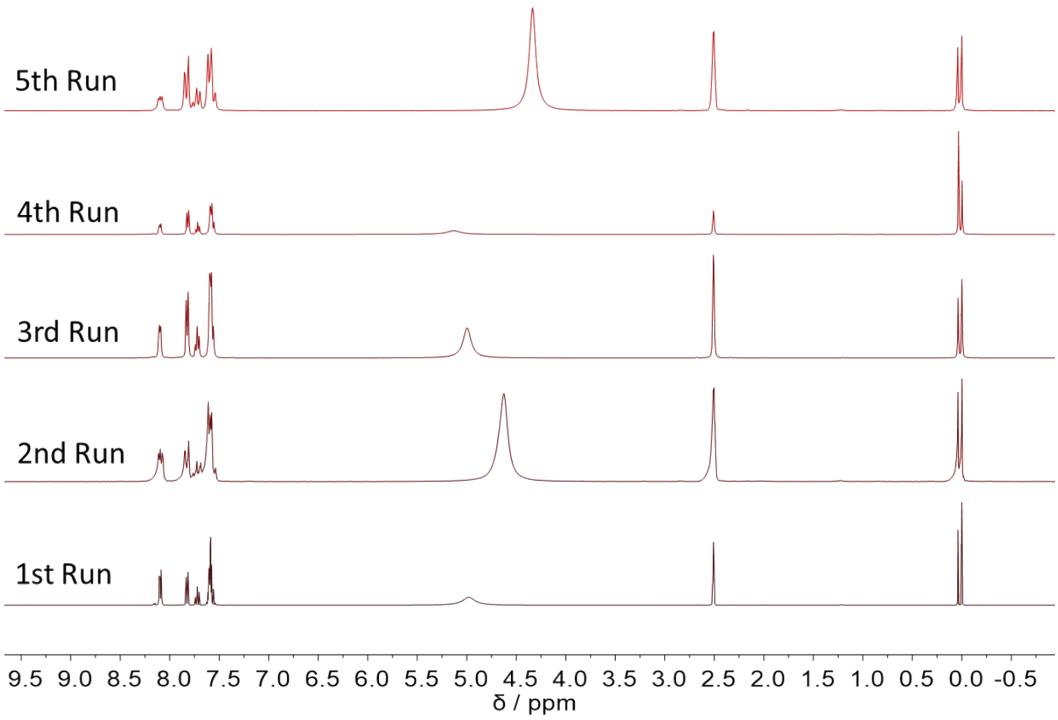


Figure S3 ^{1}H-NMR-spectra of the formation of 5-phenyltetrazole tetrazole using Polymer-bound $AlCl_3$ as catalyst under bulk conditions at 160°C; for all runs, the catalyst was recycled and used again; spectra were recorded in DMSO-d_6.

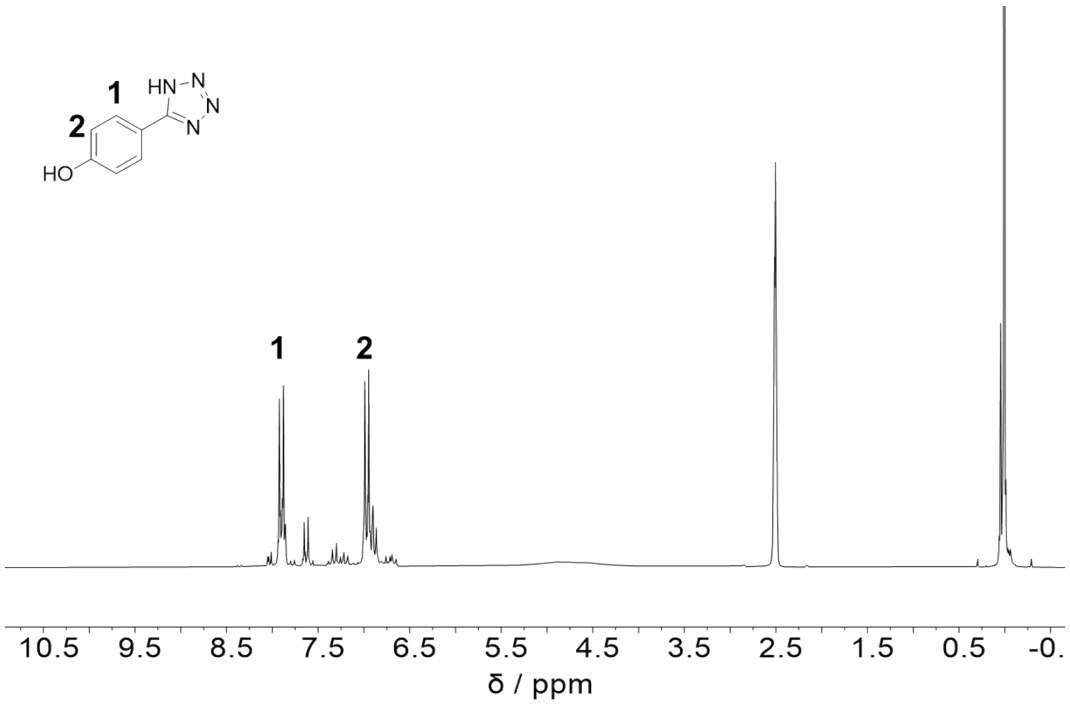


Figure S4 ^{1}H-NMR-spectrum of **3b** using polymer-bound $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6.

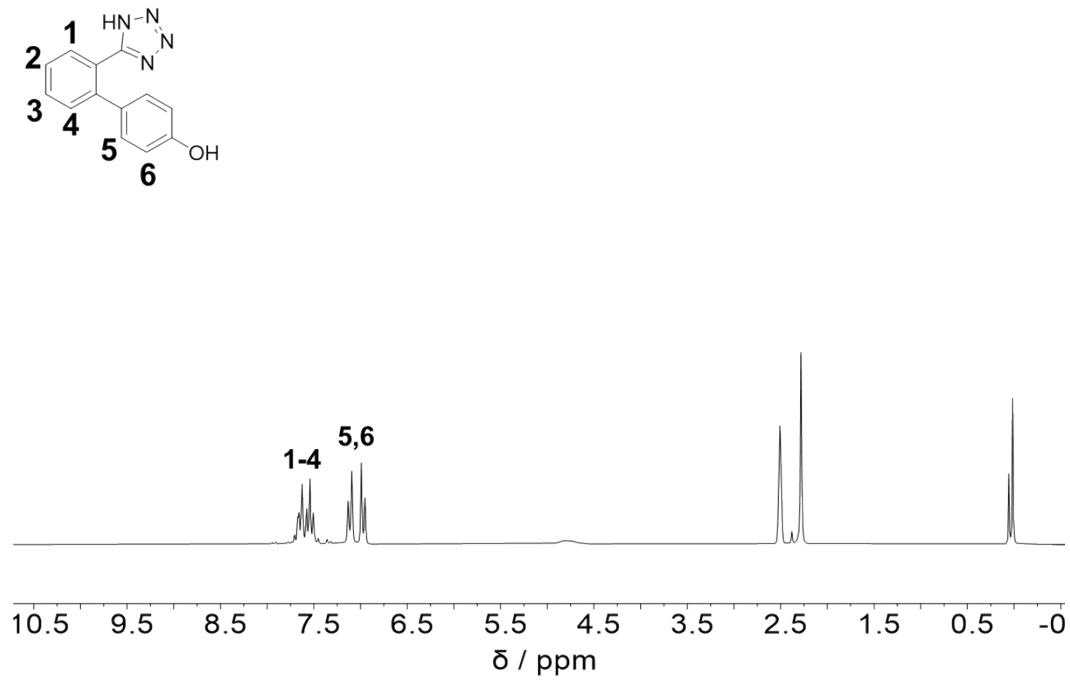


Figure S5 ^{1}H-NMR-spectrum of **3c** using polymer-bound $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6.

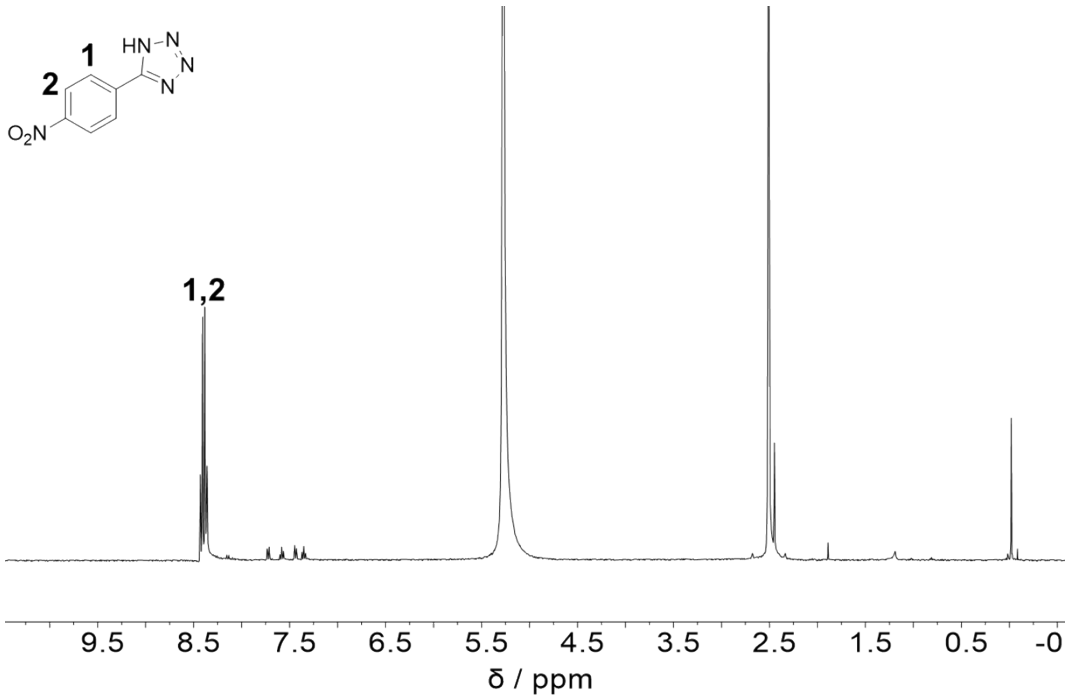
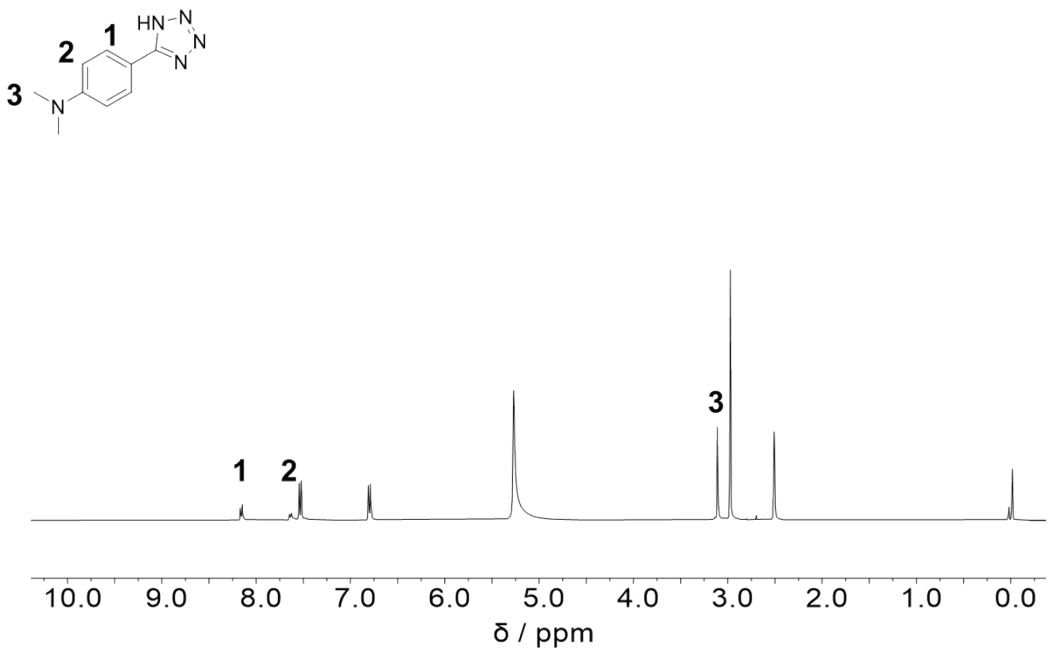


Figure S6 ^{1}H-NMR-spectrum of **3d** using polymer-bound $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6.

Figure S7 ^{1}H-NMR-spectrum of **3e** using polymer-bound $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6



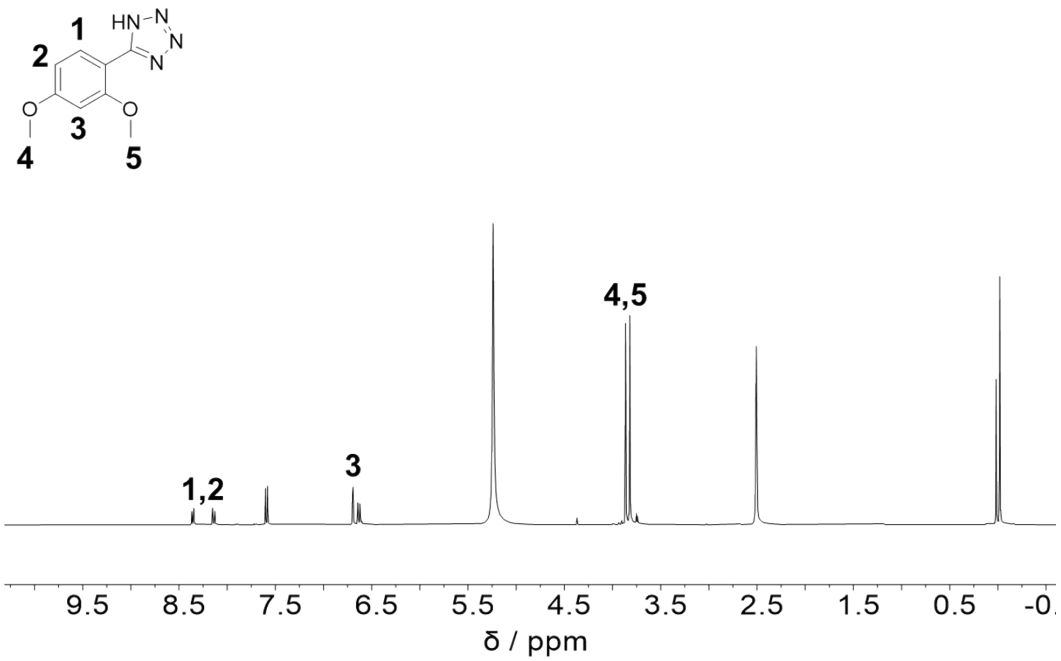


Figure S8 ^{1}H-NMR-spectrum of **3f** using polymer-bound $AlCl_3$ as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d_6

ATR-IR Spectra

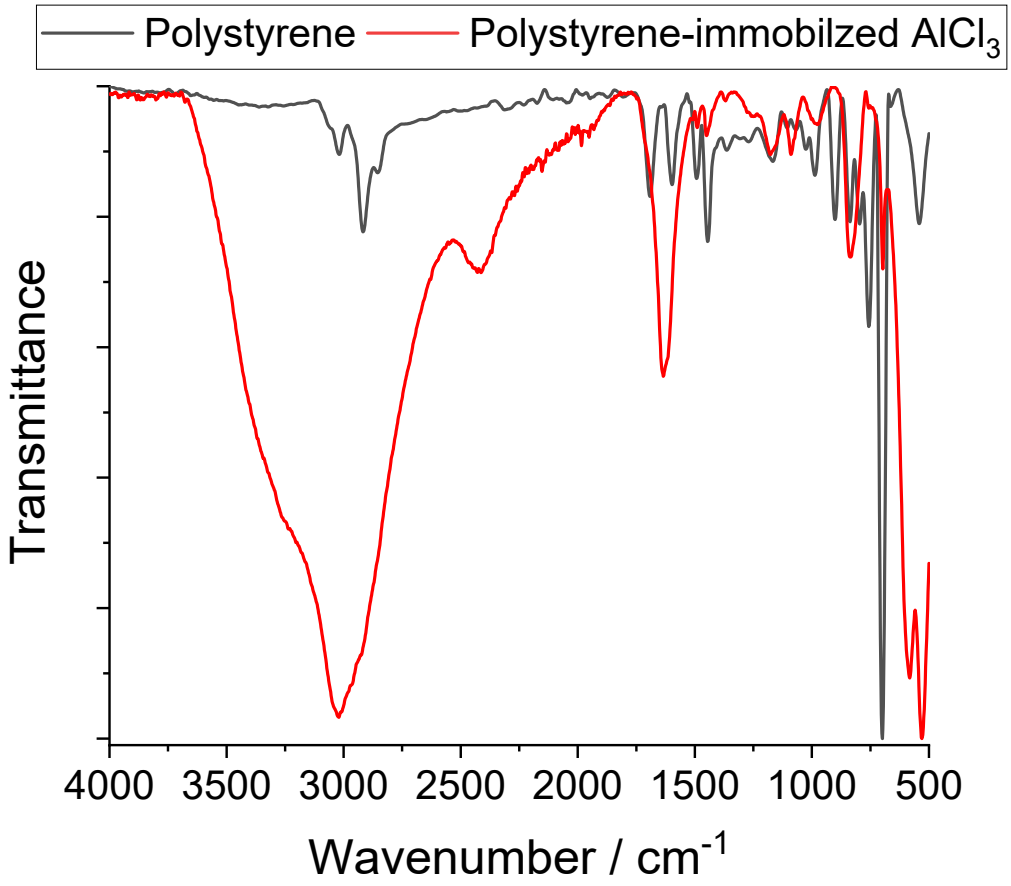


Figure S9. ART-IR spectra of polystyrene (black) and $AlCl_3$ immobilized in polystyrene (red)

Gas Sorption Measurements

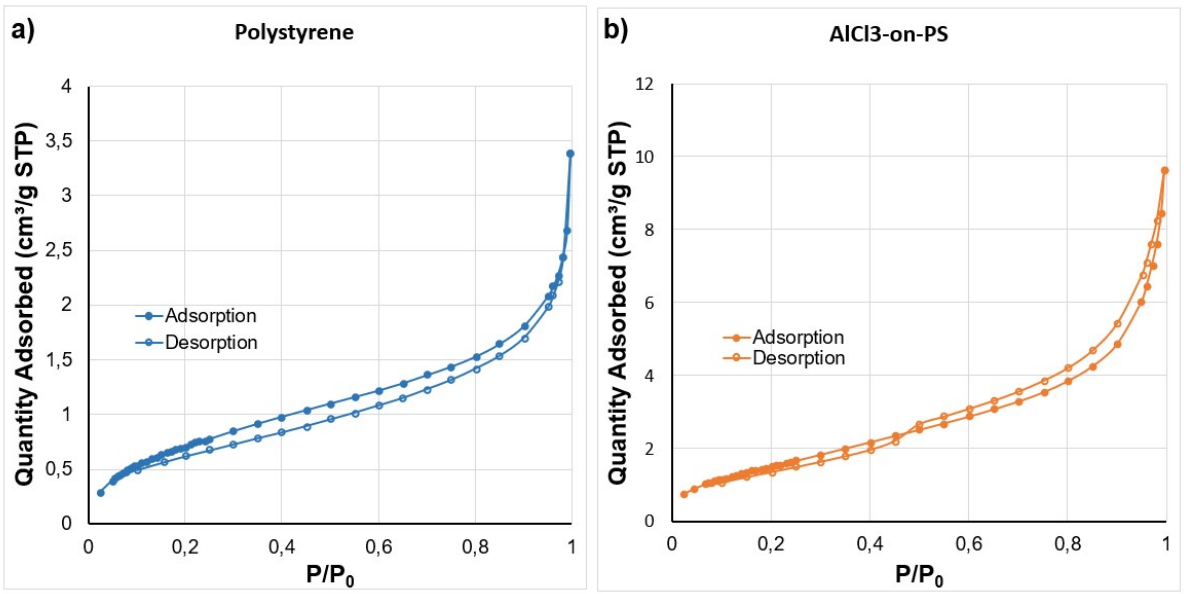


Figure S10. N2 adsorption isotherms. a) Polystyrene sample. b) AlCl3-on-PS

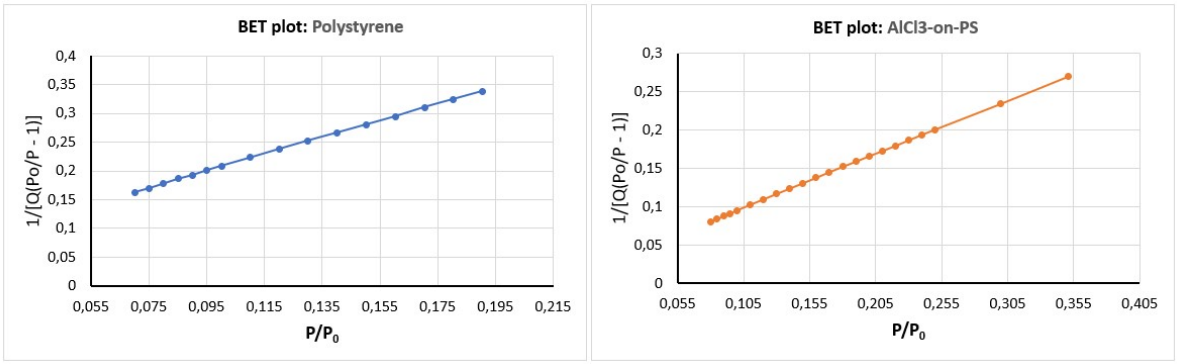


Figure S11. Brunauer-Emmett-Teller (BET) analysis

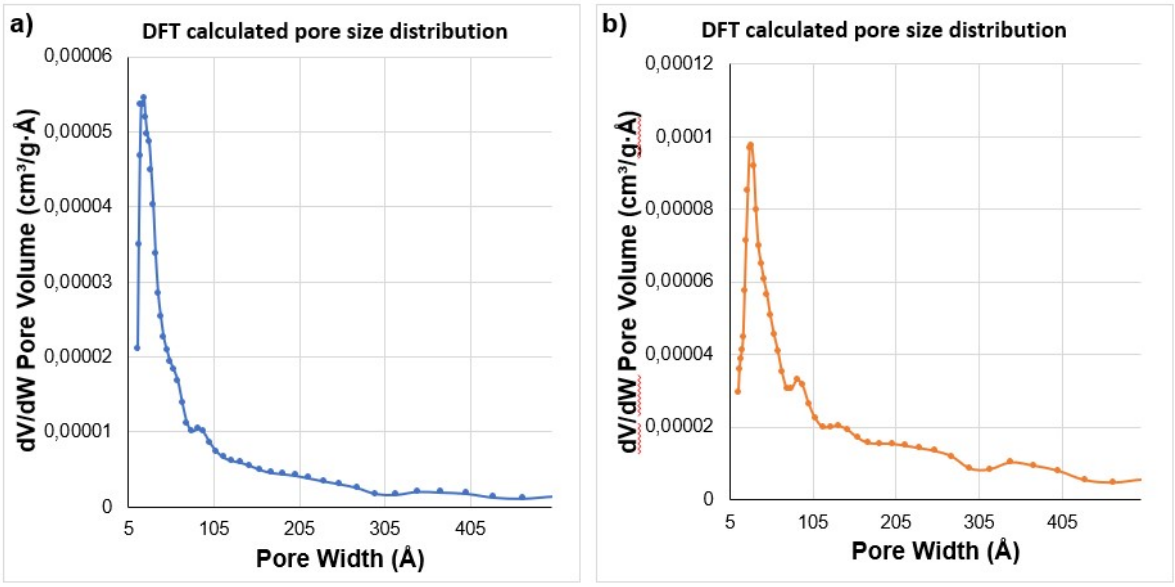


Figure S12. Pore size distribution analysis obtained from Density Functional Theory (DFT)

X-Ray Powder Diffraction Patterns

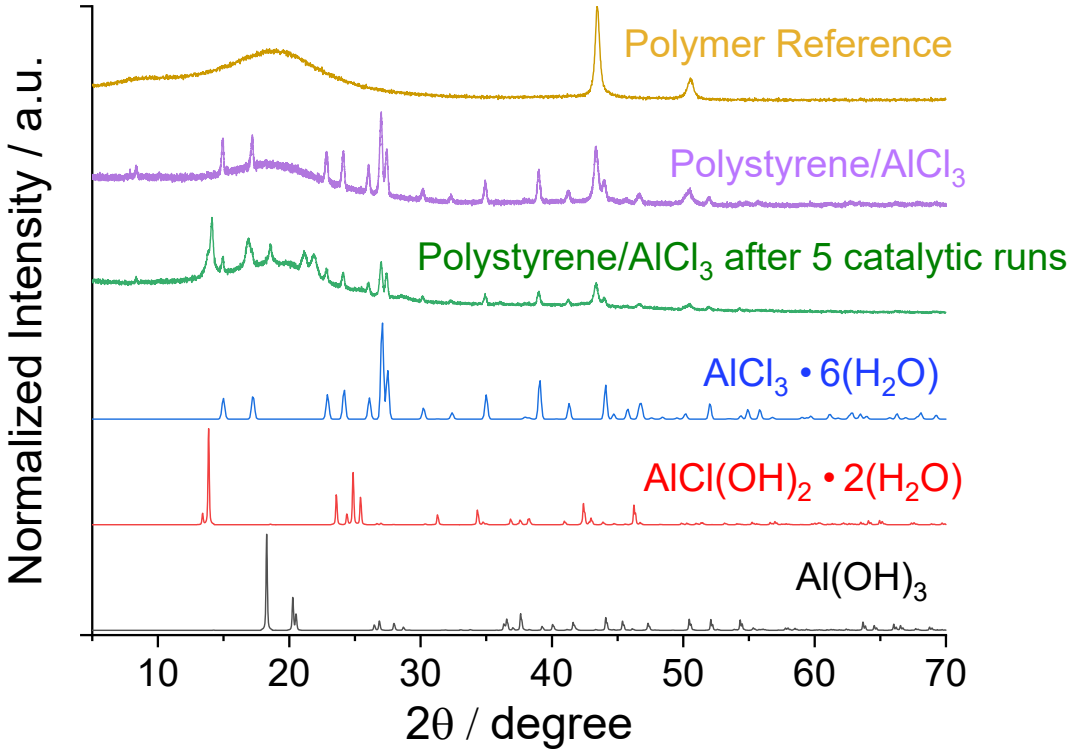


Figure S13. Normalized PXRD patterns of the polymer reference without $AlCl_3$ (yellow), the polymer-bound $AlCl_3$ composite before (violet) and after 5 catalytic runs (green). The diffractograms of $AlCl_3 \cdot 6(H_2O)$ (ICSD-22071, blue), $AlCl(OH)_2 \cdot 2(H_2O)$ (ICSD-425880, red) and $Al(OH)_3$ (ICSD-6162, black) are shown for comparison.

Optimization of $AlCl_3$ concentration

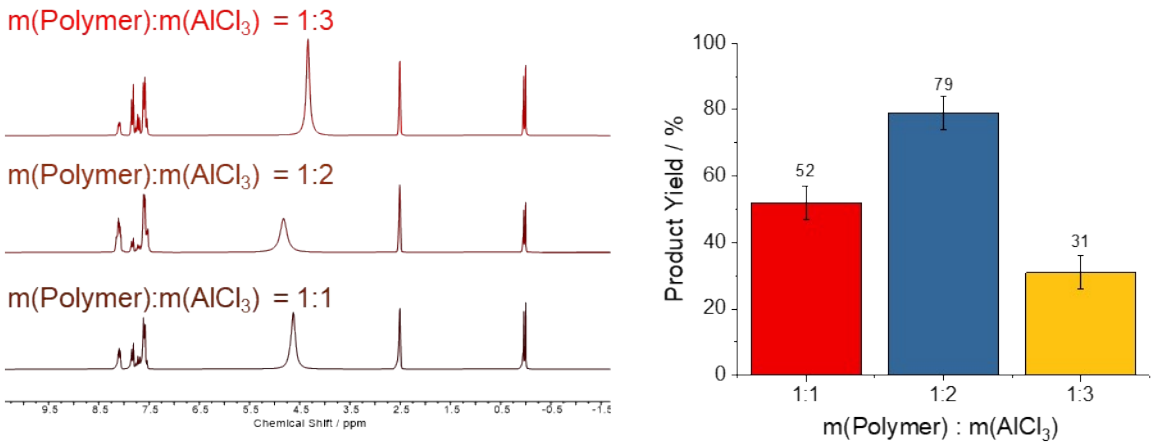


Figure S14 ^{1}H-NMR-spectra of **3a** using polymer-bound $AlCl_3$ prepared with different polymer-to-AlCl3 mass ratios as catalyst in under bulk conditions at 160°C; spectrum was recorded in DMSO-d6 (left) and comparison of the obtained product yields (right) rationalizing the 1:2 polymer:$AlCl_3$ ratio used in all further experiments