catalysts
MDPI

Supplementary Materials

C-H Bond Activation of Silyl-substituted Pyridines with Bis(phenolate)yttrium Catalysts as a facile Tool towards Hydroxyl-terminated *Michael*-type Polymers

Thomas M. Pehl [1, †], Moritz Kränzlein [1, †], Friederike Adams [1, †], Andreas Schaffer [1] and Bernhard Rieger [1,*]

[1] WACKER-Chair for Macromolecular Chemistry, Catalysis Research Center, Department of Chemistry, Technical University Munich, Lichtenbergstr. 4, 85748 Garching b. München, Germany
* Correspondence: rieger@tum.de; Tel.: +49-89-289-13570
† These authors contributed equally to this work.

1. Catalyst characterization

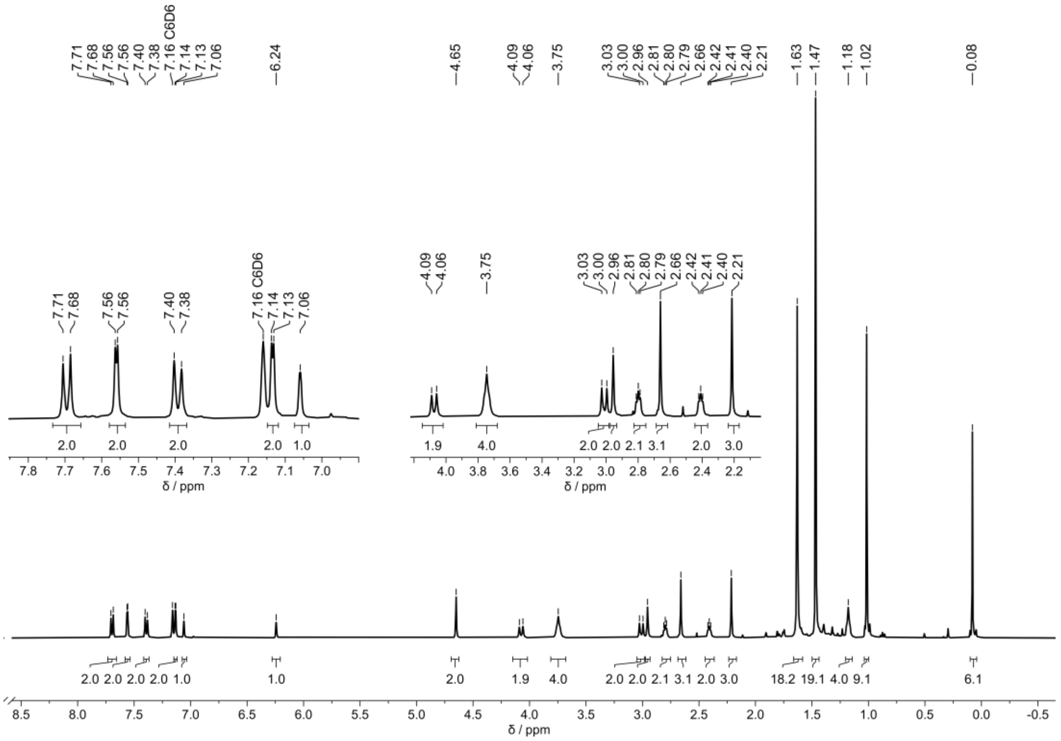


Figure S1: ^{1}H-NMR (400 MHz, C_6D_6, 300 K) of catalyst **4**.

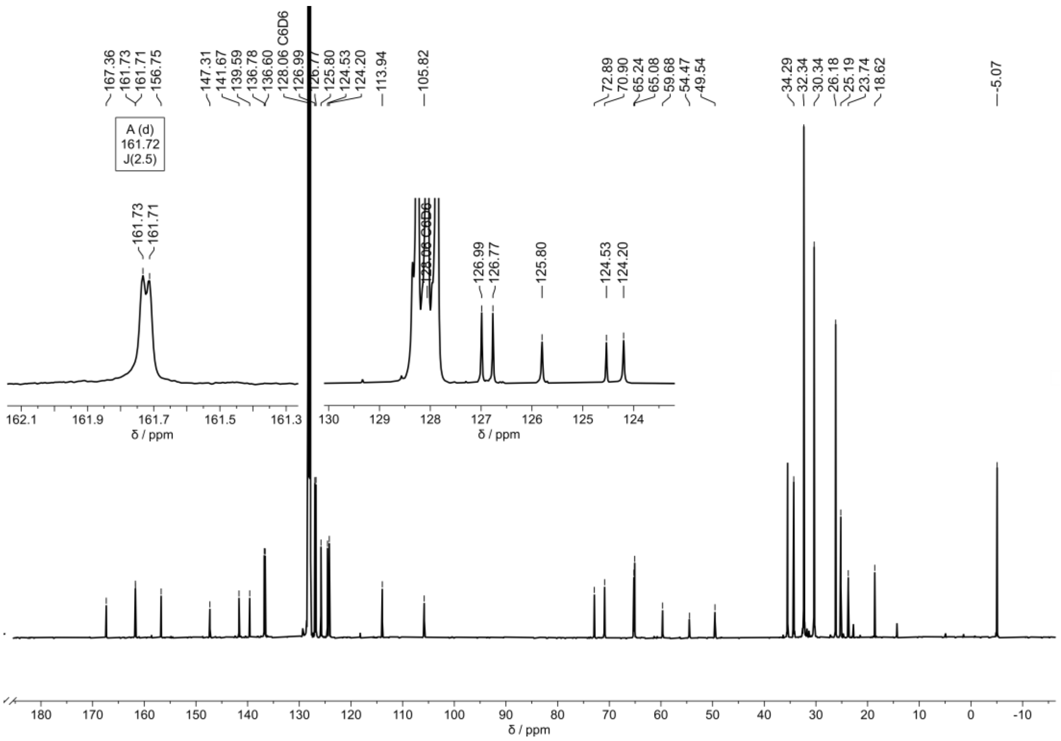


Figure S2: ^{13}C-NMR (125 MHz, C_6D_6, 300 K) of catalyst **4**.

2. End-group analysis

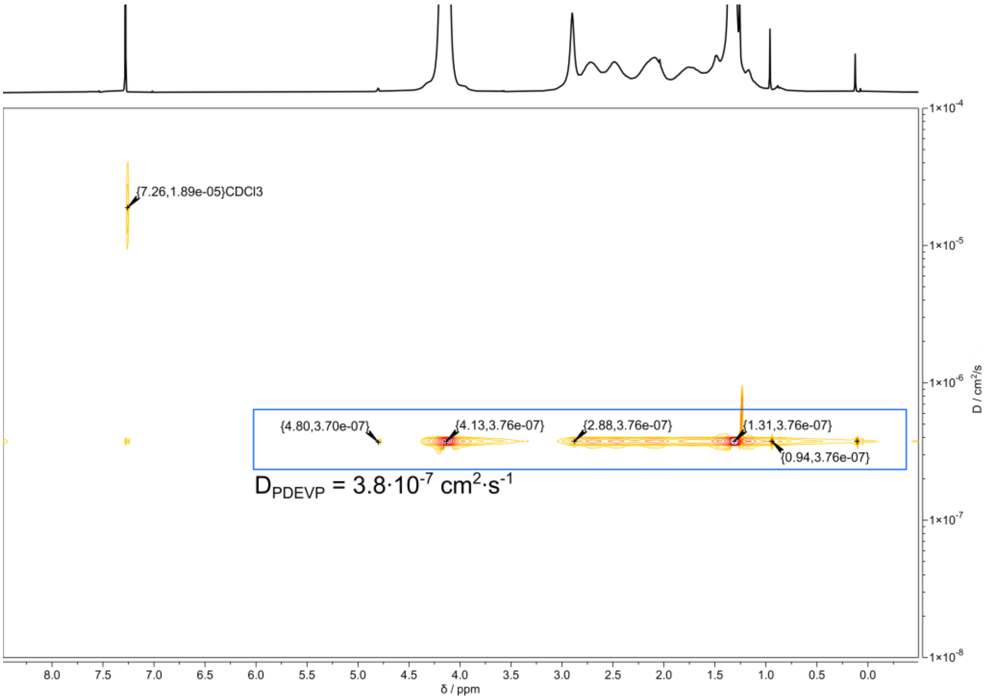


Figure S3: DOSY-NMR ($CDCl_3$, 400 MHz) of PDEVP (M_n = 43.4 kg mol^{-1}, $Đ$ = 1.11).

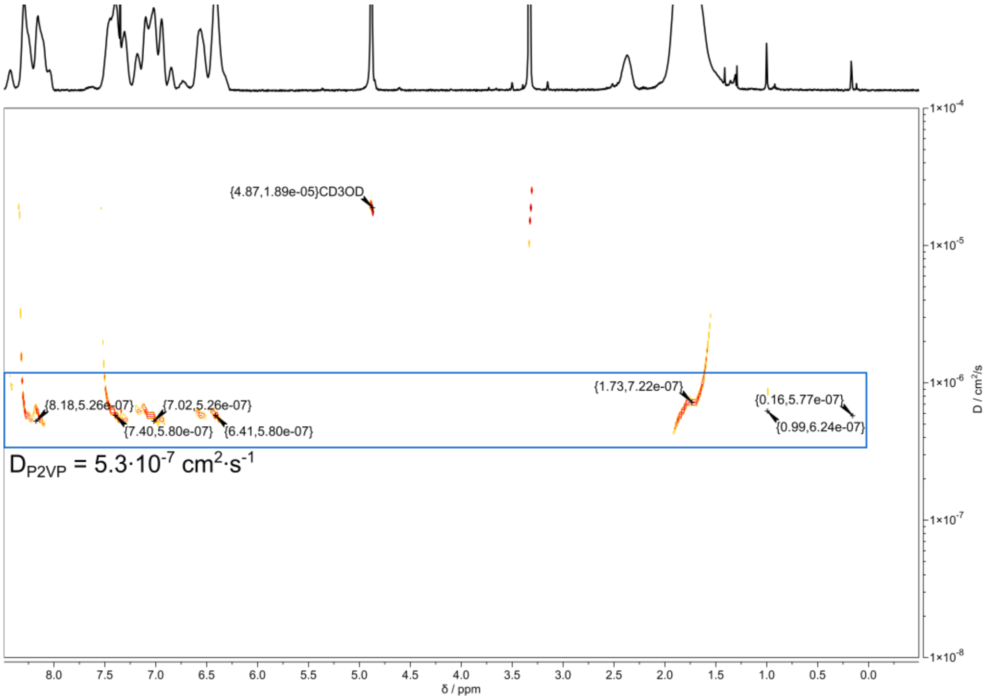


Figure S4: DOSY-NMR (MeOD, 400 MHz) of P2VP (M_n = 34.7 kg mol^{-1}, $Đ$ = 1.07).

3. Characterization of PDEVP

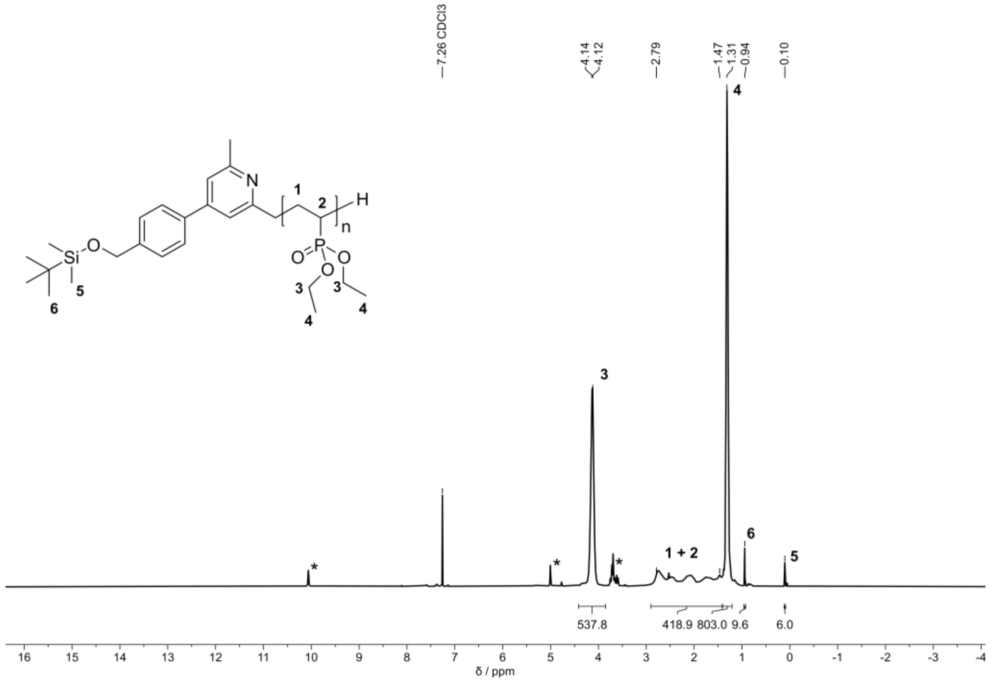


Figure S5: ^{1}H-NMR (CDCl$_3$, 400 MHz) of PDEVP produced with catalyst **4** (Table 2, entry 4, $M_{n,abs}$ = 16.6 kg/mol, $Đ$ = 1.04), impurities and artefacts are marked with *.

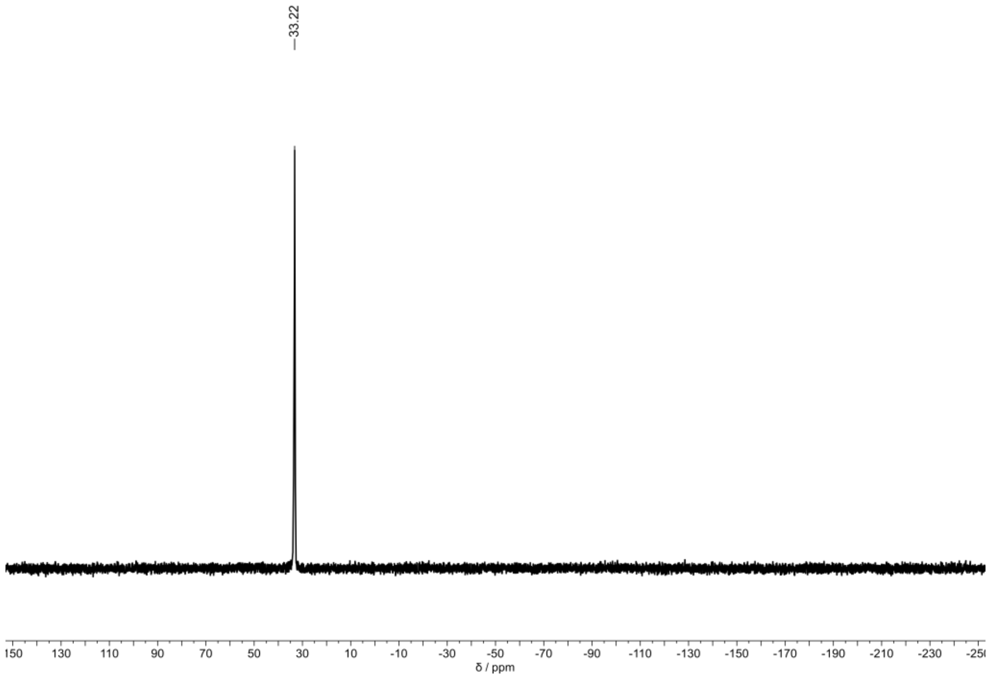


Figure S6: ^{31}P-NMR (CDCl$_3$, 162 MHz) of PDEVP produced with catalyst **4** (Table 2, entry 5, $M_{n,abs}$ = 104 kg/mol, $Đ$ = 1.33).

^{1}H-NMR (400 MHz, CDCl$_3$, 300 K): δ (ppm) = 0.10 (s, 6H, Si(CH$_3$)$_2$), 0.94 (s, 9H, Si(C(CH$_3$)$_3$)), 1.31 (m, 803H, P(OCH$_2$C*H*$_3$)$_2$), 1.47-2.79 (m, 419H, C*H*$_2$C*H*POEt$_2$), 4.12-4.14 (m, 538H, P(OC*H*$_2$CH$_3$)$_2$).
^{31}P-NMR (125 MHz, CDCl$_3$, 300 K): δ (ppm) = 33.22 (P$_{\text{side-chain}}$).

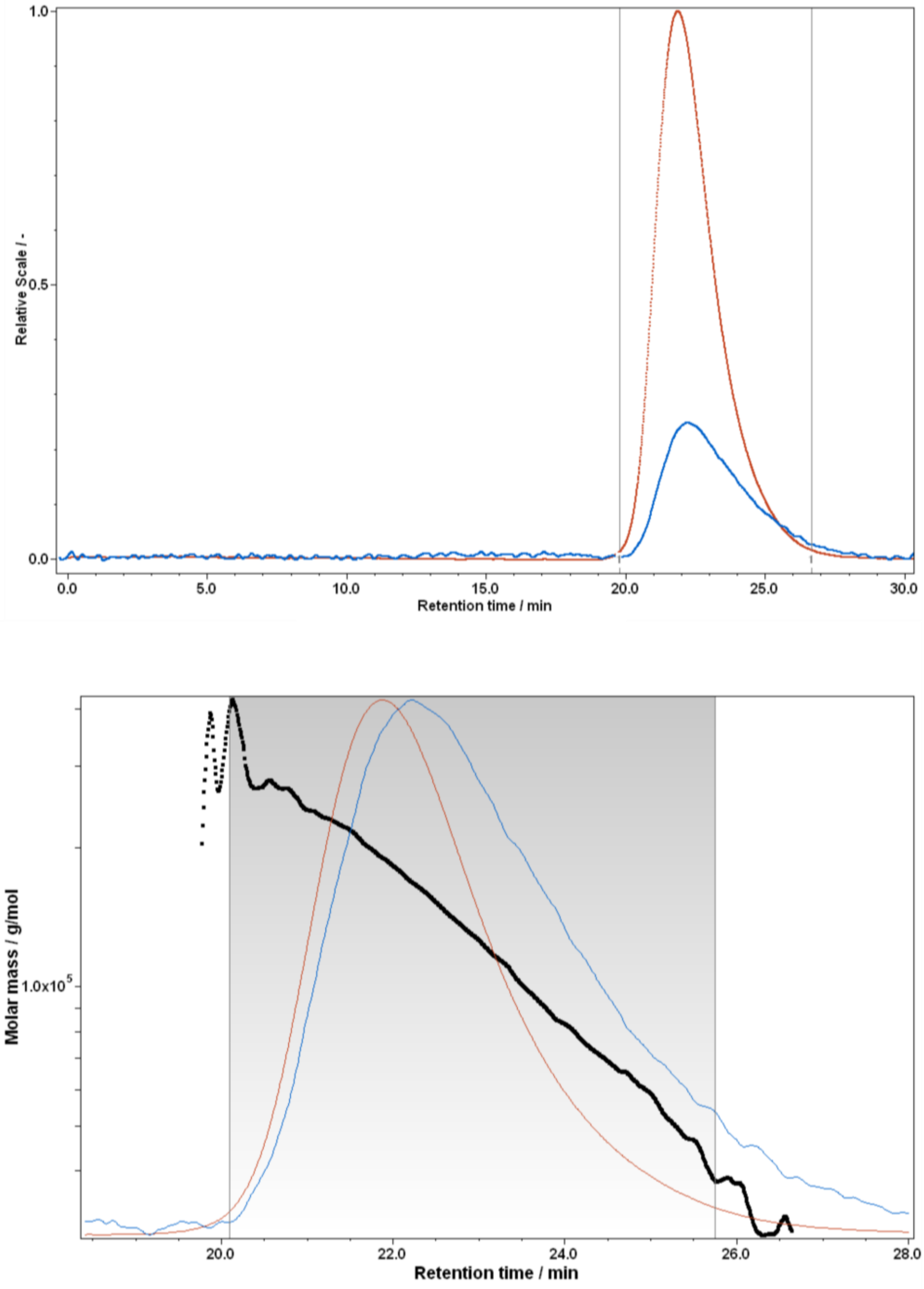


Figure S7: Representative SEC-MALS trace (top) and resulting fitting plot (bottom) for molecular weight determination of PDEVP produced with catalyst **4** (Table 2, entry 5, $M_{n,abs}$ = 104 kg/mol, $Đ$ = 1.33).

4. Characterization of Poly(2-vinylpyridine)

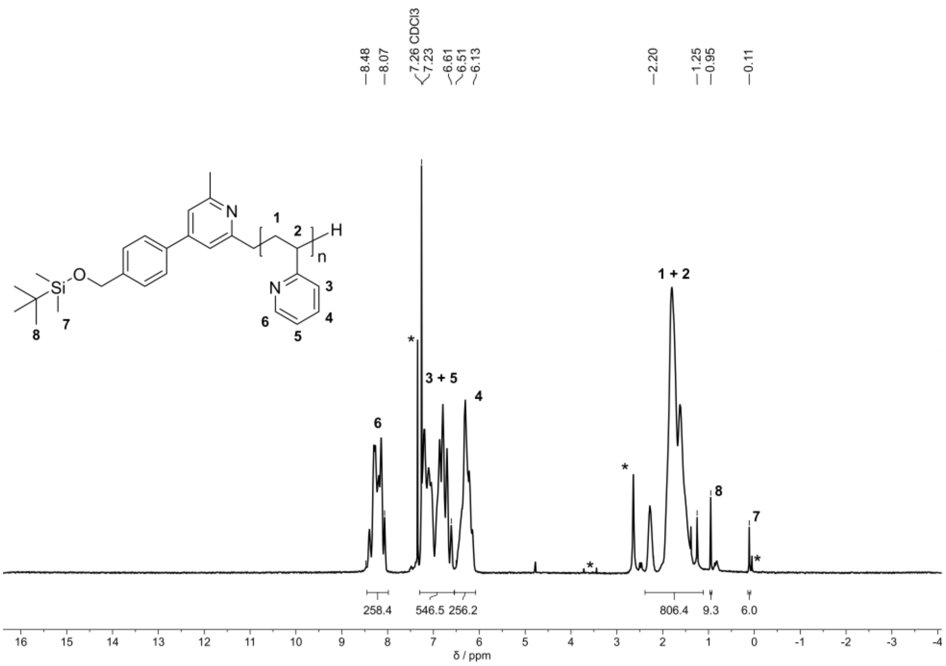


Figure S8: ^{1}H-NMR (CDCl$_3$, 400 MHz) of P2VP produced with catalyst **4** (Table 3, entry 1, $M_{n,abs}$ = 25.0 kg/mol, $Đ$ = 1.04), impurities and artefacts are marked with *.

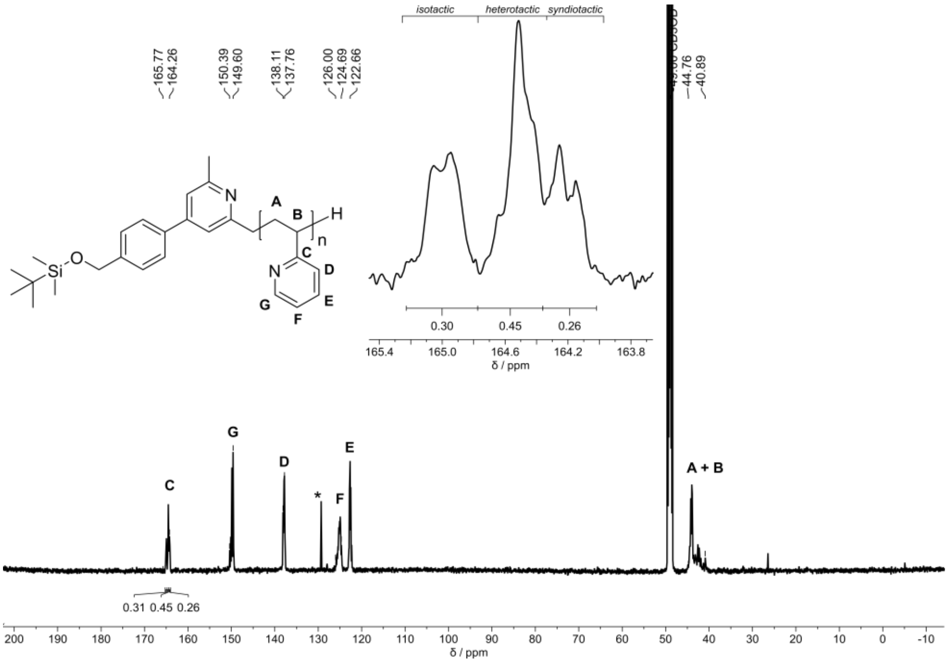


Figure S9: ^{13}C-NMR (MeOD, 500 MHz) of P2VP and section of the quaternary ^{13}C atom resonance of atactic P2VP produced with catalyst **4**, resonance assignment and microstructure determination according to Ref. [1], impurities and artefacts are marked with *.

^{1}H-NMR (400 MHz, CDCl$_3$, 300 K): δ (ppm) = 0.11 (s, 6H, Si(CH$_3$)$_2$), 0.95 (s, 9H, Si(C(CH$_3$)$_3$)), 1.25-2.20 (m, 806H, C*H*$_2$C*H*Ar), 6.13-6.50 (m, 256H, H$_{Ar}$), 6.51-7.23 (m, 456H, 2H$_{Ar}$), 8.07-8.48 (m, 258H, H$_{Ar}$).

^{13}C-NMR (100 MHz, CDCl$_3$, 300 K): δ (ppm) = 40.9-44.8 (carbon-backbone), 122.7-123.0, 124.7-126.0, 137.8-138.1, 159.6-150.4, 164.3-165.8.

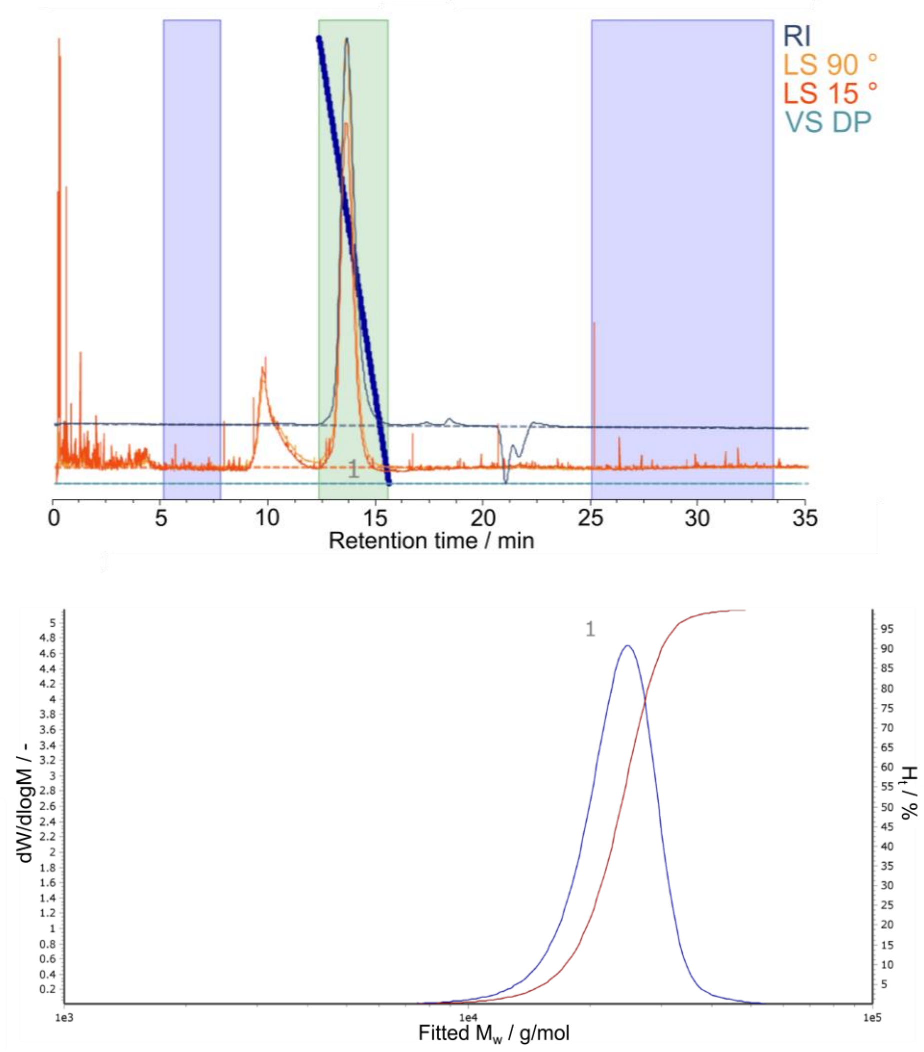


Figure S10: Representative SEC-trace (top) and distribution plot of molecular weight determination (bottom) of P2VP produced with catalyst **4** (Table 3, entry 3, $M_{n,abs}$ = 22.6 kg/mol, *Đ* = 1.06). Signals in the light scattering detectors (orange, red) with retention time below 10 min are not detectable via RI (dark blue), therefore signals do not belong to polymeric material.

5. Deprotection results

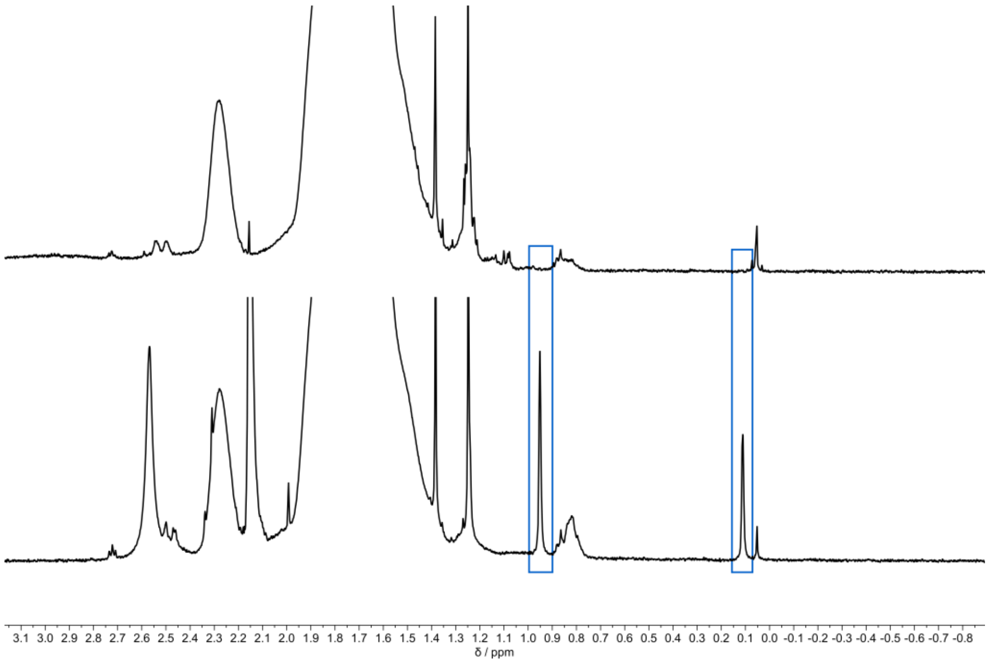


Figure S11: Representative comparison of ^{1}H-NMR spectra (silyl range, δ = -0.5 – 3.0 ppm) of protected (bottom) and deprotected (top) P2VP (Table 4, entry 2) with close-up of the silyl region (TBDMS signals marked blue).

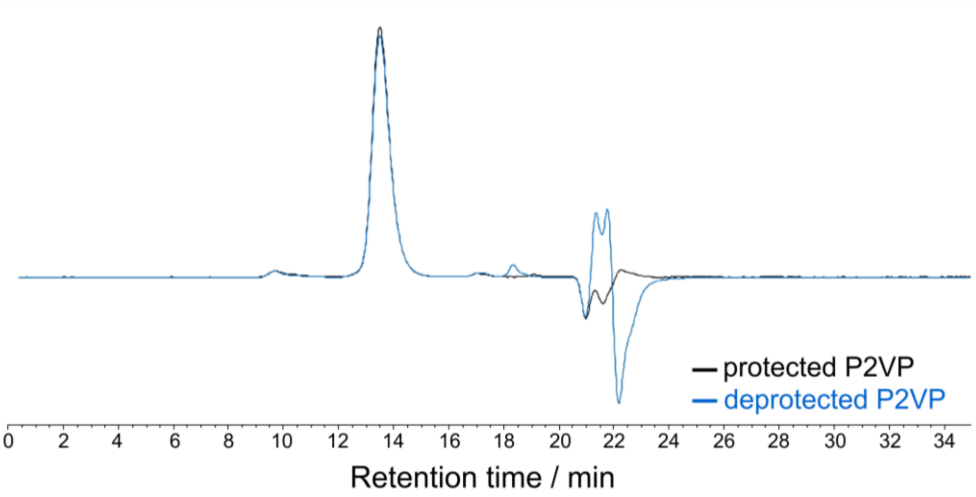


Figure S12: Overlay of SEC RI traces of P2VP protected and deprotected (Table 4, entry 2) (protected black, deprotected blue).

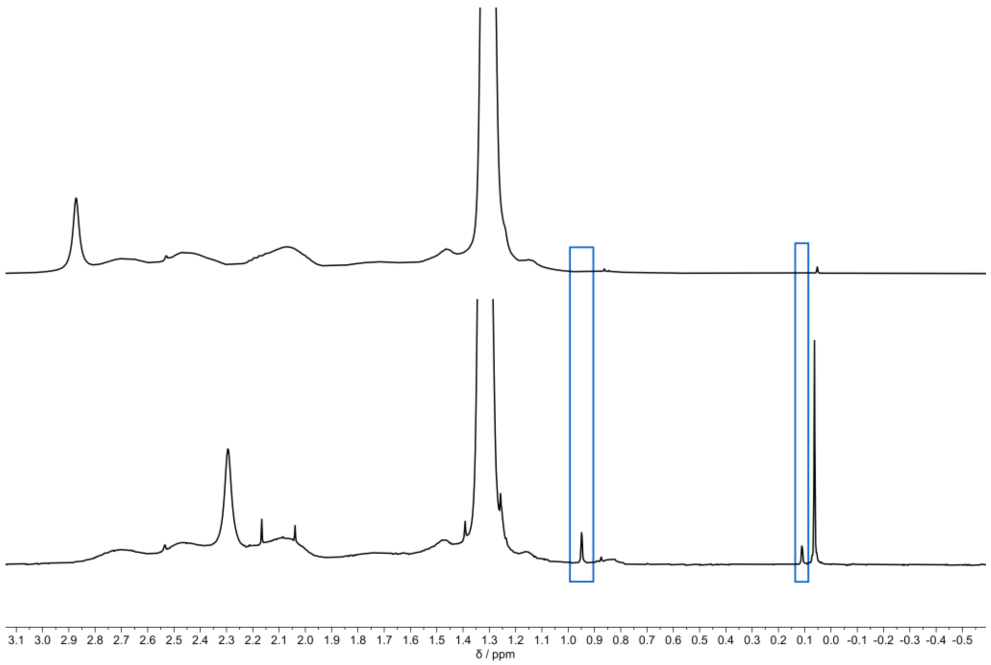


Figure S13: Representative comparison of ^{1}H-NMRs (silyl range, $\delta = -0.5 - 3.0$ ppm) of protected (bottom) and unprotected (top) PDEVP (Table 4, entry 1) with close-up of the silyl region (TBDMS signals marked blue).

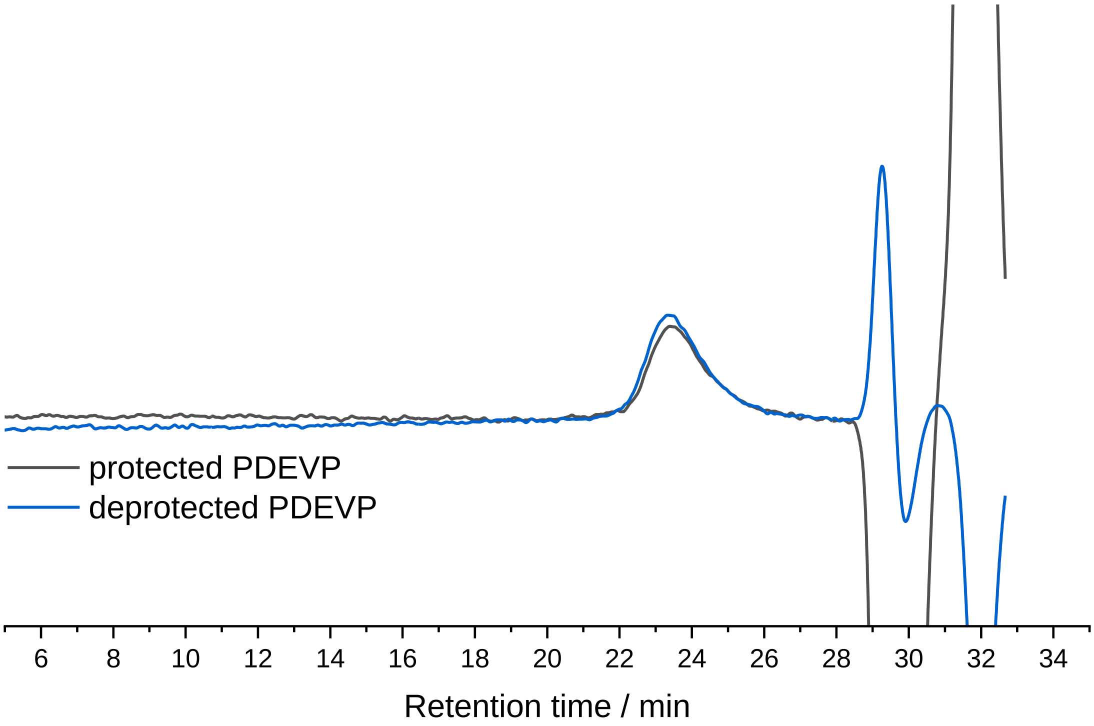
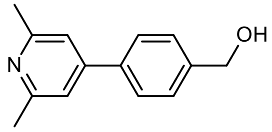


Figure S14: Overlay of SEC-MALS RI traces of PDEVP (Table 4, entry 1) protected and deprotected (protected black, deprotected blue).

6. Synthesis procedures

4-(4′-hydroxymethyl)benzyl)-2,6-dimethylpyridine [2]



1

2.95 g (19.4 mmol, 1.1 eq.) 4-(hydroxymethyl)phenyl boronic acid are suspended in 120 mL ethanol and 2.48 g (17.5 mmol, 1.0 eq.) 4-chloro-2,6-dimethylpyridine in 150 mL toluene are added. To this suspension, a saturated sodium hydrogen carbonate solution (120 mL, 1.14M, 136 mmol, 7.7 eq.) is added and the two-phase mixture is degassed while stirring by applying 20 cycles of inert gas and vacuum until boiling is observed. Under argon overpressure, 4 mol% $Pd(PPh_3)_4$ catalyst (0.82 g, 0.71 mmol, 0.04 eq.) are added before heating to 80 °C for 72 hours. After cooling to room temperature, black catalyst residue is removed via filtration and the phases are separated. The aqueous phase is extracted with 2×80 mL ethyl acetate and 1×100 mL chloroform, the organic phases are combined and dried over $MgSO_4$. The solvent is removed *in vacuo* before purifying the crude product by column chromatography (alumina *Bronkhorst* activity grade 1, $CHCl_3$:MeOH = 95:5) giving 4-(4′-hydroxymethylbenzyl)-2,6-dimethlypyridine) **1** as fine, white powder (1.84 g, 8.6 mmol, 49 %).

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 2.58 (s, 6H, CH_3), 4.76 (s, 2H, C*H*$_2$OH), 7.17 (s, 2H, $H_{Ar,Py}$), 7.46 (d, $^3J_{H,H}$ = 8.24 Hz, 2H, $H_{Ar,Benzyl}$), 7.61 (d, $^3J_{H,H}$ = 8.42 Hz, 2H, $H_{Ar,Benzyl}$).

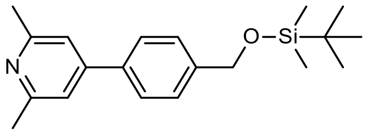
^{13}C-NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.5, 64.6, 118.5, 127.2, 127.5, 137.8, 142.1, 149.0, 158.2.

DC: R_f = 0.47 (chloroform:methanol = 95:5) [fluorescence staining]

ESI-MS: 214.29 m/z [M+H$^+$].

EA: calc: C 78.84, H 7.09, N 6.57, O 7.50.
found: C 78.33, H 7.08, N 6.52.

4-(4′-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-2,6-dimethylpyridine [2]



2

2.00 g (9.4 mmol, 1.0 eq.) unprotected pyridine **1** and 0.70 g (10.3 mmol, 1.1 eq.) imidazole are dissolved in 100 mL dry chloroform. 1.55 g (10.3 mmol, 1.1 eq.) *tert*-butyl-dimethylsilyl chloride are dissolved in 3 mL dry chloroform and are added to the alcohol mixture. The reaction solution is heated to 70 °C for 72 hours before removing the solvent *in vacuo*. 200 mL half-saturated sodium hydrogen carbonate solution (200 mL, 0.57m, 114 mmol, 12.1 eq.) are added to the crude product and the two-phase mixture is stirred for 30 min. The phases are separated and the aqueous phase is extracted with 3×150 mL benzene. The organic phases are combined and dried over $MgSO_4$. The solvent is removed, yielding 4-(4′-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-2,6-dimethylpyridine **2** as a yellow, viscous liquid (3.00 g, 9.2 mmol, 98 %).

^{1}H-NMR (400 MHz, C_6D_6, 300 K): δ (ppm) = 0.10 (s, 6H, $Si(CH_3)_2$), 1.03 (s, 9H, ^{t}Bu), 2.52 (s, 6H, CH_3), 4.66 (s, 2H, C*H*$_2$OH), 6.97 (s, 2H, $H_{Ar,Py}$), 7.36 (d, $^3J_{H,H}$ = 8.06 Hz, 2H, $H_{Ar,Benzyl}$), 7.41 (d, $^3J_{H,H}$ = 8.33 Hz, 2H, $H_{Ar,Benzyl}$).

^{13}C-NMR (100 MHz, C_6D_6, 300 K): δ (ppm) = -5.1, 18.6, 24.7, 26.1, 64.9, 118.2, 126.9, 127.3, 138.1, 142.4, 148.7, 158.6.

^{29}Si-NMR (80 MHz, C_6D_6, 300 K): δ (ppm) = 20.04.

ESI-MS: 329.0 m/z [M+H$^+$].

EA: calc: C 73.34, H 8.92, N 4.28, O 4.88, Si 8.57.
found: C 73.38, H 9.14, N 4.48.

7. References

1. Altenbuchner, P.T.; Adams, F.; Kronast, A.; Herdtweck, E.; Pöthig, A.; Rieger, B. Stereospecific catalytic precision polymerization of 2-vinylpyridine via rare earth metal-mediated group transfer polymerization with 2-methoxyethylamino-bis(phenolate)- yttrium complexes. *Polym. Chem.*, **2015**, *6*, 6796–6801.
2. Schaffer, A; Kränzlein, M.; Rieger, B. Synthesis and Application of Functional Group-Bearing Pyridyl-based Initiators to Rare-Earth Metal-Mediated Group-Transfer Polymerization. *Macromolecules* under review.