Supporting information of

Highly 2,3-selective polymerization of phenylallene and the derivatives by vanadium complexes

Xiang Gao, Jinxin Nie, Xiaojian Chen, Li Zhou, Xiaohua Hou* and Hui Zou*
Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei 230009, Anhui Province, People's Republic of China.

1. Synthesis of vanadium tricloride complexes

Synthesis of $\mathrm{V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3}$ (S1)

Into a sealed Schlenk glass tube, n-octane (40 mL) and $VOCl_3$ (4.55 g, 26.20 mmol) were added sequentially in the drybox, and 2,6-dimethylphenyl isocyanate (2.65 g, 17.40 mmol) was then added to the mixture. The mixture was placed in an oil bath preheated at 135 °C, and was stirred overnight (>12 h). CO_2 evolved was released at certain time. After the reaction, the solution was filtered through a Celite pad, and the filter cake was washed with hexane several times. The combined filtrate and the wash were placed into dryness under reduced pressure to remove volatiles. The resultant residue was dissolved in a minimum amount of hot n-hexane. Green microcrystals (4.01g, yield: 83 %) were collected from the chilled solution (placed in the freezer at -30 °C). ^{1}H NMR($CDCl_3$, 600 MHz, 25 °C): *δ* 7.01(s, 3H, Ph-H), 2.88(s, 6H, CH_3) ppm.

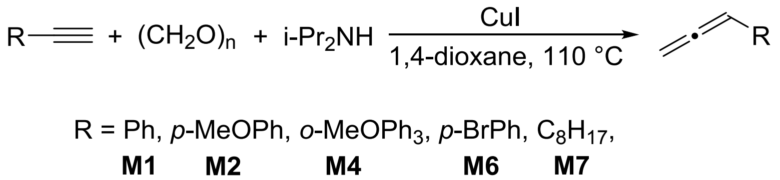
Synthesis of $\mathrm{V(N\text{-}2,4\text{-}F_2C_6H_3)Cl_3}$ (S3)

Synthesis of **L3** was carried out by the same procedure as that in **L1** except that 2,4-difluorophenyl isocyanate (2.14 g, 13.70 mmol) in place of 2,6-dimethylphenyl isocyanate was used. The product exhibited as brown solid (3.39 g, 87% yield). ^{1}H NMR($CDCl_3$, 600 MHz, 25 °C): *δ* 7.65(q, 1H, Ph-H), 6.93(m, 2H, Ph-H) ppm. ^{19}F NMR ($CDCl_3$, 600 MHz, 25 °C): *δ* -95.33, -110.00 ppm. ^{13}C NMR ($CDCl_3$, 600 MHz, 25 °C): *δ* 164.7, 163.0, 161.4, 159.7, 130.7, 111.8, 105.1 ppm.

Synthesis of $\mathrm{V(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(DME)Cl_3}$ (S2)

Into a sealed Schlenk glass tube, n-octane (25 mL) and $VOCl_3$ (2.48 g, 14.31 mmol) were added sequentially in the drybox, and 2,6-diisopropylphenylisocyanate (2.00 g, 9.54 mmol) was then added to the mixture. The mixture was placed in an oil bath preheated at 135 °C, and was stirred overnight (>12 h). CO_2 evolved was released at certain time. After the reaction, the solution was filtered through a Celite pad, and the filter cake was washed with hexane several times. Then 1 mL DME was added to the solution. The formed yellow solid was collected and dried in vacuum to obtain a yellow-brown solid (4.02 g), yield: 99 %. ^{1}H NMR($CDCl_3$, 600 MHz, 25 °C): δ 7.14(d, *J* = 7.8 Hz, 2H, m-Ph-H), 7.04 (t, 1H, p-Ph-H), 4.67 (m, 2H, CH), 3.89 (s, 4H, DME-CH_2), 3.67 (s, 6H, DME-CH_3), 1.40(d, *J* = 6.6 Hz, 12H, CH_3) ppm.

2. Synthesis of Substituted Allenes



Synthesis procedure of monomer M1: Monomer **M1** was prepared according to the literature. Paraformaldehyde (10.28 g, 343 mmol, 2.5 eq.), cuprous iodide (13.05 g, 69 mmol, 0.5 eq.) was added into a 250 mL two-neck flask. The system was evacuated and replaced with nitrogen for three times. Then diisopropylamine (24.96 g, 247 mmol, 1.8 eq.), 1,4-dioxane (130 mL) and phenylacetylene (14 g, 137 mmol, 1eq.) were sequentially added. The solution was refluxed for 18 h at 110 ºC. Then reaction flask was cooled to room temperature. 300 mL of water was added to the solution. The pH was adjusted to2 with diluted hydrochloric acid. The crude product was extracted by Et_2O (3×40 mL). The organic phases was washed with water and dried over anhydrous sodium sulfate for 1 h. The crude product was purified by silica gel chromatography. The afforded monomer **M1** was pale yellow liquid (6.56 g, yield 41%). ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C): *δ* 7.32 (d, *J* = 4.2 Hz, 4H, *om*-Ph-*H*), 7.21 (m, 1H, *p*-Ph-*H*), 6.18 (s, 1H, =C*H*), 5.17 (d, *J* = 6.6 Hz, 2H, =C*H₂*) ppm.

Monomer **M2, M4, M6** and **M7** were prepared followed the similar procedure described above, the corresponding characterization are showed below:

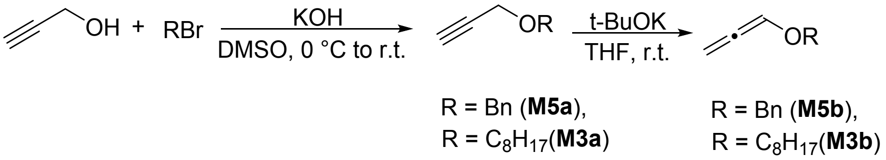
Monomer **M2**: 3.08 g of pale yellow liquid with 21% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): *δ* 7.23 (d, 2H, *o*-Ph-*H*), 6.85 (d, 2H, *m*-Ph-*H*), 6.12 (t, *J* = 7.2 Hz, 1H, =C*H*), 5.11 (d, *J* = 6.6 Hz, 2H, =C*H₂*,), 3.80 (s, 3H, OC*H₃*) ppm.

Monomer **M4**: 5.41 g of pale yellow liquid with 37% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): *δ* 7.39 (d, 1H, *3*-Ph-*H*), 7.19 (t, 1H, *4*-Ph-*H*), 6.91 (d, 1H, *5*-Ph-*H*), 6.87 (t, 1H, *6*-Ph-*H*), 6.57 (t, *J* = 7.2

Hz, 1H, =C*H*), 5.11 (d, *J* = 6.6 Hz, 2H, =C*H₂*), 3.85 (s, 3H, OC*H₃*) ppm.

Monomer **M6**: 4.49 g of pale yellow liquid with 36% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.41 (m, 2H, *o*-Ph-*H*), 7.17 (m, 2H, *m*-Ph-*H*), 6.11 (t, *J* = 7.2 Hz, 1H, =C*H*), 5.14 (d, *J* = 6.6 Hz, 2H, =CH_2) ppm.

Monomer **M7**: 2.74 g of pale yellow liquid with 36% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 5.13 (m, *J* = 10.2 Hz, 1H, =C*H*), 4.66 (m, *J* = 10.2 Hz, 2H, =CH_2), 2.00 (m, 2H, =CHCH_2), 1.44 (m, 12H, CH_2), 0.86 (t, *J* = 6.6 Hz, 3H, CH_3) ppm.



Synthesis procedure of M5a: Into a 250 mL two-neck flask, propargyl alcohol (3.74 g, 66.66 mmol) were added to DMSO solution (100 mL) containing KOH (8.42 g, 150 mmol, 3 eq.) at 0 °C. After stirring for 30 min, benzyl bromide (8.55 g, 50.0 mmol, 1 eq.) was added. The reaction mixture was then warmed slowly to room temperature and stirred for 10 h. The brown suspension was diluted with 200 mL water and extracted with diethyl ether (3 × 50 mL). The combined organic phase was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography. The monomer **M5a** was afforded as a colorless liquid (5.70 g, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.39 (m, 5H, Ph-*H*), 4.62 (s, 2H, CH_2), 4.20 (d, *J* = 2.4 Hz, 2H, OCH_2), 2.49 (t, *J* = 2.4 Hz, 1H, C*H*) ppm.

Synthesis procedure of monomer M5b: In a 250 mL two-neck flask, **M5a** (5.70 g, 39.0 mmol, 1 eq.) was added into a THF solution (100 mL) containing ^{t}BuOK (5.25 g, 46.8 mmol, 1.2 eq.) at room temperature. The suspension was stirred at room temperature for 5 h and then filtered through celite pad. The filtrate was washed with Et_2O (3 × 50 mL). Combined solution was concentrated under reduced pressure, and the crude product was purified by silica gel chromatography. The monomer **M5b** was afforded as a pale yellow liquid (4.33 g, yield 76%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.38 (m, 5H, Ph-*H*), 6.88 (t, *J* = 6.0 Hz, 1H, =C*H*), 5.51 (d, *J* = 5.4 Hz, 2H, =CH_2), 4.66 (d, *J* = 5.4 Hz, 2H, OCH_2) ppm.

M3a and **M3b** were prepared followed the similar procedure as described above, the characterization data are showed below: **M3a:** 7.89 g of colorless liquid with 70% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 4.13 (s, 2H, OCH_2), 3.50 (t, 2H, OCH_2), 2.41 (s, 1H, C*H*), 1.59 (t, 2H, OCH_2CH_2), 1.34 (m, 10H, CH_2), 0.88 (t, 3H, CH_3) ppm. **M3b**: 2.04 g of colorless liquid with 68% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 6.72 (t, *J* = 6.0 Hz, =CH, 1H), 5.42 (d, *J* = 5.4 Hz, 2H, =CH_2), 3.54 (t, *J* = 6.6 Hz, 2H, OCH_2), 1.63 (m, 2H, OCH_2CH_2), 1.26 (m, 10H, CH_2), 0.88 (t, *J* = 7.2 Hz, 3H, CH_3) ppm.

3. The additional NMR spectra of vanadium complexes

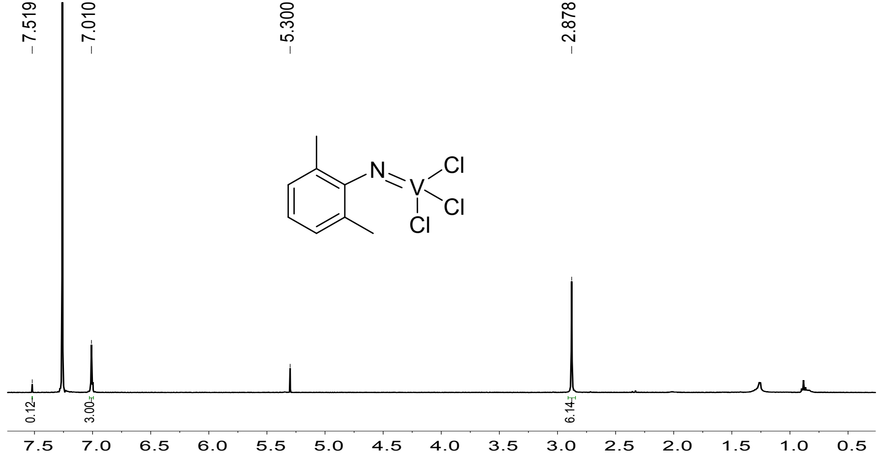


Figure S1. ^{1}H NMR (600 MHz) spectrum of ligand **S1** recorded in $CDCl_3$ at 25 °C.

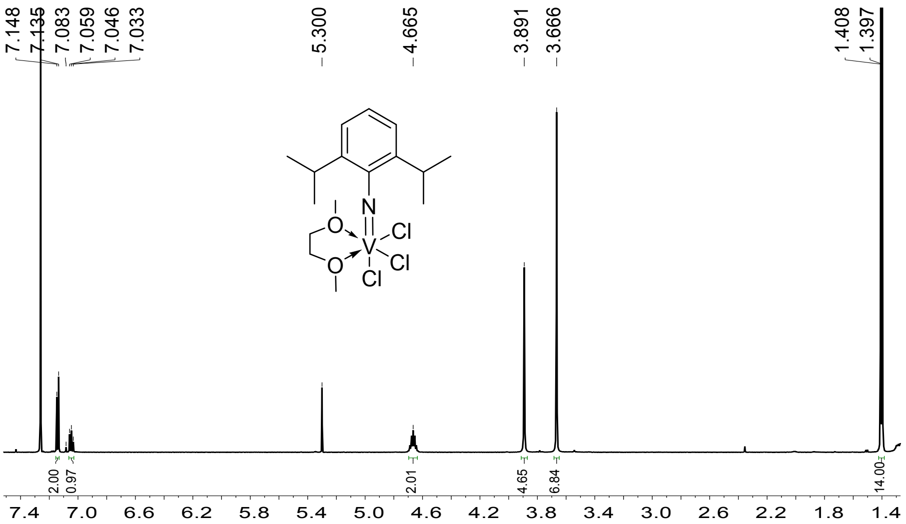


Figure S2. ^{1}H NMR (600 MHz) spectrum of ligand **S2** recorded in $CDCl_3$ at 25 °C.

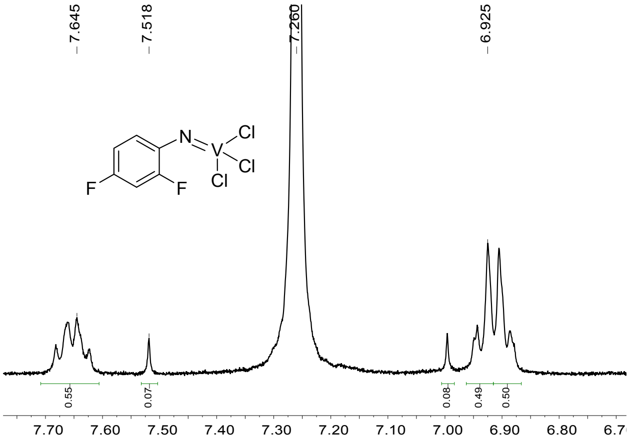


Figure S3. ^{1}H NMR (600 MHz) spectrum of ligand **S3** recorded in $CDCl_3$ at 25 °C.

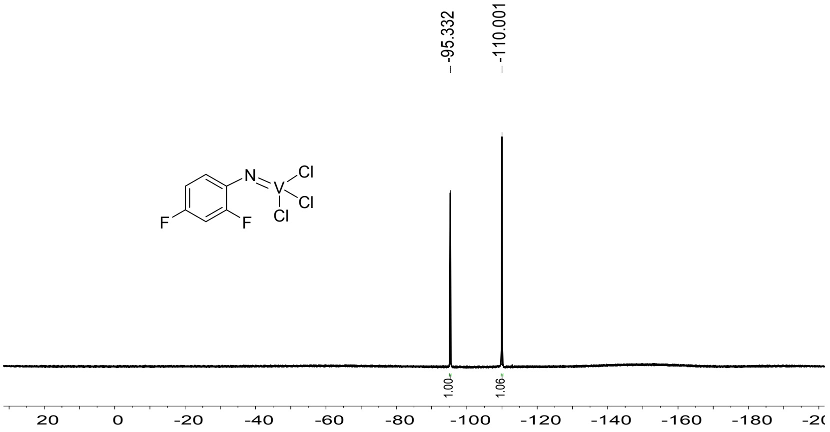


Figure S4. ^{19}F NMR (600 MHz) spectrum of ligand **S3** recorded in $CDCl_3$ at 25 °C.

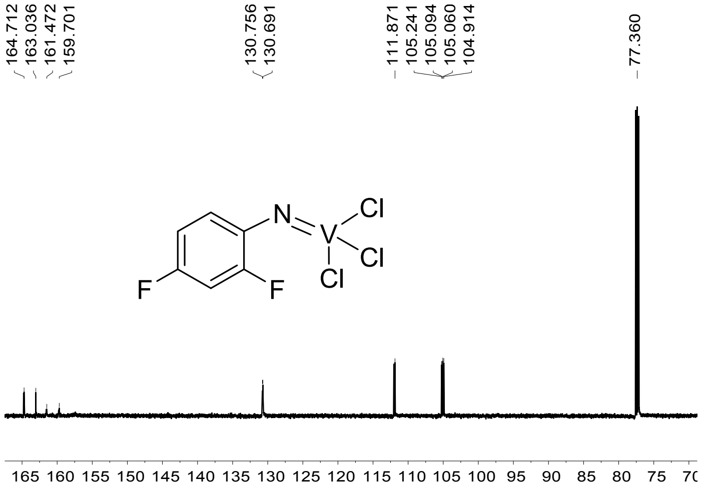


Figure S5. ^{13}C NMR (600 MHz) spectrum of ligand **S3** recorded in $CDCl_3$ at 25 °C.

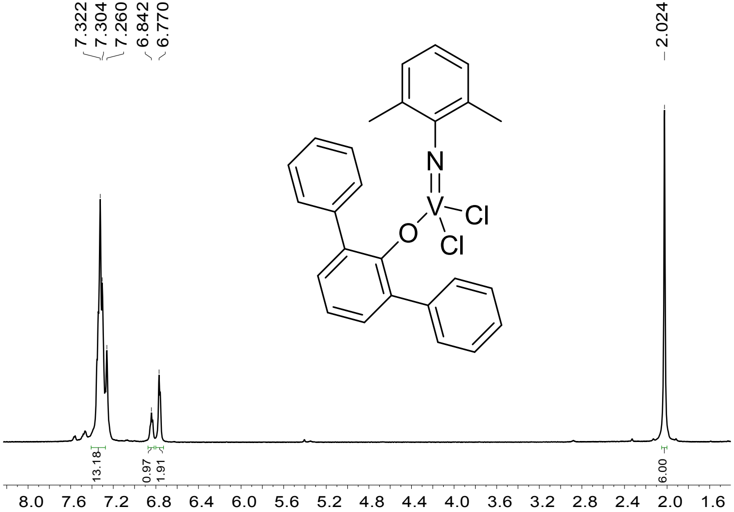


Figure S6. ^{1}H NMR (600 MHz) spectrum of catalyst **C1** recorded in $CDCl_3$ at 25 °C.

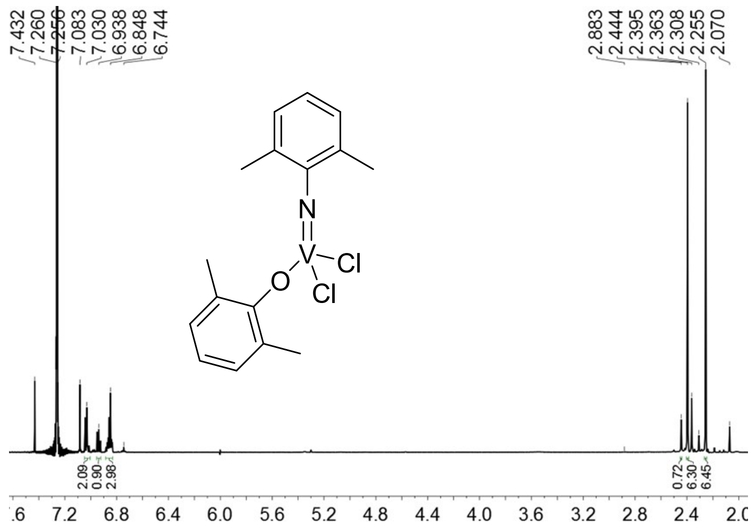


Figure S7. ^{1}H NMR (600 MHz) spectrum of catalyst **C6** recorded in $CDCl_3$ at 25 °C.

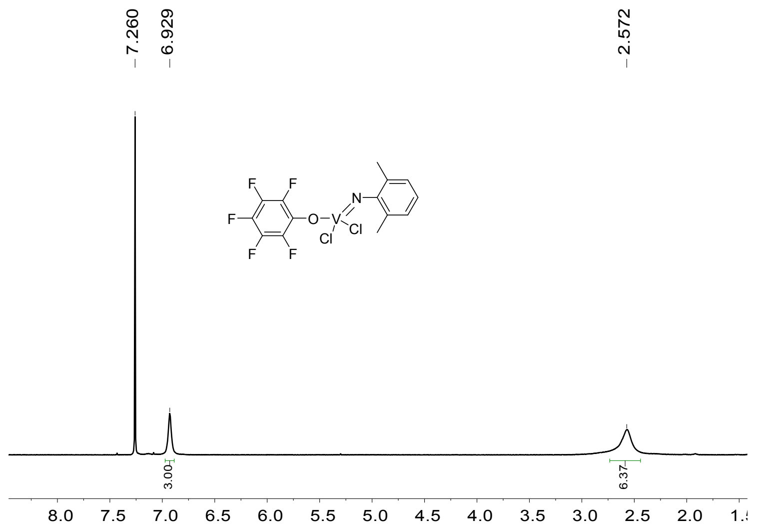


Figure S8. ^{1}H NMR (600 MHz) spectrum of catalyst **C5** recorded in $CDCl_3$ at 25 °C.

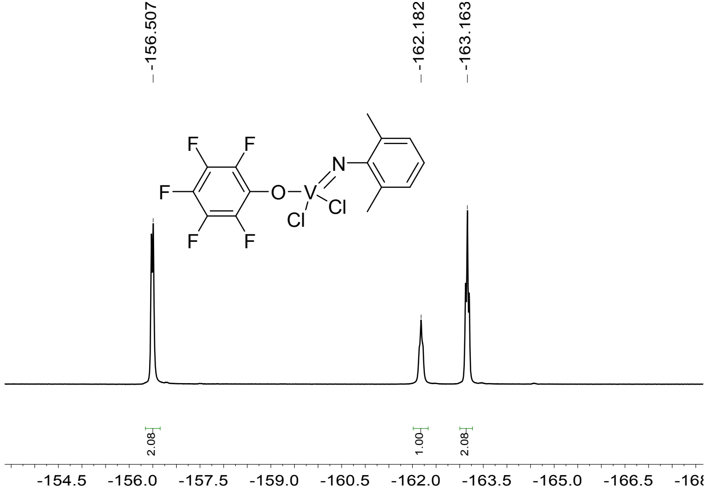


Figure S9. ^{19}F NMR (600 MHz) spectrum of catalyst **C5** recorded in $CDCl_3$ at 25 °C.

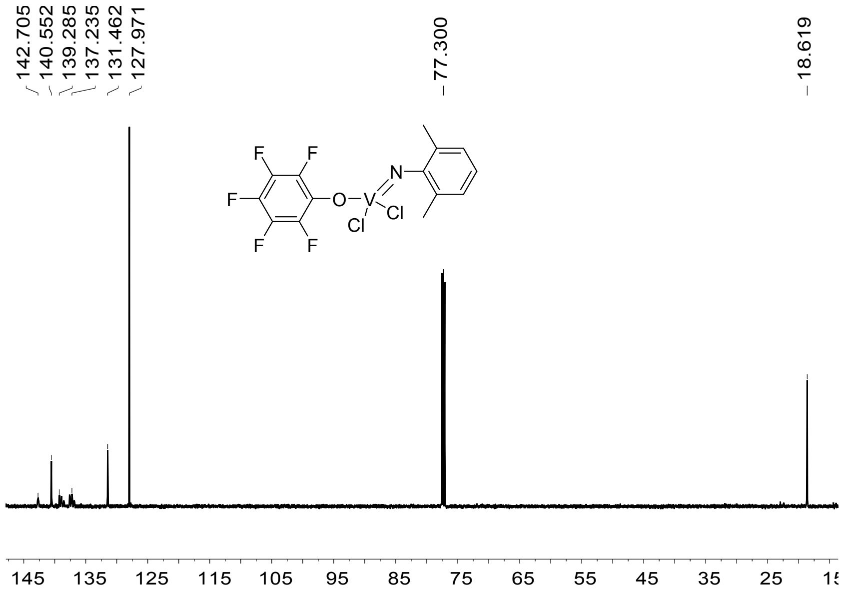


Figure S10. ^{13}C NMR (600 MHz) spectrum of catalyst **C5** recorded in $CDCl_3$ at 25 °C

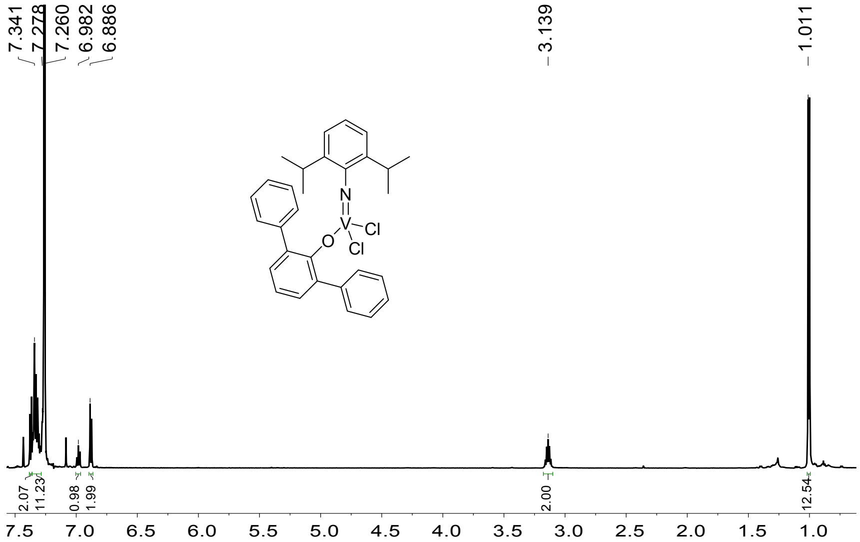


Figure S11 . ^{1}H NMR (600 MHz) spectrum of catalyst **C3** recorded in $CDCl_3$ at 25 °C.

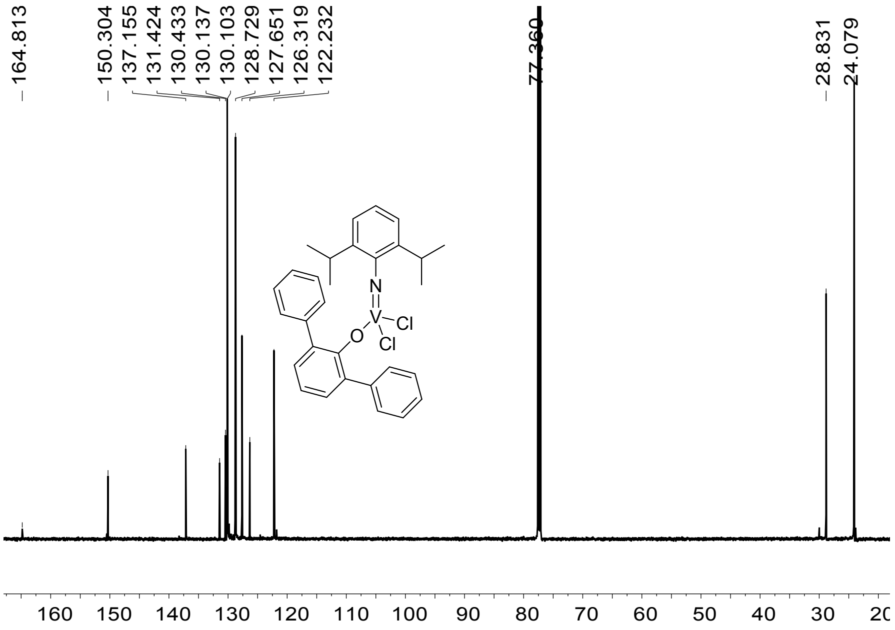


Figure S12. ^{13}C NMR (600 MHz) spectrum of catalyst **C3** recorded in $CDCl_3$ at 25 °C.

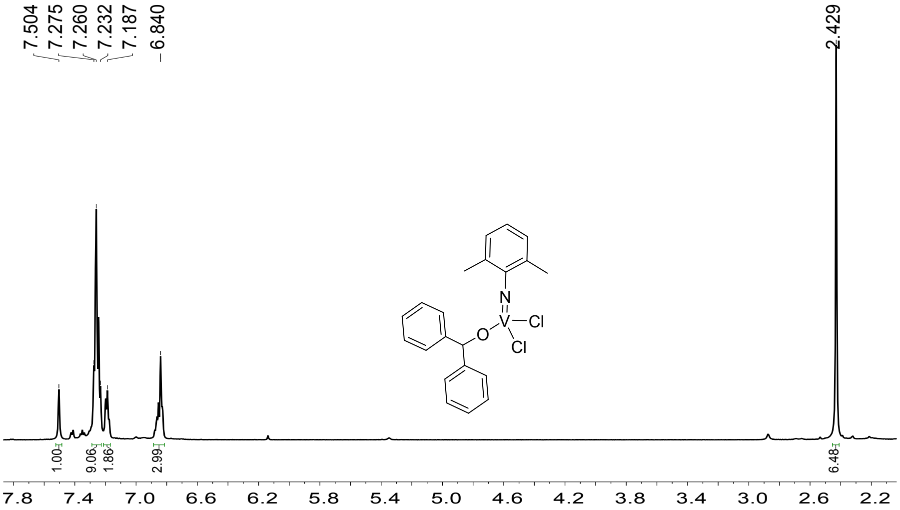


Figure S13. ^{1}H NMR (600 MHz) spectrum of catalyst **C4** recorded in $CDCl_3$ at 25 °C.

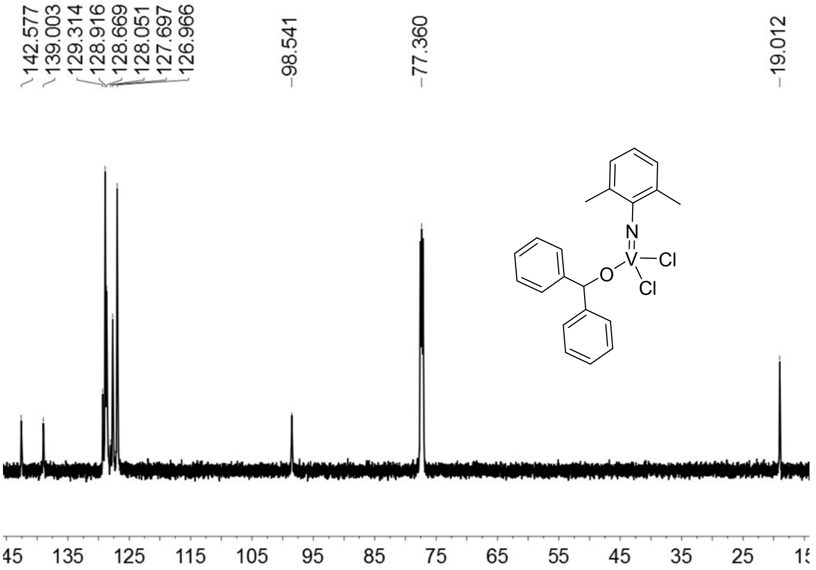


Figure S14. ^{13}C NMR (600 MHz) spectrum of catalyst **C4** recorded in CDCl$_3$ at 25 °C.

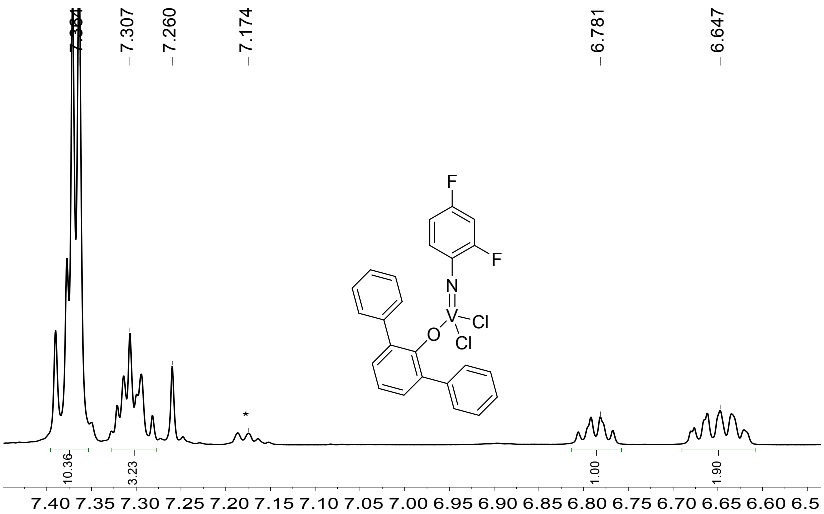


Figure S15. ^{1}H NMR (600 MHz) spectrum of catalyst **C2** recorded in CDCl$_3$ at 25 °C.

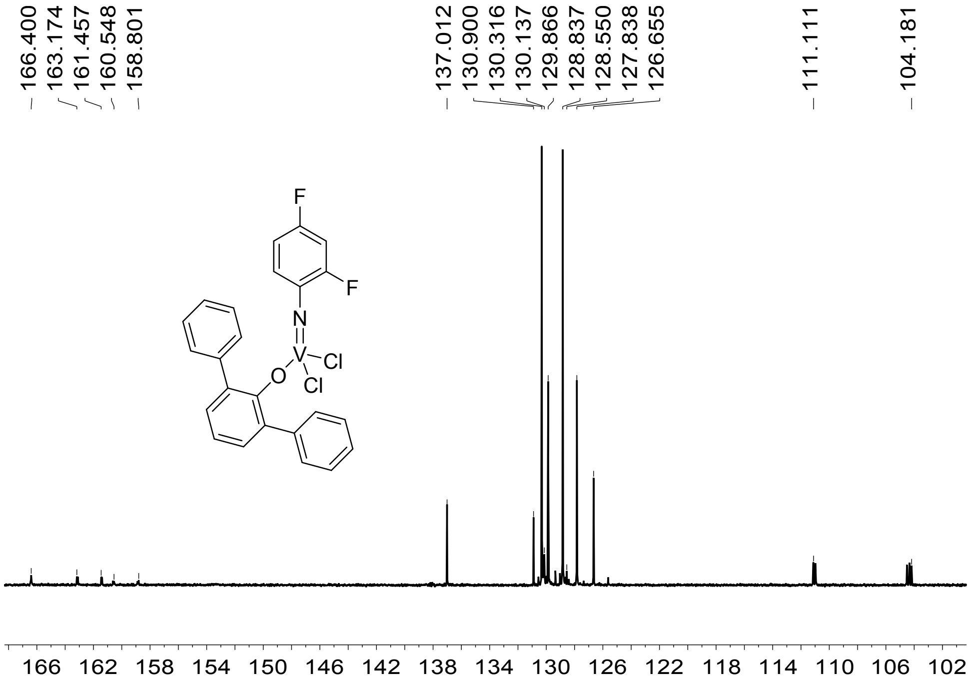


Figure S16. ^{13}C NMR (600 MHz) spectrum of catalyst **C2** recorded in $CDCl_3$ at 25 °C.

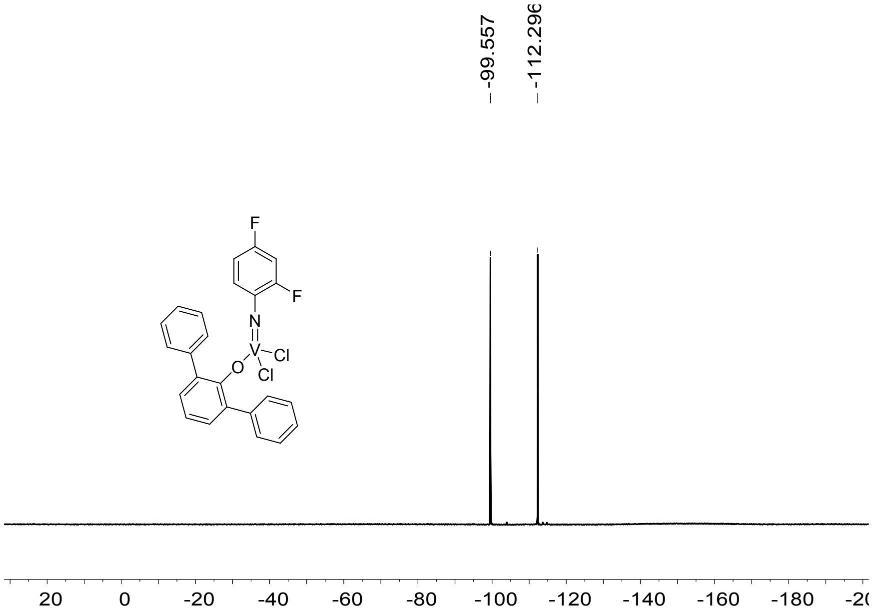


Figure S17. ^{19}F NMR (600 MHz) spectrum of catalyst **C1** recorded in $CDCl_3$ at 25 °C.

4. Characterization of polymers

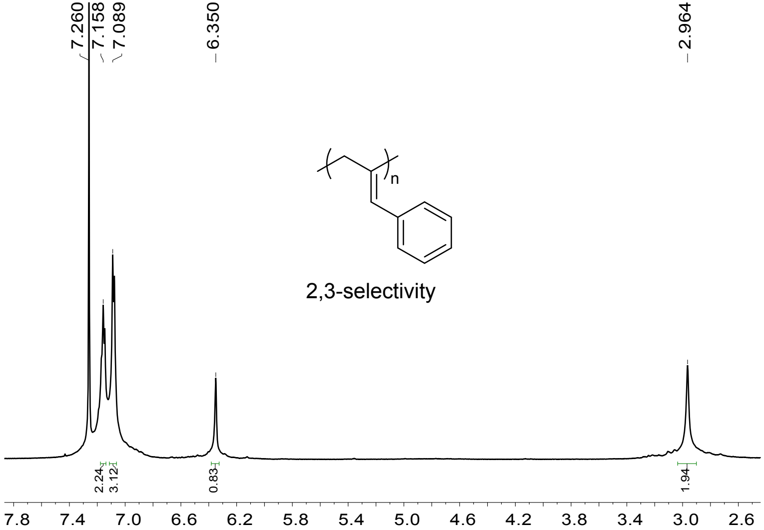


Figure S18. ^{1}H NMR (600 MHz) spectrum of polymer PPA$_{\mathbf{C1}}$ recorded in CDCl$_3$ at 25 °C.

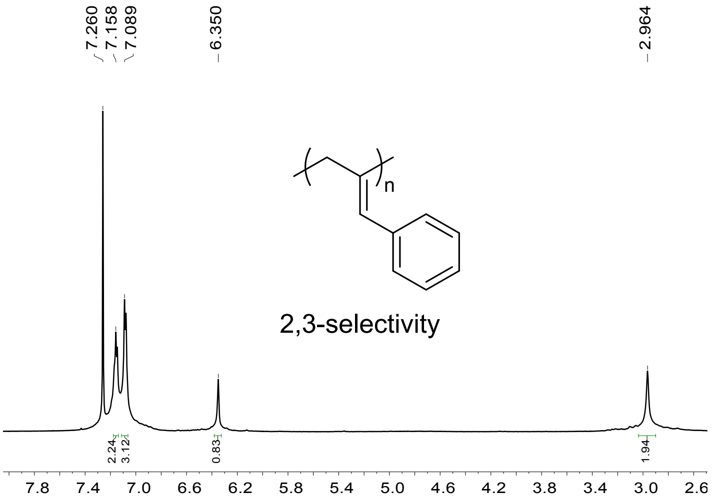


Figure S19. ^{1}H NMR (600 MHz) spectrum of polymer PPA$_{\mathbf{C1}}$ recorded in CDCl$_3$ at 25 °C.

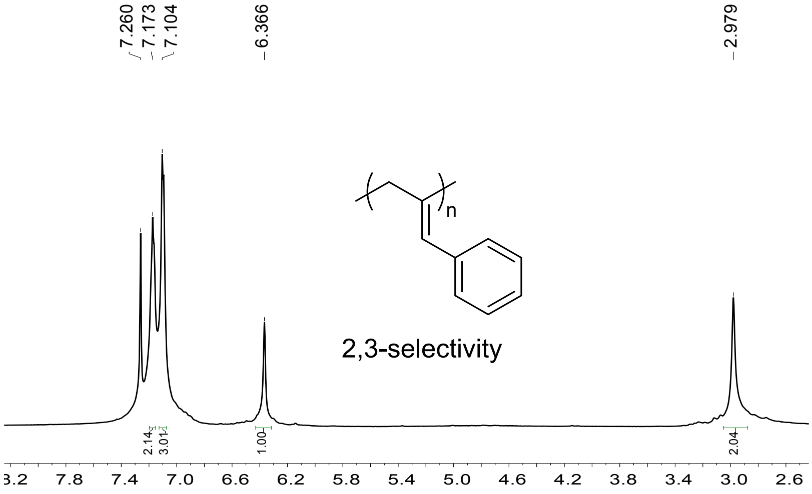


Figure S20. ^{1}H NMR (600 MHz) spectrum of polymer PPA$_{\mathbf{C6}}$ recorded in CDCl$_3$ at 25 °C.

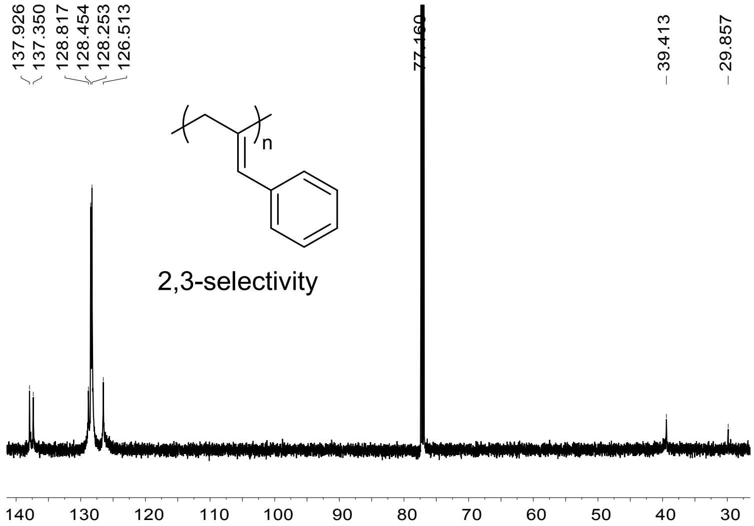


Figure S21. ^{13}C NMR (600 MHz) spectrum of polymer PPA_{C1} recorded in $CDCl_3$ at 25 °C.

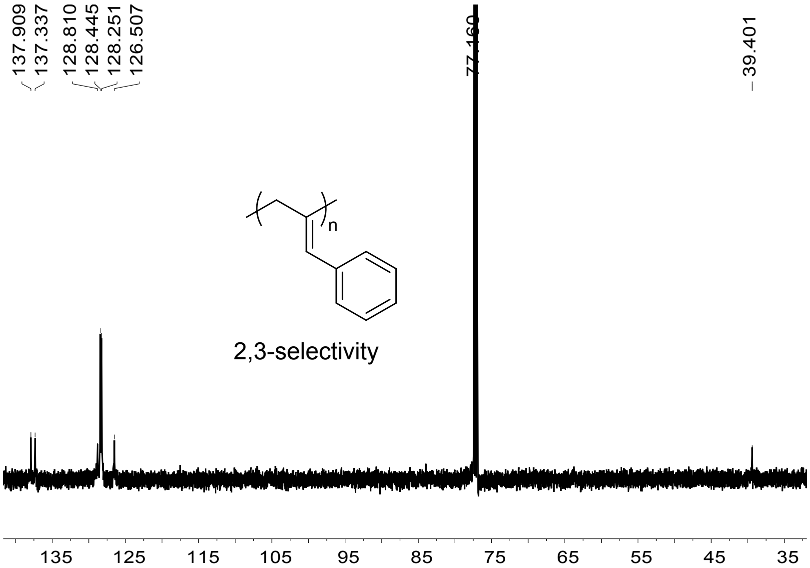


Figure S22 . ^{13}C NMR (600 MHz) spectrum of polymer PPA_{C1} recorded in $CDCl_3$ at 25 °C.

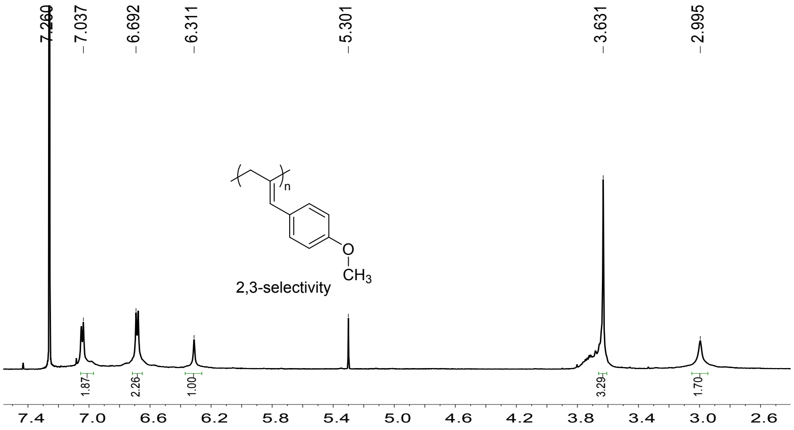


Figure S23 . ^{1}H NMR (600 MHz) spectrum of polymer P*p*MeOPA$_{C1}$ recorded in $CDCl_3$ at 25 °C.

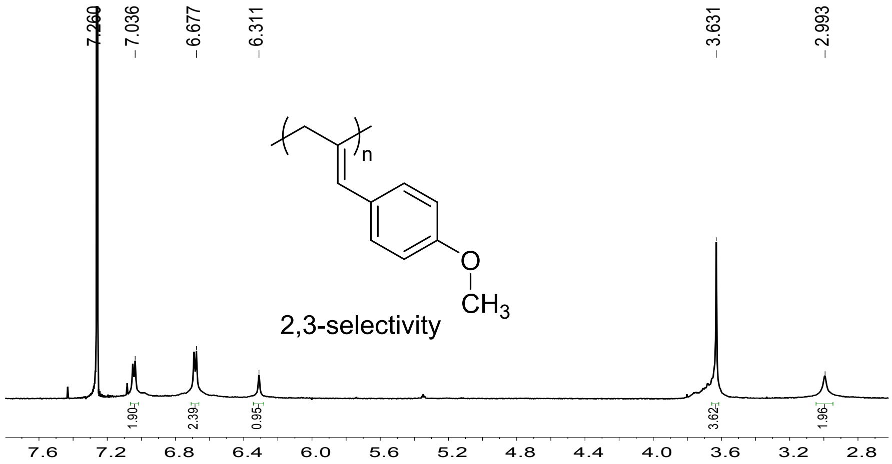


Figure S24. ^{1}H NMR (600 MHz) spectrum of polymer P*p*MeOPA$_{C1}$ recorded in $CDCl_3$ at 25 °C.

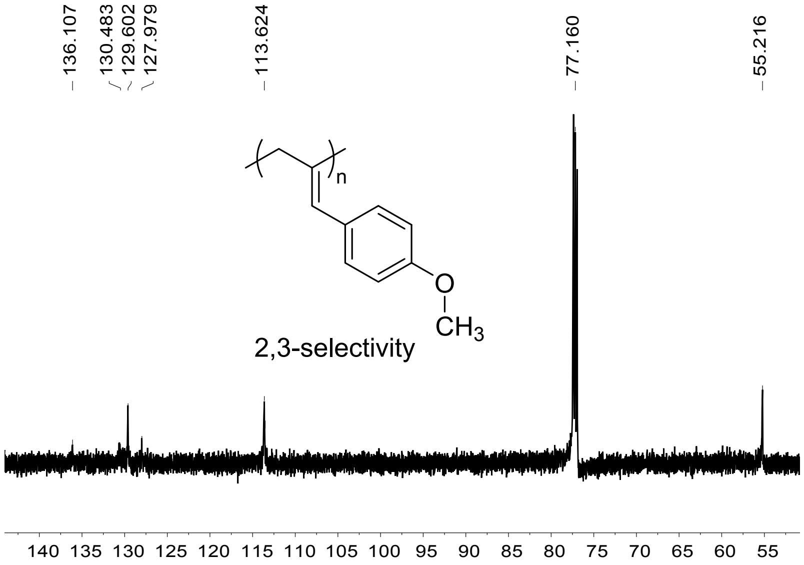


Figure S25. ^{13}C NMR (600 MHz) spectrum of polymer P*p*MeOPA$_{C1}$ recorded in $CDCl_3$ at 25 °C.

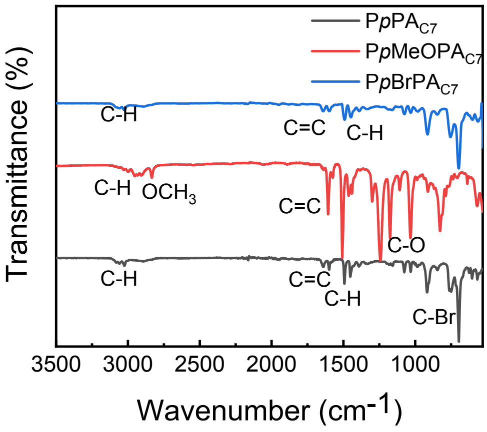


Figure S26. FT-IR spectra of PPA$_{C1}$, P*p*MeOPA$_{C1}$ and P*p*BrPA$_{C1}$ measured at 25 °C.

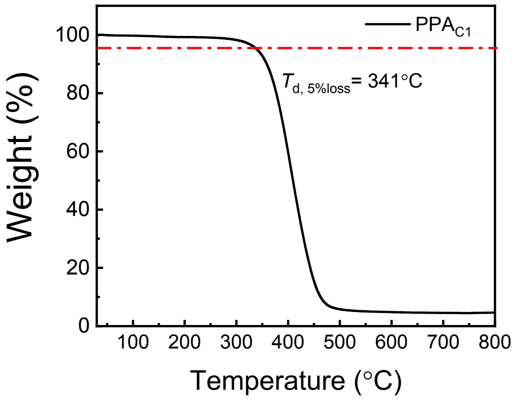


Fig S27. TGA curve at 10 °C/min heating rate for 2,3-PPA$_{\mathbf{C1}}$ (Table 1, run 6) under nitrogen atmosphere.

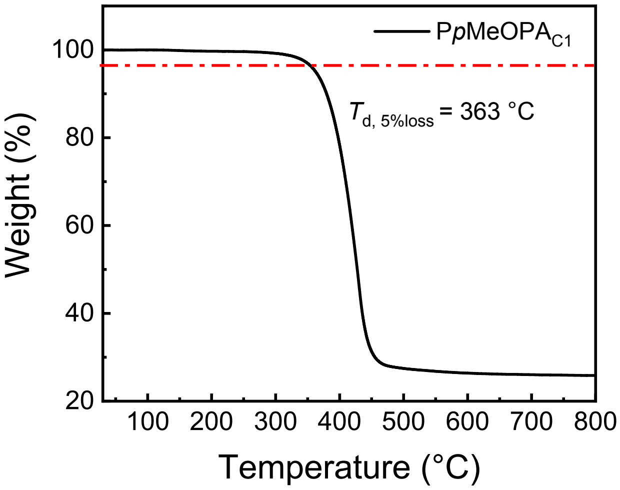


Fig S28. TGA curve at 10 °C/min heating rate for 2,3-P*p*MPA$_{\mathbf{C1}}$ (Table 4, run 7) under nitrogen atmosphere.