Electronic Supplementary Information

to accompany

Convenient route to tetraarylphosphonium polyelectrolytes via metal-catalysed P–C coupling polymerisation of aryl dihalides and diphenylphosphine

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List of Supporting Information Figures:

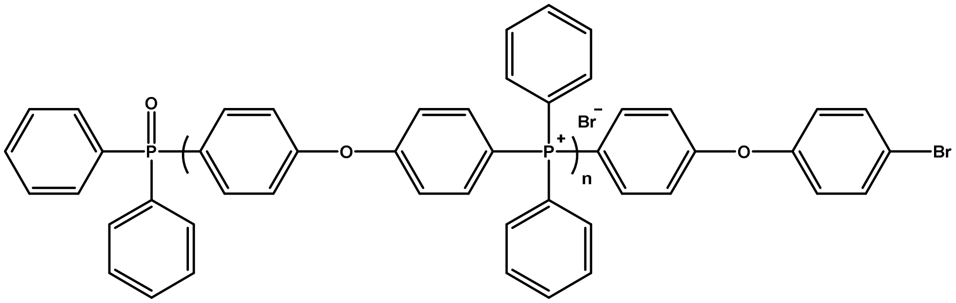
Experimental Details

General Considerations

All air-sensitive reactions were performed in an MBraun UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBraun solvent purifier. Chemicals were used without further purification after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300, 282 and 121 MHz for ^{1}H, ^{19}F and ^{31}P, respectively. Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600 from 25 °C to 800 °C with a heating rate of 20 °C min^{-1}. UV-Vis absorption spectra were acquired on a Cary 50 spectrophotometer. All NMR spectra were collected in $CDCl_3$. To assure that the ^{31}P nuclei were fully relaxed between scans and thus provide accurate integrations, the spectra with 2 s, 4 s, 8 s and 10 s delay were compared. Integration of resonances in spectra collected with a 10 s delay are identical to those collected with an 8 s delay. As a result, ^{31}P NMR spectra provided here were collected with a 10 s relaxation delay. To assure the accuracy of the chemical shift values, PPh_3 was added as an internal standard. The chemical shift of internal standard PPh_3 was set to –4.7 ppm.[1]

*Calculation of degree of polymerization (**X_n**) and number average molecular weight (**M_n**)*

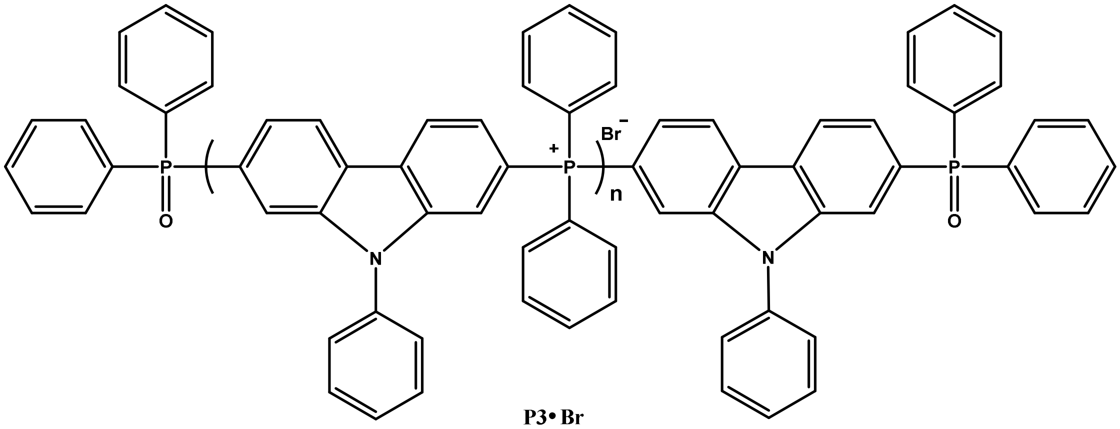
The method described here is similar to that which has been used in prior work.[2-4] In each ^{31}P-NMR spectrum, the peak of phosphine oxide was identified at ~30.00 ppm and the integrated area each of these peaks was normalized to 1.00 in the spectra provided in the ESI. If the integration for the phosphonium unit is x, the degree of polymerization (the value of n in the diagram below) is x (because each polymer chain has on average *one* phosphine-oxide end group). The M_n is then calculated by using this value of n and the molecular weight of each



P2•Br

repeat unit.

For **P3•Br** prepared by using $Pd_2(dba)_3$ as catalyst, 1.05 equivalents of diphenylphosphine was used to ensure conversion of -Br terminal groups into triarylphoshine and then phosphine oxide. Each polymer chain terminates in *two* phosphine oxide groups. To determine the number average molecular weight in this case, integration of the signal attributable to the phosphine oxide moieties is normalized to 1.00. The degree of polymerization is then twice the integration of the resonance attributable to the main chain phosphonium moieties. The M_n is then calculated by using the value of 2*n* and the molecular weight of each repeat unit.



P3• Br

Nickel (II)-catalyzed synthesis of poly(phosphonium bromide)s

P1•Br

Samples of 9,9-dioctyl-2,7-dibromofluorene (1.47 g, 2.69 mmol), diphenylphosphine (0.500 g, 2.69 mmol) and diisopropylamine (0.274 g, 2.69 mmol) were placed together in a 15 mL heavy-wall pressure tube under a nitrogen atmosphere. $NiBr_2$ (0. 0600 g, 0.270 mmol) and 6 mL anhydrous ethylene glycol were then added, and the tube was sealed with a Teflon screw cap equipped with a Viton O-ring. The sealed tube was heated at 180 °C with stirring for 24 h. After cooling down to room temperature, the reaction vessel was opened to air and 50 mL dichloromethane (DCM) was added. The mixture and then washed with 1 *M* NaBr (50 mL×2). The organic layer was dried over anhydrous $MgSO_4$ and concentrated to 10 mL by vacuum evaporation. The crude solution was added into 200 mL diethyl ether dropwise with stirring to yield a cloudy suspension. The solid was separated by vacuum filtration, and then dried in a vacuum oven overnight at 60 °C to give the desired product (1.36 g, 77.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.35-7.28 (br m, 16H), 2.53-0.32 (br m, 34H); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 30.39 (end groups), 26.13-23.01 (backbone phosphonium moieties). anal. calcd for repeat unit $C_{41}H_{50}BrP \bullet (H_2O)$ (ignoring end groups): C, 73.31; H, 7.80; found: C, 74.13; H, 7.89%

P2•Br

The synthetic procedure was the same as that used to prepare **P1•Br**, but using monomers as bis(4-bromophenyl) ether (0.882 g, 2.69 mmol) and diphenylphosphine (0.500 g, 2.69 mmol). The desired product was isolated as white powder (0.813 g, 61.1%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98-6.86 (br m, 18H); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 29.51 (end groups), 24.78-20.87 (backbone phosphonium moieties). anal. calcd for repeat unit•(H_2O) formula $C_{24}H_{20}BrO_2P$ (ignoring end groups): C, 63.87; H, 4.47; found: C, 62.10; H, 4.53%

Palladium (0)-catalyzed synthesis of poly(phosphonium bromide)s

P1•Br

The synthetic procedure was the same as $NiBr_2$ catalyzed **P1•Br**, but using $Pd_2(dba)_3$ (0.0270 mmol, 0.0280 g) as catalyst and reacting at 145 °C. The desired product was obtained as light yellow powder (1.28 g, 66.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07-7.38 (br m, 16H), 1.99-1.78 (br s, 4H), 1.29-0.36 (be m, 30H); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 30.44 (end groups), 26.16-22.94 (backbone phosphonium moieties). anal. calcd for repeat unit•(H_2O) formula $C_{41}H_{52}BrPO$ (ignoring end groups): C, 73.31; H, 7.80; found: C, 73.20; H, 7.85%

P2•Br

The synthetic procedure was the same as $NiBr_2$ catalyzed **P2•Br**, but using $Pd_2(dba)_3$ (0.0270 mmol, 0.0280 g) as catalyst and reacting under 145 °C. The desired product was obtained as yellowish white powder (0.822 g, 67.8%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.94-6.96 (br m, 18H), ^{31}P NMR (121 MHz, $CDCl_3$) δ: 29.29 (end groups), 24.51-20.72 (backbone phosphonium moieties). anal. calcd for repeat unit•H_2O $C_{24}H_{20}BrO_2P$ (ignoring end groups): C, 63.87; H, 4.47; found: C, 62.75; H, 4.53%

P3•Br

The synthetic procedure was the same as $Pd_2(dba)_3$ catalyzed **P1•Br**, but using monomers as 3, 6-dibromo-9-phenyl-9*H*-carbazole (1.25 mmol, 0.500 g), diphenylphosphine (1.31 mmol, 0.244 g). $Pd_2(dba)_3$ (0.0130 mmol, 0.0120 g) as catalyst and reacting at 145 °C for 4 h. The desired product was obtained as light grey powder (0.468 g, 71.4%). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.84-7.31 (br m, 21H); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 30.88 (end groups), 27.02-23.89 (backbone phosphonium moieties). anal. calcd for monomer•(H_2O) formula $C_{30}H_{23}BrNOP$ (ignoring end groups): C, 68.71; H,4.42; N, 2.67; found: C, 68.81; H, 4.37; N, 2.75%

Anion exchange to prepare bis(trifluoromethane)sulfonimide salts

The bis(trifluoromethane)sulfonimide [**NTf_2**]$^-$ salts of the TPELs were prepared from the bromide salts (from $NiBr_2$-catalyzed routes for **P1•Br** and **P2•Br**) via the procedures below. The degrees of polymerization reported for the bis(trifluoromethane)sulfonamide salts are slightly higher than those of the parent bromide salts in each case, presumably due to removal of some low molecular weight fractions in the rinsing of the bis(trifluoromethane)sulfonamide salts. The percentage of bromide anions that have been successfully exchanged by bis(trifluoromethane) sulfonimide anions was determined via C, H, N elemental microanalysis.

P1•[NTf_2]

A sample of **P1•Br** (0.100 g, 0.150 mmol) was dissolved in 50 mL H_2O/MeOH (1:1), and then added 10 mL bis(trifluoromethyl)sulfonimide lithium (0.100 g, 0.350 mmol) H_2O solution with stirring to form cloudy precipitation. The solid was separated by centrifugation. The supernatant liquid was removed by decantation and the sediment collected. The sediment was suspended in deionized water and collected by filtration two additional times, and the filtrand was dried in a vacuum oven at 100 °C for 24 h to obtain the anion-exchanged compound (0.131g, 100%). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 85.4% by elemental combustion microanalysis. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.43-7.29 (br m, 16H), 2.13-0.39 (br m, 34H); ^{19}F NMR (282 MHz) δ: –78.57 (-CF_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ: 29.48 (end groups), 26.58-23.34 (backbone phosphonium moieties). anal. calcd for monomer formula $C_{43}H_{50}F_6NO_4PS_2$ (ignoring end groups): C, 60.48; H, 5.90; N, 1.64; found: C, 62.26; H, 6.19; N, 1.45%.

P2•[NTf$_2$]

The procedure was the same as that used to prepare **P1•[NTf$_2$]** (0.117 g, 80.1%), but starting with **P2•Br** (0.100 g, 0.230 mmol). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 82.0% by elemental combustion microanalysis. ^1H NMR (300 MHz, $CDCl_3$) *δ*: 7.94-6.89 (br m, 18H); ^{19}F NMR (282 MHz) *δ*: –78.65 (-CF_3); ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 31.06 (end groups), 27.51-23.51 (backbone phosphonium moieties). anal. calcd for monomer formula $C_{26}H_{18}F_6NO_5PS_2$ (ignoring end groups): C, 49.29; H, 2.86; N, 2.21; found: C, 49.98; H, 2.97; N, 1.92%

P3•[NTf$_2$]

The procedure was the same as that used to prepare **P1•[NTf$_2$]** (0.102 g, 73.3%), but starting with **P3•Br** (0.100 g, 0.197 mmol). The percentage of bromide counterions that had been replaced by ditriflamide was found to be 98.5% by elemental combustion microanalysis. ^1H NMR (300 MHz, $CDCl_3$) *δ*: 8.39-7.30 (br m, 21H); ^{19}F NMR (282 MHz) *δ*: –78.78 (-CF_3); ^{31}P NMR (121 MHz, $CDCl_3$) *δ*: 30.96 (end groups), 27.50-24.5 (backbone phosphonium moieties). anal. calcd for monomer formula $C_{32}H_{21}F_6N_2O_4PS_2$ (ignoring end groups): C, 54.39; H, 3.00; N, 3.96; found: C, 56.15; H, 3.11; N, 3.95%

Stability test under basic condition

To a 50 mL round bottom flask, 20.0 mg of the polymer dissolved in 1 mL dichloromethane was slowly evaporated so that the polymer thin film was coated homogeneously on the lower part of the inner wall of the flask. The polymer film was soaking in 25 mL of 1 *M* NaOH solution for 24 h. The remaining solid was collected and then dissolved in $CDCl_3$ to collect phosphorus-31 NMR spectra. Two more sets of experiments were conducted with the same protocol by using 1 *M* NaOH at 65 °C and 6 *M* NaOH at 65 °C, cooled to room temperature prior to collection of solids.

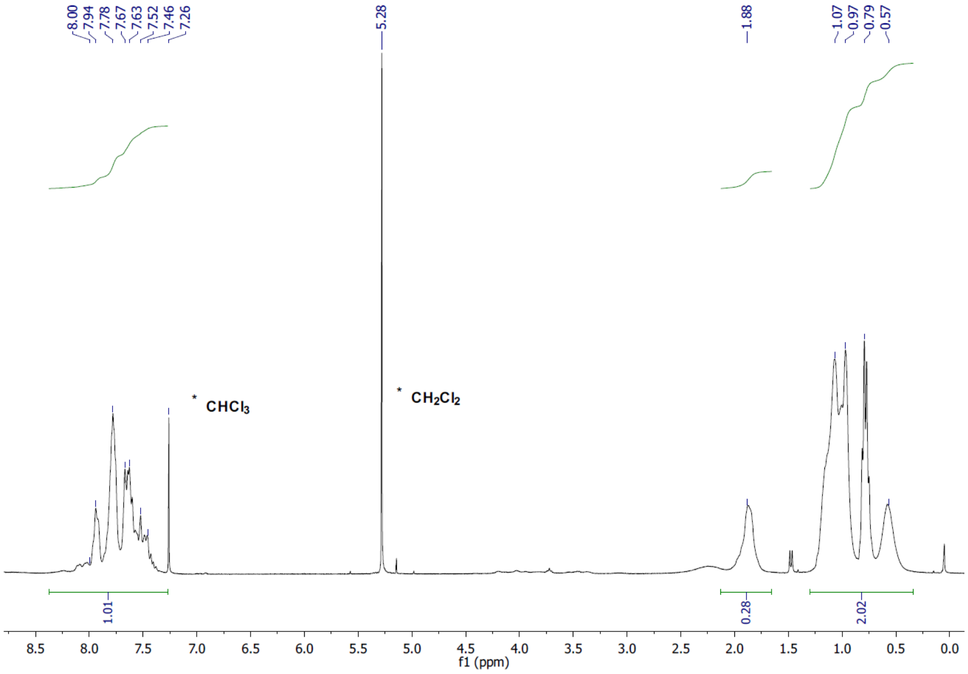


Figure S1 Proton NMR spectrum of compound **P1•Br** prepared by using $NiBr_2$ catalyst ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

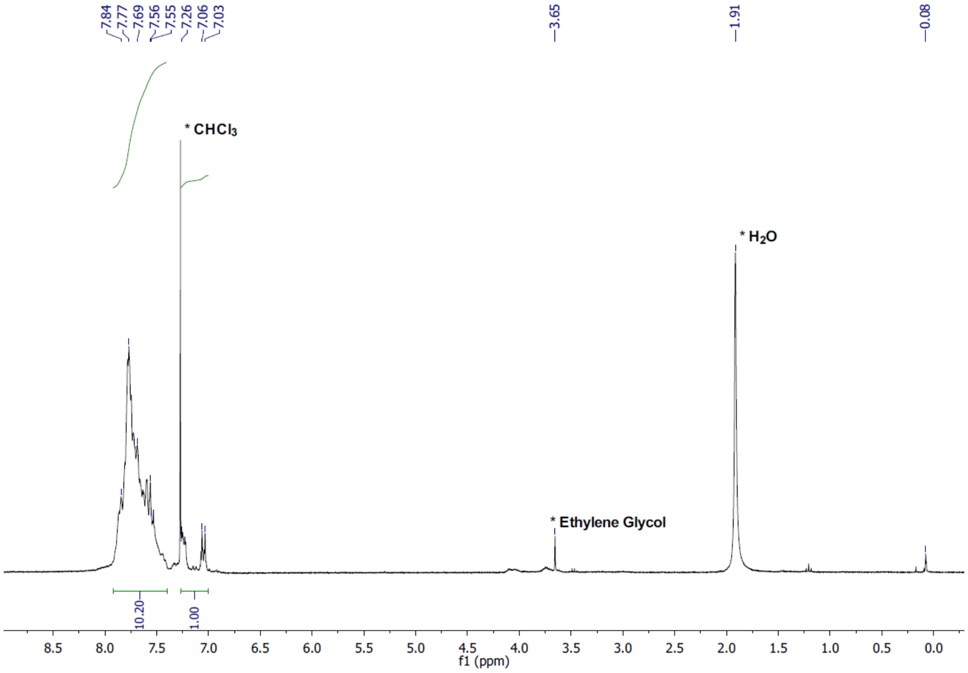


Figure S2 Proton NMR spectrum of compound **P2•Br** prepared by using $NiBr_2$ catalyst ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

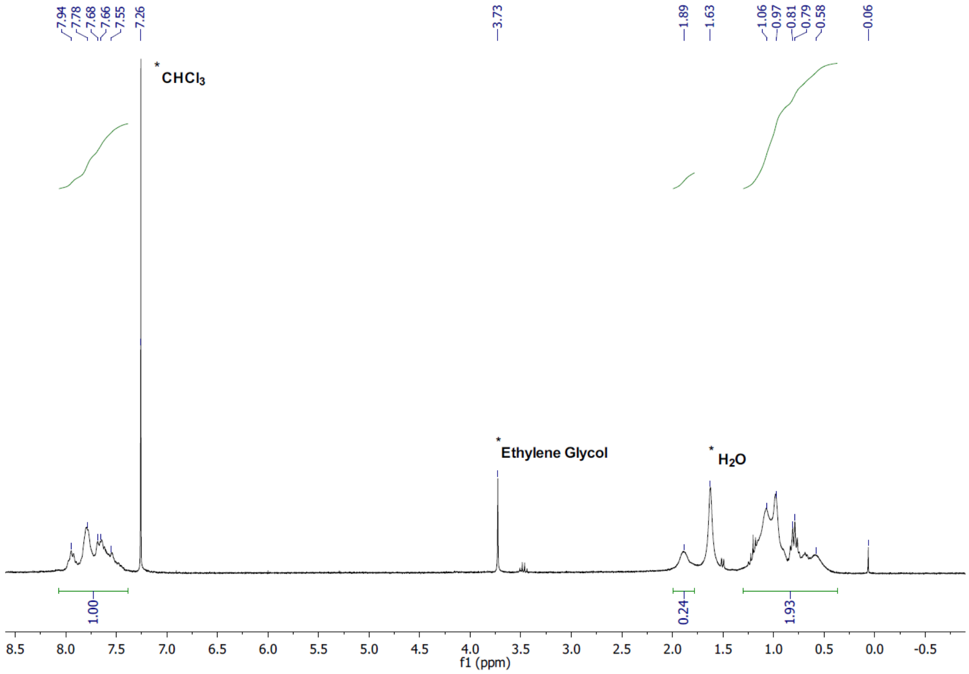


Figure S3 Proton NMR spectrum of compound **P1•Br** prepared by using $Pd_2(dba)_3$ catalyst ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

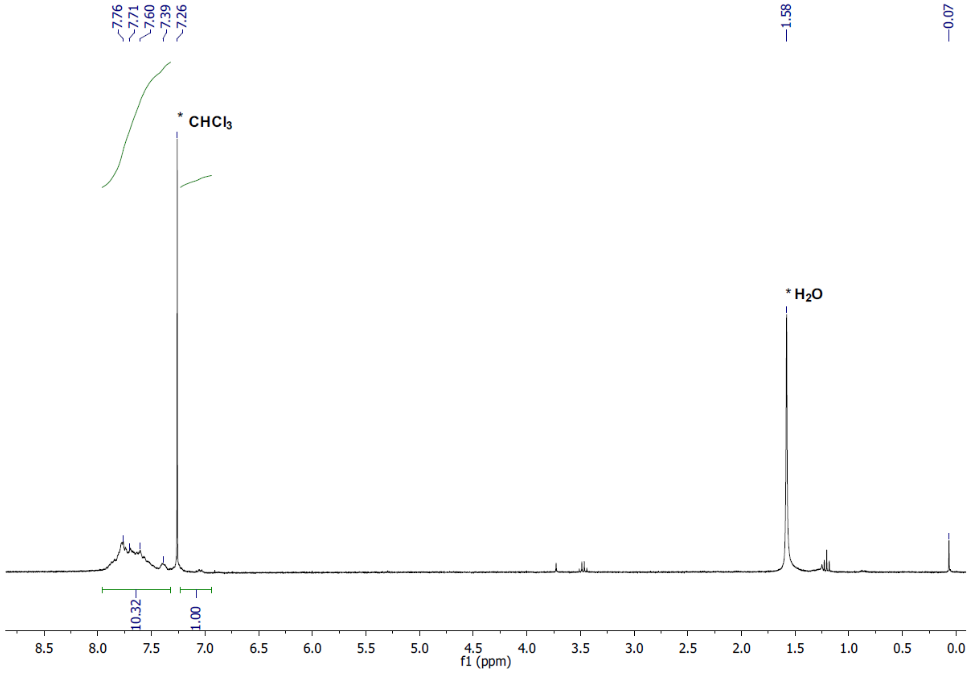


Figure S4 Proton NMR spectrum of compound **P2•Br** prepared by using $Pd_2(dba)_3$ catalyst ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

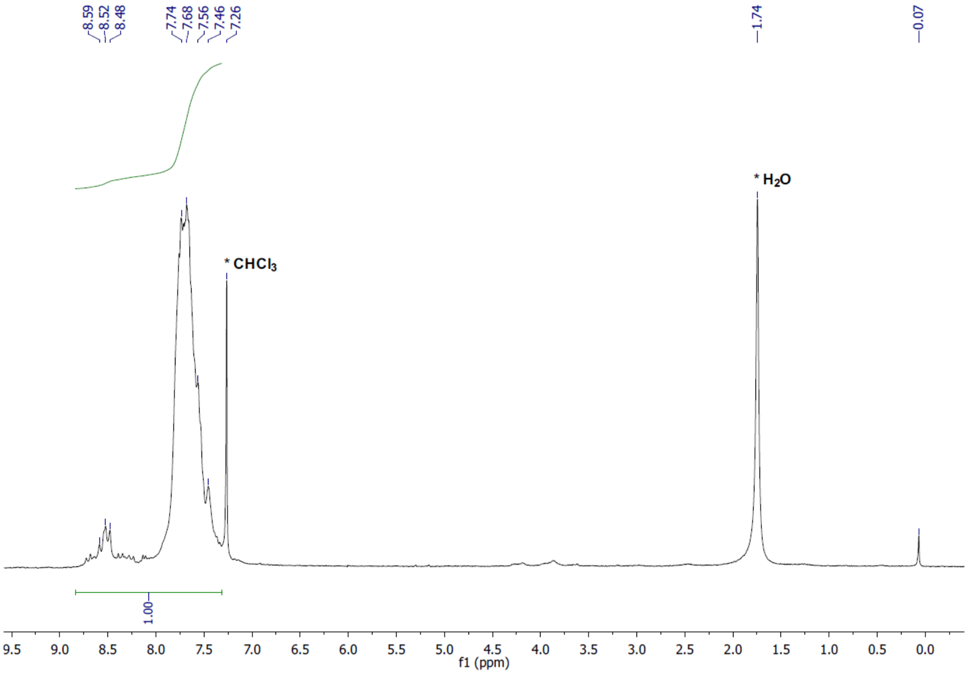


Figure S5 Proton NMR spectrum of compound **P3•Br** prepared by using $Pd_2(dba)_3$ catalyst ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

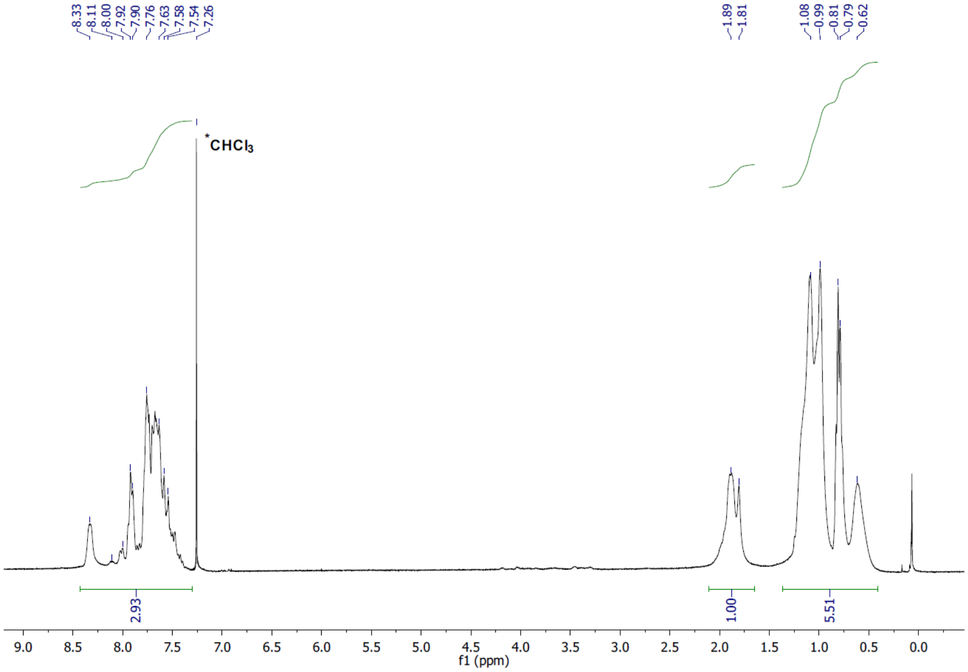


Figure S6 Proton NMR spectrum of compound **P1•NTf₂** ($CDCl_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

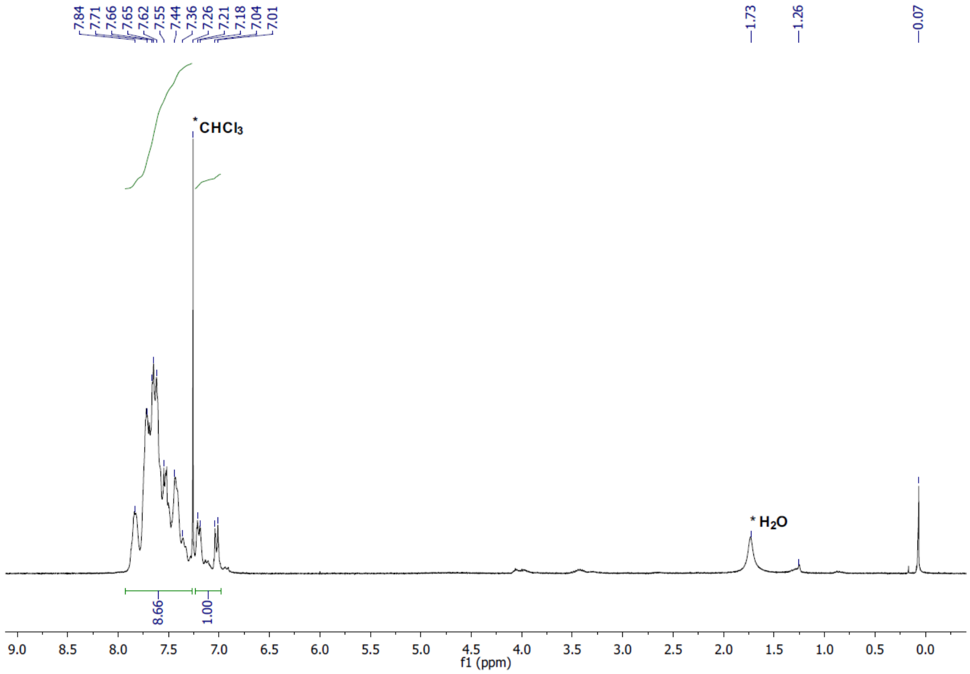


Figure S7 Proton NMR spectrum of compound **P2•NTf$_2$** (CDCl$_3$, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

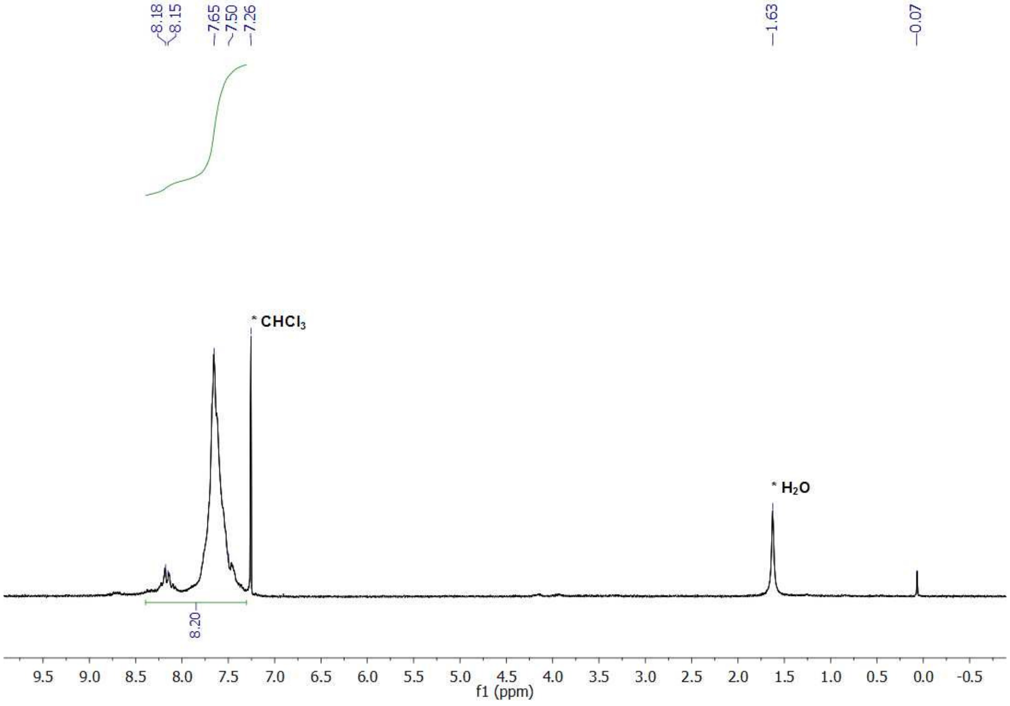


Figure S8 Proton NMR spectrum of compound **P3•NTf$_2$** (CDCl3, 300 MHz). Each peak marked with an asterisk corresponds to a solvent signal.

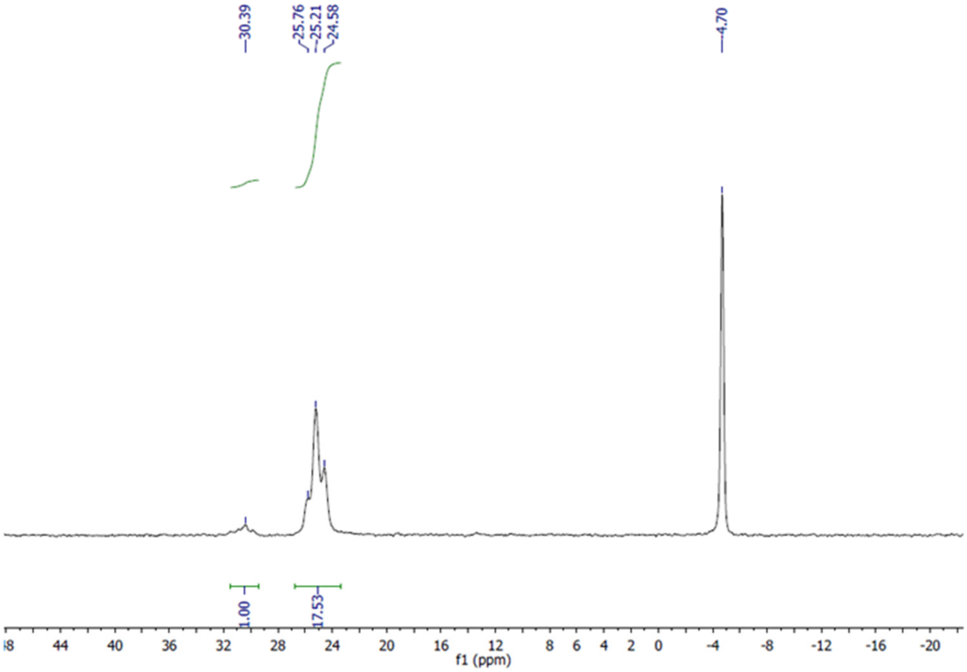


Figure S9 Phosphorus-31 NMR spectrum of compound **P1•Br** prepared by using $NiBr_2$ catalyst ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

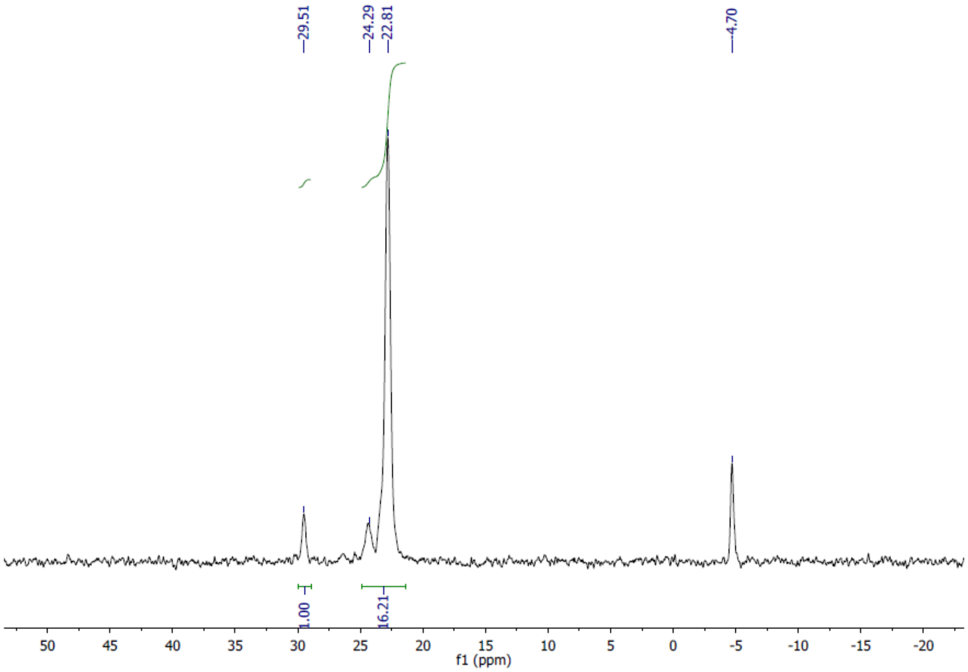


Figure S10 Phosphorus-31 NMR spectrum of compound **P2•Br** prepared by using $NiBr_2$ catalyst ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

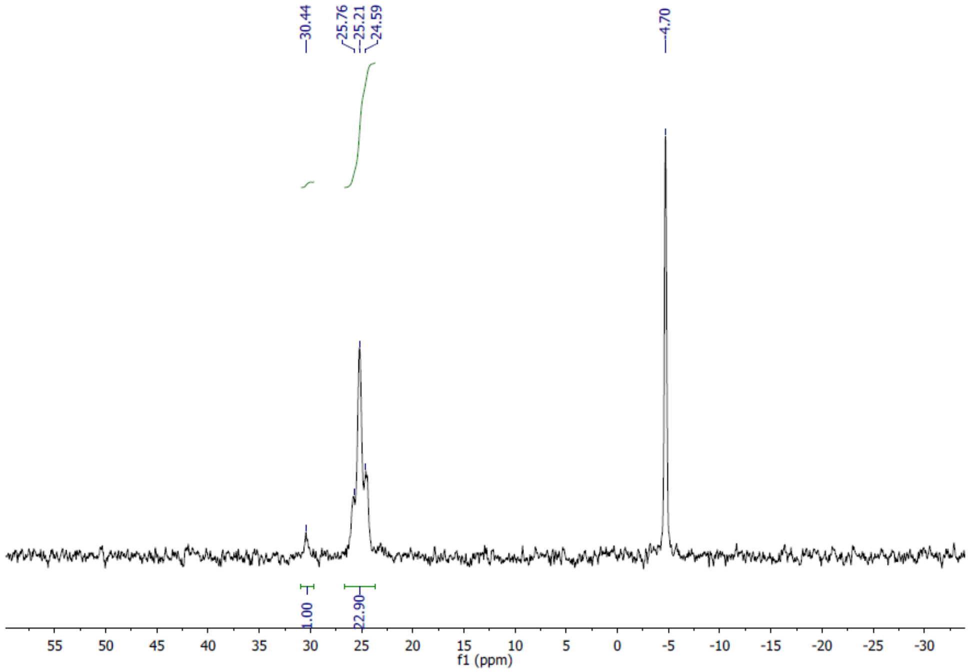


Figure S11 Phosphorus-31 NMR spectrum of compound **P1•Br** prepared by using $Pd_2(dba)_3$ catalyst ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

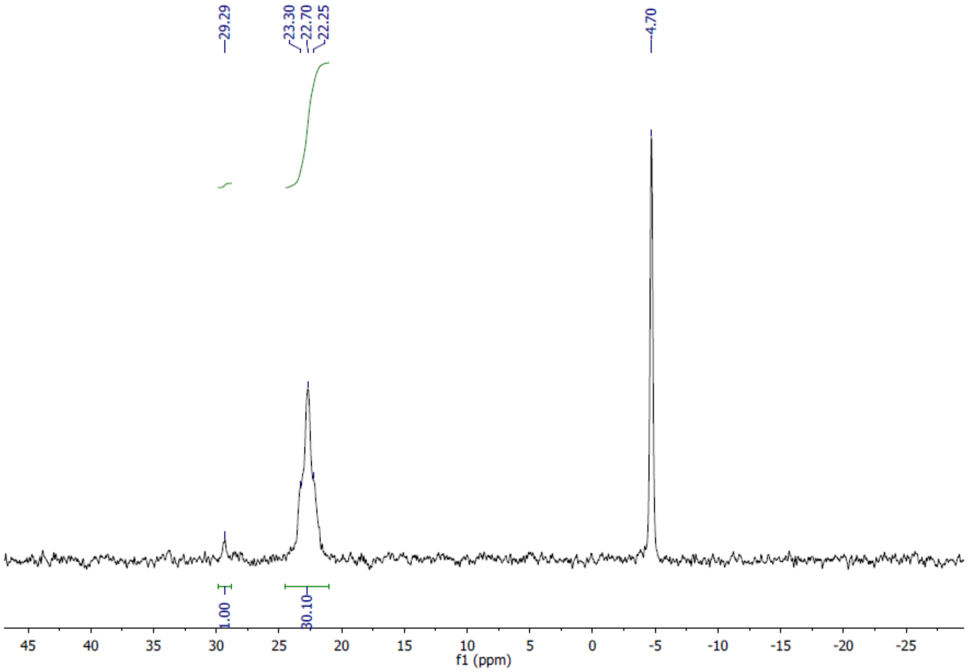


Figure S12 Phosphorus-31 NMR spectrum of compound **P2•Br** prepared by using $Pd_2(dba)_3$ catalyst ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

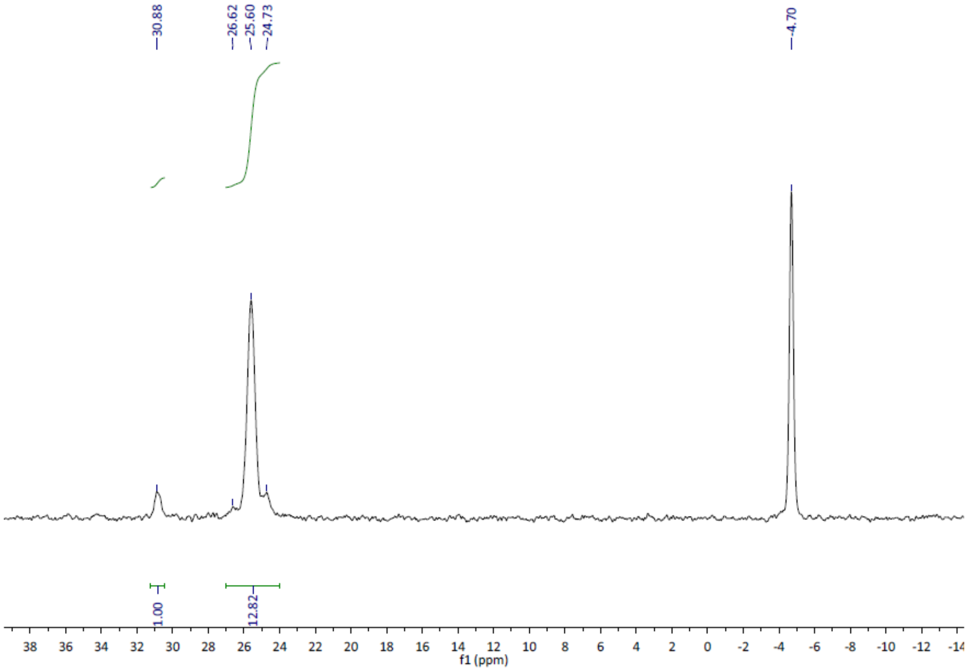


Figure S13 Phosphorus-31 NMR spectrum of compound **P3•Br** prepared by using $Pd_2(dba)_3$ catalyst with a reaction time of 4 hours ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

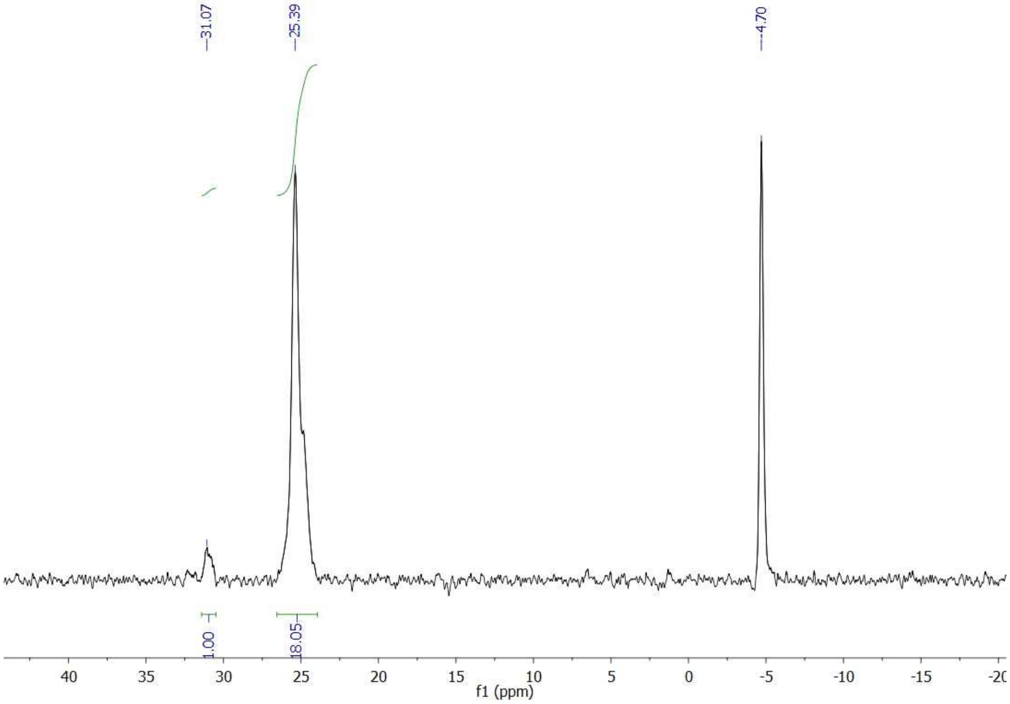


Figure S14 Phosphorus-31 NMR spectrum of compound **P1•NTf₂** ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

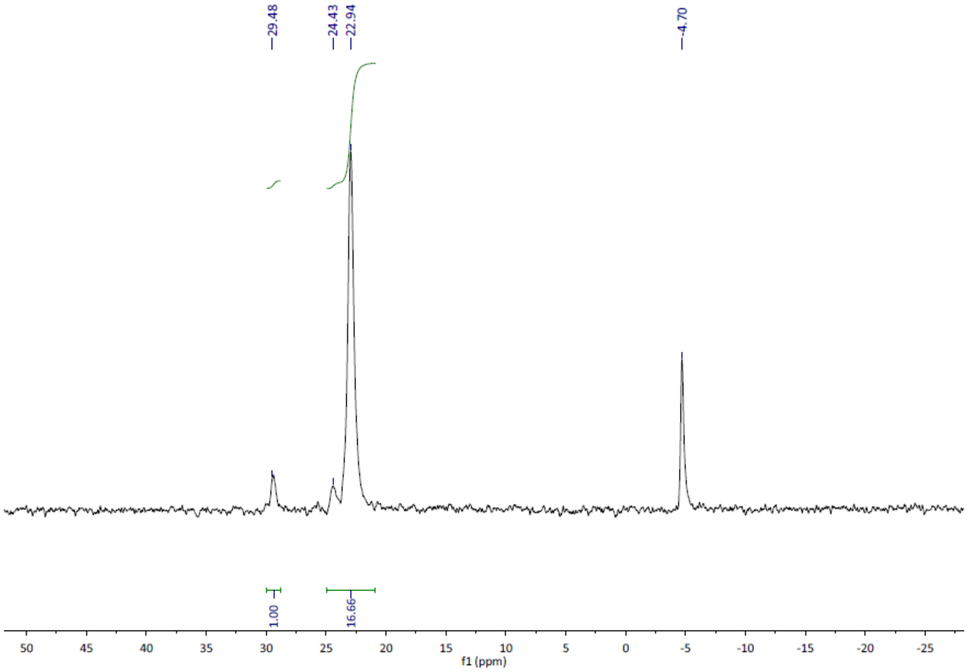


Figure S15 Phosphorus-31 NMR spectrum of compound **P2•NTf₂** ($CDCl_3$, 121 MHz). PPh_3 was used as an external standard and its chemical shift was normalized to –4.70 ppm.

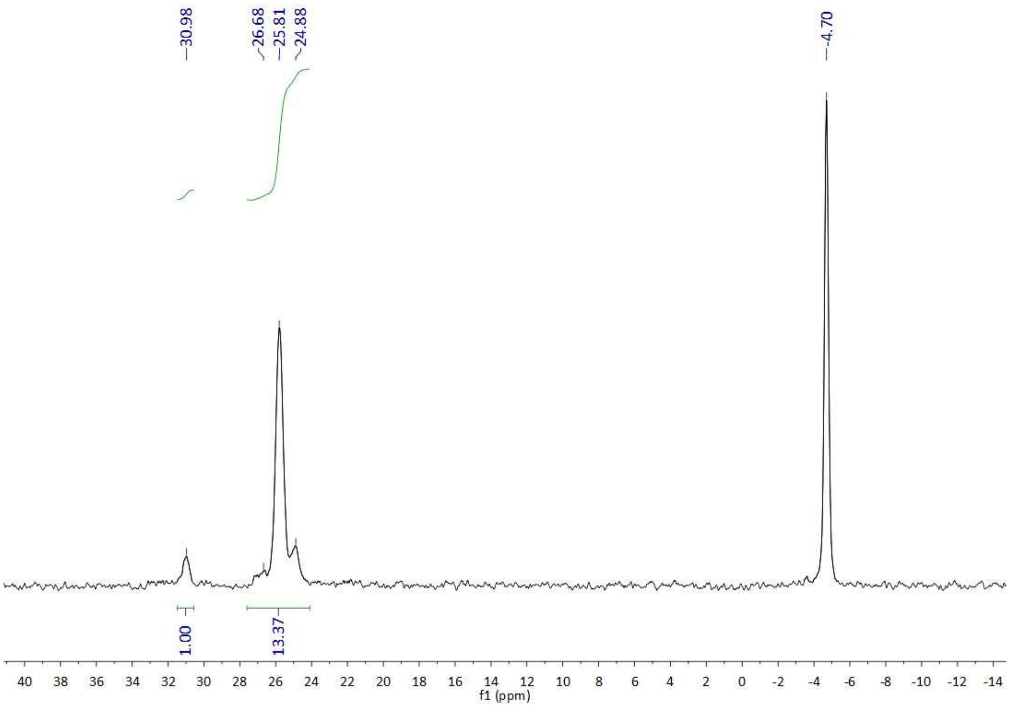


Figure S16 Phosphorus-31 NMR spectrum of compound **P3•NTf$_2$** (CDCl$_3$, 121 MHz). PPh$_3$ was used as an external standard and its chemical shift was normalized to –4.70 ppm.

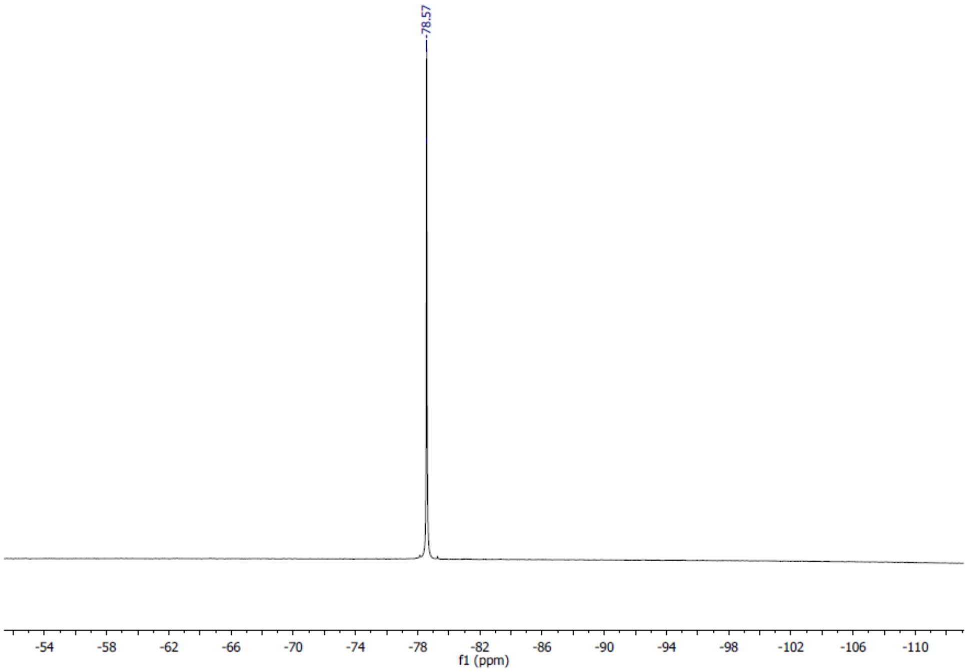


Figure S17 Fluorine-19 NMR spectrum of compound **P1•NTf₂** ($CDCl_3$, 282 MHz).

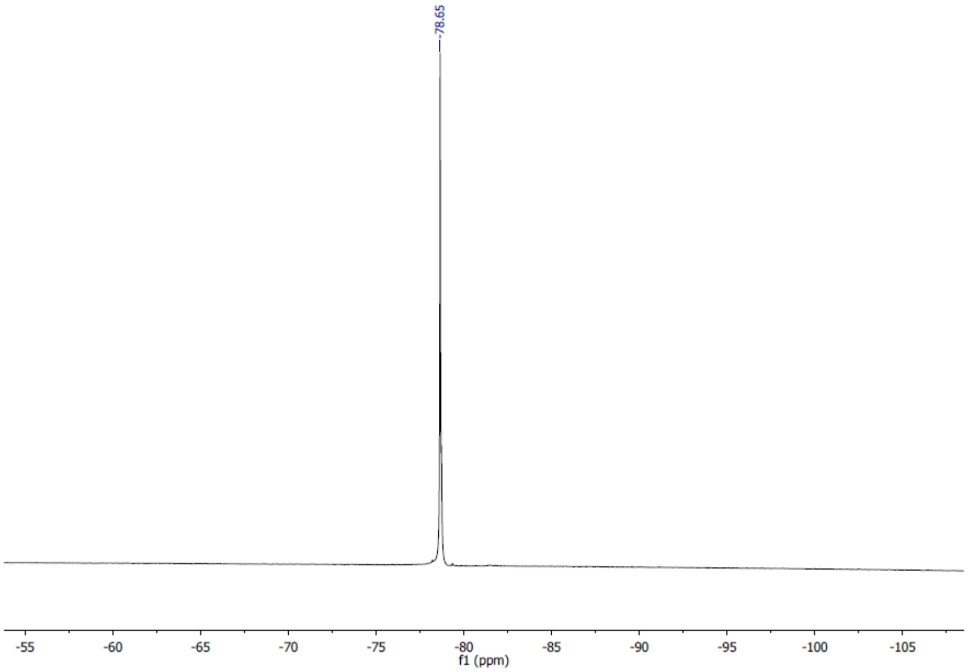


Figure S18 Fluorine-19 NMR spectrum of compound **P2•NTf₂** ($CDCl_3$, 282 MHz)

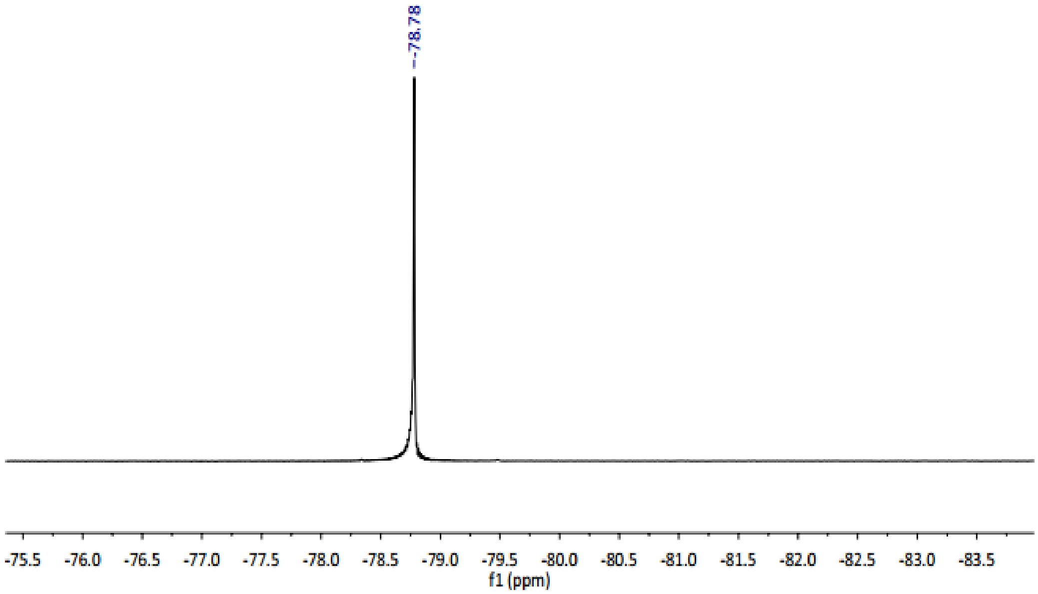


Figure S19 Fluorine-19 NMR spectrum of compound **P3•NTf₂** ($CDCl_3$, 282 MHz).

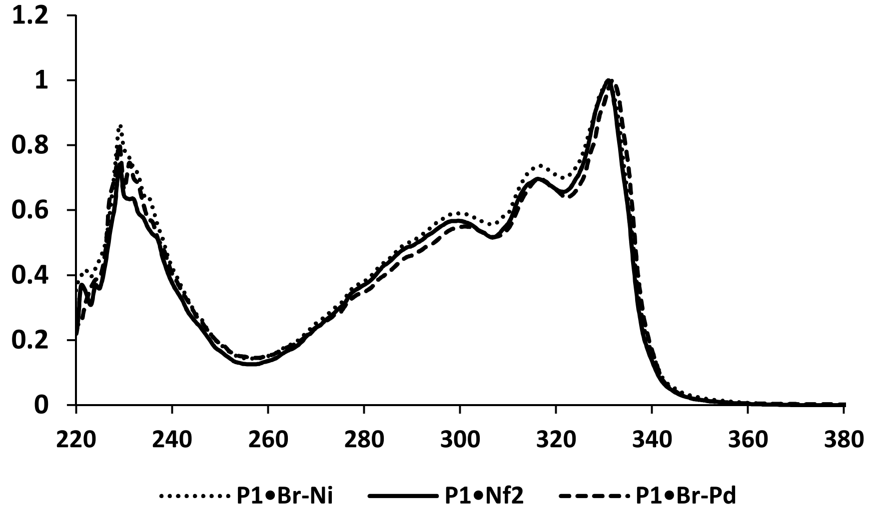


Figure S20. UV-vis absorption spectra of **P1•X (X=Br, NTf$_2$)** in dichloromethane. The metal listed in the legend is that which comprises part of the catalyst used to prepare the polymer.

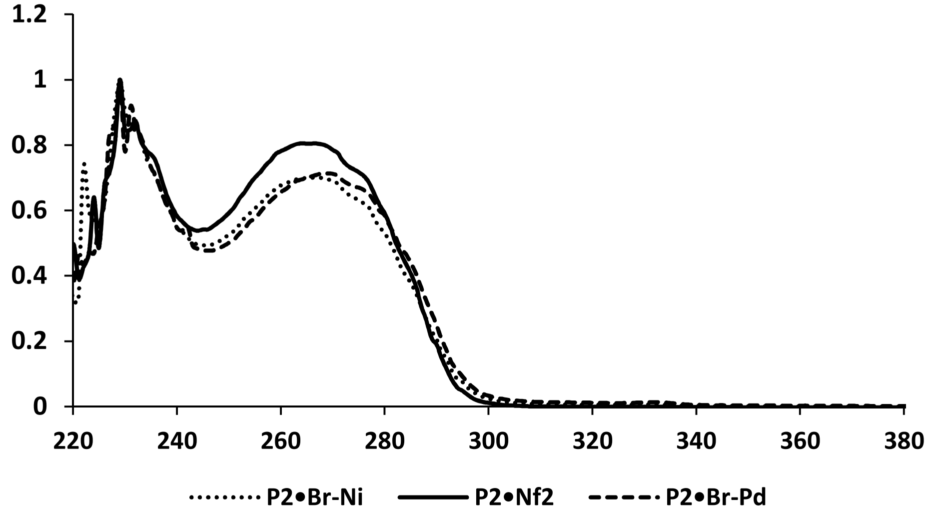


Figure S21. UV-vis absorption spectra of **P2•X (X=Br, NTf$_2$)** in dichloromethane. The metal listed in the legend is that which comprises part of the catalyst used to prepare the polymer.

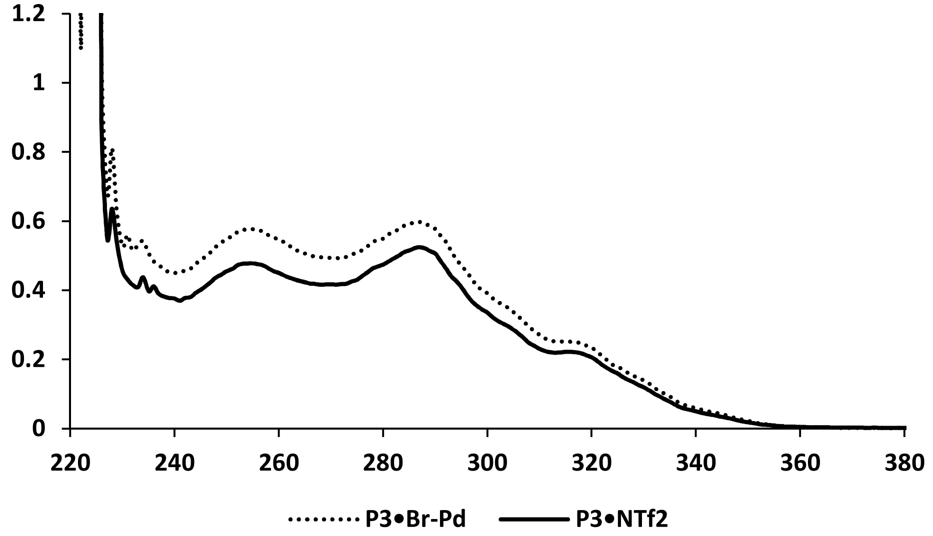


Figure 22. UV-vis absorption spectra of **P3•X (X=Br, NTf$_2$)** in dichloromethane.

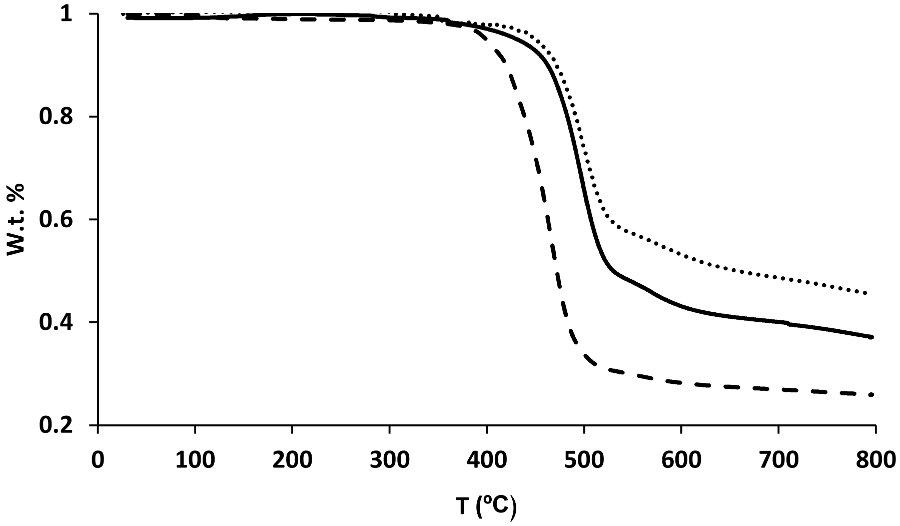


Figure 23. TGA traces of **P1•NTf₂** (dashed line), **P2•NTf₂** (solid line) and **P3•NTf₂** (dotted line)

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