Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Pd(II)-NHC coordination-driven formation of water-soluble catalytically active single chain nanoparticles

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Materials

Benzimidazole (≥95%), 4-vinylbenzyl chloride (90%), ethyl bromide (99%), lithium bis(trifluoromethane)sulfonylimide and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPAD, ≥97%) were obtained from Aldrich and used as received. The hydroxy-containing poly(ethylene oxide) monomethylester (CH_3O-PEO_{16}-OH, 800 g.mol^{-1}) was obtained from Aldrich and use as received. Azobis(2-methylpropionitrile) (AIBN, 99%) was received from Aldrich and was purified by recrystallization from methanol. Styrene and dimethylformamide were dried over CaH_2 and distilled prior to use. 1,3-Dicyclohexylcarbodiimide (DCC, 99%) was obtained from Alfa Aesar and 4-dimethylaminopyridine (DMAP; 99%) was obtained from TCI and use as received. Tetrahydrofuran (THF) was distilled over Na/benzophenone. Ethyl acetate and acetonitrile (99.7%, Aldrich) were used without further purification. Methanol was distilled over metallic Na prior to use.

Instrumental analysis

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AC-400 spectrometer in appropriate deuterated solvents. All ^{13}C measurements were performed at 298 K on a Bruker Avance III 400 spectrometer operating at 100.7 MHz and equipped with a 5 mm Bruker multinuclear direct cryoprobe. Transmission Electron Microscopy (TEM) images were recorded at Bordeaux Imaging center (BIC) on a Hitachi H7650 microscope working at 80 kV. Samples of SCNP were prepared by dropping 0.4 μL of the SCNP solution in DMSO onto a copper grid (200 mesh coated with carbon) and removing the excess after 3 minutes. Uranyl acetate was used as contrast agent. Dynamic light scattering (DLS) experiments of the micelles prepared in water were performed using an ALV CGS-3 Compact Goniometer System, equipped with a 35 mW HeNe linear polarized laser with a wavelength of 632.8 nm and an ALV/LSE-5004 light scattering electronic and Multiple Tau Digital correlator. The accessible scattering angles ranged from 30° to 150°.

Polymer molar masses were determined by Size Exclusion Chromatography (SEC) using tetrahydrofuran (THF + lithium bromide $LiTf_2N$ 10Mm) as the eluent. Measurements in THF were performed on an Ultimate 3000 system from Thermoscientific equipped with diode array detector DAD. The system also includes a multi-angle light scattering detector MALS and differential refractive index detector dRI from Wyatt technology. Polymers were separated on a PSS SDV Linear S gel columns (300 x 8 mm) (exclusion limits from 1000 Da to 150 000 Da) at a flow rate of 1 mL/min. Columns temperature was held at 36°C.

Polystyrene was used as the standard.

Synthesis of *N*-ethylbenzimidazole

Benzimidazole (6 g, 51 mmol) was dissolved in DMF (50 mL) and 5.72 g of potassium hydroxide were added (2 eq., 102 mmol). The solution was stirred for 30 minutes and 4.17 mL (6.1 g, 55 mmol) of ethyl bromide were added drop-wise. After stirring at room temperature for 24h, the solution was diluted with 50 mL of water and extracted with chloroform (6 x 25 mL). Organic phases were combined, dried over $MgSO_4$ and evaporated, yielding a yellow viscous oil (6.28 g, 43 mmol, yield = 89 %).

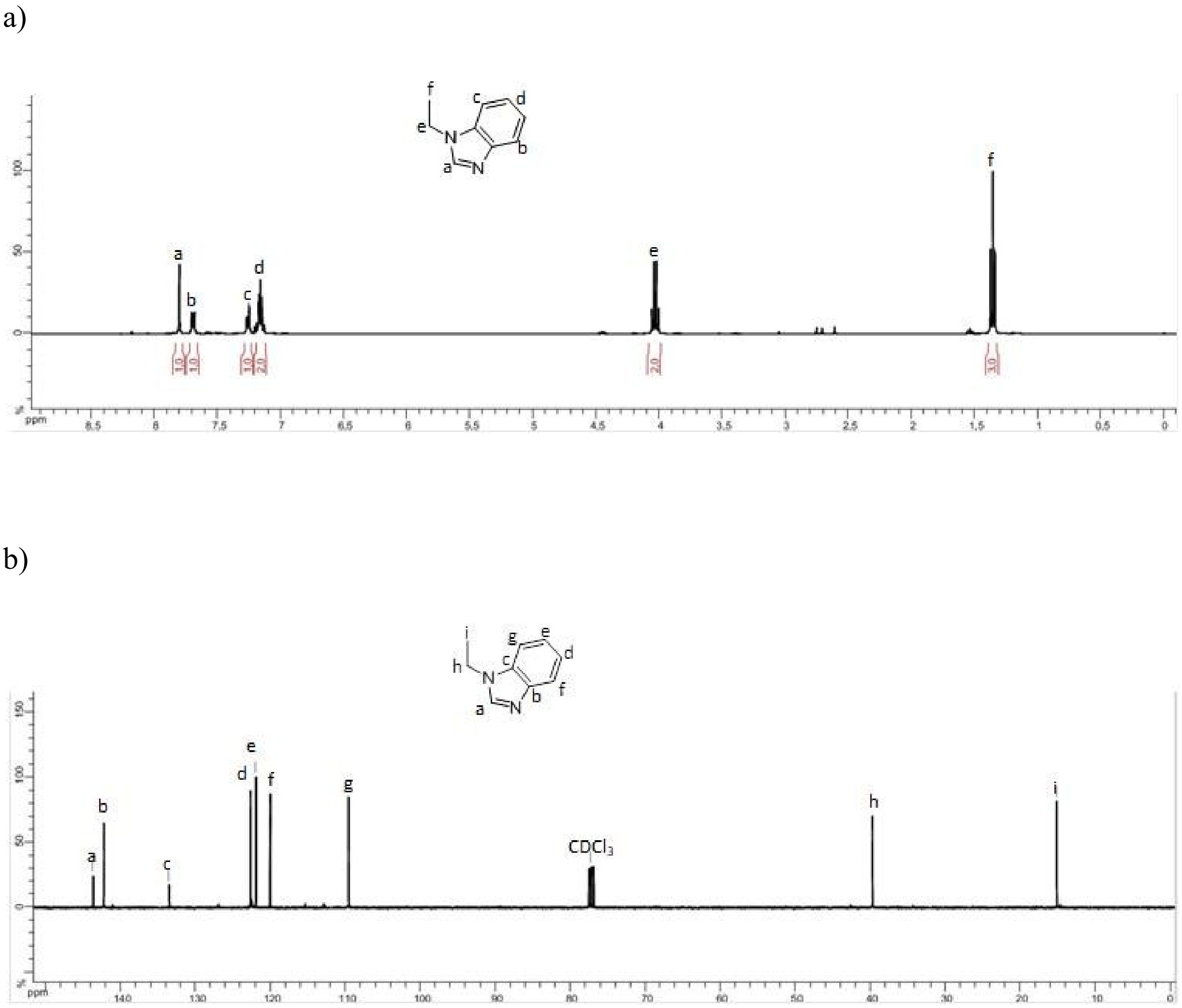


Figure S1: ^{1}H (a) and ^{13}C (b) NMR spectrum of *N*-ethylbenzimidadole **2** in $CDCl_3$

Synthesis of 4-vinylbenzylethylbenzimidazolium chloride

1-vinyl-4-chloromethylstyrene (2.90 mL, 20.8 mmol) and 2 mL (20.8 mmol) of *N*-ethylbenzimidadole were dissolved in acetonitrile (20 mL) and heated to 80 °C for 18h, giving in a yellow solution. The solvent was evaporated and the resulting white powder was washed with ethyl acetate first, then with diethyl ether. The product was dried for three hours under vacuum, yielding a white powder (5.78 g, 19.3 mmol, yield = 93%).

a)

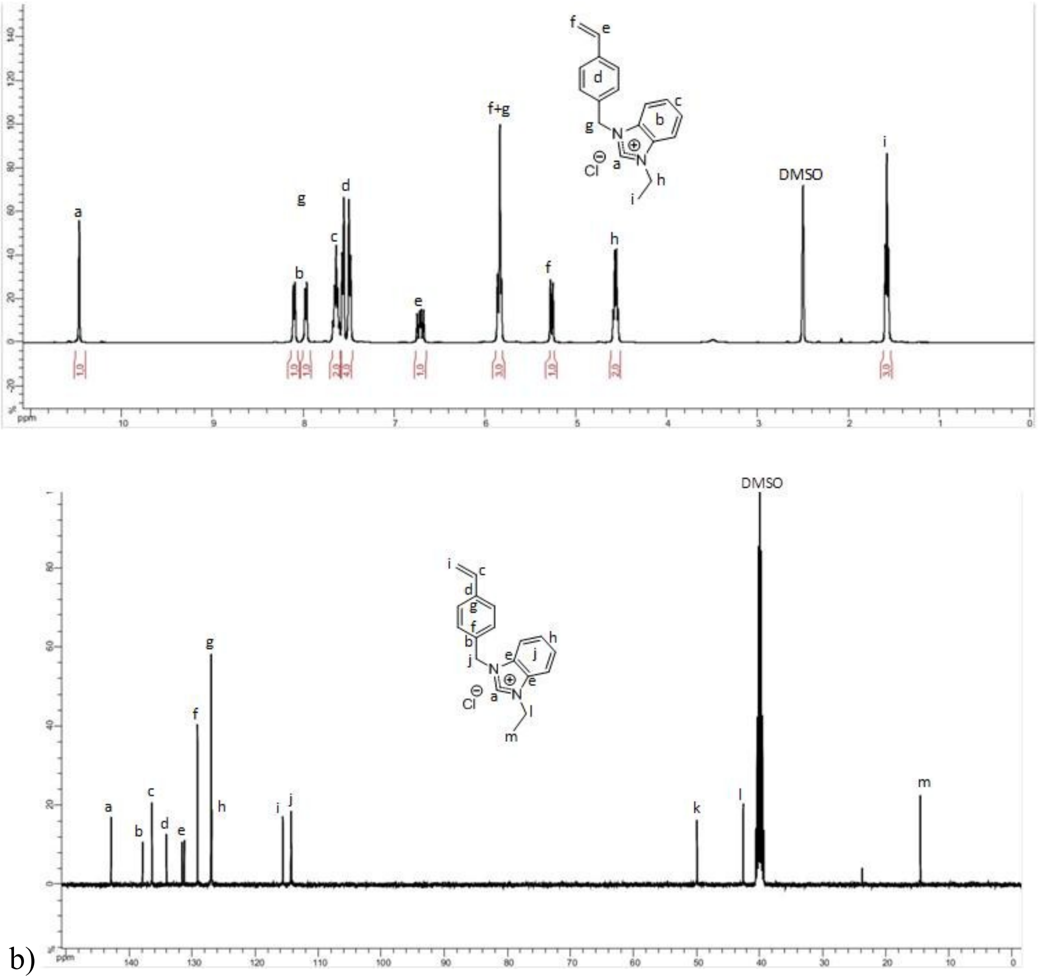


Figure S2: ^{1}H (a) and ^{13}C (b) NMR spectrum of 4-vinylbenzylethylbenzimidadolium chloride **4** in DMSO-*d6*

Synthesis of 4-vinylbenzyl-PEO$_{16}$

The hydroxy-containing poly(ethylene oxide) monomethylester (CH_3O-PEO$_{16}$-OH, 800 g.mol^{-1}) (10 g, 12.5 mmol) was dissolved in THF (30 mL) and a large excess of NaH (10 eq., 3 g, 125 mmol) was added slowly. After 30 min stirring, 1.80 mL (1.95 g, 13 mmol) of 4-vinylbenzylchloride were added drop-wise. The reaction was stirred at 50°C for 48h and then precipitated three times in a large excess of diethyl ether. The pure product was isolated as a yellow viscous oil (8.1 g, 9.3 mmol, yield = 75%).

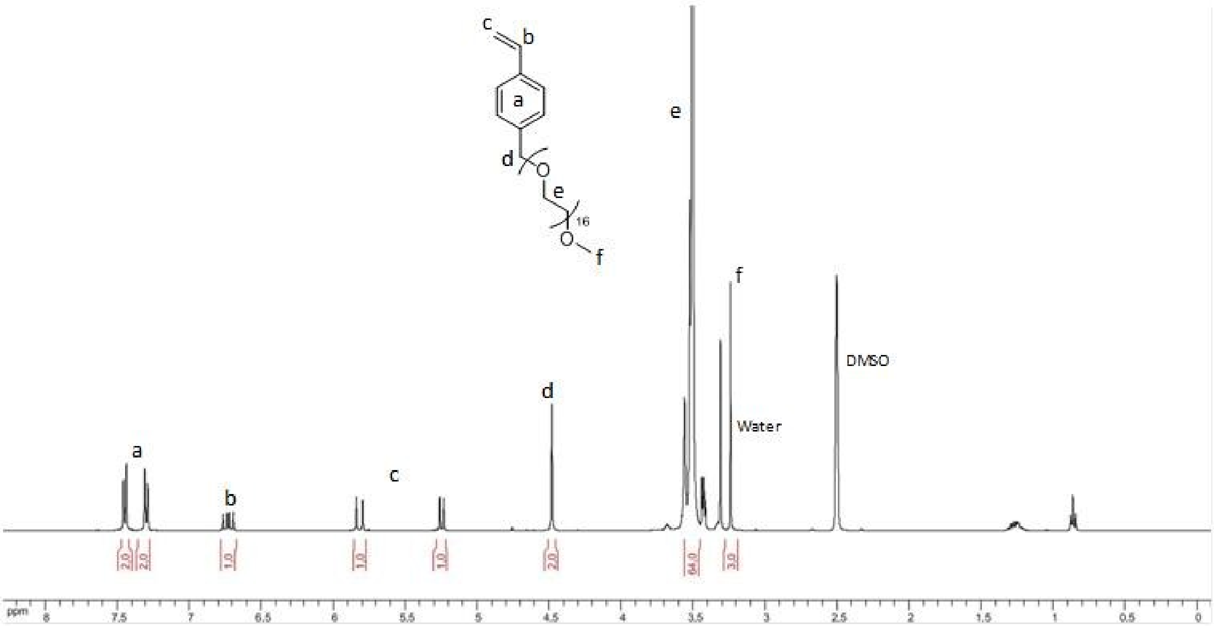


Figure S3: ^1H NMR spectrum of 4-vinylbenzyl-PEO$_{16}$ **6** in DMSO-*d6*

Synthesis of PS-*co*-PIL(Cl)-*co*-PS/PEO

The CTA (23 mg, $8.3.10^{-2}$ mmol), styrene (360 mg, 3.5 mmol) 4-vinylbenzylethylbenzimidazolium chloride (520 mg, 1.73 mmol), 4-vinylbenzyl-PEO_{16} (500 mg, 0.58 mmol), and AIBN (6.0 mg, $4.0.10^{-2}$ mmol) were dissolved in methanol. The solution was degassed by five successive freeze-pump cycles and stirred for 24h at 80 °C. The as-obtained copolymer was purified by dialysis against methanol (1 kDa membrane) and obtained as a pink powder (m = 938 mg); conversion = 81 %, yield = 68 %.

Synthesis of SCNP-Pd

PS-*co*-PIL(Cl)-*co*-PS/PEO (50 mg, 0.063 mmol) was dissolved in 100 mL DMSO and 0.5 eq. of $Pd(OAc)_2$ (7 mg, 0.0315 mmol) was added to the solution. The mixture was stirred at 120°C for three days and then purified by dialysis against methanol (1 kDa membrane) and obtained as a yellowish powder (50 mg, 0.058 mmol, yield = 90%).

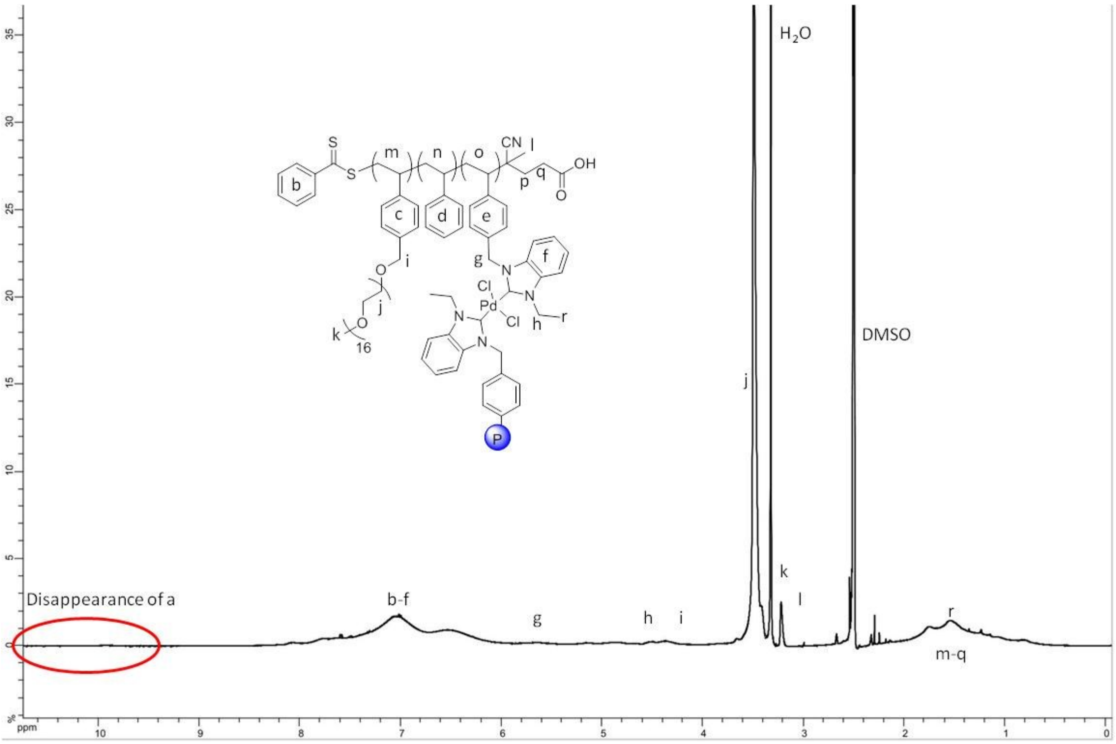


Figure S4: ^{1}H NMR spectra of SCNP **10** in DMSO-*d6*

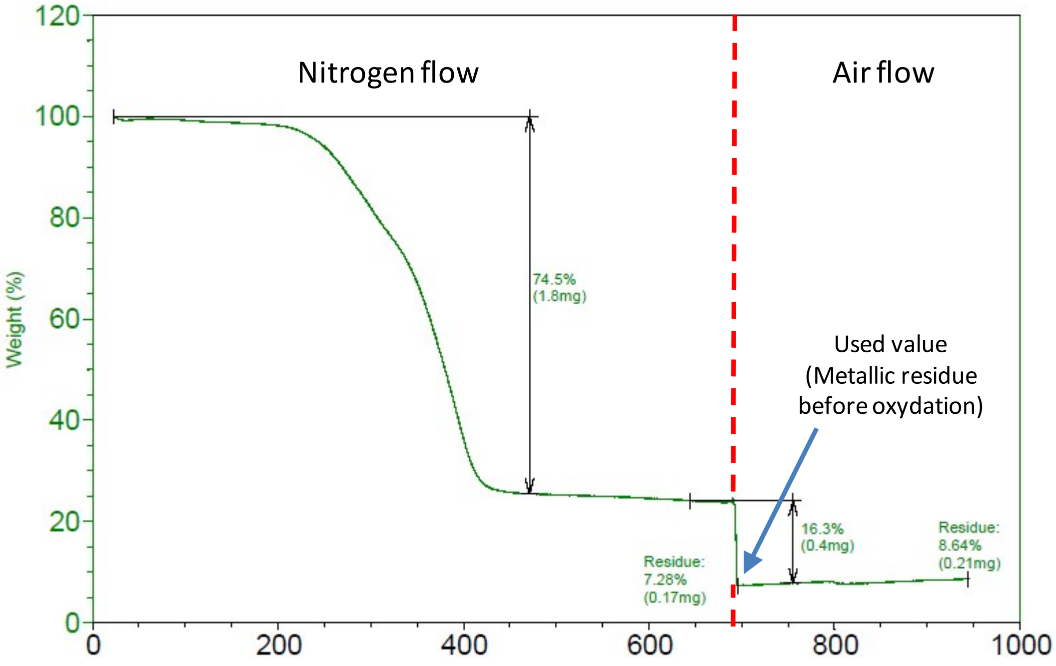


Figure S5: TGA of SCNP **10** (weight fraction of palladium in catalyst **10** was found equal to 7.14 wt.%.)

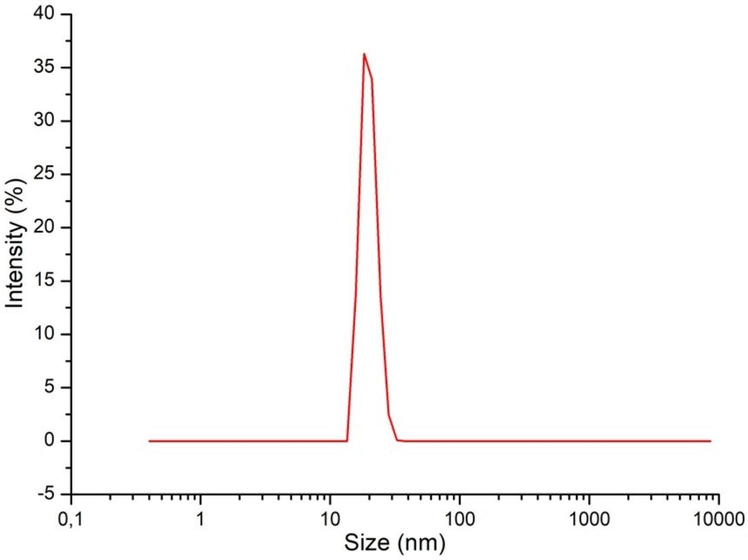
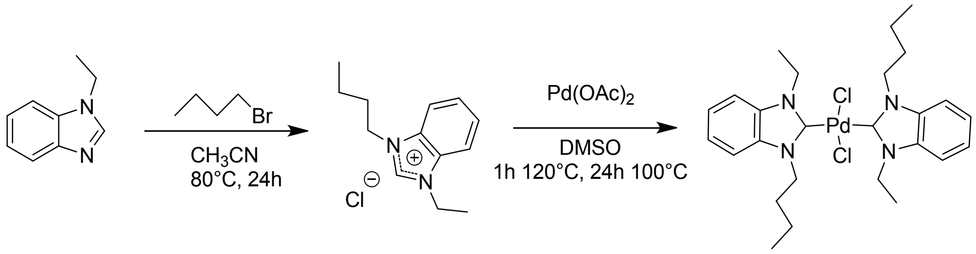


Figure S6: DLS of SCNP **10** in water (0.5 g.L^{-1})

Molecular model: bis(1-butyl-3-ethyl-1H-benzo[d]imidazol-2(3H)-ylidene)palladium(VI) chloride (10)



N-ethyl-benzimidazole (2 g, 14 mmol) was dissolved in acetonitrile (10 mL) and 1.72 mL of 1-chlorobutane (1.2 eq., 16 mmol) was added drop-wise. After stirring at 80°C for 24h, the solution was precipitated in ethyl acetate and diethylether and dried under vacuum. A white powder was obtained (0.673 g, 2.8 mmol, yield= 34%).

The next step consists to the addition of Pd(OAc)$_2$ (0.5 eq., 313 mg, 1,4 mmol) on *N*-ethyl-*N*-methylbenzimidazolium chloride (0.673 g, 2.8 mmol) in DMSO (5mL). After stirring 24h at 120°C, the resulting yellow powder was purified by successive precipitation in Et$_2$O. (0.574 g, 1.7 mmol, yield= 62%)

Suzuki coupling

In a typical experiment, SCNP-Pd (0.88 mg, 3.41.10^{-6} mol (Pd)) were introduced in a Schlenk tube. A 5 mL portion of water and then 480 mg (2.2 mmol) of iodotoluene and 401 mg (2.64 mmol) of (4-hydroxyméthyl)phénylboronique were then added. The reaction mixture was degassed 20 minutes by argon and stirred for 24 h at 110 °C. The mixture was allowed to cool down to room temperature, and was extracted three times by 5mL of diethyl ether. Organic phases were combined, dried over $MgSO_4$ and then dried under vacuum. The white solid was analyzed by ^1H NMR in CD_2Cl_2. All catalysis reactions have been carried out at least three times, and the conversion in reaction products has proven very similar, i.e. with a variation < 5%.

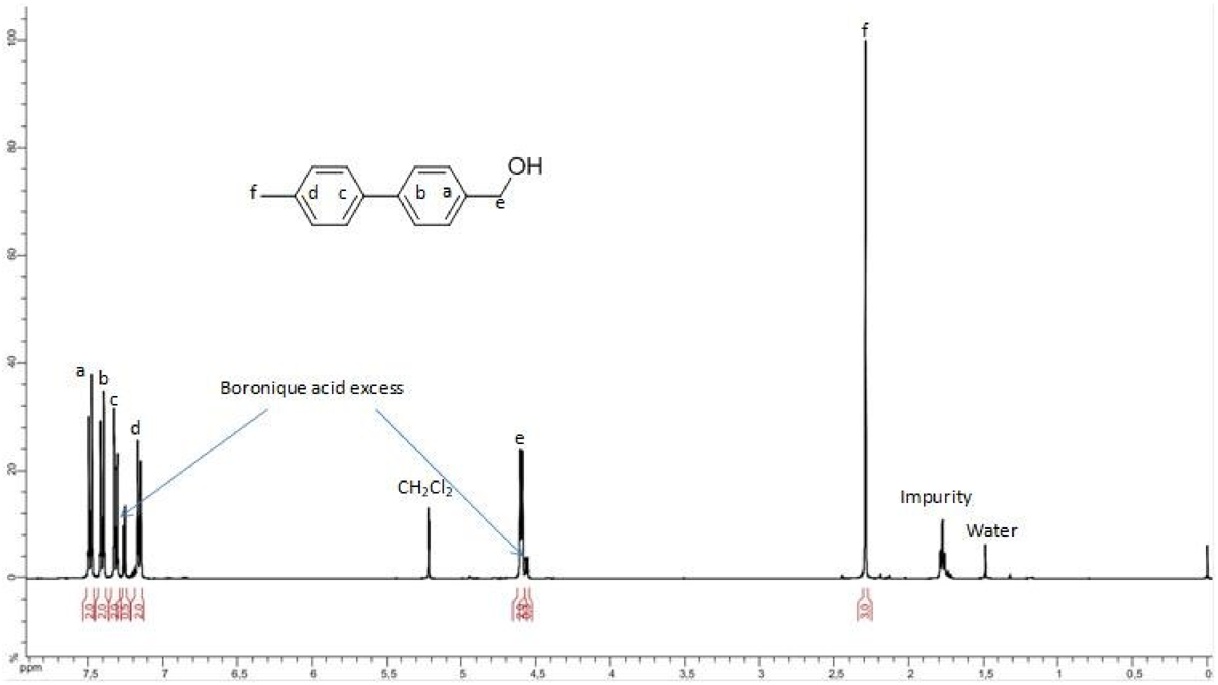


Figure S7: ^1H NMR spectrum of Suzuki coupling **13** reactions in CD_2Cl_2