Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Supporting Information

# C-C couplings in water by micellar catalysis at low loadings from a recyclable polymer-supported Pd(II)-NHC nanocatalyst

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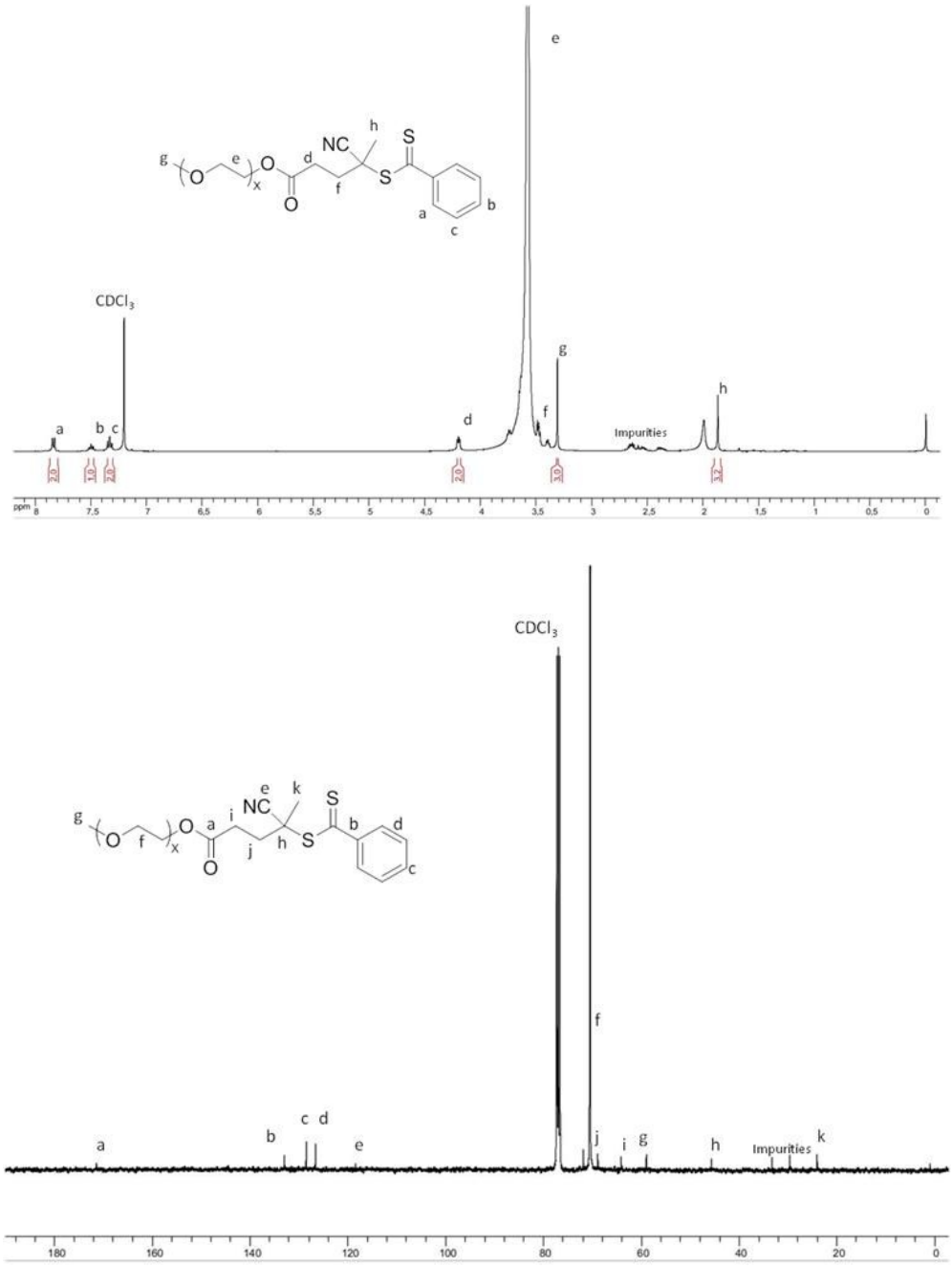



**Figure S01:** $^{1}H$ and $^{13}C$ NMR spectra of PEO-CTA macro RAFT agent **3** in $CDCl_3$.

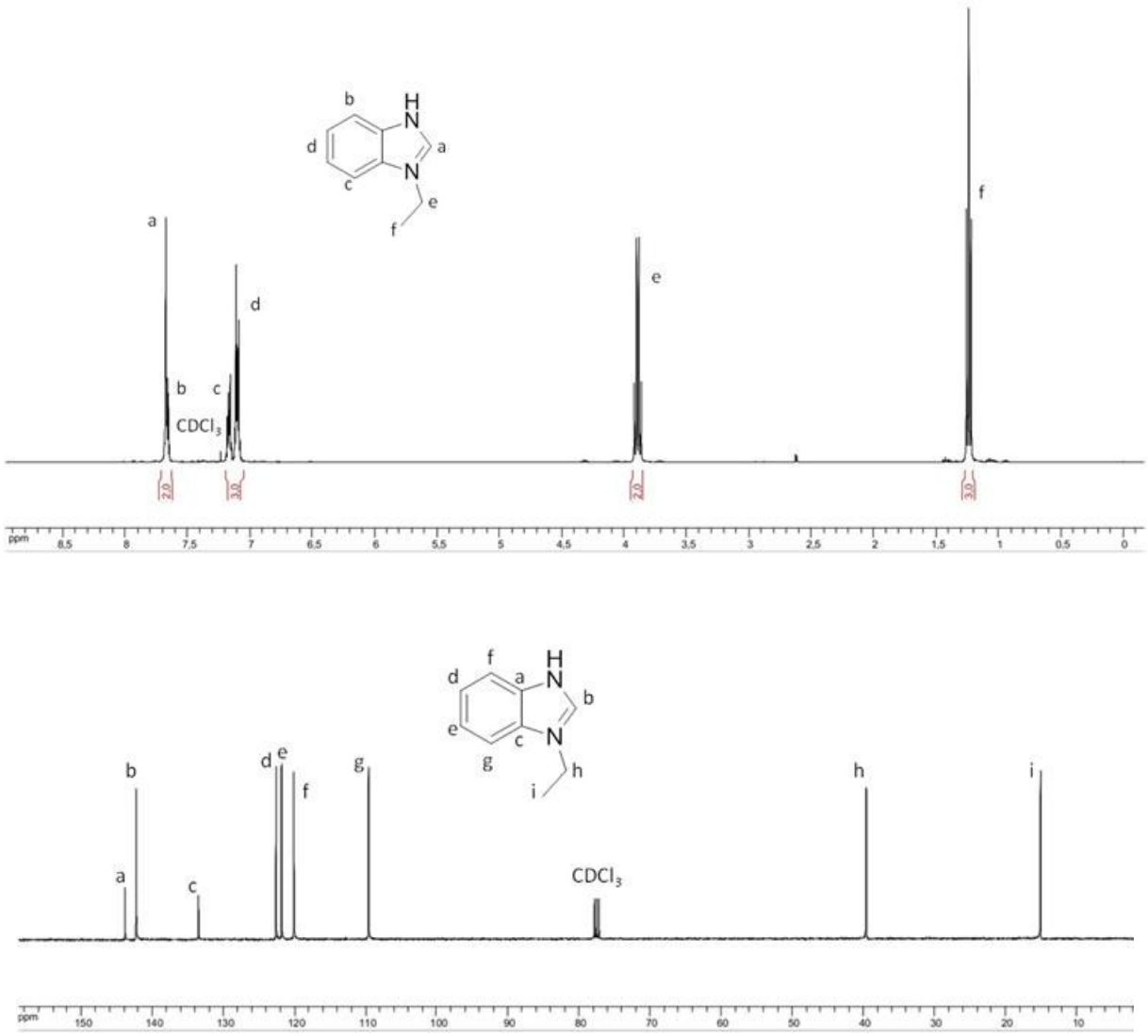



**Figure S02:** $^{1}H$ and $^{13}C$ NMR spectra of *N*-ethylbenzimidazole **5** in $CDCl_3$.

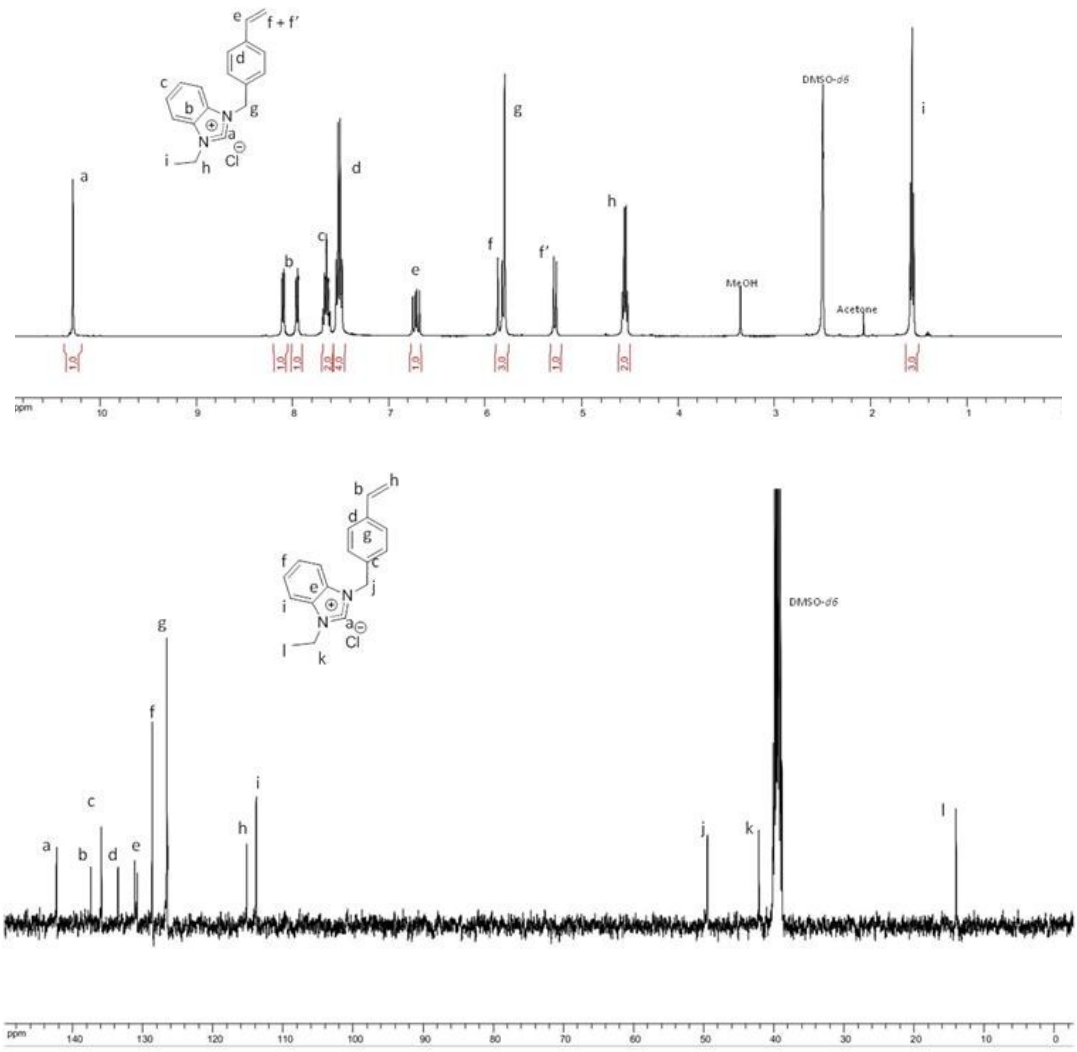



**Figure S03:** $^{1}H$ and $^{13}C$ NMR spectra of 4-vinylbenzylethylbenzimidazolium chloride **6** in DMSO-*d6*.

**Palladium insertion (8)**

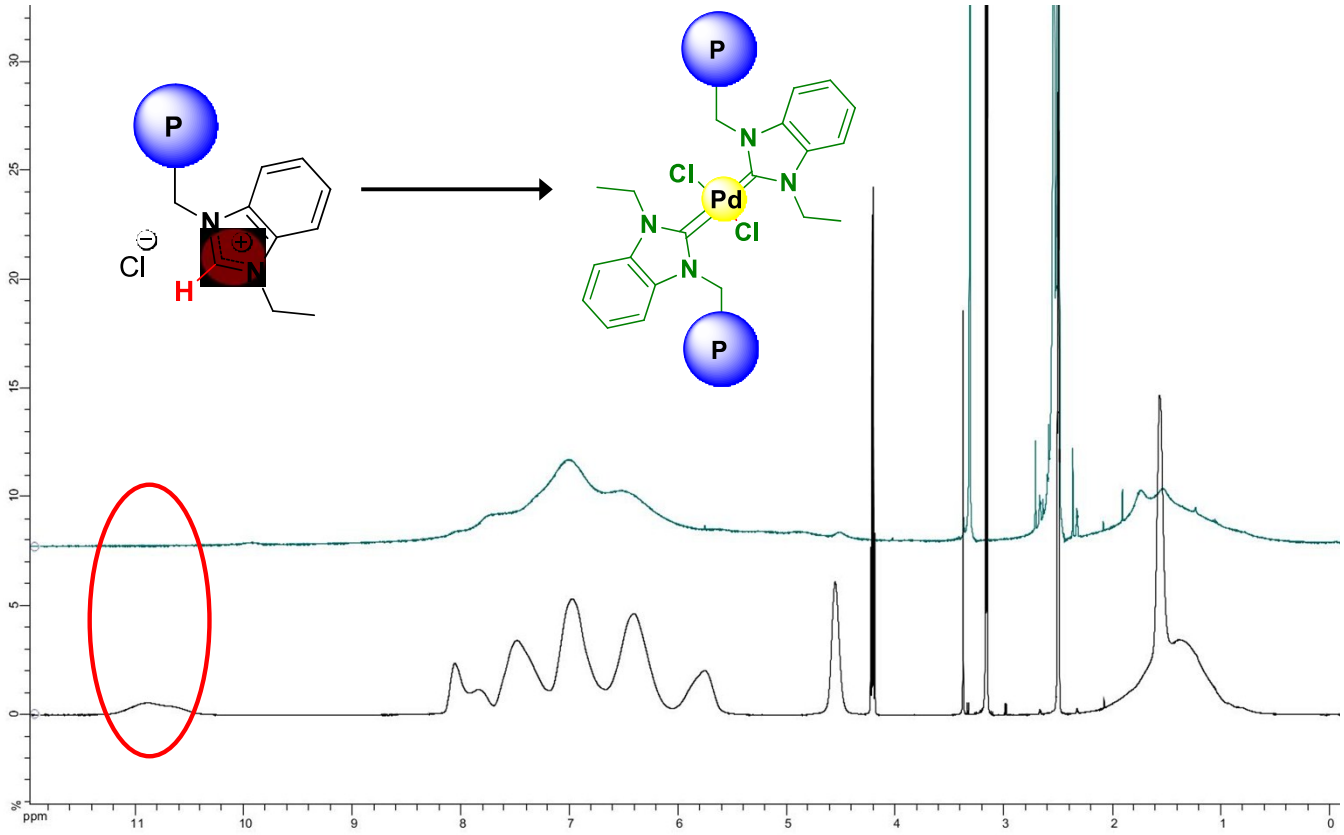
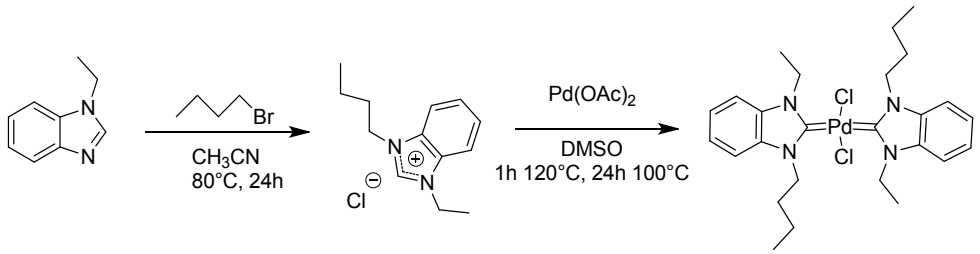



**Figure S04:** $^{1}$H NMR of $PEO_{114}$-*b*-($PS_{24}$-*co*-$PIL(Cl)_{11}$) (black) and $PEO_{114}$-*b*-($PS_{24}$-*co*-NHC-$Pd_{11}$) (green) in DMSO-*d6*.

**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 $Et_2O$. (0.574 g, 1.7 mmol, yield= 62%)

**PS-*co*-P(NHC-Pd) (11)** 4-vinylbenzylethylbenzimidazolium chloride (2.3g, 7.6 mmol), styrene (1.59g, 15 mmol) and AIBN (0.5 mol.%) were dissolved in methanol (12 mL). 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). 2.70 g, yield = 70 % (NMR $^1$H, black line).

In the second step, the PS-*co*-Poly(4-vinylbenzylethylbenzimidazolium chloride) (241 mg, 1.5 mmol) was dissolved in DMSO (2 mL) and $Pd(OAc)_2$ (0.5 eq compared to benzimidazoliums units, 50 mg, 0.22 mmol) was added. The reaction was stirred at 120°C for 48h and then precipitated three times in a large excess of $Et_2O$ and the desired product obtained as a yellow powder. 230 mg, yield = 83 % (NMR $^1$H, green line).

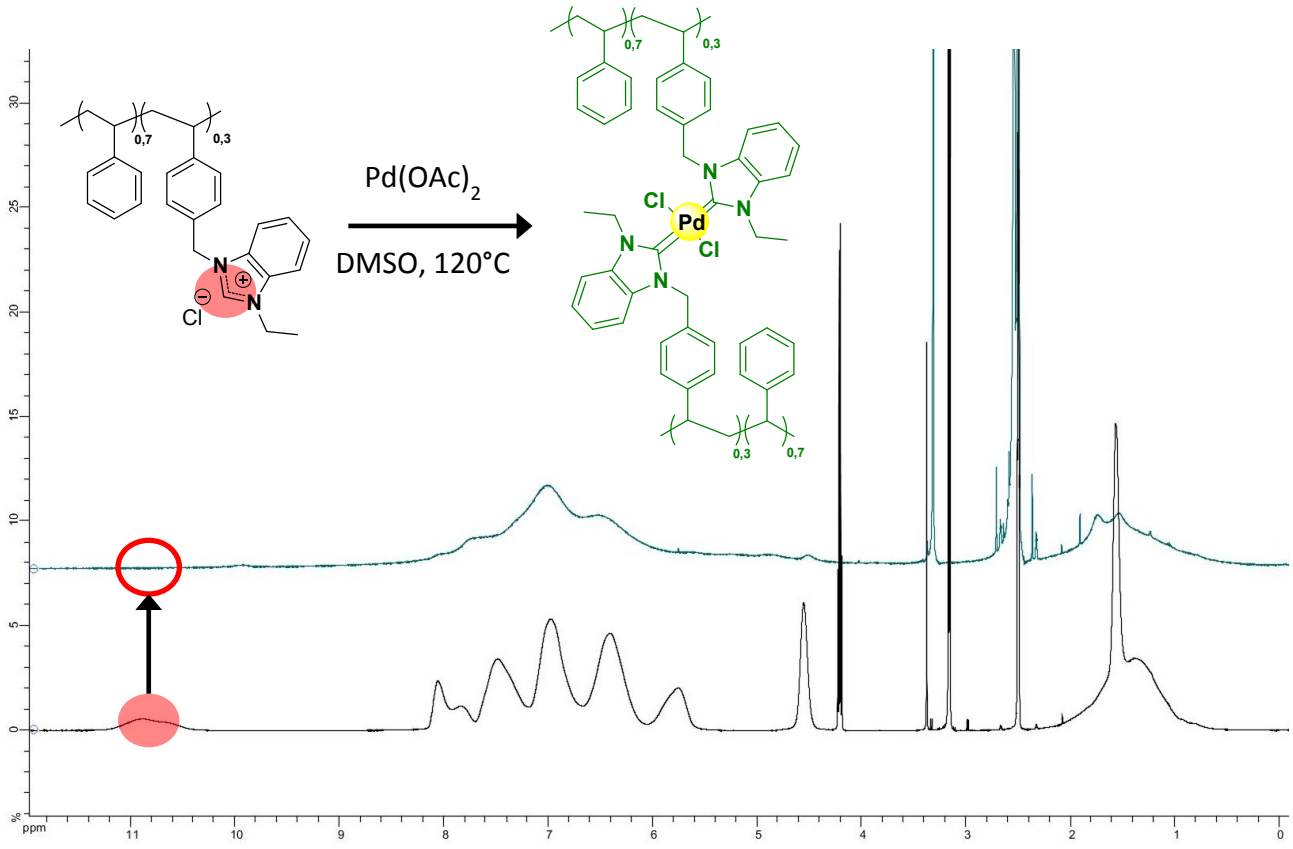



**Figure S05:** $^{1}$H NMR spectra of PS-*co*-P(NHC-Pd)

## Nanoprecipitation process

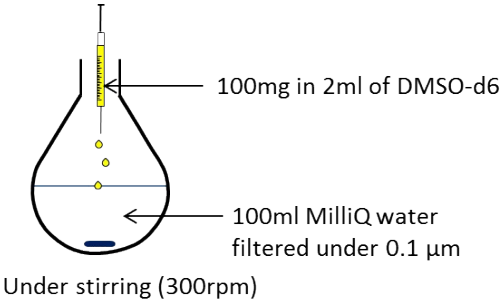



**Figure S06: Schematic nanoprecipitation process**

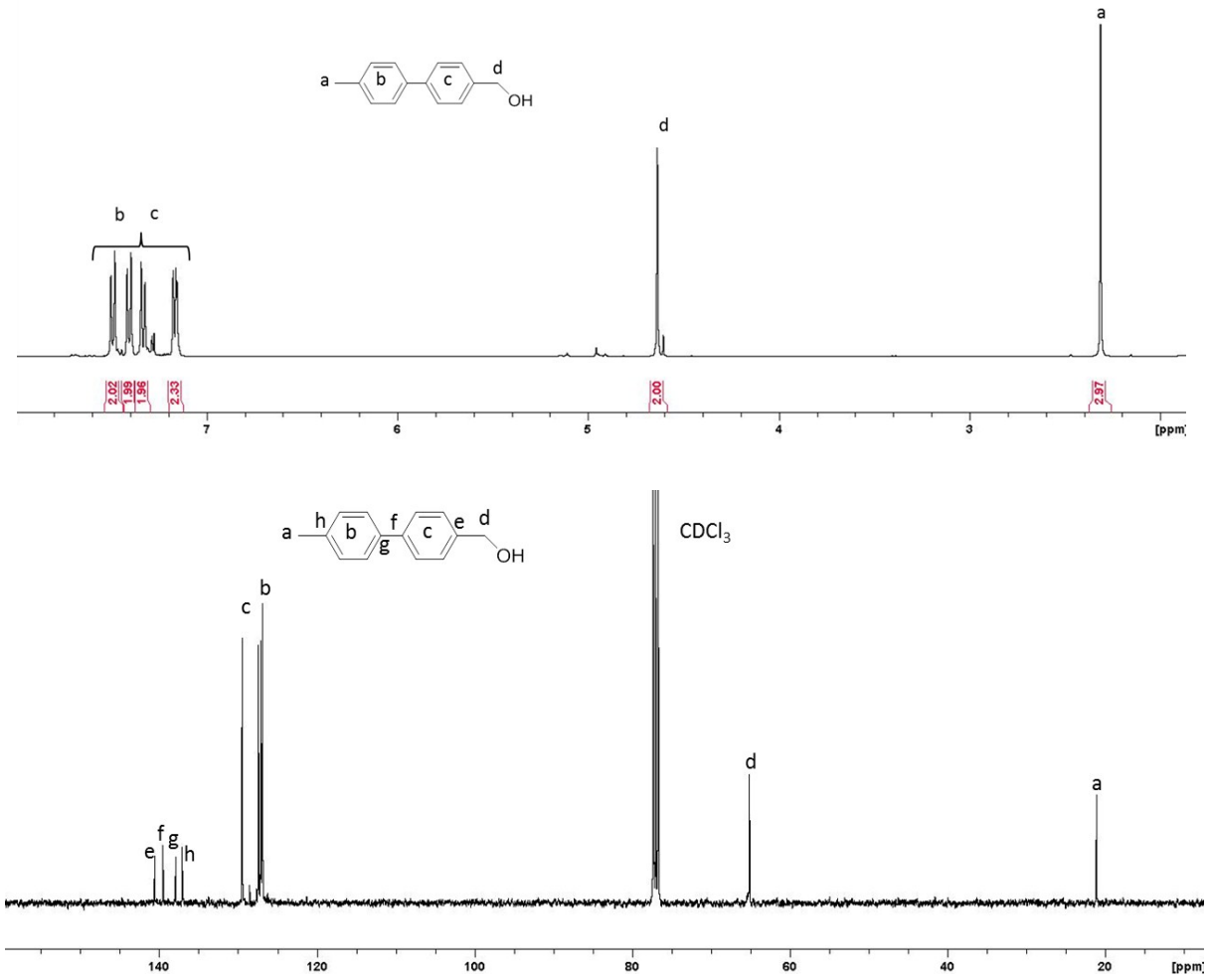



**Figure S07:** $^{1}H$ and $^{13}C$ NMR spectra of Suzuki coupling product in $CDCl_3$

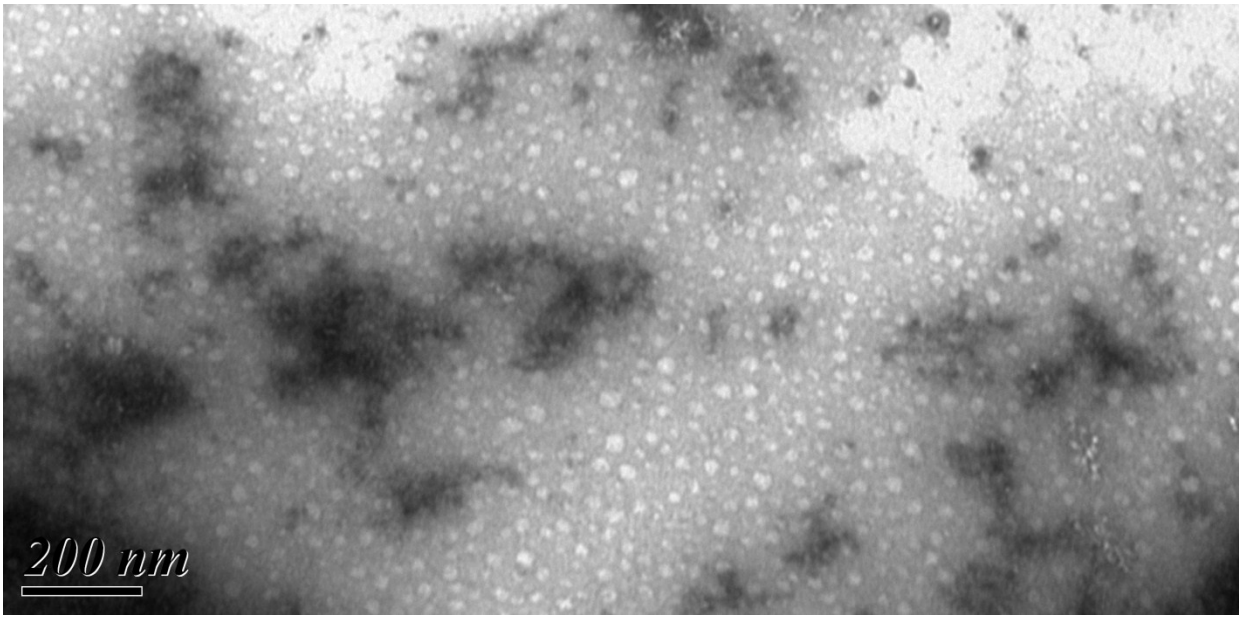
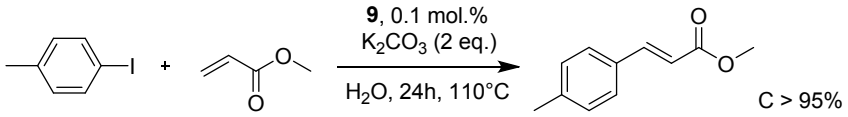



**Figure S08:** TEM picture of the resulting aqueous phase of Suzuki coupling containing micellar catalyst 9 after three extraction cycles of biphenyl product by diethyl ether.

**Heck coupling** In a typical experiment, iodotoluene (480 mg, 2.2 mmol), methyl acrylate (1.5 eq., 299 µL, 3.3 mmol) and potassium carbonate (2 eq., 608 mg, 4.4 mmol) were introduced in a Schlenk tube. 5 mL of micelles were added (cat. 0.1 mol%) and solution was stirred under argon during 20 minutes. The solution was stirred for 24 h at 110 °C. After cooling down to room temperature, the mixture was washed by ethylacetate three times, dried on MgSO4 and evaporated under vacuum during 1h. Product was analyzed by $^{1}$H NMR in $CDCl_3$. A total conversion was calculated by $^{1}$H NMR in $CDCl_3$ without any residual iodotoluene.




$^{1}$H-NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 1H), δ = 7.32 (d, 2H), δ = 7.22 (d, 2H), δ = 6.72 (d, 1H), δ = 3.15 (s, 3H), δ = 2.28 (s, 3H).

$^{13}$C-NMR (100.7 MHz, $CDCl_3$): δ = 168.0, 142.1, 140.0, 133.0, 129.5, 129.0, 112.2, 38.2, 22.5.

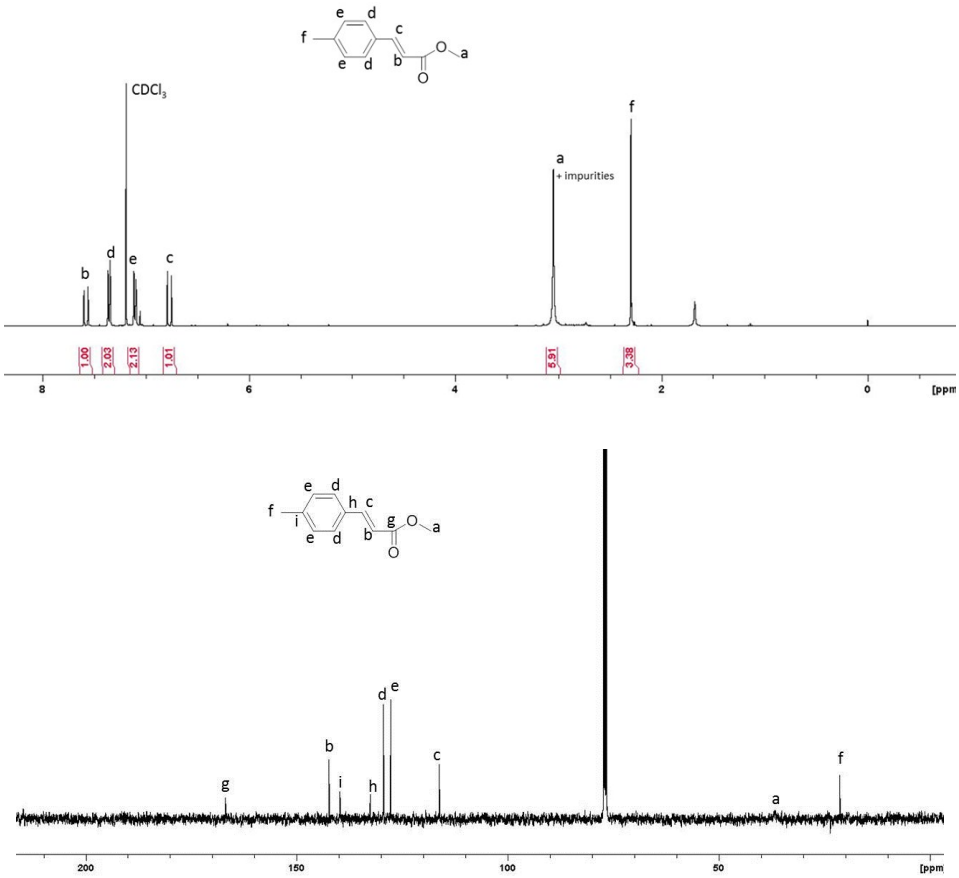
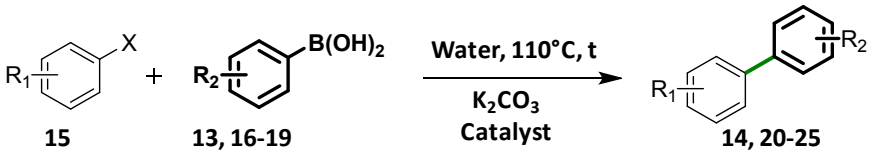
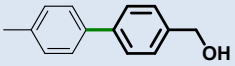
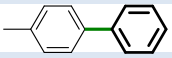
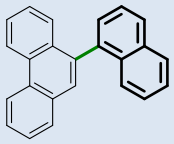
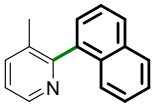
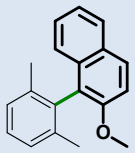
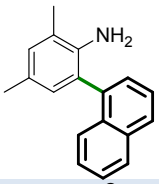
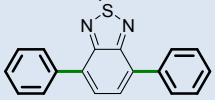


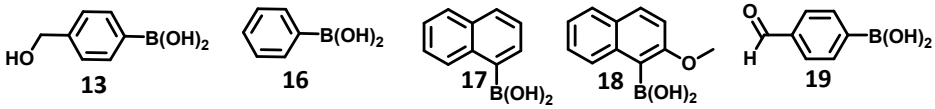

**Figure S09:** $^{1}$H and $^{13}$C NMR spectra of Heck coupling product in $CDCl_3$.

**Table S01:** Detailed substrate scope for Suzuki coupling in water




15 13, 16-19 14, 20-25

| Entry | Catalyst | Conc. (mol.%) | X | t(h) | Conv. (%) | Reaction product |
|---|---|---|---|---|---|---|
| 1 | **9** | 0.1 | I | 24 | 100 | |
| 2 | **9** | 0.1 | I | 1 | 100 | |
| 3 | **10** | 0.1 | I | 1 | 40 | |
| 4 | **9** | 0.1 | Br | 24 | 85 | **14**  |
| 5 | **9** | 0.1 | Cl | 24 | 35 | |
| 6 | **10** | 0.1 | Cl | 24 | 0 | |
| 7 | **9** | 5 | Cl | 24 | 86 | |
| 8 | **10** | 5 | Cl | 24 | 14 | |
| 9 | **9** | 0.1 | Br | 1 | 85 | **20**  |
| 10 | **9** | 0.1 | I | 1 | 98 | |
| 11 | **10** | 0.1 | I | 1 | 63 | **21**  |
| 12 | **10** | 5 | I | 1 | 86 | |
| 13 | **9** | 0.1 | Br | 1 | 97 | |
| 14 | **9** | 0.1 | I | 1 | 100 | |
| 15(b) | **9** | 0.1 | Br | 1 | 56 | **22**  |
| 15 | **9** | 0.1 | Br | 6 | 100 | |
| 16 | **9** | 0.1 | I | 1 | 100 | |
| 17 | **10** | 0.1 | I | 1 | 49 | |
| 18 | **10** | 5 | I | 1 | 52 | **23**  |
| 19(b) | **9** | 0.1 | Cl | 1 | 43 | |
| 19 | **9** | 0.1 | Cl | 6 | 100 | |
| 20 | **9** | 0.1 | Br | 6 | 100 | **24**  |
| 21 | **9** | 0.1 | Br | 1 | 100 | **25**  |



**Substrate scope for Suzuki coupling in water**

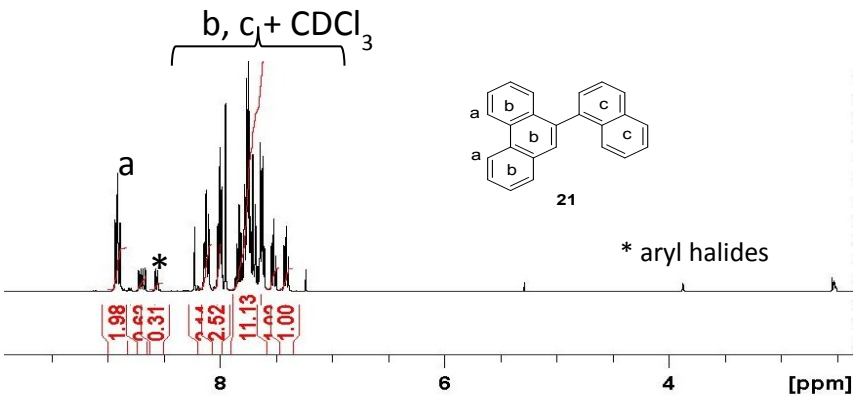



**Figure S10:** $^{1}H$ spectrum of Suzuki coupling product **21** in $CDCl_3$. **(Table 2; entry 10-13)**

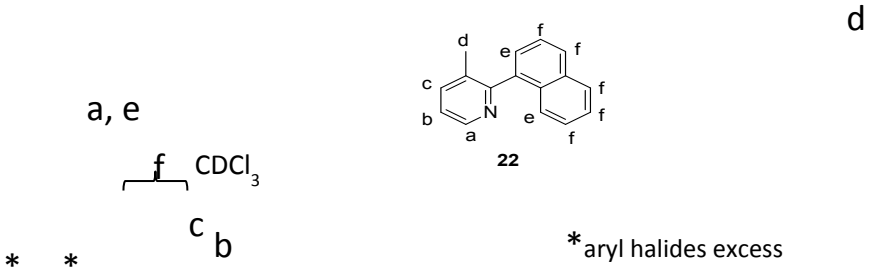



**Figure S11:** $^{1}H$ spectrum of Suzuki coupling product **22** in $CDCl_3$. **(Table 2; entry 14-15)**

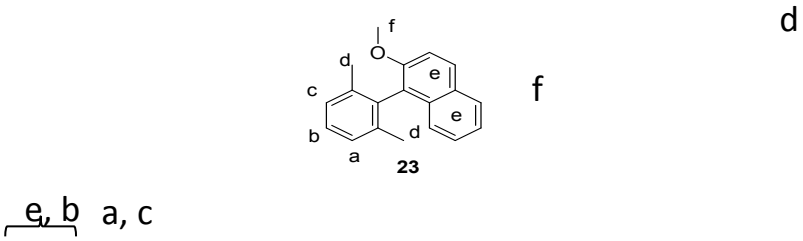



**Figure S12:** $^{1}H$ spectrum of Suzuki coupling product **23** in $CDCl_3$. **(Table 2; entry 16-19)**

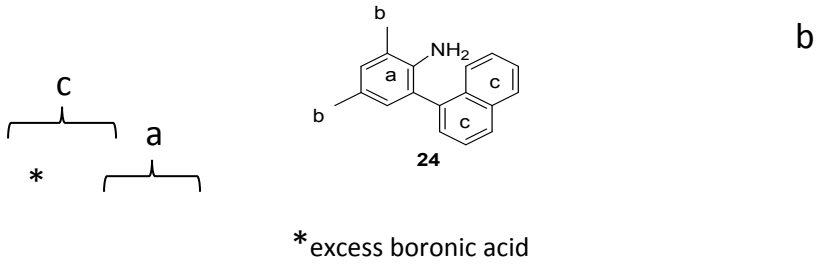



**Figure S13:** $^{1}H$ spectrum of Suzuki coupling product **24** in $CDCl_3$. **(Table 2; entry 20)**

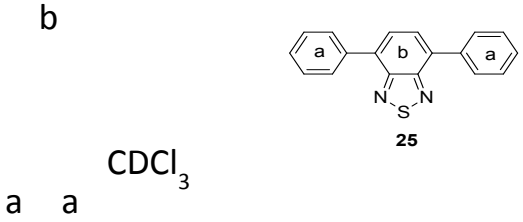



**Figure S14:** $^{1}H$ spectrum of Suzuki coupling product **25** in $CDCl_3$. **(Table 2; entry 21)**