Supplementary Materials for:

A Mild and Recyclable Nano-sized Nickel Catalyst for the Stille Reaction in Water

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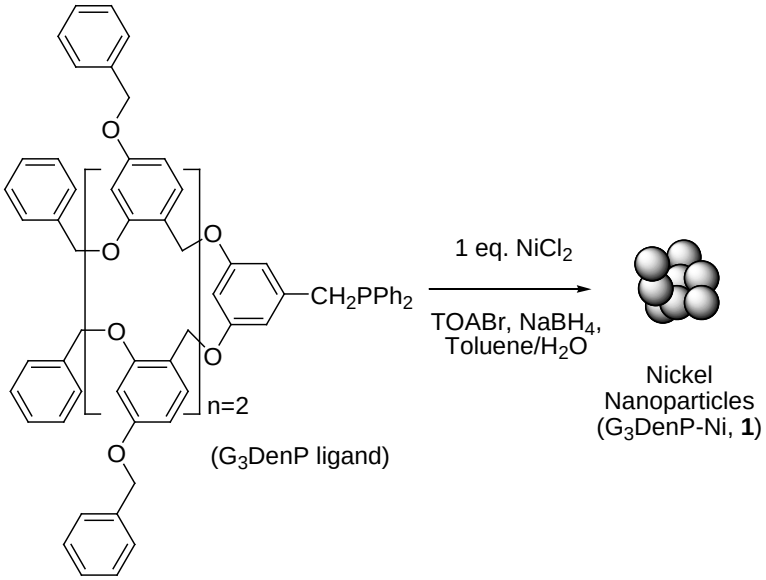
1. General Information

Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follow: THF and dioxane were distilled from sodium and benzophenone. DMF was refluxed with CaH_2 and distilled out under reduced pressure. All reactions were carried out under nitrogen or argon unless otherwise specified. Deionized water with a resistivity of 18.2 MΩ·cm was used for the catalysis. All ^{1}H-NMR (400 MHz) spectra were recorded on a Bruker-DMX 400 using $CDCl_3$ solution in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. High and Low resolution fast atom bombardment (FAB) measurements were made with a JEOL JMS-AX505HA mass spectrometer. Transmission electron microscopy (TEM): the chloroform dispersion of catalyst was drop-cast onto a 300 mesh carbon coated copper grid, and TEM pictures were taken on a FEI-Tecnai G^2 F30 at an accelerating voltage of 75 kv. The metal leaching tests were conducted on a sequential X-ray fluorescence spectrometer XRF-1700 at Tsinghua University (Shimadzu Corp., Kyoto, Japan).

2. General Procedures for Preparing G_3DenP-Ni and Purification [1]



An aqueous solution of $NiCl_2$ (0.5 mmol in 5 mL deionized water) was mixed with a solution of tetraoctylammonium bromide (TOABr, 1.25 mmol) in 10 mL toluene. The two-phase mixture was vigorously stirred until all the nickel dichloride was transferred into the organic layer. Then collected the toluene phase and purged with argon for 1 hour to remove the residual oxygen. G_3DenP ligand [2] (0.88 g, 0.5 mmol) was then added to the organic phase. A freshly degassed aqueous solution of sodium borohydride (1 mmol in 5 mL water) was slowly added with vigorous

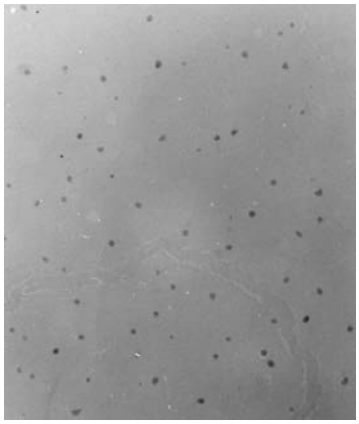
stirring. After further stirring for 3 hours, the organic phase was separated, washed with saturated brine, evaporated to afford black powders.

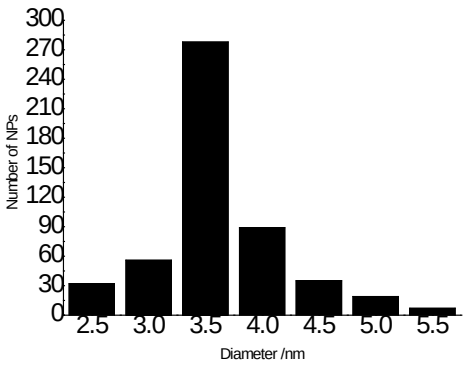
The crude nickel nanoparticles were further purified by Soxhlet extraction, which were dissolved in a minimum amount of toluene, and then placed into a Soxhlet thimble of 25 × 100 mm dimensions. 250 mL of ethanol was used as cleansing solvent. The Soxhlet extraction was run over a 12 h period under argon atmosphere and was monitored every 3 h by removing the ethanol from the round bottomed flask of the extraction equipment. After five extraction cycles, the purified nickel nanoparticles were recovered by dissolving in dichloromethane and evaporated to give black powder, which could be used directly in coupling reactions. The diameter and composition of the **G_3DenP**-Ni were determined by TEM, Element Analysis and XRF, respectively.

[1] L. Wu, J. Ling, Z.-Q. Wu, *Adv. Synth. Catal.,* 2011, **353**, 1452-1456.

[2] L. Wu, B. -L. Li, Y. -Y. Huang, H. -F. Zhou, Y. -M. He, Q. -H. Fan, *Org. Lett.,* 2006, **8**, 3605.

3. Representative Characterization of Nickel Nanoparticles (TEM Image, Size Distributions, ICP-XRF and Combustion Analysis Results)



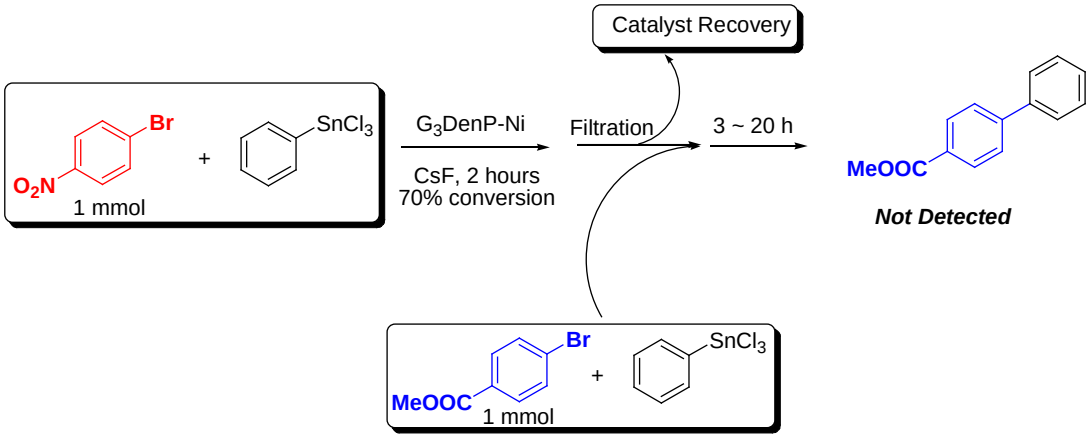


Method	Ni	C	H	N	P
XRF	3.10 %				1.69%
Element Analysis	3.22%	76.96%	5.67%	-	1.74%

The molar ratio of nickel to dendrons was calculated based on element analysis, which is about 1:1.

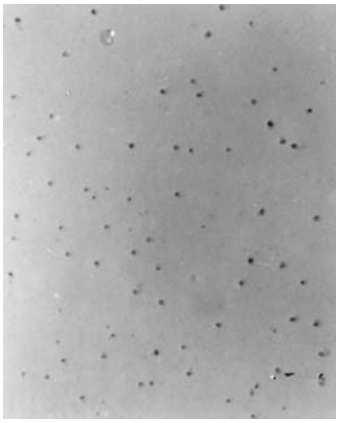
4. "Hot-filtration" Experiment

For the standard reaction of *p*-nitrobromobenzene with trichlorophenylstannane in the presence of 2 mol% **G_3DenP**-Ni, after 2 hours (70% conversion by GC), the catalyst was recovered by filtration, then added methyl 4-bromobenzoate and trichlorophenylstannane, no coupling product was detected even up to 20 hours at ambient temperature.



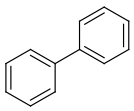
5. General Procedures for Stille Coupling and Catalyst Recycling

To a 10 mL vial under argon was added aryl halides (1 mmol), organotin (1.1 mmol), CsF (2.2 mmol), 2 mol% **G_3DenP**-Ni and 5 mL degassed deionised water. The reaction mixture was then stirred for the time listed in maitext (table 2) at room temperature. After the reaction went complete as monitoring by TLC, 50 mL hexanes was added to extract the product and precipitate the catalyst. The nano-sized catalyst was recovered by centrifugation then washed with 5 mL hexanes for three times, dried over vacuum, which can be used directly in the next run. The left-off organic phase with product was separated from the aqueous solution, and combined to determine the coupling yield after silica chromatography.

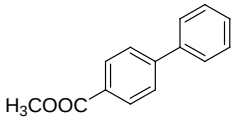


TEM image of G_3DenP-Ni after the run sixth.

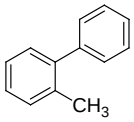
5. Representative Coupling Products Characterizations and Spectra



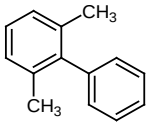
^{1}H NMR ($CDCl_3$) δ 7.230-7.36 (m, 2H), 7.40-7.45 (m, 4H), 7.55-7.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 127.2, 127.3, 128.8, 141.3.



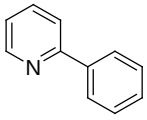
^{1}H NMR ($CDCl_3$) δ 3.95 (s, 3H), 7.40-7.50 (m, 3H), 7.61-7.68 (m, 4H), 8.11 (d, *J* = 8.63 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 52.1, 127.1, 127.3, 128.2, 128.9, 130.1, 140.0, 145.7, 167.0.



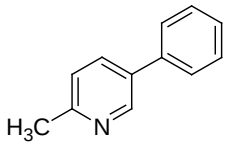
^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3H), 7.18-7.20 (m, 4H), 7.25-7.29 (m, 3H), 7.32-7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.5, 125.8, 126.8, 127.3, 128.1, 129.2, 129.8, 130.3, 135.4, 141.9, 142.0.



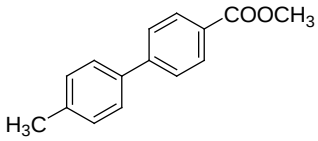
^{1}H NMR ($CDCl_3$) δ 1.20 (s, 6H), 7.05-7.13 (m, 5H), 7.26-7.29 (m, 1H), 7.33-7.45 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 20.8, 126.6, 127.0, 127.2, 127.3, 128.4, 128.7, 129.0, 136.1.



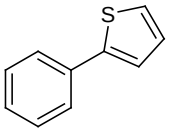
^{1}H NMR ($CDCl_3$) δ 7.21-7.25 (m, 1H), 7.41-7.50 (m, 3H), 7.73-7.76 (m, 2H), 7.98-8.01 (m, 2H), 8.69-8.70 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 120.6, 122.1, 125.9, 126.8, 127.0, 136.8, 139.3, 149.6, 157.5.



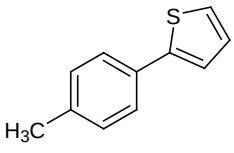
^{1}H NMR ($CDCl_3$) δ 2.59 (s, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.33-7.64 (m, 5H), 7.80 (dd, *J* =2.6 Hz, 1H), 8.75 (d, *J* = 2.6Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 20.9, 124.6, 127.8, 128.6, 129.7, 133.3, 133.8, 136.9, 143.3, 158.6.



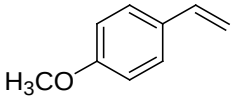
^{1}H NMR ($CDCl_3$) δ 2.33 (s, 3H), 3.86 (s, 3H), 7.19 (d, *J*= 8.1Hz, 2H), 7.45 (d, *J*= 8.1Hz, 2H), 7.57 (d, *J*= 8.25Hz), 8.02 (d, *J*= 8.25Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.2, 52.1, 126.8, 127.1, 128.6, 129.7, 130.1, 137.1, 138.1, 145.6, 167.0.



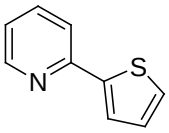
^{1}H NMR ($CDCl_3$) δ: 7.32–7.45 (m, 5H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ: 111.5, 123.8, 127.1, 127.2, 127.3, 128.5, 128.6, 142.1.



^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3H), 7.03 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J*= 5.1 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.3, 122.7, 124.3, 125.7, 127.9, 129.6, 131.6, 137.5, 144.8.



^{1}H NMR ($CDCl_3$) δ 3.82 (s, 3H), 5.13 (dd, *J* = 10.9 Hz, 1H), 5.60 (dd, J = 17.6 Hz, 1H), 6.67 (q, *J* = 17.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 55.5, 111.8, 114.1, 127.6, 130.7, 136.4, 159.6.



^{1}H NMR ($CDCl_3$) δ 7.10-7.19 (m, 2H), 7.40 (d, *J*=7.2 Hz, 1H), 7.62 (d, J =7.2 Hz, 1H), 7.66-7.71 (m, 2H), 8.58 (d, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 118.7, 121.9, 124.6, 127.6, 128.0, 136.7, 144.7, 149.5, 152.6.