Iron nanoparticles in the coupling of alkyl halides with aryl Grignard reagents.

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SUPPORTING INFORMATION

Contents

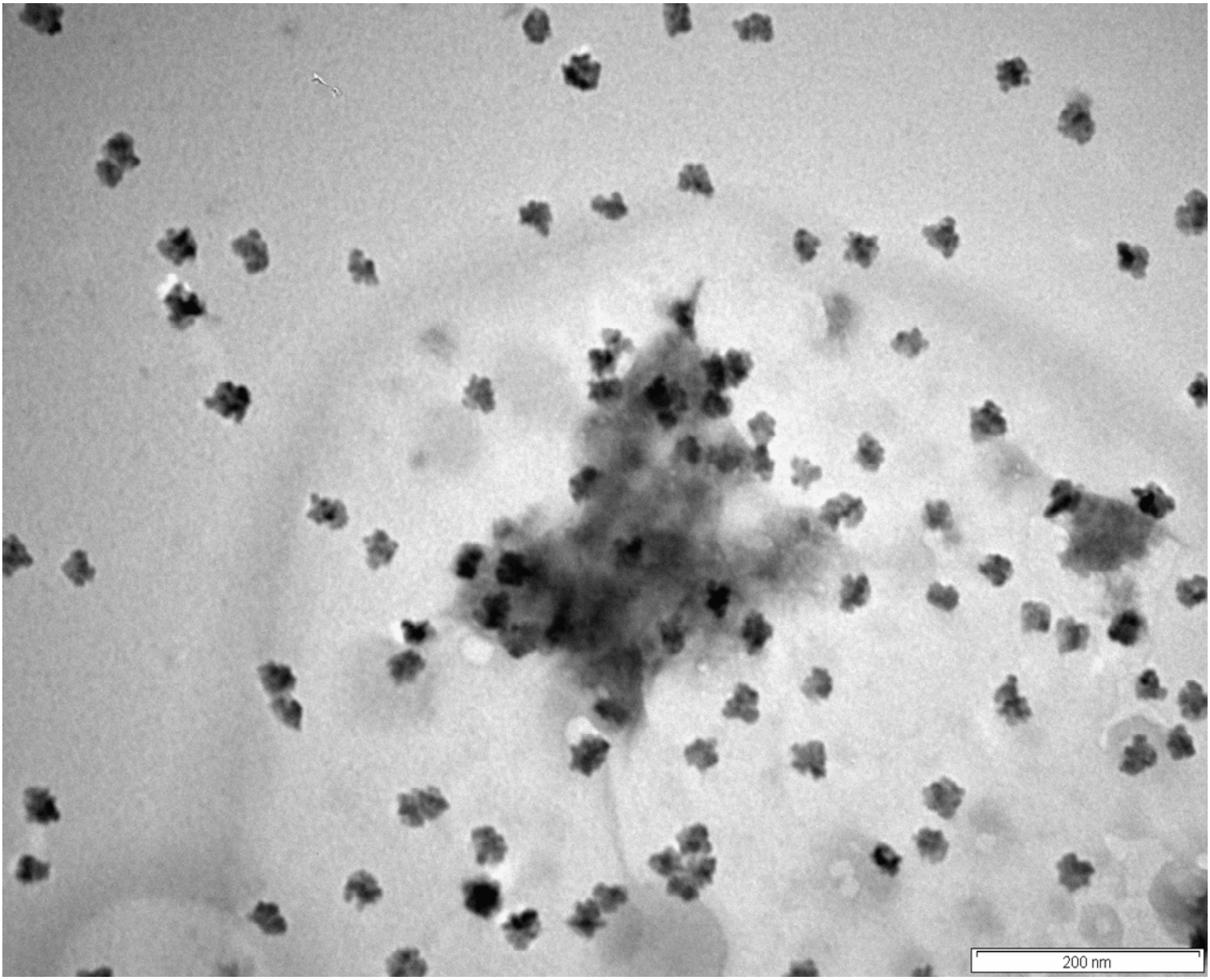
General Experimental Conditions. All reactions and manipulations of air-sensitive materials were performed under nitrogen, either in a glovebox or using standard Schlenck techniques. All solvents were dried before use. All catalytic reactions were performed on a Radleys Carousel Reactor^{TM}. This consists of twelve *ca.* 45 ml tubes which are fitted with screw-on teflon caps that are equipped with valves for the introduction of inert gas and septa for the introduction of reagents. The twelve reaction tubes sit in two stacked aluminium blocks, the lower one fits on a heater-stirrer and can be maintained at a constant temperature with a thermostat, while the upper block has water circulating which cools the top of the tubes, allowing reactions to be performed at reflux temperature.

Samples for TEM analyses were dropped onto carbon covered 3 mm Cu grids and the solvent was allowed to evaporate. The samples were imaged using a JEOL 1200EX TEM. Images were acquired using a SIS Megaview digital camera and processed using Analysis software. EDX analyses were performed using an Oxford Instruments Link Isis X-ray detector.

Coupling of cyclohexyl bromide, 1, with 4-MeC_6H_4MgBr, 2, catalysed by *in situ*-reduced $FeCl_3$-dpph. Dpph (0.05 mmol) in CH_2Cl_2 (2 ml) was added to anhydrous $FeCl_3$ (0.05 mmol) in a Radleys Carousel reaction tube and then after standing (2 mins) the solvent was removed *in vacuo*. Et_2O (3 ml) was added and the solution was stirred (~ 2 mins). CyBr (1.0 mmol) was added, the solution stirred for 5 minutes, then heated to reflux temperature (external temperature 45 °C; reaction temperature ~ 36-38 °C) and 4-MeC_6H_4MgBr (1.0 M solution in Et_2O, 2.0 ml) was added in one portion. The reaction

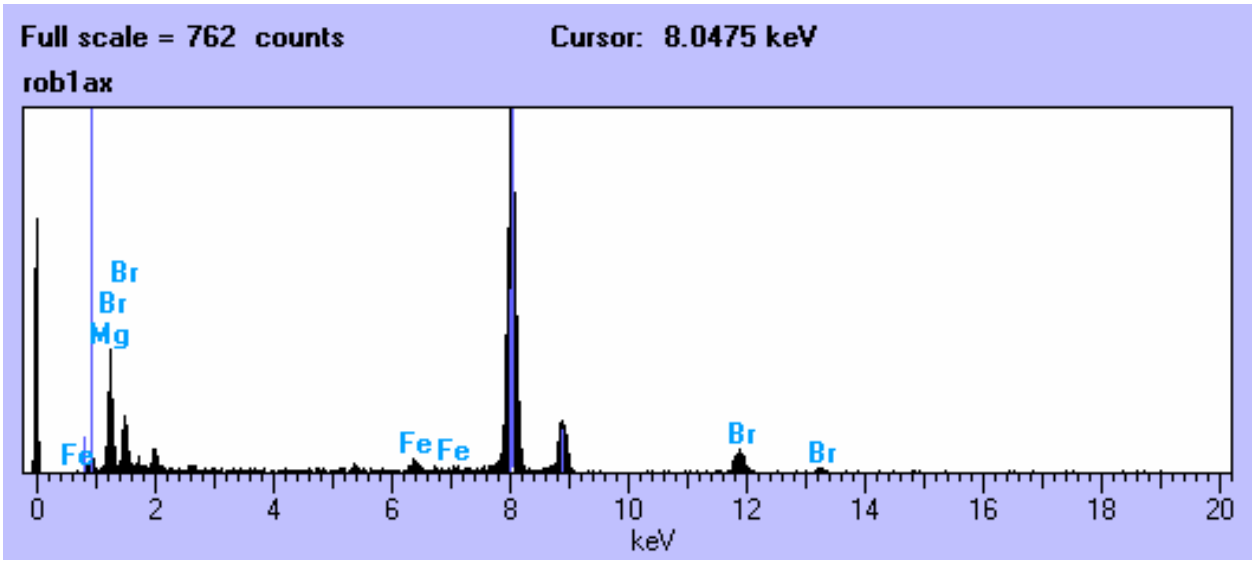
was heated for 30 mins, then allowed to cool. A sample was withdrawn for TEM analysis, the results of which are shown in figure S1.

Figure S1. TEM image of reaction mixture from the coupling of cyclohexyl bromide, **1**, with 4-MeC_6H_4MgBr, **2**, catalyzed by *in situ*-reduced $FeCl_3$-dpph (sample washed with water to remove excess MgX_2). Typical Fe particle size 5 – 12 nm.



Reaction of $FeCl_3$/dpph mixture with 4-MeC_6H_4MgBr, 2. As above but without adding the cyclohexyl bromide. The resultant mixture was analyzed by TEM, the results of which is shown in figure 1 (main paper) and the EDX spectrum is shown in figure S2.

Figure S2. EDX spectrum of sample shown in figure 1 (main paper).



General Method for the coupling of alkyl halides with aryl Grignard reagents catalysed by $FeCl_3$-PEG mixtures. A mixture of anhydrous $FeCl_3$ (0.0081 g, 0.05 mmol) and PEG (pre-dried, toluene azeotrope, M_w = 14,000 g mol^{-1}, 0.0030 g) in CH_2Cl_2 (2 ml) was stirred for 2 mins in a Radleys Carousel reaction tube and then the solvent was removed *in vacuo*. Et_2O (1 or 3 ml, to give a total solvent volume of 5 ml after addition of Grignard solution) was added and the mixture was stirred (~ 2 mins). The alkyl halide (1.0 mmol) was added, the solution stirred for 5 minutes, then heated (external temperature 45 °C) and the aryl Grignard reagent (0.5 or 1.0 M solution in Et_2O or THF, 4.0 or 2.0 ml, 2.00 mmol Grignard reagent in total) was added in one portion. The

reaction was heated for 30 mins and then quenched by the addition of water (5 ml). The mixture was extracted with CH_2Cl_2 (2 x 5 ml), dried ($MgSO_4$) and filtered. Mesitylene in CH_2Cl_2 (0.667 M, 1.00 ml) was added, the volatiles were removed under reduced pressure and the conversion to coupled product was determined by ^1H NMR spectroscopy. In all cases the spectroscopic data was in agreement with literature values. Representative products from the reactions shown in table 1, entries 4 and 21, were isolated by column chromatography (silica, cyclohexane eluent). The ^1H and ^{13}C NMR spectra of the two representative products (1-cyclohexyl-4-methylbenzene and 1-octyl-4-methylbenzene respectively) are shown in figures S3 – S6. A sample of the reaction mixture obtained in the coupling of **1** with **2** was removed for TEM analysis, the results of which are presented in figure S7.

Figure S3. ^{1}H NMR spectrum of 1-cyclohexyl-4-methylbenzene.

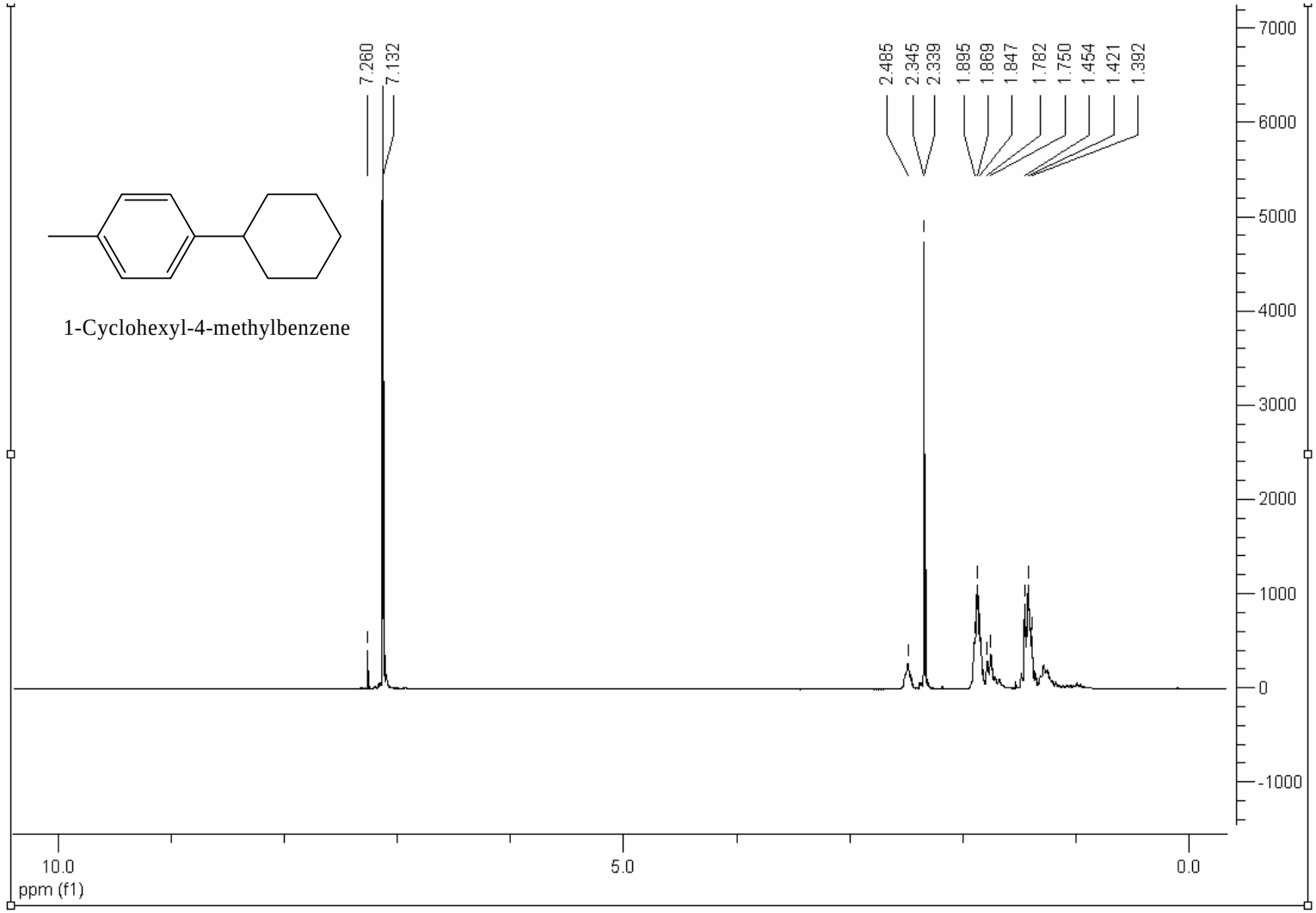


Figure S4. ^{13}C NMR spectrum of 1-cyclohexyl-4-methylbenzene.

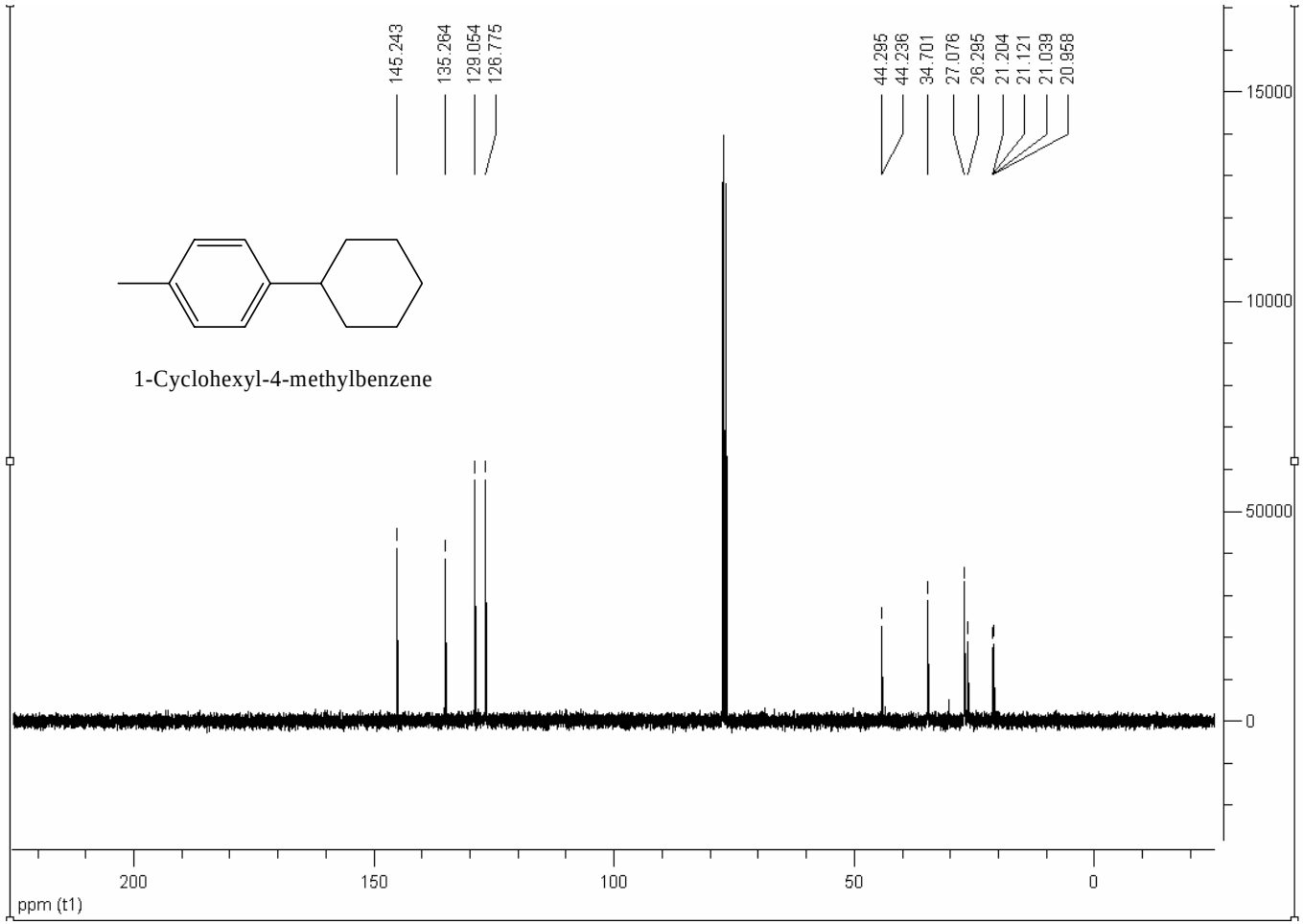


Figure S5. ^{1}H NMR spectrum of 1-octyl-4-methylbenzene.

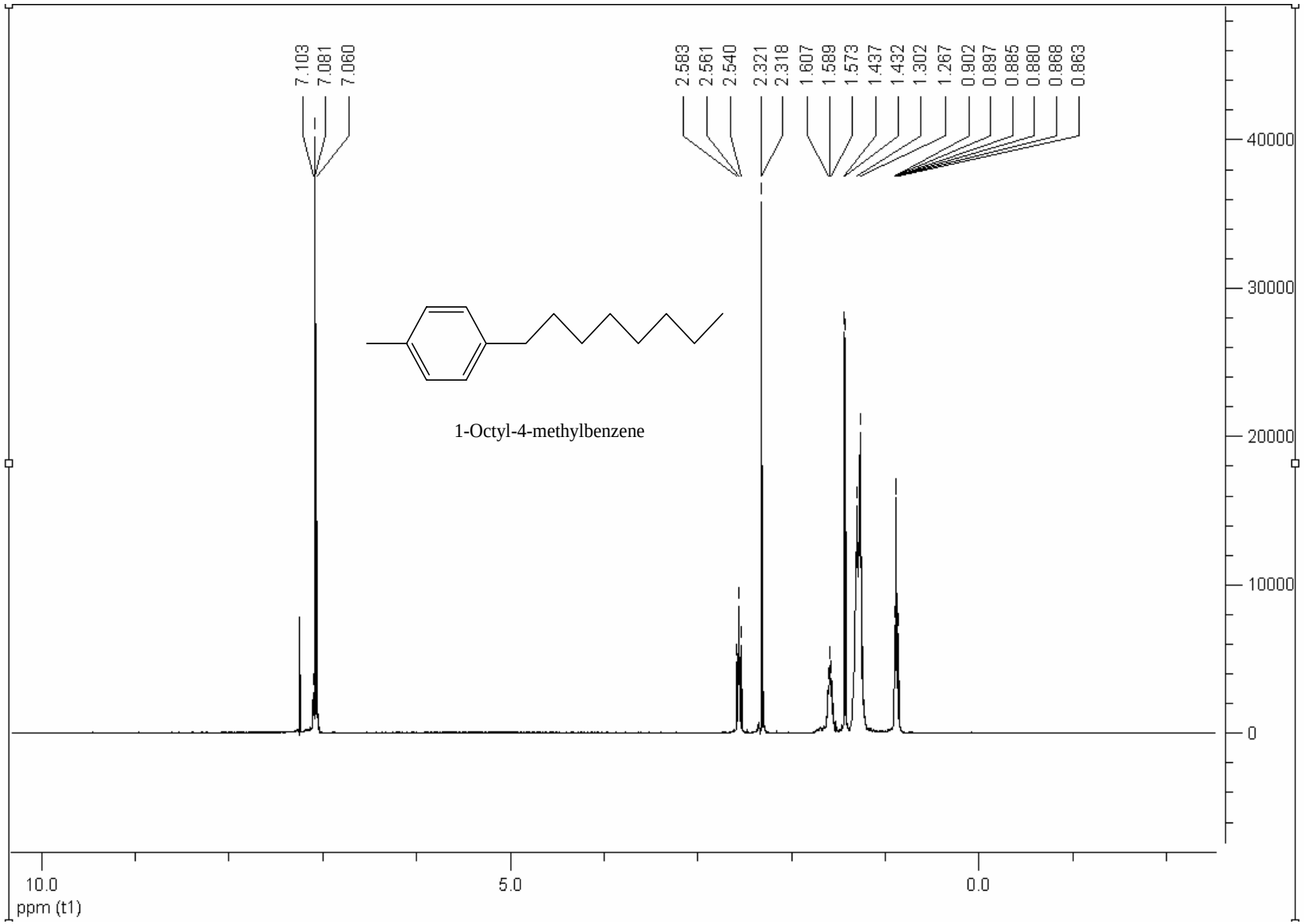


Figure S6. ^{13}C NMR spectrum of 1-octyl-4-methylbenzene.

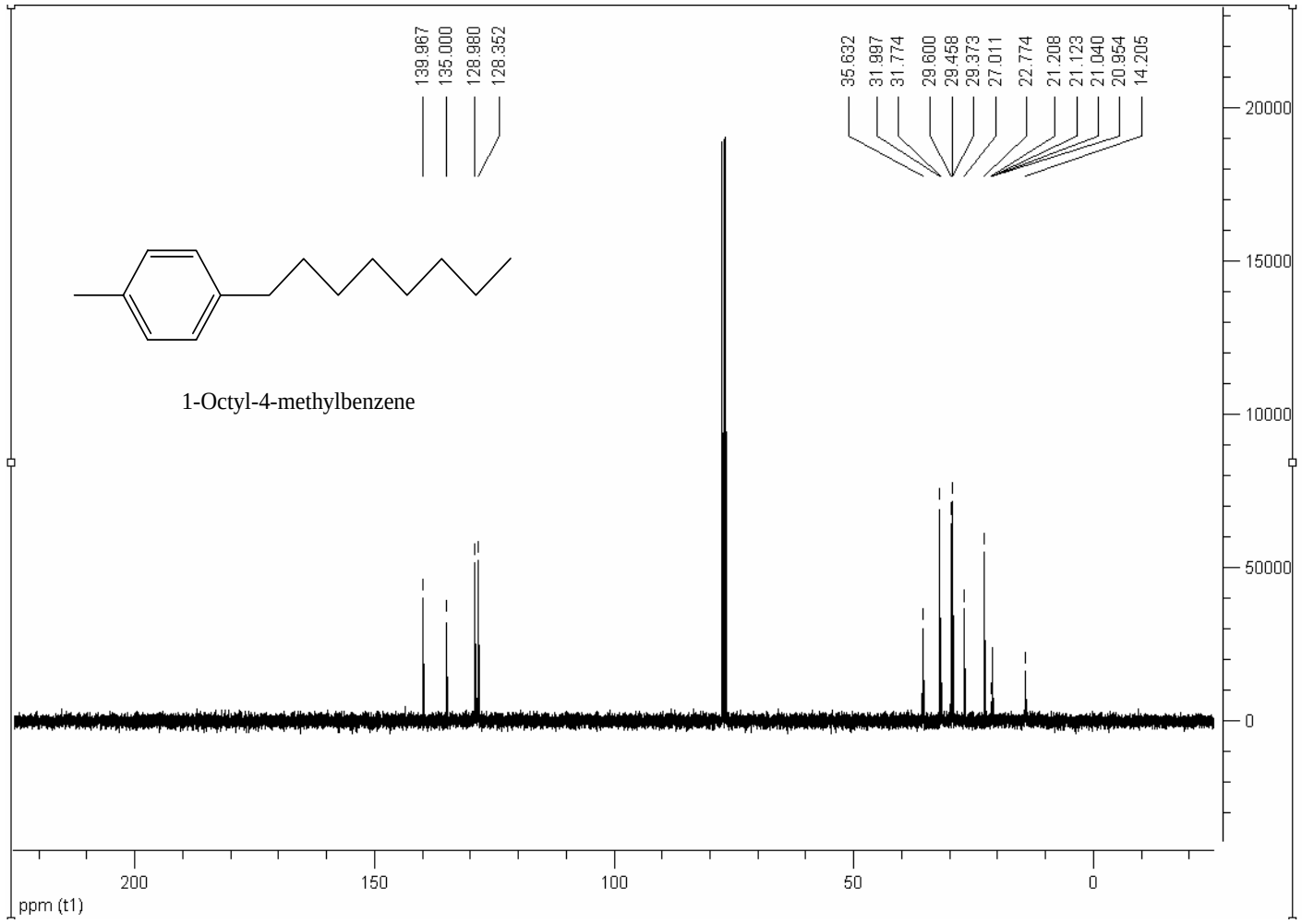
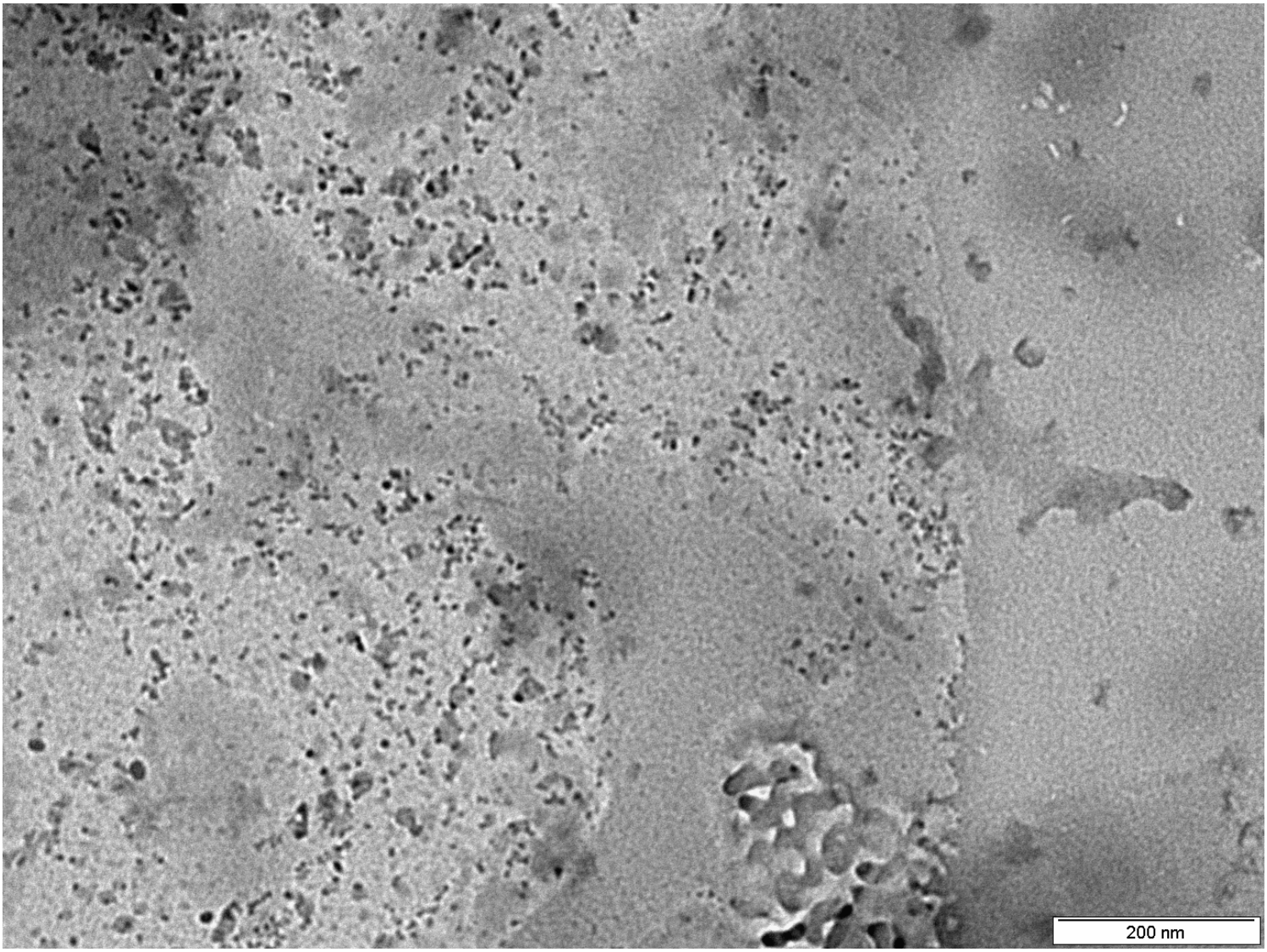
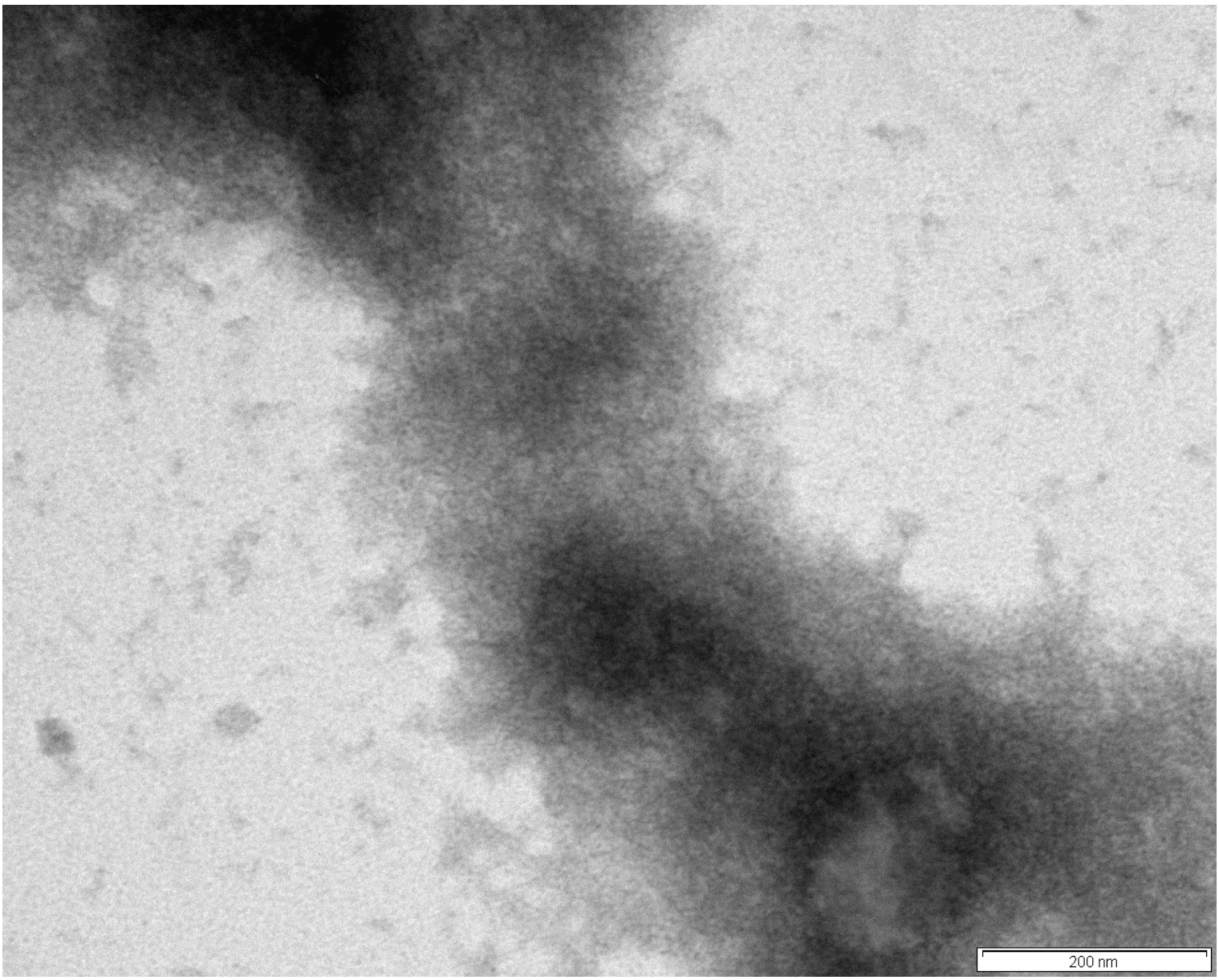


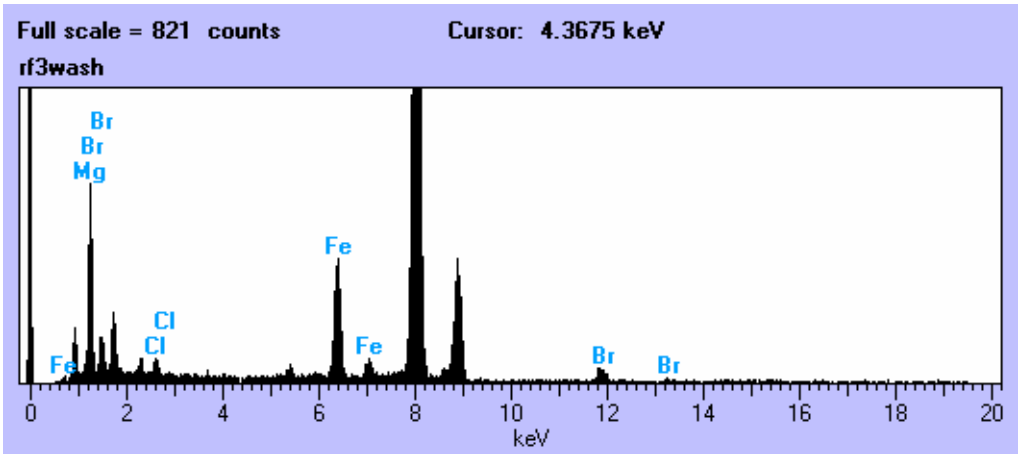
Figure S7. (a) TEM analysis of a sample from the coupling of **1** with **2**; catalyst formed *in situ* from $FeCl_3$-PEG. Typical Fe particle size 4 – 10 nm.



(b) TEM image of sample after washing with water. Typical Fe particle size 5 – 12 nm.



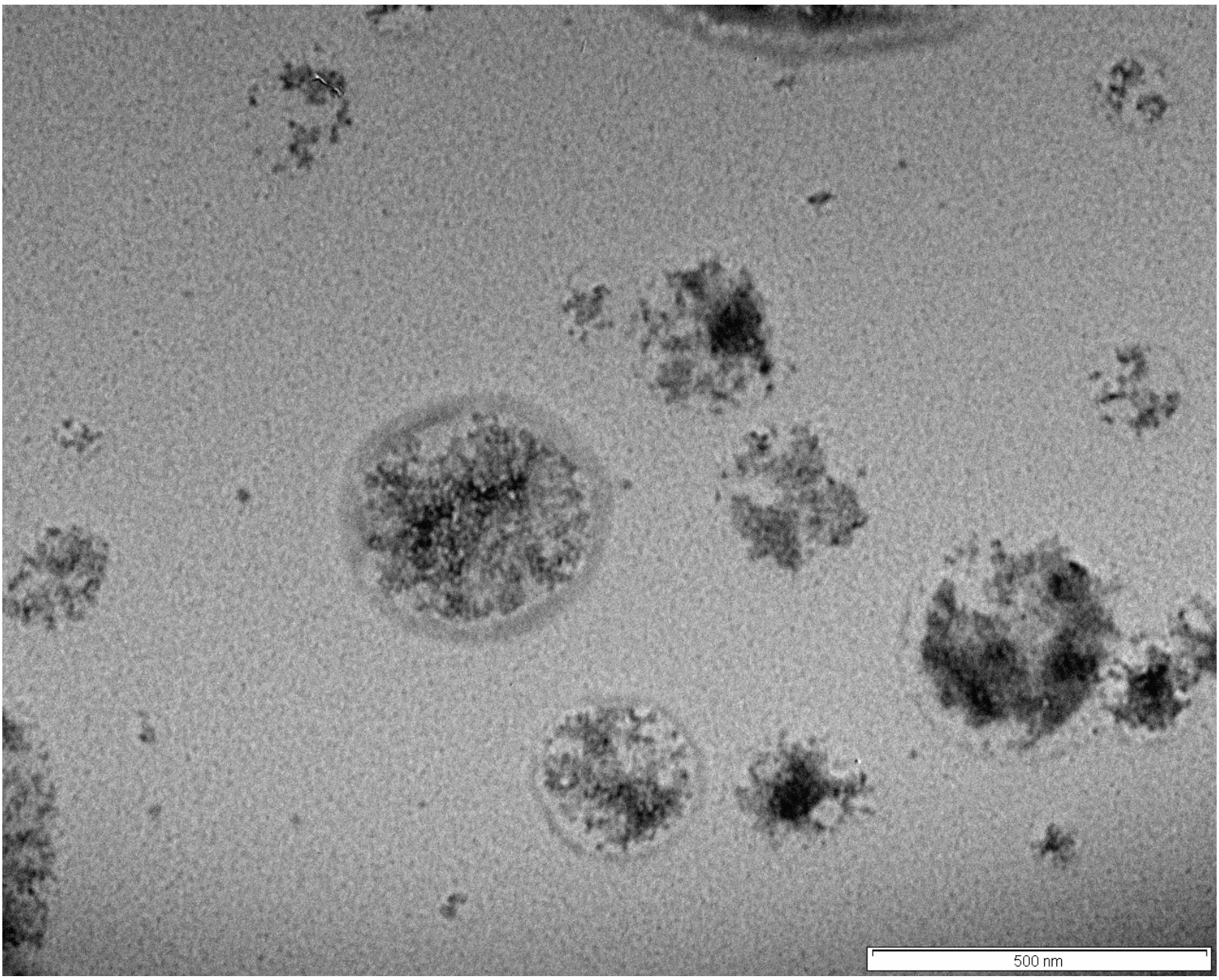
(c) EDX spectrum of sample shown in (b).



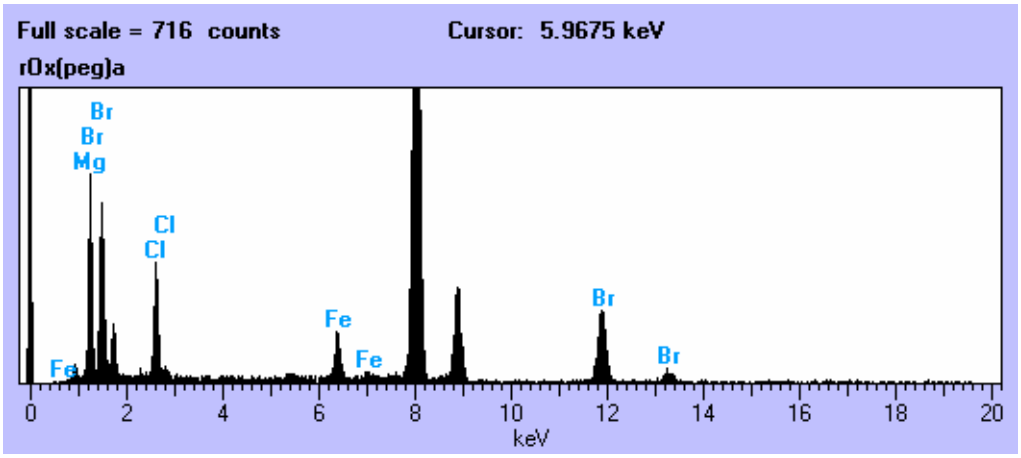
Preparation of iron nanoparticle suspension 3. A mixture of anhydrous $FeCl_3$ (0.200 g, 0.617 mmol) and PEG (pre-dried, toluene azeotrope, M_w = 14,000 g mol^{-1}, 0.075 g) in CH_2Cl_2 (5 ml) was stirred for 2 mins and then the solvent was removed *in vacuo*. Et_2O (18.75 ml) was added and the mixture was stirred (~ 2 mins) then a solution of 4-MeC_6H_4MgBr (1.0 M in Et_2O, 6.25 ml) was added in one portion and the resultant mixture was stirred a room temperature for 1 h. The resultant black suspension (figure S8) shows no signs of change after several weeks. Figure S9 shows the TEM and EDX analysis of a sample of **3**.

Figure S8. Suspension **3**.

Figure S9. (a) TEM analysis of a sample of **3**. Typical Fe particle size 7 – 13 nm.

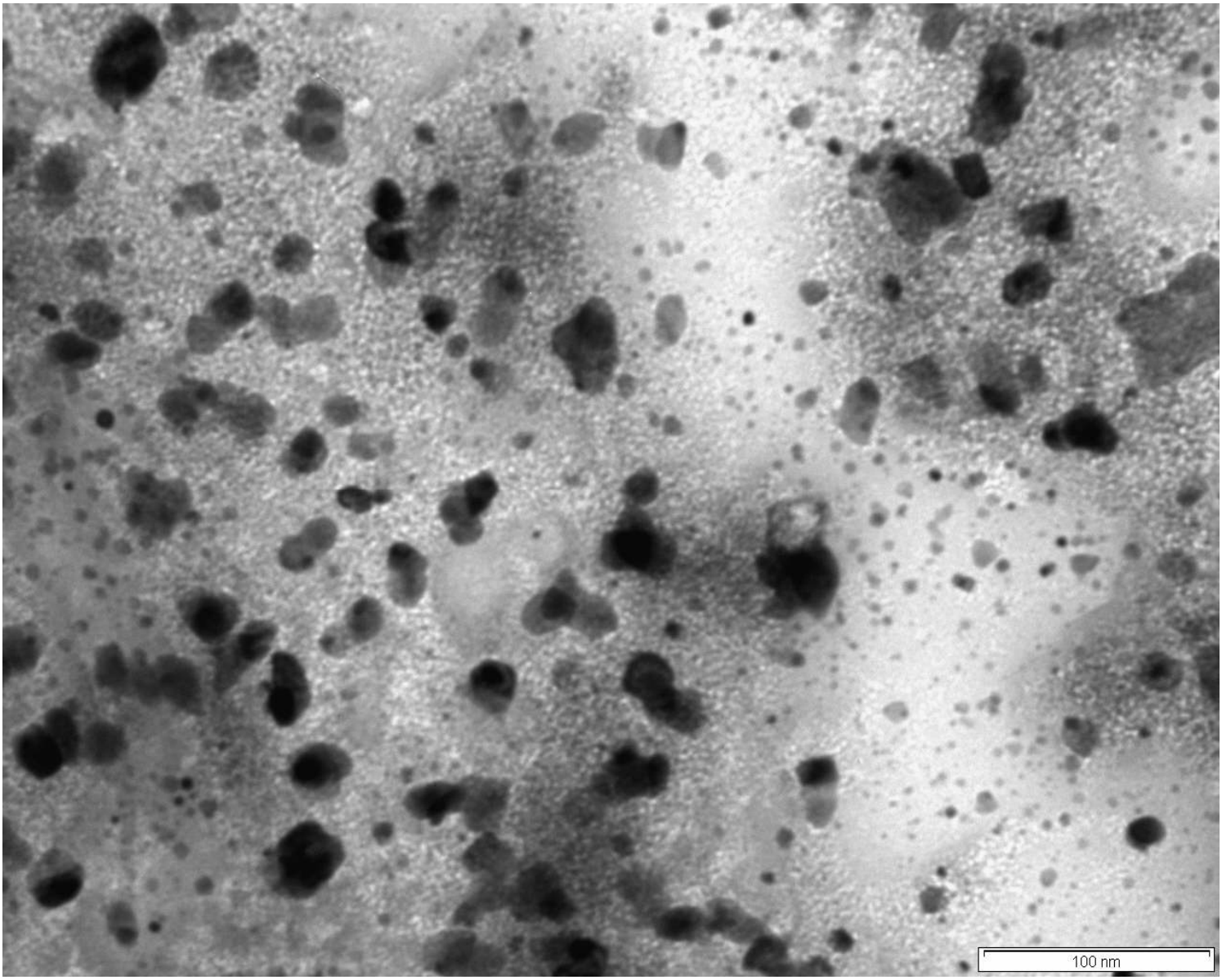


(b) EDX spectrum of sample shown in (a).

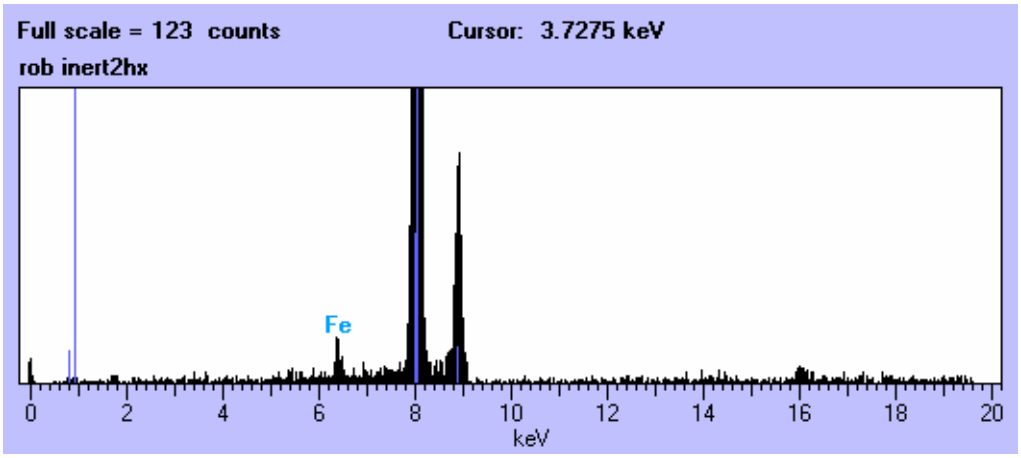


Preparation of iron nanoparticle suspension 4. As for **3** except that the aryl Grignard reagent was replaced by BuLi (2.5 M in hexane, 1.25 ml). TEM and EDX analyses are shown in figure S11.

Figure S10. (a) TEM image of a sample of **4**.



(b) EDX spectrum of **4**.



General Method for the coupling of alkyl halides with aryl Grignard reagents catalysed by 3 or 4. Suspension **3** (or **4**) (1.0 ml) and Et_2O (2 ml) were introduced to a Radleys Carousel reaction tube. The alkyl halide (1.0 mmol) was added, the solution stirred for 5 minutes, then heated to reflux temperature and then 4-MeC_6H_4MgBr (1.0 M in Et_2O, 2.0 ml) was added in one portion. The reaction was heated for 30 mins and then quenched by the addition of water (5 ml). The mixture was extracted with CH_2Cl_2 (2 x 5 ml), dried ($MgSO_4$) and filtered. Mesitylene in CH_2Cl_2 (0.667 M, 1.00 ml) was added, the volatiles removed under reduced pressure and the conversion to coupled product was determined by ^1H NMR spectroscopy.