

Electronic Supplementary Information file

Competitive Hydrosilylation in Carbon Nanoreactors: Probing the Effect of Nanoscale Confinement on Selectivity

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S1. Synthesis and selectivity of intermetallic nanoparticle catalysts

S1.1. Synthesis and characterisation of catalysts

S1.1.1. Rhodium nanoparticles (RhNP)

To a solution containing tetraoctylammonium bromide (167 mg, 0.30 mmol, 4 eq.) in toluene (10 mL) was added dropwise with vigorous stirring a solution of potassium hexachlororhodate (III) (32.0 mg, 0.74 mmol, 1 eq.) in deionised water (5 mL) resulting in a red biphasic mixture. After 10 min of stirring a solution containing sodium borohydride (30.7 mg, 0.81 mmol, 11.2 eq.) in deionised water (5 mL) was then added to the mixture, resulting in a colour change of the mixture to dark brown. Exactly 60 seconds after, dodecanethiol (35.4 μ L, 0.15 mmol, 2 eq.) was added to the mixture, which was then vigorously stirred at room temperature for 16 hr. The biphasic mixture was then separated, retaining the dark brown organic layer. This was then washed with deionised water (3 x 75 mL portions) and dried over anhydrous sodium sulphate, filtered through a cotton wool plug to give a pale brown solution, which was concentrated in vacuo down to a volume of ~ 2 mL. A large volume of ethanol (240 mL) was then added and the solution was kept at -30 °C for 16 hours. A fine dark solid was seen to have precipitated out, so the mixture was filtered and washed with ethanol (250 mL) and acetone (250 mL) and left to dry in vacuo to yield a dark solid (16.6 mg).

TEM (200 kV, "holey" carbon film): d_{NP}/nm 2.0 ± 0.3 (1.5 - 2.7) nm

SI.1.2. Intermetallic rhodium platinum nanoparticles (RhPtNP)

To a solution containing tetraoctylammonium bromide (167 mg, 0.29 mmol, 4 eq.) in toluene (10 mL) was added dropwise with vigorous stirring a solution of hexachloroplatinic acid hexahydrate (28.7 mg, 0.055 mmol, 1 eq.) in deionised water (5 mL) and potassium hexachlororhodate (III) (0.33 - 3 eq.) in deionised water (5 mL) resulting in a biphasic mixture. After 10 min of stirring a solution containing sodium borohydride (30.7 mg, 0.81 mmol, 11.2 eq.) in deionised water (5 mL) was then added to the mixture, resulting in a colour change of the mixture to dark brown. Exactly 60 seconds after, dodecanethiol (35.4 μ L, 0.15 mmol, 2 eq.) was added to the mixture, which was then vigorously stirred at room temperature for 16 hr. The biphasic mixture was then separated, retaining the dark brown organic layer. This was then washed with deionised water (3 x 75 mL portions) and dried over anhydrous sodium sulphate, filtered through a cotton wool plug to give a pale brown solution, which was concentrated in vacuo down to a volume of \sim 2 mL. A large volume of ethanol (240 mL) was then added and the solution was kept at -30 $^{\circ}$ C for 16 hours. A fine dark solid was seen to have precipitated out, so the mixture was filtered and washed with ethanol (250 mL) and acetone (250 mL) and left to dry in vacuo to yield a dark solid (5.2 - 12.3 mg).

TEM (200 kV, "holey" carbon film): d_{NP}/nm 3.4 ± 0.5 (2.3 - 4.8) nm, 2.5 ± 0.4 (1.8 - 3.1) nm, 2.1 ± 0.4 (1.4 - 3.5) nm and 3.2 ± 0.4 (2.4 - 4.2) nm for 30, 17, 12 and 10 atomic % Pt respectively in RhPtNP.

SI.1.3. Intermetallic copper platinum nanoparticles (CuPtNP)^[S1]

To a solution containing tetraoctylammonium bromide (360 mg, 0.66 mmol, 6.6 eq.) in toluene (25 mL) was added dropwise with vigorous stirring a solution of hexachloroplatinic acid hexahydrate (17.1 mg, 0.033 mmol, 0.33 eq.) in deionised water (5 mL) and copper (II) nitrate hemipentahydrate (15.6 mg, 0.067 mmol, 0.67 eq.) in deionised water (5 mL) resulting in a dark yellow biphasic mixture. After 10 min of stirring, dodecanethiol (24 μ L, 0.1 mmol, 1 eq.) was added to the mixture. After a further 10 min of stirring, a solution containing sodium borohydride (63.0 mg, 1.66 mmol, 16.6 eq.) in deionised water (5 mL) was then added to the mixture, resulting in a colour change of the mixture to dark brown, which was then vigorously stirred at room temperature for 16 hr. The biphasic mixture was then separated, retaining the dark brown organic layer. This was then washed with deionised water (3 x 75 mL portions) and dried over anhydrous sodium sulphate, filtered through a cotton wool plug to give a pale brown solution, which was concentrated in vacuo down to a volume of \sim 2 mL. A large volume of ethanol (240

mL) was then added and the solution was kept at $-30\text{ }^{\circ}\text{C}$ for 16 hours. A fine dark solid was seen to have precipitated out, so the mixture was filtered and washed with ethanol (250 mL) and acetone (250 mL) and left to dry in vacuo to yield a dark solid (2.3 mg).

TEM (200 kV, "holey" carbon film): d_{NP}/nm 2.1 ± 0.6 (1.4 – 3.8)

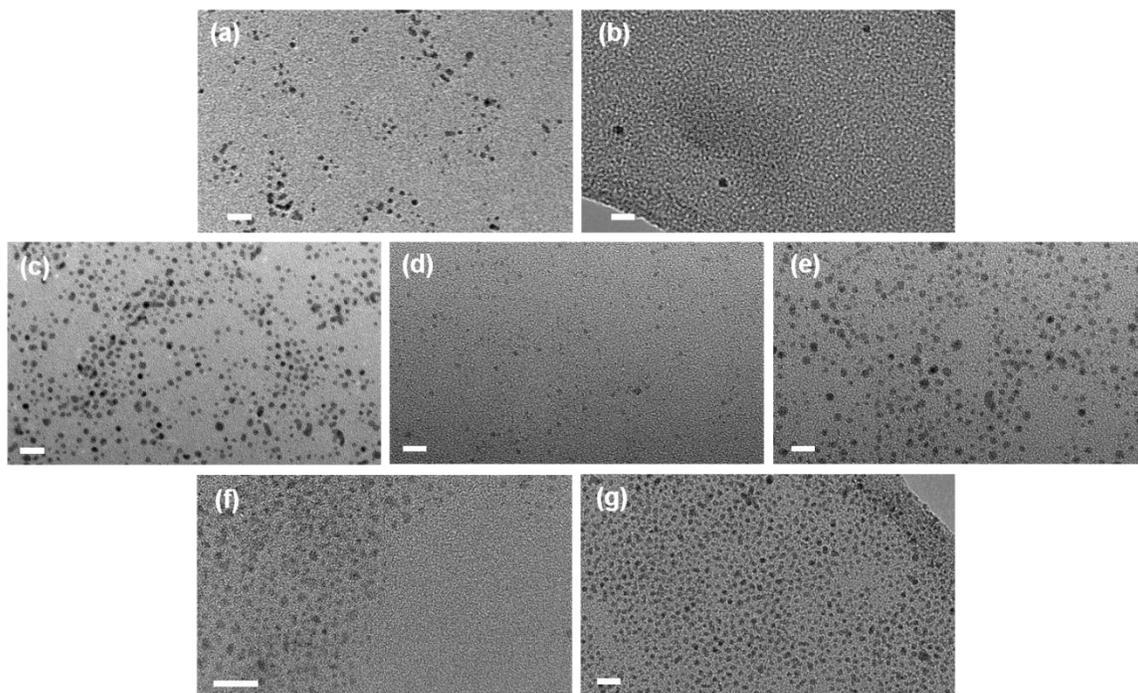


Figure S1. HR-TEM images of (a) PtNP, (b)-(e) bimetallic RhPtNP, (f) bimetallic CuPtNP and (g) RhNP consisting of (a) 100, (b) 30, (c) 17, (d) 12, (e) 10, (f) 6 and (g) 0 atomic % Pt. Scale bars are 10 nm.

S1.2. Selectivity of intermetallic nanoparticulate catalysts

Table S1. The effect of Pt content of intermetallic nanoparticle catalysts (MPtNP where M = Rh and Cu) on the selectivity for the β -addition product in the hydrosilylation of phenylacetylene by triethylsilane, showing that at very low Pt loadings (6-17 atomic %) the selectivity of the intermetallic catalyst is virtually identical to the monometallic PtNP catalyst. The error associated with measurements is $\pm 3\%$.

<i>Catalyst</i>	<i>Pt in NP / %</i>	<i>β-(E) / %</i>
RhNP	0	51
CuPtNP	6	100
RhPtNP	10	97
RhPtNP	12	96
RhPtNP	17	99
RhPtNP	30	100
PtNP	100	100

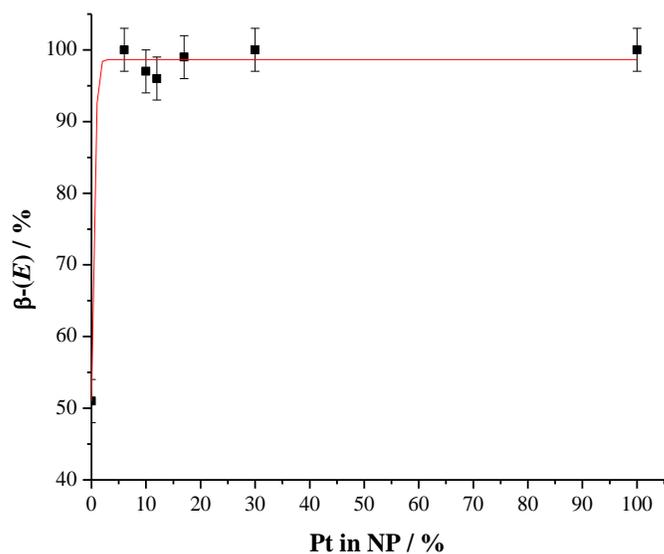


Figure S2. Graphic illustration of the effect of Pt loading on the selectivity of the hydrosilylation of phenylacetylene by triethylsilane, indicating the dominance of Pt in catalysis (i.e. high β -(E) selectivity) even at very low percentage Pt loadings.

S2. Assembly of confined and supported catalysts

S2.1. Preparation of PtNP confined in GNF (PtNP@GNF)

To a solution of platinum nanoparticles (0.32 mg) in hexane (5 mL) was added carbon nanofibres (5 mg, PR19 GNF, annealed for 1 hr at 450 °C in air). The resulting mixture was bath sonicated for 15 min at room temperature, transferred to a steel autoclave (10 mL volume) equipped with a magnetic stirrer bar and mixed with carbon dioxide (40 °C, 4000 psi) for 18 hr. During the course of the experiment, the CO₂ pressure was cycled between 1000 and 4000 psi a total of three times. The resulting solid was extracted with ethanol (10 x 5 mL), filtered through a PTFE membrane filter (0.45 µm, PTFE), washed with ethanol (50 mL), tetrahydrofuran (50 mL), chloroform (50 mL) and finally hexane (50 mL) and sucked dry in vacuo (4.6 mg).

TGA (weight residual at 900 °C, ± 1 wt.%): 5.8 wt/%

S2.2. Preparation of PtNP supported on GNF (PtNP/GNF)

To a solution of platinum nanoparticles (0.32 mg) in hexane (5 mL) was added carbon nanofibres (5 mg, PR19 GNF, as-received) and the combined mixture was bath sonicated for 30 min at room temperature. The obtained black solid was collected by vacuum filtration (0.45 µm, PTFE), washed with hexane (25 mL) and toluene (25 mL) and sucked dry in vacuo (5.2 mg).

TGA (weight residual at 900 °C, ± 1 wt.%): 6.2 wt/%

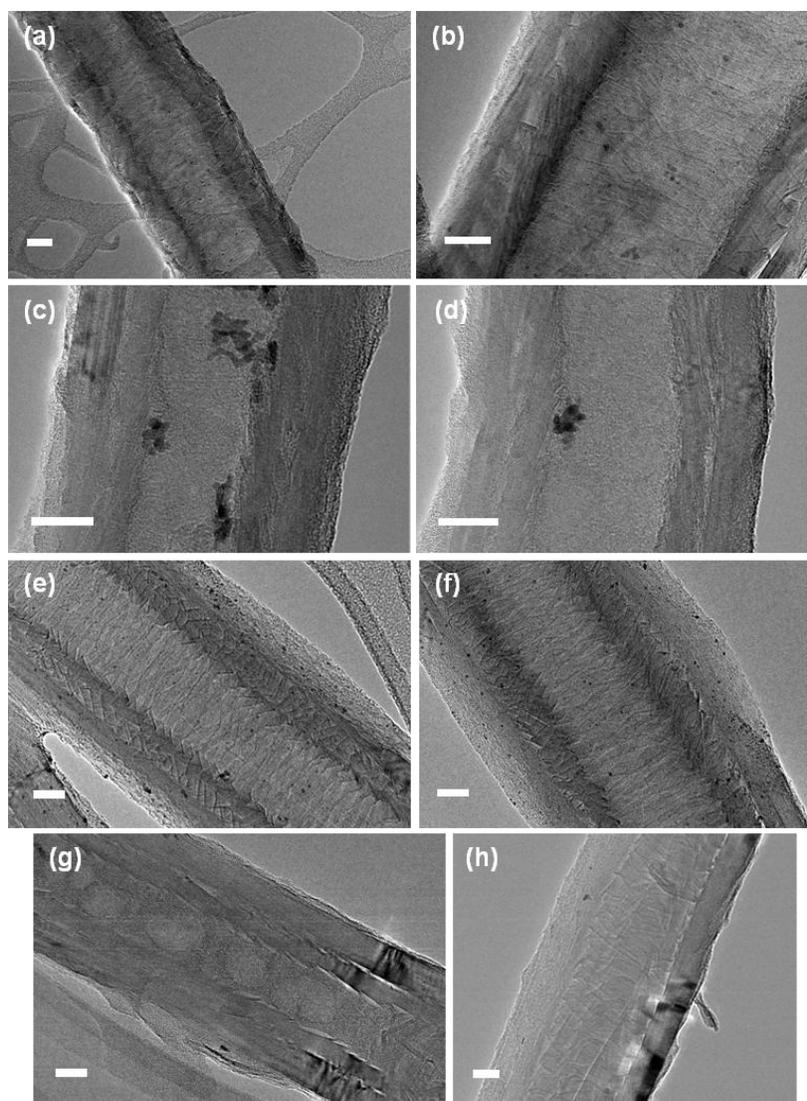


Figure S3. HR-TEM images of PtNP@GNF (a) - (b), where $d_{\text{NP}} = 2.8 \pm 0.8$ nm and PtNP@GNF after 1 cycle of catalysis (c) - (d), showing the agglomeration of PtNP at the internal graphitic step-edges ($d_{\text{NP}} = 14.2 \pm 6.8$ nm), PtNP/GNF (e) - (f), and PtNP/GNF after 1 cycle of catalysis (g) - (h), where only trace quantities of Pt were observed to remain. Scale bars are 20 nm.

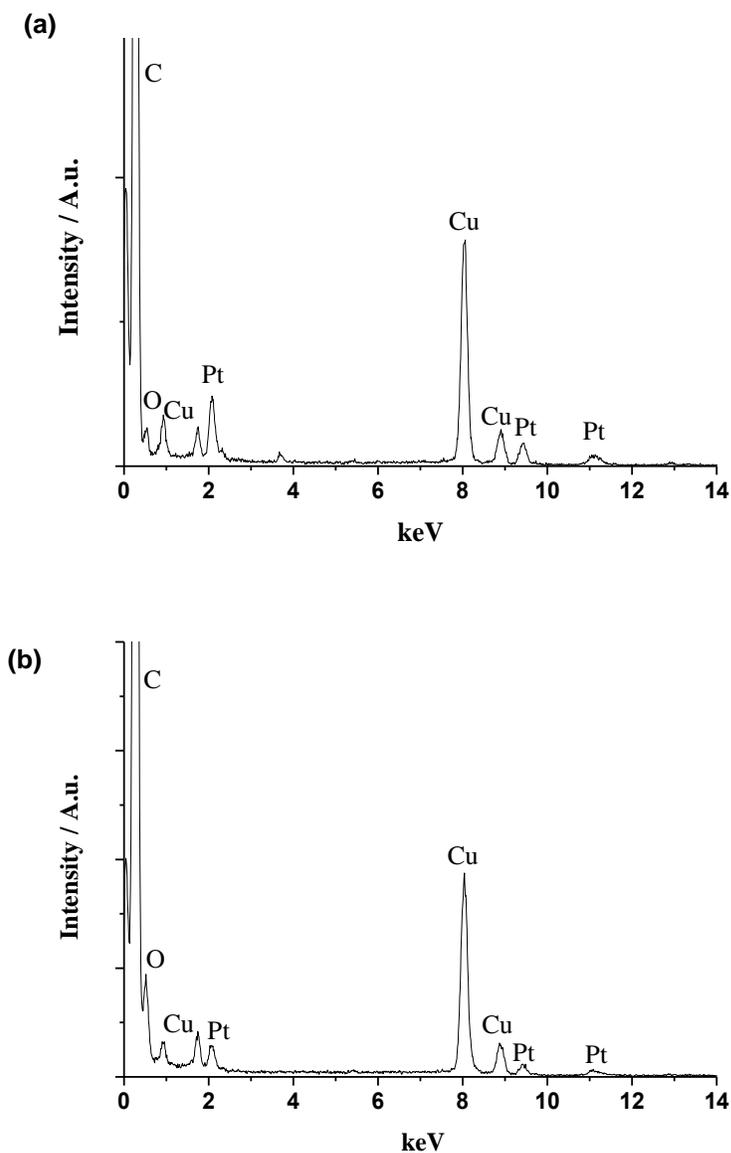


Figure S4. EDX spectra of pristine PtNP@GNF (a) and PtNP@GNF after 1 reaction cycle (b), confirming the composition of the embedded nanoparticles to be Pt. The Cu EDX peaks are due to the Cu TEM specimen grid, thus EDX analysis can only be used as a qualitative tool to confirm the presence of Pt.

S2.3. Preparation of PtNP confined in (PtNP@GNF_{short}) and supported on (PtNP/GNF_{short}) short GNF

Pristine PR19 GNF (55 mg, length >50 μm) were loaded in a stainless steel bomb (5 mL capacity) equipped with a stainless steel ball (diameter 10 mm) and milled for 90 mins at a frequency of 10 Hz. It was observed that the initially fluffy black powder had been visibly compacted into a more dense black material (GNF_{short}). PtNP were encapsulated in and supported on GNF_{short} using analogous procedures to those described in S2.1. and S2.2. respectively.

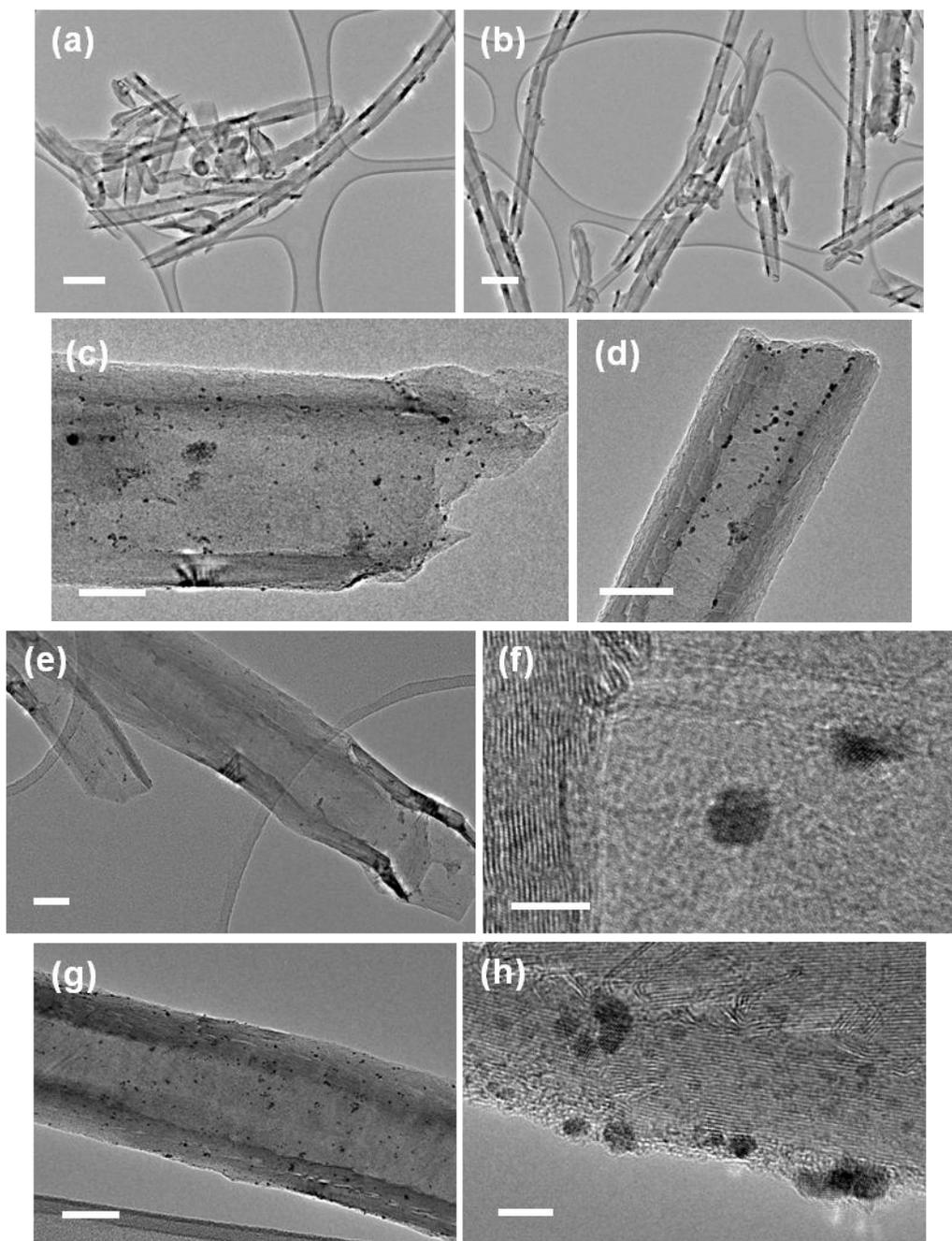


Figure S5. HR-TEM images of $\text{GNF}_{\text{short}}$, $\text{length}_{\text{GNF}}/\mu\text{m}$ Mean: 0.73 ± 0.75 (0.11 – 3.43), Median: 0.40 (a) - (b), $\text{PtNP}@GNF_{\text{short}}$, showing PtNP immobilised at the internal graphitic step-edges upon encapsulation in short GNF (c)-(f) and $\text{PtNP}/GNF_{\text{short}}$, showing PtNP anchored to the sidewalls when supported on short GNF (g)-(h). Scale bars are 200 nm (a) - (b), 50 nm (c) - (d), (e), (g) and 5 nm (f), (h).

S3. Selectivity of the hydrosilylation based on product distributions

Table S2. The selectivity for α and β products of the 3 unique PtNP catalysts in the non-competitive hydrosilylation Reactions I and II. The data shows that in both systems there is complete conversion to the α and β products and that the ratio of these products is unaffected by confinement. Data recorded after 100 hours.

Catalyst	Selectivity for α and β products			
	Reaction I		Reaction II	
	$\% (\alpha+\beta)_{DMP}$	$\alpha_{DMP} : \beta_{DMP}$	$\% (\alpha+\beta)_{TE}$	$\alpha_{TE} : \beta_{TE}$
PtNP	100	0.69	99	0.97
PtNP/GNF	100	0.62	100	0.56
PtNP@GNF	100	0.71	97	0.71

Table S3. The percentage of styrene produced using the 3 unique PtNP catalysts in Reaction I, II and III. An increase in the formation of styrene upon confinement was observed in Reactions II and III. Data recorded after 6 hours. The error associated with these measurements is $\pm 3\%$.

Catalyst	Styrene / %		
	Reaction I	Reaction II	Reaction III
PtNP	6	33	7
PtNP/GNF	6	33	7
PtNP@GNF	9	50	17
PtNP/GNF _{short}	-	-	6
PtNP@GNF _{short}	-	-	25

Table S4. The selectivity for α and β products of the 3 unique PtNP catalysts in the competitive hydrosilylation Reactions III. The data shows that there is a 3.2-fold increase in the ratio of DMP products and within this set of products, a 1.5-fold increase in $\alpha_{DMP}:\beta_{DMP}$ is seen inside the nanoreactor. Data recorded after 100 hours.

Catalyst	Competitive selectivity for α and β products		
	$(\alpha+\beta)_{DMP} : (\alpha+\beta)_{TE}$	$\alpha_{DMP} : \beta_{DMP}$	$\alpha_{TE} : \beta_{TE}$
PtNP	2.93 ± 0.09	0.56 ± 0.02	0.87 ± 0.03
PtNP/GNF	2.81 ± 0.08	0.61 ± 0.02	0.96 ± 0.03
PtNP@GNF	8.94 ± 0.27	0.94 ± 0.03	0.89 ± 0.03
PtNP/GNF _{short}	1.43 ± 0.04	0.70 ± 0.02	0.47 ± 0.02
PtNP@GNF _{short}	5.81 ± 0.17	0.80 ± 0.03	0.63 ± 0.02
PtNP@GNF _{recycled}	4.71 ± 0.14	1.40 ± 0.04	4.76 ± 0.14

S4. ^1H NMR spectroscopic analysis of hydrosilylation product distributions

Reaction I using PtNP@GNF nanoreactors

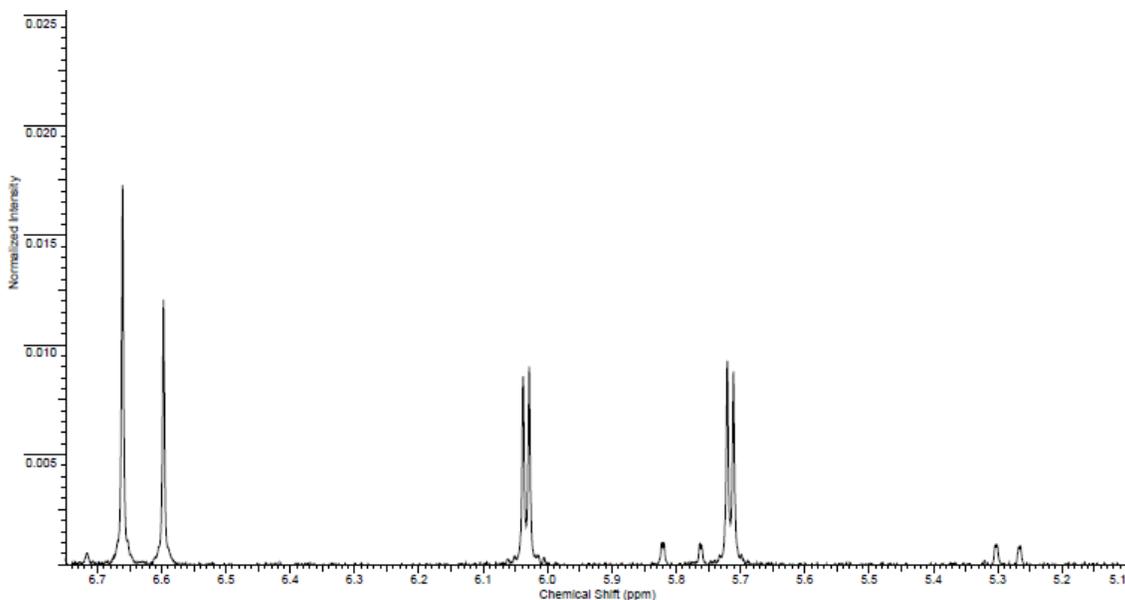


Figure S6. The products of the non-competitive hydrosilylation of phenylacetylene by dimethylphenylsilane using confined Pt catalysts.

Reaction I using PtNP/GNF catalysts

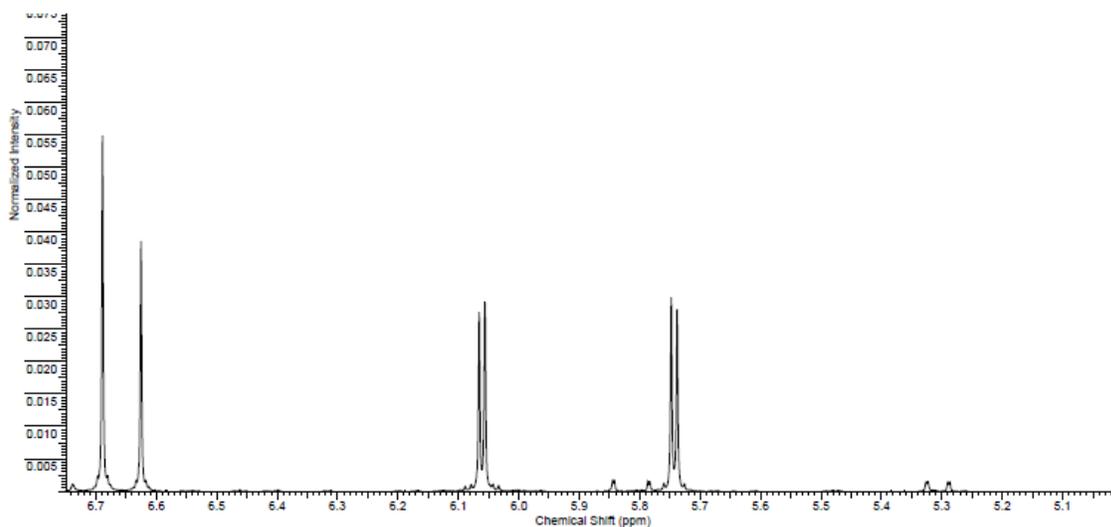


Figure S7. The products of the non-competitive hydrosilylation of phenylacetylene by dimethylphenylsilane using supported Pt catalysts.

Reaction II using PtNP@GNF nanoreactors

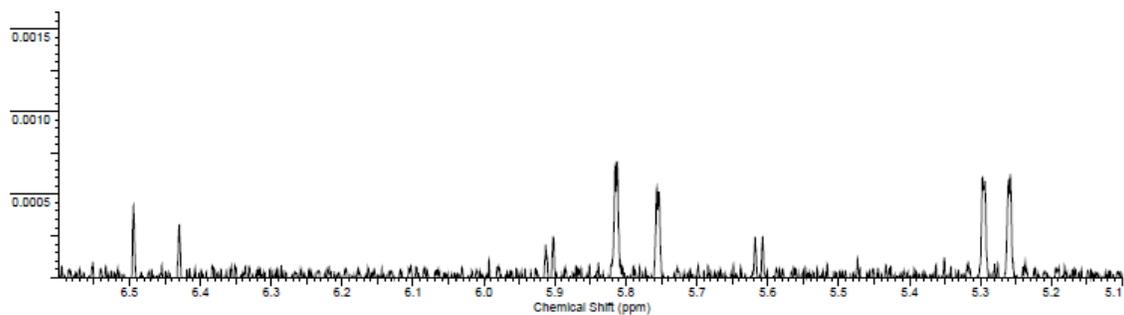


Figure S8. The products of the non-competitive hydrosilylation of phenylacetylene by triethylsilane using confined Pt catalysts.

Reaction II using PtNP/GNF catalysts

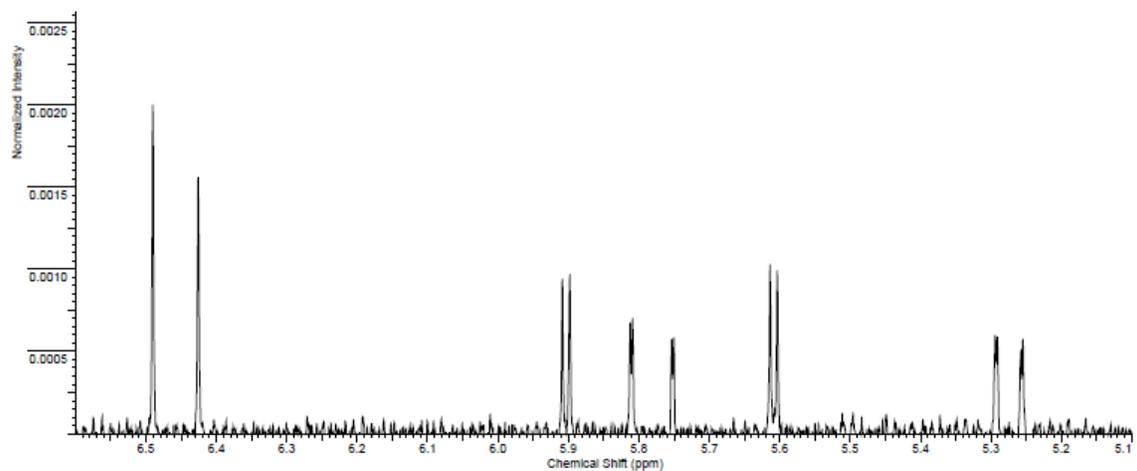


Figure S9. The products of the non-competitive hydrosilylation of phenylacetylene by triethylsilane using supported Pt catalysts.

Reaction III using PtNP@GNF nanoreactors

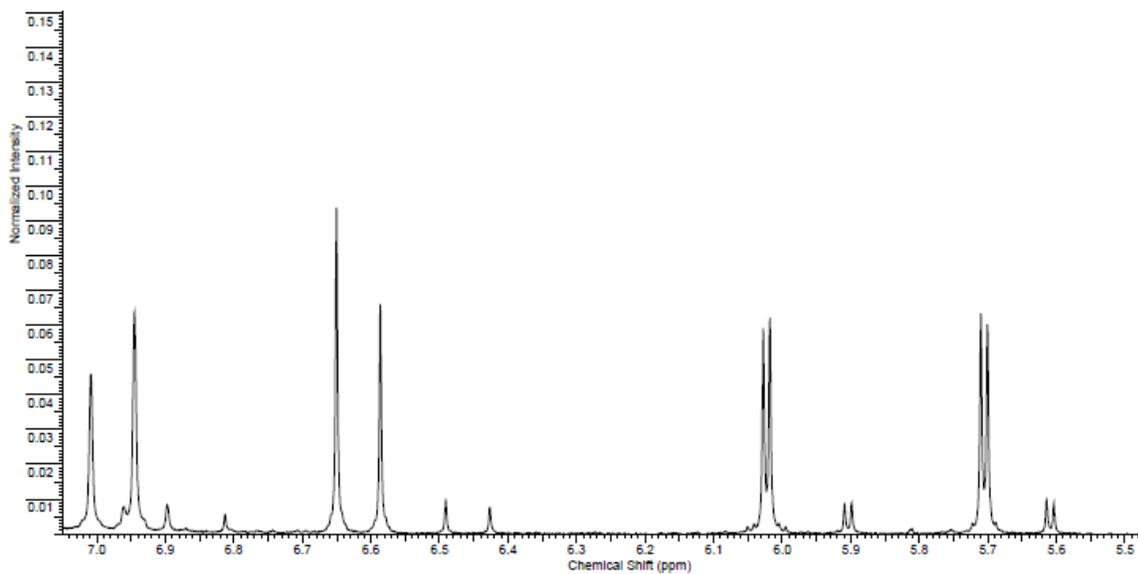


Figure S10. The products of the competitive hydrosilylation of phenylacetylene by dimethylphenylsilane and triethylsilane using confined Pt catalysts.

Reaction III using PtNP/GNF catalysts

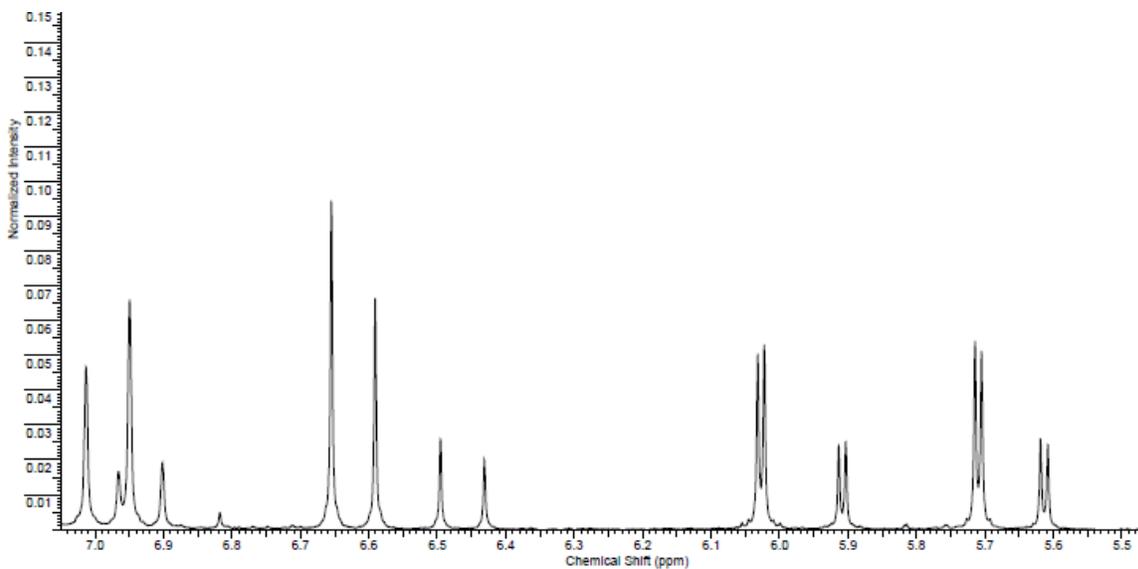


Figure S11. The products of the competitive hydrosilylation of phenylacetylene by dimethylphenylsilane and triethylsilane using supported Pt catalysts.

Reaction III using PtNP@GNF_{short} catalysts

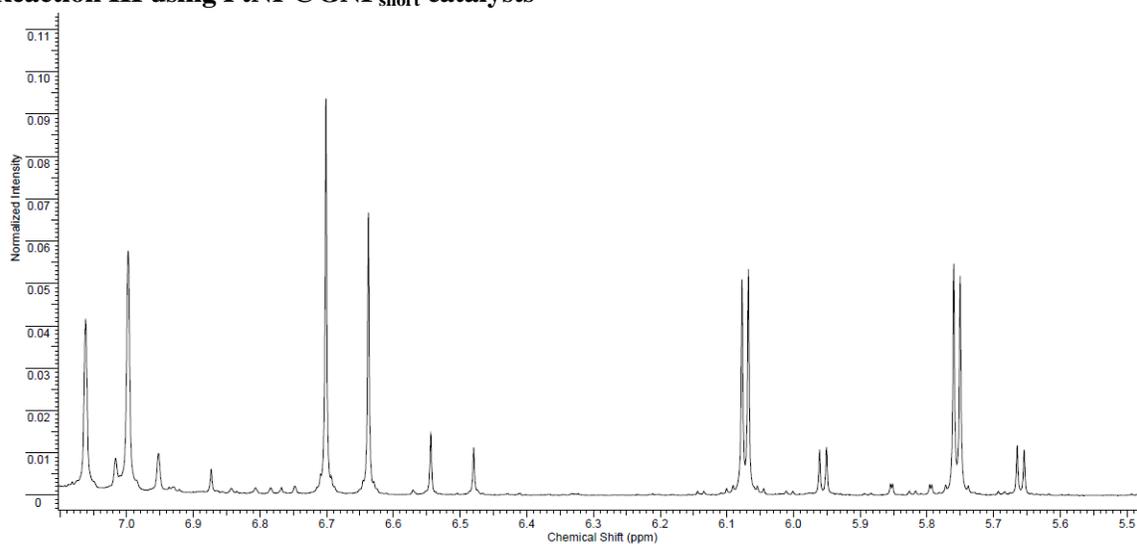


Figure S12. The products of the competitive hydrosilylation of phenylacetylene by dimethylphenylsilane and triethylsilane using Pt catalysts confined in shortened GNF.

Reaction III using PtNP/GNF_{short} catalysts

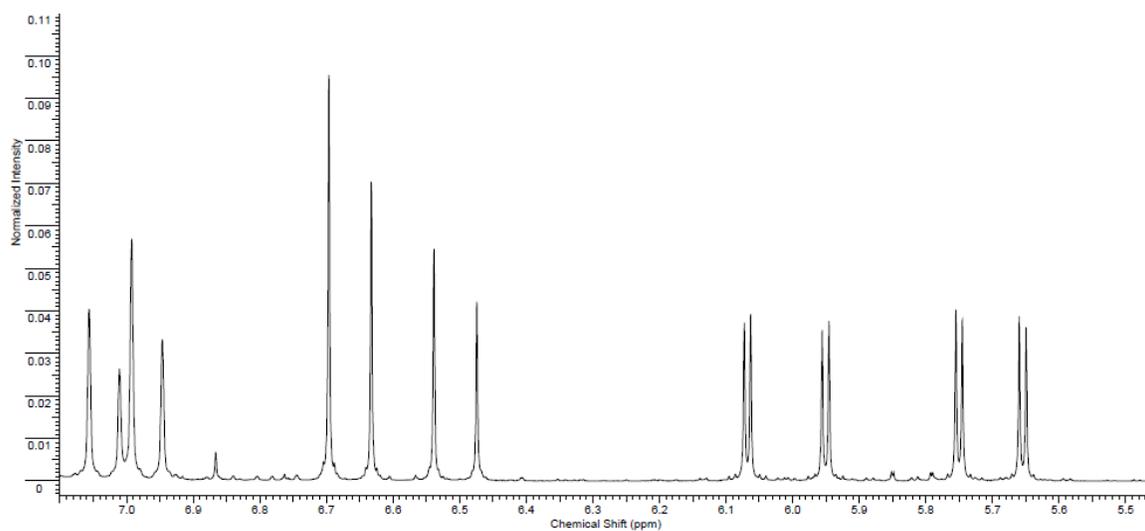


Figure S13. The products of the competitive hydrosilylation of phenylacetylene by dimethylphenylsilane and triethylsilane using Pt catalysts supported on shortened GNF.

Reaction III using recycled PtNP@GNF catalysts

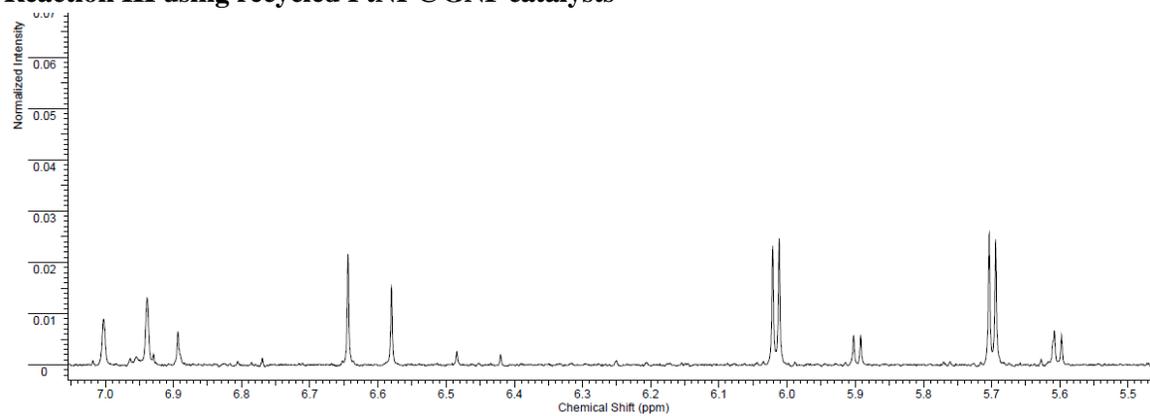


Figure S14. The products of the competitive hydrosilylation of phenylacetylene by dimethylphenylsilane and triethylsilane using recycled confined Pt catalysts.

S5. Representative GC-MS analysis of hydrosilylation product distributions

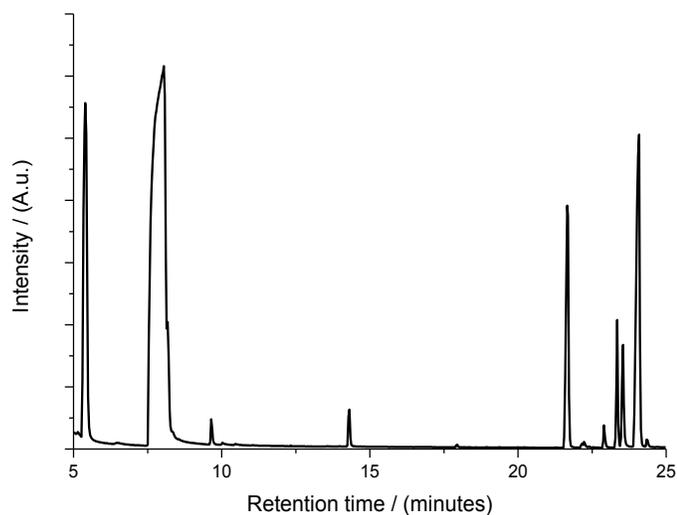


Figure S15. GC-MS of Reaction II (All unidentified peaks are due to column bleed).

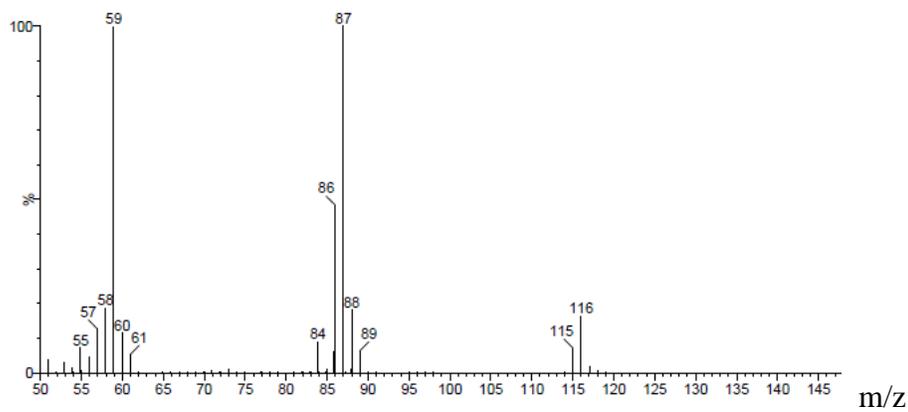


Figure S16. Peak at $t = 5.5$ min; Triethylsilane ($M^+ = 116$)

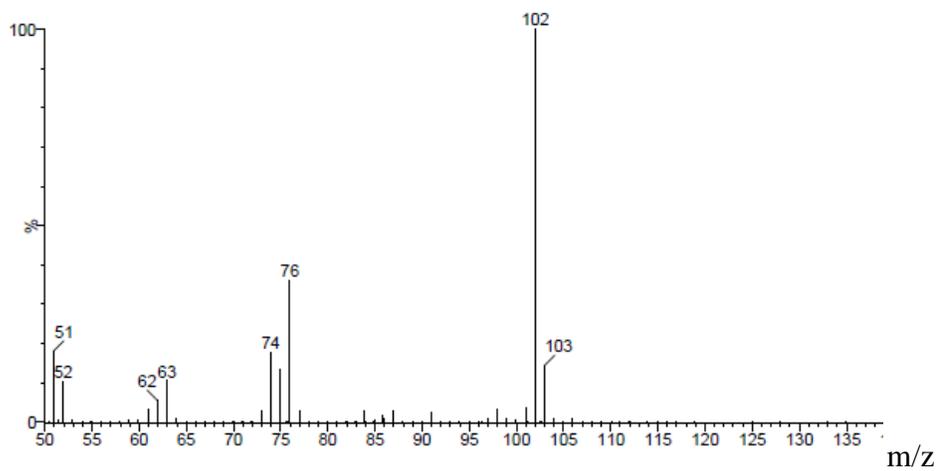


Figure S17. Peak at $t = 7.5$ min; Phenylacetylene ($M^+ = 102$).

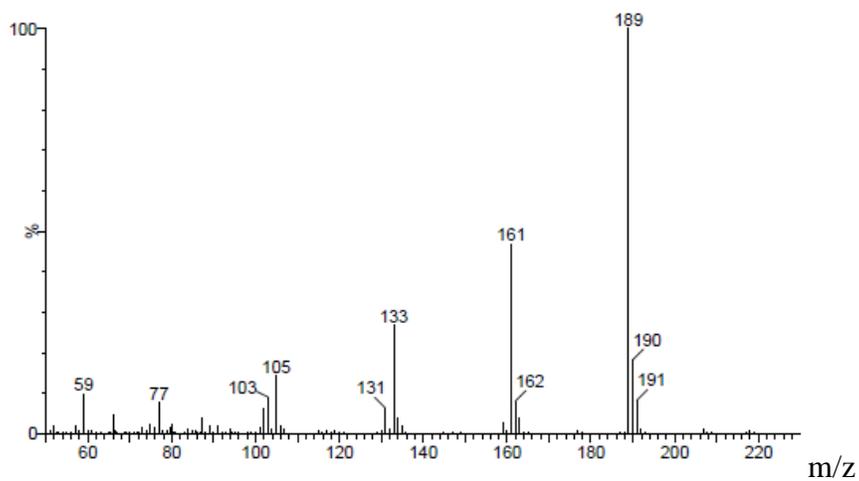


Figure S18. Peak at $t = 14.3$ min; Styrene ($M^+ = 105$, + subsequent Si (m/z 28) contamination from column).

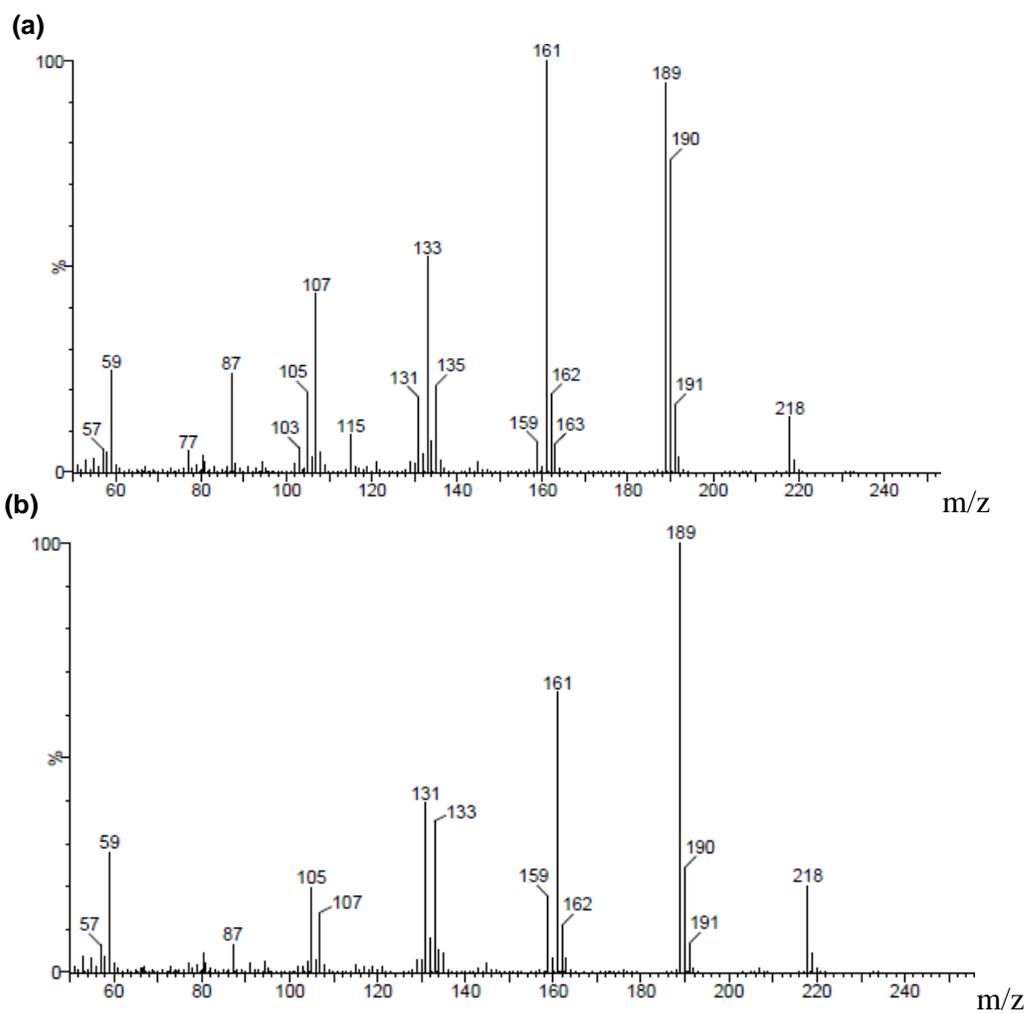


Figure S19. Peak at t = 21.7 min (a) and 24.1 min (b); α_{TE} and β_{TE} products ($M^+ = 218$)

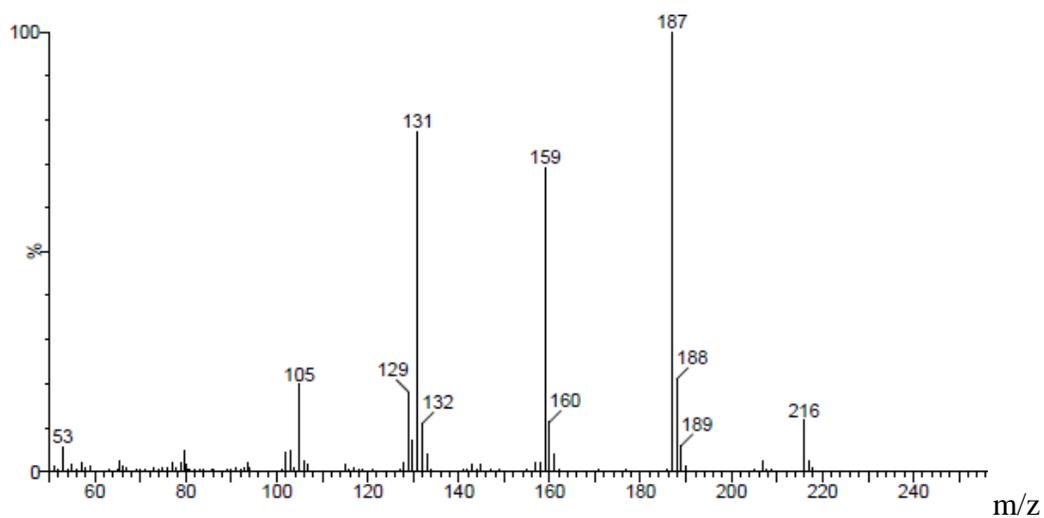


Figure S20. Peak at t = 23.4 min; Alkynylsilane_{TE} product ($M^+ = 216$).

S6. Molecular adsorption on GNF

In a typical experiment, to a solution of triethylsilane (0.03125 mmol, 1 eq.) and dimethylphenylsilane (0.03125 mmol, 1 eq.) in deuterated chloroform (5 mL) was added pristine PR19 GNF (10 mg) and the mixture bath sonicated at room temperature for 15 minutes at room temperature. The nanofibres were removed by filtration through a cotton plug and ^1H NMR spectroscopy of the filtrate was conducted. The characteristic peaks corresponding to the silane protons were then integrated and compared (δ_{H} for TE and DMP at 3.6 and 4.4 ppm respectively).

Table S5. Comparison of the adsorption of TE and DMP by GNF.

<i>Experiment</i>	<i>GNF?</i>	<i>Ratio of TE : DMP in the filtrate</i>	
		<i>Before</i>	<i>After</i>
A	×	1.00 : 1.00	1.00 : 0.99
B	✓	1.00 : 1.00	1.00 : 0.64

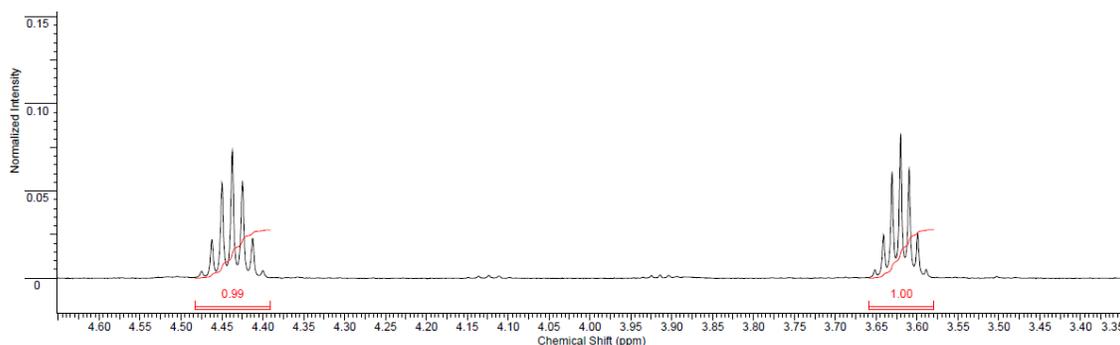


Figure S21. ^1H NMR spectrum of the filtrate in control experiment **A**, showing the presence of TE and DMP in equal quantities (red integrals) in the absence of GNF.

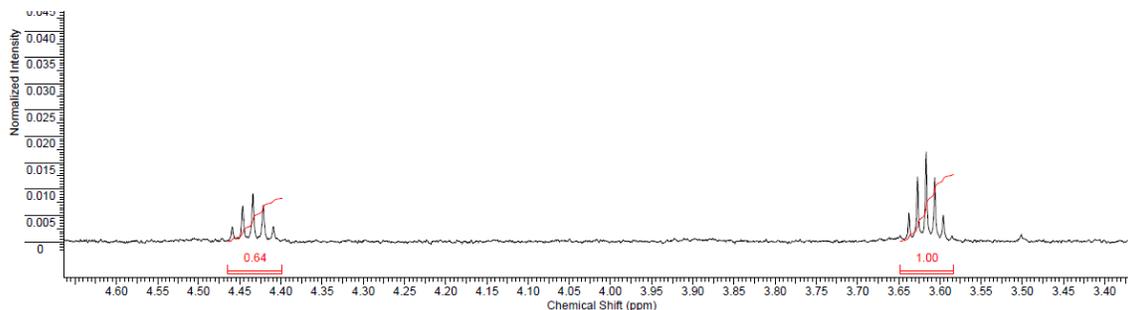


Figure S22. ^1H NMR spectrum of the filtrate in experiment **B**, showing the presence of GNF has led to a depletion of DMP associated with selective uptake of DMP over TE by GNF.

S7. References

- [S1] W. Weihua, T. Xuelin, C. Kai and C. Gengyu, *Colloids and Surfaces A*, 2006, **273**, 35.