

Supporting information

A New Pathway for Heterogenisation of Molecular Catalysts by Non-covalent Interactions with Carbon Nanoreactors

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1 ¹H NMR spectroscopic data.

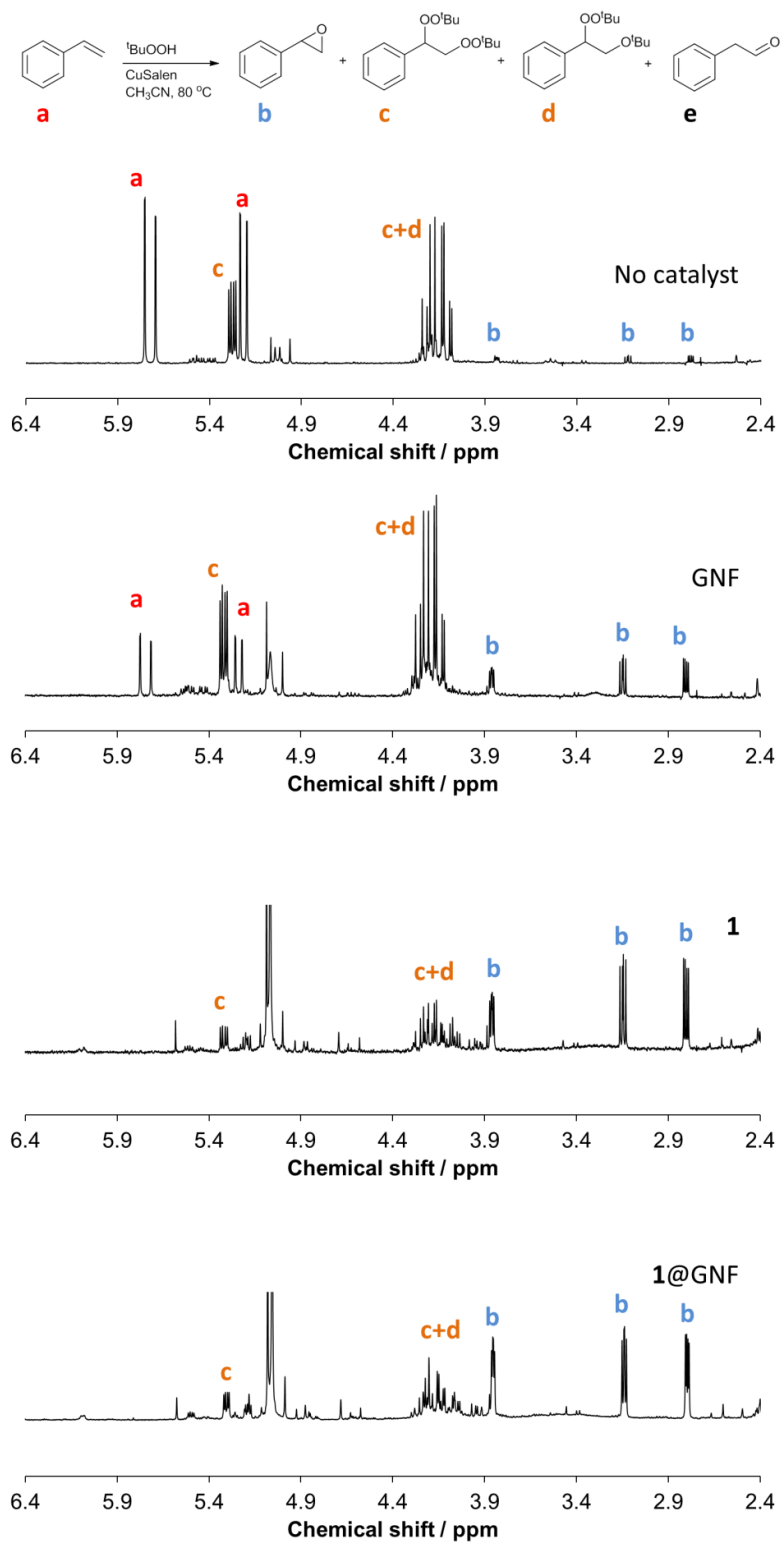


Figure S1. ¹H NMR spectra of the styrene epoxidation reaction mixture after 7 h.

2 Kinetic plots for catalytic epoxidation of styrene.

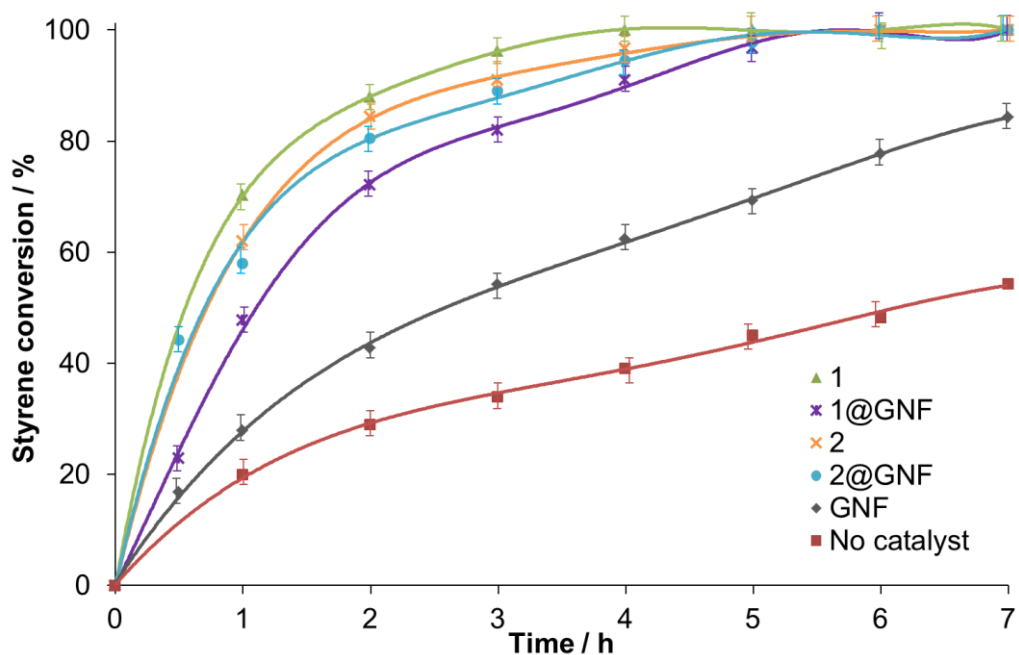


Figure S2. Conversion of styrene monitored over time catalysed by different catalysts in this study.

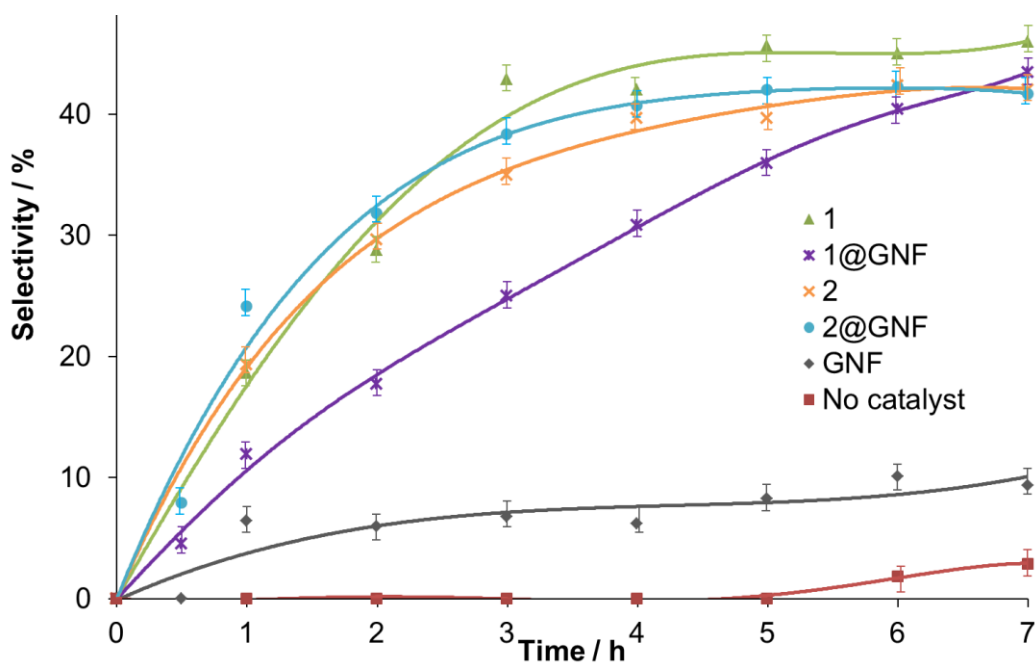


Figure S3. Selectivity for styrene epoxide defined as the ratio between the quantity of epoxide formed and styrene converted over time.

3 Catalyst loading.

Table S1. Catalyst loading in **1**@GNF and **2**@GNF compared to other carbon nanostructure immobilised molecular catalysts.

System	Method of immobilisation	Catalyst loading, mmol / g	Reference
1 @GNF ^[a]	π - π stacking interactions (fullerene-GNF)	0.03	This work
2 @GNF ^[a]	π - π stacking interactions (fullerene-GNF)	0.03	This work
Au complex/MWNT ^[b]	π - π stacking interactions (pyrene-MWNT)	0.12-0.22	i
Rh complex/MWNT ^[b]	π - π stacking interactions (pyrene-MWNT)	0.17	ii
Ru complex/SWNT ^[b]	π - π stacking interactions (pyrene-SWNT)	0.16	iii
VOSalen/SWNT ^[b]	covalent	0.08	iv
Mo complex/MWNT ^[b]	covalent	0.25-0.35	v
W complex/MWNT ^[b]	covalent	0.03	vi
Mn porphyrin/MWNT ^[b]	covalent	0.06	vii
Mn porphyrin/MWNT ^[b]	covalent	0.14	viii

^[a] the complex immobilised inside the internal channel of the corresponding nanostructure; ^[b] the complex immobilised on the outer surface of the corresponding carbon nanostructure.

4 Summary of yields for catalytic styrene epoxidation reactions with different catalysts.

Table S2. Comparison of catalytic epoxidation of styrene by different homogeneous and heterogeneous catalysts.

Catalyst	Oxidant	Styrene conversion, % ^[a]	Epoxide yield (selectivity), %	Reference
1 @GNF; 2 @GNF	^t BuOOH	100	42 (42)	This work
Cu(II)-histidine/Al-MCM-41	^t BuOOH	78	34 (53)	ix
CuSchiff base complex/polymer	^t BuOOH	67	39 (58)	x
Cu(salen)/graphene oxide	^t BuOOH	73.5	40 (54)	xi
Co(salen)/graphene oxide		70.1	25 (35)	
Cu(salen)	^t BuOOH	66.5	11 (16)	xii
Cu(salen)	Iodosyl benzene	37	5.5 (15)	xiii
Ni(salen)	^t BuOOH	57.4	8 (14)	xii
Mn(porphyrin)	^t BuOOH	80	55 (69)	xiv
Ferrierite/vanadium silicate	^t BuOOH	58	26 (51)	xv

	/O ₂			
VO(salen)/graphene oxide	O ₂	88	18 (21)	xvi
Fe(salen)/graphene oxide		76.5	37 (49)	
Co/MWNT	^t BuOOH	37	29 (79)	xvii

^[a] In CH₃CN, 50-80°C, 4-8 h reaction time.

5 Leaching test under catalytic conditions.

Leaching test were carried out using identical conditions to the catalytic reaction but in the absence of ^tBuOOH which binds to the copper(II) centre accompanied by a change of colour making it difficult to determine the catalyst concentration in solution by UV/Vis spectroscopy (Figure S4). The tests confirm that the majority of the catalyst is leached out of **2**@GNF into solution as a result of only weak interactions between **2** and the GNF whereas 97 % of molecules of **1** are retained on the GNF (Figure S5).

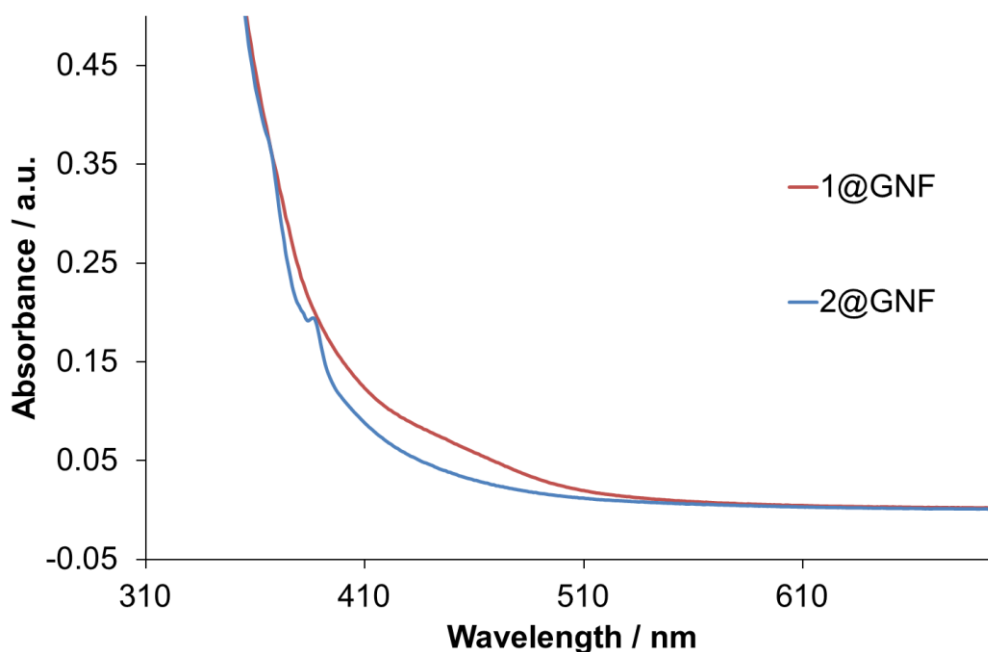


Figure S4. UV/Vis absorption spectra of reaction mixtures catalysed by **1**@GNF (red line) and **2**@GNF (blue line) under catalytic conditions in the presence of ^tBuOOH after 7 h. The spectra are almost identical and do not exhibit features corresponding to the individual CuSalen centres which interact with ^tBuOOH forming a nearly colourless solution. This hinders quantitative analysis of the reaction mixtures in solution by UV/Vis spectroscopy in the presence of ^tBuOOH.

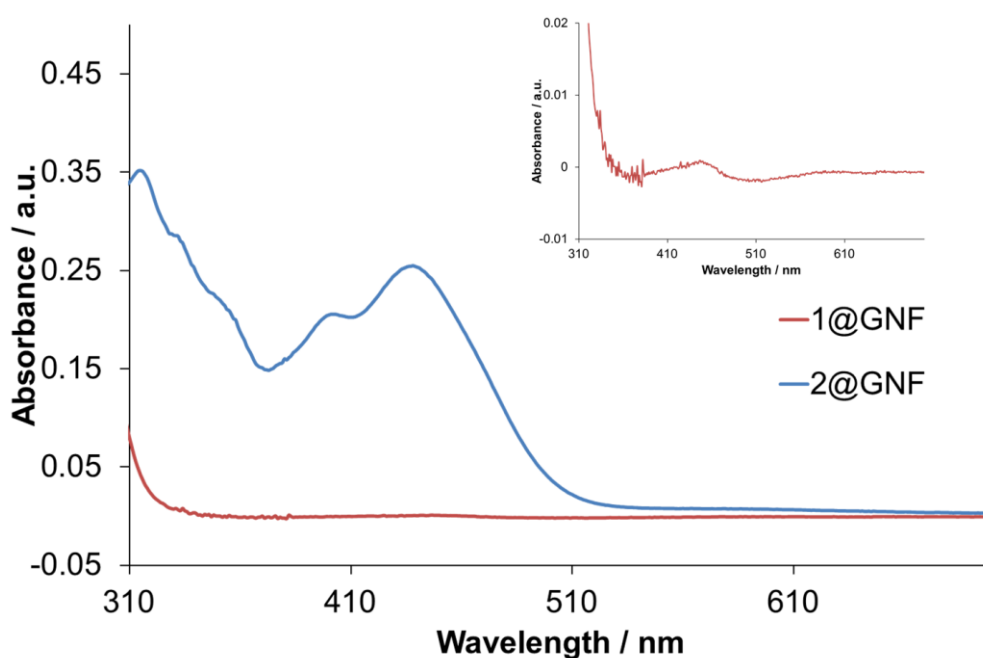


Figure S5. UV/Vis absorption spectra of reaction mixtures catalysed by **1@GNF** (red line) and **2@GNF** (blue line) under catalytic conditions in the absence of ^tBuOOH after 7 h. Inset shows enlarged UV/Vis spectrum of **1@GNF** catalysed reaction. The spectra exhibit features characteristic of the CuSalen centres and allow quantitative measurements of concentration of the corresponding catalysts in solution.

Table S3. Leaching test results for **1@GNF** and **2@GNF** performed under catalytic conditions in the absence of ^tBuOOH.

Catalyst	A (a.u., at 438 nm)	C (M)	mg of complex in solution	% of complex leached	% of complex retained on GNf
1@GNF	0.0058	2.46×10^{-7}	0.0017	3	97
2@GNF	0.2548	1.92×10^{-5}	0.0605	60	40

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