Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Thiols Make for Better Catalysts: Au Nanoparticles Supported on Functional SBA-15 for Catalysis of Ullmann-type Homocouplings

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Contents

1. Nomenclature and Abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	Name/description
NMR	nuclear magnetic resonance
GC-MS	gas chromatography mass spectrometry
TEM	transmission electron microscopy
ICP-OES	inductively coupled plasma optical emission spectrometry
TGA	thermogravimetric analysis
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
PTFE	polytetrafluoroethylene
DMF	dimethylformamide
AuNP	Au nanoparticle
H11SH	11-(triethoxysilyl)undecane-1-thiol
H2F8	1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane
H10	*n*-decyltriethoxysilane
FC	fluorocarbon chain
HC	hydrocarbon chain
UHC	Ullmann homocoupling

2. Materials and Methods

Materials

Gold(III) chloride solution (30 wt.% in dilute HCl), tetraethyl orthosilicate (TEOS, 98%), Pluronic® P-123 (M_w ~5800), 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (H2F8, 97%), 11-bromo-1-undecene (95%), 1-decene (≥ 97%), sodium hydrosulfide hydrate ($NaSH{\cdot}xH_2O$), Karstedt's Catalyst (~2% Pt in xylene), iodobenzene (98%), tetraoctylammonium bromide (98%), triphenylphosphine (≥ 98.5%), sodium borohydride ($NaBH_4$, ≥ 98%), and triethoxysilane (95%) were were purchased from Sigma-Aldrich and, unless otherwise stated, were used as received.

NMR

^1H and ^{13}C spectra were collected using a Bruker AVQ 600 MHz or 400 MHz instrument at 25 °C. Chemical shifts are reported as δ (ppm) values, and residual solvent peaks were used as the internal standard.

GC-MS

GC-MS measurements were performed on an Agilent 7820A gas chromatograph equipped with a 30m × 0.25mm DB-5MS capillary column (film thickness: 0.25 μm) and an Agilent 5975C mass-selective detector. The temperature of injection port, MSD transfer line, MS source, and MS quad were set to 220, 280, 230, and 150 °C, respectively. The oven temperature program was: 75 °C for 2.25 min; ramp to 295 °C with a rate of 25 °C/min; 295 °C for 3 min. The samples were injected into the column in split mode (50:1), and the mobile phase was He (1.0 mL/min).

TEM

TEM images were obtained on a Tecnai G2 Spirit TWIN instrument (FEI Inc.) operating at 120 kV. The samples were prepared by dropping dispersed solutions of substrates onto the carbon-coated copper grids. The solvent was allowed to dry under ambient conditions before observation. For each sample, at least five different positions were studied.

Gas sorption

Nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2420 instrument at -195.85°C. Each sample was degassed at 120°C for 12 h and back-filled with nitrogen prior to analysis. Size distribution was calculated by using the Barret-Joyner-Halenda (BJH) method of corresponding adsorption isotherms, and the surface area was determined using the Brunauer-Emmett-Teller (BET) method.

UV-Vis

Ultraviolet-visible spectra were recorded on a PerkinElmer Lambda XLS + UV-Vis spectrometer at room temperature. The scan range was 200-800 nm, and it was corrected against an appropriate background spectrum.

ICP-OES

ICP-OES measurements were conducted on a Varian 720-ES ICP Optical Emission Spectrometer. Silica samples modified with thiolate silanes were digested with HNO_3 in a microwave digestion system at 210 °C for 20 min. Au catalysts were digested with aqua regia in a microwave digestion system at 210 °C for 20 min.

TGA

TGA measurements were carried out on a TG 209 F1 Libra (Netzsch) in air using Al_2O_3 crucibles. The samples were heated from 50 °C to 800 °C at a rate of 10 °C/min.

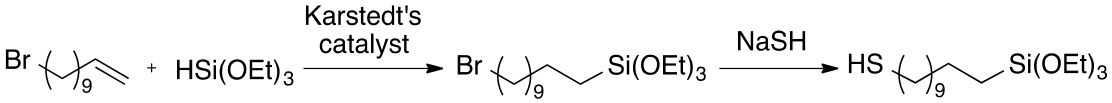
Raman

Raman spectra were obtained on a Raman microprobe (HORIBA LabRAM ARAMIS) using an excitation at 473 nm (Cobolt laser). The instrument was calibrated using a silicon standard (521 cm^{-1}).

3. Synthesis of Silanes

Synthesis of H11SH

Scheme S1. Synthesis of **H11SH**



The synthesis of H11SH was completed in two steps (Scheme S1). The first step is the hydrosilylation reaction of 11-bromo-1-undecene and triethoxysilane via Karstedt's catalyst,[1] and the second step is the thiolation of (11-bromoundecyl)triethoxysilane.[2] To remove the water of hydration, sodium hydrosulfide hydrate was dissolved in methanol at 60 °C with stirring (500 rpm). After filtration, the solution of dehydrated sodium hydrosulfide was precipitated as rapidly as possible from diethyl ether. To prevent the absorption of water, the resulting product was rapidly separated by filtration and dried under high vacuum at room temperature overnight. The dehydrated sodium hydrosulfide was kept under argon until used to prevent the quick and easy formation of sodium hydrosulfide hydrate in air.

11-bromo-1-undecene (3.000 g, 12.9 mmol) and triethoxysilane (3.165 g, 19.3 mmol) were then mixed under argon with stirring (500 rpm), and the Karstedt's catalyst (1 mL, ~0.1 mmolPt) was added to the mixture dropwise. The mixture was heated to 80 °C and the reaction was left for 12 hours. After purification by distillation, a colorless liquid was obtained. The yield was 21%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.81 (q, *J* = 6.9 Hz, 6H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.85 (p, *J* = 7.0 Hz, 2H), 1.46 – 1.19 (m, 25H), 0.66 – 0.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 58.42, 34.19, 33.32, 32.99, 29.68, 29.62, 29.57, 29.37, 28.91, 28.32, 22.89, 18.45, 10.52.

For the second step, (11-bromoundecyl)triethoxysilane (1.060 g, 2.7 mmol) and sodium hydrosulfide (0.280 g, 5.0 mmol) were combined with anhydrous methanol (10 mL) under argon and the resulting solution was stirred at room temperature for 16 hours. Afterwards, methanol was removed under vacuum and pentane (20 mL) was added to dissolve the organic silanes. The insoluble solids (NaBr and NaSH) were removed by filtration and the filtrate was evaporated under vacuum obtain the crude product. It was purified by distillation in vacuum to give a light-yellow liquid. The yield was 54%. MS (ESI) *m/z*: $[M + Na]^+$: 373.13 found.

Synthesis of H10

1-Decene (10.0 g, 71mmol) and triethoxysilane (17.6 g, 107mmol) were mixed under argon with stirring (500 rpm), and then Karstedt's catalyst (2 mL, ~0.2mmol Pt) was added dropwise. The mixture was heated to 60 °C and maintained for 12 hours. After purification by distillation, a colorless liquid was obtained. The yield was 53 %. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.86 – 3.75 (m, 6H), 1.44 – 1.12 (m, 25H), 0.91 – 0.82 (m, 3H), 0.67 – 0.56 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 58.44, 33.35, 32.07, 29.79, 29.70, 29.49, 29.41, 22.90, 22.83, 18.45, 14.26, 10.54.

4. Synthesis of Modified SBA Supports and SBA-Au Catalysts

Preparation of mesoporous SBA-15 SiO_2

SBA-15 SiO_2 was synthesized following reported procedures.[3] First, 8.0 g of Pluronic P-123 was completely dissolved in a mixture concentrated hydrochloric acid (40.2 mL, 37 wt. %) and deionized water (210 mL) in a 500 mL flask heated to 35 °C. 17.06 g of TEOS was then added and the aqueous solution was stirred vigorously for 20 hours. The temperature of the reaction was increased to 80 °C and left to stir for 24 more hours. Once complete, the reaction mixture was cooled and a white solid was collected via filtration. The solid was washed with deionized water several times and the material was allowed to dry overnight before calcination in a furnace to remove the P-123 templates (500 °C, 6 hours under air).

Modification of SBA-15 SiO_2

60 mg of SBA-15 SiO_2 and 300 mL of anhydrous toluene were mixed, and then a certain amount of silanes (Table 1, main text) were added into the solution. The reaction was run under argon and performed at 80 °C for 24 hours with vigorous stirring (500 rpm). After that, the products were collected by filtration, and sequentially washed with toluene, acetone, and ethanol (three times each). The modified hollow silica was dried under high vacuum at room temperature prior to use.

Preparation of AuNPs (Au_{101}*PPh_3)

The AuNPs were synthesized according to the reported procedures.[4-6] 2.940 g of a gold(III) chloride solution (30 wt.% in dilute HCl) was added to 60 mL of deionized water in a 500 mL round-bottomed flask equipped with a magnetic stir bar. 60 mL of toluene was then added. Tetraoctylammonium bromide (1.40 g) was added to the mixture and the toluene phase turned red; the aqueous layer was almost colorless. After stirring vigorously (1500 rpm) for 5 min, 2.30 g of triphenylphosphine was added, and then the toluene phase became cloudy white. After stirring vigorously (1500 rpm) for 10 min, 10 mL of $NaBH_4$ aqueous solution (0.20 g/mL) was freshly prepared and added rapidly with stirring (1500 rpm). The reaction was allowed to perform for 3 hours at room temperature. After that, the toluene layer was separated, washed with 100 mL of deionized water (three times), filtered to remove precipitates, and evaporated to dryness under flowing nitrogen. The crude product was dissolved in 35 mL of chloroform, and 300 mL of pentane was added to precipitate the product. The resulting precipitation was collected by filtration, and further washed with hexanes, a methanol and water mixture, pentane, and chloroform several times each. Finally, the resulting AuNPs (Au_{101}*PPh_3) were dried under high vacuum for one hour and then stored in -20 °C until further use. It should be noted that all chloroform must be filtered through basic alumina prior to use.

Synthesis of SBA-Au catalysts

SBA-15 SiO_2 or functional SBA-15 SiO_2 (50 mg) were added into a dichloromethane solution of Au_{101}*PPh_3 (10 ml, 0.10 mg/mL) while stirring (500 rpm) at room temperature for 24 hours. The products were collected by centrifugation (5000 rpm, 2 min), washed with dichloromethane three times, and dried under high vacuum at room temperature. After that, the as-synthesized Au catalysts were activated under high vacuum at 200 °C for 2 hours.

5. Characterization of Modified SBA Supports and SBA-Au Catalysts

Gas Sorption

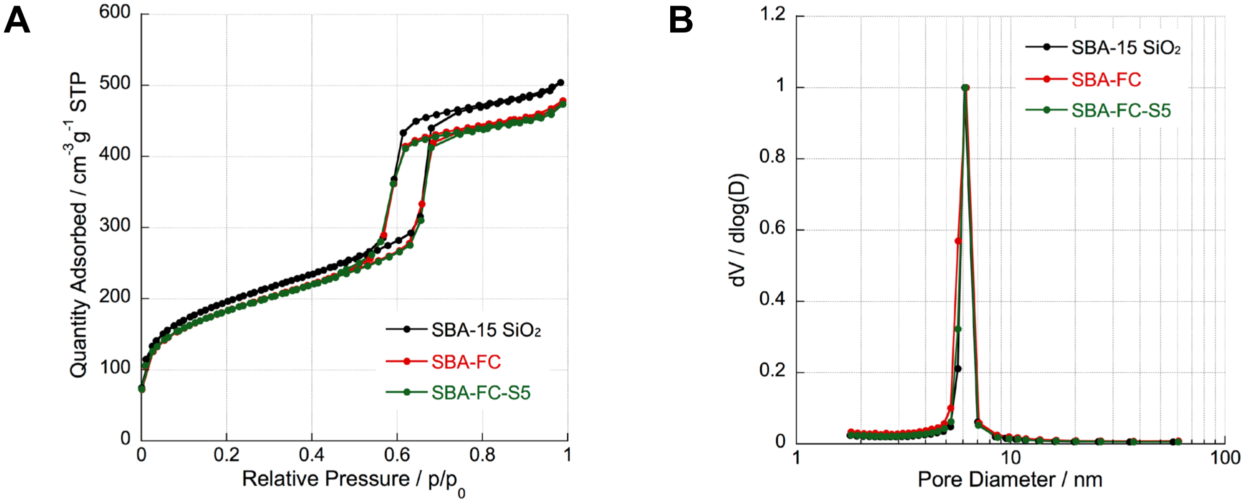


Figure S1. (A) Representative N_2 adsorption-desorption isotherms of mesoporous SiO_2, and (B) the corresponding pore diameters based on the adsorption branches. SBA-15 SiO_2 (black), **SBA-FC** (red) and **SBA-FC-S5** (green). Isotherms of SBA-15 SiO_2, **SBA-FC** and **SBA-FC-S5** exhibited the type IV isotherm and well-defined hysteresis loops of type H1 according to the IUPAC classification.[3, 7] The IUPAC type IV isotherm indicates the presence of mesoporous structures. The type H1 loop indicates the narrow distribution of pore size. The pore diameters of SBA-15 SiO_2, **SBA-FC** and **SBA-FC-S5** were almost the same.

Raman spectra

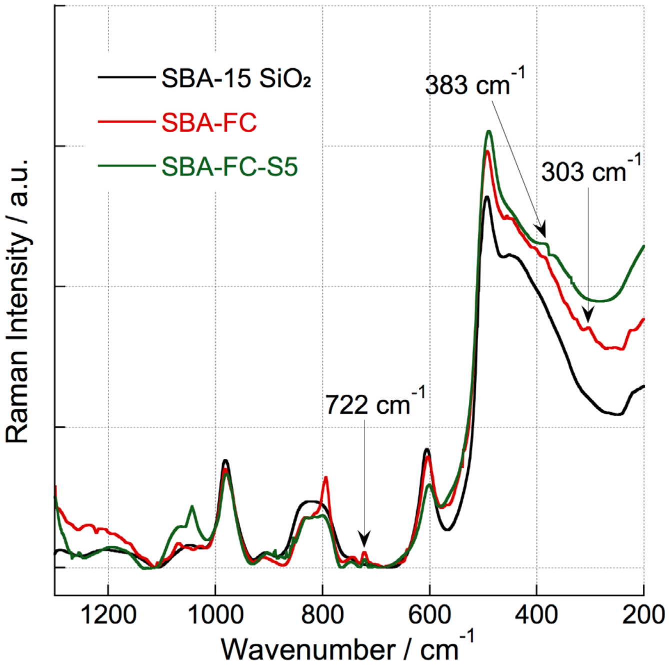


Figure S2. Raman spectra of SBA-15 SiO_2 (black), **SBA-FC** (red) and **SBA-FC-S5** (green). The characteristic peaks of $-CF_2-$ at 722 cm^{-1}, 383 cm^{-1}, and 303 cm^{-1} were observed on the spectra of **SBA-FC** and **SBA-FC-S5**.[8]

TGA

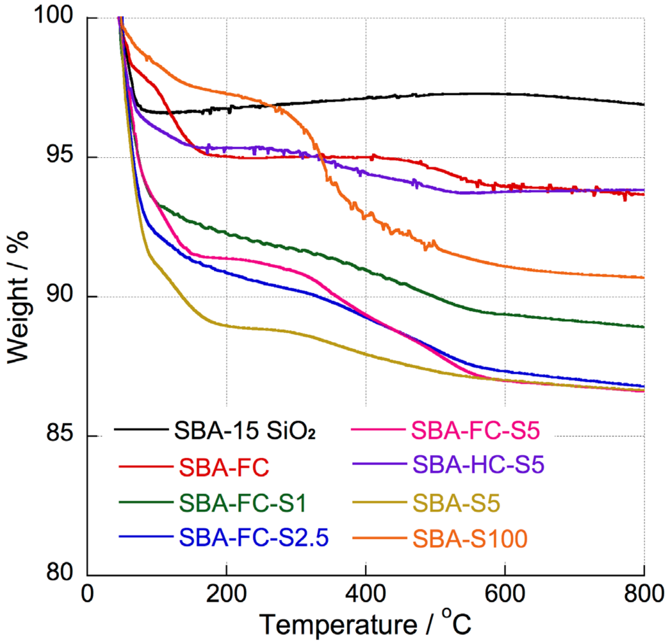


Figure S3. TGA curves of modified SBA-15 materials in air.

ICP-OES

Table S2. Au content as determined by ICP-OES.

Entry	Catalyst	Au (wt%)	Au (mmol/g)
1	**SBA-Au**	1.6	0.079
2	**SBA-FC-Au**	1.5	0.075
3	**SBA-FC-S1-Au**	1.7	0.085
4	**SBA-FC-S2.5-Au**	1.7	0.085
5	**SBA-FC-S5-Au**	1.8	0.091
6	**SBA-HC-S5-Au**	2.0	0.101
7	**SBA-S5-Au**	2.0	0.103
8	**SBA-S100-Au**	1.8	0.093

UV-Vis

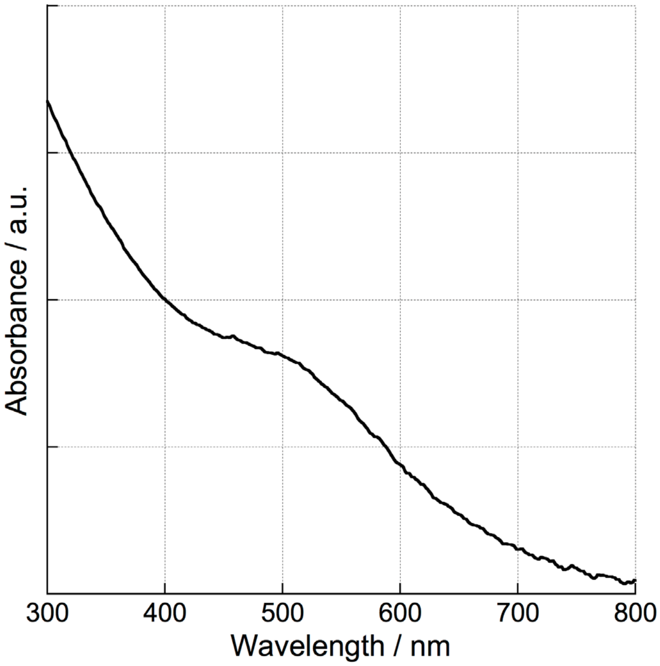


Figure S4. UV-Vis spectrum of Au_{101}*PPh_3 in dichloromethane.

TEM images

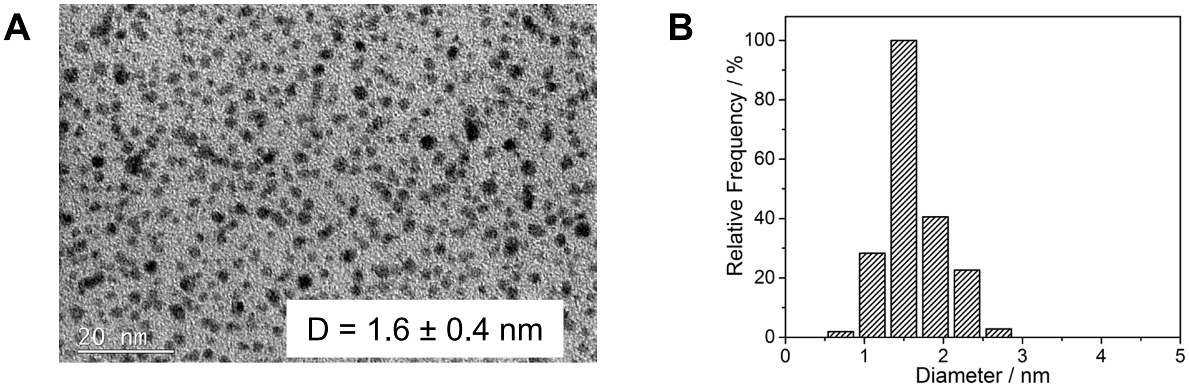


Figure S5. (A) TEM image of Au_{101}*PPh_3 and (B) the corresponding size distribution.

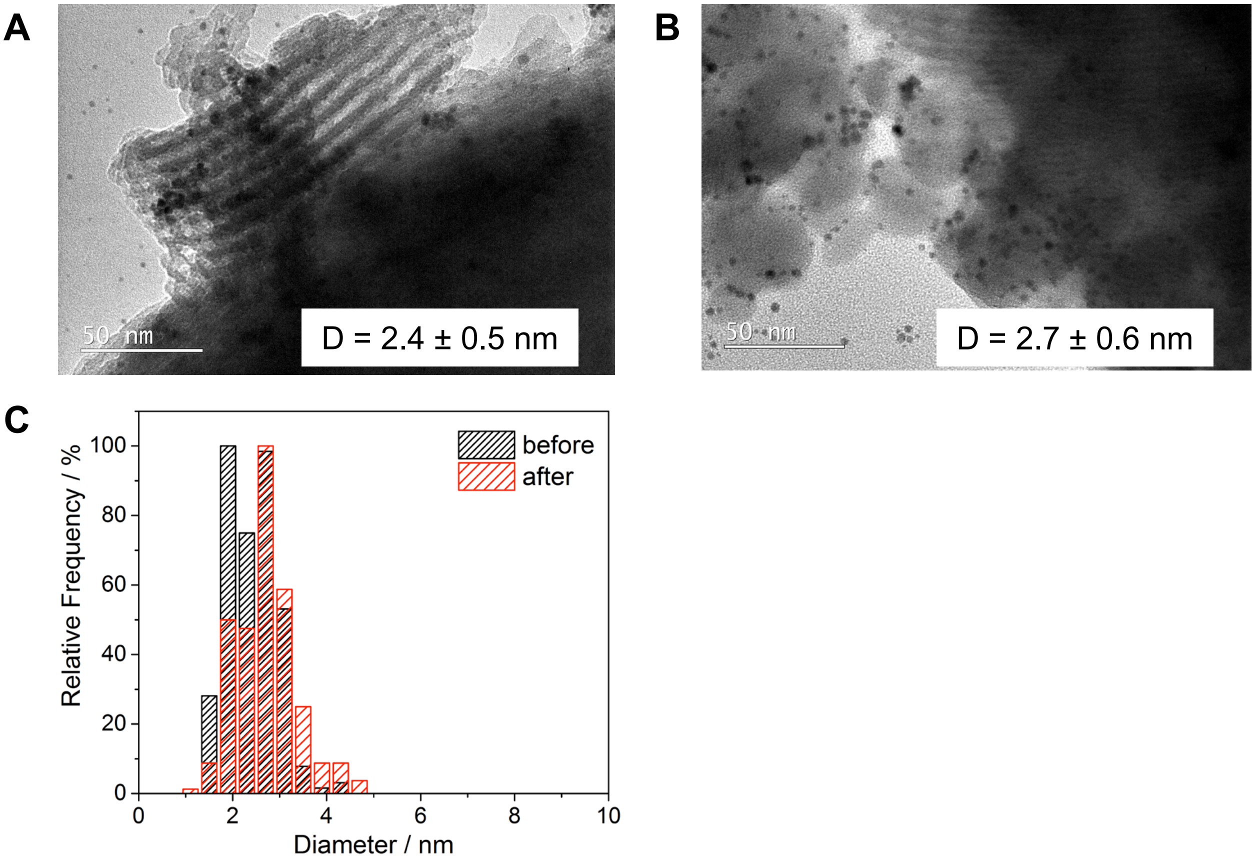


Figure S6. TEM images of **SBA-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

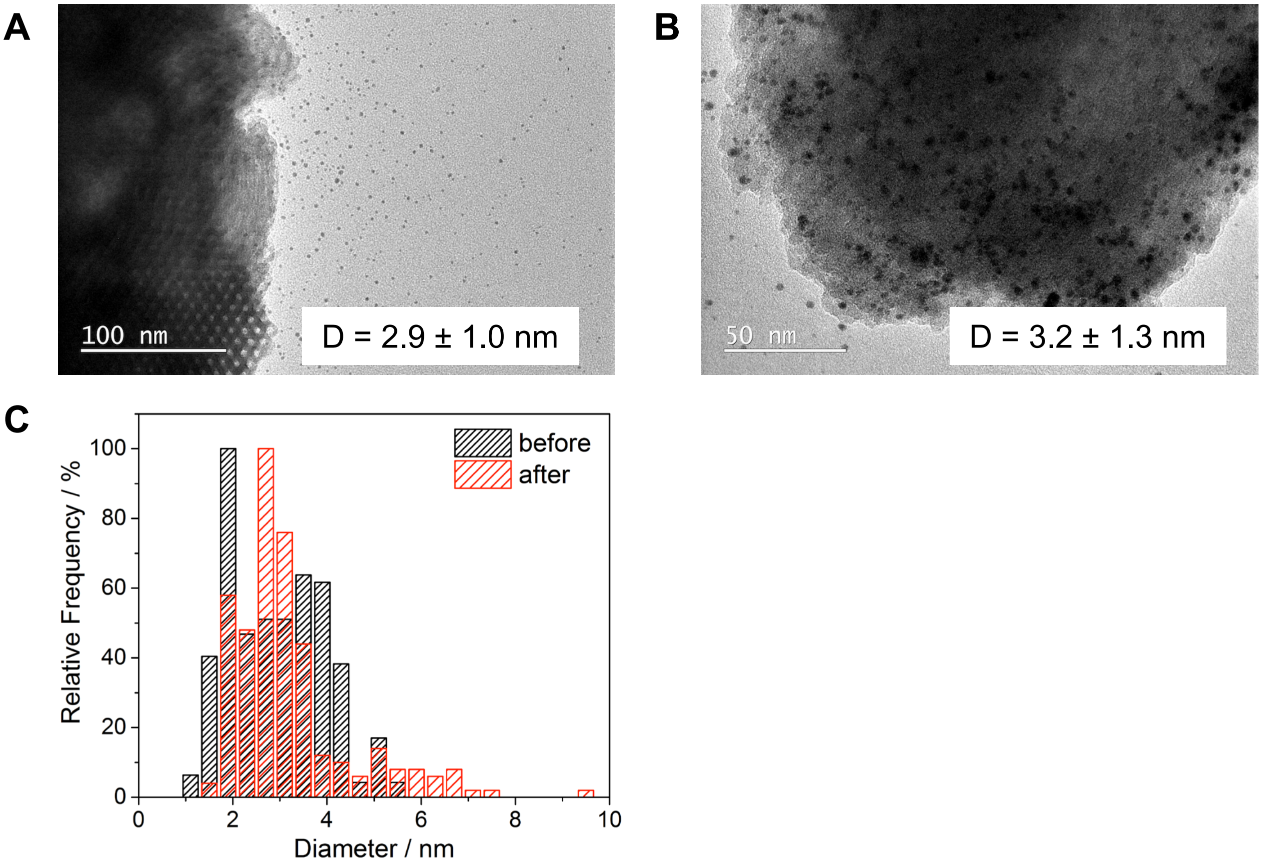


Figure S7. TEM images of **SBA-FC-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-FC-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

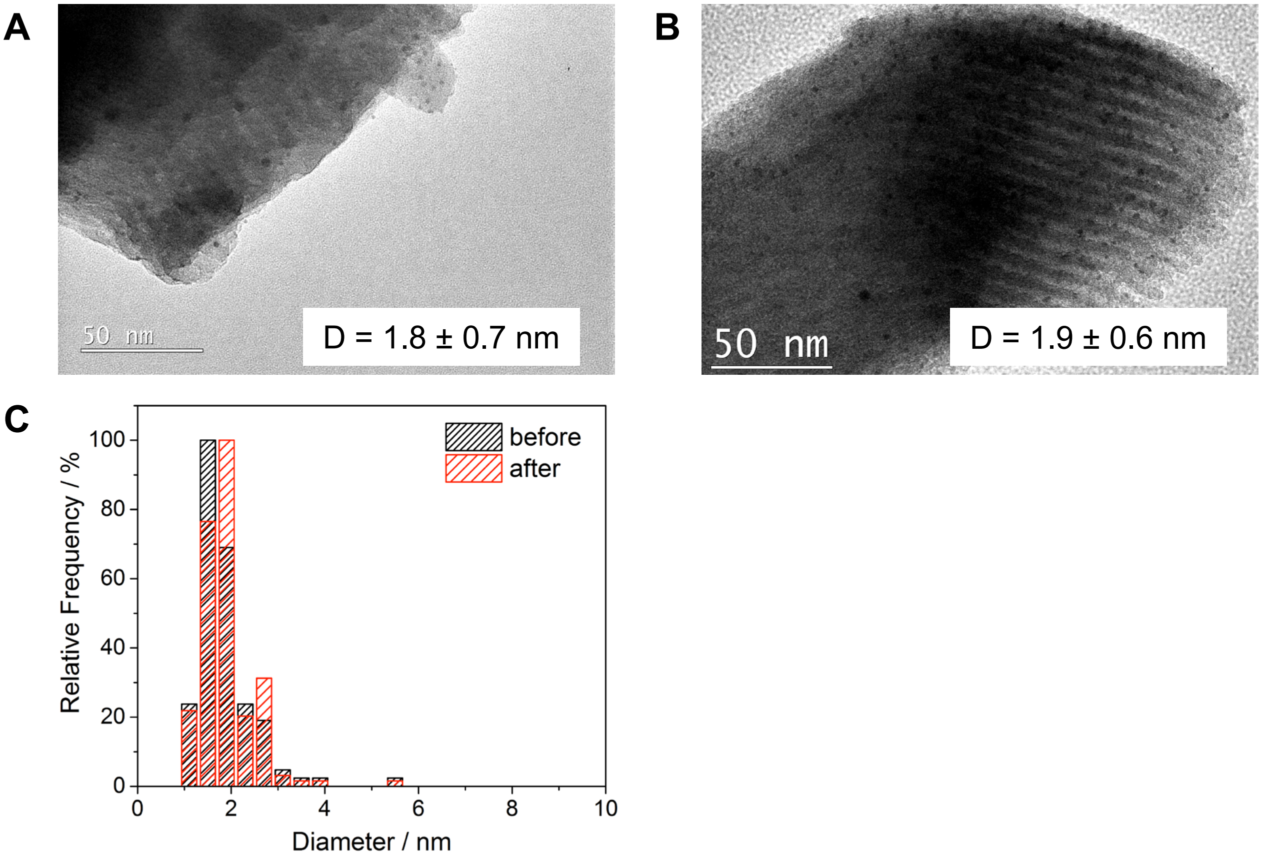


Figure S8. TEM images of **SBA-FC-S5-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-FC-S5-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

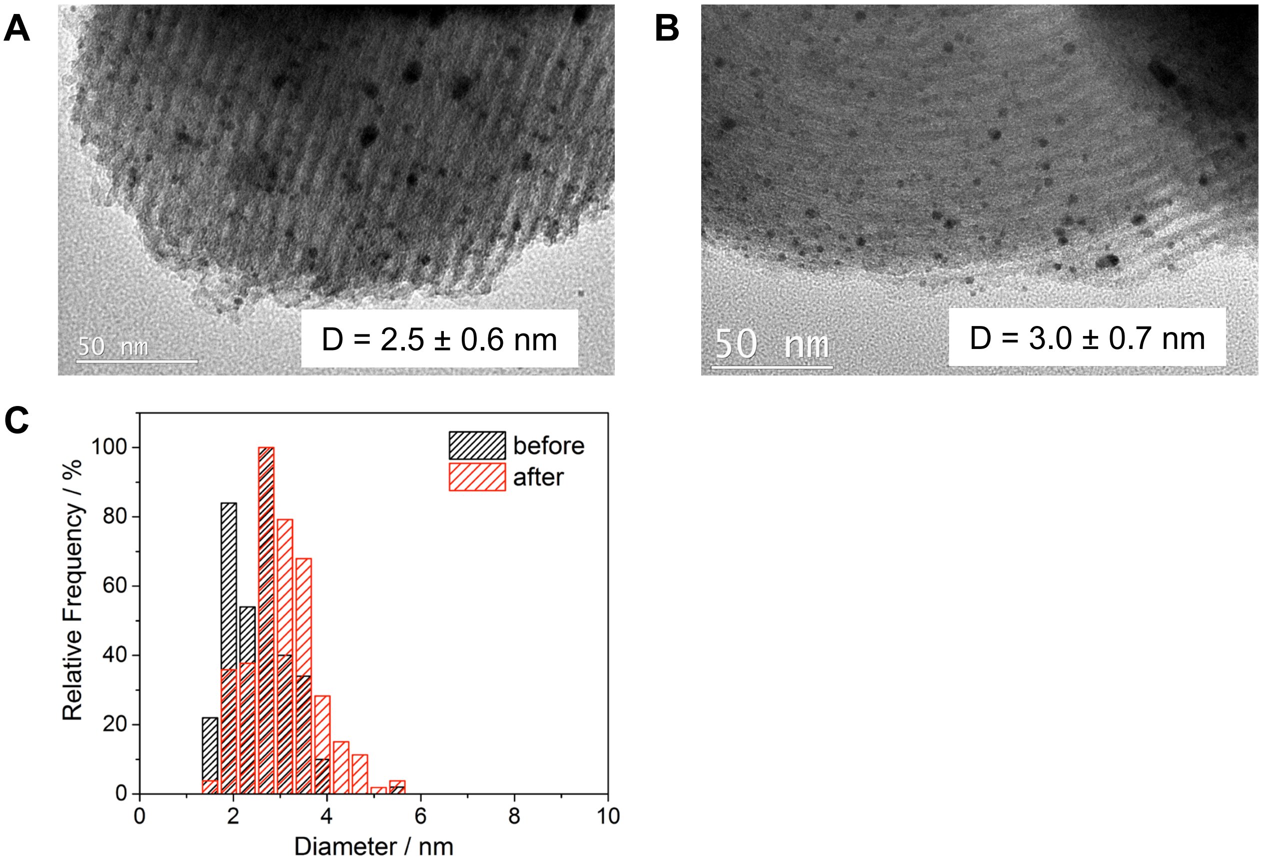


Figure S9. TEM images of **SBA-FC-S2.5-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-FC-S2.5-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

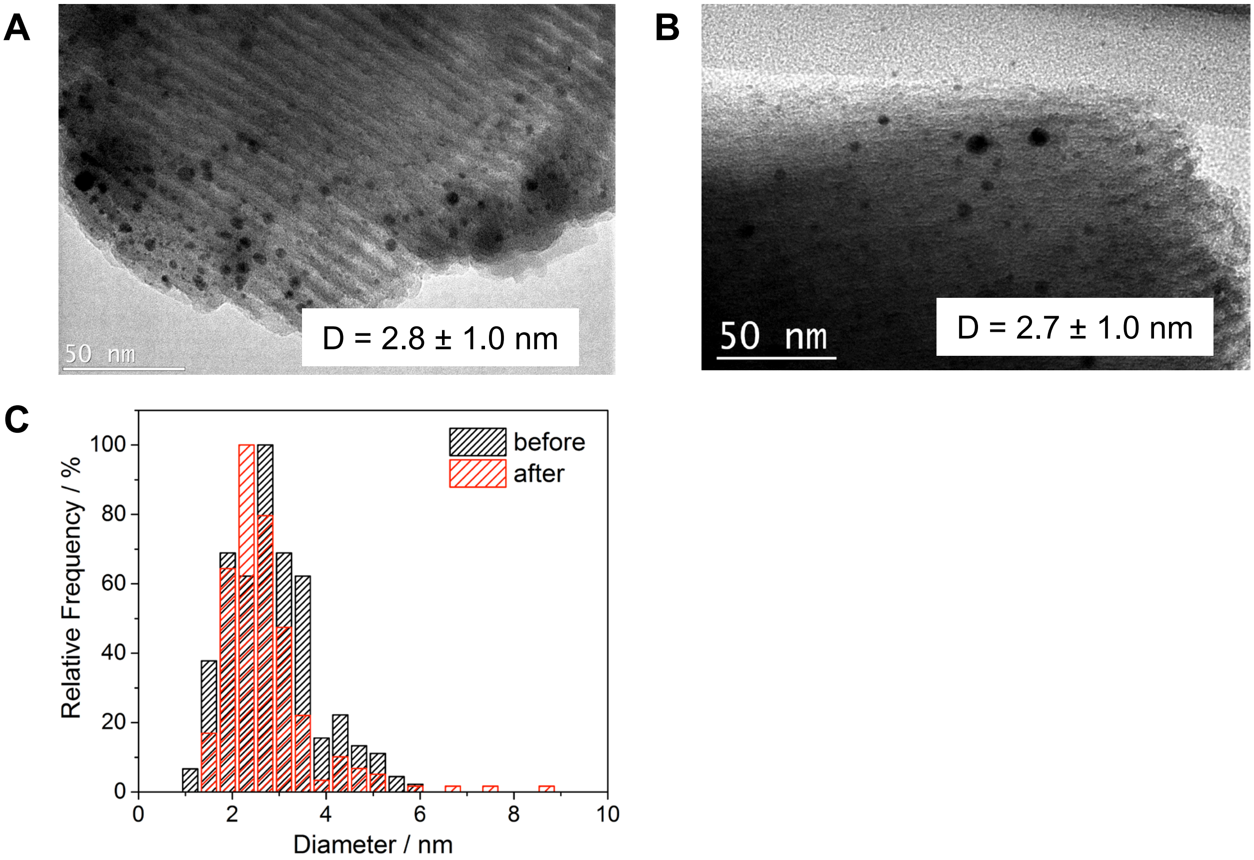


Figure S10. TEM images of **SBA-FC-S1-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-FC-S1-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

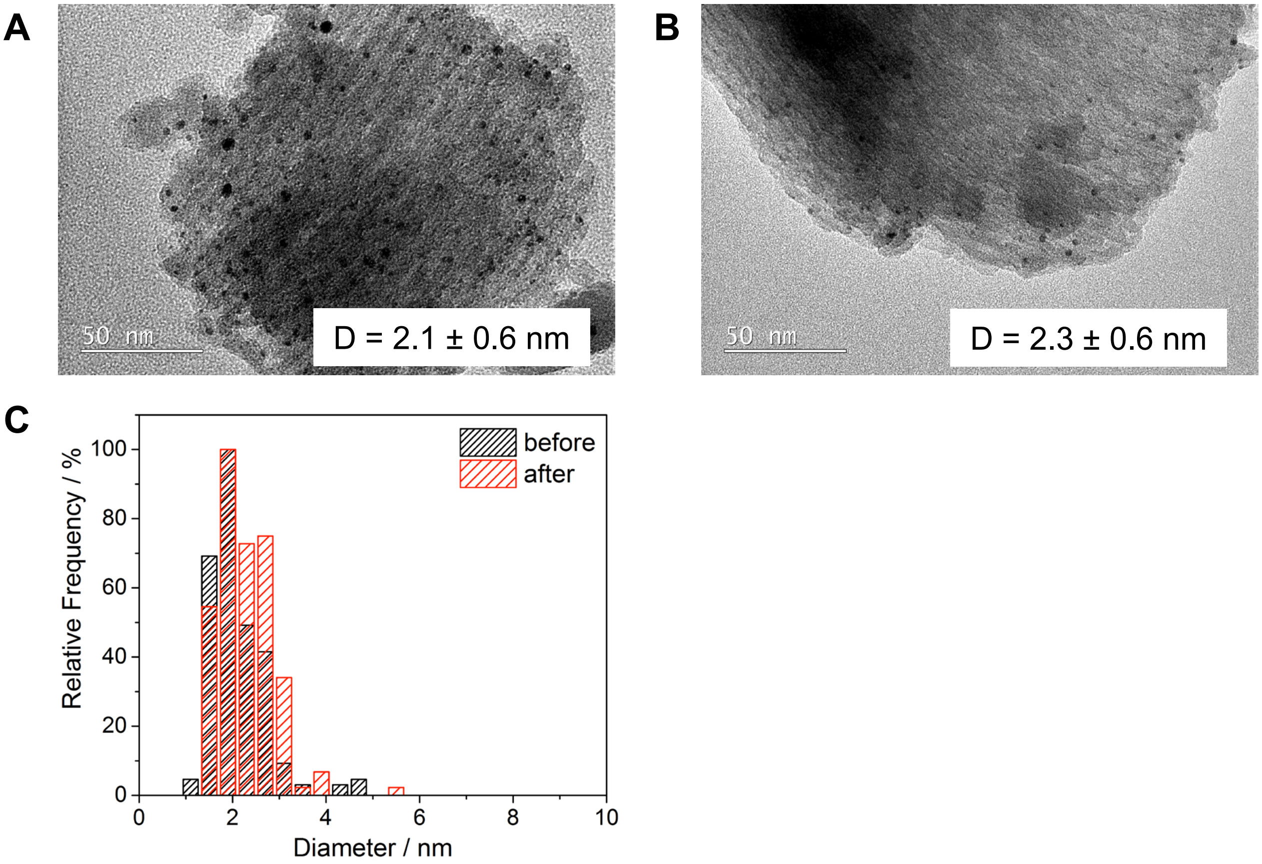


Figure S11. TEM images of **SBA-HC-S5-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-HC-S5-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

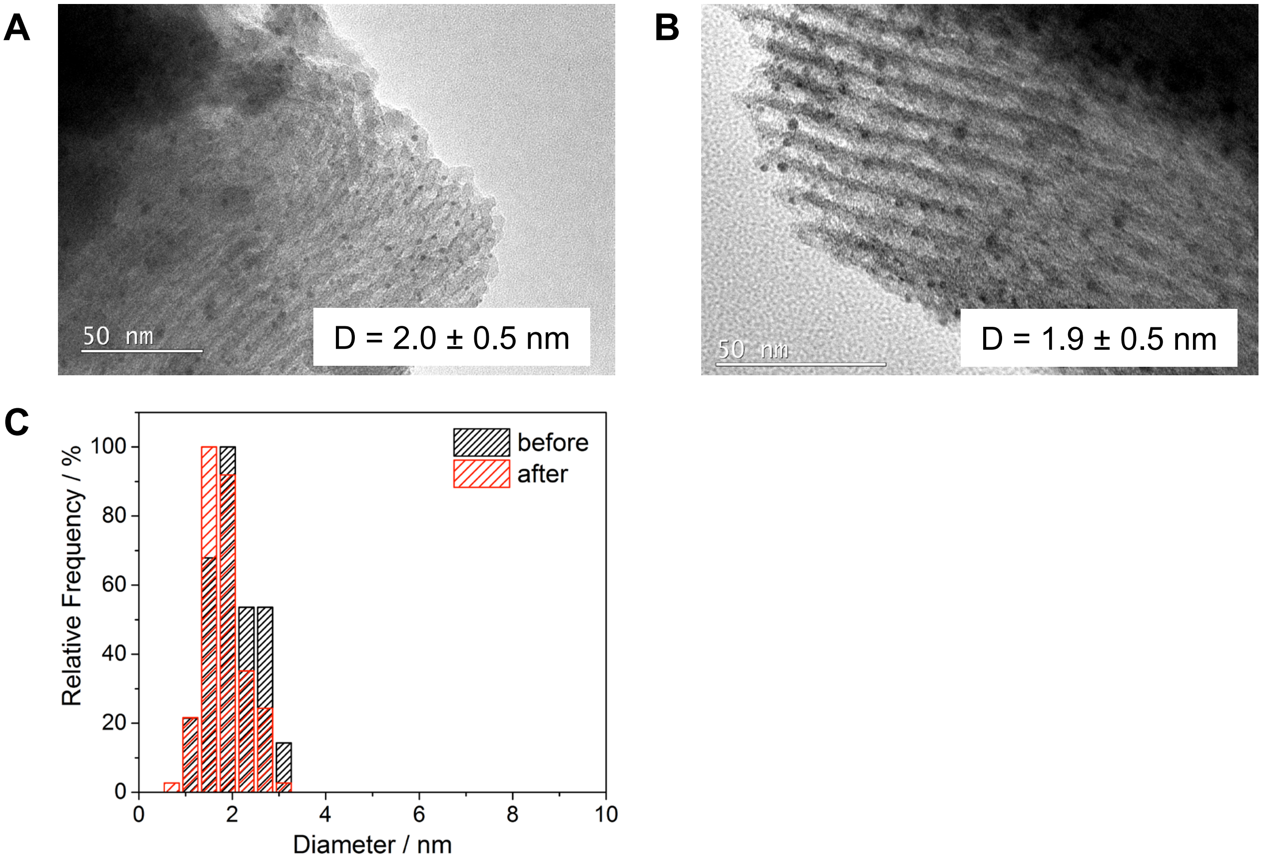


Figure S12. TEM images of **SBA-S5-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-S5-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

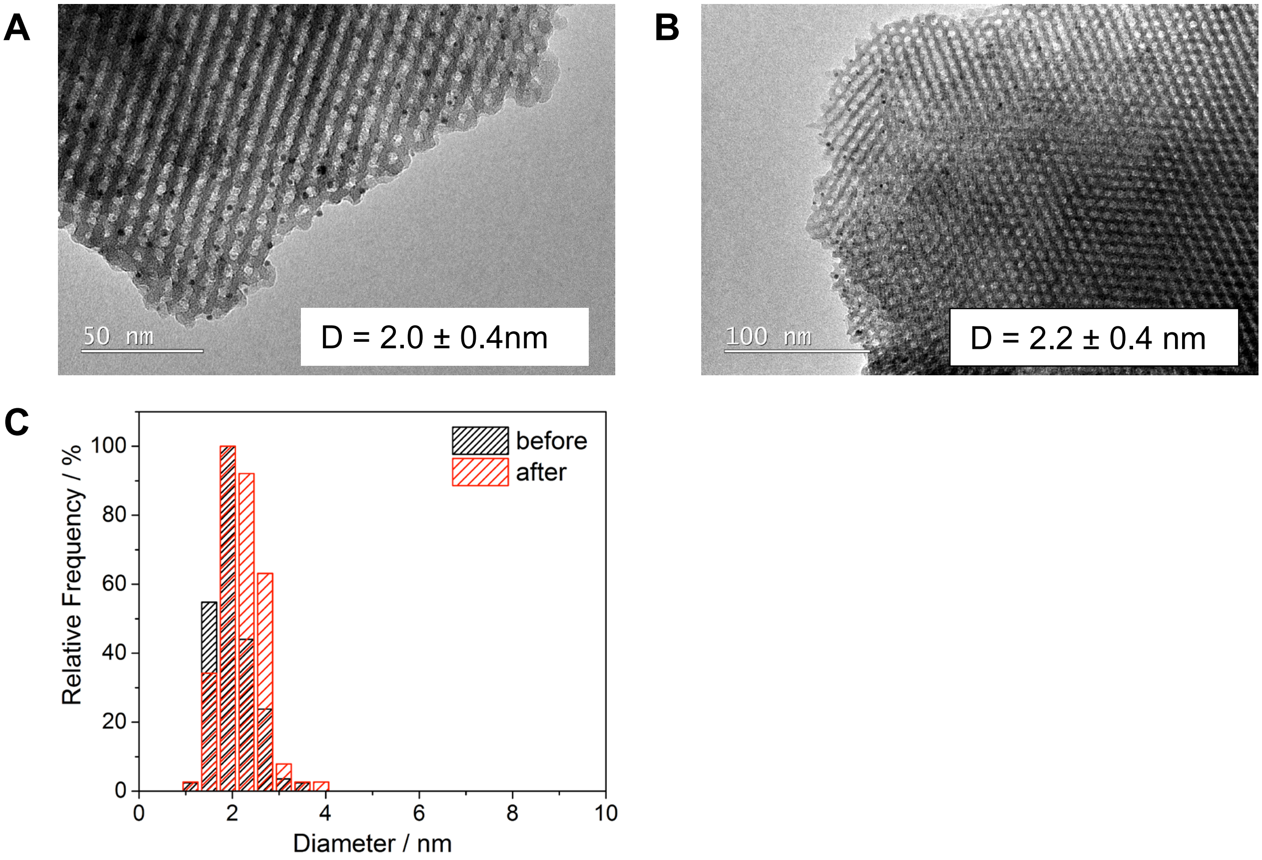


Figure S13. TEM images of **SBA-S100-Au** (A) before and (B) after thermal activation at 200 °C under vacuum. (C) The corresponding size distributions of **SBA-S100-Au** before (black) and after (red) thermal activation at 200 °C under vacuum.

6. Catalysis Experiments

General procedure:

A stock solution of DMF (20 mL) with 220 μL of iodobenzene (220 μL) and *n*-decane (200 μL) was prepared. A vial of 2 mL was charged with catalyst (2 mol% Au) and base (2 equiv). 0.5 mL of the stock solution was added. The reaction was conducted in air at 120 °C for 48 or 96 h. After cooling to room temperature, the mixture was filtered through 0.45 μm PTFE membrane, and the filtrate was collected for GC-MS. The conversion and yield were determined by GC-MS or ^{1}H NMR.

GC-MS calibration and representative GC traces

General method:

DMF solutions (2 mL) of iodobenzene (0.10, 0.20, 0.30, 0.40, and 0.50 mM) or biphenyl (0.05, 0.10, 0.15, 0.20, and 0.25 mM) were prepared. To each solution, *n*-decane (20 μL) was added as an internal standard. The ratio (r) of peak area of iodobenzene or biphenyl to that of *n*-decane was determined by GC-MS. The relationship between r and concentration (c) was obtained by linear fitting through zero.

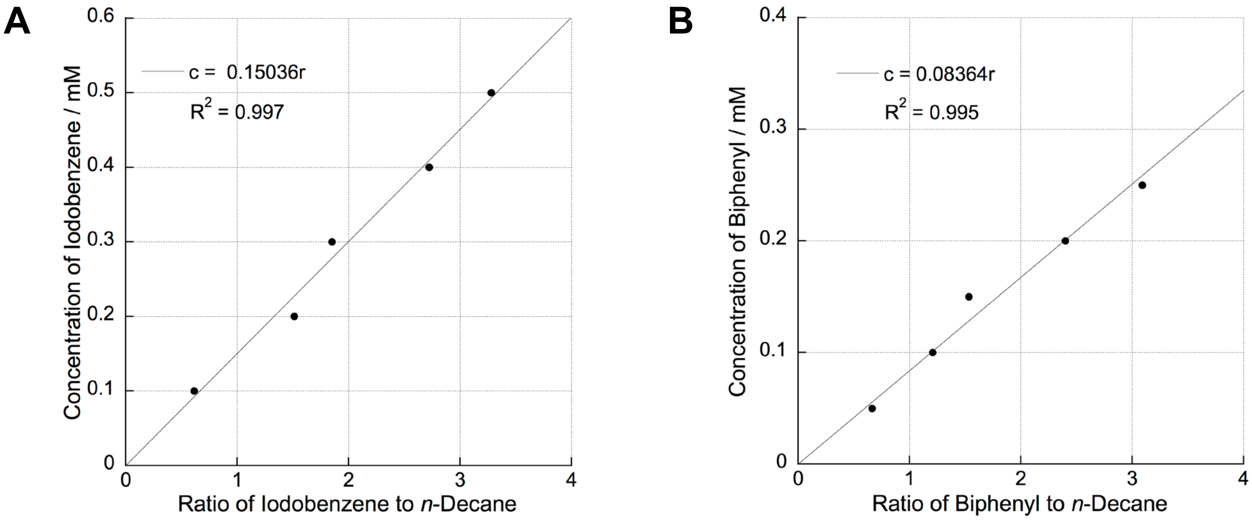


Figure S14. Calibration curves of (A) iodobenzene and (B) biphenyl with *n*-decane as an internal standard.

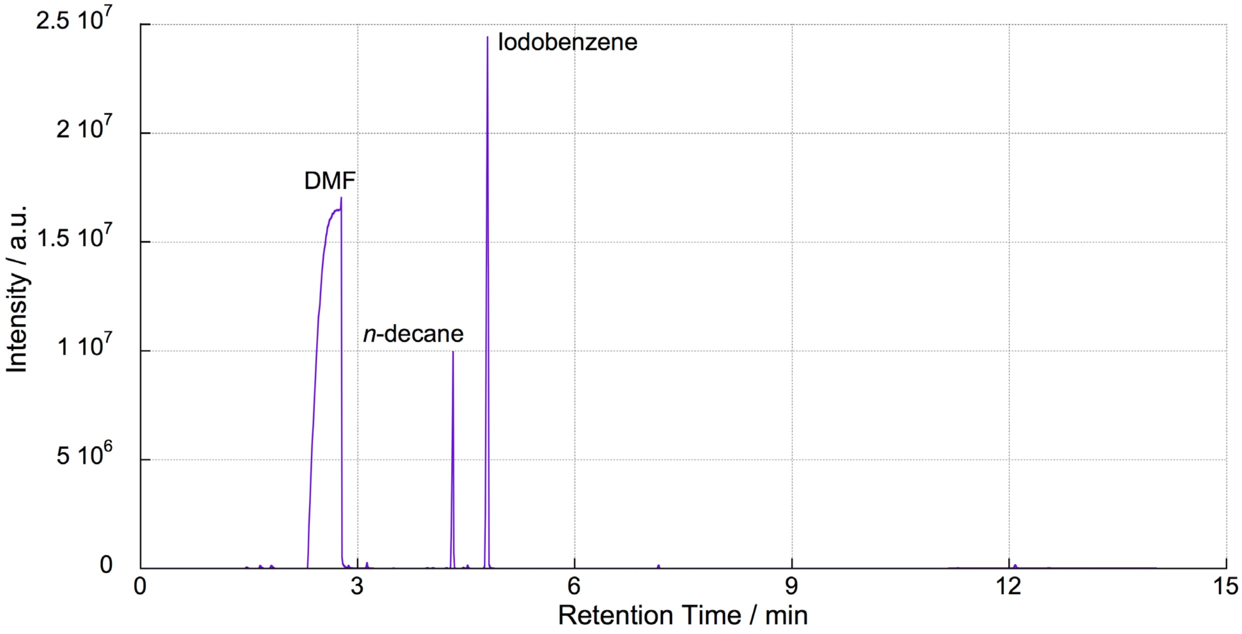


Figure S15. The GC trace of UHC by using SBA-15 SiO_2 as catalysts at 120 °C for 48 h.

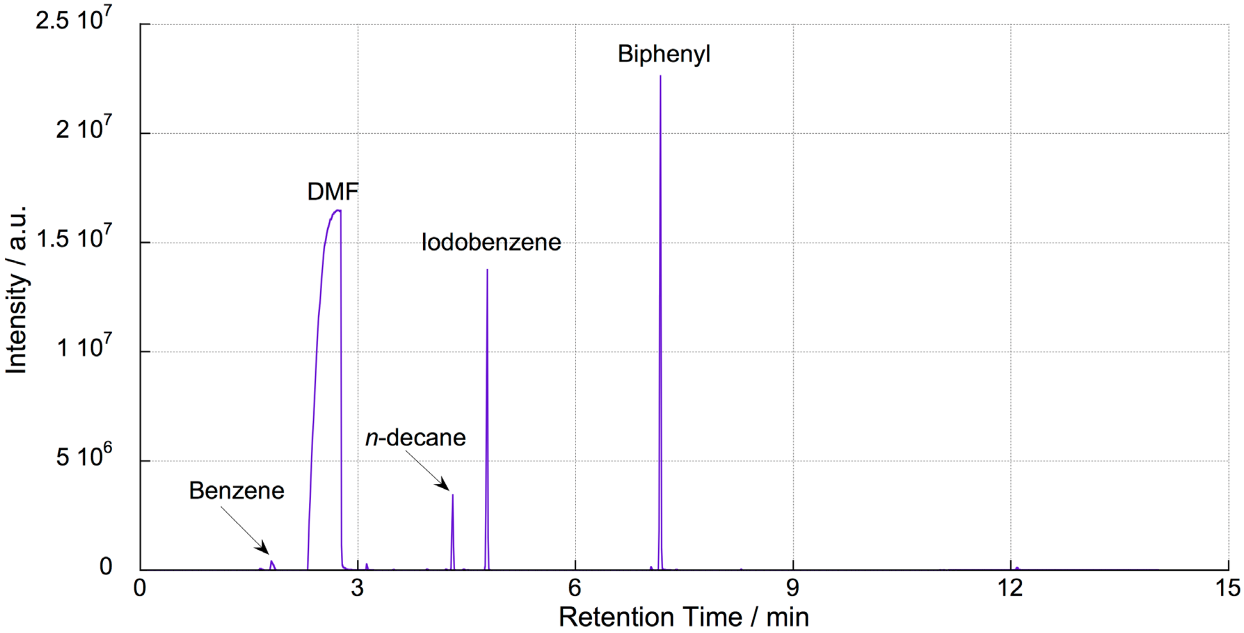
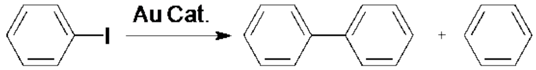


Figure S16. The GC trace of UHC by using **SBA-FC-S5-Au** as catalysts at 120 °C for 48 h.

Screening of Solvents and Bases for UHC Reactions

Table S3. The influence of base and solvent in UHCs of iodobenzene



Entry	Catalyst	Base	Solvent	Con. (%)	Sel. (%)[a]
1[b]	**SBA-FC-S5-Au**	-	DMF	9	0
2[b]	**SBA-FC-S5-Au**	K_2CO_3	DMF	49	98
3[c]	**SBA-FC-S5-Au**	K_3PO_4	NMP	31	93
4[c]	**SBA-FC-S5-Au**	K_3PO_4	DMSO	13	100

Conditions: iodobenzene (50 μmol), solvent (0.5 mL), catalyst (2 mol% equiv of Au), base (2 equiv), and *n*-decane (26 μmol) as the internal standard, 120 °C, 48 h, in air. [a] Selectivity for biphenyl. [b] Determined by GC-MS. [c] Determined by ^{1}H NMR.

Mercury Poisoning Experiments

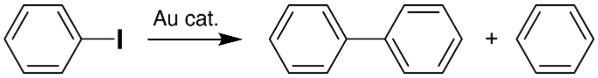
A stock solution of iodobenzene (220 μL) and *n*-decane (200 μL) in DMF (20 mL) was prepared. A vial of 2 mL was charged with 0.5 mL of the stock solution. Au_{101}*PPh_3 (2 mol% equiv of Au) and K_3PO_4 (2 equiv) were added. Mercury (~10 μL) was added either immediately, or after 24 hours. The reactions were conducted in air at 120 °C for 48 h with stirring (500 rpm). After cooling to room temperature, the mixtures were filtered through 0.45 μm PTFE membrane, and the filtrate was collected. The conversion and yield were determined by GC-MS. No conversion was observed for the reaction when mercury was added in the beginning. A conversion of 29 % was obtained when mercury was added in the middle of the reaction. These results support the hypothesis of heterogeneous nature of the operational catalyst.

Recycling

General procedure:

A stock solution of DMF (20 mL) with iodobenzene (220 μL) and *n*-decane (200 μL) was prepared. A vial of 2 mL was charged with 1 mL of the stock solution. Catalysts (2 mol% equiv of Au) and K_3PO_4 (2 equiv) were added. The reaction was conducted in air at 120 °C for 96 h with stirring (500 rpm). After cooling to room temperature, the catalysts were collected by centrifugation and then washed with DMF and deionized water. After washing, the catalysts were dried under vacuum before next run. The conversion and yield were determined by GC-MS.

Table S4. Recycling of Au_{101}*PPh_3, **SBA-Au**, and **SBA-FC-S5-Au** in UHC of iodobenzene.



entry	catalyst	cycle	conversion, %	selectivity, %
1	Au_{101}*PPh_3	1	47	77
2	Au_{101}*PPh_3	2	36	47
3	Au_{101}*PPh_3	3	14	36
4	**SBA-Au**	1	93	78
5	**SBA-Au**	2	63	32
6	**SBA-Au**	3	66	56
7	**SBA-FC-S5-Au**	1	74	98
8	**SBA-FC-S5-Au**	2	64	91
9	**SBA-FC-S5-Au**	3	35	94

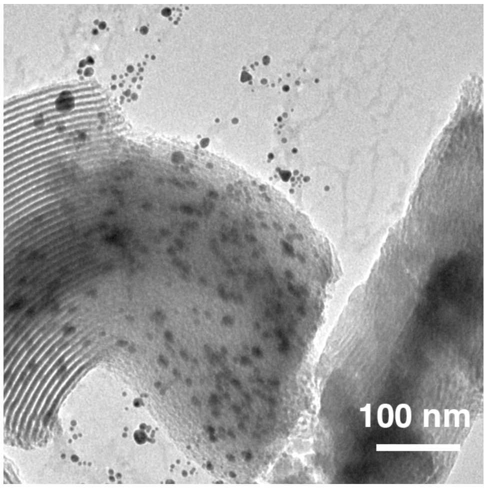


Figure S17. A TEM image of a spent sample of **SBA-FC-S5-Au** (Table S4, Entry 9). A significant number of Au NPs leached from the support can be observed. It is readily apparent that the size of NPs has increased in comparison to the pristine catalyst (Figure S8).

7. NMR Spectra

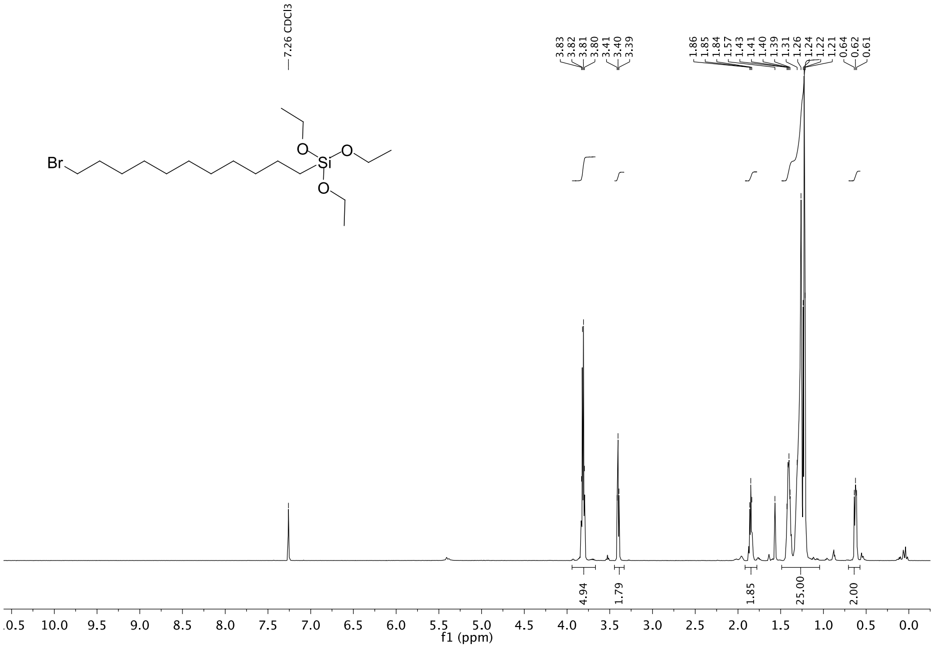


Figure S18. ^{1}H NMR spectrum of (11-bromoundecyl)triethoxysilane in $CDCl_3$.

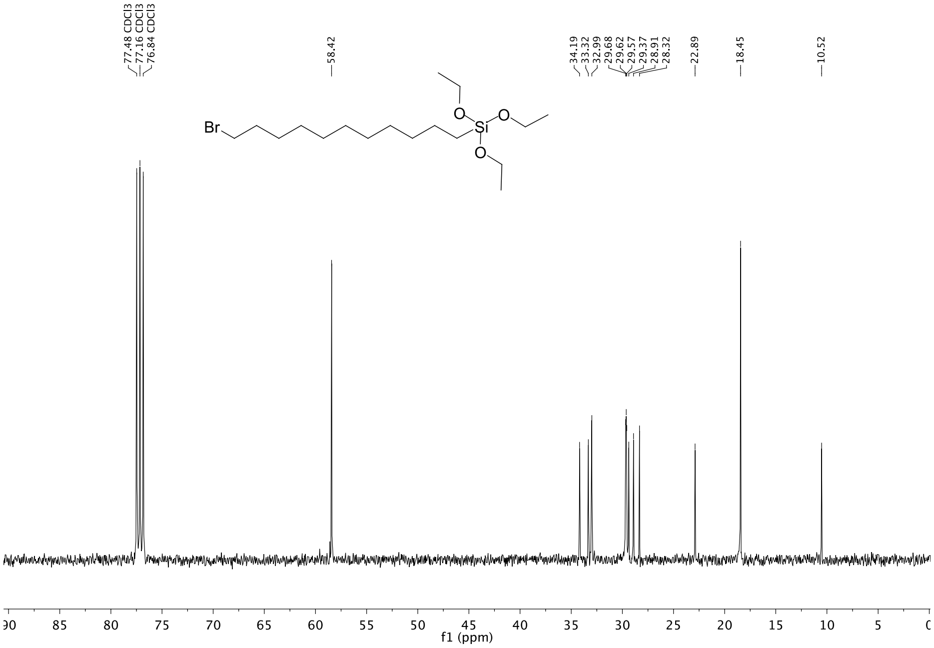


Figure S19. ^{13}C NMR spectrum of (11-bromoundecyl)triethoxysilane in $CDCl_3$.

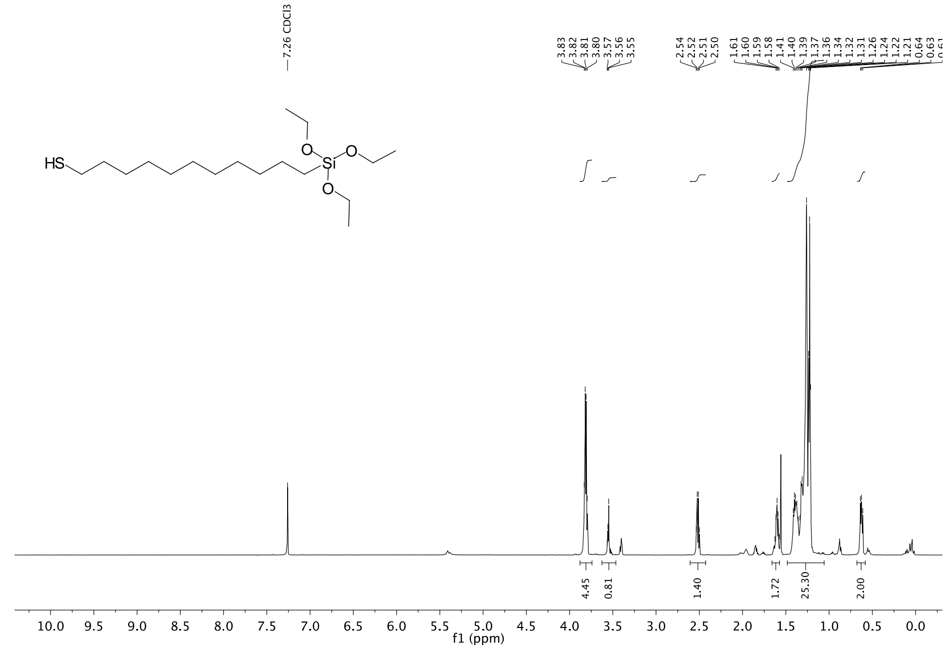


Figure S20. ^{1}H NMR spectrum of **H11SH** in CDCl$_3$.

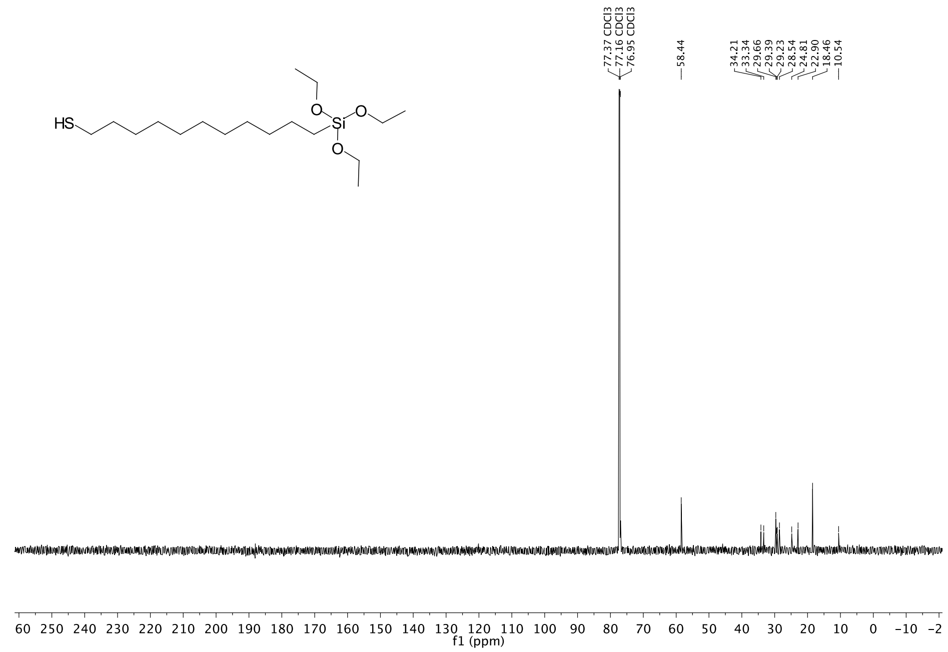


Figure S21. ^{13}C NMR spectrum of **H11SH** in CDCl$_3$.

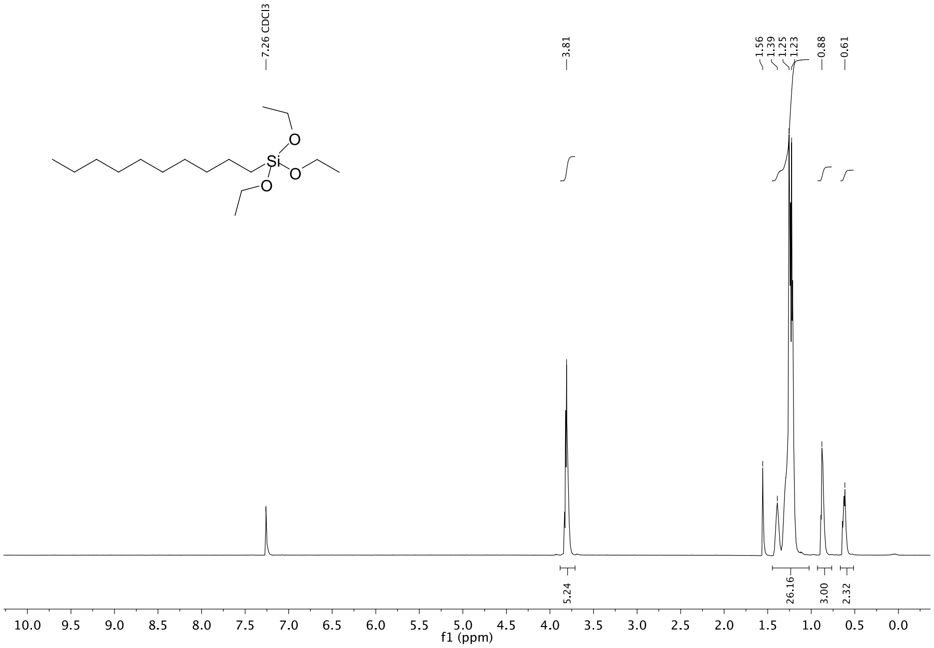


Figure S22. ^{1}H NMR spectrum of **H10** in CDCl$_3$.

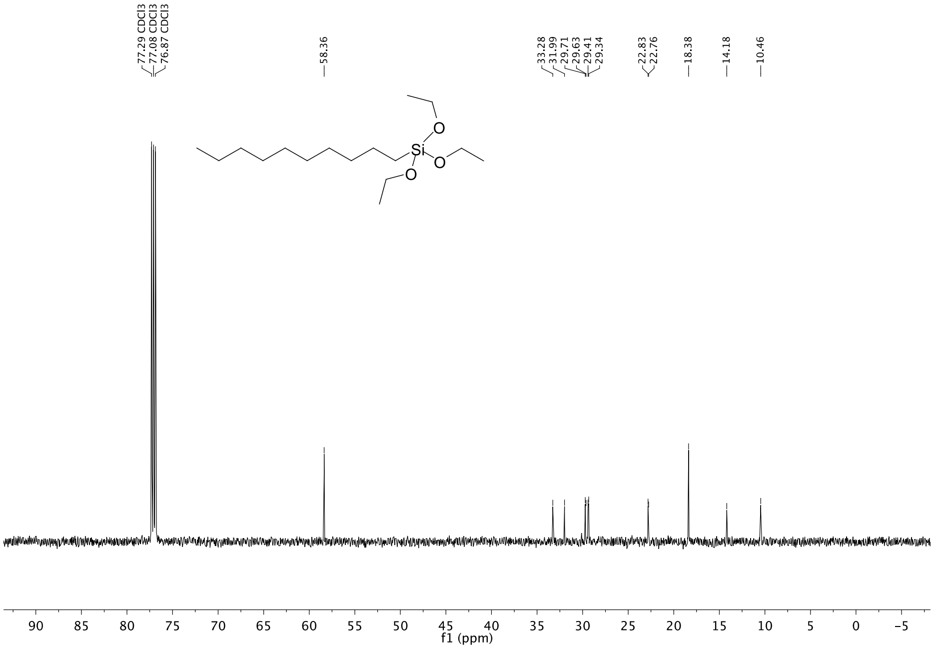


Figure S23. ^{13}C NMR spectrum of **H10** in CDCl$_3$.

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