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Insights into Dynamic Covalent Chemistry at Surfaces: From in situ Scanning Tunneling Microscopy to Solution Studies

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Contents

1. Ex-situ synthesis of compounds 5, 6, 7 and 8

General experimental procedure

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz and Bruker AMX 400 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (1H) or the internal (NMR) solvent signal (13C). Mass spectra were run using an HP5989A apparatus (EI, 70eV ionization energy) with Apollo 300 data system, a Micromass Quattro II apparatus (ESI) with MASSLYNX data system or a Thermo Finnigan LCQ Advantage apparatus (ESI/APCI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000).

Experimental and Characterization data

1.1 *N,N'*-(1,4-phenylenebis(methanylylidene))bis(3,5-di-tert-butyl aniline), 6: To a solution of terephthalaldehye (10 mg, 0.07 mmol) in ethanol (5 mL) was added 3,5-di-*tert*-butylaniline (33 mg, 0.16 mmol) and the reaction mixture was refluxed for 4 hours. The precipitate obtained was filtered, washed with ethanol (2 x 5mL) and dried under vacuum to give compound **6** (25 mg, 65%) as yellow solid. MS (EI) *m/z* 509 $[MH]^+$; HRMS (EI) calcd for $C_{36}H_{48}N_2$: 508.3817; found *m/z* = 509.3903 $[MH]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 2H), 8.02 (s, 4H), 7.33 (t, *J* = 1.6 Hz, 2H), 7.09 (d, *J* = 1.7 Hz, 4H), 1.37 (s, 36H).

1.2 4-(((4-(octadecyloxy)phenyl)imino)methyl)benzaldehyde, 5: Synthesis according to procedure leading to compound **6**. 4-(octadecyloxy)aniline (10 mg, 0.02 mmol) terephthalaldehye (9 mg, 0.06 mmol), 5 mL ethanol. Compound **5** (8 mg, 61%) was obtained as an off-white solid. MS (EI) *m/z* 478 $[MH]^+$; HRMS (EI) calcd for $C_{32}H_{47}NO_2$: 477.3607; found *m/z* = 478.3680 $[MH]^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.56 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.98 (m, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.29 (m, 30H), 0.87 (t, *J* = 6.2 Hz, 3H).

1.3 *N,N'*-(1,4-phenylenebis(methanylylidene))bis(4-octadecyloxy aniline), 7: Synthesis according to procedure leading to compound **6**. Terephthalaldehyde (18.6 mg, 0.13 mmol), 4-octadecyloxy aniline (100 mg, 0.28 mmol), 10 ml ethanol. Compound **7** (70 mg, 66%) was obtained as an off-white solid. ^{1}H NMR (400 MHz, Toluene-*d8*): δ 8.28 (s, 2H), 7.88 (s, 4H), 7.22 (d, 4H), 6.88 (d, 4H), 3.78 (t, 2H), 1.71 (t, 4H), 1.35 (m, 60H), 0.91 (m, 6H).

1.4 3,5-di-*tert*-butyl-*N*-(4-(((4-(octadecyloxy)phenyl)imino)methyl)benzylidene)aniline, 8: Synthesis according to procedure leading to compound **6.** Terephthalaldehye (5 mg, 0.035 mmol), 3,5-di-*tert*-butylaniline (7 mg, 0.0175 mmol), 4-(octadecyloxy)aniline (12 mg, 0.0175 mmol), 5 mL ethanol. Compound **8** (8 mg, 33 %) was obtained as a off-white solid. MS (EI) *m/z* 664; HRMS (EI) calcd for $C_{46}H_{68}N_2O$: 664.5332; found *m/z* = 664.4575.

2. Self-assembly of compounds 3, 5, 7 and 8 at the 1-phenyloctane/HOPG interface

General experimental procedure

4-octadecyloxyaniline was purchased from Sigma Aldrich. Compounds **5**, **7** and **8** were synthesized starting from this compound. The molecules were dissolved in 1-phenyloctane (Sigma Aldrich) at the given concentrations. All samples were subsequently dropcasted on freshly cleaved HOPG (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, OH, U.S.A.) Scanning Tunneling Microscopy (STM, Pico SPM, Agilent) measurements were performed in constant current mode at the liquid-solid interface at room temperature (20-25°C). Mechanically cut Pt/Ir wire (80/20, 0.25mm diameter) were used as STM tips. Analysis was performed after drift correction by using SPIP software (Image Metrology A/S). Corresponding molecular models were made using Hyperchem software, where the distances are based on the experimental values obtained in the STM images.

2.1 4-octadecyloxyaniline **3**

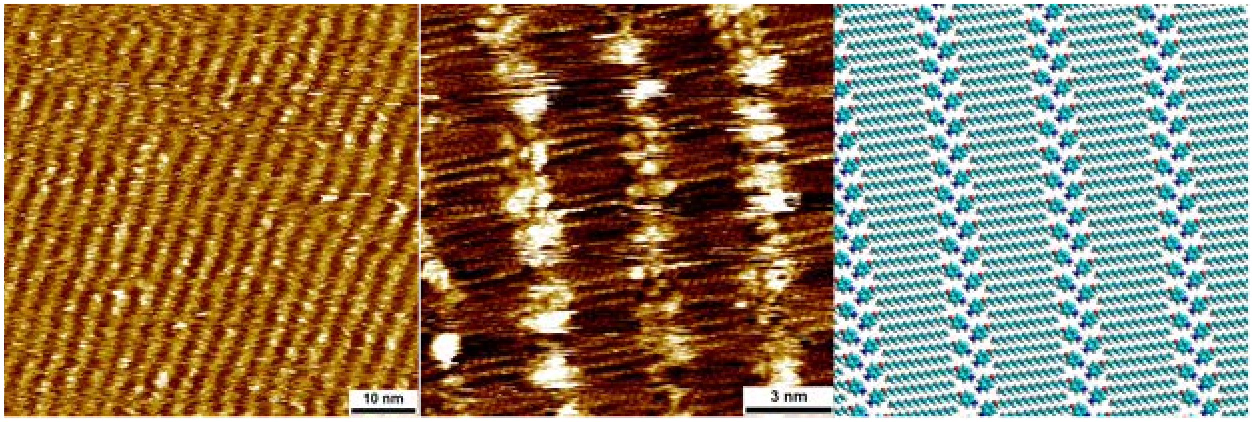


Figure S1: STM images and corresponding tentative molecular model of self-assembled monolayer of compound **3** at the phenyloctane/HOPG interface (c = 5.53*10^{-3} mol/l, V_{bias} = -0.7 V, I_{set} = 0.04 nA). Interlamellar distance is 3.51 ± 0.10 nm.

2.2 mono-imine/mono-aldehyde **5**

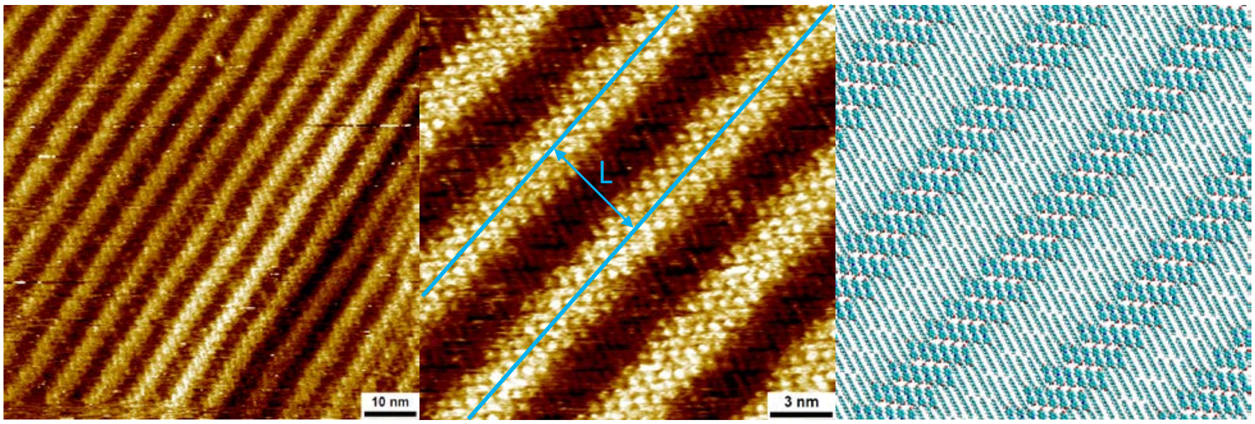


Figure S2: STM images and corresponding tentative molecular model of self-assembled monolayer of compound **5** at the phenyloctane/HOPG interface (c = $3.73*10^{-3}$ mol/l, V_{bias} = -0.7 V, I_{set} = 0.06 nA). Interlamellar distance L = 6.65 ± 0.13 nm.

2.3 bis-imine 4-octadecyloxyaniline **7**

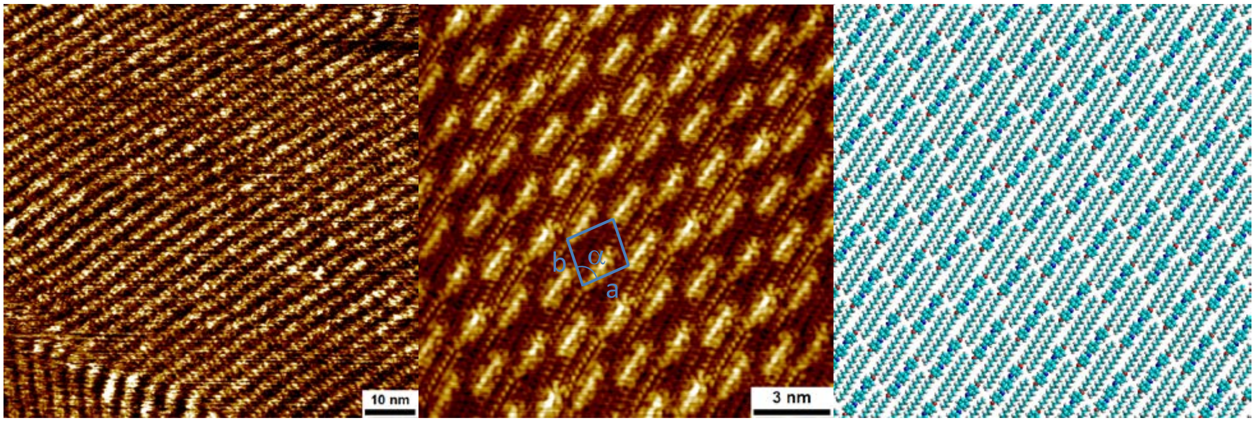


Figure S3: STM images and tentative corresponding molecular model of self-assembled monolayer of compound **7** at the phenyloctane/HOPG interface (saturated solution, V_{bias} = -0.7 V, I_{set} = 0.08 nA). Unit cell parameters: $\alpha = 88 \pm 1°$, a = 1.86 ± 0.10 nm, b = 1.91 ± 0.10 nm.

2.4 mixed-imine 4-octadecyloxyaniline **8**

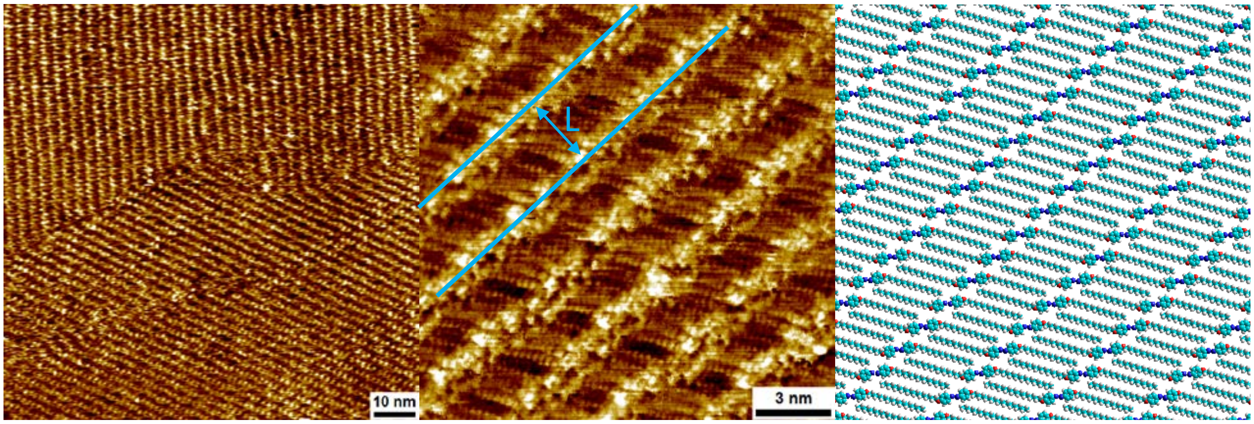
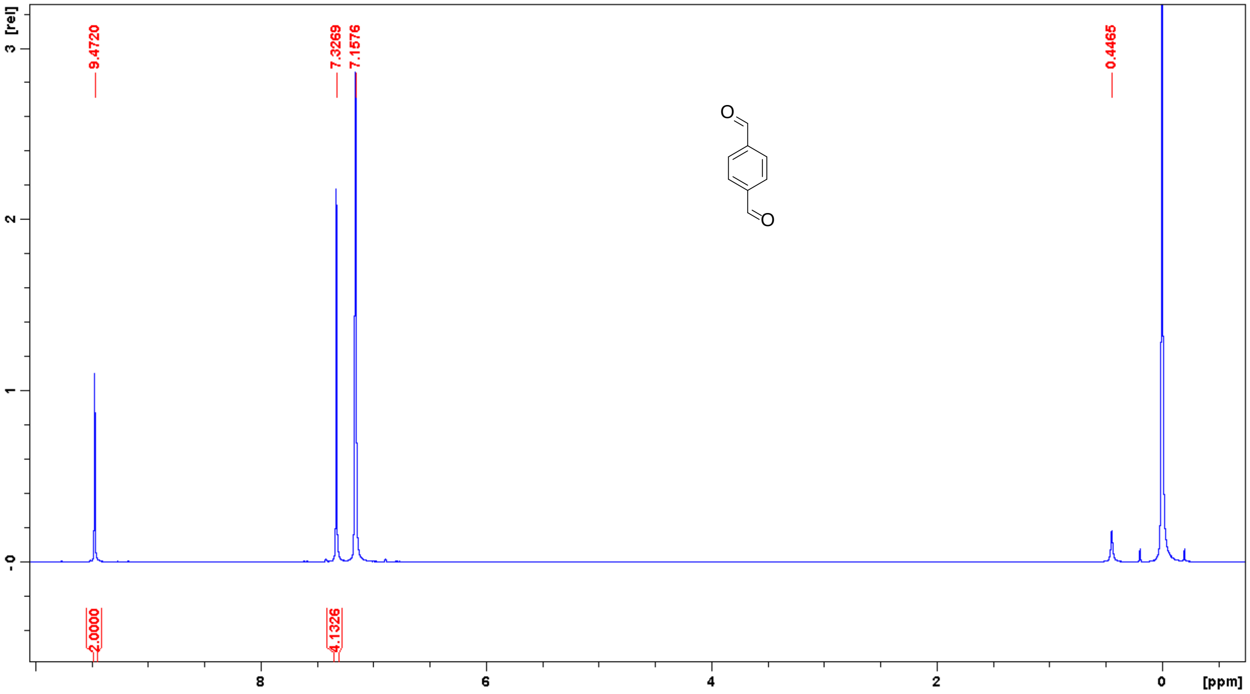


Figure S4: STM images and corresponding tentative molecular model of self-assembled monolayer of compound **8** at the phenyloctane/HOPG interface (saturated solution, V_{bias} = -1.05 V, I_{set} = 0.12 nA). Interlamellar distance L = 3.43 ± 0.10 nm. This is less than the length of a single molecule (4.14 nm) meaning that part of the molecule is pointing away from the surface into the solution. For clarity, this part is not shown in the molecular model.

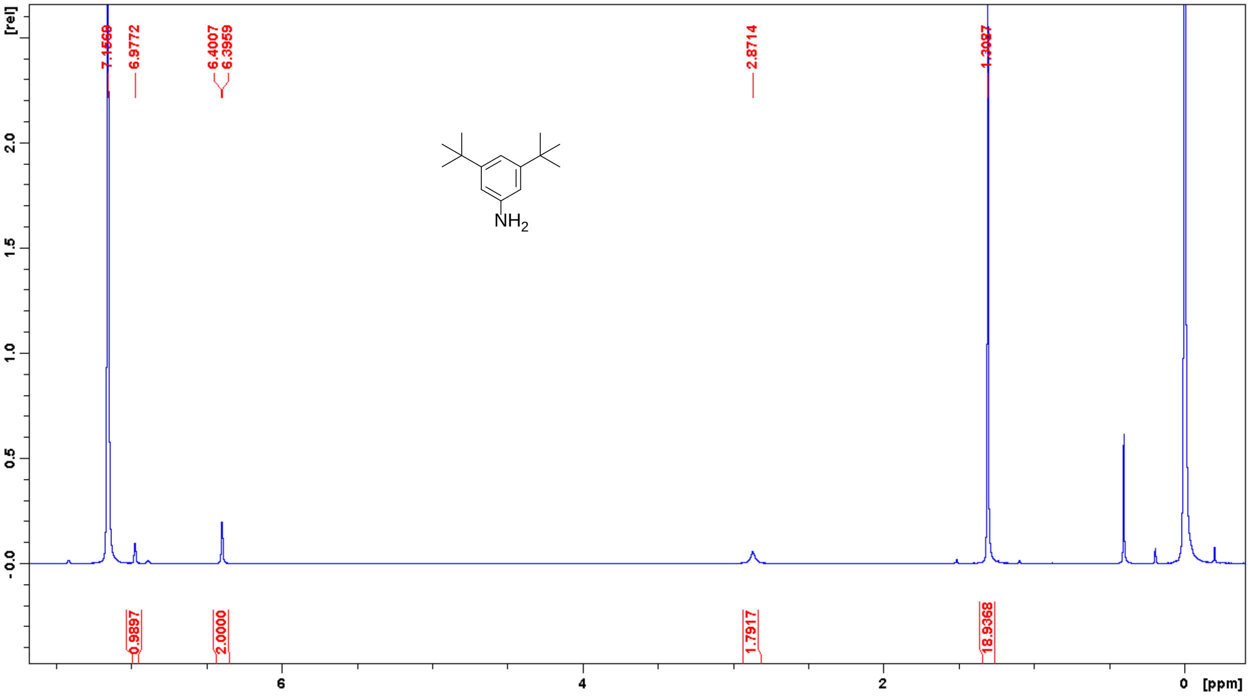
3. Reference ^{1}H-NMR-spectra (300 MHz, C_6D_6) of compounds 1, 2, 3, 5, 6 and 7

3.1 Terephthalic aldehyde, **1**



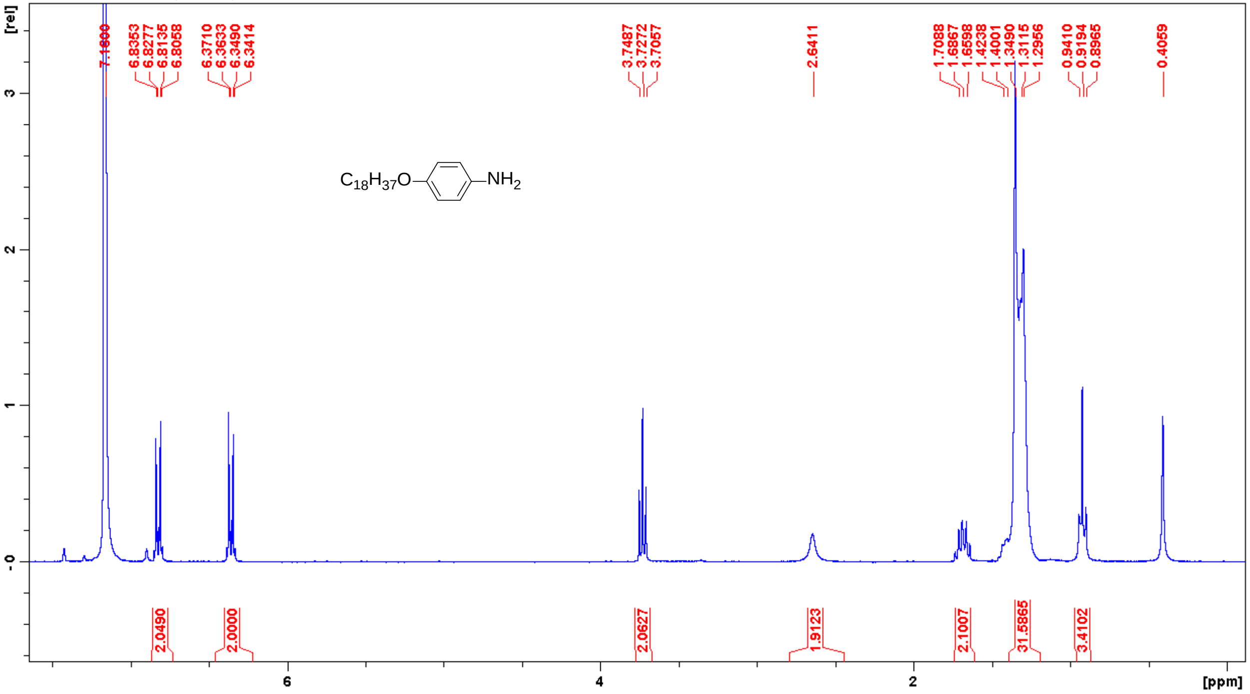
δ 9.47 (s, 2H), 7.32 (s, 4H)

3.2 3,5-di-tert-butylaniline, **2**



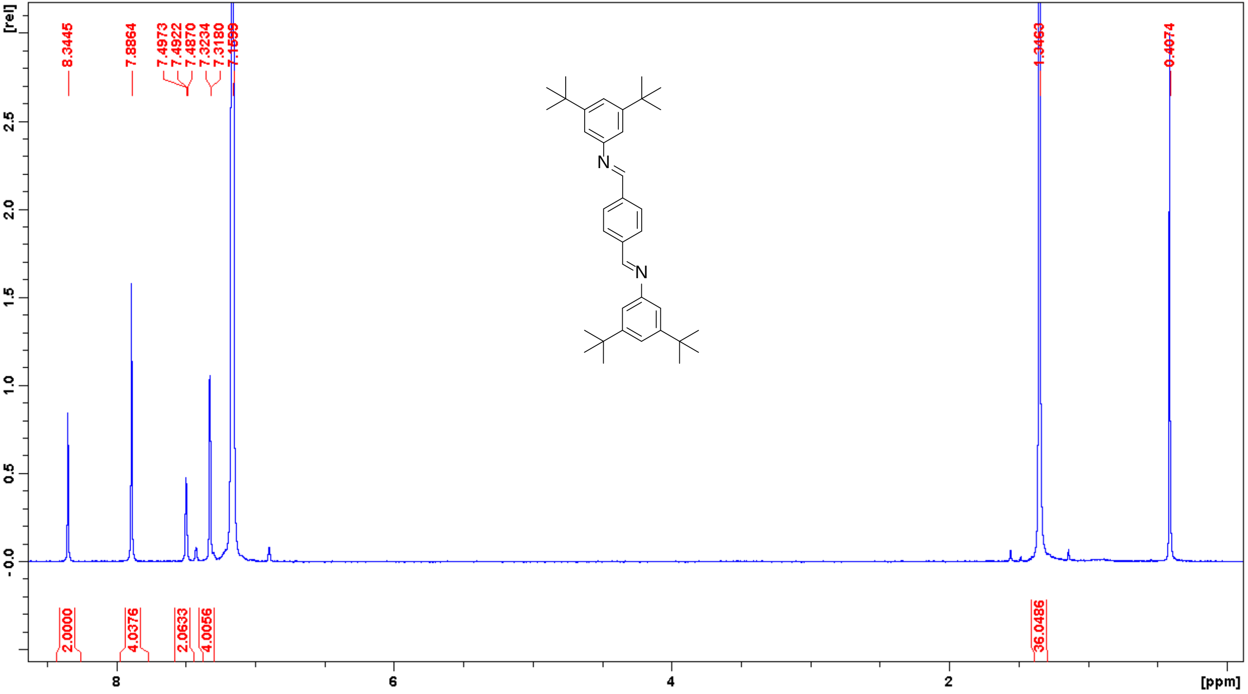
δ 6.98 (s, 1H), 6.40 (d, 2H), 2.87 (s, 2H), 1.31 (s, 18H)

3.3 4-octadecyloxy aniline, **3**



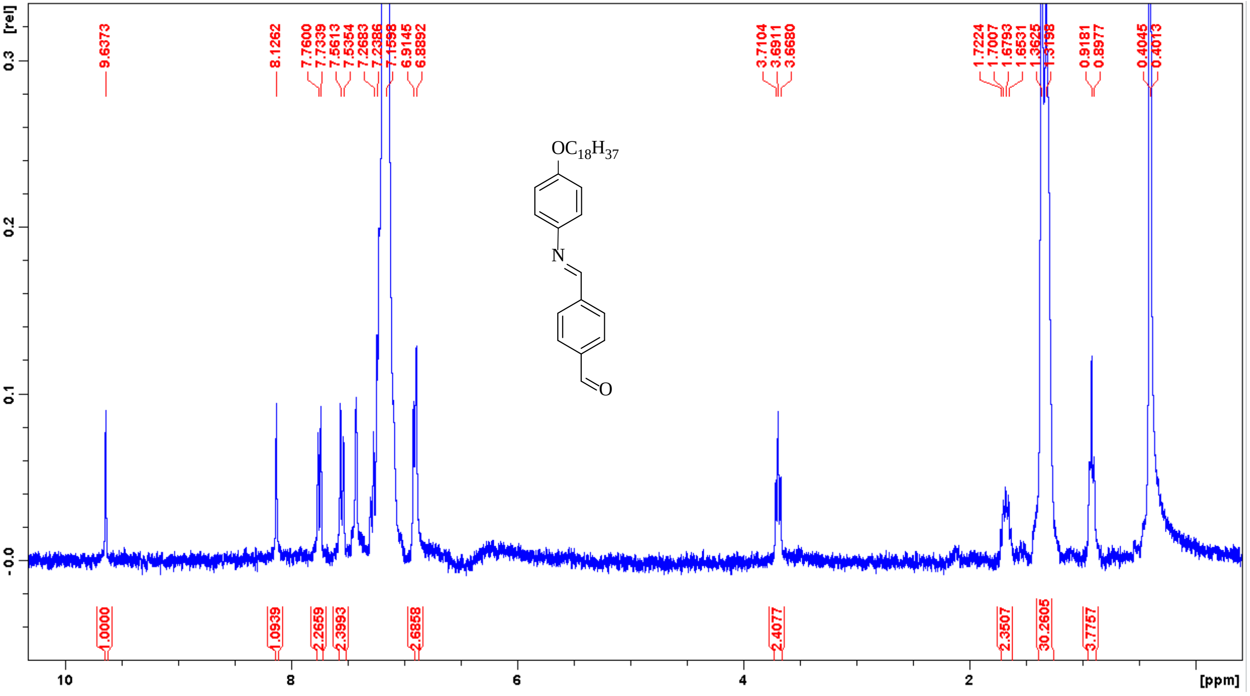
δ 6.84-6.81 (m, 2H), 6.37-6.34 (m, 2H), 3.73 (t, 2H), 2.64 (s, 2H), 1.69 (quin, 2H), 1.42-1.30 (m, 30H), 0.92 (m, 3H)

3.4 *N*,*N'*-(1,4-phenylenebis(methanylylidene))bis(3,5-di-tert-butyl aniline), **6**



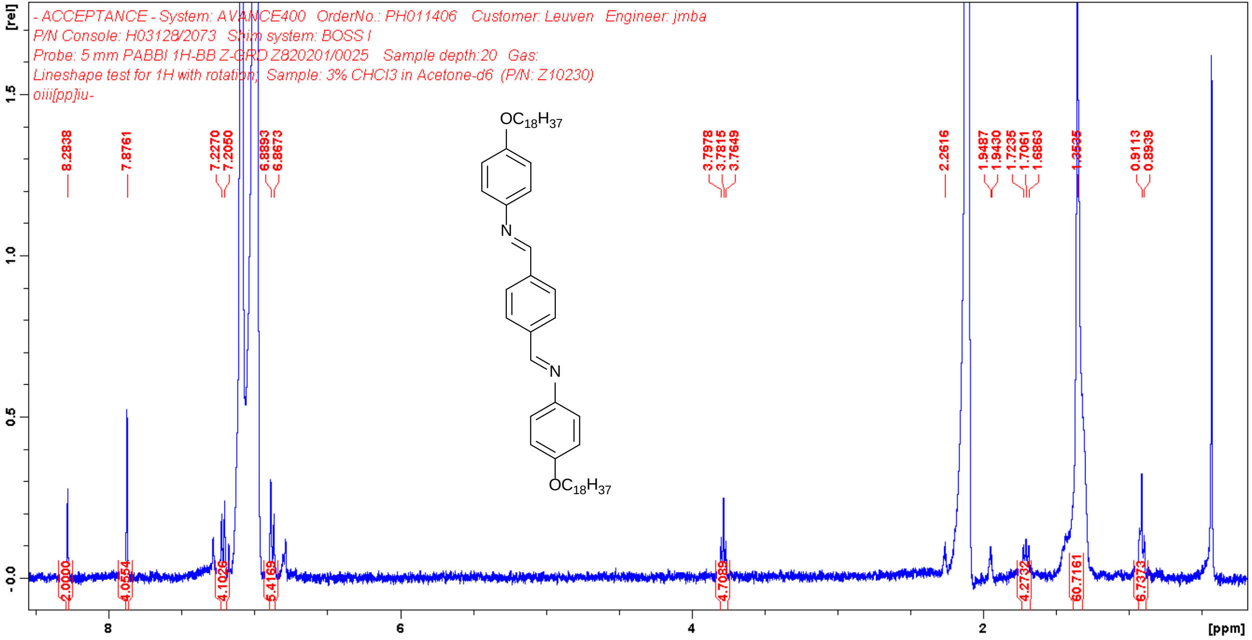
δ 8.34 (s, 2H), 7.88 (s, 4H), 7.49 (t, 2H), 7.32 (d, 4H), 1.35 (s, 36H)

3.5 4-(((4-(octadecyloxy)phenyl)imino)methyl)benzaldehyde, **5**



δ 9.64 (s, 1H), 8.13 (s, 1H), 7.74 (d, 2H), 7.55 (d, 2H), 7.27-7.24 (m, 2H), 6.90 (d, 2H), 3.69 (t, 2H), 1.68 (quin, 2H), 1.36-1.32 (m, 30H), 0.92 (m, 3H)

3.6 *N*,*N′*-(1,4-phenylenebis(methanylylidene))bis(4-octadecyloxy aniline), **7**:



δ 8.28 (s, 2H), 7.88 (s, 4H), 7.22 (d, 4H), 6.88 (d, 4H), 3.78 (t, 2H), 1.71 (t, 4H), 1.35 (m, 60H), 0.91 (m, 6H)

4. General experimental and analytical procedure for ^{1}H-NMR-experiments studying reaction A, B and C

General experimental procedure

Terephthalalaldehyde (Sigma Aldrich), 3,5-di-*tert*-butylaniline (TCI Chemicals) and 4-octadecyloxyaniline (Sigma Aldrich) were dissolved in benzene-*d6* (Sigma Aldrich) at given concentrations. For each set of experiments, a reference sample without PGC was used originating from the same solution batch to make sure that analysis was done with respect to a reliable blank sample. Porous Graphitic Carbon powder (Cheap Tubes Inc., 2 µm, 600-750 m²/g) was first dried for 3 hours at 200°C to remove an excess of adsorbed water before use. 6.50, 0.50 or 0.25 mg of PGC was added to each sample. Before NMR analysis, the samples are centrifuged and the supernatant solution is transferred to a NMR tube. If PGC is not removed from the samples, peak broadening and interference makes the analysis impossible. Silica (Across Organics), for column chromatography, 40-60 µm, 60A and amorphous carbon (Sigma Aldrich), 100 mesh were used as purchased in the same quantities as PGC.

General analytical procedure

The NMR-spectra were analyzed using the benzene peak as an internal reference. For each reaction in presence of PGC, a blank sample was used originating from the same solution batch. Since the reaction does not take place in these blank samples within the time frame we investigated, it is possible to determine the fraction of molecules of interest (products and reagents) with respect to the original amount of starting compounds. Samples in presence of PGC were first centrifuged in order to remove the solid material, which would otherwise interfere with the NMR-measurement. All compounds of interest give rise to recognizable signals either from the –CH=O or the –CH=N– protons. Therefore we used these signals to analyze the product distribution.

In this way, we can calculate the product distribution in solution. To find out the distribution between adsorbed products and the amount of molecules that is adsorbed, some extra calculations have to be made. This can be done by comparing the ratios of products to the benzene peak at ~7.16 ppm, since this is the only peak that does not change during the reaction. By comparing the ratios to benzene for the reacted and blank samples, we can find out the fraction of products that has disappeared (and thus adsorbed) from the mixture.

To calculate the distribution of adsorbed products, we start from a calibration graph for unreacted aniline **3** (figure S5). From this graph, we can calculate the amount of **3** that remains unreacted in the mixture. We already know the total fraction of products that has been adsorbed and by combining these numbers we can calculate the distribution between mono-imine **5**, bis-imine **7** and mixed-imine **8**.

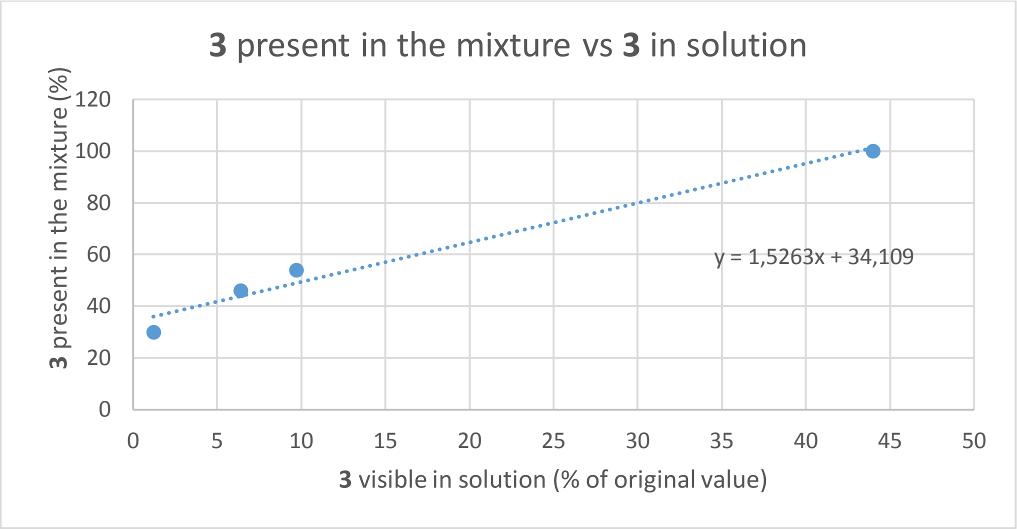
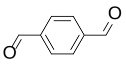


Figure S5: Calibration graph for adsorption of compound **3** on PGC. The results in this graph assume a linear relationship between the amount of compound **3** present in solution and the fraction of **3** that adsorbs on PGC. This assumption is only valid in case the original loading does not exceed 100%, since this would lead to saturation of the PGC surface. The values on the y-axis correspond to the amount of **3** that is loaded in the calibration samples, with respect to the amount that would be loaded in the reaction mixture. When PGC is added, a certain amount adsorbs on the surface. The fraction that is left in solution, after adsorption on PGC, is given on the x-axis. The graph is based on the results for 4 different amounts of **3** compared to the loaded value in reaction **C**. A linear fit of these points yields an intersect with the y-axis at the point where 0% of **3** is visible in solution, this corresponds to a fraction of 34% **3** that is capable of adsorbing in the unreacted form in reaction mixture **C**, without any observation of the compound in solution.

5. Detailed analysis of three-component reaction C in presence of PGC

5.1 6.50 mg PGC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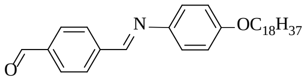

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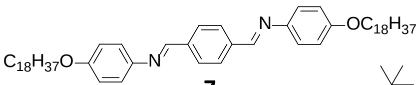

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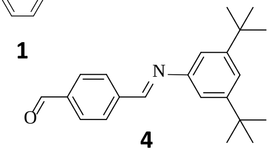

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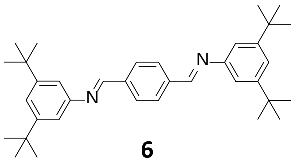

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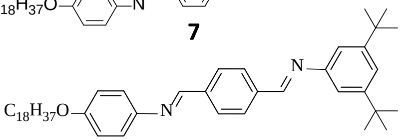

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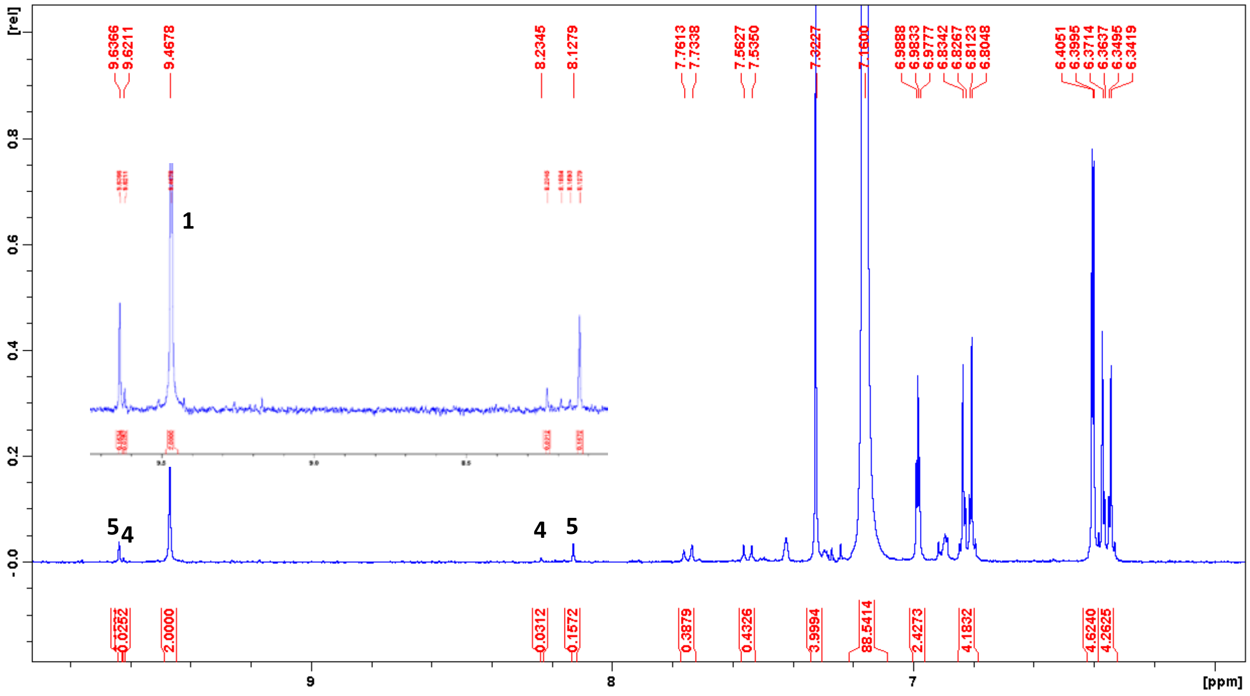
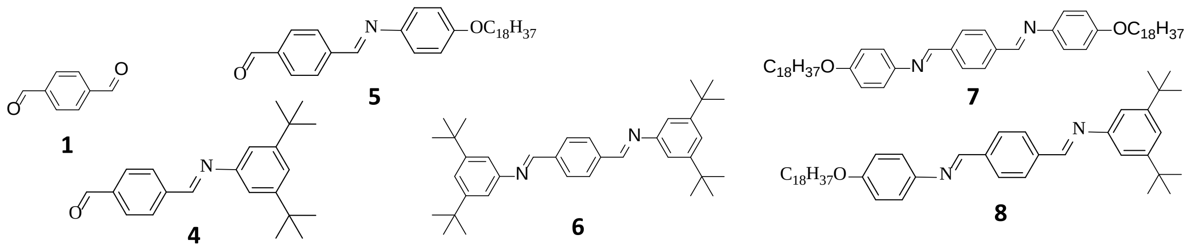


Figure S6a: ^{1}H-NMR-spectrum of reaction **C** in absence of PGC. Characteristic peaks from compounds **1**, **4** and **5** are present in the spectrum. δ 9.63 (s, 1H): –CH=O compound **5**; δ 9.62 (s, 1H): –CH=O compound **4**; δ 9.46 (s, 2H): –CH=O compound **1**; δ 8.23 (s, 1H): –CH=N– compound **4**; δ 8.13 (s, 1H), –CH=N– compound **5**.



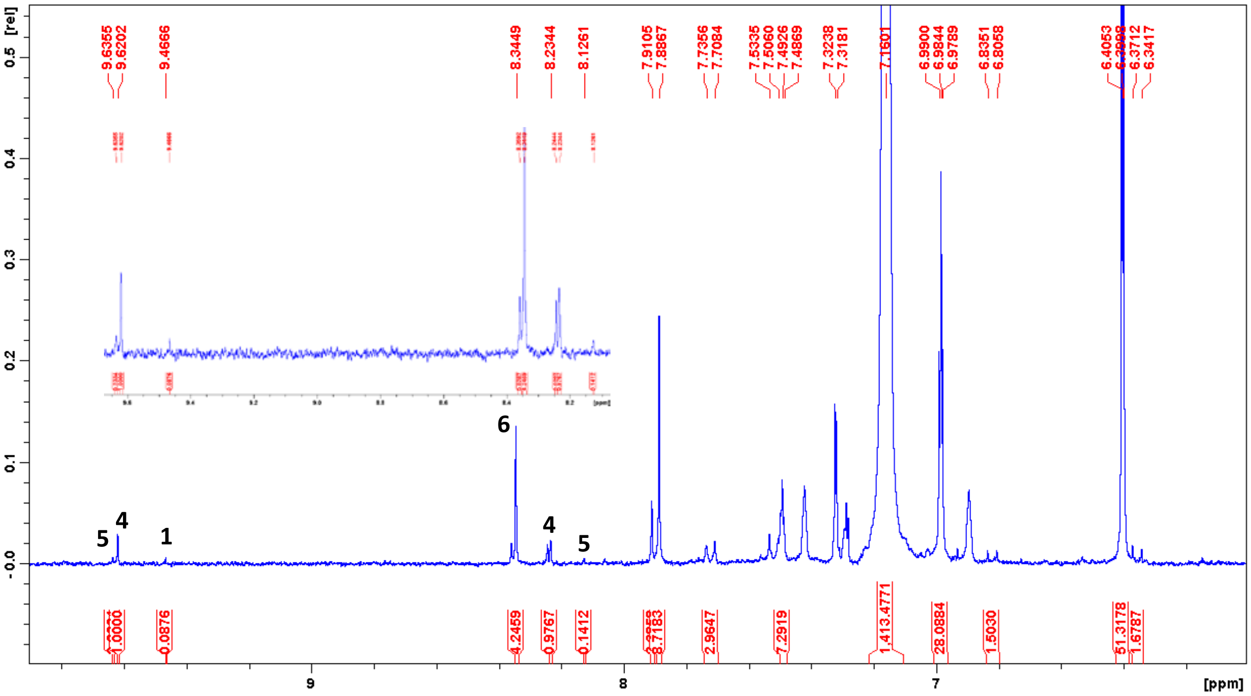


Figure S6b: ^{1}H-NMR-spectrum of reaction **C** in presence of 6.50 mg PGC. Characteristic peaks from compounds **1**, **4**, **5** and **6** are present in the spectrum. Compounds **7** and **8** are not observed because of complete adsorption on PGC. δ 9.64 (s, 1H): –CH=O compound **5**; δ 9.62 (s, 1H): –CH=O compound **4**; δ 9.46 (s, 2H): –CH=O compound **1**; δ 8.34 (s, 2H): –CH=N– compound **6**; δ 8.23 (s, 1H): –CH=N– compound **4**; δ 8.13 (s, 1H), –CH=N– compound **5**.

Table S1: Summary of the results obtained after analysis of the NMR-spectrum (figure S6b) for reaction C in presence of 6.50 mg PGC.

		Without PGC		With PGC	
Compound	Peak position	Peak intensity (converted to mole)	Fraction (%)	Peak intensity (converted to mole)	Fraction (%)
5	9.64	0.153	13	0.141	1
4	9.62	0.025	2	1.000	5
1	9.46	1.000	85	0.0438	1
6	8.34	0.000	0	2.123	11
Benzene	7.16	89		1413	
Adsorbed			0		82

The final result is obtained after averaging the numbers of 4 separate experiments:

Table S2: Average of the results obtained after analysis of 4 individual samples to study reaction C in presence of 6.50 mg PGC.

	Sample 1	Sample 2	Sample 3	Sample 4	Average
% **1** adsorbed	83 %	83 %	77 %	73 %	78 % ± 5
1 in solution	1 %	0 %	0 %	1 %	1 % ± 1
4 in solution	5 %	5 %	8 %	9 %	7 % ± 2
5 in solution	1 %	1 %	0 %	1 %	1 % ± 1
6 in solution	11 %	11 %	15 %	16 %	13 % ± 3
7 in solution	0 %	0 %	0 %	0 %	0 % ± 0
% **2** adsorbed	13 %	20 %	15 %	23 %	18 % ± 5
% **2** reacted to **4**	3 %	2 %	3 %	5 %	3 % ± 1
% **2** reacted to **6**	10 %	11 %	15 %	15 %	13 % ± 3
% **2** in solution	74 %	66 %	67 %	57 %	66 % ± 7
% **3** adsorbed	97 %	97 %	100 %	98 %	98 % ± 1
% **3** reacted to **5** (in solution)	1 %	1 %	0 %	1 %	1 % ± 1
% **3** in solution	2 %	2 %	0 %	1 %	1 % ± 1

To calculate the distribution of adsorbed products we followed the procedure as described earlier. From the calibration graph for compound **3**, we know that 36% of **3** remains unreacted in the mixture (1% in solution, 35% on PGC).
In this case there also is a small fraction of **2** that has reacted to the mixed-imine **8** and in this way adsorbed on PGC. 18% **2** is adsorbed on PGC (10% unreacted), from which 7.5% in the form of **8**. Due to the stoichiometry of the reaction (amount of anilines is twice the amount of aldehyde), this means 15% of **1** is adsorbed as **8** on PGC, leaving 78 - 15 = 63 % as a mixture of **5** and **7**.

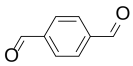
Compound **3** has adsorbed for 98% on PGC. We know that 7.5% is in the form of **8** and 35% is unreacted. This leaves 98 - 35 - 7.5 = 55.5 % as **5** and **7**.
Again, we have to consider the stoichiometry of the reaction:
63% **1** reacts with 31.5 % **3** and yields 63% **5**, leaving 55.5 - 31.5 = 24 % **3** for reaction to **7**.
48% of **5** will react to **7**, leaving 15 % **5** on PGC.

This gives rise to the following product distribution:

Table S3: Product distribution for reaction C in presence of 6.50 mg PGC.

Compound	Fraction (%)
1	1
4	7
5	16
6	13
7	48
8	15

5.2 0.50 mg PGC



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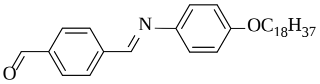

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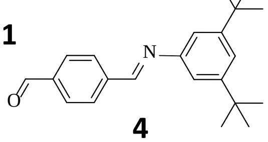

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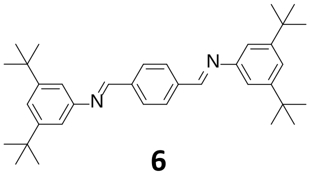

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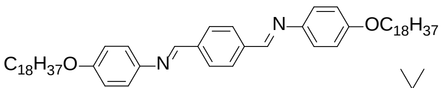

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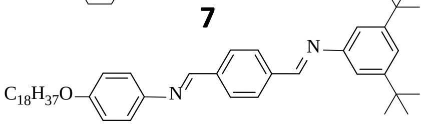

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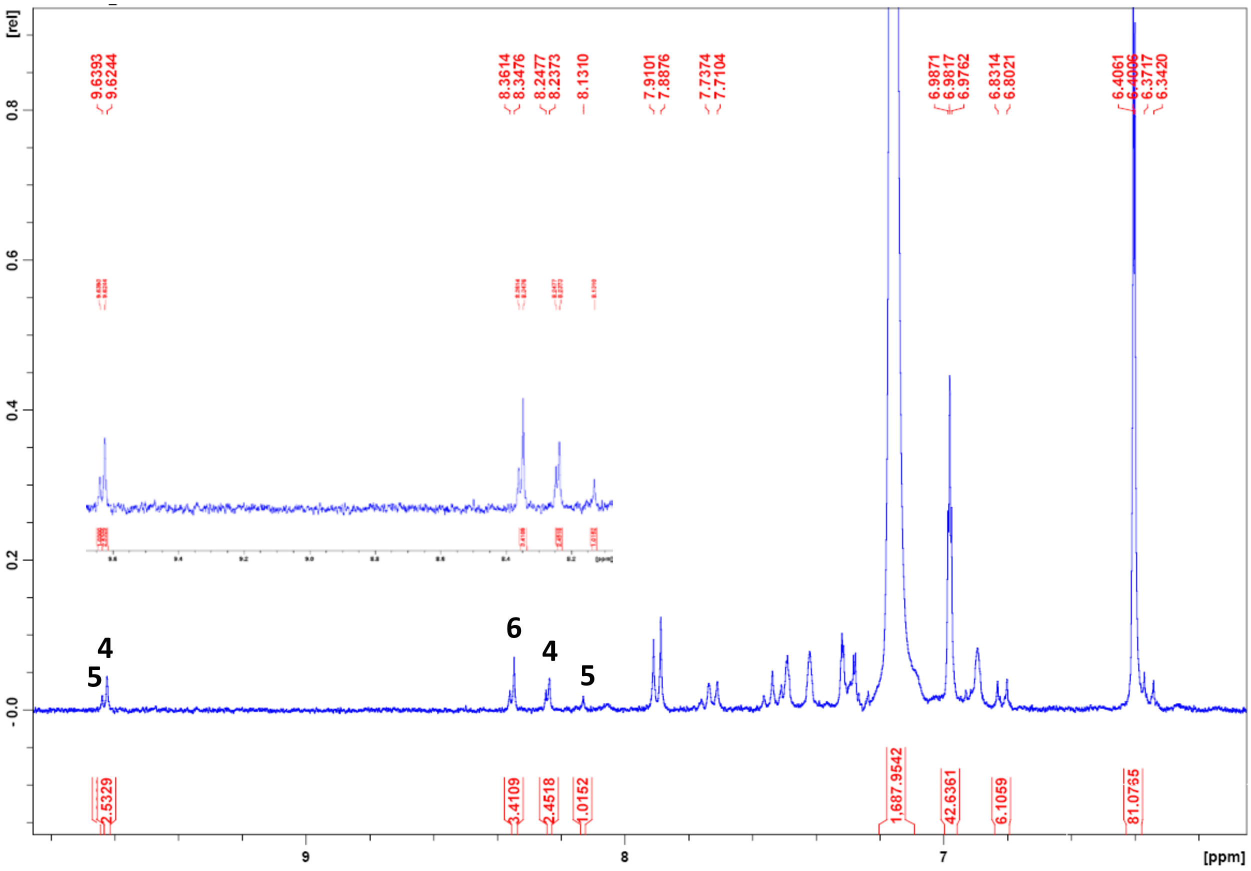


Figure S7: ^{1}H-NMR-spectrum of reaction **C** in presence of 0.50 mg PGC. Characteristic peaks from compounds **4**, **5** and **6** are present in the spectrum. Compound **7** is not observed because of complete adsorption on PGC. δ 9.64 (s, 1H): –CH=O compound **5**; δ 9.62 (s, 1H): –CH=O compound **4**; δ 8.34 (s, 2H): –CH=N– compound **6**; δ 8.23 (s, 1H): –CH=N– compound **4**; δ 8.13 (s, 1H), –CH=N– compound **5**.

Table S4: Summary of the results obtained after analysis of the NMR-spectrum (figure S7) for reaction C in presence of 0.50 mg PGC.

		Without PGC		With PGC	
Compound	Peak position	Peak intensity (converted to mole)	Fraction (%)	Peak intensity (converted to mole)	Fraction (%)
5	9.64	0.000	0	1.000	4
4	9.62	0.000	0	2.533	11
1	9.46	1.000	100	0.000	0
6	8.34	0.000	0	1.706	8
Benzene	7.16	75		1688	
Adsorbed			0		77

To calculate the distribution of adsorbed products we followed the procedure as described earlier. From the calibration graph for compound **3**, we know that 45% of **3** remains unreacted in the mixture (7% in solution, 38% on PGC).
In this case there is no aniline **2** that has adsorbed on the PGC surface. Since it can only adsorb in the form of mixed-imine **8**, we can conclude that mixed-imine **8** had not been formed.

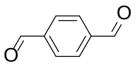
55 % of compound **3** has thus reacted with **1** to a mixture of **5** and **7**. 77 % of **1** is adsorbed on PGC in the form of **5** and **7**.
Again, we have to consider the stoichiometry of the reaction:
77% **1** reacts with 38.5 % **3** and yields 77% **5**, leaving 55 - 38.5 = 16.5 % **3** for reaction to **7**.
33 % of **5** will react to **7**, leaving 44 % **5** adsorbed on PGC.

If we combine these numbers we get the following product distribution:

Table S5: Product distribution for reaction C in presence of 0.50 mg PGC.

Compound	Fraction (%)
1	0
4	11
5	48
6	8
7	33
8	0

5.3 0.25 mg PGC



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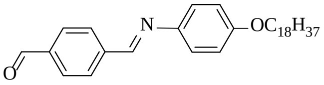

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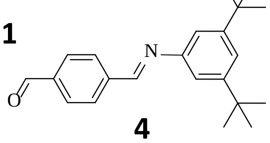

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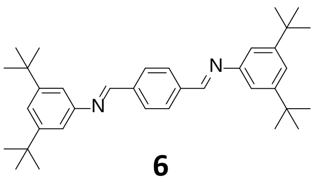

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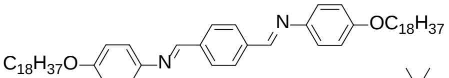

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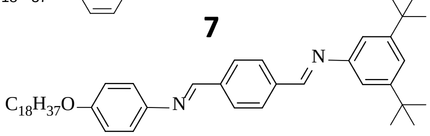

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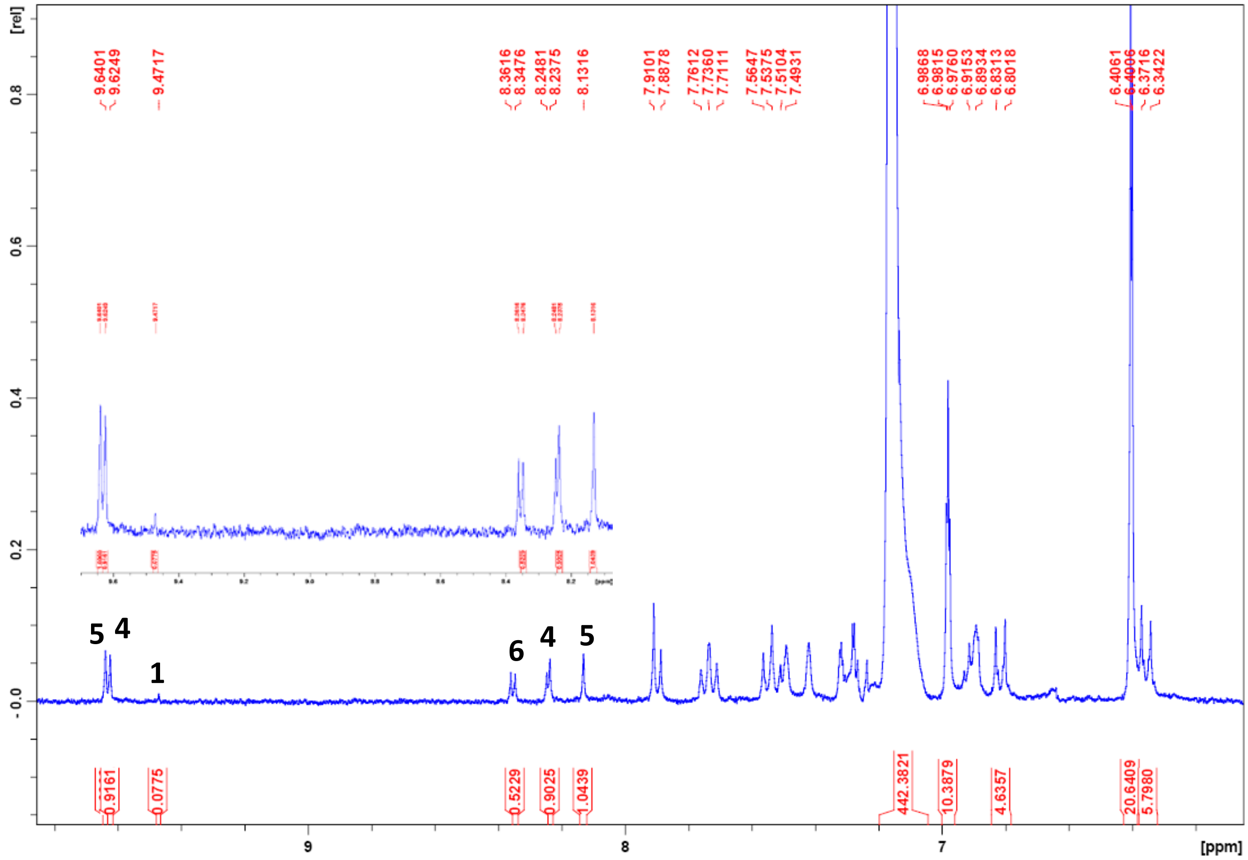


Figure S8: ^{1}H-NMR-spectrum of reaction **C** in presence of 0.25 mg PGC. Characteristic peaks from compounds **1**, **4**, **5** and **6** are present in the spectrum. Compound **7** is not formed in this case. δ 9.64 (s, 1H): –CH=O compound **5**; δ 9.62 (s, 1H): –CH=O compound **4**; δ 9.46 (s, 2H): –CH=O compound **1**; δ 8.34 (s, 2H): –CH=N– compound **6**; δ 8.23 (s, 1H): –CH=N– compound **4**; δ 8.13 (s, 1H), –CH=N– compound **5**.

Table S6: Summary of the results obtained after analysis of the NMR-spectrum (figure S8) for reaction C in presence of 0.25 mg PGC.

		Without PGC		With PGC	
Compound	Peak position	Peak intensity (converted to mole)	Fraction (%)	Peak intensity (converted to mole)	Fraction (%)
5	9.64	0.000	0	1.000	17
4	9.62	0.000	0	0.916	15
1	9.46	1.000	100	0.0388	1
6	8.34	0.000	0	0.262	5
Benzene	7.16	75		442	
Adsorbed			0		62

To calculate the distribution of adsorbed products we followed the procedure as described earlier. From the calibration graph for compound **3**, we know that 63% of **3** remains unreacted in the mixture (19% in solution, 44% on PGC).
In this case there is no aniline **2** that has adsorbed on the PGC surface. Since it can only adsorb in the form of mixed-imine **8**, we can conclude that mixed-imine **8** had not been formed.

37 % of compound **3** has thus reacted with **1** to a mixture of **5** and **7**. There already is 17 % of **5** visible in solution that contains 8 % of the reacted amount of **3**, leaving 29 % of **3** for reaction with the adsorbed fraction of **1** (62 %)
Again, we have to consider the stoichiometry of the reaction:
29 % **3** reacts with 58 % of **1** to form mono-imine **5**. This means that there is a small error on these calculations (the number is wrong by 4%), but this falls within the error bars that we considered. So we can say that there is 62% of **5** adsorbed on PGC, and no bis-imine **7** is formed.

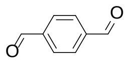
If we combine these numbers we get the following product distribution:

Table S7: Product distribution for reaction C in presence of 0.25 mg PGC.

Compound	Fraction (%)
1	1
4	15
5	79
6	5
7	0
8	0

6. Detailed analysis of two-component reactions A and B

6.1 Reaction **A**



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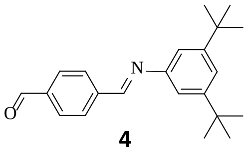

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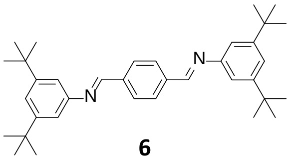

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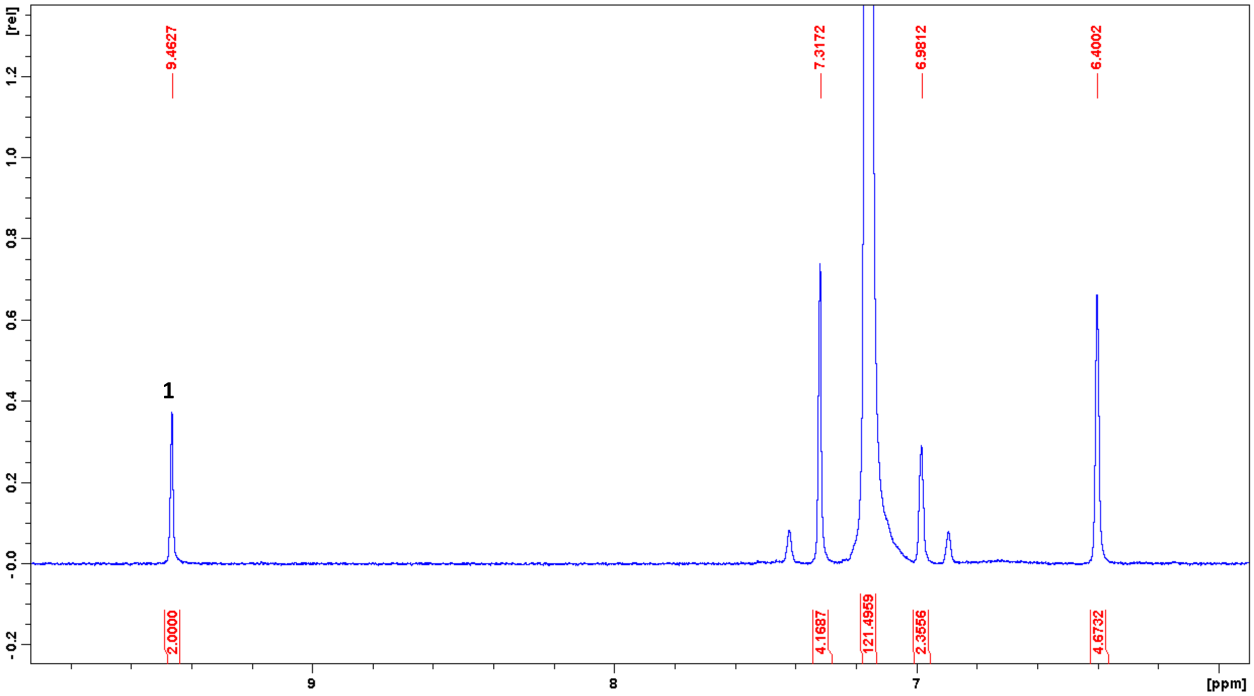
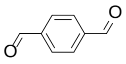
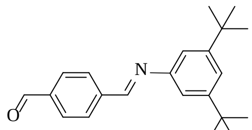


Figure S9a: ^{1}H-NMR-spectrum of reaction **A** in absence of PGC. Only the characteristic –CH=O proton that can be assigned to compound **1** is visible (δ = 9.46). There is nog sign of product **4** and **6**.



1



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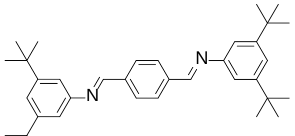

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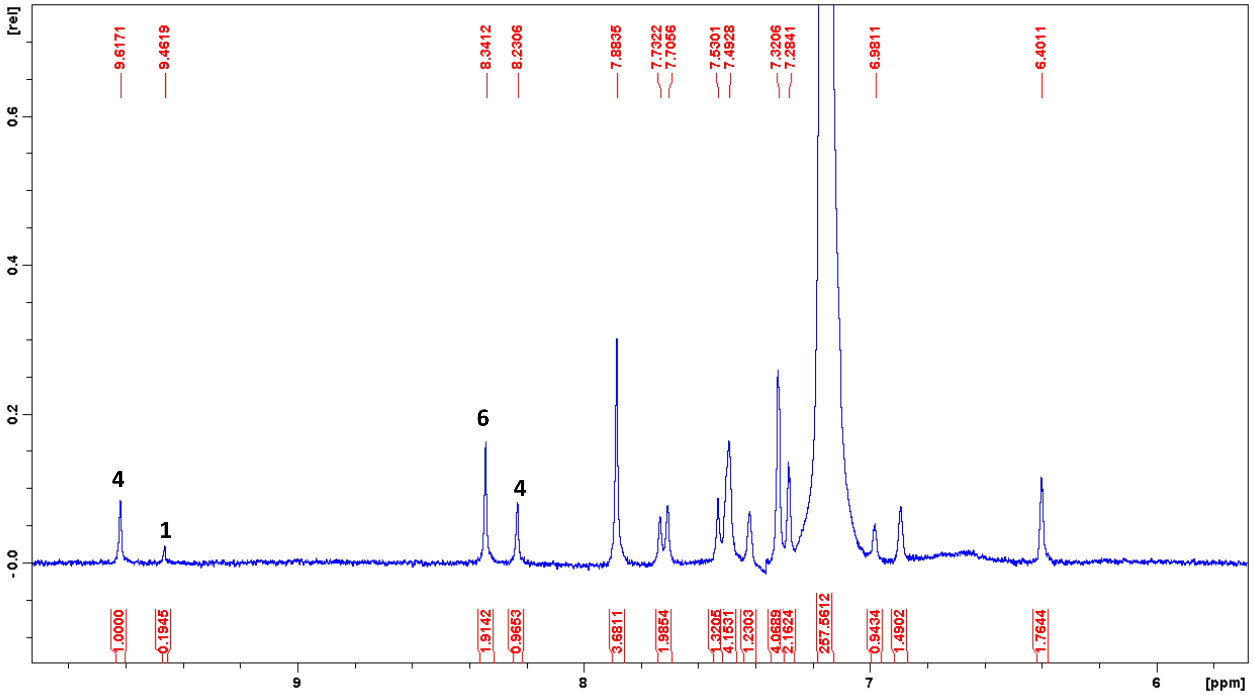


Figure S9b: ^{1}H-NMR-spectrum of reaction **A** in presence of PGC. Characteristic peaks from all three compounds of interest are present. δ 9.62 (s, 1H): –CH=O compound **4**; δ 9.46 (s, 2H): –CH=O compound **1**; δ 8.34 (s, 2H): –CH=N– compound **6**.

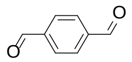
Table S8: summary of the results obtained upon analysis of the NMR-spectra for reaction A.

Compound	Peak position	Without PGC		With PGC	
		Peak intensity (converted to mole)	Fraction (%)	Peak intensity (converted to mole)	Fraction (%)
4	9.62	0.000	0	1.000	49
1	9.46	1.000	100	0.097	5
6	8.34	0.000	0	0.957	47
2					29

The fraction of unreacted **2** is calculated from the fractions of products by taking into account the stoichiometry of the reaction. 47% **6** contains 47% **2**, 49% **4** will only contain 24.5% **2**. This leads to 100 - 47 - 24.5 = 28.5 % **2**.

The final results are obtained by averaging these numbers over two separate sets of experiments.

6.2 Reaction **B**



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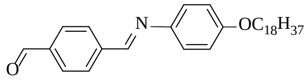

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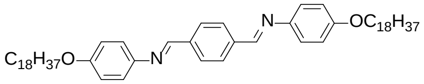

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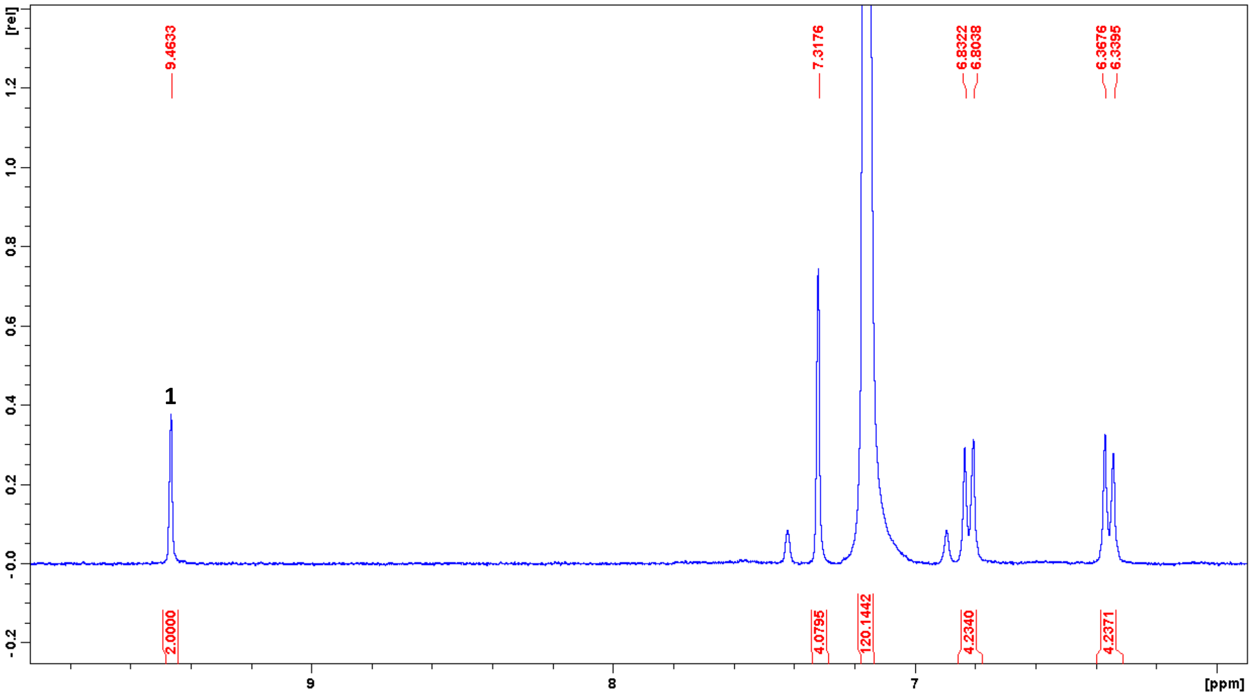

Figure S10a: ^{1}H-NMR-spectrum of reaction **B** in absence of PGC. Only the characteristic –CH=O proton that can be assigned to compound **1** is visible (δ = 9.46). There is nog sign of product **5** and **7**.

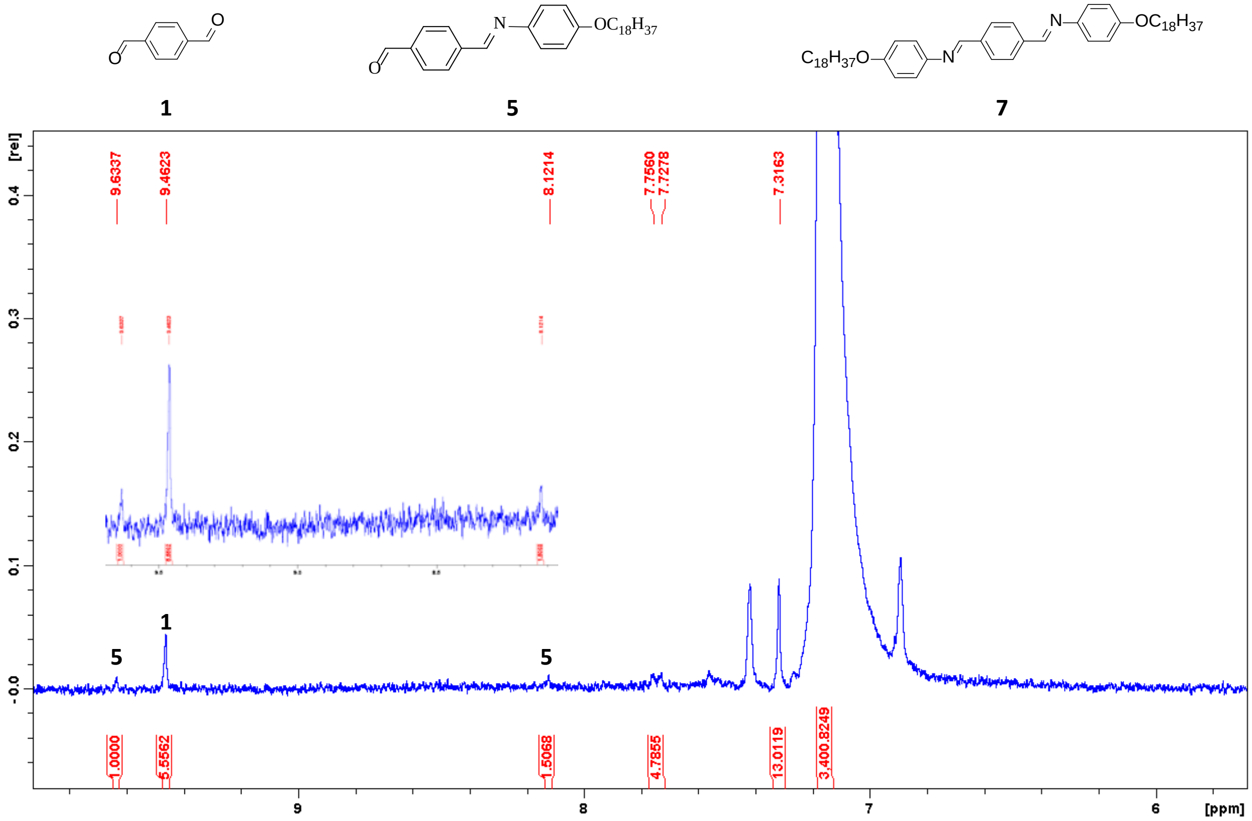

Figure S10b: ^{1}H-NMR-spectrum of reaction **B** in presence of PGC. Characteristic peaks from compounds **1** and **5** are present in the spectrum. Compound **7** cannot be identified in the spectrum due to complete adsorption of on the PGC surface. δ 9.63 (s, 1H): –CH=O compound **5**; δ 9.46 (s, 2H): –CH=O compound **1**.

Table S9: summary of the results obtained upon analysis of the NMR-spectra for reaction B.

Compound	Peak position	Without PGC		With PGC	
		Peak intensity (converted to mole)	Fraction (%)	Peak intensity (converted to mole)	Fraction (%)
5	9.64	0.000	0	1.000	26
1	9.46	1.000	100	2.778	74
7		0.000	0	0.000	0
3					
Benzene	7.16	120		2966	

We now know what the ratio of compounds in solution is, however, a large fraction of products has been adsorbed on PGC. We can calculate this amount by comparing the ratios of products to the benzene peaks. Without PGC this ratio is 0.00833, with PGC this is 0.00127. This means that 85% of the original amount of compound **1** has been adsorbed on PGC as **5** and **7**. We now have to make an estimation of the distribution between product **5** and **7** on PGC. From the calibration graph for compound **3** (figure S8) we know that there cannot be more than 34% of the loaded amount of **3** present in the reacted mixture, otherwise it would be visible in the NMR-spectrum. Therefore, at least 66% will have reacted with 85% **1** to form **5** and **7**.

85 % **1** can react with 42.5 % **3** to **5**. This leaves 23.5 % **3** that can react with 47 % **5** to form **7**. In this way the product distribution on PGC is 47 % **7** and 38 % **5**. These results are only valid under the assumption that 34% **3** remains unreacted on the surface. We cannot be completely sure about this value since it can still react with **5** to form more **7**. However, in reaction **C**, we only see 1 % **5** in solution (with 17% being adsorbed on PGC). If the amount of **5** adsorbed on PGC in reaction **B** would decrease, we would have to see a decrease in the solution as well. Therefore we can assume that it will probably will not be less than 33 % (bottom-limit). The amount of **5** cannot be more than 43 % because in this case there should be more free aniline which we would observe in the solution. This leads to an uncertainty of ± 5 % on the amounts of **5** and **7**. The final product distribution is given in table S3 below:

Table S10: Product distribution of reaction mixture B after addition of PGC.

Compound	Fraction (%)
5	42 ± 5
1	11 ± 5
7	47 ± 5
3	34 ± 5

Table S11: Compound distribution (% in solution *and* adsorbed on PGC) in a mixture of reaction A (left) and reaction B (right), in presence of PGC, 1 h after mixing the reagents.

Compound	**A**	**B**
1	7 ± 2	9 ± 5
Mono-imine	mono-imine **4** 51 ± 4	mono-imine **5** 45 ± 5
Bis-imine	bis-imine **6** 42 ± 6	bis-imine **7** 46 ± 5
Fraction of 1 adsorbed on PGC as reaction products	n/a	87 ± 5

7. Dynamics of 4-octadecyloxyaniline 3 domains changing into domains of mono-imine/mono-aldehyde 5

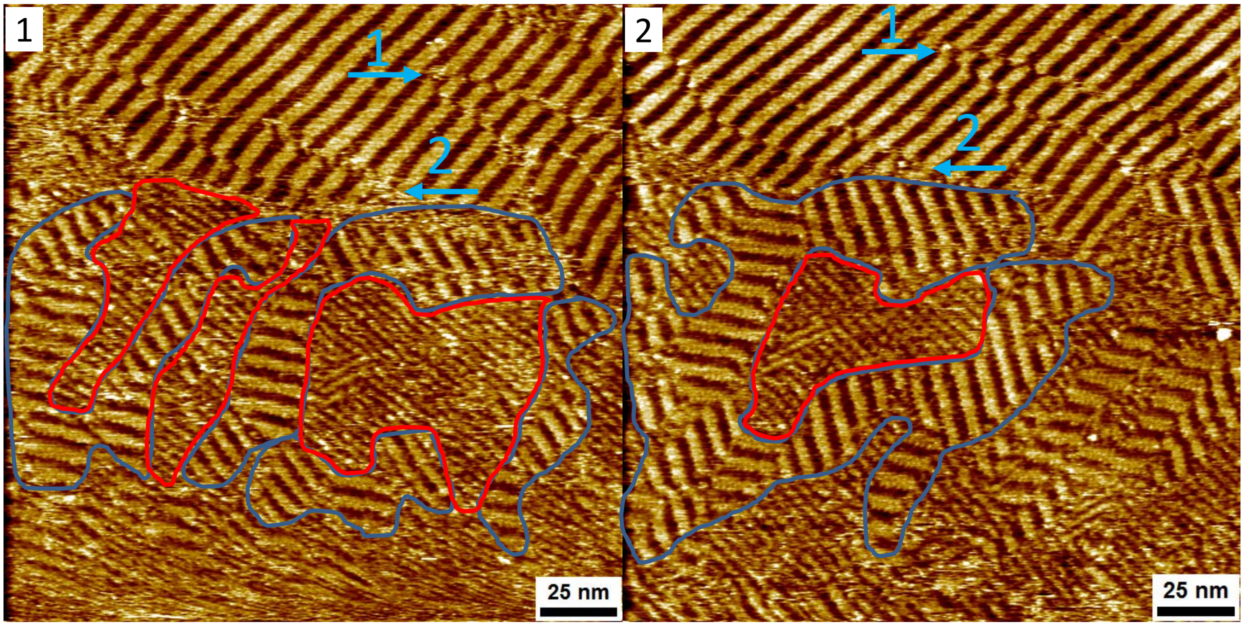

Figure S11: Image 1 and 2 are consecutive STM images of the same area on the HOPG surface. The blue arrows 1 and 2 are reference points indicating that it is the same area. Domains formed by compound **5** are circled with blue lines, the ones formed by compound **3** are circled with red lines. We can see that most of the red circled area in image 1 has been consumed by compound **5** (circled in blue) in the 2nd image, indicating dynamic exchange at the liquid/solid interface.

8. Preferential adsorption between compound 5 and 7

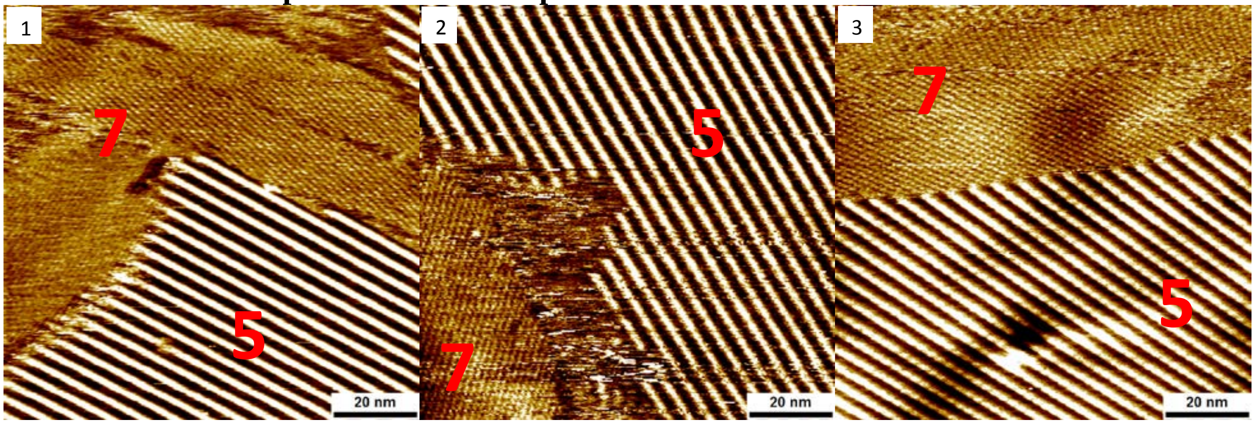

Figure S12: Preferential adsorption studies for different ratios of compound **5** and **7** from phenyloctane solutions. Image 1 shows 1:1 ratio (c = 2.01*10^{-5} M for both). Image 2 shows 2:1 ratio of **5**:**7** (c_7 = 2.94*10^{-5} M). Image 3 shows 2:1 ratio of **7**:**5** (c_5 = 0.76*10^{-5} M).

Table S12: Surface composition when mixtures of compound 5 and 7 are mixed in different ratios en dropcasted on a HOPG surface. The results are calculated based on analysis of 18 images of 100x100 nm² for each different ratio.

	% **5** on surface	% **7** on surface
1:1 ratio **5**:**7**	66	34
2:1 ratio **5**:**7**	67	33
1:2 ratio **5**:**7**	49	51

From table S1, we can see that for a 1:1 ratio of **5** and **7**, compound **5** preferentially adsorbs on HOPG. Since the surface composition does not really change when we investigate the 2:1 ratios of **5**:**7**, in seems to be that there is a saturation in the surface composition. When the ratio is changed to 2:1 in favor of compound **7**, the surface composition reaches about 50% for each compound.

These results are evidence that compound **5** preferentially adsorbs compared to compound **7**.

9. Control experiments to check acidity of PGC

Table S13: Product distribution when different amounts of acetic acid are added to a mixture of 1, 2 and 3 which is subsequently heated to 60°C and stirred for 1 h.

	Bis-aldehyde **1**	Mono-imine **4 + 5**
10 % acid	90 %	10 %
25 % acid	82 %	18 %
50 % acid	69 %	31 %

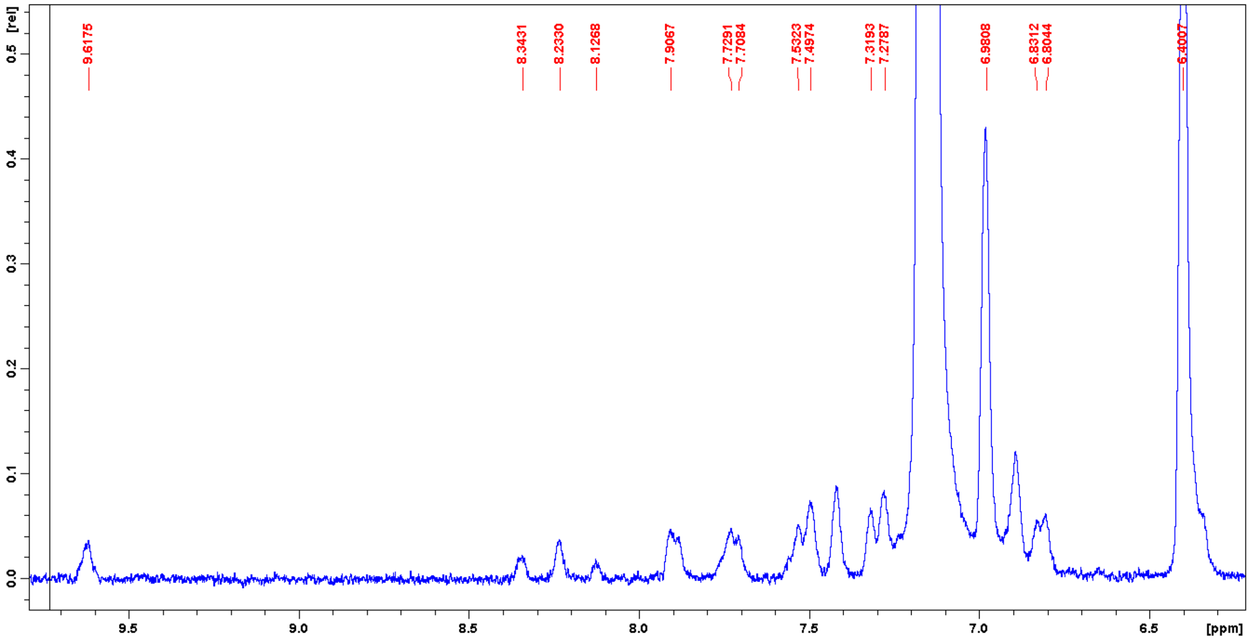

Figure S13: ^{1}H-NMR spectrum using basified PGC. Only signature peaks of compound **4** (δ 8.23), **5** (δ 8.13) and **6** (δ 8.34) can be identified. Compound **1** has been completely converted in a mixture of products, indicating that the catalytic activity remains unchanged.

10. Use of amorphous carbon and silica as high area substrates

Table S14: Comparison of PGC, amorphous carbon and silica in reaction A and B.

Reaction **A**	PGC	Amorphous carbon	SiO_2
Bis-aldehyde **1**	7 %	9 %	10 %
Mono-imine **4**	52 %	69 %	55 %
Bis-imine **6**	43 %	22 %	35 %
Reaction **B**	PGC	Amorphous carbon	SiO_2
% aldehyde adsorbed	87 %	76 %	55 %
Bis-aldehyde **1** in solution	9 %	9 %	13 %
Mono-imine **5** in solution	4 %	15 %	32 %

For all 3 substrates, the amount of compound **1** in solution is about constant, indicating that the catalytic effect is comparable. There are some differences however in product distribution and adsorption behavior of these products that can be ascribed to the different nature of the substrates.

Table S15: Comparison of PGC, amorphous carbon and silica in reaction C. The percentages in the table are relative compared to the loaded amount of compound 1.

	PGC	Amorphous carbon	SiO_2
Bis-aldehyde **1**	1 %	1 %	1 %
Mono-imine **4**	7 %	13 %	8 %
Bis-imine **6**	13 %	9 %	15 %
Total **4** + **6**	20 %	22 %	23 %
Mixed imine **8**	15 %	10 %	18 %
Mono-imine **5** (in solution)	1 %	4 %	6 %
Mono-imine **5** (adsorbed)	15 %	/	/
Bis-imine **7** (adsorbed)	48 %	/	/
Total **5** + **7**	64 %	67 %	58 %
Total adsorbed products	78 %	73 %	70 %

The ratio between compound **5** and **7** adsorbed on amorphous carbon and silica was not calculated due to the absence of a calibration graph. This would lead to a very large uncertainty on the estimated values.