

## Electronic Supplementary Information (ESI)

### Self-assembling of amino-terminated monolayers depending of the chemical structure

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## 1- General information for the organic synthesis: chemicals, solvents and methods

Commercially available reagents were used without further purification. Anhydrous DMF, toluene and acetonitrile were purchased from Aldrich (St Quentin-Fallavier, France). Karstedt's catalyst was purchased from Aldrich as a solution in xylene Pt~2% (ref: 479519). Other solvents were dried according to standard procedures over dehydrating agents (CaH<sub>2</sub> for CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and triethylamine; Na/benzophenone for THF) and distilled under an inert atmosphere immediately before use. Trimethoxysilane from Acros was distilled under an inert atmosphere immediately before use. Reactions requiring inert atmosphere were conducted under argon atmosphere. Reactions were monitored by thin-layer chromatography carried out on silica gel aluminium sheets (60F-254) using UV light at 254 nm or were revealed with potassium permanganate stain. Column chromatography was performed on VWR silica gel 60 (40-63 μm).

NMR spectra were recorded at the analysis center CESAMO (Bordeaux University). <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz, 75 MHz and 59 MHz, respectively, or on a Bruker Avance II 400 spectrometer at 400 MHz, 100 MHz and 79 MHz, respectively, or on a Bruker Avance III 600 spectrometer at 600 MHz, 150 MHz and 118 MHz, respectively. Chemical shifts (δ) are given in parts per million with respect to solvent residual peak and coupling constant (*J*) are given in Hertz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddt = doublet of doublet of triplets, br = broad signal and m = multiplet.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 using a KBr disc or pellet. ATR FTIR spectra were recorded on a Thermo-Scientific Nicolet iS10 FT-IR spectrometer.

High-resolution Mass spectra (HRMS) were performed by the CESAMO (Bordeaux, France) on a Qexactive mass spectrometer (Thermo). The instrument is equipped with an ESI source and spectra were recorded in the negative or positive mode. The spray voltage was maintained at 3200 V and capillary temperature set at 320°C. Samples were introduced by injection through a 20 μL sample loop into a 300 μL/min flow of methanol from the LC pump. Field ionization (FI) spectra were performed by the CESAMO (Bordeaux, France). The measurements were carried out on GC column coupled with a TOF mass spectrometer AccuTOF GCv by JEOL using an FI emitter with an emitter voltage of 10 Kv.

## 2- General information for the surface analysis

Contact angle were measured with a drop shape analyzer (DSA-100, Krüss, Germany) by depositing 3  $\mu\text{L}$  of milli-Q water at 20°C. The results correspond to the mean of at least 3 measurements.

AFM height images were recorded on a Bruker's Dimension Icon Atomic Force Microscope (AFM) System in PeakForce QNM® mode (Quantitative Nanomechanical Mapping) with ScanAsyst-Air tips (APEX = 2 nm, spring constant  $k = 0.4 \text{ N/M}$ ). The AFM height images are representative of three different areas.

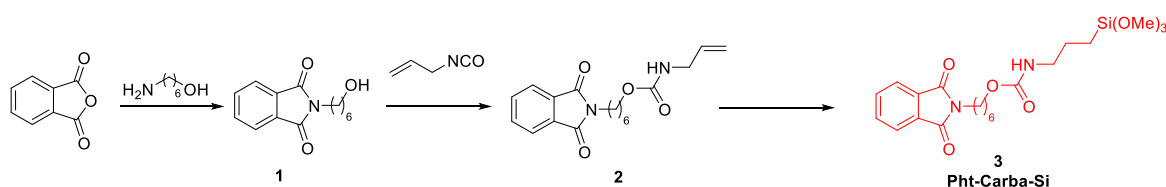
PM-IRRAS experiments were performed on a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a PM-IRRAS optical bench, following the experimental procedure previously published.<sup>1</sup> The PM-IRRAS spectra were recorded at a resolution of  $4 \text{ cm}^{-1}$  during 4 h acquisition time. The PM-IRRAS spectra were calibrated in order to be presented in IRRAS units. All spectra were collected in a dry-air atmosphere after 30 min of incubation in the chamber.

## 3- Synthesis of silylated coupling agents

### 3.1 General procedure for the hydrosilylation reaction

Experiments were carried out using Schlenk techniques under a dry and inert atmosphere of argon. To a solution of the olefin compound (0.05 mmol, 1 eq.) in anhydrous solvent (0.5 mL) were added trimethoxysilane and then Karstedt's catalyst (14  $\mu\text{L}$ , 381.48 g/mol, 0.025 eq. [Pt]). The mixture was stirred for 1 h at 60°C and then cooled to room temperature. The solvent and the excess of trimethoxysilane were removed under reduced pressure.

### 3.2 Synthesis of phthalimide carbamate silylated compound:



#### Synthesis of 2-(6-hydroxyhexyl)isoindoline-1,3-dione (1)

To a solution of phthalic anhydride (2 g, 13.5 mmol) in anhydrous DMF (15 mL) under inert atmosphere was added 6-amino-1-hexanol (1.58 g, 13.5 mmol). The mixture was stirred for 24 h at reflux, then EtOAc (100 mL) and an aqueous solution of HCl 0.1 M (50 mL) were added. The obtained

solution was extracted with EtOAc. The combined organic extracts were washed with brine, dried over MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/EtOAc 50:50). Compound **1** was obtained as a white powder (2.81 g, 84% yield). R<sub>f</sub> (Cyclohexane/EtOAc 50:50): 0.46.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 7.68 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 3.68 - 3.58 (m, 4H, CH<sub>2</sub>N and CH<sub>2</sub>O), 1.71 - 1.50 (m, 4H, 2 CH<sub>2</sub>), 1.40 - 1.20 (m, 4H, 2 CH<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6 (2 CO), 134.0 (2 CH<sub>ar</sub>), 132.2 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 62.7 (CH<sub>2</sub>OH), 37.9 (CH<sub>2</sub>N), 32.6 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 25.3 (CH<sub>2</sub>). **HRMS** (ESI): calculated for C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub>Na<sup>+</sup> ([M+Na]<sup>+</sup>): 270.1100, found 270.1110. **IR** (KBr): 3453, 2933, 2859, 1771, 1711, 1614, 1466, 1436, 1397, 1370, 1056, 720.

#### Synthesis of 6-(1,3-dioxoisindolin-2-yl)hexyl *N*-allylcarbamate (**2**)

To a solution of compound **1** (2.54 g, 10.2 mmol) in anhydrous DMF (100 mL) under inert atmosphere was added allyl isocyanate (1.1 mL, 12.7 mmol) followed by Et<sub>3</sub>N (5.7 mL, 40.8 mmol). The mixture was stirred for 26 h at 80°C and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/EtOAc 7:3 to 6:4). Compound **2** was obtained as a white powder (2.48 g, 76% yield). R<sub>f</sub> (Cyclohexane/EtOAc 50:50): 0.69.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.84 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 5.84 (ddt, *J* = 17.1, 10.6, 5.5 Hz, 1H, =CH), 5.22 - 5.10 (m, 2H, =CH<sub>2</sub>), 4.77 (br, 1H, NH), 4.05 (t, *J* = 6.5 Hz, 2H, CH<sub>2</sub>O), 3.87 - 3.73 (m, 2H, CH<sub>2</sub>NH), 3.68 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>N), 1.73 - 1.60 (m, 4H, 2 CH<sub>2</sub>), 1.40 - 1.37 (m, 4H, 2 CH<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6 (2 CO), 156.7 (CO<sub>carba</sub>), 134.8 (=CH), 134.0 (2 CH<sub>ar</sub>), 132.3 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 116.0 (=CH<sub>2</sub>), 65.0 (CH<sub>2</sub>O), 43.5 (CH<sub>2</sub>NH), 38.0 (CH<sub>2</sub>N), 28.9 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>). **HRMS** (ESI): calculated for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> ([M+Na]<sup>+</sup>): 353.1471, found 353.1475. **IR** (KBr): 2956, 2929, 2858, 1771, 1731, 1690, 1537, 1461, 1396, 1174, 720.

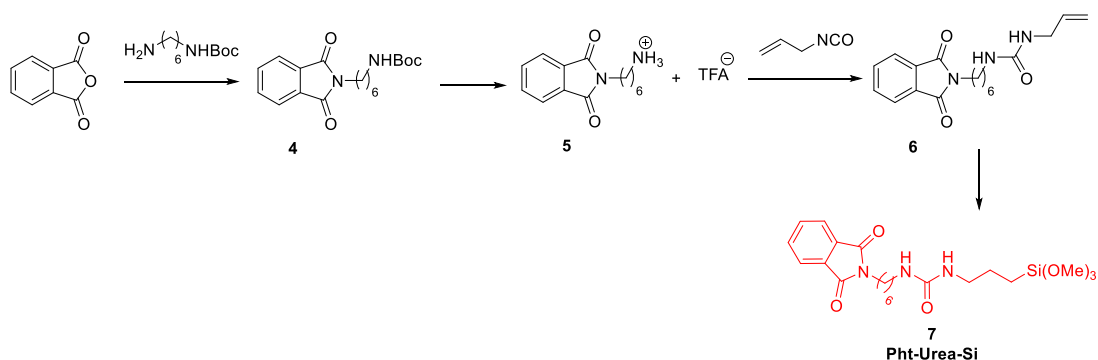
#### Synthesis of 6-(1,3-dioxoisindolin-2-yl)hexyl *N*-(3-trimethoxysilyl)propyl)carbamate (**3**)

See general procedure with trimethoxysilane as solvent.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 4.87 (br, 1H, NH), 4.01 (t, *J* = 6.5 Hz, 2H, CH<sub>2</sub>O), 3.66 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>N), 3.55 (s, 9H, 3 CH<sub>3</sub>OSi), 3.14 (q, *J* = 7.0 Hz, 2H, CH<sub>2</sub>NH), 1.69 - 1.30 (m, 10H, 5 CH<sub>2</sub>), 0.66 - 0.60 (m, 2H, CH<sub>2</sub>Si). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6 (2 CO), 156.9 (OCONH), 134.0 (2 CH<sub>ar</sub>), 132.3 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 64.8 (CH<sub>2</sub>OCONH), 50.7 (3 OCH<sub>3</sub>), 43.5 (CH<sub>2</sub>NH), 38.0 (CH<sub>2</sub>N), 29.0 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>),

25.7 (CH<sub>2</sub>) 23.3 (CH<sub>2</sub>), 6.5 (CH<sub>2</sub>Si). <sup>29</sup>Si NMR (118 MHz, CDCl<sub>3</sub>) δ (ppm): -42.3. HRMS (ESI): calculated for C<sub>21</sub>H<sub>32</sub>O<sub>7</sub>N<sub>2</sub>SiNa<sup>+</sup> ([M+Na]<sup>+</sup>): 475.18710, found 475.18590. IR (ATR): 2938, 2840, 1771, 1714, 1685, 1538, 1395, 1051, 720.

### 3.3 Synthesis of phthalimide urea silylated compound:



#### Synthesis of *tert*-butyl *N*-(6-(1,3-dioxisoindolin-2-yl)hexyl)carbamate (4)

To a solution of phthalic anhydride (1 g, 6.75 mmol) in absolute EtOH (20 mL) under inert atmosphere was added *N*-Boc-1,6-hexanediamine (1.74 g, 8.04 mmol). The mixture was stirred for 20 h at reflux then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (Cyclohexane/EtOAc 50:50). Compound **4** was obtained as a white powder (quantitative yield). R<sub>f</sub>(Cyclohexane/EtOAc 50:50): 0.70.

<sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>) δ (ppm): 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 4.52 (br, 1H, NH), 3.66 (t, 7.3 Hz, 2H, CH<sub>2</sub>N), 3.08 (q, *J* = 6.6 Hz, 2H, CH<sub>2</sub>NHBoc), 1.69 - 1.64 (m, 2H, CH<sub>2</sub>), 1.48 - 1.33 (m, 15H, *t*-Bu and 3 CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6 (2 CO), 156.1 (CO<sub>Boc</sub>), 134.0 (2 CH<sub>ar</sub>), 132.3 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 79.1 (C<sub>quat</sub>), 40.6 (CH<sub>2</sub>NH), 38.0 (CH<sub>2</sub>N), 30.0 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 28.5 (3 CH<sub>3</sub>), 26.6 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>). HRMS (ESI) calculated for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> ([M+Na]<sup>+</sup>): 369.1784, found 369.1789. IR (KBr): 3382, 2973, 2933, 2860, 1772, 1711, 1518, 1396, 1366, 1172, 1058, 720.

#### Synthesis of 6-(1,3-dioxisoindolin-2-yl)hexan-1-ammonium (5)

To a solution of compound **5** (920 mg, 2.29 mmol) in anhydrous DCM (60 mL) under inert atmosphere was added dropwise TFA (2.6 mL, 34.3 mmol). The mixture was stirred for 1 h at room temperature and then concentrated under reduced pressure. TFA traces were removed by co-evaporation under reduced pressure with toluene to give an orange solid as a salt (quantitative yield).

**<sup>1</sup>H NMR** (300 MHz, CD<sub>3</sub>OD) δ (ppm): 7.76 - 7.70 (m, 4H, 4 CH<sub>ar</sub>), 3.60 (t, *J* = 7.1 Hz, 2H, CH<sub>2</sub>N), 2.89 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), 1.68 - 1.61 (m, 4H, 2 CH<sub>2</sub>), 1.40 - 1.33 (m, 4H, 2 CH<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, MeOD) δ (ppm): 169.8 (2 CO), 135.3 (2 CH<sub>ar</sub>), 133.2 (2 C<sub>ar</sub>), 124.0 (2 CH<sub>ar</sub>), 40.5 (CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>), 38.5 (CH<sub>2</sub>N), 29.2 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 27.2 (CH<sub>2</sub>), 26.8 (CH<sub>2</sub>). **HRMS** (ESI) calculated for C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> (M<sup>+</sup>): 247.1441, found 247.1442. **IR** (ATR): 3170, 3062, 2908, 2850, 1778, 1689, 1403, 1174, 1123, 1057, 948, 712.

#### Synthesis of 1-allyl-3-(6-(1,3-dioxoisindolin-2-yl)hexyl)urea (6)

To a solution of compound **5** (757 mg, 2.1 mmol) in anhydrous DMF (40 mL) under inert atmosphere was added Et<sub>3</sub>N (440 μL, 3.15 mmol). After 30 min under stirring at room temperature, allyl isocyanate (240 μL, 2.73 mmol) was added and the mixture was stirred for 20 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (DCM/MeOH 95:5). Compound **6** was obtained as a white powder (488 mg, 71% yield). R<sub>f</sub> (EtOAc 100%): 0.55.

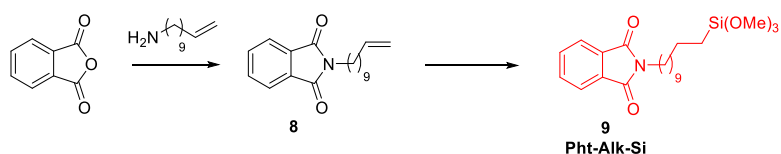
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H, 2 CH<sub>ar</sub>), 5.86 (ddt, *J* = 17.1, 10.6, 5.5 Hz, 1H, =CH), 5.23 - 5.09 (m, 2H, =CH<sub>2</sub>), 4.50 (br, 2H, 2 NH), 3.82 - 3.79 (m, 2H, CH<sub>2</sub>NH), 3.68 (t, *J* = 7.1 Hz, 2H, CH<sub>2</sub>N), 3.16 (q, *J* = 6.3 Hz, 2H, CH<sub>2</sub>NH), 1.73 - 1.63 (m, 2H, CH<sub>2</sub>), 1.49 - 1.25 (m, 6H, 3 CH<sub>2</sub>). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ (ppm): 168.7 (2 CO), 158.4 (CO<sub>urea</sub>), 135.7 (=CH), 134.1 (2 CH<sub>ar</sub>), 132.2 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 115.7 (=CH<sub>2</sub>), 43.2 (CH<sub>2</sub>NH), 40.3 (CH<sub>2</sub>NH), 37.8 (CH<sub>2</sub>N), 30.0 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.2 (CH<sub>2</sub>). **HRMS** (ESI) calculated for C<sub>18</sub>H<sub>23</sub>O<sub>3</sub>N<sub>3</sub>Na<sup>+</sup> ([M+Na]<sup>+</sup>): 352.16316, found 352.16239. **IR** (KBr): 3324, 2932, 2858, 1771, 1718, 1621, 1581, 1464, 1396, 1051, 720.

#### Synthesis of 1-(6-(1,3-dioxoisindolin-2-yl)hexyl)-3-(3-trimethoxysilyl)propyl)urea (7)

See general procedure with CHCl<sub>3</sub> as solvent and 34 μL of trimethoxysilane (0.25 mmol, 5 eq).

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.82 (dd, *J* = 5.6, 3.0 Hz, 2H, 2 CH<sub>ar</sub>), 7.70 (dd, *J* = 5.6, 3.0 Hz, 2H, 2 CH<sub>ar</sub>), 4.63 - 4.51 (m, 2H, 2 NH), 3.66 (t, *J* = 7.1 Hz, 2H, CH<sub>2</sub>N), 3.54 (s, 9H, 3 CH<sub>3</sub>OSi), 3.18 - 3.10 (m, 4H, 2 CH<sub>2</sub>NH), 1.69 - 1.34 (m, 10H, 5 CH<sub>2</sub>), 0.67 - 0.61 (m, 2H, CH<sub>2</sub>Si). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ (ppm): 168.6 (2 CO), 158.5 (CO<sub>urea</sub>), 134.0 (2 CH<sub>ar</sub>), 132.2 (2 C<sub>ar</sub>), 123.3 (2 CH<sub>ar</sub>), 50.7 (3 OCH<sub>3</sub>Si), 43.0 (CH<sub>2</sub>NH), 40.4 (CH<sub>2</sub>NH), 37.8 (CH<sub>2</sub>N), 30.0 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 6.4 (CH<sub>2</sub>Si). **<sup>29</sup>Si NMR** (79 MHz, CDCl<sub>3</sub>): δ (ppm): -42.0. **HRMS** (ESI): calculated for C<sub>21</sub>H<sub>33</sub>O<sub>6</sub>N<sub>3</sub>SiNa<sup>+</sup> ([M+Na]<sup>+</sup>): 474.20308, found 474.20190. **IR** (ATR): 2931, 2861, 1771, 1710, 1622, 1568, 1558, 1466, 1396, 1016, 785, 720.

### 3.4 Synthesis of phthalimide alkyl silylated compound:

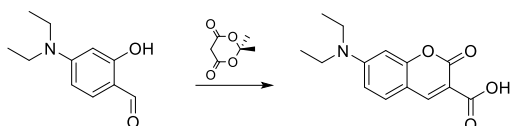


The synthesis of compound **9** was already described in the following publication:

L. Rouvière, N. Al-Hajj, J. Hunel, C. Aupetit, T. Buffeteau, L. Vellutini and E. Genin, *Langmuir*, 2022, **38**, 6464–6471.

## 4- Synthesis of fluorophore tag:

### Diethylaminocoumarin-3-carboxylic acid



In a round-bottomed flask, the 4-(diethylamino)-2-hydroxybenzaldehyde (3,865 g; 20 mmol) was dissolved in a mixture of water (15 mL) and acetone (15 mL). Meldrum's acid (1,2 eq; 3,46 g; 24 mmol) was then added. The reaction mixture was stirred and heated at 60°C for 10 h. After cooling in an ice bath for 30 min, the product was collected by filtration and washed with water (30 mL) to give reddish-orange crystals (4.75 g, 91% yield). R<sub>f</sub> (Pentane/EtOAc 10:90): 0.86.

<sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.64 (s, 1H, CH<sub>ar</sub>-4), 7.45 (d, J = 9.1 Hz, 1H, CH<sub>ar</sub>-5), 6.71 (dd, J = 9.1, 2.4 Hz, 1H, CH<sub>ar</sub>-6), 6.53 (d, J = 2.4 Hz, 1H, CH<sub>ar</sub>-8), 3.49 (q, J = 7.2 Hz, 4H, CH<sub>2</sub>), 1.26 (t, J = 7.2 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C RMN (76 MHz, CDCl<sub>3</sub>) δ (ppm): 166.08 (COOH), 165.00 (C=O), 158.60 (C-9), 154.29 (C-7), 150.83 (C-4), 132.51 (C-5), 111.49 (C-6), 109.15 (C-10), 106.19 (C-3), 97.44 (C-8), 45.93 (CH<sub>2</sub>), 12.95 (CH<sub>3</sub>).

## 5- Chemical surface modification

Substrates: SiO<sub>2</sub>/Au substrates (5 cm x 5 cm) were supplied by Optics Balzers AG. They correspond to Goldflex mirror with a SiO<sub>2</sub> protection layer (GoldflexPRO, reference 200785) and with an rms roughness of 0.9 nm. The thickness of SiO<sub>2</sub> layer, measured by ellipsometry, was 215 ± 7 Å, using a

refractive index of 1.46 (I-elli2000 NFT ellipsometer,  $\lambda=532$  nm). They were cut in squares of 2.5 cm x 2.5 cm. Wafer 1 cm x 1 cm (supplied by BT Electronics) were used as received.

Substrate cleaning procedure: Before the grafting, the substrates were intensively washed with Milli-Q water (18 M $\Omega$  cm), sonicated 15 min in chloroform then they were exposed to UV– ozone (185 – 254 nm) for 30 min and used immediately after this treatment.

Surface modification by immersion: Double shell reactor of 250 mL was used to graft under inert atmosphere and to control the temperature of the grafting bath. All glassware were washed with KOH bath during few hours then, washed with water and acetone and dried in an oven (85°C) for at least 16 h to remove water traces.

After activation, the substrate was introduced in the reactor and kept under vacuum for 1 h. The reactor was thermostated at 20°C and argon was introduced. 100 mL of anhydrous solvent was added inside the reactor, followed by the organosilane (0.05 mmol) diluted in 50 mL of solvent and TCA (0.0055 mmol) diluted in 50 mL of solvent. After 12 h to 16 h, the substrate sample was removed, sonicated in CHCl<sub>3</sub> (2 x 5 min), milli-Q H<sub>2</sub>O (2 x 5 min) and CHCl<sub>3</sub> (2 x 5 min) and finely dried under nitrogen flow.

Surface modification by spin coating: Freshly prepared azido-silylated coupling agent (0.05 mmol) was solubilized in anhydrous CHCl<sub>3</sub> HPLC grade (1.2 mL) under inert atmosphere. The stock solution (100  $\mu$ L) was diluted with CHCl<sub>3</sub> HPLC grade (0.9 mL) under inert atmosphere. 40  $\mu$ L of the freshly diluted solution of organosilane ( $4.10^{-3}$  mol.L<sup>-1</sup>) were spin-coated on the substrate rotated at 6000 rpm under 30 seconds. The sample was let at ambient temperature for the defined time in a laminar flow hood before it was washed to remove the excess of silane. The substrate sample was sonicated in CHCl<sub>3</sub> (2 x 5 min), milli-Q H<sub>2</sub>O (2 x 5 min), CHCl<sub>3</sub> (2 x 5 min), and finally dried under nitrogen flow.

## **6- Protocol for the deprotection of the phthalimide moiety**

The phthalimide SAMs was sonicated in CHCl<sub>3</sub> (2 x 5 min) and in milli-Q H<sub>2</sub>O (5 min). The slide was then introduced into a solution of MeNH<sub>2</sub> 40% in water for 4 min. The sample was sonicated in H<sub>2</sub>O (5 min), DMF/H<sub>2</sub>O (1:1 v/v) (5 min), iPrOH (5 min), CHCl<sub>3</sub> (5 min) and then dried under nitrogen flow.



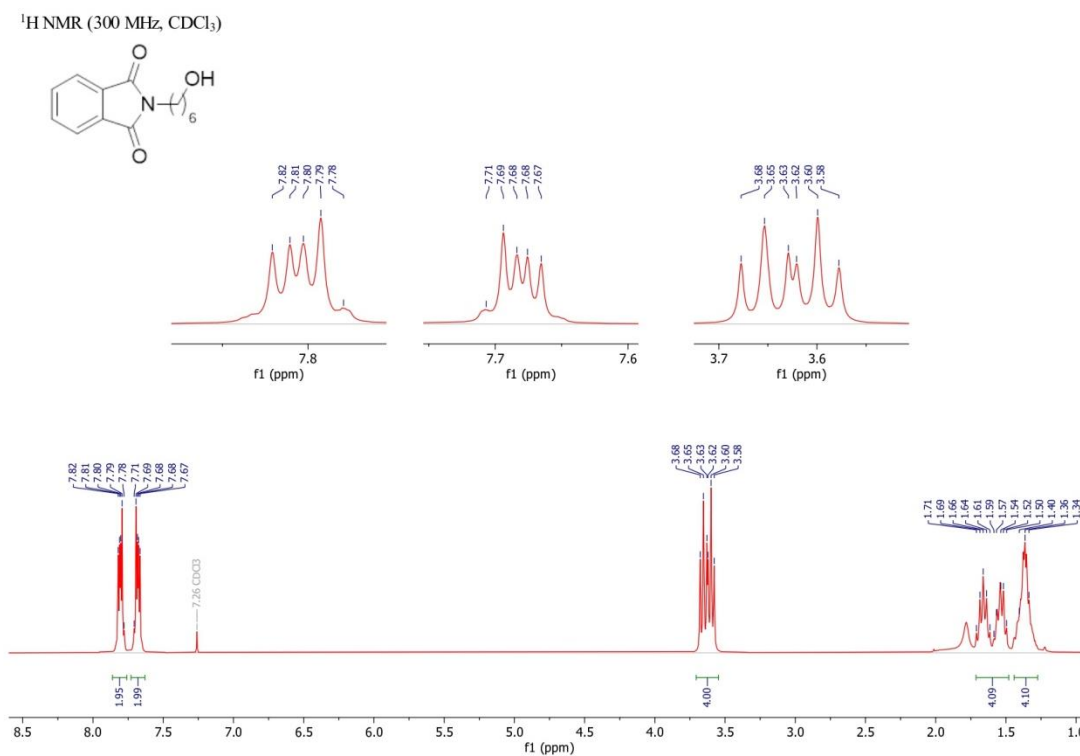
## 7- Protocol for the coumarin immobilisation on SAM-NH<sub>2</sub>

Coumarin derivative (10.5 mg, 0.04 mmol) was diluted in anhydrous DMF (6 mL). NHS (5.1 mg, 0.44 mmol) and EDC (8.4 mg, 0.44 mmol) were introduced. The mixture was stirred for 1 h at room temperature. Freshly prepared SAM-NH<sub>2</sub> was deposited in a steriplan soda-lime petri dish (diameter: 60 mm; height: 15 mm) and covered by the previously prepared activated coumarin derivative solution. Two mL of anhydrous DMF were then added to fully immerse the slide. After 24 h at room temperature under inert atmosphere on an orbital shaker, the slide was sonicated in DMF (2 x 5 min), milli-Q H<sub>2</sub>O (2 x 5 min), EtOH (2 x 5 min) and CHCl<sub>3</sub> (2x5 min), and then dried under nitrogen flow.

## 8- NMR and IR spectra of intermediate compounds and olefin precursors

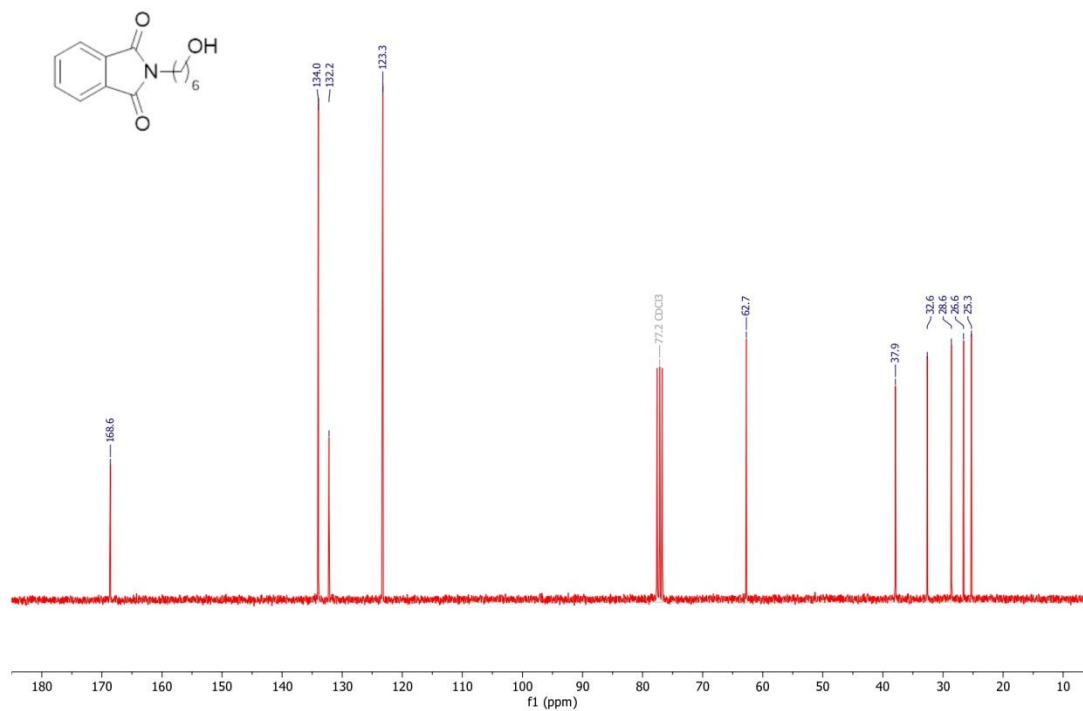
### 2-(6-hydroxyhexyl)isoindoline-1,3-dione (1)

#### <sup>1</sup>H NMR



## <sup>13</sup>C NMR

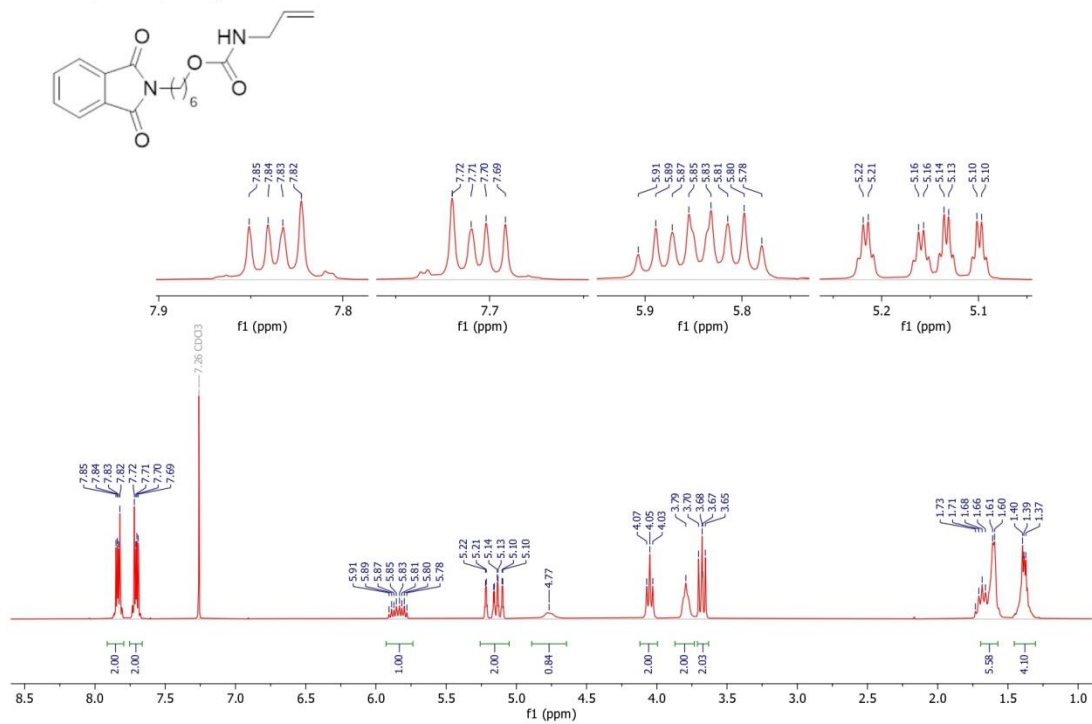
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



## 6-(1,3-dioxisoindolin-2-yl)hexyl N-allylcarbamate (2)

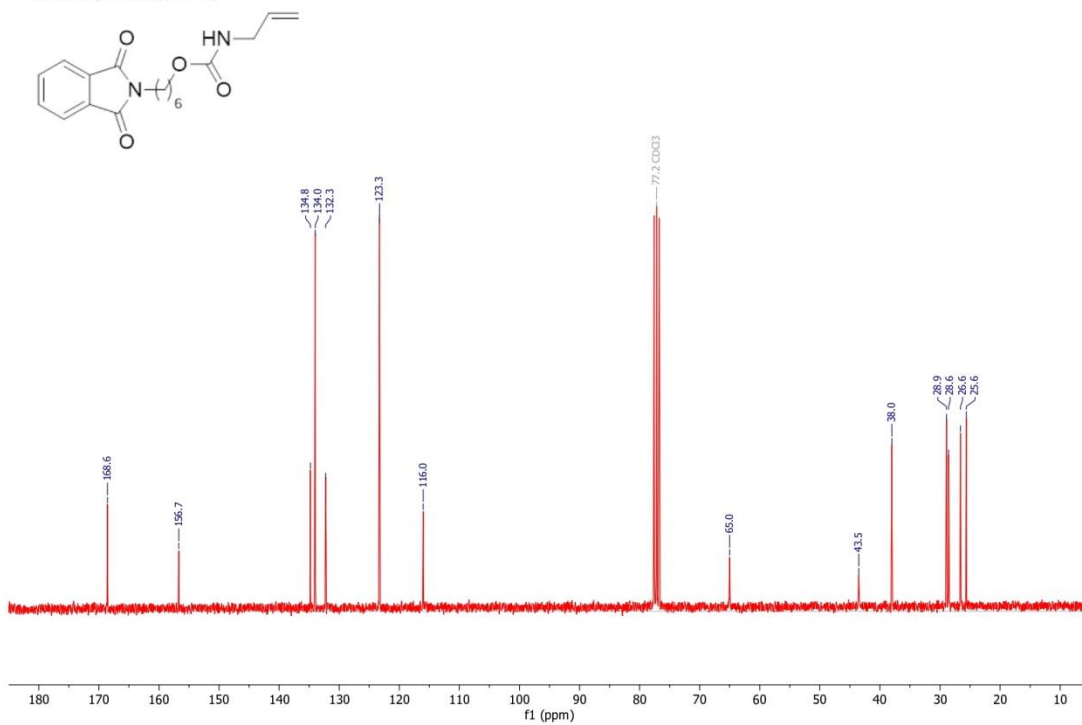
### <sup>1</sup>H NMR

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

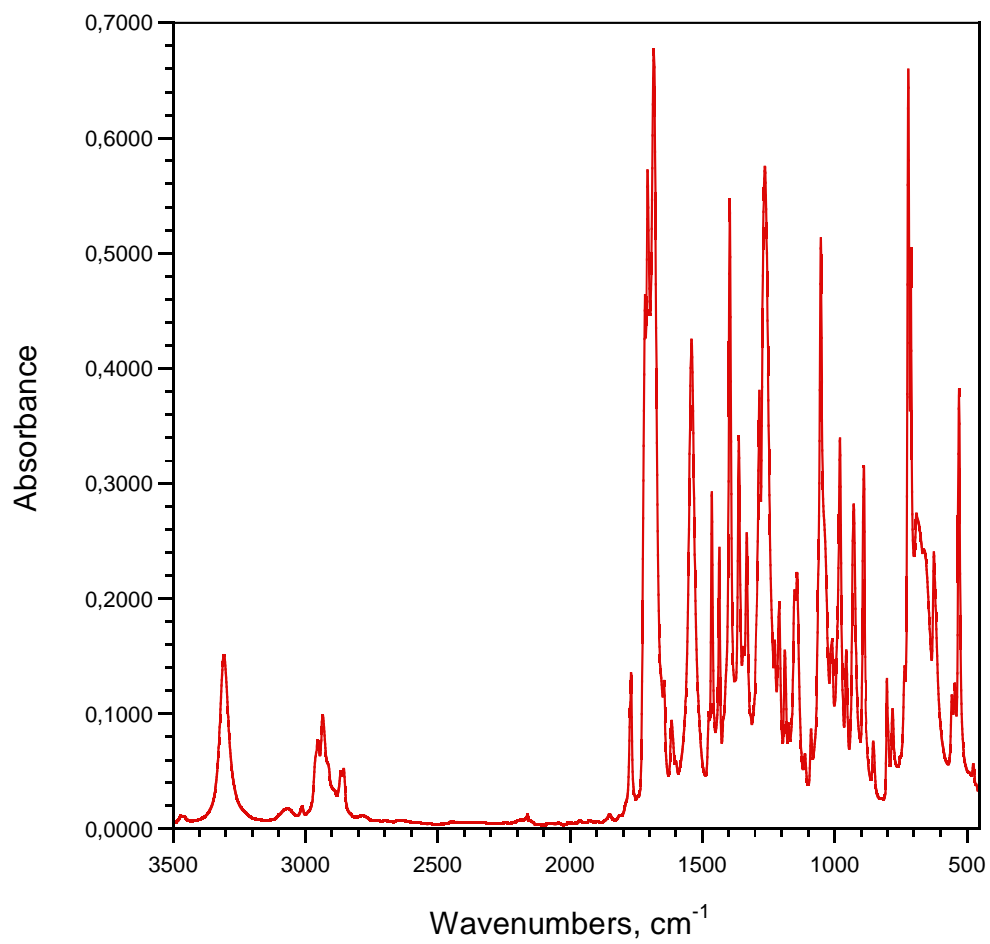


# <sup>13</sup>C NMR

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

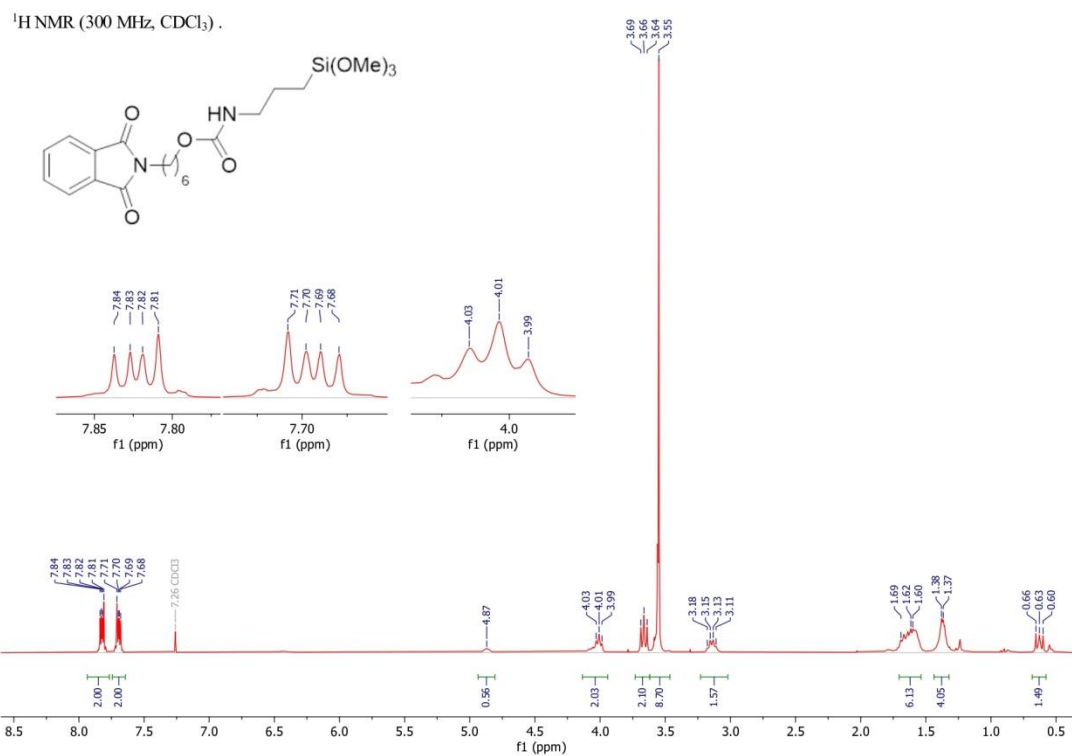


ATR-IR spectrum of compound 2

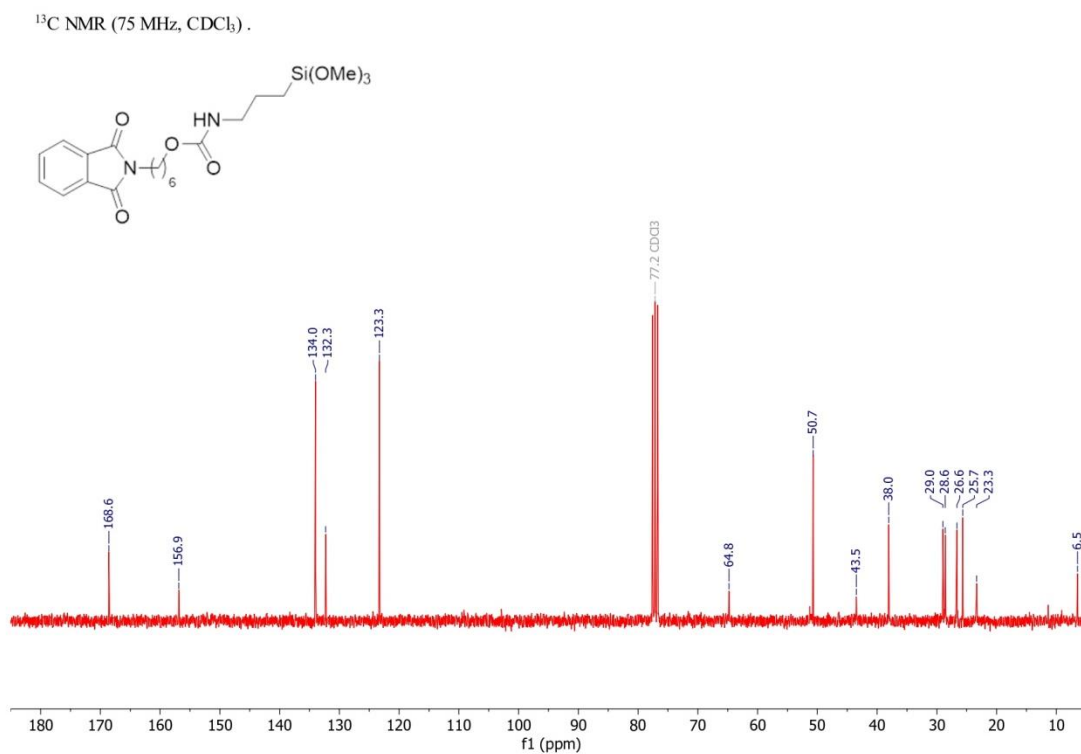


### 6-(1,3-dioxisoindolin-2-yl)hexyl *N*-(3-trimethoxysilyl)propyl)carbamate (**3**)

#### <sup>1</sup>H NMR

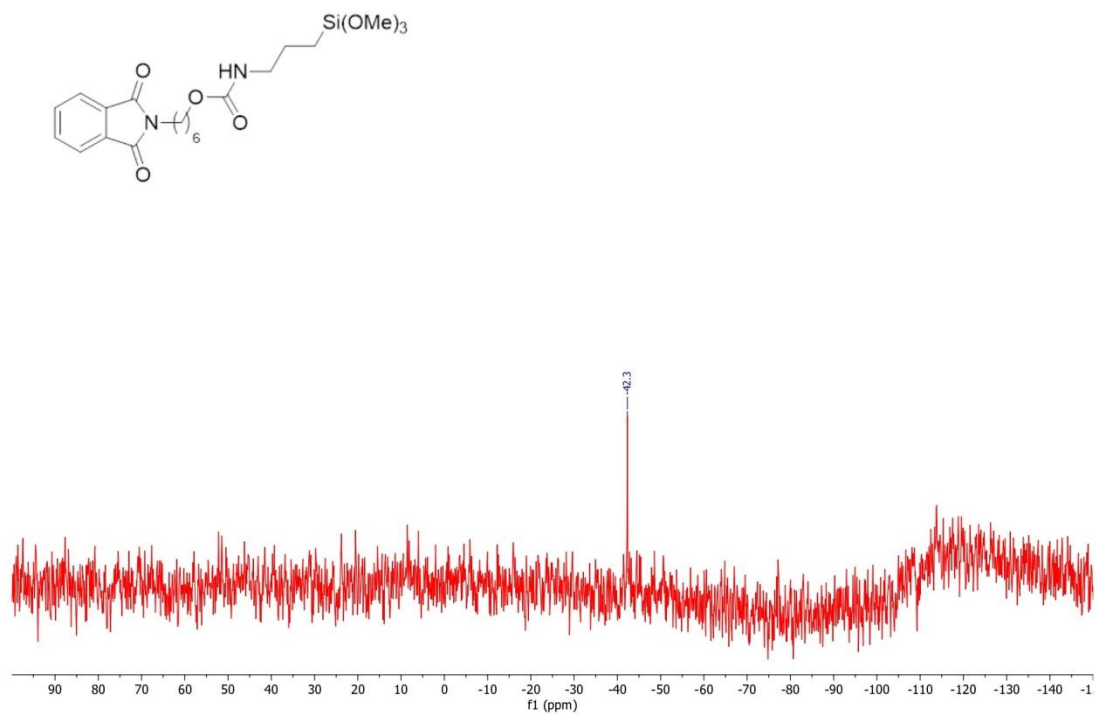


#### <sup>13</sup>C NMR



## <sup>29</sup>Si NMR

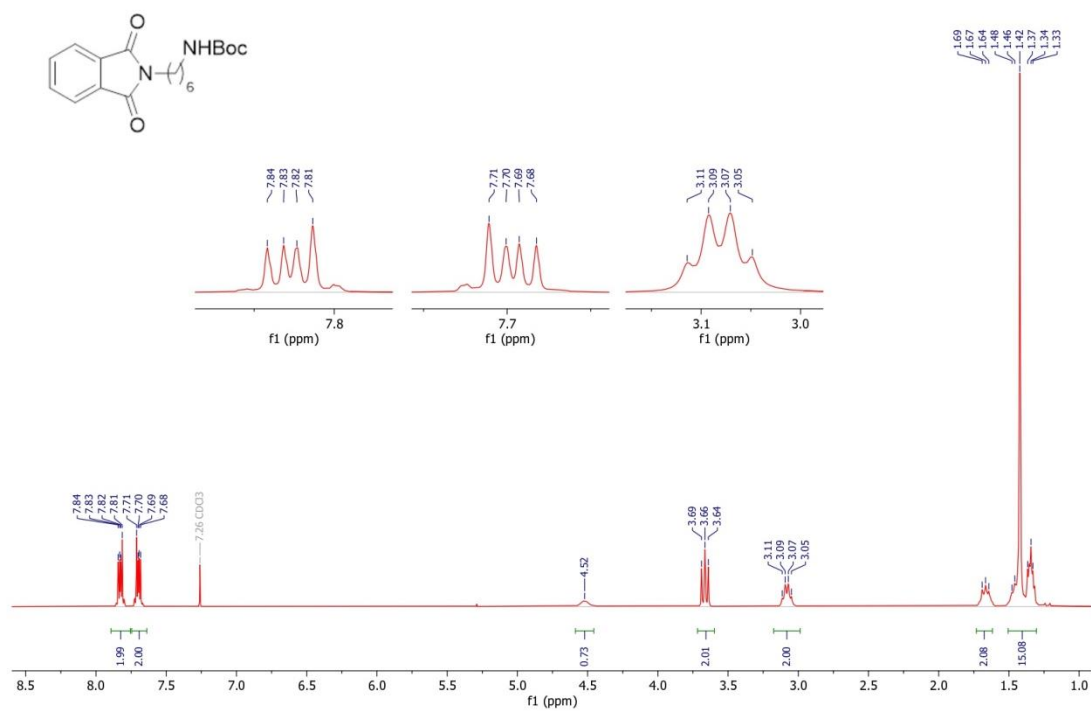
<sup>29</sup>Si NMR (118 MHz, CDCl<sub>3</sub>)



## *tert*-butyl *N*-(6-(1,3-dioxisoindolin-2-yl)hexyl)carbamate (4)

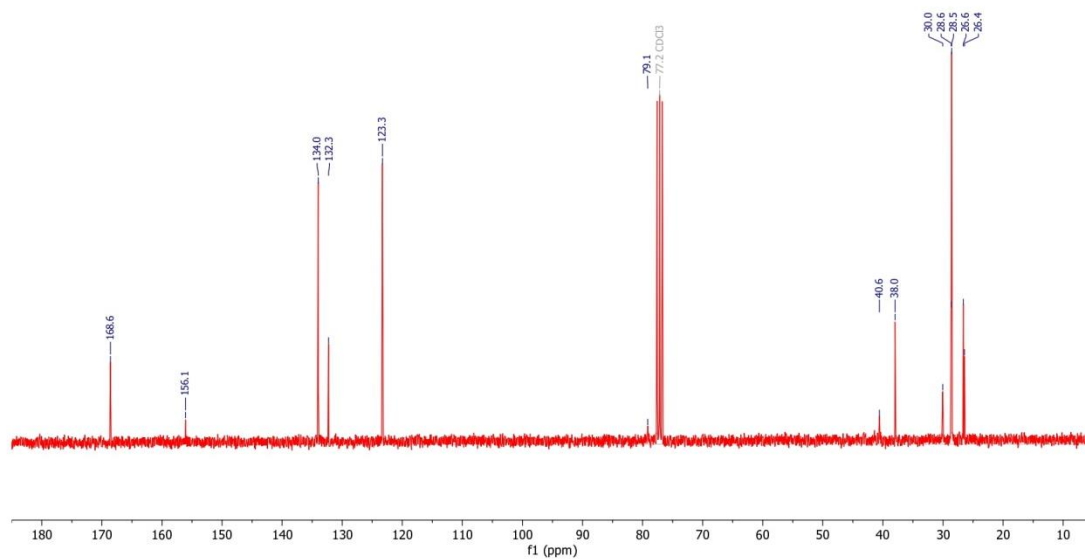
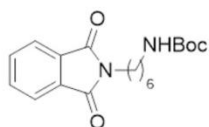
### <sup>1</sup>H NMR

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



## $^{13}\text{C}$ NMR

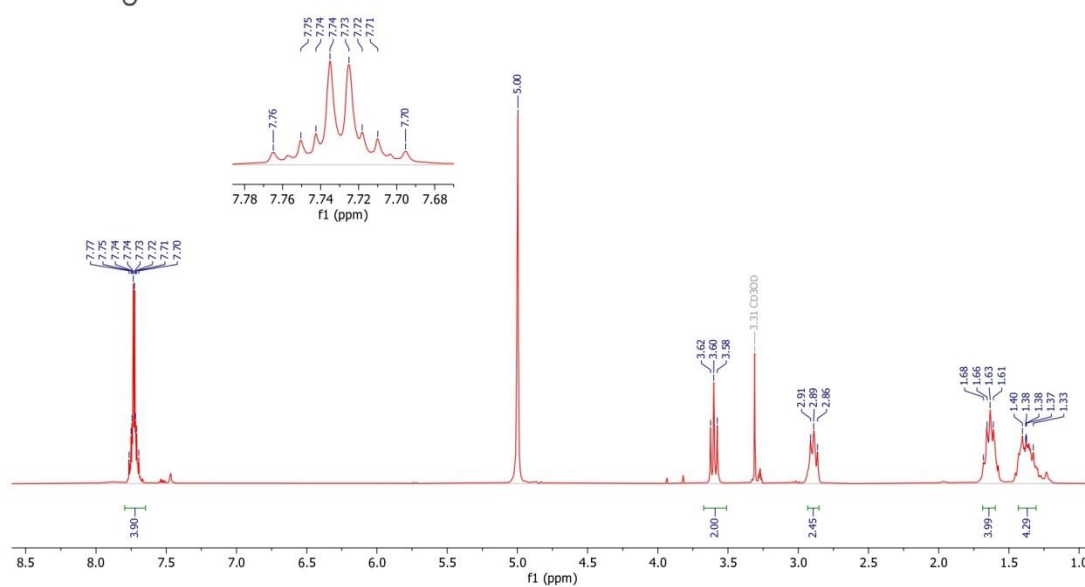
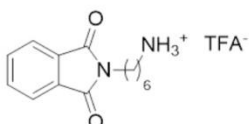
$^{13}\text{C}$  NMR (76 MHz,  $\text{CDCl}_3$ )



## 6-(1,3-dioxisoindolin-2-yl)hexan-1-ammonium (5)

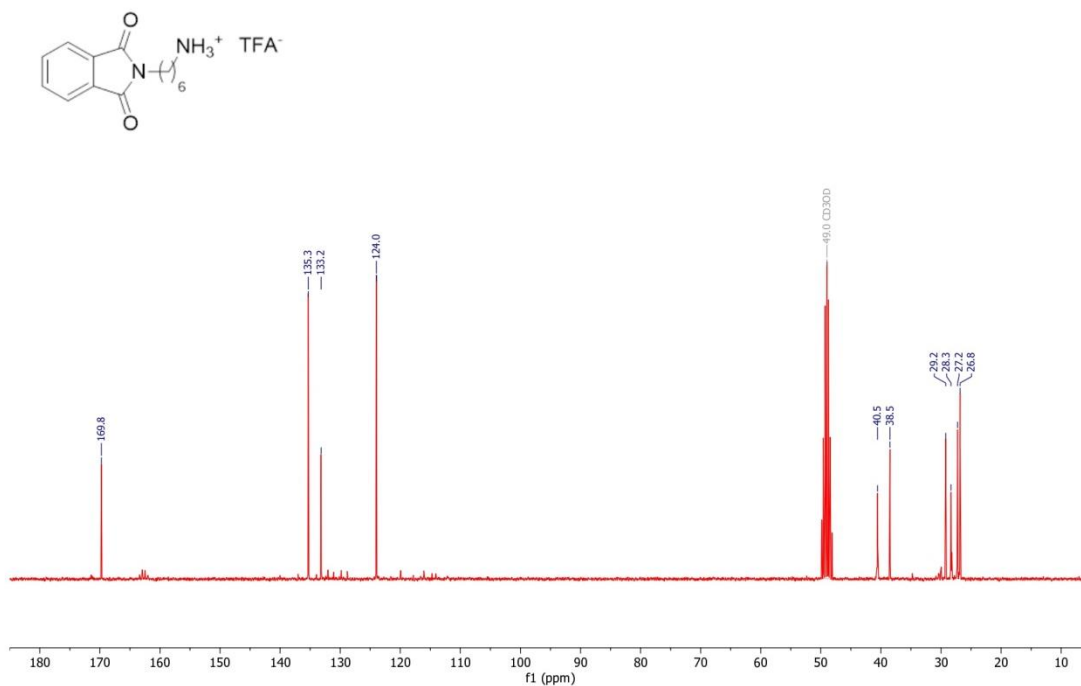
### $^1\text{H}$ NMR

$^1\text{H}$  NMR (300 MHz, MeOD)



## <sup>13</sup>C NMR

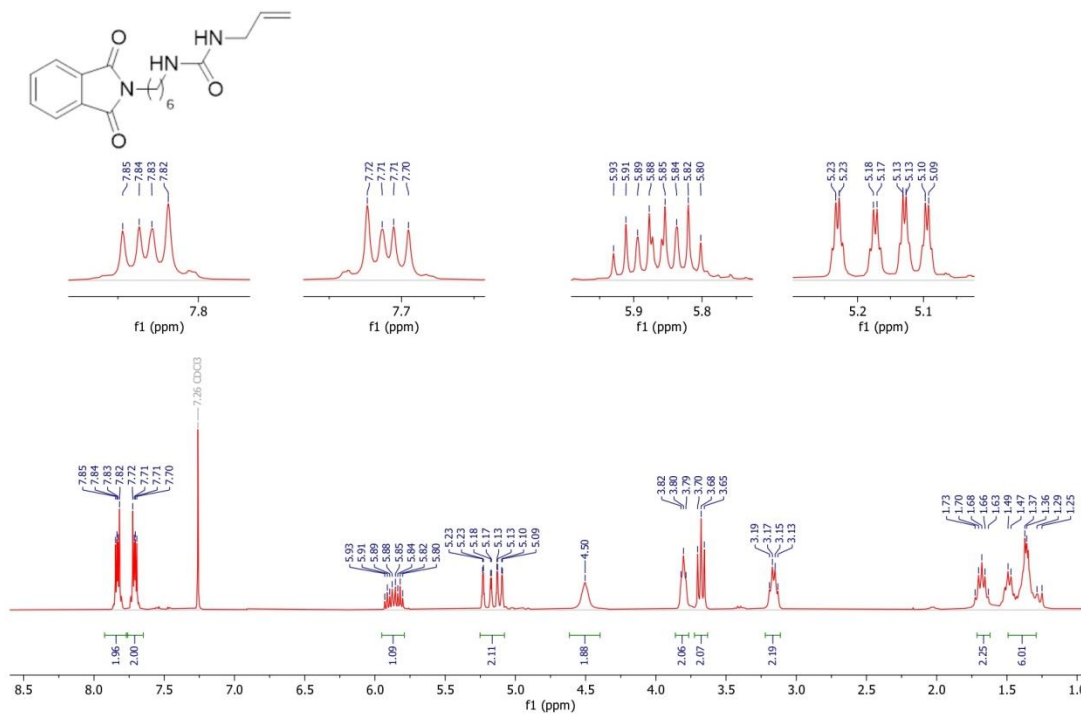
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



## 1-allyl-3-(6-(1,3-dioxisoindolin-2-yl)hexyl)urea (6)

### <sup>1</sup>H NMR

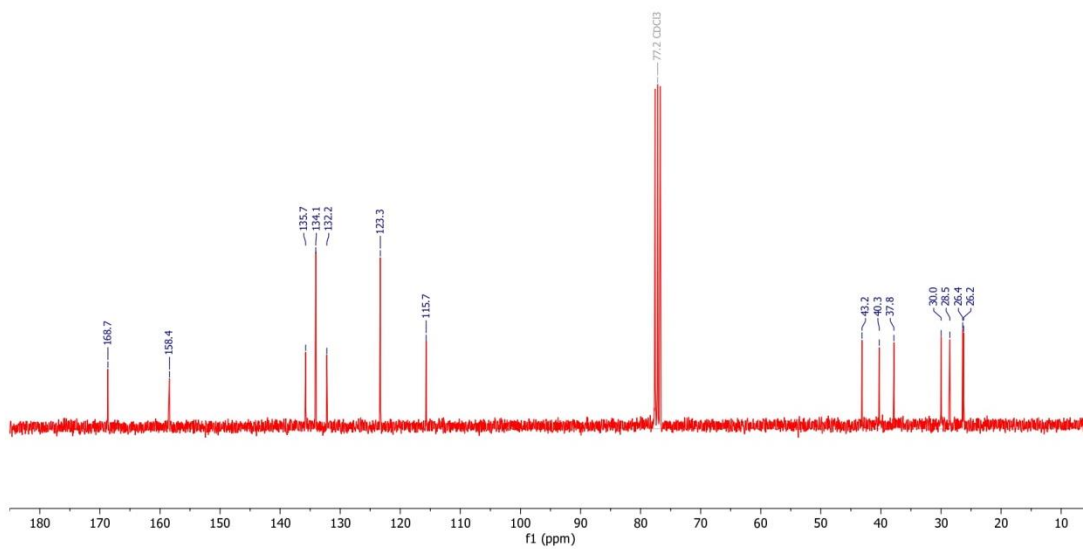
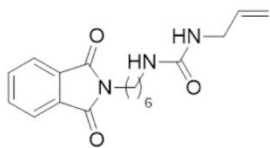
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



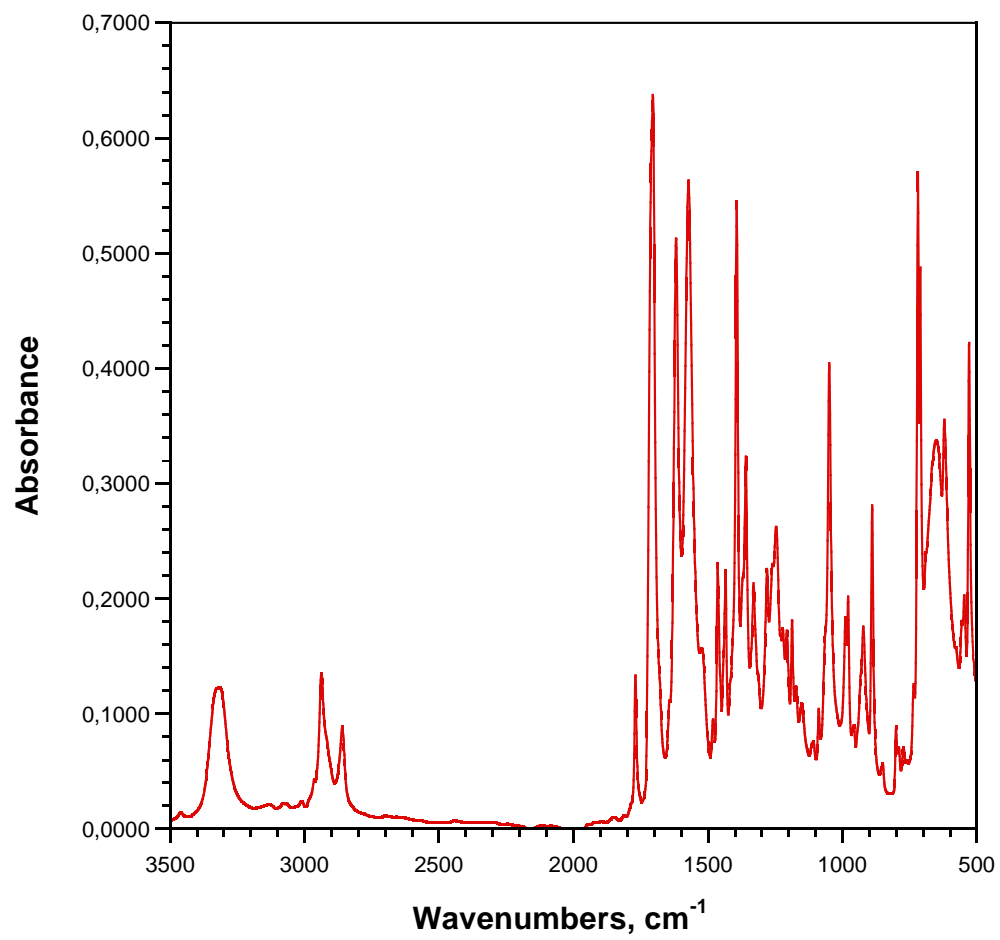


# <sup>13</sup>C NMR

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

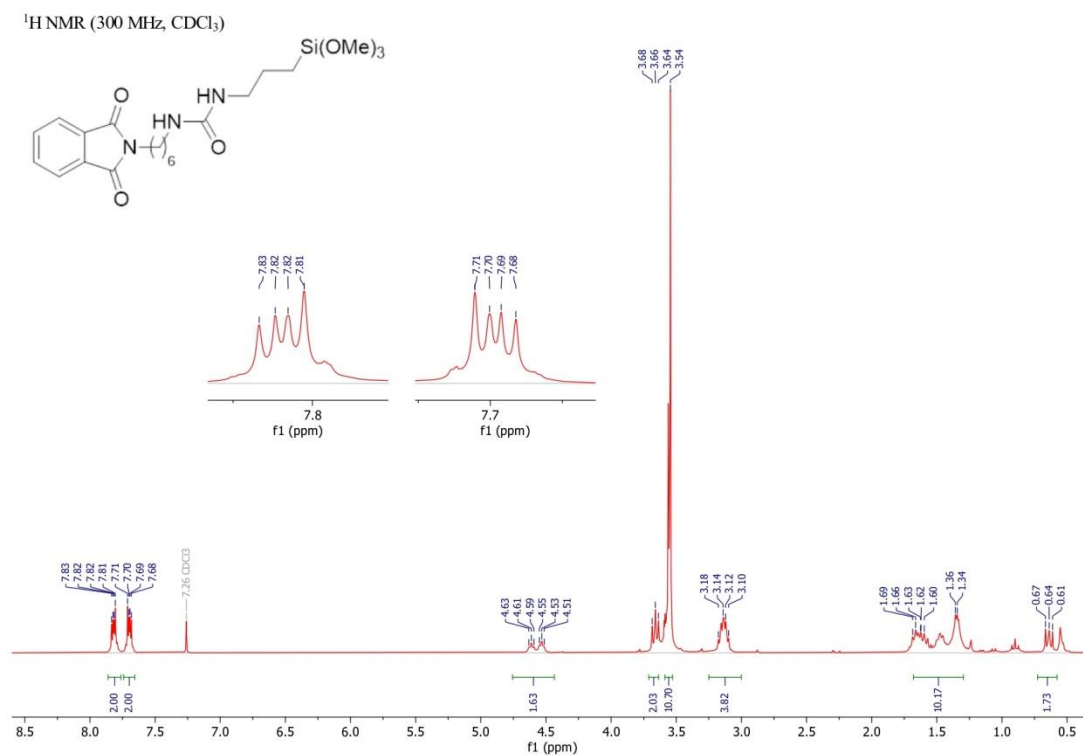


ATR-IR spectrum of compound 6

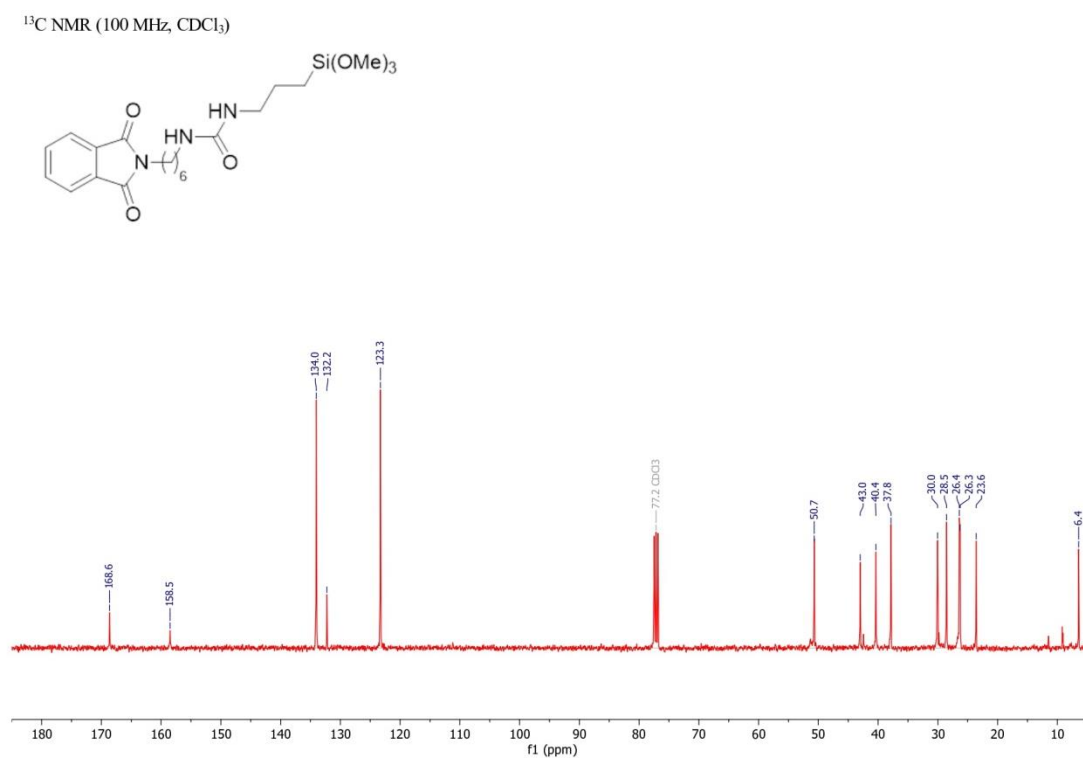


# 1-(6-(1,3-dioxisoindolin-2-yl)hexyl)-3-(3-trimethoxysilyl)propyl)urea (7)

## <sup>1</sup>H NMR

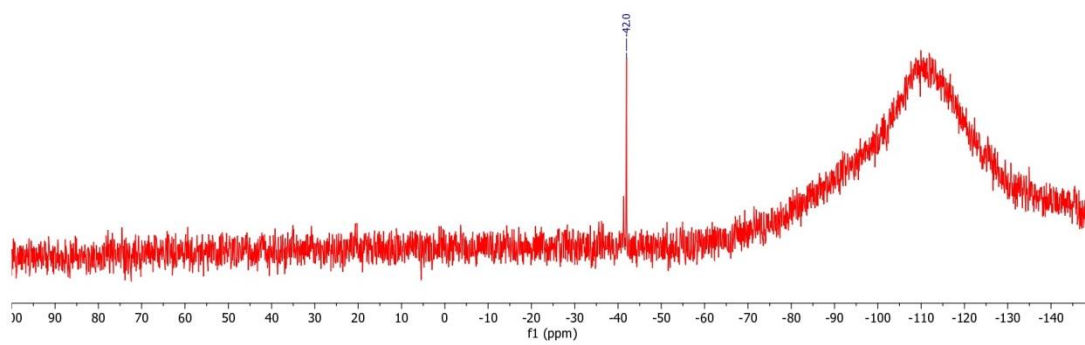
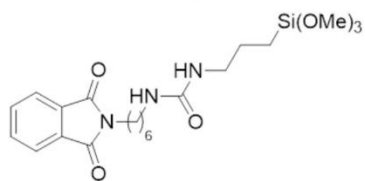


## <sup>13</sup>C NMR



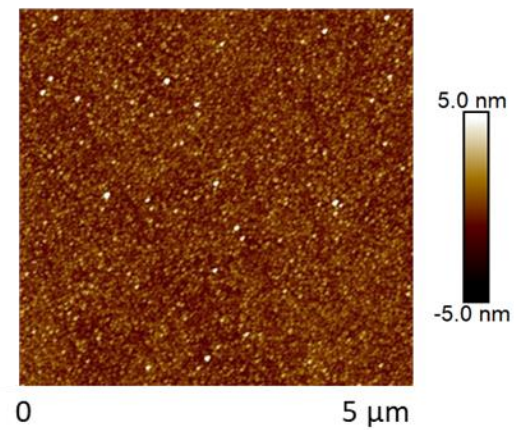
## <sup>29</sup>Si NMR

<sup>29</sup>Si NMR (79 MHz, CDCl<sub>3</sub>)

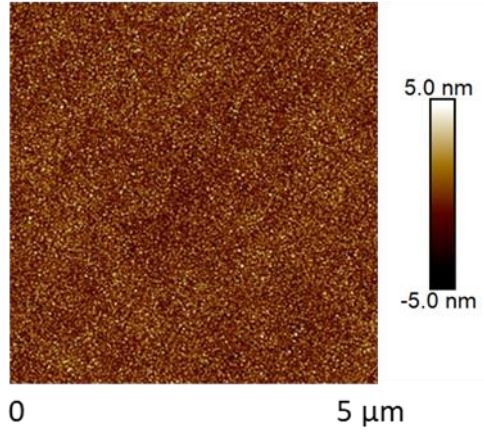


## 9- AFM height images (5 x 5 $\mu\text{m}$ ) of SAMs grafted on $\text{SiO}_2/\text{Au}$ substrate

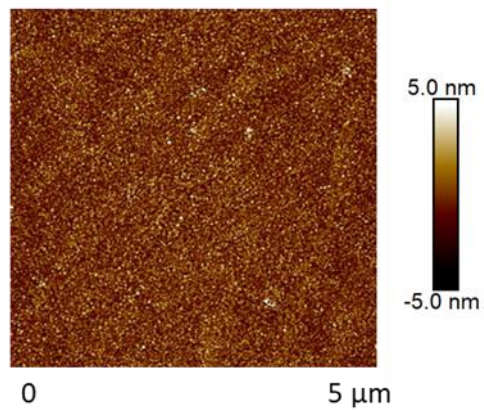
***i*SAM-Carba-Pht (RMS = 1.3 nm)**



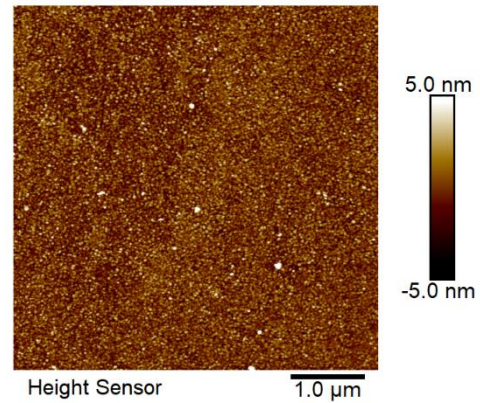
***i*SAM-Carba-NH<sub>2</sub> (RMS = 1.26 nm)**



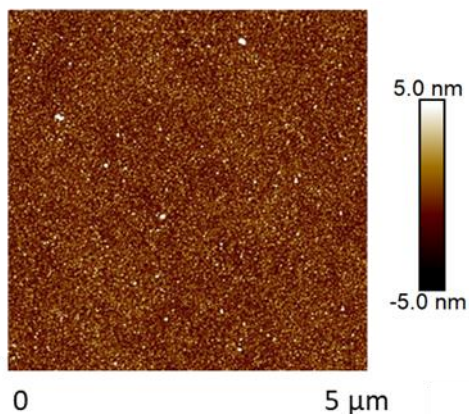
**scSAM-Carba-Pht (RMS = 1.20 nm)**



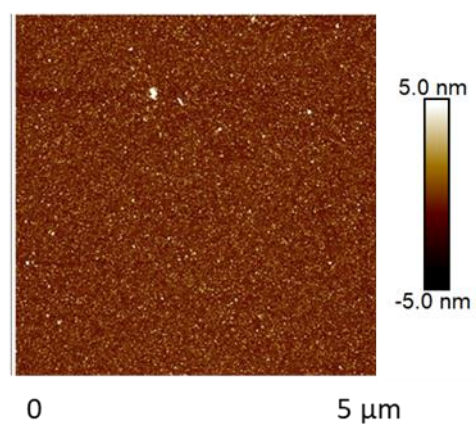
**scSAM-Carba-NH<sub>2</sub> (RMS = 1.28 nm)**



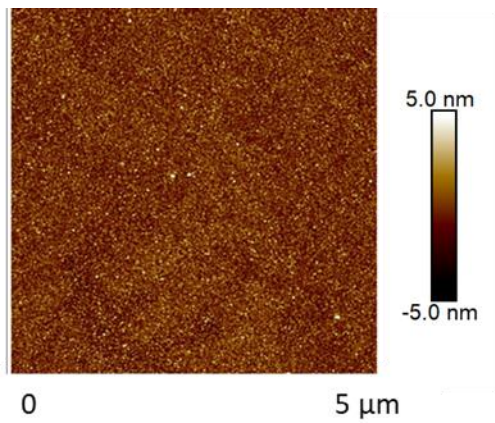
***i*SAM-Urea-Pht (RMS = 1.14 nm)**



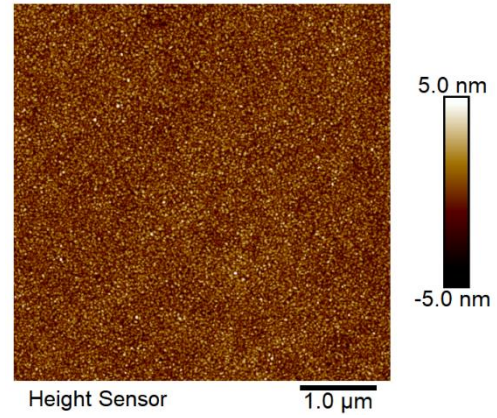
***i*SAM-Urea-NH<sub>2</sub> (RMS = 1.20 nm)**



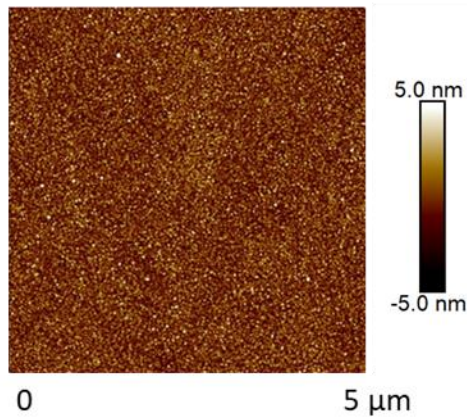
**scSAM-Urea-Pht (RMS = 1 nm)**



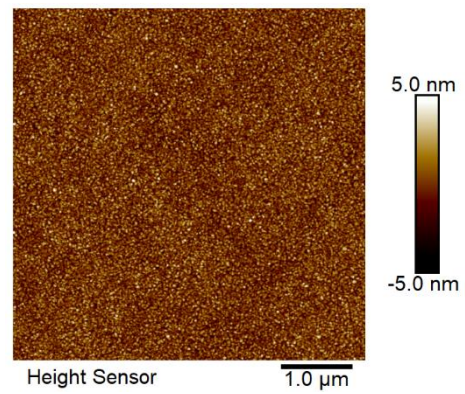
**scSAM-Urea-NH2 (RMS = 1.14 nm)**



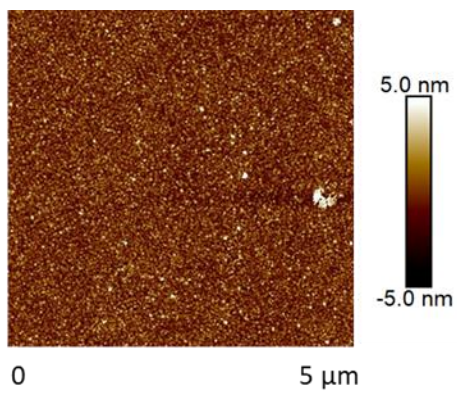
**iSAM-Alk-Pht (RMS = 1.19 nm)**



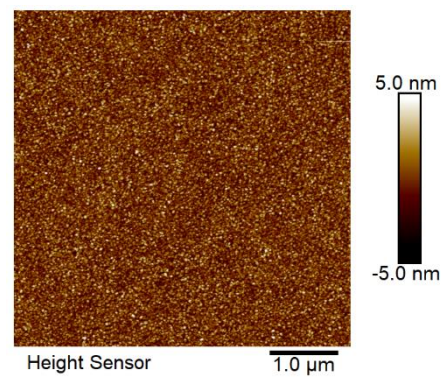
**iSAM-Alk-NH2 (RMS = 1.23 nm)**



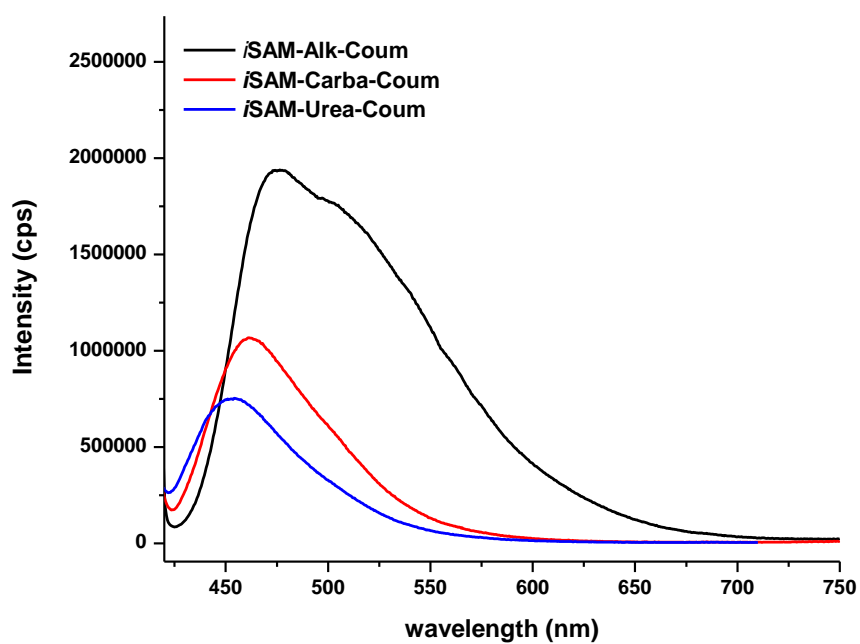
**scSAM-Alk-Pht (RMS = 1.30 nm)**



**scSAM-Alk-NH2 (RMS = 1.25 nm)**



## 10-Fluorescence spectra of *i*SAM-(alkyl or carba or urea)-Pht



<sup>1</sup> M. A. Ramin, G. Le Bourdon, N. Daugey, B. Bennetau, L. Vellutini, T. Buffeteau *Langmuir* **2011**, *27*, 6076–6084.