

## SUPPORTING INFORMATION

### **Siloxane-Containing Derivatives of Benzoic Acid: Chemical Transformation of the Carboxyl Group.**

#### **Supp.Inf.1: Methods for synthesis and characterization data**

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## 1. Materials and methods

All the starting materials were purchased from Acros and Sigma Aldrich companies. Solvents were dried and purified according to standard procedures. **1a-b** were synthesized according to known procedures. The brownish or yellowish colour of the products is most likely attributed to the cobalt salt which is contained in the acid after the oxidation due to difficulty with purification.

<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and HMBC NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer in CDCl<sub>3</sub>, (CD<sub>3</sub>)<sub>2</sub>CO, (CD<sub>3</sub>)<sub>2</sub>SO; chemical shifts are referenced to residual undeuterated solvents. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad).

High resolution mass spectra (HRMS) were registered on a Bruker Daltonics micrOTOF-Q II instrument using electrospray ionization (ESI). The measurements were acquired in a positive ion mode with the following parameters: interface capillary voltage 4500 V; mass range from m/z 50 to 3000; external calibration (Electrospray Calibrant Solution, Fluka); nebulizer pressure 0.4 Bar; flow rate 3 μL/min; nitrogen was applied as a dry gas (6L/min); interface temperature was set at 180°C. Samples were introduced into the mass spectrometer chamber via syringe injection, compounds were dissolved in acetonitrile, methanol or dichloromethane.

IR spectra were recorded on an IR spectrometer with a Fourier transformer Shimadzu IRTracer-100. Spectra were taken from thin films and transparent pellets.

Single crystals of **3al,am,bc,bi,bj,bn** and **4** were selected and studied on a Bruker QUEST diffractometer (Mo radiation) and kept at 100 K during data collection. Single crystal of **3bk** was selected and studied on a Bruker APEX-II CCD diffractometer (Mo radiation) and kept at 140 K during data collection. Single crystal of **3ah** was selected and studied on a Bruker APEX DUO CCD diffractometer (Cu radiation) and kept at 120 K during data collection. The X-ray dataset of compound **3ah** was refined as a 2-component inversion twin. All crystals were kept at 100 K during data collection. Using Olex2<sup>1</sup>, the structure was solved with the SHELXT<sup>2</sup> structure solution program using intrinsic phasing method and refined with the SHELXL<sup>3</sup> refinement package using least squares minimization procedure.

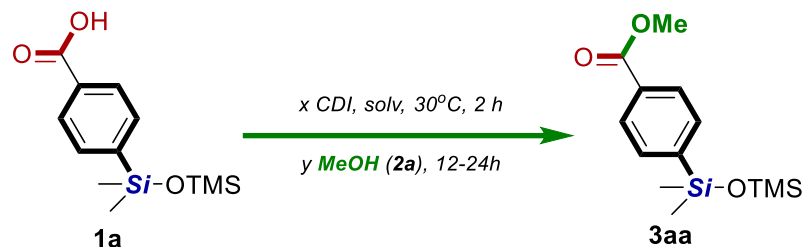
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<sup>1</sup> Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.

<sup>2</sup> Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.

<sup>3</sup> Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

## Method of synthesis and characterization data for 3aa



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion, %
1.2	2	THF	30	100
1.05	2	THF	30	100
1.05	1.05	THF	30	80
1.05	1.2	THF	30	87
1.05	2	THF	30	100

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, dry MeOH **2a** (23.9 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated, the conversion was determined by <sup>1</sup>H NMR.

### Intermediate results and comments

The use of 3% HCl for imidazole removal resulted in Si-O-Si unit destruction, therefore H<sub>2</sub>O was used instead.

An additional set of experiments showed that creating an argon layer allowed for a slightly greater conversion (100% in comparison to 92% at ambient air). The use of other devices for changing conditions such as a bubble counter and a CaCl<sub>2</sub>- tube demonstrated no changes in conversion.

\* In this and further synthesis, the brownish or yellowish product colour is most likely attributed to the cobalt salt which is contained in the acid after the oxidation due to difficulty with purification.

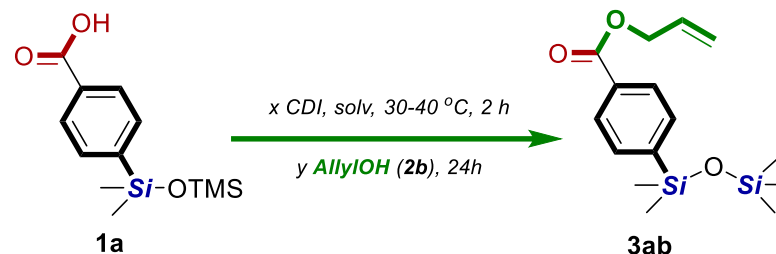
### Large-scale synthesis

Method of **3aa** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, dry MeOH **2a** (119.4 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM (dichloromethane). **3aa** was obtained a yellowish liquid with the 85% yield.

#### Characterization data for methyl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate (**3aa**):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 7.95 (d, <sup>3</sup>J=8 Hz, 2H), δ = 7.68 (d, <sup>3</sup>J=8 Hz, 2H), δ = 3.85 (s, 3H), δ = 0.33 (s, 6H), δ = 0.06 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 166.71, 146.07, 133.52, 130.79, 128.66, 52.57, 2.34, 1.06. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = 9.48, -2.06. HRMS (ESI) m/z z [M + NH<sub>4</sub>]<sup>+</sup> : calcd for [C<sub>20</sub>H<sub>26</sub>O<sub>5</sub>Si<sub>2</sub> + NH<sub>4</sub>]<sup>+</sup>, 420.1657; found, 420.1656; [M + Na]<sup>+</sup> : calcd for [C<sub>20</sub>H<sub>26</sub>O<sub>5</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 425.1211; found, 425.1214; [M + K]<sup>+</sup> : calcd for [C<sub>20</sub>H<sub>26</sub>O<sub>5</sub>Si<sub>2</sub> + K]<sup>+</sup>, 441.0950; found, 441.0948. IR (cm<sup>-1</sup>): 2957, 1938, 1730, 1601, 1557, 1499, 1436, 1389, 1314-1256, 1187-968, 876-638.

## Method of synthesis and characterization data for 3ab



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion
1.05	2	THF	30	87
1.05	2	THF	40	98

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 40 °C. After 2 hours, AllylOH **2b** (43.3 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated, the conversion was determined by <sup>1</sup>H NMR.

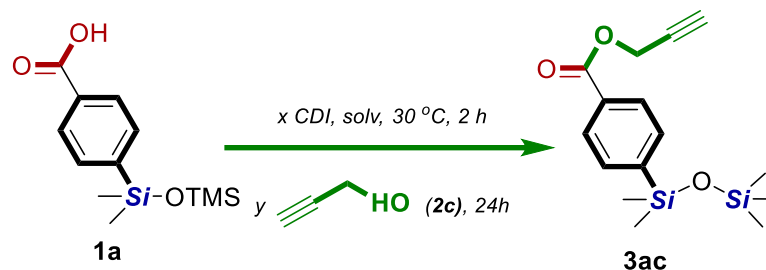
### Large-scale synthesis

Method of **3ab** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 40 °C. After 2 hours, AllylOH **2b** (216.5 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3ab** was obtained as a viscous colourless liquid with the 77% yield.

### Characterisation data for allyl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate:

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 7.98 (d, <sup>3</sup>J = 11 Hz, 2H), δ = 7.69 (d, <sup>3</sup>J = 11 Hz, 2H), δ = 6.12-5.99 (m, 1H), δ = 5.44-5.26 (m, 2H), δ = 4.81 (m, 2H), δ = 0.33 (s, 6H), δ = 0.07 (s, 8H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 165.39, 145.77, 133.11, 132.58, 130.27, 128.20, 117.82, 65.04, 1.91, 0.60. <sup>29</sup>Si NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ = 9.54, -2.03. IR (cm<sup>-1</sup>): 2958, 1724, 1558, 1389, 1275, 1186, 1095-975, 932, 876-638.

## Method of synthesis and characterization data for **3ac**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, propargyl alcohol **2c** (43.3 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 100%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3ac** was obtained as a colourless liquid.

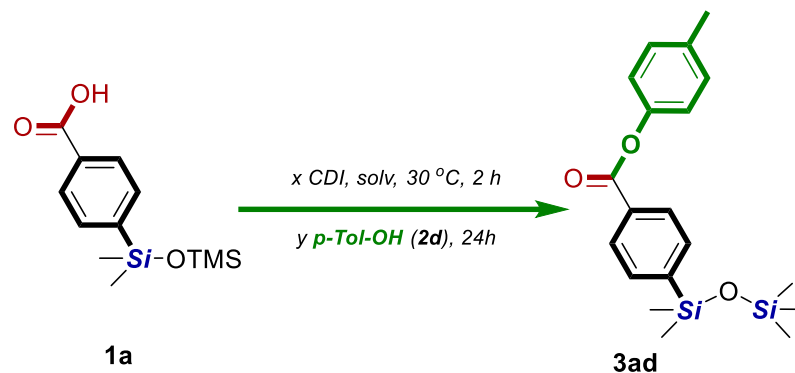
### Large-scale synthesis

Method of **3ac** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, propargyl alcohol **2c** (216.5 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM (dichloromethane). **3ac** was obtained as a colourless liquid with the 92% yield.

### Characterisation data for prop-2-yn-1-yl 4-(1,1,3,3,3-pentamethyldisiloxanyl)benzoate:

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 7.96 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.71 (d, <sup>3</sup>J=11 Hz, 2H), δ = 4.97 (d, <sup>4</sup>J=3 Hz, 2H), δ = 3.61 (m, 1H), δ = 0.34 (s, 6H), δ = 0.07 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 165.48, 146.59, 133.62, 130.14, 128.74, 78.78, 78.38, 52.94, 2.37, 1.05. <sup>29</sup>Si NMR (80 MHz, DMSO-*d*<sub>6</sub>): δ = -9.57, -2.04. IR (cm<sup>-1</sup>): 3310, 2958, 1730, 1389, 1274, 1259, 1186, 1123-982, 876-788, 757-638.

## Method of synthesis and characterization data for **3ad**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, p-cresol **2d** (80.6 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 93%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by Kugelrohr distillation at 110 °C.

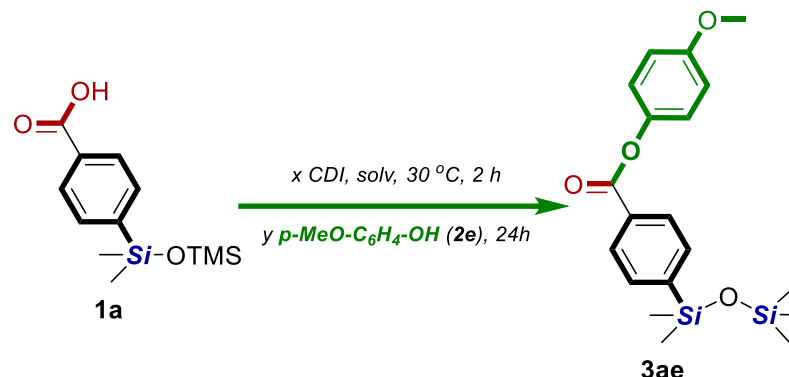
### Large-scale synthesis

Method of **3ad** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, p-cresol (402.9 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by Kugelrohr distillation at 110 °C. **3ad** was obtained as a colourless liquid with the 80% yield.

### Characterisation data for p-tolyl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate:

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 8.11 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.74 (d, <sup>3</sup>J=1 Hz, 2H), δ = 7.24 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.13 (d, <sup>3</sup>J=11 Hz, 2H), δ = 2.32 (s, 3H), δ = 0.34 (s, 6H), δ = 0.08 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 164.62, 148.37, 146.39, 135.03, 133.12, 129.80, 129.71, 128.68, 121.42, 20.34, 1.82, 0.52. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = 9.54, -2.09. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 359.1493; found, 259.1508. [M + NH<sub>4</sub>]<sup>+</sup>: calcd for [C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Si<sub>2</sub> + NH<sub>4</sub>]<sup>+</sup>, 376.1759; found, 376.1777. [M + Na]<sup>+</sup>: calcd for [C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 381.1313; found, 381.1320. [M + K]<sup>+</sup>: calcd for [C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Si<sub>2</sub> + K]<sup>+</sup>, 397.1052; found, 397.1063. IR (cm<sup>-1</sup>): 2956, 1738, 1509, 1389, 1258, 1199, 1166, 1117, -1018, 875-753.

## Method of synthesis and characterization data for 3ae



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, p-methoxyphenol **3e** (95.2 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up >90%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by Kugelrohr distillation at 110 °C.

### Large-scale synthesis

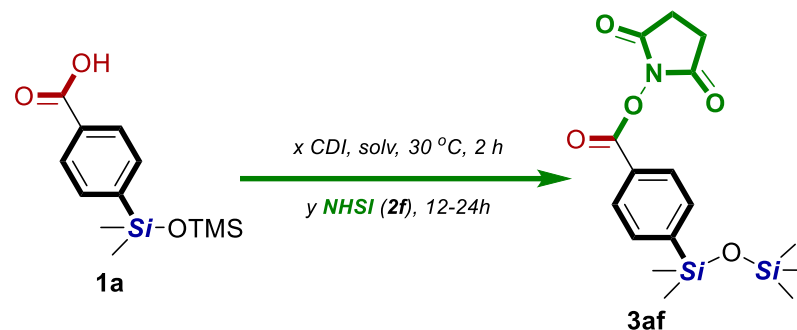
Method of **3ae** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, p-methoxyphenol **3e** (370.1 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by Kugelrohr distillation at 110 °C. **3ae** was obtained as a white powder with the 87% yield.

### Characterisation data for 4-methoxyphenyl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate:

<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>): δ = 8.16 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.80 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.23-7.17 (m, 2H), δ = 7.02-6.97 (m, 2H), δ = 3.82 (s, 3H), δ = 0.40 (s, 6H), δ = 0.13 (s, 9H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>): δ = 165.87, 158.40, 147.64, 145.50, 134.11, 131.30, 129.70, 123.44, 115.21, 55.89, 2.04, 0.89. <sup>29</sup>Si NMR (80 MHz, acetone-d<sub>6</sub>): δ = 9.38, -2.38. HRMS (ESI) m/z [M + NH<sub>4</sub>]<sup>+</sup>: calcd for [C<sub>19</sub>H<sub>26</sub>O<sub>4</sub>Si<sub>2</sub> + NH<sub>4</sub>]<sup>+</sup>, 392.1078; found, 392.1727. IR (cm<sup>-1</sup>): 2956, 2837, 1734, 1609, 1507, 1389, 1255, 1196, 1066, 871-638.



## Method of synthesis and characterization data for **3af**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, N-hydroxysuccinimide (NHSI) **3f** (85.8 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 100%. Then, the solvent was evaporated and the isolation of the product was carried out by flash-chromatography in DCM. **3af** was obtained as a colourless liquid.

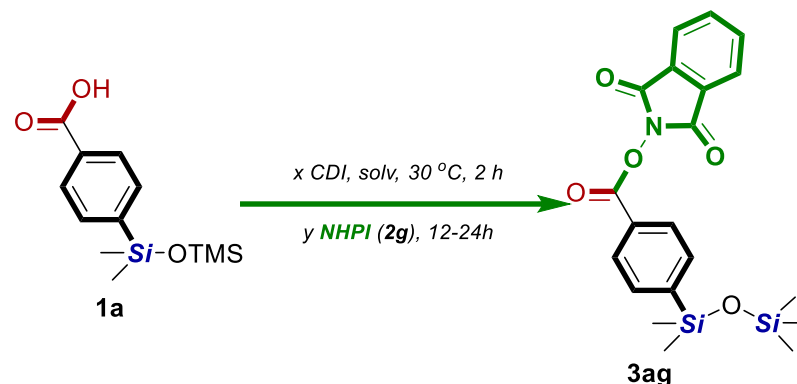
### Large-scale synthesis

Method of **3af** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, NHS **3f** (429.2 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by flash-chromatography in 80 ml of DCM. **3af** was obtained as a colourless liquid with the 60% yield.

### Characterisation data for 2,5-dioxopyrrolidin-1-yl 4-(1,1,3,3,3-pentamethyldisiloxaneyl)benzoate:

<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>): δ = 8.07 (d, <sup>3</sup>J=8 Hz, 2H), δ = 7.79 (d, <sup>3</sup>J=8 Hz, 2H), δ = 2.92 (s, 4H), δ = 0.34 (s, 6H), δ = -0.07 (s, 9H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>): δ = 170.49, 162.90, 149.68, 134.50, 129.80, 126.81, 26.38, 2.01, 0.80. <sup>29</sup>Si NMR (80 MHz, acetone-d<sub>6</sub>): δ = 9.68, -2.40. <sup>15</sup>N NMR (40 MHz, acetone-d<sub>6</sub>): δ = 198.61. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>16</sub>H<sub>23</sub>NO<sub>5</sub>Si<sub>2</sub> + H]<sup>+</sup>, 366.1188; found, 366.1190; [M + Na]<sup>+</sup>: calcd for [C<sub>16</sub>H<sub>23</sub>NO<sub>5</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 388.1007; found, 388.1015; [M + K]<sup>+</sup>: calcd for [C<sub>16</sub>H<sub>23</sub>NO<sub>5</sub>Si<sub>2</sub> + K]<sup>+</sup>, 404.0746; found, 404.0757. IR (cm<sup>-1</sup>): 2957, 1774, 1757, 1560, 1427, 1391, 1369, 1254-1186, 1111-987, 842-638.

## Method of synthesis and characterization data for **3ag**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, NHPI (121.6 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 100%. Then, the solvent was evaporated and the isolation of the product was carried out by flash-chromatography in DCM. **3ag** was obtained as a white powder.

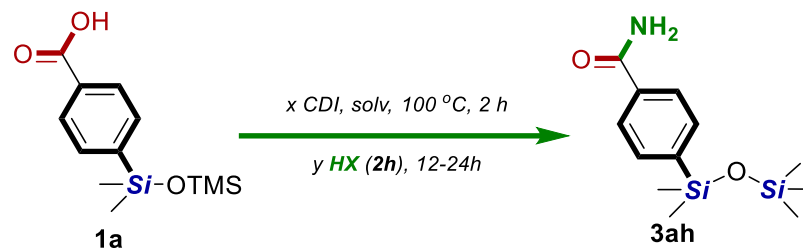
### Large-scale synthesis

Method of **3ag** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, NHPI (608.3 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by flash-chromatography in DCM. **3ag** was obtained as a white powder with the 65% yield.

### Characterisation data for 1,3-dioxoisindolin-2-yl 4-(1,1,3,3,3-pentamethyldisiloxy)benzoate:

<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>): δ = 8.15 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.94 (m, 4H), δ = 7.83 (d, <sup>3</sup>J=11 Hz, 2H), δ = 0.36 (s, 6H), δ = 0.09 (s, 9H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>): δ = 163.84, 162.76, 149.98, 136.16, 134.58, 129.96, 129.79, 126.54, 124.71, 2.04, 0.83. <sup>29</sup>Si NMR (80 MHz, acetone-d<sub>6</sub>): δ = 9.71, -2.39. <sup>15</sup>N NMR (40 MHz, acetone-d<sub>6</sub>): δ = 207.49. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub>Si<sub>2</sub> + H]<sup>+</sup>, 431.1215; found, 431.1474. IR (cm<sup>-1</sup>): 2959, 1768, 1741, 1601, 1467, 1362, 1252, 1187, 1089, 1034-1006, 877-607.

## Method of synthesis and characterization data for 3ah



Equivalent of x	Equivalent of y	HX	Solvent	Temperature, °C	Conversion, %
1.05	2	[Me <sub>3</sub> Si] <sub>2</sub> NH	THF	30	0**
1.05	4	NH <sub>3</sub> (23%)	THF	30	0
1.05	4	NH <sub>4</sub> Cl	THF	30	0
1.05	2	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	THF	30	<20% **
1.05	4	NH <sub>4</sub> OAc	THF	30	85% **
1.05	4	NH <sub>4</sub> HCO <sub>3</sub>	THF	30	90-95
1.05	2	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ( <b>2h</b> )	THF	30	90-97
1.05	4	NH <sub>4</sub> Cl	dioxane	100	50**
1.05	4	NH <sub>4</sub> OAc	dioxane	100	90**

\*\* destruction of Si-O-Si unit

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, (1) NH<sub>4</sub>X (1.492 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

### Intermediate results and comments:

The substitution of THF with dioxane took place because of a higher boiling point of dioxane. At 30 °C there is no difference in reaction efficiency in THF and in dioxane.

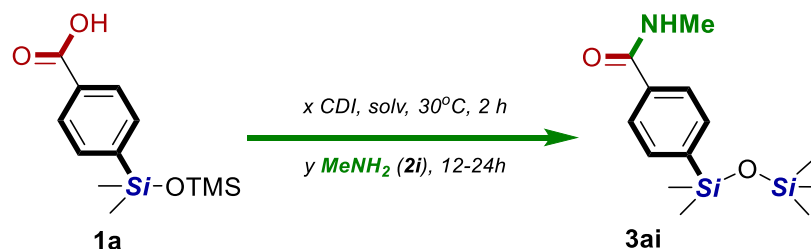
### Large-scale synthesis

Method of **3ah** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, (1) NH<sub>4</sub>HCO<sub>3</sub> (589.7 mg, 7.464 mmol, 4 eq.) or (2) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (358.3 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from EtOAc. **3ah** was obtained as a (1) 90% pure and (2) 95% pure yellowish powder with the (1) 56% and (2) 67% yields.

### Characterisation data for 4-(1,1,3,3,3-pentamethyldisiloxanyl)benzamide:

<sup>1</sup>H NMR (400 MHz, DMSO): δ = 8.00 (br s, 1H), δ = 7.87 (d, <sup>3</sup>J=8, 2H), δ = 7.59 (d, <sup>3</sup>J=8, 2H), δ = 7.41 (br s, 1H), δ = 0.31 (s, 6H), δ = 0.06 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO): δ = 167.94, 142.97, 135.10, 132.64, 126.67, 1.99, 0.74. <sup>29</sup>Si NMR (80 MHz, DMSO): δ = 9.14, -2.08. IR (cm<sup>-1</sup>): 2958, 1653, 1610, 1547, 1405, 1251, 1067, 840-685.

## Method of synthesis and characterization data for **3ai**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, MeNH<sub>2</sub> (40% aqueous solution) (115.6 mg of solution, 1.492 mmol, 4 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 100%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3ai** was obtained as a white powder.

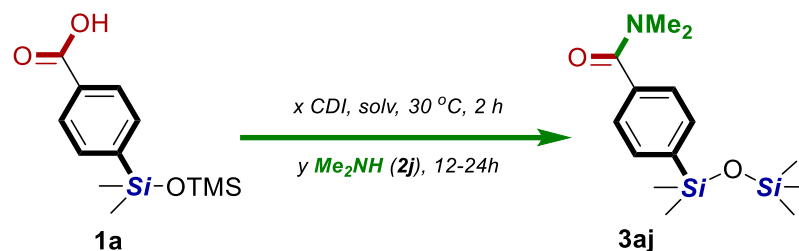
### Large-scale synthesis

Method of **3ai** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, MeNH<sub>2</sub> (40% aqueous solution) (1159.4 mg of solution, 7.464 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3ai** was obtained as a white powder with the 77% yield.

### Characterisation data for N-methyl-4-(1,1,3,3,3-pentamethyldisiloxanyl)benzamide:

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 8.43 (m, 1H), δ = 7.84 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.60 (d, <sup>3</sup>J=11 Hz, 2H), δ = 2.80 (d, <sup>3</sup>J=6 Hz, 3H), δ = 0.31 (s, 6H), δ = 0.06 (s, 7H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 166.58, 142.64, 135.32, 132.60, 126.20, 26.16, 1.87, 0.63. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = 9.62, -2.09. <sup>15</sup>N NMR (40 MHz, DMSO-d<sub>6</sub>): δ = 99.40. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>13</sub>H<sub>23</sub>NO<sub>2</sub>Si<sub>2</sub> + H]<sup>+</sup>, 282.1340; found, 282.1351. IR (cm<sup>-1</sup>): 3323, 2958, 1636, 1543, 1411, 1318, 1255, 1160-1036, 877-639.

## Method of synthesis and characterization data for **3aj**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, Me<sub>2</sub>NH (33% aqueous solution) (203.5 mg of solution, 1.492 mmol, 4 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 96%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3aj** was obtained as a white powder.

### Large-scale synthesis

Method of **3aj** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, Me<sub>2</sub>NH (33% aqueous solution) (1017.8 mg of solution, 7.464 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3aj** was obtained as a white powder with the 74% yield.

### Characterisation data for N,N-dimethyl-4-(1,1,3,3,3-pentamethyldisiloxanyl)benzamide:

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 7.59 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.40 (d, <sup>3</sup>J=11 Hz, 2H), δ = 2.99 (s, 3H), δ = 2.89 (s, 3H), δ = 0.33 (s, 6H), δ = 0.08 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 169.96, 140.68, 137.38, 132.58, 126.07, 34.60, 1.91, 0.68. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = 9.15, -2.10. It appeared to be feasible to obtain neither <sup>15</sup>N NMR nor <sup>1</sup>H – <sup>15</sup>N HMBC due to the symmetry of the molecule and <sup>15</sup>N relaxation characteristics. HRMS (ESI) m/z [M + H]<sup>+</sup> : calcd for [C<sub>14</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub> + H]<sup>+</sup>, 296.1497; found, 296.1501; [M + Na]<sup>+</sup> : calcd for [C<sub>14</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 318.1316; found, 318.1314; [M + K]<sup>+</sup> : calcd for [C<sub>14</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub> + K]<sup>+</sup>, 334.1055; found, 334.1055. IR (cm<sup>-1</sup>): 3620-3189, 2956, 1932, 1720, 1636, 1545-1394, 1257, 1118-1020, 876-676.

## Method of synthesis and characterization data for 3ak



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion, %
1.05	2	THF	30	60
1.05	4	THF	30	100

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylNH<sub>2</sub> **2k** (85.0 mg, 1.492 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

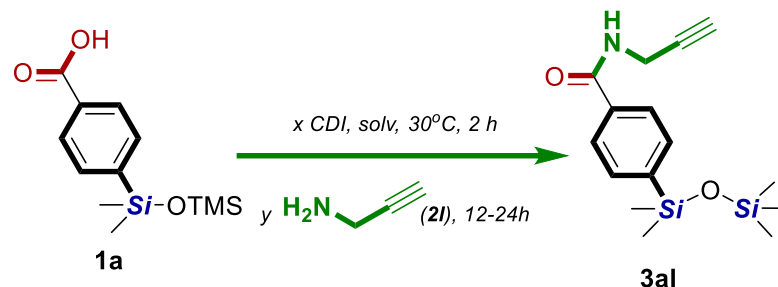
### Large-scale synthesis

Method of **3ak** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylNH<sub>2</sub> **2k** (425.4 mg, 7.464 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM (dichloromethane). **3ak** was obtained as a viscous brownish\* liquid with the 67% yield.

### Characterisation data for N-allyl-4-(1,1,3,3,3-pentamethyldisiloxanyl)benzamide:

<sup>1</sup>H NMR (400 MHz, DMSO): δ = 8.66 (t, <sup>3</sup>J=8, 1H), δ = 7.88 (d, <sup>3</sup>J=11, 2H), δ = 7.62 (d, <sup>3</sup>J=11, 2H), δ = 5.97-5.84 (m, 1H), δ = 5.21-5.07 (m, 2H), δ = 3.92 (m, 2H), δ = 0.33 (s, 6H), δ = 0.08 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO): δ = 165.99, 142.83, 135.38, 135.21, 132.62, 126.36, 115.00, 41.46, 1.90, 0.66. <sup>29</sup>Si NMR (80 MHz, DMSO): δ = 9.17, -2.08. <sup>15</sup>N NMR (40 MHz, DMSO): δ = 109.66. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>15</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub> + H]<sup>+</sup>, 282.1340; found, 282.1351. IR (cm<sup>-1</sup>): 3574-3138, 2959, 1934, 1721, 1642, 1543, 1429, 1284, 1057, 920, 816-638.

## Method of synthesis and characterization data for **3al**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, propargyl amine **2l** (40.3 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion was determined by <sup>1</sup>H NMR and made up 97%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3al** was obtained as a yellowish\* powder.

### Large-scale synthesis

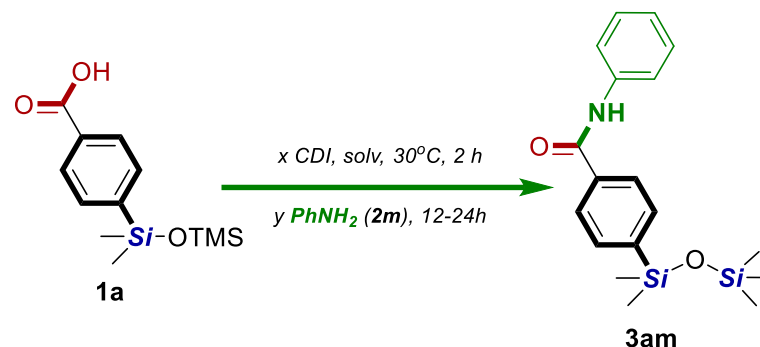
Method of **3al** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C . After 2 hours, propargyl amine **2l** (216.5 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM (dichloromethane). **3al** was obtained as a yellowish\* powder with the 86% yield.

### Characterisation data for 4-(1,1,3,3,3-pentamethyldisiloxanyl)-N-(prop-2-yn-1-yl)benzamide:

<sup>1</sup>H NMR (400 MHz, DMSO): δ = 8.92 (t, <sup>3</sup>J=7, 1H), δ = 7.86 (d, <sup>3</sup>J=11, 2H), δ = 7.62 (d, <sup>3</sup>J=11, 2H), δ = 4.08-4.06 (m, 2H), δ = 3.09 (t, <sup>4</sup>J=3, 1H), δ = 0.32 (s, 6H), δ = 0.07 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO): δ = 165.90, 143.22, 134.59, 132.69, 126.40, 81.23, 72.72, 28.45, 1.90, 0.64. <sup>29</sup>Si NMR (80 MHz, DMSO): δ = 9.23, -2.06. <sup>15</sup>N NMR (40 MHz, DMSO): δ = 107.75. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>15</sub>H<sub>23</sub>NO<sub>2</sub>Si<sub>2</sub> + H]<sup>+</sup>, 306.1340; found, 306.1340. IR (cm<sup>-1</sup>): 3327, 3236, 2959, 2120, 1638, 1542, 1423, 1313, 1250, 1112, 1063, 843-639.



## Method of synthesis and characterization data for **3am**



Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, aniline **2m** (69.4 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. The conversion was determined by <sup>1</sup>H NMR and made up 90-100%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM. **3am** was obtained as a yellowish\* powder with the 94% yield.

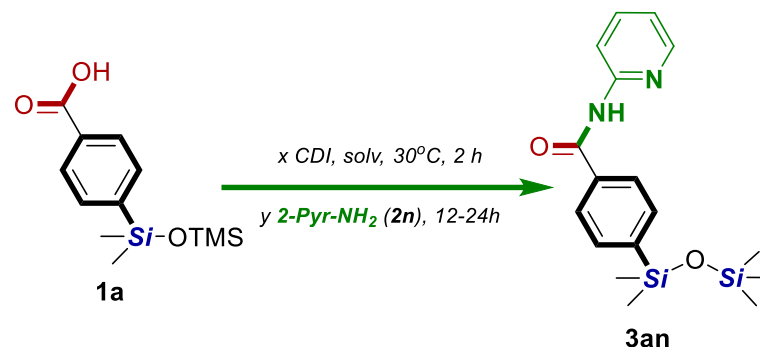
### Large-scale synthesis

Method of **3am** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, aniline **2m** (347.1 mg, 3.732 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM (dichloromethane). **3am** was obtained as a yellowish\* powder with the 94% yield.

### Characterisation data for 4-(1,1,3,3,3-pentamethyldisiloxanyl)-N-phenylbenzamide:

<sup>1</sup>H NMR (400 MHz, DMSO): δ = 10.25 (s, 1H), δ = 7.96 (d, <sup>3</sup>J=11, 2H), δ = 7.80 (d, <sup>3</sup>J=11, 2H), δ = 7.69 (d, <sup>3</sup>J=11, 2H), δ = 7.35 (t, <sup>3</sup>J=10, 2H), δ = 7.10 (t, <sup>3</sup>J=10, 1H), δ = 0.35 (s, 6H), δ = 0.10 (s, 9H). <sup>13</sup>C NMR (100 MHz, DMSO): δ = 165.56, 143.37, 139.16, 135.83, 132.70, 128.53, 126.78, 123.58, 120.27, 1.93, 0.68. <sup>29</sup>Si NMR (80 MHz, DMSO): δ = 9.29, -2.07. <sup>15</sup>N NMR (40 MHz, DMSO): δ = 128.85. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>18</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub> + H]<sup>+</sup>, 344.1497; found, 344.1505. IR (cm<sup>-1</sup>): 3305, 2956, 1640, 1602, 1540, 1496, 1444, 1330, 1253, 1082, 840-637.

## Method of synthesis and characterization data for 3an



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion
1.05	4	THF	30	50
1.05	4	THF	40	(multiple side products)
1.05	4	dioxane	100	75

The conversion was determined by  $^1\text{H}$  NMR.

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 100 °C. After 2 hours, 2-aminopyridine (70.1 mg, 0.746 mmol, 2 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by flash-chromatography in f1 – DCM/Hex 10:1 and f2 – acetone. F1 contained the pure **3an**, while f2 additionally contained the remaining acid. **3an** was obtained as a yellowish\* powder.

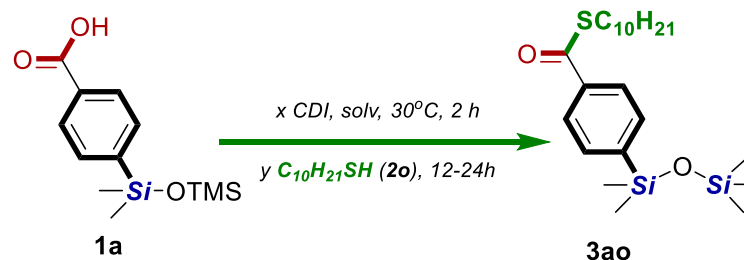
### Large-scale synthesis

Method of **3an** synthesis: **1a** (200.0 mg, 0.746 mmol), CDI (126.9 mg, 0.783 mmol, 1.05 eq) and 2 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 100 °C. After 2 hours, 2-aminopyridine (280.6 mg, 2.984 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by flash-chromatography in f1 – DCM/Hex 10:1 and f2 – acetone. F1 contained the pure **3an**, while f2 additionally contained the remaining acid. **3an** was obtained as a yellowish\* powder with the 13% yield.

**Characterisation data for 4-(1,1,3,3,3-pentamethyldisiloxanyl)-N-(pyridin-2-yl)benzamide:**

$^1\text{H}$  NMR (400 MHz, DMSO):  $\delta = 10.75$  (s, 1H),  $\delta = 8.35$  (m, 1H),  $\delta = 8.18$  (d,  $^3J=8$  Hz, 1H),  $\delta = 7.99$  (d,  $^3J=8$  Hz, 2H),  $\delta = 7.80$  (t,  $^3J=8$  Hz, 1H),  $\delta = 7.62$  (d,  $^3J=8$  Hz, 2H),  $\delta = 7.12$  (m, 1H),  $\delta = 0.30$  (s, 6H),  $\delta = 0.04$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta = 166.02, 152.20, 147.93, 143.88, 138.10, 134.90, 132.74, 127.16, 119.82, 114.71, 2.00, 0.74$ .  $^{29}\text{Si}$  NMR (80 MHz, DMSO):  $\delta = 9.31, -2.06$ . HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$  : calcd for  $[\text{C}_{17}\text{H}_{24}\text{NO}_2\text{Si}_2 + \text{H}]^+$ , 345.1449; found, 345.1452. IR ( $\text{cm}^{-1}$ ): 2958, 1675, 1584, 1539, 1442, 1313, 1253, 1313, 1253, 1077, 840-682.

## Method of synthesis and characterization data for 3ao



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion
1.05	4	THF	30	100
1.05	3	THF	30	100

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, 1-decanethiol **2o** (195.0 mg, 1.119 mmol, 3 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

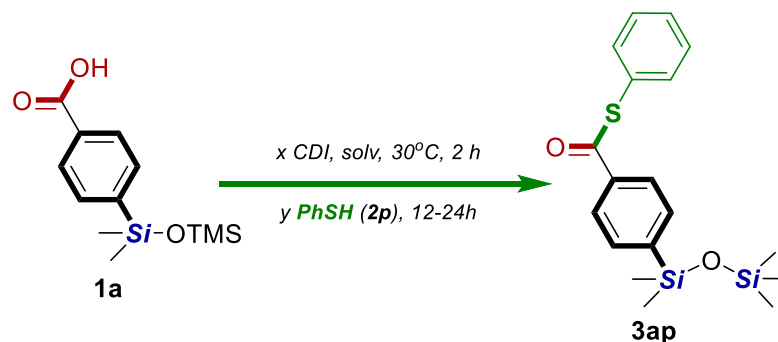
### Large-scale synthesis

Method of **3aa** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, 1-decanethiol **2o** (975.7 mg, 5.598 mmol, 3 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM followed by Kugelrohr distillation at 80 °C. **3ao** was obtained as a colourless liquid with the 80% yield (91% purity, impurities from 1-decanethiol and its dimer were hard to remove).

### Characterisation data for S-decyl 4-(1,1,3,3,3-pentamethyldisiloxanyl)benzoate:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (d, <sup>3</sup>J=11 Hz, 2H), δ = 7.63 (d, <sup>3</sup>J=11 Hz, 2H), δ = 3.08 (t, <sup>3</sup>J=10 Hz, 2H), δ = 1.73-1.63 (m, 2H), δ = 1.49-1.39 (m, 2H), δ = 1.36-1.28 (m, 13H), δ = 0.89 (m, 3H), δ = 0.34 (s, 6H), δ = 0.10 (s, 9H).  
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 192.22, 146.64, 137.69, 133.09, 126.11, 31.88, 29.57, 29.53, 29.49, 29.29, 29.15, 28.99, 28.93, 22.66, 14.08, 1.90, 0.74. <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>): δ = 9.45, -2.72. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>SSi<sub>2</sub> + H]<sup>+</sup>, 425.2360; found, 425.2368; [M + NH<sub>4</sub>]<sup>+</sup>: calcd for [C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>SSi<sub>2</sub> + NH<sub>4</sub>]<sup>+</sup>, 442.2626; found, 442.2624; [M + Na]<sup>+</sup>: calcd for [C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>SSi<sub>2</sub> + Na]<sup>+</sup>, 447.2180; found, 447.2161; [M + K]<sup>+</sup>: calcd for [C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>SSi<sub>2</sub> + K]<sup>+</sup>, 463.1919; found, 463.1914. IR (cm<sup>-1</sup>): 2956-2855, 1669, 1457, 1387, 1254, 1212, 1181, 1058, 916, 842-650.

## Method of synthesis and characterization data for 3ap



Equivalent of x	Equivalent of y	Solvent	Temperature, °C	Conversion
1.05	4	THF	30	100
1.05	3	THF	30	100

The conversion was determined by  $^1\text{H}$  NMR.

Reaction conditions: **1a** (100.0 mg, 0.373 mmol), CDI (63.5 mg, 0.392 mmol, 1.05eq) and 1 ml of THF were stirred in Schott culture tubes (H  $\times$  diam. 100 mm  $\times$  10 mm) under an argon atmosphere at 30 °C. After 2 hours, thiophenol (123.1 mg, 1.119 mmol, 3 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by  $^1\text{H}$  NMR.

### Intermediate results and comments:

The purification was complicated by the formation of diphenyl disulfide which is impossible to remove by Kugelrohr distillation at 30 °C, at higher temperatures **3ap** destruction was observed. Flash-chromatography also proved to be an ineffective method of purification. Column chromatography led to ArC(O)–SPh-unit cleavage.

### Large-scale synthesis

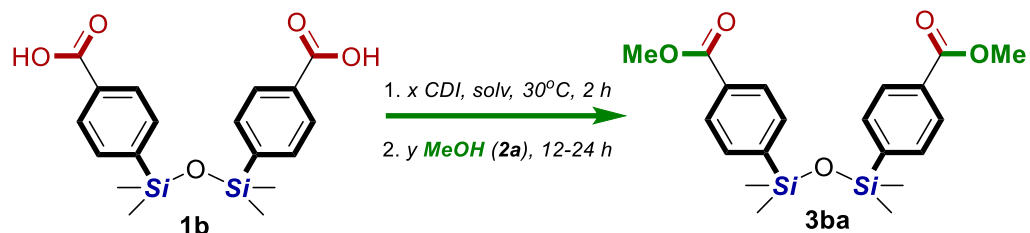
Method of **3ap** synthesis: **1a** (500.0 mg, 1.866 mmol), CDI (317.4 mg, 1.959 mmol, 1.05 eq) and 5 ml of THF were stirred in Schott culture tubes (H  $\times$  diam. 160 mm  $\times$  16 mm) under an argon atmosphere at 30 °C. After 2 hours, thiophenol (615.8 mg, 5.598 mmol, 3 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from from DCM followed by Kugelrohr distillation at 25 °C. **3ap** was obtained as a 71% pure

(impurities from thiophenol and its dimer were hard to remove) white with the 95% yield (71% purity, impurities from 1-decatethiol and its dimer were hard to remove).

**Characterisation data for S-phenyl 4-(1,1,3,3,3-pentamethyldisiloxanyl)benzothioate:**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.08$  (d,  $^3J=11$  Hz, 2H),  $\delta = 7.74$  (d,  $^3J=11$  Hz, 2H),  $\delta = 7.61$ -7.51 (m, 6H),  $\delta = 0.43$  (s, 6H),  $\delta = 0.19$  (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 190.20, 147.29, 137.02, 135.04, 133.26, 126.38, 1.93, 0.75$ .  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta = 9.63, -2.67$ . HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$ : calcd for  $[\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}_2 + \text{H}]^+$ , 361.1108; found, 361.1127;  $[\text{M} + \text{NH}_4]^+$ : calcd for  $[\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}_2 + \text{NH}_4]^+$ , 378.1374; found, 378.1376;  $[\text{M} + \text{Na}]^+$ : calcd for  $[\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}_2 + \text{Na}]^+$ , 383.0928; found, 383.0924;  $[\text{M} + \text{K}]^+$ : calcd for  $[\text{C}_{18}\text{H}_{24}\text{O}_2\text{SSi}_2 + \text{K}]^+$ , 399.0667; found, 399.0666. IR ( $\text{cm}^{-1}$ ): 3063, 2899, 1685, 1579, 1479, 1441, 1387, 1254, 1209, 1182, 1052, 903, 842-646.

## Method of synthesis and characterization data for 3ba



Equivalent of $x$ (per molecule)	Equivalent of $y$	Solvent	Temperature, °C	Conversion
2.4	4	THF	30	100
2.2	4	THF	30	100
2.05	4	THF	30	100
2.05	2.5	THF	30	87

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, dry MeOH (34.2 mg, 1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

### Large-scale synthesis

Method of **3ba** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, dry MeOH (170.88 mg, 5.340 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3ba** was obtained as a yellowish\* powder with the 77% yield.

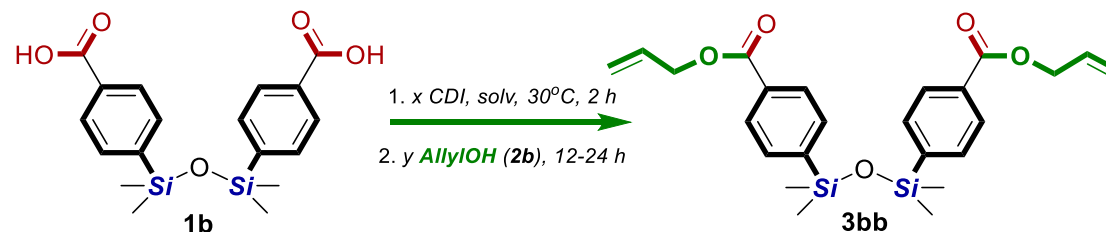
### Characterisation data for dimethyl 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibenzoate:

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 7.93 (d, <sup>3</sup>J=11 Hz, 4H), δ = 7.65 (d, <sup>3</sup>J=11 Hz, 4H), δ = 3.84 (s, 6H), δ = 0.32 (s, 12H).  
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 166.17, 145.04, 133.03, 130.38, 128.14, 52.03, 0.42. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = -

0.30. HRMS (ESI)  $m/z$   $[M + NH_4]^+$  : calcd for  $[C_{20}H_{26}O_5Si_2 + NH_4]^+$ , 420.1657; found, 420.1656;  $[M + Na]^+$  : calcd for  $[C_{20}H_{26}O_5Si_2 + Na]^+$ , 425.1211; found, 425.1214;  $[M + K]^+$  : calcd for  $[C_{20}H_{26}O_5Si_2 + K]^+$ , 441.0950; found, 441.0948. IR (cm<sup>-1</sup>): 3424, 2955, 1723, 1282, 1098.



## Method of synthesis and characterization data for 3bb



Equivalent of x (per molecule)	Equivalent of y	Solvent	Temperature, °C	Conversion
2.1	4	THF	30	72
2.1	4	THF	40	80-90

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylOH (61.9 mg, 1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

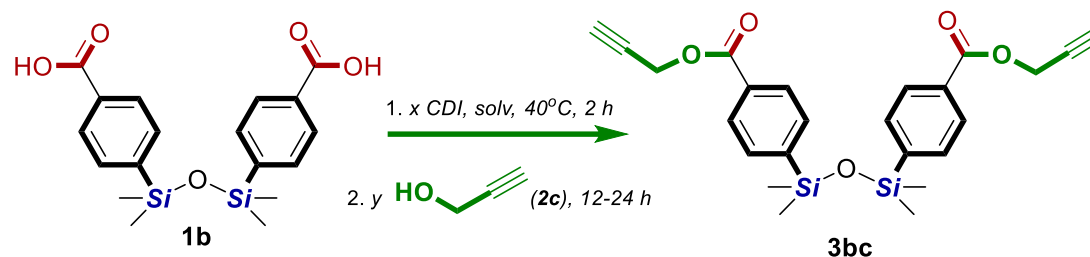
### Large-scale synthesis

Method of **3bb** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylOH (309.7 mg, 5.340 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bb** was obtained as a 71% pure yellowish\* liquid with the 90% yield.

### Characterisation data for diallyl 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibenzoate:

<sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>): δ = 8.03 (d, <sup>3</sup>J=6 Hz, 4H), δ = 7.74 (d, <sup>3</sup>J=6 Hz, 4H), δ = 6.13-6.03 (m, 2H), δ = 5.45-5.26 (m, 4H), δ = 4.83 (m, 4H), δ = 0.39 (s, 12H). <sup>13</sup>C NMR (100 MHz, acetone-d<sub>6</sub>): δ = 166.39, 146.37, 134.02, 133.56, 131.81, 129.25, 118.13, 65.96, 0.77. <sup>29</sup>Si NMR (80 MHz, acetone-d<sub>6</sub>): δ = -0.31. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>Si<sub>2</sub> + H]<sup>+</sup>, 455.1705; found, 455.1710. IR (cm<sup>-1</sup>): 3429, 3080-2900, 1942, 1717, 1649, 1601, 1557, 1498, 1455-1361, 1313-1260, 1186, 1128-663.

## Method of synthesis and characterization data for 3bc



Equivalent of x (per molecule)	Equivalent of y	Solvent	Temperature, °C	Conversion
2.1	4	THF	30	80
2.1	4	THF	40	90
2.1	4	THF	60	multiple side products

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 40 °C. After 2 hours, propargyl alcohol (59.8 mg, 1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

### Large-scale synthesis

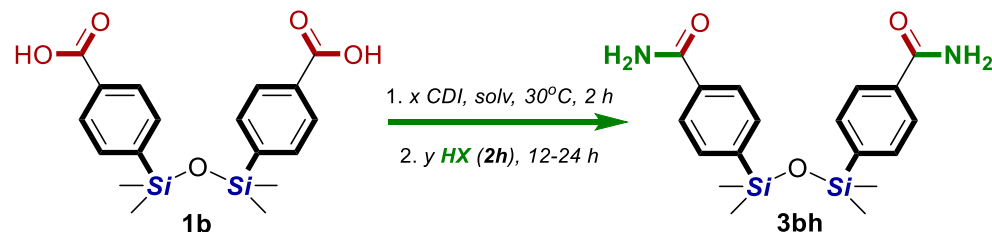
Method of **3bc** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 40 °C. After 2 hours, propargyl alcohol (299.1 mg, 5.340 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bc** was obtained as a white powder with the 70% yield.

### Characterisation data for di(prop-2-yn-1-yl) 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibenzoate:

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 7.95 (d, <sup>3</sup>J=11 Hz, 4H), δ = 7.69 (d, <sup>3</sup>J=11 Hz, 4H), δ = 4.96 (d, <sup>3</sup>J=3, 4H), δ = 3.59 (m, 1H), δ = 0.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 165.46, 146.07, 133.66, 130.25, 128.78, 78.77, 78.39, 52.96, 0.95. <sup>29</sup>Si NMR (80 MHz, DMSO): δ = -0.21. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>24</sub>H<sub>26</sub>O<sub>5</sub>Si<sub>2</sub> + H]<sup>+</sup>, 451.1392; found, 451.1391; [M + K]

$^+$  : calcd for  $[\text{C}_{24}\text{H}_{26}\text{O}_5\text{Si}_2 + \text{K}]^+$ , 489.0950; found, 489.0953;  $[\text{M} + \text{Na}]^+$  : calcd for  $[\text{C}_{24}\text{H}_{26}\text{O}_5\text{Si}_2 + \text{Na}]^+$ , 473.1211; found, 473.1206.  
IR ( $\text{cm}^{-1}$ ): 3291, 2964, 1715, 1281, 1100, 825-651.

## Method of synthesis and characterization data for 3bh



Equivalent of x (per molecule)	HX	Equivalent of y	Solvent	Temperature, °C	Conversion, %
2.1	NH <sub>3</sub> (25%)	8	THF	30	0
2.1	NH <sub>4</sub> Cl	8	THF	30	15
2.1	NH <sub>4</sub> HCO <sub>3</sub>	8	THF	30	80-85
2.1	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	4	THF	30	90
2.1	NH <sub>3</sub> (25%)	8	dioxane	100	0
2.1	NH <sub>4</sub> Cl	8	dioxane	100	90-100
2.1	NH <sub>4</sub> OAc	8	dioxane	100	80**
2.1	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4	dioxane	100	<40**

\*\*Si-O-Si unit cleavage

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of (1) THF or (2) dioxane were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at (1) 30 °C or (2) 100 °C. After 2 hours, NH<sub>4</sub>X (1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

### Large-scale synthesis

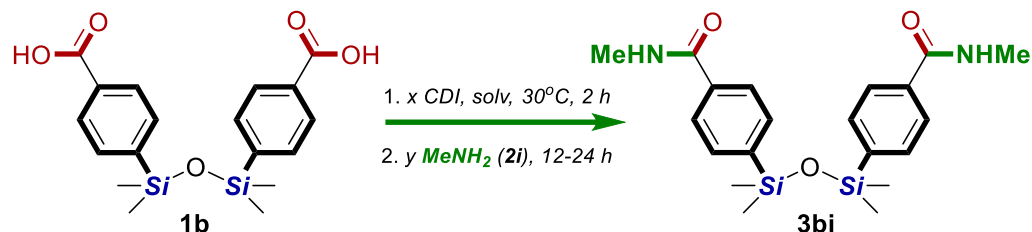
Method of **3bh** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of (1) THF or (2) dioxane were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at (1) 30 °C or (2) 100 °C. After 2 hours, (1) (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (512.6 mg, 5.340 mmol, 4 eq.) or (2) NH<sub>4</sub>Cl (582.1 mg, 2.136 mmol, 8 eq.) was added and the reaction was left

to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from EtOAc. **3bh** was obtained as a yellowish\* powder with the (1) 78% and (2) 60% yield .

**Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)dibenzamide:**

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 7.98 (br s, 2H),  $\delta$  = 7.87 (d,  $^3\text{J}$ =11 Hz, 4H),  $\delta$  = 7.61 (d,  $^3\text{J}$ =11 Hz, 4H),  $\delta$  = 7.38 (br s, 2H),  $\delta$  = 0.34 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 167.95, 142.63, 135.18, 132.66, 126.67, 0.67.  $^{29}\text{Si}$  NMR (80 MHz, DMSO- $d_6$ ):  $\delta$  = -0.56.  $^{15}\text{N}$  NMR (40 MHz, DMSO- $d_6$ ):  $\delta$  = 103.21.

## Method of synthesis and characterization data for **3bi**



Equivalent of x (per molecule)	Equivalent of y	Solvent	Temperature, °C	Conversion
2.1	4	THF	30	60-70
2.1	8	THF	30	95-100

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, MeNH<sub>2</sub> (40% aqueous solution) (165.5 mg of the solution, 2.136 mmol, 8 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by <sup>1</sup>H NMR.

### Large-scale synthesis

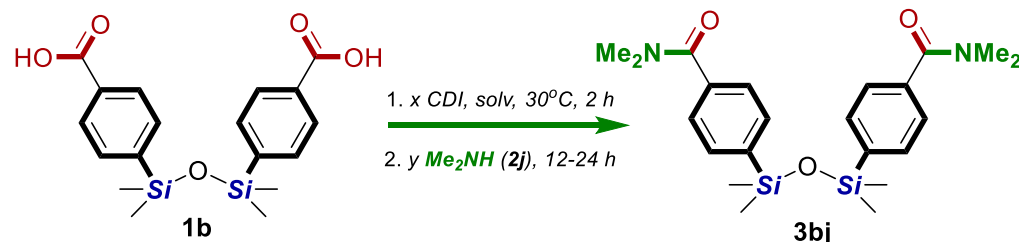
Method of **3bi** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, MeNH<sub>2</sub> (40% aqueous solution) (827.8 mg of the solution, 10.680 mmol, 8 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bi** was obtained as a yellowish powder\* with the 72% yield.

### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N-methylbenzamide):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 8.44 (m, 2H), δ = 7.83 (d, <sup>3</sup>J = 8 Hz, 4H), δ = 7.60 (d, <sup>3</sup>J = 8 Hz, 4H), δ = 2.80 (d, <sup>3</sup>J = 4.6 Hz, 6H), δ = 0.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 167.09, 142.82, 135.90, 133.18, 126.74, 26.68, 1.10. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = -0.57. <sup>15</sup>N NMR (40 MHz, DMSO-d<sub>6</sub>): δ = 99.46. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 401.1711; found, 401.1706; [M + Na]<sup>+</sup>: calcd for [C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 423.1531; found, 423.1526; [M +

$\text{K}]^+$  : calcd for  $[\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_3\text{Si}_2 + \text{K}]^+$ , 439.1270; found, 439.1263. IR ( $\text{cm}^{-1}$ ): 3325, 2958, 1635, 1545, 1411, 1319, 1254, 1111, 1067, 830, 791.

## Method of synthesis and characterization data for 3bj



Equivalent of x (per molecule)	Equivalent of y	Solvent	Temperature, °C	Conversion
2.1	4	THF	30	50
2.1	8	THF	30	70
2.1	6	THF	30	100

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at  $30^\circ\text{C}$ . After 2 hours,  $\text{Me}_2\text{NH}$  (33% aqueous solution) (218.5 mg of the solution, 1.602 mmol, 6 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by  $^1\text{H}$  NMR.

### Large-scale synthesis

Method of **3bj** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at  $30^\circ\text{C}$ . After 2 hours,  $\text{Me}_2\text{NH}$  (33% aqueous solution) (1092 mg of the solution, 8.010 mmol, 6 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bj** was obtained as a yellowish\* powder with the 97% yield.

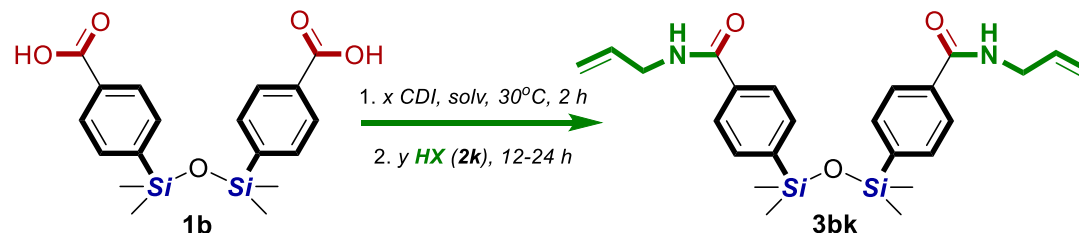
### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N,N-dimethylbenzamide):

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.58$  (d,  $^3J = 8$  Hz, 4H);  $\delta = 7.37$  (d,  $^3J = 8$  Hz, 4H);  $\delta = 2.98$  (s, 6H);  $\delta = 2.88$  (s, 6H);  $\delta = 0.33$  (s, 12H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 170.43, 140.82, 137.97, 133.13, 126.60, 35.11, 1.44$ .  $^{29}\text{Si}$  NMR (80 MHz, DMSO- $d_6$ ):  $\delta = -0.61$ .  $^{15}\text{N}$  NMR (40 MHz, DMSO- $d_6$ ):  $\delta = \text{HRMS (ESI) } m/z$   $[\text{M} + \text{H}]^+$ : calcd for  $[\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}_2 + \text{H}]^+$ , 429.2024; found, 429.2024;  $[\text{M} + \text{Na}]^+$ : calcd for  $[\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}_2 + \text{Na}]^+$ , 451.1844; found, 451.1840;  $[\text{M} + \text{K}]^+$ : calcd for  $[\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_3\text{Si}_2 + \text{K}]^+$ , 467.158; found, 467.1588. IR ( $\text{cm}^{-1}$ ): 2955, 1628, 1507-1398, 1254, 1074, 833, 790.





## Method of synthesis and characterization data for 3bk



Equivalent of x (per molecule)	Equivalent of y	Solvent	Temperature, °C	Conversion
2.1	4	THF	30	60
2.1	8	THF	30	90-100

The conversion was determined by  $^1\text{H}$  NMR.

Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H  $\times$  diam. 100 mm  $\times$  10 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylNH<sub>2</sub> (121.8 mg, 2.136 mmol, 8 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the conversion was determined by  $^1\text{H}$  NMR.

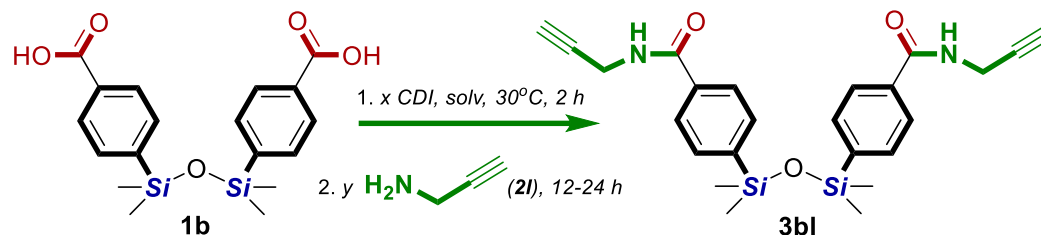
### Large-scale synthesis

Method of **3bk** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H  $\times$  diam. 160 mm  $\times$  16 mm) under an argon atmosphere at 30 °C. After 2 hours, AllylNH<sub>2</sub> (608.8 mg, 10.680 mmol, 8 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3ba** was obtained as a yellowish\* powder with the 90% yield.

### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N-allylbenzamide):

$^1\text{H}$  NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 8.69 (t,  $^3\text{J}$ =8 Hz, 2H),  $\delta$  = 7.87 (d,  $^3\text{J}$ =11 Hz, 4H),  $\delta$  = 7.62 (d,  $^3\text{J}$ =11 Hz, 4H),  $\delta$  = 5.96-5.84 (m, 2H),  $\delta$  = 5.20-5.06 (m, 4H),  $\delta$  = 3.92 (t,  $^3\text{J}$ =7 Hz, 4H),  $\delta$  = 0.33 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 173.62, 166.52, 143.00, 135.88, 133.18, 126.92, 115.54, 41.99, 1.13.  $^{29}\text{Si}$  NMR (80 MHz, DMSO-d<sub>6</sub>):  $\delta$  = -0.56.  $^{15}\text{N}$  NMR (40 MHz, DMSO-d<sub>6</sub>):  $\delta$  = 109.80. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 453.2024; found, 453.2026. IR (cm<sup>-1</sup>): 3279, 2953, 1636, 1539, 1305, 1254, 1107, 1070, 838-668.

## Method of synthesis and characterization data for **3bl**



Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, propargyl amine (58 mg, 1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 75%. Then, the solvent was evaporated and the isolation of the product was carried out by a flash-chromatography in MeCN. **3bl** was obtained as a yellowish\* powder.

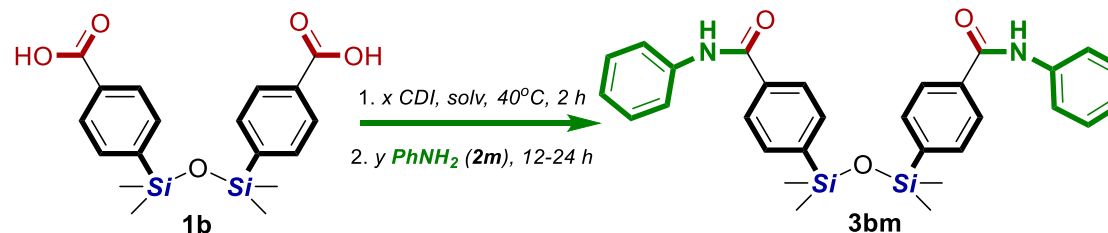
### Large-scale synthesis

Method of **3bl** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 40 °C. After 2 hours, propargyl amine (288.36 mg, 5.340 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a flash-chromatography in MeCN. **3bl** was obtained as a yellowish\* powder with the 53% yield.

### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N-(prop-2-yn-1-yl)benzamide):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 8.93 (t, <sup>3</sup>J=8 Hz, 2H), δ = 7.85 (d, <sup>3</sup>J=11 Hz, 4H), δ = 7.63 (d, <sup>3</sup>J=11 Hz, 4H), δ = 4.08-4.05 (m, 4H), δ = 3.10 (t, <sup>4</sup>J=3 Hz, 2H), δ = 0.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 165.91, 142.89, 134.68, 132.78, 126.45, 81.26, 72.79, 28.47, 0.63. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = -0.49. <sup>15</sup>N NMR (40 MHz, DMSO-d<sub>6</sub>): δ = 107.75. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 449.1711; found, 449.1729. IR (cm<sup>-1</sup>): 3339, 3234, 1640, 1543, 1313, 1258, 1112, 1065, 838, 794.

## Method of synthesis and characterization data for 3bm



Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, aniline (99.3 mg, 1.068 mmol, 4 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 84%. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bm** was obtained as a yellowish\* powder.

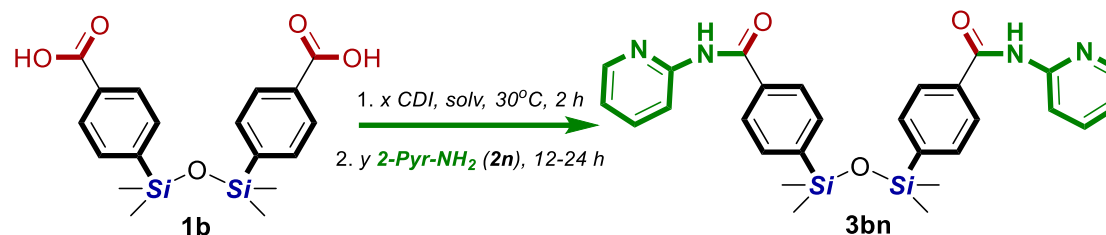
### Large-scale synthesis

**Method of 3bm synthesis:** **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 40 °C. After 2 hours, aniline (496.62 mg, 5.340 mmol, 4 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by a one-time-3% HCl wash and further water extraction from DCM. **3bm** was obtained as a yellowish\* powder with the 73% yield.

### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N-phenylbenzamide):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 10.28 (s, 2H), δ = 7.98 (d, <sup>3</sup>J=11 Hz, 4H), δ = 7.82 (d, <sup>3</sup>J=10 Hz, 4H), δ = 7.71 (d, <sup>3</sup>J=11 Hz, 4H), δ = 7.36 (t, <sup>3</sup>J=10 Hz, 4H), δ = 7.10 (t, <sup>3</sup>J=10 Hz, 2H), δ = 0.39 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 166.57, 143.02, 139.16, 135.94, 132.77, 128.56, 126.88, 123.64, 120.34, 0.69. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = -0.45. <sup>15</sup>N NMR (40 MHz, DMSO): δ = 129.14. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 525.2024; found, 525.2082; [M + K]<sup>+</sup>: calcd for [C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + K]<sup>+</sup>, 563.1583; found, 563.1574; [M + Na]<sup>+</sup>: calcd for [C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 547.1844; found, 547.1843; [M + NH<sub>4</sub>]<sup>+</sup>: calcd for [C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>Si<sub>2</sub> + NH<sub>4</sub>]<sup>+</sup>, 542.2290; found, 542.2286. IR (cm<sup>-1</sup>): 3268-2958, 1648, 1599, 1542, 1443, 1329, 1258, 1050, 832-758.

## Method of synthesis and characterization data for **3bn**



Reaction conditions: **1b** (100.0 mg, 0.267 mmol), CDI (90.8 mg, 0.561 mmol, 2.1 eq) and 1 ml of THF were stirred in Schott culture tubes (H × diam. 100 mm × 10 mm) under an argon atmosphere at 30 °C. After 2 hours, 2-aminopyridine (200.8 mg, 2.136 mmol, 8 eq.) was added and the reaction was left to stir overnight. The conversion determined by <sup>1</sup>H NMR made up 85%. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM and further column-chromatography in acetone. **3bn** was obtained as yellowish\* crystals.

### Large-scale synthesis

Method of **3bn** synthesis: **1b** (500.0 mg, 1.335 mmol), CDI (454.2 mg, 2.804 mmol, 2.1 eq) and 5 ml of THF were stirred in Schott culture tubes (H × diam. 160 mm × 16 mm) under an argon atmosphere at 30 °C. After 2 hours, 2-aminopyridine (1003.92 mg, 10.680 mmol, 8 eq.) was added and the reaction was left to stir overnight. Then, the solvent was evaporated and the isolation of the product was carried out by water extraction from DCM and further column-chromatography in acetone. **3bn** was obtained as yellowish\* crystals with the 44% yield.

### Characterisation data for 4,4'-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(N-(pyridin-2-yl)benzamide):

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 10.76 (s, 2H), δ = 8.39-8.37 (m, 2H), δ = 8.21 (m, 2H), δ = 8.03(d, <sup>3</sup>J= 11Hz, 4H), δ = 7.86-7.80 (m, 2H), δ = 7.68 (d, <sup>3</sup>J= 11 Hz, 4H), δ = 7.18-7.13 (m, 2H), δ = 0.37 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 165.97, 152.14, 147.90, 143.46, 138.06, 134.99, 132.76, 127.15, 119.79, 114.70, 0.67. <sup>29</sup>Si NMR (80 MHz, DMSO-d<sub>6</sub>): δ = -0.39. <sup>15</sup>N NMR (40 MHz, DMSO-d<sub>6</sub>): δ = 288.93, 138.27. HRMS (ESI) m/z [M + H]<sup>+</sup>: calcd for [C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>3</sub>Si<sub>2</sub> + H]<sup>+</sup>, 527.1929; found, 527.1964; [M + K]<sup>+</sup>: calcd for [C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>3</sub>Si<sub>2</sub> + K]<sup>+</sup>, 565.1488; found, 565.1482; [M + Na]<sup>+</sup>: calcd for [C<sub>28</sub>H<sub>30</sub>N<sub>4</sub>O<sub>3</sub>Si<sub>2</sub> + Na]<sup>+</sup>, 549.1749; found, 549.1746. IR (cm<sup>-1</sup>): 2957, 1676, 1582, 1539, 1437, 1306, 1254, 1074, 831, 794.

# Crystallographic data of 3ah,al,am,bc,bi,bj,bk,bn and 4.

Identification code	3bc	3bj	3al	3am	3bn	3bi	4	3bk	3ah
Empirical formula	C <sub>24</sub> H <sub>26</sub> O <sub>5</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>2</sub>	C <sub>15</sub> H <sub>23</sub> NO <sub>2</sub> Si <sub>2</sub>	C <sub>18</sub> H <sub>25</sub> NO <sub>2</sub> Si <sub>2</sub>	C <sub>28</sub> H <sub>30</sub> N <sub>4</sub> O <sub>3</sub> Si <sub>2</sub>	C <sub>30</sub> H <sub>43</sub> N <sub>3</sub> O <sub>5</sub> Si <sub>3</sub>	C <sub>37</sub> H <sub>46</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>12</sub> Si <sub>2</sub>	C <sub>24</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub> Si <sub>2</sub>	C <sub>12</sub> H <sub>21</sub> NO <sub>2</sub> Si <sub>2</sub>
Formula weight	450.63	428.67	305.52	343.57	526.74	609.94	922.04	452.69	267.48
Temperature/K	100	100	100	100	100	100	100	140	120
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	C2/c	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P-1	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P-1	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Cc
a/Å	27.3484(9)	6.1230(12)	17.612(2)	8.8577(8)	12.2575(3)	13.6295(8)	12.4163(3)	9.8135(17)	12.8516(8)
b/Å	9.8255(4)	11.555(2)	10.8605(14)	13.1585(10)	7.9709(2)	14.8131(8)	13.6044(3)	13.780(3)	12.8118(7)
c/Å	8.9313(4)	17.020(3)	9.0964(12)	18.2092(15)	28.4737(7)	17.2611(9)	14.8077(3)	18.422(4)	36.527(2)
α/°	90	90	90	89.871(3)	90	90	104.2380(10)	90	90
β/°	100.359(2)	100.03(3)	90.485(10)	76.174(3)	98.2670(10)	109.806(3)	108.8160(10)	90	90.064(3)
γ/°	90	90	90	72.851(3)	90	90	106.8640(10)	90	90
Volume/Å <sup>3</sup>	2360.83(16)	1185.8(4)	1739.9(4)	1963.9(3)	2753.07(12)	3278.8(3)	2100.61(8)	2491.3(8)	6014.2(6)
Z	4	2	4	4	4	4	2	4	16
ρ <sub>calc</sub> /cm <sup>3</sup>	1.268	1.201	1.166	1.162	1.271	1.236	1.458	1.207	1.182
μ/mm <sup>-1</sup>	0.182	0.195	0.205	0.189	0.165	0.186	1.133	0.169	2.079
Crystal size/mm <sup>3</sup>	0.11 × 0.04 × 0.04	0.07 × 0.05 × 0.03	0.32 × 0.11 × 0.06	0.12 × 0.11 × 0.09	0.21 × 0.12 × 0.11	0.23 × 0.22 × 0.19	0.15 × 0.15 × 0.12	0.23 × 0.14 × 0.12	0.43 × 0.27 × 0.06
Radiation	MoKα (λ = 0.71073)	synchrotron (λ = 0.745)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2θ range for	4.414 to 61.14	4.488 to	4.406 to	3.844 to 61.51	4.104 to	3.722 to	3.374 to	3.69 to 52.244	4.838 to

data collection/°		54.746	52.588		61.206	52.044	61.228		144.184
Reflections collected	11138	7991	17232	33236	64472	20534	31110	17722	44045
R <sub>int</sub>	0.0569	0.1065	0.1222	0.1133	0.0636	0.0777	0.0451	0.1739	0.0431
Data/restraints /parameters	3591/0/164	2342/0/140	3480/0/186	12128/0/425	8455/0/338	6415/6/492	12809/0/524	4937/0/285	9908/2/634
Goodness-of-fit on F <sup>2</sup>	1.045	1.064	1.085	0.995	1.089	1.232	1.016	1.028	1.013
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0516, wR <sub>2</sub> = 0.1057	R <sub>1</sub> = 0.0721, wR <sub>2</sub> = 0.1572	R <sub>1</sub> = 0.0786, wR <sub>2</sub> = 0.1485	R <sub>1</sub> = 0.0729, wR <sub>2</sub> = 0.1360	R <sub>1</sub> = 0.0561, wR <sub>2</sub> = 0.1362	R <sub>1</sub> = 0.1264, wR <sub>2</sub> = 0.2721	R <sub>1</sub> = 0.0436, wR <sub>2</sub> = 0.0928	R <sub>1</sub> = 0.1017, wR <sub>2</sub> = 0.1821	R <sub>1</sub> = 0.1072, wR <sub>2</sub> = 0.2802
Final R indexes [all data]	R <sub>1</sub> = 0.0938, wR <sub>2</sub> = 0.1195	R <sub>1</sub> = 0.1119, wR <sub>2</sub> = 0.1772	R <sub>1</sub> = 0.1295, wR <sub>2</sub> = 0.1663	R <sub>1</sub> = 0.1435, wR <sub>2</sub> = 0.1603	R <sub>1</sub> = 0.0658, wR <sub>2</sub> = 0.1422	R <sub>1</sub> = 0.1514, wR <sub>2</sub> = 0.2827	R <sub>1</sub> = 0.0739, wR <sub>2</sub> = 0.1055	R <sub>1</sub> = 0.1907, wR <sub>2</sub> = 0.2195	R <sub>1</sub> = 0.1088, wR <sub>2</sub> = 0.2825
Largest diff. peak/hole / e Å <sup>-3</sup>	0.32/-0.34	0.42/-0.34	0.38/-0.36	0.49/-0.54	0.62/-0.33	0.68/-0.54	0.54/-0.47	0.93/-0.32	1.35/-0.97
Flack parameter								0.1(5)	0.10(6)
CCDC number	2181701	2181709	2181708	2181703	2181704	2181707	2181705	2181702	2181706