

## Supporting information

### Cooperative Duplex Formation by Synthetic H-Bonding Oligomers

Alexander E. Stross, Giulia Iadevaia, Christopher A. Hunter\*

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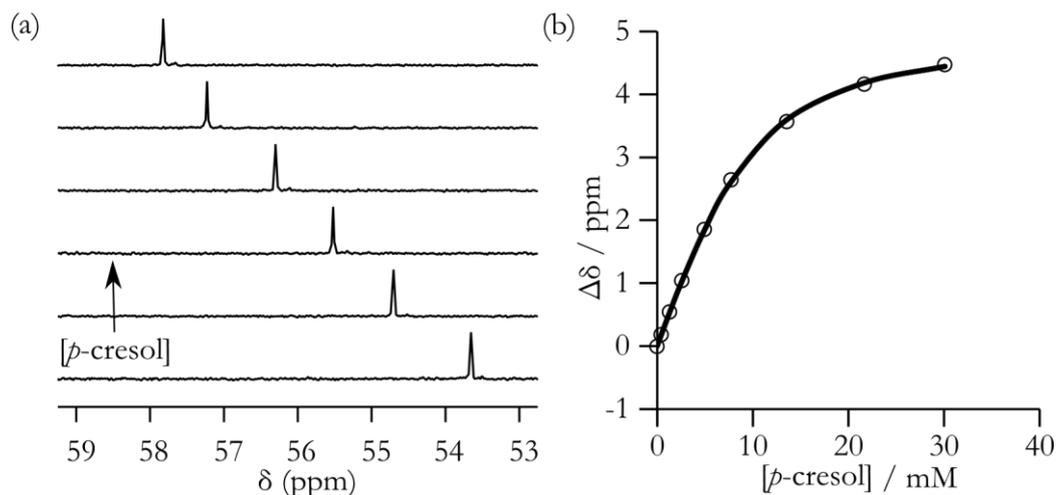
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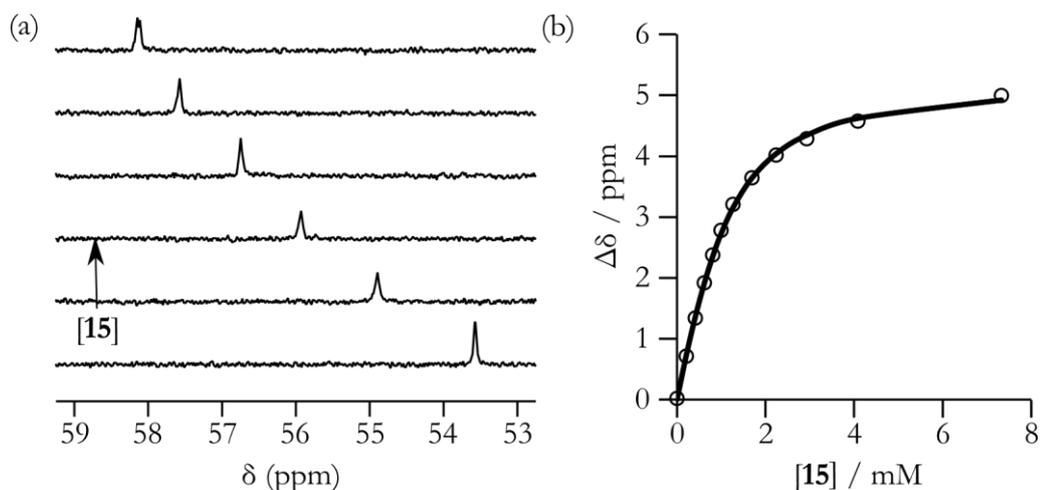
\*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW

## S1: NMR titrations

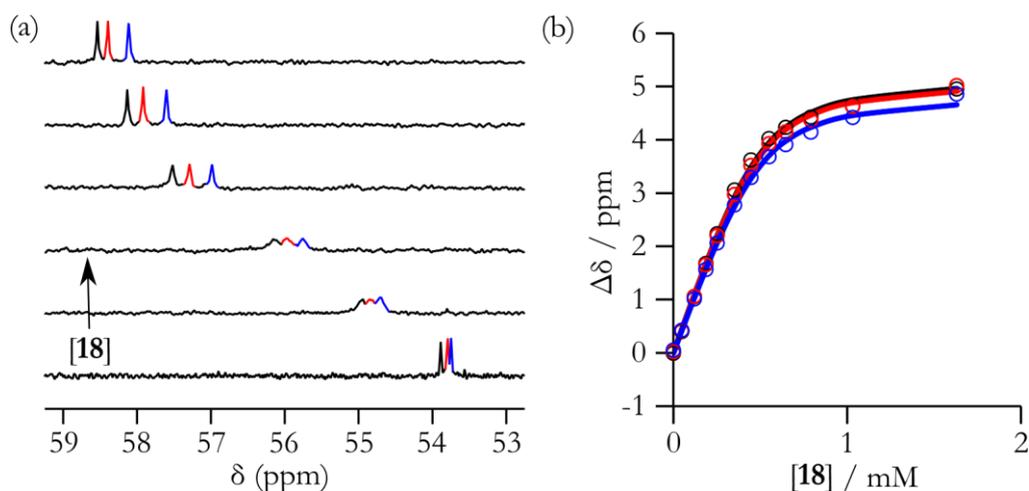
All binding constants were measured by NMR titrations. The host was dissolved in toluene- $d_8$  at a known concentration. The guest is dissolved in the host solution and made to a known concentration. A known volume of host is added to an NMR tube and the spectrum was recorded. Known volumes of guest in host solution were added to the NMR tube, and the spectra were recorded after each addition. The chemical shifts of the host spectra were monitored as a function of guest concentration and analysed using a purpose written software in Microsoft Excel. Errors were calculated as two times the standard deviation from the average value.



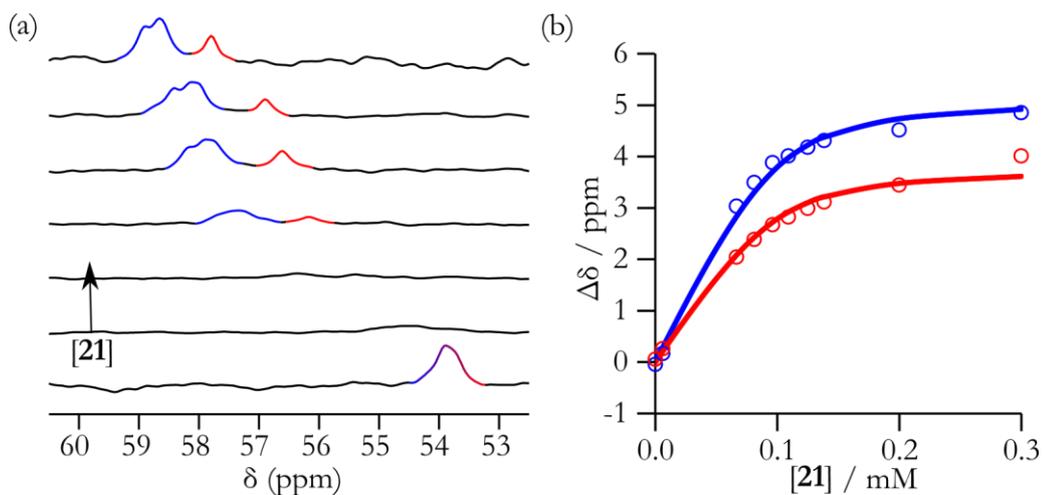
**Figure S1.**  $^1\text{H}$  NMR data for titration of *p*-cresol into **5** (9.1 mM) at 298 K in toluene- $d_8$ . (a) Example 162 MHz  $^{31}\text{P}$  NMR spectra. (b) Plot of the change in chemical shift of the  $^{31}\text{P}$  signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).



**Figure S2.**  $^{31}\text{P}$  NMR data for titration of **15** into **14** (2.0 mM) at 298 K in toluene- $d_8$ . (a) Example 162 MHz  $^{31}\text{P}$  NMR spectra. (b) Plot of the change in chemical shift of the  $^{31}\text{P}$  signal as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).



**Figure S3.**  $^{31}\text{P}$  NMR data for titration of **18** into **17** (0.5 mM) at 298 K in toluene- $d_8$ . (a) Example 162 MHz  $^{31}\text{P}$  NMR spectra. (b) Plot of the change in chemical shift of the  $^{31}\text{P}$  signals as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm).



**Figure S4.**  $^{31}\text{P}$  NMR data for titration of **21** into **20** (0.1 mM) at 298 K in toluene- $d_8$ . (a) Example 162 MHz  $^{31}\text{P}$  NMR spectra. (b) Plot of the change in chemical shift of the  $^{31}\text{P}$  signals as a function of guest concentration (the line represents the best fit to a 1:1 binding isotherm). Due to the low host concentration and peak broadening throughout the titration a high line broadening (40 Hz) was used to monitor three of the four  $^{31}\text{P}$  chemical shifts as one broad peak.

**Table S1.**  $^{31}\text{P}$  NMR chemical shifts of free host (ppm) obtained by fitting titration data measured in toluene- $d_8$  at 298 K to a 1:1 binding isotherm.

A...D	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$
5• <i>p</i> -cresol	14•15	17•18	20•21
53.7	53.6	53.9	53.9
	53.6	53.8	53.9
		53.7	53.9
			53.8

**Table S2.** Limiting complexation-induced  $^{31}\text{P}$  NMR chemical shifts of fully bound host (ppm) obtained by fitting titration data measured in toluene- $d_8$  at 298 K to a 1:1 binding isotherm.

A...D	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$	$\left[ \begin{smallmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{smallmatrix} \right]$
5• <i>p</i> -cresol	14•15	17•18	20•21
58.7	58.8	59.0	59.0
	58.8	58.7	59.0
		58.5	59.0
			57.6

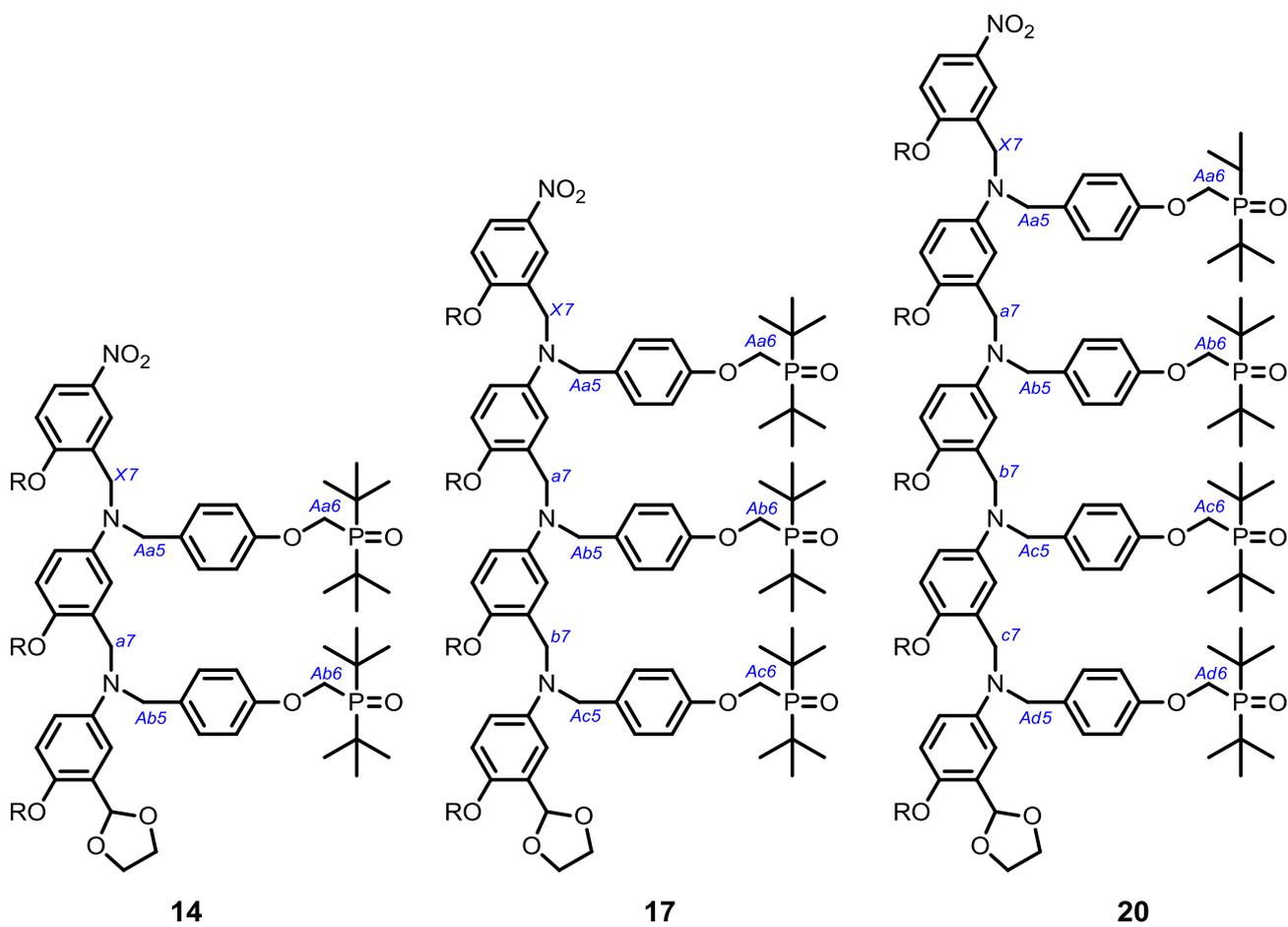


Figure S5. Proton labelling scheme. R=2-ethylhexyl

**Table S3.**  $^1\text{H}$  NMR chemical shifts of the free host (ppm) obtained by fitting titration data measured in toluene- $d_8$  at 298 K to a 1:1 binding isotherm.<sup>a</sup>

proton label	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$
	14•15	17•18	20•21
Aa6	4.2	4.2	4.3
Ab6	4.1	4.3	4.2
Ac6		4.2	4.4
Ad6			4.2
X7	4.5	4.6	4.5
a7	4.6	4.7	4.7
b7		4.7	4.7
c7			4.7
Aa5	4.4	4.4	4.3
Ab5	4.3	4.1	4.3
Ac5		4.1	4.1
Ad5			4.1

<sup>a</sup> refer to Figure S5 for proton labelling scheme

**Table S4.** Limiting complexation-induced  $^1\text{H}$  NMR chemical shifts of the free host (ppm) obtained by fitting titration data measured in toluene- $d_8$  at 298 K to a 1:1 binding isotherm.<sup>a</sup>

proton label	$\begin{bmatrix} \text{A} \\ \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \\ \text{D} \\ \text{A} \\ \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \\ \text{D} \\ \text{A} \\ \text{D} \\ \text{A} \\ \text{D} \end{bmatrix}$
	14•15	17•18	20•21
Aa6	4.3	4.4	4.5
Ab6	4.2	4.5	4.3
Ac6		4.4	4.6
Ad6			<sup>b</sup>
X7	4.5	4.6	4.5
a7	4.6	4.8	<sup>b</sup>
b7		4.8	<sup>b</sup>
c7			<sup>b</sup>
Aa5	4.3	4.3	<sup>b</sup>
Ab5	4.3	4.0	<sup>b</sup>
Ac5		4.1	4.0
Ad5			4.1

<sup>a</sup> refer to Figure S5 for numbering scheme; <sup>b</sup> signal could not be monitored due to signal overlap.

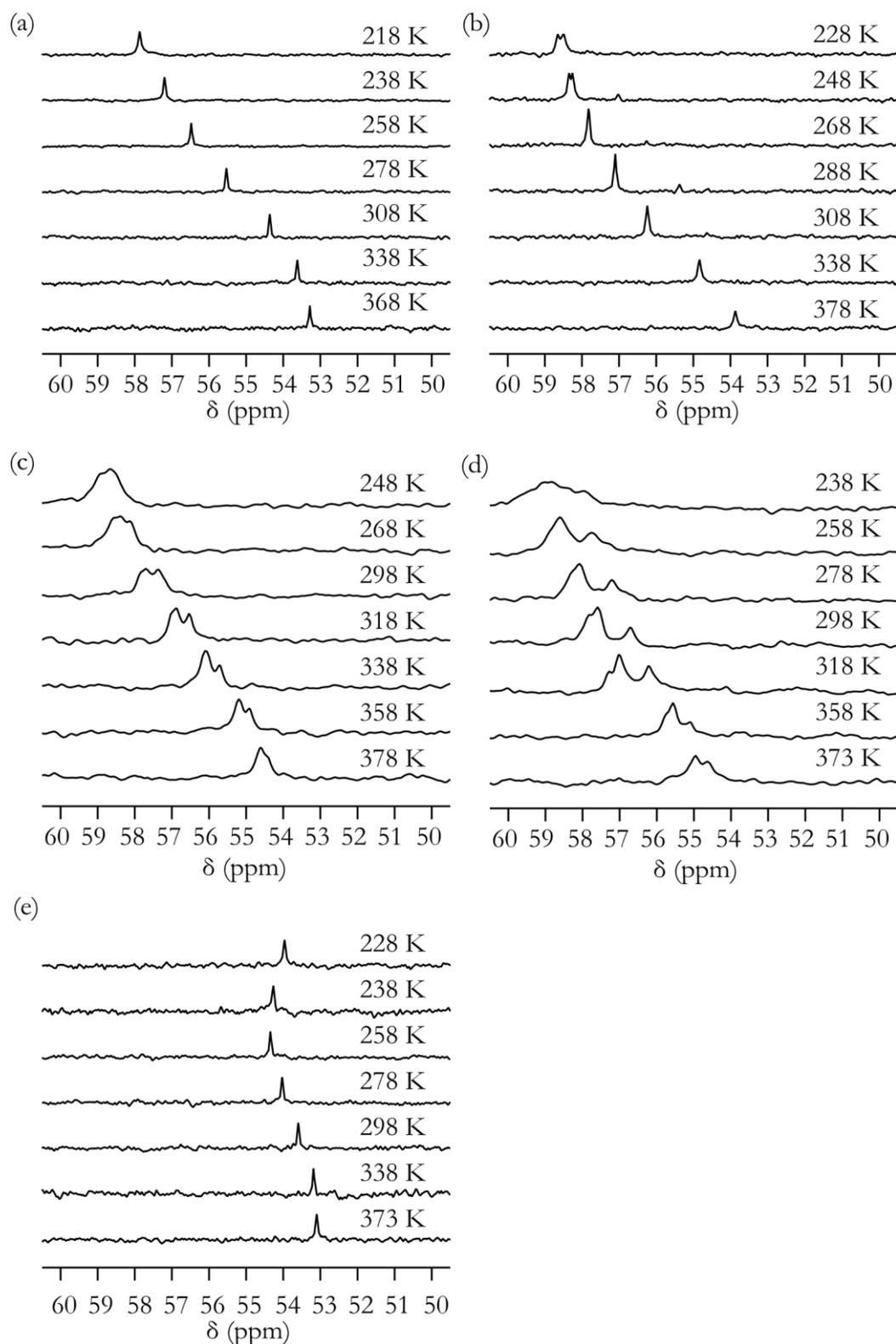
**Table S5.** Limiting complexation-induced changes in  $^1\text{H}$  NMR chemical shift changes (ppm) obtained by fitting titration data measured in toluene- $d_8$  at 298 K to a 1:1 binding isotherm.<sup>a</sup>

proton label	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$	$\begin{bmatrix} \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \\ \text{A} \cdots \text{D} \end{bmatrix}$
	14•15	17•18	20•21
Aa6	0.1	0.2	0.2
Ab6	0.1	0.2	0.1
Ac6		0.2	0.2
Ad6			
X7	0.0	0.1	0.0
a7	0.0	0.1	<sup>b</sup>
b7		0.1	<sup>b</sup>
c7			<sup>b</sup>
Aa5	-0.1	0.0	<sup>b</sup>
Ab5	0.0	-0.1	<sup>b</sup>
Ac5		-0.1	-0.1
Ad5			0.0

<sup>a</sup> refer to Figure S5 for numbering scheme; <sup>b</sup> signal could not be monitored due to signal overlap.

## Section S2: Variable temperature NMR

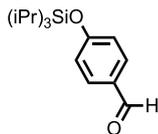
The temperature of the sample was changed using the internal thermostat of the NMR spectrometer, and the sample was allowed to equilibrate in the probe until the probe thermometer gave a stable temperature. The two chemically different  $^{31}\text{P}$  signals in **14•15** gave a single overlapping peak that began to split into two signals at lower temperatures, so for high temperatures the chemical shift at the peak maximum was used, and at lower temperatures, the average of the chemical shifts of the two peaks was used (Figure S6 (b)). Due to significant broadening of the  $^{31}\text{P}$  NMR peaks for **17•18** 40 Hz line broadening was applied to all spectra. At high temperatures where one broad peak was observed, the chemical shift was recorded at the highest point of the peak. At lower temperatures, two of the three separate signals were resolved, so the average of the chemical shifts of the peaks was used (Figure S6(c)). Even after applying the same processing (40 Hz line broadening) to the spectra of **30•27** the peaks were too broad at lower temperatures to reliably distinguish from the background noise. (Figure S6(d)). Figure S6(e) shows the  $^{31}\text{P}$  NMR spectra of phosphine oxide 1-mer **5** only (1 mM) at various temperatures.



**Figure S6.** Variable temperature 162 MHz  $^{31}\text{P}$  NMR spectra in toluene- $d_8$  for 1 mM solutions of 1:1 mixtures of (a) *p*-cresol•5; (b) 14•15; (c) 17•18; (d) 20•21; and (e) only 5. A high line broadening (40 Hz) was applied to the spectra in (c) and (d).

## Section S3: Synthesis

Synthesis of **1**<sup>1</sup>



4-Hydroxybenzaldehyde (5.01 g, 40.9 mmol, 1 equiv.) was dissolved in DMF (50 mL) and TiPS-Cl (10.1 mL, 47.1 mmol, 1.2 equiv.) and imidazole (5.58 g, 81.9 mmol, 2 equiv.) were added with stirring. After 12 hours stirring, the reaction mixture was poured onto water (100 mL), before extraction into hexane ( $5 \times 20$  mL). The organic fractions were washed several times with water ( $5 \times 100$  mL) then brine ( $1 \times 100$  mL), dried ( $\text{MgSO}_4$ ) and the solvent was removed with a rotary evaporator to yield an oil (12.8 g). The crude product was purified by flash chromatography on silica eluting with 10% EtOAc in hexane to yield a pale yellow oil (11.0 g, 96%).

**<sup>1</sup>H NMR (250 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 9.89$  (s, 1H), 7.79 (d, 2H,  $J = 9.0$ ), 6.99 (d, 2H,  $J = 9.0$ ), 1.20 – 1.38 (m, 3H), 1.07 – 1.16 (m, 18H);

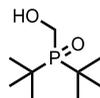
**<sup>13</sup>C NMR (63 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 190.8, 161.9, 131.9, 130.2, 120.3, 17.8, 12.7$ ;

**MS (ES+):**  $m/z$  (%) = 279 (100) [ $\text{M} + \text{H}^+$ ];

**HRMS (ES+):** calculated for  $\text{C}_{16}\text{H}_{27}\text{O}_2\text{Si}$  279.1780, found 279.1791;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2945, 2893, 2867, 2730, 1698, 1596, 1575, 1508, 1463, 1275, 1211, 1155.

## Synthesis of **2**<sup>2</sup>



Di-*tert*-butylchlorophosphine (20.0 g, 111 mmol) was dissolved in 37% aqueous formaldehyde (210 mL) and concentrated aqueous HCl (200 mL) was added and heated to 100 °C for 12 hours with stirring. The reaction mixture was cooled to room temperature before being neutralised using NaOH. The aqueous solution was washed with EtOAc (3 × 100 mL). The organic fractions were washed with brine (1 × 100 mL), dried (MgSO<sub>4</sub>) and the solvent removed using a rotary evaporator. The crude product was recrystallized in boiling hexane to yield a white solid (11.1 g, 52%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 4.05 (s, 2H), 1.28 (d, 18H, *J* = 13);

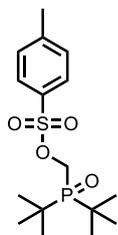
**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 54.8 (d, *J* = 62), 34.8 (d, *J* = 55), 26.4;

**<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>P</sub> = 154.0;

**MS (ES+):** *m/z* (%) = 193 (100) [M + H<sup>+</sup>];

**HRMS (ES+):** calculated for C<sub>9</sub>H<sub>22</sub>O<sub>2</sub>P 193.1357, found 193.1367;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 3142, 2957, 1474, 1129, 1120, 1064.



**2** (9.2 g, 48 mmol, 1 equiv.) was dissolved in THF 130 mL and NEt<sub>3</sub> (10 mL) at 0 °C with stirring. 4-toluenesulfonyl chloride (11.4 g, 60 mmol, 1.3 equiv.) in THF (30 mL) was added slowly over 20 minutes. After 18 hours the mixture was poured onto water (100 mL) and extracted into EtOAc (3 × 20 mL). The organic extracts were washed with water (1 × 20 mL) and brine (1 × 2 mL) before drying (MgSO<sub>4</sub>). The solvent was removed using a rotary evaporator and the crude product purified by flash chromatography on silica eluting with a gradient from 0% to 3% MeOH in DCM to yield a colourless oil, which after several days crystallised into a white amorphous solid (14.4 g, 87%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.81 (d, 2H, *J* = 8.0), 7.39 (d, 2H, *J* = 8.0), 4.27 (d, 2H, *J* = 7.0), 2.47 (s, 3H), 1.29 (d, 18H, *J* = 13.8);

**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 145.7, 131.1, 130.0, 128.2, 61.4 (d, *J* = 60.5), 35.6 (d, *J* = 58.5), 26.2, 21.6;

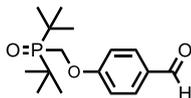
**<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>P</sub> = 56.0;

**MS (ES<sup>+</sup>):** *m/z* (%) = 347 (100) [M + H<sup>+</sup>];

**HRMS (ES<sup>+</sup>):** calculated for C<sub>16</sub>H<sub>28</sub>O<sub>4</sub>PS 347.1446, found 347.1456;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 3431, 2968, 2874, 1597, 1478, 1369, 1190, 1176, 1146, 1095, 996.

## Synthesis of **4**



4-hydroxybenzaldehyde (0.55 g, 4.5 mmol, 1 equiv.) was dissolved in DMF (20 mL) and **3** (1.70 g, 4.9 mmol, 1.1 equiv.) and Cs<sub>2</sub>CO<sub>3</sub> (2.18 g, 6.69 mmol, 1.5 equiv.) were added and the mixture heated at 80 °C for 3 days with stirring. The reaction was then poured onto water (100 mL) and extracted into EtOAc (5 × 20 mL), before being washed with water (5 × 40 mL) and brine (1 × 40 mL) and then dried (MgSO<sub>4</sub>). The solvent was removed using a rotary evaporator before the crude product was purified using flash chromatography on silica eluting with a gradient from 0% to 10% MeOH in diethyl ether to yield an amorphous white solid (0.88 g, 66%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 9.93 (s, 1H), 7.89 (d, 2H, *J* = 9.0), 7.07 (d, 2H, *J* = 9.0), 4.48 (d, 2H, *J* = 7.0), 1.40 (d, 18H, *J* = 14.0);

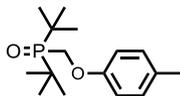
**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 190.2, 162.8 (d, *J* = 9.6), 131.8, 130.7, 114.33, 62.6 (d, *J* = 68.1), 35.2 (d, *J* = 57.6), 26.2;

**<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>P</sub> = 56.5;

**MS (ES+):** *m/z* (%) = 297 (100) [M + H<sup>+</sup>], 338 (15) [M + CH<sub>3</sub>CN], 360 (10);

**HRMS (ES+):** calculated for C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>P 297.1620, found 297.1619;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2967, 2906, 2871, 1694, 1603, 1582, 1509, 1306, 1242, 1163, 1133, 1041.



*p*-Cresol (0.21 g, 1.9 mmol, 1 equiv.) was dissolved in DMF (10 mL) and **3** (0.73 g, 2.1 mmol, 1.1 equiv.) and Cs<sub>2</sub>CO<sub>3</sub> (0.93 g, 2.86 mmol, 1.5 equiv.) were added and stirred at 80 °C for 12 h. The reaction mixture was poured onto water (100 ml) and extracted into EtOAc (5 × 20 mL), before being washed with water (5 × 20 mL), brine (1 × 20 mL) and dried (MgSO<sub>4</sub>). The solvent was removed using a rotary evaporator and the crude product was purified via flash chromatography on silica eluting with a gradient from 0% to 10% MeOH in EtOAc to yield a white amorphous solid (0.21 g, 39%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.12 (d, 2H, *J* = 8.5), 6.83 (d, 2H, *J* = 8.5), 4.37 (d, 2H, *J* = 8.0), 2.30 (s, 3H), 1.39 (d, 18H, *J* = 13.5);

**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 156.3 (d, *J* = 10.5), 131.1, 130.1, 113.1, 62.6 (d, *J* = 70.5), 35.4 (d, *J* = 56.5), 26.4, 20.4;

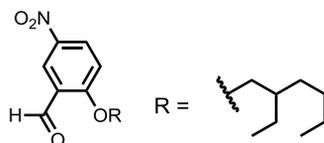
**<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>P</sub> = 56.8;

**MS (ES<sup>+</sup>):** *m/z* (%) = 283 (100) [M + H<sup>+</sup>], 346 (50), 383 (15);

**HRMS (ES<sup>+</sup>):** calculated for C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>P 283.1827, found 283.1840;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 3431, 2955, 2874, 1597, 1478, 1368, 1190, 1176, 1145, 996.

## Synthesis of **6**



2-Hydroxy-5-nitrobenzaldehyde (15 g, 90 mmol, 1 equiv.), K<sub>2</sub>CO<sub>3</sub> (18.6 g, 135 mmol, 1.5 equiv.) and 2-ethylhexyl bromide (23.9 mL, 135 mmol, 1.5 equiv.) were dissolved in DMF (100 mL) and heated to 70 °C for 4 days with stirring. The mixture was then poured onto water (100 mL) and extracted into ethyl acetate (3 × 100 mL), before being washed with water (5 × 200 mL) and finally brine (1 × 100 mL). The organic fractions were dried (MgSO<sub>4</sub>) and the solvent removed using a rotary evaporator to give the crude oil (38.8 g), which was purified by flash chromatography on silica eluting with 10% ethyl acetate in hexane to give product yellow oil (23.0 g, 91%).

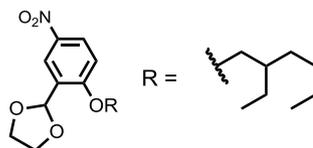
**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 10.48 (s, 1H), 8.70 (d, 1H, *J* = 3.0), 8.42 (dd, 1H, *J* = 9.0, 3.0), 7.12 (d, 1H, *J* = 9.0), 4.11 (d, 2H, *J* = 6.0), 1.86 (s, 1H), 1.23 – 1.64 (m, 8H), 0.84 – 1.03 (m, 6H);

**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 187.4, 165.4, 141.4, 124.7, 124.4, 112.9, 72.3, 39.3, 30.4, 29.0, 23.9, 22.9, 13.9, 11.0;

**MS (ES<sup>+</sup>):** *m/z* (%) = 280 (100) [M + H<sup>+</sup>], 291 (20).

**HRMS (ES<sup>+</sup>):** calculated for C<sub>15</sub>H<sub>22</sub>NO<sub>4</sub> 280.1549, found 280.1541;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2960, 2931, 2873, 1692, 1608, 1590, 1522, 1488, 1461, 1429, 1176, 1142, 1077, 1005.



**6** (14.1 g, 50.6 mmol, 1 equiv.) was dissolved in toluene (75 mL) and *p*-toluenesulfonic acid (0.19 g, 1.01 mmol, 0.02 equiv.) and ethylene glycol (9.43, 151 mmol, 3 equiv.) were added and the solution heated to reflux with stirring. The toluene/water condensate was removed using Dean-Stark apparatus until the condensate ran clear. The reaction was cooled to room temperature and poured onto water (100 mL) before being extracted into EtOAc (3 × 50 mL). The organic fractions were collected and washed with brine (1 × 100 mL), dried (MgSO<sub>4</sub>), and concentrated on a rotary evaporator. The crude product required no further purification and was isolated as a golden viscous oil (15.9 g, 96% yield).

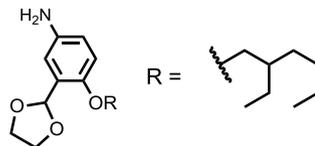
**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 8.43 (d, 1H, *J* = 3.0), 8.24 (dd, 1H, *J* = 9.0, 3.0), 6.96 (d, 1H, *J* = 9.0), 6.14 (s, 1H), 4.03 – 4.22 (m, 4H), 4.01 (d, 2H, *J* = 5.5), 1.73 – 1.89 (m, 1H), 1.24 – 1.61 (m, 8H), 0.87 – 1.00 (m, 6H);

**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 162.3, 141.1, 127.5, 126.4, 123.3, 111.2, 98.3, 71.8, 65.4, 39.2, 30.4, 29.0, 14.0, 11.0;

**MS (ES+):** *m/z* (%) = 324 (100) [M + H<sup>+</sup>].

**HRMS (ES+):** calculated for C<sub>17</sub>H<sub>26</sub>NO<sub>6</sub> 324.1811, found 324.1820.

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2959, 2931, 2875, 1613, 1596, 1518, 1494, 1463, 1340, 1270, 1105, 1067.



**7** (30.56 g, 94.51 mmol, 1 equiv., 0.2 M) was dissolved in in degassed EtOAc (475 mL) and Pd/C (2.01 g, 18.9 mmol) was added with rigorous stirring. The reaction was stirred in an atmosphere of H<sub>2</sub> overnight. The reaction is then filtered through a plug of Celite and the solvent was removed using a rotary evaporator to yield a dark red oil. The crude product was purified by flash chromatography on silica eluting with a gradient from 30% to 40% of EtOAc/hexane. The product was isolated as a yellow oil (23.4 g, 84%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 6.94 (d, 1H, *J* = 3.0), 6.76 (d, 1H, *J* = 8.5), 6.69 (dd, 1H, *J* = 8.50, 3.0), 6.12 (s, 1H), 3.98 – 4.18 (m, 4H), 3.82 (d, 2H, *J* = 5.5), 1.64 – 1.82 (m, 1H), 1.22 – 1.59 (m, 8H), 0.85 – 0.97 (m, 6H);

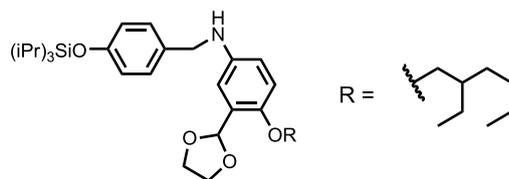
**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 150.9, 139.5, 127.0, 117.0, 114.2, 113.8, 99.2, 72.0, 65.2, 39.5, 30.5, 29.1, 23.9, 23.0, 14.0, 11.1.

**MS (ES<sup>+</sup>):** *m/z* (%) = 294 (100) [M + H<sup>+</sup>];

**HRMS (ES<sup>+</sup>):** calculated for C<sub>17</sub>H<sub>28</sub>NO<sub>3</sub>, 294.2069, found 294.2055;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 3360, 2957, 2927, 2873, 1627, 1501, 1455, 1383, 1264, 1221, 1172, 1067.

## Synthesis of **9**



**8** (4.92 g, 16.8 mmol, 1 equiv.) and **4** (5.14 g, 18.5 mmol, 1.1 equiv.) were dissolved in toluene (30 mL) with stirring and heated under Dean-Stark apparatus until the condensate ran clear. The solvent was removed using a rotary evaporator and the crude mixture was dissolved in MeOH (60 mL) and diethyl ether (30 mL) and NaBH<sub>4</sub> (1.90 g, 50.3 mmol, 3 equiv.) was added slowly at 0 °C with stirring. This mixture was stirred for 2 hours before the solution was neutralised using concentrated aqueous HCl. This solution was washed with EtOAc (5 × 30 mL) and all the organic extracts were combined and washed with brine (1 × 20 mL) and then dried (MgSO<sub>4</sub>). The crude oil was purified via flash chromatography on silica eluting with a gradient from 0% to 10% EtOAc in hexane to yield a yellow oil (8.07 g, 87%).

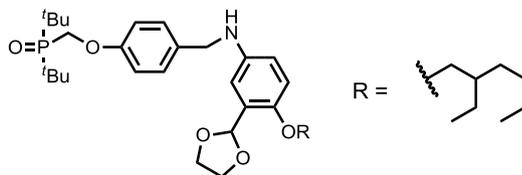
**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.21 (d, 2H, *J* = 8.5), 6.89 (d, 1H, *J* = 3.0), 6.85 (d, 2H, *J* = 9.0), 6.78 (d, 1H, *J* = 9.0), 6.60 (dd, 1H, *J* = 9.0, 3.0), 6.14 (s, 1H), 4.20 (s, 2H), 3.97 – 4.14 (m, 4H), 3.82 (d, 2H, *J* = 6.0), 1.74 (s, 1H), 1.20 – 1.56 (m, 11H), 1.11 (d, 18H, *J* = 7.0), 0.87 – 0.98 (m, 6H);

**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 155.2, 150.2, 142.2, 131.9, 128.8, 127.1, 119.9, 114.4, 113.9, 112.1, 99.4, 72.0, 65.1, 48.9, 39.5, 30.5, 29.1, 23.9, 23.1, 17.9, 14.0, 12.7, 11.1;

**MS (ES<sup>+</sup>):** *m/z* (%) = 556 (100) [M + H<sup>+</sup>];

**HRMS (ES<sup>+</sup>):** calculated for C<sub>33</sub>H<sub>54</sub>NO<sub>4</sub>Si 556.3822, found 556.3800;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2928, 2866, 1608, 1506, 1465, 1263, 1227, 1169, 1069, 913.



**4** (0.79 g, 2.7 mmol, 1 equiv.) and **8** (1.02 g, 3.5 mmol, 1.3 equiv.) were dissolved in toluene (50 mL) with stirring and heated under Dean-Stark apparatus until the condensate ran clear. The solvent was removed with a rotary evaporator and the crude mixture was dissolved in MeOH (20 mL) and NaBH<sub>4</sub> (0.61 g, 16.0 mmol, 6 equiv.) was added slowly at 0 °C with stirring. After 2 hours the solution was neutralised using concentrated aqueous HCl. This solution was washed with EtOAc (5 × 20 mL) and all the organic extracts were combined and washed with brine (1 × 20 mL) and then dried (MgSO<sub>4</sub>) and the solvent removed with a rotary evaporator. The crude oil was purified via flash chromatography on silica eluting with a gradient from 0% to 10% MeOH in EtOAc to yield a yellow oil (0.87 g, 57%).

**<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.25 (d, 2H, *J* = 8.5), 6.82 – 6.85 (m, 3H), 6.70 (d, 1H, *J* = 9.0), 6.51 (dd, 1H, *J* = 9.0, 3.0), 6.07 (s, 1H), 4.32 (d, 2H, *J* = 7.5), 4.16 (s, 2H), 3.90 – 4.05 (m, 4H), 3.75 (d, 2H, *J* = 6.0), 1.63 – 1.71 (m, 1H), 1.20 – 1.50 (m, 26H), 0.83 – 0.91 (m, 6H);

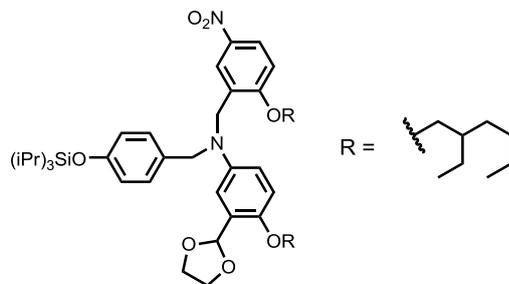
**<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 157.2 (d, *J* = 10.6), 149.7, 141.8, 132.9, 128.6, 126.7, 113.8, 113.8, 113.5, 111.8, 99.0, 71.6, 64.8, 62.3 (d, *J* = 71.0), 48.1, 39.2, 35.1 (d, *J* = 57.6), 30.2, 28.7, 26.1, 22.7, 13.8, 10.8;

**<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>P</sub> = 56.6;

**MS (ES<sup>+</sup>):** *m/z* (%) = 574 (100) [M + H<sup>+</sup>], 1148 (15);

**HRMS (ES<sup>+</sup>):** calculated for C<sub>33</sub>H<sub>53</sub>NO<sub>5</sub>P 574.3661, found 574.3642;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2956, 2927, 2871, 1691, 1601, 1506, 1468, 1392, 1226, 1136, 1069, 1040.



**9** (2.11 g, 3.8 mmol, 1 equiv.) and **6** (1.77 g, 6.3 mmol, 1.2 equiv.) were dissolved in DCE (20 mL) and  $\text{NaBH}(\text{OAc})_3$  (3.13 g, 2.8 mmol, 1.2 equiv.) was added with stirring. After 12 hours the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  solution, and extracted into  $\text{CHCl}_3$  ( $4 \times 20$  mL). All the organic fractions were washed with water ( $1 \times 20$  mL), brine ( $1 \times 10$  mL) and dried ( $\text{MgSO}_4$ ) before the solvent removed with a rotary evaporator. The crude product was purified using flash chromatography on silica eluting with a gradient from 0% to 10% of EtOAc in hexane to yield a golden yellow oil (2.48 g, 79%).

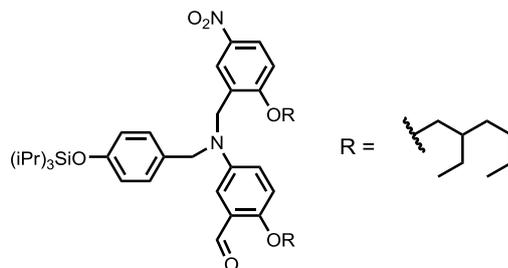
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 8.08 - 8.15$  (m, 2H), 7.12 (d, 2H,  $J = 8.5$ ), 6.97 (d, 1H,  $J = 3.0$ ), 6.90 (d, 1H,  $J = 9.5$ ), 6.81 (d, 2H,  $J = 8.5$ ), 6.74 (d, 1H,  $J = 9.0$ ), 6.60 (dd, 1H,  $J = 9.0, 3.0$ ), 6.14 (s, 1H), 4.55 (s, 2H), 4.49 (s, 2H), 3.97 (d, 2H,  $J = 6.5$ ), 3.94 (s, 4H), 3.80 (d, 2H,  $J = 6.0$ ), 1.67 – 1.84 (m, 2H), 1.17 – 1.55 (m, 19H), 1.09 (d, 18H,  $J = 7.0$ ); 0.86 – 0.97 (m, 12H);

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 161.8, 155.0, 149.9, 143.0, 141.40, 130.8, 128.80, 128.20, 126.90, 124.3, 123.5, 119.9, 114.8, 113.5, 112.3, 110.2, 99.6, 71.6, 71.3, 65.0, 55.1, 49.8, 39.4, 39.2, 30.5, 29.0, 23.9, 23.1, 22.9, 17.9, 14.1, 14.0, 12.6, 11.1$ ;

**MS (ES+):**  $m/z$  (%) = 820 (100)  $[\text{M} + \text{H}^+]$ ;

**HRMS (ES+):** calculated for  $\text{C}_{48}\text{H}_{75}\text{N}_2\text{O}_7\text{Si}$  819.5344, found 819.5344;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2921, 2852, 1660, 1633, 1610, 1595, 1508, 1465, 1378, 1340, 1264, 1076.



**11** (1.39 g, 1.7 mmol, 1 equiv.) was dissolved in  $\text{CHCl}_3$  (10 mL) and concentrated aqueous acid (10 mL) was added with stirring. After 18 hours the mixture was neutralised using aqueous  $\text{NaHCO}_3$  and the organic portion separated from the aqueous part. The aqueous layer was washed with  $\text{CHCl}_3$  ( $4 \times 10$  mL) before all organic fractions were washed with brine ( $1 \times 10$  mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator to yield a yellow oil (1.30 g, 99%) requiring no further purification.

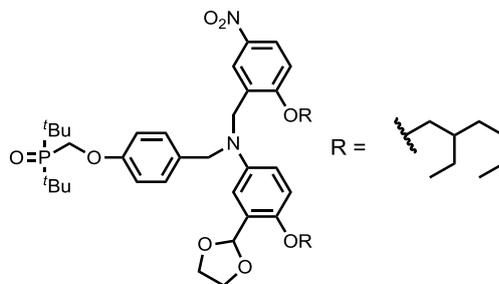
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 10.45$  (s, 1H), 8.14 (dd, 1H,  $J = 9.0, 3.0$ ), 8.01 (d, 1H,  $J = 2.5$ ), 7.17 (d, 1H,  $J = 3.0$ ), 7.10 (d, 2H,  $J = 8.5$ ), 6.89 – 6.94 (m, 2H), 6.80 – 6.87 (m, 3H), 4.57 (s, 2H), 4.54 (s, 2H), 3.99 (d, 2H,  $J = 5.5$ ), 3.89 (d, 2H,  $J = 5.5$ ), 1.69 – 1.84 (m, 2H), 1.17 – 1.59 (m, 19H), 1.09 (d, 18H,  $J = 7.0$ ), 0.86 – 0.98 (m, 12H);

**$^{13}\text{C NMR}$  (63 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 190.0, 161.9, 155.1, 154.6, 142.9, 141.4, 130.2, 128.0, 127.9, 125.3, 124.5, 123.0, 121.2, 120.1, 114.2, 110.9, 110.4, 71.5, 71.3, 54.7, 49.6, 39.5, 39.2, 30.6, 30.5, 29.1, 29.0, 24.0, 23.9, 23.0, 22.9, 17.9, 14.0, 12.6, 11.2, 11.1$ ;

**MS (ES+):**  $m/z$  (%) = 263 (40), 775 (100) [ $\text{M} + \text{H}^+$ ];

**HRMS (ES+):** calculated for  $\text{C}_{46}\text{H}_{71}\text{N}_2\text{O}_6\text{Si}$  775.5081, found 775.5060;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2956, 2925, 2858, 1684, 1610, 1591, 1508, 1463, 1341, 1266.



**10** (0.160 g, 0.28 mmol, 1 equiv.) and **6** (0.156 g, 0.56 mmol, 2 equiv.) were dissolved in DCE (1 mL) and  $\text{NaBH}(\text{OAc})_3$  (0.165 g, 0.78 mmol, 2.8 equiv.) was added with stirring. After 18 hours the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  solution, and extracted into  $\text{CHCl}_3$  ( $4 \times 10$  mL). All the organic fractions were washed with water ( $1 \times 10$  mL), brine ( $1 \times 10$  mL) and dried ( $\text{MgSO}_4$ ) before the solvent removed using a rotary evaporator. The crude product was purified using flash chromatography on silica eluting from 0% to 3% of MeOH in EtOAc to yield a pale yellow oil (0.22 g, 94%).

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}}$  = 8.12 (dd, 1H,  $J$  = 9.0, 3.0), 8.10 (d, 1H,  $J$  = 3.0), 7.22 (d, 2H,  $J$  = 9.0), 6.97 (d, 1H,  $J$  = 3.0), 6.90 (d, 1H,  $J$  = 9.0), 6.86 (d, 2H,  $J$  = 9.0), 6.74 (d, 1H,  $J$  = 9.0), 6.61 (dd, 1H,  $J$  = 9.0, 3.0), 6.11 (s, 1H), 4.56 (s, 2H), 4.50 (s, 2H), (d, 2H,  $J$  = 7.5), 3.97 (d, 2H,  $J$  = 6.0), 3.93 – 3.99 (m, 4H), 3.79 (d, 1H,  $J$  = 6.0), 1.74 – 1.82 (m, 1H), 1.67 – 1.74 (m, 1H), 1.23 – 1.54 (m, 34H), 0.85 – 0.96 (m, 12H);

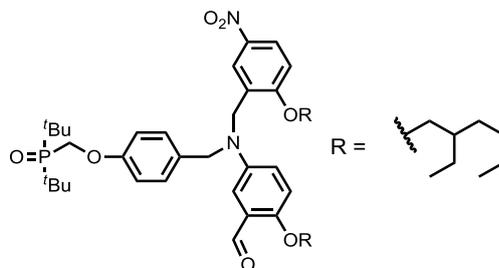
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  = 161.8, 157.4, (d,  $J$  = 10.6), 150.1, 142.7, 141.4, 132.0, 128.6, 128.5, 126.9, 124.3, 123.5, 115.1, 114.1, 113.5, 112.6, 110.3, 99.6, 71.6, 71.4, 65.0, 62.6 (d,  $J$  = 71.0), 55.0, 50.2, 39.5, 39.2, 35.4 (d,  $J$  = 57.6), 30.5, 29.0, 26.4, 23.9, 23.0, 22.9, 14.0, 11.1;

**$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{P}}$  = 56.8;

**MS (ES+):**  $m/z$  (%) = 419 (10)  $[\text{M} + 2\text{H}^+]$ , 838 (100)  $[\text{M} + \text{H}^+]$ , 860 (45)  $[\text{M} + \text{Na}^+]$ , 883 (15), 938 (30);

**HRMS (ES+):** calculated for  $\text{C}_{48}\text{H}_{74}\text{N}_2\text{O}_8\text{P}$  837.5183, found 837.5213;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2957, 2922, 2853, 1738, 1610, 1592, 1508, 1466, 1340, 1265, 1231, 1139, 1078.



**12** (0.22 g, 0.26 mmol, 1 equiv.) was dissolved in  $\text{CHCl}_3$  (10 mL) and concentrated aqueous acid (10 mL) was added with stirring. After 18 hours the mixture was neutralised using aqueous  $\text{NaHCO}_3$  and the organic portion separated from the aqueous part. The aqueous layer was washed with  $\text{CHCl}_3$  ( $3 \times 10$  mL) before all organic fractions were washed with brine ( $1 \times 10$  mL) and dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator to yield a yellow oil (0.20 g, 94%) requiring no further purification.

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 10.43$  (s, 1H), 8.12 (dd, 1H,  $J = 9.0, 3.0$ ), 7.97 (d, 1H,  $J = 3.0$ ), 7.19 (d, 2H,  $J = 8.5$ ), 7.14 (d, 1H,  $J = 3.0$ ), 6.82 – 6.95 (m, 5H), 4.59 (s, 2H), 4.55 (s, 2H), 4.35 (d, 2H,  $J = 7.5$ ), 3.99 (d, 2H,  $J = 5.5$ ), 3.87 (d, 2H,  $J = 5.5$ ), 1.66 – 1.83 (m, 2H), 1.21 – 1.56 (m, 34H), 0.83 – 0.96 (m, 12H);

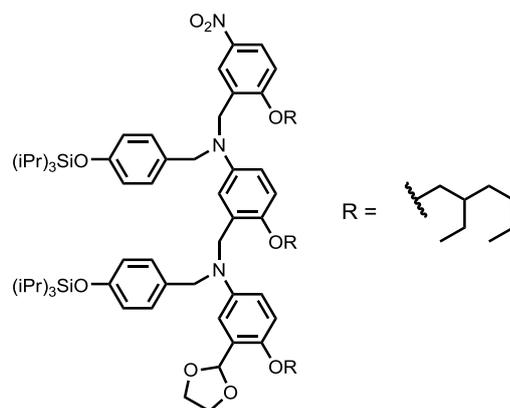
**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 189.9, 161.8, 157.4$  (d,  $J = 11.6$ ), 154.6, 142.5, 141.2, 131.1, 128.1, 127.6, 125.2, 124.5, 122.9, 121.0, 114.2, 114.1, 110.8, 110.4, 71.4, 71.1, 62.5 (d,  $J = 70.9$ ), 54.4, 49.8, 39.4, 39.1, 35.3 (d,  $J = 57.0$ ), 30.5, 30.4, 29.0, 28.9, 26.4, 23.9, 23.8, 22.9, 22.8, 14.0, 13.9, 11.1, 11.0;

**$^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{P}} = 56.6$ ;

**MS (ES+):**  $m/z$  (%) = 397 (5) [ $\text{M} + 2\text{H}^+$ ], 794 (100) [ $\text{M} + \text{H}^+$ ], 816 (65) [ $\text{M} + \text{Na}^+$ ], 839 (25), 864 (50);

**HRMS (ES+):** calculated for  $\text{C}_{46}\text{H}_{70}\text{N}_2\text{O}_7\text{P}$  793.4921, found 793.4921;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2957, 2927, 2871, 1610, 1591, 1507, 1465, 1338, 1265, 1227, 1137, 1047, 1017.



**11'** (2.02 g, 2.61 mmol, 1 equiv.) and **9** (2.90 g, 5.22 mmol, 2 equiv.) were dissolved in DCE (9 mL) and NaBH(OAc)<sub>3</sub> (1.55 g, 7.31 mmol, 2.8 equiv.) was added with stirring. After 1 day the reaction was quenched with saturated aqueous NaHCO<sub>3</sub> solution, and extracted into CHCl<sub>3</sub> (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO<sub>4</sub>) before the solvent was removed using a rotary evaporator. The crude product was purified using flash chromatography on silica eluting with a gradient from 0% to 10% of a 1:1 CHCl<sub>3</sub>/diethyl ether mix in hexane) to yield a golden yellow oil (1.86 g, 54%).

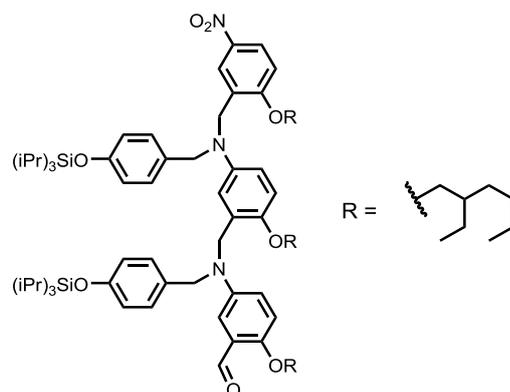
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.99 (dd, 1H, *J* = 9.0, 3.0), 7.92 (d, 1H, *J* = 3.0), 7.07 (d, 2H, *J* = 8.5), 6.99 (d, 2H, *J* = 8.5), 6.81 (d, 2H, *J* = 8.5), 6.76 (d, 2H, *J* = 8.5), 6.72 (d, 1H, *J* = 5.5), 6.67 – 6.70 (m, 2H), 6.49 – 6.54 (m, 2H), 6.37 (d, 1H, *J* = 3.0), 6.30 (dd, 1H, *J* = 9.0, 3.0), 6.10 (s, 1H), 4.49 (s, 2H), 4.39 – 4.45 (m, 4H), 4.18 (s, 2H), 3.85 – 3.93 (m, 6H), 3.73 – 3.80 (m, 4H), 1.68 – 1.79 (m, 2H), 1.60 – 1.68 (m, 1H), 1.16 – 1.54 (m, 27H), 1.08 (dd, *J* = 7.0, 2.0, 31H), 0.81 – 1.00 (m, 16H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 161.4, 154.9, 154.6, 149.1, 148.9, 143.1, 142.5, 141.2, 131.5, 131.3, 128.4, 128.1, 127.6, 127.2, 126.4, 124.2, 122.9, 119.9, 119.7, 113.4, 113.3, 112.9, 112.2, 111.3, 110.8, 110.4, 99.7, 71.7, 71.3, 70.7, 64.9, 55.6, 53.9, 50.1, 49.6, 39.6, 39.5, 39.2, 30.7, 30.5, 30.6, 29.1, 29.0, 24.0, 23.9, 23.1, 23.0, 17.9, 14.1, 14.0, 12.7, 11.2;

**MS (ES<sup>+</sup>):** *m/z* (%) = 1315 (80) [M + H<sup>+</sup>], 1337 (100) [M + Na<sup>+</sup>];

**HRMS (ES<sup>+</sup>):** calculated for C<sub>79</sub>H<sub>124</sub>N<sub>3</sub>O<sub>9</sub>Si<sub>2</sub> 1314.8876, found 1314.8842;

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2959, 2928, 2867, 1608, 1593, 1507, 1464, 1383, 1339, 1263, 1226, 1165, 1075, 1014.



**13** (0.68 g, 0.52 mmol, 1 equiv.) was dissolved in  $\text{CHCl}_3$  (10 mL) and concentrated aqueous acid (10 mL) was added with stirring. After 18 hours the mixture was neutralised using aqueous  $\text{NaHCO}_3$  and the organic portion separated from the aqueous part. The aqueous layer was washed with  $\text{CHCl}_3$  ( $3 \times 10$  mL) before all organic fractions were washed with brine ( $1 \times 10$  mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator to yield a yellow oil (0.65 g, 98%) requiring no further purification.

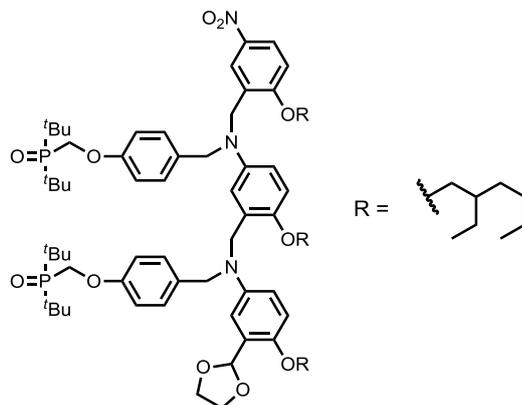
**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 10.43$  (s, 1H), 7.97 (dd, 1H,  $J = 9.0, 2.5$ ), 7.87 (d, 1H,  $J = 2.5$ ), 7.07 (d, 2H,  $J = 8.5$ ), 6.98 (d, 2H,  $J = 8.5$ ), 6.96 (d, 1H,  $J = 3.0$ ), 6.82 (d, 2H,  $J = 8.5$ ), 6.78 (d, 2H,  $J = 8.5$ ), 6.73 (d, 1H,  $J = 9.0$ ), 6.71 (d, 2H,  $J = 9.0$ ), 6.61 (s, 1H), 6.54 – 6.60 (m, 1H), 6.28 (d, 1H,  $J = 3.0$ ), 4.50 (s, 1H), 4.44 (s, 1H), 4.40 (s, 1H), 4.23 (s, 1H), 3.88 (d, 1H,  $J = 5.5$ ), 3.86 (d, 1H,  $J = 5.5$ ), 3.78 (d, 1H,  $J = 5.5$ ), 1.62 – 1.82 (m, 3H), 1.16 – 1.58 (m, 27H), 1.02 – 1.15 (m, 36H), 0.82 – 1.01 (m, 18H);

**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 190.1, 161.4, 155.0, 154.8, 153.7, 149.1, 142.9, 142.5, 141.2, 131.0, 130.7, 128.4, 128.0, 127.6, 126.4, 124.9, 124.0, 122.9, 120.1, 119.9, 113.6, 112.5, 112.2, 111.3, 110.1, 109.4, 71.4, 71.3, 70.7, 55.4, 53.8, 50.2, 49.2, 39.6, 39.5, 39.2, 30.7, 30.6, 30.5, 29.1, 29.0, 24.0, 23.9, 23.1, 23.0, 22.9, 17.9, 14.1, 12.7, 12.6, 11.2, 11.1;$

**MS (ES+):**  $m/z$  (%) = 1271 (100)  $[\text{M} + \text{H}^+]$ , 1293 (15)  $[\text{M} + \text{Na}^+]$ ;

**HRMS (ES+):** calculated for  $\text{C}_{77}\text{H}_{120}\text{N}_3\text{O}_8\text{Si}_2$  1270.8614, found 1270.8586;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2959, 2925, 2866, 1682, 1608, 1593, 1507, 1463, 1263, 1226, 1165, 1013.



**12'** (0.190 g, 0.24 mmol, 1 equiv.) and **10** (0.206 g, 0.36 mmol, 1.5 equiv.) were dissolved in DCE (900  $\mu$ L) and  $\text{NaBH}(\text{OAc})_3$  (0.142 g, 0.67 mmol, 2.8 equiv.) was added with stirring. After 2 days the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  solution, and extracted into  $\text{CHCl}_3$  ( $4 \times 10$  mL). All the organic fractions were washed with water ( $1 \times 10$  mL), brine ( $1 \times 10$  mL) and dried ( $\text{MgSO}_4$ ) before the solvent removed using a rotary evaporator. The crude product was purified using flash chromatography on silica eluting 0% to 10% MeOH in diethyl ether to yield a pale yellow oil (0.208 g, 65%).

**$^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta_{\text{H}}$  = 7.98 (dd, 1H,  $J$  = 9.0, 3.0), 7.75 (d, 1H,  $J$  = 3.0), 7.10 (d, 2H,  $J$  = 9.0), 7.06 (d, 2H,  $J$  = 8.0), 6.87 – 6.97 (m, 5H), 6.74 (d, 1H,  $J$  = 9.0), 6.64 (d, 1H,  $J$  = 3.0), 6.58 (d, 1H,  $J$  = 9.0), 6.54 (dd, 1H,  $J$  = 9.0, 3.0), 6.28 – 6.35 (m, 2H), 5.93 (s, 1H), 4.48 (s, 2H), 4.45 (s, 2H), 4.40 (s, 2H), 4.34 (d, 2H,  $J$  = 3.0), 4.33 (d, 2H,  $J$  = 3.0), 4.17 (s, 2H), 3.96 (d, 2H,  $J$  = 5.5), 3.83 (br. d., 4H,  $J$  = 2.0), 3.72 – 3.78 (m, 4H), 1.55 – 1.78 (m, 3H), 1.16 – 1.53 (m, 60H), 0.78 – 0.95 (m, 18H);

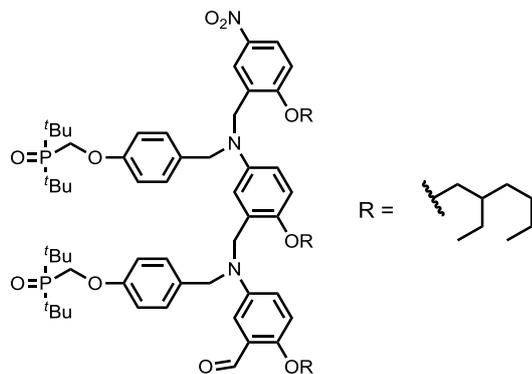
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta_{\text{C}}$  = 162.8, 158.7 (d,  $J$  = 8.5), 158.6 (d,  $J$  = 8.5), 150.1, 143.6, 143.1, 142.0, 133.5, 133.4, 129.4, 129.2, 129.1, 128.2, 127.70, 125.2, 123.5, 115.4, 115.3, 114.7, 114.4, 114.1, 113.8, 112.7, 112.2, 100.0, 72.5, 72.4, 71.8, 65.8, 63.6 (d,  $J$  = 69.4), 63.5 (d,  $J$  = 70.1), 56.1, 55.1, 51.2, 50.6, 40.6, 40., 40.2, 36.0 (d,  $J$  = 57.8), 31.5, 31.4, 30.8, 29.9, 26.9, 24.9, 24.8, 23.9, 23.8, 14.6, 14.5, 11.7;

**$^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta_{\text{P}}$  = 55.3, 55.3;

**MS (ES+):**  $m/z$  (%) = 676 (50)  $[\text{M} + 2\text{H}^+]$ , 1351 (100)  $[\text{M} + \text{H}^+]$ , 1373 (100)  $[\text{M} + \text{Na}^+]$ , 1396 (40);

**HRMS (ES+):** calculated for  $\text{C}_{79}\text{H}_{122}\text{N}_5\text{O}_{11}\text{P}_2$  1350.8555, found 1350.8549;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2958, 2927, 2871, 1680, 1610, 1592, 1505, 1465, 1432, 1392, 1264, 1225, 1174, 1135, 1044, 1017, 968.



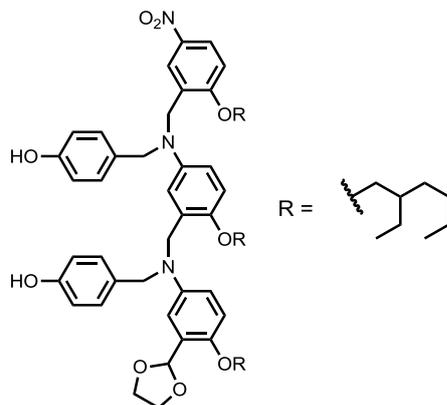
**14** (0.21 g, 0.16 mmol, 1 equiv.) was dissolved in  $\text{CHCl}_3$  (10 mL) and concentrated aqueous acid (10 mL) was added with stirring. After 3 days the mixture was neutralised using aqueous  $\text{NaHCO}_3$  and the organic portion separated from the aqueous part. The aqueous layer was washed with  $\text{CHCl}_3$  ( $3 \times 10$  mL) before all organic fractions were washed with brine ( $1 \times 10$  mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator to yield a yellow oil (0.20 g, 98%) requiring no further purification.

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 10.42$  (s, 1H), 7.96 (d, 1H,  $J = 9.0$ ), 7.84 (d, 1H,  $J = 3.0$ ), 7.16 (d, 2H,  $J = 9.0$ ), 7.06 (d, 2H,  $J = 9.0$ ), 6.79 – 6.93 (m, 5H), 6.72 (dd, 2H,  $J = 9.0, 3.5$ ), 6.64 (d, 1H,  $J = 9.5$ ), 6.60 (dd, 1H,  $J = 9.0, 3.0$ ), 6.51 – 6.57 (m, 1H), 6.26 (d, 1H,  $J = 3.0$ ), 4.51 (s, 2H), 4.45 (s, 2H), 4.43 (s, 1H), 4.32 – 4.39 (m, 4H), 4.22 (s, 2H), 3.88 (d, 2H,  $J = 5.5$ ), 3.86 (d, 2H,  $J = 5.5$ ), 3.77 (d, 2H,  $J = 5.5$ ), 1.75 (d, 2H,  $J = 7.0$ ), 1.60 – 1.69 (m, 1H), 1.18 – 1.59 (m, 60H), 0.80 – 0.99 (m, 15H);

**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 189.9, 161.3, 157.3$  (d,  $J = 11.2$ ), 157.2 (d,  $J = 10.8$ ), 153.80, 149.10, 142.6, 142.1, 141.1, 132.1, 131.6, 128.1, 128.0, 127.7, 126.2, 124.8, 124.0, 122.7, 120.0, 114.1, 113.6, 112.4, 112.2, 111.3, 110.1, 109.2, 71.3, 71.2, 70.5, 62.6 (d,  $J = 70.1$ ), 62.5 (d,  $J = 70.1$ ), 55.3, 53.6, 50.3, 49.2, 39.5, 39.4, 39.1, 35.3 (d,  $J = 57.8$ ), 30.5, 30.4, 30.3, 30.2, 29.0, 28.9, 26.4, 23.9, 23.8, 22.9, 22.8, 14.0, 13.9, 11.1;

**$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{P}} = 56.8$ ;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2958, 2928, 2872, 1683, 1592, 1508, 1466, 1339, 1265, 1229, 1176, 1138, 1081, 1047, 1014, 968.



**13** (0.321 g, 0.24 mmol, 1 equiv.) was dissolved in THF (2 mL) at 0 °C and TBAF (720  $\mu$ L, 0.72 mmol, 3 equiv.) was added with stirring. After 1 hour water (5 mL) was added and the aqueous mixture washed with diethyl ether (4  $\times$  10 mL). All organic fractions were combined and washed with brine (1  $\times$  10 mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator. The crude mixture was then purified via flash chromatography on silica eluting with a gradient from 20% to 60% of diethyl ether in hexane to yield a light red oil (0.189 g, 77%).

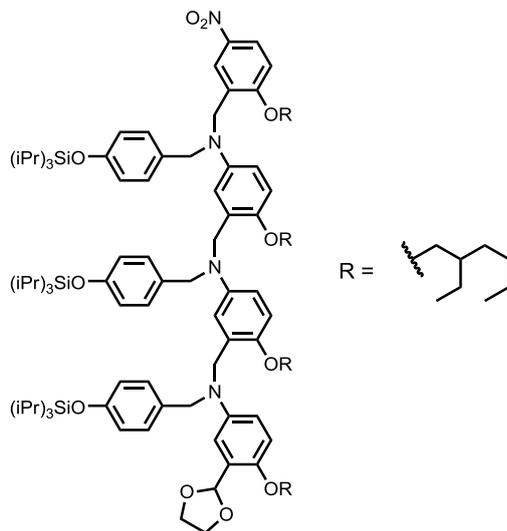
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}}$  = 8.09 (dd, 1H,  $J$  = 9.0, 2.5), 8.01 (d, 1H,  $J$  = 2.5), 7.05 (d, 2H,  $J$  = 8.5), 6.93 (d, 2H,  $J$  = 8.5), 6.87 (d, 1H,  $J$  = 9.0), 6.61 – 6.77 (m, 4H), 6.51 – 6.60 (m, 3H), 6.37 – 6.46 (m, 2H), 6.28 (dd, 1H,  $J$  = 9.0, 3.0), 6.09 (s, 1H), 4.54 (s, 2H), 4.44 (s, 2H), 4.41 (s, 2H), 4.29 (s, 2H), 3.91 – 4.06 (m, 6H), 3.80 (d, 2H,  $J$  = 6.0), 3.75 (d, 2H,  $J$  = 5.5), 1.57 – 1.82 (m, 3H), 1.18 – 1.56 (m, 24H), 0.80 – 0.98 (m, 18H);

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  = 161.7, 154.6, 154.4, 149.0, 143.1, 142.5, 141.3, 131.3, 130.5, 128.7, 128.1, 127.7, 127.4, 125.5, 124.3, 123.1, 115.8, 115.3, 113.7, 113.6, 113.5, 112.1, 111.3, 111.1, 110.4, 100.3, 71.8, 71.3, 70.7, 65.9, 65.0, 56.0, 54.5, 50.9, 49.7, 39.6, 39.5, 39.2, 30.6, 30.5, 29.1, 24.0, 23.9, 23.1, 23.0, 22.9, 14.1, 14.0, 11.1;

**MS (ES<sup>+</sup>):**  $m/z$  (%) = 853 (10), 897 (35), 959 (10), 1003 (100) [ $\text{M} + \text{H}^+$ ], 1025 (25);

**HRMS (ES<sup>+</sup>):** calculated for  $\text{C}_{61}\text{H}_{84}\text{N}_3\text{O}_6$  1002.6208, found 1002.6224;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2957, 2927, 2871, 1613, 1593, 1505, 1462, 1337, 1261, 1223, 1167, 1077, 1015, 964.



**13'** (0.885 g, 0.70 mmol, 1 equiv.) and **9** (0.774 g, 1.4 mmol, 2 equiv.) were dissolved in DCE (0.5 mL) and  $\text{NaBH}(\text{OAc})_3$  (0.413 g, 2.0 mmol, 2.8 equiv.) was added with stirring. After 2 days the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  solution, and extracted into  $\text{CHCl}_3$  ( $4 \times 10$  mL). All the organic fractions were washed with water ( $1 \times 10$  mL), brine ( $1 \times 10$  mL) and dried ( $\text{MgSO}_4$ ) before the solvent removed on a rotary evaporator. The crude product was purified using flash chromatography on silica eluting with a gradient from 0% to 5% of diethyl ether in hexane to yield a golden yellow oil (1.00 g, 79%).

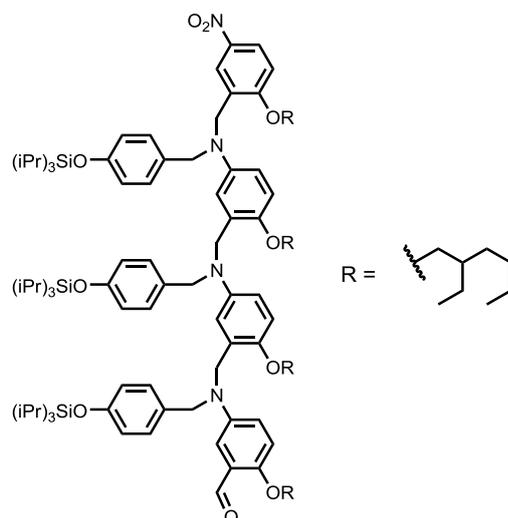
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 7.98 - 8.02$  (m, 2H), 7.05 (d, 2H,  $J = 8.5$ ), 7.00 (d, 2H,  $J = 8.5$ ), 6.96 (d, 2H,  $J = 8.5$ ), 6.89 (d, 1H,  $J = 3.0$ ), 6.82 (d, 2H,  $J = 8.5$ ), 6.79 (d, 2H,  $J = 8.5$ ), 6.77 (d, 2H,  $J = 8.5$ ), 6.72 (d, 1H,  $J = 4.0$ ), 6.71 (d, 1H,  $J = 4.0$ ), 6.69 (d, 1H,  $J = 9.0$ ), 6.59 (d, 1H,  $J = 9.0$ ), 6.51 – 6.55 (m, 2H), 6.49 (d, 1H,  $J = 2.9$ ), 6.44 (d, 1H,  $J = 3.0$ ), 6.27 – 6.30 (m, 1H), 6.18 (s, 1H), 4.50 (s, 2H), 4.48 (s, 2H), 4.46 (s, 2H), 4.44 (s, 2H), 4.10 (s, 2H), 4.07 (s, 2H), 3.92 (s, 4H), 3.79 – 3.83 (m, 6H), 3.77 (d, 2H,  $J = 5.5$ ), 1.72 (d, 4H,  $J = 6.2$ ), 1.21 – 1.57 (m, 35H), 1.04 – 1.18 (m, 54H), 0.86 – 0.99 (m, 24H);

**$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 161.4, 154.9, 154.5, 149.0, 148.9, 148.4, 143.3, 143.1, 142.6, 141.3, 131.8, 131.6, 131.7, 128.7, 128.2, 127.7, 127.6, 127.0, 126.8, 124.1, 123.2, 119.8, 119.7, 119.6, 114.2, 113.6, 113.3, 112.5, 112.2, 112.1, 111.6, 111.4, 110.9, 110.3, 99.8, 71.9, 71.3, 70.8, 70.7, 64.9, 55.4, 54.3, 53.7, 50.5, 50.2, 49.7, 39.6, 39.5, 39.2, 30.7, 30.6, 30.5, 29.1, 24.0, 23.9, 23.1, 23.0, 17.9, 14.1, 14.0, 12.6, 11.2, 11.1;$

**MS (ES<sup>+</sup>):**  $m/z$  (%) = 1810 (80) [ $\text{M} + \text{H}^+$ ], 1811 (100), 1812 (70), 1813 (40);

**HRMS (ES<sup>+</sup>):** calculated for  $\text{C}_{110}\text{H}_{173}\text{N}_4\text{O}_{11}\text{Si}_3$  1810.2409, found 1810.2484;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2959, 2929, 2867, 1608, 1508, 1465, 1340, 1264, 914.



**16** (0.89 g, 0.49 mmol, 1 equiv.) was dissolved in  $\text{CHCl}_3$  (10 mL) and concentrated aqueous acid (10 mL) was added with stirring. After 2 days the mixture was neutralised using aqueous  $\text{NaHCO}_3$  and the organic portion separated from the aqueous part. The aqueous layer was washed with  $\text{CHCl}_3$  ( $3 \times 10$  mL) before all organic fractions were washed with brine ( $1 \times 10$  mL) dried ( $\text{MgSO}_4$ ) and the solvent removed using a rotary evaporator to yield a yellow oil (0.78 g, 90%) requiring no further purification.

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}} = 10.46$  (s, 1H), 7.99 – 8.03 (m, 2H), 7.14 (d, 1H,  $J = 2.0$ ), 7.03 (d, 2H,  $J = 8.5$ ), 6.97 (d, 2H,  $J = 8.5$ ), 6.92 (d, 2H,  $J = 8.5$ ), 6.72 – 6.80 (m, 9H), 6.67 (d, 1H,  $J = 8.5$ ), 6.59 (d, 1H,  $J = 8.5$ ), 6.50 (dd, 1H,  $J = 8.5, 3.0$ ), 6.46 (d, 1H,  $J = 3.0$ ), 6.34 (d, 1H,  $J = 3.0$ ), 6.30 (dd, 1H,  $J = 9.0, 3.0$ ), 4.48 (s, 2H), 4.45 (s, 2H), 4.42 (s, 4H), 4.10 (s, 2H), 4.07 (s, 2H), 3.85 (d, 4H,  $J = 5.5$ ), 3.79 (d, 2H,  $J = 6.0$ ), 3.72 (d, 2H,  $J = 6.0$ ), 1.67 – 1.77 (m, 3H), 1.57 – 1.67 (m, 2H), 1.18 – 1.56 (m, 41H), 1.04 – 1.16 (m, 54H), 0.84 – 0.96 (m, 24H);

**$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}} = 189.9, 161.4, 154.9, 154.7, 154.6, 153.7, 149.1, 148.5, 143.4, 143.0, 142.7, 141.3, 131.7, 131.1, 131.0, 128.8, 128.2, 127.7, 127.6, 127.5, 126.2, 125.1, 124.0, 123.2, 120.7, 119.8, 119.7, 113.9, 113.2, 112.3, 112.2, 112.1, 111.4, 111.1, 110.3, 110.1, 71.4, 71.3, 70.8, 70.7, 55.4, 53.4, 50.5, 50.3, 49.6, 39.6, 39.5, 39.2, 30.7, 30.6, 30.5, 29.1, 29.0, 24.0, 23.9, 23.1, 23.0, 22.9, 17.9, 14.1, 14.0, 12.7, 12.6, 11.2, 11.1;$

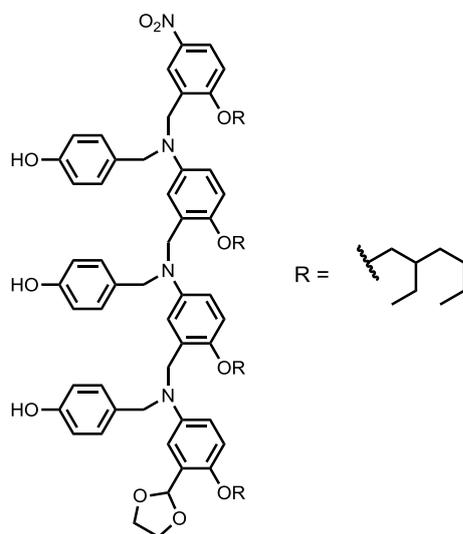
**MS (ES+):**  $m/z$  (%) = 1765 (40), 1766 (100)  $[\text{M} + \text{H}^+]$ , 1767 (95), 1768 (50), 1769 (20);

**HRMS (ES+):** calculated for  $\text{C}_{108}\text{H}_{169}\text{N}_4\text{O}_{10}\text{Si}_3$  1766.2147, found 1766.2076;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2959, 2929, 2867, 1683, 1608, 1507, 1464, 1340, 1264, 913.







**16** (0.122 g, 0.07 mmol, 1 equiv.) was dissolved in THF (2 mL) at 0 °C and TBAF (210  $\mu$ L, 0.21 mmol, 3 equiv.) was added with stirring. After 1 hour water (5 mL) was added and the aqueous mixture washed with diethyl ether ( $3 \times 10$  mL). All organic fractions were combined and washed with brine ( $1 \times 5$  mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator. The crude mixture was then purified via flash chromatography on silica eluting with a gradient from 20% to 70% of diethyl ether in hexane to yield a light red oil (0.087 g, 96%).

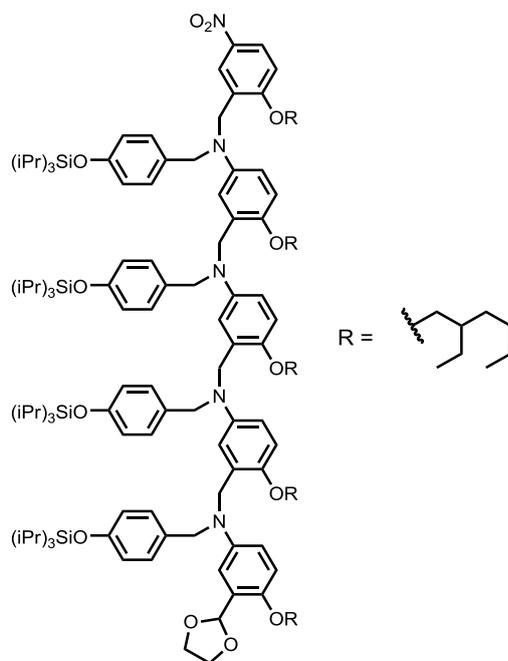
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}}$  = 8.11 (dd, 1H,  $J$  = 9.0, 3.0), 8.04 (d, 1H,  $J$  = 2.5), 6.98 (d, 2H,  $J$  = 8.5), 6.85 – 6.89 (m, 3H), 6.83 (d, 2H,  $J$  = 8.5), 6.81 (d, 1H,  $J$  = 3.5), 6.66 – 6.72 (m, 5H), 6.60 (d, 2H,  $J$  = 8.5), 6.47 – 6.51 (m, 2H), 6.37 – 6.45 (m, 4H), 6.34 (d, 1H,  $J$  = 3.0), 6.14 (s, 1H), 4.58 (s, 2H), 4.48 (s, 2H), 4.45 (s, 2H), 4.38 (s, 2H), 4.09 (s, 2H), 3.98 – 4.08 (m, 4H), 3.96 (d, 2H,  $J$  = 5.7), 3.87 (s, 2H), 3.81 (d, 2H,  $J$  = 5.7), 3.73 – 3.77 (m, 4H), 1.74 – 1.81 (m, 1H), 1.62 – 1.74 (m, 3H), 1.22 – 1.54 (m, 32H), 0.84 – 0.97 (m, 24H);

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  = 161.7, 154.7, 154.2, 154.1, 149.2, 149.0, 148.1, 143.4, 143.2, 142.3, 141.4, 131.6, 131.4, 130.5, 129.0, 128.1, 127.9, 127.5, 127.4, 126.9, 125.2, 124.3, 123.2, 115.6, 115.5, 115.3, 114.3, 113.8, 113.3, 112.6, 112.3, 112.0, 111.8, 110.8, 110.7, 110.3, 100.4, 71.7, 71.4, 71.0, 70.6, 65.0, 55.6, 54.9, 54.2, 51.3, 50.8, 49.5, 39.7, 39.5, 39.2, 30.7, 30.5, 29.1, 29.0, 24.0, 23.9, 23.8, 23.1, 23.0, 22.9, 14.1, 14.0, 11.2, 11.1, 11.0;

**MS (ES<sup>+</sup>):**  $m/z$  (%) = 565 (30), 618 (75), 671 (75), 1342 (100) [ $\text{M} + \text{H}^+$ ];

**HRMS (ES<sup>+</sup>):** calculated for  $\text{C}_{83}\text{H}_{113}\text{N}_4\text{O}_{11}$  1341.8406, found 1341.8342;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2956, 2918, 2850, 2161, 2030, 1616, 1504, 1338, 1261, 1022.



**16'** (0.815 g, 0.06 mmol, 1 equiv.) and **9** (0.713 g, 0.13 mmol, 2 equiv.) were dissolved in DCE (0.5 mL) and NaBH(OAc)<sub>3</sub> (0.038 g, 0.13 mmol, 2.8 equiv.) was added with stirring. After 2 days the reaction was quenched with saturated aqueous NaHCO<sub>3</sub> solution, and extracted into CHCl<sub>3</sub> (4 × 10 mL). All the organic fractions were washed with water (1 × 10 mL), brine (1 × 10 mL) and dried (MgSO<sub>4</sub>) before the solvent removed with a rotary evaporator. The crude product was purified using flash chromatography on silica eluting with a gradient from 3% to 5% of diethyl ether in hexane to yield a golden yellow oil (0.036 g, 26%).

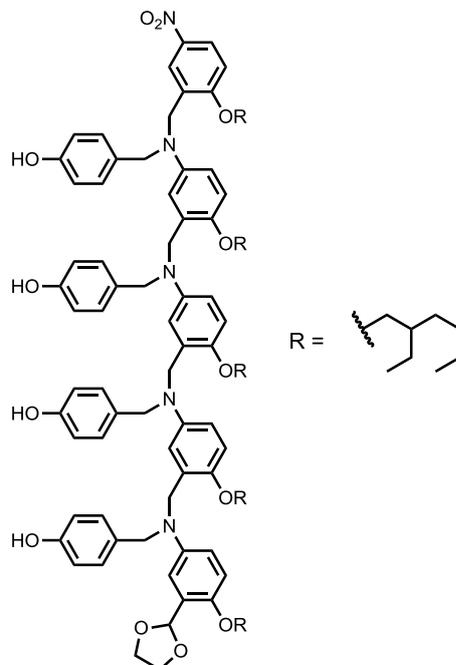
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ<sub>H</sub> = 7.96 – 8.01 (m, 2H), 7.03 (d, 2H, *J* = 8.5), 6.97 (d, 2H, *J* = 8.5), 6.89 (d, 4H, *J* = 8.5), 6.64 – 6.81 (m, 11H), 6.60 – 6.64 (m, 2H), 6.46 – 6.57 (m, 6H), 6.43 (dd, 1H, *J* = 9.0, 2.5), 6.30 (dd, 1H, *J* = 9.0, 3.0), 6.15 (s, 1H), 4.45 (s, 2H), 4.42 (s, 2H), 4.40 (s, 4H), 4.38 (s, 2H), 4.10 (s, 2H), 4.06 (s, 2H), 4.04 (s, 2H), 3.79 – 3.87 (m, 6H), 3.70 – 3.77 (m, 8H), 1.58 – 1.75 (m, 5H), 1.15 – 1.54 (m, 52H), 0.99 – 1.15 (m, 72H), 0.81 – 0.96 (m, 30H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ<sub>C</sub> = 161.4, 154.9, 154.5, 154.4, 149.2, 148.9, 148.6, 148.5, 143.4, 143.3, 142.8, 141.3, 132.1, 131.7, 131.1, 128.8, 128.3, 127.9, 127.8, 127.7, 127.3, 126.9, 126.8, 125.5, 124.0, 123.3, 119.8, 119.7, 119.6, 114.0, 113.6, 113.5, 113.3, 113.1, 112.3, 112.2, 111.8, 111.6, 111.5, 111.4, 110.1, 99.9, 71.8, 71.3, 70.9, 70.7, 64.8, 55.4, 54.5, 54.3, 53.6, 50.9, 50.4, 50.0, 49.9, 39.6, 39.5, 39.1, 30.6, 30.5, 30.3, 29.2, 29.1, 29.0, 24.0, 24.9, 23.9, 23.1, 23.0, 17.9, 14.1, 14.0, 12.6, 11.2, 11.1;

**MS (ES<sup>+</sup>):** *m/z* (%) = 2305 (50), 2306 (100) [M + H<sup>+</sup>], 2307 (95), 2308 (55), 2309 (20);

**FT-IR (thin film):** ν<sub>max</sub>/cm<sup>-1</sup> 2957, 2927, 2859, 1680, 1610, 1592, 1500, 1464, 1394, 1338, 1265, 1249, 1231, 1170, 1081, 1013, 970.





**19** (0.690 g, 0.30 mmol, 1 equiv.) was dissolved in THF (10 mL) at 0 °C and TBAF (2390  $\mu$ L, 2.4 mmol, 8 equiv.) was added with stirring. After 1 hour water (10 mL) was added and the aqueous mixture washed with diethyl ether (3  $\times$  10 mL). All organic fractions were combined and washed with brine (1  $\times$  10 mL) dried ( $\text{MgSO}_4$ ) and the solvent removed with a rotary evaporator. The crude mixture was then purified via flash chromatography on silica eluting with a gradient from 30% to 80% of diethyl ether in hexane to yield a light red oil (0.105 g, 20%).

**$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{H}}$  = 8.10 (dd, 1H,  $J$  = 9.0, 2.5), 8.04 (d, 1H,  $J$  = 2.5), 6.90 – 6.99 (m, 4H), 6.80 – 6.89 (m, 4H), 6.76 (d, 2H,  $J$  = 8.5), 6.66 – 6.73 (m, 6H), 6.56 – 6.64 (m, 5H), 6.53 (dd, 1H,  $J$  = 9.0, 3.0), 6.33 – 6.46 (m, 7H), 6.17 (s, 1H), 4.45 – 4.56 (m, 8H), 4.41 (s, 2H), 3.93 – 4.10 (m, 10H), 3.75 – 3.84 (m, 10H), 1.63 – 1.82 (m, 5H), 1.23 – 1.56 (m, 40H), 0.84 – 0.97 (m, 30H);

**$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):**  $\delta_{\text{C}}$  = 161.7, 154.5, 154.3, 154.2, 154.1, 149.2, 149.0, 148.1, 148.0, 143.6, 143.3, 143.1, 142.5, 141.4, 131.4, 131.2, 130.7, 128.8, 128.1, 128.0, 127.7, 127.6, 127.2, 126.9, 125.2, 124.3, 123.2, 115.6, 115.5, 115.3, 114.4, 113.9, 113.5, 112.9, 112.6, 112.3, 112.1, 111.8, 111.1, 110.8, 110.7, 110.3, 100.3, 71.8, 71.4, 71.3, 71.0, 70.7, 65.0, 55.4, 54.8, 54.3, 51.3, 50.8, 50.6, 49.6, 39.6, 39.5, 39.2, 30.7, 30.6, 30.5, 30.4, 29.1, 29.0, 24.0, 23.9, 23.8, 23.0, 22.9, 14.0, 11.2, 11.1, 11.0;

**MS (ES+):**  $m/z$  (%) = 484 (100), 1575 (10), 1680 (10), 1681 (50) [ $\text{M} + \text{H}^+$ ], 1682 (50), 1683 (25), 1684 (10);

**HRMS (ES+):** calculated for  $\text{C}_{105}\text{H}_{142}\text{N}_5\text{O}_{13}$  1681.0604, found 1681.0530;

**FT-IR (thin film):**  $\nu_{\text{max}}/\text{cm}^{-1}$  2957, 2927, 2858, 2163, 1613, 1593, 1505, 1464, 1339, 1264, 1225, 1168.

## Section S4: References

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- 2 H. Sun, C. A. Hunter, C. Navarro, and S. Turega, *J. Am. Chem. Soc.*, 2013, **135**, 13129–13141.