

# How secondary and tertiary amide moieties are molecular stations for dibenzo-24-crown-8 in [2]rotaxane molecular shuttles ?

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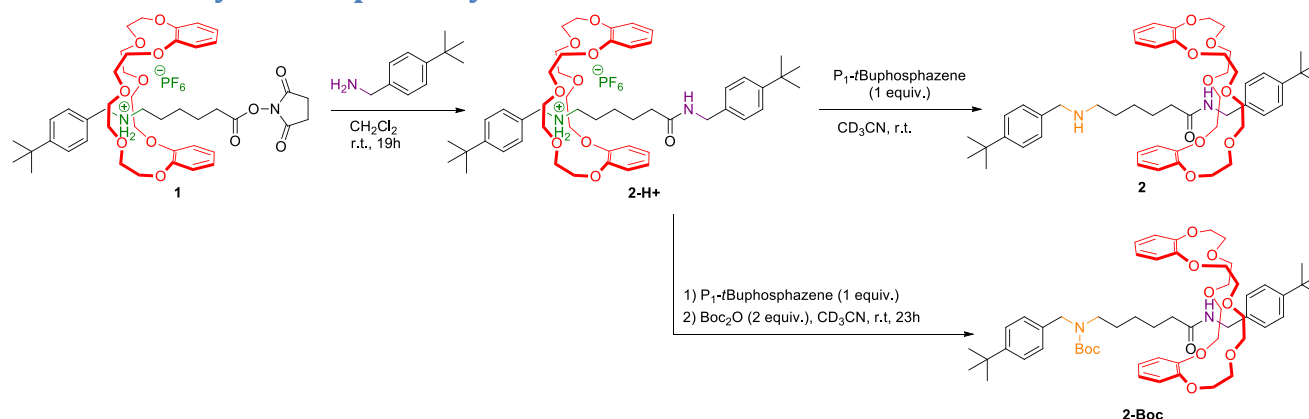
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## General methods

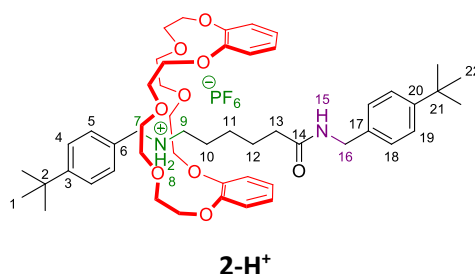
All reactions were carried out under an atmosphere of argon unless otherwise indicated. All reagents were used as received without further purification. Dichloromethane was distilled over P<sub>2</sub>O<sub>5</sub>. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates. Compounds were visualized by dipping the plates in an ethanolic solution of 10% sulphuric acid, ninhydrine or an aqueous solution of KMnO<sub>4</sub>, followed by heating. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker 500 Avance III spectrometer (respectively at 500.17 and 125.77 MHz). Chemical shifts of <sup>1</sup>H NMR and <sup>13</sup>C NMR are given by using CH<sub>3</sub>CN as references (1.94 ppm respectively for <sup>1</sup>H spectra, and 18.26 ppm respectively for <sup>13</sup>C spectra). <sup>1</sup>H assignments were deduced from 2D <sup>1</sup>H-<sup>1</sup>H NMR COSY experiments and from 2D <sup>1</sup>H-<sup>1</sup>H NMR ROESY experiments. <sup>13</sup>C assignments were deduced from 2D <sup>13</sup>C-<sup>1</sup>H NMR HSQC experiments. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), quint (quintuplet), m (multiplet). Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded respectively on a ZQ Micromass apparatus and a Q-TOF Micro apparatus.

## 1. Synthesis of [2]rotaxanes 2-H<sup>+</sup>, 2 and 2-Boc.

### 1.1. General synthetic pathway



### 1.2. Synthesis of [2]rotaxane 2-H<sup>+</sup>



To a solution of rotaxane building block **1**<sup>[1]</sup> (200 mg, 0.21 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added 4-*tert*-butylbenzyl amine (103 mg, 0.62 mmol, 3.1 equiv.). The mixture was stirred for 19h at

<sup>[1]</sup> Synthesis and characterization of **1** have already been described by F. Coutrot *et al.* in *Chem. Eur. J.*, **2016**, *22*, 8835-8847.

room temperature and evaporated to dryness. The crude was purified by chromatography on a lipophilic sephadex LH20 (CH<sub>2</sub>Cl<sub>2</sub>) to afford the pure rotaxane **2-H<sup>+</sup>** (143 mg, 53 %) as a white solid.

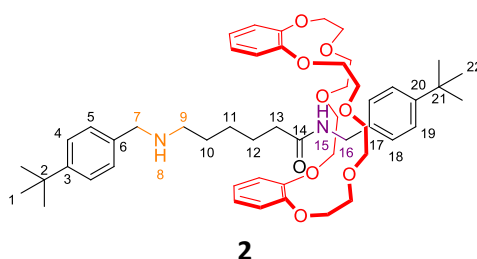
**R<sub>f</sub>**: 0.65 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.37 (d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.3 Hz, H<sub>19</sub>), 7.27 (d, 2H, <sup>3</sup>J<sub>H5-H4</sub> = 8.3 Hz, H<sub>5</sub>), 7.21 (d, 2H, <sup>3</sup>J<sub>H4-H5</sub> = 8.3 Hz, H<sub>4</sub>), 7.18 (2d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.3 Hz, H<sub>18</sub>), 7.12 (br s, 2H, H<sub>8</sub>), 6.91-6.86 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 6.59 (br t, 2H, H<sub>15</sub>), 4.55-4.50 (m, 2H, H<sub>7</sub>), 4.25 (d, 2H, <sup>3</sup>J<sub>H16-H15</sub> = 6.0 Hz, H<sub>16</sub>), 4.18-4.12 & 4.08-4.03 (2m, 2x4H, H<sub>C</sub> H<sub>C'</sub>), 3.84-3.75 (m, 8H, H<sub>D</sub> H<sub>D'</sub>), 3.67-3.61 & 3.55-3.49 (2m, 2x4H, H<sub>E</sub> H<sub>E'</sub>), 3.33-3.26 (m, 2H, H<sub>9</sub>), 1.92 (t, 2H, <sup>3</sup>J<sub>H13-H12</sub> = 7.5 Hz, H<sub>13</sub>), 1.52-1.43 (m, 2H, H<sub>10</sub>), 1.38-1.31 (m, 2H, H<sub>12</sub>), 1.29 (s, 9H, H<sub>22</sub>), 1.23 (s, 9H, H<sub>1</sub>), 1.15-1.06 (m, 2H, H<sub>11</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.0 (C<sub>14</sub>), 153.0 & 150.8 (C<sub>3</sub> C<sub>20</sub>), 148.5 (C<sub>IV</sub> arom DB24C8), 137.6 (C<sub>17</sub>), 130.5 (C<sub>5</sub>), 130.4 (C<sub>6</sub>), 128.1 (C<sub>18</sub>), 126.3 & 126.3 (C<sub>4</sub> C<sub>19</sub>), 122.3 & 113.6 (C<sub>A</sub> C<sub>B</sub>), 71.6 (C<sub>E</sub> C<sub>E'</sub>), 71.1 (C<sub>D</sub> C<sub>D'</sub>), 69.0 (C<sub>C</sub> C<sub>C'</sub>), 52.8 (C<sub>7</sub>), 49.5 (C<sub>9</sub>), 43.1 (C<sub>16</sub>), 36.2 (C<sub>13</sub>), 35.1 & 35.0 (C<sub>2</sub> C<sub>21</sub>), 31.5 (C<sub>22</sub>), 31.4 (C<sub>1</sub>), 27.0 (C<sub>10</sub>), 26.6 (C<sub>11</sub>), 25.6 (C<sub>12</sub>).

**HRMS (ESI)**: [M-PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>52</sub>H<sub>75</sub>N<sub>2</sub>O<sub>9</sub><sup>+</sup>: 871.5473, found: 871.5475.

### 1.3. Synthesis of [2]rotaxane **2**



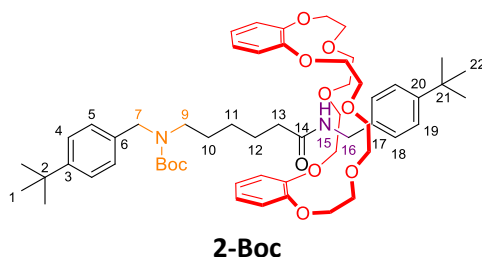
To a solution of rotaxane **2-H<sup>+</sup>** (18 mg, 0.017 mmol, 1 equiv.) in CD<sub>3</sub>CN (0.6 mL) was added P1-tBuphosphazene (4.2 mg, 0.018 mmol, 1 equiv.), directly in the NMR tube. The rotaxane **2** (quantitative conversion) was characterized without being isolated.

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.57 (d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.3Hz, H<sub>18</sub>), 7.34 (d, 2H, <sup>3</sup>J<sub>H4-H5</sub> = 8.3Hz, H<sub>4</sub>), 7.23 (br s, 1H, H<sub>15</sub>), 7.21 (d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.3Hz, H<sub>5</sub>), 7.12 (d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.3Hz, H<sub>19</sub>), 6.89-6.83 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 4.66 (br d, 2H, H<sub>16</sub>), 4.12-4.07 & 4.03-3.98 (2m, 2x4H, H<sub>C</sub> H<sub>C'</sub>), 3.72-3.67 & 3.67-3.61 (2m, 2x4H, H<sub>D</sub> H<sub>D'</sub>), 3.62 (s, 2H, H<sub>7</sub>), 3.48-3.42 & 3.23-3.17 (2m, 2x4H, H<sub>E</sub> H<sub>E'</sub>), 2.48-2.34 (m, 2H, H<sub>9</sub>), 1.95 (br t, 2H, H<sub>13</sub>), 1.43-1.35 (m, 2H, H<sub>12</sub>), 1.30-1.22 (m, 2H, H<sub>10</sub>), 1.29 (s, 9H, H<sub>1</sub>), 1.25 & 1.24 (2s, 9H, H<sub>22</sub>), 1.08-1.01 (m, 2H, H<sub>11</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.1 (C<sub>14</sub>), 150.3 & 149.4 & 149.3 (C<sub>3</sub> C<sub>20</sub> C<sub>IV</sub> arom DB24C8), 139.4 & 138.4 (C<sub>6</sub> C<sub>17</sub>), 130.1 (C<sub>18</sub>), 128.8 (C<sub>5</sub>), 126.0 (C<sub>4</sub>), 124.7 (C<sub>19</sub>), 121.6 & 113.0 (C<sub>A</sub> C<sub>B</sub>), 71.1 (C<sub>E</sub> C<sub>E'</sub>), 70.3 (C<sub>D</sub> C<sub>D'</sub>), 69.1 (C<sub>C</sub> C<sub>C'</sub>), 54.0 (C<sub>7</sub>), 50.0 (C<sub>9</sub>), 43.8 (C<sub>16</sub>), 36.8 (C<sub>13</sub>), 35.0 & 34.8 (C<sub>2</sub> C<sub>21</sub>), 32.5 (C<sub>22</sub>), 31.7 & 31.6 (C<sub>1</sub>), 30.6 (C<sub>10</sub>), 27.9 (C<sub>11</sub>), 26.0 (C<sub>12</sub>).

**HRMS (ESI)**: [M+H]<sup>+</sup> calcd for C<sub>52</sub>H<sub>75</sub>N<sub>2</sub>O<sub>9</sub><sup>+</sup>: 871.5473, found: 871.5477.

## 1.4. Synthesis of [2]rotaxane 2-Boc



To a solution of rotaxane **2-H<sup>+</sup>** (67 mg, 0.066 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) were successively added P1-tBuphosphazene (15.4 mg, 0.066 mmol, 1 equiv.) and Boc<sub>2</sub>O (32 mg, 0.146 mmol, 2.2 equiv.). The mixture was stirred for 23h at room temperature before being evaporated to dryness. The crude was purified by chromatography on a lipophilic sephadex LH20 (CH<sub>2</sub>Cl<sub>2</sub>) to afford the pure rotaxane **2-Boc** (57 mg, 89 %) as a white solid.

R<sub>f</sub>: 0.71 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

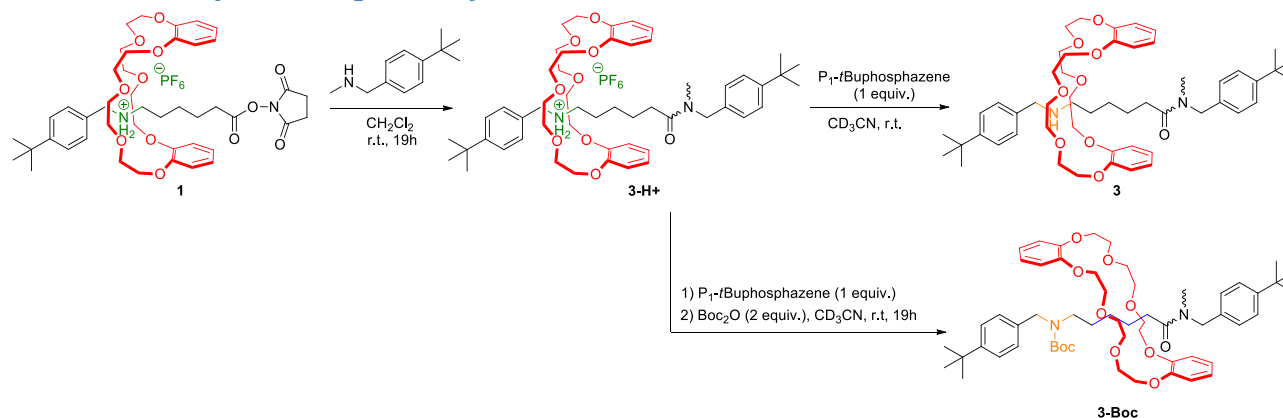
**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 7.57 (d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.3Hz, H<sub>18</sub>), 7.37 (d, 2H, <sup>3</sup>J<sub>H4-H5</sub> = 8.3Hz, H<sub>4</sub>), 7.24 (br t, 1H, H<sub>15</sub>), 7.12 (d, 2H, <sup>3</sup>J<sub>H5-H4</sub> = 8.3Hz, H<sub>5</sub>), 7.12 (d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.3Hz, H<sub>19</sub>), 6.89-6.83 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 4.65 (br d, 2H, H<sub>16</sub>), 4.28 (s, 2H, H<sub>7</sub>), 4.12-4.07 & 4.03-3.98 (2m, 2x4H, H<sub>C</sub> H<sub>C'</sub>), 3.72-3.61 (m, 8H, H<sub>D</sub> H<sub>D'</sub>), 3.48-3.42 & 3.23-3.17 (2m, 2x4H, H<sub>E</sub> H<sub>E'</sub>), 3.01-2.93 (m, 2H, H<sub>9</sub>), 1.97 (br t, 2H, H<sub>13</sub>), 1.45-1.35 (m, 2H, H<sub>12</sub>), 1.41 (br s, 9H, H<sub>Boc</sub>), 1.35-1.26 (m, 2H, H<sub>10</sub>), 1.30 (s, 9H, H<sub>1</sub>), 1.24 (s, 9H, H<sub>22</sub>), 1.02-0.94 (m, 2H, H<sub>11</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 173.1 (C<sub>14</sub>), 156.6 & 156.1 (C<sub>IV</sub> CO Boc), 150.8 & 149.4 (C<sub>3</sub> C<sub>20</sub>), 149.3 (C<sub>IV</sub> arom DB24C8), 138.4 & 137.1 (C<sub>17</sub> C<sub>6</sub>), 130.1 (C<sub>18</sub>), 128.0 (C<sub>5</sub>), 126.2 (C<sub>4</sub>), 124.7 (C<sub>19</sub>), 121.6 & 113.0 (C<sub>A</sub> C<sub>B</sub>), 79.7 (C<sub>IV</sub> Boc), 71.1 (C<sub>E</sub> C<sub>E'</sub>), 70.3 (C<sub>D</sub> C<sub>D'</sub>), 69.1 (C<sub>C</sub> C<sub>C'</sub>), 50.4 & 50.0 (C<sub>7</sub>), 47.6 & 47.2 (C<sub>9</sub>), 43.8 (C<sub>16</sub>), 36.8 (C<sub>13</sub>), 35.0 & 34.8 (C<sub>21</sub> C<sub>2</sub>), 31.7 & 31.6 (C<sub>1</sub> C<sub>22</sub>), 29.0 & 28.6 & 28.4 (C<sub>Boc</sub> C<sub>10</sub>), 27.4 (C<sub>11</sub>), 25.8 (C<sub>12</sub>).

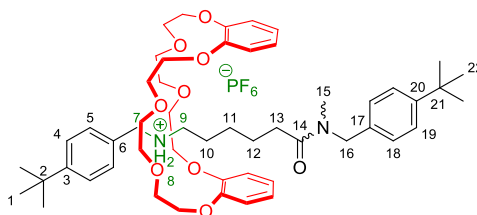
**HRMS (ESI):** [M+H]<sup>+</sup> calcd for C<sub>57</sub>H<sub>83</sub>N<sub>2</sub>O<sub>11</sub><sup>+</sup>: 971.5997, found: 971.5999.

## 2. Synthesis of [2]rotaxanes 3-H<sup>+</sup>, 3 and 3-Boc.

### 2.1. General synthetic pathway



## 2.2. Synthesis of [2]rotaxane 3-H<sup>+</sup>



**3-H<sup>+</sup> (trans/cis 61/39)**

To a solution of rotaxane building block **1**<sup>[2]</sup> (101 mg, 0.10 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added the *N*-methyl-4-*tert*-butylbenzylamine (56 mg, 0.32 mmol, 3 equiv.). The mixture was stirred for 19h at room temperature and evaporated to dryness. The crude was purified by chromatography on a lipophilic sephadex LH20 (CH<sub>2</sub>Cl<sub>2</sub>) to afford the pure rotaxane **3-H<sup>+</sup>** (74 mg, 70 %) as a white solid.

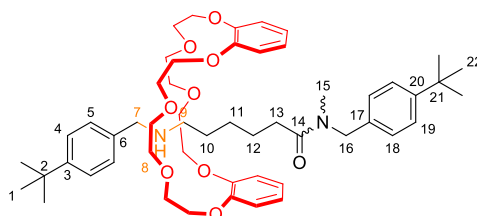
**R<sub>f</sub>**: 0.71 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.42 & 7.37 (2d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.2 Hz, H<sub>19-cis</sub> H<sub>19-trans</sub>), 7.28 (d, 2H, <sup>3</sup>J<sub>H5-H4</sub> = 8.2 Hz, H<sub>5</sub>), 7.22 (d, 2H, <sup>3</sup>J<sub>H4-H5</sub> = 8.2 Hz, H<sub>4</sub>), 7.17-7.07 (br s, 2H, H<sub>8</sub>), 7.14 & 7.09 (2d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.2 Hz, H<sub>18-trans</sub> H<sub>18-cis</sub>), 6.92-6.84 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 4.56-4.48 (m, 2H, H<sub>7</sub>), 4.46 & 4.43 (2s, 2H, H<sub>16-trans</sub> H<sub>16-cis</sub>), 4.19-4.11 & 4.09-4.01 (m, 8H, H<sub>C</sub> H<sub>C'</sub>), 3.83-3.76 (m, 8H, H<sub>D</sub> H<sub>D'</sub>), 3.69-3.60 & 3.57-3.48 (m, 8H, H<sub>E</sub> H<sub>E'</sub>), 3.38-3.31 & 3.31-3.24 (2m, 2H, H<sub>9</sub>), 2.84 & 2.82 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.08 & 2.06 (2br t, 2H, H<sub>13</sub>), 1.57-1.47 & 1.47-1.41 (2m, 2H, H<sub>10-trans</sub> H<sub>10-cis</sub>), 1.41-1.32 (m, 2H, H<sub>12</sub>), 1.30 & 1.29 (2s, 9H, H<sub>22-cis</sub> H<sub>22-trans</sub>), 1.23 (s, 9H, H<sub>1</sub>), 1.15-1.07 & 1.06-0.99 (2m, 2H, H<sub>11-trans</sub> H<sub>11-cis</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.3 & 173.1 (C<sub>14</sub>), 153.0 & 151.2 & 150.9 (C<sub>3</sub> C<sub>20</sub>), 148.5 (C<sub>IV arom DB24C8</sub>), 136.3 & 135.6 (C<sub>17</sub>), 130.4 & 130.4 (C<sub>6</sub>), 130.5 (C<sub>5</sub>), 128.3 (C<sub>18-trans</sub>), 127.1 (C<sub>18-cis</sub>), 126.6 (C<sub>19-cis</sub>), 126.3 (C<sub>4</sub> C<sub>19-trans</sub>), 122.3 & 113.5 (C<sub>A</sub> C<sub>B</sub>), 71.6 & 71.6 (C<sub>E</sub> C<sub>E'</sub>), 71.1 & 71.1 (C<sub>D</sub> C<sub>D'</sub>), 69.0 (C<sub>C</sub> C<sub>C'</sub>), 53.3 (C<sub>16-cis</sub>), 52.8 & 52.8 (C<sub>7</sub>), 50.4 (C<sub>16-trans</sub>), 49.6 (C<sub>9</sub>), 35.5 (C<sub>15-trans</sub>), 35.1 & 35.1 & 35.0 (C<sub>21</sub> C<sub>2</sub>), 34.0 (C<sub>15-cis</sub>), 33.4 & 33.1 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 31.6 & 31.4 (C<sub>22</sub> C<sub>1</sub>), 27.2 & 27.1 (C<sub>10</sub>), 26.8 & 26.7 (C<sub>11</sub>), 25.3 & 25.1 (C<sub>12</sub>).

**HRMS (ESI)**: [M-PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>53</sub>H<sub>77</sub>N<sub>2</sub>O<sub>9</sub><sup>+</sup>: 885.5629, found: 885.5632.

## 2.3. Synthesis of [2]rotaxane 3



**3 (trans/cis 59/41)**

To a solution of rotaxane **3-H<sup>+</sup>** (56 mg, 0.054 mmol, 1 equiv.) in CD<sub>3</sub>CN (0.6 mL) was added P1-*t*Buphosphazene (13 mg, 0.055 mmol, 1 equiv.), directly in the NMR tube. The rotaxane **3** (quantitative conversion) was characterized without being isolated.

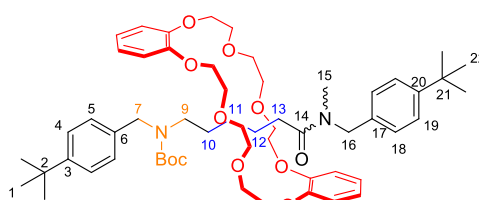
<sup>[2]</sup> Synthesis and characterization of **1** have already been described by F. Coutrot *et al.* in *Chem. Eur. J.*, **2016**, *22*, 8835-8847.

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 7.36 & 7.34 (2br d, 2H, H<sub>19</sub>), 7.21-7.15 (m, 4H, H<sub>4</sub> H<sub>5</sub>), 7.10 & 7.00 (2br d, 2H, H<sub>18-trans</sub> H<sub>18-cis</sub>), 6.89-6.82 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 4.41 & 4.37 (2s, 2H, H<sub>16-trans</sub> H<sub>16-cis</sub>), 4.14-4.02 (m, 8H, H<sub>C</sub> H<sub>C'</sub>), 3.81-3.77 & 3.77-3.73 (2m, 2x4H, H<sub>D</sub> H<sub>D'</sub>), 3.74 & 3.70 (2s, 2H, H<sub>7</sub>), 3.62-3.56 & 3.56-3.47 (2m, 8H, H<sub>E</sub> H<sub>E'</sub>), 2.75 & 2.72 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.71-2.61 (m, 2H, H<sub>9</sub>), 2.22 (br t, 2H, H<sub>13</sub>), 1.58-1.43 (m, 4H, H<sub>12</sub> H<sub>10</sub>), 1.34-1.26 (m, 2H, H<sub>11</sub>), 1.29 & 1.28 (2s, 9H, H<sub>22</sub>), 1.24 (s, 9H, H<sub>1</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 174.6 & 174.4 (C<sub>14</sub>), 150.9 & 150.7 & 149.8 (C<sub>3</sub> C<sub>20</sub>), 149.2 (C<sub>IV</sub> arom DB24C8), 136.5 & 135.9 (C<sub>6</sub> C<sub>17</sub>), 129.3 (C<sub>5</sub>), 128.3 (C<sub>18-trans</sub>), 127.2 (C<sub>18-cis</sub>), 126.5 & 126.3 (C<sub>19</sub>), 125.6 (C<sub>4</sub>), 121.7 & 113.3 & 113.2 (C<sub>A</sub> C<sub>B</sub>), 71.4 (C<sub>E</sub> C<sub>E'</sub>), 70.4 (C<sub>D</sub> C<sub>D'</sub>), 69.0 & 69.0 (C<sub>C</sub> C<sub>C'</sub>), 53.5 (C<sub>7</sub>), 53.3 (C<sub>16-cis</sub>), 50.7 (C<sub>16-trans</sub>), 50.3 (C<sub>9</sub>), 35.4 (C<sub>15-trans</sub>), 35.0 & 35.0 & 34.9 (C<sub>2</sub> C<sub>21</sub>), 34.1 & 33.9 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 33.7 (C<sub>15-cis</sub>), 31.6 & 31.6 (C<sub>22</sub> C<sub>1</sub>), 29.6 (C<sub>10</sub>), 27.7 & 27.6 (C<sub>11</sub>), 26.1 & 25.7 (C<sub>12</sub>).

**HRMS (ESI):** [M+H]<sup>+</sup> calcd for C<sub>52</sub>H<sub>75</sub>N<sub>2</sub>O<sub>9</sub><sup>+</sup>: 885.5629, found: 885.5632.

## 2.4. Synthesis of [2]rotaxane 3-Boc



**3-Boc (trans/cis 56/44)**

To a solution of rotaxane **3-H<sup>+</sup>** (56 mg, 0.054 mmol, 1 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) were successively added P1-*t*Buphosphazene (13 mg, 0.055 mmol, 1 equiv.) and Boc<sub>2</sub>O (26 mg, 0.119 mmol, 2.2 equiv.). The mixture was stirred for 19h at room temperature before being evaporated to dryness. The crude was purified by chromatography on a lipophilic sephadex LH20 (CH<sub>2</sub>Cl<sub>2</sub>) to afford the pure rotaxane **3-Boc** (50 mg, 93 %) as a white solid.

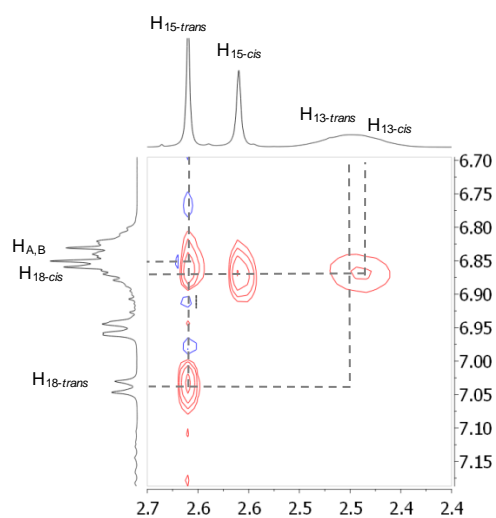
**R<sub>f</sub>:** 0.74 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 7.31-7.21 (m, 4H, H<sub>4</sub> H<sub>19</sub>), 7.04 & 6.88 (2br d, 2H, H<sub>18-trans</sub> H<sub>18-cis</sub>), 6.95 (br d, 2H, H<sub>5</sub>), 6.89-6.79 (m, 8H, H<sub>A</sub> H<sub>B</sub>), 4.34 & 4.31 (2s, 2H, H<sub>16-trans</sub> H<sub>16-cis</sub>), 4.10 (br s, 2H, H<sub>7</sub>), 4.15-4.06 & 4.06-3.99 (2m, 8H, H<sub>C</sub> H<sub>C'</sub>), 3.83-3.77 & 3.77-3.65 (2m, 8H, H<sub>D</sub> H<sub>D'</sub>), 3.61-3.56 & 3.56-3.50 (2m, 8H, H<sub>E</sub> H<sub>E'</sub>), 3.08-2.91 (m, 2H, H<sub>9</sub>), 2.66 & 2.61 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.56-2.43 (m, 2H, H<sub>13</sub>), 1.96-1.82 (m, 2H, H<sub>12</sub>), 1.73-1.62 (m, 2H, H<sub>10</sub>), 1.58-1.46 (m, 2H, H<sub>11</sub>), 1.34 (br s, 9H, H<sub>Boc</sub>), 1.29 & 1.28 & 1.27 & 1.27 (4s, 18H, H<sub>1</sub> H<sub>22</sub>).

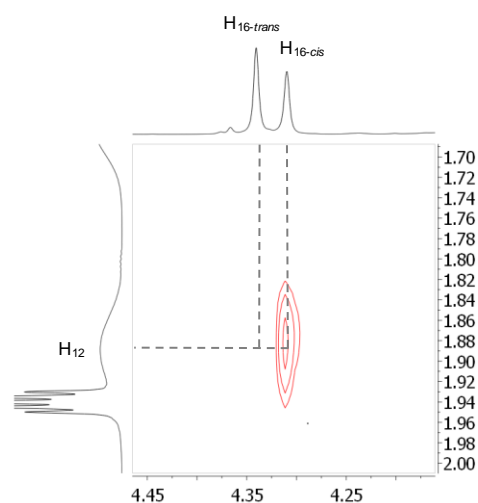
**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K):** δ ppm = 176.3 & 176.0 (C<sub>14</sub>), 156.8 & 156.2 (C<sub>IV</sub> CO Boc), 150.6 & 150.5 & 150.3 & 149.8 (C<sub>3</sub> C<sub>20</sub>), 149.4 & 149.3 (C<sub>IV</sub> arom DB24C8), 137.4 & 137.2 & 136.6 & 136.1 (C<sub>6</sub> C<sub>17</sub>), 128.2 (C<sub>18-trans</sub>), 128.0 (C<sub>5</sub>), 127.2 (C<sub>18-cis</sub>), 126.3 & 126.2 (C<sub>19-cis</sub> C<sub>19-trans</sub>), 126.0 (C<sub>4</sub>), 121.4 & 121.4 & 113.0 & 113.0 (C<sub>A</sub> C<sub>B</sub>), 79.2 (C<sub>IV</sub> Boc), 71.7 & 71.6 (C<sub>E</sub> C<sub>E'</sub>), 70.6 & 70.5 (C<sub>D</sub> C<sub>D'</sub>), 69.2 & 69.1 (C<sub>C</sub> C<sub>C'</sub>), 53.1 (C<sub>16-cis</sub>), 50.4 (C<sub>16-trans</sub>), 49.4 & 48.9 (C<sub>7</sub>), 48.1 & 47.3 (C<sub>9</sub>), 35.3 (C<sub>15-trans</sub>), 35.0 & 35.0 (C<sub>2</sub> C<sub>17</sub>), 34.7 & 34.4 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 33.2 (C<sub>15-cis</sub>), 31.6 & 31.6 (C<sub>22</sub> C<sub>1</sub>), 28.7 (C<sub>Boc</sub>), 28.3 & 27.8 (C<sub>10</sub>), 27.4 & 27.1 & 27.1 & 27.0 (C<sub>11</sub>), 26.0 & 25.8 & & 25.6 & 25.4 (C<sub>12</sub>).

**HRMS (ESI):** [M+H]<sup>+</sup> calcd for C<sub>58</sub>H<sub>85</sub>N<sub>2</sub>O<sub>11</sub><sup>+</sup>: 985.6153, found: 985.6163.

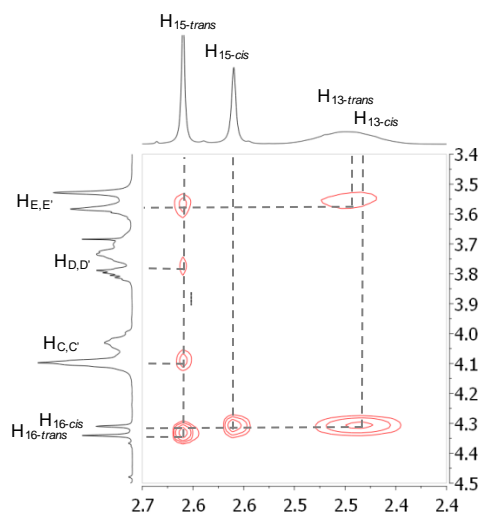
Selected 2D-ROESY  $^1\text{H}$  spectrum portions (500MHz,  $\text{CD}_3\text{CN}$ , 298K) of rotaxane 3-Boc



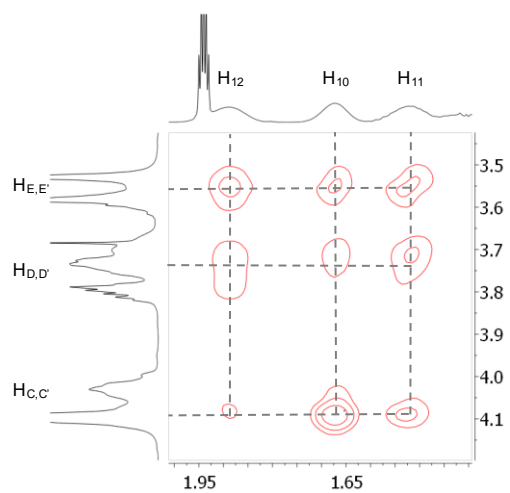
ROE correlation between the aromatic hydrogen atoms  $\text{H}_{18\text{-cis}}$  and the most acidic hydrogen atoms  $\text{H}_{13\text{-cis}}$ . The same correlation is not observed for the *trans* isomers.



ROE correlation between hydrogen atoms  $\text{H}_{16\text{-cis}}$  and hydrogen atoms  $\text{H}_{12\text{-cis}}$ . The same correlation is not observed for the *trans* isomers.



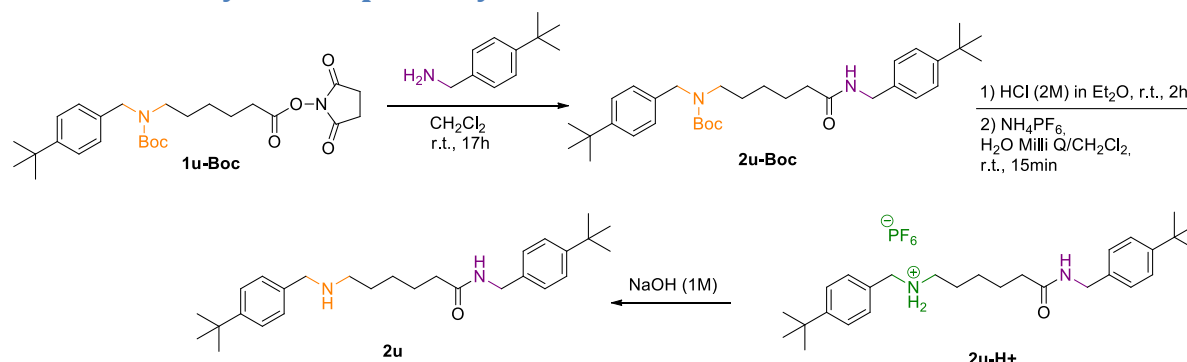
ROE correlation between the hydrogen atoms  $\text{H}_{15\text{-trans}}$  and the hydrogen atoms  $\text{H}_{\text{C-E}}$  belonging to the DB24C8. The same correlations are not observed for the *cis* isomers.



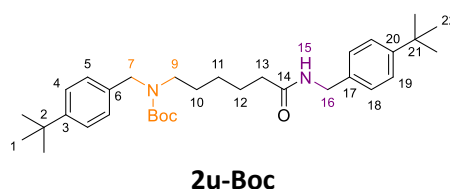
ROE correlation between the hydrogen atoms  $\text{H}_{10-12}$  and the hydrogen atoms  $\text{H}_{\text{C-E}}$  belonging to the DB24C8.

### 3. Synthesis of the uncomplexed threads **2u**, **2u-H<sup>+</sup>** and **2u-Boc**

#### 3.1. General synthetic pathway



#### 3.2. Synthesis of carbamate thread **2u-Boc**



To a solution of carbamate building block **1u-Boc**<sup>[3]</sup> (320 mg, 0.67 mmol, 1 equiv.) in dry  $\text{CH}_2\text{Cl}_2$  (20 mL) was added the 4-*tert*-butylbenzylamine (220 mg, 1.37 mmol, 2 equiv.). The mixture was stirred for 17h at room temperature before being washed with an aqueous 1M solution of HCl (2x25 mL). The combined aqueous layers were extracted with  $\text{CH}_2\text{Cl}_2$  (3x25 mL). Finally, the combined organic layers were washed with an aqueous 1M solution of NaOH (3x25 mL), dried over  $\text{MgSO}_4$ , filtrated and evaporated to afford the pure carbamate thread **2u-Boc** (347 mg, 98 %) as a colorless oil.

**R<sub>f</sub>**: 0.82 ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$  9/1).

**<sup>1</sup>H NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298K)**:  $\delta$  ppm = 7.37 & 7.35 (2br d, 4H, H<sub>19</sub> H<sub>4</sub>), 7.18 & 7.17 (2br d, 4H, H<sub>18</sub> H<sub>5</sub>), 6.77 (br s, 1H, H<sub>15</sub>), 4.35 (s, 2H, H<sub>7</sub>), 4.27 (d, 2H, <sup>3</sup>J<sub>H16-H15</sub> = 6.1Hz, H<sub>16</sub>), 3.13 (br t, 2H, H<sub>9</sub>), 2.12 (t, 2H, <sup>3</sup>J<sub>H13-H12</sub> = 7.4Hz, H<sub>13</sub>), 1.59-1.52 (m, 2H, H<sub>12</sub>), 1.52-1.43 (m, 2H, H<sub>10</sub>), 1.43 (br s, 9H, H<sub>Boc</sub>), 1.29 & 1.28 (2s, 18H, H<sub>22</sub> H<sub>1</sub>), 1.29-1.20 (m, 2H, H<sub>11</sub>).

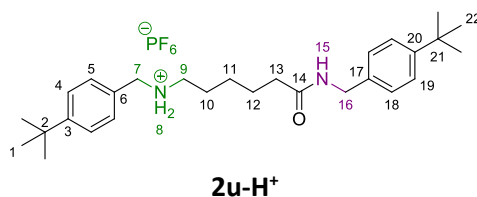
**<sup>13</sup>C NMR (126 MHz,  $\text{CD}_3\text{CN}$ , 298K)**:  $\delta$  ppm = 173.5 (C<sub>14</sub>), 156.7 & 156.3 (C<sub>IV CO Boc</sub>), 150.9 & 150.7 (C<sub>20</sub> C<sub>3</sub>), 137.7 & 137.1 (C<sub>17</sub> C<sub>6</sub>), 128.1 & 128.0 (C<sub>5</sub> C<sub>18</sub>), 126.3 (C<sub>4</sub> C<sub>19</sub>), 79.8 (C<sub>IV Boc</sub>), 50.5 & 50.1 (C<sub>7</sub>), 47.3 & 47.1 (C<sub>9</sub>), 43.0 (C<sub>16</sub>), 36.7 (C<sub>13</sub>), 35.0 (C<sub>21</sub> C<sub>2</sub>), 31.5 (C<sub>1</sub> C<sub>22</sub>), 28.6 (C<sub>Boc</sub>), 28.3 (C<sub>10</sub>), 27.0 (C<sub>11</sub>), 26.2 (C<sub>12</sub>).

**HRMS (ESI)**: [M+H]<sup>+</sup> calcd for C<sub>33</sub>H<sub>51</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 523.3900, found: 523.3903.

<sup>3</sup> Synthesis and characterization of **1u-Boc** have already been described by F. Coutrot *et al.* in *Chem. Eur. J.*, **2016**, 22, 8835-8847.



### 3.3. Synthesis of compound 2u-H<sup>+</sup>



A solution of thread **2u-Boc** (284 mg, 0.56 mmol, 1 equiv.) in 2M HCl/Et<sub>2</sub>O (5 mL) was stirred for 2h at 20°C until TLC analysis revealed no trace of starting material. The mixture was evaporated to dryness and the residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and Milli Q H<sub>2</sub>O (1 mL). NH<sub>4</sub>PF<sub>6</sub> (275 mg, 1.66 mmol, 3 equiv.) was added and the mixture was vigorously stirred for 15 minutes. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL) and the combined organic layers were dried over MgSO<sub>4</sub> and concentrated to afford compound **2u-H<sup>+</sup>** (282 mg, 89 %) as a yellow solid without further purification.

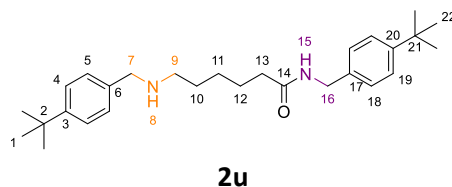
**R<sub>f</sub>**: 0.58 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.47 (br d, 2H, <sup>3</sup>J<sub>H4-H5</sub> = 8.4 Hz, H<sub>4</sub>), 7.39 (br d, 2H, <sup>3</sup>J<sub>H5-H4</sub> = 8.4 Hz, H<sub>5</sub>), 7.37 (br d, 2H, <sup>3</sup>J<sub>H19-H18</sub> = 8.4 Hz, H<sub>19</sub>), 7.28 (br s, 1H, H<sub>8</sub>), 7.17 (br d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.4 Hz, H<sub>18</sub>), 6.95 (br s, 1H, H<sub>15</sub>), 4.27 (d, 2H, <sup>3</sup>J<sub>H16-H15</sub> = 6.1 Hz, H<sub>16</sub>), 4.13-4.06 (m, 2H, H<sub>7</sub>), 3.10-3.00 (m, 2H, H<sub>9</sub>), 2.20 (t, 2H, <sup>3</sup>J<sub>H13-H12</sub> = 7.1 Hz, H<sub>13</sub>), 1.73-1.64 (m, 2H, H<sub>10</sub>), 1.62-1.53 (m, 2H, H<sub>12</sub>), 1.41-1.33 (m, 2H, H<sub>11</sub>), 1.30 & 1.29 (2s, 18H, H<sub>22</sub> H<sub>1</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 174.1 (C<sub>14</sub>), 153.7 & 150.9 (C<sub>3</sub> C<sub>20</sub>), 137.7 (C<sub>17</sub>), 130.8 (C<sub>5</sub>), 128.8 (C<sub>6</sub>), 128.0 (C<sub>18</sub>), 126.9 (C<sub>4</sub>), 126.3 (C<sub>19</sub>), 52.1 (C<sub>7</sub>), 48.2 (C<sub>9</sub>), 43.2 (C<sub>16</sub>), 35.6 (C<sub>13</sub>), 35.3 & 35.0 (C<sub>21</sub> C<sub>2</sub>), 31.5 & 31.3 (C<sub>22</sub> C<sub>1</sub>), 25.9 (C<sub>11</sub>), 25.7 (C<sub>10</sub>), 24.4 (C<sub>12</sub>).

**HRMS (ESI)**: [M-PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>O<sup>+</sup>: 423.3375, found: 423.3367.

### 3.4. Synthesis of compound 2u



A solution of compound **2u-H<sup>+</sup>** (182 mg, 0.32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was washed with an aqueous 1M solution of NaOH (5 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x5 mL) and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated to afford compound **2u** (137 mg, quantitative yield) as an orange oil.

**R<sub>f</sub>**: 0.39 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

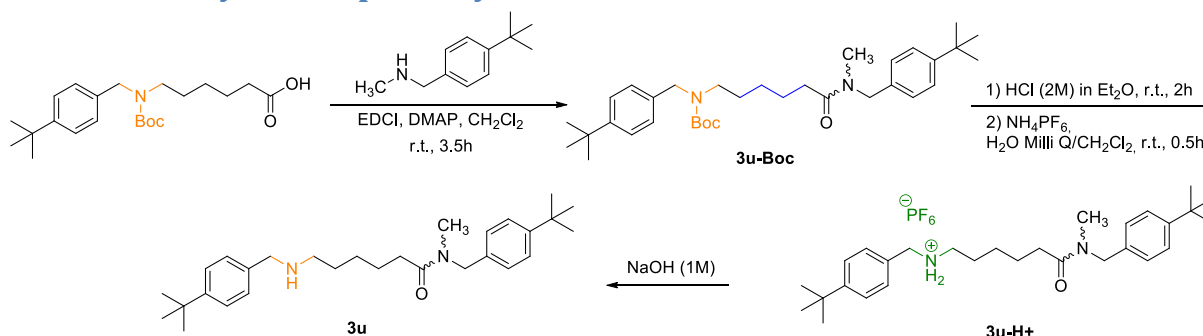
**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.36 (d, 4H, <sup>3</sup>J<sub>H19-H18</sub> = 8.1Hz <sup>3</sup>J<sub>H4-H5</sub> = 8.1Hz, H<sub>19</sub> H<sub>4</sub>), 7.24 (d, 2H, <sup>3</sup>J<sub>H5-H4</sub> = 8.1Hz, H<sub>5</sub>), 7.18 (d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.1Hz, H<sub>18</sub>), 6.77 (br s, 1H, H<sub>15</sub>), 4.27 (d, 2H, <sup>3</sup>J<sub>H9-H10</sub> = 6.0Hz, H<sub>16</sub>), 3.70 (s, 2H, H<sub>7</sub>), 2.55 (t, 2H, <sup>3</sup>J<sub>H9-H10</sub> = 7.0Hz, H<sub>9</sub>), 2.15 (t, 2H, <sup>3</sup>J<sub>H13-H12</sub> = 7.4Hz, H<sub>13</sub>), 1.61-1.53 (m, 2H, H<sub>12</sub>), 1.51-1.43 (m, 2H, H<sub>10</sub>), 1.36-1.28 (m, 2H, H<sub>11</sub>), 1.29 & 1.29 (2s, 18H, H<sub>22</sub>, H<sub>1</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.6 (C<sub>14</sub>), 150.7 & 150.5 (C<sub>3</sub> C<sub>20</sub>), 138.7 & 137.7 (C<sub>17</sub> C<sub>6</sub>), 128.8 (C<sub>5</sub>), 128.0 (C<sub>18</sub>), 126.2 & 126.1 (C<sub>4</sub> C<sub>19</sub>), 53.9 (C<sub>7</sub>), 49.8 (C<sub>9</sub>), 43.0 (C<sub>16</sub>), 36.7 (C<sub>13</sub>), 35.0 (C<sub>2</sub> C<sub>21</sub>), 31.6 & 31.5 (C<sub>1</sub> C<sub>22</sub>), 30.2 (C<sub>10</sub>), 27.5 (C<sub>11</sub>), 26.3 (C<sub>12</sub>).

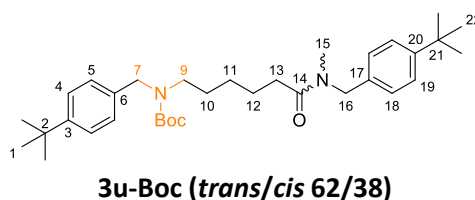
**HRMS (ESI)**: [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>O<sup>+</sup>: 423.3375, found: 423.3375.

## 4. Synthesis of the uncomplexed threads **3u**, **3u-H<sup>+</sup>** and **3u-Boc**

### 4.1. General synthetic pathway



### 4.2. Synthesis of compound **3u-Boc**



To a 0.02 M solution of carboxylic acid starting material<sup>[4]</sup> (320 mg, 0.85 mmol, 1 equiv.) and *N*-methyl-4-*tert*-butylbenzylamine (150 mg, 0.85 mmol, 1 equiv.) in dry amylene-stabilized CH<sub>2</sub>Cl<sub>2</sub> were added EDCI (243 mg, 1.27 mmol, 1.5 equiv.) and DMAP (362 mg, 2.96 mmol, 3.5 equiv.). The mixture was stirred for 3h30 at room temperature before being washed with an aqueous 1M solution of HCl (15 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and the combined organic layers were washed with an aqueous 1M solution of NaOH (3x15 mL), dried over MgSO<sub>4</sub> and concentrated. The residue was purified by silica gel chromatography (PE/EtOAc 1/1) to give thread **3u-Boc** (250 mg, 55%) as orange oil.

**R<sub>f</sub>**: 0.89 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

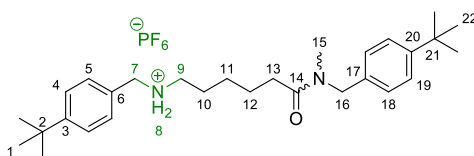
**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.42-7.34 (m, 4H, H<sub>19</sub> H<sub>4</sub>), 7.19-7.09 (m, 4H, H<sub>5</sub> H<sub>18</sub>), 4.50 & 4.48 (2s, 2H, H<sub>16</sub>), 4.37 & 4.34 (2s, 2H, H<sub>7</sub>), 3.19-3.08 (m, 2H, H<sub>9</sub>), 2.90 & 2.83 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.33 & 2.31 (2br t, 2H, H<sub>13-trans</sub> H<sub>13-cis</sub>), 1.62-1.54 (m, 2H, H<sub>12</sub>), 1.54-1.48 (m, 2H, H<sub>10</sub>), 1.48-1.37 (m, 9H, H<sub>Boc</sub>), 1.29 (s, 18H, H<sub>22</sub> H<sub>1</sub>), 1.33-1.19 (m, 2H, H<sub>11</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.7 & 173.5 (C<sub>14</sub>), 156.7 & 156.3 (C<sub>IV CO Boc</sub>), 151.2 & 150.9 (C<sub>3</sub> C<sub>20</sub>), 137.1 & 136.3 & 135.7 (C<sub>17</sub> C<sub>6</sub>), 128.2 & 128.1 & 127.2 (C<sub>5</sub> C<sub>18</sub>), 126.6 & 126.3 & 126.2 (C<sub>4</sub> C<sub>19</sub>), 79.8 (C<sub>IV Boc</sub>), 53.4 (C<sub>16-cis</sub>), 50.8 (C<sub>16-trans</sub>), 50.5 & 50.1 (C<sub>7</sub>), 47.4 & 47.1 (C<sub>9</sub>), 35.5 (C<sub>15-trans</sub>), 35.0 (C<sub>21</sub> C<sub>2</sub>), 34.0 (C<sub>15-cis</sub>), 33.7 & 33.4 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 31.6 (C<sub>22</sub> C<sub>1</sub>), 28.8 & 28.4 (C<sub>10</sub>), 28.6 (C<sub>Boc</sub>), 27.2 (C<sub>11</sub>), 25.8 & 25.6 (C<sub>12</sub>).

**HRMS (ESI)**: [M+H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>53</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>: 537.4056, found: 537.4058.

<sup>4</sup> Synthesis and characterization of carboxylic acid starting material have already been described by F. Coutrot *et al.* in *Chem. Eur. J.*, **2016**, *22*, 8835-8847.

### 4.3. Synthesis of compound 3u-H<sup>+</sup>



**3u-H<sup>+</sup> (trans/cis 64/36)**

A solution of compound **3u-Boc** (206 mg, 0.384 mmol, 1 equiv.) in 2M HCl/Et<sub>2</sub>O (10 mL) was stirred for 2h at 20°C until TLC analysis revealed no trace of starting material. The mixture was evaporated to dryness and the residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> (4 mL) and MilliQ H<sub>2</sub>O (2 mL). NH<sub>4</sub>PF<sub>6</sub> (42 mg, 1.150 mmol, 3 equiv.) was added and the mixture was vigorously stirred for 30 minutes. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL) and the combined organic layers were dried over MgSO<sub>4</sub> and concentrated to afford compound **3u-H<sup>+</sup>** (165 mg, 74%) without further purification.

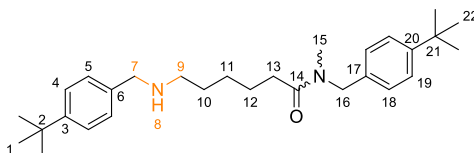
**R<sub>f</sub>**: 0.71 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.47-7.36 (m, 6H, H<sub>4</sub> H<sub>5</sub> H<sub>19</sub>), 7.12 (d, 2H, <sup>3</sup>J<sub>H18-H19</sub> = 8.1 Hz, H<sub>18</sub>), 4.50 & 4.46 (2s, 2H, H<sub>16-cis</sub> H<sub>16-trans</sub>), 4.09 (s, 2H, H<sub>7</sub>), 3.07 & 3.02 (2t, 2H, <sup>3</sup>J<sub>H9-H10</sub> = 7.2 Hz, H<sub>9-trans</sub> H<sub>9-cis</sub>), 2.91 & 2.81 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.38 & 2.35 (2t, 2H, <sup>3</sup>J<sub>H13-H12</sub> = 6.5 Hz, H<sub>13-trans</sub> H<sub>13-cis</sub>), 1.79-1.69 (m, 2H, H<sub>10</sub>), 1.58-1.49 (m, 2H, H<sub>12</sub>), 1.42-1.30 (m, 2H, H<sub>11</sub>), 1.29 & 1.25 (2s, 18H, H<sub>1</sub> H<sub>22</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 174.4 & 174.3 (C<sub>14</sub>), 153.5 & 153.5 & 151.4 & 151.1 (C<sub>3</sub> C<sub>20</sub>), 135.6 & 135.1 (C<sub>17</sub>), 130.9 (C<sub>5</sub>), 129.1 (C<sub>6</sub>), 128.3 & 127.3 & 126.8 & 126.7 & 126.7 & 126.4 (C<sub>4</sub> C<sub>18</sub> C<sub>19</sub>), 53.3 (C<sub>16-cis</sub>), 52.0 & 51.9 (C<sub>7</sub>), 51.2 (C<sub>16-trans</sub>), 47.9 & 47.8 (C<sub>9</sub>), 35.5 (C<sub>15-trans</sub>), 35.2 & 35.2 & 35.1 & 35.0 (C<sub>21</sub> C<sub>2</sub>), 34.2 (C<sub>15-cis</sub>), 32.9 & 32.8 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 31.5 & 31.4 (C<sub>22</sub> C<sub>1</sub>), 25.9 (C<sub>11-cis</sub>), 25.7 (C<sub>11-trans</sub>), 25.7 (C<sub>10-cis</sub>), 25.4 (C<sub>10-trans</sub>), 23.8 (C<sub>12-cis</sub>), 23.1 (C<sub>12-trans</sub>).

**HRMS (ESI)**: [M-PF<sub>6</sub>]<sup>+</sup> calcd for C<sub>29</sub>H<sub>45</sub>N<sub>2</sub>O<sup>+</sup>: 437.3532, found: 437.3529.

### 4.4. Synthesis of compound 3u



**3u (trans/cis 62/38)**

A solution of compound **3u-H<sup>+</sup>** (131 mg, 0.034 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was washed with an aqueous solution of NaOH 1M (5 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x5 mL) and the combined organic layers were dried over MgSO<sub>4</sub> and evaporated to afford compound **3u** (95 mg, quantitative yield) as an orange oil.

**R<sub>f</sub>**: 0.57 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9/1).

**<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 7.41-7.33 (m, 4H, H<sub>19</sub> H<sub>4</sub>), 7.26-7.21 (m, 2H, H<sub>5</sub>), 7.14 & 7.12 (2br d, 2H, H<sub>18</sub>), 4.51 & 4.48 (2s, 2H, H<sub>16-cis</sub> H<sub>16-trans</sub>), 3.69 & 3.67 (2s, 2H, H<sub>7</sub>), 2.90 & 2.83 (2s, 3H, H<sub>15-trans</sub> H<sub>15-cis</sub>), 2.55 & 2.51 (2t, 2H, <sup>3</sup>J<sub>H9-H10</sub> = 7.0Hz, H<sub>9-trans</sub> H<sub>9-cis</sub>), 2.36 & 2.33 (2br t, 2H, H<sub>13-trans</sub> H<sub>13-cis</sub>), 1.63-1.51 (m, 2H, H<sub>12</sub>), 1.53-1.58 (m, 2H, H<sub>10</sub>), 1.41-1.30 (m, 2H, H<sub>11</sub>), 1.29 (s, 18H, H<sub>1</sub> H<sub>22</sub>).

**<sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN, 298K)**: δ ppm = 173.8 & 173.6 (C<sub>14</sub>), 151.2 & 150.8 & 150.4 (C<sub>3</sub> C<sub>20</sub>), 139.1 & 136.3 & 135.7 (C<sub>17</sub> C<sub>6</sub>), 128.8 (C<sub>5</sub>), 128.3 & 127.2 (C<sub>18</sub>), 126.6 & 126.3 & 126.0 (C<sub>4</sub> C<sub>19</sub>), 54.1 & 54.0 (C<sub>7</sub>), 53.4 (C<sub>16-cis</sub>), 50.9 (C<sub>16-trans</sub>), 50.0 & 49.9 (C<sub>9</sub>), 35.6 (C<sub>15-trans</sub>), 35.1 & 35.0 (C<sub>21</sub> C<sub>2</sub>), 34.1 (C<sub>15-cis</sub>), 33.9 & 33.5 (C<sub>13-trans</sub> C<sub>13-cis</sub>), 31.8 & 31.7 (C<sub>22</sub> C<sub>1</sub>), 30.6 & 30.6 (C<sub>10</sub>), 27.9 & 27.8 (C<sub>11</sub>), 26.1 & 25.8 (C<sub>12</sub>).

**HRMS (ESI)**: [M+H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>45</sub>N<sub>2</sub>O<sup>+</sup>: 437.3532, found: 437.3531.

# SPECTRA

