Efficient catalytic vicinal diamination of arylene diimides

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Supporting Information
1. Experimental Section

1.1. General methods

Reagents were purchased at reagent grade from commercial sources and used without further purification. All air-sensitive reactions were carried out using standard Schlenk techniques under argon. Reaction solvents (THF, piperidine, dichloromethane, pyridine, triethylamine, toluene) were dried, distilled, and stored under argon according to standard methods, workup solvents were either used in "p.a." quality or purified by distillation. All solids and oils were dried overnight at RT under vacuum prior to characterization and further processing. $^1$H and $^{13}$C-NMR spectra were recorded on a Bruker DPX 300, DPX 400 and DRX 500 (300.1, 400.1, and 500.1 MHz for $^1$H and 75.5, 100.6 and 125.8 MHz for $^{13}$C). Chemical shifts are given in parts per million (ppm) referenced to residual $^1$H or $^{13}$C signals in deuterated solvents. Mass spectra were measured on a Finnigan ThermoQuest MAT 95 XL (EI-MS), a Bruker Daltonics micrOTOF-Q (ESI-MS) and a Bruker Daltronicsautoflex TOF/TOF (MALDI-MS; matrix material: DCTB, no salts added). m/z peaks smaller than 10 % (compared to the basis peak) are not reported. Thin layer chromatography was conducted on silica gel coated aluminium plates (Macherey-Nagel, Alugramm SIL G/UV254, 0.25 mm coating with fluorescence indicator). Column chromatography was performed using Silica gel Kieselgel 60 (Merck, 0.040-0.063 mm) as stationary phase. UV/Vis absorption and fluorescence emission spectra were recorded on a Perkin Elmer Lambda 18 and LS-50B Perkin Elmer spectrophotometer using 10 mm quartz cuvettes.

1.2. Synthesis

1

1 was prepared from perylenetetracarboxylic anhydride (PTCDA) according to the literature procedure described by R. Wasielewski.[1]

General procedure for the optimization of the amination of unsubstituted PDI 1 with piperidine.

The catalyst (14.8 µmol) was added to a stirred solution of 1 (30 mg, 42.2 µmol) and the additives in piperidine for 6 h or 24 h at various temperatures (rt-60°C). After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane).
Scheme 1: Direct amination and diamination of the unsubstituted PDI 1 with piperidine.

Table 1 Reaction of 1 with piperidine with several catalysts at 60 °C after 6 h.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>2a [%]</th>
<th>2b [%]</th>
<th>Overall yield [%]</th>
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<tr>
<td>1</td>
<td>-</td>
<td>H₂O, Cs₂CO₃</td>
<td>40</td>
<td>59</td>
<td>99</td>
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<tr>
<td>2</td>
<td>Mn(OAc)₃•2H₂O</td>
<td>-</td>
<td>44</td>
<td>26</td>
<td>70</td>
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<tr>
<td>3</td>
<td>Mn(OAc)₃•2H₂O</td>
<td>H₂O, Cs₂CO₃</td>
<td>53</td>
<td>10</td>
<td>63</td>
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<tr>
<td>4</td>
<td>Zn(OTf)₂</td>
<td>H₂O, Cs₂CO₃</td>
<td>70</td>
<td>7</td>
<td>77</td>
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<tr>
<td>5</td>
<td>-</td>
<td>D₂O</td>
<td>23</td>
<td>6</td>
<td>29</td>
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<tr>
<td>6</td>
<td>-</td>
<td>Glycerol</td>
<td>26</td>
<td>-</td>
<td>26</td>
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<tr>
<td>7</td>
<td>-</td>
<td>Ethyleneglycol</td>
<td>26</td>
<td>-</td>
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Table 2 Reaction of 1 with piperidine with several catalysts at 60 °C after 24h.

<table>
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<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>2a [%]</th>
<th>2b [%]</th>
<th>Overall yield [%]</th>
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<td>BINOL</td>
<td>Cs₂CO₃</td>
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<td>-</td>
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<td>BHT</td>
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<td>6</td>
<td>2,2'-Biphenol</td>
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<td>-</td>
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<td>2,4,6-Trichlorophenol</td>
<td>-</td>
<td>54</td>
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<tr>
<td>8</td>
<td>Pentfluorophenol</td>
<td>-</td>
<td>19</td>
<td>-</td>
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<tr>
<td>9</td>
<td>Cs₂CO₃</td>
<td>-</td>
<td>38</td>
<td>-</td>
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<td>Zn(OTf)₂</td>
<td>-</td>
<td>48</td>
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General procedure for the synthesis of 2a/b using water as additive.

Piperidine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol), copper(II)bromide (3.3 mg, 14.8 µmol) and cesium carbonate (13.7 mg, 42.0 µmol). The reaction mixture was stirred under air for 6 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na2SO4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane) to give 2a (9.8 mg, 12.3 µmol, 29 %; Rf: 0.45) as a green and 2b (24.8 mg, 28.3 µmol, 67 %; Rf: 0.65) as a blue solid.

2a

\(^1\text{H-NMR}\) (400 MHz, CDCl3, 298 K): \(\delta [\text{ppm}] = 9.96 (d, J = 8.4 \text{ Hz}, 1\text{H}), 8.77 (d, J = 7.9 \text{ Hz}, 1\text{H}), 8.74 (d, J = 8.3 \text{ Hz}, 1\text{H}), 8.68 (s, 1\text{H}), 8.67 – 8.61 (m, 3\text{H}), 7.50 (t, J = 7.8 \text{ Hz}, 2\text{H}), 7.38 – 7.34 (m, 4\text{H}), 3.62 – 3.55 (m, 2\text{H}), 3.10 – 3.02 (m, 2\text{H}), 2.84 – 2.72 (m, 4\text{H}), 2.0 – 1.85 (m, 6\text{H}), 1.21 – 1.18 (m, 24\text{H}).

\(^{13}\text{C-NMR}\) (100 MHz, CDCl3, 298 K): \(\delta [\text{ppm}] = 163.98, 163.91, 163.67, 163.60, 153.21, 145.82, 145.81, 136.72, 135.57, 134.68, 132.15, 131.73, 130.95, 130.78, 130.15, 129.76, 129.71, 129.64, 129.29, 127.68, 126.28, 125.94, 124.87, 124.21, 124.16, 123.81, 123.06, 122.72, 121.92, 121.44, 53.20, 29.35, 29.32, 26.04, 24.19, 24.16, 23.84.

\text{MS (MALDI TOF, matrix DCTB)} \text{C}_{53}\text{H}_{51}\text{N}_3\text{O}_4 (793.39): m/z (\%) = 793.4 (100) [M]^+.

2b

\(^1\text{H-NMR}\) (400 MHz, CDCl3, 298 K): \(\delta [\text{ppm}] = 9.81 (d, J = 8.4 \text{ Hz}, 2\text{H}), 8.68 (d, J = 8.3 \text{ Hz}, 2\text{H}), 8.47 (s, 2\text{H}), 7.50 (t, J = 7.8 \text{ Hz}, 2\text{H}), 7.36 (d, J = 7.8 \text{ Hz}, 2\text{H}), 7.35 (d, J = 7.8 \text{ Hz}, 2\text{H}), 3.01 – 2.92 (m, 4\text{H}), 3.10 – 3.02 (m, 4\text{H}), 2.80 (sept, J = 6.8 \text{ Hz}, 4\text{H}), 1.96 – 1.77 (m, 10\text{H}), 1.52 – 1.38 (m, 2\text{H}), 1.22 – 1.19 (m, 24\text{H}).

\(^{13}\text{C-NMR}\) (100 MHz, CDCl3, 298 K): \(\delta [\text{ppm}] = 163.91, 163.80, 153.70, 145.87, 145.87, 145.81, 136.59, 132.28, 131.37, 131.21, 130.86, 129.74, 129.69, 129.58, 128.54, 124.17, 124.15, 124.06, 123.62, 123.48, 123.12, 121.57, 120.45, 53.33, 29.85, 29.31, 26.04, 24.19, 24.19, 23.92.

\text{MS (MALDI TOF, matrix DCTB)} \text{C}_{58}\text{H}_{60}\text{N}_4\text{O}_4 (876.46): m/z (\%) = 876.5 (100) [M]^+.
3 a/b

Morpholine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol), copper(II)bromide (3.3 mg, 14.8 µmol) and cesium carbonate (13.7 mg, 42.0 µmol). The reaction mixture was stirred under air for 24 h at 80 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane: ethyl acetate, 100:5) to give 3a (4.5 mg, 5.6 µmol, 13 %; \( R_f: 0.22 \)) as a green and 3b (17.5 mg, 19.9 µmol, 47 %; \( R_f: 0.12 \)) as a blue solid.

3a

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta \ [ppm] = 10.15 \ (d, \ J = 8.3 \text{ Hz, 1H}), \ 8.78 \ (d, \ J = 8.0 \text{ Hz, 1H}), \ 8.74 \ (d, \ J = 8.3 \text{ Hz, 1H}), \ 8.65 \ (d, \ J = 7.6 \text{ Hz, 4H}), \ 7.51 \ (t, \ J = 7.7 \text{ Hz, 2H}), \ 7.36 \ (d, \ J = 7.9 \text{ Hz, 4H}), \ 4.09 - 3.96 \ (m, 4H), \ 3.51 - 3.48 \ (m, 2H), \ 2.81 - 2.72 \ (m, 4H), \ 1.21 - 1.18 \ (m, 24H). \]

\[ ^{13}C-NMR \ (100 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta \ [ppm] = 163.86, \ 163.77, \ 163.52, \ 163.49, \ 151.95, \ 145.79, \ 136.25, \ 135.37, \ 134.81, \ 131.95, \ 131.90, \ 130.80, \ 130.64, \ 130.11, \ 129.85, \ 129.79, \ 129.62, \ 127.75, \ 126.34, \ 125.31, \ 125.27, \ 124.33, \ 124.25, \ 124.08, \ 123.93, \ 123.13, \ 122.92, \ 122.31, \ 121.97, \ 66.78, \ 51.81, \ 29.38, \ 29.35, \ 24.20, \ 24.16. \]

**MS** (MALDI TOF, matrix DCTB) C₅₂H₄₉N₃O₅ (795.4): \( m/z \) (%): 795.4 (100) [M]+.

3b

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta \ [ppm] = 9.97 \ (d, \ J = 8.3 \text{ Hz, 2H}), \ 8.70 \ (d, \ J = 8.2 \text{ Hz, 2H}), \ 8.48 \ (s, 2H), \ 7.53 - 7.48 \ (m, 2H), \ 7.37 - 7.35 \ (m, 4H), \ 4.03 - 3.92 \ (m, 8H), \ 3.41 - 3.36 \ (m, 4H), \ 3.21 - 3.14 \ (m, 4H), \ 2.83 - 2.72 \ (m, 4H), \ 1.21 - 1.18 \ (m, 24H). \]

\[ ^{13}C-NMR \ (100 \text{ MHz, CDCl}_3, \ 298 \text{ K}): \delta \ [ppm] = 163.61, \ 163.57, \ 152.47, \ 145.80, \ 145.76, \ 135.91, \ 132.32, \ 131.28, \ 130.92, \ 130.62, \ 129.82, \ 129.71, \ 129.69, \ 128.78, \ 124.62, \ 124.22, \ 124.19, \ 123.79, \ 122.71, \ 122.36, \ 121.13, \ 66.75, \ 51.93, \ 29.36, \ 29.26, \ 24.25, \ 24.19, \ 24.15. \]

**MS** (MALDI TOF, matrix DCTB) C₅₆H₅₆N₄O₆ (880.4): \( m/z \) (%): 880.4 (100) [M]+.

4 a/b

1-Methylpiperazine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol), copper(II)bromide (3.3 mg, 14.8 µmol) and cesium carbonate (13.7 mg, 42.0 µmol). The reaction mixture was stirred under air for 24 h at 80 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane: ethyl acetate, 100:5) to give 4a (4.5 mg, 5.6 µmol, 13 %; \( R_f: 0.22 \)) as a green and 4b (17.5 mg, 19.9 µmol, 47 %; \( R_f: 0.12 \)) as a blue solid.
42.0 µmol). The reaction mixture was stirred under air for 18 h at 80 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane -> ethyl acetate) to give 4a (12.7 mg, 15.7 µmol, 37 %; Rf: 0.15) as a green and 4b (7.2 mg, 7.9 µmol, 19 %; Rf: 0.05) as a blue solid.

4a

¹H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 10.01 (d, J = 8.2 Hz, 1H), 8.78 (d, J = 8.0 Hz, 1H), 8.74 (d, J = 8.3 Hz, 1H), 8.69 − 8.61 (m, 4H), 7.54 − 7.48 (m, 2H), 7.39 − 7.34 (m, 4H), 3.69 − 3.59 (m, 2H), 3.49 (bs, 2H), 3.21 (bs, 2H), 2.90 (bs, 2H), 2.83 − 2.71 (m, 4H), 2.66 (bs, 3H), 1.23 − 1.15 (m, 24H).

¹³C-NMR (175 MHz, CDCl₃, 298 K): δ [ppm] = 163.85, 163.74, 163.56, 163.42, 145.79, 163.30, 135.41, 134.71, 131.95, 130.82, 130.63, 130.12, 129.83, 129.79, 129.56, 128.74, 127.72, 126.32, 125.43, 125.12, 124.39, 124.25, 124.23, 124.07, 123.15, 122.87, 122.31, 54.71, 29.36, 29.33, 24.21, 24.16.

MS (MALDI TOF, matrix DCTB) C₅₃H₅₂N₄O₄ (808.4): m/z (%): 808.4 (100) [M⁺].

4b

¹H-NMR (500 MHz, CDCl₃, 298 K): δ [ppm] = 9.90 (d, J = 8.2 Hz, 2H), 8.73 (d, J = 8.1 Hz, 2H), 8.48 (s, 2H), 7.56 − 7.48 (m, 2H), 7.40 − 7.33 (m, 4H), 3.89 − 3.81 (m, 4H), 3.69 − 3.53 (m, 8H), 3.34 − 3.24 (m, 4H), 3.00 (s, 3H), 2.99 (s, 3H), 2.82 − 2.66 (m, 4H), 1.23 − 1.15 (m, 24H).

MS (MALDI TOF, matrix DCTB) C₅₈H₆₂N₆O₄ (906.5): m/z (%): 906.5 (100) [M⁺].
Scheme 2: Synthesis of 1,2-diamino PDIs.

5

Ethylenediamine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol) and copper(II)bromide (3.3 mg, 14.8 µmol). The reaction mixture was stirred under air for 3 h at room temperature. Then, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH₂Cl₂) to give 5 (4.0 mg, 5.2 µmol, 12 %; Rf: 0.12) as a dark blue solid.

\[ \text{R} \]

\[ \text{1H-NMR (400 MHz, CDCl₃, 298 K): } \delta [\text{ppm}] = 10.85 (\text{bs, 1H}), 8.84 – 8.70 (\text{m, 3H}), 8.58 – 8.52 (\text{m, 2H}), 8.37 (\text{d, } J = 8.3 \text{ Hz, 1H}), 7.49 (\text{t, } J = 7.8 \text{ Hz, 2H}), 7.39 – 7.33 (\text{m, 4H}), 6.73 (\text{bs, 1H}), 3.93 – 3.85 (\text{m, 2H}), 3.64 – 3.59 (\text{m, 2H}), 2.82 – 2.69 (\text{m, 4H}), 1.22 – 1.16 (\text{m, 24H}). \]

\[ \text{13C-NMR (175 MHz, CDCl₃, 298 K): } \delta [\text{ppm}] = 171.29, 166.94, 164.04, 163.84, 163.79, 145.85, 145.80, 145.35, 137.62, 136.79, 136.70, 132.30, 132.00, 131.36, 131.26, 131.13, 130.59, 129.66, 129.52, 128.19, 127.70, 126.63, 124.20, 124.18, 122.51, 121.61, 121.29, \]
MS (MALDI TOF, matrix DCTB) $\text{C}_{50}\text{H}_{46}\text{N}_4\text{O}_4$ (766.4): $m/z$ (%) : 766.4 (100) [M]$^+$. 

6

(±)-trans-1,2-Diaminocyclohexan (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol) and copper(II)bromide (3.3 mg, 14.8 µmol). The reaction mixture was stirred under air for 3 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$) to give 6 (11.0 mg, 13.4 µmol, 32 %; $R_f$: 0.15) as a dark blue solid.

$^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 10.69 (s, 1H), 8.89 (d, $J = 8.2$ Hz, 1H), 8.74 (d, $J = 8.0$ Hz, 1H), 8.71 (d, $J = 8.1$ Hz, 1H), 8.55 – 8.48 (m, 2H), 8.33 (d, $J = 8.3$ Hz, 1H), 7.51 – 7.47 (m, 2H), 7.38 – 7.32 (m, 4H), 6.56 (s, 1H), 3.64 – 3.61 (m, 1H), 3.09 – 3.02 (m, 1H), 2.81 – 2.69 (m, 4H), 2.20 – 2.16 (m, 1H), 2.09 – 2.05 (m, 1H), 1.96 – 1.90 (m, 2H), 1.73 – 1.41 (m, 4H), 1.22 – 1.15 (m, 24H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 166.84, 164.02, 163.76, 145.88, 145.77, 145.73, 145.63, 145.35, 138.13, 136.85, 136.78, 132.21, 131.95, 131.33, 131.24, 131.03, 130.54, 129.63, 129.60, 128. 19, 127.63, 126.66, 124.25, 124.22, 124.20, 124.11, 122.41, 121.68, 121.23, 121.07, 120.23, 119.95, 119.66, 112.90, 96.55, 55.31, 54.91, 30.56, 30.25, 29.33, 29.29, 29.23, 24.26, 24.23, 24.14, 24.11, 24.09, 24.07, 24.03.

MS (MALDI TOF, matrix DCTB) $\text{C}_{54}\text{H}_{52}\text{N}_4\text{O}_4$ (820.4): $m/z$ (%) : 820.4 (100) [M]$^+$. 

7

N-Methylethylenediamine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol) and copper(II)bromide (3.0 mg, 13.4 µmol). The reaction mixture was stirred under air for 2.5 h at 60 °C. After that dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CH$_2$Cl$_2$) to give 7 (10.0 mg, 12.8 µmol, 30 %; $R_f$: 0.10) as a dark blue solid.
H-NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 10.63 (s, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.74 (d, J = 8.0 Hz, 1H), 8.58 – 8.53 (m, 2H), 8.37 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.2 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.35 (d, J = 8.2 Hz, 4H), 3.93 – 3.72 (m, 4H), 2.94 (s, 3H), 2.85 – 2.69 (m, 4H), 1.24 – 1.13 (m, 24H).

13C-NMR (100 MHz, CDCl₃, 298 K): δ [ppm] = 166.77, 164.11, 163.97, 163.89, 149.22, 145.87, 145.81, 140.06, 136.71, 136.68, 132.15, 132.01, 131.70, 131.25, 131.19, 130.20, 129.61, 129.53, 127.97, 127.72, 127.10, 124.23, 124.17, 124.14, 122.80, 121.44, 120.80, 120.04, 119.71, 119.41, 114.77, 96.69, 51.20, 45.79, 38.25, 29.8.

MS (MALDI TOF, matrix DCTB) C₅₁H₄₈N₄O₄ (780.4): m/z (%): 780.4 (100) [M]⁺.

Scheme 3: Reaction of PDI 1 with N,N’-dimethylethylenediamine.

8 a/b

N,N’-Dimethylethylenediamine (1.5 mL) and deionized water (0.1 mL) were added to 1 (30 mg, 42.2 µmol) and copper(II)bromide (3.3 mg, 14.8 µmol). The reaction mixture was stirred under air for 4 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column
chromatography on silica gel (CH$_2$Cl$_2$) to give 8a (10.0 mg, 12.6 µmol, 31 %; $R_f$: 0.10) as a dark blue solid and 8b (9.9 mg, 12.5 µmol, 30 %; $R_f$: 0.13).

8a

$^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 8.75 – 8.69 (m, 2H), 8.56 – 8.48 (m, 2H), 8.37 (d, $J$ = 8.4 Hz, 1H), 8.22 (d, $J$ = 8.2 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.36 – 7.33 (m, 4H), 4.06 – 3.97 (m, 1H), 3.90 – 3.70 (m, 3H), 3.17 (s, 3H), 2.94 (s, 3H), 2.87 – 2.71 (m, 4H), 1.26 – 1.10 (m, 24H).

$^{13}$C-NMR (125 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 164.36, 164.14, 164.03, 161.40, 148.98, 146.10, 145.88, 145.83, 145.60, 143.33, 137.02, 136.97, 132.01, 131.95, 131.65, 131.38, 131.33, 130.45, 130.16, 129.52, 129.33, 128.40, 127.83, 127.74, 127.20, 124.16, 124.11, 124.07, 124.01, 123.27, 122.51, 121.04, 120.73, 120.23, 119.58, 118.56, 50.83, 50.06, 45.77, 44.81, 29.26, 29.20, 24.39, 24.32, 24.23, 24.18, 24.15, 24.07, 23.85.

MS (MALDI TOF, matrix DCTB) C$_{52}$H$_{50}$N$_4$O$_4$ (794.4): $m/z$ (%): 794.4 (100) [M]$^+$. 

8b

$^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 8.63 (bs, 1H), 8.61 (bs, 1H), 8.57 – 8.48 (m, 4H), 7.49 (t, $J$ = 7.8 Hz, 2H), 7.37 – 7.33 (m, 4H), 3.51 (bs, 2H), 3.26 (s, 6H), 3.06 (bs, 2H), 2.77 (sept, $J$ = 6.9 Hz, 4H), 1.24 – 1.14 (m, 24H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 164.27, 163.71, 145.89, 145.82, 131.00, 129.67, 124.18, 124.17, 29.33, 29.28, 24.22, 24.20, 24.18.

MS (MALDI TOF, matrix DCTB) C$_{52}$H$_{50}$N$_4$O$_4$ (794.4): $m/z$ (%): 794.4 (100) [M]$^+$. 

9

9 was prepared from naphthalenetetracarboxylic anhydride (NTCDA) according to the literature procedure described by S. I. Pascu.[2]
**Scheme 4: Synthesis of 2,3-diamino NDIs.**

**10**

Ethylene diamine (1.5 mL) and deionized water (0.1 mL) were added to 9 (30 mg, 51.1 µmol) and copper(II) bromide (3.3 mg, 14.8 µmol). The reaction mixture was stirred under air for 20 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane) to give 10 (20.5 mg, 31.9 µmol, 84 %; Rᵣ: 0.18) as a yellow solid.

**¹H-NMR (400 MHz, CDCl₃, 298 K):** δ [ppm] = 10.63 (s, 2H), 8.46 (s, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 7.8 Hz, 4H), 3.74 (s, 4H), 2.70 (sept, J = 6.4 Hz, 4H), 1.18 – 1.16 (m, 24H).

**¹³C-NMR (100 MHz, CDCl₃, 298 K):** δ [ppm] = 166.98, 163.66, 145.72, 144.62, 130.89, 129.69, 125.69, 124.23, 123.71, 123.13, 98.14, 38.34, 29.28, 24.13, 24.11.

**MS (MALDI TOF, matrix DCTB)** C₄₀H₄₂N₄O₄ (642.32): m/z (%): 642.3 (100) [M⁺].
Table 3 Reaction of 9 with ethylenediamine with several catalysts and additives at 60 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Time [h]</th>
<th>10 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuBr₂</td>
<td>H₂O</td>
<td>20</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>H₂O</td>
<td>26</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>H₂O, Cs₂CO₃</td>
<td>-</td>
<td>24</td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>Mn(OAc)₃•2H₂O</td>
<td>-</td>
<td>24</td>
<td>70</td>
</tr>
</tbody>
</table>

N-(±)-trans-1,2-Diaminocyclohexan (1.5 mL) and deionized water (0.1 mL) were added to 9 (30 mg, 51.1 µmol) and copper(II)bromide (3.3 mg, 14.8 µmol). The reaction mixture was stirred under air for 3 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane) to give 11 (23.2 mg, 33.3 µmol, 65 %; Rᵣ: 0.20) as a yellow solid.

1H-NMR (500 MHz, CDCl₃, 298 K): δ [ppm] = 10.50 (s, 2H), 8.47 (s, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 4H), 3.43 – 3.22 (s, 2H), 2.70 (sept, J = 6.9 Hz, 4H), 2.18 – 2.10 (m, 2H), 1.93 – 1.86 (m, 2H), 1.53 – 1.43 (m, 4H), 1.18 – 1.16 (m, 24H).

13C-NMR (125 MHz, CDCl₃, 298 K): δ [ppm] = 166.92, 163.65, 145.73, 145.60, 145.00, 130.89 129.78, 125.57, 124.31, 124.29, 123.82, 123.17, 97.97, 54.08, 30.04, 29.28, 24.19, 24.18, 24.07.

MS (MALDI TOF, matrix DCTB) C₄₄H₄₈N₄O₄ (696.4): m/z (%): 696.4 (100) [M]+.

N-Methylethylenediamine (1.5 mL) and deionized water (0.1 mL) were added to 9 (30 mg, 51.1 µmol) and copper(II)bromide (4.0 mg, 17.9 µmol). The reaction mixture was stirred under air for 2 h at 60 °C. After cooling to room temperature, dichloromethane (25 mL) and water (25 mL) were added. The organic layer was separated, washed with aq HCl (10 %, 25 mL), water (25 mL), brine (25 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (dichloromethane) to give 11 (23.5 mg, 35.8 µmol, 70 %; Rᵣ: 0.15) as a yellow solid.
$^1$H-NMR (400 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 10.58 (bs, 1H), 8.45 – 8.40 (m, 2H), 7.52 – 7.46 (m, 2H), 7.37 – 7.32 (m, 4H), 3.94 – 3.88 (m, 2H), 3.74 – 3.68 (m, 2H), 3.14 (s, 3H), 2.66 – 2.78 (m, 4H), 1.19 – 1.14 (m, 24H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 166.80, 164.20, 163.82, 161.64, 148.33, 145.77, 145.73, 131.51, 130.95, 129.65, 129.54, 125.46, 125.13, 125.12, 124.22, 124.14, 123.87, 123.80, 122.70, 100.52, 96.58, 52.70, 46.37, 38.19, 29.85, 29.26, 29.24, 24.35, 24.16, 24.14, 23.91.

MS (MALDI TOF, matrix DCTB) C$_{41}$H$_{44}$N$_4$O$_4$ (656.3): $m/z$ (%): 656.4 (100) [M]+$.
2. NMR-Data

2a

Figure 1: $^1$H-NMR of 2a.

2b

Figure 2: $^1$H-NMR of 2b.
Figure 3: $^1$H-NMR of 3a.

Figure 4: $^1$H-NMR of 3b.
Figure 5: $^1$H-NMR of 4a.

Figure 6: $^1$H-NMR of 4b.
Figure 7: $^1$H-NMR of 5.

Figure 8: $^1$H-NMR of 6.
Figure 9: $^1$H-NMR of 7.

Figure 10: $^1$H-NMR of 8a.
Figure 11: $^1$H-NMR of 8b.

Figure 12: $^1$H-NMR of 10.
Figure 13: $^1$H-NMR of 11.

Figure 14: $^1$H-NMR of 12.
3. Mass Spectra

2a

![Mass Spectrum of 2a](image)

**Figure 15**: MS (Maldi-pos, DCTB) of 2a.

2b

![Mass Spectrum of 2b](image)

**Figure 16**: MS (Maldi-pos, DCTB) of 2b.
**Figure 17:** MS (Maldi-pos, DCTB) of 3a.

**Figure 18:** MS (Maldi-pos, DCTB) of 3b.
Figure 19: MS (Maldi-pos, DCTB) of 4a.

Figure 20: MS (Maldi-pos, DCTB) of 4b.
Figure 21: MS (Maldi-pos, DCTB) of 5.

Figure 22: MS (Maldi-pos, DCTB) of 6.
Figure 23: MS (Maldi-pos, DCTB) of 7.

Figure 24: MS (Maldi-pos, DCTB) of 8a.
Figure 25: MS (Maldi-pos, DCTB) of 8b.

Figure 26: MS (Maldi-pos, DCTB) of 10.
Figure 27: MS (Maldi-pos, DCTB) of 11.

Figure 28: MS (Maldi-pos, DCTB) of 12.
4. References
