

[Ta(O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-3,3'-{SiMe<sub>3</sub>})<sub>2</sub>)(NHMe<sub>2</sub>)(NMe<sub>2</sub>)<sub>3</sub>] (*S*)-4

A 50 mL flask was charged with [Ta(NMe<sub>2</sub>)<sub>5</sub>] (500 mg, 1.25 mmol), a stir bar and benzene (3 mL). This solution was stirred as (*S*)-3,3'-bis(trimethylsilyl)-2,2'-dihydroxy-1,1-dinaphthyl (536 mg, 1.25 mmol) dissolved in benzene was slowly added. This mixture was stirred for 1 hour and evaporated to dryness. The crude solid that resulted was dissolved in a minimal amount of benzene and layered with pentane affording yellow crystals (200 mg, 22%) which were washed with pentane and dried in vacuo. Anal. Calcd. for C<sub>34</sub>H<sub>53</sub>N<sub>4</sub>O<sub>2</sub>Si<sub>2</sub>Ta: C, 51.89; H, 6.79; N, 7.12. Found: C, 51.14; H, 6.54; N, 6.30. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 8.12 (s), 7.77 (d), 6.82-7.20 (m, aromatics); 3.19 (s, NMe<sub>2</sub>); 1.87 (br, NHMe<sub>2</sub>); 0.47 (s, SiMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 164.9 (Ta-O-C); 46.7 (NMe<sub>2</sub>); 40.5 (NHMe<sub>2</sub>); -0.1 (SiMe<sub>3</sub>).

[Ta(O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-3,3'-{SiMe<sub>2</sub>Ph})<sub>2</sub>)(NHMe<sub>2</sub>)(NMe<sub>2</sub>)<sub>3</sub>] (*R*)-5

A solvent sealed NMR tube was charged with [Ta(NMe<sub>2</sub>)<sub>5</sub>] and benzene-d<sub>6</sub> (~1 mL). This solution was slowly titrated with (*R*)-3,3'-bis(phenyldimethylsilyl)-2,2'-dihydroxy-1,1-dinaphthyl until reaction completion as monitored by NMR. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 8.09 (s), 7.63-7.76 (m), 6.86-7.25 (m, aromatics); 3.14 (s, NMe<sub>2</sub>); 1.98 (s, NHMe<sub>2</sub>); 0.70 (s), 0.69 (s, SiMe<sub>2</sub>Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 165.0 (Ta-O-C); 47.1 (NMe<sub>2</sub>); 39.6 (NHMe<sub>2</sub>); -0.8, -1.4 (SiMe<sub>2</sub>Ph).

[Ta(O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-3,3'-{SiMePh<sub>2</sub>})<sub>2</sub>)(NHMe<sub>2</sub>)(NMe<sub>2</sub>)<sub>3</sub>] (*R*)-6

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 7.88 (s), 7.72 (m), 7.40 (d), 6.81-7.30 (m, aromatics); 2.89 (s, NMe<sub>2</sub>); 1.81 (s, NHMe<sub>2</sub>); 1.00 (s, SiMePh<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 30°C): δ 165.8 (Ta-O-C); 46.9 (NMe<sub>2</sub>); 40.9 (NHMe<sub>2</sub>); -2.1 (SiMePh<sub>2</sub>).

[Ta(O<sub>2</sub>C<sub>20</sub>H<sub>10</sub>-3,3'-{SiPh<sub>3</sub>})<sub>2</sub>)(NHMe<sub>2</sub>)(NMe<sub>2</sub>)<sub>3</sub>] (*R,S*)-7

A solvent sealed NMR tube was charged with [Ta(NMe<sub>2</sub>)<sub>5</sub>] and benzene-d<sub>6</sub> (~1 mL). This solution was slowly titrated with racemic-3,3'-bis(triphenylsilyl)-2,2'-dihydroxy-1,1-dinaphthyl until reaction completion as monitored by NMR. Upon standing yellow crystals of 7 formed which were washed with pentane and dried in vacuo. Anal. Calcd. for C<sub>62</sub>H<sub>58</sub>N<sub>3</sub>O<sub>2</sub>Si<sub>2</sub>Ta: C, 66.83; H, 5.25; N, 3.77. Found: C, 66.81;