### **Supplementary Information for**

Polyhedral oligomeric silsesquioxane difluoroboron complexes as cooperative octo-site catalysts for the photooxidation of sulfides to sulfoxides

Mateusz Janeta\*a, Sławomir Szafera

<sup>a</sup>Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław (Poland).

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#### Section 1. Experimental section

#### Materials

All reactions were conducted under N<sub>2</sub> by using standard Schlenk techniques. N,N-Diisopropylethylamine (99%, Sigma-Aldrich), boron trifluoride diethyl etherate (98%, Alfa Aesar), quinine sulfate (Sigma Aldrich), methylene blue, 9,10-diphenylanthracene (99%, Sigma-Aldrich), methyl *p*-tolyl sulfide (99%, Sigma Aldrich), 3-bromothioanisole (97%, Sigma Aldrich), thioanisole (99%, Sigma Aldrich), 4-(methylthio)benzonitrile (98%, Sigma Aldrich) 3,3'-dimethylbenzidene (for analytical purpose), 1,10-phenanthroline (>99%, Sigma Aldrich), Na<sub>2</sub>SO<sub>4</sub> (99%, Chempur), KI (Chempur), NaN<sub>3</sub>, 1,4-diazabicyklo[2.2.2]oktan, 1,4-benzoquinone, methanol, were used as received. K<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·3H<sub>2</sub>O was recrystallized from the water before use. Dichloromethane (99%, Chempur) and triethylamine were purified via the mBraun Purification System.

#### **Known compounds**

Octa(3-aminopropyl)silsesquioxane hydrochloride,<sup>1</sup> N-n-propyl-3,5-di-tert-butylsalicylaldimine, N-n-propyl-salicylaldimine, 2-hydroxy-N-n-propyl-1-naphthaldimine, compounds POSSS-1,<sup>2</sup> POSS-2 and POSS-3<sup>3</sup> were prepared using the methods based on a previously reported procedure.



Chart S1. Structures of POSS ligands.

#### **Characterization methods**

<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded using Bruker Avance III 500 MHz or Bruker Avance III 600 MHz spectrometer equipped with broadband inverse gradient probe heads. Spectra were referred to the residual solvent signals ((CD<sub>3</sub>)<sub>2</sub>SO, 2.50; CDCl<sub>3</sub>, 7.26; (<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>SO, 39.52; <sup>13</sup>CDCl<sub>3</sub>, 77.16 ppm) as an internal reference. For <sup>29</sup>Si NMR, the chemical shifts were referenced to tetramethylsilane (TMS) ( $\delta = 0.00$  ppm), and for <sup>11</sup>B, the chemical shifts were referenced to 15% BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub> (external reference,  $\delta = 0$  ppm). <sup>19</sup>F NMR

spectra were recorded using a Jeol JNM-ECZR 500 MHz spectrometer. For <sup>19</sup>F NMR, the chemical shifts were referenced to 0.05% trifluorotoluene in CDCl<sub>3</sub> (external reference,  $\delta = -63.72$  ppm). The DRIFT spectra were recorded at room temperature using a Nicolet iS10 FT-IR (Thermo Scientific) spectrometer equipped with a Pike EasiDiff DRIFTS accessory. The spectra of samples are in the 4000 – 400 cm<sup>-1</sup> range and are averaging from 128 scans and include atmospheric correction. The spectral resolution was 4 cm<sup>-1</sup>. MALDI mass spectra were recorded on a Bruker Daltonics ultrafleXtreme or on a JMSS3000 SpiralTOF<sup>TM</sup>-plus 2.0 MALDI-TOF spectrometer. Elemental analysis (C, H, and N) was performed using a Vario EL III elemental analyser. Content of B had been determined by Inductively Coupled Plasma optical emission spectrometer. ICP measurements was performed using a ARL spectrometer model 3410 (Fisons Instruments). Before analysis a weighted sample was digested in 5 mL of piranha solution, left for 2 days and next diluted to 10 mL with distilled water.

Thermogravimetric and differential thermal analyses (simultaneous TG-DTA) were recorded on a Setaram SETSYS 16/18 instrument. Samples for thermogravimetric characterization were placed in alumina crucibles under synthetic air ( $O_2$ : $N_2 = 40$ :60) at heating rate 10 Kxmin<sup>-1</sup>. Absorption spectra in the UV-vis range were measured using a Cary 60 or JASCO v-700 spectrometer equipped with a temperature controller. Measurements were performed at 293 K on a 3.5 mL samples in a quartz cuvette with a path length of 10 mm. Emission measurements were performed using an Edinburgh Instruments FLSP 920 spectrofluorometer equipped with Hamamatsu R-928 photomultiplier and a 450 W Xe lamp as an excitation source. These spectra were measured at 295 K in quartz cuvettes. The emission spectra were corrected for the instrument response. All measurements were conducted using appropriate optical filters. Photooxidation experiments were carried out in a cylindrical quartz reactor. A medium pressure mercury lamp TQ 150 (Heraeus, Germany) with a power of 150 W and radiation flux  $\Phi$  300-600nm: 24.8W was positioned approximately 5 cm from the tube. Lamp was placed in a cooler which was supplied with water during the experiments.

#### **Syntheses**

Preparation of the POSS-tert-BF<sub>2</sub>. POSS-1 (1.00 g, 0.382 mmol) was dissolved in dry dichloromethane (40 mL). Then N,N-diisopropylethylamine (1.33 mL, 7.66 mmol, 20 equiv.) was added and the resulting mixture was stirred for 10 min at 40 °C, after which time boron trifluoride diethyl etherate (0.962 mL, 7.66 mmol, 20 equiv.) was added dropwise. The final mixture was stirred for 12h at 40 °C under nitrogen atmosphere and then cooled to room temperature. Dichloromethane (150 mL) was added and the crude mixture was washed with brine (3 x 100 mL) and then with water (100 mL). The organic layer was separated, dried over MgSO<sub>4</sub>, and evaporated to dryness. The residue was filtered through a short plug of silica gel with DCM. Solution was concentrated and then precipitated with MeOH to give the expected product in an 87% yield (1.00 g) as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (br s, 8H, CHN), 7.62 (d, J = 2.4 Hz, 8H, 4-Ar-CH), 7.33 (d, J = 2.4 Hz, 8H, 6-Ar-CH), 3.71 (t, J = 7.2 Hz, 16H, CH<sub>2</sub>N), 2.01–1.94 (m, 16H, -CH<sub>2</sub>-), 1.44 (s, 72H, tBu), 1.29 (s, 72H, tBu), 0.69 -0.66 (m, 16H, SiCH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.8 (C=N), 156.1 (C<sub>Ph</sub>-O), 142.2 (ArC-CMe<sub>3</sub>), 138.7 (ArC-CMe<sub>3</sub>), 132.9 (ArC-H), 126.0 (ArC-H), 115.6 (C), 56.8 (CH<sub>2</sub>N), 35.2 (CMe<sub>3</sub>), 34.4 (CMe<sub>3</sub>), 31.4 (-(CH<sub>3</sub>)<sub>3</sub>), 29.5 (-(CH<sub>3</sub>)<sub>3</sub>), 24.1 (-CH<sub>2</sub>-), 9.1 (SiCH<sub>2</sub>); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  0.49 (<sup>1</sup>*J*<sub>BF</sub> = 16 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -136.8 (dd, <sup>2</sup>*J*<sub>FF</sub> = 35.3 Hz,  ${}^{1}J_{\text{FB}}$  = 14.1 Hz, 2F); <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>)  $\delta$  -67.1; DRIFT (KBr):  $\tilde{v}$  = 2957 (m, v<sub>C-H</sub>), 2910 (w, v<sub>C-H</sub>), 2872 (w, v<sub>C-H</sub>), 1644 (s, v<sub>C=N</sub>), 1570 (m, v<sub>B-F</sub>), 1468 (w), 1308 (m, v<sub>B-F</sub>) o), 1192 (m), 1150 (m, v<sub>asym BF2</sub>), 1110 (s, v<sub>Si-O-Si</sub>), 1055 (s, v<sub>B-N</sub>), 939 (w, v<sub>sym BF2</sub>); MS (MALDI) m/z calcd for  $C_{144}H_{216}B_8F_{16}N_8O_{20}Si_8Na$ : 3017.4762 [M+Na]<sup>+</sup>; found: 3017.4677; C144H216B8F15N8O20Si8N: 2974.4880 [M-F]+; found: 2974.4844; elemental analysis calcd (%) for C<sub>144</sub>H<sub>216</sub>B<sub>8</sub>F<sub>16</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub> (2994.48): C, 57.76; H, 7.27; N, 3.74; found: C, 57.80; H, 7.42; N, 3.81; UV-vis (dichloromethane, 293 K) λ [nm]: 271, 367; decomposition onset temperature (T<sub>5%</sub>, 10 °C·min<sup>-1</sup>): 350 °C (air); temperature of decomposition to SiO<sub>2</sub> (determined by TGA measurement, air, 10 °C·min<sup>-1</sup>): 598 °C; ceramic yield (at 900 °C): 16.40% (calcd 15.97%).

**Preparation of the POSS-sal-BF<sub>2</sub>. POSS-2** (1.00 g, 0.583 mmol) was dissolved in dry dichloromethane (40 mL). Then N,N-diisopropylethylamine (2.03 mL, 11.7 mmol, 20 equiv.) was added and the resulting mixture was stirred for 10 min at 40 °C, after which time boron trifluoride diethyl etherate (1.47 mL, 11.7 mmol, 20 equiv.) was added dropwise. The final mixture was stirred for 2h at 40 °C under nitrogen atmosphere and then cooled to room temperature. Dichloromethane (60 mL) was added, and the crude mixture was washed with water (3 x 100 mL). The organic layer was separated, dried over MgSO<sub>4</sub> and evaporated to dryness. The residue was purified by recrystallization from DCM to give the expected product

in a 90% yield (1.10 g) as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.78 (br s, 8H, CHN), 7.59 (td, J = 7.0 Hz, J = 1.7 Hz, 8H, Ar-CH), 7.58 (dd, J = 7.8 Hz, J = 1.6 Hz, 8H, Ar-CH), 7.00 (td, J = 7.9 Hz, J = 0.8 Hz 8H, Ar-CH), 6.96 (d, J = 8.4 Hz, 8H, Ar-CH), 3.67 (t, J = 7.2 Hz, 16H, CH<sub>2</sub>N), 1.99 – 1.72 (m, 16H, –CH<sub>2</sub>–), 0.68 (t, 16H, SiCH<sub>2</sub>); <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 166.3 (C=N), 157.7 (C<sub>Ph</sub>-O), 137.7, 132.4, 119.9, 118.0, 115.4 (5C, ArC), 55.1  $(CH_2N)$ , 22.8 (- $CH_2$ -), 8.2 (Si $CH_2$ ); <sup>11</sup>B NMR (160 MHz, DMSO-d<sub>6</sub>)  $\delta$  0.39 (<sup>1</sup> $J_{BF}$  = 16 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, DMSO-d<sub>6</sub>): δ -131.4 (dd,  ${}^{2}J_{FF}$  = 33.2 Hz,  ${}^{1}J_{FB}$  = 14.2 Hz, 2F); <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>)  $\delta$  -67.1; DRIFT (KBr):  $\tilde{v}$  = 2938 (w, v<sub>C-H</sub>), 2890 (w, v<sub>C-H</sub>), 1648 (s, v<sub>C-N</sub>), 1564 (m, v<sub>B-F</sub>), 1485 (m), 1466 (w), 1415 (w), 1312 (m, v<sub>B-O</sub>), 1135 (m, v<sub>asym BF2</sub>), 1116 (s, v<sub>Si-</sub> O-Si), 1054 (s, v<sub>B-N</sub>), 938 (w, v<sub>sym BF2</sub>); MS (MALDI) m/z calcd for C<sub>80</sub>H<sub>88</sub>B<sub>8</sub>F<sub>16</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub>: 2096.4824 [M]<sup>+</sup>; found: 2096.4937; C<sub>80</sub>H<sub>88</sub>B<sub>7</sub>F<sub>12</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub>: 2009.4789 [M-BF<sub>4</sub>]<sup>+</sup>; found: 2009.4713; elemental analysis calcd (%) for C<sub>80</sub>H<sub>88</sub>B<sub>8</sub>F<sub>16</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub> (2096.75): C, 45.83; H, 4.23; N, 5.34; found: C, 45.78; H, 4.25; N, 5.30; UV-vis (dichloromethane, 293 K) λ [nm]: 281, 348; decomposition onset temperature (T<sub>5%</sub>, 10 °C·min<sup>-1</sup>): 335 °C (air), 344 °C (N<sub>2</sub>); temperature of decomposition to SiO<sub>2</sub> (determined by TGA measurement, air, 10 °C·min<sup>-1</sup>): 542 °C; ceramic vield (at 900 °C): 26.17% (calcd 22.93%).

Preparation of the POSS-npht-BF<sub>2</sub>. POSS-3 (1.00 g, 0.473 mmol) was dissolved in dry dichloromethane (40 mL). Then N,N-diisopropylethylamine (1.65 mL, 9.46 mmol, 20 equiv.) was added and the resulting mixture was stirred for 10 min at 40 °C, after which time boron trifluoride diethyl etherate (1.19 mL, 9.46 mmol, 20 equiv.) was added dropwise. The final mixture was stirred for 2h at 40 °C under nitrogen atmosphere and then cooled to room temperature. Dichloromethane (60 mL) was added, and the crude mixture was washed with water (3 x 100 mL). The organic layer was separated, dried over MgSO<sub>4</sub>, and evaporated to dryness. The residue was filtered through a short plug of silica gel with DCM. Solution was concentrated and then precipitated with MeOH to give the expected product in an 83% yield (0.975 g) as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.47 (br s, 8H, CHN), 8.26 (d,  ${}^{3}J_{HH} = 8.5$  Hz, 8H, Nph-H), 8.11 (d, J = 9.1 Hz, 8H, Nph-H), 7.86 (d,  ${}^{3}J_{HH} = 8.5$  Hz, 8H, Nph-*H*), 7.53 (t,  ${}^{3}J_{HH} = 7.6$  Hz, 8H, Nph-*H*), 7.40 (t,  ${}^{3}J_{HH} = 7.6$  Hz, 8H, Nph-*H*), 7.03 (d,  ${}^{3}J_{HH}$ = 9.1 Hz, 8H, Nph-H), 3.76 (t,  ${}^{3}J_{HH}$  = 6.5 Hz, 16H, CH<sub>2</sub>N), 1.97–1.91 (m, 16H, -CH<sub>2</sub>-), 0.74 (t,  ${}^{3}J_{\text{HH}} = 8.5 \text{ Hz}, 16\text{H}, \text{SiC}H_{2}$ ;  ${}^{13}\text{C}\{{}^{1}\text{H}\}$  NMR (126 MHz, DMSO-d<sub>6</sub>)  $\delta$  162.0 (s,  $C_{\text{Nph}}$ -O), 159.5 (s, C=N), 139.1, 131.1, 128.9, 128.7, 127.4, 124.5, 120.5, 119.4, 107.6 (9C, Nph-C), 55.4 (s, *C*H<sub>2</sub>N), 23.2 (s, *C*H<sub>2</sub>), 8.3(s, Si*C*H<sub>2</sub>); <sup>11</sup>B NMR (160 MHz, DMSO-d<sub>6</sub>)  $\delta$  0.39 (<sup>1</sup>*J*<sub>BF</sub> = 16 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -137.2 (dd, <sup>2</sup>*J*<sub>FF</sub> = 32.5 Hz, <sup>1</sup>*J*<sub>FB</sub> = 13.9 Hz, 2F); <sup>29</sup>Si NMR (99 MHz, DMSO-d<sub>6</sub>)  $\delta$  -67.0; DRIFT (KBr):  $\tilde{v} = 2935$  (w, v<sub>C-H</sub>), 2886 (w, v<sub>C-H</sub>), 1636 (s, v<sub>C-N</sub>), 1561 (m, v<sub>B-F</sub>), 1485 (m), 1470 (w), 1347 (w), 1312 (m, v<sub>B-O</sub>), 1207 (m), 1166 (m, v<sub>asym BF2</sub>), 1116 (s, v<sub>Si-O-Si</sub>), 1054 (s, v<sub>B-N</sub>), 826 (w, v<sub>sym BF2</sub>); UV–vis (dichloromethane, 293 K) λ [nm]: 271, 325, 355, 372; MS (MALDI) m/z calcd for C<sub>112</sub>H<sub>104</sub>B<sub>8</sub>F<sub>16</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub>: 2496.6089 [M ]<sup>+</sup>; found: 2495.6289; elemental analysis calcd (%) for C<sub>112</sub>H<sub>104</sub>B<sub>8</sub>F<sub>16</sub>N<sub>8</sub>O<sub>20</sub>Si<sub>8</sub> (2496.60): C, 53.87; H, 4.20; N, 4.49; found: C, 53.78; H, 4.02; N, 4.37; decomposition onset temperature (T<sub>5%</sub>, 10 °C·min<sup>-1</sup>): 339 °C (air), 340 °C (N<sub>2</sub>); temperature of decomposition to SiO<sub>2</sub> (determined by TGA measurement, air, 10 °C·min<sup>-1</sup>): 595 °C, ceramic yield (at 900 °C): 22.84% (calcd 19.25%).

Preparation of the prop-tert-BF<sub>2</sub>. N-n-propyl-3,5-di-tert-butyl-salicylaldimine (2.41 g, 11.28 mmol) was dissolved in dry dichloromethane (80 mL) then N,N-diisopropylethylamine (4.914 mL, 28.21 mmol, 2.5 equiv.) was added, the resulting mixture was stirred for 10 min at 40 °C after which boron trifluoride diethyl etherate (3.543 mL, 28.21 mmol, 2.5 equiv.) was added dropwise. The final mixture was stirred for 2h at 40 °C under a nitrogen atmosphere and then cooled to room temperature. Dichloromethane (60 mL) was added, and the crude mixture was washed with water (3 x 100 mL). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (DCM) to give the expected product in a 85% yield (3.50 g) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.16 (br s, 1H, CHN), 7.65 (d, J = 2.4 Hz, 1H, ArC-H), 7.17 (d, J = 2.4 Hz, 1H, ArC-H), 3.71 (t, J = 7.3 Hz, 2H, NCH<sub>2</sub>), 2.08 – 1.78 (m, 2H, –CH<sub>2</sub>–), 1.46 (s, 9H, –(CH<sub>3</sub>)<sub>3</sub>), 1.31 (s, 9H, –(CH<sub>3</sub>)<sub>3</sub>), 1.01 (t, J = 7.4 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  165.7 (C=N), 156.0 (Ph-O), 142.0 (ArC-CMe<sub>3</sub>), 138.6 (ArC-CMe<sub>3</sub>), 132.8 (ArC-H), 125.9 (ArC-H), 115.4 (C), 56.7 (NCH<sub>2</sub>), 35.1 (CMe<sub>3</sub>), 34.3 (CMe<sub>3</sub>), 31.3 (-(CH<sub>3</sub>)<sub>3</sub>), 29.4 (-(CH<sub>3</sub>)<sub>3</sub>), 24.0 (-CH<sub>2</sub>-), 9.0 (CH<sub>3</sub>); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  0.50 (t, <sup>1</sup>*J*<sub>BF</sub> = 17.6 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -139.3 (q,  ${}^{1}J_{\text{FB}} = 18.0 \text{ Hz}, 2\text{F}$ ; DRIFT (KBr):  $\tilde{v} = 2959 \text{ (m, v_{C-H})}, 2905 \text{ (w, v_{C-H})}, 2869 \text{ (w, v_{C-H})}, 1647 \text{ (s, v_{C-H})}$ v<sub>C=N</sub>), 1571 (m, v<sub>B-F</sub>), 1477 (w), 1338 (m, v<sub>B-O</sub>), 1101 (m, v<sub>asvm BF2</sub>), 1055 (s, v<sub>B-N</sub>), 947 (w, v<sub>svm</sub> BF2).

**Preparation of the prop-sal-BF<sub>2</sub>.** N-n-propyl-salicylaldimine (2.00 g, 11.28 mmol) was dissolved in dry dichloromethane (80 mL) and N,N-diisopropylethylamine (4.914 mL, 28.21 mmol, 2.5 equiv.) was added. The resulting mixture was stirred for 10 min at 40 °C after which time boron trifluoride diethyl etherate (3.543 mL, 28.21 mmol, 2.5 equiv.) was added dropwise. The final mixture was stirred for 2h at 40 °C under a nitrogen atmosphere and then cooled to room temperature. Dichloromethane (60 mL) was added, and the crude mixture was washed with water (3 x 100 mL). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (DCM) to give the expected

product in a 88% yield (2.10 g) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (br s, 1H, CHN), 7.52 (t, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 7.8 Hz, 2H, ArC-*H* ), 7.42 (dd, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 7.7 Hz, 1H, ArC-*H*), 6.99 (d, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 8.4 Hz, 1H, ArC-*H*), 6.92 (t, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 7.9 Hz, 1H, ArC-*H*), 3.69 (t, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 7.3 Hz, 2H, NC*H*<sub>2</sub>), 1.87 (m, 2H, –C*H*<sub>2</sub>–), 0.95 (t, <sup>3</sup>*J*<sub>*H*-*H*</sub> = 7.4 Hz, 3H, C*H*<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  164.5 (*C*=N), 158.8 (C<sub>Ph</sub>-O), 138.0 (Ar*C*–H), 131.7 (Ar*C*–H), 120.1 (Ar*C*–H), 118.9 (Ar*C*–H), 115.4 (*C*), 55.9 (NCH<sub>2</sub>), 23.2 (–CH<sub>2</sub>–), 11.1 (*C*H<sub>3</sub>); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  0.34 (t, <sup>1</sup>*J*<sub>*BF*</sub> = 16.4 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -134.7 (q, <sup>1</sup>*J*<sub>FB</sub> = 14.5 Hz, 2F); DRIFT (KBr):  $\tilde{\nu} = 2966$  (w, v<sub>C-H</sub>), 2883 (w, v<sub>C-H</sub>), 1653 (s, v<sub>C=N</sub>), 1566 (m, v<sub>B-F</sub>), 1487 (m), 1467 (w), 1420 (w), 1316 (m, v<sub>B-O</sub>), 1136 (m, v<sub>asym BF2</sub>), 1058 (s, v<sub>B-N</sub>), 950 (w, v<sub>sym BF2</sub>).

Preparation of the prop-npht-BF2. 2-Hydroxy-N-n-propyl-1-naphthaldimine (3.11 g, 11.28 mmol) was dissolved in dry dichloromethane (80 mL) and N,N-diisopropylethylamine (4.914 mL, 28.21 mmol, 2.5 equiv.) was added. The resulting mixture was stirred for 10 min at 40 °C after which time boron trifluoride diethyl etherate (3.543 mL, 28.21 mmol, 2.5 equiv.) was added dropwise. The final mixture was stirred for 2h at 40 °C under a nitrogen atmosphere and then cooled to room temperature. Dichloromethane (60 mL) was added and the crude mixture was washed with water (3 x 100 mL). The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography (DCM) to give the expected product in a 85% yield (3.10 g) as a yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.90 (m, 1H, CHN), 7.97 (dd, J = 8.7, 4.2 Hz, 2H, ArC-H), 7.78 (dd, J = 8.1, 1.3 Hz, 1H, ArC-H), 7.59 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H, ArC-H), 7.43 (ddd, J = 8.0, 6.9, 1.0 Hz, 1H, ArC-H), 7.18 (d, J = 9.1 Hz, 1H, ArC-H), 3.85 – 3.77 (m, 2H, NCH<sub>2</sub>), 2.04 – 1.92 (m, 2H, –CH<sub>2</sub>–), 1.05 (t, J = 7.4 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.4 (C<sub>Nph</sub>-O), 159.3 (C=N), 139.6, 131.3, 129.6, 129.2, 128.0, 124.8, 120.5, 119.1, 107.7 (9C, Nph-C), 56.6 (NCH<sub>2</sub>), 23.8 (-CH<sub>2</sub>-), 11.3 (*C*H<sub>3</sub>); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  0.45 (t, <sup>1</sup>*J*<sub>BF</sub> = 16.4 Hz, BF<sub>2</sub>); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -138.02 (q, <sup>1</sup>*J*<sub>FB</sub> = 13.6 Hz, 2F); DRIFT (KBr):  $\tilde{v}$  = 2966 (w, v<sub>C-H</sub>), 2936 (w, v<sub>C-H</sub>), 2877 (w, v<sub>C-H</sub>), 1641 (s, v<sub>C=N</sub>), 1565 (m, v<sub>B-F</sub>), 1475 (m), 1347 (w), 1312 (m, v<sub>B-O</sub>), 1208 (m), 1165 (m, v<sub>asym BF2</sub>), 1120 (s, v<sub>Si-O-Si</sub>), 1039 (s, v<sub>B-N</sub>), 823 (w, v<sub>sym BF2</sub>).

#### Calculation of fluorescence quantum yield

Fluorescence quantum yields were calculated using Equation (1):

$$\Phi_F = \Phi_F(ref) \times \frac{I(sample) \times OD(ref) \times n^2(sample)}{I(ref) \times OD(sample) \times n^2(ref)}$$
(1)

where *I* is the integrated fluorescence intensity, *OD* is the optical density at the excitation wavelength, *n* is the refractive index of the solvent, *ref* stands for reference standard: quinine sulfate in 0.1M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_f = 0.577$ ).<sup>4</sup>

#### Detection of <sup>1</sup>O<sub>2</sub> production in solution

9,10-diphenylanthracene (DPA) was used as an indicator for detection of  ${}^{1}O_{2}$  in solution. Tested photosensitizer (1.0×10<sup>-7</sup> mol of **POSS-imine-BF**<sub>2</sub> or 1.25×10<sup>-6</sup> of **prop-imine-BF**<sub>2</sub>) was dissolved in 10 mL of MeOH containing DPA (4.0×10<sup>-7</sup> mol). The mixture was then placed in a cuvette and irradiated (Herolab NU-15,  $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>). The absorption change of the sample at 391 nm was recorded by the UV-Vis absorption spectrophotometer.

#### Singlet oxygen (<sup>1</sup>O<sub>2</sub>) quantum yields

The singlet oxygen quantum yield  $\Phi(^{1}O_{2})$  was determined by monitoring the photooxidation of 9,10-diphenylanthracene (DPA), a well-known  $^{1}O_{2}$  scavenger that rapidly reacts to form colorless oxidized product. It absorbs in the visible region (340-410 nm) and its absorbance decreases over time as it scavenges  $^{1}O_{2}$ . The singlet oxygen quantum yields were calculated under low concentration conditions (0.036 mM photosensitizer and 0.15 mM DPA) to minimize the possibility of  $^{1}O_{2}$  quenching of by the photosensitizer. The quantum yields were determined using a relative method with methylene blue (singlet oxygen quantum yield 52%)<sup>5</sup> as the reference dye,<sup>6</sup> following the equation shown in Equation (1):

$$\Phi({}^{1}O_{2}) = \Phi({}^{1}O_{2})^{MB} \times \frac{m(sample) \times F(MB)}{m(MB) \times F(sample)}$$
(2)

In the equation  $\Phi({}^{1}O_{2})^{MB}$  represents the singlet oxygen quantum yield of methylene blue.

The parameter m is the slope of a plot with a difference in the change in the absorbance of DPA at 391 nm with the irradiation time. The absorption correction factor, F, is given by the equation  $F = 1 - 10^{-\text{OD}}$  where OD is the optical density at the irradiation wavelength.

#### Quantum efficiency photooxidation of thioanisole

The quantum yield of photooxidation of thioanisole reactions was determined at 298 K following procedures described in literature.<sup>7</sup> Thioanisole (25  $\mu$ L, 0.213 mmol) and the photocatalyst (0.133  $\mu$ mol of **POSS-imine-BF**<sub>2</sub> or 1.06  $\mu$ mol **prop-imine-BF**<sub>2</sub>, 0.5% mol loading based on the acceptor site) were added in 6 mL of methanol in a quartz tube. O<sub>2</sub> was bubbled through the mixture for 10 min. The tube was then sealed and fitted with an O<sub>2</sub> balloon.

The reaction mixture was irradiated using a medium pressure mercury vapor lamp (Heraeus TQ 150, 150 W, power density100 W/cm<sup>2</sup>, radiation flux  $\Phi$  300-600nm: 24.8W) positioned approximately 5 cm from the tube. After certain time (1-20 min) of irradiation, the solvent was evaporated. Conversions were calculated by integrating the crude <sup>1</sup>H NMR ratios of the substrate and product.

The quantum yield for product formation ( $\Phi_{\text{product}}$ ) is defined by the number of product molecules generated divided by the number of photons absorbed by the starting material (Equation (3).

$$\Phi = \frac{number of product molecules generated}{number of photons absorbed}$$
(3)

Potassium ferrioxalate solution in 0.05M H<sub>2</sub>SO<sub>4</sub> (6 mL, 0.15 M) were was placed in a quartz tube. The reaction mixture was irradiated using a medium pressure mercury vapor lamp (Heraeus TQ 150, 150 W, power density100 W/cm<sup>2</sup>, radiation flux  $\Phi$  300-600nm: 24.8W) positioned approximately 5 cm from the tube. After certain time (1-20 min) of irradiation, 1 mL of solution was diluted 0.05M H<sub>2</sub>SO<sub>4</sub> to 10 mL. 3 mL of that solution was developed by adding 0.5 mL of a 0.05M sulfuric acid solution containing 0.03M sodium acetate trihydrate and 0.003M 1,10-phenanthroline. After 1 h, the concentration of the samples was determined spectrometrically at 510 nm.

The photon flux of the lamp used was determined by standard ferrioxalate actinometry, using Equation (4).<sup>8</sup>

photon flux (F) = 
$$\frac{mole_{Fe^{2+}}}{t \times \phi \times f}$$
 (4)

Where *t* is the time of irradiation,  $\Phi$  is the quantum yield for Fe<sup>2+</sup> production in ferrioxalate actinometry ( $\Phi = 1.01$ ), and *f* is the frequency.

#### **Reactive oxygen species (ROS) trapping experiment**

Reactive oxygen species (ROS) were detected by monitoring the photooxidation of 3,3'dimethylbenzidene (DMB). DMB contains two readily oxidized amino groups and can be converted into a colored product via one electron and two electron oxidation pathways (Scheme S1). The long-wavelength absorption band of the one-electron oxidation intermediate, which forms a charge-transfer complex between the diamine (DMB) as the donor and the diimine dication (DMB<sup>2+</sup>) as the acceptor, appears at 370 nm and within the range of 550-760 nm, with a maximum at 650 nm.<sup>9</sup> Tested photosensitizer  $(1.0 \times 10^{-7} \text{ mol of POSS-imine-BF}_2 \text{ or } 1.25 \times 10^{-6} \text{ of prop-imine-BF}_2)$  was dissolved in 10 mL of DCM containing 3,3'-dimethylbenzidene (0.233 g). The solution was bubbled with oxygen for 5 minutes, placed in a quartz cuvette, and then irradiated with light (Herolab NU-15,  $\lambda_{irr} = 365 \text{ nm}$ , intensity 1.30 mW/cm<sup>2</sup>). After 90 seconds of irradiation, the UV-Vis spectrum was recorded, revealing an absorption change at 287 nm and the appearance of a new band at 360 nm, as well as within the range of 550-760 nm.

# Photocatalytic aerobic oxidation of thioanisole in the presence of POSS-imine-BF<sub>2</sub> (POSS-tert-BF<sub>2</sub>, POSS-sal-BF<sub>2</sub>, POSS-npht-BF<sub>2</sub>)

Thioanisole (50  $\mu$ L, 0.425 mmol) and **POSS-imine-BF**<sub>2</sub> (0.266  $\mu$ mol, 0.5%mol loading based on the single acceptor site) were added in 12 mL of methanol in a quartz tube. O<sub>2</sub> was bubbled through the mixture for 10 min. The tube was then sealed and fitted with an O<sub>2</sub> balloon. The reaction mixture was irradiated using a medium pressure mercury vapor lamp (Heraeus TQ 150, radiation flux  $\Phi$  300-600nm: 24.8W) positioned approximately 5 cm from the tube. After 40 minutes of irradiation, the solvent was evaporated. Conversions were calculated by integrating the crude <sup>1</sup>H NMR ratios of the substrate and product.

# Photocatalytic aerobic oxidation of thioanisole in the presence of prop-imine-BF<sub>2</sub> (prop-tert-BF<sub>2</sub>, prop-sal-BF<sub>2</sub> or prop-npht-BF<sub>2</sub>)

Thioanisole (50 µL, 0.425 mmol) and **prop-imine-BF**<sub>2</sub> (2.13 µmol, 0.5% mol loading) were added in 12 mL of methanol in a quartz tube. O<sub>2</sub> was bubbled through the mixture for 10 min. The tube was then sealed and fitted with an O<sub>2</sub> balloon. The reaction mixture was irradiated using a medium pressure mercury vapor lamp (Heraeus TQ 150, radiation flux  $\Phi$  300-600nm: 24.8W) positioned approximately 5 cm from the tube. After 40 minutes of irradiation, the solvent was evaporated. Conversions were calculated by integrating the crude <sup>1</sup>H NMR ratios of the substrate and product.

## Substrate scope for photocatalytic oxidation of various sulfides to sulfoxides in the presence of POSS-tert-BF<sub>2</sub>.

Thioether (0.425 mmol) and **POSS-tert-BF**<sub>2</sub> (0.796 mg, 0.266  $\mu$ mol, 0.5%mol loading based on the single acceptor site) were added in 12 mL of methanol in a quartz tube. O<sub>2</sub> was bubbled through the mixture for 10 min. The tube was then sealed and fitted with an O<sub>2</sub> balloon. The reaction mixture was irradiated using a medium pressure mercury vapor lamp (Heraeus TQ 150, radiation flux  $\Phi$  300-600nm: 24.8W) positioned approximately 5 cm from the tube. After 40 minutes of irradiation, the solvent was evaporated. To determine isolating yields, following the reaction the mixture was filtered through a short plug of silica gel with DCM and then evaporated. Products were identifies by <sup>1</sup>H NMR.

#### **Recycling of photocatalyst**

After completing the first reaction run, the photocatalyst was recovered by evaporation the volatiles and thoroughly washing it several times with hexane to remove any residual products or unreacted substrates. The recovered **POSS-tert-BF2** was dried under vacuum at  $80^{\circ}$ C overnight. The used photocatalyst was subsequently re-employed in the next cycle under identical conditions.

### Section 2. UV-vis spectra Reactive oxygen species (ROS) trapping experiment



Scheme S1. DMB 3,3'-dimethylbenzidene reactivity towards oxidant agents.



**Figure S1**. UV–Vis-NIR absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **POSS-tert-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



**Figure S2**. UV–vis absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **POSS-sal-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



**Figure S3**. UV–Vis-NIR absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **POSS-npht-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



**Figure S4**. UV–vis absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **prop-tert-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



**Figure S5**. UV–vis absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **prop-sal-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



**Figure S6**. UV–vis absorption spectra of the cationic radical of 3,3'-dimethylbenzidine (DMB) generated by **prop-npht-BF**<sub>2</sub> in the presence of light ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) and oxygen in DCM.



Detection of <sup>1</sup>O<sub>2</sub> production in solution

**Figure S7**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **POSS-tert-BF2** in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0 - A_t$ ,  $A_0$  - absorbance at time = 0 min and  $A_t$  - absorbance at time = t.

![](_page_16_Figure_0.jpeg)

**Figure S8**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **POSS-sal-BF**<sub>2</sub> in different interval of time and (b) plot of changes in absorption at 391 nm. Black line absorbance of **POSS-sal-BF**<sub>2</sub> before adding DPA,  $\Delta OD = A_0$ -A<sub>t</sub>, A<sub>0</sub> - absorbance at time = 0 min and A<sub>t</sub> - absorbance at time = t.

![](_page_16_Figure_2.jpeg)

**Figure S9**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **POSS-npht-BF**<sub>2</sub> in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0$ -A<sub>t</sub>, A<sub>0</sub> - absorbance at time = 0 min and A<sub>t</sub> - absorbance at time = t.

![](_page_17_Figure_0.jpeg)

**Figure S10**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **prop-tert-BF**<sub>2</sub> in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0 - A_t$ ,  $A_0$  - absorbance at time = 0 min and  $A_t$  - absorbance at time = t.

![](_page_17_Figure_2.jpeg)

**Figure S11**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **prop-sal-BF**<sub>2</sub> in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0 - A_t$ ,  $A_0$  - absorbance at time = 0 min and  $A_t$  - absorbance at time = t.

![](_page_18_Figure_0.jpeg)

**Figure S12**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of **prop-npht-BF**<sub>2</sub> in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0 - A_t$ ,  $A_0$  - absorbance at time = 0 min and  $A_t$  - absorbance at time = t.

![](_page_18_Figure_2.jpeg)

![](_page_18_Figure_3.jpeg)

**Figure S13**. (a) Changes in absorbance spectrum of DPA in MeOH upon irradiation ( $\lambda_{irr} = 365$  nm, intensity 1.30 mW/cm<sup>2</sup>) in presence of methylene blue in different interval of time and (b) plot of changes in absorption at 391 nm.  $\Delta OD = A_0 - A_t$ ,  $A_0$  - absorbance at time = 0 min and  $A_t$  - absorbance at time = t.

![](_page_19_Figure_0.jpeg)

Section 3. NMR spectra of photocatalytic aerobic oxidation of thioanisole

![](_page_19_Figure_2.jpeg)

**Figure S14.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectra of crude mixture for oxidation of thioanisole using **POSS-tert-BF**<sub>2</sub>. \* Residue methanol.

![](_page_20_Figure_0.jpeg)

**Figure S15.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained Methyl phenyl sulfoxide using **POSS-tert-BF**<sub>2</sub> as a photocatalyst (entry 4 Table 2).

![](_page_20_Figure_2.jpeg)

**Figure S16.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained 1-methyl-4-(methylsulfinyl)benzene using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

![](_page_21_Figure_0.jpeg)

**Figure S17.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained 4-(methylsulfinyl)benzonitrile using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

![](_page_21_Figure_2.jpeg)

**Figure S18.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained 1-bromo-3-(methylsulfinyl)benzene using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

![](_page_22_Figure_0.jpeg)

**Figure S19.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained 1-bromo-2-(methylsulfinyl)benzene using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

![](_page_22_Figure_2.jpeg)

**Figure S20.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained 1-(4- (methylsulfinyl)phenyl)ethan-1-one using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

![](_page_23_Figure_0.jpeg)

**Figure S21.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of obtained diphenyl sulfoxide using **POSS-tert-BF**<sub>2</sub> as a photocatalyst.

### Section 4. Characterization data POSS-tert-BF<sub>2</sub>

![](_page_24_Figure_1.jpeg)

Figure S23. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

130 120

150 140

210 200 190

180 170 160

110 100 90 δ (13C) /ppm

0 -10

40

30

20

10

50

70

80

60

![](_page_25_Figure_0.jpeg)

Figure S24. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_25_Figure_2.jpeg)

Figure S25. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_26_Figure_0.jpeg)

Figure S26. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_26_Figure_3.jpeg)

Figure S27. DOSY NMR (500 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_27_Figure_0.jpeg)

Figure S28. (<sup>1</sup>H, <sup>1</sup>H)-NOESY NMR (1D, 500 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_27_Figure_2.jpeg)

Figure S29. (<sup>1</sup>H, <sup>13</sup>C)-HSQC NMR (1D, 500 MHz, CDCl<sub>3</sub>) spectrum of POSS-tert-BF<sub>2</sub>.

![](_page_28_Figure_0.jpeg)

Figure S30. DRIFT spectrum of POSS-tert-BF2.

![](_page_28_Figure_2.jpeg)

Figure S31. MALDI mass spectrum of POSS-tert-BF2.

![](_page_29_Figure_0.jpeg)

Figure S32. Measured (top) and simulated (bottom) for  $C_{144}H_{216}B_8F_{16}N_8O_{20}Si_8$  [M+Na]<sup>+</sup> MS (MALDI) spectra of **POSS-tert-BF**<sub>2</sub>.

![](_page_30_Figure_0.jpeg)

**Figure S33.** TG (black line), and DTA (grey line) thermogram of **POSS-tert-BF**<sub>2</sub> at a heating rate of 10 °C/min. In the air atmosphere (60%  $N_2$ , 40%  $O_2$ ).

![](_page_30_Figure_2.jpeg)

Figure S34. TG (black line), and DTA (grey line) thermogram of POSS-tert-BF<sub>2</sub> at a heating rate of 10  $^{\circ}$ C/min. In nitrogen.

![](_page_31_Figure_1.jpeg)

Figure S35. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_31_Figure_3.jpeg)

Figure S36. <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_32_Figure_0.jpeg)

**Figure S37.** <sup>11</sup>B NMR (160 MHz, DMSO-d<sub>6</sub>) spectrum of **POSS-sal-BF**<sub>2</sub>. \*external reference (15% BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub>).

MJ734rek

![](_page_32_Figure_3.jpeg)

Figure S38. <sup>19</sup>F NMR (471 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

-131.37

 -131.44

![](_page_33_Figure_0.jpeg)

Figure S39. <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_33_Figure_2.jpeg)

Figure S40. DOSY NMR (500 MHz, CDCl<sub>3</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_34_Figure_0.jpeg)

Figure S41. (<sup>1</sup>H, <sup>1</sup>H)-COSY NMR (1D, 500 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_34_Figure_2.jpeg)

Figure S42. (<sup>1</sup>H, <sup>13</sup>C)-HSQC NMR (1D, 500 MHz, CDCl<sub>3</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_35_Figure_0.jpeg)

Figure S43. (<sup>1</sup>H, <sup>13</sup>C)-HMBC NMR (1D, 500 MHz, CDCl<sub>3</sub>) spectrum of POSS-sal-BF<sub>2</sub>.

![](_page_35_Figure_2.jpeg)

Figure S44. DRIFT spectrum of POSS-sal-BF2.

![](_page_36_Figure_0.jpeg)

Figure S45. MALDI mass spectrum of POSS-sal-BF2.

![](_page_36_Figure_2.jpeg)

Figure S46. Measured (top) and simulated (bottom) for  $C_{80}H_{88}B_8F_{16}N_8O_{20}Si_8$  [M] <sup>+</sup> MS (MALDI) spectra of **POSS-sal-BF**<sub>2</sub>.

![](_page_37_Figure_0.jpeg)

**Figure S47.** TG (black line), and DTA (grey line) thermogram of **POSS-sal-BF**<sub>2</sub> at a heating rate of 10 °C/min. In the air atmosphere (60%  $N_2$ , 40%  $O_2$ ).

![](_page_38_Figure_0.jpeg)

Figure S49. <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-npht-BF<sub>2</sub>.

![](_page_39_Figure_0.jpeg)

Figure S50. <sup>11</sup>B NMR (160 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-npht-BF<sub>2</sub>.

![](_page_39_Figure_2.jpeg)

Figure S51. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) spectrum of POSS-npht-BF<sub>2</sub>.

![](_page_40_Figure_0.jpeg)

Figure S52. <sup>29</sup>Si NMR (99 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-npht-BF<sub>2</sub>.

![](_page_40_Figure_2.jpeg)

Figure S53. DOSY NMR (500 MHz, DMSO-d<sub>6</sub>) spectrum of POSS-npht-BF<sub>2</sub>.

![](_page_41_Figure_0.jpeg)

Figure S1. DRIFT spectrum of POSS-npht-BF2.

![](_page_41_Figure_2.jpeg)

Figure S54. MALDI mass spectrum of POSS-npht-BF2.

![](_page_42_Figure_0.jpeg)

Figure S55. Measured (top) and simulated (bottom) for  $C_{112}H_{104}B_8F_{16}N_8O_{20}Si_8$  [M] <sup>+</sup> MS (MALDI) spectra of **POSS-npht-BF**<sub>2</sub>.

![](_page_43_Figure_0.jpeg)

**Figure S56.** TG (black line), and DTA (grey line) thermogram of **POSS-npht-BF**<sub>2</sub> at a heating rate of 10 °C/min. In the air atmosphere (60% N<sub>2</sub>, 40% O<sub>2</sub>).

![](_page_44_Figure_0.jpeg)

Figure S57. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of prop-tert-BF<sub>2</sub>.

![](_page_44_Figure_2.jpeg)

Figure S58. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of prop-tert-BF<sub>2</sub>.

![](_page_45_Figure_0.jpeg)

**Figure S59.** <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) spectrum of **prop-tert-BF2**. \*external reference (15% BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub>).

![](_page_45_Figure_2.jpeg)

Figure S60. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) spectrum of prop-tert-BF<sub>2</sub>.

![](_page_46_Figure_0.jpeg)

Figure S61. DRIFT spectrum of prop-tert-BF<sub>2</sub>.

![](_page_46_Figure_2.jpeg)

Figure S62. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of prop-sal-BF<sub>2</sub>.

![](_page_47_Figure_0.jpeg)

Figure S63. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of prop-sal-BF<sub>2</sub>.

 $\underbrace{}_{0.24}^{0.44}_{0.34}$ 

![](_page_47_Figure_3.jpeg)

**Figure S64.** <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) spectrum of **prop-sal-BF**<sub>2</sub>. \*external reference (15% BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub>).

![](_page_48_Figure_0.jpeg)

00 -80 -100 -120 δ (19F) /ppm -3 80 60 40 -160 -180 20 0 -20 -140 -200 -220 -240 -260 -40 -60 -280

Figure S65. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) spectrum of prop-sal-BF<sub>2</sub>.

![](_page_48_Figure_3.jpeg)

Figure S66. DRIFT spectrum of prop-sal-BF2.

![](_page_49_Figure_1.jpeg)

Figure S67. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of prop-npht-BF<sub>2</sub>.

![](_page_49_Figure_3.jpeg)

Figure S68. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) spectrum of prop-npht-BF<sub>2</sub>.

![](_page_50_Figure_0.jpeg)

**Figure S69.** <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) spectrum of **prop-npht-BF**<sub>2</sub>. \*external reference (15% BF<sub>3</sub>·Et<sub>2</sub>O in CDCl<sub>3</sub>).

![](_page_50_Figure_2.jpeg)

Figure S70. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) spectrum of prop-npht-BF<sub>2</sub>.

![](_page_51_Figure_0.jpeg)

Figure S71. DRIFT spectrum of prop-sal-BF2.

![](_page_51_Figure_2.jpeg)

Figure S72. Emission spectra of prop-imine-BF2. Excitation wavelength, 360 nm.

![](_page_52_Figure_0.jpeg)

**Figure S73.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectrum of **POSS-tert-BF**<sub>2</sub> after 5 cycles of photooxidation of sulfides to sulfoxides.

--- 0.49

![](_page_52_Figure_2.jpeg)

**Figure S74.** <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) spectrum of **POSS-tert-BF**<sub>2</sub> after 5 cycles of photooxidation of sulfides to sulfoxides.

to sulfoxides.					
Sample	Mass [g]	Volume [ml]	Element	Instrument data [mg/L]	Content [%]
POSS-tert-BF <sub>2</sub>	0.001	10	В	2.90	2.90

В

В

2.81

2.81

2.81

2.81

10

10

**POSS-tert-BF**<sub>2</sub>

**POSS-tert-BF**<sub>2</sub>

0.001

0.001

Table S1. The ICP-OES results of **POSS-tert-BF**<sub>2</sub> after 5 cycles of photooxidation of sulfides to sulfoxides.

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