

## Unusual Regioselective Mercuration on Metalloporphyrins and Its Potential Applications

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### Supplementary Information

#### Experimental

**Starting Materials 1a-d.** Starting materials used in this communication, **1a**,<sup>1</sup> **1b**,<sup>1</sup> **1c**,<sup>1</sup> and **1d**<sup>2</sup> were prepared to the literature.

**Chloro[10',20'-bis(3'',5''-di-*t*-butylphenyl)porphyrinato-nickel-3'-yl]mercury 2a.** Mercury trifluoroacetate (382 mg) was added to a solution of **1a** (666 mg) dissolved in dry dichloromethane (170 mL) and the reaction mixture was stirred at room temperature for 30 min. A saturated aqueous sodium chloride (7 mL) was added to the mixture and this heterogeneous mixture was stirred for further 30 min. The organic layer was washed with two portions of water and the solvent was removed under reduced pressure. The residue was purified by column chromatography eluting with a hexane-dichloromethane mixed solvent (3:1). The obtained crude product was

recrystallized from a dichloromethane-methanol mixed solvent (1:1) to give purple crystals, 288 mg (33 %; 51 mg of unreacted **1a** was recovered). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.92 (s, 1H, *meso*), 9.91 (s, 1H, *meso*), 9.24 (s, 1H, β), 9.19 (d, 1H, *J* = 4.9 Hz, β), 9.18 (d, 1H, *J* = 4.6 Hz, β), 9.16 (d, 1H, *J* = 4.9 Hz, β), 8.99 (d, 1H, *J* = 4.6 Hz, β), 8.98 (d, 1H, *J* = 4.9 Hz, β), 8.84 (d, 1H, *J* = 4.9 Hz, β), 7.95 (t, 1H, *J* = 1.8 Hz, Ar), 7.92 (d, 4H, *J* = 1.8 Hz, Ar), 7.78 (t, 1H, *J* = 1.8 Hz, Ar), 1.52 (s, 18H, *t*-Bu), and 1.51 (s, 18H, *t*-Bu) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 408 (276.0), 519 (16.9), and 552 (9.4) nm. ESI-HRMS: 978.235 (calcd. for C<sub>48</sub>H<sub>51</sub>ClHgN<sub>4</sub>Ni : 978.286).

**Chloro[10',20'-bis(3'',5''-di-*t*-butylphenyl)porphyrinato-zinc-3'-yl]mercury 2b.** Similar procedure and purification method for **2a** were employed using the following reagents and/or materials to give **2b** (33 mg, 17 %; 9 mg of unreacted **1b** was recovered): **1b** (145 mg), dry dichloromethane (50 mL), mercury trifluoroacetate (82 mg), and saturated aqueous sodium chloride (2 mL). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.33 (s, 1H, *meso*), 10.29 (s, 1H, *meso*), 9.46 (d, 1H, *J* = 4.7 Hz, β), 9.45 (d, 1H, *J* = 4.7 Hz, β), 9.43 (s, 1H, β), 9.41 (d, 1H, *J* = 4.7 Hz, β), 9.22 (d, 1H, *J* = 4.7 Hz, β), 9.21 (d, 1H, *J* = 4.7 Hz, β), 8.98 (d, 1H, *J* = 4.7 Hz, β), 8.15 (d, 2H, *J* = 1.9 Hz, Ar), 8.11 (d, 2H, *J* = 1.9 Hz, Ar), 8.03 (t, 1H, *J* = 1.9 Hz, Ar), 7.86 (t, 1H, *J* = 1.9 Hz, Ar), 1.59 (s, 18H, *t*-Bu), and 1.58 (s, 18H, *t*-Bu) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 413 (544.0), 539 (17.0), and 574 (3.6) nm. ESI-HRMS: 985.1409 (calcd. for C<sub>48</sub>H<sub>51</sub>ClHgN<sub>4</sub>Zn: 985.2878).

**Chloro[10',20'-bis(3'',5''-di-*t*-butylphenyl)porphyrin-3'-yl]mercury 2c.** Similar procedure and purification method for **2a** were employed using the following reagents and/or materials to give **2c** (30 mg, 21 %, 46 mg of unreacted starting material was recovered); **1c** (106 mg), dry dichloromethane (50 mL), mercury trifluoroacetate (132 mg), saturated aqueous sodium chloride (2 mL). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.33 (s, 1H, *meso*), 10.32 (s, 1H, *meso*), 9.46 (d, 1H, *J* = 4.7 Hz, β), 9.41 (d, 1H, *J* = 4.4 Hz, β), 9.41 (d, 1H, *J* = 4.4 Hz, β), 9.40 (s, 1H, β), 9.37 (d, 1H, *J* = 4.7 Hz, β), 9.19 (d, 1H, *J* = 4.4 Hz, β), 9.11 (d, 1H, *J* = 4.4 Hz, β), 8.97 (d, 1H, *J* = 4.7 Hz, β), 8.14 (d, 2H, *J* = 1.7 Hz, Ar), 8.10 (d, 2H, *J* = 1.7 Hz, Ar), 8.02 (t, 1H, *J* = 1.7 Hz, Ar), 7.85 (t, 1H, *J* = 1.7 Hz, Ar), 1.58 (s, 18H, *t*-Bu), 1.57 (s, 18H, *t*-Bu), -2.98 (bs, 1H, NH), and -3.01 (bs, 1H, NH) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 413 (443.0), 507 (16.6), 541 (4.4), 578 (5.3), and 632 (1.7) nm. MALDI-TOFMS: 919.21 (Calcd. for C<sub>48</sub>H<sub>53</sub>ClHgN<sub>4</sub>: 923.3743)

**Chloro(5,15-di-*n*-heptyl-porphyrinato-nickel-3'-yl)mercury 2d.** Similar procedure and purification method were performed using the following reagents and/or materials to give **2d** (12 mg, 23%, 8 mg of the unreacted starting material was recovered): **1d** (36 mg), dry dichloromethane (10 mL), mercury trifluoroacetate (42 mg), saturated aqueous sodium chloride (2 mL). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.67 (s, 1H, *meso*), 9.40 (d, 1H, *J* = 4.7 Hz, β), 9.24 (d, 1H, *J* = 4.9 Hz, β), 9.20 (d, 1H, *J* = 4.9 Hz, β), 9.16 (d, 1H, *J* = 4.7 Hz, β), 9.11 (d, 1H, *J* = 4.7 Hz, β), 8.67 (d, 1H, *J* = 4.7 Hz, β), 8.59 (s, 1H, *meso*), 8.53 (s, 1H, β), 4.56 (t, 2H, *J* = 7.8 Hz, CH<sub>2</sub>), 4.09 (t, 2H, *J* = 7.8 Hz, CH<sub>2</sub>), 2.37 (quintet, 2H, *J* = 7.83 Hz, CH<sub>2</sub>), 2.08 (quintet, 2H, *J* = 7.8 Hz, CH<sub>2</sub>), 1.51-1.25 (m, 16H, CH<sub>2</sub>), and 0.92-0.86 (m, 6H, CH<sub>3</sub>) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 409 (218.0), 523 (13.4), and 555 (5.7). ESI-HRMS: 797.9245 (M requires 798.1923).

**Mizoroki-Heck Reaction of 2a [Reaction 1: Pd(OAc)<sub>2</sub> / PPh<sub>3</sub> System]** A mixture of **2a** (27 mg), palladium acetate (6 mg), triphenylphosphine (29 mg), K<sub>2</sub>CO<sub>3</sub> (38 mg), and methyl acrylate (119 mg) was dissolved in dry THF (5 mL) and stirred at 40 °C under argon atmosphere for 24 hours. After removal the solvent under reduced pressure, the residue was chromatographed on SiO<sub>2</sub> eluting with a hexane-dichloromethane mixed solvent (1:1). The band eluted first was characterized to be scrambled product, **4** (7 mg, 32 %) and the next band to be the desired product, **5** (1 mg, 5 %). **4**: <sup>1</sup>H NMR: δ 10.11 (s, 1H, *meso*), 9.87 (s, 1H, *meso*), 9.22 (d, 1H, *J* = 15.6 Hz, alkene), 9.22 (d, 1H, *J* = 4.9 Hz, β), 9.18 (s, 1H, β), 9.15 (d, 1H, *J* = 4.9 Hz, β), 9.14 (d, 1H, *J* = 4.9 Hz, β), 8.96 (d, 1H, *J* = 4.9 Hz, β), 8.96 (d, 1H, *J* = 4.9 Hz, β), 8.96 (d, 1H, *J* = 4.9 Hz, β), 7.91 (d, 4H, *J* = 1.9 Hz, Ar), 7.80 (t, 1H, *J* = 1.9 Hz, Ar), 7.78 (t, 1H, *J* = 1.9 Hz, Ar), 7.01 (d, 1H, *J* = 15.6 Hz, alkene), 3.98 (s, 3H, OCH<sub>3</sub>), 1.53 (s, 18H, *t*-Bu), and 1.52 (s, 18H, *t*-Bu) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 423 (148), 530 (9.9), and 571(10.8) nm. ESI-HRMS: 826.3435 (Calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>4</sub>NiO<sub>2</sub> 826.3757). **5**: <sup>1</sup>H NMR: δ 9.87 (s, 1H, *meso*), 9.85 (s, 1H, *meso*), 9.32 (d, 1H, *J* = 0.9 Hz, β), 9.15 (d, 1H, *J* = 4.9 Hz, β), 9.15 (d, 1H, *J* = 4.9 Hz, β), 9.13 (d, 1H, *J* = 4.9 Hz, β), 8.97 (d, 1H, *J* = 4.9 Hz, β), 8.96 (d, 1H, *J* = 4.9 Hz, β), 8.95 (d, 1H, *J* = 4.9 Hz, β), 7.90 (d, 2H, *J* = 1.8 Hz, Ar), 7.81 (t, 1H, *J* = 1.8 Hz, Ar), 7.79 (d, 2H, *J* = 1.8 Hz, Ar), 7.77 (t, 1H, *J* = 1.8 Hz, Ar), 7.32 (dd, 1H, *J* = 15.6 and 0.9 Hz, alkene), 6.62 (d, 1H, *J* = 15.6 Hz, alkene), 3.76 (s, 3H, OCH<sub>3</sub>), 1.51 (s, 18H, *t*-Bu), 1.47 (s, 18H, *t*-Bu) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup> in CHCl<sub>3</sub>) 418 (152), 526 (10.7), 566 (8.8) nm. ESI-HRMS: 826.4094 (Calcd. for C<sub>52</sub>H<sub>56</sub>N<sub>4</sub>NiO<sub>2</sub> 826.3757).

**[Reaction 2: Pd(OAc)<sub>2</sub> / P<sup>*t*</sup>Bu<sub>2</sub>biphenyl System]** A mixture of **2a** (8 mg), palladium acetate (1 mg),

di-*t*-butyl-biphenylphosphine (5 mg), K<sub>2</sub>CO<sub>3</sub> (12 mg), and methyl acrylate (38 mg) was dissolved in dry THF (3 mL) and stirred at 50°C under argon atmosphere for 20 hours. Applying the similar work-up procedure, **4** was obtained as the sole product (5 mg, 63 %).

[*Reaction 3: Omission of the Phosphine Ligand*] A mixture of **1b** (27 mg), palladium acetate (6 mg), K<sub>2</sub>CO<sub>3</sub> (38 mg), and ethyl acrylate (119 mg) was dissolved in dry THF (5 mL) and stirred at 40°C under argon atmosphere for 9 days. Every 24 h, 6 mg of palladium acetate was added to the reaction mixture. Applying the similar work-up procedure, **5** was obtained as the sole product (11 mg, 47 %).

**3-Iodo-5,15-bis(3',5'-di-*tert*-butylphenyl)porphyrinato nickel 6.** Iodine (4 mg) was added to a solution of **2a** (17 mg) dissolved in dry THF (3 mL) and the solution was stirred for 42 hours at room temperature. After removal of the solvent under reduced pressure, the residue was chromatographed on SiO<sub>2</sub> eluting with a hexane-dichloromethane mixed solvent (3:1) and the obtained crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to give purple crystals, **6** (15 mg, quant.). <sup>1</sup>H NMR: δ 9.86 (s, 1H, *meso*), 9.73 (s, 1H, *meso*), 9.56 (s, 1H, β), 9.15 (d, 1H, *J* = 4.7 Hz, β), 9.14 (d, 1H, *J* = 4.7 Hz, β), 9.11 (d, 1H, *J* = 4.7 Hz, β), 8.98 (d, 1H, *J* = 4.7 Hz, β), 8.95 (d, 1H, *J* = 4.7 Hz, β), 8.95 (d, 1H, *J* = 4.7 Hz, β), 7.90 (d, 2H, *J* = 1.8 Hz, Ar), 7.76 (t, 2H, *J* = 1.9 Hz, Ar), 7.72 (d, 2H, *J* = 1.9 Hz, Ar), 1.51 (s, 18H, *t*-Bu), and 1.49 (s, 18H, *t*-Bu) ppm. UV/vis: λ<sub>max</sub>(ε/10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>, in CHCl<sub>3</sub>) 409 (197.0), 523 (15.0), and 553 (9.1) nm. ESI-HRMS: 868.2753 (Calcd. for C<sub>48</sub>H<sub>51</sub>IN<sub>4</sub>Ni: 868.2512).

**3-Phenyl-5,15-bis(3',5'-di-*tert*-butylphenyl)porphyrinato nickel 7.** A mixture of **6** (20 mg), phenylboronic acid ester (4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane) (7 mg), tetrakis(triphenylphosphine)palladium (3 mg), and aqueous barium hydroxide (40 mg, dissolved in 0.5 mL water) was dissolved in dry diglyme (3 mL) and stirred at 120°C under argon atmosphere for 4 days. The reaction mixture was pored into ice water and the product was extracted with chloroform. The organic layer was washed with water four times and the solvent was removed under reduced pressure. The residue was purified by SiO<sub>2</sub> chromatography eluting with a hexane-toluene mixed solvent (8:1), then preparative gel permeation high performance liquid chromatography was carried out (a Japan Analytical Industry LC-908 HPLC equipped with JAIGEL 1H+2H gel permeation columns). The obtained crude product was recrystallized from a dichloromethane-methanol mixed solvent (1:1) to give red crystals, **7** (8 mg, 42 %). <sup>1</sup>H NMR

(CDCl<sub>3</sub>)  $\delta$  9.84 (s, 1H, *meso*), 9.79 (s, 1H, *meso*), 9.15 (d, 2H,  $J = 4.9$  Hz,  $\beta$ ), 9.08 (s, 1H,  $\beta$ ), 9.05 (d, 1H,  $J = 4.9$  Hz,  $\beta$ ), 8.96 (d, 1H,  $J = 4.9$  Hz,  $\beta$ ), 8.95 (d, 1H,  $J = 4.9$  Hz,  $\beta$ ), 8.65 (d, 1H,  $J = 4.9$  Hz,  $\beta$ ), 7.91 (d, 2H,  $J = 1.7$  Hz, Ar), 7.76 (t, 1H,  $J = 1.7$  Hz, Ar), 7.55 (d, 2H,  $J = 2.0$  Hz, Ar), 7.38-7.36 (m, 2H, Ph), 7.32 (t, 1H,  $J = 2.0$  Hz, Ar), 7.14-7.12 (m, 3H, Ph) 1.51 (s, 18H, *t*-Bu), and 1.32 (s, 18H, *t*-Bu) ppm. UV/vis:  $\lambda_{\max}(\epsilon/10^3 \text{ M}^{-1}\text{cm}^{-1})$ , in CHCl<sub>3</sub>) 409 (207), 522 (15.4), and 553 (7.8) nm. HR-MALDI-TOF MS: 818.92 (Calcd. for C<sub>54</sub>H<sub>56</sub>N<sub>4</sub>Ni: 818.39).

#### Notes and References

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