#### **Supporting Information**

### Title: 2-Carbomethoxy-3-Hydroxyquinoxaline-di-N-Oxide as a Novel Ligand for the Copper-catalyzed Coupling Reaction of Phenols and Aryl Halides

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#### List of Contents

- 1. General Experimental Section (S2)
- 2. Preparation of Ligand 1, 2 and copies of <sup>1</sup>H and <sup>13</sup>C NMR of Ligand 1 (S2-S7)
- 3. Copies of <sup>1</sup>H and <sup>13</sup>C NMR of products in Table 2 (S8-S29)
- 4. Copies of <sup>1</sup>H and <sup>13</sup>C NMR of products in Table 3 (S30-S41)
- 5. Copies of <sup>1</sup>H and <sup>13</sup>C NMR of products in Table 4 (S42-S51)

**1. General Experimental Methods**: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker Avance ARX- 400. Mass spectra were performed on Kompact Axima-CFR MALDI mass spectrometers. Optical rotations were recorded on a Perkin Elmer 341 polarimeter. Anhydrous solvents were obtained as follows: DMSO from CaH<sub>2</sub>. All other solvents were reagent grade. All moisture sensitive reactions were carried out in flame dried flask under argon atmosphere.

#### **3.** Preparation of Ligands



#### 2-Carbomethoxy-3-Hydroxyquinoxaline-di-N-Oxide (L1).

To a solution of NaOCH<sub>3</sub> (0.91 g, 16.7 mmol) in dry THF (100 ml) cooled to 0 °C, dimethyl malonate (2.4 g, 17.8 mmol) was added with efficient stirring in ca. 20 min. After 30 min, the benzofuroxan (2.0 g, 14.8 mmol) in THF (50 mL) was added, and stirred at room temperature for 24 h. Subsequently, the solution was filtered, and the solid was washed with THF (3×20 ml). The remaining solid was dissolved by water (20 mL). The aqueous phase was acidified to pH=1, and extracted with ethyl acetate (3×20 ml).The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford L1 (3.9 g, 92%) as a brown solid. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  8.39 (d, *J* =8.4 Hz, 1H), 7.93 (d, *J* =8.4 Hz, 1H), 7.92-7.81 (m, 1H), 7.53-7.49 (m, 1H), 4.03 (s, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CH<sub>3</sub>OD):  $\delta$  161.2, 152.6, 135.2, 134.5, 134.0, 131.2, 126.0, 121.1, 115.0, 54.0 ppm. MS (EI, *m/z*): 237 (M<sup>+</sup>+1).



#### 2-Carbomethoxy-3-Hydroxyquinoxaline (L2).

NaH (0.4 g, 16.7 mmol) was added to CH<sub>3</sub>OH (100 mL) at 0 °C. Then, benzofuroxan (2.0 g, 14.8 mmol) was added to this solution. Subsequently, dimethyl malonate (2.4 g, 18.2 mmol) was added, and stirred at room temperature for 24 h. The solution was filtered, and the solid was washed with THF (3×20 ml). The remaining solid was dissolved by water (20 mL). The aqueous phase was acidified to pH = 1, and extracted with ethyl acetate (3×20 ml). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure, Purification by silica gel chromatography afforded **L2** (2.3 g ,75%) as a brown solid. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>):  $\delta$  7.97-7.95 (m, 1H), 7.66-7.62 (m, 1H), 7.48-7.46 (m, 1H), 7.43-7.39 (m, 1H), 4.07 (s, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  163.6, 154.6, 147.7, 133.0, 132.3, 132.0, 130.3, 125.1, 116.5, 53.3 ppm. MS (EI, *m/z*): 205 (M<sup>+</sup>+1).



L1



L1



L2



L2

# **CuI-Catalyzed Coupling Reaction of Aryl Iodides with Phenols or 2-Naphthol:** Table 2







3c









3g











3j







31





3n

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3n

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30

S26

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**3**p

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L81'EST

gyt-E405

**3**p

.

160

170

# CuI-Catalyzed Coupling Reaction of Aryl Bromide with Phenols or 2-Naphthol: Table 3

























### CuI-Catalyzed Coupling Reaction of Aryl Chloride with Phenols or 2-Naphthol: Table 4



7a

















