Supplementary data for *Dalton Transactions*

ESI for

Fe(II), Ru(II) and Re(I) complexes of endotopic, sterically non-hindering, U-shaped 8,8'-disubstituted-3,3'-biisoquinoline ligands: syntheses and spectroscopic properties

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Experimental section.

Synthesis of products neither described in the main text nor in recent publications.

Sodium diethoxyacetate **4**.

A solution of sodium hydroxyde (4.56 g, 114 mmol) in water (25 mL) was added to a solution of ethyl diethoxyacetate (20.3 mL, 20 g, 114 mmol) in ethanol (50 mL) and the resulting mixture heated at reflux for 5 hours. The mixture was evaporated to dryness, and the residue dryed *in vacuo* to give a white solid (18.66 g, 97%).

N-(2-chlorobenzyl)-2,2-diethoxyacetamide **6**.

Sodium diethoxyacetate (18.7 g, 110 mmol) was dissolved in dry diethyl ether (90 mL) and thionyl chloride (8.5 mL, 13.8 g, 115 mmol) was added to this mixture with stirring for 10 minutes at 10 °C. The reaction mixture was heated at reflux for 30 minutes and then allowed to cool. A solution of 2-chlorobenzylamine (15.6 g, 110 mmol) in toluene (60 mL) and pyridine (35 mL) was poured into this reaction mixture via a canula with vigorous stirring. This was heated at reflux for 30 minutes and then allowed to cool. The mixture was poured into ice water (~200 mL) and extracted with toluene (3 x 100 mL). The organic extracts were combined and washed firstly with a solution of hydrocholic acid (2%, 100 mL) and then with water. The solvent was evaporated and the residue purified by chromatography on silica gel by using pentane-ethyl acetate (9:1) as the eluent to give the title compound (yellow oil, 17.7 g, 59%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.38-7.34 (m, 2H), 7.26-7.21 (m, 2H), 7.04 (sb, 1H), 4.82 (s, 1H), 4.55 (d, 2H, J = 6 Hz), 3.73-3.55 (m, 4H), 1.23 (t, 6H, J = 6.9 Hz).

8-chloroisoquinolin-3-ol **7**.

N-(2-chlorobenzyl)-2,2-diethoxyacetamide (17.7 g, 65.1 mmol) was carefully added to concentrated sulfuric acid (110 mL) with stirring at about 10°C. The reaction mixture was stirred at room temperature for 16 hours, poured into ice water and filtered. The filtrate was slowly neutralized with 33% aqueous ammonium hydroxyde and the resulting precipitate was filtered, dried, and then re-crystallized in methanol to give the title compound (yellow needles, 8.34 g, 71%).

^{1}H NMR (DMSO, 300 MHz): δ = 9.12 (s, 1H), 7.73 (d, 1H, J = 8.1 Hz), 7.56 (d, 1H, J = 8 Hz), 7.46 (d, 1H, J = 7.2 Hz), 7.02 (s, 1H).

ES-MS m/z = 180.0218 (calculated 180.0216 for $C_9H_6NOCl + H^+$).