Supporting Information

## Rhodium-Grafted Hydrotalcite Catalyst for Heterogeneous 1,4-Addition Reaction of Organoboron Reagents with Electron Deficient Olefins

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**Fig. 1S** The  $k^3$ -weighted Rh K-edge EXAFS oscillations for Rh foil (dotted line, ×0.25), Rh<sub>2</sub>O<sub>3</sub> (dashed line, ×0.66), and fresh Rh/HT catalyst (solid line).



**Fig. 2S** Curve-fitting analysis was performed with the inverse FT of the 1.16 Å < r < 1.90 Å range using hexagonal Rh<sub>2</sub>O<sub>3</sub> as a standard material. The solid curve was obtained experimentally, and the dashed curve is the calculated fit.



**Fig. 3S** Curve-fitting analysis was performed with the inverse FT of the 2.21 Å < r < 2.98 Å range using Rh-(O)-Mg shell parameter. The solid curve was obtained experimentally, and the dashed curve is the calculated fit.



Fig. 4S Dependences of the initial formation rate of 3a on the amount of 1a (A) and 2a (B).

Reaction conditions for (A): **1a** 1-3 mmol, **2a** 1 mmol, Rh/HT ( $2.0 \times 10^{-2}$  g, Rh:  $4 \times 10^{-3}$  mmol), 1,4dioxane (2 mL), 1,5-COD ( $4 \times 10^{-3}$  mmol), H<sub>2</sub>O 0.1 mL, 100 °C, Ar, 30 min, for (B): **1a** 1 mmol, **2a** 1-3 mmol, Rh/HT ( $2.0 \times 10^{-2}$  g, Rh:  $4 \times 10^{-3}$  mmol), 1,4-dioxane (2 mL), 1,5-COD ( $4 \times 10^{-3}$  mmol), H<sub>2</sub>O 0.1 mL, 100 °C, Ar, 30 min,