Supplementary Material for Chemical Communications

Allosteric function facilitates template assisted olefin metathesis

Rie Wakabayashi, Yohei Kubo, Osamu Hirata, Masayuki Takeuchi* and Seiji Shinkai*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.
E-mail: taketcm@mbox.nc.kyushu-u.ac.jp, seijitcm@mbox.nc.kyushu-u.ac.jp;
Fax:+81-92-642-3611

General

All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as received. The ^{1}H spectra were recorded either on a Brucker AC 250 (250 MHz) or Brucker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer and/or a JEOL JMS HX110A high-resolution magnetic sector FAB mass spectrometer. UV-Vis and Fluorescent spectra were recorded with a Shimadzu UV-2500 PC and Hitachi F-4500 spectrophotometer, respectively.

Binding isotherm analysis

Cooperative guest-binding process was analyzed according to the Hill equation: $\log(y/(1-y)) = n\log[\text{guest}] + \log K$, where K , y and n are the association constant, the extents of complexation and Hill coefficient, respectively. From the slope and the intercept of the linear plots (Hill plot) one can estimate K and n, which are useful as measures of the cooperativity. A higher value of n is related to a higher degree of cooperativity. The maximum is equal to the number of binding sites. In the analysis of binding isotherm by Hill plot, we have evaluated the concentration of unbound guest, by assuming that 100 % 1:2 complex is formed when the absorbance change is saturated.

Measurements

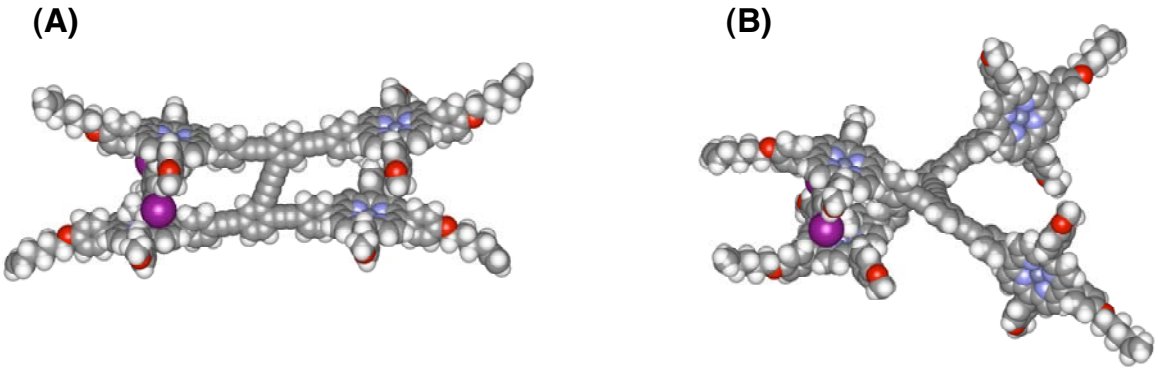

Fig. S1 The energy-minimized structures of **1b•2**. Structures (A) and (B) correspond with (A) and (B) in Scheme 1.

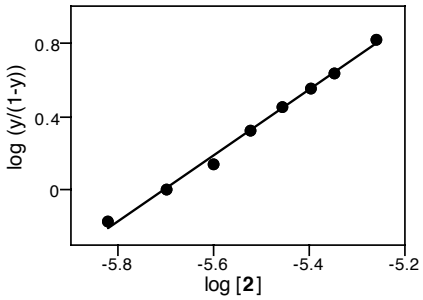

Fig. S2 Hill plot for **1b** and **2** system.

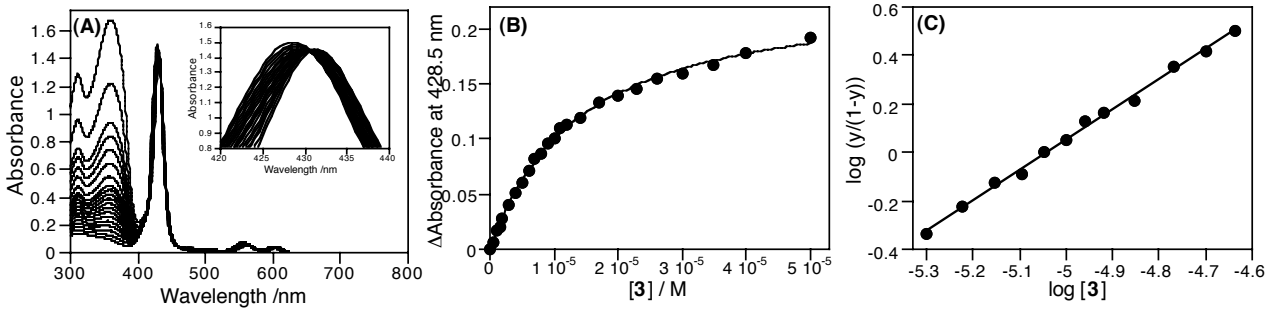

Fig. S3 (A) UV-Vis spectral change of **1b** upon addition of **3**, (B) plot of absorbance change at 428.5 nm for **1** *vs.* [**3**] and (C) Hill plot. The solid line in (B) represents a theoretical curve for 1:2 complex formation.

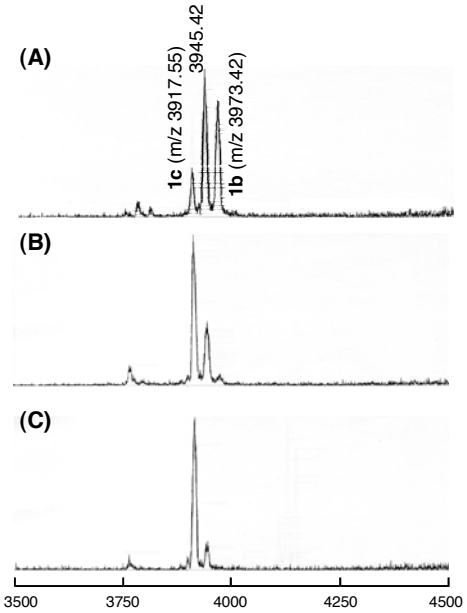

Fig. S4 MALDI TOF MS spectra of the RCM reaction mixture under the conditions of Fig. 2D after (A) 3 h, (B) 7h and (C) 12h.

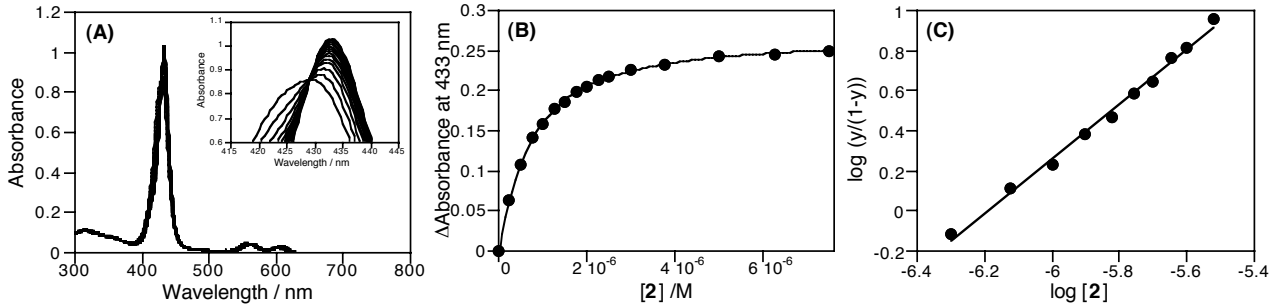

Fig. S5 (A) UV-Vis spectral change of **1c** upon addition of **2**, (B) plot of absorbance change at 433 nm for **1** *vs.* [**2**] and (C) Hill plot. The solid line in (B) represents a theoretical curve for 1:2 complex formation.

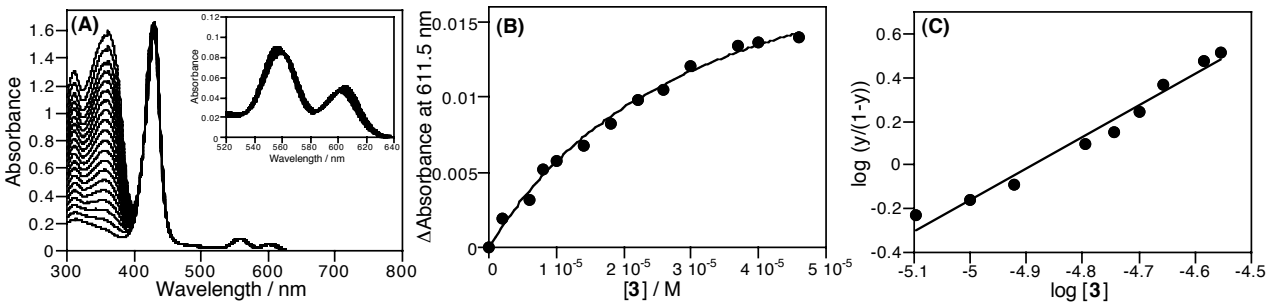

Fig. S6 (A) UV-Vis spectral change of **1c** upon addition of **3**, (B) plot of absorbance change at 611.5 nm for **1** *vs*. [**3**] and (C) Hill plot. The solid line in (B) represents a theoretical curve for 1:2 complex formation.