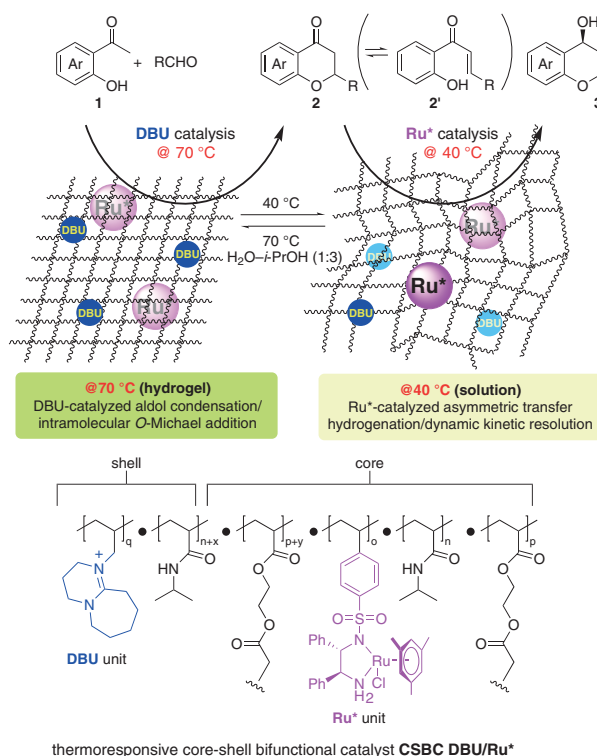


A Thermoresponsive Core-Shell Bifunctional Polymeric Catalyst: An Aldol-Michael-ATH Cascade Process

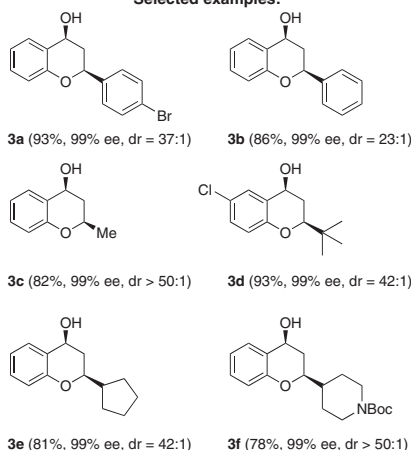


Reaction I: 2a (98% yield)
conditions: **1** (0.1 mmol), **RCHO** (**R** = 4-BrC₆H₄, 0.12 mmol)
 CSBC DBU/Ru* (0.12 mmol DBU loadings/2.5 mol% Ru loadings), HCO₂Na (0.1 mmol) in aq *i*-PrOH (4 mL),
 70 °C for 12 h.

Reaction II: 3a (95% yield, 99% ee, dr = 37:1)
conditions: **2** (0.1 mmol)
 CSBC DBU/Ru* (0.12 mmol DBU loadings), HCO₂Na (0.1 mmol) in aq *i*-PrOH (4 mL),
 40 °C for 18 h.

Reaction III: 3a (93% yield, 99% ee, dr = 37:1)
conditions: **1** (0.1 mmol), **RCHO** (**R** = 4-BrC₆H₄, 0.12 mmol)
 CSBC DBU/Ru* (0.12 mmol DBU loadings/2.5 mol% Ru loadings), HCO₂Na (0.1 mmol) in aq *i*-PrOH (4 mL),
 70 °C for 12 h then 40 °C for 18 h.

Selected examples:



Significance: A poly(*N*-isopropylmethacrylamide) (PNIPMAM)-based core-shell structured bifunctional composite (CSBC DBU/Ru*) bearing a DBU unit and a homochiral DPEN-ruthenium complex was prepared through a stepwise precipitation–polymerization procedure. CSBC DBU/Ru* promoted the aldol condensation and the subsequent intramolecular oxa-Michael addition of 2-hydroxyacetophenones (**1**) and 4-bromobenzaldehyde at 70 °C to give 2-aryl-4-chromanone **2a** (see Reaction I). CSBC DBU/Ru* also catalyzed the asymmetric transfer hydrogenation (ATH) of 4-chromanone **2a** with HCOONa to give **3a** (99% ee) (see Reaction II). When the reaction of **1** and 4-bromobenzaldehyde was carried out with CSBC DBU/Ru* at 70 °C followed by additional stirring at 40 °C, the aldol/Michael/ATH sequence took place in one pot to give 99% ee of **3a** (see Reaction III).

Comment: CSBC DBU/Ru* exists as a hydrogel in aqueous acetonitrile at 70 °C, where the inner core-tethered Ru* species is most inaccessible to show little catalytic performance, and the outer shell-tethered DBU unit promoted the aldol/oxa-Michael reactions. Ru*-catalyzed ATH smoothly proceeded in a solution of CSBC DBU/Ru* at 40 °C, where the organic substrates can diffuse into the core region of the polymer matrix. 4-Chromanone **2** is in a state of equilibrium with the retro-Michael product **2'** to realize the ATH with the dynamic kinetic resolution (DKR). Thus, the thermoresponsive property of PNIPMAM and the site-isolated core/shell immobilization of a DBU unit and a DPEN-Ru* complex enabled the direct access to chiral chromanols through the temperature-tuned aldol/Michael/ATH-DKR multi-step sequence.

SYNFACTS Contributors: Yasuhiro Uozumi, Shintaro Okumura

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