Supporting Information

A New Type of Self-Supported, Polymeric Ru-Carbene Complex for Homogeneous Catalysis and Heterogeneous Recovery: Synthesis and Catalytic Activities for Ring-Closing Metathesis

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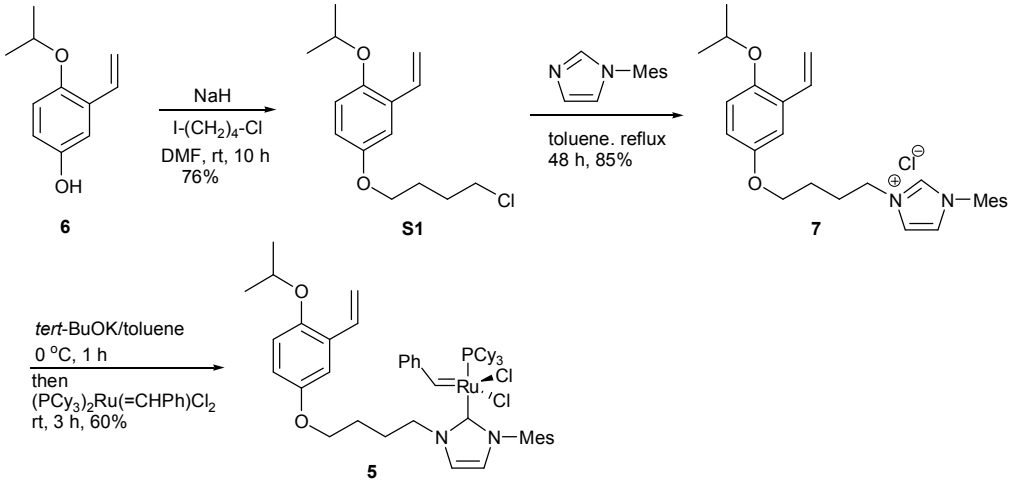
General Methods. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury VX300 NMR spectrometer (300 MHz) in given solvent. Chemical shifts were expressed in ppm with TMS as an internal standard (δ = 0 ppm) for ^{1}H NMR, coupling constants (*J*) are in Hz. The anhydrous toluene was distilled from sodium benzophenone ketyl and DMF was freshly distilled from calcium hydride. The purchased reagents are used as received without further purification. All manipulations involving air and moisture-sensitive compounds and reactions were carried out using standard Schlenk technique under nitrogen atmosphere. 4-Chloro-1-iodobutane and Grubbs' 1st generation, $(PCy_3)_2Ru(=CHPh)Cl_2$ purchased and used as received from Aldrich. 2-Isopropoxy-5-hydroxystyrene **6**[1] and 1-mesitylimidazole[2] were prepared according to the reported procedures.



Synthesis of 5-(4-chlorobutoxy)-2-isopropoxystyrene S1. To a solution of **6** (1.0 g, 5.58 mmol) in anhydrous DMF (100 mL) was added NaH (0.22 g, 5.58 mmol) at 0 ℃. After stirring for 10 min at 0 ℃, 1-chloro-4-iodiobutane (1.27 g, 5.81 mmol) was added. The resulting mixture was stirred at room temperature for 10 h, and the reaction was quenched with water, extracted with ethyl acetate. The combined organic layer was dried with Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica (EtOAc/ hexane 1:9) to give **S1** (1.14 g, 4.23 mmol, 76.3%) as a slightly yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.09 (dd, 1H, *J* = 11.1, 17.8 Hz), 7.02 (d, 1H, *J* = 3.0 Hz), 6.83 (d, 1H, *J* = 8.9 Hz), 6.75 (dd, 1H, *J* = 2.9, 8.9 Hz), 5.74 (dd, 1H, *J* = 1.3, 17.7 Hz), 5.25 (dd, 1H, *J* = 1.3, 11.1 Hz), 4.39 (sept, 1H, *J* = 6.1 Hz), 3.97 (t, 2H, *J* = 5.7 Hz), 3.62 (t, 2H, *J* = 6.2 Hz), 1.99-1.88 (m, 4H), 1.31 (d, 6H, *J* = 6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 153.1, 149.4, 131.7, 129.2, 116.9, 114.6, 114.1, 111.8, 72.2, 67.3, 44.7, 29.3, 26.7, 22.1.

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[1] Q. Yao, *Angew. Chem. Int. Ed.* **2000**, *39*, 3896.

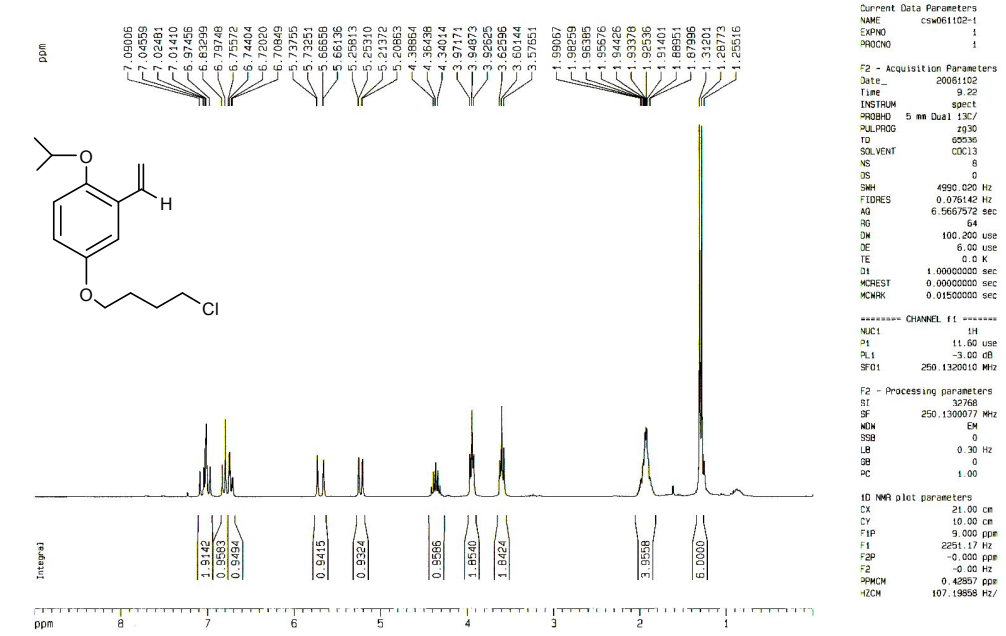
[2] E. Alclde, I Dinarés, S. Rodríguez, C. G. De Migue, *Eur. J. Org. Chem.* **2005**, *39*, 1637

Synthesis of imidazolium chloride 7. A solution of **S1** (0.9 g, 3.3 mmol), 1-mesitylimidazole (1.2 g, 6.6 mmol) in dry toluene (30 mL) was stirred at 100-110 ℃ for 48 h, then the solvent was evaporated off. The residue was purified by silica gel chromatography (dichloromethane/methanol =25/1) to afford **7** as a slightly yellow crystalline solid (1.13 g, 2.45 mmol, 84.5%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 10.88 (s, 1H), 7.68 (t, 1H, *J* = 1.7 Hz), 7.15 (t, 1H, *J* = 1.7 Hz), 7.08 (dd, 1H, *J* = 11.1, 17.8), 7.00 (s, 2H), 6.96 (s, 1H), 6.84 (d, 1H, *J* = 8.9 Hz), 6.77 (dd, 1H, *J* = 2.9, 8.9 Hz), 5.74 (dd, 1H, *J* = 1.4, 17.8 Hz), 5.27 (dd, 1H, *J* = 1.4, 11.1 Hz), 4.90 (t, 2H, *J* = 7.2 Hz), 4.37 (sept, 1H, *J* = 6.1 Hz), 4.04 (t, 2H, *J* = 5.7 Hz), 2.34 (s, 3H), 2.24 (m, 2H), 2.07 (s, 6H), 1.94 (m, 2H), 1.32 (d, 6H, *J* = 6.1 Hz). ^{13}C NMR ($CDCl_3$): δ 152.9, 149.5, 141.1, 138.6, 134.1, 131.6, 130.7, 129.8, 129.2, 123.2, 122.9, 117.0, 114.6, 114.3, 111.9, 72.2, 67.5, 49.8, 27.7, 25.9, 22.2, 21.1, 17.5.

Synthesis of Ru-carbene complex 5. ^{t}BuOK (29.5 mg, 0.26 mmol) was added to a solution of imidazolium salt **7** (0.12 g, 0.26 mmol) in dry toluene (10 mL) at 0 ^{o}C, and stirred for 1 h. To this solution, the Grubbs 1st generation $(PCy_3)_2Cl_2Ru$=CHPh (0.18 g, 0.22 mmol) was added at room temperature, and stirred for 3 h under N_2. The insoluble precipitate was filtered, and the solvent was evaporated. The residue was purified by short silica gel chromatography (EtOAc /hexane = 1/3) to afford **5** as a redish solid (0.075 g, 0.13 mmol, 60%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 19.24 (s, 1H), 7.41 (m, 2H), 7.16-6.99 (m, 6H), 6.81 (m, 4H), 6.47 (br s, 1H), 5.74 (dd, 1H, *J* = 1.3, 17.8 Hz), 5.27 (dd, 1H, *J* = 1.3, 11.1 Hz), 4.82 (t, 2H, *J* = 7.2 Hz), 4.38 (sept, 1H, *J* = 6.1 Hz), 4.07 (t, 2H, *J* = 5.7 Hz), 2.41-2.34 (m, 6H), 2.04 (m, 2H), 1.93 (m, 8H), 1.63 (m, 24H), 1.32 (d, 6H, *J* = 6.1 Hz), 1.25-1.21 (m, 6H). Note: Ru-carbene complex **5** was not enough stable to take ^{13}C NMR, see Figure S3.

Synthesis of polymeric Ru-carbene complex 4 via Ring-closing metathesis. A 10 mL oven-dried round-bottom flask equipped with a reflux condenser was charged with polymeric Ru-catalyst **5** (13.5 mg, 0.014 mmol). The flask was evacuated and filled with N_2. *N*,*N*-Diallyl-*p*-toluenesulfonamide (120.0 mg, 0.279 mmol) was then added in anhydrous CH_2Cl_2 (5.0 mL), the flask was then heated to gentle reflux for 6 h, and the solvent was evaporated. Ethyl acetate (5 mL) was added to the residue, and the precipitated polymeric Ru-complex **4** was recovered by filtration, and washed with ethyl acetate (5 mL x 2). After evaporation of the ethyl acetate, ^{1}H NMR analysis of the crude residue revealed complete conversion, and the product was isolated by flash chromatography (*n*-hexane/EA = 3/1) to afford pure product as a white crystalline (61 mg, 99%). A second run of the metathesis using the recovered polymeric Ru-complexes **4** was conducted in the same way as described for the first run. This reaction was repeated, each time using the catalyst recovered from a previous cycle. The results are listed in Table 1.

Figure S1. ^{1}H and ^{13}C NMR spectra of **S1**



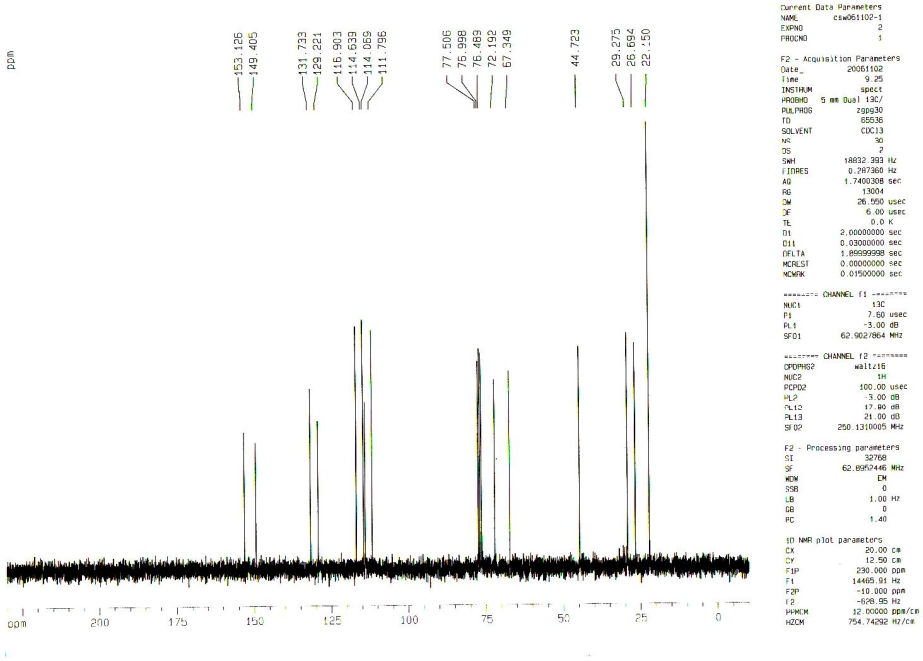


Figure S2. ^{1}H and ^{13}C NMR spectra of **7**

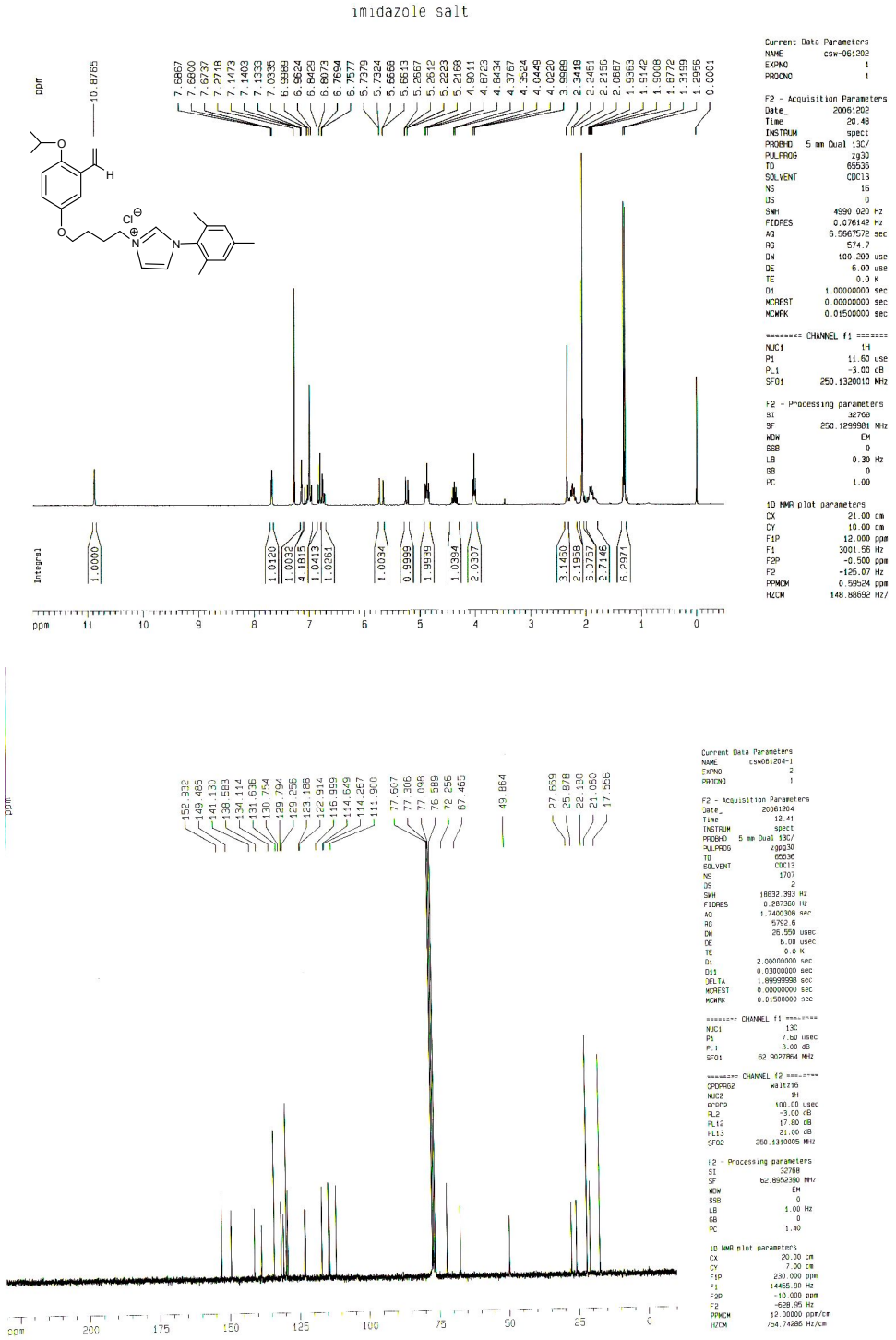


Figure S3. ^{1}H NMR ($CDCl_3$) spectra of Ru-complex **5**. top: right after separation, middle: after 5min, bottom: after 30 min.