Ruthenium porphyrin bound to a Merrifield resin as heterogeneous catalyst for the cyclooligomerization of arylethylenes.

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Supplementary Information
**Experimental**

**General Remarks:** $^1$H-NMR and $^{13}$C-NMR spectra were recorded as CDCl$_3$ solutions on a Bruker AM-300 and Bruker AM-700 instrument respectively using residual solvent signal as an internal standard. Chemical shifts are given as $\delta$ values. FAB mass spectra were measured on a VG-4 spectrometer using $m$-nitrobenzyl alcohol (NBA) as a matrix. GC mass spectra were recorded on a VG-4 spectrometer equipped with a 30 mt Supelco SPB-5 capillary column. UV/vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer in toluene solution. Silica gel 60 (70-230 and 230-400 mesh, Merck) was used for column chromatography. High-purity-grade nitrogen and argon gas were purchased from Rivoira. All other reagents and solvents were from Fluka Chem. Co., Aldrich Chem. Co. or Carlo Erba and were used as received, except where further specified.

**[5-(4-acetyloxymethylphenyl)-10,15,20-triphenylporphyrin]ruthenium(II) (2).** 500 mg (0.73 mmol) of 5-(4-acetyloxymethylphenyl)-10,15,20-triphenylporphyrin, $^1$ were dissolved in 200 ml of toluene under nitrogen and 640 mg (1 mmol) of Ru$_3$(CO)$_{12}$ were added. The mixture was refluxed for 48 hours under nitrogen and, after cooling, washed with water and evaporated to dryness under vacuum. The residue was purified on a silica gel column eluting the starting porphyrin with a petroleum ether/chloroform 1:1 mixture and then the desired metalloporphyrin with pure chloroform. The final compound was recrystallized from chloroform/methanol giving 445 mg of pure product in 75% of yield. $^1$H NMR(400 MHz, CDCl$_3$) $\delta$=8.69(s, 8H), 8.13(m, 8H), 7.74 (m, 11H), 5.42(s, 2H), 2.23(s, 3H); UV-vis (CHCl$_3$): $\lambda$max, nm 413, 529. FAB-MS: $m/z$ 813, [M-H$^+$]. Anal. calcd. for C$_{48}$H$_{32}$N$_4$O$_4$Ru: C, 70.83; H, 3.96; N, 6.88; Found: C, 70.32; H, 3.66; N, 6.62.

**[5-(4-hydroxymethylphenyl)-10,15,20-triphenylporphyrin]ruthenium(II) (3).** 400 mg (0.49 mmol) of [5-(4-acetyloxymethylphenyl)-10,15,20-triphenylporphyrin]ruthenium(II), $^2$ were dissolved under nitrogen in 50 ml of THF in a 100 ml flask. A solution of 100 mg (2.32 mmol) of
NaOH, dissolved in a minimum amount of CH₃OH, was added and the resulting mixture was stirred for two hours. Water, 200 ml, was added and the resulting solution was extracted with three 50 ml portions of CHCl₃. The organic solution was washed with water and dried on anhydrous Na₂SO₄. After evaporation of the solvent, the residue was chromatographed on a silica gel column, eluting with CHCl₃. The fraction containing the desired product was evaporated under vacuum and the residue recrystallized from CHCl₃/hexane, 1:3, affording quantitatively 378 mg of the product. ¹H NMR(400 MHz, CDCl₃) δ=8.41(s, 4H), 8.18(s, 2H), 8.14(s, 2H), 8.12(m, 7H), 7.95(m, 12H); UV-vis (CHCl₃): λmax, nm 412, 529. FAB-MS: m/z 772 [M]+. Anal.calcd. for C₄₆H₃₀N₄O₂Ru: C, 71.58; H, 3.91; N, 7.25; Found: C, 71.44; H, 4.02; N, 7.33.

**Ruthenium porphyrin-Merrifield resin adduct (4).** 100 mg(0.12 mmol) of [5-(4-hydroxymethylphenyl)-10,15,20-triphenylporphyrin]ruthenium(II), 3 were dissolved in 50 ml of anhydrous THF under nitrogen in a 100 ml flask. NaH, 46 mg(0.57 mmol), 80% oil slurry, were added and the mixture was refluxed for 1 hour. The solution was cooled to room temperature and 200 mg of, 5% chlorine content, Merrifield resin were added. The mixture was again refluxed for 12 hours, after that the solution was cooled and water, 1 mL, was carefully added. The resulting red solid was filtered and the filtrate washed with water and then with chloroform until the solvent was uncoloured. The red solid was dried under vacuum at 60° C for 3 hours. IR(nujol), cm⁻¹ 1940 (CO stretching)²; Anal. Found: C, 90.55; H, 7.53; N, 0.4, Calcd. for C₈₁H₈₁N₀.₀₄ Cl₀.₀₅: C, 90.26; H, 7.57; N, 0.52

References: