

Supporting Information For:

Molecules of ruthenium-based olefin metathesis catalysts as two- and three-photon absorbers

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General information

Apparatus and analytical methods

Thin layer chromatography: Reaction was monitored by TLC on silica gel 60 F₂₅₄ (Fluka).

Column chromatography: Merck silica gel 60 (230–400 mesh).

NMR: Spectra were recorded on a Varian Unity Plus 500 MHz spectrometer and a Bruker Avance 300 MHz in CD₂Cl₂; chemical shifts (δ) are given in parts per milion (ppm) downfield from trimethylsilane as referenced to residual protio solvent peaks, coupling constants (J) are given in Hz.

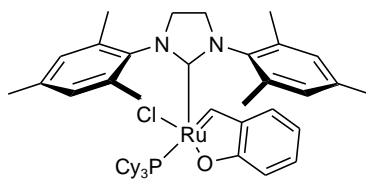
Chemicals

Complex **5** and Grubbs 2nd generation catalyst were purchased from Sigma Aldrich. Complex **4** was purchased from Strem Chemicals. All other chemicals and solvents used are commercially available and were used as received.

Synthesis of complex **6**

Grubbs 2nd generation complex (200 mg, 0.24 mmol) was dissolved in dry methylene chloride (6ml). Next (*E,Z*)-2-propenylphenol (63 mg, 0.47 mmol) and tricyclohexylphosphine (132 mg, 0.47 mmol) were added. Reaction mixture was stirred at 40°C for 5 hours. After reaction was finished (determined by TLC) solvent was removed on rotary evaporator. Crude product was purified by column chromatography on silica gel (eluent: cyclohexane to

cyclohexane/ethyl acetate 9:1). Removal of solvents afforded complex **6** as a green solid (140 mg, 72% yield).



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¹H NMR (500 MHz, CD₂Cl₂) δ ppm: 15.85 (s, 1H), 7.07 (s, 1H), 7.00-6.96 (m, 3H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.24 (s, 1H), 6.20 (t, *J* = 7.2 Hz, 1H), 4.01 – 3.96 (m, 1H), 3.83-3.70 (m, 2H), 3.64-3.59 (m, 1H), 2.63 (s, 3H), 2.54 (s, 3H), 2.50 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H), 1.66 – 1.50 (m, 13H), 1.29 (s, 3H), 1.11-0.70 (m, 20H). **¹³C NMR: (125 MHz, CD₂Cl₂) δ ppm:** 281.36, 222.21, 221.66, 180.31, 148.30, 139.54, 139.17, 138.78, 137.63, 137.32, 136.98, 134.69, 130.23, 130.05, 129.70, 129.00, 122.38, 116.17, 111.26, 32.52, 32.39, 29.45, 28.92, 28.23, 28.15, 28.12, 28.04, 27.34, 27.03, 21.33, 21.14, 19.40, 18.92, 18.66, 16.76. **³¹P NMR (124,5 MHz, CDCl₃) δ ppm:** 29.11.

Experimental method for measurements of NLO properties

Stock solutions of complexes **4**, **5** and **6** (2.1% w/w) in dichloromethane were placed in 1 mm path length Starina glass cuvettes for NLO measurements. The nonlinear absorption and refraction was measured using a laser system consisting of a Quantronix Integra-C regenerative amplifier operating as an 800 nm pump and a Quantronix-Palitra-FS BIBO crystal-based optical parametric amplifier. This system delivers wavelength tunable pulses of ~130 fs length. The repetition rate of the laser pulses was 1 kHz. The NLO properties of the samples were measured by the open-aperture (OA) and closed-aperture (CA) Z-scan technique, i.e. by moving the samples along the axis of a focused incident beam (*z* direction) and recording either the total transmittance of the sample (OA scan) or transmittance of an aperture placed in the far field after the sample (CA scan). The scans were analyzed as described in Ref.1. Results obtained for solutions of **4**, **5** and **6** were calibrated against Z-scan measurements on a fused silica plate (4.66 mm thick) and compared with the measurements on an identical glass cell filled with the solvent alone (for more details see Ref. 1). UV-Vis absorption spectra of **4**, **5** and **6** in dichloromethane for diluted stock solutions were acquired using a Jasco V-670 spectrophotometer using 1 cm quartz cuvettes.

¹ (a) M. Samoc, A. Samoc, G. T. Dalton, M. P. Cifuentes, M. G. Humphrey, P. A. Fleitz, Two-photon absorption spectra and dispersion of the complex cubic hyperpolarizability γ in organic and organometallic chromophores, in *Multiphoton Processes in Organics and Their Application*, I. Rau and F. Kajzar, eds, Old City Publishing, Philadelphia, (2011), Chapter 7, pp. 341-355; (b) M. Nyk, D. Wawrzynczyk, K. Parjaszewski, M. Samoc, *J. Phys. Chem. C*, **2011**, 115 (34), 16849.