

Supporting Information

Control of Ring Size Selectivity by Substrate directable Ring Closing Metathesis

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Experimental section

General

Experiments were conducted in dry reaction vessels under an atmosphere of dry argon. Solvents were purified by standard procedures. ¹H-NMR-spectra were recorded on a Bruker Avance DRX 400 or Bruker Avance DRX 500 in CDCl₃. Chemical shifts (δ) are reported in ppm relative to TMS with CHCl₃ (δ_H = 7.24 ppm, δ_C = 77.0 ppm) as internal standard. Coupling constants (*J*) are given in Hertz. In ¹³C-NMR-spectra the number of coupled protons was analyzed by APT or DEPT-experiments and is denoted by a number in parentheses following the δ_C value. IR spectra were recorded as films on NaCl or KBr plates. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV. Ruthenium catalysts **A** and **B** were used as purchased from Sigma-Aldrich company.

General experimental procedure for the screening of OH-protecting groups

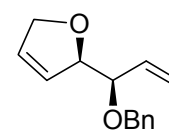
In a standardized, sealable 3 mL tube, the corresponding triene **2aa-2gb** (0.1 mmol) was dissolved in dichloromethane (2 mL) and the ruthenium catalyst was added (4.1 mg for **A**, 4.2 mg for **B**, 5 mol% each). The reaction was stirred for 20 hours at 20° C, the solvent was evaporated in vacuo and the crude reaction mixture was analyzed by ¹H-NMR spectroscopy. Dihydrofurans and dihydropyrans may be distinguished by their signals for the internal C-C-double bond. In the case of dihydrofurans, a vicinal coupling constant of approximately 6 Hertz is observed, while for dihydropyrans a value of approximately 10 Hertz is observed. In ¹³C-NMR spectra, dihydrofurans **4** and dihydropyrans **3** differ significantly in their chemical shift values for the carbon atom -CH₂O-: for dihydrofurans **4**, typically a value of approximately 75 ppm is observed, whereas for dihydropyrans **3** the chemical shift value is ca. 66 ppm.

These values are similar to those observed for structurally related compounds, which have been previously described by our group.^[1]

[1] B. Schmidt, H. Wildemann, *Eur. J. Org. Chem.* **2000**, 3145-3163.

Representative examples on preparative scale:

(R)-2-((R)-1-(benzyloxy)allyl)-2,5-dihydrofuran (4a). **2aa** (121 mg, 0.50 mmol) was dissolved in dichloromethane (10 mL). Catalyst **A** (20.5 mg, 5 mol%) was added and the reaction mixture was stirred overnight. The solvent was evaporated in vacuo, and the dark brown residue purified by column chromatography, to give 95 mg (0.44 mmol, 88%) of **4a** as a light brown oil.



HRMS (FAB) calcd. for C₁₄H₁₇O₂ (M+H⁺): 217.1229 found: 217.1235. [α]_D²⁰ = +29.2 (c 1.12, CH₂Cl₂). **MS (FAB)**: 217.0 ([M+H]⁺, 8%); 215.0 ([M-H]⁺, 5%); 91.6 (100%). **¹H-NMR (CDCl₃, 500 MHz)**: 7.38-7.26 (5 H), 5.97 (1 H, d, *J* = 6.2 Hz), 5.84-5.75 (2 H), 5.36-5.30 (2 H), 4.93 (1 H, m), 4.67 (1 H, d, *J* = 12.2 Hz), 4.65-4.61 (2 H), 4.47 (1 H, d, *J* = 12.2 Hz), 3.85 (1 H, dd, *J* = 6.7, 6.1 Hz). **¹³C-NMR (CDCl₃, 125 MHz)**: 138.5 (0), 135.0 (1), 128.2 (1), 128.1 (1), 127.5 (1), 127.3 (1), 126.5 (1), 119.2 (2), 88.0 (1), 82.3 (1), 75.6 (2), 70.4 (2). **IR (neat)**: ν = 3064 (w), 3030 (w), 2863 (m), 1774 (m), 1454 (m), 1071 (s), 932 (m), 808 (w).

Fig. 1: $^1\text{H-NMR}$ spectrum of **4a** (400 MHz, CDCl_3)

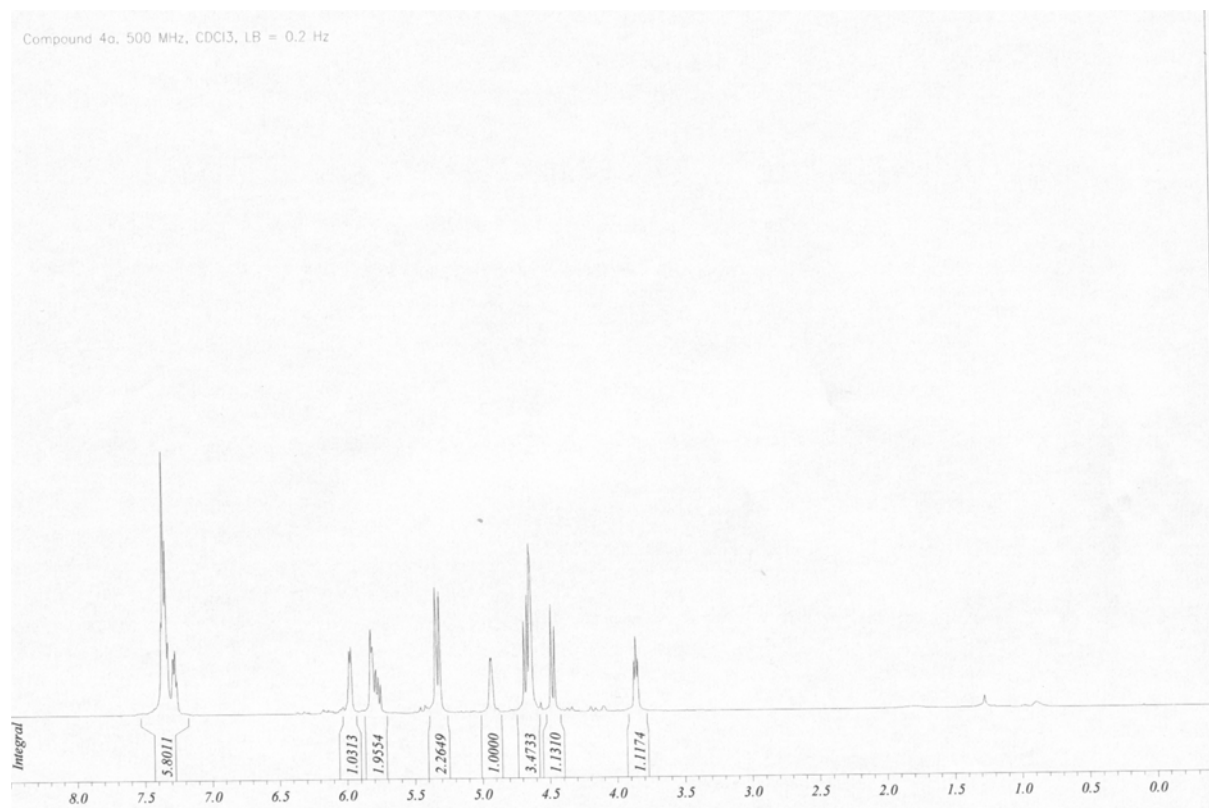


Fig. 2: $^1\text{H-NMR}$ spectrum of **4a** (400 MHz, CDCl_3); expansion of the olefinic region

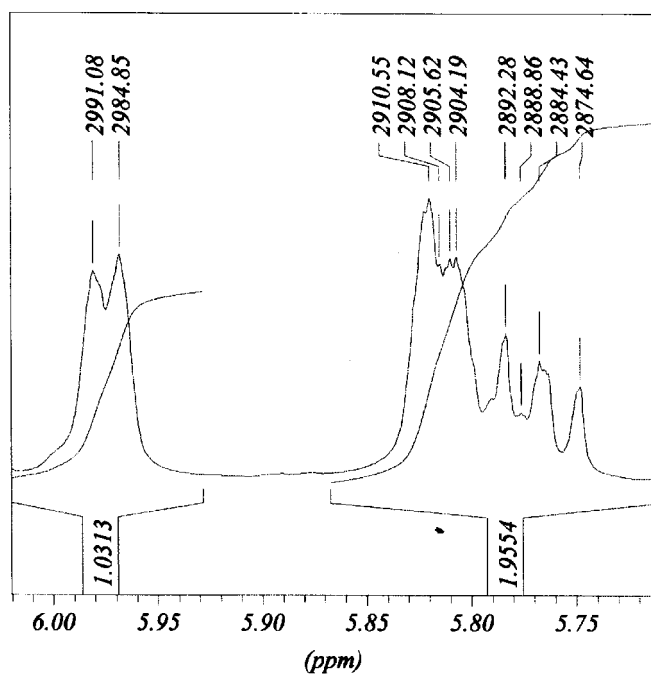
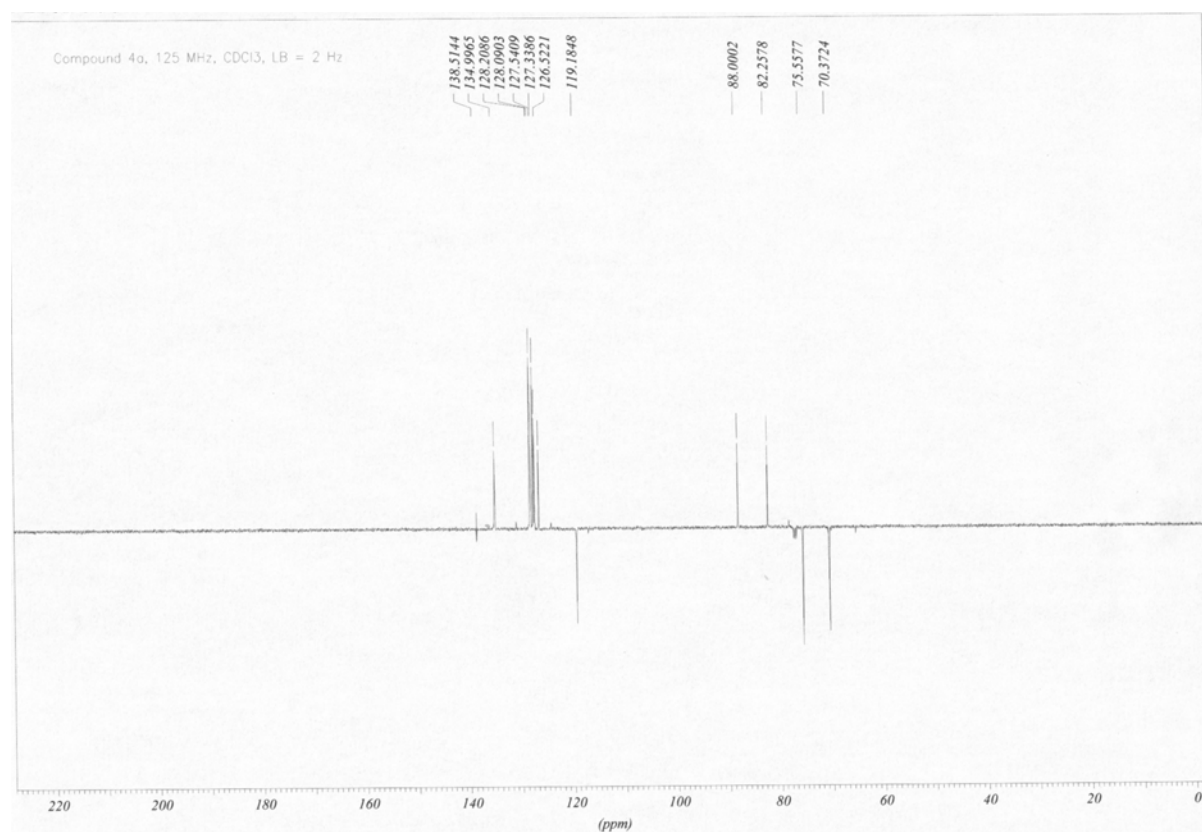
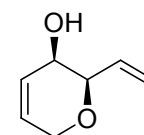


Fig. 3: ^{13}C -NMR spectrum of **4a** (100 MHz, CDCl_3)



(*2R,3R*)-3,6-dihydro-2-vinyl-2*H*-pyran-3-ol (**3g**). **2gb** (1.79 g, 10.6 mmol) was dissolved in dichloromethane (200 mL). Catalyst **A** (437 mg, 5 mol%) was added and the reaction mixture was stirred overnight. The solvent was evaporated in vacuo, and the dark brown residue purified by column chromatography, followed by Kugelrohr distillation (oven temp. 50° C at 0.23 mbar), to give 697 mg (5.5 mmol, 52%) of **3g** as a colourless oil.



Elemental Analysis calcd. for $\text{C}_7\text{H}_{10}\text{O}_2$: C 66.7%, H 8.0%, found: C 66.2%, H 8.1%. **MS (FAB)**: 127.1 ($[\text{M}+\text{H}]^+$, 20%); 109.3 ($[\text{M}-\text{OH}]^+$, 50%). $[\alpha]_{\text{D}}^{20} = -200.1$ (c 0.93, CH_2Cl_2). **^1H -NMR (CDCl_3 , 400 MHz)**: 6.05 (1 H, dddd, $J = 10.2, 5.4, 2.4, 2.2$ Hz), 5.97 (ddd, 1 H, $J = 17.4, 10.8, 5.4$ Hz), 5.94 (1 H, ddd, $J = 10.2, 3.5, 1.5$ Hz), 5.39 (1 H, ddd, $J = 17.4, 1.6, 1.6$ Hz), 5.30 (1 H, ddd, $J = 10.8, 1.5, 1.5$ Hz), 4.28 (1 H, ddd, $J = 17.1, 3.4, 1.8$ Hz), 4.19 (1 H, ddd, $J = 16.9, 3.8, 1.6$ Hz), 4.02 (1 H, m), 3.84 (1 H, s(br)). **^{13}C -NMR (CDCl_3 , 100 MHz)**: 135.0 (1), 130.2 (1), 126.6 (1), 117.2 (2), 78.4 (1), 66.0 (2), 64.5 (1). **IR (neat)**: $\nu = 3435$ (m(br)), 2926 (s), 2853 (m), 2245 (w), 1648 (w), 1446 (m), 1091 (s), 929 (m), 734 (s).

Fig. 4: $^1\text{H-NMR}$ spectrum of **3g** (500 MHz, CDCl_3)

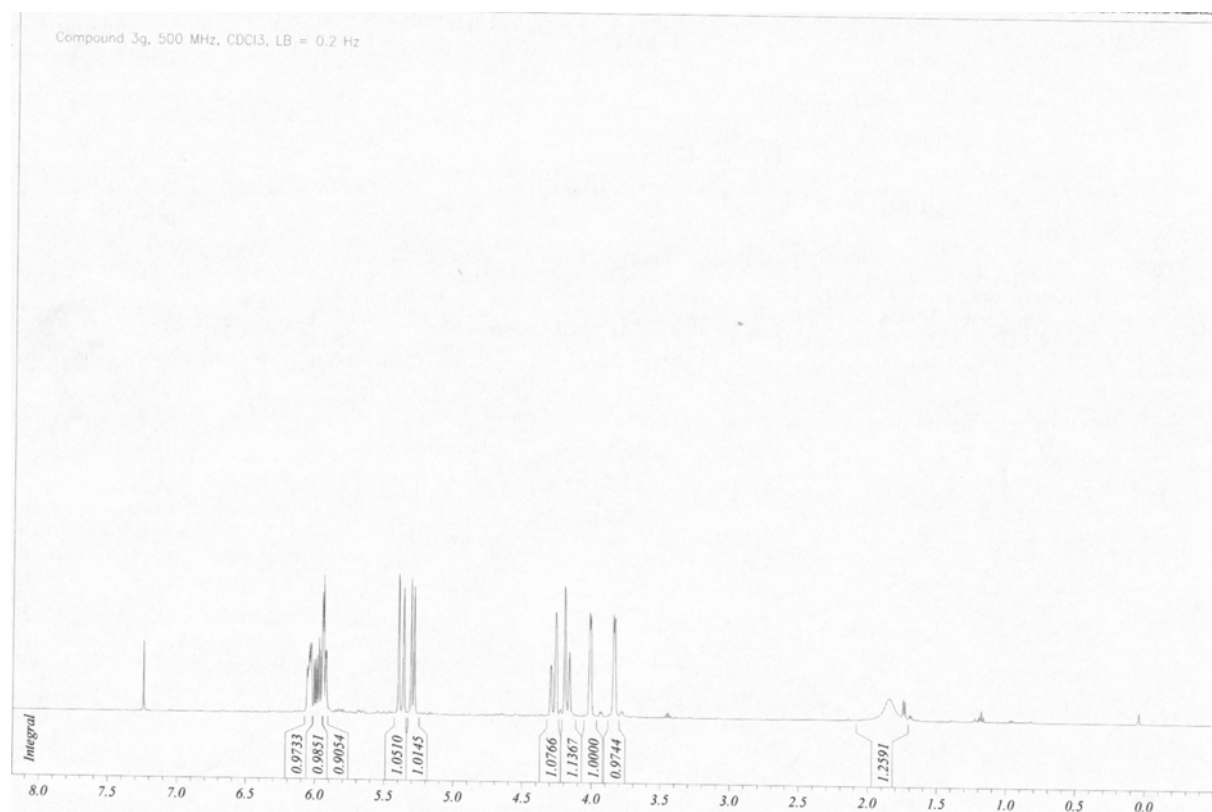


Fig. 5: $^1\text{H-NMR}$ spectrum of **3g** (500 MHz, CDCl_3); expansion of the olefinic region

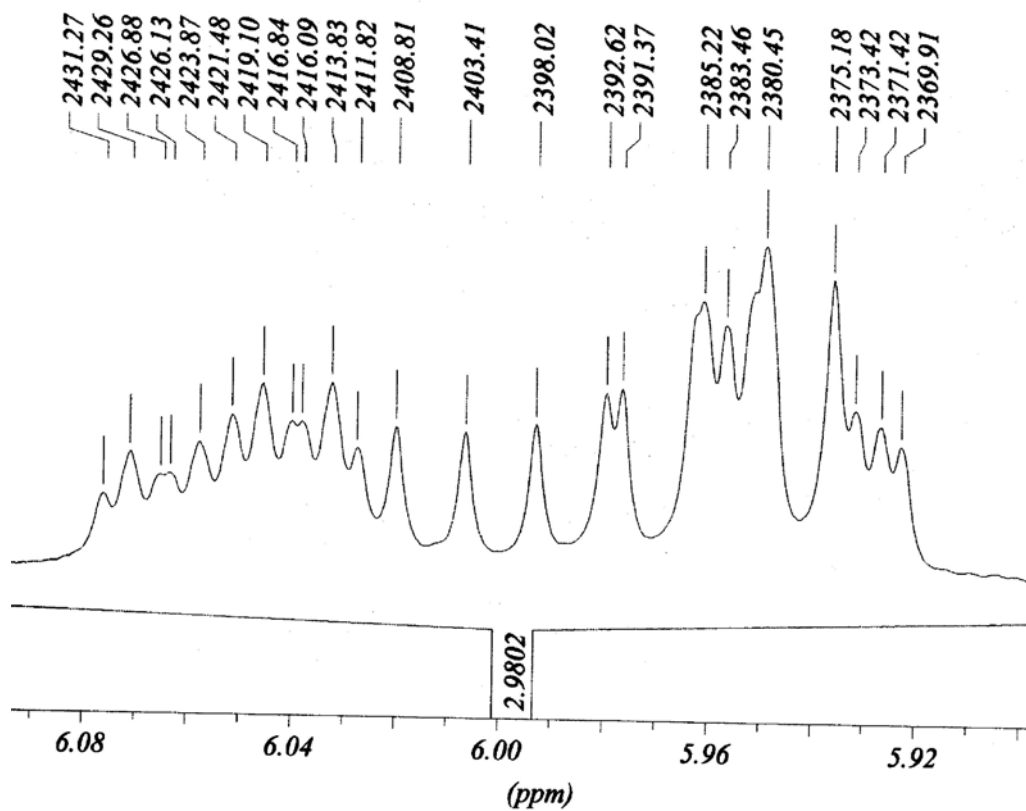


Fig. 6: ^{13}C -NMR spectrum (APT) of **3g** (125 MHz, CDCl_3)

