A New Concept for the Non Covalent Binding of a Ruthenium-based Olefin Metathesis Catalyst to Polymeric Phases: Preparation of a Catalyst on Rashig Rings

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1. General techniques

General techniques. All temperatures quoted are uncorrected. ^{1}H NMR, ^{13}C NMR, ^{1}H,^{1}H-, ^{1}H,^{13}C-COSY and HMQC spectra were recorded on Bruker DPX 200, Bruker ARX 400-NMR, Bruker AVANCE 500, Varian Gemini 200 and Varian Gemini 400 spectrometers. Chemical shift values of ^{1}H spectra are reported as values in ppm relative to residual $CHCl_3$ (δ 7.26) while chemical shift values of ^{13}C NMR spectra are reported relative to $CDCl_3$ (77.16 ppm) as internal standard if not otherwise noted. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (*J*) are quoted in Hz. Mass spectra were obtained using either LCQ Finnigan or Mariner Perseptive Biosystems, Inc. instruments, using electrospray ionisation (ESI) mode, or AMD 604 Intectra GmbH instrument, using electron impact ionisation (EI). Ion mass (m/z) signals are reported as values in atomic mass units followed, in parentheses, by the peak intensities relative to the base peak (100%). Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) were conducted using HP 6890 with HP 5 column and HP 5890 with the same column. Microanalyses were provided by Institute of Organic Chemistry, PAS, Warsaw. The Ru determination was carried out with an inductively coupled plasma mass spectrometer (ICP-MS) Thermo X7 ICP-MS (Thermo Electron GmbH, Dreieich, Germany, www.thermo.com). Reactions were monitored by TLC on silica gel 60 F_{254} (E. Merck, Darmstadt) and spots were detected either by UV-absorption or by charring with H_2SO_4/4-methoxybenzaldehyde in methanol. Flash column chromatography was performed on silica gel 60 (E. Merck, Darmstadt; 35-70 mesh). The porous glass material was obtained from ROBU Glasfilter-Geräte GmbH, Hattert, Germany (rod shaped carriers, 5 mm diameter and 11 cm length) and from Schott/QVF-engineering (Siran-glass Raschig rings). SEM-pictures were obtained with a JEOL JSM-6700F. Microwave experiments were performed in a CEM Discover LabMate^{TM} in a sealed microwave tube with an external temperature measurement (IR-sensor) at a fixed temperature. For high-throughput experiments described in Table 1 the Radleys 12 Place Heated Carousel Reaction Station (www.radleys.com) was used. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$), MeOH (Mg). All commercially available reagents were used as received. The reported compounds: diethyl 3-methylcyclopent-3-en-1,1-dicarboxylate (**12**), 2,5-dihydro-1-tosyl-1*H*-pyrole (**13**), 1,1-diphenyl-1-sila-3-cyclopentene (**22**), diethyl cyclopent-3-en-1,1-dicarboxylate (**23**), 3-

cyclopentenyl phenyl sulfone (**24**), 2,2-diphenyl-3-vinyl-2,5-dihydrofuran (**25**), dimethyl icos-10-endioate (**26**), hexose **27** and compound **28** have been previously described and were identified by comparison of their physical and spectroscopic data (^{1}H and ^{13}C NMR, MS) with those in the cited references; their purities were confirmed by TLC or GC analyses.

2. Preparation of polymeric phases

Preparation of polyvinyl benzene and its sulfonation: formation of a glass/polymer composite material C and powder A

A solution of styrene (125.19 g, 1.20 mol), divinylbenzene (16.32 g, 0.13 mol) and AIBN (1.08 g, 6.6 mmol) in a mixture of *n*-alkanes C14-C17 (1 L) was prepared. The solution was used to cover carrier materials: glass Raschig-rings or rod shaped glass carriers, placed in a round-bottom 2 L flask. This amount of monomers is sufficient for preparation of ca. 300 mL of the composite material The mass of carrier materials can differ (because of different density), but it is important that the carriers are completely submersed in the solution of monomers. A vacuum was applied for about one minute and then released to room pressure to let the monomers solution penetrate into the whole pore volume. Then the content of flask was heated at 70 °C for 12 h. During the time of polymerization the precipitation of small interconnected polymer particles occurred. The resulted glass/polymer composite material was then carefully rinsed with chloroform. The sulfonation was carried out by adding composite rings or rods to a solution of chlorosulfonic acid (40 mL) in chloroform (400 mL). After 24 h the composite material **C** was filtered-off, thoroughly rinsed with chloroform and dried under vacuum. The average capacity of the rings made by this method is 1.2 mmol/g (one ring weights 0.3-0.4 g). When rod shaped carriers (from ROBU) were used, the single rod has a capacity of about 1 mmol. The same procedure of polymerisation-precipitation and sulfonation with chlorosulfonic acid was used for preparing polymer powder **A** (3.25 mmol/g).

3. Preparation and application of catalyst 7 and supported catalysts 7A–C

4-(Diethylamino)-2-isopropoxybenzaldehyde (8)[1]

K_2CO_3 (1.24 g, 9.0 mmol) and Cs_2CO_3 (410.5 mg, 1.26 mmol) were placed in a round bottom flask. A solution of 4-(diethylamino)-2-hydroxybenzaldehyde (1.16 g, 6.0 mmol) in dry DMF (15 mL) was added. After stirring for 10 minutes at room temperature 2-iodopropane (0.9 mL, 9.0 mmol) was added. The reaction was carried out for the next 24 hours at room temperature. After pouring onto a saturated aqueous solution of K_2CO_3 the reaction mixture was extracted with MTBE. The combined organic layers were washed with 1M solution of NaOH and then with brine, dried ($MgSO_4$) and the solvent was removed under reduced pressure. Crude 4-(diethylamino)-2-isopropoxybenzaldehyde **8** was obtained as a dark red oil (1.28 g, 5.4 mmol; 91%). IR (KBr) ν/cm^{-1} ; 2976, 2930, 2867, 2836, 2758, 1658, 1587, 1547, 1521, 1471, 1146, 1406, 1391, 1356, 1299, 1129, 1238, 1210, 1106, 1076, 1015, 979, 930; ^{1}H-NMR (200 MHz, C_6D_6, C_6H_6 =7.16 ppm): δ = 10.72 (s, 1H), 8.10 (d, J = 9.2 Hz, 1H), 6.03 (dd, J = 9.2, 2.1 Hz, 1H), 5.93 (d, J = 2.1 Hz, 1H), 4.30 (septet, J = 6.0 Hz, 1H), 2.87 (q, J = 7.1 Hz, 4H), 1.09 (d, J = 6.0 Hz, 6H), 0.82 (t, J = 7.1 Hz, 6H); ^{13}C-NMR (50 MHz, C_6D_6, C_6H_6 = 128.1 ppm): δ = 186.4, 163.0, 153.6, 130.5, 116.6, 105.1, 95.7, 70.7, 44.6, 22.0, 12.6; MS (EI): m/z (%); 235 (32) [$M^{+\cdot}$], 220 (31), 192 (7),178 (100), 162 (9), 150 (14), 148 (8), 136 (2), 122 (4), 106 (2), 94 (4), 77 (5), 65 (9), 41 (9), HRMS (EI) calcd. for $C_{14}H_{21}O_2N$: 235.1572 [$M^{+\cdot}$]; found: 235.1580

N,*N*-diethyl-*N*-{3-*iso*propoxy-4-[(*E*,*Z*)-1-propenyl]-phenyl}amine (9)[1]

To a solution of dry THF (450 mL) and ethyltriphenylphosphonium bromide (22.08 g, 59.5 mmol) was added dropwise *n*-BuLi (2.5 M in hexane 25.6 mL, 63.7 mmol) at –78 °C under argon. After 15 minutes at –78 °C the solution was allowed to warm to RT and then heated at 30 °C for three hours. After this period the solution was cooled again to –78 °C and a solution of 4-(diethylamino)-2-isopropoxybenzaldehyde **8** (10.00 g, 42.5 mmol) in THF (25 mL) was added. After 30 minutes the reaction mixture was warmed to room temperature and was stirred overnight at this temperature. After pouring onto a saturated aqueous solution of $NaHCO_3$ the reaction mixture was extracted with MTBE. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography with *c*-hexane/ethyl acetate/triethyl amine

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[1] A. Michrowska, *PhD Thesis*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, 2006.

(19:1:0.2 v/v/v) as eluent to afford **9** as a yellow oil (10.30 g, 41.6 mmol, 98%; *E/Z* = 2:1). IR (film) ν /cm^{-1}; 3025, 2973, 2931, 1611, 1555, 1511, 1467, 1449, 1396, 1374, 1356, 1275, 1222, 1115, 1020, 969; isomer (*E*): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.24 (d, *J* = 8.7 Hz, 1H), 6.59 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.30-6.25 (m, 1H), 6.23 (d, *J* = 2.5 Hz, 1H), 6.00 (dq, *J* = 15.9, 6.6 Hz, 1H), 4.45 (septet, *J* = 6.2 Hz, 1H), 3.32 (q, *J* = 7.1 Hz, 4H), 1.85 (dd, *J* = 6.6, 1.7, 3H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.15 (t, *J* = 7.1 Hz, 6H); isomer (*Z*): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.5 Hz, 1 H), 6.48 (dq, *J* = 11.5, 1.7 Hz, 1H), 6.30-6.25 (m, 1H), 6.19 (d, *J* = 2.5 Hz, 1H), 5.60 (dq, *J* = 11.5, 7.1 Hz, 1H), 4.45 (septet, *J* = 6.2 Hz, 1H), 3.33 (q, *J* = 7.1 Hz, 4H), 1.85 (dd, *J* = 7.1, 1.7, 3H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.17 (t, *J* = 7.1 Hz, 6H); isomer (*E*): ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 155.8, 147.9, 130.7, 127.1, 125.8, 121.1, 116.7, 105.5, 99.4, 71.0, 44.5, 22.3, 14.8, 12.7; isomer (*Z*): ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 156.8, 147.9, 130.7, 127.1, 125.3, 122.9, 115.9, 104.3, 99.5, 71.1, 44.5, 22.3, 18.8, 12.7; MS (EI): m/z (%); 247 (48) [$M^{+\cdot}$], 232 (31), 218 (15), 205 (23), 190 (100), 178(3), 174 (5), 162 (10), 146 (3), 133 (5), 115 (3), 105 (3), 91 (4), 77 (5), 57 (5), 41 (4); HRMS (ESI) calcd. for $C_{16}H_{26}NO$ [$M+H^+$]: 248.1936, found: 248.1939; HRMS (EI) calcd. for $C_{16}H_{25}NO$: 247.1936 [$M^{+\cdot}$]; found: 247.1939; Anal. Calcd. for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. found: C, 77.58; H, 10.29; N, 5.73.

Ruthenium catalyst 7[1]

Carbene complex **2** (84.9 mg, 0.10 mmol), CuCl (14.9 mg, 0.15 mmol) and CH_2Cl_2 (14 mL) were placed in a Schlenk flask equipped with a condenser. A solution of alkene **9** (27.2 mg, 0.11 mmol) in CH_2Cl_2 (6 mL) was added and the resulting solution was stirred under argon at 40 °C for 1 h. The reaction mixture was concentrated in vacuo and the resulting material was purified by column chromatography on silica. Elution with *c*-hexane/EtOAc/Et_3N (4:1:0.1 v/v/v) removed **7** as a brown band. Removal of the solvent, washing of the minimal amount of cold *n*-pentane and drying under vacuum afforded **7** as a dark brown microcrystalline solid (53.2 mg, 0.07 mmol; 76%).

IR (KBr) ν/cm^{-1} ; 3437, 2972, 2919, 1600, 1544, 1512, 1480, 1446, 1398, 1355, 1305, 1266, 1253, 1205, 1145, 1120, 1075, 976; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 15.65 (s, 1H, 1-H), 7.04 (s, 4H, 16-H), 6.68 (d, *J* = 8.8 Hz, 1H, 3-H), 6.12 (dd, *J* = 8.8, 2.2 Hz, 1H, 4-H), 6.00 (d, *J* = 1.6 Hz, 1H, 6-H), 4.86 (septet, *J* = 6.1 Hz, 1H, 8-H), 4.15 (s, 4H, 11-H), 3.31 (q, *J* = 7.1 Hz, 4H, 18-H), 2.49 (s, 12H, 12-H), 2.38 (s, 6H, 13-H), 1.42 (d, *J* = 6.1 Hz, 6H, 9-H), 1.14 (t, *J* = 7.1 Hz, 6H, 19-H);[2] ^{13}C-NMR (125 MHz, $CDCl_3$): δ =

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[2] Assignments of the NMR signals are based on 2D ^{1}H,^{1}H and ^{1}H,^{13}C-chemical shift correlated spectra and refer to the arbitrary numbering shown on Figure 1.

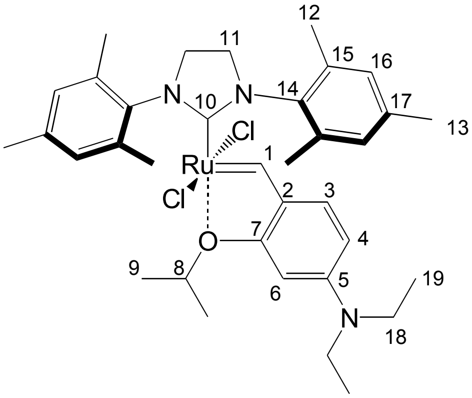

Figure 1. Arbitrary numbering used

298.0 (C-1), 216.2 (C-10), 155.8 (C-5), 150.8 (C-7), 138.8 (C-17), 138.3 (C-15), 130.5 (C-16), 129.7 (C-14), 125.6 (C-3), 115.0 (C-2), 104.3 (C-4), 96.3 (C-6), 74.4 (C-8), 55.0 (C-11), 45.5 (C-18), 25.8 (C-9), 21.5 (C-12 and C-13), 20.0 (C-11), 12.8 (C-19);[2] MS (EI): (m/z) (%) 697 (12), 582 (5), 556 (5), 554 (9), 523 (12), 439 (19), 438 (57), 353 (13), 352 (31), 307 (10), 305 (31), 304 (100), 303 (78), 301 (6), 290 (5), 289 (15), 274 (6), 233 (15), 221 (31), 220 (23), 218 (25), 207 (17), 206 (42), 192 (24), 190 (12), 179 (15), 178 (26), 176 (30), 164 (70), 162 (15), 159 (12), 158 (14), 150 (18), 148 (18), 146 (10), 136 (12), 134 (8), 91 (5), 77 (4), 43 (21), 41 (10); HRMS (EI) calcd. for $C_{35}H_{47}N_3O^{35}Cl_2{}^{102}Ru$: 697.2140 [$M^{+\cdot}$]; found: 697.2160.

General procedure for the activation of 7 by in situ salt formation and comparative olefin metathesis experiments with model dienes 10 and 11 (refer to Scheme 2).

To a solution of catalyst 7 (10.5 mg, 0.01 mmol) in CH_2Cl_2 (10 mL) in a Schlenk tube the acid (0.01 mmol) was added under argon at 21 °C. After 15 minutes a solution of diene 10 or 11 (0.30 mmol) and *n*-nonane (used as an internal standard, 34.0 mg, 0.26 mmol) was added in CH_2Cl_2 (5 mL) and the reaction mixture was stirred for 1-16 h at rt. Aliquots (0.25 mL) were taken after: 20 min., 40 min., 1 h, 1.5 h, 2 h, 4 h, 6 h and 16 h, quenched with ethyl-vinyl ether (0.25 mL, 2M in CH_2Cl_2) and analysed by GC.

Preparation of catalysts 7A-7B via direct immobilisation of 7 on sulfonated polymers A-B.

Polymer **A** (obtained by precipitation polymerisation, 3.25 mmol SO_3H/g) or **B** (Dowex® 50Wx2, 5.0 mmol SO_3H/g) was washed with 1*N* HCl and distilled water until pH of the eluent was adjusted to 7. In order to remove traces of water the polymers were washed with methanol and dried in vacuum for two days. The dry polymer (0.12 mmol) was shaken for three hours with a solution of catalyst **7** (18.3 mg, 0.026 mmol) in dichloromethane (10 mL) under argon. The polymer was filtered-off and washed with dichloromethane (5 × 2 mL). The organic layer was concentrated under reduced pressure which allowed to reisolate unreacted catalyst **7** (1.8 mg, 0.003 mmol for polymer **A** and 9.2 mg, 0.013 mmol for Dowex® 50Wx2 **B**). The resulting polymer was dried under vacuum to yield the functionalised polymers **7A** and **7B**. The loading of catalyst was determined by ICP-MS to be 0.20 mmol Ru/g of polymer (20%

of free SO_3H sites were loaded) for **7A** and 0.12 mmol Ru/g of polymer (3% of free SO_3H sites were loaded) for **7B**.

Preparation of of catalysts 7A and 7C *via* reaction of resin 14 with ruthenium complex 2

The 3-4 glass-polymer composite Raschig rings **C** (0.12 mmol) obtained by precipitation polymerisation (0.12 mmol SO_3H/g, one ring weight is 0.3-0.4 g) were added to a solution of aniline **9** (30.0 mg, 0.12 mmol) in dry dichloromethane (10 mL) and the resulted mixture was shaken under argon for one hour. After this time the polymer-composite rings were removed and washed with five portions of dichloromethane (5 mL). The resulting material was dried under reduced pressure to yield polymer **14** (0.12 mmol). To this material in CH_2Cl_2 (10 mL) Grubbs II catalyst **2** (93.0 mg, 0.11 mmol) and CuCl (16.0 mg, 0.16 mmol) were added under argon. The resulting mixture was shaken for three hours at room-temperature. The solution was filtered-off and the resulting rings were washed with five portions of CH_2Cl_2 (5 mL) and dried under vacuum to yield functionalised polymer-composite rings **7C**. The loading of catalyst was determined by ICP-MS to be 3 μmol Ru/ring. The same procedure was used for the preparation of polymer powder **7A** (loading 0.4 mmol/g).

General procedure for metathesis reactions with polymer 7A–7C

Catalyst **7A–7C** (1-10 mol%; on Raschig ring or as powder) is placed under argon in a reaction tube[3] and a solution of the substrate (0.06 mmol) was added in dry CH_2Cl_2 (20 mL/mmol). The reaction mixture was shaken for 2-24 h at 22-45 °C. At the end of the reaction (TLC or GC-monitoring) the Raschig ring was removed with a pair of tweezers or the powder was filtered and rinsed with several portions of CH_2Cl_2. The combined organic phases were concentrated under reduced pressure to yield crude products containing 21-102 ppm of residual ruthenium. Flash column chromatography (mixture of petroleum ether/ethyl acetate as eluent) was used to obtain analytically pure samples of selected products.

Studies on the stability of polymer-bound catalysts 7A–7B

Repeated reactions were carried out according to the general procedure given above using *N*-tosylated amine **11** (0.23 mmol) as a substrate. After each reaction the polymer was filtered, washed with five portions of CH_2Cl_2 (2 mL), dried under vacuum and reused for the next run. The crude products were

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[3] For high-throughput experiments with Raschig rings described in Table 1 the Radleys 12 Place Heated Carousel Reaction Station (www.radleys.com) was used.

isolated quantitatively; the amount of RCM product **13** was determined by GC.
For polymer **7A**: 1st run >99% (3 h); 2nd run 88% (4 h); 3rd run 56% (4 h); 4th run 68% (12 h); 5th run 38% (6 h); 6th run 10% (6 h). For polymer **7B**: 1st run 98% (3 h); 2nd run 33% (4 h).

Preparation of PASS*flow* column under continuous flow conditions

The PASS*flow* column of the capacity of 1 mmol was washed in a circular mode with 1*N* HCl (60 mL), distilled water (to pH 7), methanol (50 mL) and dichloromethane (100 mL). Catalyst **7** (34.4 mg, 0.05 mmol) and aniline **9** (233.0 mg, 0.95 mmol) were dissolved in CH_2Cl_2 (6 mL) and pumped through the PASS*flow* column under inert gas atmosphere for 1h in a circular mode. The column was then washed with CH_2Cl_2 until no catalyst could be detected in the solvent leaving the column.

General procedure for metathesis reactions under PASS*flow* continuous flow conditions

N-allyl-*N*-tosylprop-2-en-1-amine **11** (258.0 mg, 1.03 mmol) was dissolved in CH_2Cl_2 (4 mL) and was circulated through the PASS*flow* column (loaded with ca. 5 mol% of catalyst **7C**) under inert gas atmosphere at 40 °C for 5 h. The end of the reaction was monitored by GC analysis and the column was washed with CH_2Cl_2 until no reaction products left the column. The solution was concentrated under reduced pressure to yield the pure reaction product **13** (227.6 mg, 1.03 mmol, >99%).
Using this general procedure (**11**: 258.0 mg, 1.03 mmol; 5 h, CH_2Cl_2, 40 °C) the reactor (loaded with catalyst **7C**) was directly used again for studying its reusability: 1st run: >99%; 2nd run: 79%; 3rd run: no product **13** detected.

General procedure for reloading of catalyst 7 from Raschig rings and PASS*flow* column

Deactivated Raschig rings or a PASS*flow* column was reactivated by first washing with 1*N* HCl, H_2O (to pH 7), 1*N* NaOH, H_2O (to pH 7), 1*N* HCl, H_2O (to pH 7), dry methanol and CH_2Cl_2 followed by reloading with ligand **9** and Ru-complex **7** as described above.

Studies on the recharging ability of polymer-bound catalyst 7C

Repeated reactions with 5 mol % of polymer-bound catalyst **7C** on Raschig ring (3.0 μmol/ring) were carried out according to the general procedure (CH_2Cl_2, 45 °C, 2h) using diethyl diallylmalonate **16** (0.04 mmol) as a substrate. After 2 h of the reaction the conversion was 99% as determined by GC. The

Raschig ring was removed, washed with one portion of CH_2Cl_2 (2 mL), dried under vacuum and the catalyst was removed from the ring by washing with 1*N* HCl (60 mL), H_2O (to pH 7), 1*N* NaOH (60 mL), H_2O (to pH 7), 1*N* HCl (60 mL), H_2O (to pH 7), dry methanol (60 mL) and CH_2Cl_2 (60 mL) in the flow system with a flow rate of 2mL/min. The ring was then dried under vacuum (12 h) and reloaded with Ru-complex **7** as described above. Such "recharged" ring was used for the next runs, giving the following results: 1st recharging: loading 3.0 µmol/ring, conversion 87%; 2nd recharging: loading 3.0 µmol/ring, conversion >99%; 3rd recharging: loading 2.8 µmol/ring, conversion 99%.

4. Analytical description of products

Diethyl 3-methylcyclopent-3-en-1,1-dicarboxylate (12)[4]

Following the general procedure for polymer **7C**, diene **10** (14.5 mg, 0.06 mmol) was converted at 45 °C into the title compound **12** (12.5 mg, 0.06 mmol, 97%) within 18 h.

IR (film) ν/cm^{-1} 2982, 2937, 1733,1446, 1367, 1252, 1184, 1161, 1097, 1022, 861; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.18 (d, *J* = 1.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 4H), 2.96 (br s, 2H), 2.93 (s, 2H), 1.70 (d, *J* = 1.5 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 172.3, 137.4, 121.2, 61.4, 59.4, 44.6, 40.8, 16.0, 14.0; MS (EI): m/z (%) 226 (24), 181 (15), 153 (49),152 (100), 136 (2), 134 (3), 125 (25), 124 (25), 107 (44), 97 (8), 93 (35), 81 (25), 80 (47), 79 (64), 77 (21), 67 8.5), 55 (3), 53 (7), 39 (9); HRMS (EI) calcd. for $C_{12}H_{18}O_4$: 226.1205 [$M^{+\cdot}$]; found: 226.1210

2,5-Dihydro-1-tosyl-1*H*-pyrole (13)[5]

Following the general procedure for polymer **7C**, diene **11** (50.4 mg, 0.20 mmol) was converted at 20 °C into the title compound **13** (43.0 mg, 0.20 mmol, 96%) within 24 h.

IR (film) ν/cm^{-1} 3048, 2910, 2854, 1928, 1595, 1492, 1476, 1450, 1336, 1305, 1288, 1161, 1103, 1070, 1017, 1001, 947, 819. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.65 (d, *J* = 4.6 Hz, 2H), 4.12 (d, *J* = 4.6 Hz, 4H), 2.42 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 143.7, 134.6, 130.0, 127.7, 125.7, 55.1, 21.8; MS (EI): m/z (%); 223 (20) [$M^{+\cdot}$], 155 (25), 91 (100), 68

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[4] D. F. Taber, K. J. Frankowski, *J. Org. Chem.* **2003**, *68*, 15, 6047-6048.

[5] A. Fürstner, M. Liebl, C. Lehmann, M. Piquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 10, 1847-1857.

(80), 65 (52), 51 (12), 41 (44), 39 (52).

1,1-Diphenyl-1-sila-3-cyclopentene (22)[6]

Following the general procedure for polymer **7C**, diene **15** (15.1 mg, 0.06 mmol) was converted at 45 °C into the title compound **22** (13.4 mg, 0.06 mmol, 99%)[7] within 18h.

IR (film) ν/cm^{-1} 3068, 3047, 3005, 2931, 2870, 1641, 1621, 1427, 1402, 1150, 1114, 1055, 1029, 998, 816; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60-7.65 (m, 4H), 7.41-7.46 (m, 6H), 6.09 (s, 2H), 1.91 (d, *J* = 1.0 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 135.8, 134.7, 131.0, 129.4, 127.9, 16.8; MS (EI): m/z, (%); 236 (52) [$M^{+\cdot}$], 208 (18), 182 (43), 181 (69), 180 (15), 173 (31), 159 (13), 158 (53), 155 (6), 145 (4), 131 (5), 130 (7), 106 (10), 105 (100), 82 (3), 79 (8), 77 (31), 68 (4), 53 (11), 51 (12), 41 (4), 39 (6); HRMS (EI) calcd. for $C_{16}H_{16}Si$: 236.1021 [$M^{+\cdot}$]; found: 236.1014

Diethyl cyclopent-3-ene-1,1-dicarboxylate (23)[8]

Following the general procedure for polymer **7C**, diene **16** (13.8 mg, 0.06 mmol) was converted at 25 °C into the title compound **23** (12.1 mg, 0.06 mmol, 99%) within 24 h.

When the reaction was conducted under microwave irradiating conditions (60 °C, 200 watt, **7C** (1 mol%), 40 µL, 0.19 mmol **16**; CH_2Cl_2) the title compound **23** (21.0 mg, 0.12 mmol; 61% isolated yield) was formed within 4 minutes.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.61 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 4H), 3.01 (s, 4H), 1.24 (t, *J* = 7.1 Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 172.2, 127.8, 61.5, 61.2, 36.7, 14.1; MS (EI) : m/z, (%); 212 (43) [$M^{+\cdot}$], 199 (12), 195 (6), 173 (2), 167 (58), 166 (80), 153 (48), 149 (12), 139 (70), 138 (100), 127 (4), 125 (18), 111 (52), 110 (35), 94 (11), 93 (45), 83 (9), 79 (55), 67 (44), 66 (59), 65 (26), 55 (7).

3-cyclopentenyl phenyl sulfone (24)[9]

Following the general procedure for polymer **7C**, diene **17** (70.0 mg, 0.30 mmol) was converted at 45 °C into the title compound **24** (61.8 mg, 0.30 mmol, 99%) within 2 h.

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[6] S. Miguani, D. Damour, J. P. Bastart, G. Manuel, *Synth. Commun.* **1995**, *25*, 3855-3862.

[7] The ruthenium content in crude **22** was determined to be: 102 ppm as judged by ICP-MS

[8] D. F. Taber, K. J. Frankowski, *J. Org. Chem.* **2003**, *68*, 15, 6047-6048.

[9] C. Mioskowski, *Tetrahedron Lett*. **1994**, *30*, 5437-5440.

^{1}H-NMR (200 MHz, CDCl$_3$): δ = 7.89-7.93 (m, 2H), 7.57-7.62 (m, 3H), 5.60 (s, 2H), 3.83-3.88 (m, 1H), 2.88-2.94 and 2.60-2.64 (m, 4H); ^{13}C-NMR (50 MHz, CDCl$_3$): δ = 137.4, 132.5, 128.1, 127.4, 127.2, 60.5, 32.7; GC-MS (EI): m/z (%); 209 (1), 143 (100), 125 (17), 77 (22), 66 (95).

2,2-diphenyl-3-vinyl-2,5-dihydrofuran (25)[10]

Following the general procedure for polymer **7C**, alkene **18** (18.6 mg, 0.07 mmol) was converted at 45 °C into the title compound **25** (18.6 mg, 0.07 mmol, 99%) within 4 h.

IR (film) ν/cm^{-1} 3427, 3059, 3026, 2925, 1765, 1682, 1598, 1490, 1447, 1226, 1179, 1064, 758, 700; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.10-7.40 (m, 10H), 6.20-6.27 and 6.16-6.18 (m, 2H), 5.31 (dd, *J* = 17.7, 0.8 Hz, 1H), 5.10 (dd, *J* = 11.2, 0.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 171.1, 143.6, 143.3, 129.7, 127.9, 127.8, 124.8, 117.5, 94.5, 60.3; MS (EI): m/z (%); 248 (15) [M$^{+\cdot}$], 229 (8), 215 (9), 205 (9), 191 (13), 189 (10), 182 (22), 171 (77), 165 (17), 143 (15), 129 (10), 128 (22), 105 (100), 91 (34), 77 (43), 71 (16), 57 (20), 55 (14), 43 (41), 39 (9). HRMS (EI) *m/z* [M$^{+\cdot}$] (C$_{18}$H$_{16}$O): calcd. 248.1201; found: 248.1196.

Dimethyl icos-10-endioate (26)[11]

Following the general procedure for polymer **7C**, alkene **19** (11.3 mg, 0.06 mmol) was converted at 22 °C into the title compound **26** (20.0 mg, 0.06 mmol, 95%, *E/Z* = 1.2 : 1)[12] within 18 h.

IR (film) ν/cm^{-1} 2926, 2854, 1741, 1436, 1362, 1260, 1196, 1171, 1094, 1018, 964, 865, 799; isomer (*E*): ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.11 (m, 1H), 3.66 (s, 6H), 2.29 (t, *J* = 6.8 Hz, 4H), 1.92-1.98 (m, 4H), 1.80-1.10 (m, 24H); isomer (*Z*): ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.41 (m, 1H), 3.66 (s, 6H), 2.29 (t, *J* = 6.8 Hz, 4H), 1.92-1.98 (m, 4H), 1.80-1.10 (m, 24H); isomer (*E*): ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 174.3, 131.1, 51.4, 34.1, 32.6, 29.9, 29.8-29.1, 25.7; isomer (*Z*): ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 174.3, 131.6, 51.4, 34.1, 32.6, 29.9, 29.8-29.1, 25.7; MS (EI): m/z, (%); 368 (5) [M$^{+\cdot}$], 336 (22), 318 (14), 304 (42), 276 (7), 180 (7), 165 (9), 151 (12), 135 (14),123 (15), 109 (22), 95 (49), 81 (60), 69 (56), 55 (100), 41 (52).

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[10] A. Fürstner, M. Liebl, C. Lehmann, M. Piquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847-1857.

[11] a) L. Ruzicka, Pl. A. Platter, W. Widmer, *Helv. Chim. Acta* **1942**, *25*, 604-620, b) R. Baker, M.J. Crimnin, *Tetrahedron Lett*. **1977**, 441-444.

[12] The ruthenium content in crude **26** was determined to be 21 ppm as judged by ICP-MS

1,4-Di(4´-*O*-acetyl-2´,3´,6´-trideoxy-3´-trifluoroacetamido-α-L-*arabino*-hexopyranosyl)-2-buten-1,4-diol (27)[13]

Following the general procedure for polymer **7C**, alkene **20** (18.5 mg, 0.06 mmol) was converted at 45 °C into the title compound **27**[14] (12.0 mg after column chromatography, 0.02 mmol, 68%, *E/Z* = 11 : 1) within 24 h.

isomer (*E*): ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.76 (d, *J* = 8.4 Hz, 2H), 5.83 (t, *J* = 3.0 Hz, 2H), 4.90 (d, *J* = 3.2 Hz, 2H), 4.57 (t, *J* = 9,6 Hz, 2H), 4.51-4.44 (m, 2H), 4.20-4.16 (m, 2H), 3.99-3.93 (m, 4H), 2.27 (ddd, *J* = 12.6, 4.6, 1.2 Hz, 2H), 2.08 (s, 6H), 1.71 (dt, *J* = 12.6, 3.6 Hz, 2H), 1.19 (d, *J* = 6.4 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.0, 157.0, 128.7, 116.0, 95.4, 75.2, 67.0, 65.8, 48.0, 35.7, 20.6, 17.6; HRMS (ESI) calcd. for $C_{24}H_{32}N_2O_{10}F_6Na$ $[M+Na]^+$: 645.1859; found: 645.1850.

Methyl (3a*R*,4*S*,9a*R*)-9a-methyl-1-oxo-2,3,3a,4,5,6,9,9a-octahydro-1*H*-cyclopenta[8]annulene-4-carboxylate (28)[15]

Following the general procedure for polymer for polymer **7C**, alkene **21** (15.1 mg, 0.06 mmol) was converted at 45 °C into the title compound **28** (14.2 mg, 0.06 mmol, 99%)[16] within 16 h.

IR (film) ν/cm^{-1} 3018, 2950, 2931, 2862, 1737, 1465, 1434, 1407, 1373, 1315, 1261, 1217, 1193, 1158, 1085, 1066, 1038, 966; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.77-5.70 (m, 1H), 5.65-5.59 (m, 1H), 3.67 (s, 3H), 2.71-2.65 (m, 1H), 2.42-2.16 (m, 5H), 2.13-2.04 (m, 2H), 1.96-1.83 (m, 3H), 1.62-1.49 (m, 1H), 0.91 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 220.1, 175.3, 132.2, 126.7, 52.2, 51.3, 45.2, 41.7, 35.4, 32.0, 29.9, 23.8, 22.6, 15.8; MS (EI): m/z (%); 236 (64), 221 (7), 218 (32), 204 (21), 186 (18), 177 (30), 176 (19), 168 (100), 159 (27), 158 (29), 149 (23), 135 (22), 132 (24), 123 (21), 121 (27), 119 (32), 117 (20), 109 (26), 107 (31), 105 (35), 97 (18), 95 (43), 93 (66), 91 (50), 87 (20), 81 (39), 79 (68), 77 (39), 71 (11), 69 (24), 67 (47), 65 (18), 55 (41), 53 (32), 43 (25), 41 (74), 39 (38); HRMS (EI) *m/z* $[M^{+\cdot}]$ ($C_{14}H_{20}O_3$): calcd. 236.1412; found: 236.1410

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[13] A. Kirschning, G.-w. Chen, J. Jaunzems, M. Jesberger, M. Kalesse, M. Lindner, *Tetrahedron* **2004**, *60*, 3505-3521.

[14] The ruthenium content in crude **27** was determined to be: 77 ppm as judged by ICP-MS.

[15] M. Michalak, *PhD Thesis*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, in preparation.

[16] The ruthenium content in crude **28** was determined to be: 30 ppm as judged by ICP-MS.