Multicatalytic Processes using Diverse Transition Metals for the Synthesis of Alkenes.

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General Informations: Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware. The solvents were dried using standard methods prior to use. $\text{RhCl}(\text{PPh}_3)_3$ is commercially available, but was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 4 PPh_3 according to the literature.¹ 2-propanol and 1,4-dioxane were distilled prior to use using standard methods. Trimethylsilyldiazomethane was prepared according to the literature.^{2,3,4} The commercially available alcohols and aldehydes were purified using standard methods prior to use. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer equipped with a Golden Gate Diamond ATR and are reported in reciprocal centimeters (cm^{-1}). Only the most important and relevant frequencies are reported. ^1H NMR spectra were recorded in deuteriochloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ^{13}C NMR spectra were recorded in deuteriochloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuteriochloroform (76.9 ppm) on the δ scale. Mass spectra were obtained on a KRATOS MS-50 TC TA (FAB) or a Micromass Autospec-TOF (MAB) high resolution magnetic sector mass spectrometer by the Centre régional de spectrométrie de masse de l'Université de Montréal. The elementary analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal or by the Canadian Microanalytical Service Ltd. High performance liquid chromatography (HPLC) analyses were performed on a Hewlett Packard 1100 Series quaternary gradient pump with diode-array detector interfaced with HP Chemstation software. Analytical gas chromatography (GLC) was carried out on a Hewlett Packard 6890 series gas chromatograph equipped with a split mode capillary injector and a flame ionization detector. Unless otherwise noted, injector and detector temperatures were 250 °C and the carrier gas was hydrogen. Data are reported as follows: column type, oven temperature, and retention time (t_r).

Structure of Catalyst 1⁵

Structure of Catalyst 16⁶

Structure of DPPBE (17)⁷

¹ Osborn J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, 28, 77-79.

² Lebel, H.; Paquet, V. *J. Am. Chem. Soc.* **2004**, 126, 320-328.

³ In contrast to diazomethane, trimethylsilyldiazomethane has been shown to be *non-explosive and non-mutagenic*, thus the very careful operations used for the preparation of diazomethane are not necessary. See reference 2 for discussion.

⁴ As the quality of Aldrich's solution change from batch to batch, it is highly recommended to check the purity of commercial solution's (^1H NMR or GC-MS spectra) prior to use. For instance, we have experienced a batch that contain up to 50% of TMSCH_2Cl .

⁵ Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem., Int. Edit.* **2003**, 42, 3810-3813.

⁶ (a) Jafarpour, L.; Hillier, A. C.; Nolan, S. P. *Organometallics* **2002**, 21, 442-444. (b) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, 617, 17-27.

⁷ Yoakim, C.; Guse, I.; O'Meara, J. A.; Thavonekham, B. *Synlett* **2003**, 473-476.

Table 1. Optimization of the Reaction Conditions for the One-Pot Olefination-RCM Process.

Entry	PR_3	Additive	Conv. ^e
1	PPh_3	Oxone, 25°C	15% ^a
2	PPh_3	Oxone, 25°C	30% ^b
3	PPh_3	Oxone, 50°C	40% ^c
4	PPh_3	AlCl_3 , 50°C	$\geq 98\%$ ^a
5	DPPBE (17)	Oxone, 25°C	5% ^a
6	DPPBE (17)	Oxone, 50°C	$\geq 98\%$ ^{c,d}

^a RCM perform at 50°C ^b RCM perform at 80°C in toluene^c RCM perform at 50°C in 1,4-dioxane^d Olefination perform at 50°C in 1,4-dioxane^e Determined by GC

One-Pot Oxidation-Methylenation Procedures A and B⁸

A: One-Pot Procedure for the Oxidation-Methylenation of Aldehydes.

In a 10 mL flask, $\text{Pd}(\text{LiPr})(\text{OAc})_2 \cdot (\text{H}_2\text{O})$ (3 mg, 0.006 mmol) was added, followed by Bu_4NOAc (8 mg, 0.012) and 50 mg of powdered, activated 3Å molecular sieves. PhMe (2mL) and the primary alcohol (0.25 mmol) were then added. The flask was attached to a reflux condenser and a three way joint attached to the top of the reflux condenser. The system is evacuated and refilled with O_2 from a balloon on one end of the three way joint. This step is repeated three times. The flask is placed in an oil bath at 60°C for 12 hours. The solution is transferred, with a flat-end cannula into another flask containing a solution of chlorotris-(triphenylphosphine)rhodium (6 mg, 0.006 mmol), 2-propanol (20 μL , 0.25 mmol) and triphenylphosphine (75 mg, 0.28 mmol) in 1,4-dioxane (2 mL). The flask used for the oxidation was rinsed with 2 mL of 1,4-dioxane. To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.07 mL, 0.35 mmol). The resulting dark orange mixture was stirred at 50°C and gas evolution was observed. When the reaction is completed by GC or TLC analysis, Oxone (33 mg, 0.25 mmol) was added and the mixture was heated at 50°C for 2 h. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel with a pre-absorption.

B: One-Pot Procedure for the Oxidation-Methylenation of Ketones.

In a 10 mL flask, $\text{Pd}(\text{LiPr})(\text{OAc})_2 \cdot (\text{H}_2\text{O})$ (3 mg, 0.006 mmol) was added, followed by Bu_4NOAc (8 mg, 0.012) and 50 mg of powdered, activated 3Å molecular sieves. PhMe (2 mL) and the secondary alcohol (0.25 mmol) were then added. The flask was attached to a reflux condenser and a three way joint attached to the top of the reflux condenser. The system is evacuated and refilled with O_2 from a balloon on one end of the three way joint. This step is repeated three times. The flask is placed in an oil bath at 60°C for 12 hours. At room temperature, the condenser is replaced by septum and the solution is placed under argon. The solution is transferred with a flat-end cannula into another flask containing a solution of chlorotris-(triphenylphosphine)rhodium (6 mg, 0.006 mmol), 2-propanol (0.19 mL, 2.5 mmol) and triphenyl-

⁸ Additionnal references for stoichiometric one-pot oxidation-olefination procedures : (a) Runcie, K. A.; Taylor, R. J. K. *Chem. Commun.* **2002**, 974-975. (b) Blackburn, L.; Pei, C. X.; Taylor, R. J. K. *Synlett* **2002**, 215-218. (c) Wei, X. D.; Taylor, R. J. K. *J. Org. Chem.* **2000**, 65, 616-620. (d) Blackburn, L.; Wei, X. D.; Taylor, R. J. K. *Chem. Commun.* **1999**, 1337-1338. (e) Wei, X. D.; Taylor, R. J. K. *Tetrahedron Lett.* **1998**, 39, 3815-3818. (f) Barrett, A. G. M.; Hamprecht, D.; Ohkubo, M. *J. Org. Chem.* **1997**, 62, 9376-9378.

phosphine (75 mg, 0.28 mmol) in 1,4-dioxane (2 mL). The flask used for the oxidation was rinsed with 2 mL of 1,4-dioxane. To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.08 mL, 0.40 mmol). The resulting dark orange mixture was stirred at 50 °C and gas evolution was observed. When the reaction is completed by GC or TLC analysis, Oxone (33 mg, 0.25 mmol) was added and the mixture was heated at 50 °C for 2 h. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel with a pre-absorption.

Characterization of Products

6-(*tert*-Butyldimethylsilyloxy)-1-hexene (4). The title compound was prepared from 5-(*tert*-butyldimethylsilyloxy)-1-pentanol (50 mg, 0.23 mmol) according to the one-pot procedure **A**. The desired alkene **4** (38 mg, 78%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.48 (2% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 5.84-5.78 (m, 1H), 5.00 (d, J = 17 Hz, 1H), 4.94 (d, J = 11 Hz, 1H), 3.61 (t, J = 6 Hz, 2H), 2.09-2.04 (m, 2H), 1.55-1.50 (m, 2H), 1.47-1.41 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 114.2, 62.9, 33.4, 32.1, 25.8, 25.0, 18.2; IR (NaCl, film) 3078, 2935, 1642, 1472, 1388, 1361, 1255, 1109, 910, 842, 777, 661 cm^{-1} ; Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{OSi}$: C, 67.22; H, 12.22. Found: C, 65.94; H, 12.41.

1-Methoxy-4-vinylbenzene (6). The title compound was prepared from 4-methoxybenzyl alcohol (50 mg, 0.36 mmol) according to the one-pot procedure **A**. The desired alkene **6** (40 mg, 82%) was obtained as a colorless oil after flash chromatography (1% ether/pentane); ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 9 Hz, 1H), 6.88 (d, J = 9 Hz, 1H), 6.69 (dd, J = 18, 11 Hz, 1H), 5.62 (d, J = 18 Hz, 1H), 5.14 (d, J = 11 Hz, 1H), 3.82 (s, 3H).

5-Isopropenylbenzo[1,3]dioxole (8). The title compound was prepared from 1-benzo[1,3]dioxol-5-ylethanol⁹ (50 mg, 0.30 mmol) by the one-pot procedure **B**. The desired alkene **8** (45 mg, 92%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.27 (1% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.02-6.96 (m, 2H), 6.81-6.79 (m, 1H), 5.98 (s, 2H), 5.28 (s, 1H), 5.02 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 147.4, 143.1, 136.0, 119.5, 111.7, 108.3, 106.4, 101.4, 22.5; IR (neat) 3077, 2966, 2892, 1602, 1502, 1489, 1296, 1228, 1038, 932, 885, 811, 629 cm^{-1} . HMRS (MAB) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$ $[\text{M}]^+$: 162.068080. Found: 162.068231.

6-Benzyloxy-2-methylhexene (10).¹⁰ The title compound was prepared from 6-benzyloxyhexan-2-ol¹¹ (50 mg, 0.24 mmol) according to the one-pot procedure **B** using PPh_3 (157 mg, 0.60 mmol), 2-propanol (0.28

⁹ Takahashi, H.; Iguchi, M.; Onda, M. *Chem. Pharm. Bull.* **1985**, *33*, 4775-4782.

¹⁰ Lipshutz, B. H.; Crow, R.; Dimock, S. H.; Ellsworth, E. L.; Smith, R. A. J.; Behling, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4063-4064.

¹¹ Chong, J. M. *Tetrahedron Lett.* **1992**, *33*, 33-36.

mL, 3.6 mmol) and trimethylsilyldiazomethane (0.12 mL, 0.60 mmol). The desired alkene **10** (41 mg, 84%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.30 (2% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.30 (m, 5H), 4.73 (s, 1H), 4.70 (s, 1H), 4.54 (s, 2H), 3.51 (t, J = 6 Hz, 2H), 2.05 (t, J = 7 Hz, 2H), 1.74 (s, 3H), 1.68-1.52 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.7, 138.6, 128.2, 127.5, 127.4, 109.8, 72.8, 70.2, 37.5, 29.3, 24.1, 22.2.

2-Methylenecyclohexyl benzoate (12).¹² The title compound was prepared from 2-benzyloxycyclohexanol¹³ (50 mg, 0.24 mmol) according to the one-pot procedure **B** using PPh_3 (157 mg, 0.60 mmol), 2-propanol (0.18 mL, 2.4 mmol) and trimethylsilyldiazomethane (0.12 mL, 0.60 mmol). The desired alkene **12** (32 mg, 65%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.32 (2% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.45-7.25 (m, 5H), 4.92 (s, 1H), 4.90 (s, 1H), 4.61 (d, J = 12 Hz, 1H), 4.40 (d, J = 12 Hz, 1H), 3.88-3.85 (m, 1H), 2.43-2.34 (m, 1H), 2.15-2.07 (m, 1H), 1.93-1.30 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3, 139.0, 128.2, 127.4, 127.2, 108.7, 78.9, 69.6, 33.9, 32.2, 27.9, 22.1.

1-Benzyloxyhept-6-en-2-ol (13).¹⁴ To a solution of hept-6-en-1,2-diol¹⁵ (71.0 μL , 1.00 mmol) in MeOH (50 mL) was added dibutyltin oxide (1.24 g, 5.00 mmol). After 2 hours at reflux, the reaction mixture was evaporated to dryness and the white solid was dissolved in benzene (100 mL). Tetrabutylammonium iodide (2.77 g, 7.50 mmol) and benzyl bromide (0.65 mL, 5.50 mmol) were then added to the reaction mixture at room temperature. After 16 hours at 50 $^\circ\text{C}$, the solution was concentrated down. The desired alcohol **13** (17 mg, 51%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes); R_f 0.23 (10% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.37-7.27 (m, 5H), 5.82-5.76 (m, 1H), 5.05-4.94 (m, 2H), 4.56 (s, 2H), 3.84-3.81 (m, 1H), 3.51 (d, J = 9 Hz, 1H), 3.35 (d, J = 9 Hz, 1H), 2.34 (s (br), 1H), 2.12-2.05 (m, 2H), 1.58-1.44 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.5, 137.8, 128.3, 127.7, 127.6, 114.5, 74.5, 73.2, 70.1, 33.6, 32.4, 24.6; IR (neat) 3420 (br), 2829, 2858, 1642, 1463, 1254, 1091, 836, 631 cm^{-1} ; HMRS (FAB) calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$ $[\text{M}-1]^+$: 219.138505. Found: 219.138915.

2-Benzyloxymethyl-1,6-heptadiene (14). The title compound was prepared from 1-benzyloxyhept-6-en-2-ol (50 mg, 0.23 mmol) according to the one-pot procedure **B** using PPh_3 (160 mg, 0.45 mmol), 2-propanol (0.18 mL, 2.3 mmol) and TMSCHN_2 (0.07 mL, 0.36 mmol). The desired alkene **14** (43.5 mg, 87%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.23 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.26 (m, 5H), 5.89-5.75 (m, 1H), 5.07-4.94 (m, 4H), 4.50 (s, 2H), 3.97 (s, 2H), 2.14-2.04 (m, 4H), 1.62-1.22 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.8, 138.5, 138.3, 128.2, 127.5, 127.4, 114.5, 111.6, 72.9, 71.7, 33.3, 32.4, 26.7; HMRS (MAB) calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 216.151415. Found: 216.150687.

¹² Ren, L.; Crudden, C. M. *J. Org. Chem.* **2002**, 67, 1746-1750.

¹³ Crotti, P.; Di Bussolo, V.; Favero, L.; Pineschi, M.; Marianucci, F.; Renzi, G.; Amici, G.; Roselli, G. *Tetrahedron* **2000**, 56, 7513-7524.

¹⁴ Hofman, S.; De Baecke, G.; Kenda, B.; De Clercq, P. J. *Synthesis* **1998**, 479-489.

¹⁵ Shimizu, M.; Nemoto, H.; Kakuda, H.; Takahata, H. *Heterocycles* **2003**, 59, 245-255.

6-Benzyloxyhexane-1,5-diol (15). To a solution of 1,2,6-hexanetriol (670 mg, 5.00 mmol) in MeOH (50 mL) was added dibutyltin oxide (1.24 g, 5.00 mmol). After 2 hours at reflux, the reaction mixture was evaporated to dryness and the white solid was dissolved in benzene (100 mL). Tetrabutylammonium iodide (2.77 g, 7.50 mmol) and benzyl bromide (0.65 mL, 5.50 mmol) were then added to the reaction mixture at room temperature. After 16 hours at 50 °C, the solution was concentrated down. The desired diol **15** (0.96 g, 86%) was obtained as a colorless oil after flash chromatography (100% EtOAc); R_f 0.39 (100% EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.29 (m, 5H), 4.54 (s, 2H), 3.82-3.79 (m, 1H), 3.59 (t, J = 6 Hz, 2H), 3.48 (dd, J = 9, 3 Hz, 1H), 3.33 (dd, J = 9, 8 Hz, 1H), 2.88 (s, (br), 1H), 2.36 (s, (br), 1H), 1.58-1.39 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.8, 128.3, 127.6, 74.5, 73.2, 70.2, 62.3, 32.5, 32.3, 21.5; IR (neat) 3370 (br), 3343, 2934, 2861, 1454, 1364, 1092, 699, 631 cm^{-1} ; HMRS (FAB) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_3$ $[\text{M}+1]^+$: 225.149070. Found: 225.148681.

2-Benzyloxymethyl-1,6-heptadiene. (14). The title compound was prepared from 6-benzyloxy-hexane-1,5-diol (50 mg, 0.22 mmol) according to the one-pot procedure **B** using PPh_3 (175 mg, 0.67 mmol), 2-propanol (0.34 mL, 4.5 mmol) and trimethylsilyldiazomethane (0.16 mL, 0.78 mmol). The desired alkene **14** (26 mg, 54%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.23 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.26 (m, 5H), 5.89-5.75 (m, 1H), 5.07-4.94 (m, 4H), 4.50 (s, 2H), 3.97 (s, 2H), 2.14-2.04 (m, 4H), 1.62-1.22 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.8, 138.5, 138.3, 128.2, 127.5, 127.4, 114.5, 111.6, 72.9, 71.7, 33.3, 32.4, 26.7; IR (neat) 3075, 2930, 2857, 1641, 1454, 1092, 1073, 905, 696, 612 cm^{-1} ; HMRS (MAB) calcd for $\text{C}_{15}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 216.151415. Found: 216.150687

One-Pot Methylenation-RCM Procedures C and D

C: One-Pot Procedure for the Methylenation-RCM Reaction with PPh_3 .

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol), 2-propanol (75.0 μL , 1.00 mmol) and triphenylphosphine (0.29 g, 1.10 mmol) in 1,4-dioxane (10 mL) was added the carbonyl compound (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.82 mL, 1.40 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 50 °C. When the reaction is completed by GC or TLC analysis, AlCl_3 (133 mg, 1.00 mmol) was added and the mixture was heated at 50 °C. After 2h, catalyst **16** (85 mg, 0.10 mmol) was added and the solution was heated at 50 °C for 16 hours. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel with a pre-absorption.

D: One-Pot Procedure for the Methylenation-RCM Reaction with DPPBE.

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol) in 1,4-dioxane (10 mL) was added a solution of DPPBE in 1,4-dioxane (2.20 mL, 1.10 mmol), followed by 2-propanol (75.0 μL , 1.00 mmol) and by the carbonyl compound (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.82 mL, 1.40 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 50 °C until the reaction is completed by GC or TLC analysis. Oxone (133 mg, 1.00 mmol) was added and the mixture was heated at 50 °C. After 2h, catalyst **16** (85 mg, 0.10 mmol) was added and the solution was heated at 50 °C for 16 hours. The reaction mixture was cooled to 0 °C, prior to the addition of a solution of TBAF in THF (5.00 mL, 5.00 mmol). The resulting mixture was warmed to room temperature and stirred for 12 hours. The mixture was then diluted with dichloromethane

(30 mL), washed with 10% aqueous NaOH (15 mL) and brine (15 mL). The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude alkene was purified by flash chromatography on silica gel.

Characterization of Products

1-Benzyloxyhept-6-en-2-one (18). Oxalyl chloride (1.0 mL, 11.5 mmol) was added to a solution of dimethylsulfoxide (1.63 mL, 23.0 mmol) in dichloromethane (25 mL) at -78°C . After 15 min, a solution of 1-benzyloxyhept-6-en-2-ol (1.00 g, 4.58 mmol) in dichloromethane (25 mL) was added. The resulting mixture was stirred for 1 h at -78°C before triethylamine (6.15 mL, 48.8 mmol) was added. The cooling bath was then removed and the solution was stirred for another hour at room temperature. Saturated aqueous NH₄Cl (150 mL) was added and the aqueous layer was extracted with dichloromethane (3 x 200 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (150 mL), brine (150 mL) and dried over MgSO₄. After evaporation, the desired ketone **18** (810 mg, 81%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes); 0.18 (5% EtOAc/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.33 (m, 5H), 5.81-5.70 (m, 1H), 5.05-4.96 (m, 2H), 4.59 (s, 2H), 4.06 (s, 2H), 2.47 (t, $J = 7$ Hz, 2H), 2.10-2.03 (m, 2H), 1.73-1.68 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 208.5, 137.7, 137.1, 128.4, 127.9, 127.8, 115.2, 74.9, 73.2, 38.0, 32.9, 22.1; IR (neat) 3067, 2933, 1721, 1455, 1097, 913, 698, 630 cm⁻¹.

1-Benzyloxymethylcyclopentenyl (19). The title compound was prepared from 1-benzyloxyhept-6-en-2-one (50 mg, 0.23 mmol) according to the one-pot procedure **C** using PPh₃ (66 mg, 0.25 mmol), 2-propanol (0.18 mL, 2.3 mmol) and trimethylsilyldiazomethane (0.06 mL, 0.32 mmol). The desired alkene **19** (36 mg, 83%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (1% EtOAc/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.27 (m, 5H), 5.68 (s, 1H), 4.51 (s, 2H), 4.08 (s, 2H), 2.36 (t, $J = 7$ Hz, 4H), 1.94-1.90 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 141.3, 138.4, 129.4, 128.2, 127.5, 127.3, 71.9, 68.9, 32.8, 32.3, 23.2; IR (neat) 3030, 2924, 2846, 1455, 1091, 1073, 697 cm⁻¹; HMRS (MAB) calcd for C₁₃H₁₆O [M]⁺: 188.120115. Found: 188.120175

1-Benzyloxymethylcyclopentenyl (19). The title compound was prepared from 1-benzyloxyhept-6-en-2-one (45 mg, 0.206 mmol) according to the one-pot procedure **D**. The desired alkene **19** (34 mg, 85%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (1% EtOAc/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.27 (m, 5H), 5.68 (s, 1H), 4.51 (s, 2H), 4.08 (s, 2H), 2.36 (t, $J = 7$ Hz, 4H), 1.94-1.90 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 141.3, 138.4, 129.4, 128.2, 127.5, 127.3, 71.9, 68.9, 32.8, 32.3, 23.2; IR (neat) 3030, 2924, 2846, 1455, 1091, 1073, 697 cm⁻¹; HMRS (MAB) calcd for C₁₃H₁₆O [M]⁺: 188.120115. Found: 188.120175

6-Benzyloxy-5-oxohexanal. (20). Oxalyl chloride (44.0 μL , 0.50 mmol) was added to a solution of dimethylsulfoxide (71.0 μL , 1.00 mmol) in dichloromethane (4 mL) at -78°C . After 15 min, a solution of the diol **15** (22.0 mg, 0.10 mmol) in dichloromethane (1 mL) was added. The resulting mixture was stirred for 1 h at -78°C before triethylamine (0.27 mL, 2.00 mmol) was added. The cooling bath was then

removed and the solution was stirred for another hour at room temperature. Saturated aqueous NH_4Cl (15 mL) was added and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were washed with saturated aqueous NaHCO_3 (15 mL), brine (15 mL) and dried over MgSO_4 . After evaporation, the desired keto-aldehyde **20** (17 mg, 80%) was obtained as a colorless oil after flash chromatography (1:2 EtOAc/hexanes); R_f 0.27 (1:2 EtOAc/hexanes); ^1H NMR (300 MHz, C_6D_6) δ 9.22 (s, 1H), 7.24-7.10 (m, 5H), 4.22 (s, 2H), 3.61 (s, 2H), 2.05 (t, $J = 7$ Hz, 2H), 1.79 (t, $J = 7$ Hz, 2H), 1.62-1.58 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 204.2, 197.4, 125.8, 125.4, 125.2, 125.0, 72.4, 70.4, 40.0, 34.8, 12.8; IR (neat) 3031, 2865, 1717, 1455, 1391, 1099, 739, 699, 602 cm^{-1} ; HMRS (MAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ $[\text{M}-1]^+$: 219.102120. Found: 219.102261.

1-Benzyloxymethylcyclopentenyl (19). The title compound was prepared from 6-benzyloxy-5-oxohexanal (50 mg, 0.23 mmol) according to the one-pot procedure **C** using PPh_3 (138 mg, 0.5 mmol), 2-propanol (0.18 mL, 2.3 mmol) and trimethylsilyldiazomethane (0.13 mL, 0.57 mmol). The desired alkene **19** (28 mg, 62%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.27 (m, 5H), 5.68 (s, 1H), 4.51 (s, 2H), 4.08 (s, 2H), 2.36 (t, $J = 7$ Hz, 4H), 1.94-1.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 138.4, 129.4, 128.2, 127.5, 127.3, 71.9, 68.9, 32.8, 32.3, 23.2; IR (neat) 3030, 2924, 2846, 1455, 1091, 1073, 697 cm^{-1} ; HMRS (MAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ $[\text{M}]^+$: 188.120115. Found: 188.120175

1-Benzyloxymethylcyclopentenyl (19). The title compound was prepared from 6-benzyloxy-5-oxohexanal (100 mg, 0.42 mmol) according to the one-pot procedure **D**. The desired alkene **19** (53 mg, 66%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.27 (m, 5H), 5.68 (s, 1H), 4.51 (s, 2H), 4.08 (s, 2H), 2.36 (t, $J = 7$ Hz, 4H), 1.94-1.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 138.4, 129.4, 128.2, 127.5, 127.3, 71.9, 68.9, 32.8, 32.3, 23.2; IR (neat) 3030, 2924, 2846, 1455, 1091, 1073, 697 cm^{-1} ; HMRS (MAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ $[\text{M}]^+$: 188.120115. Found: 188.120175

2H-Chromene. (22).¹⁶ The title compound was prepared from 2-allyloxybenzaldehyde (50 mg, 0.31 mmol) according to the one-pot procedure **C**. The desired alkene **22** (38 mg, 93%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.27 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.10 (dt, $J = 8$, 2 Hz, 1H), 6.96 (dd, $J = 7$, 1 Hz, 1H), 6.87 (dt, $J = 7$, 1 Hz, 1H), 6.78 (d, $J = 8$ Hz, 1H), 6.43 (d, $J = 10$ Hz, 1H), 5.78 (dt, $J = 10$, 4 Hz, 1H), 4.83 (dd, $J = 4$, 2 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 129.0, 126.4, 121.8, 121.2, 115.6, 65.4.

2H-Chromene. (22). The title compound was prepared from 2-allyloxybenzaldehyde (50 mg, 0.31 mmol) according to the one-pot procedure **D**. The desired alkene **22** (36.5 mg, 89%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.27 (1% EtOAc/hexanes).

¹⁶ Chang, S. B.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 864-866.

1-(2,3-Dihydrobenzooxepin-7-yl)ethanone (24).¹⁷ The title compound was prepared from 5-acetyl-2-but-3-enyloxybenzaldehyde¹⁷ (50 mg, 0.23 mmol) according to the one-pot procedure C. The desired alkene **24** (34 mg, 79%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes). R_f 0.34 (10% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.82 (s, 1H), 7.74 (d, J = 8 Hz, 1H), 7.00 (d, J = 8 Hz, 1H), 6.38 (d, J = 12 Hz, 1H), 6.05-6.00 (m, 1H), 4.29 (t, J = 5 Hz, 2H), 2.71-2.57 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 196.7, 162.6, 133.7, 131.5, 131.3, 128.2, 126.2, 120.0, 69.6, 33.7, 26.3.

1-(2,3-Dihydrobenzooxepin-7-yl)ethanone. (24). The title compound was prepared from 5-acetyl-2-but-3-enyloxybenzaldehyde (50 mg, 0.23 mmol) according to the one-pot procedure D. The desired alkene **24** (34 mg, 80%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.23 (1% EtOAc/hexanes).

One-Pot Procedure for the Oxidation-Methylenation-RCM Reaction.

In a 10 mL flask, $\text{Pd}(\text{LiPr})(\text{OAc})_2 \cdot (\text{H}_2\text{O})$ (3 mg, 0.006 mmol) was added, followed by Bu_4NOAc (8 mg, 0.012) and 50 mg of powdered, activated 3 Å molecular sieves. To this 2 mL of PhMe and 1-benzyloxyhept-6-en-2-ol **13** (50 mg, 0.23 mmol) were added. The flask was attached to a reflux condenser and a three way joint attached to the top of the reflux condenser. The system is evacuated and refilled with O_2 from a balloon on one end of the three way joint. This step is repeated three times. The flask is placed in an oil bath at 60 °C for 12 hours. At room temperature, the condenser is replaced by septum and the solution is placed under argon. The solution is transferred with a flat-end cannula into another flask containing a solution of chlorotris(triphenylphosphine)rhodium (6 mg, 0.006 mmol), 2-propanol (0.18 mL, 2.3 mmol) and triphenylphosphine (65 mg, 0.25 mmol) in 1,4-dioxane (2 mL). The flask used for the oxidation was rinsed with 2 mL of 1,4-dioxane. To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.08 mL, 0.36 mmol). The resulting dark orange mixture was stirred at 50 °C and gas evolution was observed. When the reaction is completed by GC or TLC analysis, AlCl_3 (31 mg, 0.23 mmol) was added and the mixture was heated at 50 °C. After 2h, the solution is transferred with a flat-end cannula into another flask containing a solution of catalyst **16** (19 mg, 0.023 mmol) in 1,4-dioxane (1 mL) and the solution was heated at 50 °C for 16 hours. The solvent was removed under reduced pressure and the desired alkene **19** (30 mg, 70%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.27 (m, 5H), 5.68 (s, 1H), 4.51 (s, 2H), 4.08 (s, 2H), 2.36 (t, J = 7 Hz, 4H), 1.94-1.90 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.3, 138.4, 129.4, 128.2, 127.5, 127.3, 71.9, 68.9, 32.8, 32.3, 23.2; IR (neat) 3030, 2924, 2846, 1455, 1091, 1073, 697 cm^{-1} ; HMRS (MAB) calcd for $\text{C}_{13}\text{H}_{16}\text{O}$ $[\text{M}]^+$: 188.120115. Found: 188.120175.

¹⁷ Kahnberg, P.; Lee, C. W.; Grubbs, R. H.; Sterner, O. *Tetrahedron* **2002**, 58, 5203.