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Annulated butanolides by ring closing metathesis of diallyltetronic acid derivatives

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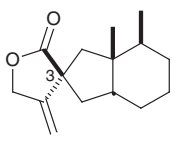
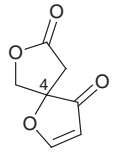
Abstract—3,3-Diallyldihydrofuran-2,4-diones **5** with two identical allyl residues were obtained by Tsuji–Trost-type Pd-catalysed allylation of either 4-*O*-allyltetronates or 3-allyltetronic acids. Allylation of sodium 3-allyltetronate with a second allyl acetate gave mixed derivatives **5** as did the Claisen rearrangement of 4-*O*-allyl 3-allyltetronates **6** under microwave conditions. Compounds **5** and **6** were converted to butanolides with 3,3-spirocyclopentenyl or 3,4-cycloalkanyl annulation by ring closing metathesis with Grubbs catalysts.

Numerous fungal and plant metabolites with spiro-annulated γ-butyrolactone structures have been reported over the last few decades. As part of our ongoing efforts towards the structural cores of the bakkanes,[1] for example bakkenolide A **1**,[2] and of compounds like longianone **2**[3] we explored the feasibility of double allylation-ring closing metathesis sequences. 3,3-Diallyldihydrofuran-2,4-diones with identical allyl residues have been obtained by allylation of tetronic acids with either allyl halides/base followed by thermal Claisen rearrangement of the intermediate 3,4-diallyl tetronates,[4,5] or with allyl acetates under Pd catalysis resulting in moderate yields or product mixtures.[6] Congeners with two different allyl residues were not accessible likewise. A single ring closing metathesis, namely of symmetrical 3,3-diallyldihydrofuran-2,4-dione has been reported.[7] In this paper we investigate the generality of such and similar approaches to 3-spiro and 4-spiro-annulated or 3,4-fused butanolides as occurring in natural products.


Bakkenolide A (**1**)


Longianone (**2**)

The most serious obstacle to using Pd-mediated allylation protocols[8] is the mobility of allyl residues attached to either the 3- or the 4-position of tetronic acids in the presence of Pd^0, which fact reflects the reversibility of the C–C bond formation step under the customary conditions. Both 3-allyltetronic acid **3**[9] and 4-*O*-allyl tetronates **4** when treated with $Pd(Ph_3P)_4$ in toluene at ca. 80 °C 'disproportionated' to give 30–40% of the corresponding 3,3-diallyldihydrofuran-2,4-diones **5** besides a similar quantity of easy to separate de-allylated tetronic acids. The latter can also be converted to **5** by reaction with an excess of external allyl acetate in the presence of Pd^0 and of a base such as DBU to increase their solubility. As depicted in Scheme 1, symmetrical 3,3-diallyldihydrofuran-2,4-diones **5a–c** were obtained in good yields from 4-*O*-allyltetronates **4** and allyl acetate.[10] 3-Allyl-3-cinnamyldihydrofuran-2,4-dione **5d**, however, was formed merely as a mixture with **5a** and 3,3-dicinnamyldihydrofuran-2,4-dione, when allyltetronate **4a** was treated with cinnamyl acetate (Scheme 1).

Yet 'mixed' 3,3-diallyl derivatives were accessible in two other ways. The first one exploits the fact that the above mentioned Pd-mediated scrambling of allyl residues requires elevated temperatures. By deprotonating 3-allyltetronic acids with sodium alkoxides well soluble sodium tetronate salts with a more strongly nucleophilic tetronate anion are obtained.[11] These in turn are readily allylated by a second external allyl acetate at 0 °C

Keywords: Tetronic acid; Metathesis; Spiro compounds; Microwave.
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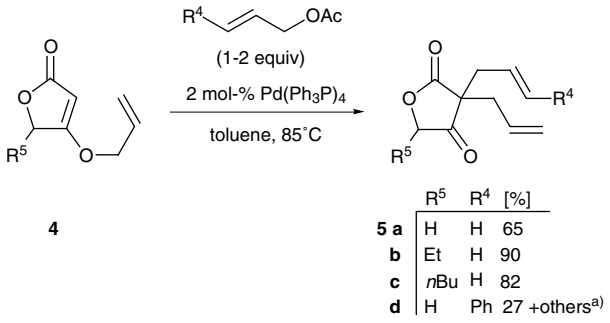


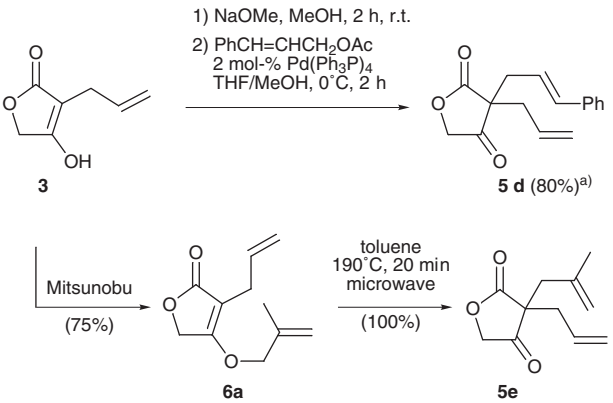
4

	R5	R4	[%]
5 a	H	H	65
b	Et	H	90
c	*n*Bu	H	82
d	H	Ph	27 +others[a)]

Scheme 1. 3,3-Diallyldihydrofuran-2,4-diones **5** from 4-*O*-allyltetronates and allyl acetates under Tsuji conditions; (a) + **5a** (26%) + 3,3-dicinnamyldihydrofuran-2,4-dione (36%).

without scrambling of the allyl residues at a noticeable degree (Scheme 2, top).[12] An alternative high-yielding route to mixed 3,3-diallyldihydrofuran-2,4-diones **5** consists of the esterification of 3-allyltetronic acids such as **3** with a different allylic alcohol[13] followed by a thermal Claisen rearrangement of the intermediate 4-*O*-allyl 3-allyltetronate **6** (Scheme 2, bottom).[14] When carried out under microwave irradiation the Claisen step proceeded quantitatively and without allyl scrambling. The esterification of **3** with methallylic alcohol to give **6a** was only possible under modified Mitsunobu conditions[15] while both the Steglich–Hassner as well as our own isourea[16] method failed completely.

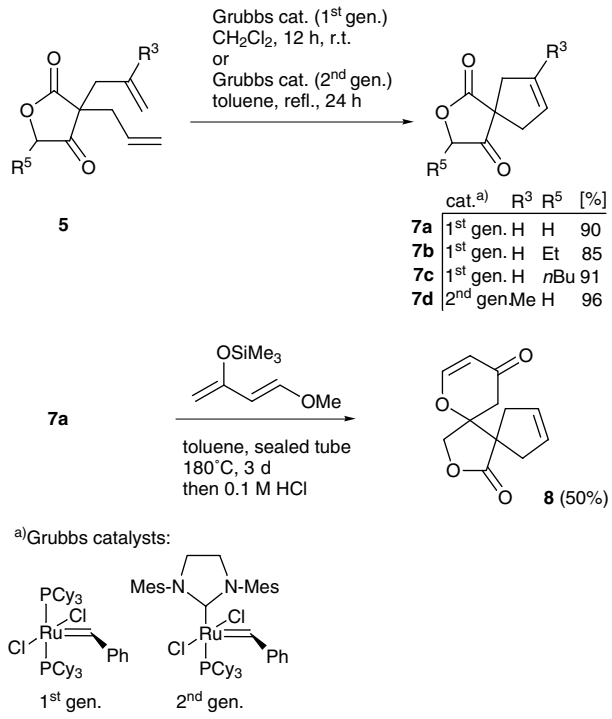
Ring closing metathesis reactions were then carried out with bis-allyl tetronates of types **5** and **6** to build up the structural target motifs of butanolides with 3,3-spirocyclopentenyl, with 4,4-spiro-oxacycloalkanyl and with 3,4-cycloalkanyl annulation. Metathesis reaction of various 3,3-diallylfurandiones **5** with Grubbs catalysts gave 3,3-spirocyclopentenyldihydrofuran-2,4-diones **7** in good to excellent yields (Scheme 3, top). While first generation catalyst $(Pcy_3)_2Cl_2Ru{=}CHPh$ was efficacious in the RCM of derivatives with two C_3H_5 residues,[17] a second generation catalyst and harsh conditions were required for the ring closure of **5e**, most likely due to sterical hinderance.[18,19] Residual Ru compounds responsible for a greyish to black hue of the crude products were removed by treatment with 4 mol % of lead tetraacetate according to Paquette et al.[20] We then treated **7a** with ethyl sorbinate in order to complete the bakkane framework via a Diels–Alder reaction with the cyclopentene. No reaction was observed under classical thermal (PhMe, sealed tube, 180 °C) nor under Lewis acid catalysed [2 mol % $Yb(OTf)_3$ or $EtAlCl_2$, 180 °C, PhMe] conditions. However, when compound **7a** was heated with Danishefsky's diene in a sealed tube in toluene the corresponding hetero-Diels Alder 3,4-dispiro adduct **8** was obtained instead in 50% yield after chromatography and recrystallisation (Scheme 3, middle).[21]



3 — **5 d** (80%)[a)]

6a — 5e

Scheme 2. Mixed 3,3-diallyldihydrofuran-2,4-diones **5d**,**e**; (a) + **5a** (8%) + 3,3-dicinnamyldihydrofuran-2,4-dione (5%).



5

	cat.[a)]	R3	R5	[%]
7a	1st gen.	H	H	90
7b	1st gen.	H	Et	85
7c	1st gen.	H	*n*Bu	91
7d	2nd gen.	Me	H	96

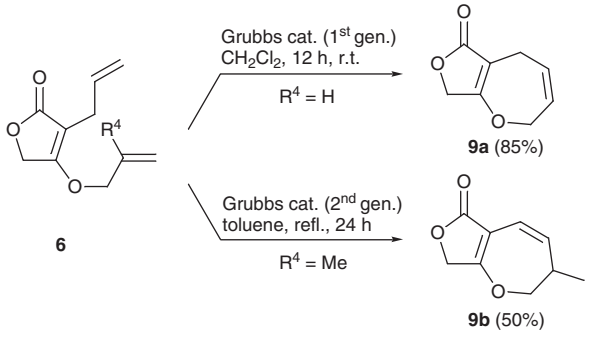
7a — **8** (50%)

[a)]Grubbs catalysts:

1st gen. 2nd gen.

Scheme 3. 3,3-Spirocyclopentenyldihydrofuran-2,4-diones **7** and 3,4-dispirobutanolide **8**.

RCM of 4-*O*-allyl 3-allyltetronates **6** led to the corresponding furo[3,4-*b*]dihydrooxepines **9**. Again, the allyl-methallyl derivative **6a** required a second generation Grubbs catalyst and forcing conditions causing a concomitant shift of the double bond into a conjugated position furnishing **9b** (Scheme 4).[17,18] Alkene



6 — **9a** (85%) — **9b** (50%)

Scheme 4. Furo[3,4-*b*]dihydrooxepines **9**.

isomerisation as a side or a follow-up reaction to metathesis processes initiated with Grubbs catalysts has been frequently reported, especially for allylic alcohols and allyl ethers.[22]

In conclusion two efficient syntheses of 3,3-diallyldihydrofurandiones-2,4 **5** with different allyl residues were developed, one by Pd-catalysed Tsuji allylation of the sodium salts of 3-allyltetronic acids, the other by Claisen rearrangement of 4-*O*-allyl 3-allyltetronates. Ring-closing metathesis of **5** with Grubbs catalysts furnished 3-spirocyclopentenyldihydrofurandiones-2,4 **7** while RCM of the 4-*O*-allyl 3-allyltetronate precursors gave furo[3,4-*b*]dihydrooxepinones **9**. In line with the known literature on RCM, the proper choice of the catalyst very much depends on the degree of substitution of the olefins.

Acknowledgements

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References and notes

1. (a) Fischer, N. H.; Oliver, E. J.; Fischer, H. D. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer: New York, 1979; Vol. 38, Chapter 2; (b) Silva, L. F. *Synthesis* **2001**, 671–689.
2. (a) Abe, N.; Onoda, R.; Shirahata, K.; Kato, T.; Woods, M. C.; Kitahara, Y. *Tetrahedron Lett.* **1968**, *9*(3), 369–373; (b) Brocksom, T. J.; Coelho, F.; Depres, J.; Greene, A. E.; Freire de Lima, M. E.; Hamelin, O.; Hartmann, B.; Kanazawa, A.; Wang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 15313–15325.
3. Edwards, R. L.; Maitland, D. J.; Oliver, C. L.; Pacey, M. S.; Shields, L.; Whalley, A. J. S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 715–719.
4. Momose, T.; Toyooka, N.; Nishio, M.; Shinoda, H.; Fujii, H.; Yanagino, H. *Heterocycles* **1999**, *51*(6), 1321–1343.
5. Kotha, S.; Mandal, K.; Deb, A. C.; Banerjee, S. *Tetrahedron Lett.* **2004**, *45*, 9603–9605.
6. (a) Prat, M.; Moreno-Mañas, M.; Ribas, J. *Tetrahedron* **1988**, *44*(23), 7205–7212; (b) Moreno-Mañas, M.; Prat, M.; Ribas, J.; Virgili, A. *Tetrahedron Lett.* **1988**, *29*(5), 581–584.
7. Kotha, S.; Deb, A. C.; Kumar, R. V. *Bioorg. Med. Chem. Lett.* **2005**, *15*(4), 1039–1043.
8. Tsuji, J. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons, 2002, p 1669.
9. Schobert, R.; Gordon, G. J.; Mullen, G.; Stehle, R. *Tetrahedron Lett.* **2004**, *45*(6), 1121–1124.
10. Compound **5a**[7] from **4a**—typical procedure: **4a**[12] (500 mg, 3.6 mmol), $Pd(Ph_3P)_4$ (80 mg, 2 mol %), allyl acetate (390 mg, 3.9 mmol) and toluene (10 mL) were stirred in the dark at 85 °C for 2 h. Filtration over Celite®, removal of the solvent and column chromatography (CC) (silica gel 60; hexane/Et_2O, 2:3, v/v; R_f 0.78) left a colourless liquid (418 mg, 65%); ν_{max} (ATR)/cm^{-1} 1802, 1752, 1214; ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (4H, d, ^3J 7.3 Hz), 4.35 (2H, s), 5.08 (2H, d, ^3J 9.7 Hz), 5.09 (2H, d, ^3J 17.3 Hz), 5.57 (2H, ddt, ^3J 7.3, 9.7, 17.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.9, 53.9, 73.2, 121.2, 129.9, 175.6, 209.9; *m/z* (EI) 180 (M^+, 2%), 139 (64%), 79 (95%), 41 (100%). Compound **5b**: R_f 0.73 (hexane/Et_2O, 3:2), red oil; ν_{max} (ATR)/cm^{-1} 1797, 1751, 1211; ^1H NMR (300 MHz, $CDCl_3$): δ 0.98 (3H, t, ^3J 7.5 Hz), 1.51–1.69 (1H, m), 1.72–1.89 (1H, m), 2.41 (4H, d, ^3J 7.7 Hz), 4.29 (1H, dd, ^3J 4.5, 8.6 Hz), 5.01–5.12 (4H, m), 5.46–5.65 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.6, 23.8, 37.9, 40.3, 54.5, 85.7, 120.8, 121.2, 129.9, 130.8, 175.3, 211.7; *m/z* (EI) 208 (M^+, 5%), 166 (33%), 79 (100%), 41 (79%). Compound **5c**: R_f 0.83 (hexane/Et_2O, 3:2), yellow oil; ν_{max} (ATR)/cm^{-1} 1798, 1755, 1214; ^1H NMR (300 MHz, $CDCl_3$): δ 0.83 (3H, t, ^3J 7.2), 1.10–1.40 (4H, m), 1.40–1.60 (1H, m), 1.65–1.87 (1H, m), 2.41 (4H, dm, ^3J 7.5 Hz), 4.34 (1H, dd, ^3J 4.3, 9.1 Hz), 5.05 (2H, m), 5.11 (2H, m), 5.45–5.70 (2H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.6, 22.0, 27.3, 30.1, 38.1, 40.3, 54.5, 84.7, 120.8, 121.2, 129.9, 130.8, 175.4, 211.9; *m/z* (EI) 236 (M^+, 5%), 194 (14%), 79 (100%), 41 (29%).
11. Sodeoka, M.; Sampe, R.; Kojima, S.; Baba, Y.; Morisaki, N.; Hashimoto, Y. *Chem. Pharm. Bull.* **2001**, *49*(2), 206–212.
12. Compound **5d** from **3**: **3** (200 mg, 1.43 mmol), NaOMe (79.5 mg, 1.43 mmol) and dry MeOH (10 mL) were stirred at rt for 2 h. The solvent was removed to give a hygroscopic sodium salt, which was re-dissolved in THF/MeOH and stirred with $Pd(Ph_3P)_4$ (32 mg, 2 mol %) and cinnamyl acetate (276 mg, 1.57 mmol) at 0 °C in the dark for 2 h. Filtration over Celite®, concentration and CC (silica gel 60; hexane/Et_2O, 2:3, v/v; R_f 0.72) left a colourless oil (292 mg, 80%); ν_{max} (ATR)/cm^{-1} 1801, 1753, 1218; ^1H NMR (300 MHz, $CDCl_3$): δ 2.48 (2H, d, ^3J 7.3 Hz), 2.59 (2H, d, ^3J 7.4 Hz), 4.30 (2H, s), 5.10 (1H, dd, ^3J 10.2, ^2J 1.5 Hz), 5.10 (1H, dd, ^3J 17.0, ^2J 1.5 Hz), 5.56 (1H, ddt, ^3J 17.0, 10.2, 7.3 Hz), 5.93 (1H, dt, ^3J 15.8, 7.4 Hz), 6.40 (1H, d, ^3J 15.8 Hz), 7.12–7.24 (5H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 38.3, 39.1, 54.3, 73.3, 120.8, 121.3, 126.4, 127.9, 128.3, 129.9, 136.0, 136.1, 175.8, 210.1; *m/z* (EI) 256 (M^+, 4%), 215 (6%), 117 (100%), 104 (35%).
13. Compound **6a** from **3**: DIAD (940 mg, 4.65 mmol) was added dropwise to Ph_3P (1.22 g, 4.65 mmol) in THF (10 mL) at −78 °C whereupon a white solid formed. **3** (500 mg, 3.57 mmol) in THF (5 mL) was slowly added at −78 °C. After addition of methallylic alcohol (390 mg, 5.41 mmol) to the clear solution it was warmed to rt while stirring and treated with aqueous $NaHCO_3$ solution (pH 10) and Et_2O (3 × 10 mL). Drying and concentrating of the organic layers and CC (silica gel 60; hexane/Et_2O, 2:3, v/v; R_f 0.57) of the residue afforded a colourless oil (519 mg, 75%); ν_{max} (ATR)/cm^{-1} 1746, 1667, 1045; ^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (3H, s), 2.94 (2H, d, ^3J 6.2 Hz), 4.49 (2H, s), 4.64 (2H, s), 4.95 (2H, m), 4.96 (2H, mc), 5.81 (1H, ddt, ^3J 6.2, 10.0, 17.0 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.7, 26.2, 65.5, 73.6, 101.2, 113.8, 115.5, 134.2, 139.2, 172.4, 174.3; *m/z* (EI) 194 (M^+, 10%), 161 (27%), 139 (60%), 55 (100%).
14. Compound **5e** from **6a**: **6a** (500 mg, 2.57 mmol) in toluene (8 mL) was irradiated in a microwave oven (CEM Discovery®) at 190 °C for 20 min. Removal of the solvent and CC (silica gel 60; hexane/Et_2O, 2:3, v/v; R_f 0.76) left a colourless oil (500 mg, 100%); ν_{max} (ATR)/cm^{-1} 1804, 1754, 1044; ^1H NMR (300 MHz, $CDCl_3$): δ 1.65 (3 H, dd, ^4J 0.9, 1.4 Hz), 2.47 (2H, ddd, ^3J 7.3, ^4J 1.4, 1.2 Hz), 2.50 (2H, s), 4.38 (2H, s), 4.68 (1H, m), 4.83 (1H, m), 5.12 (1H, m), 5.13 (1H, m), 5.60 (1H, ddt, ^3J 17.3, 9.7, 7.3 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.8, 40.3, 42.6, 54.2, 73.6, 116.1, 121.4, 129.8, 139.4, 176.2, 210.2; *m/z* (EI) 194 (M^+,

2%), 176 (50%), 139 (88%), 55 (100%). Satisfactory microanalyses (C, 0.2; H, 0.1) were obtained for **5a**–**e**.

15. Tahir, H.; Hindsgaul, O. *J. Org. Chem.* **2000**, *65*, 911–913.
16. Schobert, R.; Siegfried, S. *Synlett* **2000**, 686–687.
17. Compound **7a** from **5a**—typical procedure: **5a** (330 mg, 1.8 mmol) dissolved in dry CH_2Cl_2 (15 mL) was treated with $(Pcy_3)_2Cl_2RuCHPh$ (30 mg, 2 mol %) and the mixture was stirred for 24 h at rt. $Pb(OAc)_4$ (32 mg, 4 mol %) was added and stirring was continued for a further 20 h. Filtration over a Celite® plug (3 cm), concentration of the filtrates and CC (silica gel 60; Et_2O; R_f 0.64) left a white powder (250 mg, 90%), mp 72 °C; ν_{max} (ATR)/cm^{-1} 1781, 1745, 1246, 1047; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.70–2.92 (4H, m), 4.65 (2H, s), 5.65 (2H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 42.4, 50.8, 72.1, 127.4, 177.6, 209.3; *m*/*z* (EI) 152 (M^+, 80%), 110 (41%), 94 (33%), 66 (100%). Compound **7b**: R_f 0.63 (hexane/Et_2O, 2:3), yellow oil; ν_{max} (ATR)/cm^{-1} 1796, 1747, 1242, 1046; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (3H, t, ^3J 7.4 Hz), 1.70–1.88 (1H, m), 1.88–2.05 (1H, m), 2.68 (1H, d, ^2J 16.5 Hz), 2.74 (1H, d, ^2J 16.2 Hz), 2.86 (1H, d, ^2J 16.5 Hz), 2.86 (1H, d, ^2J 16.2 Hz), 4.70 (1H, dd, ^3J 4.8, 7.0 Hz), 5.63 (2H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 8.8, 24.7, 42.1, 43.2, 50.9, 84.7, 126.9, 127.6, 177.4, 211.7; *m*/*z* (EI) 180 (M^+, 73%), 110 (13%), 94 (95%), 66 (100%). Compound **7c**: R_f 0.59 (hexane/Et_2O, 2:3), yellow oil; ν_{max} (ATR)/cm^{-1} 1798, 1749, 1250, 1052; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (3H, t, ^3J 6.9 Hz), 1.22–1.45 (4H, m), 1.60–1.76 (1H, m), 1.77–1.95 (1H, m), 2.65 (1H, d, ^2J 15.7 Hz), 2.70 (1H, d, ^2J 15.5 Hz), 2.82 (1H, d, ^2J 15.7 Hz), 2.83 (1H, d, ^2J 15.5 Hz), 4.71 (1H, dd, ^3J 4.5, 7.9 Hz), 5.60 (2H, s); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.5, 21.9, 26.6, 30.9, 42.2, 43.1, 50.8, 83.7, 126.9, 127.5, 177.3, 211.7; *m*/*z* (EI) 208 (M^+, 21%), 110 (5%), 94 (100%), 66 (84%). Compound **9a**: R_f 0.32 (hexane/Et_2O, 2:3), white powder, mp 86 °C; ν_{max} (ATR)/cm^{-1} 1734, 1662, 1019, 921; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.08 (2H, ddd, ^3J 5.6, ^4J1.5, ^5J 1.6 Hz), 4.46 (2H, t, ^5J 1.6 Hz), 4.73 (2H, dd, ^3J 7.0, ^4J 0.4 Hz), 5.96 (1H, dtt, ^3J 7.0, 10.4, ^4J 1.5 Hz), 6.25 (1H, ddt, ^3J 5.6, 10.4, ^4J 0.4 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 22.1, 66.7, 67.6, 99.6, 125.4, 137.2, 174.1, 174.2; *m*/*z* (EI) 152 (M^+, 70%), 66 (100%), 54 (49%), 39 (59%).
18. Compound **7d** from **5e**—typical procedure: **5e** (250 mg, 1.8 mmol) dissolved in dry toluene (15 mL) was treated with benzylidene-[1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(tricyclohexylphosphane)ruthenium $C_{46}H_{65}Cl_2N_2PRu$ (44 mg, 4 mol %) and the mixture was stirred at 110 °C for 24 h. $Pb(OAc)_4$ (23 mg, 4 mol %) was added at rt and stirring was continued for a further 20 h. Workup as for **7a** gave a colourless oil of R_f 0.46 (Et_2O); ν_{max} (ATR)/cm^{-1} 1807, 1791, 1750, 1042; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72 (3H, m), 2.60 (1H, dm, ^2J 15.3 Hz), 2.73 (1H, dm, ^2J 15.3 Hz), 2.69 (1H, dm, ^2J 17 Hz), 2.81 (1H, d, ^2J 17 Hz), 4.63 (2H, d, ^5J 1.7 Hz), 5.22 (1H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 15.6, 42.6, 45.4, 51.5, 72.1, 120.7, 137.4, 177.7, 209.2; *m*/*z* (EI) 166 (M^+, 64%), 124 (41%), 93 (36%), 79 (100%). Compound **9b**: R_f 0.77 (Et_2O), colourless oil; ν_{max} (ATR)/cm^{-1} 1747, 1647, 1009; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (3H, d, ^3J 7.4 Hz), 2.77 (1H, m), 4.14 (1H, dd, ^3J 5.9, 10.9 Hz), 4.26 (1H, dd, ^3J 1.1, 10.9 Hz), 4.58 (2H, s), 5.85 (1H, dd, ^3J 5.1, 10.6 Hz), 6.05 (1H, d, ^3J 10.6 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 16.6, 37.8, 66.4, 76.8, 102.3, 117.6, 137.0, 173.0, 173.4; *m*/*z* (EI) 166 (M^+, 100%), 151 (59%), 124 (42%), 79 (74%). Satisfactory microanalyses (C, 0.2; H, 0.2) were obtained for **7a**–**c** and **9a**,**b**.
19. A similar observation has been reported recently for the RCM of 2,3-bisalkenylcyclopentanones to give [5.7]bicycles: Michalak, K.; Michalak, M.; Wicha, J. *Tetrahedron Lett.* **2005**, *46*(7), 1149–1153.
20. Paquette, L. A.; Schloss, J. D.; Efremov, I.; Fabris, F.; Gallou, F.; Méndez-Andino, J.; Yang, J. *Org. Lett.* **2000**, *2*(9), 1259–1261.
21. Compound **8**: 1-Methoxy-3-trimethylsiloxy-1,3-butadiene (490 mg, 2.84 mmol) in toluene (10 mL) was treated with **7a** (220 mg, 1.45 mmol) at 0 °C and the resulting mixture was heated in a sealed tube for 3 days at 180 °C. 15 mL of a mixture of THF (35 mL) and 0.1 N aqueous HCl (15 mL) were added at rt and stirring continued for 1 min. The residual acid solution (35 mL) was added and the resulting solution poured into AcOEt (50 mL) and treated with H_2O (25 mL). The organic layer was separated and the aqueous one was extracted with AcOEt (4 × 20 mL). The combined extracts were dried and concentrated and the residue was purified by CC (silica gel 60; Et_2O; R_f 0.53); white powder, mp 113 °C; ν_{max} (ATR)/cm^{-1} 1767, 1675, 1039, 1005; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (1H, dd, ^2J 17.2, ^4J 1.1 Hz), 2.53 (2H, m), 2.81 (1H, d, ^2J 17.2 Hz), 2.71–2.82 (1H, m), 2.84–2.95 (1H, m), 4.00 (1H, d, ^2J 10.6 Hz), 4.51 (1H, d, ^2J 10.6 Hz), 5.46 (1H, dd, ^3J 6.2, ^4J 1.1 Hz), 5.50–5.57 (1H, m), 5.70–5.77 (1H, m), 7.23 (1H, d, ^3J 6.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 35.3, 37.4, 38.6, 54.9, 71.5, 88.9, 107.2, 125.9, 130.1, 160.9, 178.8, 188.5; *m*/*z* (EI) 220 (M^+, 46%), 110 (97%), 91 (100%), 71 (91%). Found: C, 65.3; H, 5.6. $C_{12}H_{12}O_4$ requires C, 65.5; H, 5.5.
22. (a) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390–13391; (b) Bourgeois, D.; Pancrazi, A.; Nolan, S. P.; Prunet, J. *J. Organomet. Chem.* **2002**, *643*/*644*, 247–252; (c) Sworen, J. C.; Pawlowa, J. H.; Case, W.; Lever, J.; Wagener, K. B. *J. Mol. Cat. A: Chem.* **2003**, *194*, 69–78; (d) Lehman, S. E.; Schwendeman, J. E.; O'Donnell, P. M.; Wagener, K. B. *Inorg. Chim. Acta* **2003**, *345*, 190–198.