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Stereoselective Reactions of (*E*,*E*)-2,3,6,7-Tetramethyl-1,8-Bis(trimethylsilyl)-octa-2,6-diene with Aldehydes and Acyl Chlorides

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The titanium tetrachloride mediated addition reaction of (*E*,*E*)-2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)octa-2,6-diene to aldehydes and acyl chlorides is described. Aldehydes undergo simple allylation except *p*-anisaldehyde, which leads to cyclopentane resulting from double allylation. From acyl chlorides, highly substituted *meso* cyclopentanols bearing 1,3-diquaternary carbon atoms separated by a tertiary carbinol are obtained. The structures of two cyclopentanols are confirmed by X-ray analysis. From the structure of the cyclopentanols, a reaction mechanism for the double allylation of the acyl chloride by diallylsilane could be proposed.

Introduction

For thirty years, allylsilanes have become essential reagents to transfer an allyl unit to an electrophilic centre.[1] The main features of these reactions are their efficiency and regioselectivity, which is due to the SE2′ mechanism.[2] Nevertheless, with a few exceptions of commercially available compounds, generally the preparation of substituted allylsilanes is not really easy. The double silylation of dienic or trienic hydrocarbons is a particularly interesting transformation, which allows the simultaneous creation of two new Si–C bonds. This reaction constitutes a convenient route to obtain bis(silyl) unsaturated compounds that can represent useful intermediates in organic chemistry or can be used as building blocks for organic synthesis. A very simple procedure is the reductive disilylation of 1,3-dienes by lithium in the presence of chlorotrimethylsilane, which gives rise to a mixture of 1,4-bis(trimethylsilyl)-2-butene derivatives and 1,8-bis(trimethylsilyl)-2,6-octadiene derivatives.[3] A large number of compounds[4] including nonnatural steroids[5] were obtained by the reaction of various electrophiles with 1,8-bis(trimethylsilyl)-2,6-octadiene (Bistro) from the reductive dimerisation of 1,3-butadiene. The reactivity of Bistro revealed reliable high levels of diastereocontrol in spite of being a mixture of (*Z*,*Z*)- and (*Z*,*E*)-isomers.[6]

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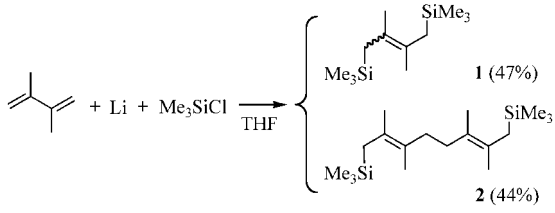
Results and Discussion

The reductive dimerisation of symmetrical 2,3-dimethyl-1,3-butadiene is attractive insofar as only two products can be obtained: 2,3-dimethyl-1,4-bis(trimethylsilyl)-2-butene (**1**) (47%) and 2,3,6,7-tetramethyl-1,8-bis(trimethylsilyl)-octa-2,6-diene (**2**) (44%) in very good overall yield (91%) – contrary to 1,3-butadiene and some other dienes, no by-products are formed (Scheme 1). These two compounds are easily separated by distillation. Compound **2** appears as a mixture of (*Z*,*E*)- (17%) and (*E*,*E*)-isomers (83%). Pleasingly, the latter crystallises on standing at –20 °C and its *trans–trans* structure was confirmed unambiguously by X-ray crystallographic analysis.[7] Only the crystallised (*E*, *E*)-isomer of **2** was used in this work.

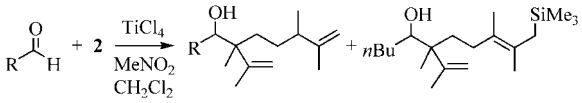


Scheme 1. Reductive dimerisation of 2,3-dimethyl-1,3-butadiene.

Reaction of 2 with Aldehydes

The $TiCl_4$ mediated reaction of **2** with aliphatic aldehydes mainly leads to dienic alcohols **3** resulting from the addition of the first allylsilane moiety to the carbonyl compound and protolysis of the second allylsilane moiety (Scheme 2). Interestingly, **3a**–**c** and **4c** are present as only

one diastereoisomer. As in the previous cases, the reaction was achieved by the addition of nitromethane (4 equiv.) to avoid the formation of some byproducts.[6b]

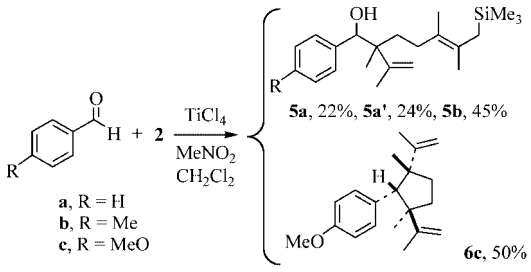


a, R = Et **3a**, 50% **4c**, 23%
b, R = *i*Pr **3b**, 30%
c, R = *n*Bu **3c**, 52%

Scheme 2. Reaction of **2** with aliphatic aldehydes.

Curiously, a different pattern occurred in the case of benzaldehyde and its derivatives. The reaction with benzaldehyde gave two diastereoisomeric silylated alcohols, **5a** and **5a′**, whereas the reaction with *p*-tolualdehyde gave two inseparable isomers, **5b**.

Interestingly, in the reaction with *p*-anisaldehyde the two allylsilane moieties took part in a cyclisation process to give rise to a single cyclopentane derivative, **6c** (Scheme 3).



a, R = H
b, R = Me
c, R = MeO

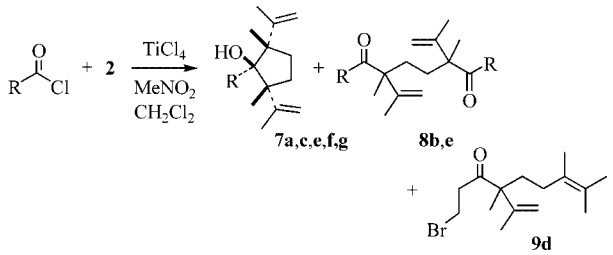
Scheme 3. Reaction of **2** with benzaldehydes.

Reaction of 2 with Acyl Chlorides

Acyl chlorides are very reactive electrophilic reagents and as in the case of Bistro,[4b] the reaction of **2** with acyl chlorides led to cyclopentanol derivatives arising from an intramolecular attack of the second allylsilane moiety. Sometimes, however, the steric enhancement induced a double acylation reaction. In fact, cyclopentanols **7** are very hindered molecules that bear 1,3-diquaternary carbon atoms separated by a tertiary carbinol (Scheme 4). The relative proportions of **7e** and **8e** can be modified by the use of an excess amount of **2** (2 equiv.): **7e**, 58% instead of 31% yield and **8e**, 22% instead of 46% yield. Compound **8b** is present as one diastereoisomer but unfortunately, X-ray analysis failed.[8]

It is worth pointing out that cyclopentanols **7** are present as only one isomer with a plane of symmetry. Structures were confirmed by X-ray crystallographic analysis of **7g** (Figure 1) and biacetyl **14** (Figure 2) resulting from cyclopentanol **7c**.

Taking in account the (*E*,*E*) geometry of diallylsilane **2** and the structure of the obtained cyclopentanols, a detailed mechanism can be proposed (Scheme 5). In the first step, diallylsilane **2** attacks the carbonyl group with an antiperiplanar arrangement of their double bonds.[2b,9] The chloride anion of the tetrahedral intermediate[10] is then substituted (SN2) by the second allylsilane moiety.



a, R = Me	**7a**, 66%	-	-
b, R = *i*Pr	-	**8b**, 2 isomers,	-
		8b$_1$ 54% and **8b**$_2$ 15%	-
c, R = -CH_2-CH_2Cl	**7c**, 44%	-	-
d, R = -CH_2-CH_2Br	-	-	**9d**, 52%
e, R = -CH_2-CH_2-CH=CH_2	**7e**, 31%	**8e** (1 isomer), 46%	-
	7e, 58%	**8e**, 22% (**2**, 2 equiv)	-
f, R = -$(CH_2)_8$-CH=CH_2	**7f**, R = -$(CH_2)_8$-CHCl-CH_3, 47%		-
g, R = Ph	**7g**, 50%	-	-

Scheme 4. Reaction of **2** with acyl chlorides.

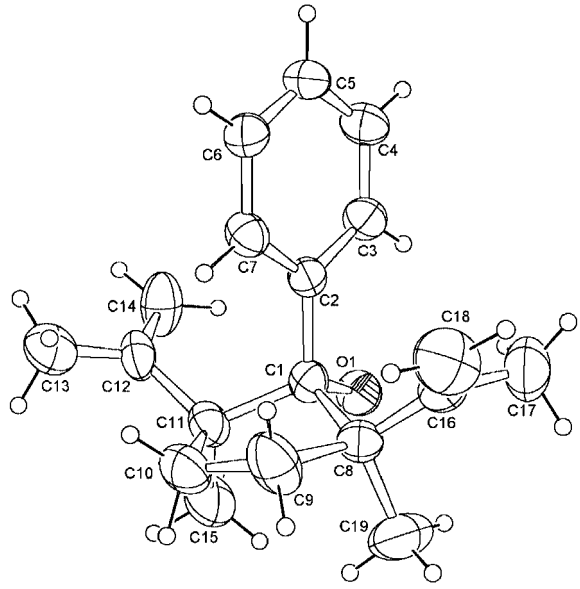


Figure 1. ORTEP diagram of cyclopentanol **7g**.[11]

The reaction of **2** with oxalyl chloride is a straightforward method for the preparation of α,α′-tetrasubstituted cyclopentanone **10** (Scheme 6); in comparison, condensation of oxalyl chloride with Bistro led to 2,5-diethylidenecyclopentanone.[3b] The decarbonylation reaction is an intriguing step,[12] but, as the phosgene does not react with **2** (or with Bistro), we can conclude that the decarbonylation occurred after the first acylation step.

Anhydrides appear to be less reactive than aldehydes and acyl chlorides. Chloroacetyl anhydride gave rise to chlorohydrin **11** in the very low yield of 10%, but the very interesting *meso*-spiro γ-lactone **12** was obtained in a moderate yield of 42% by the reaction of **2** with succinic anhydride [the corresponding (±)-spiro γ-lactone was prepared in 78% yield from Bistro] (Scheme 7).[5i] When succinyl chlo-

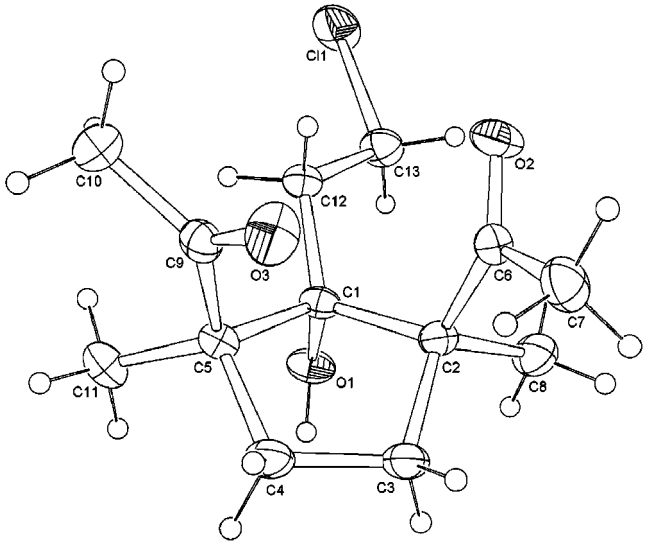
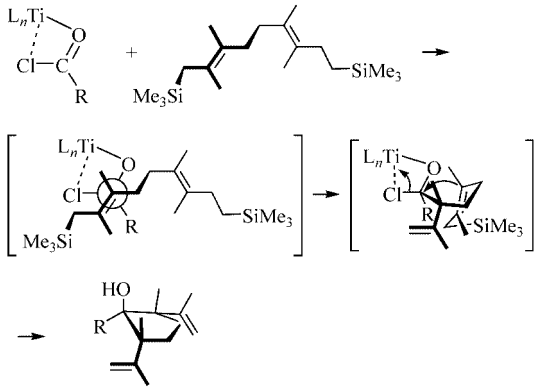
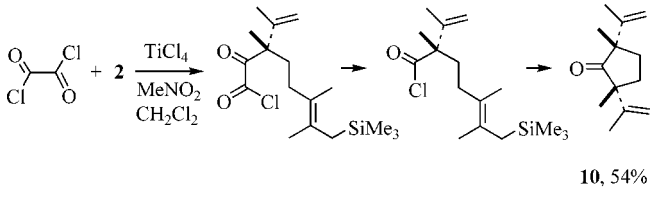


Figure 2. ORTEP diagram of bicyclic diacetylcyclopentanol **14**.



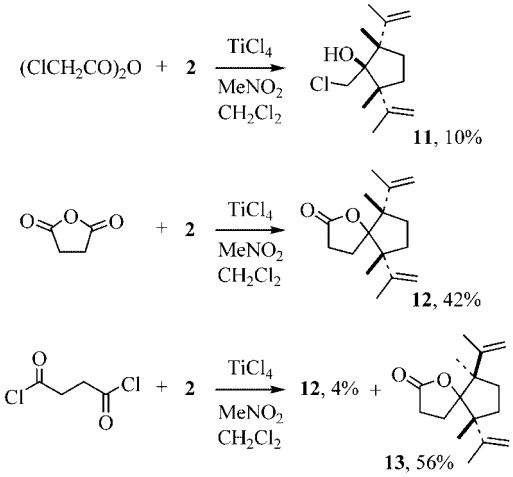
Scheme 5. Mechanism for the addition of **2** to acyl chlorides.



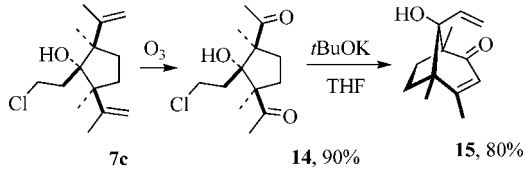
Scheme 6. Reaction of **2** with oxalyl chloride.

ride was used, (±)-spiro γ-lactone **13** was obtained in 56% yield and revealed a reversal in the stereochemistry.

The synthetic potential of cyclopentanol **7c** was succinctly explored. Ozonolysis of cyclopentanol **7c** gives rise to biacetylcyclopentanol **14** (93% yield), which is followed by an intramolecular condensation leading to bicyclic enone **15** (87% yield) (Scheme 8). The structure of **14** (and previously **7c**) with a 1,3-*cis* relationship between the two acetyl groups was confirmed by X-ray crystallographic analysis (Figure 2).



Scheme 7. Reaction of **2** with chloroacetyl anhydride, succinyl anhydride and succinyl chloride.



Scheme 8. Ozonolysis of **7c** followed by an aldolisation.

Conclusions

Finally, the remarkable easy preparation of **2** by a simple and inexpensive process, as well as the diastereoselectivity observed in its addition reaction with acyl chlorides, significantly enhances the interest of our results. The described compounds are of high synthetic potential, particularly as precursors to polycyclic molecules.

Experimental Section

General: All reactions were performed under an argon atmosphere in oven-dried glassware. TLC was performed on silica gel 60 F_{254}. Flash chromatography was performed on silica gel (230–400 mesh) obtained from Macherey–Nagel & Co. CH_2Cl_2 was distilled before use from calcium hydride and THF was distilled from sodium–benzophenone. ^1H and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ solutions at 300, and 75 MHz respectively with a Bruker AC300 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ [signals for residual $CDCl_3$ in the $CDCl_3$: 7.24 ppm for ^1H NMR and 77.16 ppm (central) for ^{13}C NMR]. Carbon–proton couplings were determined by DEPT sequence experiments. High-resolution ESI-MS analyses were performed with a Qstar Elite (Applied Biosystems SCIEX) mass spectrometer.

2,3-Dimethyl-1,4-bis(trimethylsilyl)-2-butene (1) and 2,3,6,7-Tetramethyl-1,8-bis(trimethylsilyl)octa-2,6-diene (2): A 1-L three-necked flask equipped with a thermometer, a dropping funnel, a reflux condenser connected with a stopcock to a rubber balloon filled with argon and a magnetic stirring bar was charged with anhydrous THF (250 mL). The solution was cooled to 0 °C with an ice bath and lithium metal (3 mm wires cut as pieces of 1.5 cm long, 9 g, 1.28 atom) was added. From the dropping funnel, chlorotri-

methylsilane (156 mL, 1.22 mol) was added over 15 min, which was followed by the addition of 2,3-dimethyl-1,3-butadiene (100 g, 1.22 mol) over 45 min. The solution was stirred for 6 h at 0 °C and then at room temperature overnight. Petroleum ether was added and the unreacted small pieces of lithium were removed with tweezers. The milked solution was poured onto crushed ice and, after stirring, the layers were separated. The aqueous phase was extracted with petroleum ether, and the combined organic phase was washed with water, brine and then dried with $MgSO_4$. After filtration and concentration in vacuo, the colourless residue was distilled through a 12-cm Vigreux column to give **1** (b.p. 45 °C, 0.2 Torr, 141 g, 0.58 mol, 47%) and **2** (b.p. 90–105 °C, 0.2 Torr, 85 g, 0.27 mol, 44%). The last fraction containing 83% of the (*E*,*E*)-isomer and 17% of the (*E*,*Z*)-isomer was stored at –20 °C until the major part had crystallised. The pure (*E*,*E*)-isomer was obtained by filtration. M.p. 42 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.01 (s, 18 H); 1.50 (s, 4 H), 1.59 (s, 6 H), 1.64 (s, 6 H), 2.00 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.47 (q), 19.3 (q), 20.7 (q), 25.75 (t), 33.9 (t), 125.6 (s) ppm. $C_{18}H_{38}Si_2$ (310.67): calcd. C 69.59, H 12.33; found C 69.63, H 12.41.

General Procedure for the Reaction of 2 with Aldehydes and Acyl Chlorides: A 100-mL three-necked flask equipped with a thermometer, septum cap, magnetic stirring bar, and an argon outlet was charged with anhydrous CH_2Cl_2 (11 mL) and anhydrous nitromethane (1.2 mL, 21.7 mmol). The solution was cooled to –60 °C; $TiCl_4$ (1.03 g, 0.6 mL, 5.42 mmol) was added, followed by the slow addition of aldehyde or acyl chloride (5.42 mmol). After 15 min, the mixture was cooled to –90 °C and **2** (2 g, 6.5 mmol) in CH_2Cl_2 (1 mL) was added. The mixture was stirred for 2 h at –90 °C and then slowly warmed to –60 °C and stirred until the reaction was complete. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with a saturated aqueous solution of $HNaCO_3$, brine and water. The solution was dried with $MgSO_4$, filtered and concentrated in vacuo, and the residue was purified by flash chromatography (FC; petroleum ether/diethyl ether) on silica gel.

4,7,8-Trimethyl-4-(1-methylethenyl)non-8-en-3-ol (3a): From propanal after 18 h at –60 °C. One isomer as an oil after FC (80:20). Yield: 0.60 g (50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (s, 3 H), 0.95 (s, 3 H), 0.98 (s, 3 H), 1.05–1.25 (m, 3 H), 1.35–1.45 (m, 3 H), 1.41 (s, 6 H), 2.03 (sext., *J* = 6.8 Hz, 1 H), 3.34 (br. d, *J* = 10.2 Hz, 1 H), 4.64 (s, 2 H), 4.70 (s, 1 H), 4.88 (1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4 (q), 17.1 (q), 19.5 (q), 20.26 (q), 20.32 (q), 25.0 (t), 29.6 (t), 34.2 (t), 42.5 (d), 47.7 (s), 79.4 (d), 110.05 (t), 113.3 (t), 149.0 (s), 150.6 (s) ppm. $C_{15}H_{28}O$ (224.38): calcd. C 80.29, H 12.58; found C 80.32, H 12.63.

2,4,7,8-Tetramethyl-4-(1-methylethenyl)non-8-en-3-ol (3b): From isobutyraldehyde after 24 h at –60 °C. One isomer as an oil after FC (90:10). Yield: 0.53 g (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.6 Hz 3 H), 0.88–1.03 (m, 11 H), 1.32–1.45 (m, 2 H), 1.55–1.65 (m, 7 H), 1.75–1.82 (m, 1 H), 2.05 (sept., *J* = 6.9 Hz, 1 H), 3.38 (br. d, *J* = 4.2 Hz, 1 H), 4.64 (s, 2 H), 4.74 (s, 1 H), 4.89 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8 (q), 17.3 (q), 19.05 (q), 20.05 (q), 20.1 (q), 23.7 (q), 29.0 (t), 29.2 (d), 34.9 (t), 42.0 (d), 48.1 (s), 80.8 (d), 109.6 (t), 112.9 (t), 148.7 (s), 150.1 (s) ppm. $C_{16}H_{30}O$ (238.41): calcd. C 80.61, H 12.68; found C 80.65, H 12.73.

6,9,10-Trimethyl-6-(1-methylethenyl)undec-10-en-5-ol (3c): From pentanal after 18 h at –60 °C. One isomer as an oil after FC (90:10). Yield: 0.72 g (52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.7 Hz, 3 H), 0.93 (s, 3 H), 0.97 (d, *J* = 6.3 Hz, 3 H), 1.10–1.55 (m, 9 H), 1.60 (s, 6 H), 2.03 (sext., *J* = 6.9 Hz, 1 H), 3.44 (d, *J* = 9.3 Hz, 1 H), 4.64 (s, 2 H), 4.70 (s, 1 H), 4.88 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (q, 2 C), 16.6 (q), 19.1 (q), 20.0 (q), 22.9 (t), 29.5 (t), 29.9 (t), 31.4 (t), 33.7 (t), 42.1 (d), 47.3 (s), 77.2 (d), 109.6 (t), 112.9 (t), 148.5 (s), 150.2 (s) ppm. $C_{17}H_{32}O$ (252.44): calcd. C 80.88, H 12.78; found C 80.93, H 12.81.

(9*E*)-6,9,10-Trimethyl-6-(1-methylethenyl)-11-(trimethylsilyl)undec-9-en-5-ol (4c): From pentanal after 18 h at –60 °C. One isomer as an oil after FC (90:10). Yield: 0.40 g (23%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03 (s, 9 H), 0.85–0.95 (m, 5 H), 0.98 (s, 3 H), 1.15–1.35 (m, 6 H), 1.58 (s, 6 H), 1.40–1.65 (m, 5 H), 1.75 (s, 3 H), 3.41 (br. d, *J* = 10.0 Hz, 1 H), 4.85 (s, 1 H), 5.05 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.5 (q), 14.3 (q), 16.6 (q), 18.3 (q), 19.6 (q), 21.3 (q), 23.1 (t), 25.2 (t), 29.5 (t), 29.9 (t), 30.7 (t), 33.9 (t), 47.7 (s), 75.4 (d), 114.9 (t), 124.8 (s), 125.6 (s), 148.7 (s) ppm. $C_{20}H_{40}OSi$ (324.62): calcd. C 74.00, H 12.42; found C 73.93, H 12.39.

(5*E*)-2,5,6-Trimethyl-2-(1-methylethenyl)-1-phenyl-7-(trimethylsilyl)hept-5-en-1-ol (5): From benzaldehyde after 18 h at –60 °C. Overall yield: 46% as an oil after FC (90:10). **5a**: Yield: 0.40 g (22%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.04 (s, 9 H), 0.97 (s, 3 H), 0.74–1.00 (m, 2 H), 1.54 (s, 3 H), 1.56 (s, 3 H), 1.4–1.6 (m, 4 H), 1.75 (s, 3 H), 2.12 (s, 1 H), 4.58 (s, 1 H), 4.73 (s, 1 H), 5.01 (s, 1 H), 7.24–7.28 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.5 (q), 18.3 (q), 21.1 (q), 21.3 (q), 25.2 (t), 29.4 (t), 32.7 (t), 48.0 (s), 79.0 (d), 114.3 (t), 125.1 (d), 125.5 (d), 127.3 (d), 127.5 (d, 2 C), 127.9 (d, 2 C), 141.1 (s), 147.7 (s) ppm. **5a′**: Yield: 0.44 g (24%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.03 (s, 9 H), 0.89 (m, 2 H), 0.95 (s, 3 H), 1.47–1.53 (m, 3 H), 1.53 (s, 3 H), 1.55 (s, 3 H), 1.59–1.63 (m, 2 H), 1.82 (d, *J* = 6.5 Hz, 1 H), 1.89 (s, 3 H), 2.05 (s, 1 H), 4.60 (s, 1 H), 4.99 (s, 1 H), 5.17 (s, 1 H), 7.24–7.34 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.08 (q), 17.0 (q), 18.7 (q), 20.0 (q), 21.7 (q), 25.5 (t), 29.6 (t), 34.6 (t), 49.0 (s), 78.3 (d), 116.3 (t), 125.0 (s), 126.1 (s), 127.8 (d), 128.0 (d, 2 C), 128.8 (d, 2 C), 140.8 (s), 148.8 (s) ppm. $C_{22}H_{36}OSi$ (344.61): calcd. C 76.68, H 10.53; found C 76.73, H 10.56.

(5*E*)-2,5,6-Trimethyl-2-(1-methylethenyl)-1-(4-methylphenyl)-7-(trimethylsilyl)hept-5-en-1-ol (5b): From *p*-tolualdehyde after 18 h at –60 °C. Two isomers as an oil after FC (80:20). Yield: 0.87 g (45%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = –0.08 (s, 9 H), 0.87–0.97 (m, 8 H), 1.45–1.60 (m, 7 H), 1.75–2.01 (m, 4 H), 2.33 (s, 3 H), 4.57 (4.54) (s, 1 H), 4.98 (4.96) (s, 1 H), 5.16 (5.13) (s, 1 H), 7.10 (BB′, *J* = 8.0 Hz, 2 H), 7.20 (AA′, *J* = 8.0 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.05 (q), 16.5 (16.6) (q), 19.4 (18.3) (q), 20.0 (q), 21.2 (q), 25.1 (t), 29.2 (t), 34.2 (34.0) (t), 42.0 (41.6) (q), 48.6 (48.4) (s), 77.75 (d), 115.7 (t), 124.6 (s), 125.6 (s), 128.2 (d, 4 C), 136.9 (137.4) (s), 148.6 (148.7) (s), 150.0 (150.2) (s) ppm. $C_{23}H_{38}OSi$ (358.63): calcd. C 77.03, H 10.68; found C 76.98, H 10.71.

1-(4-Methoxyphenyl)-2,5-dimethyl-2,5-bis(1-methylethenyl)cyclopentane (6c): From *p*-anisaldehyde after 40 h at –60 °C. One isomer as an oil after FC (98:2). Yield: 0.76 g (50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 3 H), 1.05–1.25 (m, 2 H), 1.40–1.60 (m, 2 H), 1.62 (s, 3 H), 1.70 (s, 6 H), 2.97 (s, 1 H), 3.76 (s, 3 H), 4.61 (s, 2 H), 4.72 (s, 2 H), 6.73 (d, *J* = 8.7 Hz, 2 H), 7.0 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (q), 21.0 (q), 21.2 (q), 21.6 (q), 31.2 (t), 37.3 (t), 45.9 (s, 2 C), 46.6 (d), 55.2 (q), 111.2 (t, 2 C), 112.6 (d, 2 C), 130.1 (d, 2 C), 138.0 (s), 151.7 (s, 2 C), 157.5 (s) ppm. ESI-HRMS: calcd. for $C_{20}H_{29}O$ $[M + H]^+$ 285.2212; found 285.2204.

1,2,5-Trimethyl-2,5-bis(1-methylethenyl)cyclopentanol (7a): From acetyl chloride after 16 h at –65 °C. One isomer as an oil after FC

(90:100). Yield: 55 g (50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (s, 3 H), 1.29 (s, 6 H), 1.54 (q, J = 6.7 Hz, 2 H), 1.60 (s, 1 H), 1.78 (s, 6 H), 2.01 (q, J = 6.7 Hz, 2 H), 4.70 (t, J = 1.3 Hz, 2 H), 4.74 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (q, 2 C), 23.9 (q, 2 C), 25.2 (q), 33.5 (t, 2 C), 53.6 (s, 2 C), 82.8 (s), 109.7 (t, 2 C), 151.3 (s, 2 C) ppm. $C_{14}H_{24}O$ (208.34): calcd. C 80.71, H 11.61; found C 80.75, H 11.58.

2,4,7,9-Tetramethyl-4,7-bis(1-methylethenyl)decan-3,8-dione (8b): From isobutyryl chloride after 16 h at –65 °C. Overall yield: 0.56 g (69%) after FC (85:15). First isomer **8b$_1$** (0.44 g, 54%), white crystals, m.p. 72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (d, J = 6.7 Hz, 6 H), 0.96 (d, J = 6.7 Hz, 6 H), 1.24 (s, 6 H), 1.30–1.45 (m, 4 H), 1.54 (s, 3 H), 1.56 (s, 3 H), 3.01 (sept., J = 6.7 Hz, 2 H), 4.94 (s, 1 H), 4.99 (s, 1 H), 5.04 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6 (q, 2 C), 20.8 (q, 4 C), 21.5 (q, 2 C), 28.1 (t), 28.4 (t), 34.3 (d, 2 C), 57.6 (s, 2 C), 114.3 (t, 2 C), 145.2 (s, 2 C), 218.0 (s, 2 C) ppm. Second isomer **8b$_2$** (0.12 g, 15%), oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93–0.99 (m, 12 H), 1.03 (s, 3 H), 1.06 (s, 3 H), 1.19 (s, 3 H), 1.55 (s, 3 H), 1.55–1.70 (m, 3 H), 2.04 (q, J = 6.8 Hz, 1 H), 2.70 (sept., J = 6.7 Hz, 1 H), 3.08–3.14 (m, 2 H), 4.74 (s, 2 H), 4.89 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (q), 19.7 (q), 32.9 (t), 40.4 (d), 46.3 (t), 77.4 (s, 2 C), 112.7 (t, 2 C), 147.7 (s, 2 C), 212.9 (s, 2 C) ppm. $C_{20}H_{34}O_2$ (306.48): calcd. C 78.38, H 11.18; found C 78.43, H 11.21.

(2*S,5*R**)-1-(2-Chloroethyl)-2,5-dimethyl-2,5-bis(1-methylethenyl)-cyclopentanol (7c):** From 3-chloropropionyl chloride after 17 h at –65 °C. One isomer as an oil after FC (90:10). Yield: 0.62 g (44%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 6 H), 1.50–1.65 (m, 4 H), 1.81 (s, 6 H), 1.96 (dd, J = 8.3, 7.8 Hz, 1 H), 2.01 (q, J = 6.4 Hz, 2 H), 3.61 (dd, J = 6.8, 2.6 Hz, 2 H), 4.80 (s, 2 H), 4.84 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9 (q, 2 C), 24.2 (q, 2 C), 33.7 (t, 2 C), 40.4 (t), 42.4 (t), 54.1 (q, 2 C), 85.6 (s), 111.3 (t, 2 C), 150.9 (s, 2 C) ppm. ESI-HRMS: calcd. for $C_{15}H_{26}ClO$ [M + H]$^+$ 257.1667; found 257.1667.

1-Bromo-4,7,8-trimethyl-4-(1-methylethenyl)non-7-en-3-one (9d): From 3-bromopropionyl chloride after 18 h at –60 °C. One isomer as an oil after FC (90:10). Yield: 0.85 g (52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (s, 3 H), 1.58 (s, 9 H), 1.66–1.70 (m, 4 H), 1.75 (s, 3 H), 2.28–2.50 (m, 4 H), 5.66 (br. s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3 (q), 18.4 (q), 20.0 (q), 20.6 (q), 24.2 (t), 24.4 (q), 30.4 (t), 35.3 (t), 37.4 (t), 51.9 (s), 123.0 (t), 124.2 (s), 127.4 (s), 138.9 (s), 215.3 (s) ppm. ESI-HRMS: calcd. for $C_{15}H_{26}{}^{79}BrO$ [M + H]$^+$ 301.1161; found 301.1159; calcd. for $C_{15}H_{26}{}^{81}BrO$ [M + H]$^+$ 303.1142; found 303.1154.

(2*S,5*R**)-1-(But-3-enyl)-2,5-dimethyl-2,5-bis(1-methylethenyl)-cyclopentanol (7e):** From 4-pentenoyl chloride after 18 h at –60 °C. One isomer as an oil after FC (95:5). Yield: 0.41 g (31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 6 H), 1.50–1.57 (m, 4 H), 1.67 (s, 1 H), 1.81 (s, 6 H), 2.07 (quint., J = 6.9 Hz, 4 H), 4.77 (br. s, 4 H), 4.84 (br. d, J = 10.2 Hz, 1 H), 4.90 (br. d, J = 16.8 Hz, 1 H), 5.69 (ddt, J = 16.8, 10.2, 6.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1 (q, 2 C), 24.8 (q, 2 C), 29.1 (t), 33.9 (t, 2 C), 36.2 (t), 54.3 (s, 2 C), 85.1 (s), 110.6 (t, 2 C), 113.8 (t), 140.2 (d), 151.6 (s, 2 C) ppm. $C_{17}H_{28}O$ (248.40): calcd. C 82.20, H 11.36; found C 82.14, H 11.31.

6,9-Dimethyl-6,9-bis(1-methylethenyl)tetradeca-1,13-dien-5,10-dione (8e): From 4-pentenoyl chloride after 18 h at –60 °C. One isomer as an oil after FC (95:5). Yield: 0.41 g (46%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 6 H), 1.39–1.48 (m, 4 H), 1.54 (s, 3 H), 1.55 (s, 3 H), 2.25 (m, 4 H), 2.43 (m, 4 H), 4.90–4.96 (m, 6 H), 5.01 (s, 2 H), 5.74 (ddt, J = 16.8, 10.2, 6.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0 (q), 20.4 (q), 28.3 (t), 28.6 (t), 36.1 (t), 56.8 (s), 113.7 (t), 115.2 (t), 137.7 (d), 146.0 (s), 212.5 (s) ppm. $C_{22}H_{34}O_2$ (330.50): calcd. C 79.95, H 10.37; found C 80.01, H 10.40. The use of two times the quantity of **2** led to **7e** (0.77 g, 58%) and **8e** (0.39 g, 22%).

(2*S,5*R**)-1-(9-Chlorodecyl)-2,5-dimethyl-2,5-bis(1-methylethenyl)-cyclopentanol (7f):** From 10-undecenoyl chloride after 18 h at –60 °C. One isomer as an oil after FC (95:5). Yield: 0.93 g (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75–1.00 (m, 6 H), 1.21 (s, 6 H), 1.10–1.30 (m, 6 H), 1.30–1.75 (m, 7 H), 1.46 (d, J = 6.6 Hz, 3 H), 1.79 (s, 6 H), 2.04 (q, J = 6.6 Hz, 2 H), 3.98 (sext., J = 6.6 Hz, 1 H), 4.73 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (q, 2 C), 24.3 (t), 25.0 (q, 2 C), 25.5 (q), 26.6 (t), 26.8 (t), 29.2 (t), 29.4 (t), 30.8 (t), 33.8 (t, 2 C), 37.2 (t), 40.5 (t), 54.3 (s, 2 C), 59.0 (d), 85.0 (s), 110.2 (t, 2 C), 151.76 (s, 2 C) ppm. ESI-HRMS: calcd. for $C_{23}H_{40}ClO$ [M – H]$^-$ 367.2774; found 367.2769.

(2*S,5*R**)-2,5-Dimethyl-2,5-bis(1-methylethenyl)-1-phenylcyclopentanol (7g):** From benzoyl chloride after 16 h at –65 °C. One isomer as white crystals after FC (95:5). Yield: 0.73 g (50%). M.p. 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 6 H), 1.39 (s, 6 H), 1.77 (½AB, J = 6.0 Hz, 2 H), 1.82 (½AB, J = 6.0 Hz, 2 H), 2.22 (s, 1 H), 2.48 (½AB, J = 6.0 Hz, 2 H), 2.53 (½AB, J = 6.0 Hz, 2 H), 4.41 (s, 1 H), 4.42 (s, 1 H), 4.62 (s, 2 H), 7.09 (br. s, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2 (q, 2 C), 26.8 (q, 2 C), 33.9 (t, 2 C), 56.5 (s, 2 C), 87.5 (s), 109.8 (t, 2 C), 125.9 (d, 4 C), 126.0 (d), 144.9 (s), 151.9 (s, 2 C) ppm. $C_{19}H_{26}O$ (270.41): calcd. C 84.39, H 9.69; found C 84.43, H 9.72.

(2*S,5*R**)-2,5-Dimethyl-2,5-bis(1-methylethenyl)cyclopentanone (10):** From oxalyl chloride and $TiCl_4$ (2.06 g, 1.2 mL, 10.84 mmol, 2 equiv.) after 24 h at –60 °C. One isomer as yellow crystals after FC (90:100). Yield: 56 g (54%). M.p. 38 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 6 H), 1.68 (m, 2 H), 1.73 (s, 6 H), 2.16 (m, 2 H), 4.68 (s, 2 H), 4.97 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (q), 21.2 (q), 31.5 (t), 58.0 (s), 114.9 (t), 144.7 (s), 203.7 (s) ppm. $C_{13}H_{20}O$ (192.30): calcd. C 81.20, H 10.48; found C 81.16, H 10.52.

1-Chloromethyl-2,5-dimethyl-2,5-bis(1-methylethenyl)cyclopentanol (11): From chloroacetyl anhydride and $TiCl_4$ (2.06 g, 1.2 mL, 10.84 mmol, 2 equiv.) after 22 h at –60 °C and 8 h at –40 °C. One isomer as an oil after FC (90:100). Yield: 14 g (10%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (s, 6 H), 1.64 (q, J = 6.8 Hz, 2 H), 1.82 (s, 6 H), 2.04 (q, J = 6.8 Hz, 2 H), 2.42 (s, 1 H), 3.66 (s, 2 H), 4.81 (s, 2 H), 4.84 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.6 (q, 2 C), 24.6 (q, 2 C), 35.9 (t, 2 C), 53.3 (t), 54.3 (s, 2 C), 83.0 (s), 111.5 (t, 2 C), 151.2 (s, 2 C) ppm. $C_{14}H_{23}ClO$ (242.78): calcd. C 69.26, H 9.55; found C 69.31, H 9.59.

(6*S,9*R**)-6,9-Dimethyl-6,9-bis(1-methylethenyl)-1-oxaspiro[4.4]-nonan-2-one (12):** From succinic anhydride after 3 d at –60 °C. One isomer as white crystals after FC (85:15). Yield: 0.56 g (42%). M.p. 78 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 6 H), 1.15–1.20 (m, 2 H), 1.72 (s, 6 H), 1.96–2.09 (m, 4 H), 2.42 (dd, J = 7.6, 2.2 Hz, 2 H), 4.80 (s, 2 H), 4.86 (s, 1 H), 4.87 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8 (q, 2 C), 25.0 (q, 2 C), 28.3 (t), 30.1 (t), 33.2 (t, 2 C), 53.7 (s, 2 C), 97.6 (s), 112.2 (t, 2 C), 150.7 (s, 2 C), 177.9 (s) ppm. $C_{16}H_{24}O_2$ (248.36): calcd. C 77.38, H 9.74; found C 77.43, H 9.80.

(6*R,9*R**)-6,9-Dimethyl-6,9-bis(1-methylethenyl)-1-oxaspiro[4.4]-nonan-2-one (13):** From succinyl chloride after 16 h at –60 °C. One isomer as an oil after FC (85:15). Yield: 0.75 g (56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 6 H), 1.25–1.60 (m, 2 H), 1.71 (s, 3 H), 1.73 (s, 3 H), 2.00–2.30 (m, 4 H), 2.31 (d, J = 8.3 Hz, 2 H), 4.77 (d, J = 3.7 Hz, 2 H), 4.89 (br. s, 2 H) ppm. ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 22.25 (q), 22.45 (q), 23.5 (q), 24.5 (q), 26.5 (t), 29.5 (t), 34.2 (t), 35.0 (t), 53.2 (s), 54.5 (s), 100.2 (s), 112.6 (t), 113.6 (t), 148.9 (s), 149.4 (s), 176.4 (s) ppm. $C_{16}H_{24}O_2$ (248.36): calcd. C 77.38, H 9.74; found C 77.41, H 9.82.

***meso*-1-(2-Chloroethyl)-2,5-bis(1-ethanone)-2,5-dimethylcyclopentanol (14):** Ozone in oxygen was bubbled through a solution of **7c** (3 g, 12 mmol) and MeOH (2.53 mL) in CH_2Cl_2 (67 mL) containing 2 drops of an ethanolic solution of "Sudan III"(Eastman Kodak) (ozonisable red dye as internal standard)[13] at –60 °C. After 2 h, the solution was colourless and argon was bubbled through it followed by the addition of dimethyl sulfide (17 mL). After the usual work up, the residue was flash chromatographed (petroleum ether/diethyl ether, 1:1) to give diketone **14** (2.83 g, 10.8 mmol, 90%) as white crystals. M.p. 62 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 6 H), 1.21–1.36 (m, 4 H), 2.17 (s, 6 H), 2.11–2.31 (m, 5 H), 3.74 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (q, 2 C), 28.1 (q, 2 C), 33.2 (t, 2 C), 39.3 (t), 41.6 (t), 62.8 (s, 2 C), 85.15 (s), 213.1 (s, 2 C) ppm.

(1*S,5*S**,8*S**)-8-Ethenyl-8-hydroxy-1,4,5-trimethylbicyclo[3.2.1]oct-3-en-2-one (15):** A 25-mL flask equipped with a septum cap, magnetic stirring bar, and an argon outlet was charged with *t*BuOK (150 mg, 1.33 mmol) and anhydrous THF (6 mL). The solution was vigorously stirred at –30 °C and diketone **14** (136 mg, 0.52 mmol) in THF (0.5 mL) was added. The solution was stirred for 3 h at room temperature. A saturated solution of NH_4Cl (10 mL) was added. The aqueous phase was extracted with diethyl ether (3 × 15 mL). The organic phases were washed with water until neutrality. After solution was dried with $MgSO_4$, filtered and concentrated in vacuo, and the residue was flash chromatographed (petroleum ether/diethyl ether, 70:30) on silica gel to give enone **15** (86 mg, 80%) as white crystals. M.p. 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 3 H), 1.38 (s, 3 H), 1.38–1.68 (m, 5 H), 1.93 (s, 3 H), 5.24 (d, J = 11.0 Hz, 1 H), 5.33 (d, J = 17.4 Hz, 1 H), 5.83 (dd, J = 17.4, 11.0 Hz, 1 H), 5.89 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 (q), 14.3 (q), 20.9 (q), 32.8 (t), 36.0 (t), 54.7 (s), 61.5 (s), 87.6 (s), 118.2 (t), 126.2 (d), 136.7 (d), 167.4 (s), 202.7 (s) ppm. $C_{13}H_{18}O_2$ (206.28): calcd. C 75.69, H 8.80; found C 75.74, H 8.83.

Table 1. Crystal data and structure refinement for **7g** and **14**.

Compound	**7g**	**14**
Formula	$C_{76}H_{64}O_4$	$C_{13}H_{21}ClO_3$
M_w	1041.27	260.75
Crystal colour	colourless	colourless
Crystal size [mm]	0.3 × 0.15 × 0.15	0.2 × 0.1 × 0.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	9.0245(2)	9.7599(9)
b [Å]	15.4984(3)	11.131(1)
c [Å]	46.959(1)	12.7674(6)
β [°]	94.233(1)	99.999(5)
V [Å^3]	6550.0(2)	1365.95(19)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.056	1.268
μ(Mo-K_α) [cm^{-1}]	0.64	2.75
No. unique data	14644	2599
No. parameters refined	721	158
No. refl. in refinement	(14644; $F^2 > 4\sigma F^2$: 4579)	(2599; $F^2 > 4\sigma F^2$: 2055)
R	0.1112[a]	0.0573[a]
wR	0.3912[b]	0.1143[c]
Goodness of fit	1.048	1.118
Residual Fourier [e Å^{-3}]	–0.260; 0.236	–0.295; 0.162

[a] $w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.2681P]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o^2) + (0.1812P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. [c] $w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 0.9311P]$ where $P = (F_o^2 + 2F_c^2)/3$.

X-ray Crystallography: CCDC-629278 (for **7g**), and -629279 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. A summary of the crystal data, data collection and refinements is given in Table 1.

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