Zirconocene-Induced Cocyclisation/Elimination Reactions of 2-Heterosubstituted 1,6-Dienes and 1,6-Enynes

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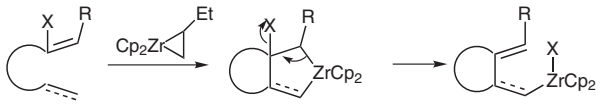
Abstract: Zirconocene-mediated cocyclisation of 2-heterosubstituted-1,6-dienes and -enynes gave zirconacycles bearing an endocyclic β-leaving group which eliminated under the reaction conditions to provide exocyclic alkylidene groups. The scope of this cyclisation/elimination has been investigated along with further elaboration of the monosubstituted zirconocene intermediates by insertion of alkenyl carbenoids.

Key words: zirconium, cyclisation, elimination, alkylidene, carbenoid insertion

The formation of zirconacycles by cocyclisation of 1,n-dienes, -enynes, and- diynes, followed by various elaborations has been developed into a powerful means to construct organic molecules.[1] To extend this chemistry we have investigated the cocyclisation of substrates bearing heteroatom substituents which undergo an endocyclic elimination reaction (Scheme 1), and report our results herein. Our substrates fall into three categories: cyclic enol ethers (dihydrofurans and dihydropyrans), acyclic enol ethers and alkenyl chlorides.



Scheme 1

Examples of the reaction described in Scheme 1 where X = Br and Cl have been reported by Waymouth[2a] and Takahashi.[2b] The reaction of zirconocene-alkyne complexes and zirconocene-alkene complexes with alkenyl ethers has been reported by Takahashi[3] and Barluenga[4] respectively and follows a closely related pathway (Scheme 2). Barluenga has also reported the related addition of zirconocene η^2-imine complexes to alkenyl ethers.[5] Marek has reported a reaction of zirconocene alkene complexes with enol ethers which follows a different pathway to afford alkenylzirconium species by overall replacement of the alkoxide.[6] Cyclisation/elimination of alkenyl ethers where the oxygen is part of the linking chain, for example as shown in Scheme 3, induced by low valent titanium is also known.[7] The elimination of exocyclic β-alkoxy groups is well known for zirconacycles.[8]

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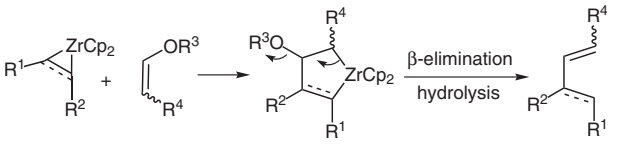
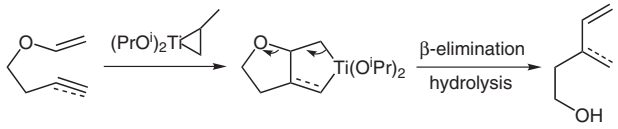
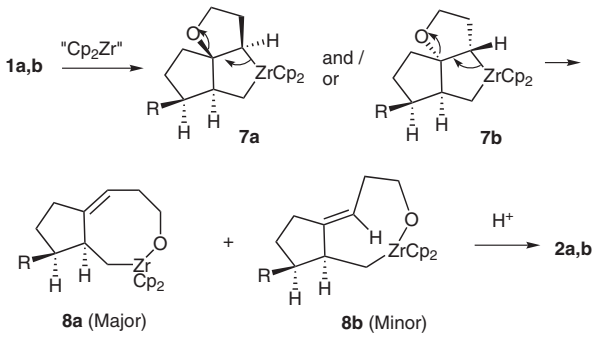


Scheme 2



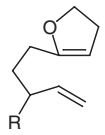
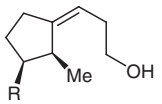
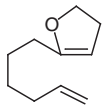
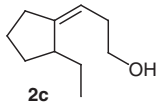
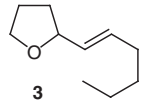
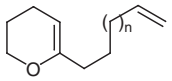
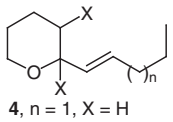
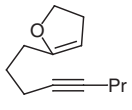
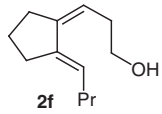
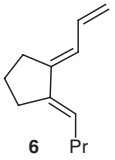
Scheme 3

We first examined the use of dihydrofuran and dihydropyran containing substrates. Alkylation of lithiated 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran with appropriate alkyl iodides[9] gave the cyclisation precursors **1a–f** (Table 1). Treatment with the Negishi 'zirconocene equivalent',[10,11] zirconocene (1-butene), generated in situ by butane elimination from dibutylzirconocene, gave the products **2–6** shown in Table 1. The products **2a** and **2b** derived by cyclisation onto dihydrofuran to give a 5-membered ring, followed by elimination, were formed in good yield. It is notable that cyclisation of the 'all carbon' analogue of **1a** is reported to fail,[12] possibly indicating the importance of the irreversible alkoxide elimination in the formation of **2a** to displace an unfavourable equilibrium between the intermediate zirconacyclopentane and the starting diene. The compound **2a** was formed as a 7:1 mixture of *Z*- and *E*-isomers corresponding to predominant anti-elimination of the intermediate zirconium alkoxide **7a** or **7b**, possibly to give the zirconacycles **8** (Scheme 4).

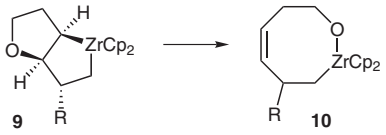


Scheme 4

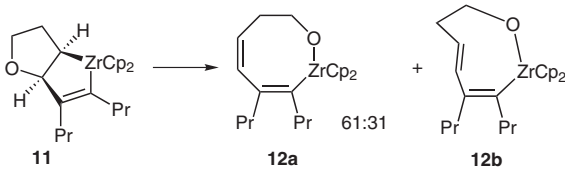
Table 1 Cyclisation/Elimination Products from Dihydrofurans and Dihydropyrans

Entry	Diene/Enyne	Product	Yield (%) (Isomers)
1	 **1a** R = H	 **2a** R = H	78 (*Z*:*E* = 7:1)
2	**1b** R = Ph	**2b** R = Ph	69 (>95% de)
3	 **1c**	 **2c**	13 (**2c**) 25 (**3**)
		 **3**	
4	 **1d** n = 1	 **4**, n = 1, X = H	31
5	**1e** n = 2	**5a** n = 2, X = H **5b** n = 2, X = D	37 (**5a**) 30 (**5b**)
6	 **1f**	 **2f**	45 (**2f**) 24 (**6**)
		 **6**	

The alkene stereochemistry assigned to **2a** is most clearly indicated by the ^{13}C chemical shift of the methine carbon (δ = 34.88 in the major and 39.27 in the minor isomer) compared with (*Z*)- and (*E*)-1-ethylidene-2-methylcyclopentane (δ = 34.4 and 39.5 respectively).[13] Although for both **7a** and **7b** the lowest energy structures[14] have a 90° Zr–C–C–O dihedral angle, there are conformers only ~3 kJ/mol higher in energy for which the dihedral angles are 140–150°, better suited to anti-elimination. In similar eliminations of monocyclic systems Barluenga obtains exclusively the *Z*-isomers **10** (Scheme 5) corresponding to an anti-elimination,[4] and Takahashi observed a 61:39 *Z*:*E* ratio of products **12** corresponding to predominant anti-elimination from **11** (Scheme 6).[3] Compound **2b** was formed as a single isomer. The *Z*-alkene stereochemistry is clear from comparison of the ^{13}C NMR with **2a**. The shown *cis*-arrangement of the phenyl and methyl groups is unexpected[15] but follows from a 6.8 Hz coupling between the C*H*Me and C*H*Ph protons. All reasonable conformers of the analogous *trans* isomer have 170–180° HCCH dihedral angles corresponding to a larger coupling constant. Indeed the methylidene analogue **19a** described later has an 11 Hz coupling between the corresponding protons.

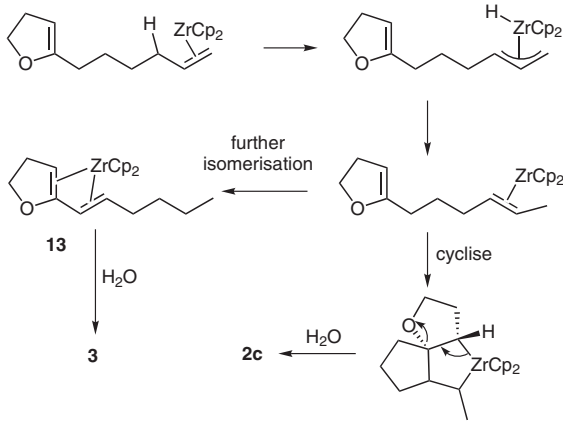


Scheme 5



Scheme 6

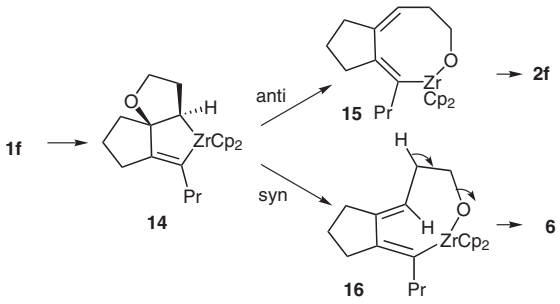
With a longer chain connecting the alkene and dihydrofuran moieties in cyclisation precursor **1c** none of the expected adduct was formed. Instead a low yield of the alkylidene cyclopentane **2c** was formed by alkene isomerisation, cyclisation, and anti-elimination (Scheme 7). The bulk of the isolated material was the allyl ether **3** resulting from multi-positional isomerisation[16] of the initially terminal alkene to form the zirconium diene complex **13** which selectively protonates at the more substituted positions (Scheme 7).[17] In a similar way the only product isolated from the dihydropyran precursors **1d** and **1e** were the allyl ethers **4** and **5**, respectively, resulting from the same multipositional isomerisation to afford zirconium diene complexes as described for the formation of **13** (Scheme 7).[16] Work-up of the reaction from **1e** with deuterium oxide gave the bis-deuterated ether **5b**.



Scheme 7

Finally cyclisation of an alkyne to a dihydrofuran to form a 5 member ring product **2f** was successful (Table 1, entry 6), but to our surprise the product **6** where a second elimination has occurred was also formed. The *E*,*Z* stereochemistry of **2f** follows from the substantial difference between the ^{13}C shifts of the alkene CH carbons (δ = 126.7

and 117.9), and the allylic cyclopentane ring carbons (δ = 36.65 and 32.87). The difference between the latter two is due to the γ-gauche effect which shifts the ring methylene adjacent to the *E*-alkylidene upfield.[18] The alkene stereochemistry of **6** follows from the ^{13}C shifts of the allylic cyclopentane ring carbons at δ = 30.47 and 31.00, both being shifted upfield by the γ-gauche effect. Data on (*E*,*E*)- and (*E*,*Z*)-1,2-diethylidenecyclopentane supports the stereochemical assignments of **2f** and **6**.[19] It is tempting to speculate that the product **16** of syn-elimination of the intermediate **14** undergoes further elimination, whereas **15** from the anti-elimination does not (Scheme 8). The minimum energy conformation of **16** is calculated by DFT[14] to be 30kJ/mol less stable than that of **15** providing some rational for the difference in behaviour. The much stronger tendency towards syn-elimination of the intermediate zirconacycle **14** (cf. **7**) may be due to the absence of low lying conformers with other than around 90° ZrCCO dihedral angles.



Scheme 8

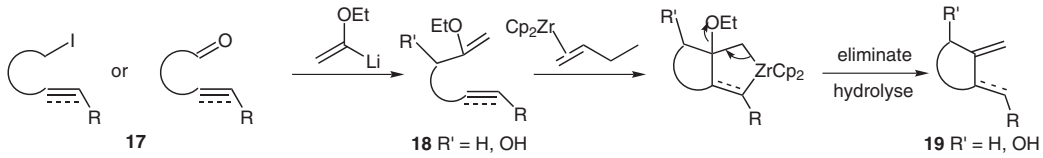
As the above results demonstrate, the trisubstituted nature of the enol ether in substrates **1** prevents cyclisation in all but the most favoured cases, so we then examined less hindered ethyl vinyl ether adducts **18**. Lithiation of ethyl vinyl ether with *tert*-butyllithium to produce 1-ethoxyvinyllithium, and subsequent alkylation[20] with aldehydes or alkyl iodides **17a–i** provide a rapid method for the synthesis of the dienes and enynes **18a–i** shown in Table 2. Cyclisation/elimination using zirconocene(1-butene) occurred as hoped for to provide a wide variety of methylidene carbocycles **19a–h** (Table 2). For alcohol-containing substrates, two equivalents of zirconocene(1-butene) were used. In many cases the cyclisations were highly diastereoselective, for example excellent diastereocontrol was observed when a phenyl group was adjacent to the newly generated chiral centre (Table 2, entries 1 and 2). In the case of the cyclisation of **18b** the hydroxyl group appeared to have no significant influence on the newly created chiral centre. For both **19a** and **19b** the *trans* stereochemistry of the phenyl and methyl groups followed from an 11 Hz coupling in the proton NMR between the adjacent vicinal hydrogens. Alcohol **18ci** (entry 3) was formed with complete 'Cram' selectivity and on cyclisation using an extra equivalent of zirconocene(1-butene) for in situ protection of the alcohol group gave **19c** with good control of the new stereocentre. The *tert*-butyldimethylsilyl protected precursor **18cii** cyclised with much poorer diastereocontrol, though to give the same major isomer of **19c**. Modest 1,3-diastereocontrol from a hydroxyl group was observed in the cyclisation of **18d** to afford **19d** (entry 5). The analogous diene lacking the ethoxy group cyclises with 3:1 diastereocontrol, but with the opposite 1,3-selectivity (hydroxyl and newly formed ring methyl group are *cis*).[21] The relative stereochemistries of **19c** and **19d** were determined by both analysis of coupling constants, and observation of substantial GOESY enhancements between the hydrogens adjacent to the hydroxyl group, and the methyl doublet. Six membered ring formation was facilitated by the 'preorganising' action of the aromatic backbone in **18e** to afford **19e** (Table 2, entry 6) – the only successful cyclisation to give a carbocyclic 6 member ring we observed in this work. There was very little diastereocontrol in the formation of **19e**, but the diastereoisomers were chromatographically separable. The lack of stereocontrol is in accord to that recently observed in cyclisation of a similar diene lacking the ethoxy group.[22] Five membered ring formation when fused to an aromatic ring (Table 2, entry 7) was poor yielding, but provided **19f** as a single diastereoisomer, although we have not yet proven which.

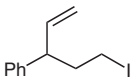
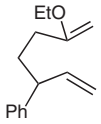
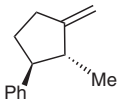
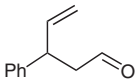
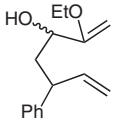
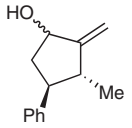
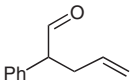
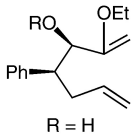
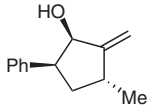
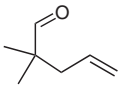
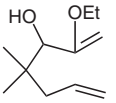
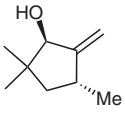
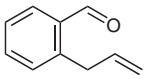
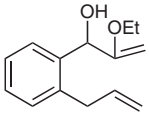
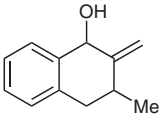
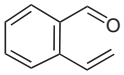
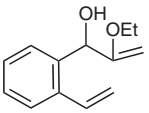
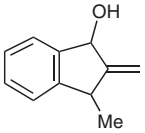
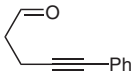
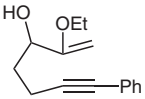
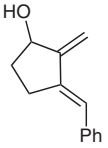
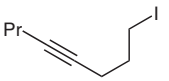
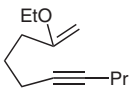
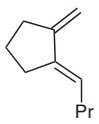
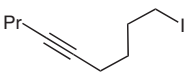
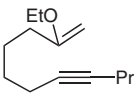
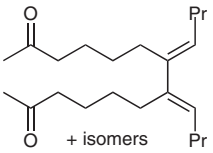
In the case of enyne cocyclisation (Table 2, entries 8–10), the five membered rings (**19g,h**) formed successfully, whereas the 1,7-enyne (**18i**) underwent dimerisation[23] showing that cyclisation from the initially formed zirconocene η^2-alkyne complex is much slower than its intermolecular addition to another alkyne.

The overall success of the cocyclisations to ethyl vinyl ether adducts in generating methylene cyclopentanes provides a viable alternative to the cocyclisation of terminal alkynes, which is not possible using the standard Negishi conditions [Cp_2Zr(1-butene)]. Although the problem can be overcome by the use of zirconocene(ethylene),[24,25] Cp_2ZrCl_2/Mg/Hg,[26] (*i*-PrO)$_2$Ti(propene)[27] or the alkenyllithium/$Cp_2ZrClMe$ method of Barluenga,[28] our route is practically more straightforward, and equally successful.

For reasons outlined below we needed to produce addition/elimination products carrying a chloro rather than alkoxy substituent on the zirconium. One example of the cocyclisation of an alkenyl chloride and an alkenyl bromide has been reported by Takahashi[2b] and Waymouth[2a] respectively. We prepared the alkenyl chlorides **20a–c** by reaction of the appropriate secondary amines with 1,2-dichloro-2-propene and carried out the cyclisation/elimination reaction with zirconocene(1-butene) to give the products **21a–c** in good yield (Table 3). In the case of cyclisation of **20b** oxidative addition of zirconocene into the carbon–chlorine bond[29] giving **22** on hydrolysis (Scheme 9) competed with the desired cyclisation. The rather unstable diene **21c** was characterised as its Diels–Alder adduct **23** (Scheme 10). The stereochemistry of **23** could not be unambiguously determined from NMR coupling constants, and that shown is suggested by comparison to a similar Diels–Alder adduct obtained by Kemp et al.[30]

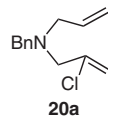
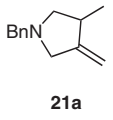
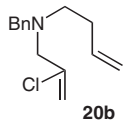
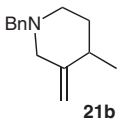
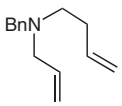
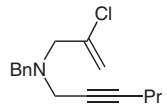
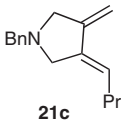
Table 2 Formation and Cyclisation of Ethyl Vinyl Ether Adducts



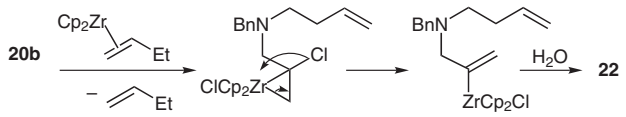
Entry	Alkylating Agent	17	Alkylated Product[a]	18	Yield (%)	Cyclised Product[b,c]	19	Yield (%)[d] (de)
1		**a**		**a**	81		**a**	72 (88)
2		**b**		**b**	72		**b**	55 (>95)
3		**c**		**ci**	70		**c**	44 (75)
4		**c**	R = $SiMe_2t$-Bu	**cii**	57[e]		**c**	47[f] (11)
5		**d**		**d**	75		**d**	74 (60)
6		**e**		**e**	70		**e**	61 (7)
7		**f**		**f**	86		**f**	26 (>95)
8		**g**		**g**	64		**g**	33
9		**h**		**h**	89		**h**	68
10		**i**		**i**	71		**i**	52[g]

[a] Alkylation conditions: H_2C=CHOEt, 1. *t*-BuLi, –70 °C, 30 min; 2. RI or RCHO, –70 to 0 °C, 3 h; 3. aq NH_4Cl.
[b] Cocyclisation conditions: 1. Cp_2ZrCl_2 + 2 *n*-BuLi, –78 to 20 °C, 3 h; 2. MeOH/aq $NaHCO_3$, 20 °C, 16 h. Two equiv of Cp_2ZrCl_2 and four equiv of *n*-BuLi were used in the cyclisation of substrates bearing free alcohol groups.
[c] Major diastereoisomer shown.
[d] Diastereoisomeric excess determined by GC.
[e] 57% yield for TBS protection of alcohol **18ci**.
[f] Yield after deprotection using TFA–H_2O–MeOH (1:1:1).
[g] Yield after hydrolysis of enol ether groups during silica gel chromatography.

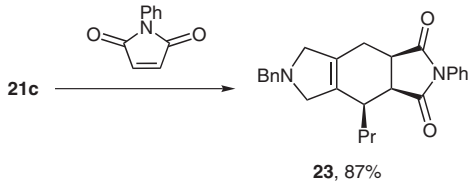
Table 3 Cyclisation/Elimination of Alkenyl Chlorides

Entry	Alkenyl Chloride	Product(s)	Yield (%)
1	 **20a**	 **21a**	71
2	 **20b**	 **21b** +  **22**	53 (**21b**), 36 (**22**)[a]
3	 **20c**	 **21c**	89

[a] Contaminated with ~25% of a further reduced product, *N*-allyl-*N*-butylbenzylamine.



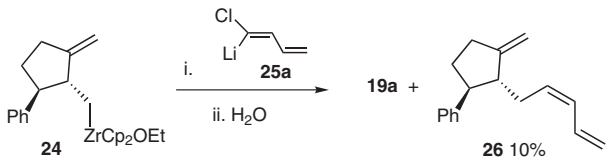
Scheme 9



Scheme 10

The cyclisation/elimination reactions described above ultimately provide a monosubstituted zirconocene, rather than the zirconacycle produced from standard enynes and diynes. We wished to exploit this opportunity for selective carbon–zirconium bond functionalisation using the carbenoid insertion chemistry we have previously developed for both zirconacycles[31] and acyclic organozirconocenes.[32] To this end, the organozirconium species **24** generated from diene **18a** was reacted with 1-chloro-1-lithio-1,3-butadiene[32] (**25a**). The main product was **19a**, but a 10% yield of the desired inserted compound **26** was isolated (Scheme 11).

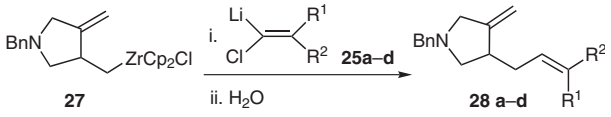
As carbenoid **25a** has been shown to insert efficiently into both zirconacycles[31b] and alkyl chlorozirconocenes,[32] we suggest the poor yield to be a consequence of the ethoxy group on the zirconium in **24**. The first stage of the carbenoid insertion is thought to be donation of a lone pair



Scheme 11

from the carbenoid into an empty orbital on the '16 electron' zirconium complex to provide an 'ate' complex. The lone pair on the ethoxy substituent will compete for this empty orbital thus inhibiting attack of the carbenoid. To combine the cocyclisation/elimination and carbenoid insertion methodologies, we turned to the product **27** derived from the cocyclisation/elimination reaction of alkenyl chloride **20a** and were delighted to find that carbenoid **25a** inserted efficiently to provide a good yield of **28a** on aqueous work-up (Table 4, entry 1). In the same way carbenoids **25b–d** inserted successfully into organozirconium **27** to afford the products **28b–d** (Table 4, entries 2–4).

Table 4 Alkenyl Carbenoid Insertion into **27**



Entry	R^1	R^2	**25**	**28**	Yield (%)[a]
1	$CH{=}CH_2$	H	**a**	**a**	75
2	(*E*)-$CH{=}CH(CH_2)_3CH_3$	H	**b**	**b**	62
3	$C{\equiv}C(CH_2)_5CH_3$	H	**c**	**c**	40
4	Me	Me	**d**	**d**	65

[a] Based on diene **20a**.

In conclusion, we have shown that zirconium mediated cocyclisation/elimination of 2-alkoxy and 2-chloro-1,6-dienes and -enynes is a useful entry to alkylidene cyclopentanes but that 1,7-dienes successfully cyclised in only two special cases. Cyclisation of substrates derived from ethyl vinyl ether is a useful alternative to the cocyclisation of terminal acetylenes in the production of methylene cyclopentanes. We have also shown an alkoxy group on zirconium to have a deactivating effect with respect to carbenoid insertion, but the corresponding alkyl zirconocene chlorides insert alkenyl carbenoids in good yield.

NMR spectra were recorded at 300 MHz (proton) and 75 MHz (carbon) on Bruker AM300 or AC300 spectrometers in $CDCl_3$ unless otherwise stated. 400 MHz (^{1}H)/100 MHz (^{13}C) spectra were acquired on a Bruker DPX400 spectrometer. The chemical shifts are reported as values in ppm relative to internal tetramethylsilane standard, or residual solvent. The following abbreviations are used to denote multiplicity and shape of signal and may be compounded: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet,

br = broad. ^{13}C NMR spectra were proton decoupled, referenced to solvent and reported with the number of attached protons (0, 1, 2, 3), this being determined by DEPT experiments. 2D (H-H and C-H COSY) and GOESY experiments were performed on the DPX400 machine to assign otherwise ambiguous signals where necessary. IR spectra were recorded on Perkin-Elmer 1600 series FTIR, Nicolet Impact 400 or Bio-Rad FTIR Spectrometers. Only absorptions characteristic of functional groups are given. Low-resolution mass spectra were recorded on a Micromass Platform quadrupole mass analyser using positive (ES^+) or negative (ES^-) ion electrospray, or atmospheric pressure chemical ionisation (APCI) from solutions in acetonitrile, or on a VG Analytical 70-250-SE double focusing mass spectrometer by chemical ionisation (CI, NH_3 reagent gas) or electron impact ionisation (EI, 70 eV). When % abundances are not given the reported peak was the only significant one. High-resolution mass spectra were obtained on the 70-250-SE using EI unless otherwise stated. Gas chromatography experiments were performed using a Hewlett Packard HP 6890 series chromatograph, using an HP-Wax column for alcohols, or a HP-5 column otherwise. The conditions were the same for both columns and all samples, and are as follows: 5 min at 60 °C, then increase at 15 °C per min to 250 °C, then 2 min at 250 °C.

Melting points were recorded on a Gallenkamp melting point apparatus, and are uncorrected. All cocyclisation reactions and experiments involving organometallics were carried out using standard Schlenk and syringe techniques. THF and ether were freshly distilled from purple solutions over sodium and benzophenone. *n*-BuLi was titrated against diphenylacetic acid. *t*-BuLi was titrated against borneol using fluorene as indicator. Ethyl vinyl ether was distilled from sodium before use. Petroleum ether used had bp 40–60 °C. Zirconocene dichloride was obtained from Aldrich co. and was not purified further, but was stored in a desiccator. Specific purifications of commercial compounds were carried out according to standard methods.[33] Microanalytical measurements were performed by the Microanalytical Department, University College London or by Medac Ltd.

The following compounds were prepared by literature methods, and had spectral data consistent with that previously reported: 1-iodo-3-phenyl-4-pentene (**17a**),[34] 3-phenyl-4-pentenal (**17b**),[35] 2-phenyl-4-pentenal (**17c**),[36] 2-allylbenzaldehyde (**17e**),[37] 2-vinylbenzaldehyde (**17f**),[38] 5-phenyl-4-pentynal (**17g**),[39] 1-iodo-4-octyne (**17h**),[40] 2-(5-hexenyl)-4,5-dihydrofuran (**1c**).[6]

Lithiation of 2,3-Dihydrofuran or 3,4-Dihydro-2*H*-pyran and Subsequent Alkylation with an Alkyl Iodide; General Procedure[9]

To a solution of 2,3-dihydrofuran (1.06 mL, 0.981 mg, 14 mmol) or 3,4-dihydro-2*H*-pyran (1.28 mL, 1.18 g, 14 mmol) in THF (8 mL) at –40 °C under argon, was added dropwise *t*-BuLi (6.1 mL of a 1.3 M solution in pentanes, 8 mmol). The solution was allowed to warm to 0 °C and stirred for 30 min before cooling to –20 °C and a solution of the alkyl iodide (6 mmol) in THF (2 mL) added. The yellow reaction mixture was allowed to warm to r.t. then refluxed for 1 h. After cooling to r.t., the solution was poured into aq sat. $NaHCO_3$ solution (10 mL) and pentane (20 mL). The aqueous layer was separated and extracted with pentane (3 × 50 mL), and the combined organic phases were dried (Na_2SO_4), filtered and concentrated. The crude products were purified by column chromatography or Kugelrohr distillation.

2-(4-Pentenyl)-4,5-dihydrofuran (1a)

Alkylation of 5-lithio-2,3-dihydrofuran with 1-iodo-4-pentene with purification by chromatography (alumina, petroleum ether) gave **1a** as a clear, colourless oil (68%).

IR (film): 1666 (s), 1640 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 5.70 (1 H, ddt, *J* = 17.0, 10.0, 6.6 Hz), 4.98 (1 H, dd, *J* = 17.0, 1.1 Hz), 4.94 (1 H, dd, *J* = 10.0, 1.1 Hz), 4.47 (1 H, t, *J* = 2.0 Hz), 4.07 (2 H, t, *J* = 9.4 Hz), 2.31 (2 H, td, *J* = 9.4, 2.0 Hz), 2.10 (2 H, t, *J* = 7.2 Hz), 1.96 (2 H, br q, *J* = 7.2 Hz), 1.58 (2 H, quintet, *J* = 7.2 Hz).

^{13}C NMR (C_6D_6): δ = 159.37 (0), 138.73 (1), 115.05 (2), 93.82 (1), 69.84 (2), 33.69 (2), 30.44 (2), 27.81 (2), 26.45 (2).

LRMS (CI): *m*/*z* (%) = 139 ($M + H^+$, 100), 121 (12), 97 (52).

HRMS (CI): *m*/*z* calcd for $C_9H_{15}O$ $(M + H)^+$: 139.1123; found: 139.1121.

5-(3-Phenyl-4-pentenyl)-2,3-dihydrofuran (1b)

Alkylation of 5-lithio-2,3-dihydrofuran with 1-iodo-3-phenyl-4-pentene with purification by Kugelrohr distillation (100 °C/0.8 mbar) gave **1b** as a viscous clear, colourless oil (83%).

IR (film): 1666 (s), 1636 (m), 1600 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 7.3–7.0 (5 H, m), 5.899 (1 H, ddd, *J* = 17.3, 10.2, 7.4 Hz), 5.036 (1 H, d, *J* = 17.2 Hz), 5.005 (1 H, d, *J* = 10.0 Hz), 4.517 (1 H, tt, *J* = 2.2, 1.3 Hz), 4.129 (2 H, t, *J* = 9.3 Hz), 3.256 (1 H, q, *J* = 7.4 Hz), 2.362 (2 H, tq, *J* = 9.4, 2.0 Hz), 2.17 (2 H, m), 2.03 (2 H, m).

^{13}C NMR (C_6D_6): δ = 159.20 (0), 144.28 (0), 142.34 (1), 128.78 (1), 127.94 (1), 126.53 (1), 114.30 (2), 93.80 (1), 69.76 (2), 49.63 (1), 32.74 (2), 30.36 (2), 26.42 (2).

LRMS (APCI): *m*/*z* (%) = 215 ($M + H^+$, 100), 214 (M^+, 50) 199 (27), 197 (54), 171 (43), 169 (52), 155 (30), 123 (56).

HRMS: *m*/*z* calcd for $C_{15}H_{18}O$ (M^+): 214.1358; found: 214.1362.

2-(4-Pentenyl)-5,6-dihydro-4*H*-pyran (1d)

Alkylation of 6-lithio-3,4-dihydro-2*H*-pyran with 1-iodo-4-pentene with purification by Kugelrohr distillation (75 °C/0.4 mbar) gave **1d** as a clear, colourless oil (91%).

IR (film): 1674 (s), 1640 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 5.83 (1 H, ddt, *J* = 16.9, 9.9, 6.6 Hz), 5.09 (1 H, dd, *J* = 16.9, 1.5 Hz), 5.03 (1 H, m), 4.52 (1 H, t, *J* = 3.7 Hz), 3.82 (2 H, t, *J* = 5.1 Hz), 2.1 (4 H, m), 1.88 (2 H, m), 1.71 (2 H, quintet, *J* = 7.4 Hz), 1.54 (2 H, quintet, *J* = 5.8 Hz).

^{13}C NMR (C_6D_6): δ = 154.59 (0), 138.83 (1), 114.66 (2), 95.20 (1), 65.87 (2), 34.14 (2), 33.42 (2), 26.60 (2), 22.67 (2), 20.51 (2).

LRMS (EI): *m*/*z* (%) = 152 (M^+, 29), 137 (6), 113 (19), 98 (77), 83 (18), 57 (100).

HRMS: *m*/*z* calcd for $C_{10}H_{16}O$ (M^+): 152.1201; found: 152.1201.

2-(5-Hexenyl)-5,6-dihydro-4*H*-pyran (1e)

Alkylation of 6-lithio-3,4-dihydro-2*H*-pyran with 1-iodo-5-hexene with purification by Kugelrohr distillation (100 °C/0.8 mbar) gave **1e** as a clear, colourless oil (83%).

IR (film): 1674 (s), 1640 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 5.75 (1 H, ddt, *J* = 16.9, 10.3, 6.6 Hz), 5.00 (1 H, d + fs, *J* = 16.9 Hz), 4.96 (1 H, d, *J* = 10.3 Hz), 4.45 (1 H, t, *J* = 3.5 Hz), 3.77 (2 H, t, *J* = 5.1 Hz), 2.06 (2 H, t, *J* = 7.4 Hz), 1.97 (2 H, m), 1.82 (2 H, q, *J* = 5.4 Hz), 1.55 (2 H, quintet, *J* = 7.5 Hz), 1.48 (2 H, quintet, *J* = 6.1 Hz), 1.35 (2 H, m).

^{13}C NMR (C_6D_6): δ = 155.21 (0), 139.40 (1), 114.82 (2), 95.37 (1), 66.28 (2), 35.02 (2), 34.32 (2), 29.09 (2), 27.24 (2), 23.10 (2), 20.94 (2).

LRMS (EI): *m*/*z* (%) = 166 (M^+, 28), 111 (100), 98 (91), 57 (88).

HRMS: *m*/*z* calcd for $C_{11}H_{18}O$ (M^+): 166.1358; found: 166.1350.

2-(4-Octynyl)-4,5-dihydrofuran (1f)
Alkylation of 5-lithio-2,3-dihydrofuran with 1-iodo-4-octyne with purification by Kugelrohr distillation (120 °C/0.7 mbar) gave **1f** as a clear, colourless oil (88%).

IR (film): 1667 (s) cm^{-1}.

^1H NMR (C_6D_6): δ = 4.590 (1 H, m), 4.152 (2 H, t, *J* = 9.2 Hz), 2.42–2.32 (4 H), 2.252 (2 H, tt, *J* = 7.2, 2.4 Hz), 2.133 (2 H, tt, *J* = 7.0, 2.4 Hz), 1.842 (2 H, quintet, *J* = 7.3 Hz), 1.505 (2 H, app. sextet, *J* = 7.2 Hz), 0.998 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR (C_6D_6): δ = 158.91 (0), 94.08 (1), 80.85 (0), 80.20 (0), 69.83 (2), 30.42 (2), 27.52 (2), 26.90 (2), 22.98 (2), 21.22 (2), 18.83 (2), 13.71 (3).

LRMS (APCI): *m*/*z* (%) = 179 ($M + H^+$, 70), 178 (M^+, 100).

HRMS: *m*/*z* calcd for $C_{12}H_{18}O$ (M^+): 178.1358; found: 178.1353.

Cocyclisation of Dienes and Enynes Using Zirconocene(1-butene); General Procedure
Method A: To a solution of $ZrCp_2Cl_2$ (321 mg, 1.1 mmol) in THF (5 mL) at –80 °C under argon was added dropwise *n*-BuLi (0.88 mL of a 2.5 M solution in hexanes, 2.2 mmol). In the case of substrates containing a free hydroxyl group, 2.2 equiv of $ZrCp_2Cl_2$ (642 mg) and 4.4 equiv of *n*-BuLi (1.76 mL) were used. After the addition of *n*-BuLi, a solution of the diene or enyne (1 mmol) in THF (2 mL) was added dropwise and the solution allowed to warm to r.t. After 3–16 h at r.t., MeOH (3 mL) and aq sat. $NaHCO_3$ solution (7 mL) were added and the cloudy white or pale yellow reaction mixture was stirred for 2–16 h. After dilution of the mixture with Et_2O (20 mL) and H_2O (20 mL), the aqueous phase was separated and extracted with Et_2O (3 × 50 mL). The combined organic phases were combined and washed with brine, dried ($MgSO_4$), filtered and concentrated.

3-[2-(*Z*)-Methylcyclopentylidene]-1-propanol (2a)
Prepared by cocyclisation of **1a** (Method A, 2.4 mmol scale). Column chromatography (silica gel, 25% Et_2O in petroleum ether) provided a clear, colourless oil (263 mg, 78%) which contained 13% of the *E*-isomer. An analytically pure sample was obtained by Kugelrohr distillation (70 °C/1 mbar).

IR (film): 3330 (br s), 1650 (w) cm^{-1}.

^1H NMR: δ = 5.18 (1 H, tq, *J* = 7.4, 1.8 Hz), 3.64 (2 H, br s), 2.71 (1 H, m), 2.32 (4 H, m), 1.84 (1 H, dq, *J* = 12.5, 7.7 Hz), 1.69 (1 H, m), 1.6 (1 H, m), 1.5 [1 H, m (obscured)], 1.40 (1 H, m), 1.02 (3 H, d, *J* = 7.4 Hz).

^{13}C NMR: δ = 152.02 (0), 115.79 (1), 62.84 (2), 35.07 (2), 34.88 (1), 33.51 (2), 32.81 (2), 24.14 (2), 20.92 (3). Minor *E*-isomer: δ = 114.63 (1), 62.57 (2), 39.27 (1), 35.59 (2), 33.15 (2), 29.44 (2), 24.04 (2), 19.17 (3), tertiary carbon at ~152 not observed.

LRMS (EI): *m*/*z* (%) = 140 (M^+, 100), 122 (19), 109 (66), 107 (84), 93 (54), 81 (81), 67 (72).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 69.98; H, 11.53.

(*Z*)-3-[(2*S,3*S**)-2-Methyl-3-phenylcyclopentylidene]propan-1-ol (2b)**
Prepared by cocyclisation of **1b** (Method A). Column chromatography (silica gel, 20% Et_2O in hexane) provided a viscous, clear colourless oil (150 mg, 69%). An analytically pure sample was obtained by Kugelrohr distillation (100 °C/1 mbar).

IR (film): 3344 (br s), 1675 (w), 1600 (m), 1580 (w) cm^{-1}.

^1H NMR (400 MHz): δ = 7.25–7.1 (5 H, m), 5.213 (1 H, tq, *J* = 7.4, 1.9 Hz), 3.585 (2 H, td, *J* = 6.5, 1.5 Hz), 2.656 (1 H, dt, *J* = 9.6, 6.6 Hz), 2.580 (1 H, quintet, *J* = 7.0 Hz), 2.2–2.4 (4 H, m), 2.014 (1 H, dtd, *J* = 12.3, 7.0, 3.3 Hz), 1.623 (1 H, dddd, *J* = 12.0, 10.5, 9.5, 7.0 Hz), 1.436 (1 H, s), 1.076 (3 H, d, *J* = 6.8 Hz).

^{13}C NMR: δ = 150.62 (0), 145.62 (0), 128.50 (1), 127.48 (1), 126.23 (1), 116.68 (1), 62.82 (2), 54.99 (1), 43.61 (1), 34.28 (2), 34.06 (2), 32.43 (2), 20.38 (3).

LRMS (ES^-): *m*/*z* = 198 ($M - H_2O$).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.48; H, 9.09.

3-[2-(*Z*)-Ethylcyclopentylidene]-1-propanol (2c) and 2-[1-(*E*)-Hexenyl]tetrahydrofuran (3)
Prepared from **1c** by Method A. After separation and purification by column chromatography (silica gel, 10% Et_2O in petroleum ether–30% Et_2O in petroleum ether) **2c** was obtained as a clear, colourless oil (20 mg, 13%) and **3** as a clear, colourless oil (39 mg, 25%).

2c
IR (film): 3343 (br s) cm^{-1}.

^1H NMR: δ = 5.200 (1 H, tq, *J* = 6.6, 1.8 Hz), 3.648 (2 H, m), 2.505 (1 H, m), 2.315 (4 H, m), 1.8–1.74 (1 H, m), 1.73–1.65 (1 H, m), 1.63–1.44 (4 H, m), 1.25 (1 H, m), 0.897 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 151.10 (0), 116.07 (2), 62.88 (2), 42.12 (1), 33.71 (2), 32.93 (2), 31.48 (2), 27.89 (2), 24.11 (2), 12.34 (3).

LRMS (APCI): *m*/*z* = 196 ($M + H^+$ + MeCN).

HRMS: *m*/*z* calcd for $C_{10}H_{18}O$ (M^+): 154.1358; found: 154.1359.

3
IR (film): 1665 (w) cm^{-1}.

^1H NMR: δ = 5.67 (1 H, dtd, *J* = 15.4, 6.6, 0.75 Hz), 5.44 (1 H, ddt, *J* = 15.1, 7.0, 1.5 Hz), 4.21 (1 H, q, *J* = 7.0 Hz), 3.89 (1 H, dt, *J* = 8.5, 7.0 Hz), 3.75 (1 H, td, *J* = 7.9, 6.2 Hz), 2.02 (2 H, q, *J* = 6.4 Hz), 1.90 (2 H, m), 1.57 (1 H, dq, *J* = 11.8, 8.1 Hz), 1.34 (5 H, m), 0.88 (3 H, t, *J* = 7.2 Hz).

^{13}C NMR: δ = 133.01 (1), 130.71 (1), 80.15 (1), 67.98 (2), 32.38 (2), 32.04 (2), 31.40 (2), 26.09 (2), 22.35 (2), 14.06 (3).

LRMS (EI): *m*/*z* (%) = 154 (M^+, 3), 111 (26), 97 (100).

HRMS: *m*/*z* calcd for $C_{10}H_{18}O$ (M^+): 154.1358; found: 154.1371.

(*E*)-2-(1-Pentenyl)tetrahydro-2*H*-pyran (4)
Prepared from **1d** by Method A (2 mmol scale). Purification by column chromatography (5% Et_2O in petroleum ether) provided a clear, colourless oil (95 mg, 31%).

IR (film): 1664 (w) cm^{-1}.

^1H NMR: δ = 5.67 (1 H, dtd, *J* = 15.5, 6.6, 0.75 Hz), 5.47 (1 H, ddt, *J* = 15.5, 6.3, 1.3 Hz), 4.01 (1 H, d + fs, *J* = 11 Hz), 3.75 (1 H, br dd, *J* = 10, 7 Hz), 3.48 (1 H, t, *J* = 11 Hz), 2.00 (2 H, q, *J* = 7.1 Hz), 1.85 (1 H, m), 1.65–1.45 (5 H, m), 1.39 (2 H, app. sextet, *J* = 7.4 Hz), 0.89 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 131.83 (1), 131.50 (1), 78.45 (1), 68.49 (2), 34.58 (2), 32.37 (2), 26.03 (2), 23.58 (2), 22.39 (2), 13.86 (3).

LRMS (APCI): *m*/*z* (%) = 196 ($M + H^+ + CH_3CN$, 52), 153 ($M + H^+ - H_2$, 100), 137 (53).

HRMS: *m*/*z* calcd for $C_{10}H_{17}O$ ($M^{+\cdot} - H$): 153.1279; found: 153.1274.

(*E*)-2-(1-Hexenyl)tetrahydro-2*H*-pyran (5a)
Prepared from **1e** by Method A (2 mmol scale). Purification by column chromatography (5% Et_2O in petroleum ether) provided a clear, colourless oil (124 mg, 37%) with data in accordance with literature values.[41]

(*E*)-2-(1-Hexenyl)-2,3-dideuterotetrahydro-2*H*-pyran (5b)
Prepared from **1e** by Method A, but with quench of the organozirconium intermediate by D_2O and MeOD. Purification by column chromatography (5% Et_2O in petroleum ether) provided a clear, colourless oil (51 mg, 30%).

IR (film): 2176 (w), 2079 (w), 1665 (w) cm^{-1}.

^1H NMR: δ = 5.66 (1 H, dt, *J* = 15.5, 6.6 Hz), 5.45 (1 H, d, *J* = 15.4 Hz), 4.00 (1 H, ddt, *J* = 11.0, 4.1, 1.8 Hz), 3.47 (1 H, td, *J* = 11.4, 2.9 Hz), 2.02 (2 H, q, *J* = 6.6 Hz), 1.83 (1 H, m), 1.52 (3 H, m), 1.34 (5 H, m), 0.88 (3 H, t, *J* = 7.2 Hz).

^{13}C NMR: δ = 132.08 (1), 131.24 (1), [78.29 (0), triplet, *J* = 15.3 Hz], 68.44 (2), 32.16 (2), [31.73 (1), triplet, *J* = 19.4 Hz], 31.40 (2), 25.98 (2), 23.45 (2), 22.37 (2), 14.07 (3).

LRMS (APCI): *m*/*z* (%) = 212 (M + MeCN + H^+, 40), 168 (M + H^+ – HD, 100), 153 (M + H^+ – H_2O, 40), 152 (M + H^+ – HDO, 20).

HRMS: *m*/*z* calcd for $C_{11}H_{18}OD_2$ (M^+):170.1640; found: 170.1650.

(*Z*)-3-[(*E*)-2-Butylidenecyclopentylidene]propan-1-ol (2f) and (1*E*,2*E*)-1-Allylidene-2-butylidenecyclopentane (6)
Prepared from enyne **1f** by Method A. After separation and purification by column chromatography (silica gel, 0 to 20 to 40% Et_2O in petroleum ether) **2f** was obtained as a clear, colourless oil (80 mg, 45%), and **6** as a clear, colourless oil (39 mg, 24%).

2f
IR (film): 3330 (br m) cm^{-1}.

^1H NMR: δ = 5.729 (1 H, t, *J* = 7.3 Hz), 5.363 (1 H, t, *J* = 7.1 Hz), 3.319 (2 H, m), 2.563 (2 H, q, *J* = 7.0 Hz), 2.42–2.33 (4 H, m), 2.077 (2 H, q, *J* = 7.4 Hz), 1.648 (2 H, quintet, *J* = 7.3 Hz), 1.5 (1 H, br, s), 1.447 (2 H, app. sextet, *J* = 7.2 Hz), 0.938 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 143.16 (0), 140.00 (0), 126.75 (1), 117.89 (1), 63.08 (2), 36.65 (2), 32.87 (2), 32.43 (2), 31.24 (2), 23.89 (2), 22.89 (2), 14.14 (3).

LRMS (APCI): *m*/*z* = 181 (M + H^+).

HRMS: *m*/*z* calcd for $C_{12}H_{20}O$ (M^+): 180.1514; found: 180.1510.

6
^1H NMR (400 MHz): δ = 6.465 (1 H, ddd, *J* = 16.9, 11.0. 10.1 Hz), 6.294 (1 H, dt, *J* = 11.2, 2.4 Hz), 5.802 (1 H, tt, *J* = 7.5 Hz, 2.6 Hz), 5.100 (1 H, dd, *J* = 16.7, 1.5 Hz), 4.956 (1 H, dd, *J* = 10.2, 1.0 Hz), 2.434 (2 H, td, *J* = 7.3, 2.4 Hz), 2.296 (2 H, tdt, *J* = 7.4, 2.4, 1.4 Hz), 2.015 (2 H, q, *J* = 7.3 Hz), 1.640 (2 H, pentet, *J* = 7.4 Hz), 0.853 (3 H, t, *J* = 7.2 Hz).

^{13}C NMR: δ = 144.20 (0), 141.09 (0), 134.99 (1), 120.53 (1), 117.73 (1), 115.35 (2), 31.90 (2), 31.00 (2), 30.47 (2), 23.98 (2), 23.01 (2), 14.17 (3).

Compound **6** decomposed before other data could be obtained.

Deprotonation of Ethyl Vinyl Ether and Subsequent Alkylation with an Alkyl Iodide or Aldehyde;[20] General Procedure
To a solution of ethyl vinyl ether (0.95 mL, 721 mg, 10 mmol) in THF (8 mL) at –70 °C under argon was added dropwise *t*-BuLi (4.7 mL of a 1.7 M solution in pentanes, 8 mmol), resulting in a bright yellow suspension. The reaction was allowed to warm, resulting in dissolution of the yellow precipitate, and disappearance of the yellow colour at around 0 °C. The resultant solution of ethoxyvinyllithium was re-cooled to –70 °C and a solution of the electrophile (5 mmol) in THF (2 mL) was added. After warming to 0 °C and stirring for 1–5 h, aq sat. NH_4Cl solution (10 mL) was added. After dilution with Et_2O (20 mL), the aqueous phase was separated and extracted with Et_2O (3 × 50 mL), and the combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated. The crude product was purified by Kugelrohr distillation (Table 2).

2-Ethoxy-5-phenyl-1,6-heptadiene (18a)
Purified by Kugelrohr distillation (100 °C/0.6 mbar) to give a clear, colourless oil (81%).

IR (film): 1652 (s), 1630 (m), 1600 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 7.3–7.0 (5 H, m), 5.923 (1 H, ddd, *J* = 17.4, 9.9, 7.7 Hz), 5.1–4.9 (2 H, m), 3.977 (1 H, s), 3.915 (1 H, s), 3.523 (2 H, q, *J* = 7.0 Hz), 3.278 (1 H, q, *J* = 7.3 Hz), 2.21 (2 H, m), 2.09 (2 H, m), 1.122 (3 H, t, *J* = 6.9 Hz).

^{13}C NMR (C_6D_6): δ = 163.36 (0), 144.45 (0), 142.50 (1), 128.73 (1), 128.09 (1), 126.46 (1), 114.20 (2), 81.04 (2), 62.67 (2), 49.63 (1), 33.63 (2), 33.51 (2), 14.52 (3).

LRMS (APCI): *m*/*z* (%) = 217 (M + H^+, 30), 215 (M + H^+ – H_2, 20), 187 (100), 171 (55).

HRMS: *m*/*z* calcd for $C_{15}H_{20}O$ (M^+): 216.1514; found: 216.1530.

2-Ethoxy-3-hydroxy-5-phenylhepta-1,6-diene (18b)
Purified by Kugelrohr distillation (130 °C/0.8 mbar) to give a clear, colourless oil (72%) as a 1:1 mixture of diastereoisomers.

IR (film): 3383 (br m), 1660 (m), 1646 (m), 1630 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 7.4–7.1 (5 H, m), 6.046 (1 H, m), 5.3–5.0 (2 H, m), 4.3–3.7 (4 H, m), 3.495 (2 H, m), 2.4–2.2 (2 H, m), 1.846 (1 H, m), 1.123 and 1.083 (3 H, each t, *J* = 7.2 Hz).

^{13}C NMR (C_6D_6): δ = 164.77 (0), 164.68 (0), 144.84 (0), 143.78 (0), 142.97 (1), 141.90 (1), 128.80 (1), 128.47 (1), 126.59 (1), 126.46 (1), 80.86 (2), 80.72 (2), 70.92 (1), 70.75 (1), 62.90 (2), 62.83 (2), 46.49 (1), 46.35 (1), 41.85 (2), 41.44 (2), 14.35 (3), 14.29 (3).

LRMS (APCI): *m*/*z* (%) = 232 (M^+, 10), 215 (100), 187 (60), 169 (70).

HRMS: *m*/*z* calcd for $C_{15}H_{20}O_2$ (M^+): 232.1463; found: 232.1457.

2-Ethoxy-3-hydroxy-4-phenyl-1,6-heptadiene (18ci)
Purified by Kugelrohr distillation (100 °C/1 mbar) to give a clear, colourless oil (70%).

IR (film): 3440 (br m), 1650 (m), 1639 (m), 1630 (m) cm^{-1}.

^1H NMR (C_6D_6): δ = 7.3–7.1 (5 H, m), 5.844 (1 H, ddt, *J* = 17.1, 10.2, 6.9 Hz), 5.154 (1 H, ddt, *J* = 17.1, 2.2, 1.5 Hz), 5.014 (1 H, ddt, *J* = 10.2, 2.2, 1.3 Hz), 4.214 (1 H, br t, *J* = 6.2 Hz), 4.154 (1 H, d, *J* = 2.0 Hz), 3.863 (1 H, d, *J* = 2.0 Hz), 3.376 (2 H, m), 3.228 (1 H, ddd, *J* = 10.9, 6.7, 4.0 Hz), 2.956 (1 H, dddt, *J* = 14.4, 7.0, 3.0, 1.5 Hz), 2.611 (1 H, dddt, *J* = 14.4, 10.9, 7.0, 1.5 Hz), 1.974 (1 H, d, *J* = 6.2 Hz), 1.068 (3 H, t, *J* = 6.9 Hz).

^{13}C NMR (C_6D_6): δ = 162.26 (0), 142.31 (0), 137.59 (1), 129.12 (1), 128.31 (1), 126.60 (1), 115.99 (2), 82.83 (2), 77.17 (1), 62.69 (2), 50.66 (1), 35.21 (2), 14.28 (3).

LRMS (APCI): *m*/*z* (%) = 232 (M^+, 30), 215 (100), 187 (60), 169 (65).

HRMS: *m*/*z* calcd for $C_{15}H_{20}O_2$ (M^+): 232.1463; found: 232.1468.

***tert*-Butyl{[1-(1-ethoxyvinyl)-2-phenyl-4-pentenyl]oxy}dimethylsilane (18cii)**
tert-Butyldimethylsilyl chloride (155 mg, 1.03 mmol) and imidazole (64 mg, 0.94 mmol) were added to a solution of **18ci** (203 mg, 0.94 mmol) in DMF (1.5 mL). The mixture was stirred 16 h, and poured into aq sat. NH_4Cl solution and Et_2O. The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried (Na_2SO_4), filtered and concentrated. The crude product was purified by column chromatography (Al_2O_3, petroleum ether) to give the desired silyl ether (186 mg, 57%).

IR (film): 1660 (w), 1640 (w), 1620 (w) cm^{-1}.

^{1}H NMR: δ = 7.3–7.1 (5 H, m), 5.817 (1 H, ddt, *J* = 17.1, 10.1, 6.8 Hz), 5.116 (1 H, d + fs, *J* = 17.4 Hz), 4.955 (1 H, d + fs, *J* = 10.1 Hz), 4.298 (1 H, d, *J* = 1.7 Hz), 4.270 (1 H, d, *J* = 5.5 Hz), 3.932 (1 H, d, *J* = 1.7 Hz), 3.390 (2 H, m), 3.317 (1 H, ddd, *J* = 11.2, 5.5, 3.7 Hz), 2.955 (1 H, ddd, *J* = 14.4, 6.8, 3.7 Hz), 2.750 (1 H, ddd, *J* = 14.4, 11.2, 6.8 Hz), 1.077 (9 H, s), 1.072 (3 H, t, *J* = 7.1 Hz), 0.078 (3 H, s), –0.147 (3 H, s).

^{13}C NMR: δ = 163.37 (0), 142.26 (0), 137.78 (1), 129.56 (1), 128.19 (1), 126.54 (1), 115.88 (2), 82.88 (2), 78.30 (1), 62.72 (2), 50.73 (1), 33.75 (2), 26.22 (3), 18.48 (0), 14.40 (3), –4.56 (3), –5.41 (3).

LRMS (APCI): *m*/*z* (%) = 301 (M + H$^+$ – EtOH, 10), 215 (M + H$^+$ – HOSiMe$_2$Bu-*i*, 25), 156 (65), 124 (100).

HRMS: *m*/*z* calcd for $C_{21}H_{34}O_2Si$ (M$^+$): 346.2328; found: 346.2328.

4,4-Dimethyl-2-ethoxy-3-hydroxy-1,6-heptadiene (18d)
Purified by Kugelrohr distillation (110 °C/1.0 mbar) to give a clear, colourless oil (75%).

IR (film): 3466 (br m), 1657 (m), 1637 (m), 1625 (m) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 6.031 (1 H, ddt, *J* = 17.9, 10.4, 7.7 Hz), 5.20–5.10 (2 H, m), 4.163 (1 H, d, *J* = 1.0 Hz), 3.990 (1 H, d, *J* = 1.0 Hz), 3.908 (1 H, d, *J* = 6.2 Hz), 3.428 (2 H, m), 2.432 (1 H, dd, *J* = 13.4, 7.7 Hz), 2.233 (1 H, dd, *J* = 13.4, 7.2 Hz), 1.990 (1 H, d, *J* = 6.2 Hz), 1.133 (3 H, s), 1.089 (3 H, s), 1.068 (3 H, t, *J* = 7.0 Hz).

^{13}C NMR (C_6D_6): δ = 163.21 (0), 136.56 (1), 117.72 (2), 83.81 (2), 79.82 (1), 63.09 (2), 44.58 (2), 38.58 (0), 24.04 (3), 23.72 (3), 14.79 (3).

LRMS (APCI): *m*/*z* (%) = 184 (M$^+$, 20), 183 (15), 167 (100).

HRMS: *m*/*z* calcd for $C_{11}H_{20}O_2$ (M$^+$): 184.1463; found: 184.1457.

1-(2-Allylphenyl)-2-ethoxy-2-propen-1-ol (18e)
Purified by Kugelrohr distillation (110 °C/1 mbar) to give a clear, colourless oil (70%).

IR (film): 3422 (br m), 1636 (m) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 7.636 (1 H, d, *J* = 6.9 Hz), 7.1–7.0 (3 H, m), 5.875 (1 H, ddt, *J* = 15.9, 9.4, 6.3 Hz), 5.325 (1 H, s), 5.0–4.9 (2 H, m), 4.298 (1 H, d, *J* = 2.2 Hz), 3.918 (1 H, d, *J* = 2.3 Hz), 3.2–3.4 (4 H, m), 2.065 (1 H, s), 0.853 (3 H, t, *J* = 7.1 Hz).

^{13}C NMR (C_6D_6): δ = 164.13 (0), 140.24 (0), 138.23 (0), 137.86 (1), 129.94 (1), 128.04 (1), 127.50 (1), 126.73 (1), 115.81 (2), 82.08 (2), 71.25 (1), 63.09 (2), 37.11 (2), 14.26 (3).

LRMS (APCI): *m*/*z* (%) = 218 (M$^+$, 10), 201 (100), 189 (15), 173 (50).

HRMS: *m*/*z* calcd for $C_{14}H_{18}O_2$ (M$^+$): 218.1307; found: 218.1306.

1-(2-Vinylphenyl)-2-ethoxy-2-propen-1-ol (18f)
Purified by Kugelrohr distillation (110 °C/0.8 mbar) to give a clear, colourless oil (86%).

IR (film): 3412 (br s), 1660 (m), 1626 (s) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 7.732 (1 H, dd, *J* = 7.7, 1.7 Hz), 7.456 (1 H, dd, *J* = 7.7, 1.5 Hz), 7.249 (1 H, dd, *J* = 17.4, 10.9 Hz), 7.203 (1 H, td, *J* = 7.7, 1.5 Hz), 7.126 (1 H, td, *J* = 7.7, 1.5 Hz), 5.587 (1 H, dd, *J* = 17.4, 1.5 Hz), 5.472 (1 H, br s), 5.214 (1 H, dd, *J* = 10.9, 1.5 Hz), 4.361 (1 H, dd, *J* = 2.3, 0.7 Hz), 4.016 (1 H, d, *J* = 2.2 Hz), 3.398 (2 H, m), 2.187 (1 H, br s), 0.961 (3 H, t, *J* = 7.1 Hz).

^{13}C NMR (C_6D_6): δ = 163.75 (0), 139.29 (0), 137.34 (0), 135.27 (1), 128.33 (1), 128.00 (1), 127.35 (1), 126.25 (1), 116.02 (2), 82.47 (2), 71.49 (1), 63.11 (2), 14.24 (3).

LRMS (APCI): *m*/*z* (%) = 200 (M + H$^+$ + MeCN – H_2O, 34), 187 (M + H$^+$ – H_2O, 100), 175 (20), 159 (85).

HRMS: *m*/*z* calcd for $C_{13}H_{16}O_2$ (M$^+$): 204.1150; found: 204.1145.

2-Ethoxy-3-hydroxy-7-phenylhepta-1-ene-6-yne (18g)
Purified by Kugelrohr distillation (150 °C/0.8 mbar) to give a clear, colourless oil (64%).

IR (film): 3417 (br m), 2240 (w), 1659 (m), 1626 (m), 1606 (w) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 7.506 (2 H, m), 7.038 (3 H, m), 4.258 (1 H, d, *J* = 2.3 Hz), 4.232 (1 H, m), 3.895 (1 H, d, *J* = 2.0 Hz), 3.420 (2 H, q, *J* = 7.0 Hz), 2.569 (1 H, dd, *J* = 7.7, 3.2 Hz), 2.546 (1 H, dd, *J* = 7.7, 1.7 Hz), 2.15–1.85 (2 H, m), 1.780 (1 H, d, *J* = 5.0 Hz), 1.035 (3 H, t, *J* = 7.1 Hz).

^{13}C NMR (C_6D_6): δ = 164.03 (0), 131.98 (1), 128.51 (1), 127.73 (1), 124.79 (0), 90.39 (0), 81.64 (0), 80.95 (2), 71.83 (1), 62.92 (2), 34.97 (2), 16.11 (2), 14.31 (3).

LRMS (APCI): *m*/*z* (%) = 231 (30), 185 (50).

HRMS: *m*/*z* calcd for $C_{15}H_{18}O_2$ (M$^+$): 230.1307; found: 230.1314.

2-Ethoxydec-1-ene-6-yne (18h)
Purified by Kugelrohr distillation (100 °C/1 mbar) to give a clear, colourless oil (89%).

IR (film): 1653 (s) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 4.046 (1 H, d, *J* = 1.5 Hz), 3.939 (1 H, d, *J* = 1.5 Hz), 3.546 (2 H, q, *J* = 7.0 Hz), 2.375 (2 H, t, *J* = 7.4 Hz), 2.261 (2 H, tt, *J* = 7.2, 2.4 Hz), 2.133 (2 H, tt, *J* = 7.0, 2.4 Hz), 1.877 (2 H, quintet, *J* = 7.2 Hz), 1.506 (2 H, sextet, *J* = 7.1 Hz), 1.156 (3 H, t, *J* = 7.0 Hz), 0.998 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR (C_6D_6): δ = 163.06 (0), 81.25 (2), 80.65 (0), 80.35 (0), 62.72 (2), 34.80 (2), 27.59 (2), 22.98 (2), 21.21 (2), 18.70 (2), 14.57 (3), 13.65 (3).

LRMS (EI): *m*/*z* (%) = 180 (M$^+$, 7), 165 (14), 152 (59), 137 (48), 119 (31), 86 (50), 58 (100).

HRMS: *m*/*z* calcd for $C_{12}H_{20}O$ (M$^+$): 180.1514; found: 180.1521.

1-Iodo-5-nonyne (17i)
Prepared in 68% yield by alkylation of 1-pentynyllithium with 1-chloro-4-iodobutane followed by conversion of chloride to iodide with NaI in acetone.

IR (film): no characteristic absorptions.

^{1}H NMR: δ = 3.218 (2 H, t, *J* = 7.0 Hz), 2.199 (2 H, tt, *J* = 7.0, 2.4 Hz), 2.123 (2 H, tt, *J* = 7.2, 2.4 Hz), 1.943 (2 H, m), 1.593 (2 H, m), 1.503 (2 H, app. sextet, *J* = 7.4 Hz), 0.970 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 81.00 (0), 79.41 (0), 32.62 (2), 29.89 (2), 22.63 (2), 20.88 (2), 17.88 (2), 13.66 (3), 6.62 (2).

HRMS: *m*/*z* calcd for $C_9H_{15}I$ (M$^+$): 250.0212; found: 250.0219.

2-Ethoxyundec-1-ene-7-yne (18i)
Purified by Kugelrohr distillation (130 °C/0.8 mbar) to give a clear, colourless oil (71%).

IR (film): 1652 (s) cm^{-1}.

^{1}H NMR (C_6D_6): δ = 3.976 (1 H, d, *J* = 1.5 Hz), 3.898 (1 H, d, *J* = 1.5 Hz), 3.524 (2 H, q, *J* = 7.0 Hz), 2.20–2.14 (4 H, m), 2.100 (2 H, tt, *J* = 7.0, 2.4 Hz), 1.744 (2 H, m), 1.63–1.41 (4 H, m), 1.136 (3 H, t, *J* = 7.2 Hz), 0.962 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR (C_6D_6): δ = 163.31 (0), 80.72 (2), 80.31 (0), 80.22 (0), 62.48 (2), 34.98 (2), 28.86 (2), 26.86 (2), 22.77 (2), 21.01 (2), 18.87 (2), 14.42 (3), 13.47 (3).

LRMS (APCI): *m*/*z* (%) = 195 (M + H$^+$, 100), 194 (M$^+$, 30).

HRMS: *m*/*z* calcd for $C_{13}H_{22}O$ (M$^+$): 194.1670; found: 194.1670.

(1*R,2*S**)-1-(2-Methyl-3-methylenecyclopentyl)benzene (19a)**
Prepared by cocyclisation of diene **18a** (Method A). Purification by column chromatography (silica gel, hexane) provided a clear, colourless oil (123 mg, 72%). The product was a 17:1 mixture of diastereoisomers, as determined by GC, t_R 13.85 min (major), 14.06 min (minor).

IR (film): 1654 (m), 1602 (m) cm^{-1}.

^1H NMR (400 MHz): δ (major diastereoisomer) = 7.3–7.1 (5 H, m), 4.844 (1 H, q, *J* = 2.3 Hz), 4.759 (1 H, q, *J* = 2.5 Hz), 2.525 (1 H, ddq, *J* = 15.7, 8.9, 2.0 Hz), 2.411 (1 H, td, *J* = 11.1, 6.3 Hz), 2.4–2.3 (2 H, m), 1.983 (1 H, dddd, *J* = 12.3, 8.1, 6.3, 1.9 Hz), 1.689 (1 H, dtd, *J* = 12.4, 10.9, 8.9 Hz), 0.929 (3 H, d, *J* = 6.2 Hz). Methyl group of minor diastereoisomer, δ = 0.629 (3 H, d, *J* = 7.0 Hz).

^{13}C NMR (100 MHz): δ (major isomer) = 157.35 (0), 144.29 (0), 128.82 (1), 127.92 (1), 126.68 (1), 104.86 (2), 54.80 (1), 46.94 (1), 33.60 (2), 32.21 (2), 16.63 (3); δ (Minor diastereoisomer (quaternaries not seen) = 128.66 (1), 128.42 (1), 126.28 (1), 105.43 (2), 49.66 (1), 43.76 (1), 31.84 (2), 28.85 (2), 16.22 (3).

LRMS (APCI): *m*/*z* = 172 (M^+, 10), 157 (100).

HRMS: *m*/*z* calcd for $C_{13}H_{16}$ (M^+): 172.1252; found: 172.1251.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.42; H, 9.39.

(1*S,3*S**,4*R**)- and (1*R**, 3*S**, 4*R**)-3-Methyl-2-methylene-4-phenyl-1-cyclopentanol (19b)**
Prepared by cocyclisation of diene **18b** (Method A). Purification by column chromatography (10% Et_2O in hexanes) provided a viscous, colourless oil (103 mg, 55%). The product was a 1:1 mixture of diastereoisomers, as determined by GC, corresponding to a 100% de; t_R 16.95 and 19.05 min.

IR (film): 3352 (br s), 1648 (w), 1601 (w) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.320 (0.5 H, dd, *J* = 2.9, 1.5 Hz), 5.248 (0.5 H, dd, *J* = 2.9, 2.2 Hz), 5.090 (0.5 H, dd, *J* = 2.2, 1.5 Hz), 5.051 (0.5 H, t, *J* = 2.6 Hz), 4.690 (0.5 H, m), 4.628 (0.5 H, tt, *J* = 6.8, 2.2 Hz), 2.914 (0.5 H, td, *J* = 11.4, 7.0 Hz), 2.669 (0.5 H, m), 2.489 (1 H, m), 2.135 (0.5 H, ddd, *J* = 13.6, 6.6, 1.8 Hz), 2.006 (0.5 H, ddd, *J* = 13.6, 11.8, 5.9 Hz), 1.796 (1 H, m), 1.449 (0.5 H, s), 1.292 (0.5 H, s), 1.105 (1.5 H, d, *J* = 6.6 Hz), 1.054 (1.5 H, d, *J* = 6.6 Hz).

^{13}C NMR: δ = 160.68 (0), 159.43 (0), 143.45 (0), 143.04 (0), 128.65 (1), 128.63 (1), 127.65 (1), 127.62 (1), 126.67 (1), 126.58 (1), 108.55 (2), 107.41 (2), 74.42 (1), 73.83 (1), 50.93 (1), 50.10 (1), 45.73 (1), 45.00 (1), 43.13 (2), 42.89 (2), 17.11 (3), 16.79 (3).

LRMS (APCI): *m*/*z* = 171 (M + H^+ – H_2O).

HRMS: *m*/*z* calcd for $C_{13}H_{16}O$ (M^+): 188.1201; found: 188.1208.

(1*S,3*S**,5*R**)-3-Methyl-2-methylene-5-phenyl-1-cyclopentanol (19c)**
Prepared by cocyclisation of diene **18ci** (Method A). Purification by column chromatography (5% Et_2O in hexanes) provided a viscous, colourless oil (82 mg, 44%). The product was a 7:1 mixture of diastereoisomers, as determined by GC; t_R 14.51 min (major), 14.20 min (minor). The major diastereoisomer has the relative stereochemistry (1*S*,3*S*,5*R*), as determined by GOESY experiments (correlation between proton adjacent to phenyl group, and methyl group). NMR data provided is for the major diastereoisomer:

IR (film): 3415 (br m), 1660 (w), 1600 (m) cm^{-1}.

^1H NMR (400 MHz): δ = 7.4–7.2 (5 H, m), 5.249 (1 H, ddd, *J* = 2.4, 1.3, 0.6 Hz), 5.094 (1 H, ddd, *J* = 2.2, 1.5, 0.7 Hz), 4.603 (1 H, d, *J* = 5.0 Hz), 3.364 (1 H, td, *J* = 7.8, 5.5 Hz), 3.0–2.9 (1 H, m), 2.461 (1 H, dtd, *J* = 12.9, 8.8, 0.3 Hz), 1.710 (1 H, dddt, *J* = 12.3, 7.2, 4.5, 0.5 Hz), 1.564 (1 H, br s), 1.200 (3 H, d, *J* = 7.1 Hz).

^{13}C NMR: δ = 159.37 (0), 139.61 (0), 128.86 (1), 128.66 (1), 126.90 (1), 109.45 (2), 77.63 (1), 48.58 (1), 35.89 (2), 34.93 (1), 22.34 (3).

LRMS (APCI): *m*/*z* = 171 (M + H^+ – H_2O).

HRMS: *m*/*z* calcd for $C_{13}H_{16}O$ (M^+): 188.1201; found: 188.1196.

The title compound was also prepared by cocyclisation of the silyl protected diene **18cii** (Method A, 0.78 mmol scale) and subsequent deprotection using TFA–H_2O–MeOH (1:1:1) by stirring for 20 h to afford **19c** (47%) as a 5:4 mixture of diastereoisomers (GC). NMR data for the minor (1*S**,3*R**,5*R**)-diastereoisomer could be distinguished:

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.319 (1 H, d, *J* = 2.0 Hz), 5.121 (1 H, s), 4.556 (1 H, d, *J* = 5.2 Hz), 3.168 (1 H, dt, *J* = 11.9, 5.7 Hz), 2.7–2.55 (1 H, m), 2.189 (1 H, dt, *J* = 11.9, 6.7 Hz), 1.912 (1 H, q, *J* = 11.8 Hz), 1.290 (3 H, d, *J* = 6.7 Hz).

^{13}C NMR: δ = 158.95 (0), 139.31 (0), 128.66 (1), 128.51 (1), 126.75 (1), 109.33 (2), 76.74 (1), 49.57 (1), 36.81 (2), 36.47 (1), 19.35 (3).

(1*S,4*S**)-2,2,4-Trimethyl-5-methylene-1-cyclopentanol (19d)**
Prepared by cocyclisation of diene **18d** (Method A). Purification by column chromatography (silica gel, 20% Et_2O in petroleum ether) provided a viscous, colourless oil (103 mg, 74%). The product was a 4:1 mixture of diastereoisomers as determined by GC; t_R 8.64 min (minor), 8.77 min (major).

IR (film): 3386 (br m), 1650 (m) cm^{-1}.

^1H NMR (400 MHz): δ (major diastereoisomer) = 5.113 (1 H, t, *J* = 2.6 Hz), 4.989 (1 H, td, *J* = 2.5, 0.6 Hz), 4.001 (1 H, q, *J* = 2.5 Hz), 2.57 (1 H, m), 1.743 (1 H, dd, *J* = 12.7, 8.2 Hz), 1.582 (1 H, br s), 1.098 (3 H, d, *J* = 6.9 Hz), 1.081 (3 H, s), 1.050 (1 H, ddq, *J* = 12.7, 10.2, 0.7 Hz), 0.791 (3 H, s); δ [minor diastereoisomer (where seen)] = 5.157 (1 H, m), 4.966 (1 H, td, *J* = 2.2, 0.6 Hz), 3.923 (1 H, t, *J* = 1.6 Hz), 1.145 (3 H, d, *J* = 7.0 Hz), 0.988 (3 H, s), 0.906 (3 H, s).

^{13}C NMR: δ (major diastereoisomer) = 159.98 (0), 106.52 (2), 82.46 (1), 45.15 (1), 41.06 (0), 33.52 (2), 26.64 (3), 21.45 (3), 19.61 (3); δ [minor diastereoisomer (where seen)] = 106.74 (2), 83.00 (1), 33.08 (2), 26.79 (3), 22.19 (3), 20.88 (3).

LRMS (APCI): *m*/*z* = 123 (M + H^+ – H_2O).

HRMS: *m*/*z* calcd for $C_9H_{16}O$ (M^+): 140.1201; found: 140.1205.

3-Methyl-2-methylene-1,2,3,4-tetrahydro-1-naphthalenol (19e)
Prepared by cocyclisation of diene **18e** (Method A, 2 mmol scale). Chromatographic separation (silica gel, 5% Et_2O in hexanes) of the diastereoisomers and purification provided a less polar isomer as a white wax (85 mg, 24%) and a more polar diastereoisomer as a white powder (130 mg, 37%), which was further purified by precipitation from MeOH–pentane. GC analysis of the crude product showed an 8:7 mixture of diastereoisomers; t_R 18.35 min (major) and 18.92 min (minor).

Less Polar Diastereoisomer
Mp 39–41°C.

IR (film): 3271(w), 1657 (m) cm^{-1}.

^1H NMR: δ = 7.604 (1 H, d, *J* = 7.0 Hz), 7.271 (1 H, td, *J* = 7.2, 1.2 Hz), 7.222 (1 H, td, *J* = 7.2, 1.7 Hz), 7.097 (1 H, dd, *J* = 7.0, 1.7 Hz), 5.283 (1 H, br s), 5.228 (1 H, br d, *J* = 3.7 Hz), 5.029 (1 H, dt, *J* = 2.2, 1.1 Hz), 2.959 (1 H, apparent q, *J* = 10.3 Hz), 2.4 (2 H, m), 2.162 (1 H, br d, *J* = 7.4 Hz), 1.278 (3 H, d, *J* = 6.2 Hz).

^{13}C NMR: δ = 153.34 (0), 139.48 (0), 136.69 (0), 128.16 (1), 127.54 (1), 127.23 (1), 126.67 (1), 105.02 (2), 72.35 (1), 39.89 (2), 33.97 (1), 18.91 (3).

LRMS (APCI): *m*/*z* = 157 (M + H^+ – H_2O).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.42; H, 8.09.

More Polar Diastereoisomer
Mp 74–75 °C.

IR (film): 3226 (br m), 1655 (w) cm^{-1}.

^1H NMR: δ = 7.5–7.1 (4 H, m), 5.207 (1 H, d, *J* = 1.0 Hz), 5.121 (1 H, br s), 5.016 (1 H, t, *J* = 1.2 Hz), 3.023 (1 H, dd, *J* = 15.6, 5.3 Hz), 2.95–2.8 (1 H, m), 2.482 (1 H, dd, *J* = 15.6, 10.5 Hz), 1.992 (1 H, br s), 1.253 (3 H, d, *J* = 6.7 Hz).

^{13}C NMR: δ = 152.62 (0), 138.06 (0), 137.05 (0), 128.85 (1), 128.49 (1), 127.95 (1), 126.66 (1), 109.31 (2), 72.89 (1), 39.67 (2), 30.99 (1), 18.22 (3).

LRMS (APCI): *m*/*z* (%) = 173 (15), 157 (100).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.02; H, 8.12.

3-Methyl-2-methylene-1-indanol (19f)
Prepared by cocyclisation of diene **18f** (Method A). Purification by column chromatography (silica gel, 10% Et_2O in petroleum ether), then further chromatography (silica gel, 10% Et_2O in hexanes) provided a single diastereoisomer of the title compound as a waxy white solid (41 mg, 26%); mp 50–52 °C.

IR (CH_2Cl_2): 3350 (br s), 1664 (w), 1609 (w) cm^{-1}.

^1H NMR: δ = 7.50–7.45 (1 H, m), 7.4–7.2 (3 H, m), 5.5 (2 H, m), 5.284 (1 H, d, *J* = 1.5 Hz), 3.884 (1 H, q, *J* = 7.1 Hz), 2.003 (1 H, br s), 1.390 (3 H, d, *J* = 7.4 Hz).

^{13}C NMR: δ = 158.80 (0), 146.73 (0), 142.83 (0), 129.14 (1), 127.51 (1), 125.13 (1), 124.05 (1), 110.71 (2), 76.22 (1), 41.84 (1), 21.34 (3).

LRMS (APCI): *m*/*z* (%) = 160 (M^+, 8), 143 (M + H^+ – H_2O, 100).

HRMS: *m*/*z* calcd for $C_{11}H_{12}O$ (M^+): 160.0888; found: 160.0887.

2-Methylene-3-[(*E*)-1-phenylmethylidene]-1-cyclopentanol (19g)
Prepared by cyclisation of the enyne **18g** (Method A). Purification by column chromatography (silica gel, 20 to 35% Et_2O in petroleum ether) provided a viscous, colourless oil (62 mg, 33%).

IR (film): 1598 (w) cm^{-1}.

^1H NMR: δ = 7.5–7.2 (5 H, m), 6.915 (1 H, t, *J* = 2.6 Hz), 5.603 (1 H, d, *J* = 1.7 Hz), 5.205 (1 H, d, *J* = 1.5 Hz), 4.618 (1 H, t, *J* = 6.2 Hz), 2.899 (1 H, dddd, *J* = 16.6, 8.2, 5.7, 2.5 Hz), 2.659 (1 H, dtd, *J* = 16.8, 7.7, 2.7 Hz), 2.101 (1 H, ddt, *J* = 13.3, 7.9, 5.7 Hz), 2.05 (1 H, br s), 1.721 (1 H, m).

^{13}C NMR: δ = 153.71 (0), 139.13 (0), 137.73 (0), 128.97 (1), 128.49 (1), 126.91 (1), 121.58 (1), 104.85 (2), 75.21 (1), 33.88 (2), 28.80 (2).

LRMS (EI): *m*/*z* (%) = 186 (M^+, 13), 168 (M^+ – H_2O, 65), 142 (68).

HRMS: *m*/*z* calcd for $C_{13}H_{14}O$ (M^+): 186.1046; found: 186.1045.

1-[(*E*)-Butylidene]-2-methylenecyclopentane (19h)
Prepared by cocyclisation of enyne **18h** (Method A). Purification by column chromatography (silica gel, hexanes), then Kugelrohr distillation (120 °C/10 mbar) provided a clear, colourless oil (92 mg, 68%) with data in accordance with literature values.[42]

Undec-7-ene-2-one Dimers 19i
Prepared by treatment of the enyne **18i** with zirconocene(1-butene) (Method A). Column chromatography (silica gel, Et_2O) provided a mixture of dimeric products (87 mg, 52%). Selected signals from the NMR spectra are listed below.

^1H NMR: δ = 5.324 (2 H, qd, *J* = 7.4, 2.5 Hz), 2.135 (3 H, s), 2.125 (3 H, s), 0.905 (3 H, t, *J* = 7.4 Hz), 0.863 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 209.33 (0), 141.54 (0), 140.82 (0), 126.53 (1), 125.74 (1), 29.99 (3), 14.25 (3), 14.08 (3).

LRMS (APCI): *m*/*z* (%) = 335 (M + H^+ 85), 317 (100).

***N*-Allyl-*N*-benzyl-*N*-(2-chloroallyl)amine (20a); Typical Procedure**
2,3-Dichloro-1-propene (3.33 g, 30 mmol) in MeCN (10 mL) was added to a suspension of K_2CO_3 (6.9 g, 50 mmol) and *N*-allylbenzylamine (2.94 g, 20 mmol) in MeCN (60 mL). The mixture was subsequently refluxed for 19 h, before cooling and dilution with H_2O and Et_2O. The aqueous phase was extracted with Et_2O, and the combined organic phases were washed with H_2O and brine, dried ($MgSO_4$), filtered and concentrated. The crude material was purified by column chromatography (silica gel, petroleum ether), then Kugelrohr distillation (120 °C/0.7 mbar) to provide a clear, colourless oil (3.282 g, 74%).

IR (film): 1634 (s) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.904 (1 H, ddt, *J* = 16.9, 10.3, 6.2 Hz), 5.512 (1 H, s), 5.368 (1 H, s), 5.3–5.15 (2 H, m), 3.684 (2 H, s), 3.259 (2 H, s), 3.164 (2 H, d, *J* = 5.9 Hz).

^{13}C NMR: δ = 140.35 (0), 139.16 (0), 135.48 (1), 128.85 (1), 128.43 (1), 127.16 (1), 117.90 (2), 113.99 (2), 59.69 (2), 57.57 (2), 56.29 (2).

LRMS (ES^+): *m*/*z* = 224 and 222 (M + H^+, 100%).

HRMS: *m*/*z* calcd for $C_{13}H_{16}NCl$ (M + H^+): 224.1565; found: 224.1552.

***N*-Benzyl-*N*-(3-butenyl)-*N*-(2-chloroallyl)amine (20b)**
Prepared by alkylation of *N*-(3-butenyl)benzylamine (0.805g, 5 mmol) with 2,3-dichloro-1-propene. Purification by column chromatography (silica gel, 10% Et_2O in petroleum ether) followed by Kugelrohr distillation (115 °C/0.7 mbar) yielded **20b** as a clear, colourless oil (681 mg, 58%).

IR (film): 1636 (s) cm^{-1}.

^1H NMR: δ = 7.35–7.15 (5 H, m), 5.719 (1 H, ddt, *J* = 16.9, 9.9, 7.0 Hz), 5.400 (1 H, s), 5.246 (1 H, s), 5.0–4.9 (2 H, m), 3.591 (2 H, s), 3.158 (2 H, s), 2.520 (2 H, t, *J* = 7.4 Hz), 2.187 (2 H, q, *J* = 7.1 Hz).

^{13}C NMR: δ = 140.45 (0), 139.33 (0), 136.81 (1), 128.83 (1), 128.40 (1), 127.13 (1), 115.79 (2), 113.88 (2), 60.28 (2), 57.99 (2), 53.06 (2), 31.81 (2).

LRMS (ES^+): *m*/*z* = 238 and 236 (M + H^+).

HRMS: *m*/*z* calcd for $C_{11}H_{13}N^{35}Cl$ (M + H^+ – C_3H_5): 194.0737; found: 194.0735.

***N*-Allyl-*N*-(2-chloro-2-propenyl)benzylamine**
Prepared from benzylamine (10.7 g, 0.1 mol) and 2,3-dichloro-1-propene. Purification by column chromatography (10% Et_2O in petroleum ether) and subsequent Kugelrohr distillation (100 °C/0.6 mbar) provided a clear, colourless oil (5.422 g, 30%).

IR (film): 1642 (s) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.382 (2 H, s), 3.782 (2 H, s), 3.446 (2 H, s), 1.854 (1 H, s).

^{13}C NMR: δ = 141.02 (0), 139.85 (0), 128.63 (1), 128.44 (1), 127.29 (1), 113.75 (2), 54.91 (2), 51.88 (2).

LRMS (ES^+): *m*/*z* = 184 and 182 (M + H^+).

HRMS: *m*/*z* calcd for $C_{10}H_{12}N^{35}Cl$ (M^+): 181.0658; found: 181.0651.

N-Benzyl-N-(2-chloroallyl)-N-(2-hexynyl)amine (20c)
Prepared by alkylation *N*-allyl-*N*-(2-chloro-2-propenyl)benzylamine (3.63 g, 20 mmol) with the mesylate of 2-hexyn-1-ol. Purification by column chromatography (silica gel, 5% Et_2O in petroleum ether), then Kugelrohr distillation (110 °C/0.4 mbar) provided **20c** as a clear, colourless oil (3.236 g, 62%).

IR (film): 1642 (s) cm^{-1}.

^1H NMR: δ = 7.5–7.2 (5 H, m), 5.526 (1 H, s), 5.384 (1 H, s), 3.708 (2 H, s), 3.370 (2 H, t, *J* = 2.2 Hz), 3.346 (2 H, s), 2.253 (2 H, tt, *J* = 7.0, 2.2 Hz), 1.604 (2 H, app. sextet, *J* = 7.2 Hz), 1.062 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 139.95 (0), 138.65 (0), 129.17 (1), 128.47 (1), 127.33 (1), 114.69 (2), 86.09 (0), 74.21 (0), 59.85 (2), 57.07 (2), 41.86 (2), 22.66 (2), 20.90 (2), 13.74 (3).

LRMS (ES^+): *m*/*z* = 264 and 262 ($M + H^+$).

Anal. Calcd for $C_{16}H_{20}NCl$: C, 73.4; H, 7.70; N, 5.35. Found: C, 73.35; H, 7.89; N, 5.37.

1-Benzyl-3-methyl-4-methylenepyrrolidine (21a)
Prepared by cocyclisation of **20a** (Method A). Purification by column chromatography (silica gel, 20% Et_2O in petroleum ether) provided a clear, colourless oil (132 mg, 71%). This compound has been synthesised previously by a different method,[27] however, no data was provided.

^1H NMR: δ = 7.4–7.2 (5 H, m), 4.905 (1 H, q, *J* = 2.2 Hz), 4.842 (1 H, q, *J* = 2.5 Hz), 3.676 (1 H, d, *J* = 13.2 Hz), 3.597 (1 H, d, *J* = 12.9 Hz), 3.466 (1 H, d, *J* = 13.2 Hz), 3.1–3.0 (2 H, m), 2.8–2.7 (1 H, m), 2.111 (1 H, t, *J* = 8.8 Hz), 1.132 (3 H, d, *J* = 6.6 Hz).

^{13}C NMR: δ = 154.08 (0), 138.96 (0), 129.01 (1), 128.42 (1), 127.17 (1), 104.06 (2), 62.44 (2), 60.83 (2), 59.63 (2), 37.67 (1), 17.82 (3).

LRMS (ES^+): *m*/*z* = 188 ($M + H^+$).

1-Benzyl-4-methyl-3-methylenepiperidine (21b) and N-Allyl-N-benzyl-N-(3-butenyl)amine (22)
Prepared by cocyclisation of diene **20b** (Method A). Separation and purification by column chromatography (silica gel, 10% Et_2O in petroleum ether) and Kugelrohr distillation (110 °C/0.7 mbar) provided **21b** as a clear, colourless oil (107 mg, 53%) with data consistent with the literature.[25] Also isolated was **22**[30] as a clear, colourless oil (72 mg, 36%), contaminated with ~20% of the further reduced product, *N*-allyl-*N*-butylbenzylamine.

1-Benzyl-3-[(Z)-butylidene]-4-methylenepyrrolidine (21c)
Prepared by cocyclisation of enyne **20c** (Method A, 3 mmol scale). Purification by column chromatography (silica gel, 10% Et_2O in petroleum ether) followed by Kugelrohr distillation (110 °C/0.8 mbar) provided a clear, colourless oil (605 mg, 89%).

IR (film): 1676 (w), 1648 (m) cm^{-1}

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.867 (1 H, tt, *J* = 7.4, 2.2 Hz), 5.264 (1 H, t, *J* = 2.2 Hz), 4.796 (1 H, s), 3.694 (2 H, s), 3.337 (2 H, d, *J* = 2.2 Hz), 3.316 (2 H, t, *J* = 2.2 Hz), 2.015 (2 H, q, *J* = 7.6 Hz), 1.434 (2 H, app. sextet, *J* = 7.4 Hz), 0.925 (3H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 145.27 (0), 138.80 (0), 136.44 (0), 129.03 (1), 128.46 (1), 127.24 (1), 120.70 (1), 100.70 (2), 60.91 (2), 60.28 (2), 57.10 (2), 31.84 (2), 22.64 (2), 14.07 (3).

LRMS (ES^+): *m*/*z* = 228 ($M + H^+$).

HRMS: *m*/*z* calcd for $C_{16}H_{21}N$ (M^+): 227.1674; found: 227.1675.

(3aS*,4R*,8aR*)-6-Benzyl-2-phenyl-4-propyl-1,2,3,3a,4,5,6,7,8,8a-decahydropyrrolo[3,4-f]isoindole-1,3-dione (23)
A solution of **13b** (125 mg, 0.55 mmol) in anhyd Et_2O (1 mL) was added dropwise to a solution of *N*-phenylmaleimide (87 mg, 0.5 mmol) in anhyd Et_2O (3 mL), and the resultant yellow solution was stirred at r.t. for 7 h. The solvent was removed in vacuo and the residue purified by column chromatography (silica gel, Et_2O) to furnish a sticky, colourless gum (173 mg, 87%).

IR (film): 1716 (s) cm^{-1}

^1H NMR: δ = 7.6–7.2 (10 H, m), 3.826 (2 H, s), 3.7–3.4 (4 H, m), 3.333 (1 H, td, *J* = 9.2, 4.4 Hz), 3.292 (1 H, dd, *J* = 8.8, 2.9 Hz), 2.764 (1 H, q, *J* = 6.5 Hz), 2.662 (1 H, d, *J* = 17.6 Hz), 2.475 (1 H, d, *J* = 16.9, 8.1 Hz), 1.8–1.3 (4 H, m), 0.920 (3 H, t, *J* = 7.4 Hz).

^{13}C NMR: δ = 179.30 (0), 177.33 (0), 139.40 (0), 136.80 (0), 132.27 (0), 132.08 (0), 129.36 (1), 128.80 (1), 128.59 (1), 127.26 (1), 126.60 (1), 62.34 (2), 61.85 (2), 60.58 (2), 44.08 (1), 39.87 (1), 35.42 (1), 31.95 (2), 21.98 (2), 21.50 (2), 14.32 (3).

LRMS (ES^+): *m*/*z* = 401 ($M + H^+$).

HRMS: *m*/*z* calcd for $C_{26}H_{28}N_2O_2$ (M^+): 400.2151; found: 400.2146.

Insertion of Alkenyl Carbenoids into Organozirconium Reagents; General Procedure
To a solution of the organozirconium species (~1 mmol) prepared by the general cocyclisation procedure (Method A) cooled to –90 °C was added the alkenyl chloride (1.3 equiv) in THF (1 mL), followed by a solution of LiTMP [1.3 equiv, prepared by addition of *n*-BuLi to a solution of 2,2,6,6-tetramethylpiperidine (1.3 equiv) in THF (4 mL) under argon at 0 °C and stirring for 30 min]. In the case of *cis*-1,4-dichloro-2-butene, 2.6 equiv of LiTMP are used. After 30 min at –90 to –80 °C, MeOH (3 mL) and aq sat. $NaHCO_3$ solution (6 mL) were added and the reaction was allowed to warm to r.t. and stirred for 16 h. The mixture was subsequently diluted with H_2O and Et_2O. The aqueous phase was extracted with Et_2O and the combined organic phases were washed with brine, dried ($MgSO_4$), filtered and concentrated.

(1R*,2S*)-1-{3-Methylene-2-[(2Z)-2,4-pentadienyl]cyclopentyl}benzene (26)
Cocyclisation of diene **18a** (1 mmol) (Method A) followed by insertion of the carbenoid derived from (*Z*)-1,4-dichloro-2-butene, aqueous work-up and purification by column chromatography (silica gel, petroleum ether) provided **26** as a clear, colourless oil (22 mg, 10%).

IR (film): 1652 (w), 1602 (w) cm^{-1}.

^1H NMR: δ = 7.4–7.1 (5 H, m), 6.527 (1 H, dddd, *J* = 16.9, 10.9, 9.9, 1.0 Hz), 6.018 (1 H, t, *J* = 11.0 Hz), 5.441 (1 H, q, *J* = 8.5 Hz), 5.177 (1 H, dd, *J* = 16.9, 1.7 Hz), 5.070 (1 H, d, *J* = 9.9 Hz), 5.006 (1 H, m), 4.928 (1 H, br q, *J* = 2.2 Hz), 2.786 (1 H, td, *J* = 10.5, 6.5 Hz), 2.69–2.52 (2 H, m), 2.50–2.33 (3 H, m), 2.081 (1 H, dddd, *J* = 12.4, 7.6, 6.7, 2.3 Hz), 1.769 (1 H, dtd, *J* = 12.4, 10.9, 8.4 Hz).

^{13}C NMR: δ = 154.79 (0), 144.54 (0), 132.68 (1), 130.40 (1), 130.37 (1), 128.54 (1), 127.82 (1), 126.40 (1), 117.14 (2), 105.77 (2), 51.35 (1), 51.15 (1), 33.92 (2), 33.11 (2), 29.71 (2).

LRMS (APCI): *m*/*z* (%) = 224 (M^+, 6), 142 (100).

HRMS: *m*/*z* calcd for $C_{17}H_{20}$ (M^+): 224.1565; found: 224.1552.

1-Benzyl-3-methylene-4-[(2Z)-2,4-pentadienyl)pyrrolidine (28a)
Prepared from **20a** (1.5 mmol) by cocyclisation (Method A) and subsequent insertion of the carbenoid produced by treatment of (*Z*)-1,4-dichloro-2-butene with 2 equiv of LiTMP. Purification by col-

umn chromatography (silica gel, 10% Et_2O in hexanes) provided a clear, colourless oil (270 mg, 75%).

IR (film): 1663 (m) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 6.657 (1 H, dddd, *J* = 16.6, 11.2, 9.9, 1.0 Hz), 6.059 (1 H, t, *J* = 11.0 Hz), 5.470 (1 H, dt, *J* = 10.4, 7.7 Hz), 5.209 (1 H, d, *J* = 16.8 Hz), 5.120 (1 H, d, *J* = 10.1 Hz), 4.946 (1 H, q, *J* = 2.2 Hz), 4.910 (1 H, q, *J* = 2.2 Hz), 3.682 (1 H, d, *J* = 12.9 Hz), 3.583 (1 H, d, *J* = 12.9 Hz), 3.369 (1 H, d, *J* = 13.4 Hz), 3.117 (1 H, d, *J* = 13.4 Hz), 2.925 (1 H, t, *J* = 7.9 Hz), 2.754 (1 H, m), 2.55–2.3 (2 H, m), 2.276 (1 H, t, *J* = 8.1 Hz).

^{13}C NMR: δ = 152.01 (0), 138.96 (0), 132.34 (1), 130.52 (2C, 1), 128.86 (1), 128.38 (1), 127.11 (1), 117.46 (2), 104.94 (2), 60.65 (2), 59.81 (2C, 2), 42.93 (1), 31.80 (2).

LRMS (ES^+): *m*/*z* = 240 ($M + H^+$).

Anal. Calcd for $C_{17}H_{21}N$: C, 85.30; H, 8.84; N, 5.85. Found: C, 84.94; H, 8.94; N, 5.90.

1-Benzyl-3-methylene-4-[(2*Z*,4*E*)-2,4-nonadienyl)pyrrolidine (28b)

Prepared by cocyclisation (Method A) of **20a** (0.8 mmol), and subsequent insertion of the carbenoid derived from (*E*,*E*)-1-chloro-1,3-octadiene. Purification by column chromatography (silica gel, 10% Et_2O in hexanes) provided a clear, colourless oil (145 mg, 62%).

IR (film): 1671 (w) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 6.331 (1 H, dd, *J* = 14.9, 11.0 Hz), 6.011 (1 H, t, *J* = 11.0 Hz), 5.698 (1 H, dt, *J* = 14.9, 7.4 Hz), 5.318 (1 H, dt, *J* = 11.0, 7.4 Hz), 4.940 (1 H, q, *J* = 2.2 Hz), 4.912 (1 H, q, *J* = 2.2 Hz), 3.662 (1 H, d, *J* = 12.9 Hz), 3.584 (1 H, d, *J* = 12.9 Hz), 3.361 (1 H, d, *J* = 13.6 Hz), 3.094 (1 H, dq, *J* = 13.2, 2.2 Hz), 2.932 (1 H, dd, *J* = 8.8, 7.4 Hz), 2.75 (1 H, m), 2.468 (1 H, dt, *J* = 14.3, 6.0 Hz), 2.334 (1 H, dt, *J* = 14.3, 8.8 Hz), 2.264 (1 H, t, *J* = 8.1 Hz), 2.129 (2 H, q, *J* = 6.6 Hz), 1.5–1.3 (4 H, m), 0.926 (3 H, t, *J* = 7.0 Hz).

^{13}C NMR: δ = 152.12 (0), 138.94 (0), 135.33 (1), 129.89 (1), 128.74 (1), 128.23 (1), 127.39 (1), 126.94 (1), 125.53 (1), 104.65 (2), 60.61 (2), 59.84 (2), 59.74 (2), 42.92 (1), 32.60 (2), 31.60 (2), 31.54 (2), 22.30 (2), 13.98 (3).

LRMS (ES^+): *m*/*z* = 296.

HRMS: *m*/*z* calcd for $C_{21}H_{29}N$ (M^+): 295.2300; found: 295.2287.

1-Benzyl-3-methylene-4-[(2*Z*)-undeca-2-en-4-ynyl)pyrrolidine (28c)

Prepared from **20a** (0.8 mmol) by cocyclisation (Method A) and subsequent insertion of the carbenoid prepared from (*E*)-1-chloro-dec-1-en-3-yne. Column chromatography (silica gel, 10% Et_2O in hexanes) provided a clear, colourless oil (102 mg, 40%).

IR (film): 2210 (w), 1665 (w) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.850 (1 H, dt, *J* = 10.3, 7.4 Hz), 5.510 (1 H, d + fs, *J* = 11.0 Hz), 4.949 (1 H, q, *J* = 2.2 Hz), 4.917 (1 H, q, *J* = 2.2 Hz), 3.668 (1 H, d, *J* = 12.5 Hz), 3.587 (1 H, d, *J* = 12.5 Hz), 3.395 (1 H, d, *J* = 13.2 Hz), 3.053 (1 H, dq, *J* = 13.2, 2.2 Hz), 2.976 (1 H, dd, *J* = 8.8, 7.4 Hz), 2.85–2.4 (3 H, m), 2.362 (2 H, td, *J* = 7.0, 2.2 Hz), 2.272 (1 H, t, *J* = 8.5 Hz), 1.6–1.25 (8 H, m), 0.915 (3 H, t, *J* = 7.0 Hz).

^{13}C NMR: δ = 151.96 (0), 140.05 (1), 139.11 (0), 128.89 (1), 128.40 (1), 127.11 (1), 110.87 (1), 104.87 (2), 95.22 (0), 77.46 (0), 60.77 (2), 60.02 (2), 59.83 (2), 42.53 (1), 33.74 (2), 31.54 (2), 29.00 (2), 28.75 (2), 22.76 (2), 19.71 (2), 14.26 (3).

LRMS (ES^+): *m*/*z* = 322 ($M + H^+$).

HRMS: *m*/*z* calcd for $C_{23}H_{31}N$ (M^+): 321.2457; found: 321.2449.

1-Benzyl-3-methylene-4-(3,3-dimethyl-2-propenyl)pyrrolidine (28d)

Prepared from diene **20a** (1 mmol) by cocyclisation (Method A) and subsequent insertion of the carbenoid derived from 1-chloro-2-methyl-1-propene. Purification by column chromatography (silica gel, 10% Et_2O in hexanes) provided a clear, colourless oil (156 mg, 65%).

IR (film): 1665 (m) cm^{-1}.

^1H NMR: δ = 7.4–7.2 (5 H, m), 5.144 (1 H, t + fs, *J* = 7.2 Hz), 4.920 (1 H, q, *J* = 2.2 Hz), 4.890 (1 H, q, *J* = 2.2 Hz), 3.673 (1 H, d, *J* = 13.2 Hz), 3.575 (1 H, d, *J* = 13.2 Hz), 3.361 (1 H, d + fs, *J* = 13.6 Hz), 3.090 (1 H, dq, *J* = 13.6, 2.3 Hz), 2.922 (1 H, dd, *J* = 8.8, 7.0 Hz), 2.78 (1 H, m), 2.298 (1 H, dt, *J* = 14.5, 7.0 Hz), 2.223 (1 H, dd, *J* = 8.8, 7.4 Hz), 2.125 (1 H, dt, *J* = 14.5, 8.1), 1.707 (3 H, d, *J* = 1.1 Hz), 1.624 (3 H, s).

^{13}C NMR: δ = 152.66 (0), 139.18 (0), 132.71 (0), 128.92 (1), 128.38 (1), 127.08 (1), 122.81 (1), 104.51 (2), 60.82 (2), 60.15 (2), 60.01 (2), 43.34 (1), 32.32 (2), 25.95 (3), 18.05 (3).

LRMS (ES^+): *m*/*z* = 242 ($M + H^+$).

HRMS: *m*/*z* calcd for $C_{17}H_{23}N$ (M^+): 241.1831; found: 241.1827.

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