Highly Substituted Homoallylvinylcyclopropanes by Indium-Mediated Reaction of α,β-Unsaturated Ketones and Aldehydes with Allylic Halides

Stephen M. Capps,[a] Timothy P. Clarke,[a] Jonathan P. H. Charmant,[a] Henning A. F. Höppe,[a] Guy C. Lloyd-Jones,*[a] Martin Murray,[a] Torren M. Peakman,[a] Rosie A. Stentiford,[a] Kenneth E. Walsh,[a] and Paul A. Worthington[b]

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Allylindium reagents, prepared from excess allylic halide (Br or I) and indium metal, react with α,β-unsaturated ketones and aldehydes to give, after aerobic acidic workup, homoallyl-substituted vinylcyclopropanes. This process was explored and developed after a chance discovery arising from a side reaction in an attempted Pd-catalysed process. The structure of the cyclopropane arising from the reaction of bis(*p*-chlorobenzylidine)acetone was confirmed by X-ray crystallography. Whilst bis-α,β–unsaturated ketones give rise to a single homoallylcyclopropane species, α,β-unsaturated ketones and aldehydes give diastereomeric mixtures whose relative stereochemistry were assigned by NOE experiments. Crotylindium reagents react with good to perfect regioselectivity to afford tetrasubstituted cyclopropanes but prenylindium reagents fail to generate the analogous pentasubstituted rings.

Introduction

Compatibility with many common organic functional groups (e.g. ROH, CO_2R) and stability towards aqueous and even mildly acidic conditions are features that make organoindium reagents of particular appeal as organometallic reagents for organic synthesis.[1] By reaction with In metal (or In halides), alkyl halides,[2] allylic halides[3] and α-haloesters[4] are readily converted into organoindium mono-, di- and sesquihalides which react with aldehydes and ketones to afford, after workup, homoallylic alcohols and β-hydroxy esters. Aqueous systems have proved to be most effective[5] (mixtures with THF, DMF, EtOH etc.) and in certain cases significant regio-, diastereo- and even enantioselectivities can be achieved. Allylindium halides also react with acyl halides (or equivalents),[6] with aryl halides[7] and with enamines, *via* acid-catalysed formation of imminium ions, to afford homoallylic amines.[8] Many other reactions, for example the carboindation of alkynes,[9] alkenes,[10] and nitriles[11] the cross-coupling of alkenyl halides,[12] reactions of organoindates and organoindium species generated *via* transmetallation[13] are also of great synthetic potential.

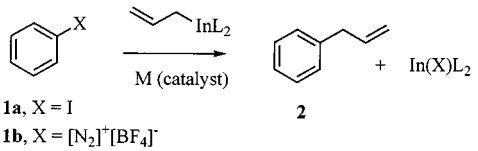
A while ago we began a research program aimed at extending the utility and range of organo-indium-mediated reactions. As part of this program we performed a feasibility study of Pd- or Ni-catalysed organoindium cross-coupling.[14] The results obtained with one particular Pd complex as a catalyst were unexpected and, serendipitously, led to the discovery of an In-mediated deoxygenative cyclopropane-forming reaction. The discovery and development of this reaction forms the subject of this paper.[15]

[a] School of Chemistry, University of Bristol,
Cantock's Close, Bristol BS8 1TS, UK
Fax: (internat.) + 44-117/929-8611
E-mail guy.lloyd-jones@bris.ac.uk
[b] Zeneca Agrochemicals, Jealott's Hill Research Station,
Bracknell, RG42 6ET, UK

Results and Discussion

Discovery of the Reaction

In initial experiments we attempted to cross-couple iodobenzene (**1a**) and benzenediazonium tetrafluoroborate (**1b**) with allylindium reagents, generated in situ from allyl iodide or bromide and indium metal, to afford allylbenzene **2** (Scheme 1).



1a, X = I
1b, X = $[N_2]^+[BF_4]^-$

2

Scheme 1. Attempted transition-metal-catalysed (M = Pd, Ni) cross-coupling of iodobenzene (**1**) with allylindium reagents to generate allylbenzene (**2**).

Control reactions for the attempted cross-coupling of **1a** and **1b** were run at 60 °C in THF or DMF or aqueous mixtures thereof, with freshly prepared "$(C_3H_5)_3In_2Br_3$",[16] and conducted in the absence of catalyst. These demonstrated that there was no product formation detectable by TLC analysis over a period of 72 h. Furthermore, addition of various Pd and Ni complexes (including: $(PPh_3)_4Pd$, $(PPh_3)_2PdCl_2$, [(dppf)Pd-allyl][OTf], (dppf)$NiCl_2$ and $(PPh_3)_2NiCl_2$) did not result in any observable catalysis of reaction. However, on addition of a THF solution containing 4 mol-% "$[(PPh_3)_2Pd(dba)(0)]$"[17] (dba = dibenzylideneacetone **3**) to **1a** (650 mg) we detected by TLC a small quantity of a new product having an R_f consistent with the

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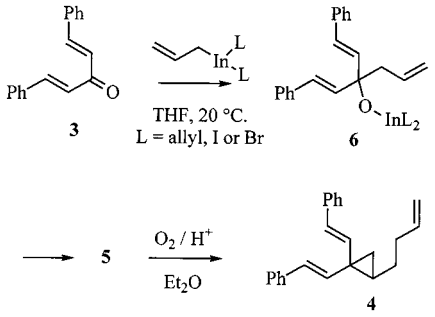
desired cross-coupling product: allylbenzene **2**. Aqueous workup and then purification by flash chromatography afforded a colourless viscous oil (<18 mg) which clearly was not **2**. The curious ^{1}H NMR spectrum of the trace of side product led us to perform a stoichiometric reaction of dba (**3**) with $(C_3H_5)_3In_2Br_3$ (1: 1 ratio) in THF (Scheme 2).



Scheme 2. Possible sequence of events leading to the generation of **4** from **3**. Intermediate **6** is suggested on the basis of NMR observation ([D_8]THF) of a symmetrical allyl-adduct. Due to very broad and unassignable NMR signals, a structure has not yet been suggested for intermediate **5**.

The dba **3** reacted rapidly and completely with the $(C_3H_5)_3In_2Br_3$ and aqueous workup [Et_2O/1 M HCl (aq.)] then column chromatography afforded a material identical with that isolated from the attempted Pd-catalysed cross-coupling reaction. The high-field ^{1}H NMR shifts of some of the protons of the product and the low $^1J_{CC}$ coupling constants of the carbon atoms associated (by long and short range $^{13}C^1H$ correlation) with these higher-field ^{1}H NMR signals were very indicative of a cyclopropane ring. This conclusion was supported by the observation of a sharp IR band at 3060 cm^{-1} characteristic of a cyclopropane ring methylene group. Further NMR analysis (PECSY, DEPT, 2D-^{13}C INADEQUATE, NOE studies and selective ^{1}H decoupling) suggested the structure to be (±) 2-(3"-butenyl)-1,1-bis[(*E*)-2′-phenylethenyl]cyclopropane **4**[18] – a molecule formally resulting from the deoxygenative combination of two allyl units with the ketonic carbon atom of **3**. The yield of analytically pure cyclopropane **4** was variable and ranged from 20–62%. Selected NOE data and $^1J_{CC}$ coupling constants for **4** are shown in Figure 1.

The NOE data indicates that the C(1) *E*-PhCH=CH– substituent which is *anti* to the homoallylic unit at C(2) is rotated away from the *syn*-*E*-PhCH=CH– substituent and lies under the cyclopropane ring. This orientation was also observed for other products (vide infra) in which a vinylic group is attached to a quaternary C(1).

To study the formation of **4** in more detail, we added THF solutions of $(C_3H_5)_3In_2Br_3$ to **3** in THF and then took samples at regular intervals to assay by TLC (hexane/EtOAc, 12:1; Merck silica gel 60 Hf254). At 25 °C (or indeed at –30 °C), soon after addition of the allylindium reagent, TLC indicated there was little or no trace of ketone **3** (R_f 0.5), a highly variable quantity of an intermediate **5** (R_f 0.4) which fluoresced at 365 nm and the hydrocarbon **4** (R_f 0.9). However, after a long series of erratic results it became clear that much of the chemistry was occurring on the TLC plate rather than in the reaction flask. For example, after sampling the reaction mixture and 'spotting' this onto the TLC plate – where both the THF could evaporate and the residue gain intimate contact with air – the spotted sample changed from a pale yellow colour to deep red and then slowly faded to yellow again. Furthermore, "streaking" was often observed on the TLC plate between **5** and **4** – indicating that the conversion of **5** to **4** was occurring upon development of the plate with the eluent. However, deliberate exposure of the reaction mixture to air or UV light or addition of water did not induce conversion of **5** to **4** and we concluded that both the removal of the THF and contact with air (in the presence of acid) were required. This conclusion was tested by addition of the reaction mixture (*via* cannula) to a pre-solvated silica-gel column under nitrogen and collection of a compound **5** whose ^{1}H NMR spectrum ($CDCl_3$, 25 °C) consisted solely of a series of very broadened resonances in the aromatic and alkyl regions. The broadening could have been due to either some fluxional process or a nonfluxional statistical distribution (e.g. polymeric material such as alkyl indium halide polymers).

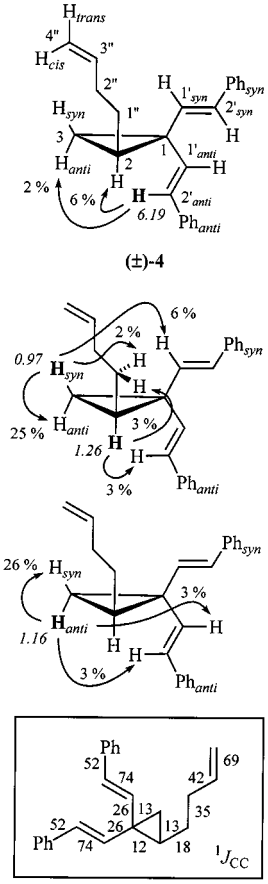


Figure 1. Numbering scheme and selected ^{1}H NMR NOE-difference data ($CDCl_3$, 400 MHz) for **4**. Protons irradiated are in bold (chemical shifts are italicised) with NOE difference values (%) and connectivities indicated by arrows. Inset: $^1J_{CC}$ coupling constants extracted by analysis of $^{13}C\{^1H\}$ NMR, ^{13}C-satellites. The small couplings (12–13 Hz) between C(1), C(2) and C(3) confirm the proposed cyclopropane ring and confirm the nonring carbons to which they are joined (to which there are $^1J_{CC}$ couplings of 18 and 26 Hz). The 69–74 Hz couplings between the sp^2, 42–52 Hz between sp^2-sp^3 and 35 Hz between sp^3-sp^3 carbons are 'normal' values.

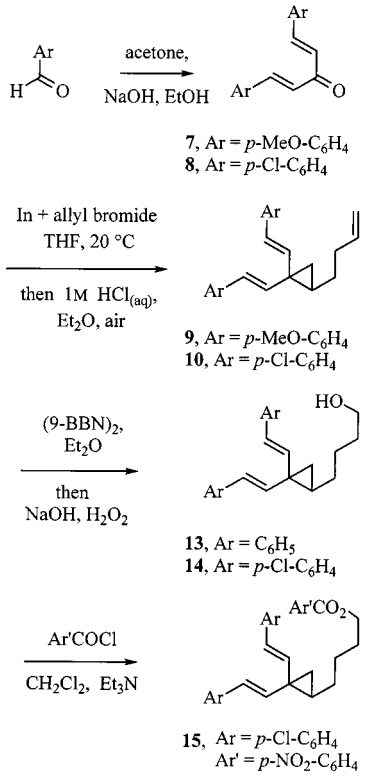
The spectrum could not be assigned and thus far the identity of **5** has remained elusive.

Through a series of NMR studies in [D_8]THF, it became clear that the unidentified intermediate **5** was not in fact the initial product of reaction of dba **3** with $(C_3H_5)_3In_2Br_3$. This seemed more likely to be a homoallylic indium alkoxide of type **6** which would be generated by [1,2]-addition of allylindium species to the carbonyl group of dba **3**. The symmetrical nature of the adduct **6** being manifested in a single, well-resolved, AB system for the two nondiastereotopic styryl proton sets and a clean $ABCX_2$ allyl signal. A separate experiment employing the allylic indium dihalide $(C_3H_5)_2In_2I_4$[19] (prepared from allyl iodide and indium(I) iodide) gave similar results (clean conversion of **3** to **6**). Subsequent removal of the [D_8]THF (0.1 Torr) from the initially pale yellow solution left a yellow oil that suddenly became deep brown as the last traces of THF were removed. Addition then removal of toluene afforded a pale brown oil that redissolved in [D_8]THF to give a grey-green solution. All of the resonances assigned to **6** had disappeared when the ^{1}H NMR spectrum of this solution was recorded. The spectrum consisted solely of two very broad resonances with chemical shifts in the aromatic and alkyl regions. Thus we suspected that upon removal of THF the intermediate **5** was being generated from **6** and that subsequent allyl transfer/rearrangement (on aerobic acidic workup in Et_2O) led to cyclopropane **4** (Scheme 2).

We later discovered that we could attain improved yields of **4** by addition of the sodium salt of allyl alcohol (C_3H_5ONa) before workup. Control experiments revealed that this was not arising through allyl transfer from the alkoxide. KBr has been employed to prepare the more volatile dialkylindium halides by inducing disproportionative alkyl exchange between indium centers in alkylindium sesquihalide complexes[20] and more recently, Reetz and Haning[21] reported on increased (or reversed) diastereoselectivities for the addition of allylindium sesquibromide to aldehydes and ketones by employing bulky lithium alkoxides to induce "ate" complex formation. Thus we suspected that the improved yields of **4** may be due to the formation of indium "ate" complexes and accordingly found that the addition of one equivalent of LiBr after complete consumption of **3** resulted in a fairly exothermic reaction. When this reaction was worked-up in air by addition of ether and then HCl (1 M), **4** was isolated in 83% yield by chromatography. When workup was performed with ether and water this failed to generate **4** until acid (HCl (aq) 1 M) was introduced. By employing NaOH (instead of LiBr) and then using the usual acid aerobic aqueous workup we isolated **4** in 82% yield.

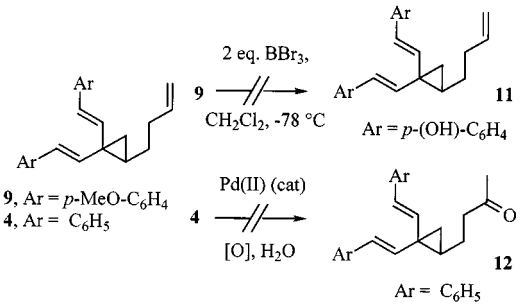
Confirmation of the Structure of the Homoallylcyclopropanation Reaction by X-ray Crystallography

Given the unusual and unprecedented direct generation of a vinylcyclopropane from an α,β-unsaturated ketone (i.e. **4** from **3**) we wished to confirm the structure of **4** by X-ray crystallography. However, not surprisingly, **4** was an oil and we therefore attempted to make analogues or derivatives of **4** that contained functionality that might engender crystallinity. Cyclopropanes **9** (60%) and **10** (79%) were readily prepared as viscous oils from ketones **7** and **8** respectively (Scheme 3), emphasising the utility of the homoallylvinylcyclopropanation reaction since the core of the molecules are constructed from acetone (*p*-methoxy- and *p*-chlorobenzaldehyde → **7** and **8**) and two allyl units in two laboratory steps.



Scheme 3. Rapid construction of homoallyldivinylcyclopropanes **9** and **10** in two steps from arylaldehydes **7** and **8** and attempted generation of crystalline derivatives and analogues of **4** for X-ray analysis. Chemo- and regio-selective hydroboration-oxidation gave alcohols **13** and **14** as oils. Esterification of **14** gave *p*-nitrobenzoate derivative **15** (63%) which could not be crystallised. However, although both **9** and **10** were initially oils, cyclopropane **10** was eventually crystallised from MeOH/diethyl ether.

Attempted demethylation of the aryl ethers in cyclopropane **9**, to afford what was hoped would be a more polar bisphenol **11**, effected near-complete destruction of the substrate **9** – presumably by reaction of the vinylcyclopropane unit with the Lewis-acidic BBr_3 (Scheme 4). We next tested



Scheme 4. Attempted generation of polar derivatives of **4** or analogue **9**. BBr_3-mediated demethylation completely degraded **9**, whilst Wacker oxidation of **4** failed to proceed.

the possibility of derivatising homoallylcyclopropane **4** by selective functionalisation of allyl group – preferably in a way that would not generate diastereomeric products. Pd-catalysed Wacker-type oxidation of **4** failed to give ketone **12** under a variety of conditions (Scheme 4).

However, a chemo- and regio-selective hydroboration of **4** with $(9\text{-BBN})_2$ afforded primary alcohol **13** in good yield (Scheme 3) but as an oil. Hydroboration of the bis-*p*-chloro compound **10** afforded the alcohol **14**, which was then esterified to afford *p*-nitrobenzoate **15**. However, although a semi-solid we were unable to crystallise **15** from a range of solvents. Finally, we returned to **10** (the bis-*p*-chloro analogue of the parent cyclopropane **4**) which on prolonged storage had solidified. Slow concentration of a solution of cyclopropane **10** in $MeOH/Et_2O$ afforded needles (m.p. 60–62 °C) some of which were just large enough for single crystal X-ray diffraction. The molecular structure, which confirms formation of **10**, is presented in Figure 2.

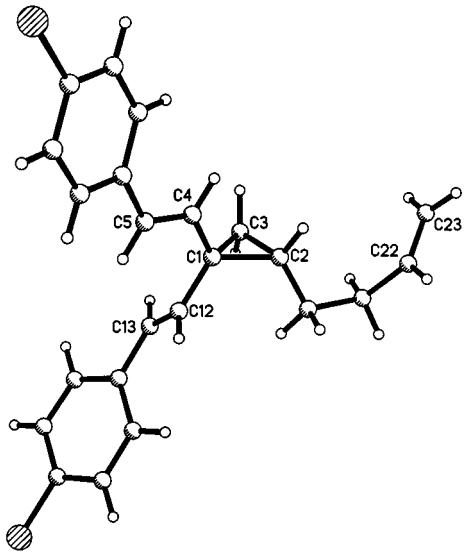


Figure 2. Single crystal X-ray structure of **10** ($C_{23}H_{22}Cl_2$, unit cell parameters: a = 20.840(5) b = 6.0414(18) c = 31.686(10) β = 96.38(3), space group $P21/n$). Crystallographic data for **10** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134689. ***Note:*** the crystallographic numbering scheme is different to that used in the text and experimental sections.

The shortest of the cyclopropane bond lengths [1.523(6) Å] is found between C(2) and C(3) along the edge of the triangle where there is least steric clash [compare C(1)–C(2) and C(1)–C(3) = 1.564(6) and 1.541(6) resp.]. The presence of the homoallyl chain appears to slightly elongate the bonding of C(1) to the *syn*-*p*-chlorostyryl group [compare *anti* C(1)–C(4) = 1.469(6), *syn* C(1)–C(12) = 1.482(6) Å], but within the styryl group there is little effect, e.g. compare CH=CH bonds [*anti* C(4)–C(5) = 1.327(6), *syn* C(12)–C(13) = 1.329(5) Å]. Finally, the position of the vinylic double bond at the terminus of the homoallyl chain is clearly shown by a C(22)–C(23) distance of 1.331(7) Å.

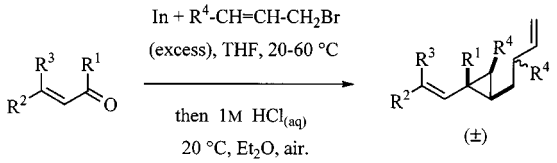
Non-Dibenzylideneacetone-Type Substrates

Butsugan *et al.* have reported extensively on the reactions of ketones and aldehydes with allylindium reagents. Notably, α,β−unsaturated ketones and aldehydes had been reported to undergo simple indium-mediated [1,2]-allylation reactions with no mention of cyclopropane or hydrocarbon products.[22] Therefore we were very interested to test whether the reaction performed under our homoallylcyclopropanation (HAC) conditions was restricted to dibenzylideneacetone **3** (or derivatives **7** and **8**).

Using the standard procedure we had developed for the HAC of **3**, **7** and **8**, we were able to prepare cyclopropanes **17**, **19**, **21** and **23** from phorone (**16**), benzylideneacetone (**18**), cyclopentenone (**20**) and cinnamaldehyde (**22**) respectively (Table 1, entries 4–7).

Notably, both the rate of cyclopropane formation upon workup (H_3O^+/O_2) and the isolated yield decreased

Table 1. Yields and (where appropriate) ratios of major/minor diastereomers for indium-mediated homoallylcyclopropanation (HAC) reactions of α,β-unsaturated ketones and aldehydes with allyl or crotyl bromide.



Entry	Substrate	R^1	R^2	R^3	R^4	Product	*dr*[a]	Yield (%)[b]
1	**3**	*E*-styryl	C_6H_5–	H	H	**4**	– [c]	83
2	**7**	*E*-*p*-MeO–styryl	*p*-MeO–C_6H_4-	H	H	**9**	– [c]	60
3	**8**	*E*-*p*-Cl–styryl	*p*-Cl–C_6H_4-	H	H	**10**	– [c]	79
4	**16**	$CH{=}CH(CH_3)_2$	CH_3	CH_3	H	**17**	– [c]	92
5	**18**	CH_3	C_6H_5–	H	H	**19**	1/1	78
6	**20**	CH_2–R^3	H	–CH_2-	H	**21**	4/1	49
7	**22**	H	C_6H_5–	H	H	**23**	2/1	52[d]
8	**3**	*E*-styryl	C_6H_5–	H	CH_3	**24**	81/19[e]	79
9	**16**	$CH{=}CH(CH_3)_2$	CH_3	CH_3	CH_3	**25**	88/12[e]	53

For structure of major diastereomer see text. Diastereomer ratio [for C(1)/C(2) or C(2)/C(3) relative stereocentres only] by ^1H NMR or ^{13}C NMR analysis. – [b] Yield of analytically pure material obtained after chromatography on silica-gel or by kugelrohr distillation. – [c] No diastereoisomerism due to single stereogenic centre [C(2)]. – [d] Yield after modified workup procedure – see experimental section. Yield under standard conditions <28%. – [e] Ratio of the two major *cis* isomers [at C(2)–C(3)] to the two minor *trans* isomers.

through the series **17** (95%), **4** (83%), **19** (79%), **21** (49%) and **23** (< 28%). This series is consistent with removal of allylic stabilisation from the respective intermediates prior to cyclopropane ring closure: from the initial bis allylic systems (phorone **16** and dba **3**) a double bond is removed and replaced with alkyl (**18**), the aryl ring removed (**20**) and the alkyl replaced with H (**22**). The yield of **23** from the reaction of cinnamaldehyde **22** with $(C_3H_5)_3In_2Br_3$/LiBr was nearly doubled (ca. 52%) by quenching the reaction (Et_2O, 1 M HCl), evaporating the ether and refluxing the residue, under air, in chloroform.

Cyclopropanes **19**, **21** and **23** were obtained as diastereomeric mixtures in ratios of 1:1, 4:1 and 2:1 respectively. The relative structures of the diastereomers of **19** and **23** were assigned by NOE difference experiments (Figure 3) and these were later confirmed by reactivity studies in ring-closing metathesis.[23] The styryl-group on C(1) of the cinnamaldehyde-derived cyclopropane (**23**) displayed a noticeably different set of NOE contacts to the apparently similar **19**. These results are indicative of a different time-average orientation of the group, relative to the cyclopropane ring, between the two systems (**19** versus **23**). This difference may be ascribed to $A^{1,3}$-strain – see inset to Figure 3. For the spiro-compound **21**, due to close chemical shifts, the NOE difference spectra observed for the two diastereomers were ambiguous and the relative stereochemistry could not be assigned with confidence by this method. PNOSY was therefore employed to establish NOE contacts.

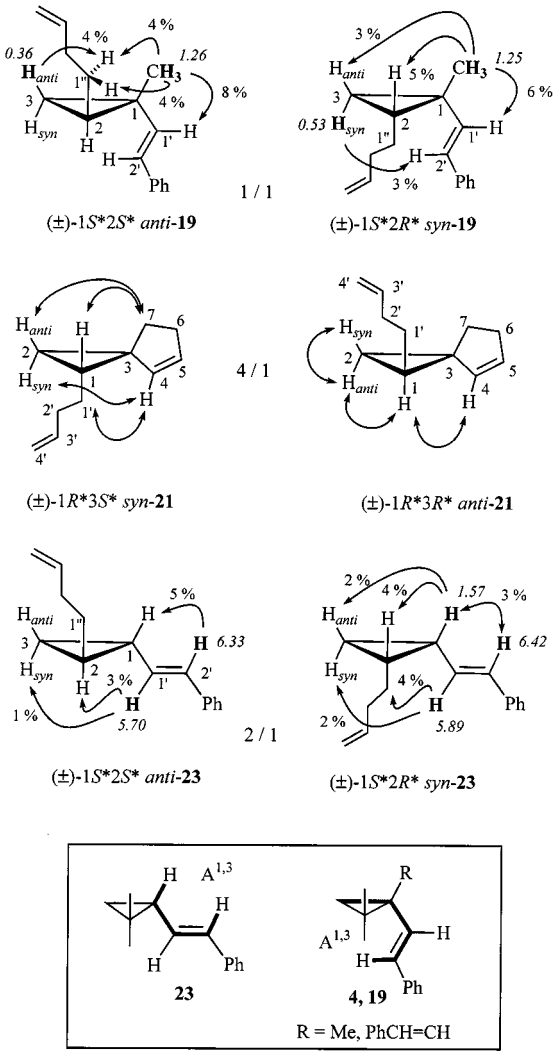


Figure 3. Selected ^1H NMR NOE-difference data ($CDCl_3$, 400 MHz) for **19** and **23** and selected NOE contacts (PNOSY, $CDCl_3$, 500 MHz) for **21** that establish the relative stereochemical identities for each pair of diastereomers. For NOE difference experiments, protons irradiated are in bold (chemical shifts are italicised) with NOE difference values (%) and connectivities indicated by arrows. Inset: $A^{1,3}$-strain may control the predominant location of the styryl group in **4** and **19** as compared to **23**.

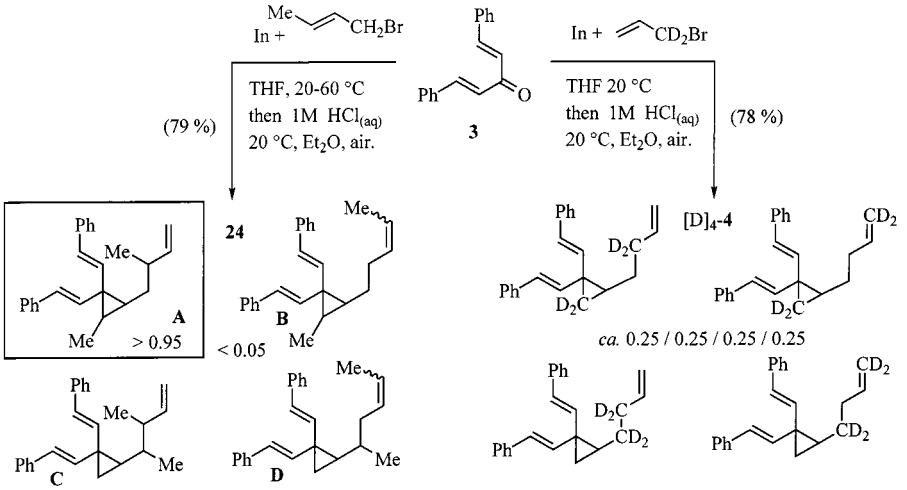
Crotyl- and Prenyl-Type Indium Reagents

We have also reacted dba **3** with more substituted allylindium species. As a preliminary study we prepared 1,1-$[D]_2$-allyl bromide and reacted this with dba **3** and indium under the HAC conditions. Consistent with the postulated construction of **4** from two allyl units, the reaction gave $[D]_4$-**4** (78% yield) with no evidence by MS for any deuterium exchange ($[D]_3$, $[D]_5$ etc.). Analysis of $[D]_4$-**4** by ^1H, ^2H and ^{13}C-NMR indicated that four regioisotopomers had been obtained in approximately equal ratio (Scheme 5, right hand side). The HAC reaction is therefore not regiospecific with regard to the initial allylic halide and thus the $[D]_2$ unit can appear at either termini of the two dideuterioallyl units used in the construction of $[D]_4$-**4**.

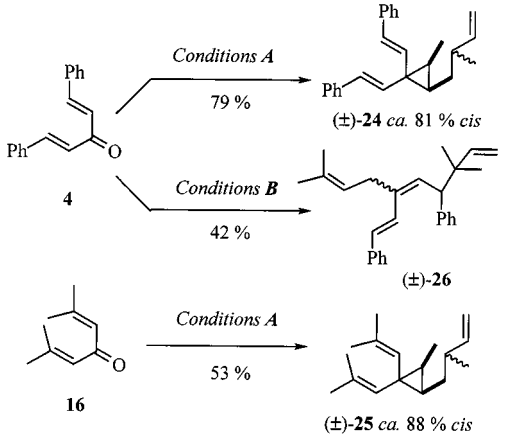
Consequently, reaction of **3** with crotyl bromide/indium could lead to four possible regioisomers [**A**-**D**] (Scheme 5, left hand side). Each regioisomer has three stereogenic centres and can exist as four diastereoisomers, therefore, the reaction could generate a total of 16 racemic isomers. The reaction proceeded smoothly under the standard conditions and workup then chromatography afforded hydrocarbon **24** analytically pure and in 79% yield. It was clear from preliminary ^1H- and ^{13}C-NMR spectra of both the crude and purified product that a range of isomers was present. However, based on careful examination of the ^{13}C-DEPT spectrum in which only CHMe (no CH_2) cyclopropyl carbons and CH_2 (no CHMe) terminal allyl carbons were evident, we were able to conclude that the reaction afforded essentially a single regioisomer (**A**) with greater than 95% regioselectivity.

This highly regioselective reaction, which generates two *cis*-related tertiary carbon centres both of which are adjacent to a quaternary carbon centre, reproducibly gave **24** in up to 79% yields on a multigram scale using the standard procedure (Scheme 6, and Table 1, entry 8). Despite many attempts, we were unable to separate any of the diastereomers of **24** by chromatography on silica gel that had been impregnated with Ag^+.[24]

Similar reaction with phorone **16** afforded highly substituted **25** in 53% yield (Scheme 6 and Table 1, entry 9). Again careful examination of the ^{13}C-DEPT spectrum indicated that the major product (>90%) was the regioisomer in which the C(3) and C(2′′) centres bear the methyl groups – in direct analogy to **24**.



Scheme 5. Homoallylcyclopropanation with dideuterio-allyl (right hand scheme) and crotyl (left-hand scheme) indium reagents. Reaction of 1,1-$[D]_2$-allyl bromide and dba **3** affords all four regioisotopomeric products of $[D]_4$-**4** in 78% yield. Excess 1,1-$[D]_2$-allyl bromide is recovered unscrambled but ^{2}H-NMR analysis of intermediate indium-allyl species indicates an equal mixture of 1,1-$[D]_2$- and 3,3-$[D]_2$-isotopomers. The reaction with crotyl bromide is very regioselective giving a single isomer **A** (>95%) in 79% yield.



Scheme 6. Homoallylcyclopropanation with crotyl- and prenylindium reagents. Conditions **A**: 4 equiv. In + 4 equiv. crotyl bromide THF, 60 °C, 3–4 h. Then 1 M HCl(aq), 20 °C, Et_2O, air, 30 min. Conditions **B**: 4 equiv. In + 4 equiv. prenyl bromide THF, 60 °C, 3–4 h. Then 1 M HCl(aq), 20 °C, Et_2O, air, 30 min. Highly substituted **24** and **25** are obtained as >95% and >90% single regioisomers respectively.

Assignment of the relative stereochemistry of the diastereomers of **24** was frustrated by the observation of very closely overlapping sets of multiplets in the 500 MHz ^{1}H NMR spectra in most solvents. In $[D_6]$acetone, a small degree of chemical shift dispersion was observed and we could determine that all four diastereomers had been obtained in a ratio of *ca.* 56/25/16.5/2.5%. Using 2D NOESY at 500 MHz we were able to identify spacial relationships between some of the protons (Figure 4 left hand side) as well as chemical shifts within overlapping sets of multiplets. The latter were employed for spectral simulation of the ^{1}H NMR of the major diastereomer (56%) which allowed confirmation of the assignment of *cis* stereochemistry at the cyclopropane ring since a 9.5 Hz coupling between the two ring protons was required for satisfactory simulation. The same *cis* relationship was observed in the second most abundant diastereomer (25%) and thus the overall diastereoselectivity at the cyclopropane centre is 81% *cis*.[25]

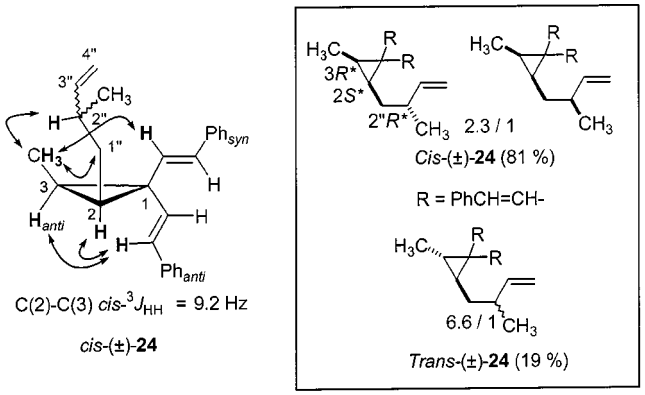


Figure 4. Left hand side: selected ^{1}H NMR NOE contacts (PNOSY, $[D_6]$acetone, 500 MHz) observed for of the two major diastereomers of **24** (*cis*-(±)-**24**) that establish the *cis* relationship between the homoallyl chain at C(2) and the methyl group located on the cyclopropane C(3)-carbon. NOE contacts between the C(3)-methyl group and the allylic proton at C(2′) were inconclusive due to free rotation about C(2)–C(1′). Boxed area: relative stereochemical assignments for the C(2′) stereogenic centre based on NOE experiments of a derivative (see text).

Due to free rotation about the C(2)–C(1′) and C(1′)–C(2′) bonds, the NOESY data of **24** was ambiguous regarding the relative stereochemistry at the allylic stereogenic centre [C(2′)]. We eventually solved this problem by employing Ru-catalysed ring closing metathesis (RCM) to generate a structure in which the conformational mobility of the allylic carbon was restricted by annelation.[23] This procedure allowed complete assignment of the relative configuration of the two major diastereomers (Figure 4, boxed area). The ^{13}C-NMR spectrum of **25** suggests that all four diastereomers of the major (>90%) regioisomer are obtained (*ca.* 55/33/9/3 based on $CH{=}CH_2$) with very similar ^{13}C-NMR chemical shifts for the two major isomers (88%). Analysis of the ^{1}H NMR spectrum (simulation) of the major isomer of **25** allowed tentative assignment of the stereo-

chemistry at the cyclopropane ring. A $^3J_{HH}$ coupling constant of 9.5 Hz is required at C(3)–H suggesting that the stereochemistry is the same as **24** and thus high *cis*-selectivity is observed in both examples.

When the steric demands of ring-formation were increased from crotyl to prenyl, cyclopropanes were not formed (Scheme 6). Under the usual conditions, reaction of **3** with dimethyl allyl bromide/indium afforded the terpene-like structure **26** – as a mixture of *cis* and *trans* isomers (1.0/1.2), whose stereochemical identities were determined by NOE difference experiments (Figure 5).

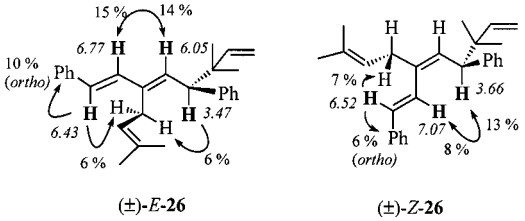


Figure 5. Selected ^{1}H NMR NOE data (NOE difference, $CDCl_3$, 400 MHz) for **26** that establish the geometric (*cis*/*trans*) identities of the two isomers. Protons irradiated are in bold (chemical shifts are italicised) with NOE difference values (%) and connectivities indicated by arrows.

Conclusions

By isolation and identification (predominantly by NMR) of a minor side product **4** arising from reaction of a co-ligand (dba **3**, 8 mol-%) of a Pd-catalyst with an allylindium reagent, we have discovered a novel homoallylcyclopropanation (HAC) reaction. In Pd-catalysed reactions involving $[Pd_2(dba)_3.dba]$ as a pro-catalyst, the dba (**3**) liberated in situ is often considered to be inert and solely a spectator ligand. However, here as elsewhere[26] this has proved not to be the case. In the work described herein, the reaction was far removed from our original intended cross-coupling reaction[27] and completely unexpected given the literature at that time on the reaction of allylindium reagents with α,β-unsaturated ketones. When performed stoichiometrically, and under slightly improved conditions, the reaction affords cyclopropane **4** in over 80% yield from ketone **3**. Analogous compounds with functionalised aromatic rings are also readily prepared using the HAC reaction and the homoallylcyclopropyl structure was confirmed by X-ray crystallography of **10**, the bis-*para*-chloro analogue of **4.**

Furthermore, a range of other α,β-unsaturated ketones and aldehydes have also proven to undergo the reaction. However, thus far the reaction appears restricted to α,β-unsaturated carbonyl compounds. Using these other substrates a range of homoallylcyclopropanes (**17**, **19**, **21**, and **23**) can be obtained in yields that range from moderate (**23**, 52%) through to excellent (**17**, 92%) with a range of diastereoselectivities. With crotylindium reagents, the crowded structures **24** and **25** are obtained with very high regioselectivity. The relative stereochemistry of **24** (>95% a single regioisomer) was studied in detail and the two major diastereomers (81%) determined to be those with a *cis* arrangement of the 2-methylbut-3-enyl chain and the methyl group about the cyclopropane ring. The stereochemistry of **25** is suggested to be *cis* at C(3) in the two major isomers (ca. 88%). Whilst the products obtainable from the HAC reaction are, so far, somewhat restricted in range, it is remarkable that molecules as complex as **24** and **25** can be obtained in two laboratory steps from such simple reactants as acetone, benzaldehyde and crotyl bromide.

Future work will concentrate on further elucidation of the mechanism of these intriguing reactions, on the development of enantioselective or stereospecific HAC reactions and on the development of HAC reactions in which two differing allylic groups are transferred.

Experimental Section

General: Solvents and reagents were purified by standard procedures. Anhydrous solvents were purchased from Fluka or Aldrich and used as received. When appropriate, reactions were carried out under nitrogen or argon using standard Schlenk techniques. – NMR experiments were performed on JEOL Delta 270, Lambda 300, JEOL GX400 and JEOL Alpha 500 instruments. Chemical shift, multiplicities, assignments and coupling constants are based on a combination of some or all of the following: ^{1}H^{1}H COSY, PECSY, DEPT, ^{13}C^{1}H COSY (long and short range), NOE difference, PNOSY, $^1J_{CC}$ and $^1J_{CH}$ coupling. In cases where spectra were significantly second order, overlapping or complicated, iterative simulations (*g*-NMR) were performed until a satisfactory fit was obtained (in these cases chemical shifts and coupling constants are denoted "*simul.*"). – Mass spectra were obtained using both CI and EI sources on a Fisons Micromass Autospec mass spectrometer. – Elemental analysis of the compounds were performed by the analytical service of the School of Chemistry, University of Bristol. Some of the oily hydrocarbon reaction products, whilst homogeneous by ^{1}H and ^{13}C NMR, gave slightly unsatisfactory elemental analyses – even after kugelrohr distillation. However, in all cases high-resolution mass spectra (HRMS) were satisfactory. – IR spectra: Perkin–Elmer 1600 FT, samples were prepared as thin films on NaCl or as KBr discs, absorptions are reported in cm^{-1} as strong (s), medium (m) or weak (w). – Flash column chromatography: Merck silica gel 60 eluting with a constant gravity head of ca. 15 cm solvent. – TLC: 0.25 mm, Merck silica gel 60 F254 visualising at 254 nm or with acidic (H_2SO_4) aq. $KMnO_4$ solution (ca. 2%). *Substrates:* Phorone (**16**), benzylideneacetone (**18**), cyclopentenone (**20**) and cinnamaldehyde (**22**) were obtained commercially. Dibenzylideneacetone (**4**), bis(*p*-methoxybenzylidene)acetone (**7**) and bis(*p*-chlorobenzylidene)acetone (**8**) were prepared by reaction of two equivalents of the appropriate arylaldehyde with acetone in ethanolic aqueous NaOH and then recrystallisation of the precipitated product from EtOAc. Allyl (and crotyl or prenyl) indium reagents were prepared by the mildly exothermic reaction of allyl, crotyl or prenyl bromide (ca. 3 M in anhydrous THF or DMF) with indium metal (ratio 3:2) under nitrogen or argon. This takes between 30 min and 2 h to reach completion and often not all of the In metal is completely consumed.[16] If the In powder (100 mesh 99.99%, Aldrich) is placed under vacuum prior to addition of anhydrous THF and freshly distilled allyl bromide, sometimes no reaction occurs. Presumably surface water is responsible for initiation of reaction.

X-ray Crystallography: X-ray measurements were made using a Bruker SMART CCD area detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å). Crystallographic data (excluding structure factors) for the structure of **10** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134689. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk).

Homoallylcyclopropanation (HAC) Reactions

(±)-2-(3′′-Butenyl)-1,1-bis[(*E*)-2′-phenylethenyl]cyclopropane (4): Under nitrogen, THF (2 mL) was added to indium powder (100 mesh, 99.99%, Aldrich, 459 mg, 4 mmol), the resulting suspension was treated with allyl bromide (0.53 mL, 6.09 mmol) and stirred vigorously. An exothermic reaction occurred immediately and after 90 min, ≥ 95% of the In powder had reacted. Dibenzylideneacetone (**3**) (235 mg, 1 mmol) was added as a solid and the resulting green/yellow solution stirred for 90 min or until no trace of **3** could be detected by TLC. LiBr was added (347 mg, 4 mmol) and an exothermic reaction resulted. The solution was left stirring overnight and then air admitted to the reaction vessel followed immediately by addition of ether (60 mL) and then 1 M HCl (20 mL) in four portions. The resulting biphasic mixture was shaken vigorously at 5–10 min intervals until TLC indicated no further generation of **4**. The organic phase was separated, dried ($MgSO_4$) and evaporated. The residue was extracted with hexane and applied to a pre-solvated silica-gel column (2.5 × 25 cm). Elution with hexane/EtOAc (40:1) collecting 28 × 30 mL fractions afforded **4**, 249 mg (83%) as a viscous colourless oil. – IR (NaCl): $\tilde{\nu}$ = 3059 (m), 3025 (m), 2924 (m), 2924 (m), 2854 (m), 1944 (w), 1873 (w), 1801 (w), 1742 (w), 1639 (m), 1599 (m), 1493 (m), 1447 (m), 1327 (w), 1250 (w), 1210 (w), 1179 (w), 1156 (w), 1073 (w), 1028 (w), 964 (s), 910 (m). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.97 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.7 Hz, $^3J_{(H,H)anti}$ = 6.1 Hz, C(3)H$_{syn}$]; 1.17 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.6 Hz; $^3J_{(H,H)syn}$ = 8.5 Hz, C(3)H$_{anti}$]; 1.25 [*dddd*, 1 H, $^3J_{(H,H)}$ = 8.5, 7.4, 6.8, 6.1 Hz, C(2)H]; 1.48 [*dddd*, 1 H, $^2J_{(H,H)}$ = 13.8 Hz; $^3J_{(H,H)}$ = 7.4, 6.8, 6.8 Hz, C(1′′)H$_{anti}$]; 1.54 [*dddd*, $^2J_{(H,H)}$ = 13.8 Hz; $^3J_{(H,H)}$ = 7.4, 7.4, 7.2 Hz, C(1′′)H$_{syn}$]; 2.16 [*ddddd*, 2 H, $^3J_{(H,H)}$ 7.3; 7.3, 7.3 Hz, $^4J_{(H,H)}$ = 1.3, 1.1 Hz, C(2′′)H$_2$]; 4.96 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.0 Hz; $^3J_{(H,H)}$ = 10.3 Hz; $^4J_{(H,H)}$ = 1.1 Hz, C(4′′)H$_{cis}$]; 5.02 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.0 Hz; $^3J_{(H,H)}$ = 17.1 Hz; $^4J_{(H,H)}$ = 1 Hz, C(4′′)H$_{trans}$]; 5.83 [*ddt*, 1 H, $^3J_{(H,H)}$ = 17.1, 10.3, 6.8 Hz, C(3′′)H]; 6.18 [*d*, 1 H, $^3J_{(H,H)}$ = 15.9 Hz, C(2′$_{anti}$)H]; 6.36 [*d*, 1 H, $^3J_{(H,H)}$ = 15.9 Hz, C(1′$_{anti}$)H]; 6.39 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′$_{syn}$)H]; 6.47 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′$_{syn}$)H]; 7.15 [*tt*, 1 H, $^3J_{(H,H)}$ = 7.2; $^4J_{(H,H)}$ = 1.3, *p*-CH$_{arom.anti}$]; 7.19 [*tt*, 1 H, $^3J_{(H,H)}$ = 7.3; $^4J_{(H,H)}$ = 1.4 Hz, *p*-CH$_{arom.syn}$]; 7.26 (m, 2 H, *m*-CH$_{arom.anti}$); 7.29 (m, 2 H, *m*-CH$_{arom.syn}$); 7.32 (m, 2 H, *o*-CH$_{arom.anti}$); 7.38 (m, 2 H, *o*-CH$_{arom.syn}$). – ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 19.9 [C(3)H$_2$]; 28.7 [C(2)H]; 28.9 [C(1′′)H$_2$]; 29.9 [C(1)]; 33.9 [C(2′′)H$_2$]; 114.7 [C(4′′)H$_2$]; 125.9 (*o*-CH$_{arom.anti}$); 126.1 (*o*-CH$_{arom.syn}$); 126.9 (*p*-CH$_{arom.anti}$); 127.2 (*p*-CH$_{arom.syn}$); 127.4 [C(1′)H$_{syn}$]; 128.6 (*m*-CH$_{arom.anti}$); 128.7 (*m*-CH$_{arom.syn}$); 130.0 [C(1′)H$_{anti}$]; 131.7 [C(2′)H$_{syn}$]; 136.2 [C(2′)$_{anti}$]; 137.6 (*i*-C$_{arom.syn}$); 137.7 (*i*-C$_{arom.anti}$); 138.5 [C(3′′)H]. – MS(EI); *m*/*z* (%): 300 [M]$^+$ (42), 257 (46), 245 (24), 229 (8), 218 (12), 215 (30), 209 (14), 202 (18), 179 (10), 167 (46), 156 (6), 153 (30), 141 (46), 128 (38), 115 (46), 103 (14), 91 (100), 77 (18), 65 (10), 55 (6). – TLC: R_f = 0.88 (hexane/EtOAc, 9:1). $C_{23}H_{24}$ (300.44): calcd. C 91.94, H 8.05%; found C 91.59, H 8.30%.

(±)-2-(3′′-Butenyl)-1,1-bis[(*E*)-2′-*p*-methoxyphenylethenyl]cyclopropane (9): Reaction as for **4** except (*E*,*E*)-1,5-bis(*p*-methoxyphenyl)penta-1,4-diene-3-one **(7)** (100.0 mg, 0.3 mmol) instead of **3** to yield **9** as a colourless oil, 73.0 mg (60%). – IR (NaCl): $\tilde{\nu}$ = 3000 (w), 2931 (w), 2834 (w), 2359 (w), 1638 (w), 1605 (m), 1510 (s), 1463 (m), 1301 (m), 1248 (s), 1174 (m), 1108 (w), 1036 (m), 994 (w), 962 (w), 912 (w), 827 (m). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.92 [*dd*, 1 H, $^2J_{(H,H)}$ = 5.1 Hz, $^3J_{(H,H)anti}$ = 5.1 Hz, C(3)H$_{syn}$]; 1.10 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4, $^3J_{(H,H)syn}$ = 8.2 Hz, C(3)H$_{anti}$]; 1.21 [m, 1 H, C(2)H]; 1.50 [m, 2 H, C(1′′)H$_2$]; 2.15 [*ddd*, 2 H, $^3J_{(H,H)}$ = 6.5, 7.7, 7.7 Hz, C(2′′)H$_2$]; 3.77 (s, 3 H, OCH$_3$); 3.79 (s, 3 H, OCH$_3$); 5.00 [m, 2 H, C(4′′)H$_2$]; 5.82 [m, 1 H, C(3′′)H]; 6.03 [*d*, 1 H, $^3J_{(H,H)trans}$ = 15.9 Hz, C(2′$_{anti}$)H]; 6.31 [*d*, 1 H, $^3J_{(H,H)trans}$ = 15.9 Hz, C(1′$_{anti}$)H]; 6.44 [*d*, 1 H, $^3J_{(H,H)trans}$ = 16.2 Hz, C(1′$_{syn}$)H]; 6.62 [*d*, 1 H, $^3J_{(H,H)trans}$ = 16.2 Hz, C(2′$_{syn}$)H]; 6.81 [m, 2 H, *AA′ of AA′BB′* $J_{(H,H)}$ = 9.1 Hz, CH$_{arom}$]; 6.86 [m, 2 H, *AA′ of AA′BB′* $J_{(H,H)}$ = 9.1 Hz, CH$_{arom}$]; 7.26 [m, 2 H, *AA′ of AA′BB′* $J_{(H,H)}$ = 9.1 Hz, CH$_{arom}$]; 7.33 [m, 2 H, *AA′ of AA′BB′* $J_{(H,H)}$ = 9.1 Hz, CH$_{arom}$]. – ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 19.8 [C(3)H$_2$]; 28.4 [C(2)H]; 29.0 [C(1′′)H$_2$]; 29.8 [C(1)]; 38.3 [C(2′′)H$_2$]; 55.2 (OCH$_3$); 55.3 (OCH$_3$); 113.9 (CH$_{arom}$); 114.0 (CH$_{arom}$); 116.2 [C(4′′)H$_2$]; 126.4 [C(1′)H$_{syn}$]; 126.9 (CH$_{arom}$); 127.3 (CH$_{arom}$); 130.3 [C(2′) H$_{syn}$]; 131.0 [C(1′)H$_{anti}$]; 134.5 [C(2′)H$_{anti}$]; 135.3 (2 × C$_{arom}$); 136.9 [C(3′′)H$_2$]; 157.9, 158.9 (2 × C$_{arom}$–O). – MS(CI); *m*/*z* (%): 361 [M + H]$^+$ (22), 360 [M]$^+$ (24), 319 (100), 305 (12), 279 (10), 253 (29), 212 (8), 161 (43), 121 (55). – HRMS(CI): $C_{25}H_{28}O_2$ requires 360.2092, found 360.2089. – TLC: R_f = 0.37 (hexane/EtOAc, 19:1).

(±)-2-(3′′-Butenyl)-1,1-bis[(*E*)-2′-*p*-chlorophenylethenyl]cyclopropane (10): Reaction as for **4** except (*E*,*E*)-1,5-bis(*p*-chlorophenyl)penta-1,4-diene-3-one (**8**) (203 mg, 0.67 mmol) instead of **3** to yield **10** (196 mg, 79%). Crystallisation from MeOH/Et_2O afforded colourless needles, m.p 60–62 °C. – IR (KBr): $\tilde{\nu}$ = 3026 (m), 2926 (m), 2848 (w), 1891 (w), 1641 (m), 1591 (w), 1491 (s), 1441 (w), 1402 (m), 1319 (w), 1252 (w), 1180 (w), 1091 (s), 1013 (m), 963 (m), 907 (m), 846 (w), 813 (m), 735 (m). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.96 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.7 Hz, $^3J_{(H,H)}$ = 6.0 Hz, C(3)H$_{syn}$]; 1.17 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.7 Hz, $^3J_{(H,H)}$ = 8.4 Hz, C(3)H$_{anti}$]; 1.26 [m, 1 H, C(2)H]; 1.50 [m, 1 H, C(1′′)H$_2$]; 2.15 [m, 1 H, C(2′′)H$_2$]; 4.95 [*dddd*, 1 H, $^3J_{(H,H)}$ = 10.1 Hz, $^2J_{(H,H)}$ = 2.0 Hz, $^4J_{(H,H)}$ = 1.1, 1.1 Hz, C(4′′)H$_{cis}$]; 5.02 [*dddd*, 1 H, $^3J_{(H,H)}$ = 18.7 Hz, $^2J_{(H,H)}$ = 2.0 Hz, $^4J_{(H,H)}$ = 1.1, 1.1 Hz, C(4′′)H$_{trans}$]; 5.82 [*dddd*, 1 H, $^3J_{(H,H)}$ = 16.8, 10.1, 6.9, 6.9 Hz, C(3′′)H]; 6.13 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′$_{anti}$) H]; 6.29 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′$_{anti}$)H]; 6.34 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′$_{syn}$) H]; 6.41 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′$_{syn}$)H]; 7.29 [m, 4 H, CH$_{arom}$]; 7.26 (m, 4 H, CH$_{arom}$). – ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 20.1 [C(3)H$_2$]; 28.9 [C(2)H]; 28.9 [C(1′′) H$_2$]; 29.9 [C(1)]; 33.9 [C(2′′) H$_2$]; 114.8 [C(4′′)H$_2$]; 126.3 [C(1′)H$_{anti}$]; 127.0 (CH$_{arom}$); 127.2 (CH$_{arom}$); 128.6 (CH$_{arom}$); 128.7 (CH$_{arom}$); 130.6 and 130.6 [C(1′)H$_{syn}$ and C(2′)H$_{syn}$]; 132.4 (C$_{arom}$); 132.8 (C$_{arom}$); 135.9 (C$_{arom}$); 136.0 (C$_{arom}$); 136.6 [C(2′)H$_{anti}$]; 138.3 [C(3′′) CH]. – MS(EI); *m*/*z* (%): 368 [M]$^+$ (31), 235 (39), 313 (19), 287 (26), 243 (20), 229 (16), 215 (37), 201 (18), 189 (20), 175 (25), 165 (30), 153 (27), 139 (20), 125 (100). – HRMS(CI): $C_{23}H_{23}{}^{35}Cl_2$ calcd. 369.1177, found 369.1194. – TLC: R_f = 0.69 (9: 1 hexane/EtOAc). – $C_{23}H_{23}Cl_2$ (371.12): calcd. C 74.80, H 6.00%; found: C 74.78, H 5.94%.

(±)-2-(3′′-Butenyl)-1,1-bis[1′-(2′-methyl)propenyl]cyclopropane (17): Reaction as for **4** except phorone **16** (156 μL, 138.2 mg, 1 mmol, Aldrich 97%) used instead of **3** to yield after kugelrohr distillation (0.1 Torr, oven T: 90 °C), **17**, 188 mg (92%) as a mobile colourless oil. – IR (NaCl): $\tilde{\nu}$ = 3067 (w), 2966 (s), 2925 (s), 2856 (m), 2360 (w), 1640 (w), 1446 (m), 1374 (m), 991 (w), 909 (m), 855 (w). – ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.32 [m, 1 H, C(3)H$_{syn}$]; 0.82 [m, 2

H, C(3)H_{anti} and C(2)H]; 1.14 and 1.61 [2 × m, 2 × 1 H, C(1′′)H_2]; 1.61 [*d*, 3 H,$^4J_{(H,H)}$ = 1.5 Hz, C(3′$_{syn}$)H_3]; 1.67 [*d*, 3 H,$^4J_{(H,H)}$ = 1.5 Hz, C(2′$_{syn}$)–CH_3]; 1.67 [*d*, 3 H,$^4J_{(H,H)}$ = 1.5 Hz, C(3′$_{anti}$)H_3]; 1.69 [*d*, 3 H,$^4J_{(H,H)}$ = 1.4 Hz, C(2′$_{anti}$)–CH_3]; 2.15 [m, 2 H, C(2′′)H_2]; 4.93 [*dddd*, $^2J_{(H,H)}$ = 2.1 Hz, $^3J_{(H,H)}$ = 10.2 Hz, $^4J_{(H,H)}$ = 1.2, 1.2 Hz, C(4′′)H_{cis}]; 5.01 [*dddd*, $^2J_{(H,H)}$ = 2.1 Hz, $^3J_{(H,H)}$ = 16.9 Hz, $^4J_{(H,H)}$ = 1.5, 1.5 Hz, C(4′′)H_{trans}]; 5.270 [*sept*, 1 H, $^4J_{(H,H)}$ = 1.5 Hz, C(1′)H_{syn}]; 5.272 [*sept*, 1 H, $^4J_{(H,H)}$ = 1.4 Hz, C(1′)H_{anti}]; 5.85 [*dddd*, 1 H, $^3J_{(H,H)}$ = 16.9, 10.2, 6.7, 6.7 Hz, C(3′′)H]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 19.1 [(C2′$_{syn}$)–CH_3]; 19.3 [(C2′$_{anti}$)–CH_3]; 22.5 [C(3)H_2]; 23.6 (C1); 25.4 (C3′$_{syn}$); 25.5 (C3′$_{anti}$); 26.2 [C(2)H]; 29.9 (C1′′); 33.9 (C2′′); 114.2 (C4′′); 125.5 (C1′$_{anti}$); 130.5 (C1′$_{syn}$); 132.8 (C2′$_{syn}$); 135.2 (C2′$_{anti}$); 139.1 (C3′′). – MS(CI); *m*/*z* (%): 205 $[M + H]^+$ (1), 204 $[M]^+$ (2), 203 $[M – H]^+$ (2), 189 (4), 163 (4), 149 (3), 135 (3), 121 (5), 85 (100), 71 (35), 57 (58). – HRMS(EI) calcd. for $(M – H)^+$ ($C_{15}H_{23}$): 203.1795, found 203.1800. – HRMS(CI) calcd. for $C_{15}H_{24}$ 204.1878, found 204.1873. – TLC: R_f = 0.80 (19: 1 hexane/EtOAc).

(±)-2-(3′′-Butenyl)-1-methyl-1-[(*E*)-2′-phenylethenyl]cyclopropanes (19$_{syn}$) and (19$_{anti}$): Reaction as for **4** except benzylideneacetone **18** (146.2 mg, 1 mmol) instead of **3** to yield **19**, 169 mg (79%) as a colourless oil. – IR (NaCl): ṽ = 3060 (m), 3011 (m), 2966 (m), 2925 (s), 2858 (m), 1942 (w), 1872 (w), 1804 (w), 1705 (w), 1641 (s), 1601 (w), 1494 (m), 1447 (m), 1381 (w), 1325 (w), 1203 (w), 1156 (w), 1072 (w), 1027 (w), 993 (m), 962 (s), 909 (s), 846 (w), 748 (s), 693 (s). – **(±)-1*S**,2*R** (*syn*)-19 :** ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.53 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)trans}$ = 5.6 Hz, C(3)H_{syn}]; 0.83 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)cis}$ = 8.3 Hz, C(3)H_{anti}]; 0.92 [*ddt*, 1 H, $^3J_{(H,H)}$ = 5.6, 6.8, 8.3 Hz, C(2)H]; 1.25 (s, 3 H, CH_3); 1.50 [*ddt*, 2 H, $^2J_{(H,H)}$ = 13.8 Hz, $^3J_{(H,H)}$ = 7.4, 6.8, C(1′′)H_2]; 2.14 [*dddt*, 2 H, $^3J_{(H,H)}$ 7.4, 6 Hz, $^4J_{(H,H)}$ = 1.7, 1.3 Hz, C(2′′)H_2]; 4.96 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.2 Hz; $^3J_{(H,H)}$ = 10.0 Hz; $^4J_{(H,H)}$ = 1.3 Hz, C(4′′)H_{cis}]; 5.03 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.2 Hz; $^3J_{(H,H)}$ = 17.1 Hz; $^4J_{(H,H)}$ = 1.7 Hz, C(4′′)H_{trans}]; 5.86 [*ddt*, 1 H, $^3J_{(H,H)}$ = 17.1, 10.0, 6 Hz, C(3′′)H]; 6.10 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′)H]; 6.39 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′)H]; 7.13 (m, 2 H, *o*-$CH_{arom.}$); 7.24 (m, 2 H, *m*-$CH_{arom.}$); 7.3 (m, 1 H, *p*-$CH_{arom.}$). – **(±)-1*S**,2*S** (*anti*)-19:** ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.36 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)trans}$ = 5.3 Hz, C(3)H_{anti}]; 0.89 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)cis}$ = 8.8 Hz, C(3)H_{syn}]; 0.92 [*dddd*, 1 H, $^3J_{(H,H)}$ = 5.3, 6.5, 6.8, 8.8 Hz, C(2)H]; 1.26 (s, 3 H, CH_3); 1.46 [*ddt,* 1 H, $^2J_{(H,H)}$ = 13.6 Hz, $^3J_{(H,H)}$ = 6.8, 6 Hz, C(1′′)$H_{pro\text{-}S}$]; 1.56 [*ddt,* 1 H, $^2J_{(H,H)}$ = 13.6, $^3J_{(H,H)}$ = 6.5, 6 Hz, C(1′′)$H_{pro\text{-}R}$]; 2.13 [*ddddd*, 2 H,$^3J_{(H,H)}$ 6, 6, 6 Hz, $^4J_{(H,H)}$ = 1.7, 1.3 Hz, C(2′′)H_2]; 4.94 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.2 Hz; $^3J_{(H,H)}$ = 10.0 Hz; $^4J_{(H,H)}$ = 1.3 Hz, C(4′′)H_{cis}]; 5.00 [*ddt*, 1 H, $^2J_{(H,H)}$ = 2.2 Hz; $^3J_{(H,H)}$ = 17.1 Hz; $^4J_{(H,H)}$ = 1.7 Hz, C(4′′)H_{trans}]; 5.82 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′)H]; 5.86 [*ddt*, 1 H, $^3J_{(H,H)}$ = 17.1, 10.0, 6 Hz, C(3′′)H]; 6.29 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′)H]; 7.13 (m, 2 H, *o*-$CH_{arom.}$); 7.24 (m, 2 H, *m*-$CH_{arom.}$); 7.3 (m, 1 H, *p*-$CH_{arom.}$). – **(±)-1*S**,2*R** (*syn*)-19:** $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 21.7 [C(3)H_2]; 22.2 [C(2)H]; 23.6 (CH_3); 27.9 [C(1)]; 29.3 [C(1′′)H_2]; 34.1 [C(2′′)H_2]; 114.6 [C(4′′)H_2]; 125.8 (*o*-$CH_{arom.}$); 126.4 (*p*-$CH_{arom.}$); 127.6 [C(1′)H]; 128.6 (*m*-$CH_{arom.}$); 134.9 [C(2′)H]; 138.6 (*i*-$C_{arom.}$); 140.4 [C(3′′)H]. **(±)-1*R**,2*R** (*anti*)-19:**: $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 16.1 (CH_3); 21.5 [C(3)H_2]; 21.7 [C(2)H]; 26.2 [C(1)]; 28.8 [C(1′′)H_2]; 34.0 [C(2′′)H_2]; 114.5 [C(4′′)H_2]; 124.5 [C(1′)H]; 125.6 (*o*-$CH_{arom.}$); 126.0 (*p*-$CH_{arom.}$); 128.6 (*m*-$CH_{arom.}$); 138.6 (*i*-$C_{arom.}$); 138.6 [C(2′)H]; 140.4 [C(3′′)H]. – MS(EI); *m*/*z* (%): 212 $[M]^+$ (37), 197 (16), 183 (14), 169 (29), 157 (15), 143 (17), 129 (45), 115 (13), 91 (38), 84 (100), 77 (7). – TLC: R_f = 0.84 (9:1 hexane/EtOAc). – $C_{16}H_{20}$ (212.33): calcd. C 90.51, H 9.49%; found C 90.64, H 9.79%.

(*Z*)-Spiro[2.4]-1-(3′-Butenyl)hept-4-enes (21$_{syn}$ and 21$_{anti}$): Reaction as for **4** except cyclopent-2-ene-1-one (**20**) (411 mg, 5 mmol) instead of **3** to yield **21**, 363 mg (49%) as a colourless oil. – IR (NaCl): ṽ = 2928 (m), 1640 (m), 1442 (m), 1276 (m), 1245 (m), 997 (m), 910 (s). – **Major (80%) (±)-1*R**,3*S**-('*syn*') isomer only:** ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.40 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)}$ = 5.5 Hz, C(2)H_{syn}]; 0.75 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)}$ = 8.5 Hz, C(2)H_{anti}]; 0.87 [*dddd*, 1 H, $^3J_{(H,H)}$ = 8.5, 7.5, 7.5, 5.5 Hz, C(1)H]; 1.45 [*ddd*, 2 H, $^3J_{(H,H)}$ = 7.5, 7.5, 7.5 Hz, C(1′)H_2]; 1.83 [*dd*, 2 H, $^3J_{(H,H)}$ = 6.9, 6.9 Hz, C(7)H_2]; 2.13 [m, 2 H, C(2′)H_2]; 2.45 [*dddd*, 2 H, $^3J_{(H,H)}$ = 6.9, 6.9, 2.2 Hz, $^4J_{(H,H)}$ = 1.8 Hz, C(6)H_2]; 4.95 [*dddd*, 1 H, $^2J_{(H,H)}$ = 1.9 Hz, $^3J_{(H,H)}$ = 10.1 Hz, $^4J_{(H,H)}$ = 1.5, 1.5 Hz, C(4′)H_{cis}]; 5.00 [*dddd*, 1 H, $^2J_{(H,H)}$ = 1.9 Hz, $^3J_{(H,H)}$ = 16.9 Hz, $^4J_{(H,H)}$ = 1.5, 1.5 Hz, C(4′)H_{trans}]; 5.42 [*ddd*, 1 H, $^3J_{(H,H)}$ = 5.7 Hz, $^4J_{(H,H)}$ = 1.8, 1.8 Hz, C(4)H]; 5.75 [*ddd*, 1 H, $^3J_{(H,H)}$ = 5.7, 2.2, 2.2 Hz, C(5)H]; 5.84 [*dddd*, 1 H, $^3J_{(H,H)}$ = 16.9, 10.1, 6.8, 6.8 Hz, C(3′)H]. – $^{13}C\{^1H\}$NMR ($CDCl_3$, 75 MHz): δ = 19.9 [C(2)H_2]; 25.3 [C(1)H]; 29.8 [C(3)]; 30.7 [C(1′)H_2]; 31.5 [C(6)H_2]; 33.9 [C(2′)H_2]; 34.1 [(C(7)H_2]; 114.3 [(C4′)H_2]; 130.4 [C(5)H]; 133.8 [C(4)H]; 139.0 [(C3′)H]. – MS(EI); *m*/*z* (%): 147 $[M – H]^+$ (15), 133 (10), 123 (16), 107 (38), 95 (27), 91 (70), 84 (87), 79 (100), 67 (44), 55 (53). – HRMS(EI): $C_{11}H_{15}$ $[M – H^+]$ calcd. 147.1174, found 147.1172. – TLC: R_f = 0.94 (2:1 hexane/EtOAc).

(±)-2-(3′′-Butenyl)-1-[(*E*)-2′-phenylethenyl]cyclopropanes (23$_{syn}$) and (23$_{anti}$): Reaction as for **4** except cinnamaldehyde (**22**) (136 mg, 1 mmol) instead of **3** with a modified workup. Thus, after addition of ether and acid, the ether phase was separated and the volatiles removed in vacuo. The residue was dissolved in $CHCl_3$ (ca. 20 mL) and 15 mL 1 M HCl added. The two phase mixture was refluxed for 12 h prior to purification in the usual manner to yield **23**, 103 mg (52%) as a colourless oil. – IR (NaCl): ṽ = 3048 (m), 3013 (m), 2966 (w), 2919 (m), 2343 (w), 1942 (w), 1872 (w), 1790 (w), 1643 (m), 1596 (w), 1490 (m), 1443 (m), 1320 (w), 1255 (w), 1208 (w), 1155 (w), 1067 (w), 1020 (w), 991 (m), 955 (s), 908 (s), 808 (w), 738 (m), 691 (s). – **Major (66%) (±)-1*S**,2*S**-*anti* isomer only:** ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.62 [*ddd*, 1 H, $^2J_{(H,H)}$ = 4.6 Hz, $^3J_{(H,H)}$ = 8.3, 5.5 Hz, C(3)H_{anti}]; 0.69 [*ddd*, 1 H, $^2J_{(H,H)}$ = 4.6 Hz, $^3J_{(H,H)}$ = 8.2, 4.8 Hz, C(3)H_{syn}]; 0.88 [m, 1 H, C(2)H]; 1.31 (m, 1 H, C(2)H]; 1.41 [m, 2 H, C(1′′)H_2]; 2.17 [m, 2 H, C(2′′)H_2]; 4.95 [*dt*, 1 H, $^3J_{(H,H)}$ = 10.3 Hz, $^4J_{(H,H)}$ = 1.1 Hz, C(4′′)H_{cis}]; 5.02 [*dt*, 1 H, $^3J_{(H,H)}$ = 17.0 Hz, $^4J_{(H,H)}$ = 1.1 Hz, C(4′′)H_{trans}]; 5.77 [*dd*, 1 H, $^3J_{(H,H)}$ = 15.9, 8.8 Hz, C(1′)H]; 5.85 [*dddd,* 1 H, $^3J_{(H,H)}$ = 17.0, 10.3, 6.6, 6.6 Hz, C(3′′)H]; 6.41 [*d*, 1 H, $^3J_{(H,H)}$ = 15.9 Hz, C(2′)H]; 7.21 (m, 5 H, CH_{arom}). – **Major (66%) (±)-1*S**,2*S**-*anti* isomer only:** $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 14.5 [C(3)H_2]; 21.2 [C(2)H]; 22.3 [C(1)H]; 33.4 [C(1′′)H_2]; 33.6 [C(2′′)H_2]; 114.5 [C(4′′)H_2]; 125.6, 126.4 (2 × CH_{arom}); 126.9 [C(2′)H]; 128.4 (CH_{arom}); 134.4 [C(1′)H]; 138.7 [C(3′′)H]. – MS(EI); *m*/*z* (%): 198 $[M]^+$ (42), 169 (10), 156 (36), 143 (45), 130 (88), 129 (98), 128 (69), 115 (74), 104 (15), 91 (100), 79(25), 65 (12). – HRMS(EI) $C_{15}H_{18}$ calcd. 198.1409, found 198.1404. – TLC: R_f = 0.84 (9:1 hexane/EtOAc).

(±)-2-[3′′-(2′′-Methyl)butenyl)]-3-methyl-1,1-bis[(*E*)-2′-phenylethenyl]cyclopropane (24): Reaction as for **4** except crotyl bromide (6.3 mL, 61 mmol, Aldrich 85% *trans*) used instead of allyl bromide to yield **24**, 2.81 g (79%) as a colourless oil. The diastereoisomeric mixture of **24** could not be separated by chromatography on silica gel that had been impregnated with $AgNO_3$. ^1H- and ^{13}C-NMR assignments are given for the major diastereomer [(±)-*cis*-(2*S**,3*R**, 2′′*R**)] and are based on extensive spectral simulation (^1H) and subsequent DEPT and CH correlation (long and short range). –

IR (NaCl): ṽ = 3070 (m), 3024 (m), 2938 (m), 2868 (m), 2363 (w), 1943 (w), 1874 (w), 1804 (w), 1638 (m), 1599 (m), 1493 (m), 1448 (m), 1417 (w), 1378 (w), 1099 (w), 1072 (w), 1028 (w), 964 (m), 911 (m), 834 (w), 745 (m), 692 (s). – ^{1}H NMR ([D$_6$]acetone, 500 MHz): δ = 1.07 [*d*, 3 H, $^3J_{(H,H)}$ = 6.8 Hz, C(2′′)–CH$_3$]; 1.20 [*d*, 3 H, $^3J_{(H,H)}$ = 6.5 Hz, C(3)–CH$_3$]; 1.40 [*simul. ddd*, 1 H, $^3J_{(H,H)}$ = 9.5, 7.4, 6.2, C(2)H]; 1.49 [*simul. dq*, 1 H, $^3J_{(H,H)}$ = 9.5, 6.5, C(3)H]; 1.50 [*simul. ddd*, 1 H, $^2J_{(H,H)}$ = 13.9, $^3J_{(H,H)}$ = 7.4, 6.5, C(1′′)*H*H]; 1.63 [*simul. ddd*, 1 H, $^2J_{(H,H)}$ = 13.9, $^3J_{(H,H)}$ = 6.5, 6.2, C(1′′)H*H*]; 2.30 [*dddddq*, 1 H, $^3J_{(H,H)}$ = 6.5, 6.5, 6.8, 7.5, $^4J_{(H,H)}$ = 1.2, 0.9, C(2′′)H]; 4.93 [*ddd*, 1 H, $^2J_{(H,H)}$ = 1.9, $^3J_{(H,H)}$ = 10.2 Hz, $^4J_{(H,H)}$ = 0.9 Hz, C(4′′)H$_{cis}$]; 5.04 [*ddd*, 1 H, $^2J_{(H,H)}$ = 1.9 Hz, $^3J_{(H,H)}$ = 17.2 Hz, $^4J_{(H,H)}$ = 1.2 Hz, C(4′′)H$_{trans}$]; 5.86 [*ddd*, 1 H, $^3J_{(H,H)}$ = 17.2, 10.2, 7.5 Hz, C(3′′)H]; 6.32 [*d*, 1 H, $^3J_{(H,H)}$ = 16.3 Hz, C(1′$_{syn}$)H]; 6.41 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′$_{anti}$)H]; 6.53 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′$_{anti}$)H]; 6.62 [*d*, 1 H, $^3J_{(H,H)}$ = 16.3 Hz, C(2′$_{syn}$)H]; 7.19 (m, 1 H, *p*-CH$_{arom\ anti}$); 7.20 (m, 1 H, *p*-CH$_{arom syn}$); 7.29 (m, 2 H, *m*-CH$_{arom\ syn}$); 7.31 (m, 2 H, *m*-CH$_{arom\ anti}$); 7.42 (m, 2 H, *o*-CH$_{arom\ anti}$); 7.46 (m, 2 H, *o*-CH$_{arom\ syn}$). – ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 9.6 [C(3)CH$_3$]; 20.0 [C(2′′)CH$_3$]; 25.1 [C(3)H]; 29.4 (C(2)H]; 30.6 [C(1)]; 31.3 [C(1′′)H$_2$]; 38.2 [C(2′′)H]; 112.7 (C(4′′)H$_2$]; 125.8 (2 × CH$_{arom}$); 126.7 (2 × CH$_{arom}$); 126.9 [C(1′$_{anti}$)-H]; 128.0 [C(1′$_{syn}$)H]; 128.2 (2 × CH$_{arom}$); 133.4 [C(2′$_{syn}$)H]; 136.8 [C(2′$_{anti}$)H]; 137.7, 138.0 (2 × C$_{arom}$); 144.4 [C(3′′)H]. – MS(EI); *m*/*z* (%): 328 [M]$^+$ (38), 313 (6), 271 (62), 259 (36), 245 (14), 237 (24), 231 (14), 218 (20), 215 (38), 202 (26), 195 (18), 181 (35), 169 (57), 155 (35), 141 (40), 128 (33), 115 (46), 105 (30), 91 (100), 84 (26), 77 (18), 65 (10), 55 (30). – TLC: R_f = 0.67 (9:1 hexane/EtOAc). – C$_{25}$H$_{28}$ (328.49): calcd. C 91.41, H 8.59%; found C 91.72, H 8.60%.

(±)-2-[3′′-(2′′-Methyl)butenyl)]-3-methyl-1,1-bis[1′-(2′-methyl)-propenyl]cyclopropane (25): Reaction as for **24** except phorone **16** (400 mg, 2.9 mmol, Aldrich 97%) used instead of **3** to yield after chromatography (40:1 hexane/EtOAc) **25**, 350 mg (52%) as a colourless oil. – IR (NaCl): ṽ = 2973 (s), 2934 (s), 1720 (m), 1688 (m), 1674 (m), 1633 (s), 1557 (w), 1446 (m), 1378 (m), 1222 (m), 1114 (m), 1032 (m), 996 (m), 912 (m), 869 (m), 770 (m). **Major (55%) diastereomer only:** ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.84 [*simul. dq*, 1 H, $^3J_{(H,H)}$ = 9.5, 6.5 Hz, C(3)–H]; 0.90 [*simul. d*, 3 H, $^3J_{(H,H)}$ = 6.5 Hz, C(3)–CH$_3$]; 0.95 [*simul. ddd*, 1 H, $^3J_{(H,H)}$ = 9.5, 7.0, 3.5 Hz, C(2)–H]; 1.025 [*d*, 3 H, $^3J_{(H,H)}$ = 7.0 Hz, C(2′′)–CH$_3$]; 1.03 [*simul. ddd*, 1 H, $^2J_{(H,H)}$ = 14.0 Hz, $^3J_{(H,H)}$ = 7.0, 7.0 Hz, C(1′′)–HH]; 1.40 [*ddd*, 1 H, $^2J_{(H,H)}$ = 14.0 Hz, $^3J_{(H,H)}$ = 7.7, 3.5 Hz, C(1′′)–H*H*]; 1.60 and 1.64 [*d*, 3 H, $^4J_{(H,H)}$ = 1.1 Hz, *syn* and *anti* C(2′)–CH$_3$]; 1.64 and 1.70 [*d*, 3 H, $^4J_{(H,H)}$ = 1.1 Hz, *syn* and *anti* C(3′)–H$_3$]; 2.15 [*dddq*, 1 H, $^3J_{(H,H)}$ = 7.7, 7.0, 7.0, 5.6 Hz, C(2′′)–H]; 4.91 [*ddq*, 1 H, $^2J_{(H,H)}$ = 2.0 Hz, $^3J_{(H,H)}$ = 10.3 Hz, $^4J_{(H,H)}$ = 1.3 Hz, C(4′′)H$_{cis}$]; 4.97 [*ddq*, 1 H, $^2J_{(H,H)}$ = 2.0 Hz, $^3J_{(H,H)}$ = 15.3 Hz, $^4J_{(H,H)}$ = 1.3 Hz, C(4′′)H$_{trans}$]; 5.19 and 5.34 [*sept*, 1 H, $^4J_{(H,H)}$ = 1.1 Hz, *syn* and *anti* C(2′)–H]; 5.76 [*ddd*, 1 H, $^3J_{(H,H)}$ = 15.3, 10.3, 5.6 Hz, C(3′′)–H]. – **Major (55%) diastereomer only:** ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ = 9.4 [C(3)–CH$_3$]; 19.4 and 20.1 [*syn* and *anti* C(2′)–CH$_3$]; 20.3 [C(2′′)–CH$_3$]; 23.3 [C(3)]; 25.1 [C(1)]; 25.2 and 25.4 [*syn* and *anti* C(3′)]; 27.0 [C(2)]; 31.6 [C(1′′)]; 38.2 [C(2′′)], 112.3 [C(4′′)]; 122.0 and 132.6 [*syn* and *anti* C(1′)]; 131.9 [*syn*-C(2′)]; 136.1 (*anti*-C(2′)]; 144.9 [C(3′′)]. – MS(EI); *m*/*z* (%): 231[M – H]$^+$ (7), 217 (10), 189 (11), 181 (9), 177 (25), 163 (30), 149 (32), 135 (40), 121 (69), 107 (63), 95 (48), 91 (53), 83 (64), 69 (69), 59 (55). – HRMS(EI), C$_{17}$H$_{28}$: calcd. 232.2191, found 232.2191. – TLC: R_f = 0.33 (19:1 hexane/EtOAc).

3,3,9-Trimethyl-4-phenyl-6-[(*E*)-2′-phenylethenyl]-1,5,8-decatrienes (*E*-26) and (*Z*-26): Reaction as for **4** except dimethylallyl bromide (0.702 mL, 9.09 mmol, Aldrich 96% purity) used instead of allyl bromide to yield a 1.2: 1 mixture of *E*-**26** and *Z*-**26**, 150 mg (42%) as a colourless oil. – IR (NaCl): ṽ = 3070 (w), 3026 (m), 2965 (s), 2925 (m), 1704 (w), 1638 (w), 1598 (w), 1494 (m), 1450 (m), 1414 (w), 1377 (m), 1168 (w), 1101 (w), 1072 (w), 1009 (w), 958 (m), 913 (m), 776 (w), 748 (m), 717 (m), 692 (s). – ***E*-26:** ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.97 and 1.03 [s, 3 H, C(3)(CH$_3$)$_2$); 1.68 [*d*, 3 H, $^4J_{(H,H)}$ = 1.4 Hz, C(10)H$_3$), 1.74 [*d*, 3 H, $^4J_{(H,H)}$ = 1.4 Hz, [C(9)CH$_3$]; 2.99 [m, 2 H, $^3J_{(H,H)}$ = 6.9 Hz, $^4J_{(H,H)}$ = 0.7 Hz, C(7)H$_2$]; 3.47 [*d*, 1 H, $^3J_{(H,H)}$ = 10.3 Hz, C(4)H]; 4.92 [*dd*, 1 H, $^2J_{(H,H)}$ = 1.5 Hz, $^3J_{(H,H)}$ = 17.5 Hz, C(1)H*Htrans*]; 5.02 [*dd*, 1 H, $^2J_{(H,H)}$ = 1.5 Hz, $^3J_{(H,H)}$ = 10.8 Hz, C(1)H*Hcis*]; 5.20 [*t-sept*, 1 H, $^3J_{(H,H)}$ = 6.9 Hz, $^4J_{(H,H)}$ = 1.4 Hz, C(8)H]; 5.87 [*dd*, 1H $^3J_{(H,H)}$ = 17.5, 10.8 Hz, C(2)H]; 6.06 [*d*, 1 H, $^3J_{(H,H)}$ = 10.3 Hz, C(5)H]; 6.43 [*d*, 1 H, $^3J_{(H,H)}$ = 16.2 Hz, C(1′)H]; 6.43 [*d*, 1 H, $^3J_{(H,H)}$ = 16.2 Hz, C(2′)H]; 7.23 (m, 10 H, 2 × C$_6$H$_5$). ***Z*-26:** ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.97 and 1.04 [s, 3 H, C(3)(CH$_3$)$_2$]; 1.63 [*d*, 3 H, $^4J_{(H,H)}$ = 1.3 Hz, C(10)H$_3$]; 1.74 [*d*, 3 H, $^4J_{(H,H)}$ = 1.1 Hz, C(9)CH$_3$]; 2.97 [m, 2 H, $^3J_{(H,H)}$ = 6.8 Hz, C(7)H$_2$]; 3.66 [*d*, 1 H, $^3J_{(H,H)}$ = 10.3 Hz, C(4)H]; 4.87 [*tqq*, 1 H, $^3J_{(H,H)}$ = 6.9 Hz, $^4J_{(H,H)}$ = 1.3, 1.1 Hz, C(8)H]; 4.90 [*dd*, 1 H, $^2J_{(H,H)}$ = 1.5 Hz, $^3J_{(H,H)}$ = 17.5 Hz, C(1)H*Htrans*]; 5.01 [*dd*, 1 H, $^2J_{(H,H)}$ = 1.5 Hz, $^3J_{(H,H)}$ = 10.8 Hz, C(1)H*Hcis*]; 5.86 [*dd*, 1 H, $^3J_{(H,H)}$ = 17.5, 10.8 Hz, C(2)H]; 5.90 [*d*, 1 H, $^3J_{(H,H)}$ = 10.3 Hz, C(5)H]; 6.52 [*d*, 1 H, $^3J_{(H,H)}$ = 16.3 Hz, C(2′)H], 7.08 [*d*, 1 H, $^3J_{(H,H)}$ = 16.3 Hz, C(1′)H]; 7.23 (m, 10 H, 2 × C$_6$H$_5$-). – ***E*-26:** ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 17.8 [C(9)*C*H$_3$]; 18.1 [C(10)]; 33.1 [C(7)]; 54.3 [C(4)]; 40.4 [C(3)]; 112.1 [C(1)]; 122.7 [C(8)]; 126.5 [C(2′)]; 133.0 [C(1′)]; 132.6 [C(6)]; 134.4 [C(5)]; 142.2 [C(9)]; 145.9 [C(2)]. ***Z*-26:** ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 25.5 [C(9)*C*H$_3$]; 25.7 [C(10); 26.4 [C(7)]; 53.4 [C(4)]; 40.6 [C(3)]; 112.0 [C(1)]; 122.5 [C(8)]; 125.6 [C(1′)]; 128.7 [C(2′)]; 131.3 [C(6)]; 131.6 [C(5)]; 142.6 [C(9)]; 145.8 [C(2)]. ***E*-26 and *Z*-26:** ^{13}C{^{1}H} NMR (CDCl$_3$, 75 MHz): δ = 126.2, 126.4, 127.6, 127.7 (*o*-CH$_{arom.}$); 126.1, 127.0, 127.3 and 128.7 (*p*-CH$_{arom.}$); 127.4, 128.5, 129.5, 129.6 (*m*-CH$_{arom.}$); 135.8, 137.9, 138.0 and 138.2 (*i*-C$_{arom.}$). – MS(EI); *m*/*z* (%): 355 [M – H]$^+$ (3), 287 (100), 245 (15), 231 (12), 215 (22), 196 (16), 181 (20), 167 (30), 153 (16), 145 (14), 141 (24), 128 (20), 117 (44), 105 (18), 91 (48), 77 (14), 69 (58), 53 (14). – TLC: R_f = 0.87 (9:1 hexane/EtOAc). – C$_{27}$H$_{32}$ (356.54): calcd. C 90.95, H 9.05%; found C 90.91, H 9.29%.

Derivatisation of Homoallyl Chain of Cyclopropanes 4 and 10

(±)-2-(4′′-Hydroxy-3′′-butenyl)-1,1-bis[(*E*)-2′-phenylethenyl]-cyclopropane (13): To a stirred solution of **4** (1.025 g, (3.41 mmol) in THF (15 mL) was added 9-BBN, 1.0 g, (8.2 mmol) under argon. After 15 min the starting material had been consumed (TLC, hexane/EtOAc, 9:1) and ethanol was added (25 mL). After 10 min 3 M NaOH was added (25 mL) and the mixture cooled to 0 °C. After a further 20 min H_2O_2 (30%, 14 mL) was added and the reaction warmed to room temp. The resulting biphasic mixture was extracted with diethyl ether (4 × 40 mL) and the extract washed with saturated brine solution (2 × 20 mL) and water (2 × 20 mL) then dried ($MgSO_4$) and the solvent removed in vacuo. The resulting oil was purified by flash chromatography (hexane:EtOAc, 2:1) to yield **13** as a yellow oil, 0.816 g, (75%). – IR (NaCl): ṽ = 3583 (w), 3346 (br m), 3079 (w), 3057 w, 3024 (m), 2995 (w), 2931 (s), 2856 (m), 2360 (w), 1945 (w), 1874 (w), 1802 (w), 1746 (w), 1639 (m), 1598 (m), 1493 (m), 1447 (m), 1058 (m), 1029 (m), 964 (s), 911 (w), 839 (w), 747 (s), 693 (s). – ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 0.97 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.5 Hz, $^3J_{(H,H)}$ = 5.6 Hz, C(3)H$_{syn}$]; 1.15 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.5 Hz, $^3J_{(H,H)}$ = 8.5 Hz, C(3)H$_{anti}$]; 1.22 [m, 1 H, C(2)H]; 1.35–1.65 [m, 7 H, C(1′′)H$_2$, C(2′′)H$_2$, C(3′′)H$_2$, OH]; 3.61 [*t*, 2 H,

$^3J_{(H,H)}$ = 6.4 Hz, C(4′′)H_2]; 6.18 [*d*, 1 H, $^3J_{(H,H)}$ = 16 Hz, C(2′$_{anti}$)H]; 6.36[*d*, 1 H, $^3J_{(H,H)}$ = 16 Hz, C(1′$_{anti}$)H]; 6.39[*d*, 1 H, $^3J_{(H,H)}$ = 16 Hz, C(1′$_{syn}$)H]; 6.48 [*d*, 1 H, $^3J_{(H,H)}$ = 16 Hz, C(2′$_{syn}$)H]; 7.13–7.42 (m, 10 H, CH_{arom}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 19.9 [C(3)H_2]; 25.8 [C(1′′)H_2]; 29.1 [C(2′′)H_2]; 29.2 [C(2)H]; 29.8 [C(1)]; 32.4 [C(2′′)H_2]; 62.8 [C(4′′)H_2]; 125.8, 126.0 (2 × *o*-CH_{arom}); 126.8, 127.1 (2 × *p*-CH_{arom}); 127.3 [C(1′$_{anti}$)H]; 130.0 [C(2′$_{anti}$)H]; 131.6 [C(2′$_{syn}$)H]; 136.2 [C(2′$_{anti}$)H]; 137.5, 137.6 (2 × *i*-C_{arom}). – MS(EI); *m/z* (%): 318 $[M]^+$ (86), 300 (10), 257 (20), 245 (90), 231 (34), 219 (54); 215 (48), 209 (26), 202 (20), 181 (20), 167 (56), 153 (44), 141 (63), 128 (45), 115 (46), 103 (20), 91 (100), 85 (44), 77 (18). – HRMS(EI), $C_{23}H_{26}O$: calcd. 318.1984, found 318.1987. – HRMS(CI) $[M + H]^+$ $C_{23}H_{27}O$: calcd. 319.2062, found 319.2060. – TLC: R_f = 0.46 (hexane/EtOAc, 2:1).

(±)-2-(4′′-Hydroxy-3′′-butenyl)-1,1-bis[(*E*)-2′-*p*-chlorophenylethenyl]cyclopropane (14): Prepared in an identical manner to **13** but from **10** (0.23 g, 0.63 mmol) to yield **12** as a yellow oil, 227.0 mg, (94%). – IR (NaCl): ṽ = 3381 *br*, 3026 (w), 2933 (m), 2858 (m), 2326 (w), 1894 (w), 1639 (m), 1490 (s), 1404 (m), 1264 (m), 1178 (w), 1090 (s), 1012 (m), 966 (m), 816 (m), 738 (m). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.96 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)}$ = 5.7 Hz, C(3)H_{syn}]; 1.80 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.4 Hz, $^3J_{(H,H)}$ = 8.4 Hz, C(3)H_{anti}]; 1.22 [m, 1 H, C(2)H]; 1.45 [m, 4 H, C(2′′)H_2 and C(1′′)H_2]; 1.56 [m, 2 H, C(3′′)H_2]; 1.76 (*br* s, 1 H, OH); 3.60 [*t*, 2H; $^3J_{(H,H)}$ = 6.2 Hz, C(4′′)H_2]; 6.13 [*d*, 1 H,$^3J_{(H,H)trans}$ = 16.0 Hz, C(1′)H]; 6.28 [*d*, 1 H,$^3J_{(H,H)trans}$ = 16.0 Hz, C(2′)H]; 6.34 [*d*, 1 H,$^3J_{(H,H)trans}$ = 16.0 Hz, C(1′)H]; 6.41 [*d*, 1 H,$^3J_{(H,H)trans}$ = 16.0 Hz, C(2′)H]; 7.29 (m, 8 H, CH_{arom}). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ =20.0 [C(3)H]; 25.8 and 29.0, [C(1′′)H_2 and C(2′′)H_2]; 29.3 [C(2)H]; 29.8 [C(1)]; 32.3 [C(3′′)H_2]; 62.7 [C(4′′)H_2]; 126.1 [C(2′)H]; 126.9, 127.1, 128.5, 128.6 (4 × CH_{arom}); 130.5 and 130.4 [C(2′)H and C(1′)H]; 135.8, 136.0, (2 × *i*-C_{arom}); 132.2, 132.6 (2 × Cl–C_{arom}); 136.6 [C(1′)H]. – MS(EI); *m/z* (%): 386 $[M]^+$ (50), 313 (45), 287 (55), 252 (20), 243 (19), 229 (21), 215 (41), 201 (20), 189 (20), 175 (39), 165 (39), 153 (38), 139 (28), 125 (100). – HRMS (EI), $C_{23}H_{25}Cl_2O$: calcd. 386.1204, found 386.1202. – TLC: R_f = 0.1 (hexane/EtOAc, 9:1). – $C_{23}H_{25}Cl_2O$ (387.34): calcd. C 71.32, H 6.24%; found: C 71.05, H 6.28.

4-Bis[(*E*)-2′-*p*-Chlorophenylethenyl]cyclopropylbutyl *p*-Nitrobenzoate (15): (±)-2-(3′′-butenyl-4′′-hydroxy)-1,1-bis[(*E*)-2′-*p*-chlorophenylethenyl]cyclopropane (**14**) 120 mg (0.31 mmol), Et_3N 63 mg (0.62 mmol) and *p*-nitrobenzoyl chloride 68 mg (0.37 mmol) were added to CH_2Cl_2 (1 mL) to afford a partial solution. On addition of DMAP (1–2 mg) all material dissolved to afford a yellow solution. After 3.5 h. TLC indicates there was still **14** present and a further 35 mg (0.19 mmol) of *p*-nitrobenzoyl chloride was added. After further 2 h, TLC indicated >95% conversion of **14** and 5 mL of HCl (aq) 1 M was added. The mixture was extracted with CH_2Cl_2 (4 × 20 mL) and the extracts washed with two 20 mL portions of saturated brine then dried ($MgSO_4$). Removal of the volatiles in vacuo afforded a yellow oil. Purification by column chromatography on silica-gel afforded **15**, 105 mg (63%) as a viscous oil. – IR (NaCl): ṽ = 3025 (m), 2935 (m), 2857 (m), 2360 (w), 1896 (w), 1723 (s), 1639 (m), 1608 (m), 1526 (s), 1490 (s), 1461 (m), 1406 (m), 1348 (s), 1319 (m), 1275 (s), 1177 (w), 1118 (s), 1102 (s), 1013 (s), 966 (s), 909 (m), 872 (m), 842 (m), 812 (s), 784 (m), 719 (s). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.99 [*dd*, 1 H, $^2J_{(H,H)}$ = 4.6 Hz, $^3J_{(H,H)}$ = 5.7 Hz, C(3)H_{syn}]; 1.18 [m, 1 H, C(3)H_{anti}]; 1.25 [m, 1 H, C(2)H]; 1.45 [m, 2 H, C(1′′)H_2]; 1.57 [m, 2 H, C(2′′)H_2]; 1.82 [m, 2 H, C(3′′)H_2]; 4.36 [*dd*, 2 H, $^3J_{(H,H)}$ = 6.6, 6.6, C(4′)H_2]; 6.15 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′)H]; 6.29 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′)H]; 6.34 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(1′)H]; 6.43 [*d*, 1 H, $^3J_{(H,H)}$ = 16.0 Hz, C(2′)H]; 7.25 [m, 10 H, CH_{arom}]; 8.14 (AA′BB′, J_{AB} = 9.2, CH_{arom} benzoate); 8.25 (AA′BB′, J_{AB} = 9.2 Hz, CH_{arom} benzoate). – $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 20.1 [C(3)H]; 26.0 [C(2′′)H_2]; 28.3 [C(3′′)H_2]; 28.9 [C(1′′)H_2]; 29.1 [C(2)H]; 29.8 (C1); 65.8 [C(4′′)H_2]; 123.4 [2 × CH_{arom} (benzoate)]; 126.4 [C(1′)H], 127.0 (2 × CH_{arom}); 127.1 (2 × CH_{arom}); 128.6 (2 × CH_{arom}); 128.7 (2 × CH_{arom}); 130.3 [C(1′)H]; 130.5 [2 × CH_{arom} (benzoate)]; 130.6 [C(2′)H]; 132.4, 132.8, 135.6, 135.7, 135.9 (5 × C_{arom}); 136.4 [C(2′)H]; 150.4 (C_{arom}–N); 164.6 (CO_2). – MS(EI); *m/z* (%): 535 $[M]^+$ {fits predicted isotope cluster: 535 (calc. 35, obs. 35), 536 (12, 12), 537 (25, 25), 538 (8, 8), 539 (5, 5), 540(1, 2), 541 (1, 0)), 518 (13), 410 (14), 368 (9), 327 (14), 313 (20), 300 (7), 287 (80), 265 (18), 252 (27), 243 (30), 229 (20), 215 (40), 201 (20), 191 (30), 175 (42), 165 (33), 150 (53), 141 (18), 125 (100), 115 (24), 104 (46), 92 (20), 81 (20), 76 (20), 69 (1), 67 (10), 55 (10). – HRMS(CI), $^{12}C_{30}{}^1H_{28}{}^{35}Cl_2{}^{14}N^{16}O_4$: calcd. 536.1395, found 536.1411. – TLC: R_f = 0.24 (hexane/EtOAc, 9:1).

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