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Palladium-Catalysed Oligocyclisations of 2-Bromododeca-1,11-diene-6-ynes[1]

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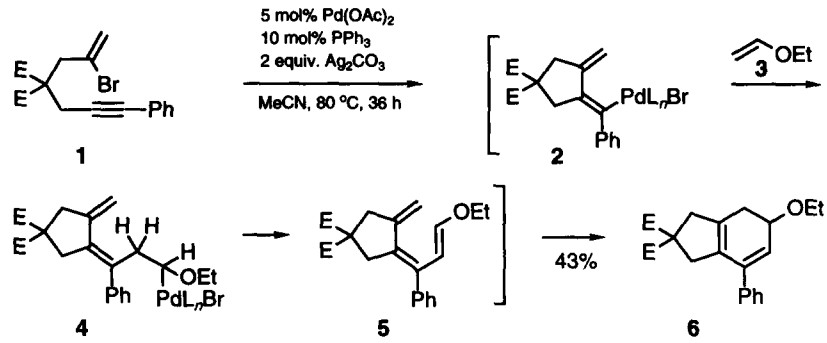
Abstract: Variously substituted 2-bromo-dodeca-1,11-diene-6-ynes under palladium-catalysis undergo (i) biscyclisation followed by (a) 6π-electrocyclic rearrangement to give [1,2:3,4]bisannelated cyclohexadiene derivatives (*cis/trans*-**7**-Me → *cis/trans*-**21**-Me, **9** → **20**-Me, **14**-Me → **19**-Me, **14**-All → **22+23**, **15a–e** → **24a–e**, **27** → **28**, *E,E*-**37** → **38+39**, **42** → **43**), (b) Diels-Alder reaction to bicyclo[4.1.0]hept-2-enes (*E/Z*-**54** → **52**), *or* (ii) tetracyclisation to a tetracyclo[6.3.1.$0^{1,8}$.$0^{2,6}$]dodec-2-ene (**58** → **60**), simply controlled by the type of substituents and substitution pattern on the starting dienyne as well as the reaction conditions. Copyright © 1996 Elsevier Science Ltd

Introduction

Sequential transformations have become a rapidly expanding area of research.[2] The formation of several carbon-carbon bonds by a combination of different reaction types in a single experimental operation is a highly attractive method of enhancing the efficiency of organic synthesis. In this respect the potential of transition metal-catalysed coupling reactions is well known and has been greatly probed and extended in recent years.[3] In particular the Heck reaction has gained considerable importance in intra-, inter-, and even mixed inter-intramolecular carbon-carbon bond coupling sequences of open-chain precursors.[4] Indeed, due to several modern improvements it has developed from a simple coupling reaction for alkenes with alkenyl and aryl halides into an impressively useful synthetic tool. Based on the working hypothesis for the mechanism of the Heck reaction[4h] with the assumed occurrence of certain alkenyl-palladium intermediates, one can conceive of combinations of several consecutive Heck type and other reactions which ought to be applicable for the efficient construction of complex oligocyclic molecules. We report herein on the palladium-catalysed transformations of various 2-bromododeca-1,11-diene-6-ynes which can give tricyclic systems with a central six- and two annelated five-membered rings by a reaction cascade of two Heck type couplings and a subsequent 6π-electrocyclisation. The scope and limitations of this reaction with regard to the substitution pattern and the presence of heteroatoms in the substrates are presented.

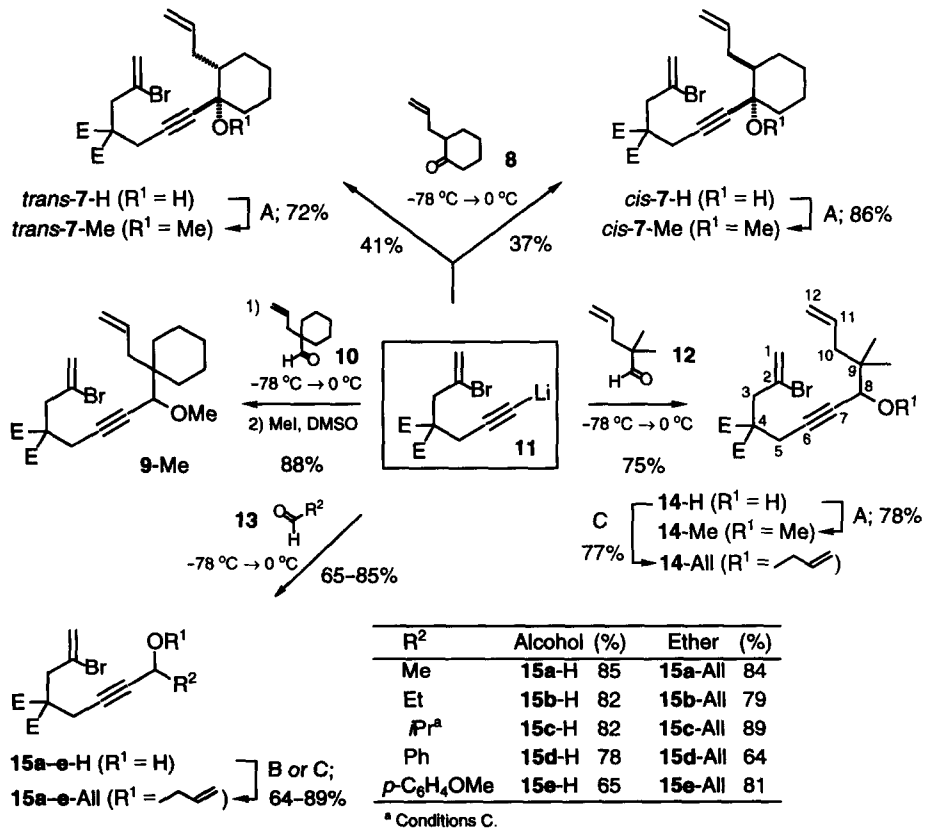
The Basic Tricyclisation Cascade

In close analogy to the finding by Negishi et al. that the 2-bromohept-1-ene-6-yne **1** can be coupled with alkenes leading to indene derivatives,[5] we recently discovered that, when subjected to Heck reaction conditions (5 mol% $Pd(OAc)_2$, 10 mol% PPh_3, 2 equiv. Ag_2CO_3, MeCN, 80 °C, 36 h), various enol ethers, such as ethyl vinyl ether (**3**), can be coupled with **1**, to give five-membered ring annelated cyclohexadienes such as **6**. This transformation may be envisaged to proceed via intramolecular cyclisation of enyne **1** to the palladium-alkenyl intermediate **2**, which is trapped intermolecularly by excess alkene, giving the alkyl palladium species **4**. β-Hydride elimination from **4** then leads to the conjugated hexatriene **5**, which undergoes a thermal electrocyclic rearrangement to the final cyclohexadiene **6** in 43% yield (**Scheme 1**). It was essential to use silver(I) carbonate instead of the cheaper potassium carbonate to prevent palladium-catalysed double bond isomerisation.[6] The reaction temperature plays a critical role in determining the type of product, as higher temperatures (110–120 °C) usually afford aromatized bicyclic compounds.[7] The intra-intermolecular



Scheme 1. E = CO_2Et.

sequence of two Heck reactions and a 6π-electrocyclisation complement the sequence of an intramolecular palladium-catalysed cyclisation of 2-bromo-1,6- as well as 2-bromo-1,7-dienes and a Diels-Alder reaction of the resulting 1,2-bismethylenecyclopentanes with alkenes to yield bicyclo[4.3.0]non-1(6)-enes and bicyclo-[4.4.0]dec-1(6)-enes, respectively.[1d,e]



R^2	Alcohol	(%)	Ether	(%)
Me	**15a**-H	85	**15a**-All	84
Et	**15b**-H	82	**15b**-All	79
*i*Pr[a]	**15c**-H	82	**15c**-All	89
Ph	**15d**-H	78	**15d**-All	64
p-C_6H_4OMe	**15e**-H	65	**15e**-All	81

[a] Conditions C.

Scheme 2. E = CO_2Et. A: 1) *n*BuLi, THF, –78 °C → 0 °C; 2) MeI, DMSO, 10 °C, 3 h. – B: 50% NaOH, nBu_4NI (1 mol%), allyl bromide, CH_2Cl_2, 20 °C, 6–11 h. – C: 1) *n*BuLi, THF, –78 °C → –10 °C; 2) allyl bromide, DMSO, 0 °C, 30 min.

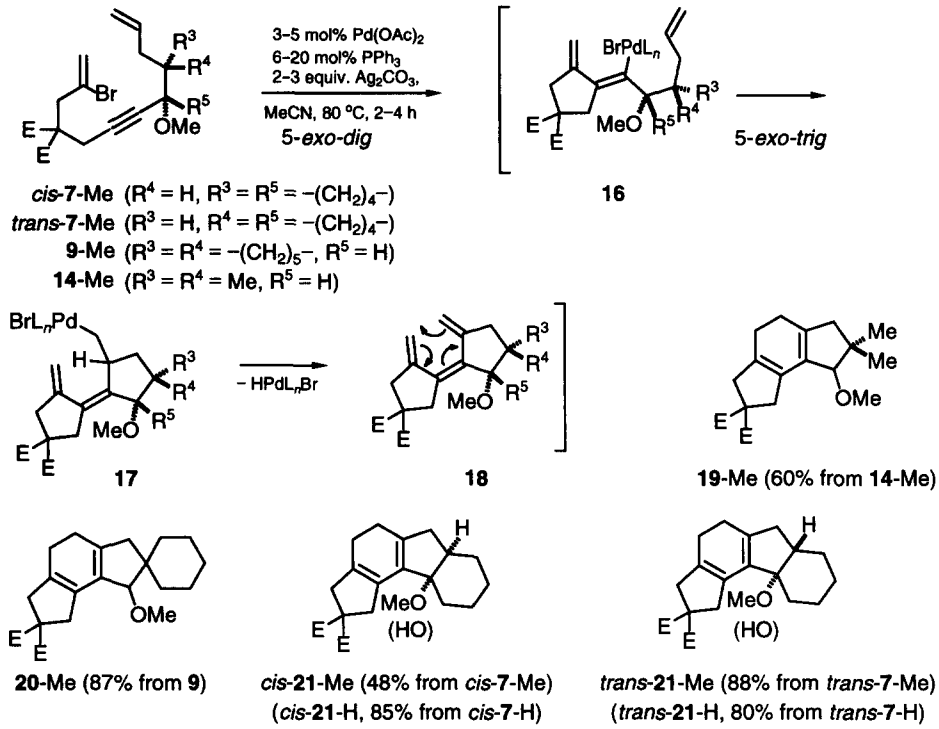
The logical extension of the intra-intermolecular domino transformation was to tether the external alkene onto the enyne system and make the whole cascade a completely intramolecular process.[8] Suitable 2-bromododeca-1,11-diene-6-ynes[9] should undergo a 5-*exo-dig* cyclisation as observed for 2-bromoenynes (see **Scheme 1**), ensuing intramolecular 5-*exo-trig* attack upon the tethered double bond and a 6π-electrocyclisation should eventually lead to tricyclic products.

The dienynes used were generally synthesized from unsaturated aldehydes or ketones and 2-bromo-4,4-bis(ethoxycarbonyl)-1-heptene-6-yne. This was achieved by the addition of the aldehyde or ketone to the lithium derivative **11** of this terminal acetylene. The resulting secondary or tertiary alcohols were usually transformed to the corresponding methyl ethers. Dienynes *cis/trans*-**7**-Me[10] and **14**-Me were thus prepared by treatment of the lithium acetylide **11** with 2-allylcyclohexanone (**8**)[11] and 2,2-dimethylpentenal (**12**),[12] respectively, which gave the 2-bromo-dodeca-1,11-diene-6-yne-8-ols *cis/trans*-**7**-H (78%) and **14**-H (75%) in good yields. The diastereomeric mixture of *cis/trans*-**7**-H was separated by column chromatography. Deprotonation of the hydroxy functionality in each of them with *n*-butyllithium at low temperature and addition of methyl iodide in dimethylsulfoxide afforded the corresponding methyl ethers *cis*-**7**-Me (86%), *trans*-**7**-Me (72%), and **14**-Me (78%), respectively. Another precursor for the palladium-catalysed cascade reaction **9**-Me was synthesized in the same way from 1-allylcyclohexylcarbaldehyde (**10**)[13] and **11**, except that the resulting alkoxide was directly methylated with methyl iodide without an intervening work-up.

With a view to ultimately forming oxygen containing oligocyclic compounds, a series of 2-bromo-9-oxadecadienynes **15**-All was synthesized. Treatment of the lithium acetylide **11** with aldehydes **13a–e** gave the secondary alcohols **15a–e**-H (65–85% yield), which were converted to the corresponding allyl ethers **15a–e**-All by treatment with allyl bromide in the presence of 50% aqueous sodium hydroxide in dichloromethane under phase transfer catalysis (nBu$_4$NI) (64–89% yield). As an additional model compound with an oxygen in the chain, which is also an all carbon 2-bromodecadienyne, the allyl ether **14**-All was prepared (77% yield) from the secondary alcohol **14**-H (**Scheme 2**).

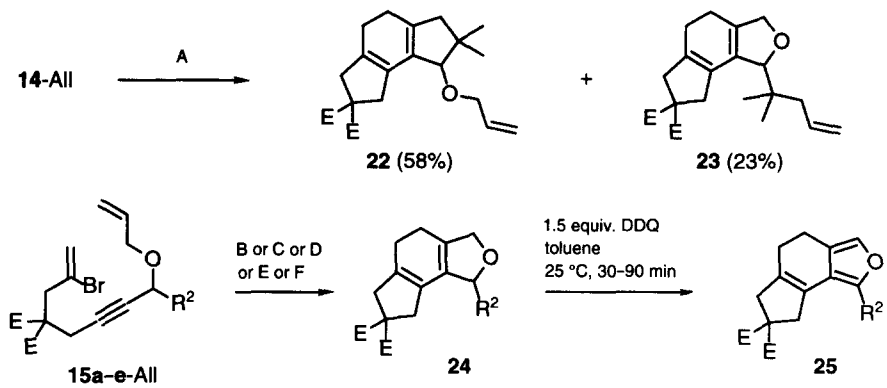
Treatment of the methoxybromodienyne **14**-Me with the catalyst as above (5 mol% of $Pd(OAc)_2$, 20 mol% of PPh_3, Ag_2CO_3, MeCN, 80 °C, 3 h) gave the bisannelated cyclohexadiene **19**-Me in 60% isolated yield. This confirms that an initial palladium-catalysed 5-*exo-dig* cyclisation generates an alkenylpalladium intermediate **16**, which then cyclizes in a 5-*exo-trig* mode to the alkylpalladium species **17**. Ensuing β-hydride elimination eventually gives the hexatriene intermediate **18**, and its 6π-electrocyclic rearrangement under the reaction conditions yields the observed tricycle **19**-Me.

The efficiency of this domino process is nicely demonstrated by the cleanly proceeding palladium-catalysed transformation of the spirocyclic precursor **9** to the tetracyclic compound **20**-Me in 87% yield. Even when the dienyne precursor contains a cyclohexane ring as in *cis/trans*-**7**-Me, which could conceivably cause steric problems during the palladium catalysed ring formation as a consequence of restricted conformational mobility, the reaction proceeds smoothly. Treatment of *cis/trans*-**7**-Me under the above mentioned conditions gives the corresponding tetracyclic compounds *cis*-**21**-Me and *trans*-**21**-Me in yields of 48% and 88%, respectively (**Scheme 3**). The exceptionally low yield of *cis*-**21**-Me was not inherent, as the corresponding tetracyclic tertiary allylic alcohol *cis*-**21**-H was obtained from the unprotected secondary propargyl alcohol *cis*-**7**-H in 85% yield.



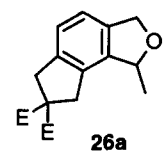
Scheme 3. E = CO_2Et.

The intramolecular competition between the oxygen containing and the all-carbon pentenyl tether in the allyl ether **14**-All from **14**-H was won by the latter, as the palladium-catalysed tricyclisation gave the carbocyclic compound **22** with the allyloxy side-chain intact and the heterotricycle **23** in a ratio of 2:1 according to the ^1H NMR spectrum of the crude product mixture (total yield 93%[14]). After column chromatography, **22** and **23** were isolated in 58 and 23% yield, respectively. The significantly greater loss of **23** during chromatography is apparently due to a greater sensitivity of this product. In this case the formation of the fully carbocyclic over the dihydrofuran system is probably favoured by the *gem*-dimethyl substitution at C-9 (**Scheme 4**). This benefit from a Thorpe-Ingold effect, is also evident in the high yields from the tricyclisations of 2-bromo-9-oxadodecadienynes **15**-All, at least of the alkyl substituted examples **15a–c**-All (**Scheme 4**). It is remarkable that the dihydrofuran-annelated cyclohexadienes **24** are dehydrogenated by 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ) in toluene to the corresponding furan-annelated compounds **25** in up to 84% yield; only from the methyl substituted precursor **24a** was the corresponding dihydrofuran-annelated benzene derivative obtained as a by-product (36%).[15]



R^2	Product	(%)	Conditions	Furan	(%)
Me	**24a**	84	B	**25a**	55[a]
Et	**24b**	81	C	**25b**	64
*i*Pr	**24c**	95	D	**25c**	84
Ph	**24d**	51	E	—[b]	
p-C_6H_4OMe	**24e**	25	F	—[b]	

[a] In addition, 36% of the benzoaromatic compound **26a** was isolated. – [b] Not performed.



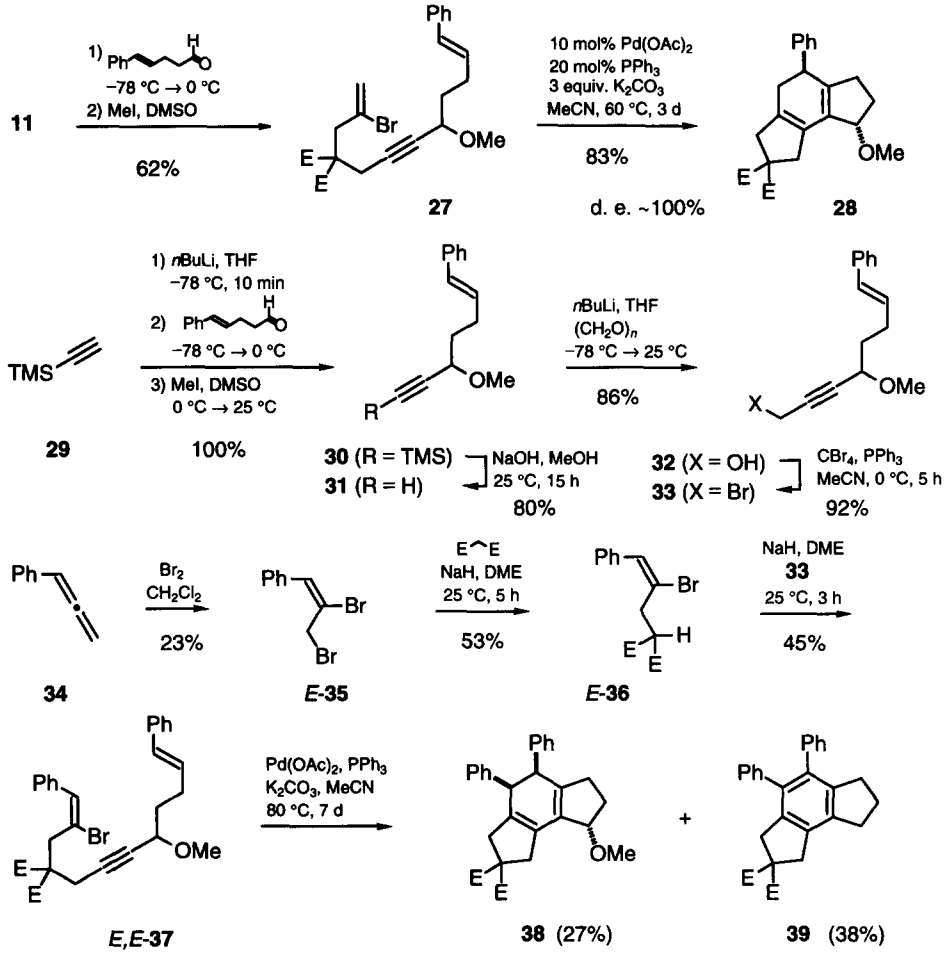
Scheme 4. E = CO_2Et. A: 5 mol% $Pd(OAc)_2$, 10 mol% PPh_3, 3 equiv. Ag_2CO_3, MeCN, 60 °C, 6 h. – B: Same as A, but 80 °C, 9 h. – C: 10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 2 equiv. Ag_2CO_3, MeCN, 80 °C, 6 h. – D: Same as A, but 3 equiv. Ag_2CO_3, 4 h. – E: Same as C, but 12 h. – F: Same as C, but 110 °C, 7 h.

The Stereochemical Outcome of the Reaction Cascade

In order to test for possible diastereoselectivity in the formation of two new stereogenic centers due to the known stereospecificity of the 6π-electrocyclisation process,[16] which is the final step in this reaction cascade, the terminally mono- and disubstituted 2-bromododecadienynes **27** and *E,E*-**37** were synthesized (**Scheme 5**).

To access compound **27**, the enyne **11** was coupled with *trans*-5-phenyl-4-pentenal[17] and the resulting alkoxide trapped with methyl iodide, as for other alkoxide intermediates above, to give **27** in a yield of 62%. The preparation of 1,12-bisphenyl-substituted dienyne *E,E*-**37** required a modification of this strategy. Coupling of the 1-phenyl-substituted analogue of bromoenyne **11** with 5-phenyl-4-hexenal failed, presumably because of halogen metal exchange at the bromoalkenyl unit after addition of *n*-butyllithium. Neither lowering the temperature (–90 to –100 °C), nor the use of lithium diisopropylamide (LDA) instead of *n*-butyllithium as the base resulted in a successful coupling reaction. The synthesis of *E,E*-**37** was, however, achieved by consecutive alkylation of diethyl malonate with the two appropriate alkyl bromides *E*-**35** and **33**, one bearing the 2-bromoalkene and the other the enyne unit. For the synthesis of **33**, lithium trimethylsilylacetylide was added to *trans*-5-phenyl-4-pentenal, and the resulting alkoxide methylated by subsequent addition of methyl iodide, to give the crude TMS-protected enyne **30**, which was directly desilylated to **31** under basic conditions (NaOH, MeOH, 25 °C, 15 h) in an overall yield of 80%. Hydroxymethylation (*n*-butyllithium, paraformaldehyde, –78 °C, 86%) of **31** and exchange of the hydroxy group in **32** for bromide with carbon tetrabromide/triphenylphosphane[18] at 0 °C yielded 1-bromooctenyne **33** (92%). (*E*)-1,2-Dibromo-3-phenyl-2-propene (*E*-**35**) was prepared from phenylpropadiene[19a] (**34**) by bromination in dichloromethane[19b] and chromatographic separation from the (*Z*)-isomer. It was found to be rather sensitive towards (*E/Z*)-isomerisation, and had to be used immediately after chromatography. Therefore freshly purified (*E*)-**35** was

used to alkylate diethyl sodiomalonate first, and to avoid the transformation of undesired *Z*-**36** during this reaction by isomerisation of the (*E*)-dibromide *E*-**35** prior to malonate alkylation, the reaction was quenched before completion, and the mixture worked-up; this gave the sufficiently stable *E*-**36** in moderate yield (53%). The assembly of dienyne *E,E*-**37** was completed by alkylating the deprotonated (NaH/DME) malonate *E*-**36** with the propargyl bromide **33** (45% yield).



Scheme 5. E = CO_2Et. – TMS = $SiMe_3$.

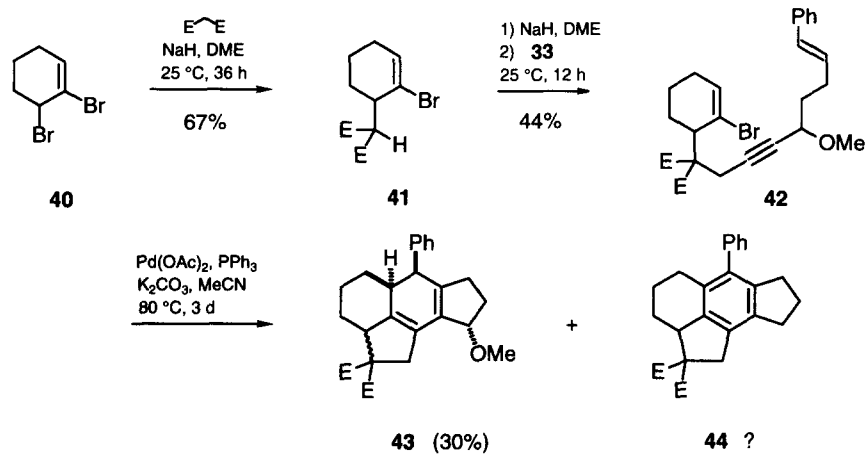
Under palladium-catalysis (10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 3 equiv. K_2CO_3, 60 °C, 3 d) compound **27** afforded only the expected tricycle **28** in a yield of 83% as a single diastereomer with the phenyl and methoxy groups in a *trans* orientation.[3d,20] The palladium-catalysed reaction cascade leading to the 1,3,5-hexatriene intermediate, which finally undergoes the 6π-electrocyclisation, is not adversely effected by the terminal phenyl group on the alkene tether. In addition its presence revealed the remarkable influence of the methoxy group on the rotaselectivity of the electrocyclic rearrangement.[21] Only one of the two disrotatory movements, that are allowed under thermal conditions according to the Woodward-Hoffmann rules,[16c] takes place, bringing the methoxy and the phenyl group highly selectively into a *trans* relationship (**Scheme 5**).[22]

When *E,E*-**37** was treated with $Pd(OAc)_2$, PPh_3, and K_2CO_3 in deoxygenated acetonitrile at 80 °C, a considerably longer reaction time of 7 d was neccessary for total consumption of starting material. Two

products of similar polarity were obtained, the aromatized system **39** without the methoxy group at what was formerly C-8 in **37** and the expected cyclohexadiene **38** as a single diastereomer. Apparently, the final ring formation in this case is also directed by the methoxy substituent and thus the relative configuration of three new stereocenters is controlled. The cyclohexadiene derivative **38** turned out to be quite sensitive towards oxidation when exposed to air, and it decomposed upon standing. The major product **39** can be rationalized as arising from **38** by 1,4-elimination of methanol under the reaction conditions, probably initiated by deprotonation in the benzylic-allylic position and subsequent isomerisation of the resulting cross-conjugated tricyclic triene.

The Influence of Additional Substituents on the Reaction Mode

In order to further explore scope and limitations of this tricyclisation protocol, several other differently substituted 2-bromododeca-1,11-diene-6-ynes were prepared. The readily accessible 8-bromo-5-methoxy-1-phenyloct-1-ene-6-yne **33** was coupled to the 2-bromocyclohexenyl-substituted malonate **41**, which was prepared from diethyl malonate and 2,3-dibromocyclohexene (**40**) in 67% yield. The bromodienyne **42** was obtained in moderate yield (44%), and when subjected to the cyclisation conditions (10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 2 equiv. K_2CO_3, MeCN, 80 °C, 3 d), gave two products, one of which decomposed rapidly after isolation. The more polar of the two products was identified by NMR studies as the expected tetracyclic system **43**. However, its steadily proceeding decomposition prevented the verification of the assumed relative configuration. The unidentified less polar second product was probably the aromatic compound **44** by close analogy with the formation of **39** from *E,E*-**37**. The lability of **43** may be attributed to the phenyl substituent on the cyclohexadiene ring, which makes it more prone to oxidation (**Scheme 6**).

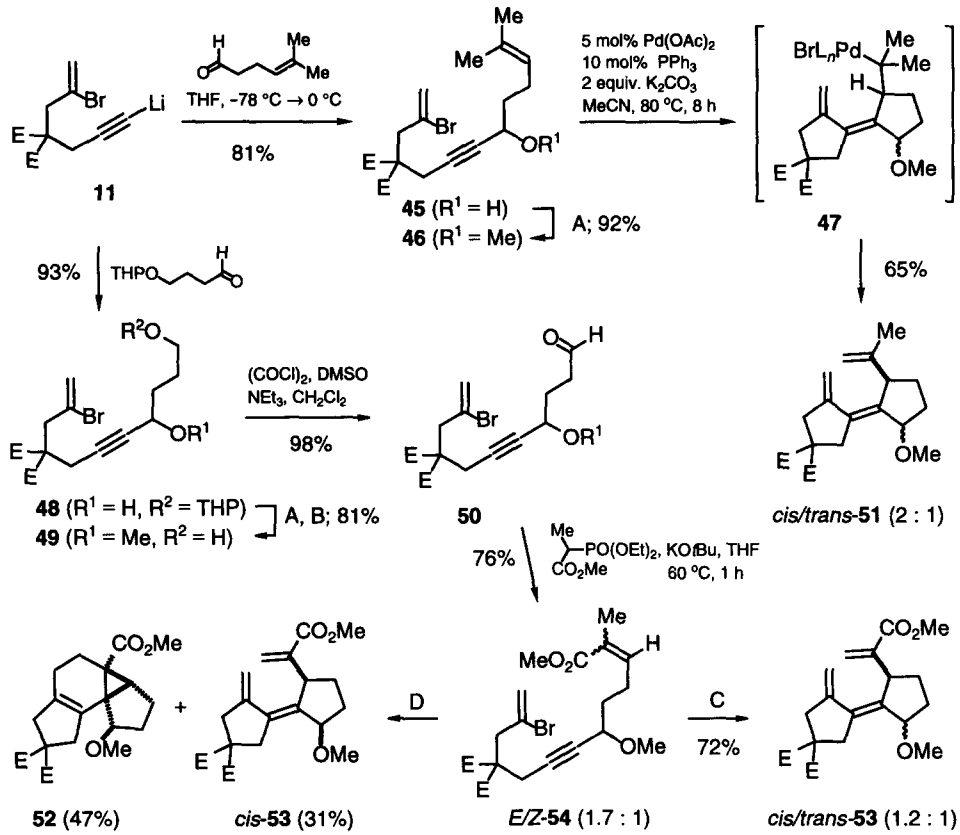


Scheme 6. E = CO_2Et.

This methodology is also limited by the fact that alkyl substituents *cis* to the bromine atom on C-1 of the 2-bromodienyne prevent the electrocyclic rearrangement from proceeding after the initial palladium-catalysed biscyclisation has occurred.[23] To study the effect of aliphatic substituents on the other terminus of the dienyne, the model compound **46** with two methyl groups at C-12 was prepared by adding **11** to 5-methyl-4-hexenal,[24] and methylating the resulting alcohol **45** (81% yield) using the standard procedure (*n*BuLi, THF, then MeI, DMSO, 92% yield).

Another model compound with one methyl and one methoxycarbonyl group at C-12 was prepared, starting with the adduct of **11** to 4-(tetrahydropyranyloxy)butanal.[25] The secondary alcohol **48** (93% yield) was transformed to the corresponding methyl ether, and the primary alcohol functionality was deprotected

with 2 M hydrochloric acid in methanol to give **49** (81% overall yield). Swern oxidation (oxalyl chloride/DMSO, NEt_3, CH_2Cl_2)[26] afforded the aldehyde **50** in excellent yield (98%), which was converted to the 2-bromodienyne *E/Z*-**54** in 76% yield (*E/Z*-ratio 1.7:1) via a Wittig-Horner olefination with diethyl 1-(methoxycarbonyl)ethylphosphonate (**Scheme 7**).[27]



Scheme 7. E = CO_2Et. – A: 1) *n*BuLi, THF, –78 °C; 2) MeI, DMSO, 0 °C. – B: 2 N HCl, MeOH, 25 °C. – C: 3 mol% $Pd(OAc)_2$, 12 mol% PPh_3, 2 equiv. Ag_2CO_3, MeCN, 80 °C, 8 h. – D: 11 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 3 equiv. K_2CO_3, MeCN, 130 °C, 14 h.

Treatment of the dimethyl derivative **46** with the standard palladium catalyst (10 mol% $Pd(OAc)_2$, 20 mol% PPh_3, 2 equiv. K_2CO_3, MeCN, 80 °C, 8 h) yielded a 2:1 mixture of the two diastereomeric bicyclopentenylidene derivatives *cis/trans*-**51**. Thus, β-hydride elimination in the *tert*-alkylpalladium intermediate **47** did not proceed in the usual way to give a conjugated 1,3,5-hexatriene, set up for 6π-electrocyclisation, but from one of the six primary C–H positions to yield the non-conjugated 1,3,6-heptatriene **51**, and isomerization to the conjugated 1,3,5-heptatriene apparently did not take place (**Scheme 7**). The triene **51** cannot undergo a 6π-electrocyclic rearrangement. The analogous 1,3,6-heptatriene *cis/trans*-**53** (1.2:1) was obtained under palladium catalysis in the presence of silver carbonate from *E/Z*-**54** at 80 °C. However, when this reaction was run at 130 °C in the presence of potassium carbonate, only the *cis*-disubstituted bicyclopentylidene derivative *cis*-**53** was isolated as such (31%), while the *trans*-isomer had undergone an intramolecular Diels-Alder reaction to give the tetracyclic compound **52** (**Scheme 7**). The configuration and structure of **52**, isolated in 47% yield, was proved by an X-ray crystal structure analysis (see **Figure 1**).[28]

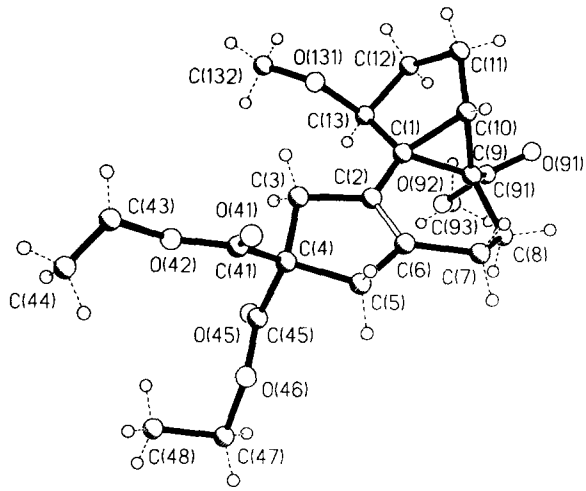
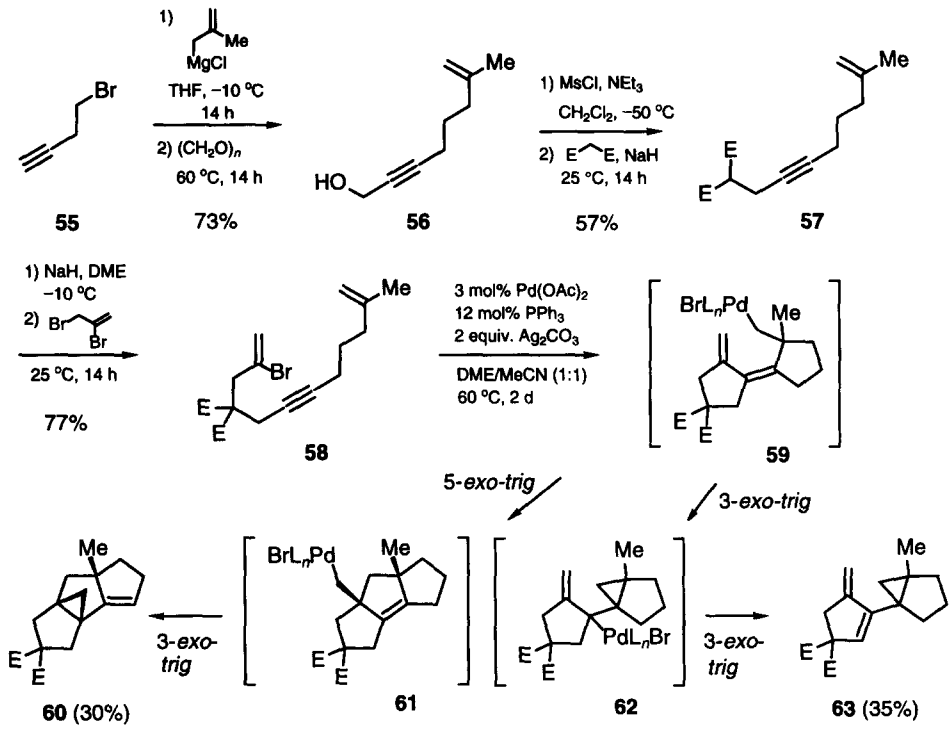


Fig. 1. Molecular structure of diethyl 13-methoxy-9-methoxycarbonyltetracyclo[7.4.0.0^{1,10}.0^{2,6}]tridec-2(6)-ene-4,4-dicarboxylate (**52**) in the crystal.[28] Monoclinic crystal of space group $P2_1/c$, Z = 4, unit cell dimensions a = 13.029(4) Å, b = 9.784(3) Å, c = 17.154(4) Å, V = 2167.4(11) Å^3, 4605 reflexions collected with 7°<2Θ<45°, R_w = 12.59%.

Varying the substitution pattern at C-11 rather than C-12 of the terminal double bond would conceivably affect the reaction mode of the dienyne system. For instance a methyl group at this position would not interfere with either the 5-*exo-dig*, or the 5-*exo-trig* cyclisation, leading to the biscyclized intermediate, but the β-hydride elimination as the final step of the palladium-catalysed cascade would be prevented. If no suitable hydrogen were present, as in all of the previous examples, the neopentylpalladium intermediate would have to find another reaction mode, e. g. by attack on one of the adjacent double bonds. To prove this hypothesis, the 2-bromodienyne **58** was prepared from 4-bromo-1-butyne **55**. Treatment with two equivalents of β-methylallylmagnesium chloride in THF and subsequent trapping of the resulting alkynylmagnesium chloride with paraformaldehyde yielded **56** (73%), which was mesylated at –50 °C (MsCl, NEt_3, CH_2Cl_2). Deprotonated (with NaH in DME) diethyl malonate was reacted with the crude mesylate to afford the enyne **57** in 57% yield. The synthesis of the cyclisation precursor **58** was concluded by alkylation of **57** after deprotonation with sodium hydride in DME with 2,3-dibromopropene (77% yield).

When **58** was subjected to the cyclisation conditions (3 mol% $Pd(OAc)_2$, 12 mol% PPh_3, 2 equiv. Ag_2CO_3, DME/MeCN 1:1, 60 °C, 2 d), three products were observed, two of which were isolated by column chromatography. One was the tetracycle **60** (30%), which was apparently formed by a 5-*exo-trig* cyclisation of the neopentylpalladium intermediate **59** to the tricyclic neopentylpalladium bromide **61**, in which β-hydride elimination was still precluded, so that attack of the remaining double bond in a sterically favoured 3-*exo-trig* mode occurred. Finally β-hydride elimination afforded the cyclopropane-bridged triquinane derivative **60**. The second product (35% yield) was the bicyclo[3.1.0]hexane derivate **63**, apparently formed from **59** by a 3-*exo-trig* attack on the nearest double bond, and ensuing β-hydride elimination (**Scheme 8**).



Scheme 8. E = CO_2Et.

Conclusion

Under palladium catalysis 2-bromododeca-1,11-diene-6-ynes undergo two consecutive Heck type cyclisations to conjugated 2,2'-dimethylene-1,1-bicyclopentylidenes, and these react further to give bisannelated cyclohexa-1,3-dienes by 6π-electrocyclisation under the same conditions (60–80 °C). This methodology allows the facile construction of tricyclic skeletons consisting of a central six- and two vicinally annelated five-membered carbo- or heterocycles. A substituent in the second ring formed controls the relative configuration of a new stereogenic center in the third ring by exerting a rotaselectivity on the 6π-electrocyclisation step. With an alkyl substituent at C-12 of the 2-bromododecadienynes, the palladium-catalysed cyclisation leads to 2-methylene-2'-vinyl-1,1'-bicyclopentylidenes, which can undergo an intramolecular Diels-Alder reaction, when the vinyl group is activated by an electron withdrawing group. A substituent at C-11 totally prevents the β-hydride elimination, which normally leads to the conjugated 1,3,5-hexatrienes, and causes two more cyclisation steps to occur, eventually leading to an interesting tetracyclic skeleton containing a bridging cyclopropane ring.

Research on such palladium-catalysed cascade reactions is continuing in our laboratories. Forthcoming results on the cyclisation of homologous 2-bromotrideca-1,12-diene-7-ynes and 2-bromotetradeca-1,13-diene-7-ynes will be published elsewhere in due course.

Experimental Part

^{1}H NMR: Bruker AM 250 (250 MHz), WH 270 (270 MHz), Jeol EX 400 (400 MHz), Varian VXR 200 (200 MHz), VXR 500 S (500 MHz), δ = 0 for tetramethylsilane as internal standard, 7.26 for chloroform. – ^{13}C NMR: Bruker AM 250 (62.9 MHz), Jeol EX 400 (100.6 MHz) Varian VXR 500 S (125.7 MHz), δ = 77.00 for deuteriochloroform, * = assignment is interchangeable. The multiplicities of ^{13}C NMR signals were determined with the help of either DEPT- (Distortionless Enhancement by Polarisation Transfer) or APT-techniques (Attached Proton Test) and are designated as follows: CH_3, CH = (+) (DEPT and APT), CH_2 = (–) (DEPT and APT), quaternary C = (–) (APT) or (C_{quat}) (DEPT). – IR: Bruker IFS 66, Perkin-Elmer 298. – MS: Varian MAT CH 7, MAT 731. – HRMS: Varian MAT 311 A. The molecular composition was determined by high resolution mass spectrometry with preselected ion peak matching at R >> 10000 to be within ± 2 ppm of the exact masses. – Melting points: Büchi 510, uncorrected. – Column chromatography was performed on Macherey-Nagel silica gel 230–240 mesh, thin layer chromatography on Macherey-Nagel Fertigfolien Alugram Sil G/UV$_{254}$. – Microanalyses: Mikroanalytisches Laboratorium des Instituts für Organische Chemie der Georg-August-Universität Göttingen. – All operations were performed under nitrogen. Diethyl ether and THF were dried by distillation from sodium or potassium/benzophenone, dimethylsulfoxide, acetonitrile, dimethoxyethane and triethylamine by distillation from calcium hydride. The following abbreviations have been used: PE = petroleum ether bp. 40–60 °C, DMSO = dimethylsulfoxide, DME = 1,2-dimethoxyethane.

General Procedure 1 (GP 1a,b) for the Addition of Diethyl 1-Lithio-6-bromo-6-heptene-1-yne-4,4-dicarboxylate to Aldehydes and Ketones: *n*-Butyllithium (1.05 mmol, in *n*-hexane) is added dropwise to a well stirred solution of diethyl 6-bromo-6-heptene-1-yne-4,4-dicarboxylate (1 mmol) in THF (10 mL) at –78 °C. Stirring is continued for 30 min and the aldehyde (1.05 mmol) added dropwise. (a) The reaction mixture is allowed to warm up to 0 °C, water is added (20 mL) and the aqueous phase is extracted with Et_2O (3 × 20 mL). The organic layer is washed with brine (25 mL), dried over magnesium sulfate and concentrated under vacuum. The residue is purified by chromatography on silica gel as indicated below. *Or* (b) the reaction mixture is warmed up slowly to 0 °C, DMSO (10 mL) and methyl iodide (1 mL) are added in one portion and stirring is continued for 2 h at 10 °C. The reaction mixture is poured into water (40 mL) and extracted with Et_2O (3 × 50 mL). The organic layer is washed with water (2 × 50 mL) and brine (20 mL), dried over magnesium sulfate and concentrated under vacuum, followed by column chromatography on silica gel.

General Procedure (GP 2a,b) for Palladium-Catalysed Oligocyclisations: To a solution of vinyl bromide (1 mmol) in deoxygenated acetonitrile (10 mL) in a screw cap pyrex bottle are added 2–10 mol% palladium(II) acetate, 4–20 mol% triphenylphosphane and 2–3 equiv. of base. The sealed bottle is heated to 60–130 °C for 2 h–3 d. After cooling to room temperature the reaction mixture is (a) poured into water (50 mL) and extracted with dichloromethane. The organic phases are washed with brine (50 mL) and dried over magnesium sulfate. Removal of the solvents yields the crude product, which is chromatographed on silica gel. *Or* (b) the reaction mixture is concentrated under vacuum to approximately 1–2 mL residue (not until dryness !), which is directly chromatographed on silica gel.

General Procedure (GP 3) for the Alkylation of Malonates with Alkyl Bromides: A suspension of sodium hydride (15 mmol, 1.2 equiv., 60% in mineral oil) in DME (50 mL) is treated with diethyl malonate (12.5 mmol, 1 equiv.) dropwise at room temperature. After the gas formation has finished, the alkyl bromide (12.5 mmol) is added in one portion and the reaction mixture further stirred for 1–48 h. It is poured into water (20 mL), the aqueous layer is extracted with Et_2O (3 × 30 mL) and the combined organic layers are washed with brine (20 mL). Drying over magnesium sulfate and concentration under vacuum are followed by chromatography on silica gel.

Diethyl 5-Ethoxy-7-phenyl-1,3,4,5-tetrahydroindene-2,2-dicarboxylate (**6**): In accordance with GP 2b 6-bromo-4,4-bis(ethoxycarbonyl)-1-phenyl-6-heptene-1-yne[5] (**1**) (210 mg, 0.534 mmol), palladium acetate (6 mg, 5 mol%), triphenylphosphane (14 mg, 10 mol%), and silver(I) carbonate (294 mg, 1.07 mmol, 2 equiv.) were treated in acetonitrile (15 mL). Additional to GP 2b freshly distilled ethyl vinyl ether (2 mL)

was added, after which the carefully closed pyrex-bottle was heated to 80 °C for 1 d. Chromatography of the crude product on silica gel (40 g, column 2.5 × 25 cm, PE/Et_2O 10 : 1 + 2 vol% triethylamine) yielded **6** (88 mg, 43%) as a colourless oil (R_f = 0.39 in PE/Et_2O 2 : 1). – IR (film): ν = 3056 cm^{-1} (CH), 2978 (CH), 2934, 2872, 1732, 1662, 1492, 1464, 1444, 1390, 1366, 1254, 1192, 1116, 1096, 1072, 1002, 916, 860, 788, 762, 734, 702, 646. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7 Hz, 3 H, $CHOCH_2CH_3$), 1.22 (t, ^3J = 7 Hz, 3 H, CH_3), 1.23 (t, ^3J = 7 Hz, 3 H, CH_3), 2.46–2.51 (m, 2 H, 4-H), 3.08 (bs, 2 H, 1-H*), 3.16 (bs, 2 H, 3-H*), 3.54 (q, ^3J = 7 Hz, 2 H, $CHOCH_2$), 4.12–4.23 (mc, 4 H, OCH_2), 4.32 (ddd, ^3J = 8, ^3J = 8, ^3J = 4 Hz, 1 H, 5-H), 5.78 (d, ^3J = 4 Hz, 1 H, 6-H), 7.27–7.38 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.94 (+, CH_3), 15.64 (+, $CHOCH_2CH_3$), 30.10 (–, C-4), 40.67 and 43.34 (–, C-1, C-3), 58.37 (C_{quat}, C-2), 61.48 and 61.52 (–, OCH_2), 62.80 (–, $CHOCH_2$), 72.51 (+, C-5), 123.69 (+, C-6), 127.13 (+, C-Ph), 127.55 (+, C-Ph), 128.03 (+, C-Ph), 129.74 (C_{quat}), 134.29 (C_{quat}), 138.25 (C_{quat}), 139.84 (C_{quat}), 171.73 and 172.11 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 384 (13) [M^+], 338 (57) [$M^+ - C_2H_5OH$], 310 (9), 264 (99), 237 (44), 191 (100), 165 (30), 115 (7), 91 (3), 45 (3). – $C_{23}H_{28}O_5$: calcd 384.1937 (correct HRMS). – $C_{23}H_{28}O_5$ (384.5): Anal. Calcd for C 71.85, H 7.34; found: C 71.67, H 7.38.

Diethyl 2-Bromo-9,9-dimethyl-8-hydroxydodeca-1,11-diene-6-yne-4,4-dicarboxylate (**14**-H): According to GP 1, to a solution of diethyl 6-bromo-6-heptene-1-yne-4,4-dicarboxylate (2.00 g, 6.3 mmol)[5] in THF (20 mL) *n*-butyllithium (2.94 mL, 6.9 mmol, 2.34 M in *n*-hexane) and 2,2-dimethyl-4-pentenal (**12**) (708 mg, 6.3 mmol)[12] were added. After standard work-up, the crude product was chromatographed on silica gel (70 g, column 2.5 × 35 cm, PE/Et_2O 10 : 1) to yield **14**-H (2.03 g, 75%) as a colourless oil (R_f = 0.19 in PE/Et_2O 3 : 1). – IR (film): ν = 3520 cm^{-1} (OH), 3080 (C=CH_2), 2980, 2240, 1740 (C=O), 1640 (C=C), 1370, 1200, 1060, 920, 865. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, 9-CH_3), 0.94 (s, 3 H, 9-CH_3), 1.27 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.84 (d, ^3J = 6.0 Hz, 1 H, OH), 2.10 (mc, 2 H, 10-H), 2.98 (d, ^5J = 2.0 Hz, 2 H, 5-H), 3.28 (s, 2 H, 3-H), 4.03 (dt, ^5J = 2.0, ^3J = 6.0 Hz, 1 H, 8-H), 4.22 (m, 4 H, OCH_2CH_3), 5.06 (d, ^3J = 11.4 Hz, 1 H, 12-H), 5.07 (d, ^3J = 15.7 Hz, 1 H, 12-H), 5.61 (d, J = 1.6 Hz, 1 H, 1-H), 5.80 (bs, 1 H, 1-H), 5.82 (m, 1 H, 11-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 22.4 (+, 9-CH_3), 22.6 (+, 9-CH_3), 22.6 (–), 38.6 (C_{quat}, C-9), 42.7 (–), 42.8 (–), 56.3 (C_{quat}, C-4), 61.9 (–, OCH_2CH_3), 70.2 (+, C-8), 80.9 (C_{quat}), 83.6 (C_{quat}), 117.6 (–, C-12), 122.4 (–, C-1), 126.5 (C_{quat}, C-2), 134.8 (+, C-11), 169.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 401/399 (2), 349 (44) [M^+ – Br], 273 (28), 267 (36), 237 (33), 225 (27), 153 (64), 91 (46), 55 (100). – Anal. Calcd for $C_{20}H_{29}BrO_5$ (429.3): C 55.95, H 6.81, Br 18.61; found: C 56.19, H 6.88, Br 18.08.

Diethyl 2-Bromo-9,9-dimethyl-8-methoxydodeca-1,11-diene-6-yne-4,4-dicarboxylate (**14**-Me): *n*-Butyllithium (0.52 mL, 1.2 mmol, 2.36 M in *n*-hexane) was added to a solution of **14**-H (500 mg, 1.2 mmol) in THF (20 mL) at –78 °C, and the solution was warmed slowly to 0 °C. DMSO (20 mL) and methyl iodide (1 mL) were added dropwise and the reaction mixture was stirred at 10 °C for 3 h. Then it was poured into water (50 mL), the aqueous phase was extracted with Et_2O (3 × 50 mL) and the combined organic phases were washed with water (3 × 50 mL) and brine (50 mL). After drying over magnesium sulfate, solvents were removed under vacuum and the crude material chromatographed on silica gel (30 g, column 2.5 × 20 cm, PE/Et_2O 10 : 1) to give **14**-Me (403 mg, 78%) as a colourless oil (R_f = 0.25). – IR (film): ν = 3070 cm^{-1} (C=CH_2), 2960, 2930, 2820, 1750 (C=O), 1625 (C=C), 1430, 1285, 1190, 1095, 1010, 905, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, 9-CH_3), 0.89 (s, 3 H, 9-CH_3), 1.23 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 2.04 (m, 2 H, 10-H), 2.96 (d, ^5J = 1.9 Hz, 2 H, 5-H), 3.26 (s, 2 H, 3-H), 3.30 (s, 3 H, OCH_3), 3.50 (t, ^5J = 1.9 Hz, 1 H, 8-H), 4.16 (m, 4 H, OCH_2CH_3), 4.97 (m, 1 H, 12-H), 5.02 (bs, 1 H, 12-H), 5.57 (bs, 1 H, 1-H), 5.76 (bs, 1 H, 1-H), 5.76 (m, 1 H, 11-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 22.6 (–), 22.7 (+, 9-CH_3), 23.1 (+, 9-CH_3), 38.2 (C_{quat}, C-9), 42.9 (–), 43.8 (–), 56.3 (C_{quat}, C-4), 57.0 (+, OCH_3), 61.9 (–, OCH_2CH_3), 79.2 (+, C-8), 81.3 (C_{quat}), 81.4 (C_{quat}), 117.3 (–, C-12), 122.3 (–, C-1), 126.6 (C_{quat}, C-2), 134.8 (+, C-11), 169.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 444/442 [M^+], 429/427 (5/4) [$M^+ - CH_3$], 359 (16), 329/327 (18/19), 285/287 (36/37), 255 (25), 207 (38), 178 (48), 134 (40), 91 (57), 55 (100). –

$C_{21}H_{31}BrO_5$: calcd 442.1354 (correct HRMS). – Anal. Calcd for $C_{21}H_{31}BrO_5$ (443.4): C 56.89, H 7.05; found: C 56.75, H 6.87.

1-[7'-Bromo-5',5'-bis(ethoxycarbonyl)-1'-methoxyoct-7'-ene-2'-ynyl]-1-(2''-propenyl)cyclohexane (**9**-Me): A solution of diethyl 6-bromo-6-heptene-1-yne-4,4-dicarboxylate (1.50 g, 4.72 mmol) in THF (25 mL) was treated in accordance with GP 1b with *n*-butyllithium (2.10 mL, 5.0 mmol, 2.36 M in *n*-hexane) and 1-allylcyclohexylcarbaldehyde (**10**) (754 mg, 5.0 mmol). After warming up to 0 °C DMSO (25 mL) and methyl iodide (2.11 g, 14.9 mmol) were added and stirring was continued for 3 h at 40 °C. Standard work-up and chromatography of the crude product on silica gel (60 g, column 2.5 × 35 cm, PE/Et_2O 30 : 1) yielded **9**-Me (2.01 g, 88%) as a colourless oil (R_f = 0.44 in PE/Et_2O 4 : 1). – IR (film): ν = 3080 cm^{-1} (C=CH_2), 2990, 2940, 2860, 1740 (C=O), 1640 (C=C), 1450, 1290, 1220, 920, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.32–1.52 (m, 10 H, cyclohexyl-H), 2.23 (mc, 2 H, 1''-H), 3.00 (d, ^5J = 1.9 Hz, 2 H, 4'-H), 3.29 (s, 2 H, 6'-H), 3.32 (s, 3 H, OCH_3), 3.71 (t, ^5J = 1.8 Hz, 1 H, 1'-H), 4.19 (m, 4 H, OCH_2CH_3), 4.99 (bs, 1 H, 3''-H), 5.05 (bs, 1 H, 3''-H), 5.60 (d, *J* = 1.5 Hz, 1 H, 8'-H), 5.76 (m, 1 H, 2''-H), 5.79 (bs, 1 H, 8'-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 21.3 (–), 21.4 (–), 22.6 (–), 26.0 (–), 29.9 (–), 30.8 (–), 36.9 (–), 40.7 (C_{quat}, C-1), 42.9 (–, C-6'), 56.3 (C_{quat}, C-5'), 57.1 (+, OCH_3), 61.9 (–, OCH_2CH_3), 77.5 (+, C-1'), 81.2 (C_{quat}), 81.9 (C_{quat}), 117.1 (–, C-3''), 122.3 (–, C-8'), 126.7 (C_{quat}, C-7'), 135.0 (+, C-2''), 169.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 484/482 (1/1) [M^+], 423 (6), 404 (18), 361 (24), 319 (80), 237 (100), 163 (23), 135 (38), 111 (54), 91 (44), 43 (36). – $C_{24}H_{35}BrO_5$: calcd 482.1667 (correct HRMS).

***cis*- and *trans*-1-[6'-Bromo-4',4'-bis(ethoxycarbonyl)-6'-heptene-1'-ynyl]-1-hydroxy-2-(2''-propenyl)cyclohexane** (*cis- and trans*-**7**-H): According to GP 1a 2-(2-propenyl)cyclohexanone (**8**) (1.12 g, 8.1 mmol), *n*-butyllithium (3.60 mL, 8.5 mmol, 2.36 M in *n*-hexane), and 6-bromo-6-heptene-1-yne-4,4-dicarboxylate (2.57 g, 8.1 mmol) were reacted in THF (30 mL). After standard work-up, the crude product was chromatographed on silica gel (225 g, column 3.5 × 70 cm, PE/Et_2O 9 : 1) to give *trans*-**7**-H (1.50 g, 41%, R_f = 0.25 in PE/Et_2O 1 : 1) and *cis*-**7**-H (1.35 g, 37%, R_f = 0.20 in PE/Et_2O 1 : 1) as colourless oils. *trans*-**7**-H: IR (film): ν = 3550 cm^{-1} (OH), 3080 (C=CH_2), 2950, 1735 (C=O), 1635 (C=C), 1440, 1375, 920, 865. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.17 (m, 6 H, CH_2CH_3), 1.54 (m, 8 H), 1.95 (m, 3 H), 2.52 (d, ^2J = 12.2 Hz, 1 H, 1''-H), 2.90 (s, 2 H, 3'-H), 3.23 (s, 2 H, 5'-H), 4.17 (m, 4 H, OCH_2CH_3), 4.94–5.04 (m, 2 H, 3''-H), 5.56 (bs, 1 H, 7'-H), 5.75 (bs, 1 H, 7'-H), 5.76 (m, 1 H, 2''-H). – ^{13}C-NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 21.1 (–), 22.4 (–), 24.8 (–), 25.7 (–), 35.1 (–), 39.9 (–), 42.8 (–, C-5'), 45.7 (+, C-2), 56.3 (C_{quat}, C-4'), 61.8 (–, OCH_2CH_3), 69.8 (C_{quat}, C-1), 78.1 (C_{quat}), 88.8 (C_{quat}), 115.8 (–, C-3''), 122.2 (–, C-7'), 126.6 (C_{quat}, C-6'), 137.6 (+, C-2''), 169.0 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 456/454 (3/2) [M^+], 427/425 (7/6), 409/407 (20/19), 375 (78) [M^+ – Br], 357 (100), 335 (55), 301 (38), 283 (86), 255 (47), 199 (33), 159 (35), 115 (34), 91 (62), 55 (47), 41 (96). – $C_{22}H_{31}BrO_5$: calcd 454.1354 (correct HRMS). – Anal. Calcd for $C_{22}H_{31}BrO_5$ (455.4): C 58.02, H 6.86, Br 17.55; found: C 57.93, H 6.76, Br 17.12. – *cis*-**7**-H: IR (film): ν = 3420 cm^{-1} (OH), 3070 (C=CH_2), 2930, 2860, 2240, 1725 (C=O), 1625 (C=C), 1370, 1290, 1190, 1040, 735. – ^1H NMR (250 MHz, $CDCl_3$): 1.23 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.37–1.91 (m, 10 H), 2.53–2.57 (m, 2 H), 2.95 (s, 2 H, 3'-H), 3.25 (s, 2 H, 5'-H), 4.18 (m, 4 H, OCH_2CH_3), 4.94–5.07 (m, 2 H, 3''-H), 5.57 (d, *J* = 1.5 Hz, 1 H, 7'-H), 5.77 (bs, 1 H, 7'-H), 5.79 (m, 1 H, 2''-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 22.4 (–), 23.9 (–), 25.3 (–), 29.2 (–), 35.7 (–), 41.4 (–), 42.7 (–, C-5'), 47.4 (+, C-2), 56.2 (C_{quat}, C-4'), 61.8 (–, OCH_2CH_3), 72.8 (C_{quat}, C-1), 80.7 (C_{quat}), 85.0 (C_{quat}), 116.0 (–, C-3''), 122.3 (–, C-7'), 126.4 (C_{quat}, C-6'), 138.0 (+, C-2''), 169.0 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 418 (4), 361 (22), 342 (11), 305 (46), 262 (22), 153 (34), 139 (59), 113 (58), 83 (37), 74 (43), 57 (83), 43 (100). – Anal. Calcd for $C_{22}H_{31}BrO_5$ (455.4): C 58.02, H 6.86, Br 17.55; found: C 58.15, H 7.01, Br 17.28.

***trans*-1-[6'-Bromo-4',4'-bis(ethoxycarbonyl)-6'-heptene-1'-ynyl]-1-methoxy-2-(2''-propenyl)cyclohexane** (*trans*-**7**-Me): According to the preparation of **14**-Me, a solution of *trans*-**7**-H (1.00 g, 2.2 mmol) in THF (30 mL) was treated with *n*-butyllithium (1.0 mL, 2.4 mmol, 2.36 M in *n*-hexane), methyl iodide

(1.0 mL), and DMSO (20 mL). Standard work-up and chromatography on silica gel (35 g, column 2.5 × 20 cm, PE/Et_2O 16 : 1) gave *trans*-**7**-Me (0.74 g, 72%) as a colourless oil (R_f = 0.59 in PE/Et_2O 1 : 1). – IR (film): ν = 2940 cm^{-1}, 2240, 1740 (C=O), 1640 (C=C), 1445, 1380, 1150, 915, 865. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 1.26–1.54 (m, 8 H), 1.68–2.03 (m, 2 H), 2.50 (m, 1 H), 2.90 (s, 2 H, 3'-H), 3.18 (s, 3 H, OCH_3), 3.21 (s, 2 H, 5'-H), 4.13 (m, 4 H, OCH_2CH_3), 4.87–4.96 (m, 2 H, 3"-H), 5.54 (d, J = 1.5 Hz, 1 H, 7'-H), 5.69 (m, 1 H, 2"-H), 5.71 (bs, 1 H, 7'-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 21.0 (–), 22.3 (–), 24.3 (–), 25.5 (–), 34.1 (–), 34.4 (–), 42.7 (–, C-5'), 45.5 (+, C-2), 50.4 (+, OCH_3), 56.2 (C_{quat}, C-4'), 61.7 (–, OCH_2CH_3), 75.2 (C_{quat}), 80.1 (C_{quat}), 85.4 (C_{quat}), 115.2 (–, C-3"), 122.1 (–, C-7'), 126.6 (C_{quat}, C-6'), 137.9 (+, C-2"), 168.9 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 441/439 (6/5), 409/407 (14/13), 389 (16) [M^+ – Br], 315 (19), 283 (25), 237 (100), 205 (77), 153 (40), 135 (45), 112 (90), 111 (61), 91 (85), 77 (60), 41 (66). – Anal. Calcd for $C_{23}H_{33}BrO_5$ (469.4): C 58.85, H 7.09, Br 17.02; found: C 59.03, H 7.15, Br 17.09.

***cis*-1-[6'-Bromo-4',4'-bis(ethoxycarbonyl)-6'-heptene-1'-ynyl]-1-methoxy-2-(2"-propenyl)cyclohexane** (*cis*-**7**-Me): According to the preparation of **14**-Me, a solution of *cis*-**7**-H (1.00 g, 2.2 mmol) in THF (30 mL) was treated with *n*-butyllithium (1.0 mL, 2.4 mmol, 2.36 M in *n*-hexane), methyl iodide (1.0 mL), and DMSO (20 mL). Standard work-up and chromatography of the crude product on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 16 : 1) gave *cis*-**7**-Me (0.88 g, 86%) as a colourless oil (R_f = 0.59 in PE/Et_2O 1 : 1). – IR (film): ν = 3080 cm^{-1} ($C=CH_2$), 2940, 1740 (C=O), 1635 (C=C), 1445, 1435, 1290, 1050, 1095, 915, 865. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.25–1.76 (m, 9 H, cyclohexyl-H and 1"-H), 2.05 (d, ^2J = 11.1 Hz, 1 H, 1"-H), 2.54 (m, 1 H, 2-H), 2.96 (s, 2 H, 3'-H), 3.23 (bs, 5 H, OCH_3 and 5'-H), 4.13 (m, 4 H, OCH_2CH_3), 4.86–5.04 (m, 2 H, 3"-H), 5.54 (d, J = 1.5 Hz, 1 H, 7'-H), 5.65 (m, 1 H, 2"-H), 5.71 (bs, 1 H, 7'-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 22.4 (–), 23.5 (–), 25.1 (–), 28.3 (–), 34.8 (–), 35.9 (–), 42.7 (–, C-5'), 46.4 (+, C-2), 50.5 (+, OCH_3), 56.3 (C_{quat}, C-4'), 61.8 (–, OCH_2CH_3), 77.8 (C_{quat}), 82.2 (C_{quat}, C-1), 82.7 (C_{quat}), 115.4 (–, C-3"), 122.1 (–, C-7'), 126.6 (C_{quat}, C-6'), 137.8 (+, C-2"), 168.9 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 409/407 (12/11), 389 (15) [M^+ – Br], 283 (25), 237 (100), 220 (15), 205 (75), 135 (50), 112 (80), 91 (95). – Anal. Calcd for $C_{23}H_{33}BrO_5$ (469.4): C 58.85, H 7.09, Br 17.02; found: C 58.85, H 7.12, Br 17.09.

Diethyl 2-Bromo-8-hydroxynon-1-ene-6-yne-4,4-dicarboxylate (**15a**-H): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (10.0 g, 32.0 mmol), *n*-butyllithium (18.8 mL, 32.0 mmol, 1.7 M in hexane) and ethanal (1.54 g, 35.0 mmol) were reacted in THF (150 mL). Chromatography of the crude product on silica gel (250 g, column 4 × 40 cm, PE/Et_2O 3 : 1) afforded **15a**-H (9.68 g, 85%) as a colourless oil (R_f = 0.13). – IR (film): ν = 3413 cm^{-1} (OH), 2980, 2931 (C–H), 1735 (C=O), 1626 (C=C), 1446, 1292, 1147, 1014, 900, 858. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.26 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.39 (d, ^3J = 6.5 Hz, 3 H, 9-H), 2.17 (bs, 1 H, OH), 2.97 (d, ^5J = 1.3 Hz, 2 H, 5-H), 3.24 (s, 2 H, 3-H), 4.20 (mc, 5 H, 2 × OCH_2CH_3, H-8), 5.61 (d, ^2J = 1.3 Hz, 1 H, 1-H), 5.85 (d, ^2J = 1.3 Hz, 1 H, 1-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 13.86 (+, 2 × OCH_2CH_3), 21.93 (–, C-3), 22.30 (+, C-9), 41.37 (–, C-5), 55.97 (C_{quat}, C-4), 61.83 (–, 2 × OCH_2CH_3), 64.10 (+, C-8), 79.32 (C_{quat}, C-6), 81.57 (C_{quat}, C-7), 122.36 (–, C-1), 126.38 (C_{quat}, C-2), 168.91 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 281 (100) [M^+ – Br], 207 (47), 161 (51), 137 (53), 91 (41), 43 (82) [$C_3H_7^+$].

Diethyl 2-Bromo-8-hydroxydeca-1-ene-6-yne-4,4-dicarboxylate (**15b**-H): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (10.0 g, 32.0 mmol), *n*-butyllithium (15.0 mL, 33.0 mmol, 2.20 M in hexane) and propanal (1.98 g, 34.0 mmol) were reacted in THF (150 mL). Chromatography of the crude product on silica gel (250 g, column 4 × 40 cm, PE/Et_2O 3 : 1) afforded **15b**-H (9.70 g, 82%) as a colourless oil (R_f = 0.15). – IR (film): ν = 3482 cm^{-1} (OH), 2970, 2936 (C–H), 1738 (C=O), 1628 (C=C), 1466, 1292, 1217, 1043, 901. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.3 Hz, 3 H, 10-H), 1.28 (t, ^3J = 7.1 Hz, 6 H, 2 × OCH_2CH_3), 1.65 (mc, 2 H, 9-H), 2.13 (bs, 1 H, OH), 2.95 (d, ^5J = 1.6 Hz, 2 H, 5-H), 3.23 (s, 2 H, 3-H), 4.21 (mc, 5 H, 2 × OCH_2CH_3, 8-H), 5.61 (d, ^2J = 1.6 Hz, 1 H, 1-H), 5.81 (d, ^2J = 1.6 Hz, 1 H, 1-H). –

^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 9.31 (+, C-10), 13.91 (+, 2 × OCH_2CH_3), 22.36 (–, C-3), 30.95 (–, C-9), 42.73 (–, C-5), 56.08 (C_{quat}, C-4), 61.97 (–, 2 × OCH_2CH_3), 63.61 (+, C-8), 79.45 (C_{quat}, C-6), 85.03 (C_{quat}, C-7), 122.56 (–, C-1), 126.38 (C_{quat}, C-2), 169.17 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 359/357 (37/36), 313/311 (15/14), 285/283 (81/76), 257/255 (41/39), 203 (38), 175 (41), 131 (75), 91 (100), 57 (61).

Diethyl 2-Bromo-8-hydroxy-8-phenyloct-1-ene-6-yne-4,4-dicarboxylate (**15d**-H): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (9.31 g, 29.4 mmol), *n*-butyllithium (14.1 mL, 30.0 mmol, 2.13 M in hexane), and benzaldehyde (3.40 g, 32.0 mmol) were reacted in THF (150 mL). Chromatography of the crude product on silica gel (250 g, column 4 × 40 cm, PE/Et_2O 5 : 1) afforded **15d**-H (9.68 g, 78%) as a colourless oil (R_f = 0.22, PE/Et_2O 3 : 1). – IR (film): ν = 3264 cm^{-1} (OH), 3037, 2907 (C–H), 1734 (C=O), 1626 (C=C), 1429, 1044, 758, 700, 640. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.2 Hz, 6 H, 2 × OCH_2CH_3), 2.71 (d, ^3J = 6.2 Hz, 1 H, OH), 2.99 (d, ^5J = 2.0 Hz, 2 H, 5-H), 3.26 (s, 2 H, 3-H), 4.19 (mc, 4 H, 2 × OCH_2CH_3), 5.39 (br. d, ^3J = 6.2 Hz, 1 H, 8-H), 5.56 (d, ^2J = 1.5 Hz, 1 H, 1-H), 5.70 (d, ^2J = 1.5 Hz, 1 H, 1-H), 7.35–7.52 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.85 (+, 2 × OCH_2CH_3), 22.47 (–, C-3), 42.76 (–, C-5), 56.02 (C_{quat}, C-4), 62.00 (–, 2 × OCH_2CH_3), 64.42 (+, C-8), 81.43 (C_{quat}, C-6), 83.92 (C_{quat}, C-7), 122.67 (–, C-1), 126.23 (C_{quat}, C-2), 126.45, 128.21, 128.46 (+, C-Ph), 140.71 (C_{quat}, C-Ph), 169.15 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 343 (45) [M^+ – Br], 269 (98), 251 (55), 223 (75), 195 (100), 179 (45), 115 (25), 105 (85), 77 (48) [$C_6H_5^+$], 43 (8) [$C_3H_7^+$].

Diethyl 2-Bromo-8-hydroxy-8-(p-methoxyphenyl)oct-1-ene-6-yne-4,4-dicarboxylate (**15e**-H): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (9.70 g, 30.6 mmol), *n*-butyllithium (13.1 mL, 31.0 mmol, 2.36 M in hexane), and anisaldehyde (3.85 g, 28.3 mmol) were reacted in THF (200 mL). Chromatography of the crude product on silica gel (250 g, column 5 × 25 cm, PE/Et_2O 3 : 1) afforded **15e**-H (8.30 g, 65%) as a colourless oil (R_f = 0.42, PE/Et_2O 1 : 1). – IR (film): ν = 3282 cm^{-1} (OH), 2980, 2936 (C–H), 1734 (C=O), 1611 (C=C), 1512, 1194, 1039, 855, 569. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.2 Hz, 6 H, 2 × OCH_2CH_3), 2.94 (d, ^5J = 1.8 Hz, 2 H, 5-H), 3.20 (bs, 1 H, OH), 3.22 (s, 2 H, 3-H), 3.75 (s, 3 H, OCH_3), 4.14 (q, ^3J = 7.2 Hz, 4 H, 2 × OCH_2CH_3), 5.32 (br. d, *J* = 6.1 Hz, 1 H, 8-H), 5.52 (d, ^2J = 1.5 Hz, 1 H, 1-H), 5.72 (d, ^2J = 1.5 Hz, 1 H, 1-H), 6.83 (d, ^3J = 8.5 Hz, 2 H, *o*-Ar-H), 7.35 (d, ^3J = 8.5 Hz, 2 H, *m*-Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.70 (+, 2 × OCH_2CH_3), 22.32 (–, C-3), 42.60 (–, C-5), 55.04 (+, OCH_3), 55.83 (C_{quat}, C-4), 61.86 (–, 2 × OCH_2CH_3), 63.70 (+, C-8), 80.71 (C_{quat}, C-6), 84.11 (C_{quat}, C-7), 113.55 (+, 2 × *o*-C-Ar), 122.61 (–, C-1), 126.05 (C_{quat}, C-2), 127.78 (+, 2 × *m*-C-Ar), 133.02 (C_{quat}, C-Ar), 159.23 (C_{quat}, C-Ar), 169.05 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 454/452 (2/2) [M^+], 409/407 (1/1), 393/391 (8/8), 373 (28) [M^+ – Br], 323/327 (7/7), 281 (45), 225 (75), 137/135 (98/100) [$C_4H_8Br^+$], 109 (18), 81/79 (23) [Br^+], 56 (66).

Diethyl 8-Allyloxy-2-bromo-9,9-dimethyldodeca-1,11-diene-6-yne-4,4-dicarboxylate (**14**-All): To a solution of **14**-H (800 mg, 1.86 mmol) in THF (30 mL) *n*-butyllithium (0.8 mL, 1.9 mmol, 2.36 M in *n*-hexane) was added dropwise at –78 °C, after which stirring was continued for 10 min. The reaction mixture was heated to –10 °C, DMSO (20 mL) was added in one portion and afterwards allyl bromide (0.7 mL, 8.1 mmol) at 0 °C. The reaction mixture was further stirred for 30 min, water (10 mL) was added and the aqueous layer extracted with Et_2O (2 × 20 mL). After washing with brine (30 mL) and drying over magnesium sulfate, the solvents were removed under vacuum and the crude product purified by chromatography on silica gel (70 g, column 1.5 × 30 cm, PE/Et_2O 7 : 1) to yield **14**-All (672 mg, 77%) as a colourless oil (R_f = 0.12). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.25 (t, 6 H, CH_2CH_3), 2.10 (mc, 2 H, 10-H), 2.98 (d, ^4J = 1.8 Hz, 2 H, 3-H), 3.27 (s, 2 H, 5-H), 3.68 (dd, 1 H, OCH_2CHCH_2), 3.84 (dd, 1 H, OCH_2CHCH_2), 4.23 (m, 5 H, 8-H, CH_2CH_3), 4.98 (m, 1 H, 12-H), 5.04 (m, 1 H, 12-H), 5.14 (bd, 1 H, OCH_2CHCH_2), 5.25 (bd, 1 H, OCH_2CHCH_2), 5.60 (d, ^4J = 1.8 Hz, 1 H, 1-H), 5.81 (m, 3 H, 1-H, OCH_2CHCH_2, 11-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.90 (+, CH_2CH_3), 22.52 (–, C-3), 22.82 (+, CH_3), 23.14 (+, CH_3), 38.20 (C_{quat}, C-9), 42.84 (–, C-5), 42.95 (–, C-10), 56.20 (C_{quat}, C-4), 61.86

(–, CH_2CH_3), 69.85 (–, OCH_2CHCH_2), 76.38 (+, C-8), 81.21 (C_{quat}, C-6), 81.52 (C_{quat}, C-7), 116.63 (–, OCH_2CHCH_2), 117.34 (–, C-12), 122.36 (–, C-1), 126.58 (C_{quat}, C-2), 134.68 (+, OCH_2CHCH_2), 134.87 (+, C-11), 169.09 (C_{quat}, CO_2Et). – MS (70 eV), *m/z* (%): 470/468 (1/2) [M^+], 441/439 (3/4) [$M^+ - C_2H_5$], 429/427 (7/8) [$M^+ - C_3H_5$], 389 (61) [$M^+ - Br$], 345 (20), 327 (78), 271 (17), 265 (39), 255 (55), 241 (40), 227 (30), 163 (27), 159 (39), 131 (36), 91 (53), 55 (89), 41 (100). – Anal. Calcd for $C_{23}H_{33}BrO_5$ (469.4): C 58.85, H 7.09, Br 17.02; found: C 59.23, H 7.19, Br 16.57.

Diethyl 8-Allyloxy-2-bromonon-1-ene-6-yne-4,4-dicarboxylate (**15a**-All): To a solution of **15a**-H (3.87 g, 10.7 mmol) in dichloromethane (100 mL) were added tetrabutylammonium iodide (40 mg, 1 mol%), allyl bromide (1.45 g, 12 mmol), and a sodium hydroxide solution (100 mL, 50% NaOH in water). After stirring for 6 h at room temperature, water was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with brine (100 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (200 g, column 4 × 30 cm, PE/Et_2O 5 : 1) to give **15a**-All (3.61 g, 84%) as a colourless oil (R_f = 0.28, PE/Et_2O 3 : 1). – IR (film): ν = 2979 cm^{-1}, 2937 (C–H), 1738 (C=O), 1632 (C=C), 1464, 1427, 1367, 1215, 1121, 1015, 900. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.27 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 1.41 (d, ^3J = 6.7 Hz, 3 H, 9-H), 2.98 (d, ^5J = 1.7 Hz, 2 H, 5-H), 3.26 (s, 2 H, 3-H), 3.83–3.95 (m, 2 H, OCH_2CHCH_2), 4.23 (mc, 5 H, 2 × OCH_2CH_3, 8-H), 5.17 (dd, $^3J_{cis}$ = 10.4, ^2J = 1.8 Hz, 1 H, OCH_2CHCH_2), 5.31 (dd, $^3J_{trans}$ = 17.2, ^2J = 1.8 Hz, 1 H, OCH_2CHCH_2), 5.62 (d, ^2J = 1.1 Hz, 1 H, 1-H), 5.88 (bs, 1 H, 1-H), 5.90–5.96 (m, 1 H, OCH_2CHCH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.88 (+, 2 × OCH_2CH_3), 22.10 (–, C-3), 22.37 (+, CH_3), 42.67 (–, C-5), 55.93 (C_{quat}, C-4), 61.54 (–, 2 × OCH_2CH_3), 64.25 (+, C-8), 69.15 (–, OCH_2CHCH_2), 79.21 (C_{quat}, C-6), 83.73 (C_{quat}, C-7), 117.10 (–, OCH_2CHCH_2), 122.3 (–, C-1), 126.34 (C_{quat}, C-2), 134.26 (+, OCH_2CHCH_2), 168.90 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 345/343 (15/18), 271/269 (57/61), 243/241 (40/42), 189 (36), 117/115 (82/98), 91 (58), 77 (35), 43 (100) [$C_3H_7^+$].

Diethyl 8-Allyloxy-2-bromodec-1-ene-6-yne-4,4-dicarboxylate (**15b**-All): To a solution of **15b**-H (4.01 g, 10.7 mmol) in dichloromethane (100 mL) were added tetrabutylammonium iodide (40 mg, 1 mol%), allyl bromide (1.45 g, 12 mmol), and a sodium hydroxide solution (100 mL, 50% NaOH in water). After stirring for 7 h at room temperature, water was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic phases were washed with brine (100 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (200 g, column 4 × 30 cm, PE/Et_2O 5 : 1) to give **15b**-All (3.51 g, 79%) as a colourless oil (R_f = 0.16). – IR (film): ν = 2978 cm^{-1}, 2935 (C–H), 1738 (C=O), 1626 (C=C), 1464, 1288, 1215, 1067, 900. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, ^3J = 7.5 Hz, 3 H, 10-H), 1.26 (t, ^3J = 7.2 Hz, 6 H, 2 × OCH_2CH_3), 1.62–1.72 (m, 2 H, 9-H), 2.96 (d, ^5J = 1.8 Hz, 2 H, 5-H), 3.28 (s, 2 H, 3-H), 3.86–3.98 (m, 2 H, OCH_2CHCH_2), 4.24 (mc, 5 H, 2 × OCH_2CH_3, 8-H), 5.09 (dd, $^3J_{cis}$ = 10.4, ^2J = 1.6 Hz, 1 H, OCH_2CHCH_2), 5.20 (dd, $^3J_{trans}$ = 17.2, ^2J = 1.6 Hz, 1 H, OCH_2CHCH_2), 5.54 (d, ^2J = 1.3 Hz, 1 H, 1-H), 5.72 (bs, 1 H, 1-H), 5.88–5.90 (m, 1 H, OCH_2CHCH_2). – ^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 8.39 (+, C-10), 13.76 (+, 2 × OCH_2CH_3), 22.30 (–, C-3), 28.84 (–, C-9), 42.64 (–, C-5), 56.00 (C_{quat}, C-4), 61.68 (–, 2 × OCH_2CH_3), 69.16 (–, OCH_2CHCH_2), 69.87 (+, C-8), 80.10 (C_{quat}, C-6), 82.79 (C_{quat}, C-7), 116.82 (–, OCH_2CHCH_2), 122.20 (–, C-1), 126.42 (C_{quat}, C-2), 134.42 (+, OCH_2CHCH_2), 168.86 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 387/385 (9/11), 335 (43) [$M^+ - Br$], 255 (31), 205/203 (37/39), 131 (77), 91 (74), 57 (75), 41 (100).

Diethyl 8-Allyloxy-2-bromo-9-methyldec-1-ene-6-yne-4,4-dicarboxylate (**15c**-All): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (2.00 g, 6.31 mmol), *n*-butyllithium (2.70 mL, 6.62 mmol, 2.45 M in *n*-hexane), and isobutyraldehyde (546 mg, 7.57 mmol) were reacted in THF (30 mL). Chromatography of the crude product on silica gel (90 g, column 2 × 30 cm, PE/Et_2O 1 : 1) yielded diethyl 2-bromo-8-hydroxy-9-methyldec-1-ene-6-yne-4,4-dicarboxylate (**15c**-H) (2.01 g, 82%) as a yellow oil (R_f = 0.60). – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.69 (d, ^3J = 6.2 Hz, 6 H, CH_3), 1.03 (t, ^3J = 7.1 Hz, 6 H,

CH_2CH_3), 1.58 (bs, 1 H, OH), 1.87 (m, 1 H, 9-H), 2.74 (d, J = 2.2 Hz, 2 H, 3-H), 3.05 (s, 2 H, 5-H), 3.80 (bs, 1 H, 8-H), 3.98 (m, 4 H, CH_2CH_3), 5.38 (d, J = 1.2 Hz, 1 H, 1-H), 5.56 (bs, 1 H, 1-H). – MS (70 eV), *m/z* (%): 347/345 (3/3) [$M^+ - C_3H_7$], 327 (10), 310 (20), 309 (100) [M^+ – Br], 299 (8), 291 (8), 271 (14), 253 (20), 245 (18), 235 (55), 225 (26), 216 (24), 189 (32), 173 (12), 172 (21), 147 (22), 145 (24), 119 (32), 97 (23), 93 (63), 91 (45), 79 (20), 71 (79), 69 (20), 55 (28), 43 (96) [$C_3H_7^+$]. – A solution of **15c**-H (1.00 g, 2.57 mmol) in THF (30 mL) was treated dropwise with *n*-butyllithium (1.1 mL, 2.70 mmol, 2.45 M in *n*-hexane) at –78 °C. The reaction mixture was warmed to –10 °C, during which it became yellowish. DMSO (30 mL) and allyl bromide (0.9 mL, 10 mmol) were added at 0 °C and stirring was continued for 30 min. After the addition of water (10 mL) and Et_2O (100 mL), the organic layer was washed with water (2 × 20 mL) and the aqueous phase extracted with Et_2O (3 × 50 mL). Washing with brine (100 mL), drying over magnesium sulfate and removal of the solvents under vacuum gave the crude product, which was chromatographed on silica gel (60 g, column 2 × 20 cm, PE/Et_2O 3 : 1) to yield **15c**-All (0.98 g, 89%) as a colourless oil (R_f = 0.32). – IR (film): ν = 3081 cm^{-1}, 2979, 2936, 2906, 2873, 2217, 1735 (C=O), 1676, 1653, 1647, 1626, 1466, 1447, 1428, 1387, 1367, 1350, 1324, 1289, 1252, 1215, 1191, 1148, 1113, 1066, 1013, 902, 856, 563. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.93 (d, ^3J = 6.5 Hz, 3 H, CH_3), 0.96 (d, ^3J = 6.5 Hz, 3 H, CH_3), 1.25 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.88 (m, 1 H, 9-H), 2.96 (d, J = 1.7 Hz, 2 H, 3-H), 3.26 (s, 2 H, 5-H), 3.82 (m, 1 H, OCH_2CHCH_2), 3.85 (m, 1 H, OCH_2CHCH_2), 4.15 (m, 5 H, CH_2CH_3, 8-H), 5.18 (m, 1 H, OCH_2CHCH_2), 5.29 (m, 1 H, OCH_2CHCH_2), 5.61 (m, 1 H, 1-H), 5.80 (s, 1 H, 1-H), 5.84 (m, 1 H, OCH_2CHCH_2). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.80 (+, CH_2CH_3), 17.59 (+, CH_3), 18.42 (+, CH_3), 22.34 (–, C-3), 32.89 (+, C-9), 42.68 (–, C-5), 55.98 (C_{quat}, C-4), 61.79 (–, CH_2CH_3), 69.37 (–, OCH_2CHCH_2), 74.18 (+, C-8), 80.70 (C_{quat}), 81.55 (C_{quat}), 116.87 (–, OCH_2CHCH_2), 122.34 (–, C-1), 126.40 (C_{quat}, C-2), 134.46 (+, OCH_2CHCH_2), 169.00 (C_{quat}, CO_2Et). – MS (70 eV), *m/z* (%): 387/385 (40/36) [$M^+ - C_3H_7$], 349 (70) [M^+ – Br], 327 (56), 309 (26), 291 (14), 255 (26), 243 (17), 231 (17), 220 (17), 203 (13), 163 (17), 145 (21), 131 (22), 111 (23), 93 (28), 91 (27), 79 (17), 71 (60), 69 (16), 55 (23), 43 (59) [$C_3H_7^+$], 41 (100). – Anal. Calcd for $C_{20}H_{29}BrO_5$ (429.4): C 55.95, H 6.81, Br 18.61; found: C 55.96, H 6.79, Br 18.49.

Diethyl 8-Allyloxyphenyl-2-bromooct-1-ene-6-yne-4,4-dicarboxylate (**15d**-All): To a solution of **15d**-H (2.00 g, 4.73 mmol) in dichloromethane (80 mL) were added tetrabutylammonium iodide (18 mg, 1 mol%), allyl bromide (0.61 g, 5.00 mmol), and a sodium hydroxide solution (80 mL, 50% NaOH in water). After stirring for 11 h at room temperature, water was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic phases washed with brine (100 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (150 g, column 2 × 30 cm, PE/Et_2O 5 : 1) to give **15d**-All (1.40 g, 64%) as a colourless oil (R_f = 0.54, PE/Et_2O 3 : 1). – IR (film): ν = 2981 cm^{-1}, 2936 (C–H), 1734 (C=O), 1626 (C=C), 1452, 1194, 1068, 917, 700, 546. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.16 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 2.95 (d, ^5J = 2.0 Hz, 2 H, 5-H), 3.21 (s, 2 H, 3-H), 3.92–4.22 (m, 7 H, OCH_2CHCH_2, 2 × OCH_2CH_3, 8-H), 5.06–5.11 (m, 1 H, OCH_2CHCH_2), 5.12 (dd, $^3J_{cis}$ = 12.0, ^2J = 1.6 Hz, 1 H, OCH_2CHCH_2), 5.25 (dd, $^3J_{trans}$ = 17.2, ^2J = 1.6 Hz, 1 H, OCH_2CHCH_2), 5.49 (d, ^2J = 1.6 Hz, 1 H, 1-H), 5.62 (d, ^2J = 1.6 Hz, 1 H, 1-H), 7.21–7.41 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.82 (+, 2 × OCH_2CH_3), 22.50 (–, C-3), 42.78 (–, C-5), 56.00 (C_{quat}, C-4), 61.88 (–, 2 × OCH_2CH_3), 68.85 (–, OCH_2CHCH_2), 70.44 (+, C-8), 81.71 (C_{quat}, C-6), 82.38 (C_{quat}, C-7), 117.52 (–, OCH_2CHCH_2), 122.50 (–, C-1), 126.31 (C_{quat}, C-2), 127.18, 128.20, 128.30 (+, C-Ph), 134.31 (+, OCH_2CHCH_2), 138.62 (C_{quat}, C-Ph), 168.98 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 383 (6) [M^+ – Br], 325 (2), 274 (3), 257 (20), 211 (12), 155 (8), 122 (18), 105 (100), 77 (35), 51 (14).

Diethyl 8-Allyloxy-8-(*p*-methoxyphenyl)-2-bromooct-1-ene-6-yne-4,4-dicarboxylate (**15e**-All): To a solution of **15e**-H (4.00 g, 8.82 mmol) in dichloromethane (100 mL) were added tetrabutylammonium iodide (33 mg, 1 mol%), allyl bromide (1.21 g, 10 mmol), and a sodium hydroxide solution (100 mL, 50% NaOH in water). After stirring for 7 h at room temperature, water was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (4 × 30 mL) and the combined organic phases were washed

with brine (100 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (200 g, column 5 × 20 cm, PE/Et_2O 4 : 1) to give **15e**-All (3.51 g, 81%) as a colourless oil (R_f = 0.23). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.1 Hz, 6 H, 2 × OCH_2CH_3), 3.01 (d, ^5J = 1.8 Hz, 2 H, 5-H), 3.28 (s, 2 H, 3-H), 3.75 (s, 3 H, OCH_3), 3.93–4.23 (m, 6 H, OCH_2CHCH_2, 2 × OCH_2CH_3), 5.10 (bs, 1 H, 8-H), 5.16 (dd, $^3J_{cis}$ = 10.3, ^2J = 1.3 Hz, 1 H, OCH_2CHCH_2), 5.27 (dd, $^3J_{trans}$ = 17.2, ^2J = 1.3 Hz, 1 H, OCH_2CHCH_2), 5.55 (d, ^2J = 1.5 Hz, 1 H, 1-H), 5.70 (d, ^2J = 1.5 Hz, 1 H, 1-H), 5.89 (mc, 1 H, OCH_2CHCH_2), 6.85 (d, ^3J = 8.7 Hz, 2 H, *o*-Ar-H), 7.36 (d, ^3J = 8.7 Hz, 2 H, *m*-Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.69 (+, 2 × OCH_2CH_3), 22.36 (–, C-3), 42.64 (–, C-5), 54.97 (+, OCH_3), 55.85 (C_{quat}, C-4), 61.72 (–, 2 × OCH_2CH_3), 68.48 (–, OCH_2CHCH_2), 69.90 (+, C-8), 81.79 (C_{quat}, C-6), 81.95 (C_{quat}, C-7), 113.46 (+, 2 × *o*-C-Ar), 117.20 (–, OCH_2CHCH_2), 122.38 (–, C-1), 126.05 (C_{quat}, C-2), 128.48 (+, 2 × *m*-C-Ar), 133.82 (+, OCH_2CHCH_2), 134.13, 159.38 (C_{quat}, 2 × C-Ar), 168.82 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 494/492 (1/1) [M^+], 413 (40) [M^+ – Br], 355 (38), 339 (23), 281 (60), 209 (39), 165 (43), 135 (100), 121 (20), 77 (17), 41 (10).

Diethyl 3-Methoxy-4,4-dimethyltricyclo[7.3.0.0^{2,6}]dodeca-1(9),2(6)-diene-11,11-dicarboxylate (**19**-Me): A solution of **14**-Me (400 mg, 0.9 mmol) in acetonitrile (10 mL) was reacted according to GP 2b with palladium acetate (11 mg, 5 mol%), triphenylphosphane (47 mg, 20 mol%) and silver(I) carbonate (489 mg, 2 equiv.) for 3 h at 80 °C. The crude product was purified on silica gel (8 g, column 1 × 15 cm, PE/Et_2O 16 : 1) to give **19**-Me (197 mg, 60%) as a colourless oil (R_f = 0.20 in PE/Et_2O 10 : 1). – IR (film): ν = 2930 cm^{-1}, 2830, 1740 (C=O), 1670 (C=C), 1470, 1445, 1390, 1370, 1260, 1185, 1165, 1100, 1055, 1025, 870. – ^1H NMR (67.9 MHz, $CDCl_3$): δ = 1.10 (bs, 6 H, 4-CH_3), 1.24 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.25 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.97 (d, ^2J = 17.1 Hz, 1 H, 5-H), 2.13–2.34 [m, 5 H, 5(7,8)-H], 2.28–3.24 [m, 4 H, 10(12)-H], 3.40 (s, 3 H, OCH_3), 3.78 (bs, 1 H, 3-H), 4.17 (q, ^3J = 7.0 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_2CH_3), 23.0 (+, 4-CH_3), 23.7 (–), 24.5 (–), 30.2 (+, 4-CH_3), 39.7 (–), 42.1 (C_{quat}, C-4), 43.2 (–), 49.7 (–), 58.4 (+, OCH_3), 58.9 (C_{quat}, C-11), 61.37 (–), 61.42 (–), 93.2 (+, C-3), 129.0 (C_{quat}), 131.2 (C_{quat}, 2 C), 138.7 (C_{quat}), 172.1 (C_{quat}), 172.6 (C_{quat}). – MS (70 eV), *m/z* (%): 362 (4) [M^+], 289 (3), 257 (100), 211 (18), 183 (43), 128 (16), 119 (20), 105 (12), 77 (5), 41 (3). – $C_{21}H_{30}O_5$: calcd 362.2093 (correct HRMS). – Anal. Calcd for $C_{21}H_{30}O_5$ (362.5): C 69.59, H 8.34; found: C 69.61, H 8.51.

Diethyl Spiro[cyclohexane-1,1'-(2'-methoxytricyclo[7.4.0.0.$^{4',8'}$]dodeca-3'(11'),4'(8)-diene-6',6'-dicarboxylate (**20**-Me): According to GP 2b, to a solution of **9**-Me (400 mg, 0.83 mmol) in acetonitrile (10 mL) palladium acetate (6 mg, 3 mol%), triphenylphosphane (12 mg, 6 mol%) and silver(I) carbonate (448 mg, 2 equiv.) were added. The mixture was heated for 4 h at 80 °C. Standard work-up and chromatography on silica gel (20 g, column 2.5 × 20 cm, PE/Et_2O 16 : 1) gave **20**-Me (290 mg, 87%) as a colourless oil. – IR (film): ν = 2960 cm^{-1}, 1730 (C=O), 1440, 1370, 1250, 1180, 1100, 1020, 965, 925, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.22 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.27–1.56 [m, 10 H, 2(3,4,5,6)-H], 2.03 (d, ^2J = 17.2 Hz, 1 H, 12'-H), 2.15–2.26 [m, 5 H, 12'(9',10')-H], 2.93–3.11 [m, 4 H, 7'(5')-H], 3.37 (s, 3 H, OCH_3), 3.78 (bs, 1 H, 2'-H), 4.14 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.17 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 23.4 (–), 23.5 (–), 23.6 (–), 24.6 (–), 26.2 (–), 31.6 (–), 38.2 (–), 39.8 (–), 43.1 (–), 45.2 (–), 45.8 (C_{quat}, C-1), 58.3 (+, OCH_3), 58.8 (C_{quat}, C-6'), 61.3 (–, OCH_2CH_3), 93.1 (+, C-2'), 128.8 (C_{quat}), 130.9 (C_{quat}), 131.1 (C_{quat}), 138.9 (C_{quat}), 172.0 (C_{quat}, C=O), 172.4 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 402 (5) [M^+], 370 (47), 329 (4), 297 (100), 296 (44), 251 (10), 223 (32), 167 (7), 129 (6), 91 (3). – $C_{24}H_{34}O_5$: calcd 402.2406 (correct HRMS). – Anal. Calcd for $C_{24}H_{34}O_5$ (402.5): C 71.61, H 8.51; found: C 71.71, H 8.46.

Diethyl *cis*-10a-Methoxy-3,4,5,6,6a,7,8,9,10,10a-decahydro-1*H*-cyclopenta[*c*]fluorene-2,2-dicarboxylate (*cis*-**21**-Me): According to GP 2b, to a solution of *cis*-**7**-Me (300 mg, 0.64 mmol) in acetonitrile (10 mL) palladium acetate (5 mg, 3 mol%), triphenylphosphane (11 mg, 7 mol%), and silver(I) carbonate (346 mg, 2 equiv.) were added. The mixture was heated for 4 h at 80 °C. Standard work-up and filtration of

the crude product through silica gel (5 g, Et_2O) yielded *cis*-**21**-Me (120 mg, 48%) as a colourless oil. – IR (film): ν = 2980 cm^{-1}, 2920, 1730 (C=O), 1635 (C=C), 1620 (C=C), 1445, 1390, 1370, 1250, 1190, 1100, 1070, 1055, 1015, 865, 805. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.14–1.22 (m, 6 H, CH_2CH_3), 1.40–2.03 (m, 10 H), 2.10–2.30 (m, 5 H), 2.89 (bs, 2 H), 2.99 (s, 3 H, OCH_3), 3.00–3.10 (m, 2 H), 4.10–4.25 (m, 4 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_2CH_3), 21.1 (–), 23.8 (–), 24.1 (–), 24.6 (–), 26.2 (–), 31.0 (–), 37.6 (–), 40.6 (–), 42.7 (–), 50.2 (+), 51.1 (+), 58.9 (C_{quat}, C-2), 61.5 (–, OCH_2CH_3), 84.4 (C_{quat}, C-10a), 123.3 (C_{quat}), 128.5 (C_{quat}), 132.0 (C_{quat}), 143.0 (C_{quat}), 172.2 (C_{quat}, C=O), 172.3 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 354 (80), 282 (57), 280 (100), 253 (18), 207 (46), 165 (26), 143 (12), 105 (15), 41 (12). – Anal. Calcd for $C_{23}H_{32}O_5$ (388.5): C 71.11, H 8.30; found: C 70.99, H 8.35.

Diethyl *trans*-10a-Methoxy-3,4,5,6,6a,7,8,9,10,10a-decahydro-1*H*-cyclopenta[*c*]fluorene-2,2-dicarboxylate (*trans*-**21**-Me): According to GP 2b, to a solution of *trans*-**7**-Me (300 mg, 0.64 mmol) in acetonitrile (10 mL) palladium acetate (5 mg, 3 mol%), triphenylphosphane (11 mg, 7 mol%), and silver(I) carbonate (346 mg, 2 equiv.) were added. The mixture was heated for 4 h at 80 °C. Standard work-up and filtration of the crude product through silica gel (5 g, Et_2O) yielded *trans*-**21**-Me (220 mg, 88%) as a colourless oil. – IR (film): ν = 2970 cm^{-1}, 2920, 1735 (C=O), 1440, 1365, 1275, 1245, 1185, 1155, 1095, 1070, 860, 800. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.25 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.28–1.90 (m, 8 H), 1.95–2.10 (m, 1 H), 2.23–2.34 (m, 6 H), 2.97 (bs, 2 H), 3.10 (s, 3 H, OCH_3), 3.10–3.16 (m, 2 H), 4.17 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.18 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_2CH_3), 19.9 (–), 20.9 (–), 23.7 (–), 24.9 (–), 25.6 (–), 33.6 (–), 37.5 (–), 37.9 (+, C-6a), 39.3 (–), 42.7 (–), 50.2 (+, OCH_3), 58.9 (C_{quat}, C-2), 61.3 (–, OCH_2CH_3), 87.5 (C_{quat}, C-10a), 128.0 (C_{quat}), 131.7 (C_{quat}), 135.3 (C_{quat}), 137.8 (C_{quat}), 172.3 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 356 (18), 357 (20), 354 (90), 282 (78), 280 (100), 253 (22), 208 (27), 207 (45), 165 (23), 143 (33), 69 (18). – Anal. Calcd for $C_{23}H_{32}O_5$ (388.5): C 71.11, H 8.30; found: C 71.03, H 8.20.

Diethyl *trans*-10a-Hydroxy-3,4,5,6,6a,7,8,9,10,10a-decahydro-1*H*-cyclopenta[*c*]fluorene-2,2-dicarboxylate (*trans*-**21**-H): According to GP 2b a solution of *trans*-**7**-H (300 mg, 0.7 mmol) in acetonitrile (10 mL) was treated with palladium acetate (5 mg, 3 mol%), triphenylphosphane (11 mg, 6 mol%), and silver carbonate (385 mg, 2 equiv.) for 3 h at 80 °C. The reaction mixture was concentrated, rapidly (!) filtered through silica gel (3 g) with ether to yield 197 mg (80%) of *trans*-**21**-H as a colourless oil. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.40–1.75 (m, 9 H), 1.98–2.03 (m, 2 H), 2.14–2.24 (m, 5 H), 2.75–3.00 (m, 2 H), 3.80 (bs, 2 H), 4.03–4.15 (m, 4 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.7 (+, CH_2CH_3), 21.0 (–), 23.4 (–), 24.0 (–), 24.5 (–), 25.9 (–), 34.7 (–), 36.2 (–), 39.5 (–), 42.5 (–), 49.2 (+, C-6a), 58.5 (C_{quat}, C-2), 61.1 (–, OCH_2CH_3), 80.3 (C_{quat}, C-10a), 127.7 (C_{quat}), 131.4 (C_{quat}), 138.2 (C_{quat}), 140.2 (C_{quat}), 171.9 (C_{quat}, C=O), 171.9 (C_{quat}, C=O).

Diethyl *cis*-10a-Hydroxy-3,4,5,6,6a,7,8,9,10,10a-decahydro-1*H*-cyclopenta[*c*]fluorene-2,2-dicarboxylate (*cis*-**21**-H): According to GP 2b a solution of *cis*-**7**-H (328 mg, 0.72 mmol) in acetonitrile (20 mL) was treated with palladium acetate (5 mg, 3 mol%), triphenylphosphane (11 mg, 6 mol%), and silver carbonate (392 mg, 2 equiv.) for 3 h at 80 °C. The reaction mixture was concentrated, rapidly (!) filtered through silica gel (3 g) with ether to yield 229 mg (85%) of *cis*-**21**-H as a colourless oil. – ^1H NMR (250 MHz, $CDCl_3$): 1.24 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.25 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.30–2.09 (m, 10 H), 2.23 (bs, 5 H), 2.35 (dd, ^3J = 6.4, ^2J = 15.4 Hz, 1 H, 6-H), 2.93 (d, ^2J = 16.5 Hz, 1 H, 1-H), 2.99 (d, ^2J = 16.6 Hz, 1 H, 1-H), 3.21 (bs, 2 H), 4.14–4.24 (m, 4 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 20.5 (–), 21.9 (–), 23.6 (–), 24.6 (–), 26.7 (–), 34.1 (–), 37.5 (–), 39.3 (–), 42.6 (–), 46.8 (+, C-6a), 58.7 (C_{quat}, C-2), 61.2 (–, OCH_2CH_3), 82.2 (C_{quat}, C-10a), 127.7 (C_{quat}), 131.8 (C_{quat}), 136.7 (C_{quat}), 137.5 (C_{quat}), 172.2 (C_{quat}, C=O), 172.3 (C_{quat}, C=O).

Diethyl 3-Allyloxy-4,4-dimethyltricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (22) and Diethyl 3-[1'-(1',1'-Dimethyl-3'-butenyl)]-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (23): According to GP 2b **14**-All (200 mg, 0.43 mmol) was treated with palladium acetate (5 mg, 5 mol%), triphenylphosphane (11 mg, 10 mol%), and silver(I) carbonate (356 mg, 3 equiv.) in acetonitrile (10 mL) at 80 °C for 6 h. The reaction mixture was filtered through a plug of celite, silica gel (treated before with triethylamine and washed with PE), and charcoal prior to concentration. Chromatography of the residue on silica gel (60 g, column 2 × 20 cm, PE/Et_2O 3 : 1) gave **22** (97 mg, 58%, R_f = 0.43) and **23** (38 mg, 23%, R_f = 0.30) as colourless oils. **22**: ^{1}H NMR (250 MHz, C_6D_6): δ = 0.92 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.02 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.84 (d, ^2J = 17.0 Hz, 1 H, 10-H), 1.98 (m, 4 H, 7-H, 8-H), 2.15 (d, ^2J = 17.0 Hz, 1 H, 10-H), 3.22 (m, 2 H, 12-H), 3.54 (m, 2 H, 5-H), 3.94 (m, 7 H, CH_2CH_3, 3-H, OCH_2CHCH_2), 4.98 (m, 1 H, OCH_2CHCH_2), 5.03 (m, 1 H, OCH_2CHCH_2), 5.90 (m, 1 H, OCH_2CHCH_2). – ^{13}C NMR (62.9 MHz, C_6D_6, plus DEPT): δ = 14.02 (+, CH_2CH_3), 23.73 (+, CH_3), 23.88 (–), 24.76 (–), 29.92 (+, CH_3), 40.49 (–), 42.39 (C_{quat}, C-4), 43.68 (–), 49.94 (–), 59.28 (C_{quat}, C-11), 61.27 (–, CH_2CH_3), 61.32 (–, CH_2CH_3), 71.72 (–, OCH_2CHCH_2), 91.50 (+, C-3), 115.51 (–, OCH_2CHCH_2), 129.81 (C_{quat}), 131.37 (C_{quat}), 132.25 (C_{quat}), 135.98 (C_{quat}), 137.73 (+, OCH_2CHCH_2), 172.05 (C_{quat}, CO_2Et), 172.36 (C_{quat}, CO_2Et). – MS (70 eV), *m/z* (%): 388 (12) [M$^+$], 330 (55), 318 (5), 284 (3), 257 (100), 220 (31), 205 (100), 184 (33), 164 (37), 143 (76), 129 (18), 91 (42), 57 (27). – Anal. Calcd for $C_{23}H_{32}O_5$ (388.5): C 71.11, H 8.30; found: C 71.00, H 8.48. – **23**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (s, 3 H, CH_3), 0.85 (s, 3 H, CH_3), 1.23 (m, 6 H, CH_2CH_3), 2.06 (m, 2 H, CH_2CHCH_2), 2.22 (m, 4 H, 7-H, 8-H), 2.99 (m, 4 H, 10-H, 12-H), 4.19 (m, 4 H, CH_2CH_3), 4.51 (m, 3 H, 3-H, 5-H), 5.14 (m, 2 H, CH_2CHCH_2), 5.35 (m, 1 H, CH_2CHCH_2).

Diethyl 3-Methyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (24a): According to GP 2b **15a**-All (2.170 g, 5.407 mmol) was treated with palladium acetate (61 mg, 5 mol%), triphenylphosphane (142 mg, 10 mol%), and silver(I) carbonate (2.98 g, 2 equiv.) in acetonitrile (120 mL) at 80 °C for 9 h. The reaction mixture was filtered through a plug of celite, silica gel, and charcoal prior to concentration. Chromatography of the residue on silica gel (150 g, column 4 × 30 cm, PE/Et_2O 5 : 1) gave **24a** (1.455 g, 84%) as a colourless oil (R_f = 0.16). – IR (film): ν = 2976 cm^{-1}, 2930 (C–H), 1737 (C=O), 1446, 1367, 1250, 1181, 1070, 1011, 945, 862, 844. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.0 Hz, 6 H, 2 × OCH_2CH_3), 1.29 (d, ^3J = 6.2 Hz, 3 H, CH_3), 2.30 (bs, 4 H, 10-H, 12-H), 2.93–3.19 (m, 4 H, 7-H, 8-H), 4.27 (q, ^3J = 7.0 Hz, 4 H, 2 × OCH_2CH_3), 4.48 (d, ^2J = 12.5 Hz, 1 H, 5-H), 4.81 (dd, ^2J = 12.5, ^4J = 1.5 Hz, 1 H, 5-H), 4.91 (bs, 1 H, 3-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 13.87 (+, 2 × OCH_2CH_3), 20.44 (–, C-10*), 21.62 (+, CH_3), 23.54 (–, C-12*), 39.25, 42.73 (–, C-8, C-7), 58.58 (C_{quat}, C-11), 61.47 (–, 2 × OCH_2CH_3), 75.19 (–, C-5), 80.84 (+, C-3), 125.82 (C_{quat}, C-2), 130.82 (C_{quat}, C-6), 132.45 (C_{quat}, C-1), 132.98 (C_{quat}, C-9), 171.88 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 274 (19), 258 (63), 231 (41), 185 (48), 173 (63), 115 (39), 91 (18), 43 (100) [$C_3H_7^+$]. – Anal. Calcd for $C_{18}H_{22}O_5$ (318.4 = aromatised product): C 67.91, H 6.97; found: C 67.88, H 7.08.

Diethyl 3-Ethyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (24b): According to GP 2b **15b**-All (460 mg, 1.108 mmol) was treated with palladium acetate (25 mg, 10 mol%), triphenylphosphane (58 mg, 20 mol%), and silver(I) carbonate (0.61 g, 2 equiv.) in acetonitrile (40 mL) at 80 °C for 6 h. The reaction mixture was filtered through a plug of celite, silica gel, and charcoal prior to concentration. Chromatography of the residue on silica gel (30 g, column 2 × 20 cm, PE/Et_2O 10 : 1) gave **24b** (300 mg, 81%) as a colourless oil (R_f = 0.22, PE/Et_2O 4 : 1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.33 (t, ^3J = 6.9 Hz, 6 H, 2 × OCH_2CH_3), 1.52–1.63 (m, 1 H, CH_2CH_3), 1.78–1.88 (m, 1 H, CH_2CH_3), 2.38 (bs, 4 H, 10-H, 12-H), 3.01–3.20 (m, 4 H, 7-H, 8-H), 4.27 (q, ^3J = 6.9 Hz, 4 H, 2 × OCH_2CH_3), 4.56–4.72 (m, 2 H, 5-H), 4.92 (bs, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 8.66 (+, CH_2CH_3), 13.94 (+, 2 × OCH_2CH_3), 20.52, 23.65 (–, C-10, C-12), 28.15 (–, CH_2CH_3), 39.41, 42.78 (–, C-8, C-7), 58.72 (C_{quat}, C-11), 61.52 (–, 2 × OCH_2CH_3), 75.84 (–, C-5), 80.71 (+, C-3), 126.05 (C_{quat}, C-2), 130.65 (C_{quat}, C-6), 131.67 (C_{quat}, C-1), 132.93 (C_{quat}, C-9), 171.96 (C_{quat}, 2 × CO_2Et). – MS

(70 eV), *m/z* (%): 334 (9) [M+], 305 (100) [M+ – C_2H_5], 275 (11), 259 (8), 229 (23), 157 (10), 128 (8), 57 (5), 44 (7). – Anal. Calcd for $C_{19}H_{26}O_5$ (334.4): C 68.24, H 7.84; found: C 68.22, H 7.73.

Diethyl 3-Isopropyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (24c): According to GP 2b **15c**-All (300 mg, 0.70 mmol) was treated with palladium acetate (8 mg, 5 mol%), triphenylphosphane (18 mg, 10 mol%), and silver(I) carbonate (579 mg, 3 equiv.) in acetonitrile (15 mL) at 60 °C for 4 h. The reaction mixture was filtered through a plug of celite, silica gel (treated before with triethylamine and washed with PE), and charcoal prior to concentration. Chromatography of the residue on silica gel (60 g, column 2 × 20 cm, PE/Et_2O 4 : 1) gave **24c** (232 mg, 95%) as a colourless oil (R_f = 0.22). – IR (film): ν = 2962 cm^{-1}, 2871, 2830, 1722, 1628, 1465, 1445, 1383, 1366, 1251, 1180, 1097, 1069, 1035, 947, 932, 890, 861, 831, 806, 733, 632, 583, 521, 458, 418, 410. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.71 [d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.02 [d, ^3J = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.23 (t, ^3J = 7.2 Hz, 6 H, OCH$_2$CH_3), 1.81 [sept, ^3J = 6.9, ^3J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 2.27 (s, 4 H, 10-H, 12-H), 3.01 (m, 4 H, 7-H, 8-H), 4.18 (2 q, ^3J = 7.2 Hz, 4 H, OCH_2CH$_3$), 4.51 (d, 2 H, 5-H), 4.73 (m, 1 H, 3-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.96 (+, CH_2CH_3), 14.59 [+, CH(CH_3)$_2$], 19.91 [+, CH(CH_3)$_2$], 20.52 (–), 23.66 (–), 32.45 [+, CH(CH$_3$)$_2$], 39.56 (–, C-8), 42.76 (–, C-7), 58.75 (C_{quat}, C-11), 61.55 (–, CH_2CH$_3$), 76.49 (–, C-5), 89.51 (+, C-3), 126.13 (C_{quat}, C-2), 130.38 (C_{quat}, C-6), 131.86 (C_{quat}, C-1), 132.97 (C_{quat}, C-9), 172.00 (C_{quat}, CO_2Et).

Diethyl 3-Phenyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (24d): According to GP 2b **15d**-All (800 mg, 1.727 mmol) was treated with palladium acetate (39 mg, 10 mol%), triphenylphosphane (91 mg, 20 mol%), and silver(I) carbonate (0.95 g, 2 equiv.) in acetonitrile (60 mL) at 80 °C for 12 h. The reaction mixture was filtered through a plug of celite, silica gel, and charcoal prior to concentration. Chromatography of the residue on silica gel (50 g, column 3 × 25 cm, PE/Et_2O 8 : 1) gave **24d** (337 mg, 51%) as a colourless oil (R_f = 0.17, PE/Et_2O 3 : 1). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3), 2.31–2.38 (m, 5 H, 7-H, 10-H, 12-H), 2.78–2.95 (m, 3 H, 7-H, 8-H), 4.04 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.16 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.67 (d, ^2J = 13.0 Hz, 1 H, 5-H), 4.81 (dd, ^2J = 13.0, ^4J = 1.4 Hz, 1 H, 5-H), 5.70 (bs, 1 H, 3-H), 7.23–7.36 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.82, 13.93 (+, 2 × OCH$_2$CH_3), 20.66, 23.62 (–, C-10, C-12), 39.04, 42.76 (–, C-8, C-7), 58.60 (C_{quat}, C-11), 61.33, 61.52 (–, 2 × OCH_2CH$_3$), 76.36 (–, C-5), 87.28 (+, C-3), 126.22 (C_{quat}, C-2), 127.45, 128.15, 128.43 (+, C-Ph), 131.33 (C_{quat}, C-6), 131.87 (C_{quat}, C-1), 133.31 (C_{quat}, C-9), 141.35 (C_{quat}, C-Ph), 171.73, 172.01 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 382 (10) [M+], 309 (5), 277 (6), 254 (3), 205 (10), 179 (10), 105 (45), 74 (100), 44 (18). – Anal. Calcd for $C_{23}H_{26}O_5$ (382.5): C 72.23, H 6.85; found: C 70.68, H 6.97. – HRMS: calcd 382.1780 (correct HRMS).

Diethyl 3-*p*-Methoxyphenyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2(6),1(9)-diene-11,11-dicarboxylate (24e): According to GP 2b **15e**-All (185 mg, 0.408 mmol) was treated with palladium acetate (9 mg, 11 mol%), triphenylphosphane (21 mg, 21 mol%), and silver(I) carbonate (0.23 g, 2.2 equiv.) in acetonitrile (10 mL) at 110 °C for 7 h. The reaction mixture was filtered through a plug of celite, silica gel, and charcoal prior to concentration. Chromatography of the residue on silica gel (20 g, column 1.5 × 20 cm, PE/Et_2O 4 : 1) gave **24e** (38 mg, 25%) as a colourless oil (R_f = 0.15). – IR (film): ν = 2962 cm^{-1} (C–H), 1725, 1513, 1261, 899, 721, 651. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3), 1.21 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3), 2.20–2.59 (m, 5 H, 7-H, 10-H, 12-H), 2.71–3.04 (m, 3 H, 7-H, 8-H), 3.79 (s, 3 H, OCH_3), 4.07 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.17 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.64 (d, ^2J = 13.1 Hz, 1 H, 5-H), 4.80 (dd, ^2J = 13.1, ^4J = 1.8 Hz, 1 H, 5-H), 5.67 (bs, 1 H, 3-H), 6.89 (d, ^3J = 6.8 Hz, 2 H, *o*-Ar-H), 7.17 (d, ^3J = 6.8 Hz, 2 H, *m*-Ar-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.84, 13.96 (2 × OCH$_2$CH_3), 20.73, 23.69 (C-10, C-12), 39.10, 42.82 (C-8, C-7), 55.19 (OCH_3), 58.68 (C-11), 61.37, 61.54 (OCH_2CH$_3$), 76.06 (C-5), 86.81 (C-3), 113.87 (C-Ar), 126.38 (C-2), 128.76 (C-Ar), 131.32 (C-6), 131.88 (C-1), 133.27 (C-9), 133.54 (C-Ar), 159.53 (C-Ar), 171.81, 172.05 (2 × CO_2Et). – MS (70 eV), *m/z* (%): 412 (42) [M+], 336 (15), 263 (21), 235 (18), 203 (12), 135 (100), 57 (42), 41 (14). – $C_{24}H_{28}O_6$: calcd 412.1886 (correct HRMS).

Diethyl 3-Methyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2,5,1(9)-triene-11,11-dicarboxylate (25a): To a solution of **24a** (1.20 g, 3.75 mmol) in toluene (150 mL) was slowly (1 h) added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.28 g, 5.64 mmol), and the mixture was stirred for additional 30 min at room temperature. The yellow reaction mixture was diluted with Et_2O and washed with sodium hydroxide solution (50 mL, 1% NaOH in water). The aqueous layer was extracted with Et_2O (4 × 50 mL) and the combined organic phases were washed with brine (100 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (100 g, column 3.5 × 25 cm, PE/Et_2O 6 : 1) to give **25a** (656 mg, 55%, R_f = 0.24) and the benzoaromatic product **26a** (429 mg, 36%, R_f = 0.17) as colourless oils. – **25a**: IR (film): ν = 2977 cm^{-1} (C–H), 1731 (C=O), 1368, 1249, 1186, 1072, 833. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 6 H, 2 × OCH_2CH_3), 2.12 (bs, 2 H, 8-H), 2.32 (s, 3 H, CH_3), 2.62 (t, ^3J = 6.2 Hz, 2 H, 7-H), 3.09 (s, 2 H, 10-H*), 3.32 (s, 2 H, 12-H*), 4.22 (q, ^3J = 7.1 Hz, 4 H, 2 × OCH_2CH_3), 6.98 (s, 1 H, 5-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 12.86 (–, C-10*), 14.01 (+, 2 × OCH_2CH_3), 18.24 (–, C-12*), 24.31 (+, CH_3), 40.04, 43.33 (–, C-8, C-7), 58.51 (C_{quat}, C-11), 61.62 (–, 2 × OCH_2CH_3), 115.53 (C_{quat}, C-9), 120.71 (C_{quat}, C-1), 124.93 (C_{quat}, C-6), 132.94 (C_{quat}, C-2), 134.50 (+, C-5), 143.92 (C_{quat}, C-3), 172.17 (C_{quat}, 2 × CO_2Et). – Anal. Calcd for $C_{18}H_{22}O_5$ (318.4): C 67.91, H 6.97; found: C 67.81, H 7.11. – **26a**: IR (film): ν = 2977 cm^{-1} (C–H), 1731 (C=O), 1368, 1249, 1186, 1072. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.27 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3), 1.29 (d, ^3J = 6.6 Hz, 3 H, CH_3), 3.38–3.63 (m, 4 H, 10-H, 12-H), 4.26 (mc, 4 H, 2 × OCH_2CH_3), 4.98 (d, ^2J = 12.1 Hz, 1 H, 5-H), 5.11 (d, ^2J = 12.1 Hz, 1 H, 5-H), 5.34 (bs, 1 H, 3-H), 7.05 (d, ^3J = 7.6 Hz, 1 H, 7-H*), 7.10 (d, ^3J = 7.6 Hz, 1 H, 8-H*). – ^{13}C NMR (100.6 MHz, $CDCl_3$, plus DEPT): δ = 14.29 (+, 2 × OCH_2CH_3), 21.02, 38.60 (–, C-10, C-12), 40.24 (+, CH_3), 60.98 (C_{quat}, C-11), 62.10 (–, 2 × OCH_2CH_3), 72.61 (–, C-5), 79.76 (+, C-3), 115.59 (C_{quat}, C-9), 119.96 (C_{quat}, C-1), 123.58 (C_{quat}, C-6), 133.33 (C_{quat}, C-2), 138.45, 139.23 (+, C-7, C-8), 171.77 (C_{quat}, 2 × CO_2Et).

Diethyl 3-Ethyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2,5,1(9)-triene-11,11-dicarboxylate (25b): To a solution of **24b** (79 mg, 0.236 mmol) in toluene (30 mL) was slowly (1 h) added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (80 mg, 0.352 mmol), and the mixture was stirred for additional 30 min at room temperature. The yellow reaction mixture was diluted with Et_2O and washed with sodium hydroxide solution (30 mL, 1% NaOH in water). The aqueous layer was extracted with Et_2O (4 × 25 mL) and the combined organic phases were washed with brine (50 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (20 g, column 1.5 × 15 cm, PE/Et_2O 5 : 1) to give **25b** (50 mg, 64%) as a colourless oil (R_f = 0.39, PE/Et_2O 4 : 1). – IR (film): ν = 2990 cm^{-1} (C–H), 1733 (C=O), 1556, 1533, 1367, 1015, 762, 665. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22–1.29 (m, 9 H, 2 × OCH_2CH_3, CH_2CH_3), 2.26 (bs, 2 H, 8-H), 2.51–2.63 (m, 4 H, 7-H, CH_2CH_3), 3.06 (s, 2 H, 10-H*), 3.29 (s, 2 H, 12-H*), 4.21 (q, ^3J = 7.1 Hz, 4 H, 2 × OCH_2CH_3), 6.99 (s, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.56 (+, CH_2CH_3), 14.02 (+, 2 × OCH_2CH_3), 18.23, 20.80 (–, C-10, C-12), 24.32 (–, CH_2CH_3), 40.17, 43.32 (–, C-7, C-8), 58.58 (C_{quat}, C-11), 61.58 (–, 2 × OCH_2CH_3), 114.56 (C_{quat}, C-9), 120.52 (C_{quat}, C-1), 124.98 (C_{quat}, C-6), 133.03 (C_{quat}, C-2), 134.56 (+, C-5), 149.32 (C_{quat}, C-3), 172.15 (C_{quat}, 2 × CO_2Et). – MS (70 eV), *m/z* (%): 332 (52) [M$^+$], 258 (100), 185 (41), 171 (18), 105 (22), 77 (23), 41 (19). – $C_{19}H_{24}O_5$: calcd 332.1623 (correct HRMS).

Diethyl 3-Isopropyl-4-oxatricyclo[7.3.0^{2,6}.0^{1,9}]dodeca-2,5,1(9)-triene-11,11-dicarboxylate (25c): A solution of **24c** (100 mg, 0.29 mmol) in toluene (20 mL) was reacted with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (69 mg, 0.30 mmol) for 30 min at room temperature. The yellow reaction mixture was diluted with Et_2O and washed with sodium hydroxide solution (10 mL, 1% NaOH in water). The aqueous layer was extracted with Et_2O (3 × 20 mL) and the combined organic phases washed with brine (30 mL) and dried over magnesium sulfate. Removal of the solvents was followed by chromatography of the residue on silica gel (30 g, column 2 × 10 cm, PE/Et_2O 3 : 1) to give **25c** (84 mg, 84%) as a yellowish oil. – IR (film): ν = 2968 cm^{-1}, 2924, 2864, 1727 (C=O), 1682 (C=C–O), 1454, 1424, 1376, 1356, 1298, 1250 (=C–O–C), 1182,

1152, 1111, 1068, 1009, 909, 833. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.24 (2 d, ^3J = 7.0 Hz, 6 H, CH_3), 1.28 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 2.24 (m, 2 H, 8-H), 2.61 (dt, ^3J = 7.5, ^4J = 1.5 Hz, 2 H, 7-H), 3.06 (t, ^4J = 1.5 Hz, 2 H, 10-H), 3.11 [sept, ^3J = 7.0 Hz, 1 H, $CH(CH_3)_2$], 3.31 (mc, 2 H, 12-H), 4.22 (2 q, ^3J = 7.1 Hz, 4 H, CH_2CH_3), 7.00 (d, ^4J = 1.5 Hz, 1 H, 5-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.00 (+, CH_2CH_3), 18.18 (–), 21.79 [+, $CH(CH_3)_2$], 24.28 (–), 27.27 [+, $CH(CH_3)_2$], 40.29 (–), 43.26 (–), 58.52 (C_{quat}, C-11), 61.58 (–, CH_2CH_3), 113.43 (C_{quat}), 120.27 (C_{quat}), 124.94 (C_{quat}), 132.97 (C_{quat}), 134.34 (+, C-5), 152.54 (C_{quat}, C-3), 172.14 (C_{quat}, CO_2Et). – MS (70 eV), *m/z* (%): 346 (11) [M^+], 331 (3) [$M^+ - CH_3$], 304 (2), 272 (13), 257 (9), 238 (2), 230 (7), 199 (8), 185 (4), 165 (8), 143 (100), 129 (5), 97 (5), 91 (24), 83 (11), 69 (27), 55 (15), 41 (24). – Anal. Calcd for $C_{20}H_{26}O_5$ (346.4): C 69.34, H 7.56; found: C 69.25, H 7.66.

Diethyl (*E*)-2-Bromo-8-methoxy-12-phenyl-1,11-dodecadiene-6-yne-4,4-dicarboxylate (27): According to GP 1b diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (2.00 g, 6.3 mmol), 5-phenyl-4-pentenal[17] (1.01 g, 6.3 mmol), *n*-butyllithium (2.80 mL, 6.6 mmol, 2.36 M in *n*-hexane), and methyl iodide (3.0 mL) were reacted in THF and DMSO (30 mL each). After standard work-up, the crude material was chromatographed on silica gel (95 g, column 2.5 × 35 cm, PE/Et_2O 16 : 1 to 4 : 1) to yield **27** (1.91 g, 62%) as a colourless oil (R_f = 0.35 in PE/Et_2O 4 : 1). – IR (film): ν = 3075 cm^{-1} (C=CH), 3050 (C=CH), 3020 (C=CH), 2970, 2925, 2815, 2240 (C≡C), 1735 (C=O), 1623 (C=C), 1595 (C=C), 1440, 1425, 1365, 1285, 1210, 1185, 905, 855, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.82 (mc, 2 H, 9-H), 2.33 (mc, 2 H, 10-H), 3.00 (d, ^5J = 1.8 Hz, 2 H, 5-H), 3.30 (s, 2 H, 3-H), 3.36 (s, 3 H, OCH_3), 3.96 (tt, ^5J = 1.7, ^3J = 6.6 Hz, 1 H, 8-H), 4.20 (mc, 4 H, OCH_2CH_3), 5.61 (d, J = 1.5 Hz, 1 H, 1-H), 5.80 (d, J = 1.0 Hz, 1 H, 1-H), 6.18 (dt, ^3J = 6.8 and 15.8 Hz, 1 H, 11-H), 6.42 (d, ^3J = 15.9 Hz, 1 H, 12-H), 7.15–7.36 (m, 5 H, Ph-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 22.4 (–), 28.5 (–), 35.3 (–), 42.7 (–), 56.0 (+, OCH_3), 56.2 (C_{quat}, C-4), 61.8 (–, OCH_2CH_3), 70.4 (+, C-8), 80.6 (C_{quat}), 82.5 (C_{quat}), 122.4 (–, C-1), 125.8 (+), 126.4 (C_{quat}, C-2), 126.8 (+), 128.4 (+), 129.3 (+), 130.5 (+), 137.5 (C_{quat}, Ar-C), 168.9 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 492/490 (8/9) [M^+], 411 (5) [M^+ – Br], 337 (22), 305 (20), 295 (46), 235 (33), 207 (22), 129 (30), 117 (95), 91 (100), 77 (62), 51 (28). – $C_{25}H_{31}BrO_5$: calcd 490.1354 (correct HRMS). – $C_{25}H_{31}BrO_5$ (491.4): C 61.10, H 6.36, Br 16.26; found: C 60.97, H 6.31, Br 16.01.

(*E*)-5-Methoxy-1-phenylhept-1-ene-6-yne (31): Analogously to GP 1b trimethylsilylacetylene (3.27 g, 33.3 mmol), (*E*)-5-phenyl-4-pentenal[17] (5.34 g, 33.3 mmol), *n*-butyllithium (15.01 mL, 36.6 mmol, 2.44 N in *n*-hexane), and methyl iodide (5 mL) were reacted in THF (150 mL) and DMSO (150 mL). Work-up yielded (*E*)-5-methoxy-1-phenyl-7-trimethylsilylhept-1-ene-6-yne (**30**) (9.03 g, 100%) as a slightly yellow oil, that was used without further purification. – IR (film): ν = 3082 cm^{-1} (=CH), 3069, 3026, 2956 (CH), 2938, 2902, 2168 (C≡C), 1652 (C=C), 1598, 1494, 1448, 1410, 1334, 1250, 1160, 1108, 1072, 966, 846, 760, 694. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.24 (s, 9 H, CH_3Si), 1.85–1.96 (m, 2 H, 4-H), 2.42 (q, ^3J = 7 Hz, 2 H, 3-H), 3.45 (s, 3 H, OCH_3), 4.03 (t, ^3J = 7 Hz, 1 H, 5-H), 6.26 (dt, ^3J = 16, ^3J = 6 Hz, 1 H, 2-H), 6.45 (d, ^3J = 16 Hz, 1 H, 1-H), 7.20–7.39 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 0.06 ($SiCH_3$), 28.67 (C-4), 35.05 (C-3), 56.33 (OCH_3), 70.89 (C-5), 90.88 (C-6*), 104.31 (C-7*), 125.95 (C-Ph), 126.92, 128.45 (C-Ph), 129.59, 130.58, 137.67 (C-Ph). – A solution of **30** (9.00 g, 33.1 mmol) in methanol (100 mL) was treated with sodium hydroxide solution (1 mL, 10% in water) and stirred for 15 h at room temperature, after which the reaction mixture was poured into water (100 mL) and extracted with Et_2O (3 × 40 mL). The combined organic layers were washed with brine (20 mL) and dried over magnesium sulfate. Removal of the solvents under vacuum and chromatography of the residue on silica gel (160 g, column 5 × 50 cm, PE/Et_2O 15 : 1) afforded **31** (5.28 g, 80%) as a colourless oil (R_f = 0.67 in PE/Et_2O 5 : 1). – IR (film): ν = 3294 cm^{-1} (≡CH), 3082 (=CH), 3058, 3026, 2988 (CH), 2934, 2824, 1598, 1494, 1448, 1336, 1196, 1162, 1108, 1072, 966, 742, 694, 638. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (mc, 2 H, 4-H), 2.41 (q, ^3J = 7 Hz, 2 H, 3-H), 2.48 (d, ^4J = 2 Hz, 1 H, 7-H), 3.45 (s, 3 H, OCH_3), 4.01 (dt, ^3J = 7, ^4J = 2 Hz, 1 H, 5-H), 6.23 (dt, ^3J = 16, ^3J = 6 Hz, 1 H, 2-H), 6.45 (d, ^3J = 16 Hz, 1 H, 1-H), 7.19–7.40 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT):

δ = 28.53 (–, C-4), 35.06 (–, C-3), 56.43 (+, OCH_3), 70.30 (+, OCH), 74.02 (C_{quat}, C-6), 82.45 (+, C-7), 125.95 (+, C-Ph), 126.95 (+), 128.46 (+, C-Ph), 129.38 (+), 130.68 (+), 137.60 (C_{quat}, C-Ph). – MS (EI, 70 eV), *m/z* (%): 200 (2) [M^+], 167 (100), 142 (64), 129 (40), 117 (35), 115 (56), 91 (42), 69 (20), 51 (7). – $C_{14}H_{16}O$: calcd 200.1201 (correct HRMS).

(*E*)-8-Bromo-5-methoxy-1-phenyloct-1-ene-6-yne (33): To a solution of (*E*)-5-methoxy-1-phenylhept-1-ene-6-yne (**31**) (5.27 g, 26.3 mmol) in THF (120 mL) was added *n*-butyllithium (11.9 mL, 29.0 mmol, 2.44 N in *n*-hexane) dropwise at –78 °C. After completion the red reaction mixture was stirred for further 15 min and paraformaldehyde (1.58 g, 52.6 mmol, 2 equiv.) added in one portion. The heterogeneous mixture was allowed to come to room temperature and stirring was continued for 10 h, during which it became yellow and homogeneous. The reaction mixture was poured into water (50 mL) and extracted with Et_2O (4 × 30 mL). Washing of the combined organic extracts with brine (30 mL) and drying over magnesium sulfate was followed by concentration under vacuum. The crude product was purified on silica gel (70 g, column 4 × 25 cm, PE/Et_2O 2 : 1) to give (*E*)-4-methoxy-8-phenyloct-7-ene-2-yne-1-ol (**32**) (5.23 g, 86%) as a colourless oil (R_f = 0.58 in PE/Et_2O 1 : 3). – IR (film): ν = 3384 cm^{-1} (OH), 3030 (arom. CH), 2982 (CH), 2936, 2862, 1856, 1494, 1448, 1338, 1128, 1102, 1054, 1022, 966, 746, 694, 616. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.92 (mc, 2 H, 5-H), 2.10 (bs, 1 H, OH), 2.38 (q, ^3J = 7 Hz, 2 H, 6-H), 3.42 (s, 3 H, OCH_3), 4.04 (m, 1 H, 4-H), 4.33 (bs, 2 H, 1-H), 6.21 (dt, ^3J = 16, ^3J = 6 Hz, 1 H, 7-H), 6.44 (d, ^3J = 16 Hz, 1 H, 8-H), 7.19–7.37 (m, 5 H, Ph-H). – ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 25.54 (C-5), 28.59 (C-6), 50.96 (C-1), 56.43 (OCH_3), 70.50 (OCH), 84.20 (C-2*), 84.43 (C-3*), 125.91 (C-Ph), 126.94, 128.45 (C-Ph), 129.34, 130.62, 137.59 (C-Ph). – MS (EI, 70 eV), *m/z* (%): 199 (9) [$M^+ - OCH_3$], 182 (14), 179 (20), 167 (47), 154 (100), 141 (27), 129 (25), 117 (37), 115 (50), 91 (60), 77 (12), 71 (17), 41 (18). – $C_{15}H_{18}O_2$: calcd. 230.1307 (correct HRMS). – To a solution of **32** (4.73 g, 20.5 mmol) and carbon tetrabromide (10.2 g, 30.8 mmol, 1.5 equiv.) in acetonitrile (200 mL) triphenylphosphane (8.08 g, 30.8 mmol, 1.5 equiv.) was added portionwise at 0 °C and the reaction mixture stirred for 5 h. The solvent was partially removed under vacuum and the remaining residue (about 50 mL) filtered. The filtrate was further concentrated under vacuum and the crude product chromatographed on silica gel (60 g, column 4 × 20 cm, PE/Et_2O 10 : 1) to afford **33** (5.54 g, 92%) as a slightly yellowish oil (R_f = 0.76 in PE/Et_2O 5 : 1), that must be stored at –30 °C to preserve it from decomposition. – ^1H-NMR (250 MHz, $CDCl_3$): δ = 1.78–2.00 (m, 2 H, 4-H), 2.38 (q, ^3J = 7 Hz, 2 H, 3-H), 3.42 (s, 3 H, OCH_3), 3.97 (d, ^5J = 2 Hz, 2 H, 8-H), 4.06 (mc, 1 H, 5-H), 6.20 (dt, ^3J = 16, ^3J = 6 Hz, 1 H, 2-H), 6.43 (d, ^3J = 16 Hz, 1 H, 1-H), 7.17–7.38 (m, 5 H, Ph-H). – ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 14.27 (C-8), 28.56 (C-4), 34.89 (C-3), 56.61 (OCH_3), 70.51 (C-5), 81.23 (C-6*), 85.67 (C-7*), 125.95 (C-Ph), 126.98, 128.47 (C-Ph), 129.31, 130.73, 137.54 (C-Ph). – MS (EI, 70 eV), *m/z* (%): 261/259 (1/1), 236/234 (7/7), 181 (100), 155 (76), 121 (44), 117/115 (62/58), 91 (95), 77 (29), 71 (34), 65 (28).

Ethyl (*E*)-4-Bromo-2-ethoxycarbonyl-5-phenyl-4-pentenecarboxylate (*E*-**36**): To a solution of phenylpropadiene[19d] (6.5 g, 56 mmol) in dichloromethane (200 mL) was added slowly at room temperature a solution of bromine (8.9 g, 56 mmol) in dichloromethane (100 mL). The solvent was immediately removed under vacuum and below 30 °C to give the crude (*E*/*Z*)-mixture of products, which was chromatographed on silica gel (200 g, column 6 × 50 cm, PE/Et_2O 20 : 1) to yield pure (*E*)-1,2-dibromo-3-phenyl-2-propene (*E*-**35**) (3.5 g, 23%, R_f = 0.70 in PE/Et_2O 2 : 1), accompanied by the (*Z*)-isomer (*Z*-**35**) (4.8 g, 32%, R_f = 0.66 in PE/Et_2O 2 : 1) and a fraction of both isomers (3.2 g, 21%), which was not further separated. *E*-**35**: ^1H NMR (250 MHz, $CDCl_3$): δ = 4.38 (s, 2 H, 1-H), 7.08 (s, 1 H, 3-H), 7.28–7.40 (m, 5 H, Ph-H). – ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 35.16 (C-1), 121.52, 127.89 (C-Ph), 128.63, 130.54 (C-Ph), 135.14 (C-Ph), 136.67 (C-3). The (*E*)-isomer was very prone to partial isomerisation into the (*Z*)-isomer and therefore used immediately after preparation. – According to GP 3 a suspension of sodium hydride (609 mg, 15.2 mmol, 1.2 equiv., 60% in mineral oil) in DME (50 mL) was treated with diethyl malonate (2.03 g, 12.7 mmol, 1 equiv.) dropwise at room temperature. After the formation of gas had finished, *E*-**35** (3.5 g, 12.7 mmol) was added and stirring continued for 5 h. Standard work-up and purification by chromatography on silica gel (100 g, column 5 × 30 cm, PE/Et_2O 25 : 1) afforded *E*-**36** (2.41 g, 53%) as a slightly yellow oil (R_f = 0.61 in

PE/Et_2O 2 : 1). – IR (film): ν = 3030 cm^{-1} (=CH), 2980 (CH), 1730 (C=O), 1628 (C=C), 1446, 1370, 1240, 1183, 1160, 1100, 1040, 926, 865, 760, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19 (t, ^3J = 7 Hz, 6 H, CH_3), 3.27 (d, ^3J = 8 Hz, 2 H, 3-H), 3.91 (t, ^3J = 8 Hz, 1 H, 2-H), 4.03–4.23 (m, 4 H, OCH_2), 7.08 (s, 1 H, 5-H), 7.19–7.38 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.88 (CH_3), 34.71 (C-3), 50.99 (C-2), 61.59 (OCH_2), 124.94 (C-4), 127.55 (C-Ph), 128.15 (C-Ph), 128.51 (C-Ph), 135.21, 135.68, 168.13 (C=O). – MS (EI, 70 eV), *m/z* (%): 356/354 (0.1/0.1) [M^+], 311/309 (3/3), 275 (100) [M^+ – Br], 247 (14), 201 (58), 173 (27), 128 (33), 115 (50), 91 (21), 69 (22), 43 (32). – Anal. Calcd for $C_{16}H_{19}BrO_4$ (355.2): C 54.10, H 5.39; found: C 54.06, H 5.24.

2-Bromo-4,4-bis(ethoxycarbonyl)-8-methoxy-1,12-diphenyldodeca-1(*E*),11(*E*)-diene-6-yne (*E,E*-**37**): According to GP 3 *E*-**36** (1.09 g, 3.07 mmol), (*E*)-8-bromo-5-methoxy-1-phenyl-oct-1-ene-6-yne (**33**) (897 mg, 3.06 mmol), and sodium hydride (134 mg, 3.36 mmol, 1.1 equiv., 60% in mineral oil) were reacted in DME (40 mL). The crude product was chromatographed on silica gel (35 g, column 2 × 25 cm, PE/Et_2O 20 : 1) to yield *E,E*-**37** (777 mg, 45%) as a colourless oil (R_f = 0.59 in PE/Et_2O 2 : 1). – IR (film): ν = 3078 cm^{-1} (=CH), 2952 (CH), 2842, 1728 (C=O), 1438, 1376, 1242, 1228, 1182, 1092, 1066, 960, 788, 750, 700, 636. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7 Hz, 6 H, CH_3), 1.42–1.67 (m, 2 H, 9-H), 2.18 (q, ^3J = 7 Hz, 2 H, 10-H), 2.99 (s, 2 H, 5-H), 3.15 (s, 3 H, OCH_3), 3.44 (m, 1 H, 8-H), 3.68 (s, 2 H, 3-H), 4.00–4.24 (mc, 4 H, OCH_2), 6.13 (dt, ^3J = 16, ^3J = 7 Hz, 1 H, 11-H), 6.38 (d, ^3J = 16 Hz, 1 H, 12-H), 7.16 (s, 1 H, 1-H), 7.18–7.34 (m, 10 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.69 (+, CH_3), 22.44 (–, C-5), 28.37 (–, C-9), 34.94 (–, C-10), 36.62 (–, C-3), 55.90 (+, OCH_3), 57.01 (C_{quat}, C-4), 61.72 (–, OCH_2), 69.86 (+, C-8), 80.40 (C_{quat}, C-6*), 81.79 (C_{quat}, C-7*), 122.38 (C_{quat}, C-2), 125.75 (+, C-Ph), 126.75 (+), 127.38 (+), 128.32 (+, C-Ph), 128.38 (+, 2 C-Ph), 129.51 (+), 130.28 (+), 135.77 (C_{quat}, C-Ph), 137.36 (+, C-Ph), 137.53 (C_{quat}, C-Ph), 169.07 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 568/566 (7/7) [M^+], 488 (7), 455 (3), 413 (16), 371 (35), 307 (8), 265 (8), 209 (14), 199 (35), 165 (41), 117 (58), 115 (100), 91 (62), 77 (30). – $C_{31}H_{35}BrO_5$: calcd 566.1668; found: 566.1667 (HRMS).

Diethyl *trans*-3-Methoxy-7-phenyltricyclo[7.3.0.0^{2,6}]dodeca-1(9),2(6)-diene-11,11-dicarboxylate (**28**): According to GP 2b, to a solution of **27** (500 mg, 1.02 mmol) in acetonitrile (10 mL) were added palladium acetate (24 mg, 10 mol%), triphenylphosphane (53 mg, 20 mol%), and potassium carbonate (422 mg, 3 equiv.). The mixture was heated for 3 d at 60 °C. Standard work-up and chromatography on silica gel (10 g, column 1 × 15 cm, PE/Et_2O 8 : 1) gave **28** (347 mg, 83%, R_f = 0.24 in PE/Et_2O 4 : 1) as a colourless oil. – IR (film): ν = 3080 cm^{-1} (C=CH), 3050 (C=CH), 2930, 2245 (C≡C), 1735 (C=O), 1600 (C=C), 1550, 1440, 1365, 1240, 1180, 1155, 910, 860, 770, 730, 705, 650. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.78–1.89 (m, 1 H), 2.03–2.16 (m, 2 H), 2.28–2.41 (m, 2 H), 2.68–2.79 (m, 1 H, 8-H), 2.87 (d, ^2J = 17.6 Hz, 1 H, 12-H), 3.13 (d, ^2J = 17.7 Hz, 1 H, 12-H), 3.16–3.26 (m, 3 H, 10- and 7-H), 3.31 (s, 3 H, OCH_3), 3.66 (t, ^3J = 9.1 Hz, 1 H, 3-H), 4.18 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 4.19 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 7.12–7.40 (m, 5 H, Ph-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.0 (CH_2CH_3), 28.8, 31.9, 33.2, 39.4, 42.3, 43.0, 55.3, 58.9, 61.4, 85.1, 126.3, 127.5, 128.4, 128.6, 131.2, 132.6, 142.6, 144.6, 171.9 (C=O), 172.3 (C=O). – MS (70 eV), *m/z* (%): 410 (2) [M^+], 378 (8), 305 (20), 304 (14), 231 (18), 160 (15), 127 (40), 117 (60), 115 (70), 104 (100), 91 (86), 84 (88), 55 (31). – $C_{25}H_{30}O_5$: calcd 410.2093 (correct HRMS).

4,4-Bis(ethoxycarbonyl)-7,8-diphenyltricyclo[7.3.0^{1,9}.0^{2,6}]dodeca-1,6,8-triene (**39**) **and 4,4-Bis(ethoxycarbonyl)-12-methoxy-7,8-diphenyltricyclo[7.3.0^{1,9}.0^{2,6}]dodeca-1(9),2(6)-diene** (**38**): According to GP 2b 2-bromo-4,4-bis(ethoxycarbonyl)-8-methoxy-1,12-diphenyldodeca-1(*E*),11(*E*)-diene-6-yne (*E,E*-**37**) (650 mg, 1.15 mmol), palladium acetate (26 mg, 10 mol%), triphenylphosphane (60 mg, 20 mol%), and potassium carbonate (320 mg, 2.32 mmol, 2 equiv.) were reacted in acetonitrile (20 mL) for 7 d at 80 °C. Chromatography of the filtered and concentrated reaction mixture on silica gel (20 g, column 1 × 30 cm, PE/Et_2O 10 : 1) gave **39** (200 mg, 38 %, R_f = 0.52 in PE/Et_2O 2 : 1) and **38** (151 mg, 27%, R_f = 0.23 in PE/Et_2O 2 : 1) as colourless oils. **39**: IR (film): ν = 3056 cm^{-1} (=CH), 2978 (CH), 2960, 2938, 2906, 1732

(C=O), 1602 (C=C), 1444, 1366, 1296, 1264, 1240, 1188, 1158, 1098, 1070, 1030, 1014, 912, 862, 734, 706. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7 Hz, 6 H, CH_3), 2.06 (quint, ^3J = 7 Hz, 2 H, 11-H), 2.73 (t, ^3J = 7 Hz, 2 H, 10-H*), 2.93 (t, ^3J = 7 Hz, 2 H, 12-H*), 3.43 (s, 2 H, 3-H**), 3.63 (s, 2 H, 5-H**), 4.19 (q, ^3J = 7 Hz, 4 H, OCH_2), 6.98–7.24 (m, 10 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.99 (+, CH_3), 25.28 (–, CH_2), 31.51 (–, CH_2), 32.92 (–, CH_2), 39.48 (–, CH_2), 40.55 (–, CH_2), 60.19 (C_{quat}, C-4), 61.61 (–, OCH_2), 125.91 (+, C-Ph), 126.03 (+, C-Ph), 127.39 (+, C-Ph), 127.59 (+, C-Ph), 130.02 (+, 2 C-Ph), 134.68 (C_{quat}), 135.36 (C_{quat}), 136.28 (C_{quat}), 137.28 (C_{quat}), 138.72 (C_{quat}), 139.86 (C_{quat}), 140.20 (C_{quat}), 142.55 (C_{quat}), 171.79 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 452 (13), 381 (68) [$M^+ - CO_2Et$], 354 (10), 335 (15), 307 (62), 279 (33), 215 (16), 202 (11), 129 (17), 102 (18), 91 (35), 84 (100), 57 (36), 55 (27), 51 (26), 47 (49), 43 (56), 41 (40). – $C_{30}H_{30}O_4$: calcd 454.2144 (correct HRMS). – Anal. Calcd for $C_{30}H_{30}O_4$ (454.6): C 79.27, H 6.65; found: C 79.20, H 6.71. – **38**: IR (film): ν = 3084 cm^{-1} (=CH), 3062, 3028, 2980 (CH), 2936, 2902, 2848, 1740 (C=O), 1730, 1660 (C=C), 1602, 1492, 1452, 1392, 1366, 1298, 1252, 1184, 1158, 1076, 1052, 1032, 1012, 942, 914, 778, 734, 704. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7 Hz, 3 H, CH_3), 1.23 (t, ^3J = 7 Hz, 3 H, CH_3), 1.85–1.95 (m, 1 H, CH_2), 2.05–2.19 (m, 2 H, CH_2), 2.22–2.41 (m, 1 H, CH_2), 2.85 (s, 2 H, 3-H), 3.36 (bs, 5 H, OCH_3, 5-H), 3.86 (d, ^3J = 9.8 Hz, 1 H, 7-H*), 4.00 (d, ^3J = 9.7 Hz, 1 H, 8-H*), 4.17 (q, ^3J = 7 Hz, 2 H, OCH_2), 4.18 (q, ^3J = 7 Hz, 2 H, OCH_2), 4.73 (mc, 1 H, 12-H), 6.58–6.67 (m, 4 H, Ph-H), 7.01–7.24 (m, 6 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.92 (+, 2 C, CH_3), 29.11 (–, CH_2), 32.10 (–, CH_2), 39.58 (–, CH_2), 41.72 (–, CH_2), 49.30 (+, C-7*), 49.81 (+, C-8*), 55.51 (+, OCH_3), 59.07 (C_{quat}, C-4), 61.40 (–, 2 C, OCH_2), 85.14 (+, C-12), 126.16 (+, C-Ph), 126.30 (+, C-Ph), 127.40 (+, 2 C-Ph), 129.51 (C_{quat}, C-Ph), 129.60 (+, C-Ph), 130.80 (+, C-Ph), 133.30 (C_{quat}), 134.41 (C_{quat}), 138.16 (C_{quat}), 138.55 (C_{quat}), 143.72 (C_{quat}), 171.78 (C_{quat}, C=O), 172.24 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 486 (2) [M^+], 455 (13) [$M^+ - OCH_3$], 382 (16), 307 (13), 84 (100), 47 (34). – $C_{31}H_{34}O_5$: calcd 486.2406 (correct HRMS).

Diethyl 2-(2-Bromocyclohex-2-enyl)malonate (41): According to GP 3 diethyl malonate (4.40 g, 27.5 mmol), 2,3-dibromocyclohexene (**40**) (6.0 g, 25 mmol), and sodium hydride (1.0 g, 25 mmol, 60% in mineral oil) were reacted in DME (50 mL) for 36 h. The crude product was purified on silica gel (250 g, column 6 × 40 cm, PE/Et_2O 15 : 1) to afford **41** (5.38 g, 67%) as a colourless oil (R_f = 0.63 in PE/Et_2O 2 : 1). – IR (Film): ν = 2980 cm^{-1} (CH), 2935, 1730 (C=O), 1642 (C=C), 1450, 1370, 1330, 1250, 1220, 1180, 1145, 1105, 1035, 980, 940, 895, 888, 875, 810, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19–1.26 (m, 6 H, CH_3), 1.42–1.72 (m, 2 H, 5'-H), 1.79–2.07 (m, 4 H, 4'-H, 6'-H), 3.02–3.11 (m, 1 H, 1'-H), 3.95 (d, ^3J = 5 Hz, 1 H, 2-H), 4.06–4.20 (m, 4 H, OCH_2), 6.12–6.17 (m, 1 H, 3'-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.92 (+, CH_3), 20.08 (–, CH_2), 26.41 (–, CH_2), 27.39 (–, CH_2), 42.19 (+, C-1'), 54.09 (+, C-2), 60.98 (–, OCH_2), 61.40 (–, OCH_2), 123.67 (C_{quat}, C-2'), 132.72 (+, C-3'), 167.69 (C_{quat}, C=O), 168.51 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 320/318 (0.5/0.4) [M^+], 275/273 (8/8) [$M^+ - OC_2H_5$], 266/244 (7/7), 240 (22), 239 (100) [M^+ – Br], 211 (12), 193 (8), 165 (68), 162/160 (30/30), 137 (38), 115 (40), 91 (18), 79 (28), 55 (10), 43 (6). – $C_{13}H_{19}BrO_4$: calcd 318.0467; found: 318.0466 (HRMS).

Ethyl (*E*)-2-(2-Bromocyclohex-2-enyl)-2-ethoxycarbonyl-6-methoxy-10-phenyldec-9-ene-4-yne-carboxylate (42): According to GP 3 **41** (858 mg, 2.69 mmol) was treated with sodium hydride (118 mg, 2.96 mmol, 1.1 equiv., 60%) in DME (30 mL) for 5 h, after which (*E*)-8-bromo-5-methoxy-1-phenyloct-1-ene-6-yne (**33**) (788 mg, 2.69 mmol, 1 equiv.) was added in one portion. Stirring was continued for 12 h. Standard work-up and chromatography on silica gel (15 g, column 1 × 25 cm, PE/Et_2O 10 : 1) yielded **42** (624 mg, 44%) as a colourless oil (R_f = 0.45 in PE/Et_2O 2 : 1). – IR (Film): ν = 3030 cm^{-1} (=CH), 2980 (CH), 2940, 1730 (C=O), 1450, 1371, 1340, 1306, 1270, 1235, 1200, 1108, 1045, 970, 750, 700. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7 Hz, 6 H, CH_3), 1.58 (mc, 1 H, CH_2), 1.69–1.88 (m, 3 H, CH_2), 1.92–2.05 (m, 4 H, CH_2), 2.36 (q, ^3J = 7 Hz, 2 H, 8-H), 2.94 (d, ^2J = 17 Hz, 1 H, 3-H), 3.10 (d, ^2J = 17 Hz, 1 H, 3-H), 3.38 (s, 3 H, OCH_3), 3.63 (mc, 1 H, 1'-H), 3.97 (mc, 1 H, 6-H), 4.22 (q, ^3J = 7 Hz, 4 H, OCH_2), 6.20 (dt, ^3J = 16, ^3J = 7 Hz, 1 H, 9-H), 6.26 (m, 1 H, 3'-H), 6.41 (d, ^3J = 16 Hz, 1 H, 10-H), 7.13–7.38 (m, 5 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 13.78 (+, CH_3), 13.86 (+, CH_3), 20.44 (–, CH_2), 23.88 (–, CH_2), 27.26

(–, CH_2), 27.52 (–, CH_2), 28.62 (–, CH_2), 35.26 (–, CH_2), 45.46 (+, C-1'), 56.19 (+, C-6), 60.18 (C_{quat}, C-2), 61.66 (–, 2 C, OCH_2), 70.59 (+, OCH_3), 81.16 (C_{quat}, C-4*), 82.57 (C_{quat}, C-5*), 122.33 (C_{quat}, C-2'), 125.86 (+, C-Ph), 126.83 (+), 128.39 (+, C-Ph), 129.59 (+), 130.43 (+), 134.67 (+), 137.59 (C_{quat}, C-Ph), 169.27 (C_{quat}, C=O), 169.46 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 532/530 (13/12) [M^+], 451 (11) [M^+ – Br], 377 (21), 335 (72), 275 (41), 247 (36), 209 (30), 163 (30), 129 (37), 117 (100), 91 (78), 79 (63), 51 (17). – $C_{28}H_{35}BrO_5$: calcd 530.1668 (correct HRMS).

13,13-Bis(ethoxycarbonyl)-3-methoxy-7-phenyltetracyclo[6.6.1.$0^{2,6}$.$0^{12,15}$]pentadeca-1(15),2(6)-diene (43): According to GP 2b **42** (418 mg, 0.786 mmol) was treated with palladium acetate (18 mg, 10 mol%), triphenylphosphane (41 mg, 20 mol%), and potassium carbonate (217 mg, 1.57 mmol, 2 equiv.) in acetonitrile (15 mL) at 80 °C for 3 d. The crude product mixture was chromatographed on silica gel (20 g, column 1 × 35 cm, PE/Et_2O 20 : 1) to give 69 mg of a not securely identified compound [R_f = 0.41 in PE/Et_2O 2 : 1, ^1H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7 Hz, 3 H, CH_3), 1.32 (t, ^3J = 7 Hz, 3 H, CH_3), 1.61–1.81 (m, 2 H), 1.96–2.06 (m, 2 H), 2.07–2.34 (m, 2 H), 2.36–2.52 (m, 2 H), 2.71–2.83 (m, 1 H), 3.29 (d, ^2J = 17 Hz, 1 H), 3.39 (s, 3 H, OCH_3), 3.41–3.49 (m, 1 H), 3.63 (d, ^2J = 17 Hz, 1 H), 3.78–3.84 (m, 1 H), 4.06–4.20 (m, 4 H, OCH_2), 4.94 (dd, ^3J = 6, ^3J = 4 Hz, 1 H, OCH), 7.17–7.41 (m, 5 H, Ph-H), probably the aromatic compound **44**] and **43** (108 mg, 30%) as a colourless oil (R_f = 0.30 in PE/Et_2O 2 : 1). – IR (film): ν = 3024 cm^{-1}, 2978 (CH), 2938, 2904, 1730 (C=O), 1600 (C=C), 1492, 1452, 1388, 1366, 1298, 1252, 1182, 1092, 1036, 914, 732, 704, 646. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7 Hz, 3 H, CH_3), 1.27 (t, ^3J = 7 Hz, 3 H, CH_3), 1.33–1.41 (m, 2 H), 1.65–1.74 (m, 3 H), 1.88–1.94 (m, 3 H), 2.04–2.11 (m, 2 H), 2.43–2.52 (m, 1 H), 2.79–2.88 (m, 1 H), 3.05 (m, 1 H), 3.35–3.45 (m, 2 H), 3.37 (s, 3 H, OCH_3), 4.18 (m, 4 H, OCH_2), 4.64 (bs, 1 H, 3-H), 6.95–6.99 (m, 2 H, Ph-H), 7.18–7.22 (m, 3 H, Ph-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, plus DEPT): δ = 14.00 (+, CH_3), 14.10 (+, CH_3), 20.44 (–, CH_2), 21.47 (–, CH_2), 23.12 (–, CH_2), 29.35 (–, CH_2), 31.69 (–, CH_2), 37.08 (+, CH), 39.75 (–, CH_2), 45.85 (+, CH), 46.84 (+, CH), 54.55 (+, C-3), 60.77 (–, OCH_2), 61.10 (–, OCH_2), 64.36 (C_{quat}, C-13), 84.11 (+, OCH_3), 125.66 (C_{quat}), 126.58 (+, C-Ph), 128.07 (+, C-Ph), 128.44 (+, C-Ph), 132.93 (C_{quat}), 137.69 (C_{quat}), 138.45 (C_{quat}), 145.32 (C_{quat}), 170.40 (C_{quat}, C=O), 172.04 (C_{quat}, C=O). – MS (EI, 70 eV), *m/z* (%): 450 (1) [M^+], 377 (11), 275 (32), 247 (26), 129 (29), 117 (54), 79 (43), 51 (100). – $C_{28}H_{34}O_5$: calcd 450.2406 (correct HRMS).

Diethyl 2-Bromo-8-methoxy-12-methyltrideca-1,11-diene-6-yne-4,4-dicarboxylate (46): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (2.00 g, 6.31 mmol) was treated with *n*-butyllithium (2.80 mL, 6.61 mmol, 2.36 M in *n*-hexane), and 5-methyl-4-hexenal[24] (708 mg, 6.31 mmol) in THF (30 mL). Purification of the crude product on silica gel (50 g, column 2.5 × 20 cm, PE/Et_2O 4 : 1) afforded diethyl 2-bromo-8-hydroxy-12-methyltridec-1,11-diene-6-yne-4,4-dicarboxylate (**45**) (2.18 g, 81%) as a colourless oil (R_f = 0.31 in PE/Et_2O 1 : 1). – IR (Film): ν = 3400 cm^{-1} (OH), 2920, 1740 (C=O), 1640 (C=C), 1425, 1365, 1270, 1065, 900, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.61 (bs, 3 H, 12-CH_3), 1.67 (bs, 3 H, 12-CH_3), 1.67 (m, 2 H, 9-H), 1.94 (d, ^3J = 5.7 Hz, 1 H, OH), 2.09 (m, 2 H, 10-H), 2.94 (d, ^5J = 1.9 Hz, 2 H, 5-H), 3.16 (s, 2 H, 3-H), 4.20 (m, 4 H, OCH_2CH_3), 4.29 (m, 1 H, 8-H), 5.09 (qt, ^4J = 1.3, ^3J = 7.2 Hz, 1 H, 11-H), 5.60 (d, *J* = 1.5 Hz, 1 H, 1-H), 5.79 (bs, 1 H, 1-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 17.7 (+, CH_3), 22.4 (–), 23.7 (–), 25.7 (+, CH_3), 37.9 (–), 42.7 (–), 56.1 (C_{quat}, C-4), 61.9 (–, OCH_2CH_3), 62.1 (+, C-8), 79.6 (C_{quat}), 85.2 (C_{quat}), 122.5 (–, C-1), 123.2 (+, C-11), 126.4 (C_{quat}, C-2), 132.6 (C_{quat}, C-12), 169.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 237 (31), 220 (15), 205 (51), 143 (23), 111 (27), 95 (37), 81 (43), 69 (79), 55 (100), 41 (84). – To a solution of **45** (1.88 g, 4.4 mmol) in THF (20 mL) *n*-butyllithium (1.95 mL, 4.6 mmol, 2.36 M in *n*-hexane) was added at –78 °C and the reaction mixture slowly warmed to 0 °C. DMSO (20 mL) and methyl iodide (1 mL) were added dropwise and stirring was continued at 10 °C for 3 h. The reaction mixture was poured into water (50 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with water (3 × 50 mL) and brine (50 mL), dried over magnesium sulfate and concentrated in a rotary evaporator under vacuum. The residue was chromatographed on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 16 : 1) to afford **46** (1.78 g, 92%) as a colourless oil (R_f = 0.47 in PE/Et_2O 4 : 1). – IR (film): ν = 2960 cm^{-1}, 2920, 1740 (C=O), 1650

(C=C), 1445, 1430, 1370, 1290, 1215, 1190, 1100, 1070, 1045, 1015, 900, 860. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.57 (bs, 3 H, 12-CH_3), 1.60 (m, 2 H, 9-H), 1.65 (bs, 3 H, 12-CH_3), 2.04 (m, 2 H, 10-H), 2.94 (d, ^5J = 1.8 Hz, 2 H, 5-H), 3.25 (s, 2 H, 3-H), 3.31 (s, 3 H, OCH_3), 3.83 (tt, ^5J = 1.9, ^3J = 6.6 Hz, 1 H, 8-H), 4.18 (m, 4 H, OCH_2CH_3), 5.05 (t, ^3J = 7.3 Hz, 1 H, 11-H), 5.57 (bs, 1 H, 1-H), 5.76 (bs, 1 H, 1-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 17.5 (+, CH_3), 22.4 (–), 23.7 (–), 25.6 (+, CH_3), 35.8 (–), 42.7 (–, C-3), 56.1 (C_{quat}, C-4), 56.1 (+, OCH_3), 61.8 (–, OCH_2CH_3), 70.5 (+, C-8), 80.3 (C_{quat}), 82.8 (C_{quat}), 122.4 (–, C-1), 123.1 (+, C-11), 126.5 (C_{quat}, C-2), 132.3 (C_{quat}, C-12), 169.0 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 444/442 [M$^+$], 427 (3), 402 (11), 361 (60), 329 (51), 287 (84), 255 (57), 227 (36), 207 (72), 178 (62), 134 (56), 91 (59), 55 (100). – $C_{21}H_{31}BrO_5$: calcd 442.1354 (correct HRMS). – Anal. Calcd for $C_{21}H_{31}BrO_5$ (443.4): C 56.89, H 7.05, Br 18.02; found: C 56.92, H 6.88, Br 18.33.

Diethyl *cis/trans*-2'-Isopropenyl-5'-methoxy-5-methylenebicyclopentylidene-3,3-dicarboxylate (*cis/trans*-**51**): According to GP 2a **46** (400 mg, 0.90 mmol), palladium acetate (11 mg, 5 mol%), triphenylphosphane (24 mg, 10 mol%), and potassium carbonate (249 mg, 2 equiv.) were reacted in acetonitrile (10 mL) for 8 h at 80 °C. The crude product was purified on silica gel (10 g, column 1 × 15 cm, PE/Et_2O 16 : 1) to yield *cis/trans*-**51** (213 mg, 65%) as a colourless mixture of diastereomers (2 : 1). – IR (film): ν = 3080 cm^{-1} (C=CH), 2970, 2820, 1730 (C=O), 1645 (C=C), 1625 (C=C), 1600 (C=C), 1450, 1370, 1350, 1250, 1190, 1165, 1075, 1025, 895, 870, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (m, 6 H, CH_2CH_3), 1.50–2.10 (m, 4 H), 1.69 (bs, 3 H, CH_3), 2.85–3.20 (m, 5 H), 3.28 (s, 2 H, OCH_3), 3.30 (s, 1 H, OCH_3), 4.10–4.22 (m, 5 H, OCH_2CH_3), 4.41 (bs, 0.67 H), 4.61 (bs, 0.67 H), 4.68 (bs, 0.67 H), 4.87 (bs, 0.67 H), 4.99 (bs, 0.33 H), 5.05 (bs, 1 H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 21.2 (+, CH_3), 21.9 (+, CH_3), 27.2 (–), 29.9 (–), 40.1 (–), 40.3 (–), 42.1 (–), 42.8 (–), 49.4 (+, C-2'), 49.8 (+, C-2'), 56.2 (+, OCH_3), 57.5 (C_{quat}, C-3), 61.3 (–, OCH_2CH_3), 83.8 (+, C-5'), 84.2 (+, C-5'), 110.5 (–), 110.9 (–), 111.1 (–), 111.2 (–), 134.9 (C_{quat}), 135.6 (C_{quat}), 140.4 (C_{quat}), 140.8 (C_{quat}), 143.6 (C_{quat}), 144.0 (C_{quat}), 144.1 (C_{quat}), 145.2 (C_{quat}), 171.3 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 362 (4) (M$^+$), 330 (19), 315 (23), 257 (26), 256 (30), 239 (30), 183 (38), 119 (28), 59 (86), 60 (100), 46 (50), 45 (53), 43 (78). – Anal. Calcd for $C_{21}H_{30}O_5$ (362.5): C 69.59, H 8.34; found: C 69.42, H 8.32.

The more polar isomer was enriched by chromatography on silica gel (20 g, column 2.5 × 20 cm, PE/Et_2O 16 : 1): IR (film): ν = 3080 cm^{-1} (C=CH), 2970, 2820, 1730 (C=O), 1645 (C=C), 1625 (C=C), 1600 (C=C), 1450, 1350, 1190, 1165, 1075, 1025, 895, 870, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (m, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.54–1.85 (m, 4 H), 1.69 (s, 3 H, CH_3), 1.90–2.05 (m, 1 H, 2'-H), 2.90 (d, ^2J = 17.1 Hz, 1 H), 3.07 (dt, ^4J = 1.5, ^2J = 17.1 Hz, 1 H), 3.14 (bs, 2 H), 3.30 (s, 3 H, OCH_3), 4.08–4.25 (m, 5 H, OCH_2CH_3 und 5'-H), 4.42 (bs, 1 H), 4.62 (bs, 1 H), 4.88 (bs, 1 H), 5.06 (bs, 1 H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): 13.9 (+, CH_2CH_3), 21.9 (+, CH_3), 27.3 (–), 30.0 (–), 40.3 (–), 42.8 (–), 49.8 (+, C-2'), 56.2 (+, OCH_3), 57.6 (C_{quat}), 61.3 (–, OCH_2CH_3), 84.3 (+, C-5'), 110.5 (–), 111.2 (–), 135.6 (C_{quat}), 140.8 (C_{quat}), 143.6 (C_{quat}), 144.0 (C_{quat}), 171.2 (C_{quat}, C=O), 171.3 (C_{quat}, C=O).

Diethyl 2-Bromo-8-hydroxy-11-(tetrahydropyranyl-2-oxy)-1-undecene-6-yne-4,4-dicarboxylate (**48**): According to GP 1a diethyl 2-bromohept-1-ene-6-yne-4,4-dicarboxylate (2.50 g, 7.9 mmol) in THF (20 mL) was treated with *n*-butyllithium (3.67 mL, 8.7 mmol, 2.36 M in *n*-hexane) and 4-(tetrahydropyranyl-2-oxy)-butanal[25] (1.43 g, 8.3 mmol). Work-up and purification of the crude product on silica gel (90 g, column 2.5 × 35 cm, Et_2O) afforded a diastereomeric mixture of **48** (3.62 g, 93%) as a colourless oil (R_f = 0.55 in PE/Et_2O 1 : 3). – IR (film): ν = 3420 cm^{-1} (OH), 2950, 2860, 1730 (C=O), 1635 (C=C), 1430, 1370, 910, 865, 815. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 1.48–1.81 (m, 10 H, THP-, 9- and 10-H), 2.90 (d, ^5J = 1.7 Hz, 2 H, 5-H), 2.94 (bs, 1 H, OH), 3.23 (s, 2 H, 3-H), 3.37–3.49 (m, 2 H, OCH_2 and 11-H), 3.71–3.85 (m, 2 H, OCH_2 and 11-H), 4.18 (mc, 4 H, OCH_2CH_3), 4.34 (bs, 1 H, 8-H), 4.56 (bs, 1 H, OCHO), 5.57 (d, *J* = 1.4 Hz, 1 H, 1-H), 5.79 (bs, 1 H, 1-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.9 (+, CH_2CH_3), 19.3 (–), 22.3 (–), 25.3 (–), 25.4 (–), 30.5 (–), 35.2 (–), 42.7 (–), 56.0 (C_{quat}, C-

4), 61.9 (–, OCH_2), 61.9 (+, C-8), 62.0 (–, OCH_2), 62.1 (–, OCH_2), 67.0 (–, OCH_2), 67.1 (–, OCH_2), 79.2 (C_{quat}), 85.1 (C_{quat}), 98.6 (+, OCHO), 122.5 (–, C-1), 126.1 (C_{quat}), 169.1 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 387 (2), 307 (4), 279 (3), 190 (6), 153 (24), 97 (17), 85 (100), 71 (48), 41 (17).

Diethyl 2-Bromo-8-methoxy-1-undecene-6-yne-11-ol-4,4-dicarboxylate (49): According to the preparation of **14**-Me, a solution of **48** (7.03 g, 14.4 mmol) in THF (80 mL) was treated with *n*-butyllithium (6.7 mL, 15.8 mmol, 2.36 M in *n*-hexane), methyl iodide (5.0 mL), and DMSO (80 mL). Standard work-up gave the crude product, which was dissolved in wet methanol (300 mL). Hydrochloric acid (4 mL, 2 N) was added and the reaction mixture stirred for 2 h at room temperature. It was poured into water (200 mL) and extracted with dichloromethane (3 × 100 mL). Washing of the combined organic layers with brine (100 mL), drying over magnesium sulfate, removal of the solvents and chromatography on silica gel (95 g, column 2.5 × 35 cm, Et_2O) gave **49** (4.84 g, 81%) as a colourless oil (R_f = 0.18 in PE/Et_2O 1 : 3). – IR (film): ν = 3400 cm^{-1} (OH), 2900, 1720 (C=O), 1625 (C=C), 1430, 1370, 1285, 945, 905, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 1.56–1.73 (m, 4 H, 9- and 10-H), 2.49 (bs, 1 H, OH), 2.88 (d, ^5J = 1.7 Hz, 2 H, 5-H), 3.19 (bs, 2 H, 3-H), 3.28 (s, 3 H, OCH_3), 3.56 (t, ^3J = 5.8 Hz, 2 H, 11-H), 3.88 (tt, ^5J = 1.6, ^3J = 5.9 Hz, 1 H, 8-H), 4.14 (mc, 4 H, OCH_2CH_3), 5.53 (d, *J* = 1.5 Hz, 1 H, 1-H), 5.71 (bs, 1 H, 1-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.7 (+, CH_2CH_3), 22.3 (–), 28.3 (–), 32.2 (–), 42.6 (–, C-3), 56.0 (+, OCH_3), 56.1 (C_{quat}, C-4), 61.8 (–, OCH_2), 62.0 (–, OCH_2), 70.9 (+, C-8), 80.6 (C_{quat}), 82.3 (C_{quat}), 122.3 (–, C-1), 126.3 (C_{quat}, C-2), 169.0 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 361/359 (19/19), 339 (63), 307 (89), 285 (29), 279 (30), 233 (100), 206 (35), 205 (53), 178 (35), 161 (32), 140 (67), 117 (41), 109 (68), 91 (65), 85 (61), 71 (89), 55 (63), 41 (67). – Anal. Calcd for $C_{18}H_{27}BrO_6$ (419.3): C 51.56, H 6.49, Br 19.06; found: C 51.75, H 6.59, Br 17.80.

Diethyl 2-Bromo-8-methoxy-1-undecene-6-yne-11-al-4,4-dicarboxylate (50): To a solution of oxalyl chloride (0.36 mL, 4.2 mmol) in dichloromethane (10 mL) DMSO (0.61 mL, 7.8 mmol) was added dropwise at –60 °C and stirring was continued until the evolution of gas was finished. Then **49** (1.50 g, 3.6 mmol) was added slowly, during which a colourless precipitate was formed, and further stirred for additional 15 min at –60 °C, after which triethylamine (2.51 mL, 17.8 mmol) was added in one portion. The reaction mixture was warmed to room temperature and the resulting suspension poured into water (15 mL) and extracted with Et_2O (3 × 15 mL). Washing of the combined organic extracts with water (2 × 10 mL) and brine (10 mL), drying over magnesium sulfate and concentration under vacuum gave the crude product. It was purified by chromatography on silica gel (50 g, column 2.5 × 20 cm, PE/Et_2O 1 : 1) to yield **50** (1.46 g, 98%), which became brownish after a few hours (R_f = 0.59 in Et_2O). – IR (film): ν = 2950 cm^{-1}, 2710, 2210 (C≡C), 1700 (C=O), 1620 (C=C), 900, 850, 760, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 1.93 (mc, 2 H, 9-H), 2.53 (t, ^3J = 7.1 Hz, 2 H, 10-H), 2.91 (d, ^5J = 1.9 Hz, 2 H, 5-H), 3.21 (s, 2 H, 3-H), 3.28 (s, 3 H, OCH_3), 3.94 (tt, ^5J = 1.8, ^3J = 6.0 Hz, 1 H, 8-H), 4.15 (mc, 4 H, OCH_2CH_3), 5.56 (d, *J* = 1.6 Hz, 1 H, 1-H), 5.72 (bs, 1 H, 1-H), 9.71 (t, ^3J = 1.4 Hz, 1 H, 11-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 13.8 (+, CH_2CH_3), 22.3 (–), 28.2 (–), 39.4 (–), 42.6 (–, C-3), 55.9 (+, OCH_3), 56.2 (C_{quat}, C-4), 61.8 (–, OCH_2), 69.8 (+, C-8), 81.1 (C_{quat}), 81.7 (C_{quat}), 122.3 (–, C-1), 126.3 (C_{quat}, C-2), 168.9 (C_{quat}, C=O), 201.4 (+, C-11). – MS (70 eV), *m/z* (%): 418/416 (1/1) [M^+], 389/387 (4/4), 367 (9), 337 (26), 285 (20), 254 (21), 231 (30), 205 (37), 178 (36), 161 (39), 153 (44), 125 (47), 115 (57), 107 (63), 91 (89), 71 (74), 55 (76), 41 (100). – $C_{18}H_{25}BrO_6$: calcd 416.0834 (correct HRMS).

Methyl (*E,Z*)-12-Bromo-10,10-bis(ethoxycarbonyl)-6-methoxy-2-methyl-2,12-tridecadiene-7-yne-carboxylate (*E/Z*-54): To a solution of diethyl 1-(methoxycarbonyl)ethylphosphonate[27] (500 mg, 2.23 mmol) in THF (20 mL) was given potassium *tert*-butoxide (251 mg, 2.24 mmol) and stirred for 1 h. Compound **50** (886 mg, 2.12 mmol) was added and the reaction mixture heated under reflux for 1 h, after which it was poured into water (100 mL) and extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with brine (50 mL), dried over magnesium sulfate and concentrated under vacuum. The residue was purified on silica gel (40 g, column 2.5 × 20 cm, gradient PE/Et_2O 10 : 1 to 5 : 1) to give *E/Z*-**54** (785 mg,

76%) as a mixture of *E/Z*-isomers (ratio 1.67 : 1, R_f = 0.25 and 0.26 in PE/Et_2O 5 : 2). – IR (film): ν = 2930 cm^{-1}, 1710 (C=O), 1620 (C=C), 1420, 890, 850, 740. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.65–1.84 (m, 5 H, 2-CH_3 and 5-H), 2.25 (mc, ^3J = 7.5 Hz, 1.25 H, 4-H), 2.51 (m, ^3J = 7.4 Hz, 0.75 H, 4-H), 2.93 (bs, 2 H, 9-H), 3.23 (bs, 2 H, 11-H), 3.29 (s, 3 H, OCH_3), 3.68 (s, 3 H, CO_2CH_3), 3.85 (t, ^3J = 6.3 Hz, 1 H, 6-H), 4.17 (mc, 4 H, OCH_2CH_3), 5.56 (bs, 1 H, 13-H), 5.74 (bs, 0.6 H, 13-H), 5.75 (bs, 0.4 H, 13-H), 5.87 (t, ^3J = 7.4 Hz, 0.4 H, 3-H), 6.68 (t, ^3J = 7.4 Hz, 0.6 H, 3-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 12.2 (+, 2-CH_3), 13.8 (+, CH_2CH_3), 20.5 (+, 2-CH_3), 22.3 (–), 24.2 (–), 25.5 (–), 34.4 (–), 35.3 (–), 42.7 (–), 51.1 (+, OCH_3), 51.6 (+, OCH_3), 56.0 (+, CO_2CH_3), 56.1 (+, CO_2CH_3), 56.2 (C_{quat}, C-10), 61.8 (–, OCH_2CH_3), 70.2 (+, C-6), 70.6 (+, C-6), 80.5 (C_{quat}), 80.8 (C_{quat}), 82.2 (C_{quat}), 82.4 (C_{quat}), 122.3 (–, C-13), 122.4 (–, C-13), 126.4 (C_{quat}, C-12), 127.5 (C_{quat}, C-2), 128.3 (C_{quat}, C-2), 140.9 (+, C-3), 141.7 (+, C-3), 168.1 (C_{quat}, C=O), 168.4 (C_{quat}, C=O), 168.9 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 488/486 (6/5) [M^+], 457 (10), 407 (85), 367 (30), 347 (30), 315 (42), 301 (46), 287 (36), 269 (47), 255 (63), 161 (70), 141 (67), 115 (100), 98 (62), 65 (80). – $C_{22}H_{31}BrO_7$: calcd 486.1253 (correct HRMS).

After second chromatography on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 10 : 1), pure *(E)*-isomer was obtained (R_f = 0.25 in PE/Et_2O 5 : 2). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.0 Hz, 6 H, CH_2CH_3), 1.74–1.78 (m, 2 H, 5-H), 1.82 (bs, 3 H, 2-CH_3), 2.28 (mc, 2 H, 4-H), 2.96 (d, ^5J = 1.7 Hz, 2 H, 9-H), 3.26 (s, 2 H, 11-H), 3.33 (s, 3 H, OCH_3), 3.71 (s, 3 H, CO_2CH_3), 3.87 (mc, 1 H, 6-H), 4.20 (mc, 4 H, OCH_2CH_3), 5.59 (d, *J* = 1.4 Hz, 1 H, 13-H), 5.76 (bs, 1 H, 13-H), 6.71 (t, ^3J = 7.5 Hz, 1 H, 3-H).

Diethyl *cis/trans*-2'-(1-Methoxycarbonylvinyl)-5'-methoxy-5-methylenebicyclopentylidene-3,3-dicarboxylate (*cis/trans*-**53**): According to GP 2a *E/Z*-**54** (250 mg, 0.51 mmol), palladium acetate (4 mg, 3 mol%), triphenylphosphane (16 mg, 12 mol%), and silver(I) carbonate (279 mg, 2 equiv.) were reacted in acetonitrile (10 mL) at 80 °C for 8 h. Work-up and purification of the crude product on silica gel (18 g, column 2.5 × 20 cm, PE/Et_2O 4 : 1) afforded *cis/trans*-**53** (150 mg, 72%, ratio 1.2 : 1) as a colourless oil (R_f = 0.27 in PE/Et_2O 1 : 1). – IR (film): ν = 2990 cm^{-1}, 2880, 1730 (C=O), 1630 (C=C), 1445, 1375, 1260, 1190, 1105, 870. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19–1.26 (m, 6 H, CH_2CH_3), 1.53–2.40 (m, 4 H, 3'- and 4'-H), 2.91–3.27 (m, 4 H, 2- and 4-H), 3.32 (bs, 3 H, OCH_3), 3.64–3.71 (m, 1 H, 2'-H), 3.75 (bs, 3 H, CO_2CH_3), 3.85 (d, ^3J = 7.5 Hz, 0.59 H, 5'-H), 4.05 (d, ^3J = 7.5 Hz, 0.41 H, 5'-H), 4.14–4.26 (m, 4 H, OCH_2CH_3), 4.88 (bs, 1 H), 5.04 (bs, 0.59 H), 5.07 (bs, 0.41 H), 5.22 (bs, 0.41 H), 5.58 (bs, 0.59 H), 6.02 (bs, 0.59 H), 6.11 (bs, 0.41 H). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 14.0, 26.7, 29.3, 40.0, 40.7, 42.2, 42.8, 43.9, 44.1, 51.8 (2 signals), 56.3, 56.4, 57.5 (2 signals), 61.5, 83.7, 84.3, 111.0, 112.0, 124.0, 125.3, 135.3, 136.5, 139.1, 139.2, 139.5, 140.6, 143.5, 143.9, 167.5 (2 signals), 171.0, 171.3, 171.4. – MS (70 eV), *m/z* (%): 406 (2) [M^+], 374 (6), 315 (8), 300 (29), 241 (38), 221 (22), 220 (18), 169 (18), 167 (28), 141 (14), 85 (100), 71 (44). – $C_{22}H_{30}O_7$: calcd 406.1991 (correct HRMS).

Diethyl *cis*-2'-(1-Methoxycarbonylvinyl)-5'-methoxy-5-methylenebicyclopentylidene-3,3-dicarboxylate (*cis*-**53**) **and Diethyl 13-Methoxy-9-methoxycarbonyltetracyclo[7.4.0.0^{1,10}.0^{2,6}]tridec-2(6)-ene-4,4-dicarboxylate** (**52**): According to GP 1a *E/Z*-**54** (400 mg, 0.82 mmol), palladium acetate (20 mg, 11 mol%), triphenylphosphane (43 mg, 20 mol%), and potassium carbonate (340 mg, 3 equiv.) were reacted in acetonitrile (10 mL) at 130 °C for 14 h. The crude product mixture was chromatographed on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 8 : 1) to give *cis*-**53** (103 mg, 31%, R_f = 0.40 in PE/Et_2O 1 : 1) and **52** (158 mg, 47%, R_f = 0.35 in PE/Et_2O 1 : 1) as colourless oils. *cis*-**53**: IR (film): ν = 2990 cm^{-1}, 2880, 1730 (C=O), 1630 (C=C), 1445, 1375, 1260, 1190, 1105, 870. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.53–2.00 (m, 4 H, 3'- and 4'-H), 2.99 (bs, 2 H, 4-H), 3.03 (d, ^2J = 17.5 Hz, 1 H, 2-H), 3.22 (d, ^2J = 17.6 Hz, 1 H, 2-H), 3.32 (s, 3 H, OCH_3), 3.71 (bs, 1 H, 2'-H), 3.75 (s, 3 H, CO_2CH_3), 3.85 (d, ^3J = 7.5 Hz, 1 H, 5'-H), 4.15–4.26 (m, 4 H, OCH_2CH_3), 4.89 (bs, 1 H, 5-CH_2), 5.04 (bs, 1 H, 5-CH_2), 5.58 (bs, 1 H), 6.02 (bs, 1 H). – MS (70 eV), *m/z* (%): 406 (2) [M^+], 374 (6), 315 (8), 300 (29), 241 (38), 221 (22), 220 (18), 169 (18), 167 (28), 141 (14), 85 (100), 71 (44). – $C_{22}H_{30}O_7$: calcd 406.1991 (correct HRMS). – Anal. Calcd for $C_{22}H_{30}O_7$ (406.5): C 65.01, H 7.44; found: C 65.05, H 7.46. – **52**: IR (film): ν = 2920 cm^{-1}, 1730 (C=O),

1435, 1367, 1240, 860. – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93–1.00 (m, 1 H, 10-H), 1.23 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.73–1.87 (m, 4 H), 1.92 (d, J = 4.8 Hz, 1 H), 1.97–2.05 (m, 3 H), 2.79 (d, ^2J = 17.0 Hz, 1 H, 5-H), 3.00 (d, ^2J = 17.0 Hz, 1 H, 5-H), 3.26 (d, ^2J = 17.5 Hz, 1 H, 3-H), 3.27 (s, 3 H, OCH_3), 3.34 (d, ^2J = 17.5 Hz, 1 H, 3-H), 3.64 (s, 3 H, CO_2CH_3), 3.75 (d, ^3J = 4.5 Hz, 1 H, 13-H), 4.18 (mc, ^3J = 7.1 Hz, 4 H, OCH_2CH_3). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_2CH_3), 21.9 (–), 23.8 (–), 27.1 (–), 28.1 (–), 33.6 (+, C-10), 35.1 (C_{quat}), 37.6 (C_{quat}), 43.2 (–), 43.4 (–), 52.0 (+, OCH_3), 55.8 (+, OCH_3), 58.0 (C_{quat}, C-4), 61.25 (–, OCH_2), 61.29 (–, OCH_2), 84.0 (+, C-13), 129.7 (C_{quat}), 131.3 (C_{quat}), 172.4 (C_{quat}, C=O), 172.6 (C_{quat}, C=O), 173.5 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 406 (3) [M^+], 300 (2), 241 (7), 195 (1), 167 (3), 97 (3), 57 (10), 43 (100), 41 (25). – $C_{22}H_{30}O_7$: calcd. 406.1991 (correct HRMS). – Anal. Calcd for $C_{22}H_{30}O_7$ (406.5): C 65.01, H 7.44; found: C 65.17, H 7.47.

7-Methyl-7-octene-2-yne-1-ol (**56**): To 2-methallylmagnesium chloride (23 mL, 32.7 mmol, 1.42 M in THF) a solution of 4-bromo-1-butyne (**55**) (2.00 g, 15.0 mmol) in THF (100 mL) was added at –10 °C, at which temperature stirring was continued for 14 h. After addition of paraformaldehyde (1.35 g, 45.0 mmol), the reaction mixture was heated under reflux for 14 h, cooled down to room temperature and poured into ice water (100 mL). The organic layer was washed with hydrochloric acid and the aqueous phase extracted with Et_2O (3 × 100 mL). Washing of the combined organic layers with sat. potassium hydrogen carbonate solution (100 mL) and brine (100 mL) yielded after drying over magnesium sulfate and concentration under vacuum the crude product. It was chromatographed on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 8 : 1) to yield **56** (1.52 g, 73%) as a colourless oil. – IR (film): ν = 3340 cm^{-1} (OH), 3090 (C=CH), 2950, 2240, 1655 (C=C), 1430, 1140, 1020, 890. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.54 (m, 2 H, 5-H), 1.60 (s, 3 H, 7-CH_3), 1.99 (t, ^3J = 7.3 Hz, 2 H, 6-H), 2.10 (tt, ^5J = 2.4, ^3J = 7.3 Hz, 2 H, 4-H), 2.53 (bs, 1 H, OH), 4.13 (t, ^5J = 2.4 Hz, 2 H, 1-H), 4.58 (bs, 1 H, 8-H), 4.60 (bs, 1 H, 8-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 18.3 (+, 7-CH_3), 22.3 (–), 26.5 (–), 36.8 (–), 51.4 (–, C-1), 86.3 (C_{quat}), 78.5 (C_{quat}), 110.4 (–, C-8), 144.9 (C_{quat}, C-7). – MS (70 eV), *m/z* (%): 137 (1) [M^+ – H], 123 (35), 119 (17), 109 (24), 105 (100), 95 (42), 91 (56), 79 (55), 67 (56), 53 (42), 41 (97). – Anal. Calcd for $C_9H_{14}O$ (138.2): C 78.21, H 10.21; found: C 78.08, H 10.12.

Diethyl 7-Methyl-7-octene-2-ynylmalonate (**57**): To a solution of **56** (1.50 g, 10.9 mmol) and triethylamine (2.60 mL, 18.4 mmol) in dichloromethane (20 mL) was added dropwise at –50 °C methanesulfonyl chloride (0.9 mL, 11 mmol), after which the reaction mixture was warmed up to 0 °C and poured into ice water (20 mL). The aqueous phase was extracted with dichloromethane (3 × 20 mL) and the combined organic layers washed with brine (50 mL), dried over magnesium sulfate and concentrated under reduced pressure. The residue was diluted with DME (10 mL) and added dropwise to a solution of diethyl malonate sodium salt, prepared from diethyl malonate (1.88 g, 11.7 mmol) and sodium hydride (336 mg, 11.2 mmol, 80% in mineral oil) in DME. The reaction mixture was stirred for 14 h at room temperature, poured into water (20 mL) and extracted with Et_2O (3 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried over magnesium sulfate and concentrated under vacuum. The residue was chromatographed on silica gel (150 g, column 2.5 × 79 cm, PE/Et_2O 25 :1) to yield **57** (1.74 g, 57%) as a colourless oil (R_f = 0.36 in PE/Et_2O 4 : 1). – IR (film): ν = 3090 cm^{-1} (C=CH), 2950, 1740 (C=O), 1655 (C=C), 1450, 1240, 1040, 900. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.57 (mc, 2 H, 5'-H), 1.69 (s, 3 H, 7'-CH_3), 2.01–2.14 (m, 4 H, 4'- and 6'-H), 2.73 (dt, ^5J = 2.2, ^3J = 7.8 Hz, 2 H, 1'-H), 3.50 (t, ^3J = 7.8 Hz, 1 H, 2-H), 4.20 (q, ^3J = 7.0 Hz, 4 H, OCH_2CH_3), 4.66 (bs, 1 H, 8'-H), 4.69 (bs, 1 H, 8'-H).

Diethyl 2-Bromo-11-methyl-1,11-dodecadiene-6-yne-4,4-dicarboxylate (**58**): *Variant A*: To a suspension of sodium hydride (184 mg, 6.13 mmol, 80% in mineral oil) in DME (20 mL) **57** (1.64 g, 5.8 mmol) was added slowly at –10 °C, at which temperature stirring was continued until the formation of gas was nearly finished (~30 min). 2,3-Dibromopropene (1.29 g, 6.45 mmol) was added and the reaction mixture stirred over night at room temperature. The suspension was poured into water (20 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with brine (20 mL), dried over magnesium sulfate and concentrated under vacuum. The crude product was purified by chromatography on silica gel (30 g, column

2.5 × 20 cm, PE/Et_2O 32 : 1) to give **58** (1.80 g, 77%) as a colourless oil, which became brownish upon standing.

Variant B: To a solution of **56** (750 mg, 5.43 mmol) and triethylamine (1.28 mL, 9.22 mmol) in dichloromethane (10 mL) methanesulfonyl chloride (0.45 mL, 5.8 mmol) was added at –60 °C. The reaction mixture was allowed to warm up to 0 °C slowly and was poured into ice water (20 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over magnesium sulfate and concentrated under vacuum (water bath temperature < 40 °C). The crude product was diluted with DME (3 mL) and quickly given to a solution of diethyl malonate sodium salt in DME, prepared from diethyl malonate (0.913 g, 5.70 mmol) and sodium hydride (173 mg, 5.77 mmol, 80% in white oil) in DME. Stirring was continued for 2 h at room temperature, the reaction mixture was cooled to 0 °C and sodium hydride (173 mg, 5.77 mmol, 80% in mineral oil) was added. After the evolution of gas was finished, 2,3-dibromopropene (1.09 g, 5.45 mmol) was added and the mixture stirred further for 2 h. The reaction mixture was given into water (50 mL), extracted with Et_2O (3 × 50 mL) and washed with brine (50 mL). Drying over magnesium sulfate and removal of the solvents under vacuum gave the crude product, which was purified by chromatography on silica gel (100 g, column 2.5 × 35 cm, PE/Et_2O 32 : 1) to yield **58** (1.65 g, 76%) as a colourless oil (R_f = 0.48 in PE/Et_2O 4 : 1). – IR (film): ν = 3080 cm^{-1} (C=CH), 2980, 2950, 1735 (C=O), 1650 (C=C), 1635 (C=C), 1440, 1375, 1330, 1295, 1260, 1220, 1195, 1160, 1075, 1050, 1020, 900, 860. – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 1.59 (mc, 2 H, 9-H), 1.71 (s, 3 H, 11-CH_3), 2.04–2.18 (m, 4 H, 8- and 10-H), 2.88 (t, ^5J = 2.2 Hz, 2 H, 5-H), 3.28 (s, 2 H, 3-H), 4.20 (m, 4 H, OCH_2CH_3), 4.71 (bs, 1 H, 12-H), 4.72 (bs, 1 H, 12-H), 5.61 (d, J = 1.5 Hz, 1 H, 1-H), 5.80 (bs, 1 H, 1-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, plus APT): δ = 14.0 (+, CH_2CH_3), 18.2 (–), 22.3 (+, 11-CH_3), 22.5 (–), 26.9 (–), 36.7 (–), 42.8 (–), 56.3 (–, C-4), 61.8 (–, OCH_2CH_3), 74.6 (–, C-6*), 83.9 (–, C-7*), 110.5 (–, C-12), 122.3 (–, C-1), 126.8 (–, C-2), 144.8 (–, C-11), 169.3 (–, C=O). – MS (70 eV), *m/z* (%): 371/369 (2/1.9), 319 (21), 245 (83), 199 (35), 171 (41), 123 (57), 121 (47), 105 (33), 95 (100), 91 (37), 81 (43), 69 (40), 55 (59), 41 (75). – Anal. Calcd for $C_{19}H_{27}BrO_4$ (399.3): C 57.15, H 6.82, Br 20.01; found: C 57.32, H 6.74, Br 19.92.

4,4-Bis(ethoxycarbonyl)-8-methyltetracyclo[6.3.0.$1^{2,6}$.$0^{2,6}$]-1(11)-dodecene (60) and 1-[3-Bis(ethoxycarbonyl)-5-methylenecyclopent-1-ene-1-yl]-5-methylbicyclo[3.1.0]hexane (63): According to GP 2a, to a solution of **58** (584 mg, 1.46 mmol) in acetonitrile (10 mL) and dimethoxyethane (10 mL) were added palladium acetate (10 mg, 3 mol%), triphenylphosphane (46 mg, 12 mol%), and silver(I) carbonate (806 mg, 2 equiv.). The mixture was heated for 2 d at 60 °C. Standard work-up and chromatography on silica gel (40 g, column 2.5 × 20 cm, PE/Et_2O 30 : 1) gave **60** (142 mg, 30%, R_f = 0.45 in PE/Et_2O 4 : 1) and **63** (165 mg, 35%, R_f = 0.42 in PE/Et_2O 4 : 1), both as colourless oils. **60**: IR (film): ν = 3060 cm^{-1} (C=CH), 2990, 2860, 1738 (C=O), 1662 (C=C), 1450, 1377, 1250, 1190, 1085, 1022, 920, 870, 800, 740. – ^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, ^2J = 6.3 Hz, 1 H, 12-H), 1.04 (s, 3 H, 8-CH_3), 1.24 (m, 6 H, CH_2CH_3), 1.31 (d, ^2J = 6.3 Hz, 1 H, 12-H), 1.67 (d, ^2J = 12.0 Hz, 1 H, 7-H), 1.80 (m, 3 H, 7- and 9-H), 2.31 (ddd, ^3J = 3.8 and 7.8, ^2J = 15.0 Hz, 1 H, 10-H), 2.36 (dd, ^5J = 1.4, ^2J = 13.7 Hz, 1 H, 3-H), 2.47 (dd, ^5J = 1.5, ^2J = 13.6 Hz, 1 H, 3-H), 2.51 (d, ^2J = 13.5 Hz, 1 H, 5-H), 2.58 (d, ^2J = 13.5 Hz, 1 H, 5-H), 2.65 (dddd, ^3J = 1.5, 6.0 and 9.5, ^2J = 15.1 Hz, 1 H, 10-H), 4.15 (m, 4 H, OCH_2CH_3), 5.31 (dd, ^3J = 1.5, ^3J = 3.8 Hz, 1 H, 11-H). – ^{13}C NMR (125.7 MHz, $CDCl_3$, plus APT): δ = 14.0 (+, CH_2CH_3), 23.3 (–), 25.9 (+, 8-CH_3), 35.0 (–), 37.6 (–), 38.4 (–), 40.5 (–), 44.6 (–), 45.1 (–), 47.1 (–), 59.7 (–, C-4), 61.5 (–, OCH_2CH_3), 61.6 (–, OCH_2CH_3), 67.5 (–), 116.4 (+, C-11), 159.0 (–, C-1), 171.6 (–, C=O), 172.3 (–, C=O). – MS (70 eV), *m/z* (%): 318 (58) [M^+], 246 (31), 245 (39), 244 (41), 173 (35), 171 (100), 129 (30), 95 (60), 91 (23), 81 (20), 55 (13), 41 (16). – Anal. Calcd for $C_{19}H_{26}O_4$ (318.4): C 71.67, H 8.23; found: C 71.55, H 8.33. – **63**: IR (film): ν = 3095 cm^{-1} (C=CH), 3060 (C=CH), 2945, 2860, 1735 (C=O), 1640 (C=C), 1450, 1390, 1375, 1295, 1250, 1180, 1100, 1075, 1050, 880, 860. – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.41 (d, ^2J = 4.3 Hz, 1 H, 6-H), 0.75 (d, ^2J = 4.4 Hz, 1 H, 6-H), 1.03 (s, 3 H, 5-CH_3), 1.24 (m, 6 H, CH_2CH_3), 1.54–2.07 (m, 6 H, 2-, 3- and 4-H), 3.19 (dd, ^4J = 1.7 Hz, ^4J = 1.7 Hz, 2 H, 4'-H), 4.19 (m, 4 H, OCH_2CH_3), 4.87 (d, ^4J = 1.9 Hz, 1 H, 5'-CH_2), 4.95 (d, ^4J = 1.5 Hz, 1 H, 5'-CH_2), 5.93 (s, 1 H, 2'-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, plus DEPT): δ = 14.0 (+, CH_2CH_3), 17.9 (+), 18.7

(–), 21.9 (–), 29.9 (C_{quat}), 31.0 (C_{quat}), 32.9 (–), 34.9 (–), 38.7 (–), 61.5 (–, OCH_2CH_3), 63.4 (C_{quat}, C-3'), 104.9 (–, 5'-CH_2), 133.5 (+, C-2'), 149.3 (C_{quat}), 150.4 (C_{quat}), 170.7 (C_{quat}, C=O). – MS (70 eV), *m/z* (%): 318 (11) [M^+], 272 (7), 246 (22), 245 (100), 199 (22), 171 (48), 129 (12), 81 (14). – Anal. Calcd for $C_{19}H_{26}O_4$ (318.4): C 71.67, H 8.23; found: C 71.55, H 8.33.

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