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Palladium-catalysed reactions of conjugated enyne oxiranes with organoborons: A diastereoselective method of the synthesis of 2,4,5-trienol derivatives

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ABSTRACT

A palladium-catalysed reaction of conjugated enyne oxiranes with organoboron reagents is described. This method allows aryl-substituted vinylallenes containing a hydroxyl group on the allylic position to be synthesized, with good diastereomeric ratios, under mild conditions.

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1. Introduction

Allenes are highly versatile reagents, with broad utility as building blocks to a diverse array of high-value products.¹ In addition, there are quite a number of biologically active natural products and pharmaceutical agents that contain an allene moiety.^{1a,b} Therefore it is of interest to develop mild and selective methods to synthesise allenes with diverse substitution patterns^{2,3} that can be elaborated into specific targets.^{1c,4}

Our group has recently developed general palladium-catalysed methods to synthesise functionalized tetra-substituted allenes in a series of studies of conjugated enyne compounds.⁵ This work was initiated with studies of enynes containing a carbonate-leaving group on the allylic carbon. These enynes react with CO/ROH combinations or organoboron reagents to afford esters and aryl- or alkenyl-substituted vinylallenes, respectively (Scheme 1).^{5a-c}

We then extended the alkoxyacylation to conjugated enynes carrying an oxirane moiety to synthesise functionalized vinylallenes, thereby allowing the formation of 7-hydroxy-2,3,5-trienoates stereoselectively (Scheme 1).^{5d,6}

We demonstrate in this study that enyne oxiranes are compliant reagents for Miyaura-Suzuki-type reactions⁷ and thus produce aryl- or alkenyl-substituted vinylallenes bearing a hydroxyl group on the allylic position (Scheme 2).

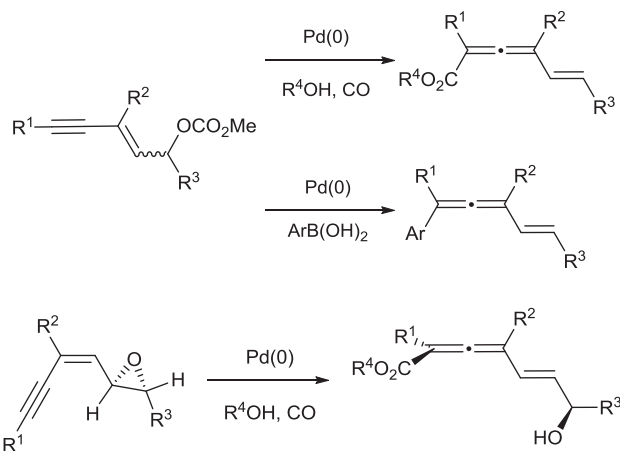
2. Results and discussion

A promising result was obtained in the reaction of the enyne oxirane **1a**, which had a dimethyl group on the oxirane terminus, with phenylboronic acid in the presence of Pd(PPh₃)₄ (3 mol%) in a THF/water (2:1) mixture at 50 °C. This reaction resulted in complete conversion in 1.5 h and furnished the phenyl-substituted vinylallene **3aa**, which had a hydroxyl group on the allylic position (Scheme 3).

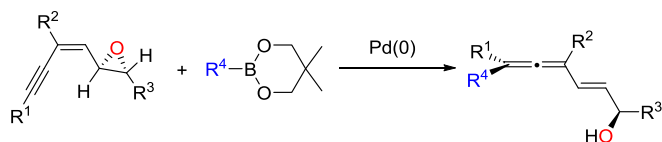
Based on this promising result, the optimization studies with the enyne oxirane **1b**, which had a disubstituted oxirane ring, were carried out so that the stereoselectivity of the process could be evaluated with respect to the relative configurations of the axially-chiral allenyl moiety and the hydroxyl-substituted chirality centre (Scheme 4). However, interestingly, the reaction of this substrate with phenylboronic acid under the aforementioned conditions led only to a condensation product. Other organoboron reagents, such as PhBF₃K and (PhBO)₃ also shared the same fate.

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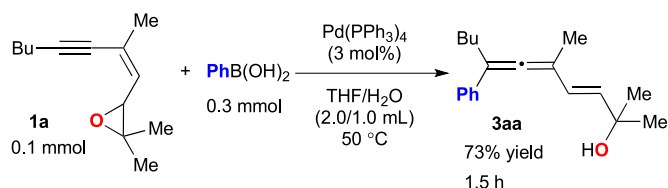
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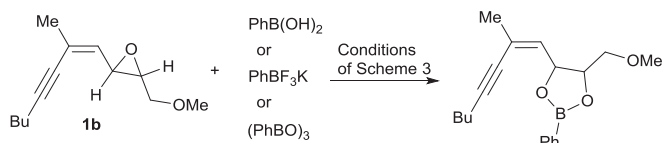
Scheme 1. Palladium-catalysed alkoxy carbonylation and Miyaura-Suzuki type reactions of enyne carbonates and enyne oxiranes.⁵



Scheme 2. This study: Palladium-catalysed arylation of enyne oxiranes.



Scheme 3. Palladium-catalysed reaction of **1a** and phenylboronic acid.



Scheme 4. Palladium-catalysed reaction of **1b** and organoborons.

Palladium-catalysed condensation of allylic oxiranes with organoboronic acids has been previously documented,⁸ so the latter two reagents were probably also partially hydrolysed to phenylboronic acid under aqueous conditions. Encouragingly, the desired vinylallene product **3ba** could be obtained with a moderate yield (67%) and diastereomeric ratio (dr) of 79:21, as determined by ¹H NMR, with the use of the $NaBPh_4$ reagent (Table 1, entry 1). Increasing the THF/water ratio improved the reaction efficiency and dr to some extent (entry 2). However, lowering the reaction temperature to 25 °C resulted in a significant reduction in the yield and led to the formation of the allylic substitution product **4ba** (entry 3). The neopentyl glycol ester of phenylboronic acid (**2a**) was also compatible—when reacting with **1b** at 25 °C in the presence of $Pd(PPh_3)_4$ or $Pd_2(dba)_3 \cdot CHCl_3 / PPh_3$ (3 mol% Pd; P/Pd = 4.5:1) catalyst systems, neither the condensation by-product formation nor **4ba** were observed to form and, thus, **3ba** could be obtained with a good yield, but with a non-satisfactory dr (entries 4 and 5).

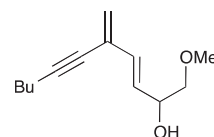
Several mono and bidentate ligands were surveyed in an attempt to improve the efficacy and stereoselectivity for the reaction of **1b** and **2a** (see the supporting file), among which the most promising ligands that provided dr levels greater than 80:20 are listed in Table 2.

The reactions in the presence of TFP, PPh_2Me , $AsPh_3$, $dppf$, $dppp$, and $dppb$ ligands were either unaffordably slow or had unsatisfactory yields (entries 1–6). The best performance in terms of the **3ba** yield and reaction rate was achieved by the use of DPEPhos ligand, albeit with somewhat lessened stereoselectivity (entry 7).

Gratifyingly, the presence of a base additive has been found to be beneficial for the level of stereoselectivity (see the supporting file) and the organic bases usually performed better than inorganic bases (entries 8–10). The additive (*i*-Pr)₂EtN was determined to be the most suitable base and even better diastereoselectivities were achieved by using larger amounts of the base (entries 11 and 12).

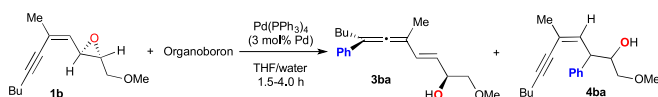
Having completed the optimization study, we surveyed the scope of the method against an array of neopentyl glycol esters of arylboronic acids with a variety of substitution patterns under the conditions of entry 11 of Table 2, which was judged to be sufficient for the selective formation of the desired product **3**. The palladium-catalysed reaction of **1b** and organoboron reagents (**2b–e**) substituted with an electron donating group gave the expected vinylallenes in good yields and stereoselectivities in relatively short reaction periods, regardless of the substitution pattern of **2** (Table 3, entries 1–4). However, the allylic substitution product **4bf** was the main product of the reaction carried out with the highly encumbered 2,6-dimethyl substituted organoboron **2f**, and therefore, yielded the desired **3bf** in low yield (entry 5).

Both electron-poor organoboron reagents (entries 6–8) and naphthylborons (entries 9 and 10) were competent reagents in terms of process efficiency and stereoselective formation of respective products. The reactions proceeded slower when the former organoboron reagents were used. The method was less stereoselective for alkenylboron reagents, whereas the structurally interesting divinylallene product **3bl** could be isolated with a synthetically useful dr (83:17) when using (*E*)-1-pentenylboronic ester (entry 11). On the other hand, the reaction with (*E*)-styrylboronic ester proceeded with remarkably low diastereomeric selectivity (entry 12). Interestingly, a β -hydride elimination product was the sole product of the reaction performed in the presence of 3-thienylboron (**2n**) (entry 13).



The enyne oxirane component of the reaction was also varied, usually with similar success (Table 4). The substrate **1a** showed a better performance under the optimized conditions. Hence, **3aa** could be obtained in high yield (entry 1). The method was also suitable to the synthesis of the vinylallene with a primary allylic alcohol portion (**3ca**), although it was obtained in a relatively lower yield (entry 2). While the pendant oxygen functionality within R³ group could also be used in benzyl- or silyl-protected forms effectively, the protection of the hydroxyl functionality was not compulsory, although there was some reduction in yield without such protection (entries 3–5). The presence of a larger group in R³, such as 2-methoxypropan-2-yl group (**1g**), was also well-tolerated by the method (entry 6). However, the reaction was dramatically decelerated when there was only one methyl group at the oxirane terminus (**1h**) (entry 7).

Table 1
Effect of Organoboron type and other reaction parameters.^a



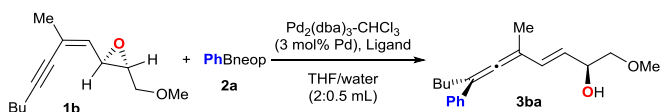
Entry	Organo-boron	THF/water (mL)	Temp. (°C)	Yield (%) ^b 3ba:4ba	dr of 3ba ^b
1	NaBPh ₄	2:1	50	67:-	79:21
2	NaBPh ₄	2:0.5	50	75:-	83:17
3	NaBPh ₄	2:0.5	25	31:33	N.D.
4	PhNeop	2:0.5	25	77:-	73:27
5 ^c	PhNeop	2:0.5	25	81:-	76:24

^a Reagents and conditions: **1b** (0.1 mmol), organoboron (0.3 mmol).

^b Determined by ¹H NMR using *p*-anisaldehyde as the internal standard.

^c Performed using Pd₂(dba)₃-CHCl₃/PPh₃ (3 mol% Pd, P/Pd = 4.5:1) combination.

Table 2
Optimization studies.^a



Entry	Ligand ^b	Base (eq)	Time (h)	Yield (%) ^c	dr ^c
1	TFP	—	15	65	85:15
2	PPh ₂ Me	—	23	70	85:15
3	AsPh ₃	—	20	66	82:18
4	dppe	—	30	81	84:16
5	dppp	—	72	70	82:18
6	dppb	—	40	48	83:17
7	DPEPhos	—	1.5	92	80:20
8	DPEPhos	NaHCO ₃ (2)	3.5	96	87:13
9	DPEPhos	Et ₃ N (2)	5	90	89:11
10	DPEPhos	(<i>i</i> -Pr) ₂ EtN (2)	2	90	90:10
11	DPEPhos	(<i>i</i> -Pr) ₂ EtN (4)	4	92 ^d	91:9
12	DPEPhos	(<i>i</i> -Pr) ₂ EtN (6)	6	89	92:8

^a Reagents and conditions: **1b** (0.1 mmol), **2a** (0.3 mmol) at 25 °C.

^b P (or As)/Pd: 4.5:1; TFP: tri(2-furyl)phosphine; dppe: 1,2-Bis(di-phenylphosphino)-ethane; dppp: 1,3-Bis(di-phenylphosphino)propane; dppb: 1,4-Bis(di-phenylphosphino)butane; DPEPhos: Bis[2-(di-phenylphosphino)-phenyl] ether.

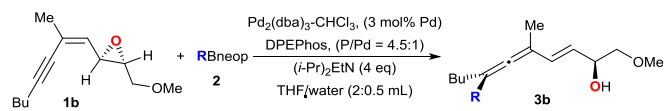
^c Determined by ¹H NMR using *p*-anisaldehyde as the internal standard.

^d Yield of isolated product is provided.

The reactions proceeded smoothly with enyne oxiranes bearing a terminal alkyne moiety (**1i**) and those bearing methyl (**1j**), phenyl (**1k**), or ester (**1l**) groups on the alkynyl terminus (R¹) (entries 8–11). However, the regioselectivity of the method was sensitive to the size of the R¹ and R² group on the alkenyl carbon that was in the vicinity of the alkynyl moiety (entries 12–17). When either group was larger than Bu, the formation of the desired vinylallene products was accompanied by the corresponding allylic substitution products **4**, with varying yields of 9–16% for enynes where R¹ was Cy (**1m**) or *t*-Bu (**1n**) or R² was Cy (**1q**) under the standard conditions. However, the formation of these by-products could be minimized by using Ph₃P, albeit with a decrease of dr of the product. On the other hand, the formation of **4ra** was almost exclusive when R² was *t*-Bu and the DPEphos ligand was used, and **3ra** formation was not satisfactory even using the Ph₃P ligand (entry 17).

The diastereomeric forms of the products **3** were estimated by comparison with NMR spectra of **3la** (entry 11) and its diastereomeric form **3la'** synthesized in another study^{5d} (see the supporting information).

Table 3
The reaction of **1b** with various organoboronic esters.^a



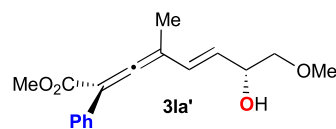
Entry	R	Time (h)	Yield (%)	dr ^b
1	<i>p</i> -MeC ₆ H ₄ 2b	1.5	93 3bb	92:8
2	<i>m</i> -MeC ₆ H ₄ 2c	2	72 3bc	90:10
3	<i>o</i> -MeC ₆ H ₄ 2d	1.5	87 3bd	92:8
4	<i>p</i> -OMeC ₆ H ₄ 2e	1.5	95 3be	91:9
5 ^c	2,6-Me ₂ C ₆ H ₄ 2f	20	28 3bf	74:26
6	<i>p</i> -CF ₃ C ₆ H ₄ 2g	12	81 3bg	92:8
7	<i>m</i> -ClC ₆ H ₄ 2h	9	78 3bh	90:10
8	<i>o</i> -FC ₆ H ₄ 2i	6	83 3bi	92:8
9	1-Naphthyl 2j	1.5	93 3bj	91:9
10	2-Naphthyl 2k	2	88 3bk	91:9
11	(<i>E</i>)-1-Pentenyl 2l	4	63 3bl	83:17
12	(<i>E</i>)-Styryl 2m	6	73 3bm	70:30
13 ^d	3-Thienyl 2n	3	trace 3bn	—

^a Reagents and conditions: **1b** (0.1 mmol), **2** (0.3 mmol) at 25 °C.

^b Determined by ¹H NMR.

^c The reaction also yielded 43% of **4bf**.

^d A β-hydride elimination product was the only product of this reaction.

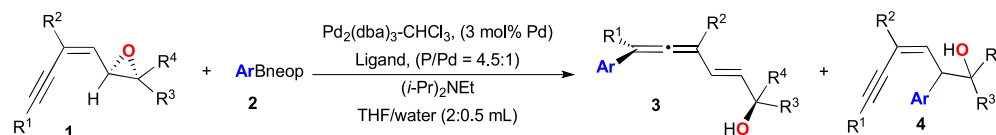


The scope of the method was also evaluated for an enyne oxirane with an (*E*)-configured alkenyl moiety (*E*-**1b**); the reaction of this reagent with **2a** proceeded with low stereoselectivity and produced **3ba'**, the diastereomer of **3ba**, with a 76:24 dr (**Scheme 5**).

Finally the method was also examined for substrate **1s**, which had an endocyclic double bond. However, unlike its acyclic counterparts listed herein, its reaction with **2a** under the standard conditions resulted in only a mixture of 3,5-dienone structure (**5sa**) and the typical allyl-substituted by-product **4sa**; therefore the expected product of vinylallene **3sa** could not be isolated (**Scheme 6**). This vinylallene **3sa** would have been precursor to **5sa**, and after it was formed, it would have undergone successive isomerization and tautomerization steps to form **5sa** products.

It has been shown in previous studies that vinylallenes can be

Table 4
Arylation of enyne oxiranes.^a

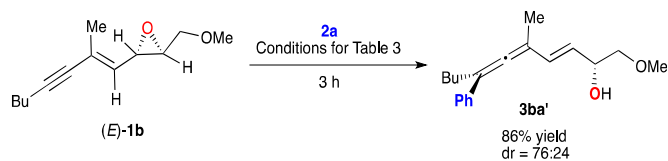
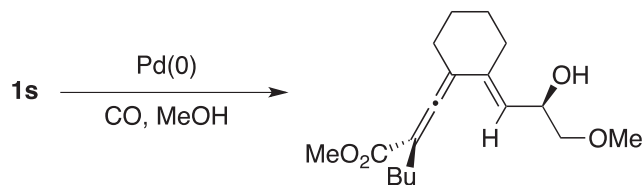


Entry	Product	Time (h)	Yield 3 (%)	dr ^b	Entry	Product	Time (h)	Yield 3 (%)	dr ^b
1		1.5	91	—	12		8 (5) ^c	71 (73) ^c	92:8 (85:15) ^c
2		2	78	—				9 (trace) ^c	N.D.
3		1.5	78	91:9	13		16 (10) ^c	68 (71) ^c	92:8 (88:12) ^c
4		2.5	88	90:10				11 (5) ^c	N.D.
5		2	87	92:8	14		4	67	89:11
6		2	87	92:8	15		1.5	88	92:8
7		16	73	91:9	16		3 (2) ^c	68 (72) ^c	88:12 (85:15) ^c
8		1	74	91:9				16 (trace) ^c	N.D.
9		1	93	92:8	17		8 (3) ^c	Trace (16) ^c	N.D. (85:15) ^c
10		3	93	91:9				62 (61) ^c	83:17 (81:19) ^c
11		2	89	89:11					

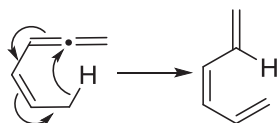
^a Reagents and conditions: **1** (0.1 mmol), **2** (0.3 mmol), and DPEPhos ligand at 25 °C. The oxirane ring is in the form of *E*-configuration where it is applicable.

^b Determined by ¹H NMR.

^c Ph₃P ligand was used in these reactions.

Scheme 5. The reaction of (*E*)-**1b** and **2a**.Scheme 7. Pd-catalysed alkoxy carbonylation of **1s**.^{5d}

converted to conjugated trienes via thermally induced [1,5]-sigmatropic hydrogen shift.⁹

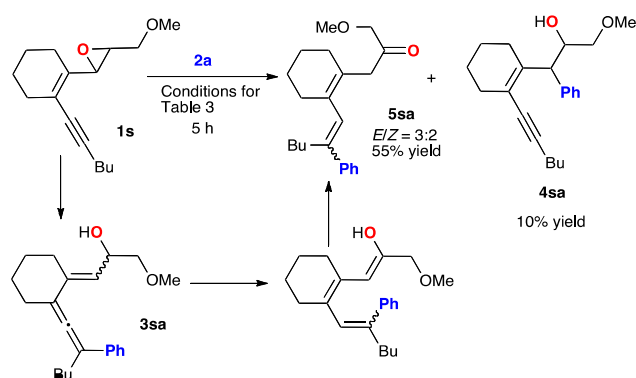
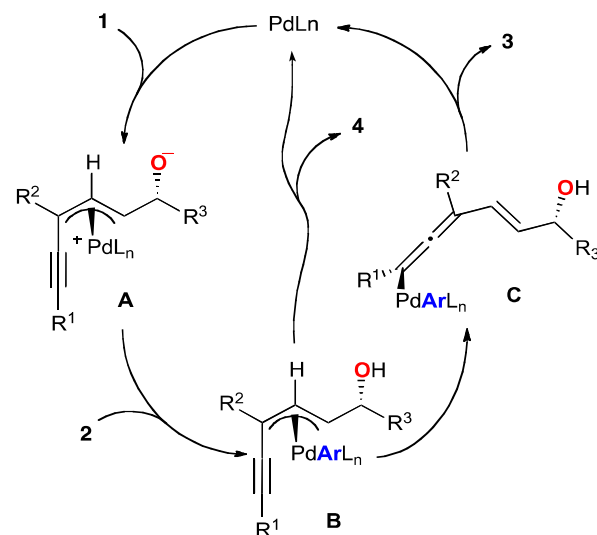


A hydrogen shift in this way requires that the alkenyl moiety of **3sa** be present in the (*Z*)-configuration, but we do not know its exact configuration in fact. Whereas, in our previous study, the palladium-catalysed alkoxy carbonylation of **1s** had yielded the corresponding ester functionalized vinylallene with exclusively (*E*)-configuration and no traces of a triene product could be detected in that study (Scheme 7).^{5d}

Considering that similar mechanisms are proposed for both alkoxy carbonylation^{5d} and arylation (this study, Scheme 8) reactions, we cannot envisage any possibility that could lead to the formation of **3sa** in (*Z*) configuration. Presumably both the locked *s-cis* conformational structure of **3sa** and the apparent π -conjugated nature of the trienol intermediate may have favored an isomerization process.

As for the reaction mechanism, as suggested in our previous reports⁵ the catalytic cycle could begin with the formation of a π -allylpalladium intermediate in anti-form (**A**), which has the R^3 group oriented syn with respect to the middle allylic C–H so that vinylallene products can ultimately form in (*E*)-configuration (Scheme 8). Then, this allyl-ligated palladium species **A** and organoboron **2** should undergo transmetalation to form the intermediate **B**.¹⁰ The subsequent migration of the palladium unit over the intermediate **B** to the distal alkenyl carbon mainly by retention of the configuration, affords a σ -allenylpalladium complex (**C**)¹¹ and the final reductive elimination step then completes the cycle, resulting in the target product **3**. In cases where **B** has R^1 or R^2 groups relatively large in size or increased crowding around the palladium core metal, such a palladium shift would be less favourable and, therefore, **B** would preferentially undergo reductive elimination to furnish the by-product **4**.

The loss of stereochemical integrity of the resulting products

Scheme 6. Palladium-catalysed reaction of **1s** and **2a**.

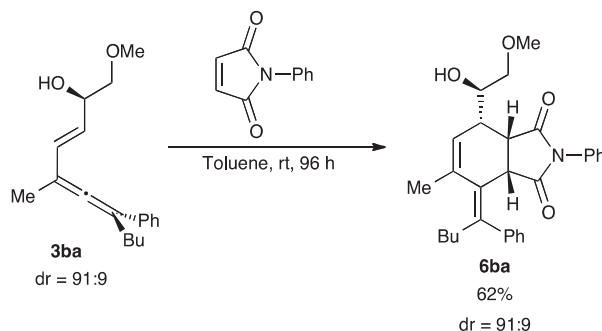
Scheme 8. Proposed mechanism.

probably took place during the course of the reaction cycle, because it was observed that the vinylallene **3ba** was configurationally stable under the reaction conditions¹²; subjecting the purified **3ba** again to the standard conditions for 3 days had no influence on its original diastereomeric ratio of 91:9.^{3b,5c}

Evidently, the vinylallene structures of this study are well-suited to Diels-Alder reactions, as the reaction of **3ba** (dr = 91:9) with *N*-phenylmaleimide proceeded with virtually complete facial- and endo-selectivity to furnish a structurally interesting adduct **6ba** in two diastereomeric forms (91:9) (Scheme 9). The structure of the major diastereomeric form was elucidated by NOE studies.

3. Conclusion

We have demonstrated that the palladium-catalysed reactions of enyne oxiranes and organoboronic esters can be carried out with good stereoselectivity under mild conditions, yielding 2,4,5-trienol

Scheme 9. The Diels-Alder reaction of the vinylallene **3ba** with *N*-phenylmaleimide.

derivatives. One product served as a substrate for a Diels-Alder reaction with high stereospecificity and stereoselectivity.

4. Experimental section

4.1. General

The synthesis procedure of the starting enyne oxirane compound **1c**¹³ and others^{5d} can be found elsewhere. The solvents were dried and purified following standard procedures. All of the reaction products were isolated by silica-gel column chromatography and analysed by GC–MS, NMR, FTIR, and HRMS techniques. NMR (400 MHz) spectra were recorded in CDCl₃ or C₆D₆. With C₆D₆ solvent, the ¹H NMR signals of diastereomers were usually resolved adequately, allowing determination of diastereomeric ratios (dr) smoothly. In contrast, when using CDCl₃ solvent, diastereomeric signals were all overlapped. The coupling constants of olefinic protons and NOE studies confirmed (*E*)-configured structures for **3**. Infrared spectra were obtained by the ATR method with neat samples. High-resolution mass spectral analyses of new compounds were performed using ESI-LTQ Orbitrap and an ESI-Q-TOF mass spectrometers.

4.2. General method for the synthesis of neopentyl borates (**2**)

The dry THF (1 mL) solution of organoboronic acid (10 mmol), 2,2-dimethylpropan-1,3-diol (11 mmol, 1.2 g), and MgSO₄ (14 mmol, 1.7 g) mixture was stirred overnight at room temperature under Ar. The crude mixture was concentrated under a reduced pressure and neopentyl borate ester derivative (**2**) was purified on a silica gel column with yields varying in the range of 76–97% (hexane/ethyl acetate as the eluent).

4.3. General procedures for catalytic reactions

A palladium complex, ligand, and the dry THF (half of the volume necessary for the reaction) were added successively into a Schlenk apparatus that is attached to an Ar line and stirred 15 min at 25 °C. Then, the dry THF (remaining half volume) solution of organoboron, enyne oxirane (**1**), and degassed water were added successively. The mixture was stirred magnetically in a preheated water or an oil bath. When the reaction was complete, as judged by TLC analysis, the solvent was evaporated under reduced atmosphere and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate), affording the product **3** as colourless oil unless otherwise mentioned. In the case of optimization studies, the reaction mixture was filtered through a short silica gel column, washed with Et₂O, dried with MgSO₄ and evaporated under reduced atmosphere. The residue was analysed by ¹H NMR using *p*-anisaldehyde as the internal standard. Aldehyde and methoxy hydrogen signals were used in the quantitative analyses.

4.3.1. (*E*)-2,5-Dimethyl-7-phenylundeca-3,5,6-trien-2-ol (**3aa**)

¹H NMR (400 MHz, CDCl₃) δ: 7.37–7.34 (m, 2H), 7.33–7.38 (m, 2H), 7.17–7.21 (m, 1H), 6.23 (d, *J* = 15.9 Hz, 1H), 5.76 (d, *J* = 15.9 Hz, 1H), 2.45 (t, *J* = 8.0 Hz, 2H), 1.91 (s, 3H), 1.54–1.39 (m, 4H), 1.38 (s, 6H), 0.92 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 208.1, 137.4, 136.3, 128.5, 126.7, 126.3, 125.5, 105.3, 102.5, 71.2, 30.2, 30.1, 30.0, 22.6, 15.6, 14.2; FTIR (ν_{max}/cm⁻¹): 3356, 2923, 1609, 1362, 1142, 974, 763, 692; MS (EI, *m/z*): 270(<5, M⁺), 252(6), 195(10), 165(12), 153(15), 141(40), 128(23), 115(35), 91(62), 77(50), 59(100); HRMS (ESI), C₁₉H₂₅ [(M-H₂O)+H]⁺: 253.1951 (calculated), 253.1952 (found).

4.3.2. ((2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-phenylundeca-3,5,6-trien-2-ol (**3ba**)

Isolated as a 91:9 mixture of diastereomers; white crystal; m.p. 46.4–47.8 °C; ¹H NMR (400 MHz, C₆D₆) δ: 7.43 (dd, *J* = 8.8, 1.6 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.55 (dd, *J* = 15.8, 1.6 Hz, 1H), 5.63 (dd, *J* = 15.8, 5.9 Hz, 1H), 4.35–4.31 (m, 1H), 3.14 (dd, A of ABX, *J*_{AB} = 9.6 Hz, *J*_{AX} = 3.8 Hz, 1H), 3.11 (dd, B of ABX, *J*_{AB} = 9.6 Hz, *J*_{BX} = 8.3 Hz, 1H), 3.01 (s, 3H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.86 (s, 3H), 1.55–1.48 (m, 2H), 1.37–1.28 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, C₆D₆) δ: 208.8, 138.0, 130.4, 129.1, 128.6, 127.3, 127.1, 106.3, 103.4, 77.5, 71.7, 59.0, 30.8, 30.7, 23.1, 15.9, 14.5; FTIR (ν_{max}/cm⁻¹): 3426, 2938, 1923, 1455, 1198, 1126, 968, 770, 697; MS (EI, *m/z*): 286(8, M⁺), 236(8), 198(15), 169(40), 129(45), 115(52), 91(100), 77(88), 56(84); HRMS (ESI) C₁₉H₂₇O₂ [M+H]⁺: 287.2006 (calculated); 287.2008 (found).

4.3.3. (2*S*,6*R*,*E*)-1-methoxy-5-methyl-7-phenylundeca-3,5,6-trien-2-ol (**3ba'**)

Isolated as a 76:24 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.45–7.41 (m, 2H), 7.20–7.15 (m, 2H), 7.08–7.04 (m, 1H), 6.55 (dd, *J* = 15.8, 1.4 Hz, 1H), 5.633 (dd, *J* = 15.8, 6.0 Hz, 1H), 4.35–4.30 (m, 1H), 3.14 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 3.4 Hz, 1H), 3.11 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 7.9 Hz, 1H), 3.01 (s, 3H), 2.40 (t, *J* = 7.2 Hz, 2H), 1.86 (s, 3H), 1.57–1.48 (m, 2H), 1.38–1.28 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.8, 138.0, 130.5, 129.06, 127.3, 127.1, 106.3, 103.4, 77.5, 71.7, 58.9, 30.81, 30.75, 23.2, 15.9, 14.5; FTIR (ν_{max}/cm⁻¹): 3428, 2931, 2163, 1925, 1438, 1115, 973, 761, 692; MS (EI, *m/z*): 286(<5, M⁺) 241(20), 223(25), 199(30), 181(45), 169(100), 91(70), 77(20), 45(50).

4.3.4. (*Z*)-1-Methoxy-5-methyl-3-phenylundec-4-en-6-yn-2-ol (**4ba**)

¹H NMR (400 MHz, CDCl₃): δ 7.34–7.24 (m, 5H), 5.75 (d, *J* = 10.2 Hz, 1H), 4.09 (t, *J* = 8.4 Hz, 1H), 3.95 (t, *J* = 9.6 Hz, 1H), 3.54 (dd, *J* = 9.8, 2.7 Hz, 1H), 3.39–3.30 (m, 4H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.55–1.44 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.0, 134.7, 128.7, 128.3, 126.7, 120.2, 94.9, 79.5, 75.2, 73.0, 59.1, 50.5, 30.9, 23.7, 22.0, 19.2, 13.6.

4.3.5. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(*p*-tolyl)undeca-3,5,6-trien-2-ol (**3bb**)

Isolated as a 92:8 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.41 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.56 (dd, *J* = 15.8, 1.0 Hz, 1H), 5.63 (dd, *J* = 15.8, 6.1 Hz, 1H), 4.34–4.28 (m, 1H), 3.14 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 8.2 Hz, 1H), 3.10 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 3.5 Hz, 1H), 3.00 (s, 3H), 2.43 (t, *J* = 8 Hz, 2H), 2.14 (s, 3H), 1.87 (s, 3H), 1.54 (quint, *J* = 7.2 Hz, 2H), 1.37–1.30 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.6, 136.8, 135.1, 130.7, 129.8, 128.3, 127.1, 106.2, 103.3, 77.5, 71.7, 58.9, 30.9, 30.6, 23.2, 21.4, 16.0, 14.5; FTIR (ν_{max}/cm⁻¹): 3444, 2923, 1523, 1441, 1197, 1123, 961, 831, 603; MS (EI, *m/z*): 300(15, M⁺), 282(5), 225(30), 193(30), 155(50), 141(30), 105(20), 91(15), 44(100); HRMS (ESI): C₂₀H₂₈O₂Na [M+Na]⁺: 323.1982 (calculated), 323.1983 (found).

4.3.6. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(*m*-tolyl)undeca-3,5,6-trien-2-ol (**3bc**)

Isolated as a 90:10 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.36 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.17–7.13 (m, 1H), 6.92 (dt, *J* = 7.4, 0.8 Hz, 1H), 6.58 (dd, *J* = 15.9, 1.4 Hz, 1H), 5.63 (dd, *J* = 15.9, 5.6 Hz, 1H), 4.34–4.30 (m, 1H), 3.13 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 7.8 Hz, 1H), 3.10 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 3.6 Hz, 1H), 3.00 (s, 3H), 2.44 (t, *J* = 6.4 Hz, 2H), 2.27 (bs, 1H), 2.14 (s, 3H), 1.88 (s, 3H), 1.59–1.51 (m, 2H), 1.40–1.30 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.8, 138.4, 138.0,

130.6, 129.1, 128.5, 128.2, 127.8, 124.3, 106.4, 103.2, 77.5, 71.7, 58.9, 30.9, 30.8, 23.2, 21.9, 16.0, 14.5; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3435, 2922, 1606, 1470, 1258, 1107, 956, 797, 699; MS (EI, m/z): 300(5, M^+), 237(15), 195(40), 183(85), 143(45), 105(100), 91(40), 77(25), 45(40); HRMS (ESI) $C_{20}H_{29}O_2$ [$M+H$] $^+$: 301.2162 (calculated), 301.2164 (found).

4.3.7. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(*o*-tolyl)undeca-3,5,6-trien-2-ol (**3bd**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.26 (d, $J = 6.7$ Hz, 1H), 7.11–7.04 (m, 3H), 6.58 (dd, $J = 15.7$, 1.6 Hz, 1H), 5.54 (dd, $J = 15.7$, 5.9 Hz, 1H), 4.34–4.29 (m, 1H), 3.13 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 7.7$ Hz, 1H), 3.09 (dd, B of ABX, $J_{AB} = 9.4$ Hz, $J_{BX} = 3.7$ Hz, 1H), 3.00 (s, 3H), 2.35 (s, 3H), 2.33 (td, $J = 7.2$, 2.8 Hz, 2H), 1.80 (s, 3H), 1.50–1.42 (m, 2H), 1.36–1.26 (m, 2H), 0.84 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 206.9, 138.6, 136.3, 131.2, 130.9, 128.8, 127.9, 127.5, 126.6, 104.9, 100.5, 77.5, 71.6, 58.9, 34.7, 30.7, 23.1, 21.2, 16.0, 14.5; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3413, 2922, 1449, 1190, 1142, 959, 756, 728; MS (EI, m/z): 300(20, M^+), 282(5), 225(30), 193(30), 155(50), 141(30), 105(20), 91(15), 44(100); HRMS (ESI) $C_{20}H_{28}O_2Na$ [$M+Na$] $^+$: 323.1982 (calculated), 323.1984 (found).

4.3.8. (2*S*,6*S*,*E*)-1-methoxy-7-(4-methoxyphenyl)-5-methylundeca-3,5,6-trien-2-ol (**3be**)

Isolated as a 91:9 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.38 (d, $J = 9.2$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 6.58 (dd, $J = 15.8$, 1.4 Hz, 1H), 5.64 (dd, $J = 15.7$, 5.9 Hz, 1H), 4.37–4.32 (m, 1H), 3.33 (s, 3H), 3.16 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 4.3$ Hz, 1H), 3.12 (dd, B of ABX, $J_{AB} = 9.4$ Hz, $J_{BX} = 7.6$ Hz, 1H), 3.015 (s, 3H), 2.42 (t, $J = 6.8$ Hz, 2H), 1.89 (s, 3H), 1.60–1.51 (m, 2H), 1.40–1.31 (m, 2H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.4, 159.6, 130.9, 130.1, 128.24, 128.19, 114.7, 105.9, 103.3, 77.5, 71.7, 59.0, 55.2, 31.0, 30.9, 23.2, 16.1, 14.5; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3444, 2931, 2867, 1925, 1613, 1512, 1454, 1247, 1174, 1120, 1041, 967, 835, 597; MS (EI, m/z): 316(10, M^+), 259(80), 209(100), 171(95), 121(75), 44(90); HRMS (ESI) $C_{20}H_{29}O_3$ [$M+H$] $^+$: 317.2111 (calculated), 317.2112 (found).

4.3.9. (2*S*,6*S*,*E*)-7-(2,6-dimethylphenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bf**)

Isolated as a 74:26 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.06–6.96 (m, 3H), 6.65 (d, $J = 15.8$ Hz, 1H), 5.52 (dd, 15.8, 5.9, 1H), 4.35–4.31 (m, 1H), 3.13 (dd, A of ABX, $J_{AB} = 9.2$ Hz, $J_{AX} = 7.8$ Hz, 1H), 3.08 (dd, B of ABX, $J_{AB} = 9.2$ Hz, $J_{BX} = 3.5$ Hz, 1H), 3.00 (s, 3H), 2.34 (s, 6H), 2.13–2.07 (m, 2H), 1.77 (s, 3H), 1.55–1.48 (m, 2H), 1.37–1.26 (m, 2H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 204.8, 138.9, 136.0, 130.7, 128.3, 127.7, 127.5, 104.1, 100.8, 77.5, 71.6, 58.9, 34.1, 30.5, 23.3, 20.8, 15.7, 14.6; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3421, 2944, 1470, 1386, 1190, 1129, 956, 760; MS (EI, m/z): 314(50, M^+), 269(60), 197(45), 157(30), 119(55), 45(100); HRMS (ESI) $C_{21}H_{31}O_2$ [$M+H$] $^+$: 315.2319 (calculated); 315.2320 (found).

4.3.10. (*Z*)-3-(2,6-dimethylphenyl)-1-methoxy-5-methylundec-4-en-6-yn-2-ol (**3bf**)

^1H NMR (400 MHz, C_6D_6) δ : 7.05–6.96 (m, 3H), 6.35 (d, $J = 8.0$ Hz, 1H), 4.69 (t, $J = 8.0$ Hz, 1H), 4.31–4.23 (m, 1H), 3.20–3.16 (dd, $J = 9.4$, 2.8 Hz, 1H), 3.14–3.07 (m, 1H), 2.92 (s, 3H), 2.69–2.28 (bs, 6H), 2.11 (t, $J = 6.8$ Hz, 2H), 1.87 (s, 3H), 1.40–1.18 (m, 4H), 0.77 (t, $J = 8.0$ Hz, 3H); FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3451, 2912, 1460, 1391, 1122, 767; ^{13}C NMR (101 MHz, C_6D_6) δ : 139.5, 137.1, 126.9, 120.8, 95.2, 81.4, 75.4, 73.1, 58.9, 46.7, 31.5, 24.5, 22.8 (bs), 22.6, 20.0, 14.1; ^1H NMR (400 MHz, CD_3Cl) δ : 7.02–6.97 (m, 3H), 6.14 (d, $J = 8.0$ Hz, 1H), 4.43 (t, $J = 8.0$ Hz, 1H), 4.29–4.22 (m, 1H), 3.28 (s, 3H), 3.28–3.22 (m, 1H), 3.14–3.09 (m, 1H), 2.43 (s, 6H), 2.29 (t, $J = 8.0$ Hz, 2H), 1.86 (s, 3H), 1.51–1.33 (m, 4H), 0.90 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (101 MHz, CD_3Cl) δ : 138.0, 135.0, 126.5, 121.3, 95.1, 80.2, 74.7, 72.5,

59.1, 46.2, 30.9, 24.2, 22.3 (bs), 22.2, 19.5, 13.8; (EI, m/z): 314(<5, M^+), 269(15), 239(100), 198(55), 183(85), 169(95), 119(40), 55(40); HRMS (ESI) $C_{21}H_{30}O_2$ [$M+H$] $^+$: 315.2319 (calculated); 315.2320 (found).

4.3.11. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(4-(trifluoromethyl)phenyl)undeca-3,5,6-trien-2-ol (**3bg**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.37 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 7.8$ Hz, 2H), 6.54 (dd, $J = 15.7$, 1.6 Hz, 1H), 5.63 (dd, $J = 15.7$, 5.5 Hz, 1H), 4.32 (dt, $J = 3.8$, 1.8 Hz, 1H), 3.15 (dd, A of ABX, $J_{AB} = 11.8$ Hz, $J_{AX} = 9.6$ Hz, 1H), 3.09 (dd, B of ABX, $J_{AB} = 11.8$ Hz, $J_{BX} = 2.1$ Hz, 1H), 3.00 (s, 3H), 2.24 (t, $J = 7.2$ Hz, 2H), 1.82 (s, 3H), 1.48–1.40 (m, 2H), 1.36–1.27 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); ^1H NMR (400 MHz, $CDCl_3$) δ : 7.53 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 6.35 (d, $J = 16.0$ Hz, 1H), 5.63 (dd, $J = 16.0$, 8.0 Hz, 1H), 4.45–4.37 (m, 1H), 3.50–3.46 (m, 1H), 3.42 (s, 3H), 3.37–3.30 (m, 1H), 2.5 (bs, 1H), 2.44 (t, $J = 8.0$ Hz, 2H), 1.92 (s, 3H), 1.52–1.35 (m, 4H), 0.92 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 208.8, 140.9, 130.3, 128.5 (q, $J_{C-F} = 32$ Hz), 127.1, 126.3, 125.2 (q, $J_{C-F} = 16$ Hz), 124.3 (q, $J_{C-F} = 270$ Hz), 104.7, 103.1, 76.5, 71.2, 59.1, 29.9, 29.8, 22.4, 15.2, 14.0; ^{19}F NMR (326.27 MHz, $CDCl_3$) δ : -62.4; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3435, 2941, 2862, 1609, 1326, 1160, 1133, 1071, 833, 612; MS (EI, m/z): 354(<1, M^+), 309(35), 291(30), 267(45), 249(60), 237(90), 159(85), 109(45), 55(40), 45(100); HRMS (ESI) $C_{20}H_{25}F_3O_2$ [$M+H$] $^+$: 355.1784 (calculated); 355.1781 (found).

4.3.12. (2*S*,6*S*,*E*)-7-(3-chlorophenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bh**)

Isolated as a 90:10 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.53 (t, $J = 2.0$ Hz, 1H), 7.17 (dd, $J = 1.6$, 0.8 Hz, 1H), 7.04 (ddd, $J = 7.9$, 2.1, 1.0 Hz, 1H), 6.87 (t, $J = 8.0$ Hz, 1H), 6.49 (dd, $J = 15.7$, 1.6 Hz, 1H), 5.60 (dd, $J = 15.7$, 5.9 Hz, 1H), 4.31–4.29 (m, 1H), 3.12 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 7.7$ Hz, 1H), 3.08 (dd, B of ABX, $J_{AB} = 9.4$ Hz, $J_{BX} = 3.7$ Hz, 1H), 3.00 (s, 3H), 2.30 (bs, 1H), 2.22 (t, $J = 7.6$ Hz, 2H), 1.78 (s, 3H), 1.47–1.38 (m, 2H), 1.27 (sext, $J = 7.6$ Hz, 2H), 0.82 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.8, 140.2, 135.3, 130.3, 129.7, 129.1, 127.3, 126.96, 126.93, 125.24, 105.4, 104.0, 77.4, 71.5, 59.0, 30.6, 30.4, 23.0, 15.7, 14.5; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3406, 2930, 1617, 1480, 1109, 972, 783, 686; MS (EI, m/z): 320(5, M^+), 257(15), 203(45), 165(35), 125(40), 44(100); HRMS (ESI) $C_{19}H_{25}ClO_2Na$ [$M+Na$] $^+$: 343.1441 (calculated), 343.1439 (found).

4.3.13. (2*S*,6*S*,*E*)-7-(2-fluorophenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bi**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.25–7.21 (m, 1H), 6.85–6.80 (m, 3H), 6.59 (dd, $J = 15.9$, 1.4 Hz, 1H), 5.59 (dd, $J = 15.9$, 5.9 Hz, 1H), 4.33–4.29 (m, 1H), 3.13 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 8.2$ Hz, 1H), 3.09 (dd, B of ABX, $J_{AB} = 9.4$ Hz, $J_{BX} = 3.6$ Hz, 1H), 3.00 (s, 3H), 2.47 (t, $J = 7.4$ Hz, 2H), 2.30 (bs, 1H), 1.85 (s, 3H), 1.52–1.44 (m, 2H), 1.32 (sext, $J = 8.0$ Hz, 2H), 0.83 (t, $J = 7.2$ Hz, 3H); ^1H NMR (400 MHz, $CDCl_3$) δ : 7.27–7.15 (m, 2H), 7.09–6.98 (m, 2H), 6.36 (d, $J = 16.0$ Hz, 1H), 5.55 (dd, $J = 16.0$, 8.0 Hz, 1H), 4.42–4.37 (m, 1H), 3.49–3.45 (m, 1H), 3.41 (s, 3H), 3.36–3.31 (m, 1H), 2.42 (t, $J = 8.0$ Hz, 2H), 1.87 (s, 3H), 1.65 (bs, 1H), 1.43–1.19 (m, 4H), 0.89 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 208.7, 160.2 (d, $J_{C-F} = 247.3$ Hz), 131.3, 129.8 (d, $J_{C-F} = 3.8$ Hz), 128.4 (d, $J_{C-F} = 8.3$ Hz), 126.4, 125.7 (d, $J_{C-F} = 12.9$ Hz), 124.0 (d, $J_{C-F} = 3.8$ Hz), 116.1 (d, $J_{C-F} = 22.8$ Hz), 100.7, 100.5, 76.7, 71.4, 59.2, 32.0, 30.2, 22.4, 15.5, 14.1; ^{19}F NMR (326.27 MHz, $CDCl_3$) δ : -114.0; FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3425, 2923, 1487, 1440, 1196, 1110, 971, 752; MS (EI, m/z): 304(5, M^+), 259(15), 199(25), 187(60), 133(25), 109(100), 45(35); HRMS (ESI) $C_{19}H_{26}FO_2$ [$M+H$] $^+$: 305.1911 (calculated), 305.1913 (found).

4.3.14. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(naphthalen-1-yl)undeca-3,5,6-trien-2-ol (**3bj**)

Isolated as a 91:9 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 8.39 (d, *J* = 8.6 Hz, 1H), 7.66 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.41–7.37 (m, 2H), 7.29–7.24 (m, 2H), 6.67 (dd, *J* = 15.8, 1.4 Hz, 1H), 5.54 (dd, *J* = 15.8, 5.7 Hz, 1H), 4.35–4.30 (m, 1H), 3.13 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 8.1 Hz, 1H), 3.08 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 3.7 Hz, 1H), 3.00 (s, 3H), 2.47 (td, *J* = 7.5, 1.8 Hz, 2H), 1.84 (s, 3H), 1.524 (quint, *J* = 7.2 Hz, 2H), 1.33 (sext, *J* = 7.6 Hz, 2H), 0.83 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 207.3, 137.6, 135.0, 132.4, 130.8, 129.2, 128.1, 126.6, 126.4, 126.32, 126.1, 104.5, 100.7, 77.5, 71.6, 58.9, 35.5, 31.0, 23.1, 16.1, 14.5; FTIR (ν_{max}/cm⁻¹): 3435, 2922, 1946, 1470, 1206, 1129, 986, 804, 782; MS (EI, *m/z*): 336 (20, M⁺), 273(30), 261(55), 229(100), 217(65), 202(80), 165(60), 141(35), 44(95); HRMS (ESI) C₂₃H₂₈O₂Na [M+Na]⁺: 359.1982 (calculated), 359.1983 (found).

4.3.15. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-(naphthalen-2-yl)undeca-3,5,6-trien-2-ol (**3bk**)

Isolated as a 91:9 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.84 (s, 1H), 7.71 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.68–7.60 (m, 3H), 7.26 (quint, *J* = 7.1, 1.6 Hz, 2H), 6.62 (dd, *J* = 15.8, 1.4 Hz, 1H), 5.67 (dd, *J* = 15.8, 5.9 Hz, 1H), 4.37–4.33 (m, 1H), 3.15 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 7.8 Hz, 1H), 3.12 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 3.5 Hz, 1H), 3.01 (s, 3H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.35 (bs, 1H), 1.91 (s, 3H), 1.63–1.56 (m, 2H), 1.38 (sext, *J* = 7.6 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 209.6, 135.4, 134.7, 133.5, 130.3, 128.8, 128.7, 126.7, 126.5, 126.3, 124.6, 106.6, 103.8, 77.5, 71.7, 59.0, 30.8, 30.7, 23.2, 16.0, 14.6; FTIR (ν_{max}/cm⁻¹): 3451, 2950, 1449, 1363, 1122, 959, 863, 825, 747; MS (EI, *m/z*): 336(15, M⁺), 291(30), 261(30), 219(80), 207(55), 165(45), 141(100), 73(50), 45(60); HRMS (ESI) C₂₃H₂₈O₂Na [M+Na]⁺: 359.1982 (calculated), 359.1983 (found).

4.3.16. (2*S*,3*E*,6*S*,8*E*)-7-butyl-1-methoxy-5-methylundeca-3,5,6,8-tetraen-2-ol (**3bl**)

Isolated as a 83:17 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 6.53 (dd, *J* = 15.1, 1.0 Hz, 1H), 6.09 (d, *J* = 16.0 Hz, 1H), 5.65 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.58 (dd, *J* = 15.7, 5.6 Hz, 1H), 4.33–4.29 (m, 1H), 3.13 (dd, A of ABX, *J*_{AB} = 9.5 Hz, *J*_{AX} = 7.8 Hz, 1H), 3.09 (dd, B of ABX, *J*_{AB} = 9.5 Hz, *J*_{BX} = 4.0 Hz, 1H), 3.00 (s, 3H), 2.20 (t, *J* = 7.2 Hz, 2H), 2.02 (q, *J* = 6.5 Hz, 2H), 1.84 (s, 3H), 1.56–1.48 (m, 2H), 1.39–1.29 (m, 4H), 0.87 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 210.5, 131.0, 129.6, 128.7, 127.8, 105.3, 101.2, 77.5, 71.6, 58.9, 35.8, 30.7, 29.6, 23.4, 23.3, 16.2, 14.6, 14.3; FTIR (ν_{max}/cm⁻¹): 3442, 2927, 1480, 1261, 1113, 958, 796; MS (EI, *m/z*): 278(10), 233(25), 161(30), 119(45), 105(100), 93(60), 55(55); HRMS (ESI) C₁₉H₃₂O₂Na [M+Na]⁺: 315.2319 (calculated), 315.2320 (found).

4.3.17. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-((*E*)-styryl)undeca-3,5,6-trien-2-ol (**3bm**)

Isolated as a 70:30 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.27–7.23 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.05–7.02 (m, 1H), 6.83 (d, *J* = 16.4 Hz, 1H), 6.58 (d, *J* = 16.4 Hz, 1H), 6.57 (dd, *J* = 15.8, 0.4 Hz, 1H), 5.64 (ddd, *J* = 16.0, 5.6, 0.8 Hz, 1H), 5.64 (ddd, *J* = 16.0, 5.6, 0.8 Hz, 1H), 4.36–4.31 (m, 1H), 3.14 (dd, A of ABX, *J*_{AB} = 9.4 Hz, *J*_{AX} = 7.7 Hz, 1H), 3.10 (dd, B of ABX, *J*_{AB} = 9.4 Hz, *J*_{BX} = 3.6 Hz, 1H), 3.00 (s, 3H), 2.26 (t, *J* = 7.2 Hz, 2H), 1.86 (s, 3H), 1.57–1.50 (m, 2H), 1.39–1.30 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 212.4, 138.4, 130.4, 129.2, 127.84, 127.80, 127.0, 106.0, 101.6, 77.4, 71.6, 59.0, 30.6, 29.4, 23.2, 16.1, 14.6; FTIR (ν_{max}/cm⁻¹): 3435, 2923, 1460, 1142, 957, 753, 693; MS (EI, *m/z*): 312(40), 267(35), 223(15), 195(80), 165(60), 115(50), 91(100), 32(60); HRMS (ESI) C₂₁H₂₉O₂ [M+H]⁺: 313.2161 (calculated),

313.2178 (found).

4.3.18. (*E*)-4-Methyl-6-phenyldeca-2,4,5-trien-1-ol (**3ca**)

¹H NMR (400 MHz, C₆D₆) δ: 7.45 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.07 (td, *J* = 7.6, 0.8 Hz, 1H), 6.29 (d, *J* = 15.6 Hz, 1H), 5.59 (dtd, *J* = 15.6, 5.8, 0.8 Hz, 1H), 3.90 (d, *J* = 5.8 Hz, 2H), 2.41 (t, 7.4 Hz, 2H), 1.83 (s, 3H), 1.54 (quin, *J* = 7.4 Hz, 2H), 1.39–1.30 (m, 2H), 0.87 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.6, 138.0, 129.7, 129.12, 129.07, 127.4, 127.0, 106.3, 103.4, 63.8, 30.8, 30.7, 23.2, 15.9, 14.5; FTIR (ν_{max}/cm⁻¹): 3345, 2912, 1488, 1449, 1305, 978, 689; MS (EI, *m/z*): 242(<5, M⁺), 224(5), 200(15), 169(100), 154(20), 141(25), 128(20), 115(20), 91(30), 41(5); HRMS (ESI) C₁₇H₂₂ONa [M+Na]⁺: 265.1563 (calculated), 265.1569 (found).

4.3.19. (2*S*,6*S*,*E*)-5-methyl-7-phenylundeca-3,5,6-triene-1,2-diol (**3da**)

Isolated as a 91:9 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.45–7.42 (m, 2H), 7.21–7.16 (m, 2H), 7.08–7.04 (m, 1H), 6.42 (dd, *J* = 15.6, 1.6 Hz, 1H), 5.50 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.05–4.02 (m, 1H), 3.40–3.37 (m, 1H), 3.30–3.24 (m, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 1.82 (d, *J* = 0.8 Hz, 3H), 1.55–1.48 (m, 2H), 1.38–1.28 (m, 2H), 0.86 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.9, 137.9, 130.9, 129.1, 127.4, 127.1, 106.4, 103.3, 73.8, 67.2, 30.8, 30.7, 23.2, 15.9, 14.5; MS (EI, *m/z*): 256(25), 239(27), 112(95), 83(40), 70(75), 57(100), 43(65); FTIR (ν_{max}/cm⁻¹): 3365, 2951, 2920, 2862, 1925, 1597, 1454, 1079, 1031, 967, 750, 698; HRMS (ESI) C₁₈H₂₅O₂ [M+H]⁺: 273.1849 (calculated), 273.1851 (found).

4.3.20. (2*S*,6*S*,*E*)-1-(benzyloxy)-5-methyl-7-phenylundeca-3,5,6-trien-2-ol (**3ea**)

Isolated as a 90:10 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.44 (d, *J* = 7.8 Hz, 2H), 7.20–7.14 (m, 6H), 7.11–7.05 (m, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 5.60 (dd, *J* = 15.9, 5.9 Hz, 1H), 4.39–4.34 (m, 1H), 4.24 (s, 2H), 3.28 (dd, A of ABX, *J*_{AB} = 9.3 Hz, *J*_{AX} = 7.9 Hz, 1H), 3.21 (dd, B of ABX, *J*_{AB} = 9.3 Hz, *J*_{BX} = 3.8 Hz, 1H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.25 (bs, 1H), 1.85 (s, 3H), 1.51 (quint, *J* = 7.4 Hz, 2H), 1.32 (sext, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.8, 139.0, 137.9, 130.5, 129.1, 129.0, 128.5, 128.3, 128.2, 127.4, 127.1, 106.3, 103.4, 75.1, 73.6, 71.8, 30.8, 30.7, 23.2, 15.9, 14.5; FTIR (ν_{max}/cm⁻¹): 3435, 2915, 1503, 1450, 1142, 983, 763, 674; MS (EI, *m/z*): 362(<5, M⁺), 320(5), 253(10), 197(20), 181(25), 169(45), 129(20), 91(100), 69(35), 41(40); HRMS (ESI) C₂₅H₃₀O₂Na [M+Na]⁺: 385.2138 (calculated), 385.2138 (found).

4.3.21. (2*S*,6*S*,*E*)-1-((*tert*-butyldimethylsilyloxy)-5-methyl-7-phenylundeca-3,5,6-trien-2-ol (**3fa**)

Isolated as a 92:8 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.44 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.58 (dd, *J* = 15.9, 1.2 Hz, 1H), 5.65 (dd, *J* = 15.9, 6.1 Hz, 1H), 4.25 (bs, 1H), 3.53 (dd, A of ABX, *J*_{AB} = 9.9 Hz, *J*_{AX} = 7.3 Hz, 1H), 3.43 (dd, B of ABX, *J*_{AB} = 9.9 Hz, *J*_{BX} = 3.7 Hz, 1H), 2.39 (t, *J* = 7.6 Hz, 2H), 2.32 (d, *J* = 3.1 Hz, 1H), 1.89 (s, 3H), 1.52 (quint, *J* = 7.6 Hz, 2H), 1.38–1.29 (m, 2H), 0.91 (s, 9H), 0.86 (t, *J* = 7.2 Hz, 3H), -0.01 (s, 6H); ¹³C NMR (101 MHz, C₆D₆) δ: 208.8, 137.9, 134.9, 131.5, 130.6, 129.1, 127.4, 127.1, 106.3, 103.4, 73.5, 68.2, 30.8, 30.7, 26.4, 23.2, 21.9, 18.8, 16.0, 14.5, -4.9; FTIR (ν_{max}/cm⁻¹): 3426, 2915, 1468, 1318, 1256, 1115, 851, 772, 683; MS (EI, *m/z*): 386(<1, M⁺), 311(5), 237(30), 195(35), 181(55), 169(30), 105(35), 91(55), 75(100); HRMS (ESI) C₂₄H₃₉O₂Si [M+H]⁺: 387.2714 (calculated), 387.2716 (found).

4.3.22. (3*S*,7*S*,*E*)-2-methoxy-2,6-dimethyl-8-phenylundeca-4,6,7-trien-3-ol (**3ga**)

Isolated as a 92:8 mixture of diastereomers; ¹H NMR (400 MHz, C₆D₆) δ: 7.44 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H, minor), 7.18 (t,

$J = 7.6$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.54 (d, $J = 15.6$ Hz, 1H), 5.77 (ddd, $J = 15.7, 6.6, 0.8$ Hz, 1H), 4.06 (d, $J = 6.4$ Hz, 1H), 2.92 (s, 3H), 2.55 (bs, 1H), 1.879 (s, 3H), 1.51 (quint, $J = 7.6$ Hz, 2H), 1.32 (sext, $J = 7.6$ Hz, 2H), 1.03 (s, 3H), 0.97 (s, 3H), 0.85 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.7, 138.0, 134.9, 131.3, 129.1, 127.3, 127.1, 106.2, 103.5, 78.7, 78.0, 72.4, 49.4, 30.8, 23.1, 21.9, 21.1, 19.9, 16.0, 14.5; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3438, 2920, 1480, 1384, 1067, 962, 761, 708; MS (EI, m/z): 314(<1, M^+), 242(5), 91(5), 115(5), 73(100); HRMS (ESI) $\text{C}_{21}\text{H}_{31}\text{O}_2$ $[\text{M}+\text{H}]^+$: 315.2318 (calculated), 315.2327 (found).

4.3.23. (2*R*,6*S*,*E*)-5-methyl-7-phenylundeca-3,5,6-trien-2-ol (**3ha**)

Isolated as a 91:9 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.46 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.30 (d, $J = 15.7$ Hz, 1H), 5.59 (ddd, $J = 15.7, 6.4, 0.8$ Hz, 1H), 4.14–4.08 (m, 1H), 2.42 (t, $J = 7.2$ Hz, 2H), 1.85 (d, $J = 0.8$ Hz, 3H), 1.54 (quint, $J = 7.2$ Hz, 2H), 1.39–1.30 (m, 2H), 1.12 (d, $J = 6.4$ Hz, 3H), 0.86 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.7, 138.0, 134.1, 129.1, 128.3, 127.4, 127.0, 106.2, 103.3, 69.0, 30.8, 30.7, 24.1, 23.15, 16.0, 14.5; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3332, 2972, 2920, 1501, 1427, 1089, 982, 782, 708; MS (EI, m/z): 256(<5, M^+), 238(5), 196(10), 181(15), 169(100), 155(25), 141(25), 129(20), 115(20), 91(25), 77(10), 43(25); HRMS (ESI) $\text{C}_{18}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}]^+$: 257.1899 (calculated), 257.1907 (found).

4.3.24. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-phenylhepta-3,5,6-trien-2-ol (**3ia**)

Isolated as a 91:9 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.23 (d, $J = 6.8$ Hz, 2H), 7.11 (t, $J = 7.6$ Hz, 2H), 7.01 (t, $J = 7.2$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 6.20 (s, 1H), 5.62 (ddt, $J = 15.6, 5.6, 1.2$ Hz, 1H), 4.28 (bs, 1H), 3.11–3.08 (m, 1H), 3.00 (s, 3H), 3.02–2.90 (m, 1H), 2.16 (bs, 1H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 210.0, 135.4, 129.3, 128.6, 128.3, 127.7, 127.59, 110.7, 104.1, 77.3, 71.6, 59.0, 15.7; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3412, 2929, 1506, 1471, 1118, 966, 753, 683; MS (EI, m/z): 230(15, M^+), 185(100), 165(30), 152(45), 129(60), 115(50), 91(40), 77(30), 45(30); HRMS (ESI) $\text{C}_{15}\text{H}_{19}\text{O}_2$ $[\text{M}+\text{H}]^+$: 231.1379 (calculated), 231.1385 (found).

4.3.25. (2*S*,6*S*,*E*)-1-methoxy-5-methyl-7-phenylocta-3,5,6-trien-2-ol (**3ja**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.39 (d, $J = 8.4$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 2H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.51 (d, $J = 15.6$ Hz, 1H), 5.63 (ddd, $J = 15.8, 5.9, 0.8$ Hz, 1H), 4.33–4.29 (m, 1H), 3.13 (dd, A of ABX, $J_{AB} = 8.7$ Hz, $J_{AX} = 6.8$ Hz, 1H), 3.11 (dd, B of ABX, $J_{AB} = 8.7$ Hz, $J_{BX} = 3.4$ Hz, 1H), 3.01 (s, 3H), 2.36 (bs, 1H), 1.97 (s, 3H), 1.83 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.9, 138.1, 130.4, 129.0, 128.7, 127.3, 126.7, 102.2, 101.0, 77.4, 71.7, 59.0, 17.5, 15.8; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432, 2922, 1498, 1449, 1135, 1027, 978, 767, 689, 593; MS (EI, m/z): 244(10, M^+), 199(100), 181(35), 166(45), 128(35), 105(20), 91(30), 77(20), 45(25); HRMS (ESI) $\text{C}_{16}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 245.1535 (calculated), 245.1536 (found).

4.3.26. (2*S*,6*S*,*E*)-1-methoxy-7-(4-methoxyphenyl)-5-methyl-7-phenylhepta-3,5,6-trien-2-ol (**3ke**)

Isolated as a 91:9 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.52–7.46 (m, 2H), 7.40–7.36 (m, 1H), 7.38 (d, $J = 8.8$ Hz, 1H), 7.18–7.14 (m, 2H), 7.10–7.06 (m, 1H), 6.79–6.75 (m, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 6.58 (dd, $J = 15.8, 1.4$ Hz, 1H), 5.63 (dd, $J = 15.8, 5.9$ Hz, 1H), 4.30 (q, $J = 5.6$ Hz, 1H), 3.29 (s, 3H), 3.11 (dd, A of ABX, $J_{AB} = 8.6$ Hz, $J_{AX} = 5.8$ Hz, 1H), 3.08 (dd, B of ABX, $J_{AB} = 8.6$ Hz, $J_{BX} = 2.4$ Hz, 1H), 3.00 (s, 3H), 2.31 (bs, 1H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 210.5, 160.0, 138.2, 130.59, 130.0, 129.9, 129.43, 129.2, 129.1, 127.9, 114.7, 110.3, 103.2, 77.4, 71.6, 59.0, 55.2, 16.0; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3432, 2931, 1507, 1267, 1180, 1122, 1036, 978, 834, 767, 700; MS (EI, m/z): 336 (30, M^+), 291(100), 262(65), 247(40),

183(30), 155(25), 30(25), 45(45); HRMS (ESI) $\text{C}_{22}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$: 337.1798 (calculated), 337.1799 (found).

4.3.27. Methyl (3*R*,7*S*,*E*)-7-hydroxy-8-methoxy-4-methyl-2-phenylocta-2,3,5-trienoate (**3la**)

Isolated as a 89:11 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.74–7.70 (m, 2H), 7.18–7.12 (m, 2H), 7.05–7.01 (m, 1H), 6.38 (dd, $J = 15.8, 1.2$ Hz, 1H), 5.55 (dd, $J = 15.8, 5.6$ Hz, 1H), 4.20–4.14 (m, 1H), 3.36 (s, 3H), 3.00–2.93 (m, 2H), 2.94 (s, 3H), 2.04 (bs, 1H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 216.7, 166.5, 139.9, 131.1, 129.4, 129.0, 128.3, 127.0, 105.2, 103.4, 77.1, 71.4, 59.0, 52.2, 15.0; MS (EI, m/z): 288(<5, M^+), 256(3), 211(5), 183(5), 155(17), 115(8), 89(4), 77(9), 51(5), 45(100); FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3419, 2922, 2851, 1926, 1716, 1492, 1434, 1369, 1321, 1273, 1195, 1171, 1123, 1062, 1039, 964, 918, 898, 781, 694; HRMS (ESI) $\text{C}_{17}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 289.1434 (calculated), 289.1439 (found).

4.3.28. (2*S*,6*S*,*E*)-7-cyclohexyl-1-methoxy-5-methyl-7-phenylhepta-3,5,6-trien-2-ol (**3ma**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.43 (d, $J = 8.2$ Hz, 2H), 7.19 (d, $J = 7.2$ Hz, 2H), 7.08–7.04 (m, 1H), 6.57 (d, $J = 15.7$ Hz, 1H), 5.63 (ddd, $J = 15.7, 5.9, 0.8$ Hz, 1H), 4.36–4.32 (m, 1H), 3.15 (dd, A of ABX, $J_{AB} = 9.2$ Hz, $J_{AX} = 7.1$ Hz, 1H), 3.11 (dd, B of ABX, $J_{AB} = 9.2$ Hz, $J_{BX} = 3.6$ Hz, 1H), 3.01 (s, 3H), 1.48–1.41 (m, 1H), 2.34 (bs, 1H), 1.96–1.93 (m, 2H), 1.86 (d, $J = 0.8$ Hz, 3H), 1.72–1.58 (m, 3H), 1.30–1.08 (m, 5H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.6, 137.7, 130.7, 129.1, 128.3, 127.6, 127.3, 112.7, 104.2, 77.5, 71.7, 59.0, 39.3, 33.8, 33.8, 27.3, 27.3, 27.0, 16.1; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3444, 2923, 2858, 1506, 1458, 1123, 953, 774, 701; MS (EI, m/z): 312(10, M^+), 267(70), 181(100), 141(50), 91(80), 45(60); HRMS (ESI) $\text{C}_{21}\text{H}_{29}\text{O}_2$ $[\text{M}+\text{H}]^+$: 313.2161 (calculated), 313.2178 (found).

4.3.29. (2*S*,6*S*,*E*)-1-methoxy-5,8,8-trimethyl-7-phenylnona-3,5,6-trien-2-ol (**3na**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.30–7.27 (m, 2H), 7.14–7.12 (m, 2H), 7.09–7.05 (m, 1H), 6.59 (dd, $J = 15.7, 1.2$ Hz, 1H), 5.51 (dd, $J = 16.0, 4.3$ Hz, 1H), 4.35–4.31 (m, 1H), 3.13 (dd, A of ABX, $J_{AB} = 9.3$ Hz, $J_{AX} = 8.1$ Hz, 1H), 3.08 (dd, B of ABX, $J_{AB} = 9.3$ Hz, $J_{BX} = 3.7$ Hz, 1H), 3.00 (s, 3H), 2.24 (bs, 1H), 1.77 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ : 206.1, 138.5, 131.2, 130.2, 128.9, 128.5, 127.7, 127.3, 127.1, 100.9, 77.5, 71.6, 58.9, 35.7, 31.8, 30.5, 16.4; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3422, 2960, 1460, 1199, 1132, 969, 709; MS (EI, m/z): 286 (10, M^+), 241(75), 197(100), 165(35), 141(40), 105(85), 57(95); HRMS (ESI) $\text{C}_{19}\text{H}_{27}\text{O}_2$ $[\text{M}+\text{H}]^+$: 287.2005 (calculated), 287.2016 (found).

4.3.30. (*Z*)-1-Methoxy-5,8,8-trimethyl-3-phenylnon-4-en-6-yn-2-ol (**4na**)

^1H NMR (400 MHz, C_6D_6) δ : 7.40 (d, 7.8 Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 7.6$ Hz, 1H), 6.12 (dd, $J = 9.6, 1.4$ Hz, 1H), 4.26 (dd, $J = 9.8, 6.0$ Hz, 1H), 4.10–4.06 (m, 1H), 3.30 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 7.1$ Hz, 1H), 3.23 (dd, B of ABX, $J_{AB} = 9.4$ Hz, $J_{BX} = 3.4$ Hz, 1H), 3.00 (s, 3H), 2.22 (s, 1H), 1.80 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ : 143.4, 136.4, 129.1, 128.3, 127.0, 121.1, 102.8, 79.7, 75.8, 74.6, 59.0, 50.4, 31.6, 28.6, 24.0; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3446, 2910, 1459, 1364, 1117, 1079, 688; MS (EI, m/z): 268(5), 212(100), 197(65), 169(65), 155(95), 141(35), 91(55), 41(40).

4.3.31. (2*S*,6*S*,*E*)-1-methoxy-7-phenylundeca-3,5,6-trien-2-ol (**3oa**)

Isolated as a 89:11 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.44 (d, $J = 7.0$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 2H), 7.06 (t, $J = 7.2$ Hz, 1H), 6.37 (ddd, $J = 15.3, 10.6, 1.2$ Hz, 1H), 6.16 (dt, $J = 10.6, 2.9$ Hz, 1H), 5.61 (dd, $J = 15.5, 5.7$ Hz, 1H), 4.27–4.23 (m, 1H), 3.09 (dd, A of ABX, $J_{AB} = 9.4$ Hz, $J_{AX} = 8.1$ Hz, 1H), 3.05 (dd, B of ABX,

$J_{AB} = 9.4$ Hz, $J_{BX} = 3.6$ Hz, 1H), 2.98 (s, 3H), 2.39–2.34 (m, 2H), 2.24 (bs, 1H), 1.52 (quint, $J = 7.2$ Hz, 2H), 1.32 (sext, $J = 7.6$ Hz, 2H), 0.85 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 209.0, 137.3, 131.6, 129.1, 128.5, 127.5, 127.1, 108.2, 97.6, 77.2, 71.3, 58.9, 30.8, 30.5, 23.2, 14.5; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3426, 2932, 1450, 1133, 974, 772, 701; MS (EI, m/z): 272(<5, M^+); 254(5), 227(20), 209(20), 185(65), 167(55), 155(75), 141(70), 129(65), 115(70), 91(100), 77(30), 45(50).

4.3.32. (2S,6S,E)-5-butyl-1-((tert-butylidimethylsilyloxy)-7-phenylundeca-3,5,6-trien-2-ol (**3pa**)

Isolated as a 92:8 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.48 (d, $J = 8.8$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 6.8$ Hz, 1H), 6.54 (d, $J = 15.7$ Hz, 1H), 5.80 (ddd, $J = 15.7$, 6.0, 0.4 Hz, 1H), 4.27 (bs, 1H), 3.55 (dd, A of ABX, $J_{AB} = 9.8$ Hz, $J_{AX} = 7.6$ Hz, 1H), 3.45 (dd, B of ABX, $J_{AB} = 9.8$ Hz, $J_{BX} = 3.4$ Hz, 1H), 2.44 (t, $J = 7.2$ Hz, 2H), 2.29 (t, $J = 8.0$ Hz, 2H), 1.64–1.54 (m, 4H), 1.40–1.29 (m, 4H), 0.91 (s, 9H), 0.87 (t, $J = 7.6$ Hz, 3H), 0.85 (t, $J = 7.6$ Hz, 3H), -0.01 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ : 208.2, 137.9, 130.2, 129.1, 128.3, 127.4, 126.9, 108.6, 108.0, 73.6, 68.2, 31.0, 30.9, 30.8, 29.8, 26.4, 23.5, 23.3, 18.8, 14.5, 14.5, -4.9 ; MS (EI, m/z): 371(10), 336(5), 315(20), 296(25), 279(25), 212(20), 168(45), 116(60), 91(55), 75(100), 56(95); FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3437, 2917, 1451, 1272, 1093, 849, 776, 685. HRMS (ESI) $\text{C}_{27}\text{H}_{44}\text{O}_2\text{SiNa}^+$ [$\text{M}+\text{Na}$] $^+$: 451.3003 (calculated), 451.300 (found).

4.3.33. (2S,6S,E)-5-cyclohexyl-1-methoxy-7-phenylundeca-3,5,6-trien-2-ol (**3qa**)

Isolated as a 88:12 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.51 (d, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.07 (t, $J = 7.2$ Hz, 1H), 6.39 (dd, $J = 16.0$, 1.2 Hz, 1H), 5.86 (dd, $J = 16.0$, 5.9 Hz, 1H), 4.35–4.31 (m, 1H), 3.14 (dd, A of ABX, $J_{AB} = 9.5$ Hz, $J_{AX} = 8.9$ Hz, 1H), 3.10 (dd, B of ABX, $J_{AB} = 9.5$ Hz, $J_{BX} = 4.0$ Hz, 1H), 2.99 (s, 3H), 2.46–2.42 (m, 2H), 2.29 (bs, 1H), 2.26–2.22 (m, 1H), 2.07–2.04 (m, 2H), 1.71–1.56 (m, 4H), 1.39–1.06 (m, 7H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 207.1, 138.0, 129.1, 128.9, 128.3, 127.3, 126.7, 114.4, 109.0, 77.5, 71.8, 58.9, 39.3, 33.8, 33.7, 31.1, 30.8, 27.3, 27.3, 27.0, 23.4, 14.5; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3446, 2918, 2846, 1424, 1142, 1000, 777, 683; MS (EI, m/z): 336(10), 309(35), 279(45), 207(40), 155(50), 91(100), 55(55), 32(55); HRMS (ESI) $\text{C}_{24}\text{H}_{35}\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 355.2631 (calculated), 355.2642 (found).

4.3.34. (Z)-5-Cyclohexyl-1-methoxy-3-phenylundec-4-en-6-yn-2-ol (**4qa**)

^1H NMR (400 MHz, C_6D_6) δ : 7.45 (d, $J = 7.8$ Hz, 2H), 7.20 (t, $J = 7.8$ Hz, 2H), 7.08 (t, $J = 7.2$ Hz, 1H), 6.22 (d, $J = 9.8$ Hz, 1H), 4.34 (dd, $J = 9.8$, 5.5 Hz, 1H), 4.14 (bs, 1H), 3.39–3.25 (m, 2H), 3.04 (s, 3H), 2.21 (t, $J = 6.4$ Hz, 2H), 2.08 (t, $J = 12.0$ Hz, 1H), 1.84 (dd, $J = 26.4$, 12.4 Hz, 2H), 1.71–1.65 (m, 2H), 1.58–1.29 (m, 7H), 1.22–1.08 (m, 3H), 0.82 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 143.6, 132.2, 129.1, 129.0, 128.3, 127.0, 95.9, 79.6, 75.9, 74.6, 59.1, 49.9, 46.4, 33.1, 32.9, 31.7, 27.1, 27.0, 26.8, 22.6, 19.9, 14.1; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3469, 2940, 1459, 1269, 1089, 876, 697; MS (EI, m/z): 336(<5), 279(65), 223(55), 197(60), 155(100), 115(40), 91(85), 55(35).

4.3.35. (2S,6R,E)-5-(tert-butyl)-1-methoxy-7-phenylundeca-3,5,6-trien-2-ol (**3ra**)

Isolated as a 85:15 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.52 (d, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.06 (t, $J = 8.0$ Hz, 1H), 6.42 (dd, $J = 15.5$, 1.4 Hz, 1H), 6.02 (dd, $J = 15.6$, 5.2 Hz, 1H), 4.31 (bs, 1H), 3.04 (dd, A of ABX, $J_{AB} = 7.7$ Hz, $J_{AX} = 7.3$ Hz, 1H), 3.01 (dd, B of ABX, $J_{AB} = 7.7$ Hz, $J_{BX} = 1.3$ Hz, 1H), 2.93 (s, 3H), 2.47–2.42 (m, 2H), 2.24 (bs, 1H), 1.61 (quint, $J = 7.6$ Hz, 2H), 1.55 (s, 3H), 1.39–1.33 (m, 2H), 1.19 (s, 9H), 0.89 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 203.0, 138.2, 130.8, 129.2, 128.3,

127.2, 126.4, 125.7, 117.3, 109.3, 77.4, 71.5, 58.8, 34.9, 31.0, 30.8, 30.1, 23.4, 14.6; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3421, 2867, 1453, 1379, 1242, 1155, 806, 701; MS (EI, m/z): 309(<5), 253(20), 212(20), 197(65), 155(95), 140(60), 105(40), 91(100), 69(40), 57(95).

4.3.36. (Z)-5-(tert-butyl)-1-methoxy-3-phenylundec-4-en-6-yn-2-ol (**4ra**)

Isolated as a 83:17 mixture of diastereomers; ^1H NMR (400 MHz, C_6D_6) δ : 7.44 (d, 7.8 Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.06 (td, $J = 8.0$, 1.2 Hz, 1H), 6.33 (d, $J = 9.8$ Hz, 1H), 4.37 (dd, $J = 9.6$, 5.7 Hz, 1H), 4.17–4.12 (m, 1H), 3.34 (dd, A of ABX, $J_{AB} = 9.3$ Hz, $J_{AX} = 7.3$ Hz, 1H), 3.28 (dd, B of ABX, $J_{AB} = 9.3$ Hz, $J_{BX} = 3.6$ Hz, 1H), 3.02 (s, 3H), 2.28 (s, 1H), 2.21 (t, $J = 6.5$ Hz, 2H), 1.44–1.31 (m, 4H), 1.22 (s, 9H), 0.82 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 143.6, 136.1, 131.7, 129.1, 129.0, 127.0, 96.5, 79.5, 75.9, 74.6, 59.0, 50.2, 36.5, 31.7, 29.9, 22.6, 19.8, 14.1; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3452, 2958, 2923, 1468, 1354, 1115, 763, 710; MS (EI, m/z): 328(<1, M^+), 310(5), 253(25), 197(65), 155(100), 91(40), 57(25).

4.3.37. 1-Methoxy-3-(2-(2-phenylhex-1-en-1-yl)cyclohex-1-en-1-yl)propan-2-one (**5sa**)

(E): ^1H NMR (400 MHz, C_6D_6) δ : 7.35 (d, $J = 7.6$ Hz, 2H), 7.20–7.16 (m, 2H), 7.11 (d, $J = 8.0$ Hz, 1H), 6.14 (s, 1H), 3.61 (d, $J = 0.8$ Hz, 2H), 3.15 (s, 2H), 3.02 (s, 3H), 2.51 (t, $J = 7.2$ Hz, 2H), 2.08 (d, $J = 9.2$ Hz, 4H), 1.58 (bs, 4H), 1.35–1.21 (m, 4H), 0.80 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 206.0, 142.9, 142.5, 133.5, 129.0, 128.7, 128.3, 128.1, 127.2, 78.0, 59.2, 45.3, 39.4, 31.1, 30.7, 30.4, 23.6, 23.4, 22.8, 14.4; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2922, 1738, 1440, 1209, 1094, 767, 700; MS (EI, m/z): 326(10, M^+); 281(25), 238(95), 181(55), 129(30), 91(100), 45(35).

(Z): ^1H NMR (400 MHz, C_6D_6) δ : 7.31 (d, $J = 8.0$ Hz, 2H), 7.20–7.16 (m, 2H), 7.08–7.03 (m, 1H), 6.12 (s, 1H), 3.67 (d, $J = 0.8$ Hz, 2H), 3.12 (s, 2H), 3.08 (s, 3H), 2.40 (t, $J = 7.2$ Hz, 2H), 1.96 (bs, 2H), 1.87 (bs, 2H), 1.48–1.36 (m, 4H), 1.38 (s, 4H), 0.82 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ : 205.8, 143.1, 142.0, 133.5, 129.5, 128.5, 128.0, 127.7, 78.0, 59.2, 45.2, 39.4, 31.3, 31.0, 30.4, 23.7, 23.4, 22.8, 14.4; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2922, 1738, 1440, 1209, 1094, 767, 700; MS (EI, m/z): 326(20, M^+); 281(25), 238(95), 181(60), 141(35), 91(100), 45(35).

4.3.38. (3aS,7S,7aS,E)-7-((R)-1-hydroxy-2-methoxyethyl)-5-methyl-2-phenyl-4-(1-phenylpentylidene)-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (**6ba**)

Isolated as a 91:9 mixture of diastereomers; ^1H NMR (400 MHz, CDCl_3) δ : 7.46–7.42 (m, 3H), 7.37 (t, $J = 7.6$ Hz, 3H), 7.32–7.29 (m, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.00 (d, $J = 2.4$ Hz, 1H), 4.30 (q, $J = 5.5$ Hz, 1H), 3.93 (d, $J = 8.6$ Hz, 1H), 3.64–3.56 (m, 2H), 3.41 (s, 3H), 3.14 (dd, $J = 8.6$, 5.9 Hz, 1H), 2.56–2.48 (m, 1H), 2.40–2.33 (m, 2H), 2.06 (t, $J = 1.6$ Hz, 3H), 1.34–1.24 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ : 178.8, 177.0, 143.6, 140.8, 138.4, 131.8, 129.1, 128.8, 128.24, 128.16, 127.3, 126.5, 126.0, 74.8, 69.7, 59.1, 47.1, 44.9, 40.0, 36.0, 30.5, 22.9, 22.2, 13.9; FTIR ($\nu_{\text{max}}/\text{cm}^{-1}$): 2954, 2849, 1724, 1512, 1367, 1209, 1128, 71; MS (EI, m/z): 441(90), 385(50), 328(40), 237(20), 207(30), 181(100), 145(90), 91(90), 45(35). HRMS (EI) $\text{C}_{29}\text{H}_{34}\text{NO}_4$ [$\text{M}+\text{H}$] $^+$: 460.2482 (calculated); 460.2482 (found).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.tet.2018.05.030>.

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