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PII: S0040-4020(18)30549-0

DOI: 10.1016/j.tet.2018.05.030

Reference: TET 29537

To appear in: *Tetrahedron*

Received Date: 12 September 2017

Revised Date: 26 January 2018

Accepted Date: 11 May 2018

Please cite this article as: Ziyanak Fı, Kuş M, Alkan-Karadeniz L, Artok L, Palladium-catalysed reactions of conjugated enyne oxiranes with organoborons: A diastereoselective method of the synthesis of 2,4,5-trienol derivatives, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.05.030.

Graphical Abstract

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[a]*Department of Chemistry, Faculty of Science, Izmir Institute of Technology, Urla, Izmir 35430, Turkey*
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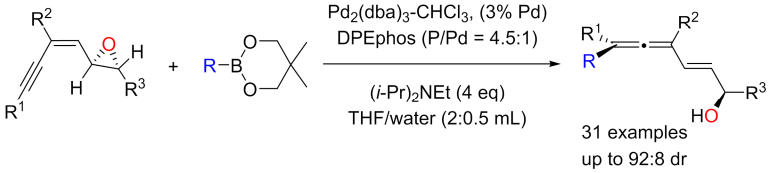

Tetrahedron
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Palladium-catalysed reactions of conjugated enyne oxiranes with organoborons: A diastereoselective method of the synthesis of 2,4,5-trienol derivatives

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

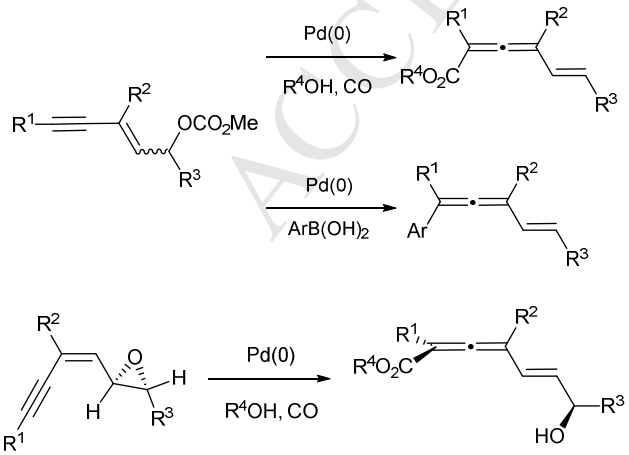
Keywords:
Allene
Vinylallene
2,4,5-trienol
Enyne oxirane
Organoboron

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 synthesised, with good diastereomeric ratios, under mild conditions.

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]

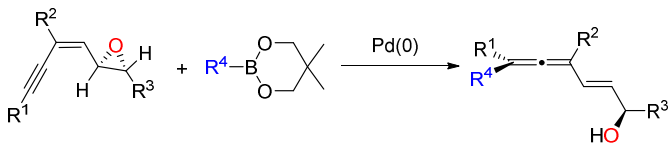


Scheme 1. Palladium-catalysed alkoxycarbonylation and Miyaura-Suzuki type reactions of enyne carbonates and enyne oxiranes.[5]

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 alkoxycarbonylation to conjugated enynes carrying an oxirane moiety to synthesize 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 reactions[7] and thus produce aryl- or alkenyl-substituted vinylallenes bearing a hydroxyl group on the allylic position (Scheme 2).



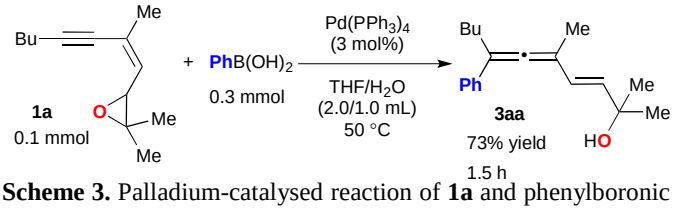
Scheme 2. This study: Palladium-catalysed arylation of enyne oxiranes.

2. Results and discussion

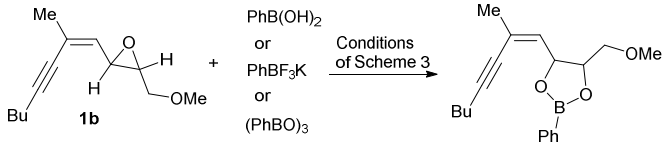
A promising result was obtained in the reaction of the enyne oxirane **1a**, which had a dimethyl group on the oxirane terminus, with phenylboronic acid in the presence of $Pd(PPh_3)_4$ (3 mol%) in

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 optimisation 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 $PhBF_3K$ and $(PhBO)_3$ also shared the same fate.



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



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

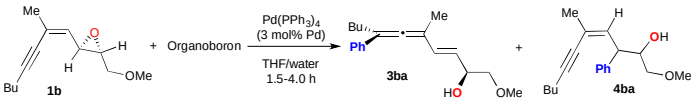
Palladium-catalysed condensation of allylic oxiranes with organoboronic acids has been previously documented,[8] so the latter two reagents were probably also partially hydrolysed to phenylboronic acid under aqueous conditions. Encouragingly, the desired vinylallene product **3ba** could be obtained with a moderate yield (67%) and diastereomeric ratio (dr) of 79:21, as determined by ^{1}H 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 $Pd_2(dba)_3$-$CHCl_3$/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, $AsPh_3$, dppe, 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 $(i\text{-Pr})_2$EtN was

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



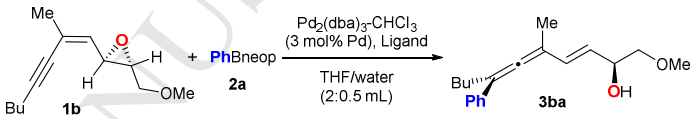
Entry	Organo-boron	THF/water (mL)	Temp. (°C)	Yield (%)[b] **3ba**:**4ba**	dr of **3ba**[b]
1	$NaBPh_4$	2:1	50	67:-	79:11
2	$NaBPh_4$	2:0.5	50	75:-	83:17
3	$NaBPh_4$	2:0.5	25	31:33	N.D.
4	PhNeop	2:0.5	25	77:-	73:27
5[c]	PhNeop	2:0.5	25	81:-	76:24

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

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

[c]Performed using $Pd_2(dba)_3$-$CHCl_3$/PPh_3 (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_2Me	–	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	87:12
9	DPEPhos	Et_3N (2)	5	90	89:11
10	DPEPhos	$(i\text{-Pr})_2$EtN (2)	2	90	90:10
11	DPEPhos	$(i\text{-Pr})_2$EtN (4)	4	92[d]	91:9
12	DPEPhos	$(i\text{-Pr})_2$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(diphenylphosphino)propane; dppb: 1,4-Bis-(diphenylphosphino)butane; DPEPhos: Bis[(2-diphe-nylphosphino)-phenyl] ether.

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

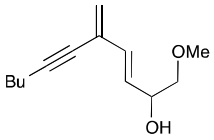
[d]Yield of isolated product is provided.

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

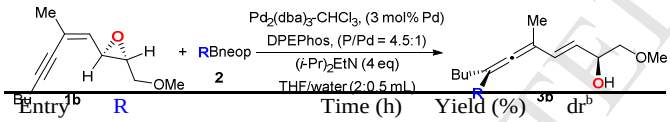
expected vinylallenes in good yields and stereoselectivities in relatively short reaction periods, regardless of the substitution pattern of **2** (Table 3, entries 1-4). However, the allylic substitution product **4bf** was the main product of the reaction carried out with the highly encumbered 2,6-dimethyl 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 R^3 group could also be used in benzyl- or silyl-protected

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



Entry	R	Time (h)	Yield (%)	dr[b]
1	*p*-MeC_6H_4 **2b**	1.5	93 **3bb**	92:8
2	*m*-MeC_6H_4 **2c**	2	72 **3bc**	90:10
3	*o*-MeC_6H_4 **2d**	1.5	87 **3bd**	92:8
4	*p*-$OMeC_6H_4$ **2e**	1.5	95 **3be**	91:9
5[c]	2,6-$Me_2C_6H_4$ **2f**	20	28 **3bf**	74:26
6	*p*-$CF_3C_6H_4$ **2g**	12	81 **3bg**	92:8
7	*m*-ClC_6H_4 **2h**	9	78 **3bh**	90:10
8	*o*-FC_6H_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	(*E*)-1-Pentenyl **2l**	4	63 **3bl**	83:17
12	(*E*)-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 ^{1}H NMR.

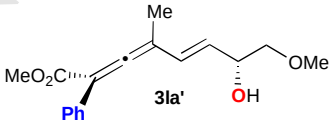
[c]The reaction also yielded 43% of **4bf**.

[d]A *β*-hydride elimination product was the only product of this reaction.

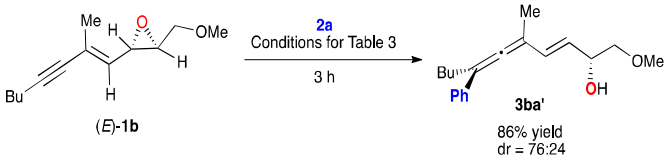
forms effectively, the protection of the hydroxyl functionality was not compulsory, although there was some reduction in yield without such protection (entries 3-5). The presence of a larger group in R^3, such as 2-methoxypropan-2-yl group (**1g**), was also well-tolerated by the method (entry 6). However, the reaction was dramatically decelerated when there was only one methyl group at the oxirane terminus (**1h**) (entry 7).

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 (R^1) (entries 8–11). However, the regioselectivity of the method was sensitive to the size of the R^1 and R^2 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 R^1 was Cy (**1m**) or *t*-Bu (**1n**) or R^2 was Cy (**1q**) under the standard conditions. However, the formation of these by-products could be minimized by using Ph_3P, albeit with a decrease of dr of the product. On the other hand, the formation of **4ra** was almost exclusive when R^2 was *t*-Bu and the DPEphos ligand was used, and **3ra** formation was not satisfactory even using the Ph_3P ligand (entry 17).

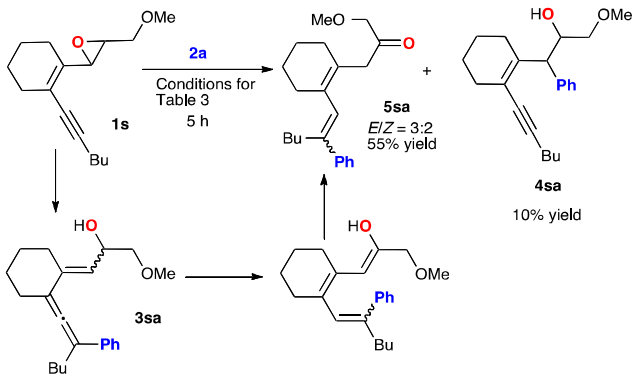
The diastereomeric forms of the products **3** were estimated by comparison with NMR spectra of **3la** (entry 11) and its diastereomeric form **3la'** synthesized in another study[5d] (see the supporting information).



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).

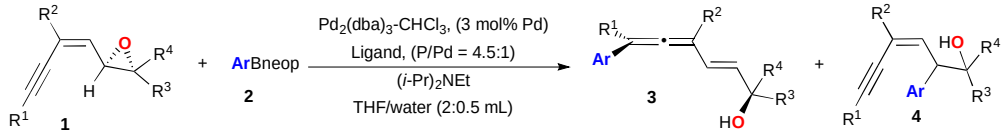


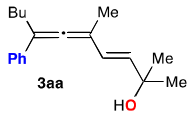
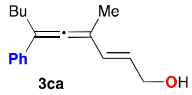
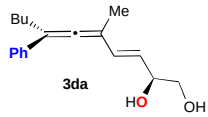
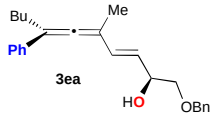
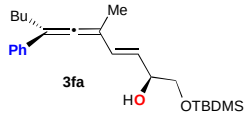
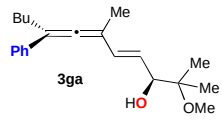
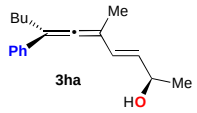
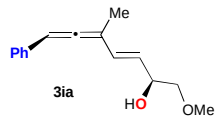
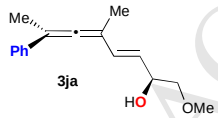
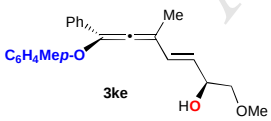
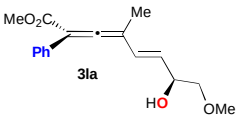
Scheme 5. The reaction of (*E*)-**1b** and **2a**.

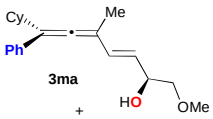
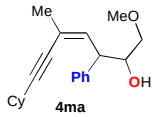
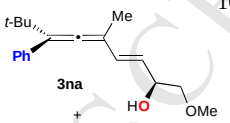
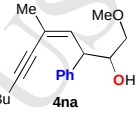
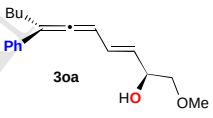
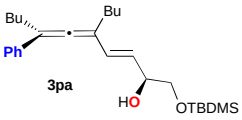
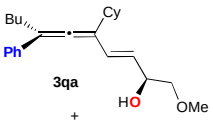
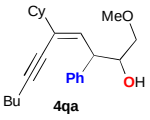
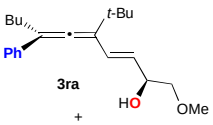
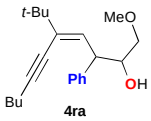


Scheme 6. Palladium-catalysed reaction of **1s** and **2a**.

Table 4. Arylation of enyne oxiranes.[a]



Entry	Product	Time (h)	Yield **3** (%)	dr[b]
1	 **3aa**	1.5	91	-
2	 **3ca**	2	78	-
3	 **3da**	1.5	78	91:9
4	 **3ea**	2.5	88	90:10
5	 **3fa**	2	87	92:8
6	 **3ga**	2	87	92:8
7	 **3ha**	16	73	91:9
8	 **3ia**	1	74	91:9
9	 **3ja**	1	93	92:8
10	 **3ke**	3	93	91:9
11	 **3la**	2	89	89:11

Entry	Product	Time (h)	Yield **3** (%)	dr[b]
12	 **3ma** +  **4ma**	8 (5)[c]	71 (73)[c] 9 (trace)[c]	92:8 (85:15)[c] N.D.
13	 **3na** +  **4na**	16 (10)[c]	68 (71)[c] 11 (5)[c]	92:8 (88:12)[c] N.D.
14	 **3oa**	4	67	89:11
15	 **3pa**	1.5	88	92:8
16	 **3qa** +  **4qa**	3 (2)[c]	68 (72)[c] 16 (trace)[c]	88:12 (85:15)[c] N.D.
17	 **3ra** +  **4ra**	8 (3)[c]	Trace (16)[c] 62 (61)[c]	N.D. (85:15)[c] 83:17 (81:19)[c]

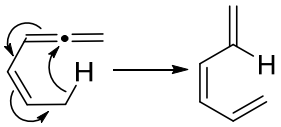
[a]Reagents and conditions: **1** (0.1 mmol), **2** (0.3 mmol), and DPEPhos ligand at 25 °C. The oxirane ring is in the form of *E*-configuration where it is applicable.

[b]Determined by ^{1}H NMR.

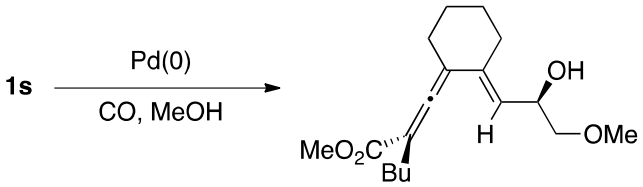
[c]Ph_3P ligand was used in these reactions.

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 isomerisation and tautomarization steps to form **5sa** products.

It has been shown in previous studies that vinylallenes can be 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 an our previous study, the palladium-catalysed alkoxycarbonylation 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]



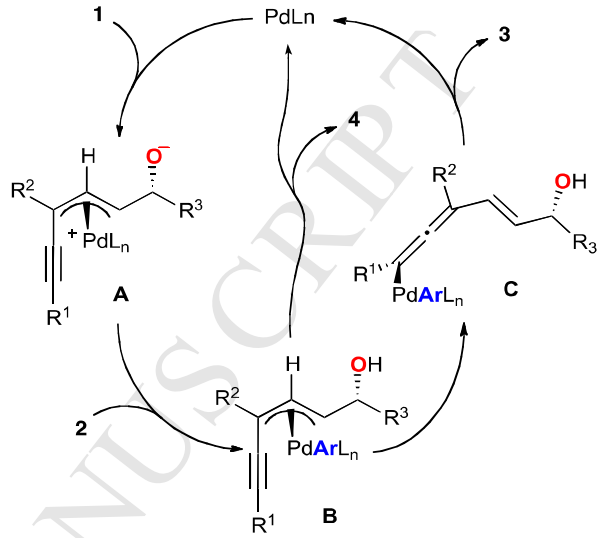
Scheme 7. Pd-catalysed alkoxycarbonylation of **1s**.[5d]

Considering that similar mechanisms are proposed for both alkoxycarbonylation[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.

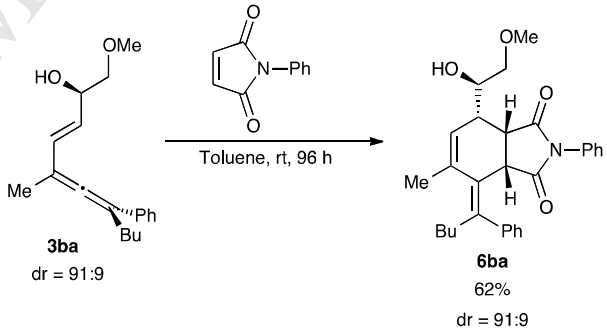
As for the reaction mechanism, as suggested in our previous reports[5] the catalytic cycle could begin with the formation of a π-allylpalladium intermediate in anti-form (**A**), which has the R^3 group oriented syn with respect to the middle allylic C−H so that vinylallene products can ultimately form 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 alkynyl 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 probably took place during the course of the reaction cycle, because it was observed that the vinylallene **3ba** was configurationally stable under the reaction conditions;[12] 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.



Scheme 8. Proposed mechanism.



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

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 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 $CDCl_3$ or C_6D_6. With C_6D_6 solvent, the ^1H NMR signals of diastereomers were usually resolved adequately, allowing

determination of diastereomeric ratios (dr) smoothly. In contrast, when using $CDCl_3$ 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 $MgSO_4$ (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 minutes 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 Et_2O, dried with $MgSO_4$ and evaporated under reduced atmosphere. The residue was analysed by ^{1}H 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**)*

^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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), $C_{19}H_{25}$ $[(M-H_2O)+H]^+$: 253.1951 (calculated), 253.1952 (found).

*4.3.2. ((2S,6S,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; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (100 MHz, C_6D_6) 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) $C_{19}H_{27}O_2$ $[M+H]^+$: 287.2006 (calculated); 287.2008 (found).

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

Isolated as a 76:24 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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**)*

^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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. (2S,6S,E)-1-methoxy-5-methyl-7-(p-tolyl)undeca-3,5,6-trien-2-ol (**3bb**)*

Isolated as a 92:8 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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): $C_{20}H_{28}O_2Na$ $[M+Na]^+$: 323.1982 (calculated), 323.1983 (found).

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

Isolated as a 90:10 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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 (ν_{max}/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. (2S,6S,E)-1-methoxy-5-methyl-7-(o-tolyl)undeca-3,5,6-trien-2-ol (**3bd**)*

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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 (ν_{max}/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. (2S,6S,E)-1-methoxy-7-(4-methoxyphenyl)-5-methylundeca-3,5,6-trien-2-ol (**3be**)*

Isolated as a 91:9 mixture of diastereomers; ^{1}H 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 (ν_{max}/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. (2S,6S,E)-7-(2,6-dimethylphenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bf**)*

Isolated as a 74:26 mixture of diastereomers; ^{1}H 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 (ν_{max}/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 (**4bf**)*

^{1}H 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 (ν_{max}/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; ^{1}H 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. (2S,6S,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; ^{1}H 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); ^{1}H 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 (ν_{max}/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. (2S,6S,E)-7-(3-chlorophenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bh**)*

Isolated as a 90:10 mixture of diastereomers; ^{1}H 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 (ν_{max}/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. (2S,6S,E)-7-(2-fluorophenyl)-1-methoxy-5-methylundeca-3,5,6-trien-2-ol (**3bi**)*

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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); ^{1}H 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 (ν_{max}/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. (2S,6S,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; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{23}H_{28}O_2Na$ $[M+Na]^+$: 359.1982 (calculated), 359.1983 (found).

*4.3.15. (2S,6S,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; ^{1}H NMR (400 MHz, C_6D_6): 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); ^{13}C NMR (101 MHz, C_6D_6): 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) $C_{23}H_{28}O_2Na$ $[M+Na]^+$: 359.1982 (calculated), 359.1983 (found).

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

Isolated as a 83:17 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{19}H_{32}O_2Na$ $[M+Na]^+$: 315.2319 (calculated), 315.2320 (found).

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

Isolated as a 70:30 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{21}H_{29}O_2$ $[M+H]^+$: 313.2161 (calculated), 313.2178 (found).

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

^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{17}H_{22}ONa$ $[M+Na]^+$: 265.1563 (calculated), 265.1569 (found).

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

Isolated as a 91:9 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) δ: 7.45-7.42 (m, 2H), 7.21-7.16 (m, 2 H), 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{18}H_{25}O_2$ $[M+H]^+$: 273.1849 (calculated), 273.1851 (found).

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

Isolated as a 90:10 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101 MHz, C_6D_6) 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) $C_{25}H_{30}O_2Na$ $[M+Na]^+$: 385.2138 (calculated), 385.2138 (found).

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

Isolated as a 92:8 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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); ^{13}C NMR (101

MHz, C_6D_6) 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) $C_{24}H_{39}O_2Si$ $[M+H]^+$: 387.2714 (calculated), 387.2716 (found).

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

Isolated as a 92:8 mixture of diastereomers; ^{1}H NMR (400 MHz, C_6D_6) 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 (ν_{max}/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) $C_{21}H_{31}O_2$ $[M+H]^+$: 315.2318 (calculated), 315.2327 (found).

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

Isolated as a 91:9 mixture of diastereomers; ^{1}H 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 (ν_{max}/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) $C_{18}H_{25}O$ $[M+H]^+$: 257.1899 (calculated), 257.1907 (found).

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

Isolated as a 91:9 mixture of diastereomers; ^{1}H 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 (ν_{max}/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) $C_{15}H_{19}O_2$ $[M+H]^+$: 231.1379 (calculated), 231.1385 (found).

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

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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 (ν_{max}/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) $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1535 (calculated), 245.1536 (found).

*4.3.26. (2S,6S,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; ^{1}H 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 (ν_{max}/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) $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798 (calculated), 337.1799 (found).

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

Isolated as a 89:11 mixture of diastereomers; ^{1}H 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 (ν_{max}/cm^{-1}): 3419, 2922, 2851, 1926, 1716, 1492, 1434, 1369, 1321, 1273, 1195, 1171, 1123, 1062, 1039, 964, 918, 898, 781, 694; HRMS (ESI) $C_{17}H_{21}O_4$ $[M+H]^+$: 289.1434 (calculated), 289.1439 (found).

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

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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} = 7.7 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 (ν_{max}/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) $C_{21}H_{29}O_2$ $[M+H]^+$: 313.2161 (calculated), 313.2178 (found).

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

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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 (ν_{max}/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) $C_{19}H_{27}O_2$ $[M+H]^+$: 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**)*

^{1}H 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 (ν_{max}/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. (2S,6S,E)-1-methoxy-7-phenylundeca-3,5,6-trien-2-ol (**3oa**)*

Isolated as a 89:11 mixture of diastereomers; ^{1}H 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 (ν_{max}/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-butyldimethylsilyl)oxy)-7-phenylundeca-3,5,6-trien-2-ol (**3pa**)*

Isolated as a 92:8 mixture of diastereomers; ^{1}H 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 (ν_{max}/cm^{-1}): 3437, 2917, 1451, 1272, 1093, 849, 776, 685. HRMS (ESI) $C_{27}H_{44}O_2SiNa^+$ $[M+Na]^+$: 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; ^{1}H 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 (ν_{max}/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) $C_{24}H_{35}O_2$ $[M+H]^+$: 355.2631 (calculated), 355.2642 (found).

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

^{1}H 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 (ν_{max}/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; ^{1}H 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 (ν_{max}/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; ^{1}H 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 (ν_{max}/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*): ^{1}H 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 (ν_{max}/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*): ^{1}H 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 (ν_{max}/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; ^{1}H 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 (ν_{max}/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) $C_{29}H_{34}NO_4$ $[M+H]^+$: 460.2482 (calculated); 460.2482 (found).

Acknowledgments

The financial support of the Scientific and Technological Research Council of Turkey and Federal Ministry of Education and Research (Germany) via the Intensified Cooperation Program (201T092) is gratefully acknowledged. We thank the Mass Spectrometry Laboratory of Dortmund University of Technology and the Environmental Research Centre of Izmir Institute of Technology for HRMS analyses and GC-MS analyses of a part of samples.

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Supplementary Material Supplementary data related to this article can be found at http://dx.doi.org/