Enantioselective Synthesis of Chromans for the Preparation of Enantiopure Vitamin E and Analogues

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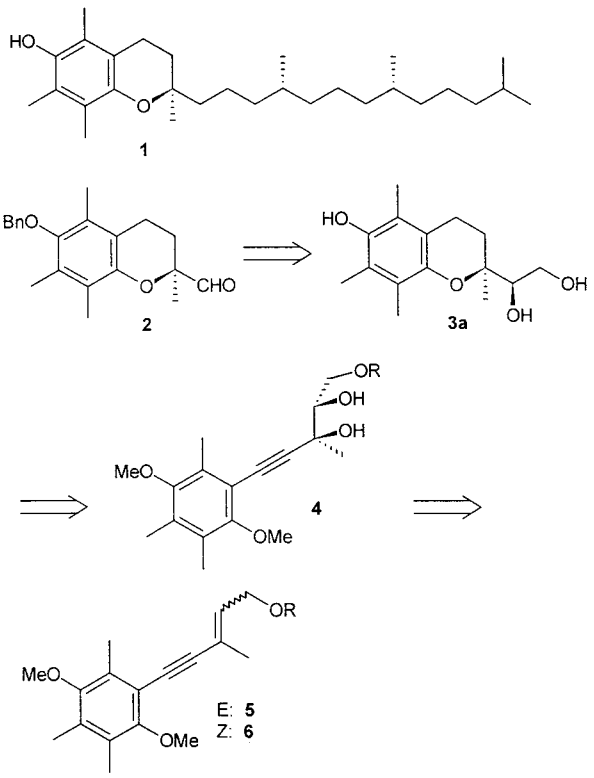
Dedicated to Professor Hans J. Schäfer on the occasion of his 60th birthday.

Coupling of the differently protected (hydroxymethyl)enynes **11a–e** and **12a–c** with the iodoarene **7** in the presence of catalytic amounts of $Pd(PPh_3)_4$ afforded the arylenynes **5a–e** and **6a–c** which were transformed into the monoprotected chiral trihydroxy compounds **13a–d** and **14a,b** by Sharpless bishydroxylation with >95% ee for **13a–d**, 91% ee for **14b** and 64% ee for **14a**. A 5-step transformation of **13a** led to the desired chroman derivative **3a** which was cleaved to give the aldehyde **2** a known precursor for the enantioselective synthesis of vitamin E.

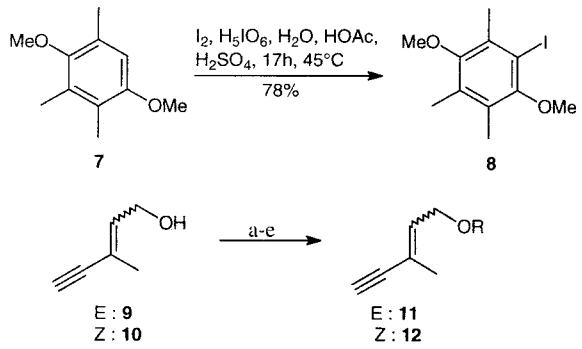
Vitamin E (**1**) possesses strong antioxidant and radical-scavenging properties in a lipophilic medium.[1] Thus, the deficiency of this vitamin causes a degeneration of cells of the nervous system and muscles; also a greater risk of getting cancer is assumed.[2] So far, synthetic vitamin E is offered only as a mixture of all eight possible stereoisomers. Therefore, there is a considerable interest in the diastereo- and enantioselective synthesis[3] of vitamin E and the preparation of structurally related compounds.[4] In the meantime, a few fat- and water-soluble compounds[5] with equal antioxidative activity have been synthesised and some of them are cardioselective.[6]

In this paper we describe a stereoselective access to chromanylethanediol **3a** which can be employed in the preparation of enantiopure vitamin E[7] as well as of various vitamin E analogues according to the functionalisation of the three hydroxy groups. Thus, the aldehyde **2**, easily obtained from **3a** by oxidative cleavage of the diol, is a known precursor[8] of vitamin E. Our retrosynthetic analysis of **3a** led to the triol derivative **4**, which was accessible from the (*E*)-enynes **5** by a Sharpless bishydroxylation.[9] In addition, we have also investigated the bishydroxylation of the (*Z*)-compounds **6**.

The synthesis of **5** and **6** was achieved starting from the known arene **7**.[10] Iodination[11] of **7** with I_2/HIO_4 to give **8**, followed by reaction with the enynes **11a–e** and **12a–c** afforded **5a–e** and **6a–c**, respectively, usually in good yields. The best results in the coupling reaction were obtained using a modified procedure reported by Negishi[12] with the zinc salt of **11** and **12**, prepared in situ from the lithium salt, in the presence of catalytic amounts of $Pd(PPh_3)_4$. It is necessary to use DMPU in the preparation of the lithium salt of **11** and **12** with BuLi in THF for stabilisation. Astoundingly, in the case of **11d** and **12b** with the *p*-methoxyphenyl protecting group the yields never exceeded 30% although careful optimisation was carried out. As byproducts in the coupling, varying amounts of the dimeric alkyne were found, which were sometimes difficult to separate. For the synthesis of **11a–e** and **12a–c** commercially available **9** and **10** were used and transformed into the corresponding ethers by known procedures.[13–15]



Scheme 1



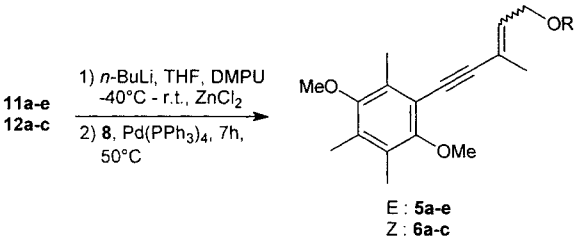
a) NaH, THF, BnBr, TBAI, 4h, 30 °C
b) NaH, THF, *p*-methoxybenzyl bromide, TBAI, 4h, 30 °C
c) Thexyldimethylsilyl chloride, imidazole, CH_2Cl_2, 18h, 0 °C, r.t.
d) Diisopropyl azodicarboxylate, PPh_3, *p*-methoxyphenol, CH_2Cl_2, 4h, r.t.
e) DHP, pyridinium *p*-toluenesulfonate, CH_2Cl_2, 2h, r.t.

Scheme 2

Table 1. Synthesis of the Enynes **11/12** from **9/10**

Product	Configuration	Conditions	Protecting group	Yield (%)
11a	*E*	a	Bn	89
11b	*E*	b	PMB	87
11c	*E*	c	TexDMS	94
11d	*E*	d	PMP	93
11e	*E*	e	THP	97
12a	*Z*	c	TexDMS	93
12b	*Z*	d	PMP	89
12c	*Z*	e	THP	96

Bn: Benzyl: PMB: *p*-methoxybenzyl: PMP: *p*-methoxyphenyl; TexDMS: Thexyldimethylsilyl: THP: tetrahydropyranyl

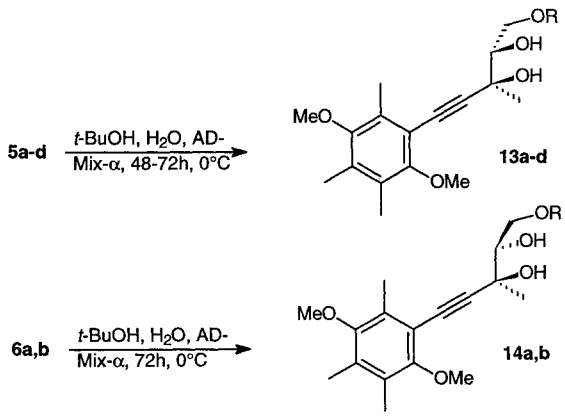


Scheme 3

Table 2. Synthesis of **5a-e** and **6a-c** from **11a-e** and **12a-c**

Product	**5a**	**5b**	**5c**	**5d**	**5e**	**6a**	**6b**	**6c**
Yield (%)	73	66	77	28	75	70	21	62

The asymmetric bishydroxylation[16] of **5a–d** and **6a,b** was performed under standard conditions as described by Sharpless (*t*-BuOH, H_2O, AD-Mix-α [$(DHQ)_2PHAL$], 0 °C) to give the diols **13a–d** and **14a,b** in good yields and high enantioselectivity.



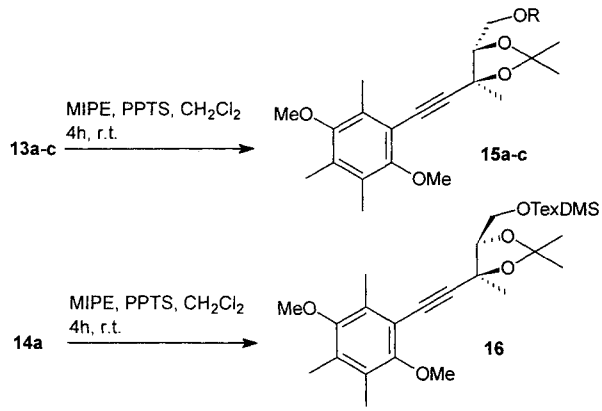
Scheme 4

Table 3. Synthesis of the Diols **13a-d** and **14a,b** from the Enynes **5a-d** and **6a,b**

Substrate	Product	Yield (%)	ee (%)
5a	**13a**	85	> 95
5b	**13b**	78	> 95
5c	**13c**	76	> 95
5d	**13d**	55	> 95
6a	**14a**	55	64
6b	**14b**	32	91

The enantiomeric excess of the diols **13a–d** and **14a,b** was determined by NMR analysis (^1H and ^{19}F) of the corresponding Mosher esters;[17] the obtained selectivity depends on the protecting group and the configuration of the double bond. As expected, and in accordance with the work of Sharpless,[16] the (*Z*)-trisubstituted alkenes **6a,b** gave in all cases lower enantiomeric excess than the (*E*)-alkenes, which led to the enantiomerically pure diols **13a–d** with > 95 % ee (by NMR analysis). Furthermore, we found that for the (*Z*)-enyne **6a** with the thexyldimethylsilyl protecting group, a worse facial discrimination is observed as compared to the (*Z*)-enyne **6b** with the *p*-methoxyphenyl group. We assign this effect to an increased steric bulkiness of the silyl ether causing unfavourable steric interaction in the binding pocket[18] of the catalyst.

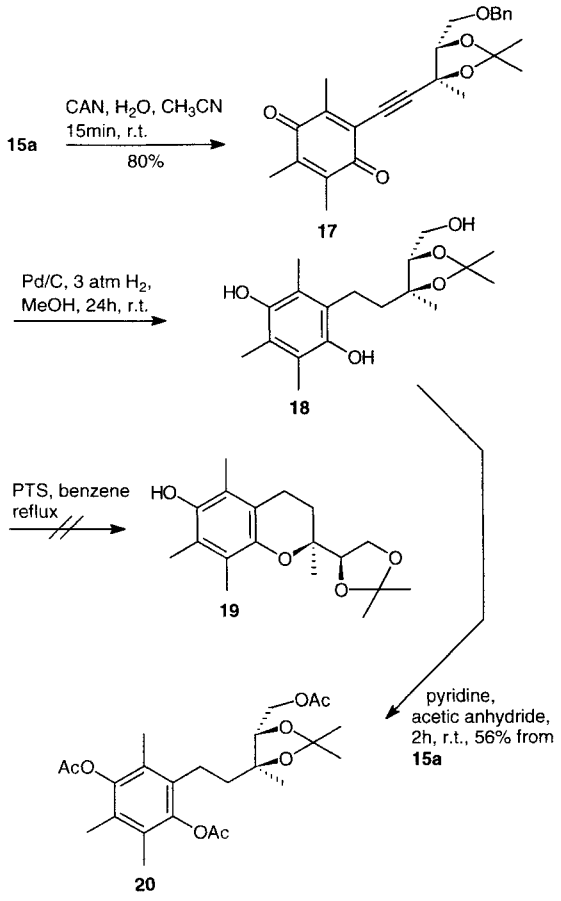
The diols **13a–c** and **14a** were easily converted into the corresponding acetonides **15a–c** and **16** in 82–89 % yield with methyl isopropenyl ether (MIPE) in CH_2Cl_2 in the presence of catalytic amounts of pyridinium *p*-toluenesulfonate.



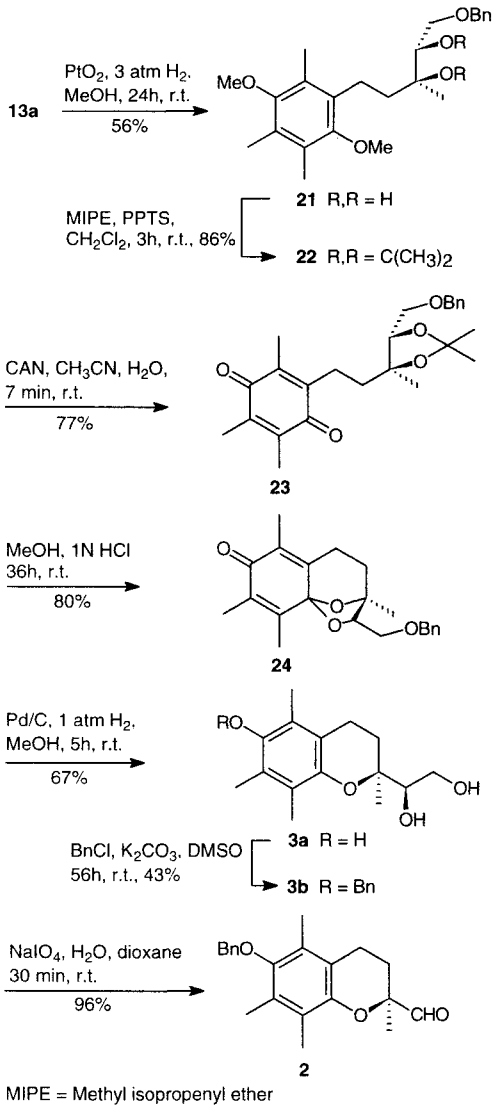
Scheme 5

For the synthesis of the desired aldehyde **2**[8] the triol derivative **15a** was oxidatively demethylated with cerium ammonium nitrate (CAN) in aqueous acetonitrile to give the quinone **17** in 90 % yield. Reduction with H_2/Pd/C led to rearomatisation, cleavage of the benzyl ether and reduction of the triple bond to give **18**. It was our hope that under treatment with an acid, **18** would undergo a transacetalisation and a stereoselective ring closure via a tertiary carbocation. Despite various efforts using dif-

ferent reaction conditions and acids however, the desired product **19** was not obtained. The formation of the intermediate **18** was confirmed by its conversion into the triacetate **20** with acetic anhydride in pyridine in 56% yield.



Scheme 6



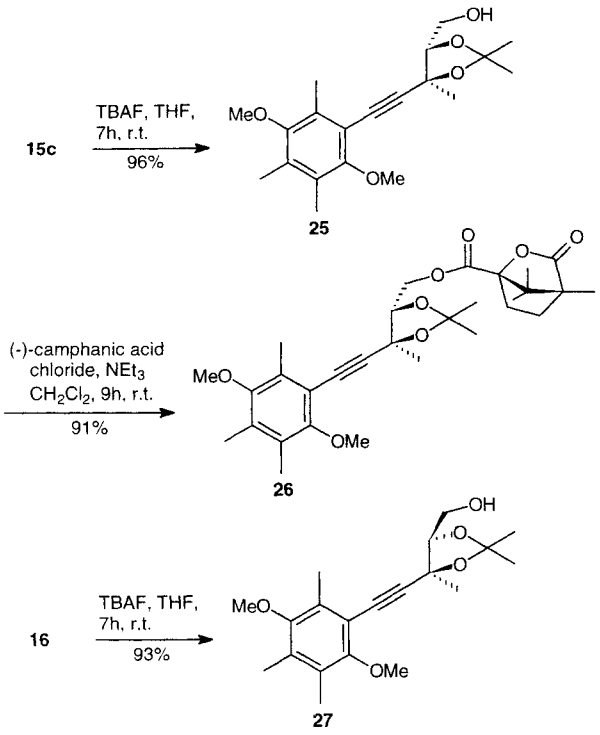
Scheme 7

Due to the failure to transform **15a** into **2**, we now used **13a** for the synthesis of **2**, which was successful. Reduction of the triple bond in **13a** with Adams catalyst in methanol followed by acetalisation with methyl isopropenyl ether under PPTS catalysis gave **22** via **21** in 48% overall yield. Oxidative demethylation to give **23** in 77% yield and treatment with methanol/aqueous hydrochloric acid afforded the tricyclic acetal **24** in 80% yield. Hydrogenation with H_2/Pd/C led to rearomatisation under regioselective cleavage of the acetal and the benzyl ether to afford **3a** in 67% yield. Selective benzylation[19] of the phenol with benzyl chloride/potassium carbonate in DMSO and oxidative cleavage of the diol accomplished the synthesis of aldehyde **2**, which is a known vitamin E precursor.[8]

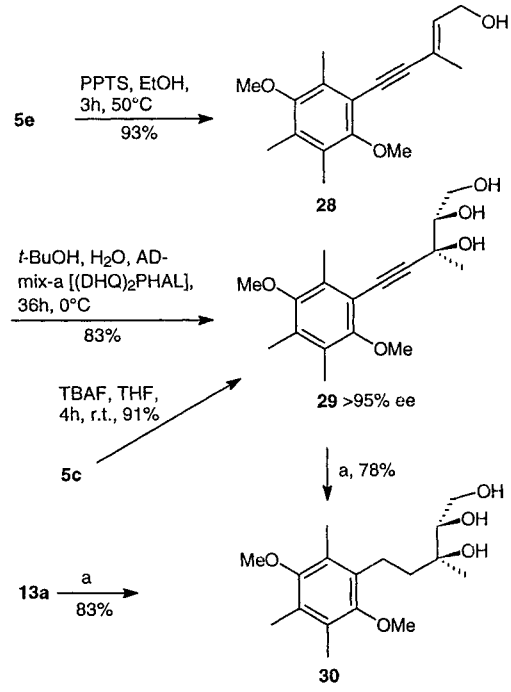
The determination of the absolute configuration of the triol derivatives was achieved by X-ray structure analysis of the camphanic acid ester **26**. Cleavage of the silyl ethers in **15c** and **16** with TBAF[13] in THF furnished the compounds **25** and **27** with a free primary hydroxy group in 96 and 93% yield, respectively, of which **25** was transformed into the crystalline ester **26** in 91% yield using (−)-camphanic acid chloride.[20]

In addition to the bishydroxylation of the protected enynes **5a–d** and **6a,b** we also used **28** with a free hydroxy group, which was obtained[15] from **5e** by treatment with PPTS in ethanol in 93% yield. Bishydroxylation of **28** under standard conditions gave the triol **29** in good yield and excellent enantioselectivity which can also be synthesised from **5c** using TBAF in THF in 91% yield. Hydrogenation[8] of both **29** and **13a** with H_2/Pd/C led to the saturated compound **30**.

In conclusion, we have shown that the diastereomeric enynes **5a–d** and **6a,b**, both easily accessible, can be transformed into the chiral triol derivatives **13a–d** and **14a,b**. Using the (*E*)-alkenes **5a–d** to give **13a–d**, the enantioselectivity was >95% in all cases: **14b** was obtained with ee >91%. Compound **13a** was transformed into the aldehyde **2** which is a known precursor of vita-



Scheme 8



a) Pd/C, MeOH, 3 atm H_2, 18h, r.t.

Scheme 9

min E. The scope of the described approach is quite high, since not only the diastereopure and in most cases enantiopure diols **13** and **14** can be obtained in a straightforward way but also their enantiomers could easily be prepared by using quinidine as the chiral ligand in the Sharpless bishydroxylation. Thus, all four stereoisomers of the triols are accessible. Furthermore, the obtained enantiopure compounds are good substrates for the synthesis of vitamin E analogues.

All reactions were carried out in an inert atmosphere. ^{1}H NMR and ^{13}C NMR spectra: Varian XL-200, VXR-200, Bruker AMX-300, Varian VXR-500S. IR: Bruker IFS-25. MS and HMRS: MAT 95. Elemental analyses: analytical laboratory of the University of Göttingen. Column chromatography: Macherey, Nagel & Co. Kieselgel 60 (0.063–0.200 mm). Analytical TLC: Macherey, Nagel & Co. (SIL G/UV_{254}). Solvents (distilled from): Et_2O (KOH or Na/benzophenone), petroleum ether bp 40–80 °C (KOH), EtOAc (CaH_2), THF ($LiAlH_4$). Satisfactory elemental analyses (C, H ± 0.4%) or correct HMRS were obtained for all new compounds.

(*E*)-1-Benzyloxy-3-methylpent-2-en-4-yne (11a):
To a solution of NaH (820 mg, 20.5 mmol, 60% suspension in mineral oil) in THF (8 mL) was added **9** (2.06 mL, 20.0 mmol) in THF (8 mL) dropwise at r.t. After the evolution of gas had ceased, BnBr (2.37 mL, 20.0 mmol) in THF (8 mL) and TBAI (200 mg, 0.54 mmol) were added and the solution was stirred for 4 h at 30 °C, H_2O was added and the mixture extracted with Et_2O (2 × 100 mL) and the combined organic layers were washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The crude product was purified by distillation; yield: 3.31 g (89%); colorless oil: bp 110 °C/1 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.81 (s, 3H), 2.83 (s, 3H), 4.10 (d, J = 7 Hz, 2H), 4.49 (s, 2H), 6.10 (t, J = 7 Hz, 1H), 7.26–7.40 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.42, 65.81, 72.14, 75.18, 85.67, 120.3, 127.6, 127.6, 128.3, 134.9, 137.9.

IR (film): ν = 3292 (C≡C*H*), 3064 (C=C*H*), 2096 (C≡C), 1636 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%) = 186 (12, M^+).

(*E*)-1-(4-Methoxybenzyloxy)-3-methylpent-2-en-4-yne (11b):
To a solution of NaH (820 mg, 20.5 mmol, 60% suspension in mineral oil) in THF (8 mL) was added **9** (2.06 mL, 20.0 mmol) in THF (8 mL) dropwise at r.t. After the evolution of gas had ceased 4-methoxybenzyl bromide (4.04 g, 20.0 mmol) in THF (8 mL) and TBAI (200 mg, 0.54 mmol) were added and the solution was stirred for 4 h at 30 °C. H_2O was added and the mixture extracted with Et_2O (2 × 100 mL) and the combined organic layers were washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The crude product was purified by distillation; yield: 3.76 g (87%); colorless oil: bp 105 °C/0.05 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.80 (s, 3H), 2.82 (s, 3H), 3.80 (s, 3H), 4.06 (d, J = 7 Hz, 2H), 4.44 (s, 2H), 6.08 (t, J = 7 Hz, 1H), 6.78 (m_c, 2H), 7.27 (m_c, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.48, 55.15, 65.57, 71.86, 75.13, 85.76, 113.7, 120.2, 129.3, 130.0, 135.1, 159.1.

IR (film): ν = 3288 (C≡C*H*), 3034 (C=C*H*), 2096 (C≡C), 1612, 1514 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%) = 216 (9, M^+), 135 (67), 121 (100).

Silylation of Alcohols; (*E*)-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-3-methylpent-2-en-4-yne (11c): Typical Procedure 1:
To a solution of thexyldimethylsilyl chloride (4.21 mL, 21.0 mmol) and imidazole (2.01 g, 29.0 mmol) in CH_2Cl_2 (25 mL) was added at 0 °C **9** (2.06 mL, 20 mmol) in CH_2Cl_2 (10 mL). Warming up within 18 h was followed by dilution with CH_2Cl_2 (25 mL) and extraction with cold H_2O (2 × 100 mL). The solution was washed with brine, dried (Na_2SO_4) and concentrated. The crude product was purified by distillation; yield: 4.48 g (94%); colorless oil: bp 60 °C/0.02 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 6H), 0.82 (s, 6H, 1′-H), 0.86 (d, J = 7 Hz, 6H), 1.59 (sept, J = 7 Hz, 1H), 1.77 (s, 3H), 2.77 (s, 1H), 4.19 (d, J = 7 Hz, 2H), 5.97 (t, J = 7 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −3.12, 17.38, 18.49, 20.30, 25.16, 34.15, 59.61, 74.47, 86.10, 117.5, 138.7.

IR (film): ν = 3314 (C≡C*H*), 3034 (C=C*H*), 2098 (C≡C), 1636 (C=C) cm^{-1}

MS (70 eV, EI): *m/z* (%): 139 (42), 75 (100).

(Z)-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-3-methylpent-2-en-4-yne **(12a)**:

Reaction of **10** according to Typical Procedure 1; yield: 93%; colorless oil: bp 50°C/0.01 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.12 (s, 6H), 0.84 (s, 6H), 0.88 (d, J = 7 Hz, 6H), 1.62 (sept, J = 7 Hz, 1H), 1.77 (s, 3H), 3.14 (s, 1H), 4.35 (d, J = 7 Hz, 2H), 5.85 (t, J = 7 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −3.12, 18.48, 20.33, 22.80, 25.15, 34.14, 61.87, 81.80, 82.01, 117.4, 138.7.

IR (film): ν = 3310 (C≡C*H*), 3028 (C=C*H*), 1636 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 153 (26), 75 (100).

Mitsunobo-Type Phenylation of Alcohols; (*E*)-(4-Methoxyphenoxy)-3-methylpent-2-en-4-yne (11d); Typical Procedure 2:

To an ice-cold solution of **9** (1.03 mL, 10.0 mmol), PPh_3 (3.6 g, 13.7 mmol) and 4-methoxyphenol (3.85 g, 31.0 mmol) was added diisopropyl azodicarboxylate (2.71 mL, 13.7 mmol) and the solution was stirred for 4 h at r. t. The solvent was evaporated and the residue subjected to column filtration (200 g silica gel, EtOAc/petroleum ether 10:1) and distillation; yield: 1.88 g (93%); colorless oil, which solidified in the refrigerator; bp 92°C/0.01 mbar; mp 41°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.91 (d, J = 1 Hz, 3H), 2.86 (s, 1H), 3.77 (s, 3H), 4.56 (d, J = 7 Hz, 2H), 6.16 (dt, J = 7, 1 Hz, 1H), 6.81 (s, 4H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.64, 55.63, 64.89, 75.61, 85.49, 114.6, 115.6, 120.7, 133.8, 152.4, 154.0.

IR (film): ν = 3272 (C≡C*H*), 3038 (C=C*H*), 2094 (C≡C), 1618, 1510 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 202 (23, M^+), 124 (100).

(Z)-(4-Methoxyphenoxy)-3-methylpent-2-en-4-yne **(12b)**:

Reaction of **10** according to Typical Procedure 2; yield: 89%; colorless oil: bp 87°C/0.01 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90 (s, 3H), 3.22 (s, 1H), 3.74 (s, 3H), 4.69 (d, J = 7 Hz, 2H), 5.96 (t, J = 7 Hz, 1H), 6.84 (s, 4H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.92, 55.56, 66.86, 80.83, 83.03, 114.6, 115.5, 120.9, 134.2, 152.5, 153.8.

IR (film): ν = 3246 (C≡C*H*), 3042 (C=C*H*), 2088 (C≡C), 1628, 1590, 1504 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 202 (16, M^+), 124 (100).

THP-Protection of Alcohols; (*E*)-2-(3-Methylpent-2-en-4-yn-1-yl)oxytetrahydropyran (11e); Typical Procedure 3:

To a solution of **9** (2.57 mL, 25.0 mmol) in CH_2Cl_2 (150 mL) was added dihydropyran (3.41 mL, 37.5 mmol) and PPTS (627 mg, 2.50 mmol) and the solution was stirred at r.t. for 2 h. Et_2O (125 mL) was added and the organic phase was washed with half-saturated brine, dried (Na_2SO_4) and concentrated. The crude product was purified by distillation; yield: 4.32 g (97%); colorless oil: bp 90°C/3.5 mbar.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.92 (m, 6H), 1.85 (t, J = 1.5 Hz, 3H), 2.84 (s, 1H), 3.52 (m_c, 1H), 3.87 (m_c, 1H), 4.11 (ddd, J = 12, 7, 1 Hz, 1H), 4.28 (ddd, J = 12, 7, 1 Hz, 1H), 4.63 (t, J = 4 Hz, 1H), 6.07 (dt, J = 7, 1.5 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.47, 19.43, 25.43, 30.69, 62.13, 62.95, 75.11, 85.87, 97.86, 120.2, 134.9.

(Z)-2-(3-Methylpent-2-en-4-yn-1-yl)oxytetrahydropyran **(12c)**:

Reaction of **10** according to Typical Procedure 3; yield: 96%; colorless oil: bp 60°C/0.35 mbar.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.44–1.94 (m, 6H), 1.90 (t, J = 1 Hz, 3H), 3.16 (s, 1H), 3.52 (m_c, 1H), 3.90 (m_c, 1H), 4.24 (ddd, J = 12, 7, 1 Hz, 1H), 4.41 (ddd, J = 12, 7, 1 Hz, 1H), 4.65 (t, J = 4 Hz, 1H), 5.93 (dt, J = 7, 1.5 Hz, 1H).

Modified Negishi-Coupling of Alkynes; (*E*)-2-[5-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-2-en-4-yn-1-yl]oxytetrahydropyran (5e); Typical Procedure 4:

Solution I: A degassed solution of **10** (1.35 g, 7.50 mmol) in THF (8 mL) and DMPU (1.26 mL, 10 mmol) was cooled to −40°C and treated with a 2.3 M solution of BuLi in hexane (3.26 mL, 7.50 mmol). The solution was warmed up to r.t. and $ZnCl_2$ (1 M solution in THF, 8 mL) was added. After 5 min solution I was added to solution II.

Solution II: $Pd(PPh_3)_4$ (250 mg, 0.21 mmol) was dissolved in degassed THF (8 mL) under Ar and stirred for 5 min, then **8** (1.83 g, 6 mmol) was added. The solution was stirred for 20 min whereupon solution I was added with a syringe and the mixture heated to 47°C for 7 h. The solution was cooled and diluted with Et_2O (100 mL) then the organic layer was washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The residue was subjected to column chromatography (300 g silica gel, *t*-BuOMe/petroleum ether 12:1); yield: 1.61 g (75%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.88 (m, 6H), 1.97 (d, J = 1 Hz, 3H), 2.16 (s, 3H), 2.20 (s, 3H), 2.34 (s, 3H), 3.52 (m_c, 1H), 3.64 (s, 3H), 3.72 (s, 3H), 3.90 (m_c, 1H), 4.16 (ddd, J = 12, 7, 1 Hz), 4.35 (ddd, J = 12, 7, 1 Hz), 4.67 (t, J = 7 Hz, 1H), 6.07 (dt, J = 7, 1 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.43, 12.98, 14.15, 19.43, 25.48, 25.63, 30.62, 60.06, 60.65, 63.22, 67.95, 83.11, 97.91, 99.05, 105.5, 121.9, 128.2, 131.6, 132.6, 152.7, 155.5.

IR (film): ν = 2198 (C≡C), 1632 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%) = 358 (48, M^+), 274 (17), 258 (52), 243 (100), 85 (63).

(E)-1-(5-Benzyloxy-3-methylpent-3-en-1-yn-1-yl)-2,5-dimethoxy-3,4,6-trimethylbenzene **(5a)**:

Reaction of **11a** according to Typical Procedure 4; yield: 73%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.16 (s, 3H), 2.20 (s, 3H), 2.33 (s, 3H), 3.63 (s, 3H), 3.81 (s, 3H), 4.16 (d, J = 7 Hz, 2H), 4.54 (s, 2H), 6.11 (t, J = 7 Hz, 1H), 7.23–7.39 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.28, 12.83, 14.01, 17.70, 59.87, 60.38, 66.11, 72.19, 83.07, 98.83, 115.3, 121.9, 127.5, 127.6, 128.2, 128.1, 131.1, 131.4, 132.5, 138.0, 152.5, 155.3.

IR (film): ν = 2196 (C≡C), 1630 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 364 (31, M^+), 91 (100).

(E)-1-[5-(4-Methoxybenzyloxy)-3-methylpent-3-en-1-yn-1-yl]-2,5-dimethoxy-3,4,6-trimethylbenzene **(5b)**:

Reaction of **11b** according to Typical Procedure 4; yield: 66%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 (s, 3H), 2.16 (s, 3H), 2.20 (s, 3H), 2.34 (s, 3H), 3.65 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 4.13 (d, J = 7 Hz, 2H), 4.47 (s, 2H), 6.10 (t, J = 7 Hz, 1H), 6.88 (d, J = 8 Hz, 2H), 7.28 (d, J = 8 Hz, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.15, 12.70, 13.98, 17.57, 54.86, 59.71, 60.22, 65.71, 76.36, 82.92, 98.78, 113.5, 115.2, 121.6, 127.9, 129.1, 130.8, 131.3, 132.6, 152.5, 155.3, 159.0.

IR (film): ν = 2198 (C≡C), 1612 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 394 (16, M^+), 273 (37), 258 (72), 121 (100).

(E)-1-[5-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-3-methylpent-3-en-1-yn-1-yl]-2,5-dimethoxy-3,4,6-trimethylbenzene **(5c)**:

Reaction of **11c** according to Typical Procedure 4; yield: 77%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 6H), 0.84 (s, 6H), 0.87 (d, J = 7 Hz, 6H), 1.62 (sept, J = 7 Hz, 1H), 1.89 (s, 3H), 2.16 (s, 3H), 2.23 (s, 3H), 2.32 (s, 3H), 3.62 (s, 3H), 3.80 (s, 3H), 4.27 (d, J = 7 Hz, 2H), 6.01 (t, J = 7 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −3.23, 12.40, 12.94, 14.11, 17.68, 18.47, 20.30, 25.17, 34.10, 60.04, 60.51, 60.60, 82.41, 99.25, 115.5, 119.0, 128.2, 131.0, 131.4, 136.4, 152.6, 155.4.

IR (film): ν = 2190 (C≡C), 1632 (C=C), 1378 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 331 (100).

(E)-1-[5-(4-Methoxyphenoxy)-3-methylpent-3-en-1-yn-1-yl]-2,5-dimethoxy-3,4,6-trimethylbenzene **(5d)**:

Reaction of **11d** according to Typical Procedure 4; yield: 28%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3H), 2.16 (s, 3H), 2.19 (s, 3H), 2.36 (s, 3H), 3.64 (s, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 4.61 (d, J = 7 Hz, 2H), 6.17 (t, J = 7 Hz, 1H), 6.81–6.90 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.43, 13.05, 14.16, 18.02, 55.68, 60.07, 60.59, 65.19, 83.63, 98.64, 114.6, 115.3, 115.6, 122.4, 128.2, 131.2, 131.3, 131.7, 152.6, 154.0, 155.5.

IR (film): ν = 2196 (C≡C), 1622 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%): 380 (4, M^+), 257 (100), 123 (21).

(Z)-1-[5-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-3-methylpent-3-en-1-yn-1-yl]-2,5-dimethoxy-3,4,6-trimethylbenzene **(6a)**:

Reaction of **12a** according to Typical Procedure 4; yield: 70%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 6H), 0.83 (s, 6H), 0.86 (d, J = 7 Hz, 6H), 1.62 (sept, J = 7 Hz, 1H), 1.97 (s, 3H), 2.15 (s, 3H), 2.18 (s, 3H), 2.33 (s, 3H), 3.63 (s, 3H), 3.80 (s, 3H), 4.47 (d, J = 7 Hz, 2H), 5.97 (t, J = 7 Hz, 1H).

IR (film): ν = 2196 (C≡C), 1632 (C=C), 1378 (C(CH$_3$)$_2$) cm^{-1}.

MS (70 eV, EI): m/z (%): 331 (100).

(Z)-1-[5-(4-Methoxyphenoxy)-3-methylpent-3-en-1-yn-1-yl]-2,5-dimethoxy-3,4,6-trimethylbenzene **(6b)**:

Reaction of **12b** according to Typical Procedure 4; yield: 21%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3H), 2.17 (s, 3H), 2.22 (s, 3H), 2.35 (s, 3H), 3.64 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 4.83 (d, J = 7 Hz, 2H), 5.95 (t, J = 7 Hz, 1H), 6.83–6.93 (m, 4H).

IR (film): ν = 2198 (C≡C), 1630 (C=C), 1508 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%): 380 (2, M^+), 257 (100), 123 (19).

(Z)-2-[5-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-2-en-4-yn-1-yl]oxytetrahydropyran **(6c)**:

Reaction of **12c** according to Typical Procedure 4; yield: 62%; colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46–1.97 (m, 6H), 2.03 (d, J = 1 Hz, 3H), 2.16 (s, 3H), 2.20 (s, 3H), 2.35 (s, 3H), 3.51 (m_c, 1H), 3.65 (s, 3H), 3.82 (s, 3H), 3.91 (m_c, 1H), 4.38 (ddd, J = 12, 7, 1 Hz), 4.54 (ddd, J = 12, 7, 1 Hz), 4.68 (t, J = 7 Hz, 1H), 5.88 (dt, J = 7, 1 Hz).

IR (film): ν = 2192 (C≡C), 1630 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%) = 358 (36, M^+), 85 (100).

Sharpless Bishydroxylation of Enynes; (2*S*,3*S*)-1-(4-Methoxyphenoxy)-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol (13d); Typical Procedure 5:

AD-mix-α [(DHQ)$_2$PHAL] (0.49 g) was dissolved in *t*-BuOH/H$_2$O (3.5 mL, 1:1) and cooled to 0°C. Compound **5d** (134 mg, 0.35 mmol) was added and the solution was stirred at this temperature for 48–72 h (TLC). The solution was treated with Na_2SO_3 (0.53 g), stirred for 1 h at r.t. and extracted with CH_2Cl_2 (1 × 10 mL, 3 × 5 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:1) to give **9c** (80 mg, 55%) as a white solid; mp 96°C; $[\alpha]_D^{20}$ −13.5 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.68 (s, 3H), 2.14 (s, 3H), 2.18 (s, 3H), 2.33 (s, 3H), 2.87 (d, J = 7 Hz, 1H), 3.05 (s, 1H), 3.63 (s, 3H), 3.77 (s, 3H), 3.78 (s, 3H), 4.07–4.15 (m, 2H), 4.33–4.40 (m, 1H), 6.80–6.93 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.32, 12.87, 14.13, 25.33, 55.62, 59.97, 60.58, 69.82, 75.66, 76.57, 80.63, 97.49, 114.4, 114.6, 115.7, 128.3, 131.3, 132.2, 152.6, 152.7, 154.2, 155.6.

IR (KBr): ν = 2198 (C≡C), 1630 (C=C), 1508 (C=C) cm^{-1}.

MS (CI, NH_3): m/z (%): 432 (100, $M^+ + NH_4$).

(2S,3S)-1-Benzyloxy-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol **(13a)**:

Reaction of **5a** according to Typical Procedure 5; yield: 85%; white solid, mp 74°C, $[\alpha]_D^{20}$ +2.4 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 2.14 (s, 3H), 2.19 (s, 3H), 2.30 (s, 3H), 2.68 (br s, 1H), 3.62 (s, 3H), 3.66–3.78 (m, 1H), 3.75 (s, 3H), 3.86–3.95 (m, 2H), 3.97 (s, 1H), 4.60 (s, 2H), 6.88 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.43, 12.98, 14.23, 25.61, 60.08, 60.64, 70.87, 71.36, 73.65, 75.45, 80.42, 97.67, 114.6, 127.8, 127.8, 128.5, 128.3, 131.4, 132.1, 137.6, 152.8, 155.7.

IR (KBr): ν = 3328 (OH), 2222 (C≡C) cm^{-1}.

MS (70 eV, EI): m/z (%): 398 (5, M^+), 247 (37), 91 (53), 43 (100).

(2S,3S)-1-(4-Methoxybenzyloxy)-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol **(13b)**:

Reaction of **5b** according to Typical Procedure 5; yield: 78%; white solid: mp 71°C; $[\alpha]_D^{20}$ +5.2 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 2.14 (s, 3H), 2.19 (s, 3H), 2.30 (s, 3H), 2.61 (d, J = 6 Hz, 1H), 3.48 (s, 1H), 3.63 (s, 3H), 3.63 (s, 3H), 3.63–3.72 (m, 1H), 3.79 (s, 3H), 3.83–3.95 (m, 2H), 4.53 (s, 2H), 6.86 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.38, 12.93, 14.18, 20.94, 55.11, 60.41, 60.56, 70.62, 71.23, 73.13, 75.57, 80.17, 98.06, 113.8, 114.8, 128.2, 129.8, 129.4, 131.3, 131.9, 152.7, 155.5, 159.3.

IR (KBr): ν = 3442 (OH), 2224 (C≡C), 1514 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%): 428 (34, M^+), 410 (30), 246 (100), 121 (57).

(2S,3S)-1-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol **(13c)**:

Reaction of **5c** according to Typical Procedure 5; yield 76%; colorless oil; $[\alpha]_D^{20}$ +3.5 (c = 2.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 6H), 0.86 (s, 6H), 0.88 (d, J = 7 Hz, 6H), 1.63 (sept, J = 7 Hz, 1H), 1.64 (s, 3H), 2.14 (s, 3H), 2.18 (s, 3H), 2.35 (s, 3H), 2.59 (d, J = 7 Hz, 1H), 3.65 (s, 3H), 3.73 (t, J = 6 Hz, 1H), 3.79 (s, 3H), 3.84 (dd, J = 9.6, 6 Hz, 1H), 3.98 (dd, J = 9.6, 6 Hz, 1H).

IR (film): ν = 3448 (OH), 2224 (C≡C), 1376 (C(CH$_3$)$_2$) cm^{-1}.

MS (70 eV, EI): m/z (%): 450 (6, M^+), 347 (47), 247 (47), 231 (68), 75 (100).

(2R,3S)-1-[(2,3-Dimethyl-2-butyl)dimethylsilyloxy]-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol **(14a)**:

Reaction of **6a** according to Typical Procedure 5; yield: 55%; colorless oil, $[\alpha]_D^{20}$ −15.3 (c = 2.0, $CHCl_3$).

^{1}H NMR (300 MHz, CD_3OD): δ = 0.15 (s, 6H), 0.87 (s, 6H), 0.90 (d, J = 7 Hz, 6H), 1.64 (s, 3H), 1.65 (sept, J = 7 Hz, 1H), 2.14 (s, 3H), 2.19 (s, 3H), 2.31 (s, 3H), 3.63 (s, 3H), 3.58–3.64 (m, 1H), 3.79 (s, 3H), 3.89 (dd, J = 10.2, 3.8 Hz, 1H), 3.98 (dd, J = 10.2, 3.8 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = −3.63, 12.35, 12.90, 14.17, 18.42, 20.12, 25.02, 22.87, 26.46, 34.00, 59.98, 60.48, 62.27, 70.77, 75.35, 80.54, 97.87, 114.5, 128.2, 131.2, 131.9, 152.6, 155.6.

IR (film): ν = 3408 (OH), 2226 (C≡C), 1378 (C(CH$_3$)$_2$) cm^{-1}.

MS (70 eV, EI): m/z (%): 450 (21, M^+), 347 (96), 247 (64), 231 (100).

(2R,3S)-1-(4-Methoxyphenoxy)-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-2,3-diol **(14b)**:

Reaction of **6b** according to Typical Procedure 5; yield: 32%; white solid: mp 114°C; $[\alpha]_D^{20}$ −12.6 (c = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (s, 3H), 2.13 (s, 3H), 2.18 (s, 3H), 2.30 (s, 3H), 2.92 (d, J = 7 Hz, 1H), 3.29 (s, 1H), 3.62 (s, 3H), 3.75 (s, 3H), 3.78 (s, 3H), 3.93–4.00 (m, 1H), 4.31 (dd, J = 10, 3.5 Hz, 1H), 4.43 (dd, J = 10, 7 Hz, 1H), 6.80–6.93 (m, 4H).

IR (KBr): ν = 2198 (C≡C), 1630 (C=C), 1508 (C=C) cm^{-1}.

MS (70 eV, EI): m/z (%): 414 (82, M^+), 246 (100), 190 (68), 124 (83).

(2S,3S)-5-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-4-yne-1,2,3-triol **(29)**:

Reaction of **28** according to Typical Procedure 5; yield: 83%; white solid, mp 105°C (hexane/*t*-BuOMe), $[\alpha]_D^{20}$ −4.8 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 2.14 (s, 3H), 2.20 (s, 3H), 2.32 (s, 3H), 2.72 (s, 1H), 3.24 (d, *J* = 7 Hz, 1H), 3.30 (s, 1H), 3.64 (s, 3H), 3.77 (s, 3H), 3.80 (dd, *J* = 12, 7 Hz, 1H), 3.87 (d, *J* = 7 Hz, 1H), 3.95 (dd, *J* = 12, 7 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.40, 12.95, 14.17, 25.12, 60.04, 60.76, 63.01, 70.41, 77.36, 80.23, 97.89, 114.5, 128.2, 131.4, 132.2, 152.8, 155.3.

IR (KBr): ν = 3406 (OH), 2226 (C≡C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 308 (42, M^+), 247 (100).

Acetalisation of Diols with Methyl Isopropenyl Ether; (4*S*,5*S*)-5-[(2,3-Dimethyl-2-butyl)dimethylsilyloxymethyl]-2,2,4-trimethyl-4-(2,5-dimethoxy-3,4,6-trimethylphenylethynyl)-1,3-dioxolane (15c); Typical Procedure 6:

To a solution of **13c** (575 mg, 1.28 mmol) in CH_2Cl_2 (6 mL) was added methyl isopropenyl ether (0.26 mL, 2.80 mmol) and PPTS (50 mg, 0.20 mmol) and the solution was stirred at r.t. for 4 h. The mixture was diluted with Et_2O and washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (EtOAc/petroleum ether 10:1) to give **15c** (550 mg, 87%) as a colorless oil, $[\alpha]_D^{20}$ −22.0 (*c* = 2.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10 (s, 6H), 0.80 (s, 6H), 0.82 (d, *J* = 7 Hz, 6H), 1.43 (s, 3H), 1.58 (sept, *J* = 7 Hz, 1H), 1.53 (s), 1.54 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 2.30 (s, 3H), 3.61 (s, 3H), 4.79 (d, *J* = 7 Hz, 1H), 3.79 (s, 3H), 4.49 (dd, *J* = 7, 7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.68, 12.10, 12.65, 13.86, 18.25, 20.02, 23.12, 24.87, 25.50, 28.05, 33.91, 59.66, 60.18, 61.42, 75.48, 79.20, 83.40, 98.71, 108.7, 114.6, 127.9, 131.1, 131.5, 152.4, 155.6.

IR (film): ν = 2984, 2938 (CH), 2226 (C≡C), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 490 (7, M^+), 347 (63), 231 (100).

(4S,5S)-5-Benzyloxymethyl-2,2,4-trimethyl-4-(2,5-dimethoxy-3,4,6-trimethylphenylethynyl)-1,3-dioxolane **(15a)**:

Reaction of **13a** according to Typical Procedure 6; yield: 83%; colorless oil, $[\alpha]_D^{20}$ −24.8 (*c* = 3.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (s, 6H), 1.54 (s, 3H), 2.12 (s, 3H), 2.18 (s, 3H), 2.31 (s, 3H), 3.60–3.75 (m, 2H), 3.61 (s, 3H), 3.76 (s, 3H), 3.55 (d, *J* = 12 Hz, 1H), 3.55–3.61 (m, 1H), 4.69 (d, *J* = 12 Hz, 1H), 7.23–7.40 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.40, 12.99, 14.11, 23.53, 25.80, 28.22, 60.08, 60.53, 68.55, 73.54, 75.37, 79.72, 82.01, 97.72, 109.4, 114.6, 127.7, 127.7, 128.3, 128.2, 131.4, 132.0, 137.8, 152.6, 155.7.

IR (film): ν = 2988, 2936 (CH), 2226 (C≡C), 1376 ($C(CH_3)$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 438 (53, M^+), 230 (66), 215 (100), 91 (92).

(4S,5S)-5-(4-Methoxybenzyloxymethyl)-2,2,4-trimethyl-4-(2,5-dimethoxy-3,4,6-trimethylphenylethynyl)-1,3-dioxolane **(15b)**:

Reaction of **13b** according to Typical Procedure 6; yield: 89%; colorless oil, $[\alpha]_D^{20}$ −24.4 (*c* = 2.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 6H), 1.54 (s, 3H), 2.12 (s, 3H), 2.18 (s, 3H), 2.30 (s, 3H), 3.57–3.70 (m, 2H), 3.62 (s, 3H), 3.74 (s, 3H), 3.78 (s, 3H), 4.48 (d, *J* = 12 Hz, 1H), 4.53 (dd, *J* = 7, 5 Hz, 1H), 4.61 (d, *J* = 12 Hz, 1H), 6.85 (d, *J* = 8 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.41, 12.99, 14.12, 23.53, 25.80, 28.22, 55.23, 60.10, 60.56, 68.18, 73.19, 75.37, 79.70, 82.02, 97.76, 109.4, 113.8, 114.6, 128.3, 129.5, 129.8, 131.5, 132.0, 152.6, 155.7, 159.2.

IR (film): ν = 2988, 2936 (CH), 2226 (C≡C), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 468 (18, M^+), 215 (53), 121 (100).

(4S,5R)-5-[(2,3-Dimethyl-2-butyl)dimethylsilyloxymethyl]-2,2,4-trimethyl-4-(2,5-dimethoxy-3,4,6-trimethylphenylethynyl)-1,3-dioxolane **(16)**:

Reaction of **14a** according to Typical Procedure 6; yield: 82%; colorless oil, $[\alpha]_D^{20}$ +27.0 (*c* = 4.47, $CHCl_3$).

^{1}H NMR (300 MHz, C_6D_6): δ = 0.15 (s, 6H), 0.91 (s, 6H), 0.93 (d, *J* = 7 Hz, 6H), 1.49 (s, 3H), 1.65 (sept, *J* = 7 Hz, 1H), 1.73 (s, 3H), 1.78 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.52 (s, 3H), 3.30 (s, 3H), 3.77 (s, 3H), 4.03 (dd, *J* = 7, 7 Hz, 1H), 4.27 (d, *J* = 7 Hz, 2H).

IR (film): ν = 2980, 2936 (CH), 2222 (C≡C), 1374 ($C(CH_3)$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 490 (11, M^+), 347 (100), 245 (86), 231 (95).

(4S,5S)-5-Benzyloxymethyl-2,2,4-trimethyl-4-(2,5-dimethoxy-3,4,6-trimethylphenylethyl)-1,3-dioxolane **(22)**:

Reaction of **21** according to Typical Procedure 6; yield: 86%; colorless oil, $[\alpha]_D^{20}$ + 1.8 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, C_6D_6): δ = 1.31 (s, 3H), 1.38 (s, 3H), 1.51 (s, 3H), 1.51–1.77 (m, 2H), 2.13 (s, 3H), 2.15 (s, 3H), 2.33 (s, 3H), 2.96–3.04 (m, 2H), 3.40 (s, 3H), 3.50 (s, 3H), 3.47–3.54 (m, 1H), 3.71 (dd, *J* = 10, 7 Hz, 1H), 4.23–4.30 (m, 2H, 5-H), 4.35 (d, *J* = 12 Hz, 1H), 7.05–7.27 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.18, 12.83, 12.96, 21.14, 22.28, 27.14, 29.02, 40.43, 59.64, 60.62, 69.50, 73.50, 80.44, 82.33, 107.59, 127.71, 128.19, 128.53, 132.57, 153.56, 153.85.

IR (film): ν = 3030 (ArH), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 442 (100, M^+), 206 (81), 193 (93).

Oxidative Demethylation with Cerium Ammonium Nitrate; (2-[(4*S*,5*S*)-5-Benzyloxymethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl-ethynyl]-3,5,6-trimethyl-1,4-benzoquinone (17); Typical Procedure 7:

To a solution of **15a** (250 mg, 0.63 mmol) in CH_3CN (2.5 mL) was added CAN (690 mg, 1.26 mmol) in H_2O (2.5 mL) over a period of 5 min. After 7 min the mixture was extracted with $CHCl_3$ (2 × 10 mL), dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (EtOAc/petroleum ether 6:1) to give **17g** (207 mg, 80%) as a yellow oil.

^{1}H NMR (300 MHz, C_6D_6): δ = 1.42 (s, 3H), 1.53 (s, 3H), 1.56 (s, 6H), 1.57, 1.59 (s, 3H), 2.05 (s, 3H), 3.61 (d, *J* = 7 Hz, 2H), 4.28 (d, *J* = 12 Hz, 1H), 4.37 (d, *J* = 12 Hz, 1H), 4.72 (dd, *J* = 7, 7 Hz, 1H), 7.05–7.30 (m, 5H).

^{13}C NMR (50 MHz, C_6D_6): δ = 12.36, 14.96, 23.51, 26.13, 28.63, 69.06, 73.67, 76.06, 77.81, 82.46, 108.0, 110.0, 127.7, 128.0, 128.8, 138.8, 140.5, 141.0, 146.9, 182.8, 186.0.

IR (film): ν = 3030 (ArH), 1650 (C=O), 1602 (C=C), 1376 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 258 (58), 200 (74), 91 (100).

2-[(4S,5S)-5-Benzyloxymethyl-2,2,4-trimethyl-1,3-dioxolan-4-ylethyl]-3,5,6-trimethyl-1,4-benzoquinone **(23)**:

Reaction of **22** according to Typical Procedure 7; yield: 77%; yellow solid, $[\alpha]_D^{20}$ −2.0 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 3H), 1.32 (s, 3H), 1.45 (s, 3H), 1.14–1.60 (m_c, 1H), 1.65–1.71 (m_c, 1H), 1.71, 1.72 (s, 3H), 1.89 (s, 3H), 2.56–2.75 (m_c, 2H), 3.45 (dd, *J* = 10, 7 Hz, 1H), 3.54 (dd, *J* = 10, 7 Hz, 1H), 4.16 (dd, *J* = 7, 7 Hz, 1H), 4.24 (d, *J* = 12 Hz, 1H), 4.34 (d, *J* = 12 Hz, 1H), 7.05–7.30 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.93, 12.21, 12.29, 20.98, 21.81, 27.24, 29.06, 38.95, 69.41, 73.68, 80.70, 82.22, 107.85, 127.94, 127.99, 128.73, 138.80, 140.25, 140.31, 144.36, 186.66, 187.27.

IR (KBr): ν = 3038 (ArH), 1636 (C=O), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 91 (100).

4-Acetoxy-2-{2-[(4*S*,5*R*)-5-acetoxymethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl]ethyl}-3,5,6-trimethylphenyl Acetate (20):

To a solution of **17** (300 mg, 0.73 mmol) in MeOH (2 mL) was added Pd/C (22 mg, 10%) and stirred for 24 h in an atmosphere of H_2 (3 atm). After filtration under Ar the solvent was evaporated and the residue was taken up in a degassed mixture of CH_2Cl_2 (3 mL), pyridine (2 mL) and Ac_2O (1 mL). This solution was stirred for 2 h at r.t., then H_2O (3 mL) was added and the mixture was extracted with Et_2O (2 × 15 mL). The combined organic phases were washed with 1 M HCl, diluted $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated. The residue was subjected to column chromatography (EtOAc/petroleum ether 7:2); yield: 190 mg (59%); white solid; mp 89°C (hexane); $[\alpha]_D^{20}$ −8.8 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 3H), 1.38 (s, 3H), 1.49 (s, 3H), 1.53–1.77 (m, 2H), 2.02, 2.03, 2.08, 2.09 (4s, 4 × 3H), 2.34 (s, 6H), 2.46–2.88 (m, 2H), 3.97–4.04 (m, 1H), 4.09–4.23 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.27, 13.11, 20.42, 20.49, 20.75, 20.80, 22.11, 26.92, 28.53, 38.57, 63.07, 79.23, 81.39, 108.1, 126.7, 127.6, 127.8, 130.6, 145.4, 146.0, 168.9, 169.3, 170.8.

IR (KBr): ν = 2982 (CH), 1756 (C=O), 1372 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 450 (21, M^+), 408 (46), 366 (25), 308 (100).

(2*S*,3*S*)-1-Benzyloxy-5-(2,5-dimethoxy-3,4,6-trimethylphenyl)-3-methylpentane-2,3-diol (21):

A mixture of **13a** (250 mg, 0.63 mmol) and PtO_2 (16 mg, 63 μmol) in MeOH (4 mL) was stirred under an atmosphere of H_2 (3 atm) for 24 h. After filtration from the catalyst the solution was concentrated. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether 2:1); yield: 142 mg (56%); white solid; $[\alpha]_D^{20}$ −5.5 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 3H), 1.56–1.65 (m_c, 2H), 2.17 (s, 6H), 2.22 (s, 3H), 2.65–2.73 (m_c, 2H), 2.75 (s, 1H), 2.83 (s, 3H), 3.60–3.73 (m, 3H, 2-H), 3.64 (s, 3H), 3.69 (s, 3H).

IR (KBr): ν = 3458 (OH), 3028, 2976 (CH) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 402 (18, M^+), 251 (38), 193 (100), 91 (37).

(9*S*,10*S*)-10-(Benzyloxymethyl)-2,3,5,9-tetramethyl-11,12-dioxatricyclo[7.2.1.0^{1,6}]dodeca-2,5-dien-4-one (24):

A solution of **23** (71 mg, 0.17 mmol) in MeOH (1.5 mL) and 1 M HCl (0.37 mL) was stirred at r.t. for 48 h. The mixture was diluted with CH_2Cl_2 (10 mL) and the organic phase was washed with $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated. The residue was subjected to column chromatography (EtOAc/petroleum ether 8:1); yield: 49 mg (80%); colorless oil, $[\alpha]_D^{20}$ −43.0 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 3H), 1.21–1.30 (m, 1H), 1.39–1.53 (m, 1H), 1.80 (s, 3H), 1.81 (s, 3H), 1.89 (s, 3H), 2.17–2.27 (m, 2H), 3.48 (d, *J* = 7 Hz, 2H), 4.12 (t, *J* = 7 Hz, 1H), 4.30 (s, 2H), 7.08–7.31 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.52, 11.88, 13.15, 19.86, 22.41, 36.91, 70.62, 73.52, 79.32, 81.51, 99.51, 127.9, 128.3, 128.6, 134.8, 138.6, 144.8, 147.3, 184.5.

IR (film): ν = 1682, 1642 (C=O), 1604 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 354 (18, M^+), 233 (100).

(2*S*,2′*S*)-1-(6-Hydroxy-2,5,7,8-tetramethylchroman-2-yl)ethane-1,2-diol (3a):

A mixture of **24** (19 mg, 53 μmol) and Pd/C (20 mg, 10%) in MeOH (8 mL) was stirred under an atmosphere of H_2 for 3 h. After filtration from the catalyst and evaporation of the solvent, the crude diol was purified by column chromatography (EtOAc/petroleum ether 1:1) to give **3a** (9.5 mg, 67%) as a white solid; $[\alpha]_D^{20}$ −13.3 (*c* = 0.84, MeOH).

^{1}H NMR (300 MHz, CD_3OD): δ = 1.16 (s, 3H), 1.79–1.95 (m, 2H), 2.04 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 2.51–2.70 (m, 2H), 3.66 (t, *J* = 7 Hz, 2H), 3.87 (d, *J* = 7 Hz, 1H).

^{13}C NMR (75 MHz, CD_3OD): δ = 11.80, 12.05, 12.75, 20.03, 21.21, 28.11, 63.73, 77.21, 78.80, 118.4, 122.0, 123.3, 124.5, 146.2, 146.3.

MS (70 eV, EI): *m/z* (%): 266 (42, M^+), 205 (100), 165 (48).

(2*S*,2′*S*)-1-(6-Benzyloxy-2,5,7,8-tetramethylchroman-2-yl)ethane-1,2-diol (3b):

To a solution of **3a** (170 mg, 0.64 mmol) in DMSO (3 mL) was added K_2CO_3 (138 mg, 1.00 mmol) and BnCl (0.22 mL, 1.92 mmol). After stirring for 72 h at r.t. and 4 h at 40°C, H_2O was added followed by subsequent Et_2O extraction (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether 1:1) to give **3b** (96 mg, 43%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 3H), 1.73–1.85 (m, 1H), 1.98–2.15 (m, 1H), 2.10 (s, 3H), 2.15 (s, 3H), 2.23 (s, 3H), 2.31 (t, *J* = 6 Hz, 1H), 2.56 (d, *J* = 6 Hz, 1H), 2.59–2.74 (m, 2H), 3.71–3.93 (m, 3H, 1-H), 4.69 (s, 2H), 7.31–7.53 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.00, 12.87, 12.88, 19.40, 19.94, 27.93, 62.66, 74.78, 76.48, 76.81, 117.67, 122.88, 126.38, 127.74, 127.87, 128.39, 128.49, 137.78, 146.67, 148.74.

MS (70 eV, EI): *m/z* (%): 365 (33), 265 (100), 229 (23), 165 (23).

(2*S*)-6-Benzyloxy-2,5,7,8-tetramethylchroman-2-carbaldehyde (2):

To a solution of **3b** (100 mg, 0.28 mmol) in dioxane/H_2O (3 mL, 1:1) $NaIO_4$ (120 mg, 0.56 mmol) was added, the mixture stirred for 30 min at r.t. and after addition of H_2O (20 mL), extracted with Et_2O (3 × 10 mL). The combined organic phases were washed, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether 8:1) to give **2** (87 mg, 96%) as white solid, mp 53°C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 (s, 3H), 1.76–1.89 (m, 1H), 2.13 (s, 3H), 2.20 (s, 3H), 2.21–2.32 (m, 1H), 2.26 (s, 3H), 2.51–2.61 (m, 2H), 4.69 (s, 2H), 7.31–7.52 (m, 5H).

Cleavage of Silyl Ethers with TBAF; (4*S*,5*S*)-[5-(2,5-Dimethoxy-3,4,6-trimethylphenylethynyl)-2,2,5-trimethyl-1,3-dioxolan-4-yl]-methanol (25); Typical Procedure 8:

To a solution of **15c** (100 mg, 0.20 mmol) in THF (3 mL) was added TBAF (189 mg, 0.60 mmol). After stirring for 7 h at r.t., Et_2O (10 mL) and H_2O (10 mL) were added. The organic phase was washed with aq $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated. The residue was subjected to column chromatography (EtOAc/petroleum ether 6:1); yield: 67 mg (96%); white solid; mp 101°C (hexane); $[\alpha]_D^{20}$ −12.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 3H), 1.54 (s, 3H), 1.57 (s, 3H), 1.82 (dd, *J* = 7, 7 Hz, 1H), 2.16 (s, 3H), 2.19 (s, 3H), 2.33 (s, 3H), 3.69 (s, 3H), 3.80 (s, 3H), 3.78–3.87 (m, 2H), 4.48 (dd, *J* = 6, 5 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.41, 13.00, 14.15, 23.55, 25.86, 28.26, 60.11, 60.68, 61.35, 75.30, 79.78, 83.54, 97.79, 109.5, 114.5, 128.3, 131.5, 132.2, 152.7, 155.7.

IR (KBr): ν = 3448 (OH); 2228 (C≡C), 1558 (C=C), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 348 (100, M^+), 315 (14), 247 (34), 215 (48), 169 (31).

(4R,5S)-[5-(2,5-Dimethoxy-3,4,6-trimethylphenylethynyl)-2,2,5-trimethyl-1,3-dioxolan-4-yl]methanol **(27)**:

Reaction of **16** according to Typical Procedure 8; yield: 93%; white solid; $[\alpha]_D^{20}$ +13.3 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 3H), 1.60 (s, 3H), 1.74 (s, 3H), 1.82 (dd, *J* = 7, 7 Hz, 1H), 2.16 (s, 3H), 2.20 (s, 3H), 2.33 (s, 3H), 3.64 (s, 3H), 3.79 (s, 3H), 3.98–4.13 (m, 3H, 1-H).

IR (KBr): ν = 3484 (OH), 2222 (C≡C), 1562 (C=C), 1374 ($C(CH_3)_2$) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 348 (11, M^+), 247 (34), 215 (21).

(−)-Camphanic Acid 5-(2,5-Dimethoxy-3,4,6-trimethylphenylethynyl)-(4*S*,5*R*)-2,2,5-trimethyl-1,3-dioxolan-4-yl Methyl Ester (27):

To a solution of **25** (245 mg, 0.70 mmol) in CH_2Cl_2/Et_3N (5:1, 5 mL) was added camphanic acid chloride (216 mg, 1.00 mmol). The mixture was stirred for 9 h and stopped by addition of H_2O (5 mL) and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were washed with 2 M HCl, aq $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated. The residue was subjected to column chromatography (EtOAc/petroleum ether 2:1); yield: 337 mg (91%); white solid; mp 105°C (hexane/*t*-BuOMe); $[\alpha]_D^{20}$ −12.2 (*c* = 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98, 1.08, 1.13, 1.50, 1.55, 1.59 (6s, 6 × 3H), 1.66 (ddd, *J* = 17.0, 9.0, 4.0 Hz, 1H), 1.89 (ddd, *J* = 17.0, 10.5, 4.5 Hz, 1H), 2.03 (ddd, *J* = 18.0, 9.0, 4.5 Hz, 1H), 2.16 (s, 3H), 2.20 (s, 3H), 2.32 (s, 3H), 2.45 (ddd, *J* = 18.0, 10.5, 4.0 Hz, 1H), 3.64 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 4.43 (ddd, *J* = 11.0, 7.0, 4.5 Hz, 1H), 4.59 (dd, *J* = 7.0, 4.5 Hz, 1H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 9.69, 12.40, 13.01, 14.16, 16.64, 16.71, 23.65, 25.82, 28.22, 28.88, 30.57, 54.29, 54.75, 60.07, 60.61, 63.20, 75.32, 80.31, 80.58, 91.00, 97.08, 109.8, 114.3, 128.3, 131.4, 132.3, 152.6, 155.6, 167.0, 177.9.

IR (KBr): $\nu = 2226$ (C≡C), 1792 (C=O), 1760 (C=O), 1376 [$C(CH_3)_2$] cm^{-1}.

MS (70 eV, EI): *m/z* (%): 528 (100, M^+).

(*E*)-5-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-3-methylpent-2-en-4-yn-1-ol (28):

PPTS (13 mg, 50 μmol) and **5e** (90 mg, 0.25 mmol) were dissolved in anhyd EtOH (3 mL) and stirred at 50 °C for 3 h. After evaporation of the solvent the residue was purified by chromatography (EtOAc/petroleum ether 4:1) to give **28** (64 mg, 93 %) as a white solid; mp 77 °C (hexane).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.70$ (s, 1 H), 1.97 (d, $J = 1$ Hz, 3 H), 2.15 (s, 3 H), 2.20 (s, 3 H), 2.34 (s, 3 H), 3.64 (s, 3 H), 3.72 (s, 3 H), 4.29 (d, $J = 7$ Hz, 2 H), 6.11 (dt, $J = 7$, 1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 12.44$, 13.00, 14.14, 17.66, 59.23, 60.09, 60.58, 83.28, 98.83, 115.3, 121.4, 128.3, 131.1, 131.6, 134.6, 152.7, 155.4.

IR (KBr): $\nu = 3418$ (OH), 2190 (C≡C), 1670 (C=C) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 274 (100, M^+), 246 (79), 231 (70).

(2*S*,3*S*)-5-(2,5-Dimethoxy-3,4,6-trimethylphenyl)-3-methylpentane-1,2,3-triol (30):

A solution of **29** (195 mg, 0.50 mmol) and 10 % Pd/C (15 mg) was stirred under H_2 (3 atm) for 18 h. After filtration from the catalyst, the solvent was evaporated and the crude triol was purified by column chromatography (EtOAc/petroleum ether 4:1) to give **30** (121 mg, 78 %) as a white solid; mp 97.5 °C (EtOAc/hexane); $[\alpha]_D^{20}$ +0.0 ($c = 1.0$, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.24$ (s, 3 H), 1.71 (m_c, 2 H), 2.16 (s, 6 H), 2.22 (s, 3 H), 2.66 (m_c, 3 H), 2.80 (br s, 1 H), 3.11 (br s, 1 H), 3.65 (s, 3 H), 3.72 (s, 3 H), 3.79 (d, $J = 7$ Hz, 2 H).

IR (KBr): $\nu = 3408$, 3360 (OH) cm^{-1}.

MS (70 eV, EI): *m/z* (%): 312 (25, M^+), 193 (100).

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