Efficient and General Preparation of Pyranostilbenes: First Total Synthesis of Artocarbene and Pawhuskin B

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Abstract: An efficient and general synthesis providing pyranostilbenes in moderate yields has been developed. It consists of the reaction of pinosylvin with the appropriate α,β-unsaturated aldehyde catalyzed by ethylenediamine diacetate. As an application of this methodology, biologically active natural products artocarbene and pawhuskin B were synthesized by a convergent sequence from commercially available aldehydes.

Key words: heterocycles, alkenes, phenols, artocarbene, pawhuskin B

Compounds containing the benzopyran moiety are widely distributed throughout nature,[1] possess many biological activities,[2] and are used as versatile intermediates in organic and natural product synthesis.[3] Molecules bearing the stilbene moiety are also widely found in nature[4] and have a variety of interesting biological activities and properties, including antimicrobial,[5] antimalarial,[6] antioxidant,[7] antileukemic,[8] anti-platelet aggregative,[9] anticarcinogenic,[10] anti-HIV,[11] protein tyrosine kinase inhibitory,[12] anti-inflammatory,[13] antimutagenic,[14] antifungal,[15] and hepatoprotective[16] activities.

In particular, pyranostilbenes with the benzopyran moiety on the stilbene are also found in nature.[17–20] Among these, artocarbene (**1**; Figure 1) was isolated from the tropical evergreen *Artocarpus incisus*, distributed throughout Thailand.[6,17] This plant has been used in folk medicine for the treatment of tapeworm infection[6] and has been shown to possess antimalarial[6] and antityrosinase[18] activities. Pawhuskin B (**2**; Figure 1) was isolated from *Dalea purpurea*, which was used by Plains Indians to ward off disease and for unspecified ailments together pawhuskins A and C.[19] It has a high affinity for the opioid receptor in bioassay testing.[19] Recently, a synthetic approach for natural pawhuskin C without a benzopyran ring has been reported.[20] Natural compounds **3**–**5** (Figure 1) were isolated from the roots of *Lonchocarpus utilus*, used as an insecticide and pesticide,[21] and have shown potent inhibition of NADH:ubiquinone oxidoreductase and phorbol ester induced ornithine decarboxylase activities.[21] This range of important biological activities and properties has stimulated research into the synthesis of molecules with a benzopyran moiety on the stilbene. The structures of these natural products **1**–**5** have been established by spectral analysis, but no synthetic approaches for the formation of pyranostilbenes have been reported.

Recently, we developed a new and useful methodology for preparing a variety of benzopyrans using reactions of resorcinols with α,β-unsaturated aldehydes catalyzed by ethylenediamine diacetate (EDDA).[22] These reactions involve cycloadditions through a 6π-electrocyclization or hetero-Diels–Alder reaction[22] and provide a rapid route for the synthesis of benzopyran derivatives with a variety of substituents on the pyranyl ring. As part of an ongoing study of the synthetic efficacy of this methodology, we describe herein an efficient and general synthesis of a variety of pyranostilbene derivatives through a domino aldol-type reaction and 6π-electrocyclization reaction.

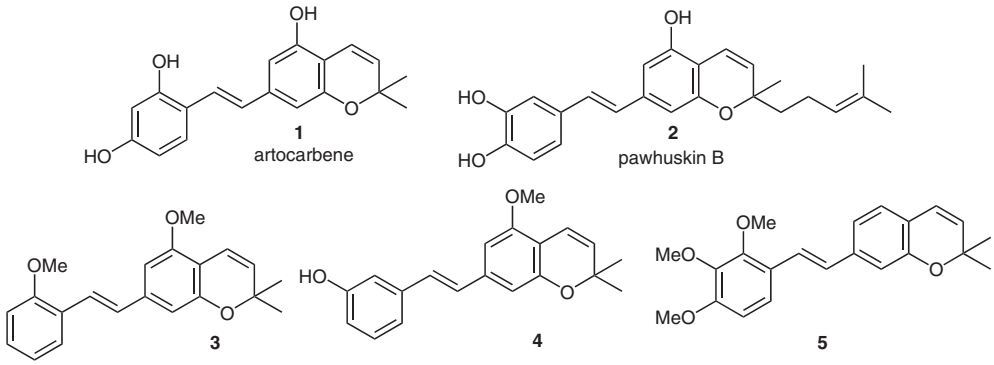

Figure 1 Naturally occurring compounds **1**–**5** with benzopyran on the stilbene nucleus

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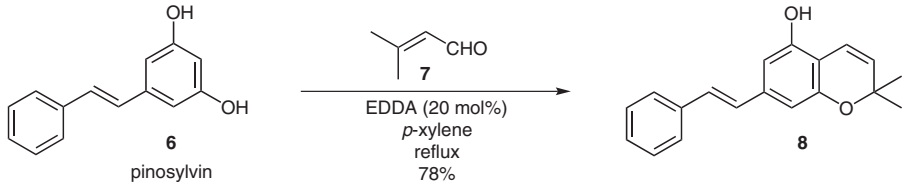
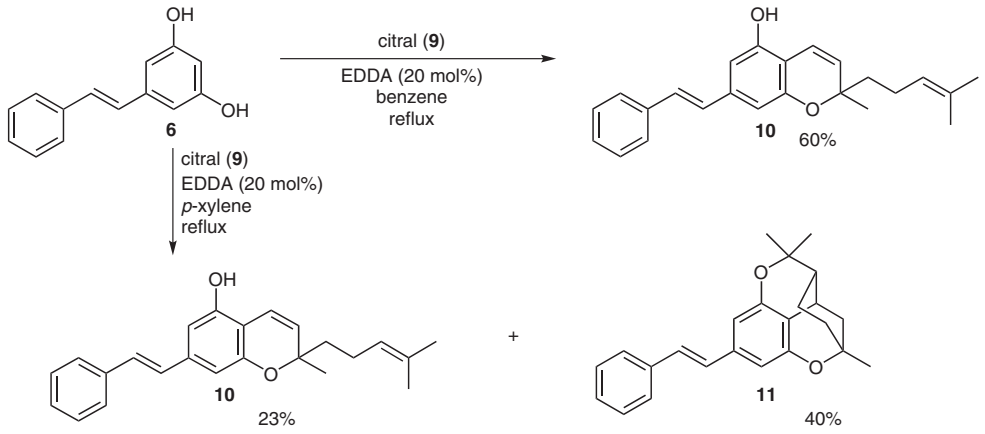


Scheme 1 Reaction of pinosylvin (**6**) with 3-methylbut-2-enal (**7**) in the presence of ethylenediamine diacetate



Scheme 2 Reaction of pinosylvin (**6**) with citral (**9**) in the presence of ethylenediamine diacetate

We also report on the first total synthesis of the naturally occurring artocarbene (**1**) and pawhuskin B (**2**).

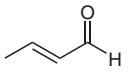
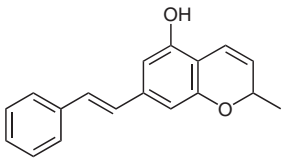
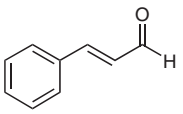
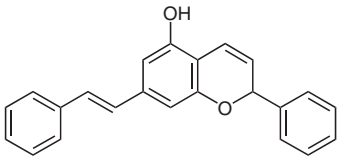
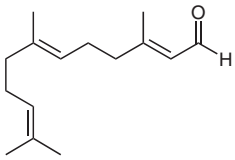
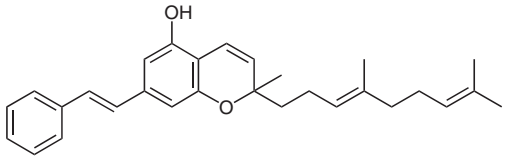
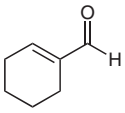
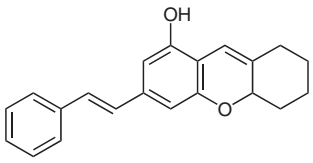
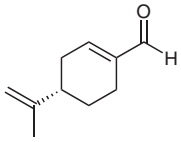
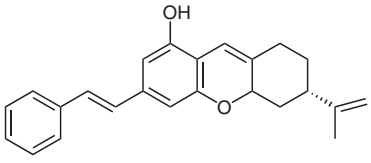
We first investigated the synthesis of pyranostilbene derivatives using pinosylvin (**6**) as starting material (Scheme 1). Reaction of **6** with 3-methylbut-2-enal (**7**) in the presence of ethylenediamine diacetate (20 mol%) in refluxing *p*-xylene for eight hours afforded benzopyran **8** in 78% yield through a domino aldol-type reaction and a 6π-electrocyclization reaction.[22a] Compound **8** was easily separated by column chromatography and characterized by spectroscopic analyses. In the ^{1}H NMR spectrum, two vinyl protons on the 2*H*-pyranyl ring were observed at δ = 6.60 (d, *J* = 9.8 Hz, 1 H) and 5.59 (d, *J* = 9.8 Hz, 1 H).

As shown in Scheme 2, reaction of pinosylvin (**6**) with 3,7-dimethylocta-2,6-dienal (citral, **9**) in refluxing benzene for ten hours afforded the desired product **10** in 60% yield. It is interesting that when the temperature was raised to 138 °C for ten hours by the use of *p*-xylene as solvent, both product **10** (23%) and tetracycle **11** (40%) were produced (Scheme 2). The two compounds were easily separated by column chromatography and characterized by spectroscopic analyses on the basis of data reported in the literature.[19,23] The ^{1}H NMR spectrum of compound **10** showed the two vinyl protons on the 2*H*-pyranyl ring at δ = 6.59 (d, *J* = 9.8 Hz, 1 H) and 5.49 (d, *J* = 9.8 Hz, 1 H), whereas the ^{1}H NMR spectrum of compound **11** showed a methine proton of benzylic position at δ = 2.83 as a broad singlet. Further support for the structural assignment of tetracycle **11** was obtained from its ^{13}C NMR spectrum, which clearly showed the expected two quaternary carbons on the two tetrahydropyranyl rings at δ = 83.8 and 74.7.

Additional reactions of pinosylvin (**6**) with several types of α,β-unsaturated aldehydes **12**–**16** were carried out in the presence of ethylenediamine diacetate (20 mol%) in refluxing benzene or *p*-xylene (Table 1). Reaction of **6** with crotonaldehyde (**12**) for 12 hours afforded adduct **17** in 43% yield (entry 1), whereas treatment with *trans*-cinnamaldehyde (**13**) in refluxing benzene for 12 hours afforded compound **18** in 79% yield (entry 2). In the case of *trans*,*trans*-farnesal (**14**), bearing a long chain, the reaction in refluxing benzene for 12 hours produced the desired product **19** in 58% yield (entry 3). With the other α,β-unsaturated aldehydes **15** and **16**, containing cyclohexene rings, the cycloaddition reactions were also successful (entries 4 and 5). Thus, the reactions of **6** with cyclohex-1-ene-1-carboxaldehyde (**15**) and (–)-perillaldehyde (**16**) in refluxing *p*-xylene provided the corresponding adducts **20** and **21** in 67 and 79% yields, respectively, as single compounds (entries 4 and 5). These reactions provide a rapid route for the synthesis of pyranostilbenes with a variety of substituents on the 2*H*-pyranyl rings.

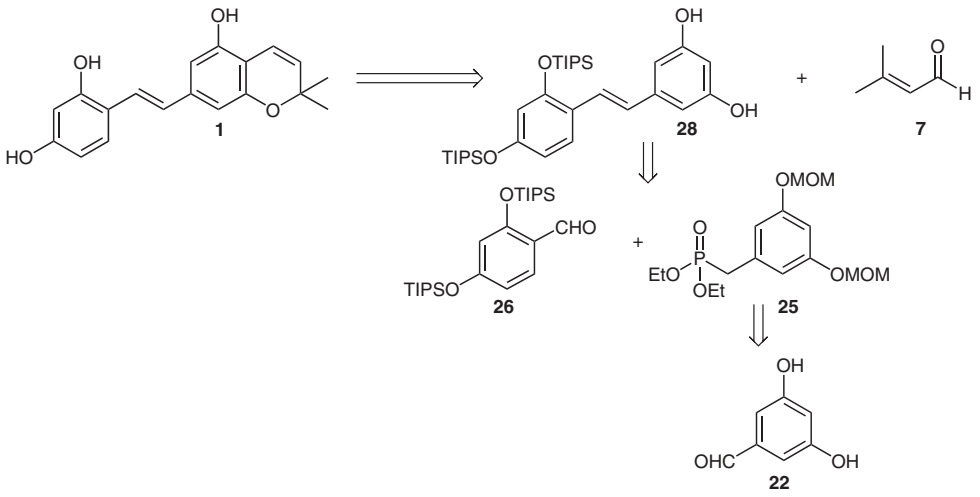
As an application of this methodology, the total syntheses of naturally occurring artocarbene (**1**) and pawhuskin B (**2**) were attempted. Scheme 3 shows the retrosynthetic analysis for artocarbene (**1**) through disconnection. Artocarbene (**1**) can be prepared by a benzopyran-formation reaction of *trans*-stilbene **28** with 3-methylbut-2-enal (**7**) through the domino aldol-type reaction and 6π-electrocyclization reaction described above. Compound **28** can be readily generated by a Horner–Wadsworth–Emmons reaction of benzaldehyde **26** and benzylic phosphonate **25**. Aldehyde **26** can be prepared from commercially available 2,4-dihydroxybenzaldehyde, while phosphonate **25**

Table 1 Reactions of Pinosylvin (**6**) with α,β-Unsaturated Aldehydes **12**–**16**

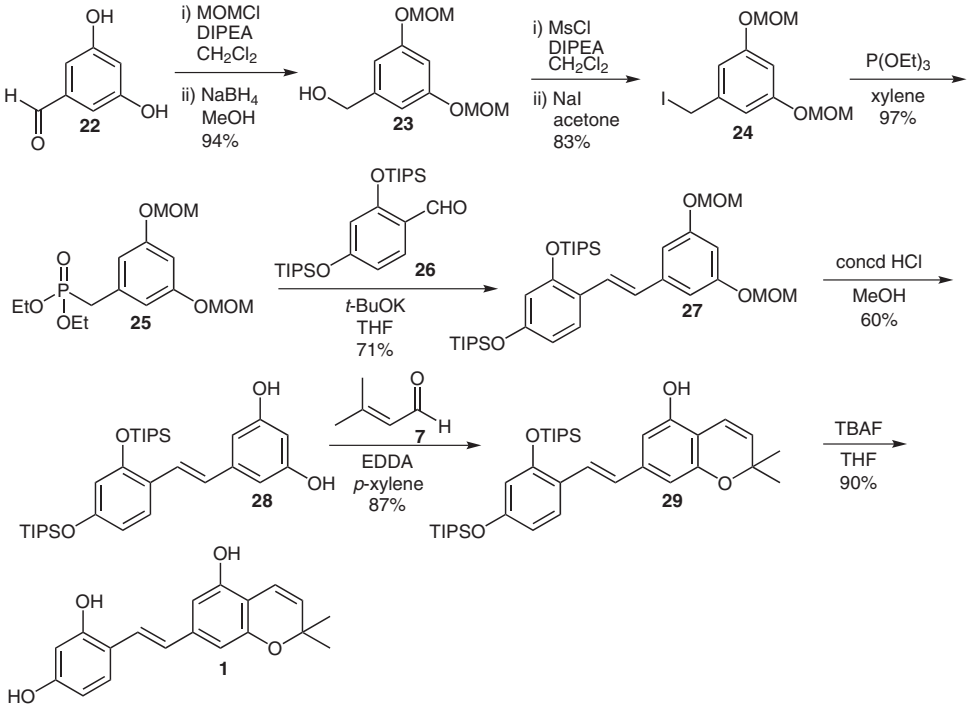
Entry	α,β-Unsaturated aldehyde	Conditions	Product	Yield (%)
1	**12** 	benzene, reflux, 12 h	**17** 	43
2	**13** 	benzene, reflux, 12 h	**18** 	79
3	**14** 	benzene, reflux, 12 h	**19** 	58
4	**15** 	*p*-xylene, reflux, 12 h	**20** 	67
5	**16** 	*p*-xylene, reflux, 12 h	**21** 	79

may be derived from commercially available 3,5-dihydroxybenzaldehyde (**22**).

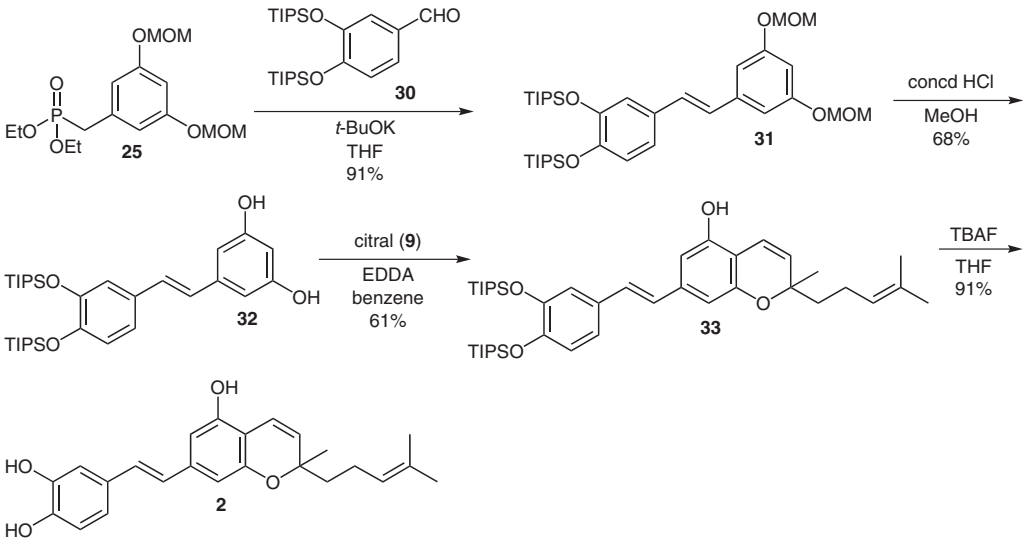
The synthetic approach of artocarbene (**1**) is shown in Scheme 4. Protection of aldehyde **22** with chloromethyl methyl ether under basic conditions provided by *N*,*N*-diisopropylethylamine, followed by reduction with sodium borohydride gave the protected benzyl alcohol **23** in 94% yield (2 steps). Alcohol **23** was then converted into the corresponding iodide **24** in 83% yield (2 steps) by a sequence consisting of mesylate formation followed by displacement with sodium iodide. Reaction of iodide **24** with triethyl phosphite in refluxing xylene for five hours afforded the desired phosphonate **25** in 97% yield. The Horner–Wadsworth–Emmons reaction of phosphonate **25** with benzaldehyde **26** in the presence of potassium *tert*-butoxide in tetrahydrofuran gave the desired *trans*-stilbene **27** in 71% yield.[24] Deprotection of the two methoxymethyl ethers of compound **27** with concentrated



Scheme 3 Retrosynthetic analysis for artocarbene (**1**)



Scheme 4 Total synthesis of artocarbene (**1**)



Scheme 5 Total synthesis of pawhuskin B (**2**)

hydrochloric acid in methanol at room temperature for ten hours afforded compound **28** in 60% yield. Reaction of **28** with 3-methylbut-2-enal (**7**) in the presence of ethylenediamine diacetate (20 mol%) in refluxing xylene for eight hours gave adduct **29** (87%). Removal of the two silyl ether groups with tetrabutylammonium fluoride provided artocarbene (**1**) in 90% yield. The spectroscopic data of synthetic material **1** was in agreement with the reported data.[17]

Next, the total synthesis of pawhuskin B (**2**) (Scheme 5) began with phosphonate **25**, prepared as described above. The Horner–Wadsworth–Emmons reaction of phosphonate **25** with benzaldehyde **30**, prepared from 3,4-dihydroxybenzaldehyde, provided *trans*-stilbene **31** in 91% yield.[24] Deprotection of the two methoxymethyl ethers was accomplished with concentrated hydrochloric acid in methanol at room temperature for ten hours to afford compound **32** (68%). Treatment of **32** with citral (**9**) catalyzed by ethylenediamine diacetate (20 mol%) in refluxing benzene for 12 hours gave adduct **33** in 61% yield. Removal of the two silyl ethers with tetrabutylammonium fluoride in tetrahydrofuran at room temperature for five hours gave pawhuskin B (**2**) in 91% yield. The spectroscopic data of synthetic compound **2** are identical to those of the natural product reported in the literature.[19]

In conclusion, we have described reactions for the formation of pyranostilbene derivatives starting from pinosylvin (**6**) and α,β-unsaturated aldehydes **12**–**16** in the

presence of ethylenediamine diacetate. As an application of this new methodology, the first total syntheses of natural products artocarbene (**1**) and pawhuskin B (**2**) were accomplished by a convergent sequence. The required *trans*-stilbenes **28** and **32**, key intermediates in the syntheses of these two natural products, were prepared in a straightforward manner by Horner–Wadsworth–Emmons reactions of the corresponding phosphonates synthesized from commercially available aldehydes.

All experiments were carried out under a N_2 atmosphere. Precoated silica gel plates (Merck, Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed on silica gel 9385 (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Model ARX (300 and 75 MHz, respectively) spectrometer; samples were prepared in $CDCl_3$ or acetone-d_6. IR spectra were recorded on a Jasco FTIR 5300 spectrophotometer. HRMS and MS spectra were carried out at the Korea Basic Science Institute.

Pyranostilbenes; General Procedure

EDDA (18 mg, 0.1 mmol) was added to a soln of pinosylvin (**6**; 0.5 mmol) and the appropriate α,β-unsaturated aldehyde (1.0–1.5 mmol) in benzene (10 mL) or *p*-xylene (10 mL). The mixture was refluxed for 8–12 h, and the subsequent removal of the solvent left an oily residue, which was purified by column chromatography (silica gel) to give the product.

(*E*)-2,2-Dimethyl-7-styryl-2*H*-chromen-5-ol (8)

The reaction of **6** (106 mg, 0.5 mmol) with 3-methylbut-2-enal (**7**; 84 mg, 1.0 mmol) in refluxing *p*-xylene (10 mL) for 8 h afforded compound **8**.

Yield: 109 mg (78%); solid; mp 138–140 °C.

IR (KBr): 3372, 2976, 1615, 1566, 1451, 1424, 1360, 1323, 1275, 1248, 1113, 1046, 957, 868, 826, 777 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.6 Hz, 2 H), 7.32 (dd, *J* = 8.6, 8.4 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 1 H), 7.01 (d, *J* = 16.3 Hz, 1 H), 6.89 (d, *J* = 16.3 Hz, 1 H), 6.60 (s, 1 H), 6.60 (d, *J* = 9.8 Hz, 1 H), 6.46 (s, 1 H), 5.59 (d, *J* = 9.8 Hz, 1 H), 1.42 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.1, 151.3, 138.4, 137.1, 129.3, 129.0, 128.6, 128.1, 127.7, 126.5, 116.3, 109.3, 107.3, 106.2, 76.1, 27.8.

MS (EI, 70 eV): *m*/*z* (%) = 278 [M$^+$] (17), 277 (3), 265 (2), 264 (20), 263 (100), 155 (2), 132 (4), 91 (4).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{19}H_{18}O_2$: 278.1307; found: 278.1309.

(*E*)-2-Methyl-2-(4-methylpent-3-enyl)-7-styryl-2*H*-chromen-5-ol (10)

The reaction of **6** (106 mg, 0.5 mmol) with citral (**9**; 152 mg, 1.0 mmol) in refluxing benzene (10 mL) for 10 h afforded compound **10**.

Yield: 104 mg (60%); oil.

IR (neat): 3409, 2970, 2921, 1613, 1567, 1429, 1343, 1263, 1198, 1143, 1083, 1058, 960, 824, 749 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.6 Hz, 2 H), 7.26 (dd, *J* = 8.6, 8.4 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 1 H), 6.96 (d, *J* = 16.3 Hz, 1 H), 6.83 (d, *J* = 16.3 Hz, 1 H), 6.59 (d, *J* = 9.8 Hz, 1 H), 6.55 (s, 1 H), 6.39 (s, 1 H), 5.49 (*J* = 9.8 Hz, 1 H), 5.10–4.98 (m, 2 H), 2.18–1.99 (m, 2 H), 1.75–1.63 (m, 2 H), 1.60 (s, 3 H), 1.53 (s, 3 H), 1.34 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 151.4, 138.3, 137.2, 131.7, 128.9, 128.7, 128.2, 128.1, 127.7, 126.5, 124.1, 116.8, 109.2, 107.1, 106.1, 78.4, 41.1, 26.3, 25.7, 22.7, 17.6.

MS (EI, 70 eV): *m*/*z* (%) = 346 [M$^+$] (9), 264 (19), 263 (100), 150 (3), 107 (3), 77 (3), 69 (9), 58 (5).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{24}H_{26}O_2$: 346.1933; found: 346.1936.

Compounds 10 and 11

The reaction of **6** (106 mg, 0.5 mmol) with citral (**9**; 152 mg, 1.0 mmol) in refluxing *p*-xylene (10 mL) for 10 h afforded compounds **10** and **11**.

Yield (**10**): 40 mg (23%); yield (**11**): 69 mg (40%).

Compound 11

Oil.

IR (neat): 3026, 2975, 2930, 1610, 1578, 1449, 1424, 1352, 1314, 1130, 1065, 997, 963, 909, 883, 827, 733 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 7.8 Hz, 2 H), 7.27 (dd, *J* = 7.8, 7.5 Hz, 2 H), 7.15 (d, *J* = 7.5 Hz, 1 H), 6.94 (s, 2 H), 6.60 (s, 1 H), 6.57 (s, 1 H), 2.83 (br s, 1 H), 2.24–1.98 (m, 2 H), 1.79 (d, *J* = 13.2 Hz, 2 H), 1.48 (s, 3 H), 1.41–1.36 (m, 1 H), 1.33 (s, 3 H), 1.25–1.18 (m, 1 H), 0.98 (s, 3 H), 0.74–0.61 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 156.9, 137.4, 136.8, 129.2, 128.6, 128.2, 127.3, 126.4, 116.9, 107.8, 107.4, 83.8, 74.7, 46.7, 37.3, 35.2, 29.7, 29.0, 28.3, 23.8, 22.1.

MS (EI, 70 eV): *m*/*z* (%) = 346 [M$^+$] (30), 331 (7), 303 (5), 265 (10), 264 (22), 263 (100), 151 (10), 123 (7), 109 (5), 91 (7), 69 (31).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{24}H_{26}O_2$: 346.1933; found: 346.1929.

(*E*)-2-Methyl-7-styryl-2*H*-chromen-5-ol (17)

The reaction of **6** (106 mg, 0.5 mmol) with crotonaldehyde (**12**; 105 mg, 1.5 mmol) in refluxing benzene (10 mL) for 12 h afforded compound **17**.

Yield: 57 mg (43%); solid; mp 92–93 °C.

IR (KBr): 3425, 2969, 2925, 1615, 1569, 1429, 1296, 1105, 1065, 960, 868, 823, 750 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.8 Hz, 2 H), 7.35 (dd, *J* = 7.8, 7.5 Hz, 2 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 7.03 (d, *J* = 16.2 Hz, 1 H), 6.92 (d, *J* = 16.2 Hz, 1 H), 6.71 (d, *J* = 9.8 Hz, 1 H), 6.64 (s, 1 H), 6.48 (d, *J* = 2.0 Hz, 1 H), 5.66 (dd, *J* = 9.8, 3.3 Hz, 1 H), 5.05–4.90 (m, 1 H), 1.47 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 151.4, 138.4, 137.0, 129.0, 128.6, 128.1, 127.7, 126.5, 125.3, 117.9, 109.9, 106.9, 106.4, 71.3, 21.0.

MS (EI, 70 eV): *m*/*z* (%) = 264 [M$^+$] (37), 263 (30), 250 (19), 249 (100), 155 (28), 116 (9), 91 (31), 69 (11), 59 (12).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{16}O_2$: 264.1150; found: 264.1146.

(*E*)-2-Phenyl-7-styryl-2*H*-chromen-5-ol (18)

The reaction of **6** (106 mg, 0.5 mmol) with *trans*-cinnamaldehyde (**13**; 198 mg, 1.5 mmol) in refluxing benzene (10 mL) for 12 h afforded compound **18**.

Yield: 129 mg (79%); solid; mp 55–56 °C.

IR (KBr): 3339, 1615, 1564, 1352, 1202, 1144, 1073, 1019, 949, 822, 764, 704 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.17 (m, 10 H), 6.90 (d, *J* = 16.2 Hz, 1 H), 6.78 (d, *J* = 16.2 Hz, 1 H), 6.77 (d, *J* = 9.8 Hz, 1

H), 6.54 (s, 1 H), 6.40 (s, 1 H), 5.79 (br s, 1 H), 5.70 (d, *J* = 9.8 Hz, 1 H), 5.25 (br s, 1 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 154.4, 153.3, 141.3, 138.8, 137.3, 128.7, 128.6, 128.5, 128.4, 128.1, 127.6, 126.9, 126.5, 122.7, 118.5, 109.6, 106.7, 105.5, 76.3.

MS (EI, 70 eV): *m*/*z* (%) = 326 [M$^+$] (100), 325 (81), 249 (31), 225 (16), 165 (8), 115 (8), 105 (14), 91 (14), 86 (22), 84 (33), 77 (11), 58 (8).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{23}H_{18}O_2$: 326.1307; found: 326.1307.

2-[(*E*)-4,8-Dimethylnona-3,7-dienyl]-2-methyl-7-[(*E*)-styryl]-2*H*-chromen-5-ol (19)

The reaction of **6** (106 mg, 0.5 mmol) with *trans*,*trans*-farnesal (**14**; 220 mg, 1.0 mmol) in refluxing benzene (10 mL) for 12 h afforded compound **19**.

Yield: 120 mg (58%); oil.

IR (neat): 3366, 2967, 1612, 1427, 1329, 1070, 960, 823 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.1 Hz, 2 H), 7.31 (dd, *J* = 8.4, 8.1 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 16.3 Hz, 1 H), 6.86 (d, *J* = 16.3 Hz, 1 H), 6.63 (d, *J* = 9.8 Hz, 1 H), 6.59 (s, 1 H), 6.42 (s, 1 H), 5.53 (d, *J* = 9.8 Hz, 1 H), 5.33 (br s, 1 H), 5.12–5.03 (m, 2 H), 2.19–1.86 (m, 6 H), 1.80–1.68 (m, 2 H), 1.65 (s, 3 H), 1.56 (s, 6 H), 1.38 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 151.4, 138.3, 137.2, 135.3, 131.3, 128.9, 128.7, 128.2, 128.1, 127.6, 126.5, 124.3, 123.9, 116.7, 109.2, 107.1, 106.0, 78.5, 41.1, 39.7, 26.7, 26.3, 25.7, 22.6, 17.7, 16.0.

MS (EI, 70 eV): *m*/*z* (%) = 414 [M$^+$] (10), 265 (4), 264 (19), 263 (100), 69 (6).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{29}H_{34}O_2$: 414.2559; found: 414.2563.

(*E*)-6-Styryl-2,3,4,4a-tetrahydro-1*H*-xanthen-8-ol (20)

The reaction of **6** (106 mg, 0.5 mmol) with cyclohex-1-ene-1-carboxaldehyde (**15**; 110 mg, 1.0 mmol) in refluxing *p*-xylene (10 mL) for 12 h afforded compound **20**.

Yield: 102 mg (67%); oil.

IR (neat): 3397, 2930, 1613, 1570, 1431, 1335, 1182, 1155, 1073, 1012, 959, 819, 752, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.20 (m, 5 H), 6.97 (d, *J* = 16.2 Hz, 1 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 6.53 (s, 1 H), 6.42 (s, 1 H), 6.34 (s, 1 H), 5.15 (br s, 1 H), 4.93–4.89 (m, 1 H), 2.47 (d, *J* = 13.8 Hz, 1 H), 2.25–2.21 (m, 1 H), 1.91–1.70 (m, 3 H), 1.54–1.30 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.9, 150.5, 137.2, 137.1, 136.6, 128.6, 128.4, 128.2, 127.5, 126.5, 110.1, 109.3, 106.4, 105.9, 76.6, 35.0, 33.2, 26.7, 24.3.

MS (EI, 70 eV): *m*/*z* (%) = 304 [M$^+$] (94), 303 (85), 276 (28), 275 (100), 125 (14), 109 (36), 86 (23), 84 (35), 81 (13), 58 (35).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{21}H_{20}O_2$: 304.1463; found: 304.1462.

3-[(*S*)-Isopropenyl]-6-[(*E*)-styryl]-2,3,4,4a-tetrahydro-1*H*-xanthen-8-ol (21)

The reaction of **6** (106 mg, 0.5 mmol) with (–)-perillaldehyde (**16**; 150 mg, 1.0 mmol) in refluxing *p*-xylene (10 mL) for 8 h afforded compound **21**.

Yield: 136 mg (79%); oil.

IR (neat): 3400, 2934, 1614, 1579, 1427, 1331, 1163, 1065, 960, 889, 822, 750 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.5 Hz, 2 H), 7.35 (dd, *J* = 7.5, 7.3 Hz, 2 H), 7.27 (d, *J* = 7.3 Hz, 1 H), 6.99 (d, *J* = 16.2 Hz, 1 H), 6.89 (d, *J* = 16.2 Hz, 1 H), 6.59 (s, 1 H), 6.51 (br s, 1 H), 6.45 (s, 1 H), 5.01 (dd, *J* = 11.1, 5.1 Hz, 1 H), 4.79 (s, 2 H), 2.55 (d, *J* = 14.7 Hz, 1 H), 2.34–2.29 (m, 1 H), 2.21–2.13 (m, 2 H), 1.90–1.73 (m, 3 H), 1.79 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 153.8, 150.7, 148.3, 137.2, 137.1, 135.5, 128.6, 128.4, 128.2, 127.5, 126.5, 110.5, 109.3, 106.7, 105.8, 76.6, 43.1, 39.6, 32.4, 31.7, 20.7.

MS (EI, 70 eV): *m*/*z* (%) = 344 [M$^+$] (100), 343 (64), 329 (23), 315 (21), 301 (5), 276 (25), 275 (51), 262 (38), 165 (10), 149 (12), 115 (10), 91 (13), 83 (11), 69 (14).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{24}H_{24}O_2$: 344.1776; found: 344.1778.

3,5-Bis(methoxymethoxy)benzyl Alcohol (23)
Protected Benzaldehyde Intermediate

MOMCl (1.761 g, 22.0 mmol) was added to a soln of **22** (1.380 g, 10.0 mmol) and DIPEA (5.160 g, 40.0 mmol) in anhyd CH_2Cl_2 (30 mL) at r.t. The mixture was stirred at r.t. for 10 h, and then H_2O (20 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the combined organic extracts were washed with sat. aq NH_4Cl (30 mL) and H_2O (20 mL), dried ($MgSO_4$), and evaporated in vacuo. Flash chromatography (silica gel, hexane–EtOAc, 5:1) afforded the protected benzaldehyde.

Yield: 2.215 g (98%); oil.

IR (neat): 2955, 2830, 2732, 1702, 1600, 1465, 1389, 1297, 1214, 1153, 1084, 1033, 927, 856, 726 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.88 (s, 1 H), 7.18 (s, 2 H), 6.94 (s, 1 H), 5.18 (s, 4 H), 3.46 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 158.7, 138.4, 111.1, 110.4, 90.4, 56.2.

Compound 23

The protected benzaldehyde (2.054 g, 9.1 mmol) in MeOH (3 mL) was added dropwise to a suspension of $NaBH_4$ (0.344 g, 9.1 mmol) in MeOH (20 mL) at 0 °C. The mixture was allowed to stir at r.t. for 3 h and then quenched by addition of H_2O (30 mL). The mixture was acidified with 2 N aq HCl (30 mL) and extracted with EtOAc (3 × 40 mL). The organic layer was washed with H_2O (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, hexane–EtOAc, 1:1); this gave protected alcohol **23**.

Yield: 1.992 g (96%); oil.

IR (neat): 3419, 2953, 1604, 1462, 1294, 1149, 1082, 1034, 924, 846, 702 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.67 (s, 2 H), 6.61 (s, 1 H), 5.12 (s, 4 H), 4.57 (s, 2 H), 3.44 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 143.5, 107.9, 104.0, 94.3, 65.0, 56.0.

MS (EI, 70 eV): *m*/*z* (%) = 228 [M$^+$] (100), 198 (9), 183 (5), 168 (15), 167 (6), 152 (7), 107 (4).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{11}H_{16}O_5$: 228.0998; found: 228.1000.

3,5-Bis(methoxymethoxy)benzyl Iodide (24)

MsCl (0.916 g, 8.0 mmol) was added dropwise to a soln of alcohol **23** (1.789 g, 7.8 mmol) and DIPEA (2.012 g, 15.6 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was allowed to stir at r.t. for 10 h and then quenched by the addition of H_2O (30 mL). The reaction mixture was extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with NH_4Cl soln (30 mL), H_2O (30 mL), and

brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. A mixture of the resulting residue and NaI (3.507, 23.4 mmol) in acetone (50 mL) was stirred for 10 h. The removal of the solvent under reduced pressure left an oily residue, which was then purified by column chromatography (silica gel, hexane–EtOAc, 5:1) to give product **24**.

Yield: 2.188 g (83%); oil.

IR (neat): 3022, 2935, 1601, 1457, 1364, 1179, 1151, 1024, 967, 867, 808, 744 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.70 (s, 2 H), 6.60 (s, 1 H), 5.12 (s, 4 H), 4.35 (s, 2 H), 3.45 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.2, 141.2, 110.0, 104.4, 94.4, 56.0, 5.2.

HRMS–FAB: *m*/*z* $[M + H]^+$ calcd for $C_{11}H_{16}O_4I$: 339.0093; found: 339.0091.

Diethyl [3,5-Bis(methoxymethoxy)benzyl]phosphonate (25)

$P(OEt)_3$ (1 mL) was added to a soln of **24** (2.025 g, 6.0 mmol) in *p*-xylene (10 mL) at r.t. The mixture was heated at 100 °C for 5 h. The removal of the solvent under reduced pressure left an oily residue, which was then purified by column chromatography (silica gel, hexane–EtOAc, 1:1) to give product **25**.

Yield: 2.024 g (97%); oil.

IR (neat): 3457, 2982, 1602, 1464, 1400, 1150, 1029, 965, 857, 792 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.61–6.58 (m, 3 H), 5.10 (m, 4 H), 4.05–3.95 (m, 4 H), 3.42 (s, 6 H), 3.01 (d, J_{PH} = 21.6 Hz, 2 H), 1.26–1.21 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 133.6, 111.1, 103.4, 94.3, 62.1, 55.9, 33.9 (d, J_{CP} = 138.1 Hz), 16.2.

MS (EI, 70 eV): *m*/*z* (%) = 348 $[M^+]$ (100), 318 (28), 317 (22), 316 (94), 315 (27), 287 (42), 271 (25), 232 (24), 229 (20), 160 (21).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{15}H_{25}O_7P$: 348.1338; found: 348.1335.

(*E*)-3,5-Bis(methoxymethoxy)-2′,4′-bis(triisopropylsiloxy)stilbene (27)

t-BuOK (0.717 g, 6.4 mmol) was added to a soln of **25** (1.055 g, 3.0 mmol) and aldehyde **26** (1.440 g, 3.2 mmol) in THF (30 mL) at 0 °C, and the mixture was stirred at 0 °C for a further 30 min. The mixture was quenched by the addition of H_2O (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with NH_4Cl soln (30 mL), H_2O (30 mL), and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The removal of the solvent under reduced pressure left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 20:1) to give product **27**.

Yield: 1.465 g (71%); oil.

IR (neat): 2948, 2866, 1595, 1495, 1309, 1182, 1149, 1080, 1035, 986, 889, 840, 760 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 16.5 Hz, 1 H), 7.42 (d, *J* = 8.4 Hz, 1 H), 6.83 (d, *J* = 16.5 Hz, 1 H), 6.82 (d, *J* = 2.0 Hz, 2 H), 6.58 (t, *J* = 2.0 H z, 1 H), 6.49 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.38 (d, *J* = 2.0 Hz, 1 H), 5.15 (s, 4 H), 3.47 (s, 6 H), 1.33–1.16 (m, 6 H), 1.13–1.03 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 156.7, 154.5, 140.6, 126.4, 125.7, 124.4, 121.5, 113.6, 110.8, 107.5, 103.9, 94.5, 56.0, 18.0, 17.9, 17.7, 13.0, 12.7, 12.0.

MS (EI, 70 eV): *m*/*z* (%) = 644 $[M^+]$ (100), 601 (12), 407 (23), 87 (10), 73 (15), 59 (14), 57 (10).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{36}H_{60}O_6Si_2$: 644.3928; found: 644.3925.

(*E*)-3,5-Dihydroxy-2′,4′-bis(triisopropylsiloxy)stilbene (28)

Concd HCl (5 drops) was added to a soln of **27** (1.305 g, 2.0 mmol) in MeOH (10 mL), and the mixture was stirred at r.t. for 10 h. Removal of the solvent under reduced pressure left an oily residue, which was then diluted with H_2O (30 mL). The mixture was extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with sat. aq $NaHCO_3$ (30 mL), H_2O (30 mL), and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Removal of the solvent under reduced pressure left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 7:1) to give **28**.

Yield: 0.668 g (60%); oil.

IR (neat): 3389, 2948, 2868, 1596, 1511, 1302, 1155, 996, 890, 742 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 16.5 H, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 6.77 (d, *J* = 16.5 Hz, 1 H), 6.52 (d, *J* = 2.0 Hz, 2 H), 6.49 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.39 (d, *J* = 2.0 Hz, 1 H), 6.21 (d, *J* = 2.0 Hz, 1 H), 1.32–1.16 (m, 6 H), 1.13–1.07 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 156.7, 154.5, 140.1, 126.6, 125.5, 124.6, 121.5, 113.6, 110.8, 105.8, 101.6, 18.0, 17.9, 17.8, 13.2, 12.9, 12.7, 12.6.

MS (EI, 70 eV): *m*/*z* (%) = 556 $[M^+]$ (100), 515 (12), 514 (29), 513 (71), 207 (10), 186 (12), 87 (11), 73 (13), 59 (16).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{32}H_{52}O_4Si_2$: 556.3404; found: 556.3403.

(*E*)-7-[2,4-Bis(triisopropylsiloxy)styryl]-2,2-dimethyl-2*H*-chromen-5-ol (29)

EDDA (5 mg, 0.03 mmol) was added to a soln of stilbene **28** (0.167 g, 0.3 mmol) and 3-methylbut-2-enal (**7**; 0.051 g, 0.6 mmol) in *p*-xylene (10 mL). The mixture was refluxed for 8 h and the solvent was removed; this left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 10:1) to give **29**.

Yield: 0.162 g (87%); oil.

IR (neat): 3415, 2949, 2868, 1600, 1497, 1425, 1311, 1250, 1113, 1060, 1003, 890, 772 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.4 H, 1 H), 7.38 (d, *J* = 16.5 Hz, 1 H), 6.75 (d, *J* = 16.5 Hz, 1 H), 6.60 (d, *J* = 9.8 Hz, 1 H), 6.54 (s, 1 H), 6.49 (dd, *J* = 8.4, 2.0 Hz, 1 H), 6.42 (s, 1 H), 6.39 (d, *J* = 2.0 Hz, 1 H), 5.56 (d, *J* = 9.8 HZ, 1 H), 1.42 (s, 6 H), 1.34–1.19 (m, 6 H), 1.17–1.08 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6, 154.5, 154.1, 151.3, 139.6, 128.8, 126.7, 125.8, 124.2, 121.7, 116.4, 113.5, 110.8, 108.7, 107.4, 105.4, 75.9, 27.8, 18.0, 17.8, 17.7, 13.0, 12.7.

MS (EI, 70 eV): *m*/*z* (%) = 622 $[M^+]$ (100), 608 (17), 607 (33), 579 (20), 407 (19), 254 (11), 155 (27), 91 (29).

HRMS (EI): *m*/*z* $[M^+]$ calcd for $C_{37}H_{58}O_4Si_2$: 622.3874; found: 622.3871.

Artocarbene (1)

A 1.0 M soln of TBAF in THF (0.6 mL, 0.6 mmol) was added to a soln of **29** (0.151 g, 0.2 mmol) in THF (10 mL) and the mixture was stirred at r.t. for 5 h. The mixture was then quenched by the addition of sat. aq NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Removal of the solvent under reduced pressure left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 2:1) to give **1**.

Yield: 0.068 g (90%); solid.

IR (KBr): 3411, 2977, 1610, 1516, 1456, 1264, 1117, 1060, 971, 837, 773 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.40 (s, 2 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.33 (d, *J* = 16.5 Hz, 1 H), 7.32 (s, 1 H), 6.87 (d, *J* = 16.5 Hz, 1 H), 6.65 (d, *J* = 9.9 Hz, 1 H), 6.57 (s, 1 H), 6.47 (s, 1 H), 6.43 (d, *J* = 2.4 Hz, 1 H), 6.38 (dd, *J* = 8.4, 2.4 Hz, 1 H), 5.59 (d, *J* = 9.9 Hz, 1 H), 1.37 (s, 6 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 160.0, 157.8, 155.8, 154.8, 141.5 129.6, 129.1, 126.8, 125.3, 118.7, 118.0, 110.2, 109.3, 107.3, 107.0 104.4, 77.1, 28.8.

(*E*)-3,5-Bis(methoxymethoxy)-3′,4′-bis(triisopropylsiloxy)stilbene (31)

t-BuOK (0.494 g, 4.4 mmol) was added to a soln of **25** (1.392 g, 4.0 mmol) and the benzaldehyde **30** (1.532 g, 4.4 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min, then quenched by the addition of H_2O (40 mL), and extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with aq NH_4Cl (30 mL), H_2O (30 mL), and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The removal of the solvent under reduced pressure left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 20:1) to give product **31**.

Yield: 2.583 g (91%); oil.

IR (neat): 2948, 2867, 1593, 1511, 1463, 1287, 1223, 1981, 1036, 888, 849 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.97–6.89 (m, 3 H), 6.81–6.79 (m, 3 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 6.62 (t, *J* = 2.0 H, 1 H), 5.17 (s, 4 H), 3.48 (s, 6 H), 1.34–1.23 (m, 6 H), 1.13–1.03 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 147.2, 147.1, 140.0, 130.1, 129.5, 126.0, 119.9, 119.6, 118.0, 107.7, 103.7, 94.5, 56.1, 18.0. 17.9, 17.7, 13.2, 12.3.

MS (EI, 70 eV): *m*/*z* (%) = 644 [M^+] (12), 487 (12), 252 (19), 251 (100), 207 (7), 180 (7), 179 (50), 165 (11), 157 (7), 131 (7), 75 (11).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{36}H_{60}O_6Si_2$: 644.3928; found: 644.3925.

(*E*)-3,5-Dihydroxy-3′,4′-bis(triisopropylsiloxy)stilbene (32)

Concd HCl (5 drops) was added to a soln of **31** (1.290 mg, 2.0 mmol) in MeOH (10 mL) and the mixture was stirred at r.t. for 10 h. The removal of the solvent under reduced pressure left an oily residue, which was then diluted with H_2O (30 mL). The mixture was extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with sat. aq $NaHCO_3$ (30 mL), H_2O (30 mL), and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Removal of the solvent under reduced pressure left an oily residue, which was then purified by column chromatography (silica gel, hexane–EtOAc, 4:1) to give **32**.

Yield: 0.757 g (68%); oil.

IR (neat): 3372, 2946, 2867, 1596, 1512, 1465, 1069, 995, 887, 850, 739 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.96 (d, *J* = 2.0 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 6.89 (d, *J* = 16.2 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.70 (d, *J* = 16.2 Hz, 1 H), 6.54 (d, *J* = 2.0 Hz, 2 H), 6.23 (t, *J* = 2.0 Hz, 1 H), 1.34–1.23 (m, 6 H), 1.13–1.03 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 147.2, 146.9, 140.5, 129.9, 129.6, 125.5, 119.9, 119.6, 118.0, 106.1, 101.9, 18.0, 17.9, 13.1, 12.9.

MS (EI, 70 eV): *m*/*z* (%) = 556 [M^+] (100), 356 (21), 158 (13), 157 (85), 129 (14), 116 (10), 115 (87), 101 (13), 87 (41), 75 (15), 73 (410, 59 (56), 58 (45).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{32}H_{52}O_4Si_2$: 556.3404; found: 556.3407.

(*E*)-7-[3,4-Bis(triisopropylsiloxy)styryl]-2-methyl-2-(4-methylpent-3-enyl)-2*H*-chromen-5-ol (33)

EDDA (4.0 mg) was added to a soln of stilbene **32** (0.223, 0.4 mmol) and citral (**9**; 0.122 g, 0.8 mmol) in benzene (10 mL). The reaction mixture was refluxed for 12 h; removal of the solvent left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 20:1) to give **33**.

Yield: 0.169 g (61%); oil.

IR (neat): 3431, 2947, 2868, 1611, 1512, 1301, 1131, 1082, 999, 899 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 2.0 Hz, 1 H), 6.87 (d, *J* = 16.2 Hz, 1 H), 6.87 (dd, *J* = 8.1, 2.0 Hz, 1 H), 6.77 (d, *J* = 8.1 Hz, 1 H), 6.66 (d, *J* = 16.2 Hz, 1 H), 6.63 (d, *J* = 9.9 Hz, 1 H), 6.56 (br s, 1 H), 6.40 (br s, 1 H), 5.52 (d, *J* = 9.9 Hz, 1 H), 5.11–5.06 (m, 1 H), 2.16–2.10 (m, 2 H), 1.74–1.69 (m, 2 H), 1.65 (s, 3 H), 1.57 (s, 3 H), 1.38 (s, 3 H), 1.33–1.24 (m, 6 H), 1.12–1.08 (m, 36 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.3, 151.3, 147.1, 147.0, 138.8, 131.7, 130.2, 128.9, 127.9, 125.8, 124.1, 119.9, 119.5, 117.9, 116.8, 108.7, 106.9, 105.6, 78.4, 41.2, 26.3, 25.7, 22.8, 18.0, 17.9, 17.6, 13.2.

MS (EI, 70 eV): *m*/*z* (%) = 690 [M^+] (70), 609 (21), 608 (52), 607 (100), 408 (10), 407 (31), 157 (12), 115 (22), 87 (18), 73 (20), 59 (23).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{42}H_{66}O_4Si_2$: 690.4500; found: 690.4496.

Pawhuskin B (2)

A 1.0 M soln of TBAF in THF (0.6 mL, 0.6 mmol) was added to a soln of **33** (0.151 g, 0.2 mmol) in THF (10 mL) and the mixture was stirred at r.t. for 5 h. The reaction mixture was quenched by the addition of sat. aq NH_4Cl (30 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layer was washed with H_2O (30 mL) and brine (30 mL), dried ($MgSO_4$), and concentrated under reduced pressure. Removal of the solvent under reduced pressure left an oily residue, which was purified by column chromatography (silica gel, hexane–EtOAc, 2:1) to give **2**.

Yield: 0.075 g (91%); oil.

IR (neat): 3387, 2937, 1609, 1518, 1442, 1366, 1273, 1195, 1096, 979, 827, 738 cm^{-1}.

^1H NMR (300 MHz, acetone-d_6): δ = 8.11 (br s, 2 H), 7.07 (d, *J* = 2.0 Hz, 1 H), 6.97 (d, *J* = 16.5 Hz, 1 H), 6.91 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 6.79 (d, *J* = 16.5 Hz, 1 H), 6.71 (d, *J* = 9.9 Hz, 1 H), 6.55 (s, 1 H), 6.51 (s, 1 H), 5.59 (d, *J* = 9.9 Hz, 1 H), 5.14–5.09 (m, 1 H), 2.16–2.03 (m, 2 H), 1.72–1.66 (m, 2 H), 1.63 (s, 3 H), 1.57 (s, 3 H), 1.36 (s, 3 H).

^{13}C NMR (75 MHz, acetone-d_6): δ = 155.5, 154.2, 146.4, 140.0, 132.1, 130.9, 129.7, 128.2, 126.8, 125.4, 120.3, 118.5, 116.5, 114.1, 109.8, 106.9, 106.5, 78.9, 42.1, 26.8, 26.0, 23.7, 17.9.

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