Palladium-Catalyzed Routes to Geranylated or Farnesylated Phenolic Stilbenes: Synthesis of Pawhuskin C and Schweinfurthin J

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Abstract: Starting from double MOM-protected phloroglucinol, the facile total syntheses of bioactive natural products pawhuskin C and schweinfurthin J were accomplished in good overall yields. The Heck, Stille, or Suzuki coupling reactions of two different electron-rich phenolic segments bearing geranylated or farnesylated units were involved in the decisive step. The Sonogashira coupling reaction followed by palladium-catalyzed chemo- and stereoselective *cis*-reduction of an alkyne unit and subsequent isomerization to give the desired natural products is also described.

Key words: total synthesis, natural products, geranylated or farnesylated stilbenes, palladium-catalyzed coupling reactions, phloroglucinol

A large number of prenylated, geranylated, and farnesylated phenolic compounds exist in nature and they constitute structurally interesting and biologically important structural architectures.[1–6] A few representative examples of such naturally occurring bioactive phenolic stilbenes are depicted in Figure 1.[7–10] In the synthesis of these target compounds holding free prenyl, geranyl, or farnesyl chains, the formation of benzofurans or benzopyrans, cycloaddition products, regioisomeric mixtures, and polymeric gums are common difficulties.[1–5] Pawhuskin C (**1**) was isolated from *Dalea purpurea* and exhibits opioid activity, while schweinfurthin J (**2**) was from *Macaranga schweinfurthii* and exhibits anticancer activity.[7,8] Structural scrutiny revealed that pawhuskin C could be the biogenetic precursor of schweinfurthin G, while schweinfurthin J is the farnesyl derivative of naturally occurring potent anticancer agent resveratrol.[7,11] To date, only one synthesis of pawhuskin C (**1**) has been published.[12] It was accomplished using an *ortho*-lithiation strategy to install the geranyl chain and subsequent appropriate Horner–Wadsworth–Emmons condensation to form the desired *trans*-stilbene. The palladium-catalyzed C–C coupling reactions of substrates bearing prenylated, geranylated, or farnesylated phenolic segments to form stilbenes are not known in the literature.[13–15] The synthesis of natural products **1** and **2** would be feasible via the uncommon aromatic Claisen rearrangement of the geranyl or farnesyl unit followed by Heck, Stille, Suzuki, or Sonogashira coupling reactions pathways. Herein we report our results for the synthesis of these stilbene natural products (Schemes 1 and 2).

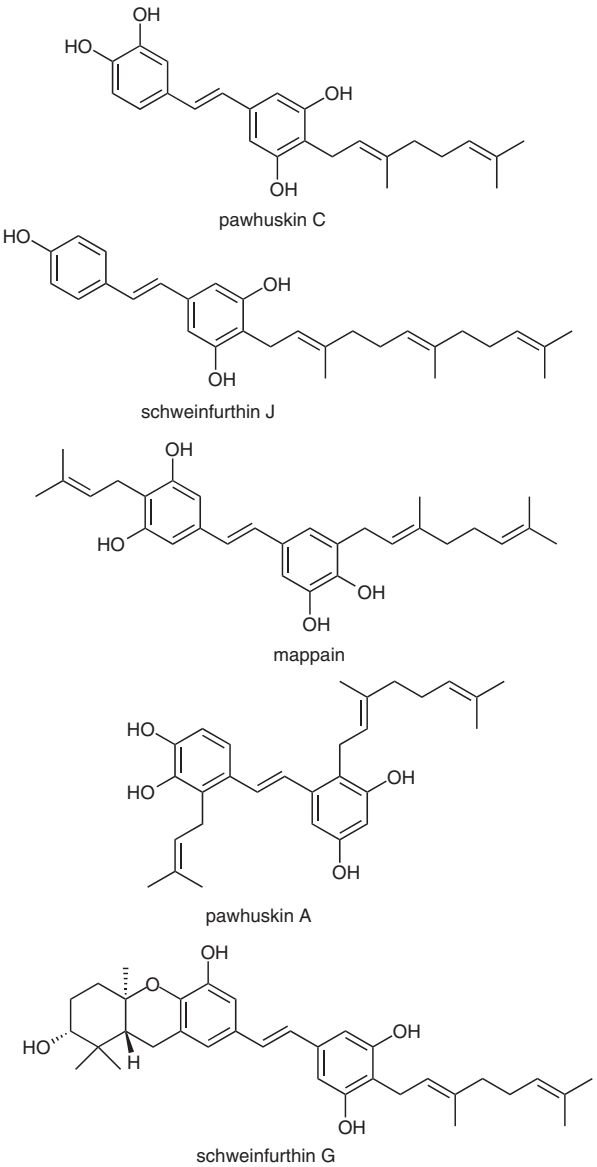

Figure 1 Naturally occurring prenylated, geranylated, or farnesylated phenolic stilbenes.

The double methoxymethyl-protected (MOM) symmetrical phenol **3**[16] on reaction with geranyl bromide or farnesyl bromide in the presence of potassium carbonate in *N*,*N*-dimethylformamide provided the expected O-geranylated or O-farnesylated products **4a**,**b** in 76–78% yields (Scheme 1). The products **4a**,**b** underwent a defined Claisen rearrangement in refluxing *N*,*N*-dimethylaniline

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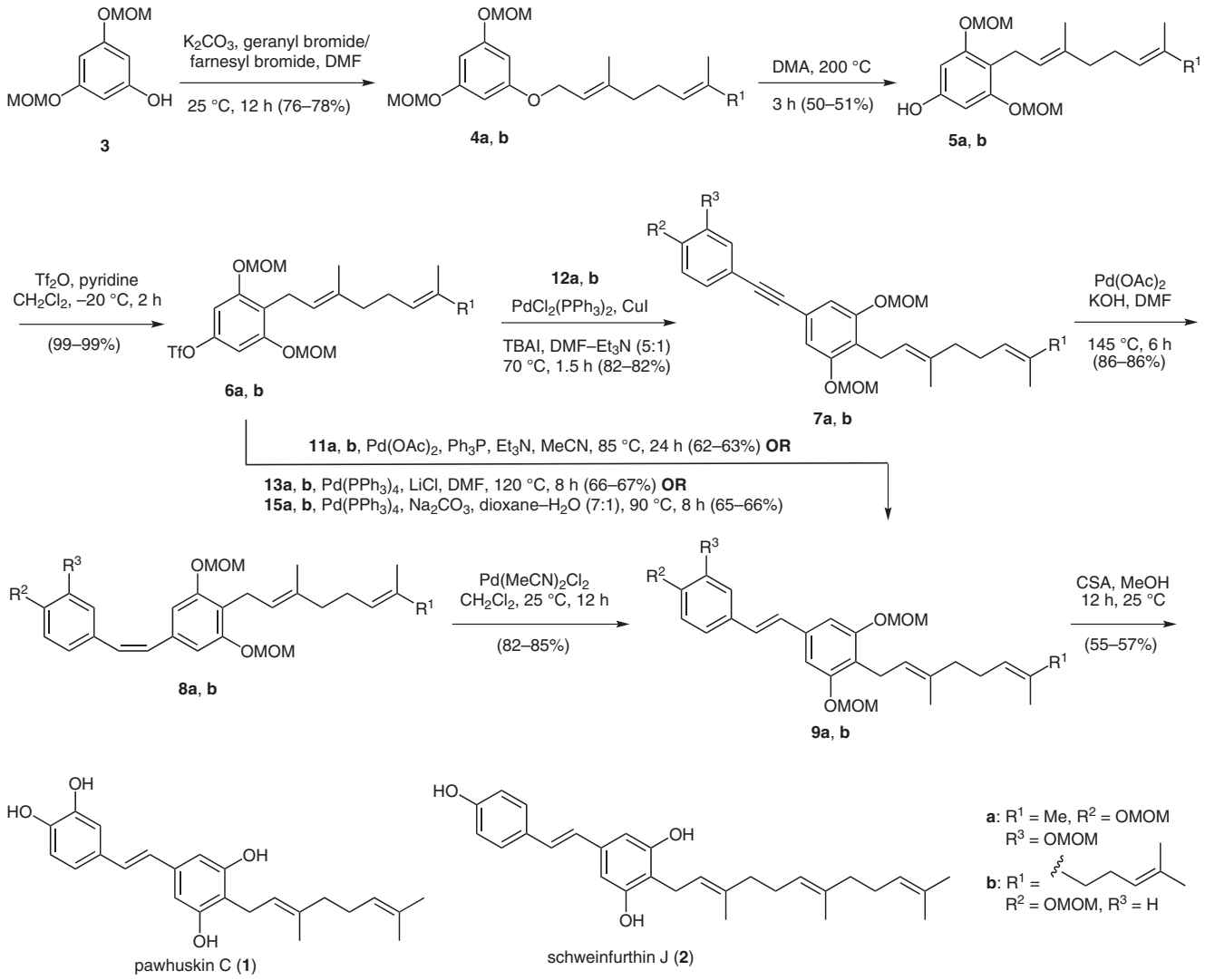
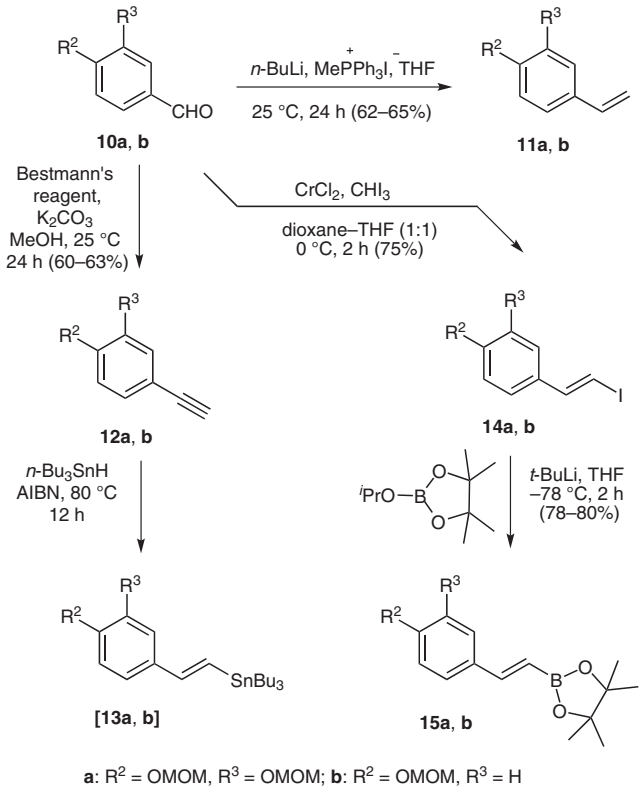


Scheme 1 Synthesis of bioactive natural and unnatural geranylated or farnesylated phenolic stilbenes.

(DMA) furnishing only the corresponding *p*-geranylated or *p*-farnesylated *trans* products **5a**,**b** in 50–51% yields along with 30–35% recovery of the starting material. In this reaction, we also noticed the decomposition of the starting material to the extent of 10–15%, while under forced conditions we noticed excessive decomposition. To the best of our knowledge, very few examples of such this aromatic Claisen rearrangement to install the geranyl or farnesyl unit are known in literature.[17–19] The free phenolic groups in compounds **5a**,**b** were transformed to the good triflyloxy leaving group by treatment with triflic anhydride/pyridine to obtain **6a**,**b** both in 99% yield. Subsequently, the Heck, Stille, and Suzuki coupling reactions of the building blocks **6a**,**b** with appropriate coupling partners from Scheme 2 were deliberated to obtain the products **9a**,**b**.[20–25] As depicted in Scheme 2, the Heck and Sonogashira coupling partners **11** and **12** were respectively prepared from **10a**,**b** by using Wittig or Ohira–Bestmann's reagents;[26–28] the radical hydrostannation of **12a**,**b** provided the desired Stille coupling regioisomers **13a**,**b**;[29] and the Suzuki coupling partners were also obtained from **10a**,**b** via Takai olefination to form vinyl iodides **14a**,**b** and subsequent conversion into 2-vinyl-substituted pinacolboranes **15a**,**b**.[30,31] The above-mentioned palladium-catalyzed Heck, Stille, or Suzuki coupling reactions of **6a**,**b** with **11a**,**b**, **13a**,**b**, and **15a**,**b** were selective and exclusively provided the desired products **9a**,**b** in good yields (62–67%). Interestingly, all of these palladium-catalyzed coupling reactions involving electron-rich substrates were equally efficient in yielding the desired stilbenes. A systematic study of the Sonogashira coupling between **6a** and **12a** was also planned to provide selectively both *cis*- and *trans*-stilbenes.[32–34] Initial attempts to couple the phenolic compounds **6a** and **12a** under standard coupling conditions resulted in dimerization of the alkyne unit. A literature search revealed that the present observation matches with the report of Boger et al.[35] that such type of electron-rich compounds are relatively less reactive. An in situ exchange of triflyloxy to iodo using excess tetrabutylammonium iodide was necessary for Sonogashira coupling reactions of the two electron-rich segments **6a**,**b** and **12a**,**b**; fortunately, these coupling conditions yielded the desired products **7a**,**b** both in 82% yield. Efforts to convert the alkyne unit in

7a,**b** into *trans*-**9a**,**b** using diisobutylaluminum hydride were unsuccessful and resulted in the recovery of the starting materials.[36] At this stage, the recently reported palladium-catalyzed transfer semihydrogenation conditions for the reduction of the C≡C bond to the C=C bond were examined.[37] The reaction of alkynes **7a**,**b** with *N*,*N*-dimethylformamide and potassium hydroxide in the presence of palladium(II) acetate exclusively supplied the corresponding *cis*-stilbenes **8a**,**b** both in 86% yield. The *cis*-geometry of the C=C bond in products **8a**,**b** was confirmed on the basis of the chemical shift and coupling constants of the corresponding vinylic protons. Using the method reported by Spencer et al.,[38a] palladium(II)-catalyzed *cis*-to-*trans* isomerization of the C=C bond in **8a**,**b** formed the required products **9a**,**b** in 82–85% yields. On the basis of the reports of Sen et al.,[38b,c] we feel that neryl-substituted analogues of **8a** will also form the corresponding product **9a** via the *Z*-to-*E* C=C bond isomerization (allylic rearrangement). Finally, the acid-catalyzed global deprotection of methoxymethyl groups in **9a**,**b** delivered the desired natural products pawhuskin C (**1**) and schweinfurthin J (**2**) in 55–57% yields. The obtained analytical and spectral data for the natural products **1** and **2** were in complete agreement with the reported data.[7,8,12] The natural products **1** and **2** were obtained via partially separate routes in five and seven linear steps with 14–15% and 12–14% overall yields.



Scheme 2 Synthesis of Heck, Sonogashira, Stille, and Suzuki coupling blocks.

In summary, we have demonstrated a new route to bioactive polyene natural products pawhuskin C and schweinfurthin J by using Heck, Stille, Suzuki, or Sonogashira coupling reactions as the key steps. The present approach provides an easy access to the both geometrically pure *cis*- and *trans*-stilbene isomers. We feel that Heck, Stille, or Suzuki coupling reactions will provide access to nerylated *trans*-stilbenes and the Sonogashira coupling reaction will provide access to nerylated *cis*-stilbenes. Hence the described synthetic strategy is general in nature and will be useful for the preparation of some of the desired natural and unnatural stilbene analogues, congeners, and the corresponding benzofuran or benzopyran architectures for structure–activity relationship studies.

^{1}H NMR spectra were recorded on 200 MHz and 500 MHz spectrometers using TMS as an internal standard. ^{13}C NMR spectra were recorded on 200 (50 MHz), 400 (100 MHz), and 500 (125 MHz) spectrometers. Mass spectra were recorded on an MS-TOF mass spectrometer. HRMS (ESI) were recorded on Orbitrap (quadrupole plus ion trap) and TOF mass analyzer. IR spectra were recorded on an FT-IR spectrophotometer. Column chromatographic separations were carried out on silica gel (60–120, 100–200, and 230–400 mesh); petroleum ether = PE. Commercially available *n*-BuLi, $CrCl_2$, CHI_3, *n*-Bu_3SnH, AIBN, *t*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, DMA, Tf_2O, TBAI, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$, $Pd(PPh_3)_4$, $Pd(MeCN)_2Cl_2$, and camphorsulfonic acid (CSA) were used.

1,2-Bis(methoxymethoxy)-4-vinylbenzene (11a); Typical Procedure

To a stirred soln of $MePh_3PI$ (2.68 g, 6.63 mmol) in THF (30 mL) at 0 °C was added 1.60 M *n*-BuLi in hexane (4.0 mL, 6.41 mmol) and the mixture was stirred for 45 min under argon. A soln of aldehyde **10a**[39a] (500 mg, 2.21 mmol) in THF (10 mL) was added dropwise and the mixture was stirred at 25 °C for 24 h. The reaction was quenched with sat. NH_4Cl (5 mL), and THF was removed in vacuo. The residue was dissolved in EtOAc (25 mL), and EtOAc soln was washed with H_2O (5 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was subjected to column chromatography (silica gel, PE–EtOAc, 9:1) to afford pure **11a** as a thick oil;[39b] yield: 307 mg (62%).

IR (neat): 1631, 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.51 (s, 3 H), 3.53 (s, 3 H), 5.16 (dd, *J* = 10, 2 Hz, 1 H), 5.23 (s, 2 H), 5.25 (s, 2 H), 5.62 (dd, *J* = 18, 2 Hz, 1 H), 6.64 (dd, *J* = 18, 10 Hz, 1 H), 7.01 (dd, *J* = 8, 2 Hz, 1 H), 7.12 (d, *J* = 8 Hz, 1 H), 7.25 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.21, 56.23, 95.4, 95.5, 112.7, 114.2, 116.5, 120.7, 132.5, 136.2, 147.0, 147.3.

MS (ESI): *m*/*z* = 247 [M + Na]$^+$.

1-(Methoxymethoxy)-4-vinylbenzene (11b)

Following the typical procedure for **11a** using **10b**[40a] (500 mg, 3.01 mmol), $MePh_3PI$ (3.65 g, 9.03 mmol), and 1.60 M *n*-BuLi in hexane (5.45 mL, 8.73 mmol) gave **11b** as a thick oil;[40b] yield: 329 mg (65%).

IR (neat): 1629, 1606 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.48 (s, 3 H), 5.16 (d, *J* = 10 Hz, 1 H), 5.18 (s, 2 H), 5.64 (d, *J* = 18 Hz, 1 H), 6.68 (dd, *J* = 18, 10 Hz, 1 H), 7.00 (d, *J* = 8 Hz, 2 H), 7.35 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.0, 94.4, 112.1, 116.2, 127.3, 131.5, 136.1, 156.9.

MS (ESI): *m*/*z* = 165 [M + H]$^+$.

4-Ethynyl-1,2-bis(methoxymethoxy)benzene (12a); Typical Procedure

To a stirred soln of **10a** (3.00 g, 13.27 mmol) and Ohira–Bestmann's reagent (6.41 g, 39.82 mmol) in MeOH (80 mL) was added K_2CO_3 (9.17 g, 66.37 mmol) and the mixture was stirred at 25 °C for 24 h under argon. The mixture was concentrated in vacuo, and EtOAc (50 mL) was added to the residue. The EtOAc soln was washed with H_2O (15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 9:1) to afford pure **12a** as a thick oil; yield: 1.76 g (60%).

IR (neat): 3286, 2105, 1600 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.01 (s, 1 H), 3.51 (s, 3 H), 3.52 (s, 3 H), 5.23 (s, 2 H), 5.25 (s, 2 H), 7.09–7.14 (m, 2 H), 7.31 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.2 (2 C), 76.1, 83.3, 95.1, 95.4, 115.9, 116.0, 120.2, 126.8, 146.7, 148.0.

MS (ESI): *m*/*z* = 223 $[M + H]^+$, 245 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{14}NaO_4$: 245.0790; found: 245.0784.

1-Ethynyl-4-(methoxymethoxy)benzene (12b)

Following the typical procedure for **12a** using **10b** (3.00 g, 18.07 mmol), Ohira–Bestmann's reagent (8.72 g, 54.21 mmol), and K_2CO_3 (12.48 g, 90.36 mmol) gave **12b** as a thick oil;[40b] yield: 1.84 g (63%).

IR (neat): 3288, 2107, 1604 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 3.01 (s, 1 H), 3.47 (s, 3 H), 5.18 (s, 2 H), 6.93–7.03 (m, 2 H), 7.38–7.47 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.1, 76.0, 83.5, 94.2, 115.3, 116.1, 133.5, 157.5.

MS (ESI): *m*/*z* = 163 $[M + H]^+$, 185 $[M + Na]^+$.

(*E*)-4-(2-Iodovinyl)-1,2-bis(methoxymethoxy)benzene (14a); Typical Procedure

To a vigorously stirred suspension of $CrCl_2$ (4.35 g, 35.39 mmol) in THF–dioxane (1:1, 60 mL) at 0 °C was added a soln of aldehyde **10a** (1.00 g, 4.42 mmol) in THF–dioxane (1:1, 20 mL) under argon. After 5 min, CHI_3 (6.09 g, 15.48 mmol) in THF–dioxane (1:1, 10 mL) soln was added to the mixture. After 2 h at 0 °C, H_2O (80 mL) and EtOAc (80 mL) were added to the mixture and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 × 40 mL) and the combined organic layers were washed with brine (15 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 19:1) to afford pure (*E*)-vinyl iodide **14a** as a thick oil; yield: 1.16 g (75%).

IR ($CHCl_3$): 1601 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = (*E*/*Z* 94:6): 3.51 (s, 3 H), 3.52 (s, 3 H), 5.23 (s, 4 H), 6.68 (d, *J* = 14 Hz, 1 H), 6.89 (dd, *J* = 8, 2 Hz, 1 H), 7.10 (d, *J* = 8 Hz, 1 H), 7.13 (d, *J* = 2 Hz, 1 H), 7.33 (d, *J* = 16 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.2 (2 C), 75.0, 95.3, 95.5, 113.9, 116.4, 120.6, 132.5, 144.2, 147.3, 147.5.

MS (ESI): *m*/*z* = 373 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{12}H_{15}INaO_4$: 372.9913; found: 372.9904.

(*E*)-1-(2-Iodovinyl)-4-(methoxymethoxy)benzene (14b)

Following the typical procedure for **14a** using $CrCl_2$ (5.92 g, 48.19 mmol), aldehyde **10b** (1.00 g, 6.02 mmol), CHI_3 (8.30 g, 21.08 mmol) gave **14b** as a thick oil; yield: 1.31 g (75%).

IR ($CHCl_3$): 1605 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = (*E*/*Z* 93:7):3.47 (s, 3 H), 5.17 (s, 2 H), 6.66 (d, *J* = 14 Hz, 1 H), 6.94–7.04 (m, 2 H), 7.18–7.29 (m, 2 H), 7.36 (d, *J* = 16 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 56.1, 74.2, 94.3, 116.3, 127.2, 131.8, 144.2, 157.3.

MS (ESI): *m*/*z* = 313 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{12}IO_2$: 290.9882; found: 290.9871.

(*E*)-2-[3,4-Bis(methoxymethoxy)styryl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15a); Typical Procedure

To a stirred soln of vinyl iodide **14a** (500 mg, 1.42 mmol) in THF (10 mL) at –78 °C was added 1.30 M *t*-BuLi in hexane (1.53 mL, 1.99 mmol) and the mixture was stirred for 45 min under argon. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.32 mL, 1.99 mmol) was added dropwise and the mixture was stirred at –78 °C for 2 h. The reaction was quenched with sat. NH_4Cl (2 mL) and THF was removed in vacuo. The obtained residue was dissolved in EtOAc (25 mL) and the EtOAc soln was washed with H_2O (5 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 9:1) to afford pure vinyl boronate **15a** as a thick oil; yield: 390 mg (78%).

IR (neat): 1625, 1602 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 (s, 12 H), 3.44 (s, 6 H), 5.16 (s, 2 H), 5.17 (s, 2 H), 5.98 (d, *J* = 18 Hz, 1 H), 7.04 (s, 2 H), 7.18–7.32 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.8, 56.1, 56.2, 83.3, 95.2, 95.5, 115.0, 116.1, 121.9, 132.2, 147.2, 148.0, 148.9.

MS (ESI): *m*/*z* = 351 $[M + H]^+$, 373 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{27}BNaO_6$: 373.1798; found: 373.1800.

(*E*)-2-[4-(Methoxymethoxy)styryl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)

Following the typical procedure for **15a** using vinyl iodide **14b** (500 mg, 1.72 mmol), 1.3 M *t*-BuLi in hexane (1.85 mL, 2.41 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.49 mL, 2.41 mmol) gave **15b** as a thick oil; yield: 400 mg (80%).

IR ($CHCl_3$): 1626, 1604 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.28 (s, 12 H), 3.44 (s, 3 H), 5.15 (s, 2 H), 6.00 (d, *J* = 18 Hz, 1 H), 6.97 (d, *J* = 10 Hz, 2 H), 7.32 (d, *J* = 20 Hz, 1 H), 7.40 (d, *J* = 10 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.8, 56.0, 83.2, 94.3, 116.2, 128.4, 130.2, 131.5, 148.9, 157.9.

MS (ESI): *m*/*z* = 291 $[M + H]^+$, 313 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{24}BO_4$: 291.1768; found: 291.1750.

(*E*)-1-[(3,7-Dimethylocta-2,6-dienyl)oxy]-3,5-bis(methoxymethoxy)benzene (4a); Typical Procedure

To a stirred soln of **3** (2.00 g, 9.34 mmol) and geranyl bromide (4.05 g, 18.69 mmol) in DMF (40 mL) was added K_2CO_3 (6.45 g, 46.72 mmol) and the mixture was stirred at 25 °C for 12 h under argon. To the mixture was added EtOAc (100 mL) and the EtOAc soln was washed with brine (3 × 25 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 19:1) to afford pure **4a** as a thick oil; yield: 2.48 g (76%).

IR (neat): 1602 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.61 (s, 3 H), 1.68 (s, 3 H), 1.73 (s, 3 H), 2.00–2.20 (m, 4 H), 3.47 (s, 6 H), 4.49 (d, *J* = 8 Hz, 2 H), 5.00–5.20 (m, 1 H), 5.13 (s, 4 H), 5.47 (t, *J* = 6 Hz, 1 H), 6.27–6.38 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.6, 17.7, 25.6, 26.3, 39.5, 56.0, 64.9, 94.5, 96.9, 97.2, 119.3, 123.8, 131.8, 141.3, 158.9, 160.6.

MS (ESI): *m*/*z* = 351 $[M + H]^+$, 373 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{31}O_5$: 351.2171; found: 351.2159.

1,3-Bis(methoxymethoxy)-5-{[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]oxy}benzene (4b)

Following the typical procedure for **4a** using **3** (2.00 g, 9.34 mmol), farnesyl bromide (5.32 g, 18.70 mmol), and K_2CO_3 (6.45 g, 46.72 mmol) gave **4b** as a thick oil; yield: 3.04 g (78%).

IR (neat): 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.60 (s, 6 H), 1.68 (s, 3 H), 1.73 (s, 3 H), 1.90–2.20 (m, 8 H), 3.47 (s, 6 H), 4.49 (d, *J* = 6 Hz, 2 H), 5.00–5.20 (m, 2 H), 5.13 (s, 4 H), 5.47 (t, *J* = 8 Hz, 1 H), 6.27–6.38 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 16.6, 17.7, 25.7, 26.2, 26.7, 39.5, 39.7, 56.0, 64.9, 94.4, 96.8, 97.2, 119.2, 123.7, 124.3, 131.3, 135.4, 141.3, 158.9, 160.6.

MS (ESI): *m*/*z* = 419 $[M + H]^+$, 441 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{38}NaO_5$: 441.2617; found: 441.2607.

(*E*)-4-(3,7-Dimethylocta-2,6-dienyl)-3,5-bis(methoxymethoxy)phenol (5a); Typical Procedure

DMA (5 mL) was added to **4a** (500 mg, 1.43 mmol) and the mixture was refluxed for 3 h under argon. The mixture was allowed to attain r.t. To the mixture was added EtOAc (40 mL) and the soln was washed with dil HCl (2 × 10 mL), H_2O (3 × 10 mL), and brine (10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure **5a** as a thick oil; yield: 250 mg (50%).

IR ($CHCl_3$): 3394, 1603 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.65 (s, 3 H), 1.76 (s, 3 H), 1.85–2.20 (m, 4 H), 3.30 (d, *J* = 8 Hz, 2 H), 3.46 (s, 6 H), 5.00–5.25 (m, 2 H), 5.14 (s, 4 H), 5.48 (br s, 1 H), 6.31 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 17.6, 22.1, 25.7, 26.7, 39.8, 55.9, 94.3, 96.0, 112.4, 123.2, 124.4, 131.2, 134.2, 154.8, 156.2.

MS (ESI): *m*/*z* = 373 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{31}O_5$: 351.2171; found: 351.2172.

3,5-Bis(methoxymethoxy)-4-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]phenol (5b)

Following the typical procedure for **5a** using **4b** (500 mg, 1.19 mmol) gave **5b** as a thick oil; yield: 255 mg (51%).

IR (neat): 3398, 1606 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 1.76 (s, 3 H), 1.85–2.15 (m, 8 H), 3.31 (d, *J* = 6 Hz, 2 H), 3.46 (s, 6 H), 5.00–5.25 (m, 3 H), 5.14 (s, 4 H), 6.31 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.9, 16.0, 17.7, 22.1, 25.7, 26.66, 26.71, 39.7, 39.8, 55.9, 94.3, 96.0, 112.4, 123.2, 124.3, 124.4, 131.3, 134.2, 134.8, 154.8, 156.2.

MS (ESI): *m*/*z* = 419 $[M + H]^+$, 441 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{25}H_{39}O_5$: 419.2797; found: 419.2798.

(*E*)-4-(3,7-Dimethylocta-2,6-dienyl)-3,5-bis(methoxymethoxy)phenyl Trifluoromethanesulfonate (6a); Typical Procedure

To a stirred soln of **5a** (250 mg, 0.71 mmol) in CH_2Cl_2 (5 mL) at –20 °C was added pyridine (0.11 mL, 1.42 mmol) in a dropwise fashion under an argon atmosphere and the mixture was stirred at –20 °C for 30 min, which was followed by the addition of Tf_2O (0.18 mL, 1.07 mmol) and the mixture was stirred at –20 °C for a further 2 h. The reaction was quenched with ice-cooled H_2O and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 97:3) to afford pure triflate **6a** as a thick oil; yield: 340 mg (99%).

IR (neat): 1612 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.56 (s, 3 H), 1.64 (s, 3 H), 1.77 (s, 3 H), 1.85–2.15 (m, 4 H), 3.36 (d, *J* = 8 Hz, 2 H), 3.46 (s, 6 H), 5.05 (t, *J* = 6 Hz, 1 H), 5.15 (t, *J* = 6 Hz, 1 H), 5.18 (s, 4 H), 6.72 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 17.6, 22.5, 25.6, 26.6, 39.7, 56.1, 94.6, 101.7, 120.3, 121.6, 124.2, 131.4, 135.4, 148.0, 156.0.

MS (ESI): *m*/*z* = 505 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{29}F_3NaO_7S$: 505.1484; found: 505.1498.

3,5-Bis(methoxymethoxy)-4-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]phenyl Trifluoromethanesulfonate (6b)

Following the typical procedure for **6a** using **5b** (250 mg, 0.59 mmol), pyridine (0.09 mL, 1.19 mmol), and Tf_2O (0.15 mL, 0.89 mmol) gave **6b** as a thick oil; yield: 325 mg (99%).

IR (neat): 1612 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 6 H), 1.68 (s, 3 H), 1.77 (s, 3 H), 1.85–2.20 (m, 8 H), 3.37 (d, *J* = 6 Hz, 2 H), 3.46 (s, 6 H), 5.00–5.25 (m, 3 H), 5.18 (s, 4 H), 6.72 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 16.1, 17.6, 22.5, 25.7, 26.6, 26.7, 39.7, 39.8, 56.1, 94.6, 101.7, 120.4, 121.6, 124.1, 124.3, 131.3, 135.0, 135.2, 135.5, 148.0, 156.0.

MS (ESI): *m*/*z* = 573 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{38}F_3O_7S$: 551.2290; found: 551.2296.

(*E*)-5-{[(3,4-Bis(methoxymethoxy)phenyl]ethynyl}-2-(3,7-dimethylocta-2,6-dienyl)-1,3-bis(methoxymethoxy)benzene (7a); Typical Procedure

To a stirred soln of triflate **6a** (300 mg, 0.62 mmol), $PdCl_2(PPh_3)_2$ (43 mg, 10 mol%), CuI (35 mg, 30 mol%), and TBAI (689 mg, 1.86 mmol) in DMF–Et_3N (5:1, 8 mL) under argon at 70 °C was added alkyne **12a** (193 mg, 0.87 mmol) in DMF–Et_3N (5:1, 4 mL) over a period of 1 h. The mixture was allowed to stir for an additional 30 min and then it was cooled to 25 °C. The mixture was diluted with EtOAc (50 mL) and the EtOAc soln was washed with brine (3 × 20 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure **7a** as a thick oil; yield: 282 mg (82%).

IR ($CHCl_3$): 2401, 1597 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.65 (s, 3 H), 1.78 (s, 3 H), 1.85–2.15 (m, 4 H), 3.40 (d, *J* = 8 Hz, 2 H), 3.48 (s, 6 H), 3.52 (s, 3 H), 3.54 (s, 3 H), 5.06 (t, *J* = 6 Hz, 1 H), 5.13–5.25 (m, 1 H), 5.20 (s, 4 H), 5.25 (s, 4 H), 6.95 (s, 2 H), 7.05–7.20 (m, 2 H), 7.33 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 17.6, 22.7, 25.6, 26.7, 39.8, 56.0, 56.2 (2 C), 88.3, 88.5, 94.4, 95.2, 95.4, 111.1, 116.2, 117.3, 119.6, 121.1, 121.5, 122.2, 124.3, 126.2, 131.2, 134.9, 146.8, 147.5, 155.4.

MS (ESI): *m*/*z* = 555 $[M + H]^+$, 577 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{32}H_{42}NaO_8$: 577.2777; found: 577.2770.

1,3-Bis(methoxymethoxy)-5-{[4-(methoxymethoxy)phenyl]ethynyl}-2-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzene (7b)

Following the typical procedure for **7a** using triflate **6b** (300 mg, 0.54 mmol), $PdCl_2(PPh_3)_2$ (38 mg, 10 mol%), CuI (31 mg, 30 mol%), TBAI (604 mg, 1.63 mmol), and alkyne **12b** (123 mg, 0.76 mmol) gave **7b** as a thick oil; yield: 251 mg (82%).

IR ($CHCl_3$): 2401, 1598 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 1.78 (s, 3 H), 1.85–2.50 (m, 8 H), 3.40 (d, *J* = 8 Hz, 2 H), 3.48 (s, 9 H), 5.08 (t, *J* = 6 Hz, 1 H), 5.10–5.25 (m, 2 H), 5.19 (s, 2 H), 5.20 (s, 4 H), 6.94 (s, 2 H), 6.95–7.05 (m, 2 H), 7.40–7.50 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 16.1, 17.7, 22.7, 25.7, 26.6, 26.7, 39.7, 39.8, 56.0, 56.1, 88.4, 88.5, 94.3, 94.4, 111.1, 116.1, 116.7, 121.0, 121.7, 122.2, 124.2, 124.4, 131.3, 133.0, 135.0, 155.4, 157.1.

MS (ESI): *m*/*z* = 585 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{35}H_{46}NaO_6$: 585.3192; found: 585.3191.

5-[(*Z*)-3,4-Bis(methoxymethoxy)styryl]-2-[(*E*)-3,7-dimethylocta-2,6-dienyl]-1,3-bis(methoxymethoxy)benzene (8a); Typical Procedure

Compound **7a** (200 mg, 0.36 mmol), KOH (30 mg, 0.54 mmol), $Pd(OAc)_2$ (4.0 mg, 5 mol%), and DMF (2 mL) were placed in a thick-walled Pyrex screw-cap tube (10 mL) under argon and the capped tube was heated in an oil bath at 145 °C under stirring for 6 h. The mixture was cooled to 25 °C and diluted with EtOAc (25 mL). The EtOAc soln was washed with brine (3 × 10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure *cis*-stilbene **8a** as a thick oil; yield: 172 mg (86%).

IR ($CHCl_3$): 1638 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.50 (s, 3 H), 1.58 (s, 3 H), 1.69 (s, 3 H), 1.80–2.05 (m, 4 H), 3.29 (d, *J* = 8 Hz, 2 H), 3.33 (s, 9 H), 3.42 (s, 3 H), 4.96 (s, 4 H), 4.99 (s, 2 H), 5.05–5.25 (m, 2 H), 5.13 (s, 2 H), 6.40 (s, 2 H), 6.59 (s, 2 H), 6.75–7.00 (m, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 17.6, 22.6, 25.6, 26.7, 39.8, 55.8, 56.0, 56.1, 94.5, 95.4 (2 C), 108.7, 116.4, 117.6, 119.3, 122.7, 123.3, 124.4, 129.5, 129.7, 131.2, 131.9, 134.5, 136.0, 146.3, 146.8, 155.4.

MS (ESI): *m*/*z* = 557 $[M + H]^+$, 579 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{32}H_{44}NaO_8$: 579.2934; found: 579.2924.

1,3-Bis(methoxymethoxy)-5-[(*Z*)-4-(methoxymethoxy)styryl]-2-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzene (8b)

Following the typical procedure for **8a** using **7b** (200 mg, 0.35 mmol), KOH (30 mg, 0.53 mmol), and $Pd(OAc)_2$ (4.0 mg, 5 mol%) gave **8b** as a thick oil; yield: 172 mg (86%).

IR ($CHCl_3$): 1604 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 1.77 (s, 3 H), 1.85–2.15 (m, 8 H), 3.36 (d, *J* = 6 Hz, 2 H), 3.39 (s, 6 H), 3.46 (s, 3 H), 5.01 (s, 4 H), 5.05–5.27 (m, 3 H), 5.15 (s, 2 H), 6.42 (d, *J* = 12 Hz, 1 H), 6.50 (d, *J* = 12 Hz, 1 H), 6.67 (s, 2 H), 6.90 (d, *J* = 8 Hz, 2 H), 7.22 (d, *J* = 8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.9, 16.1, 17.7, 22.6, 25.7, 26.65, 26.71, 39.7, 39.8, 55.8, 55.9, 94.3, 94.4, 108.8, 115.9, 119.3, 122.7, 124.3, 124.4, 129.2, 129.5, 130.2, 131.0, 131.2, 134.6, 134.8, 136.0, 155.4, 156.2.

MS (ESI): *m*/*z* = 565 $[M + H]^+$, 587 $[M + Na]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{35}H_{48}NaO_6$: 587.3349; found: 587.3352.

5-[(*E*)-3,4-Bis(methoxymethoxy)styryl]-2-[(*E*)-3,7-dimethylocta-2,6-dienyl]-1,3-bis(methoxymethoxy)benzene (9a); Typical Procedures

C=C Bond isomerization: To a stirred soln of the *cis*-stilbene **8a** (100 mg, 0.18 mmol) in CH_2Cl_2 (0.4 mL) was added $PdCl_2(MeCN)_2$ (4.6 mg, 10 mol%) and the mixture was stirred at 25 °C for 12 h under argon. The mixture was diluted with Et_2O (20 mL), filtered through a short pad of Celite and washed with Et_2O (10 mL), and the filtrate was concentrated in vacuo. The residue was subjected to column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure *trans*-stilbene **9a** as a thick oil; yield: 82 mg (82%).

Heck coupling: Triflate **6a** (100 mg, 0.20 mmol) and styrene **11a** (69 mg, 0.31 mmol) were dissolved in MeCN (2 mL). Et_3N (1 mL), $Pd(OAc)_2$ (4.6 mg, 10 mol%), and Ph_3P (27 mg, 50 mol%) were added to the stirred mixture. The mixture was heated at 85 °C for 24 h under argon. The mixture was concentrated in vacuo and the residue was subjected to column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure *trans*-stilbene **9a** as a thick oil; yield: 71 mg (62%).

Stille coupling: Triflate **6a** (100 mg, 0.20 mmol) and stannate **13a** (159 mg, 0.31 mmol) were dissolved in DMF (2 mL) in a thick-walled Pyrex screw-cap tube (10 mL) under argon. $Pd(PPh_3)_4$ (12 mg, 5 mol%) and LiCl (44 mg, 1.031 mmol) were added to this mixture and the capped tube was heated in an oil bath at 120 °C with stirring for 8 h. To the mixture was added EtOAc (20 mL) and the EtOAc soln was washed with brine (3 × 10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure *trans*-stilbene **9a** as a thick oil; yield: 76 mg (66%).

Suzuki coupling: To a mixture of triflate **6a** (100 mg, 0.20 mmol) and boronate **15a** (108 mg, 0.31 mmol) in dioxane–H_2O (2 mL, 7:1) were added $Pd(PPh_3)_4$ (12 mg, 5 mol%) and Na_2CO_3 (109 mg, 1.037 mmol) in a thick-walled Pyrex screw-cap tube (10 mL). The mixture was heated at 90 °C for 8 h and then concentrated in vacuo to give a residue. EtOAc (20 mL) was added to the residue and the organic layer was washed with H_2O (5 mL) and brine (5 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 4:1) to afford pure *trans*-stilbene **9a** as a thick oil; yield: 74 mg (65%).

IR ($CHCl_3$): 1599 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.65 (s, 3 H), 1.79 (s, 3 H), 1.85–2.15 (m, 4 H), 3.40 (d, *J* = 8 Hz, 2 H), 3.50 (s, 6 H), 3.53 (s, 3 H), 3.56 (s, 3 H), 5.00–5.15 (m, 1 H), 5.15–5.30 (m, 1 H), 5.24 (s, 4 H), 5.25 (s, 2 H), 5.29 (s, 2 H), 6.92 (s, 2 H), 6.90–7.18 (m, 4 H), 7.33 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.0, 17.6, 22.7, 25.6, 26.7, 39.8, 56.0, 56.16, 56.19, 94.4, 95.4 (2 C), 106.0, 114.2, 116.5, 119.7, 120.9, 122.5, 124.3, 127.6, 127.7, 131.2, 132.1, 134.6, 136.7, 146.8, 147.4, 155.8.

MS (ESI): *m*/*z* = 579 $[M + Na]^+$.

1,3-Bis(methoxymethoxy)-5-[(*E*)-4-(methoxymethoxy)styryl]-2-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzene (9b)

C=C Bond isomerization: Following the typical procedure for **9a** using *cis*-stilbene **8b** (150 mg, 0.26 mmol), $PdCl_2(MeCN)_2$ (6.8 mg, 10 mol%) gave **9b** as a thick oil; yield: 127 mg (85%).

Heck coupling: Following the typical procedure for **9a** using triflate **6b** (100 mg, 0.18 mmol), styrene **11b** (45 mg, 0.27 mmol), Et_3N (1 mL), $Pd(OAc)_2$ (4.0 mg, 10 mol%), and Ph_3P (24 mg, 50 mol%) gave **9b** as a thick oil; yield: 64 mg (63%).

Stille coupling: Following the typical procedure for **9a** using triflate **6b** (100 mg, 0.18 mmol), stannate **13b** (123 mg, 0.27 mmol), $Pd(PPh_3)_4$ (10 mg, 5 mol%), and LiCl (39 mg, 0.90 mmol) gave **9b** as a thick oil; yield: 68 mg (67%).

Suzuki coupling: Following the typical procedure for **9a** using triflate **6b** (100 mg, 0.18 mmol), boronate **15b** (79 mg, 0.27 mmol),

$Pd(PPh_3)_4$ (10 mg, 5 mol%), and Na_2CO_3 (96 mg, 0.90 mmol) gave **9b** as a thick oil; yield: 67 mg (66%).

IR ($CHCl_3$): 1601 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.59 (s, 3 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.81 (s, 3 H), 1.92–2.00 (m, 4 H), 2.00–2.11 (m, 4 H), 3.43 (d, *J* = 5 Hz, 2 H), 3.50 (s, 3 H), 3.52 (s, 6 H), 5.06–5.14 (m, 2 H), 5.20 (s, 2 H), 5.22–5.28 (m, 1 H), 5.25 (s, 4 H), 6.94 (d, *J* = 15 Hz, 1 H), 6.94 (s, 2 H), 7.02 (d, *J* = 15 Hz, 1 H), 7.03 (d, *J* = 10 Hz, 2 H), 7.45 (d, *J* = 10 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.9, 16.1, 17.6, 22.7, 25.6, 26.6, 26.7, 39.7, 39.8, 55.9 (2 C), 94.4, 94.5, 106.0, 116.4, 119.7, 122.6, 124.2, 124.4, 127.2, 127.6, 127.7, 131.2, 131.3, 134.6, 134.8, 136.5, 155.9, 156.8.

MS (ESI): *m*/*z* = 565 $[M + H]^+$.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{35}H_{48}NaO_6$: 587.3349; found: 587.3358.

4-{(*E*)-4-[(*E*)-3,7-Dimethylocta-2,6-dienyl}-3,5-dihydroxystyryl}benzene-1,2-diol (Pawhuskin C, 1); Typical Procedure

To a stirred soln of *trans*-stilbene **9a** (80 mg, 0.14 mmol) in MeOH (10 mL) was added CSA (5 mg, cat.) and the mixture was stirred at 25 °C for 12 h under an argon atmosphere. The reaction was quenched by addition of sat. $NaHCO_3$ and concentrated in vacuo. To the residue was added EtOAc (20 mL) and the EtOAc soln was washed with brine (5 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, PE–EtOAc, 1:1) to afford pure pawhuskin C (**1**) as a yellow solid; yield: 30 mg (55%); mp 144–146 °C (Lit.[7] 148–152 °C).

IR ($CHCl_3$): 3423, 1619 cm^{-1}.

^1H NMR (200 MHz, acetone-d_6): δ = 1.57 (s, 3 H), 1.62 (s, 3 H), 1.78 (s, 3 H), 1.90–2.15 (m, 4 H), 3.37 (d, *J* = 8 Hz, 2 H), 5.09 (t, *J* = 6 Hz, 1 H), 5.33 (t, *J* = 6 Hz, 1 H), 6.58 (s, 2 H), 6.70–6.92 (m, 4 H), 7.04 (d, *J* = 2 Hz, 1 H), 7.75–8.15 (br s, 4 H).

^{13}C NMR (100 MHz, acetone-d_6): δ = 16.4, 17.9, 23.2, 26.0, 27.6, 40.8, 105.8, 113.8, 115.4, 116.4, 119.9, 124.4, 125.4, 127.1, 128.5, 131.0, 131.7, 134.7, 137.4, 146.1, 146.3, 157.2.

MS (ESI): *m*/*z* = 381 $[M + H]^+$, 403 $[M + Na]^+$.

5-[(*E*)-4-Hydroxystyryl]-2-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trienyl]benzene-1,3-diol (Schweinfurthin J, 2)

Following the typical procedure for **1** using **9b** (100 mg, 0.17 mmol) gave **2** as a yellow solid; yield: 43 mg (57%); mp 118–120 °C.

IR ($CHCl_3$): 3423, 1630, 1605 cm^{-1}.

^1H NMR (500 MHz, CD_3OD): δ = 1.56 (s, 6 H), 1.63 (s, 3 H), 1.77 (s, 3 H), 1.90 (t, *J* = 10 Hz, 2 H), 1.96 (q, *J* = 10 Hz, 2 H), 2.01 (t, *J* = 10 Hz, 2 H), 2.07 (q, *J* = 10 Hz, 2 H), 3.30 (d, *J* = 10 Hz, 2 H), 5.03–5.10 (m, 1 H), 5.08 (t, *J* = 10 Hz, 1 H), 5.26 (t, *J* = 10 Hz, 1 H), 6.46 (s, 2 H), 6.75 (d, *J* = 15 Hz, 1 H), 6.76 (d, *J* = 10 Hz, 2 H), 6.90 (d, *J* = 15 Hz, 1 H), 7.32 (d, *J* = 10 Hz, 2 H).

^{13}C NMR (125 MHz; CD_3OD): δ = 16.1, 16.3, 17.8, 23.2, 25.9, 27.6, 27.8, 40.8, 41.0, 105.7, 115.8, 116.5, 124.7, 125.5, 125.6, 127.3, 128.2, 128.6, 130.7, 131.9, 134.7, 135.8, 137.6, 157.2, 158.1.

MS (ESI): *m*/*z* = 433 $[M + H]^+$, 455 $[M + Na]^+$.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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