Supporting Information for:

Stannylation Cycloaddition of Enynes Catalyzed by Palladium–Iminophosphine

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere or in a dry box under a nitrogen atmosphere. Flash column chromatography was performed using Merck silica gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian INOVA 500 (¹H NMR, 500 MHz; ¹³C NMR, 126 MHz), JEOL EX-270 (¹H, 270 MHz; ¹³C, 67.8 MHz; ¹¹⁹Sn, 101 MHz), or Varian Mercury 200 (¹H, 200 MHz; ¹³C, 50.3 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR, CHCl₃ at 7.26 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm) or Me₄Sn (¹¹⁹Sn NMR, at 0 ppm) as the external standard. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, br t = broad triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. GC analysis was performed on a Shimadzu GC 14B equipped with an OV-

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1701 column (25 m x 0.25 mm, pressure = 570 kPa, detector = FID, 290 °C) with helium gas as a carrier. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H using chloroform as an eluent. High-resolution mass spectra were obtained with a JEOL JMS-700 (EI and CI) or JEOL JMS-HX110A (FAB+) spectrometer.

Chemicals. Unless otherwise noted, commercially available reagents were used without purification. Solvents were distilled from a suitable drying reagent as follows: sodium/benzophenone ketyl for toluene and THF; calcium hydride for dichloromethane. Anhydrous NMP and DMF were purchased from Aldrich and used without further purification. Hexabutyldistannoxane,¹ *N*-(2-diphenylphosphinobenzylidene)cyclohexylamine (**1**),² Cp(allyl)Pd,³ 2-heptyl-1-buten-3-yne (**2b**),⁴ ethyl (*Z*)-2-penten-4-ynoate (**2g**),⁵ 1-decen-3-yne (**2i**),⁶ and methyl 4-penten-2-ynyl ether (**2j**)⁷ were prepared according to reported procedures. 1-Penten-3-yne (**2h**)⁸ and ethyl (*Z*)-2-undecen-4-ynoate⁹ were prepared by the procedure similar to those reported, starting with 3-pentyn-1-ol or 1-octyne respectively.

Preparation of enynes, 2c–2f. A general procedure.⁴ To a solution of *t*-BuOK (19.8 g, 176 mmol) in THF (48 mL) was added a 1.6 M *n*-BuLi solution in hexane (110 mL, 176 mmol) at –80 °C. This solution was transferred dropwise to a solution of 2-methyl-1-buten-3-yne (5.3 g, 80 mmol) in THF (48 mL) at –80 °C via cannula. The resulting mixture was stirred for 30 min at –78 °C, warmed to 5 °C for 10 min, and then cooled at –20 °C. A solution of LiBr (15.3 g, 176 mmol) in THF (48 mL) was added to the mixture. The mixture was stirred for 10 min at –20 °C before an alkyl bromide (40 mmol) was added at –70 °C. The resulting mixture was warmed at –10 °C in 10 min. After the bromide was all consumed as confirmed by GC, the reaction was quenched by an aqueous NH₄Cl saturated solution (72 mL) at –40 °C. The resulting bilayer solution was extracted with diethyl ether. Combined ethereal extracts were washed with brine and dried over anhydrous MgSO₄. After removal of the solvent, the residue was distilled under vacuum.

2-(Phenylethyl)-1-buten-3-yne (2c). The reaction using benzyl bromide (6.8 g, 40 mmol) gave the title compound (3.8 g, 61%) as a colorless oil, bp 67 °C (3.0 mmHg), R_f 0.63 (hexane). ^1H NMR (200 MHz, CDCl_3) δ 7.33–7.16 (m, 5H), 5.43 (s, 1H), 5.27 (s, 1H), 2.98 (s, 1H), 2.90 (t, $J = 7.9$ Hz, 2H), 2.50 (t, $J = 7.9$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 141.1, 129.8, 128.3, 128.2, 125.8, 123.2, 83.8, 77.3, 38.9, 34.4; Anal. Calcd for $\text{C}_{12}\text{H}_{12}$; C, 92.26; H, 7.74. Found: C, 92.02; H, 7.90.

2-Ethynyl-1,6-heptadiene (2d). Reaction using 1-bromo-3-butene (5.4 g, 40 mmol) gave 1.48 g (40%) of the title compound as a colorless oil, bp 71 °C (80 mmHg), R_f 0.50 (hexane). ^1H NMR (200 MHz, CDCl_3) δ 5.90–5.70 (m, 1H), 5.42 (s, 1H), 5.29 (s, 1H), 5.07–4.93 (m, 2H), 2.87 (s, 1H), 2.17 (t, $J = 7.5$ Hz, 2H), 2.05 (t, $J = 7.1$ Hz, 2H), 1.63 (tt, $J = 7.5, 7.1$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 138.2, 130.4, 122.7, 114.7, 84.0, 76.8, 36.3, 32.9, 27.1; HRMS (CI) Calcd for C_9H_{13} ; $\text{M}^+ + \text{H}$, 121.1017. Found: m/z 121.1016.

2-Ethynyl-6-trimethylsilyl-1-hexen-5-yne (2e). Reaction using 3-bromo-1-(trimethylsilyl)propene (4.8 g, 25 mmol) gave 0.99 g (22%) of the title compound as a colorless oil, bp 58 °C (4.0 mmHg), R_f 0.75 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, CDCl_3) δ 5.45 (s, 1H), 5.35 (s, 1H), 2.88 (s, 1H), 2.50–2.31 (m, 4H), 0.17 (s, 9H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 128.7, 123.6, 105.9, 85.2, 77.4, 36.3, 35.4, 19.1, 0.2; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{16}\text{Si}$; M^+ , 176.1021. Found: m/z 176.1020.

3-[(*tert*-Butyldimethylsilyloxy)propyl]-1-buten-3-yne (2f). Reaction using (2-bromoethoxy)-*tert*-butyldimethylsilane (8.4 g, 35 mmol) afforded 4.1 g (52%) of the title compound as a colorless oil, bp 68 °C (3.0 mmHg), R_f 0.75 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, CDCl_3) δ 5.42 (s, 1H), 5.31 (s, 1H), 3.62 (t, $J = 6.3$ Hz, 2H), 2.87 (s, 1H), 2.23 (t, $J = 7.5$ Hz, 2H), 1.75 (tt, $J = 7.5, 6.3$ Hz, 2H), 0.90 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (67.8 MHz,

CDCl₃) δ 130.2, 122.8, 84.0, 76.9, 62.1, 33.3, 31.0, 26.0, 18.4, -5.2; Anal. Calcd for C₁₃H₂₄OSi; C, 69.58; H, 10.78. Found: C, 69.63; H, 10.50.

Preparation of 7-octen-5-ynenitrile (2k). To a mixture of PdCl₂(PPh₃)₂ (84 mg, 0.12 mmol) and CuI (11.4 mg, 60 μ mol) in Et₃N (44 mL) were added 5-hexynenitrile (1.12 g, 12.0 mmol) and a 1.0 M vinyl bromide solution in THF (14.4 mL, 14.4 mmol) successively. The resulting mixture was stirred at room temperature for 6.5 h, and then aqueous NaHCO₃ saturated solution was added. The bilayer mixture was extracted with diethyl ether, and combined organic layers were washed with brine. Concentration in vacuo followed by flash chromatography on silica gel (hexane–ethyl acetate = 4:1) gave the title compound (1.01g, 70%) as a colorless oil, R_f 0.31 (hexane–ethyl acetate = 5:1). ¹H NMR (200 MHz, CDCl₃) δ 5.77 (ddt, *J* = 13.0, 8.1, 1.6 Hz, 1H), 5.58 (dd, *J* = 13.0, 1.6 Hz, 1H), 5.44 (dd, *J* = 8.1, 1.6 Hz, 1H), 2.51 (t, *J* = 7.1 Hz, 2H), 2.50 (t, *J* = 6.7 Hz, 2H), 1.89 (tt, *J* = 7.1, 6.7 Hz, 2H); ¹³C NMR (67.8 MHz, CDCl₃) δ 126.4, 119.0, 116.9, 87.6, 81.0, 24.6, 18.5, 16.3; Anal. Calcd for C₈H₉N; C, 80.63; H, 7.61. Found: C, 80.86; H, 7.77.

Optimization of stannylating reagents. A solution of [(η^3 -allyl)PdCl]₂ (0.90 mg, 2.5 μ mol) and **1** (1.9 mg, 5.0 μ mol) in THF (0.15 mL) were added sequentially an organostannane (0.10 mmol) and 2-methyl-1-buten-3-yne (**2a**) (20 mg, 0.30 mmol), and the resulting mixture was stirred at 50 °C for 24 h. The mixture was filtered through a Florisil pad, and mixed with tridecane (28 mg, 0.15 mmol). After yield of **4a** was determined by GC assay, the solvent was removed in vacuo, and Me₄Sn (18 mg, 0.10 mmol) was added to the residue to estimate yield of **3a** by ¹¹⁹Sn NMR. Results are summarized in Table S1.

Table S1. Stannylation Dimerization of 2-Methyl-1-buten-3-yne (**2a**)

entry	organostannane	yield of 3a (%) ^a	yield of 4a (%) ^b
1	Ph-C≡C-SnBu ₃	57	11
2 ^c	(Bu ₃ Sn) ₂ O	74	11
3 ^{c,d}	(Bu ₃ Sn) ₂ O	81 (81) ^e	14
4 ^c	Bu ₃ Sn-C≡C-SnBu ₃	67	15
5	Me ₂ NSnBu ₃	61	8
6	EtOSnBu ₃	52	13
7	(Allyl)SnBu ₃	46	15
8	(vinyl)SnBu ₃	30	40
9 ^c	(Bu ₃ Sn) ₂	30	37
10	HSnBu ₃	30	40
11	ClSnBu ₃	0	0

^a Determined by ¹¹⁹Sn NMR using Me₄Sn as an internal standard. ^b Determined by GC using tridecane as an internal standard. ^c 0.15 mmol of an organostannane was used. ^d Cp(allyl)Pd (5.0 mol%), **1** (5.0 mol%), and maleic anhydride (7.5 mol%) were used as a catalyst. ^e Isolated yield based on Bu₃Sn group.

Optimization of catalysts, additives, and solvents. To a solution of a palladium complex (5.0 μmol of Pd), a ligand (5.0 μmol), and an additive (7.5 μmol) in a solvent (0.15 mL) were added 2-phenylethyl-1-buten-3-yne (**2c**) (46 mg, 0.30 mmol) and hexabutyldistannoxane (30 mg, 50 μmol), and the resulting mixture was stirred at 50 °C for 6 h before filtration through a Florisil pad. Tetradecane (30 mg, 0.15 mmol) was added to the filtrate. Yield of **4c** was estimated by GC. After removal of the solvent, Me₄Sn (18 mg, 0.10 mmol) was added, and the residue was analyzed by ¹¹⁹Sn NMR to determine yields of **3c** and **3c'**. Results are summarized in Table S2.

Table S2. Stannylation Dimerization of 2-Phenylethyl-1-buten-3-yne

entry	catalyst	ligand	additive	solvent	yield (%)		
					3c ^a	3c' ^a	4c ^b
1	1/2 [(η ³ -allyl)PdCl] ₂	1a	none	THF	46	19	25
2	1/2 [(η ³ -allyl)PdCl] ₂	1a	MA ^c	THF	51	5	15
3	1/2 Pd ₂ (dba) ₃	1a	none	THF	69	14	41
4	1/2 Pd ₂ (dba) ₃	1a	MA ^c	THF	52	5	27
5	Cp(allyl)Pd	1a	none	THF	35	12	10
6	Cp(allyl)Pd	1a	MA ^c	THF	78	0	18
7	Cp(allyl)Pd	1a	MA ^c	toluene	65	7	44
8	Cp(allyl)Pd	1a	MA ^c	DMF	79	0	38
9	Cp(allyl)Pd	1a	4-F-styrene	THF	62	0	23
10	Cp(allyl)Pd	1a	DMAD ^d	THF	53	0	14
11	Cp(allyl)Pd	1b	MA ^c	THF	66	7	27
12	Cp(allyl)Pd	1c	MA ^c	THF	43	0	7
13	Cp(allyl)Pd	1d	MA ^c	THF	29	5	10
14	Cp(allyl)Pd	1e	MA ^c	THF	54	7	26
15	Cp(allyl)Pd	1f	MA ^c	THF	60	0	21
16	1/2 Pd ₂ (dba) ₃	1g	none	toluene	2	0	41
17	1/2 Pd ₂ (dba) ₃	1h	none	toluene	13	10	21
18	Cp(allyl)Pd	1i	MA ^c	THF	65	0	41
19	Cp(allyl)Pd	dppp	MA ^c	THF	1	0	0
20	Cp(allyl)Pd	PPh ₃	MA ^c	THF	33	5	69
21	Cp(allyl)Pd	none	MA ^c	THF	0	0	1

^a Determined by ¹¹⁹Sn NMR using Me₄Sn as an internal standard. ^b Determined by GC using tetradecane as an internal standard. ^c Maleic anhydride. ^d Dimethyl acetylenedicarboxylate.

Stannylation dimerization of enynes. A general procedure. To a solution of Cp(allyl)Pd (3.2 mg, 15 μ mol for enynes **2a–2g**; 13 mg, 60 μ mol for enynes **2h–2k**), **1** (5.6 mg, 15 μ mol for enynes **2a–2g**; 22 mg, 60 μ mol for enynes **2h–2k**), and maleic anhydride (2.2 mg, 23 μ mol for enynes **2a–2g**; 8.8 mg, 90 μ mol for enynes **2h–2k**) in THF were added sequentially (Bu₃Sn)₂O (89 mg, 0.15 mmol) and an enyne (0.90 mmol). The resulting mixture was stirred at 50 °C (for enynes **2a–2g**) or 80 °C (for enynes **2h–2k**) for 24 h, and then filtered through a Florisil pad. Concentration in vacuo followed by flash chromatography (hexane–ethyl acetate with 0.3–1.0% Et₃N) and by preparative GPC gave desired products **3a–3k**.

2-Methyl-5-(propen-2-yl)-1-(tributylstannyl)benzene (3a). A colorless oil, *R*_f 0.67 (hexane–ethyl acetate = 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 2.1 Hz, ³*J*_{H–Sn} = 45.2 Hz, 1H), 7.33 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 5.33 (q, *J* = 0.7 Hz, 1H), 5.05 (dq, *J* = 1.5, 1.5 Hz, 1H), 2.40 (s, 3H), 2.16 (dd, *J* = 1.5, 0.7 Hz, 3H), 1.63–1.47 (m, 6H), 1.40–1.31 (m, 6H), 1.17–1.03 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ¹³C NMR (50.3 MHz, CDCl₃) δ 144.0, 143.4, 141.8, 137.5, 133.5, 128.6, 125.5, 111.4, 29.2, 27.4, 24.6, 21.9, 13.7, 10.0; ¹¹⁹Sn{¹H} NMR (101 MHz, CDCl₃) δ –40.2; Anal. Calcd for C₂₂H₃₈Sn; C, 62.73; H, 9.09. Found: C, 62.72; H, 8.82.

5-(1-Octen-2-yl)-2-pentyl-1-(tributylstannyl)benzene (3b). A colorless oil, *R*_f 0.60 (hexane). ¹H NMR (200 MHz, CDCl₃) δ 7.44 (d, *J* = 1.9 Hz, 1H), 7.32 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 5.25 (s, 1H), 5.01 (s, 1H), 2.58 (t, *J* = 8.1 Hz, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 1.63–0.85 (m, 53H); ¹³C NMR (67.8 MHz, CDCl₃) δ 148.73, 148.70, 141.2, 137.6, 134.1, 127.5, 126.0, 110.9, 39.3, 35.5, 32.6, 32.0, 31.9, 30.0, 29.5, 29.4, 29.30, 29.26, 29.1, 28.6, 27.6, 27.1, 22.8, 14.2, 13.8, 10.6; ¹¹⁹Sn{¹H} NMR (101 MHz, CDCl₃) δ –41.6; Anal. Calcd for C₃₄H₆₂Sn; C, 69.27; H, 10.60. Found: C, 69.50; H, 10.60.

5-(4-Phenyl-1-buten-2-yl)-2-(2-phenylethyl)-1-(tributylstannyl)benzene (3c). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 50:1). ^1H NMR (200 MHz, CDCl_3) δ 7.51 (d, J = 1.8 Hz, 1H), 7.39–7.18 (m, 12H), 5.29 (s, 1H), 5.04 (s, 1H), 2.93 (s, 4H), 2.81 (s, 4H), 1.59–0.83 (m, 27H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 147.8, 147.7, 141.9, 141.6, 141.5, 137.6, 134.3, 128.32, 128.29, 128.21, 128.18, 127.8, 126.1, 125.9, 125.7, 111.9, 40.7, 38.6, 37.5, 35.0, 29.3, 27.5, 13.8, 10.6; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –40.9; Anal. Calcd for $\text{C}_{36}\text{H}_{50}\text{Sn}$; C, 71.89; H, 8.38. Found: C, 71.87; H, 8.44.

5-(1,6-Heptadien-2-yl)-2-(4-pentenyl)-1-(tributylstannyl)benzene (3d). A colorless oil, R_f 0.45 (hexane). ^1H NMR (200 MHz, CDCl_3) δ 7.44 (d, J = 2.1 Hz, 1H), 7.32 (dd, J = 7.9, 2.1 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 5.97–5.73 (m, 2H), 5.27 (d, J = 1.4 Hz, 1H), 4.93–5.12 (m, 5H), 2.64–2.48 (m, 4H), 2.23–2.06 (m, 4H), 1.79–0.87 (m, 31H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 148.3, 148.2, 141.4, 138.5, 138.3, 137.6, 134.1, 127.5, 126.0, 114.7, 114.6, 111.3, 38.5, 34.8, 34.0, 33.5, 31.5, 29.2, 27.7, 27.5, 13.8, 10.5; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –41.2; Anal. Calcd for $\text{C}_{30}\text{H}_{50}\text{Sn}$; C, 68.06; H, 9.52. Found: C, 68.35; H, 9.45.

2-(4-Trimethylsilyl-3-butynyl)-5-(6-trimethylsilyl-1-hexen-5-yn-2-yl)-1-(tributylstannyl)benzene (3e). A pale yellow oil, R_f 0.15 (hexane–ethyl acetate = 50:1). ^1H NMR (270 MHz, CDCl_3) δ 7.41 (d, J = 1.5 Hz, 1H), 7.29 (dd, J = 6.0, 1.5 Hz, 1H), 7.21 (d, J = 6.0 Hz, 1H), 5.29 (s, 1H), 5.07 (s, 1H), 2.83 (t, J = 5.9 Hz, 2H), 2.70 (t, J = 5.7 Hz, 2H), 2.44 (t, J = 5.9 Hz, 2H), 2.37 (t, J = 5.7 Hz, 2H), 1.60–0.88 (m, 27H), 0.15 (s, 18H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 146.7, 146.6, 141.8, 137.4, 134.2, 127.8, 126.0, 112.4, 106.6, 106.4, 85.1, 84.9, 38.2, 34.8, 29.2, 27.5, 22.8, 19.5, 13.8, 10.5, 0.3, 0.2; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –41.1; Anal. Calcd for $\text{C}_{34}\text{H}_{58}\text{Si}_2\text{Sn}$; C, 63.64; H, 9.11. Found: C, 63.87; H, 8.87.

5-[5-(*tert*-Butyldimethylsilyloxy)-1-penten-2-yl]-2-[3-(*tert*-butyldimethylsilyloxy)propyl]-1-(tributylstannyl)benzene

(3f). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 50:1). ^1H NMR (200 MHz, CDCl_3) δ 7.44 (d, $J = 2.1$ Hz, 1H), 7.32 (dd, $J = 7.9, 2.1$ Hz, 1H), 7.19 (d, $J = 7.9$ Hz, 1H), 5.27 (s, 1H), 5.04 (s, 1H), 3.71 (t, $J = 6.4$ Hz, 2H), 3.64 (t, $J = 6.4$ Hz, 2H),

2.69–2.53 (m, 4H), 1.86–0.91 (m, 49H), 0.45 (s, 12H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 148.2, 148.0, 141.4, 137.5, 134.1, 127.6, 126.0, 111.3, 63.0, 62.7, 35.4, 31.6, 31.5, 29.3, 27.5, 26.1, 18.5, 18.4, 13.8, 10.5, –5.1, –5.2; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –40.9; Anal. Calcd for $\text{C}_{38}\text{H}_{74}\text{O}_2\text{Si}_2\text{Sn}$; C, 61.85; H, 10.11. Found: C, 62.00; H, 9.89.

Ethyl

5-[(*Z*)-2-(ethoxycarbonyl)ethenyl]-3-

(tributylstannyl)benzoate (3g). A colorless oil, R_f 0.24

(hexane–ethyl acetate = 20:1). ^1H NMR (500 MHz, CDCl_3) δ 8.11 (td, $J = 1.7, 0.5$ Hz, 1H), 8.08 (s, $J_{\text{H-Sn}} = 36.1$ Hz, 1H), 7.76

(t, $J = 1.0$ Hz, $J_{\text{H-Sn}} = 36.6$ Hz, 1H), 6.97 (d, $J = 12.6$ Hz, 1H), 6.00 (d, $J = 12.6$ Hz, 1H), 4.38 (q, $J = 7.1$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 1.61–1.45 (m, 6H), 1.39 (t, $J = 7.1$ Hz, 3H), 1.37–1.29 (m, 6H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.16–1.01 (m, 6H), 0.89 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 166.6, 165.8, 142.1, 141.9, 141.3, 137.4, 134.3, 130.1, 129.2, 120.7, 60.9, 60.4, 29.1, 27.4, 14.4, 14.1, 13.7, 9.8; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –38.8; Anal. Calcd for $\text{C}_{26}\text{H}_{42}\text{O}_4\text{Sn}$; C, 58.12; H, 7.88. Found: C, 57.94; H, 7.61.

2,6-Dimethyl-3-(tributylstannyl)styrene (3h). A pale yellow oil,

R_f 0.48 (hexane). ^1H NMR (200 MHz, CDCl_3) δ 7.19 (d, $J = 7.4$ Hz, 1H), 7.03 (d, $J = 7.4$ Hz, 1H), 6.72 (dd, $J = 18.0, 11.6$ Hz, 1H), 5.53 (dd, $J = 11.6, 2.0$ Hz, 1H), 5.23 (dd, $J = 18.0, 2.0$ Hz, 1H), 2.35

(s, 3H), 2.30 (s, 3H), 1.60–0.85 (m, 27H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 142.0, 139.7, 138.0, 136.1, 135.9, 135.0, 127.2, 119.1, 29.2, 27.4, 26.9, 24.0, 13.7, 10.2; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –41.4; Anal. Calcd for $\text{C}_{22}\text{H}_{38}\text{Sn}$; C, 62.73; H, 9.09. Found: C, 62.73; H, 9.33.

2,6-Dihexyl-3-(tributylstannyl)styrene (3i). A pale yellow oil, R_f 0.60 (hexane). ^1H NMR (500 MHz, CDCl_3) δ 7.21 (d, $J = 7.6$ Hz, $J_{\text{H-Sn}} = 43.7$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.78 (dd, $J = 18.0$, 11.5 Hz, 1H), 5.47 (dd, $J = 11.5$, 2.3 Hz, 1H), 5.21 (dd, $J = 18.0$, 2.3 Hz, 1H), 2.61–2.53 (m, 4H), 1.58–1.23 (m, 28H), 1.11–0.96 (m, 6H), 0.93–0.84 (m, 15H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 147.3, 140.9, 138.6, 137.6, 135.7, 135.4, 126.1, 118.7, 38.1, 33.9, 31.88, 31.85, 31.8, 31.2, 30.1, 29.6, 29.3, 27.6, 22.78, 22.75, 22.7, 14.2, 13.8, 10.7; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –43.1; Anal. Calcd for $\text{C}_{32}\text{H}_{58}\text{Sn}$; C, 68.45; H, 10.41. Found: C, 68.70; H, 10.56.

2,6-Bis(methoxymethyl)-3-(tributylstannyl)styrene (3j). A colorless oil, R_f 0.21 (hexane–ethyl acetate = 15:1). ^1H NMR (200 MHz, CDCl_3) δ 7.41 (d, $J = 7.5$ Hz, 1H), 7.31 (d, $J = 7.5$ Hz, 1H), 6.84 (dd, $J = 17.9$, 11.2 Hz, 1H), 5.55 (dd, $J = 11.2$, 2.2 Hz, 1H), 5.29 (dd, $J = 17.9$, 2.2 Hz, 1H), 4.43 (s, 4H), 3.38 (s, 3H), 3.34 (s, 3H), 1.58–0.85 (m, 27H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 142.3, 141.7, 137.6, 135.7, 135.4, 133.9, 127.0, 120.2, 74.0, 72.9, 58.2, 57.9, 29.2, 27.6, 13.8, 10.9; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –41.8; Anal. Calcd for $\text{C}_{24}\text{H}_{42}\text{O}_2\text{Sn}$; C, 59.89; H, 8.80. Found: C, 59.79; H, 8.80.

2,6-Bis(3-cyanopropyl)-3-(tributylstannyl)styrene (3k). A pale yellow oil, R_f 0.45 (hexane–ethyl acetate = 2:1). ^1H NMR (200 MHz, CDCl_3) δ 7.27 (d, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.80 (dd, $J = 17.9$, 11.4 Hz, 1H), 5.60 (dd, $J = 11.4$, 2.0 Hz, 1H), 5.27 (dd, $J = 17.9$, 2.0 Hz, 1H), 2.81–2.69 (m, 4H), 2.37 (t, $J = 7.0$ Hz, 2H), 2.33 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 144.9, 140.3, 138.0, 137.9, 135.9, 134.7, 126.8, 120.3, 119.4, 36.5, 32.3, 29.1, 27.4, 26.8, 26.3, 17.4, 16.9, 13.7, 10.7; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ –40.8; HRMS (FAB+) Calcd for $\text{C}_{24}\text{H}_{35}\text{N}_2^{120}\text{Sn}$: $\text{M}^+ - \text{Bu}$, 471.1822. Found: m/z 471.1819.

Stannylation cross-cycloaddition of **2a** and ethyl (Z)-2-

undecen-4-ynoate. To a solution of Cp(allyl)Pd (1.6 mg, 7.5 μ mol) and **1** (5.6 mg, 15.0 μ mol) in THF were added sequentially (Bu₃Sn)₂O (89 mg, 0.15 mmol), **2a** (30 mg, 0.45

mmol), and ethyl (Z)-2-undecen-4-ynoate (94 mg, 0.45 mmol). The resulting mixture was stirred at 50 °C for 24 h, and then filtered through a Florisil pad. Concentration in vacuo followed by flash chromatography (hexane–ethyl acetate = 40:1 with 0.3% Et₃N) and by preparative GPC gave ethyl 3-[(Z)-2-(ethoxycarbonyl)ethenyl]-4-hexyl-6-methyl-1-(tributylstannyl)benzene (**5**) (127 mg, 89%) as a colorless oil, R_f 0.35 (hexane–ethyl acetate = 10:1). ¹H NMR (500 MHz, CDCl₃) δ 7.24 (s, $J_{\text{H-Sn}}$ = 44.2 Hz, 1H), 7.15 (d, J = 12.0 Hz, 1H), 6.98 (s, 1H), 5.96 (d, J = 12.0 Hz, 1H), 4.04 (q, J = 7.0 Hz, 2H), 2.51 (t, J = 8.0 Hz, 2H), 2.35 (s, 3H), 1.54–1.47 (m, 8H), 1.33 (q, J = 2.9 Hz, 6H), 1.28 (m, 6H), 1.09 (t, J = 7.3 Hz, 3H), 1.03 (t, J = 8.3 Hz, 6H), 0.874 (t, J = 7.3 Hz, 9H), 0.868 (t, J = 6.8 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.3, 145.0, 143.1, 140.7, 137.9, 137.0, 131.5, 129.2, 120.6, 59.9, 33.7, 31.7, 30.7, 29.3, 29.1, 27.4, 24.8, 22.6, 14.1, 14.0, 13.6, 9.8; ¹¹⁹Sn{¹H} NMR (101 MHz, CDCl₃) δ –40.7; Anal. Calcd for C₃₀H₅₂O₂Sn; C, 63.95; H, 9.30. Found: C, 63.81; H, 9.35.

Stannylation cross-cycloaddition of **2a** and 1,4-diphenylbutadiyne.

To a solution of Cp(allyl)Pd (3.2 mg, 15 μ mol) and **1** (11 mg, 30 μ mol) in THF were added sequentially (Bu₃Sn)₂O (89 mg, 0.15 mmol), **2a** (30 mg, 0.45 mmol), and 1,4-diphenylbutadiyne (91 mg, 0.45 mmol). The resulting mixture was stirred at 50 °C for 24 h, and then filtered through a Florisil pad.

Concentration in vacuo followed by flash chromatography (hexane–ethyl acetate = 40:1 with 1.0% Et₃N) and by preparative GPC gave 6-methyl-4-phenyl-3-phenylethynyl-1-(tributylstannyl)benzene (**6**) (141 mg, 85%) as a colorless oil, R_f 0.50 (hexane–ethyl acetate = 20:1). ¹H NMR (400 MHz, CDCl₃) δ 7.70–7.66 (m, 2H), 7.64 (s, $J_{\text{H-Sn}}$ = 42.8 Hz, 1H), 7.48–7.42 (m, 2H), 7.40–7.23 (m, 7H), 2.45 (s, 3H), 1.65–1.48 (m, 6H), 1.43–1.32 (m, 6H), 1.24–1.05 (m, 6H), 0.92 (t, J = 7.2 Hz, 9H); ¹³C NMR (67.8 MHz, CDCl₃) δ 145.1, 143.4,

140.72, 140.67, 140.5, 131.2, 129.59, 129.56, 129.2, 128.0, 127.7, 127.2, 123.7, 117.9, 91.5, 90.0, 29.2, 27.5, 25.1, 13.7, 10.2; $^{119}\text{Sn}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ -39.5; Anal. Calcd for $\text{C}_{33}\text{H}_{42}\text{Sn}$; C, 71.11; H, 7.59. Found: C, 71.12; H, 7.84.

Structural determination. The structures of the products were determined by a combination of NOE experiments, $J_{\text{H-H}}$ and $J_{\text{H-Sn}}$ values of aromatic hydrogens, and protodestannylation leading to known compounds. Representative examples are shown in Scheme S1.

Scheme S1. Representative structural characterization of the products

Synthesis of Alcyopteroicin N.

Cross-coupling reaction of **3h with methyl α -(bromomethyl)acrylate.** To a mixture of $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 10 μmol) and PPh_3 (11 mg, 20 μmol) in NMP were added **3h** (84 mg, 0.20 mmol) and methyl α -(bromomethyl)acrylate (38 mg, 0.21 mmol), and the resulting mixture was stirred at 100 °C for 3 h. The mixture was diluted with diethyl ether and washed with aqueous 1 M KF solution for three times. The aqueous layers were extracted with diethyl ether, and the combined organic layer was dried over anhydrous MgSO_4 . After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate = 20:1) to give **7** (0.17 mmol, 87%) as a yellow oil, R_f 0.45 (hexane–ethyl acetate = 2:1). ^1H NMR (200 MHz, CDCl_3) δ 7.00 (d, J = 7.7 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.69 (dd, J = 18.0, 11.4 Hz, 1H), 6.22 (s, 1H), 5.55 (dd, J = 11.4, 2.0 Hz, 1H), 5.26–5.10 (m, 2H), 3.78 (s, 3H), 3.60 (s, 2H), 2.27 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 167.7, 139.3, 138.7, 135.8, 134.3, 134.17, 134.15, 128.6, 127.4, 125.9, 119.5, 51.9, 35.7, 20.9, 16.5; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$; C, 78.23; H, 7.88. Found: C, 78.50; H, 8.05.

1,4-Reduction followed by α -methylation of **7.**¹² To a suspension of CuI (7.6 mg, 40 μmol) in THF was added 1 M MeLi solution in diethyl ether (40 μL , 40 μmol), and the resulting mixture was stirred for 30 min. The mixture was cooled to –50 °C, and 1 M DIBAL-H solution in hexane (1.2 mL, 1.2 mmol) and HMPA (0.4 mL) were added. After 1 h, **5** (94 mg, 0.41 μmol) was added at –50 °C, and the resulting mixture was stirred for 1 h, warmed at –10 °C. To this was added MeI (115 mg, 0.81 mmol), and the resulting mixture was stirred for 25 h at –10 °C before quenching with H_2O . Extraction with diethyl ether followed by drying the combined organic layer over anhydrous MgSO_4 and concentration in vacuo gave a residue, which was purified by flash chromatography on silica gel (hexane–ethyl acetate = 10:1) to give **8** (99 mg, 99%) as a colorless oil, R_f 0.35 (hexane–ethyl acetate = 10:1). ^1H NMR (200 MHz, CDCl_3) δ 6.96 (d, J = 7.8 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.75 (dd, J = 17.9, 11.4 Hz, 1H), 5.53 (dd, J = 11.4, 2.1 Hz, 1H), 5.18 (dd, J = 17.9, 2.1 Hz, 1H), 3.68 (s,

3H), 2.94 (s, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 178.1, 138.6, 136.1, 134.6, 133.7, 133.6, 129.1, 126.8, 119.2, 51.7, 44.2, 42.5, 25.1, 21.0, 17.6; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: M^+ , 246.1620. Found: m/z 246.1623.

Hydroboration of 8. To a solution of **8** (4.9 mg, 20 μmol) in THF was added 1 M $\text{Me}_2\text{CHCMe}_2\text{BH}_2$ solution in THF¹³ (0.10 mL, 0.10 mmol) at 0 $^\circ\text{C}$, and the resulting mixture was stirred at 0 $^\circ\text{C}$ for 3 h. To this were added water (0.30 mL), aqueous 3 M NaOH solution (0.50 mL), and aqueous 30% H_2O_2 solution (1.0 mL).

The resulting mixture was stirred at room temperature for 3 h before dilution with diethyl ether, and then an aqueous 1 M HCl. Extraction with diethyl ether and drying combined organic layers over anhydrous MgSO_4 , and concentration in vacuo followed by flash chromatography on silica gel (hexane–ethyl acetate = 2:1) gave **9** (4.2 mg, 79%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 2:1). ^1H NMR (200 MHz, CDCl_3) δ 6.93 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 3.74 (dt, J = 8.0, 5.0 Hz, 2H), 3.64 (s, 3H), 2.98 (t, J = 8.0 Hz, 2H), 2.93 (s, 2H), 2.32 (s, 3H), 2.27 (s, 3H), 1.43 (t, J = 5.0 Hz, 1H), 1.17 (s, 6H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 178.3, 135.8, 135.1, 134.9, 134.3, 128.9, 127.3, 61.6, 51.7, 44.2, 42.7, 33.4, 24.9, 20.2, 16.2; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: M^+ , 264.1725. Found: m/z 264.1732.

Hydrolysis of 9. A mixture of **7** (26 mg, 98 μmol) and LiOH (24 mg, 0.98 mmol) in H_2O –MeOH (9:1) was stirred at 50 $^\circ\text{C}$ for 12 h. The resulting mixture was washed with hexane, and the aqueous layer was acidified with aqueous 1 M HCl solution and extracted

with diethyl ether. The combined organic layers were dried over anhydrous MgSO_4 , and the solvent was removed in vacuo to give a crude 3-[3-(2-hydroxyethyl)-2,4-dimethylphenyl]-2,2-dimethylpropanoic acid, which was used for the next step without further purification.

Acetylation of 3-[3-(2-hydroxyethyl)-2,4-dimethylphenyl]-2,2-dimethylpropanoic acid. To a solution of the title compound (23 mg, 93 μ mol) in CH_2Cl_2 (1.0 ml) were added acetic anhydride (96 mg, 0.94 mmol) and pyridine (37 mg, 0.47 mmol), and the resulting mixture was stirred at room temperature for 9 h. The mixture was washed with aqueous 1 M HCl solution and concentrated in vacuo to give crude 3-[3-(2-acetoxyethyl)-2,4-dimethylphenyl]-2,2-dimethylpropanoic acid (26 mg, 97%), which was used for the next without further purification.

Intramolecular Friedel-Crafts acylation. To a solution of 3-[3-(2-acetoxyethyl)-2,4-dimethylphenyl]-2,2-dimethylpropanoic acid (26 mg, 90 μ mol) in CH_2Cl_2 (1.0 mL) was added SOCl_2 (54 mg, 0.45 mmol) at room temperature, and the resulting mixture was stirred for 1 h at room temperature and then for 3 h at 40 $^\circ\text{C}$. The solvent and unreacted SOCl_2 were removed in vacuo. To the residue were added CH_2Cl_2 (1.0 mL) and AlCl_3 (14 mg, 0.11 mmol). The resulting mixture was stirred at 40 $^\circ\text{C}$ for 3 h before the reaction was quenched with water. The mixture was extracted with diethyl ether, and the combined organic layers were dried over anhydrous MgSO_4 . The solvent was removed to give a residue, which was purified by flash chromatography on silica gel (hexane–ethyl acetate = 5:1) to give **10** (25 mg, 92% for 3 steps) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 5:1). ^1H NMR (200 MHz, CDCl_3) δ 7.45 (s, 1H), 4.17 (t, J = 7.7 Hz, 2H), 3.09 (t, J = 7.7 Hz, 2H), 2.86 (s, 2H), 2.42 (s, 3H), 2.32 (s, 3H), 2.07 (s, 3H), 1.23 (s, 6H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 211.4, 170.8, 149.4, 141.3, 136.8, 134.3, 133.4, 123.1, 62.5, 45.5, 42.4, 29.5, 25.5, 21.1, 20.4, 14.9; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_3$: M^+ , 274.1569. Found: m/z 274.1570.

Deacetylation of 10. To a solution of **10** (24 mg, 88 μ mol) in H_2O – MeOH (1:1, 1.0 mL) was added K_2CO_3 (61 mg, 0.44 mmol), and the mixture was stirred at room temperature for 1 h before dilution with water. The resulting mixture was extracted with

diethyl ether. After removal of the solvent, the residue was purified by flash chromatography on silica gel (hexane–ethyl acetate = 2:1) followed by preparative GPC afforded alcyopterosin N (17 mg, 83%) as a colorless solid, mp 107.3–107.9 °C (lit.¹⁴ 103–104 °C), R_f 0.25 (hexane–ethyl acetate = 1:1). ^1H NMR (200 MHz, CDCl_3) δ 7.44 (s, 1H), 3.81 (t, J = 7.4 Hz, 2H), 3.06 (t, J = 7.4 Hz, 2H), 2.86 (s, 2H), 2.41 (s, 3H), 2.31 (s, 3H), 1.61 (bs, 1H), 1.22 (s, 6H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 211.7, 149.6, 142.4, 136.9, 134.4, 133.3, 123.2, 61.4, 45.5, 42.4, 33.3, 25.4, 20.5, 14.9; IR (KBr) 3472, 2961, 2922, 2359, 2341, 1692, 1605, 1042 cm^{-1} . The spectral data are in good agreement with those reported.¹⁴

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^1H NMR (200 MHz)

2d

¹³C NMR (67.8 MHz)

2d

36.323
32.900
27.108

83.993
77.461
77.000
76.835
76.523

138.197
130.430
122.746
114.715

^1H NMR (200 MHz)

2e

^{13}C NMR (67.8 MHz)

67.80 MHz
135.00 KHz
5200.0 Hz
4.2 us
30.7 us
0.2000 ms
1.0 sec

100.00
BCM
Bilevel. complete. decoupling
1H

TH5
C:\WINNMR98\COMMON\DEFAULT

64.60 KHz
59.0 Hz
205
30
262
1995
16 Hz

¹H NMR (200 MHz)

8

MENUF
OBNUC 13C67.80 MHz
135.00 KHz
5200.0 Hz
4.2 us
30.7 us
0.2000 ms
1.0 sec¹³C NMR (67.8 MHz)

8

17.597
20.986
26.05142.395
44.238
51.74176.539
77.000
77.477119.175
126.810
129.064
133.606
133.672
134.577
136.124
138.592

178.134

BCM
Bilevel. complete. decoupling
1H270.05 MHz
112.00 KHz
5800.0 Hz
50 us
511C:\WINNMR98\COMMON\DEFAULT
TH564.60 KHz
59.0 Hz
200
27
349
1098
16 Hz

PPM

10

20

30

40

50

60

70

80

90

100

110

120

130

140

150

160

170

180

190

200

¹H NMR (200 MHz)

¹³C NMR (50.3 MHz)

^1H NMR (200 MHz)

MENUF
OBNUC 13C67.80 MHz
135.00 KHz
5200.0 Hz
4.2 us
30.7 us
0.2000 ms
1.0 secPOINT 16384
SPO 16384
TIMES 100000

DUMMY 1

FREQU 18315.0 Hz

FLT 9150 Hz

DELAY 21.9 us

ACQTM 0.895 sec

PD 2.105 sec

ADBIT 16.00

RGAIN 32

BF 0.16 Hz

T1 0.00

T2 0.00

T3 90.00

T4 100.00

BCM

Bilevel. complete. decoupling

1H

270.05 MHz

112.00 KHz

5800.0 Hz

50 us

511

C:\WINNMR98\COMMON\DEFAULT

TH5

64.60 KHz

59.0 Hz

200

20

6

982

22 Hz

CSPED

FILDC

FILDF

PPM

10

¹H NMR (200 MHz)

alcyopterosin N

¹³C NMR (50.3 MHz)

alcyopterosin N