Supporting Information

for

Synthesis of cross-conjugated trienes by rhodium-catalyzed dimerization of monosubstituted allenes

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General Methods: All reactions were carried out under an argon atmosphere unless otherwise noted. Infrared spectra were recorded on a Shimadzu FTIR DR-8000 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury vx400 (¹H at 400 MHz and ¹³C at 100 MHz) spectrometer using CHCl₃ (¹H, δ = 7.26) and CDCl₃ (¹³C, δ = 77.0) as an internal standard unless otherwise noted. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI), a Thermofisher OrbitrapXL (ESI, APCI corona), or JMS-HX110A (FAB) spectrometer. Flash column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed on silica gel plates with PF254 indicator (Merck).

Materials: Toluene was distilled from sodium/benzophenone ketyl. [RhCl(cod)]₂ was prepared according to the literature procedure [1]. 1,2-Bis(diphenylphosphino)ethane (TCI) was used as received from commercial sources. Undeca-1,2-diene (**1a**) [2], nona-1,2-diene (**1b**) [2], penta-3,4-dien-1-ylbenzene (**1c**) [2], buta-2,3-dien-1-ylcyclohexane (**1d**) [2], 5-bezyloxy-penta-1,2-diene (**1e**) [3], 7-benzyloxy-hepta-1,2-diene (**1f**) [3], 7-(*tert*-butyldimetylsiloxy)-hepta-1,2-diene (**1g**) [3], hepta-5,6-dien-1-ol (**1h**) [3], octa-6,7-dienenitrile (**1i**) [3], propa-1,2-dien-1-ylcyclohexane (**1j**) [2] were prepared according to the literature procedures.

1h [4]: IR (neat): 3314, 2934, 2860, 1956, 1435 cm⁻¹; ¹H NMR: 1.36 (br s, 1H), 1.43–1.54 (m, 2H), 1.56–1.68 (m, 2H), 1.98–2.08 (m, 2H), 3.60–3.70 (m, 1H), 4.66 (dt, J = 6.8, 3.2 Hz, 2H), 5.10 (quint, J = 6.8 Hz); ¹³C NMR: 25.1, 27.9, 32.1, 62.8, 74.8, 89.7, 208.5; HRMS (APCI corona): Calcd for C₇H₁₃O, M+H⁺ 113.0966. Found m/z 113.0964.

1i: IR (neat): 2937, 2860, 2245, 1956, 1425 cm⁻¹; ¹H NMR: $\delta = 1.52-1.64$ (m, 2H), 1.65–1.76 (m, 2H), 2.00–2.08 (m, 2H), 2.35 (t, J = 7.2 Hz, 2H), 4.68 (dt, J = 6.8, 3.2 Hz, 2H), 5.08 (quint, J = 6.8 Hz, 1H); ¹³C NMR: $\delta = 16.9$, 24.6, 27.2, 27.7, 75.3, 88.9, 119.7, 208.5; HRMS (ESI⁺): Calcd for C₈H₁₁NNa, M+Na⁺ 144.0789. Found *m*/*z* 144.0784.

General procedures for the rhodium-catalyzed dimerization of monosubstituted allenes 1.

To a side-arm tube equipped with a stirrer bar, was added $[RhCl(cod)]_2$ (4.9 mg, 2.5 mol %) and dppe (7.7 mg, 5 mol %). The tube was evacuated and refilled with argon three times. Then, toluene (4mL) and substrate 1 (0.4 mmol) were added via syringe and the tube was closed. After heating at 130 °C for 6 h, the reaction mixture was cooled to room temperature, passed through a pad of Florisil(R) and eluted with ethyl acetate (ca 90–100mL). The filtrate was concentrated under reduced pressure and the residue purified by preparative thin-layer chromatography to give product 3. Although the isolated 3 was relatively labile, it could be kept a -30 °C for days without any detectable decomposition or polymerization.

3a: IR (neat): 2924, 2853, 1463 cm⁻¹; ¹H NMR: $\delta = 0.88$ (t, J = 7.2 Hz, 6H), 1.18–1.46 (m, 24H), 2.09 (q, J = 7.2 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 4.89 (d, J = 1.6 Hz, 1H), 4.95 (s, 2H), 4.98 (s, 1H), 5.74 (dt, J = 15.6, 6.8 Hz, 1H), 6.06 (d, J = 15.2 Hz, 1H); ¹³C NMR: $\delta = 14.09$, 14.11, 22.67, 22.69, 28.2, 29.2, 29.3, 29.35, 29.38, 29.5, 29.6, 29.7, 31.8, 31.9, 32.8, 35.4, 112.1, 112.8, 130.3, 133.3, 148.5, 148.9; HRMS (EI⁺): Calcd for C₂₂H₄₀, M⁺ 304.3130. Found *m*/*z* 304.3138.

3b: IR (neat): 2925, 2855, 1467 cm⁻¹; ¹H NMR: $\delta = 0.88$ (t, J = 6.8 Hz, 3H), 0.89 (t, J = 6.4 Hz, 3H), 1.20–1.46 (m, 16H), 2.09 (q, J = 7.2 Hz, 2H), 2.20 (t, J = 7.2 Hz, 2H), 4.90 (s, 1H), 4.95 (s, 2H), 4.98 (s, 1H), 5.74 (dt, J = 15.6, 6.8 Hz, 1H), 6.06 (d, J = 15.6 Hz, 1H); ¹³C NMR: $\delta = 14.06$, 14.11, 22.5, 22.7, 28.2, 28.9, 29.2, 29.3, 31.4, 31.9, 32.8, 35.4, 112.1, 112.8, 130.3, 133.4, 148.4, 148.9; HRMS (EI⁺): Calcd for C₁₈H₃₂, M⁺ 248.2504. Found *m*/*z* 248.2494.

3c: IR (neat): 3025, 2936, 1495, 1452 cm⁻¹; ¹H NMR: $\delta = 1.74$ (quint, J = 7.6 Hz, 2H), 2.26 (t, J = 7.6 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 3.44 (d, J = 6.8 Hz, 2H), 4.95 (d, J = 2.0 Hz, 1H), 4.97–5.02 (m, 2H), 5.04 (d, J = 1.6 Hz, 1H), 5.90 (dt, J = 15.6, 6.8 Hz, 1H), 6.15 (d, J = 15.2 Hz, 1H), 7.14–7.32 (m, 10H); ¹³C NMR: $\delta = 29.9$, 35.0, 35.5, 39.1, 113.2, 113.5, 125.6, 126.0, 128.2, 128.4, 128.6, 131.3, 131.7, 140.2, 142.4, 147.8, 148.0; HRMS (EI⁺): Calcd for C₂₂H₂₄, M⁺ 288.1878. Found *m*/*z* 288.1872.

3d: IR (neat): 2922, 2851, 1448 cm⁻¹; ¹H NMR: $\delta = 0.80-0.94$ (m, 2H), 1.04–1.36 (m, 11H), 1.60–1.78 (m, 10H), 1.96–2.08 (m, 1H), 2.21 (t, *J* = 7.2 Hz, 2H), 4.90 (d, *J* = 2.4 Hz, 1H), 4.95 (s, 2H), 4.99 (d, *J* = 1.6 Hz, 1H), 5.69 (dd, *J* = 15.6, 7.2 Hz, 1H), 6.02 (d, *J* = 15.6 Hz, 1H); ¹³C NMR: $\delta = 26.0, 26.2, 26.4, 26.7, 32.6, 32.8, 33.3, 36.0, 37.4, 40.8, 112.1, 112.6, 127.7, 139.0, 148.6, 149.2; HRMS (EI⁺): Calcd for C₂₀H₃₂, M⁺ 272.2504. Found$ *m/z*272.2498.

3e: IR (neat): 2925, 2854, 1454, 1362, 1074 cm⁻¹; ¹H NMR: $\delta = 1.75$ (quint, J = 6.8 Hz, 2H), 2.33 (t, J = 7.6 Hz, 2H), 3.48 (t, J = 6.8 Hz, 2H), 4.09 (d, J = 6.0 Hz, 2H), 4.50 (s, 2H), 4.53 (s, 2H), 4.99 (s, 1H), 5.02 (s, 2H), 5.12 (s, 1H), 5.87 (dt, J = 15.6, 6.8 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 7.22–7.40 (m, 10H); ¹³C NMR: $\delta = 28.2$, 31.8, 69.8, 70.5, 72.1, 72.9, 113.8, 114.5, 127.5, 127.6, 127.8, 128.3, 128.4, 132.8, 138.2, 138.6, 147.1, 147.3; HRMS (FAB⁺): Calcd for C₂₄H₂₈O₂Na, M+Na⁺ 371.1987. Found *m/z* 371.1992.

3f: IR (neat): 2935, 2855, 1453, 1103 cm⁻¹; ¹H NMR: $\delta = 1.34-1.48$ (m, 4H), 1.63 (quint, J = 7.2 Hz, 2H), 1.74 (quint, J = 7.2 Hz, 2H), 2.16–2.26 (m, 4H), 3.47 (t, J = 6.4 Hz, 2H), 3.49 (t, J = 6.4 Hz, 2H), 4.51 (s, 2H), 4.51 (s, 2 H), 4.91 (s, 1H), 4.95 (s, 2H), 5.00 (s, 1H), 5.74 (dt, J = 15.6, 6.8 Hz, 1H), 6.08 (d, J = 16.0 Hz, 1H), 7.24–7.40 (m, 10H); ¹³C NMR: $\delta = 25.9$, 28.0, 29.26, 29.31, 29.6, 35.2, 69.6, 70.4, 72.8, 72.9, 112.5, 113.0, 127.4, 127.5, 127.6, 128.31, 128.33, 130.8, 132.3, 138.5, 138.6, 148.1, 148.5; HRMS (ESI⁺): Calcd for C₂₈H₃₆O₂Na, M+Na⁺ 427.2613. Found *m*/*z* 427.2584.

3g: IR (neat): 2930, 1472, 1256, 1104 cm⁻¹; ¹H NMR: $\delta = 0.05$ (s, 12H), 0.89 (s, 18H), 1.20–1.70 (m, 8H), 2.10–2.30 (m, 4H), 3.52–3.69 (m, 4H), 4.90 (s, 1H), 4.95 (s, 2H), 4.98 (s, 1H), 5.73 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.08 (d, *J* = 15.6 Hz, 1H); ¹³C NMR: $\delta = -5.30$, -5.27, 18.3, 18.4, 25.5, 25.96, 25.97, 28.0, 29.0, 32.3, 32.7, 35.4, 62.5, 63.2, 112.4, 113.0, 130.6, 132.6, 148.2, 148.6; HRMS (EI⁺): Calcd for C₂₆H₅₂O₂Si₂, M⁺ 452.3506. Found *m*/*z* 452.3504.

3h: IR (neat): 3300, 2934, 2860, 1435 cm⁻¹; ¹H NMR: $\delta = 1.30-1.74$ (m, 8H), 2.14–2.26 (m, 4H), 3.58–3.70 (m, 4H), 4.91 (d, J = 2.0 Hz, 1H), 4.95 (s, 1H), 4.96 (s, 1H), 4.99 (s, 1H), 5.75 (dt, J = 15.6, 7.2 Hz, 1H), 6.10 (d, J = 15.6 Hz, 1H); ¹³C NMR: $\delta = 25.3$, 27.8, 29.0, 32.0, 32.5, 35.3, 62.3, 62.8, 112.7, 113.2, 130.9, 132.2, 148.0, 148.3; HRMS (FAB⁺): Calcd for C₁₄H₂₄O₂Na, M+Na⁺ 247.1674. Found *m*/*z* 247.1669.

3i: IR (neat): 2936, 2863, 2245, 1585, 1424 cm⁻¹; ¹H NMR: $\delta = 1.38-1.50$ (m, 4H), 1.66 (quint, *J* = 6.8 Hz, 2H), 1.78 (quint, *J* = 7.2 Hz, 2H), 2.18–2.40 (m, 8H), 4.95 (s, 1H), 4.97 (s, 1H), 4.98 (s, 1H), 5.04 (s, 1H), 5.65 (dt, *J* = 15.2, 7.2 Hz, 1H), 6.14 (d, *J* = 15.6 Hz, 1H); ¹³C NMR: $\delta = 16.5$, 17.1, 24.8, 25.2, 27.2, 28.2, 31.4, 34.9, 113.5, 113.8, 119.5, 119.7, 129.9, 132.4, 147.4, 147.6; HRMS (EI⁺): Calcd for C₁₆H₂₁N₂, M–H⁺ 241.1699. Found *m*/*z* 241.1694.

3j: IR (neat): 2921, 2851, 1448 cm⁻¹; ¹H NMR: $\delta = 0.80-0.94$ (m, 2H), 1.06–1.76 (m, 15H), 2.10–2.26 (m, 6H), 4.86 (d, J = 0.8 Hz, 1H), 4.88 (d, J = 0.8 Hz, 1H), 5.09 (d, J = 2.4 Hz, 1H), 5.20 (d, J = 1.6 Hz, 1H), 5.71 (s, 1H); ¹³C NMR: $\delta = 26.4$, 26.6, 26.8, 28.1, 28.8, 29.7, 33.5, 36.2, 37.3, 42.1, 113.5, 114.5, 121.8, 143.0, 144.9, 146.8; HRMS (EI⁺): Calcd for C₁₈H₂₈, M⁺ 244.2191. Found *m*/*z* 244.2188.

Procedure for Diels–Alder reaction of *N*-phenyl-1,2,4-triazoline-3,5-dione (4) with 3a.

To a side-arm tube equipped with a stirrer bar, was added *N*-phenyl-1,2,4-triazoline-3,5-dione (4, 62.1 mg, 0.36 mmol, 2.4 equiv). The tube was evacuated and refilled with argon three times. Then, toluene (1.5 mL) and **3a** (46.6 mg, 0.15 mmol) were added via syringe, and the tube was closed. After stirring at 0 °C for 1 h, the solvent was removed by evaporation and the residue purified by preparative thin-layer chromatography (hexane:ethyl acetate = 3:1) to give the two isomeric bisadducts (**5a**, 74.3 mg, 0.11 mmol, 75% major) and (**5a'**, 5.3 mg, 0.01 mmol, 6% minor).

5a: IR (KBr): 2926, 2855, 1772, 1718, 1503, 1419 cm⁻¹; ¹H NMR: $\delta = 0.80-0.92$ (m, 6H), 1.16–1.52 (m, 24H), 1.88–1.99 (m, 1H), 2.16–2.40 (m, 3H), 3.98 (d, J = 13.6 Hz, 1H), 4.06–4.20 (m, 2H), 4.52–4.58 (m, 1H), 4.83–4.93 (m, 1H), 4.94 (d, J = 13.6 Hz, 1H) 7.34–7.56 (m, 10H); ¹³C NMR: $\delta = 14.0$, 14.1, 22.56, 22.61, 25.3, 28.7, 29.1, 29.2, 29.3, 29.38, 29.40, 30.9, 31.7, 31.8, 33.4, 44.8, 46.2, 57.4, 58.5, 119.3, 125.3, 125.4, 128.1, 128.5, 129.1, 129.3, 130.7, 131.4, 132.6, 149.4, 152.5, 152.7, 153.2; HRMS (ESI⁺): Calcd for C₃₈H₅₁N₆O₄, M+H⁺ 655.3972. Found *m*/*z* 655.3975.

5a': IR (KBr): 2923, 2855, 1773, 1719, 1600, 1502, 1413 cm⁻¹; ¹H NMR: $\delta = 0.80-0.94$ (m, 6H), 1.14–1.46 (m, 24H), 1.74–1.94 (m, 2H), 2.04–2.16 (m, 1H), 2.38–2.48 (m, 1H), 3.39 (d, *J* = 12.0 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 4.56 (d, *J* = 13.2 Hz, 1H), 4.58–4.66 (m, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 6.24 (d, *J* = 4.4 Hz, 1H), 7.34–7.56 (m, 10H); ¹³C NMR: $\delta = 14.07$, 14.09, 22.56, 22.64, 23.6, 25.0, 29.0, 29.19, 29.25, 29.4, 29.5, 31.0, 31.7, 31.8, 31.9, 47.2, 52.4, 52.5, 61.8, 125.41, 125.43, 126.1, 128.0, 128.37, 128.44, 129.2, 130.8, 131.0, 150.2, 151.4, 151.8, 152.0; HRMS (EI⁺): Calcd for C₃₈H₅₀N₆O₄, M⁺ 654.3894. Found *m/z* 654.3923.

Procedure for Diels-Alder reaction of tetracyanoethylene (6) with 3a.

To a side-arm tube equipped with a stirrer bar, was added tetracyanoethylene (6, 51.5 mg, 0.40 mmol, 2.7 equiv). The tube was evacuated and refilled with argon three times. Then, toluene (1.5 mL) and **3a** (46.1 mg, 0.15 mmol) were added via syringe and the tube was closed. After stirring at 60 °C for 24 h, the solvent was removed by evaporation and the residue purified by preparative thin-layer chromatography (hexane:ethyl acetate = 3:1) to give an isomeric mixture of **7a** and **7a'** (52.7 mg, 0.12 mmol, 62% major, 19% minor).

7a: IR (neat): 2927, 2855, 1611, 1467 cm⁻¹; ¹H NMR: $\delta = 0.82-0.96$ (m, 6H), 1.20–1.78 (m, 25H), 1.92–2.02 (m, 1H), 2.24 (t, J = 7.6 Hz, 2H) 3.07-3.14 (m, 1H), 3.18 (d, J = 17.6 Hz, 1H), 3.29 (d, J = 17.2 Hz, 1H), 5.08 (s, 1H), 5.15 (s, 1H), 5.79–5.83 (m, 1H); ¹³C NMR: $\delta = 22.8$, 22.9, 26.8, 28.4, 29.1, 29.4, 29.5, 29.57, 29.61, 29.7, 31.8, 32.1, 32.2, 33.5, 33.7, 39.3, 41.9, 43.9, 109.1, 110.6, 111.4, 111.6, 114.4, 120.7, 131.2, 144.9; HRMS (EI⁺): Calcd for C₂₈H₄₀N₄, M⁺ 432.3253. Found *m*/*z* 432.3249.

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