Supporting Information

Biaryl Synthesis from Two Different Aryl Halides with Tri(2-furyl)germane

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Instrumentation and Materials

¹H NMR (300 MHz) and ¹³C NMR (75.3 MHz) spectra were taken on Varian GEMINI 300 and Mercury 300 spectrometers. ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tri(2-furyl)germane (**1**)¹ and tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃•CHCl₃)² were prepared according to the literature.

Experimental Section

A Typical Procedure for Synthesis of Aryltri(2-furyl)germane.

Palladium(II) acetate (11 mg, 0.050 mmol), 1,1'-bis(diphenylphosphino)ferrocene (28 mg, 0.050 mmol), and cesium carbonate (0.36 g, 1.1 mmol) were placed in a 20-mL flask under argon, and then DMF (5 mL) was added at room temperature. After the mixture was stirred for 5 min, iodobenzene (0.13 mL, 1.2 mmol) and DMF solution (5 mL) of tri(2-furyl)germane (**1**, 0.27 g, 1.0 mmol) were

¹ Nakamura, T.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. *Synlett* **1999**, 1415.

² Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, 65, 253.

sequentially added to the suspension. The mixture was stirred at room temperature for 1.5 h. Water was added and the mixture was extracted with ethyl acetate (20 mL $\times$ 3). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by silica gel column chromatography (hexane/AcOEt = 20/1) to afford tri(2-furyl)phenylgermane (**2a**, 0.29 g, 0.83 mmol) in 83% yield.

Characterization Data

Tri(2-furyl)phenylgermane (2a): IR (nujol) 2345, 1549, 1433, 1362, 1205, 1150, 1005, 897, 748 cm⁻¹; ¹H NMR (CDCl₃) δ 6.49 (dd, J = 3.0, 1.8 Hz, 3H), 6.83 (d, J = 3.0 Hz, 3H), 7.38–7.46 (m, 3H), 7.63–7.67 (m, 2H), 7.77 (d, J = 1.8 Hz, 3H); ¹³C NMR (CDCl₃) δ 109.89, 121.99, 128.56, 130.01, 133.27, 134.49, 147.85, 152.40. Found: C, 61.32; H, 4.06%. Calcd for C₁₈H₁₄GeO₃: C, 61.61; H, 4.02%.

Tri(2-furyl)-4-methoxyphenylgermane (2b): IR (nujol) 1593, 1501, 1462, 1250, 1182, 1148, 1097, 1001, 897, 748 cm⁻¹; ¹H NMR (CDCl₃) δ 3.83 (s, 3H), 6.49 (dd, J = 3.3, 1.8 Hz, 3H), 6.82 (d, J = 3.3 Hz, 3H), 6.97 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.77 (d, J = 1.8 Hz, 3H); ¹³C NMR (CDCl₃) δ 55.05, 109.86, 114.36, 121.83, 123.83, 135.90, 147.77, 152.79, 161.24. Found: C, 59.93; H, 4.34%. Calcd for C₁₉H₁₆GeO₄: C, 59.91; H, 4.23%.

Tri(2-furyl)-3-methoxyphenylgermane (2c): IR (neat) 3125, 2937, 1549, 1479, 1418, 1362, 1234, 1103, 1043, 1005, 897, 820, 746, 694 cm⁻¹; ¹H NMR (CDCl₃) δ 3.79 (s, 3H), 6.49 (dd, J = 3.3, 1.8 Hz, 3H), 6.83 (d, J = 3.3 Hz, 3H), 6.97 (dd, J = 8.1, 3.0 Hz, 1H), 7.19–7.22 (m, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.35 (dd, J = 7.8, 7.5 Hz, 1H), 7.77 (d, J = 1.8 Hz, 3H); ¹³C NMR (CDCl₃) δ 55.09, 109.87, 115.45, 119.92, 122.01, 126.72, 129.63, 134.62, 147.85, 152.36, 159.54. Found: C, 60.02; H, 4.18%. Calcd for C₁₉H₁₆GeO₄: C, 59.91; H, 4.23%.

Tri(2-furyl)-4-methylphenylgemane (2d): IR (neat) 3115, 2922, 1599, 1549, 1454, 1362, 1205, 1151,

1101, 1005, 897 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.38 (s, 3H), 6.49 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.83 (d, $J = 3.3$ Hz, 3H), 7.24 (d, $J = 7.8$ Hz, 2H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.77 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 21.40, 109.85, 121.86, 129.40, 129.56, 134.46, 140.04, 147.77, 152.71. Found: C, 62.54; H, 4.47%. Calcd for $\text{C}_{19}\text{H}_{16}\text{GeO}_3$: C, 62.26; H, 4.42%.

Tri(2-furyl)-2-methylphenylgermane (2e): IR (neat) 1549, 1452, 1362, 1205, 1150, 1101, 1005, 897, 745 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.33 (s, 3H), 6.50 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.83 (d, $J = 3.3$ Hz, 3H), 7.17–7.27 (m, 2H), 7.32–7.38 (m, 1H), 7.45 (d, $J = 7.5$ Hz, 1H), 7.78 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 22.58, 109.96, 121.88, 125.57, 130.28, 130.35, 132.54, 135.50, 144.00, 147.63, 152.89. Found: C, 62.26; H, 4.59%. Calcd for $\text{C}_{19}\text{H}_{16}\text{GeO}_3$: C, 62.54; H, 4.42%.

Tri(2-furyl)-4-(*N,N*-dimethylamino)phenylgermane (2f): IR (nujol) 1597, 1549, 1454, 1366, 1204, 1101, 1003, 897, 802, 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.98 (s, 6H), 6.47 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.77 (d, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 3.3$ Hz, 3H), 7.50 (d, $J = 8.7$ Hz, 2H), 7.75 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 39.98, 109.74, 112.41, 117.72, 121.55, 135.39, 147.54, 151.68, 153.44. Found: C, 61.08; H, 4.91%. Calcd for $\text{C}_{20}\text{H}_{19}\text{GeNO}_3$: C, 60.97; H, 4.86%.

(*E*)-6-Tri(2-furyl)germyl-6-dodecene (2g): IR (neat) 2928, 1549, 1456, 1205, 1150, 1003, 897, 743 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80 (t, $J = 6.9$ Hz, 3H), 0.89 (t, $J = 6.9$ Hz, 3H), 1.10–1.44 (m, 12H), 2.16 (dt, $J = 7.2, 7.2$ Hz, 2H), 2.30 (t, $J = 7.2$ Hz, 2H), 5.90 (t, $J = 7.2$ Hz, 1H), 6.46 (dd, $J = 3.0, 1.8$ Hz, 3H), 6.76 (d, $J = 3.0$ Hz, 3H), 7.74 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 13.83, 13.91, 22.24, 22.40, 28.56, 28.92, 29.01, 30.54, 31.49, 31.62, 109.74, 121.39, 135.08, 144.07, 147.38, 153.75. Found: C, 65.53; H, 7.49%. Calcd for $\text{C}_{24}\text{H}_{32}\text{GeO}_3$: C, 65.35; H, 7.31%.

2-Tri(2-furyl)germyl-2-propen-1-ol (2h): IR (neat) 3383, 2860, 2256, 1551, 1454, 1362, 1207, 1151, 1101, 1005, 897 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.71 (bs, 1H), 4.44 (dd, $J = 1.8, 1.5$ Hz, 2H), 5.62 (dt, $J = 1.5, 1.5$ Hz, 1H), 6.06 (dt, $J = 1.5, 1.8$ Hz, 1H), 6.48 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.83 (d, $J = 3.3$ Hz, 3H),

7.75 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 66.65, 109.99, 121.87, 126.76, 145.73, 147.72, 152.12. Found: C, 54.55; H, 4.09%. Calcd for $\text{C}_{15}\text{H}_{14}\text{GeO}_4$: C, 54.45; H, 4.26%.

2-Tri(2-furyl)germylpropene (2i): IR (neat) 2953, 1549, 1447, 1362, 1205, 1150, 1101, 1005, 930, 897, 745 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.07 (dd, $J = 1.5, 1.5$ Hz, 3H), 5.47–5.48 (m, 1H), 5.83–5.84 (m, 1H), 6.47 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.80 (d, $J = 3.3$ Hz, 3H), 7.75 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 23.23, 109.82, 121.61, 128.21, 141.27, 147.63, 152.56. Found: C, 56.94; H, 4.73%. Calcd for $\text{C}_{15}\text{H}_{14}\text{GeO}_3$: C, 57.22; H, 4.48%.

(E)-1-Tri(2-furyl)germylpropene (2j): IR (neat) 1738, 1620, 1551, 1454, 1362, 1205, 1150, 1101, 1005, 897 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.97 (dd, $J = 6.0, 1.5$ Hz, 3H), 6.11 (dq, $J = 18.0, 1.5$ Hz, 1H), 6.43 (dq, $J = 18.0, 6.0$ Hz, 1H), 6.51 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.83 (d, $J = 3.3$ Hz, 3H), 7.78 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 22.10, 109.78, 121.26, 121.51, 146.96, 147.50, 153.09. Found: C, 57.18; H, 4.64%. Calcd for $\text{C}_{15}\text{H}_{14}\text{GeO}_3$: C, 57.22; H, 4.48%.

α -Tri(2-furyl)germylstyrene (2k): IR (neat) 3059, 1549, 1493, 1452, 1362, 1205, 1151, 1101, 1005, 897, 746 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.77 (d, $J = 1.5$ Hz, 1H), 6.22 (d, $J = 1.5$ Hz, 1H), 6.46 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.74 (d, $J = 3.3$ Hz, 3H), 7.23–7.36 (m, 5H), 7.74 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 109.92, 122.04, 127.07, 127.37, 128.35, 129.76, 141.88, 145.36, 147.69, 152.44. Found: C, 63.95; H, 4.25%. Calcd for $\text{C}_{20}\text{H}_{16}\text{GeO}_3$: C, 63.73; H, 4.28%.

(E)- β -Tri(2-furyl)germylstyrene (2l): IR (neat) 2249, 1604, 1573, 1495, 1342, 1205, 1151, 1101, 1005, 908, 733 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.48–6.51 (m, 3H), 6.81 (d, $J = 18.6$ Hz, 1H), 6.85–6.86 (m, 3H), 7.15 (d, $J = 18.6$ Hz, 1H), 7.27–7.37 (m, 3H), 7.48 (d, $J = 6.9$ Hz, 2H), 7.75–7.78 (m, 3H); ^{13}C NMR (CDCl_3) δ 109.89, 119.82, 121.57, 126.85, 128.61, 128.75, 137.38, 147.69, 147.74, 152.59. Found: C, 63.86; H, 4.35%. Calcd for $\text{C}_{20}\text{H}_{16}\text{GeO}_3$: C, 63.73; H, 4.28%.

Tri(2-furyl)-2-pyridylgermane (2m): IR (nujol) 2350, 1572, 1452, 1205, 1101, 898, 748 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.50 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.93 (d, $J = 3.3$ Hz, 3H), 7.26–7.32 (m, 1H), 7.64–7.66 (m, 2H), 7.78 (d, $J = 1.8$ Hz, 3H), 8.83 (d, $J = 4.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 109.97, 122.32, 123.89, 130.64, 135.02, 147.87, 151.03, 151.73, 161.90. Found: C, 57.94; H, 3.80%. Calcd for $\text{C}_{17}\text{H}_{13}\text{GeNO}_3$: C, 58.03; H, 3.72%.

(E)-1-Tri(2-furyl)germyl-1-octene (2n): IR (neat) 2928, 2856, 1616, 1549, 1454, 1362, 1205, 1151, 1101, 1003, 897, 885, 816, 694, 596 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, $J = 6.9$ Hz, 3H), 1.10–1.52 (m, 8H), 2.23 (dt, $J = 6.3, 6.3$ Hz, 2H), 6.02 (d, $J = 18.3$ Hz, 1H), 6.34 (dt, $J = 18.3, 6.3$ Hz, 1H), 6.46 (dd, $J = 3.3, 1.8$ Hz, 3H), 6.78 (d, $J = 3.3$ Hz, 3H), 7.74 (d, $J = 1.8$ Hz, 3H); ^{13}C NMR (CDCl_3) δ 13.93, 22.47, 28.16, 28.72, 31.56, 36.35, 109.79, 119.49, 121.25, 147.54, 152.31, 153.22. Found: C, 62.42; H, 6.40%. Calcd for $\text{C}_{20}\text{H}_{24}\text{GeO}_3$: C, 62.40; H, 6.28%.

A Typical Procedure for Cross-Coupling Reaction of Aryltri(2-furyl)germane with Aryl Halides.

Tetrabutylammonium fluoride (1.0 M THF solution, 4.0 mL, 4.0 mmol) was added to a solution of tri(2-furyl)-4-methoxyphenylgermane (**2b**, 0.38g, 1.0 mmol) and iodobenzene (0.13 mL, 1.2 mmol) in *N*-methyl-2-pyrrolidinone (5 mL), and the mixture was stirred at room temperature under argon. After 5 min, a mixture of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (10 mg, 0.010 mmol) and tri(2-furyl)phosphine (4.6 mg, 0.020 mmol) in NMP (5 mL) was introduced to the reaction mixture. The whole mixture was heated at 100 °C. After being stirred for 5 h, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 , and then concentrated. The residue was purified on a silica gel column to give 4-methoxybiphenyl (**3a**, 0.17 g, 0.90 mmol) in 90% yield.

All biaryls are known compounds.

3a, **3f**, **3h** and **3i** are commercially available.

Registry No. **3c**, 27331-33-5; **3j**, 352032-26-9; **3l**, 28665-60-3

Spectral data for **3b**³, **3d**⁴, **3e**⁵, **3g**⁶, and **3k**⁷ were found in the literature.

One-Pot Synthesis of Unsymmetrical Biaryl.

A DMF solution of tri(2-furyl)germane (**1**, 0.27 g, 1.0 mmol) and 4-iodoanisole (0.25g, 1.05 mmol) were treated with Pd(OAc)₂ (11 mg, 0.050 mmol), DPPF (28 mg, 0.050 mmol), and Cs₂CO₃ (0.36 g, 1.1 mmol) in DMF at room temperature. After 1 h, iodobenzene (0.13 mL, 1.2 mmol), TBAF (1.0 M THF solution, 4.0 mL, 4.0 mmol), and NMP (10 mL) were introduced, and then the reaction mixture was heated at 100 °C for 10 h. Aqueous workup followed by silica gel column purification afforded the desired product **3a** in 34% yield.

³ Badone, D.; Baroni, M.; Cardamone, R.; Ielmini, A.; Guzzi, U. *J. Org. Chem.* **1997**, 62, 7170.

⁴ Saito, S.; Oh-tani, S.; Miyaura, N. *J. Org. Chem.* **1997**, 62, 8024.

⁵ Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, 58, 5434.

⁶ Zapf, A.; Beller, M. *Chem. Eur. J.* **2000**, 6, 1830.

⁷ Hatanaka, Y.; Goda, K.; Okahara, Y.; Hiyama, T. *Tetrahedron* **1994**, 50, 8301.