Preparation and Reaction of 2-Aryl-3-silyl-1,3-butadiene

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General procedure for preparation of 2-Aryl-3-silyl-1,3-butadiene. Preparation of 6a.

Under Ar atmosphere, Ni(cod)_2 (0.02 mmol, 2 mol%) and P(2-furyl)_3 (0.03 mmol, 3 mol%) were stirred in THF (0.3 ml) for 10 min at 0 °C. Then bis(iodozincio)methane (**5a**) (1.2 mmol, 1.2 eq.), 3-trimethylsilyl-1-benzyloxy-2-propyne (**1a**) (1.0 mmol) and iodobenzene (1.2 mmol, 1.2 eq.) were added subsequently and the mixture was stirred for 10 h at 25 °C. After the mixture was cooled to 0 °C, hexane/AcOEt (5 / 1, 20 mL) was added. After an addition of sat. NH_4Cl aq, the mixture was extracted with hexane / AcOEt (5 / 1). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 2-Trimethylsilyl-3-phenyl-1,3-butadiene (**6a**) as colorless oil.

2-Trimethylsilyl-3-phenyl-1,3-butadiene (6a): ^1H NMR (500MHz, CDCl_3) δ 7.34 – 7.24 (m, 5H), 5.73 (d, J = 3.5 Hz, 1H), 5.58 (d, J = 3.5 Hz, 1H), 5.21 (d, J = 2.0 Hz, 1H), 4.99 (d, J = 2.0 Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 153.9, 153.1, 140.9, 128.0, 127.9, 127.4, 127.3, -1.0.

2-(p-Tolyl)-3-trimethylsilyl-1,3-butadiene (6b): ^1H NMR (500MHz, CDCl_3) δ 7.23 – 7.22 (m, 2H), 7.11 – 7.10 (m, 2H), 5.72 (d, $J = 3.5$ Hz, 1H), 5.57 (d, $J = 3.5$ Hz, 1H), 5.18 (d, $J = 1.5$ Hz, 1H), 4.93 (d, $J = 1.5$ Hz, 1H), 2.34 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 154.0, 152.9, 137.9, 137.2, 128.7, 127.7, 127.2, 110.6, 21.1, -1.0

2-(4-Methoxyphenyl)-3-trimethylsilyl-1,3-butadiene (6c): ^1H NMR (500MHz, CDCl_3) δ 7.28 – 7.25 (m, 2H), 6.85 – 6.82 (m, 2H), 5.72 (d, $J = 3.5$ Hz, 1H), 5.56 (d, $J = 3.5$ Hz, 1H), 5.14 (d, $J = 2.0$ Hz, 1H), 4.89 (d, $J = 2.0$ Hz, 1H), 3.81 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 159.1, 154.2, 152.5, 133.3, 128.5, 127.5, 113.3, 109.7, 55.2, -1.0

2-(4-Trifluoromethylphenyl)-3-trimethylsilyl-1,3-butadiene (6d): ^1H NMR (500MHz, CDCl_3) δ 7.56 – 7.55 (m, 2H), 7.44 – 7.43 (m, 2H), 5.72 (d, $J = 3.5$ Hz, 1H), 5.63 (d, $J = 3.5$ Hz, 1H), 5.28 (d, $J = 1.5$ Hz, 1H), 5.10 (d, $J = 1.5$ Hz, 1H), 0.02(s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 153.2, 151.9, 144.5, 129.5, 128.7, 127.6, 125.3, 125.0(q), 113.3, -1.0

6d (^1H NMR)

6d (^{13}C NMR)

2-(4-Bromophenyl)-3-trimethylsilyl-1,3-butadiene (6e): ^1H NMR (500MHz, CDCl_3) δ 7.43 – 7.41 (m, 2H), 7.21 – 7.19 (m, 2H), 5.71 (d, $J = 3.0$ Hz, 1H), 5.59 (d, $J = 3.0$ Hz, 1H), 5.21 (d, $J = 1.5$ Hz, 1H), 5.00 (d, $J = 1.5$ Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 153.4, 152.0, 139.8, 131.1, 129.0, 128.3, 121.5, 111.9, -1.0

2-(4-Cyanophenyl)-3-trimethylsilyl-1,3-butadiene (6f): ^1H NMR (500MHz, CDCl_3) δ 7.61 – 7.58 (m, 2H), 7.44 – 7.42 (m, 2H), 5.72 (d, $J = 3.0$ Hz, 1H), 5.64 (d, $J = 3.0$ Hz, 1H), 5.31 (d, $J = 1.5$ Hz, 1H), 5.13 (d, $J = 1.5$ Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125MHz, CDCl_3) δ 152.9, 151.5, 145.5, 131.9, 129.1, 127.9, 119.0, 114.1, 111.0, -1.1

2-Dimethylphenylsilyl-3-phenyl-1,3-butadiene (7b): ^1H NMR (500MHz, CDCl_3) δ 7.50 – 7.47 (m, 2H), 7.34 – 7.30 (m, 3H), 7.28 – 7.22 (m, 5H), 5.82 (d, $J = 3.5$ Hz, 1H), 5.62 (d, $J = 3.5$ Hz, 1H), 5.17 (d, $J = 2.0$ Hz, 1H), 4.97 (d, $J = 2.0$ Hz, 1H), 0.29 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ 152.6, 151.6, 140.9, 138.1, 133.9, 130.1, 128.9, 127.9, 127.63, 127.57, 127.4, 112.6, -2.4

2-(2,6-Dimethoxyphenyldimethylsilyl)-3-phenyl-1,3-butadiene (7d): ^1H NMR (500MHz, CDCl_3) δ 7.27 – 7.17 (m, 6H), 6.43 (d, $J = 8.0$ Hz, 2H), 5.66 (d, $J = 3.5$ Hz, 1H), 5.55 (d, $J = 3.5$ Hz, 1H), 5.10 (d, $J = 2.0$ Hz, 1H), 4.99 (d, $J = 2.0$ Hz, 1H), 3.67 (s, 6H), 0.33 (s, 6H); ^{13}C NMR (125MHz, CDCl_3) δ 165.4, 153.6, 153.1, 141.5, 131.6, 127.7, 127.6, 127.3, 126.9, 112.4, 111.8, 103.4, 55.1, 0.9

(2,6-(MeO) $_2$ C $_6$ H $_3$)Me $_2$
7d (^1H NMR)

Reaction of 2-Aryl-3-silyl-1,3-butadiene.

To a solution of 2-(2,6-Dimethoxyphenyldimethylsilyl)-3-phenyl-1,3-butadiene (**7d**) (0.5 mmol) in hexane (1 ml), $\text{BF}_3\cdot 2\text{AcOH}$ (0.6 mmol, 1.2 eq.) was added at 0 °C and the mixture was stirred for 1 h at 0 °C. Then sat. NaHCO_3 was added and the mixture was extracted with hexane. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. As a crude product, 2-Fluorodimethylsilyl-3-phenyl-1,3-butadiene (**8a**) was obtained in 68% yield.

To a solution of **8a** (0.16 mmol) and 4-iodotoluene (0.16 mmol, 1.0 eq.) in THF (0.5 ml), TBAF (0.32 mmol, 2.0 eq., 1.0 M solution in THF) was added and the mixture was stirred for 3 min at 25 °C. Then $\text{Pd}_2(\text{dba})_3$ (0.008 mmol, 5 mol%) was added and the mixture was stirred for 2 h at 25 °C. The mixture was cooled to 0 °C, diluted by Et_2O , added sat. NaHCO_3 and extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 2-(p-tolyl)-3-phenyl-1,3-butadiene (**9**) as colorless oil in 40% yield.

2-(4-Methylphenyl)-3-phenyl-1,3-butadiene (9): ^1H NMR (500MHz, CDCl_3) δ 7.40 – 7.38 (m, 2H), 7.30 – 7.20 (m, 5H), 7.07 (d, $J = 7.5$ Hz, 2H), 5.54 (d, $J = 2.0$ Hz, 1H), 5.52 (d, $J = 2.0$ Hz, 1H), 5.31 (d, $J = 1.5$ Hz, 1H), 5.27 (d, $J = 1.5$ Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (125MHz, CDCl_3) δ 149.9, 149.6, 140.2, 137.24, 137.20, 128.9, 128.1, 127.44, 127.41, 127.3, 116.1, 115.6, 21.1

9 (^1H NMR)

9 (^{13}C NMR)

General procedure for preparation of Bis(3-trimethylsilyl-1,3-butadien-2-yl)benzene (or biphenyl).**Preparation of 11a.**

Under Ar atmosphere, Ni(cod)₂ (0.02 mmol, 4 mol%) and P(2-furyl)₃ (0.03 mmol, 6 mol%) were stirred in THF (0.3 ml) for 10 min at 0 °C. Then bis(iodozincio)methane (**5a**) (0.6 mmol, 1.2 eq.), 3-trimethylsilyl-1-benzyloxy-2-propyne (**1a**) (0.5 mmol) and 1,4-diiodobenzene (**10a**) (0.2 mmol, 0.4 eq.) were added subsequently and the mixture was stirred for 24 h at 25 °C. The mixture was cooled to 0 °C, diluted by hexane / AcOEt (5 / 1, 30 mL). After an addition of sat. NH₄Cl aq and extracted with hexane / AcOEt (5 / 1). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Purification on a neutral silica-gel column chromatography gave 1,4-bis(3-trimethylsilyl-1,3-butadien-2-yl)benzene (**11a**) as white solid.

1,4-Bis(3-trimethylsilyl-1,3-butadien-2-yl)benzene (11a): ^1H NMR (500MHz, CDCl_3) δ 7.27 (s, 4H), 5.74 (d, $J = 3.5$ Hz, 2H), 5.57 (d, $J = 3.5$ Hz, 2H), 5.22 (d, $J = 2.0$ Hz, 2H), 4.97 (d, $J = 2.0$ Hz, 2H), -0.01 (s, 18H); ^{13}C NMR (125MHz, CDCl_3) δ 154.0, 152.9, 139.9, 127.7, 127.0, 110.0, -1.0

11a (^1H NMR)

11a (^{13}C NMR)

1,3-Bis(3-trimethylsilyl-1,3-butadien-2-yl)benzene (11b): ^1H NMR (500MHz, CDCl_3) δ 7.31 – 7.30 (m, 1H), 7.23 – 7.22 (m, 3H), 5.73 (d, $J = 3.5$ Hz, 2H), 5.58 (d, $J = 3.5$ Hz, 2H), 5.21 (d, $J = 2.0$ Hz, 2H), 4.99 (d, $J = 2.0$ Hz, 2H), 0.01 (s, 18H); ^{13}C NMR (125MHz, CDCl_3) δ 153.8, 153.1, 140.6, 127.9, 127.6, 126.6, 126.3, 111.4, -1.0

11b (^1H NMR)

11b (^{13}C NMR)

4,4'-Bis(3-trimethylsilyl-1,3-butadien-2-yl)biphenyl (11c): ^1H NMR (500MHz, CDCl_3) δ 7.57 – 7.55 (m, 4H), 7.42 – 7.39 (m, 4H), 5.77 (d, $J = 3.5$ Hz, 2H), 5.62 (d, $J = 3.5$ Hz, 2H), 5.28 (d, $J = 2.0$ Hz, 2H), 5.01 (d, $J = 2.0$ Hz, 2H), 0.04 (s, 18H); ^{13}C NMR (125MHz, CDCl_3) δ 153.8, 152.6, 139.8, 139.7, 128.0, 127.7, 126.5, 111.3, -1.0

11c (^1H NMR)

11c (^{13}C NMR)