A facile preparation of 4-aryl-3-[(*tert*-butyldimethylsilyl)oxymethyl]furans

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A series of aryl bromides undergo a palladium-catalyzed coupling reaction with 3-[(*tert*-butyldimethylsilyl)oxymethyl]-4-(tri-*n*-butylstannyl)furan to provide 4-aryl-3-[(*tert*-butyldimethylsilyl)oxymethyl]furans in moderate to good yields.

Key words: palladium, cross-couplings, stannanes, 3,4-disubstituted furans.

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Des réactions de couplage, catalysées par le palladium, entre divers bromures d'aryle et le [(*tert*-butyldiméthylsilyl)oxyméthyl]-3-(triméthylstannyl)-4-furanne conduisent avec des rendements relativement faibles aux aryl-4-[(*tert*-butyldiméthylsilyl)oxyméthyl]-3-furannes.

Mots clés : palladium, couplage croisé, stannanes, furannes disubstitués en positions 3 et 4.

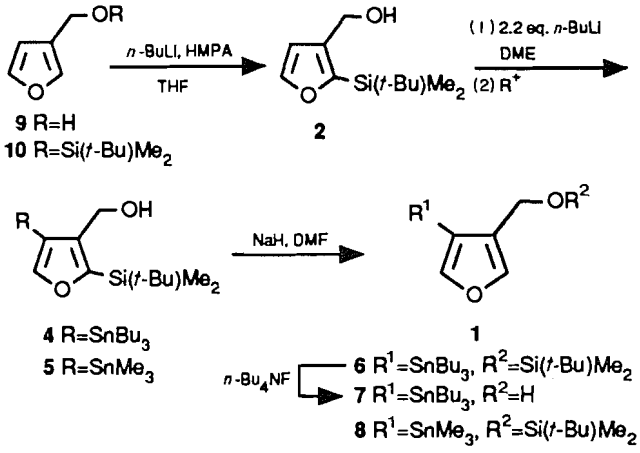
[Traduit par la rédaction]

The preparation of 3,4-disubstituted furans is a formidable task since furan derivatives tend to lithiate (1) and add electrophiles (2) in the C-2 and C-5 positions. Elaborate methods for the preparation of 3,4-disubstituted furans have therefore been developed to overcome these tendencies. Some of these include inter- (3) and intra-molecular (4) Diels–Alder–retro-Diels–Alder sequences, synthesis of the furan ring from acyclic (5) and cyclic (6) precursors, and chemical modifications of commercially available 3,4-furandicarboxylic acid (7). We have recently described a simple preparation of 3,4-disubstituted furans **1** (8) via a regiospecific C-4 lithiation of 2-(*tert*-butyldimethylsilyl)-3-(hydroxymethyl)furan **2** (Scheme 1). Quenching the dianion with electrophiles followed by a carbon to oxygen silyl migration afforded 3,4-disubstituted furans **1** in good yields.

The scope of these procedures does not include the preparation of 4-aryl-3-substituted furans. Since furan rings can be converted to a variety of other ring systems (Scheme 2), we sought a general method for the preparation of 4-aryl-3-substituted furans for further elaboration into natural products such as Heritol **3**, the ichthyotoxic constituent of the mangrove plant *Heritiera littoralis* (9).

A suitable method for the introduction of aryl groups at the C-4 position of furan rings could involve the palladium-catalyzed coupling reaction between aryl halides and organostannanes developed by Stille and co-workers (10). Recent reports of successful arylhalide–arylstannyl couplings (11) and the lack of examples reported utilizing stannylfurans (12)[3] led us to study the palladium-catalyzed coupling reaction between various arylbromides and stannylfurans **4–7** (Scheme 1). We herein report our findings.

Stannylfurans **4–8** were prepared as outlined in Scheme 1. Thus, 3-(hydroxymethyl)furan **9** was silylated to provide the silyl alcohol **10** (95%) (15). Treatment of **10** with 1.7 equivalents



SCHEME 1

of *n*-butyllithium (THF, HMPA) provided furan **2** (87%) via a 1,4 O→C silyl migration (8*a*). Regiospecific lithiation of furan **2** at C-4 with 2.2 equivalents of *n*-butyllithium (DME, 0°C), followed by trapping of the dianion with either tri-*n*-butyl- or trimethyl-stannyl chloride (1.1 equivalents), provided stannylfurans **4** (89%) and **5** respectively (8*b*). A 1,4 C→O silyl migration of compounds **4** and **5** (NaH, DMF) provided stannylfurans **6** and **8** respectively (>95%) (8*c*). Desilylation of furan **6** with tetra-*n*-butylammonium fluoride (THF, room temperature) afforded alcohol **7** (88%).

Stannylfuran **4** was initially employed in the coupling reaction with bromobenzene (1.1 equiv.) and tetrakis(triphenylphosphine)palladium(0) (TTPP, 2 mol%) in refluxing toluene. Analysis of the reaction mixture after 5 h indicated that only 50% of the bromobenzene had reacted. The addition of another 2 mol% of palladium catalyst and refluxing for another 6 h were required to provide coupled furan **11** (51%) and 10% of destannylated furan **2** (Scheme 3). The long reaction time, poor yield of furan **11**, and the presence of destannylated furan **2** are in contrast to results reported from typical coupling reactions using bromobenzene (10, 11*g*). No improvement in the yield

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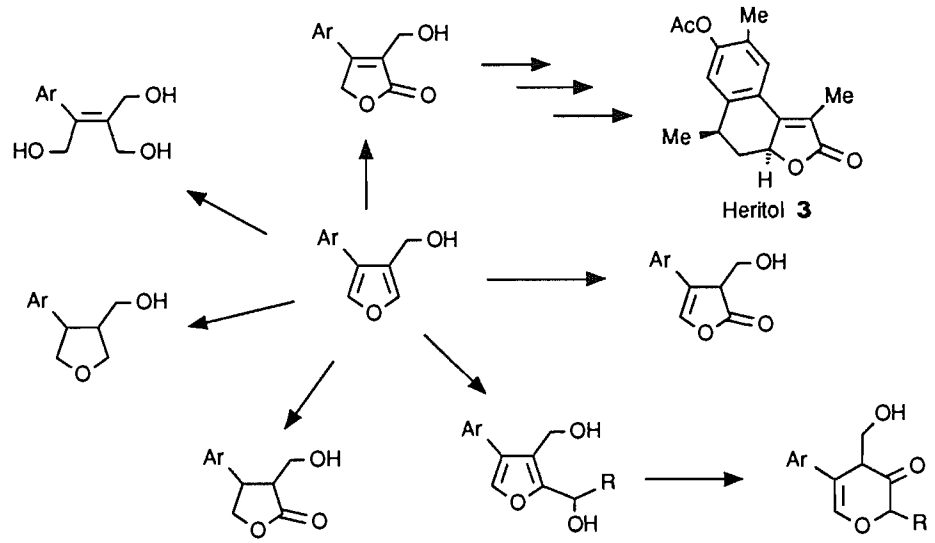
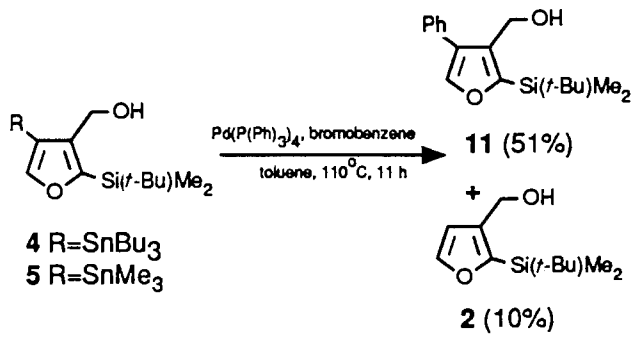
[3]Furylzinc and furylboronic acids have been used in palladium-catalyzed coupling reactions, see refs. 13 and 14 respectively.



SCHEME 2



SCHEME 3

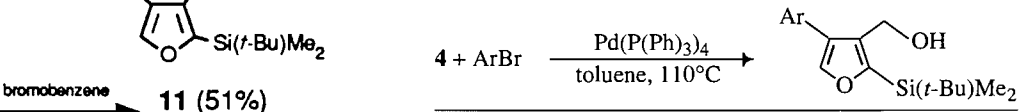
of furan **11** was observed when the trimethylstannylfuran **5** was employed with bromobenzene under identical conditions; destannylated furan **2** was also isolated (11%). These observations were not limited to bromobenzene, as both 3-bromotoluene and 2-bromonaphthalene coupled with furan **4** to provide furans **12** and **13** respectively in poor yields (Table 1).

The disappointing results obtained for the coupling reactions of furans **4** and **5** were overcome by the use of furan **6** as the starting material. Compound **6** coupled smoothly with bromobenzene to provide coupled furan **14** in 90% yield within 1 h (Table 2). Destannylated furan **10** (Scheme 1) was neither detected (by ^{1}H NMR) nor isolated.

The coupling reaction was extended to a number of aromatic bromides (Table 2). In general, yields were high, and reaction times were short (1–6 h, entries 1, 2, 5, and 7). Exceptions were noted when sterically hindered aryl bromides were employed (entries 3, 4, and 6). Longer reaction times and, in the case of bromomesitylene, additional palladium catalyst were required for the reaction to proceed to completion. The absence of any coupled product from the reaction with 2-bromopyridine was surprising since it has been used successfully in other palladium-catalyzed couplings (16). The reaction also failed for 1-bromo-2-methoxybenzene despite the addition of more catalyst after 6 and 12 h.[4] This result may be due to both steric interactions and electronic factors (6).

[4]It is well documented that couplings with methoxy-substituted aryl bromides proceed slowly, and usually require additional catalyst, see ref. 10.

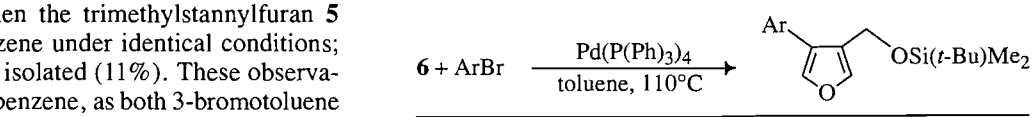
TABLE 1. Palladium-catalyzed coupling reactions of furan **4**



	ArBr	Time (h)	Yield (%)
1.	Bromobenzene	18	**11** (51)[a]
2.	3-Bromotoluene	18	**12** (55)[a]
3.	2-Bromonaphthalene	18	**13** (46)[a]

[a](10–12%) Destannylated furan **2** was also isolated.

TABLE 2. Palladium-catalyzed coupling reactions of furan **6**

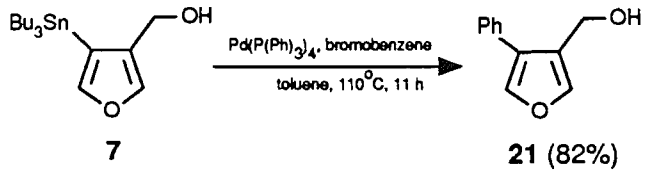


	ArBr	Time (h)	Yield (%)
1.	Bromobenzene	1	**14** (90)
2.	2-Bromobenzaldehyde	1	**15** (85)
3.	2-Bromomesitylene	6[a]	**16** (55)
4.	1-Bromo-2-methylbenzene	4	**17** (80)
5.	4-Bromobiphenyl	3	**18** (70)
6.	1-Bromo-2-methylnaphthalene	3	**19** (82)
7.	1-Bromo-4-chlorobenzene	1	**20** (88)
8.	2-Bromopyridine	18[b]	n.r.[c]
9.	1-Bromo-2-methoxybenzene	18[b]	n.r.[d]

[a]Added more catalyst after 3 h.
[b]Added more catalyst after 6 and 12 h.
[c]Recovered 80% of furan **6**.
[d]Recovered 20% of furan **6**.

The poor results observed for stannyl furans **4** and **5** are in contrast to results reported from typical coupling reactions with bromobenzene. These observations could be due to the presence of the unprotected hydroxymethyl group at C-3 and (or) the bulky *tert*-butyldimethylsilyl moiety at C-2 of furans **4** and **5** (Scheme 1). Further experiments were performed to elucidate the reason for our observation.

To determine if the free hydroxyl group in our systems was responsible, we coupled stannyl furan **7** with bromobenzene



SCHEME 4

(Scheme 4) under the same conditions used for furans **4** and **5**. Coupled product **21** was obtained in 82% yield after 3 h (110°C); no destannylated furan **9** (Scheme 1) was observed (by ^{1}H NMR). This result clearly indicates that the hydroxyl group was not interfering with the reaction. Echavarren and Stille reported similar results with palladium-catalyzed cross-couplings between aryl triflates and vinyl stannanes containing free hydroxyl groups (17).

The presence of the *tert*-butyldimethyl silyl group at C-2 of furans **4** and **5** was shown to be responsible for the destannylation of furans **4** and **5**. Refluxing either furan **4** or **5** in toluene for 12 h in the absence of both the palladium catalyst and bromobenzene provided destannylated furan **2** in 13% yield. Stannylated furans **6** and **7**, and **8** (with no C-2 silyl group), did not provide destannylated furans **10** and **9** respectively under identical conditions. Furans **4** and **5** were also found to undergo facile protiodestannylation (18) when treated with 0.1% aqueous HCl (THF, 10 min) while furans **6–8** showed no signs of protiodestannylation after 1 h under identical conditions.

Examination of molecular models indicated that the trisubstituted compound **4** is sterically congested. These unfavourable steric interactions are not observed in stannyl furans **6–8** since the furan rings are only disubstituted (at C-3 and C-4). In the absence of a substituent at C-2, the C-3 moiety can rotate away from the stannyl group, thereby reducing the steric interactions in furans **6–8** when compared to furans **4** and **5**. Thus protiodestannylation occurs to relieve the strong steric interaction among the substituents in furans **4** and **5**. In addition, the hindered nature of furan **4** may be the reason for the longer reaction times (18 h vs. 1 h for furan **6**) required for the cross-coupling with bromobenzene (Table 1).

We have therefore shown that 4-aryl-3-substituted furans can be prepared via a palladium-catalyzed coupling reaction. The reactions are simple to perform and the products are easily purified. In addition, the silyl-protected hydroxymethyl group on the furan ring can be modified to convert the products from the coupling reaction into other 3,4-disubstituted furans. Synthetic applications of this methodology towards Hertiol **3** are currently in progress.

Experimental

Nuclear magnetic resonance spectra were obtained with a Bruker AC300 spectrometer using deuterochloroform as solvent (and internal standard). All ^{1}H NMR and ^{13}C NMR spectra were obtained at 300 and 75 MHz respectively. Infrared spectra were obtained with a Nicolet 5DK-FTIR spectrometer. Low and high resolution mass spectra were obtained with either a Varian CH5 or VG 7070F and a Kratos MS80RFA spectrometer respectively. Elemental analyses were performed by either Guelph Chemical Laboratories, Guelph, Ontario, or at the University of Calgary.

Flash column chromatography was performed using E. Merck silica gel (230–400 mesh A.S.T.M.) by the method developed by Still *et al.* (19). All solvents were dried and distilled prior to use.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]furan (**10**)*

To a solution of *tert*-butyldimethylsilyl chloride (6.1 g, 40 mmol) in DMF (20 mL) at 0°C under an atmosphere of argon was added imidazole (5.7 g, 84 mmol) and 3-hydroxymethylfuran **9** (3.6 g, 37 mmol). After 12 h at 25°C, diethyl ether and aqueous sodium chloride were added. The organic layer was washed six times with saturated aqueous sodium chloride, dried (Na_2SO_4), and the solvent removed *in vacuo* to afford, after distillation, a clear colourless oil **10** (95%), bp 106–109°C/20 Torr (1 Torr = 133.3 Pa); IR (neat): 1063 cm^{-1}; ^{1}H NMR δ: −0.04 (s, 6H), 0.81 (s, 9H), 4.54 (s, 2H), 6.42 (m, 1H), 7.51 (m, 2H); ^{13}C NMR δ: −2.85, 18.21, 25.80, 57.52, 109.66, 125.85, 139.38, 143.14; mass spectrum, *m/e*: 212 (M$^{\cdot+}$). Anal. calcd. for $C_{11}H_{20}O_2Si$: C 62.21, H 9.49; found: C 62.34, H 9.43.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)furan (**2**)*

To a mixture of furan **10** (0.69 g, 3.3 mmol) and HMPA (0.62 mL, 3.6 mmol) dissolved in THF (10 mL) under an atmosphere of argon at −78°C was added *n*-butyllithium (1.43 mL, 2.5 M in hexane, 3.6 mmol). The solution was allowed to come to room temperature over 6 h and stirred at room temperature overnight. Saturated ammonium chloride was added and the solution extracted with diethyl ether. The organic layer was washed three times with saturated copper sulfate, dried (Na_2SO_4), and the solvent removed *in vacuo* to afford, after distillation, a white crystalline solid **2** (87%), bp 75–78°C/0.02 Torr; IR (KBr): 3319, 1070 cm^{-1}; ^{1}H NMR δ: 0.01 (s, 6H), 0.89 (s, 9H), 1.5 (bs, 1H), 4.57 (s, 2H), 6.46 (d, 1H, *J* = 1.8 Hz), 7.57 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR δ: −5.73, 18.12, 25.69, 57.10, 110.52, 135.87, 146.69, 154.96; mass spectrum, *m/e*: 212 (M$^{\cdot+}$). Anal. calcd. for $C_{11}H_{20}O_2Si$: C 62.21, H 9.49; found: C 62.27, H 9.47.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)-4-(tri-*n*-butylstannyl)furan (**4**)*

To a solution of furan **2** (1.5 g, 6.9 mmol) in dry DME (20 mL) at −78°C under an atmosphere of argon was added *n*-butyllithium (7.6 mL, 2.0 M in hexane, 15.2 mmol). After 15 min at 0°C, tri-*n*-butylstannyl chloride (1.9 mL, 6.9 mmol) was added and the solution stirred for 1 h. Saturated ammonium chloride was added, the solution extracted with ethyl acetate, and the solvent removed *in vacuo* to afford, after silica gel column (petroleum ether/ethyl acetate 20:1) and distillation, stannylated furan **4** (89%) as a clear colourless oil, bp 148–150°C/0.12 Torr; IR (neat): 3425, 1464, 1251 cm^{-1}; ^{1}H NMR δ: 0.28 (s, 6H), 0.87 (t, 9H, *J* = 4.1 Hz), 0.88 (s, 9H), 0.94 (t, 6H, *J* = 3.7 Hz), 1.2–1.4 (m, 6H), 1.44–1.55 (m, 6H), 2.05 (s, 1H), 4.50 (s, 2H), 7.35 (s, 1H); ^{13}C NMR δ: −5.52, 9.95, 13.65, 17.33, 26.37, 27.29, 29.18, 58.30, 115.75, 141.02, 151.53, 154.78(s); mass spectrum, *m/e*: 444 (M$^{\cdot+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{19}H_{37}O_2Si^{120}Sn$ (M$^{\cdot+}$ − *t*-Bu): 445.1585; found (M$^{\cdot+}$ − *t*-Bu): 445.1578.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)-4-(trimethylstannyl)furan (**5**)*

The above procedure was used, followed by quenching the dianion with trimethylstannyl chloride. Work-up provided furan **5** (88%) as a clear colourless oil, bp 88–92°C/0.04 Torr; IR (neat): 3450, 1471, 972 cm^{-1}; ^{1}H NMR δ: 0.30 (s, 9H, $J_{H,Sn}$ = 54.6 and 57.1 Hz), 0.30 (s, 6H), 0.92 (s, 9H), 4.57 (s, 2H), 7.40 (s, 1H); ^{13}C NMR δ: −8.77, −5.48, 17.32, 26.40, 58.12, 116.50, 140.89, 151.59, 154.54; mass spectrum, *m/e*: 361 (M$^{\cdot+}$ − Me); HRMS (EI) calcd. for $C_{13}H_{25}O_2Si^{120}Sn$ (M$^{\cdot+}$ − Me): 361.0653; found: 361.0625.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(tri-*n*-butylstannyl)furan (**6**)*

To a solution of stannylfuran **4** (0.32 g, 0.63 mmol) in dry DMF (1 mL) was added sodium hydride (0.8 mg, 0.04 mmol) under an atmosphere of argon. After 5 min at 25°C, diethyl ether and saturated sodium chloride were added. The diethyl ether was washed six times with saturated sodium chloride, dried (Na_2SO_4), and the solvent removed *in vacuo* to afford, after distillation, compound **6** (98%) as a clear colourless oil, bp 138°C/0.21 Torr; IR (neat): 1464, 1254, 1106, 1073, 1040, 842 cm^{-1}; ^{1}H NMR δ: 0.08 (s, 6H), 0.89 (t, 9H, *J* = 7.0 Hz), 0.92 (s, 9H), 1.05 (t, 6H, *J* = 5.1 Hz), 1.43 (m, 6H), 1.51 (m, 6H), 4.55 (s, 2H), 7.14 (s, 1H), 7.44 (s, 1H); ^{13}C NMR δ: −5.25, 9.71, 13.65, 18.48, 25.98, 27.32, 29.14, 59.11, 114.14, 130.77,

139.63, 147.82; mass spectrum, *m/e*: 444 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{19}H_{37}O_2Si^{120}Sn$ ($M^{\bullet+}$ − *t*-Bu): 445.1585; found ($M^{\bullet+}$ − *t*-Bu): 445.1594.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(trimethylstannyl)furan (**8**)*

The above procedure was followed using furan **5** to afford furan **8** (88%) after work-up and distillation, bp 78–82°C/0.04 Torr; IR (neat): 1257, 1074, 839 cm^{-1}; ^1H NMR δ: 0.08 (s, 6H), 0.28 (s, 9H, $J_{H,Sn}$ = 55.0 and 57.3 Hz), 4.56 (s, 2H), 7.17 (s, 1H), 7.44 (s, 1H); ^{13}C NMR δ: −9.03, −5.15, 18.51, 26.03, 58.53, 115.59, 130.50, 139.67, 147.92; mass spectrum, *m/e*: 361 ($M^{\bullet+}$ − Me); HRMS (EI) calcd. for $C_{13}H_{25}O_2Si^{120}Sn$ ($M^{\bullet+}$ − Me): 361.0653; found: 361.0638.

*3-(Hydroxymethyl)-4-(tri-*n*-butylstannyl)furan (**7**)*

To a solution of furan **6** (100 mg) in THF (5 mL) at 0°C was added 1.1 equivalents of tetra-*n*-butylammonium fluoride. After 5 h at 0°C, diethyl ether and saturated ammonium chloride were added. The organic layer was separated, dried, and removed *in vacuo* to leave an oil. Flash chromatography (silica gel, EtOAc/pet. ether 1:5) followed by distillation provided furan **7** (92%) as a colourless oil, bp 80–84°C/0.04 Torr; IR (neat): 3423, 1496, 1040 cm^{-1}; ^1H NMR δ: 1.92 (t, 9H), 1.08 (m, 6H), 1.38 (m, 6H), 1.51 (m, 6H), 4.51 (s, 2H), 7.18 (s, 1H), 7.52 (s, 1H); ^{13}C NMR δ: 9.58, 13.59, 27.24, 29.11, 58.05, 114.97, 130.31, 140.02, 148.17; mass spectrum, *m/e*: 331 ($M^{\bullet+}$ − *n*-Bu); HRMS (EI) calcd. for $C_{13}H_{23}O_2{}^{120}Sn$ ($M^{\bullet+}$ − *n*-Bu): 331.0724; found: 331.0755.

General tin coupling procedure

To a solution of a stannylated furan (82 mg, 0.16 mmol) in dry toluene (2 mL) were added an aryl bromide (0.18 mmol) and tetrakis(triphenylphosphine)palladium(0) (2 mol%). The mixture was refluxed. After the appropriate time (Table 1 or 2) either the solution was worked up or more catalyst was added. The work-up was as follows: the solution was cooled to room temperature, water (1 mL) added, and the mixture filtered through Celite. The mixture was extracted with diethyl ether, dried (Na_2SO_4), and the solvent removed *in vacuo*. Silica gel chromatography (petroleum ether/ethyl acetate 50:1), followed by either a distillation or recrystallization, afforded coupled products.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)-4-phenyl furan (**11**)*

Yield 51%; bp 105°C/0.3 Torr; IR (neat): 3450, 1488, 1254, 1099, 999, 829, 782 cm^{-1}; ^1H NMR δ: 0.35 (s, 6H), 0.94 (s, 9H), 1.6 (bs, 1H), 4.60 (s, 2H), 7.27–7.31 (m, 1H), 7.36–7.41 (m, 2H), 7.52–7.55 (m, 2H), 7.70 (s, 1H); ^{13}C NMR δ: −5.55, 17.51, 26.41, 55.13, 127.11, 127.25, 128.27, 128.72, 132.29, 133.93, 144.00, 158.09; mass spectrum, *m/e*: 231 ($M^{\bullet+}$ − *t*-Bu): HRMS (EI) calcd. for $C_{13}H_{15}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 231.0842; found ($M^{\bullet+}$ − *t*-Bu): 231.0836.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)-4-(3-methylphenyl)-furan (**12**)*

Yield 55%; bp 120–125°C/0.05 Torr; IR (neat): 3431, 1608, 1471, 1251 cm^{-1}; ^1H NMR δ: 0.38 (s, 6H), 0.97 (s, 9H), 2.40 (s, 3H), 4.63 (s, 2H), 7.27 (m, 1H), 7.3–7.5 (m, 2H), 7.35 (s, 1H), 7.71 (m, 1H); ^{13}C NMR δ: −5.53, 17.27, 21.45, 26.44, 55.20, 125.37, 127.16, 127.69, 128.81, 129.03, 132.21, 134.06, 136.25, 143.96, 157.92; mass spectrum, *m/e*: 245 ($M^{\bullet+}$ − *t*-Bu). Anal. calcd. for $C_{18}H_{26}O_2Si$: C 71.47, H 8.67; found: C 71.37, H 8.79.

*2-(*tert*-Butyldimethylsilyl)-3-(hydroxymethyl)-4-(2-naphthyl)furan (**13**)*

Yield 46%; bp 155–160°C/0.05 Torr; IR (neat): 3456, 1601, 1392 cm^{-1}; ^1H NMR δ: 0.41 (s, 6H), 1.01 (s, 9H), 4.42 (s, 1H), 7.40–7.55 (m, 4H), 7.71 (s, 1H), 7.8–8.0 (m, 3H); ^{13}C NMR δ: −5.55, 17.37, 26.54, 55.51, 124.52, 125.36, 125.73, 125.94, 126.26, 128.07, 128.11, 128.35, 129.63, 132.70, 133.60, 136.10, 145.09, 157.10; mass spectrum, *m/e*: 281 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{17}H_{17}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 281.0998; found: 281.0980.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-phenylfuran (**14**)*

Yield 90%; bp 89°C/0.03 Torr; IR (neat): 1468, 1255, 1095, 1074, 857, 776 cm^{-1}; ^1H NMR δ: 0.08 (s, 6H), 0.93 (s, 9H), 4.68 (s, 2H), 7.27–7.31 (m, 1H), 7.35–7.41 (m, 2H), 7.45–7.55 (m, 4H); ^{13}C NMR δ: −5.29, 19.23, 25.86, 56.53, 124.42, 126.23, 127.01, 127.89, 128.59, 132.38, 139.95, 141.73; mass spectrum, *m/e*: 288 ($M^{\bullet+}$), 231 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{13}H_{15}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 231.0842; found ($M^{\bullet+}$ − *t*-Bu): 231.0859.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(2-formylphenyl)furan (**15**)*

Yield 85%; bp 82–85°C/0.02 Torr; IR (neat): 1694, 1468, 1256, 1075, 839, 774 cm^{-1}; ^1H NMR δ: −0.05 (s, 6H), 0.82 (s, 9H), 0.47 (s, 2H), 7.40–7.71 (m, 5H), 8.01 (dd, 1H, *J* = 8.1 and 2.3 Hz), 10.05 (s, 1H); ^{13}C NMR δ: −5.58, 16.21, 25.77, 58.09, 121.66, 125.79, 127.43, 128.1, 131.8, 133.51, 134.86, 135.7, 141.23, 141.98, 192.12; mass spectrum, *m/e*: 259 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{14}H_{15}O_3Si$ ($M^{\bullet+}$ − *t*-Bu): 259.0791; found ($M^{\bullet+}$ − *t*-Bu): 259.0795.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(2,4,6-trimethylphenyl)-furan (**16**)*

Yield 55%; bp 90°C/0.07 Torr; IR (neat): 1471, 1256, 1078, 849 cm^{-1}; ^1H NMR δ: −0.1 (s, 6H), 0.83 (s, 9H), 2.05 (s, 6H), 2.29 (s, 3H), 4.29 (s, 2H), 6.89 (s, 2H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR δ: −5.74, 19.4, 20.58, 21.01, 25.84, 56.94, 123.00, 125.64, 127.85, 128.08, 137.07, 137.76, 139.79, 140.66; mass spectrum, *m/e*: 330 ($M^{\bullet+}$), 273 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{16}H_{21}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 273.1311; found ($M^{\bullet+}$ − *t*-Bu): 273.1324.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(2-methylphenyl)furan (**17**)*

Yield 80%; bp 85°C/0.1 Torr; IR (neat): 1550, 1082, 841, 780 cm^{-1}; ^1H NMR δ: −0.06 (s, 6H), 0.84 (s, 9H), 2.23 (s, 3H), 4.42 (s, 2H), 7.12–7.25 (m, 4H), 7.30 (d, 1H, *J* = 1.3 Hz), 7.45 (d, 1H, *J* = 1.3 Hz); ^{13}C NMR δ: −5.59, 18.28, 20.33, 25.83, 56.65, 124.59, 125.46, 125.69, 127.56, 129.98, 130.60, 131.60, 137.01, 140.38, 140.57; mass spectrum, *m/e*: 245 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{14}H_{17}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 245.0998; found ($M^{\bullet+}$ − *t*-Bu): 245.0991.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-[4-(phenyl)phenyl]furan (**18**)*

Yield 70%; bp 95°C/0.13 Torr; IR (neat): 1470, 1256, 1075, 838, 765 cm^{-1}; ^1H NMR δ: 0.11 (s, 6H), 0.92 (s, 9H), 4.71 (s, 2H), 7.31–7.63 (m, 11H); ^{13}C NMR δ: −5.30, 18.25, 25.83, 56.49, 124.40, 125.91, 126.99, 127.27, 128.21, 128.55, 128.76, 139.83. 140.02, 140.76, 141.18, 141.83; mass spectrum, *m/e*: 364 ($M^{\bullet+}$), 307 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{19}H_{19}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 307.1155; found ($M^{\bullet+}$ − *t*-Bu): 307.1152.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(2-methylnaphthyl)furan (**19**)*

Yield 82%; bp 103°C/0.09 Torr; IR (neat): 1470, 1256, 1084, 838, 793, 743 cm^{-1}; ^1H NMR δ: −0.28 (s, 3H), −0.25 (s, 3H), 0.74 (s, 9H), 2.32 (s, 3H), 4.25 (s, 2H), 7.35–7.45 (m, 5H), 7.60 (s, 1H), 7.75–7.82 (m, 2H); ^{13}C NMR δ: −5.90, 18.22, 20.78, 25.76, 56.87, 121.87, 124.81, 125.79, 126.00, 126.59, 127.71, 128.40, 131.89, 133.65, 135.20, 140.74, 140.99; mass spectrum, *m/e*: 352 ($M^{\bullet+}$), 295 ($M^{\bullet+}$ − *t*-Bu); HRMS (EI) calcd. for $C_{18}H_{19}O_2Si$ ($M^{\bullet+}$ − *t*-Bu): 295.1155; found ($M^{\bullet+}$ − *t*-Bu): 295.1164.

*3-[(*tert*-Butyldimethylsilyl)oxymethyl]-4-(4-chlorophenyl)furan (**20**)*

Yield 88%; bp 95°C/0.1 Torr; IR (neat): 1515, 1092, 837 cm^{-1}; ^1H NMR δ: 0.07 (s, 6H), 0.89 (s, 9H), 4.60 (s, 2H), 7.33 (d, 2H, *J* = 4.8 Hz), 7.43 (d, 2H, *J* = 1.3 Hz), 7.48 d, 2H, *J* = 4.8 Hz), 7.53 (d, 1H, *J* = 1.3 Hz); ^{13}C NMR δ: −5.30, 18.25, 25.82, 56.16, 124.14, 125.43, 128.73, 129.16, 130.83, 132.90, 140.06, 141.98; mass spectrum, *m/e*: 265 ($M^{\bullet+}$ − *t*-Bu), 230 ($M^{\bullet+}$ − *t*-Bu − Cl); HRMS (EI) calcd. for $C_{13}H_{14}O_2SiCl$ ($M^{\bullet+}$ − *t*-Bu): 265.5293; found ($M^{\bullet+}$ − *t*-Bu): 265.5281.

*3-(Hydroxymethyl)-4-(phenyl)furan (**21**)*

Yield 82%; bp 70–72°C/0.04 Torr; IR (KBr): 3338, 1601, 1051 cm^{-1}; ^1H NMR δ: 4.65 (s, 2H), 7.3–7.6 (m, 7H); ^{13}C NMR δ: 55.20, 123.68, 126.81, 127.4, 128.34, 129.15, 131.61, 139.85, 141.62; mass spectrum, *m/e*: 174 ($M^{\bullet+}$); HRMS (EI) calcd. for $C_{11}H_{10}O_2$: 174.0680; found: 174.0672.

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