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Regioselective Synthesis of Highly Substituted Furans *via* Tantalum-Alkyne Complexes.

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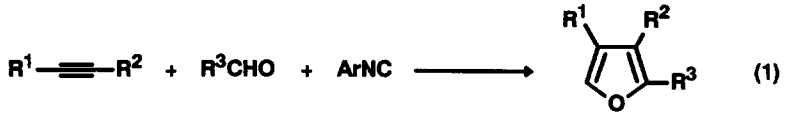
Abstract: *A variety of 2,3,4-trisubstituted furans are prepared by treatment of tantalum-alkyne complexes with aldehydes followed by addition of an isocyanide in DME-PhH-THF (1:1:1). The regioselectivity of the reaction depends on the bulkiness of substituents on acetylenes and the bulkier substituents tend to possess 4-position of the produced furans. 4-Trialkylsilyl-substituted furans are produced exclusively when trialkylsilylacetylenes are employed.*

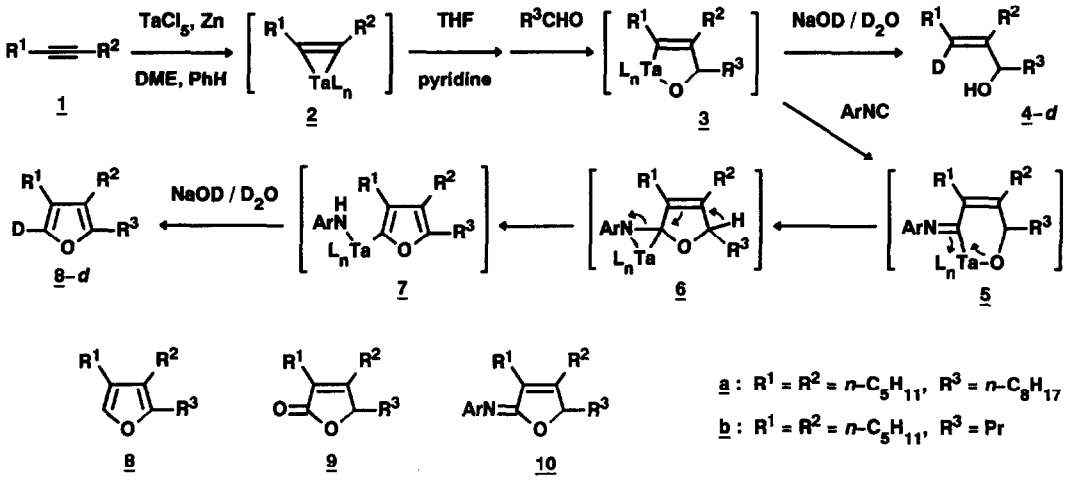
Furan skeletons[1] are observed in many naturally occurring compounds[2] and moreover, they are important compounds as synthetic intermediates[1,3] such as diene components of the Diels-Alder reaction and latent 1,4-diketone moieties. Because regioselective introduction of carbon substituents into a simple furan is rather difficult,[4] they are sometimes prepared from acyclic precursors.[5] We disclose here a regioselective preparation of highly substituted furans from three components, i.e. acetylenes, aldehydes, and an isocyanide by means of low-valent tantalum (eq. 1).



(1)

Insertion of carbon monoxide[6] or isocyanide[7] into metal-carbon bonds is a typical method for introducing one carbon unit into organometallic compounds. Although the insertion of isocyanide into tantalum-carbon bonds was first recognized in 1974,[8] the process has not been utilized in organic synthesis. Recently, we found a general and simple method for the preparation of tantalum-alkyne complexes[9,10] derived from low-valent tantalum and acetylenes. These complexes react with carbonyl compounds in a stereoselective manner to yield (E)-allylic alcohols.[9c,10e] In this reaction, oxatantalacyclopentene **3** was postulated as an intermediate, because quenching the reaction mixture of **3a** ($R^1=R^2=n\text{-}C_5H_{11}$,

Scheme 1



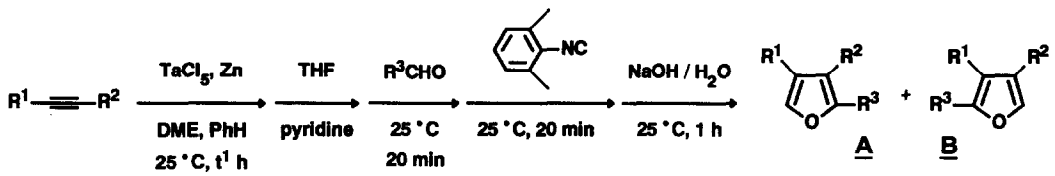
R^3=*n*-C_8H_{17}) with alkaline D_2O furnished 3-deuterated allylic alcohol **4a-*d*** in 86% yield (94% deuterated).[11] Thus we tried to examine the insertion of an isocyanide into the tantalum–carbon bond of the complex **3** (Scheme 1).

Reactive tantalacyclopropene **2a** (R^1=R^2=*n*-C_5H_{11}) was generated by the reaction between 6-dodecyne (1.0 equiv) and the low-valent tantalum derived from $TaCl_5$ (2.0 equiv) and zinc (3.0 equiv) in a mixed solvent of 1,2-dimethoxyethane (DME) and benzene at 25 °C. Successive addition of THF, pyridine, and nonanal (1.2 equiv) to the reaction mixture gave oxatantalacyclopentene **3a** (not isolated).[9c] Treatment of **3a** with 2,6-dimethylphenyl isocyanide (1.0 equiv) at 25 °C for 20 min afforded a furan **8a** in 66% yield.[9d] Neither a butenolide[12] **9a** nor an imino lactone[13] **10a** was formed.[14]

Yields of furans were critically dependent on the amounts of the isocyanide and the charge of excess isocyanide retarded the formation of furans.[15] For example, treatment of **3a** with 2.0 equiv of the isocyanide gave **8a** in 40% yield along with unreacted allylic alcohol **4a** in 15% yield. Decomposition of the furan **8a** took place gradually in the reaction mixture. Yield of the furan **8a** in the reaction between **3a** and 1.2 equiv of the isocyanide monitored by GLPC are as follows: 66% yield, 20 min; 55% yield, 1h; 31% yield, 14h. The reaction also took place with either cyanotrimethylsilane or carbon monoxide (ca. 1.2 atom), but the desired furan **8a** was obtained in only 29% and 13% yields, respectively.

The reaction proceeded under mild conditions and 2,3,4-trisubstituted furans were produced (Table 1).[16] The yield of the furan was rather low when aliphatic isocyanide was used (run 3). The regioselectivities of the reactions are determined at the insertion step of aldehydes into tantalacyclopropene **2** and are controlled by bulkiness of the substituents of the acetylenes.[9c] (Trialkylsilyl)acetylenes gave one of the regioisomers under high stereocontrol (runs 6 and 8). Because the formation of tantalum–alkyne complexes having bulky substituents was slow, 4 equiv of low-valent tantalum and 2 equiv of isocyanide were employed (runs 5, 6, and 8). Regiochemistry of the furan derived from a tantalum-1-dodecyne complex was confirmed by ^1H NMR analysis (run 1).[17] Trialkylsilyl-substituted furans were desilylated with a $(HF)_x$-pyridine complex [5h] and the regiochemistries were ascertained by comparison with the authentic compounds obtained from the corresponding terminal alkynes.

Table 1. Synthesis of Furans from Alkynes, Aldehydes, and Isocyanides.[a]

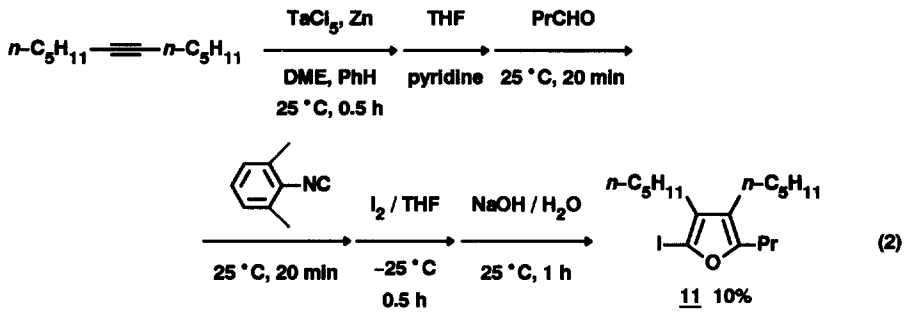


Run	R^1	R^2	R^3	Ar	t^1 / h	Yield / %[b]	A / B[c]
1	n-$C_{10}H_{21}$	H	n-C_3H_7	2,6-$Me_2(C_6H_3)$	0.5	8[d]	>99 / <1
2	n-C_5H_{11}	n-C_5H_{11}	n-C_8H_{17}		0.5	66	--
3				[$Me_3CCH_2CMe_2NC$]	0.5	28	--
4	c-C_6H_{11}	n-C_6H_{13}	n-C_5H_{11}	2,6-$Me_2(C_6H_3)$	2	55	69 / 31
5	t-Bu	n-C_7H_{15}	n-C_3H_7		5	40[f]	98 / 2
6	Me_3Si	n-$C_{10}H_{21}$			2	57	94 / 6[g]
7		Ph			3.5	42[f]	>99 / <1[g]
8	t-$BuMe_2Si$	n-$C_{10}H_{21}$			3.5	54[f,h]	>99 / <1[g]

a) Reactions were carried out on a 1 mmol scale. Conditions: 2.0 equiv of $TaCl_5$, 3.0 equiv of zinc, 4.0 equiv of pyridine, 1.2 equiv of aldehyde, 1.0 equiv of isonitrile, DME-PhH-THF (1:1:1), 25 °C. b) Isolated yields. c) Reference 19. d) Polymer of 1-dodecyne was produced in the reaction of 1-dodecyne with the low-valent tantalum, and remained until workup. Half equiv of the isonitrile was used. e) Reaction was conducted without pyridine. f) Conditions: 4.0 equiv of $TaCl_5$, 6.0 equiv of zinc, 8.0 equiv of pyridine, 2.0 equiv of isonitrile. g) Reference 5h. h) The reaction mixture was stirred at 25 °C for 40 min after addition of the isonitrile.

Plausible mechanisms for the reaction are outlined in Scheme 1. Insertion of an isocyanide into the carbon-tantalum bond of **3** would produce a tantalacycle **5**.[8,10d] Migration of oxygen from tantalum to the imino carbon would give a η^2-acylimidoyl complex **6**,[18] which would produce 2-furyltantalum **7** *via* oxygen-assisted elimination of NAr. The affinity of tantalum for heteroatoms and hence the formation the η^2-acylimidoyl complex **6** is the driving force for this migration process. The presence of the 2-furyltantalum **7** was ascertained by the fact that quenching of the reaction mixture of **7b** with alkaline D_2O afforded 2-deuterated furan **8b-*d*** (R^1=R^2=n-C_5H_{11}, R^3=n-C_3H_7, 47% yield, 91% deuterated).[11]

Although the postulated 2-furyltantalum **7** could not be trapped completely, quenching with iodine at -25 °C produced 2-iodofuran **11** in 10% yield (eq 2).



Experimental

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Benzene, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone just before use and 2,6-lutidine was distilled from KOH. Internal alkynes were prepared according to the standard procedure described in ref 20. 2,6-Dimethylphenylisocyanide was prepared according to the standard procedure described in ref 21. Zinc dust (GR grade) purchased from Wako Pure Chemical Industries, Ltd., was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying *in vacuo* according to the literature.[22] Distillation of small amounts of products was performed with a Büchi Kugelrohr, and boiling points are indicated by an air bath temperature without correction. IR spectra were determined with a JASCO IR-810 spectrometer. Mass spectra were obtained with a Hitachi M-80 mass spectrometer. ^1H and ^{13}C NMR spectra were determined with a Varian XL-200 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Column chromatography was done with silica gel (200 mesh). GLPC was performed with a Hitachi 163 gas chromatograph using a SE-30 capillary column. Elemental analysis were performed by the staff at the Elemental Analyses Center of Kyoto University.

General Procedure for the Synthesis of Furans. In a 50-mL reaction flask was placed $TaCl_5$ (0.72 g, 2.0 mmol) under an argon atmosphere. To the salt was added at 25 °C benzene (5 mL) and DME (5mL) successively. Zinc (0.20 g, 3.0 mmol) was added to stirring a pale yellow solution of $TaCl_5$ in DME and benzene and the resulting mixture was stirred at 25 °C for 40 min. The color of the mixture turned to greenish dark blue with a slightly exothermic process. To the mixture was added at 25 °C a solution of an alkyne (1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C. After consumption of the alkyne was confirmed by TLC, THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 15 min, carbonyl compound (1.2 mmol) was added, and the resulting mixture was stirred at 25 °C for 20 min. To this mixture was added 2,6-dimethylphenyl isocyanide (0.13 g, 1.0 mmol) at 25 °C and the reaction mixture was stirred at 25 °C for an additional 20 min. Aqueous NaOH solution (15%, 2 mL) was added, and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was removed by filtration with Hyflo-Super Cel^R and washed well with ethyl acetate (3x5 mL). Organic extracts were concentrated *in vacuo*, diluted with hexane, dried over $MgSO_4$ and concentrated *in vacuo* again. Purification by column chromatography on silica gel using hexane as eluent gave a furan.

4-Decyl-2-propylfuran. Bp 55-57 °C (bath temp, 0.10 Torr); IR (neat): 2954, 2922, 2852, 1546, 1466, 1459, 1123, 940, 797, 738, 721 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8-1.0 (m, 6H), 1.2-1.8 (m, 18H), 2.31 (t,

J=7.0 Hz, 2H), 2.54 (t, J=7.3 Hz, 2H), 5.87 (d, J=0.7 Hz, 1H), 7.06 (d, J=0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.1, 21.3, 22.7, 25.0, 29.4, 29.5, 29.6, 30.0, 30.2, 31.9, 106.4, 126.0, 136.6, 156.3; MS *m/z* (real intensity): 250 (M^+, 8), 137 (22), 124 (100), 67 (12). Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08. Found: C, 81.64; H, 12.20. The regiochemistry was confirmed by ^{1}H MNR analysis.[15]

2-Octyl-3,4-dipentylfuran (8a). Bp 69–67 °C (bath temp, 0.15 Torr); IR (neat): 2954, 2924, 2854, 1730, 1561, 1466, 1378, 1274, 1135, 1073, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.1 (m, 9H), 1.2–1.7 (m, 24H), 2.2–2.3 (m, 4H), 2.51 (t, J=7.3 Hz, 2H), 7.02 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.8, 23.3, 23.4, 24.2, 24.7, 27.1, 29.4, 29.8, 30.0, 30.1, 31.2, 32.5, 32.6, 119.4, 126.5, 136.7, 152.3; MS *m/z* (real intensity): 320 (M^+, 100), 264 (61), 179 (64), 151 (84), 109 (47). Anal. Calcd for $C_{22}H_{40}O$: C, 82.43; H, 12.58. Found C, 82.70; H, 12.81.

4-Cyclohexyl-3-hexyl-2-pentylfuran (A) and 3-Cyclohexyl-4-hexyl-2-pentylfuran (B). The regioisomer ratio was determined by capillary GLPC analysis (column temp 150 °C, t_r=29.5 min (**A**) and 30.5 min (**B**)) (**A**/**B**=69/31). Bp 90–92 °C (bath temp, 0.10 Torr); IR (neat, mixture of **A**/**B**=69/31): 2952, 2924, 2852, 1459, 1449, 1379, 1261, 1142, 889, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–2.0 (m, 24H), 2.2–2.3 (m, 3H), 2.4–2.6 (m, 2H), 6.977 (s, 1H(**B**)), 6.984 (s, 1H(**A**)); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.1, 22.5, 22.7, 23.6, 24.7, 26.3, 26.4, 26.9, 27.3, 28.4, 28.8, 29.3, 29.4, 29.45, 29.50, 31.1, 31.6, 31.65, 31.70, 31.8, 33.1, 34.3, 35.5, 118.1 (**A**), 123.2 (**B**), 125.5 (**B**), 131.8 (**A**), 135.1 (**A**), 136.1 (**B**), 151.1 (**B**), 151.5 (**A**); MS *m/z* (real intensity): 304 (M^+, 54), 247 (48), 234 (53), 191 (100), 177 (35), 109 (54), 81 (43). Anal. Calcd for $C_{21}H_{36}O$: C, 82.83; H, 11.92. Found: C, 82.99; H, 12.22.

4-*tert*-Butyl-3-heptyl-2-propylfuran. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed and the regiochemistry ratio was determined by ^{1}H NMR analysis. Bp 80–82 °C (bath temp, 0.60 Torr); IR (neat): 2956, 2926, 2860, 1466, 1389, 1379, 1362, 1205, 1147, 1133, 1096, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.26 (s, 9H), 1.2–1.7 (m, 12H), 2.4–2.5 (m, 4H), 6.97 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.1, 21.8, 22.7, 24.8, 28.5, 29.1, 29.2, 30.2, 30.7, 31.4, 31.9, 118.5, 134.4, 134.7, 153.0; MS *m/z* (real intensity): 264 (M^+, 23), 179 (48), 165 (27), 151 (46), 138 (49), 91 (22), 57 (100). Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20. Found: C, 81.83; H, 12.36.

3-Decyl-4-trimethylsilyl-2-propylfuran (A) and 4-Decyl-3-trimethylsilyl-2-propylfuran (B). The regioisomer ratio was determined by capillary GLPC analysis (190 °C, t_r=4.5 min (**A**) and t_r=5.4 min (**B**) (**A**/**B**=94/6). Bp 100–102 °C (bath temp, 0.40 Torr); IR (neat, mixture of **A**/**B**=94/6): 2954, 2924, 2852, 1506, 1465, 1458, 1249, 1139, 1123, 837, 753, 689 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 9H(**A**)), 0.24 (s, 9H(**B**)), 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.3–2.4 (m, 2H), 2.4–2.5 (m, 2H), 7.09 (s, 1H(**B**)), 7.11 (s, 1H(**A**)); ^{13}C NMR ($CDCl_3$): δ −0.14, 14.0, 14.1, 22.0, 22.7, 25.6, 28.0, 29.4, 29.5, 29.6, 29.8, 31.8, 31.9, 111.8 (**B**), 119.5 (**A**), 122.7 (**A**) 130.3 (**B**), 136.8 (**B**), 145.5 (**A**), 152.3 (**A**), 161.7 (**B**); MS *m/z* (real intensity): 322 (M^+, 10), 195 (22), 167 (15), 154 (23), 75 (30), 73 (100). Anal. Calcd for $C_{20}H_{38}OSi$: C, 74.46; H, 11.87. Found: C, 74.20; H, 12.16. The sample was desilylated with $(HF)_x$–Py[5h] and its regiochemistry was ascertained by comparison with the product from 1-dodecyne.

4-Trimethylsilyl-3-Phenyl-2-propylfuran. Bp 55–57 °C (bath temp, 0.15 Torr); IR (neat): 2956, 2898, 2870, 1508, 1249, 1164, 1120, 978, 838, 768, 754, 700, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.02 (s, 9H), 0.87 (t, J=7.3 Hz, 3H), 1.5–1.7 (m, 2H), 2.51 (t, J=7.3 Hz, 2H), 7.2–7.4 (m, 6H); ^{13}C NMR ($CDCl_3$): δ −0.31, 13.8, 22.0, 28.0, 120.4, 125.4, 126.7, 127.9, 130.0, 135.7, 145.6, 152.9; MS *m/z* (real intensity): 258 (M^+, 36), 243 (32), 229 (34), 75 (40), 73 (100). Anal. Calcd for $C_{16}H_{22}OSi$: C, 74.36; H, 8.58. Found: C,

74.20; H, 8.45. The sample was desilylated with $(HF)_x$-Py[5h] and its regiochemistry was ascertained by comparison with the product from phenylacetylene.

4-*tert*-Butyldimethylsilyl-3-decyl-2-propylfuran. $TaCl_5$ (4.0 equiv), zinc (6.0 equiv), and pyridine (8.0 equiv) were employed. Bp 75–77 °C (bath temp, 0.30 Torr); IR (neat); 2952, 2924, 2852, 1501, 1465, 1249, 1141, 1126, 832, 821, 807, 769, 672 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.18 (s, 6H), 0.87 (s, 9H), 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.3–2.4 (m, 2H), 2.51 (t, *J*=7.3 Hz, 2H), 7.12 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.0, 14.2, 17.0, 22.0, 22.8, 26.1, 26.8, 28.2, 29.4, 29.6, 29.7, 30.0, 32.0, 32.2, 116.5, 123.0, 146.3, 152.1; MS *m/z* (real intensity): 364 (M^+, 9), 308 (26), 307 (100), 181 (57), 75 (35), 73 (33). Anal. Calcd for $C_{23}H_{44}OSi$: C, 75.75; H, 12.16. Found: C, 75.96; H, 12.33. The sample was desilylated with $(HF)_x$-Py[5h] and its regiochemistry was ascertained by comparison with the product from 1-dodecyne.

3,4-Dipentyl-2-iodo-5-propylfuran (11). To a stirring solution of $TaCl_5$ (0.72 g, 2.0 mmol) in a mixed solvent of DME and benzene (1:1, 10 mL) at 25 °C under an argon atmosphere was added zinc (0.20 g, 3.0 mmol) and the mixture was stirred at 25 °C for 40 min. To the mixture was added at 25 °C a solution of 6-dodecyne (0.17 g, 1.0 mmol) in DME and benzene (1:1, 2 mL) and the whole mixture was stirred at 25 °C for 30 min. THF (6 mL) and pyridine (0.32 mL, 4.0 mmol) were added successively to the mixture. After the reaction mixture was stirred at 25 °C for 15 min, butanal (0.086 g, 1.2 mmol) was added to the mixture and the resulting mixture was stirred at 25 °C for an additional 20 min. To this mixture was added 2,6-dimethylphenyl isocyanide (0.13 g, 1.0 mmol) at 25 °C and the reaction mixture was stirred at 25 °C for an additional 20 min. To the mixture was added at −25 °C a solution of I_2 (1.3g, 5.0 mmol) in THF (6 mL) and the whole mixture was stirred at −25 °C for 30 min. Aqueous NaOH solution (15%, 2 mL) was added at −25 °C and the mixture was stirred at 25 °C for an additional 1 h. The deposited white solid was filtered off with Hyflo-Super Cel[R] and washed well with ethyl acetate (3X5 mL). The organic extracts were washed with saturated $NaHSO_3$ (10 mL) and brine (10 mL). Organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by column chromatography on silica gel with hexane gave 0.038 g (10%) of 3,4-dipentyl-2-iodo-5-propylfuran. Bp 90–92 °C (bath temp, 0.30 Torr); IR (neat): 2954, 2928, 2856, 1625, 1459, 1378, 1168, 1133, 1094, 1002 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 9H), 1.2–1.8 (m, 14H), 2.24 (t, *J*=8.7 Hz, 2H), 2.27 (t, *J*=9.2 Hz, 2H), 2.51 (t, *J*=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.0, 22.0, 22.5, 23.8, 25.5, 28.6, 29.5, 30.5, 31.7, 85.4, 121.0, 131.7, 157.2; MS *m/z* (real intensity): 376 (M^+, 98), 347 (19), 249 (100), 193 (35).

Typical Procedure for Protodesilylation: A mixture of 3-Decyl-4-trimethylsilyl-2-propylfuran and 4-decyl-2-propyl-3-trimethylsilylfuran (0.16 g, 0.5 mmol, a 94/6 mixture) in THF (3 mL) was placed in a Teflon beaker. Pyridine poly(hydrogenfluoride) (1.5 mL, 68% HF) was added in one portion, and the resulting mixture was allowed to stir at 25 °C for 1 h. The reaction mixture was carefully added to a stirred, ice-cooled mixture of hexane (20 mL) and saturated $NaHCO_3$ solution (20 mL) (Evolution of CO_2). After 5 min, solid $NaHCO_3$ was added in portions until the aqueous phase became saturated. The organic layer was then separated and the aqueous layer was extracted with hexane (2x20 mL). The combined organic extracts were washed twice with water and brine. The crude product was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by column chromatography on silica gel afforded a mixture of 3-decyl-2-propylfuran and 4-decyl-2-propylfuran in 88% combined yield (0.11 g, 0.44 mmol, 94/6)

3-Decyl-2-propylfuran: Bp 55–57 °C (bath temp, 0.10 Torr); IR (neat): 2956, 2924, 2852, 1734, 1654, 1509, 1459, 1145, 722 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.8–1.0 (m, 6H), 1.2–1.7 (m, 18H), 2.31 (t, *J*=7.0

Hz, 2H), 2.52 (t, *J*=7.3 Hz, 2H), 6.19 (d, *J*=1.7 Hz, 1H), 7.22 (d, *J*=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 13.8, 14.2, 22.0, 22.7, 24.7, 28.0, 29.4, 29.5, 29.7, 30.7, 32.0, 111.3, 119.0, 140.0, 151.0; MS *m/z* (real intensity): 250 (M^+, 13), 223 (15), 137 (20), 124 (58), 123 (45), 95 (100), 82 (59). Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.08. Found: C, 81.84; H, 12.32.

3-Phenyl-2-propylfuran: Bp 50–52 °C (bath temp, 0.10 Torr); IR (neat): 2958, 2928, 2870, 1518, 1459, 1147, 1132, 960, 764, 732, 696, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.95 (t, *J*=7.3 Hz, 3H), 1.7–1.8 (m, 2H), 2.75 (t, *J*=7.3 Hz, 2H), 6.49 (d, *J*=1.7 Hz, 1H), 7.2–7.4 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 13.9, 21.8, 28.9, 111.2, 120.9, 126.3, 127.8, 128.5, 134.3, 140.4, 151.8; MS *m/z* (real intensity): 186 (M^+, 34), 157 (74), 129 (32), 128 (31), 58 (100). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.91; H, 7.35.

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