A novel cyclization reaction between 2,3-bis(trimethylsilyl)buta-1,3-diene and acyl chlorides with straightforward formation of polysubstituted furans

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GENERAL

GC analyses were performed on a gas chromatograph equipped with a SE-30 (methyl silicone, 30 m x 0.25 mm id) capillary column. MS spectra were recorded on a Shimadzu GCMS-QP 5000 spectrometer. ^1H NMR and ^13C NMR spectra were recorded in CDCl_3 at 500 MHz and at 125.7 MHz, respectively, using the residual proton peak of CDCl_3 at 7.24 ppm as reference for ^1H spectra and the signals of CDCl_3 at 77 ppm for ^13C spectra. Elemental analyses were done by a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Dichloromethane was distilled over P_2O_5 immediately prior to use. 2,3-bis(trimethylsilyl)buta-1,3-diene 4 was prepared according to the literature. Acyl chlorides 5a-g, AlCl_3 and BF_3 etherate were commercial products. Column chromatography was performed using silica gel 60, 40-63 μm from Machery-Nagel, alumina 15-50 μm from Fluka.

2-Methyl-5-phenylfuran (7a)^ii

A CH_2Cl_2 solution (18 ml) of freshly distilled benzoyl chloride 5a (0.319 g, 2.27 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl_3 (0.303 g, 2.27 mmol) in 6 ml of CH_2Cl_2. When the mixture became clear, a CH_2Cl_2 solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol) was slowly (over about 20 minutes) added maintaining the temperature to 0 °C. Immediately after the addition, the reaction was quenched with saturated aqueous NH_4Cl solution (30 ml) and extracted with CH_2Cl_2 (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na_2CO_3 solution, dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9.8:0.2 as eluent) obtaining 7a as a white solid (m.p. : 39-40 °C from ethanol/water) (0.150 g, 63% yield) which was fully characterized by NMR spectroscopy and mass spectrometry.

^1H-NMR (CDCl_3, 500 MHz): δ (ppm): 2.35 (d, J = 0.9 Hz, 3H), 6.03-6.07 (m, 1H), 6.54 (d, J = 3.1 1H), 7.20-7.24 (m, 1H), 7.36 (t like, J = 7.7 2H), 7.62 (dd, J = 7.7, 1.3 Hz 2H).

The ^1H NMR multiplet at 6.03-6.07 ppm, showing long range coupling with the methyl group protons, was attributed to the hydrogen atom in the 3 position of the furan ring.
Decoupling by irradiation at 2.35 ppm (methyl group) resolved the multiplet in a doublet centered at 6.05 ppm, with J = 3.1 Hz, confirming the attribution.

$^{13}$C-NMR (CDCl$_3$, 125 MHz): $\delta$(ppm): 13.7, 105.8, 107.6, 123.3, 126.7, 128.6, 131.2, 151.9, 152.3

MS [m/z (%)]: 158[M$^+$(90)], 129(21), 115(47), 105(19), 89(13), 77(28), 64(18), 51(17), 43(100).


GC-MS analysis of the reaction mixture revealed the presence, besides 7a, of a second product with a molecular mass 230 uma, corresponding to that of 7a (158 uma) with an hydrogen atom substituted by a trimethylsilyl group (73 uma). This silylated product was converted into 7a during work-up and chromatographic purification.

Quenching the reaction mixture with an aqueous saturated solution of sodium carbonate (30 ml), instead of ammonium chloride, and performing chromatographic purification over a basic alumina column with petroleum ether as the eluent afforded, besides 7a (0.102 g, 43% yield), the silylated compound (0.073 g, 21% yield) as a white solid. On the basis of the spectroscopic data reported below, this compound was identified as 2-methyl-3-trimethylsilyl-5-phenyl furan 6a. In particular, the position of the trimethylsilyl group was attributed on the basis of comparison between the $^1$H NMR spectra of 6a and 7a (disappearance of the 6.05 ppm H absorbance in the 6a spectrum, that was attributed to the H atom in the 3 position of the 7a spectrum). The structure of 6a was confirmed by NOE experiments (see pag. 23 and pag. 24 below).

MS [m/z (%)]: 230[M$^+$(84)], 215(100), 141(10), 108(25), 75(28), 43(50).

$^1$H-NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 0.26 (s, 9H), 2.40 (s, 3H), 6.52 (s, 1H), 7.18-7.22 (m, 1H), 7.32-7.37 (m, 2H), 7.61-7.64 (m, 2H).

$^{13}$C-NMR (CDCl$_3$, 125 MHz): $\delta$(ppm): -0.6, 14.5, 110.3, 114.7, 123.3, 126.6, 128.5, 130.9, 152.0, 156.6.

Anal. Calcd for: C$_{14}$H$_{18}$OSi: C, 72.99; H, 7.88. Found: 73.21; H, 8.01.

**2-Methyl-3-trimethylsilyl-5-thiophen-2-yl-furan (6b)**

A CH$_2$Cl$_2$ solution (18 ml) of freshly distilled acyl chloride 5b (0.333 g, 2.27 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl$_3$ (0.303 g, 2.27 mmol) in 6 ml of CH$_2$Cl$_2$. When the mixture became clear, a CH$_2$Cl$_2$ solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol) was slowly (over about 20 minutes) added maintaining the temperature to 0 °C. After complete addition at 0°C, the mixture was stirred at the same temperature and the progress of the reaction was monitored by GC-MS analysis. After
disappearance of the starting compound 4 (75 min), the mixture was quenched with saturated aqueous NH₄Cl solution (30 ml) and extracted with CH₂Cl₂ (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na₂CO₃ solution, dried over Na₂SO₄ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether / ethyl acetate 9 : 1 as eluent) obtaining a yellow oil (0.185g, 52% yield) which was fully characterized by NMR spectroscopy and mass spectrometry analysis, and identified as 2-methyl-3-trimethylsilyl-5-thiophen-2-yl-furan 6b.

1H-NMR (CDCl₃, 500 MHz): δ (ppm): 0.35(s, 9H), 2.47 (s, 3H), 6.47 (s, 1H), 7.09 (dd, J = 5.1, 3.6 Hz, 1H), 7.25 (dd, J = 5.1, 1.1 Hz, 1H), 7.27(dd, J = 3.6, 1.1 Hz, 1H).

13C-NMR (CDCl₃,125 MHz): δ(ppm): -0.6, 14.4, 110.3, 114.8, 121.5, 123.2, 127.5, 133.9, 147.5, 156.1
MS [m/z (%)]: 236[M⁺(70)], 221(65), 147(16), 141(14), 111(24), 103(9), 75(32), 73(35), 59(11), 43 (100)
Anal. Calcd for: C₁₂H₁₆OSSi: C, 60.97; H, 6.82; S, 13.56. Found: C, 60.80; H, 6.71; S, 13.41.

The structure of 6b was confirmed by NOE experiments (see pag. 23 and pag. 25 below).

2-Methyl-5-thiophen-2-yl-furan (7b)

2-Methyl-3-trimethylsilyl-5-thiophen-2-yl-furan 6b was desilylated according to the following procedure. 0.10 ml of BF₃·Et₂O (d = 1.13 g/ml, 0.113 g, 0.80 mmol) were slowly added under a nitrogen atmosphere to a CH₂Cl₂ solution (15 ml) of 6b (0.185 g, 0.78 mmol) at room temperature. After disappearance of the starting compound (about 3 h) monitored by gas-chromatographic analysis, the mixture was quenched with water (15 ml) and extracted with CH₂Cl₂ (3x40 ml). The organic layers were washed several times with a saturated aqueous NaHCO₃ solution, dried over Na₂SO₄ and concentrated under reduced pressure. 0.128 g of a yellow oil (100% yield) were isolated as the pure compound 7b, which was fully characterized by NMR spectroscopy and mass spectrometry.

1H-NMR (CDCl₃, 500 MHz): δ(ppm): 2.37 (d, J ~ 1Hz, 3H), 6.03-6.05 (m, 1H), 6.41 (d, J = 3.6 Hz, 1H), 7.03 (dd, J = 5.2, 3.6 Hz, 1H), 7.19 (dd J = 5.2, 1.6 Hz, 1H), 7.22 (dd, 3.6, 1.6 Hz, 1H).

13C-NMR (CDCl₃,125 MHz): δ(ppm): 13.5, 105.8, 107.5, 121. 6, 123.2, 127.4, 134.1, 147.7, 151.5
MS [m/z (%)]: 164[M⁺(100)], 135(34), 121(52), 91(14), 77(19), 63(10), 43 (99)
(E)-2-methyl-3-trimethylsilyl-5-styryl-furan (6c)

A CH$_2$Cl$_2$ solution (18 ml) of cinnamoyl chloride $5c$ (0.756 g, 4.54 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl$_3$ (0.605 g, 4.54 mmol) in 6 ml of CH$_2$Cl$_2$ in a three-necked flask. When the solution obtained became clear, a CH$_2$Cl$_2$ solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene $4$ (0.300 g, 1.51 mmol) was slowly added (over about 20 min) maintaining the temperature at 0°C. After complete addition, the mixture was quenched with saturated aqueous NH$_4$Cl solution (30 ml) and extracted with CH$_2$Cl$_2$ (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na$_2$CO$_3$ solution, dried over Na$_2$SO$_4$ and concentrated. The crude product obtained was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9 : 1 as eluent) obtaining a yellow oil (0.313 g, 81% yield) which was fully characterized by NMR spectroscopy and mass spectrometry and identified as (E)-2-methyl-3-trimethylsilyl-5-styryl-furan 6c.

$^1$H-NMR (CDCl$_3$, 500 MHz): $\delta$ (ppm): 0.27(s, 9H), 2.41 (s, 3H), 6.25 (s, 1H), 6.85 (d, J = 16.2 Hz, 1H), 6.96 (d, J = 16.2 Hz, 1H), 7.21-7.26 (m, 2H) 7.32-7.37(m, 2H), 7.45-7.49 (m, 1H).

$^{13}$C-NMR (CDCl$_3$,125 MHz): $\delta$(ppm): -0.5, 14.6, 114.6, 116.4, 123.8, 125.4, 126.1, 127.1, 128.6, 137.4, 151.5, 157.0.

MS [m/z (%)]: 256[M$^+$(37)], 241(24), 121(12), 75(47), 73(36), 59(16), 45(59), 43(100).

Anal. Calcd for: C$_{16}$H$_{20}$OSi: C, 74.95; H, 7.86. Found: C, 75.17; H, 8.02.

The structure of 6c was confirmed by NOE experiments (see pag. 23 and pag. 26 below).

(E)-2-Methyl-5-styryl-furan (7c)$^*$

(E)-2-Methyl-3-trimethylsilyl-5-styryl-furan 6c was desilylated according to the following procedure. 0.16 ml of BF$_3$Et$_2$O (d = 1.13 g/ml, 0.181 g, 1.28 mmol)were slowly added under a nitrogen atmosphere to a CH$_2$Cl$_2$ solution (15 ml) of the 6c (0.313 g, 1.22 mmol) at room temperature. After disappearance of starting compound (about 3 h) monitored by gas-chromatographic analysis, the mixture was quenched with water (15 ml) and extracted with CH$_2$Cl$_2$ (3x40 ml). The organic extracts were washed several times with saturated aqueous NaHCO$_3$, dried over Na$_2$SO$_4$ and concentrated under reduced pressure. 0.224 g of a yellow oil (100% yield) were
isolated as the pure compound 7c, which was fully characterized by NMR spectroscopy and mass spectrometry.

\[^{1}\text{H-NMR (CDCl}_3, 500 \text{ MHz)}: \delta(ppm): 2.36 \text{ (bs, 3H), 6.01-6.02 (m, 1H), 6.24 (d, J = 2.9 Hz, 1H), 6.84 (d, J = 16.3 Hz, 1H), 6.96 (d, J = 16.3 Hz, 1H) 7.21-7.24(m, 1H),7.31-7.36 (m, 2H), 7.44-7.48 (m, 2H).}\]

\[^{13}\text{C-NMR (CDCl}_3, 125 \text{ MHz)}: \delta(ppm): 13.8, 107.8, 109.9, 116.6, 125.4, 126.1, 127.2, 128.6, 137.3, 151.7, 152.3.}\]

MS [m/z (%)]: 184[M^+(67)], 169(18), 141(88), 115(30), 91(7), 77(15), 63(10), 43(100).

Anal. Calcd for: C\text{13}H\text{12}O: C, 84.75; H, 6.57. Found: C, 84.62; H, 6.49.

2-Methyl-3-trimethylsilyl-5-naphthalen-2-yl-furan (6d)

A CH\text{2}Cl\text{2} solution (18 ml) of acyl chloride 5d (0.433 g, 2.27 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl\text{3} (0.303 g, 2.27 mmol) in 6 ml of CH\text{2}Cl\text{2}. When the solution became clear a CH\text{2}Cl\text{2} solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol) was slowly added (over about 20 minutes), maintaining the temperature at 0°C. After complete addition at 0°C, the mixture was stirred at the same temperature and the reaction was monitored by GC analysis. After disappearance of 4 (30 min), the mixture was quenched with saturated aqueous NH\text{4}Cl solution (30 ml) and extracted with CH\text{2}Cl\text{2} (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na\text{2}CO\text{3} solution and filtered. The resulting solution was dried over Na\text{2}SO\text{4} and concentrated. The crude product was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9.5 : 0.5 as eluent) obtaining a yellow oil (0.253 g, 60 % yield) that was fully characterized by NMR spectroscopy and mass spectrometry and identified as 2-methyl-3-trimethylsilyl-5-naphtalen-2-yl-furan 6d.

\[^{1}\text{H-NMR (CDCl}_3, 500 \text{ MHz)}: \delta(ppm): 0.32(s, 9H), 2.48(s, 3H), 6.68 (s, 1H), 7.41-7.51 (m, 2H), 7.73-7.88(m, 4H), 8.11 (s, 1H).}\]

\[^{13}\text{C-NMR (CDCl}_3, 125 \text{ MHz)}: \delta(ppm): -0.5, 14.6, 111.0 115.0, 121.3, 122.3, 125.5, 126.3, 127.7, 128.0, 128.2, 128.3, 132.4, 133.7, 152.1, 156.9.}\]

MS [m/z (%)]: 280[M^+(100)], 265 (90), 235(8), 191(15), 189(23), 155(51), 133(77), 75(52), 73(71), 45(79), 43(50).


The structure of 6d was confirmed by NOE experiments (see pag. 23 and pag. 27 below).
2-Methyl-5-naphthalen-2-yl-furan (7d)
2-Methyl-3-trimethylsilyl-5-naphtalen-2-yl-furan 6d was desilylated according to the following procedure. 0.12 ml of BF3.Et2O (d = 1.13 g/ml, 0.147 g, 0.95 mmol) were slowly added under a nitrogen atmosphere to a CH2Cl2 solution (15 ml) of the silylated furan (0.253 g, 0.90 mmol) at room temperature. After disappearance of the starting compound (about 3 h) monitored by gas-chromatographic analysis, the mixture was quenched with water (15 ml) and extracted with CH2Cl2 (3x40 ml). The organic extracts were washed several times with saturated aqueous NaHCO3, dried over Na2SO4 and concentrated under reduced pressure. 0.183 g of a yellow oil (98% yield) were isolated as the pure compound 7d, which was fully characterized by NMR spectroscopy and mass spectrometry.

1H-NMR (CDCl3, 500 MHz): δ(ppm): 2.45 (bs, 3H), 6.13-6.15 (m, 1H), 6.69 (d, J = 3.1 Hz, 1H), 7.44-7.53 (m, 2H), 7.75-7.92 (m, 4H), 8.14 (s, 1H).
MS [m/z (%)]: 208[M+(100)], 207 (25), 179(16), 165(50), 164(12), 127(10), 104(24), 89(9), 63(7), 51(10), 43 (43).

5-Biphen-4-yl-2-methyl-3-trimethylsilyl-furan (6e)
A CH2Cl2 solution (18 ml) of acyl chloride 5e (0.660 g, 3.05 mmol) was added, under a nitrogen atmosphere, to a stirred suspension of anhydrous AlCl3 (0.407 g, 3.05 mmol) in 6 ml of CH2Cl2 maintained at room temperature. When the solution obtained became clear, it was cooled at 0°C and a CH2Cl2 solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol) was slowly added (over about 20 minutes). After addition completion, the reaction was quenched with saturated aqueous NH4Cl solution (30 ml) and extracted with CH2Cl2 (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na2CO3 solution, dried over Na2SO4 and concentrated. The residue was purified by silica gel column chromatography (petroleum ether as eluent) obtaining a white solid (m.p. 75-76°C, from ethanol) (0.342 g, 74% yield) that was fully characterized by NMR spectroscopy and mass spectrometry and identified as 5-biphen-4-yl-2-methyl-3-trimethylsilyl-furan (6e).
\( ^1\text{H-NMR (CDCl}_3, 500 \text{ MHz): } \delta \text{ (ppm): } 0.3(\text{s, 9H}), 2.42(\text{s, 3H}), 6.58 (\text{s, 1H}), 7.35 (\text{t di t, } J = 7.3, 1.2 \text{ Hz, 1H}), 7.45(\text{t like, } J = 7.3 \text{ Hz, 2H}), 7.58-7.64 (\text{m, 4H}), 7.70 (\text{d like, } J = 8.5 \text{ Hz, 2H}). \)

\( ^{13}\text{C-NMR (CDCl}_3, 125 \text{ MHz): } \delta \text{ (ppm): } -0.5, 14.5, 110.5, 114.9, 127.8, 126.8, 127.1, 127.2, 128.7, 130.0, 139.2, 151.8, 156.7. \)

MS [m/z (%)]: 306[M+(100)], 291(74), 215(7), 202(7), 181(7), 153(12), 146(34), 75(21), 73(19), 45(21).


The structure of \(6e\) was confirmed by NOE experiments (see pag. 23 and pag. 28 below).

**2-Biphen-4-yl-5-methyl-furan (7e)**

5-Biphen-4-yl-2-methyl-3-trimethylsilyl-furan \((6e)\) was desilylated according to the following procedure. 0.15 ml of BF\(_3\)·Et\(_2\)O \((d = 1.13, 0.169 \text{ g, 1.19 mmol})\) were slowly added under a nitrogen atmosphere to a CH\(_2\)Cl\(_2\) solution (15 ml) of the silylated furan \((0.342 \text{ g, 1.12 mmol})\) at room temperature. After disappearance of the starting compound (about 3 h) monitored by gas-chromatographic analysis, the mixture was quenched with water and extracted with CH\(_2\)Cl\(_2\) (3x40 ml). The organic layers were washed several times with saturated aqueous NaHCO\(_3\), dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. 0.259 g of a light yellow solid (m.p. 110-111°C, from ethanol-water) (99% yield) were isolated as the pure compound \(7e\), that was fully characterized by NMR spectroscopy and mass spectrometry.

\( ^1\text{H-NMR (CDCl}_3, 500 \text{ MHz): } \delta \text{ (ppm): } 2.40 (\text{bs, 3H}), 6.09 (\text{m, 1H}), 6.59 (\text{d, } J = 3.5 \text{ Hz, 1H}), 7.36 (\text{t like, } J = 7.4 \text{ Hz, 1H}), 7.46 (\text{t like, } J = 7.7 \text{ Hz, 2H}), 7.63 (\text{t like, } J = 8.2 \text{ Hz, 4H}), 7.71 (\text{d like, } J = 8.4 \text{ Hz, 2H}). \)

\( ^{13}\text{C-NMR (CDCl}_3,125 \text{ MHz): } \delta \text{ (ppm): } 13.7, 106.1, 107.8, 123.6, 126.8, 127.2, 127.3, 128.7, 130.1, 139.3, 140.7, 152.0, 152.1. \)

MS [m/z (%)]: 234[M\(^+\)(100)], 191(33), 165(8), 152(15), 117(20), 89(5), 76(11), 43(62).

Anal. calcd for: C\(_{17}\)H\(_{14}\)O: C, 87.15; H, 6.02. Found: C, 87.31; H, 6.11.

**2-Cyclohexyl-5-methyl-furan (7f)**

A CH\(_2\)Cl\(_2\) solution (18 ml) of acyl chloride \(5f\) \((0.333 \text{ g, 2.27 mmol})\) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl\(_3\) \((0.303 \text{ g, 2.27 mmol})\) in 6 ml of CH\(_2\)Cl\(_2\). When the solution became clear, a CH\(_2\)Cl\(_2\) solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene \(4\) \((0.300 \text{ g, 1.51 mmol})\) was slowly added (over about 20 minutes) maintaining the
temperature at 0°C. After addition completion, the reaction was quenched with saturated aqueous NH₄Cl solution (30 ml) and extracted with CH₂Cl₂ (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na₂CO₃ solution, dried over Na₂SO₄ and concentrated. The crude product obtained was purified by silica gel column chromatography (petroleum ether as eluent) obtaining 7f as a colorless oil (0.178 g, 72% yield) that was fully characterized by NMR spectroscopy and mass spectrometry.

1H-NMR (CDCl₃, 500 MHz): δ (ppm): 1.23-1.45 (m, 5H), 1.70-1.77 (m, 1H), 1.78-1.87 (m, 2H), 2.01-2.08 (m, 2H), 2.28 (s, 3H), 2.56-2.64 (m, 1H), 5.84 (d, J = 2.5 Hz, 1H), 5.86-5.88 (m, 1H).

13C-NMR (CDCl₃, 125 MHz): δ(ppm): 13.4, 26.0, 26.2, 31.7, 37.2, 103.0, 105.5, 149.7, 159.3.

MS [m/z (%)]: 164[M⁺(27)], 149(3), 121(100), 108(23), 95(33), 77(12), 55(27), 53(11), 43 (89).


2-Methyl-5-pentyl-furan (7g)iv
A CH₂Cl₂ solution (18 ml) of acyl chloride 5g (0.306 g, 2.27 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl₃ (0.303 g, 2.27 mmol) in 6 ml of CH₂Cl₂. When the solution became clear, a CH₂Cl₂ solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol) was added slowly (over about 20 minutes) maintaining the temperature to 0°C.

After addition completion, the reaction was quenched with saturated aqueous NH₄Cl solution (30 ml) and extracted with CH₂Cl₂ (3x40 ml). The organic extracts were washed several times with a saturated aqueous Na₂CO₃ solution, dried over Na₂SO₄ and concentrated. The crude product obtained was purified by silica gel column chromatography (petroleum ether/ethyl acetate 9.5 : 0.5 as eluent) obtaining 7g as a colorless oil (0.114 g, 50% yield) which was fully characterized by NMR spectroscopy and mass spectrometry.

1H-NMR (CDCl₃, 500 MHz): δ (ppm): 0.91(t like, J = 7.2 Hz, 3H), 1.29-1.37 (m, 4H), 1.58-1.68 (m, 2H), 2.26 (s, 3H), 2.57 (t, J = 7.6 Hz, 2H), 5.84 (s, 2H).

13C-NMR (CDCl₃, 125 MHz): δ(ppm): 13.4, 14.0, 22.4, 27.8, 28.0, 31.4, 105.1, 105.7, 150.0, 154.8.

MS [m/z (%)]: 152[M⁺(9)], 96(10), 95(100), 81(3), 79(2), 67(3), 53(4), 43 (35), 41(16).

Anal. calcd for: C₁₀H₁₆O: C, 80.44; H, 10.59. Found: C, 78.71; H, 10.45.

Mixture of 3-Benzoyl-5-methyl-2-phenylfuranv and 3-benzoyl-2-methyl-5-phenyl furan (8a,b)
A CH₂Cl₂ solution (48 ml) of freshly distilled benzoyl chloride 5a (0.849 g, 6.04 mmol) was added, under a nitrogen atmosphere, to a cold (0°C), stirred suspension of anhydrous AlCl₃ (0.805 g, 6.04
mmol) in 16 ml of CH$_2$Cl$_2$. When the solution obtained became clear, it was slowly added to a cold (0 °C) CH$_2$Cl$_2$ solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene 4 (0.300 g, 1.51 mmol), maintaining the temperature at 0°C.

After complete addition, the mixture was stirred at the same temperature for 20 hours. Then, it was quenched with saturated aqueous NH$_4$Cl solution (60 ml) and extracted with CH$_2$Cl$_2$ (3x100 ml). The organic extracts were washed several times with a saturated aqueous Na$_2$CO$_3$ solution, dried over Na$_2$SO$_4$ and concentrated. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate 9.5:0.5 as eluent) obtaining a mixture of 8a and 8b as a white solid (0.246 g, 62% yield) which was fully characterized by NMR spectroscopy and mass spectrometry analysis.

$^1$H-NMR (CDCl$_3$, 500 MHz): δ (ppm): 2.40 (d, J ~ 1Hz, 3H, CH$_3$ isomer 1), 2.61 (s, 3H, CH$_3$ isomer 2), 6.30 (q like, J ~ 1Hz, 1H, H furan isomer 1), 6.82 (s, 1H, H furan isomer 2), 7.50-7.86 (20H, 10 H phenyl isomer 1 and 10 H phenyl isomer 2).

MS [m/z (%)]: Isomer 1: 262[M$^+$ (59)], 261(33), 105(89), 77(100), 51(38), 43(43).
Isomer 2: 262[M$^+$ (73)], 261(35), 115(24), 105(86), 77(100), 51(47), 43(52).
Supplementary Material (ESI) for Chemical Communications
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2-methyl-1,3-trimethylylallyl-5-phenyl furan 6a
2-Methyl-5-phenylthioren
a) Furan proton signals of compound 7a, showing the long-range coupling between the proton in 3-position (6.05 ppm) and the methyl group.

b) Same region as above with decoupling by irradiation at 2.35 ppm (methyl group). The multiplet at 6.05 ppm is resolved in a doublet.
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Determination of the structure of silyl furans 6a-e by means of NOE experiments

The structure of furans 6a-e was confirmed by means of NOE experiments, by applying selective $^1$H preirradiations within a double pulsed field gradient spin-echo NOE (DPFGSE-NOE) sequence. Figure 1 reports the $^1$HNMR spectrum of furan 6a (trace a), together with two DPFGSE-NOE spectra recorded with selective preirradiations of the signal of furan proton at $\delta = 6.52$ ppm (trace b) and of the signal of the trimethylsilyl protons at $\delta = 0.26$ ppm (trace c). A positive NOE was detected for the signal of the ortho phenyl and of the trimethylsilyl protons, when the selective preirradiation was applied to the signal of the furan proton (trace b). When the preirradiation was applied to the signal of the trimethylsilyl protons, a positive NOE was evidenced for the signals of the methyl group and of the furan proton (trace c). These results confirm the close proximity of the furan proton to the phenyl ring and to the trimethylsilyl group, as expected for the proposed structure of the furan 6a. Similar NOE experiments were also performed with compounds 6b-e (see figures 2 to 5). In all cases the NOE spectra are in agreement with the proposed structures.
Figure 1. a) $^1$HNMR spectrum of furan 6a. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.52$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.26$ ppm.
Figure 2. a) $^1$HNMR spectrum of furan 6b. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.39$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.28$ ppm.
Figure 3. a) $^1$HNMR spectrum of furan 6c. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.28$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.26$ ppm.
**Figure 4.** a) $^1$HNMR spectrum of furan 6d. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.28$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.26$ ppm.
Figure 5. a) $^1$HNMR spectrum of furan 6e. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.57$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.29$ ppm.