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. ^{1}H NMR and ^{13}C 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 ^{1}H spectra and the signals of $CDCl_3$ at 77 ppm for ^{13}C 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.[i] 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.

^{1}H-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 ^{1}H 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): δ(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).
Anal. Calcd for: $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.67; H = 6.51.
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): δ (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): δ(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_2Cl_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_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. 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 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 : 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**.

^{1}H-NMR ($CDCl_3$, 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).

^{13}C-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: $C_{12}H_{16}OSSi$: 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 $BF_3{\cdot}Et_2O$ (d = 1.13 g/ml, 0.113 g, 0.80 mmol) were slowly added under a nitrogen atmosphere to a CH_2Cl_2 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 CH_2Cl_2 (3x40 ml). The organic layers were washed several times with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4 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.

^{1}H-NMR ($CDCl_3$, 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).

^{13}C-NMR ($CDCl_3$,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)

Anal. Calcd. For C_9H_8OS: C, 65.82; H, 4.91; S, 19.53. Found: C, 65.73; H, 4.85; S, 19.48.

(*E*)-2-methyl-3-trimethylsilyl-5-styryl-furan (6c)

A CH_2Cl_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_2Cl_2 in a three-necked flask. When the solution obtained 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 added (over about 20 min) maintaining the temperature at 0°C. After complete addition, the mixture 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 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 spectromety and identified as (*E*)-2-methyl-3-trimethylsilyl-5-styryl-furan **6c.**

^{1}H-NMR ($CDCl_3$, 500 MHz): δ (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): δ(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)[ii]

(*E*)-2-Methyl-3-trimethylsilyl-5-styryl-furan **6c** was desilylated according to the following procedure. 0.16 ml of $BF_3 \cdot Et_2O$ (d = 1.13 g/ml, 0.181 g, 1.28 mmol)were slowly added under a nitrogen atmosphere to a CH_2Cl_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_2Cl_2 (3x40 ml). The organic extracts were washed several times with saturated aqueous $NaHCO_3$, dried over Na_2SO_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}H-NMR ($CDCl_3$, 500 MHz): δ(ppm): 2.36 (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}C-NMR ($CDCl_3$, 125 MHz): δ(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: $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.62; H, 6.49.

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

A CH_2Cl_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 $AlCl_3$ (0.303 g, 2.27 mmol) in 6 ml of CH_2Cl_2. When the solution 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 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_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 and filtered. The resulting solution was dried over Na_2SO_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}H-NMR ($CDCl_3$, 500 MHz): δ (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}C-NMR ($CDCl_3$, 125 MHz): δ(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).

Anal. Calcd for: $C_{18}H_{20}OSi$: C, 77.09; H, 7.19. Found: C, 77.23; H, 7.27.

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 $BF_3 \cdot Et_2O$ (d = 1.13 g/ml, 0.147 g, 0.95 mmol) were slowly added under a nitrogen atmosphere to a CH_2Cl_2 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 CH_2Cl_2 (3x40 ml). The organic extracts were washed several times with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 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.

^{1}H-NMR ($CDCl_3$, 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).

Anal. Calcd for: $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.77, H, 5.99.

5-Biphen-4-yl-2-methyl-3-trimethylsilyl-furan (6e)

A CH_2Cl_2 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 $AlCl_3$ (0.407 g, 3.05 mmol) in 6 ml of CH_2Cl_2 maintained at room temperature. When the solution obtained became clear, it was cooled at 0°C and 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 added (over about 20 minutes). After addition completion, 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 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}H-NMR ($CDCl_3$, 500 MHz): δ (ppm): 0.3(s, 9H), 2.42(s, 3H), 6.58 (s, 1H), 7.35 (t di t, J = 7.3, 1.2 Hz, 1H), 7.45(t like, J = 7.3 Hz, 2H), 7.58-7.64 (m, 4H), 7.70 (d like, J = 8.5 Hz, 2H).

^{13}C-NMR ($CDCl_3$, 125 MHz): δ(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).

Anal. Calcd for: $C_{20}H_{22}OSi$: C, 78,38; H, 7.24. Found: C, 78.22; H, 7.12.

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 $BF_3 \cdot Et_2O$ (d = 1.13, 0.169 g, 1.19 mmol) were slowly added under a nitrogen atmosphere to a CH_2Cl_2 solution (15 ml) of the silylated furan (0.342 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_2Cl_2 (3x40 ml). The organic layers were washed several times with saturated aqueous $NaHCO_3$, dried over Na_2SO_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}H-NMR ($CDCl_3$, 500 MHz): δ(ppm): 2.40 (bs, 3H), 6.09 (m, 1H), 6.59 (d, J = 3.5 Hz, 1H), 7.36 (t like, J = 7.4 Hz, 1H), 7.46 (t like, J = 7.7 Hz, 2H), 7.63 (t like, J = 8.2 Hz, 4H), 7.71 (d like, J = 8.4 Hz, 2H).

^{13}C-NMR ($CDCl_3$,125 MHz): δ(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)[iii]

A CH_2Cl_2 solution (18 ml) of acyl chloride **5f** (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_2Cl_2. When the solution 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 added (over about 20 minutes) maintaining the

temperature at 0°C. After addition completion, 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 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.

^{1}H-NMR ($CDCl_3$, 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).

^{13}C-NMR ($CDCl_3$, 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).

Anal. Calcd for: $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.69; H, 9.99.

2-Methyl-5-pentyl-furan (7g)[iv]

A CH_2Cl_2 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 $AlCl_3$ (0.303 g, 2.27 mmol) in 6 ml of CH_2Cl_2. When the solution 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 added slowly (over about 20 minutes) maintaining the temperature to 0°C.

After addition completion, 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 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.

^{1}H-NMR ($CDCl_3$, 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).

^{13}C-NMR ($CDCl_3$, 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: $C_{10}H_{16}O$, C, 78.90; H, 10.59. Found: C, 78.71; H, 10.45.

Mixture of 3-Benzoyl-5-methyl-2-phenylfuran[v] and 3-benzoyl-2-methyl-5-phenyl furan (8a,b)

A CH_2Cl_2 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 $AlCl_3$ (0.805 g, 6.04

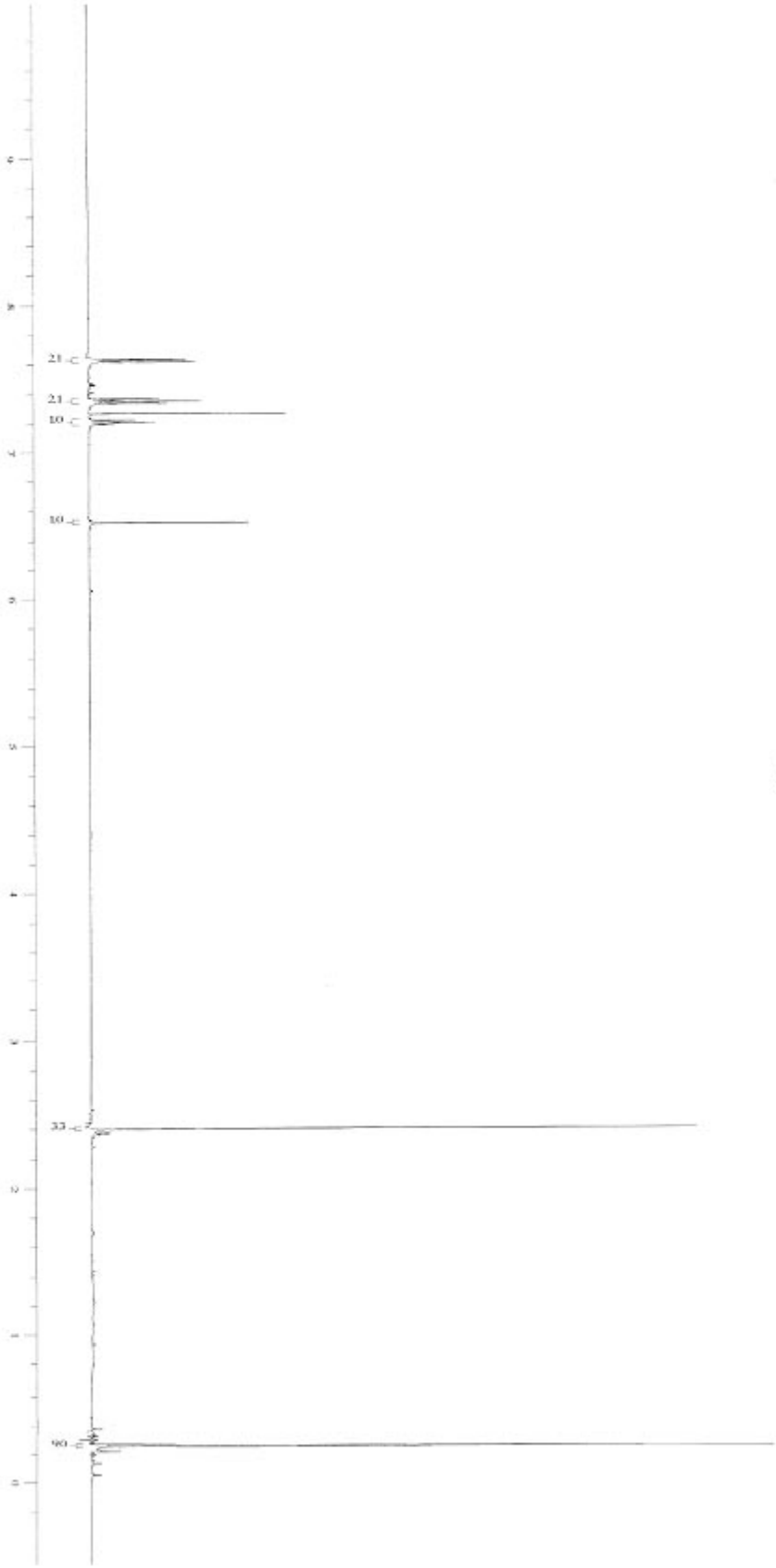
mmol) in 16 ml of CH_2Cl_2. When the solution obtained became clear, it was slowly added to a cold (0 °C) CH_2Cl_2 solution (6 ml) of 2,3-bis(trimethylsilyl)buta-1,3-diene **4** (0.300 g, 1.51 mmol), maintaining the temperature at 0°C.

After complete addition, the mixture was stirred at the same temperature for 20 hours. Then, it was quenched with saturated aqueous NH_4Cl solution (60 ml) and extracted with CH_2Cl_2 (3x100 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 9.5:0.5 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).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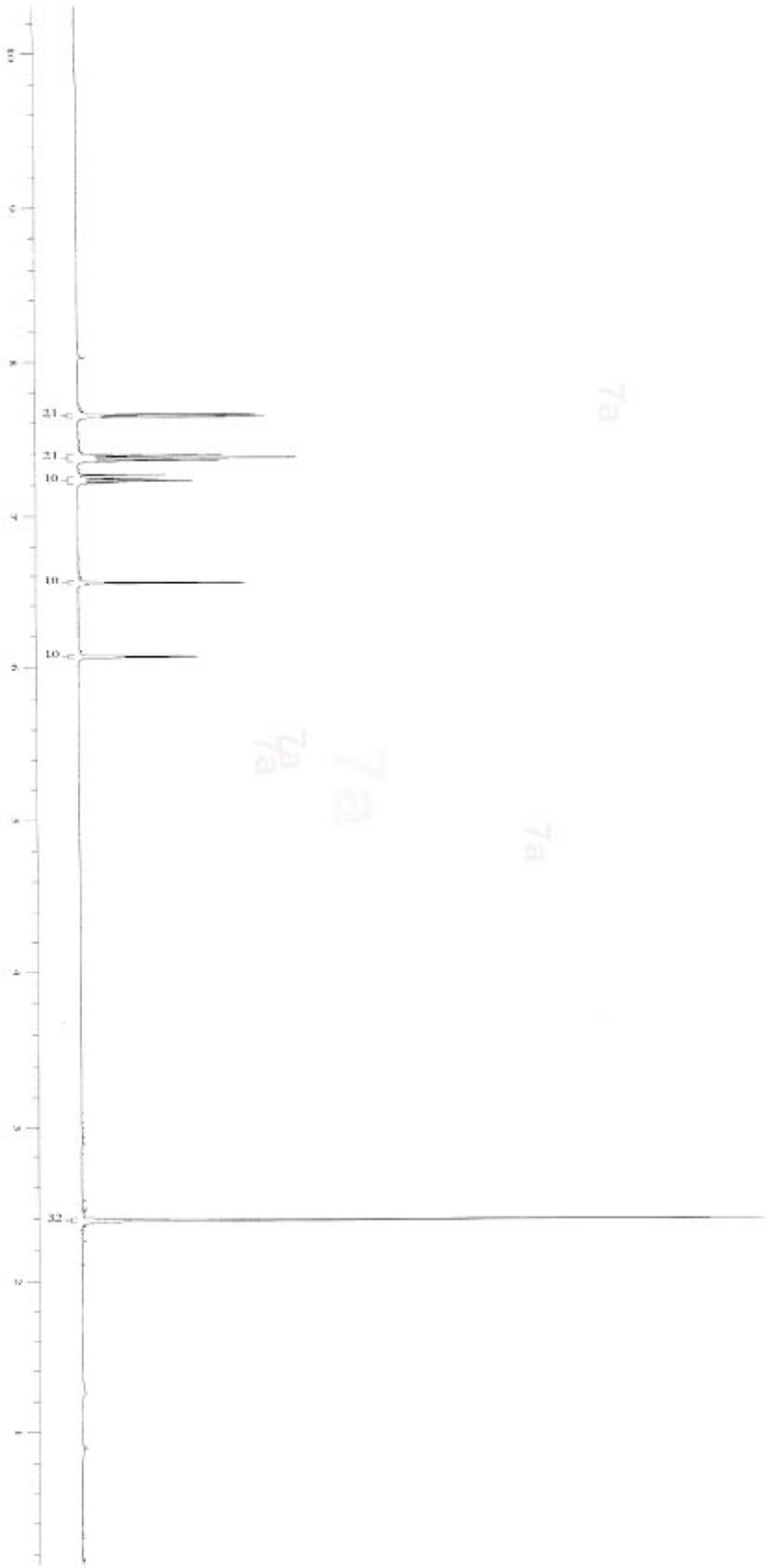
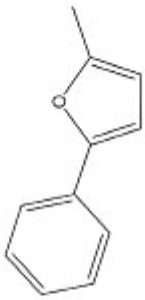
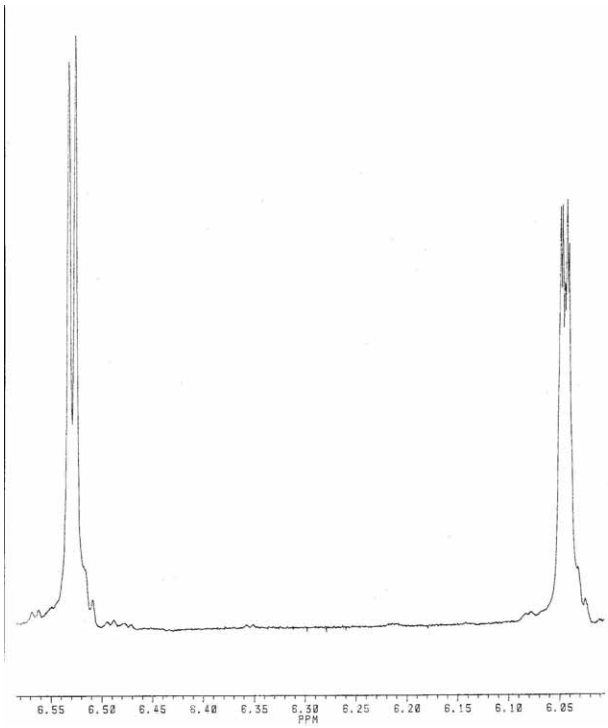
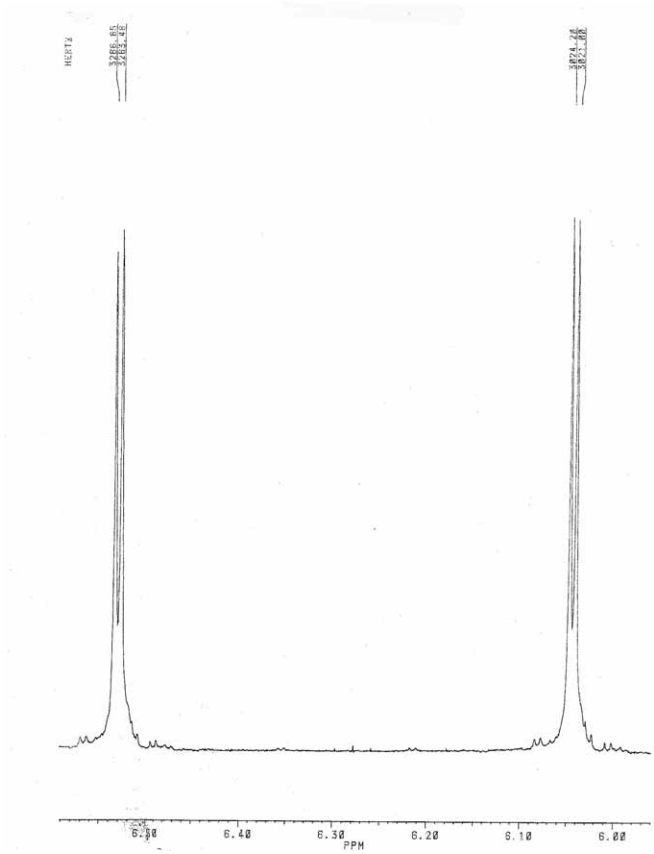


2-Methyl-5-phenylfuran **7a**



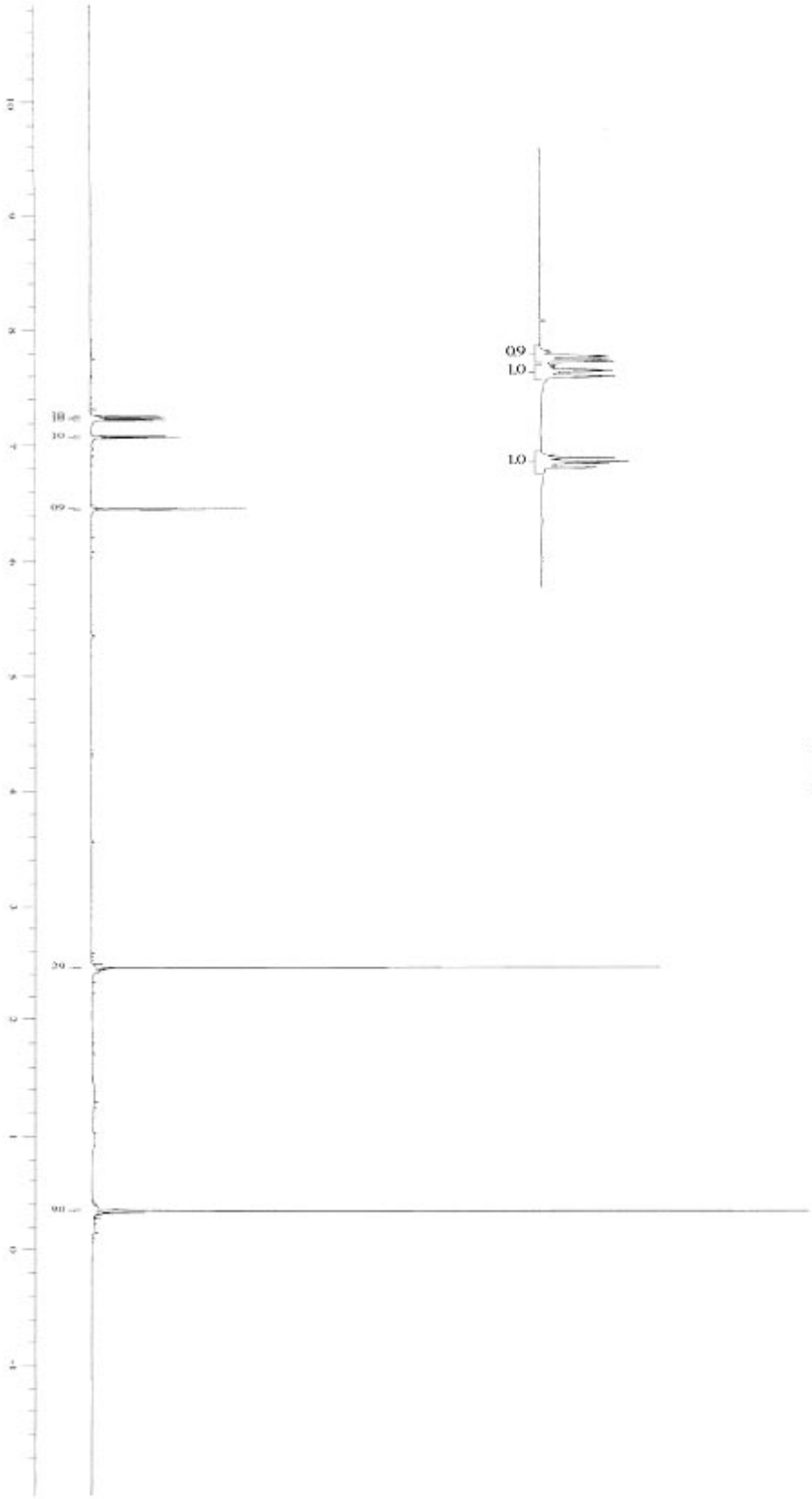


a

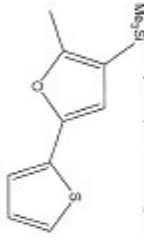


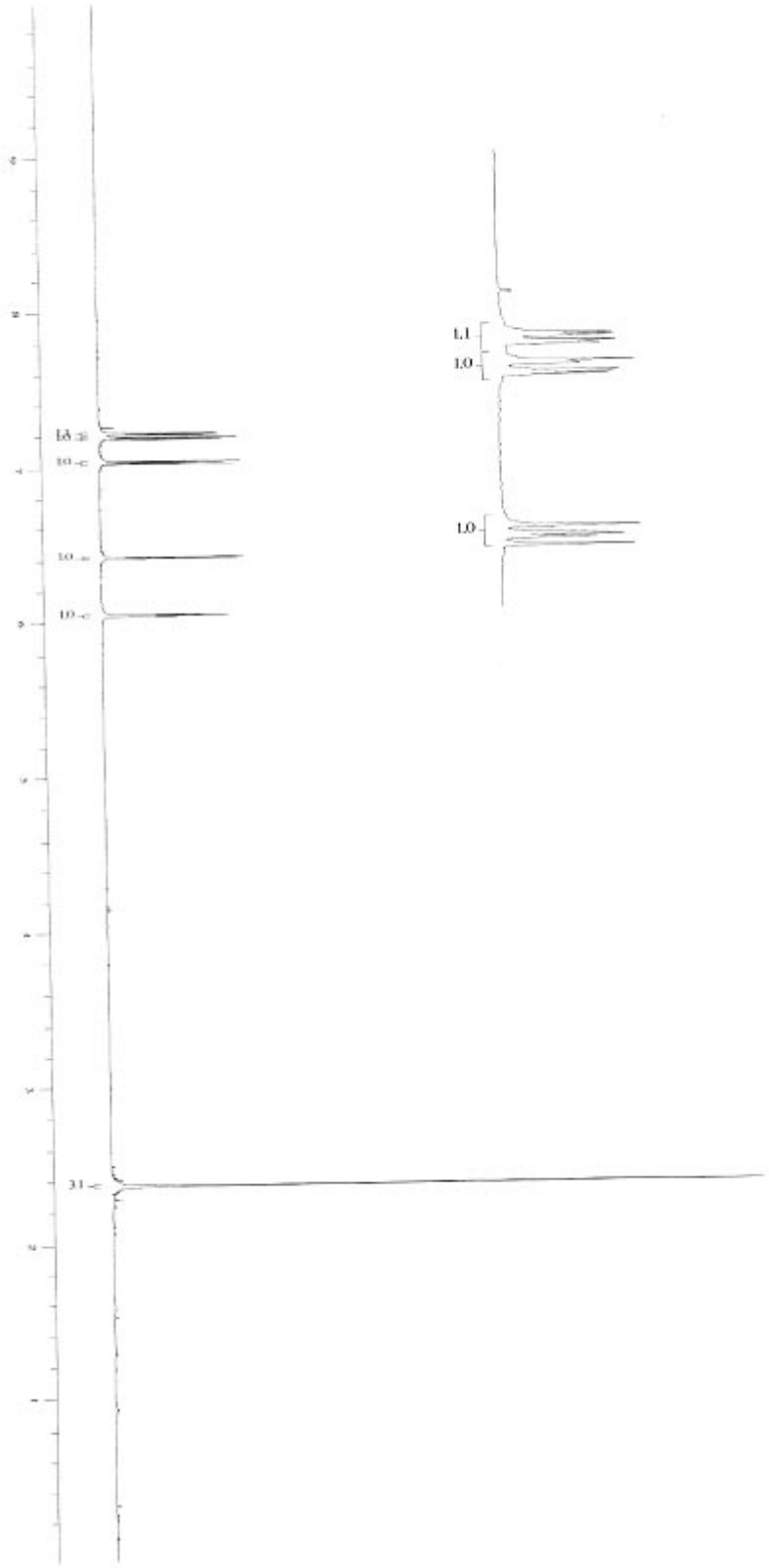
b

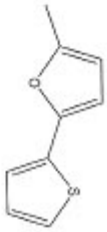
a) Furan proton signals of compound **7a**, showing the long-range coupling between the proton in 3-position (6.05 ppm) and the methyl group.
b) Same region as above with decoupling by irradiation at 2.35 ppm (methyl group). The multiplet at 6.05 ppm is resolved in a doublet.



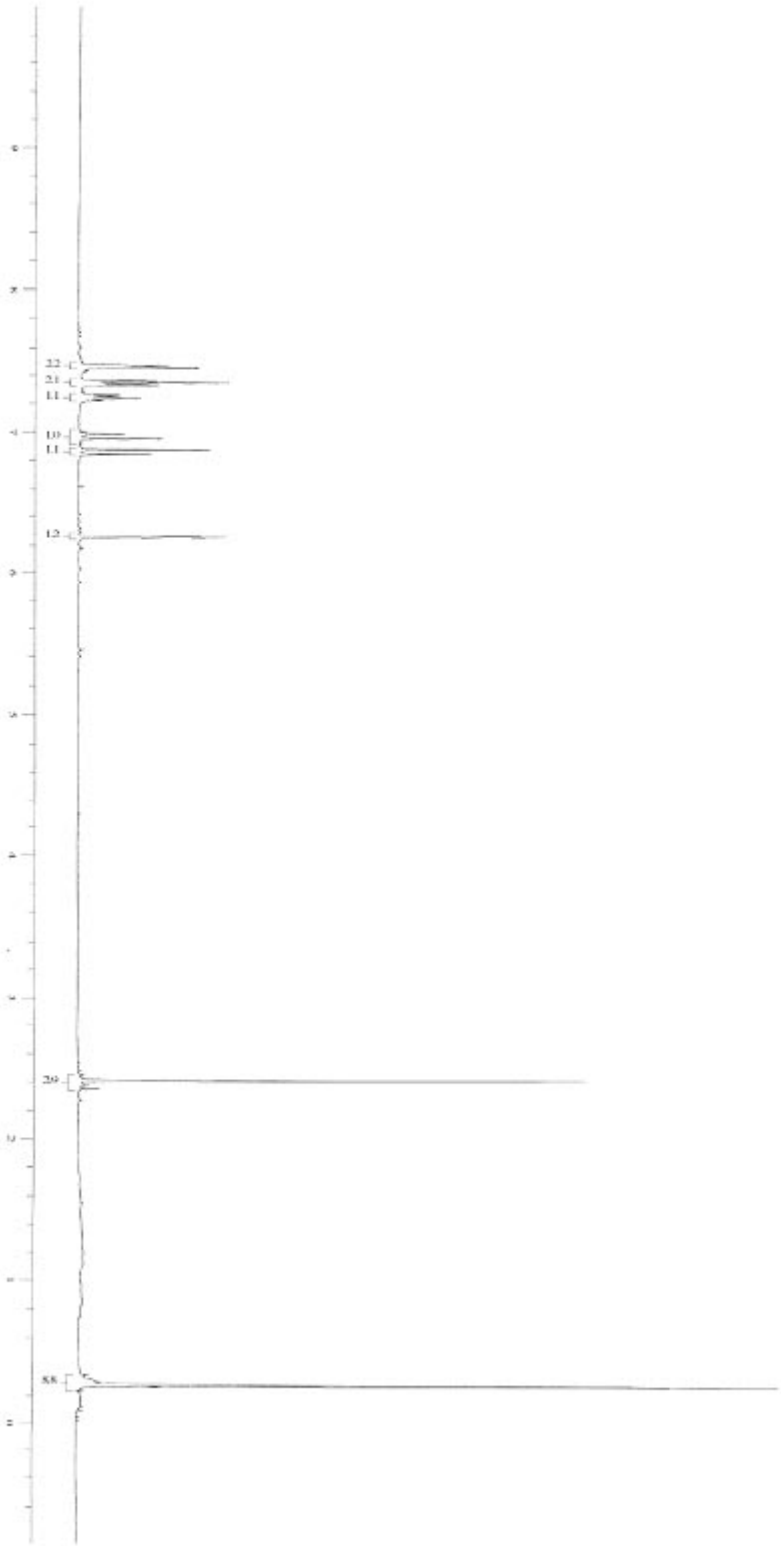
2-Methyl-3-trimethylsilyl-5-thiophen-2-yl-furan **6b**

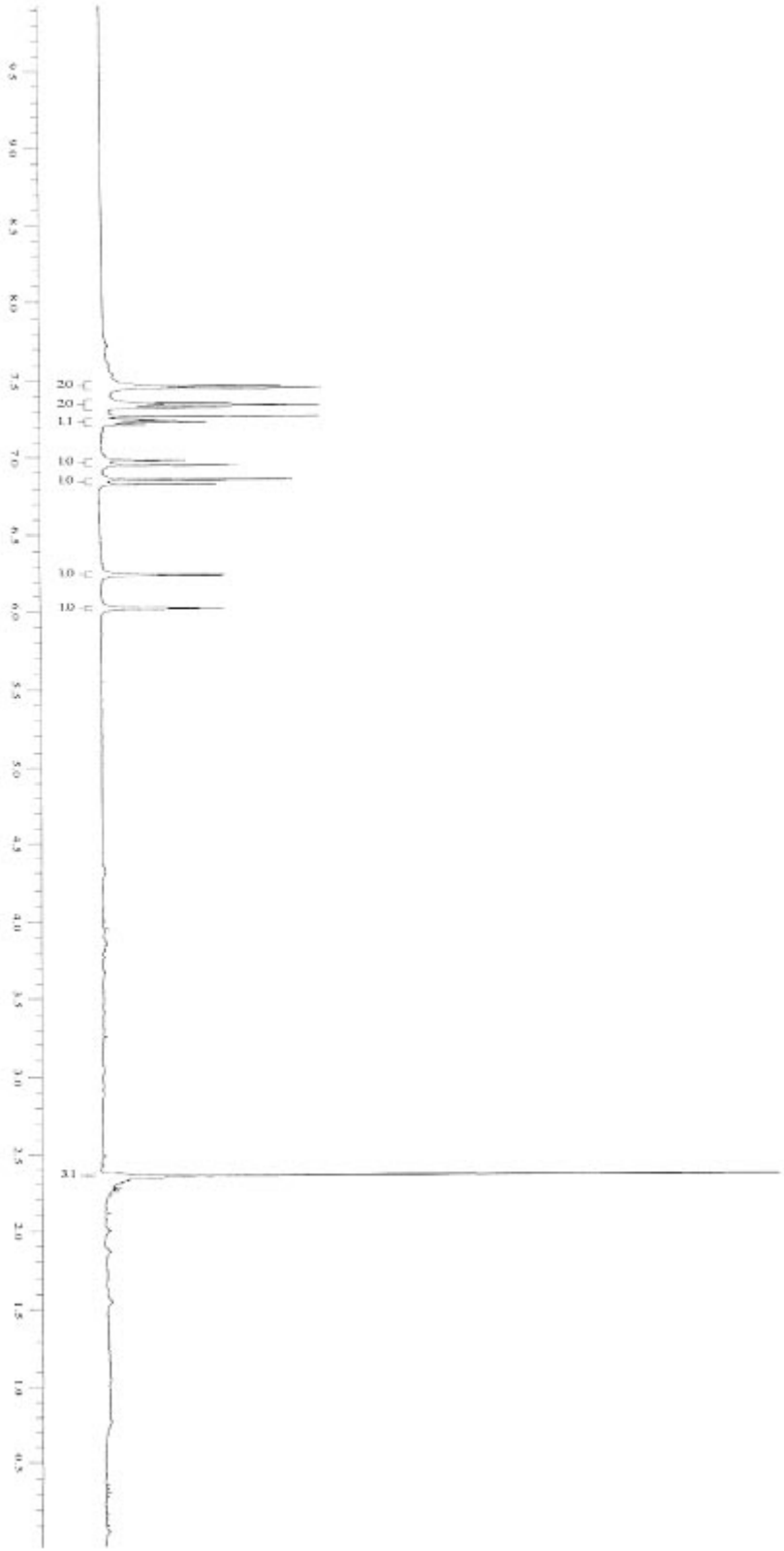




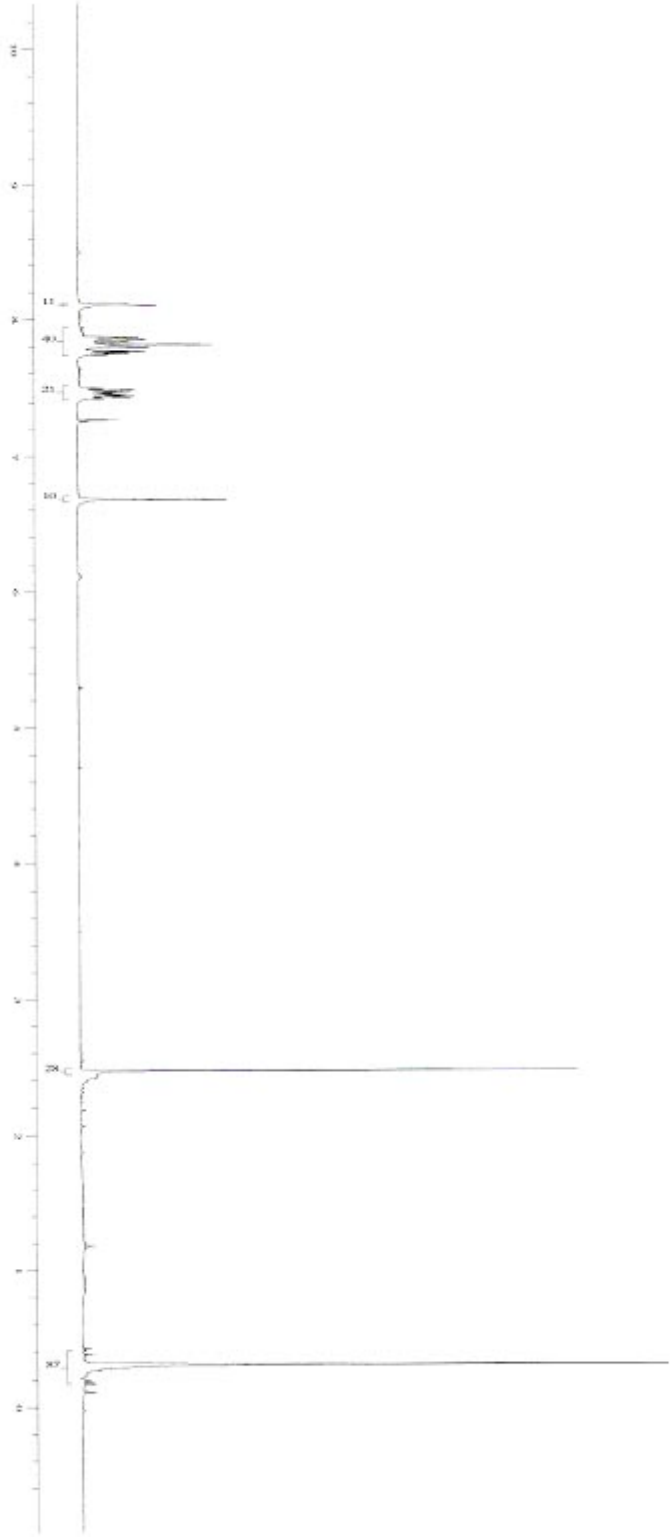


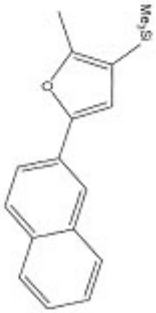
2-Methyl-5-thiophen-2-yl-furan **7b**


Me3Si
(E)-2-Methyl-3-trimethylsilyl-5-styryl-furan 6c
2.2
2.1
1.1
1.0
1.1
1.2
2.9
8.8

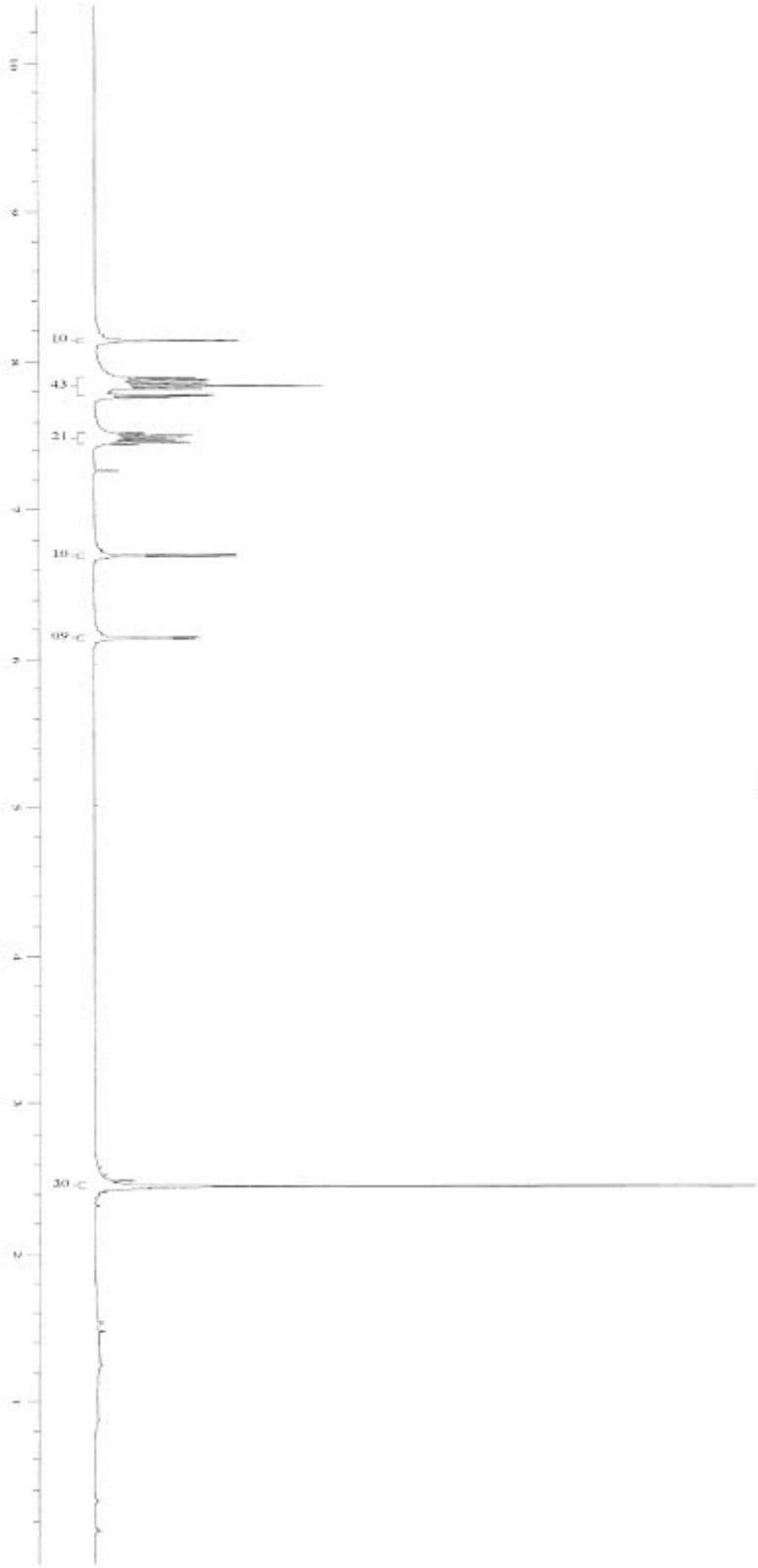


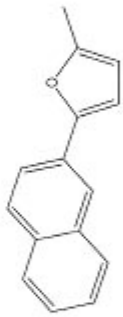
(E)-2-Methyl-5-styryl-furan **7c**



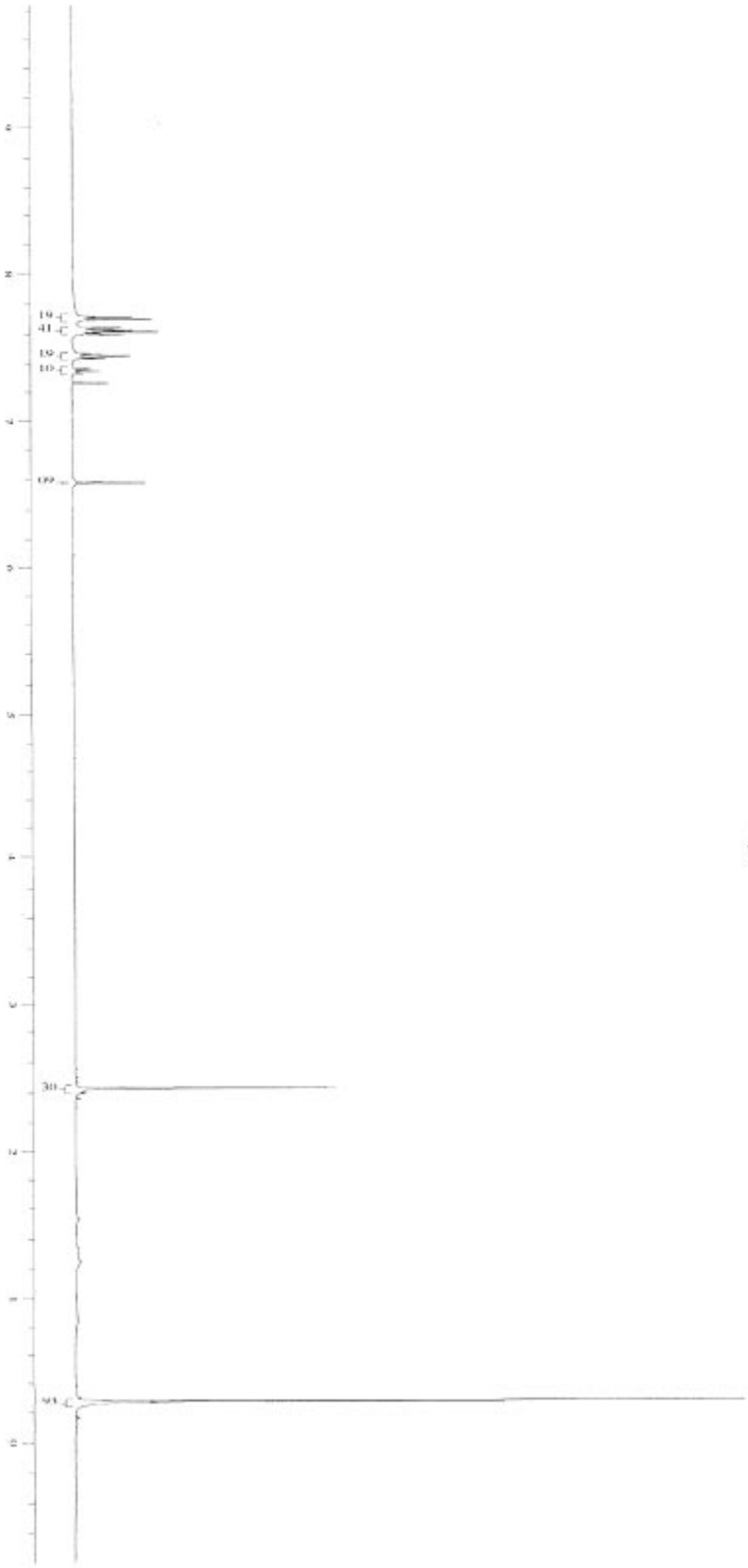


2-methyl-3-trimethylsilyl-5-naphtalen-2-yl-furan **6d**

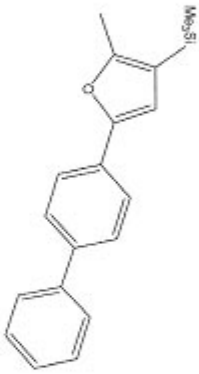


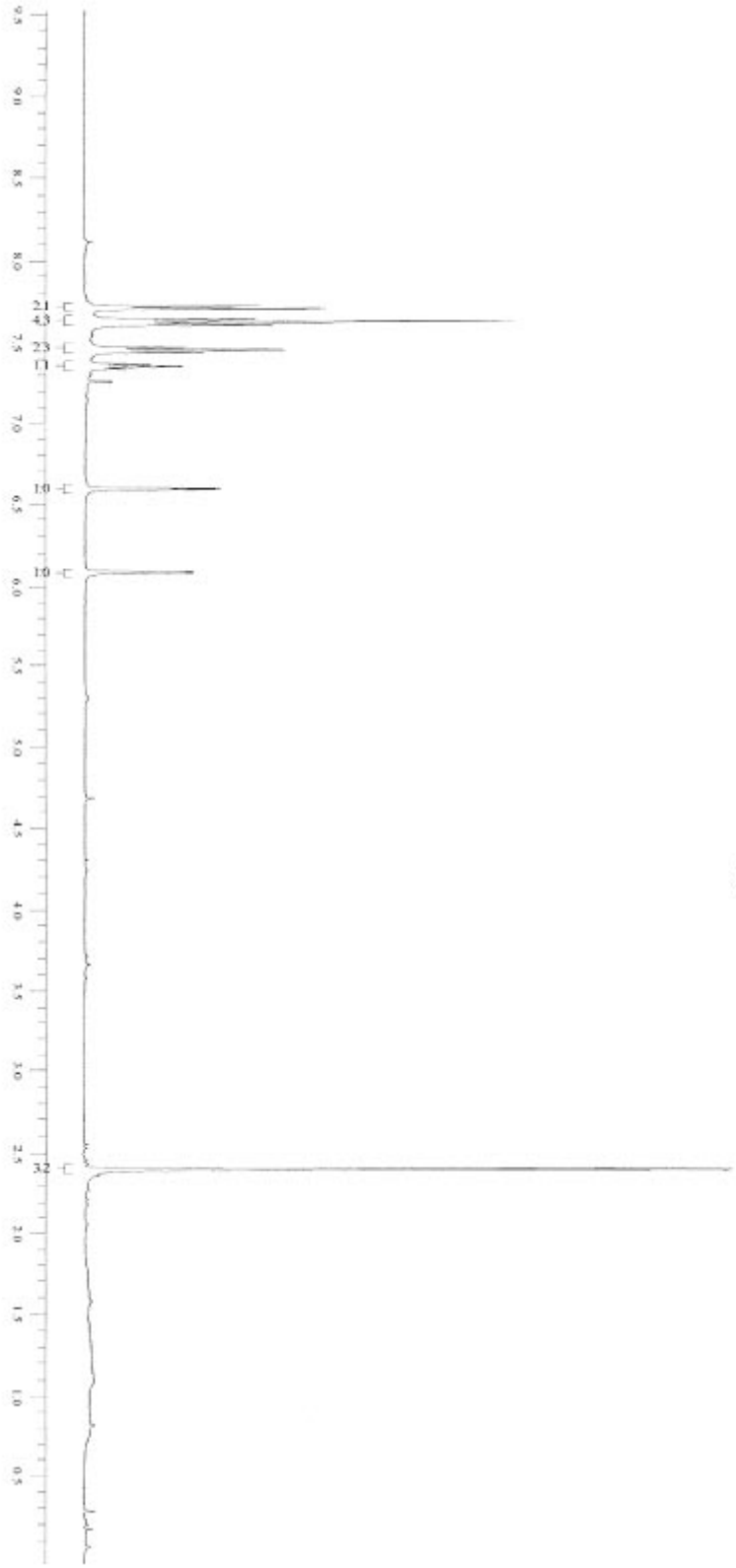


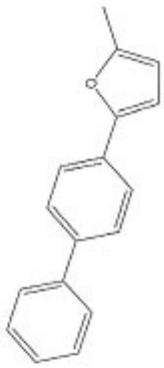
2-Methyl-5-naphthalen-2-yl-furan **7d**



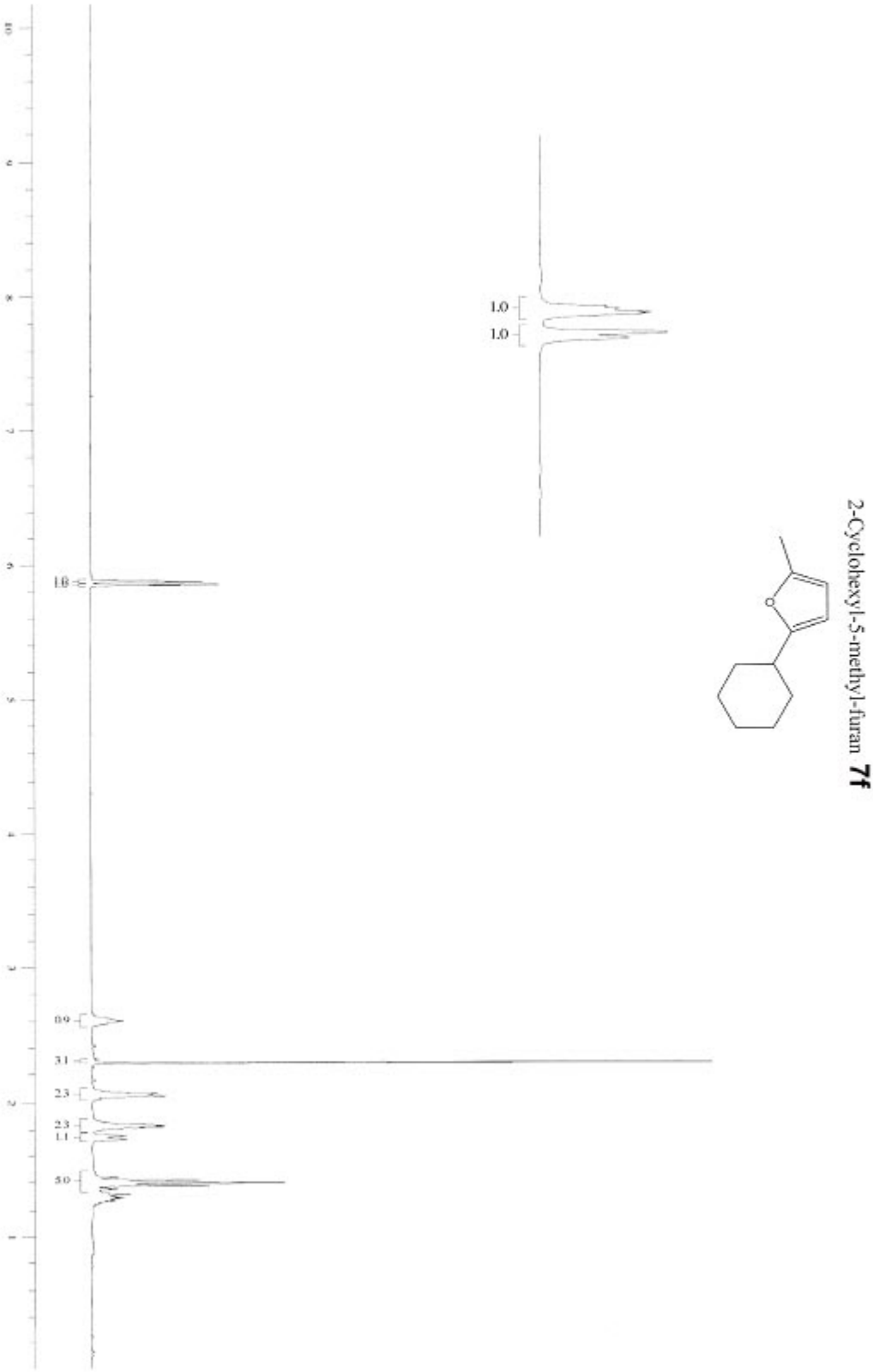
5-Biphen-4-yl-2-methyl-3-trimethylsilyl-furan **6e**

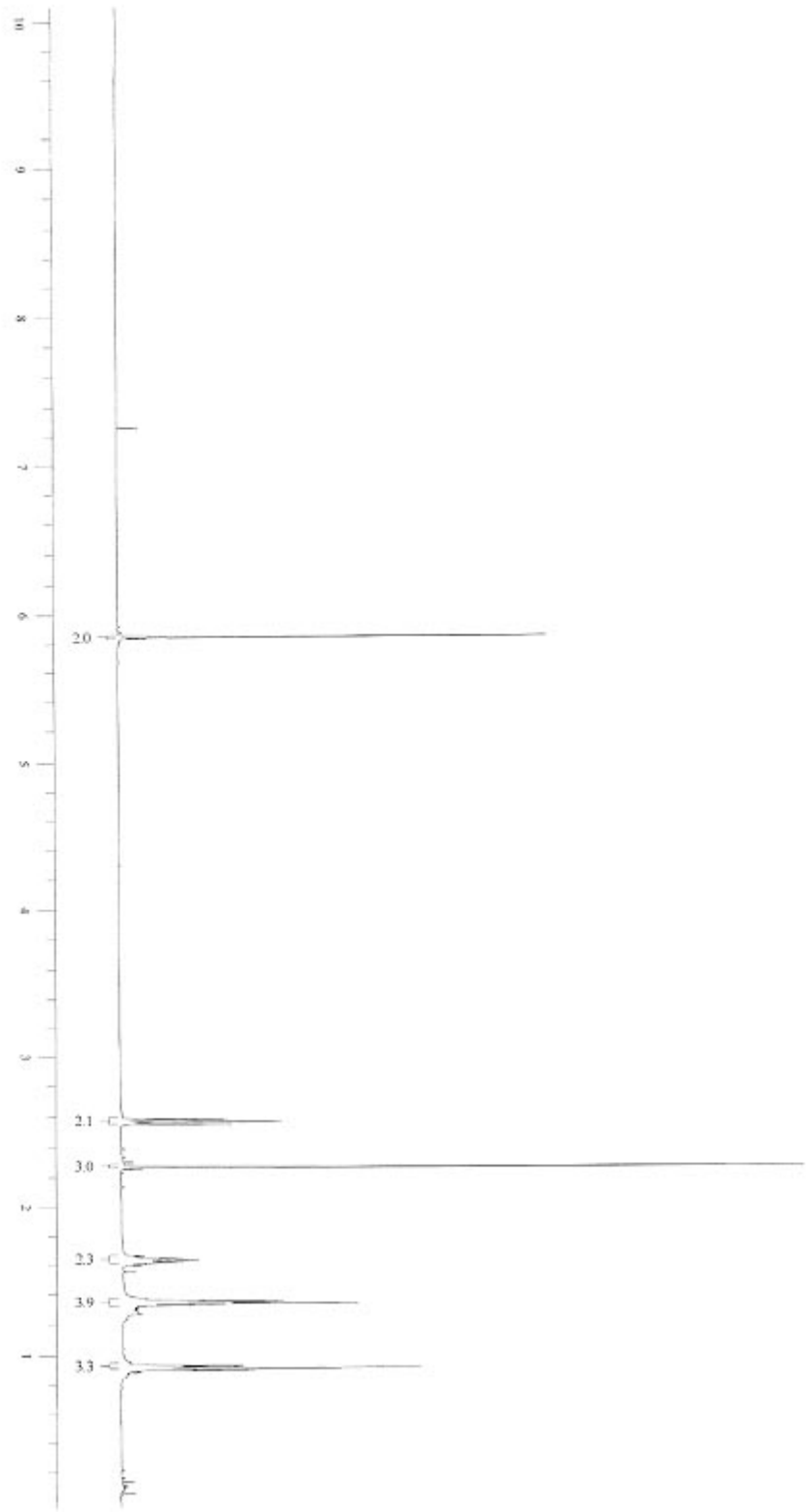






2-Biphen-4-yl-5-methyl-furan **7e**


2-Cyclohexyl-5-methyl-furan 7f
1.0
1.0
1.0
0.9
3.1
2.3
2.3
1.1
5.0



2-methyl-5-pentyl-furan **7g**

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.[vi]

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.

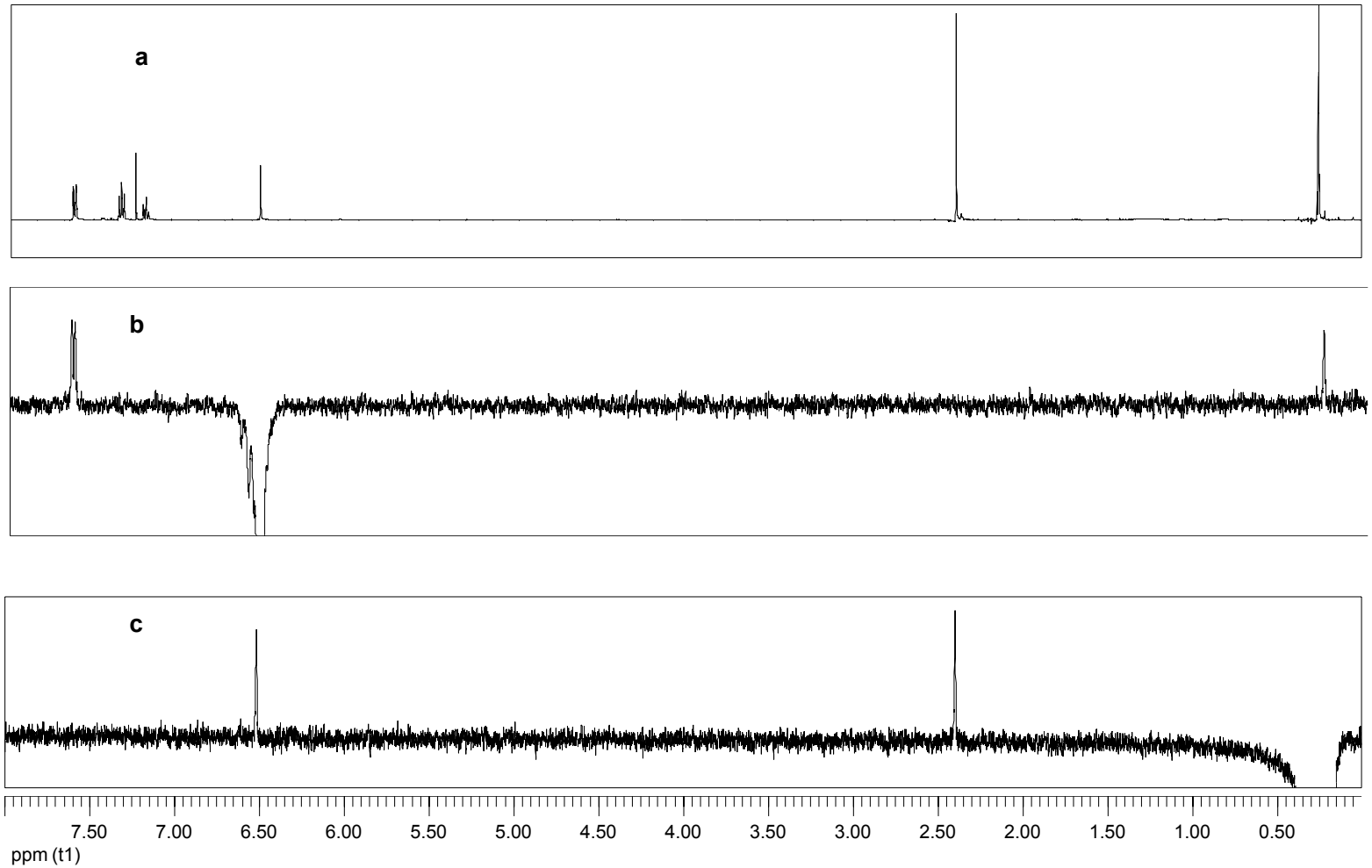


Figure 1. a) ^{1}HNMR spectrum of furan **6a**. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.52$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.26$ ppm.

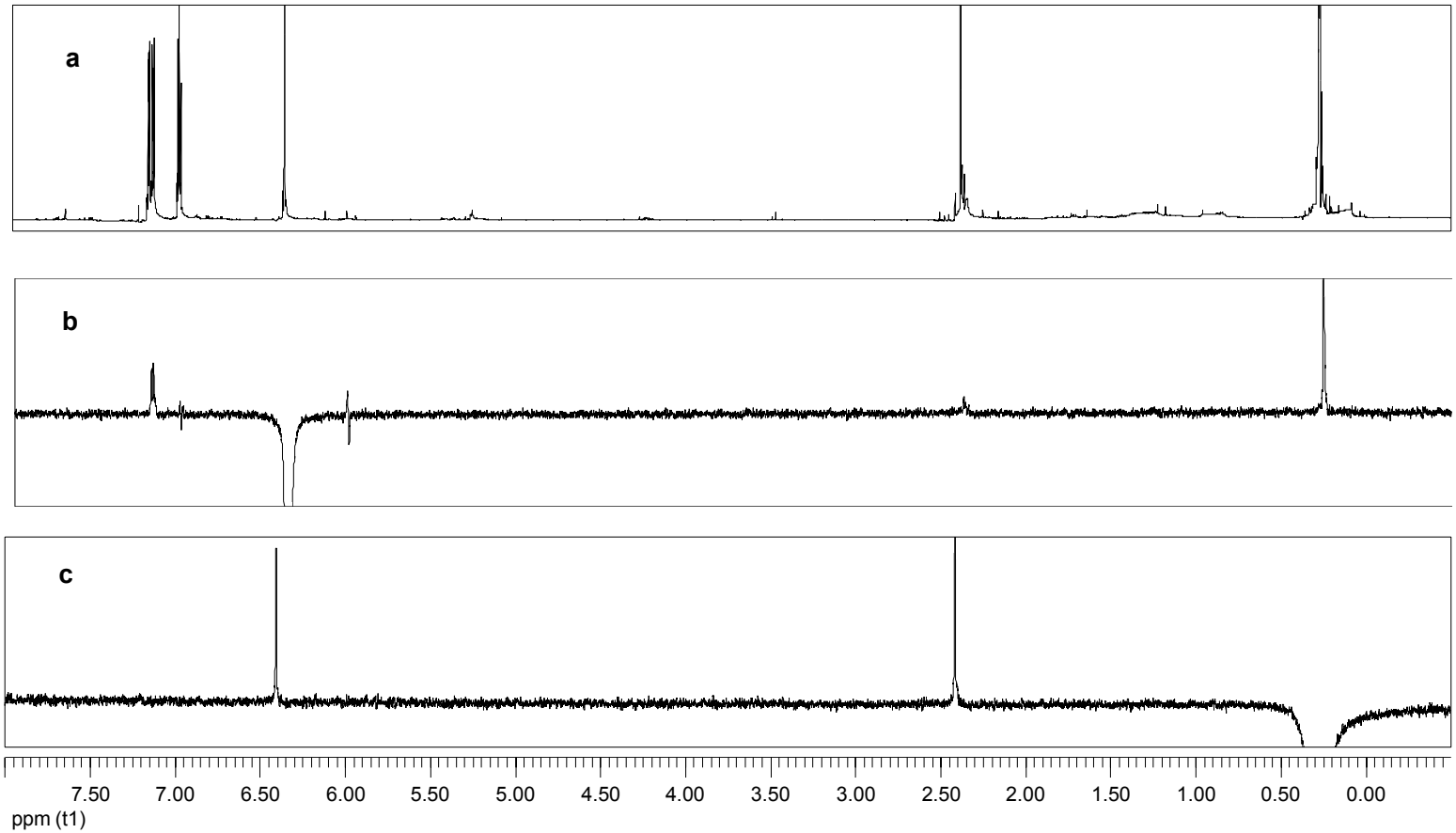


Figure 2. a) ^{1}HNMR spectrum of furan **6b**. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.39$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.28$ ppm.

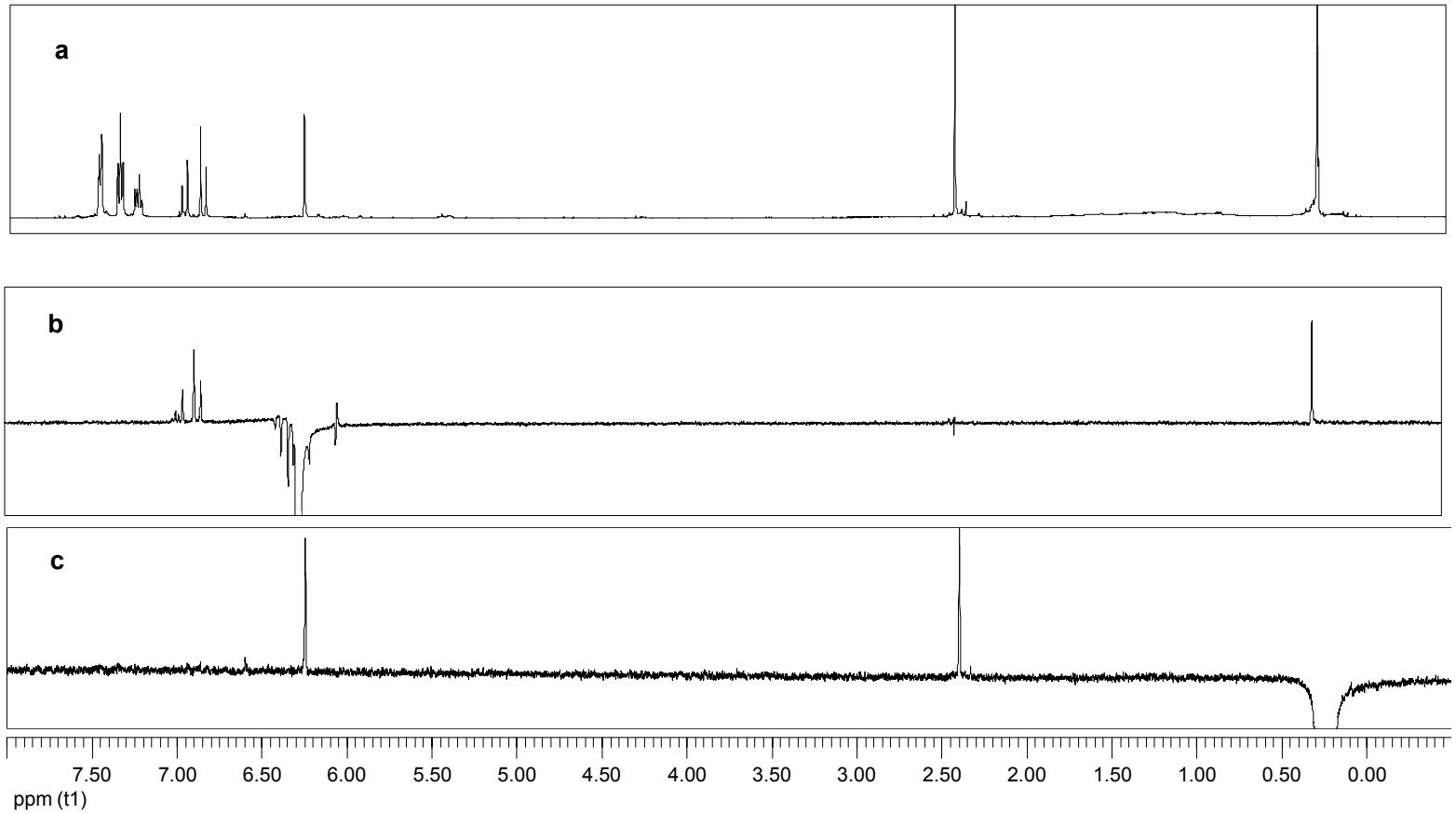


Figure 3. a) ^{1}HNMR spectrum of furan **6c**. b) DPFGSE-NOE spectrum with selective preirradiation at δ = 6.28 ppm. c) DPFGSE-NOE spectrum with selective preirradiation at δ = 0.26 ppm.

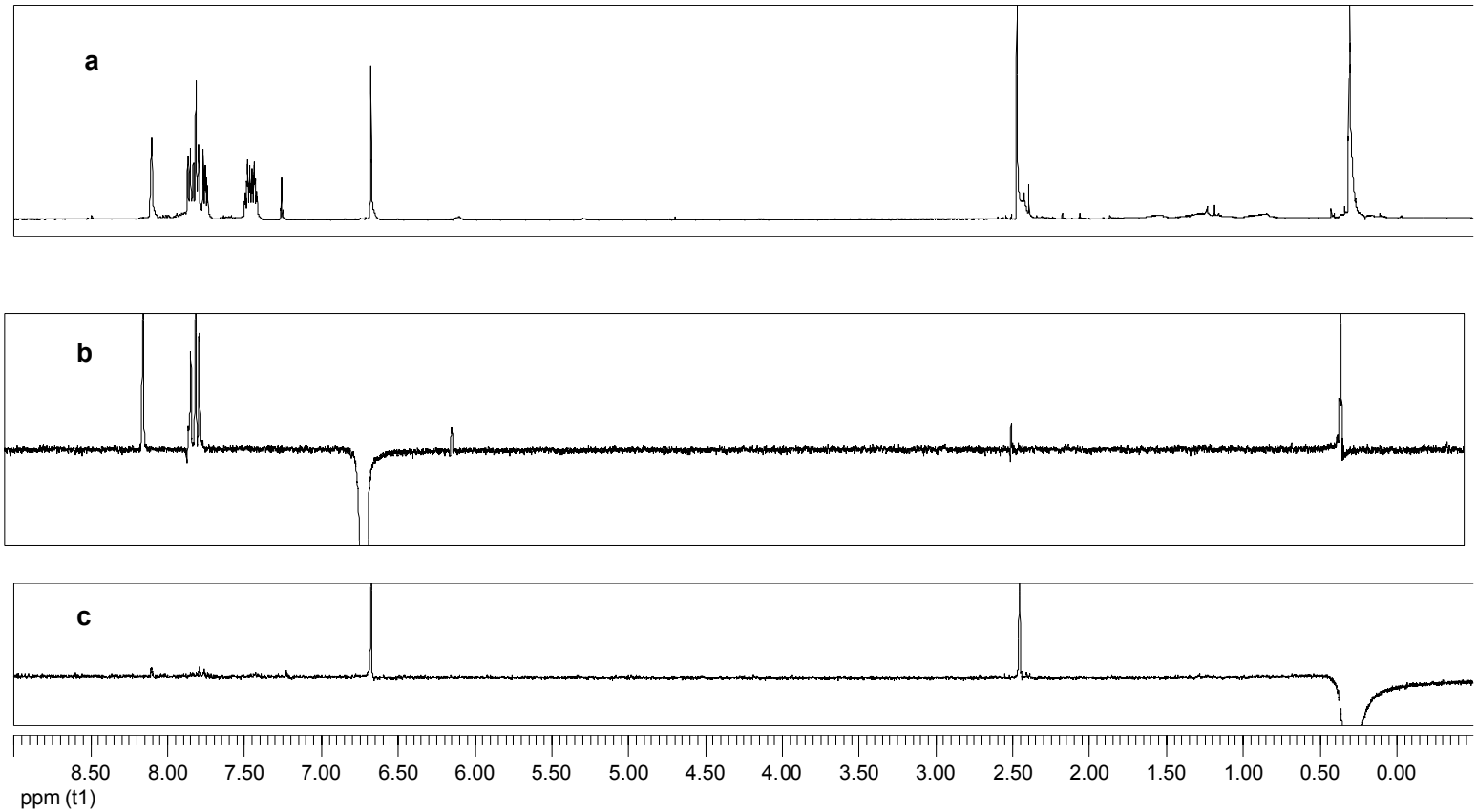


Figure 4. a) ^{1}HNMR spectrum of furan **6d**. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.28$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.26$ ppm.

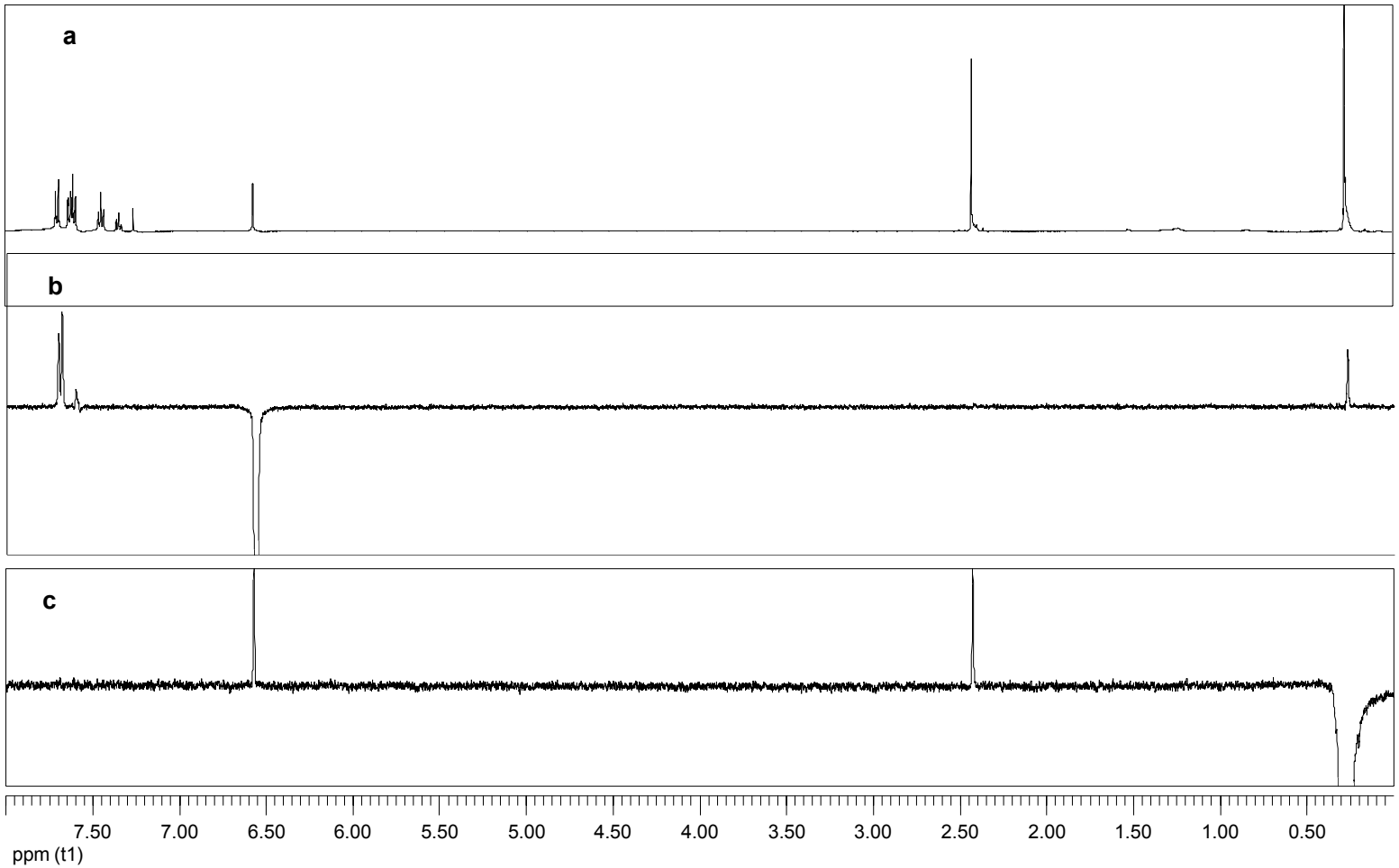


Figure 5. a) ^{1}HNMR spectrum of furan **6e**. b) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 6.57$ ppm. c) DPFGSE-NOE spectrum with selective preirradiation at $\delta = 0.29$ ppm.

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[ii] Alickmann, D.; Fröhlich, R.; Maulitz, A.H.; Würthwein, E.-U. *Eur. J. Org. Chem.* **2002**, 1523.
[iii] Fleming, I.; Morgan, I.T.; Sarkar, A.K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2749.
[iv] Zhou, C. Y.; Chan, P. W. H.; Che, C. M. *Org. Lett.* **2006**, 8, 2, 325.
[v] Tiecco, M.; Testaferri, L.; Tingoli, M.; Marini, F. *J. Org. Chem.* **1993**, *58*, 1349.
[vi] Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: New York, 1989; p 264.