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Synthesis, metallation and nucleophilic reactivity of 2,6-bis(trialkylsilyl)-*4H*-thiopyrans†

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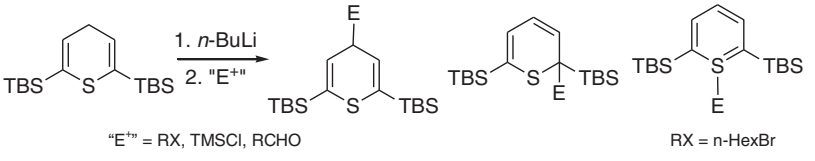
We report herein (i) the synthesis of 2,6-bis(trialkylsilyl)-4H-thiopyrans by thionation-cylisation of 1,5-bis(acylsilanes) and (ii) the lithiation of these thiopyrans and reaction of their lithium salt with various electrophiles. Most reaction led to alkylation at carbons in position 4 and 2, the former being generally more regioselective. Partial reaction at sulfur atom occurred in case of *n*-hexyl bromide. An effective and totally regioselective trimethylsilylation led to a 2,4,6-tris(trialkylsilyl)-4H-thiopyran. Its lithium salt exhibited also interesting properties: Peterson olefination products were formed under reaction with aldehyde, and a stable thiabenzene was effectively obtained with *n*-hexylbromide. The role of the silyl substituents was decisive to explain the particular aspects of the reactivity of these silyl substituted thiopyrans.



Keywords: 4H-thiopyran; thiabenzene; organosilicon; organosulfur; sulfur heterocycles

1. Introduction

Since the first report on the synthesis of *4H*-thiopyran in 1962 (*1*), several papers described the synthesis and the chemistry of analogues variously substituted, generally on positions 2,6 and/or 4. 4H-Thiopyrans may be considered as both hydride donors and proton donors. Thiopyrilium salts are produced under oxidative conditions (Cl_2, I_2, PCl_5, $Ph_3C^+ClO_4^-$) (*2*). Metallation of thiopyrans gives a conjugated nucleophilic intermediate which can be alkylated, acylated or silylated more or less regioselectively (*3–5*). Thiopyrilium salts are themselves good precursors for the preparation of further substituted derivatives by electrophilic addition (*6*).

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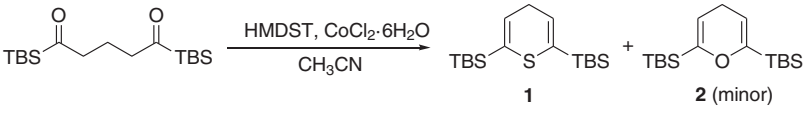
We reported several years ago preliminary results on the synthesis (*7*) and some properties (*8*) of unprecedented 2,6-bis(trialkysilyl)-*4H*-thiopyrans. These compounds were obtained from the corresponding 1,5-bis(trialkylsilyl)pentan-1,5-diones by a two-step *one-pot* procedure, Co(II) catalyzed thionation by hexamethyldisilathiane (HMDST) (*9*) – cyclocondensation, as depicted in Scheme 1 for the bis(*t*-butyldimethylsilyl) derivative **1**. We report herein the optimization of the synthesis of **1**, its metallation and subsequent nucleophilic reactions.



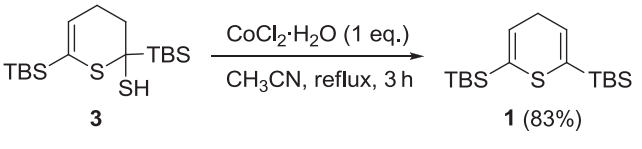
Scheme 1. Synthesis of 2,6-bis(*t*-butyldimethylsilyl)-*4H*-thiopyran **1** (*7*).

2. Results and discussion

2.1. *Optimization of the synthesis of 2,6-bis(trialkylsilyl)-4H-thiopyrans*

The study of the chemical properties of bis(trialkylsilyl)-4H-pyrans required their synthesis at a multigram scale. As reported in our preliminary paper (*7*), a minor amount of bis(trialkyslyl)-*4H*-pyran **2** was present as a by-product beside the expected thiopyran analogue. The difficult separation was a drawback we had to overcome before scaling up the reaction. The occurrence of 4H-pyran may be explained either by the acidic medium due to the presence of Co(II) salt and to the increasing temperature because of the exothermicity of the reaction. 1,5-Bis(acylsilanes) are known to give intramolecular reaction in acidic medium or by heating to give 2,6-(trialkylsilyl)-*4H*-pyrans (*10*).

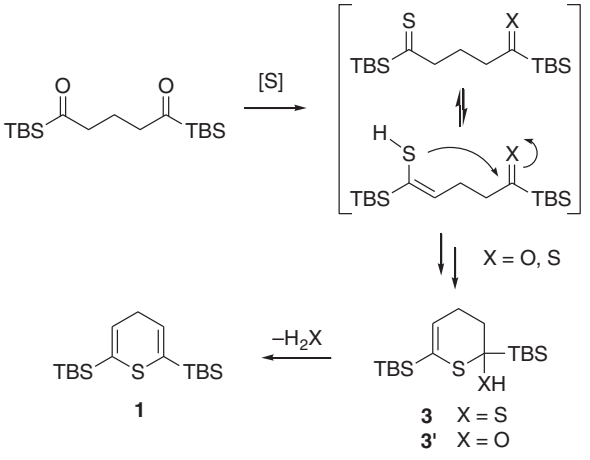
The first attempt to scale up the preparation of 2,6-bis-(*t*-butyldimethylsilyl)-*4H*-thiopyran **1** under the preliminary reported conditions allowed the isolation of a considerable amount of the intermediate dithiolactol type compound **3** (such an intermediate had also been observed in case of the preparation of the homologous 2,7-bis(trialkylsilyl)-4,5-dihydrothiepine, see (*7*)). The intermediate character of **3**, which has been isolated and characterized, was corroborated by its conversion to the corresponding thiopyran by refluxing an acetonitrile solution of **3** under similar Co(II) salt activation (Scheme 2). The overall synthetic pathway is depicted in Scheme 3, where compound **3′**, the oxygenated analogue of **3**, was also mentioned as a possible intermediate, although it has not been identified in the crude mixture.



Scheme 2. Transformation of intermediate **3** into *4H*-thiopyran **1**.

Finally, the synthesis was improved by adding slowly the catalyst to reactants and keeping the reaction at room temperature for one night. The black material formed during the reaction was removed by filtration before a further treatment with fresh cobalt catalyst in acetonitrile. Evaporation and filtration of the residue through a pad of silica using diethyl ether as eluent, gave compound **1** (yield: 83%) as 97% pure material (contaminated by 3% of *4H*-pyran).

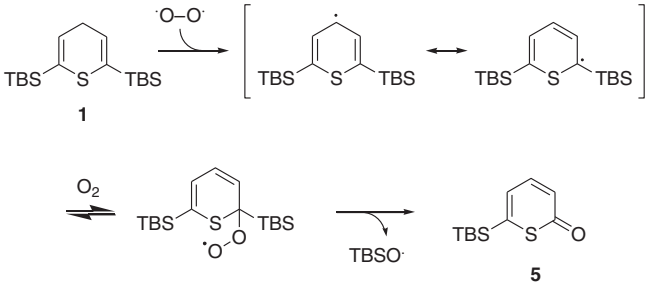
Similarly, the bis(trimethylsilyl) derivative **4** was prepared (see Section 4). The yield was lower (54%) probably because of its higher volatility.



Scheme 3. Overall synthetic pathway of *4H*-thiopyran **1**.

2.2. *Stability of 2,6-bis(trialkysilyl)-4H-thiopyrans*

Compound **1** was unstable and turned to brown oil when exposed to air. It was stored at −10°C, in the dark and under argon after three vacuum-argon cycles. Nevertheless, the material became brown in about three weeks. A filtration through a pad of silica gel using hexanes as eluant usually allows to obtain a colorless or pale yellow oil while the brown material stays on the top of the silica pad. After filtration, enough amount of this brown material was recovered for analysis (elution with diethylether). The very main component of this material proved to be the oxidation product **5**, which was characterized after a further purification by preparative thin layer chromatography (TLC). A plausible mechanism explaining this oxidation process is depicted in Scheme 4.



Scheme 4. Possible mechanism for the formation of compound **5**.

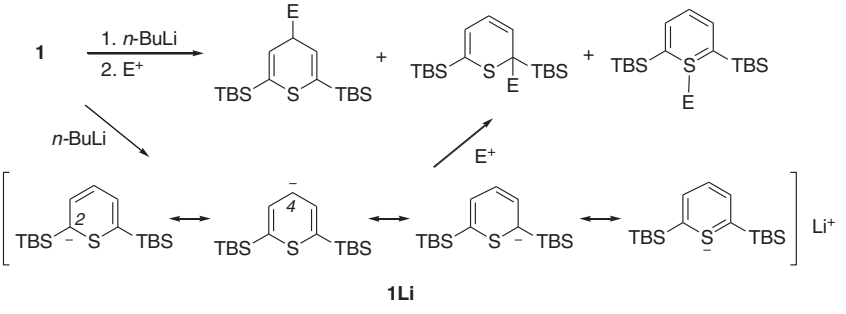
2.3. *Lithiation and nucleophilic reactions*

Treatment of 2,6-substituted-*4H*-thiopyran with a strong base was expected to give a conjugated species with several reaction sites. Usually C2 and C4 are concerned by such reaction. According to the literature, the regioselectivity depends on both substituents and electrophilic reactant. Unsubstituted lithiated *4H*-thiopyran reacted selectively with benzylchloride at C4 position (*3*) whereas alkylation with cyclohexylbromide led to a 15/85 mixture of C4 and C2 branched compounds (*4*). Similarly, after treatment with $NaNH_2$ or *t*-BuLi, 2,4,6-triphenyl-*4H*-thiopyran and -2*H*-thiopyran are methylated, benzylated or acylated selectively at C4, whereas deuteration occurred exclusively

at C2. In contrast, lithiated 2,6-diphenyl-*4H*-thiopyran was deuterated selectively at C4. The same regioselectivity was observed for trimethylsilylation (*5*).

Thus, the precise prediction of the alkylation of deprotonated 2,6-bis(trialkylsilyl)-4H-thiopyrans was not obvious and justified this exploratory study. Moreover, although they have never been mentioned with this type of reaction, products resulting from alkylation at sulfur could theoretically be expected, as proved the results we are reporting here (vide supra). Such a reaction would lead to compound which may be considered as sulfur ylide, even if they are usually presented as thiabenzenes (*11*). Thiabenzenes are formed from reaction of thiopyrillium salts with nucleophiles. They are usually unstable at room temperature, and their observation is favored when the ylide carbon bears a stabilizing group like aryl or carbonyl one. In our case, the presence of the trialkylsilyl group could play such a role.

n-Butyllithium was used as a base and a variety of electrophilic reactants were investigated. The lithium salt **1Li** was formed instantaneously at 0°C, giving a deep red solution, a color which seems to corroborate the contribution of a carbon–sulfur double bond in the canonical forms of the intermediate anion. The plausible pathways are depicted in Scheme 5.



Scheme 5. Tandem lithiation of *4H*-thiopyran **1** – nucleophilic substitution.

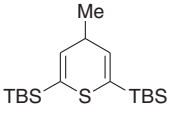
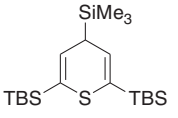
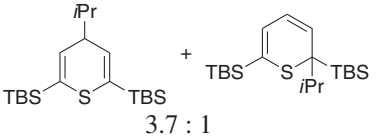
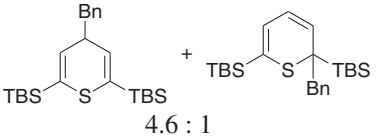
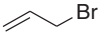
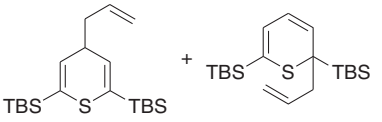
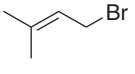
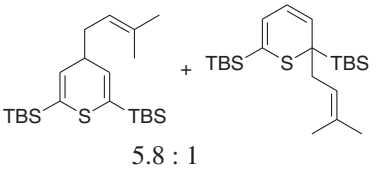
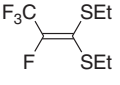
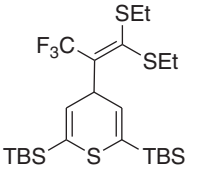
2.3.1. *Reaction of lithium salt **1Li** with halogenated reagents*

The results obtained by reaction of **1Li** with halogenated derivatives are summarized in Table 1. The regioselectivity of the reaction of the lithium salt **1Li** with halogenated derivatives depends on the reactant structure. Methylation and trimethylsilylation occurred exclusively at the 4 position, giving almost quantitatively compounds **6** and **7**, respectively (Table 1: Entries 1 and 2). Similarly, protonation of **1Li** occurred exclusively at C4 on acidic hydrolysis. A mixture of two isomers were produced from isopropyl-(**8a** + **8b**), benzyl-(**9a** + **9b**), allyl-(**10a** + **10b**) and prenyl bromide (**11a** + **11b**) (Entries 3–6). The yields are moderate and the 4-substituted-4H-thiopyran is the major isomer except for allyl derivative where the reaction was quantitative and led to the 2-allyl thiopyran **10b** as the major isomer. This particular behavior could be due to the contribution of a sigmatropic rearrangement subsequent to either 4-allyl- or S-allyl substituted derivatives.

The product **12** reported in Entry 7 results from the regioselective reaction of **1Li** with a perfluoroketene dithiocetal. This type of compound reacts with various electrophiles according to an addition–elimination process leading to the substitution of the β fluorine (*12*).

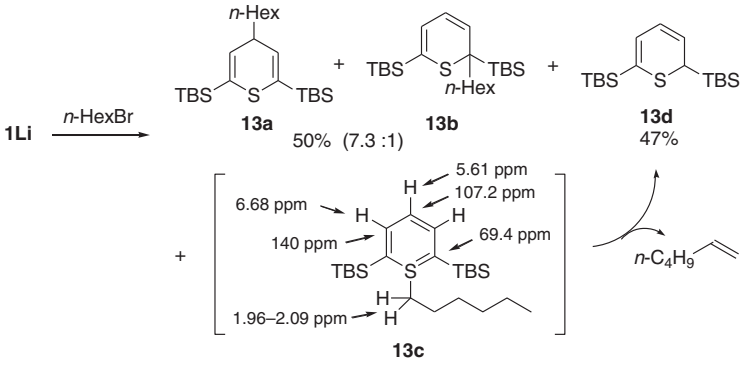
The reaction between **1Li** and hexyl bromide is of particular interest (Scheme 6). Whereas a thiabenzene type intermediate was simply mentioned as a hypothesis in the allylation case, *S*-alkylation proved to contribute to the hexylation products. In addition to the product alkylated at position 4 (**13a**) and 2 (**13b**), a significant amount of the thiabenzene product **13c** was detected. Compound **13c** survived to aqueous work up. It was stable enough to be observed via ^{1}H-NMR but decomposed in $CDCl_3$ solution. The selected nuclear magnetic resonance (NMR) data reported in

Table 1. Reaction of **1Li** with halogenated derivatives.

Entry	R-X		Product(s)	Yield (%)[a]
1	Me-I	**6**		98
2	Me_3Si-Cl	**7**		99
3	*i*Pr-Br	**8a** + **8b**	 3.7 : 1	50
4	Bn-Br	**9a** + **9b**	 4.6 : 1	56
5		**10a** + **10b**	 1 : 1.8	99
6		**11a** + **11b**	 5.8 : 1	39
7		**12**		70

Note: [a]Isolated yield.

Scheme 6 are consistent with those reported in the literature for thiabenzenes (*11h*). Separation of the reaction components over silica gel chromatography gave the *C*-alkylation products **13a** and **13b**, whereas **13c** was totally converted to the 2*H*-thiopyran **13d**, isomer of the starting material. This transformation could be explained by a sequential or concerted intramolecular elimination (Scheme 6).



Scheme 6. Reaction of **1Li** with *n*-hexyl bromide.

2.3.2. *Reaction of lithium salt **1Li** with carbonyl derivatives*

Two types of products could be expected from the reaction of the lithium salt **1Li** with carbonyl derivatives. Besides addition via the position 4, reaction at carbon 2 bearing the silyl group could lead to an addition or a Peterson olefination product. The results obtained from various carbonyl compounds are summarized in Table 2.

All compounds considered in this study reacted selectively at position 4. Reaction with pivalaldehyde and benzaldehyde gave the alcohol adducts **14** and **15**, respectively, in good to excellent yields (Entries 1 and 2). With a view to a possible approach to a highly conjugated compound, terephtalaldehyde was reacted in similar conditions and gave the diol **16** (Entry 3). Unfortunately, attempts to induce dehydration via mesylation or tosylation failed. A conjugate addition took place using butenolide as reactant giving the lactone derivative **17** (Entry 4). The last experiment with benzophenone followed a different pathway (Entry 5). The bis-*4H*-thiopyran **18** was formed in high yield. The most probable pathway consists in an electron transfer from the anion to benzophenone, giving a highly stabilized radical which dimerizes (Scheme 7). Similar coupling was reported for related compounds (*13*).

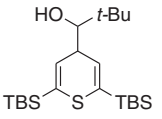
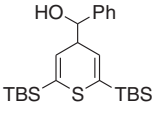
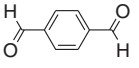
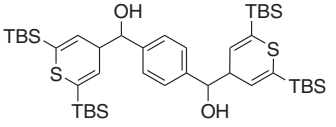
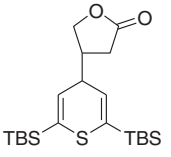
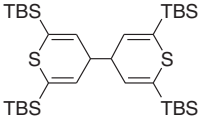
2.3.3. *Metallation and nucleophilic reactions from tris(trialkylsilyl)-4H-thiopyran **7***

Further stabilization of the lithium salt anion by a third trialkysilyl group in the 4 position prompted us to consider the reactivity of bis(t-butyldimethylsilyl)-4-trimethylsilyl-*4H*-pyran in similar conditions. The lithium salt **7Li** reacted with benzaldehyde as electrophile, but the reaction did not stop at the addition step. A subsequent Peterson type elimination took place giving almost quantitative yield of an equimolar mixture of the benzylidene derivatives **19** and **20** (Scheme 8).

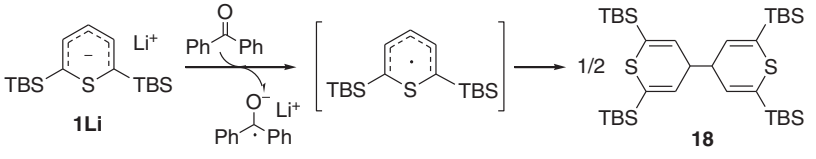
As observed with the analogue **1Li**, the salt **7Li** reacted with *n*-hexyl bromide according to a particular pathway, giving the thiabenzene **21** (Scheme 9). The NMR data (reported in the molecular structure **21**) are consistent with reported data for thiabenzene structures with, in particular, the signal at 64.2 ppm for ylidic carbon 2 (*11h*). The presence of a third trialkylsilyl group in conjugate position undoubtedly favored the effective formation of **21** and its stabilization.

It is worth noting that few thiopyran derivatives appeared to be not very stable, turning to black especially when exposed to the day light at room temperature, leading to unidentified degradation products.

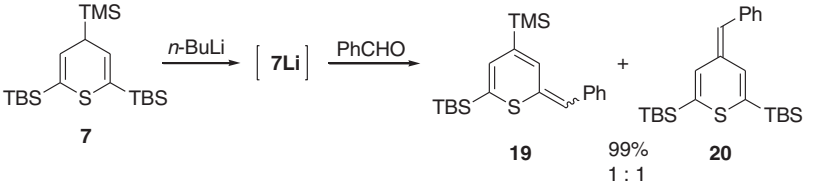
Table 2. Reaction of **1Li** with carbonyl compounds.

Entry	Carbonyl compound		Product	Yield (%)[a]
1	*t*-Bu-CHO	**14**		98
2	Ph-CHO	**15**		75
3		**16**[b]		65
4		**17**		53
5	Ph-CO-Ph	**18**		83

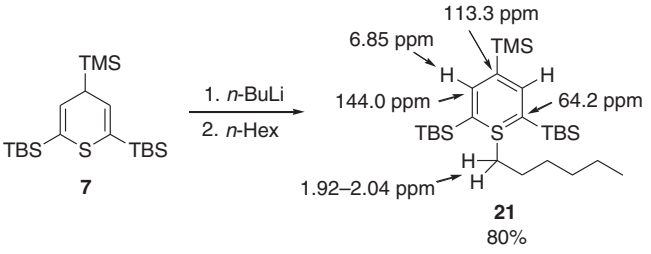
Notes: [a]Isolated yield.
[b]Mixture (1:1) of diastereomers.



Scheme 7. Possible pathway for the formation of dimer **18**.



Scheme 8. Reaction of **7Li** with benzaldehyde.



Scheme 9. Reaction of **7Li** with *n*-hexyl bromide.

3. Conclusion

2,6-Bis(trialkylsilyl)-4H-thiopyrans constitute a new and interesting class of sulfur heterocycles. Their metallation converts them to a nucleophile which behaves most often like classically substituted 4H-thiopyrans. Thus, simple alkylation reactions proceed at positions 2 and 4 (mainly). On the other hand, in some cases, the reaction follows a particular way, due to the stabilizing effect of silicon, as for the easy formation of thiabenzenes, or to its oxophilicity, as for the occurrence of Peterson process on addition to aldehydes. As expected, this effect is enhanced by the presence of a third silyl group in position 4. Whereas thiabenzenes are generally the result of addition of a nucleophile on a pyrilium salt, the 2,6-bis- and 2,4,6-tris(trialkylsilyl) substituted thiopyrans may be converted into thiabenzene via reaction of their lithium salt with *n*-hexyl bromide.

4. Experimental section

4.1. *General remarks*

Reagents and solvents were used without further purification. All reactions were monitored by TLC with Merck silica gel 60 F254 0.25 mm plates and revealed using ultra violet light. Purification of 4H-thiopyran derivatives was carried out using flash silica gel column chromatography (70–200 μm). The purity of synthetic products was established by NMR spectroscopic data and mass spectra (MS) analysis. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-250 spectrometer, in deuteriochloroform if not mentioned. Chemical shifts are reported as δ in units of parts per million (ppm) relative to internal standards: tetramethylsilane (δ 0.00 ppm) or chloroform (δ 7.27 ppm) for ^{1}H, 77.0 ppm (central line) for ^{13}C NMR spectra. Coupling constants are reported in Hertz (Hz), multiplicities are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broaded. Low resolution MS were obtained with a mass spectrometer coupled with gas chromatography (GC-MS) Thermoquest Trace GC 2000 series, in electronic impact (EI) mode. High resolution mass spectra (HRMS) were recorded on a Q-TOF Micromass spectrometer in positive electrospray mode (ES^{+}, EC 30V).

4.2. *Typical procedure for the synthesis of 2,6-bis(t-butyldimethylsilyl)-4H-thiopyran (1)*

To a solution of 1,5-bis(*t*-butyldimethylsilyl)pentan-1,5-dione (4.34 g, 13.2 mmol) in CH_3CN (35 mL) cooled at 0°C, were added HMDST (11.2 mL, 52.8 mmol) and a solution of $CoCl_2 \cdot 6H_2O$ (6.3 g, 26.4 mmol) in CH_3CN (97 mL), under a N_2 atmosphere. The reaction mixture was stirred overnight at room temperature, then the solvent was evaporated and the residual material was filtered through a pad of silica gel using diethyl ether as eluant. The filtrate was evaporated, giving a pale yellow oil which was dissolved in CH_3CN (14 mL). After addition of $CoCl_2 \cdot 6H_2O$

(1.4 g, 5.8 mmol), the solution was heated at reflux for 3 h. The solvent was evaporated and the resulting mixture was filtered through a pad of silica gel using diethyl ether as eluent. The filtrate was evaporated and the residue was purified by flash chromatography (eluent: hexanes) affording 4H-thiopyran **1** (3.58 g, 83%, 97% pure) as a colorless oil which slowly crystallized at 20°C.

2,6-Bis(*t*-butyldimethylsilyl)-*4H*-thiopyran (**1**): this compound has been described in Ref (*7*).

4.2.1. *2,6-Bis-(t-butyldimethylsilyl)-3,4-dihydro-2H-thiopyran-2-thiol (3)*

This compound was isolated (flash chromatography, hexanes, Rf: 0.5) as a colorless oil in 20% yield from a preliminary experiment stopped before the additional $CoCl_2$ treatment. ^{1}H-NMR ($CDCl_3$): $\delta = 0.08$ (3H, s), 0.09 (3H, s), 0.17 (3H, s), 0.20 (3H, s), 0.90 (9H, s), 1.06 (9H, s), 1.94–2.26 (3H, m), 2.29 (1H, s), 2.63 (1H, dddd, $J = 18.3$, 11.4, 5.9, 2.5 Hz), 6.07 (1H, dd, $J = 8.5$, 2.7 Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -7.3$ (CH_3), -7.2 (CH_3), -6.6 (CH_3), -6.2 (CH_3), 17.2 (C_q), 19.5 (C_q), 20.2 (CH_2), 26.8 (CH_3), 28.5 (CH_3), 32.0 (CH_2), 39.5 (C_q), 128.4 (CH), 129.2 (C_q). MS (EI): m/z 360 (M^+, 1), 326 (M^+-H_2S, 13), 269 (M^+-(*t*-Bu), 51), 73 (100). HRMS (ES^+): calcd for $C_{17}H_{37}S_2Si_2$ ($M^+ + H$) m/z 361.1875, found: 361.1868.

4.3. *Typical optimized procedure for the synthesis of 2,6-bis(trimethylsilyl)-4H-thiopyran (4)*

To a solution of 1,5-bis(trimethylsilyl)pentan-1,5-dione (1.00 g, 4.1 mmol) in CH_3CN (11 mL) cooled at 0°C, were added under a N_2 atmosphere HMDST (3.5 mL, 16.5 mmol) and a solution of $CoCl_2{\cdot}6H_2O$ (2.00 g, 8.2 mmol) in CH_3CN (30 mL). The reaction mixture was stirred overnight at room temperature, then the solvent was evaporated and the residual material was filtered through a pad of silica gel using diethyl ether as eluant. The filtrate was evaporated to give a yellow pale oil. Flash chromatography (hexanes, Rf: 0.85) afforded 536 mg (54%) of **4** as a colorless oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.15$ (18H, s), 2.68 (2H, t, $J = 4.5$ Hz), 6.01 (2H, t, $J = 4.5$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -1.7$ (CH_3), 29 (CH_2), 128 (CH), 137 (C_q). MS (EI): m/z 241 ($M^+ - 1$, 85), 227 ($M^+ - 15$, 49), 169 (M^+-$SiMe_3$, 34), 154 (M^+-$SiMe_3$-15, 76), 73 (100). HRMS (ES^+): calcd for $C_{11}H_{23}SSi_2$ ($M^+ + H$) m/z 243.1059, found 243.1048.

4.4. *6-(t-Butyldimethylsilyl)-thiopyran-2-one (5)*

Filtration on silica gel (eluent: diethylether). ^{1}H-NMR ($CDCl_3$): $\delta = 0.28$ (6H, s), 0.92 (9H, s), 6.47 (1H, d, $J = 10.4$ Hz), 6.96 (1H, d, $J = 7.1$ Hz), 7.35 (1H, dd, $J = 10.4$, 7.1 Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.3$ (CH_3), 17.0 (C_q), 26.3 (CH_3), 124.5 (CH), 125.2 (CH), 139.9 (CH), 155.9 (C_q), 186.5 (C_q). IR (neat): 1731, 1644 cm^{-1}. MS (EI): m/z 226 (M^+, 24), 169 (M^+-(*t*-Bu), 99), 141 (100). HRMS (ES^+): calcd for $C_{11}H_{19}OSSi$ (M^++H) m/z 227.0926, found 227.0925.

4.5. *Typical procedure for the reaction of lithium salt 1Li with electrophilic reagent*

To a 0°C cooled solution of *4H*-thiopyran **1** (102 mg, 0.31 mmol) in tetrahydrofuran (THF) (2 mL) was added *n*-BuLi (0.37 mmol), 1.2 equivalent of a 2.5 M solution in hexane). The deeply red colored solution was stirred for 0.5 h at 0°C then a solution (53 mg, 0.37 mmol) of MeI in THF (1 mL) was added. The deep red color disappeared at the end of the addition, and the resulting yellow solution was stirred for 10 min. at 0°C and for 0.5 h at room temperature. Water (2 mL) was then added. The solution was extracted three times with diethyl ether (3×10 mL) and the organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography or preparative TLC.

4.5.1. *2,6-Bis-(t-butyldimethylsilyl)-4-methyl-4H-thiopyran (6)*

Filtration on silica gel (eluent: hexanes, Rf: 0.85). Yield: 98% (122 mg). ^{1}H-NMR ($CDCl_3$): $\delta = 0.13$ (6H, s), 0.14 (6H, s), 0.90 (18H, s), 1.30 (3H, d, $J = 7.2$ Hz), 2.35–2.41 (1H, m), 5.81 (2H, d, $J = 3.3$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.1$ (CH_3), -5.8 (CH_3), 17.0 (Cq), 19.2 (CH_3), 26.8 (CH_3), 33.5 (CH), 133.3 (C_q), 135.4 (CH). MS (EI): m/z 340 (M^+, 4), 325 (100), 73 (64). HRMS (ES^+): calcd for $C_{18}H_{37}SSi_2$ ($M^+ + H$) m/z 341.2154, found: 341.2152.

4.5.2. *2,6-Bis-(t-butyldimethylsilyl)-4-trimethylsilyl-4H-thiopyran (7)*

Filtration on silica gel (eluent: hexanes, Rf: 0.90). Yield: 99% (198 mg). ^{1}H-NMR ($CDCl_3$): $\delta = 0.11$ (12H, s), 0.92 (18H, s), 2.63 (1H, t, $J = 6.6$ Hz), 5.84 (2H, d, $J = 6.6$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.01$ (CH_3), -6.0 (CH_3), 17.1 (C_q), 26.8 (CH_3), 36.7 (CH), 127.2 (Cq), 131.3 (CH). MS (EI): m/z 398 (M^+, 33), 325 (M^+-$SiMe_3$, 97), 283 (M^+-(*t*-Bu)Me_2, 100), 73 (98). HRMS (ES^+): calcd for $C_{20}H_{43}SSi_3$ ($M^+ + H$) m/z: 399.2393, found 399.2391.

4.5.3. *2,6-Bis-(t-butyldimethylsilyl)-4-isopropyl-4H-thiopyran (8a) and 2,6-bis-(t-butyldimethylsilyl)-2-isopropyl-2H-thiopyran (8b)*

Filtration on silica gel (eluent: hexanes, Rf: 0.80). Yield: 50% (45 mg). Mixture (3.7:1) of **8a** and **8b**. Yellow oil. Compound **8a**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.10$ (12H, s), 0.91 (18H, s), 0.97 (6H, d, $J = 6.7$ Hz), 1.82–1.98 (1H, m), 2.44 (1H, dt, $J = 5.7, 4.4$ Hz), 5.90 (2H, d, $J = 4.4$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.0$ (CH_3), -5.9 (CH_3), 17.1 (C_q), 19.9 (CH_3), 26.9 (CH_3), 31.6 (CH), 44.5 (CH), 132.0 (CH), 132.9 (C_q). MS (EI): m/z 366 (M^+-2, 7), 325 (M^+-(*i*-Pr), 100), 73 (31). Compound **8b**: selected data: HRMS (ES^+): calcd for $C_{20}H_{41}SSi_2$ ($M^+ + H$) m/z 369.2467, found: 369.2474.

4.5.4. *4-Benzyl-2,6-bis-(t-butyldimethysilyl)-4H-thiopyran (9a) and 2-Benzyl-2,6-bis-(t-butyldimethysilyl)-2H-thiopyran (9b)*

Filtration on silica gel (eluent: hexanes, Rf: 0.8–0.9). Yield: 56% (57 mg). Mixture (4.6:1) of **9a** and **9b.** Oil. Compound **9a**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.09$ (6H, s), 0.10 (6H, s), 0.88 (18H, s), 2.75–2.82 (2H, m), 2.89–3.00 (1H, m), 5.86 (2H, d, $J = 4.3$ Hz), 7.12–7.32 (5H, m). ^{13}C-NMR ($CDCl_3$): $\delta = -6.0$ (CH_3), 17.0 (C_q), 26.8 (CH_3), 38.7 (CH_2), 39.6 (CH), 125.9 (CH), 127.1 (CH), 128.1 (CH), 132.7 (CH), 133.3 (C_q), 139.7 (C_q). MS (EI): m/z 414 (M^+-2, 11), 325 (M^+-$PhCH_2$, 100), 267 (24), 91 (11), 73 (32). HRMS (ES^+) calcd for $C_{24}H_{41}SSi_2$ ($M^+ + H$) m/z 417.2467, found: 417.2471. Compound **9b**: ^{1}H-NMR ($CDCl_3$): $\delta = -0.01$ (6H, s), 0.26 (6H, s), 0.73 (9H, s), 0.96 (9H, s), 2.76–2.91 (2H, m), 5.24 (1H, d, $J = 10.0$ Hz), 5.39 (1H, d, $J = 5.0$ Hz), 5.61 (1H, dd, $J = 10.0, 5.0$ Hz), 7.00–7.25 (5H, m).

4.5.5. *4-Allyl-2,6-bis-(t-butyldimethylsilyl)-4H-thiopyran (10a) and 2-allyl-2,6-bis-(t-butyldimethylsilyl)-2H-thiopyran (10b)*

Filtration on silica gel (eluent: hexanes, Rf: 0.8–0.9). Yield: 99% (89 mg). Mixture (1:1.8) of **10a** and **10b**. Oil. Compound **10a**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.12$ (12H, s), 0.89 (18H, s), 2.35–2.40 (2H, m), 2.50–2.59 (1H, m), 5.05 (1H, d, $J = 9.6$ Hz), 5.07 (1H, d, $J = 18.3$ Hz), 5.77–5.91 (1H, m), 5.86 (2H, $J = 3.6$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.0$ (CH_3), -5.9 (CH_3), 17.0 (C_q), 26.7 (CH_3), 37.7 (CH_2), 37.9 (CH), 116.4 (CH_2), 133.1 (CH), 133.6 (C_q), 136.2 (CH). MS (EI): m/z 366 (M^+, 2), 351 (M^+-Me, 3), 325 (100), 73 (48). Compound **10b**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.09$

(6H, s), 0.11 (3H, s), 0.15 (3H, s), 0.93 (9H, s), 1.02 (9H, s), 2.26–2.46 (2H, m), 5.04–5.07 (2H, m), 5.32 (1H, d, $J = 10.3$ Hz), 5.80–5.86 (1H, m), 5.96–5.99 (1H, m), 6.06–6.23 (1H, m). ^{13}C-NMR ($CDCl_3$): $\delta = -6.9$ (CH_3), -6.7 (CH_3), -6.6 (CH_3), -6.1 (CH_3), 17.3 (C_q), 19.3 (C_q), 26.8 (CH_3), 28.5 (CH_3), 34.9 (C_q), 43.5 (CH_2), 116.6 (CH_2), 123.3 (CH), 123.7 (CH), 126.5 (CH), 133.1 (C_q), 135.6 (CH). MS (EI): m/z 366 (M^+, 2), 351 (M^+-Me, 3), 325 (100), 73 (48). HRMS (ES^+) calcd for $C_{20}H_{39}SSi_2$ ($M^+ + H$) m/z 367.2311, found 367.2310.

4.5.6. *2,6-Bis-(t-butyldimethylsilyl)-4-(3-methyl-but-2-enyl)-4H-thiopyran (11a) and 2,6-bis-(t-butyldimethylsilyl)-2-(3-methyl-but-2-enyl)-2H-thiopyran (11b)*

Filtration on silica gel (eluent: hexanes, Rf: 0.8–0.9). Yield: 39% (22 mg). Mixture (5.8:1) of **11a** and **11b**. Oil. Compound **11a**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.12$ (12H, s), 0.90 (18H, s), 1.63 (3H, s), 1.71 (3H, s), 2.27–2.32 (2H, m), 2.48–2.54 (1H, m), 5.15–5.25 (1H, m), 5.85 (2H, d, $J = 3.7$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.1$ (CH_3), -5.9 (CH_3), 17.0 (C_q), 18.0 (CH_3), 25.8 (CH_3), 26.7 (CH_3), 32.0 (CH_2), 38.6 (CH), 122.1 (CH), 133.1 (C_q), 133.6 (CH), 133.6 (C_q). MS (EI): m/z 392 (M^+-2, 6), 325 (100), 73 (43). Compound **11b**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.02$ (6H, s), 0.22 (6H, s), 0.70 (9H, s), 0.95 (9H, s), 1.46 (3H, s), 1.48 (3H, s), 2.10–2.40 (2H, m), 5.20 (1H, d, $J = 10$ Hz), 5.41 (1H, m), 5.68 (1H, dd, $J = 10, 5$ Hz), 5.86 (1H, d, $J = 5$ Hz). HRMS (ES^+) calcd for $C_{22}H_{43}SSi_2$ ($M^+ + H$) m/z 395.2624, found 395.2619.

4.5.7. *4-(2,2-Bis-ethylsulfanyl-1-trifluoromethyl-vinyl)-2,6-bis-(t-butyldimethyl-silyl)-4H-thiopyran (12)*

Filtration on silica gel (eluent: hexanes). Yield: 70% (38 mg). Oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.13$ (6H, s), 0.16 (6H, s), 0.91 (18H, s), 1.21 (3H, t, $J = 7.4$ Hz), 1.29 (3H, t, $J = 7.3$ Hz), 2.79–2.94 (4H, m), 4.18 (1H, brs), 5.72 (2H, brs). ^{13}C-NMR ($CDCl_3$): $\delta = -6.2$ (CH_3), -5.6 (CH_3), 14.6 (CH_3), 14.8 (CH_3), 17.1, (C_q), 26.7 (CH_3), 28.2 (CH_2), 28.7 (CH_2), 45.1 (CH), 123.5 (CF_3, q, $^1J = 276$ Hz), 131.3 (CH), 131.9 (C_q), 137.7 (C_q, q, $^2J = 26$ Hz), 144.1 (C_q). ^{19}F-NMR ($CDCl_3$): $\delta = -53.0$ (s). MS (EI): m/z 539 (M^+-1, 1), 511 (M^+-Et, 3), 449 (100). HRMS (ES^+) calcd for $C_{24}H_{44}F_3S_3Si_2$ ($M^+ + H$) m/z 541.2096, found 541.2090.

4.5.8. *2,6-Bis-(t-butyldimethylsilyl)-4-hexyl-4H-thiopyran (13a), 2,6-bis-(t-butyldimethyl-silyl)-2-hexyl-2H-thiopyran (13b), and 2,6-bis-(t-butyldimethylsilyl)-2H-thiopyran (13d)*

Filtration on silica gel (eluent: hexanes, Rf: 0.85) leading to 50% (31 mg) of a mixture (7.3:1) of **13a** and **13b** (oil) and 47% (23 mg) of 2*H*-thiopyran **13d**. Compound **13a**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.13$ (12H, s), 0.83–0.91 (3H, m), 0.90 (18H, s), 1.06–1.62 (10H, m), 2.39–2.48 (1H, m), 5.87 (2H, d, $J = 3.9$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.0$ (CH_3), -5.8 (CH_3), 14.1 (CH_3), 17.0 (C_q), 22.6 (CH_2), 26.8 (CH_3), 26.9 (CH_2), 29.5 (CH_2), 31.8 (CH_2), 33.4 (CH_2), 38.6 (CH), 133.0 (C_q), 134.0 (CH). MS (EI): m/z 409 (M^+-1, 4), 351, (8), 325 (100), 73 (39). Compound **13b**: ^{1}H-NMR ($CDCl_3$): $\delta = 0.11$ (6H, s), 0.16 (6H, s), 0.88 (9H, s), 0.92 (9H, s), 0.85–0.90 (3H, m), 1.21–2.04 (10H, m), 5.36 (1H, dd, $J = 7.5, 5.0$ Hz), 5.87 (1H, d, $J = 7.5$ Hz), 6.14 (1H, d, $J = 5.0$ Hz). HRMS (ES^+) calcd for $C_{23}H_{47}SSi_2$ (M^++H) m/z 411.2937, found 411.2942. Compound **13d**: oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.10$ (6H, s), 0.14 (6H, s), 0.95 (18H, s), 2.72 (1H, dd, $J = 5.3, 2.0$ Hz), 5.50 (1H, dd, $J = 9.7, 5.3$ Hz), 5.93 (1H, ddd, $J = 9.7, 5.6, 2.0$ Hz), 6.26 (1H, d, $J = 5.6$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -7.2$ (CH_3), -7.0 (CH_3), -6.2 (CH_3), -5.9 (CH_3), 17.0 (C_q), 17.5 (C_q), 26.8 (CH_3), 27.1 (CH_3), 41.4 (CH), 118.8 (CH), 125.8 (CH), 130.5 (CH), 134.0 (C_q), 136.1 (C_q). MS (EI): m/z 326 (M^+, 22), 269 (M^+-(*t*-Bu), 7), 211 (100), 73 (75).

4.5.9. *[2,6-Bis-(t-butyldimethylsilyl)-4H-thiopyran-4-yl]-phenylmethanol (14)*

Filtration on silica gel (eluent: hexanes). Yield: 98%. Oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.06$ (3H, s), 0.10 (3H, s), 0.15 (6H, s), 0.88 (9H, s), 0.92 (9H, s), 2.13 (1H, brs), 3.20–3.26 (1H, m), 4.74 (1H, d, $J = 7.3$ Hz), 5.64 (1H, d, $J = 5.2$ Hz), 6.02 (1H, d, $J = 5.2$ Hz), 7.27–7.37 (5H, m). ^{13}C-NMR ($CDCl_3$): $\delta = -6.1$ (CH_3), -6.0 (CH_3), -5.9 (CH_3), 17.0 (C_q), 26.8 (CH_3), 45.7 (CH), 74.7 (CH), 126.6 (CH), 127.5 (CH), 128.1 (CH), 128.8 (CH), 129.3 (CH), 134.7 (C_q), 135.0 (C_q), 142.2 (C_q). HRMS (ES^+) calcd for $C_{42}H_{75}O_2S_2Si_4$ ($M^+ + H$) m/z 787.4286, found: 787.4276.

4.5.10. *1-[2,6-Bis-(t-butyldimethylsilyl)-4H-thiopyran-4-yl]-2,2-dimethyl-propan-1-ol (15)*

Filtration on silica gel (eluent: hexanes). Yield: 75%. Oil. H-NMR ($CDCl_3$): $\delta = 0.14$ (12H, s), 0.90 (9H, s), 0.91 (9H, s), 0.98 (9H, s), 1.79 (1H, brs), 2.88–2.93 (1H, m), 3.4–3.49 (1H, brs), 5.93 (1H, d, $J = 5.0$ Hz), 6.05 (1H, d, $J = 5.0$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -5.9$ (CH_3), -5.8(CH_3), 17.0 (C_q), 26.8 (CH_3), 26.9 (CH_3), 35.7 (C_q), 41.4 (CH), 81.7 (CH), 129.7 (CH), 133.0 (CH), 134.5 (C_q), 135.8 (C_q). HRMS (ES^+) calcd for $C_{22}H_{45}OSSi_2$ ($M^+ + H$) m/z 413.2730, found 413.2733.

4.5.11. *[2,6-Bis-(t-butyldimethylsilyl)-4H-thiopyran-4-yl]-(4-{[2,6-bis-(t-butyldimethylsilyl)-4H-thiopyran-4-yl]-hydroxymethyl}-phenyl)-methanol (16)*

Filtration on silica gel (eluent: hexanes). Yield: 65%. Mixture (1:1) of diastereomers. Oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.05$ (6H, s), 0.06 (6H, s), 0.09 (6H, s), 0.10 (6H, s), 0.14 (12H, s), 0.15 (12H, s), 0.87 (18H, s), 0.88 (18H, s), 0.91 (18H, s), 0.92 (18H, s), 2.17 (4H, brs), 3.18–3.27 (4H, m), 4.71–4.77 (4H, m), 5.60 (2H, d, $J = 5.4$ Hz), 5.68 (2H, d, $J = 5.1$ Hz), 5.97 (2H, d, $J = 5.1$ Hz), 6.04 (2H, d, $J = 5.4$ Hz), 7.30 (4H, s), 7.31 (4H, s). ^{13}C-NMR ($CDCl_3$): $\delta = -6.1$ (CH_3), -5.9 (CH_3), 17.0 (C_q), 26.7 (CH_3), 45.7 (CH), 45.8 (CH), 74.2 (CH), 74.6 (CH), 126.3 (CH), 126.4 (CH), 128.5 (CH), 128.7 (CH), 129.3, (CH), 129.3 (CH), 134.6 (C_q), 134.8 (C_q), 135.1 (C_q), 135.1 (C_q), 141.5 (C_q), 141.6 (C_q). HRMS (ES^+) calcd for $C_{42}H_{75}O_2S_2Si_4$ ($M^+ + H$) m/z 787.4286, found: 787.4276.

4.5.12. *[4-[2,6-Bis-(t-butyldimethylsilyl)-4H-thiopyran-4-yl]-dihydrofuran-2-one (17)*

Filtration on silica gel (eluent: hexanes). Yield: 53%. Oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.13$ (6H, s), 0.14 (6H, s), 0.89 (18H, s), 2.42 (1H, dd, $J = 17.5$, 7.6 Hz), 2.54 (1H, dd, $J = 17.5$, 8.2 Hz), 2.75–2.90 (1H, m), 2.96 (1H, dt, $J = 7.9$, 5.4 Hz), 4.19 (1H, dd, $J = 9.2$, 6.6 Hz), 4.34 (1H, dd, $J = 9.2$, 7.3 Hz), 5.85 (2H, d, $J = 5.4$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.2$ (CH_3), -6.0 (CH_3), 16.9 (C_q), 26.7 (CH_3), 32.0 (CH_2), 38.1 (CH), 39.5 (CH), 71.3 (CH_2), 127.9 (CH), 128.0 (CH), 136.2 (C_q), 136.4 (C_q), 176.9 (C_q). MS (EI): m/z 325 (100), 269 (40), 211 (23), 73 (89).

4.5.13. *2,6,2′,6′-Tetrakis-(t-butyldimethylsilyl)-4H,4′H-[4,4′]bithiopyranyl (18)*

Filtration on silica gel (eluent: hexanes). Yield: 83%. Oil. ^{1}H-NMR ($CDCl_3$): $\delta = 0.11$ (12H, s), 0.12 (12H, s), 0.89 (36H, s), 3.03 (2H, t, $J = 2.5$ Hz), 5.92 (4H, d, $J = 2.5$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = -6.2$ (CH_3), -5.9 (CH_3), 17.0 (C_q), 26.7 (CH_3), 41.4 (CH), 131.5 (CH), 134.0 (C_q). HRMS (ES^+) calcd for $C_{34}H_{67}S_2Si_4$ ($M^+ + H$) m/z 651.3761, found 651.3741.

4.5.14. *2-Benzylidene-6-(t-butyldimethylsilyl)-4-trimethylsilyl-2H-thiopyran (19) and 4-Benzylidene-2,6-bis-(t-butyldimethylsilyl)-4H-thiopyran (20)*

Purification by preparative TLC on silica gel (eluent: hexanes, Rf: 0.4). Yield: 99% (71 mg). Mixture (1:1) of **19** and **20**. Oil. GC-MS (EI): compound **19** m/z 372 (M^+, 36), 73 (100); compound **20** m/z 414 (M^+, 48), 73 (100). ^{13}C-NMR ($CDCl_3$) of **19** + **20**: $\delta = -6.5$ (CH_3), -6.4 (CH_3), -2.2 (CH_3), 17.2 (C_q), 17.3 (C_q), 26.6 (CH_3), 26.7 (CH_3), 119.4 (CH), 120.6 (CH), 125.4 (CH), 125.8 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.2 (CH), 128.7 (CH), 129.2 (CH), 129.4 (C_q), 130.8 (C_q), 131.3 (CH), 133.3 (C_q), 133.5 (C_q), 135.6 (CH), 136.5 (C_q), 137.2 (C_q), 138.0 (C_q).

4.5.15. *2,6-Bis-(t-butyldimethylsilyl)-1-hexyl-4-trimethylsilyl-4H-thiopyran (21)*

Purification by preparative TLC on silica gel (eluent: hexanes, Rf: 0.54).Yield: 80%. Oil. ^{1}H-NMR ($CDCl_3$): $\delta = -0.04$ (9H, s), 0.00 (6H, s), 0.10 (6H, s), 0.75 (18H, s), 0.85–0.90 (3H, m), 1.15–1.50 (10H, m), 1.92–2.03 (2H, m), 6.85 (2H, s). ^{13}C-NMR ($CDCl_3$): $\delta = -5.0$ (CH_3), -4.9 (CH_3), -0.6 (CH_3), 14.0 (CH_3), 17.8 (C_q), 22.4 (CH_2), 26.7 (CH_2), 28.1 (CH_2), 31.3 (CH_2), 37.6 (CH_2), 64.2 (C_q), 113.3 (C_q), 144.0. MS (EI): m/z 483 (M^+, 18), 73 (100).

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