Preparation of *para*-Terphenylylalkanethiols with Different Chain Lengths

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Abstract: Terphenylylalkanethiols with different chain length were synthesized using palladium-catalyzed cross-coupling reactions. While the thiols with two and three methylene groups were obtained via photoaddition of thiopivalic acid to the respective alkenes, the longer terphenylylalkanethiols were synthesized by two consecutive Kumada cross-coupling reactions followed by a Mitsunobu reaction for the introduction of the sulfur functionality.

Key words: cross-coupling, Mitsunobu reaction, self-assembly, thiols, arylations

Self-assembled monolayers (SAM), in particular of thiols on gold, are used in a variety of fields like electrochemistry,[1,2] biosensors,[3,4] or surface patterning.[5–7] They are also promising candidates for the construction of molecular electronic devices.[8,9] Although these monolayers are widely used, some of their fundamental properties are still not fully understood. We wanted to investigate the influence of mutual interactions between aromatic and aliphatic substructures, respectively, on the structure of the monolayers. For this, we needed to synthesize a series of alkanethiols with a terphenyl headgroup in order to explore the influence of odd and even numbered alkyl chains and if this can overcome the relatively strong interactions of the terphenyl groups (Figure 1).

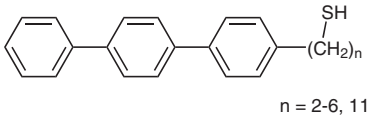
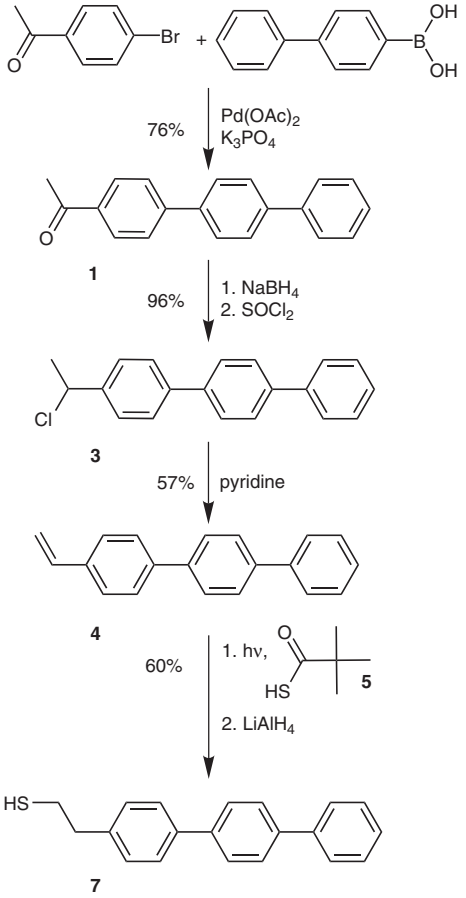


Figure 1 General structure of terphenylylalkanethiols studied

In a previous study, we published the synthesis of 4-terphenylthiol and (4-terphenylyl)methanethiol.[10] For the longer alkyl derivatives, we intended to use the well established photoaddition of thiocarboxylic acids to terminal alkenes (followed by hydrolysis) to introduce the thiol groups.

In order to obtain the C_2-derivative **7**, the carbon framework was built up by Suzuki cross-coupling of 4-biphenylboronic acid with 4-bromoacetophenone (Scheme 1). Ketone **1**[11] was reduced to the alcohol which was transformed to the chloride **3** before elimination to afford 4-vinylterphenyl **4** (this compound has been obtained before using a series of low-yield steps starting from terphenyl[12]). This somewhat complicated route had to be chosen, since the Pd-assisted coupling of a 4-halostyrene would have yielded the Heck product instead of the desired Suzuki product. Photoaddition of thiopivalic acid (**5**) to the vinyl group followed by reductive cleavage of the ester yielded 22% of the thiol **7** overall in six steps.



Scheme 1

The synthesis of 3-(4-terphenylyl)propanethiol (**11**) commenced with Kumada cross-coupling of the mono Grignard compound of 1,4-dibromobenzene with allyl bromide leading to a mixture of mono- and disubstituted product and unreacted starting material.[13] By means of distillation **8** was enriched. A second Kumada cross-coupling of **8** with 4-bromobiphenyl lead to **9** in 59% yield. Photoaddition of thioacetic acid followed by saponification of the ester **10** gave **11**[14] (Scheme 2).

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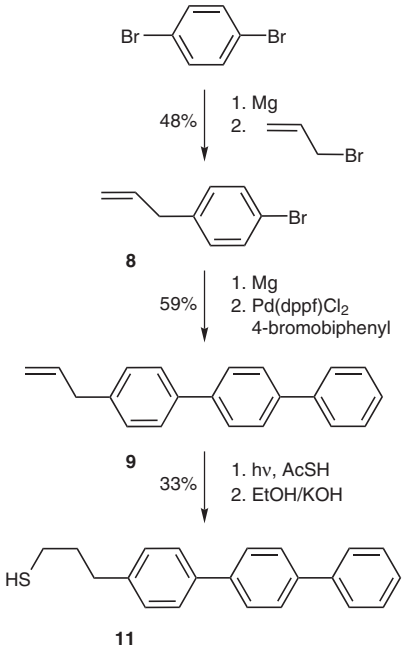
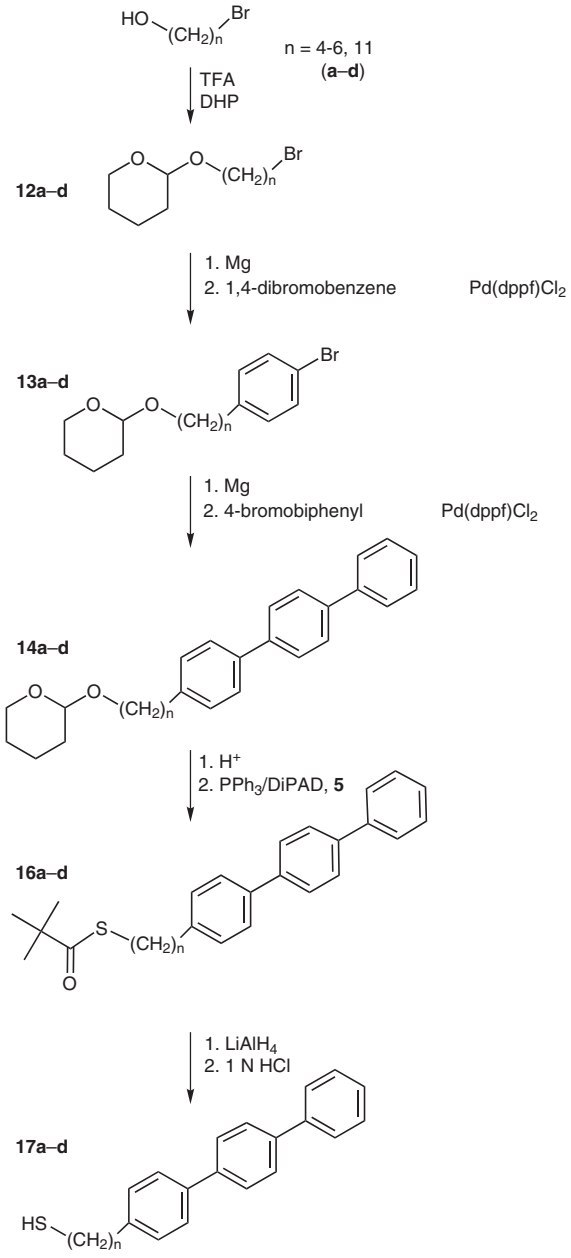


Scheme 2

For the synthesis of ω-*p*-terphenyl substituted alkanethiols with a chain length larger than three carbon atoms this protocol could not be used since we observed a significant amount of alkene isomerization during the Pd-mediated coupling steps. Therefore we decided to modify our approach by using ω-alkanol derivatives, which do not isomerize during the coupling steps, as precursors for the thiols.

The modified protocol started with the protection of easily available ω-bromoalkanols as THP-ethers.[15] The bromides were converted to the Grignard reagents and coupled under palladium catalysis with an excess of 1,4-dibromobenzene. The resulting compounds were again converted to the Grignard reagents and coupled under palladium catalysis with 4-bromobiphenyl. **14a–d** were deprotected and transformed via a Mitsunobu reaction[16,17] into thioesters **16a–d**. The esters could be reductively cleaved using $LiAlH_4$ yielding thiols **17a–d** Scheme 3). The analytical and spectral data of thiols **7**, **11**, and **17a–d** prepared are listed in Table 1.

In conclusion, using different approaches, we were able to obtain terphenylylalkanethiols with chainlengths between two and eleven methylene groups. While the thiols with two and three methylene groups could be obtained by addition of thioacids to the respective alkenes, a different approach had to be taken for the longer derivatives due to a notorious tendency for the isomerization of the double bond. This alternative approach starts from ω-bromoalkanols using the Kumada cross-coupling for the assembly of the carbon back-bone. These thiols will be tested as new compounds for the construction of self-assembled monolayers.



Scheme 3

Unless otherwise stated all reactions were carried out under N_2 using anhyd solvents. Biphenyl-4-boronic acid, 6-bromohexanol, 11-bromoundecanol, 4-bromobiphenyl, and 4-bromoacetophenone were purchased from Aldrich and were used as received. Commercially available thioacetic acid was distilled and kept under N_2.

The syntheses of 4-bromobutanol,[18] 5-bromopentanol,[19] and $Pd(dppf)Cl_2$[19,20] were carried out according to the literature.

[1.1′;4′.1″]Terphenyl-4-ylethanone (1)

A mixture of 4-bromoacetophenone (2.0 g, 10 mmol), biphenyl-4-boronic acid (2.0 g, 11 mmol), K_3PO_4 (5.2 g, 20 mmol) and $Pd(OAc)_2$ (45 mg, 0.20 mmol) in toluene (50 mL) was heated at 80 °C under stirring for 24 h. After hydrolysis with 1 M HCl (30 mL), the suspension was extracted with CH_2Cl_2 (150 mL) until the entire solid residue was dissolved. The solvent was removed in vacuum and the crude product was purified by column chromatog-

Table 1 Thiols **7**,**11**,**17a–d** Prepared

Product[a]	Yield (%)	Mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS *m*/*z* (%)
7	95	222–225	1.44 (t, *J* = 7.8, 1 H, SH), 2.84 (q, *J* = 7.4, 2 H, CH_2), 2.99 (t, *J* = 7.5, 2 H, CH_2), 7.28–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′)	–	290.3 (52, M^+), 256.2 (8, $M^+ - H_2S$), 243.2 (100, terphenylmethylene cation)
11	83	175–176	1.40 (t, *J* = 7.8, 1 H, SH), 1.99 (quint, *J* = 7.4, 2 H, CH_2), 2.59 (q, *J* = 7.4, 2 H, CH_2S), 2.79 (t, *J* = 7.5, 2 H, CH_2), 7.30–7.64 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′)	24.3 ($C\text{-}1_{chain}$), 34.7 ($C\text{-}3_{chain}$), 36.6 ($C\text{-}2_{chain}$), 127.4–129.6 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 139.0–141.5 (C-1, C-4, C-1′, C-4′, C-1″)	304.3 (100, M^+), 270.3 (14, $M^+ - H_2S$), 243.3 (76, terphenylmethylene cation)
17a	93	178	1.36 (t, *J* = 7.8, 1 H, SH), 1.65-1.83 (m, 4 H_{aliph}-H-2, H-3), 2.58 (q, *J* = 6.8, 2 H_{aliph}-H-1), 2.68 (t, *J* = 7.2, aliph-H-4), 7.25–7.64 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′)	26.1 ($C\text{-}1_{chain}$), 31.0 ($C\text{-}3_{chain}$), 34.7 ($C\text{-}2_{chain}$), 35.8 ($C\text{-}4_{chain}$), 127.5, 127.6, 127.9, 128.0, 128.1, 129.6, 129.7, (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 139.0, 140.7, 140.9, 141.6, 142.4 (C-1, C-4, C-1′, C-4′, C-1″)	318.1 (100, M^+), 284.2 (2, $M^+ - H_2S$), 243.1 (76, terphenylmethylene cation)
17b	90	179	1.34 (t, *J* = 7.8, 1 H, SH), 1.43–1.54 (m, 4 H_{aliph}-H-2, H-3), 1.68 (quint, *J* = 7.3, 2 H_{aliph}-H-4), 2.54 (q, *J* = 6.8, 2 H_{aliph}-H-1), 2.67 (t, 7.6, aliph-H-5), 7.25–7.64 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).	26.0 ($C\text{-}1_{chain}$), 28.8 ($C\text{-}3_{chain}$), 31.8 ($C\text{-}4_{chain}$), 34.9 ($C\text{-}2_{chain}$), 36.1 ($C\text{-}5_{chain}$), 127.4, 127.5, 127.8, 127.9, 127.9, 129.4, 129.5 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 138.8, 140.5, 140.7, 141.5, 142.5 (C-1, C-4, C-1′, C-4′, C-1″)	332.2 (100, M^+), 298.2 (2, $M^+ - H_2S$), 243.1 (93, terphenylmethylene cation)
17c	79	157	1.33 (t, *J* = 7.8, 1 H, SH), 1.43–1.54 (m, 4 H_{aliph}-H-2, H-3), 1.67 (quint, *J* = 7.3, 2 H_{aliph}-H-4), 2.53 (q, 6.8, 2 H_{aliph}-H-1), 2.66 (t, *J* = 7.6, aliph-H-5), 7.24–7.64 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CHarom-H-2′, H-3′, H-5′, H-6′)	26.0 ($C\text{-}1_{chain}$), 29.0 ($C\text{-}3_{chain}$), 29.6 ($C\text{-}4_{chain}$), 32.2 ($C\text{-}5_{chain}$), 34.9 ($C\text{-}2_{chain}$), 36.2 ($C\text{-}6_{chain}$), 127.3, 127.4, 127.8, 127.9, 127.9, 129.4, 129.5 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 139.0, 140.7, 140.8, 141.6, 142.4 (C-1, C-4, C-1′, C-4′, C-1″)	346.2 (100, M^+), 312.2 (1, $M^+ - H_2S$), 243.1 (98, terphenylmethylene cation)
17d	81	168–170	1.24–1.36 (m, 15 H_{aliph}-H-3 to H-9, SH), 1.58–1.67 (m, 4 H_{aliph}-H-2, H-10), 2.52 (q, *J* = 7.4, 2 H, aliph-H-1), 2.65 (t, *J* = 7.8, 2 H, aliph-H-11), 7.29–7.66 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.68 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′)	25.7 ($C\text{-}1_{chain}$), 29.4 ($C\text{-}3_{chain}$), 30.0 ($C\text{-}4_{chain}$), 30.4 ($C\text{-}5_{chain}$), 30.5 ($C\text{-}2_{chain}$), 30.6 ($C\text{-}6_{chain}$), 32.5, 35.1, 36.6, 127.9, 128.1, 128.3, 128.3, 128.4, (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 139.0, 140.8, 141.1, 141.8, 143.2 (C-1, C-4, C-1′, C-4′, C-1″)	416 (100, M^+), 382.2 (2, $M^+ - H_2S$), 243.1 (86, terphenylmethylene cation)

raphy on silica gel with CH_2Cl_2 followed by crystallization from EtOH; yield: 2.1 g (76%); white solid.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 2.66 (s, 3 H, CH_3), 7.34–7.67 (m, 5 H, CH_{arom}-H-2″ to H-6″), 7.71 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′), 7.74 (d, *J* = 8.4 Hz, 2 H, CH_{arom}-H-2, H-6), 8.06 (d, *J* = 8.4 Hz, 2 H, CH_{arom}-H-3, H-5).

1-[1.1′;4′.1″]Terphenyl-4-ylethanol (2)

Compound **1** (2.9 g, 11 mmol) was dissolved in a mixture of THF (200 mL) and H_2O (10 mL). During a period of 1 h, $NaBH_4$ (3 g, 0.08 mol) was added and the mixture was stirred overnight. After hydrolysis with 6 M HCl (50 mL), the organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (4 × 50 mL). The solvent of the combined organic phases was removed. The residue was dissolved in acetone and filtered over alumina. After removal of the solvent a white solid was obtained; yield: 2.9 g (99%); mp 204 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.56 (d, *J* = 6.4 Hz, 3 H, CH_3), 4.98 (q, *J* = 6.4 Hz, 1 H, aliph-CH), 7.36–7.66 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.68 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

4-(1-Chloroethyl)-[1.1′;4′.1″]terphenyl (3)

The alcohol **2** (2.9 g, 11 mmol), $SOCl_2$ (150 mL), and DMF (1 drop) were heated to reflux overnight. After removal of the volatiles in vacuo, a white solid was obtained; yield: 3.0 g (97%).

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.90 (d, *J* = 6.8 Hz, 3 H, CH_3), 5.17 (q, *J* = 6.8 Hz, 1 H, aliph-CH), 7.36–7.66 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.68 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

MS (EI): *m*/*z* (%) = 292.1 (40, M^+), 257.1 (100, $[M - Cl]^+$).

4-Vinyl-[1.1′; 4′.1″]terphenyl (4)
Terphenyl **3** (3.0 g, 10 mmol) was dissolved in pyridine (50 mL) and refluxed overnight. After cooling, CH_2Cl_2 (100 mL) was added and the solution was washed with brine (2 × 50 mL). The solvent was removed and the residue was filtered over silica gel (hexane–CH_2Cl_2, 1:1); yield: 1.5 g (57%); white solid; mp 227 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 5.29 (d, *J* = 11 Hz, 1 H, =CH_2), 5.81 (d, *J* = 17.5 Hz, 1 H, =CH_2), 6.75 (dd, *J* = 17.5 Hz, 11 Hz, 1 H, =CH), 7.32–7.67 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.69 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

Thiopivalic Acid (5)
A solution of Na (17 g, 0.74 mol) in EtOH (250 mL) was saturated with gaseous H_2S (ca. 2 h). To this, pivaloyl chloride (31.5 mL, 256 mmol) was added within 30 min leading to a fierce reaction. A white precipitate and copious amounts of H_2S were formed.

The EtOH was removed in vacuum and the residue was hydrolyzed with 3 M HCl (450 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (4 × 75 mL) and the combined organic phases were distilled using a Vigreux column under reduced pressure; yield: 20.64 g (66%); bp 45 °C/100 mbar (Lit.[21] bp 118–120 °C/1 bar); clear liquid with a pungent stench.

IR (KBr): 2971 (C–H), 2935 (C–H), 2872 (C–H), 2563 (C–H), 1693 (C=O), 1478 (C–H), 1462 (C–H), 1395 (C–H), 1367 (C–H). [Lit.[22] 2550 (S–H), 1683 cm^{-1} (C=O)].

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.25 (s, 9 H, CH_3), 4.10 (s, 1 H, SH) [Lit.[21] δ = 2.53 (s, 9 H, CH_3), 7.8 (s, 1 H, SH)].

^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$/TMS): δ = 27.73 (CH_3), 47.76 [*C*(CH_3)$_3$], 205.79 (C*C*OSH). [Lit.[22] δ = 26.4 (q, CH_3), 48.5 [s, *C*(CH_3)$_3$], 198.0 (CCOSH)].

Thiopivalic Acid *S*-(2-[1.1′;4′.1″]terphenyl-4-ylethyl) Ester (6)
A solution of **4** (1.5 g, 5.9 mmol) and thiopivalic acid (2.0 mL, 2.0 g; 17 mmol) in THF (40 mL) was irradiated with a 25 W mercury lamp. After 12 h, the solvent and the excess thioacid were removed in vacuo; yield: 1.4 g (63%); white solid; mp 174–175 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.25 (s, 9 H, CH_3), 2.84–2.95 (m, 2 H, CH_2), 3.07–3.17 (m, 2 H, CH_2), 7.28–7.66 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.68 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$/TMS): δ = 27.4 (CH_3), 29.9 (CH_2), 35.6 (CH_2), 46.4 [$C(CH_3)_3$], 127.0, 127.3, 127.5, 127.6, 128.2, 128.8, 129.0, 129.1 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 138.8, 139.4, 139.8, 140.0, 140.7 (C-1, C-4, C-1′, C-4′, C-1″), 206.8 (C=O).

2-[1.1′;4′.1″]Terphenyl-4-ylethan-1-thiol (7)
The thio ester **6** was reductively cleaved according to the typical procedure described for **17b** at the end of this section. For analytical data, see Table 1.

4-Allylbromobenzene (8)
1,4-Dibromobenzene (18 g, 75 mmol) in Et_2O (50 mL) was added dropwise to Mg (2.0 g, 82 mmol). The refluxing mixture was stirred until it again reached r.t. The solution was decanted into another dry flask and allyl bromide (7.2 mL, 10 g, 83 mmol) was carefully added. *The reaction is strongly exothermic!* When the reaction mixture had reached r.t., it was hydrolyzed with aq sat. NH_4Cl solution (20 mL). The aqueous phase was removed and extracted with Et_2O (4 × 25 mL). The combined organic phases were concentrated and the residue was distilled under reduced pressure using a Vigreux column (1,4-dibromobenzene sublimed into the whole apparatus). A clear liquid was obtained as main fraction at 90–150 °C/15 mbar, which was stored over night at –15 °C. 1,4-Dibromobenzene crystallized and was removed by filtration. The obtained clear liquid (8.5 g) was a mixture of 1,4-diallylbenzene and 4-allylbromobenzene (83% w/w); bp 93 °C/18 mbar (Lit.[14] bp 96 °C/16 mbar).

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 3.32–3.39 (m, 2 H, CH_2), 5.01–5.11 (m, 2 H, =CH_2), 5.83–6.03 (m, 1 H, =CH), 7.06 (d, *J* = 8.5 Hz, 2 H_{arom}), 7.41 (d, *J* = 8.5 Hz, 2 H_{arom}).

The ^{1}H NMR data of the impurities present are given below.

1,4-Dibromobenzene
^{1}H NMR ($CDCl_3$/TMS): δ = 7.36 (s).

1,4-Diallylbenzene
^{1}H NMR ($CDCl_3$/TMS): δ = 3.32–3.39 (m, 2 H, CH_2), 5.01–5.11 (m, 2 H, =CH_2), 5.83–6.03 (m, 1 H, =CH), 7.12 (s, 4 H_{arom}).

4-Allyl-[1.1′;4′.1″]terphenyl (9)
A Grignard solution was prepared from 4-allylbromobenzene (**8**; 2.0 g, 10 mmol) and Mg (260 mg, 11 mmol) in Et_2O (20 mL). After refluxing for 2 h, the reaction mixture was diluted with THF (20 mL). In another flask, a mixture of THF (20 mL), 4-bromobiphenyl (2.3 g, 10 mmol) and Pd(dppf)Cl_2 (60 mg, 0.082 mmol) was prepared. The Grignard reagent was added dropwise to this mixture, which was then stirred overnight. After hydrolysis with 0.1 M HCl, the aqueous phase was separated and extracted with CH_2Cl_2 (3 × 50 mL). The solvent of the combined organic phases was removed in vacuo and the crude product was filtered over silica gel with CH_2Cl_2 as eluent. After removal of the solvent in vacuo the product was obtained as a white solid; yield: 1.6 g (59%).

^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 3.43–3.46 (m, 2 H, =CH_2), 5.08–5.18 (m, 2 H, CH_2), 5.92–6.12 (m, 1 H, =CH), 7.25–7.62 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

Thioacetic Acid *S*-(3-[1.1′;4′.1″]terphenyl-4-ylpropyl) Ester (10)
A solution of **8** (1.0 g, 3.7 mmol) and thioacetic acid (1.0 mL, 1.0 g, 18 mmol) in CH_2Cl_2 (10 mL) was irradiated with a 150 W mercury lamp. After 12 h, the solvent and the excess thioacetic acid were removed in vacuum. Purification of the crude product by column chromatography on silica gel with CH_2Cl_2–hexane (1:1) followed by crystallization from glacial HOAc gave a white solid; yield: 0.5 g (39%); mp 175 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.95 (tt, 2 H, *J* = 7.6, 7.2 Hz, CH_2), 2.35 (s, 3 H, CH_3), 2.75 (t, *J* = 7.6 Hz, 2 H, CH_2), 2.93 (t, *J* = 7.3 Hz, 2 H, CH_2), 7.25–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CHarom-H-2′, H-3′, H-5′, H-6′).

3-[1.1′;4′.1″]Terphenyl-4-yl-propan-1-thiol (11)
A mixture of **9** (0.80 g, 2.3 mmol), powdered KOH (0.50 g, 7.6 mmol), THF (50 mL) and H_2O (10 mL) was refluxed overnight and then acidified with 1 M HCl. The aqueous phase was extracted with CH_2Cl_2 (4 ×) and the combined organic layers were concentrated in vacuum. Purification of the crude product by column chromatography on silica gel with CH_2Cl_2–hexane (1:1) gave a white solid; yield: 0.60 g (83%) (Table 1).

Protection of ω-Bromoalkan-1-ols; 2-(5-Bromopentyloxy)tetrahydropyran (12b); Typical Procedure
To a solution of ω-bromopentan-1-ol (10 g, 60 mmol) in CH_2Cl_2 (35 mL) were added trifluoroacetic acid (1 drop) and 3,4-dihydro-2*H*-pyran (9.8 g, 0.12 mol). The reaction mixture was stirred overnight in the dark. After concentration in vacuo, the crude product was filtered over alumina (hexane–CH_2Cl_2, 1:1). Evaporation of the solvent afforded a pale yellow liquid; yield: 13.0 g (86%); bp 90 °C/0.01 mbar.

The ^{1}H NMR data were in accord with literature values.[22]

2-(4-Bromobutyloxy)tetrahydropyran (12a)
Yield: 3.5 g (50%); bp 85 °C/0.01 mbar; pale yellow liquid.

The ^{1}H NMR data were in accord with literature values.[15]

2-(6-Bromohexyloxy)tetrahydropyran (12c)
Yield: 3.9 g (95%); clear liquid.

The ^{1}H NMR data were in accord with literature values.[15]

MS-EI: *m*/*z* (%) = 263.0 (5, M^+ – H), 163.0 (4, BrC_6H_{12}-cation), 85.0 (100, tetrahydropyran-H).

2-(11-Bromoundecyloxy)tetrahydropyran (12d)
Yield: 6.86 g (96%); clear liquid.

The analytical data were in accord with literature values.[23]

Kumada Cross-Coupling of sp^2,sp^3-Carbon Atoms; 2-[5-(4-Bromophenyl)pentyloxy]tetrahydropyran (13b); Typical Procedure
A solution of **12b** (6.4 g, 26 mmol) in THF (30 mL) was added dropwise to Mg (1.0 g, 42 mmol) and the mixture was refluxed for 1 h. This solution was added dropwise to a solution of 1,4-dibromobenzene (13 g, 54 mmol) and Pd(dppf)Cl_2 (80 mg, 0.11 mmol) in THF (50 mL). During the addition the mixture turned from an orange suspension to a red solution, which turned after some minutes to yellow. After stirring overnight, the mixture was hydrolyzed with conc. NH_4OH/NH_4Cl-buffer. The aqueous layer was extracted with CH_2Cl_2 (3 ×) and the combined organic phases were dried (Na_2CO_3). The solvent and the excess 1,4-dibromobenzene were removed in vacuo. The crude product was filtered over alumina (hexane–CH_2Cl_2, 9:1). Evaporation of the solvent afforded a clear liquid; yield: 3.52 g (42%).

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.25–1.84 (series of m, 12 H, H-2$_{chain}$, H-3$_{chain}$, H-4$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.57 (t, *J* = 7.6 Hz, 2 H, H-5$_{chain}$), 3.32–3.90 (series of m, 4 H, H-1$_{chain}$, H-6$_{ring}$), 4.55 (m, 2 H, H-2$_{ring}$), 7.04 (d, *J* = 8.4 Hz, 2 H, CH$_{arom}$-H-3, H-5), 7.38 (d, *J* = 8.4 Hz, 2 H, CH$_{arom}$-H-2, H-6).

2-[4-(4-Bromophenyl)butyloxy]tetrahydropyran (13a)
Yield: 1.6 g (34%); colorless liquid.

^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ = 1.33–1.84 (series of m, 10 H, H-2$_{chain}$, H-3$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.60 (t, *J* = 7.1 Hz, 2 H, H-4$_{chain}$), 3.34–3.93 (series of m, 4 H, H-1$_{chain}$, H-6$_{ring}$), 4.56 (m, 2 H, H-2$_{ring}$), 7.05 (d, *J* = 8.4, 2.3 Hz, 2 H, CH$_{arom}$-H-3, H-5), 7.39 (d, *J* = 8.4 Hz, 2 H, CH$_{arom}$-H-2, H-6).

2-[6-(4-Bromophenyl)hexyloxy]tetrahydropyran (13c)
Yield: 2.7 g (54%); clear liquid.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.27–1.85 (series of m, 14 H, H-2$_{chain}$, H-3$_{chain}$, H-4$_{chain}$, H-5$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.56 (t, *J* = 7.6 Hz, 2 H, H-6$_{chain}$), 3.31–3.92 (series of m, 4 H, H-1$_{chain}$, H-6$_{ring}$), 4.57 (m, 2 H, H-2$_{ring}$), 7.04 (d, *J* = 8.3 Hz, 2.3 Hz, 2 H, CH$_{arom}$-H-3, H-5), 7.38 (d, *J* = 8.3 Hz, 2 H, CH$_{arom}$-H-2, H-6).

2-[11-(4-Bromophenyl)undecyloxy]tetrahydropyran (13d)
Yield: 2.16 g (44%); yellowish liquid.

^{1}H NMR (200 MHz, C_6D_6): δ = 0.21–1.50 (series of m, 22 H, H-3$_{chain}$ to H-10$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 1.50–1.92 (m, 2 H, H-2$_{chain}$), 2.53 (t, *J* = 7.6 Hz, 2 H, H-11$_{chain}$), 3.45–3.50 (m, 2 H, H-6$_{ring}$), 3.89–3.99 (m, 2 H, H-1$_{chain}$), 4.32 (m, 1 H, H-2$_{ring}$), 6.88 (d, *J* = 8.3 Hz, 2 H, CH$_{arom}$-H-3, H-5), 7.17 (d, *J* = 8.4 Hz, 2 H, CH$_{arom}$-H-2, H-6).

Kumada Cross-Coupling of sp^2,sp^2-Carbon Atoms; 2-(5-[1.1′;4′.1″]Terphenyl-4-ylpentyloxy)tetrahydropyran (14b); Typical Procedure
A Grignard solution, prepared from 4-bromobiphenyl (2.8 g, 12 mmol) and Mg (0.50 g, 21 mmol) in THF (25 mL) was added dropwise to a solution of **13b** (3.5 g, 11 mmol) and Pd(dppf)Cl_2 (50 mg, 0.068 mmol) in THF (30 mL). During the addition the mixture turned from an orange suspension to a red solution. When the addition was complete, the mixture turned pale brown and a white precipitate was formed. After stirring overnight, the mixture was hydrolyzed with conc. NH_4OH/NH_4Cl-buffer. The aqueous layer was extracted with CH_2Cl_2 (3 ×) and the combined organic phases were dried (Na_2CO_3). The solvent was removed in vacuo. The crude product was filtered over alumina (hexane–CH_2Cl_2, 1:1). Evaporation of the solvent and crystallization of the residue from hexane afforded a yellow solid; yield: 3.0 g (63%).

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.45–1.77 (series of m, 12 H, H-2$_{chain}$, H-3$_{chain}$, H-4$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.70 (t, *J* = 7.6 Hz, 2 H, H-5$_{chain}$), 3.40–3.84 (series of m, 4 H, H-1$_{chain}$, H-6$_{ring}$), 4.60 (m, 2 H, H-2$_{ring}$), 7.27–7.65 (m, 9 H, CH$_{arom}$-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.69 (s, 4 H, CH$_{arom}$-H-2′, H-3′, H-5′, H-6′).

2-(4-[1.1′;4′.1″]Terphenyl-4-ylbutyloxy)tetrahydropyran (14a)
Yield: 2.8 g (51%); white solid.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.43–1.83 (series of m, 10 H, H-2$_{chain}$, H-3$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.70 (t, 7.3 Hz, 2 H, H-4$_{chain}$), 3.38–3.93 (series of m, 4 H, H-1$_{chain}$, H-6$_{Ring}$), 4.57 (m, 2 H, H-2$_{ring}$), 7.30–7.64 (m, 9 H, CH$_{arom}$-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.66 (s, 4 H, CH$_{arom}$-H-2′, H-3′, H-5′, H-6′).

2-(6-[1.1′;4′.1″]Terphenyl-4-ylhexyloxy)tetrahydropyran (14c)
Yield: 1.9 g (59%); white solid.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.40–1.76 (series of m, 14 H, H-2$_{chain}$, H-3$_{chain}$, H-4$_{chain}$, H-5$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 2.66 (t, *J* = 7.6 Hz, 2 H, H-6$_{chain}$), 3.34–3.87 (series of m, 4 H, H-1$_{chain}$, H-6$_{ring}$), 4.58 (m, 2 H, H-2$_{ring}$), 7.25–7.63 (m, 9 H, CH$_{arom}$-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH$_{arom}$-H-2′, H-3′, H-5′, H-6′).

2-(11-[1.1′;4′.1″]Terphenyl-4-ylundecyloxy)tetrahydropyran (14d)
Yield: 0.47 g (26%); white solid.

^{1}H NMR (400 MHz, C_6D_6): δ = 0.21–1.90 (m, 22 H, H-3$_{chain}$ to H-10$_{chain}$, H-3$_{ring}$, H-4$_{ring}$, H-5$_{ring}$), 1.50–1.72 (m, 2 H, H-2$_{chain}$) 2.52–2.63 (t, *J* = 7.7 Hz, 2 H, H-11$_{chain}$), 3.30–3.45 (m, 2 H, H-1$_{chain}$), 3.81–3.92 (m, 2 H, H-6$_{ring}$), 4.63 (m, 1 H, H-2$_{ring}$), 7.11–7.64 (m, 9 H, CH$_{arom}$-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.60 (s, 4 H, CH$_{arom}$-H-2′, H-3′, H-5′, H-6′).

Deprotection of ω-Terphenylalkan-1-ols; 5-[1.1′;4′.1″]Terphenyl-4-ylpentan-1-ol (15b); Typical Procedure
To a solution of **14b** (3.0 g, 7.5 mmol) in THF (40 mL) and H_2O (10 mL) was added conc. HCl (3 mL). The cloudy solution became clear after 30 min. After another 30 min, the solution turned light yellow and a white precipitate was formed. The mixture was stirred overnight and extracted with CH_2Cl_2 (3 ×). The solvents were removed in vacuo. The residue was washed with hot hexane to give a yellow solid; yield: 1.8 g (76%).

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.22–1.79 (series of m, 6 H, H-2$_{chain}$, H-3$_{chain}$, H-4$_{chain}$), 2.68 (t, *J* = 7.6 Hz, 2 H, H-5$_{chain}$), 3.66 (t, *J* = 6.3 Hz, 2 H, H-1$_{chain}$), 7.25–7.64 (m, 9 H, CH$_{arom}$-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH$_{arom}$-H-2′, H-3′, H-5′, H-6′).

4-[1.1′;4′.1″]Terphenyl-4-ylbutan-1-ol (15a)
Yield: 2.0 g (90%); pale orange solid.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.62–1.78 (series of m, 4 H, H-2_{chain}, H-3_{chain}), 2.71 (t, *J* = 7.2 Hz, 2 H, H-4_{chain}), 3.70 (t, *J* = 6.2 Hz, 2 H, H-1_{chain}), 7.30–7.64 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

6-[1.1′;4′.1″]Terphenyl-4-ylhexan-1-ol (15c)
Yield: 1.3 g (82%); white solid; mp 180 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.25–1.59 (series of m, 8 H, H-2_{chain} to H-5_{chain}), 2.67 (t, *J* = 7.8 Hz, 2 H, H-6_{chain}), 3.66 (t, *J* = 6.3 Hz, 2 H, H-1_{chain}), 7.25–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

11-[1,1′;4′,1″]Terphenyl-4-ylundecan-1-ol (15d)
Yield: 0.30 g (77%); white wax.

^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 1.20–1.73 (series of m, 18 H, H-2_{chain} to H-10_{chain}), 2.67 (t, *J* = 7.8 Hz, 2 H, H-11_{chain}), 3.67 (t, *J* = 6.3 Hz, 2 H, H-1_{chain}), 7.20–7.65 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.67 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

Thio-Mitsunobu Reaction; Thiopivalic Acid *S*-(5-[1.1′;4′.1″]terphenyl-4-ylpentyl) Ester (16b); Typical Procedure
A solution of Ph_3P (2.9 g, 11 mmol) in THF (30 mL) was cooled to 0 °C. Diisopropyl azodicarboxylate (2.3 mL, 12 mmol) was added dropwise and a yellow precipitate was formed. To the cooled mixture, a suspension of **15b** (1.8 g, 11 mmol) and thiopivalic acid (**5**; 1.3 mL, 11 mmol) in THF (60 mL) was added slowly. The cooling was removed and the mixture was stirred for 1 h. After refluxing for 2 h, the solvent was removed. The residue was mixed with EtOH, which was afterwards removed in vacuo. The residue was subjected to flash chromatography (silica gel, hexane–CH_2Cl_2, 4:1 → 2:1) to give a crude product, which was crystallized from EtOH giving a white solid; yield: 1.2 g (26%); mp 149 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.23 (s, 9 H, CH_3), 1.47–1.69 (series of m, 6 H, H-2_{chain}, H-3_{chain}, H-4_{chain}), 2.66 (t, *J* = 7.6 Hz, 2 H, H-5_{chain}), 2.84 (t, *J* = 7.2 Hz, 2 H, H-1_{chain}), 7.24–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.66 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$/TMS): δ = 27.4 (CH_3), 28.4 (C-3_{chain}), 28.5 (C-2_{chain}), 29.4 (C-4_{chain}), 30.9 (C-1_{chain}), 35.4 (C-5_{chain}), 46.4 [*C*(CH_3)$_3$], 126.8, 126.9, 127.2, 127.4, 128.7, 128.8 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 138.0, 139.7, 139.9, 140.6, 141.7 (C-1, C-4, C-1′, C-4′, C-1″), 206.9 (C=O).

Thiopivalic Acid *S*-(4-[1.1′;4′.1″]terphenyl-4-ylbutyl) Ester (16a)
Yield: 1.5 g (56%); white solid; mp 156 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.23 (s, 9 H, CH_3), 1.63–1.75 (series of m, 4 H, H-2_{chain}, H-3_{chain}), 2.68 (t, *J* = 7.3 Hz, 2 H, H-4_{chain}), 2.88 (t, *J* = 7.0 Hz, 2 H, H-1_{chain}), 7.24–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.66 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$/TMS): δ = 27.4 (CH_3), 28.3 (C-2_{chain}), 29.2 (C-3_{chain}), 30.6 (C-1_{chain}), 35.0 (C-4_{chain}), 46.4 [C(*C*H_3)$_3$], 126.9, 127.0, 127.3, 127.5, 128.8, 128.9 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 138.2, 139.9, 140.0, 140.7, 141.4 (C-1, C-4, C-1′, C-4′, C-1″), 207.0 (C=O).

Thiopivalic Acid *S*-(6-[1.1′;4′.1″]terphenyl-4-ylhexyl) Ester (16c)
Yield: 1.0 g (60%); white solid; mp 144 °C.

^{1}H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.23 (s, 9 H, CH_3), 1.24–1.65 (series of m, 8 H, H-2_{chain}, H-3_{chain}, H-4_{chain}, H-5_{chain}), 2.65 (t, *J* = 7.6 Hz, 2 H, H-6_{chain}), 2.83 (t, *J* = 7.2 Hz, 2 H, H-1_{chain}), 7.24–7.63 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.66 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$/TMS): δ = 27.4 (CH_3), 28.5 (C-3_{chain}), 28.7 (C-4_{chain}), 28.8 (C-2_{chain}), 29.5 (C-5_{chain}), 31.3 (C-1_{chain}), 35.5 (C-6_{chain}), 46.4 [*C*(CH_3)$_3$], 126.8, 126.9, 127.2, 127.4, 128.7, 128.8 (C-2, C-3, C-5, C-6, C-2′, C-3′, C-5′, C-6′, C-2″ to C-6″), 137.9, 139.7, 140.0, 140.7, 141.9 (C-1, C-4, C-1′, C-4′, C-1″), 206.9 (C=O).

Thiopivalic Acid *S*-(11-[1.1′;4′.1″]terphenyl-4-yl-undecyl) Ester (16d)
Yield: 0.20 g (53%); white solid; mp 123–124 °C.

^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 1.20 (s, 9 H, CH_3), 1.25–1.90 (series of m, 18 H, H-2_{chain} to H-10_{chain}), 2.66 (t, *J* = 7.8 Hz, 2 H, H-11_{chain}), 2.83 (t, *J* = 7.4 Hz, 2 H, H-1_{chain}), 7.20–7.66 (m, 9 H, CH_{arom}-H-2, H-3, H-5, H-6, H-2″ to H-6″), 7.68 (s, 4 H, CH_{arom}-H-2′, H-3′, H-5′, H-6′).

Reductive Cleavage of Thio Esters 6, 16a–d; 5-[1.1′;4′.1″]Terphenyl-4-ylpentan-1-thiol (17b); Typical Procedure
To a suspension of $LiAlH_4$ (0.34 g, 9.0 mmol) in THF (5 mL) was added slowly a solution of thioester **15b** (1.2 g, 2.9 mmol) in THF (50 mL). After 1 h, the mixture was hydrolyzed with 1 M HCl (20 mL) and extracted with CH_2Cl_2 (3 × 75 mL). After the removal of the solvent, the crude product was filtered over silica gel (hexane–CH_2Cl_2, 1:1). Evaporation of the solvent afforded a white solid; yield: 0.88 g (90%). For analytical data, see Table 1.

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