# Synthesis of a Rigid Tetrahedral Linker with Thioether End Groups

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**Abstract:** The synthesis of a tetrahedral thio end-functionalized rigid oligo(*p*-phenylene ethynylene) (OPE) based on a convergent approach is reported.

**Key words:** alkynes, cross-coupling, nanostructures

There has been increasing interest in the synthesis and self-assembly of noble metal nanoparticles in recent years. In particular, gold and silver particles have gathered attention because they feature a localized surface plasmon resonance in the visible region and because of their high environmental stability.[1] Their tunable size and structure allows devices with tailor-made optical properties to be fabricated that could be used in applications for energy conversion,[2] medicinal therapy,[3] sensors,[4] and optical devices.[5] Moreover, their optical response is not only governed by their dimension or shape but, in fact, also by the spatial arrangement of the particles to each other. Hence, it is crucial to implement methods that enable the precise formation of ordered plasmonic nanoparticle assemblies. Top-down approaches involve the pattering of large preformed metal structures, whereas the top-up strategy utilizes patterned surfaces that are subsequently functionalized with nanoparticles. The bottom-up approach relies on the assembly of nanoparticles, for example through chemical reactions or electrostatic interactions. Click,[6] Diels–Alder,[7] and oligonucleotide[8] reactions have successfully been used to create clusters with a precise number of particles. Moreover, mediated by polymers, clusters with dozens of particles can be synthesized.[9] Thiols, and to a lesser extent amines, show strong affinity towards gold surfaces. Molecules with a defined geometry, for example thio end-functionalized linear linkers therefore allow ordered nanoparticle structures to be created. The electromagnetic interactions between the particles and, hence, the optical response is strongly dependent on the interparticle distance. As a result, a pivotal point is to utilize molecules with a defined distance between the functional moieties. Whereas α,ω-alkane thiols have been employed to assemble gold nanoparticles, the flexibility of the alkyl chain prevents a stable gap between the particles.[10] To avoid this problem, rigid linker molecules based on arylene vinylenes and arylene ethynylenes were introduced as a design principle.[11] However, until now, uncertainty remained over the exact binding mode of such linkers. Yan and co-workers reported the synthesis of rigid quadratic and trigonal planar linkers but, instead of binding three or four gold nanoparticles, the chelating effect allowed only two particles to be bridged.[12] In contrast, Novak et al. reported the successful formation of dimers and trimers with similar linkers.[13]

Here we report the synthesis of a tetrahedral molecule. By attaching **8** to a large gold nanoparticle surface, the most probable structure is that three arms bind to the surface of the particle. The fourth arm stands out perpendicular to the surface and is able to bind another particle. If instead, compared to the linker size, small nanoparticles are employed, each arm would be able to bind one particle, resulting in a tetrahedral cluster.

Different strategies can be utilized to create these kinds of linkers.[14] In the divergent approach, starting from a tetraphenylmethane core, in consecutive steps more phenyl ethynylene units could be coupled onto the core. However, side reactions or incomplete functionalization of all arms results in structures with similar properties (e.g., $R_f$ values) and, as a result, separation of these impurities from the desired product becomes an increasingly tedious task the longer the arm becomes. The second strategy involves the convergent approach, whereby the arm is synthesized first, followed by final attachment to the core.

An acetylene-functionalized core and an iodo-functionalized arm could be coupled through a Sonogashira reaction. Star-star coupling of the core, however, leads to a complex mixture of byproducts. Hence, a more versatile approach is the utilization of an iodo-substituted core and the respective arm. The creation of large rigid OPE structures can be accomplished in most cases by utilizing the bifunctional compound **C**, which can be coupled onto an acetylene moiety through a Sonogashira reaction (Scheme 1).[15] Subsequent cleavage of the $SiMe_3$ protecting group followed by reaction with **C** allows the number of repeating units to be increased in consecutive steps. Another strategy involves the orthogonal deprotection of compound **B**, which can be converted either into compound **C** or into compound **D**.[16] The latter can be coupled with the corresponding iodo compound followed by conversion of the triazene moiety with, for example iodomethane to give the elongated iodo compound.

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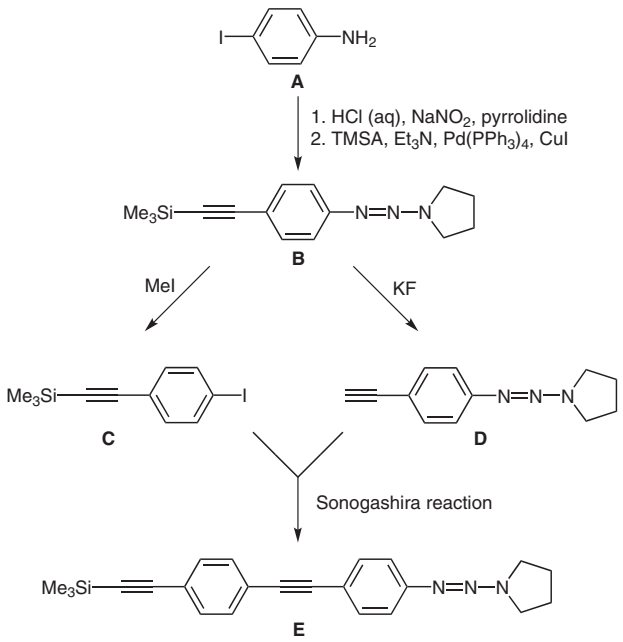
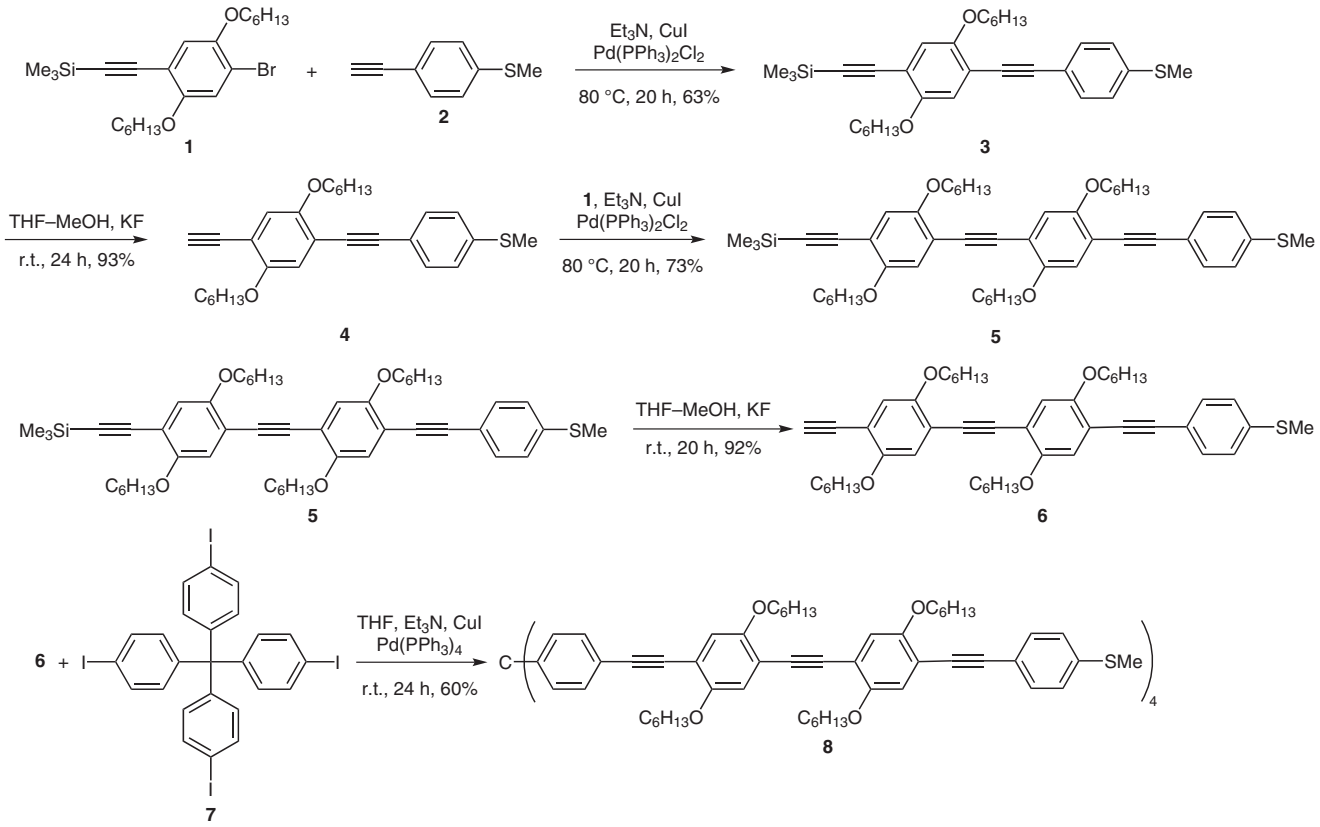



**Scheme 1** Schematic representation of the synthesis of OPEs[14]

*p*-Iodoaniline (**A**) is a common starting material for both approaches; however, incorporation of side chains that improve the solubility is difficult to achieve. For an increasing number of repeating units, the solubility of the OPEs decreases due to extensive π-stacking. Experiments conducted with linear linkers devoid of side-chains showed only poor solubility, which hampers purification as well as potential applications.

Hydroquinone was found to be a suitable starting material for linkers with increased solubility because it allows the introduction of long alkyl side chains through etherification of the hydroxyl groups. Moreover, halogenation with *N*-bromosuccinimide (NBS) and iodine followed by a Sonogashira reaction gave compound **1**, which is similar in its structure to **C**. The strength of the gold–sulfur interaction is, to a large extent, dependent on the nature of the thio moiety.[17]

Thiol groups and disulfides bind most strongly; however, they interfere with the palladium-catalyzed cross-coupling reaction. Whereas thioacetates can be utilized as protecting groups for thiols, we found that they are also cleaved off to a significant extent during the reaction, thus hampering multiple consecutive synthetic steps with this moiety. Hence, although offering a less strong gold–sulfur interaction, thioethers were chosen due to their good chemical stability. Therefore, **1** was coupled with *p*-ethynylthioanisole **2** in a Sonogashira reaction to give **3** as a yellow solid (Scheme 2). It should be noted that **1** can contain substantial amounts of the disubstituted trimethylsilylacetylene (TMSA) compound where the bromine is additionally substituted by TMSA. Both are difficult to separate by column chromatography, however, upon subsequent coupling with **2** only the bromo-substituted compound reacts. Compound **3** can then easily be separated from the disubstituted compound by column chromatog-




**Scheme 2** Schematic representation of the synthesis of the tetrahedral linker

raphy. The conversion of the reaction and the attachment of the phenylene-ethynylene units can be easily followed by thin-layer chromatography. Both the $R_f$ value and the fluorescence of the product change significantly as the length of the conjugated π system increases. In the following step, cleavage of the trimethylsilyl group was achieved through conversion with potassium fluoride under an inert atmosphere to yield acetylene **4**. Subsequently, a second Sonogashira reaction was applied to react **4** with compound **1** to give **5** in 73% yield. Cleavage of the trimethylsilyl groups was accomplished in the same way as described before to yield the linker arm **6**. Through a Sonogashira reaction of the arm with tetrakis(4-iodophenylmethane) **7**, finally the tetrahedral linker **8** could be synthesized. The compound shows good solubility in common organic solvents such as chloroform, tetrahydrofuran and *N*,*N*-dimethylformamide.

In conclusion, a novel, rigid tetrahedral linker for the potential self-assembly of gold nanoparticles has been synthesized. The formation of plasmonic superstructures with this compound is under investigation.

Reagents and solvents were purchased from Carl Roth, Sigma–Aldrich, Fluka, Merck and VWR. All chemicals were used as received. THF was distilled over sodium/benzophenone under an argon atmosphere. Triethylamine was distilled over KOH under an argon atmosphere. $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AC 300 at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) and were calibrated against residual protiosolvent. ESI-Q-TOF-MS measurements were performed with a micrOTOF (Bruker Daltonics) mass spectrometer. Elemental analyses were carried out with a Vario ELIII – Elementar Euro and an EA from HekaTech. Melting points were determined with a Stuart SMP3. IR spectra were measured with a Shimadzu IRAffinity-1 FTIR-spectrophotometer. Compounds **1**,[18] **2**,[19] and **7**[20] were prepared as reported.

**[(2,5-Bis(hexyloxy)-4-{[4-(methylthio)phenyl]ethynyl}phenyl)ethynyl]trimethylsilane (3)**

Compound **1** (3.06 g, 6.75 mmol), **2** (1 g, 6.75 mmol), and CuI (13 mg, 6.8 μmol) were dissolved in $Et_3N$ (50 mL). The solution was purged with argon for 1 h and subsequently $Pd(PPh_3)_2Cl_2$ (48 mg, 6.8 μmol) was added. The solution was heated to 80 °C and stirred at this temperature for 20 h. The solvent was then removed under reduced pressure and the residue was dissolved in $CHCl_3$ (100 mL). The organic phase was washed three times with $H_2O$, dried over $Na_2SO_4$ and finally the solvent was removed under reduced pressure. The crude product was purified by column chromatography ($SiO_2$; $CH_2Cl_2$–hexane, 1:1) to obtain **3**.

Yield: 2.2 g (63%); yellow solid; mp 67 °C.

IR (FTIR): 2940, 2859, 2156, 1504, 1389, 1215, 1030, 891, 837, 810, 760, 637 cm$^{-1}$.

$^1$H NMR (300 MHz, $CD_2Cl_2$): δ = 7.46 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.00 (s, 1 H), 6.96 (s, 1 H), 4.02 (m, 4 H, 2 × $OCH_2$), 2.54 (s, 3 H, $SCH_3$), 1.84 (m, 4 H, 2 × $CH_2$), 1.58 (m, 4 H, 2 × $CH_2$), 1.39 (m, 8 H, 4 × $CH_2$), 0.94 (m, 6 H, 2 × $CH_3$), 0.29 (s, 9 H, 3 × $SiCH_3$).

$^{13}$C NMR (75 MHz, $CD_2Cl_2$): δ = 155.4, 154.7, 141.09, 133.01, 127.01, 120.76, 118.43, 118.09, 115.49, 114.88, 102.47, 101.26, 95.82, 87.23, 70.88, 70.84, 32.91, 32.89, 30.62, 30.6, 27.02, 27.0, 23.95, 16.38, 15.14, 15.12, 0.91.

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{32}H_{44}O_2SSiNa^+$: 543.2723; found: 543.2712.

Anal. Calcd for $C_{32}H_{44}O_2SSi$: C, 73.79; H, 8.51; S, 6.16. Found: C, 74.00; H, 8.46; S, 6.16.

**(4-{[4-Ethynyl-2,5-bis(hexyloxy)phenyl]ethynyl}phenyl)(methyl)sulfane (4)**

Compound **3** (970 mg, 1.86 mmol) and KF (540 mg, 9.29 mmol) were dissolved in a 1:1 mixture of MeOH and THF (40 mL). After stirring at r.t. under an argon atmosphere for 24 h, toluene (100 mL) was added and the mixture was washed three times with $H_2O$ and then dried with $Na_2SO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography ($SiO_2$; $CHCl_3$–hexane, 1:1) to obtain **4**.

Yield: 780 mg (93%); yellow solid; mp 81 °C.

IR (FTIR): 3287, 2940, 2851, 2357, 1504, 1389, 1273, 1219, 1030, 864, 818, 733, 637 cm$^{-1}$.

$^1$H NMR (300 MHz, $CD_2Cl_2$): δ = 7.44 (d, *J* = 8.2 Hz, 2 H), 7.22 (d, *J* = 8.2 Hz, 2 H), 6.99 (s, 1 H), 6.98 (s, 1 H), 3.99 (m, 4 H, 2 × $OCH_2$), 3.38 (s, 1 H, CH), 2.50 (s, 3 H, $SCH_3$), 1.80 (m, 4 H, 2 × $CH_2$), 1.54 (m, 4 H, 2 × $CH_2$), 1.36 (m, 8 H, 4 × $CH_2$), 0.91 (m, 6 H, 2 × $CH_3$).

$^{13}$C NMR (75 MHz, $CD_2Cl_2$): δ = 154.39, 153.59, 140.08, 131.94, 125.93, 119.62, 117.95, 116.88, 114.81, 112.59, 94.79, 86.02, 82.35, 80.19, 69.87, 69.81, 31.81, 31.76, 29.51, 29.38, 25.94, 25.81, 22.87, 22.82, 15.29, 14.03, 14.02.

HRMS (ESI): *m*/*z* [M + H] calcd for $[C_{29}H_{36}O_2S + H]^+$: 449.2509; found: 449.2488.

Anal. Calcd for $C_{29}H_{36}O_2S$: C, 77.63; H, 8.09; S, 7.15. Found: C, 77.66; H, 8.30; S, 6.95.

**({4-[(2,5-Bis(hexyloxy)-4-{[4-(methylthio)phenyl]ethynyl}phenyl)ethynyl]-2,5-bis(hexyloxy)phenyl}ethynyl)trimethylsilane (5)**

Compound **4** (1.2 g, 2.67 mmol) and **1** (1.21 g, 2.67 mmol) were dissolved in $Et_3N$ (50 mL). The solution was purged with argon for 45 min, then $Pd(PPh_3)_2Cl_2$ (18.9 mg 2.67 μmol) and CuI (5 mg, 2.67 μmol) were added and the solution was heated to 80 °C and stirred at this temperature overnight. $Et_2O$ (100 mL) was added and the mixture was washed with $H_2O$ (3 × 100 mL). The organic phase was then dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography ($SiO_2$; $CHCl_3$–hexane, 1:1) and then recrystallized from EtOH to obtain **5**.

Yield: 1.6 g (73%); yellow solid; mp 70 °C.

IR (FTIR): 2947, 2851, 2361, 2149, 1497, 1389, 1273, 1215, 1034, 841 cm$^{-1}$.

$^1$H NMR (300 MHz, $CD_2Cl_2$): δ = 7.48 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.2 Hz, 2 H), 7.05 (s, 1 H), 7.04 (s, 1 H), 7.00 (s, 1 H), 6.98 (s, 1 H), 4.04 (m, 8 H, 4 × $OCH_2$), 2.54 (s, 3 H, $SCH_3$), 1.87 (m, 8 H, 4 $CH_2$), 1.56 (m, 8 H, 2 $CH_2$), 1.39 (m, 16 H, 8 × $CH_2$), 0.94 (m, 12 H, 4 × $CH_3$), 0.29 (s, 9 H, 3 × $SiCH_3$).

$^{13}$C NMR (75 MHz, $CD_2Cl_2$): δ = 154.68, 154.14, 154.07, 153.91, 140.37, 132.29, 126.31, 120.08, 117.81, 117.59, 117.54, 117.41, 114.91, 114.63, 114.48, 114.34, 101.76, 100.62, 95.2, 92.05, 91.87, 86.67, 70.26, 70.24, 70.17, 70.1, 32.2, 29.92, 29.86, 26.34, 26.29, 26.26, 26.24, 23.24, 15.66, 14.40, 0.19.

HRMS (ESI): *m*/*z* [M + H] calcd for $[C_{52}H_{72}O_4SSi + H]^+$: 821.4993; found: 821.4938.

Anal. Calcd for $C_{52}H_{72}O_4SSi$: C, 76.05; H, 8.84; S, 3.9. Found: C, 76.35; H, 8.86; S, 4.29.

**{4-[(4-{[4-Ethynyl-2,5-bis(hexyloxy)phenyl]ethynyl}-2,5-bis(hexyloxy)phenyl)ethynyl]phenyl}(methyl)sulfane (6)**

Compound **5** (830 mg, 1.01 mmol) and KF (460 mg, 7.91 mmol) were dissolved in a 1:1 mixture of MeOH and THF (40 mL). After stirring at r.t. under an argon atmosphere overnight, toluene (100 mL) was added to the solution. The mixture was washed three times

with $H_2O$, then dried with $Na_2SO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography ($SiO_2$; $CH_2Cl_2$–hexane, 1:1) to obtain **6**.

Yield: 700 mg (92%); yellow solid; mp 82 °C.

IR (FTIR): 3291, 2920, 2851, 2361, 1732, 1505, 1420, 1389, 1204, 1030, 860, 818, 617 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 7.45 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 7.05–6.95 (m, 4 H), 4.01 (m, 8 H, 4 × $OCH_2$), 3.39 (s, 1 H, CH), 2.51 (s, 3 H, $SCH_3$), 1.84 (m, 8 H, 4 × $CH_2$), 1.52 (m, 8 H, 4 × $CH_2$), 1.36 (m, 16 H, 8 × $CH_2$), 0.90 (m, 12 H, 4 × $CH_3$).

$^{13}C$ NMR (75 MHz, $CD_2Cl_2$): δ = 155.11, 154.51, 154.46, 154.23, 140.74, 132.66, 126.68, 120.44, 118.81, 117.92, 117.84, 117.79, 115.68, 115.07, 114.78, 113.49, 95.58, 92.43, 92.06, 87.01, 83.15, 80.91, 70.68, 70.63, 70.56, 70.53, 32.55, 32.49, 30.29, 30.22, 30.21, 30.13, 26.70, 26.60, 26.55, 23.59, 23.54, 16.03, 14.76.

HRMS (ESI): *m/z* [M + H] calcd for $[C_{49}H_{64}O_4S + H]^+$: 749.4598; found: 749.4546.

Anal. Calcd for $C_{49}H_{64}O_4S$: C, 78.56; H, 8.61; S, 4.28. Found: C, 78.79; H, 8.84; S, 4.05.

**Tetrakis[4-({4-[(2,5-bis(hexyloxy)-4-{[4-(methylthio)phenyl]ethynyl}phenyl)ethynyl]-2,5-bis-(hexyloxy)phenyl}ethynyl)phenyl]methane (8)**

Compound **6** (280 mg, 0.37 mmol), **7** (70 mg, 85.5 µmol), $Pd(PPh_3)_4$ (23 mg, 20 µmol) and CuI (3.8 mg, 20 µmol) were dissolved in THF (5 mL). The solution was purged 20 min with nitrogen and subsequently $Et_3N$ (5 mL) was added. The solution was stirred at r.t. for 24 h, then heated to 80 °C for 3 h. Subsequently, the solvent was removed under reduced pressure and the crude product was purified by column chromatography ($SiO_2$; $CH_2Cl_2$–hexane, 3:2) to obtain **8**.

Yield: 170 mg (60%); dark-yellow solid; mp 90 °C.

IR (FTIR): 2929, 2859, 2361, 1732, 1508, 1420, 1377, 1277, 1215, 1018, 860, 818 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CD_2Cl_2$): δ = 7.46 (m, 16 H), 7.22 (m, 16 H), 7.10–7.03 (m, 16 H), 4.05 (m, 32 H, 16 × $OCH_2$), 2.51 (s, 12 H, 4 × $SCH_3$), 1.86 (m, 32 H, 16 × $CH_2$), 1.53 (m, 32 H, 16 × $CH_2$), 1.36 (m, 64 H, 32 × $CH_2$), 0.90 (m, 48 H, 16 × $CH_3$).

$^{13}C$ NMR (75 MHz, $CD_2Cl_2$): δ = 153.72, 153.57, 153.50, 146.06, 139.79, 131.72, 130.97, 125.73, 121.50, 119.51, 116.99, 116.95, 116.84, 114.16, 114.04, 113.94, 113.88, 94.62, 94.41, 91.52, 92.42, 86.43, 86.10, 69.70, 69.63, 69.60, 65.00, 31.63, 30.59, 29.34, 29.29, 25.75, 25.68, 22.66, 15.09, 13.83.

HRMS (ESI): *m/z* [M + H] calcd for $[C_{221}H_{268}O_{16}S_4 + H]^+$: 3308.9174; found: 3309.2124.

Anal. Calcd for $C_{221}H_{268}O_{16}S_4$: C, 80.22; H, 8.16; S, 3.88. Found: C, 80.10; H, 8.36; S: 3.96.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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