

Facile Convergent Route to Molecular Caltrops

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The convergent syntheses of molecular caltrops are described starting from tetraethyl orthosilicate and using organolithium additions and Pd/Cu-catalyzed coupling methods. The caltrop core is based on a tetrahedral silicon atom, and there are three legs each bearing sulfur-tipped feet for adhesion to metallic surfaces. The forth prong (arm) is non-sulfur-bearing for projection upward from the surface. Rigid phenyleneethynylene segments are used for the legs and arms. These organosilicon caltrops may have utility as scanning probe microscopy tips.

Introduction

Scanning probe microscopy (SPM), which includes primarily scanning tunneling microscopy (STM) and atomic force microscopy (AFM), has become a critical tool for atomic-scale imaging. The application of these techniques has tremendously impacted chemistry, physics, biology, and materials science.¹ However, SPM has limited resolution for tightly spaced pattern imaging or atomically sharp surface asperities.^{2,3} This resolution deficiency results, in part, from the limited aspect ratio of the SPM tip. Since imaging sharp surface contours will be important as molecular systems for nanotechnology and biology are further investigated, a rigid and high aspect ratio tip configuration must be developed. An advance in imaging probe technology was achieved by attaching carbon nanotubes to the probe tip; however, methodologies for functionalization of the nanotube ends and for adhesion of the nanotubes to the cantilever surfaces are in their infancy.⁴ As part of our studies directed toward imaging molecular electronic device architectures,^{3,5} we describe here precisely defined molecular caltrops that may act as SPM probe tips. A classical caltrop is a tetrahedrally arranged four-pointed device such that three of the prongs naturally form a tripod on the ground while the fourth prong projects

upward when the caltrop is deployed. Iron-made versions of these structures were formerly used to impede the progress of advancing enemy cavalry while similar tools with hollow prongs have been used to erect rapid road- and airstrip-barricades. The molecular caltrops here were prepared by a facile convergent route based on a tetrahedral silicon atom core with three legs bearing thiol-tipped feet for adhesion to a metallic surface such as Au, Pt–Ir, or Ga–As.^{3,6} The thiols are protected with acetyl groups to prevent their premature oxidative coupling; we previously demonstrated the efficacy of NH₄OH-based removal of the acetyl groups during self-assembled monolayer (SAM) formation.^{3,5,7} The fourth prong is a non-sulfur-bearing arm for projection upward from the surface. Rigid phenyleneethynylene segments are used for the prong arms. The suitability of these molecular caltrops to serve as SPM tips will depend on several factors including the rigidity of the framework,⁸ the overall conductances^{3,5} (which is critical for STM but not AFM), the ability to be well dispersed on a surface via insertion into SAMs of short alkane thiols,³ and the propensity of the three sulfur-bearing arms to align toward the surface with the fourth arm projected upward. All of these factors are molecular length-dependent and an illustration of the proposed tip functionalization approach is depicted in Scheme 1. The results of SPM tip usage will be considered separately from the synthetic details described here.⁹

Results and Discussion

The caltrops with varying arm and leg lengths and tips were rapidly synthesized in a convergent manner as shown in Scheme 2. Slow addition of (*p*-iodophenyl)-lithium, generated in situ by lithium–halogen exchange of *p*-diiodobenzene in ether using *n*-BuLi, to tetraethyl

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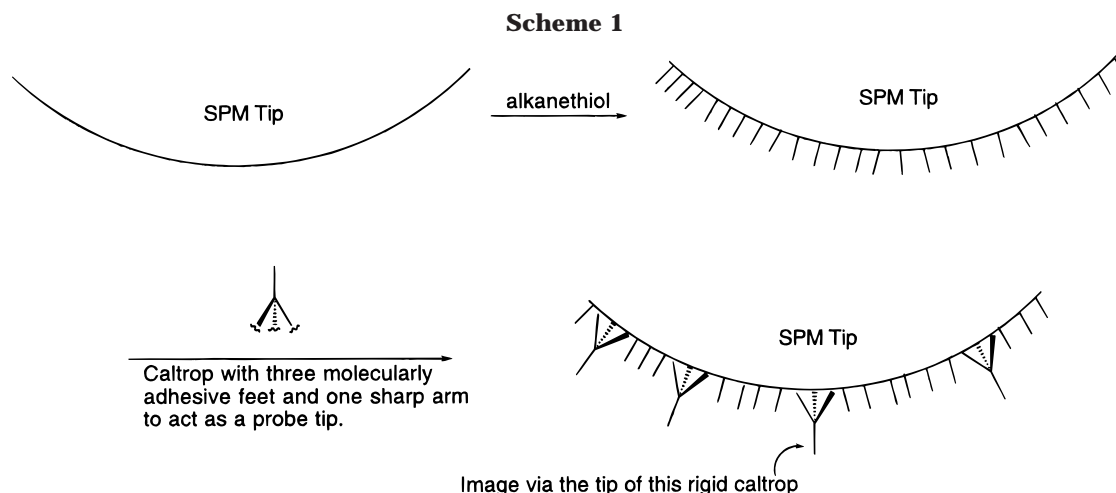
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orthosilicate afforded ethoxytri(*p*-iodophenyl)silane (**1**).¹⁰ The use of THF instead of ether as the reaction solvent gave exclusively tetra(*p*-iodophenyl)silane. Lithium-halogen exchange of 1-bromo-4-(trimethylsilylethynyl)benzene with *tert*-BuLi followed by quenching with **1** provided **2**. Attempts to prepare **2** through a one-pot transformation from *p*-diiodobenzene in ether or THF failed; only 1-iodo-4-(trimethylsilylethynyl)benzene and tetra(*p*-iodophenyl)silane were afforded via an unexpected lithium-halogen exchange process. The three legs bearing the adhesion moieties were affixed in a single pot using Pd/Cu couplings¹¹ of **2** and 1-ethynyl-4-(thioacetyl)benzene to produce the caltrop **3** with a trimethylsilyl tip. Desilylation of **3** using tetra(*n*-butyl)ammonium fluoride (TBAF), acetic anhydride and acetic acid gave the proton-tipped caltrop **4**. Deletion of the acetic anhydride during desilylation resulted in significant loss of the acetyl moieties on sulfur.^{8,12} Again, Pd/Cu coupling of **4** with 4-iodonitrobenzene afforded **5**. The terminal nitro group will provide an efficient handle for monitoring the tilt angle of the caltrop's tip-arm via grazing angle IR.³ Since we have prepared numerous oligo(phenyleneethynylene)s ranging from 10 to 140 nm via iterative doubling strategies,⁸ we demonstrated the efficacy of **4** to serve as base for tip-elongation using Pd/Cu-catalyzed coupling with 1-iodo-4-(trimethylsilylethynyl)benzene to afford **6** and its desilylated counterpart **7**.

Therefore, the molecular caltrop could be rapidly prepared with varying tip moieties and differing arm lengths to serve as potential SPM tips. The silicon core provides a suitable template for the required construction of the three legs and the probe arm, each length being

variable using differing oligo(phenyleneethynylene)s. Although the caltrop feet used here are based upon protected thiols, the methodology would permit the incorporation of numerous surface binding moieties.¹³

Experimental Section

General. Unless otherwise noted, all operations were carried out under a dry, oxygen-free nitrogen atmosphere. Combustion analyses were obtained from Atlantic Microlab, Inc. Alkyl lithium reagents were obtained from FMC and (trimethylsilyl)acetylene was obtained from FAR Research Inc., Melbourne, FL. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Bulk grade hexane was distilled prior to use. Flash chromatography was carried out using 230–400 mesh silica gel from EM Science. Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F254 with a layer thickness of 0.25 mm purchased from EM Science.

Ethoxytri(*p*-iodophenyl)silane (1**).** To a suspension of *p*-diiodobenzene (13.2 g, 40.0 mmol) in ether (250 mL) at -78°C was added *n*-BuLi (19.25 mL, 31.00 mmol, 1.61 N in hexane) via syringe pump (0.57 mL/min for the first 15 mL, and 0.32 mL/min for the next 4.25 mL). After the addition, the pale yellow slurry was stirred for 1 h and added via cannula to a precooled solution (-78°C) of tetraethyl orthosilicate (2.23 mL, 10.00 mmol) in ether (30 mL). The resulting clear solution was stirred for 30 min at -78°C and 3 h at room temperature. 1 N HCl (30 mL, 30 mmol) was added. The organic layer was separated and washed with water (2 \times) and brine (1 \times). The aqueous solution was extracted with ether (2 \times). The combined organic fractions were dried over magnesium sulfate and filtered. Removal of solvent in vacuo gave a crystalline white solid. The solid was purified by flash chromatography (silica gel, hexane) to give **1** (3.89 g, 57%) as a white solid. Mp = 174–175 $^{\circ}\text{C}$. FTIR (KBr) 2964, 2872, 1569, 1477 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 6 H), 7.28 (d, $J = 8.2$ Hz, 6 H), 3.82 (q, $J = 7.0$ Hz, 2 H), 1.21 (t, $J = 7.0$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 137.26, 136.73, 132.75, 98.05, 60.00, 18.42. HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{I}_3\text{OSi}$: 681.8183. Found: 681.8165.

Tris(4-iodophenyl)-(4-(trimethylsilylethynyl)phenyl)silane (2**).** To a solution of bromo-4-(trimethylsilylethynyl)benzene¹² (1.01 g, 4.00 mmol) in ether (15 mL) at -78°C was added dropwise *t*-BuLi (4.32 mL, 8.00 mmol, 1.85 M in pentane). The solution was stirred for 45 min and added slowly via cannula to a precooled (-78°C) solution of **1** (2.05 g, 3.00 mmol) in THF (15 mL). The flask and cannula were rinsed with ether (10 mL), and the solution was added to the reaction mixture. The resultant clear yellow solution was stirred for

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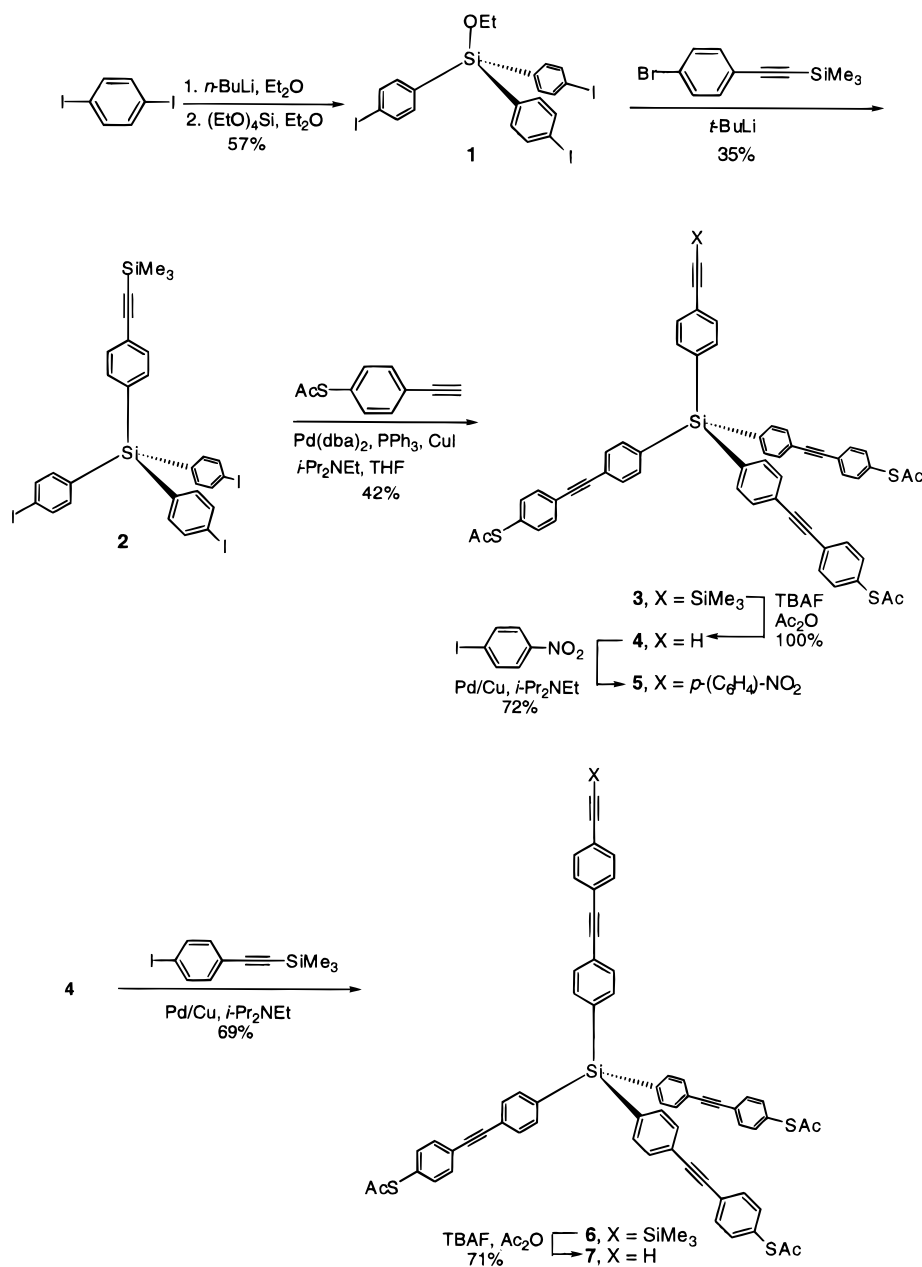
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Scheme 2



1.5 h at -78°C and poured into water. The organic layer was separated and washed with water (1 \times) and brine (1 \times). The aqueous solution was extracted with ether (2 \times). The combined organic fractions were dried over magnesium sulfate and filtered. Removal of solvent in vacuo followed by flash chromatography (silica gel, hexane) gave **2** (0.85 g, 35%) as a white solid. $\text{Mp} = 168^\circ\text{C}$ (decomp). FTIR (cast) 3067, 2954, 2154, 1564, 1539, 1477 cm^{-1} . $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.71 (d, $J = 8.2$ Hz, 6 H), 7.45 (d, $J = 8.3$ Hz, 2 H), 7.39 (d, $J = 8.3$ Hz, 2 H), 7.17 (d, $J = 8.2$ Hz, 6 H), 0.24 (s, 9 H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 137.85, 137.50, 136.07, 133.11, 132.22, 131.67, 125.17, 104.90, 98.17, 96.37, 0.29. HRMS calcd for $\text{C}_{29}\text{H}_{25}\text{I}_3\text{-Si}_2$: 809.8629. Found: 809.8632.

General Procedure for Pd/Cu Coupling Reactions between Terminal Alkynes and Aryl Iodides. To an oven-dried glass vessel containing the terminal alkyne, aryl iodide, Pd catalyst, copper iodide, and triphenylphosphine were added THF and the amine in a drybox which was filled with nitrogen. The mixture was stirred at room temperature. The reaction mixture was then poured into water, and the aqueous layer was extracted with ether, ethyl acetate or dichloromethane (3 \times). The combined organic solution was washed with water

(2 \times) and dried over magnesium sulfate. The solvent was removed in vacuo, and the residues were purified by column chromatography on silica gel.

Caltrop 3. See the general coupling procedure. The compounds used were **2** (0.772 g, 0.950 mmol), 1-thioacetyl-4-(trimethylsilylethynyl)benzene (0.88 g, 5.00 mmol), $\text{Pd}(\text{dba})_2$ (0.082 g, 0.140 mmol), PPh_3 (0.147 g, 0.560 mmol), CuI (0.053 g, 0.280 mmol), $i\text{-Pr}_2\text{NEt}$ (0.66 mL, 3.8 mmol), and THF (10 mL). The reaction mixture was stirred at room temperature for 3 d. Flash chromatography (silica gel, hexane/ $\text{Et}_2\text{O} = 2/1$) gave **3** (0.377 g, 42%) as a white solid. FTIR (cast) 3067, 2954, 2154, 1713, 1595, 1539, 1503, 1482, 1395 cm^{-1} . $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.58 (d, $J = 8.4$ Hz, 6 H), 7.56–7.52 (overlapping, 16 H), 7.41 (d, $J = 8.5$ Hz, 6 H), 2.42 (s, 9 H), 0.28 (s, 9 H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 193.34, 136.24, 136.10, 134.29, 133.84, 133.69, 132.31, 131.49, 131.20, 128.41, 124.90, 124.68, 124.31, 104.88, 96.05, 90.91, 90.17, 30.34, 0.04. LRMS calcd for $\text{C}_{59}\text{H}_{46}\text{O}_3\text{S}_3\text{Si}_2$: 954. Found: 954. Anal. Calcd for $\text{C}_{59}\text{H}_{46}\text{O}_3\text{S}_3\text{-Si}_2$: C, 74.17; H, 4.85. Found: C, 74.24; H, 4.78.

Caltrop 4. A mixture of TBAF (4 mL, 4 mmol, 1.0 M in THF), acetic anhydride (0.38 mL, 4.00 mmol), and acetic acid (0.23 mL, 4.00 mmol) was added to a solution of **3** (0.735 g,

0.770 mmol) in THF (10 mL). The green-yellow solution was stirred for 50 min and then poured into water. The mixture was washed with water (2 \times) and brine (1 \times). The combined aqueous solution was extracted with ether (1 \times). The combined organic solution was dried over magnesium sulfate and filtered. Removal of solvent in vacuo followed by flash chromatography (silica gel, hexane/ethyl acetate = 2/1) gave **4** as a white solid (0.68 g, 100%). FTIR (cast) 3292, 3067, 3015, 1708, 1595, 1539, 1497, 1482, 1395 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.56 (d, J = 8.6 Hz, 6 H), 7.55–7.52 (m, 16 H), 7.40 (d, J = 8.4, 6 H), 3.16 (s, 1 H), 2.42 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 193.40, 136.19, 134.25, 133.69, 132.27, 131.63, 131.17, 128.34, 124.66, 124.28, 123.84, 90.82, 90.11, 83.43, 78.68, 30.32. LRMS calcd for $\text{C}_{56}\text{H}_{38}\text{O}_3\text{S}_3\text{Si}$: 882. Found: 882. Anal. Calcd for $\text{C}_{56}\text{H}_{38}\text{O}_3\text{S}_3\text{Si}$: C, 76.16; H, 4.34. Found: C, 76.00; H, 4.36.

1-Iodo-4-(trimethylsilylethynyl)benzene.¹⁴ See the general coupling procedure. The compounds used were *p*-diiodobenzene (13.2 g, 40.0 mmol), (trimethylsilyl)acetylene (4.24 mL, 30.00 mmol), $\text{Pd}(\text{dba})_2$ (0.86 g, 1.50 mmol), PPh_3 (1.57 g, 6.00 mmol), CuI (0.57 g, 3.00 mmol), *i*- Pr_2NEt (20.9 mL, 120.0 mmol), and THF (30 mL). The mixture was stirred at room temperature for 1.5 d. Flash chromatography (silica gel, hexane) gave 4.75 g (53%) of the title compound as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 7.62 (d, J = 8.6 Hz, 2 H), 7.16 (d, J = 8.6 Hz, 2 H), 0.22 (s, 9 H).

Caltrop 5. See the general coupling procedure. The compounds used were **4** (0.224 g, 0.250 mmol), *p*-iodonitrobenzene (0.25 g, 1.00 mmol), $\text{Pd}(\text{dba})_2$ (0.008 g, 0.013 mmol), PPh_3 (0.014 g, 0.052 mmol), CuI (0.005 g, 0.026 mmol), *i*- Pr_2NEt (0.09 mL, 0.50 mmol), and THF (8 mL). The reaction mixture was stirred at room temperature for 17 h. Flash chromatography (silica gel, cyclohexane/ethyl acetate = 4/1) gave **5** (0.182 g, 72%) as a yellow solid. FTIR (cast) 3067, 3026, 2215, 1708, 1595, 1518, 1503, 1395 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 8.21 (d, J = 8.8, 2 H), 7.66 (d, J = 8.8, 2 H), 7.59–7.55 (overlapping, 22 H), 7.40 (d, J = 8.2 Hz, 6 H), 2.42 (s, 9 H). ^{13}C NMR (75 MHz, CDCl_3) δ 193.01, 146.83, 136.05, 135.94, 134.65, 134.00, 133.32, 132.16, 132.02, 131.02, 130.95, 129.73, 128.14, 124.50, 124.01, 123.54, 123.45, 94.19, 90.58, 89.99, 88.68, 30.25. LRMS calcd for $\text{C}_{62}\text{H}_{41}\text{NO}_5\text{S}_3\text{Si}$: 1003. Found: 1003. Anal. Calcd for $\text{C}_{62}\text{H}_{41}\text{NO}_5\text{S}_3\text{Si}$: C, 74.15; H, 4.11; N, 1.39. Found: C, 73.92; H, 4.15; N, 1.37.

Caltrop 6. See the general coupling procedure. The compounds used were **4** (0.416 g, 0.47 mmol), 1-iodo-4-(trimeth-

ylsilylethynyl)benzene (0.56 g, 1.88 mmol), $\text{Pd}(\text{dba})_2$ (0.014 g, 0.024 mmol), PPh_3 (0.025 g, 0.096 mmol), CuI (0.009 g, 0.048 mmol), *i*- Pr_2NEt (0.16 mL, 0.94 mmol), and THF (11 mL). The reaction mixture was stirred at room temperature for 24 h. Flash chromatography (silica gel, hexane/ethyl acetate = 4/1) gave **6** (0.34 g, 69%) as a yellow solid. FTIR (cast) 3067, 3026, 2964, 2154, 1713, 1595, 1539, 1503, 1482, 1395 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 7.59–7.57 (overlapping, 22 H), 7.48 (s, 4 H), 7.41 (d, J = 8.2, 6 H), 2.42 (s, 9 H), 0.28 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3) δ 193.02, 136.00, 134.05, 133.57, 133.48, 132.06, 131.74, 131.31, 130.97, 130.91, 128.17, 124.56, 124.47, 124.09, 122.98, 122.91, 104.49, 96.35, 90.97, 90.72, 90.40, 89.99, 30.28, 0.00. LRMS calcd for $\text{C}_{67}\text{H}_{50}\text{O}_3\text{S}_3\text{Si}_2$: 1054. Found: 1054. Anal. Calcd for $\text{C}_{67}\text{H}_{50}\text{O}_3\text{S}_3\text{Si}_2$: C, 76.24; H, 4.77. Found: C, 76.30; H, 4.88.

Caltrop 7. A mixture of TBAF (1 mL, 1 mmol, 1.0 M in THF), acetic anhydride (0.1 mL, 1 mmol), and acetic acid (0.06 mL, 1.00 mmol) was added to a solution of **6** (0.215 g, 0.200 mmol) in THF (5 mL). The solution was stirred for 30 min and then poured into water. The mixture was washed with water (2 \times) and brine (1 \times). The combined aqueous solution was extracted with methylene chloride (1 \times). The combined organic solution was dried over magnesium sulfate and filtered. Removal of solvent in vacuo followed by flash chromatography (silica gel, hexane/methylene chloride/ether = 10/10/1) gave **7** as a white solid (0.139 g, 71%). FTIR (cast) 3292, 3067, 3015, 2923, 1708, 1595, 1533, 1503, 1482, 1395 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) 7.58–7.55 (m, 22 H), 7.48 (m, 4 H), 7.40 (d, J = 8.5 Hz, 6 H), 3.17 (s, 1 H), 2.42 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3) δ 193.38, 136.16, 134.21, 133.72, 132.22, 132.06, 131.53, 131.10, 131.06, 128.27, 124.59, 124.25, 123.48, 122.06, 91.08, 90.76, 90.23, 90.02, 83.20, 79.02, 30.27. LRMS calcd for $\text{C}_{64}\text{H}_{42}\text{O}_3\text{S}_3\text{Si}$: 982. Found: 982. Anal. Calcd for $\text{C}_{64}\text{H}_{42}\text{O}_3\text{S}_3\text{Si}$: C, 78.17; H, 4.31. Found: C, 77.44; H, 4.34.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **3**–**7** (10 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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