Soluble Ferrocene Conjugates for Incorporation into Self-Assembled Monolayers

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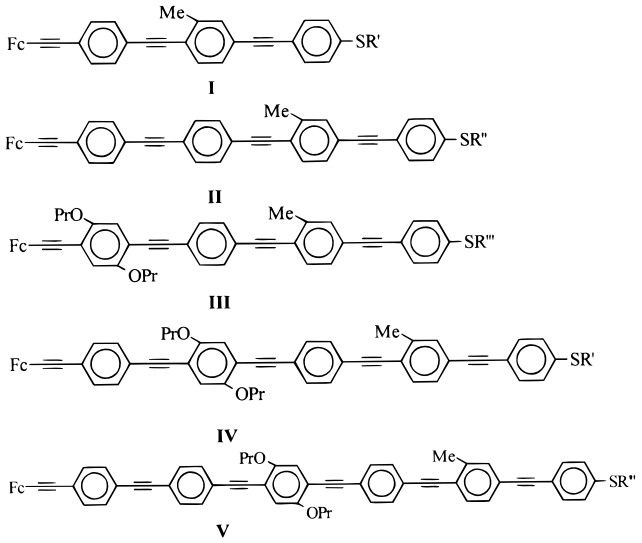
A series of phenylethynyl oligomers (**I**−**V**) possessing a ferrocene and thiol at each termini have been synthesized. These oligomers have been designed to overcome the inherent insolubility of this class of complexes by substitution at the phenyl groups with methyl and propoxy substituents. Several new reactions for preparing arenethiol-protected compounds are described. Interestingly, the generation of an arenethiol anion during base- or fluoride-catalyzed deprotection has been characterized.

Introduction

Recent work on long-range electron-transfer reactions through DNA suggested that an electrochemical nucleic acid sensor could be developed.[1−14] During the coarse of our investigations into the development of this class of sensor, we have designed and synthesized a series of conjugated arenethiol molecular wires that are chemisorbed onto gold surfaces. In particular, we are interested in the ferrocene-terminated oligo(phenylethynyl)arenethiols as target molecules for exploring conductivity of molecular wires that bridge ferrocene complexes to electrodes.

Chart 1



Fc = Ferrocene R' = CH_2CH_2Pyr R" = CH_2CH_2TMS R''' = CH_2CH_2TBDMS

Molecular wires based on oligo(phenylethynyl) derivatives have been extensively studied by several research groups;[7,9−13,17] especially, Tour and co-workers[9] have contributed significantly to the synthesis of asymmetric arenethiol adsorbates. For closely related molecules, Sita and co-workers[12,13] have reported the synthesis of ferrocene-$[C{\equiv}C{-}C_6H_4]_n$-SAc (n = 1, 2, 3, Ac = acetyl) by the palladium-catalyzed Heck reactions[14−16] using acetyl as a protecting group for arylthiols. To our knowledge, there has not been any report of the preparation of a phenylethynyl oligomer (n > 3) with the same structural features, presumably because of the poor solubility of unsubstituted oligomers and the high lability of the acetyl group for arenethiols to the basic conditions and elevated temperature, commonly used for the aryl coupling reactions.

We report here the design and synthesis of a series of conductive oligomers, **I**−**V** (Chart 1), by using novel protecting groups for arenethiols, 2-(4-pyridinyl)ethyl and

(1) Meade, T. J. In *Interactions of Metal Ions with Nucleotides, Nucleic Acids, and Their Constituents*; Asigel, Sigel, H., Eds.; Marcel Dekker: New York, 1996; Vol. 32, *Metal Inons in Biological Systems* pp 453−478.
(2) Holmlin, R. E.; Danlike, P. J.; Barton, J. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 3714−2730.
(3) Meade, T. J.; Kayyem, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 352−354.
(4) Wilson, E. K. *Chem Eng. News* **1998**, *May 25*, 47−49.
(5) Armitage, B.; Yu, C. J.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9854−9859.
(6) Lewis, F. D.; Wu, T. F.; Zhang, Y. F.; Letsinger, R. L.; Greenfield, S. R.; Wasielewski, M. R. *Science* **1997**, *277*, 673−676.
(7) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529−9534.
(8) Chidsey, C. E. D. *Science* **1991**, *251*, 919−922.
(9) For synthesis of conjugated oligomers, see: (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537−553, and references therein. (b) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6901−6921. (c) Pearson, D., Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376−1387. (c) Jones, L., II; Schemm, J. S.; Tour, J. M. *J. Org. Chem.* **1996**, *62*, 1388−1410.
(10) (a) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1995**, *118*, 2721−2732. (b) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem.* Soc. **1997**, *119*, 10563−10564. (c) Zehner, R. W.; Sita, L. R. *Langmuir* **1997**, *13*, 2973−2979.
(11) (a) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841. (b) Bharathi, P.; Patel, U.; Kawaguchi, T.; Peask, D. J.; Moore, J. S. *Macromolecules* **1995**, *28*, 5955. (c) Nelson, J. C.; Young, J. K.; Moore, J. S. *J. Org. Chem.* **1996**, *61*, 8160. (d) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635−9644.
(12) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808−4815.
(13) Hsung, R. P.; Babcock, J. R.; Chidsey, C. E. D.; Sita, L. R. *Tetrahedron Lett.* **1995**, *36*, 4525−4528.
(14) Heck, R. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 4, pp 833−863.
(15) Heck, R. F. *Org. React.* **1982**, *27*, 345.
(16) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

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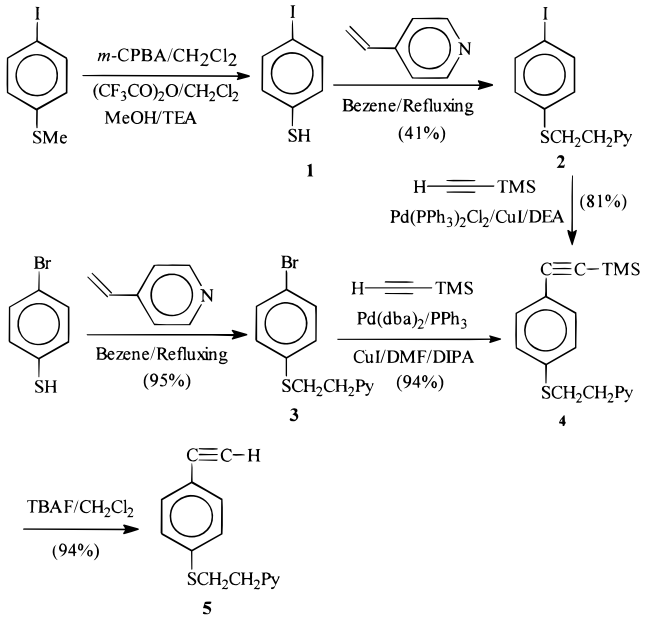
Scheme 1



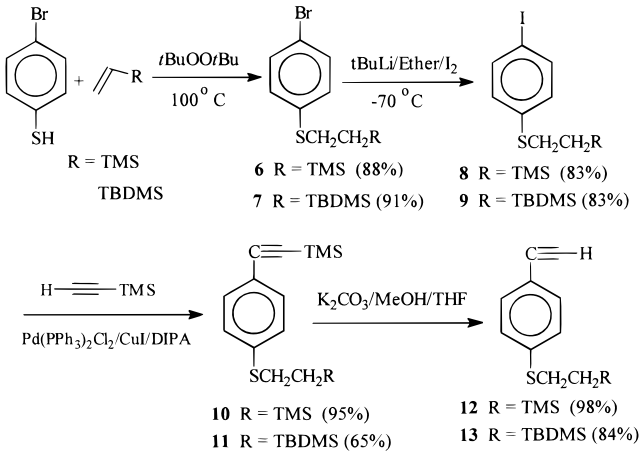
2-(trialkylsilyl)ethyl, that can tolerate a range of experimental conditions and can still be easily removed under very mild conditions whenever thiols are needed. In addition, we report a method for introducing two different substitution groups on benzene rings in the phenylethynyl groups for increasing solubility of the target compounds. The electrochemical properties of monolayers of these molecules on gold electrodes have been studied and are described separately.[18]

Results and Discussion

To successfully synthesize the soluble and asymmetrical ferrocene-terminated phenylethynyl oligomers, three key issues must be addressed. The first is to protect the arenethiols with the right protecting groups, the second is to introduce appropriate substituents onto the phenyl groups, and the last is to construct the oligomers with the right sequences.

Arenethiol Protection. The choice of the protection groups for arenethiols is crucial for the successful synthesis of soluble "molecular wires". Typical arenethiol protecting groups, such as methyl or ethyl group,[12,13] bind too strongly, while acetyl groups bind too weakly.[9−13] Ideally, the best protecting groups should be stable under a variety of many experimental conditions while being easily removed under mild conditions. We introduce here two new types of protecting groups with these characteristics, 2-(4-pyridinyl)ethyl and 2-(trialkylsilyl)ethyl, as described in (Scheme 1). While these protecting groups are used in the literature,[18−21] they have not been previously been used to protect arenethiols for use in the formation of SAMs. Compound **1**, 4-iodothiophenol, which

Scheme 2

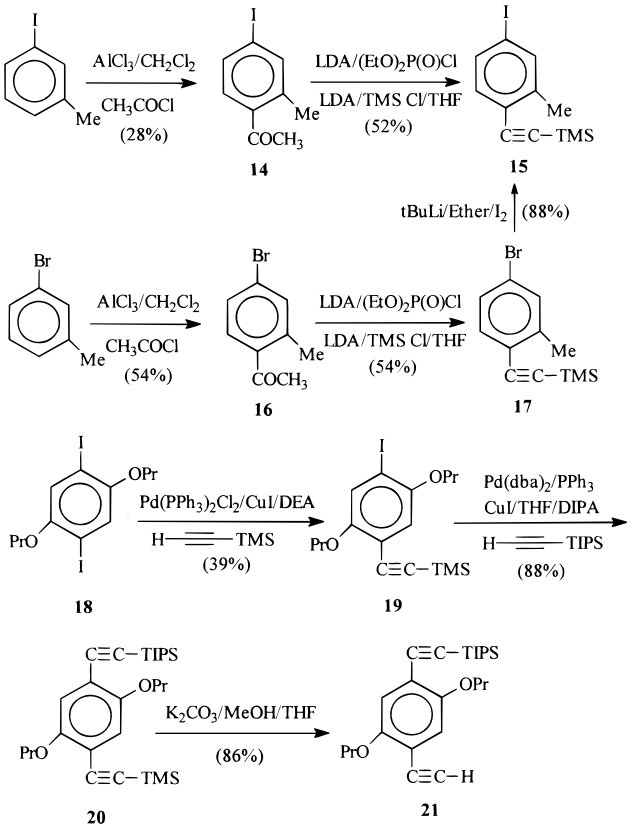


was prepared from a Pummerer rearrangement of the corresponding sulfoxide utilizing an adopted procedure,[22] was reacted with *p*-vinylpyridine under refluxing conditions to afford compound **2** with a yield of 46%. Although compound **1** was previously reported[12] to be synthesized via the reduction of pipsyl chloride, the process could not be successfully repeated in our lab. Apparently, the synthesis route starting with 4-iodothioanisole is not ideal due to low yield and multistep reactions. To get better yield with fewer steps of the reactions, we employed the commercially available 4-bromothiophenol for the same addition reaction in which compound **3** was obtained in excellent yield (95%). To couple trimethylsilylacetylene to the iodo derivative **2** utilizing the mild catalyst $Pd(PPh_3)_2Cl_2$ is easy and straightforward and proceeds with a high yield of 81%. However, many attempts to run the same cross-coupling reaction starting with bromo derivative **3** by varying different Pd catalysts, combinations of solvents, temperatures, and reaction times failed. After numerous trials, it was found that an unusually high percentage (>10% in molarity relative to **3**) of $Pd(dba)_2/PPh_3$, in combination with DMF/diisopropylamine, high temperature (60 °C), and long reaction time (at least 16 h), is crucial to successfully couple compound **3** with trimethylsilylacetylene to form the desired product **4,** with a yield of 94%. The compound **5,** obtained from the desilylation of **4** by either fluoride in CH_2Cl_2 or potassium carbonate in methanol, was used as one of the possible thiol-protected starting units to build the oligomers.

The 2-(trialkylsilyl)ethyl as protecting group for the thiols can be introduced by the reaction of either trimethylvinylsilane or dimethyl-*tert*-butylvinylsilane with 4-bromothiophenol in the presence of a catalytic amount of *tert*-butyl peroxide as free radical initiator (Scheme 2) to afford the desired (β-addition) compound **6** (88%) or **7** (91%). In addition, the above reactions also produced a very small amount (<3%) of the undesired (α-addition) products (structures not shown), as indicated by GC−MS. The observation here is consistent with that in the literature.[24] After halogen exchange, the iodo derivatives **8** and **9** were obtained in excellent yields (coincidentally, 83%). After coupling to trimethylsilylacetylene, followed

(17) Hoger, S.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2713−2716.
(18) Creager, S.; Yu, C. J.; Bamdad, C.; O'Connor, S.; Maclean, T.; Lam, E.; Chong, Y.; Kayyem, J. F.; Gozin, M. *J. Am. Chem. Soc.* **1999**, *121*, 1059−1064.
(19) Young, R. N.; Gauthier, J. Y.; Coombs, W. *Tetrahedron Lett.* **1984**, 1753−1756.
(20) Katritzky, A. R.; Khan, G. R.; Schwarz, O. A. *Tetrahedron Lett.* **1984**, 1223−1226.
(21) Katritzky, A. R.; Takahashi, I.; Marson, C. M. *J. Org. Chem.* **1986**, *51*, 4914−4920.
(22) Koreeda, M.; Yang, W. *J. Am. Chem. Soc.* **1994**, *116*, 10793−10794.
(23) Takeda, H.; Shimada, S.; Ohnishi, S.; Nakanishi, F.; Matsuda, H. *Tetrahedron Lett.* **1998**, *39*, 3701−3704.
(24) Wetterlin, K. *Acta Chem. Scand.* **1964**, *18*, 899−903.

Scheme 3

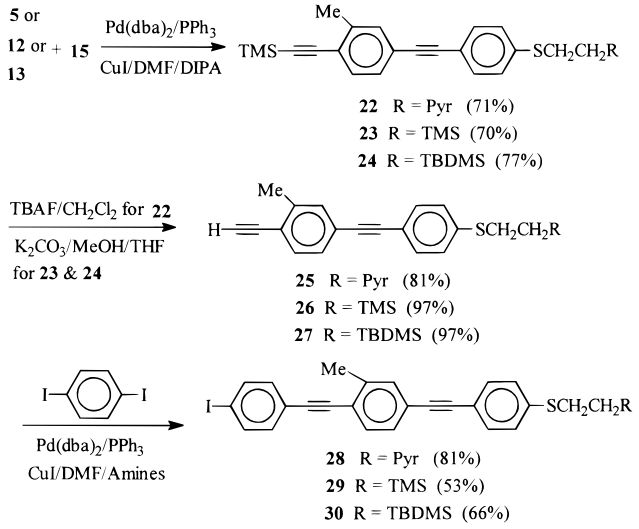


by desilylation, the compound **12** or **13** was obtained. The advantage of **13** over **12** as the starting unit in preparing elongated oligomers is that the dimethyl-*tert*-butylsilylethyl-terminated multiple-unit phenylethynyl oligomers have better solubility in common organic solvents. The study on deprotection of those groups will be discussed in a later section.

Synthesis of Substituted Monomers. A characteristic property of the oligo(phenylethynyl) derivatives is their high degree of symmetry and they can easily crystallize, which accounts for their limited solubility. If a substituent, is introduced onto one or more of the benzene rings, the symmetry of the molecules is disrupted and the solubility of the compounds in organic solvents is greatly improved. On this basis, two types of substituted groups were considered. The first is the methyl group, which might help break the symmetry of molecules, but hopefully has little or no effect on the assembly of target compounds onto gold surfaces due to its small size. The second is the propoxy group, which might help increase dramatically the compounds' solubility due to its flexibility.

The synthesis of the substituted monomer **15** is described in Scheme 3 where the acylation of either 3-iodotoluene or 3-bromotoluene under standard Friedel–Crafts conditions[25,26] gave products **14** or **16** and their isomers (structures not shown), which were converted to the corresponding acetylene derivatives **15** or **17** using the published procedure.[27] The acylation of 3-iodotoluene or 3-bromotoluene gave only two isomers, the desired

Scheme 4



product and the undesired isomer (2-(iodo or bromo)-4-methylacetophenone), which can be separated from the desired isomer using a silica gel column. From ^{1}H NMR chemical shifts and integrals, the structures of **14** or **16** and their isomers can be assigned. In the case of 3-iodotoluene as starting material, the yield of the desired product **14** is very low because of the severe deiodination of either starting material or the product or both, so that the synthesis route involving 3-bromotoluene is preferred, even though it involves one additional step. The transformation of **17** to **15** was predicted.

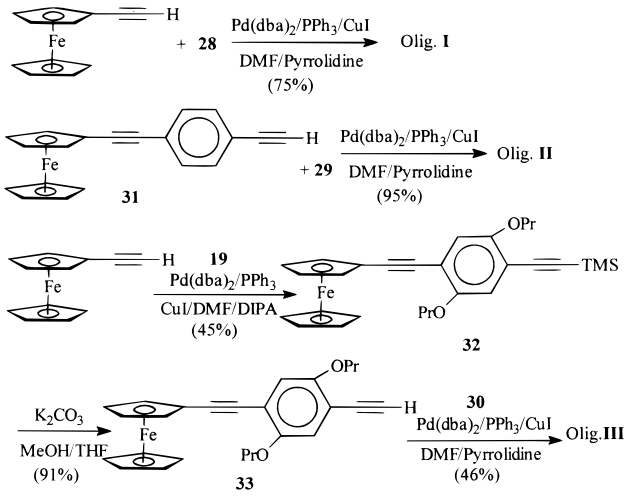
The preparation of the second substituted monomer was carried out, starting with the known compound **18**.[28,29] Compound **18** is partially coupled to trimethylsilylacetylene, followed by coupling to triisopropylsilylacetylene to afford **20**. The selective desilylation of **20** provided the asymmetrical monomer **21**, which is very useful for attaching different groups on both ends, as seen in Scheme 3. A compound similar to **21** has been synthesized in one pot by Hoger and Enkelmann.[17]

Building Oligomers. There are two possible strategies[9] for building multiunit unsymmetrical oligo(phenylethynyl) derivatives: (i) the stepwise iterative approach, and (ii) the combination of the stepwise iterative approach for the small pieces and a convergent approach for final assembly of a large piece. We have found that the second strategy is much more efficient than the first one, especially more so in the case in which a large oligomer was coupled to a small monomer. In this regard, it is logical to synthesize the iodo-terminated universal three-unit oligomers with different protection groups for arenethiols as basic units, as depicted in Scheme 4. The syntheses of **28**, **29**, and **30** were accomplished in a straightforward manner, with good yields, involving two palladium-catalyzed Heck reactions and one desilylation reaction.

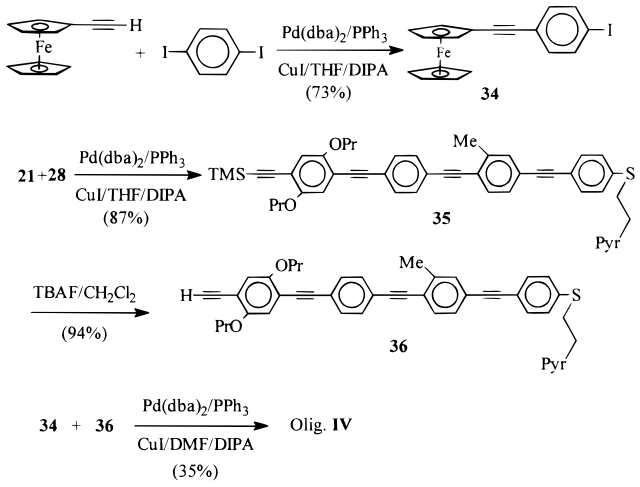
Once all building blocks are prepared, the target compounds can be constructed. The synthesis of the first oligomer **I** is depicted in Scheme 5, where ferrocenyl-

(25) Friedman, L.; Honour, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 6344–6349.
(26) Olah, G. A.; Kobayashi, S. *J. Am. Chem. Soc.* **1971**, *93*, 6964–6967.
(27) Negishi, E.; King, A. O.; Tour, J. M. *Org. Synth.* **1985**, *64*, 44.
(28) Zhao, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593–12602.
(29) Zhao, Q.; Carroll, P.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294.

Scheme 5



Scheme 6

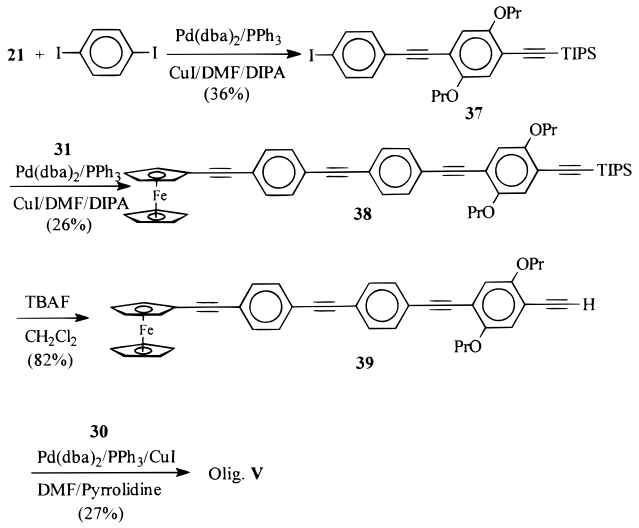


acetylene[30,31] was coupled to compound **28** to give **I** in excellent yield. For oligomers **II** and **III**, which have the same length but different substituents on the benzene rings in the phenylethynyl bridge, the first step was to build one-unit ferrocene **31**, which is prepared using the literature procedure,[12] and **33,** which is prepared by reacting ferrocenylacetylene to compound **19**, followed by desilylation using potassium carbonate. Oligomers **II** and **III** were then constructed by reactions of **31** to **29** and **33** to **30** with good to excellent yields, as illustrated in Scheme 5.

The strategy for oligomer **IV** is to synthesize an iodo-terminated one-unit ferrocene **34** via the reaction of ferrocenylacetylene to 1,4-diiodobenzene, and a four-unit oligomer, **36,** via the coupling of **21** to **28**, followed by desilylation. The subsequent coupling between **34** and **36** was catalyzed by the Pd(0) complex to form **IV** with a relatively low yield, as seen in Scheme 6.

The final target, oligomer **V**, has six phenylethynyl units and is the most complicated and tedious to make, involving many reaction steps. As illustrated in Scheme 7, the asymmetrical monomer **21** was coupled to 1,4-diiodobenzene, followed by coupling to one-unit ferrocene

Scheme 7



31, producing compound **38** with a low yield (25.8%). Compound **39** with three units, obtained from the desilylation of **38**, was then coupled to compound **30** to form oligomer **V** in a relatively poor yield. By investigating the lengths of oligomers and their yields in the final coupling, it is apparent that the more phenylethynyl units the synthesized oligomers have, the more complicated the syntheses are and the lower the yields are. The common problem associated with the low yield is that the terminal acetylenes dimerized themselves under the Heck cross-coupling conditions. Despite these limitations, the present reactions offer the best and only route thus far described for preparing soluble, asymmetrically substituted arylthiol adsorbates of this size suitable for use in preparing electroactive SAMs.

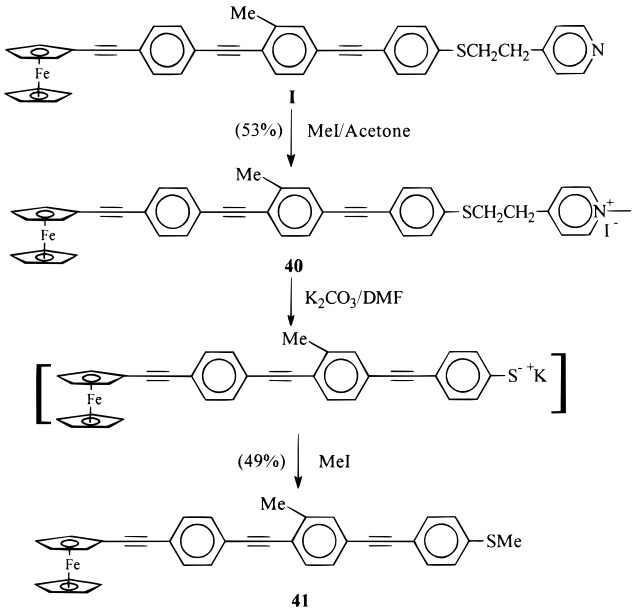
Removal of Protection Groups for Arenethiols. The protection groups chosen in this work for arenethiols are stable in the experimental conditions. For the 2-(4-pyridinyl)ethyl group, the first step in deprotecting the thiol is to convert the compounds to the corresponding pyridinium iodides by reaction with iodomethane in acetone as solvent. The formation of the pyridinium salts actually is an activation process in which β-hydrogen of the ethyl group becomes acidic due to the nitrogen cation on the pyridine ring. When the salt products were stirred with a base (either organic base, such as TEA and $(CH_3CH_2)_2NH$, or inorganic base, such as K_2CO_3 and $NaHCO_3$), in organic solvents, for example, acetone, DMF, or THF, for 2 h, the salts were consumed and new products, arenethiolate anions, were formed.

To provide the evidence for the generation of the arenethiolate anion, a good electrophile, such as CH_3I, was used as a trapping reagent. As exemplified in Scheme 8, the activated form, **40**, of the oligomer **I** was mixed with a suspension of potassium carbonate and DMF, followed by addition of a large excess of methyl iodide. The product was isolated and analyzed by ^1H NMR and FAB mass spectra. ^1H NMR spectra clearly showed the disappearance of the 2-(4-pyridinyl)ethyl group and formation of a new peak at 2.547 ppm assigned to CH_3 attached to sulfur. These data coupled with an indicated mass of 546.11 identified the isolated product as compound **41**. The result of the trapping experiment confirmed the generation of the arenethiolate anion.

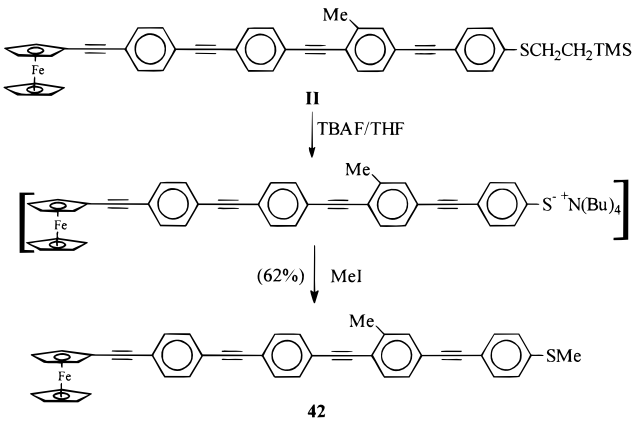
The solvent systems that have been tested for the deprotection of arenethiols include K_2CO_3/DMF, K_2CO_3/

(30) Rosenblum, M.; Brawn, N.; Papenmerier, J.; Applebaum, M. *J. Organomet. Chem.* **1966**, *6*, 173−180.
(31) Doisneau, G.; Balavoine, G.; Fillebeen-Khan, T. *J. Organomet Chem.* **1992**, *425*, 113−117.

Scheme 8



Scheme 9



acetone, TEA/acetone, TEA/CH_3CH_2OH, TEA/THF, and TEA/CH_2Cl_2. It was interesting to note that the deprotection in TEA/CH_2Cl_2 gave the CH_2Cl_2-trapped product in which CH_2Cl_2 acted as an electrophile. The mechanism of formation for the thiolate anion is the base-catalyzed β-elimination of sulfur in the pyridinium salt, which is consistent with the literature result.[20]

For the 2-(trialkylsilyl)ethyl group, prior to deprotection, there is no activation process. Scheme 9 presents the reaction of oligomer **II** with tetrabutylammonium fluoride in THF, and the consequential trapping reaction by methyl iodide. The product was also isolated and characterized by ^{1}H NMR and mass spectrometry. The structure of the isolated product was assigned to **42**, on the basis of its ^{1}H NMR and mass spectra. The isolation of **42** also indicated the generation of the arylthiolate anion from the fluoride-induced β-elimination of 2-(trialkylsilyl)ethyl group, which is known in the literature.[22,23]

Oligomers **III**, **IV**, and **V** can be deprotected in the same manner.[34] The experimental results demonstrate that both types of protection groups are quite labile either to bases upon activation or to the fluorides and are very useful to protect the unsaturated thiols, such as arenethiols, alkenylthiols, and alkynylthiols.[23]

Experimental Section

Materials. Diisopropylamine, diethylamine, 1,2-dichloroethane, triethylamine (TEA), pyrrolidine, $Pd(PPh_3)_2Cl_2$, copper iodide, 3-chloroperoxybenoic acid (*m*CPBA), trifluoroacetic anhydride, vinyltrimethylsilane, *tert*-butyl peroxide, 1.7 M *tert*-butyllithium (*t*-BuLi) pentane solution, 3-iodotoluene, 3-bromotoluene, 2.0 M lithium diisopropylamide (LDA) THF solution, diethylchlorophosphate, and triisopropylsilylacetylene were purchased from Aldrich and used as received. Methanol, dichloromethane, hexane, ethyl acetate, benzene, sodium thiosulfate, ether, and sodium sulfate were purchased from EM Science and used as received. Triphenylphosphine, 1-bromothiophenol, trimethylsilylacetylene, and iodine were purchased from Lancaster and used as received. Dimethylformamide (DMF), 4-vinylpyridine, tetrahydrofuran (THF), and trimethylchlorosilane were purchased from Fluka and used as received. Aluminum chloride and 4-iodothioanisol were purchased from Acros and used as received. Edetate disodium (EDTA) was purchased from J. T. Baker and used as received. Vinyl(*tert*-butyl)dimethylsilane was purchased from Gelest and used as received. $Pd(dba)_2$ was prepared following the literature procedure.[30,31]

Instrumentation. Spectra were recorded with the following spectrometers: GC/MS performed at 70 eV with a 50 m × 0.2 mm capillary column programmed at 140 °C for 1 min and then 280 °C at 10 °C min^{-1}, NMR (300 MHz, ^{1}H; 75 MHz, ^{13}C). Mass spectrometry was provided by Mass Consortium at San Diego using either electrospray or high-resolution FAB.

General Procedure for the Palladium-Catalyzed Coupling Reactions. A solution of aryl iodides or aryl bromides, terminal acetylenes, $Pd(PPh_3)_2Cl_2$ or $Pd(dba)_2PPh_3$, and CuI in either diethylamine or amine-containing mixtures, such as THF/diethylamine, DMF/diethylamine, DMF/TEA, THF/diisopropylamine, DMF/diisopropylamine, and DMF/pyrrolidine, as solvents was degassed well by argon and stirred at 25−60 °C for 3 h to overnight, depending on the specific reactions performed. The conditions for each reaction are specified herein by the catalyst, solvents, temperature, and reaction time. After removing the solvents, the residue was used either for column chromatography separation or for the treatment in which the dichloromethane solution of the residue was stirred with the saturated EDTA aqueous solution for 3 h to overnight. This procedure effectively removed the copper impurities that interfered with column separation in some cases when the products contained pyridinyl and/or propoxy groups. The solvent systems for purifying the products are variable and are specified in the actual reactions.

General Procedure for Desilylation. Two reagents were used to remove the silyl groups. For TBAF as desilylation reagent, the procedure is as follows: A solution of the substrate in dichloromethane was cooled in an ice−water bath. Into this cold solution was added 1.2 equiv of 1.0 M TBAF THF solution. The resulting solution was stirred at the same temperature for another 1 h, washed once with water, dried over sodium sulfate, and then concentrated on a rotavapor. The crude product was used for column separation. When potassium carbonate is used as desilylation reagent, the procedure is as follows: To a mixture of 200−300 mL of 50% THF/methanol were added the substrate and a certain amount of potassium carbonate. The resulting suspension was stirred at room temperature for 2−3 h and diluted by adding 400 mL of dichloromethane and 400 mL of water. Upon shaking well, the organic layer was separated, dried over sodium sulfate and concentrated in vacuo. The crude product was used for column purification.

(32) Takahashi, Y.; Ito, T.; Sakai, S.; Ishi. Y. *Chem Commun*. **1970**, 1065−1066.

(33) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth*. **1972**, 134−136.

(34) In our studies on the electrochemical properties of these target molecules, the oligomers **I**−**V** self-assemble onto gold surfaces by in situ deprotection, published separately.[18]

Synthesis of 4-Iodothiophenol (1). A solution of 6.0 g (24.00 mmol) of 4-iodothioanisole in 300 mL of CH_2Cl_2 was cooled in an ice−water bath. To the cooled solution was added 6.05 g (35.05 mmol) of *m*CPBA. After stirring for 30 min, 3.0 g (40.49 mmol) of $Ca(OH)_2$ was added and the resulting precipitate was filtered. To the filtrate was added 7 mL (49.56 mmol) of $(CF_3CO)_2O$, and the solution was refluxed for 1.5 h. After evaporating off the solvent, the residue was dissolved in 200 mL of 50% methanol/TEA. The solvent was then evaporated, and the residue was further dried. The compound was used immediately for the next step without further purification and analysis in order to avoid oxidation.

Synthesis of 2-(4-Pyridinyl)ethyl-4′-iodophenyl Sulfide (2). The dried residue (**1**) was dissolved in 70 mL of benzene and the solution washed once with 60 mL of a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted once with 40 mL of benzene. The combined organic extracts were dried over sodium sulfate and filtered off. To the benzene solution was added 7.7 mL (7.21 mmol) of 4-vinylpyridine, and the reaction mixture was refluxed overnight. The benzene was evaporated, and the residue was dissolved in CH_2Cl_2 for column chromatography. The crude product was purified on a 150 g silica gel column, packing with 20% ethyl acetate/hexane and eluting with 20−60% ethyl acetate/hexane. The desired fractions were pooled and concentrated to afford 3.4 g (41.5%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93 (t, J = 7.2 Hz, 2H), 3.19 (t, J = 7.2 Hz, 2H), 7.11−7.71 (m, 6H), 8.69 (d, J = 7.7 Hz, 2H); GC−MS *m*/*z* (relative intensity) 341.

Synthesis of 2-(4-Pyridynyl)ethyl-4′-bromophenyl Sulfide (3). A solution of 14.0 g (74.06 mmol) of 1-bromothiophenol and 11 mL (103.01 mmol) of 4-vinylpyridine in 200 mL of benzene was refluxed overnight. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 for column chromatography. The crude product was purified on a 250 g silica gel column, packing with 20% ethyl acetate/hexane and eluted with 20−60% ethyl acetate/hexane. The desired fractions were pooled and evaporated to afford 20.78 g (95.0%) of the title product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (t, J = 7.2 Hz, 2H), 3.19 (t, J = 7.2 Hz, 2H), 7.15−7.48 (m, 6H), 8.56 (d, J = 7.7 Hz, 2H); GC−MS *m*/*z* (relative intensity) 295 (36).

Synthesis of 2-(4-Pyridinyl)ethyl-4′-[(trimethylsilyl)-ethynyl]phenyl Sulfide (4) from 2. Compound **4** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 1.70 g (4.98 mmol) of **2**, 100 mg (0.14 mmol) of $Pd(PPh_3)_2Cl_2$, 100 mg (0.53 mmol) of CuI, and 0.95 mL (6.72 mmol) of trimethylsilylacetylene in 35 mL of diethylamine. The reaction mixture was stirred for 2 h at 55 °C and worked up. The crude product was purified on a 150 g silica gel column, packing with hexane and eluting with 0−50% ethyl acetate/hexane. The desired fractions were pooled and concentrated to afford 1.27 g (81.4%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H), 2.91 (t, J = 7.2 Hz, 2H), 3.17 (t, J = 7.2 Hz, 2H), 7.15−7.49 (m, 6H), 8.56 (br s, 2H); GC−MS *m*/*z* (relative intensity) 311 (100).

Synthesis of 2-(4-Pyridinyl)ethyl-4′-[(trimethylsilyl)-ethynyl]phenyl Sulfide (4) from 3. Compound **4** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 3.0 g (10.20 mmol) of **3**, 2.45 mL (17.33 mmol) of trimethylsilylacetylene, 590 mg (1.01 mmol) of $Pd(dba)_2$, 2.0 g (7.57 mmol) of triphenylphosphine, 300 mg (1.57 mmol) of CuI in 120 mL of DMF, and 30 mL of diisopropylamine. The reaction mixture was stirred at 60 °C overnight and worked up. The crude product was purified on a 150 g silica gel column, packing with hexane and eluting with 0−50% ethyl acetate/hexane. The desired fractions were pooled and concentrated to afford 3.00 g (94.0%) of the title compound. Characterization and analysis of this compound is the same as above.

Synthesis of 2-(4-Pyridinyl)ethyl-4′-(ethynyl)phenyl Sulfide (5). Compound **5** was prepared following the general procedure for desilylation using 2.6 g (8.35 mmol) of **4** and 9 mL (9.00 mmol) of 1.0 M TBAF THF solution in 150 mL of CH_2Cl_2. The reaction mixture was stirred for 1.5 h and worked up. The crude product was purified on a 50 g silica gel column, packing with 50% ethyl acetate/hexane, eluting with the same solvents. The desired fractions were pooled and concentrated to afford 1.87 g (94.1%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.95 (t, J = 7.2 Hz, 2H), 3.10 (s, 1H), 3.19 (t, J = 7.2 Hz, 2H), 7.15−7.40 (m, 6H), 8.56 (d, J = 7.7 Hz, 2H); GC−MS *m*/*z* (relative intensity) 239 (87).

Synthesis of 2-(Trimethylsilyl)ethyl-4′-bromophenyl Sulfide (6). To a Schlenk tube was added 13.55 g (71.7 mmol) of 4-bromothiophenol, 12.67 mL (82.20 mmol) of vinyltrimethylsilane, and 1.88 mL (10.00 mmol) of *tert*-butyl peroxide under argon. The reaction mixture was stirred at 100 °C for 10 h. The reaction mixture was diluted by adding 200 mL of hexane, and the hexane solution was washed once with a 10% sodium hydroxide aqueous solution. The organic layer was separated, dried over sodium sulfate, and then concentrated for column chromatography. The crude product was purified on a 270 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 18.3 g (88.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.94−0.98 (m, 2H), 2.95−3.01 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H); GC−MS *m*/*z* (relative intensity) 290 (4), 288 (3).

Synthesis of 2-(*tert*-Butyldimethylsilyl)ethyl-4′-bromophenyl Sulfide (7). To a Schlenk tube was added 5.55 g (29.36 mmol) of 4-bromothiophenol, 6.6 mL (35.05 mmol) of vinyl(*tert*-butyl)dimethylsilane, and 0.5 mL (2.66 mmol) of *tert*-butyl peroxide under argon. The reaction mixture was stirred at 100 °C for 10 h. The reaction mixture was then diluted by adding 200 mL of hexane, and the hexane solution washed once with a 10% sodium hydroxide aqueous solution. The organic layer was separated, dried over sodium sulfate, and then concentrated for column chromatography. The crude product was purified on a 250 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 8.86 g (91.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.91 (s, 9H), 0.94−1.04 (m, 2H), 2.95−3.01 (m, 2H), 7.20 (d, J = 8.7 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H); GC−MS *m*/*z* (relative intensity) 275 (15), 273 (14).

Synthesis of 2-(Trimethylsilyl)ethyl-4′-iodophenyl Sulfide (8). A solution of 18.17 g (62.87 mmol) of compound **6** in 400 mL of dry ether was cooled to −78 °C in the presence of argon. To this solution containing **6** was added 80 mL of 1.7 M *t*-BuLi pentane solution, and the reaction mixture was stirred at −78 °C for 40 min. A second solution of 21.0 g (82.73 mmol) of iodine in 400 mL of dry ether was cooled to −78 °C under argon, and the cooled iodine solution was then transferred into the cooled reaction mixture starting with **6**. After stirring for 10 min at −78 °C the reaction mixture was warmed to 0 °C and stirring continued for another 30 min. The reaction mixture was then washed with a sodium thiosulfate solution until the iodine color disappeared. The ether layer was separated, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 250 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 17.4 g (83.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.0.94−0.98 (m, 2H), 2.97−3.02 (t, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H); GC−MS *m*/*z* (relative intensity) 336 (19).

Synthesis of 2-(*tert*-Butyldimethyl)ethyl-4′-iodophenyl Sulfide (9). A solution of 22.1 g (66.70 mmol) of **7** in 500 mL of dry ether was cooled to −78 °C. To this cooled solution was added 88 mL (149.60 mmol) of 1.7 M *t*-BuLi pentane solution in the presence of argon, and then the reaction mixture was stirred for 1 h. A separate solution of 22.0 g (86.68 mmol) of iodine in 300 mL of dry ether was also cooled to −78 °C and added to the reaction mixture starting with **7**. This reaction mixture was stirred for 10 min at −78 °C, and then stirring continued for 30 min at 0 °C. The solution was then washed with a sodium thiosulfate solution until the iodine color disappeared. The ether layer was separated, dried over sodium sulfate, and then concentrated for column chromatography. The crude product was purified on a 230 g silica gel column, packing and eluting with hexane. The desired fractions were

pooled and concentrated to afford 21.1 g (83.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.93 (s, 9H), 0.94−1.00 (m, 2H), 2.95−3.01 (t, J = 8.7 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H); GC−MS *m*/*z* (relative intensity) 378 (2).

Synthesis of 2-(Trimethylsilyl)ethyl-4′-[(trimethylsily)-ethynyl]phenyl Sulfide (10). Compound **10** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 7.5 g (22.32 mmol) of **8**, 469 mg (0.67 mmol) of $Pd(PPh_3)_2Cl_2$, and 469 mg (2.46 mmol) of CuI in 300 mL of diethylamine. The reaction mixture was stirred at 50 °C for 1.5 h and worked up. The crude product was purified on a 150 g silica gel column, packing with hexane and eluting with 10−40% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 6.50 g (95.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.25 (s, 9H), 0.90−0.95 (m, 2H), 2.93−2.99 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H); GC−MS *m*/*z* (relative intensity) 306 (7).

Synthesis of 2-(*tert*-Butyldimethyl)ethyl-4′-[(trimethylsilyl)ethynyl]phenyl Sulfide (11). Compound **11** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 10.0 g (26.43 mmol) of **9**, 4.1 mL (29.01 mmol) of trimethylsilylacetylene, 0.43 g (0.61 mmol) of $Pd(PPh_3)_2Cl_2$, and 0.43 g (2.25 mmol) of CuI in 350 mL of diethylamine. The reaction mixture was stirred at 55 °C for 1 h and then worked up. The crude product was purified on a 250 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 6.0 g (65.5%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.24 (s, 9H), 0.87 (s, 9H), 0.90−0.97 (m, 2H), 2.93−2.99 (m, 2H), 7.16−7.38 (m, 4H); GC−MS *m*/*z* (relative intensity) 348 (3).

Synthesis of 2-(Trimethylsilyl)ethyl-4′-(ethynyl)phenyl Sulfide (12). Compound **12** was prepared following the general procedure for desilylation using 14.67 g (47.92 mmol) of **10** and 10.7 g (7.75 mmol) of potassium carbonate in 240 mL of 50% CH_3OH/THF. The reaction mixture was stirred at room temperature for 1 h and worked up. The crude product was purified on a 150 g silica gel column, packing with hexane and eluting with 10% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 10.23 g (98.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9H), 0.91−0.97 (m, 2H), 2.97−3.00 (m, 2H), 3.10 (s, 1H), 7.20−7.41 (m, 4H); GC−MS *m*/*z* (relative intensity) 234 (9).

Synthesis of 2-(*tert*-butyldimethyl)ethyl-4′-(ethynyl)-phenyl Sulfide (13). Compound **13** was prepared following the general procedure for desilylation using 6.0 g (17.21 mmol) of **11** and 10.0 g (7.25 mmol) of potassium carbonate in 200 mL of 50% CH_3OH/THF. The reaction mixture was stirred at room temperature for 1.5 h and worked up. The crude product was purified on a 100 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 4.0 g (84.1%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.87 (s, 9H), 0.94−0.98 (m, 2H), 2.95−2.98 (m, 2H), 3.08 (s, 1H), 7.19−7.42 (m, 4H); GC−MS *m*/*z* (relative intensity) 276 (1).

Synthesis of 2-Methyl-4-iodoacetophenone (14). To a suspension of 12.0 g (89.98 mmol) of $AlCl_3$ in 200 mL of dichloroethane was added 6.4 mL (0.19 mol) of acetyl chloride under argon. When the suspension dissolved, a solution of 15 g (68.79 mmol) of 3-iodotoluene in 50 mL of dichloroethane was added dropwise. After stirring at room temperature for 1 h and then at 50 °C for 2 h, the solution was diluted by adding 100 mL of CH_2Cl_2 and washed twice with a saturated ammonium chloride solution and then with a 5% sodium bicarbonate solution. The organic layer was then separated, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 240 g silica gel column, packing with hexane and eluting with 500 mL of hexane, 500 mL of 1% ether/hexane, 1.0 L of 2% ether/hexane, and 2.5 L of 3% ether/hexane. Two isomers were formed. The first peak from GC−MS analysis is the desired isomer. The desired fractions were pooled and concentrated to afford 5.1 g (28.5%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 2.56 (s, 3H), 7.39−7.65 (m, 3H); GC−MS *m*/*z* (relative intensity) 260 (53).

Synthesis of 2-(Trimethylsilyl)ethyl-4-iodotoluene (15) from 14. To 25 mL of dry THF cooled to −78 °C was added 14 mL (28.00 mmol) 2.0 M LDA THF solution under argon. To this mixture was added a solution of 6.34 g (24.38 mmol) of **(14)** in 25 mL of THF dropwise. After the addition was complete the reaction mixture was stirred at −78 °C for 1 h, then 4 mL (27.68 mmol) of diethylchlorophosphate was added, and stirring was continued for 15 min at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h. The reaction mixture was cooled again to −78 °C, and 29 mL (56.0 mmol) of 2.0 M LDA THF was added dropwise. Once addition of LDA was complete, the reaction mixture was warmed to room temperature and stirred for an additional 3 h. The reaction mixture was recooled to −20 °C, 9 mL (70.9 mmol) of trimethylsilyl chloride was added, and the mixture was stirred at room temperature overnight. The solution was then poured into 200 mL of 5% $KHCO_3$ aqueous solution and 300 mL of ether. The organic layer was separated, and the aqueous phase was then extracted again with 300 mL of ether. The combined ether extracts were dried over sodium sulfate and concentrated for column chromatography. The crude product was purified on a 250 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 4.0 g (52.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H), 2.37 (s, 3H), 7.13 (d, J = 8.4 Hz, 1H), 7.44−7.57 (m, 2H); GC−MS *m*/*z* (relative intensity) 314 (53).

Synthesis of 2-(Trimethylsilyl)ethyl-4-iodotoluene (15) from 17. To a solution of 26.6 g (0.10 mol) of **17** in 400 mL of ether cooled to −78 °C was added 128.7 mL (0.22 mol) of *t*-BuLi pentane solution. The reaction mixture was stirred at −78 °C for 30 min. Another solution of 33.2 g (0.13 mol) of I_2 in 400 mL of ether was cooled to −78 °C and was added into the cold reaction mixture starting with **17**. The resulting mixture was then allowed to warm to 0 °C, stirred for 10 min, and washed with 10% sodium thiosulfate aqueous solution to remove any excess iodine. The organic layer was then separated, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 250 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 27.6 g (88.1%) of the title compound. Characterization and analysis of this compound is the same as above.

Synthesis of 2-Methyl-4-bromoacetophenone (16). To a suspension of 20.0 g (0.15 mol) of $AlCl_3$ in 250 mL of CH_2Cl_2 was added 10.7 mL (0.15 mol) of acetyl chloride under argon. After the suspension was dissolved, 20.0 g (0.12 mol) of 3-bromotoluene was added and the reaction mixture was stirred overnight at room temperature. The reaction mixture was washed twice with a saturated ammonium chloride solution. The organic layer was then separated, filtered through Celite, and dried over sodium sulfate. The crude product was purified on a 220 g silica gel column, packing with hexane and eluting with 1 L of hexane, 500 mL of 10% CH_2Cl_2/hexane, 1.0 L of 20% CH_2Cl_2/hexane, and 2.5 L of 30% CH_2Cl_2/hexane. Two isomers were formed. The first peak from GC−MS analysis is the desired isomer. The desired fractions were pooled and concentrated to afford 13.4 g (53.8%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (s, 3H), 2.58 (s, 3H), 7.38−7.58 (m, 3H); GC−MS *m*/*z* (relative intensity) 214 (33), 212 (33).

Synthesis of 2-(Trimethylsilyl)ethyl-4-bromotoluene (17). To 50 mL of dry THF cooled to −78 °C was added 34 mL (68.00 mmol) of 2.0 M LDA THF solution under argon. To this mixture was added a solution of 13.3 g (62.41 mmol) of **16** in 50 mL of THF dropwise. After the addition of compound **16** solution was complete the reaction mixture was stirred at −78 °C for 1 h, then 11.9 mL (82.34 mmol) of diethylchlorophosphate was added, and stirring continued for 15 min at −78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was recooled to −78 °C, and 69.0 mL (0.14 mol) of 2.0 M LDA THF solution was added dropwise. Once addition of LDA solution was complete,

the reaction mixture was warmed to room temperature. After stirring for 3 h, the reaction mixture was then cooled to −20 °C, 14.3 mL (0.11 mol) of trimethylsilyl chloride was added, and stirring continued at room temperature overnight. The solution was then poured into 400 mL of the saturated sodium chloride aqueous solution and 1.0 L of ether. The organic layer was separated, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 300 g silica gel column, packing and eluting with hexane. The desired fractions were pooled and concentrated to afford 9.03 g (54.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 9H), 2.42 (s, 3H), 7.20−7.37 (m, 3H); GC−MS *m*/*z* (relative intensity) 268 (30), 266 (29).

Synthesis of 2-Iodo-5-(trimethylsily)ethynyl-1,4-dipropoxybenzene (19). A solution of 6.46 g (14.51 mmol) of **18**, which was prepared from the literature procedure,[26,27] 2.15 mL (15.21 mmol) of trimethylsilylacetylene, 600 mg (0.86 mmol) of $Pd(PPh_3)_2Cl_2$, and 300 mg (1.57 mmol) of CuI in 350 mL of diisopropylamine was stirred at 70 °C for 2.5 h under argon. The solvent was removed, and 300 mL of hexane was added to the residue. The precipitated solids were filtered off, and the solution was evaporated to dryness for column chromatography. The crude product was purified on a 150 g silica gel column, packing with hexane and eluting with 0−10% CH_2Cl_2/hexane. The desired fractions were pooled and evaporated to afford 2.33 g (39.0%) of the title product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 9H), 1.07 (t, J = 7.2 Hz, 6H), 1.78−1.86 (m, 4H), 3.91 (t, J = 6.3 Hz, 4H), 6.84 (s, 2H); GC−MS *m*/*z* (relative intensity) 416 (79).

Synthesis of 2-(Triisopropylsilyl)ethynyl-5-(trimethylsily)ethynyl-1,4-dipropoxybenzene (20). Compound **20** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 1.5 g (3.61 mmol) of **19**, 0.79 g (4.33 mmol) of triisopropylsilylacetylene, 150 mg (0.26 mmol) of $Pd(dba)_2$, 500 mg (1.91 mmol) of PPh_3, and 1.0 g (5.25 mmol) of CuI in 80 mL of THF and 80 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 3 h and worked up. The crude product was purified on a 100 g silica gel column, packing with hexane eluting with 0−10% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 1.5 g (88.0%) of the title compound. Characterization and analysis of this compound will be reported after desilylation.

Synthesis of 2-(Triisopropylsilyl)ethynyl-5-ethynyl-1,4-dipropoxybenzene (21). Compound **21** was prepared following the general procedure for desilylation using 1.8 g (3.83 mmol) of **20** and 4.5 g of potassium carbonate in 200 mL of 50% CH_3OH/THF. The reaction mixture was stirred at room temperature for 1.5 h and worked up. The crude product was purified on a 100 g silica gel column, packing with 10% CH_2Cl_2/hexane and eluting with 10−20% of CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 1.3 g (85.5%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, J = 7.5 Hz, 3H), 1.05 (t, J = 7.5 Hz, 3H), 1.14 (br s, 21H), 1.74−1.89 (m, 4H), 3.32 (s, 1H), 3.90 (t, J = 6.6 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 6.91 (s, 2H); GC−MS *m*/*z* (relative intensity) 398 (100).

Synthesis of Compound 22. Compound **22** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 252 mg (0.44 mmol) of $Pd(dba)_2$, 700 mg (2.67 mmol) of PPh_3, and 800 mg (4.20 mmol) of CuI, 1.5 g (6.35 mmol) of **5**, and 2.2 g (7.00 mmol) of **15** in 60 mL of diisopropylamine and 15 mL of THF. The reaction mixture was stirred at 60 °C for 4 h and worked up. The crude product was purified on a 100 g silica gel column, packing with CH_2Cl_2 and eluting with 0−20% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 1.89 g (71.0%) of the title compound. Characterization and analysis of this compound will be reported after desilylation.

Synthesis of Compound 23. Compound **23** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 428 mg (0.74 mmol) of $Pd(dba)_2$, 878 mg (3.35 mmol) of PPh_3, and 428 mg (2.25 mmol) of CuI, 8.7 g (37.15 mmol) of **12**, and 11.7 g (37.26 mmol) of **15** in 200 mL of diisopropylamine and 100 mL of DMF. The reaction mixture was stirred at 60 °C for 2 h and worked up. The crude product was purified on a 200 g silica gel column, packing with hexane and eluting with 0−20% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 11.0 g (70.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.71 (s, 9H), 0.92−1.05 (m, 2H), 2.48 (s, 3H), 3.01−3.07 (m, 2H), 7.24−7.47 (m, 7H). Anal. Calcd for $(C_{25}H_{32}SSi_2 + Na)^+$: 443.18. Found: 445.

Synthesis of Compound 24. Compound **24** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 640 mg (1.11 mmol) of $Pd(dba)_2$, 1.25 g (4.77 mmol) of PPh_3, 640 mg (3.36 mmol) of CuI, 6.2 g (26.48 mmol) of **12**, and 7.32 g (23.29 mmol) of **15** in 150 mL of DMF and 200 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 2.5 h and worked up. The crude product was purified on a 220 g silica gel column, packing with hexane and eluting with 0−10% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 8.06 g (77.4%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.31 (s, 9H), 0.92 (s, 9H), 0.93−1.05 (m, 2H), 2.46 (s, 3H), 3.00−3.06 (m, 2H), 7.26−7.48 (m, 7H). Anal. Calcd for $(C_{28}H_{38}SSi_2 + Na)^+$: 485.22. Found: 485.

Synthesis of Compound 25. Compound **25** was prepared following the general procedure for desilylation using 0.74 g (1.74 mmol) of **22** and 2.2 mL (2.2 mmol) of a 1.0 M TBAF THF solution and 150 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min and worked up. The crude product was purified on a 50 g silica gel column, packing with 50% ethyl acetate/CH_2Cl_2 and eluting with the same solvents. The desired fractions were pooled and concentrated to afford 0.5 g (81.3%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 3H), 2.98 (t, J = 7.8 Hz, 2H), 3.25 (t, J = 7.8 Hz, 2H), 3.41 (s, 1H), 7.20−7.50 (m, 9H), 8.60 (br s, 2H). Anal. Calcd for $(C_{24}H_{19}NS + H)^+$: 354.12. Found: 354.

Synthesis of Compound 26. Compound **26** was prepared following the general procedure for desilylation using 11.0 g (26.17 mmol) of **23** and 10.0 g (72.5 mmol) of potassium carbonate in 240 mL of 50% THF/CH_3OH. The reaction mixture was stirred for 1.5 h and worked up. The crude product was purified on a 200 g silica gel column, packing with hexane and eluting with a 0−10% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 8.85 g (97.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.92−1.05 (m, 2H), 2.48 (s, 3H), 3.01−3.07 (m, 2H), 3.44 (s, 1H), 7.24−7.47 (m, 7H). Anal. Calcd for $(C_{22}H_{24}SSi + Na)^+$: 371.14. Found: 373.

Synthesis of Compound 27. Compound **27** was prepared following the general procedure for desilylation using 8.0 g (17.28 mmol) of **24** and 10.0 g (72.5 mmol) of potassium carbonate in 80 mL of THF and 150 mL of methanol. The reaction mixture was stirred for 2 h and worked up. The crude product was purified on a 220 g silica gel column, packing with hexane and eluting with a 0−15% CH_2Cl_2/hexane. Then desired fractions were pooled and concentrated to afford 6.60 g (97.6%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.041 (s, 6H), 0.92 (s, 9H), 1.00−1.03 (m, 2H), 2.49 (s, 3H), 3.03−3.06 (m, 2H), 3.41 (s, 1H), 7.26−7.48 (m, 7H). Anal. Calcd for $(C_{25}H_{30}SSi + K)^+$: 429.18. Found: 429.

Synthesis of Compound 28. Compound **28** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 350 mg (0.61 mmol) of $Pd(dba)_2$, 1.0 g (3.82 mmol) of PPh_3, and 260 mg (1.37 mmol) of CuI, 2.4 g (6.79 mmol) of **25**, and 13.5 g (40.92 mmol) of diiodobenzene in 200 mL of diisopropylamine and 200 mL of THF. The reaction mixture was stirred at 60 °C for 16 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 100 g silica gel column, packing with CH_2Cl_2 and eluting with 0−30% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 3.04 g (81.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 3.26 (t, J = 7.2 Hz, 2H), 7.18−7.49 (m, 11H), 7.74 (d, J = 8.4 Hz, 2H), 8.58 (d, J = 6.0 Hz, 2H). Anal. Calcd for $(C_{30}H_{22}INS + H)^+$: 556.05. Found: 556.

Synthesis of Compound 29. Compound **29** was prepared following the general procedure for the palladium-catalyzed

coupling reaction using 210 mg (0.37 mmol) of $Pd(dba)_2$, 431 mg (1.65 mol) of PPh_3, and 200 mg (1.05 mmol) of CuI, 3.0 g (8.6 mmol) of **26**, and 12.0 g (36.0 mmol) of diiodobenzene in 175 mL of DMF and 125 mL of pyrrolidine. The reaction mixture was stirred at 60 °C for 16 h and worked up. The crude product was purified on a 250 g silica gel column, packing with hexane and eluting with of 0−20% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 2.48 g (53.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.94−1.02 (m, 2H), 2.53 (s, 3H), 3.01−3.08 (m, 2H), 7.27−7.53 (m, 9H), 7.74 (d, J = 8.1 Hz, 2H). Anal. Calcd for $(C_{28}H_{27}ISSi + H)^+$: 551.06. Found: 551.

Synthesis of Compound 30. Compound **30** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 350 mg (0.61 mmol) of $Pd(dba)_2$, 670 mg (2.56 mmol) of PPh_3, and 350 mg (1.83 mmol) of CuI, 4.0 g (10.23 mmol) of (**27**), and 33.8 g (0.10 mol) of diiodobenzene in 600 mL of DMF and 300 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 3 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 240 g silica gel column, packing with hexane and eluting with 0−20% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 3.98 g (65.8%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 6H), 0.92 (s, 9H), 0.98−1.03 (m, 2H), 2.53 (s, 3H), 3.02−3.07 (m, 2H), 7.27−7.51 (m, 9H), 7.74 (d, J = 8.4 Hz, 2H). Anal. Calcd for $(C_{31}H_{33}ISSi + H)^+$: 593.11. Found: 593.

Synthesis of Compound 32. Compound **32** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 70 mg (0.12 mmol) $Pd(dba)_2$, 140 mg (0.53 mmol) of triphenylphosphine, 70 mg (0.37 mmol) of CuI, 1.0 g (2.4 mmol) of **19**, and 0.61 g (2.9 mmol) of ferrocenylacetylene in 75 mL of DMF and 75 mL of diisopropylamine. The reaction mixture was stirred at 55 °C for 3 h and worked up, followed by the treatment of the EDTA solution. The crude product was purified on a 100 g silica gel column, packing with hexane and eluting with 0−30% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 0.53 g (44.5%) of the title compound. Characterization and analysis of this compound will be reported after desilylation.

Synthesis of Compound 33. Compound **33** was prepared following the general procedure for desilylation using 0.53 g (1.06 mmol) of **32** and 8.0 g (57.88 mmol) of potassium carbonate in 100 mL of 50% THF/CH_3OH. The reaction mixture was stirred at room temperature for 2 h and worked up. The crude product was purified on a 50 g silica gel column, packing with hexane and eluting with 0−50% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 0.41 g (91.1%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.81−1.96 (m, 4H), 3.38 (s, 1H), 4.00 (t, J = 6.6 Hz), 4.01(t, J = 6.6 Hz, 2H), 4.30−4.56 (m, 9H), 6.99 (d, J = 3.3 Hz, 2H). Anal. Calcd for $(C_{26}H_{26}FeO + Na)^+$: 449.13. Found: 449.

Synthesis of Compound 34. Compound **34** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 230 mg (0.40 mmol) of $Pd(dba)_2$, 442 mg (1.69 mmol) of triphenylphosphine, 200 mg (1.05 mmol) of CuI, 3.1 g (14.76 mmol) of ferrocenylacetylene, and 16.0 g (48.50 mmol) of diiodobenzene in 150 mL of THF and 100 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 16 h and worked up. The crude product was purified on a 300 g silica gel column, packing in hexane, eluting with hexane until all diiodobenzene is out, and eluting then with 20% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 3.76 g (73.4%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24−4.50 (m, 9H), 7.20 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz). Anal. Calcd for $(C_{18}H_{13}Fe + H)^+$ and $(C_{18}H_{13}Fe - H)^-$: 412.94 and 411.94. Found: 412 and 410.

Synthesis of Compound 35. Compound **35** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 56 mg (0.01 mmol) of $Pd(dba)_2$, 108 mg (0.41 mmol) of triphenylphosphine, 50 mg (0.26 mmol) of CuI, 0.63 g (1.57 mmol) of **21**, and 0.76 g (1.37 mmol) of **28** in 50 mL of THF and 50 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 16 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 50 g silica gel column, packing in CH_2Cl_2 and eluting with 0−30% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 0.98 g (86.6%) of the title compound. Characterization and analysis of this compound will be reported after desilylation.

Synthesis of Compound 36. Compound **36** was prepared following the general procedure for desilylation using 0.98 g (1.19 mmol) of **35** and 1.5 mL (1.50 mmol) of 1.0 M TBAF THF and 50 mL of CH_2Cl_2. The reaction mixture was stirred for 1 h and worked up. The crude product was purified on a 30 g silica gel column, packing with CH_2Cl_2 and eluting with 0−30% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 0.74 g (93.6%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08−1.18 (m, 6H), 1.83−1.95 (m, 4H), 2.56 (s, 3H), 2.98 (t, J = 7.8 Hz, 2H), 3.25 (t, J = 7.8 Hz, 2H), 3.40 (s, 1H), 4.00−4.05 (m, 4H), 7.03−7.55 (m, 15H), 8.57 (d, J = 5.4 Hz, 2H). Anal. Calcd for $(C_{46}H_{39}NO_2S + Na)^+$: 692.27. Found: 692.

Synthesis of Compound 37. Compound **37** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 140 mg (0.24 mmol) of $Pd(dba)_2$, 280 mg (1.07 mmol) of triphenylphosphine, 140 mg (0.74 mmol) of CuI, 1.2 g (3.01 mmol) of **21**, and 9.93 g (30.10 mmol) of diiodobenzene in 300 mL of DMF and 140 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 4 h and worked up. The crude product was purified on a 200 g silica gel column, packing with hexane, eluting with hexane until the diiodobenzene is out of the column, and then eluting with 0−30% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 0.65 g (36.1%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H), 1.18 (br s, 21H), 1.81−1.94 (m, 4H), 3.97 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.6 Hz, 2H), 6.98 (s, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H). Anal. Calcd for $(C_{31}H_{41}IO_2S + Na)^+$: 623.19. Found: 623.

Synthesis of Compound 38. Compound **38** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 100 mg (0.17 mmol) of $Pd(dba)_2$, 200 mg (0.77 mmol) of triphenylphosphine, 100 mg (0.53 mmol) of CuI, 0.47 g (1.51 mmol) of **31**, which is prepared in the literature procedure,[12] and 0.60 g (1.00 mmol) of **37** in 250 mL of DMF and 150 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 16 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 50 g silica gel column, packing with hexane and eluting with of 0−40% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 200 mg (25.8%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.19 (br s, 21H), 1.83−1.95 (m, 4H), 3.98 (t, J = 6.6 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 4.30−4.56 (m, 9H), 6.99 (br s, 2H), 7.51−7.54 (m, 8H). Anal. Calcd for $(C_{51}H_{54}FeO_2Si + Na)^+$: 805.32. Found: 805.

Synthesis of Compound 39. Compound **39** was prepared following the general procedure for desilylation using 200 mg (0.25 mmol) of **38** and 0.31 mL (0.31 mmol) of 1.0 M TBAF THF solution in 50 mL of THF. The reaction mixture was stirred at room temperature for 2 h and worked up. The crude product was purified on a 50 g silica gel column, packing with hexane and eluting with 0−30% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 130 mg (81.8%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (t, J = 6.9 Hz, 3H), 1.14 (t, J = 6.9 Hz, 3H), 1.825−1.97 (m, 4H), 3.40 (s, 1H), 4.01 (t, J = 6.6 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 4.30−4.56 (m, 9H), 7.03 (s, 1H), 7.04 (s, 1H), 7.52 (br s, 4H), 7.55 (br s, 4H). Anal. Calcd for $(C_{42}H_{34}FeO_2 + Na)^+$ and $(C_{42}H_{34}FeO_2 - H)^-$: 649.19 and 625.19. Found: 649 and 625.

Synthesis of Compound 40. A solution of 0.93 g (1.46 mmol) of **I** and 2 mL (3.21 mmol) of iodomethane in 200 mL of acetone was stirred at room temperature overnight. The solution was concentrated to half its volume and diluted by adding 200 mL of hexane. The yellow precipitate was formed, filtered off, and dried to afford 0.60 g (53.0%) of the title

compound: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.15 (s, 3H), 2.56 (s, 3H), 3.29 (t, J = 6.3 Hz, 2H), 3.40 (t, J = 6.3 Hz, 2H), 4.30−4.60 (m, 9H), 7.36−7.56 (m, 11H), 7.91 (d, J = 6.6 Hz, 2H), 9.02 (d, J = 6.6 Hz, 2H). Anal. Calcd for $(C_{43}H_{34}FeSN)^+$: 652.17. Found: 652.

Synthesis of Compound 41. To 60 mL of DMF was added 0.18 g (0.22 mmol) of **(40)** under argon. To this solution was added 2.0 g (14.47 mmol) of potassium carbonate and 1.5 mL of water. After stirring at room temperature for 1.2 h, 6 mL (96.38 mmol) of iodomethane was added and stirring continued for 40 min. The reaction mixture was diluted by adding 600 mL of CH_2Cl_2 and washed once with 400 mL of water. After separating the organic layer, the aqueous layer was extracted twice with 200 mL of CH_2Cl_2. The combined organic extracts were washed once with water, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 88 g silica gel column, packing with hexane and eluting with 20−50% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 58.5 mg (48.7%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.547 (s, 3H), 2.553 (s, 3H), 4.29−4.56 (m, 9H), 7.24−7.52 (m, 11H). HRMS calcd for $C_{36}H_{26}FeS$: 546.1104. Found: 546.1100.

Synthesis of Compound 42. To 40 mg (0.06 mmol) of **II** was added 5.0 mL (5.00 mmol) of TBAF THF solution under argon, and the resulting red solution was stirred for 45 min. To this reaction mixture was added 1.5 mL (24.09 mmol) of iodomethane, and the mixture was stirred another 20 min. The solution was diluted by adding 60 mL of dichloromethane and 10 mL of water. Upon shaking well, the organic layer was separated, dried over sodium sulfate, and concentrated for column chromatography. The crude product was purified on a 53 g silica gel column, packing with hexane and eluting with 50% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated. The yellow product was then precipitated from hexane to afford 22 mg (61.9%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.548 (s, 3H), 2.557 (s, 3H), 4.29−4.56 (m, 9H), 7.24−7.56 (m, 15H). Anal. Calcd for $(C_{44}H_{30}FeS + K)^+$, $(C_{44}H_{30}FeS + Na)^+$, $(C_{44}H_{30}FeS - H)^-$: 685.24, 669.13, 645.13. Found 685, 669, 645.

Synthesis of Compound I. Compound **I** was prepared following the general procedure for the palladium-catalyzed coupling using 55 mg (0.0.96 mmol) of $Pd(dba)_2$, 112 mg (0.43 mmol) of triphenylphosphine, 55 mg (0.29 mmol) of CuI, 1.06 g (1.91 mmol) of **28**, and 0.5 g (2.4 mmol) of ferrocenylacetylene in 75 mL of DMF and 75 mL of pyrrolidine. The reaction mixture was stirred for 16 h at 60 °C and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 60 g silica gel column, packing with CH_2Cl_2 and eluting with 0−20% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 0.91 g (74.6%) of the title compound: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.55 (s, 3H), 3.01 (t, J = 7.2 Hz, 2H), 3.27 (t, J = 7.2 Hz, 2H), 4.29−4.60 (m, 9H), 7.18−7.56 (m, 13H), 8.53 (d, J = 5.7 Hz, 2H). HRMS calcd for $(C_{42}H_{31}FeNS + H)^+$: 638.1605. Found: 638.1622.

Synthesis of Compound II. Compound **II** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 47 mg (0.08 mmol) of $Pd(dba)_2$, 90 mg (0.34 mmol) of triphenylphosphine, 35 mg (0.18 mmol) of CuI, 0.34 g (1.09 mmol) of **31**, which is prepared in the literature procedure,[12] and 0.45 g (0.82 mmol) of **29** in 50 mL of DMF and 25 mL of pyrrolidine. The reaction mixture was stirred at 60 °C for 4 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 120 g silica gel column, packing with hexane and eluting with 0−20% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 0.60 g (95.0%) of the title compound. The desired fractions were pooled and concentrated to afford 2.48 g (53.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.94−1.02 (m, 2H), 2.53 (s, 3H), 3.01−3.08 (m, 2H), 4.29−4.57 (m, 9H), 7.27−7.78 (m, 15H). HRMS calcd for $(C_{48}H_{40}FeSSi + H)^+$: 733.2048. Found: 733.2021.

Synthesis of Compound III. Compound **III** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 100 mg (0.17 mmol) of $Pd(dba)_2$, 200 mg (0.76 mmol) of triphenylphosphine, 100 mg (0.53 mmol) of CuI, 0.65 g (1.10 mmol) of **30**, and 0.41 g (0.97 mmol) of **33** in 100 mL of DMF, 60 mL of THF, and 100 mL of diisopropylamine. The reaction mixture was stirred at 60 °C for 4 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 110 g silica gel column, packing with hexane and eluting with 0−50% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to afford 0.40 g (46.5%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.89 (s, 9H), 0.94−1.00 (m, 2H), 1.15 (t, J = 7.5 Hz, 3H), 1.17 (t, J = 7.5 Hz, 3H), 1.79−1.93 (m, 4H), 2.52 (s, 3H), 2.99−3.05 (m, 2H), 4.03 (t, J = 6.3 Hz, 2H), 4.04 (t, J = 6.3 Hz, 2H), 4.25 (s, 5H), 4.27 (t, J = 1.8 Hz, 2H), 4.51 (t, J = 1.8 Hz, 2H), 6.98 (s, 1H), 7.01 (s, 1H), 7.24−7.55 (m, 11H). HRMS calcd for $C_{57}H_{58}FeO_2SSi$: 890.3276. Found: 890.3241.

Synthesis of Compound IV. Compound **IV** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 30 mg (0.05 mmol) of $Pd(dba)_2$, 58 mg (0.22 mmol) of triphenylphosphine, 30 mg (0.16 mmol) of CuI, 0.40 g (0.60 mmol) of **36**, and 0.50 g (0.98 mmol) of **34** in 60 mL of DMF and 40 mL of diisopropylamine. The reaction mixture was stirred at 65 °C for 4 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 35 g silica gel column, packing with CH_2Cl_2 and eluting with 0−25% ethyl acetate/CH_2Cl_2. The desired fractions were pooled and concentrated to afford 0.20 g (35.0%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.5 Hz, 6H), 1.94 (sextet, J = 6.6 Hz, 4H), 2.56 (s, 3H), 2.99 (t, J = 7.8 Hz, 2H), 3.26 (t, J = 7.8 Hz, 2H), 4.06 (t, J = 7.2 Hz, 4H), 4.30(br s, 7H), 4.56 (s, 2H), 7.07 (s, 2H), 7.21−7.56 (m, 17H), 8.61 (br s, 2H). HRMS calcd for $(C_{64}H_{51}FeNO_2S + H)^+$: 954.3068. Found: 954.3036.

Synthesis of Compound V. Compound **V** was prepared following the general procedure for the palladium-catalyzed coupling reaction using 100 mg (0.17 mmol) of $Pd(dba)_2$, 200 mg (0.76 mmol) of triphenylphosphine, 100 mg (0.53 mmol) of CuI, 130 mg (0.20 mmol) of **39**, and 162 mg (0.27 mmol) of **30** in 50 mL of DMF and 50 mL of pyrrolidine. The reaction mixture was stirred at 60 °C for 16 h and worked up, followed by the treatment of EDTA solution. The crude product was purified on a 60 g silica gel column, packing with hexane and eluting with 0−30% CH_2Cl_2/hexane. The desired fractions were pooled and concentrated to 50 mg (27.2%) of the title compound: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.89 (s, 9H), 0.94−1.00 (m, 2H), 1.12 (t, J = 7.5 Hz, 6H), 1.90 (sextet, J = 6.6 Hz, 4H), 2.52 (s, 3H), 2.97−3.03 (m, 2H), 4.02 (t, J = 6.6 Hz, 4H), 4.27−4.52 (m, 9H), 7.03 (s, 2H), 7.23−7.52 (m, 19H). HRMS calcd for $(C_{73}H_{66}FeO_2SSi + H)^+$: 1091.3980. Found: 1091.4018.

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Supporting Information Available: Proton NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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