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En Route to Surface-Bound Electric Field-Driven Molecular Motors

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Four caltrop-shaped molecules that might be useful as surface-bound electric field-driven molecular motors have been synthesized. The caltrops are comprised of a pair of electron donor−acceptor arms and a tripod base. The molecular arms are based on a carbazole or oligo(phenylene ethynylene) core with a strong net dipole. The tripod base uses a silicon atom as its core. The legs of the tripod bear sulfur-tipped bonding units, as acetyl-protected benzylic thiols, for bonding to a gold surface. The geometry of the tripod base allows the caltrop to project upward from a metallic surface after self-assembly. Ellipsometric studies show that self-assembled monolayers of the caltrops are formed on Au surfaces with molecular thicknesses consistent with the desired upright-shaft arrangement. As a result, the zwitterionic molecular arms might be controllable when electric fields are applied around the caltrops, thereby constituting field-driven motors.

Introduction

Nature has elegantly constructed mechanical-like devices at the micron-scale such as those in bacteria.[1−4] Like their macroscopic analogues, these tiny machines perform numerous functions. In achieving controlled rotary[1,2] or translational[3,4] movement under the influence of external stimuli, the natural micron-sized devices can be highly efficient. Yet they are sufficiently complicated that reproducing them artificially is beyond present technologies. Nevertheless, the pursuit of constructing nanosized machines to augment the basic functions of their natural counterparts has continued since the concept was first proposed by Feynman around half a century ago.[5−7] Recent developments in organic synthetic methodologies have allowed chemists to successfully build several prototypes of nanosized machines in a "bottom-up" approach.[8] For example, several man-made molecular motors have been reported that can convert external energy into arranged movement such as ordered rotary[9−11] or translational[12,13] motion. The energy sources most commonly used are chemical[9,14,15] and light energy.[10−12] Modest AC fields can be used to influence and monitor intramolecular rotary motion.[16] We have been interested in the force and energy that a dipolar unit generates under the influence of external electric stimuli. The change of orientation of dipolar units, originating from intramolecular rotary motion, could be detected according to the conformation of the molecules.[17−19] In this paper we detail our design and synthesis of a series of caltrop-shaped molecules with donor−acceptor functionality, which might behave as electric field-driven molecular motors. In all cases, the molecules have thiol-based end groups for adhesion to a metallic surface, and the efficiency for their controlled surface assembly is discussed.

In our system (Figure 1), the movement of a molecule is restricted by attaching the molecule to a surface via a tripod.[20−23] The molecular caltrops are tetrahedral in shape and can assemble upright on a metallic surface

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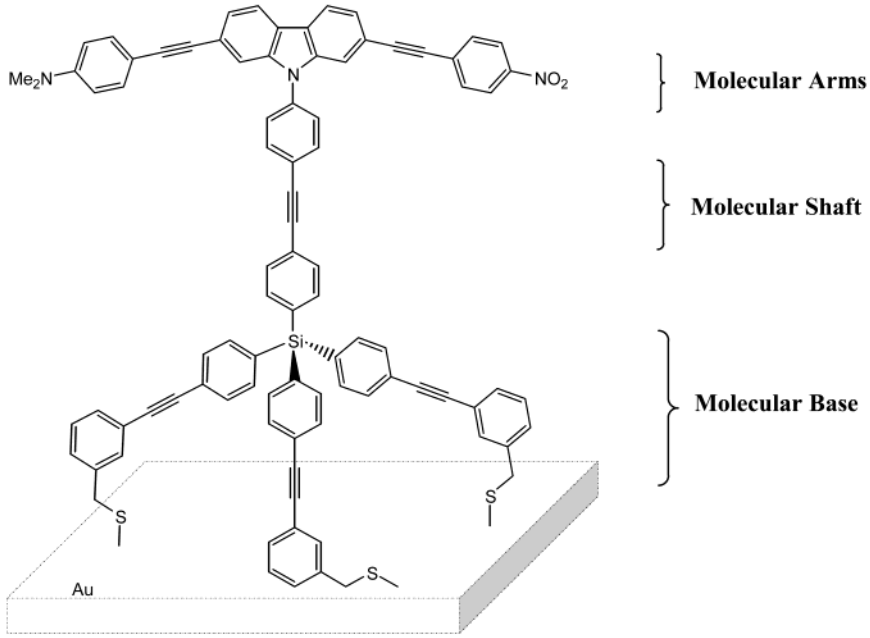

FIGURE 1. Design of electrically driven molecular motor that is assembled on a gold surface.

(such as Au) in the form of self-assembled monolayers (SAMs). Each of the three legs of the tripodal platform bears a sulfur-tipped adhesion unit, delivered via an acetyl-protected benzylic thiol. The acetyl groups can be readily deprotected in situ to afford free thiols during the self-assembly process. Once assembled on a metallic surface, the molecule has no translational degree of freedom. Instead, the top part (the molecular arms) is able to rotate about the oligomeric phenylene ethynylene axis of the molecule (the molecular shaft). With donor−acceptor functionality attached, the arm possesses a strong net dipole moment, with the hope of influencing this dipole to control rotation when subjected to oscillating electric fields.[16]

The molecular arms in three of the caltrops are based on carbazole cores. Functionalized carbazoles have been used as chromophores and building blocks in organic photoconductors and photorefractive materials.[24,25] The spectroscopic properties of carbazole and its derivatives have been widely studied,[26,27] which might allow us to track the movement of the molecular arms by coupled microscopic/spectroscopic methods.[28] Controlling the angle of the arms by the positions of substitution on the carbazole and the length of the arms by the number of conjugated phenylene ethynylene groups allows several arrangements to be considered. In caltrops **1**−**3** in Figure 2, one end of the arms carry an *N*,*N*-dimethylamino moiety and the other end a nitro group for the strong net dipole. Naturally, the strength of the dipole depends on the separation distance and the electronic arrangement around the carbazole. In caltrop **4**, we sought to have the arms generate another degree of measurable propeller-like motion that is off-angle to the shaft rotation. The arms and the base are connected together via the molecular shaft, a rigid oligomeric phenylene ethynylene. This shaft also separates the arms from the metallic surface to reduce possible interactions between them.

We previously synthesized some caltrops that could be useful as AFM tips; they had no molecular arms atop the shafts.[23] However, our previous study showed that the caltrops with *para*-phenylenethiol-terminated tripods were tilted when attached to the gold surface because only two of the three potential Au−S bonds could form. The modified molecular tripod base used here has benzylic thiols at *meta*-positions relative to the ethynylene groups, thereby permitting the proper orientation for assembly.

Results and Discussion

Synthesis of the Molecular Tripod Base. The construction of the molecular base began with the synthesis of **7**, which was made from 3-iodobenzyl alcohol (Scheme 1).

The synthesis of the silicon core is shown in Scheme 2. We have previously reported preparation of **8** by lithiation of 1,4-diiodobenzene and addition of the phenyllithium to tetraethyl orthosilicate.[23] It is imperative that the reaction be conducted in ether and not THF; otherwise, only traces of **8** are afforded. Coupling of **8** with 3 equiv of **7** gave **9**. The 4-iodophenylene moiety of **10** was introduced by addition of *n*-butyllithium to the mixture of 1,4-diiodobenzene, **9**, and THF at −78 °C. Neither the addition of 4-iodophenyllithium, generated in situ by lithium−halogen exchange, to **9** nor the reverse addition gave **10**. Removal of the three TBDMS groups

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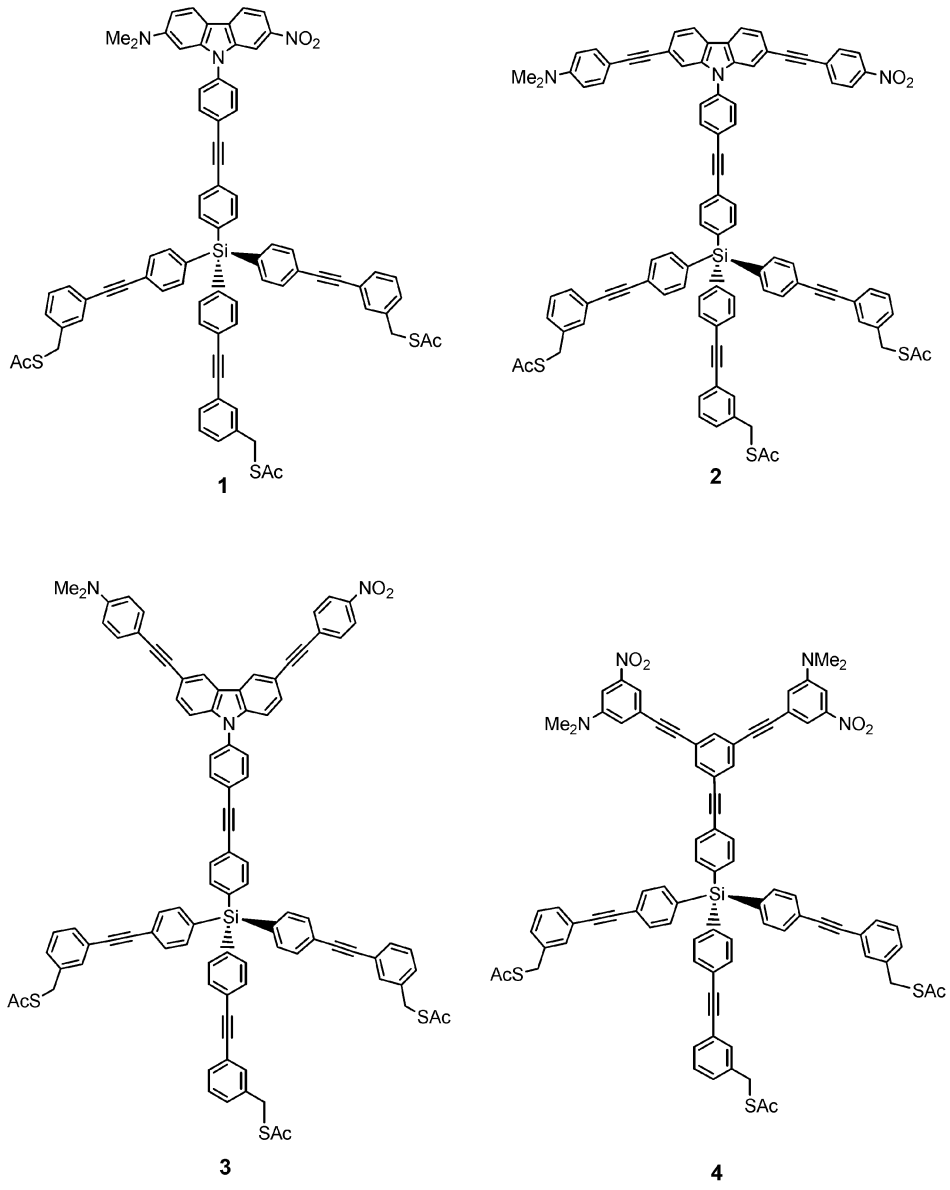
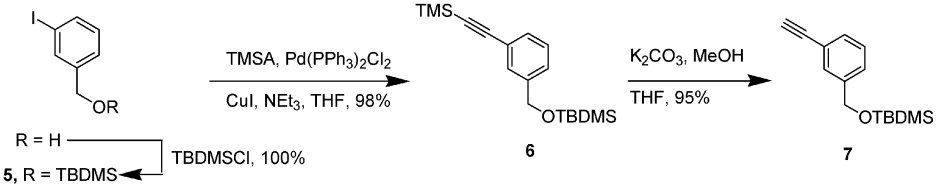


FIGURE 2. Structures of molecular caltrops **1**−**4**.

SCHEME 1



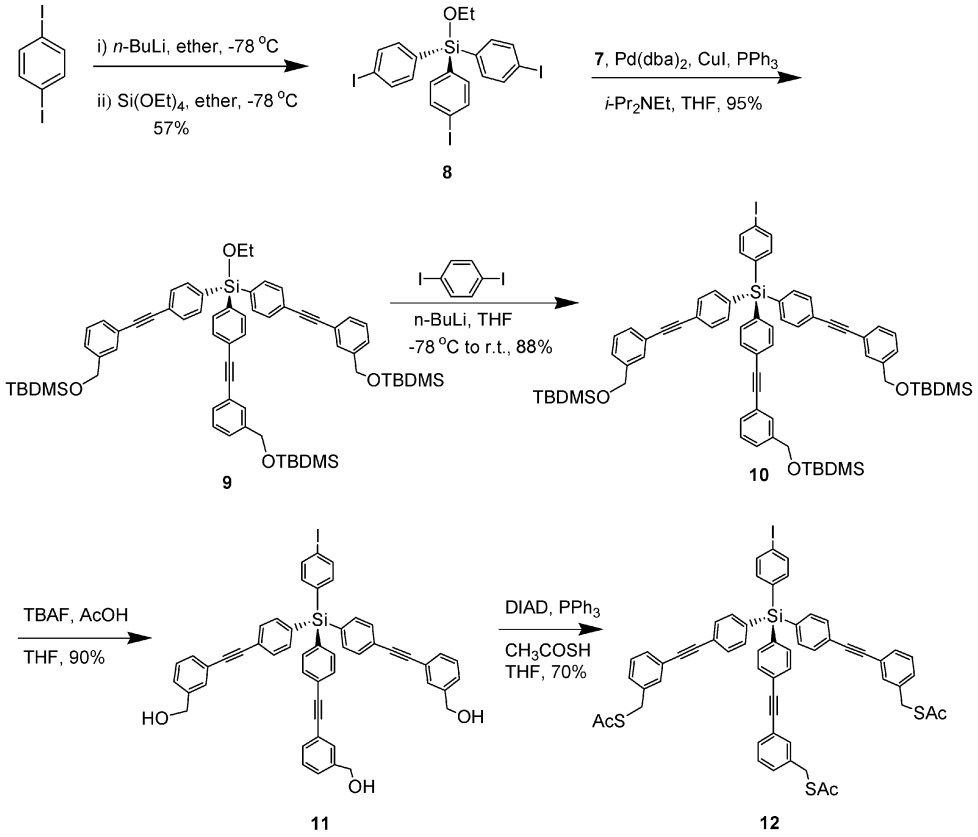
from **10** was completed by TBAF buffered with acetic acid. When the reaction mixture was not buffered, the central silicon atom in **10** was fully disrupted. The triol **11** was converted to trithiolacetate **12** by a Mitsunobu-type reaction.

The thiol groups of **12** are protected by acetyl groups, which will be removed during the SAM formation process. The molecular tripod base **12** contains an aryl iodide moiety that allows coupling with different molecular shafts to produce various final products for studying structure−activity relationships.

Synthesis of Molecular Arms. The arms of caltrop **1** are based on a 2,7-disubstituted carbazole core. As shown in Scheme 3, lithiation of 4-bromo-*N*,*N*-dimethylaniline followed by treatment with tributyltin chloride gives **13**.[29] Stille coupling of **13** and 2-bromo-5-nitroaniline produces **14**. The azide **15** was made from **14** through displacement of the diazonium salt. Thermal decomposition of azide **15** in kerosene gives the function-

(29) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434−5444.

SCHEME 2



alized carbazole **16**.[30] Cu-catalyzed coupling of **16** with 1,4-diodobenzene affords **17**. Palladium-catalyzed coupling of **17** with TMSA followed by deprotection of the terminal alkyne affords **19**, the "molecular arms" of caltrop **1**. Caltrop **1** was synthesized by Sonogashira coupling of **19** and tripod base **12**.

The arms of caltrop **2** have the same carbazole regiochemistry in relation to the shaft as that in caltrop **1**, but **2**'s arms are longer. Since 2,7-dibromocarbazole (**22**) cannot be conveniently made via bromination of carbazole, **22** is prepared in three steps (Scheme 4). Ullmann coupling of 2,5-dibromo-3-nitrobenzene gives **20**,[31] which is subsequently reduced to the diamine **21**.[31] Cyclization of **21** in hot acid gives **22**.[32] The nucleophilic aromatic substitution reaction of **22** and 4-fluoronitrobenzene affords **23** that is reduced to **24**.

The synthesis of the donor part of **2**'s molecular arms starts with the reductive alkylation of 4-iodoaniline to give **25** (Scheme 5).[33] Further coupling of **25** with TMSA affords **26**.[34] Desilylation of **26** gives **27**,[35] which will be used as the donor side of molecular arms of caltrops **2** and **3**.

As shown in Scheme 6, the amino group of **24** was converted to the iodo group through a Sandmeyer reaction. Pd-catalyzed coupling of **28** with 1 equiv of TMSA gave the dibromo compound **29**. This iodide coupling reaction had quite good selectivity with little reaction seen at the symmetrical bromo positions. Further coupling of **29** with 1 equiv of **27** gave the monocoupled product **30**. The yield of this coupling reaction was depressed due to the selectivity problems; however, 40−50% of **29** could be recovered. Several attempts to couple **30** with (4-nitrophenyl)ethyne[44] failed to yield **32**. Lithium−halogen exchange of **30** gave the aryl iodide **31**. Coupling of **31** successfully afforded **32** in good yield. Removal of the TMS group of **32** gave the free alkyne **33** that was ready for coupling with **12** (molecular base), yielding caltrop **2**.

As shown in Scheme 7, preparation of arms of caltrop **3** starts with **34**, which was made according to Moore's procedure.[24] Iodination of **34** by Sandmeyer reaction affords **35**[24] that was coupled with TMSA to give **36**. Coupling of **36** with 1 equiv of 1-ethynyl-4-nitrobenzene gave **37** in a low yield of 36%. However, 50−60% of **36** could be recovered. Further Pd-catalyzed coupling of **37** and **27** afforded **38**, desilylation of which gave **39** that was coupled with the tripod base **12** to afford molecular caltrop **3**.

The synthesis of caltrop **4** (Scheme 8) began with the literature-based preparation of 1,3-dibromo-5-(trimethylsilylethynyl)benzene (**40**[36]) and **41**.[37] Partial reduction of 1,3-dinitro-5-bromobenzene[38] gave **41**. The *N*,*N*-di-

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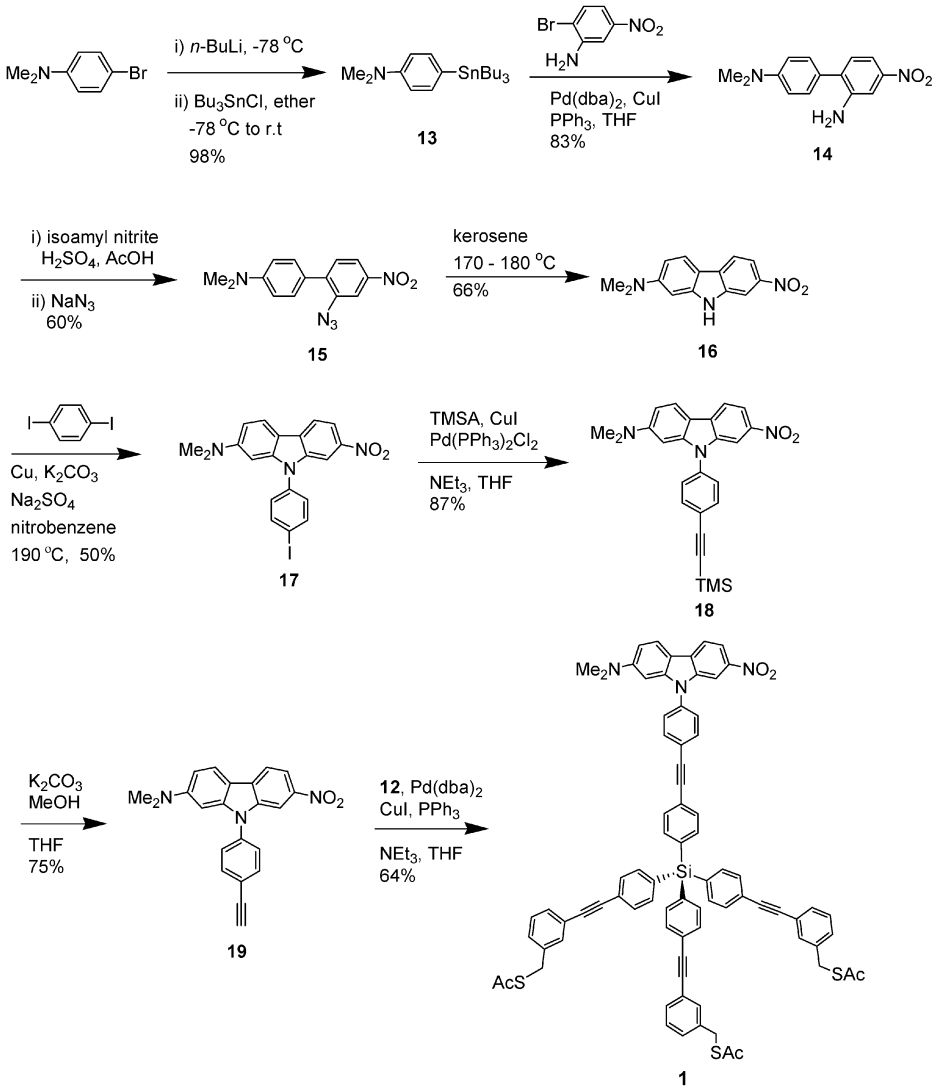
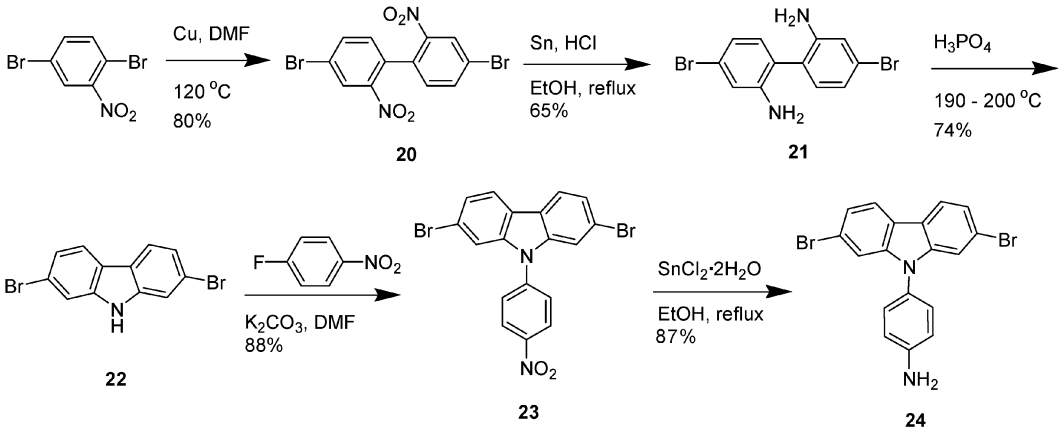
SCHEME 3



SCHEME 4



methylation of aniline **41** gave **42**[39] followed by Pd-catalyzed coupling to afford the silyl-protected alkyne **43**, desilylation of which afforded **44**. Coupling of **44** with **40** gave **45** (the arms of the caltrop) that was desilylated to give **46** and coupled with **12** to afford the desired caltrop **4**.

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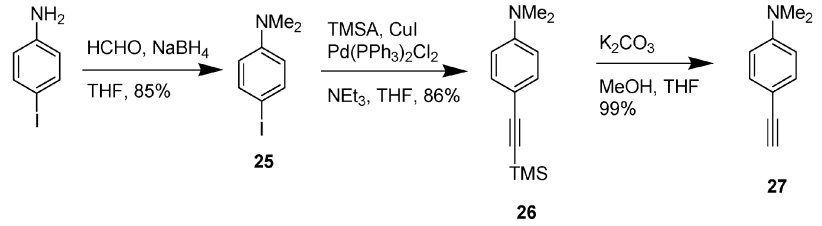
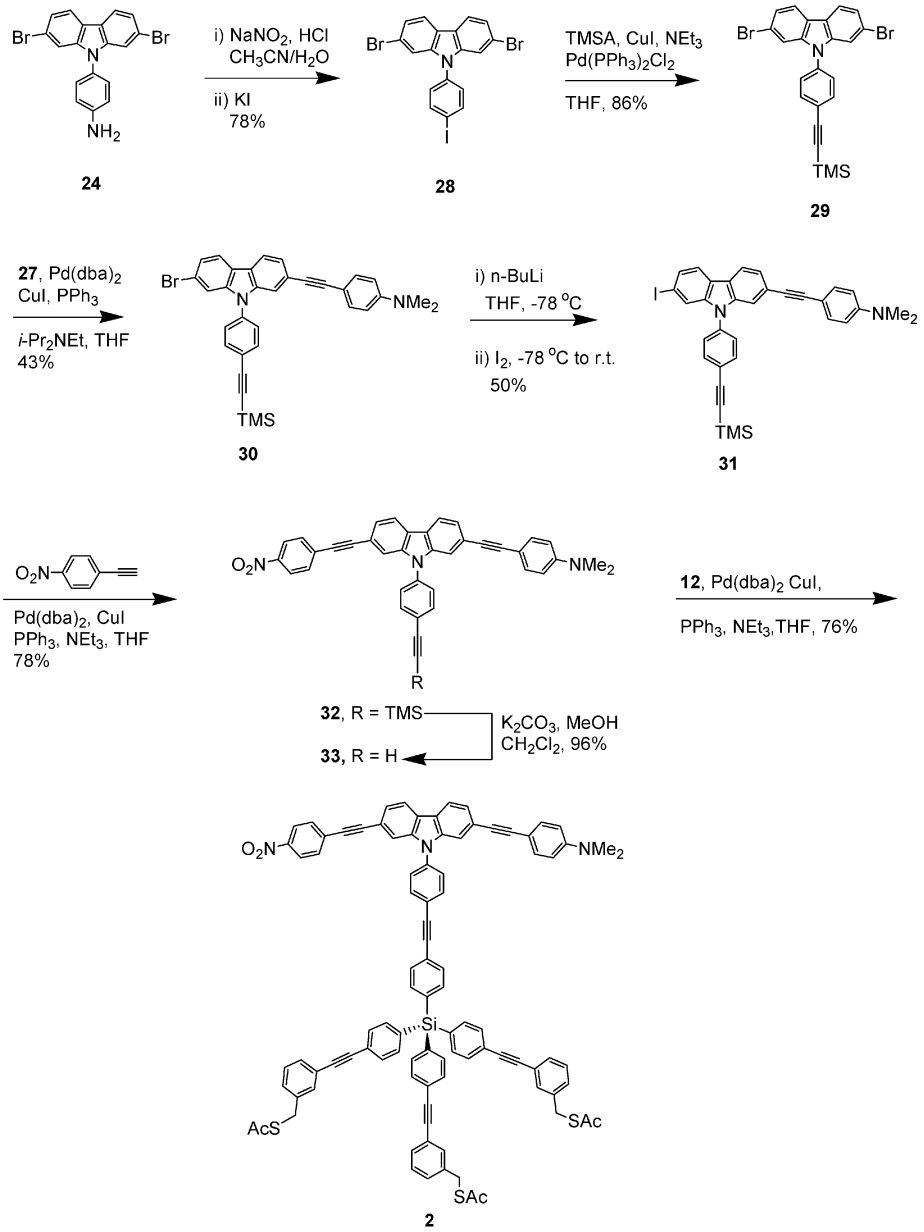
SCHEME 5

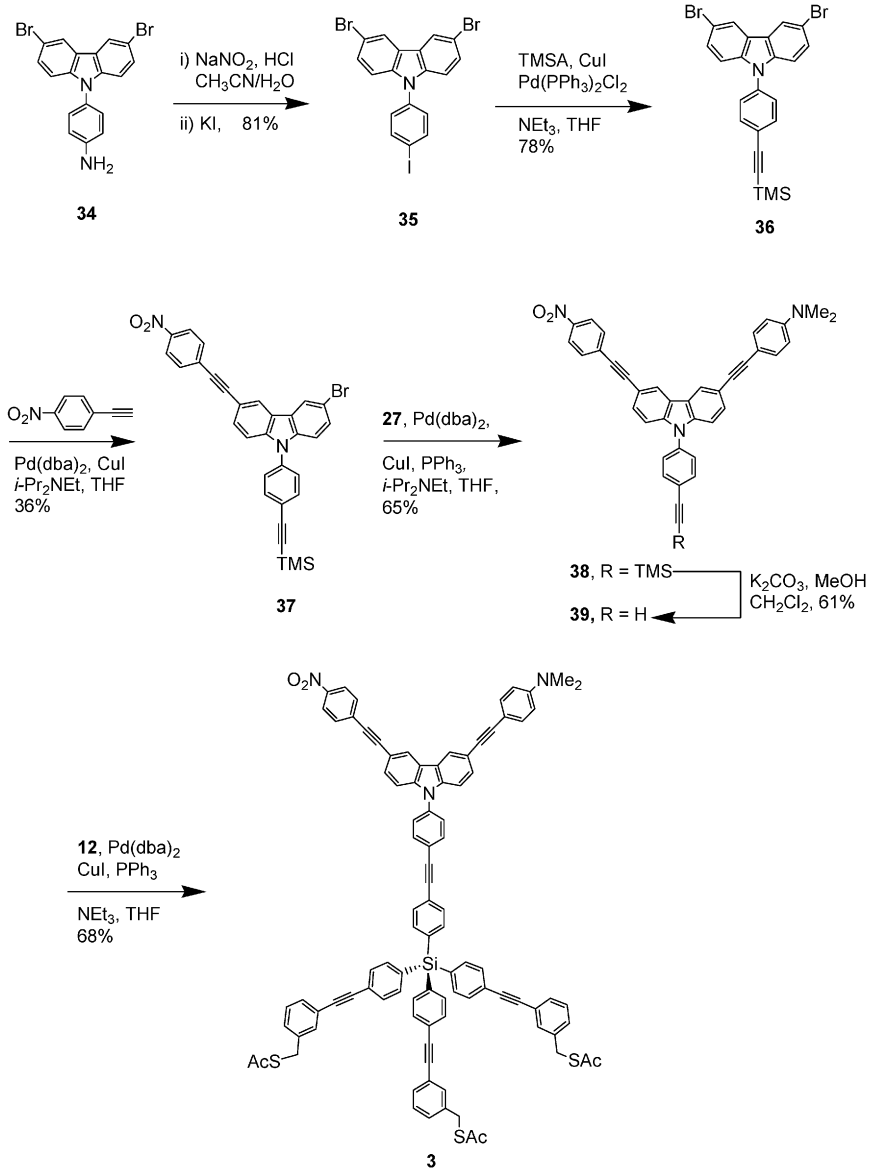


SCHEME 6



Using the selective addition of aryllithium reagents to tetraethyl orthosilicate, along with transition-metal-catalyzed coupling reactions, we have synthesized four caltrop-shaped molecules that can potentially serve as molecular motors. These caltrops were designed with tripod bases containing protected thiols that should allow the molecules to form Au−S bonds to gold surfaces. The arms bear donor−acceptor functionalities, which should make them controllable by an external electric field, to be confirmed by testing. The synthetic methodology developed will permit us to easily adjust the structure of the motors, varying such characteristics as the functional groups of the molecular arms, the length of the molecular shafts, and the binding moieties of the molecular base. Using the results of the surface testing as feedback to our synthetic strategy, we can maximize the

SCHEME 7



performance of the caltrop-shaped molecules as molecular motors or rotors in outer low-frequency oscillating electric fields and on different surfaces.

Self-Assembly. The four caltrops bear thiolacetate-terminated ends for adhesion to a metallic surface so that their behavior can ultimately be studied in the presence of electric fields. We will use lithographic techniques to pattern small regions of Au surfaces on which the caltrops will be deposited. The formation of monolayers is crucial in order to be able to determine the orientation of the molecular arms and to detect any movement when an electric field is applied. Codeposition or insertion into short alkanethiolate matrixes might be needed to keep the molecular arms of adjacent molecules from interacting.

In prior work, we have developed both acid- and base-catalyzed thiol deprotection methods for the in situ generation of thiols during the self-assembly process, and we exploit the acid-catalyzed deprotection method here.[40] A fresh vapor-deposited Au surface (on silicon with a Cr-adhesion layer) was incubated with a solution of each caltrop in the presence of dilute sulfuric acid for 2−6 h to generate SAMs that were investigated by ellipsometry, the results of which are shown in Table 1. The predicted heights are based upon minimized structures by Spartan using force field MMFF94. Our results show that the thicknesses of the SAMs are consistent with the calcu-

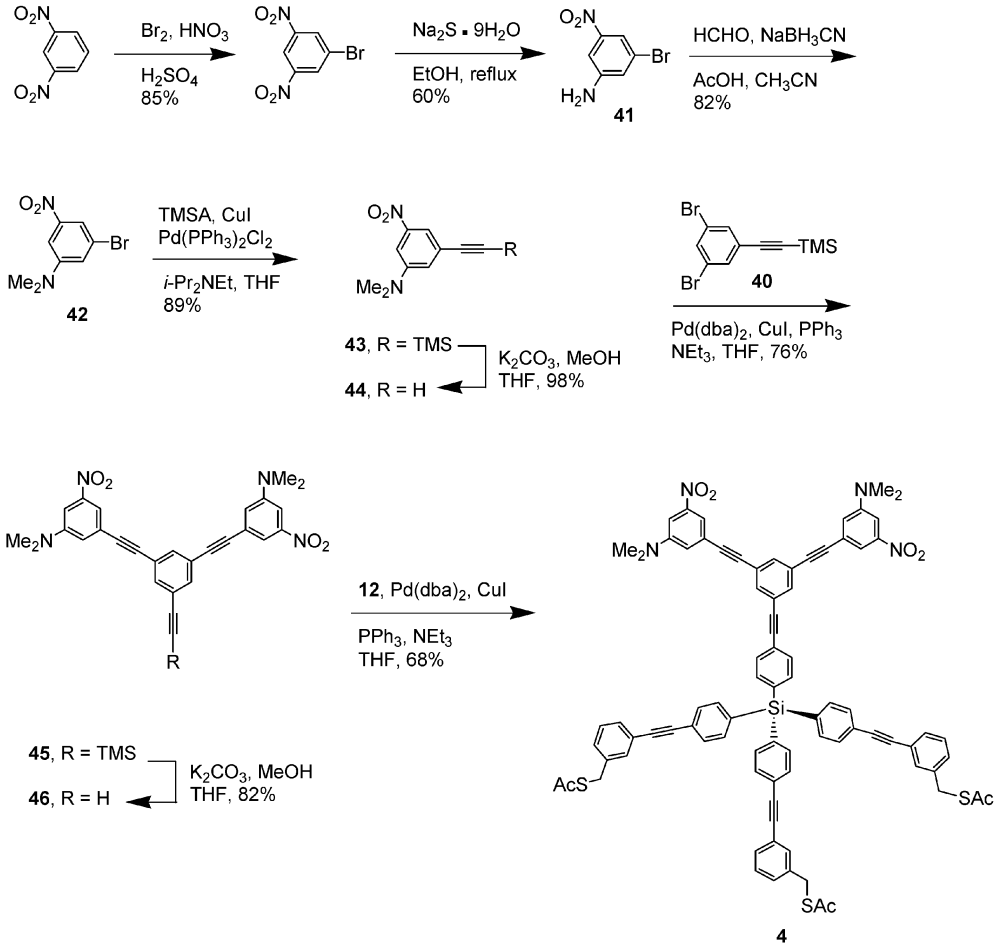
TABLE 1. Theoretical and Actual Self-Assembled Monolayer Thicknesses of 1−4 on Au Surfaces[a]

caltrop	conc (mM)	time (h)	theoretical height (Å)	thickness of SAM (Å)
1	1.0	6	29	26
2	1.0	4	25	22
3	0.5	2	31	31
4	1.0	4	25	25

[a] Comparison of the theoretical thickness (Spartan, estimating the Au−S bond to be 2.4 Å) with the ellipsometrically obtained thicknesses of the monolayers assembled on Au surfaces. Acid-promoted self-assembly of caltrops where $[H_2SO_4] = 60$ mM.[40]

(40) Cai, L.; Yao, Y.; Yang, J.; Price, D. W.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 2905−2909.

SCHEME 8



lated heights (Table 1). Clearly, the benzylic thiols that are *meta*-oriented to the extended base permit self-assembly in a well-controlled fashion. Previously, when we had made caltrops (without the molecular arms)[23] that had arylthiols *para*-oriented to the extended base, self-assembly was inconsistent (unpublished results); the ellipsometric thicknesses and surface IR studies suggest that two of the thiols would bind while the third projected off the surface.

Conclusions

We have designed and successfully synthesized four caltrop-shaped molecules that bear donor−acceptor functionalities. Our ellipsometry results show that the thiol moieties on the legs of the molecular caltrops allow them to form SAMs on Au surfaces, with heights that are consistent with a monolayer structure. Once assembled, the structures of these molecules should allow the top donor−acceptor part (molecular arms) to rotate in response to an outer oscillating electric field in testing that is now underway.[28]

Experimental Section

General. All reactions were performed under an atmosphere of N_2 unless otherwise stated. All chemicals were used as received from commercial resources without further purification unless otherwise stated. The palladium catalysts used in coupling reactions were prepared according to literature methods.[41−43] THF and diethyl ether were distilled from sodium and benzophenone under a N_2 atmosphere. NEt_3 and *N*,*N*-diisopropylethylamine were distilled from calcium hydride under a N_2 atmosphere. Column chromatography was carried out on silica gel (grade 60, mesh size 230−400, EM Science). Thin-layer chromatography (TLC) was performed using glass silica gel plates (40 F_{254} 0.25 mm layer thicknesses, Merck). Infrared spectra (IR) assignments have 2 cm^{-1} resolution. The *para*-substituted benzene ring protons (AA′XX′ system) were reported as doublets. The residual solvent ($CDCl_3$) proton signal was used as an internal standard for spectra (δ 7.28 for ^1H and δ 77.5 for ^{13}C) unless otherwise stated. All compounds were named using the Beilstein Autonom feature of Beilstein Commander software.

General Procedure for Palladium-Catalyzed Coupling Reaction of Terminal Alkynes and Aryl Bromides or Aryl Iodides. The palladium catalysts $Pd(dba)_2$[41] and $Pd(PPh_3)_2Cl_2$[42,43] were prepared according to literature procedures. An oven-dried screw-cap tube was charged with the aryl halide (1 mol), palladium catalysts ($Pd(dba)_2$ or $Pd(PPh_3)_2Cl_2$) (3−5 mol %), and CuI (3−5 mol %). The ligand PPh_3 (12−20 mol %) was also added if the catalyst was $Pd(dba)_2$. The tube was capped with a septum, evacuated, and back-filled with N_2 three times. Triethylamine or *N*,*N*-diisopropylethylamine was added via syringe. A solution of the terminal alkyne in

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THF was transferred via cannula to the tube. The tube was then capped with its screw cap and the solution was stirred. According to the reactivity of alkyne and aryl halide, the reaction temperature varied from room temperature to 70 °C, and the reaction time varied from 2 h to 3 days. The reaction mixture was then cooled to room temperature and poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O three times, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford the coupled product.

General Procedure for Deprotection of Trimethylsilyl-Protected Alkynes. To a stirring solution of the TMS-protected alkyne in THF were added at room temperature K_2CO_3 (0.5−1 equiv) and MeOH/THF (1:1). After the reaction mixture was stirred at room temperature for 2−4 h, it was filtered and the solvent was removed in vacuo. The residue was passed through a plug of silica gel to afford the terminal alkyne.

Chemical Assembly of Caltrops on Gold Surfaces. To the freshly prepared solution of caltrop (0.5−1.0 mM) in CH_2Cl_2 (1.5 mL) was added H_2SO_4 (concentrated, 5.0 μL). The cleaned Au substrate was immersed into the solution at room temperature for 2−6 h. The gold sample was removed from the solution and washed with H_2O, followed by CH_3CN and EtOH, and then dried by blowing with N_2. Monolayer thickness was determined by using a Gaertner LSE ellipsometer. The He−Ne laser (6328 Å) light had an incidence angle of 70°. The thickness was calculated on the basis of the refractive index of $N_f = 1.55$ and $K_f = 0$. The measurement of blank Au substrate was carried out before assembly to obtain N_s and K_s values of the substrate. The thickness of the monolayer was measured immediately after assembly, washing, and drying. The theoretical height was obtained from molecular models minimized by SPARTAN SGI version 5.1.3, using force field MMFF94, with the following assumptions: a Au−S−C bond angle of 97°, 2.4 Å for the Au−S bond length, and perpendicular positioning of molecular shafts relative to the Au surface.

***tert*-Butyl(3-iodobenzyloxy)dimethylsilane (5).** A mixture of 3-iodobenzyl alcohol (9.17 g, 39.2 mmol), TBDMSCl (7.1 g, 47 mmol), and imidazole (3.1 g, 47 mmol) was dissolved in CH_2Cl_2 (250 mL). The reaction mixture was stirred in room temperature for 2 h and then poured into H_2O. The organic layer was washed with H_2O (three times) and dried over $MgSO_4$ and the solvent removed in vacuo. The residue was filtered through a plug of silica gel to afford **5** as a clear oil (13.7 g, 100%): IR (KBr) 2953, 1105, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (s, 1H), 7.59 (d, 1H, J = 7.7 Hz), 7.30 (t, 1H, J = 7.7 Hz), 7.09 (t, 1H, J = 7.7 Hz), 4.71 (s, 2H), 0.97 (s, 9H), 0.13 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 136.3, 135.5, 130.4, 125.6, 94.7, 64.5, 26.3, 18.8, −4.8; HRMS calcd for $C_{13}H_{21}IOSi$ 348.0406, found 348.0400.

1-(*tert*-Butyldimethylsilanyloxymethyl)-3-trimethylsilanylethynylbenzene (6). According to the general coupling procedure, **5** (8.89 g, 25.5 mmol), TMSA (4.4 mL, 31 mmol), $Pd(PPh_3)_2Cl_2$ (0.181 g, 0.258 mmol), CuI (0.097 g, 0.51 mmol), NEt_3 (20 mL), and THF (40 mL) were employed at room temperature to give **6** (7.98 g, 98%) as a yellow oil: R_f = 0.27 (hexanes/CH_2Cl_2, 5:1); IR (KBr) 3064, 2956, 2153, 1158, 1107, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45−7.30 (m, 4H), 4.74 (s, 2H), 0.99 (s, 9H), 0.30 (s, 9H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.9, 130.9, 129.9, 128.6, 126.7, 123.3, 105.7, 94.2, 64.9, 26.4, 18.8, 0.4, −4.8; HRMS calcd for $C_{18}H_{30}OSi_2$ 318.1835, found 318.1809.

***tert*-Butyl(3-ethynylbenzyloxy)dimethylsilane (7).** According to the general deprotection procedure, **6** (5.641 g, 17.67 mmol), K_2CO_3 (1.22 g, 8.84 mmol), CH_3OH (50 mL), and THF (50 mL) were employed to give **7** (4.15 g, 95%) as a yellow oil: R_f = 0.29 (hexanes/CH_2Cl_2, 5:1); IR (KBr) 3303, 2955, 2100, 1105, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.53−7.34 (m, 4H), 4.78 (s, 2H), 3.13 (s, 1H), 1.02 (s, 9H), 0.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.1, 131.1, 130.1, 128.7, 127.0, 122.4, 84.3, 77.4, 64.9, 26.4, 18.9, −4.8; HRMS calcd for $C_{15}H_{22}OSi$ 246.1440, found 246.1436.

Ethoxytri{4-[3-(*tert*-butyldimethylsilanyloxymethyl)-phenylethynyl]phenyl}silane (9). According to the general coupling procedure, **8**[23] (0.153 g, 0.220 mmol), **7** (0.32 g, 1.3 mmol), $Pd(dba)_2$ (0.019 g, 0.033 mmol), CuI (0.006 g, 0.03 mmol), PPh_3 (0.029 g, 0.11 mmol), *i*-Pr_2NEt (5 mL), and THF (15 mL) were employed at room temperature for 2 days to give **9** as a yellow sticky oil (0.223 g, 95%): R_f = 0.31 (hexanes/CH_2Cl_2, 2:1); IR (KBr) 3064, 2931, 2208 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, 6H, J = 8.2 Hz), 7.61 (d, 6H, J = 8.2 Hz), 7.54 (d, 3H, J = 1.4 Hz), 7.47 (td, 3H, J = 4.5 Hz, 1.4 Hz), 7.36 (m, 6H), 4.79 (s, 6H), 3.94 (q, 2H, J = 6.9 Hz), 1.31 (t, 3H, J = 6.9 Hz), 1.00 (s, 27H), 0.17 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 135.6, 134.59, 131.4, 130.7, 129.7, 128.7, 126.6, 125.6, 123.3, 91.3, 89.5, 65.0, 60.4, 26.4, 18.8, 18.7, −4.8; LRMS calcd for $C_{65}H_{80}O_4Si_4$ 1036.51, found 1036.51.

Tris{4-[3-(*tert*-butyldimethylsilanyloxymethyl)phenylethynyl]phenyl}-4′-iodophenylsilane (10). An oven-dried 50 mL round-bottom flask was charged with **9** (1.25 g, 1.20 mmol), diiodobenzene (0.495 g, 1.50 mmol), and THF (20 mL). The solution was cooled to −78 °C. *n*-BuLi (2.39 M in hexane, 0.61 mL) was added dropwise via syringe. The reaction mixture was stirred at −78 °C after the addition. The dry ice bath was allowed to warm to room temperature overnight. The reaction mixture was poured into H_2O, and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **10** as a slightly yellow clear oil (1.06 g, 88%): R_f = 0.17 (hexanes/CH_2Cl_2, 3:1); IR (KBr) 2952, 2929, 2211, 1102, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 2H, J = 8.0), 7.60−7.54 (m, 15H), 7.47 (td, 3H, J = 4.6 Hz, 1.1 Hz), 7.36 (d, 6H, J = 5.0 Hz), 7.31 (d, 2H, J = 8.0 Hz), 4.78 (s, 6H), 1.00 (s, 27H), 0.17 (s, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2, 138.3, 137.7, 136.6, 133.7, 133.2, 131.5, 130.7, 129.7, 128.8, 126.7, 125.5, 123.3, 98.0, 91.5, 89.4, 65.0, 26.4, 18.9, −4.8; MALDI-TOF MS *m*/*z* (matrix: dithranol; AgOTf added) found 1303 (M + Ag^+), calcd for $C_{69}H_{79}IO_3Si_4Ag$ 1303.

Tris{4-[3-(hydroxymethyl)phenylethynyl]phenyl}-4′-iodophenylsilane (11). To the solution of **10** (0.795 g, 0.665 mmol) in THF (100 mL) was added AcOH (0.15 mL, 2.7 mmol), followed by TBAF (1 M in THF, 2.66 mL, 2.66 mmol). The reaction mixture was stirred at room temperature for 28 h. The reaction mixture was poured into H_2O, and the mixture was extracted with EtOAc. The organic layer was washed with H_2O and brine, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography to afford **11** (0.51 g, 90%) as a white oil that solidified slowly at room temperature: R_f = 0.25 (hexanes/EtOAC, 1:2); mp 169−171 °C; IR (KBr) 3414 (br), 2360, 1099, 1007 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, 2H, J = 8.0 Hz), 7.59−7.53 (m. 15H), 7.50 (td, 3H, J = 5.4 Hz, 1.5 Hz), 7.37 (d, 6H, J = 4.7 Hz), 7.29 (d, 2H, J = 7.6 Hz), 4.72 (s, 6H), 1.88 (br, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.6, 138.2, 137.7, 136.5, 133.7, 133.0, 131.5, 131.3, 130.5, 129.0, 127.4, 125.4, 123.7, 98.0, 91.1, 89.7, 65.2; LRMS calcd for $C_{51}H_{37}O_3ISi$ 852, found 852.

Tripod Base 12. To a solution of PPh_3 (3.343 g, 12.76 mmol) in THF (50 mL), cooled to 0 °C, was added diisopropyl azodicarboxylate (DIAD) (2.51 mL, 12.8 mmol). A white precipitate formed after stirring at 0 °C for 5 min. The mixture was stirred at 0 °C for 30 min, and then a solution of **11** (0.544 g, 0.640 mmol) and thiolacetic acid (0.92 mL, 12.8 mmol) in THF (20 mL) was added dropwise by pipet. The reaction mixture became orange, then green, and finally brown during the addition. The flask that held **11** was rinsed with THF (5 mL × 2), and the rinses were also added to the reaction mixture. The reaction mixture was stirred in an ice bath throughout the addition, and the ice bath was then allowed to warm to room temperature. After 4.5 h, the reaction mixture was poured into H_2O and extracted with EtOAc. The organic

layer was washed with H_2O and brine, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography to afford **12** (0.463 g, 70%) as a colorless sticky oil. The oil solidified slowly at room temperature to a white solid: $R_f = 0.35$ (hexanes/EtOAC, 4:1); mp 59−61 °C; IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, 2H, $J = 8.1$ Hz), 7.58−7.49 (m, 15H), 7.44 (dt, 3H, $J = 6.3$ Hz, 2.5 Hz), 7.31−7.28 (m, 8H), 4.14 (s, 6H), 2.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.2, 138.4, 138.2, 137.7, 136.5, 133.7, 133.1, 132.4, 131.5, 131.0, 129.4, 129.1, 125.3, 123.8, 98.0, 90.9, 89.8, 33.4, 30.7; MALDI-TOF MS *m*/*z* (matrix: dithranol; AgOTf added) found 1135 ($M + Ag^+$), calcd for $C_{57}H_{43}IO_3S_3SiAg$ 1135.

Dimethyl-(4′-nitro-2′-amino-biphenyl-4-yl)-amine (14). A screw cap tube was charged with **13**[29] (4.71 g, 11.5 mmol), 2-bromo-5-nitroaniline (1.55 g, 7.14 mmol), $Pd(dba)_2$ (0.122 g, 0.212 mmol), CuI (0.081 g, 0.43 mmol), and PPh_3 (0.223 g, 0.851 mmol). The mixture was degassed and back-filled with N_2. THF (50 mL) was added, and the reaction mixture was heated at 85 °C for 21 h. The reaction mixture was cooled to room temperature, stirred with aqueous KF (saturated 15 mL) overnight, and filtered. The solid was discarded after washing with EtOAc (three times). The liquid was poured into H_2O and extracted with EtOAc. The combined organic layer was washed with H_2O and brine, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography to afford **14** as a red solid (1.51 g, 83%): $R_f = 0.36$ (hexanes/EtOAc, 3:1); mp 198−199 °C; IR (KBr) 3417, 3323, 1504, 1335 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.64 (dd, 1H, $J = 8.3$ Hz, 2.2 Hz), 7.58 (d, 1H, $J = 2.3$ Hz), 7.36 (d, 2H, $J = 8.7$ Hz), 7.23 (d, 1H, $J = 8.3$ Hz), 6.83 (d, 2H, $J = 8.7$ Hz), 4.10 (br, 2H), 3.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 147.8, 145.0, 134.5, 131.1, 129.8, 125.1, 113.8, 113.0, 109.9, 40.8; HRMS calcd for $C_{14}H_{15}N_3O_2$ 257.1164, found 257.1162.

Dimethyl-(4′-nitro-2′-azido-biphenyl-4-yl)-amine (15). To the dark red mixture of **14** (3.63 g, 14.1 mmol), AcOH (70 mL), and H_2SO_4 (concentrated, 14 mL), cooled to 0 °C, while stirring, was added dropwise isoamyl nitrite (2.1 mL, 15.5 mmol) over a period of 5 min. The reaction mixture was stirred at 0 °C for 25 min and then at room temperature for 1 h. H_2O (100 mL) was added to form a dark aqueous solution. Excess aqueous urea (saturated 6 g) was added to destroy the remaining nitrous acid, followed by Norit-A (2.5 g). The dark suspension was stirred at 0 °C for 15 min and filtered. The dark aqueous solution, after filtration, was stirred in an ice bath while saturated aqueous NaN_3 (1.83 g, 28.2 mmol) was added dropwise. N_2 evolved at once. The reaction mixture turned from dark to a clear brown solution during the addition. The reaction mixture was kept stirring in an ice bath for 3 h after addition of the NaN_3. Na_2CO_3 (powder, 100 g) was added slowly to the reaction mixture. The resulting red suspension was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with saturated aqueous $NaHCO_3$ and H_2O, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **15** as a red solid (2.28 g, 57%, a yield as high as 60% was obtained): $R_f = 0.25$ (hexanes/EtOAC, 8:1); mp 167−168 °C; IR (KBr) 2118, 1514, 1342 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, 1H, $J = 2.2$ Hz), 8.04 (dd, 1H, $J = 8.5$ Hz, 2.2 Hz), 7.50 (d, 1H, $J = 8.5$ Hz), 7.43 (d, 2H, $J = 8.9$ Hz), 6.80 (d, 2H, $J = 8.9$ Hz), 3.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.1, 147.1, 140.8, 138.6, 131.6, 130.7, 123.7, 120.3, 114.5, 112.2, 40.7; HRMS calcd for $C_{14}H_{13}N_5O_2$ 283.1069, found 283.1071.

Dimethyl(7-nitro-9*H*-carbazol-2-yl)amine (16). Odorless kerosene (250 mL) was purified by shaking with concentrated H_2SO_4 (3 × 30 mL). The red powder of **15** (1.958 g, 6.919 mmol) was added portionwise to hot kerosene (250 mL) while stirring at 170−190 °C. The heat was maintained for 5 min after the final addition. The reaction mixture was then cooled to room temperature and chilled in a refrigerator. The red solid was collected by filtration, and washed with petroleum ether (3 × 10 mL). Recrystallization from benzene gave **16** as a red solid (0.851 g, 48%, a yield as high as 66% was obtained): $R_f = 0.24$ (hexanes/EtOAC, 4:1); mp 245−246 °C; IR (KBr) 3379, 1509, 1335 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, 1H, $J = 1.9$ Hz), 8.12 (dd + br, 2H, $J = 8.6$ Hz, 2.0 Hz), 7.93 (d, 1H, $J = 8.8$ Hz), 7.92 (d, 1H, $J = 8.6$ Hz), 6.81 (dd, 1H, $J = 8.8$ Hz, 2.2 Hz), 6.66 (d, 1H, $J = 2.1$ Hz), 3.12 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 152.2, 145.7, 143.6, 139.0, 129.8, 123.1, 119.0, 114.9, 112.5, 108.8, 106.6, 93.2, 41.2; HRMS calcd for $C_{14}H_{13}N_3O_2$ 255.1008, found 255.1008.

[9-(4-Iodophenyl)-7-nitro-9*H*-carbazol-2-yl]dimethylamine (17). The mixture of **16** (52.7 mg, 0.207 mmol), 1,4-diiodobenzene (208 mg, 0.630 mmol), Cu powder (29 mg, 0.021 mmol), K_2CO_3 (29 mg, 0.21 mmol), Na_2SO_4 (30 mg, 0.21 mmol), and nitrobenzene (10 mL) was heated at 190 °C for 23 h. After the mixture was cooled, most of the nitrobenzene was removed by vacuum distillation. The residue was passed through a column of silica gel. The desired product **17** was isolated as a red solid (48 mg, 50%): $R_f = 0.37$ (hexanes/CH_2Cl_2, 3:2); mp 250−251 °C; IR (KBr) 1493, 1298 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16 (dd, 1H, $J = 8.5$ Hz, 2.0 Hz), 8.10 (d, 1H, $J = 1.9$ Hz), 8.01−7.95 (m, 4H), 7.33 (d, 2H, $J = 8.6$ Hz), 6.84 (dd, 1H, $J = 8.8$ Hz, 2.2 Hz), 6.48 (d, 1H, $J = 2.1$ Hz), 3.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 145.9, 144.4, 139.9, 139.8, 136.9, 130.0, 129.5, 122.7, 118.5, 116.5, 112.6, 109.0, 105.5, 93.6, 91.6, 41.2; HRMS calcd for $C_{20}H_{16}IN_3O_2$ 457.0287, found 457.0291.

Dimethyl[7-nitro-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazol-2-yl]amine (18). According to the general coupling procedure, **17** (48 mg, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.005 mmol), CuI (1 mg, 0.005 mmol), TMSA (50 μL, 0.35 mmol), NEt_3 (5 mL), and THF (5 mL) were employed at room temperature to give **18** as an orange solid (39 mg, 87%): $R_f = 0.36$ (hexanes/CH_2Cl_2, 3:2); mp > 232 °C dec; IR (KBr) 2158, 1508, 1328 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.16−8.13 (m, 2H), 7.98 (d, 1H, $J = 8.8$ Hz), 7.97 (d, 1H, $J = 8.4$ Hz), 7.77 (d, 2H, $J = 8.5$ Hz), 7.53 (d, 2H, $J = 8.5$ Hz), 6.84 (dd, 1H, $J = 8.8$ Hz, 2.2 Hz), 6.50 (d, 1H, $J = 2.1$ Hz), 3.06 (s, 6H), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.0, 145.9, 144.5, 139.9, 137.1, 134.3, 130.0, 127.3, 123.5, 122.6, 118.5, 116.4, 112.7, 109.0, 105.7, 104.3, 96.5, 91.8, 41.2, 0.33; HRMS calcd for $C_{25}H_{25}N_3O_2Si$ 427.1716, found 427.1719.

[9-(4-Ethynylphenyl)-7-nitro-9*H*-carbazol-2-yl]dimethylamine (19). According to the general deprotection procedure, **18** (74 mg, 0.17 mmol), K_2CO_3 (12 mg, 0.086 mmol), MeOH (20 mL), and THF (20 mL) were employed to give **19** as an orange solid (45 mg, 75%): $R_f = 0.26$ (hexanes/CH_2Cl_2, 3:2); IR (KBr) 3278, 2360, 1509, 1318 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.17−8.15 (m, 2H), 7.99 (d, 1H, $J = 8.8$ Hz), 7.98 (d, 1H, $J = 8.5$ Hz), 7.80 (d, 2H, $J = 8.5$ Hz), 7.56 (d, 2H, $J = 8.5$ Hz), 6.85 (dd, 1H, $J = 8.8$ Hz, 2.2 Hz), 6.52 (d, 1H, $J = 2.2$ Hz), 3.24 (s, 1H), 3.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 145.9, 144.5, 139.9, 137.5, 134.5, 130.0, 127.4, 122.7, 122.5, 118.5, 116.5, 112.7, 109.1, 105.6, 91.8, 83.0, 79.1, 41.2; HRMS calcd for $C_{22}H_{17}N_3O_2$ 355.1321, found 355.1320.

Caltrop 1. According to the general coupling procedure, **19** (42 mg, 0.12 mmol), **12** (121 mg, 0.120 mmol), $Pd(dba)_2$ (4 mg, 0.006 mmol), CuI (1 mg, 0.006 mmol), PPh_3 (6.3 mg, 0.024 mmol), NEt_3 (5 mL), and THF (5 mL) were employed to give **1** as an orange solid (96 mg, 64%): $R_f = 0.23$ (hexanes/EtOAc, 2:1); mp 103−106 °C; IR (KBr) 1689, 1511, 1321 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.19−8.16 (m, 2H), 7.98 (d + d, 2H, $J = 8.6$ Hz, $J = 8.4$ Hz), 7.86 (d, 2H, $J = 8.4$ Hz), 7.67−7.29 (m, 30H), 6.85 (dd, 1H, $J = 8.8$ Hz, $J = 2.0$ Hz), 6.57 (d, 1H, $J = 1.8$ Hz), 4.15 (s, 6H), 3.07 (s, 6H), 2.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz, missing one aromatic C due to overlap) δ 195.3, 152.1, 145.9, 144.5, 139.9, 138.5, 137.2, 136.7, 136.6, 134.5, 134.0, 134.0, 132.4, 131.6, 131.5, 131.0, 130.0, 129.4, 129.1, 127.5, 125.3, 125.0, 123.8, 123.4, 118.5, 116.5, 112.7, 109.1, 105.7, 91.8, 91.1, 91.0, 90.2, 89.9, 41.2, 33.5, 30.8;

MALDI-TOF MS *m*/*z* (matrix: sinapinic acid) found 1253 (M^+) and 1162 (M^+ − SAc), calcd for $C_{79}H_{59}N_3O_5S_3Si$: 1253.

2,7-Dibromo-9-(4-nitrophenyl)-9*H*-carbazole (23). To a flask charged with 2,7-dibromocabazole (**22**)[31,32] (4.99 g, 15.3 mmol) and K_2CO_3 (10.56 g, 76.52 mmol) was added 4-fluoronitrobenzene (6.5 mL, 61.4 mmol) and DMF (80 mL). The reaction mixture was heated at reflux in DMF overnight, cooled to room temperature, and poured into H_2O (500 mL). The yellow solid was collected by filtration. The crude material was recrystallized from benzene to afford the product as a light yellow solid (5.89 g, 86%, a yield as high as 88% was obtained): R_f = 0.25 (hexanes/CH_2Cl_2, 3:1); mp 229−230 °C; IR (KBr) 3073, 1588, 1514, 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.56 (d, 2H, J = 8.9 Hz), 7.98 (d, 2H, J = 8.3 Hz), 7.77 (d, 2H, J = 9.0 Hz), 7.58 (d, 2H, J = 1.5 Hz), 7.49 (dd, 2H, J = 8.3 Hz, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.0, 142.8, 141.3, 127.5, 126.3, 125.2, 122.8, 122.2, 120.9, 113.3; HRMS calcd for $C_{18}H_{10}Br_2N_2O_2$ 445.9090, found 445.9091.

4-(2,7-Dibromocarbazol-9-yl)phenylamine (24). The mixture of **23** (5.89 g, 13.2 mmol), $SnCl_2 \cdot 2H_2O$ (14.9 g, 660 mmol), and ethanol (200 mL) was heated at 78−80 °C overnight and then cooled to room temperature. Most of the ethanol was removed in vacuo. An aqueous solution of saturated NaOH (25 g) was poured into the reaction mixture slowly while the mixture was cooled in an ice bath and stirred vigorously. The white solid was collected by filtration. The solid was extracted with benzene several times. The combined benzene solution was dried over $MgSO_4$ and filtered and the solvent removed in vacuo. Recrystallization from benzene gave the desired product as ivory crystals (4.78 g, 87%): R_f = 0.35 (hexanes/CH_2Cl_2, 1:1); mp 185.5−187 °C; IR (KBr) 3469, 3381 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, 2H, J = 8.3 Hz), 7.44 (d, 2H, J = 1.6 Hz), 7.38 (dd, 2H, J = 8.3 Hz, 1.7 Hz), 7.22 (d, 2H, J = 8.7 Hz), 6.89 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 142.9, 128.9, 127.0, 123.6, 121.8, 121.7, 120.2, 116.4, 113.5; HRMS calcd for $C_{18}H_{12}N_2Br_2$ 415.9348, found 415.9338.

2,7-Dibromo-9-(4-iodophenyl)-9*H*-carbazole (28). The mixture of **24** (2.54 g, 6.11 mmol), CH_3CN (50 mL), and H_2O (50 mL) was stirred in an ice bath while concentrated HCl (3 mL) was added dropwise over 5 min. The reaction mixture turned from white to yellow. To this mixture, still in an ice bath, was added a solution of $NaNO_2$ (0.842 g, 12.2 mmol) in 50 mL of H_2O. The reaction mixture turned from yellow to orange. The reaction mixture was then stirred at room temperature for 50 min. A solution of KI (5.06 g, 30.5 mmol) in 100 mL of H_2O was added. The reaction mixture was then heated to boiling until no more purple or brown vapor was evolved. After cooling to room temperature, the reaction mixture was poured into H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with aqueous Na_2SO_3, followed by H_2O, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography to afford **28** (2.35 g, 71%, a yield as high as 78% was obtained) as a white crystalline solid: R_f = 0.48 (hexanes/CH_2Cl_2, 5:1); mp 189.5−190.5 °C; IR (KBr) 2360, 1491 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, 2H, J = 8.6 Hz), 7.95 (d, 2H, J = 8.3 Hz), 7.49 (d, 2H, J = 1.6 Hz), 7.43 (dd, 2H, J = 8.3 Hz, 1.6 Hz), 7.27 (d, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141,9, 139.9, 136.6, 129.3, 124.4, 122.2, 122.0, 120.5, 113.3, 93.7; HRMS calcd for $C_{18}H_{10}Br_2NI$ 524.8225, found 524.8216.

2,7-Dibromo-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazole (29). According to the general coupling procedure, **28** (0.615 g, 1.17 mmol) was coupled with TMSA (0.25 mL, 1.75 mmol) in the presence of $Pd(PPh_3)_2Cl_2$ (41 mg, 0.58 mmol), CuI (11 mg, 0.058 mmol), NEt_3 (10 mL), and THF (25 mL) at room temperature for 40 h to give the product **29** as a white solid (0.49 g, 84%, a yield as high as 86% was obtained): R_f = 0.31 (hexanes/CH_2Cl_2, 10:1); mp 241−242 °C; IR (KBr) 2161 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 2H, J = 8.3 Hz), 7.74 (d, 2H, J = 8.6 Hz), 7.50 (d, 2H, J = 1.5 Hz), 7.48 (d, 2H, J = 8.6 Hz), 7.43 (dd, 2H, J = 8.3, 1.7 Hz), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.9, 136.7, 134.2, 127.2, 124.3, 123.7, 122.2, 121.9, 120.5, 113.4, 104.2, 96.6, 0.36; HRMS calcd for $C_{23}H_{19}Br_2NSi$ 494.9654, found 494.9649.

{**4-[7-Bromo-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazol-2-ylethynyl]phenyl**}**dimethylamine (30).** According to the general coupling procedure, **29** (0.379 g, 0.766 mmol) was coupled with **27**[35] (0.11 g, 0.76 mmol) in the presence of $Pd(dba)_2$ (22 mg, 0.038 mmol), CuI (7 mg, 0.04 mmol), PPh_3 (40 mg, 0.15 mmol), *i*-Pr_2NEt (5 mL), and THF (15 mL) at 60 °C for 11 h to give **30** (0.186 g, 43%) as a yellow solid: R_f = 0.43 (hexanes/EtOAc, 10:1); mp 224−225 °C; IR (KBr) 2204, 2160 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, 1H, J = 8.1 Hz), 7.95 (d, 1H, J = 8.3 Hz), 7.75 (d, 2H, J = 8.6 Hz), 7.51 (m, 4H), 7.48 (dd, 1H, J = 8.1, 1.3 Hz), 7.45 (m, 3H), 6.68 (d, 2H, J = 8.6 Hz), 3.02 (s, 6H), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 142.3, 141.0, 137.1, 134.1, 133.1, 127.3, 124.6, 124.0, 123.3, 122.7, 122.6, 122.5, 122.0, 120.6, 120.3, 113.3, 113.0, 112.2, 110.3, 104.4, 96.3, 91.4, 88.6, 40.6, 0.35; HRMS calcd for $C_{33}H_{29}N_2BrSi$ 560.1284, found 560.1287.

{**4-[7-Iodo-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazol-2-ylethynyl]phenyl**}**dimethylamine (31).** A dry flask charged with a solution of **30** (0.214 g, 0.382 mmol) in THF (10 mL) was cooled to −78 °C, and *n*-BuLi (2.39 M in pentane, 0.19 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 30 min. A solution of I_2 (0.135 g, 0.531 mmol) in THF (10 mL) was added. The dry ice bath was then allowed to warm to room temperature overnight. The reaction mixture was poured into aqueous Na_2SO_3 and extracted with EtOAc; the organic layer was washed with H_2O three times, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **31** as a white solid (0.116 g, 50%): R_f = 0.43 (hexanes/EtOAc, 10:1); IR (KBr) 2203, 2158 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 8.1 Hz), 7.75 (d, 2H, J = 8.5 Hz), 7.71 (d, 1H, J = 1.2 Hz), 7.60 (dd, 1H, J = 8.2 Hz, 1.4 Hz), 7.52−7.44 (m, 6H), 6.68 (d, 2H, J = 8.7 Hz), 3.02 (s, 6H), 0.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 142.5, 140.7, 137.1, 134.1, 133.1, 133.0, 129.7, 127.3, 124.5, 123.3, 123.2, 122.7, 122.6, 122.2, 120.6, 119.2, 113.0, 112.2, 110.3, 104.4, 96.3, 91.2, 88.6, 40.6, 0.36; HRMS calcd for $C_{33}H_{29}IN_2Si$ 608.1145, found 608.1137.

Dimethyl-{4-[7-(4-nitrophenylethynyl)-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazol-2-ylethynyl]phenyl}-amine (32). According to the general coupling procedure, **31** (0.274 g, 0.450 mmol) was coupled with (4-nitrophenyl)ethyne[44] (0.11 g, 0.75 mmol) in the presence of $Pd(dba)_2$ (0.014 g, 0.024 mmol), CuI (0.005 g, 0.02 mmol), PPh_3 (0.025 g, 0.096 mmol), NEt_3 (5 mL), and THF (15 mL) at room temperature for 15 h to give **32** (0.235 g, 78%) as red crystals: R_f = 0.42 (hexanes/CH_2Cl_2, 1:1); mp 206−208 °C; IR (KBr) 2359, 2341, 2205, 1514, 1384 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, 2H, J = 8.8 Hz), 8.07 (d + d, 2H, J = 8.3 Hz, 8.2 Hz), 7.77 (d, 2H, J = 8.3 Hz), 7.67 (d, 2H, J = 8.3 Hz), 7.57−7.42 (m, 8H), 6.68 (d, 2H, J = 8.5 Hz), 3.06 (s, 6H), 0.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 147.2, 141.6, 141.1, 137.2, 134.1, 133.2, 132.6, 130.8, 127.3, 124.6, 124.6, 124.5, 124.1, 123.3, 123.0, 122.6, 121.0, 120.9, 119.7, 113.7, 113.0, 112.2, 110.3, 104.4, 96.5, 96.3, 91.8, 88.7, 88.2, 40.6, 0.38; HRMS calcd for $C_{41}H_{33}N_3O_2Si$ 627.2342, found 627.2335.

{**4-[9-(4-Ethynylphenyl)-7-(4-nitrophenylethynyl)-9*H*-carbazol-2-ylethynyl]phenyl**}**dimethylamine (33).** According to the general deprotection procedure, **32** (9.4 mg, 0.014 mmol) with K_2CO_3 (1.9 mg, 0.014 mmol), MeOH (10 mL), and CH_2Cl_2 (10 mL) gave **33** (8.0 mg, 96%) as a red solid: R_f = 0.41 (hexanes/CH_2Cl_2, 1:1); mp 247−249 °C dec; IR (KBr) 3276, 2205, 1512, 1389 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.11 (d, 1H, J = 6.4 Hz), 8.09 (d, 1H, J = 6.5 Hz), 7.80 (d, 2H, J = 6.6 Hz), 7.69 (d, 2H, J = 6.8 Hz), 7.60−7.43 (m, 8H), 6.68 (d, 2H,

(44) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, *8*, 627−630.

J = 7.0 Hz), 3.24 (s, 1H), 3.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 147.3, 141.6, 141.1, 137.6, 134.4, 133.2, 132.6, 130.8, 127.5, 124.7, 124.7, 124.6, 124.1, 123.1, 122.6, 122.3, 121.0, 119.7, 113.7, 113.0, 112.2, 110.2, 96.4, 91.8, 88.6, 88.2, 83.1, 78.9, 40.6; HRMS calcd for $C_{38}H_{25}N_3O_2$ 555.1947, found 555.1942.

Caltrop 2. According to the general coupling procedure, **12** (0.250 g, 0.243 mmol) and **33** (0.151 g, 0.272 mmol) were coupled in the presence of $Pd(dba)_2$ (8.0 mg, 0.014 mmol), CuI (2.7 mg, 0.014 mmol), PPh_3 (14 mg, 0.054 mmol), NEt_3 (5 mL), and THF (15 mL) at room temperature for 34 h to give **2** as a red solid (0.147 g, 42%, a yield as high as 76% was obtained): R_f = 0.20 (hexanes/EtOAc, 3:1); mp > 130 °C dec; IR (KBr) 2203, 1689, 1515, 1337, 1098 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, 2H, J = 8.9 Hz), 8.10 (d, 1H, J = 8.0 Hz), 8.07 (d, 1H, J = 8.1 Hz), 7.85 (d, 2H, J = 8.52 Hz), 7.70−7.44 (m, 34H), 7.33−7.29 (m, 4H), 6.68 (d, 2H, J = 8.8 Hz), 4.14 (s, 6H), 3.02 (s, 6H), 2.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, missing one aromatic C due to overlap) δ 195.3, 150.5, 147.2, 141.6, 141.1, 138.5, 137.2, 136.7, 136.6, 134.4, 134.0, 133.9, 133.2, 132.6, 132.4, 131.8, 131.6, 131.5, 131.0, 130.8, 129.5, 129.1, 127.5, 125.3, 125.0, 124.7, 124.7, 124.6, 124.1, 123.8, 123.2, 123.1, 122.7, 121.0, 119.7, 113.8, 113.0, 112.2, 110.2, 96.5, 91.9, 91.0, 90.3, 89.9, 88.8, 88.2, 40.6, 33.5, 30.8; MALDI-TOF MS *m/z* (matrix: dithranol) found 1454, calcd for $C_{95}H_{67}N_3O_5S_3Si$ 1454.

3,6-Dibromo-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazole (36). According to the general coupling procedure, **35**[24] (4.393 g, 8.834 mmol) was coupled with TMSA (1.3 mL, 9.2 mmol) in the presence of $Pd(PPh_3)_2Cl_2$ (0.116 g, 0.166 mmol), CuI (0.032 g, 0.17 mmol), NEt_3 (30 mL), and THF (50 mL) at room temperature to give **36** as a white solid (3.41 g, 78%): R_f = 0.22 (hexanes); mp 236−238 °C; IR (KBr) 2162, 1509 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, 2H, J = 1.7 Hz), 7.72 (d, 2H, J = 8.5 Hz), 7.53 (dd, 2H, J = 8.7 Hz, J = 1.9 Hz), 7.47 (d, 2H, J = 8.5 Hz), 7.26 (d, 2H, J = 8.8 Hz), 0.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9, 137.1, 134.1, 129.9, 126.9, 124.5, 123.7, 123.3, 113.8, 111.8, 104.3, 96.5, 0.37; HRMS calcd for $C_{23}H_{19}Br_2NSi$: 494.9654, found 494.9663.

3-(4-Nitrophenylethynyl)-6-bromo-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazole (37). According to the general coupling procedure, **36** (1.385 g, 2.46 mmol) and 4-nitrophenylethyne (0.726 g, 4.93 mmol) were coupled in the presence of $Pd(dba)_2$ (0.080 g, 0.14 mmol), CuI (0.027 g, 0.14 mmol), PPh_3 (0.147 g, 0.561 mmol), *i*-Pr_2NEt (20 mL), and THF (50 mL) at 80 °C to give **37** as a yellow solid (0.56 g, 36%): R_f = 0.40 (hexanes/CH_2Cl_2, 2:1); mp 227−228 °C; IR (KBr) 2192, 2155, 1506, 1338 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28−8.22 (m, 4H), 7.73 (d, 2H, J = 8.5 Hz), 7.68 (d, 2H, J = 8.8 Hz), 7.61 (dd, 1H, J = 8.5 Hz, J = 1.5 Hz), 7.53 (dd, 1H, J = 8.7 Hz, J = 1.9 Hz), 7.47 (d, 2H, J = 8.5 Hz), 7.35 (d, 1H, J = 8.5 Hz), 7.26 (d, 1H, J = 8.7 Hz), 0.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 141.3, 140.1, 136.9, 134.1, 132.4, 131.1, 130.9, 129.9, 127.0, 125.0, 125.0, 124.1, 123.7, 123.5, 123.0, 114.4, 114.1, 111.9, 110.6, 104.2, 96.6, 96.4, 87.3, 0.35; HRMS calcd for $C_{31}H_{23}BrN_2O_2Si$ 564.0698, found 564.0703.

Dimethyl-{4-[6-(4-nitrophenylethynyl)-9-(4-trimethylsilanylethynylphenyl)-9*H*-carbazol-3-ylethynyl]phenyl}-amine (38). According to the general coupling procedure, **37** (0.613 g, 1.09 mmol) and **27** (0.48 g, 3.3 mmol) were coupled in the presence of $Pd(dba)_2$ (0.044 g, 0.077 mmol), CuI (0.015 g, 0.077 mmol), PPh_3 (0.081 g, 0.31 mmol), *i*-Pr_2NEt (10 mL), and THF (30 mL) to give **38** as a red solid (0.451 g, 65%): R_f = 0.28 (hexanes/CH_2Cl_2, 3:2); mp > 143 °C (decomp.); IR (KBr) 2202, 2154, 1514, 1338 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (m, 2H), 8.21 (d, 2H, J = 8.9 Hz), 7.72 (d, 2H, J = 8.5 Hz), 7.68 (d, 2H, J = 8.9 Hz), 7.59 (m, 2H), 7.48 (m, 4H), 7.33 (d, 1H, J = 8.5 Hz), 7.31 (d, 1H, J = 8.5 Hz), 6.70 (d, 2H, J = 8.9 Hz), 3.01 (s, 6H), 0.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.4, 147.0, 141.3, 140.5, 137.1, 134.0, 133.1, 132.4, 131.2, 130.6, 130.5, 127.0, 125.0, 124.1, 124.0, 123.7, 123.3, 123.2, 117.1, 114.3, 112.3, 110.7, 110.5, 110.4, 104.4, 96.7, 96.4, 90.0, 88.3, 87.3, 40.6, 0.40; HRMS calcd for $C_{41}H_{33}N_3O_2Si$ 627.2342, found 627.2338.

{4-[9-(4-Ethynylphenyl)-6-(4-nitrophenylethynyl)-9*H*-carbazol-3-ylethynyl]phenyl}dimethylamine (39). According to the general deprotection procedure, **38** (0.235 g, 0.374 mmol) in the presence of K_2CO_3 (0.026 g, 0.19 mmol), MeOH (30 mL), and THF (30 mL) for 3 h gave **39** as a red solid (0.126 g, 61%): R_f = 0.22 (hexanes/CH_2Cl_2, 3:2); IR (KBr) 3283, 2922, 2203, 1512, 1338 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.29 (m, 2H), 8.22 (d, 2H, J = 8.7 Hz), 7.76 (d, 2H, J = 8.3 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.60 (m, 2H), 7.52 (d, 2H, J = 8.3 Hz), 7.49 (d, 2H, J = 8.7 Hz), 7.35 (m, 2H), 6.71 (d, 2H, J = 8.7 Hz), 3.24 (s, 1H), 3.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.4, 147.0, 141.3, 140.5, 137.5, 134.3, 133.1, 132.4, 131.2, 130.6, 130.5, 127.1, 125.0, 124.1, 124.0, 123.8, 123.4, 122.2, 117.2, 114.3, 112.3, 110.7, 110.5, 110.4, 96.6, 90.0, 88.3, 87.3, 83.1, 79.1, 40.6; HRMS calcd for $C_{38}H_{25}N_3O_2$ 555.1947, found 555.1946.

Caltrop 3. According to the general coupling procedure, **39** (0.126 g, 0.227 mmol) was coupled with **12** (0.105 g, 0.102 mmol) in the presence of $Pd(dba)_2$ (2.9 mg, 0.0050 mmol), CuI (1 mg, 0.005 mmol), PPh_3 (5 mg, 0.02 mmol), NEt_3 (10 mL), and THF (10 mL) to give **3** as a red solid (0.101 g, 68%): R_f = 0.33 (hexanes/EtOAc, 2:1); mp 143−146 °C; IR (KBr) 2201, 1688, 1515, 1338 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.33 (m, 2H), 8.24 (d, 2H, J = 8.7 Hz), 7.82 (d, 2H, J = 8.3 Hz), 7.71 (d, 2H, J = 8.7 Hz), 7.65−7.30 (m, 36H), 6.71 (d, 2H, J = 8.8 Hz), 4.15 (s, 6H), 3.02 (s, 6H), 2.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.3, 150.4, 147.1, 141.4, 140.6, 138.5, 137.1, 136.7, 136.6, 134.7, 134.5, 134.0, 133.8, 133.1, 132.4, 132.4, 131.6, 131.5, 131.2, 131.0, 130.6, 130.5, 129.4, 129.1, 127.2, 125.3, 125.0, 125.0, 124.1, 123.8, 123.4, 123.2, 117.2, 114.3, 112.3, 110.7, 110.6, 110.5, 96.7, 91.0, 91.0, 90.2, 90.0, 89.8, 88.3, 88.2, 87.3, 40.6, 33.5, 30.8; MALDI-TOF MS *m/z* (matrix: sinapinic acid) found 1455 (M + H$^+$), calcd for $C_{95}H_{67}N_3O_5S_3Si$ 1454.

(3-Bromo-5-nitrophenyl)dimethylamine (42).[39] To an orange solution of **41**[39] (1.423 g, 6.557 mmol) in CH_3CN (100 mL) was added formaldehyde (37% w/w aqueous, 1.6 mL), followed by $NaBH_3CN$ (1.26 g, 20.0 mmol) and AcOH (6.6 mL). The reaction mixture was stirred at room-temperature overnight. Then, a second portion of reagents, formaldehyde (37% w/w aqueous, 1.6 mL), $NaBH_3CN$ (1.26 g, 20.0 mmol), and AcOH (6.6 mL) were added. Monitoring the reaction by TLC showed the starting material (**41**) to be totally consumed after stirring at room temperature for 24 h. The reaction mixture was poured into H_2O and extracted with EtOAc. The organic layer was washed with H_2O (two times), aqueous Na_2CO_3 (two times), and brine (two times) and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash column chromatography to afford **42** as a red solid (1.315 g, 82%): R_f = 0.46 (hexanes/EtOAc, 8:1); mp 100−101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (pseudo-t, 1H, J = 1.8 Hz); 7.42 (pseudo-t, 1H, J = 2.2 Hz), 7.05 (pseudo-t, 1H, J = 2.2 Hz), 3.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.6, 150.0, 123.6, 120.1, 113.7, 105.5, 40.7.

Dimethyl-(3-nitro-5-trimethylsilanylethynylphenyl)-amine (43). According to the general coupling procedure, **42** (0.286 g, 1.18 mmol) was coupled with TMSA (0.34 mL, 2.4 mmol) in the presence of $Pd(PPh_3)_2Cl_2$ (33 mg, 0.047 mmol), CuI (8.9 mg, 0.047 mmol), i-Pr_2NEt (5 mL), and THF (10 mL) at 50 °C overnight to give **43** as yellow crystals (0.276 g, 89%): R_f = 0.41 (hexanes/CH_2Cl_2, 3:1); mp 102.5−103.5 °C; IR (KBr) 2156, 1529, 1343 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (pseudo-t, 1H, J = 1.8 Hz), 7.40 (pseudo-t, 1H, J = 2.2 Hz), 6.98 (dd, 1H, J = 2.5 Hz, 1.0 Hz), 3.03 (s, 6H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 149.5, 125.0, 120.5, 114.4, 106.6, 104.0, 95.8, 40.7, 0.24; HRMS calcd for $C_{13}H_{18}N_2O_2Si$ 262.1137, found 262.1134.

(3-Ethynyl-5-nitrophenyl)dimethylamine (44). According to the general deprotection procedure, **43** (0.276 g, 1.05 mmol) was treated with K_2CO_3 (0.073 g, 0.52 mmol), MeOH (30 mL), and THF (30 mL) to give **44** as an orange solid (0.196

g, 98%): $R_f = 0.30$ (hexanes/CH_2Cl_2, 3:1); mp 180.5−181.5 °C; IR (KBr) 3287, 1539, 1349 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.57 (pseudo-t, 1H, $J = 1.8$ Hz), 7.41 (pseudo-t, 1H, $J = 2.3$ Hz), 6.99 (dd, 1H, $J = 2.5$ Hz, 1.0 Hz), 3.12 (s, 1H), 3.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 149.5, 124.0, 120.7, 114.2, 106.8, 82.8, 78.5, 40.6; HRMS calcd for $C_{10}H_{10}N_2O_2$: 190.0742. Found: 190.0740.

{**3,5-Bis[3-(*N*,*N*-dimethyl)amino-5-nitrophenylethynyl]-phenylethynyl**}**trimethylsilane (45).** According to the general coupling procedure, **40**[36] (0.199 g, 0.599 mmol) was coupled with **44** (0.251 g, 1.32 mmol) in the presence of $Pd(dba)_2$ (27 mg, 0.048 mmol), CuI (9.1 mg, 0.048 mmol), PPh_3 (0.050 g, 0.19 mmol), NEt_3 (10 mL), and THF (15 mL) to give **45** (0.25 g, 76%) as a yellow solid: $R_f = 0.41$ (hexanes/EtOAc, 3:1); mp 253−254 °C; IR (KBr) 2162, 1533, 1342 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68 (m, 3H), 7.65 (d, 2H, $J = 1.6$ Hz), 7.50 (t, 2H, $J = 2.3$ Hz), 7.07 (dd, 2H, $J = 2.5$ Hz, 1.2 Hz), 3.09 (s, 12H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 149.7, 135.3, 134.8, 124.7, 124.6, 123.8, 120.2, 114.1, 106.8, 103.3, 96.7, 89.8, 88.7, 40.8, 0.24; HRMS calcd for $C_{31}H_{30}N_4O_4Si$ 550.2043, found 550.2037.

1-Ethynyl-3,5-bis-[3-(*N*,*N*-dimethyl)amino-5-nitrophenylethynyl]-benzene (46). According to the general deprotection procedure, **45** (0.064 g, 0.17 mmol) with K_2CO_3 (0.008 g, 0.06 mmol), MeOH (20 mL), and THF (20 mL) gave **46** (0.045 g, 82%) as a yellow solid: $R_f = 0.34$ (hexanes/EtOAc, 3:1); mp > 248 °C dec; IR (KBr) 3247, 1530, 1341 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.72 (t, 1H, $J = 1.5$ Hz), 7.67 (m, 4H), 7.50 (t, 2H, $J = 2.3$ Hz), 7.08 (dd, 2H, $J = 2.5$ Hz, 1.1 Hz), 3.17 (s, 1H), 3.08 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9, 149.7, 135.4, 135.2, 124.6, 123.9, 123.6, 120.2, 114.1, 106.9, 90.0, 88.5, 82.1, 79.2, 40.8; HRMS calcd for $C_{28}H_{22}N_4O_4$ 478.1641, found 478.1642.

Caltrop 4. According to the general coupling procedure, **46** (0.075 g, 0.157 mmol) was coupled with **12** (0.093 g, 0.091 mmol) in the presence of $Pd(dba)_2$ (2.6 mg, 0.0045 mmol), CuI (0.8 mg, 0.005 mmol), PPh_3 (0.0047 g, 0.018 mmol), NEt_3 (5 mL), and THF (5 mL) to give caltrop **4** as a yellow solid (0.084 g, 68%): $R_f = 0.23$ (hexanes/EtOAc, 2:1); mp > 108 °C dec; IR (KBr) 1691, 1533, 1343 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, 2H, $J = 1.4$ Hz), 7.70 (m, 3H), 7.60−7.56 (m, 16H), 7.50 (m, 5H), 7.45 (dt, 3H, $J = 6.3$ Hz, 2.2 Hz), 7.32 (m, 6H), 7.09 (q, 2H), 4.14 (s, 6H), 3.08 (s, 12H), 2.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz, missing one aromatic C due to overlap) δ 195.5, 150.8, 149.7, 138.4, 136.7, 136.6, 135.0, 134.8, 134.7, 133.9, 132.4, 131.6, 131.5, 131.0, 129.4, 129.1, 125.3, 124.7, 124.5, 123.9, 123.8, 120.3, 114.2, 106.9, 91.2, 90.9, 89.9, 89.8, 89.3, 88.8, 40.8, 33.5, 30.8; MS *m*/*z* (CI) found 1377.6 ($M + H^+$), calcd for $C_{85}H_{64}N_4O_7S_3Si$ 1377.4.

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Supporting Information Available: Copies of ^1H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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