Synthesis and testing of new end-functionalized oligomers for molecular electronics

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Abstract—Several new classes of oligomers have been synthesized with functionalities designed to aid in the understanding of molecular device behavior, specifically when molecules are interfaced between proximal electronic probes. The compounds synthesized are series of azobenzenes, bipyridines and oligo(phenylene vinylene)s that bear acetyl-protected thiols for ultimate attachment to metallic surfaces. Some initial electrochemical and solid-state test results are also reported.

1. Introduction

Due to physical and economic constraints, silicon based semiconductor technology is rapidly nearing a production brick wall.1 As the miniaturization of solid-state silicon circuitry continues in order to increase speed, capacity and computing power, a point will be reached at which processors can no longer be made smaller, faster and cheaper. It has been proposed that by incorporating organic molecules into functioning molecular circuits, one may overcome many of the challenges that complimentary metal-oxide semiconductor (CMOS) technology is facing.2 Work performed in the molecular electronics field has demonstrated that single molecules exhibit reversible switching behavior, which may lead researchers to molecular memory and logic devices.3–5 Our research has centered around oligo(phenylene ethynylene)s (OPEs) which, with the redox active nitro group, have demonstrated negative differential resistance (NDR) at variable temperatures.2 Several new classes of potential molecular electronics molecules have been synthesized in our laboratory in order to develop further understanding of the switching process.6–9 In this paper, we will discuss our synthetic work on azobenzene derivatives, pyridine systems, and oligo(phenylene vinylene)s (OPVs) that have been synthesized as possible device candidates and that all bear protected thiol end groups for self-assembled attachment to metallic probes. Due to the additional redox center of azobenzenes, the electron deficient nature of pyridyl oligomers, and the high electrical transport seen in OPVs,10 these molecules are good candidates to study device behavior.

In addition to these syntheses, we performed electrochemical testing of selected compounds, a method found to be useful for qualitative comparisons of molecular electronic devices.11 We also include some results obtained from planar test devices using the bipyridyl compounds which show a resetable on-off state and NDR behavior.

2. Azobenzenes

It has been shown that OPEs containing a redox aromatic nitro functionality exhibit NDR at various temperatures.3 The proposed mechanism is that the redox center contributes to the switching behavior of the mononitro OPE.12 However, other theories have recently been put forth for NDR behavior including molecule/metal-based contact variations that could result in NDR-like performance.13,14 By incorporating an azo functionality into an OPE, an additional redox center is created where switching behavior is likely to be observed.

In addition to the redox active site, azobenzenes are known to change between the \( E \) and \( Z \) configurations when irradiated with light, giving rise to other probable switching mechanisms,15 although we are not exploiting that manifold here.

The azobenzene derivatives synthesized are shown in
As shown in Scheme 2, coupling 5 with 4-ethyl-1-thioacetylbenzene\textsuperscript{17} afforded the expected dicycled product 2. Since our experiments have shown that compounds without thoacetyl (‘alligator clips’ for adhesion to metallic surfaces after acetyl removal) produced cleaner electrochemical results that are still quantitatively similar to the sulfur-bearing systems,\textsuperscript{11} we made 6 by coupling phenyl-acetylene to 5 under the same conditions as those used to make 2. It is important to note that in both of these coupling reactions, none of the hydrazo product was obtained.

Figure 2 shows the cyclic voltamgram (CV) of 6. It is evident from the data that the azo linkage contains an additional redox center compared to the unfunctionalized OPE (vide infra). From Figure 2, there are two clear reduction peaks at \(-1.3\) and \(-2.1\) V as well as smaller features at \(-1.4\) and \(-1.8\) V. The reductions are reasonably reversible. However, because oxygen and water were not rigorously excluded, this data was used, as we have done in our prior work, only for comparison between molecules and to make relative assessments regarding solid-state behavior.

Figure 3 shows the CV of the dinitro azo compound 3 with multiple reduction peaks at \(-1.3\), \(-2.0\) and \(-2.3\) V and a small peak at \(-1.8\) V. We are currently awaiting solid-state testing of these compounds in order to assess their applicability for molecular electronics.

### 3. Pyridyl devices

By replacing the phenyl\textsuperscript{18} or biphenyl\textsuperscript{19} core of the OPE

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**Figure 1.** Azobenzene derivatized compounds 1–3 and hydrazo compound 4.

**Figure 1 as compounds 1–3** as well as the hydrazo compound 4.

Compound 1 was synthesized from \(p\)-iodoaniline as shown in Scheme 1. Oxidizing \(p\)-iodoaniline using potassium permanganate and copper(II) sulfate afforded 5 in a lower than expected yield.\textsuperscript{16} Attempts to replace the diiodide using tert-butyllithium at \(-78^\circ\text{C}\), followed by adding sulfur and quenching with acetyl chloride were met with no success. However, using \(n\)-butyllithium, 1 was afforded, albeit in low yield.

**Scheme 1.** Synthesis of substituted azobenzene 1.

**Scheme 2.** Synthesis of compounds 2 and 6.

Compounds 3 and 4 were synthesized from 2-nitro-4-iodoaniline as shown in Scheme 3. 2-Nitro-4-iodoaniline was oxidatively coupled using mercury(II) oxide and iodine\textsuperscript{18} to afford the azo derivative 7, exclusively as the \(E\) isomer, in low yield. This poor yield is presumably due to the low reactivity of the electron deficient aniline and the sterically hindered azo product. 7 was then subjected to palladium-catalyzed coupling with 4-ethyl-1-thioacetylbenzene to yield both the azo compound 3, and the hydrazo product 4.

**Figure 3.** CV of the dinitro azo compound 3 with multiple reduction peaks at \(-1.3\), \(-2.0\) and \(-2.3\) V and a small peak at \(-1.8\) V. We are currently awaiting solid-state testing of these compounds in order to assess their applicability for molecular electronics.
molecule with one or two pyridine moieties, we surmise that the LUMO will be lowered, producing a better match with the Fermi level of the metal contact and higher current through the device.\(^\text{12,19}\) In addition, due to the absence of the 2- and 2'-steric interactions, less inter-ring twisting in the bipyridyl system would be present. Molecular modeling (AM1 theory) indicates a reduction of the dihedral angle from 45.5\(^\circ\) for the 2-2'-dinitro-biphenyl system to 35.1\(^\circ\) for the 2-2'-dinitro-bipyridyl system. This will ultimately increase the overlap of the extended \(\pi\)-orbitals, lowering the resistance through the molecule. The pyridyl based systems synthesized are shown in Figure 4.

Scheme 4 shows the synthesis of the target compound \(8\) with two thioacetates. The dinitro-bipyridyl compound \(11\) was obtained by an Ullmann\(^\text{20}\) coupling of commercially available 2-chloro-3-nitropyridine.\(^\text{21}\) \(11\) was brominated under harsh conditions, presumably necessary due to the electron deficient nature of the system,\(^\text{22}\) to afford \(12\). \(12\) was coupled with trimethylsilylacetylene in fair yield to afford the dicoupled product \(13\). Deprotection of the terminal alkynes was accomplished using potassium carbonate and the resulting bis-alkyne was then coupled with 4-((thioacetyl)iodobenzene\(^\text{23}\) to afford the target \(8\). Also shown in Scheme 4 is the synthesis of the unfunctionalized compound \(14\) (for CV) accomplished by coupling intermediate \(12\) with phenylacetylene.

Scheme 5 shows the synthesis of the dinitro-bipyridyl compound \(9\) with one thioacetate. Intermediate \(12\) was first coupled to trimethylsilylacetylene to afford \(15\) and then coupled to phenylacetylene to yield \(16\). \(16\) was then deprotected with potassium carbonate and coupled to 4-((thioacetyl)iodobenzene\(^\text{23}\) to afford the target \(9\). The solid-state test results of compounds \(8\) and \(9\) are discussed later in this paper.

Scheme 6 shows the synthesis of the 3'-nitro-pyridine molecule \(10\). 2-Amino-5-bromopyridine was nitrated to give the mononitro compound \(17\).\(^\text{24}\) \(17\) was converted to the dibromo compound \(18\),\(^\text{25}\) coupled with phenylacetylene, trimethylsilylacetylene, deprotected and finally coupled with 4-((thioacetyl)iodobenzene to afford \(10\).

4. Oligo(phenylene vinylene)

In an attempt to design more efficient molecular devices...
(lower impedance, larger ON:OFF ratios and longer electronic hold times), several features need to be optimized. In order to achieve the highest efficiency in terms of energy used, transport needs to be maximized across a molecular device. To date, most of our research has focused on OPE-based devices.\textsuperscript{1,2} Recent work by Chidsey et al.\textsuperscript{10} has shown that electrical transport is higher through OPVs than through OPEs. Similar results, both theoretically and experimentally, have been obtained by Shashidhar et al.\textsuperscript{26} To study OPVs in a molecular electronic device, three new OPVs were synthesized as shown in Figure 5.

Initially 4-vinylphenyl thioacetate (25) was chosen as the group to carry the alligator clip. 25 was previously
The synthesis of 25 began by refluxing vinyl magnesium bromide with tributyltin chloride to produce the vinyl stannane 24. A subsequent Stille coupling produced 25.

The attempted synthesis of 21 began with a Heck coupling of 4-iodo-2-nitroaniline with styrene to produce 2-nitro-4-styrylaniline. Diazotization of 26 produced 27 in high yield, which was then halogenated with I₂ and NaI to afford 28. Disappointingly, the Heck coupling of 28 with 25 yielded no desired product and instead formed 29.

In an effort to avoid the sulfur deprotection and thioether formation, 24 was coupled to 28 to form 30 in excellent yield as shown in Scheme 9. However, 30 was not reactive under the Heck conditions to form the desired 21.

In order to overcome the problems with the acetyl-protecting group, the ethyltrimethylsilyl group was used to protect the sulfur. Coupling of 2-(trimethylsilyl)ethyl-4'-bromophenyl sulfide directly with 24 did not afford the desired compound, and in fact only resulted in recovery of starting material. This may be due to the fact that the aryl bromide is electron rich and slow to couple with the stannane under Stille conditions. With this in mind, the aryl bromide was converted to an aryl iodide by lithiating and quenching with diiodoethane to form 31. Coupling 31...


Figure 5. OPV based potential devices.
with 24 resulted in the formation of the desired alligator clip 32 in high yield as shown in Scheme 10.

Compound 33 was synthesized by coupling 28 with 32 under Heck conditions as shown in Scheme 11.

In order to examine the effects of a nitro group in the OPV system, an unfunctionalized wire was synthesized. The synthesis of 22 began by coupling 4-bromiodobenzene with styrene to produce 34 as shown in Scheme 12.
Compound 34 was then coupled with 32 to afford 35 in high yield.

The mononitro OPV containing two alligator clips, 23, was synthesized by dicoupling 2,5-dibromonitrobenzene with 32 under Heck conditions to afford the desired compound 36 as shown in Scheme 13.

With the completed ethyltrimethylsilyl-protected compounds in hand, initial assembly experiments using in situ deprotection failed to form adequate self-assembled monolayers (SAMs). It was determined that the acetyl precursor was preferred for the in situ deprotection and assembly. Replacement of the ethyltrimethylsilyl group with the acetyl group was accomplished using 10 equiv. of TBAF for deprotection followed by the addition of 20 equiv. of acetyl chloride, thereby affording the desired acetyl protected compounds 21, 22, and 23 as shown in Scheme 14.

The CVs of compounds 21 and 22 were compared to the CVs of the corresponding OPEs which have been shown to have NDR behavior if mononitro-substituted.11 As shown in Figure 6, both the unfunctionalized OPVs and the OPEs (Fig. 6(a) and (c), respectively) have first reduction potentials at −1.2 V and another small reduction feature at −2.3 V. However, nitro-containing OPVs and OPEs (Fig. 6(b) and (d), respectively), as observed for compound 3, show multiple reduction events due to the nitro group being able to undergo further electron reduction and corresponding oxidations.11 We note the first reduction potentials of the unsubstituted and mononitro OPVs and OPEs are not significantly different, suggesting the LUMO of the mononitro compound was not lowered. However, previous calculations have shown the LUMO differences to be quite significant in non-electrolytic media, resulting in proposals for the observed switching behavior in solid-state systems.12

The CV differences between the OPVs (Fig. 6(a) and (b)) and their corresponding OPEs (Fig. 6(c) and (d)) are subtle enough that one would expect similar behaviors in device embodiments. This subtle difference was unexpected based on reports.10,26,32–36 Therefore, we await solid-state testing in order to definitively evaluate the differences between the OPVs and their corresponding OPEs.37

5. Planar testbed results

Compounds 8 and 9 have been tested for device behavior using the planar device testbed wherein a SAM of the compound is made on a lithographically patterned Au substrate followed by Au evaporation atop the SAM structure.3,4,11 The device size can range from 1 to 5 μm². As shown in Figure 7, compound 8 exhibited reproducible NDR in both sweep directions at room temperature. Previously, NDR had been reported only in the positive direction (in the negative sweep direction, the NDR was far...
less pronounced) for the mononitro OPE device and sharp voltage peaks were only seen at low temperatures. A device built from compound 9 also exhibited reproducible NDR in the testbed as well as a resetable state as shown in Figure 8. The first voltage sweep reveals NDR in the positive direction at a peak voltage of 1.5 V and a peak current of ~50 pA. However, the NDR peak weakens noticeably upon subsequent voltage sweeps in the range of 0–2.5 V. After an applied negative voltage pulse, the NDR returns to the original peak current and device behavior is returned to the system. The ‘resetability’ of the dinitro-bipyridyl system is similar to the device behavior observed with the mononitro OPE, where after an applied negative voltage pulse, NDR returns to the system.

6. Summary

Several new classes of oligomers have been synthesized bearing functionalities to interface between proximal electronic probes for molecular electronics studies. The

![Figure 6. Cyclic voltametry results for OPVs 21 (a) and 22 (b) and their corresponding OPEs (c) and (d), respectively.](image)

![Figure 7. Positive and negative NDR in the dinitro-bipyridyl device built from 8. T=300 K.](image)

![Figure 8. A resetable state is observed for a device built from 9. After the first sweep, the current is reduced dramatically as seen in voltage sweeps 2–8. Following the 8th sweep, a negative voltage pulse of ~2.5 V (not shown) is given to restore NDR to the device, as seen in the 9th voltage sweep. T=300 K.](image)
compounds synthesized were series of azobenzenes, bipyridines and oligo(phenylene vinylene)s. Some initial electrochemical results point to electrical similarities between these oligomers and previously prepared OPEs. Initial solid-state test results are also reported for the new class of bipyridines which show encouraging resetable NDR behavior at room temperature.

7. Experimental

7.1. General

All reactions were performed under an atmosphere of N₂ unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexanes were distilled. Triethylamine (TEA), diisopropylethylamine (DIEA) and CH₂Cl₂ were distilled from CaH₂ under N₂. Silica gel plates were 250 µm thick, 40 F254 grade obtained from EM Science. Silica gel was grade 60 (230–400 mesh) from EM Science. Mass spectrometry was performed at Rice University’s Mass Spectrometry lab. All new compounds were named using the Beilstein Autonom feature.

7.2. General procedure for electrochemical testing of compounds

The CVs were performed on a BAS CV-50W using a glassy carbon electrode as the working electrode, platinum wire as the auxiliary electrode, and a Ag/AgNO₃ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1 M in n-Bu₄NBF₄. The scan rate was 0.1 V/s at 25°C. Oxygen and water were not rigorously excluded from the vessels.

7.3. General procedure for coupling a terminal alkyne with an aryl halide (Castro–Stephens/Sonogashira protocol)³⁸

To an oven dried screw cap tube with a magnetic stir bar were added the aryl halide, bis(triphenylphosphine)palladium(II) dichloride (5 mol% based on aryl halide), and copper(I) iodide (10 mol% based on aryl halide). The vessel was then sealed with a rubber septum, evacuated and backfilled with N₂ (3X). A cosolvent of THF was added followed by the amine. The terminal alkyne was then added and the reaction was heated, if necessary, until the aryl halide was consumed as judged by TLC. The reaction vessel was cooled to room temperature and quenched with water. The organic layer was diluted with CH₂Cl₂ and washed with brine (3X). The solvent was removed in vacuo. The crude product was then purified by flash chromatography (silica gel).

7.4. General Stille coupling reaction procedure³⁹

To an oven dried screw cap tube or round-bottom flask, all solids including the aryl halide (bromide or iodide), and palladium catalyst were added. The atmosphere was removed via vacuum and replaced with dry N₂ (3X). THF and tin compounds were added and the reaction was heated in an oil bath while stirring. Upon cooling, all solvents were removed in vacuo.

7.5. General Heck coupling procedure³⁰

To an oven dried glass screw cap tube or round-bottom flask all solids including the aryl halide (bromide or iodide), alkene, base (if solid), and palladium(II) acetate catalyst were added. The atmosphere was removed via vacuum and replaced with dry N₂ (3X). Solvent and remaining liquids were added and the reaction was heated in an oil bath while stirring. Upon cooling, the reaction was quenched with the addition of water. The reaction mixture was extracted with a suitable organic solvent (3X). The organic layer was dried with MgSO₄ and filtered. The solvent was then removed in vacuo.

7.6. General procedure for the deprotection of trimethylsilyl protected alkynes³⁹

To a round-bottom flask equipped with a stir bar were added the protected alkyne, K₂CO₃ (5 equiv. per protected alkyne), methanol, and CH₂Cl₂. The reaction was stirred, and upon completion, the reaction mixture was diluted with CH₂Cl₂ and washed with brine (3X). The organic layer was dried over MgSO₄ and the solvent removed in vacuo.

7.7. General procedure for the diazotization of anilines with nitrosonium tetrafluoroborate in the acetonitrile–sulfolane system³⁰

NOBF₄ was weighed out in a N₂-filled dry box and placed in a round-bottom flask equipped with a magnetic stirring bar and sealed with a septum. Acetonitrile and sulfolane were injected in a 5 to 1 volume ratio and the resulting suspension was cooled in a dry ice/acetonate bath to −40°C. The solution of the aniline was prepared by adding warm sulfolane (45–50°C) to the amine under a N₂ blanket, sonication for 1 min and subsequent addition of acetonitrile (10–20% by volume). The aniline solution was then added to the nitrosonium salt suspension over a period of 10 min. The reaction mixture was kept at −40°C for 30 min and was then allowed to warm to the room temperature. At this point, the diazonium salt was precipitated by the addition of ether or CH₂Cl₂, collected by filtration, washed with ether or CH₂Cl₂ and dried. Additional purification of the salt was accomplished by re-precipitation from DMSO by CH₂Cl₂ and/or ether addition.

7.7.1. Thioacetic acid S-[4-(4-acetylsulfanyl-phenylazo)-phenyl] ester (1)

To a 100 mL round-bottom flask was added bis-(4-iodo-phenyl)-diazene (5)⁶ (0.50 g, 1.15 mmol). THF (50 mL) was added and the solution cooled to −78°C. n-Butyllithium (1.04 mL of a 2.21 M solution in hexanes) was added dropwise. The mixture was kept at −78°C and stirred for 45 min. With a strong backfill of N₂, the septum was removed, sulfur powder (0.078 g, 2.419 mmol) was quickly added, and the septum replaced. The reaction mixture was warmed to 0°C and stirred for 10 min. The mixture was recooled to −78°C and acetyl chloride (0.20 mL, 2.76 mmol) was added. The solution was allowed to warm to room temperature overnight and the next day it was poured into H₂O (100 mL) and extracted
with CH₂Cl₂ (3X). The organic extracts were combined, washed with brine, dried over anhydrous MgSO₄, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the product (0.025 g, 7%). Mp: 162–164°C. IR (KBr) 3018.9, 1698.9, 1215.3, 1115.9, 756.7, 667.4 cm⁻¹. ¹H NMR (400 MHz, CDC1₃) δ 7.93 (d, J = 8.8 Hz, 4H), 7.59 (d, J = 8.8 Hz, 4H), 2.48 (s, 6H). ¹³C NMR (100 MHz, CDC1₃) δ 193.8, 152.4, 134.7, 133.0, 132.7, 128.9, 125.8, 124.6, 30.8. HRMS calcd for C₁₈H₁₄N₂O₅S₂: 330.0496. Found: 330.0495.

7.7.2. Thioacetic acid S-[4-(4-[4-(4-acetylsulfanyl-phenyl ethynyl)-phenylazo]-phenylethylnyl)-phenyl] -phenyl) ester (2). Bis-(4-iodo-phenyl)-diazene (7) (0.69 g, 1.59 mmol) was coupled to 4-ethynyl-1-thioacetylbenzene (0.63 g, 3.57 mmol) following the general coupling procedure at 50–60°C for 20 min. The mixture was poured into ether and washed with a saturated aqueous ammonium chloride solution. The organic layer was dried using anhydrous MgSO₄ and concentrated in vacuo. The remaining solid was dissolved in hot CH₂Cl₂ and filtered. The filtrate was washed with brine, dried over anhydrous MgSO₄, and concentrated in vacuo. The remaining solid was recrystallized from CH₂Cl₂ followed by the addition of hexanes (100 mL). Care was taken to remove only mainly the more volatile CH₂Cl₂ and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the desired product as an orange solid (0.105 g, 15%). Mp: decomposes at 246°C. IR (KBr) 3018.9, 1698.9, 1215.3, 1115.9, 756.7, 667.0 cm⁻¹. ¹H NMR (400 MHz, CDC1₃) δ 7.35 (d, J = 9 Hz, 4H), 7.69 (d, J = 9 Hz, 4H), 7.6 (d, J = 9 Hz, 4H), 2.45 (s, 6H). ¹³C NMR (100 MHz, CDC1₃) δ 193.8, 152.4, 134.7, 133.0, 128.9, 125.8, 124.6, 123.5, 91.7, 91.4, 30.7. HRMS calcd for C₃₂H₂₃N₂O₅S₂: 623.1059. Found: 623.1054.

7.7.3. Thioacetic acid S-[4-(4-[4-(4-acetylsulfanyl-phenyl ethynyl)-phenylazo]-3-nitro-phenylethynyl]-phenyl] -phenyl) ester (3). Bis-(4-iodo-2-nitro-phenylazo)-[4-(4-acetylsulfanyl-phenyl) ester (8). The filtrate and MeOH washings from 3 were combined and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CH₂Cl₂ followed by the addition of hexanes (100 mL). Care was taken to remove only mainly the more volatile CH₂Cl₂ in vacuo. The solid was vacuum filtered and washed with hexanes. The solid was purified by flash chromatography, silica gel (CH₂Cl₂) to afford 4 as an orange solid (0.105 g, 59%). Mp: 226–232°C. IR (KBr) 3370.9, 3018.9, 2399.7, 1715.0, 1528.9, 1426.4, 1215.5, 929.0, 769.9, 667.8 cm⁻¹. ¹H NMR (400 MHz, CDC1₃) δ 9.34 (s, 2H), 8.45 (d, J = 2.4 Hz, 2H), 7.64 (dd, J = 9.0 Hz, 2H), 7.54 (d, J = 9.4 Hz, 4H), 7.42 (d, J = 9.4 Hz, 4H), 7.19 (d, J = 9.4 Hz, 2H), 2.45 (s, 6H). ¹³C NMR (100 MHz, CDC1₃) δ 193.8, 144.8, 139.7, 134.7, 133.0, 132.5, 130.3, 128.9, 124.2, 114.8, 114.7, 89.5, 88.9, 30.7. HRMS calcd for C₃₂H₂₄N₂O₅S₂: 623.1059. Found: 623.1054.

7.7.5. Bis-(4-iodo-phenyl)-diazene (5).¹⁶ Potassium permanganate (7.50 g, 86.3 mmol) and copper(II) sulfate pentahydrate (7.50 g, 30.0 mmol) were ground until homogenous and added to a 500 mL round-bottom flask containing 4-iodoaniline (4.38 g, 20.0 mmol) and a magnetic stir bar. CHCl₃ (200 mL) was added and the suspension was allowed to stir for 4 days. Upon completion, the reaction was filtered through a silica gel plug, washed with CHCl₃, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH₂Cl₂) afforded the desired product as an orange solid (1.25 g, 15%). ¹H NMR (400 MHz, CDC1₃) δ 7.86 (d, J = 9 Hz, 4H), 7.64 (d, J = 9 Hz, 4H).

7.7.6. Bis-(4-phenylethynyl-phenyl)-diazene (6). Bis-(4-iodo-phenyl)-diazene (5) (0.25 g, 0.58 mmol) was coupled to phenylacetylene (0.15 mL, 1.38 mmol) according to the general procedure. Flash chromatography, silica gel (5:1 hexanes/CH₂Cl₂) afforded the product (0.088 g, 40%). Mp: decomposes at 246°C. IR (KBr) 3019.1, 2399.9, 1215.3, 769.3, 668.8 cm⁻¹. ¹H NMR (400 MHz, CDC1₃) δ 7.94 (d, J = 6.4 Hz, 4H), 7.69 (d, J = 6.4 Hz, 4H), 7.58 (m, 4H), 7.39 (m, 6H). ¹³C NMR (100 MHz, CDC1₃) δ 152.2, 132.9, 132.1, 129.1, 128.9, 126.7, 123.5, 123.3, 92.6, 89.6. HRMS calcd for C₃₈H₃₈N₂O₈S: 530.1470. Found: 530.1469.

7.7.7. Bis-(4-iodo-2-nitro-phenyl)-diazene (7). To a 250 mL round-bottom flask charged with a magnetic stir bar was added 4-iodo-2-nitroaniline (2.00 g, 7.58 mmol), mercury(II) oxide (2.46 g, 11.36 mmol), and iodine (2.88 g, 11.36 mmol). CH₂Cl₂ (80 mL) was added and the reaction mixture was allowed to stir overnight. The next day the suspension was filtered through a silica gel plug and washed with copious amounts of CH₂Cl₂. The filtrate was then washed with a saturated aqueous solution of sodium thiosulfate, dried over anhydrous MgSO₄, and the solvent removed in vacuo. Flash chromatography, silica gel (1:1 petroleum ether/diethyl ether) afforded the product as brown crystals (0.15 g, 4%). Mp: 244°C. IR (KBr) 3076.3, 3019.1, 1517.1, 1336.1, 1215.1, 1090.6, 840.0, 756.3, 666.5 cm⁻¹. ¹H NMR (400 MHz, CDC1₃) δ 8.31 (d, J = 2.0 Hz, 2H), 8.05 (dd, J = 8.1, 2.0 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H). ¹³C NMR (100 MHz, CDC1₃) δ 148.4, 144.8, 143.3, 133.6, 120.3, 97.6. HRMS calcd for C₁₂H₁₂N₂O₃: 523.8478. Found: 523.8492.

7.7.8. Thioacetic acid S-[4-(5-[4-(4-acetylsulfanyl-phenyl ethynyl)-phenyl]-3,3-dinitro-[2,2]bipyridinyl-5-ylthiophenyl]-phenyl] ester (8). Compound 13 (1.6 g, 3.7 mmol), potassium carbonate (4.5 g, 33 mmol), methanol (15 mL) and dichloromethane (15 mL) were used following the general deprotection method. A short silica gel plug (1:1 hexanes/CH₂Cl₂) afforded the desired product as a brown solid (1.06 g, 99% yield). ¹H NMR (200 MHz, CDC1₃) δ 8.88 (d,
J = 1.8 Hz, 2H), 8.58 (d, J = 1.8 Hz, 2H), 3.45 (s, 2H). The deprotected material (1.06 g, 3.65 mmol) was then immediately coupled according to the general procedure using bis(dibenzyldieneacetone)palladium (0.11 g, 0.18 mmol), copper(I) iodide (0.07 g, 0.37 mmol), triphenylphosphine (0.20 g, 0.74 mmol), THF (18 mL), DIEA (2.5 mL, 15 mmol), and 4-(thioacetyl)iodobenzene1 (3.05 g, 10.95 mmol). The tube was placed in a 50°C oil bath for 1 h. Flash chromatography, silica gel (CH2Cl2) gave the desired product as an orange-yellow solid (0.41 g, 55%). Mp: decomposes at 110°C. IR (KBr) 3357.2, 2930.0, 2869.5, 1578.4, 1548.0, 1488.8, 1404.9, 1379.5, 1348.4, 1347.4, 1344.3, 1223.8, 827.9, 756.8, 688.0, 619.8, 526.9 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ 8.90 (d, J = 1.9 Hz, 1H), 8.45 (d, J = 1.9 Hz, 1H), 7.68 (m, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.43 (m, 5H), 2.44 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 193.4, 155.6, 146.6, 136.1, 134.8, 134.7, 133.1, 132.8, 130.7, 130.4, 129.0, 122.9, 121.7, 120.1, 100.2, 96.4, 85.7, 85.6, 30.8. HRMS calcd for C32H26N4O9S2: 594.0664. Found: 594.0666.

7.7.9. Thioacetic acid S-[4-(3,3-dinitro-5'-phenylethnyl-2,2'-bipyrindinyl-5'-yethylthynyl)-phenyl] ester (9). Compound 16 (0.51 g, 1.15 mmol), potassium carbonate (1.59 g, 11.5 mmol), methanol (15 mL), and dichloromethane (15 mL) were used following the general deprotection method to give the desired product as a reddish brown solid (0.41 g, 98%). The deprotected material (0.40 g, 1.09 mmol) was then immediately coupled according to the general procedure given using bis(dibenzyldieneacetone)-palladium (0.03 g, 0.05 mmol), copper(I) iodide (0.02 g, 0.11 mmol), triphenylphosphine (0.06 g, 0.22 mmol), THF (10 mL), DIEA (0.38 mL, 2.18 mmol), and 4-(thioacetyl)iodobenzene1 (0.51 g, 1.82 mmol). The tube was placed in a 50°C oil bath for 3 h. Column chromatography, silica gel (1:1 hexanes/CH2Cl2 then ethyl acetate) and precipitation from CH2Cl2 and hexanes gave the desired product as an orange solid (0.41 g, 55%). Mp: decomposes at 110°C. IR (KBr) 3394.5, 3057.1, 2211.6, 1705.2, 1542.8, 1487.5, 1446.0, 1351.6, 1108.2, 1084.1, 954.2, 829.1, 619.1, 598.1, 544.3, cm⁻¹. 1H NMR (200 MHz, CDCl3) δ 8.93 (d, J = 1.7 Hz, 2H), 8.62 (d, J = 1.8 Hz, 2H), 7.60 (d, J = 7.6 Hz, 4H), 7.45 (d, J = 7.6 Hz, 4H), 2.44 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 193.3, 155.2, 149.4, 144.1, 135.4, 134.8, 132.9, 130.5, 122.8, 122.2, 96.0, 85.2, 30.8. HRMS calcd for C30H18N4O6S2: 594.0668. Found: 594.0664.

7.7.10. Thioacetic acid S-[4-(5-nitro-6-phenylethynyl)-phenyl] ester (10). To a 50 mL round-bottom flask containing a stir bar was added KBr (120 g, 0.62 g, 1.89 mmol) and THF (10 mL). Acetic acid (0.51 g, 1.15 mmol), potassium carbonate (120 g, 0.62 g, 1.89 mmol) was then added and the screwcap affixed. The mixture was heated in a 80°C oil bath for 24 h. Flash chromatography, silica gel (CH2Cl2) followed by precipitation from CH2Cl2 in hexanes gave the desired product as an orange-yellow solid (0.41 g, 98%). Mp: decomposes at 110°C. IR (KBr) 3394.5, 3057.1, 2211.6, 1705.2, 1542.8, 1487.5, 1446.0, 1351.6, 1108.2, 1084.1, 954.2, 829.1, 619.1, 598.1, 544.3, cm⁻¹. 1H NMR (200 MHz, CDCl3) δ 8.93 (d, J = 1.7 Hz, 2H), 8.62 (d, J = 1.8 Hz, 2H), 7.60 (d, J = 7.6 Hz, 4H), 7.45 (d, J = 7.6 Hz, 4H), 2.44 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 193.3, 155.2, 149.4, 144.1, 135.4, 134.8, 132.9, 130.5, 122.8, 122.2, 96.0, 85.2, 30.8. HRMS calcd for C30H18N4O6S2: 594.0668. Found: 594.0664.

7.7.11. 3,3'-Dinitro-[2,2']bipyridinyl (11). To a 250 mL round-bottom flask equipped with a reflux condenser and stir bar was added 2-chloro-3-nitropyridine (12.0 g, 75.8 mmol) in dimethylformamide (50 mL). Copper bronze (12.0 g, 189.0 mmol) was added slowly and the mixture was heated to 145°C for 5.5 h. The reaction was then poured onto ice and filtered. The remaining filtrate was extracted in a Soxhlet extractor with acetonitrile for 4 days. The acetonitrile was then poured into a large amount of dilute ammonium hydroxide solution to precipitate the product, which was then filtered. The solid was dissolved in CH2Cl2 and washed with dilute ammonium hydroxide solution. The organic layers were combined and dried over anhydrous MgSO4 and the solvent removed in vacuo to give a brown-yellow solid (5.8 g, 62%). Mp: 208–210°C. 1H NMR (400 MHz, DMSO) δ 8.93 (dd, J = 3.6, 1.2 Hz, 2H), 8.72 (dd, J = 7.2, 1.1 Hz, 2H), 7.88 (dd, J = 3.6, 4.8 Hz, 2H).
7.7.13. 3,3'-Dinitro-5,5'-bis-trimethylsilanylenyl-[2,2']-dinitro-bipyridinyl (13). Compound 12 (3.51 g, 8.69 mmol) was coupled with TMSA (1.72 mL, 12.17 mmol) following the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.3 g, 0.43 mmol), copper(I) iodide (0.16 g, 0.86 mmol), THF (6 mL), and DIEA (6.05 mL, 34.76 mmol) were combined and the mixture was stirred at room temperature for 3 h. Column chromatography, silica gel (1:1 hexanes/CH_2Cl_2) afforded the product as a dark yellow solid (1.64 g, 43%). Mp: decomposes at 226 °C.

7.7.14. 3,3'-Dinitro-5,5'-bis-phenylethynyl-[2,2']bipyridinyl (14). Compound 12 (0.21 g, 0.52 mmol) was coupled with phenylacetylene (0.23 mL, 2.08 mmol) following the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.02 g, 0.03 mmol), copper(I) iodide (0.01 g, 0.06 mmol), THF (1 mL), and DIEA (0.36 mL, 2.08 mmole) were added and the tube was capped and heated in a 50°C oil bath for 1 h then allowed to stir for 15 h at room temperature. Column chromatography, silica gel (1:1 hexanes/CH_2Cl_2) afforded the product as a dark yellow solid (1.32 g, 60%). Mp: 83–85 °C.

7.7.15. 5'-Bromo-3,3'-dinitro-5,5'-trimethylsilanylenyl-[2,2']bipyridinyl (15). Compound 12 (0.34 g, 0.84 mmol) was coupled with TMSA (0.99 mL, 8.48 mmol) following the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.03 g, 0.04 mmol), copper(I) iodide (0.015 g, 0.08 mmol), THF (5 mL), and DIEA (0.29 mL, 1.68 mmol) were combined and the mixture was allowed to stir at room temperature for 1 h. Column chromatography, silica gel (1:1 hexanes/CH_2Cl_2) afforded the product as a yellow solid (0.25 g, 71%). Mp: 157–159°C.

7.7.16. 3,3'-Dinitro-5,5'-phenylethynyl-5-trimethylsilanylenyl-[2,2']bipyridinyl (16). Compound 15 (0.63 g, 1.49 mmol) was coupled with phenylacetylene (0.33 mL, 3.0 mmol) according to the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.05 g, 0.07 mmol), copper(I) iodide (0.03 g, 0.14 mmol), THF (5 mL), and DIEA (0.78 mL, 4.5 mmol) were combined and the mixture was heated in a 55°C oil bath for 3.5 h. Column chromatography, silica gel (1:1 hexanes/CH_2Cl_2) afforded the product as a brown-yellow solid (0.51 g, 77%). IR (KBr) 3060.9, 2958.3, 2217.2, 2141.1, 1595.7, 1542.8, 1442.9, 1349.4, 1248.9, 1028.7, 912.5, 848.8, 759.1, 684.9, 524.2 cm⁻¹. 1H NMR (400 MHz, CDCl_3) δ 8.87 (d, J = 2.1 Hz, 2H), 8.55 (d, J = 2.1 Hz, 2H), 7.58 (m, 2H), 7.40 (m, 3H), 0.31 (s, 9H). 13C NMR (100 MHz, CDCl_3) δ 155.6, 155.2, 149.4, 149.1, 144.1, 143.9, 135.7, 135.2, 132.4, 130.2, 129.1, 122.6, 122.3, 121.8, 103.8, 98.7, 97.0, 83.8, 0.0. HRMS calcd for: C_23H_18N_4O_4Si: 442.1097. Found: 442.1095.

7.7.17. 5-Bromo-3-nitro-pyridin-2-ylamine (17). To a 250 mL round-bottom flask was added sulfuric acid (60 mL) and a stir bar and the mixture was cooled to 0°C. 4-Bromo-2-aminopyridine (10.0 g, 57.8 mmol) was then added slowly. Fuming nitric acid (1.9 mL) was then added dropwise and the solution began to turn yellow. The solution was stirred for 1 h at 0°C, 1.5 h at room temperature, and 1 h at 50°C (during which time it turned orange-red). The mixture was poured onto ice, neutralized, and the precipitate filtered and washed with cold water to give a dark yellow solid (10.4 g, 83%). Mp: decomposes at 180°C. 1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 2.3 Hz, 1H), 8.40 (d, J = 2.3 Hz, 1H). 1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 2.3 Hz, 1H). 1H NMR (400 MHz, CDCl_3) δ 8.57 (d, J = 2.3 Hz, 1H).
organics were dried over MgSO4, filtered, and the solvent (10 mL) and extracted with ethyl acetate (20 mL). The purple solution changed to light yellow. The solution was Acetyl chloride was added (0.5 mL, 6.4 mmol) and the dark purple and the solution was allowed stirred for 1 h. Column chromatography, silica gel (1:2 hexanes/CH2Cl2) afforded the product as a dark yellow solid (0.62 g, 44%). Mp: 78–79°C. IR (KBr) 3057.4, 2955.8, 2896.1, 2217.6, 2159.9, 1595.4, 1543.9, 1491.4, 1448.1, 1346.2, 1247.1, 1187.9, 1157.7, 1070.7, 960.4, 918.7, 842.8, 806.7, 766.4, 751.2, 685.1, 631.6, 561.4, 529.6 cm⁻¹. ¹H NMR (400 MHz, CDCl3) δ 8.79 (d, J=2.0 Hz, 1H), 8.35 (d, J=2.0 Hz, 1H), 7.64 (m, 2H), 7.37 (m, 3H), 0.26 (s, 9H), 13C NMR (100 MHz, CDCl3) δ 156.0, 146.5, 136.1, 135.2, 131.3, 129.0, 121.7, 120.2, 104.0, 100.0, 99.1, 85.6, 0.0. HRMS calcd for C18H19NO2Si: 320.0983. Found: 320.0981.

7.7.21. Thioacetic acid S-[4-(2-(2-nitro-4-phenyl)-vinyl)-phenyl] ester (21). To a large test-tube equipped with a stir bar was added 33 (0.15 g, 0.32 mmol) and THF (4 mL). To the solution was added dropwise TBAF (3.2 mL, 1 M in THF). The solution changed from light yellow to blood-red and it was allowed to stir for 1 h. The solution was added dropwise TBAF (4.8 mL, 1 M in THF). The solution changed from light yellow to dark purple and it was allowed to stir for 1 h. Acetyl chloride (0.6 mL, 8 mmol) was added and the dark purple solution changed to light yellow. The solution was allowed to stir for 15 min and then worked up with water (10 mL) and extracted with ethyl acetate (20 mL). The organics were dried over MgSO4, filtered, and the solvent was removed in vacuo. The crude product was purified by running the material through a plug of silica to yield the desired compound as a bright yellow solid (0.12 g, 95%). Mp: 170–180°C. IR (KBr) 3429.3, 3025.2, 1697.3, 1520.6, 1403.3, 1349.0, 1118.3, 1088.2, 1011.0, 946.5, 828.2, 618.5, 552.6 cm⁻¹. ¹H NMR (400 MHz, CDCl3) δ 8.08 (d, J=1.6 Hz, 1H), 7.75 (d, J=8.0 Hz, 1H), 7.71 (dd, J=8.0, 1.6 Hz, 1H), 7.62 (d, J=16.4 Hz, 1H), 7.58–7.54 (m, 3H), 7.42 (d, J=8.0 Hz, 4H), 7.18–7.10 (m, 3H), 2.43 (s, 3H), 2.42 (s, 3H), ¹³C NMR (100 MHz, CDCl3) δ 194.0, 194.0, 148.7, 137.8, 137.7, 135.0, 135.0, 131.6, 130.8, 130.7, 128.6, 128.4, 127.9, 127.7, 127.4, 124.8, 122.8, 30.5. HRMS calcd for C18H16N2O2Si: 302.0978. Found: 302.0976.

7.7.22. Thioacetic acid S-[4-(2-(2-(4-acyethylsulfanyl)-vinyl)-3-nitro-phenyl)-vinyl]-phenyl ester (23). To a large test-tube equipped with a stir bar was added 36 (0.12 g, 0.20 mmol) and THF (3 mL). To the solution was added dropwise TBAF (4.0 mL, 1 M in THF). The solution changed from yellow to dark purple and it was allowed to stir for 1 h. Acetyl chloride (0.6 mL, 8 mmol) was added and the dark purple solution changed to light yellow. The solution was allowed to stir for 15 min and then worked up with water (10 mL) and extracted with ethyl acetate (20 mL). The organics were dried over MgSO4, filtered, and the solvent was removed in vacuo. The crude product was purified by running the material through a plug of silica to yield the desired compound as a bright yellow solid (0.036 g, 36%). Mp: 170–180°C. IR (KBr) 3429.3, 3025.2, 1697.3, 1520.6, 1403.3, 1349.0, 1118.3, 1088.2, 1011.0, 946.5, 828.2, 618.5, 552.6 cm⁻¹. ¹H NMR (400 MHz, CDCl3) δ 8.08 (d, J=1.6 Hz, 1H), 7.75 (d, J=8.0 Hz, 1H), 7.71 (dd, J=8.0, 1.6 Hz, 1H), 7.62 (d, J=16.4 Hz, 1H), 7.58–7.54 (m, 3H), 7.42 (d, J=8.0 Hz, 4H), 7.18–7.10 (m, 3H), 2.43 (s, 3H), 2.42 (s, 3H), ¹³C NMR (100 MHz, CDCl3) δ 194.0, 194.0, 148.7, 137.8, 137.7, 135.0, 135.0, 131.6, 130.8, 130.7, 128.6, 128.4, 127.9, 127.7, 127.4, 124.8, 122.8, 30.5. HRMS calcd for C24H19NO3S: 401.1084. Found: 401.1084.
IR (KBr) 3087.9, 3008.5, 2956.8, 2922.6, 2853.8, 1708.7, 1629.2, 1593.3, 1491.8, 1420.9, 1395.3, 1352.6, 1269.1, 1141.0, 1093.1, 1013.3, 989.9, 949.9, 913.8, 837.0, 738.0, 610.1 cm\(^{-1}\). 

To a 250 mL round-bottom flask was added 4-Iodo-2-nitroaniline (5.28 g, 20.00 mmol), palladium(II) acetate (0.05 g, 0.20 mmol), styrene (2.8 mL, 24.0 mmol), DIEA (8.7 mL, 50.0 mmol), and acetonitrile (50 mL) were coupled at 80 °C and stirring overnight, cooled and quenched with sodium thiosulfate (50 mL) and extracted with ether (20 mL). The crude product was purified via flash column chromatography, silica gel (1:1 CH\(_2\)Cl\(_2\)/petroleum ether) to yield 0.14 g (39%) of the titled compound. Mp: 88–90 °C. 

IR (KBr) 3425.6, 3023.0, 2924.6, 1628.4, 1593.3, 1517.4, 1393.1, 1331.7, 1290.0, 1243.7, 1106.3, 1044.0, 958.6, 909.9, 814.9, 750.9, 690.0, 566.0, 538.5, 454.2 cm\(^{-1}\). 


C\(_{22}\)H\(_{17}\)NO\(_2\)S: 359.0980. Found: 359.0981.

C\(_{14}\)H\(_{12}\)N\(_2\)O\(_2\): 240.0899. Found: 240.0900.

C\(_{16}\)H\(_{13}\)NO\(_2\): 251.0946. Found: 251.0947.

C\(_{22}\)H\(_{17}\)NO\(_2\)S: 359.0980. Found: 359.0981.
column chromatography, silica gel (hexanes) to yield 1.94 g (81%) of a pale yellow liquid. 1H NMR (400 MHz, CDCl3) δ 7.56 (dt, J = 8.6, 2.5 Hz, 2H), 7.01 (dt, J = 8.6, 2.5 Hz, 2H), 2.93–2.89 (m, 2H), 0.94–0.89 (m, 2H), 0.02 (s, 9H).

7.7.32. Trimethyl-[2-(4-vinylphenylsulfanyl)ethyl]silane (32). Bis(dibenzylideneacetone)palladium (0.15 g, 0.26 mmol), 31 (1.71 g, 5.10 mmol), trimethylarsene (0.16 g, 0.51 mmol), tributylvinylstannane (1.71 g, 5.40 mmol), BHT (1 crystal) and THF (15 mL) were coupled according to the general Stille coupling procedure above. The crude product was purified via flash column chromatography, silica gel (hexanes) to yield 0.973 g (81%) of a pale yellow liquid. IR (KBr) 3068.2, 3007.4, 2952.4, 2916.2, 1540.0, 1496.0, 1419.6, 1397.2, 1250.6, 1161.8, 1092.2, 1010.1, 989.4, 893.0, 755.4, 694.5, 474.7 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ 7.31 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.65 (dd, J = 17.6, 10.9 Hz, 1H), 6.69 (dd, J = 17.5, 0.8 Hz, 1H), 5.20 (dd, J = 10.9, 0.9 Hz, 2H), 2.96–2.92 (m, 2H), 0.94–0.87 (m, 2H), 0.02 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 137.2, 136.6, 135.5, 129.3, 127.0, 113.8, 29.7, 17.3, –1.4. HRMS calcd for C14H11BrSi: 258.0044. Found: 258.0044.

7.7.33. Trimethyl-[2-(4-[2-(2-nitro-4-styryl-phenyl)-vinyl]-phenyl-sulfanyl}ethyl]-silane (33). Palladium(II) acetate (0.009 g, 0.040 mmol), K2CO3 (0.095 g, 0.69 mmol), tetrabutylammonium bromide (0.372 g, 1.12 mmol), 28 (0.270 g, 0.77 mmol), 32 (0.218 g, 0.92 mmol) and DMF (7 mL) were coupled according to the general Heck coupling procedure above. The crude product was purified via flash column chromatography, silica gel (1:3 CH2Cl2/hexanes) to yield 0.259 g (73%) of a yellow solid. IR (KBr) 3424.9, 3024.3, 2950.6, 1621.8, 1589.2, 1521.1, 1347.2, 1248.8, 1090.1, 1012.2, 962.1, 858.8, 824.2, 757.8, 692.6 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ 8.04 (d, J = 2.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 8.4, 1.6, 1H), 7.56–7.51 (m, 3H), 7.44 (d, J = 8.2 Hz, 2H), 7.39–7.36 (m, 3H), 7.32–7.27 (m, 2H), 7.20 (d, J = 16.4, 1H), 7.07 (dd, J = 16.4, 2.0 Hz, 2H), 3.80–3.76 (m, 2H), 0.96–0.92 (m, 2H), 0.04 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 148.7, 138.7, 138.0, 136.8, 134.3, 133.4, 131.8, 131.8, 130.8, 129.3, 129.0, 128.9, 128.4, 127.8, 127.2, 126.3, 122.9, 122.8, 29.6, 17.2, –1.3. HRMS calcd for C26H22NOSSi: 459.1688. Found: 459.1687.

7.7.34. 4-Ethenylphenylbromobenzene (34). Palladium (II) acetate (0.22 g, 1.0 mmol), K2CO3 (0.24 g, 1.80 mmol), tetrabutylammonium bromide (0.935 g, 1.12 mmol), styrene (2.31 mL, 20.0 mmol), 4-bromiodobenzene (5.66 g, 20.0 mmol) and DMF (50 mL) were coupled according to the general Heck coupling procedure above. The crude product was purified via flash column chromatography, silica gel (hexanes) to yield 3.11 g (60%) of a white solid. IR: 2952.4, 2916.2, 1627.3, 1594.0, 1490.6, 1419.6, 1397.2, 1250.6, 1161.8, 1092.2, 1010.1, 989.4, 833.0, 755.4, 694.5, 474.7 cm⁻¹. 1H NMR (400 MHz, CDCl3) δ 8.02 (d, J = 1.6 Hz, 1H), 7.73 (d, J = 8.0, 1.6 Hz, 1H), 7.66 (dd, J = 8.4, 1.6 Hz, 1H), 7.53 (d, J = 16.0 Hz, 1H), 7.45–7.42 (m, 4H), 7.28–7.26 (m, 4H), 7.14 (d, J = 16.4 Hz, 1H), 7.06 (d, J = 16.0 Hz, 1H), 7.03 (d, J = 16.4 Hz, 1H), 3.00–2.96 (m, 4H), 0.96–0.92 (m, 4H), 0.04 (s, 18H). 13C NMR (100 MHz, CDCl3) δ 148.7, 138.8, 138.6, 138.0, 134.0, 133.4, 131.7, 131.1, 130.1, 128.9, 128.9, 128.4, 127.9, 127.6, 125.6, 122.8, 127.7, 30.1, 29.5, 17.2, –1.6. HRMS calcd for C32H24NO2SSi2: 591.2117. Found: 591.2114.

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