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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 active 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

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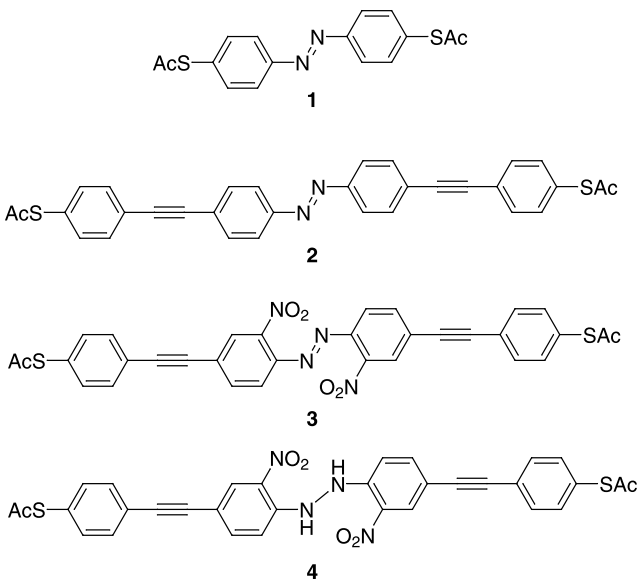
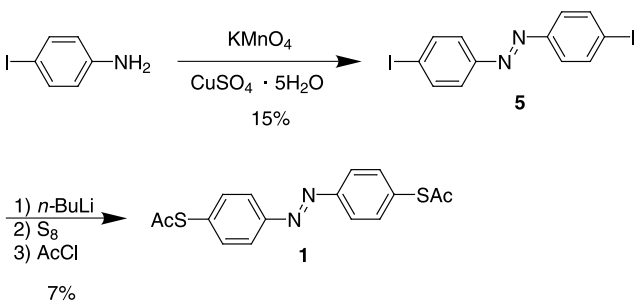


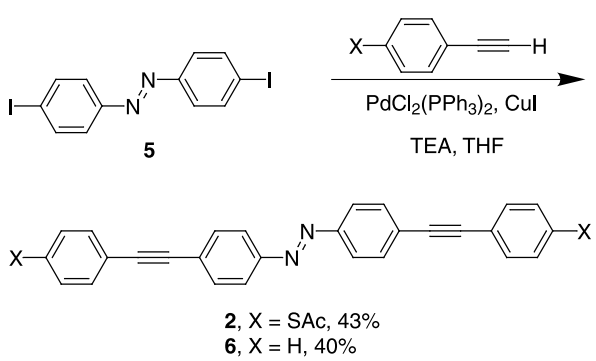
Figure 1. Azobenzene derivatized compounds **1**–**3** and hydrazo compound **4**.

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 expect yield.[16] Attempts to replace the diiodide using *tert*-butyllithium at −78°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**.

As shown in Scheme 2, coupling **5** with 4-ethynyl-1-thioacetylbenzene[17] afforded the expected dicoupled product **2**. Since our experiments have shown that compounds without thioacetyl ('alligator clips' for adhesion to metallic surfaces after acetyl removal) produced cleaner electrochemical results that are still quantitatively similar to the sulfur-bearing systems,[11] we made **6** by coupling phenylacetylene 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 voltamagram (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.

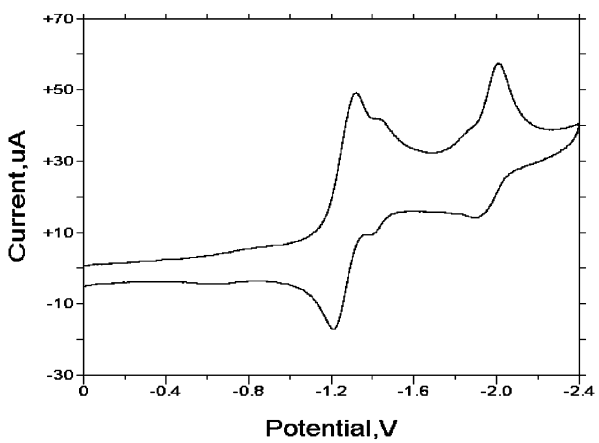


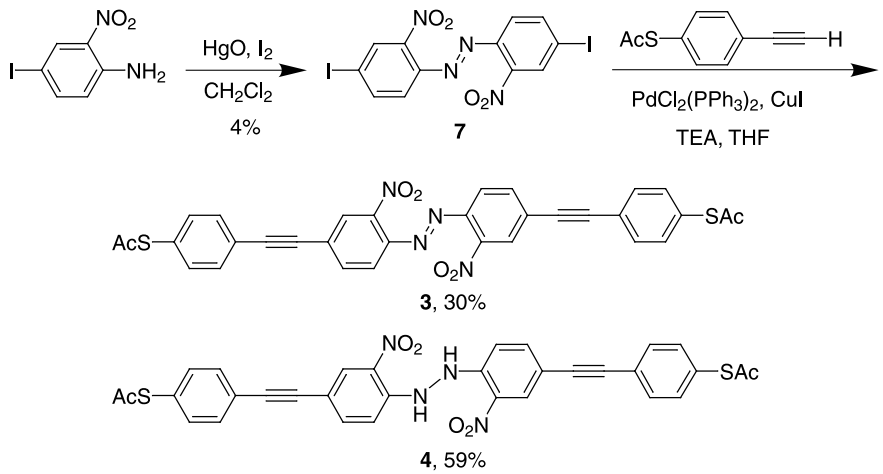
Figure 2. CV of compound **6**.

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[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 stericly hindered azo product. **7** was then subjected to palladium-catalyzed coupling with 4-ethynyl-1-thioacetylbenzene to yield both the azo compound **3**, and the hydrazo product **4**.

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[8] or biphenyl[9] core of the OPE



Scheme 3. Synthesis of compounds **3** and **4**.

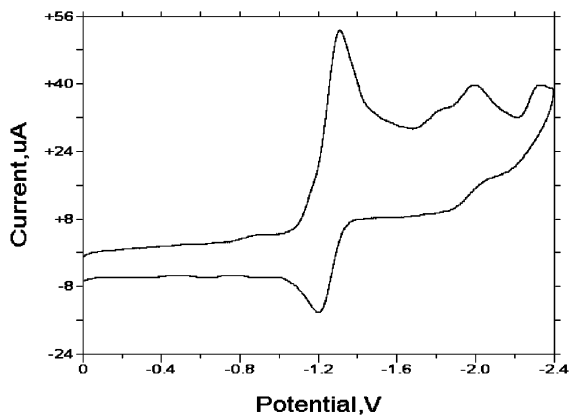


Figure 3. CV of the dinitro azo compound **3**.

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.[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° for the 2-2′-dinitro-biphenyl system to 35.1° for the 2-2′-dinitro-bipyridyl system. This will ultimately increase the overlap of the extended π-orbitals, lowering the resistance through the molecule. The pyridyl based systems synthesized are shown in Figure 4.

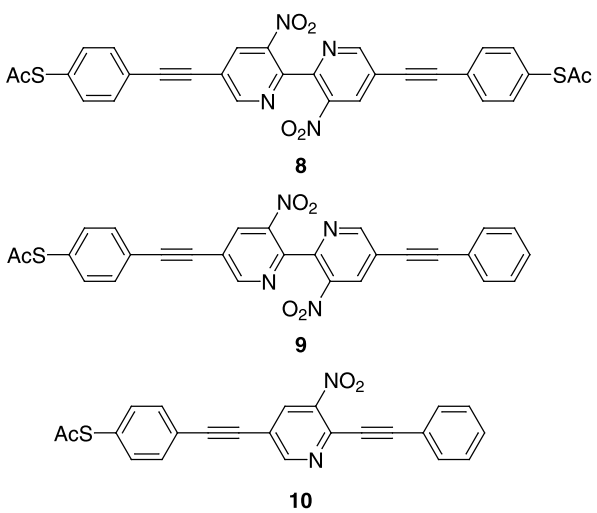


Figure 4. Pyridyl based targets **8**–**10**.

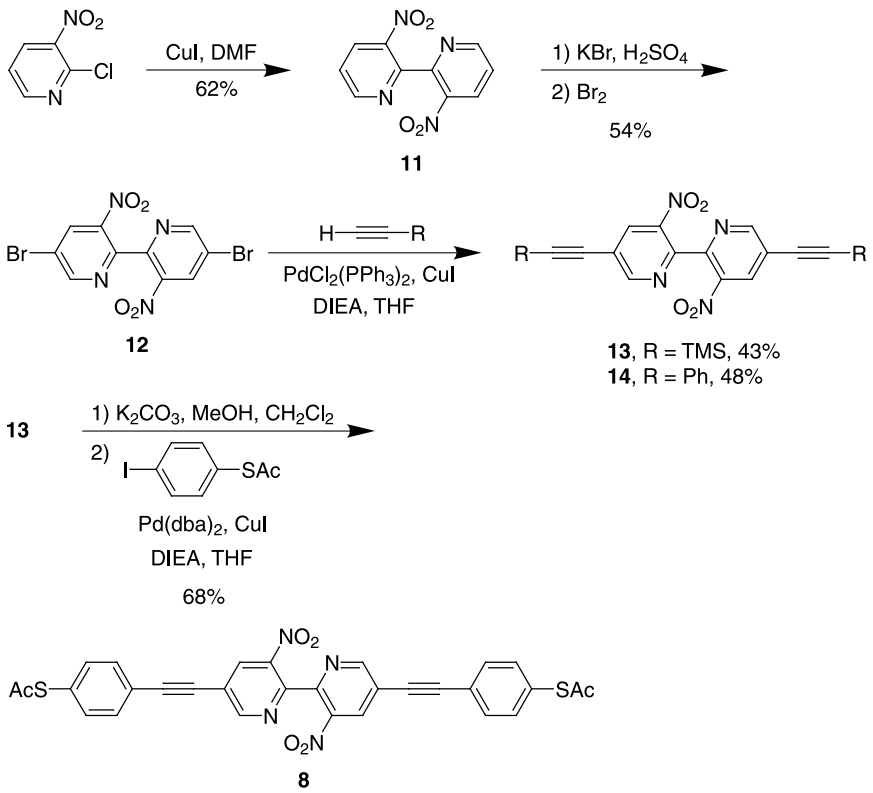
Scheme 4 shows the synthesis of the target compound **8** with two thioacetates. The dinitro-bipyridyl compound **11** was obtained by an Ullmann[20] coupling of commercially available 2-chloro-3-nitropyridine.[21] **11** was brominated under harsh conditions, presumably necessary due to the electron deficient nature of the system,[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[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 to afford the target compound **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**.[24] **17** was converted to the dibromo compound **18**,[25] coupled with phenylacetylene, trimethylsilylacetylene, deprotected and finally coupled with 4-(thioacetyl)iodobenzene to afford **10**.

4. Oligo(phenylene vinylene)s

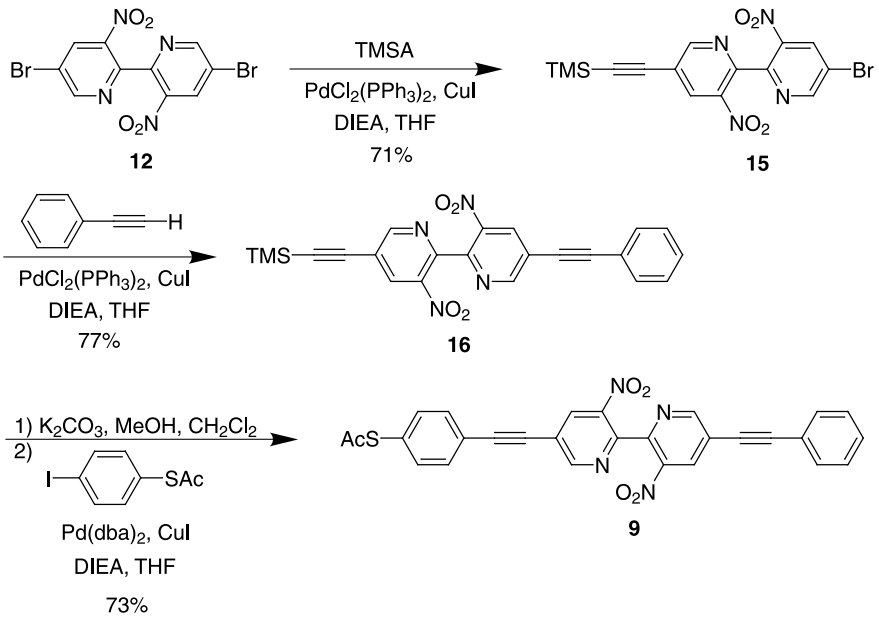
In an attempt to design more efficient molecular devices



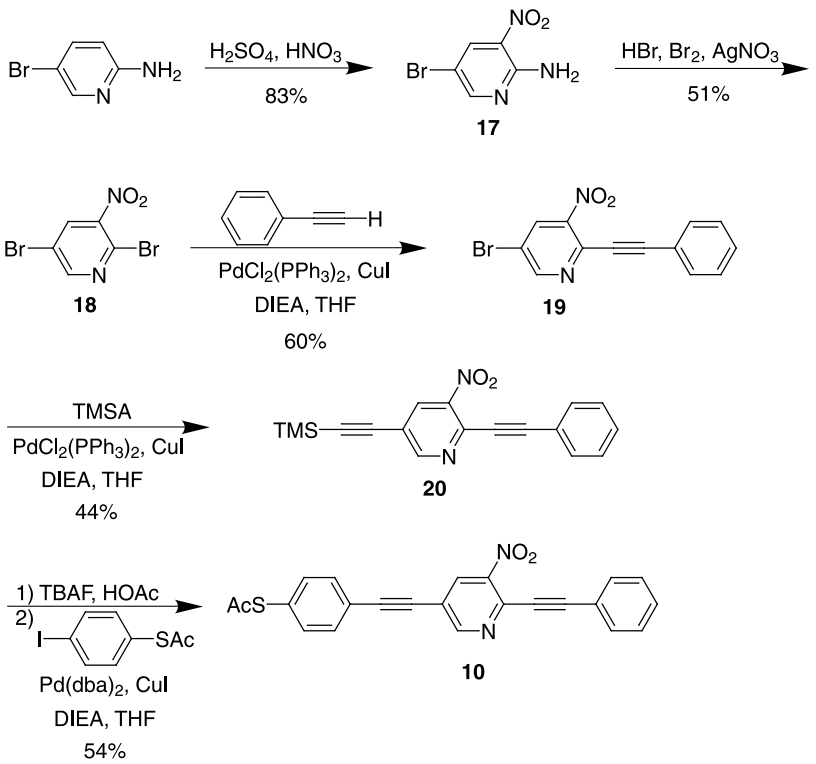
Scheme 4. Synthesis of the dithioacetate dinitro-bipyridyl **8** and the unfunctionalized derivative **14**.

(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.[1,2] Recent work by Chidsey et al.[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.[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



Scheme 5. Synthesis of the monothioacetate dinitro-bipyridyl compound **9**.



Scheme 6. Synthesis of the mononitro-monothioacetate pyridine compound **10**.

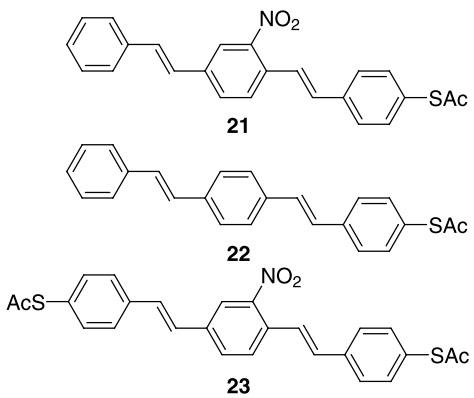


Figure 5. OPV based potential devices.

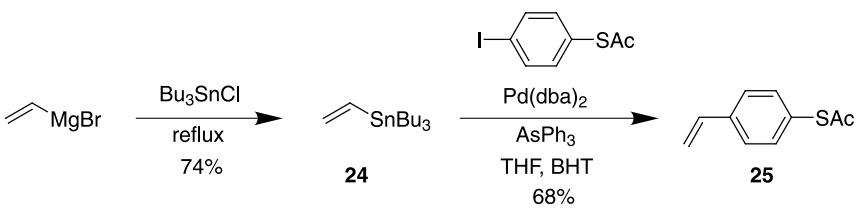
synthesized by Overberger and Lebovits,[27] however, their synthesis required extreme temperatures in excess of 460°C. Our route, in Scheme 7, is higher yielding and more easily accessed.

The synthesis of **25** began by refluxing vinyl magnesium bromide with tributyltin chloride to produce the vinyl stannane **24**.[28] A subsequent Stille[29] coupling produced **25**.

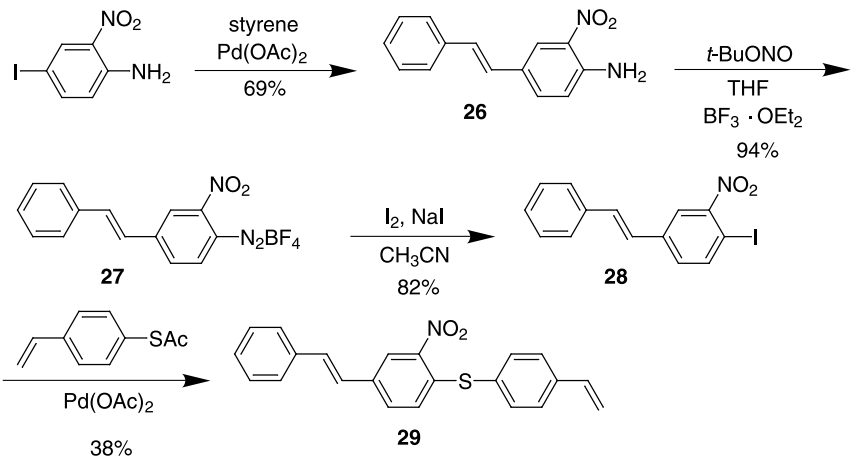
Initial attempts to synthesize **21** resulted in the formation of arylthioether **29** as shown in Scheme 8. The attempted synthesis of **21** began with a Heck[30] coupling of 4-iodo-2-nitroaniline with styrene to produce 2-nitro-4-styrylaniline. Diazotization of **26** produced **27** in high yield, which was then halogenated with I_2 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**.

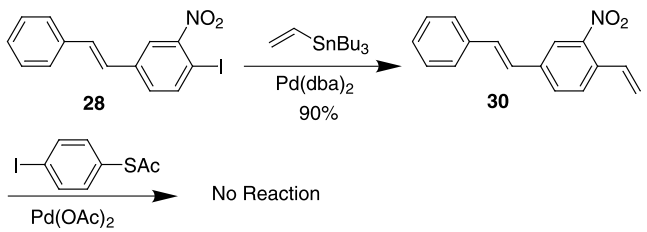
In order to overcome the problems with the acetyl-protecting group, the ethyltrimethylsilyl group was used to protect the sulfur. Coupling of 2-(trimethylsilyl)ethyl-4′-bromophenyl sulfide[31] directly with **24** did not afford the desired compound, and in fact only resulted in recovery of starting 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**.[31] Coupling **31**



Scheme 7. Synthesis of alligator clip **25**.



Scheme 8. Attempted synthesis of **21**.

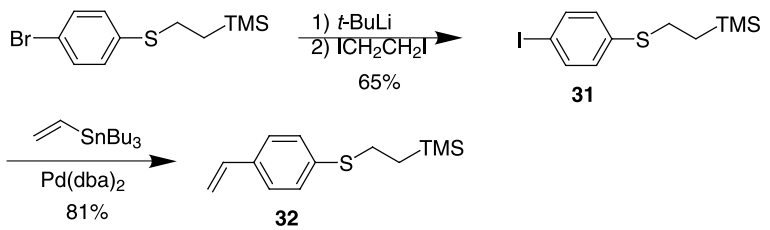


Scheme 9. Attempted synthesis of **21** from **28**.

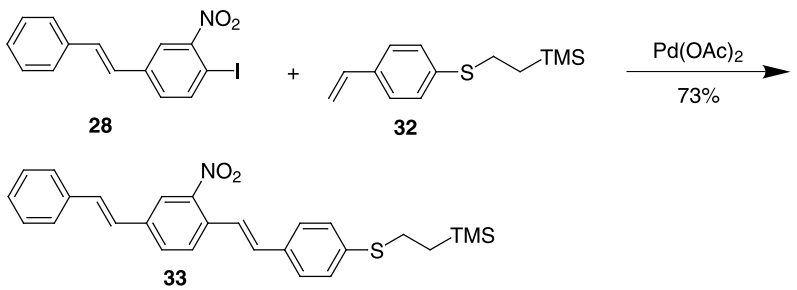
with **24** resulted in the formation of the desired alligator clip **32** in high yield as shown in Scheme 10.

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

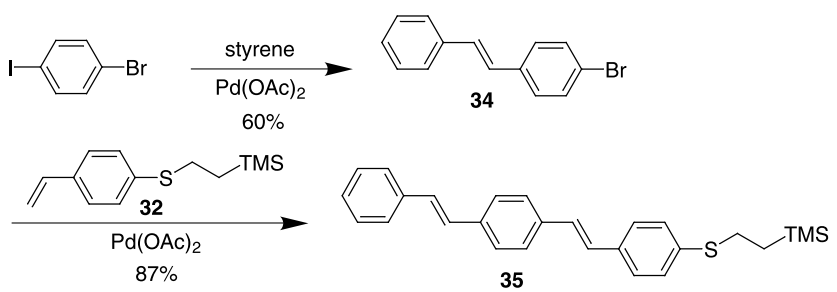
In order to examine the effects of a nitro group in the OPV system, an unfunctionalized wire was synthesized. The synthesis of **22** began by coupling 4-bromoiodobenzene with styrene to produce **34** as shown in Scheme 12.



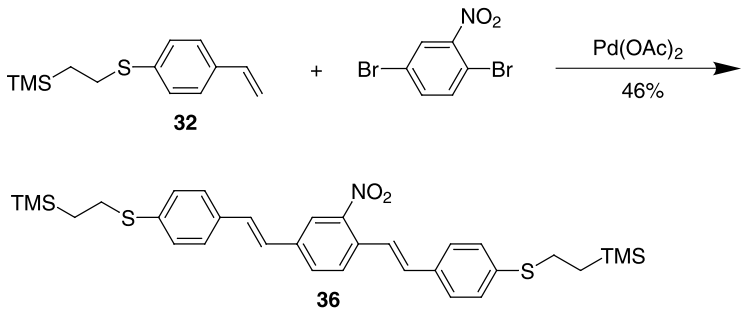
Scheme 10. The synthesis of alligator clip **32**.



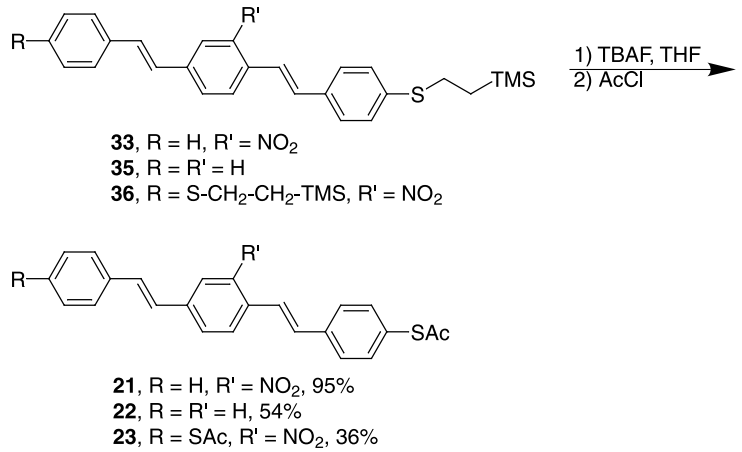
Scheme 11. Synthesis of compound **33**.



Scheme 12. Synthesis of compound **35**.



Scheme 13. Synthesis of compound **36**.



Scheme 14. Deprotection of the ethyltrimethylsilyl groups to afford **21**, **22** and **23**.

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,[31] 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 μm^2. 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

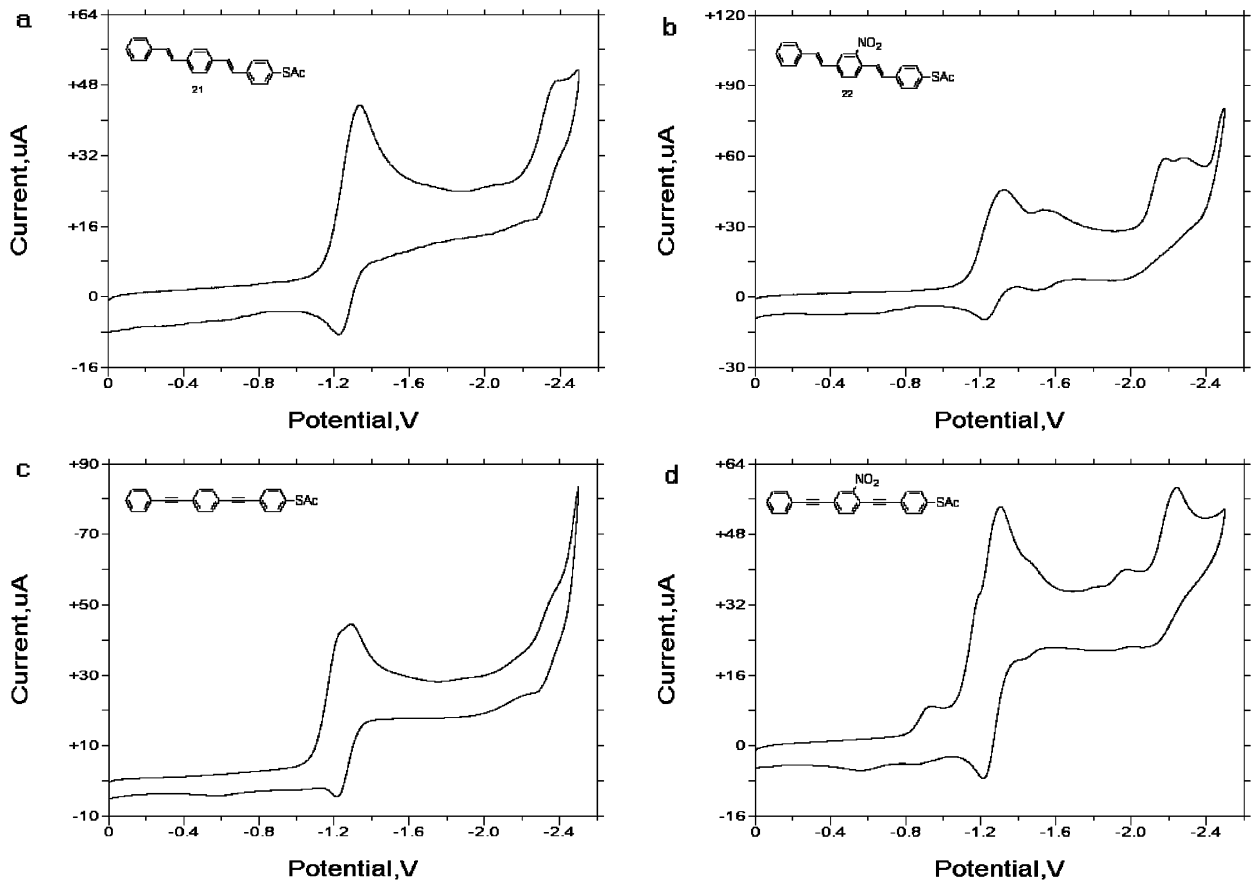


Figure 6. Cyclic voltametry results for OPVs **21** (a) and **22** (b) and their corresponding OPEs (c) and (d), respectively.

less pronounced) for the mononitro OPE device and sharp voltage peaks were only seen at low temperatures.[3]

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 'resetablility' 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.[4]

6. Summary

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

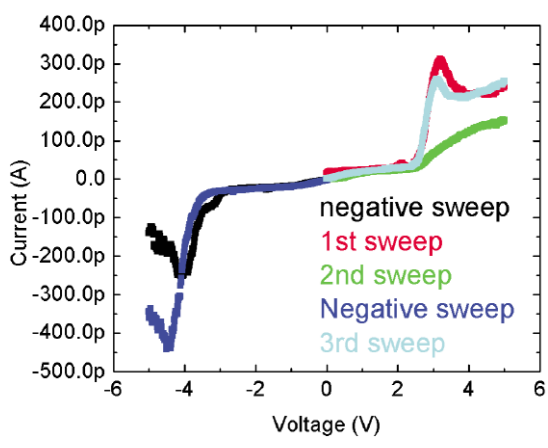


Figure 7. Positive and negative NDR in the dinitro-bipyridyl device built from **8**. T=300 K.

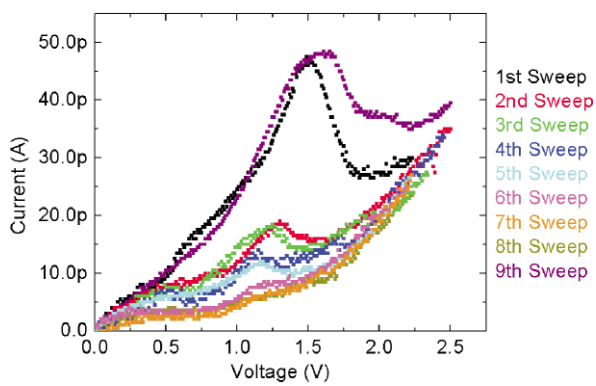


Figure 8. A resetable state is observed for a device built from **9**. After the first sweep, the current is reduced dramatically as seen in voltage sweeps 2–8. Following the 8th sweep, a negative voltage pulse of ~2.5 V (not shown) is given to restore NDR to the device, as seen in the 9th voltage sweep. T=300 K.

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 N_2 unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexanes were distilled. Triethylamine (TEA), diisopropylethylamine (DIEA) and CH_2Cl_2 were distilled from CaH_2 under N_2. Silica gel plates were 250 μm thick, 40 F_{254} 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 $Ag/AgNO_3$ non-aqueous reference electrode. The solutions were 1 mM in DMF and 0.1 M in *n*-Bu_4NBF_4. The scan rate was 0.1 V/s at 23°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 N_2 (3×). 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 CH_2Cl_2 and washed with a saturated solution of NH_4Cl. The organic layer was dried using anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was then purified by flash chromatography (silica gel).

7.4. General Stille coupling reaction procedure[29]

To an oven dried screwcap 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 N_2 (3×). 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 procedure[30]

To an oven dried glass screwcap 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 N_2 (3×). 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 (3×). The organic layer was dried with $MgSO_4$ and filtered. The solvent was then removed in vacuo.

7.6. General procedure for the deprotection of trimethylsilyl protected alkynes[39]

To a round-bottom flask equipped with a stir bar were added the protected alkyne, K_2CO_3 (5 equiv. per protected alkyne), methanol, and CH_2Cl_2. The reaction was stirred, and upon completion, the reaction mixture was diluted with CH_2Cl_2 and washed with brine (3×). The organic layer was dried over $MgSO_4$, and the solvent removed in vacuo.

7.7. General procedure for the diazotization of anilines with nitrosonium tetrafluoroborate in the acetonitrile–sulfolane system[40]

$NOBF_4$[39] was weighed out in a N_2-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/acetone bath to −40°C. The solution of the aniline was prepared by adding warm sulfolane (45–50°C) to the amine under a N_2 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 CH_2Cl_2, collected by filtration, washed with ether or CH_2Cl_2 and dried. Additional purification of the salt was accomplished by re-precipitation from DMSO by CH_2Cl_2 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**)[16] (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 N_2, 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 H_2O (100 mL) and extracted

with CH_2Cl_2 (3×). The organic extracts were combined, washed with brine, dried over anhydrous $MgSO_4$, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH_2Cl_2) 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, $CDCl_3$) δ 7.97 (d, J=8.8 Hz, 4H), 7.59 (d, J=8.8 Hz, 4H), 2.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 153.0, 135.4, 131.8, 124.0, 30.8. HRMS calcd for $C_{16}H_{14}N_2O_2S_2$: 330.0496. Found: 330.0495.

7.7.2. Thioacetic acid *S*-(4-{4-[4-(4-acetylsulfanyl-phenylethynyl)-phenylazo]-phenylethynyl}-phenyl) ester (2). Bis-(4-iodo-phenyl)-diazene (**5**)[16] (0.69 g, 1.59 mmol) was coupled to 4-ethynyl-1-thioacetylbenzene[1] (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 $MgSO_4$ and concentrated in vacuo. The remaining solid was dissolved in hot CH_2Cl_2 and filtered. The filtrate was concentrated to afford the product (0.36 g, 43%). Mp: decomposes at 246°C. IR (KBr) 3051.7, 2923.0, 2206.6, 1911.7, 1692.0, 1594.4, 1557.4, 1497.5, 1479.5, 1396.5, 1353.5, 1297.5, 1282.8, 1261.4, 1221.0, 1181.4, 1154.1, 1110.3, 1012.2, 951.0, 852.3, 823.8, 734.3, 708.4, 622.7 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 7.95 (d, J=9 Hz, 4H), 7.69 (d, J=9 Hz, 4H), 7.6 (d, J=9 Hz, 4H), 7.43 (d, J=9 Hz, 4H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 152.4, 134.7, 133.0, 132.7, 128.9, 125.8, 124.6, 123.5, 91.7, 91.4, 30.7. HRMS calcd for $C_{32}H_{22}N_2O_2S_2$: 530.1123. Found: 530.1122.

7.7.3. Thioacetic acid *S*-(4-{4-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenylazo]-3-nitro-phenylethynyl}-phenyl) ester (3). Bis-(4-iodo-2-nitro-phenyl)-diazene (**7**) (0.100 g, 0.286 mmol) was coupled to 4-ethynyl-1-thioacetylbenzene[1] (0.11 g, 2.29 mmol) according to the general coupling procedure. After 30 min the reaction was complete and poured into CH_2Cl_2 (100 mL) and MeOH (100 mL). Care was taken to remove mainly the more volatile CH_2Cl_2 on the rotovap. The precipitate was vacuum filtered and washed with MeOH to afford **3** (0.06 g, 30%). Mp: decomposes at 350°C. IR (KBr) 2359.5, 2341.3, 1714.9, 1529.2, 1087.8, 772.0, 667.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J=1.9 Hz, 2H), 7.82 (dd, J=7.6, 1.9 Hz, 2H), 7.73 (d, J=7.6 Hz, 2H), 7.62 (d, J=9.0 Hz, 4H), 7.46 (d, J=9.0 Hz, 4H), 2.47 (s, 6H). Repeated attempts to obtain the ^{13}C NMR, even at 125 MHz, were unsuccessful due to the insolubility of the material. HRMS calcd for $C_{32}H_{20}N_4O_6S_2$: 620.0824. Found: 620.0820.

7.7.4. Thioacetic acid *S*-[4-(4-{*N*′-[4-(4-acetylsulfanyl-phenylethynyl)-2-nitro-phenyl]-hydrazino}-3-nitro-phenylethynyl)-phenyl] ester (4). 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 CH_2Cl_2 followed by the addition of hexanes (100 mL). Care was taken to remove only mainly the more volatile CH_2Cl_2 in vacuo. The solid was vacuum filtered and washed with hexanes. The solid was purified by flash chromatography, silica gel (CH_2Cl_2) 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, $CDCl_3$) δ 9.34 (s, 2H), 8.45 (d, J=2.4 Hz, 2H), 7.64 (dd, J=9.0, 2.4 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{32}H_{23}N_4O_6S_2$: 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. $CHCl_3$ (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 $CHCl_3$, and the solvent was removed in vacuo. Flash chromatography, silica gel (CH_2Cl_2) afforded the desired product as an orange solid (1.25 g, 15%). ^1H NMR (400 MHz, $CDCl_3$) 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/CH_2Cl_2) 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, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 132.9, 132.1, 129.1, 128.9, 126.7, 123.5, 123.3, 92.6, 89.6. HRMS calcd for $C_{28}H_{18}N_2$: 382.1470. Found: 382.1469.

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). CH_2Cl_2 (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 CH_2Cl_2. The filtrate was then washed with a saturated aqueous solution of sodium thiosulfate, dried over anhydrous $MgSO_4$, 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, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 144.8, 143.3, 133.6, 120.3, 97.6. HRMS calcd for $C_{12}H_6N_4O_4I_2$: 523.8478. Found: 523.8492.

7.7.8. Thioacetic acid *S*-{4-[5′-(4-acetylsulfanyl-phenylethynyl)-3,3′-dinitro-[2,2′]bipyridinyl-5-ylethynyl]-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/CH_2Cl_2) afforded the desired product as a brown solid (1.06 g, 99% yield). ^1H NMR (200 MHz, $CDCl_3$) 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(dibenzylideneacetone)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)iodobenzene[1] (3.05 g, 10.95 mmol). The tube was placed in a 50°C oil bath for 1 h. Flash chromatography, silica gel (CH_2Cl_2) gave the desired product as an orange-yellow solid (1.51 g, 69%). Mp: 198–199°C. IR (KBr) 3394.5, 3057.1, 2212.6, 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, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{30}H_{18}N_4O_6S_2$: 594.0668. Found: 594.0664.

7.7.9. Thioacetic acid *S*-[4-(3,3′-dinitro-5′-phenylethynyl-[2,2′]bipyridinyl-5-ylethynyl)-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(dibenzylideneacetone)-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)-iodobenzene[1] (0.36 g, 1.31 mmol). The tube was placed in a 55–60°C oil bath for 2 h. Flash chromatography, silica gel (CH_2Cl_2) followed by precipitation from CH_2Cl_2 in hexanes gave the desired product as an orange-yellow solid (0.41 g, 74% yield). Mp: 161–162°C. IR (KBr) 3442.2, 3245.4, 3071.3, 2210.8, 1709.4, 1595.7, 1543.0, 1488.6, 1444.6, 1349.3, 1110.2, 1078.7, 1028.9, 943.0, 908.3, 821.7, 764.9, 617.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (m, 2H), 8.61 (m, 2H), 7.60 (m, 3H), 7.43 (m, 6H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 155.1, 149.4, 149.1, 144.2, 135.3, 135.2, 134.7, 132.9, 132.4, 130.6, 130.2, 129.0, 122.8, 122.6, 122.1, 121.8, 97.0, 96.0, 85.2, 83.8, 30.7. HRMS calcd for $C_{28}H_{16}N_4O_5S$: 520.0841. Found: 520.0839.

7.7.10. Thioacetic acid *S*-[4-(5-nitro-6-phenylethynyl-pyridin-3ylethynyl)-phenyl] ester (10). To a 50 mL round-bottom flask containing a stir bar was added **20** (0.62 g, 1.89 mmol) and THF (10 mL). Acetic acid (0.22 mL, 3.78 mmol) and then 1.0 M TBAF in THF were then added and the reaction was allowed to stir for 15 min. The reaction was then poured into water and the product extracted with CH_2Cl_2 (3×). The organic layers were combined and dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The product was purified by column chromatography; silica gel (CH_2Cl_2) afforded the product as a light yellow solid (0.47 g, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J=1.9 Hz, 1H), 8.42 (d, J=1.9 Hz, 1H), 7.67 (m, 2H), 7.40 (m, 3H), 3.44 (s, 1H). The deprotected material (0.47 g, 1.82 mmol) was then coupled according to the general procedure using bis(dibenzylideneacetone)-palladium (0.05 g, 0.09 mmol), copper(I) iodide (0.03 g, 0.18 mmol), triphenylphosphine (0.10 g, 0.37 mmol), THF (10 mL), DIEA (0.38 mL, 2.18 mmol), and 4-(thioacetyl)-iodobenzene[1] (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/CH_2Cl_2 then ethyl acetate) and precipitation from CH_2Cl_2 and hexanes gave the desired product as an orange solid (0.41 g, 55%). Mp: decomposes at 110°C. IR (KBr) 3042.4, 2929.7, 2215.3, 2151.2, 1712.4, 1696.4, 1665.5, 1647.5, 1588.3, 1540.3, 1490.4, 1448.8, 1379.5, 1348.4, 1244.3, 1123.8, 827.9, 756.8, 688.0, 619.8, 526.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J=1.9 Hz, 1H), 8.45 (d, J=1.9 Hz, 1H), 7.68 (m, 2H), 7.58 (d, J=8.8 Hz, 2H), 7.43 (m, 5H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{23}H_{14}N_2O_3S$: 398.0725. Found: 398.0723.

7.7.11. 3,3′-Dinitro-[2,2′]bipyridinyl (11).[21] To a 250 mL round-bottom flask equipped with a reflux condenser and stir bar was added 2-chloro-3-nitropyridene (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 CH_2Cl_2 and washed with dilute ammonium hydroxide solution. The organic layers were combined and dried over anhydrous $MgSO_4$ 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).

7.7.12. 5,5′-Dibromo-3,3′-dinitro-[2,2′]bipyridinyl (12).[22] To a 100 mL round-bottom flask was added **11** (3.9 g, 15.8 mmol) and a stir bar. Dry methanol (25 mL) and dry CH_2Cl_2 (25 mL) were added and cooled to 0°C. To a three-necked 500 mL round-bottom flask was added KBr (120 g, 1008.4 mmol) and an addition funnel with H_2SO_4 (conc., 90 mL) was placed on top. The system was then sealed with rubber septas and the two flasks connected via a cannula. The H_2SO_4 was slowly added over 20 min (the temperature must stay below 75°C to prevent formation of Br_2). The precipitate that formed was filtered off and the solution re-subjected to HBr. This affords the salt as a light yellow powder. The salt and a stir bar were then added to a screwcap tube and the vessel sealed with a rubber septum, evacuated and backfilled with N_2 (3×). Br_2 (5 mL) was then added and the screwcap affixed. The mixture was heated in a 165°C oil bath for 24 h. The reaction mixture was cooled and poured into a saturated solution of sodium thiosulfate to remove excess bromine. The crude product was extracted with CH_2Cl_2 (3×) and the organic layers were combined and dried over anhydrous $MgSO_4$ and the solvent removed in vacuo. The crude product was purified by column chromatography, silica gel (1:2 hexanes/CH_2Cl_2) to afford the desired product as a white-yellow solid (3.46 g, 54%). Mp: 158–160°C. IR (KBr) 3065.9, 2869.5, 1578.2, 1545.2, 1426.6, 1346.4, 1234.0, 1103.0, 1025.6, 897.1, 879.1, 788.8,

753.7, 649.2, 551.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J=2.2 Hz, 2H), 8.68 (d, J=2.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 149.0, 144.2, 136.0, 121.3. HRMS calcd for $C_{10}H_4Br_2N_4O_4$: 403.8581. Found: 403.8580.

7.7.13. 3,3′-Dinitro-5,5′-bis-trimethylsilanylethynyl-[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: 157–159°C. IR (KBr) 3083.6, 2956.5, 2896.5, 2156.5, 1594.8, 1542.8, 1448.0, 1382.9, 1358.6, 1248.0, 1191.7, 1029.8, 950.2, 918.5, 843.6, 759.9, 696.3, 641.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J=1.9 Hz, 2H), 8.52 (d, J=1.9 Hz, 2H), 0.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 149.4, 143.9, 135.7, 122.2, 103.8, 98.7, 0.0. HRMS calcd for $C_{20}H_{22}N_4O_4Si_2$: 438.1180. Found: 438.1180.

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 mmol) 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 (0.13 g, 48%). Mp: decomposes at 226°C. IR (KBr) 3068.0, 2209.4, 1544.0, 1489.0, 1442.5, 1350.3, 1029.9, 909.4, 821.9, 764.3, 689.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, J=1.8 Hz, 2H), 8.60 (d, J=1.8 Hz, 2H), 7.58 (m, 4H), 7.41 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 149.1, 144.2, 135.2, 132.4, 130.1, 129.0, 122.5, 121.8, 97.0, 83.8. HRMS calcd for $C_{26}H_{14}N_4O_4$: 446.1015. Found: 446.1014.

7.7.15. 5′-Bromo-3,3′-dinitro-5-trimethylsilanylethynyl-[2,2′]bipyridinyl (15). Compound **12** (0.34 g, 0.84 mmol) was coupled with TMSA (0.09 mL, 0.84 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%). IR (KBr) 3069.4, 2960.2, 2359.8, 1585.4, 1543.7, 1436.8, 1344.3, 1249.9, 1105.2, 1029.1, 848.3, 812.6, 784.7, 764.0, 646.9 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J=2.0 Hz, 1H), 8.83 (d, J=2.0 Hz, 1H), 8.67 (d, J=2.0 Hz, 1H), 8.53 (d, J=2.0 Hz, 1H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 154.6, 149.4, 149.0, 144.3, 143.8, 135.9, 135.7, 122.4, 121.1, 104.0, 98.6, 0.0. HRMS calcd for $C_{15}H_{13}BrN_4O_4Si$: 419.9890. Found: 419.9884.

7.7.16. 3,3′-Dinitro-5′-phenylethynyl-5-trimethylsilanyl-ethynyl-[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, 689.4, 524.1 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). ^{13}C 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: $C_{23}H_{18}N_4O_4Si$: 442.1097. Found: 442.1095.

7.7.17. 5-Bromo-3-nitro-pyridin-2-ylamine (17).[24] 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), 6.79 (br s, 2H).

7.7.18. 2,5-Dibromo-3-nitro-pyridine (18).[25] To a 50 mL round-bottom flask was added **17** (0.5 g, 2.3 mmol) in HBr (2 mL, 48%) with a stir bar. This was cooled to 0°C and bromine (0.41 mL, 8.0 mmol) was added followed by sodium nitrite (0.47 g, 6.9 mmol). After 0.5 h, the solution was warmed to room temperature and an additional portion of sodium nitrite (1 g, 14.5 mmol), HBr (1 mL, 48%) and water (2 mL). After the bubbling stopped, the solution was made alkaline and sodium thiosulfite was added to remove excess bromine. The product was then extracted with CH_2Cl_2 (3×). The organic layers were combined and dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo to give a yellow solid (0.33 g, 51%). Mp: 93–94°C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J=2.2 Hz, 1H), 8.25 (d, J=2.2 Hz, 1H).

7.7.19. 5-Bromo-3-nitro-2-phenylethynyl-pyridine (19). Compound **18** (2.05 g, 7.27 mmol) was coupled to phenylacetylene (0.80 mL, 7.27 mmol) according to the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.15 g, 0.21 mmol), copper(I) iodide (0.08 g, 0.43 mmol), THF (10 mL), and DIEA (2.5 mL, 14.5 mmol) were combined and the reaction mixture was allowed to stir for 2 h at room temperature. Column chromatography, silica gel (1:1 hexanes/CH_2Cl_2) afforded the product as dark yellow flakes (1.32 g, 60%). Mp: 83–85°C. IR (KBr) 3071.3, 2218.4, 1577.4, 1544.6, 1513.7, 1487.0, 1434.8, 1369.0, 1334.9, 1218.9, 1151.0, 1100.0, 1070.5, 913.9, 892.7, 836.9, 755.7, 687.1, 518.8 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J=2.0 Hz, 1H), 8.52 (d, J=2.2 Hz, 1H), 7.66 (m, 2H), 7.40 (m, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 155.1, 136.1, 135.3, 133.0, 130.7, 129.0, 121.5, 119.1, 99.7, 84.9. HRMS calcd for $C_{13}H_7BrN_2O_2$: 301.9695. Found: 301.9691.

7.7.20. 3-Nitro-2-phenylethynyl-5-trimethylsilanylethynyl-pyridene (20). Compound **19** (1.3 g, 4.28 mmol) was coupled with TMSA (0.73 mL, 5.14 mmol) following the general coupling procedure. Bis(triphenylphosphine)palladium(II) dichloride (0.09 g, 0.13 mmol), copper(I) iodide (0.05 g, 0.26 mmol), THF (10 mL), and DIEA (1.49 mL, 8.56 mmol) were combined and the mixture was allowed to stir at room temperature for 2 h. Column chromatography, silica gel (1:2 hexanes/CH_2Cl_2) 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, 862.2, 842.8, 806.7, 766.4, 751.2, 685.1, 631.6, 561.4, 529.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 146.5, 136.1, 135.2, 133.1, 130.6, 129.0, 121.7, 120.2, 104.0, 100.0, 99.1, 85.6, 0.0. HRMS calcd for $C_{18}H_{16}N_2O_2Si$: 320.0983. Found: 320.0981.

7.7.21. Thioacetic acid *S*-{4-[2-(2-nitro-4-styryl-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 orange to dark purple and the solution was allowed stirred for 1 h. Acetyl chloride was added (0.5 mL, 6.4 mmol) 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 $MgSO_4$, 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: 128–131°C. IR (KBr) 3027.5, 2923.6, 1706.5, 1634.6, 1523.1, 1492.8, 1449.2, 1406.1, 1347.1, 1318.5, 1283.2, 1258.3, 1215.6, 1187.6, 1121.7, 1088.3, 1011.4, 965.5, 906.0, 814.2, 751.1, 690.0, 615.8, 564.9, 529.4 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J=1.6 Hz, 1H), 7.74 (d J=8.4 Hz, 1H), 7.70 (dd, J=8.4, 1.6 Hz, 1H), 7.62 (d, J=16.0 Hz, 1H), 7.57–7.48 (m, 4H), 7.42–7.36 (m, 4H), 7.30 (tt, J=7.2, 2.0 Hz, 1H), 7.21 (d, J=16.0 Hz, 1H), 7.09 (dd, J=16.0, 2.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 148.8, 138.5, 138.1, 136.7, 135.2, 132.8, 132.0, 131.5, 130.9, 129.3, 129.0, 128.7, 128.5, 128.1, 127.3, 126.2, 125.1, 122.8, 30.7. HRMS calcd for $C_{24}H_{19}NO_3S$: 401.1086. Found: 401.1084.

7.7.22. Thioacetic acid *S*-{4-[2-(4-styrylphenyl)-vinyl]-phenyl} ester (22). To a large test-tube equipped with a stir bar was added **35** (0.20 g, 0.48 mmol) and THF (5 mL). To the solution was added dropwise TBAF (4.8 mL, 1 M in THF). The solution changed from light yellow to blood-red and stirring was continued for 1 h. Acetyl chloride (0.7 mL, 9.6 mmol) was added and the solution changed to light yellow. After stirring for an additional 15 min the mixture was worked up with water (10 mL) and extracted with ethyl acetate (20 mL). The organics were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by running the material through a plug of silica to afford the desired product as a bright yellow solid (0.09 g, 54%). Mp: 200–210°C dec. IR (KBr) 3022.9, 1699.5, 1589.0, 1510.3, 1488.1, 1447.7, 1417.5, 1352.6, 1120.7, 1011.2, 967.2, 945.8, 861.8, 826.2, 754.4, 691.9, 615.9, 549.2 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 8H), 7.39–7.33 (m, 4H), 7.27–7.23 (m, 1H), 7.12–7.11 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 139.0, 137.7, 137.5, 136.7, 135.1, 130.2, 129.3, 129.1, 128.6, 128.1, 127.9, 127.6, 127.4, 127.3, 127.2, 127.0, 30.6. HRMS calcd for $C_{24}H_{20}OS$: 356.1235. Found: 356.1237.

7.7.23. Thioacetic acid *S*-[4-(2-{4-[2-(4-acetylsulfanyl-phenyl)-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 $MgSO_4$, 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 dec. 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, $CDCl_3$) 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), 7.18–7.08 (m, 3H), 2.43 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 194.0, 148.7, 137.8, 137.7, 135.0, 135.0, 132.9, 131.6, 130.8, 130.7, 128.6, 128.4, 128.2, 127.9, 127.7, 127.4, 124.8, 122.8, 30.5. HRMS calcd for $C_{26}H_{21}NO_4S_2$: 475.0912. Found: 475.0912.

7.7.24. Tributylvinylstannane (24).[27] Vinyl magnesium bromide (100.0 mL of a 1 M solution in THF) and tributyltin chloride (13.8 mL, 50.0 mmol) were added to a N_2 purged 250 mL round-bottom flask equipped with a stir bar and a condenser. The solution was heated at reflux overnight and then cooled to room temperature. NH_4Cl (aq) (80 mL) was added slowly to the mixture and the organics were decanted into a 500 mL round-bottom flask. The remaining aqueous layer was washed with ether (4×50 mL) and the ether was decanted into the round-bottom. The product was purified by distilling at 115°C at 2.5 mm Hg to yield the desired product as a clear liquid (11.79 g, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.45 (dd, J=20.8, 14.1 Hz, 1H), 6.13 (dd, J=14.0, 3.7 Hz, 1H), 5.64 (dd, J=20.7, 3.6 Hz, 1H), 1.49 (m, 6H), 1.29 (sex, J=7.2 Hz, 6H), 0.87 (m, 15H).

7.7.25. 4-Vinylbenzenethioacetate (25).[26] 4-(Thioacetyl)-iodobenzene[1] (1.92 g, 6.92 mmol), bis(dibenzylideneacetone)-palladium (0.120 g, 0.21 mmol), triphenylarsene (0.129 g, 0.42 mmol), tributylvinylstannane **24** (2.12 mL, 7.27 mmol), and THF (15 mL) were coupled according to the general Stille coupling procedure. The crude product was purified via column chromatography, silica gel (1:1 CH_2Cl_2/petroleum ether) to yield 0.844 g (68%) of a yellow oil.

IR (KBr) 3087.9, 3008.5, 2956.8, 2922.6, 2853.8, 1708.7, 1629.2, 1593.3, 1491.8, 1420.9, 1395.5, 1352.6, 1269.1, 1114.0, 1093.0, 1013.1, 989.9, 949.9, 913.8, 837.0, 738.0, 610.1 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dt, J=8.2, 1.8 Hz, 2H), 7.34 (dt, J=8.2, 1.9 Hz, 2H), 6.70 (dd, J=17.7, 10.9 Hz, 1H), 5.78 (dd, J=17.6, 0.8 Hz, 1H), 5.31 (dt, J=10.9, 0.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 139.2, 136.4, 135.0, 127.5, 127.4, 115.9, 30.6.

7.7.26. 2-Nitro-4-styrylaniline (26). 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 according to the general Heck coupling reaction above. The crude product was purified via flash column chromatography, silica gel (1:1 CH_2Cl_2/hexanes) to yield 3.30 g, (69%) of a bright red solid. Mp: 202–206°C dec. IR (KBr) 3466.5, 3338.7, 3177.5, 3024.5, 1639.4, 1596.5, 1554.3, 1519.6, 1468.9, 1410.9, 1346.3, 1272.1, 1223.8, 1191.9, 1175.8, 1093.3, 957.4, 927.3, 825.6, 749.5, 689.9, 625.3, 553.5, 509.6 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J=2.4 Hz, 1H), 7.58 (dd, J=8.4, 2.0 Hz, 1H), 7.48–7.46 (m, 2H), 7.34 (td, J=7.2, 1.6 Hz, 2H), 7.26–7.22 (m, 1H), 6.80 (d, J=8.4, 1H), 6.12 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.4, 133.7, 132.6, 129.2, 128.2, 128.2, 127.5, 126.8, 126.8, 124.5, 119.6. HRMS calcd for $C_{14}H_{12}N_2O_2$: 240.0899. Found: 240.0900.

7.7.27. 2-Nitro-4-styrylbenzenediazonium tetrafluoroborate (27). Boron trifluoride etherate (2.10 mL, 16.64 mmol) was added to a 100 mL round-bottom flask and the temperature was reduced to −30°C. **26** (1.00 g, 4.16 mmol) in THF (20 mL) was added dropwise to the round-bottom flask. *tert*-Butylnitrite (1.73 mL, 14.56 mmol) in THF (15 mL) was then added dropwise and the temperature was allowed to rise to −5°C for 30 min. Ether (25 mL) was then added and the orange precipitate was then collected via a fritted funnel and washed with ether (20 mL) to yield 1.31 g (94%) of desired product that was taken directly on to the next step without characterization.

7.7.28. 5-Ethenylphenyl-2-iodonitrobenzene (28). Iodine (0.75 g, 2.95 mmol), sodium iodide (0.88 g, 5.90 mmol), and acetonitrile (25 mL) were added to a 250 mL round-bottom flask equipped with a stir bar. **27** was added in one portion to the round-bottom flask. The mixture was allowed to stir until the N_2 evolution ceased (15 min). A saturated solution of sodium thiosulfate (50 mL) and CH_2Cl_2 (50 mL) were then added and stirred for 20 min. The layers were separated and the organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude material was purified via flash column chromatography, silica gel (1:1 CH_2Cl_2/hexanes) to yield 0.85 g (82%) of a yellow solid. Mp: 77–80°C. IR (KBr) 3057.7, 3025.0, 1633.4, 1545.6, 1524.0, 1466.4, 1353.6, 1329.7, 1109.0, 1013.2, 963.9, 892.7, 818.0, 751.2, 688.0, 553.7, 516.7 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J=8.1 Hz, 1H), 7.51 (m, 2H), 7.37 (m, 3H), 7.31 (dd, J=7.2, 1.4 Hz, 1H), 7.20 (d, J=16.3 Hz, 1H), 7.01 (d, J=16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 142.4, 139.5, 136.4, 132.8, 131.2, 129.3, 129.2, 127.3, 125.5, 123.3, 84.1. HRMS calcd for $C_{14}H_{10}INO_2$: 350.9756. Found: 350.9755.

7.7.29. 2-Nitro-4-styryl-1-(4-vinyl-phenylsulfanyl)-benzene (29). Palladium(II) acetate (11 mg, 0.050 mmol) and BHT (1 crystal) were added to a 25 mL round-bottom flask. The atmosphere was removed and replaced with N_2 and a solution of **25** (0.18 g, 1.0 mmol), **28** (0.35 g, 1.0 mmol), and DIEA (0.19 mL, 1.1 mmol) in DMF (5 mL) was then added via cannula to the round-bottom flask. The reaction mixture was heated to 85°C overnight, cooled and quenched with water (20 mL) and extracted with ether (20 mL). The layers were separated and the organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude material was purified via flash column chromatography, silica gel (1:1 CH_2Cl_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}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J=2.0 Hz, 1H), 7.54–7.43 (m, 7H), 7.37–7.33 (m, 2H), 7.30–7.28 (m, 1H), 7.12 (d, J=16.0 Hz, 1H), 7.01 (d, J=16.4 Hz, 1H), 6.86 (d, J=8.4 Hz, 1H), 6.75 (dd, J=17.6, 10.8 Hz, 1H), 5.85 (dd, J=17.6, 0.4 Hz, 1H), 5.38 (dd, J=10.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 139.7, 138.3, 136.8, 136.3, 136.2, 135.4, 131.3, 131.3, 130.7, 129.2, 129.1, 128.8, 128.2, 127.1, 125.9, 123.6, 116.4. HRMS calcd for $C_{22}H_{17}NO_2S$: 359.0980. Found: 359.0981.

7.7.30. 2-Ethenyl-5-ethenylphenylnitrobenzene (30). Bis-(dibenzylideneacetone)palladium (0.081 g, 0.14 mmol), **28** (1.00 g, 2.85 mmol), triphenylarsene (0.086 g, 0.28 mmol), tributylvinylstannane (0.948 g, 2.99 mmol), BHT (1 crystal) and THF (10 mL) were reacted according to the general Stille coupling procedure above. The crude product was purified via flash column chromatography, silica gel (3:1 hexanes/CH_2Cl_2) to yield 0.646 g, (90%) of a yellow solid. Mp: 76–77°C. IR (KBr) 3078.1, 3055.3, 3026.2, 2945.1, 2925.1, 1627.1, 1543.6, 1520.6, 1491.2, 1448.2, 1415.7, 1351.6, 1149.6, 1072.5, 968.4, 922.9, 866.0, 833.1, 814.2, 752.8, 690.5, 619.6, 556.1, 511.0 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J=1.8 Hz, 1H), 7.68 (dd, J=8.2, 1.9 Hz, 1H), 7.61 (d, J=8.2 Hz, 1H), 7.52 (m, 2H), 7.37 (m, 2H), 7.30 (tt, J=7.3, 2.2 Hz, 1H), 7.19 (d, J=16.3 Hz, 1H), 7.15 (dt, J=17.3, 11.0 Hz, 1H), 7.07 (d, J=16.3 Hz, 1H), 5.77 (dd, J=17.3, 0.9 Hz, 1H), 5.48 (dd, J=10.9, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 138.5, 136.7, 132.5, 132.1, 131.9, 130.9, 129.3, 129.0, 128.9, 127.2, 126.2, 122.4, 119.1. HRMS calcd for $C_{16}H_{13}NO_2$: 251.0946. Found: 251.0947.

7.7.31. [2-(4-Iodophenylsulfanyl)ethyl]trimethylsilane (31).[30] To a 250 mL round-bottom flask was added 2-(trimethylsilyl)ethyl-4′-bromophenyl sulfide (3.00 g, 10.35 mmol) and THF (30 mL). The solution was cooled to −78°C and *tert*-butyllithium (10.5 mL of a 1.7 M solution in pentane) was added dropwise. The solution was stirred at −78°C for 20 min. Diiodoethane (2.77 g, 9.82 mmol) in THF (15 mL) was added and the reaction mixture was allowed to warm to room temperature over 20 min. The reaction was quenched with a saturated solution of sodium thiosulfate (50 mL) and extracted with ether (3×30 mL). The layers were separated and the organic phase was dried over $MgSO_4$, filtered and the solvent removed in vacuo. The crude product was purified via flash

column chromatography, silica gel (hexanes) to yield 1.94 g (65%) of a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) 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), triphenylarsene (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, 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}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J=8.6 Hz, 2H), 7.24 (d, J=8.4 Hz, 2H), 6.65 (dd, J=17.6, 10.09 Hz, 1H), 6.69 (dd, J=17.5, 0.8 Hz, 1H), 5.20 (dd, J=10.9, 0.9 Hz, 1H), 2.96–2.92 (m, 2H), 0.94–0.87 (m, 2H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.6, 135.5, 129.3, 127.0, 113.8, 29.9, 17.3, −1.4. HRMS calcd for $C_{13}H_20SSi$: 236.1055. Found: 236.1055.

7.7.33. Trimethyl-(2-{4-[2-(2-nitro-4-styryl-phenyl)-vinyl]-phenylsulfanyl}-ethyl)-silane (33). Palladium(II) acetate (0.009 g, 0.040 mmol), K_2CO_3 (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 CH_2Cl_2/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}. ^{1}H NMR (400 MHz, $CDCl_3$) 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 Hz, 2H), 7.39–7.36 (m, 3H), 7.32–7.26 (m, 3H), 7.20 (d, J=16.4, 1H), 7.07 (dd, J=16.4, 3.6 Hz, 2H), 3.00–2.96 (m, 2H), 0.96–0.92 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{27}H_{29}NO_2SSi$: 459.1688. Found: 459.1687.

7.7.34. 4-Ethenylphenylbromobenzene (34). Palladium (II) acetate (0.22 g, 1.0 mmol), K_2CO_3 (2.49 g, 18.0 mmol), tetrabutylammonium bromide (9.35 g, 1.12 mmol), styrene (2.31 mL, 20.0 mmol), 4-bromoiodobenzene (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. Mp: 122–126°C. IR (KBr) 3079.2, 3019.9, 1578.6, 1489.5, 1447.3, 1399.2, 1327.8, 1302.0, 1215.2, 1183.2, 1072.4, 1004.6, 966.8, 863.4, 813.0, 749.6, 689.1, 525.9 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (m, 4H), 7.38–7.33 (m, 4H), 7.26 (tt, J=7.2, 1.2 Hz, 1H), 7.09 (d, J=16.4 Hz, 1H), 7.01 (d, J=16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.7, 132.2, 129.8, 129.2, 128, 8.4, 128.3, 127.8, 127.0, 121.7. HRMS calcd for $C_{14}H_{11}Br$: 258.0044. Found: 258.0044.

7.7.35. Trimethyl-(2-{4-[2-(4-styryl-phenyl)-vinyl]-phenylsulfanyl}-ethyl)-silane (35). Palladium(II) acetate (0.023 g, 0.10 mmol), K_2CO_3 (0.258 g, 1.87 mmol), tetrabutylammonium bromide (0.974 g, 3.02 mmol), **32** (0.541 g, 2.29 mmol), **34** (0.539 g, 2.08 mmol) and DMF (10 mL) were reacted overnight at 105°C according to the general Heck coupling procedure above. The crude product was purified via flash column chromatography, silica gel (hexanes) to yield 0.754 g (87%) of a pale yellow green solid. Mp: 240–250°C dec. IR (KBr) 3021.8, 2950.4, 1584.4, 1510.4, 1489.6, 1444.4, 1416.1, 1247.0, 1162.5, 1089.2, 1009.5, 965.9, 823.5, 751.7, 689.9, 545.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 6H), 7.42 (d, J=8.4 Hz, 2H), 7.35 (t, J=7.6 Hz, 2H), 7.27 (d, J=8.4 Hz, 2H), 7.14–7.06 (m, 4H), 2.99–2.94 (m, 2H), 0.95–0.91 (m, 2H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.2, 137.1, 137.1, 135.3, 129.4, 129.1, 129.0, 128.7, 128.4, 128.2, 128.1, 127.3, 127.3, 127.2, 126.9, 29.9, 17.3, −1.3. HRMS calcd for $C_{27}H_{30}SSi$: 414.1838. Found: 414.1838.

7.7.36. 2-Nitro-1,4-bis-{2-[4-(2-trimethylsilanyl-ethylsulfanyl)-phenyl]-vinyl}-benzene (36). Palladium(II) acetate (0.045 g, 0.20 mmol), K_2CO_3 (0.498 g, 3.60 mmol), tetrabutylammonium bromide (1.87 g, 5.80 mmol), **32** (1.04 g, 4.40 mmol), 2,5-dibromonitrobenzene (0.56 g, 2.0 mmol) and DMF (10 mL) were combined overnight at 90°C according to the general Heck coupling procedure above. The crude product was purified via flash column chromatography, silica gel (3:1 hexanes/CH_2Cl_2) to yield 0.54 g (46%) of a yellow-orange solid. Mp: 114–120°C. IR (KBr) 3022.1, 2950.6, 1621.3, 1589.8, 1519.7, 1493.9, 1404.9, 1349.5, 1248.4, 1186.7, 1165.3, 1090.2, 1012.4, 962.1, 895.3, 859.5, 830.0, 758.5, 726.2, 690.9, 545.0, 505.2 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J=1.6 Hz, 1H), 7.73 (d, J= 8.0, 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). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 138.8, 138.6, 138.0, 134.2, 134.0, 133.3, 131.7, 131.1, 130.1, 128.9, 128.9, 128.4, 127.9, 127.6, 125.6, 122.8, 122.7, 30.1, 29.5, 17.2, −1.6. HRMS calcd for $C_{32}H_{41}NO_2S_2Si_2$: 591.2117. Found: 591.2114.

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