

Synthesis and properties of conjugated phenylene ethynylene derivatives

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Abstract

Fourteen new conjugated phenylene ethynylene derivatives as potential molecular electronic devices are presented here. These new compounds were synthesized by convergent synthetic methodologies which are based on Sonogashira and Suzuki couplings. The synthesized compounds were identified by ^1H NMR, ^{13}C NMR, IR, HRMS and elemental analysis. The UV-vis maximum absorption spectra were in the range of 304-321 nm in CHCl_3 . Cyclic voltammetry (CV) test results showed two distinct reduction peaks.

Keywords: Suzuki reaction, Sonogashira reaction, spectra properties, electrochemical properties

Introduction

In the past few years, molecular electronics has attracted much interest of chemists and physicists.¹ Rigid rod conjugated oligo(phenylene ethynylene)s (OPEs) are one family of molecules that have interesting molecular electronic properties.² OPEs derivatives containing thiol groups can form self-assembled monolayers (SAMs) on the surface of Au, Ag or other metals.³ SAMs plays an important role in the constructure ordered nanostructure in molecular electronics. Chemical functionalization of OPEs with nitro groups and terminal sulfur groups exhibits negative differential resistance (NDR) and molecular random access memory effects.⁴ Numerous theoretical studies of the nitro group effect and electron transport behavior are still under investigation.⁵ Several groups⁶ have been pursuing the ultimate miniaturization of electronic components, synthesizing diverse organic molecules that can be used as electronic devices. Since then, considerable work has been focused on their synthesis.⁷

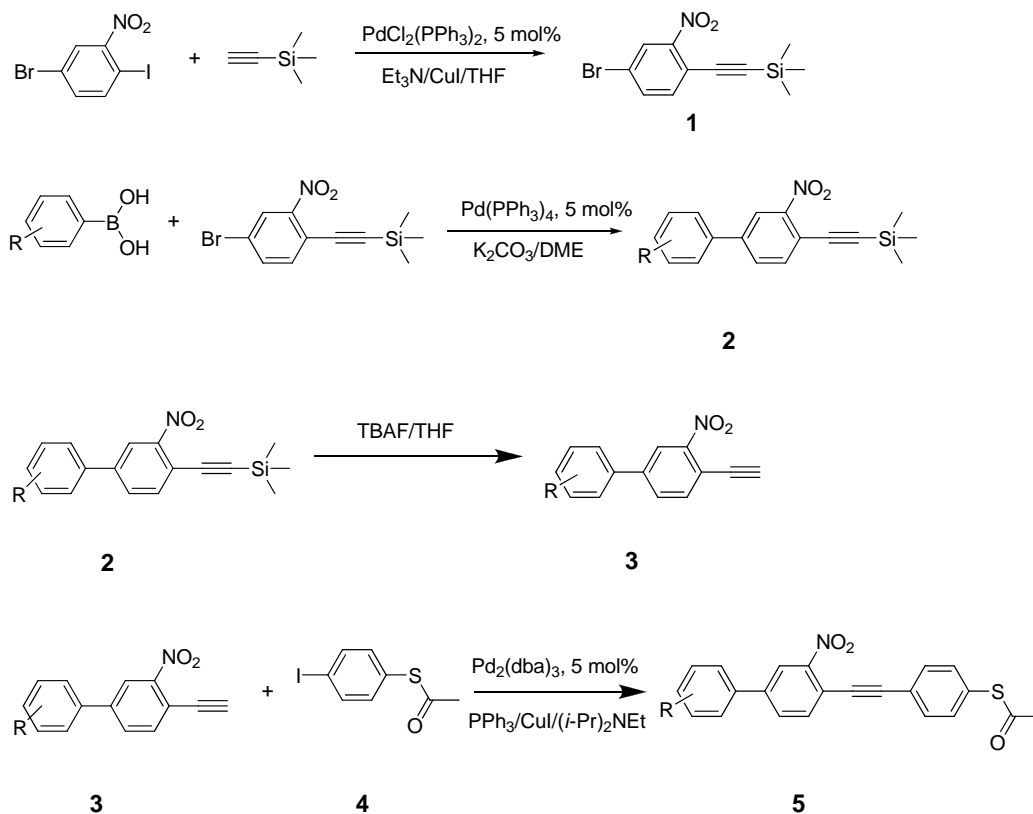
Here, new conjugated phenylene ethynylene derivatives containing protected thiol end

groups are designed and synthesized. These new compounds could be used as potential molecular electronics devices. Target compounds are synthesized using convergent synthetic methodologies which are based on Sonogashira⁸ and Suzuki⁹ couplings for aryl-ethynyl and aryl-aryl bond formations. In addition to these syntheses, the spectroscopic and electrochemical properties of these compounds were also tested.

Results and Discussion

Synthesis

The synthetic route of conjugated phenylene ethynylene derivatives **5** is outlined in Scheme 1. The central core of 4-bromo-1-iodo-2-nitrobenzene was synthesized according to the literature methods.^{7g} Compound **1** was synthesized according to the literature methods^{7g,10} in 91% yields. Then compound **1** reacted with substituted phenylboronic acid to furnish compounds **2** in moderate (17-84%) yields.



Scheme 1. The synthetic route of target compounds **5**.

Synthesis of compounds **2** was carried out using 5 mol % tetrakis(triphenylphosphine)

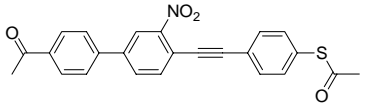
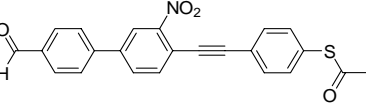
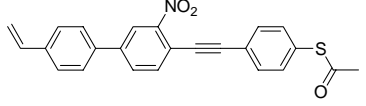
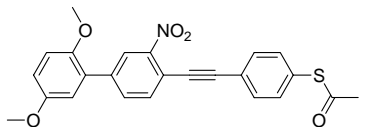
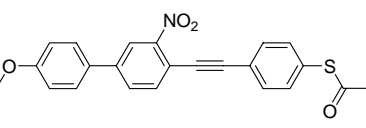
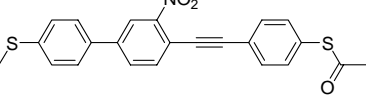
palladium(0) as catalyst and potassium carbonate (K_2CO_3) as base in 1,2-dimethoxyethane (DME) and H_2O at reflux temperature. Terminal alkyne **3h** was also achieved in this step when R was 4-acetyl group and the yield was 31%.

Sequentially, the compounds **2** were desilylated using tetrabutylammonium fluoride (TBAF) to furnish the terminal alkynes **3** in moderate to high (31-97%) yields. Finally, conjugated phenylene ethynylene derivatives **5** can readily be achieved by reaction of the corresponding terminal alkynes **3** with the protected-thiol “alligator clip” **4**^{7a,11} using palladium catalyzed Sonogashira cross coupling reaction. Reaction was carried out using tris(dibenzylideneacetone)dipalladium(0) (5 mol% based on aryl halide) as catalyst, copper(I) iodide (10 mol% based on aryl halide) as co-catalyst and triphenyl phosphine (20 mol% based on aryl halide) as ligand in tetrahydrofuran at 50 °C with *N,N*-diisopropylethylamine as base. The structure and isolated yields of products **5** are shown in Table 1. The yields of product **5** are from 12 to 79%. It is found that the yields were the highest when R was 4-thiomethyl group **5m**.

Table 1. Data of conjugated phenylene ethynylene derivatives **5**

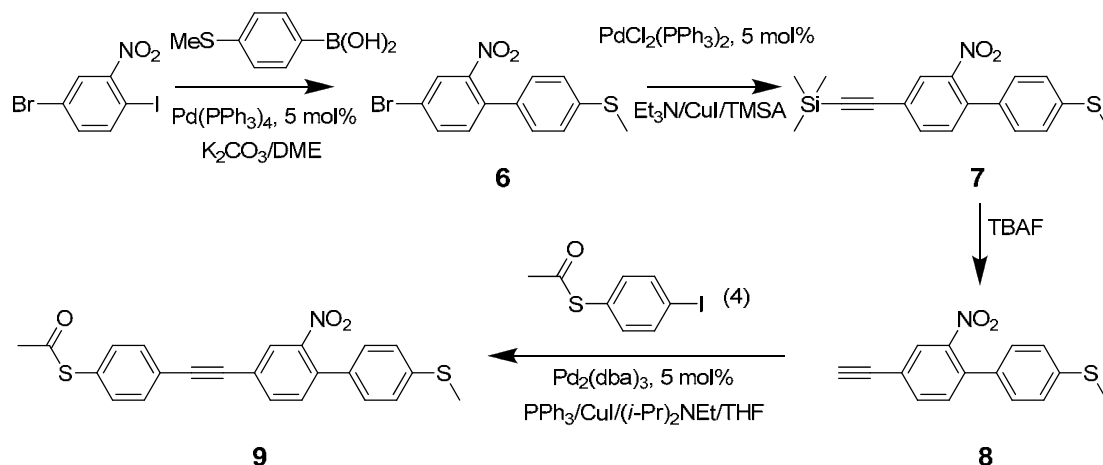
Compounds	Structure	Yields (%)
5a		27
5b		53
5c		37
5d		61
5e		45
5f		52
5g		26

Table 1. Continued

Compounds	Structure	Yields (%)
5h		22
5i		38
5j		12
5k		22
5l		44
5m		79

Variation of functional groups, both number and location can have a profound influence on the electronic properties of the compounds.¹² Considering this, the derivatives **9** was prepared using a protocol similar to that described above.

4-Bromo-1-iodo-2-nitrobenzene was highly selectively coupled with 4-(methylthio)phenyl boronic acid to give cross-coupling product of compound **6** in 87% yield. Next **6** was coupled with trimethylsilylacetylene (TMSA) to afford **7**, and then deprotected with TBAF to furnish **8**. A final coupling with the protected-thiol “alligator clip” **4** afforded the desired product **9** in 45% yields.



Scheme 2. The synthetic route to target compound **9**.

UV-vis spectral properties

In order to study the optical properties of these compounds, the UV-vis absorption spectra were tested in CHCl₃ solution. The UV-vis maximum absorption wavelength ($\lambda_{\text{abs}}^{\text{max}}$) and molar absorption coefficient (ϵ) of compounds **5a-m** and **9** are presented in Table 2. The $\lambda_{\text{abs}}^{\text{max}}$ of compounds **5a-m** and **9** was in the range of 304~321 nm. When R was H (**5b**, entry 2), $\lambda_{\text{abs}}^{\text{max}}$

Table 2. The spectral properties of compounds **5a-m** and **9**

Entry	Compounds	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	ϵ (L/mol/cm)
1	5a	304	2.63×10^4
2	5b	307	2.44×10^4
3	5c	310	2.11×10^4
4	5d	310	2.14×10^4
5	5e	312	2.46×10^4
6	5f	312	2.52×10^4
7	5g	312	1.69×10^4
8	5h	314	2.89×10^4
9	5i	315	2.47×10^4
10	5j	316	2.26×10^4
11	5k	316	2.0×10^4
12	5l	316	3.30×10^4
13	5m	321	3.54×10^4
14	9	314	3.60×10^4

was 307 nm. Introducing electron-donating substituted groups (R= 4-ethyl (**5e**), 2,5-dimethoxy (**5k**), 4-methoxy (**5l**), 4-thiomethyl (**5m**), and compound **9**; entry 5, 11-14) caused bathochromic

shift of 5~14 nm compared with **5b**. While substituted groups R was electron-withdrawing groups (R= 4-fluoro (**5c**), 4-trifluoromethyl (**5d**), 4-chloro (**5f**), 4-cyano (**5g**), 4-acetyl (**5h**), 4-formyl (**5i**), and 4-vinyl (**5j**); entry 3, 4, 6-10), $\lambda_{\text{abs}}^{\text{max}}$ generated bathochromic shift of 3~9 nm compared with **5b**. However when R was 2,3-dimethoxy (**5a**, entry 1), $\lambda_{\text{abs}}^{\text{max}}$ caused hypsochromic shift of 3 nm compared with **5b**. From this it can be seen that variation of substituted groups R had effect on spectral properties and the largest bathochromic shift in $\lambda_{\text{abs}}^{\text{max}}$ occurred when R was thiomethyl group (**5m**, entry 13).

Cyclic voltammetry

Cyclic voltammetry (CV) can help us understand how some of molecules might behave as switches and memory elements.¹³ Hence the new products' electrochemical properties were tested by CV measurements. The CV was performed at room temperature on a CHI-650C voltametric analyzer using a glassy carbon electrode as working electrode, with an Ag/AgCl reference electrode. The solutions were 1 mmol in CH₂Cl₂ and 0.1 M tetrabutylammonium perchlorate (n-Bu₄NClO₄) with a scan rate of 0.1 V/s.

CV test results of selected compounds **5a**, **5b**, **5m** and **9** are listed in Figure 1. It is found that the four compounds showed the first reductions potential at -1.1 V and the second reduction potential at -1.82 V (**5a**), -1.63 V (**5b**), -1.71 V (**5m**) and -1.73 V (**9**). These gave the potential difference of 0.72 V (**5a**), 0.53 V (**5b**), 0.61 V (**5m**) and 0.63 V (**9**). The first reduction peaks of four compounds appear to be reversible in this system. The CV of unsubstituted **5b** were compared to the CV of substituted **5a**, **5m** and **9** in the side of phenyl ring, the first reduction potential of **5b** are approximately the same as **5a**, **5m** and **9**. However, the second reduction potential of **5b** is higher than **5a**, **5m** and **9**.

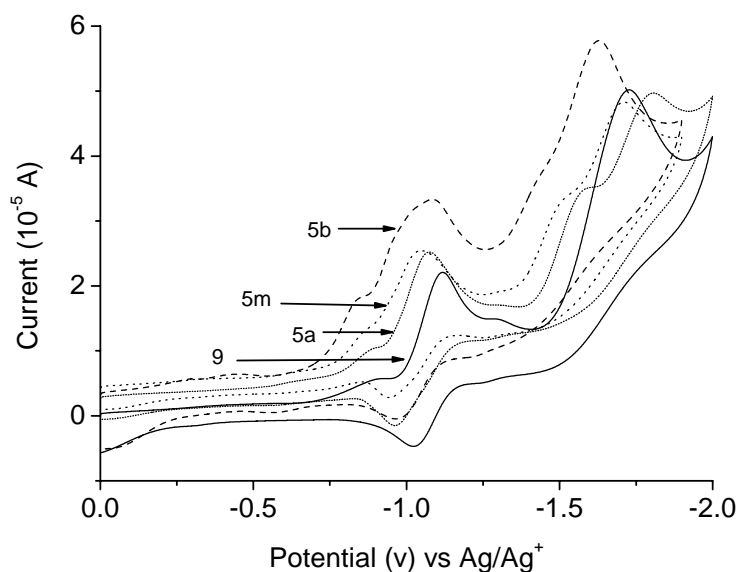


Figure 1. Cyclic voltammetry of selected compounds **5a**, **5b**, **5m** and **9**.

The first and the second reduction potentials of these four compounds are drastically reduced compared with the reference reported “nitroaniline compound **1**”¹³ (the first reduction potential at -1.7 V and the second reduction potential at -2.3 V). This might provide for a solid-state device with lower operating voltages than the “nitroaniline compound **1**” devices.

Summary

Fourteen novel conjugated phenylene ethynylene derivatives are designed and synthesized using convergent synthetic methodologies that are based on Sonogashira and Suzuki couplings for aryl-ethynyl and aryl-aryl bond formations. Each structure bears one nitro moiety and the “alligator clips”. It was found that UV-vis maximal absorption spectra were in the range of 304~321 nm and compounds **5m** (R=SMe) have the largest $\lambda_{\text{abs}}^{\text{max}}$ than other compounds. From CV reduction curves we can see that selected compounds showed two obvious distinct reduction peaks. Work on further applications is currently underway in our laboratory.

Experimental Section

General. Unless stated otherwise, reactions were performed in dry, nitrogen-flushed glassware, using freshly distilled solvents. Reagent grade tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. Reagent grade chloroform (CHCl_3) and ethyl acetate (EtOAc) was used without further distillation. All other commercially available reagents were used as received. Silica gel for thin-layer chromatography was used from Qingdao Haiyang Chemical Co. Ltd. Melting points were measured by a XT5 melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 500MHz spectrometer using TMS as an internal reference. Chemical shift values (δ) were given in ppm. Infrared spectra were obtained on a NEXUS670 spectrophotometer using potassium bromide pellets and are reported as wave numbers (cm^{-1}). High Resolution mass spectra were performed on a GCT Premier spectrometer.

General procedure for the Suzuki cross coupling reaction

Aryl halide, aryl boronic acid and tetrakis(triphenylphosphine) palladium(0) (5 mol% based on aryl halide).were added in sequence to a round bottom flask equipped with a magnetic stir bar. Then the vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen (3 \times). DME was added followed by aqueous K_2CO_3 . The reaction heated at 85°C and monitored by TLC. The reaction vessel was cooled to room temperature and the mixture quenched with water and extracted with organic solvents (3 \times). The combined organic layers were dried over anhydrous MgSO_4 and the solvent was removed in vacuo. The crude product was then purified by flash chromatography.

General procedure for alkaline deprotection of trimethylsilyl-protected alkynes

The TMS-protected alkyne was added to an open round bottom flask equipped with a stirring bar and tetrabutylammonium fluoride (TBAF) buffered with a mixture of acetic acid (AcOH) and acetic anhydride (Ac₂O). THF was added to dissolve the organic compound. The reaction was monitored by TLC until deprotection was complete. The reaction was quenched with water and extracted with organic solvents (3×). The combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed in vacuo. The crude product was then purified by flash chromatography.

General procedure for the Sonogashira cross coupling reaction

The aryl halide, tris(dibenzylideneacetone)dipalladium(0) (5 mol% based on aryl halide) or bis(triphenylphosphine)palladium(II) dichloride (5 mol% based on aryl halide), and copper(I) iodide (10 mol% based on aryl halide), triphenyl phosphine (20 mol% based on aryl halide, if necessary) were added in sequence to a round bottom flask equipped with a magnetic stir bar. Then the vessel was sealed with rubber septum, evacuated and backfilled with nitrogen (3×). THF was added followed by Hünig's base or TEA. The terminal alkyne was then added and the reaction was heated if necessary (monitored by TLC). The reaction vessel was cooled to room temperature and the mixture quenched with water. The organic layer was diluted with organic solvent and washed with a saturated solution of NH₄Cl (3×). The combined aqueous layers were extracted with organic solvent (3×), dried over anhydrous MgSO₄ and the solvent was removed in vacuo. The crude product was then purified by flash chromatography

4'-Ethynyl-2,3-dimethoxy-3'-nitrobiphenyl (3a). The general Suzuki cross coupling procedure was followed using **1** (0.594 g, 2 mmol), 2,3-dimethoxyphenylboronic acid (0.728 g, 4 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1156 g, 0.1 mmol), K₂CO₃ (aq. 2M 1.05 mL), DME (10 mL) at 85 °C for 10h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=15/1) furnished ((2',3'-dimethoxy-3-nitrobiphenyl-4-yl)ethynyl)trimethylsilane (**2a**) as a colorless oil (0.5321 g, 75% yield). It was used directly for the next step. The general deprotection protocol was followed using **2a** (0.5321 g, 1.5 mmol), TBAF (0.5828 g, 2.25 mmol), AcOH (0.18 g, 3 mmol), Ac₂O (0.306 g, 3 mmol), THF (10 mL) at r.t. for 30min. Purification by flash chromatography (petroleum ether/CH₂Cl₂=8/1) furnished a white solid (0.4059 g, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.53 (s, 1 H, CH), 3.65 (s, 3 H, CH₃), 3.93 (s, 3 H, CH₃), 6.96 (q, 1 H, *J* = 1.5 Hz, Ar-H), 6.99 (q, 1 H, *J* = 1 Hz, Ar-H), 7.16 (t, 1 H, *J* = 8 Hz, Ar-H), 7.72 (d, 1 H, *J* = 8 Hz, Ar-H), 7.82 (q, 1 H, *J* = 1 Hz, Ar-H), 8.26 (d, 1 H, *J* = 1 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 56.0, 60.8, 78.8, 85.1, 113.2, 115.8, 121.9, 124.6, 125.3, 132.5, 133.6, 135.1, 139.9, 146.6, 150.2, 153.3. Anal. Calcd for C₁₆H₁₃NO₄: C, 67.84; H, 4.63; N, 4.94; Found: C, 67.92; H, 4.85; N, 5.02.

4-Ethynyl-3-nitrobiphenyl (3b). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), phenylboronic acid (0.732 g, 6 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=40/1) furnished

trimethyl((3-nitrophenyl-4-yl)ethynyl)silane (**2b**) as an orange oil (0.49 g, 55% yield). It was used directly for the next step. The general deprotection protocol was followed using **2b** (0.49 g, 1.66 mmol), TBAF (0.6453 g, 2.49 mmol), AcOH (0.1992 g, 3.32 mmol), Ac₂O (0.3386 g, 3.32 mmol), THF (10 mL) at r.t. for 40min. Purification by flash chromatography (petroleum ether/CH₂Cl₂=15/1) furnished a pale yellow solid (0.2125 g, 57% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.55 (s, 1 H, CH), 7.43-7.46 (m, 1 H, Ar-H), 7.48-7.51 (m, 2 H, Ar-H), 7.61-7.65 (m, 2 H, Ar-H), 7.75 (d, 1 H, *J* = 8.1 Hz, Ar-H), 7.81 (q, 1 H, *J* = 1.8 Hz, Ar-H), 8.27 (d, 1 H, *J* = 1.75 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.5, 85.4, 115.8, 122.8, 127.0, 128.9, 129.2, 130.9, 135.8, 137.7, 142.7, 150.7. Anal. Calcd for C₁₄H₉NO₂: C, 75.33; H, 4.06; N, 6.27; Found: C, 75.22; H, 4.19; N, 6.15.

4-Ethynyl-4'-fluoro-3-nitrophenyl (3c). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-fluorophenylboronic acid (0.84 g, 6 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1272 g, 0.11 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 3h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished ((4'-fluoro-3-nitrophenyl-4-yl)ethynyl)trimethylsilane (**2c**) as colorless oil (0.4628 g, 49% yield). It was used directly for the next step. The general deprotection protocol was followed using **2c** (0.4628 g, 1.48 mmol), TBAF (0.5744 g, 2.22 mmol), AcOH (0.1776 g, 3 mmol), Ac₂O (0.3019 g, 3 mmol), THF (10 mL) at r.t. for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=8/1) furnished a white solid (0.2994 g, 84% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.55 (s, 1 H, CH), 7.17-7.20 (m, 2 H, Ar-H), 7.57-7.59 (m, 2 H, Ar-H), 7.75 (q, 2 H, *J* = 1.25 Hz, Ar-H), 8.21 (d, 1 H, *J* = 1.0 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.4, 85.6, 115.9, 116.2, 116.4 (d, *J* = 22.5 Hz), 122.7, 128.8, 128.9 (d, *J* = 8.75 Hz), 130.8, 133.9, 134.0 (d, *J* = 8.75 Hz), 135.9, 141.7, 162.3, 164.3 (d, *J* = 248.75 Hz). Anal. Calcd for C₁₄H₈FNO₂: C, 69.71; H, 3.34; N, 5.81; Found: C, 69.82; H, 3.47; N, 5.98.

4-Ethynyl-3-nitro-4'-(trifluoromethyl)biphenyl (3d). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-trifluorophenylboronic acid (0.8963 g, 4.5 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 1.5h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=15/1) furnished trimethyl((3-nitro-4'-(trifluoromethyl)biphenyl-4-yl)ethynyl)silane (**2d**) as a pale yellow oil (0.628 g, 58% yield). It was used directly for the next step. The general deprotection protocol was followed using **2d** (0.3701 g, 1.02 mmol), TBAF (0.3963 g, 1.53 mmol), AcOH (0.1224 g, 2.04 mmol), Ac₂O (0.2081 g, 2.04 mmol), THF (10 mL) at r.t. for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished a pale yellow solid (0.2887 g, 97% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.60 (s, 1 H, CH), 7.72-7.80 (m, 4 H, Ar-H), 7.83 (q, 2 H, *J* = 1.4 Hz, Ar-H), 8.29 (d, 1 H, *J* = 1.4 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.3, 86.2, 116.9, 123.1, 126.2, 126.2, 126.3, 127.5, 131.1, 136.1, 141.1, 141.3. Anal. Calcd for C₁₅H₈F₃NO₂: C, 61.86; H, 2.77; N, 4.81; Found: C, 61.97; H, 2.89; N, 4.75.

4'-Ethyl-4-ethynyl-3-nitrophenyl (3e). The general Suzuki cross coupling procedure was followed using **1** (0.297 g, 1 mmol), 4-ethylphenylboronic acid (0.3 g, 2 mmol),

tetrakis(triphenylphosphine) palladium(0) (0.0578 g, 0.05 mmol), K₂CO₃ (aq. 2M 0.55 mL), DME (10 mL) at 85 °C for 1h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished ((4'-ethyl-3-nitrobiphenyl-4-yl)ethynyl)trimethylsilane (**2e**) as a pale yellow oil (0.2712 g, 84% yield). It was used directly for the next step. The general deprotection protocol was followed using **2e** (0.5206 g, 1.61 mmol), TBAF (0.6216 g, 2.42 mmol), AcOH (0.192 g, 3.22 mmol), Ac₂O (0.3264 g, 3.22 mmol), THF (10 mL) at r.t. for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished a pale yellow solid (0.3144 g, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 1.31 (t, 3 H, *J* = 7.6 Hz, CH₃), 2.75 (q, 2 H, *J* = 7.6 Hz, CH₂), 3.56 (s, 1 H, CH), 7.35 (d, 2 H, *J* = 8.05 Hz, Ar-H), 7.57 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.75 (d, 1 H, *J* = 8.05 Hz, Ar-H), 7.82 (q, 1 H, *J* = 1.7 Hz, Ar-H), 8.28 (d, 1 H, *J* = 1.65 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 15.4, 28.5, 78.6, 85.2, 115.5, 122.6, 126.9, 128.8, 130.7, 135.1, 135.8, 142.7, 145.4, 150.7. Anal. Calcd for C₁₆H₁₃NO₂: C, 76.48; H, 5.21; N, 5.57; Found: C, 76.34; H, 5.19; N, 5.45.

4'-Chloro-4-ethynyl-3-nitrobiphenyl (3f). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-chlorophenylboronic acid (0.6234 g, 4 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 3h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=5/1) furnished ((4'-chloro-3-nitrobiphenyl-4-yl)ethynyl)trimethylsilane (**2f**) as a yellow solid (0.2168 g, 22% yield). It was used directly for the next step. The general deprotection protocol was followed using **2f** (0.2168 g, 0.66 mmol), TBAF (0.2589 g, 1 mmol), AcOH (0.08 g, 1.3 mmol), Ac₂O (0.1346 g, 1.3 mmol), THF (10 mL) at r.t. for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=3/1) furnished a yellow solid (0.17 g, 91% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.57 (s, 1 H, CH), 7.47 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.55 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.74-7.78 (m, 2 H, Ar-H), 8.23 (d, 1 H, *J* = 1.2 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.4, 85.8, 116.2, 122.7, 128.3, 129.5, 130.8, 135.3, 136.0, 136.1, 141.4, 150.7. Anal. Calcd for C₁₄H₈ClNO₂: C, 65.26; H, 3.13; N, 5.44; Found: C, 65.20; H, 3.19; N, 5.52.

4'-Ethynyl-3'-nitrobiphenyl-4-carbonitrile (3g). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-cyanophenylboronic acid (0.3563 g, 2.4 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=3/1) furnished (**2g**) as a pale yellow solid (0.177 g, 23% yield based on boronic acid). It was used directly for the next step. The general deprotection protocol was followed using **2g** (0.177 g, 0.55 mmol), TBAF (0.2149 g, 0.83 mmol), AcOH (0.066 g, 1.1 mmol), Ac₂O (0.1122 g, 1.1 mmol), THF (10 mL) at r.t. for 1h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=1/1) furnished a yellow solid (0.1267 g, 93% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.60 (s, 1 H, CH), 7.73 (d, 2 H, *J* = 8 Hz, Ar-H), 7.80 (d, 4 H, *J* = 9 Hz, Ar-H), 8.27 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.1, 86.6, 112.9, 117.4, 118.2, 123.1, 127.8, 130.9, 133.0, 136.2, 140.5, 142.1, 150.9. Anal. Calcd for C₁₅H₈N₂O₂: C, 72.58; H, 3.25; N, 11.28; Found: C, 72.34; H, 3.43; N, 11.05.

1-(4'-Ethynyl-3'-nitrobiphenyl-4-yl)ethanone (3h). The general Suzuki cross coupling

procedure was followed using **1** (0.4638 g, 1.5 mmol), 4-acetylphenylboronic acid (0.492 g, 3 mmol), tetrakis(triphenylphosphine) palladium(0) (0.0867 g, 0.075 mmol), K₂CO₃ (aq. 2M 0.8 mL), DME (10 mL) at 85 °C for 2.5h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=8/1) furnished a white solid (0.1254 g). The structure is characterized as **3h** using NMR and the overall yield is 31% of the two steps. ¹H NMR (500 MHz, CDCl₃) δ 2.66 (s, 3 H, CH₃), 3.60 (s, 1 H, CH), 7.72 (d, 2 H, *J* = 8.25 Hz, Ar-H), 7.79 (d, 1 H, *J* = 8.05 Hz, Ar-H), 7.85 (q, 1 H, *J* = 1.7 Hz, Ar-H), 8.09 (d, 2 H, *J* = 8.3 Hz, Ar-H), 8.31 (d, 1 H, *J* = 1.6 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 26.7, 78.3, 86.2, 116.9, 123.1, 127.3, 129.2, 131.1, 136.1, 137.2, 141.3, 142.0, 150.8, 197.3. Anal. Calcd for C₁₆H₁₁NO₃: C, 72.45; H, 4.18; N, 5.28; Found: C, 72.56; H, 4.29; N, 5.09.

4'-Ethyne-3'-nitrobiphenyl-4-carbaldehyde (3i). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-formylphenylboronic acid (0.937 g, 6 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K₂CO₃ (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=2/1) furnished 3'-nitro-4'-((trimethylsilyl)ethynyl)biphenyl-4-carbaldehyde (**2i**) as a pale yellow solid (0.5537 g, 57% yield). It was used directly for the next step. The general deprotection protocol was followed using **2i** (0.5537 g, 1.72 mmol), TBAF (0.6681 g, 2.58 mmol), AcOH (0.2064 g, 3.44 mmol), Ac₂O (0.3509 g, 3.44 mmol), THF (10 mL) at r.t. for 2h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=1/1) furnished a yellow solid (0.3796 g, 88% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.61 (s, 1 H, CH), 7.80-7.96 (m, 4 H, Ar-H), 8.02 (d, 2 H, *J* = 7.5 Hz, Ar-H), 8.32 (s, 1 H, Ar-H), 10.10 (s, 1 H, CHO). ¹³C NMR (125 MHz, CDCl₃) δ 78.3, 86.4, 123.2, 127.7, 127.9, 130.5, 131.2, 136.2, 136.4, 141.1, 143.4, 191.4. Anal. Calcd for C₁₅H₉NO₃: C, 71.71; H, 3.61; N, 5.58; Found: C, 71.61; H, 3.83; N, 5.42.

4-Ethyne-3-nitro-4'-vinylbiphenyl (3j). The general Suzuki cross coupling procedure was followed using **1** (0.594 g, 2 mmol), 4-vinylphenylboronic acid (0.444 g, 3 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1156 g, 0.1 mmol), K₂CO₃ (aq. 2M 1.05 mL), DME (10 mL) at 85 °C for 4.5h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished trimethyl((3-nitro-4'-vinylbiphenyl-4-yl)ethynyl)silane (**2j**) as a pale yellow oil (0.0689 g, 11% yield). It was used directly for the next step. The general deprotection protocol was followed using **2j** (0.0689 g, 0.21 mmol), TBAF (0.10 g, 0.32 mmol), AcOH (0.03 g, 0.42 mmol), Ac₂O (0.045 g, 0.42 mmol), THF (10 mL) at r.t. for 1h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=8/1) furnished a yellow solid (0.0574 g, 96% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.55 (s, 1 H, CH), 5.35 (d, 1 H, *J* = 11 Hz, CH), 5.84 (d, 1 H, *J* = 17 Hz, CH), 6.77 (q, 1 H, *J* = 11 Hz, CH), 7.53 (d, 2 H, *J* = 9 Hz, Ar-H), 7.59 (d, 2 H, *J* = 9 Hz, Ar-H), 7.74 (d, 1 H, *J* = 8 Hz, Ar-H), 7.81 (q, 1 H, *J* = 1.5 Hz, Ar-H), 8.27 (d, 1 H, *J* = 2 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 78.6, 85.5, 115.2, 115.8, 122.7, 127.1, 127.2, 130.7, 135.9, 135.9, 136.9, 138.4, 142.2, 150.8. Anal. Calcd for C₁₆H₁₁NO₂: C, 77.10; H, 4.45; N, 5.62; Found: C, 77.26; H, 4.69; N, 5.49.

4'-Ethyne-2,5-dimethoxy-3'-nitrobiphenyl (3k). The general Suzuki cross coupling procedure was followed using **1** (0.1485 g, 0.5 mmol), 2,5-dimethoxyphenylboronic acid (0.127 g, 0.7

mmol), tetrakis(triphenylphosphine) palladium(0) (0.0289 g, 0.025 mmol), K_2CO_3 (aq. 2M 0.3 mL), DME (10 mL) at 85 °C for 10h. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =15/1) furnished (2',5'-dimethoxy-3-nitrobiphenyl-4-yl)ethynyl)trimethylsilane (**2k**) as a pale yellow oil (0.0836 g, 47% yield). It was used directly for the next step. The general deprotection protocol was followed using **2k** (0.0836 g, 0.24 mmol), TBAF (0.0915 g, 0.36 mmol), AcOH (0.03 g, 0.5 mmol), Ac_2O (0.05 g, 0.5 mmol), THF (10 mL) at r.t. for 1h. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =3/1) furnished a yellow solid (0.0591 g, 87% yield). 1H NMR (500 MHz, $CDCl_3$) δ 3.52 (s, 1 H, CH), 3.78 (s, 3 H, CH_3), 3.82 (s, 3 H, CH_3), 6.89-6.96 (m, 3 H, Ar-H), 7.70 (d, 1 H, $J = 8.05$ Hz, Ar-H), 7.76 (q, 1 H, $J = 1.7$ Hz, Ar-H), 8.25 (d, 1 H, $J = 1.55$ Hz, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.9, 56.2, 78.8, 84.9, 112.8, 114.8, 115.6, 116.3, 125.5, 128.0, 133.6, 135.0, 140.1, 150.1, 150.6, 153.9. Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.94; Found: C, 67.70; H, 4.79; N, 4.86.

4-Ethynyl-4'-methoxy-3-nitrobiphenyl (3l). The general Suzuki cross coupling procedure was followed using **1** (0.4455 g, 1.5 mmol), 4-methoxyphenylboronic acid (0.456 g, 3 mmol), tetrakis(triphenylphosphine) palladium(0) (0.0867 g, 0.075 mmol), K_2CO_3 (aq. 2M 0.8 mL), DME (10 mL) at 85 °C for 2h. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =10/1) furnished ((4'-methoxy-3-nitrobiphenyl-4-yl)ethynyl)trimethylsilane (**2l**) as a pale yellow oil (0.4071 g, 84% yield). It was used directly for the next step. The general deprotection protocol was followed using **2l** (0.3559 g, 1.1 mmol), TBAF (0.4274 g, 1.65 mmol), AcOH (0.132 g, 2.2 mmol), Ac_2O (0.2244 g, 2.2 mmol), THF (10 mL) at r.t. for 1h. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =10/1) furnished a yellow solid (0.26 g, 93% yield). 1H NMR (500 MHz, $CDCl_3$) δ 3.53 (s, 1 H, CH), 3.87 (s, 3 H, CH_3), 7.02 (d, 2 H, $J = 1.9$ Hz, Ar-H), 7.56 (q, 2 H, $J = 1.9$ Hz, Ar-H), 7.71 (d, 1 H, $J = 8.05$ Hz, Ar-H), 7.76 (q, 1 H, $J = 1.8$ Hz, Ar-H), 8.22 (d, 1 H, $J = 1.75$ Hz, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 78.7, 85.1, 114.7, 115.1, 122.2, 128.2, 130.1, 130.4, 135.8, 142.3, 150.8, 160.4. Anal. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53; Found: C, 71.22; H, 4.47; N, 5.45.

(4'-Ethynyl-3'-nitrobiphenyl-4-yl)(methyl)sulfane (3m). The general Suzuki cross coupling procedure was followed using **1** (0.891 g, 3 mmol), 4-(methylthio)phenylboronic acid (1 g, 6 mmol), tetrakis(triphenylphosphine) palladium(0) (0.1734 g, 0.15 mmol), K_2CO_3 (aq. 2M 1.55 mL), DME (10 mL) at 85 °C for 23h. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =15/1) furnished trimethyl((4'-(methylthio)-3-nitrobiphenyl-4-yl)ethynyl)silane (**2m**) as a yellow solid (0.17 g, 17% yield). It was used directly for the next step. The general deprotection protocol was followed using **2m** (0.17 g, 0.5 mmol), TBAF (0.1943 g, 0.75 mmol), AcOH (0.06 g, 1 mmol), Ac_2O (0.102 g, 1 mmol), THF (10 mL) at r.t. for 30min. Purification by flash chromatography (petroleum ether/ CH_2Cl_2 =3/1) furnished a yellow solid (0.1122 g, 83% yield). 1H NMR (500 MHz, $CDCl_3$) δ 2.53 (s, 3 H, CH_3), 3.59 (s, 1 H, CH), 7.35 (d, 2 H, $J = 8.35$ Hz, Ar-H), 7.54 (d, 2 H, $J = 8.35$ Hz, Ar-H), 7.73 (d, 1 H, $J = 8.1$ Hz, Ar-H), 7.78 (q, 1 H, $J = 1.4$ Hz, Ar-H), 8.24 (s, 1 H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.4, 78.6, 85.4, 115.6, 122.4, 126.7, 127.2, 130.5, 134.1, 135.9, 140.3, 142.0, 150.7. Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20; Found: C, 66.72; H, 4.19; N, 5.11.

S-4-((2',3'-Dimethoxy-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5a). The general Sonogashira cross coupling procedure was followed using **3a** (0.4059 g, 1.43 mmol), CuI (0.0272 g, 0.14 mmol), Pd₂(dba)₃ (0.0655 g, 0.07 mmol), PPh₃ (0.0749 g, 0.3 mmol), **4** (0.3975 g, 1.43 mmol), (*i*-Pr)₂NEt (0.7379 g, 5.7 mmol), THF (10 mL) at 50 °C for 24h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.1668 g, 27% yield) as yellow solid. Mp 85.8-87.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 3.67 (s, 3 H, CH₃), 3.94 (s, 3 H, CH₃), 6.98-7.01 (m, 2 H, Ar-H), 7.17 (t, 1 H, *J* = 8 Hz, Ar-H), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.64 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.75 (d, 1 H, *J* = 8 Hz, Ar-H), 7.85 (q, 1 H, *J* = 1.5 Hz, Ar-H), 8.32 (d, 1 H, *J* = 1.5 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 56.0 (q), 60.8 (q), 86.5 (s), 96.2 (s), 113.0 (d), 116.7 (d), 121.8 (d), 123.7 (s), 124.5 (d), 125.4 (d), 128.3 (s), 129.2 (s), 132.5 (d), 132.6 (s), 133.7 (d), 134.2 (d), 139.4 (s), 146.6 (s), 149.5 (s), 153.3 (s), 193.1 (s). FT-IR (KBr) 625 (w), 751 (m), 781 (m), 824 (w), 957 (w), 1001 (m), 1038 (w), 1094 (w), 1119 (m), 1266 (m), 1344 (m), 1385 (s), 1469 (m), 1524 (m), 1543 (m), 1621 (m), 1709 (m), 2926 (w) cm⁻¹. HRMS *m/z*: calcd for C₂₄H₁₉NO₅S 433.0984, found 433.0985. Anal. Calcd for C₂₄H₁₉NO₅S: C, 66.50; H, 4.42; N, 3.23; Found: C, 66.73; H, 4.55; N, 3.12.

S-4-((3-Nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5b). The general Sonogashira cross coupling procedure was followed using **3b** (0.223 g, 1 mmol), CuI (0.019 g, 0.1 mmol), Pd₂(dba)₃ (0.0458 g, 0.05 mmol), PPh₃ (0.0524 g, 0.2 mmol), **4** (0.278 g, 1 mmol), (*i*-Pr)₂NEt (0.516 g, 4 mmol), THF (10 mL) at 50 °C for 17h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.1978 g, 53% yield) as yellow solid. Mp 133.7-134.8 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.41-7.47 (m, 2 H, Ar-H), 7.50-7.54 (m, 2 H, Ar-H), 7.62-7.64 (m, 4 H, Ar-H), 7.77 (d, 1 H, *J* = 8.1 Hz, Ar-H), 7.80-7.85 (m, 2 H, Ar-H), 8.33 (d, 1H, *J* = 1.7 Hz, Ar-H). FT-IR (KBr) 623 (w), 699 (w), 761 (m), 826 (m), 951 (w), 1015 (w), 1118 (m), 1265 (w), 1342 (s), 1389 (w), 1490 (w), 1524 (s), 1544 (s), 1696 (s) cm⁻¹. HRMS *m/z*: calcd for C₂₂H₁₅NO₃S 373.0773, found 373.0783. Anal. Calcd for C₂₂H₁₅NO₃S: C, 70.76; H, 4.05; N, 3.75; Found: C, 70.67; H, 4.23; N, 3.58.

S-4-((4'-Fluoro-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5c). The general Sonogashira cross coupling procedure was followed using **3c** (0.2994 g, 1.24 mmol), CuI (0.03 g, 0.12 mmol), Pd₂(dba)₃ (0.06 g, 0.06 mmol), PPh₃ (0.065 g, 0.25 mmol), **4** (0.3454 g, 1.24 mmol), (*i*-Pr)₂NEt (0.645 g, 5 mmol), THF (10 mL) at 50 °C for 22h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.1799 g, 37% yield) as brown solid. Mp 109.7-111.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.19 (t, 2 H, *J* = 8.5 Hz, Ar-H), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.60-7.64 (m, 4 H, Ar-H), 7.75-7.80 (m, 2 H, Ar-H), 8.28 (d, 1 H, *J* = 1.5 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 86.2 (s), 96.7 (s), 116.3 (d, *J* = 21.25 Hz), 116.9 (s), 122.9 (d), 123.5 (s), 128.8 (d, *J* = 8.75 Hz), 129.3 (s), 130.9 (d), 132.5 (d), 134.0 (s), 134.2 (d), 135.1 (d), 141.1 (s), 150.0 (s), 164.3 (d, *J* = 247.5 Hz), 193.1 (s). FT-IR (KBr) 620 (m), 759 (w), 826 (s), 947 (m), 1011 (w), 1111 (m), 1163 (m), 1232 (m), 1286 (w), 1348 (s), 1387 (w), 1517 (s), 1544 (s), 1601 (w), 1700 (s) cm⁻¹. HRMS *m/z*: calcd for C₂₂H₁₄NO₃SF 391.0678, found 391.0677. Anal. Calcd for C₂₂H₁₄FNO₃S: C, 67.51; H, 3.61; N, 3.58; Found: C, 67.23; H, 4.05; N, 3.42.

S-4-((3-Nitro-4'-(trifluoromethyl)biphenyl-4-yl)ethynyl)phenyl ethanethioate (5d). The general Sonogashira cross coupling procedure was followed using **3d** (0.3801 g, 1.3 mmol), CuI (0.03 g, 0.13 mmol), Pd₂(dba)₃ (0.06 g, 0.065 mmol), PPh₃ (0.0681 g, 0.26 mmol), **4** (0.3631 g, 1.3 mmol), (*i*-Pr)₂NEt (0.6708 g, 5.2 mmol), THF (10 mL) at 50 °C for 26h. Flash chromatography (petroleum ether/CH₂Cl₂=1/1) yielded the desired adduct (0.351 g, 61% yield) as yellow solid. Mp 101.1-102.4 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.44 (d, 2 H, *J* = 8.15 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8.2 Hz, Ar-H), 7.74-7.78 (m, 4 H, Ar-H), 7.80-7.85 (m, 2 H, Ar-H), 8.34 (d, 1 H, *J* = 1.65 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 86.0 (s), 97.4 (s), 117.9 (s), 123.3 (d), 123.4 (s), 126.2 (d), 127.4 (d), 129.0 (s), 129.6 (s), 131.2 (d), 132.5 (d), 134.2 (d), 135.3 (d), 140.5 (s), 141.3 (s), 150.1 (s), 193.0 (s). FT-IR (KBr) 615 (m), 830 (m), 947 (w), 1012 (w), 1074 (m), 1119 (s), 1165 (m), 1266 (w), 1325 (s), 1520 (m), 1543 (m), 1616 (w), 1706 (m) cm⁻¹. HRMS m/z: calcd for C₂₃H₁₄NO₃SF₃ 441.0646, found 441.0645. Anal. Calcd for C₂₃H₁₄F₃NO₃S: C, 62.58; H, 3.20; N, 3.17; Found: C, 62.63; H, 3.04; N, 3.32.

S-4-((4'-Ethyl-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5e). The general Sonogashira cross coupling procedure was followed using **3e** (0.1255 g, 0.5 mmol), CuI (0.01 g, 0.05 mmol), Pd₂(dba)₃ (0.0229 g, 0.025 mmol), PPh₃ (0.0262 g, 0.1 mmol), **4** (0.1529 g, 0.55 mmol), (*i*-Pr)₂NEt (0.258 g, 2 mmol), THF (10 mL) at 50 °C for 7h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.09 g, 45% yield) as yellow solid. Mp 90.6-91.4 °C. ¹H NMR (500 MHz, CDCl₃) δ 1.29 (t, 3 H, *J* = 7.6 Hz, CH₃), 2.44 (s, 3 H, CH₃), 2.72 (q, 2 H, *J* = 7.6 Hz, CH₂), 7.34 (t, 2 H, *J* = 8.1 Hz, Ar-H), 7.43 (t, 2 H, *J* = 1.65 Hz, Ar-H), 7.55 (t, 2 H, *J* = 8.6 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.75 (d, 1 H, *J* = 8.1 Hz, Ar-H), 7.82 (q, 1 H, *J* = 1.8 Hz, Ar-H), 8.31 (d, 1 H, *J* = 1.8 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 15.4 (q), 28.6 (t), 30.3 (q), 86.5 (s), 96.4 (s), 116.5 (s), 122.8 (d), 123.7 (s), 126.9 (d), 128.8 (d), 129.2 (s), 130.8 (d), 132.5 (d), 134.2 (d), 135.0 (d), 135.2 (s), 142.1 (s), 145.4 (s), 150.0 (s), 193.1 (s). FT-IR (KBr) 616 (s), 754 (w), 825 (s), 951 (m), 1013 (w), 1114 (m), 1266 (w), 1345 (s), 1389 (m), 1519 (s), 1538 (s), 1708 (s), 2871 (w), 2928 (w), 2964 (w) cm⁻¹. HRMS m/z: calcd for C₂₄H₁₉NO₃S 401.1086, found 401.1082. Anal. Calcd for C₂₄H₁₉NO₃S: C, 71.80; H, 4.77; N, 3.49; Found: C, 71.93; H, 4.87; N, 3.29.

S-4-((4'-Chloro-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5f). The general Sonogashira cross coupling procedure was followed using **3f** (0.385 g, 1.5 mmol), CuI (0.03 g, 0.15 mmol), Pd₂(dba)₃ (0.0687 g, 0.075 mmol), PPh₃ (0.0786 g, 0.3 mmol), **4** (0.417 g, 1.5 mmol), (*i*-Pr)₂NEt (0.774 g, 6 mmol), THF (10 mL) at 50 °C for 35.5h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.3183 g, 52% yield) as yellow solid. Mp 115.9-117.3 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.45 (q, 4 H, *J* = 7.2 Hz, Ar-H), 7.60 (q, 4 H, *J* = 6.5 Hz, Ar-H), 7.76-7.80 (m, 2 H, Ar-H), 8.29 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 86.2 (s), 96.9 (s), 117.2 (s), 122.9 (d), 123.5 (s), 128.2 (d), 129.4 (s), 129.5 (d), 130.8 (d), 132.5 (d), 134.2 (d), 135.1 (d), 135.2 (s), 136.3 (s), 140.8 (s), 150.0 (s), 193.1 (s). FT-IR (KBr) 613 (m), 778 (w), 826 (s), 939 (m), 1011 (m), 1088 (s), 1279 (w), 1334 (s), 1389 (w), 1414 (w), 1487 (s), 1540 (s), 1704 (s), 2922 (w) cm⁻¹. HRMS m/z: calcd for C₂₂H₁₄NO₃SCl 407.0383, found 407.0386. Anal. Calcd for C₂₂H₁₄ClNO₃S: C, 64.78; H, 3.46; N,

3.43; Found: C, 64.59; H, 3.57; N, 3.29.

S-4-((4'-Cyano-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5g). The general Sonogashira cross coupling procedure was followed using **3g** (0.2069 g, 0.83 mmol), CuI (0.0158 g, 0.1 mmol), Pd₂(dba)₃ (0.038 g, 0.4 mmol), PPh₃ (0.0435 g, 0.2 mmol), **4** (0.2307 g, 0.83 mmol), (*i*-Pr)₂NEt (0.4283 g, 3.32 mmol), THF (10 mL) at 50 °C for 48h. Flash chromatography (CH₂Cl₂) yielded the desired adduct (0.0849 g, 26% yield) as yellow solid. Mp 153.1-154.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8 Hz, Ar-H), 7.75 (d, 2 H, *J* = 8 Hz, Ar-H), 7.81 (q, 4 H, *J* = 6.5 Hz, Ar-H), 8.33 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 85.9 (s), 97.8 (s), 112.7 (s), 118.3 (s), 118.4 (s), 123.3 (s), 123.3 (d), 127.7 (d), 131.1 (d), 132.6 (d), 133.0 (d), 134.3 (d), 135.4 (d), 137.4 (s), 139.8 (s), 142.2 (s), 150.1 (s), 193.0 (s). FT-IR (KBr) 623 (m), 757 (w), 825 (s), 957 (w), 1012 (w), 1119 (m), 1253 (w), 1286 (w), 1343 (s), 1388 (m), 1531 (s), 1607 (w), 1697 (s), 2224 (m, CN), 2922 (w), 3089 (w) cm⁻¹. MS (EI) *m/z*: 398. Anal. Calcd for C₂₃H₁₄N₂O₃S: C, 69.33; H, 3.54; N, 7.03; Found: C, 69.25; H, 3.59; N, 6.89.

S-4-((4'-Acetyl-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5h). The general Sonogashira cross coupling procedure was followed using **3h** (0.1621 g, 0.61 mmol), CuI (0.0116 g, 0.06 mmol), Pd₂(dba)₃ (0.0279 g, 0.03 mmol), PPh₃ (0.0387 g, 0.12 mmol), **4** (0.17 g, 0.61 mmol), (*i*-Pr)₂NEt (0.3148 g, 2.5 mmol), THF (10 mL) at 50 °C for 19h. Flash chromatography (CH₂Cl₂) yielded the desired adduct (0.0548 g, 22% yield) as yellow solid. Mp 90.1-91.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 2.66 (s, 3 H, CH₃), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8 Hz, Ar-H), 7.74 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.80 (d, 1 H, *J* = 8 Hz, Ar-H), 7.87 (d, 1 H, *J* = 8 Hz, Ar-H), 8.08 (d, 2 H, *J* = 8 Hz, Ar-H), 8.36 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 26.3 (q), 30.3 (q), 86.1 (s), 97.3 (s), 117.8 (s), 123.3 (d), 123.4 (s), 127.2 (d), 129.2 (d), 129.5 (s), 131.1 (d), 132.5 (d), 134.2 (d), 135.2 (d), 137.1 (s), 140.6 (s), 142.1 (s), 150.0 (s), 193.0 (s), 197.3 (s). FT-IR (KBr) 591 (m), 823 (s), 952 (m), 1011 (w), 1082 (m), 1116 (m), 1188 (w), 1266 (s), 1349 (s), 1390 (m), 1493 (m), 1526 (s), 1600 (m), 1680 (s), 1709 (m), 2962 (w) cm⁻¹. Anal. Calcd for C₂₄H₁₇NO₄S: C, 69.38; H, 4.12; N, 3.37; Found: C, 69.24; H, 4.26; N, 3.29.

S-4-((4'-Formyl-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5i). The general Sonogashira cross coupling procedure was followed using **3i** (0.125 g, 0.5 mmol), CuI (0.01 g, 0.05 mmol), Pd₂(dba)₃ (0.0229 g, 0.025 mmol), PPh₃ (0.0262 g, 0.1 mmol), **4** (0.139 g, 0.5 mmol), (*i*-Pr)₂NEt (0.258 g, 2 mmol), THF (10 mL) at 50 °C for 12h. Flash chromatography (CH₂Cl₂) yielded the desired adduct (0.0769 g, 38% yield) as yellow solid. Mp 146.1-147.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.81 (q, 3 H, *J* = 3 Hz, Ar-H), 7.88 (q, 1 H, *J* = 2 Hz, Ar-H), 8.01 (d, 2 H, *J* = 8.5 Hz, Ar-H), 8.37 (d, 1 H, *J* = 1.5 Hz, Ar-H), 10.09 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 86.1 (s), 97.6 (s), 118.1 (s), 123.4 (s), 123.4 (d), 127.7 (d), 129.6 (s), 130.5 (d), 131.2 (d), 132.6 (d), 134.3 (d), 135.3 (d), 136.3 (s), 140.5 (s), 143.5 (s), 150.1 (s), 191.5 (d), 193.0 (s). FT-IR (KBr) 619 (m), 763 (m), 821 (s), 956 (w), 1014 (w), 1122 (m), 1176 (m), 1216 (m), 1349 (m), 1389 (w), 1528 (m), 1604 (m), 1698 (s), 2725 (w), 2922 (w), 3087 (w) cm⁻¹. HRMS *m/z*:

calcd for C₂₃H₁₅NO₄S 401.0722, found 401.0715. Anal. Calcd for C₂₃H₁₅NO₄S: C, 68.81; H, 3.77; N, 3.49; Found: C, 68.69; H, 3.54; N, 3.36.

S-4-((3-Nitro-4'-vinylbiphenyl-4-yl)ethynyl)phenyl ethanethioate (5j). The general Sonogashira cross coupling procedure was followed using **3j** (0.1312 g, 0.53 mmol), CuI (0.01 g, 0.05 mmol), Pd₂(dba)₃ (0.0243 g, 0.025 mmol), PPh₃ (0.0278 g, 0.16 mmol), **4** (0.1473 g, 0.53 mmol), (*i*-Pr)₂NEt (0.2735 g, 2.1 mmol), THF (10 mL) at 50 °C for 24h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.0259 g, 12% yield) as yellow solid. Mp 82.2-82.9 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 5.35 (d, 1 H, *J* = 11 Hz, CH), 5.85 (d, 1 H, *J* = 17.5 Hz, CH), 6.78 (q, 1 H, *J* = 10.75 Hz, CH), 7.44 (d, 2 H, *J* = 8 Hz, Ar-H), 7.54 (d, 2 H, *J* = 8 Hz, Ar-H), 7.63 (t, 4 H, *J* = 8.5 Hz, Ar-H), 7.77 (d, 1 H, *J* = 8 Hz, Ar-H), 7.85 (q, 1 H, *J* = 1.5 Hz, Ar-H), 8.34 (d, 1 H, *J* = 1.5 Hz, Ar-H). FT-IR (KBr) 613 (m), 693 (w), 750 (w), 825 (s), 953 (w), 1018 (m), 1089 (m), 1261 (m), 1346 (m), 1390 (w), 1536 (m), 1621 (w), 1652 (w), 1708 (s), 2921 (w), 2962 (w) cm⁻¹. HRMS *m/z*: calcd for C₂₄H₁₇NO₃S 399.0929, found 399.0922. Anal. Calcd for C₂₄H₁₇NO₃S: C, 72.16; H, 4.29; N, 3.51; Found: C, 72.28; H, 4.36; N, 3.43.

S-4-((2',5'-Dimethoxy-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5k). The general Sonogashira cross coupling procedure was followed using **3k** (0.0591 g, 0.21 mmol), CuI (0.004 g, 0.02 mmol), Pd₂(dba)₃ (0.01 g, 0.01 mmol), PPh₃ (0.011 g, 0.04 mmol), **4** (0.0584 g, 0.21 mmol), (*i*-Pr)₂NEt (0.1084 g, 0.84 mmol), THF (10 mL) at 50 °C for 48h. Flash chromatography (petroleum ether/CH₂Cl₂=1/1) yielded the desired adduct (0.02 g, 22% yield) as yellow semisolid. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 3.79 (s, 3 H, CH₃), 3.82 (s, 3 H, CH₃), 6.92-6.97 (m, 3 H, Ar-H), 7.41-7.44 (m, 2 H, Ar-H), 7.62-7.64 (m, 2 H, Ar-H), 7.70-7.73 (m, 1 H, Ar-H), 7.76-7.80 (m, 1 H, Ar-H), 8.30 (q, 1 H, *J* = 1.5 Hz, Ar-H). FT-IR (KBr) 695 (w), 763 (w), 830 (m), 1020 (m), 1179 (m), 1214 (m), 1262 (m), 1341 (s), 1386 (m), 1492 (s), 1524 (s), 1585 (w), 1617 (m), 1649 (w), 1707 (m), 2835 (w), 2925 (m) cm⁻¹. HRMS *m/z*: calcd for C₂₄H₁₉NO₅S 433.0984, found 433.0989.

S-4-((4'-Methoxy-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5l). The general Sonogashira cross coupling procedure was followed using **3l** (0.30 g, 1.2 mmol), CuI (0.0224 g, 0.12 mmol), Pd₂(dba)₃ (0.0596 g, 0.06 mmol), PPh₃ (0.0654 g, 0.36 mmol), **4** (0.3365 g, 1.2 mmol), (*i*-Pr)₂NEt (0.6601 g, 4.7 mmol), THF (10 mL) at 50 °C for 16h. Flash chromatography (petroleum ether/CH₂Cl₂=1/1) yielded the desired adduct (0.2072 g, 44% yield) as yellow solid. Mp 80.5-81.6 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 3.87 (s, 3 H, CH₃), 7.02 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.43 (q, 2 H, *J* = 7.5 Hz, Ar-H), 7.60 (q, 4 H, *J* = 8.25 Hz, Ar-H), 7.76 (q, 2 H, *J* = 8 Hz, Ar-H), 8.28 (s, 1 H, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 30.3 (q), 55.4 (q), 86.5 (s), 96.3 (s), 114.7 (d), 116.0 (s), 122.4 (d), 123.7 (s), 128.2 (d), 129.2 (s), 130.2 (s), 130.4 (d), 132.5 (d), 134.2 (d), 134.9 (d), 141.8 (s), 150.0 (s), 160.4 (s), 193.1 (s). FT-IR (KBr) 616 (m), 825 (s), 949 (w), 1021 (m), 1112 (m), 1181 (m), 1253 (s), 1290 (m), 1344 (m), 1515 (s), 1542 (m), 1604 (s), 1705 (s), 2836 (w), 2926 (w), 2960 (w) cm⁻¹. HRMS *m/z*: calcd for C₂₃H₁₇NO₄S 403.0878, found 403.0888. Anal. Calcd for C₂₃H₁₇NO₄S: C, 68.47; H, 4.25; N, 3.47; Found: C, 68.29; H, 4.37; N, 3.37.

S-4-((4'-(Methylthio)-3-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (5m). The general Sonogashira cross coupling procedure was followed using **3m** (0.1122 g, 0.42 mmol), CuI (0.008 g, 0.04 mmol), Pd₂(dba)₃ (0.0192 g, 0.02 mmol), PPh₃ (0.022 g, 0.08 mmol), **4** (0.1168 g, 0.42 mmol), (*i*-Pr)₂NEt (0.2167 g, 1.7 mmol), THF (10 mL) at 50 °C for 24h. Flash chromatography (petroleum ether/CH₂Cl₂=1/1) yielded the desired adduct (0.1404 g, 79% yield) as yellow solid. Mp 88.3-89.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 2.54 (s, 3 H, CH₃), 7.35 (d, 2 H, *J* = 8.05 Hz, Ar-H), 7.43 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.56 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.63 (d, 2 H, *J* = 8.1 Hz, Ar-H), 7.73-7.82 (m, 2 H, Ar-H), 8.30 (d, 1 H, *J* = 1.3 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 15.5 (q), 30.3 (q), 86.4 (s), 96.6 (s), 116.6 (s), 122.6 (d), 123.6 (s), 126.8 (d), 127.2 (d), 129.0 (s), 129.3 (s), 130.6 (d), 132.5 (d), 134.2 (d), 135.1 (d), 140.2 (s), 141.5 (s), 150.1 (s), 193.1 (s). FT-IR (KBr) 617 (m), 815 (s), 951 (w), 1011 (w), 1094 (m), 1278 (w), 1340 (s), 1388 (m), 1489 (m), 1538 (s), 1617 (w), 1702 (s), 2853 (w), 2921 (w), 3066 (w) cm⁻¹. HRMS *m/z*: calcd for C₂₃H₁₇NO₃S₂ 419.0650, found 419.0652. Anal. Calcd for C₂₃H₁₇NO₃S₂: C, 65.85; H, 4.08; N, 3.34; Found: C, 65.78; H, 4.19; N, 3.21.

Trimethyl((4'-(methylthio)-2-nitrobiphenyl-4-yl)ethynyl)silane (7). The general Sonogashira cross coupling procedure was followed using **6** (0.2193 g, 0.7 mmol), CuI (0.005 g, 0.03 mmol), PdCl₂(PPh₃)₂ (0.0238 g, 0.03 mmol), ethynyltrimethylsilane (0.1 g, 1 mmol), TEA (0.2747 g, 2.7 mmol), THF (10 mL) at reflux for 11h. Flash chromatography (petroleum ether/CH₂Cl₂=15/1) yielded the desired adduct (0.2315 g, 97% yield) as yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 0.29 (s, 9 H, CH₃), 2.51 (s, 3 H, CH₃), 7.22 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.28 (d, 2 H, *J* = 8.5 Hz, Ar-H), 7.36 (d, 1 H, *J* = 8 Hz, Ar-H), 7.64 (q, 1 H, *J* = 1.5 Hz, Ar-H), 7.90 (d, 1 H, *J* = 1.5 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃) δ 1.0, 15.4, 98.0, 102.0, 123.6, 126.4, 127.4, 128.2, 131.7, 133.1, 135.2, 135.3, 139.7, 149.0. FT-IR (KBr) 758 (m), 810 (s), 846 (s), 1022 (m), 1096 (m), 1256 (m), 1356 (m), 1478 (m), 1541 (m), 1595 (w), 2960 (w) cm⁻¹. Anal. Calcd for C₁₈H₁₉NO₂SSi: C, 63.31; H, 5.61; N, 4.10; Found: C, 63.20; H, 5.82; N, 4.03.

(4'-Ethynyl-2'-nitrobiphenyl-4-yl)(methyl)sulfane (8). The general deprotection protocol was followed using **7** (0.2319 g, 0.7 mmol), TBAF (0.2642 g, 1.02 mmol), AcOH (0.0816 g, 1.36 mmol), Ac₂O (0.1387 g, 1.36 mmol), THF (10 mL) at r.t. for 1h. Purification by flash chromatography (petroleum ether/CH₂Cl₂=10/1) furnished a pale yellow solid (0.1471 g, 80% yield). ¹H NMR (500 MHz, CDCl₃) δ 2.51 (s, 3 H, CH₃), 3.23 (s, 1 H, CH), 7.22 (d, 2 H, *J* = 8.35 Hz, Ar-H), 7.29 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.39 (d, 1 H, *J* = 7.95 Hz, Ar-H), 7.68 (q, 1 H, *J* = 1.4 Hz, Ar-H), 7.93 (d, 1 H, *J* = 1.1 Hz, Ar-H). FT-IR (KBr) 815 (w), 1020 (w), 1099 (w), 1170 (m), 1262 (w), 1353 (m), 1405 (m), 1568 (s), 1663 (m) cm⁻¹. Anal. Calcd for C₁₅H₁₁NO₂S: C, 66.89; H, 4.12; N, 5.20; Found: C, 66.77; H, 4.24; N, 5.24.

S-4-((4'-(Methylthio)-2-nitrobiphenyl-4-yl)ethynyl)phenyl ethanethioate (9). The general Sonogashira cross coupling procedure was followed using **8** (0.1471 g, 0.55 mmol), CuI (0.0105 g, 0.06 mmol), Pd₂(dba)₃ (0.0252 g, 0.03 mmol), PPh₃ (0.03 g, 0.11 mmol), **4** (0.152 g, 0.55 mmol), (*i*-Pr)₂NEt (0.2838 g, 2.2 mmol), THF (10 mL) at 50 °C for 48h. Flash chromatography (petroleum ether/CH₂Cl₂=3/1) yielded the desired adduct (0.1044 g, 45% yield) as yellow solid. Mp 77.4-77.9 °C. ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3 H, CH₃), 2.52 (s, 3 H, CH₃), 7.24-7.26

(m, 2 H, Ar-H), 7.30 (d, 2 H, $J = 8.35$ Hz, Ar-H), 7.41-7.44 (m, 3 H, Ar-H), 7.58 (d, 2 H, $J = 8.25$ Hz, Ar-H), 7.72 (q, 1 H, $J = 1.6$ Hz, Ar-H), 7.98 (d, 1 H, $J = 1.45$ Hz, Ar-H). ^{13}C NMR (125 MHz, CDCl_3) δ 15.4 (q), 30.3 (q), 88.3 (s), 91.4 (s), 123.3 (s), 123.4 (s), 126.4 (d), 127.0 (d), 128.2 (d), 128.9 (s), 131.9 (d), 132.3 (d), 133.0 (s), 134.3 (d), 134.9 (d), 135.4 (s), 139.7 (s), 149.1 (s), 193.1 (s). FT-IR (KBr) 822 (s), 952 (m), 1095 (m), 1188 (w), 1262 (w), 1355 (m), 1431 (w), 1486 (m), 1534 (s), 1593 (w), 1709 (s), 2855 (w), 2921 (w), 2961 (w) cm^{-1} . HRMS m/z : calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_3\text{S}_2$ 419.0650, found 419.0650. Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_3\text{S}_2$: C, 65.85; H, 4.08; N, 3.34; Found: C, 65.72; H, 4.21; N, 3.24.

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