

Sonogashira coupling with aqueous ammonia directed to the synthesis of azotolane derivatives

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Abstract—Sonogashira coupling with aqueous ammonia is tolerable for the reaction of aryl iodides or terminal alkynes bearing an azobenzene group. The reaction of (4-heptyloxyphenyl)ethyne with (4-heptyloxyphenyl)-(4-iodophenyl)diazene in the presence of 1 mol% of $\text{PdCl}_2(\text{PPh}_3)_2$, 2 mol% of CuI , and 2 equiv of 0.5 M aqueous ammonia gives the corresponding azotolane in 87% isolated yield after stirring at room temperature for 15 h.

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1. Introduction

Organic holographic materials recently attract considerable interest for storage and reconstruction of three-dimensional image in the organic compound.^{1,2} Azotolanes,³ which contain a carbon–carbon triple bond as well as an azobenzene group, are potentially important component of holographic materials since these compounds show liquid crystalline and highly birefringent characteristics that enable photo-induced order-disorder change to form holographic gratings of high diffraction efficiency.^{1a,4} Hence, the synthetic methodology for azotolanes that is tolerable to various functional groups would be the key for flexible and efficient design of the target molecule.

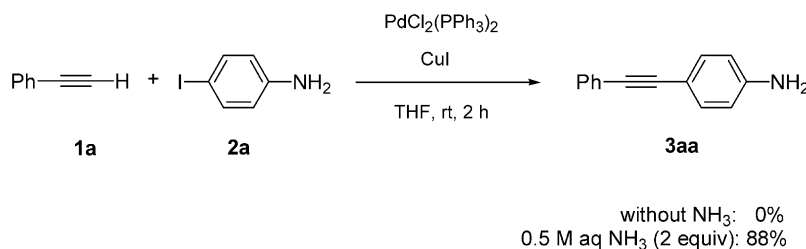
We have recently shown that the Sonogashira coupling takes place with aqueous ammonia to afford a variety of substituted alkynes highly efficiently.^{5,6} Our concern has thus turned to apply the reaction for substrates bearing an azobenzene moiety leading to azotolane derivatives.³

Herein, we report that the Sonogashira coupling with aqueous ammonia takes place efficiently with several substrates bearing an azobenzene group.

2. Results and discussion

Prior to the coupling reaction to synthesize azotolanes, we studied the Sonogashira coupling with a substrate bearing a protic functional group such as NH_2 or OH in aryl halide with aqueous ammonia.⁷

The reaction of phenylethyne (**1a**) with 4-amino-1-iodobenzene (**2a**) was carried out in the presence of 1 mol% of $\text{PdCl}_2(\text{PPh}_3)_2$, 2 mol% of CuI and 2 equiv of 0.5 M aqueous ammonia. The coupling product **3aa** was obtained in 88% isolated yield after stirring at room temperature for 2 h in THF. On the other hand, no reaction was found to take place in the absence of ammonia suggesting that the presence of



Scheme 1.

Keywords: Azotolane; Aqueous ammonia; Sonogashira; Palladium; Terminal alkynes.

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Table 1. Cross coupling of terminal alkynes, R-C≡CH, with aryl halides bearing a protic functional group^a

Alkyne (R)	Aryl halide	Time, h	3, %Yield
1a (Ph)	I-C ₆ H ₄ -2-NH ₂ (2b)	3.5	3ab , 87
	I-C ₆ H ₄ -2-OH (2c)	4	3ac , 97
	I-C ₆ H ₄ -4-OH (2d)	2	3ad , 96
	Br-C ₆ H ₄ -4-NH ₂ (2a')	12	3aa , 86 ^b
	Br-C ₆ H ₄ -2-NH ₂ (2b')	19	3ab , 72 ^b
	Br-C ₆ H ₄ -3-NH ₂ (2e')	30	3ae , 83 ^b
	Br-C ₆ H ₄ -4-OH (2d')	17	3ad , 80 ^b
	Br-C ₆ H ₄ -3-OH (2f')	24	3af , 77 ^b
1b (Me ₃ Si)	2a	2	3ba , 86
	2b	3.5	3bb , 77
	2c	16	3bc , 63
	2d	3	3bd , 92

^a Unless noted, the reaction was carried out with 0.5 mmol aryl halide, 0.6 mmol alkyne, and 1 mL of 0.5 M aq NH₃ in the presence of 1 mol% of PdCl₂(PPh₃)₂, 2 mol% of CuI in THF at room temperature.

^b The reaction was performed at 60 °C with 3 mol% of PdCl₂(PPh₃)₂ and 2 mol% of CuI. Instead of aq. NH₃, 0.5 M of aq. 2-ethanolamine (2 equiv) was employed.

the amino group in the aryl halide could not be a surrogate promoter for ammonia as shown in [Scheme 1](#).

[Table 1](#) summarizes the results of the cross-coupling reaction of terminal alkynes with various aryl halides bearing an amino or hydroxy group at room temperature in the presence of 2 equiv of 0.5 M aqueous ammonia. The reaction of **1a** with 2-amino-1-iodobenzene (**2b**) similarly proceeded to give **3ab** in 87%. Use of aryl iodides bearing a hydroxy group, 2-hydroxy-1-iodobenzene (**2c**)⁸ and 4-hydroxy-1-iodobenzene (**2d**) also resulted in giving the coupling products **3ac** and **3ad** in 97 and 96% yields, respectively. Aryl bromides bearing an amino (**2a'**, **2b'** and **2e'**) or hydroxy group (**2d'** and **2f'**) effected the reaction, which was carried out at 60 °C using an aqueous solution of 2-ethanolamine instead of ammonia.⁹ In addition, the reaction of trimethylsilylethyne (**1b**) with several aryl iodides took place to afford the coupling products in excellent yields.

Studies on the reaction bearing an amino group on the aromatic group of aryl alkynes were then carried out. As summarized in [Scheme 2](#), the reaction of (4-aminophenyl)ethyne (**1c**) with 4-methoxy-1-iodobenzene (**2g**) was found to proceed to give **3cg** in 74% yield after stirring at room temperature for 4 h. The coupling reaction of terminal alkyne **1c** and aryl halide **2a**, both of which possessed an amino group on the aromatic group, proceeded to afford **3ca**.

The Sonogashira coupling with aqueous ammonia was applied for the reaction of aryl alkynes **1** and aryl iodide bearing an azo group **4**. As summarized in [Table 2](#), the reaction was found to take place smoothly. With **4a** bearing an *n*-heptyloxy group the coupling reaction of

trimethylsilylethyne (**1b**) and (4-cyanophenyl)ethyne (**1d**) afforded the corresponding azotolanes **5ba** and **5da** in 87 and 79% yields, respectively. Worthy of note is that aryl iodide **4b**, which possesses a phenolic hydroxy group as well as an azo group, also undergoes the coupling reaction. Azotolanes bearing a hydroxy group **5bb**, **5eb**, and **5fb** can be converted into various ethers.¹⁰ Subsequently, introduction of an alkyl group of different chain length would be applicable for the library of tail groups.

[Scheme 3](#) represents that azotolanes can be synthesized with different pathways. Treatment of **4a** with **1g** with the palladium/copper catalyst system in the presence of aqueous ammonia afforded azotolane **5ga** in 87% yield after stirring at room temperature for 14 h. On the other hand, azo alkyne **1h** and aryl iodide **2h** also effected the reaction to furnish the identical product with that of the former reaction in 79% yield. These results show that the reaction with aqueous ammonia proceeds by employing terminal alkynes bearing an azo group as well as aryl halides.

It is also remarkable that sila-Sonogashira coupling,¹¹ which is the reaction of trimethylsilylalkyne with aryl triflate was found to take place. The reaction of **5ba** with 4-cyanobenzene triflate afforded **5da** in 81% yield with the Pd(0)/CuCl catalyst system in DMF at 80 °C ([Scheme 4](#)).

3. Conclusion

Coupling reactions of alkynes with aryl halides, in which an azo group is incorporated in the molecule, produce azotolanes in good to excellent yields. The reaction was also found to be applicable for substrates bearing a protic functional group such as NH₂ or OH on the aromatic ring.

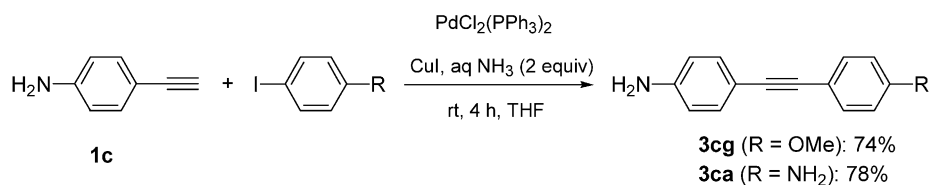
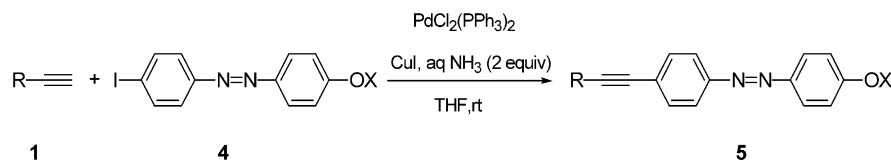
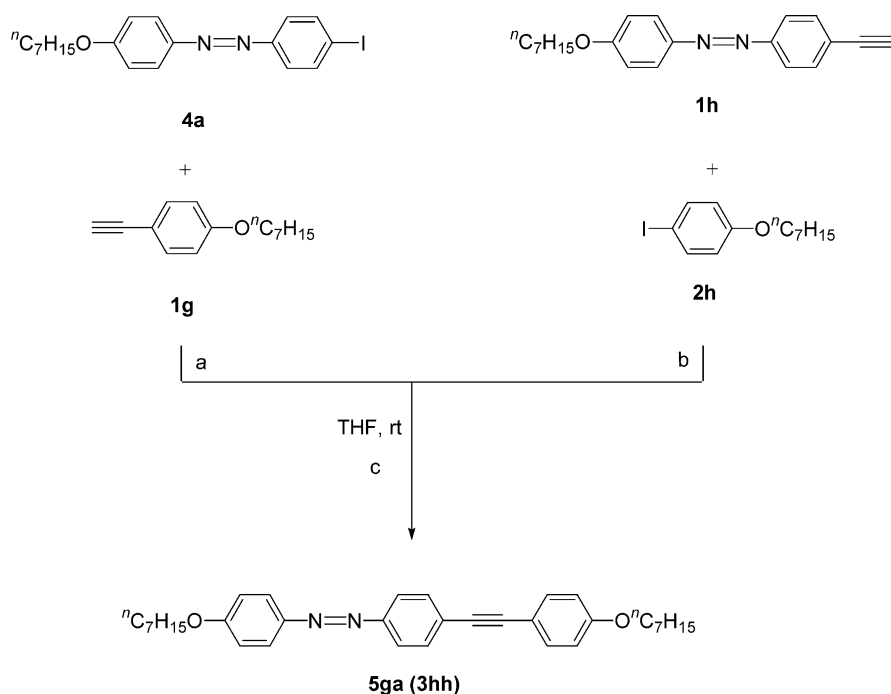
**Scheme 2.**

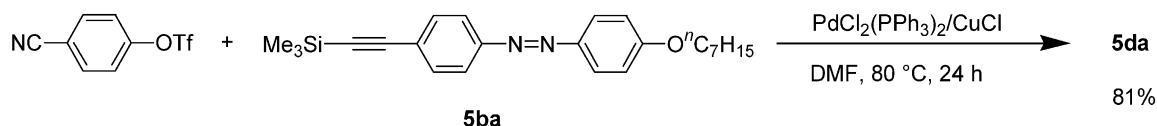
Table 2. Sonogashira coupling of aryl iodide bearing an azo group **4** with aqueous ammonia^a

Alkyne (R)	Iodide (X)	Time, h	5 , %yield
1b (Me ₃ Si)	4a (ⁿ C ₇ H ₁₅)	5	5ba , 87
1d (4-NC-C ₆ H ₄)	4a	16	5da , 79
1b	4b (H)	3	5bb , 90
1e (<i>t</i> -Bu)	4b	18	5eb , 76
1f (ⁿ C ₆ H ₁₃)	4b	24	5fb , 77

^a The reaction was carried out with 0.5 mmol aryl halide, 0.6 mmol alkyne, and 1 mL of 0.5 M aq. NH₃ in the presence of 1 mol% of PdCl₂(PPh₃)₂, 2 mol% of CuI in THF at room temperature.



a. 87% (15 h). b. 79% (14 h) c. PdCl₂(PPh₃)₂ (1 mol %), CuI (2 mol %), 0.5 M aq NH₃ (2 equiv)

Scheme 3.**Scheme 4.**

Since isolation and purification procedures for the reaction with aqueous ammonia are quite simple compared with those of conventional Sonogashira conditions, the reaction provides a practical azotolane synthesis that enables to design derivatives bearing a wide range of functional groups and alkyl groups with different chain length directed toward holographic materials of high performance.

4. Experimental

4.1. General

All reactions were performed under an atmosphere of argon using standard Schlenk tubes. Melting points were recorded using an Electrothermal melting point apparatus. Infrared

spectra were recorded on Shimadzu FT/IR-8100 spectrometer and presented in cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer in CDCl_3 . The ^1H (300 MHz) and ^{13}C (75 MHz) chemical shifts were referenced to residual CHCl_3 (δ 7.26 ppm) for ^1H and (77.0 ppm) for ^{13}C . High resolution mass spectra (HRMS) were recorded using JEOL JMS-700 (70 eV). Elemental analyses were carried out at the Elemental Analysis Center of Tokyo Institute of Technology using a Yanaco MT-5 CHN auto recorder and SX-Elements Micro Analyzer.

4.2. General method for the cross coupling of terminal alkynes with aryl halides bearing a protic functional group

To $\text{PdCl}_2(\text{PPh}_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), and **2** (0.5 mmol) in 3 mL of THF was added **1** (0.6 mmol) at room temperature. A 0.5 M solution of aqueous ammonia (2 mL, 1 mmol) was then added dropwise and stirring was continued for the period given in Table 1 at room temperature. Two phases of the resulting mixture were separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel (hexanes–ethyl acetate) to furnish the corresponding coupling product in good to excellent yields.

4.2.1. 4-(Phenylethynyl)aniline (3aa).¹² Purified by chromatography on silica gel (30:1 hexanes–ethyl acetate) afforded **3aa** in 88% yield (85 mg, 0.44 mmol).

The following coupling products were obtained in a manner described above: 2-(phenylethynyl)aniline (**3ab**),¹³ 2-(phenylethynyl)phenol (**3ac**),¹⁴ 4-(phenylethynyl)phenol (**3ad**),¹⁵ 3-(phenylethynyl)aniline (**3ae**),^{7b} 3-(phenylethynyl)phenol (**3af**),¹⁶ 4-(trimethylsilylethynyl)aniline (**3ba**),¹⁷ 2-(trimethylsilylethynyl)aniline (**3bb**),¹⁸ 2-(trimethylsilylethynyl)phenol (**3bc**),¹⁹ 4-(trimethylsilylethynyl)phenol (**3bd**).²⁰

4.3. General procedure for Sonogashira-coupling reaction of 4-aminophenylethyne with aryl iodides

To $\text{PdCl}_2(\text{PPh}_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), and **2** (0.5 mmol) in 3 mL of THF was added 4-aminophenylethyne (**1c**) (63.5 mg, 0.5 mmol) at room temperature under an argon atmosphere. A 0.5 M solution of aqueous ammonia (2 mL, 1 mmol) was then added dropwise and stirring was continued for the period given in Scheme 2 at room temperature. Two phases of the resulting mixture were separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel (hexanes–ethyl acetate) to furnish the corresponding coupling product in good yield.

4.3.1. 4-(4-Methoxyphenylethynyl)aniline (3cg). Purified by flash chromatography on silica gel (50:1 hexanes–ethyl acetate) to afford 83 mg of **3cg** (74%) as a white solid. Mp 140–141 °C. IR (KBr) 3447, 3359, 3034, 3011, 2211, 1607 cm^{-1} . ^1H NMR (CDCl_3) δ 3.82 (s, 3H), 3.80–3.83 (br,

2H), 6.63 (d, $J=8.1$ Hz, 2H), 6.86 (d, $J=8.7$ Hz, 2H), 7.32 (d, $J=8.1$ Hz, 2H), 7.43 (d, $J=8.7$ Hz, 2H). ^{13}C NMR (CDCl_3) 55.24, 87.11, 88.59, 112.96, 113.90, 114.75, 116.02, 132.74 (br), 146.36, 159.17. HRMS (EI) m/z Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$ 223.0997, found 223.0978.

The following coupling product was obtained in a manner described above: bis-(4-aminophenyl)ethyne (**3ca**).²¹

4.4. (4-Heptyloxyphenyl)-(4-iodophenyl)diazene (4a)

To a solution of KOH (2.94 mmol) and 4-iodoazophenol (1.47 mmol) in 4 mL DMSO was added 1-iodoheptane (2.2 mmol). The resulting mixture was then stirred for 2.5 h at room temperature. After the reaction was complete, the resulting mixture was extracted with chloroform (3×15 mL) and the combined organic layer was dried over anhydrous MgSO_4 , and concentrated in vacuo. The residue was purified by flash chromatography using (10:1 hexanes–ethyl acetate) to afford 551 mg of **4a** (93%) as an orange solid. Mp 112–113 °C. IR (KBr) 2953, 2857, 1605.0, 1584, 1559 cm^{-1} . ^1H NMR (CDCl_3) δ 0.90 (t, $J=6.9$ Hz, 3H), 1.31–1.50 (m, 8H), 1.79–1.85 (m, 2H), 4.04 (t, $J=6.6$ Hz, 2H), 7.00 (d, $J=9.0$ Hz, 2H), 7.61 (d, $J=9.0$ Hz, 2H), 7.84 (d, $J=9.0$ Hz, 2H), 7.90 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) 14.09, 22.60, 25.95, 29.04, 29.16, 31.75, 68.38, 96.60, 114.75, 124.20, 124.96, 138.22, 146.60, 152.03, 162.05. HRMS (EI) m/z Calcd for $\text{C}_{14}\text{H}_{13}\text{IN}_2\text{O}$ 422.0855, found 422.0846.

4.5. General procedure for Sonogashira coupling of aryl iodide bearing an azobenzene moiety with aqueous ammonia

To $\text{PdCl}_2(\text{PPh}_3)_2$ (3.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), and **4** (0.5 mmol) in 3 mL of THF was added **1** (0.6 mmol) at room temperature. A 0.5 M solution of aqueous ammonia (2 mL, 1 mmol) was then added dropwise and stirring was continued for the period given in Table 2 at room temperature. Two phases of the resulting mixture were separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was concentrated under reduced pressure to leave a crude solid, which was purified by chromatography on silica gel (hexanes–ethyl acetate) to furnish the corresponding coupling product in good to excellent yield.

4.5.1. (4-Heptyloxyphenyl)-{(4-trimethylsilylethynyl)-phenyl}diazene (5ba). Purified by chromatography on silica gel (20:1 hexanes–ethyl acetate) to furnish 170.8 mg of **5ba** (87%) as an orange solid. Mp 93–94 °C. IR (KBr) 2955, 2938, 2924, 2867, 2161, 1605, 1584 cm^{-1} . ^1H NMR (CDCl_3) δ 0.27 (s, 9H), 0.90 (t, $J=6.6$ Hz, 3H), 1.32–1.51 (m, 8H), 1.79–1.86 (m, 2H), 4.04 (t, $J=6.6$ Hz, 2H), 7.00 (d, $J=9.0$ Hz, 2H), 7.58 (d, $J=9.0$ Hz, 2H), 7.81 (d, $J=9.0$ Hz, 2H), 7.90 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 0.08, 14.07, 22.59, 25.95, 29.03, 29.16, 31.75, 68.32, 96.49, 104.83, 114.69, 122.45, 124.89, 132.33, 132.72, 146.82, 152.07, 161.95. HRMS (EI) m/z Calcd for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{OSi}$ 392.2284, found 392.2280.

4.5.2. 4-[4-(4-Heptyloxyphenylazo)phenylethynyl]benzonitrile (5da). Purified by chromatography on silica gel (5:1

hexanes–ethyl acetate) to furnish 110 mg of **5da** (79%) as an orange solid. Mp 171–172 °C. IR (KBr) 2940, 2872, 2855, 2226, 2213, 1601, 1580 cm^{-1} . ^1H NMR (CDCl_3) δ 0.90 (t, $J=7.2$ Hz, 3H), 1.34–1.51 (m, 8H), 1.79–1.86 (m, 2H), 4.05 (t, $J=6.6$ Hz, 2H), 7.01 (d, $J=9.0$ Hz, 2H), 7.62–7.68 (m, 6H), 7.90 (d, $J=8.4$ Hz, 2H), 7.93 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) 14.06, 22.58, 25.94, 29.01, 29.14, 31.74, 68.39, 89.58, 93.59, 111.65, 114.76, 118.45, 122.69, 123.86, 125.00, 127.97, 132.05, 132.08, 132.60, 146.81, 152.48, 162.14. HRMS (EI) m/z Calcd for $\text{C}_{28}\text{H}_{27}\text{N}_3\text{O}$ 421.2154, found 421.2142.

4.5.3. 4-[(4-Trimethylsilylethynyl)phenylazo]phenol (5bb). Purified by chromatography on silica gel (10:1 hexanes–ethyl acetate) to furnish 132.4 mg of **5bb** (90%) as an orange solid. Mp 129–130 °C. IR (KBr) 3170 (br), 2957, 2155, 1603, 1593 cm^{-1} . ^1H NMR (CDCl_3) δ 0.27 (s, 9H), 5.27 (brs, 1H), 6.96 (d, $J=9.0$ Hz, 2H), 7.59 (d, $J=8.1$ Hz, 2H), 7.82 (d, $J=8.1$ Hz, 2H), 7.89 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) δ -0.10, 96.77, 104.77, 115.90, 122.48, 125.16, 132.78, 147.09, 151.91, 158.57. HRMS (EI) m/z Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{OSi}$ 294.1188, found 294.1194.

4.5.4. 4-[4-(3,3-Dimethylbut-1-ynyl)phenylazo]phenol (5eb). Purified by chromatography on silica gel (10:1 hexanes–ethyl acetate) to furnish 107 mg of **5eb** (76%) as an orange solid. Mp 154–155 °C. IR (KBr) 3235 (br), 2967, 2929, 2865, 2234, 1593 cm^{-1} . ^1H NMR (CDCl_3) δ 1.34 (s, 9H), 5.18 (brs, 1H), 6.94 (d, $J=9.0$ Hz, 2H), 7.50 (d, $J=8.7$ Hz, 2H), 7.80 (d, $J=8.7$ Hz, 2H), 7.87 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) 28.08, 30.94, 79.05, 101.15, 115.91, 122.45, 125.02, 126.37, 132.32, 147.04, 151.32, 158.54. HRMS (EI) m/z Calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}$ 278.1419, found 278.1411.

4.5.5. 4-(4-Oct-1-ynylphenylazo)phenol (5fb). Purified by chromatography on silica gel (10:1 hexanes–ethyl acetate) to furnish 118 mg of **5fb** (77%) as an orange solid. Mp 103–104 °C. IR (KBr) 3320 (br), 2957, 2930, 2857, 2226, 1595 cm^{-1} . ^1H NMR (CDCl_3) δ 0.92 (t, $J=6.6$ Hz, 3H), 1.31–1.66 (m, 8H), 2.44 (t, $J=7.2$ Hz, 2H), 5.38 (brs, 1H), 6.94 (d, $J=8.7$ Hz, 2H), 7.51 (d, $J=8.7$ Hz, 2H), 7.81 (d, $J=8.7$ Hz, 2H), 7.88 (d, $J=8.7$ Hz, 2H). ^{13}C NMR (CDCl_3) 14.03, 19.54, 22.52, 28.61 (br), 31.32, 80.55, 93.25, 115.91, 122.48, 125.04, 126.40, 132.31, 147.02, 151.33, 158.54. HRMS (EI) m/z Calcd for $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}$ 306.1732, found 306.1729.

4.5.6. (4-Heptyloxyphenylazo)-phenylethyne (1h). To a solution of **5bb** (196 mg, 0.5 mmol) in 3 mL methanol was added K_2CO_3 (26.6 mg, 0.19 mmol). The stirring was continued at room temperature for 40 min. The solvent was then evaporated under reduce pressure and the resulted crude sample subjected to aqueous workup and purified through flash chromatography (hexanes–ethyl acetate 10:1) afforded 134.5 mg of **1h** (84%) as a red solid. Mp 89 °C. IR (KBr) 3285, 2961, 2936, 2924, 2872, 2859, 1603, 1586 cm^{-1} . ^1H NMR (CDCl_3) δ 0.90 (t, $J=6.9$ Hz, 3H), 1.32–1.48 (m, 8H), 1.83 (quint, $J=8.4$ Hz, 2H), 3.21 (s, 1H), 4.05 (t, $J=6.6$ Hz, 2H), 7.00 (d, $J=9.0$ Hz, 2H), 7.61 (d, $J=8.4$ Hz, 2H), 7.84 (d, $J=8.4$ Hz, 2H), 7.91 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) 14.06, 22.59, 25.95, 29.03, 29.16, 31.75, 68.37, 79.04, 82.96, 114.72, 122.49, 122.61,

123.83, 124.94, 132.90, 146.80, 152.36, 162.02. HRMS (EI) m/z Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}$ 320.1889, found 320.1892.

4.5.7. (4-Heptyloxyphenyl)-[4-(4-heptyloxyphenylethynyl)phenyl]diazene (5ga). Purified by chromatography on silica gel (20:1 hexanes–ethyl acetate) to furnish 110 mg of **5ga** (86%) as an orange solid. Mp 173–174 °C. IR (KBr) 2953, 2936, 2924, 2872, 2861, 2215, 1603, 1584 cm^{-1} . ^1H NMR (CDCl_3) δ 0.90 (t, $J=6.6$ Hz, 6H), 1.25–1.51 (m, 16H), 1.74–1.87 (m, 4H), 3.98 (t, $J=6.6$ Hz, 2H), 4.04 (t, $J=6.6$ Hz, 2H), 6.88 (d, $J=9.0$ Hz, 2H), 7.0 (d, $J=9.0$ Hz, 2H), 7.48 (d, $J=8.4$ Hz, 2H), 7.62 (d, $J=8.4$ Hz, 2H), 7.86 (d, $J=9.0$ Hz, 2H), 7.91 (d, $J=9.0$ Hz, 2H). ^{13}C NMR (CDCl_3) 14.06, 22.60, 25.98, 29.04, 29.20, 31.77, 68.13, 68.41, 88.07, 91.84, 114.62, 114.76, 114.90, 122.61, 124.84, 125.67, 132.15, 133.13, 146.96, 151.79, 159.47, 161.91. Anal. Calcd for $\text{C}_{34}\text{H}_{42}\text{N}_2\text{O}_2$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.56; H, 8.23; N, 5.38.

4.6. Coupling of 5ba with 4-cyanobenzene triflate

To 25 mL Schlenk tube under argon atmosphere were added $\text{PdCl}_2(\text{PPh}_3)_2$ (17.5 mg, 0.025 mmol), CuCl (4.95 mg, 0.05 mmol), 4-cyanobenzene triflate (125.6 mg, 0.5 mmol), and **5ba** (196.3 mg, 0.5 mmol) in 3 mL of DMF at room temperature. The stirring was continued for 24 h in an oil bath at 80 °C. The resulting mixture was then cooled down and followed the general aqueous workup. The crude product was then purified by chromatography on silica gel (hexanes–ethyl acetate) to furnish 113 mg of **5da** (81%).

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