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Efficient Synthesis of a Complete Donor/Acceptor bis(Aryl)diyne Family

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Efficient Synthesis of a Complete Donor/Acceptor *bis*(Aryl)diyne Family

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ABSTRACT

A facile route to a family of *bis*(aryl)diynes containing both an electron donating pyridine ring and an electron accepting iodobenzene has been developed. The convergent synthesis involves the coupling of 2-, 3-, or 4-bromopyridine with TMS-acetylene, followed by deprotection to form the first half of the molecule. Similarly, 2-, 3-, or 4-iodoaniline was coupled to TMS-acetylene

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after protection of the amine group as a diethyltriazine. After conversion of the triazine to an iodine, deprotection of the acetylene and formation of the corresponding bromophenylacetylene, the two halves of the molecule were coupled under Cadiot-Chodkiewicz conditions. Nine new compounds were prepared, each of which was found to thermally polymerize from the melt. None of the compounds underwent photochemical polymerization in the solid-state.

Key Words: Diacetylene; Charge-transfer; Cross-coupling.

INTRODUCTION

The 1,3-butadiyne or diacetylene (DA) moiety is responsible for some unique and important chemistry. In addition to its role in various natural products.^[1] the DA group can undergo polymerization to form highly conjugated materials with interesting optical, nonlinear optical and electrical properties.^[2] If the DA-containing monomer crystallizes with the proper packing geometry (described in the literature^[3]) this polymerization can be topotactic, leading to highly crystalline polymers. Connection of the DA termini directly to aromatic rings leads to extended conjugation, but the rigidity of the system decreases the likelihood of solid-state polymerization. This is particularly true for heterocyclic DAs, where polymerizable compounds are extremely rare.^[4] Still, bis(aryl)DAs have been widely investigated for use in supramolecular synthesis, particularly in the realm of molecular electronics,^[5] conjugated macrocycles^[6] and as ligands for organometallic structures.^[7] Perhaps the reason for this interest is the relatively few degrees of freedom in the compounds, which makes the design of very large systems conceptually simple.

RESULTS AND DISCUSSION

As part of an ongoing crystal engineering effort, we found it necessary to prepare the nine possible isomers of DA 1 (Sch. 1). In addition to the structural features found in all *bis*(aryl)DAs, this family of compounds can form $N \cdots I$ halogen bonds^[8] (or X-bonds) with themselves or with other donors or acceptors. Of course, the pyridine lone pair is

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Scheme 1. Target compounds: a) 4-I, 4-py; b) 4-I, 3-py; c) 4-I, 2-py; d) 3-I, 4-py; e) 3-I, 3-py; f) 3-I, 2-py; g) 2-I, 4-py; h) 2-I, 3-py; i) 2-I, 2-py.

also available for coordination to metal centers, while the iodine provides a convenient site for further structural elaboration.

While none of the members of this family have been previously reported, DAs are generally prepared by the coupling or cross-coupling of terminal acetylenes. Therefore, we designed a convergent synthesis making use of the previously reported iodophenylacetylenes and the ethynylpyridines. In order to prevent homocoupling by this route, however, one of the acetylenes must be brominated.

Several synthetic routes to 2-, 3-, and 4-ethynylpyridine have been previously reported, as these compounds have been used to construct a number of polymeric and supramolecular species. Dehydrohalogenation of vinylpyridines has been successful, but involves several steps from available starting materials, suffers from low yields and involves difficult purifications.^[9] Direct palladium/copper catalyzed coupling of 2-methyl-3-butyn-2-ol and the commercially available bromopyridines, 2a-c, proceeds in excellent yields, but the subsequent deprotection step does not.^[10] The Stang group used TMS-protected acetylene in a similar coupling reaction to prepare 3c, but the deprotection step was again problematic, limiting the overall yield to only 50%.^[11] We prepared compounds **3a–c** using the same starting materials (Sch. 2), but effected the deprotection by stirring it in a methanolic KOH solution rather than TBAF/THF. This improved the yields to 85-90% overall and permitted easy purification of the products. Bromination of the ethynylpyridines to give 4a-c was also efficient, but the products lacked thermal and photochemical stability and the route was not pursued.

The synthesis of the iodophenylacetylene precursors has also been reported. Takahashi et al coupled TMS-acetylene to 4-iodoaniline, followed by conversion of the amino group to an iodine using Sandmeyer conditions and then deprotection of the acetylene.^[12] Similar strategies have been used by others, however, the yields, particularly of products **7b** and **7c**, are modest.^[13] In developing routes to large phenylacetylene macrocycles, the Moore group choose to first convert anilines to phenyltriazines (Sch. 3) before reaction at the iodine.^[14] Using a slight

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Scheme 2. Reagents and conditions: a) (Ph₃P)₂PdCl₂, CuI, *i*-Pr₂NH, TMS-acetylene; b) KOH, MeOH/CH₂Cl₂; c) NBS, AgNO₃, acetone.



Legend: a= 4-I, b= 3-I, c= 2-I

Scheme 3. Reagents and conditions: a) HCl/CH_3CN ; b) $NaNO_2/H_2O$; c) K_2CO_3/DEA ; d) $(Ph_3P)_2PdCl_2$, CuI, Et₃N, TMS-acetylene; e) CH_3I , $120^{\circ}C$; f) KOH, MeOH/CH₂Cl₂; g) NBS, AgNO₃, acetone.

modification of these conditions, we were able to prepare 7a-c in overall yields of 60–65%, significantly higher than the more direct route, despite the additional step. Once again, in our hands the methanolic KOH deprotection method gave superior results to TBAF/THF or K₂CO₃. Conversion to the bromoacetylenes **8a–c** by treatment with NBS and AgNO₃ proceeded in approximately 90% yield in each case.

DAs 1a-i were prepared by Cadiot-Chodkiewicz coupling^[15] of the appropriate combinations of 3a-c and 8a-c. The ethynylpyridines were added to a solution of CuCl (cat.), 70% aqueous ethylamine and hydroxylamine hydrochloride in methanol. The bromoethynyl-iodobenzene was then added slowly to this solution while maintaining

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a constant temperature between 30 and 35° C. In each case, column chromatography afforded a small amount of starting material as well as the desired DA product. While the formation of symmetrical DA dimer side products have commonly been reported during Cadiot-Chodkiewicz cross-couplings, in only one case, the reaction of **3a** with **8b**, was the presence of a homo-coupled DA detected (the dimer of **3a**). This compound could be cleanly separated from the desired unsymmetrical DA by column chromatography.

Yields for the DAs were good, ranging from 70–88% for the single coupling step. Each DA was stable under ambient conditions, with the exception of **1f** and **1i**. These compounds initially crystallized as yellow solids, but gradually darkened in the presence of room light. Exposure of the solid DAs to UV radiation resulted in the slight darkening of some material, but there was no evidence of topopolymerization (characterized by the formation of intensely absorbing blue or red phases). This was expected, not only because the polymerization is rare in *bis*(aryl)DA's, but also because the compounds are expected to exhibit N…I X-bonding in the solid state, inhibiting the molecular motions required during the reaction.^[8d]

The thermal behavior of compounds **1a-i** were also explored by differential scanning calorimetry and thermal gravimetric analysis. All compounds displayed generally similar behavior. The first thermal event was the melting of the solid, usually accompanied by a small mass loss (on the order of 1-5%). The melting points varied from 65°C to 160°C, with the more linear compounds, such as 1a-c, melting towards the high end of the range, while the less linear compounds, such as 1h, and 1i, melted towards the low end. The melting points were more sensitive to iodine position than to nitrogen position. At higher temperature, an exothermic event occurred, again accompanied by a small mass loss (1-15%). This usually occurred with an onset temperature of around 220°C, but could be as high as 240°C or as low as 130°C. Based on these data and hot stage optical microscopy, we attribute the exothermic event to a thermallyinduced polymerization in the melt. Often, some of the monomer would evaporate during this process, before it could be locked into the matrix. Finally, between 310 and 325°C the samples evaporated, presumably concomitant with the decomposition of the polymer.

In summary, nine new *bis*(aryl)DA supramolecular building blocks have been synthesized in good yields and characterized by spectroscopic and thermal methods. The DAs do not undergo photochemical topopolymerization, but do polymerize in the melt. **MA**

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EXPERIMENTAL

All reagents were obtained from commercial sources and used without further purification unless mentioned elsewhere. Diisopropylamine. diethylamine, triethylamine, acetonitrile, and dichloromethane were distilled from calcium hydride under a nitrogen atmosphere. Methanol and acetone were dried over activated 3Å molecular sieves. All ¹H and ¹³CNMR spectra were obtained on a Bruker AC-300 Fourier Transform Spectrometer using deuterated chloroform (CDCl₃) as the solvent. Chemical shifts are reported in parts per million (δ) downfield relative to tetramethylsilane (TMS). GC-MS analyses were performed on a Hewlett-Packard 5970 Series Mass Selective Detector with a Hewlett-Packard 5890A Gas Chromatograph. Elemental analyses of selected compounds were obtained from Atlantic Microlab, INC, P.O. Box 2288, Norcross, Georgia, 30091. UV-vis absorption spectra were recorded on a Shimadzu UV-2101PC UV-vis Scanning Spectrophotometer. Thermal gravimetric analyses were performed on a Mettler-Toledo TGA (SDTA851^e) instrument with the Star^e software package (ver 6.0). Differential scanning calorimetry was performed on a Mettler-Toledo TGA DSC820 instrument with the Star^e software package (ver 6.0). The TGA samples had a mass of approximately 5 mg each and all calculations were performed on data represented as percent loss of starting mass. For onset calculations, the samples were heated at a constant rate of 5°C min⁻¹ from 25°C until all of the material had evaporated. Mass loss and onset calculations were performed by standard methods. Experiments were performed under nitrogen gas (50 mL/min). The DSC samples had a mass of approximately 5 mg each and were heated at a constant rate of 5° C min⁻¹ from 25°C until all of the material had evaporated. Experiments were performed under nitrogen gas with a flow of 50 mL/min.

4-[2-(Trimethylsilyl)ethynyl]pyridine. 4-Bromopyridine hydrochloride (1.00 g, 5.1 mmol), *bis*(triphenylphosphine)palladium(II) chloride (0.09 g, 2.5 mol%) and copper iodide (0.024 g, 2.5 mol%) were placed in a three-neck round bottom flask. The flask was flushed with nitrogen and diisopropylamine (10 mL) was added into the flask while stirring at 40°C, followed by the addition of trimethylsilylacetylene (0.8 mL, 5.7 mmol). After 12 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and a clear solid (87% yield) was obtained by Kugelrohr distillation (95°C/3 mmHg). Spectral data were consistent with literature reports.^[5]

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General Procedure for 3-[2-(Trimethylsilyl)ethynyl]pyridine and 2-[2-(Trimethylsilyl)ethynyl]pyridine

In a three neck round bottom flask, the appropriate bromopyridine (1.00 mL, 10.5 mmol), *bis*(triphenylphosphine)palladium(II) chloride (0.18 g, 2.5 mol%) and copper iodide (0.050 g, 2.5 mol%) were added. The flask was flushed with nitrogen and diisopropylamine (17 mL) was added into the flask while stirring at 30°C, followed by trimethylsilylace-tylene (1.7 mL, 11.6 mmol). After 3 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the product was obtained by Kugelrohr distillation (95°C/3 mm Hg).

3-[2-(Trimethylsilyl)ethynyl]pyridine. Colorless oil, 93% yield. $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.59 (s, 1H), 8.42 (d, J = 6.0 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.11 (dd, J = 6.4 Hz, 1H), 0.18 (s, 9H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 152.49 (CH), 148.56 (CH), 138.58 (CH), 122.69 (CH), 120.14, 101.36, 98.03, 0.00 (CH). GC-MS, m/z (relative intensity): 175 (21), 160 (100).

2-[2-(Trimethylsilyl)ethynyl]pyridine. Colorless oil, 91% yield. $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.20 (d, J = 4.1 Hz, 1H), 7.27 (m, 1H), 7.09 (m, 1H), 6.85 (m, 1H), 0.20 (s, 9H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 148.89 (CH), 142.04, 135.08 (CH), 126.24 (CH), 122.07 (CH), 102.93, 93.45, 0.00 (CH). GC-MS, m/z (relative intensity): 175 (21), 160 (100).

4-, 3-, and 2-Ethynylpyridines (3a-c): General Procedure

In a nitrogen flushed three neck round bottom flask, potassium hydroxide (0.64 g, 11.4 mmol) was added to methanol (10 mL), dichloromethane (5 mL) and 2-, 3-, or 4-[2-(trimethylsilyl)-ethynyl]pyridine (1.00 g, 5.7 mmol). After 2 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The remaining solution was then passed through a silica gel plug, eluting with dichloromethane. The solvent was removed under reduced pressure yielding the pure product (90, 86, and 85% yield, respectively). Spectral data were consistent with literature reports.^[9b]

1-(2,3, and 4-Iodophenyl)-3,3-diethyltriazene: General Procedure

In a 25 mL three-neck round bottom flask fitted to a reflux condenser, 2-, 3-, or 4-iodoaniline (1.00 g, 4.6 mmol), acetonitrile (5 mL) and 6 M HCl

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(1.8 mL) were heated and stirred under nitrogen at 70°C for 15 min. The mixture was then allowed to cool to room temperature, and then cooled further in an ice bath until the temperature of the mixture was about 15° C. To this cooled solution was added a solution of sodium nitrite (0.41 g, 5.9 mmol) in water (1 mL). The resultant solution was allowed to stir for 15 min. In a separate 50 mL three-neck round bottom flask, potassium carbonate (3.17 g, 22.9 mmol), diethylamine (0.72 mL, 6.9 mmol), water (6.6 mL) and acetonitrile (2.2 mL) were stirred under nitrogen in an ice bath for 20 min. The first solution was then poured slowly into the second solution and allowed to stir for 10 min. The ice bath was removed and the resulting solution was allowed to stir an additional hour. The organic phase was extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure oil was isolated by column chromatography.

1-(4-Iodophenyl)-3,3-diethyltriazene. Red oil (silica gel, 3:2 hexane/ chloroform, R_f =0.44, 94% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.61 (d, J=6.9 Hz, 2H), 7.18 (d, J=6.9 Hz, 2H), 3.73 (q, J=7.1, 4H), 1.25 (t, J=6.9 Hz, 6H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.81, 137.58 (CH), 123.38 (CH), 88.89, 45.52 (CH), 13.12 (CH). GC-MS, m/z (relative intensity): 303 (12), 231 (35), 203 (100), 50 (21).

1-(3-Iodophenyl)-3,3-diethyltriazene. Brown oil (silica gel, 3:2 hexane/ chloroform, R_f =0.44, 96% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.81 (s, 1H), 7.44 (d, J=7.6 Hz, 1H), 7.38 (d, J=8.4 Hz, 1H), 7.04 (dd, J=8.0 Hz, 1H), 3.74 (q, J=7.1 Hz, 4H), 1.25 (t, J=6.5 Hz, 6H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 152.40, 133.50 (CH), 130.18 (CH), 128.81 (CH), 120.27 (CH), 94.48, 48.92 (CH), 41.56 (CH), 12.90 (CH). GC-MS, m/z (relative intensity): 303 (12), 231 (35), 203 (100), 50 (21).

1-(2-Iodophenyl)-3,3-diethyltriazene. Red oil (silica gel, 3:2 hexane/ chloroform, R_f =0.44, 92% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.86 (d, J=6.7 Hz, 1H), 7.36 (d, J=6.5 Hz, 1H), 7.29 (dd, J=6.9 Hz, 1H), 6.85 (dd, J=6.2 Hz, 1H), 3.79 (q, J=7.2 Hz, 4H), 1.33 (t, J=7.1Hz, 6H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.27, 138.88 (CH), 128.50 (CH), 126.40 (CH), 117.41 (CH), 96.52, 49.01 (CH), 42.05 (CH), 14.44 (CH), 10.98 (CH). GC-MS, m/z (relative intensity): 303 (12), 231 (35), 203 (100), 50 (21).

1-[2-, 3-, and 4-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3diethyltriazene (6a-c): General Procedure

In a three neck round bottom flask, 1-(2-, 3-, or 4-iodophenyl)-3, 3-diethyltriazene (1.00 g, 3.3 mmol), *bis*(triphenylphosphine)palladium(II)

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chloride (0.058 g, 2.5 mol%) and copper iodide (0.016 g, 2.5 mol%) were added. The flask was flushed with nitrogen and triethylamine (12 mL) was added via syringe into the flask, followed by trimethylsilylacetylene (0.47 mL, 3.6 mmol). After 3 h at 30° C, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure oil was isolated by performing column chromatography.

1-[4-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (6a). Brown oil (silica gel, 4:1 hexane/chloroform, R_f =0.91, 95% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.42 (d, J=5.8 Hz, 2H), 7.33 (d, J=5.8 Hz, 2H), 3.74 (q, J=7.1 Hz, 4H), 1.25 (t, J=6.8 Hz, 6h), 0.24 (s, 9H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 151.12, 132.63 (CH), 120.19 (CH), 119.21, 105.78, 93.41, 42.18 (CH), 13.01 (CH), 0.00 (CH). GC-MS, m/z (relative intensity): 273 (28), 201 (25), 173 (100), 158 (35), 145 (36), 79 (14).

1-[3-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (6b). Yellow oil (silica gel, 4:1 hexane/chloroform, R_f =0.91, 93% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.56 (s, 1H), 7.38 (m, 2H), 7.25 (m, 1H), 3.73 (q, J=7.1 Hz, 4H), 1.24 (t, J=7.0 Hz, 6H), 0.27 (s, 9H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.97, 128.54 (CH), 128.34 (CH), 123.66 (CH), 123.34, 121.03 (CH), 105.50, 93.23, 45.54 (CH), 12.68 (CH), 0.00 (CH). GC-MS, m/z (relative intensity): 273 (28), 201 (25), 173 (100), 158 (35), 145 (36), 79 (14).

1-[2-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (6c). Orange oil (silica gel, 4:1 hexane/chloroform, R_f =0.91, 91% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.46 (m, 1H), 7.38 (m, 1H), 7.23 (m, 1H), 7.02 (m, 1H), 3.77 (q, *J*=7.1 Hz, 4H), 1.29 (t, *J*=7.1 Hz, 6H), 0.24 (s, 9H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 152.73, 133.16 (CH), 129.01 (CH), 124.48 (CH), 117.92, 116.70 (CH), 103.52, 97.72, 48.97 (CH), 41.69 (CH), 14.77 (CH), 11.64 (CH), 0.00 (CH). GC-MS, *m/z* (relative intensity): 273 (28), 201 (25), 173 (100), 158 (35), 145 (36), 79 (14).

1-[2-(Trimethylsilyl)ethynyl]-2-,3-, or 4-iodobenzene: General Procedure

1-[2-, 3-, or 4-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (1.00 g, 3.7 mmol) and methyl iodide (20 mL) were sealed in a heavy walled flask under nitrogen and heated at 110°C for 4 days. The reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure product was isolated by column chromatography (silica gel, 3:2 hexane/dichloromethane). Yields were 86, 85,

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and 90%, respectively. Spectroscopic data were consistent with literature reports.^[13]

1-Ethynyl-2-, 3-, and 4-iodobenzene (7a-c): General Procedure

In a nitrogen flushed three neck round bottom flask, potassium hydroxide (0.37 g, 6.6 mmol) was added to methanol (10 mL), dichloromethane (5 mL) and 1-[2-(trimethylsilyl)ethynyl]-2-, 3-, or 4-iodobenzene (1.00 g, 3.3 mmol). After stirring for 2 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure product was isolated by column chromatography (silica gel, 4:1 hexane/dichloromethane) and recrystallized from hexane. Yields were 83, 80, and 87%, respectively. Spectroscopic data were consistent with literature reports.^[13]

1-(2-Bromoethynyl)-2-, 3-, and 4-iodobenzene (8a-c): General Procedure

In a nitrogen flushed three-neck round bottom flask, acetone (25 mL) was added into a mixture of 1-ethynyl-2,3, or 4-iodobenzene (1.00 g, 4.4 mmol), *N*-bromosuccinimide (0.94 g, 5.3 mmol) and silver nitrate (0.12 g). After stirring for 6 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure product was isolated by column chromatography.

1-(2-Bromoethynyl)-4-iodobenzene (8a). White solid recrystallized from methanol (silica gel, 4:1 hexane/dichloromethane, R_f =0.81, 93% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.63 (d, J=8.3 Hz, 2H), 7.14 (d, J=8.3 Hz, 2H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 137.52 (CH), 133.44 (CH), 122.09, 94.86, 79.16, 51.77. Elemental Analysis Calculated for C₈H₄IBr: C, 31.31; H, 1.31. Found: C, 32.05; H, 1.47.

1-(2-Bromoethynyl)-3-iodobenzene (8b). Yellow solid recrystallized from methanol (silica gel, 4:1 hexane/dichloromethane, $R_f = 0.81$, 89% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.86 (s, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.06, (dd, J = 7.8 Hz, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 140.49 (CH), 137.66 (CH), 131.01 (CH), 129.71 (CH), 124.59, 93.58, 78.37, 51.68. Elemental Analysis Calculated for C₈H₄IBr: C, 31.31; H, 1.31. Found: C, 31.90; H, 1.34.

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1-(2-Bromoethynyl)-2-iodobenzene (8c). Yellow solid recrystallized from methanol (silica gel, 4:1 hexane/dichloromethane, $R_f = 0.81$, 87% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 7.79 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.26 (m, 1H), 6.98 (m, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 138.57 (CH), 133.11 (CH), 129.69 (CH), 129.11, 127.66 (CH), 100.54, 82.04, 54.26. Elemental Analysis Calculated for C₈H₄IBr: C, 31.31; H, 1.31. Found: C, 31.73; H, 1.40.

1-[2-, 3-, and 4-Iodophenyl]-4-[2-,3-, and 4-pyridyl]buta-1,3-diyne (1a-i)

In a nitrogen flushed three-neck round bottom flask, methanol (5 mL) was added into a measured amount of hydroxylamine hydrochloride (0.007 g, 0.1 mmol) and copper(I) chloride (0.01 g, 0.1 mmol) and stirred for 5 min. A 70% aqueous solution of ethylamine (1.2 mL) was then slowly dropped into the solution and allowed to stir for five more minutes. A solution of 2-, 3-, or 4-ethynylpyridine (0.1 g, 0.97 mmol) dissolved in a mixture of methanol (2 mL) and dichloromethane (1 mL) was then slowly added into the flask dropwise. After ten minutes, a separate solution of 1-(2-bromoethynyl)-2-, 3-, or 4-iodobenzene (0.33 g, 1.1 mmol) of dissolved in a mixture of methanol (1 mL) and dichloromethane (2 mL) was slowly added into the flask at 35°C. After 6 h, the reaction mixture was quenched with water; extracted with dichloromethane, dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the pure solid was isolated by column chromatography and recrystallized from chloroform/hexane.

1-[4-Iodophenyl]-4-[4-pyridyl]buta-1,3-diyne (1a). White solid (silica gel, 1:1 hexane/chloroform, $R_f = 0.20$, 82% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.62 (d, J = 6.0 Hz, 2H), 7.71 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 5.9 Hz, 2H), 7.25 (d, J = 6.3 Hz, 2H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 149.90 (CH), 137.80 (CH), 133.89 (CH), 139.93, 136.01 (CH), 120.87, 96.45, 79.04, 77.89, 76.22, 74.65. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.50; H, 2.71; N, 4.15. UV $\lambda_{\rm max}$ (ethanol): 318.5 nm.

1-[4-Iodophenyl]-4-[3-pyridyl]buta-1,3-diyne (1b). White solid (silica gel, 1:1 hexane/chloroform, R_f =0.20, 84% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.76 (s, 1H), 8.58 (m, 1H), 7.79–7.81 (m, 1H), 7.68–7.71 (m, 2H), 7.30–7.23 (m, 3H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 153.18 (CH), 149.43 (CH), 139.38 (CH), 137.81 (CH), 133.93 (CH), 123.15 (CH), 120.91, 119.14, 96.04, 81.77, 78.78, 77.13, 74.81. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 55.01; H, 2.82; N, 4.41. UV $\lambda_{\rm max}$ (ethanol): 313.5 nm.

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1-[4-Iodophenyl]-4-[2-pyridyl]buta-1,3-diyne (1c). White solid (silica gel, 1:1 hexane/chloroform, R_f =0.20, 70% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.63 (m, 1H), 7.65–7.71 (m, 3H), 7.52 (d, J=7.8 Hz, 1H), 7.24–7.30 (m, 3H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.39 (CH), 142.15, 137.70 (CH), 136.15 (CH), 133.94 (CH), 128.11 (CH), 123.58 (CH), 120.83, 95.96, 81.37, 80.90, 74.90, 73.46. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.62; H, 2.81; N, 4.31. UV $\lambda_{\rm max}$ (ethanol): 238.5 nm.

1-[3-Iodophenyl]-4-[4-pyridyl]buta-1,3-diyne (1d). White solid (silica gel, 1:1 hexane/chloroform, $R_f = 0.20$, 88% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.61 (m, 2H), 7.87 (s, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 5.1 Hz, 2H), 7.07 (dd, J = 7.8 Hz, 1H), 7.35 (d, J = 5.1 Hz, 2H), 7.07 (dd, J = 7.8 Hz, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 149.94 (CH), 141.09 (CH), 138.83 (CH), 131.79 (CH), 130.11, 129.88 (CH), 126.18, 123.26 (CH), 93.78, 81.76, 79.09, 77.92, 74.42. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.83; H, 2.41; N, 4.19. UV $\lambda_{\rm max}$ (ethanol): 245.0 nm.

1-[3-Iodophenyl]-4-[3-pyridyl]buta-1,3-diyne (1e). White solid (silica gel, 1:1 hexane/chloroform, $R_f = 0.20$, 80% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.71 (s, 1H), 8.53 (d, J = 4.1 Hz, 1H), 7.82 (s, 1H), 7.74 (d, J = 6.6 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.20-7.24 (m, 1H), 7.02 (dd, J = 7.8 Hz, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 152.99 (CH), 149.24 (CH), 140.83 (CH), 139.21 (CH), 138.40 (CH), 131.52 (CH), 129.82 (CH), 123.31, 122.94 (CH), 118.87, 93.60, 80.67, 78.70, 76.81, 74.59. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.72; H, 2.50; N, 4.39. UV $\lambda_{\rm max}$ (ethanol): 301.5 nm.

1-[3-Iodophenyl]-4-[2-pyridyl]buta-1,3-diyne (1f). Yellow solid (silica gel, 1:1 hexane/chloroform, R_f =0.20, 70% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.55 (d, J=4.6 Hz, 1H), 7.81 (s, 1H), 7.58–7.66 (m, 2H), 7.38–7.51 (m, 2H), 7.20–7.24 (m, 1H), 7.01 (dd, J=7.9 Hz, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.23 (CH), 141.88, 140.83 (CH), 138.42 (CH), 136.03 (CH), 131.61 (CH), 129.80 (CH), 128.04 (CH), 123.51 (CH), 123.23, 93.51, 80.87, 80.29, 74.67, 73.18. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.80; H, 2.43; N, 4.35. UV $\lambda_{\rm max}$ (ethanol): 306.5 nm. **Unstable solid, turns brown/black under ambient conditions.

1-[2-Iodophenyl]-4-[4-pyridyl]buta-1,3-diyne (1g). Yellow solid (silica gel, 1:1 hexane/chloroform, R_f = 0.20, 81% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.60 (d, J = 4.7 Hz, 2H), 7.84 (d, J = 8.1Hz, 1H), 7.51 (d, J = 6.4 Hz, 1H), 7.29–7.37 (m, 3H), 7.03–7.08 (m, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 149.86 (CH), 138.93 (CH), 134.07 (CH), 130.67 (CH), 129.88, 127.92, 127.91 (CH), 126.02 (CH), 100.87, 84.80, 79.77, 77.99, 76.37. Elemental Analysis

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Calculated for $C_{15}H_8NI$: C, 54.74; H, 2.45; N, 4.26. Found: C, 55.00; H, 2.45; N, 4.25. UV λ_{max} (ethanol): 241.0 nm.

1-[2-Iodophenyl]-4-[3-pyridyl]buta-1,3-diyne (**1h**). Yellow solid (silica gel, 1:1 hexane/chloroform, R_f =0.20, 79% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.74 (s, 1H), 8.56 (d, J=3.8 Hz, 1H), 7.77–7.83 (m, 2H), 7.48–7.51 (m, 1H), 7.23–7.32 (m, 2H), 7.00–7.05 (m, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 153.05 (CH), 149.29 (CH), 139.28 (CH), 138.84 (CH), 133.94 (CH), 130.43 (CH), 128.19, 127.84 (CH), 123.01 (CH), 119.02, 100.84, 83.89, 79.54, 77.01, 76.83. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.46; H, 2.80; N, 4.46. UV λ_{max} (ethanol): 311.5 nm.

1-[2-Iodophenyl]-4-[2-pyridyl]buta-1,3-diyne (1i). Yellow solid (silica gel, 1:1 hexane/chloroform, R_f =0.20, 72% yield). $\delta_{\rm H}$ (300 MHz, CDCl₃): 8.55 (d, J=4.67 Hz, 1H), 7.78 (d, J=8.04 Hz, 1H), 7.59–7.65 (m, 1H), 7.40–7.48 (m, 2H), 7.0–7.264 (m, 2H), 7.00 (dd, J=7.6 Hz, 1H). $\delta_{\rm C}$ (75 MHz, CDCl₃): 150.19 (CH), 141.88, 138.71 (CH), 136.03 (CH), 133.91 (CH), 131.80, 130.38 (CH), 127.97 (CH), 127.73 (CH), 123.49 (CH), 100.75, 84.44, 81.63, 76.72, 73.36. Elemental Analysis Calculated for C₁₅H₈NI: C, 54.74; H, 2.45; N, 4.26. Found: C, 54.97; H, 2.31; N, 4.40. UV $\lambda_{\rm max}$ (ethanol): 316.50 nm. **Unstable solid, turns brown/black under ambient conditions.

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