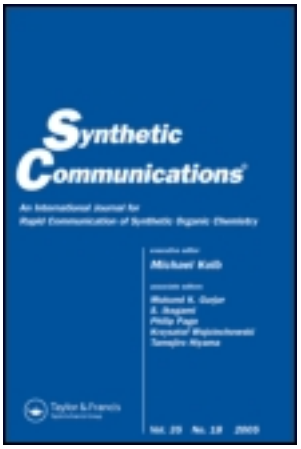

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Facile Synthesis of Functionalized Bis(arylethynyl)benzene Derivatives via Sila-Sonogashira Reaction

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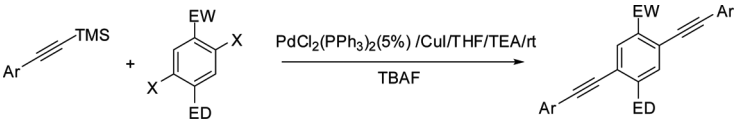
FACILE SYNTHESIS OF FUNCTIONALIZED BIS(ARYLETHYNYL)BENZENE DERIVATIVES VIA SILA–SONOGASHIRA REACTION

Zhang-Lin Zhou, Lihua Zhao, Sean Zhang, Kent Vincent, Sity Lam, and Dick Henze
Hewlett-Packard Laboratories, Palo Alto, California, USA

GRAPHICAL ABSTRACT



Abstract *This article describes a facile synthesis of a new series of symmetrical bis(arylethynyl)benzene derivatives via a one-pot coupling reaction between trialkylsilyl protected arylalkynyes and aryldihalides bearing both electron-withdrawing (EW) and electron-donating groups (ED) in the presence of $PdCl_2(PPh_3)_2$(5%) / CuI/tetrabutylammonium fluoride / triethylamine / tetrahydrofuran (sila–Sonogashira reaction) at room temperature.*

Keywords Bis(arylethynyl)benzene derivatives; cross-coupling reaction; Sila–Sonogashira reaction

INTRODUCTION

Functionalized conjugated bis(arylethynyl)benzene derivatives have received increased attention because of their potential in optical and electrical applications. During the course of searching for new targets for molecular electronics and molecular display applications, there was a need to synthesize functionalized conjugated bis(arylethynyl)benzene derivatives bearing either electron-withdrawing (EW) and/or electron-donating (ED) groups in large quantities. Among a large number of synthetic methods developed for these types of materials, the Sonogashira palladium-catalyzed cross-coupling reaction[1] has been proved to be a powerful method for the formation of shape-persistent arylethynylenes.[2] This method has been employed in the generation of scaffolds leading to molecular electronic devices,[3] dendrimers,[4] dehydrobenzannulenes,[5] foldamers,[6] and polymers.[7] The Sonogashira cross-coupling reaction has been a reliable, high-yielding reaction

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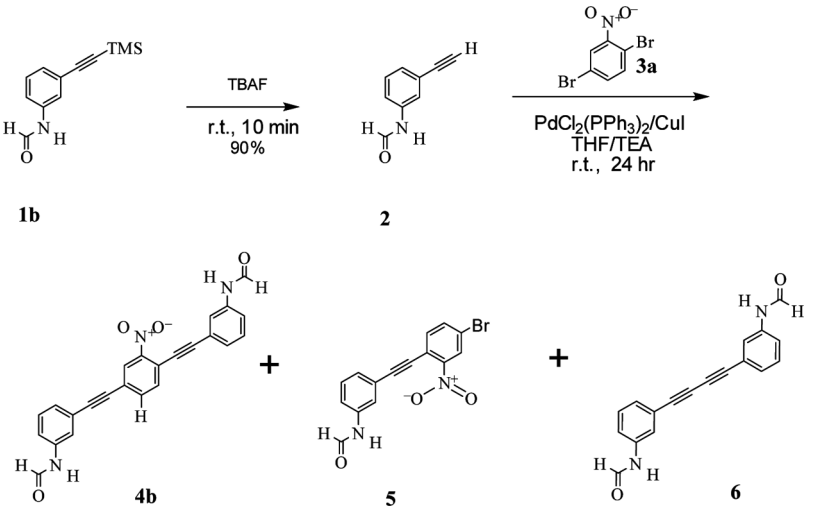
that is tolerant of a wide variety of functional groups. However, the use of the traditional Sonogashira reaction to effect iterative synthesis often requires stepwise deprotection of terminal acetylenes and coupling reactions, which normally result in much lower yields.[8] Thus, it is necessary to develop a more efficient method to synthesize such functionalized bis(arylethynyl)benzene derivatives in better yields for potential molecular electronics and display applications.

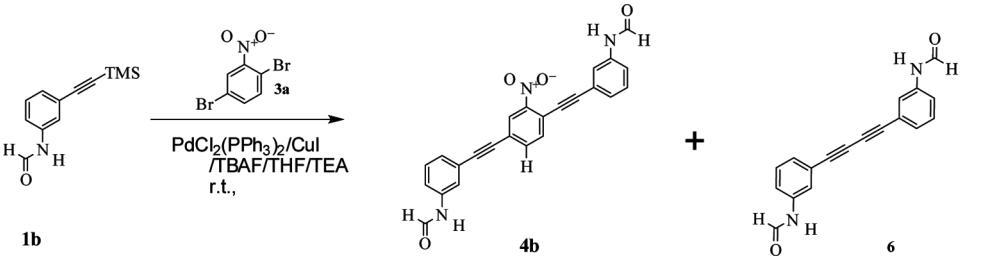
There have been several published reports recently to achieve Sonogashirsa cross-coupling reactions in one step via the Sila–Sonogashira reaction.[9] However, most of these published papers used special reagents,[9a] special catalysts,[9e,f] traditional heating,[9b,c] and/or microwave heating.[9d] Moreover, most of them also needed either aryl iodides or activated aryl bromides as substrates. We report herein a very efficient catalyst system for the Sila–Sonogashira coupling reaction, consisting of $PdCl_2(PPh_3)_2$(5%)/CuI/tetrabutylammonium fluoride (TBAF)/triethylamine (TEA)/tetrahydrofuran (THF) to generate symmetrical bisarylethynyes derivatives bearing both EW and ED groups at room temperature in good yields.

Initially, we tried to follow the traditional Sonogashira approach to make the functionalized bisarylethynyes derivatives.[10] Thus, we carried out the deprotection reaction of the trimethylsilyl (TMS) group of 3-(trimethylsilylethynyl)formanilide (**1b**) by 1 equiv. of TBAF under argon (Ar) at room temperature (r.t.) within 10 min, affording acetylene **2** in 90% yield. Subsequent coupling reaction of acetylene **2** with 2,5-dibrormonitrobenzene (**3a**) by 5% equivalent of $PdCl_2(PPh_3)_2$/CuI as catalysts at room temperature under Ar resulted in a mixture of 6% of the desired bis-coupling product (**4b**), 42% of monocoupling product (**5**), and 28% of homocoupling by-product (**6**) (Scheme 1).

To minimize the undesired homocoupling reaction, we used a one-pot process by combining both deprotection and coupling steps in one step under Ar. When a solution of TMS protected compound **1**, dibromide **3a**, $PdCl_2(PPh_3)_2$/CuI, and



Scheme 1. Deprotection of 3-(trimethylsilylethynyl)formanilide (**1b**) and subsequent coupling reaction with 2,5-dibromonitrobenzene (**3a**).

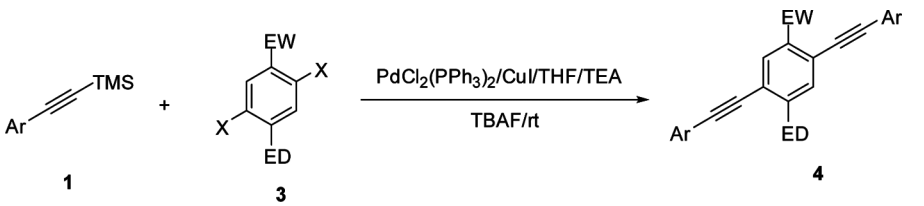


Scheme 2. One-pot coupling reaction of 3-(trimethylsilylethynyl)formanilide (**1b**) and with 2,5-dibromonitrobenzene (**3a**).

TEA in THF is treated with TBAF at room temperature, a blue color appeared. The reaction was completed within 2 h at room temperature. Around 80% of mixed products of the desired bis-coupling product (**4b**) and the homocoupling by-product (**6**) were obtained in the ratio of 83/17. No monocoupled side product **5** was detected. Around 62% of the pure desired bis-coupled product (**4b**) can be isolated after flash chromatography (Scheme 2).

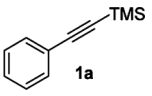
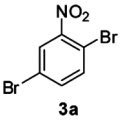
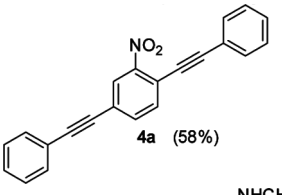
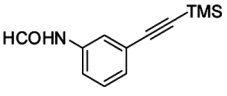
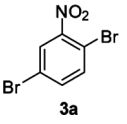
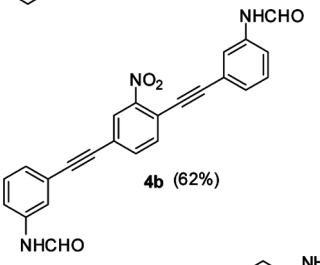
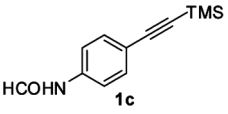
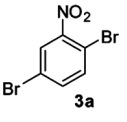
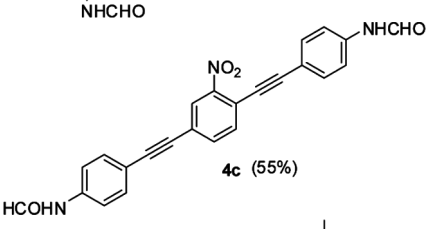
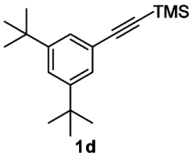
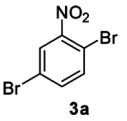
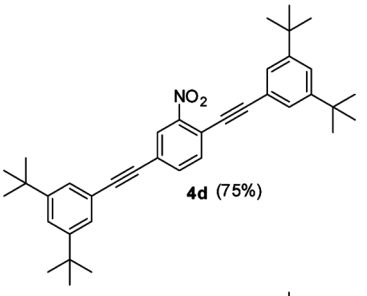
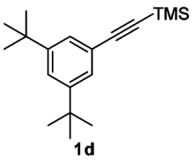
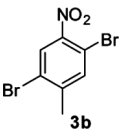
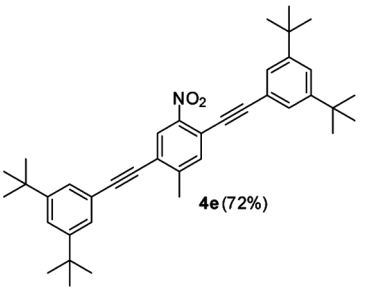
Based on these results, we found that $PdCl_2(PPh_3)_2$ (5%)/CuI/TBAF/TEA/THF is a very efficient system to promote a one-pot Sonogashira coupling reaction to generate functionalized bis(arylethynyl)benzene derivatives. We successfully used this method to synthesize a series of such bis(arylethynyl)benzene derivatives with both EW and/or ED groups (Scheme 3), which provided us various potential targets for evaluation of molecular electronics and display applications.

Table 1 describes 12 examples of this one-pot Sonogashira coupling method to synthesize functionalized conjugated bisarylethynylbenzene derivatives in good isolated yields (58–85%) at room temperature. This is extremely high overall yield considering that this is a single combination of three-step reactions. Simple trimethylsilyl protected phenylethynylacetylene (**1a**) coupled with 2,5-dibromonitrobenzene in this condition afforded the desired bis-coupled product (**4a**) in 58% yield, without the complication of homocoupling product. Both protected 3- and 4-formamidophenylacetylenes reacted with 2,5-dibromonitrobenzene nicely, giving the corresponding bis-coupled products **4b** and **4c** respectively. Based on the ^{1}H NMR spectra of **4b** and **4c**, these two products are the mixtures of two tautomers of formamide and enol. Sterically hindered trimethylsilyl protected 3,5-tert-butylphenylacetylene (**1d**) can react with various aryldihalides either with EW and/or ED groups (**3a, 3b, 3c**, and **3d**) to give rise to the corresponding desired bis-coupled products in very good



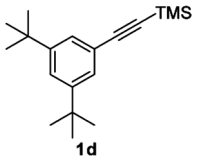
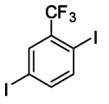
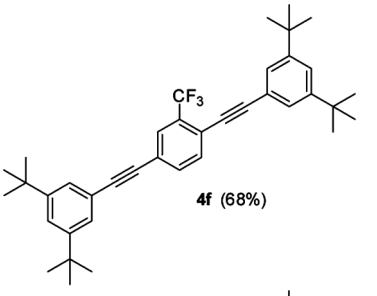
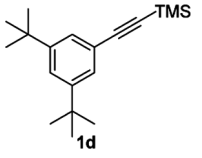
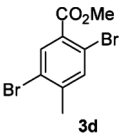
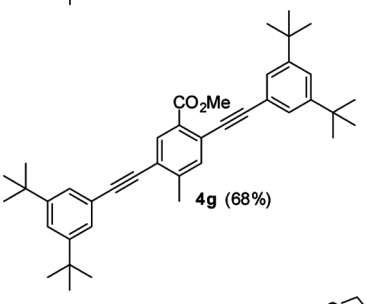
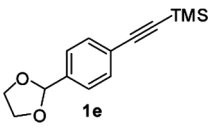
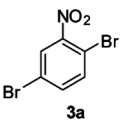
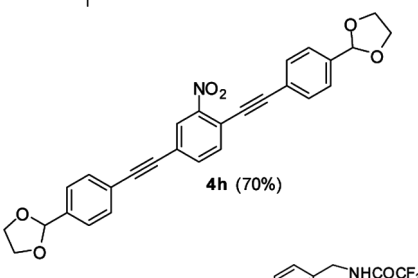
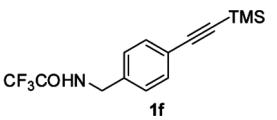
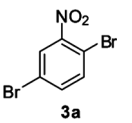
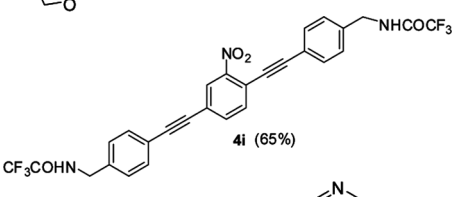
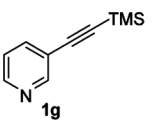
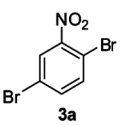
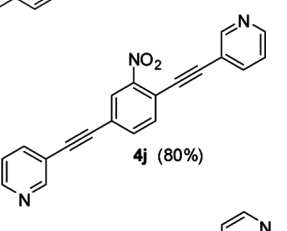
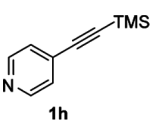
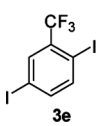
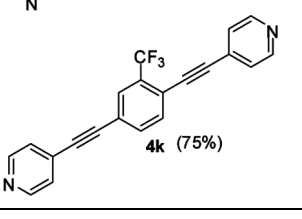
Scheme 3. General examples of one-pot coupling reaction of aryldihalides with TMS-protected arylethynes.

Table 1. Examples of one-pot coupling reaction of aryldihalides with TMS-protected arylethynes

Entry	Arylethynes	Aryldihalides	Product (isolated yield)
1	 **1a**	 **3a**	 **4a** (58%)
2	 **1b**	 **3a**	 **4b** (62%)
3	 **1c**	 **3a**	 **4c** (55%)
4	 **1d**	 **3a**	 **4d** (75%)
5	 **1d**	 **3b**	 **4e** (72%)

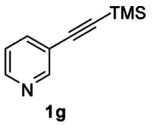
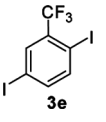
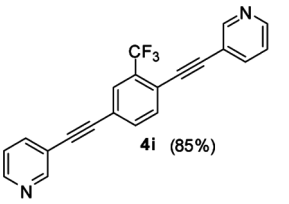
(*Continued*)

Table 1. Continued

Entry	Arylethynes	Aryldihalides	Product (isolated yield)
6	 **1d**	 **3c**	 **4f** (68%)
7	 **1d**	 **3d**	 **4g** (68%)
8	 **1e**	 **3a**	 **4h** (70%)
9	 **1f**	 **3a**	 **4i** (65%)
10	 **1g**	 **3a**	 **4j** (80%)
11	 **1h**	 **3e**	 **4k** (75%)

(*Continued*)

Table 1. Continued

Entry	Arylethynes	Aryldihalides	Product (isolated yield)
12	 **1g**	 **3e**	 **4i** (85%)

yields without any detected side products such as homocoupling product or monocoupling product. These are very significant results, because traditional Sonogashira coupling reactions very often gave only monocoupled product, especially when dihalides were inactivated by electron-donating groups such as **3b** and **3d**. As for the substrates that are precursors to aldehyde and amine **1e** and **1f**, both coupling reactions with 2,5-dibromonitrobenzene (**3a**) went smoothly to give the desired products **4h** and **4i** in 70% and 65% yields respectively, which can be further liberated to give reactive conjugated bisarylethynylbenzene derivatives. The last three examples demonstrated heterocyclic ring systems such as trimethylsilyl protected 3- or 4-pyridylacetylenes (**1g** and **1h**) can also couple with dihalides in the same condition, giving rise to the corresponding bis-coupled products (**4j-4l**) in good yields.

In summary, we have developed a very efficient catalyst system, $PdCl_2(PPh_3)_2$(5%)/CuI/TBAF/TEA/THF, for a one-pot Sila–Sonogashira reaction between trimethylsilyl protected arylacetylenes with aryldihalide bearing both EW and/or ED groups at room temperature. This method greatly improves the synthesis of these highly functionalized symmetrical bis(arylethynyl)benzene derivatives and provides easy access to these novel targets in large quantities for evaluation of molecular electronics and potential display applications.

EXPERIMENTAL

Typical Procedure for Synthesis of Symmetrical Bis(arylethynyl)benzene Derivatives: Synthesis of 1,4-Bis[3′,5′-di-*tert*-butylphenylethynyl]-5-methly-2-methoxy Carbonylbenzene (4g)

Tetrabutylammonium fluoride (2.5 mL) was added to a solution of 1-[3′,5′-di-*tert*-butylphenyl-2-trimethylsilylacetylene (**1d**) (572 mg, 2.0 mmol), methyl 2,5-dibromo-4-methylbenzoate (**3d**) (308 mg, 1.0 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.1 mmol), and CuI (20 mg, 0.1 mmol) in 10 mL of triethylamine and 10 mL of tetrahydrofuran. The resulting solution was stirred at room temperature overnight. Then, the mixture was partitioned between ethyl acetate and water (50 ml/50 ml). The aqueous layer was extracted with ethyl acetate (50 mL). The combined organic layer was washed with water and brine and dried over sodium sulfate. Filtration of sodium sulfate and evaporation of the solvent followed by purification by flash chromatography gave the desired compound **4g** as a pale yellow solid: 390 mg (68%). ^{1}H NMR

($CDCl_3$, 300 MHz) δ 8.15 (s, 1 H), 7.55 (s, 1 H), 7.38–7.42 (m, 6 H), 3.97 (s, 3 H), 2.56 (s, 3 H), 1.34 (s, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 151.2, 151.1, 144.1, 135.2, 134.4, 129.4, 126.2, 126.1, 123.4, 122.4, 122.2, 96.9, 87.4, 86.2, 52.4, 35.1, 31.6, 20.9; IR (neat) ν (cm^{-1}) 2970, 2871, 2210, 1742, 1590, 1252, 877. Anal. calcd. for $C_{41}H_{50}O_2$: C, 85.67; H, 8.77. Found: C, 85.51; H, 8.72.

1,4-Bis[phenylethynyl]-2-nitrobenzene (4a)

Yield: 58%; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.21 (m, 1 H), 7.68 (m, 2 H), 7.57 (m, 5 H), 7.39 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 135.2, 134.5, 132.5, 132.1, 132.0, 131.8, 129.4, 129.2, 128.8, 128.7, 128.5, 128.4, 127.6, 124.1, 122.2, 122.1, 118.0, 98.9, 93.6, 86.9, 84.9; IR (neat) ν (cm^{-1}) 2930, 2220, 1540, 1351, 756. Anal. calcd. for $C_{22}H_{13}NO_2$: C, 81.72; H, 4.05; N, 4.33. Found: C, 81.56; H, 4.03; N, 4.29.

1,4-Bis[3′-formamidophenylethynyl]-2-nitrobenzene (4b)

Yield: 62%; ^1H NMR (DMSO-d_6, 300 MHz) δ 10.38–10.25 (m, 2 H), 8.85 (m, 0.5 H), 8.31 (m, 2 H), 7.94–7.89 (m, 3.5 H), 7.50 (m, 2 H), 7.45–7.31 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 160.4, 149.9, 149.8, 139.4, 139.1, 139.0, 135.3, 130.6, 130.5, 130.1, 130.0, 127.8, 127.4, 127.3, 123.8, 122.7, 122.2, 121.0, 120.7, 120.4, 120.3, 117.1, 98.2, 93.5, 87.4, 84.9; IR (neat) ν (cm^{-1}) 3272, 3090, 2890, 1691, 1540, 1400, 792. Anal. calcd. for $C_{24}H_{15}N_3O_4 \cdot 0.25H_2O$: C, 69.64; H, 3.77; N, 10.15. Found: C, 69.61; H, 3.59; N, 10.04.

1,4-Bis[4′-formamidophenylethynyl]-2-nitrobenzene (4c)

Yield: 55%; ^1H NMR (DMSO-d_6, 300 MHz) δ 10.47–10.39 (m, 2 H), 8.88 (m, 0.5 H), 8.31–8.24 (m, 2.5 H), 7.83 (m, 2 H), 7.66 (m, 3 H), 7.55 (m, 4 H), 7.28 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 160.4, 149.6, 140.0, 139.7, 136.0, 135.1, 133.6, 133.5, 133.2, 133.1, 127.6, 123.7, 119.7, 119.6, 117.6, 117.2, 116.4, 116.3, 98.8, 93.9, 87.0, 84.7; IR (neat) ν (cm^{-1}) 3260, 3010, 2220, 1705, 1610, 1532, 1301, 838. Anal. calcd. for $C_{24}H_{15}N_3O_4 \cdot 0.25H_2O$: C, 69.64; H, 3.77; N, 10.15. Found: C, 69.42; H, 3.64; N, 10.02.

1,4-Bis[3′,5′-di-*tert*-butylphenylethynyl]-2-nitrobenzene (4d)

Yield: 75%; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.43–7.26 (m, 5 H), 5.45 (s, 2 H), 2.46 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 149.3, 135.2, 134.5, 127.6, 126.3, 126.1, 124.1, 124.0, 123.7, 121.3, 121.1, 118.1, 100.2, 94.7, 85.8, 83.8, 34.9; IR (neat) ν (cm^{-1}) 2970, 2871, 2220, 1592, 1540, 1360, 877. Anal. calcd. for $C_{38}H_{45}NO_2$: C, 83.32; H, 8.28; N, 2.56. Found: C, 83.20; H, 8.21; N, 2.53.

1,4-Bis[3′,5′-di-*tert*-butylphenylethynyl]-5-methyl-2-nitrobenzene (4e)

Yield: 72%; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.25 (s, 1 H), 7.60 (s, 1 H), 7.40–7.48 (m, 6 H), 2.60 (s, 3 H), 1.35 (s, 36 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 151.0, 145.4,

135.2, 128.0, 126.3, 125.9, 124.0, 123.8, 123.7, 121.5, 121.4, 118.1, 99.5, 98.2, 84.9, 84.1, 34.9, 31.3; IR (neat) ν (cm^{-1}) 2960, 2872, 2215, 1590, 1360, 1340, 877. Anal. calcd. for $C_{39}H_{47}NO_2$: C, 83.38; H, 8.43; N, 2.49. Found: C, 83.30; H, 8.50; N, 2.48.

1,4-Bis[3′,5′-di-*tert*-butylphenylethynyl]-2-trifluoromethylbenzene (4f)

Yield: 68%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (s, 1 H), 7.66 (s, 2 H), 7.44 (m, 2 H), 7.40 (m, 4 H), 1.35 (s, 36 H); ^{13}C NMR (75 MHz, CDCl3) δ 151.0, 134.0, 133.7, 129.1, 129.0, 126.0, 123.5, 123.4, 123.3, 121.6, 121.5, 97.9, 93.7, 86.7, 84.2, 34.8, 31.3; ^{19}F NMR (282 MHz, CDCl3) δ −62.6; IR (neat) ν (cm^{-1}) 2970, 2871, 2220, 1590, 1170, 1142, 876. Anal. calcd. for $C_{39}H_{45}F_3$: C, 82.07; H, 7.95; F, 9.99. Found: C, 81.91; H, 7.92; F, 9.78.

1,4-Bis[4′-(1″,3″-dioxolan-2″-yl)phenylethynyl]-2-nitrobenzene (4h)

Yield: 70%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.23 (s, 1 H), 7.70 (m, 2 H), 7.61 (m, 4 H), 7.49 (m, 4 H), 5.84 (s, 2 H), 4.15–4.05 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 139.2, 139.0, 135.3, 134.5, 132.1, 131.8, 127.7, 126.7, 126.6, 124.1, 123.0, 122.9, 118.0, 103.1, 98.6, 93.3, 87.3, 85.3, 65.4; IR (neat) ν (cm^{-1}) 2971, 2890, 2220, 1542, 1350, 1083, 832. Anal. calcd. for $C_{28}H_{21}NO_6$: C, 71.94; H, 4.53; N, 3.00. Found: C, 71.95; H, 4.43; N, 3.01.

1,4-Bis[4′(trifluoromethylacetamidoethyl)phenylethynyl]-2-nitrobenzene (4i)

Yield: 65%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 10.03 (t, $J = 1.8$ Hz, 2 H), 8.27 (s, 1H), 7.87 (m, 2H), 7.58 (m, 4 H), 7.35 (m, 4 H), 4.43 (d, $J = 8.7$ Hz, 4 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 157.2, 156.7, 149.7, 139.8, 139.5, 136.1, 135.2, 133.0, 132.3, 128.3, 128.2, 123.8, 120.8, 120.7, 118.3, 117.2, 114.5, 98.3, 93.6, 87.5, 85.1, 42.8; ^{19}F NMR (282 MHz, DMSO-d_6) δ −74.4; IR (neat) ν (cm^{-1}) 3362, 3090, 2215, 1722, 1542, 1350, 1220, 1180, 835. Anal. calcd. for $C_{28}H_{17}F_6N_3O_4$: C, 58.65; H, 2.99; N, 7.33. Found: C, 58.52; H, 3.00; N, 7.16.

1,4-Bis[3′-pyridylethynyl]-2-nitrobenzene (4j)

Yield: 80%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.84 (d, $J = 8.4$ Hz, 2 H), 8.63 (d, $J = 3.9$ Hz, 2 H), 8.28 (d, $J = 0.6$ Hz, 1 H), 7.91–7.84 (m, 2 H), 7.75 (m, 2H), 7.37–7.27 (m, 2H); ^{13}C NMR (75 MHz, CDCl3) δ 152.5, 152.4, 149.7, 149.5, 139.0, 138.7, 135.5, 134.7, 127.8, 123.9, 123.2, 119.4, 119.2, 117.8, 95.4, 90.3, 89.8, 87.7 IR (neat) ν (cm^{-1}) 3040, 2220, 1542, 1520, 1411, 1350, 1020, 800. Anal. calcd. for $C_{20}H_{11}N_3O_2$: C, 73.84; H, 3.41; N, 12.92. Found: C, 73.71; H, 3.35; N, 12.72.

1,4-Bis[4′-pyridylethynyl]-2-trifluoromethylbenzene (4k)

Yield: 75%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66 (dd, $J_1 = 6.3$ Hz, $J_2 = 0.6$ Hz, 4 H), 7.89 (s, 1 H), 7.70 (s, 2 H), 7.39 (dd, $J_1 = 4.5$ Hz, $J_2 = 1.8$ Hz, 4 H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 149.9, 134.5, 134.1, 132.5, 132.1, 132.0, 130.3, 129.4, 128.6, 128.4, 125.5, 124.7, 123.1, 121.2, 120.9, 93.9, 91.6, 90.0, 88.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.6; IR (neat) ν (cm^{-1}) 3041, 2220, 1590, 1142, 1050, 814. Anal. calcd. for $C_{21}H_{11}F_3N_2$: C, 72.41; H, 3.18; N, 8.04. Found: C, 72.42; H, 3.18; N, 7.54.

1,4-Bis[3′-pyridylethynyl]-2-trifluoromethylbenzene (4l)

Yield: 85%; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.79 (s, 2 H), 8.59 (m, 2 H), 7.87–7.81 (m, 3 H), 7.69 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 149.2, 149.3, 138.6, 134.3, 133.9, 132.2, 132.1, 132.0, 131.9, 129.2, 129.1, 128.6, 128.4, 124.8, 123.1, 120.7, 119.6 93.4, 90.8, 89.3, 88.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.6; IR (neat) ν (cm^{-1}) 3040, 2220, 1510, 1180, 1110, 800. Anal. calcd. for $C_{21}H_{11}F_3N_2$: C, 72.41; H, 3.18; N, 8.04. Found: C, 71.97; H, 3.17; N, 7.78.

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