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

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Abstract: This paper 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/TBAF/TEA/THF (sila-Sonogashira reaction) at room temperature.

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Functionalized conjugated bis(arylethynyl)benzene derivatives have received increased attention due to their potential in optical and electrical applications. During the course of searching new targets towards molecular electronics and molecular display application, there was a need to synthesize functionalized conjugated bis(arylethynyl)benzene derivatives either bearing both 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

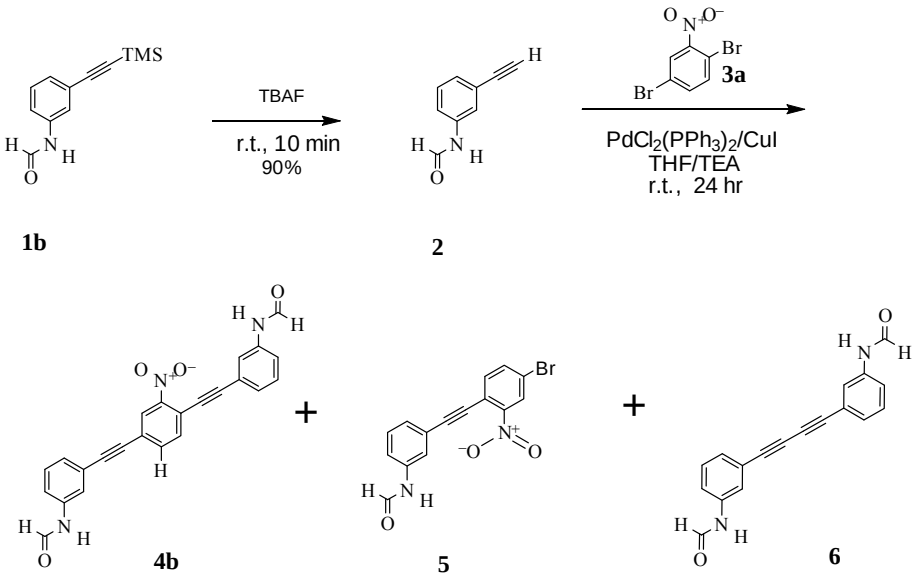
employed in the generation of scaffolds leading to molecular electronic devices,[3] dendrimers,[4] dehydrobenzannulenes,[5] foldamers,[6] or polymers.[7] The Sonogashira cross-coupling reaction has been a reliable, high-yielding reaction that is tolerant of a wide variety of functional groups. However, the use of the traditional Sonogashira reaction to effect iterative synthesis often requires stepwise deprotection of terminal acetylenes and coupling reactions, which normally resulted in much lower yields.[8] Thus it is necessary to develop a more efficient method to synthesize such functionalized bis(arylethynyl)benzene derivatives in higher yields for potential molecular electronics and display applications. .

There have been several published reports recently to achieve Sonogashirs cross-coupling reactions in one step via sila-Sonogashira reaction.[9] However, most of these published papers used either 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/TBAF/TEA/THF to generate symmetrical bisarylethynyes derivatives bearing both EW and ED groups at room temperature in high yields.

Initially, we tried to follow the traditional Sonogashira approach to make this functionalized bisarylethynyes derivatives.[10] Thus, we carried out the deprotection reaction of trimethylsilyl-(TMS) group of 3-(trimethylsilylethynyl) formanilide (**1b**) by one equiv. of tetrabutylammonium fluoride (TBAF) under Argon (Ar) at room temperature within 10 minutes, 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

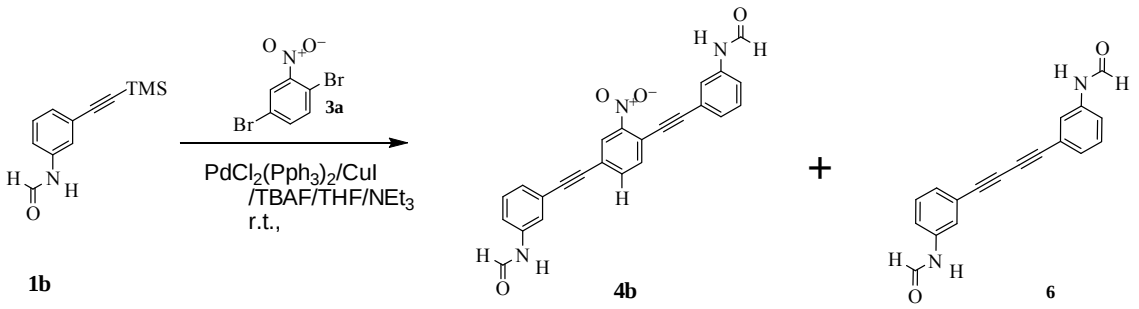
temperature under Ar resulted in a mixture of 6% of the desired bis-coupling product (**4b**), 42% of mono-coupling product (**5**) and 28% of homo-coupling by-product (**6**) (**Scheme 1**).

Scheme 1



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

Scheme 2



Based on the above 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.

Scheme 3

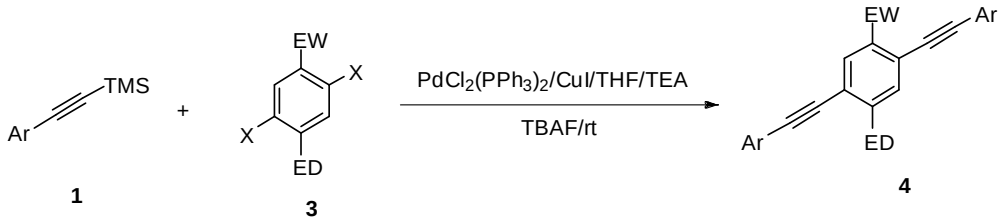
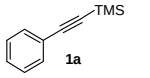
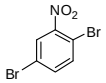
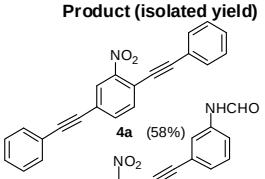
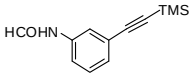
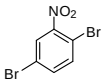
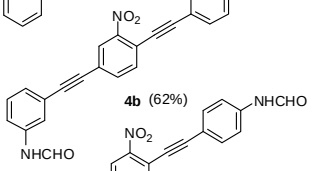
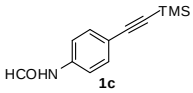
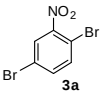
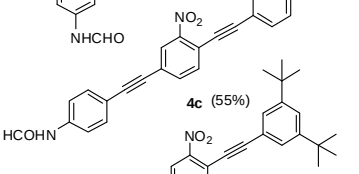
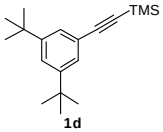
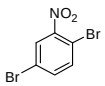
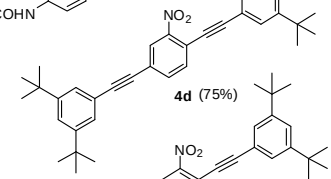
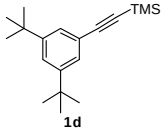
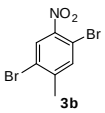
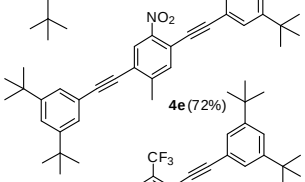
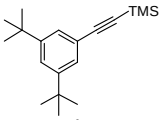
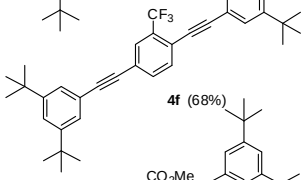
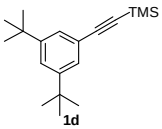
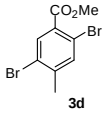
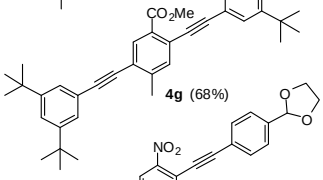
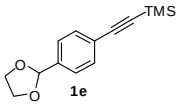
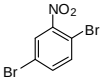
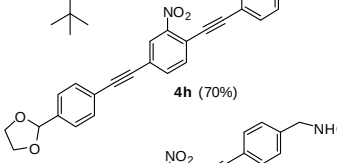
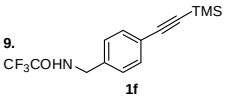
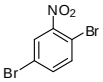
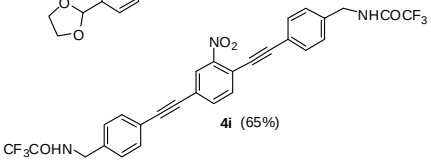
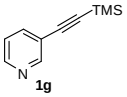
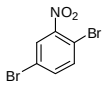
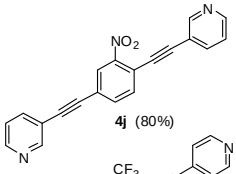
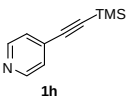
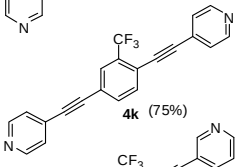
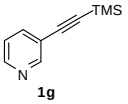
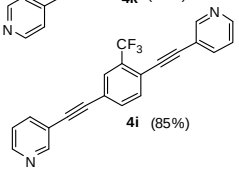


Table 1 describes twelve examples of this one-pot Sonogashira coupling method to synthesize functionalized conjugated bisarylethynylbenzene derivatives in high isolated yields

(58–85%) at room temperature. This is extremely high overall yield considering 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 homo-coupling 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 high yields without any side-products such as homo-coupling product or mono-coupling product detected. These are very significant results, since traditional Sonogashira coupling reactions very often gave only mono-coupled 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% yield 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 high yields.

Table 1

Examples of one-pot coupling reaction of aryldihalides with TMS-protected arylethyne

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%)
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%)
12.	 **1g**	 **3e**	 **4i** (85%)

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 the easy access to these novel targets in large quantities for evaluation of molecular electronics and potential display applications.

Experimentals

A 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)

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), CuI (20 mg, 0.1 mmol), in 10 mL of triethylamine and 10 mL of tetrahydrofuran was added 2.5 mL of tetrabutylammonium fluoride. The resulted solution was stirred at room temperature for overnight. Then, the mixture was partitioned between ethyl acetate and water (50ml/50 ml). The aqueous layer was extracted with ethyl acetate (50 mL). The combined organic layer was washed with water, brine and dried over sodium sulfate. Filtration off 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%). ^1H 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}); 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%; ^{1}H 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, CDCl3) 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}); 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%; ^{1}H 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, CDCl3) 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}); Anal. Calcd for $C_{24}H_{15}N_3O_4.0.25H_2O$.: 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%; ^{1}H 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}); Anal. Calcd for $C_{24}H_{15}N_3O_4.0.25H_2O$.: 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%; ^{1}H 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, CDCl3) 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}); 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-methly-2-nitrobenzene (4e) Yield: 72%; ^{1}H 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, CDCl3) 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, 84.134.9, 31.3; IR (neat) ν (cm^{-1}); 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}); 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}); 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= 1.8Hz, 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}) ; 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}); 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, CDCl3) 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}); 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 (4i) 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, CDCl3) 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, CDCl3) δ -62.6; IR (neat) ν (cm^{-1}); 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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