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Regioselective Synthesis of Tetraalkynylarenes by Consecutive Dual Sonogashira Coupling Reactions of the Bis(triflate) of 4,5-Diiodobenzene-1,2-diol

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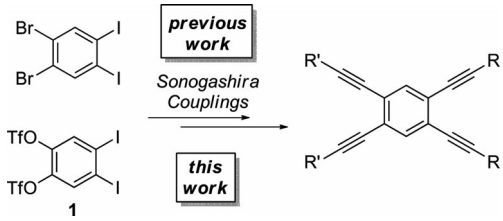
The regioselective synthesis of nonsymmetric tetraalkynylarenes has been readily achieved through consecutive sets of Sonagashira cross-coupling reactions of the bis(triflate) derivative of 4,5-diiodobenzene-1,2-diol. The initial coupling reactions proceeded with nearly complete selectivity for the reaction at the Ar–I linkages. Subsequent coupling reactions at the Ar–OTf linkages were efficiently conducted. The tetraalkynylarene products are of interest as components of organic molecular materials.

Introduction

The palladium-catalyzed cross-coupling reactions of aryl halides or triflates with terminal alkynes is a popular method for the synthesis of arylalkynes.[1] One class of reaction products, tetraalkynylarenes, is of particular interest in the field of organic materials.[2] Tetraalkynylbenzenes containing four identical alkyne side-chains can be prepared from nonselective coupling reactions of tetrahaloarenes.[3] However, regio-defined synthesis of unsymmetrical tetraalkynylarenes also requires control of the sequence of cross-coupling steps. A reported solution to this challenge exploits the greater reactivity of aryl iodides relative to aryl bromides.[1,2] However, in some cases, the sequential coupling reactions of iodo/bromoarenes have resulted in low yields of tetraalkynylarenes, presumably reflecting the lower reactivity and cross-coupling efficiency of aryl bromides and/or the corresponding requirement for more forcing reaction conditions.[4] Indeed, in the course of investigations requiring the preparation of unsymmetrical tetraalkynes, we found that attempted two-fold Sonagashira cross-coupling of model 1,2-dibromoarenes failed to give bis(alkyne) products. As a result, we became interested in the possibility of performing consecutive dual Sonogashira coupling reactions with an arene bearing both *ortho*-diiodide and *ortho*-bis(triflate) units.

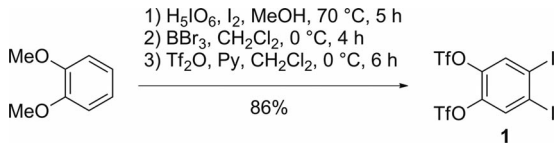
The higher reactivity of aryl iodides relative to aryl triflates as substrates for C–C cross-coupling reactions is well established,[5] and we were encouraged by a few reports describing the successful use of arene-1,2-diyl bis(triflates) as substrates for Sonogashira coupling reactions.[6] Herein, we report the synthesis of the bis(triflate) ester of 4,5-diiodobenzene-1,2-diol and the application of this previously unreported electrophile in the regiocontrolled synthesis of tetraalkynylarenes (Scheme 1).



Scheme 1. Synthetic approach to tetraalkynylarenes.

Results and Discussion

Diiodo bis(triflate) **1** was readily prepared in three steps from 1,2-dimethoxybenzene as shown in Scheme 2. Electrophilic iodination of 1,2-dimethoxybenzene proceeded in 86% yield.[7] Bis(demethylation), followed by disulfonylation of the resulting catechol proceeded quantitatively to furnish **1**. We used this procedure to prepare up to 20 g of **1**, which is stable in the dark at room temperature for months.



Scheme 2. Synthesis of **1**.

The selectivity of Sonagashira coupling reactions of **1** was investigated by using the benzyl ether of 4-pentynol as a model alkyne (Table 1). $[PdCl_2(PPh_3)_2]$ proved to be an efficient catalyst at a loading of 6 mol-% (Entry 1). Good

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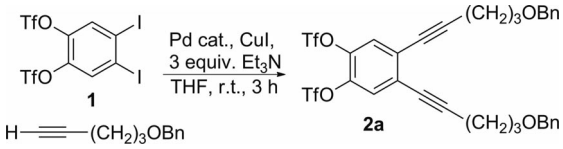
yields of the 1,2-bis(alkynyl) product could be obtained at lower catalyst loadings but at the cost of extended reaction times (Entry 4). Complete conversion of the starting material at lower catalyst loadings could be achieved by performing the reaction at higher temperatures (Entry 5), but these conditions resulted in the formation of copious amounts of byproducts that were difficult to separate from the desired diyne. Alternative sources of Pd^{II} or Pd^{0} provided lower conversions and only trace amounts of the product (Entries 8 and 9). A 2:1 ratio of Cu^{I}/Pd^{II} proved optimal for the transformation. Complete selectivity for the coupling of the aryl iodides was found when 2.3 equiv. of alkyne were used; no appreciable amounts of products resulting from coupling to the triflates were detected. However, performing the reaction in the presence of a large excess (5 equiv.) of alkyne did lead to the formation of significant amounts of inseparable byproducts, which appeared to include the tri- and tetraalkynylbenzene (not shown).

Table 1. Optimization of the alkyne coupling reaction with **1**.[a]



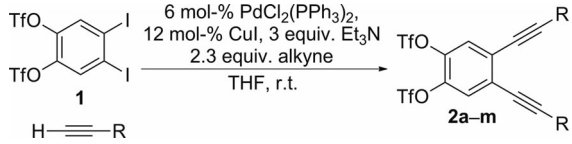
Entry	Pd cat. (amount [mol-%])	Alkyne equiv.	Conv. [%]	Yield[b] [%]
1	$[PdCl_2(PPh_3)_2]$ (6)	2.3	>99	84
2	$[PdCl_2(PPh_3)_2]$ (3)	2.3	68	16
3	$[PdCl_2(PPh_3)_2]$ (1)	2.3	67	2
4[c]	$[PdCl_2(PPh_3)_2]$ (3)	2.3	>99	70
5[d]	$[PdCl_2(PPh_3)_2]$ (3)	2.3	>99	nd
6	$[PdCl_2(PPh_3)_2]$ (6)	2.1	>95	69
7	$[PdCl_2(PPh_3)_2]$ (6)	2.5	>99	81
8	$[Pd(PPh_3)_4]$ (6)	2.3	52	trace
9	$[PdCl_2(dppf)]$ (6)	2.3	47	trace

[a] Reagents: **1** (0.4 mmol), CuI/Pd (2:1); nd = not determined. [b] Isolated yield. [c] Time = 10 h. [d] T = 60 °C.

The selectivity of the reaction is significant. One might envisage that the introduction of an alkyne in the first Sonagashira coupling might direct the second coupling away from the *ortho* iodide and towards one of the electron-deficient, but sterically unencumbered triflate units; electron-poor aryl halides are typically favored as electrophiles in alkyne cross-coupling reactions.[8] However, the selective Sonogashira coupling of aryl iodides in the presence of aryl triflates has previously been demonstrated.[5] Interestingly, the reaction of **1** with only 1.1 equiv. of (4-methoxyphenyl)-ethyne under typical reaction conditions generated the diyne and monoyne in a 1.3:1 ratio in a combined yield of 81% (not shown). The modest preference for dialkynylation could reflect a directing effect of the *ortho*-alkyne[9] or, alternatively, a more facile insertion into the hindered aryl iodide due to the diffusion-controlled proximity of the Pd catalyst to the electrophile.[10]

With the optimized reaction conditions in hand, we investigated the scope of the selective cross-coupling reaction of **1** with a variety of alkynes (Table 2). Although most reactions were complete in 3 h, some alkynes required longer times for the complete consumption of the starting material (Entries 2 and 14). The reactions proceeded smoothly with alkynes functionalized with esters (Entry 2), nitriles (Entry 3), silyl ethers (Entry 4), alkyl chlorides (Entry 5), THP ethers (Entry 10), and an acetal (Entry 12). Aromatic alkynes also proved to be excellent coupling partners (Entries 7–9). Coupling reactions with nonpolar alkynes (e.g., heptyne) appeared to proceed to completion (TLC); however, because of the difficulty in completely separating the products from recovered alkyne and nonpolar byproducts by silica chromatography, these examples are not reported. Cross-coupling with a tertiary propargyl alcohol proceeded in good yield (Entry 11), whereas reactions with unhindered propargyl ethers (Entries 13 and 14) provided lower yields of the bis(alkynes). Given the frequent application of propargyl alcohols and ethers as nucleophiles in Sonagashira coupling reactions,[1] we are uncertain as to why their use has limitations in this setting.

Table 2. Substrate scope for the selective coupling of **1**.[a]



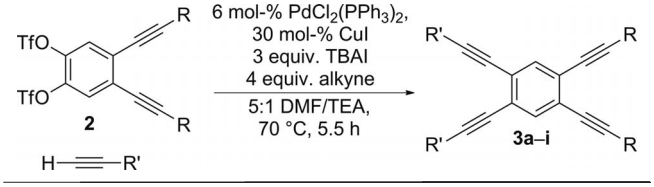
Entry	R	t [h]	Product, yield[b] [%]
1	$(CH_2)_3OBn$	3	**2a**, 84
2	$(CH_2)_3OBz$	5	**2b**, 71
3	$(CH_2)_3CN$	3	**2c**, 78
4	$(CH_2)_4OTBS$	3	**2d**, 94
5	$(CH_2)_4Cl$	3	**2e**, 76
6	TIPS	3	**2f**, 46
7	4-$MeOC_6H_4$	3	**2g**, 78
8	2-Py	3	**2h**, 69
9	2-Py	3	**2h**, 84[c]
10	$(CH_2)_2OTHP$	3	**2i**, 85
11	$C(CH_3)_2OH$	3	**2j**, 72
12	$CH(OEt)_2$	3	**2k**, 69
13	CH_2OBz	3	**2l**, 46
14	CH_2OBn	5	**2m**, 43

[a] Reagents: **1** (0.4 mmol), THF (1 mL). [b] Isolated yield. [c] On a 3.2 mmol scale.

We next investigated the conditions for displacing both triflates in a second set of Sonogashira coupling reactions (Table 3). By using conditions related to those reported by Powell and Rychnovsky,[6a] diyne **2a** was coupled with the TBS ether of 5-hexynol to yield tetrayne **3a** in 72% yield (Entry 1). Further modification of the reported conditions did not lead to any notable improvement (data not shown). The scope of the second set of coupling reactions was then investigated (Entries 2–9).

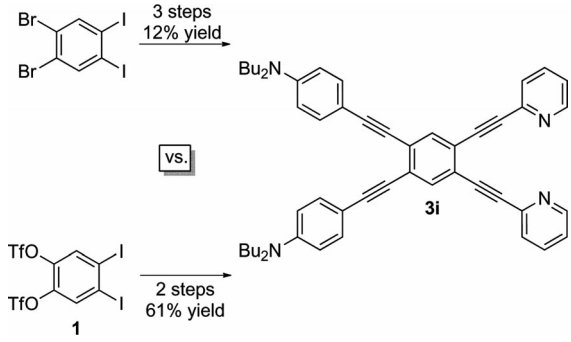
Finally, we compared our new approach directly against an existing methodology for the synthesis of **3i**, a target previously prepared in four steps and 11% yield from 1,2-dibromo-4,5-diiodobenzene (Scheme 3).[2a] By using our method, **3i** could be prepared from diiododitriflate **1** in two steps and 61% yield (or five steps and 53% overall yield from 1,2-dimethoxybenzene).

Table 3. Synthesis of tetraalkynylarenes by dual coupling of dialkynylarenediyl bis(triflates).[a]



Entry	R	R′	Product, yield[b] [%]
1	$(CH_2)_3OBn$	$(CH_2)_4OTBS$	**3a**, 72
2	$(CH_2)_3OBn$	$(CH_2)_3OBz$	**3b**, 64
3	$(CH_2)_3OBn$	TMS	**3c**, 64
4	$(CH_2)_3OBn$	Ph	**3d**, 83
5	$(CH_2)_3OBn$	4-$MeOC_6H_4$	**3e**, 79
6	$(CH_2)_3OBn$	4-FC_6H_4	**3f**, 74
7[c]	$(CH_2)_4OTBS$	$(CH_2)_3OBz$	**3g**, 68
8	4-$MeOC_6H_4$	TMS	**3h**, 57
9	2-Py	4-$(Bu_2N)C_6H_4$	**3i**, 73

[a] Reagents and conditions: on a 0.25 mmol scale, DMF/TEA (5:1) (1.5 mL), sealed vial. [b] Isolated yield. [c] KI (3 equiv.) used instead of TBAI.



Scheme 3. Comparison of the protocol developed here with an existing methodology.

Conclusions

The selective Sonogashira cross-coupling reaction of 1,2-diiodobenzene-4,5-diyl bis(triflate) proceeds with almost complete selectivity displacing both iodine atoms to furnish a 4,5-bis(alkynyl)benzene-1,2-diyl bis(triflate), which can be subjected to a second set of alkyne coupling reactions to efficiently give nonsymmetric 1,2,4,5-tetraalkynylarenes. Structurally related 1,2-diyl bis(triflates) have been shown to undergo dual Suzuki coupling reactions,[6b] which suggests our results could potentially be extended to other transition-metal-catalyzed cross-coupling reactions.

Experimental Section

General: All the reactions were carried out in flame-dried glassware under dry nitrogen with magnetic stirring. Solvents were used as purchased with the exception of THF and CH_2Cl_2, which were distilled from Na/Ph_2CO and CaH_2, respectively. TLC was performed on 0.25 mm hard-layer silica G plates; developed plates were visualized with a UV lamp and/or by staining: vanillin (general stain, after charring), 1% aq. $KMnO_4$ (for unsaturated compounds), I_2, or phosphomolybdic acid (general stain, after charring). NMR spectra were recorded in $CDCl_3$ (by using residual $CHCl_3$: δ = 7.286 ppm) at 300/400/500/600 MHz (^{1}H) or 75/100/125/150 MHz (^{13}C), as indicated. ^{1}H NMR chemical shifts are reported as δ in ppm as follows: chemical shift [multiplicity, coupling constant(s) in Hz, integration]. ^{13}C NMR chemical shifts are reported as δ in ppm. IR spectra were recorded as neat ATR films with selected absorbances reported in wavenumbers (cm^{-1}).

1,2-Diiodo-4,5-dimethoxybenzene: This compound was prepared according to the procedure of Lacour et al.[7] H_5IO_6 (0.41 equiv., 25.6 mmol, 5.84 g) and MeOH (36 mL) were added to a flame-dried 100 mL round-bottomed flask equipped with a short air condenser. The mixture was stirred at room temp., and then I_2 (0.8 equiv., 50.2 mmol, 12.76 g) was added. The reaction mixture was stirred vigorously for 10 min, after which 1,2-dimethoxybenzene (1 equiv., 63 mmol, 8.7 g, 8.0 mL) was added in one portion through a syringe. The reaction mixture was heated at 70 °C in an oil bath for 5 h, which resulted in the formation of a white solid that made stirring difficult; however, the reaction proceeded even without efficient stirring. The hot solution was poured into dilute aqueous $Na_2S_2O_5$ (ca. 100 mL), and the mixture was cooled to room temp. The solid collected by filtration through a glass frit was washed quickly with two 30 mL portions of cold MeOH and dried in vacuo to afford 1,2-diiodo-4,5-dimethoxybenzene (21.07 g, 54 mmol, 86%) as a white solid that was deemed pure by NMR spectroscopy and used without further purification. R_f = 0.49 (20% ethyl acetate/hexane). M.p. 134.5–136.0 °C (ref.[7] 134 °C). ^{1}H NMR (600 MHz): δ = 7.25 (s, 2 H), 3.85 (s, 6 H) ppm. ^{13}C NMR (150 MHz): δ = 149.6, 121.7, 96.1, 56.2 ppm.

1,2-Dihydroxy-4,5-diiodobenzene: A flame-dried 250 mL round-bottomed flask was charged with 1,2-diiodo-4,5-dimethoxybenzene (1 equiv., 10 mmol, 3.90 g) and then evacuated/back-filled with nitrogen (3 ×) before addition of CH_2Cl_2 (70 mL). The solution was cooled to 0 °C, and BBr_3 (2.5 equiv., 25 mmol, 25 mL of a 1.0 M solution in CH_2Cl_2) was added through a syringe pump over 20 min. The reaction mixture was stirred at 0 °C for 4 h and then quenched with H_2O (50 mL). The separated aqueous layer was extracted with Et_2O (2 × 75 mL). The combined organic layers were dried with $MgSO_4$, filtered through a pad of silica, and concentrated in vacuo to afford 1,2-dihydroxy-4,5-diiodobenzene (3.61 g, 9.99 mmol, quant.) as an off-white solid that was deemed pure by NMR spectroscopy and used without further purification. R_f = 0.50 (50% ethyl acetate/hexane). M.p. 116.0–116.5 °C. ^{1}H NMR (400 MHz, [D_6]acetone): δ = 8.48 (br. s, 2 H), 7.38 (s, 2 H) ppm. ^{13}C NMR (150 MHz, [D_6]acetone): δ = 146.5, 125.6, 93.7 ppm.

4,5-Diiodo-1,2-phenylene Bis(trifluoromethanesulfonate) (1): 1,2-Dihydroxy-4,5-diiodobenzene (1 equiv., 7.85 mmol, 2.84 g), CH_2Cl_2 (55 mL), and pyridine (5 equiv., 39 mmol, 3.10 g, 3.16 mL) were added to a flame-dried 100 mL round-bottomed flask. The solution was cooled to 0 °C, and Tf_2O (2.2 equiv., 17.3 mmol, 4.88 g, 2.91 mL) was added dropwise through a syringe over 10 min. The reaction mixture was stirred for 6 h, while warming to ambient temperature, then cooled to 0 °C, and quenched with H_2O (30 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried with $MgSO_4$ and filtered through a tall pad of silica. The pad was washed carefully with CH_2Cl_2 to avoid the elution of impurities, and the filtrate was concentrated in vacuo to afford **1** (4.90 g, 7.82 mmol, quant.) as an off-white solid that was deemed pure by NMR spectroscopy and used without further purification. (Note: For reactions in which small amounts of impurities were observed after filtration, the product could be obtained in pure form by column chromatography utilizing 10% ethyl acetate/hexane as the mobile phase.) R_f

= 0.60 (10% ethyl acetate/hexane). M.p. 46.5–47.7 °C. ^{1}H NMR (400 MHz): δ = 7.91 (s, 2 H) ppm. ^{13}C NMR (100 MHz): δ = 139.6, 133.4, 118.5 (q, $J_{C,F}$ = 321.0 Hz), 108.0 ppm. FTIR: $\tilde{\nu}$ = 1429, 1335, 1215, 1125, 1105, 868, 788, 745, 689 cm^{-1}. HRMS (ESI): calcd. for $C_8H_2F_6I_2NaO_6S_2$ [M + Na]$^+$ 648.7184; found 648.7164.

General Procedure A. Sonogashira Coupling of 1: A flame-dried 8 mL vial fitted with a screw-top septum cap was charged with [Pd(PPh$_3$)$_2$Cl$_2$] (0.06 equiv., 0.024 mmol, 16.8 mg), CuI (0.12 equiv., 0.048 mmol, 9.2 mg), and **1** (1 equiv., 0.40 mmol, 250 mg) and then evacuated/back-filled with nitrogen (3 ×). A solution of the alkyne (2.3 equiv., 0.92 mmol) in THF (1 mL) was then added, followed by Et$_3$N (3 equiv., 1.2 mmol, 0.17 mL). The mixture was stirred at room temp. for the required time (3–5 h) until the reaction was complete (TLC) and then filtered through a plug of silica, which was washed with Et$_2$O. The combined eluents were concentrated in vacuo and purified by flash chromatography (ethyl acetate/hexane) to afford the diyne.

4,5-Bis(5-benzyloxypent-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2a): Yield: 241 mg, 0.336 mmol, 84%. Mobile phase: step gradient hexane to 10% ethyl acetate/hexane. R_f = 0.27 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.42 (s, 2 H), 7.27–7.39 (10 H), 4.56 (s, 4 H), 3.65 (t, J = 6.0 Hz, 4 H), 2.62 (t, J = 7.1 Hz, 4 H), 1.92–1.98 (m, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 138.8, 138.3, 128.4, 128.2, 127.59, 127.56, 126.3, 118.5 (q, $J_{C,F}$ = 321.1 Hz), 98.1, 77.4, 73.0, 68.5, 28.6, 16.5 ppm. FTIR: $\tilde{\nu}$ = 2859, 2230, 1489, 1433, 1210, 1178, 1135, 1080, 732 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{28}F_6O_8S_2Na$ [M + Na]$^+$ 741.1027; found 741.1039.

5,5′-[4,5-Bis(trifluoromethylsulfonyloxy)-1,2-phenylene]dipent-4-ynyl Dibenzoate (2b): Yield: 211 mg, 0.284 mmol, 71%. Mobile phase: step gradient hexane to 12% ethyl acetate/hexane. R_f = 0.20 (10% ethyl acetate/hexane). ^{1}H NMR (400 MHz): δ = 8.01–8.11 (4 H), 7.53–7.60 (2 H), 7.39–7.48 (6 H), 4.51 (t, J = 6.3 Hz, 4 H), 2.71 (t, J = 7.0 Hz, 4 H), 2.12 (quint, J = 6.5 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 166.5, 138.9, 133.0, 130.1, 129.6, 128.4, 128.0, 126.5, 118.5 (q, $J_{C,F}$ = 321.4 Hz), 97.2, 77.8, 63.5, 27.6, 16.7 ppm. FTIR: $\tilde{\nu}$ = 2210, 1716, 1489, 1433, 1271, 1246, 1209, 1177, 1134, 1085, 1070, 1027, 863, 808, 708 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{24}F_6O_{10}S_2Na$ [M + Na]$^+$ 769.0613; found 769.0609.

4,5-Bis(5-cyanopent-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2c): Yield: 173 mg, 0.312 mmol, 78%. M.p. 56.8–58.0 °C. Mobile phase: step gradient 25–35% ethyl acetate/hexane. R_f = 0.35 (40% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.49 (s, 2 H), 2.73 (t, J = 6.7 Hz, 4 H), 2.62 (t, J = 6.7 Hz, 4 H), 2.03 (quint, J = 6.7 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 139.2, 127.5, 126.7, 121.7, 118.5 (q, $J_{C,F}$ = 321.0 Hz), 95.4, 78.7, 24.2, 18.6, 16.2 ppm. FTIR: $\tilde{\nu}$ = 2231, 1490, 1431, 1401, 1246, 1223, 1212, 1131, 1084, 907, 858, 799, 749 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{14}F_6N_2O_6S_2Na$ [M + Na]$^+$ 579.0095; found 579.0092.

4,5-Bis[6-(*tert*-butyldimethylsilyloxy)hex-1-ynyl]-1,2-phenylene Bis(trifluoromethanesulfonate) (2d): Yield: 298 mg, 0.376 mmol, 94%. Mobile phase: step gradient hexane to 2% ethyl acetate/hexane. R_f = 0.27 (2.5% ethyl acetate/hexane). ^{1}H NMR (400 MHz): δ = 7.44 (s, 2 H), 3.66–3.72 (4 H), 2.49–2.61 (4 H), 1.66–1.77 (8 H), 0.92 (s, 18 H), 0.08 (s, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 138.8, 128.3, 126.3, 118.5 (q, $J_{C,F}$ = 320.9 Hz), 98.6, 77.3, 62.5, 31.9, 25.9, 24.9, 19.4, 18.3, –5.3 ppm. FTIR: $\tilde{\nu}$ = 2945, 2930, 2858, 2230, 1489, 1436, 11247, 1211, 1179, 1137, 1087, 834, 807, 774 cm^{-1}. HRMS (ESI): calcd. for $C_{32}H_{48}F_6O_8S_2Na$ [M + Na]$^+$ 817.2131; found 817.2120.

4,5-Bis(6-chlorohex-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2e): Yield: 185 mg, 0.304 mmol, 76%. Mobile phase: 4% ethyl acetate/hexane, R_f = 0.27 (5% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.46 (s, 2 H), 3.63 (t, J = 6.6 Hz, 4 H), 2.57 (t, J = 7.0 Hz, 4 H), 1.97–2.04 (4 H), 1.80–1.86 (4 H) ppm. ^{13}C NMR (150 MHz): δ = 138.9, 128.0, 126.5, 118.5 (q, $J_{C,F}$ = 320.7 Hz), 97.7, 77.7, 44.4, 31.6, 25.6, 19.0 ppm. FTIR: $\tilde{\nu}$ = 2946, 2230, 1489, 1432, 1302, 1246, 1209, 1179, 1085, 862, 802, 597 cm^{-1}. HRMS (ESI): calcd. for $C_{20}H_{18}F_6O_8S_2Cl_2Na$ [M + Na]$^+$ 624.9724; found 624.9716.

4,5-Bis[2-(triisopropylsilyl)ethynyl]-1,2-phenylene Bis(trifluoromethanesulfonate) (2f): Yield: 136 mg, 0.184 mmol, 46%. M.p. 42.3–43.5 °C. Mobile phase: 100% hexane. R_f = 0.43 (100% hexane). ^{1}H NMR (600 MHz): δ = 7.52 (s, 2 H), 1.14–1.21 (42 H) ppm. ^{13}C NMR (150 MHz): δ = 139.3, 128.0, 127.3, 118.5 (q, $J_{C,F}$ = 320.9 Hz), 102.1, 100.7, 18.7, 11.2 ppm. FTIR: $\tilde{\nu}$ = 2944, 2867, 2363, 1485, 1436, 1385, 1211, 1167, 1135, 881, 834, 574 cm^{-1}. HRMS (EI): calcd. for $C_{30}H_{44}F_6O_6S_2Si_2Na$ [M]$^+$ 734.2022; found 734.2020.

4,5-Bis[2-(4-methoxyphenyl)ethynyl]-1,2-phenylene Bis(trifluoromethanesulfonate) (2g): Yield: 197 mg, 0.312 mmol, 78%. M.p. 113.4–114.3 °C. Mobile phase: step gradient hexane to 7% ethyl acetate/hexane. R_f = 0.30 (10% ethyl acetate/hexane). ^{1}H NMR (400 MHz): δ = 7.59 (s, 2 H), 7.51–7.57 (4 H), 6.90–6.97 (4 H), 3.88 (s, 6 H) ppm. ^{13}C NMR (150 MHz): δ = 160.6, 139.0, 133.5, 127.8, 125.9, 118.5 (q, $J_{C,F}$ = 321.0 Hz), 114.3, 114.0, 97.7, 84.6, 55.4 ppm. FTIR: $\tilde{\nu}$ = 2205, 1605, 1513, 1485, 1435, 1414, 1290, 1248, 1213, 1130, 1027, 896, 828 cm^{-1}. HRMS (ESI): calcd. for $C_{26}H_{16}F_6O_8S_2Na$ [M + Na]$^+$ 657.0088; found 657.0083.

4,5-Bis[2-(pyridin-2-yl)ethynyl]-1,2-phenylene Bis(trifluoromethanesulfonate) (2h): Yield: 158 mg, 0.276 mmol, 69%. M.p. 119.1–120.2 °C. Mobile phase: 40% ethyl acetate/hexane. R_f = 0.30 (40% ethyl acetate/hexane). ^{1}H NMR (400 MHz): δ = 8.65–8.77 (2 H), 7.67–7.83 (6 H), 7.31–7.40 (m, 2 H) ppm. ^{13}C NMR (150 MHz): δ = 150.4, 142.2, 140.0, 136.3, 128.1, 127.3, 126.8, 123.8, 118.5 (q, $J_{C,F}$ = 320.8 Hz), 96.4, 84.2 ppm. FTIR: $\tilde{\nu}$ = 1581, 1561, 1493, 1429, 1208, 1131, 1054, 1040, 904, 885, 833, 782, 732 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{10}F_6N_2O_6S_2Na$ [M + Na]$^+$ 598.9782; found 598.9783.

4,5-Bis[4-(tetrahydro-2*H*-pyran-2-yloxy)but-1-ynyl]-1,2-phenylene Bis(trifluoromethanesulfonate) (2i): Yield: 230 mg, 0.340 mmol, 85%. Mobile phase: step gradient 10–20% ethyl acetate/hexane. R_f = 0.22 (15% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.45 (s, 2 H), 4.69–4.73 (2 H), 3.88–3.98 (4 H), 3.69 (dt, J = 9.7, 7.0 Hz, 2 H), 3.52–3.58 (2 H), 2.81 (t, J = 7.0 Hz, 4 H), 1.81–1.91 (2 H), 1.71–1.79 (2 H), 1.51–1.69 (8 H) ppm. ^{13}C NMR (150 MHz): δ = 138.9, 128.0, 126.4, 118.5 (q, $J_{C,F}$ = 320.4 Hz), 98.9, 95.6, 77.8, 65.3, 62.2, 30.5, 25.4, 21.2, 19.4 ppm. FTIR: $\tilde{\nu}$ = 2944, 2873, 2234, 1489, 1434, 1247, 1210, 1180, 1133, 1082, 976, 892, 859, 804, 733 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{28}F_6O_{10}S_2Na$ [M + Na]$^+$ 701.0926; found 701.0925.

4,5-Bis(3-hydroxy-3-methylbut-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2j): Yield: 155 mg, 0.288 mmol, 72%. Mobile phase: step gradient 30–40% ethyl acetate/hexane. R_f = 0.22 (30% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.48 (s, 2 H), 3.65 (br. s, 2 H), 1.66 (s, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 139.3, 127.5, 125.8, 118.5 (q, $J_{C,F}$ = 321.0 Hz), 102.2, 78.2, 65.6, 31.1 ppm. FTIR: $\tilde{\nu}$ = 3371, 2985, 1486, 1431, 1210, 1134, 1062, 952, 866, 826, 799, 734 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{16}F_6O_8S_2Na$ [M + Na]$^+$ 561.0088; found 561.0094.

4,5-Bis(3,3-diethoxyprop-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2k): Yield: 172 mg, 0.276 mmol, 69%. Mobile phase: step gradient hexane to 5% ethyl acetate/hexane. R_f = 0.22

(5% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.58 (s, 2 H), 5.52 (s, 2 H), 3.79–3.9 (4 H), 3.64–3.74 (4 H), 1.29 (t, J = 7.2 Hz, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 139.8, 127.0, 126.7, 118.5 (q, $J_{C,F}$ = 320.9 Hz), 92.51, 91.5, 80.3, 61.3, 15.1 ppm. FTIR: $\tilde{\nu}$ = 3675, 2979, 2901, 1490, 1435, 1248, 1211, 1178, 1135, 1076, 1050, 868, 814 cm^{-1}. HRMS (ESI): calcd. for $C_{22}H_{24}F_6O_{10}S_2Na$ [M + Na]$^+$ 649.0613; found 649.0610.

3,3′-[4,5-Bis(trifluoromethylsulfonyloxy)-1,2-phenylene]diprop-2-ynyl Dibenzoate (2l): Yield: 127 mg, 0.184 mmol, 46%. M.p. 78.4–79.5 °C. Mobile phase: step gradient hexane to 8% ethyl acetate/hexane. R_f = 0.35 (10% ethyl acetate/hexane). ^{1}H NMR (400 MHz): δ = 8.04–8.17 (4 H), 7.54–7.64 (4 H), 7.42–7.53 (4 H), 5.18 (s, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 165.7, 139.8, 133.5, 129.8, 129.3, 128.5, 127.1, 126.8, 118.5 (q, $J_{C,F}$ = 320.8 Hz), 91.6, 81.7, 52.7 ppm. FTIR: $\tilde{\nu}$ = 1724, 1490, 1434, 1265, 1246, 1210, 1177, 1134, 1089, 1069, 869, 803, 709 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{16}F_6O_{10}S_2Na$ [M + Na]$^+$ 712.9987; found 712.9988.

4,5-Bis(3-benzyloxyprop-1-ynyl)-1,2-phenylene Bis(trifluoromethanesulfonate) (2m): Yield: 114 mg, 0.172 mmol, 43%. Mobile phase: step gradient hexane to 10% ethyl acetate/hexane. R_f = 0.27 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.55 (s, 2 H), 7.30–7.43 (10 H), 4.67 (s, 4 H), 4.43 (s, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 139.6, 137.1, 128.5, 128.11, 128.07, 127.2, 126.8, 118.5 (q, $J_{C,F}$ = 320.4 Hz), 93.5, 82.2, 72.0, 57.6 ppm. FTIR: $\tilde{\nu}$ = 3676, 2988, 2901, 1489, 1433, 1247, 1209, 1178, 1133, 1072, 864, 807, 737 cm^{-1}. HRMS (ESI): calcd. for $C_{28}H_{20}F_6O_8S_2Na$ [M + Na]$^+$ 685.0402; found 685.0397.

General Procedure B. Sonogashira Coupling of Bis(triflates): A flame-dried 8 mL vial fitted with a septum-containing screw-top cap was charged with [Pd(PPh$_3$)$_2$Cl$_2$] (0.06 equiv., 0.015 mmol, 10.6 mg), CuI (0.3 equiv., 0.075 mmol, 14.3 mg), and Bu$_4$NI (3 equiv., 0.75 mmol, 277 mg). The vessel was evacuated/back-filled with nitrogen (3×), after which was added a solution of the bis(triflate) (1 equiv., 0.25 mmol) in DMF/TEA (5:1, 1 mL). The mixture was stirred at room temp. for 5 min, whereupon a solution of alkyne (4 equiv., 1 mmol) in DMF/TEA (5:1, 0.5 mL) was added. The capped vial was placed in an oil bath (70 °C) for 5.5 h and then cooled to room temp. The reaction mixture was filtered through a plug of silica, which was washed with Et$_2$O. The combined eluents were concentrated in vacuo and purified by flash chromatography.

1,2-Bis(5-benzyloxypent-1-ynyl)-4,5-bis(6-*tert*-butyldimethylsilyloxyhex-1-ynyl)benzene (3a): Yield: 151 mg, 0.18 mmol, 72%. Mobile phase: 6% ethyl acetate/hexane. R_f = 0.54 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.32–7.40 (10 H), 7.27–7.31 (2 H), 4.55 (s, 4 H), 3.69 (t, J = 5.9 Hz, 4 H), 3.65 (t, J = 6.2 Hz, 4 H), 2.59 (t, J = 7.0 Hz, 4 H), 2.51 (t, J = 6.6 Hz, 4 H), 1.93 (quint, J = 6.7 Hz, 4 H), 1.67–1.78 (8 H), 0.93 (s, 18 H), 0.09 (s, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 138.5, 135.2, 128.4, 127.60, 127.56, 125.2, 125.0, 95.4, 94.7, 79.2, 79.1, 73.0, 68.8, 62.7, 32.0, 28.9, 26.0, 25.1, 19.5, 18.4, 16.6, –5.3 ppm. FTIR: $\tilde{\nu}$ = 2928, 2855, 2209, 1487, 1253, 1102, 900, 834, 774, 733, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{54}H_{74}O_4Si_2Na$ [M + Na]$^+$ 865.5023; found 865.5006.

5,5′-[4,5-Bis(5-benzyloxypent-1-ynyl)-1,2-phenylene]dipent-4-ynyl Dibenzoate (3b): Yield: 127 mg, 0.16 mmol, 64%. Mobile phase: 15% ethyl acetate/hexane. R_f = 0.39 (20% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 8.04–8.10 (4 H), 7.54–7.60 (2 H), 7.42–7.47 (4 H), 7.39–7.41 (2 H), 7.33–7.38 (8 H), 7.27–7.31 (2 H), 4.55 (s, 4 H), 4.53 (t, J = 6.3 Hz, 4 H), 3.66 (t, J = 6.2 Hz, 4 H), 2.70 (t, J = 7.0 Hz, 4 H), 2.60 (t, J = 7.0 Hz, 4 H), 2.11 (quint, J = 6.6 Hz, 4 H), 1.94 (quint, J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 166.5, 138.5, 135.3, 133.0, 130.2, 129.6, 128.38, 128.36, 127.60, 127.56, 125.3, 124.9, 95.0, 93.9, 79.6, 79.1, 73.0, 68.7, 63.7, 28.9, 28.0, 16.7, 16.6 ppm. FTIR: $\tilde{\nu}$ = 3675, 2988, 2972, 2901, 2229, 1716, 1451, 1394, 1269, 1107, 1068, 1027, 900 cm^{-1}. HRMS (ESI): calcd. for $C_{54}H_{50}O_6Na$ [M + Na]$^+$ 817.3505; found 817.3503.

1,2-Bis(5-benzyloxypent-1-ynyl)-4,5-bis(2-trimethylsilylethynyl)benzene (3c): Yield: 98 mg, 0.16 mmol, 64%. Mobile phase: 6% ethyl acetate/hexane. R_f = 0.41 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.48 (s, 2 H), 7.28–7.41 (10 H), 4.56 (s, 4 H), 3.66 (t, J = 6.1 Hz, 4 H), 2.61 (t, J = 7.0 Hz, 4 H), 1.94 (quint, J = 6.4 Hz, 4 H), 0.32 (s, 18 H) ppm. ^{13}C NMR (150 MHz): δ = 138.5, 135.6, 128.4, 127.62, 127.61, 126.0, 124.5, 102.4, 100.0, 95.6, 79.0, 73.0, 68.7, 28.9, 16.6, 0.01 ppm. FTIR: $\tilde{\nu}$ = 2956, 2856, 2226, 2155, 1481, 1454, 1249, 1103, 1077, 1028, 839, 758, 731, 696, 635 cm^{-1}. HRMS (ESI): calcd. for $C_{40}H_{46}O_2Si_2Na$ [M + Na]$^+$ 637.2934; found 637.2922.

1,2-Bis(5-benzyloxypent-1-ynyl)-4,5-bis(2-phenylethynyl)benzene (3d): Yield: 130 mg, 0.208 mmol, 83%. Mobile phase: step gradient 5–10% ethyl acetate/hexane. R_f = 0.32 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.57–7.63 (6 H), 7.34–7.42 (14 H), 7.29–7.34 (2 H), 4.58 (s, 4 H), 3.69 (t, J = 6.1 Hz, 4 H), 2.64 (t, J = 7.0 Hz, 4 H), 1.97 (quint, J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 138.5, 135.1, 131.7, 128.7, 128.5, 128.4, 127.63, 127.61, 125.9, 124.6, 123.1, 95.6, 94.9, 87.6, 79.2, 73.0, 68.7, 28.9, 16.6 ppm. FTIR: $\tilde{\nu}$ = 2856, 2224, 1597, 1497, 1364, 1102, 1076, 1027, 899, 754, 734, 688 cm^{-1}. HRMS (ESI): calcd. for $C_{46}H_{38}O_6Na$ [M + Na]$^+$ 645.2770; found 645.2759.

1,2-Bis(5-benzyloxypent-1-ynyl)-4,5-bis[2-(4-methoxyphenyl)ethynyl]benzene (3e): Yield: 135 mg, 0.198 mmol, 79%. Mobile phase: 15% ethyl acetate/hexane. R_f = 0.37 (20% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.49–7.56 (6 H), 7.34–7.42 (8 H), 7.28–7.38 (2 H), 6.88–6.93 (4 H), 4.56 (s, 4 H), 3.86 (s, 6 H), 3.68 (t, J = 6.1 Hz, 4 H), 2.62 (t, J = 7.0 Hz, 4 H), 1.95 (quint, J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 159.2, 138.5, 134.8, 133.2, 128.4, 127.62, 127.59, 125.5, 124.7, 115.3, 114.1, 95.2, 94.9, 86.6, 79.3, 73, 68.7, 55.3, 28.9, 16.6 ppm. FTIR: $\tilde{\nu}$ = 2932, 2857, 2209, 1604, 1568, 1511, 1289, 1246, 1172, 1141, 1104, 1027, 899, 829, 734, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{48}H_{42}O_4Na$ [M + Na]$^+$ 705.2981; found 705.2974.

1,2-Bis(5-benzyloxypent-1-ynyl)-4,5-bis[2-(4-fluorophenyl)ethynyl]benzene (3f): Yield: 122 mg, 0.185 mmol, 74%. Mobile phase: 8% ethyl acetate/hexane. R_f = 0.36 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 7.52–7.58 (6 H), 7.34–7.42 (8 H), 7.28–7.34 (2 H), 7.05–7.11 (4 H), 4.57 (s, 4 H), 3.68 (t, J = 6.1 Hz, 4 H), 2.63 (t, J = 7.0 Hz, 4 H), 1.96 (quint, J = 6.6 Hz, 4 H) ppm. ^{13}C NMR (150 MHz): δ = 162.8 (d, $J_{C,F}$ = 250.5 Hz), 138.5, 135.0, 133.5 (d, $J_{C,F}$ = 8.6 Hz), 128.4, 127.61, 127.60, 126.0, 124.3, 119.2 (d, $J_{C,F}$ = 4.4 Hz), 115.8 (d, $J_{C,F}$ = 22.5 Hz), 95.7, 93.7, 87.3, 79.1, 73.0, 68.7, 28.9, 16.6 ppm. FTIR: $\tilde{\nu}$ = 2926, 2856, 2225, 1600, 1567, 1507, 1227, 1155, 1102, 899, 833, 792, 734, 696 cm^{-1}. HRMS (ESI): calcd. for $C_{46}H_{36}F_2O_2Na$ [M + Na]$^+$ 681.2581; found 681.2567.

5,5′-{4,5-Bis[6-(*tert*-butyldimethylsilyloxy)hex-1-ynyl]-1,2-phenylene}dipent-4-ynyl Dibenzoate (3g): Yield: 149 mg, 0.170 mmol, 68%. Mobile phase: 6% ethyl acetate/hexane. R_f = 0.36 (10% ethyl acetate/hexane). ^{1}H NMR (600 MHz): δ = 8.03–8.08 (4 H), 7.34–7.42 (8 H), 7.52–7.59 (2 H), 7.38–7.47 (6 H), 4.50 (t, J = 6.3 Hz, 4 H), 3.68 (t, J = 6.0 Hz, 4 H), 2.67 (t, J = 6.8 Hz, 4 H), 2.50 (t, J = 6.5 Hz, 4 H), 2.09 (quint, J = 6.5 Hz, 4 H), 1.65–1.77 (8 H), 0.92 (s, 18 H), 0.07 (s, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 166.5, 135.2, 132.9, 130.2, 129.6, 128.3, 125.4, 124.8, 95.6, 93.8, 79.6, 79.0, 63.7, 62.6, 31.9, 28.0, 26.0, 25.1, 19.5, 18.3, 16.6, –5.3 ppm. FTIR: $\tilde{\nu}$ = 2951, 2928, 2856, 2231, 1719, 1270, 1107, 1070, 834, 709 cm^{-1}.

HRMS (ESI): calcd. for $C_{54}H_{70}O_6Si_2Na$ $[M + Na]^+$ 893.4609; found 893.4631.

1,2-Bis[2-(4-methoxyphenyl)ethynyl]-4,5-bis(2-trimethylsilylethynyl)-benzene (3h): Yield: 76 mg, 0.143 mmol, 57%. Mobile phase: 4% ethyl acetate/hexane. R_f = 0.38 (10% ethyl acetate/hexane). ^1H NMR (600 MHz): δ = 7.66 (s, 2 H), 7.47–7.55 (4 H), 6.86–6.93 (4 H), 3.85 (s, 6 H), 0.31 (s, 18 H) ppm. ^{13}C NMR (150 MHz): δ = 160.0, 135.2, 133.2, 125.6, 124.8, 115.1, 114.1, 102.4, 100.4, 95.7, 86.4, 55.3, 0.0 ppm. FTIR: $\tilde{\nu}$ = 2959, 2213, 2156, 1605, 1513, 1290, 1246, 1167, 1031, 828 cm^{-1}. HRMS (EI): calcd. for $C_{34}H_{34}O_2Si_2$ $[M]^+$ 530.2097; found 530.2093.

1,2-Bis{2-[4-(dibutylamino)phenyl]ethynyl}-4,5-bis[2-(2-pyridyl)-ethynyl]benzene (3i): Yield: 134 mg, 0.183 mmol, 73%. Mobile phase: 35% ethyl acetate/hexane. R_f = 0.35 (40% ethyl acetate/hexane). ^1H NMR (600 MHz): δ = 8.64–8.70 (2 H), 7.78 (s, 2 H), 7.73 (d, J = 7.6 Hz, 2 H), 7.67 (td, J = 7.8, 1.9 Hz, 2 H), 7.45 (d, J = 8.7 Hz, 2 H), 7.23–7.28 (2 H), 6.61 (d, J = 8.7 Hz, 4 H), 3.32 (t, J = 7.9 Hz, 8 H), 1.61 (quint, J = 7.8 Hz, 8 H), 1.39 (sext, J = 7.6 Hz, 8 H), 0.99 (t, J = 7.3 Hz, 12 H) ppm. ^{13}C NMR (150 MHz): δ = 150.1, 148.3, 143.5, 136.1, 134.8, 133.3, 127.8, 126.7, 123.4, 122.9, 111.2, 108.5, 98.0, 93.9, 87.4, 86.0, 50.7, 29.4, 20.3, 14.0 ppm.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for all compounds.

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