Synthesis of Difunctional Triarylethanes with Pendent Ethynyl Groups: Monomers for Crosslinkable Condensation Polymers[1]

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Synthetic schemes have been developed and optimized for the preparation of groups of 4,4′-diamino- and 4,4′-dihydroxytriarylethanes with an ethynyl group pendent on the third aryl group. Palladium-(0)-catalyzed reaction of an aryl halide moiety with an acetylene is used for the attachment of the ethynyl group. The third aryl group is either a phenyl or a phenoxyphenyl group, while the other end of the ethynyl group is either unprotected or bears an *n*-butyl or phenyl group. The variations in the structure of the third aryl group and the cap on its acetylene group are chosen to probe their influence on the mechanical properties of the resulting crosslinked thermoplastics.

Introduction

Engineering thermoplastics such as polyarylates, poly(arylene ether)s, and polyimides find unique technological applications as matrices in composites, adhesives, films, and coatings.[2-5] This is because they possess an excellent combination of mechanical and physical properties. When used as functional and structural materials, these thermoplastics are frequently subjected to high temperatures, high stress and strain, and exposure to various environmental elements including fluids. Under these working conditions, linear engineering polymers are known to suffer from solvent sensitivity under stress and swelling by fluids and creep under load at temperatures below their glass transition temperatures (Tgs).

One of the best methods of improving the mechanical properties and stability of high performance thermoplastics is crosslinking.[6] Of the crosslinking techniques, the use of pendent acetylene or acetylene caps as the reactive function for curing[2-5,7] is significant for the following reasons: (a) the acetylene group can be attached efficiently, (b) the curing process occurs by an addition reaction which generates no effluents in the body of fabricated large parts. Therefore, in efforts to improve the applicability of high performance polymers, crosslinking through acetylenic groups is one of the methods of choice. We were consequently interested in developing efficient schemes for the synthesis of acetylene-containing difunctional monomers with high aromatic content for use in the preparation of condensation polymers. Linear polymers arising from an initial condensation polymerization of these monomers through their condensable functional groups (NH_2, OH) would be expected to undergo crosslinking during curing of fabricated objects by the addition reaction of the acetylenic groups.

We have developed and optimized schemes for the synthesis of 12 difunctional triarylethanes, each bearing an ethynyl group. We report here the details of the syntheses and purification of these monomers. Results from the polymerization of some of these monomers and crosslinking studies of the resulting linear polymers have been presented[8] and are reported elsewhere.[9]

Results and Discussion

Scheme 1 illustrates two strategies for the synthesis of difunctional triarylethanes with pendent ethynyl groups. Both strategies begin with the conversion of the aryl dihalides 1 and 8 to the *p*-haloaryl ketones 2 and 9. At this point, two pathways A and B were compared for the conversion of 2 to the final structure 5, 6.

Preparation of the 4-Haloaryl Ketones. The *p*-halo ketones **2a**,[10] **2b**,[11] and 9 were prepared by monolithiation of the aryl dihalides 1 and 8 followed by low-temperature trapping of the appropriate aryllithium with ethyl or methyl trifluoroacetate (ETFA or MTFA). Highest yields were obtained (96% **2a**) by carrying out the aqueous acid quench at between −40 to −30 °C. As expected, we found that with 1,4-dibromobenzene only monolithiation occurred, even when up to 4 equiv of n-BuLi per mole of *p*-dihalobenzene was used. The *p*-iodoaryl ketone **2b**[11] was prepared from 1,4-diiodobenzene by the same method.

4-Bromophenyl ether 8 required a slightly higher temperature for lithiation and was converted, in high yield, to the bromo ketone 9 when the lithiation was conducted

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Scheme 1

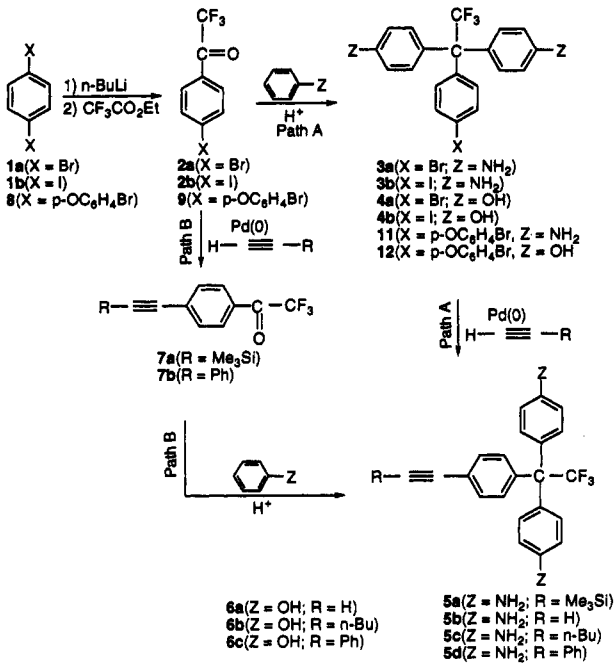


Table 1. Effect of Different Acids on the Condensation of 2a with Phenol

entry	acid catalyst	mol %	% yield of 4a
1	$HCl/HS(CH_2)_2CO_2H$	100	0
2	CF_3SO_3H	100	80
3	CF_3SO_3H	2	80
4	*p*-TsOH	6	60
5	BF_3-Et_2O	6	60

at between −50 and −40 °C, followed by the addition of ETFA at −78 °C and quenching at −30 °C. In this reaction, bis[4-(4-bromophenoxy)phenyl](trifluoromethyl)carbinol (**10**) was always a minor product.

Condensation of the 4-Haloaryl Ketones with Aniline and Phenol (Path A). The synthesis of difunctional 2,2-diarylpropanes and 2,2,2-triarylethanes from nonenolizable ketones usually involves their acid-catalyzed condensation with phenols and arylamines.[12] The efficiency of these reactions is known to depend on the nature of the ketone and the acid catalyst. Some of the catalysts that have been reported as effective include CF_3SO_3H, BF_3, *p*-TsOH,[13] $AlCl_3$,[12] and HCl/3-mercaptopropionic acid system.[14]

Refluxing the *p*-halo ketones **2a**, **2b**, and **9** with aniline and aniline hydrochloride[13] led to good yields of the diaminotriaryl bromides **3a** and **11** and the iodo analog **3b**. Of the catalysts that were tested for the condensation between the *p*-haloaryl ketones and phenol, trifluoromethanesulfonic acid (TfA) gave the best results in terms of catalytic efficiency and yield. This is shown in Table 1 for the condensation with **2a**.

Pd(0)-Catalyzed Ethynylation of 4,4′-Diaminotriaryl Halides (Path A). The halide (bromide or iodide) group of vinyl and aryl halides is usually replaced by an ethynyl group through Pd(0)-catalyzed reactions.[15] Uncapped acetylenes such as **5b** are the most reactive ethynyl groups in cross-linking reactions. At the outset it was not known whether the acetylenic group of these monomers would survive the temperature for condensation polymerization of the diamines to polyimides. We therefore initially targeted **5b** in order to address the survivability uncertainty.

Table 2. Reaction Conditions and Product Yields for the Ethynylation of Diaminotriaryl Halides 3a, 3b, and 11

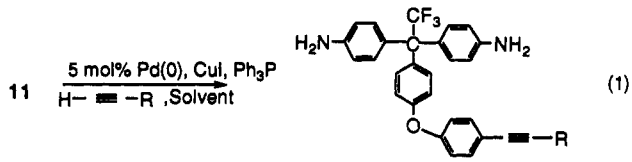
halide	alkyne	solvent	catalyst[a]	product	% yield
3a	TMSA	Et_3N/NMP (3:1)	C_1	**5b**	79
3a	TMSA	Et_3N/NMP (3:1)	C_1	**5a**	82
3b	TMSA	Et_3N/NMP (3:1)	C_1	**5a**	54
3a	1-hexyne	Et_3N/NMP (3:1)	C_2	**5c**	62
3b	P—≡—H	Et_3N/NMP (3:1)	C_1	**5d**	58
11	TMSA	NMP	C_2	**13**	61
11	1-hexyne	NMP	C_2	**14**	54
11	Ph—≡—H	NMP	C_2	**15**	75

[a] C_1 = tetrakis(triphenylphosphine)palladium(0) and CuI; C_2 = tetrakis(triphenylphosphine)palladium(0), CuI, and Ph_3P. For each reaction, all catalyst components are either 4 or 5 mol % relative to the halide substrate.

Pd(0)-catalyzed coupling of the bromide **3a** with TMSA in tertiary amine solvents such as triethylamine (Et_3N) and *N*-methylpyrrolidine (NMP) resulted in incomplete conversion of the bromide even when up to 5 mol % of palladium catalyst was employed in the presence of CuI. All efforts to separate the ethynylation product from unreacted triaryl halide were unsuccessful. In order to obtain the monomers with high purity, it was therefore necessary to determine conditions that would lead to total conversion of the bromide to the ethynyl derivative since it would not be possible to remove any unreacted bromide from the resulting monomers. Complete halide conversions were obtained under the conditions given in Table 2.

For **5b** the crude ethynylation adduct **5a** was subjected to desilylation after which chromatographic purification was undertaken. Subsequent polyimide generation from the uncapped diaminotriaryl acetylene **5b** demonstrated that the ethynyl group of our target monomers would survive the conditions of condensation polymerization.[9]

The reactivity trend of the acetylenes was similar in the ethynylation of the phenoxytriaryl bromide **11** (eq 1). The reaction conditions and product yields are summarized in Table 2.



(1)

13: R = H(Me_3Si)
14: R = n-Bu
15: R = Ph

Pd(0)-Catalyzed Ethynylation of 4,4′-Dihydroxytriaryl Halides (Path A). The ethynylations of **4a** with TMSA and 1-hexyne were driven to completion in Et_3N using 4 mol % each of Pd(0) catalyst and CuI. The uncapped dihydroxytriaryl acetylene **6a** was obtained in 80% yield from the halide while the hexynyl adduct **6b**

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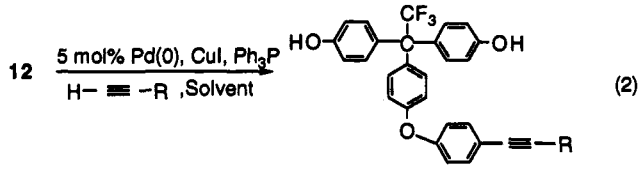
Table 3. Reaction Conditions and Product Yields for the Ethynylation of Dihydroxytriaryl Halides 4a, 4b, and 12

halide	alkyne	solvent	catalyst[a]	product	% yield
4a	TMSA	Et_3N	C_1	**6a**	80
4a	1-hexyne	Et_3N	C_1	**6b**	78
4b	Ph—≡—H	Et_3N	C_1	**6c**	78
12	1-hexyne	Et_3N	C_2	**16**	85
12	Ph—≡—H	Et_3N	C_2	**17**	83
12	TMSA	NMP	C_2	**18**	66

[a] C_1 = tetrakis(triphenylphosphine)palladium(0) and CuI; C_2 = tetrakis(triphenylphosphine)palladium(0), CuI, and Ph_3P. For each reaction, all catalyst components are either 4 or 5 mol % relative to the halide substrate.

was obtained in 78% yield. All attempts to drive the ethynylation of the bromide **4a** with phenylacetylene to completion failed. Use of the dihydroxytriaryl iodide **4b**, however, led to the phenylethynyl derivative **6c** uncontaminated with unreacted halide, in 78% yield.

Ethynylation of the dihydroxytriarylphenoxy bromide **12** with any of the acetylenes required the presence of Ph_3P for the exhaustive replacement of the bromide group either in Et_3N or NMP (eq 2). Reactions with phenyl-

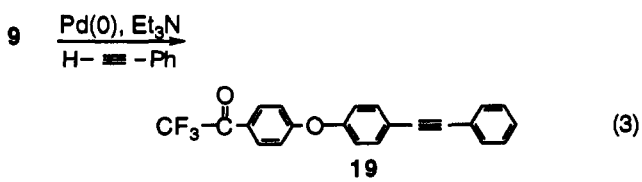


(2)

16: R = n-Bu
17: R = Ph
18: R = H(Me_3Si)

acetylene and 1-hexyne leading to **16** and **17**, respectively, went to completion in either solvent when fresh Pd catalyst was used. Yields were always lower in NMP than in Et_3N. The uncapped acetylene **18** was obtained using TMSA in the usual two-step sequence as similar analogs. The reaction conditions and yields for the ethynylations of the dihydroxytriaryl halides are summarized in Table 3.

The Ethynylation–Condensation Pathway from the Ketoaryl Halides (Path B). It was anticipated that the carbonyl group of the *p*-haloaryl ketones **2a**, **2b**, and **9** would make them more reactive in the Pd(0)-catalyzed ethynylation reactions.[16] This was found to be true. For example, the bromide **2a** was ethynylated with TMSA and phenylacetylene in Et_3N in the presence of 2 mol % of Pd(0) catalyst only to give **7a** and **7b**, respectively, in very high yields (see Scheme 1). The bromophenoxy ketone **9** was coupled with phenylacetylene under similar reaction conditions to give **19** (eq 3) in good yield.



(3)

19

When *p*-ethynylaryl ketones **7a**, **7b**, and **19** were subjected to acid-catalyzed condensation with aniline or phenol, the reaction, in most cases, did not lead to the expected products. It was only in the condensation of **7b** with aniline that the desired monomer **5d** was obtained. Condensation of the trimethylsilyl adduct **7a** (see Scheme 1) with aniline in the presence of aniline hydrochloride, followed by steam distillation under basic conditions, gave an unidentified solid with mp above 250 °C and insoluble in $CDCl_3$. The mass spectrum (MS) of this material showed a highest mass of 1104 amu (expected mass of **5b** is 366 amu). Its ^1H NMR in deuterated acetone showed that the trimethylsilyl group had been lost, most probably during the basic steam distillation. Attempted condensation of 4-[4-(phenylethynyl)phenoxy]trifluoroacetophenone (**19**) with aniline or **7b** with phenol resulted in mixtures in which addition of 1 mol of aniline or phenol to the ethynyl group had occurred as well as the expected condensation with the carbonyl group. For example, MS of the product mixture from the reaction of **7b** with phenol showed a parent peak at 538 amu which corresponds to the mass of **6c** + PhOH (i.e., 444 + 94 amu). In the reaction between **19** and aniline, a parent peak of 628 amu, corresponding to **15** + $PhNH_2$ (i.e., 535 + 93 amu), was observed. The crude products could not be purified for further identification.

Conclusion

It is obvious from these results that the ethynylation–condensation pathway does not offer access to the ethynyl monomers except in the case of the reaction between aniline and the ethynyl ketone **7b**. This is due to an accompanying addition of phenol or aniline to the triple bond during the acid-catalyzed condensation reaction. Even though the reactivity of the triaryl bromides toward Pd(0)-catalyzed ethynylation is much lower than that of the aryl ketones, optimal conditions were still found to drive the reaction to completion. The condensation/ethynylation pathway, therefore, represents the one general synthetic route to these ethynylated condensation monomers.

Experimental Section

General Procedures. Diethyl ether for metal–halogen-exchange reactions was distilled from sodium benzophenone ketyl under nitrogen atmosphere. Aniline hydrochloride was purified by decolorizing a methanol solution with Norit-A. Aniline was freshly distilled before use. Other solvents and reagents were used as purchased from either Aldrich Chemical Co. or Alfa/Johnson Matthey Co. Apparatus for metal-exchange reactions was always flame-dried and cooled under nitrogen before addition of reagents and solvent. All reactions were run under nitrogen except in those cases where the reaction flask was sealed with a rubber septum. Thin-layer chromatography (TLC) was run with Kodak TLC silica gel sheets with fluorescent indicator, and column chromatographic separations were run with silica gel, 70–230 mesh (ASTM) from EM Science.

Melting points (mp) were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. ^1H NMR were recorded at 60 MHz on a Varian EM360A 60 NMR spectrometer. Chemical shifts are reported in parts per million from tetramethylsilane as an internal standard. Infrared spectra of liquids were obtained neat while those of solids were obtained as KBr pellets on a Nicolet 510 FT-IR spectrometer. Low- and high-resolution mass spectral analyses were performed at 70 eV on a VG-7070 E-HF and a Finnigan 4500 GC–MS spectrometer. Elemental analyses were performed by Galbraith Microanalytical Laboratory, Nashville, TN.

The modified procedure for the preparation of **2a**,[10] **2b**,[11] the procedures and characterization data for **3a,b**, **4a**, **5b–d**, **4b**, and **6a–c** have been reported.[9]

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1,1-Bis(4-aminophenyl)-1-[4-[(trimethylsilyl)ethynyl]-phenyl]-2,2,2-trifluoroethane (5a). In a mixture of 30 mL of Et_3N and 10 mL of NMP was dissolved 3.68 g (7.86 mmol) of **3b**. To this solution were added 0.43 g (0.37 mmol, 5 mol %) and 0.07 g (0.37 mmol, 5 mol %) of tetrakis(triphenylphosphine)palladium-(0) [$L_4Pd(0)$] and CuI, respectively, and 1.88 g (19.18 mmol) of TMSA. The flask was sealed with a rubber septum which was additionally secured with copper wire. The mixture was stirred at 80 °C for 24 h. The solution was decanted from the solid sticking to the flask into another flask and concentrated, and the residue was redissolved in ether. After the ether solution was washed with water, dried over $MgSO_4$, filtered, and concentrated, the residue was chromatographed. Elution with benzene removed faster moving components. Continued elution with 50 vol % of ether in benzene gave **5a** as a viscous oil that foamed up under vacuum and dried into a gray fluffy solid weighing 1.85 g (54%). Analytical samples were obtained by a second chromatography using 20 vol % of ether in benzene. The fluffy solid from this second chromatography was vacuum dried at room temperature overnight and then vacuum heat-dried at 80 °C for 3 h. This process removed benzene that was found (^1H NMR) retained in the product even after vacuum drying at room temperature: mp 85–95 °C (orange liquid); IR (cm^{-1}) 3452, 3359, 2150, 1609, 1502, 1211, 1125, 819; ^1H NMR ($CDCl_3$, external TMS standard) δ 0.22 (s, 9 H), 3.60 (br s, 4 H), 6.28–7.43 (two AB quartets, 12 H); MS *m/z* (relative intensity) 438 (M^+, 30), 369 ($M^+ - CF_3$, 100), 274 (70); IR ($CDCl_3$) 3440 cm^{-1} (d, NH_2); high-resolution MS calcd for $C_{25}H_{25}F_3N_2Si$ 438.1739, found 438.1739. **5a** was also prepared from **3a** as a bright yellow fluffy solid in 82% yield under the same reaction conditions.

4-[(Trimethylsilyl)ethynyl]trifluoroacetophenone (7a). To a solution of 4.83 g (19.02 mmol) of **2a** in 20 mL of Et_3N were added 0.16 g (0.14 mmol, 0.74 mol %) of $L_4Pd(0)$ and 2.25 g (22.93 mmol) of TMSA. The flask was sealed with a secured rubber septum and heated at 80 °C for 3 h. During this period, a white precipitate developed in the reaction mixture which increased in size and darkened with time. After 3 h, the suspension was filtered and the filtrate was concentrated. The residue was taken up in ether and the ether solution was washed with 1 N HCl and dried ($MgSO_4$). Removal of solvent was followed by column chromatography with hexane as eluent to obtain 4.55 g (87%) of **7a**: mp 41–2 °C (hexane); IR (cm^{-1}) 1715, 1600, 1161, 847; ^1H NMR ($CDCl_3$, external TMS) δ 0.28 (s, 9 H), 7.28–7.97 (AB q, 4 H); MS *m/z* (relative intensity) 270 (M^+,10), 255 (100), 158 (18). Anal. Calcd for $C_{13}H_{13}F_3OSi$: C, 57.76; H, 4.85. Found: C, 57.22; H, 5.22.

4-(Phenylethynyl)trifluoroacetophenone (7b) was prepared and purified by a similar procedure as for **7a** using phenylacetylene instead of TMSA. Differences in procedure include the use of a reflux condenser and a reaction time of 12 h. The yield of **7b** was 90%: mp 80–1 °C (hexane); IR (cm^{-1}) 2204, 1707, 1586, 1196, 1117; ^1H NMR ($CDCl_3$) δ 7.89 (d, 2 H), 7.60–7.03 (m, 7 H); MS *m/z* (relative intensity) 274 (M^+, 73), 205 (100), 176 (40). Anal. Calcd for $C_{16}H_9F_3O$: C, 70.07; H, 3.31. Found: C, 70.32; H, 3.21.

4-(4-Bromophenoxy)trifluoroacetophenone (9). Into an appropriately dried flask was placed 50.29 g (152.39 mmol) of 4-bromophenyl ether **8**. A pressure-equalizing addition funnel with a rubber septum was attached to one neck, a nitrogen line to another, and the third neck was covered with a rubber septum. Anhydrous ether (200 mL) was added by syringe into the flask, and then 100 mL of 1.6 M n-BuLi in hexanes was introduced into the addition funnel. The setup was brought to a bath temperature of −40 °C by adding bits of dry ice to an acetone bath, causing the bromo ether to precipitate out of solution. To this stirred suspension was added, dropwise, the n-BuLi solution over 35 min. The suspension became a solution toward the end of addition of the n-BuLi. This solution was stirred for 1 h at between −50 to −40 °C and then cooled to −78 °C. To this solution was added, by syringe, in less than 5 min, 30 g (211.27 mmol) of ETFA. After being allowed to warm to 0 °C (~6 h), the reaction mixture was cooled to −30 °C, and 40 mL of saturated NH_4Cl was added dropwise, followed by 40 mL of 6 N HCl. The suspension was stirred until it warmed to room temperature.

The aqueous layer was separated, and the ether solution was washed twice with distilled water and then dried ($MgSO_4$) and concentrated. The residual liquid was chromatographed with hexane to obtain 45.08 g (86%) of **9** as a moderately viscuous, colorless liquid: ^1H NMR ($CDCl_3$) δ 6.90 (unsym q, 4 H), 7.38 (unsym d, 2 H), 7.92 (unsym d, 2 H); IR (neat) 1710, 1583, 1469, 1169 cm^{-1}; MS *m/z* (relative intensity) 346 ($M^+ + 2$, 10), 344 (M^+, 10), 277 ($M^+ + 2 - CF_3$, 30), 275 ($M^+ - CF_3$, 30), 139 (100). Anal. Calcd for $C_{14}H_8BrF_3O_2$: C, 48.72; H, 2.34; Br, 23.15. Found: C, 49.08; H, 2.33; Br, 23.15. Some of the carbinol **10** was recovered from the column by eluting with ether: ^1H NMR ($CDCl_3$) δ 2.97 (br s, 1 H), 6.70 (unsym m, 8 H), 7.22 (unsym m, 8 H); MS *m/z* (relative intensity) 596 ($M^+ + 4$, 5), 594 ($M^+ + 2$, 10), 592 (M^+, 5), 527 (30), 525 (60), 523 (30), 277 (70), 275 (70), 168 (100).

1,1-Bis(4-aminophenyl)-1-[4-(4-bromophenoxy)phenyl]-2,2,2-trifluoroethane (11). This compound was prepared in 70% yield from **9** according to the procedure for **3a**.[9] Chromatographic purification was effected by initial elution with benzene to remove mobile impurities, followed by a 9:1 mixture of benzene and ether. The form of **11** varied from fluffy yellow to purple powder. All forms gave an intense purple solution in benzene. Analytical samples were prepared by recrystallization from benzene and vacuum heat-drying at 90 °C for 1 h to remove residual benzene. An ashy-white solid resulted: mp 179–80 °C; IR (cm^{-1}) 3438, 3328, 1896, 1611, 1469, 1105, 806; ^1H NMR ($CDCl_3$) δ 3.53 (br s, 4 H), 6.26–6.97 (two AB q, 12 H), 7.00–7.40 (AB q, 4 H); MS *m/z* (relative intensity) 514 ($M^+ + 2$, 20), 512 (M^+, 20), 445 ($M^+ + 2 - CF_3$, 100), 443 ($M^+ - CF_3$, 100), 364 (15). Anal. Calcd for $C_{26}H_{20}BrF_3N_2O$: C, 60.83; H, 3.93; Br, 15.56. Found: C, 61.03; H, 4.05; Br, 15.71.

1,1-Bis(4-hydroxyphenyl)-1-[4-(4-bromophenoxy)phenyl]-2,2,2-trifluoroethane (12). Bromo ketone **9** (10.06 g, 29.07 mmol) and 55 g (581 mmol) of crystalline phenol were heated in a flask attached to a reflux condenser until a stirrable solution resulted. To this solution was added 0.45 g (0.32 mmol, 0.9 mol %) of TfA, and the mixture was heated at 100 °C for 72 h. The resulting mixture was steam-distilled until the distillate was clear. The solid residue was filtered from the hot water and washed many times with hot water to give granules of **12** as an off-white solid. The mass was vacuum dried overnight at room temperature to remove traces of moisture. The weight of **12** was 14.36 g (96%). Analytical samples were obtained by dissolving the granules in a mixture of hexane/CH_2Cl_2 and allowing the CH_2Cl_2 to evaporate, leaving **12** to precipitate out of hexane: mp 193–5 °C; IR (cm^{-1}) 3342 (broad), 1601, 1494, 1231, 1131, 819; ^1H NMR ($CDCl_3$) δ 6.56–7.47 (three AB q, 16 H), 7.73 (br s, 2 H); MS *m/z* (relative intensity) 516 ($M^+ + 2$, 20), 514 (M^+, 20), 447 (100), 445 (100), 366 (22). Anal. Calcd for $C_{26}H_{18}BrF_3O_3$: C, 60.60; H, 3.52; Br, 15.51. Found: C, 60.88; H, 3.85; Br, 15.38.

1,1-Bis(4-aminophenyl)-1-[4-(4-ethynylphenoxy)phenyl]-2,2,2-trifluoroethane (13). In a procedure similar to the preparation of **5b**,[9] 5 mol % each of $L_4Pd(0)$, CuI, and Ph_3P catalyzed the coupling of TMSA (100% excess) with the aryl bromide **11** in NMP at 90 °C for 41 h. The crude intermediate was desilylated also as for **5b**. Chromatographic purification started with elution with benzene, followed by a 9:1 mixture of benzene and ether, respectively. The product was a foamy yellow mass under vacuum but turned into an orange gel when the vacuum was released. Leaving the mass under vaccum for 12–24 h usually left a fluffy solid that did not collapse into a gel on removal of the vacuum, but ^1H NMR showed that benzene was still included in the dry solid. To remove residual benzene, the product was redissolved in a 1:1 mixture of MeOH/ether. Removal of the solvent mixture gave a more compact solid which was vacuum dried at room temperature for 12 h to obtain pure **13** in 61% yield as a yellow solid: mp the solid started to shrink at 80 °C, softened into an orange glass at 86 °C, and melted at 105 °C; IR (cm^{-1}) 3447, 3276, 1608, 1488, 1231, 1117, 811; ^1H NMR ($CDCl_3$) δ 3.00 (s, 1 H), 3.60 (br s, 4 H), 6.24–7.57 (m, 16 H); MS *m/z* (relative intensity) 458 (M^+, 15), 389 ($M^+ - CF_3$, 100). Anal. Calcd for $C_{28}H_{21}F_3N_2O$: C, 73.35; H, 4.62; N, 6.11. Found: C, 73.47; H, 4.96; N, 5.99.

1,1-Bis(4-aminophenyl)-1-[4-(4-hexynylphenoxy)phenyl]-2,2,2-trifluoroethane (14). This compound was prepared and purified in 54% yield, as a yellow solid, through the coupling of **11** with 1-hexyne (200% excess) using the same procedure as for the intermediate to **13** and the purification routine for **13**: mp the solid started to soften at 63 °C, became a transparent yellow

glass at 72 °C, and melted at 84 °C; IR (cm^{-1}) 3450, 3364, 2915, 1611, 1483, 1212, 1127, 813; ^1H NMR ($CDCl_3$) δ 0.93 (m, 3 H), 1.47 (m, 4 H), 2.30 (m, 2 H), 3.53 (br s, 4 H), 6.20–7.34 (unresolved AB qs, 16 H); MS *m/z* (relative intensity) 514 (M^+, 18), 445 ($M^+ - CF_3$, 100), 365 (60). Anal. Calcd for $C_{32}H_{29}F_3N_2O$: C, 74.69; H, 5.68; N, 5.44. Found: C, 74.83; H, 5.76; N, 5.23.

1,1-Bis(4-aminophenyl)-1-[4-[4-(phenylethynyl)phenoxy]-phenyl]-2,2,2-trifluoroethane (15). A solution of 11 (2.49 g, 4.84 mmol), fresh $L_4Pd(0)$ (0.28 g, 0.24 mmol, 5 mol %), CuI (0.05 g, 0.30 mmol, 6 mol %), Ph_3P (0.06 g, 0.23 mmol, 5 mol %), and 1.02 g (10 mmol) of phenylacetylene in 15 mL of pyrrolidine was refluxed at 95 °C for 72 h. After the reaction mixture was concentrated, the residue was extracted with ether many times until the extracts were colorless. All ether extracts were collected and washed with water until the aqueous layer was no longer yellow. The ether solution was dried ($MgSO_4$) and concentrated under vacuum to give a bright yellow foamy mass that collapsed to a gel on release of vacuum. This crude was chromatographed slowly using benzene. The first fraction, which was a dark brown viscuous oil, was discarded. A second fraction from continued elution with benzene was redissolved in 1:1 MeOH/ether and concentrated to remove residual benzene. Vacuum drying at room temperature for 24 h gave 1.95 g (75%) of 15 as a yellow solid: mp softened and shrank into an opaque yellow glass at 183 °C and melted into an orange liquid at 188–90 °C; IR (cm^{-1}) 3464, 3371, 1618, 1497, 1250, 1126, 806; ^1H NMR ($CDCl_3$) δ 3.50 (br s, 4 H), 6.24–7.62 (unresolved, 21 H); MS *m/z* (relative intensity) 534 (M^+, 20), 465 ($M^+ - CF_3$, 100). Anal. Calcd for $C_{34}H_{25}F_3N_2O$: C, 76.39; H, 4.71; N, 5.24. Found: C, 76.04; H, 4.71; N, 5.20.

1,1-Bis(4-hydroxyphenyl)-1-[4-(4-hexynylphenoxy)phenyl]-2,2,2-trifluoroethane (16). To a solution of 2.51 g (4.86 mmol) of 12 in 50 mL of Et_3N were added 0.27 g (0.38 mmol, 8 mol %) of $(Ph_3P)_2PdCl_2$, 0.07 g (0.37 mmol, 8 mol %) of CuI, 0.10 g (0.38 mmol, 8 mol %) of Ph_3P, and 1.68 g (20.49 mmol) of 1-hexyne. The flask was securely sealed with a rubber septum, and the stirred mixture was heated at 90 °C for 72 h. After the reaction mixture was concentrated, it was extracted with ether and the ether extract was washed with 4 N HCl, followed by distilled water. Washing with water was repeated until washings showed a negative Cl test. A beilstein test on the ether solution was negative, indicating no residual 12. The solution was dried ($MgSO_4$) and concentrated to give a dark granular crust weighing 3.30 g. This crude product was chromatographed using benzene to elute faster moving impurities. Change of eluent to 9:1 benzene/ether gave 16 which, after redissolving in 1:1 ether/MeOH to remove residual benzene and vacuum drying at room temperature for 24 h, weighed 2.13 g (85%): mp melted into white cloudy liquid at 169–71 °C which clarified at 176 °C; IR (cm^{-1}) 3331 (broad), 2950, 1901, 1595, 1481, 1168, 820; ^1H NMR (C_3D_6O/$CDCl_3$) δ 0.92 (m, 3 H), 1.50 (m, 4 H), 3.20 (m, 2 H), 6.48–7.00 (m, 14 H), 7.00–7.34 (two split peaks, 2 H), 8.34 (br s, 2 H); MS *m/z* (relative intensity) 516 (M^+, 30), 447 ($M^+ - CF_3$, 100), 367 (22). Anal. Calcd for $C_{32}H_{27}F_3O_3$: C, 74.41; H, 5.27. Found: C, 74.47; H, 5.19. A chloroform (better with $CDCl_3$) solution of 16 yields a tan white precipitate on standing which is a purer granular product.

1,1-Bis(4-hydroxyphenyl)-1-[4-[4-(phenylethynyl)phenoxy]-phenyl]-2,2,2-trifluoroethane (17). This compound was prepared and purified in 83% yield by the same procedure as 16. Phenylacetylene and 4 mol % of L_4Pd, CuI, and Ph_3P were used. The reaction time was 48 h. Alkaline extraction of the crude product, followed by aqueous acid regeneration, may be used to remove neutral impurities before chromatography. As in the case of 16, the product 17 dissolved initially in $CHCl_3$ or $CDCl_3$ but soon dropped out of solution. Analytical samples were obtained by this process: mp 203–5 °C; IR (cm^{-1}) 3350 (broad), 1597, 1497, 1234, 1141, 820; ^1H NMR (C_3D_6O/$CDCl_3$) δ 6.50–7.00 (m, 12 H), 7.03–7.70 (m, 9 H); OH protons were not observable; MS *m/z* (relative intensity) 536 (M^+, 45), 468 (35), 467 ($M^+ - CF_3$, 100). Anal. Calcd for $C_{34}H_{23}F_3O_3$: C, 76.11; H, 4.32. Found: C, 75.96; H, 4.36.

1,1-Bis(4-hydroxyphenyl)-1-[4-(4-ethynylphenoxy)phenyl]-2,2,2-trifluoroethane (18). The coupling of 15 with TMSA was carried out in NMP using similar procedure as for 17. The crude coupling adduct was desilylated as described for 13. The eluent for complete chromatographic purification was benzene. The product 18, obtained in 66% yield, was subjected to two methods of removing residual benzene (i.e., vacuum heat-drying and treatment with 1:1 MeOH/ether): mp 165–8 °C ($CDCl_3$ precipitated, vacuum dried); IR (cm^{-1}) 3359 (broad), 2100, 1592, 1493, 1188, 825; ^1H NMR (C_3D_6O)/$CDCl_3$, external TMS standard) δ 3.40 (s, 1 H), 6.50–7.00 (unresolved AB qs, 14 H), 7.35 (two split peaks, 2 H), 8.37 (br s, 2 H); MS *m/z* (relative intensity) 460 (M^+, 40), 391 ($M^+ - CF_3$, 100), 365 (15). Anal. Calcd for $C_{28}H_{19}F_3O_3$: C, 73.04; H, 4.16. Found: C, 72.95; H, 4.24.

4-[4-(Phenylethynyl)phenoxy]trifluoroacetophenone (19) was prepared from the bromide 9 and phenylacetylene as in the procedure for 7b. The amounts of $L_4Pd(0)$ and CuI were 1 mol % and 2 mol %, respectively, and the reaction time was 48 h of reflux. Chromatographic purification involved initial elution of mobile impurities with benzene, followed by a 9:1 mixture of benzene and ether, respectively. The product was obtained in 74% yield, and recrystallization from 9:1 hexane/ether gave 19 as white spherical granules: mp 94–3 °C; IR (cm^{-1}) 2211, 1706, 1585, 1500, 1200, 1145, 818; ^1H NMR ($CDCl_3$) δ 6.76–7.67 (unresolved m, 11 H), 7.90 (two s, 2 H); MS *m/z* (relative intensity) 366 (M^+, 30), 297 ($M^+ - CF_3$, 80). Anal. Calcd for $C_{22}H_{13}F_3O_2$: C, 72.13; H, 3.58. Found: C, 72.06; H, 3.55.

Condensation of 7b with Aniline: The Alternate Route to 5c. The (phenylethynyl)aryl ketone 7b (20.58 g, 75.11 mmol) was heated at 90 °C for 5 days with aniline (125 mL) and aniline hydrochloride (18 g, 138 mmol), followed by reflux for 24 h. The resulting dark purple mixture was allowed to cool to room temperature and then carefully neutralized with 12 g (138 mmol) of $NaHCO_3$. Steam distillation was conducted until the distillate was clear. On cooling, the semisolid black residue was dissolved in ether. The intense purple solution was washed several times with water and then dried ($MgSO_4$). Solvent removal left a dark syrup which was applied to a column. Elution with benzene removed three faster moving minor components before the eluent was changed to 9:1 benzene/ether. A purple-colored 5c was obtained which was redissolved in MeOH and decolorized with Norit-A to obtain 23.53 g of an ashy-white solid (71%) after vacuum drying at room temperature for 24 h. This 5c gave a purple solution in benzene like all the other products of condensation with aniline (i.e., the diaminotriaryl halides), whereas all diaminotriaryl acetylenes prepared by final ethynylation step gave yellow solutions. The 5c resulting from this pathway had a higher mp also than that generated by the condensation/coupling sequence. It started to shrink at 78 °C, softened into a glass at 108 °C, and melted at 120 °C. The TLC, ^1H NMR, and MS of the two samples were, however, identical in every way.

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