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Combinatorial synthesis of oligo(phenylene ethynylene)s

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Abstract—The combinatorial synthesis of oligo(phenylene ethynylene) tetramers, both in solution and on solid support, is described. These products are of interest for molecular electronics applications. An iterative sequence, coupling of aryl halides to alkynes under Sonogashira conditions, was used. Five monomers functionalized with electron-donating or electron-withdrawing groups were synthesized, and used to generate a library of 25 trimers in a solution-phase based process. A library of 24 tetramers was prepared by subsequent protodesilylation and coupling with the alligator clip 4-iodo-1-thioacetylbenzene. The solution-phase based sequence was successfully adapted to a higher yielding directed split-and-pool solid-phase process, with average yields of 78–86% for each step over seven steps. A triazene linker group was used to attach the starting monomer to the polymer beads. At the completion of the solid-phase-based process, traceless cleavage of trimers from the resin was achieved by sonication of the resin in 10% HCl/THF solution. The released products were then poised for the final step in the sequence, attachment of the alligator clip.

1. Introduction

Combinatorial chemistry is one of the fastest growing fields in chemistry because combinatorial-based processes can rapidly generate large libraries of small molecules.[1] This methodology has been extensively utilized[2] for the synthesis of potential drug candidates, but lately the combinatorial approach has been applied to materials research,[3] mainly on inorganic solid-state materials, polymeric materials, and catalytic systems, in order to speed discovery and development. A combinatorial process coupled with effective screening techniques can yield a great deal of information concerning the activity of the synthesized compounds in the desired application. Collection and analysis of large data sets can produce structure–activity relationships (SAR) that can lead to optimization of the molecular properties through a feedback loop of synthesis and screening.

Research in the field of molecular electronics[4] is targeted to the development of molecules that can function as wires or switches, with the eventual goal of replacing present solid-state-based devices. In 1974, Aviram and Ratner first proposed[5] that a single organic molecule could act as a rectifier of electrical current. Since then, considerable effort has been expended to synthesize and study a variety of molecules as potential molecular electronics candidates. Recently, we have been concentrating on the synthesis and testing of conjugated oligo(phenylene ethynylene)s (OPEs).[6] OPEs, in self-assembled monolayers (SAMs) on metallic surfaces, can behave as molecular wires conducting electrical currents, as devices showing negative differential resistance (NDR), and/or as memory components retaining electrical bits of information,[6] depending on their functionality and structure.

Most of the OPEs we have synthesized to date have been 'trimers' containing three aromatic rings.[6] In the present work, we report on our efforts to expand OPE space to include a large group of tetramers (compounds with four aromatic rings), synthesized using combinatorial chemistry.

2. Results and discussion

2.1. Monomer synthesis

In order to develop SAR data, monomers with electron-donating groups (EDGs), such as alkyl or alkoxy, or electron-withdrawing groups (EWGs), such as F, CN, and CF_3, were designed and synthesized. The five scaffold monomers were synthesized as shown in Scheme 1. Sonogashira coupling[7] of aniline derivatives **1a**–**e**[8] with trimethylsilylacetylene (TMSA) in Et_3N gave high yields of the products **2a**–**e**. Without further purification, **2a**–**e** were converted to the corresponding diazonium salts using the method of Doyle et al.,[9] followed by quenching with NaI and I_2[10] to give the desired monomers **3a**–**e** in good yields.

2.2. Oligomer syntheses in solution

Synthesis of a library of 25 tetramers of OPEs was carried

Keywords: tetramers; oligomer; molecular electronics.

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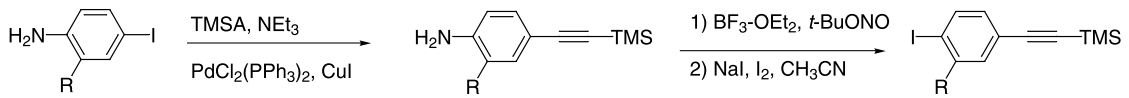
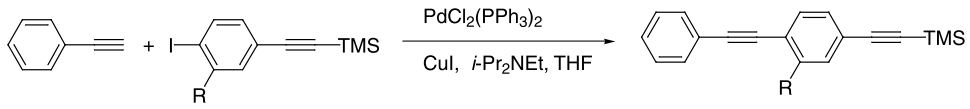


1a, R = H
1b, R = F
1c, R = CN
1d, R = CF_3
1e, R = Et

2a, R = H
2b, R = F
2c, R = CN
2d, R = CF_3
2e, R = Et

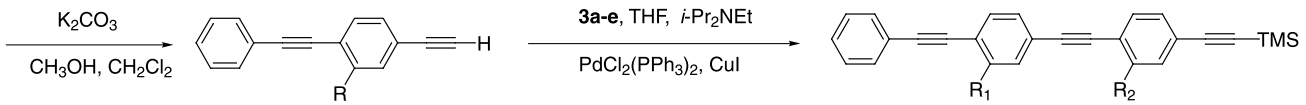
3a, R = H, 78%
3b, R = F, 85%
3c, R = CN, 70%
3d, R = CF_3, 67%
3e, R = Et, 86%

Scheme 1.



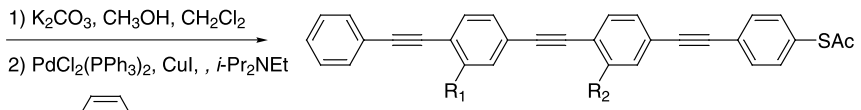
3a, R = H
3b, R = F
3c, R = CN
3d, R = CF_3
3e, R = Et

4a, R = H, 90%
4b, R = F, 88%
4c, R = CN, 81%
4d, R = CF_3, 87%
4e, R = Et, 82%



5a, R = H, 96%
5b, R = F, 95%
5c, R = CN, 91%
5d, R = CF_3, 93%
5e, R = Et, 94%

6a-e, R_1 = H, R_2 = H, F, CN, CF_3, or Et
7a-e, R_1 = F, R_2 = H, F, CN, CF_3, or Et
8a-e, R_1 = CN, R_2 = H, F, CN, CF_3, or Et
9a-e, R_1 = CF_3, R_2 = H, F, CN, CF_3, or Et
10a-e, R_1 = Et, R_2 = H, F, CN, CF_3, or Et



11

12 a-e, R_1 = H, R_2 = F, CN, CF_3, or Et
13 a-e, R_1 = F, R_2 = H, F, CN, CF_3, or Et
14 a-e, R_1 = CN, R_2 = H, F, CN, CF_3, or Et
15 a-e, R_1 = CF_3, R_2 = H, F, CN, CF_3, or Et
16 a-e, R_1 = Et, R_2 = H, F, CN, CF_3, or Et

Scheme 2.

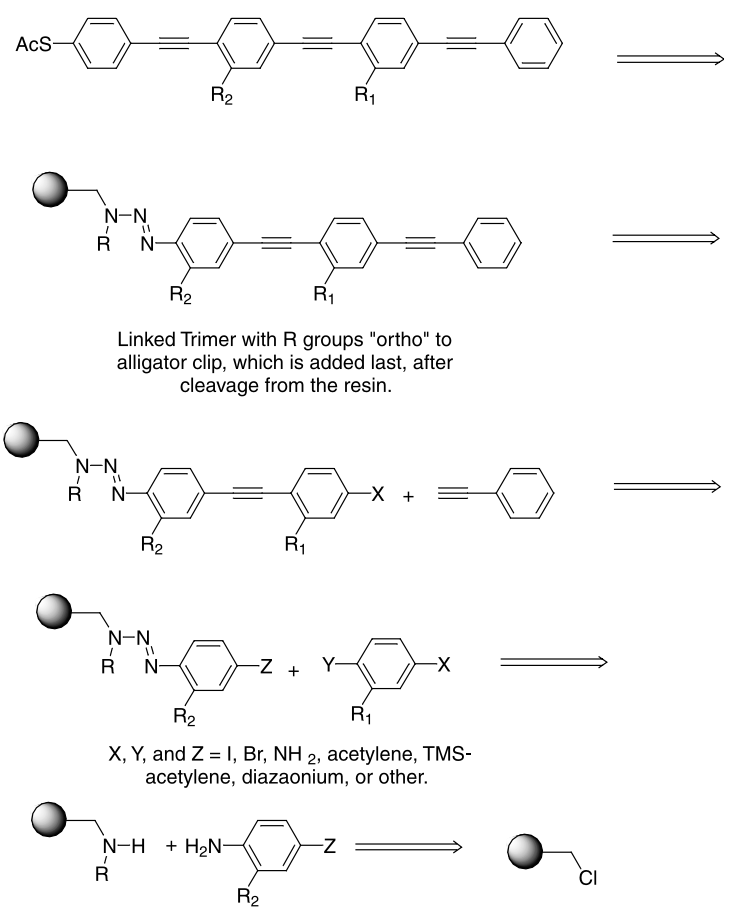
out by a combinatorial approach with the monomers **3a–e**. The solution phase synthesis of tetramers is outlined in Scheme 2.

Sonogashira coupling five monomers **3a–e** to phenylacetylene afforded five corresponding dimers **4a–e** in excellent yield. Protodesilylation[11,12] of the terminal alkynes **4a–e** with potassium carbonate in CH_3OH and CH_2Cl_2 gave **5a–e** followed by a set of reactions in which each of the five alkynes **5a–e** was subjected to coupling with the five monomers **3a–e** to generate a library of 25 trimers. The coupling reaction of monomers bearing CF_3 or Et required higher temperatures and longer reaction times, and they gave lower yields. The relatively lower yields in this coupling may be caused by steric effects. The final step in the process is the attachment of 1-iodo-4-thioacetylbenzene **11**,[11] the alligator clip. A library of 24 potential molecular devices **12b–e** and **13a–e** to **16a–e** were

Table 1. Isolated yields of solution-phase synthesized trimers (**6–10**) and tetramers (**12–16**)

	R_1=H	R_1=F	R_1=CN	R_1=CF_3	R_1=Et
R_2=H	**6a** (44%)	**7a** (86%)	**8a** (72%)	**9a** (75%)	**10a** (52%)
	12a[a]	**13a** (38%)	**14a** (58%)	**15a** (40%)	**16a** (46%)
R_2=F	**6b** (66%)	**7b** (87%)	**8b** (88%)	**9b** (77%)	**10b** (70%)
	12b (43%)	**13b** (41%)	**14b** (42%)	**15b** (36%)	**16b** (53%)
R_2=CN	**6c** (84%)	**7c** (97%)	**8c** (77%)	**9c** (70%)	**10c** (69%)
	12c (41%)	**13c** (48%)	**14c** (42%)	**15c** (26%)	**16c** (46%)
R_2=CF_3	**6d** (71%)	**7d** (62%)	**8d** (72%)	**9d** (51%)	**10d** (64%)
	12d (47%)	**13d** (41%)	**14d** (30%)	**15d** (56%)	**16d** (51%)
R_2=Et	**6e** (55%)	**7e** (54%)	**8e** (71%)	**9e** (68%)	**10e** (51%)
	12e (47%)	**13e** (48%)	**14e** (43%)	**15e** (21%)	**16e** (37%)

[a] **12a** was not prepared because of low solubility of **6a**.



Scheme 3. Retrosynthetic analysis.

obtained in moderate yields (Table 1). Unsubstituted tetramer **12a** was not prepared due to the low solubility of trimer **6a**. Tetramers bearing only one functional group in the two central phenyl units exhibited low solubility in organic solvents.

2.3. Oligomer syntheses on a solid support

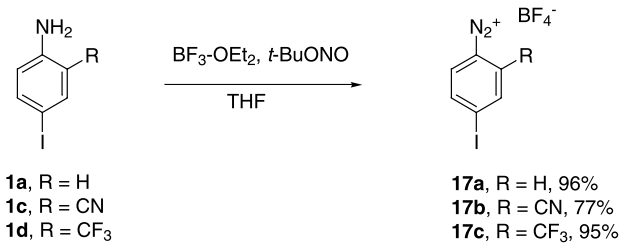
The advantages of employing solid phase synthesis for the preparation of conjugated oligomers instead of solution phase synthesis have been demonstrated by many research groups.[12,13] Advantages include higher overall yields as well as rapid purification processes, since time-consuming chromatography, a bottleneck in conventional solution-phase-based chemistry, is avoided. We hoped to quickly adapt the optimized solution phase chemistry to the solid phase synthesis of the same or similar library, which would allow us to compare yields of the two processes.

An important issue in the design of a solid-phase combinatorial synthesis is to choose the proper linker for placing the starting monomer on the resin. The triazene linkage has been used by us[12] and other research groups.[14–16] The linker is stable under the various reaction conditions encountered in the synthesis. The triazene linker can be cleaved using a variety of conditions that yield soluble products with different functionalities. Trifluoroacetic acid (TFA)[15] cleavage gives the aromatic diazonium salt, while cleavage using iodomethane[12,14,16] produces the corresponding aryl iodide. Each of these functionalities can serve as a handle for further manipulation using standard transition metal-catalyzed coupling conditions to add additional monomeric units. The third method, traceless cleavage using 10% HCl in THF,[17] converts the triazene linker into a C–H bond[15a] to give the corresponding arenes.

The a priori retrosynthetic approach to the solid phase combinatorial syntheses of the library of target OPEs is outlined in Scheme 3. The tetramers would be synthesized from the set of immobilized trimers by first cleaving the trimers and then adding the alligator clip moiety. The trimers would be synthesized using an iterative approach where each monomer is derived from anilines **1a–e** via the appropriate chemical manipulations, which could be varied depending on yields and other problems that might be encountered during the synthesis. Anilines **1a–e** were either commercially available, or were obtainable via a short synthesis from commercially available products.

The first step in the solid phase synthesis of the OPEs was attachment of the starting monomers to the resin. The functionalized diazonium salts **17a–c** were prepared[9] in high yields from the corresponding aniline derivatives **1a**, **c**, and **d**, respectively (Scheme 4).

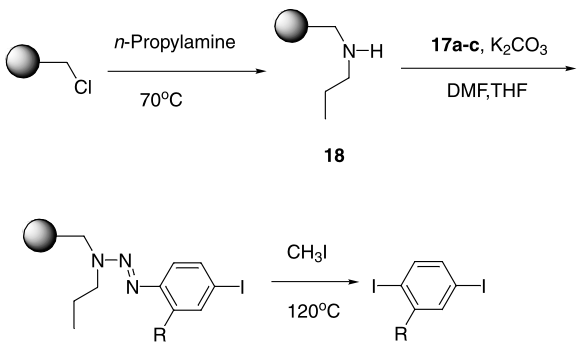
Propylaminomethylate polystyrene **18** was prepared by heating a suspension of Merrifield resin with *n*-propylamine in a screw cap tube at 70°C for 3–4 days.[14] Functionalized diazonium salts **17a–c** were reacted with resin **18** in DMF–THF solution in the presence of K_2CO_3 to form the



1a, R = H
1c, R = CN
1d, R = CF_3

17a, R = H, 96%
17b, R = CN, 77%
17c, R = CF_3, 95%

Scheme 4.



19a, R = H
19b, R = CN
19c, R = CF_3

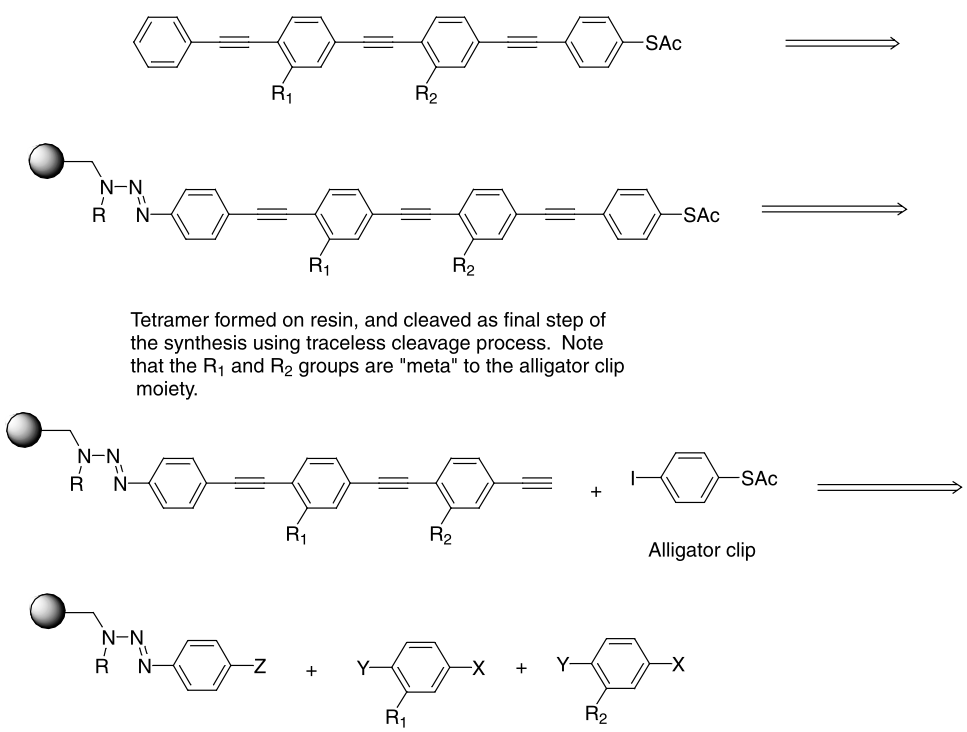
20a, R = H, 70% over 3 steps
20b, R = CN, 35% over 3 steps
20c, R = CF_3, 36% over 3 steps

Scheme 5.

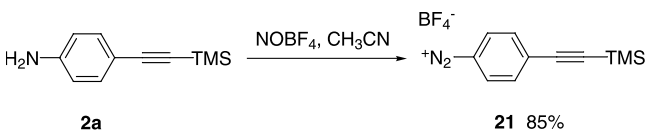
corresponding resin-immobilized triazene-linked monomers **19a–c**, respectively (Scheme 5). The attachment procedure was repeated to maximize the loading and a total of 2–3 equiv. of diazonium salts were used. Small portions of resin were taken out and cleaved to give the corresponding diiodobenzene derivatives **20a–c** to monitor the loading. This method was found to be more accurate than elemental analysis or weight changes in calculating yields and loading.[14,18]

Treatment of resin-bound monomer **19a** with iodomethane in a screw cap tube at 120°C for 24 h liberated 1,4-diiodobenzene **20a** in 70% yield over three steps. This result indicated that the first two steps were achieved in high loadings. Unfortunately, cleavage of resin-bound monomer **19b** in iodomethane at 120°C only gave 7–16% yields **20b** over three steps; various reaction times from 12 to 60 h were screened but did not improve the yield. Slightly higher yields (29–35%) were obtained by adding CH_3CN co-solvent. Similar low yields were obtained from the liberation of resin-bound monomer **19c** to give **20c**. We suspect that the *ortho*-EWG functional groups adjacent to the triazene moiety caused the lower yields; steric hindrance may also be a factor. We therefore sought to begin with a scaffold in which the functionalized aromatic ring was further removed from the triazene moiety.

As shown in the retrosynthetic analysis in Scheme 6, we altered our synthetic pathway such that the two aromatic rings containing the functionality were further removed from the triazene linker. For the highest efficiency and to take advantage of the easier handling afforded a solid phase-based system, it was preferable to attach the alligator



Scheme 6. Retrosynthetic analysis.



2a **21** 85%

Scheme 7.

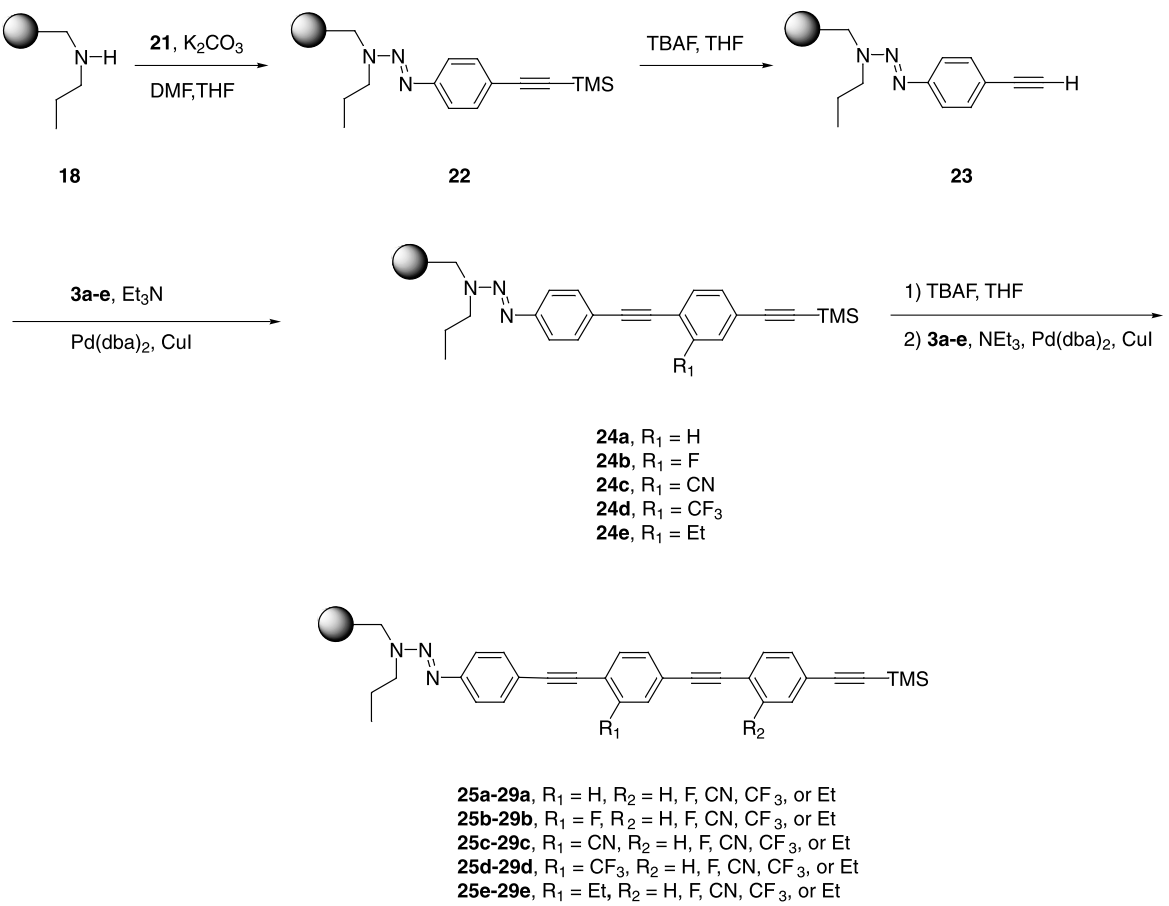
clip before cleavage from the resin. Therefore, the last step would be traceless cleavage. The success of this route depended on the survival of the thiol protection group. Note that if we were successful, this route would produce a set of tetramers in which the functional groups were *meta* to the alligator clip, a different set than that produced in the solution phase work. Retrosynthetically, the procedure would utilize the same monomers **1a**–**e** as before.

The linker diazonium salt **21** was prepared in high yield from diazotization of 4-(trimethylsilylethynyl)aniline (**2a**) with $NOBF_4$[19] (Scheme 7).

Diazonium salt **21** was then reacted with resin **18** in DMF–THF solution in the presence of K_2CO_3 to give the corresponding triazene monomer **22** (Scheme 8). The terminal alkyne in resin **22** was revealed by treatment with a solution of tetrabutylammonium fluoride (TBAF) in THF to remove the TMS-protecting group and give the corresponding resin-bound alkyne **23**.[12,14] Infrared analysis was used as a simple, non-destructive method to monitor oligomer synthesis. The IR spectra were assigned as follows: 2153 cm^{-1} (medium) carbon–carbon stretch of the trimethylsilylethynyl group; 3317 cm^{-1} (strong) alkynyl carbon-hydrogen stretch; and 2106 cm^{-1} (weak) alkyne carbon–carbon stretch.

The preparation of resin-bound alkyne **23** was followed by a parallel synthesis. The subsequent directed sort, split, and pool synthesis of individual oligomers was performed in small reactors constructed of polypropylene mesh flow-through walls, specifically MacroKans,[20] using a unique identification system.[21] Resin-bound monomer **23** sealed in MacroKans were subjected to a Pd/Cu-catalyzed cross-coupling with monomers **3a**–**e** in Et_3N. The catalyst solution ($Pd(dba)_2$/PPh_3/CuI)[12,14] was pre-mixed at 70°C for 2 h prior to use. The suspended MacroKans were heated with the catalyst in a screw cap tube at 65°C for 44–48 h. At the completion of the coupling reaction, the MacroKans were collected and washed according to a literature procedure.[12,14] The next step in the process was to pool one (or more) of each resin-bound dimer **24a**–**e** for another split-and-pool combinatorial reaction with monomers **3a**–**e**. Resin-bound dimers **24a**–**e** were deprotected with a solution of TBAF in THF to give the corresponding resin-bound alkynes, followed by a subsequent Pd/Cu-catalyzed cross-coupling with monomers **3a**–**e** to afford a library of 25 different polymer-supported trimers **25a**–**e** to **29a**–**e**.

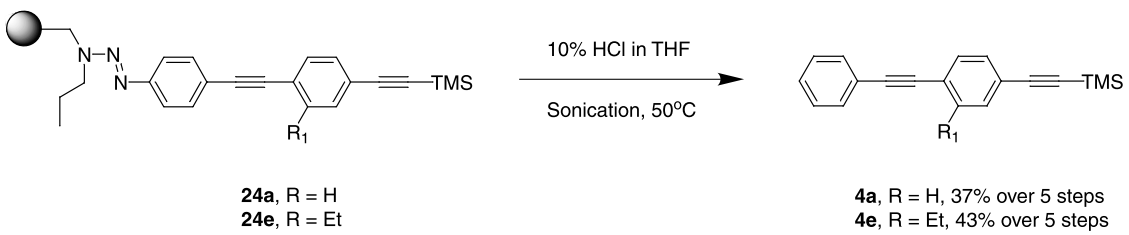
In order to monitor resin loading, **24a** and **24e** were liberated via traceless cleavage[15a] by sonication at 50°C using 10% HCl in THF solution (Scheme 9). The isolated yields of **4a** and **4e** (over five steps from Merrifield resin)



24a, R_1 = H
24b, R_1 = F
24c, R_1 = CN
24d, R_1 = CF_3
24e, R_1 = Et

25a-29a, R_1 = H, R_2 = H, F, CN, CF_3, or Et
25b-29b, R_1 = F, R_2 = H, F, CN, CF_3, or Et
25c-29c, R_1 = CN, R_2 = H, F, CN, CF_3, or Et
25d-29d, R_1 = CF_3, R_2 = H, F, CN, CF_3, or Et
25e-29e, R_1 = Et, R_2 = H, F, CN, CF_3, or Et

Scheme 8.



24a, R = H
24e, R = Et

4a, R = H, 37% over 5 steps
4e, R = Et, 43% over 5 steps

Scheme 9.

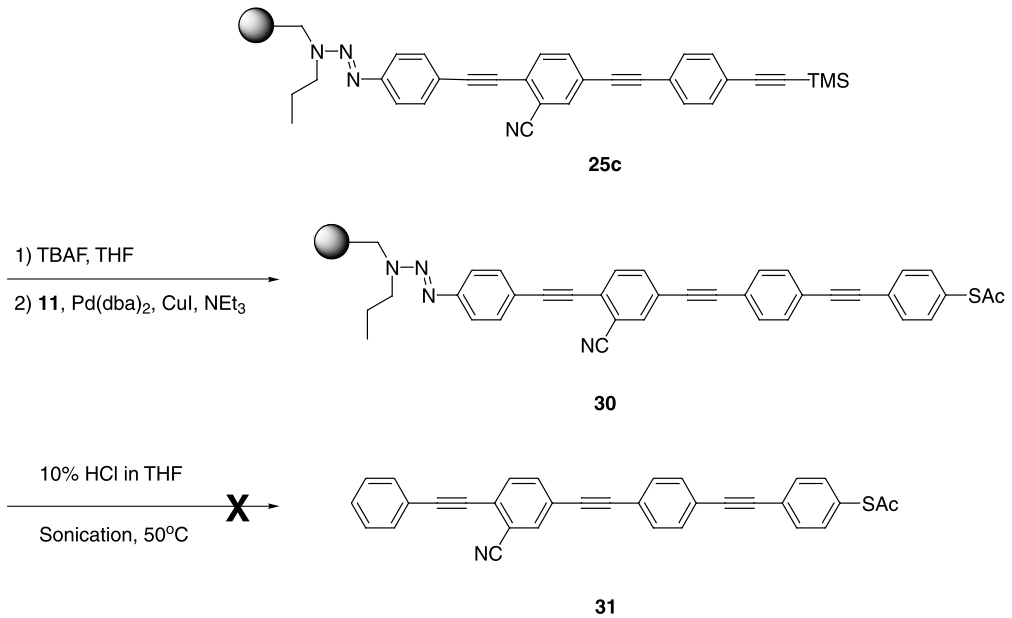
were 37% and 43%, respectively. This result indicates that high loadings and cleavage (>82%, on average) were achieved in each step.

Before the cleavage to release the desired library of products, the last step of the planned synthesis was to attach alligator clip **11** (Scheme 10). Deprotection of **25c** using TBAF in THF gave the free alkyne that was subsequently coupled with **11** under standard conditions to give **30**. Unfortunately, after exposure of the resin-bound **30** to 10% HCl in THF at 50°C under sonication, the ^{1}H NMR spectra of crude liberation product **31** indicated a plethora of products. One of the possible side-reactions would be hydrolysis of the thioester to form intermediate sulfides that would subsequently couple in the presence of oxygen to form insoluble disulfides.

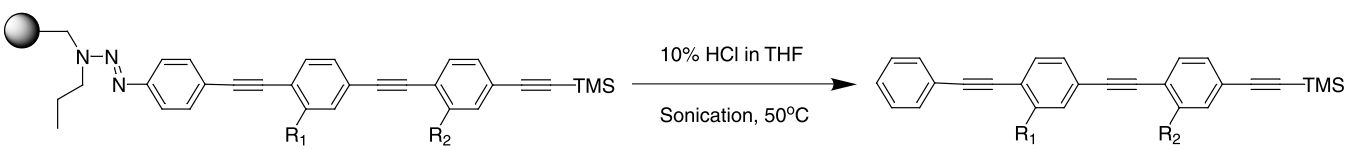
Since the alligator clip did not survive the cleavage reaction, we decided to liberate the trimers prior to the coupling with the alligator clip. The traceless cleavage method was applied to the polymer-supported trimers **25a–e** to **29a–e** to afford products **6a–e** to **10a–e** that we had previously taken on to the tetramer stage in the solution phase. (Scheme 11). The final isolated yields of trimers over seven steps from commercially available Merrifield resin ranged from 18 to 34%, an average of 78–86% yield over each step (Table 2).

3. Summary

We demonstrated the combinatorial synthesis of oligo(phenylene ethynylene)s both in solution phase and on solid



Scheme 10.



25a-29a, R_1 = H, R_2 = H, F, CN, CF_3, or Et
25b-29b, R_1 = F, R_2 = H, F, CN, CF_3, or Et
25c-29c, R_1 = CN, R_2 = H, F, CN, CF_3, or Et
25d-29d, R_1 = CF_3, R_2 = H, F, CN, CF_3, or Et
25e-29e, R_1 = Et, R_2 = H, F, CN, CF_3, or Et

6a-e, R_1 = H, R_2 = H, F, CN, CF_3, or Et
7a-e, R_1 = F, R_2 = H, F, CN, CF_3, or Et
8a-e, R_1 = CN, R_2 = H, F, CN, CF_3, or Et
9a-e, R_1 = CF_3, R_2 = H, F, CN, CF_3, or Et
10a-e, R_1 = Et, R_2 = H, F, CN, CF_3, or Et

Scheme 11.

Table 2. Overall yields of solid-phase synthesized trimers

	R_1=H	R_1=F	R_1=CN	R_1=CF_3	R_1=Et
R_2=H	**6a**, 30% (33 mg)	**7a**, 23% (26 mg)	**8a**, 32% (37 mg)	**9a**, 24% (41 mg)	**10a**, 27% (32 mg)
R_2=F	**6b**, 31% (36 mg)	**7b**, 33% (40 mg)	**8b**, 34% (42 mg)	**9b**, 33% (45 mg)	**10b**, 24% (30 mg)
R_2=CN	**6c**, 33% (39 mg)	**7c**, 29% (35 mg)	**8c**, 25% (30 mg)	**9c**, 28% (39 mg)	**10c**, 18% (25 mg)
R_2=CF_3	**6d**, 34% (44 mg)	**7d**, 31% (42 mg)	**8d**, 29% (40 mg)	**9d**, 32% (48 mg)	**10d**, 23% (28 mg)
R_2=Et	**6e**, 27% (32 mg)	**7e**, 23% (28 mg)	**8e**, 26% (32 mg)	**9e**, 22% (30 mg)	**10e**, 18% (23 mg)

Yields are based on isolated products after chromatographic purification (amount shown in parentheses) and calculated according to the loading of original resin.

supports. The construction of oligomers was accomplished by following an iterative approach using the Sonogashira coupling of aryl halides to alkynes as the capstone reaction. Five monomers with electron-donating groups (H, Et) or electron-withdrawing groups (F, CN, or CF_3) were synthesized and used to generate a library of 25 trimers by a directed sortsplit-and-pool synthesis. The coupling reaction with the monomers bearing CF_3 or Et functional groups required higher temperatures and longer reaction times, and gave lower yields. A library of 24 tetramers bearing a thioacetyl end group was synthesized from those 25 trimers. We found that the solid-phase combinatorial synthesis offered advantages over the conventional solution-phase approach by maximizing overall yields and facilitating the purification process through avoidance of time-consuming chromatography. Functional groups ortho to the triazene linkage group produced lower yields when the scaffold was removed from the resin, necessitating an easy redesign of the synthesis. Traceless cleavage from the resin was effectively achieved via sonication of resin-bound oligomer in 10% HCl in THF. An average yield of 78–86% (for each step over seven steps in the solid-phase combinatorial synthesis) was obtained. This study presents a fast combinatorial synthesis of OPEs incorporating a diversity of substituent groups. Testing of these diverse libraries in molecular electronics applications will allow us to deduce structure-activity relationships.

4. Experimental

4.1. General procedure

All reactions were performed under an atmosphere of nitrogen unless otherwise stated. Unless otherwise noted, all chemicals were used as received without further purification. Merrifield resin (1.1 mmol Cl^-/g, 1% cross-linker divinylbenzene copolymer, 70–90 mesh) was obtained from Aldrich Chemical Co. MacroKans were obtained from IRORI.[20] The Pd/Cu couplings were conducted in a manner analogous to that described by Suffert.[7c] THF and diethyl ether were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. Triethylamine, *N*,*N*-diisopropylethylamine and acetonitrile were distilled over calcium hydride under nitrogen. Column chromatography was carried out using Silica gel (grade 60, 230–400 mesh from EM Science). Thin layer chromatography (TLC) was performed using glass-backed silica gel plates (40 F_{254} 0.25 mm layer thickness, Merck). Infrared (IR) spectra assignments have 2 cm^{-1} resolution. FT-IR characterizations of the polymer-supported reactions were carried out by placing ca. 10 mg of the polymer-supported material on a NaCl plate. After the beads were swollen with 2–3 drops of CCl_4, a second NaCl plate was pressed onto the beads, and an FTIR spectrum was recorded.

4.2. General procedure for the coupling of aniline derivatives with trimethylsilylacetylene

To a stirring solution in a septum-capped tube of the aniline derivative was added at room temperature bis(triphenylphosphine)palladium(II) dichloride (0.5 mol%), copper(I) iodide (1 mol%) in triethylamine, and TMSA (1.07 equiv.). The tube was capped and the solution was stirred overnight. The reaction mixture was filtered and the filtrate was washed with ether. The combined organic phase was then washed with NH_4Cl (2 M) (2×), brine and dried over Na_2SO_4 to give the desired product.

4.2.1. 4-Trimethylsilylethynylaniline (2a).[8b] According to the general procedure, 4-iodoaniline **1a** (25.0 g, 114 mmol), bis(triphenylphosphine)palladium(II) dichloride (400 mg, 0.57 mmol, 0.5 mol%), copper(I) iodide (217 mg, 1.14 mmol, 1 mol%), and TMSA (17.3 mL, 122 mmol, 1.07 equiv.) in triethylamine (200 mL) gave the desired product (21.3 g, 113 mmol, 99%).

4.2.2. 2-Fluoro-4-trimethylsilylethynylaniline (2b). According to the general procedure, **1b** (12.0 g, 50.6 mmol), bis(triphenylphosphine)palladium(II) dichloride (178 mg, 0.253 mmol, 0.5 mol%), copper(I) iodide (96 mg, 0.506 mmol, 1 mol%) and TMSA (7.7 mL, 54.5 mmol, 1.07 equiv.) in triethylamine (120 mL) gave the desired product (10.4 g, 50.1 mmol, 99%). IR (KBr) 3439, 3393, 2148 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ7.08–7.14 (m, 2H), 6.68 (dd, J=1.0, 8.2 Hz, 1H), 3.95 (br s, 2H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ150.9 (d, J_{C-F}=239 Hz), 135.8 (d, J_{C-F}=12 Hz), 129.2 (d, J_{C-F}=3 Hz), 119.1 (d, J_{C-F}=20 Hz), 116.5 (d, J_{C-F}=4 Hz), 113.1 (d, J_{C-F}=8 Hz), 105.1 (d, J_{C-F}=26 Hz), 92.6, 0.4; HRMS calcd for $C_{11}H_{14}FSi$: 207.0880. Found: 207.0877.

4.2.3. 2-Amino-5-trimethylsilylethynylbenzonitrile (2c). According to the general procedure, **1c** (23.5 g, 104.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (338 mg, 0.48 mmol, 0.5 mol%), copper(I) iodide (183 mg, 0.96 mmol, 1 mol%) and TMSA (14.6 mL, 103 mmol, 1.07 equiv.) in triethylamine (200 mL) gave the desired product (20.5 g, 95.6 mmol, 91%). IR (KBr) 3447, 3352, 2219, 2145 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J=1.9 Hz, 1H), 7.42 (dd, J=1.9, 8.6 Hz, 1H), 6.67 (d, J=8.6 Hz, 1H), 4.59 (br s, 2H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 137.8, 136.4, 117.2, 115.5,

113.1, 103.8, 96.1, 93.7, 0.4; HRMS calcd for $C_{12}H_{14}N_2Si$: 214.0926. Found: 214.0924.

4.2.4. 2-Trifluoromethyl-4-trimethylsilylethynylaniline (2d). According to the general procedure, **1d** (30.0 g, 104.5 mmol), bis(triphenylphosphine)palladium(II) dichloride (367 mg, 0.52 mmol, 0.5 mol%), copper(I) iodide (199 mg, 1.04 mmol, 1 mol%) and TMSA (15.8 mL, 112 mmol, 1.07 equiv.) in triethylamine (200 mL) gave the desired product (26.8 g, 104 mmol, 99%). IR (KBr) 3486, 3396, 2150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J=1.8 Hz, 1H), 7.40 (dd, J=1.8, 8.5 Hz, 1H), 6.66 (d, J=8.5 Hz, 1H), 4.33 (br s, 2H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 136.6, 131.0 (q, J_{C-F}=5 Hz), 124.8 (q, J_{C-F}=272 Hz), 117.2, 113.7 (q, J_{C-F}=30 Hz), 112.4, 104.8, 93.2, 0.4; HRMS calcd for $C_{12}H_{14}F_3NSi$: 257.0848. Found: 257.0845.

4.2.5. 2-Ethyl-4-trimethylsilylethynylaniline (2e). According to the general procedure, **1e** (7.4 g, 30 mmol), bis(triphenylphosphine)palladium(II) dichloride (105 mg, 0.15 mmol, 0.5 mol%), copper(I) iodide (57 mg, 0.3 mmol, 1 mol%) and TMSA (4.5 mL, 31.8 mmol, 1.07 equiv.) in triethylamine (80 mL) gave the desired product (6.5 g, 29.9 mmol, 99%). IR (neat) 3480, 2140 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J=1.8 Hz, 1H), 7.14 (dd, J=1.8, 8.1 Hz, 1H), 6.53 (d, J=8.1 Hz, 1H), 3.74 (br s, 2H), 2.43 (q, J=7.5 Hz, 2H), 1.21 (t, J=7.5 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 132.6, 131.3, 127.9, 115.2, 113.0, 106.9, 91.5, 24.1, 13.1, 0.6; HRMS calcd for $C_{13}H_{19}NSi$: 217.1287. Found: 217.1285.

4.3. General procedure for the conversion of aniline derivatives into iodoarenes through the diazonium salt[22]

To a round-bottom flask fitted with an addition funnel and nitrogen inlet was added boron trifluoride etherate (4 equiv.) which was then chilled in a dry ice-acetone bath (−20°C). To the reaction flask was added dropwise over 5 min a solution of the aniline derivative (1 equiv.) in dry ether, followed by a solution of *tert*-butylnitrite (3.5 equiv.) in dry ether over 30 min. The chilled mixture was stirred an additional 10 min, and the cold bath was allowed to warm to 5°C over 20 min. To the mixture was added diethyl ether, and the mixture was chilled in an ice-bath for 15 min. The solid was collected by filtration, washed with chilled (0–5°C) diethyl ether, and dried to give diazonium salt. After briefly air-drying, the diazonium salt was dissolved in CH_3CN and then added dropwise via cannula to a solution of NaI (1.1 equiv.) and I_2 (0.1 equiv.) in CH_3CN. The mixture was stirred at rt for 1 h, then $Na_2S_2O_3$ (aq) (2 M) was added to the mixture. The mixture was extracted with CH_2Cl_2 (3×), and the organic phase was washed with brine and dried over Na_2SO_4. The crude product was purified by column chromatography (silica gel) with hexane or a hexane/EtOAc mixture to give the desired product.

4.3.1. (4-Iodo-phenylethynyl)trimethylsilane (3a).[23] According to the general procedure, 13.2 g (44 mmol, 78%) of **3a** was produced from **2a** (10.7 g, 56.5 mmol).

4.3.2. (3-Fluoro-4-iodophenylethynyl)trimethylsilane (3b). According to the general procedure, 8.97 g (28.2 mmol, 85%) of **3b** was produced from **2b** (6.9 g, 33.3 mmol). IR (neat) 2160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J=6.6, 8.1 Hz, 1H), 7.16 (dd, J=1.7, 8.5 Hz, 1H), 7.00 (dd, J=1.7, 8.6 Hz, 1H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F}=246 Hz), 139.1 (d, J_{C-F}=2 Hz), 129.1 (d, J_{C-F}=3 Hz), 125.2 (d, J_{C-F}=8 Hz), 118.6 (d, J_{C-F}=25 Hz), 102.6 (d, J_{C-F}=3 Hz), 96.9, 81.8 (d, J_{C-F}=26 Hz), −0.2; HRMS calcd for $C_{11}H_{12}FISi$: 317.9737. Found: 317.9737.

4.3.3. 2-Iodo-5-trimethylsilanylethynylbenzonitrile (3c). According to the general procedure, 9.6 g (29.5 mmol, 70%) of **3c** was produced from **2c** (9.0 g, 42 mmol). IR (neat) 2233, 2151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=8.3 Hz, 1H), 7.66 (d, J=2.0 Hz, 1H), 7.31 (dd, J=2.0, 8.3 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.1, 136.5, 124.2, 121.0, 118.7, 101.6, 99.1, 98.1, −0.1; HRMS calcd for $C_{12}H_{12}INSi$: 324.9784. Found: 324.9784.

4.3.4. (4-Iodo-3-trifluoromethylphenylethynyl)trimethylsilane (3d). According to the general procedure, 8.6 g (23.4 mmol, 67%) of **3d** was produced from **2d** (9.0 g, 35 mmol). IR (neat) 2164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=8.2 Hz, 1H), 7.74 (d, J=1.8 Hz, 1H), 7.26 (dd, J=1.8, 8.2 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.7, 134.0 (q, J_{C-F}=31 Hz), 130.5 (q, J_{C-F}=6 Hz), 123.8, 122.9 (q, J_{C-F}=274 Hz), 102.6, 98.1, 91.0 (q, J_{C-F}=2 Hz), −0.4; HRMS calcd for $C_{12}H_{12}F_3INSi$: 367.9705. Found: 367.9702.

4.3.5. (3-Ethyl-4-iodophenylethynyl)trimethylsilane (3e). According to the general procedure, 9.72 g (29.6 mmol, 86%) of **3e** was produced from **2e** (7.5 g, 34.5 mmol). IR (neat) 2160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J=8.1 Hz, 1H), 7.33 (d, J=8.1 Hz, 1H), 6.98 (dd, J=2.0, 8.1 Hz, 1H), 2.71 (q, J=7.5 Hz, 2H), 1.22 (t, J=7.5 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 139.8, 132.2, 131.2, 123.9, 104.8, 101.3, 95.8, 34.5, 14.9, 0.5; HRMS calcd for $C_{13}H_{17}ISi$: 328.0144. Found: 328.0142.

4.4. General procedure for the coupling of a terminal alkyne with an aryl halide utilizing a palladium-copper cross-coupling (Sonogashira protocol)

To a stirring solution of the aryl halide (1 equiv.), bis(triphenylphosphine)palladium(II) dichloride (2 mol%), copper(I) iodide (4 mol%), and addition triphenylphosphine (only used at temperature >25°C, 2 equiv. based on Pd) in THF was added the terminal alkyne (1–2 equiv.) followed by the amine (4 equiv. based on the aryl halide) at rt (unless otherwise stated) under nitrogen in a screw cap tube. The tube was flushed with nitrogen, capped, and allowed to stir 24 h. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with dichloromethane. After drying the combined organic layers over sodium sulfate, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel) with hexanes or hexane/EtOAc mixtures to give the desired product.

4.4.1. Trimethyl(4-phenylethynylphenylethynyl)silane (4a).[6b] **3a** (1.2 g, 4 mmol), phenylacetylene (0.48 mL,

4.4 mmol), bis(triphenylphosphine)palladium(II) dichloride (56 mg, 0.08 mmol), copper(I) iodide (30 mg, 0.16 mmol), and *N*,*N*-diisopropylethylamine (2.8 mL, 16.0 mmol) in THF (40 mL) for 1 d gave the desired product (0.99 g, 90%).

4.4.2. (3-Fluoro-4-phenylethynylphenylethynyl)trimethylsilane (4b). 3b (2.65 g, 8.33 mmol), phenylacetylene (0.87 mL, 7.92 mmol), bis(triphenylphosphine)palladium(II) dichloride (56 mg, 0.08 mmol), copper(I) iodide (30 mg, 0.16 mmol), and *N*,*N*-diisopropylethylamine (5.5 mL, 31.6 mmol) in THF (40 mL) for 1 d gave the desired product (2.05 g, 88%). IR (KBr) 2216, 2154 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.59 (m, 2H), 7.46 (dd, J=8, 8 Hz, 1H), 7.38–7.40 (m, 3H), 7.21–7.26 (m, 2H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F}= 252 Hz), 133.5 (d, J_{C-F}=2 Hz), 132.1, 129.8, 128.8, 128.1 (d, J_{C-F}=3 Hz), 125.1 (d, J_{C-F}=6 Hz), 123.1, 119.2 (d, J_{C-F}=23 Hz), 112.8 (d, J_{C-F}=16 Hz), 103.7 (d, J_{C-F}= 3 Hz), 97.8, 96.5 (d, J_{C-F}=4 Hz), 82.8, 0.2; HRMS calcd for $C_{19}H_{17}FSi$: 292.1084. Found: 292.1082.

4.4.3. 2-Phenylethynyl-5-trimethylsilanylethynylbenzonitrile (4c). 3c (2.14 g, 6.58 mmol), phenylacetylene (0.69 mL, 6.28 mmol), bis(triphenylphosphine)palladium(II) dichloride (44 mg, 0.06 mmol), copper(I) iodide (24 mg, 0.12 mmol), and *N*,*N*-diisopropylethylamine (4.4 mL, 25.2 mmol) in THF (30 mL) for 1 d gave the desired product (1.52 g, 81%). IR (KBr) 2230, 2211, 2152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J=1.6 Hz, 1H), 7.62–7.65 (m, 5H), 7.57 (d, J=8.2 Hz, 1H), 7.36–7.43 (m, 3H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.8, 132.5, 132.4, 129.9, 128.9, 127.0, 124.0, 122.2, 117.2, 115.9, 102.6, 99.5, 98.3, 86.0, 0.2; HRMS calcd for $C_{20}H_{17}NSi$: 299.1130. Found: 299.1134.

4.4.4. Trimethyl-(4-phenylethynyl-3-trifluoromethylphenylethynyl)silane (4d). 3d (3.23 g, 8.77 mmol), phenyl acetylene (1.06 mL, 9.65 mmol), bis(triphenylphosphine)-palladium(II) dichloride (123 mg, 0.17 mmol), copper(I) iodide (67 mg, 0.35 mmol), triphenylphosphine (92 mg, 0.35 mmol), and *N*,*N*-diisopropylethylamine (6.1 mL, 35.0 mmol) in THF (45 mL) at 40°C for 3 d gave the desired product (2.61 g, 87%). IR (KBr) 2210, 2159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 1H), 7.56–7.60 (m, 2H), 7.54–7.56 (m, 2H), 7.36–7.40 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 134.0, 132.1, 132.0 (q, J_{C-F}=31 Hz), 129.9 (q, J_{C-F}=5 Hz), 129.4, 128.8, 123.6 (q, J_{C-F}=274 Hz), 123.4, 122.9, 121.7 (q, J_{C-F}= 2 Hz), 103.6, 98.5, 97.2 (q, J_{C-F}=2 Hz), 85.6, 0.2; HRMS calcd for $C_{20}H_{17}F_3Si$: 342.1051. Found: 342.1054.

4.4.5. (3-Ethyl-4-phenylethynylphenylethynyl)trimethylsilane (4e). 3e (2.65 g, 8.07 mmol), phenylacetylene (0.93 mL, 8.47 mmol), bis(triphenylphosphine)palladium(II) dichloride (93 mg, 0.16 mmol), copper(I) iodide (61 mg, 0.32 mmol), triphenylphosphine (212 mg, 0.81 mmol), and *N*,*N*-diisopropylethylamine (5.6 mL, 32.1 mmol) in THF (40 mL) at 40°C for 3 d gave the desired product (2.01 g, 82%). IR (KBr) 2210, 2157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.56 (m, 2H), 7.45 (d, J=7.9 Hz, 1H), 7.35–7.40 (m, 4H), 7.30 (dd, J=1.7, 7.9 Hz, 1H), 2.86 (q, J=7.6 Hz, 2H), 1.32 (t, J=7.6 Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 132.4, 131.9, 131.8, 129.6, 128.8, 128.7, 123.8, 123.4, 105.5, 96.0, 95.0, 88.2, 28.0, 15.0, 0.4; HRMS calcd for $C_{21}H_{22}Si$: 302.1491. Found: 302.1492.

4.5. General procedures for the desilylation of alkynes

The silylated alkyne (1 equiv.) was dissolved in CH_3OH or CH_2Cl_2/CH_3OH mixtures. Potassium carbonate (2 equiv.) was added, and the reaction was stirred overnight. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with CH_2Cl_2. After drying the combined organic layers over Na_2SO_4, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel) with hexanes or hexane/EtOAc mixtures to give the desired product.

4.5.1. 1-Ethynyl-4-phenylethynylbenzene (5a). 4a (1.3 g, 4.7 mmol), CH_3OH (20 mL), CH_2Cl_2 (20 mL), and potassium carbonate (1.3 g, 9.4 mmol) afforded 0.92 g (96%) of the title compound. IR (KBr) 3276 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.58 (m, 2H), 7.43–7.52 (m, 4H), 7.37–7.40 (m, 3H), 3.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 132.2, 132.0, 129.0, 128.9, 124.3, 123.4, 122.4, 91.9, 89.4, 83.8, 79.5; HRMS calcd for $C_{16}H_{10}$: 202.0782. Found: 202.0784.

4.5.2. 4-Ethynyl-2-fluoro-1-phenylethynylbenzene (5b). 4b (1.2 g, 4.1 mmol), CH_3OH (15 mL), CH_2Cl_2 (15 mL), and potassium carbonate (1.13 g, 8.2 mmol) afforded 0.748 g (83%) of the title compound. IR (KBr) 3267, 2216 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.60 (m, 2H), 7.48 (dd, J=7.6, 7.6 Hz, 1H), 7.37–7.41 (m, 3H), 7.24–7.28 (m, 2H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F}=253 Hz), 133.6, 132.2, 129.3, 128.8, 128.2 (d, J_{C-F}=4 Hz), 124.0 (d, J_{C-F}=9 Hz), 123.0, 119.4 (d, J_{C-F}=23 Hz), 113.3 (d, J_{C-F}=16 Hz), 96.7 (d, J_{C-F}=4 Hz), 82.7, 82.5 (d, J_{C-F}=3 Hz), 80.2; HRMS calcd for $C_{16}H_9F$: 220.0688. Found: 220.0690.

4.5.3. 5-Ethynyl-2-phenylethynylbenzonitrile (5c). 4c (425 mg, 1.4 mmol), CH_3OH (10 mL), CH_2Cl_2 (10 mL), and potassium carbonate (392 mg, 2.8 mmol) afforded 295 mg (91%) of the title compound. IR (KBr) 3262, 2234, 2207 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=1.6 Hz, 1H), 7.66 (dd, J=1.6, 8.2 Hz, 1H), 7.63–7.65 (m, 2H), 7.60 (d, J=8.2 Hz, 1H), 7.39–7.45 (m, 3H), 3.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 136.0, 132.5, 132.4, 129.9, 128.9, 127.6, 123.0, 122.2, 117.1, 116.1, 85.8, 81.5; HRMS calcd for $C_{17}H_9N$: 227.0735. Found: 227.0737.

4.5.4. 4-Ethynyl-1-phenylethynyl-2-trifluoromethylbenzene (5d). 4d (1.23 g, 3.59 mmol), CH_3OH (35 mL), and potassium carbonate (0.99 g, 7.16 mmol) afforded 0.9 g (93%) of the title compound. IR (KBr) 2218, 2197 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.60 (br s, 2H), 7.55–7.59 (m, 2H), 7.38–7.42 (m, 3H), 3.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.1, 132.2, 132.0 (q, J_{C-F}=31 Hz), 130.0 (q, J_{C-F}=5 Hz), 122.8, 122.5 (q, J_{C-F}=274 Hz), 122.4, 122.2 (q, J_{C-F}=2 Hz), 97.5 (q, J_{C-F}=2 Hz), 85.5, 82.4, 80.8; HRMS calcd for $C_{17}H_9F_3$: 270.0656. Found: 270.0652

4.5.5. 2-Ethyl-4-ethynyl-1-phenylethynylbenzene (5e). 4e (1.43 g, 4.7 mmol), CH_3OH (25 mL), and potassium carbonate (1.3 g, 9.4 mmol) afforded 1.02 g (94%) of the title compound. IR (neat) 3292, 2202 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.58 (m, 2H), 7.48 (d, J=7.9 Hz, 1H), 7.37–7.42 (m, 4H), 7.34 (dd, J=1.6, 7.9 Hz, 1H), 3.18 (s, 1H), 2.90 (q, J=7.6 Hz, 2H), 1.33 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 132.5, 132.1, 132.0, 129.9, 128.9, 128.8, 123.7, 123.5, 122.4, 95.2, 88.2, 84.1, 78.9, 28.1, 15.0; HRMS calcd for $C_{18}H_{14}$: 230.1096. Found: 230.1093.

4.5.6. Trimethyl[4-(4-phenylethynylphenylethynyl)phenylethynyl]silane (6a). 5a (250 mg, 1.24 mmol), **3a** (742 mg, 2.47 mmol), bis(triphenylphosphine)palladium(II) dichloride (17 mg, 0.024 mmol), copper(I) iodide (9 mg, 0.047 mmol), and *N*,*N*-diisopropylethylamine (860 μL, 4.94 mmol) in THF (8 mL) for 1 d gave the desired product (205 mg, 44%). IR (KBr) 2152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 7H), 7.45–7.51 (m, 3H), 7.37–7.41 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.3, 132.1, 132.0, 131.9, 131.8, 128.9, 128.8, 123.8, 123.6, 123.5, 123.4, 123.2, 105.0, 96.9, 91.8, 91.4, 89.4, 0.3; HRMS calcd for $C_{27}H_{22}Si$: 374.1491. Found: 374.1488.

4.5.7. [3-Fluoro-4-(4-phenylethynylphenylethynyl)phenylethynyl]trimethylsilane (6b). 5a (240 mg, 1.19 mmol), **3b** (756 mg, 2.38 mmol), bis(triphenylphosphine)-palladium(II) dichloride (17 mg, 0.024 mmol), copper(I) iodide (9 mg, 0.047 mmol), and *N*,*N*-diisopropylethylamine (830 μL, 4.76 mmol) in THF (8 mL) for 1 d gave the desired product (310 mg, 66%). IR (KBr) 2211, 2152 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53–7.58 (m, 6H), 7.46 (dd, J=7.6, 7.6 Hz, 1H), 7.37–7.40 (m, 3H), 7.21–7.26 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F}=252 Hz), 133.5, 132.1, 132.0, 129.9, 128.9, 128.8, 128.1 (d, J_{C-F}=3 Hz), 125.4, 125.3, 124.1, 123.4, 122.8, 119.2 (d, J_{C-F}=23 Hz), 112.5 (d, J_{C-F}=16 Hz), 103.6 (d, J_{C-F}=3 Hz), 98.0, 96.2 (d, J_{C-F}=4 Hz), 91.9, 89.4, 84.6, 0.2; HRMS calcd for $C_{27}H_{21}FSi$: 392.1396. Found: 392.1394.

4.5.8. 2-(4-Phenylethynylphenylethynyl)-5-trimethylsilanylethynylbenzonitrile (6c). 5a (150 mg, 0.74 mmol), **3c** (241 mg, 0.74 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (6 mg, 0.032 mmol), and *N*,*N*-diisopropylethylamine (517 μL, 2.96 mmol) in THF (8 mL) for 1 d gave the desired product (248 mg, 84%). IR (KBr) 2230, 2210, 2149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J=1.2 Hz, 1H), 7.63 (dd, J=1.7, 8.2 Hz, 1H), 7.58–7.61 (m, 2H), 7.52–7.57 (m, 5H), 7.37–7.40 (m, 3H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.9, 132.1, 132.0, 131.9, 129.0, 128.8, 126.8, 124.8, 124.2, 123.3, 121.9, 117.2, 115.9, 102.5, 99.8, 97.8, 92.4, 89.4, 87.6, 0.1; HRMS calcd for $C_{28}H_{21}NSi$: 399.1443. Found: 399.1436.

4.5.9. Trimethyl[4-(4-phenylethynylphenylethynyl)-3-trifluoromethylphenyl-ethynyl]silane (6d). 5a (150 mg, 0.74 mmol), **3d** (410 mg, 1.11 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (8 mg, 0.03 mmol), and *N*,*N*-diisopropylethylamine (517 μL, 2.96 mmol) in THF (8 mL) at 50°C for 7 d gave the desired product (233 mg, 71%). IR (KBr) 2210, 2157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.51–7.60 (m, 8H), 7.36–7.41 (m, 3H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 134.0, 132.1, 132.0, 131.9 (q, J_{C-F}=31 Hz), 129.9 (q, J_{C-F}=5 Hz), 129.0, 128.8, 124.4, 123.7, 123.4, 123.3 (q, J_{C-F}=274 Hz), 122.6, 121.4 (q, J_{C-F}=2 Hz), 103.6, 98.7, 96.9, 92.2, 89.5, 87.4, 0.2; HRMS calcd for $C_{28}H_{21}F_3Si$: 442.1365. Found: 442.1366.

4.5.10. [3-Ethyl-4-(4-phenylethynylphenylethynyl)phenylethynyl]trimethylsilane (6e). 5a (155 mg, 0.77 mmol), **3e** (330 mg, 1.0 mmol), bis(triphenylphosphine)palladium(II) dichloride (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (8 mg, 0.03 mmol), and *N*,*N*-diisopropylethylamine (517 μL, 2.96 mmol) in THF (8 mL) at 50°C for 5 d gave the desired product (171 mg, 55%). IR (KBr) 2156 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51–7.58 (m, 6H), 7.46 (d, J=7.9 Hz, 1H), 7.37–7.41 (m, 4H), 7.31 (dd, J=1.4, 7.9 Hz, 1H), 2.88 (q, J=7.6 Hz, 2H), 1.33 (t, J=7.6 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 132.4, 132.1, 132.0, 131.9, 131.8, 129.7, 128.9, 128.8, 123.7, 123.6, 123.5, 123.4, 122.8, 105.4, 96.2, 94.7, 91.8, 90.1, 89.5, 28.0, 15.0, 0.4; HRMS calcd for $C_{29}H_{26}Si$: 402.1804. Found: 402.1798.

4.5.11. [4-(3-Fluoro-4-phenylethynylphenylethynyl)phenylethynyl]trimethylsilane (7a). 5b (185 mg, 0.84 mmol), **3a** (252 mg, 0.84 mmol), bis(triphenylphosphine)palladium(II) dichloride (18 mg, 0.026 mmol), copper(I) iodide (10 mg, 0.052 mmol), and *N*,*N*-diisopropylethylamine (586 μL, 3.36 mmol) in THF (8 mL) for 1 d gave the desired product (285 mg, 86%). IR (KBr) 2210, 2154 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56–7.59 (m, 2H), 7.48 (dd, J=7.6, 7.6 Hz, 1H), 7.38–7.40 (m, 3H), 7.24–7.28 (m, 2H), 0.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5 (d, J_{C-F}=252 Hz), 133.7, 132.4, 132.1, 131.9, 129.2, 128.8, 127.7 (d, J_{C-F}=3 Hz), 125.0 (d, J_{C-F}=9 Hz), 123.9, 123.0 (d, J_{C-F}=11 Hz), 118.8 (d, J_{C-F}=23 Hz), 112.8 (d, J_{C-F}=16 Hz), 104.9, 97.1, 96.6 (d, J_{C-F}=3 Hz), 92.0, 90.2 (d, J_{C-F}=4 Hz), 0.3; HRMS calcd for $C_{27}H_{21}FSi$: 392.1396. Found: 392.1397.

4.5.12. [3-Fluoro-4-(3-fluoro-4-phenylethynylphenylethynyl)phenylethynyl]-trimethylsilane (7b). 5b (150 mg, 0.68 mmol), **3b** (217 mg, 0.68 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (5 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (474 μL, 2.72 mmol) in THF (8 mL) for 1 d gave the desired product (231 mg, 82%). IR (KBr) 2209, 2153 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.60 (m, 2H), 7.52 (dd, J=7.6, 7.6 Hz, 1H), 7.45 (dd, J=7.6, 7.6 Hz, 1H), 7.22–7.27 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F}=252 Hz), 162.4 (d, J_{C-F}=252 Hz), 133.7, 133.6, 133.5, 133.4, 132.2, 129.2, 128.8, 128.2 (d, J_{C-F}=4 Hz), 128.8 (d, J_{C-F}=4 Hz), 127.7 (d, J_{C-F}=9 Hz), 124.6 (d, J_{C-F}=9 Hz), 123.0, 119.2 (d, J_{C-F}=22 Hz), 118.9 (d, J_{C-F}=22 Hz), 113.1 (d, J_{C-F}=16 Hz), 112.1 (d, J_{C-F}=16 Hz), 103.5 (d, J_{C-F}=3 Hz), 98.3, 96.8 (d, J_{C-F}=3 Hz), 95.0 (d, J_{C-F}=3 Hz), 94.9 (d, J_{C-F}=3 Hz), 85.4, 82.8, 0.2; HRMS calcd for $C_{26}H_{17}F_2Si$: 410.1302. Found: 410.1302.

4.5.13. 2-(3-Fluoro-4-phenylethynylphenylethynyl)-5-trimethylsilanylethynyl-benzonitrile (7c). 5b (150 mg, 0.68 mmol), **3c** (221 mg, 0.68 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (5 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (474 μL, 2.72 mmol) in THF (8 mL) for 1 d gave the desired product (275 mg, 97%). IR (KBr) 2231, 2217, 2152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J=1.3 Hz, 1H), 7.62 (dd, J=1.6, 8.2 Hz, 1H), 7.57–7.61 (m, 3H), 7.53 (dd, J=7.4, 7.4 Hz, 1H), 7.37–7.41 (m, 4H), 7.34 (dd, J=1.4, 9.5 Hz, 1H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F}=253 Hz), 135.6, 135.3, 133.2, 133.1, 131.9, 131.6, 128.7, 128.2, 127.6 (d, J_{C-F}=3 Hz), 125.6, 124.0, 123.0 (d, J_{C-F}=9 Hz), 122.3, 118.5 (d, J_{C-F}=22 Hz), 116.4, 115.4, 113.2 (d, J_{C-F}=16 Hz), 101.8, 99.4, 96.6 (d, J_{C-F}=3 Hz), 95.8 (d, J_{C-F}=3 Hz), 87.6, 82.2, −0.4; HRMS calcd for $C_{28}H_{20}FNSi$: 417.1349. Found: 417.1346.

4.5.14. [4-(3-Fluoro-4-phenylethynylphenylethynyl)-3-trifluoromethyl-phenylethynyl]trimethylsilane (7d). 5b (150 mg, 0.68 mmol), **3d** (251 mg, 0.68 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (5 mg, 0.026 mmol), triphenylphosphine (8 mg, 0.03 mmol), and *N*,*N*-diisopropylethylamine (474 μL, 2.72 mmol) in THF (8 mL) at 50°C for 7 d gave the desired product (195 mg, 62%). IR (KBr) 2207, 2159 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J=0.4 Hz, 1H), 7.60–7.62 (m, 2H), 7.56–7.60 (m, 2H), 7.53 (dd, J=7.5, 7.5 Hz, 1H), 7.38–7.42 (m, 3H), 7.30–7.34 (m, 2H), 0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F}=252 Hz), 134.9, 134.1, 133.8, 133.7, 132.2, 132.1 (q, J_{C-F}=31 Hz), 129.9 (q, J_{C-F}=5 Hz), 129.3, 128.8, 127.8 (d, J_{C-F}=3 Hz), 124.4, 124.3, 124.1, 123.5 (q, J_{C-F}=274 Hz), 123.1, 120.9 (q, J_{C-F}=2 Hz), 118.9 (d, J_{C-F}=22 Hz), 113.4 (d, J_{C-F}=16 Hz), 103.4, 99.0, 97.0 (d, J_{C-F}=3 Hz), 95.5 (d, J_{C-F}=3 Hz), 88.0, 82.9, 0.2; HRMS calcd for $C_{28}H_{20}F4Si$: 460.1270. Found: 460.1273.

4.5.15. [3-Ethyl-4-(3-fluoro-4-phenylethynylphenylethynyl)phenylethynyl]-trimethylsilane (7e). 5b (150 mg, 0.68 mmol), **3e** (223 mg, 0.68 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (5 mg, 0.026 mmol), triphenylphosphine (8 mg, 0.03 mmol), and *N*,*N*-diisopropylethylamine (474 μL, 2.72 mmol) in THF (8 mL) at 50°C for 4 d gave the desired product (150 mg, 54%). IR (KBr) 2219, 2152, 2131 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.61 (m, 2H), 7.52 (dd, J=7.5, 7.5 Hz, 1H), 7.46 (d, J=7.9 Hz, 1H), 7.36–7.42 (m, 4H), 7.26–7.34 (m, 3H), 2.89 (q, J=7.6 Hz, 2H), 1.33 (t, J=7.6 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F}=252 Hz), 133.7, 133.6, 132.5, 132.0, 129.7, 129.2, 128.8, 127.6 (d, J_{C-F}=3 Hz), 124.0, 123.1, 122.3, 118.6 (d, J_{C-F}=22 Hz), 112.6 (d, J_{C-F}=16 Hz), 105.3, 96.6 (d, J_{C-F}=3 Hz), 96.5, 93.5 (d, J_{C-F}=3 Hz), 90.9, 82.9, 28.0, 15.0, 0.4; HRMS calcd for $C_{29}H_{25}FSi$: 420.1710. Found: 420.1711.

4.5.16. 2-Phenylethynyl-5-(4-trimethylsilanylethynyl-phenylethynyl)benzonitrile (8a). 5c (150 mg, 0.66 mmol), **3a** (208 mg, 0.69 mmol), bis(triphenylphosphine)palladium(II) dichloride (9 mg, 0.013 mmol), copper(I) iodide (5 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (460 μL, 2.64 mmol) in THF (4 mL) for 22 h gave the desired product (190 mg, 72%). IR (KBr) 2233, 2211, 2152 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J=1.6 Hz, 1H), 7.69 (dd, J=1.6, 8.2 Hz, 1H), 7.61–7.65 (m, 3H), 7.49 (br, 4H), 7.39–7.45 (m, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.8, 135.5, 132.6, 132.5, 132.4, 132.0, 129.9, 128.9, 127.0, 124.3, 123.9, 122.5, 122.3, 117.2, 116.2, 104.8, 98.4, 97.4, 93.3, 89.1, 86.0, 0.3; HRMS calcd for $C_{28}H_{21}NSi$: 399.1443. Found: 399.1446.

4.5.17. 5-(2-Fluoro-4-trimethylsilanylethynylphenylethynyl)-2-phenylethynyl-benzonitrile (8b). 5c (180 mg, 0.79 mmol), **3b** (252 mg, 0.79 mmol), bis(triphenylphosphine)palladium(II) dichloride (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), and *N*,*N*-diisopropylethylamine (550 μL, 3.16 mmol) in THF (8 mL) for 1 d gave the desired product (293 mg, 88%). IR (KBr) 2231, 2210, 2149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J=1.7, 0.3 Hz, 1H), 7.72 (dd, J=1.7, 8.2 Hz, 1H), 7.62–7.66 (m, 3H), 7.46 (dd, J=7.6, 7.6 Hz, 1H), 7.39–7.46 (m, 3H), 7.23–7.28 (m, 2H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F}=252 Hz), 135.8, 135.5, 133.6, 133.5, 132.6, 132.5, 129.9, 128.9, 128.2 (d, J_{C-F}=3 Hz), 127.3, 126.1 (d, J_{C-F}=9 Hz), 123.5, 122.2, 119.3 (d, J_{C-F}=22 Hz), 117.2, 116.2, 111.6 (d, J_{C-F}=16 Hz), 103.4 (d, J_{C-F}=3 Hz), 98.7, 98.6, 93.8 (d, J_{C-F}=3 Hz), 86.7, 86.0, 0.2; HRMS calcd for $C_{28}H_{20}FNSi$: 417.1349. Found: 417.1349.

4.5.18. 2-(3-Cyano-4-phenylethynylphenylethynyl)-5-trimethylsilanylethynyl-benzonitrile (8c). 5c (126 mg, 0.55 mmol), **3c** (189 mg, 0.58 mmol), bis(triphenylphosphine)palladium(II) dichloride (12 mg, 0.017 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (9 mg, 0.034 mmol), and *N*,*N*-diisopropylethylamine (380 μL, 2.18 mmol) in THF (4 mL) at 40°C for 3 d gave the desired product (182 mg, 77%). IR (KBr) 2196, 1704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J=0.5, 1.7 Hz, 1H), 7.78 (dd, J=1.7, 8.3 Hz, 1H), 7.76 (dd, J=0.5, 1.7 Hz, 1H), 7.62–7.67 (m, 4H), 7.57 (dd, J=0.5, 8.1 Hz, 1H), 7.37–7.42 (m, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 136.0, 135.9, 132.6, 132.5, 130.0, 128.9, 128.0, 125.7, 125.0, 122.6, 122.1, 117.0, 116.9, 116.3, 116.2, 102.3, 100.4, 99.0, 95.1, 89.3, 85.9, 0.1; HRMS calcd for $C_{29}H_{20}N_2Si$: 424.1396. Found: 424.1391.

4.5.19. 2-Phenylethynyl-5-(2-trifluoromethyl-4-trimethylsilanylethynyl-phenylethynyl)benzonitrile (8d). 5c (130 mg, 0.57 mmol), **3d** (220 mg, 0.6 mmol), bis(triphenylphosphine)palladium(II) dichloride (12 mg, 0.017 mmol), copper(I) iodide (7 mg, 0.037 mmol), triphenylphosphine (9 mg, 0.034 mmol), and *N*,*N*-diisopropylethylamine (400 μL, 2.30 mmol) in THF (4 mL) at 40°C for 2 d gave the desired product (192 mg, 72%). IR (KBr) 2231, 2209, 2156 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J=0.5, 1.7 Hz, 1H), 7.80 (br s, 1H), 7.69 (dd, J=1.7, 8.2 Hz, 1H), 7.62–7.65 (m, 5H), 7.37–7.42 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 135.5, 135.0, 134.1, 132.6, 132.5, 132.2 (q, J_{C-F}=31 Hz), 130.0 (q, J_{C-F}= 5 Hz), 129.9, 127.6, 124.5, 123.4 (q, J_{C-F}=274 Hz), 123.3, 122.2, 120.4 (q, J_{C-F}=2 Hz), 117.1, 116.2, 103.3, 99.4,

98.8, 94.2, 89.2, 86.0, 0.2; HRMS calcd for $C_{29}H_{20}F_3NSi$: 467.1317. Found: 467.1313.

4.5.20. 5-(2-Ethyl-4-trimethylsilanylethynylphenylethynyl)-2-phenylethynyl-benzonitrile (8e). 5c (180 mg, 0.79 mmol), **3e** (260 mg, 0.79 mmol), bis(triphenylphosphine)palladium(II) dichloride (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (8 mg, 0.03 mmol), and *N*,*N*-diisopropylethylamine (550 μL, 3.16 mmol) in THF (7 mL) at 50°C for 5 d gave the desired product (242 mg, 71%). IR (KBr) 2230, 2215, 2152 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J=1.6 Hz, 1H), 7.68 (dd, J=1.6, 1.78.1 Hz, 1H), 7.61–7.69 (m, 3H), 7.43 (d, J=8.1 Hz, 2H), 7.40–7.43 (m, 4H), 7.32 (dd, J=1.6, 7.9 Hz, 1H), 2.86 (q, J=7.6 Hz, 2H), 1.32 (t, J=7.6 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 135.6, 135.3, 132.6, 132.5, 132.4, 132.0, 129.9, 129.8, 128.9, 126.8, 124.4, 124.2, 122.3, 121.9, 117.3, 116.2, 105.2, 98.4, 96.8, 92.4, 92.2, 86.0, 28.0, 15.0, 0.4; HRMS calcd for $C_{30}H_{25}NSi$: 427.1756. Found: 427.1747.

4.5.21. Trimethyl[4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-phenylethynyl]silane (9a). 5d (150 mg, 0.55 mmol), **3a** (167 mg, 0.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (8 mg, 0.011 mmol), copper(I) iodide (4 mg, 0.021 mmol), and *N*,*N*-diisopropylethylamine (387 μL, 2.22 mmol) in THF (6 mL) for 1 d gave the desired product (185 mg, 75%). IR (KBr) 2211, 2149 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.64–7.68 (m, 2H), 7.57–7.60 (m, 2H), 7.48–7.52 (m, 4H), 7.39–7.42 (m, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.5, 134.2, 132.4, 132.1 (q, J_{C-F}=31 Hz), 132.0, 129.5 (q, J_{C-F}=5 Hz), 129.4, 128.9, 124.1, 123.5 (q, J_{C-F}=274 Hz), 123.4, 123.0, 122.9, 121.6 (q, J_{C-F}=2 Hz), 104.9, 97.4, 97.2, 92.6, 90.1, 85.7, 0.3; HRMS calcd for $C_{28}H_{21}F_3Si$: 442.1364. Found: 442.1364.

4.5.22. [3-Fluoro-4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-phenylethynyl]-trimethyl-silane (9b). 5d (150 mg, 0.55 mmol), **3b** (177 mg, 0.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (8 mg, 0.011 mmol), copper(I) iodide (4 mg, 0.021 mmol), and *N*,*N*-diisopropylethylamine (387 μL, 2.22 mmol) in THF (8 mL) for 1 d gave the desired product (198 mg, 77%). IR (KBr) 2204, 2151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J=0.5 Hz, 1H), 7.64–7.69 (m, 2H), 7.55–7.59 (m, 2H), 7.46 (dd, J=7.5, 7.5 Hz, 1H), 7.38–7.41 (m, 3H), 7.23–7.28 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F}=252 Hz), 134.6, 134.2, 133.6, 133.5, 132.1 (q, J_{C-F}=31 Hz), 129.5 (q, J_{C-F}=5 Hz), 129.5, 128.5, 128.1(d, J_{C-F}=3 Hz), 126.0, 125.9, 123.5 (q, J_{C-F}=274 Hz), 123.0, 122.9, 122.1 (q, J_{C-F}=2 Hz), 119.3 (d, J_{C-F}=23 Hz), 112.0 (d, J_{C-F}=16 Hz), 103.5 (d, J_{C-F}=3 Hz), 98.4, 97.6, 94.7 (d, J_{C-F}=3 Hz), 86.0, 85.7, 0.2; HRMS calcd for $C_{28}H_{20}F_4Si$: 460.1270. Found: 460.1266.

4.5.23. 2-(4-Phenylethynyl-3-trifluoromethylphenylethynyl)-5-trimethylsilanylethynylbenzonitrile (9c). 5d (150 mg, 0.55 mmol), **3c** (180 mg, 0.55 mmol), bis(triphenylphosphine)palladium(II) dichloride (8 mg, 0.011 mmol), copper(I) iodide (4 mg, 0.021 mmol), and *N*,*N*-diisopropylethylamine (387 μL, 2.22 mmol) in THF (6 mL) for 1 d gave the desired product (182 mg, 70%). IR (KBr) 2231, 2210, 2154 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.78 (d, J=1.3 Hz, 1H), 7.75 (dd, J=1.3, 8.1 Hz, 1H), 7.68 (d, J=8.1 Hz, 1H), 7.64 (dd, J=1.6, 8.1 Hz, 1H), 7.56–7.60 (m, 3H), 7.39–7.42 (m, 3H), 0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 135.9, 135.0, 134.3, 132.6, 132.3 (q, J_{C-F}=31 Hz), 132.2, 129.7 (q, J_{C-F}=5 Hz), 129.6, 128.9, 126.1, 124.8, 123.4 (q, J_{C-F}=274 Hz), 122.8, 122.7 (q, J_{C-F}=2 Hz), 122.0, 117.0, 116.1, 102.4, 100.2, 98.2, 96.2, 88.6, 85.6, 0.1; HRMS calcd for $C_{29}H_{20}F_3NSi$: 467.1317. Found: 467.1314.

4.5.24. Trimethyl[4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-3-trifluoromethylphenylethynyl]silane (9d). 5d (225 mg, 0.83 mmol), **3d** (260 mg, 0.79 mmol), bis(triphenylphosphine)palladium(II) dichloride (17 mg, 0.024 mmol), copper(I) iodide (9 mg, 0.047 mmol), triphenylphosphine (13 mg, 0.049 mmol), and *N*,*N*-diisopropylethylamine (580 μL, 3.32 mmol) in THF (5 mL) at 50°C for 3 d gave the desired product (230 mg, 51%). IR (KBr) 2202, 2158 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (br s, 1H), 7.79 (d, J=0.7 Hz, 1H), 7.66 (d, J=1.1 Hz, 2H), 7.61 (d, J=1.1 Hz, 2H), 7.55–7.59 (m, 2H), 7.35–7.40 (m, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 134.6, 134.2, 134.1, 132.3 (q, J_{C-F}=31 Hz), 132.2 (q, J_{C-F}=31 Hz), 132.1, 129.9 (q, J_{C-F}=5 Hz), 129.4 (q, J_{C-F}=5 Hz), 128.9, 124.9, 124.8, 124.2, 123.6 (q, J_{C-F}=274 Hz), 123.5 (q, J_{C-F}=274 Hz), 122.8, 122.7, 122.3 (q, J_{C-F}=2 Hz), 120.7 (q, J_{C-F}=2 Hz), 103.4, 99.1, 97.7, 95.2, 88.5, 85.6, 0.2; HRMS calcd for $C_{29}H_{20}F_6Si$: 510.1238. Found: 510.1234.

4.5.25. [3-Ethyl-4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-phenylethynyl]trimethylsilane (9e). 5d (180 mg, 0.67 mmol), **3e** (219 mg, 0.67 mmol), bis(triphenylphosphine)palladium(II) dichloride (9 mg, 0.013 mmol), copper(I) iodide (5 mg, 0.026 mmol), triphenylphosphine (7 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (550 μL, 3.16 mmol) in THF (7 mL) at 50°C for 4 d gave the desired product (213 mg, 68%). IR (KBr) 2216, 2154 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.56–7.64 (m, 2H), 7.52–7.55 (m, 2H), 7.42 (d, J=7.9 Hz, 1H), 7.34–7.38 (m, 4H), 7.27 (dd, J=1.6, 7.9 Hz, 1H), 2.83 (q, J=7.6 Hz, 2H), 1.28 (t, J=7.6 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 134.4, 134.2, 132.6, 132.3 (q, J_{C-F}=31 Hz), 132.2, 132.0, 129.7, 129.5, 129.3 (q, J_{C-F}=5 Hz), 128.9, 125.0, 123.6, 123.5 (q, J_{C-F}=274 Hz), 122.9, 122.2, 121.5 (q, J_{C-F}=2 Hz), 105.2, 97.3, 96.6, 93.3, 91.4, 85.7, 28.0, 15.0, 0.4; HRMS calcd for $C_{30}H_{25}F_3Si$: 470.1678. Found: 470.1678.

4.5.26. [4-(3-Ethyl-4-phenylethynylphenylethynyl)-phenylethynyl]trimethylsilane (10a). 5e (150 mg, 0.65 mmol), **3a** (196 mg, 0.65 mmol), bis(triphenylphosphine)palladium(II) dichloride (9 mg, 0.013 mmol), copper(I) iodide (5 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (454 μL, 2.60 mmol) in THF (8 mL) for 1 d gave the desired product (136 mg, 52%). IR (KBr) 2201, 2154 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55–7.58 (m, 2H), 7.51 (d, J=7.9 Hz, 1H), 7.43–7.50 (m, 4H), 7.44 (d, J=1.3 Hz, 1H), 7.35–7.42 (m, 4H), 2.92 (q, J=7.6 Hz, 2H), 1.35 (t, J=7.6 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 132.5, 132.3, 131.9, 131.8, 131.5, 129.3,

128.8, 123.7, 123.6, 123.4, 123.3, 123.1, 105.0, 96.8, 95.1, 91.8, 90.8, 88.2, 28.0, 15.0, 0.3; HRMS calcd for $C_{29}H_{26}Si$: 402.1804. Found: 402.1800.

4.5.27. [4-(3-Ethyl-4-phenylethynylphenylethynyl)-3-fluorophenylethynyl]trimethyl-silane (10b). 5e (160 mg, 0.69 mmol), **3b** (221 mg, 0.69 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.014 mmol), copper(I) iodide (4 mg, 0.026 mmol), and *N*,*N*-diisopropylethylamine (484 μL, 2.78 mmol) in THF (8 mL) for 1 d gave the desired product (206 mg, 70%). IR (KBr) 2205, 2150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.59 (m, 2H), 7.53 (d, J=7.9 Hz, 1H), 7.46–7.49 (m, 2H), 7.37–7.42 (m, 4H), 7.23–7.27 (m, 2H), 2.93 (q, J=7.6 Hz, 2H), 1.37 (t, J=7.6 Hz, 3H), 0.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F}=252 Hz), 146.7, 133.5, 132.5, 132.0, 131.6, 129.4, 128.8, 128.1 (d, J_{C-F}=3 Hz), 125.3, 125.2, 123.7, 123.5, 122.9, 119.2 (d, J_{C-F}=23 Hz), 112.7 (d, J_{C-F}=16 Hz), 103.7 (d, J_{C-F}=3 Hz), 98.0, 96.6 (d, J_{C-F}=3 Hz), 88.2, 84.2, 28.0, 15.0, 0.2; HRMS calcd for $C_{29}H_{25}FSi$: 420.1710. Found: 420.1706.

4.5.28. 2-(3-Ethyl-4-phenylethynylphenylethynyl)-5-trimethylsilanylethynyl-benzonitrile (10c). 5e (175 mg, 0.76 mmol), **3c** (247 mg, 0.76 mmol), bis(triphenylphosphine)palladium(II) dichloride (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), and *N*,*N*-diisopropylethylamine (530 μL, 3.04 mmol) in THF (8 mL) for 1 d gave the desired product (225 mg, 69%). IR (KBr) 2230, 2201, 2149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J=0.6, 1.6 Hz, 1H), 7.62 (dd, J=1.6, 8.2 Hz, 1H), 7.51–7.58 (m, 5H), 7.43 (dd, J=1.6, 7.9 Hz, 1H), 7.37–7.41 (m, 3H), 2.92 (q, J=7.6 Hz, 2H), 1.36 (t, J=7.6 Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 136.2, 135.8, 132.6, 132.4, 132.0, 131.9, 129.7, 128.9, 128.8, 126.9, 124.2, 124.1, 123.6, 122.0, 117.2, 115.9, 102.6, 99.7, 98.3, 95.7, 88.1, 87.1, 28.0, 15.0, 0.1; HRMS calcd for $C_{30}H_{25}NSi$: 427.1756. Found: 427.1755.

4.5.29. [4-(3-Ethyl-4-phenylethynylphenylethynyl)-3-trifluoromethylphenylethynyl]-trimethylsilane (10d). 5e (180 mg, 0.78 mmol), **3d** (432 mg, 1.17 mmol), bis(triphenylphosphine)palladium(II) dichloride 2 (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (8 mg, 0.032 mmol), and *N*,*N*-diisopropylethylamine (545 μL, 3.13 mmol) in THF (8 mL) at 50°C for 7 d gave the desired product (235 mg, 64%). IR (KBr) 2200, 2157 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.58–7.62 (m, 2H), 7.55–7.57 (m, 2H), 7.51 (d, J=7.9 Hz, 1H), 7.44 (dd, J=0.5, 1.5 Hz, 1H), 7.37–7.40 (m, 4H), 2.93 (q, J=7.6 Hz, 2H), 1.35 (t, J=7.6 Hz, 3H), 0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 134.9, 134.0, 132.6, 132.1 (q, J_{C-F}=31 Hz), 132.0, 131.6, 129.6 (q, J_{C-F}=5 Hz), 129.5, 128.9, 128.8, 123.8, 123.7, 123.6 (q, J_{C-F}=274 Hz), 123.5, 122.8, 121.6 (q, J_{C-F}=2 Hz), 103.6, 98.6, 97.3, 95.5, 88.2, 86.9, 28.1, 15.0, 0.2; HRMS calcd for $C_{30}H_{25}F_3Si$: 470.1678. Found: 470.1681.

4.5.30. [3-Ethyl-4-(3-ethyl-4-phenylethynylphenylethynyl)phenylethynyl]trimethyl-silane (10e). 5e (180 mg, 0.78 mmol), **3e** (385 mg, 1.17 mmol), bis(triphenyl phosphine)palladium(II) dichloride (11 mg, 0.016 mmol), copper(I) iodide (6 mg, 0.032 mmol), triphenylphosphine (8 mg, 0.032 mmol), and *N*,*N*-diisopropylethylamine (545 μL, 3.13 mmol) in THF (8 mL) at 50°C for 4 d gave the desired product (170 mg, 51%). IR (KBr) 2200, 2155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.58 (m, 2H), 7.51 (d, J=8.0 Hz, 1H), 7.45 (d, J=8.4 Hz, 1H), 7.41–7.43 (m, 2H), 7.35–7.40 (m, 4H), 7.35 (dd, J=1.7, 8.0 Hz, 1H), 7.30 (dd, J=1.7, 8.0 Hz, 1H), 2.91 (q, J=7.6 Hz, 2H), 2.90 (q, J=7.6 Hz, 2H), 1.35 (t, J=7.6 Hz, 3H), 1.33 (t, J=7.6 Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.5, 132.5, 132.4, 131.9, 131.8, 131.4, 129.7, 129.2, 128.8, 128.7, 123.8, 123.6, 123.5, 123.0, 122.9, 105.5, 96.2, 95.1, 95.0, 89.6, 89.3, 28.1, 28.0, 15.0, 14.9, 0.4; HRMS calcd for $C_{31}H_{30}Si$: 430.2117. Found: 430.2120.

4.6. General procedure for the preparation of tetramer thioacetate

The silylated alkyne was deprotected as described previously. Without further purification, the trimer alkyne was subjected to coupling with the alligator clip as follows: To a stirring solution of the 1-iodo-4-thioacetylbenzene (**11**) (1–2 equiv.), bis(triphenylphosphine)palladium(II) dichloride (3 mol%), and copper(I) iodide (6 mol%) in THF was added the terminal alkyne followed by the amine (4 equiv. based on the alkyne) at room temperature under nitrogen in a screw cap tube. The tube was flushed with nitrogen, capped, and allowed to stir 24 h. The reaction mixture was then subjected to an aqueous workup and the aqueous layer extracted with dichloromethane. After drying the combined organic layers over sodium sulfate, the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel) with hexane/EtOAc mixtures to give desired product.

4.6.1. Thioacetic acid *S*-{4-[3-fluoro-4-(4-phenylethynyl-phenylethynyl-phenylethynyl]phenyl} ester (12b). 75 mg (43%) of **12b** as yellow solid, mp 196–202°C, was produced from **6b** (145 mg, 0.37 mmol) and **11** (205 mg, 0.74 mmol). IR (KBr) 2204, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53–7.59 (m, 8H), 7.52 (dd, J=7.6, 7.6 Hz, 1H) 7.43 (d, J=8.4 Hz, 2H), 7.37–7.41 (m, 3H), 7.28–7.34 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 162.5 (d, J_{C-F}=252 Hz), 134.7, 133.6, 132.6, 132.1, 132.0, 129.2, 128.9, 128.8, 127.8 (d, J_{C-F}=3 Hz), 125.1, 125.0, 124.2, 124.1, 123.4, 122.8, 118.9 (d, J_{C-F}=23 Hz), 112.6 (d, J_{C-F}=16 Hz), 96.5, 96.3 (d, J_{C-F}=3 Hz), 92.0, 91.8, 89.9 (d, J_{C-F}=3 Hz), 89.4, 84.7, 30.7; HRMS calcd for $C_{32}H_{19}FOS$: 470.1140. Found: 470.1141.

4.6.2. Thioacetic acid *S*-{4-[3-cyano-4-(4-phenylethynyl-phenylethynyl)-phenylethynyl]phenyl} ester (12c). 72 mg (41%) of **12c** as yellow solid, mp 199–201°C, was produced from **6c** (148 mg, 0.37 mmol) and **11** (122 mg, 0.44 mmol). IR (KBr) 2223, 2209, 1706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J=1.5 Hz, 1H), 7.71 (dd, J=1.7, 8.2 Hz, 1H), 7.55–7.65 (m, 9H), 7.45 (d, J=8.4 Hz, 1H), 7.37–7.41 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 135.8, 135.6, 134.7, 132.7, 132.5, 132.4, 132.1, 132.0, 129.6, 129.0, 128.8, 126.8, 124.9, 124.0, 123.7, 123.3, 121.9, 117.2, 116.1, 98.0, 93.0, 92.4, 89.4, 88.8, 87.7, 30.8; HRMS calcd for $C_{33}H_{19}NOS$: 477.1187. Found: 477.1193.

4.6.3. Thioacetic acid *S*-{4-[4-(4-phenylethynylphenylethynyl)-3-trifluoromethyl-phenylethynyl]phenyl} ester (12d). 88 mg (47%) of **12d** as yellow solid, mp 201°C (dec.), was produced from **6d** (158 mg, 0.36 mmol) and **11** (142 mg, 0.51 mmol). IR (KBr) 2214, 1703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (br s, 1H), 7.68 (br s, 2H), 7.56–7.61 (m, 8H), 7.44 (d, J=8.4 Hz, 2H), 7.36–7.41 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 134.7, 134.6, 134.2, 132.7, 132.2 (q, J_{C-F}=31 Hz), 132.21, 132.0, 129.6 (q, J_{C-F}=5 Hz), 129.3, 129.0, 128.8, 124.4, 124.0, 123.5 (q, J_{C-F}=274 Hz), 123.4, 123.3, 122.6, 121.5 (q, J_{C-F}=2 Hz), 97.0, 92.3, 92.1, 89.8, 89.4, 87.4, 30.7; HRMS calcd for $C_{33}H_{19}F_3OS$: 520.1109. Found: 520.1109.

4.6.4. Thioacetic acid *S*-{4-[3-ethyl-4-(4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (12e). 72 mg (47%) of **12e** as yellow solid, mp 176–184°C, was produced from **6e** (128 mg, 0.32 mmol) and **11** (131 mg, 0.47 mmol). IR (KBr) 2200, 1694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.60 (m, 9H), 7.45–7.46 (m, 1H), 7.43 (d, J=8.4 Hz, 2H), 7.37–7.41 (m, 4H), 2.91 (q, J=7.6 Hz, 2H), 2.47 (s, 3H), 1.34 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 146.7, 134.7, 132.6, 132.5, 132.1, 132.0, 131.9, 131.6, 129.4, 128.9, 128.8, 128.6, 124.8, 123.7, 123.5, 123.4, 122.9, 94.9, 91.8, 91.5, 90.6, 90.2, 89.6, 30.7, 28.1, 15.0; HRMS calcd for $C_{34}H_{24}OS$: 480.1548. Found: 480.1457.

4.6.5. Thioacetic acid *S*-{4-[4-(3-fluoro-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (13a). 82 mg (38%) of **13a** as yellow solid, mp 202–205°C, was produced from **7a** (180 mg, 0.46 mmol) and **11** (120 mg, 0.43 mmol). IR (KBr) 2212, 1692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.56–7.60 (m, 4H), 7.50–7.56 (m, 4H), 7.52 (dd, J=7.6, 7.6 Hz, 1H) 7.44 (d, J=8.4 Hz, 2H), 7.35–7.40 (m, 3H), 7.31–7.35 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 162.5 (d, J_{C-F}=252 Hz), 133.7, 133.6, 132.6, 132.2, 132.1, 132.0, 129.2, 128.8, 127.7 (d, J_{C-F}=4 Hz), 125.0 (d, J_{C-F}=9 Hz), 124.6, 123.7, 123.1, 118.8 (d, J_{C-F}=23 Hz), 112.8 (d, J_{C-F}=16 Hz), 96.6 (d, J_{C-F}=3 Hz), 92.0, 91.2, 91.0, 90.4 (d, J_{C-F}=4 Hz), 82.9, 30.7; HRMS; HRMS calcd for $C_{32}H_{19}FOS$: 470.1140. Found: 470.1143.

4.6.6. Thioacetic acid *S*-{4-[3-fluoro-4-(3-fluoro-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (13b). 30 mg (23%) of **13b** as yellow solid, mp 203–207°C, was produced from **7b** (112 mg, 0.28 mmol) and **11** (75 mg, 0.27 mmol). IR (KBr) 2208, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57–7.60 (m, 4H), 7.52 (dd, J=7.3, 14.8 Hz, 2H) 7.44 (d, J=8.4 Hz, 2H), 7.37–7.41 (m, 3H), 7.30–7.37 (m, 4H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 162.6 (d, J_{C-F}=252 Hz), 162.5 (d, J_{C-F}=252 Hz), 134.7, 133.7, 132.7, 132.2, 129.2 (d, J_{C-F}=4 Hz), 128.9, 127.9 (d, J_{C-F}=4 Hz), 127.8, 125.5 (d, J_{C-F}=9 Hz), 124.4 (d, J_{C-F}=9 Hz), 124.1, 123.0, 119.0 (d, J_{C-F}=22 Hz), 118.9 (d, J_{C-F}=22 Hz), 113.1 (d, J_{C-F}=16 Hz), 112.1 (d, J_{C-F}=16 Hz), 96.8 (d, J_{C-F}=3 Hz), 96.5, 95.1 (d, J_{C-F}=3 Hz), 92.0, 89.8 (d, J_{C-F}=3 Hz), 85.4, 82.8, 30.7; HRMS calcd for $C_{32}H_{18}F_2OS$: 488.1046. Found: 488.1034.

4.6.7. Thioacetic acid *S*-{4-[3-cyano-4-(3-fluoro-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (13c). 65 mg (48%) of **13c** as yellow solid, mp 192–195°C, was produced from **7c** (115 mg, 0.28 mmol) and **11** (76 mg, 0.27 mmol). IR (KBr) 2228, 2208, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J=1.7 Hz, 1H), 7.68 (dd, J=1.6, 8.2 Hz, 1H), 7.59 (d, J=8.2 Hz, 1H), 7.52–7.56 (m, 4H), 7.50 (dd, J=7.7, 7.7 Hz, 1H), 7.41 (d, J=8.4 Hz, 2H), 7.31–7.37 (m, 5H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 162.5 (d, J_{C-F}=252 Hz), 135.9, 135.6, 134.7, 133.9, 133.8, 132.7, 132.6, 132.2, 129.7, 129.3, 128.8, 128.2 (d, J_{C-F}=3 Hz), 126.3, 124.4, 123.6 (d, J_{C-F}=9 Hz), 123.0, 119.1 (d, J_{C-F}=23 Hz), 117.0, 116.3, 113.9 (d, J_{C-F}=16 Hz), 97.3 (d, J_{C-F}=3 Hz), 96.6 (d, J_{C-F}=3 Hz), 93.3, 88.7, 88.2, 82.8, 30.8; HRMS calcd for $C_{33}H_{18}FNOS$: 495.1093. Found: 495.1096.

4.6.8. Thioacetic acid *S*-{4-[4-(3-fluoro-4-phenylethynylphenylethynyl)-3-trifluoromethylphenylethynyl]phenyl} ester (13d). 80 mg (41%) of **13d** as yellow solid, mp 188–190°C, was produced from **7d** (166 mg, 0.36 mmol) and **11** (97 mg, 0.35 mmol). IR (KBr) 2210, 1700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.63–7.67 (m, 2H), 7.59–7.61 (m, 4H), 7.53 (dd, J=7.6, 7.6 Hz, 1H), 7.44 (d, J=8.3 Hz, 2H), 7.38–7.41 (m, 3H), 7.29–7.34 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 162.5 (d, J_{C-F}=252 Hz), 134.7, 134.6, 134.2, 133.7, 133.6, 123.7, 132.3 (q, J_{C-F}=31 Hz), 132.2, 129.6 (q, J_{C-F}=5 Hz), 129.4, 128.8, 127.9 (d, J_{C-F}=3 Hz), 124.4, 124.3, 123.9, 123.8, 123.4 (q, J_{C-F}=274 Hz), 120.9 (q, J_{C-F}=2 Hz), 118.9 (d, J_{C-F}=22 Hz), 113.4 (d, J_{C-F}=16 Hz), 97.0 (d, J_{C-F}=3 Hz), 96.6 (d, J_{C-F}=3 Hz), 92.5, 89.7, 88.1, 82.8, 30.7; HRMS calcd for $C_{33}H_{18}F_4OS$: 538.1014. Found: 538.1014.

4.6.9. Thioacetic acid *S*-{4-[3-ethyl-4-(3-fluoro-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (13e). 62 mg (48%) of **13e** as yellow solid, mp 150–152°C, was produced from **7e** (110 mg, 0.26 mmol) and **11** (68 mg, 0.24 mmol). IR (KBr) 2218, 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.61 (m, 4H), 7.50–7.54 (m, 2H), 7.46 (br, 1H), 7.43 (d, J=8.2 Hz, 2H), 7.36–7.42 (m, 4H), 2.91 (q, J=7.6 Hz, 2H), 2.47 (s, 3H), 1.33 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 162.5 (d, J_{C-F}=252 Hz), 146.9, 134.6, 133.7, 133.6, 132.7, 132.6, 132.2, 131.6, 129.4, 129.2, 128.8, 128.7, 127.6 (d, J_{C-F}= 3 Hz), 125.3, 125.2, 124.7, 123.8, 123.1, 122.4, 118.6 (d, J_{C-F}=23 Hz), 112.6 (d, J_{C-F}=16 Hz), 96.6 (d, J_{C-F}= 3 Hz), 93.7 (d, J_{C-F}=3 Hz), 91.4, 90.9, 90.7, 83.0, 30.7, 28.0, 15.0; HRMS calcd for $C_{34}H_{23}FOS$: 498.1454. Found: 498.1453.

4.6.10. Thioacetic acid *S*-{4-[4-(3-cyano-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (14a). 105 mg (58%) of **14a** as yellow solid, mp 204–205°C, was produced from **8a** (125 mg, 0.38 mmol) and **11** (111 mg, 0.4 mmol). IR (KBr) 2228, 2213, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J=1.8 Hz, 1H), 7.70 (dd, J=1.7, 8.2 Hz, 1H), 7.61–7.65 (m, 3H), 7.57 (d, J=8.4 Hz, 2H), 7.53–7.56 (m, 4H), 7.41 (d, J=8.4 Hz, 2H), 7.40–7.42 (m, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 135.8, 135.5, 134.7, 132.6, 132.5, 132.4, 132.2, 132.1, 129.9, 128.8, 127.0, 124.5, 124.1, 123.9, 122.6, 122.2, 117.2, 116.2, 98.4, 93.3, 91.4, 90.9, 89.2, 86.0, 30.7; HRMS calcd for $C_{33}H_{19}NOS$: 477.1187. Found: 477.1184.

4.6.11. Thioacetic acid *S*-{4-[4-(3-cyano-4-phenylethynylphenylethynyl)-3-fluoro-phenylethynyl]phenyl} ester (14b). 62 mg (42%) of **14b** as yellow solid, mp 207–208°C, was produced from **8b** (125 mg, 0.3 mmol) and **11** (78 mg, 0.28 mmol). IR (KBr) 2231, 2210, 1695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J=1.6 Hz, 1H), 7.74 (dd, J=1.6, 8.2 Hz, 1H), 7.62–7.66 (m, 3H), 7.57 (dd, J=7.6, 7.6 Hz, 1H), 7.43 (d, J=8.4 Hz, 2H), 7.41–7.43 (m, 3H), 7.30–7.35 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 162.2 (d, J_{C-F}=252 Hz), 135.1, 134.2, 133.3, 133.2, 132.2, 132.1, 132.0, 129.5, 128.9, 128.5, 127.5 (d, J_{C-F}=3 Hz), 126.9, 125.5 (d, J_{C-F}=9 Hz), 123.6, 123.1, 121.8, 118.5 (d, J_{C-F}=22 Hz), 116.7, 115.7, 111.3 (d, J_{C-F}=16 Hz), 98.2, 93.5 (d, J_{C-F}=3 Hz), 91.8, 89.3 (d, J_{C-F}=3 Hz), 86.3, 85.5, 30.3; HRMS calcd for $C_{33}H_{18}FNOS$: 495.1093. Found: 495.1095.

4.6.12. Thioacetic acid *S*-{4-[3-cyano-4-(3-cyano-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (14c). 49 mg (42%) of **14c** as yellow solid was produced from **8c** (100 mg, 0.24 mmol) and **11** (65 mg, 0.23 mmol). IR (KBr) 2231, 2209, 1706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J=1.4 Hz, 1H), 7.86 (d, J=1.4 Hz, 1H), 7.80 (dd, J=1.6, 8.2 Hz, 1H), 7.74 (dd, J=1.6, 8.2 Hz, 1H), 7.69 (d, J=1.4 Hz, 1H), 7.65–7.69 (m, 4H), 7.59 (d, J=8.4 Hz, 2H), 7.45 (d, J=8.4 Hz, 2H), 7.40–7.44 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 136.0, 135.9, 135.8, 135.7, 134.7, 132.7, 132.6, 132.5, 130.0, 129.8, 128.9, 128.1, 125.8, 124.8, 123.5, 122.6, 122.1, 117.0, 116.9, 116.4, 116.3, 99.1, 95.3, 93.6, 89.3, 88.6, 86.0, 30.7; HRMS calcd for $C_{34}H_{18}N_2OS$: 502.1140. Found: 502.1140.

4.6.13. Thioacetic acid *S*-{4-[4-(3-cyano-4-phenylethynylphenylethynyl)-3-trifluoromethylphenylethynyl]phenyl} ester (14d). 32 mg (30%) of **14d** as yellow solid, mp 162–164°C, was produced from **8d** (90 mg, 0.19 mmol) and **11** (53 mg, 0.19 mmol). IR (KBr) 2230, 2210, 1703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J=0.6 Hz, 1H), 7.84 (d, J=1.5 Hz, 1H), 7.72 (dd, J=1.7, 13.1 Hz, 1H), 7.69 (d, J=1.4 Hz, 1H), 7.68 (s, 1H) 7.63–7.66 (m, 3H), 7.60 (d, J=8.4 Hz, 2H), 7.45 (d, J=8.4 Hz, 2H), 7.38–7.44 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 135.9, 135.6, 134.7, 134.3, 132.7, 132.6, 132.5, 132.4 (q, J_{C-F}=31 Hz), 130.0, 129.7 (q, J_{C-F}= 5 Hz), 129.5, 128.9, 127.6, 124.3, 123.9, 123.4 (q, J_{C-F}=274 Hz), 123.3, 122.2, 120.5, 120.4 (q, J_{C-F}= 2 Hz), 98.8, 94.4, 92.8, 89.5, 89.2, 86.0, 30.8; HRMS calcd for $C_{34}H_{18}F_3NOS$: 545.1061. Found: 545.1060.

4.6.14. Thioacetic acid *S*-{4-[4-(3-cyano-4-phenylethynylphenylethynyl)-3-ethyl-phenylethynyl]phenyl} ester (14e). 61 mg (43%) of **14e** as yellow solid, mp 144–146°C, was produced from **8e** (120 mg, 0.28 mmol) and **11** (75 mg, 0.27 mmol). IR (KBr) 2229, 2212, 1706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J=1.6, 0.4 Hz, 1H), 7.69 (dd, J=1.6, 8.1 Hz, 1H), 7.64–7.68 (m, 3H), 7.60 (d, J=8.4 Hz, 2H), 7.53 (d, J=8.0 Hz, 1H), 7.39 (m, 7H), 2.91 (q, J=7.6 Hz, 2H), 2.49 (s, 3H), 1.37 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 147.0, 135.6, 135.3, 134.6, 132.8, 132.6, 132.5, 132.4, 132.3, 131.7, 129.9, 129.5, 128.9, 128.8, 126.9, 124.6, 124.2, 124.1, 122.3, 121.9, 117.3, 116.2, 98.4, 92.6, 92.3, 91.3, 91.0, 86.0, 30.7, 28.0, 15.0; HRMS calcd for $C_{35}H_{23}NOS$: 505.1500. Found: 505.1501.

4.6.15. Thioacetic acid *S*-{4-[4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-phenylethynyl]phenyl} ester (15a). 60 mg (40%) of **15a** as yellow solid, mp 192–194°C, was produced from **9a** (128 mg, 0.29 mmol) and **11** (80 mg, 0.29 mmol). IR (KBr) 2212, 1697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.67 (d, J=1.1 Hz, 2H), 7.58–7.60 (m, 4H), 7.56 (br, 2H), 7.43 (d, J=8.4 Hz, 2H), 7.39–7.5422 (m, 3H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 134.7, 134.5, 134.2, 133.5, 132.6, 132.3 (q, J_{C-F}=31 Hz), 132.2, 132.1, 132.0, 129.6 (q, J_{C-F}=5 Hz), 129.5, 128.9, 124.6, 123.8, 123.5 (q, J_{C-F}=274 Hz), 123.4, 122.9, 121.7 (q, J_{C-F}=2 Hz), 97.4, 92.6, 91.3, 91.0, 90.2, 85.7, 30.7; HRMS calcd for $C_{33}H_{19}F_3OS$: 520.1109. Found: 520.1107.

4.6.16. Thioacetic acid *S*-{4-[3-fluoro-4-(4-phenylethynyl-3-trifluoromethyl-phenylethynyl)phenylethynyl]phenyl} ester (15b). 56 mg (36%) of **15b** as yellow solid, mp 178–180°C, was produced from **9b** (132 mg, 0.29 mmol) and **11** (77 mg, 0.28 mmol). IR (KBr) 2205, 1699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.69–7.72 (m, 2H), 7.58–7.60 (m, 4H), 7.53 (dd, J=7.7, 7.7 Hz, 1H), 7.44 (d, J=8.4 Hz, 2H), 7.40–7.42 (m, 3H), 7.34–7.35 (m, 1H), 7.30–7.33 (m, 1H), 2.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 162.6 (d, J_{C-F}=252 Hz), 134.7, 134.6, 134.2, 133.7, 132.7, 132.3 (q, J_{C-F}=31 Hz), 132.2, 129.6 (q, J_{C-F}=5 Hz), 129.5, 129.3, 128.9, 127.9 (d, J_{C-F}=3 Hz), 125.7, 125.6, 124.1, 123.5 (q, J_{C-F}=274 Hz), 122.9, 122.8, 122.0, (q, J_{C-F}=2 Hz), 119.0 (d, J_{C-F}= 23 Hz), 112.0 (d, J_{C-F}=16 Hz), 97.6, 94.8 (d, J_{C-F}=3 Hz), 92.1, 89.9 (d, J_{C-F}=3 Hz), 85.9, 85.6, 30.7; HRMS calcd for $C_{33}H_{18}F_4OS$: 538.1014. Found: 538.1013.

4.6.17. Thioacetic acid *S*-{4-[3-cyano-4-(4-phenylethynyl-3-trifluoromethyl-phenylethynyl)phenylethynyl]phenyl} ester (15c). 35 mg (26%) of **15c** as yellow solid, mp 177–176°C, was produced from **9c** (116 mg, 0.25 mmol) and **11** (68 mg, 0.24 mmol). IR (KBr) 2229, 2229, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (br s, 1H), 7.84 (d, J=1.1 Hz, 1H), 7.75 (dd, J=1.5, 8.1 Hz, 1H), 7.71 (dd, J=1.6, 8.1 Hz, 1H), 7.68 (d, J=8.1 Hz, 1H), 7.63 (d, J=8.2 Hz, 1H), 7.56–7.58 (m, 4H), 7.43 (d, J=8.4 Hz, 1H), 7.38–7.41 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.5, 135.9, 135.6, 135.0, 134.7, 134.3, 132.7, 132.3 (q, J_{C-F}=31 Hz), 132.2, 129.7 (q, J_{C-F}=5 Hz), 129.6, 128.9, 126.1, 124.6, 123.6, 123.5 (q, J_{C-F}= 274 Hz), 122.8, 122.8, 122.0, 117.0, 116.3, 98.0, 96.3, 93.4, 88.7, 88.6, 85.6, 30.8; HRMS calcd for $C_{34}H_{18}F_3NOS$: 545.1061. Found: 545.1062.

4.6.18. Thioacetic acid *S*-{4-[4-(4-phenylethynyl-3-trifluoromethylphenylethynyl)-3-trifluoromethylphenylethynyl]phenyl} ester (15d). 125 mg (56%) of **15d** as yellow solid, mp 181–183°C, was produced from **9d** (195 mg, 0.38 mmol) and **11** (106 mg, 0.38 mmol). IR (KBr) 2206, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J=0.6 Hz, 1H), 7.86 (br s, 1H), 7.68–7.72 (m, 4H), 7.56–7.60 (m, 4H), 7.44 (d, J=8.4 Hz, 2H), 7.39–7.42 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 134.7, 134.6, 134.3, 134.2, 132.7, 132.4 (q, J_{C-F}=31 Hz),

132.3 (q, J_{C-F}=31 Hz), 132.2, 129.6 (q, J_{C-F}=5 Hz), 129.5, 129.4 (q, J_{C-F}=5 Hz), 128.9, 124.0, 123.9, 122.8, 122.7, 123.5 (q, J_{C-F}=274 Hz), 123.4 (q, J_{C-F}=274 Hz), 122.4 (q, J_{C-F}=2 Hz), 120.8 (q, J_{C-F}=2 Hz), 97.7, 95.3, 92.6, 89.6, 88.5, 85.6, 30.7; HRMS calcd for $C_{34}H_{18}F_6OS$: 588.0982. Found: 588.0984.

4.6.19. Thioacetic acid *S*-{4-[3-ethyl-4-(4-phenylethynyl-3-trifluoromethyl-phenylethynyl)phenylethynyl]phenyl} ester (15e). 34 mg (21%) of **15e** as yellow solid, mp 167–172°C, was produced from **9e** (142 mg, 0.30 mmol) and **11** (122 mg, 0.3 mmol). IR (KBr) 2219, 1696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.69–7.71 (m, 2H), 7.58–7.61 (m, 4H), 7.53 (d, *J*=7.9 Hz, 1H), 7.47 (d, *J*=1.1 Hz, 1H), 7.44 (d, *J*=8.4 Hz, 1H), 7.39–7.43 (m, 4H), 2.91 (q, *J*=7.6 Hz, 2H), 2.47 (s, 3H), 1.36 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.7, 146.9, 134.6, 134.4, 134.2, 132.7, 132.6, 132.4 (q, J_{C-F}=31 Hz), 132.2, 131.6, 129.4, 129.3 (q, J_{C-F}=5 Hz), 128.8, 128.7, 124.7, 123.9, 123.6, 123.5 (q, J_{C-F}=274 Hz), 123.0, 122.3, 121.6 (q, J_{C-F} F=2 Hz), 97.3, 93.4, 91.4, 91.3, 90.8, 85.7, 30.7, 28.0, 15.0; HRMS calcd for $C_{35}H_{23}F_3OS$: 548.1422. Found: 548.1423.

4.6.20. Thioacetic acid *S*-{4-[4-(3-ethyl-4-phenylethynyl-phenylethynyl)-phenylethynyl]phenyl} ester (16a). 14 mg (12%) of **16a** as yellow solid, mp 129–131°C, was produced from **10a** (98 mg, 0.24 mmol) and **11** (67 mg, 0.24 mmol). IR (KBr) 2203, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.60 (m, 9H), 7.43–7.46 (m, 3H), 7.36–7.41 (m, 4H), 2.92 (q, *J*=7.6 Hz, 2H), 2.47 (s, 3H), 1.36 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 146.2, 134.2, 132.4, 132.2, 132.1, 132.0, 131.6, 131.58, 131.55, 131.5, 131.1, 128.9, 128.4, 128.3, 127.2, 124.3, 123.3, 122.8, 122.7, 122.6, 94.7, 91.5, 90.7, 90.5, 90.4, 87.8, 30.3, 27.6, 14.5; HRMS calcd for $C_{34}H_{24}OS$: 480.1548. Found: 480.1544.

4.6.21. Thioacetic acid S-{4-[4-(3-ethyl-4-phenylethynyl-phenylethynyl)-3-fluoro-phenylethynyl]phenyl} ester (16b). 88 mg (53%) of **16b** as yellow solid, mp 172–170°C, was produced from **10b** (140 mg, 0.33 mmol) and **11** (88 mg, 0.32 mmol). IR (KBr) 2205, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.60 (m, 4H), 7.50–7.54 (m, 2H), 7.47 (d, *J*=1.0 Hz, 1H), 7.44 (d, *J*=8.4 Hz, 1H), 7.35–7.40 (m, 4H), 7.29–7.33 (m, 2H), 2.91 (q, *J*=7.6 Hz, 2H), 2.47 (s, 3H), 1.36 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 162.5 (d, J_{C-F}=252 Hz), 146.7, 134.7, 133.7, 133.6, 132.7, 132.5, 131.9, 131.6, 129.4, 129.2, 128.8, 127.8 (d, J_{C-F}=3 Hz), 125.0, 124.9, 124.2, 123.7, 123.5, 122.9, 119.0 (d, J_{C-F}=23 Hz), 112.7 (d, J_{C-F}= 16 Hz), 96.8 (d, J_{C-F}=3 Hz), 95.3, 91.7, 90.0 (d, J_{C-F}=3 Hz), 88.2, 84.2, 30.7, 28.1, 15.0; HRMS calcd for $C_{34}H_{23}OSF$: 498.1454. Found: 498.1456.

4.6.22. Thioacetic acid *S*-{4-[3-cyano-4-(3-ethyl-4-phenylethynylphenylethynyl)-phenylethynyl]phenyl} ester (16c). 75 mg (46%) of **16c** as yellow solid, mp 180–183°C, was produced from **10c** (138 mg, 0.32 mmol) and **11** (103 mg, 0.37 mmol). IR (KBr) 2228, 2197, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J*=1.6 Hz, 1H), 7.71 (dd, *J*=1.6, 8.2 Hz, 1H), 7.63 (d, *J*=9.7 Hz, 1H), 7.52–7.60 (m, 6H), 7.43–7.47 (m, 3H), 2.94 (q, *J*=7.6 Hz, 2H), 2.48 (s, 3H), 1.36 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 146.8, 135.9, 135.6, 134.7, 132.7, 132.5, 132.0, 131.9, 129.8, 129.6, 128.9, 128.8, 126.9, 124.2, 123.9, 123.7, 123.6, 122.0, 117.2, 116.1, 98.4, 95.7, 93.0, 88.9, 88.1, 87.2, 30.8, 28.1, 15.0; HRMS calcd for $C_{35}H_{23}NOS$: 505.1500. Found: 505.1497.

4.6.23. Thioacetic acid *S*-{4-[4-(3-ethyl-4-phenylethynyl-phenylethynyl)-3-trifluoromethylphenylethynyl]phenyl} ester (16d). 98 mg (51%) of **16d** as yellow solid, mp 185–188°C, was produced from **10d** (165 mg, 0.35 mmol) and **11** (80 mg, 0.29 mmol). IR (KBr) 2192, 1694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.68 (d, *J*=1.0 Hz, 1H), 7.60 (d, *J*=8.4 Hz, 2H), 7.55–7.59 (m, 2H), 7.52 (d, *J*=7.9 Hz, 1H), 7.42–7.46 (m, 3H), 7.37–7.41 (m, 4H), 2.92 (q, *J*=7.6 Hz, 2H), 2.48 (s, 3H), 1.36 (t, *J*=7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 146.8, 134.7, 134.6, 134.2, 132.7, 132.5, 132.2 (q, J_{C-F}=31 Hz), 131.9, 131.6, 129.6 (q, J_{C-F}=5 Hz), 129.4, 129.3, 128.9, 128.8, 124.0, 123.7, 123.6, 123.5 (q, J_{C-F}=274 Hz), 123.3, 122.7, 121.6 (q, J_{C-F}=2 Hz), 97.4, 95.4, 92.2, 89.9, 88.2, 86.9, 30.7, 28.1, 15.0; HRMS calcd for $C_{35}H_{23}OSF_3$: 548.1422. Found: 548.1423.

4.6.24. Thioacetic acid *S*-{4-[3-ethyl-4-(3-ethyl-4-phenyl-ethynylphenylethynyl)-phenylethynyl]phenyl} ester (16e). 48 mg (37%) of **16e** as yellow solid, mp 141–144°C, was produced from **10e** (110 mg, 0.25 mmol) and **11** (70 mg, 0.25 mmol). IR (KBr) 2199, 1692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53–7.58 (m, 4H), 7.49 (dd, *J*=9.9, 1.8 Hz, 2H), 7.38–7.44 (m, 4H), 7.34–7.37 (m, 5H), 2.90 (q, *J*=7.6 Hz, 4H), 2.44 (s, 3H), 1.34 (t, *J*=7.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 146.8, 146.7, 134.6, 132.6, 132.5, 132.4, 131.9, 131.6, 131.4, 129.4, 129.2, 128.8, 128.6, 124.8, 123.8, 123.6, 123.3, 123.1, 123.0, 95.2, 95.1, 91.5, 90.5, 89.6, 88.3, 30.7, 28.1, 28.0, 15.1, 15.0; HRMS calcd for $C_{36}H_{28}OS$: 508.1861. Found: 508.1860.

4.7. General procedure for the diazonium formation

To a round-bottom flask fitted with an addition funnel and nitrogen inlet was added boron trifluoride etherate (4 equiv.) which was then chilled in a dry ice-acetone bath (−20°C). To the reaction flask was added dropwise over 5 min a solution of the aniline derivative (1 equiv.) in dry THF, followed by a solution of *tert*-butylnitrite (3.5 equiv.) in dry THF over 30 min. The chilled mixture was stirred an additional 10 min, and the cold bath was allowed to warm to 5°C over 20 min. To the mixture was added diethyl ether, and the mixture was chilled in an ice-bath for 15 min. The solid was collected by filtration, washed with chilled (0–5°C) diethyl ether, and dried in vacuo to give the desired product.

4.7.1. 4-Iodobenzenediazonium tetrafluoroborate (17a).[23] According to the general procedure, 7.0 g (96%) of **17a** was produced from **1a** (5.0 g, 22.8 mmol).

4.7.2. 2-Cyano-4-iodobenzenediazonium tetrafluoroborate (17b). According to the general procedure, 6.5 g (77%) of **17b** was produced from **1c** (6.0 g, 25.7 mmol). IR (KBr) 2284, 2244 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.76 (d, *J*=1.7 Hz, 1H), 8.65 (dd, *J*=1.7, 8.8 Hz, 1H), 8.42

(d, J=8.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN) δ 146.8, 146.2, 135.2, 116.6, 115.3, 114.7, 111.3; FAB HRMS calcd for (M - BF_4^-) $C_7H_3N_3I$: 255.9372. Found: 255.9379.

4.7.3. 2-Trifluoromethyl-4-iodobenzenediazonium tetrafluoroborate (17c). According to the general procedure, 3.83 g (95%) of **17c** was produced from **1d** (3.0 g, 10.4 mmol). IR (KBr) 2290 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.71 (d, J=1.6 Hz, 1H), 8.66 (dd, J=1.6, 8.7 Hz, 1H), 8.46 (d, J=8.7 Hz, 1H); ^{13}C NMR (125 MHz, CD_3CN) δ 146.3, 141.1 (q, J_{C-F}=4 Hz), 136.2, 130.5 (q, J_{C-F}=36 Hz), 120.9 (q, J_{C-F}=275 Hz), 115.7, 111.8; FAB HRMS calcd for (M−BF_4^-) $C_7H_3N_2IF_3$: 298.9293. Found: 298.9292.

4.7.4. Propylaminomethylated polystyrene (1% cross-linked divinylbenzene copolymer, 7–90 mesh) (18).[14] A suspension of chloromethyl polystyrene: 1% divinylbenzene copolymer beads (54 g, 1.1 mequiv./g of chlorine, 70–90 mesh) and *n*-propylamine (350 mL) were degassed and heated at 70°C with stirring for 4 d in a screw cap tube. The polymer was transferred to a coarse sintered glass filter using CH_2Cl_2 and washed with CH_2Cl_2 (500 mL). The resin was thoroughly washed with the following protocol to remove noncovalently-bound material: the resin was stirred slowly with dioxane/2N NaOH (1/1, v/v, 500 mL) at 70°C for 30 min, and the solvent was removed by aspiration through a coarse sintered glass filter. This was repeated once more with dioxane/2N NaOH (1/1, v/v, 500 mL), twice each with dioxane/H_2O (1/1, v/v, 500 mL), DMF (500 mL), CH_3OH (500 mL), and finally benzene (500 mL). The resin was then washed with hot CH_3OH (800 mL), hot benzene (800 mL), hot CH_3OH (800 mL), hot CH_2Cl_2 (800 mL) and 400 mL of CH_3OH and dried in vauco to a constant mass to give 53.97 g.

4.8. General procedure for the polymer-supported triazene formation

To a chilled (0°C) suspension of propylaminomethyl polystyrene resin (**18**) and finely ground potassium carbonate (2 equiv.) in DMF–THF was added the diazonium salt with stirring at 0°C for 5 min and rt for 1 h. The suspension was transferred to a fritted filter using DMF and washed sequentially with 120 mL of the following solvents: CH_3OH, H_2O, CH_3OH, THF, CH_3OH. The loading procedure was repeated twice and the resin was dried in vacuo to a constant mass to give desired functional polymer beads.

4.8.1. 1-(4-Iodo-phenyl)-3-propyl-3-(benzyl-supported) triazene (19a). According to the general procedure, resin **18** (3.00 g), potassium carbonate (0.83 g, 6 mmol), and 4-iodo-benzenediazonium tetrafluoroborate (**17a**) (0.954 g, 3 mmol) in DMF–THF (25 mL–25 mL) gave desired polymer beads 3.72 g.

4.8.2. 1-(2-Cyano-4-iodophenyl)-3-propyl-3-(benzyl-supported) triazene (19b). According to the general procedure, resin **18** (4.00 g), potassium carbonate (1.1 g, 8 mmol), and 2-cyano-4-iodo-benzenediazonium tetrafluoroborate (**17b**) (1.37 g, 4 mmol) in DMF–THF (25 mL–25 mL) gave desired polymer beads 4.89 g.

4.8.3. 1-(2-Trifluoromethyl-4-iodophenyl)-3-propyl-3-(benzyl-supported) triazene (19c). According to the general procedure, resin **18** (3.00 g), potassium carbonate (0.83 g, 6 mmol), and 2-trifluoromethyl-4-iodo-benzenediazonium tetrafluoroborate (**17c**) (1.16 g, 3 mmol) in DMF–THF (25 mL–25 mL) gave desired polymer beads 3.60 g.

4.9. General procedure for the cleavage of polymer-supported triazene using iodomethane

A thick-walled oven-dried screw cap tube was charged with a suspension of the polymer-supported triazene and iodomethane. The tube was flushed with nitrogen, capped, and heated to 120°C for 24 h without stirring. The reaction mixture was cooled and passed through a fritted filter before the resin was introduced to hot CH_2Cl_2 (3×) to extract any residual product trapped in the polymer matrix. The product was purified by chromatography with hexane or a hexane/EtOAc mixture to give the product.

4.9.1. 1,4-Diiodobenzene (20a). According to the general procedure, 1-(4-iodophenyl)-3-propyl-3-(benzyl-supported) triazene (**19a**) (300 mg) in iodomethane (4.5 mL) gave the product (62 mg, 70% yield over three steps from Merrifield resin 1.1 mequiv./g).

4.9.2. 2-Cyano-1,4-diiodobenzene (20b). According to the general procedure, 1-(2-cyano-4-iodophenyl)-3-propyl-3-(benzyl-supported) triazene (**19b**) (300 mg) in CH_3I–CH_3CN (2.5 mL–2.5 mL) at 120°C for 18 h gave the product (33 mg, 35% yield over three steps from Merrifield resin 1.1 mequiv./g). IR (KBr) 2230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J=2.0 Hz, 1H), 7.62 (d, J=8.4 Hz, 1H), 7.57 (dd, J=2.0, 8.4 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 142.8, 141.2, 123.0, 118.2, 98.0, 93.1; HRMS calcd for $C_7H_3NI_2$: 354.8355. Found: 354.8352.

4.9.3. 2-Trifluoromethyl-1,4-diiodobenzene (20c). According to the general procedure, 1-(2-trifluoromethyl-4-iodophenyl)-3-propyl-3-(benzyl-supported) triazene (**19c**) (300 mg) in CH_3I–CH_3CN (2.5 mL–2.5 mL) at 110°C for 24 h gave the product (37 mg, 36% yield over three steps from Merrifield resin 1.1 mequiv./g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J=2.0 Hz, 1H), 7.74 (d, J=8.2 Hz, 1H), 7.53 (dd, J=2.0, 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 142.3, 136.8 (q, J_{C-F}=6 Hz), 135.8 (q, J_{C-F}=31 Hz), 122.0 (q, J_{C-F}=274 Hz), 93.4, 90.7; HRMS calcd for $C_7H_3F_3I_2$: 397.8276. Found: 397.8272.

4.9.4. 4-(Trimethylsilyl)ethynylbenzenediazonium tetrafluoroborate (21). To a cooled solution of $NOBF_4$ (5.75 g, 49 mmol, 1.05 equiv.) in 50 mL CH_3CN at −40°C was added dropwise over 15 min **2a** (8.86 g, 46.8 mmol) in 60 mL CH_3CN, and the mixture was stirred at −40°C for another 50 min. Ether was added to this mixture to precipitate the product. The precipitate was collected by filtration, washed with chilled ether, and dried in vacuo to give the product (11.5 g, 85%), a yellow solid. IR (KBr) 2290 cm^{-1}; ^{1}H NMR (400 MHz, CD_3CN) δ 8.46 (d, J=9.2 Hz, 2H), 7.90 (d, J=9.2 Hz, 2H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 137.3, 135.4, 133.8, 114.2,

109.6, 102.6, −0.5; FAB HRMS calcd for ($M-BF_4^-$) $C_{11}H_{13}N_2SiI$: 201.0848. Found: 201.0850.

4.9.5. 1-(4-(2-(Trimethylsilyl)ethynyl)phenyl)-3-propyl-3-(benzyl-supported) triazene (22). According to the general procedure, 4-(trimethylsilyl)ethynyl-benzenediazonium tetrafluoroborate **21** (5.65 g, 19.6 mmol), potassium carbonate (5.4 g, 39.1 mmol), and resin **18** (19.6 g) in DMF–THF (80 mL–80 mL) were allowed to react; the loading procedure was repeated twice (2.8 and 1.6 g of **21** were used, respectively) and the product was dried in vacuo to a constant mass to give desired polymer beads **22**, 23.96 g. IR 2153 cm^{-1}.

4.9.6. 1-(4-Ethynyl)phenyl)-3-propyl-3-(benzyl-supported) triazene (23). To a suspension of polymer-supported aryl(trimethylsilyl)alkyne **22** (23.96 g) and THF (9 mL/g of polymer) in an Erlenmeyer flask was added a solution of TBAF (50 mL, 50 mmol, 1.0 M in THF). The suspension was swirled periodically for 25 min. The polymer was then transferred to a pre-weighed fritted filter using THF, washed sequentially (ca. 30 mL/g polymer) with THF followed by CH_3OH, and dried to constant mass in a vacuum oven at 60°C for 36 h to give desired polymer beads 22.11 g. IR 3317, 2106 cm^{-1}.

Macrokans loading. Resin **23** was distributed into 50 Macrokans (300 mg each). The Macrokans were then split into five groups each containing 10 Macrokans. Each group was subjected to coupling with the corresponding aryl halides (**3a–e**) (Scheme 8) under the following procedure.

4.10. General procedure for cross-coupling of resin-bound terminal alkyne with aryl halide monomers

To a heavy-walled flask equipped with a nitrogen inlet was added 10 Macrokans. The flask was evacuated and back-filled with dry nitrogen 3×. In a separate flask, a catalyst solution consisting of tris(dibenzylideneacetone)dipalladium(0) (138 mg, 0.24 mmol), copper(I) iodide (46 mg, 0.24 mmol), and triphenylphosphine (252 mg, 0.96 mmol) in dry triethylamine (50 mL) was degassed and stirred at 70°C for 2 h. The supernatant from this catalyst solution was transferred via cannula to the reaction flask containing the Macrokans. To the mixture was added one of the aryl halides **3a–e** (15 mmol). The flask was sealed and kept at 65°C for 44 h with stirring. The Macrokans were collected and washed sequentially with 100 mL of the following solvents: CH_2Cl_2, DMF, 0.05 M solution of sodium diethyl dithiocarbamate in 99/1 DMF/diisopropylethylamine, DMF, CH_2Cl_2, CH_3OH, and dried in vacuo.

4.11. General procedures for the desilylation of polymer-supported dimers

To a suspension of 10 Macrokans containing polymer-supported aryl(trimethylsilyl)alkyne **24** and THF (50 mL) in an Erlenmeyer flask was added a solution of TBAF (20 mL, 20 mmol, 1.0 M in THF). The suspension was stirred for 30 min. The Macrokans were collected and washed sequentially (100 mL) with THF followed by CH_3OH, and dried in vacuo.

4.12. Polymer-supported trimer formation

The above Macrokans were re-split into five new groups by combining two Macrokans from each of the previous groups. Each of the five new groups was subjected to coupling with the previous five aryl halides (**3a–e**) by following the previous general procedure.

4.13. Traceless cleavage of resin

A suspension of polymer-supported trimer **25a–e** to **29a–e** in 4 mL of 10% conc. HCl/THF solution was treated with ultrasound in a sonicator bath at 50°C for 10 min. The resulting slurry was filtered and the resin residue was washed with EtOAc and THF. The organic phase was then washed with H_2O (2×), brine, and dried over Na_2SO_4. The crude product was purified by column chromatography (silica gel) with hexanes or a hexane/EtOAc mixture to give the desired product.

4.13.1. Trimethyl-(4-phenylethynylphenylethynyl)silane (4a).[6b] 30 mg (37% yield over five steps from Merrifield resin) of product was obtained. The yield was calculated according to the loading of original resin.

4.13.2. (3-Ethyl-4-phenylethynylphenylethynyl)trimethylsilane (4e). 36 mg (41% yield over five steps from Merrifield resin) of product was obtained. The yield was calculated according to the loading of original resin.

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