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Preparative Fluorous Mixture Synthesis of Diazonium-Functionalized Oligo(phenylene vinylene)s

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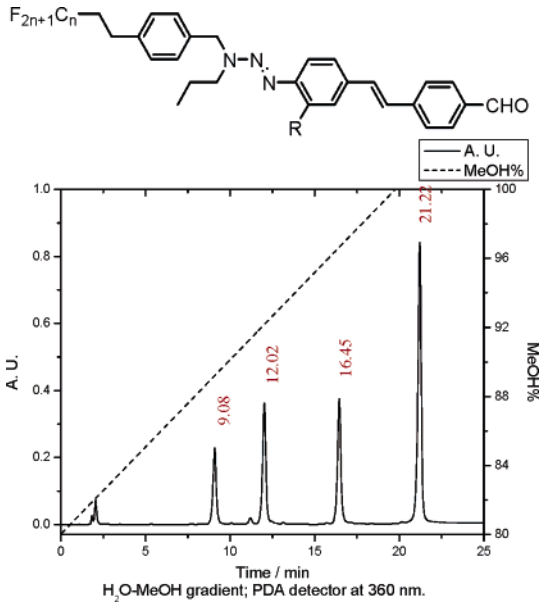

A series of building blocks for the synthesis of oligo(phenylene vinylene)s (OPVs) and hybrid oligomers were prepared, and alternating Heck coupling and Horner−Wadswoth−Emmons (HWE) reactions were used to couple the building blocks. Model studies were carried out to optimize the reaction strategies. The products were made to bear aryl diazonium functionalities that allow them to be used as surface grafting moieties in hybrid silicon/molecule assemblies. A library of OPV and hybrid oligomer tetramers was synthesized using fluorous mixture synthesis (FMS). The fluorous tags, which are secondary amines bearing different numbers of fluorine atoms, were synthesized and used as phase tags in mixture synthesis. The tags and substrates were anchored together by triazene linkages. The mixture synthesis was monitored by analytical HPLC on a fluorous column, and isolation of final OPV and hybrid oligomer tetramers was achieved by preparative HPLC. At the end of the FMS, after demixing, the tagged products were detagged by cleaving the triazene linkage and generating a series of aryl diazonium compounds. The fluorous tags could be recovered and reused. The NMR spectra of the 1-aryl-3,3-dialkyltriazenes are discussed.

Introduction

Combinatorial synthesis is a tool to generate libraries of materials[1] and catalysts.[2] A large number of new organic materials have been made combinatorially, such as dendrimers,[3] fluorescent dyes,[4] and conjugated oligomers.[5] Instead of making a huge number of similar molecules and taking great effort to find the ones of interest, nowadays combinatorial synthesis is shifting to make more focused libraries.[6] Organic molecules that possess conjugated systems have been widely studied for their electronic and optical properties.[7] In recent years, several conjugated oligomer libraries have been made, such as oligo(phenylene ethynylene)s,[8] oligothiophenes,[9] oligo(triacetylene)s, and oligo(phenylene triacetylene)s.[10]

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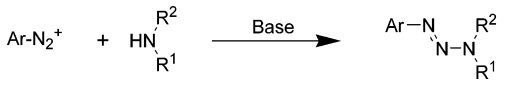
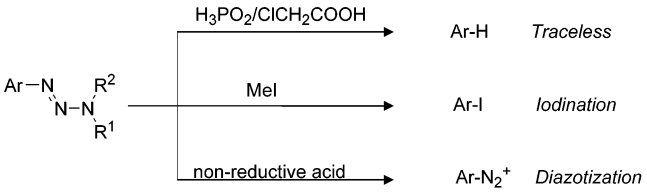
The poly(phenylene vinylenes) (PPVs) constitute a class of interesting conjugated systems. They show a range of electrical and optical properties[11,12] that make them useful as light-emitting diodes (LEDs), semiconductive or photoconductive devices, and in related applications.[13,14] However, the solubility of PPVs limited their processing and further development.[15] Although soluble PPVs have been made, the structure of PPV backbones cannot be finely tuned to achieve certain functions. Hence oligo(phenylene vinylene)s (OPVs) were developed as substitutes for PPVs because they have similar properties to PPVs and their structure can be finely controlled.[14] Changing functional groups on the backbone of an OPV will result in a change of its electrical and optical performance. Unfortunately, how the substituents will affect the physical properties of the OPV is not always predictable. Most new materials are found by screening. For conjugated oligomers, the sequence of repeat units also has an impact on their properties.[16] In this paper, we describe our effort to synthesize a library of OPV tetramers and hybrid oligomers on a preparative scale so that they can be screened in future work. To our knowledge, this is the first OPV library synthesized by combinatorial chemistry.

Molecules derived from aryl diazonium salts have been assembled on metal and semiconductor surfaces.[17,18]

SCHEME 1



SCHEME 2



When attached to surfaces, a direct M−C bond was formed. This attachment mode is complementary to the conventional thiolate "alligator clip" for the attachment of molecules to surfaces because the M−S−C moiety has one additional σ bond between the metal surface and the conjugate molecule, possibly hindering electronic transport between them. Also, the surface−molecule bonds formed by deposition of aryl diazoniums give monolayers on complementary technologically interesting surfaces, such as silicon and GaAs.[18] Hence, OPVs and hybrid oligomers bearing diazonium functionality became the targets of the combinatorial-based syntheses described here.

Combinatorial synthesis dramatically increases throughput by binding the substrates to a resin (for solid-supported combinatorial synthesis) or phase-tags (for solution-phase combinatorial synthesis). The linkage is important since it will have to tolerate all transformations and should be easily cleaved at the end of the synthesis. We chose the widely used triazene moiety as the linkage for both solid- and solution-phase combinatorial syntheses,[19−21] Scheme 1 shows the formation of a triazene linkage.

Since both the amine and diazonium group are protected at the same time, triazenes can serve as protection groups for both functionalities.[22] Triazenes have been converted to aryl diazonium salts, with further reactions carried out in situ,[23] and to other functionalities.[24] Scheme 2 shows the most common conversions of the triazene linker in combinatorial synthesis applications. These processes, while cleaving the triazene linkage, also release the linked products from their solid support (for solid-supported synthesis) or phase tag (for solution phase synthesis).

As shown in Scheme 2, for aryl triazenes (Ar-N=N-NR^{1}R^2), reductive cleavage of the triazene

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group gives aromatic hydrocarbons (Ar-H). This strategy has been used in natural product synthesis.[25] When used in combinatorial chemistry, the triazene group is displaced by a proton after treating the linkage with a reductive acid.[26] This is called traceless cleavage.[21] Heating a molecule containing the triazene moiety in iodomethane converts it into an aryl iodide, which provides an active site for further chemistry.[8] A non-reductive acid, such as HOAc or trifluoroacetic acid (TFA), cleaves the same bond formed during synthesis of triazene, giving back the aryl diazonium salt and the amine.[27,28] Although there are a few cases in the combinatorial literature of the conversion of triazene groups to synthesize aryl diazonium salts,[27] this conversion was limited to the regeneration of diazonium functionalized resins.[29,30] Our work is the first to make aryl diazonium libraries.

In applying our earlier work[8c] to the synthesis of OPVs, we found that the use of solid-phase organic synthesis (SPOS) in combinatorial synthesis suffered from several known bottlenecks, such as unfavorable heterogeneous reaction kinetics, limited resin loading capacity, the need for a large excess of reagent that cannot always be recovered, and the necessity for releasing the product from the resin in order to monitor the reaction progress. Solution-phase combinatorial chemistry has become a viable alternative to SPOS, since it has advantages of both homogeneous reaction kinetics and combinatorial high-throughput[31] and includes soluble polymer-supported organic synthesis (SPSOS),[32] biphasic catalysis,[33] ionic liquids,[34−36] fluorous synthesis,[37] phase extraction,[38] precipitation auxiliary labels,[39] and others.

Fluorous technologies for high-throughput organic synthesis have been in development since the mid-1990s.[40] Fluorous synthesis is similar to solid-phase synthesis in concept,[37] yet it is more like traditional solution phase synthesis in practice. In the earlier years of fluorous mixture synthesis (FMS),[41] purification of products was done by fluorous extraction.[42] A significant advancement in FMS technology was made when fluorous reverse phase silica gel (Fluoro*Flash*) began to be used for separation.[43] Fluoro*Flash* HPLC columns have C_8F_{17} functionalized silica gel as the stationary phase. Therefore, the mobility of a molecule on this silica gel depends on the number of fluorine atoms it possesses. In a HPLC separation of a mixture of different fluorous compounds, molecules with increasing fluorous content have longer retention times. The use of fluorous HPLC to isolate products allows light fluorous synthesis with fewer fluorines (F% < 40 wt %).[44] The compounds that contain no fluorine atoms are treated as inert and have no interaction with the Fluoro*Flash* column.

FMS can be done in one-pot consecutive reactions, which means mixed components are taken through a multistep synthesis and separated at the end of the synthesis. If we begin with a specific number of tagged substrates, the same number of products is generated in one-pot FMS. The library size one-pot FMS can generate is limited. But the process is good for the synthesis of a more focused library, such as preparative combinatorial synthesis.

Combining FMS with split-parallel synthesis techniques, larger libraries with more diversity can be synthesized.[45] In this technique, intermediates from FMS sequences could be split into several portions and different reactions are carried out on each portion.

At this stage, FMS addresses many of the SPOS problems since reactions are done homogeneously; due to the lipophilicity of the perfluoroalkyl chains, the solubility of tagged substrates is equal to or better than their untagged counterparts.[40] In addition, reaction scale-up is similar to ordinary solution-phase organic synthesis, optimization of reaction protocols can be easier than SPOS, the fluorous tags are stable in common organic reactions and have minimal effect on the reactivity of the tagged substrates, a large excess of reagents is not required, and TLC, NMR, IR, and GC−MS can be used to monitor the reaction process without cleaving the products from their support.

There are five stages involved in FMS,[41] as shown in Scheme 3 for our synthesis of OPV tetramers and hybrid oligomers. (1) Tagging: a series of diazonium functionalized aryl iodides (building blocks 1−4 (BB1−BB4)) are tagged *separately* with a corresponding number of secondary amine fluorous tags.[46] (2) Mixing: the tagged substrates are mixed. (3) Synthesis: the OPV oligomers are extended by alternating Heck coupling and HWE reactions. (4) Demixing: the mixture of tagged OPV tetramers are separated by fluorous HPLC; since the fluorine content is known, the order of separation can be predicted. (5) Detagging: the isolated products with tags are converted to the final diazonium salt OPV tetramer products by *separately* removing their tags.

If we have n_1 R^1s, n_2 R^2s, n_3 R^3s and n_4 R^4s, by the split-parallel technique,[45] a library of $n_1 \times n_2 \times n_3 \times n_4$ compounds could be made.

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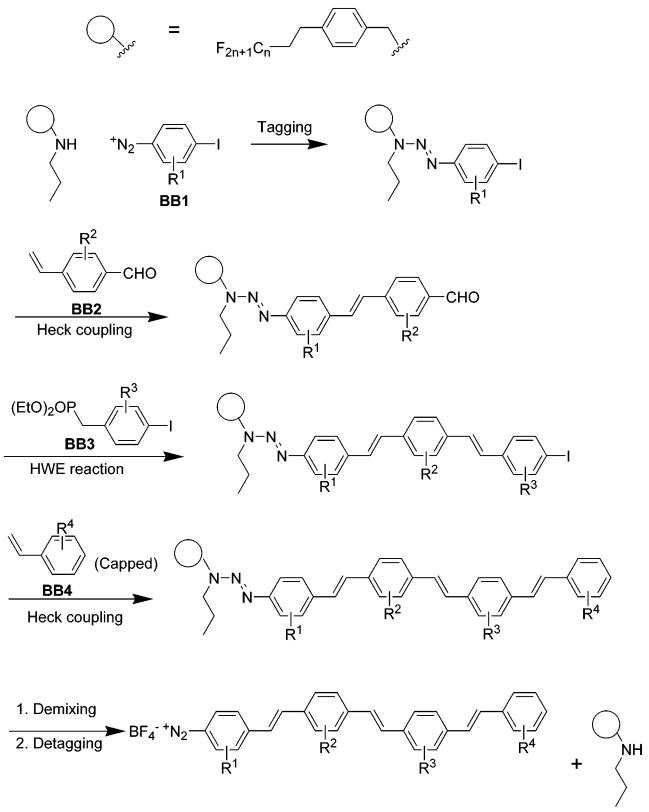
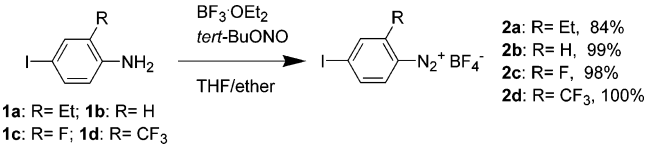
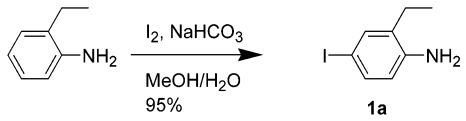
SCHEME 3



SCHEME 4



SCHEME 5



Results and Discussion

Synthesis of Fluorous Tags. The synthesis of the fluorous tags began with formation of the diazonium salts **2a**, **2b**,[47] **2c**, and **2d**,[48] achieved by treating the corresponding substituted anilines under Doyle−Bryker conditions,[49] as shown in Scheme 4.

Except for **1b**, which is commercially available, the 4-iodoanilines **1a**,[50] **1c**,[51,52] and **1d**[52] were prepared by iodination of substituted anilines. As an example, the procedure for synthesizing **1a** is shown in Scheme 5.

The chosen tag is composed of a perfluoroalkyl chain and a secondary amine connected by a phenylene group. An ethylene spacer was placed between the perfluoroalkyl chain and the benzene ring and a methylene spacer between the amine and the benzene ring to minimize effects of the perfluoroalkyl chain on the chemistry of the substrate.

Scheme 6 shows the synthesis of the tag precursor compound **4**. It was made in two steps quantitatively from 4-bromobenzyl bromide: amination of the benzyl bromide using *n*-propylamine, followed by protection of the benzylamine. In the first reaction, a large excess of *n*-propylamine had to be used to limit tertiary amine and quaternary ammonium salt formation. The excess *n*-propylamine was recovered and reused in subsequent amination reactions.

Heck coupling between bromide **4** and 1*H*,1*H*,2*H*-perfluoroalkenes required an effective palladacycle catalyst[53] which generally proved to be superior to $Pd(OAc)_2$. Its structure and synthesis is shown in Scheme 7. Scheme 8 shows the synthesis of the fluoro tags in *separate* reaction pots. Hydrogenation of the coupled alkenes (**5a**−**d**) in *separate* reaction pots was done by a modified literature procedure.[46] Removal of the Boc groups on **6a**−**d** in separate reactions gave secondary amines **7a**−**d** as fluorous tags for aryl iodides. Each fluorous tag was synthesized separately and was used to tag different aryl iodides separately.

Scheme 9 shows tagging of each of the aryl iodides in *separate* pots. Each aryl diazonium salt **2** was tagged with a different fluorine-containing tag **7**. Treating the solution of the diazonium salt and the amine with base in acetonitrile completed the tagging; for the longer perfluoroalkyl chain amines (**7c** and **7d**), THF had to be added to dissolve the amines.

Synthesis of Other Building Blocks. Our strategy for growing OPV and hybrid oligomers was to use alternating Heck and HWE reactions. Building blocks were made separately, and put together sequentially to make oligomers. Each internal building block had two active sites, one for Heck coupling and one for HWE reaction. The terminal building blocks had one active site for either one of the two key reactions. The first building block will be linked to a fluorous tag. The last building block will serve to endcap the oligomer, so as to prevent further growth of the chain. The diversity of the library is achieved by substituting various functional groups on the building blocks.

To demonstrate this strategy, we made a library of *p*-OPV tetramers and hybrid oligomers. The first building block (BB1 in Scheme 3) of the tetramer is the tagged substrate **8a**−**d**, which contains aryl iodides as the Heck coupling candidates. The second building block (BB2 in Scheme 3) had a vinyl group to couple with the tagged aryl iodide and an aldehyde group for further oligomer growth. Four BB2s (**9**, **12**, **16**, and **19**) were prepared, bearing different functionalities.

The simplest BB2 is 4-vinylbenzaldehyde (**9**).[54] As shown in Scheme 10, both 4-bromostyrene and 4-chlorostyrene were used to prepare **9** via a Grignard reagent.[55]

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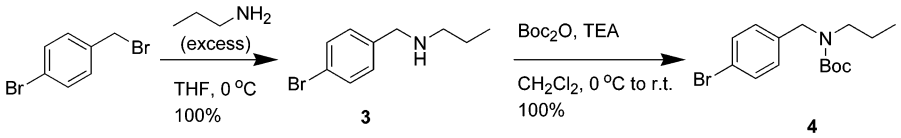
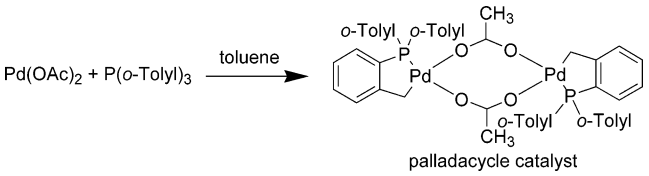
SCHEME 6



SCHEME 7



BB2 **12** has two ethyl groups to increase solubility of the oligomers (Scheme 11). Its synthesis began from 4-ethylacetophenone. Reduction of the ketone followed by iodination of 1,4-diethylbenzene gave **10**.[56] Monolithiation of **10** and quenching the aryllithium with anhydrous DMF afforded benzaldehyde **11**. A Stille coupling of **11** with vinyltributyltin[57] gave **12**.

2,5-Dialkoxy groups on OPV and PPV backbones are known to not only increase the solubility of the derivatives but also provide better photoreactivity and photoconductivity properties.[7,14] BB2 **16** is such a building block, which was made in four steps from *p*-hydroquinone (Scheme 12). Dibutylation of the hydroquinone dianion gave 1,4-dibutoxybenzene **13**, which was iodinated to give **14**.[58] Preparation of **15** followed Yu's procedure.[13] Compound **16** was made from **15** via a Stille coupling.

3,4-Ethylenedioxylthiophene (EDOT) has attracted interest as a building block for conducting polymers and oligomers. Since it is a derivative of thiophene, it shares thiophene's electronic and optical properties[59] and is superior to thiophene in that it is more stable and easier to process.[60] To increase the diversity of the conjugated oligomer library, we chose to make hybrid oligomers of EDOT and OPV. Synthesis of EDOT containing BB2 **19** (Scheme 13) began with commercially available EDOT. The aldehyde **17** was prepared according to a literature procedure.[61] Bromination of **17** gave **18**. A Stille coupling reaction converted **18** to BB2 **19**.

The third building block (BB3 in Scheme 3) in oligomer growth has a benzyl phosphonate group for HWE reaction, and an aryl iodide for the Heck coupling. Three kinds of BB3 were prepared for the library. The simplest BB3 **21** (Scheme 14) has no other substituents. Synthesis of **20**[62] and **21**[63] followed literature procedures.

Another BB3 **25** bears two ethyl groups to solubilize oligomers (Scheme 15). It was synthesized from **10** in four steps. Benzoic acid **22** was made from diiodide **10** via lithiation followed by a CO_2 quenching; it was reduced to the benzyl alcohol **23** in high yield. The benzyl alcohol was converted to the benzyl bromide **24**. **24** was then converted to **25** via a Michaelis–Arbuzov reaction[64,65] in high yield. The same strategy was used to synthesize 2,5-dibutoxy-functionalized BB3 **28** (Scheme 16).

All the transformations in Scheme 16 have quite high yields and nicely characterized products except for **27**, which is unstable in the solid state. As soon as solid **27** formed in air, the white crystal began to smoke and become dark. In solution **27** was reasonably stable. Conversion of **27** to **28** must be done before **27** decomposes and yields as high as 97% were obtained.

The last building block, BB4 (see Scheme 3) in the OPV tetramer synthesis, is a group of functionalized styrenes. Since BB4 has no functional groups for HWE reaction, the oligomer growth would be endcapped after adding BB4. Except for styrene, which is commercially available, the other functionalized styrenes were synthesized.

The syntheses of BB4 **30**[66] and **31**[67] are shown in Scheme 17. **30** was made by a Negishi coupling[68] from **29**.[69] 4-Nitrostyrene **31** was synthesized according to a literature procedure for dehydration.[67]

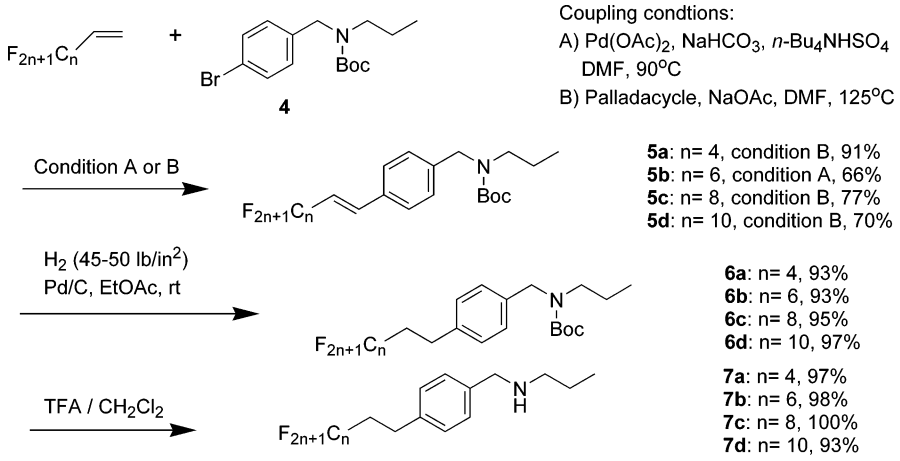
Scheme 18 shows synthesis of a BB4, 1,3-dinitrostyrene (**34**). 1,3-Dinitro-5-bromobenzene (**32**) was made by bromination of 1,3-dinitrobenzene, following a modified literature procedure.[70,71] Stille- and Negishi-type reactions were tried to make **34** from **32**, neither of which gave good yields because of incomplete conversion of **32**. Therefore **32** was subjected to halogen exchange to give **33** using the recently reported procedure by Buchwald.[72] Negishi coupling on **33** gave **34** with complete consumption of **33**.

Table 1 is a summary of the building blocks synthesized. For the planned combinatorial synthesis of an OPV tetramer and hybrid oligomer library, we have prepared the following: four fluorous tags, four BB1s, four BB2s, three BB3s, and four BB4s. If the split-parallel techniques were fully applied, the total library size could be $4 \times 4 \times 3 \times 4 = 192$.

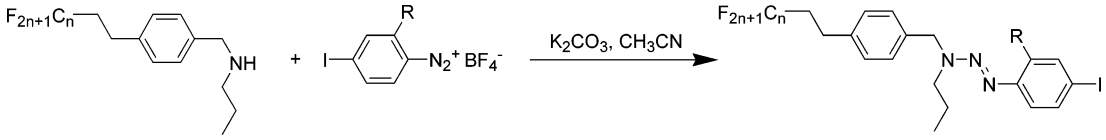
Model Studies. Reaction optimization is crucial for combinatorial syntheses. For SPOS, the optimization of reaction yield is necessary. For solution-phase combina-

(55) Leebrick, J. R.; Ramsden, H. E. *J. Am. Chem. Soc.* **1958**, *23*, 935–936.
(56) Yao, Y. Ph.D. Thesis, University of South Carolina, Columbia, SC, 1998.
(57) Seyferth, D.; Stone, F. G. A. *J. Am. Chem. Soc.* **1957**, *79*, 515–517.
(58) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281–5286.
(59) Roncali, J. *Chem. Rev.* **1992**, *92*, 711–738.
(60) Sankaran, B.; Reynolds, J. R. *Macromolecules* **1997**, *30*, 2582–2588.
(61) Mohanakrishnan, A. K.; Hucke, A.; Lyon, M. A.; Lakshmikantham, M. V.; Cava, M. P. *Tetrahedron* **1999**, *55*, 11745–11754.
(62) Sloviter, H. A. *J. Am. Chem. Soc.* **1949**, *71*, 3360–3361.
(63) Kung, H. F.; Lee, C.-W.; Zhuang, Z.-P.; Kung, M.-P.; Hou, C.; Plossl, K. *J. Am. Chem. Soc.* **2001**, *123*, 12740–12741.
(64) Arbuzov, A. E. *J. Russ. Phys. Chem. Soc.* **1906**, *38*, 687.
(65) Michaelis, A.; Kaehne, R. *Ber.* **1898**, *31*, 1048.
(66) Murata, M.; Kawakita, K.; Asana, T.; Watanabe, S.; Masuda, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 825–830.
(67) Zhuo, J.-C.; Wyler, H. *Helv. Chim. Acta* **1999**, *82*, 1122–1134.
(68) Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821–1823.
(69) Jalil, A. A.; Kurono, N.; Tokuda, M. *Tetrahedron* **2002**, *58*, 7447–7484.
(70) Andrievskii, A. M.; Gorelik, M. V.; Avidon, S. V.; Al'tman, E. S. *Russ. J. Org. Chem.* **1993**, *29*, 1519–1524.
(71) Jian, H.; Tour, J. M. *J. Org. Chem.* **2003**, *68*, 5091–5103.
(72) Klapars, A.; Buchward, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844–14845.

SCHEME 8



SCHEME 9



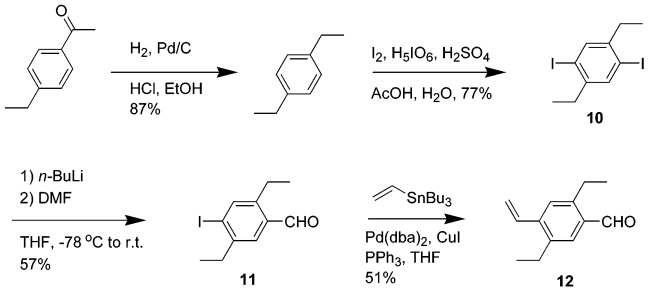
7a: n= 4
7b: n= 6
7c: n= 8
7d: n= 10

2a: R= Et
2b: R= H
2c: R= F
2d: R= CF_3

8a: n= 4, R= Et, 73%
8b: n= 6, R= H, 100%
8c: n= 8, R= F, 84%
8d: n= 10, R= CF_3, 99%

SCHEME 10

SCHEME 11



torial synthesis, even though it is not as important as for SPOS, model studies are still necessary to test the reaction conditions.

Unfortunately, there are no universal coupling conditions that will work for every imaginable substrate. For the attachment of a BB2 or BB4 to a BB1 or BB3 substrate using Heck coupling conditions, we always used $Pd(OAc)_2$ as the catalyst, but there are two ligand choices. One is the traditional ligand P(*o*-tolyl)$_3$. The other is a ligand-free process using a tetrabutylammonium salt as a phase-transfer catalyst. Usually either of these two conditions could work. But there were some cases in which one of them worked much better than the other. Thus, the model studies proved essential. It is even more important to do model studies for the attachment of a BB3 to a BB2 using HWE reaction. Only the proper combination of base and solvent could make the reaction efficient.

The model studies were expected to provide useful information for both solid-phase and solution-phase combinatorial synthesis. In the model studies, the triazene linkage and fluorous tags were simplified to a 3,3-diethyltriazene group. The yields were obtained using a ~1:1 ratio of building blocks. The purpose of these model studies was to determine if side reactions took place. We expected that the yields would be higher in the combinatorial synthesis because an excess of one coupling building block would be used.

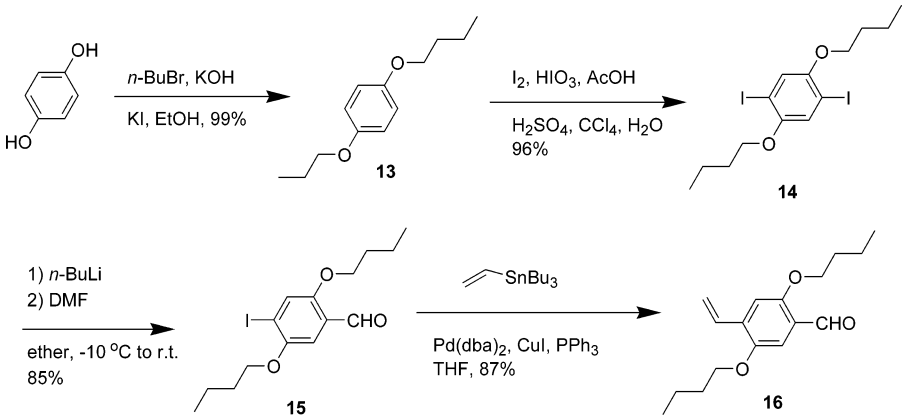
The 3,3-diethyltriazene compounds, as models of BB1, were synthesized from the aniline **1a** (Scheme 19) or from the diazonium salt **2b**−**d**. Discussion about their NMR spectra can be found below.

The first OPV trimer **37** (Scheme 20) was synthesized by Heck coupling of **35b** and **9**, followed by HWE reaction with **21**. The poor solubility of **37** made further reaction impractical. This model study established that OPV trimers must bear solubilizing groups to enable further functionalization.

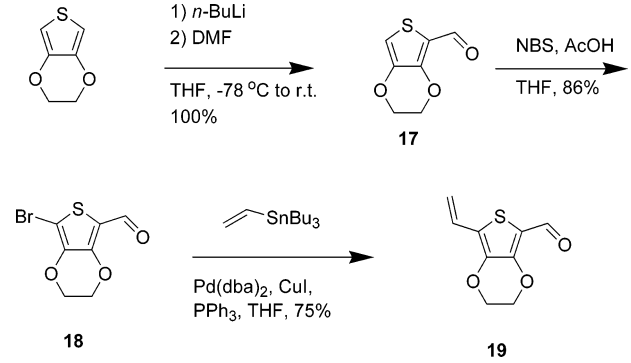
The two ethyl groups on the backbone of OPV trimer **38** dramatically increased its solubility. Compound **38** was synthesized from HWE reaction of **36** with **25** (Scheme 21). It was extended to tetramer **39**, which also had good solubility.

Dimer **40** was made from **35b** and **16** (Scheme 22). But Heck coupling of **16** with aryl iodides always gave 1,1- and *cis*-olefin isomers. The best yields for Heck coupling between such substrates was 30−40% both in our hands and in the literature.[13] This dimer could not be used in the combinatorial synthesis process until further optimization was completed.

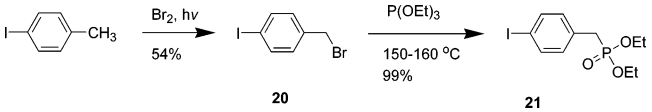
SCHEME 12



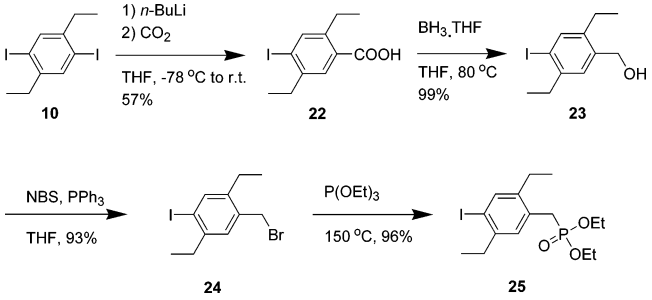
SCHEME 13



SCHEME 14



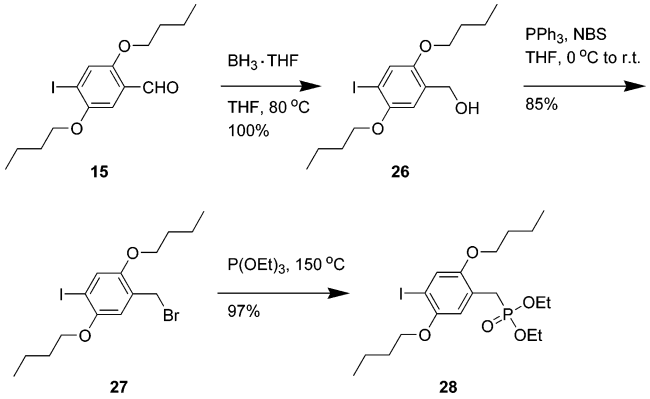
SCHEME 15



A model study of EDOT-based BB2 **19** is shown in Scheme 23. Heck coupling of aryl iodide **35b** and **19** gave **41**. The yield (72%) was better than the reactions between aryl iodides and styrenes. However, under common HWE conditions (NaH in DME), reaction between dimer **41** and BB3 **21** did not give clean trimer product **42**. After trying different combinations of bases (*t*-BuOK and NaH) and solvents (DME, THF, and DMF), we found that NaH in DMF gave the best yield. The electron-rich EDOT-containing hybrid oligomers, such as trimer **42**, are unstable in air and sensitive to acid.

The presence of cyano groups on the vinylene linkage of the electron-rich OPV backbone greatly lowers the electronic band gap of the oligomer.[73] It is believed that incorporation of 2,5-dialkoxyphenylene, EDOT, and cyano vinylene groups in one conjugated oligomer backbone could make a material with good optical and electrical characteristics.[74] The model study shown in Scheme 24 was done to make such an oligomer, **45**. Dichloromethylation of 1,4-dibutoxybenzene gave **43**, which was subjected to a substitution reaction to afford dicyano compound **44**. A Knoevenagel condensation between **44** and **19** gave hybrid oligomer **45**. Compound **45** is sensitive to acid, light, and air.

SCHEME 16



The last model study carried out was to make a diazonium-functionalized trimer **48** (Scheme 25). This trimer has an ethyl group for solubility, which came from the BB1 **35a**. Heck coupling of **35a** with **9**, followed by HWE reaction with **21**, gave triazene trimer **47**. The triazene group was converted to the diazonium salt with HBF_4. The triazene acted as a protected form of the diazonium group in these processes. With the information provided to us by the model studies we moved on to the combinatorial syntheses of the OPVs.

Mixture Synthesis. For the two basic coupling reactions involved in our synthetic strategy (Heck reaction and HWE reaction), similar substrates require similar reaction conditions. Using mixture synthesis technology to grow OPV oligomers takes advantage of this fact. Four reactions are done in one pot. The following syntheses were carried out by starting with *mixtures* of four substrates **8a**−**d**. Each coupling reaction generated a

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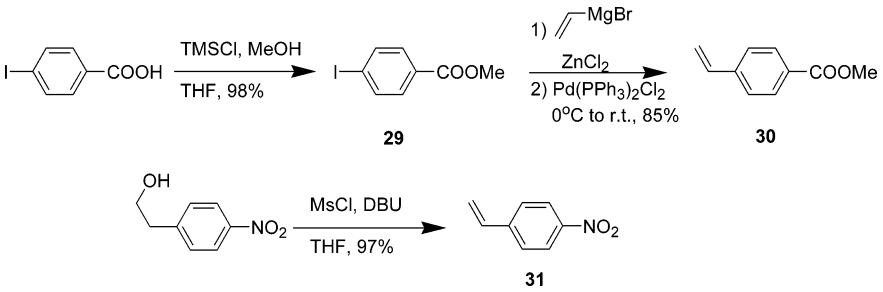
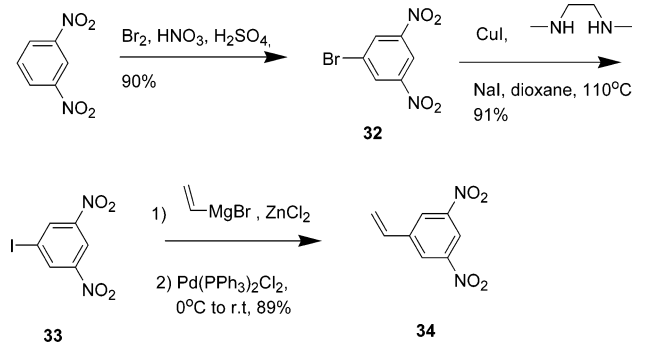
(74) Pepitone, M. F.; Hardaker, S. S.; Gregory, R. V. *Chem. Mater.* **2003**, *15*, 557−563.

SCHEME 17



SCHEME 18



mixture of four fluoro-tagged products. Each mixture synthesis reaction was monitored by analytical HPLC on a Fluoro*Flash* column. The compounds with no fluorous content, which include excess reagents, building blocks and side products, had no interaction with the fluorous column and eluted first. The intermediate mixtures were usually neither isolated nor characterized. Therefore the yields of the individual reaction steps were not calculated. Only the final products were isolated by preparative HPLC on a Fluoro*Flash* column. After isolation, the tetramers with fluoro tags were fully characterized, and overall yields were calculated, while further detagging followed in some cases.

The mixture of **8a**−**d** coupled with **9** to afford a mixture of four fluoro-tagged dimers **49a**−**d** (Scheme 26). The mixture of **49a**−**d** was split into several portions. One portion was extended to trimers **50a**−**d** by a HWE reaction. The final stage of OPV tetramer growth was a Heck coupling with an endcapping styrene derivative **31**. The mixture of four tetramers was isolated by preparative HPLC. To prove that the correct intermediates were generated in the mixture synthesis, a small amount of **49b** was isolated from the mixture of **49a**−**d** by preparative HPLC. Compound **49b** was also synthesized *separately* by Heck coupling of **8b** and **9** under the same conditions. These two products were identical by NMR spectroscopic analysis.

The mixture of trimers **50a**−**d** was split to two portions. One portion was extended to tetramers with a nitro terminus **51a**−**d** (Scheme 26). The other portion coupled with the carbomethoxy styrene derivative **30** to give a tetramer mixture of **52a**−**d** (Scheme 27).

Another portion of the dimer mixture **49a**−**d** was extended to dibutoxy-functionalized trimers **53a**−**d**, which were further extended to the tetramer mixture **54a**−**d** by coupling with *p*-nitrostyrene (Scheme 28).

The third portion of **49a**−**d** was subjected to a HWE reaction with building block **21** (Scheme 29). The trimers **55a**−**d** have higher solubility than their untagged counterparts because of the lipophilicity of the tags (perfluoroalkyl chains). Analytical HPLC showed four nicely distributed product peaks. However, after extension to the tetramers **56a**−**d**, the solubility of the mixture was too low to be isolated by preparative HPLC.

Scheme 30 shows the synthesis of hybrid oligomers of phenylene-vinylene and the EDOT derivative. The mixture **8a**−**d** coupled with **19** to give dimers **57a**−**d**. Extending these dimers to trimers **58a**−**d** followed the conditions of the model study from Scheme 24. The trimers were extended to tetramers **59a**−**d** by coupling with *p*-nitrostyrene (**31**). The solubilities of EDOT containing hybrid oligomers were much higher than those of the OPVs. Even without any solubilizing group on the oligomer backbone, the tetramers were easily dissolved in common organic solvents.

The trimer mixture **58a**−**d** was split into three portions. In addition to the extension to a mixture of tetramers with a nitro terminus, as shown in Scheme 30, the trimer mixture was also coupled with styrene or carbomethoxy styrene derivative **30** to give other tetramer mixtures (Scheme 31).

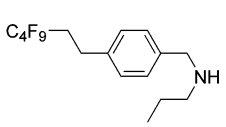
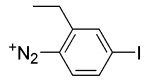
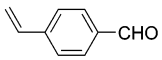
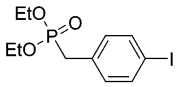
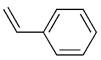
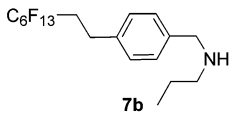
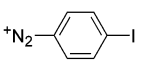
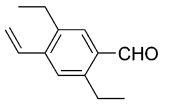
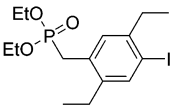
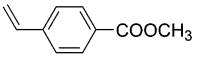
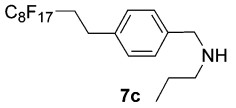
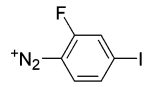
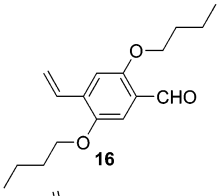
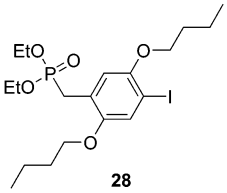
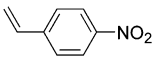
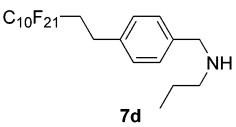
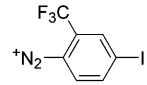
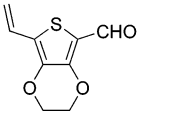
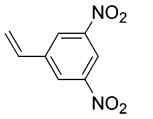
The EDOT-containing tetramers **59a**−**d**, **60a**−**d**, and **61a**−**d** were not successfully separated by using H_2O−CH_3CN or H_2O−MeOH solvent mixtures because of their poor solubility in these systems. The preparative separation could however be achieved by using a THF-based system. Except for **59d**, each isolated fraction was a mixture of desired product and polymers. The EDOT-containing hybrid oligomers are known to be unstable because of their low oxidation potentials.[75] The free radicals generated by THF hydroperoxides during separation may have contributed to the polymerization of EDOT-containing products, although mass spectrometric analysis verified the presence of the desired tetramers.

The preceding mixture syntheses all generated mixtures of OPV tetramers (or hybrid oligomers with EDOT). The final products were isolated at the end of synthetic route by preparative HPLC. The isolated tetramers with their tags were then detagged *separately* by HBF_4 to give diazonium salts.

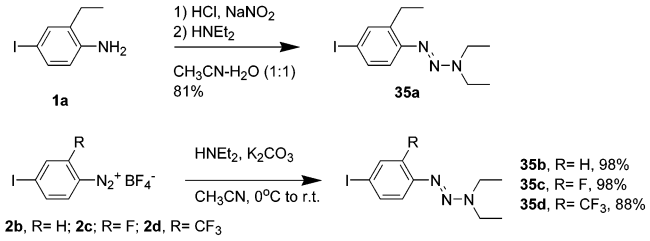
HBF_4 was used to cleave the tag and give the aryl diazonium salt because the diazonium salts with a BF_4^- counterion are more stable than other forms. As shown in Scheme 32, the tetramer with fluoro tag **51b** was treated with HBF_4·OMe_2 complex. The diazonium functionalized tetramer **62b** was generated in 60% yield from

(75) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481−494.

TABLE 1. Building Blocks for OPV Library Synthesis

Fluorous Tags	Tagged Diazonium Salt (BB1)	Heck Coupling Candidate (BB2)	HWE Reaction Candidate (BB3)	Heck Coupling Candidate (BB4)
 **7a**	 **2a**	 **9**	 **21**	
 **7b**	 **2b**	 **12**	 **25**	 **30**
 **7c**	 **2c**	 **16**	 **28**	 **31**
 **7d**	 **2d**	 **19**		 **34**

SCHEME 19



51b, and the fluorous tag **7b** was recovered in 82% yield from **51b**. The overall yield of the diazonium salt **62b** was 30% for four steps (from **8b**).

The diazonium salts, even in their BF_4^- form, decomposed slowly during storage at −20 °C. Thus, they were generally stored in their protected triazene form, as fluorous tagged tetramers. In-situ cleavage of a triazene linkage and assembly of the resulting diazonium salt will be performed on metallic or semiconducting surfaces. This is under study in our laboratory, as is the screening of the products.

Table 2 is a summary of OPV tetramers synthesized by FMS and isolated by preparative HPLC.

UV−vis of the OPV Tetramers. The normalized UV−vis absorption spectra of selected fluoro-tagged OPV tetramers are shown in Figure 1. All of the fluoro-tagged tetramers show broad and strong absorption in the visible region.

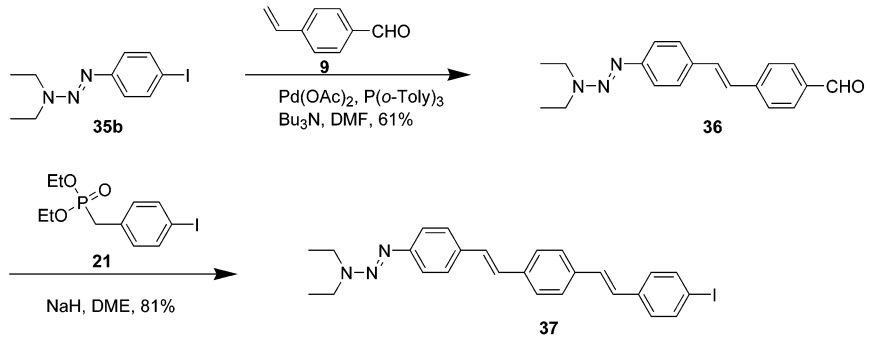
The diethyl functionalized OPVs (**51b**−**d, 52c,d**) show absorption maximum at 401−408 nm. Compared to OPV tetramers of similar substitution, the end groups (triazene and nitro/carboxyl) red-shifted the absorption maxima about 20 nm.[76] The absorption maximum of dibutoxy functionalized OPVs (**54b** and **54c**) was red-shifted about 30 nm to 440 nm, compared to the OPV tetramers of similar substitution.[77] The absorption maximum of the EDOT-containing hybrid oligomer **59d** was further red-shifted to 465 nm. This value is between that of the OPVs and the alternating copolymers made using EDOT and 1,2-vinylene as repeat units.[78]

NMR Spectra of 1-Aryl-3,3-Dialkyltriazenes

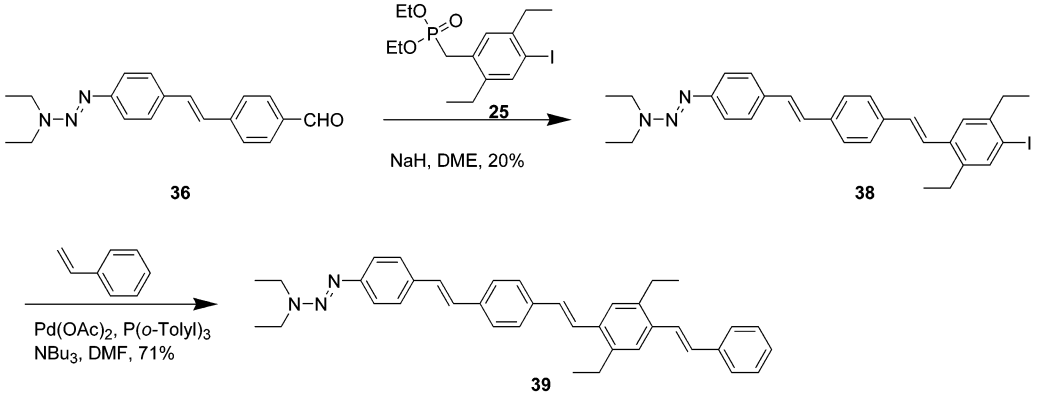
Triazene [diazoamino group, $R^1-N1{=}N2-N3(R^2R^3)$] is the fundamental active group in a range of applications, from antitumor medicines[79,80] to molecular electronics.[81] The triazene moiety is a good chromophore, with a deep color in solution and a low melting point. It is known that the triazene group tends to adopt a trans configuration about the N1=N2 double bond in the ground state.[82] However, the N1=N2 conformation is highly dependent on the electronic and steric effects of

(76) Schenk, R.; Gregorius H.; Meerholz, K.; Heinze, J.; Müllen, K. *J. Am. Chem. Soc.* **1991**, *113*, 2634−2647.
(77) Wang, S.; Oldham, W. J. Jr.; Hudack, R. A., Jr.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695−5709.
(78) Fu, Y.; Cheng, H.; Elsenbaumer, R. L. *Chem. Mater.* **1997**, *9*, 1720−1724.
(79) For a review about triazene in medicinal chemistry: *Triazenes: Chemical, Biological and Clinical Aspects*; Giraldi, T., Connors, T. A., Carter, G., Eds.; Plenum: New York, 1990.
(80) Carvalho and co-workers have published a series concerning triazene drug metabolites; Part 15: Carvalho, E.; Iley, J.; Perry, M. d. J.; Rosa, E. *Pharm. Res.* **1998**, *15*, 931−935.
(81) Martin, P. J. In *An Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press: New York, 1995; Chapter 6.
(82) The conclusion is from: (a) Benson, F. R. *The High Nitrogen Compounds*; John Wiley & Sons: New York, 1984; pp 49−50. Experimental support: (b) Kondrashev, Y. D. *Kristallografiya* **1961**, *6*, 515.

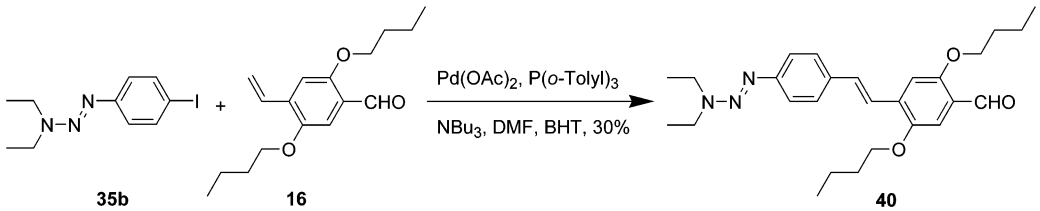
SCHEME 20



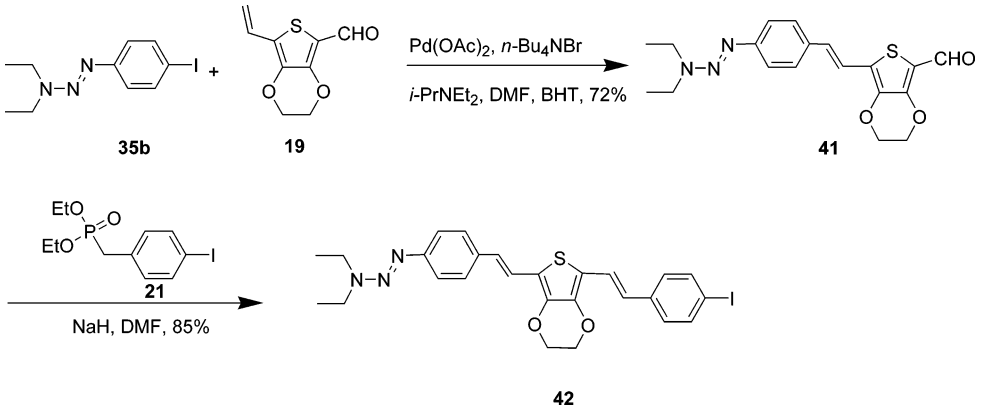
SCHEME 21



SCHEME 22



SCHEME 23



the substituent groups.[83] The reversible *E*/*Z* isomerization can be thermally or photochemically induced, and the interconversion process can be catalyzed by acid or base and solvents can have effects on the relative rates of interconversion.[84,85] In addition to the possible N1=N2 isomerism, rotation about the N2−N3 bond makes the system more complicated. The rotational isomerism about the N2−N3 bond has been observed experimentally,[86] and is supported by calculations.[87] The ^{1}H NMR

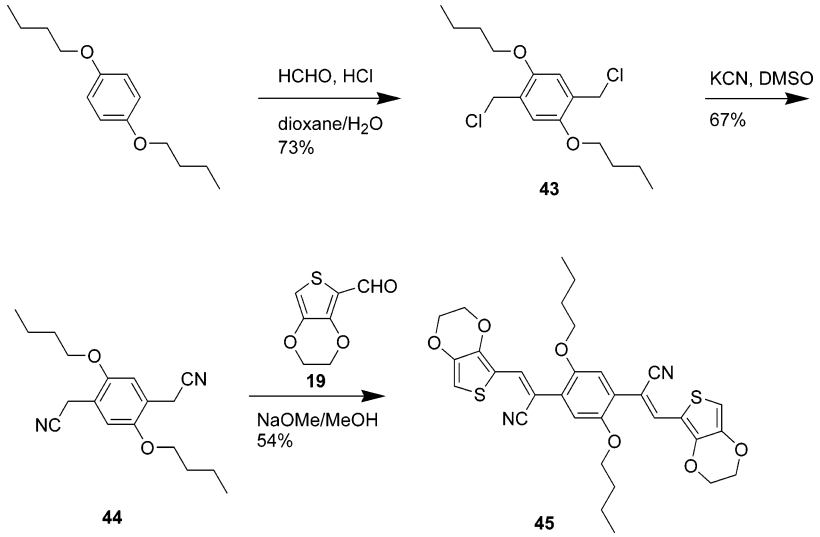
(83) Howell, J. M.; Kirschenbaum, L. J. *J. Am. Chem. Soc.* **1976**, *98*, 877−885.

(84) Barra, M.; Chen, N. *J. Org. Chem.* **2000**, *65*, 5739−5744 And references about N3 sp^3 center inversion therein.

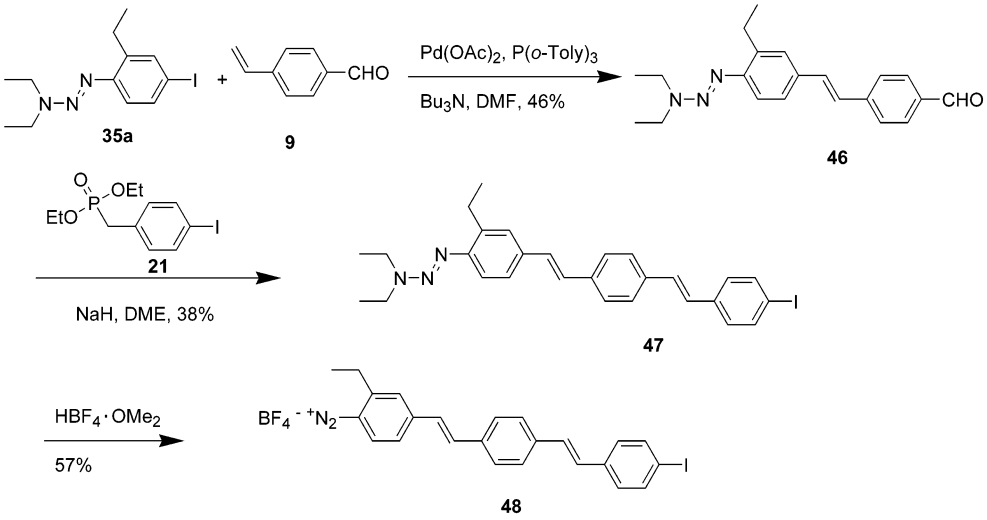
(85) Chen, N.; Barra, M.; Lee, I.; Chahal, N. *J. Org. Chem.* **2002**, *67*, 2271−2277.

(86) LaFrance, R. J.; Manning, H. W.; Vaughan, K. *J. Org. Chem.* **1985**, *50*, 2229−2232.

SCHEME 24



SCHEME 25



and ^{13}C NMR signal of substituents on N3 are usually significantly broadened, evidence of restricted N2−N3 bond rotation. In earlier years, the origin of the rotational barrier was ascribed to partial π-bond formation between N2 and N3.[88] Recent studies considered the isomerism to originate from the inversion of the N3 sp^3 center, since the rotation around N2−N3 has a relatively high energy barrier.[84] In fact, both of these factors could contribute to the rotational isomerism. Which energy barrier is lower depends on the electronic and steric effect of the substituents.

As a result of the isomerism, a triazene compound can exist as a mixture of a number of rotamers. For each *E*/*Z* isomer, there are several rotamers. Scheme 33 demonstrates the triazene isomerization process and the major rotamers, using **8a**−**d** as an example. The stereodescriptor *E*/*Z* is assigned to specify the N1=N2 space arrangement, and *cis*/*trans* is used to specify N2−N3 space arrangement.

For aryl triazenes (Ar-N1=N2-N3<), the N1=N2 rotation is further restricted due to conjugation of the double bond with the aromatic ring.[88] In these cases, at room temperature, N2−N3 rotation is usually at a rate that produces broad NMR signals for N3 substituents, especially carbons and protons neighboring N3 (e.g., CH_2* in Scheme 34). The *cis* and *trans* CH_2* are usually not differentiated, producing a broad peak in the ^{1}H NMR. The ^{13}C NMR of C* gives rise to a broad and weak signal that it is usually not observed at room temperature.

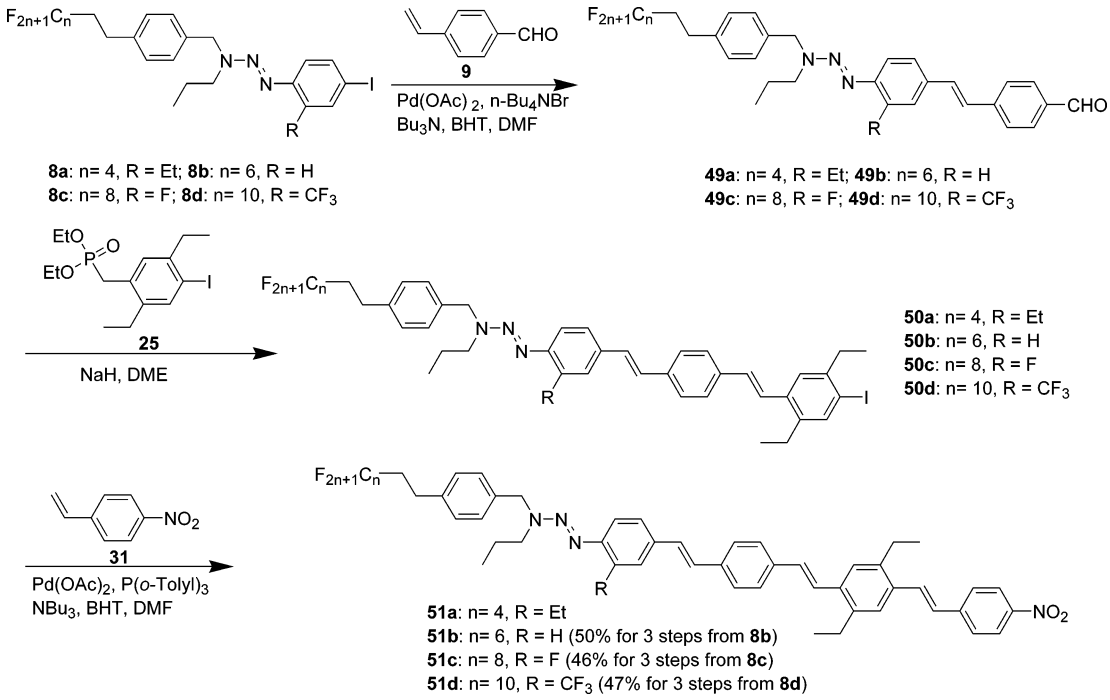
Any molecular dynamic process is expected to be temperature dependent. At low temperature, the rate of bond rotation is decreased. When the N2−N3 rotation is slow enough, the *cis* and *trans* C* can be differentiated. Variable-temperature NMR studies of triazenes confirmed that distinct *cis* and *trans* C* signals can be resolved at about 250 K, and fine coupling structures of ^{1}H NMR signals appear at lower temperatures.[88,89] The electronic and steric effects of substituents on the aro-

(87) Pye, C. C.; Vaughan, K.; Glister, J. F. *Can. J. Chem.* **2002**, *80*, 447−454 and references about more calculation studies therein.

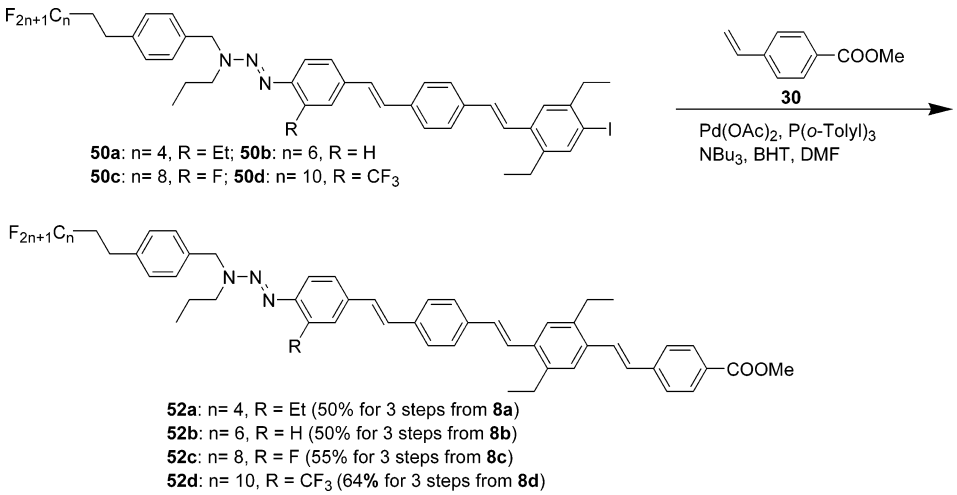
(88) Akhtar, M. H.; McDaniel, R. S.; Feser, M.; Oehlschlager, A. C. *Tetrahedron* **1968**, *24*, 3389−3906.

(89) Hooper, D. L.; Pottie, I. R.; Vacheresse, M.; Vaughan, K. *Can. J. Chem.* **1998**, *76*, 125−135.

SCHEME 26



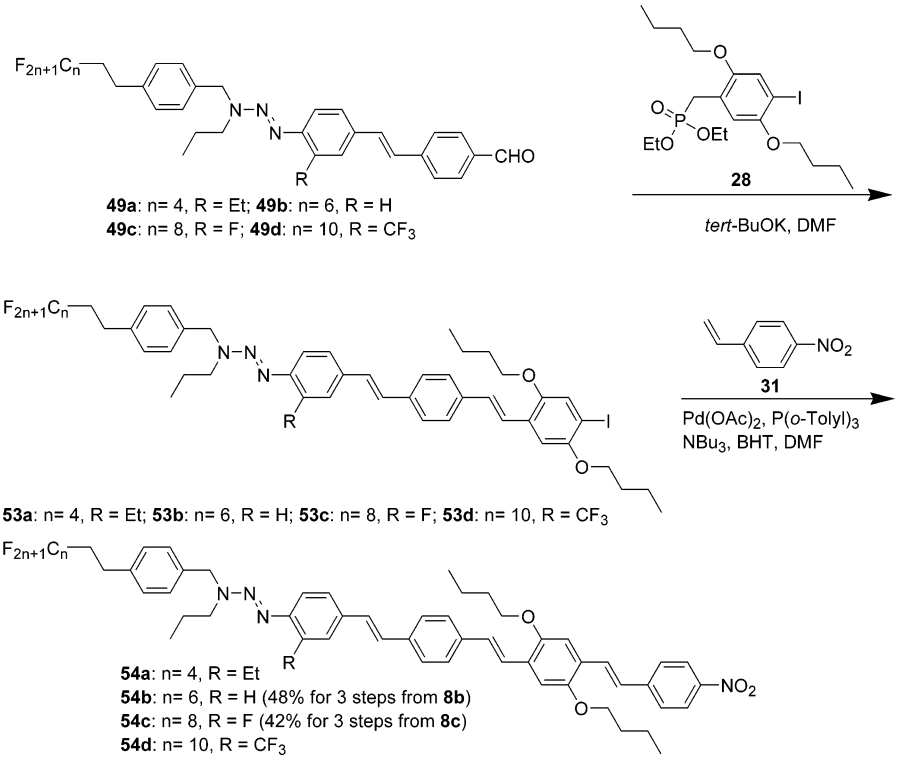
SCHEME 27



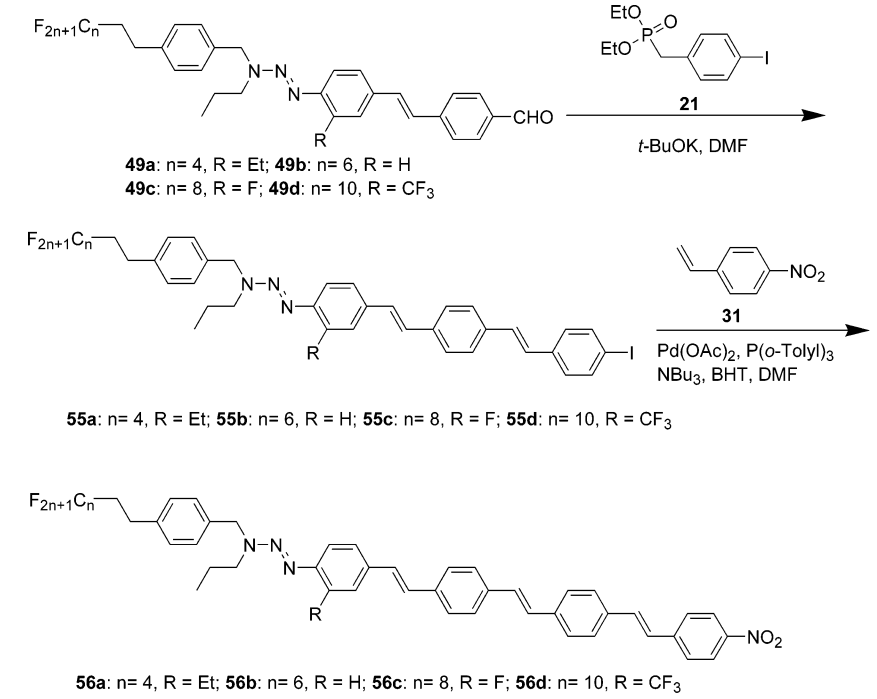
matic rings also influence the N2−N3 rotational isomerism. The presence of a strong electron-withdrawing group on the aromatic ring promotes the formation of 1,3-dipolar compounds (Scheme 34, bottom left and right). Under these circumstances, N2−N3 rotation is restricted to the point where CH_2* is either *cis* or *trans* to N1, and the signals due to CH_2* (both ^{1}H and ^{13}C NMR) in the *cis* and *trans* rotamers are distinct at room temperature.[89] Figures 2 and 3 compare the *N*-ethyl resonance of the two 1-aryl-3,3-diethyltriazene compounds **35b** and **35d**. When there is no electron-withdrawing group on the aryl ring, the *N*-ethyl groups have a broad $-CH_3$ ^{1}H NMR signal (Figure 2a). The ^{13}C signals of the *N*-ethyl groups average out as very weak bumps (Figure 3a). With enough scans in the FT-NMR analysis, two groups of resonances could be observed, due to the moieties *cis* and *trans* to the aryl group. When there is an electron-withdrawing group, $-CF_3$, in the aromatic ring, the two ethyl groups are differentiated in both ^{1}H and ^{13}C NMR (Figure 2b and 3b). An electron-withdrawing group reduces the rate of N2−N3 rotation, and the ethyl groups have to take a position either *cis* or *trans* to the aryl group.

In aryl triazenes, the signals due to the aromatic protons fall into two categories: (1) when the two N3 substituents are similar in size; (2) when one of the N3 substituents is much larger than the other. When the two N3 substituents are similar in size, the signals due to aromatic nuclei are all observed as usual. They exhibit sharp, well-resolved peaks and expected coupling patterns. More important is that the signals are not temperature dependent. The magnetic field of the aromatic ring changes little in different rotamers, and the aromatic nuclei are usually not affected by triazene isomerization. In compounds **35a**−**d**, when both the N3 substituents are ethyl groups, each aromatic carbon gives a sharp peak in the ^{13}C NMR spectrum. But when the two N3 substituents are significantly different in size, rotation about

SCHEME 28



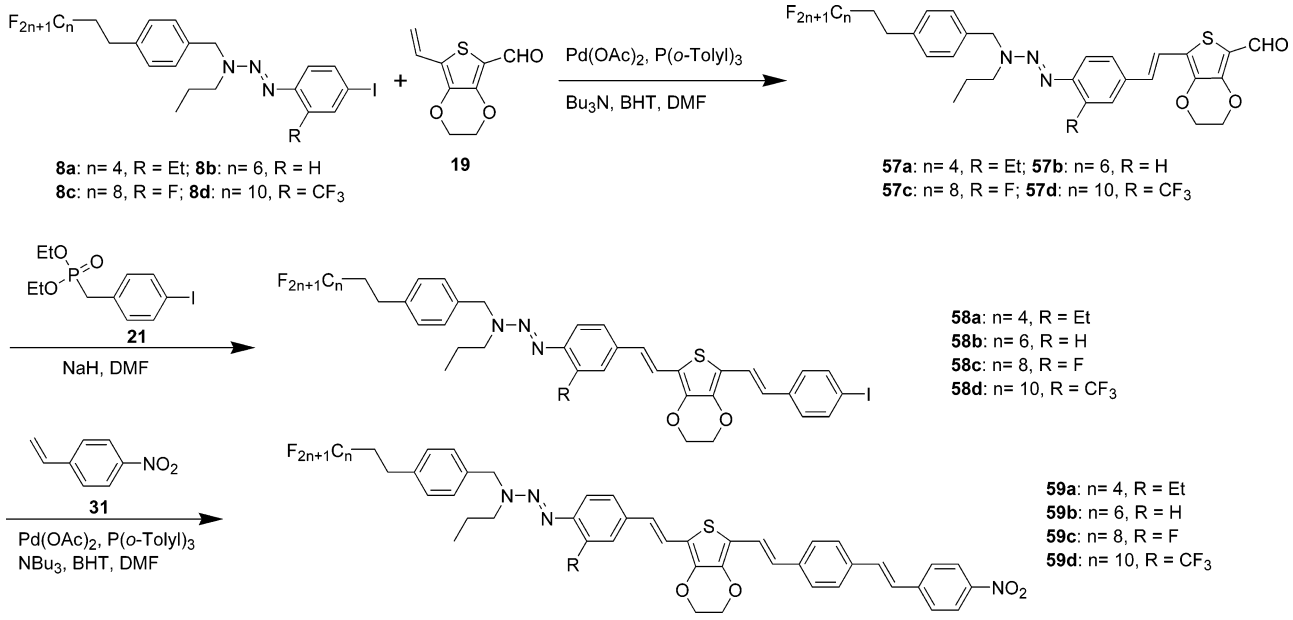
SCHEME 29



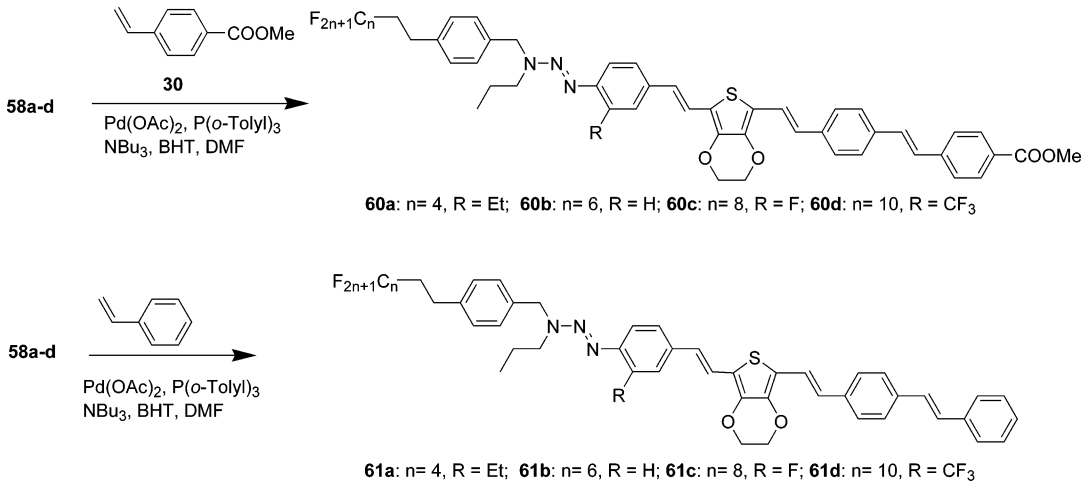
the N2−N3 bond is restricted, giving two stereoisomers that are distinguishable by NMR. This is the case for compounds **8a**−**d**. Under these conditions, a greater number of aromatic signals are resolved, due to the dynamic equilibrium of the rotamers.

When the two N3 substituents are significantly different in size, not only are the protons and carbons on the aromatic ring affected, the signals arising from aryl substituents are also put in different magnetic fields in different rotamers. From Scheme 33, we can see that there are two positions for the ortho aryl substituent R: *cis* and *trans* to the larger N3 substituents. These two positions should give rise to two NMR signals for each set of nuclei in R. However, in combination with its electron effect, an electron donating R gives broad, averaged ^{1}H signals. And each carbon in electron donating R gives a single ^{13}C signal (e.g., ^{1}H and ^{13}C NMR of **8a**, R = Et).

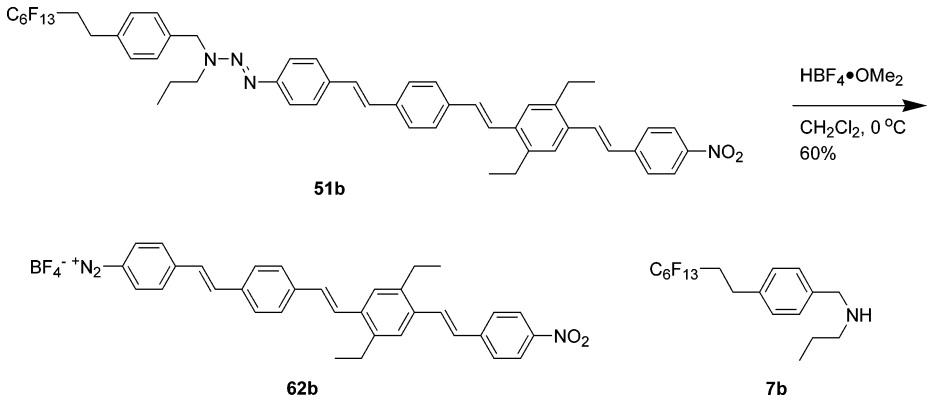
SCHEME 30



SCHEME 31



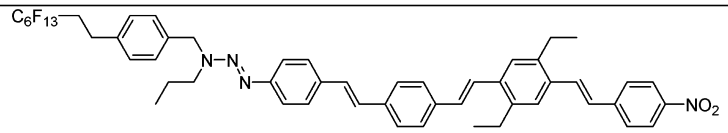
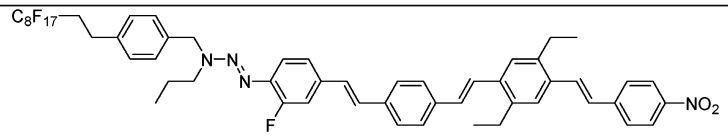
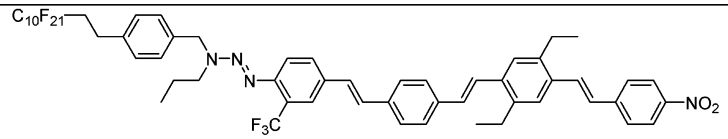
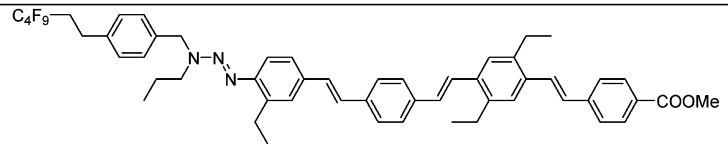
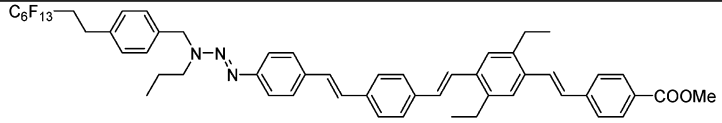
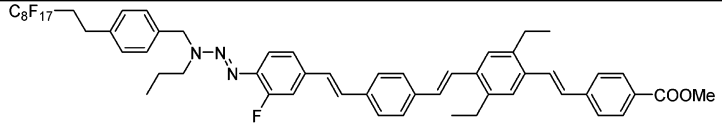
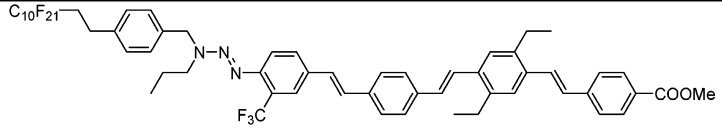
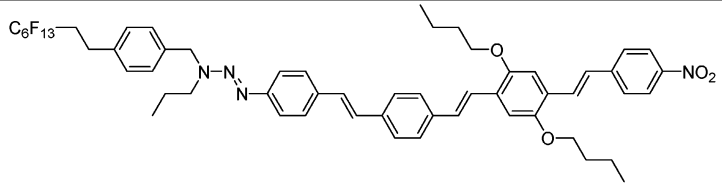
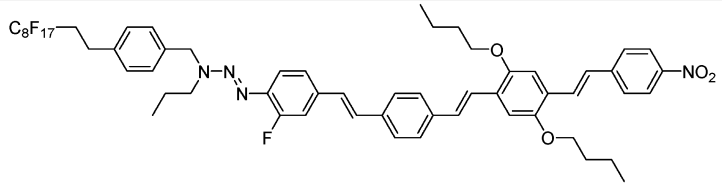
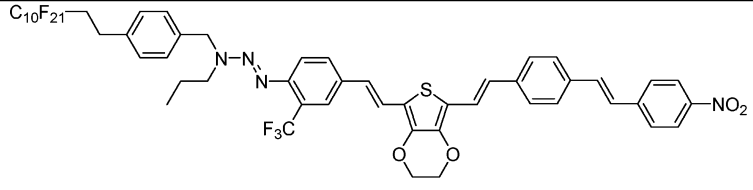
SCHEME 32



If the substituent R contains fluorine atoms, the *cis* and *trans* isomers can produce distinct signals in ^{19}F NMR spectra. Figure 4 compares the ^{19}F NMR of two Ar-F-type triazene compounds **35c** and **8c**. When the two N3 substituents are both ethyl groups, the fluorine gives a multiplet due to coupling with protons on the aromatic ring (Figure 4a). When the two N3 substituents are different in size, two multiplets are observed, indicating an equilibrium between *cis* and *trans* isomers (Figure 4b).

Figure 5 compares the ^{19}F NMR of two *o*-CF_3 aryl triazene compounds **35d** and **8d**. When the two N3 substituents are both ethyl groups, the CF_3 group gives

TABLE 2. Isolated OPV Tetramers

	Structure	Yield[a]
51b		50%
51c		46%
51d		47%
52a		50%
52b		50%
52c		55%
52d		64%
54b		48%
54c		42%
59d		22%

[a] Overall yields for three steps from **8a**−**d**, based on isolated products.

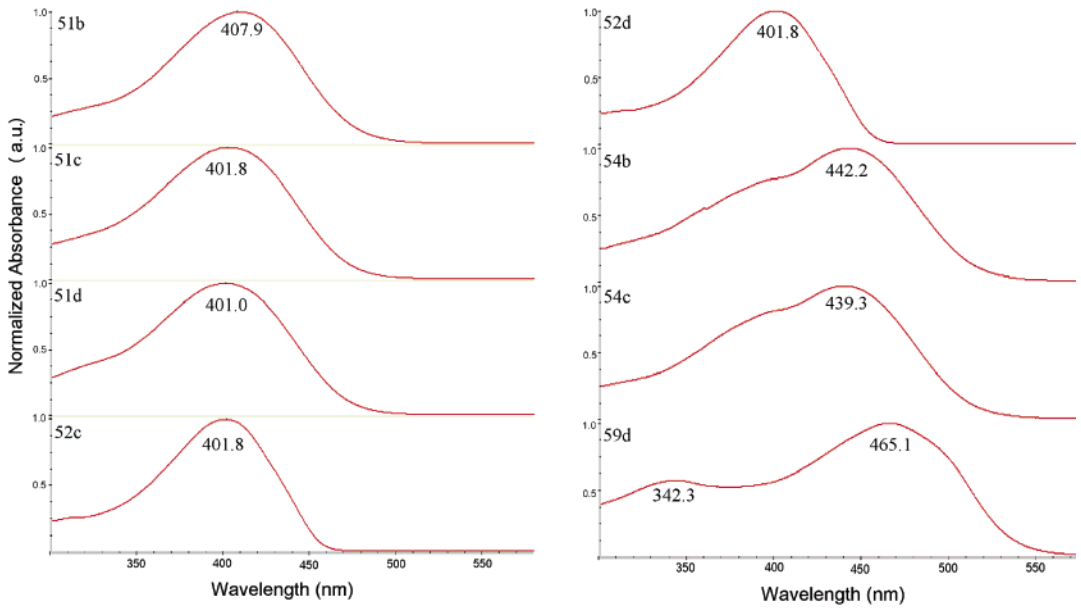
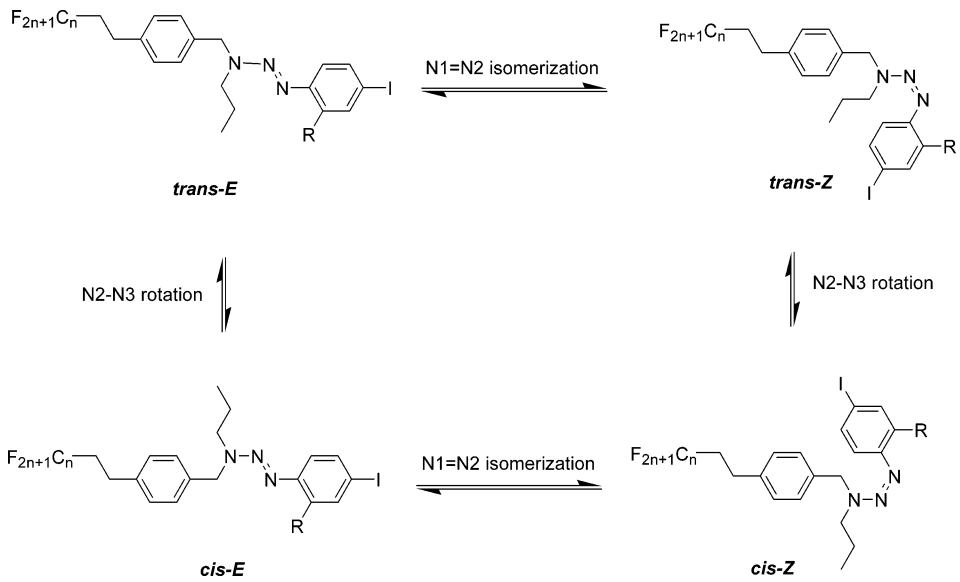


FIGURE 1. UV−vis absorption spectra (normalized to peak height) of selected fluoro-tagged OPV tetramers (~10^{-5} M solution in CH_2Cl_2).

SCHEME 33

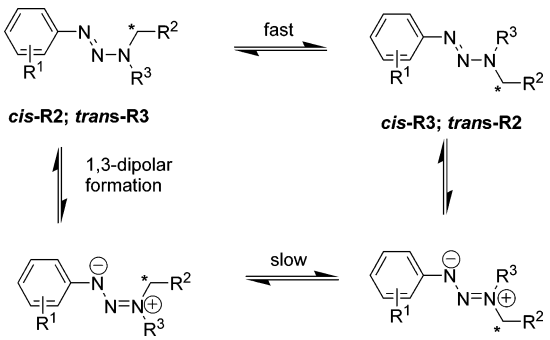


a sharp singlet (Figure 5a). When the two N3 substituents are different in size, two singlets are observed, indicating an equilibrium between *cis* and *trans* isomers (Figure 5b). From the ^{19}F peak intensity of the two isomers, the *cis*/*trans* ratio can be calculated.

Conclusions

We have outlined a method of synthesizing a library of diazonium-functionalized OPV tetramers using FMS technology. Alternating Heck coupling and HWE reaction were used to grow OPVs and hybrid oligomers. Model studies were used to optimize the reaction strategies and OPVs and hybrid oligomers bearing aryl diazonium functionalities were synthesized. FMS technology successfully generated a library of OPVs and

SCHEME 34



hybrid oligomers and was superior to SPOS techniques. Analytical HPLC was used to monitor the mixture

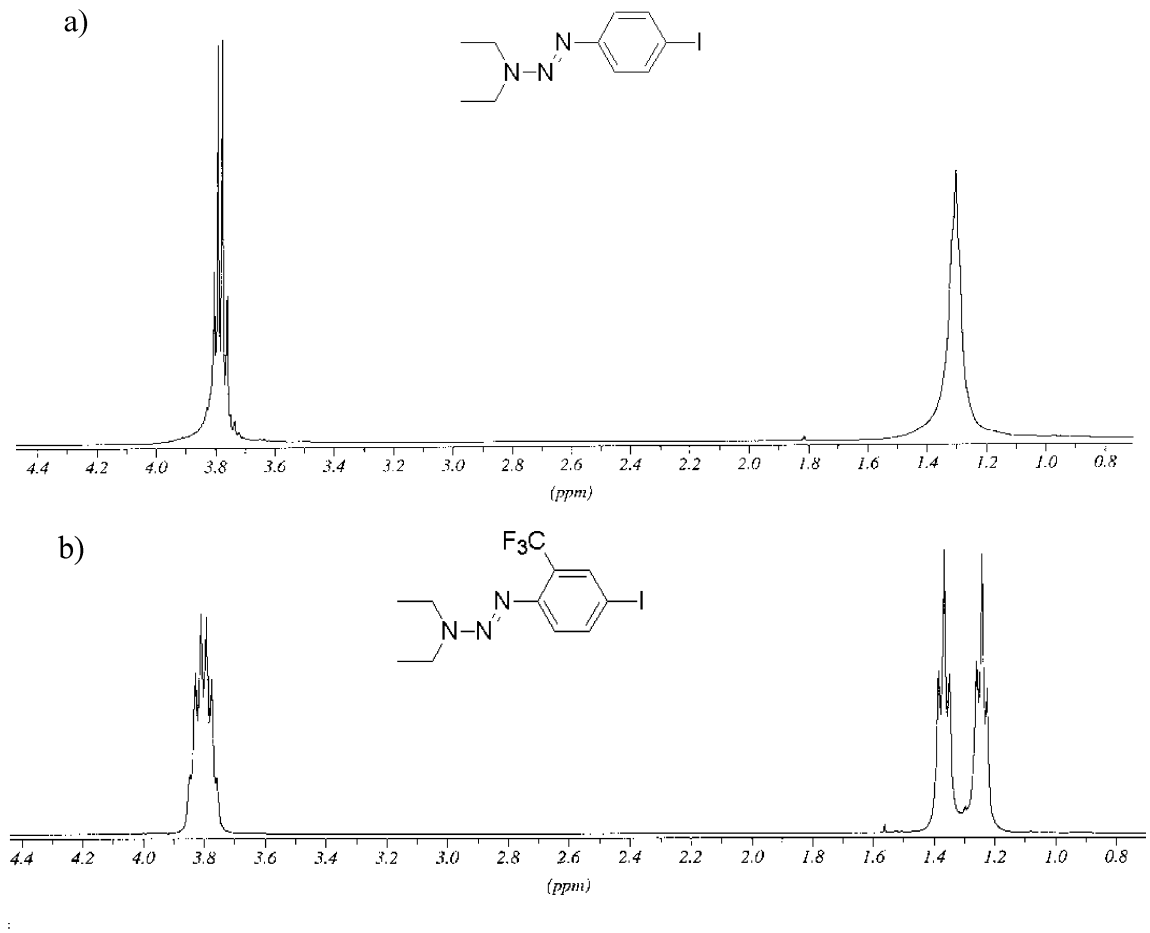


FIGURE 2. ^{1}H NMR spectra of 1-aryl-3,3-diethyltriazene compounds in the *N*-ethyl resonance region (400 MHz, $CDCl_3$): (a) without any electron-withdrawing group on the aryl ring; (b) with an electron-withdrawing group on the aryl ring.

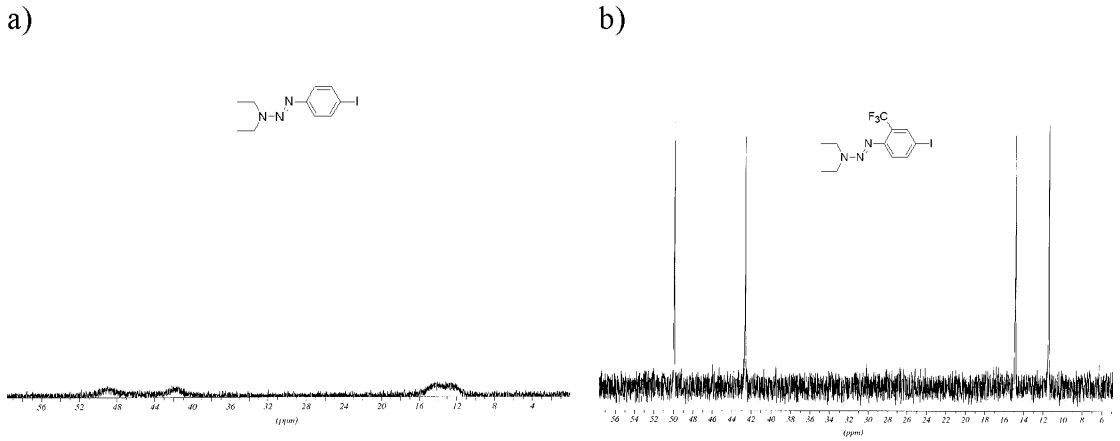


FIGURE 3. ^{13}C NMR spectra of 1-aryl-3,3-diethyltriazene compounds in the *N*-ethyl resonance region (100 MHz, $CDCl_3$): (a) without any electron-withdrawing group on the aryl ring; (b) with an electron-withdrawing group on the aryl ring.

synthesis and final products were isolated by preparative HPLC. Although we did not synthesize all the possible tetrameric OPVs and hybrid oliogmers in this library, the efficiency of the approach was proven. Provided with the appropriate building blocks, longer OPVs or OPV-EDOT hybrid oligomers could be synthesized using this method. Screening results of the OPV and hybrid oligomer products in molecular electronic and optoelectronic applications will be reported in due course.

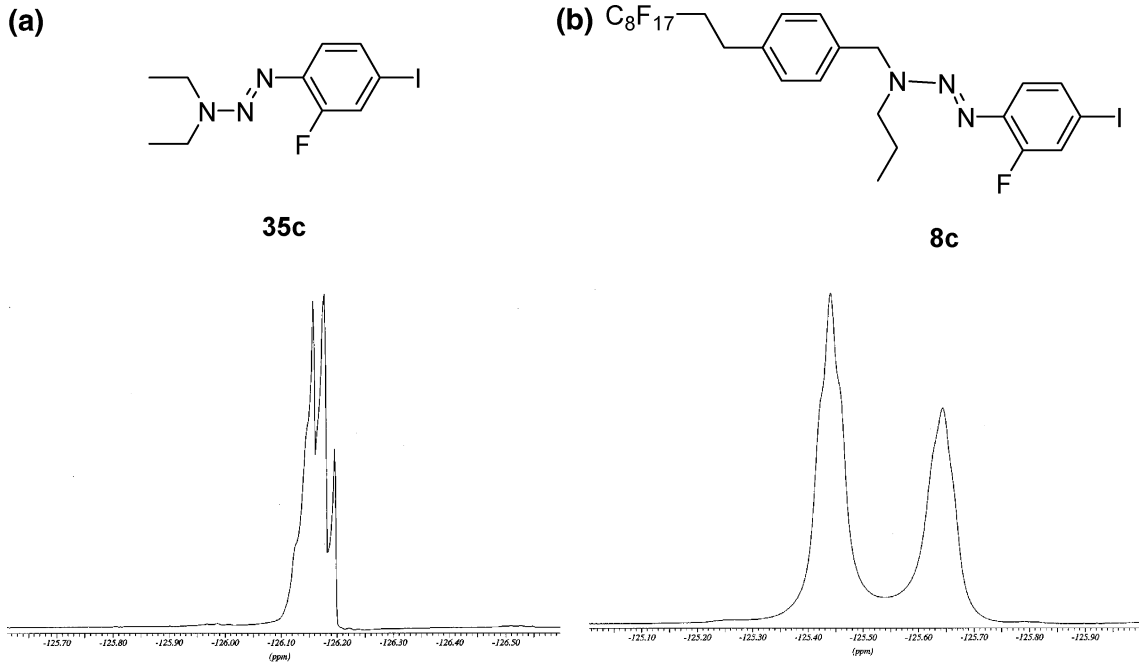


FIGURE 4. ^{19}F NMR of Ar-F triazene compounds (470.5 MHz, $CDCl_3$): (a) ^{19}F NMR of **35c**; (b) ^{19}F NMR of **8c**.

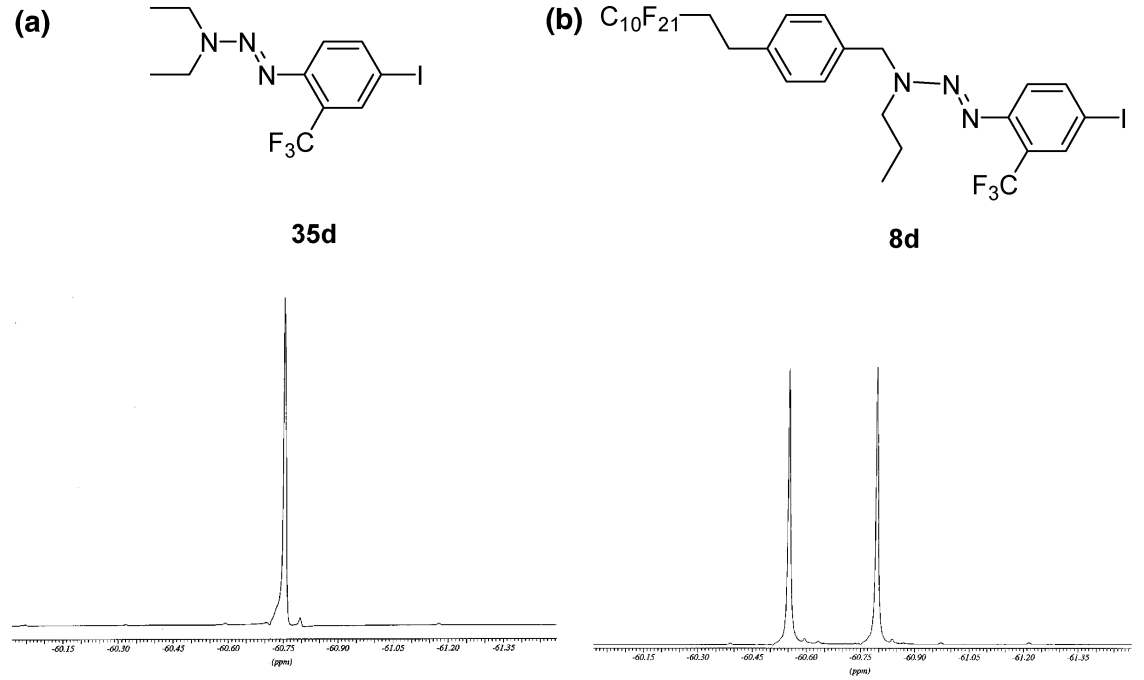


FIGURE 5. ^{19}F NMR of Ar-CF_3 triazene compounds (470.5 MHz, $CDCl_3$): (a) ^{19}F NMR of **35d**; (b) ^{19}F NMR of **8d**.

Experimental Section

2-Ethyl-4-iodoaniline (1a).[50] To the solution of 2-ethylaniline (42.81 g, 353.3 mmol) in MeOH (200 mL), cooled in an ice bath, was added a solution of $NaHCO_3$ (47.48 g, 565.2 mmol)/H_2O (200 mL). I_2 (89.67 g, 353.3 mmol) was then added portionwise over 30 min. The reaction mixture was stirred at room temperature for 2 h, poured into water in a separatory funnel, and extracted with EtOAc. The organic layer was washed with Na_2SO_3 (satd aq) twice, H_2O twice, and brine once and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was passed through a plug of silica gel to give **1a** (82.82 g, 95%) as dark unstable liquid: IR (KBr, neat) 3469 (br), 3381 (m), 2964 (s), 2871 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, J = 2.1 Hz, 1H), 7.32 (dd, J = 2.1, 8.3 Hz, 1H), 6.47 (d, J = 8.3 Hz, 1H), 3.64 (br, 2H), 2.47 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 137.1, 135.8, 131.1, 117.8, 80.4, 24.1, 13.1; LRMS for $C_8H_{10}IN$ (EI) *m/z* (peak intensity, assignment) 247 (100, M^+), 232 (90, $M^+ - CH_3$); HRMS calcd for $C_8H_{10}IN$ 246.9858, found 246.9851.

2-Ethyl-4-iodobenzenediazonium Tetrafluoroborate (2a). According to the general procedure for the diazotization of anilines, **1a** (13.15 g, 53.22 mmol), $BF_3{\cdot}OEt_2$ (27.0 mL, 213 mmol), *t*-BuONO (22.3 mL, 186 mmol), THF (50 mL), and ether (300 mL) gave **2a** as a white solid (15.4 g, 84%): mp > 91 °C dec; IR (KBr) 3009 (m), 2973 (m), 2274 (s), 2244 (s), 1056

(s, br), 822 (m) cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 8.26 (d, J = 1.4 Hz, 1H), 8.14 (dd, J = 8.7, 1.5 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 2.95 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H); ^{13}C NMR (CD_3CN, 100 MHz) δ 151.2, 142.3, 140.3, 133.6, 115.0, 114.6, 26.3, 13.8; FAB HRMS calcd for $C_8H_8IN_2^+$ 258.9732, found 258.8633.

2-Fluoro-4-iodobenzenediazonium Tetrafluoroborate (2c). According to the general procedure for the diazotization of anilines, **1c** (5.663 g, 23.89 mmol), $BF_3{\cdot}OEt_2$ (12.1 mL, 95.6 mmol), *t*-BuONO (10.0 mL, 83.6 mmol), THF (50 mL), and ether (150 mL) gave **2c** as a white pale solid (7.86 g, 98%): mp > 150 °C dec; IR (KBr) 3104 (m), 2270 (s), 1051 (s, br), 827 (m) cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 8.26 (m, 1H), 8.16 (m, 2H); ^{13}C NMR (CD_3CN, 125 MHz) δ 161.8, 159.6, 138.8 (d, J_{C-F} = 3.3 Hz), 133.6 (d, J_{C-F} = 3.9 Hz), 130.1 (d, J_{C-F} = 17.1 Hz), 117.4 (d, J_{C-F} = 8.5 Hz); FAB HRMS calcd for $C_6H_3FIN_2^+$ 248.9325, found 248.8257.

***N*-(4-Bromobenzyl)propan-1-amine (3).**[91] A flask charged with *n*-propylamine (250 mL) was cooled in an ice bath. 4-Bromobenzyl bromide (9.93 g, 39.7 mmol) was divided into four portions. One portion was dissolved in a minimum amount of THF (3 mL). The solution was added dropwise to the *n*-propylamine while stirring. The reaction mixture was then stirred at room temperature for 1 h. *n*-Propylamine was then recovered by distillation, and reused to react with another portion of 4-bromobenzyl bromide. This was done four times. The residues of the distillations were then combined, diluted with EtOAc, and poured into water in a separatory funnel. The organic layer was washed with H_2O three times and brine once, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was passed through a plug of silica gel to afford **3** as slightly yellow liquid (9.06 g, 100%): R_f = 0.19 (hexanes/EtOAc = 1/1); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 3.76 (s, 2H), 2.59 (t, J = 7.3 Hz, 2H), 1.53 (sext, J = 7.3 Hz, 2H), 1.26 (br, 1H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.1, 131.8, 130.2, 121.0, 53.7, 51.7, 23.6, 12.2.

***tert*-Butyl 4-Bromobenzylpropylcarbamate (4).** To the solution of **3** (9.06 g, 39.7 mmol) in CH_2Cl_2 (80 mL), cooled to 0 °C, was added via syringe a solution of Boc_2O (10.71 g, 47.61 mmol) in CH_2Cl_2 (20 mL), followed by NEt_3 (6.7 mL, 48 mmol). The reaction mixture was then stirred in room temperature for 4.5 h and concentrated in vacuo. The residue was partitioned between EtOAc and water in a separatory funnel. The organic layer was then washed with H_2O three times and brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **4** as a clear liquid (13.0 g, 100%): R_f = 0.32 (hexanes/CH_2Cl_2 = 1/1); IR (KBr, neat) 2969(s), 1682 (s), 795 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d-br, J = 8.1 Hz, 2H), 7.09 (br, 2H), 4.35 (s, 2H), 3.14 and 3.07 (2 s, br, 2H), 1.44 (m, 11H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, at room temperature, some Cs are multiplets because of amide isomerization) δ 156.3 (m), 138.2 (m), 131.9, 129.4 (2m), 121.2, 80.0, 50.0 (2m), 48.8 (m), 28.6, 21.7 (m), 11.7; HRMS calcd for $C_{15}H_{23}BrNO_2$ 328.0912, found 328.0901; LRMS for $C_{15}H_{23}BrNO_2$ (EI) *m/z* (peak intensity, assignment) 271 (77, $M^+ - t$-Bu), 273 (77, $M^+ - t$-Bu), 169 (100, $BrC_7H_6^+$), 171 (100, $BrC_7H_6^+$), 57 (73, t-Bu^+).

5a. According to the general coupling procedure B, **4** (3.116 g, 9.463 mmol), 1*H*,1*H*,2*H*-perfluoro-1-hexene (2.0 mL, 12 mmol), palladacycle (0.178 g, 0.190 mmol), NaOAc (1.012 g, 12.34 mmol), and DMF (25 mL) gave **5a** (4.26 g, 91%) as a slightly yellow oil: IR (KBr, neat) 2971 (s), 1693 (s), 1235−1133 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.1 Hz, 2H), 7.28 (br, 2H), 7.18 (dm, J = 16.1 Hz, 1H), 6.20 (m, 1H), 4.47 (s, 2H), 3.22 and 3.12 (2 s, 2H), 1.47 (m, 11H), 0.87 (t, J = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.6 (m, 3F), −111.8 (m, 2F), −124.7 (m, 2F), −126.3 (m, 2F); LRMS for $C_{21}H_{24}F_9NO_2$ (EI) *m/z* (peak intensity, assignment): 437 (20, $M^+ - C_4H_8$), 335 (100, M^+ − Boc − *n*-PrN), 57 (35, t-Bu^+).

5b. According to the general coupling procedure A, **4** (1.413 g, 4.305 mmol), 1*H*,1*H*,2*H*-perfluoro-1-octene (1.0 mL, 4.7 mmol), $Pd(OAc)_2$ (0.0146 g, 0.0650 mmol), $NaHCO_3$ (0.904 g, 10.7 mmol), *n*-Bu_4NHSO_4 (1.46 g, 4.30 mmol), and DMF (20 mL) gave **5b** (1.69 g, 66%) as a slightly yellow oil: IR (KBr, neat) 2972 (s), 1691 (s), 1300−1064 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.1 Hz, 2H), 7.28 (br, 2H), 7.18 (dm, J = 16.1 Hz, 1H), 6.20 (m, 1H), 4.47 (s, 2H), 3.22 and 3.13 (2 s, 2H), 1.47 (m, 11H), 0.88 (t, J = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.3 (t, 3F), −111.5 (m, 2F), −122.1 (m, 2F), −123.4 (m, 2F), −123.7 (m, 2F), −126.7 (m, 2F); HRMS (CI) calcd for $C_{23}H_{25}F_{13}NO_2$ (M + H) 594.1678, found 594.1596; LRMS for $C_{23}H_{24}F_{13}NO_2$ (EI) *m/z* (peak intensity, assignment) 537 (16, $M^+ - C_4H_8$), 435 (100, M^+ − Boc − *n*-PrN), 57 (5, t-Bu^+).

5c. According to the general coupling procedure B, **4** (1.129 g, 3.439 mmol), 1*H*,1*H*,2*H*-perfluoro-1-docene (1.0 mL, 3.8 mmol), palladacycle (0.032 g, 0.034 mmol), NaOAc (0.367 g, 4.47 mmol), and DMF (20 mL) gave **5c** (1.8 g, 77%) as a slightly yellow oil, which solidified slowly at room temperature: mp 57−58 °C; IR (KBr) 3044 (m), 2975 (s), 1688 (s), 1251−1050 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.1 Hz, 2H), 7.28 (br, 2H), 7.17 (dm, J = 16.1 Hz, 1H), 6.20 (m, 1H), 4.47 (s, 2H), 3.21 and 3.12 (2 br, 2H), 1.47 (m, 11H), 0.87 (t, J = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.7 (t, J = 10.1 Hz, 3F), −111.8 (m, 2F), −122.1 (m, 2F), −122.7 (m, 4F), −123.5 (m, 2F), −123.9 (m, 2F), −126.9 (m, 2F); HRMS calcd for $C_{25}H_{24}F_{17}NO_2$ 693.1536, found 693.1537; LRMS for $C_{25}H_{24}F_{17}NO_2$ (EI) *m/z* (peak intensity, assignment) 637 (10, $M^+ - C_4H_8$), 535 (100, M^+ − Boc − *n*-PrN), 57 (15, t-Bu^+).

5d. According to the general coupling procedure B, **4** (1.476 g, 4.497 mmol), 1*H*,1*H*,2*H*-perfluoro1-dodecene (2.72 g, 4.98 mmol), palladacycle (0.042 g, 0.045 mmol), NaOAc (0.480 g, 5.85 mmol), and DMF (25 mL) gave **5d** (2.5 g, 70%) as a white solid: mp 71−72 °C; IR (KBr) 2983 (s), 1689 (s), 1305−1152 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, J = 8.1 Hz, 2H), 7.28 (br, 2H), 7.18 (dm, J = 16.1 Hz, 1H), 6.20 (m, 1H), 4.47 (s, 2H), 3.21 and 3.12 (2 br, 2H), 1.47 (m, 11H), 0.87 (t, J = 7.1 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.3 (t, J = 9.6 Hz, 3F), −111.5 (m, 2F), −122.9 (m, 2F), −122.3 (m, 8F), −123.2 (m, 2F), −123.7 (m, 2F), −126.6 (m, 2F); LRMS for $C_{27}H_{24}F_{21}NO_2$ (EI) *m/z* (peak intensity, assignment) 635 (100, M^+ − Boc − *n*-PrN), 57 (10, t-Bu^+).

6a. According to the general procedure for hydrogenation, **5a** (5.99 g, 12.1 mmol), Pd (10% on charcoal, 1.55 g), and EtOAc (80 mL) gave **6a** (5.56 g, 93%) as a clear oil: IR (KBr) 2971 (s), 1697 (s), 1305−1088 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.18 (m, 4H), 4.43 (s, 2H), 3.18 and 3.11 (2 br, 2H), 2.94−2.88 (m, 2H), 2.45−2.31 (m, 2H), 1.48 (m, 11H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, some Cs are missing or multiplets because of isomerization of carbamate) δ 138.3, 128.5, 80.0, 50.0 (m), 48.8, 33.3 (t, J_{C-F} = 22.1 Hz), 26.52 (t, J_{C-F} = 4.0 Hz), 21.6 (m), 11.7; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.6 (t, J = 8.9 Hz, 3F), −115.4 (m, 2F), −125.0 (m, 2F), −126.6 (m, 2F); HRMS (CI) calcd for $C_{21}H_{27}F_9NO_2$ (M + H) 496.1898, found 496.1785; HRMS (EI) calcd for $C_{21}H_{26}F_9NO_2$ 495.1820, found 495.1820.

6b. According to the general procedure for hydrogenation, **5b** (1.69 g, 2.85 mmol), Pd (10% on charcoal, 0.364 g), and EtOAc (15 mL) gave **6b** (1.58 g, 93%) as a clear oil: IR (KBr): 2971 (s), 1694 (s), 1367−1088 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.19 (m, 4H), 4.43 (s, 2H), 3.17 and 3.12 (2 br, 2H), 2.94 and 2.90 (m, 2H), 2.45−2.33 (m, 2H), 1.50 (m, 11H), 0.87 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.5 (m, 3F), −115.3 (m, 2F), −122.5 (m, 2F), −123.5 (m, 2F), −124.1 (m, 2F), −126.8 (m, 2F); HRMS calcd for $C_{23}H_{26}F_{13}NO_2$ 595.1756, found 595.1749; LRMS (EI) *m/z* (peak intensity,

(90) Fluoro*Flash* HPLC columns were purchased from Fluorous Technologies, Inc., Pittsburgh, PA

(91) Kerdesky, F. A. J.; Haight, A.; Narayanan, B. A.; Nordeen, C. W.; Scarpetti, D.; Seif, L. S.; Wittenberger, S.; Morton, H. E. *Synth. Commun.* **1993**, *23*, 2027−2039.

assignment) 595 (1, M^+), 437 (100, M^+ − Boc − C_3H_7N), 57 (15, *t*-Bu^+).

6c. According to the general procedure for hydrogenation, **5c** (4.01 g, 5.78 mmol), Pd (10% on charcoal, 0.738 g), and EtOAc (50 mL) gave **6c** (3.83 g, 95%) as a clear oil: IR (KBr, neat) 2972 (m), 1692 (s), 1243−1146 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.20 (m, 4H), 4.45 (s, 2H), 3.19 and 3.12 (2 br, 2H), 2.95−2.90 (m, 2H), 2.44−2.34 (m, 2H), 1.49 (m, 11H), 0.87 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.65 (t, J = 9.4 Hz, 3F), −115.4 (m, 2F), −122.4 (m, 2F), −122.7 (m, 4F), −123.5 (m, 2F), −124.2 (m, 2F), −126.9 (m, 2F); LRMS for $C_{25}H_{26}F_{17}NO_2$ (EI) *m/z* (peak intensity, assignment) 695 (5, M^+), 594 (15, M^+ − Boc), 537 (100, M^+ − Boc − NHC_3H_7).

6d. According to the general procedure for hydrogenation, **5d** (5.219 g, 6.577 mmol), Pd (10% on charcoal, 0.840 g), and EtOAc (60 mL) gave **6d** (5.07 g, 97%) as a clear oil, which solidified slowly at room temperature to give a white solid: mp 66−67 °C; IR (KBr) 2972 (m), 1688 (s), 1244−1149 (s), 882 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.18 (m, 4H), 4.43 (s, 2H), 3.18 and 3.11 (2 br, 2H), 2.94−2.89 (m, 2H), 2.45−2.33 (m, 2H), 1.48 (m, 11H), 0.87 (t, J = 7.3 Hz, 3H); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.4 (t, J = 10.1 Hz, 3F), −115.2 (m, 2F), −122.4 (m, 10F), −123.3 (m, 2F), −124.1 (m, 2F), −126.8 (m, 2F); HRMS calcd for $C_{27}H_{26}F_{21}NO_2$ 795.1628, found 795.1613.

7a. According to the general procedure for amine deprotection, **6a** (5.56 g, 11.2 mmol), TFA (5 mL), and CH_2Cl_2 (50 mL) gave **7a** (4.31 g, 97%) as a slightly yellow oil: IR (KBr) 3305 (br), 2961 (m), 1357−1134 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.80 (s, 2H), 2.96−2.91 (m, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.48−2.32 (m, 2H), 1.56 (sext, J = 7.5 Hz, 2H), 1.45 (br, 1H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 139.6, 138.1, 129.0, 128.7, 54.1, 51.8, 33.4 (t, J_{C-F} = 21.9 Hz), 26.5 (t, J_{C-F} = 4.3 Hz), 23.6, 12.1; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.8 (m, 3F), −115.5 (m, 2F), −125.1 (m, 2F), −126.7 (m, 2F); HRMS calcd for $C_{16}H_{18}NF_9$ 395.1295, found 395.1292.

7b. According to the general procedure for amine deprotection, **6b** (4.18 g, 7.02 mmol), TFA (5 mL) and CH_2Cl_2 (50 mL) gave **7b** (3.41 g, 98%) as a slightly yellow oil: IR (KBr) 3303 (br), 2961 (m), 1366−1118 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 3.80 (s, 2H), 2.96−2.91 (m, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.45−2.34 (m, 2H), 1.56 (sext + br, J = 7.5 Hz, 2H+1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 139.6, 138.2, 129.0, 128.8, 54.1, 51.8, 33.5 (t, J_{C-F} = 22.0 Hz), 26.6 (t, J_{C-F} = 4.2 Hz), 23.6, 12.2; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.6 (t, J = 10.1 Hz, 3F), −115.3 (m, 2F), −122.5 (m, 2F), −123.5 (m, 2F), −124.2 (m, 2F), −126.8 (m, 2F); HRMS calcd for $C_{18}H_{18}F_{13}N$ 495.1232, found 495.1225.

7c. According to the general procedure for amine deprotection, **6c** (1.69 g, 2.43 mmol), TFA (3 mL), and CH_2Cl_2 (30 mL) gave **7c** (1.44 g, 100%) as a slightly yellow oil at room temperature, which solidified upon refrigeration: IR (KBr) 3306 (br), 2961 (m), 1330−1115 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 3.80 (s, 2H), 2.94−2.90 (m, 2H), 2.63 (t, J = 7.5 Hz, 2H), 2.48−2.32 (m, 2H), 1.56 (sext, J = 7.5 Hz, 2H), 1.46 (br, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 139.6, 138.2, 129.0, 128.8, 54.1, 51.9, 33.5 (t, J_{C-F} = 21.9 Hz), 26.6 (t, J_{C-F} = 4.3 Hz), 23.7, 12.2; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.8 (t, J = 9.4 Hz, 3F), −115.4 (m, 2F), −122.5 (m, 2F), −122.7 (m, 4F), −123.5 (m, 2F), −124.2 (m, 2F), −127.0 (m, 2F); LRMS for $C_{20}H_{18}F_{17}N$ (EI) *m/z* (peak intensity, assignment) 595 (55, M^+), 566 (90, $M^+ - C_2H_5$), 537 (100, $M^+ - NHC_3H_7$).

7d. According to the general procedure for amine deprotection, **6d** (0.964 g, 1.21 mmol), TFA (3 mL), and CH_2Cl_2 (30 mL) gave **7d** (0.784 g, 93%) as a white solid: mp 60−61 °C; IR (KBr) 3340 (br), 2963 (m), 1210−1150 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 3.80 (s, 2H), 2.94−2.90 (m, 2H), 2.64 (t, J = 7.5 Hz, 2H), 2.45−2.32 (m, 2H), 1.57 (sext, J = 7.5 Hz, 2H), 1.39 (br, 1H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 139.7, 138.2, 129.0, 128.7, 54.1, 51.9, 33.5 (t, J_{C-F} = 21.9 Hz), 26.5 (t, J_{C-F} = 4.3 Hz), 23.7, 12.0; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.4 (t, J = 10.1 Hz, 3F), −115.2 (m, 2F), −122.2 (m, 10F), −123.2 (m, 2F), −124.0 (m, 2F), −126.7 (m, 2F); HRMS calcd for $C_{24}H_{21}F_{13}IN_3$ 725.0573, found 725.0582.

8a. According to the general procedure for triazene formation, **2a** (4.53 g, 13.1 mmol), **7a** (4.31 g, 10.9 mmol), K_2CO_3 (3.05 g, 22.1 mmol), and CH_3CN (100 mL) gave **8a** (5.19 g, 73%) as an orange oil: R_f = 0.43 (hexanes/CH_2Cl_2 = 8/1); IR (KBr) 2966 (s), 1455−1097 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.54 (m, 1H), 7.49 (dd, J = 8.4 Hz, 1.8 Hz, 1H), 7.27−7.19 (m, 5H), 4.94 (s, 2H), 3.74 (br, 1H), 2.97−2.91 (m, 2H), 2.72 (br, 2H), 2.47−2.32 (m, 2H), 1.73 (br, 2H), 1.12 (br, 3H), 0.95 (br-m, 3H); ^{13}C NMR (CDCl3, 100 MHz; two aromatic C's not observed because of triazene rotamer interconversion; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 148.2, 141.8, 138.4, 135.7, 129.0, 128.6, 119.1, 90.5, 33.3 (t, J_{C-F} = 21.9 Hz), 32.1, 26.5 (t, J_{C-F} = 4.3 Hz), 25.0, 23.1, 15.6, 14.6, 11.9; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −80.2 (m, 3F), −114.0 (m, 2F), −123.7 (m, 2F), −125.2 (m, 2F); HRMS calcd for $C_{24}H_{25}IN_3F_9$ 653.0949, found 653.0941.

8b. According to the general procedure for triazene formation, **2b** (0.931 g, 2.93 mmol), **7b** (1.21 g, 2.44 mmol), K_2CO_3 (0.674 g, 4.88 mmol), and CH_3CN (50 mL) gave **8b** (1.77 g, 100%) as an orange oil: R_f = 0.49 (hexanes/CH_2Cl_2 = 4/1); IR (KBr) 2966 (m), 1239−1120 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.7 Hz, 2H), 7.28−7.20 (m, 6H), 4.97 (s, 2H), 3.68 (br-s, 2H), 2.97−2.93 (m, 2H), 2.49−2.32 (m, 2H), 1.72 (br-s, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz; one aromatic C not observed because of triazene rotamer interconversion; the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 151.0, 138.3, 129.0, 128.9, 123.2, 123.2, 90.0, 33.4 (t, J_{C-F} = 22.0 Hz), 32.1, 26.6 (t, J_{C-F} = 4.1 Hz), 23.2, 14.6, 11.9; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −80.1 (m, 3F), −113.9 (m, 2F), −121.2 (m, 2F), −122.1 (m, 2F), −122.8 (m, 2F), −125.4 (m, 2F); HRMS calcd for $C_{24}H_{21}F_{13}IN_3$ 725.0573, found 725.0574.

8c. According to the general procedure for triazene formation, **2c** (1.74 g, 5.17 mmol), **7c** (2.37 g, 3.98 mmol), K_2CO_3 (1.10 g, 7.96 mmol), and CH_3CN (50 mL), together with THF (50 mL) gave **8c** (2.82 g, 84%) as a pinkish solid: R_f = 0.33 (hexanes/CH_2Cl_2 = 8/1); mp 62−63 °C; IR (KBr) 2971 (m), 1290−1100 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.49−7.43 (m, 2H), 7.35−7.15 (m, 5H), 5.00 (br-s, 2H), 3.76 and 3.68 (2 s, 2H), 2.95 (m, 2H), 2.49−2.30 (m, 2H), 1.78 and 1.70 (2 br-s, 2H), 0.97 (m, 3H); ^{13}C NMR is complicated because of triazene rotamer interconversion and overlap of perfluoro carbons with aromatic carbons; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.7 (t, J = 9.9 Hz, 3F), −115.3 (m, 2F), −122.4 (m, 2F), −122.6 (m, 4F), −123.5 (m, 2F), −124.1 (m, 2H), −125.5 (2m, because of N=N *E/Z* interconversion, 1F, Ph-*F*), −126.9 (m, 2F); HRMS calcd for $C_{26}H_{20}IN_3F_{18}$ 843.0414, found 843.0446.

8d. According to the general procedure for triazene formation, **2d** (0.347 g, 0.899 mmol), **7d** (0.521 g, 0.749 mmol), K_2CO_3 (0.207 g, 1.50 mmol), and CH_3CN (30 mL), together with THF (30 mL), gave **8d** (0.74 g, 99%) as a yellow solid: R_f = 0.56 (hexanes/CH_2Cl_2 = 6/1); mp 75−76 °C; IR (KBr) 2960 (m), 1350−1080 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ7.95 (d, J = 8.2 Hz, 1H), 7.87 (pseudo-t, J = 7.4 Hz, 1H), 7.42 (2d, J = 8.6 Hz, 1H), 7.27−7.16 (m, 4H), 5.02 and 4.95 (2 s, 2H), 3.75 and 3.61 (2t, J = 7.3 Hz, 2H), 2.99−2.88 (m, 2H), 2.47−

2.30 (m, 2H), 1.78 and 1.62 (2 sext, J = 7.4 Hz, 2H), 0.97 and 0.89 (2t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, the signals due to perfluoro carbons were not picked because of strong C−F coupling and overlap) δ 148.8, 141.6, 139.5 and 138.8 (2 s, *cis* and *trans*), 135.5 (q, J = 5.1 Hz), 134.9, 129.2 and 129.2 (2 s, *cis* and *trans*), 128.9 and128.8 (2 s, *cis* and *trans*), 120.1 and 119.7 (2 s, *cis* and *trans*), 88.2, 59.1 and 56.5 (2 s, *cis* and *trans*), 50.2 and 49.4 (2 s, *cis* and *trans*), 33.4 (t, J_{C-F} = 22.9 Hz), 26.6 (m), 22.5 and 19.3 (2 s, *cis* and *trans*), 11.9 and11.7 (2 s, *cis* and *trans*); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −60.6 and −60.8 (2 s, 3F, Ar-CF_3), −81.4 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.4 (m, 10F), −123.2 (m, 2F), −124.0 (m, 2F), −126.7 (m, 2F); HRMS calcd for $C_{29}H_{20}F_{24}IN_3$ 993.0319, found 993.0317.

2,5-Diethyl-4-iodobenzaldehyde (11). In an oven-dried three-neck flask were charged **10**[56] (6.46 g, 16.73 mmol) and THF (100 mL). The solution was cooled to −78 °C to form a white slurry. To this mixture was added dropwise *n*-BuLi (2.03 M in hexane, 8.47 mL) over 20 min. The mixture was then stirred at −78 °C for 4 h. DMF (anhydrous, 3.9 mL, 50 mmol) was added in one portion. The reaction temperature was allowed to increase to room temperature over 6 h and then poured into water and partitioned. The aqueous layer was extracted with CH_2Cl_2 twice. The organic layers were combined, dried over $MgSO_4$, and filtered, and solvent was removed in vacuo. The residue was purified by column chromatography to afford **11** as a clear oil (2.49 g, 52%; a yield as high as 57% was obtained) at room temperature, which solidified under refrigeration: R_f = 0.33 (hexanes/CH_2Cl_2 = 3/1); IR (KBr) 2967 (s), 1699 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.20 (s, 1H), 7.76 (s, 1H), 7.59 (s, 1H), 2.94 (q, J = 7.5 Hz, 2H), 2.73 (q, J = 7.5 Hz, 2H), 1.22 (2t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.2, 145.7, 145.2, 141.5, 133.8, 130.9, 109.1, 33.9, 25.0, 16.6, 14.7; HRMS calcd for $C_{11}H_{13}IO$ 288.0011, found 288.0013.

2,5-Diethyl-4-vinylbenzaldehyde (12). An oven-dried screw-cap tube was charged with $Pd(dba)_2$ (0.0995 g, 0.173 mmol), CuI (0.0659 g, 0.346 mmol), PPh_3 (0.181 g, 0.691 mmol), and BHT (one crystal). The tube was septum-capped, evacuated, and back-filled with N_2 three times. A solution of **11** (2.49 g, 8.64 mmol) and vinyltributyltin (3.07 g, 9.68 mmol) in THF (25 mL) was transferred to the tube via cannula. The tube was then capped with its screw cap, and the solution was stirred in an oil bath at 80 °C for 16 h. The reaction mixture was then cooled to room temperature, and KF (0.8 g) was added. The mixture was stirred at room temperature overnight and poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O three times and brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **12** (0.83 g, 51%) as a clear oil: R_f = 0.32 (hexanes/CH_2Cl_2 =2/1); IR (KBr) 2966 (s), 1693 (s), 1604 (m), 919 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.25 (s, 1H), 7.64 (s, 1H), 7.40 (s, 1H), 7.00 (dd, J = 17.4 Hz, 11.0 Hz, 1H), 5.80 (dd, J = 17.4 Hz, 1.2 Hz, 1H), 5.45 (dd, J = 11.0 Hz, 1.1 Hz, 1H), 3.05 (q, J = 7.5 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.4, 145.0, 142.1, 140.0, 134.2, 133.2, 132.5, 127.8, 118.4, 26.1, 25.8, 16.9, 15.5; HRMS calcd for $C_{13}H_{16}O$ 188.1201, found 188.1203.

2,5-Dibutoxy-4-iodobenzaldehyde (15). A solution of **14**[61] (8.81 g, 18.58 mmol) in diethyl ether (180 mL) was cooled to −10 °C. To this solution was added dropwise *n*-BuLi (2.03 M in hexane, 9.15 mL) over 20 min. The reaction mixture was stirred in an ice/brine bath at −8 to −5 °C for 1 h. DMF (anhydrous, 2.2 mL, 29 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature over 6 h and then poured into water in a separatory funnel. The organic layer was washed with H_2O three times and brine once and dried over $MgSO_4$, and the solvent was removed in vacuo. After concentration, the yellow oil was diluted with hexanes (80 mL) and chilled in the refrigerator overnight. The product crystallized as a yellow solid and was collected by filtration, washed with hexanes twice, and dried in air to give **15** (5.96 g, 85%) as a yellow crystalline solid: mp 73.5−74.5 °C; IR (KBr) 2956 (m), 2866 (m), 1669 (s), 1210 (s), 1036 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.44 (s, 1H), 7.47 (s, 1H), 7.20 (s, 1H), 4.04 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 1.82 (m, 4H), 1.53 (m, 4H), 1.02 (t, J = 7.4 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.5, 156.1, 152.5, 125.5, 124.9, 109.1, 97.1, 69.9, 69.5, 31.53, 31.51, 19.7, 19.6, 14.23, 14.19; HRMS calcd for $C_{15}H_{21}IO_3$ 376.0535, found 376.0536.

2,5-Dibutoxy-4-vinylbenzaldehyde (16). An oven-dried screw-cap tube was charged with **15** (0.890 g, 3.61 mmol), $Pd(dba)_2$ (0.027 g, 0.047 mmol), CuI (0.018 g, 0.094 mmol), PPh_3 (0.049 g, 0.19 mmol). and BHT (one crystal). The tube was septum-capped, evacuated and back-filled with N_2 three times. A solution of vinyltributyltin (0.900 g, 2.84 mmol) in THF (15 mL) was transferred to the tube via cannula. The tube was then capped with its screw cap, and the solution was stirred in an oil bath at 80 °C for 19 h. The reaction mixture was then cooled to room temperature and poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O twice and brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography and then recrystallized from MeOH to afford **16** (0.57 g, 87%) as yellow fluorescent crystals: R_f = 0.44 (hexanes/CH_2Cl_2 = 1/1); mp 47−48 °C; IR (KBr) 2953 (m), 1665 (s), 1210 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.45 (s, 1H), 7.30 (s, 1H), 7.11−7.04 (s+dd, J = 11.1 Hz, 17.7 Hz, 2H), 5.87 (dd, J = 17.8 Hz, 0.9 Hz, 1H), 5.43 (dd, J = 11.1 Hz, 0.9 Hz, 1H), 4.08 (t, J = 6.4 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 1.82 (2 quint, J = 6.5 Hz, 4H), 1.52 (m, 4H), 1.00 (2t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.7, 156.6, 150.9, 134.8, 131.8, 124.9, 118.0, 111.2, 110.4, 69.3, 69.1, 31.75, 31.73, 19.8, 19.7, 14.31, 14.28; HRMS calcd for $C_{17}H_{24}O_3$ 276.1725, found 276.1727.

7-Bromo-2,3-dihydrothieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (18). To the mixture of **17**[61] (0.208 g, 1.22 mmol), AcOH (10 mL), and THF (10 mL), cooled in an ice bath, was portionwise added NBS (0.228 g, 1.28 mmol). The reaction mixture was stirred at room temperature for 17 h, poured into H_2O in a separatory funnel, and extracted with EtOAc. The organic layer was washed with H_2O three times, Na_2CO_3 (satd aq) twice, and brine once, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was recrystallized from CH_2Cl_2/hexanes to afford **18** (0.262 g, 86%) as a slightly yellow solid: R_f = 0.27 (hexanes/EtOAc = 3/1); mp 141−142 °C; IR (KBr) 1358 (m), 2947 (m), 1638 (s), 1085 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.84 (s, 1H), 4.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.3, 148.1, 140.7, 119.0, 102.2, 65.7, 65.3; HRMS calcd for $C_7H_5SBrO_3$ 247.9143, found 247.9138.

2,3-Dihydro-7-vinylthieno[3,4-*b*][1,4]dioxine-5-carbaldehyde (19). An oven-dried screw-cap tube was charged with **18** (0.262 g, 1.05 mmol), $Pd(dba)_2$ (0.012 g, 0.021 mmol), CuI (0.0080 0.042 mmol), PPh_3 (0.022 g, 0.084 mmol), and BHT (one crystal). The tube was septum-capped, evacuated, and back-filled with N_2 three times. A solution of vinyltributyltin (0.399 g, 1.26 mmol) in THF (15 mL) was transferred to the tube via cannula. The tube was then capped with its screw cap, and the solution was stirred in oil bath at 80 °C for 44 h. The reaction mixture was then cooled to room temperature. KF (0.9 g) in H_2O (5 mL) was added. The mixture was stirred under N_2 atmosphere for 20 h, poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O twice, brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography, then recrystallized from EtOAc/hexanes to afford **19** (0.154 g, 75%) as white crystals: R_f = 0.31 (hexanes/EtOAc = 3/1); mp >110 °C dec; IR (KBr) 2951 (m), 1641 (s), 1084 (s), 902 (m)

cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.91 (s, 1H), 6.75 (dd, J = 17.5 Hz, 11.1 Hz, 1H), 5.75 (dd, J = 17.5 Hz, 0.5 Hz, 1H), 5.37 (dd, J = 11.1 Hz, 0.5 Hz, 1H), 4.38 (m, 2H), 4.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.1, 148.9, 139.1, 127.9, 126.0, 117.5, 116.1, 65.7, 64.9; HRMS calcd for $C_9H_8SO_3$ 196.0194, found 196.0193. Anal. Calcd: C, 55.09; H, 4.11; S, 16.34. Found: C, 54.81; H, 4.13; S, 16.31.

2,5-Diethyl-4-iodobenzoic Acid (22). A solution of **10**[56] (18.11 g, 46.92 mmol) in THF (200 mL) was cooled to −78 °C. To this mixture was added dropwise *n*-BuLi (2.19 M in hexanes, 21.4 mL) over 40 min. The reaction mixture was stirred at −78 °C for 1 h. Excess crushed dry ice was poured into the reaction mixture under a N_2 atmosphere. The dry ice bath was removed, and the reaction mixture was allowed to warm to room temperature and then quenched with H_2O. THF was removed in vacuo. The residue was transferred into aqueous NaOH (2 M, 200 mL). The basic aqueous layer was washed with $CHCl_3$ three times, ether once, then acidified by adding HCl (concd, 40 mL) in an ice bath. A white precipitate formed during the acidification. The white solid was collected by filtration, washed with H_2O three times, and dried under vacuum to afford **22** (8.11 g, 57%): mp 134−135 °C (lit.[92] mp 134−135 °C); IR (KBr) 3060−2500 (s), 2970 (m), 1690 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.2 (br, 1H), 7.87 (s, 1H), 7.80 (s, 1H), 2.98 (q, J = 7.5 Hz, 2H), 2.76 (q, J = 7.5 Hz, 2H), 1.25 (2t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.2, 146.5, 144.9, 141.9, 131.5, 128.4, 107.7, 34.0, 27.4, 16.2, 14.9; HRMS calcd for $C_{11}H_{13}IO_2$ 303.9960, found 303.9966.

(2,5-Diethyl-4-iodophenyl)methanol (23). To the solution of **22** (4.57 g, 15.01 mmol) in THF (100 mL), was added BH_3·THF (1.0 M in THF, 18 mL) at room temperature while stirring. The reaction mixture was then heated at 75−80 °C for 2.5 h, cooled to room temperature, and poured into H_2O in a separatory funnel. The mixture was partitioned, and the aqueous phase was extracted with CH_2Cl_2 twice. The combined organic layer was dried over $MgSO_4$ and filtered, and the solvents were removed in vacuo. The residue was purified by column chromatography to afford **23** (4.302 g, 99%) as white crystals: mp 53−55 °C; IR (KBr) 3278 (br), 2962 (m), 1043 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (s, 1H), 7.21 (s, 1H), 4.55 (s, 2H, C*H*$_2$OH, this signal shifts with OH group, could also be observed at 4.61 when δ-O*H* = 2.39), 3.14 (br, 1H), 2.71 (q, J = 7.5 Hz, 2H), 2.56 (q, J = 7.5 Hz, 2H), 1.22 (2t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.3, 141.6, 139.3, 138.7, 128.1, 99.9, 62.4, 34.0, 24.6, 15.4, 15.1; HRMS calcd for $C_{11}H_{15}IO$ 290.0168, found 290.0165.

1-(Bromomethyl)-2,5-diethyl-4-iodobenzene (24). To the clear solution of **23** (4.302 g, 14.83 mmol) and PPh_3 (4.667 g, 17.79 mmol) in THF (80 mL) was added portionwise NBS (3.167 g, 17.79 mmol) while stirring in an ice bath. A white precipitate formed immediately. The reaction mixture was then stirred at room temperature for 15 min, poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O twice and brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was passed through a plug of silica gel to afford **24** (4.89 g, 93%) as white crystals: R_f = 0.43 (hexanes 100%); mp 29−30 °C; IR (KBr) 2965 (s), 1209(s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.68 (s, 1H), 7.17 (s, 1H), 4.49 (s, 2H), 2.71 (2q, J = 7.5 Hz, 4H), 1.29 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.7, 142.5, 139.9, 135.9, 130.4, 101.8, 33.9, 31.5, 24.7, 15.2, 14.9; HRMS calcd for $C_{11}H_{14}BrI$ 351.9324, found 351.9327.

Diethyl (2,5-Diethyl-4-iodophenyl)methylphosphonate (25). The mixture of **24** (0.35 g, 0.99 mmol) and $P(OEt)_3$ (2.0 mL, 12 mmol) was heated in a pressure tube at 150−160 °C for 5 h. Afterward, most of excess $P(OEt)_3$ was removed in vacuo (∼2 mmHg). The residue was purified by column chromatography to afford **25** (0.39 g, 96%) as a clear oil: R_f = 0.28 (hexanes/EtOAc = 1/1); IR (KBr, neat) 2968 (s), 1251 (s), 1051 and 1025 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (s, 1H), 7.05 (d, J_{P-H} = 2.6 Hz, 1H), 3.93 (m, 4H), 3.03 (d, J_{P-H} = 22.1 Hz, 2H), 2.58 (m, 4H), 1.18−1.10 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9 (d, J_{C-P} = 3.7 Hz), 142.4 (d, J_{C-P} = 6.3 Hz), 139.2 (d, J_{C-P} = 3.2 Hz), 130.9 (d, J_{C-P} = 5.4 Hz), 130.0 (d, J_{C-P} = 9.1 Hz), 99.0 (d, J_{C-P} = 4.7 Hz), 62.2 (d, J_{C-P} = 6.8 Hz), 33.6, 30.2 (d, J_{C-P} = 137.8 Hz), 25.1, 16.5 (d, J_{C-P} = 5.8 Hz), 14.8, 14.7; HRMS calcd for $C_{15}H_{24}IO_3P$ 410.0508, found 410.0514.

(2,5-Dibutoxy-4-iodophenyl)methanol (26). To the solution of **15** (5.96 g, 15.8 mmol) in THF (100 mL) was added BH_3·THF (1.0 M THF, 19.0 mL) at room temperature. The mixture was heated at 80 °C for 80 min, then concentrated in vacuo. The residue was passed through a plug of silica gel to afford **26** (6.01 g, 100%) as a white crystalline solid: R_f = 0.35 (hexanes/EtOAc = 5/1); mp 44.5−45.5 °C; IR (KBr) 3264 (s, br), 2956 (s), 1205 (s), 1037 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.25 (s, 1H), 6.83 (s, 1H), 4.64 (s, 2H), 3.98 (t, J = 6.4 Hz, 2H), 3.96 (t, J = 6.4 Hz, 2H), 2.32 (br, 1H), 1.79 (2 quint, J = 6.5 Hz, 4H), 1.53 (2 sext, J = 7.5 Hz, 4H), 0.99 (2t, J = 7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.5, 151.7, 130.9, 122.6, 113.3, 85.4, 70.4, 69.0, 62.3, 31.82, 31.79, 19.80, 19.78, 14.32, 14.30; HRMS calcd for $C_{15}H_{23}IO_3$ 378.0692, found 378.0689.

1-(Bromomethyl)-2,5-dibutoxy-4-iodobenzene (27). To the clear solution of **26** (1.186 g, 3.135 mmol) and PPh_3 (0.987 g, 3.76 mmol) in THF (40 mL), was added portionwise NBS (0.670 g, 3.762 mmol) while stirring in an ice bath. A precipitate formed immediately. The reaction mixture was then stirred at room temperature for 40 min and poured into H_2O in a separatory funnel, and the aqueous layer was extracted with EtOAc. The organic layer was washed with H_2O twice and brine twice, dried over $MgSO_4$, and filtered, and the solvent was removed in vacuo. The residue was passed through a plug of silica gel to afford **27** (1.175 g, 85%) as white crystals. When dried, the white solid immediately turned dark in air. Compound **27** was reasonably stable in solution but began to decompose quickly when the pristine solid was isolated. Thus, some characterization data on this compound could not be obtained: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (s, 1H), 6.82 (s, 1H), 4.52 (s, 2H), 3.99 (2t, J = 6.4 Hz, 4H), 1.82 (m, 4H), 1.56 (m, 4H), 1.02 and 1.00 (2t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.4, 151.9, 127.6, 123.7, 114.9, 87.9, 70.3, 69.4, 31.81, 31.79, 29.1, 19.82, 19.76, 14.4, 14.3.

Diethyl (2,5-Dibutoxy-4-iodophenyl)methylphosphonate (28). The mixture of **27** (1.175 g, 2.663 mmol) and $P(OEt)_3$ (1.5 mL, 8.7 mmol) was heated in a pressure tube at 150 °C for 4 h. The reaction mixture was cooled to room temperature and purified by column chromatography to afford **28** (1.282 g, 97%) as a clear oil: R_f = 0.24 (hexanes/EtOAc = 1/1); IR (KBr) 2958 (m), 1211 (s), 1028 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12 (s, 1H), 6.77 (d, J_{P-H} = 2.6 Hz, 1H), 3.93 (2q, J = 7.2 Hz, 4H), 3.85 (t, J = 6.4 Hz, 2H), 3.79 (t, J = 6.4 Hz, 2H), 3.08 (d, J_{P-H} = 21.8 Hz, 2H), 1.66 (m, 4H), 1.40 (m, 4H), 1.14 (t, J = 7.1 Hz, 6H), 0.87 (2t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9 (d, J_{P-C} = 3.2 Hz), 151.5 (d, J_{P-C} = 7.0 Hz), 122.7 (d, J_{P-C} = 2.8 Hz), 121.6 (d, J_{P-C} = 9.1 Hz), 115.3 (d, J_{P-C} = 5.0 Hz), 84.7 (d, J_{P-C} = 4.5 Hz), 69.8, 69.0, 62.1 (d, J_{P-C} = 6.3 Hz), 31.6, 31.5, 26.6 (d, J_{P-C} = 138.6 Hz), 19.5, 19.4, 16.5 (d, J_{P-C} = 6.2 Hz), 14.0 (2C, overlap); HRMS calcd for $C_{19}H_{32}IO_5P$ 498.1032, found 498.1035.

5-Bromo-1,3-dinitrobenzene (32).[70,71] To the mixture of 1,3-dinitrobenzene (29.964 g, 178.24 mmol), Br_2 (4.76 mL, 92.7 mmol), and HNO_3 (concd 56 mL), cooled in an ice bath, was added H_2SO_4 (200 mL) slowly while stirring. The reaction mixture was heated to 80 °C for 2 h (monitored by TLC, until minimum starting material remained), cooled to room temperature, and poured into ice. The pale solid was collected by filtration and washed with H_2O until the washings were neutral. The crude product was recrystallized from EtOH to give **32** (37.61 g, 85%) as a slightly yellow solid: R_f = 0.62 (hexanes/EtOAc = 4/1) (1,3-dinitrobenzene has R_f = 0.32 on

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TLC under the same conditions); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.03 (t, J = 2.0 Hz, 1H), 8.74 (d, J = 2.0 Hz, 2H).

5-Iodo-1,3-dinitrobenzene (33).[93,94] A screw-cap tube charged with **32** (3.029 g, 12.26 mmol), NaI (3.677 g, 24.53 mmol), and CuI (0.117 g, 0.613 mmol) was evacuated and back-filled with N_2 three times. *N,N′*-Dimethylethylenediamine (0.13 mL, 1.2 mmol) was added via syringe, followed by 1,4-dioxane (50 mL, previously dried over 4 Å molecular sieves and flushed with N_2 for at least 2 h). The tube was sealed with its screw cap and heated at 110 °C for 31 h. The reaction mixture was cooled back to room temperature, diluted with aqueous ammonia (30%, 8 mL), poured into water in a separatory funnel, and extracted with EtOAc. The organic layer was washed with H_2O three times and brine once, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by column chromatography to give **33** (3.28 g, 91%) as a white solid: R_f = 0.44 (hexanes/EtOAc = 8/1); mp 102−103 °C (lit.[90] mp 104.5−105.5 °C, lit.[91] mp 101−102 °C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.04 (t, J = 2.0 Hz, 1H), 8.90 (d, J = 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.0, 138.2, 118.9, 93.9.

3,5-Dinitrostyrene (34).[95] A two-neck flask charged with $ZnCl_2$ (2.34 g, 17.2 mmol) under vacuum was heated over a Bunson burner until the $ZnCl_2$ melted and began to sublime. The flask was then allowed to cool to room temperature under vacuum and back-filled with N_2. THF (10 mL) was added via syringe to dissolve the $ZnCl_2$. The white slurry was cooled to 0 °C, and vinylmagnesium bromide (1M in THF, 10.3 mL) was added slowly over 10 min. The mixture was then stirred at room temperature for 1 h. A solution of **33** (2.02 g, 6.87 mmol), $Pd(PPh_3)_2Cl_2$ (0.0964 g, 0.137 mmol), and BHT (one crystal) in THF (50 mL) was cannulated into the mixture above. The reaction mixture was stirred at room temperature for 18 h and quenched with NH_4Cl (satd aq, 10 mL). The mixture was poured into water in a separatory funnel and extracted with CH_2Cl_2 three times. The combined organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography to afford **34** (1.19 g, 89%) as a slightly yellow solid: R_f = 0.38 (hexanes/EtOAc = 8/1); mp 89−90 °C (lit.[92] mp 88 °C); IR (KBr) 3098 (m), 1534 (s), 1345 (s), 907 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.91 (t, J = 2.0 Hz, 1H), 8.56 (d, J = 2.0 Hz, 2H), 6.87 (dd, J = 17.5, 11.1 Hz, 1H), 6.10 (d, J = 17.5 Hz, 1H), 5.68 (d, J = 11.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.3, 141.7, 133.4, 126.3, 120.8, 117.8; HRMS calcd for $C_8H_6N_2O_4$ 194.0328, found 194.0326.

35a. To the dark solution of **1a** (13.22 g, 53.50 mmol) in a mixed solvent of H_2O−CH_3CN (1:1, 100 mL), cooled in ice bath, was added HCl (concd, 17.7 mL). A precipitate formed at once. To the mixture above, while efficiently stirring, was added dropwise a solution of $NaNO_2$ (5.538 g, 80.26 mmol) in H_2O (20 mL) over 20 min. The dark red mixture was stirred at 0 °C for 15 min, room temperature 1.5 h, then poured into a solution of K_2CO_3 (36.9 g, 267 mmol)/$HNEt_2$ (11.0 mL, 107 mmol)/H_2O (100 mL). The resulting mixture was stirred at room temperature for 2 h, poured into H_2O in a separatory funnel, and extracted with CH_2Cl_2 three times. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The residue was purified by column to give **35a** (14.34 g, 81%) as a dark orange oil: R_f = 0.25 (hexanes 100%); IR (KBr, neat) 2970 (m), 1465−1202 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56 (d, J = 2.1 Hz, 1H), 7.49 (dd, J = 2.1 Hz, 8.4 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 3.78 (q, J = 7.1 Hz, 4H), 2.85 (q, J = 7.5 Hz, 2H), 1.31 (t-br, J = 7.0 Hz, 6H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.6, 141.4, 138.1, 135.6, 118.9, 89.9, 25.0, 15.7; HRMS calcd for $C_{12}H_{18}IN_3$ 331.0545, found 331.0544.

35b.[96] To mixture of K_2CO_3 (6.62 g, 48.0 mmol)/$HNEt_2$ (3.3 mL, 32 mmol)/H_2O (40 mL), cooled in an ice bath, was added the solution of **2b**[47] (5.10 g, 16.0 mmol) in CH_3CN (100 mL). The reaction mixture was stirred in an ice bath that was allowed to warm to room temperature overnight. The reaction mixture was poured into water in a separatory funnel and extracted with EtOAc. The organic layer was washed with H_2O twice and brine once, concentrated in vacuo, and purified by column to afford **35b** (4.75 g, 98%) as an orange oil: R_f = 0.43 (hexanes/CH_2Cl_2 = 3/1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 3.77 (q, J = 7.1 Hz, 4H), 1.30 (br-t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 138.2, 123.0, 89.5.

35c. To the mixture of K_2CO_3 (6.46 g, 46.8 mmol)/$HNEt_2$ (3.6 mL, 35 mmol)/CH_3CN (80 mL), cooled in ice bath, was added portionwise **2c** (7.86 g, 23.4 mmol). The reaction mixture was then stirred in an ice bath that was allowed to warm to room temperature overnight. The reaction mixture was poured into H_2O in a separatory funnel and extracted with EtOAc. The organic layer was washed with H_2O twice and brine once, concentrated in vacuo, and purified by column to afford **35c** (6.76 g, 90%, a yield as high as 98% was obtained) as an orange oil: R_f = 0.52 (hexanes/CH_2Cl_2 = 3/1); IR (KBr, neat) 2975 (m), 1476−1102 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (dd, $^3J_{F-H}$ = 10.3 Hz, $^4J_{H-H}$ = 1.9 Hz, 1H), 7.39 (dm, $^3J_{H-H}$ = 8.5 Hz, 1H), 7.20 (t, $^4J_{F-H}$ = $^3J_{H-H}$ = 8.4 Hz, 1H), 3.79 (q, J = 7.2 Hz, 4H), 1.33 and 1.26 (2 br, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.5 (d, J_{C-F} = 252.8 Hz), 139.8 (d, J_{C-F} = 7.5 Hz), 133.7 (d, J_{C-F} = 3.8 Hz), 125.7 (d, J_{C-F} = 22.9 Hz), 121.1 (d, J_{C-F} = 2.4 Hz), 87.7 (d, J_{C-F} = 7.6 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −126.2 (m, 1F); HRMS calcd for $C_{10}H_{13}IN_3F$ 321.0138, found 321.0136.

35d. To the mixture of K_2CO_3 (2.86 g, 20.8 mmol)/$HNEt_2$ (1.6 mL, 16 mmol)/H_2O (50 mL)/CH_3CN (50 mL), cooled in ice bath, was portionwise added **2d**[48] (4.01 g, 10.4 mmol). The reaction mixture was then stirred in an ice bath that was allowed to warm to room temperature overnight. The reaction mixture was poured into H_2O in a separatory funnel and extracted with EtOAc. The organic layer was washed with H_2O twice and brine once, concentrated in vacuo and purified by column to afford **35d** (3.40 g, 88%) as a red oil: R_f = 0.25 (hexanes 100%); IR (KBr, neat): 2977 (m), 1467−1139 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 1.9 Hz, 1H), 7.77 (dd, J = 8.6 Hz, 1.9 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 3.84−3.75 (m, 4H), 1.37 (q, J = 7.1 Hz, 3H), 1.24 (q, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 141.4, 135.4 (q, J_{C-F} = 5.7 Hz), 125.7 (q, J_{C-F} = 29.8 Hz), 123.8 (q, J_{C-F} = 272.7 Hz), 119.6, 87.5, 49.9, 42.6, 14.9, 11.5; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −60.8 (s, 3F); HRMS calcd for $C_{11}H_{13}IN_3F_3$ 371.0106, found 371.0102.

4-[4-(3,3-Diethyl)triazene]styrylbenzaldehyde (36). According to the general coupling procedure C, **35b** (1.271 g, 4.193 mmol) was coupled with **9**[54] (0.554 g, 4.19 mmol) in the presence of $Pd(OAc)_2$ (0.047 g, 0.21 mmol), P(*o*-tolyl)$_3$ (0.256 g, 0.841 mmol), DMF (20 mL), and NBu_3 (5.0 mL, 21 mmol) at 90 °C for 49 h to give **36** (0.79 g, 61%) as a yellow solid: R_f = 0.41 (hexanes/EtOAc = 5/1); mp 149−150 °C; IR (KBr) 2936 (m), 2977 (m), 1696 (s), 970 (s), 835 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.00 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 16.3 Hz, 1H), 7.11 (d, J = 16.3 Hz, 1H), 3.81 (q, J = 7.1 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.0, 151.9, 144.3, 135.4, 133.7, 132.7, 130.7, 128.0, 127.1, 126.2, 121.2; HRMS calcd for $C_{19}H_{21}N_3O$ 307.1685, found 307.1686.

37. According to the general HWE reaction procedure, **36** (0.096 g, 0.31 mmol), **21**[63] (0.130 g, 0.350 mmol), NaH (0.014 g, 60% in mineral oil, 0.34 mmol), and DME (10 mL) gave **37**

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(0.13 g, 81%) as a yellow solid: R_f = 0.41 (hexanes/CH_2Cl_2 = 1/1); mp >200 °C dec; IR (KBr) 2918 (m), 968 (s), 838 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.54−7.43 (m, 8H), 7.28 (d, J = 8.3 Hz, 2H), 7.18−7.00 (m, 4H), 3.81 (q, J = 7.2 Hz, 4H), 1.30 (t, J = 7.2 Hz, 6H); the solubility of this compound was too low to obtain a good ^{13}C NMR; HRMS calcd for $C_{26}H_{26}IN_3$ 507.1171, found 507.1178.

38. According to the general HWE reaction procedure, **36** (0.083 g, 0.27 mmol), **25** (0.166 g, 0.405 mmol), NaH (0.0162 g, 60% in mineral oil, 0.405 mmol), and DME (10 mL) at room temperature for 16 h gave **38** (0.030 g, 20%) as a yellow solid: R_f = 0.32 (hexanes/CH_2Cl_2 = 3/1); mp 104−106 °C; IR (KBr) 2960 (m), 2924 (m), 960 (s), 833 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.67 (s, 1H), 7.53−7.45 (m, 9H), 7.30 (d, J = 15.9 Hz, 1H), 7.18−7.02 (m, 3H), 3.81 (q, J = 7.2 Hz, 4H), 2.80−2.71 (m, 4H), 1.33−1.24 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3, 144.6, 141.8, 139.9, 137.7, 136.9, 136.6, 134.6, 130.6, 129.2, 127.6, 127.4, 127.22, 127.17, 125.9, 125.5, 121.2, 99.8, 34.2, 26.1, 15.7, 15.3; HRMS calcd for $C_{30}H_{34}IN_3$ 563.1797, found 563.1799.

39. According to the general coupling procedure C, **38** (41 mg, 0.073 mmol), styrene (0.083 mL, 0.73 mmol), $Pd(OAc)_2$ (0.8 mg, 0.004 mmol), P(*o*-tolyl)$_3$ (4.4 mg, 0.015 mmol), DMF (5 mL), and NBu_3 (0.26 mL, 1.1 mmol) at 80 °C for 17 h gave **39** (28 mg, 71%) as a yellow solid: R_f = 0.27 (hexanes/CH_2Cl_2 = 2/1); mp 170−172 °C; IR (KBr) 3022 (m), 2961 (m), 962 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.58−7.49 (m, 10H), 7.46−7.39 (m, 6H), 7.30 (dm, J = 7.4 Hz, 1H), 7.19−7.06 (m, 4H), 3.81 (q, J = 7.2 Hz, 4H), 2.85 (2q, J = 7.5 Hz, 4H), 1.32 (m, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz, 1 aliphatic and 2 aromatic peaks missing because of overlap, triazene *N*-ethyl carbons were broadened and not observed) δ 151.3, 140.3, 138.3, 137.5, 137.3, 135.6, 135.5, 134.6, 130.0, 129.7, 129.2, 129.0, 128.0, 127.6, 127.3, 127.2, 127.0, 126.5, 126.44, 126.41, 126.0, 121.1, 26.8 (2 Cs overlap), 16.22, 16.20; HRMS calcd for $C_{38}H_{41}N_3$ 539.3300, found 539.3300.

2,5-Dibutoxyl-4-[4-(3,3-diethyl)triazene]styrylbenzaldehyde (40). According to the general coupling procedure C, **16** (0.754 g, 2.73 mmol) coupled with **35b** (0.992 g, 3.27 mmol) in the presence of $Pd(OAc)_2$ (0.0294 g, 0.131 mmol), P(*o*-Toly)$_3$ (0.159 g, 0.523 mmol), NBu_3 (3 mL, 16 mmol), and DMF (15 mL), at 80 °C for 19 h, to give **40** (0.372 g, 30%) as a yellow solid: R_f = 0.29 (hexanes/CH_2Cl_2 = 1/1); mp 97−98 °C; IR (KBr) 2955 (s), 2934 (s), 1669 (s), 1205 (s), 978 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 10.46 (s, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.47−7.43 (m, 3H), 7.34 (s, 1H), 7.28 (s, 1H), 7.22 (d, J = 17.0 Hz, 1H), 4.14 (t, J = 6.4 Hz, 2H), 4.06 (t, J = 6.5 Hz, 2H), 3.80 (q, J = 7.2 Hz, 4H), 1.89−1.84 (m, 4H), 1.60−1.54 (m, 4H), 1.30 (t, J = 7.1 Hz, 6H), 1.03 (t, J = 7.3 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.6, 156.8, 151.8, 151.1, 135.3, 134.5, 132.8, 128.1, 124.4, 121.8, 121.2, 110.7, 110.5, 69.35, 69.27, 31.8 (2C, overlap), 19.9, 19.8, 14.4, 14.3; HRMS calcd for $C_{27}H_{37}N_3O_3$ 451.2835, found 451.2841.

41. According to the general coupling procedure A, **35b** (0.276 g, 0.991 mmol), **19** (0.149 g, 0.759 mmol), $Pd(OAc)_2$ (5.2 mg, 0.023 mmol), *n*-Bu_4NBr (0.245 g, 0.759 mmol), *i*-$PrNEt_2$ (0.8 mL, 5 mmol), DMF (10 mL), and a crystal of BHT gave **41** (0.20 g, 72%). Recrystallization from CH_2Cl_2/hexanes afforded bronze shiny crystals: R_f = 0.25 (hexanes/EtOAc = 3/1); mp 179.5−180.5 °C; IR (KBr) 2972 (m), 1628 (s), 1274 (s), 1080 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.89 (s, 1H), 7.47 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 16.2 Hz, 1H), 7.09 (d, J = 16.2 Hz, 1H), 4.39 (m, 2H), 4.37 (m, 2H), 3.79 (q, J = 7.1 Hz, 4H), 1.29 (br-t, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.8, 152.0, 149.2, 138.8, 133.5, 132.3, 129.3, 128.0, 121.3, 116.2, 115.6, 65.9, 65.0; HRMS calcd for $C_{19}H_{21}SN_3O_3$ 371.1304, found 371.1304.

42. According to the general HWE reaction procedure, **41** (0.016 g, 0.043 mmol), **21**[63] (0.031 g, 0.086 mmol), NaH (5.2 mg, 60% in mineral oil, 0.13 mmol), and DMF (10 mL) gave **42** (0.021 g, 85%) as an orange solid: R_f = 0.26 (hexanes/EtOAc = 5/1); mp >145 °C dec; IR (KBr) 2923 (m), 1083 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 16.1 Hz, 1H), 7.13 (d, J = 16.1 Hz, 1H), 6.86 (d, J = 16.2 Hz, 1H), 6.73 (d, J = 16.2 Hz, 1H), 4.33 (s, 4H), 3.79 (q, J = 7.0 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H); decomposed while obtaining ^{13}C NMR in $CDCl_3$.

1,4-Dibutoxy-2,5-bischloromethylbenzene (43).[97,98] A three-neck flask was charged a mixture of 1,4-dibutoxylbenzene[90] (2.609 g, 11.73 mmol), formaldehyde (37% w/w aq, 7.1 mL, 88 mmol), dioxane (30 mL), and HCl (conc, 6.0 mL). The reaction mixture was heated at 65 °C for 9 h. HCl gas freshly generated from NaCl and H_2SO_4 (concd) was continuously introduced to the reaction mixture throughout the process. The reaction mixture was cooled back to room temperature, poured into water, and extracted with EtOAc. The organic layer was washed with H_2O three times, Na_2CO_3 (satd aq) twice,and brine once, dried over $MgSO_4$, and filtered and the solvent removed in vacuo. The residue was purified by flash column to give **43** (2.75 g, 73%) as white crystals: R_f = 0.54 (hexanes/CH_2Cl_2 = 3/1); mp 87−88 °C (lit.[97] mp 84−86 °C); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.93 (s, 2H), 4.65 (s, 4H), 4.01 (t, J = 6.4 Hz, 4H), 1.80 (sext, J = 6.6 Hz, 4H), 1.54 (m, 4H), 1.01 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.1, 127.5, 114.8, 69.3, 41.9, 31.9, 19.8, 14.4; HRMS calcd for $C_{16}H_{24}Cl_2O_2$ 318.1153, found 318.1157.

(2,5-Dibutoxy-4-cyanomethylphenyl)acetonitrile (44).[99] To the solution of **47** (2.039 g, 6.386 mmol) in DMSO (50 mL) was added KCN (1.081 g, 16.60 mmol). The reaction mixture was stirred at room temperature for 8 h and then poured into cold water in an ice bath. The white precipitate was collected by filtration, washed thoroughly with H_2O, and dried under vacuum. Recrystallization from EtOH afforded **44** (4.07 g, 78%) as a white solid: R_f = 0.15 (hexanes/CH_2Cl_2 = 3/1); mp 107−108 °C (lit.[99] 106−107 °C); IR (KBr) 2960 (s), 2940 (s), 2250 (s), 1225 (s), 1043 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.93 (s, 2H), 4.00 (t, J = 6.4 Hz, 4H), 3.71 (s, 4H), 1.80 (sext, J = 6.4 Hz, 4H), 1.51 (m, 4H), 1.00 (t, J = 7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 119.6, 118.3, 113.1, 69.1, 31.8, 19.8, 19.1, 14.3; HRMS calcd for $C_{18}H_{24}N_2O_2$ 300.1838, found 300.1838.

1,4-Bis[1-cyano-2-{(3,4-(ethylenedioxy)thien-2-yl}vinyl]-2,5-dibutoxybenzene (45). To the mixture of **44** (0.118 g, 0.394 mmol), **19** (0.134 g, 0.787 mmol), and MeOH (40 mL) was added NaOMe (0.043 g, 0.787 mmol). The reaction mixture was heated at 60 °C for 25 h. MeOH was removed in vacuo. The residue was diluted with CH_2Cl_2, washed with H_2O three times, dried over $MgSO_4$,and filtered and solvent removed in vacuo. The residue was recrystallized in MeOH to give **45** (0.128 g, 54%) as a yellow solid: R_f = 0.52 (hexanes/EtOAc = 2/1); mp > 200 °C dec; IR (KBr) 2959 (m), 2209 (s), 1216 (s), 1067 (s), 850 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.26 (s, 2H), 7.11 (s, 2H), 6.63 (s, 2H), 4.33 (m, 4H), 4.27 (m, 4H), 4.08 (t, J = 6.1 Hz, 4H), 1.87 (m, 4H), 1.57 (m, 4H), 1.00 (t, 6H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.0, 144.8, 141.9, 135.1, 124.2, 119.5, 114.7, 114.4, 105.5, 101.8, 69.7, 65.7, 65.0, 31.9, 19.9, 14.5; HRMS calcd for $C_{32}H_{32}N_2O_6S_2$ 604.1702, found 604.1690.

4-[3-Ethyl-4-(3,3-Diethyl)triazene]styrylbenzaldehyde (46). According to the general coupling procedure A, **35a** (1.48 g, 4.47 mmol), **9**[54] (0.537 g, 4.06 mmol), $Pd(OAc)_2$, *n*-Bu_4NBr (1.31 g, 4.06 mmol), NBu_3 (2.9 mL, 12 mmol), and DMF (20 mL) at 95 °C for 32 h gave **46** (0.690 g, 46%) as a dark sticky oil: R_f = 0.30 (hexanes/CH_2Cl_2 = 1/1); IR (KBr) 2969 (m), 1696 (s), 1593 (m), 1096 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.97 (s, 1H), 7.84 (d, J = 8.2 Hz, 2H), 7.61 (d, J =

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8.2 Hz, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.38 (dd, J = 8.3 Hz, 2.0 Hz, 1H), 7.24 (d, J = 16.3 Hz, 1H), 7.08 (d, J = 16.3 Hz, 1H), 3.80 (q, J = 7.2 Hz, 4H), 2.95 (q, J = 7.5 Hz, 2H), 1.34−1.30 (m, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.7, 149.1, 144.2, 139.2, 135.2, 133.5, 132.8, 130.4, 128.2, 126.9, 125.7, 125.5, 117.0, 25.3, 15.8; HRMS calcd for $C_{21}H_{25}N_3O$ 335.1998, found 335.1990.

47. According to the general HWE reaction procedure, **46** (0.705 g, 2.10 mmol), **21**[63] (0.992 g, 2.73 mmol), NaH (0.420 g, 60% in mineral oil, 10.5 mmol), and THF (60 mL) at room temperature for 2.5 h gave **47** (0.426 g, 38%) as a yellow solid: R_f = 0.34 (hexanes/CH_2Cl_2 = 3/1); mp 182−183 °C; IR (KBr) 3017 (m), 2964 (m), 1087 (s), 965 (s), 834 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (d, J = 8.4 Hz, 2H), 7.52 (m, 4H), 7.42 (d, J = 8.3 Hz, 1H), 7.38 (d, J = 1.7 Hz, 1H), 7.35 (dd, J = 8.3 Hz, 1.7 Hz, 1H), 7.28 (overlap with solvent peak, d, J = 8.4 Hz, 2H), 7.18−7.06 (overlap of 4 doublets, J = 16.3 Hz, 4H), 3.80 (q, J = 7.2 Hz, 4H), 2.90 (q, J = 7.5 Hz, 2H), 1.35−1.25 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.6, 139.3, 138.2, 138.0, 137.4, 136.2, 134.5, 129.7, 129.6, 128.6, 127.9, 127.5, 127.4, 127.1, 126.9, 125.3, 117.1, 93.1, 25.5, 16.0; HRMS calcd for $C_{28}H_{30}IN_3$ 535.1484, found 535.1481.

48. A centrifuge tube charged with the solution of **47** (0.121 g, 0.226 mmol) in CH_2Cl_2 (3 mL) was cooled at 0 °C. To this solution was added HBF_4·OMe_2 (0.11 mL, 0.90 mmol) via a syringe. The reaction mixture turned red immediately. The mixture was kept in an ice bath for 30 min, and intermittent sonication was applied during this period. The reaction mixture was centrifuged, and the liquid was decanted. The solid was washed with ether twice, dissolved in a minimum amount of CH_3CN, and precipitated by adding ether. The diazonium salt **48** (0.053 g, 57%) was collected by filtration as a red solid: IR (KBr) 2236 (s), 1578 (s), 1051 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.61 (d, J = 8.7 Hz, 1H), 8.05 (s, 1H), 8.01 (d, J = 8.7 Hz, 1H), 7.87−7.71 (m, 7H), 7.55 (d, J = 16.3 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.35 (m, 2H), 3.05 (q, J = 7.5 Hz, 2H), 1.39 (t, J = 7.5 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.5, 150.0, 139.3, 138.8, 138.4, 137.4, 136.0, 134.2, 129.59, 129.56, 129.4, 129.2, 128.8, 128.1, 127.2, 126.7, 111.2, 94.8, 25.6, 13.8.

49a−d. According to the general coupling procedure A, a mixture of **8a** (0.185 g, 0.283 mmol), **8b** (0.221 g, 0.305 mmol), **8c** (0.184 g, 0.218 mmol), and **8d** (0.202 g, 0.203 mmol) was coupled with **9**[54] (0.199 g, 1.51 mmol) in the presence of $Pd(OAc)_2$ (0.0091 g, 0.040 mmol), n-Bu_4NBr (0.326 g, 1.01 mmol), NBu_3 (0.71 mL, 3.0 mmol), BHT (one crystal), and DMF (15 mL) to give the mixture of **49a−d** as a yellow solid (0.55 g, crude). The product mixture gave four major fluorous peaks corresponding to the four products in the analytical HPLC (Figure 6).

49b. According to the general coupling procedure A, **8b** (0.821 g, 1.13 mmol), **9**[54] (0.164 g, 1.24 mmol), $Pd(OAc)_2$ (0.013 g, 0.056 mmol), n-Bu_4NBr (0.364 g, 1.13 mmol), NBu_3 (0.81 mL, 3.4 mmol), and DMF (15 mL) gave **49b** (0.723 g, 88%) as a yellow solid: R_f = 0.27 (hexanes/CH_2Cl_2 = 3/2); mp 124.5−125.5 °C; IR (KBr) 2963 (m), 1701 (s), 1592 (m), 1257−1139 (s), 970 (m), 840 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.01 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.31−7.10 (m, 6H), 4.98 (s, 2H), 3.68 (s-br, 2H), 2.93 (m, 2H), 2.39 (m, 2H), 1.71 (t-br, 2H), 0.94 (t, J = 7.3 Hz, 3H); HRMS calcd for $C_{33}H_{28}F_{13}N_3O$ 729.2025, found 729.2557. Anal. Calcd: C, 54.33; H, 3.87. Found: C, 54.37; H, 3.82.

50a−d. According to the general HWE reaction procedure, the mixture of **49a−d** (crude, 0.295 g), **25** (0.313 g, 0.764 mmol), NaH (0.076 g, 60% in mineral oil, 1.9 mmol), and DME (20 mL) gave **50a−d** as a yellow solid (0.16 g, crude). The analytical HPLC gave four major fluorous peaks corresponding to the four coupled products (Figure 7).

51a−d. According to the general coupling procedure C, the mixture of **50a−d** (crude, 0.16 g), **31**[67] (0.048 g, 0.32 mmol), $Pd(OAc)_2$ (0.0018 g, 0.0078 mmol), P(o-tolyl)$_3$ (0.0096 g, 0.031

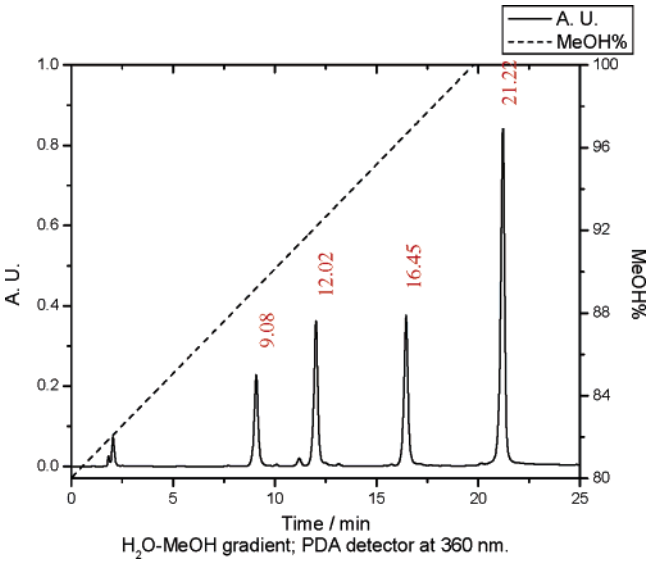

FIGURE 6. HPLC results of the mixture **49a−d**. Gradient conditions: H_2O−MeOH (MeOH from 80% to 100% in 20 min). Compound (retention time): **49a** (9.08 min); **49b** (12.02 min); **49c** (16.45 min); **49d** (21.22 min).

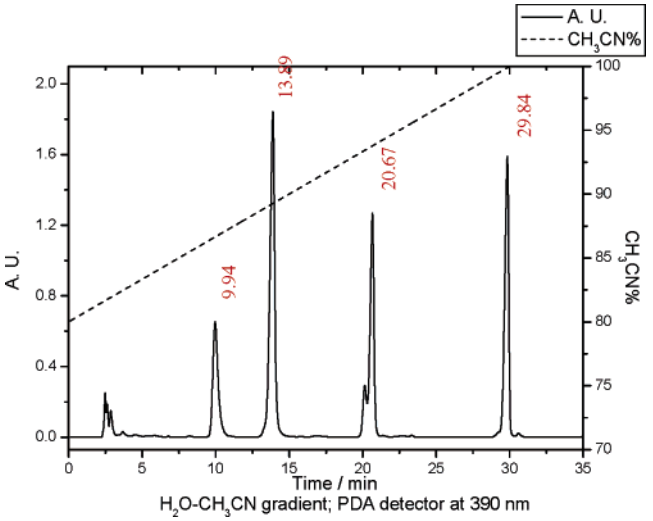

FIGURE 7. HPLC results of the mixture **50a−d**. Gradient conditions: H_2O−CH_3CN (CH_3CN from 80% to 100% in 30 min). Compound (retention time): **50a** (9.94 min); **50b** (13.89 min); **50c** (20.67 min); **50d** (29.84 min).

mmol), NBu_3 (0.38 mL, 1.6 mmol), BHT (one crystal), and DMF (15 mL) give a mixture of **51a−d** as an orange solid (~0.21 g, crude). Product analysis by HPLC gave four major fluorous peaks corresponding to the four coupled products (Figure 8). The peak attributed to **51a** was small, indicating a low yield or unstable product. **51b**, **51c**, and **51d** were isolated by preparative HPLC.

51b. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 50% for three steps (from **8b**): mp > 100 °C dec; IR (KBr) 2961 (m), 2926 (m), 1508 (s), 1339 (s), 960 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, J = 8.8 Hz, 2H, Ar-*H*, *o*-NO_2), 7.68 (d, J = 8.8 Hz, 2H), 7.59−7.48 (m, 11H), 7.39 (d, J = 16.0 Hz, 1H, *trans* alkene-*H*), 7.28−7.09 (m, 8H), 4.98 (s, 2H, benzyl-*H*), 3.65 (br-t, 2H, $NCH_2CH_2CH_3$), 2.96−2.92 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.86 (q, J = 7.5 Hz, 4H, Ar-CH_2CH_3), 2.45−2.33 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.72 (br, 2H, $NCH_2CH_2CH_3$), 1.33 (t, J = 7.5 Hz, 6H, Ar-CH_2CH_3), 0.95 (t, 3H, J = 7.3 Hz, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz)

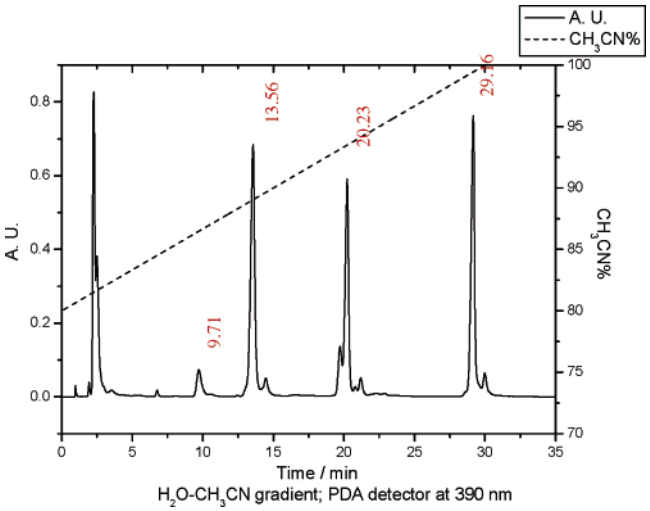

FIGURE 8. HPLC results of the mixture **51a**−**d**. Gradient conditions: H_2O-CH_3CN (CH_3CN from 80% to 100% in 30 min). Compound (retention time): **51a** (9.71 min); **51b** (13.56 min); **51c** (20.23 min); **51d** (29.16 min).

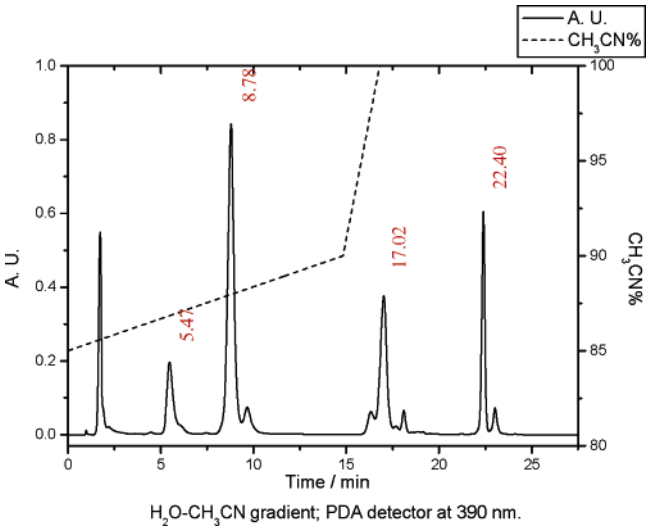

FIGURE 9. HPLC results of the mixture **52a**−**d**. Gradient conditions: H_2O-CH_3CN (CH_3CN from 85% to 90% in 15 min, then to 100% in 2 min). Compound (retention time): **52a** (5.47 min); **52b** (8.78 min); **52c** (17.02 min); **52d** (22.40 min).

δ −81.3 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.4 (m, 2F), −123.4 (m, 2F), −124.0 (m, 2F), −126.6 (m, 2F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{52}H_{47}F_{13}N_4O_2$ 1006.3, found 1006.2.

51c. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 46% for three steps (from **8c**): mp >120 °C dec; IR (KBr) 2925 (m), 1508 (s), 1339 (s), 1203 (s), 957 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, J = 8.8 Hz, 2H, Ar-*H*, *o*-NO_2), 7.67 (d, J = 8.8 Hz, 2H), 7.59−7.47 (m, 8H), 7.41 (d, J = 16.1 Hz, 1H, *trans* alkene-*H*), 7.28−7.06 (m, 10H), 4.99 (s, 2H, benzyl-*H*), 3.71 (br-t, 2H, $NCH_2CH_2CH_3$), 2.95−2.92 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.86 (q, J = 7.6 Hz, 4H, Ar-CH_2CH_3), 2.45−2.37 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.74 (br, 2H, $NCH_2CH_2CH_3$), 1.33 (t, J = 7.6 Hz, 6H, Ar-CH_2CH_3), 0.95 (br, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.2 (t, J = 10.1 Hz, 3F), −115.5 (m, 2F), −121.9 (m, 2F), −122.2 (m, 4F), −123.2 (m, 2F), −124.0 (m, 2F), −126.6 (m, 2F), −128.1 and −128.3 (2m, 1F, *cis* and *trans* Ar-*F*); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{54}H_{46}F_{18}N_4O_2$ 1124.3, found 1124.3.

51d. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 47% for three steps (from **8d**): mp 147−149 °C; IR (KBr) 2925 (m), 1517 (s), 1340 (s), 961 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.26 (d, J = 8.6 Hz, 2H, Ar-*H*, *o*-NO_2), 7.81 (m, 1H, Ar-*H*, *o*-CF_3), 7.68 (d, J = 8.7 Hz, 2H), 7.59−7.47 (m, 7H), 7.39 (d, J = 16.0 Hz, 1H, *trans* alkene-*H*), 7.28−7.09 (m, 10H), 5.03 and 4.98 (2 s, 2H, benzyl-*H*), 3.77 and 3.64 (2 br, 2H, $NCH_2CH_2CH_3$), 2.93 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.86 (q, J = 7.5 Hz, 4H, Ar-CH_2CH_3), 2.39 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.79 and 1.59 (2 br, 2H, $NCH_2CH_2CH_3$), 1.33 (t, J = 7.5 Hz, 6H, Ar-CH_2CH_3), 0.95 (t, 3H, J = 7.3 Hz, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −60.3 and −60.5 (2 s, 3F, *cis* and *trans* Ar−CF_3), −81.2 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.2 (m, 10F), −123.2 (m, 2F), −124.0 (m, 2F), −126.6 (m, 2F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{57}H_{46}F_{24}N_4O_2$ 1274.3, found 1275.5.

52a−**d.** According to the general coupling procedure C, the mixture of **50a**−**d** (crude, 0.29 g), **30**[66] (0.094 g, 0.58 mmol), $Pd(OAc)_2$ (0.0034 g, 0.015 mmol), P(*o*-tolyl)$_3$ (0.018 g, 0.060 mmol), NBu_3 (0.70 mL, 3.0 mmol), BHT (one crystal), and DMF (20 mL) give a mixture of **52a**−**d** as a yellow solid (~0.38 g, crude). Analytical HPLC analysis gave four major fluorous peaks corresponding to the four coupled products (Figure 9), and each was isolated by preparative HPLC.

52a. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 50% for three steps (from **8a**): ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H, Ar-*H*, *o*-$COOCH_3$), 7.62 (d, J = 8.3 Hz, 2H), 7.57−7.50 (m, 10H), 7.42 (d, J = 16.0 Hz, 1H, *trans* alkene-*H*), 7.32−7.08 (m, 8H), 4.98 (s, 2H, benzyl-*H*), 3.96 (s, 3H, Ar-$COOCH_3$), 3.68 (br, 2H, $NCH_2CH_2CH_3$), 2.95−2.92 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.86 (m, 6H, Ar−CH_2CH_3), 2.45−2.33 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.72 (br, 2H, $NCH_2CH_2CH_3$), 1.33 (m, 9H, Ar-CH_2CH_3), 0.95 (t-br, J = 7.2 Hz, 3H, $NCH_2CH_2CH_3$).

52b. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 50% for three steps (from **8b**): ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H, Ar-*H*, *o*-$COOCH_3$), 7.61 (d, J = 8.3 Hz, 2H), 7.57−7.50 (m, 10H), 7.42 (d, J = 16.0 Hz, 1H, *trans* alkene-*H*), 7.32−7.08 (m, 9H), 4.98 (s, 2H, benzyl-*H*), 3.96 (s, 3H, Ar-$COOCH_3$), 3.68 (br, 2H, $NCH_2CH_2CH_3$), 2.95−2.91 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.86 (q, J = 7.6 Hz, 4H, Ar-CH_2CH_3), 2.45−2.33 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.72 (br, 2H, $NCH_2CH_2CH_3$), 1.33 (t, J = 7.6 Hz, 6H, Ar-CH_2CH_3), 0.95 (t-br, J = 7.2 Hz, 3H, $NCH_2CH_2CH_3$).

52c. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 55% for three steps (from **8c**): mp 108−110 °C; IR (KBr) 2960 (m), 1719 (s), 1205 (s), 960 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.2 Hz, 2H, Ar-*H*, *o*-$COOCH_3$), 7.61 (d, J = 8.3 Hz, 2H), 7.57−7.50 (m, 8H), 7.42 (d, J = 16.0 Hz, 1H, *trans* alkene-*H*), 7.32−7.21 (m, 6H), 7.12−7.08 (m, 4H), 4.99 (s, 2H, benzyl-*H*), 3.96 (s, 3H, Ar-$COOCH_3$), 3.73 (br, 2H, $NCH_2CH_2CH_3$), 2.93−2.88 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.85 (q, J = 7.5 Hz, 4H, Ar-CH_2CH_3), 2.45−2.33 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.75 (br, 2H, $NCH_2CH_2CH_3$), 1.33 (t, J = 7.5 Hz, 6H, Ar-CH_2CH_3), 0.95 (br, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.2 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.2 (m, 2F), −122.4 (m, 4F), −123.2 (m, 2F), −123.9 (m, 2F), −126.6 (m, 2F), −128.1 and −128.3 (2m, 1F, *cis* and *trans* Ar-*F*); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{54}H_{45}F_{18}N_3O_2$ 1109.3, found 1109.5.

52d. Isolated by preparative HPLC on Fluoro*Flash* column; the overall yield was 64% for three steps (from **8d**): mp 170−172 °C; IR (KBr) 2965 (m), 1725 (s), 1212 (s), 961 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, J = 8.2 Hz, 2H, Ar-*H*, *o*-$COOCH_3$), 7.81 (m, 1H, Ar-*H*, *o*-CF_3), 7.68−7.49 (m, 11H), 7.42 (d, J = 16.1 Hz, 1H, *trans* alkene-*H*), 7.32−7.21 (m, 8H), 5.02 and 4.97 (2 s, 2H, benzyl-*H*), 3.95 (s, 3H, Ar-$COOCH_3$), 3.77 and 3.63 (2 m, 2H, $NCH_2CH_2CH_3$), 2.93−2.88 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.85 (q, J = 7.5 Hz, 4H, Ar-CH_2CH_3), 2.45−2.33 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.78 and 1.63 (2 m, 2H,

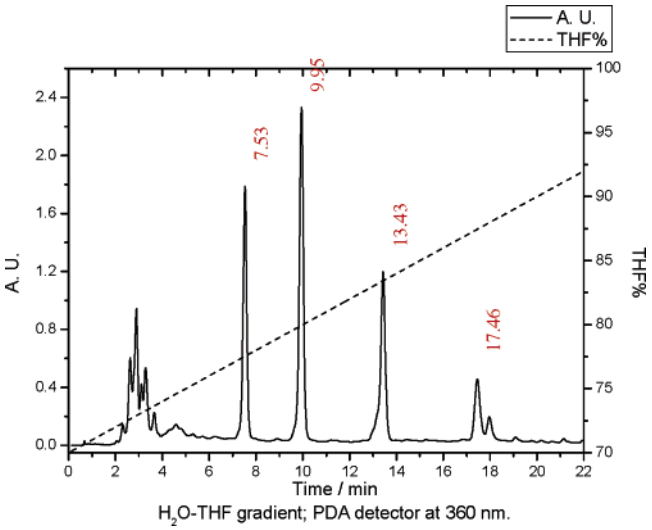

FIGURE 10. HPLC results of the mixture **53a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **53a** (7.53 min); **53b** (9.95 min); **53c** (13.43 min); **53d** (17.46 min).

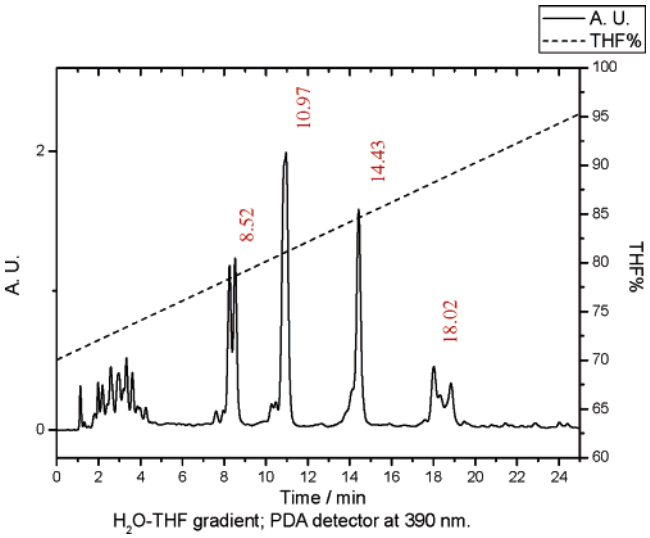

FIGURE 11. HPLC results of the mixture **54a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **54a** (8.52 min); **54b** (10.97 min); **54c** (14.43 min); **54d** or other $C_{10}F_{21}$ tagged products (18.02 min).

$NCH_2CH_2CH_3$), 1.32 (t, J = 7.5 Hz, 6H, Ar-CH_2CH_3), 0.97 and 0.90 (2 t, J = 7.3 Hz, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −80.3 and −60.5 (2 s, 3F), −81.2 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.2 (m, 10F), −123.2 (m, 2F), −123.9 (m, 2F), −126.6 (m, 2F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{59}H_{49}F_{24}N_3O_2$ 1287.3, found 1287.4.

53a−**d.** According to the general HWE reaction procedure, the mixture of **49a**−**d** (crude, 0.503 g), **28** (0.611 g, 1.23 mmol), *t*-BuOK (0.303 g, 2.70 mmol), and DMF (30 mL) gave **53a**−**d** as an orange solid (0.55 g, crude). Analysis by HPLC gave four major fluorous peaks as four coupled products (Figure 10). From Figure 10, there are a significant number of $C_{10}F_{21}$ tagged compounds present. Thus, side products of **53d** were formed in this coupling reaction.

54a−**d.** According to the general coupling procedure C, the mixture of **53a**−**d** (crude, 0.48 g), **31**[67] (0.268 g, 1.80 mmol), $Pd(OAc)_2$ (0.0081 g, 0.036 mmol), P(*o*-tolyl)$_3$ (0.0438 g, 0.144 mmol), NEt_3 (0.70 mL, 5.0 mmol), BHT (one crystal) and DMF (20 mL) give a mixture of **54a**−**d** as a yellow solid (∼0.75 g, crude). Analysis by HPLC gave four major fluorous peaks corresponding to the four coupled products (Figure 11). From Figure 11, we can see that at least two C_4F_9 tagged products were formed, one of which was presumably **54a**. The tetramers **54b** and **54c** were collected after preparative HPLC. Because the $C_{10}F_{21}$ tagged trimer was not pure, the group of $C_{10}F_{21}$ peaks was a mixture of compounds and **54d** was not isolated. Only **54b** and **54c** were isolated by preparative HPLC.

54b. Isolated by preparative HPLC on Fluoro*Flash* column; red solid; the overall yield was 48% for three steps (from **8b**): mp 100−102 °C; IR (KBr) 2956 (m), 1513 (s), 1338 (s), 1205 (s), 963 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H, Ar-*H*, *o*-NO_2), 7.70−7.67 (m, 3H), 7.57−7.48 (m, 6H), 7.28−7.08 (m, 13H), 4.99 (s, 2H, benzyl-*H*), 4.13 and 4.11 (2t, J = 7.4 Hz, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 3.69 (br, 2H, $NCH_2CH_2CH_3$), 2.95−2.92 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.46−2.34 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.93 (m, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 1.76 (br, 2H, $NCH_2CH_2CH_3$), 1.63 (m, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 1.07 (t, J = 7.4 Hz, 6H, Ar-$OCH_2CH_2CH_2CH_3$), 0.95 (br, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.3 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.4 (m, 2F), −123.4 (m, 2F), −124.0 (m, 2F), −126.6 (m, 2F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{56}H_{55}F_{13}N_4O_4$ 1094.4, found 1094.6.

54c. Isolated by preparative HPLC on Fluoro*Flash* column; red solid; the overall yield was 42% for three steps (from **8c**):

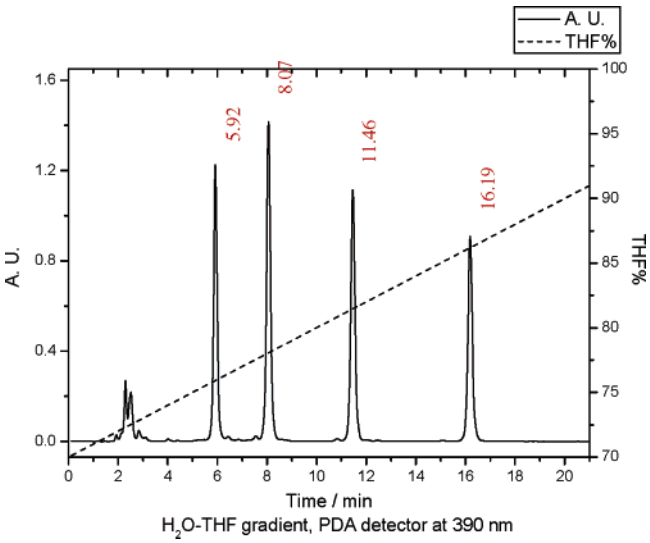

FIGURE 12. HPLC results of the mixture **55a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **55a** (5.92 min); **55b** (8.07 min); **55c** (11.46 min); **55d** (16.19 min).

mp 105−107 °C; IR (KBr) 2959 (m), 1513 (s), 1338 (s), 1205 (s), 962 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, J = 8.8 Hz, 2H, Ar-*H*, *o*-NO_2), 7.68−7.64 (m, 3H), 7.59−7.50 (m, 6H), 7.28−7.09 (m, 12H), 4.99 (s, 2H, benzyl-*H*), 4.13 and 4.10 (2t, J = 7.4 Hz, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 3.71 (br, 2H, $NCH_2CH_2CH_3$), 2.98−2.91 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.46−2.32 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.92 (m, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 1.75 (br, 2H, $NCH_2CH_2CH_3$), 1.63 (m, 4H, Ar-$OCH_2CH_2CH_2CH_3$), 1.07 (t, J = 7.4 Hz, 6H, Ar-$OCH_2CH_2CH_2CH_3$), 0.95 (br, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −81.2 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.2 (m, 2F), −122.4 (m, 4F), −123.2 (m, 2F), −124.0 (m, 2F), −126.6 (m, 2F), −128.1 and −128.3 (2 s, 1F, *cis* and *trans* Ar-F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{58}H_{54}F_{18}N_4O_4$ 1212.4, found 1212.5.

55a−**d.** According to the general HWE reaction procedure, the mixture of **49a**−**d** (0.469 g, crude), **21**[63] (0.282 g, 0.777

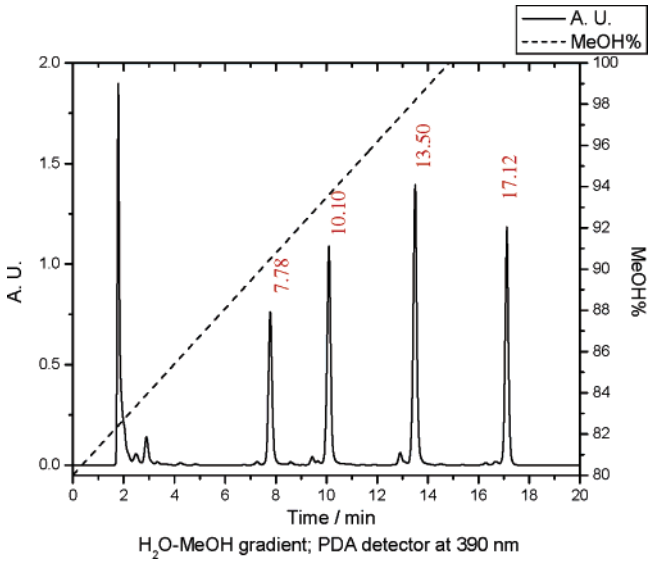

FIGURE 13. HPLC results of the mixture **57a**−**d**. Gradient conditions: H_2O−MeOH (MeOH from 80% to 100% in 15 min). Compound (retention time): **57a** (7.78 min); **57b** (10.10 min); **57c** (13.50 min); **57d** (17.12 min).

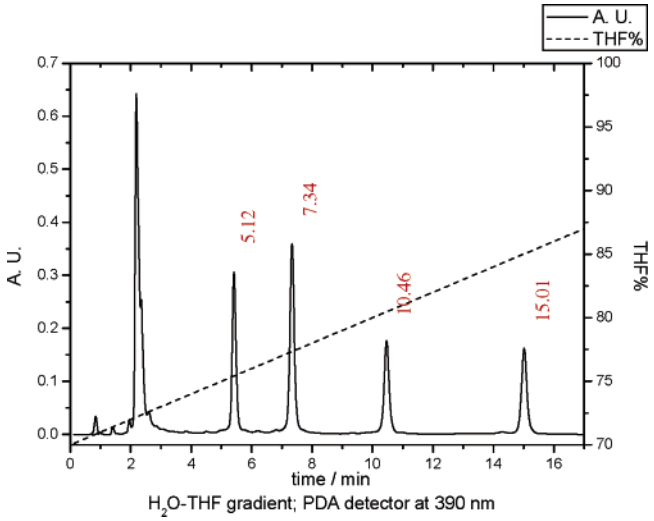

FIGURE 14. HPLC results of the mixture **58a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **58a** (5.21 min); **58b** (7.34 min); **58c** (10.46 min); **58d** (15.01 min).

mmol), NaH (0.072 g, 60% in mineral oil, 1.8 mmol) and DME (15 mL) gave **55a**−**d** as a yellow solid (0.50 g, crude). The analytical HPLC gave four major fluorous peaks corresponding to the four coupled products (Figure 12).

56a−**d.** According to the general coupling procedure C, the mixture of **55a**−**d** (0.50 g, crude), **31**[67] (0.152 g, 1.02 mmol), $Pd(OAc)_2$ (0.0046 g, 0.020 mmol), P(*o*-tolyl)$_3$ (0.025 g, 0.082 mmol), NEt_3 (0.35 mL, 2.5 mmol), and DMF (10 mL) gave mixture **56a**−**d** as a yellow solid (0.65 g, crude). The mixture was extremely insoluble; thus, HPLC analyses were not obtained.

57a−**d.** According to the general coupling procedure C, the mixture of **8a** (0.103 g, 0.158 mmol), **8b** (0.106 g, 0.146 mmol), **8c** (0.078 g, 0.092 mmol), **8d** (0.070 g, 0.070 mmol), $Pd(OAc)_2$ (0.0051 g, 0.023 mmol), P(*o*-tolyl)$_3$ (0.028 g, 0.093 mmol), NBu_3 (0.55 mL, 2.3 mmol), BHT (one crystal), and DMF (20 mL) gave a mixture of **57a**−**d** as an orange solid (0.29 g, crude).

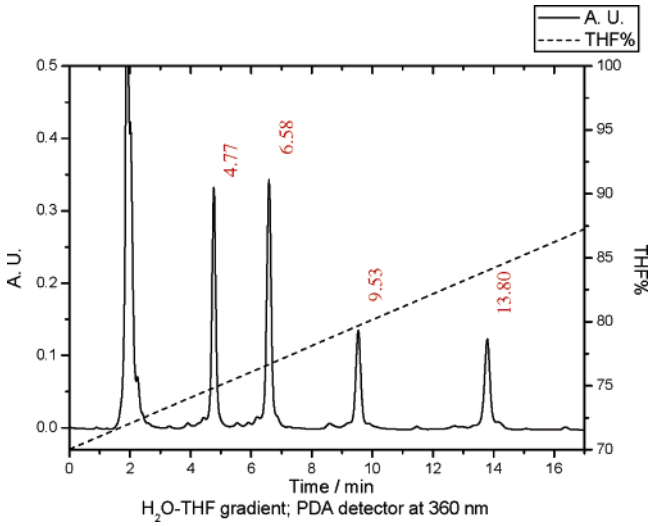

FIGURE 15. HPLC results of the mixture **59a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **59a** (4.77 min); **59b** (6.58 min); **59c** (9.53 min); **59d** (13.80 min).

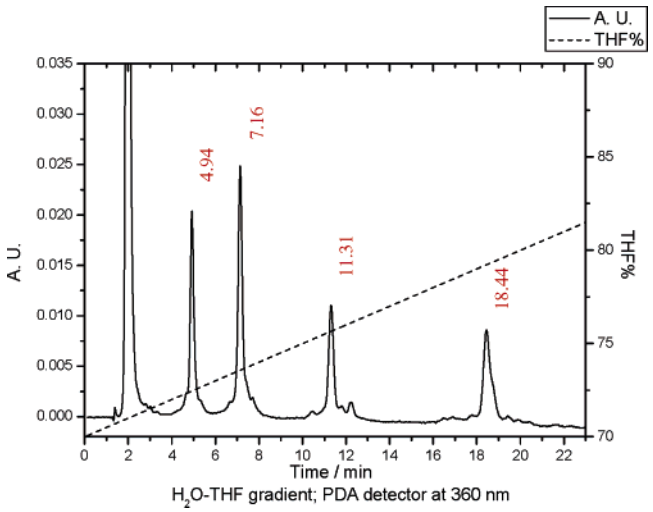

FIGURE 16. HPLC results of the mixture **60a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **60a** (4.94 min); **60b** (7.16 min); **60c** (11.31 min); **60d** (18.44 min).

The products mixture gave four major fluorous peaks corresponding to the four coupled products in the analytical HPLC (Figure 13).

58a−**d.** According to the general HWE reaction procedure, the mixture of **57a**−**d** (crude, 0.269 g), **21**[63] (0.231 g, 0.636 mmol), NaH (0.0382 g, 60% in mineral oil, 0.954 mmol), and DMF (30 mL) gave **58a**−**d** as an orange solid (0.230 g, crude). The analytical HPLC gave four major fluorous peaks corresponding to the four coupled products (Figure 14).

59a−**d.** According to the general coupling procedure C, the mixture of **58a**−**d** (crude, 0.143 g), **31**[67] (0.0509 g, 0.341 mmol), $Pd(OAc)_2$ (1.5 mg, 0.0068 mmol), P(*o*-tolyl)$_3$ (8.3 g, 0.027 mmol), NBu_3 (0.24 mL, 1.1 mmol), BHT (one crystal), and DMF (20 mL) gave a mixture of **59a**−**d** as a red solid (~0.19 g, crude). Analytical HPLC of the product gave four major fluorous peaks corresponding to the four coupled products (Figure 15). Because of poor solubility, the preparative HPLC isolation could only be achieved using THF-based eluents. Only **59d** was successfully isolated. The isolated fractions of **59b** and **59c** were mixtures of the desired products and side prod-

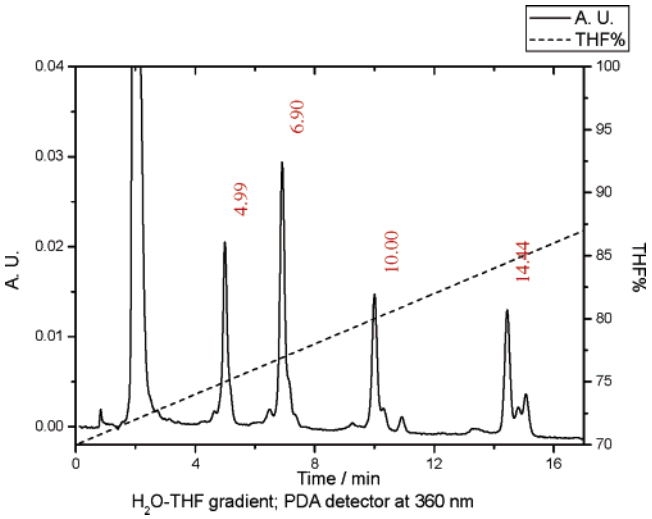

FIGURE 17. HPLC results of the mixture **61a**−**d**. Gradient conditions: H_2O−THF (THF from 70% to 100% in 30 min). Compound (retention time): **61a** (4.99 min); **61b** (6.90 min); **61c** (10.00 min); **61d** (14.44 min).

ucts. MS verified the presence of desired **59b** and **59c**: **59b**, MALDI-TOF MS *m/z* (Matrix: dithranol), calcd for $C_{48}H_{39}F_{13}N_4O_4S$ 1014.2, found 1014.9; **59c**, MALDI-TOF MS *m/z* (matrix: dithranol), calcd for $C_{50}H_{38}F_{18}N_4O_4S$ 1132.2, found 1132.7.

59d. Isolated by preparative HPLC on Fluoro*Flash* column; brown solid; the overall yield was 22% for three steps (from **8d**): mp >200 °C dec; IR (KBr) 2923 (m), 1515 (s), 1340 (s), 1213 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 2H, Ar-*H*, *o*-NO_2), 7.72 (m, 1H, Ar-*H*, *o*-CF_3), 7.65 (d, J = 8.8 Hz, 2H), 7.57−7.48 (m, 5H), 7.32−7.15 (m, 10H), 6.86 (d, J = 16.1 Hz, 2H, alkene-*H*), 5.01 and 4.97 (2 s, 2H, benzyl-*H*), 4.36 (s, 4H, OCH_2CH_2O), 3.76 and 3.62 (2-m, 2H, $NCH_2CH_2CH_3$), 2.93 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 2.38 (m, 2H, $C_6F_{13}CH_2CH_2$-Ar), 1.78 and 1.63 (2m, 2H, $NCH_2CH_2CH_3$), 0.97 and 0.90 (2m, 3H, $NCH_2CH_2CH_3$); ^{19}F NMR ($CDCl_3$, 470 MHz) δ −60.3 and −60.6 (2 s, 3F), −81.2 (t, J = 10.1 Hz, 3F), −115.1 (m, 2F), −122.2 (m, 10F), −123.2 (m, 2F), −123.9 (m, 2F), −126.6 (m, 2F); MALDI-TOF MS *m/z* (matrix: dithranol) calcd for $C_{53}H_{38}F_{24}N_4O_4S$ 1282.2, found 1282.9.

60a−**d.** According to the general coupling procedure C, the mixture of **58a**−**d** (crude, 0.061 g), **30**[66] (0.019 mL, 0.12 mmol), $Pd(OAc)_2$ (0.0011 g, 0.0049 mmol), P(*o*-tolyl)$_3$ (0.0056 g, 0.018 mmol), NBu_3 (0.20 mL, 0.84 mmol), BHT (one crystal), and DMF (8 mL) gave a mixture of **60a**−**d** as a red solid (~0.079 g, crude). Analytical HPLC of the product gave four major fluorous peaks corresponding to the four coupled products (Figure 16).

61a−**d.** According to the general coupling procedure C, the mixture of **58a**−**d** (crude, 0.064 g), styrene (0.020 mL, 0.20 mmol), $Pd(OAc)_2$ (0.0011 g, 0.0049 mmol), P(*o*-tolyl)$_3$ (0.0061 g, 0.020 mmol), NBu_3 (0.20 mL, 0.84 mmol), BHT (one crystal) and DMF (8 mL) gave a mixture of **61a**−**d** as a red solid. HPLC analysis of the mixture gave four major fluorous peaks corresponding to the four coupled products (Figure 17).

62b. The solution of **51b** (0.024 g, 0.024 mmol) in CH_2Cl_2 (2.5 mL) was cooled to 0 °C. $HBF_4{\cdot}OMe_2$ (0.1 mL, 0.8 mmol) was added via a syringe. The reaction mixture immediately turned red. The mixture was stirred in an ice bath for 10 min. Anhydrous CH_3CN (2 mL, twice) was added to extract the reaction mixture. The solid salt of the amine tag **7b** was isolated from the CH_3CN extract, and **7b** was recovered after a basic workup (9.8 mg, 82%). The extraction solution was concentrated, and adding ether precipitated a red solid. The precipitate was recrystallized from CH_3CN/ether. The diazonium salt **62b** (8.6 mg, 60%) was collected by filtration as a red solid: IR (KBr) 2928 (m), 2336 (w), 1570 (s), 1373 (s) cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 8.38 (d, J = 9.0 Hz, 2H), 8.22 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 9.0 Hz, 2H), 7.78 (d, J = 8.7 Hz, 2H), 7.73−7.60 (m, 8H), 7.54 (d, J = 16.2 Hz, 1H), 7.42 (d, J = 16.2 Hz, 1H), 7.27 (d, J = 16.7 Hz, 1H), 7.22 (d, J = 16.7 Hz, 1H), 2.86 (2q, J = 7.5 Hz, 4H), 1.26 (2t, J = 7.5 Hz, 6H); ^{13}C NMR (CD_3CN, 100 MHz) δ 152.8, 148.2, 145.8, 142.3, 141.9, 141.2, 140.5, 137.0, 136.3, 135.8, 134.3, 131.4, 130.4, 130.2, 129.9, 128.8, 128.6, 128.5, 128.3, 127.8, 127.6, 126.6, 125.4, 110.1, 27.1 (2C, overlap), 16.7, 16.6.

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Supporting Information Available: ^1H, ^{13}C, and ^{19}F NMR spectra of selected compounds as well as general reaction procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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