JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

ortho-Perfluoroalkylation and Ethoxycarbonyldifluoromethylation of Aromatic Triazenes

Andreas Hafner,[†] Angela Bihlmeier,[‡] Martin Nieger,[§] Wim Klopper,[‡] and Stefan Bräse*[,†,∥]

[†]Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Campus South, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany

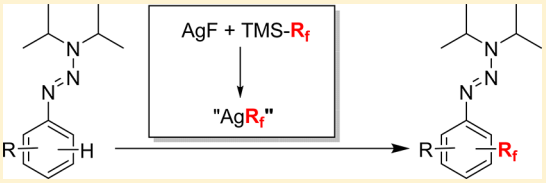
[‡]Institute of Physical Chemistry, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

[§]Laboratory of Inorganic Chemistry, Department of Chemistry, PO Box 55, FIN-00014, University of Helsinki, Finland

[∥]Institute of Toxicology and Genetics, KIT, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Supporting Information

ABSTRACT: A robust protocol for perfluoroalkylation and ethoxycarbonyldifluoromethylation of functionalized aromatic triazenes is described. Using silver(I)-fluoride and different fluorinated (trimethyl)-silyl substituted species, it was possible to synthesize various *ortho*-fluorinated triazenes in good yields via simple *CH*-substitution. Initial reactions under solvent-free (neat) conditions indicate a stabilizing interaction between "AgR_f" and the triazene moiety, which may be responsible for the good yields and regioselectivity. The transformation possibilities of the triazene moiety make these reactions interesting for the synthesis of fluorinated building blocks. In addition, quantum chemical calculations suggest that the stabilization of the radical intermediate in the *ortho*-position is distinctly more favored for aromatic triazenes than for other aromatic substrates.



INTRODUCTION

Aromatic compounds bearing fluorinated groups are important structures in pharmaceutical and agrochemical research, due to their unique chemical and physical properties. For example, perfluoroalkylated groups are completely unknown to living organisms, which results in a high stability for fluorinated molecules against metabolization. This is one reason for their importance in terms of bioisosteric replacement of, for example, electron-withdrawing groups.[1]

Therefore, perfluoroalkyl groups—first of all, the trifluoromethyl group—are a common structural motif in pharmaceutical and agrochemical compounds. Thus, many methods were reported dealing with the direct introduction of this moiety into aromatic and heteroaromatic compounds. Most methods are based on in situ generated "$CuCF_3$"[2] or on Pd-catalyzed[3] cross-coupling reactions. While many metal-mediated trifluoromethylation reactions require halogenated arenes as reactant, methods based on radical CF_3 sources do not need prior functionalization and react under simple *CH*-substitution.[4] However, radical pathways often lead to a mixture of products. Recently, our group[5] as well as Sanford and coworkers[6] reported a silver-mediated trifluoromethylation reaction. Noteworthy, in the meantime, several other groups also reported silver-mediated trifluoromethylation protocols.[7] Although these reactions are based on an in situ generated metallic "$AgCF_3$" species, they also tolerate halogenated groups—most interestingly, iodides. We could show that especially aromatic triazenes are suitable substrates for this kind of trifluoromethylation (Scheme 1a) as they give good yields and a high *ortho* regioselectivity—in particular, when *para*-functionalized triazenes were used.[5]

Experiments with radical inhibitors and initiators conducted by the Sanford group indicated that radical intermediates are involved,[6] which could be confirmed by our own experiments. Because of the easy setup of this reaction—the "$AgCF_3$" species was generated simply by using commercially available silver(I)-fluoride and (trifluoromethyl)trimethylsilane (TMS-CF_3)—and of the straightforward reaction pathway, we investigated whether it were possible to expand this transformation to other fluorinated substrates.

Herein, we present novel and facile protocols for the pentafluoroethylation, heptafluoropropylation, and ethoxycarbonyldifluoromethylation of functionalized aromatic triazenes as well as new insights into the mechanism of these reactions.

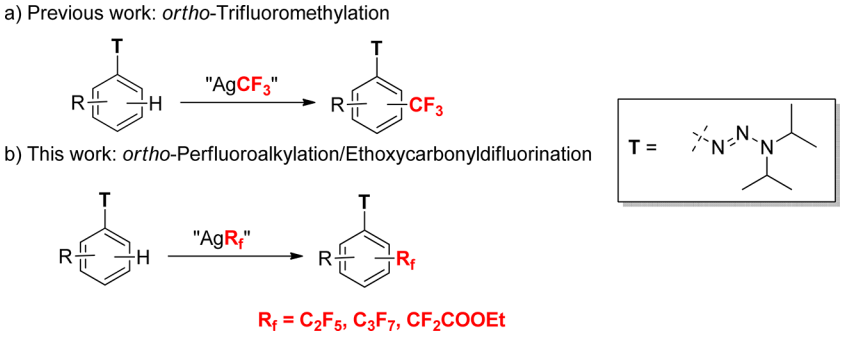
RESULTS AND DISCUSSION

While looking for a new transformation protocol to convert triazenes into the corresponding CF_3-arenes, we found that addition of an Ag(I) salt leads to formation of the *ortho*-trifluoromethylated aromatic triazene. After optimization of the reaction conditions, we investigated that this reaction worked best when "$AgCF_3$" was generated in perfluorohexane. This was surprising because perfluorohexane has no stabilizing effects on metallic species. When the reaction was performed in more chelating solvents, such as dimethylformamide (DMF) or

Received: May 24, 2013
Published: July 12, 2013

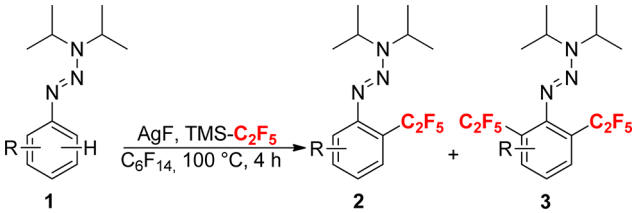
   dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

Scheme 1. Perfluoroalkylation of Aromatic Triazenes



acetonitrile, at 100 °C, perfluoroethylated byproducts were observed.[8] Encouraged by these findings, we imagined that this protocol, which is generally based on a "AgR_f" species, is not only suitable for the trifluoromethylation reaction but also for the introduction of other perfluoroalkylated chains. Therefore, it was reasonable to test whether a simple change of the perfluoroalkyl source would allow access to other "AgR_f" species, leading to further perfluoroalkylated aromatic triazenes. The required aromatic triazenes for this conversion can be easily synthesized by a one-step procedure starting from commercially available aniline derivatives.[9] Triazenes, as stable protected diazonium salts, can be isolated and stored and are known to undergo a number of further transformations on the aromatic core.[10] Furthermore, the triazene moiety itself offers access to various functional groups (e.g., halides, amines, alcohols), which makes them versatile intermediates in organic synthesis.[11] Hence, we synthesized several functionalized aromatic triazenes and started to explore the pentafluoroethylation using (pentafluoroethyl)trimethylsilane (TMS-C_2F_5) instead of TMS-CF_3. In analogy to the generation of "$AgCF_3$", the preparation of "AgC_2F_5" is known in solvents such as DMF and triethylamine.[12] Thus, "AgC_2F_5" was generated in situ in the presence of the triazene using TMS-C_2F_5/AgF in perfluorohexane as solvent. As shown in Table 1,

Table 1. Pentafluoroethylation of Different Aromatic Triazenes[d]



1 2 3

entry	R	mono-*ortho* **2** (%)[a]	di-*ortho* **3** (%)[a]	yield (%)[c]
a[b]	4-I	62	17	79
b[b]	4-Br	53	10	63
c[b]	4-Cl	43	12	55
d	4-F	64	traces	64
e	4-COOEt	45	11	56
f	2-Me, 4-CN	69		69
g	2-I	43		43

[a]Isolated yields. [b]Mono- and di-*ortho*-pentafluoroethylated products could not be separated by column chromatography. [c]Combined yields of isolated mono- and di-*ortho*-fluorinated products. [d]Reaction conditions: **1** (0.40 mmol), TMS-C_2F_5 (0.80 mmol), AgF (1.60 mmol), C_6F_{14} (1 mL), 100 °C, 4 h.

the desired conversion occurred in good yields under precipitation of elemental silver. In analogy to the trifluoromethylation reaction, the pentafluoroethylation also showed a high *ortho* selectivity, especially when *para*-substituted triazenes were used (**1a−1e**).

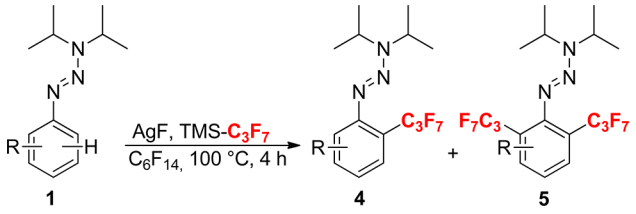
When the *para*-position was not blocked by a prior introduced functional group, the *para*, *ortho*-disubstituted triazene was found as a major side product (∼14%) along with the *ortho*-pentafluoroethylated as the main product. Functional groups, such as iodides, bromides, fluorides, and chlorides as well as ethoxy or nitrile groups, are tolerated, which make these compounds interesting for further functionalization, such as cross-coupling reactions. Surprisingly, the ratio between mono- and di-*ortho*-pentafluoroethylated products differed significantly between the *para*-halogenated triazenes **1a−1c** and the *para*-fluoro-substituted triazene **1d**. Whereas triazenes **1a−1c** showed between 10% and 17% of di-*ortho*-pentafluoroethylated byproduct, only trace amounts of di-*ortho*-substituted byproduct could be isolated in the case of the *para*-fluorotriazene **1d**. Recently, the Sanford group showed that, in general, the transfer of a C_3F_7-group to benzene is possible using Ag(I).[6] Starting from commercially available TMS-C_3F_7 and AgF, this reaction could be also accomplished in presence of different functionalized aromatic triazenes under our conditions. In analogy to the prior reaction, the corresponding perfluoro-alkylated triazenes were obtained in good yields (41−77%, for the *ortho*-position) and good *ortho* selectivity (Table 2). In the case of triazene **1g**, the *para*, *ortho*-disubstituted triazene was also found as a major side product (∼16%).

With these results in hand, we tried to expand this kind of reaction to other fluorinated TMS-sources, such as difluoromethyl precursors. Lately, TMS-CF_2H, which is easily prepared from TMS-CF_3 and $NaBH_4$,[13] was introduced as a difluoromethylation agent for aromatic halides.[14] However, when we tested the difluoromethylation of aromatic triazenes under our conditions, only traces of the desired product could be observed via GCMS analysis. Neither an increase of the TMS-CF_2H or the AgF equivalents nor an elongation of the reaction time did lead to higher conversion.

Amii and co-workers reported the use of TMS-CF_2COOEt as a precursor for the generation of difluoromethyl groups.[15] Following their one-step procedure, this agent could be obtained starting from commercially available $ClCF_2COOEt$. However, using the latter fluorinating agent under the previously optimized reaction conditions resulted in only poor yield (32% mono-*ortho*-ethoxycarbonyldifluoromethylated product in the case of triazene **1b**). We, therefore, doubled the TMS-CF_2COOEt equivalents and elongated the reaction time.

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

Table 2. Heptafluoropropylation of Different Aromatic Triazenes[d]



entry	R	mono-*ortho* **4** (%)[a]	di-*ortho* **5** (%)[a]	yield (%)[c]
a[b]	4-I	50	19	69
b[b]	4-Br	64	13	77
c[b]	4-Cl	52	8	60
d[b]	4-F	49	7	56
e	4-COOEt	43	18	61
f	2-Me, 4-CN	70		70
g	2-I	41		41

[a]Isolated yields. [b]Mono- and di-*ortho*-heptafluoropropylated products could not be separated by column chromatography. [c]Combined yields of isolated mono- and di-*ortho*-fluorinated products. [d]Reaction conditions: **1** (0.40 mmol), TMS-C_3F_7 (0.80 mmol), AgF (1.60 mmol), C_6F_{14} (1 mL), 100 °C, 4 h.

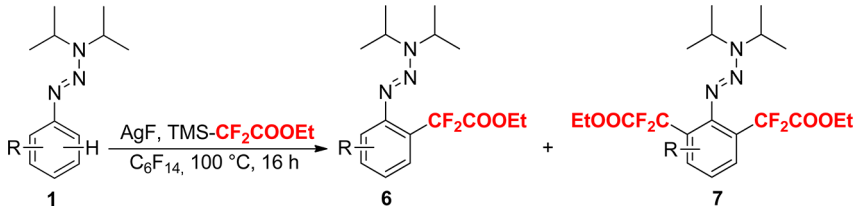
After these modifications, the desired ethoxycarbonylated products could be obtained in good yields (Table 3).

It is interesting to note that triazenes **1c**, **1d**, and **1e** yielded more di-*ortho*-substituted triazene (**7c**, **7d**, **7e**) than mono-substituted triazene (**6c**, **6d**, **6e**), which might be a result of the higher equivalents of the fluorinating source. Nonetheless, this observation along with the different ratios between the *ortho* and di-*ortho* products in the perfluoroalkylation reactions could be also explained by the nonhomogeneous reaction media. In fact, fluorinated solvents, such as perfluorohexane, show in general nearly no solubility for nonfluorinated substrates and act most probably just as an inert heat carrier. Aromatic triazenes are also not soluble in perfluorohexane, but after the reactions were completed, the formerly colorless perfluorohexane phases were colored slightly yellow, which might be explained by the partial solubility of the perfluoroalkylated triazenes (most probably the diperfluoroalkylated triazenes).

It is known that perfluoroalkyl silver compounds decompose to radical intermediates.[16] Nevertheless, until recently, it was not possible to use these perfluoroalkyl radicals for synthetic purposes like aromatic substitution reactions. Because of the fact that aromatic triazenes show such promising results in aromatic perfluoroalkylation reactions under these conditions, we imagined that somehow the "$AgCF_3$" species is stabilized by coordination to the triazene moiety, since stabilization of "$AgCF_3$" through N-donor solvents, such as triethylamine or acetonitrile, is known. Furthermore, such a coordination could also explain the high *ortho* selectivity because of the proximity to the *ortho*-position. Naumann et al. showed that, in solution, an equilibrium between $AgCF_3$ and $[Ag(CF_3)_2]^-$ exists, and its ratio depends on the donor ability of the solvent.[12] For example, this equilibrium is completely shifted toward the neutral species in triethylamine. Therefore, we investigated whether there is an influence on this equilibrium in the presence of aromatic triazenes. In acetonitrile, both species can be observed by ^{19}F NMR spectroscopy, and the ratio between the neutral and ionic species was found to be 1:3.9. When 1 equiv of triazene **1c** was added, this equilibrium slightly changed to 1:3.3 (see the Supporting Information). Compared to the influence of triethylamine, these observations do not clearly indicate an interaction. Therefore, we further examined the trifluoromethylation reaction under solvent-free (neat) conditions and in triethylamine as solvent. We thought that, if there is an interaction between $AgCF_3$ and the triazene moiety that is responsible for the good yields and good selectivity compared to other substrates, the reaction should be suppressed, on one hand, when a strong stabilizing donor solvent, such as triethylamine, is present, whereas, on the other hand, the reaction should work under neat conditions comparable to our standard protocol. These assumptions could be confirmed: while the reaction proceeds smoothly under neat conditions, the reaction was completely suppressed in triethylamine (Scheme 2). Recently, we could also show that the *ortho* selectivity is lost when sterically more demanding silver organyls are used, which can be explained by the fact that the steric hindrance of these substrates does not allow coordination to the triazene moiety.[17]

Nevertheless, when we wanted to expand the substrate spectrum to other aromatic substrates, such as electron-rich anilines (primary and tertiary) and electron-poor aromatic nitriles or azides, no conversion was observed via ^{19}F NMR spectroscopy. Only anisoles and thioanisoles led to a

Table 3. Ethoxycarbonyldifluoromethylation of Different Aromatic Triazenes[c]

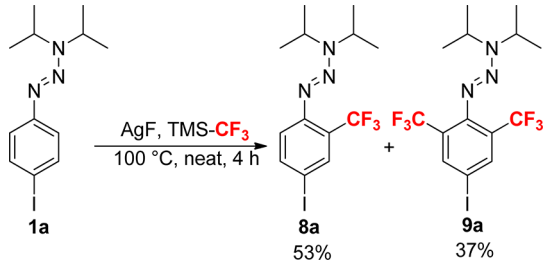


entry	R	mono-*ortho* **6** (%)[a]	di-*ortho* **7** (%)[a]	yield (%)[b]
a	4-I	28	28	56
b	4-Br	36	32	68
c	4-Cl	24	29	53
d	4-F	26	36	62
e	4-COOEt	20	28	48
f	4-CN	28	13	41

[a]Isolated yields. [b]Combined yields of isolated mono- and di-*ortho*-fluorinated products. [c]Reaction conditions: **1** (0.40 mmol), TMS-CF_2COOEt (1.60 mmol), AgF (1.60 mmol), C_6F_{14} (1 mL), 100 °C, 4 h.

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

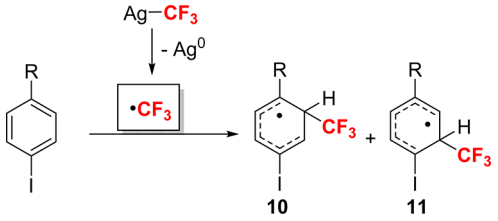
Scheme 2. Trifluoromethylation of the Triazene 1a under Solvent-Free Conditions[a]



[a]Reaction conditions: **1a** (0.40 mmol), TMS-CF_3 (0.80 mmol), AgF (1.60 mmol), 100 °C, 4 h. Isolated yields are shown. For the molecular structure of **9a**, see the Supporting Information.

conversion of around 40%. However, compared to *para*-substituted aromatic triazenes, 4-iodoanisole and 4-bromothioanisole showed only a slight preference for the *ortho*-position (in both cases, ∼30%) over the *meta*-position (∼10% for both cases) (results not shown). These observations were surprising because we expected some sort of interaction between $AgCF_3$ and these compounds under our conditions as well. Therefore, we performed quantum chemical calculations of the reaction energies for the addition of a trifluoromethyl radical toward these arenes. As it is shown in Table 4, the reaction energies for the *para*-substituted aromatic

Table 4. Reaction Energies (TPSS; B3LYP in Brackets; Reaction Energy = $-[E_{product} - E_{reactant}]$) for the Addition of a Trifluoromethyl Radical to Various 4-Iodosubstituted Aromatic Compounds[a]



entry	R	*ortho* **10**	*meta* **11**	Δ*E* (*ortho* − *meta*)
a	CN	50 (51)	38 (39)	12 (12)
b	N_3	54 (55)	42 (44)	12 (11)
c	OMe	57 (59)	48 (49)	9 (10)
d	$N_3(iPr)_2$	73 (72)	45 (56)	28 (26)

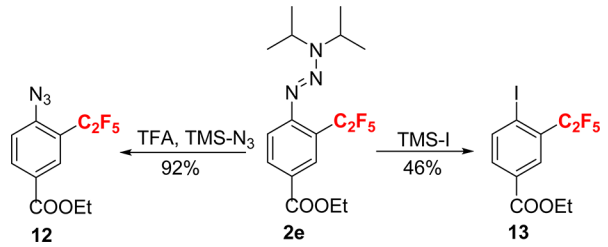
[a]All values are given in kJ/mol.

nitrile and azide are lower than those for anisole and significantly lower than those for aromatic triazenes. These values directly reflect the ability of the radical intermediate to stabilize the unpaired electron, for example, via delocalization. Especially for triazenes, much higher reaction energies for the *ortho*-substitution have been calculated. Therefore, stabilizing effects of the triazene moiety via, for example, delocalization, could be also responsible for the higher *ortho* selectivity compared to the anisole substrate where the energy difference for *ortho*- and *meta*-substitution is much smaller. However, for a more thorough understanding of the reactivity and selectivity, it might be necessary to identify the structures and relative energies of the corresponding transition states. Another mechanism, such as an oxidative aromatic substitution mechanism, can also not be ruled out, but seems to be rather unlikely under our reaction conditions.[18]

On the basis of these results, we propose that the high yields (compared to other arenes) as well as the good regioselectivity of these reactions in the presence of triazenes can be explained by (i) a coordination of a neutral $AgCF_3$ species toward the triazene moiety, which enables the generation of a CF_3 radical next to the *ortho*-position of the aromatic core, and (ii) a good stabilization of the radical intermediate by the triazene moiety.

As previously mentioned, aromatic triazenes offer various functionalization possibilities, which makes this reaction interesting for the synthesis of fluorinated building blocks. Exemplarily, the conversion of the pentafluoroethylated triazene **2e** to the corresponding azide[19] (**12**) and iodide[20] (**13**) is shown in Scheme 3.

Scheme 3. Transformation of the Triazene Moiety into the Azide 12 and the Iodide 13



CONCLUSION

In conclusion, we report pentafluoroethylation, heptafluoropropylation, and ethoxycarbonyldifluoromethylation of functionalized aromatic triazenes by simple *CH*-substitution. In all cases, the desired fluorinated products could be obtained in a high *ortho* selectivity and mostly good yields. The transformation possibilities of the triazene moiety make these reactions interesting for the synthesis of fluorinated building blocks. Furthermore, we could show that the similar trifluoromethylation reaction is also possible under neat conditions, whereas this reaction is completely suppressed in triethylamine as a solvent. These observations, combined with the fact that nonfluorinated triazenes showed nearly no solubility in perfluorohexane, indicate a stabilizing interaction between AgR_f and the triazene moiety. This kind of coordination might be responsible for the good regioselectivity of these transformations. Nevertheless, first quantum chemical calculations suggest that the stabilization of the radical intermediate plays also an important role in terms of reactivity and selectivity, but further investigations are necessary to get a more thorough understanding.

EXPERIMENTAL SECTION

Computational Details. All calculations presented in this work were performed using density functional theory methods as implemented in the TURBOMOLE program package.[21] The structures of reactants and radical intermediates were optimized with the TPSS[22] and B3LYP[23] functionals in combination with the dhf-TZVP[24]basis set employing tight convergence criteria (SCF energy: 10^{-8} E_h; energy gradient: 10^{-5} E_h/a_0), fine quadrature grids (m5),[25] and including the derivatives of quadrature weights. In the case of TPSS, the efficient resolution-of-the-identity (RI) approximation for two-electron Coulomb integrals was used. Vibrational frequencies for all species were computed in the harmonic approximation, and the reported reaction energies are zero-point vibrational energy corrected.

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

General Procedure for the Perfluoroethylation of Triazenes. A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol) of AgF and the triazene (0.40 mmol). The reaction vessel was closed, and perfluorohexane (1 mL) was added via syringe under an argon atmosphere. A 154 mg (0.80 mmol) portion of TMS-C_2F_5 was then added, and the suspension was heated to 100 °C. The reaction mixture was stirred for 4 h. The solution was then cooled to room temperature, and ethyl acetate was added and was stirred for 5 min. The solution was poured into a flask, and silica gel was added. Finally, the solvent was removed in vacuum and the crude product was purified by flash column chromatography (silica gel, solvent).

*(E)-1-(4-Iodo-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2a**) and (E)-1-(4-Iodo-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**3a**).* The product was obtained as an inseparable mixture (3.6:1, determined by ^{19}F NMR) of (*E*)-1-(4-iodo-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-iodo-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 151 mg of a mixture (62% mono-*ortho*, 17% di-*ortho*). R_f = 0.43 (**2a**) (cyclohexane) and R_f = 0.48 (**3a**) (cyclohexane). Data for **2a**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, ^3J = 6.8 Hz, 6 H), 1.39 (d, ^3J = 6.6 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 5.17 (sept, ^3J = 6.8 Hz, 1 H), 7.30 (d, ^3J = 8.7 Hz, 1 H), 7.74 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1 H), 7.84 (d, ^4J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.4, 49.7, 87.1, 112.7 (tq, ^1J = 256.6 Hz, ^2J = 39.7 Hz), 118.4 (qt, ^1J = 287.4 Hz, ^2J = 39.0 Hz), 119.6, 123.1 (t, ^2J = 21.9 Hz), 136.5 (t, ^3J = 9.5 Hz), 141.1, 150.2 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.8 (m, 3 F), −108.9 (m, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 449 (54) [M^+], 348 (20) [$M^+ - C_6H_{14}N$], 320 (46) [$M^+ - C_6H_{14}N_3$], 271 (100) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{14}H_{17}IN_3F_5$ [M^+]): calcd, 449.0387; found, 449.0388. Data for **3a**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 6.8 Hz, 6 H), 1.28 (d, ^3J = 6.6 Hz, 6 H), 3.96 (sept, ^3J = 6.6 Hz, 1 H), 5.17 (sept, ^3J = 6.8 Hz, 1 H), 8.02 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.0, 45.7, 49.1, 86.3, 124.6 (t, ^2J = 22.1 Hz), 140.8 (t, ^3J = 8.8 Hz), 153.3 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.8 (m, 6 F), −106.8 (m, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 527 (21) [M^+], 466 (5) [$M^+ - C_6H_{14}N$], 438 (9) [$M^+ - C_6H_{14}N_3$], 388 (38) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{16}H_{16}IN_3F_{10}$ [M^+]): calcd, 527.0229; found, 527.0226. IR (KBr, mixture of **2a** and **3a**): $\tilde{\nu}$ = 2977 (w), 2935 (w), 1562 (vw), 1470 (w), 1414 (m), 1393 (w), 1367 (w), 1327 (w), 1292 (w), 1274 (w), 1199 (m), 1159 (w), 1129 (w), 1097 (w), 1071 (w), 1030 (w), 976 (w), 888 (vw), 828 (vw), 750 (vw), 691 (vw), 652 (vw), 549 (vw) cm^{-1}.

*(E)-1-(4-Bromo-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2b**) and (E)-1-(4-Bromo-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**3b**).* The product was obtained as an inseparable mixture (5.7:1, determined by ^{19}F NMR) of (*E*)-1-(4-bromo-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-bromo-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 104 mg of a mixture (53% mono-*ortho*, 10% di-*ortho*). R_f = 0.28 (**2b**/**3b**) (cyclohexane). Data for **2b**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.40 (d, ^3J = 6.6 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 5.17 (sept, ^3J = 6.8 Hz, 1 H), 7.46 (d, ^3J = 8.8 Hz, 1 H), 7.54 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1 H), 7.68 (d, ^4J = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.4, 49.7, 113.9 (tq, ^1J = 256.7 Hz, ^2J = 39.6 Hz), 116.9, 119.4, 119.5 (qt, ^1J = 287.2 Hz, ^2J = 39.0 Hz), 122.8 (t, ^2J = 22.1 Hz), 130.7 (t, ^3J = 9.6 Hz), 135.2, 149.6 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.8 (m, 3 F, CF_3), −109.0 (m, 2 F, CF_2) ppm. MS (70 eV, EI), *m*/*z* (%): 401 (8) [M^+], 301 (8) [$M^+ - C_6H_{14}N$], 273 (13) [$M^+ - C_6H_{14}N_3$], 222 (44) [$M^+ - C_6H_{14}N_1Br$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{14}H_{17}BrN_3F_5$ [M^+]): calcd, 401.0526; found, 401.0524. Data for **3b**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.28 (d, ^3J = 6.6 Hz, 6 H), 3.97 (sept, ^3J = 6.6 Hz, 1 H), 5.18 (sept, ^3J = 6.8 Hz, 1 H), 7.87 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.1, 45.7, 49.1, 116.8, 124.5 (t, ^2J = 22.3 Hz), 135.1 (t, ^3J = 8.8 Hz), 152.7 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.8 (m, 6 F), −106.8 (m, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 519 (2) [M^+], 340 (7) [$M^+ - C_6H_{14}NBr$]. HRMS ($C_{16}H_{16}IN_3F_{10}$ [M^+]): calcd, 519.0368; found, 519.0369. IR (KBr, mixture of **2b** and **3b**): $\tilde{\nu}$ = 2978 (w), 2936 (w), 2874 (vw), 1569 (vw), 1473 (m), 1396 (m), 1368 (m), 1327 (w), 1296 (w), 1271 (m), 1200 (s), 1158 (m), 1128 (m), 1095 (m), 1068 (m), 1031 (m), 980 (m), 887 (w), 829 (w), 750 (vw), 697 (w), 655 (vw), 551 (w) cm^{-1}.

*(E)-1-(4-Chloro-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2c**) and (E)-1-(4-Chloro-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**3c**).* The product was obtained as an inseparable mixture (3.6:1, determined by ^{19}F NMR) of (*E*)-1-(4-chloro-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-chloro-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 84 mg of a mixture (43% mono-*ortho*, 12% di-*ortho*). R_f = 0.52 (**2c**/**3c**) (cyclohexane/ethyl acetate = 90:1). Data for **2c**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, ^3J = 6.8 Hz, 6 H), 1.40 (d, ^3J = 6.6 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 5.18 (sept, ^3J = 6.8 Hz, 1 H), 7.40 (dd, ^3J = 8.8 Hz, ^4J = 2.3 Hz, 1 H), 7.51−7.54 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.3, 49.6, 114.0 (tq, ^1J = 256.3 Hz, ^2J = 39.7 Hz), 119.1, 119.3 (qt, ^1J = 287.2 Hz, ^2J = 39.0 Hz), 122.4 (t, ^2J = 22.2 Hz), 127.8 (t, ^3J = 9.6 Hz), 129.4, 132.3, 149.2 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.9 (m, 3 F), −109.1 (m, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 357 (10) [M^+], 257 (27) [$M^+ - C_6H_{14}N$], 229 (22) [$M^+ - C_6H_{14}N_3$], 179 (63) [$M^+ - C_7H_{14}F_2N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{14}H_{17}ClN_3F_5$ [M^+]): calcd, 357.1031; found, 357.1032. Data for **3c**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.28 (d, ^3J = 6.6 Hz, 6 H), 3.97 (sept, ^3J = 6.6 Hz, 1 H), 5.19 (sept, ^3J = 6.8 Hz, 1 H), 7.73 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.1, 45.7, 49.0, 113.2 (tq, ^1J = 257.8 Hz, ^2J = 39.4 Hz), 119.1 (qt, ^1J = 287.5 Hz, ^2J = 38.3 Hz), 124.3 (t, ^2J = 22.2 Hz), 129.8, 132.3 (t, ^3J = 9.1 Hz), 152.2 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.86 (m, 6 F), −106.96 (m, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 475 (20) [M^+], 375 (10) [$M^+ - C_6H_{14}N$], 347 (11) [$M^+ - C_6H_{14}N_3$], 297 (49) [$M^+ - C_7H_{14}F_2N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{16}H_{16}ClN_3F_{10}$ [M^+]): calcd, 475.0873; found, 475.0870. IR (KBr, mixture of **2c** and **3c**): $\tilde{\nu}$ = 2979 (m), 2937 (w), 1573 (w), 1476 (m), 1425 (m), 1399 (m), 1368 (m), 1328 (m), 1298 (m), 1270 (m), 1202 (s), 1159 (m), 1129 (m), 1100 (m), 1069 (m), 1031 (m), 985 (m), 912 (w), 888 (w), 857 (w), 832 (w), 795 (vw), 765 (w), 750 (w), 709 (w), 662 (w), 613 (w), 593 (w), 555 (w), 441 (vw) cm^{-1}.

*(E)-1-(4-Fluoro-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2d**).* The product was obtained after flash column chromatography (cyclohexane) as a slightly yellow oil. 87 mg (64%). R_f = 0.39 (cyclohexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, ^3J = 6.8 Hz, 6 H), 1.39 (d, ^3J = 6.5 Hz, 6 H), 4.02 (sept, ^3J = 6.5 Hz, 1 H), 5.16 (sept, ^3J = 6.8 Hz, 1 H), 7.17−7.20 (m, 1 H), 7.25−7.28 (m, 1 H), 7.51−7.55 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.8, 47.1, 49.4, 114.6 (dt, ^2J = 25.4 Hz, ^3J = 9.5 Hz), 119.3 (d, ^2J = 21.8 Hz), 119.34 (d, ^3J = 7.7 Hz), 147.0, 159.4 (d, ^1J = 243.8 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.9 (m, 3 F), −109.0 (m, 2 F), −118.5 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 2978 (vw), 1612 (vw), 1488 (w), 1405 (m), 1368 (w), 1312 (w), 1266 (w), 1253 (w), 1207 (m), 1157 (w), 1119 (w), 1097 (w), 1063 (w), 1032 (w), 1002 (w), 913 (vw), 866 (w), 825 (w), 742 (w), 674 (vw), 621 (vw), 603 (vw), 567 (w), 533 (vw), 489 (vw), 449 (vw), 421 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 341 (57) [M^+], 241 (37) [$M^+ - C_6H_{14}N$], 213 (35) [$M^+ - C_6H_{14}N_3$], 163 (100) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{14}H_{17}N_3F_6$ [M^+]): calcd, 341.1326; found, 341.1324.

*(E)-1-(4-Ethoxycarbonyl-2-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 70:1) as a yellow oil. 71 mg (45%). R_f = 0.21 (cyclohexane/ethyl acetate = 90:1). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (d, ^3J = 6.8 Hz, 6 H), 1.40 (t, ^3J = 7.1 Hz, 3 H), 1.41 (d, ^3J = 6.6 Hz, 6 H), 4.08 (sept, ^3J = 6.6 Hz, 1 H), 4.38 (q, ^3J = 7.1 Hz, 2 H), 5.23 (sept, ^3J = 6.8 Hz, 1 H), 7.62 (d, ^3J = 8.6 Hz, 1 H), 8.10 (dd, ^3J = 8.6 Hz, ^4J = 1.9 Hz, 1 H), 8.26 (d, ^4J = 1.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 19.1, 23.7, 47.8, 50.0, 61.0, 114.3 (tq, ^1J = 256.2 Hz, ^2J = 39.6 Hz), 117.5, 119.6 (qt, ^1J = 287.3 Hz, ^2J = 39.2 Hz), 121.1 (t, ^2J = 22.2 Hz), 125.9, 130.0 (t, ^3J = 9.3 Hz), 133.4, 153.8, 165.8 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ =

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

−82.8 (m, 3 F), −109.0 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2980 (m), 2937 (w), 1719 (s), 1609 (m), 1468 (m), 1400 (s), 1366 (s), 1301 (m), 1251 (s), 1198 (s), 1158 (m), 1128 (s), 1068 (m), 1029 (m), 994 (m), 925 (w), 891 (m), 853 (m), 772 (w), 741 (w), 696 (w), 657 (w), 553 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 395 (32) [M^+], 350 (11) [$M^+ - C_2H_5O$], 295 (6) [$M^+ - C_6H_{14}N$], 267 (48) [$M^+ - C_6H_{14}N_3$], 217 (100) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{17}H_{22}O_2N_3F_5$ [M^+]): calcd, 395.1632; found, 395.1633.

*(E)-1-(4-Ethoxycarbonyl-2,6-bis(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**3e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 70:1) as a yellow oil. 22 mg (11%). R_f = 0.29 (cyclohexane/ethyl acetate = 90:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.30 (d, ^3J = 6.6 Hz, 6 H), 1.42 (t, ^3J = 7.1 Hz, 3 H), 3.99 (sept, ^3J = 6.6 Hz, 1 H), 4.43 (q, ^3J = 7.1 Hz, 2 H), 5.20 (sept, ^3J = 6.8 Hz, 1 H), 8.42 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 19.1, 23.1, 45.9, 49.2, 61.8, 113.6 (tq, ^1J = 257.3 Hz, ^2J = 39.3 Hz), 119.0 (qt, ^1J = 287.0 Hz, ^2J = 38.7 Hz), 123.0 (t, ^2J = 22.3 Hz), 126.4, 133.4 (t, ^3J = 8.7 Hz), 157.1, 164.4 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.8 (s, 6 F), −106.8 (s, 4 F) ppm. IR (KBr): $\tilde{\nu}$ = 2980 (m), 2932 (m), 1730 (s), 1612 (m), 1433 (s), 1369 (s), 1327 (m), 1206 (s), 1162 (s), 1132 (s), 1088 (m), 1031 (s), 991 (w), 930 (w), 912 (w), 897 (w), 882 (w), 768 (w), 755 (w), 738 (w), 717 (w), 700 (m), 638 (vw), 572 (vw), 540 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 513 (28) [M^+], 468 (10) [$M^+ - C_2H_5O$], 413 (9) [$M^+ - C_6H_{14}N$], 385 (29) [$M^+ - C_6H_{14}N_3$], 335 (100) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{19}H_{21}O_2N_3F_{10}$ [M^+]): calcd, 513.1474; found, 513.1475.

*(E)-1-(2-Pentafluoroethyl-4-cyano-6-(methyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2f**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 90:1) as a yellow oil. 100 mg (69%). R_f = 0.21 (cyclohexane/ethyl acetate = 90:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, ^3J = 6.8 Hz, 6 H), 1.31 (d, ^3J = 6.6 Hz, 6 H), 2.21 (s, 3 H), 4.02 (sept, ^3J = 6.6 Hz, 1 H), 5.24 (sept, ^3J = 6.8 Hz, 1 H), 7.62 (s, 1 *H*), 7.71 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 19.7, 23.7, 46.2, 49.2, 107.4, 113.7 (tq, ^1J = 256.8 Hz, ^2J = 39.7 Hz), 118.3, 119,0 (qt, ^1J = 287.0 Hz, ^2J = 38.8 Hz), 122.7 (t, ^2J = 22.1 Hz), 129.9 (t, ^3J = 9.3 Hz), 133.0, 137.7, 154.7 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.9 (m, 3 F), −108.8 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2979 (w), 2936 (w), 2876 (vw), 2229 (w), 1604 (w), 1469 (w), 1407 (m), 1368 (m), 1309 (w), 1257 (w), 1228 (m), 1169 (m), 1119 (m), 1036 (m), 1000 (w), 894 (m), 828 (w), 763 (vw), 726 (vw), 608 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 362 (20) [M^+], 262 (6) [$M^+ - C_6H_{14}N$], 234 (36) [$M^+ - C_6H_{14}N_3$] 184 (100) [$M^+ - C_7H_{14}N_3F_2$]. HRMS ($C_{16}H_{19}N_4F_5$ [M^+]): calcd, 362.1529; found, 362.1529.

*(E)-1-(2-Iodo-6-(pentafluoroethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**2g**).* The product was obtained after flash column chromatography (cyclohexane) as a yellow oil. 78 mg (43%). R_f = 0.18 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.37 (d, ^3J = 6.6 Hz, 6 H), 4.03 (sept, ^3J = 6.6 Hz, 1 H), 5.18 (sept, ^3J = 6.8 Hz, 1 H), 6.95 (t, ^3J = 7.9 Hz, 1 H), 7.54 (d, ^3J = 7.9 Hz, 1 H), 8.04 (d, ^3J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.7, 46.2, 49.3, 93.7, 113.6 (tq, ^1J = 256.5 Hz, ^2J = 39.3 Hz), 119.1 (qt, ^1J = 287.1 Hz, ^2J = 38.9 Hz), 121.9 (t, ^2J = 22.0 Hz), 125.7, 128.3 (t, ^3J = 8.3 Hz), 143.3, 153.1 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −83.2 (s, 3 F), −108.5 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2976 (m), 2934 (w), 1586 (w), 1468 (m), 1421 (m), 1405 (m), 1382 (m), 1368 (m), 1329 (m), 1279 (m), 1195 (s), 1148 (m), 1132 (m), 1097 (m), 1079 (m), 1032 (m), 978 (m), 916 (w), 776 (w), 759 (w), 727 (w), 698 (m), 658 (vw), 549 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 449 (61) [M^+], 321 (12) [$M^+ - C_6H_{14}N_3$] 271 (15) [$M^+ - C_7H_{14}N_3F_2$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{14}H_{17}IN_3F_5$ [M^+]): calcd, 449.0387; found, 449.0389.

General Procedure for the Perfluoropropylation of Triazenes. A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol) of AgF and the triazene (0.40 mmol). The reaction vessel was closed, and perfluorohexane (1 mL) was added via syringe under an argon atmosphere. A 0.16 mL (195 mg, 0.80 mmol) portion of TMS-C_3F_7 was added, and the suspension was heated to 100 °C. The reaction mixture was stirred for 4 h. The solution was then cooled to room temperature, and ethyl acetate was added and was stirred for 5 min. The solution was poured into a flask, and silica gel was added. Finally, the solvent was removed in vacuum, and the crude product was purified by flash column chromatography (silica gel, solvent). Note: ^{13}C NMR analysis of the perfluoropropyl group was not possible due to the complexity of the signals.

*(E)-1-(4-Iodo-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4a**) and (E)-1-(4-Iodo-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**5a**).* The product was obtained as an inseparable mixture (2.7:1, determined by ^{19}F NMR) of (*E*)-1-(4-iodo-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-iodo-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 148 mg of a mixture (50% mono-*ortho*, 19% di-*ortho*). R_f = 0.45 (**4a**/**5a**) (cyclohexane). Data for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, ^3J = 6.8 Hz, 6 H), 1.37 (d, ^3J = 6.6 Hz, 6 H), 4.03 (sept, ^3J = 6.6 Hz, 1 H), 5.16 (sept, ^3J = 6.8 Hz, 1 H), 7.29 (d, ^3J = 8.7 Hz, 1 H), 7.73 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1 H), 7.82 (d, ^4J = 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.3, 49.6, 87.0, 119.6, 123.1 (t, ^2J = 22.2 Hz), 136.7 (t, ^3J = 9.7 Hz), 141.1, 150.5 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.33 (t, ^3J = 10.0 Hz, 3 F), −105.6 (m, 2 F), −124.1 (s, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 499 (35) [M^+], 398 (8) [$M^+ - C_6H_{14}N$], 370 (15) [$M^+ - C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{15}H_{17}IN_3F_7$ [M^+]): calcd, 499.0355; found, 499.0357. Data for **5a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, ^3J = 6.8 Hz, 6 H), 1.28 (d, ^3J = 6.6 Hz, 6 H), 3.94 (sept, ^3J = 6.6 Hz, 1 H), 5.21 (sept, ^3J = 6.8 Hz, 1 H, C*H*), 8.02 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.1, 45.2, 48.8, 86.3, 124.6 (t, ^2J = 22.2 Hz), 141.1 (t, ^3J = 8.6 Hz), 154.0 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.2 Hz, 6 F), −103.5 (m, 4 F), −124.4 (s, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 667 (43) [M^+], 566 (2) [$M^+ - C_6H_{14}N$], 538 (12) [$M^+ - C_6H_{14}N_3$]. HRMS ($C_{18}H_{16}IN_3F_{14}$ [M^+]): calcd, 667.0165; found, 667.0163. IR (KBr, mixture of **4a** and **5a**): $\tilde{\nu}$ = 2979 (m), 2937 (w), 1563 (vw), 1470 (m), 1416 (s), 1393 (m), 1382 (m), 1368 (m), 1345 (s), 1273 (m), 1229 (vs), 1199 (s), 1158 (m), 1127 (m), 1110 (s), 1073 (w), 1053 (m), 1031 (m), 959 (w), 940 (w), 909 (m), 877 (m), 853 (vw), 828 (w), 750 (w), 725 (w), 690 (w), 550 (w) cm^{-1}.

*(E)-1-(4-Bromo-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4b**) and (E)-1-(4-Bromo-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**5b**).* The product was obtained as an inseparable mixture (5:1, determined by ^{19}F NMR) of (*E*)-1-(4-bromo-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-bromo-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 148 mg of a mixture (64% mono-*ortho*, 13% di-*ortho*). R_f = 0.44 (**4b**/**5b**) (cyclohexane). Data for **4b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H,), 1.40 (d, ^3J = 6.6 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 5.17 (sept, ^3J = 6.8 Hz, 1 H), 7.46 (d, ^3J = 8.8 Hz, 1 H), 7.55 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1 H), 7.65 (d, ^3J = 2.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.3, 49.6, 116.8, 119.4, 122.8 (t, ^2J = 22.3 Hz), 130.8 (t, ^3J = 9.8 Hz), 135.3, 149.8 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.4 (t, ^3J = 10.0 Hz, 3 F, CF_3), −105.7 (m, 2 F), −124.2 (m, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 451 (8) [M^+], 351 (1) [$M^+ - C_6H_{14}N$], 325 (2) [$M^+ - C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{15}H_{17}BrN_3F_7$ [M^+]): calcd, 451.0494; found, 451.0497. Data for **5b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, ^3J = 6.8 Hz, 6 H), 1.27 (d, ^3J = 6.6 Hz, 6 H), 3.95 (sept, ^3J = 6.6 Hz, 1 H), 5.23 (sept, ^3J = 6.8 Hz, 1 H), 7.87 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.1, 45.2, 48.8, 116.7, 124.6 (t, ^2J = 22.7 Hz), 132.5 (t, ^3J = 9.0 Hz), 153.4 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.1 Hz, 6 F), −103.6 (m, 4 F), 124.4 (m, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 619 (4) [M^+], 519 (1) [$M^+ - C_6H_{14}N$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{18}H_{16}BrN_3F_{14}$ [M^+]): calcd, 619.0304; found, 619.0303. IR (KBr, mixture of **4b** and **5b**): $\tilde{\nu}$ = 2979 (m), 2937 (w), 2875 (w), 1568 (w), 1473 (m), 1421 (s), 1396 (s), 1383 (s), 1369 (s), 1345 (s), 1271 (s), 1228 (s), 1196 (s), 1158 (m), 1127 (s), 1111 (s), 1054 (m), 1031 (m), 959 (w), 941 (m), 911 (m), 878 (m), 854 (w), 829 (m), 778 (w), 749 (m), 726 (w), 694 (m), 651 (w) cm^{-1}.

dx.doi.org/10.1021/jo401145g | *J. Org. Chem.* 2013, 78, 7938−7948

*(E)-1-(4-Chloro-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4c**) and (E)-1-(4-Chloro-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**5c**).* The product was obtained as an inseparable mixture (6.8:1, determined by ^{19}F NMR) of (*E*)-1-(4-chloro-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-chloro-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane/ethyl acetate = 90:1) as a yellow oil. 103 mg of a mixture (52% mono-*ortho*, 8% di-*ortho*). R_f = 0.75 (**4c**/**5c**) (cyclohexane/ethyl acetate =90:1). Data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.40 (d, ^3J = 6.6 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 5.16 (sept, ^3J = 6.8 Hz, 1 H), 7.42 (dd, ^3J = 8.8 Hz, ^4J = 2.2 Hz, 1 H), 7.50−7.52 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 47.3, 49.6, 119.1, 122.5 (t, ^2J = 22.6 Hz), 128.0 (t, ^3J = 9.8 Hz), 129.4, 132.4, 149.4 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.0 Hz, 3 F), −105.7 (m, 2 F), −124.2 (m, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 407 (31) [M^+], 307 (17) [$M^+ - C_6H_{14}N$], 278 (40) [$M^+ - C_6H_{14}N_3$], 229 (28) [$M^+ - C_7H_{14}F_2N_3$], 179 (62) [$M^+ - C_8H_{14}F_4N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{15}H_{17}ClN_3F_7$ [M^+]): calcd, 407.0999; found, 407.0997. Data for **5c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, ^3J = 6.8 Hz, 6 H), 1.27 (d, ^3J = 6.6 Hz, 6 H), 3.95 (sept, ^3J = 6.6 Hz, 1 H), 5.23 (sept, ^3J = 6.8 Hz, 1 H), 7.72 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.1, 45.2, 48.8, 124.3 (t, ^2J = 22.9 Hz), 129.7, 132.5 (t, ^3J = 9.3 Hz), 152.9 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.1 Hz, 6 F), −103.7 (m, 4 F), −124.4 (m, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 575 (5) [M^+], 475 (4) [$M^+ - C_6H_{14}N$], 447 (5) [$M^+ - C_6H_{14}N_3$], 397 (4) [$M^+ - C_7H_{14}F_2N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{18}H_{16}ClN_3F_{14}$ [M^+]): calcd, 575.0809; found, 575.0808. IR (KBr, mixture of **4c** and **5c**): $\tilde{\nu}$ = 2979 (w), 2937 (w), 1475 (w), 1423 (m), 1399 (m), 1368 (w), 1346 (m), 1295 (w), 1269 (m), 1227 (m), 1195 (m), 1158 (w), 1127 (w), 1111 (m), 1054 (w), 1031 (w), 944 (w), 917 (w), 880 (w), 854 (vw), 831 (w), 786 (vw), 749 (w), 706 (w), 682 (vw), 579 (vw), 551 (vw) cm^{-1}.

*(E)-1-(4-Fluoro-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4d**) and (E)-1-(4-Fluoro-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**5d**).* The product was obtained as an inseparable mixture (6.8:1, determined by ^{19}F NMR) of (*E*)-1-(4-fluoro-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene and (*E*)-1-(4-fluoro-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene after flash column chromatography (cyclohexane) as a yellow oil. 91 mg of a mixture (49% mono-*ortho*, 7% di-*ortho*). R_f = 0.32 (**4d**/**5d**) (cyclohexane). Data for **4d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.39 (d, ^3J = 6.6 Hz, 6 H), 4.02 (sept, ^3J = 6.6 Hz, 1 H), 5.16 (sept, ^3J = 6.8 Hz, 1 H), 7.16−7.21 (m, 1 H), 7.24−7.27 (m, 1 H), 7.52−7.56 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 23.8, 47.0, 49.4, 114.8 (dt, ^2J = 25.5 Hz, ^3J = 9.8 Hz), 119.37 (d, ^3J = 7.8 Hz), 119.44 (d, ^2J = 21.9 Hz), 122.4 (dt, ^2J = 22.6 Hz, ^3J = 6.9 Hz), 147.3, 159.3 (d, ^1J = 243.9 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.4 (t, ^3J = 9.9 Hz, 3 F), −105.7 (m, 2 F), −118.6 (s, 1 F), −124.3 (s, 2 F) ppm. MS (70 eV, EI), *m*/*z* (%): 391 (25) [M^+], 291 (26) [$M^+ - C_6H_{14}N$], 263 (34) [$M^+ - C_6H_{14}N_3$], 213 (22) [$M^+ - C_7H_{14}N_3F_2$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{15}H_{17}N_3F_8$ [M^+]): calcd, 391.1294; found, 391.1293. Data for **5d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.8 Hz, 6 H), 1.28 (d, ^3J = 6.6 Hz, 6 H), 3.95 (sept, ^3J = 6.6 Hz, 1 H), 5.24 (sept, ^3J = 6.8 Hz, 1 H), 8.02 (d, ^3J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.1, 45.1, 48.7, 119.8 (d, ^2J = 25.1 Hz), 124.4 (dt, ^2J = 23.2 Hz, ^3J = 6.1 Hz), 133.0, 158.1 (d, ^1J = 245.2 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.1 Hz, 6 F), −103.7 (m, 4 F), −116.5 (s, 1 F), −124.5 (s, 4 F) ppm. MS (70 eV, EI), *m*/*z* (%): 560 (100) [M^+ + H]. HRMS ($C_{18}H_{17}N_3F_{15}$ [M^+ + H]): calcd, 560.1183; found, 560.1185. IR (KBr, mixture of **4d** and **5d**): $\tilde{\nu}$ = 2980 (s), 2937 (w), 1611 (s), 1489 (m), 1433 (m), 1408 (s), 1383 (m), 1369 (m), 1347 (m), 1311 (m), 1267 (m), 1253 (m), 1226 (s), 1182 (s), 1158 (m), 1109 (m), 1049 (w),1032 (m), 981 (w), 965 (w), 950 (m), 913 (w), 880 (w), 857 (w), 838 (m), 822 (w), 748 (m), 684 (w), 625 (vw) cm^{-1}.

*(E)-1-(4-Ethoxycarbonyl-2-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 90:1) as a yellow oil. 77 mg (43%). R_f = 0.31 (cyclohexane/ethyl acetate = 70:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (d, ^3J = 6.8 Hz, 6 H), 1.40 (t, ^3J = 7.1 Hz, 3 H), 1.41 (d, ^3J = 6.6 Hz, 6 H), 4.08 (sept, ^3J = 6.6 Hz, 1 H), 4.38 (q, ^3J = 7.1 Hz, 2 H), 5.23 (sept, ^3J = 6.8 Hz, 1 H), 7.61 (d, ^3J = 8.6 Hz, 1 H), 8.11 (dd, ^3J = 8.6 Hz, ^4J = 1.8 Hz, 1 H), 8.24 (d, ^4J = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 19.1, 23.8, 47.7, 49.9, 61.1, 117.5, 121.1 (t, ^2J = 22.2 Hz), 125.9, 130.2 (t, ^3J = 9.5 Hz), 133.4, 154.0, 165.8 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (t, ^3J = 10.0 Hz, 3 F), −105.7 (m, 2 F), −124.2 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2981 (m), 2937 (w), 1720 (s), 1608 (m), 1573 (w), 1468 (w), 1401 (s), 1383 (m), 1366 (m), 1346 (m), 1300 (m), 1250 (s), 1225 (s), 1195 (s), 1158 (m), 1109 (s), 1054 (w), 1030 (m), 955 (w), 940 (w), 922 (w), 856 (w), 773 (w), 749 (w), 694 (w), 654 (vw), 576 (w), 554 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 445 (28) [M^+], 400 (7) [$M^+ - C_2H_5O$], 345 (4) [$M^+ - C_6H_{14}N$], 317 (23) [$M^+ - C_6H_{14}N_3$], 217 (10) [$M^+ - C_8H_{14}N_3F_4$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{18}H_{22}O_2N_3F_7$ [M^+]): calcd, 445.1600; found, 445.1602.

*(E)-1-(4-Ethoxycarbonyl-2,6-bis(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**5e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 70:1) as a yellow oil. 42 mg (18%). R_f = 0.43 (cyclohexane/ethyl acetate = 70:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, ^3J = 6.8 Hz, 6 H), 1.30 (d, ^3J = 6.6 Hz, 6 H), 1.42 (t, ^3J = 7.1 Hz, 3 H), 3.97 (sept, ^3J = 6.6 Hz, 1 H), 4.45 (q, ^3J = 7.1 Hz, 2 H), 5.24 (sept, ^3J = 6.8 Hz, 1 H), 8.41 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 18.9, 23.1, 45.4, 48.9, 61.8, 123.1 (t, ^2J = 22.5 Hz), 126.5, 133.7 (t, ^3J = 8.6 Hz), 157.8, 164.4 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.2 (t, ^3J = 10.2 Hz, 6 F), −103.6 (m, 4 F), −124.4 (s, 4 F, $CF_2CF_2CF_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3094 (vw), 2983 (s), 2940 (m), 2878 (w), 1730 (s), 1612 (m), 1577 (w), 1434 (s), 1370 (s), 1345 (s), 1320 (s), 1230 (s), 1159 (s), 1113 (s), 1075 (s), 1054 (m), 1031 (m), 965 (m), 950 (m), 926 (m), 911 (w), 869 (m), 768 (m), 751 (m), 739 (w), 726 (m), 696 (m), 582 (w), 538 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 613 (16) [M^+], 513 (3) [$M^+ - C_6H_{14}N$], 485 (8) [$M^+ - C_6H_{14}N_3$], 385 (6) [$M^+ - C_8H_{14}N_3F_4$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{21}H_{21}O_2N_3F_{14}$ [M^+]): calcd, 613.1410; found, 613.1407.

*(E)-1-(2-Heptafluoropropyl-4-cyano-6-(methyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4f**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 90:1) as a yellow oil. 115 mg (70%). R_f = 0.11 (cyclohexane/ethyl acetate = 90:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.32 (d, ^3J = 6.6 Hz, 6 H), 2.21 (s, 3 H), 4.02 (sept, ^3J = 6.6 Hz, 1 H), 5.27 (sept, ^3J = 6.8 Hz, 1 H), 7.63 (s, 1 H), 7.69 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 19.8, 23.7, 46.0, 49.1, 107.3, 118.3, 122.8 (t, ^2J = 22.2 Hz), 130.2 (t, ^3J = 9.6 Hz), 132.9, 137.8, 154.9 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.29 (t, ^3J = 10.2 Hz, 3 F, CF_3), −105.6 (m, 2 F), −124.4 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2979 (m), 2937 (w), 2230 (w), 1603 (w), 1469 (m), 1408 (m), 1382 (m), 1368 (m), 1348 (m), 1308 (w), 1257 (m), 1229 (s), 1206 (s), 1160 (m), 1113 (s), 1032 (w), 1011 (w), 965 (w), 945 (m), 894 (w), 809 (w), 739 (w), 722 (w), 586 (vw), 514 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 412 (32) [M^+], 312 (16) [$M^+ - C_6H_{14}N$], 284 (100) [$M^+ - C_6H_{14}N_3$], 234 (36) [$M^+ - C_7H_{14}N_3F_2$], 184 (92) [$M^+ - C_8H_{14}N_3F_4$]. HRMS ($C_{17}H_{19}N_4F_7$ [M^+]): calcd, 412.1497; found, 412.1499.

*(E)-1-(2-Iodo-6-(heptafluoropropyl)phenyl)-3,3-diisopropyltriaz-1-ene (**4g**).* The product was obtained after flash column chromatography (cyclohexane) as a yellow oil. 83 mg (41%). R_f = 0.12 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, ^3J = 6.8 Hz, 6 H), 1.36 (d, ^3J = 6.6 Hz, 6 H), 4.02 (sept, ^3J = 6.6 Hz, 1 H), 5.20 (sept, ^3J = 6.8 Hz, 1 H), 6.95 (t, ^3J = 7.9 Hz, 1 H), 7.52 (d, ^3J = 7.9 Hz, 1 H), 8.05 (d, ^3J = 7.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.8, 46.0, 49.3, 93.5, 122.1 (t, ^2J = 22.1 Hz), 125.7, 128.5 (t, ^3J = 8.8 Hz), 143.4, 153.3 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −80.3 (s, 3 F), −105.3 (m, 2 F), −124.6 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2977 (s), 1585 (w), 1468 (w), 1420 (m), 1368 (m), 1345 (m), 1269 (m), 1228 (s), 1206 (m), 1158 (m), 1130 (m), 1111 (m), 1076 (w), 1060 (w), 1031 (w), 939 (w), 922 (w), 892 (m), 772 (w), 753 (w), 732 (w), 697 (m), 589 (vw), 547 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 499 (24) [M^+], 399 (5) [$M^+ - C_6H_{14}N$], 371 (34) [$M^+ - C_6H_{14}N_3$],

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

244 (41) [$M^+ - C_7H_{14}N_3I$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{15}H_{17}IN_3F_7$ [M^+]): calcd, 499.0355; found, 499.0354.

General Procedure for the Ethoxycarbonyldifluoromethylation of Triazenes. A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol) of AgF and the triazene (0.40 mmol). The reaction vessel was closed, and perfluorohexane (1 mL) was added via syringe under an argon atmosphere. A 315 mg (1.60 mmol) portion of TMS-CF_2COOEt was then added, and the suspension was heated to 100 °C. The reaction mixture was stirred for 16 h. The solution was then cooled to room temperature, and ethyl acetate was added and was stirred for 5 min. The solution was poured into a flask, and silica gel was added. Finally, the solvent was removed in vacuum, and the crude product was purified by flash column chromatography (silica gel, solvent).

*(E)-1-(4-Iodo-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6a**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as a slightly yellow oil. 51 mg (28%). R_f = 0.30 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.8 Hz, 6 H), 1.22 (t, ^3J = 7.1 Hz, 3 H), 1.37 (d, ^3J = 6.6 Hz, 6 H), 4.00 (sept, ^3J = 6.6 Hz, 1 H), 4.22 (q, ^3J = 7.1 Hz, 2 H), 5.05 (sept, ^3J = 6.8 Hz, 1 H), 7.29 (d, ^3J = 8.7 Hz, 1 H), 7.70 (dd, ^3J = 8.7 Hz, ^4J = 1.9 Hz, 1 H), 7.98 (d, ^3J = 1.9 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.2, 24.0, 47.3, 49.1, 62.3, 87.4, 112.3 (t, ^1J = 247.6 Hz), 128.5 (t, ^2J = 23.2 Hz), 117.8, 134.2 (t, ^3J = 8.6 Hz), 140.1, 148.2 (t, ^3J = 4.3 Hz), 163.7 (t, ^3J = 34.4 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −101.6 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2976 (w), 2925 (w), 1772 (w), 1469 (w), 1396 (m), 1381 (w), 1366 (w), 1289 (w), 1264 (w), 1240 (m), 1216 (w), 1156 (w), 1095 (m), 1082 (m), 1058 (w), 1029 (m), 890 (vw), 825 (w), 761 (w), 690 (vw), 595 (vw), 557 (vw), 452 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 453 (13) [M^+], 100 (78) [$C_6H_{14}N$], 43 (100). HRMS ($C_{16}H_{22}N_3O_2F_2I$ [M^+]): calcd, 453.0724; found, 453.0727.

*(E)-1-(4-Iodo-2,6-bis(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**7a**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1) as an orange solid. 65 mg (28%). R_f = 0.21 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.23 (t, ^3J = 7.1 Hz, 6 H), 1.30 (d, ^3J = 6.7 Hz, 6 H), 3.97 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 4.99 (sept, ^3J = 6.8 Hz, 1 H), 8.10 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 22.8, 46.3, 49.9, 62.6, 86.8, 111.7 (t, ^1J = 249.1 Hz), 128.6 (t, ^2J = 23.7 Hz), 137.5 (t, ^3J = 9.1 Hz), 149.1 (t, ^3J = 3.4 Hz), 162.8 (t, ^2J = 34.1 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.1 (s, 2 F) ppm. IR (ATR): $\tilde{\nu}$ = 2983 (vw), 2939 (vw), 1769 (m), 1452 (w), 1416 (w), 1400 (w), 1383 (w), 1369 (w), 1296 (w), 1278 (w), 1229 (m), 1190 (w), 1152 (m), 1115 (m), 1094 (m), 1068 (m), 1031 (w), 1011 (w), 917 (vw), 888 (w), 858 (w), 839 (w), 804 (vw), 782 (w), 761 (w), 737 (w), 688 (w), 636 (vw), 618 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 575 (27) [M^+], 475 (4) [$M^+ - C_6H_{14}N$], 100 (100). HRMS ($C_{20}H_{26}IN_3O_4F_4$ [M^+]): calcd, 575.0904; found, 575.0903.

*(E)-1-(4-Bromo-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6b**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 70:1) as a slightly yellow oil. 58 mg (36%). R_f = 0.28 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.8 Hz, 6 H), 1.21 (t, ^3J = 7.1 Hz, 3 H), 1.37 (d, ^3J = 6.6 Hz, 6 H), 4.00 (sept, ^3J = 6.6 Hz, 1 H), 4.22 (q, ^3J = 7.1 Hz, 2 H), 5.05 (sept, ^3J = 6.8 Hz, 1 H), 7.42 (d, ^3J = 8.7 Hz, 1 H), 7.50 (dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz, 1 H), 7.81 (d, ^3J = 2.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.2, 24.0, 47.3, 49.0, 62.3, 112.4 (t, ^1J = 247.7 Hz), 117.0, 117.5, 128.2 (t, ^2J = 23.2 Hz), 128.4 (t, ^3J = 8.6 Hz), 134.2, 147.5 (t, ^3J = 4.2 Hz), 163.7 (t, ^3J = 34.2 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −101.6 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2979 (m), 2935 (w), 1774 (s), 1689 (vw), 1471 (m), 1400 (s), 1382 (m), 1368 (m), 1292 (m), 1263 (m), 1242 (m), 1217 (m), 1157 (m), 1133 (m), 1112 (m), 1095 (m), 1062 (w), 1017 (w), 888 (vw), 828 (w), 763 (w), 695 (vw), 568 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 405 (12) [M^+], 305 (4) [$M^+ - C_6H_{14}N$], 146 (100). HRMS ($C_{16}H_{22}BrN_3O_2F_2$ [M^+]): calcd, 405.0863; found, 405.0860.

*(E)-1-(4-Bromo-2,6-bis(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**7b**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 70:1) as a nearly white solid. 68 mg (32%). R_f = 0.19 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.23 (t, ^3J = 7.1 Hz, 6 H), 1.31 (d, ^3J = 6.7 Hz, 6 H), 3.97 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 5.00 (sept, ^3J = 6.8 Hz, 1 H), 7.93 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 22.8, 46.3, 49.9, 62.6, 111.8 (t, ^1J = 249.1 Hz), 116.8, 128.6 (t, ^2J = 23.8 Hz), 131.8 (t, ^3J = 9.1 Hz), 148.5, 162.7 (t, ^3J = 34.2 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.2 (s, 4 F) ppm. IR (ATR): $\tilde{\nu}$ = 2982 (vw), 1768 (w), 1453 (vw), 1416 (w), 1400 (w), 1369 (w), 1297 (w), 1229 (w), 1189 (w), 1153 (w), 1113 (w), 1094 (w), 1070 (w), 1032 (w), 1014 (w), 913 (vw), 888 (w), 859 (w), 841 (vw), 808 (vw), 783 (vw), 765 (w), 738 (w), 696 (w), 621 (vw), 567 (vw), 550 (vw), 532 (w), 473 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 527 (61) [M^+], 427 (30) [$M^+ - C_6H_{14}N$], 315 (100). HRMS ($C_{20}H_{26}BrN_3O_4F_4$ [M^+]): calcd, 527.1041; found, 527.1038.

*(E)-1-(4-Chloro-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6c**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1−20:1) as a yellow oil. 35 mg (24%). R_f = 0.23 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, ^3J = 6.7 Hz, 6 H), 1.21 (t, ^3J = 7.1 Hz, 3 H), 1.37 (d, ^3J = 6.6 Hz, 6 H), 4.00 (sept, ^3J = 6.6 Hz, 1 H), 5.07 (sept, ^3J = 6.7 Hz, 1 H), 7.35 (dd, ^3J = 8.7 Hz, ^4J = 2.3 Hz, 1 H), 7.49 (d, ^3J = 8.7 Hz, 1 H), 7.66 (d, ^3J = 2.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 19.2, 24.0, 47.2 (+, CH), 49.0, 62.3, 112.5 (t, ^1J = 247.6 Hz), 117.2, 125.5 (t, ^3J = 8.6 Hz), 127.9 (t, ^2J = 23.3 Hz), 129.4, 131.3, 147.1 (t, ^3J = 4.3 Hz), 163.7 (t, ^3J = 34.1 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −101.7 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2977 (m), 1771 (m), 1546 (vw), 1473 (m), 1399 (s), 1366 (m), 1292 (m), 1259 (m), 1241 (m), 1216 (m), 1156 (m), 1131 (m), 1094 (s), 1064 (m), 1015 (m), 912 (w), 887 (w), 859 (w), 828 (m), 762 (m), 703 (w), 661 (w), 599 (vw), 580 (w), 546 (w); 491 (w), 405 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 361 (12) [M^+], 261 (6) [$M^+ - C_6H_{14}N$], 205 (100). HRMS ($C_{16}H_{22}ClN_3O_2F_2$ [M^+]): calcd, 361.1368; found, 361.1370.

*(E)-1-(4-Chloro-2,6-bis(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**7c**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 50:1−20:1) as a yellow oil. 56 mg (29%). R_f = 0.14 (cyclohexane/ethyl acetate = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.24 (t, ^3J = 7.1 Hz, 6 H), 1.31 (d, ^3J = 6.7 Hz, 6 H), 3.97 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 5.01 (sept, ^3J = 6.8 Hz, 1 H), 7.79 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.3, 22.8, 46.2, 49.9, 62.6, 111.9 (t, ^1J = 249.1 Hz), 128.4 (t, ^2J = 23.8 Hz), 128.9 (t, ^3J = 9.2 Hz), 129.5, 148.0 (t, ^3J = 3.4 Hz), 162.8 (t, ^3J = 34.3 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.2 (s, 4 F) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (vw), 2982 (w), 2938 (w), 1775 (m), 1415 (m), 1384 (w), 1369 (m), 1286 (m), 1232 (m), 1192 (w), 1158 (m), 1132 (m), 1098 (m), 1070 (m), 1020 (w), 890 (w), 864 (vw), 772 (w), 739 (w), 710 (w), 579 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 483 (2) [M^+], 383 (1) [$M^+ - C_6H_{14}N$], 43 (100). HRMS ($C_{20}H_{26}ClN_3O_4F_4$ [M^+]): calcd, 483.1547; found, 483.1550.

*(E)-1-(4-Fluoro-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6d**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 30:1) as a yellow oil. 45 mg (33%). R_f = 0.36 (cyclohexane/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, ^3J = 6.5 Hz, 6 H), 1.22 (t, ^3J = 7.1 Hz, 6 H), 1.37 (d, ^3J = 6.7 Hz, 6 H), 3.98 (sept, ^3J = 6.5 Hz, 1 H), 4.23 (q, ^3J = 7.1 Hz, 2 H), 5.04 (sept, ^3J = 6.7 Hz, 1 H), 7.08−7.15 (m, 1 H), 7.40 (dd, ^3J = 9.0 Hz, ^4J = 2.8 Hz, 1 H), 7.52 (dd, ^3J = 8.9 Hz, ^4J = 5.1 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 24.0, 47.0, 48.8, 62.3, 112.4 (t, ^1J = 247.7 Hz), 112.4 (dt, ^2J = 25.2 Hz, ^3J = 8.6 Hz), 117.4 (d, ^3J = 7.7 Hz), 118.1 (d, ^2J = 22.6 Hz), 127.9 (td, ^2J = 23.7 Hz, ^3J = 7.4 Hz), 144.9 (td, ^3J = 4.3 Hz, ^4J = 3.1 Hz), 159.6 (d, ^1J = 159.6 Hz), 163.7 (t, ^3J = 34.3 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −101.4 (s, 2 F), −118.2 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (vw), 2979 (w), 2936 (w), 1774 (m), 1611 (w), 1486 (w), 1412 (m),

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

1383 (w), 1303 (w), 1255 (m), 1216 (w), 1178 (m), 1158 (w), 1124 (m), 1097 (m), 1072 (w), 1021 (w), 916 (w), 878 (w), 830 (w), 764 (w), 730 (w), 674 (vw), 613 (vw), 601 (vw), 574 (vw), 550 (vw), 496 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 345 (32) [M^+], 245 (18) [$M^+ - C_6H_{14}N$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{16}H_{22}N_3O_2F_3$ [M^+]): calcd, 345.1664; found, 345.1663.

*(E)-1-(4-Fluoro-2,6-bis(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**7d**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 30:1) as a yellow oil. 59 mg (32%). R_f = 0.24 (cyclohexane/ethyl acetate = 10:1). Slightly contaminated with (*E*)-1-(4-fluoro-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, ^3J = 6.8 Hz, 6 H), 1.23 (t, ^3J = 7.1 Hz, 6 H), 1.30 (t, ^3J = 6.7 Hz, 6 H), 3.96 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 5.00 (sept, ^3J = 6.8 Hz, 1 H), 7.53 (d, ^3J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 19.3, 22.8, 45.9, 49.6, 62.6, 116.0 (dt, ^2J = 25.0 Hz, ^3J = 9.0 Hz), 128.6 (dt, ^2J = 24.2 Hz, ^3J = 7.2 Hz), 145.7 (dt, ^3J = 7.2 Hz, ^4J = 3.6 Hz), 158.6 (d, ^1J = 244.6 Hz), 162.7 (t, ^3J = 34.2 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.2 (s, 4 F), −116.9 (s, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (vw), 2983 (w), 2939 (w), 1775 (s), 1614 (w), 1461 (m), 1416 (m), 1370 (m), 1330 (w), 1300 (m), 1232 (m), 1157 (m), 1123 (m), 1097 (m), 1026 (m), 925 (w), 910 (w), 884 (w), 858 (w), 827 (w), 784 (w), 738 (w), 697 (vw), 611 (vw), 538 (vw), 423 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 467 (53) [M^+], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{20}H_{26}N_3O_4F_5$ [M^+]): calcd, 467.1843; found, 467.1841.

*(E)-1-(4-Ethoxycarbonyl-2-(ethoxycarbonyldifluoromethyl)-phenyl)-3,3-diisopropyltriaz-1-ene (**6e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 30:1) as a slightly yellow oil. 32 mg (20%). R_f = 0.20 (cyclohexane/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.1 Hz, 3 H), 1.21 (d, ^3J = 6.6 Hz, 6 H), 1.39 (d, ^3J = 6.9 Hz, 6 H), 4.04 (sept, ^3J = 6.6 Hz, 1 H), 4.22 (q, ^3J = 7.1 Hz, 2 H), 4.38 (q, ^3J = 7.1 Hz, 2 H), 5.11 (sept, ^3J = 6.8 Hz, 1 H), 7.58 (d, ^3J = 8.6 Hz, 1 H), 8.08 (dd, ^3J = 8.6 Hz, ^4J = 1.8 Hz, 1 H), 8.38 (d, ^3J = 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.4, 19.2, 23.9, 47.7, 49.4, 60.9, 62.2, 112.8 (t, ^1J = 247.1 Hz), 115.6, 125.8, 126.5 (t, ^2J = 23.4 Hz), 127.4 (t, ^3J = 8.2 Hz), 132.6, 151.9 (t, ^4J = 4.0 Hz), 163.9 (t, ^3J = 34.4 Hz), 166.1 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −101.7 (s, 4 F) ppm. IR (KBr): $\tilde{\nu}$ = 2979 (w), 1764 (s), 1711 (s), 1607 (m), 1464 (w), 1413 (m), 1393 (s), 1364 (s), 1284 (m), 1251 (s), 1210 (s), 1155 (m), 1133 (m), 1093 (s), 1066 (s), 1016 (s), 928 (m), 862 (m), 775 (m), 745 (m), 696 (m), 655 (w), 574 (m), 493 (w), 444 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 399 (15) [M^+], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{19}H_{27}N_3O_4F_2$ [M^+]): calcd, 399.1969; found, 399.1968.

*(E)-1-(4-Ethoxycarbonyl-2,6-bis(ethoxycarbonyldifluoromethyl)-phenyl)-3,3-diisopropyltriaz-1-ene (**7e**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 30:1) as a white solid. 58 mg (28%). R_f = 0.10 (cyclohexane/ethyl acetate = 10:1).^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.1 Hz, 6 H), 1.23 (t, ^3J = 6.8 Hz, 3 H), 1.33 (d, ^3J = 6.7 Hz, 6 H), 1.41 (t, ^3J = 7.1 Hz, 3 H), 4.00 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 4.41 (q, ^3J = 7.1 Hz, 2 H), 5.01 (sept, ^3J = 6.8 Hz, 1 H), 8.49 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 14.3, 19.2, 22.7, 46.7, 50.3, 61.4, 62.6, 112.3 (t, ^1J = 248.6 Hz), 125.9, 126.9 (t, ^2J = 23.8 Hz), 130.3 (t, ^3J = 8.9 Hz), 152.7 (t, ^3J = 3.2 Hz), 162.0 (t, ^3J = 34.2 Hz), 165.2 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.8 (s, 4 F) ppm. IR (ATR): $\tilde{\nu}$ = 3440 (vw), 2979 (w), 2936 (w), 1774 (m), 1611 (w), 1486 (w), 1412 (m), 1383 (w), 1368 (w), 1303 (w), 1255 (m), 1216 (w), 1178 (m), 1158 (w), 1124 (m), 1097 (m), 1072 (w), 1021 (w), 916 (w), 878 (w), 830 (w), 764 (w), 730 (w), 674 (vw), 613 (vw), 601 (vw), 574 (vw), 550 (vw), 496 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 521 (39) [M^+], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{23}H_{31}N_3O_6F_4$ [M^+]): calcd, 521.2148; found, 521.2148.

*(E)-1-(4-Cyano-2-(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**6f**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 20:1−10:1) as a yellow oil. 40 mg (28%). R_f = 0.15 (cyclohexane/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.2 Hz, 3 H), 1.23 (d, ^3J = 6.8 Hz, 6 H), 1.40 (d, ^3J = 6.6 Hz, 6 H), 4.07 (sept, ^3J = 6.6 Hz, 1 H), 4.22 (q, ^3J = 7.1 Hz, 2 H), 5.11 (sept, ^3J = 6.8 Hz, 1 H), 7.63 (d, ^3J = 8.6 Hz, 1 H), 7.66 (dd, ^3J = 8.6 Hz, ^4J = 1.7 Hz, 1 H), 7.97 (d, ^4J = 1.7 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.1, 23.9, 48.2, 49.2, 62.5, 106.9, 112.1 (t, ^1J = 248.1 Hz), 116.5, 118.9, 127.4 (t, ^2J = 23.7 Hz), 130.1 (t, ^3J = 8.4 Hz), 134.8, 151.8 (t, ^3J = 4.0 Hz), 163.3 (t, ^3J = 34.2 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −102.5 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2977 (w), 2937 (w), 2219 (w), 1773 (m), 1604 (w), 1483 (w), 1463 (w), 1421 (w), 1365 (m), 1290 (m), 1270 (m), 1247 (m), 1224 (m), 1199 (w), 1168 (m), 1136 (m), 1095 (m), 1070 (m), 1020 (m), 916 (w), 857 (w), 831 (m), 766 (m), 746 (w), 719 (w), 674 (w), 616 (w), 592 (w), 579 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 352 (75) [M^+], 252 (23) [$M^+ - C_6H_{14}N_3$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{17}H_{22}N_4O_2F_2$ [M^+]): calcd, 352.1710; found, 352.1710.

*(E)-1-(4-Cyano-2,6-bis(ethoxycarbonyldifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**7f**).* The product was obtained after flash column chromatography (cyclohexane/ethyl acetate = 20:1−10:1) as a yellow oil. 24 mg (13%). R_f = 0.09 (cyclohexane/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.1 Hz, 6 H), 1.24 (d, ^3J = 6.8 Hz, 6 H), 1.33 (t, ^3J = 6.7 Hz, 6 H), 4.04 (sept, ^3J = 6.7 Hz, 1 H), 4.20 (q, ^3J = 7.1 Hz, 4 H), 4.98 (sept, ^3J = 6.8 Hz, 1 H), 8.08 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.1, 22.6, 47.4, 50.9, 62.9, 107.4, 111.8 (t, ^1J = 249.4 Hz), 117.9, 127.9 (t, ^2J = 24.0 Hz), 132.8 (t, ^3J = 9.2 Hz), 152.4 (t, ^3J = 3.2 Hz), 162.5 (t, ^2J = 34.1 Hz) ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −98.9 (s, 4 F) ppm. IR (KBr): $\tilde{\nu}$ = 3442 (vw), 3091 (vw), 2983 (m), 2938 (w), 2230 (w), 1776 (s), 1610 (w), 1572 (vw), 1460 (w), 1418 (m), 1397 (m), 1382 (m), 1368 (m), 1299 (m), 1251 (m), 1234 (m), 1198 (w), 1172 (m), 1127 (m), 1096 (m), 1026 (m), 908 (w), 856 (w), 823 (vw), 782 (w), 740 (w), 721 (w), 622 (vw), 594 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 474 (71) [M^+], 374 (24) [$M^+ - C_6H_{14}N$], 100 (100) [$C_6H_{14}N$]. HRMS ($C_{21}H_{26}N_4O_4F_4$ [M^+]): calcd, 474.1890; found, 474.1888.

General Procedure for the Trifluoromethylation of Triazenes under Neat Conditions. A vial equipped with a septum and a stirring bar was charged with 202 mg (1.60 mmol) of AgF and the triazene (0.40 mmol). The reaction vessel was closed, and then 0.12 mL (114 mg, 0.80 mmol) of TMS-CF_3 was added and the suspension was heated to 100 °C. The reaction mixture was stirred for 4 h. The solution was then cooled to room temperature, and ethyl acetate was added and was stirred for 5 min. The solution was poured into a flask, and silica gel was added. Finally, the solvent was removed in vacuum, and the crude product was purified by flash column chromatography.

*(E)-1-(4-Iodo-2-(trifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**8a**).* The product was obtained after flash column chromatography (cyclohexane) as a yellow oil. 84 mg (53%). R_f = 0.40 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.39 (d, ^3J = 6.6 Hz, 6 H), 4.06 (sept, ^3J = 6.6 Hz, 1 H), 5.08 (sept, ^3J = 6.8 Hz, 1 H), 7.34 (d, ^3J = 8.7 Hz, 1 H), 7.73 (dd, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 1 H), 7.91 (d, ^4J = 1.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1, 23.7, 48.0, 50.5, 86.4, 118.9, 123.9 (q, ^1J = 273.8 Hz), 125.1 (q, ^2J = 30.1 Hz), 134.9 (q, ^3J = 5.7 Hz), 140.9, 149.1 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −60.2 (s, 3 F) ppm. IR (KBr): $\tilde{\nu}$ = 3443 (vw), 2976 (w), 2933 (w), 1587 (vw), 1470 (m), 1397 (s), 1382 (m), 1367 (m), 1307 (m), 1274 (m), 1256 (m), 1230 (m), 1198 (m), 1126 (s), 1097 (m), 1047 (m), 1030 (m), 892 (w), 829 (w), 741 (vw), 682 (w), 645 (vw), 611 (vw), 577 (vw), 545 (w), 495 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 399 (17) [M^+], 299 (8) [$M^+ - C_6H_{14}N$], 271 (100) [$M^+ - C_6H_{14}N_3$], 144 (6) [$M^+ - C_6H_{14}N_3I$]. HRMS ($C_{13}H_{17}IN_3F_3$ [M^+]): calcd, 399.0419; found, 399.0420.

*(E)-1-(4-Iodo-2,6-bis(trifluoromethyl)phenyl)-3,3-diisopropyltriaz-1-ene (**9a**).* The product was obtained after flash column chromatography (cyclohexane) as a yellow solid. 69 mg (37%). R_f = 0.28 (cyclohexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (d, ^3J = 6.8 Hz, 6 H, CH_3), 1.31 (d, ^3J = 6.6 Hz, 6 H), 4.01 (sept, ^3J = 6.6 Hz, 1 H), 5.13 (sept, ^3J = 6.8 Hz, 1 H), 8.09 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0, 23.0, 47.0, 50.0, 85.6, 122.5 (q, ^1J = 274.3 Hz), 125.8 (q, ^2J = 31.0 Hz), 138.9 (q, ^3J = 5.7 Hz), 150.6 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −58.8 (s, 6 F) ppm. IR (ATR): $\tilde{\nu}$ = 2975 (w), 2934 (w), 1818 (vw), 1575 (w), 1456 (w), 1409 (s), 1383

dx.doi.org/10.1021/jo401145g | J. Org. Chem. 2013, 78, 7938−7948

(m), 1367 (m), 1328 (m), 1289 (m), 1259 (m), 1230 (s), 1169 (s), 1128 (s), 1099 (s), 1026 (m), 895 (m), 860 (w), 835 (m), 803 (w), 763 (m), 678 (m), 648 (w), 586 (w), 534 (w), 506 (w), 462 (w) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 467 (53) [M^+], 367 (23) [$M^+ - C_6H_{14}N$], 339 (100) [$M^+ - C_6H_{14}N_3$]. HRMS ($C_{14}H_{16}IN_3F_6$ [M^+]): calcd, 467.0293; found, 467.0291.

*1-Azido-4-(ethoxycarbonyl)-2-(pentafluoroethyl)benzene (**12**).* A vial equipped with a septum and a stirring bar was charged with the triazene **2e** (50 mg, 0.126 mmol). The reaction vessel was closed, and abs. dichloromethane (1 mL) was added via syringe under an argon atmosphere. The solution was cooled down to 0 °C, and 0.08 mL of TMS-N_3 (72.9 mg, 0.63 mmol, 5.00 equiv) and 0.10 mL of TFA (143 mg, 1.26 mmol, 1.00 equiv) were added via syringe. After 1 h of stirring at room temperature, the solvent was reduced under vacuum. The pure compound could be obtained after flash column chromatography (silica gel, cyclohexane/ethyl acetate = 30:1) as a yellow oil. 36 mg (92%). R_f = 0.21 (cyclohexane/ethyl acetate = 90:1). Note: ^{13}C NMR analysis of the perfluoroethyl group was not possible due to the complexity of the signals. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, ^3J = 7.1 Hz, 3 H), 4.40 (q, ^3J = 7.1 Hz, 2 H), 7.34 (d, ^3J = 8.3 Hz), 8.23−8.25 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3, 61.6, 119.2 (t, ^2J = 23.5 Hz), 131.0 (t, ^3J = 8.5 Hz), 119.8, 127.1, 134.3, 143.7, 164.6 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −83.6 (m, 3 F), −111.5 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 2986 (w), 2422 (w), 2132 (s), 1724 (s), 1611 (m), 1580 (w), 1497 (m), 1414 (w); 1392 (w), 1369 (m), 1331 (m), 1301 (s), 1271 (m), 1241 (s), 1204 (s), 1119 (m), 1074 (m), 1023 (m), 995 (m), 927 (w), 885 (w), 837 (w), 765 (m), 738 (vw), 707 (w), 665 (w), 643 (vw), 624 (vw), 537 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 309 (20) [M^+], 281 (100) [$M^+ - N_2$]. HRMS ($C_{11}H_8O_2N_3F_5$ [M^+]): calcd, 309.0536; found, 309.0539.

*1-Iodo-4-(ethoxycarbonyl)-2-(pentafluoroethyl)benzene (**13**).* A vial equipped with a septum and a stirring bar was charged with the triazene **2e** (50 mg, 0.126 mmol). The reaction vessel was closed, and abs. dichloromethane (1 mL) was added via syringe under an argon atmosphere. A 0.11 mL (152 mg, 0.76 mmol) portion of TMS-I was then added, and the solution was heated to 100 °C for 16 h. The solution was then cooled to room temperature and concentrated in vacuum. The pure product could be obtained after flash column chromatography (silica gel, cyclohexane/ethyl acetate = 30:1) as a yellow oil. 23 mg (46%). R_f = 0.26 (cyclohexane/ethyl acetate = 20:1). Note: ^{13}C NMR analysis of the perfluoroethyl group was not possible due to the complexity of the signals. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 (t, ^3J = 7.13 Hz, 3 H), 4.41 (q, ^3J = 7.3 Hz, 2 H), 7.80 (dd, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 1 H), 8.18 (d, ^3J = 8.2 Hz, 1 H), 8.20 (bs, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 61.8, 96.8, 130.7 (t, ^3J = 8.7 Hz), 130.8, 131.7 (t, ^2J = 23.0 Hz), 133.2, 143.6, 164.9 ppm. ^{19}F NMR (367 MHz, $CDCl_3$): δ = −82.5 (m, 3 F), −110.1 (m, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 3441 (vw), 2985 (vw), 1726 (w), 1598 (w), 1467 (vw), 1369 (w), 1308 (w), 1251 (w), 1206 (m), 1157 (w), 1132 (w), 1094 (w), 1018 (w), 993 (w), 921 (vw), 858 (vw), 759 (w), 731 (vw), 705 (vw), 660 (vw) cm^{-1}. MS (70 eV, EI), *m*/*z* (%): 393 (100) [M^+], 348 (97) [$M^+ - OC_2H_5$]. HRMS ($C_{11}H_8IO_2F_5$ [M^+]): calcd, 393.9489; found, 393.9488.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray data, spectroscopic data, and NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: braese@kit.edu. Fax: + 49 721 608 48581. Tel: + 49 721 608 42903.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Landesgraduiertenförderung Baden-Württemberg (fellowship to A.H.). The authors also acknowledge support from the Deutsche Forschungsgemeinschaft through the Center for Functional Nanostructures (CFN, project no. C3.3).

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