DOI: 10.1002/ejoc.201301538

4-(Pentafluorosulfanyl)benzenediazonium Tetrafluoroborate: A Versatile Launch Pad for the Synthesis of Aromatic SF_5 Compounds via Cross Coupling, Azo Coupling, Homocoupling, Dediazoniation, and Click Chemistry

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Keywords: Click chemistry / Diazo compounds / Azo coupling / Cross-coupling / Solvolysis / Fluorine / Sulfur

The reagent 4-(pentafluorosulfanyl)benzenediazonium tetrafluoroborate (**1**) was synthesized and isolated as a stable salt for the first time; its application in a wide assortment of transformations was subsequently investigated. A series of novel SF_5-bearing alkenes, alkynes, and biaryl derivatives were synthesized by employing Heck–Matsuda, Sonogashira, and Suzuki coupling protocols. Dediazoniation with TMSX (X = Hal; N_3; and CN) and NH_4SCN in [BMIM][BF_4] as solvent furnished the corresponding *p*-SF_5–C_6H_4X derivatives. The azide derivative *p*-SF_5–$C_6H_4N_3$ entered into click chemistry with phenylacetylenes to furnish the corresponding triazoles. The 4,4′-bis(pentafluorosulfanyl)biphenyl was synthesized by homo-coupling using $Pd(OAc)_2$. The corresponding azo compounds were obtained through azo-coupling with reactive aromatic nucleophiles (1,3-dimethoxybenzene, 1,3,5-trimethoxybenzene, 1,2,4-trimethoxybenzene, aniline and phenol). Fluorodediazoniation in [BMIM][PF_6] and [BMIM][BF_4] selectively furnished the fluoro derivative *p*-SF_5–C_6H_4F. Dediazoniation in [BMIM][NTf_2] gave *p*-SF_5–$C_6H_4OS(O)(CF_3)$=NSO_2CF_3 as the major and *p*-SF_5–C_6H_4-NTf_2 as the minor products. Homolytic dediazoniation in MeCN/NaI gave the unsymmetrical biaryls *p*-SF_5–C_6H_4-Ar (ArH = mesitylene and *p*-xylene) along with *p*-SF_5–C_6H_4I. Analysis of the dediazoniation product mixtures indicated that dediazoniation of *p*-SF_5–$C_6H_4N_2^+$ BF_4^- in low nucleophilicity, highly ionizing, solvents (TfOH, TFE, HFIP, TFAH) is mainly heterolytic, while in MeOH it is mainly homolytic. The isodesmic reaction *p*-SF_5–$C_6H_4^+$ + R-C_6H_5 → SF_5–C_6H_5 + *p*-R-$C_6H_4^+$ (with R = NO_2, CF_3, H) was gauged by DFT at various levels and by PCM.

Introduction

The presence of the pentafluorosulfanyl (SF_5) group imparts a number of favorable physical and chemical characteristics including thermal, hydrolytic, and chemical stability, high density, high electronegativity, and high lipophilicity. These favorable characteristics have prompted a high degree of interest in SF_5-organics for potential applications in the biomedical and materials fields.[1]

As a substituent on an aromatic ring the SF_5 group acts as a sterically demanding, strongly electron-withdrawing/deactivating group. A major drawback in the development of synthetic chemistry of SF_5-arenes has been the lack of practical methods that avoid the use of exotic/hazardous reagents and harsh conditions. In early pioneering studies Sheppard synthesized the parent (pentafluorosulfanyl)benzene and its *p*-nitro derivative in modest yields by reacting the corresponding aryl disulfides or aryl sulfur trifluorides with excess AgF_2 in chlorofluorocarbon solvent at elevated temperatures in a copper reactor.[2] This method was later employed by Thrasher et al.[3] to prepare various substituted derivatives of $PhSF_5$ in modest overall yields. Subsequent methods reported from other laboratories involved elemental fluorination starting with the corresponding bis-nitrophenyl disulfide,[4] and high pressure reactions with gaseous SF_5 halides.[5,6] The 3-nitro derivative is accessible by direct electrophilic nitration of $PhSF_5$.[2,4,5] A recent method reported by Umemoto et al.[7] involves synthesis of $ArSF_4Cl$ from ArSSAr or ArSH by reaction with Cl_2/KF or CsF and subsequent transformation to $ArSF_5$ by ZnF_2/heat. The commercial availability of parent $PhSF_5$ and a few other derivatives, notably the *p*-Me, the *p*-NH_2, and the *m*- and *p*-NO_2 derivatives,[8] has, to some extent, remedied preparatory problems.

The strongly deactivating effect of SF_5 group makes $PhSF_5$ amenable to S_NAr chemistry notably with alkoxides and thiolate,[9a] and by vicarious nucleophilic substitution of hydrogen.[9b–9d] By contrast, the S_EAr chemistry of SF_5-aromatics has remained under-developed. In early work by Philip et al.,[4a] the 3-iodo and 4-iodo derivatives were synthesized by in-situ diazotization and reaction with KI, and were shown to enter into cross coupling reactions in repre-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301538

sentative cases. Formation of an SF_5-based azo-dye by in-situ diazotization and coupling to $PhNMe_2$ was reported by Kirsch and Hahn.[4c] However, the $F_5S–C_6H_4N_2^+$ salt was never isolated in earlier studies to allow its use as a key building block for the synthesis of other SF_5-aromatics using diazonium ion chemistry.

In relation to our continuing interest in diazonium ion chemistry and dediazoniation,[10–13] and in the application of ArN_2^+ in ligand coupling reactions,[14] we report here on the synthesis and isolation of 4-(pentafluorosulfanyl) benzenediazonium tetrafluoroborate **1** as a stable salt. Moreover, we explore the utility of **1** as a versatile building block for the synthesis of a host of aromatic SF_5 compounds by cross coupling, azo-coupling, homocoupling, dediazoniation, and click chemistry.

Results and Discussion

Synthesis and Isolation of 4-(Pentafluorosulfanyl)phenyldiazonium Tetrafluoroborate (1)

In early trials diazonium salt **1** could not be isolated by classical diazotization of the amine.[15] Diazotization could be effected by using $NaNO_2/HBF_4$ but the resulting diazonium salt would not precipitate out of solution following dilution of the aqueous solution with ether, dichloromethane, or hexane. "Dry" diazotization as previously reported by Doyle and Bryker,[16] using *tert*-butyl nitrite/$BF_3{\cdot}OEt_2$ in cold CH_2Cl_2 (Figure 1), successfully afforded the diazonium salt as a colorless precipitate which, following purification with MeCN/ether, furnished the diazonium salt as a pale-yellow solid. Tetrafluoroborate salt **1** is highly stable and can be stored at room temperature for extended periods. The $\nu_{N–N}$ frequency of **1** was observed at 2309 cm^{-1}, consistent with the extreme deactivating inductive effect of the *p*-SF_5 group. For comparison purposes it is instructive to note that the $\nu_{N–N}$ frequency for 4-$NO_2C_6H_4N_2^+$ is at 2280 cm^{-1}.[17] Attempts were made to obtain an X-ray structure for the diazonium salt but the crystals did not diffract well enough to render viable crystallographic data.

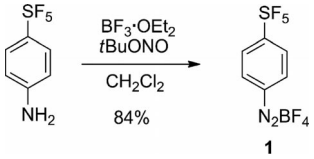
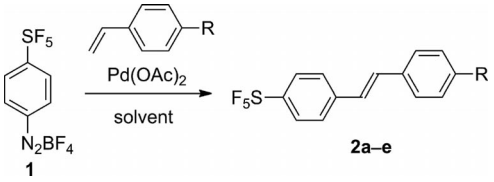


Figure 1. Synthesis of diazonium salts from 4-(pentafluorsulfanyl)-aniline.

Heck–Matsuda Arylation

The *p*-SF_5 substituted diazonium salt entered into Heck–Matsuda coupling reaction with styrene and 4-substituted styrenes in the presence of catalytic $Pd(OAc)_2$ in ethanol to give corresponding 4′-substituted 4-(pentafluorosulfanyl)stilbenes **2a**–**e** (Table 1). Heck coupling in [BMIM][BF_4] ionic liquid[14] instead of EtOH resulted in lower isolated yields due to the increased formation of homo-coupling products (styrene dimer and oligomers) that could not be effectively separated from the desired stilbene.

Table 1. Heck–Matsuda arylation with styrenes.



R	Solvent	Temp. [°C]	Time [h]	Yield[a] [%]
H (**2a**)	95% EtOH	70	15	77
H (**2a**)	[BMIM][BF_4]	r.t.	22	23
F (**2b**)	95% EtOH	70	5	77
CH_3 (**2c**)	95% EtOH	70	5	82
Cl (**2d**)	95% EtOH	r.t.	24	65
CH_3COO (**2e**)	95% EtOH	r.t.	14	64

[a] Isolated yield after SiO_2 column chromatography.

Colorless crystals suitable for X-ray analysis were obtained from **2e** and the structure is shown in Figure 2. There are three crystallographically unique molecules per unit cell with an oxygen disordered over two positions in the third molecule.

Diazonium salt **1** reacted with methyl acrylate in the presence of $Pd(OAc)_2$ in 95% EtOH to give methyl *trans*-3-[4-(pentafluorosulfanyl)phenyl]prop-2-enoate **3** in 85% isolated yield with no *cis* isomer being observed (Figure 3).

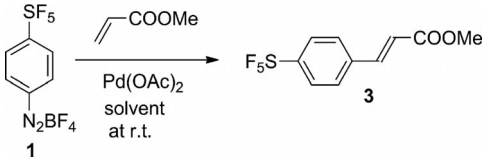


Figure 3. Heck coupling with methyl acrylate.

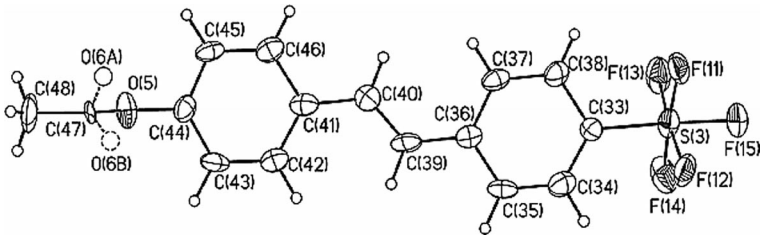
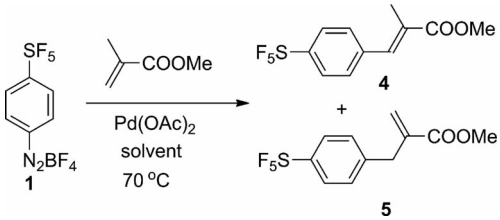


Figure 2. X-ray structure of **2e**.

The coupling reaction with methyl methacrylate gave a mixture of two isomeric products namely methyl 2-methyl-3-[4-(pentafluorosulfanyl)phenyl]prop-2-enoate **4** and methyl 2-{[4-(pentafluorosulfanyl)phenyl]methyl}prop-2-enoate **5** in a 1:2 ratio in 78% isolated yield (Table 2). Optimal yields were obtained after 18 h at room temp. in EtOH. A near quantitative yield was reached at room temp. when using [BMIM][BF_4] as the solvent although increased formation of isomer **5** was also noted with these reaction conditions.

Table 2. Heck–Matsuda arylation with methyl methacrylate.



Solvent	Temp. [°C]	Time [h]	Ratio of **4**/**5**	Yield[a] [%]
95% EtOH	70	4	1:2	47%
95% EtOH	70	2	1:2	78%
95% EtOH	r.t.	18	1:2	84%
[BMIM][BF_4]	r.t.	16	1:3	99%

[a] Combined yield after SiO_2 column chromatography.

Attempted syntheses of **6** by Heck coupling of **1** with ethyl cinnamate in EtOH, MeOH, or in [BMIM][BF_4] as solvent at room temp. or by heating at 70 °C were unsuccessful (Figure 4).

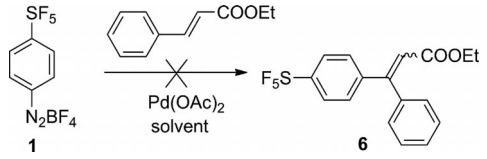
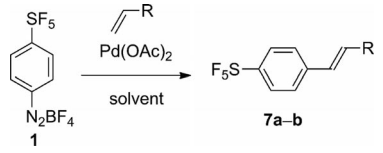


Figure 4. Attempted couplings with ethyl cinnamate.

In representative cases, diazonium salt **1** enabled coupling with fluorous olefins to give novel polyfluorinated adducts **7a** and **7b** (Table 3).

Table 3. Heck arylation with fluoroalkenes.



R	Solvent	Temp. [°C]	Time [h]	Yield[a] [%]
$(CF_2)_3CF_3$ (**7a**)	95% EtOH	r.t.	24	81%
$(CF_2)_3CF_3$ (**7a**)	95% EtOH	r.t.	20	69%
$(CF_2)_3CF_3$ (**7a**)	[BMIM][BF_4]	r.t.	17	0%[b]
$(CF_2)_3CF_3$ (**7a**)	[BMIM][BF_4]	70	20	13%[b]
$(CF_2)_5CF_3$ (**7b**)	95% EtOH	r.t.	16	83%

[a] Isolated yield after SiO_2 column chromatography. [b] After extraction with hexane.

Attempted coupling of **7a** with **1** in EtOH failed to produce the desired highly fluorinated adduct **8** even after stirring for one week at room temp. or by heating at 70 °C (Figure 5).

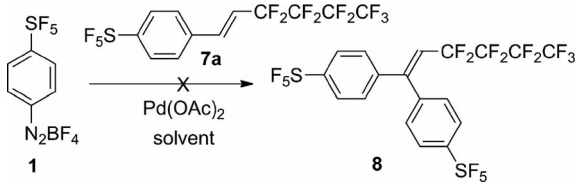
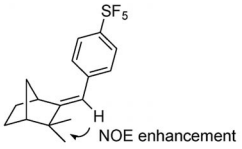
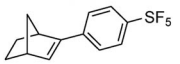
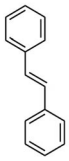
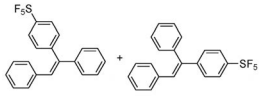


Figure 5. Attempted synthesis of **8**.

To further expand the scope of the Heck–Matsuda reaction, coupling of **1** with camphene, norbornene, and *trans*-stilbene was also investigated. Whereas coupling with camphene afforded **9** in respectable isolated yield, compound **10** could not be obtained by coupling to norbornene. Coupling with *trans*-stilbene gave an inseparable isomeric mixture of **11** and **12** (as indicated by NMR)[18a] (Table 4).

Table 4. Heck arylation with reactive alkenes.

Alkene	Solvent	Temp.	Time	Product (yield)[a]
	95% EtOH	r.t.	16 h	 **9** (89%)
	95% EtOH	70 °C	1.5 h	 **10** (0%)
	95% EtOH	70 °C	40 min	 **11** + **12** (45% by NMR)

[a] Isolated yield after SiO_2 column chromatography.

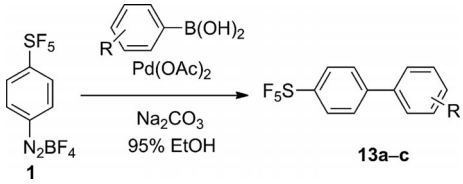
Suzuki Coupling

In selected cases, diazonium salt **1** was allowed to react with Ar-B(OH)$_2$ under standard Suzuki coupling conditions. These reactions yielded corresponding biaryl derivatives **13a**–**c** in isolated yields ranging from 27–59% (Table 5).

Biaryl Synthesis by Homocoupling

The 1,4′-bis(pentafluorsulfanyl)biphenyl (**14**) was successfully obtained in near quantitative yield by homocoupling using Pd(OAc)$_2$ in MeOH solvent (Figure 6). It is worth noting that Kirsch and Hahn accidentally obtained compound **14** in 6% yield while attempting to metalate *p*-$BrC_6H_4SF_5$ with *n*BuLi/THF.[4d] The X-ray structure of biaryl species **14** is shown in Figure 7.

Table 5. Suzuki-coupling with **1**.



R	Temp. [°C]	Time [h]	Yield[a] [%]
4-CF_3 (**13a**)	70	3	27
3,4,5-F_3 (**13b**)	r.t.	24	44
3,5-Me_2 (**13c**)	r.t.	20	59

[a] Isolated yield after SiO_2 column chromatography.

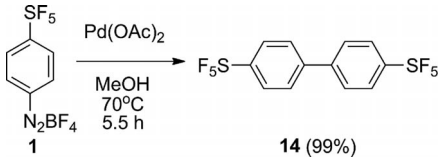
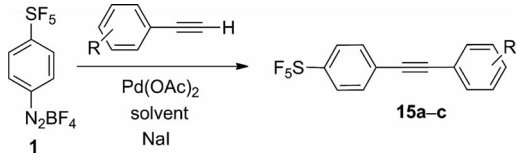


Figure 6. Biaryl synthesis through homocoupling chemistry.

Sonogashira Coupling with Phenylacetylenes

Sonogashira coupling with phenylacetylene and its mono- and bis-trifluoromethyl derivatives employing $Pd(OAc)_2$/NaI[18b] in 95% EtOH/Et_3N as solvent at 70 °C resulted in modest isolated yields of adducts **15a**–**c** (Table 6). In control experiments no conversion was observed in CH_3CN/Et_3N/PPh_3 at 70 °C. Reactions using EtOH alone or EtOH/Na_2CO_3 at room temp. in the absence of NaI also failed to afford the desired coupling products.

Table 6. Sonogashira coupling with phenylacetylenes.



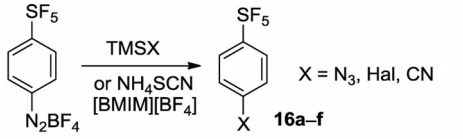
R	Solvent	Temp. [°C]	Yield[a] [%]
H (**15a**)	95% EtOH, Et_3N	70	9
2-CF_3 (**15b**)	95% EtOH, Et_3N	70	15
3,5-$(CF_3)_2$ (**15c**)	95% EtOH, Et_3N	70	17

[a] Isolated yield after SiO_2 column chromatography.

Halo-, Azido-, and Cyano-dediazoniation and Thiocyanation in IL Solvent

Reaction of SF_5-diazonium salt **1** with TMSX (X = N_3, I) and with NH_4SCN in [BMIM][BF_4] solvent provided convenient access to compounds **16** through a dediazoniation route.[13] Reaction with TMSBr, TMSCl, and TMSCN/KF, on the other hand, generated only traces of targeted SF_5 compounds (Table 7). Fortunately, the X-ray structure of thiocyanate derivative **16c** was successfully obtained and is shown in Figure 8.

Table 7. Reaction of **1** with TMSX (X = N_3, I, Br, Cl, CN) and with NH_4SCN in [BMIM][BF_4].



Reagent	Temp.	Time	Product	Yield[a]
$TMSN_3$ (**16a**)	r.t.	0.1 h	F_5S–C_6H_4–N_3	86%
TMSI (**16b**)	r.t.	0.1 h	F_5S–C_6H_4–I	40%
NH_4SCN (**16c**)	70 °C	0.5 h	F_5S–C_6H_4–SCN	31%
TMSCl (**16d**)	r.t.	2 d	F_5S–C_6H_4–Cl	trace[b]
TMSBr (**16e**)	r.t.	3 d	F_5S–C_6H_4–Br	9%
TMSCN/KF (**16f**)	r.t.	2 d	F_5S–C_6H_4–CN	trace[b]

[a] Isolated yield by SiO_2 column chromatography. [b] Detected by GC–MS.

Synthesis of the Triazole-Derivative by Click Chemistry

Azide derivative **16a** was found to take part in click chemistry with phenylacetylene and its CF_3-substituted derivatives when using Cu-Zn nanopowder as catalyst,[19] to give the corresponding triazole derivatives in isolated yields ranging from 52–63% (Table 8).

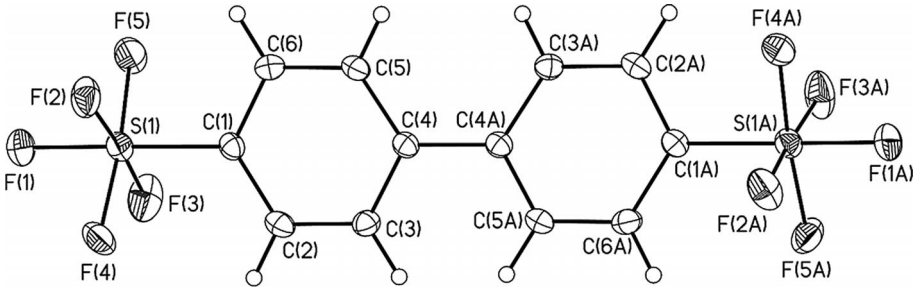


Figure 7. X-ray structure of biaryl species **14**.

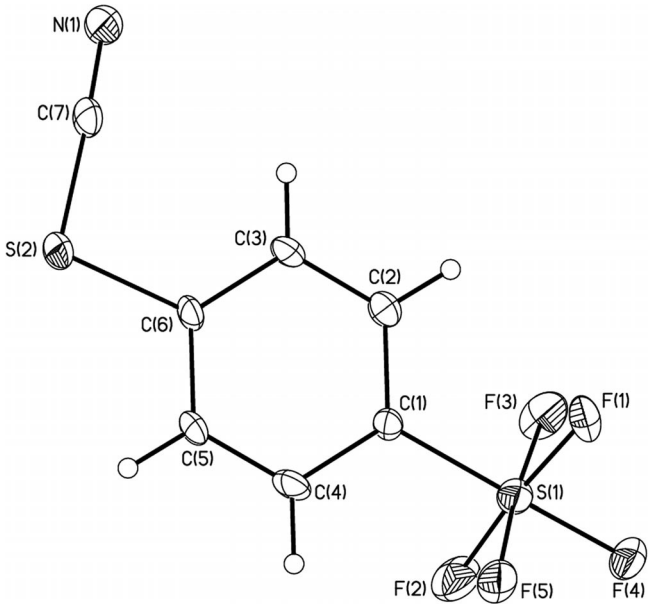
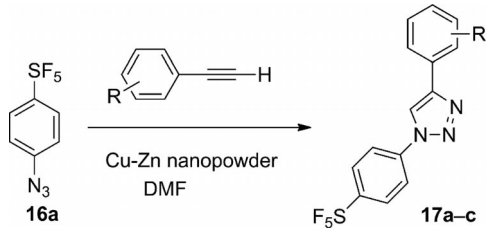


Figure 8. X-ray structure of the thiocyanate derivative **16c**.

Table 8. Synthesis of triazole derivatives **17** by click chemistry.



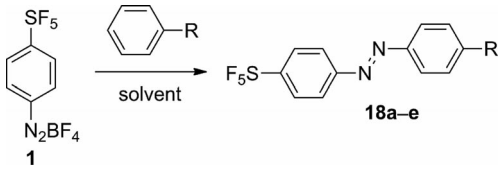
R	Temp. [°C]	Time [h]	Yield[a] [%]
H (**17a**)	70	19	52
2-CF_3 (**17b**)	70	19	65
2,5-$(CF_3)_2$ (**17c**)	70	19	63

[a] Isolated yield after SiO_2 column chromatography.

Diazonium Coupling

The SF_5-diazonium salt took part in azo-coupling chemistries with dimethoxy- and isomeric trimethoxybenzenes in EtOH solvent, simply by mixing at room temp. to give corresponding diazo derivatives **18** in 72–98% isolated yields (Table 9). Coupling reactions with less reactive arenes (phenol and aniline) were much slower and required prolonged reaction times. Attempted diazo-coupling with anisole, 1-methylnaphthalene, 9-methylanthracene, anthracene, 2,6-lutidine, and benzyl cyanide under a variety of conditions were unsuccessful.

Table 9. Synthesis of diazo derivatives **18** by azo-coupling.



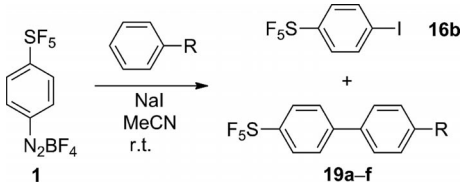
R	Solvent	Temp. [°C]	Time	Yield[a] [%]
2,4-$(MeO)_2$ (**18a**)	95% EtOH	r.t.	2 weeks	98
2,4,6-$(MeO)_3$ (**18b**)	95% EtOH	r.t.	6 min	75
2,4,5-$(MeO)_3$ (**18c**)	95% EtOH	r.t.	6 min	72
4-HO (**18d**)	CH_3CN	70	16 h	0[b]
4-HO (**18d**)	CH_3CN + AcONa	r.t.	1 month	62
4-NH_2 (**18e**)	95% EtOH	r.t.	20 d	22

[a] Isolated yield after SiO_2 column chromatography. [b] NMR monitoring.

Synthesis of Biaryls by Homolytic Dediazoniation

Homoytic dediazoniation can, in principle, serve as an alternative route to Suzuki coupling for the synthesis of unsymmetrical biaryls. Dediazoniation of **1** in MeCN/NaI[20] at room temperature in the presence of reactive arenes (mesitylene, *p*-xylene, and anisole) led to formation of desired unsymmetrical SF_5-biaryls **19** in modest yields (Table 10). Notably, formation of iodo derivatives **16b** was a competing reaction.

Table 10. Synthesis of biaryl derivatives by homolytic dediazoniation.



R	Yield of **19**[a]
2,4,6-Me_3 (**19a**)	31% (**16b**; 60%)
2,5-Me_2 (**19b**)	14% (**16b**; 14%)
2,3,5,6-Me_4 (**19c**)	2%
2,3,4,5,6-Me_5 (**19d**)	trace[b]
MeO (**19e**)	*ortho* (13%), *meta* (4%), *para* (5%)[c]
Et (**19f**)	0%

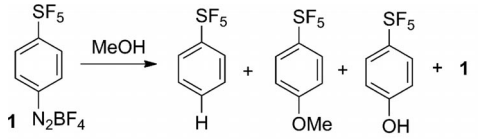
[a] Isolated yield after SiO_2 column chromatography. [b] GC–MS. [c] As determined by NMR spectroscopy.

Dediazoniation Under Solvolytic Conditions

Solvolytic dediazoniation of **1** was studied in MeOH, TFE, TfOH, TFAH, HFIP, and in [BMIM][X] ionic liquids with X = PF_6, BF_4, and NTf_2 as counterions, and the progress of each reaction was monitored by ^1H and ^{19}F NMR spectroscopy.

Solvolysis in MeOH

Diazonium salt **1** reacted slowly in MeOH at room temperature to give Ph–SF_5 as a major product along with *p*-SF_5–C_6H_4OH and *p*-SF_5–C_6H_4OMe as minor products. The rate of dediazoniation was found to increase in warm MeOH; the reaction was nearly complete after 90 min. The observed product distribution (Scheme 1) is consistent with homolytic dediazoniation as the predominant mechanistic pathway.[21]

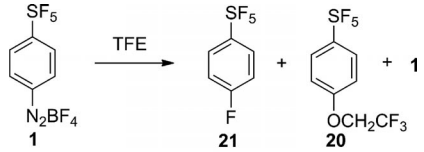


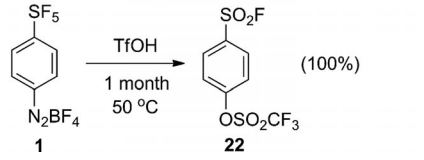
13 days at r.t.	77%	5%	18%	<1%
30 days at r.t.	62%	5%	33%	<1%
50 days at r.t.	65%	5%	30%	<1%
1.5 h at 50 °C	55%	7%	38%	9%

Scheme 1. Dediazoniation in MeOH.

Solvolysis in TFE

Solvolysis of diazonium salt **1** in TFE was very slow at room temperature; even after a reaction time of 7 d 94% of **1** remained unreacted. The rate of reaction could be improved by heating at 70 °C (Scheme 2) for four hours. Formation of *p*-SF_5–C_6H_4-OCH_2CF_3 **20** and *p*-SF_5–C_6H_4-F **21** is consistent with heterolytic dediazoniation.[22a] Compound **20**, the major product in the mixture, was obtained in 29% isolated yield.





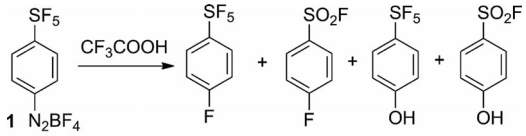
Scheme 2. Dediazoniation in TFE and TfOH.

Solvolysis in TfOH

The diazonium salt remained unreacted in TfOH after 3 d of stirring at room temperature. However, dediazoniation proceeded slowly at 50 °C over the course of 1 month to furnish triflate derivative **22** (Scheme 2), with concomitant transformation of the SF_5 moiety to SO_2F. Under these conditions **22** was found to be generated cleanly (>95% by NMR) and was isolated in quantitative yield. The results are consistent with heterolytic dediazoniation in TFE and in TfOH.

Solvolysis in TFAH

Solvolytic dediazoniation of **1** in TFAH was studied at 70 °C. Concomitant transformation of the SF_5 moiety to its SO_2F congener was again observed. The ester *p*-SF_5–C_6H_4-$OCOCF_3$ was not detected among the products. The evolution of the solvolytic products, as monitored by NMR (Scheme 3), suggests a heterolytic dediazoniation mechanism and oxidation of the SF_5 functionality to SO_2F as major events.



70 °C, 12h	2%	56%	40%	2%
70 °C, 1 d	5%	67%	23%	5%
70 °C, 3 d	<2%	55%	<2%	45%

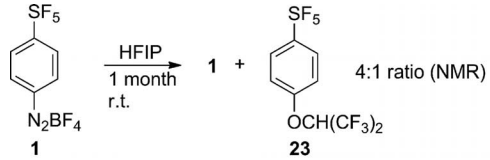
Scheme 3. Dediazoniation in TFAH.

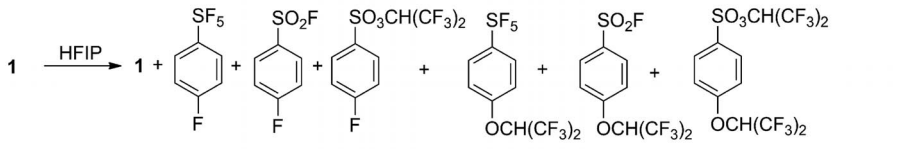
Solvolysis in HFIP

Solvolysis of **1** in HFIP was very slow at room temperature. After stirring for 1 month *p*-SF_5–C_6H_4-$OCH(CF_3)_2$ **23** was detected by NMR together with unreacted **1**. To speed up the process, the reaction was followed at 60 °C where competing oxidation led to a complex mixture which was analyzed by ^1H and ^{19}F NMR (Scheme 4). The solvolytic products observed in HFIP are in accord with a heterolytic mechanism.

Solvolysis in Ionic Liquids

Solvolytic dediazoniation in [BMIM][BF_4] and [BMIM][PF_6] provides easy access to *p*-SF_5–C_6H_4-F **21** through fluorodediazoniation.[12] Reactions were performed at 50 °C and 70 °C and proceeded to completion within a matter of days. In line with related earlier studies,[13] solvolytic dediazoniaton of **1** in [BMIM][NTf_2] gave **25** as the





3 h; 60 °C	17%	17%	24%	9%	7%	24%	2%	by NMR
4 h; 60 °C	-	-	13%	14%	2%	19%	8%	after SiO_2 column

Scheme 4. Dediazoniation in HFIP.

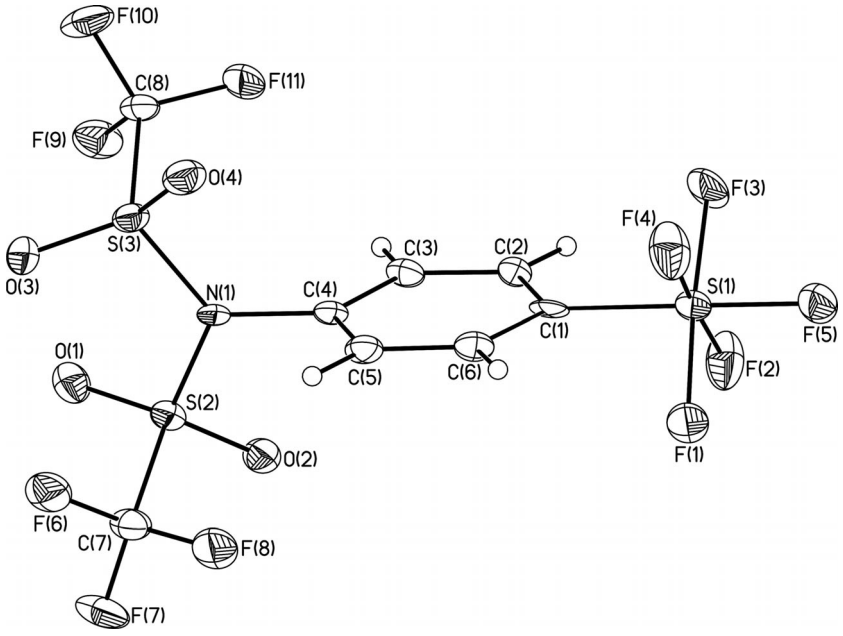
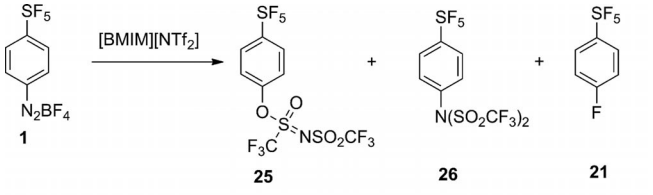


Figure 9. X-ray structure of the NTf_2 adduct **26**.

major and **26** as the minor trapping products consistent with the ambident nucleophilic character of NTf_2 anion. Minor amounts of the fluorodediazoniation product *p*-SF_5–C_6H_4-F **21** were also formed at higher temperatures (Scheme 5).



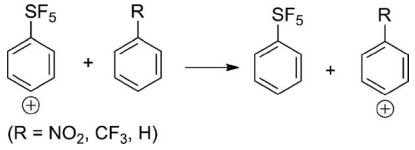
50 °C, 17 h	27%	4%	not observed
50 °C, 67 h	74%	10%	not observed
	(88 : 12 after hexane extraction)		
70 °C, 15h	77%	8%	15%
	(79 : 13 : 8 after hexane extraction)		

Scheme 5. Dediazoniation in [BMIM][NTf_2].

Compound **25** was isolated as an oil, and attempts to crystallize it were unsuccessful. By contrast, minor product **26** was isolated as a crystalline solid and its X-ray structure successfully determined thus validating initial structure assignments (Figure 9).

Collectively, product analysis of dediazoniation reactions with **1** in highly ionizing low nuclephilicity solvents (TFE, HFIP), protic acids (TfOH, TFAH) and imidazolium ionic liquids underscore the significance of heterolytic dediazoniation and point to the involvement of SF_5–$C_6H_4^+$ as a critical intermediate. Homolytic dediazoniation was found to be significant only in the MeOH case.

To elucidate the relative stability of *p*-SF_5–$C_6H_4^+$ the isodesmic reaction (Scheme 6) was determined by DFT calculations at various levels for both the singlet and triplet phenyl cation species, with R = NO_2, CF_3, and H (see Supporting Information).



Scheme 6. Isodesmic reaction.

Solvent effects were also considered using PCM calculations. The computed relative energies imply the relative stability order as Ph^+ >> *p*-$CF_3C_6H_4^+$ > *p*-NO_2–$C_6H_4^+$ ≈ *p*-F_5S-$C_6H_4^+$ for the phenyl cation intermediates. In concert with an earlier DFT study of aryl cations,[22b] the singlet 4-R-phenyl cations are more stable than the corresponding triplet cations. Whereas a *p*-NO_2 group is more effective in stabilizing the singlet state relative to triplet state, a *p*-SF_5 group stabilizes the singlet and triplet phenyl cations to the same extent.

Conclusions

The utility of 4-(pentafluorosulfanyl)phenyl diazonium tetrafluoroborate **1** as a versatile launch pad for the synthesis of a wide range of SF_5-aromatics through the application of diazonium ion chemistry that enables cross coupling, azo-coupling, homocoupling, dediazoniation and click chemistry has been demonstrated. Significantly, the present approach has potential to significantly expand the library of SF_5-aromatics for further applications in the biomedical and materials fields.

Experimental Section

General: NMR spectra were recorded with a 500 MHz spectrometer at room temperature (^{1}H: 500 MHz, ^{19}F: 470 MHz, ^{13}C: 125 MHz). IR data were collected with an FT-IR instrument. Electron ionization mass spectra (EI-MS) were measured using a GC–MS instruments. All reagents were commercially available and were used without purification.

4-(Pentafluorosulfanyl)benzenediazonium Tetrafluoroborate (1): A solution of 1-(pentafluorosulfanyl)benzene (495.9 mg, 2.263 mmol) in CH_2Cl_2 (10 mL) was added dropwise to $BF_3{\cdot}OEt_2$ (493.3 mg, 3.476 mmol) in a flask cooled with an ice-water bath. *tert*-Butyl nitrite (300.1 mg, 2.910 mmol) in 2 mL of CH_2Cl_2 was added dropwise and stirred at 0 °C for 1 h. The precipitated colorless crystals were isolated by filtration. The crystals was dissolve in CH_3CN (0.4 mL) and precipitated by addition of ether to give pale yellow solid crystals, which were washed with diethyl ether. Removal of the solvent under vacuum afforded the title compound as pale yellow crystals (605.1 mg, 84%): IR (ATR): $\tilde{\nu}$ = 2924, 2852, 2309, 1574, 1418, 1304, 1053, 768 cm^{-1}. ^{1}H NMR (500 MHz, CD_3CN): δ = 8.72 (d, J = 9.2 Hz, 2 H), 8.40 (d, J = 9.2 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 160.4, (C), 134.4 (2CH), 129.5 (2CH), 120.4 (C) ppm. ^{19}F NMR (470 MHz, CD_3CN): δ = 77.7 (quint, J = 151 Hz, 1 F), 60.9 (d, J = 151 Hz, 4 F), –151.5 (s, 4 F) ppm.

(*E*)-4-(Pentafluorosulfanyl)stilbene 2a. i) EtOH as Solvent: A solution of **1** (10.0 mg, 0.0315 mmol) in 0.4 mL of 95% aqueous ethanol was added dropwise to a solution of styrene (6.5 mg, 0.062 mmol) and palladium(II) acetate (0.5 mg, 0.002 mmol) in 0.11 g of 95% aqueous ethanol. The reaction mixture was heated by an oil bath at 70 °C for 15 h. After cooling, the mixture was filtered through a pad of Celite 545 and purified by SiO_2 column chromatography (9:1 hexane/CH_2Cl_2) to give **2a** (7.4 mg, 77% yield) as colorless crystals; m.p. 121.6–122.0 °C. IR (ATR): $\tilde{\nu}$ = 3028, 1593, 1499, 1450, 1096, 964 cm^{-1}. MS (GC, EI): m/z = 306 [M$^+$], 179. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.5 Hz, 2 H), 7.56 (d, J = 8.5 Hz, 2 H), 7.53 (d, J = 7.4 Hz, 2 H), 7.39 (t, J = 7.4 Hz, 2 H), 7.31 (t, J = 7.4 Hz, 1 H), 7.19 (d, J = 16.4 Hz, 1 H), 7.09 (d, J = 16.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5 (C), 140.6 (C), 136.4 (C), 132.0 (CH), 128.8 (2CH), 128.5 (CH), 126.8 (2CH), 126.3 (5CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 89.9 (quint, J = 150.2 Hz, 1 F), 61.0 (d, J = 150.2 Hz, 4 F) ppm.

ii) [BMIM][BF_4] as Solvent: Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (10.5 mg, 0.0330 mmol) and styrene (29.0 mg, 0.278 mmol) in 96.6 mg of [BMIM][BF_4]. The mixture was stirred at room temp. for 22 h and was extracted with diethyl ether (0.5 mL × 3). The solvent of the combined organic layer was evaporated to give a brown oil, which was purified by SiO_2 column chromatography (9:1 hexane/CH_2Cl_2) to give **2a** (2.3 mg, 23% yield) as colorless crystals.

(*E*)-4-Fluoro-4′-(pentafluorosulfanyl)stilbene (2b): A solution of **1** (10.4 mg, 0.0315 mmol) in 0.4 mL of 95% aqueous ethanol was added dropwise to a solution of 4-fluorostyrene (9.8 mg, 0.080 mmol) and palladium(II) acetate (0.2 mg, 0.0009 mmol) in 0.10 g of 95% aqueous ethanol. The reaction mixture was heated on an oil bath at 70 °C for 5 h. After cooling, the mixture was filtered through a pad of Celite 545 and purified by SiO_2 column chromatography (9:1 hexane/CH_2Cl_2) to give **2b** (8.2 mg, 77% yield) as colorless crystals; m.p. 85.0–86.2 °C. IR (ATR): $\tilde{\nu}$ = 1593, 1508, 1236, 1159, 1099, 964, 831, 818 cm^{-1}. MS (GC, EI): m/z = 324 [M$^+$], 197 [M$^+$ SF_5], 177. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.8 Hz, 2 H), 7.55 (d, J = 8.5 Hz, 2 H), 7.51 (dd, J = 8.8, 5.4 Hz, 2 H), 7.15 (d, J = 16.4 Hz, 1 H), 7.08 (d, J = 8.7 Hz, 2 H), 7.01 (d, J = 16.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8 (C), 152.3 (C), 140.4 (C), 132.6 (C), 130.7 (CH), 128.4 (2CH), 126.3 (2CH), 126.2 (2CH), 126.2 (CH), 115.8 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.9 (quint, J = 150.2 Hz, 1 F), 63.0 (d, J = 150.2 Hz, 4 F), –112.7 (m, 1 F) ppm.

(*E*)-4-Methyl-4′-(pentafluorosulfanyl)stilbene (2c): A solution of **1** (10.0 mg, 0.0315 mmol) in 0.4 mL of 95% aqueous ethanol was added dropwise to a solution of 4-methylstyrene (9.0 mg, 0.076 mmol) and palladium(II) acetate (0.2 mg, 0.0009 mmol) in 0.12 g of 95% aqueous ethanol. The reaction mixture was heated on an oil bath at 70 °C for 5 h. After cooling, the mixture was filtered through a pad of Celite 545 and purified by SiO_2 column chromatography (9:1 hexane/CH_2Cl_2) to give **2c** (8.3 mg, 82% yield) as colorless crystals; m.p. 165.2–166.5 °C. IR (ATR): $\tilde{\nu}$ = 1593, 1514, 1450, 1416, 1329, 1265, 1098, 972, 962, 841 cm^{-1}. MS (GC, EI): m/z = 320 [M$^+$], 193 [M$^+$ – F_5S], 178 [M$^+$ – CH_3F_5S]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.8 Hz, 2 H), 7.54 (d, J = 8.5 Hz, 2 H), 7.43 (d, J = 8.1 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 16.4 Hz, 1 H), 7.04 (d, J = 16.4 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.3 (C), 140.8 (C), 138.6 (C), 133.6 (C), 131.9 (CH), 129.5 (2CH), 126.7 (2CH), 126.3 (2CH), 126.2 (2CH), 125.3 (CH), 21.3 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.1 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F) ppm.

(*E*)-4-Chloro-4′-(pentafluorosulfanyl)stilbene (2d): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (10.76 mg, 0.0337 mmol) and 4-chlorostyrene (19.0 mg, 0.137 mmol) in 0.18 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 1 d. The mixture was filtered through a pad of Celite 545 with CH_2Cl_2 and purified by SiO_2 column chromatography with hexane as eluent to give **2d** (7.5 mg, 65% yield) as colorless crystals; m.p. 119.8–120.8 °C. MS (GC, EI): m/z = 340 [M$^+$], 321, 232, 213, 196, 178 [M$^+$ ClF_5S]. IR (ATR): $\tilde{\nu}$ = 1589, 1495, 1414, 1094, 970, 831 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.7 Hz, 2 H), 7.55 (d, J = 8.7 Hz, 2 H), 7.46 (d, J = 8.5 Hz, 2 H), 7.35 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 16.4 Hz, 1 H), 7.06 (d, J = 16.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.7 (C), 140.2 (C), 134.9 (C), 134.1 (C), 130.6 (CH), 129.0 (2CH), 128.0 (2CH), 126.9 (CH), 126.4 (4CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.8 (quint, J = 150 Hz, 1 F), 63.0 (d, J = 150 Hz, 4 F) ppm.

(*E*)-4-Acetoxy-4′-(pentafluorosulfanyl)stilbene (2e): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (11.6 mg, 0.0365 mmol) and 4-acetoxystyrene (11.5 mg, 0.0709 mmol) in 0.22 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 14 h, filtered through a pad of Celite 545 with CH_2Cl_2, and purified by SiO_2 column chromatography (1:1 hexane/CH_2Cl_2) to give **2e** (8.5 mg, 64% yield) as colorless crystals; m.p. 177.5–178.5 °C. MS (GC, EI): m/z = 364 [M$^+$], 322 [M$^+$ – $COCH_2$], 194, 165. IR (ATR): $\tilde{\nu}$ = 1759, 1593, 1508, 1373, 1223, 833 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.7 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.7 Hz, 2 H), 7.16 (d, J = 16.4 Hz, 1 H), 7.12 (d, J = 8.4 Hz, 2 H), 7.04 (d, J = 16.4 Hz, 1 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.4 (C), 152.6 (C), 150.7 (C), 140.4 (C), 134.2 (C), 130.9 (CH), 127.8 (2CH), 126.6 (CH), 126.3 (4CH), 122.0 (2CH), 21.1 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.9 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F) ppm.

Methyl (*E*)-3-[4-(Pentafluorosulfanyl)phenyl]prop-2-enoate (3):[4a] Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (10.9 mg, 0.0343 mmol) and methyl acrylate (15.6 mg,

0.181 mmol) in 0.18 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 18 h, filtered through a pad of Celite 545 with CH_2Cl_2, and purified by SiO_2 column chromatography (6:4 hexane/CH_2Cl_2) to give **3** (8.4 mg, 85% yield) as colorless crystals; m.p. 80.5–81.5 °C. MS (GC, EI): *m*/*z* = 288 [M^+], 269 [M^+ – F], 257, 130, 102. IR (ATR): $\tilde{\nu}$ = 1701, 1640, 1439, 1317, 1213, 1101, 999, 845, 816 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.7 Hz, 2 H), 7.68 (d, *J* = 16.1 Hz, 1 H), 7.60 (d, *J* = 8.7 Hz, 2 H), 7.61 (d, *J* = 16.1 Hz, 1 H), 3.83 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7 (C), 154.6 (C), 142.5 (CH), 137.5 (C), 128.0 (2CH), 126.6 (2CH), 121.1 (CH), 52.0 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.7 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F) ppm.

Methyl (*E*)-2-Methyl-3-(pentafluorosulfanyl)prop-2-enoate 4 and Methyl 2-{[4-(Pentafluorosulfanyl)phenyl]methyl}prop-2-enoate (5):

i) In EtOH. Method a: A solution of **1** (10.2 mg, 0.0321 mmol) in 0.4 mL of 95% aqueous ethanol was added dropwise to a solution of methyl methacrylate (8.9 mg, 0.089 mmol) and palladium(II) acetate (0.2 mg, 0.0009 mmol) in 0.12 g of 95% aqueous ethanol. The reaction mixture was heated on an oil bath at 70 °C for 4 h. After cooling, the mixture was filtered through a pad of Celite 545. Removal of the solvent gave a brown oil, whose NMR analysis showed the formation of **4** and **5** in 1: 2 ratio (17.8 mg). The products were purified by SiO_2 column chromatography (6:4 hexane/CH_2Cl_2). The first eluted product was **5** (colorless oil; 1.2 mg, 12%). The second fraction was a mixture of **5** and **4** (pale yellow oil; 1:1 ratio, 2.8 mg, 29%), and the next fraction was pure **4** (pale yellow oil; 0.6 mg, 6%).

Method b: To a solution of **1** (20.8 mg, 0.0654 mmol) and methyl methacrylate (19.0 mg, 0.190 mmol) in 0.76 g mL of 95% aqueous ethanol was added palladium(II) acetate (0.5 mg, 0.002 mmol). The reaction mixture was heated on an oil bath at 70 °C for 2 h. After cooling, the mixture was filtered through a pad of Celite 545 to give a pale brown oil, whose NMR analysis showed the formation of **4** and **5** in 1:2 ratio (32.7 mg). The products were purified by SiO_2 column chromatography (7:3 hexane/CH_2Cl_2) to give a mixture of both compounds (15.5 mg) as colorless oil (78%). Subsequent preparative TLC (1:1 hexane/CH_2Cl_2) separation of the mixture gave: The first eluted product was **5** (colorless oil; 9.6 mg, 48%). The second fraction was a mixture of the two compounds (pale yellow oil; 1:1 ratio, 11.1 mg, 56%) and the next fraction was pure **4** (pale yellow oil; 1.8 mg, 9%).

ii) in [BMIM][BF_4]: To a solution of **1** (11.3 mg, 0.0355 mmol) and methyl methacrylate (20.0 mg, 0.200 mmol) in 0.11 g of [BMIM][BF_4] was added palladium(II) acetate (0.5 mg, 0.002 mmol). The reaction mixture was stirred at room temp. for 16 h. NMR analysis of the reaction mixture showed the formation of **4** and **5** in 1:3 ratio and complete consumption of the diazonium ion. The reaction mixture was extracted with diethyl ether and the solvent was evaporated to give a pale-brown oil. The products were purified by SiO_2 column chromatography (8:2 hexane/CH_2Cl_2) to give a mixture of the two compounds (10.6 mg) as colorless oil (99%).

Methyl 2-Methylidene-3-(pentafluorosulfanyl)propanoate (4): IR (ATR): $\tilde{\nu}$ = 2916, 2849, 1717, 1439, 1261, 1117, 847 cm^{-1}. MS (GC, EI): *m*/*z* = 302 [M^+], 242 [$M^+ - C_2H_4O_2$], 115 [$M^+ - C_2H_4F_5O_2S$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.5 Hz, 2 H), 7.30 (d, *J* = 8.5 Hz, 2 H), 6.29 (s, 1 H), 5.56 (s, 1 H), 3.74 (s, 3 H), 3.68 (s, 2 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.3 (quint, *J* = 150.2 Hz, 1 F), 63.2 (d, *J* = 150.2 Hz, 4 F) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.5 (C), 153.1 (C), 139.2 (C), 136.5 (CH), 131.1 (C), 129.6 (2CH), 126.0 (2CH) ppm.

Methyl 2-{[4-(Pentafluorosulfanyl)phenyl]methyl}prop-2-enoate (5): IR (ATR): $\tilde{\nu}$ = 2955, 1721, 1632, 1441, 1207, 1142, 1099, 840 cm^{-1}. MS (GC, EI): *m*/*z* = 302 [M^+], 116 [$M^+ - C_2H_3F_5O_2S$], 115 [$M^+ - C_2H_4F_5O_2S$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.5 Hz, 2 H), 7.66 (s, 1 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 3.84 (s, CH_3), 2.11 (s, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9 (C), 152.3 (C), 142.8 (C), 138.9 (C), 129.1 (2CH), 127.2 (CH_2), 126.0 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.1 (quint, *J* = 150.2 Hz, 1 F), 62.8 (d, *J* = 150.2 Hz, 4 F) ppm.

(*E*)-3,3,4,4,5,5,6,6,6-Nonafluoro-1-[4-(pentafluorosulfanyl)phenyl]-hex-1-ene (7a): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (15.0 mg, 0.0472 mmol) and 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene (8.9 mg, 0.089 mmol) in 0.44 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 1 d and filtered through a pad of Celite 545. Removal of the solvent gave a pale yellow oil which was purified by SiO_2 column chromatography with hexane to give **7a** as colorless oil (17.1 mg; 81%): IR (ATR): $\tilde{\nu}$ = 2918, 2849, 1663, 1234, 1134, 844 cm^{-1}. MS (GC, EI): *m*/*z* = 448 [M^+], 429 [M^+ – F], 302 [$M^+ - SF_6$], 279 [$M^+ - C_3F_7$], 152 [$M^+ - C_3F_{12}S$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.7 Hz, 2 H), 7.57 (d, *J* = 8.7 Hz, 2 H), 7.20 (d, *J* = 16.2 Hz, 1 H), 6.30 (dt, *J* = 16.2, 12.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7 (C), 137.7 (CH), 136.5 (C), 127.8 (2CH), 126.7 (2CH), 117.7 (CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.4 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F), –81.0 (s, 3 F), –112.0 (s, 2 F), –124.0 (s, 2 F), –125.7 (s, 2 F) ppm.

(*E*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-[4′-(pentafluorothio)-phenyl]oct-1-ene (7b): Palladium(II) acetate (1.0 mg, 0.0045 mmol) was added to a solution of **1** (22.4 mg, 0.0704 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,8-undecacfluorooct-1-ene (35.4 mg, 0.102 mmol) in 0.45 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 16 h, and filtered through a pad of Celite 545 with a help of hexane. Removal of the solvent gave a pale brown oil, which was purified by SiO_2 column chromatography with hexane to give **7b** as colorless oil (31.9 mg; 83%): IR (ATR): $\tilde{\nu}$ = 1238, 1190, 1144, 844 cm^{-1}. MS (GC, EI): *m*/*z* = 548 [M^+], 529 [M^+ – F], 421 [$M^+ - SF_5$], 402 [$M^+ - SF_6$], 279 [$M^+ - C_5F_{11}$], 152 [$M^+ - C_5F_{16}S$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.6 Hz, 2 H), 7.57 (d, *J* = 8.6 Hz, 2 H), 7.20 (d, *J* = 16.2 Hz, 1 H), 6.30 (dt, *J* = 16.2, 11.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7 (C), 137.6 (CH), 136.6 (C), 127.8 (2CH), 126.7 (2CH), 117.8 (CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.4 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F), –80.8 (s, 3 F), –111.8 (s, 2 F), –121.6 (s, 2 F), –122.9 (s, 2 F), –123.2 (s, 2 F), –126.2 (s, 2 F) ppm.

Camphene Adduct 9: Palladium(II) acetate (0.3 mg, 0.001 mmol) was added to a solution of **1** (12.9 mg, 0.0406 mmol) and camphene (7.7 mg, 0.057 mmol) in 0.27 g of 95% aqueous ethanol. The reaction mixture was stirred at room temperature for 16 h, and filtered through a pad of Celite 545 with the help of hexane. Removal of the solvent gave a colorless oil, which was purified by SiO_2 column chromatography using hexane to give the adduct **9** as colorless oil (12.2 mg; 89%): IR (ATR): $\tilde{\nu}$ = 2965, 1655, 1597, 1495, 1460, 1383, 1101, 841 cm^{-1}. MS (GC, EI): *m*/*z* = 338 [M^+], 323 [$M^+ - CH_3$], 309 [$M^+ - C_2H_5$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 6.00 (s, 1 H), 3.21 (d, *J* = 4.7 Hz, 1 H), 1.99 (d, *J* = 2.2 Hz, 1 H), 1.84 (m, 1 H), 1.76 (m, 1 H), 1.72 (m, 1 H), 1.51 (m, 1 H), 1.41 (m, 1 H), 1.30 (d, *J* = 10.0 Hz, 1 H), 1.13 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163 (C), 151.0 (C), 142.5 (C), 127.8 (2CH), 125.7 (2CH), 114.7 (CH), 47.4 (CH), 43.6 (C), 42.6 (CH), 38.0 (CH_2), 28.9 (CH_3), 27.7 (CH_2),

26.1 (CH_3), 23.7 (CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.6 (quint, J = 150 Hz, 1 F), 63.2 (d, J = 150 Hz, 4 F) ppm.

Reaction with Stilbene: Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a solution of **1** (11.1 mg, 0.0349 mmol) and stilbene (8.0 mg, 0.044 mmol) in 0.21 g of 95% aqueous ethanol. The reaction mixture was heated an oil bath at 70 °C for 40 min, and filtered through a pad of Celite 545 with the help of hexane. Removal of the solvent gave a colorless crystalline solid, which was purified by SiO_2 column chromatography using hexane/CH_2Cl_2 (8:2) to give a mixture of stilbene, and (*Z*)-, and (*E*)-1,2-diphenyl-1-(pentafluorosulfanyl)phenylethenes (**11** and **12**) (5:2:3 ratio) as colorless crystals (10.1 mg; yield of the adducts, **11** and **12**, 45%).

11: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.5 Hz, 2 H), 7.40–7.26 (m, 6 H), 7.19–7.14 (m, 4 H), 7.05–7.02 (m, 2 H), 7.04 (s, 1 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.7 (quint, J = 150 Hz, 1 F), 63.0 (d, J = 150 Hz, 4 F) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.2 (C), 142.5 (C), 140.6 (C), 136.6 (C), 130.9 (2CH), 129.8 (CH), 129.5 (2CH), 128.4 (2CH), 128.2 (2CH), 128.0 (CH), 127.6 (2CH), 127.3 (CH), 126.2 (2CH) ppm.

12: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.5 Hz, 2 H), 7.40–7.26 (m, 6 H), 7.19–7.14 (m, 4 H), 7.05–7.02 (m, 2 H), 7.01 (s, 1 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.9 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.7 (C), 140.6 (C), 139.3 (C), 136.6 (C), 130.5 (CH), 130.2 (2CH), 129.7 (2CH), 128.9 (2CH), 128.1 (2CH), 127.9 (CH), 127.6 (2CH), 127.4 (CH), 125.8 (2CH) ppm.

4-(Pentafluorosulfanyl)-4′-(trifluoromethyl)biphenyl (13a): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a mixture of **1** (10.8 mg, 0.0340 mmol), 4-(trifluoromethyl)phenylboronic acid (7.3 mg, 0.038 mmol), and Na_2CO_3 (5.9 mg, 0.056 mmol) in 0.20 g of 95% aqueous ethanol. The reaction mixture was stirred at 70 °C for 3 h, and filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a brown crystalline solid, which was purified by SiO_2 column chromatography with hexane to give the title compound **13a** as colorless crystals (3.2 mg; 27%); m.p. 123.5–125.0 °C. IR (ATR): $\tilde{\nu}$ = 2924, 1618, 1492, 1395, 1327, 1171, 1107, 1072, 837, 814 cm^{-1}. MS (GC, EI): m/z = 348 [M^+], 329 [M^+ – F], 239. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.8 Hz, 2 H), 7.75 (d, J = 8.8 Hz, 2 H), 7.69 (d, J = 8.8 Hz, 2 H), 7.67 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5 (C), 143.0 (C), 142.5 (C), 130.5 (q, J = 33 Hz), 127.7 (2CH), 127.5 (2CH), 126.6 (2CH), 126.0 (2CH), 124.0 (q, J = 272 Hz, C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.2 (quint, J = 150 Hz, 1 F), 63.0 (d, J = 150 Hz, 4 F), –62.6 (s, 3 F) ppm.

3,4,5-Trifluoro-4′-(pentafluorosulfanyl)biphenyl (13b): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a mixture of **1** (14.7 mg, 0.0462 mmol), 3,4,5-trifluorophenylboronic acid (7.1 mg, 0.040 mmol), and Na_2CO_3 (15.1 mg, 0.14 mmol) in 0.69 g of 95% aqueous ethanol. The reaction mixture was stirred at room temp. for 1 d, and filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a brown crystalline solid which was purified by SiO_2 column chromatography with hexane to give **13b** as a colorless oil (6.0 mg; 44%), which subsequently gave colorless crystals (from hexane); m.p. 46.5–48.8 °C. IR (ATR): $\tilde{\nu}$ = 1618, 1579, 1537, 1506, 1496, 1449, 1396, 1363, 1254, 1105, 1051, 828 cm^{-1}. MS (GC, EI): m/z = 334 [M^+], 315 [M^+ – F], 226, 206. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.5 Hz, 2 H), 7.58 (d, J = 8.5 Hz, 2 H), 7.20 (t, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5 (C), 151.5 (d, J = 251 Hz, C), 141.4 (C), 140.0 (d, J = 254 Hz, C), 135.0 (C), 127.1 (2CH), 126.8 (2CH), 111.5 (d, J = 17 Hz, 2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.9 (quint, J = 150 Hz, 1 F), 63.0 (d, J = 150 Hz, 4 F), –132.9 (d, J = 8 Hz, 2 F), –160.3 (t, J = 8 Hz, 1 F) ppm.

3,5-Dimethyl-4′-(pentafluorosulfanyl)biphenyl (13c): Palladium(II) acetate (0.5 mg, 0.002 mmol) was added to a mixture of **1** (12.2 mg, 0.0384 mmol), 3,5-dimethylphenylboronic acid (5.2 mg, 0.035 mmol), and Na_2CO_3 (6.7 mg, 0.063 mmol) in 0.48 g of 95% aqueous ethanol. The reaction mixture was stirred at room temp. for 20 h and filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a brown crystalline solid which was purified by SiO_2 column chromatography with hexane to give **13c** (6.3 mg) as a colorless oil (59%): IR (ATR): $\tilde{\nu}$ = 3024, 2920, 2853, 1599, 1468, 1379, 1105, 822 cm^{-1}. MS (GC, EI): m/z = 308 [M^+], 293 [M^+ – CH_3], 289 [M^+ – F], 199, 203, 164. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, J = 8.5 Hz, 2 H), 7.63 (d, J = 8.5 Hz, 2 H), 7.19 (s, 2 H), 7.06 (s, 1 H), 2.39 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8 (C), 144.8 (C), 139.1 (C), 138.6 (2 C), 130.0 (CH), 127.2 (2CH), 126.2 (2CH), 125.2 (2CH), 21.4 ($2CH_3$) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.9 (quint, J = 150 Hz, 1 F), 63.2 (d, J = 150 Hz, 4 F) ppm.

1,4′-Bis(pentafluorosulfanyl)biphenyl (14):[4d] Palladium(II) acetate (0.3 mg, 0.001 mmol) was added to a solution of **1** (14.5 mg, 0.0384 mmol) in 0.15 g of methanol. The reaction mixture was stirred at 70 °C for 5.5 h and filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a colorless crystalline solid which was purified by SiO_2 column chromatography with hexane to give **14** (7.7 mg) as colorless crystals (99%); m.p. 196.0–197.0 °C (in sealed tube). IR (ATR): $\tilde{\nu}$ = 3007, 2992, 1599, 1481, 1391, 1277, 1260, 1101, 831, 810 cm^{-1}. MS (GC, EI): m/z = 406 [M^+], 387 [M^+ – F], 282, 190. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.6 Hz, 2 H), 7.66 (d, J = 8.6 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7 (C), 142.3 (C), 127.6 (2CH), 126.7 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.0 (quint, J = 150 Hz, 1 F), 63.0 (d, J = 150 Hz, 4 F) ppm.

1-(Pentafluorosulfanyl)-4-(phenylethynyl)benzene (15a):[4a] Diazonium salt **1** (11.7 mg, 0.0368 mmol) was added to a mixture of phenylacetylene (11.4 mg, 0.0805 mmol), sodium iodide (9.8 mg, 0.065 mmol), and $Pd(OAc)_2$ (0.5 mg, 0.002 mmol) in 0.23 g of 95% ethanol. Then triethylamine (10.6 mg, 0.077 mmol) was added to the mixture. The reaction mixture was stirred at 70 °C for 22 h, then filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a pale yellow crystalline solid which were purified by SiO_2 column chromatography with hexane to give **15a** as a colorless oil (1.0 mg; 9%); m.p. 88.0–89.0 °C. IR (ATR): $\tilde{\nu}$ = 2926, 2222, 1603, 1503, 1445, 1402, 1094, 835 cm^{-1}. MS (GC, EI): m/z = 304 [M^+], 196. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, J = 9.0 Hz, 2 H), 7.60 (d, J = 9.0 Hz, 2 H), 7.55 (m, 2 H), 7.39–7.37 (m, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0 (C), 131.8 (2CH), 131.6 (2CH), 129.0 (CH), 128.5 (2CH), 127.0 (C), 126.0 (2CH), 122.2 (C), 92.2 (C), 87.2 (C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.0 (quint, J = 150 Hz, 1 F), 62.7 (d, J = 150 Hz, 4 F) ppm.

1-(Pentafluorosulfanyl)-4-[(2-trifluoromethyl)phenylethynyl]benzene (15b): Sodium iodide (9.8 mg, 0.065 mmol) was added portion-wise to a solution of **1** (10.4 mg, 0.0327 mmol) in 0.17 g of 95% ethanol. To the mixture, triethylamine (7.8 mg, 0.077 mmol), (2-trifluoromethyl)phenylacetylene (13.7 mg, 0.0805 mmol), and $Pd(OAc)_2$ (0.5 mg, 0.002 mmol) were subsequently added. The reaction mixture was stirred at 70 °C for 4 h, then filtered through a pad of SiO_2 with the help of hexane. Removal of the solvent gave a brown oil which was purified by SiO_2 column chromatography with hexane to give **15b** as a colorless oil (1.8 mg; 15%): IR (ATR): $\tilde{\nu}$ = 2232, 1605, 1503, 1323, 1261, 1175, 1134, 1111, 829 cm^{-1}. MS (GC,

EI): *m*/*z* = 372 [M+], 353 [M+ – F], 264, 243. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 6 H), 7.56 (t, *J* = 7.8 Hz, 1 H), 7.48 (t, *J* = 7.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5 (C), 133.9 (C), 131.8 (q, *J* = 34 Hz, C), 131.7 (2CH), 131.5 (CH), 128.7 (CH), 126.4 (C), 126.1 (3CH), 123.4 (q, *J* = 274 Hz, C), 120.5 (C), 92.5 (C), 88.1 (C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.8 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F), –62.3 (s, 3 F) ppm.

1-(Pentafluorosulfanyl)-4-[(3,5-trifluoromethyl)phenylethynyl]benzene (15c): Sodium iodide (9.3 mg, 0.062 mmol) was added portionwise to a solution of **1** (15.4 mg, 0.0484 mmol) in 0.15 g of 95% ethanol. To the mixture, triethylamine (10.0 mg, 0.0988 mmol), 3,5-di(trifluoromethyl)phenylacetylene (15.1 mg, 0.0634 mmol), and $Pd(OAc)_2$ (0.3 mg, 0.001 mmol) were subsequently added. The reaction mixture was stirred at 70 °C for 4 h, then filtered through a pad of SiO_2 with the help of hexane. Removal of solvent gave a brown oil which was purified by SiO_2 column chromatography with hexane to give **15c** as a colorless oil (3.6 mg; 17%): IR (ATR): ṽ = 2231, 1615, 1599, 1498, 1387, 1279, 1180, 1138, 833 cm^{-1}. MS (GC, EI): *m*/*z* = 440 [M+], 421 [M+ – F], 332. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (s, 2 H), 7.87 (s, 1 H), 7.79 (d, *J* = 8.7 Hz, 2 H), 7.64 (d, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8 (C), 132.1 (q, *J* = 34 Hz, 2 C), 131.9 (2CH), 131.6 (2CH), 126.3 (2CH), 125.5 (C), 124.7 (C), 122.8 (q, *J* = 273 Hz, C), 122.3 (CH), 90.4 (C), 88.8 (C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.4 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F), –63.1 (s, 6 F) ppm.

4-(Pentafluorosulfanyl)phenyl Azide (16a):[2] Trimethylsilyl azide (6.5 mg, 0.056 mmol) was added to a solution of **1** (10.2 mg, 0.0321 mmol) in [BMIM][BF_4] (65.0 mg). After stirring for 5 min, the mixture was extracted with hexane (0.5 mL × 3) and the combined extracts was evaporated to give pure **16a** as a colorless oil (6.8 mg, 86%): IR (ATR): ṽ = 2124, 2099, 1586, 1501, 1287, 843 cm^{-1}. MS (GC, EI): *m*/*z* = 245 [M+], 219 [M+ – CN], 200 [M+ – CFN], 111. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 9.0 Hz, 2 H), 7.08 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.3 (C), 143.3 (C), 127.7 (2CH), 118.9 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.4 (quint, *J* = 150 Hz, 1 F), 63.5 (d, *J* = 150 Hz, 4 F) ppm.

1-Iodo-4-(pentafluorosulfanyl)benzene 16b:[4a] Trimethylsilyl iodide (15.0 mg, 0.0750 mmol) was added to a solution of **1** (11.0 mg, 0.0346 mmol) in [BMIM][BF_4] (67.6 mg). After stirring for 5 min the mixture was extracted with hexane (0.5 mL × 3) and the combined extracts was evaporated to give pure **16b** as a colorless oil (4.6 mg, 40%): MS (GC, EI): *m*/*z* = 330 [M+], 311 [M+ F], 222, 96. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 2 H), 7.48 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.9 (2CH), 127.5 (2CH), 98.2 (C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.5 (quint, *J* = 151 Hz, 1 F), 62.8 (d, *J* = 151 Hz, 4 F) ppm.

4-(Pentafluorosulfanyl)phenyl Thiocyanate (16c): A solution of ammonium thiocyanate (7.3 mg, 0.096 mmol) and **1** (10.1 mg, 0.0318 mmol) in 0.29 g of MeCN was heated at 70 °C for 0.5 h. After cooling, the mixture was filtered through SiO_2 with CH_2Cl_2 and the solvent was evaporated to give a pale yellow oil, whose purification by SiO_2 column chromatography with 9:1 hexane/CH_2Cl_2 furnished pure **16c** as colorless crystals (2.6 mg, 31%); m.p. 67.2–68.2 °C. IR (ATR): ṽ = 3103, 2162, 1585, 1479, 1402, 1105, 1082, 837 cm^{-1}. MS (GC, EI): *m*/*z* = 261 [M+], 242 [M+ – F], 153, 133. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0 (C), 129.6 (C), 128.7 (2CH), 127.8 (2CH), 108.6 (C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 82.5 (quint, *J* = 151 Hz, 1 F), 62.9 (d, *J* = 151 Hz, 4 F) ppm.

Reaction of 1 with TMSCl: Trimethylsilyl chloride (6.0 mg, 0.055 mmol) was added to a solution of **1** (11.0 mg, 0.0346 mmol) in [BMIM][BF_4] (62.1 mg). After stirring for 2 d the mixture was extracted with hexane (0.5 mL × 3) and the combined extracts was analyzed by GC–MS to show the formation of small amount of: **16d:**[2,7] MS (GC, EI) *m*/*z* = 238 and 240 (M+), 221, 219, 132, 130.

Reaction of 1 with TMSBr: Trimethylsilyl bromide (9.8 mg, 0.064 mmol) was added to a solution of **1** (10.0 mg, 0.0315 mmol) in [BMIM][BF_4] (57.4 mg). After stirring for 3 d the mixture was extracted with hexane (0.5 mL × 3) and the combined extracts was analyzed by GC–MS to show the formation of **16e**. The removal of the solvent gave as **16e**[2,26,27] as a colorless oil (0.5 mg, 6%).

Reaction of 1 with TMSCN/KF: Trimethylsilyl cyanide (10.8 mg, 0.109 mmol) and KF (3.5 mg, 0.060 mmol) were added to a solution of **1** (10.7 mg, 0.0337 mmol) in [BMIM][BF_4] (55.0 mg). After stirring for 2 d the mixture was extracted with hexane (0.5 mL × 3) and the combined extracts was analyzed by GC–MS to show the formation of small amount of **16f**: MS (GC, EI): *m*/*z* = 229 [M+], 210 [M+ – F], 121.

1-(4-Pentafluorosulfanyl)phenyl-4-phenyl-1*H*-1,2,3-triazole (17a): Cu-Zn (60/40) alloy nanopowder (<150 nm) (5.2 mg) was added into a solution of **16c** (7.2 mg, 0.033 mmol) and phenylethyne (9.2 mg, 0.090 mmol). The mixture was heated at 70 °C for 19 h, then cooled to room temp. and filtered through Celite with the help of CH_2Cl_2. Evaporation of solvent produced a pale yellow crystalline solid which was washed with hexane to give pale yellow crystals of pure **17a** (4.0 mg, 39%). The hexane solution was evaporated to give a pale yellow oil which was purified by SiO_2 column chromatography with hexane/EtOAc (7:3) to furnish additional amounts of **17a** (colorless crystals; 1.3 mg, 13%); m.p. 246.0–247.2 °C. IR (ATR): ṽ = 3123, 1596, 1504, 1483, 1458, 1436, 1410, 1230, 1101, 1089, 830 cm^{-1}. MS (GC, EI): *m*/*z* = 347 [M+], 319 [M+ – N_2], 211, 192, 165, 116, 90. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (s, 1 H), 7.98 (d, *J* = 9.8 Hz, 1 H), 7.95 (d, *J* = 9.8 Hz, 2 H), 7.93 (d, *J* = 7.3 Hz, 2 H), 7.49 (t, *J* = 7.3 Hz, 2 H), 7.41 (t, *J* = 7.3 Hz, 1 H) ppm. ^{1}H NMR (500 MHz, [D_6]acetone): δ = 9.30 (s, 1 H), 8.28 (d, *J* = 9.2 Hz, 1 H), 8.20 (d, *J* = 9.2 Hz, 2 H), 8.03 (d, *J* = 7.6 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, [D_6]acetone): δ = 151.4 (C), 148.3 (C), 139.4 (C), 130.5 (C), 129.0 (2CH), 128.4 (CH), 128.0 (2CH), 125.6 (2CH), 120.3 (2CH), 118.9 (CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.1 (quint, *J* = 150 Hz, 1 F), 63.1 (d, *J* = 150 Hz, 4 F) ppm. ^{19}F NMR (470 MHz, [D_6]acetone): δ = 83.5 (quint, *J* = 148 Hz, 1 F), 62.6 (d, *J* = 148 Hz, 4 F) ppm.

1-(4-Pentafluorosulfanyl)phenyl-4-[2-(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole (17b): Cu-Zn (60/40) alloy nanopowder (<150 nm) (6.7 mg) was added to a solution of **16c** (8.0 mg, 0.033 mmol) and [2-(trifluoromethyl)phenyl]ethyne (10.1 mg, 0.0591 mmol). The mixture was heated at 70 °C for 19 h, then cooled to room temp. and filtered through Celite using CH_2Cl_2. Removal of solvent gave a pale green oil, which was purified by SiO_2 column chromatography using hexane/EtOAc (8:2) to give **17b** as colorless crystals (9.1 mg, 65%); m.p. 92.5–93.0 °C. IR (ATR): ṽ = 1601, 1515, 1409, 1315, 1177, 1125, 1036, 833 cm^{-1}. MS (GC, EI): *m*/*z* = 415 [M+], 396 [M+ – F], 387 [M+ – N_2], 368. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (s, 1 H), 8.05 (d, *J* = 7.8 Hz, 1 H), 7.98 (d, *J* = 9.4 Hz, 2 H), 7.95 (d, *J* = 9.4 Hz, 2 H), 7.82 (d, *J* = 7.8 Hz, 1 H), 7.70 (t, *J* = 7.6 Hz, 1 H), 7.56 (t, *J* = 7.6 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3 (C), 145.5 (C), 138.6 (C), 132.2 (CH), 131.7 (CH), 128.9 (CH), 128.5 (C), 128.0 (2CH), 127.4 (q, *J* = 30 Hz, C),

126.3 (CH), 124.1 (q, J = 274 Hz, C), 120.6 (CH), 120.3 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.0 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F), –58.6 (s, 3 F) ppm.

1-(4-Pentafluorosulfanyl)phenyl-4-[3,5-bis(trifluoromethyl)phenyl]-1*H*-1,2,3-triazole (17c): Cu-Zn (60/40) alloy nanopowder (<150 nm) (6.9 mg) was added into a solution of **16c** (5.5 mg, 0.022 mmol) and [3,5-bis(trifluoromethyl)phenyl]ethyne (10.2 mg, 0.0428 mmol). The mixture was heated at 70 °C for 19 h, then cooled to room temp. and filtered through Celite using CH_2Cl_2. Removal of the solvent gave a pale yellow oil, which was purified by SiO_2 column chromatography with hexane/EtOAc (8:2) to give **17c** as colorless crystals (6.9 mg, 63%); m.p. 169.0–169.5 °C. MS (GC, EI): m/z = 483 [M^+], 464 [M^+ – F], 455 [M^+ N_2], 348, 328. IR (ATR): $\tilde{\nu}$ = 1669, 1601, 1514, 1373, 1330, 1278, 1177, 1134, 833 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 8.38 (s, 2 H), 8.01 (d, J = 9.3 Hz, 2 H), 7.97 (d, J = 9.3 Hz, 2 H), 7.90 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7 (C), 146.3 (C), 138.4 (C), 132.5 (q, J = 24 Hz, 2 C), 131.8 (C), 128.1 (2CH), 125.9 (2CH), 123.0 (q, J = 273 Hz, 2 C), 122.2 (CH), 120.2 (2CH), 118.4 (CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 82.7 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F), –63.0 (s, 6 F) ppm.

(*E*)-2,4-Dimethoxy-4′-(pentafluorosulfanyl)azobenzene (18a): Diazonium salt **1** (9.8 mg, 0.030 mmol) in 1 mL of 95% aqueous ethanol was added to a solution of 1,3-dimethoxybenzene (8.7 mg, 0.063 mmol) in 0.5 mL of 95% aqueous ethanol. After 2 weeks, the solvent was evaporated to give a red oil, whose purification by SiO_2 column chromatography (1:1 hexane/CH_2Cl_2) afforded **18a** as orange crystals (10.8 mg, 98%); m.p. 88.0–88.5 °C. IR (ATR): $\tilde{\nu}$ = 2943, 1600, 1496, 1471, 1294, 1253, 1211, 767 cm^{-1}. MS (GC, EI): m/z = 368 [M^+], 241 [M^+ – SF_5], 165 [M^+ – $C_6H_4SF_5$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, J = 9.0 Hz, 2 H), 7.86 (d, J = 9.0 Hz, 2 H), 7.78 (d, J = 9.0 Hz, 1 H), 6.60 (d, J = 2.4 Hz, 1 H), 6.56 (dd, J = 9.0, 2.4 Hz, 1 H), 4.03 (s, 3 H), 3.91 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.8 (C), 159.5 (C), 154.4 (C), 154.1 (C), 136.7 (C), 126.9 (2CH), 122.5 (2CH), 118.2 (CH), 105.9 (CH), 98.9 (CH), 56.3 (CH_3), 55.7 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.3 (quint, J = 150 Hz, 1 F), 63.2 (d, J = 150 Hz, 4 F) ppm.

(*E*)-2,4,6-Trimethoxy-4′-(pentafluorosulfanyl)azobenzene (18b): Diazonium salt **1** (11.9 mg, 0.0374 mmol) and 1,3,5-trimethoxybenzene (6.6 mg, 0.039 mmol) were dissolved in 0.18 g of 95% aqueous ethanol. After 0.1 h, a red solid precipitated which was filtered. The red precipitate was purified by SiO_2 column chromatography (7:3 hexane/ethyl acetate) to afford **18b** as a red oil (11.2 mg, 75%): IR (ATR): $\tilde{\nu}$ = 2943, 1599, 1456, 1335, 1207, 1151, 1126, 837 cm^{-1}. MS (GC, EI): m/z = 398 [M^+], 271 [M^+ – SF_5], 195, 152. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.3 Hz, 2 H), 7.85 (d, J = 9.3 Hz, 2 H), 6.23 (s, 2 H), 3.93 (s, 6 H), 3.92 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.4 (C), 156.4 (2 C), 154.6 (C), 153.9 (C), 127.1 (C), 126.9 (2CH), 122.0 (2CH), 91.4 (2CH), 56.6 ($2CH_3$), 55.7 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.5 (quint, J = 150 Hz, 1 F), 63.3 (d, J = 150 Hz, 4 F) ppm.

(*E*)-2,4,5-Trimethoxy-4′-(pentafluorosulfanyl)azobenzene (18c): Diazonium salt **1** (14.1 mg, 0.0443 mmol) and 1,2,4-trimethoxybenzene (15.6 mg, 0.0928 mmol) were dissolved in 0.148 g of 95% aqueous ethanol. After 0.1 h, a red solid precipitated. After filtration the red solid was purified by SiO_2 column chromatography (7:3 hexane/ethyl acetate) to give **18c** as a red oil (12.8 mg, 72%): IR (ATR): $\tilde{\nu}$ = 2941, 1607, 1598, 1505, 1472, 1436, 1269, 1209, 1126, 1093, 1030, 839, 824 cm^{-1}. MS (GC, EI): m/z = 398 [M^+], 140, 110. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.0 Hz, 2 H), 7.86 (d, J = 9.0 Hz, 2 H), 7.44 (s, 1 H), 6.64 (s, 1 H), 4.07 (s, 3 H), 4.01 (s, 3 H), 3.93 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.74 (C), 154.70 (C), 154.3 (C), 154.0 (C), 144.1 (C), 135.1 (C), 126.9 (2CH), 122.4 (2CH), 98.8 (CH), 97.5 (CH), 57.6 (CH_3), 56.22 (CH_3), 56.17 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.4 (quint, J = 150 Hz, 1 F), 63.3 (d, J = 150 Hz, 4 F) ppm.

(*E*)-4-Hydroxy-4′-(pentafluorosulfanyl)azobenzene (18d): Diazonium salt **1** (11.6 mg, 0.0365 mmol), phenol (9.5 mg, 0.10 mmol), and sodium acetate (10.2 mg, 0.124 mmol) were dissolved in 0.21 g of acetonitrile. After 1 month, the solution was filtered through Celite 545. Evaporation of the solvent gave a red oil, which was purified by SiO_2 column chromatography (9:1 hexane/ethyl acetate) and following preparative TLC (SiO_2, CH_2Cl_2) afforded **18d** as yellow-orange crystals (7.3 mg, 62%); m.p. 110.0–111.0 °C. IR (ATR): $\tilde{\nu}$ = 3261, 1593, 1505, 1467, 1436, 1402, 1271, 1235, 1142, 1094, 829 cm^{-1}. MS (GC, EI): m/z = 324 [M^+], 305 [M^+ – F], 197, 121, 93, 65. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.88 (m, 6 H), 6.97 (d, J = 8.8 Hz, 2 H), 5.50 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.1 (C), 154.4 (C), 153.7 (C), 147.0 (C), 127.0 (2CH), 125.6 (2CH), 122.5 (2CH), 116.0 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.1 (quint, J = 150 Hz, 1 F), 63.2 (d, J = 150 Hz, 4 F) ppm.

(*E*)-4-Amino-4′-(pentafluorosulfanyl)azobenzene (18e): Diazonium salt **1** (11.1 mg, 0.0349 mmol) and aniline (32.0 mg, 0.344 mmol) were dissolved in 0.19 g of 95% ethanol. After 20 d, the solution was filtered through Celite 545. Evaporation of the solvent gave an orange oil, which was purified by SiO_2 column chromatography (8:2 hexane/ethyl acetate) and following preparative TLC (SiO_2, CH_2Cl_2) afforded **18e** as orange crystals (2.5 mg, 22%); m.p. 153.0–154.5 °C. IR (ATR): $\tilde{\nu}$ = 3417, 2915, 1666, 1628, 1603, 1507, 1398, 1302, 1148, 1092, 834 cm^{-1}. MS (GC, EI): m/z = 323 [M^+], 197, 120, 94, 65. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.88–7.82 (m, 6 H), 6.76 (d, J = 8.8 Hz, 2 H), 2.20 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1 (C), 150.5 (C), 145.3 (C), 126.9 (2CH), 125.8 (2CH), 122.2 (2CH), 114.5 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.4 (quint, J = 150 Hz, 1 F), 63.2 (d, J = 150 Hz, 4 F) ppm.

2,4,6-Trimethyl-4′-(pentafluorosulfanyl)biphenyl (19a): Sodium iodide (5.2 mg, 0.035 mmol) was added portion-wise to a solution of **1** (10.4 mg, 0.0327 mmol) and mesitylene (33.6 mg, 0.280 mmol) in CH_3CN (0.14 g). The reaction mixture was filtered through Celite 545 by using CH_2Cl_2. The solvent was evaporated to give pale-red oil. NMR analysis indicated the formation of a 2:1 mixture of **16b** and **19a** which were separated by SiO_2 column chromatography using hexane to give **16b** as colorless crystals (6.5 mg, 60%) and **19a** as colorless crystals (3.3 mg, 31%).

16b: ^1H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.8 Hz, 2 H), 7.48 (d, J = 8.8 Hz, 2 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 83.5 (quint, J = 150 Hz, 1 F), 62.8 (d, J = 150 Hz, 4 F) ppm.

19a: M.p. 121.8–122.8 °C. MS (GC, EI): m/z = 322 [M^+], 307 [M^+ – CH_3], 195 [M^+ – SF_5], 180 [M^+ – CH_3SF_5]. IR (ATR): $\tilde{\nu}$ = 2292, 1612, 1476, 1396, 1096, 765 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.6 Hz, 2 H), 7.24 (d, J = 8.6 Hz, 2 H), 6.96 (s, 2 H), 2.34 (s, 3 H), 1.99 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.4 (C), 145.0 (C), 137.4 (C), 136.9 (2 C), 135.6 (2CH), 129.7 (2CH), 128.3 (2CH), 126.1 (2CH), 21.0 (CH_3), 20.7 ($2CH_3$) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.0 (quint, J = 150 Hz, 1 F), 63.1 (d, J = 150 Hz, 4 F) ppm.

2,5-Dimethyl-4′-(pentafluorosulfanyl)biphenyl (19b): Sodium iodide (5.5 mg, 0.037 mmol) was added portion-wise to a solution of **1** (9.9 mg, 0.031 mmol) and *p*-xylene (60.1 mg, 0.566 mmol) in

CH_3CN (0.11 g). The reaction mixture was filtered through Celite 545 using CH_2Cl_2. The solvent was evaporated to give a brown oil, which was purified by SiO_2 column chromatography with hexane to afford **16b** (1.4 mg, 14%) and **19b** as a colorless oil (1.3 mg, 14%): MS (GC, EI): *m*/*z* = 308 [M^+], 181 [$M^+ – SF_5$]. IR (ATR): $\tilde{\nu}$ = 2924, 1599, 1493, 1456, 1395, 1099, 833 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.5 Hz, 2 H), 7.40 (d, *J* = 8.5 Hz, 2 H), 7.18 (d, *J* = 8.3 Hz, 1 H), 7.12 (d, *J* = 8.3 Hz, 1 H), 7.02 (s, 1 H), 2.36 (s, 3 H), 2.22 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0 (C), 145.6 (C), 139.5 (C), 132.0 (C), 130.5 (CH), 130.2 (CH), 129.4 (2CH), 128.8 (CH), 125.7 (2CH), 20.9 (CH_3), 19.8 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.9 (quint, *J* = 150 Hz, 1 F), 63.2 (d, *J* = 150 Hz, 4 F) ppm.

2,3,5,6-Tetramethyl-4′-(pentafluorothio)biphenyl (19c): NaI (5.7 mg, 0.038 mmol) was added portion-wise to a solution of **1** (12.0 mg, 0.0377 mmol) and 1,2,4,5-tetramethylbenzene (8.6 mg, 0.064 mmol) in CH_3CN (0.17 g). The reaction mixture was filtered through Celite 545 using CH_2Cl_2. The solvent was evaporated to give (a) a mixture containing 1,2,4,5-tetramethylbenzene and **16b** (13.8 mg), and (b) the desired **19c** as colorless crystals in very low yield (0.3 mg, 2%).

19c: M.p. 166.0–167.0 °C. MS (GC, EI): *m*/*z* = 336 [M^+], 321 [$M^+ – CH_3$], 194 [$M^+ – CH_3SF_5$]. IR (ATR): $\tilde{\nu}$ = 2924, 2852, 1603, 1462, 1096, 843, 810 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.7 Hz, 2 H), 7.22 (d, *J* = 8.7 Hz, 2 H), 7.03 (s, 1 H), 2.27 (s, 6 H), 1.86 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.3 (C), 146.2 (C), 140.0 (C), 133.8 (2 C), 131.5 (2 C), 131.1 (CH), 129.7 (2CH), 126.0 (2CH), 20.1 (CH_3), 17.2 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.0 (quint, *J* = 150 Hz, 1 F), 63.2 (d, *J* = 150 Hz, 4 F) ppm.

2-Methoxy-4′-(pentafluorosulfanyl)biphenyl, 3-Methoxy-4′-(pentafluorosulfanyl)biphenyl, and 4-Methoxy-4′-(pentafluorosulfanyl)biphenyl (19e) (Isomer Mixture): NaI (22.0 mg, 0.147 mmol) was added portion-wise to a solution of **1** (31.0 mg, 0.0974 mmol) and anisole (96.0 mg, 0.888 mmol) in CH_3CN (53.5 mg). The reaction mixture was neutralized with Na_2CO_3 and filtered through Celite 545 using hexane. The solvent was evaporated to give a pale yellow oil, Silica column chromatography with hexane afforded **16b** (15.3 mg, 48%), 2-methoxy-4′-(pentafluorosulfanyl)biphenyl as colorless crystals (4.0 mg, 13%), 3-methoxy-4′-(pentafluorosulfanyl)biphenyl as a colorless oil (0.2 mg, 1%), a fraction containing both 3-methoxy-4′-(pentafluorosulfanyl)biphenyl and 4-methoxy-4′-(pentafluorosulfanyl)biphenyl (1:1) as colorless oil (2.0 mg, 7%), and 4-methoxy-4′-(pentafluorosulfanyl)biphenyl as colorless crystals (0.7 mg, 2%).

2-Methoxy-4′-(pentafluorosulfanyl)biphenyl (*ortho*): Colorless crystals; m.p. 80.5–81.5 °C. IR (ATR): $\tilde{\nu}$ = 2944, 2841, 1601, 1485, 1400, 1264, 1244, 831 cm^{-1}. MS (GC, EI): *m*/*z* = 310 [M^+], 291 [$M^+ – F$], 204, 168, 139. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H), 7.38 (td, *J* = 7.8, 1.7 Hz, 1 H), 7.30 (dd, *J* = 7.5, 1.7 Hz, 1 H), 7.06 (td, *J* = 8.5, 1.0 Hz, 1 H) 7.01 (d, *J* = 8.3 Hz), 3.83 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.3 (C), 152.4 (C), 142.0 (C), 130.7 (C), 129.7 (3CH), 128.4 (CH), 125.6 (2CH), 121.0 (CH), 111.3 (CH), 55.5 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.0 (quint, *J* = 150 Hz, 1 F), 63.1 (d, *J* = 150 Hz, 4 F) ppm.

3-Methoxy-4′-(pentafluorosulfanyl)biphenyl (*meta*): Colorless oil. IR (ATR): $\tilde{\nu}$ = 2916, 2849, 1740, 1599, 1572, 1487, 1463, 1397, 1224, 1102, 1030, 833 cm^{-1}. MS (GC, EI): *m*/*z* = 310 [M^+], 202, 172, 159, 154, 139. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.8 Hz, 2 H), 7.65 (d, *J* = 8.8 Hz, 2 H), 7.40 (t, *J* = 8.0 Hz, 1 H), 7.17 (d, *J* = 8.0 Hz, 1 H), 7.10 (t, *J* = 2.0 Hz, 1 H), 6.96 (dd, *J* = 8.0, 2.0 Hz, 1 H), 3.88 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0 (C), 152.9 (C), 144.4 (C), 140.5 (C), 130.1 (CH), 127.3 (2CH), 126.4 (2CH), 119.7 (CH), 113.6 (CH), 113.2 (CH), 55.4 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.8 (quint, *J* = 150 Hz, 1 F), 63.1 (d, *J* = 150 Hz, 4 F) ppm.

4-Methoxy-4′-(pentafluorosulfanyl)biphenyl (*para*): Colorless crystals; m.p. 102.0–104.0 °C. IR (ATR): $\tilde{\nu}$ = 2921, 2850, 1740, 1609, 1493, 1467, 1398, 1298, 1261, 1184, 1103, 1037, 830 cm^{-1}. MS (GC, EI): *m*/*z* = 310 [M^+], 202, 187, 158, 139. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.8 Hz, 2 H), 7.61 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.00 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.0 (C), 152.3 (C), 144.1 (C), 131.4 (C), 128.4 (2CH), 126.6 (2CH), 126.4 (2CH), 114.5 (2CH), 55.4 (CH_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.0 (quint, *J* = 150 Hz, 1 F), 63.2 (d, *J* = 150 Hz, 4 F) ppm.

Solvolytic Dediazoniations

i) In Methanol: Diazonium salt **1** (22.5 mg, 0.0314 mmol) was dissolved in methanol (0.82 mL). After 13 d stirring at room temp. a portion of the solution was diluted with $CDCl_3$ and analyzed by NMR, which indicated the formation of 1-fluoro-4-(pentafluorosulfanyl)benzene **21**,[7] 1-methoxy-4-(pentafluorosulfanyl)-benzene,[9a] and 4-(pentafluorosulfanyl)phenol.[9a]

4-(Pentafluorosulfanyl)phenol: Pale-brown oil. MS (GC, EI): *m*/*z* = 220 [M^+], 201 [$M^+ – F$], 112, 84. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.9 Hz, 2 H), 6.86 (d, *J* = 8.9 Hz, 2 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 86.0 (quint, *J* = 150 Hz, 1 F), 64.2 (d, *J* = 150 Hz, 4 F) ppm.

ii) in 2,2,2-Trifluroethanol TFE: Diazonium salt **1** (24.1 mg, 0.0314 mmol) was dissolved in TFE (90.5 mg, 0.400 mmol) and the mixture was heated at 70 °C for 4 h. NMR analysis of the reaction mixture indicated the formation of 1-fluoro-4-(pentafluorosulfanyl)benzene (**21**),[7] 1-(pentafluorosulfanyl)-4-(2,2,2-trifluoroethoxy)benzene (**20**),[9a] and unreacted **1** in 39:56:5 ratio. Most of the solvent was evaporated to give a pale yellow oil, whose SiO_2 column chromatography with hexane/CH_2Cl_2 (9:1) afforded **20** as a colorless oil (6.6 mg, 29%): MS (GC, EI): *m*/*z* = 302 [M^+], 283 [$M^+ – F$]. IR (ATR): $\tilde{\nu}$ = 2951, 1593, 1504, 1288, 1248, 1163, 1103, 837 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 9.2 Hz, 2 H), 6.98 (t, *J* = 9.2 Hz, 2 H), 4.40 (q, *J* = 7.9 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8 (C), 148.1 (C), 128.0 (2CH), 122.9 (q, *J* = 278 Hz, CF_3), 114.5 (2CH), 65.7 (q, *J* = 36 Hz, CH_2) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 85.0 (quint, *J* = 150 Hz, 1 F), 64.0 (d, *J* = 150 Hz, 4 F) ppm.

1-Fluoro-4-(pentafluorosulfanyl)benzene (21): MS (GC, EI): *m*/*z* = 222 [M^+], 203 [$M^+ – F$]. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (dd, *J* = 8.8, 4.7 Hz, 2 H), 7.47 (t, *J* = 8.8 Hz, 2 H) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.1 (quint, *J* = 150 Hz, 1 F), 62.6 (d, *J* = 150 Hz, 4 F), –107.1 (s, 1 F) ppm.

iii) In Triflic Acid: Diazonium salt **1** (7.1 mg, 0.022 mmol) was dissolved in TfOH (0.27 g) and the mixture was heated at 50 °C for 1 month. After cooling, a portion of the mixture was diluted with $CDCl_3$ and analyzed by NMR showing the formation of 4-(fluorosulfonyl)phenyl trifluoromethanesulfonate **22**. The mixture was diluted with CH_2Cl_2, washed with 10% Na_2CO_3 aq. and dried with $MgSO_4$. Most of the solvent was evaporated to give a pale yellow oil, which was purified by SiO_2 column chromatography with hexane/CH_2Cl_2 (7:3) to afforded **22** as a colorless oil (6.9 mg, 100%). MS (GC, EI): *m*/*z* = 308 [M^+], 289 [$M^+ – F$]. IR (ATR): $\tilde{\nu}$ = 3107, 1587, 1486, 1418, 1213, 1136, 881 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 9.0 Hz, 2 H), 7.57 (d, *J* = 9.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9 (C), 133.2 (C),

131.2 (2CH), 123.0 (2CH). ^{19}F NMR (470 MHz, $CDCl_3$): δ = 66.6 (s, 1 F), –72.5 (s, 3 F) ppm.

iv) In 1,1,1,3,3,3-hexafluoro-2-propanol HFIP: Diazonium salt **1** (106.8 mg, 0.3359 mmol) was dissolved in HFIP (7.16 g) and the mixture was heated at 60 °C for 4 h. After cooling, Na_2CO_3 was added and the mixture was filtered. Most of the solvent was evaporated to give a pale-yellow oil, which was purified by SiO_2 column chromatography with hexane/CH_2Cl_2 (9:1) to afford 1-(pentafluorosulfanyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]benzene (colorless oil; 2.0 mg, 1.6%), 1-fluoro-4-(fluorosulfonyl)benzene[23] (colorless oil; 7.7 mg, 13%), and 2,2,2-trifluoro-1-(trifluoromethyl)-ethyl 4-fluorophenylsulfonate[28] (colorless oil; 15.7 mg, 14.3%). Elution with hexane/CH_2Cl_2 (8:2) gave 1-(fluorosulfonyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]benzene (colorless oil, 6.6 mg, 6.0%), a 2:1 mixture of 1-(fluorosulfonyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]benzene and 2,2,2-trifluoro-1-(trifluoromethyl)ethyl-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phenylsulfonate (colorless oil, 27.2 mg, 19.1%), and 4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phenylsulfonate (colorless oil, 3.8 mg, 2.4%).

1-(Pentafluorothio)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-benzene: Colorless oil. MS (GC, EI): *m/z* = 370 [M^+], 361 [M^+ – F], 262, 224, 111, 83. IR (ATR): $\tilde{\nu}$ = 1596, 1502, 1369, 1291, 1244, 1199, 1105, 846 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 9.1 Hz, 2 H), 7.14 (d, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6 (C), 149.7 (C), 128.3 (2CH), 120.2 (q, *J* = 285 Hz, 2 C), 116.6 (2CH), 75.4 (m, CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 84.0 (quint, *J* = 151 Hz, 1 F), 63.6 (d, *J* = 151 Hz, 4 F), –73.4 (d, *J* = 5 Hz, 6 F) ppm.

1-Fluoro-4-(fluorosulfonyl)benzene: Colorless oil. IR (ATR): $\tilde{\nu}$ = 1593, 1498, 1416, 1210, 836, 768 cm^{-1}. MS (GC, EI): *m/z* = 178 [M^+], 159 [M^+ – F], 111, 83, 75. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 9.1, 4.9 Hz, 2 H), 7.33 (t, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8 (d, *J* = 260 Hz, C), 131.5 (d, *J* = 10 Hz, 2CH), 129.0 (d, *J* = 26 Hz, C), 117.2 (d, *J* = 23 Hz, 2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 66.8 (s, 1 F), –99.3 (m, 1 F) ppm.

2,2,2-Trifluoro-1-(trifluoromethyl)ethyl 4-Fluorophenylsulfonate: Colorless oil. IR (ATR): $\tilde{\nu}$ = 1593, 1498, 1375, 1363, 1290, 1234, 1204, 1191, 1066, 880, 837, 793 cm^{-1}. MS (GC, EI): *m/z* = 326 [M^+], 159, 111, 75. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 8.9, 4.9 Hz, 2 H), 7.30 (dd, *J* = 8.9, 8.0 Hz, 2 H), 5.28 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6 (d, *J* = 260 Hz, C), 131.2 (d, *J* = 10 Hz, 2CH), 130.4 (d, *J* = 3 Hz, C), 119.7 (q, *J* = 284 Hz, 2 C), 117.1 (d, *J* = 23 Hz, 2CH), 72.0 (m, C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 73.1 (d, *J* = 6 Hz, 1 F), –100 (m, 1 F) ppm.

1-(Fluorosulfonyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]-benzene: Colorless oil. IR (ATR): $\tilde{\nu}$ = 1596, 1498, 1290, 1248, 1211, 1200, 1180, 1103, 900, 776 cm^{-1}. MS (GC, EI): *m/z* = 326 [M^+], 307 [M^+ – F], 259, 224, 92. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.9 Hz, 2 H), 7.29 (d, *J* = 8.9 Hz, 2 H), 5.00 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.8 (C), 131.3 (2CH), 128.6 (d, *J* = 29 Hz, C), 120.5 (q, *J* = 279 Hz, 2 C), 117.4 (2CH), 74.8 (m, C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 66.8 (s, 1 F), –73.2 (d, *J* = 6 Hz, 6 F) ppm.

2,2,2-Trifluoro-1-(trifluoromethyl)ethyl-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phenylsulfonate: Colorless oil. IR (ATR): $\tilde{\nu}$ = 1589, 1496, 1375, 1291, 1240, 1198, 1175, 1104, 1065, 881, 798 cm^{-1}. MS (GC, EI): *m/z* = 474 [M^+], 326, 307, 259, 243, 111. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.9 Hz, 2 H), 7.27 (d, *J* = 8.9 Hz, 2 H), 5.29 (m, 1 H), 4.99 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.5 (C), 131.0 (2CH), 130.6 (C), 120.6 (q, *J* = 283 Hz, C), 119.7 (q, *J* = 280 Hz, C) 117.4 (2CH), 74.9 (m, C), 72.0 (m, C) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –73.1 (d, *J* = 6 Hz, 6 F), –73.2 (d, *J* = 6 Hz, 6 F) ppm.

v) In CF_3COOH (TFAH): Diazonium salt **1** (29.7 mg, 0.0934 mmol) was dissolved in TFAH (0.96 g) and the mixture was heated with 70 °C for 12 h. After cooling, a portion of the mixture was diluted with $CDCl_3$ and analyzed by NMR which indicated the formation of 1-fluoro-4-(pentafluorosulfanyl)benzene,[7] 1-fluoro-4-(fluorosulfonyl)benzene,[23] 4-(pentafluorosulfanyl)phenol,[9a] and 4-(fluorosulfonyl)phenol.[24,25] Most of the solvent was evaporated to give a pale yellow oil, which was purified by SiO_2 column chromatography with hexane/EtOAc (9:1) to afford: 4-(pentafluorosulfanyl)phenol, 4-(fluorosulfonyl)phenol (colorless oil; 3.5 mg), and 4-(fluorosulfonyl)phenol (colorless oil; 2.4 mg, 15%).

4-(Fluorosulfonyl)phenol: Colorless oil. MS (GC, EI): *m/z* = 176 [M^+], 157 [M^+ – F], 109, 81, 65, 63. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 2.89 (br. s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.9 (C), 131.2 (2CH), 131.1 (C), 116.4 (2CH) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 67.2 (s, 1 F) ppm.

vi) In [BMIM][NTf_2]: Diazaonium salt **1** (44.8 mg, 0.141 mmol) was dissolved in [BMIM][NTf_2] (0.4514 g, 1.076 mmol) and the mixture was heated at 70 °C for 15 h. NMR analysis of the reaction mixture indicated the formation of **25** and **26** and **21** in a 77:8:15 ratio. The mixture was extracted with hexane and the solvent was evaporated to give a pale yellow oil, whose SiO_2 column chromatography with hexane/CH_2Cl_2 (8:2) afforded **26** (colorless crystals; 2.0 mg, 3%) and **25** (colorless oil; 24.3 mg, 36%).

25: MS (GC, EI): *m/z* = 483 [M^+], 464 [M^+ – F]. IR (ATR): $\tilde{\nu}$ = 1495, 1395, 1343, 1219, 1130, 1076, 839 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.1 Hz, 2 H), 7.48 (t, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9 (C), 149.6 (C), 129.0 (2CH), 122.4 (2CH), 118.7 (q, *J* = 221 Hz, CF_3), 118.6 (q, *J* = 221 Hz, CF_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 81.6 (quint, *J* = 150 Hz, 1 F), 63.1 (d, *J* = 150 Hz, 4 F), –72.5 (s, 3 F), –77.8 (s, 3 F) ppm.

26: Dec. 245.0 °C (in a sealed tube). MS (GC, EI): *m/z* = 483 [M^+], 464 [M^+ – F]. IR (ATR): $\tilde{\nu}$ = 1449, 1232, 1219, 1117, 837 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.7 Hz, 2 H), 7.54 (t, *J* = 8.7 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7 (C), 134.4 (C), 131.6 (2CH), 127.9 (2CH), 121.7 (q, *J* = 222 Hz, CF_3) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = 81.3 (quint, *J* = 150 Hz, 1 F), 62.7 (d, *J* = 150 Hz, 4 F), –70.4 (s, 6 F) ppm.

vii) In [BMIM][BF_4] and [BMIM][PF_6]: Diazonium salt **1** (10.1 mg, 0.0318 mmol) was dissolved in the IL (90 mg) and the mixture was heated to 70 °C in an oil bath for 8 h. NMR analysis of the reaction mixture indicated quantitative formation of fluoro derivative **21**.[7,23]

Computational Methods: Structures were optimized using a C_1 molecular point group by the density function theory (DFT) method[29] at B3LYP/6-31G(d) level and B3LYP/6-311+G(d,p) using the Gaussian 03 package.[30] All computed geometries were verified by frequency calculations to have no imaginary frequencies. The solvent effect was estimated by the polarized continuum model (PCM).[31–33] Energies are summarized in Tables S1 and S2.

CCDC-965267 (for **26**), -965268 (for **2e**), -965269 (for **14**), and -965270 (for **16c**) contain the supplementary crystallographic data

for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures S1–S133 (Selected ^{1}H, ^{19}F, ^{13}C NMR, and IR spectra). Tables S1 and S2 (Energy data), and Tables S3–S8 (Cartesian Coordinates for the optimized Structure by the DFT method).

Acknowledgments

The authors thank the University of North Florida for research support.

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Received: October 10, 2013
Published Online: January 8, 2014

