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Pentafluorophenylation of Aromatics with Pentafluorophenyl Perfluoro- and Polyfluoroalkanesulfonates. A Photoinduced Electron-Transfer Cation Diradical Coupling Process

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Irradiation of pentafluorophenyl perfluoro- and polyfluoroalkanesulfonates **1** with arenes, aromatic ethers, anilines, pyrroles, indoles, and phenols results in the corresponding pentafluorophenylated aromatic compounds. An electron-transfer mechanism is proposed.

Introduction

Arylation of aromatic substrates is one of the most important classes of radical chemistry and has been studied extensively both mechanistically and synthetically.[1] However, arylation of pentafluorobenzenes from the reaction of diaroyl peroxide, used as an aryl radical source in perfluorobenzenes, has not been as thoroughly investigated.[2] Due to the lack of availability of the pentafluorophenyl radical, few pentafluorophenylations of aromatics have been reported. Heating dipentafluorobenzoyl peroxide in hexafluorobenzene gave a very low yield of perfluorobiphenyl.[3] Pentafluorophenylation of benzene or toluene with pentafluoroiodobenzene afforded the corresponding pentafluorobiphenyls only after prolonged irradiation (150 h).[4] In connection with our previous work on perfluoroalkylations of aromatics and heterocyclic compounds with perfluoroalkyl iodides through single-electron transfer (SET) reactions,[5] we have chosen pentafluorophenyl perfluoro- and polyfluoroalkanesulfonates ($R_fSO_3C_6F_5$, **1**) as pentafluorophenylating agents, as it is known that their analogues are good electron acceptors.[6] Furthermore, if the radical anion of **1** is formed, its dissociation to pentafluorophenyl radical and perfluoro- and polyfluoroalkanesulfonate anion will provide another C–O bond cleavage pathway for polyfluorophenol through its sulfonate derivative **1**.[7] This paper presents the results of the reaction of **1** with arenes, methoxybenzenes, anilines, pyrroles, indoles, and phenols.

Results and Discussion

Irradiation of pentafluorophenyl perfluoro- and polyfluoroalkanesulfonates **1** in aromatic compounds (such as benzene, toluene, *m*- or *p*-xylene, isopropylbenzene, and mesitylene) gave the corresponding pentafluorophenylated regioisomers in high yields (Scheme I). Direct irradiation of **1** for hours in the absence of arenes gave no products, and the residue appeared only as tar. The reaction temperature of the mixture of **1** and **2** rose to 80 °C within about 0.5 h when irradiated. The same mixture, when heated at 80 °C without irradiation for several hours, gave no products, indicating that UV irradiation is essential to the reaction. The results are shown in Table I.

It was found that the pentafluorophenylation always occurs at the ortho or para position relative to the substituent of **2**, the majority of products being ortho substituted. The variation in the R_f groups showed little influence on the yields (see Table I).

Similarly, treatment of anisole (**6a**) or dimethoxybenzene (**6b**) with **1** gave pentafluorophenylated products **7** in good yields (Scheme II). The reaction with anisole was carried out with anisole as solvent, whereas the reaction with *p*-dimethoxybenzene took place in DMF. No pentafluorobenzene **4** byproduct was found in either of these two reactions.

Anilines **8** underwent the same reaction with **1** affording *o*- and *p*-(pentafluorophenyl)anilines but no meta-substituted derivatives (Scheme III). The reaction proceeded with neat **8**. The reaction gave lower yields when acetonitrile was used as the solvent.

Besides the main products, a small amount of pentafluorobenzene (**4**) was also obtained. It was also found that **8a**, **8b**, and *N*-ethylaniline are produced from the reaction of **8b**, **8c** and **8d**, respectively. The results of the reaction are given in Table II.

Pyrroles **10** and indoles **12** reacted with **1** in acetonitrile under similar conditions, giving the corresponding coupling products (Scheme IV). In the reactions of **10a**, **10b**, and **12a**, the major product were 2-pentafluorophenylated derivatives, and none of these reactions gave *N*-pentafluorophenylated compounds. The reactions of indoles did not afford phenyl ring substituted products. Under similar conditions, imidazoles and pyridines reacted with **1** resulting only in the formation of the S–O bond cleavage product, pentafluorophenol, probably because of the greater basicity of these compounds.

In order to elucidate the reaction mechanism, inhibition studies were carried out. For example, on addition of SET scavengers, *p*-dinitrobenzene (*p*-DNB), and *t*-Bu_2NO or free-radical inhibitor, hydroquinone (HQ), to the reaction mixtures, the reaction was significantly suppressed (entries 7–9 in Table I, entries 7–9 in Table II). The existence of C_6F_5 radical was established by the observation of small

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[1] (a) Nonhebel, D. C.; Walton, J. C. *Free Radical Chemistry*; Cambridge University Press: Cambridge, 1974; p 417. (b) Sainsburg, M. *Tetrahedron* **1980**, *36*, 3327. (c) Mattay, J. Topics in Current Chemistry; Springer-Verlag: Berlin, 1990; Vol. 156, p 59. (d) Norris, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, L., Eds.; Pergamon Press: New York, 1991; Vol. 4, p 469.

[2] Kobrina, L. S. Russ. *Chem. Rev.* **1977**, *46*, 660.

[3] Clart, P. A.; Williams, G. H.; Coulson, J. *J. Chem. Soc. C* **1968**, 341; *Chem. Ind.* **1965**, 228.

[4] Birchall, J. M.; Hazard, R.; Haszeldine, R. N.; Wakalski, W. W. *J. Chem. Soc. C* **1967**, 47.

[5] Chen, Q.-Y.; Li, Z.-T. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1443.

[6] Chen, Q.-Y.; Chen, M.-F. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1071 and references cited therein.

[7] We have found that $Pd(PPh_3)_2Cl_2/NEt_3/DMF$ or $Pd(0)/NEt_3$ can catalyze the alkynyl dehydroxylation of polyfluorophenols through polyfluorophenyl perfluoroalkanesulfonates with alkynes; see Chen, Q.-Y.; Li, Z.-T. *J. Chem. Soc., Perkin Trans 1* **1992**, 2931.

0022-3263/93/1958-2599$04.00/0

Scheme I

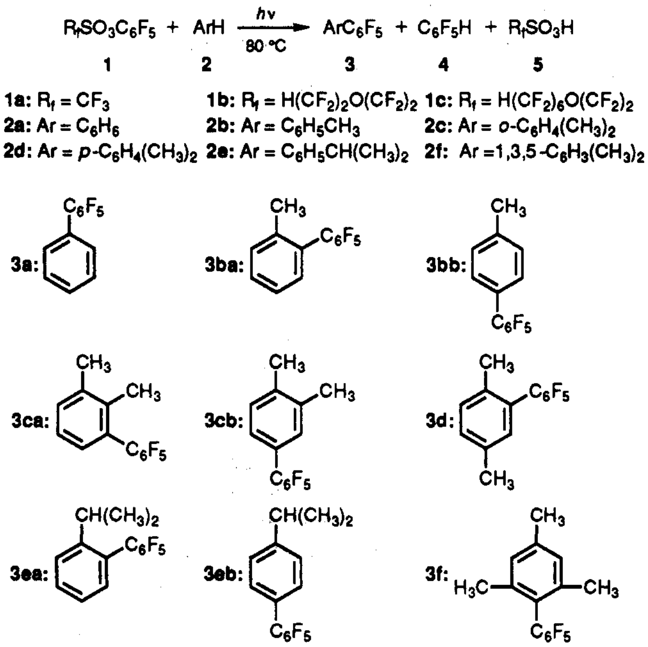
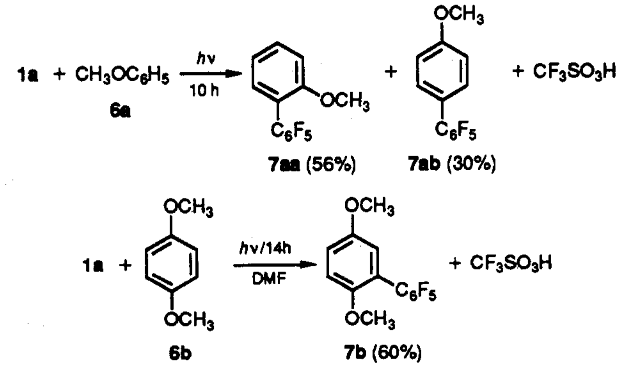


Table I. Photoinduced Reaction between 1 and Arenes 2

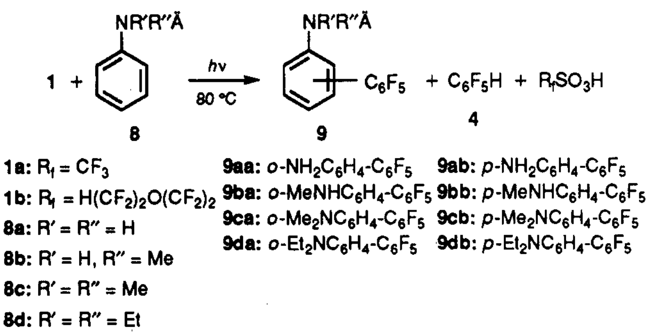
entry	1	2	time (h)	products^a (%)				4^b
1	1a	2a	20	3a	65			0
2	1b	2a	20		60			0
3	1c	2a	20		62			0
4	1a	2b	12	3ba	54	3bb	32	5
5	1b	2b	12		49		31	3
6	1c	2b	12		46		32	4
7^c	1a	2b	12		34		20	4
8^d	1a	2b	12		29		22	3
9^e	1a	2b	12		32		19	3
10	1b	2c	11	3ca	42	3cb	40	4
11	1a	2d	18	3d	70			6
12	1b	2d	18		71			6
13	1a	2e	24	3ea	38	3eb	34	7
14	1b	2f	26	3f	72			8

^{a} Isolated yields bsaed on 1. ^{b} Determined by ^{19}F-NMR except entries 3 and 4. ^{c} 20 mol % of *p*-DNB was added. ^{d} 20 mol % of *t*-Bu$_2$NO was added. ^{e} 20 mol % of HQ was added.

Scheme II



Scheme III



amounts of C$_6$F$_5$Cl when tetrachloromethane was added to the reactions of **1a** with **2b** and **1a** with **8c**. The latter also afforded chloroform. All of these results indicate that the reaction mechanism involves a photoinduced electron-transfer process (PET). However, the products ArC$_6$F$_5$ **3b–f** obtained from the reaction of **1** with arenes **2b–f** were interesting because the photoinduced electron-transfer reaction between aromatic electron acceptors and methylbenzenes (electron donors) usually gives benzyl-substituted products as well as bibenzyl depending on the affinity of the acceptor.[8] The mechanism proposed suggests that the initial step is a PET process followed by proton transfer to yield a radical pair. The coupling of the radical pair yields a benzyl substitution product as well as bibenzyl.

The fact that neither benzylpentafluorobenzenes nor biphenyls were obtained in our case is more consistent with a mechanism involving a PET process which is followed, not by proton transfer, but rather by coupling of pentafluorophenyl radical with toluene radical cation pair (Scheme V). The absence of proton transfer in this reaction may result from the low basicity of the anion radical of **1** and the high reactivity of pentafluorophenyl radical. The lack of CF$_3$SO$_3$-substituted aromatic derivatives in the reaction seems to indicate fast decomposition of the radical anion and the inertness of sulfonate ion CF$_3$SO$_3^-$.[9] This explanation is not unprecedented. Mariano has observed the arylation of toluene with 2-arylpyrrolinium perchlorates in methanol, but not in acetonitrile, under UV irradiation, by a cation radical pair coupling process.[10] However, the solvent effect was not observed in our cases, as the product distribution was nearly unchanged whether in methanol, acetonitrile, or neat.

Like Mariano's results,[10a] the formation of ortho(major) and para but no meta products in the pentafluorophenylation of arenes, anisole, and anilines can also be rationalized by the intermediacy of pentafluorophenyl radical attacking the ring positions of highest odd electron density (i.e., ortho and para).

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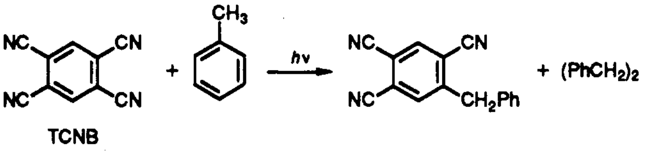
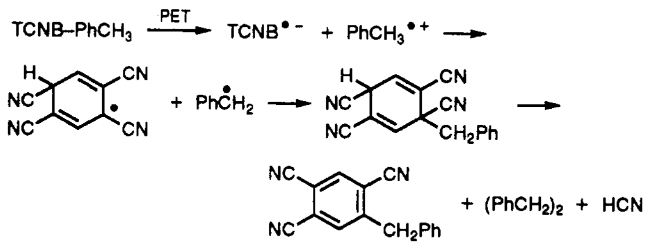
[8] For a review, see Albini, A.; Sulpizio, A. In *Photoinduced Electron transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. 3, pp 89–133. An example is the reaction of tetracyanobenzene (TCNB) with toluene:



This reaction mechanism was proposed as follows:



Lewis, F. D.; Pesrisce, J. R. *Tetrahedron* 1986, *42*, 6207.

[9] For comparison, see: Yamaoko, T.; Adachi, H.; Matsumoto, K.; Watanabe, H. *J. Chem. Soc., Perkin Trans 2* 1990, 1709.

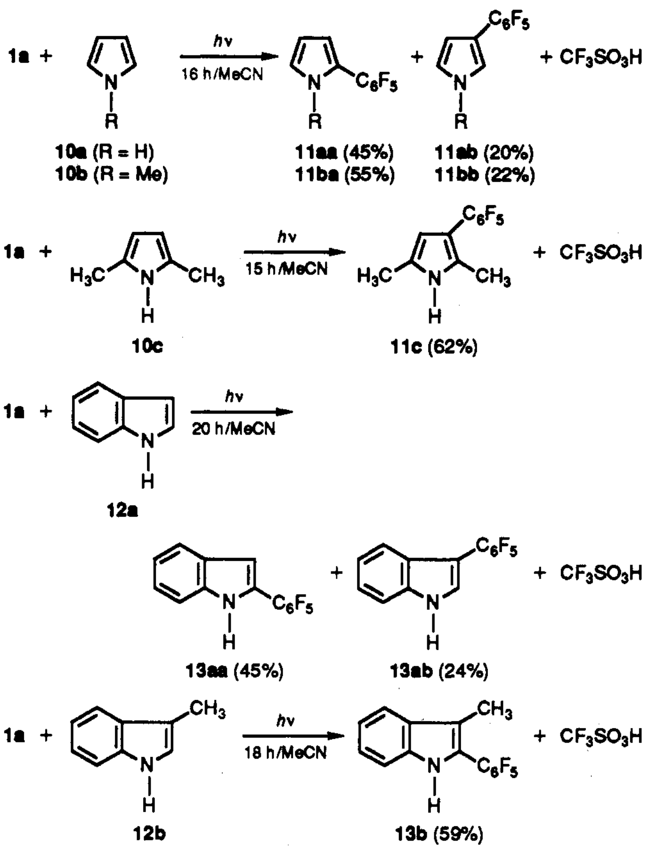
[10] (a) Borg, R. M.; Hueckeroth, R. O.; Lan, A. J. Y.; Quillan, S. L.; Mariano, P. S. *J. Am. Chem. Soc.* 1987, *109*, 2728. (b) Cho, I. S.; Tu, C. L.; Mariano, P. S. *Ibid.* 1990, *112*, 3594.

Table II. Photoinduced Reaction of 1 and Anilines 8

entry	1	8	time (h)	products^a (%)				4	other (%)	
1	1a	8a	12	**9aa**	45	**9ab**	32	3		
2	1b	8a	12		46		30	2		
3	1a	8b	10	**9ba**	50	**9bb**	36	10	8a	9
4	1b		10		45		35	11		
5	1a	8c	8	**9ca**	50	**9cb**	35	12	8b	10
6	1b		8		45		35	10		
7^b	1b		8		34		28	14		
8^c	1b		8		32		20	12		
9^d	1b		8		28		18	14		
10	1a	8d	9	**9da**	47	**9db**	40	10		12^e
11	1b		9		48		36	12		

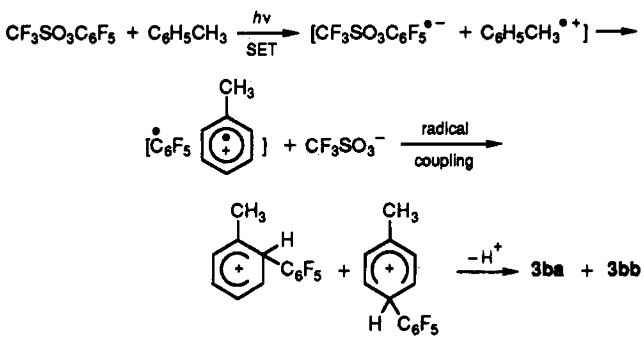
^{a} Isolated yield based on 1. ^{b} 20 mol % of p-DNB was added. ^{c} 20 mol % of t-Bu_2NO was added. ^{d} 20 mol % of HQ was added. ^{e} The yield of N-ethylaniline.

Scheme IV

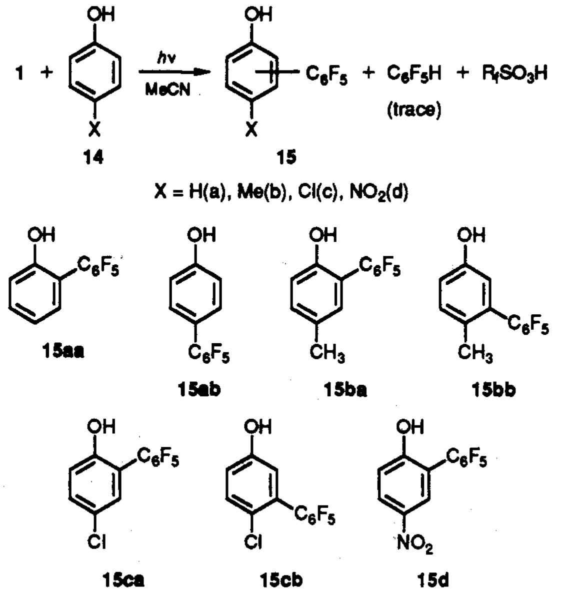


The fact that phenols are electron-rich aromatic compounds, and the observation that hydroquinone significantly suppressed the reaction of 1 with arenes and anilines, prompted us to study the reactions of phenols with 1. Although it has been reported that sodium phenoxide reacts with phenyl halides in an $S_{RN}1$ mechanism,[11] similar results were not obtianed in the case of sodium phenoxide and 1. Instead, the S–O bond cleavage product, pentafluorophenol, was observed, presumably resulting from a simple nucleophilic substitution. However, irradiating an acetonitrile solution of phenols and 1 did give biphenyls (Scheme VI). In the reaction of **14a**, only ortho- and para-substituted products **15aa** and **15ab** were obtained, while the reaction of **14d** gave product **15d** exclusively in low yield. None of these reactions gave pentafluorophenoxyl derivatives. The representative results are shown in Table III.

Scheme V



Scheme VI



Hydroquinones **16** also react with 1 resulting in the formation of products **17** (Scheme VII). Similar to the reaction of C_6F_5I with toluene and benzene, a small amount of byproduct **4** was observed in reactions of 1 with arenes and anilines, but not with benzene, anisoles, and pyrroles. The fact that **8a**, **8b**, and N-ethylaniline were produced from the reaction of corresponding **8b**, **8c**, and **8d** with 1 suggests the possibility that the pentafluorophenyl radical formed during the reaction abstracts a hydrogen atom from the α-carbon of the alkyl group of **8**. For example, see Scheme VIII. Earlier papers also reported that **8b** was obtained from photoinduced reactions of **8c** with aryl halides[12] or diphenyl ketone.[13] However, this result needs more study. Furthermore, the possibility of protonation of $C_6F_5^-$, generated from the reduction of $C_6F_5^\bullet$ by substrates, cannot be excluded.

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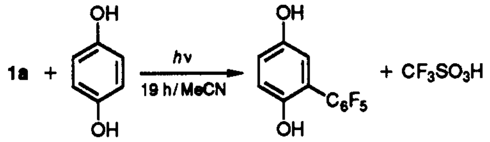
(11) (a) Alam, N.; Amatove, C.; Combellas, C.; Thiebaunt, A.; Verpeaux, J.-N. *Tetrahedron Lett.* 1987, *28*, 6171. (b) Baumgartner, M. T.; Pierini, A. B.; Rossi, R. A. *Tetrahedron Lett.* 1982, *33*, 2323. (c) Beumgelmans, R.; Chastanet, J.; *Tetrahedron Lett.* 1991, *32*, 3487.

Table III. Photoinduced Reaction of 1 with Phenols 14 in MeCN

entry	1 (1:14)^a	phenols	time (h)	products^b (%)	
1	**1a**	**14a**	20	**15aa** (40)	**11ab** (35)
2	**1b** (1:1)	**14a**	20	**15aa** (20)	**15ab** (14)
3	**1b** (1:2)	**14a**	20	**15aa** (32)	**15ab** (24)
4	**1b**	**14a**	20	**15aa** (40)	**15ab** (32)
5	**1b** (1:5)	**14a**	20	**15aa** (44)	**15ab** (34)
6^c	**1b**	**14a**	16	**15aa** (38)	**15ab** (31)
7	**1c**	**14a**	20	**15aa** (36)	**15ab** (30)
8	**1a**	**14b**	19	**15ba** (50)	**15bb** (30)
9	**1b**	**14b**	19	**15ba** (47)	**15bb** (28)
10	**1c**	**14b**	19	**15ba** (42)	**15bb** (26)
11^d	**1b**	**14b**	19	**15ba** (24)	**15bb** (18)
12^e	**1b**	**14b**	19	**15ba** (25)	**15bb** (15)
13	**1a**	**14c**	22	**15ca** (56)	**15cb** (10)
14	**1b**	**14c**	22	**15ca** (55)	**15cb** (10)
15	**1b**	**14d**	24	**15d** (12)^f	

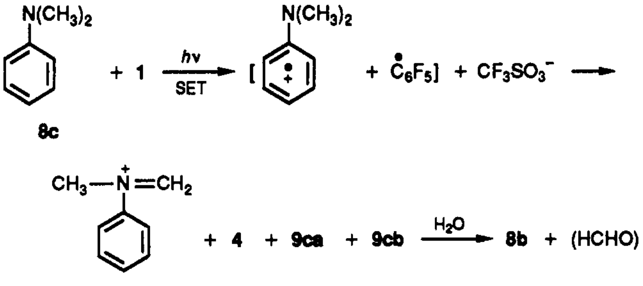
^{a} 1:14 = 1:3 unless otherwise noted. ^{b} Isolated yields based on 1. ^{c} The reaction proceeded in DMF. ^{d} 20 mol % of *p*-DNB was added. ^{e} 20 mol % of *t*-Bu_2NO was added. ^{f} The yield was determined by ^{19}F-NMR.

Scheme VII



16 **17** (53%)

Scheme VIII



8c

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were recorded on an XL-200 instrument using TMS as an external standard. ^{19}F NMR spectra were taken on a Varian EM-360 NMR instrument at 60 MHz using CF_3COOH as an external standard. IR spectra were obtained on a Shimadzu-440 model using KBr pellets. Mass spectra were recorded on a Finnigan-4401 instrument and are reported as *m/z* (relative intensity). All reagents were purified before use. Silica gel (10–40 μm) was used for column chromatography. All the reactions were carried out under an atmosphere of nitrogen. 1 was prepared according to ref 14.

Typical Procedure for the Reaction of 1 with Arenes 2. A solution of **1a** (1.58 g, 5 mmol) and toluene (20 mL) in a Pyrex flask fitted with a dry ice condenser, with stirring, was irradiated by a 450-W medium pressure Hg lamp at a distance of 8 cm for 12 h. The temperature rose to 80 °C as a result of the irradiation (no reaction occurred when the solution was stirred at 80 °C for hours without irradiating). Distillation gave 40 mg (5%) of 4. After toluene was removed, the residue was chromatographed using ether/petroleum ether (1:10) as eluent. 0.70 g (54%) of **2′-methyl-2,3,4,5,6-pentafluorobiphenyl (3ba)** and 0.41 g (32%) of **4′-methyl-2,3,4,5,6-pentafluorobiphenyl (3bb)** were obtained. Irradiating a mixture of **1a** (1.58 g, 5 mmol), toluene (10 mL), and CCl_4 (10 mL) for 12 h gave 50% of **3ba and 3bb**, **4** (3%), and chloropentafluorobenzene (3%). **3ba**: mp 39–40 °C (lit.[4] mp 38–39.5 °C); IR 2965, 1520, 1505, 1185, 990 and 825 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.32 (3 H, s), 7.10–7.32 (2 H, m), 7.40 (1 H, m), 7.64 (1 H, m); ^{19}F-NMR ($CDCl_3$) δ 73.9 (2 F, s), 82.5 (1 F, t), 88.6 (2 F, t); MS 259 ($M^+ + 1$, 100), 258 (M^+, 36.37), 257 (42.73), 239 (20.00). **3bb**: mp 117–119 °C (lit.[4] mp 118 °C); IR 2960, 1525, 1500, 1495, 1200, 1050, and 815 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.32 (3 H, s), 7.22 (2 H, d, *J* = 8 Hz), 7.65 (2 H, d, *J* = 8 Hz); ^{19}F-NMR ($CDCl_3$) δ 68.4 (2 F, d), 82.0 (1 F, t), 88.4 (2 F, t); MS 259 ($M^+ + 1$, 100), 258 (M^+, 54.02), 238 (15.78), 219 (23.45). The reaction proceeded in lower yields when using methanol or cyclohexane as the solvent with the ratios of the products **3ba** and **3bb** being nearly unchanged. When product **3ba** or **3bb** was heated at 80 °C for hours, there was no change (detected by ^{1}H-NMR and ^{19}F-NMR).

2,3,4,5,6-Pentafluorobiphenyl (3a): mp 111–112 °C (lit.[4] mp 112 °C); IR 1540, 1495, 1065, 990, and 795 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.54; ^{19}F-NMR ($CDCl_3$) δ 66.0 (2 F, d), 80.2 (1 F, t), 87.2 (2 F, t); MS 244 (M^+, 100), 225 (14.00), 224 (25.90), 205 (10.55), 122 (7.56).

2′,3′-Dimethyl-2,3,4,5,6-pentafluorobiphenyl (3ca) and 3′,4′-Dimethyl-2,3,4,5,6-pentafluorobiphenyl (3cb). 3ca: mp 47 °C; IR 2955, 1650, 1525, 1455, 1380, 1100, 990, 860, and 770 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.12 (3 H, s), 2.26 (3 H, s), 7.14–7.32 (2 H, m), 7.41 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 63.4 (2 F, d), 79.6 (1 F, t), 86.2 (2 F, t); MS 273 ($M^+ + 1$, 26.45), 272 (M^+, 100), 257 (46.24), 237 (12.45). Anal. Calcd for $C_{14}H_9F_5$: C, 61.76; H, 3.33; F, 34.91. Found: C, 62.02; H, 3.38; F, 34.63. **3cb**: mp 54 °C; IR 2960, 1655, 1495, 1440, 1330, 1145, 900, 860, and 790 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.20 (3 H, s), 2.24 (3 H, s), 7.18 (1 H, m), 7.45 (1 H, m), 7.63 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 62.9 (2 F, d), 79.5 (1 F, t), 86.0 (2 F, t); MS 273 ($M^+ + 1$, 46.24), 272 (M^+, 100), 257 (41.24), 155 (10.24). Anal. Calcd for $C_{14}H_9F_5$: C, 61.76; H, 3.33; F, 34.91. Found: C, 61.87; H, 3.14; F, 34.67.

2′,5′-Dimethyl-2,3,4,5,6-pentafluorobiphenyl (3d): mp 59–61 °C; IR 2950, 1520, 1495, 1320, 1130, 990, 925, 815, and 795 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.14 (3 H, s), 2.37 (3 H, s), 7.24 (3 H, m); ^{19}F-NMR ($CDCl_3$) δ 64.0 (2 F, d), 79.0 (1 F, t), 85.8 (2 F, t); MS 273 ($M^+ + 1$, 13.70), 272 (M^+, 100), 257 (58.32), 237 (39.76), 155 (15.32). Anal. Calcd for $C_{14}H_9F_5$: C, 61.76; H, 3.33; F, 34.91. Found: C, 61.70; H, 3.01; F, 34.60.

2′-Isopropyl-2,3,4,5,6-pentafluorobiphenyl (3ea) and 4′-Isopropyl-2,3,4,5,6-pentafluorobiphenyl (3eb). 3ea: mp 45 °C; IR 2965, 1650, 1600, 1520, 1320, 990, 860, and 760 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 1.32 (6 H, d, *J* = 7 Hz), 3.05 (1 H, m), 7.24 (2 H, m), 7.35 (1 H, m), 7.58 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 68.6 (2 F, d), 82.6 (1 F, t), 88.6 (2 F, t); MS 287 ($M^+ + 1$, 37.88), 286 (M^+, 33.65), 272 (100), 251 (49.14), 201 (32.09), 77 (24.40). Anal. Calcd for $C_{15}H_{11}F_5$: C, 62.92; H, 3.88; F, 33.20. Found: C, 62.53; H, 3.95; F, 32.87. **3eb**: mp 125 °C; IR 2965, 1605, 1455, 1275, 985, 795 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 1.34 (6 H, d, 7 Hz), 3.09 (1 H, m), 7.34 (2 H, d, *J* = 9 Hz), 7.60 (2 H, d, *J* = 9 Hz); ^{19}F-NMR (acetone-d_6) δ 66.0 (2 F, d), 82.5 (1 F, t), 88.5 (2 F, t); MS 287 ($M^+ + 1$, 7.47), 286 (M^+, 42.69), 272 (14.68), 271 (100), 251 (25.48), 77 (11.32). Anal. Calcd for $C_{15}H_{11}F_5$: C, 62.92; H, 3.88; F, 33.20. Found: C, 62.84; H, 3.98; F, 33.13.

2′,4′,6′-Trimethyl-2,3,4,5,6-pentafluorobiphenyl (3f): mp 44.5–46 °C; IR 2950, 1615, 1520, 1505, 1200, 990, and 835 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.10 (6 H, s), 2.36 (3 H, s), 7.10 (2 H, s); ^{19}F-NMR (acetone-d_6) δ 66.1 (2 F, d), 81.9 (1 F, t), 88.2 (2 F, t); MS 287 ($M^+ + 1$, 17.84), 286 (M^+, 100), 271 (82.52), 251 (29.69), 91 (12.84), 77 (10.25). Anal. Calcd for $C_{15}H_{11}F_5$: C, 62.92; H, 3.88; F, 33.20. Found: C, 63.11; H, 3.71; F, 33.18.

Reaction of 1a with Anisole (6a). 1a (1.58 g, 5 mmol) in **6a** (20 mL) was irradiated as above for 10 h. After **6a** was removed, the residue was directly chromatographed to give 0.77 g (56%) of **2′-methoxy-2,3,4,5,6-pentafluorobiphenyl (7aa)** and 0.41 g (30%) of **4′-methoxy-2,3,4,5,6-pentafluorobiphenyl (7ab). 7aa**: mp 47–48 °C (lit.[15] mp 46–47.5 °C); IR 1650, 1510, 1440,

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1300, 1180, 1025, 945, and 760 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 3.32 (3 H, s), 7.01–7.48 (4 H, m); ^{19}F-NMR (acetone-d_6) δ 68.5 (2 F, d), 82.7 (1 F, t), 88.6 (2 F, t); MS 275 (M^+ + 1, 23.85), 274 (M^+, 78.29), 259 (13.77), 231 (100), 205 (26.53). **7ab**: mp 123 °C (lit.[16] mp 123–124 °C); IR 1650, 1600, 1520, 1430, 1250, 1060, 990, and 860 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 3.30 (3 H, s), 6.99 (2 H, d, J = 8 Hz), 7.48 (2 H, d, J = 8 Hz); ^{19}F-NMR (acetone-d_6) δ 64.4 (2 F, d), 82.5 (1 F, t), 88.6 (2 F, t); MS 275 (M^+ + 1, 16.99), 274 (M^+, 100), 259 (19.96), 231 (61.71), 205 (17.29).

Reaction of 1a with 1,4-Dimethoxybenzene (6b). A mixture of **1a** (1.58 g, 5 mmol) and **6b** (2.76 g, 20 mmol) in DMF (15 mL) was irradiated as above for 14 h. After workup, 0.91 g (60%) of **2′,5′-dimethoxy-2,3,4,5,6-pentafluorobiphenyl (7c)** was obtained: mp 62 °C; IR 2960, 1655, 1470, 1230, 1180, 1045, 990, and 720 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 3.82 (3 H, s), 3.92 (3 H, s), 7.08 (2 H, m), 7.35 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 64.6 (2 F, d), 81.2 (1 F, t), 87.2 (2 F, t); MS 305 (M^+ + 1, 17.03), 304 (M^+, 100), 261 (29.10), 138 (95.03), 123 (99.42). Anal. Calcd for $C_{14}H_9O_2F_5$: C, 55.27; H, 2.99; F, 31.23. Found: C, 55.34; H, 2.87; F, 30.98.

Typical Procedure for the Reaction of 1 and Anilines 8. **1a** (1.58 g, 5 mmol) and **8c** (10 mL) were added to a Pyrex flask fitted with a dry ice condenser. The mixture was irradiated, with stirring, by a 450-W medium-pressure Hg lamp for 6 h. ^{19}F-NMR indicated that **1a** had reacted completely. 100 mg (12%) of pentafluorobenzene was obtained by distillation. Unreacted **8c** contaminated with about 10% of **8b** (based on 1) as identified by GC was removed under reduced pressure. The residue was extracted with ether (50 mL), and the mixture was washed with 5% Na_2CO_3 solution (10 mL × 3) and saturated NaCl solution (10 mL) and then dried over $MgSO_4$. After the ether was distilled, the oily residue was chromatographed using ether/petroleum (1:5) as an eluent. 0.72 g (50%) of **9ca** and 0.50 g (35%) of **9cb** were obtained. Under similar conditions, adding CCl_4 (1 mL) produced C_6F_5 Cl (6%) and $CHCl_3$ (4%). **9ca**: mp 56–7 °C; IR 2960, 1620, 1550, 1425, 1340, 995, and 780 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.64 (6 H, s), 7.05 (2 H, m), 7.40 (1 H, m), 7.65 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 62.4 (2 F, d), 80.8 (1 F, t), 87.2 (2 F, t); MS 288 (M^+ + 1, 14.72), 287 (M^+, 99.73), 286 (100), 271 (13.23), 143 (35.82), 43 (11.09). Anal. Calcd for $C_{14}H_{10}NF_5$: C, 58.53; H, 3.52; N, 4.88; F, 33.07. Found: C, 58.53; H, 3.42; N, 4.75; F, 33.07. **9cb**: mp 158 °C (lit.[17] mp 158–160 °C); IR 2960, 1615, 1510, 1490, 1320, 1230, 1065, 820 and 780 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.72 (6 H, s), 6.92 (2 H, d, J = 8.5 Hz), 7.62 (2 H, d, J = 8.5 Hz); ^{19}F-NMR (acetone-d_6) δ 60.2 (2 F, d), 80.0 (1 F, t), 86.4 (2 F, t); MS 288 (M^+ + 1, 15.58), 287 (M^+, 84.43), 286 (100), 271 (14.46), 243 (12.01), 143 (31.13). The reactions of 1 with **8a**, **8b** and **8d** were similar to that of 1 with **8c**. **8a** (9%) formed in the reaction of 1 with **8b** and *N*-ethylaniline (12%) formed in the reaction of 1 with **8d** were identified also by GC.

2′-Amino-2,3,4,5,6-pentafluorobiphenyl (9aa) and 4′-Amino-2,3,4,5,6-pentafluorobiphenyl (9ab). **9aa**: mp 86–88 °C; IR 3400, 3050, 1650, 1500, 1425, 1360, 1260, 1010, 990, and 820 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.40 (2 H, w), 7.10 (2 H, m), 7.38 (1 H, m), 7.62 (1 H, m); ^{19}F-NMR ($CDCl_3$) δ 65.0 (2 F, d), 85.6 (1 F, t), 88.2 (2 F, t); MS 260 (M^+ + 1, 14.20), 259 (M^+, 100), 240 (24.26). Anal. Calcd for $C_{12}H_6NF_5$: C, 55.61; H, 2.34; N, 5.41; F, 36.65. Found: C, 55.60; H, 2.26; N, 5.32; F, 36.62. **9ab**: mp 134 °C (lit.[17] mp 135–136 °C); ^{1}H-NMR ($CDCl_3$) δ 3.60 (2 H, w), 6.74 (2 H, d, J = 8 Hz), 7.68 (2 H, d, J = 8 Hz); ^{19}F-NMR ($CDCl_3$) δ 61.2 (2 F, d), 80.4 (1 F, t), 87.5 (2 F, t); MS 260 (M^+ + 1, 86.40), 259 (M^+, 100), 240 (12.06).

2′-(Methylamino)-2,3,4,5,6-pentafluorobiphenyl (9ba) and 4′-(Methylamino)-2,3,4,5,6-pentafluorobiphenyl (9bb). **9ba**: mp 75 °C; IR 3420, 1605, 1585, 1490, 1310, 1245, 980, and 865 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.45 (3 H, s), 3.21 (1 H, w), 6.99–7.14 (2 H, m), 7.40 (1 H, m), 7.68 (1 H, m); ^{19}F-NMR ($CDCl_3$) δ 63.2 (2 F, d), 82.4 (1 F, t), 88.4 (2 F, t); MS 274 (M^+ + 1, 16.80), 273 (M^+, 100), 258 (24.67). Anal. Calcd for $C_{13}H_8NF_5$: C, 57.14; H, 2.96; N, 5.13; F, 34.77. Found: C, 57.09; H, 2.84; N, 5.02; F, 34.42. **9bb**: mp 142 °C; IR 3450, 1510, 1325, 1300, 1245, 990, and 865 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.60 (3 H, s), 3.42 (1 H, w), 6.92 (2 H, d, J = 8 Hz), 7.60 (2 H, d, J = 8 Hz); ^{19}F-NMR ($CDCl_3$) δ 60.5 (2 F, d), 81.7 (1 F, t), 88.0 (2 F, t); MS 274 (M^+ + 1, 64.25), 273 (M^+, 100). Anal. Calcd for $C_{13}H_8NF_5$: C, 57.14; H, 2.96; N, 5.13; F, 34.77. Found: C, 57.00; H, 2.91; N, 5.04; F, 34.52.

2′-(Diethylamino)-2,3,4,5,6-pentafluorobiphenyl (9da) and 4′-Diethyl-2,3,4,5,6-pentafluorobiphenyl (9db). **9da**: mp 60–62 °C IR 2960, 2870, 1605, 1505, 1485, 1390, and 985 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 1.34 (6 H, t, J = 7 Hz), 2.68 (4 H, q, J = 7 Hz), 7.14 (2 H, m), 7.36 (1 H, m), 8.57 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 62.0 (2 F, d), 80.1 (1 F, t), 87.4 (2 F, t); MS 316 (M^+ + 1, 15.89), 315 (M^+, 36.95), 301 (13.57), 300 (100), 272 (38.08). Anal. Calcd for $C_{16}H_{14}NF_5$: C, 60.94; H, 4.48; N, 4.44; F, 30.13. Found: C, 60.59; H, 4.18; N, 4.28; F, 29.96. **9db**: mp 158 °C; IR 2960, 1620, 1545, 1460, 1350, 980 and 870 cm^{-1}; ^{1}H-NMR (acetone-d_6 δ 1.38 (6 H, 5, J = 7 Hz), 2.70 (4 H, q, J = 7 Hz), 6.90 (2 H, d, J = 8 Hz), 7.42 (2 H, d, J = 8 Hz); ^{19}F-NMR (acetone-d_6) δ 60.2 (2 F, d), 79.4 (1 F, t), 87.2 (2 F, t); MS 316 (M^+ + 1, 47.71), 315 (M^+, 100), 301 (22.77), 300 (68.71), 272 (42.36). Anal. Calcd For $C_{16}H_{14}NF_5$: C, 60.94; H, 4.48; N, 4.44; F, 30.13. Found: C, 60.68; H, 4.32; N, 4.42; F, 30.05.

The Reaction of 1 with Pyrroles 10. A mixture of **1a** (1.58 g, 5 mmol), **10b** (4 mL), and MeCN (10 mL) was irradiated as above for 13 h. After workup, 0.70 g (55%) of **1-methyl-2-(2,3,4,5-pentafluorophenyl)pyrrole (11ba)** and 0.28 g (22%) of **1-methyl-3-(2,3,4,5,6-pentafluorophenyl)pyrrole (11bb)** were obtained. **11ba**: mp 87–88 °C; IR 1510, 1495, 1410, 1360, 1280, 1120, and 990 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 2.95 (3 H, s), 5.61 (2 H, m), 6.33 (1 H, m); ^{19}F-NMR (acetone-*d36*) δ 63.3 (2 F, d), 81.5 (1 F, t), 88.6 (2 F, t); MS 248 (M^+ + 1, 14.60), 247 (M^+, 100), 246 (30.69), 205 (21.88). Anal. Calcd for $C_{11}H_5NF_5$: C, 53.45; H, 2.45; N, 5.67; F, 38.43. Found: C, 53.48; H, 2.19; N, 5.52; F, 38.23. **11bb**: mp 94 °C; IR 1550, 1480, 1235, 1175, 1060, 985, and 800 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 3.47 (3 H, s), 6.20 (2 H, m), 6.95 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 67.0 (2 F, d), 80.8 (1 F, t), 89.2 (2 F, t); MS 248 (M^+ + 1, 18.02), 247 (M^+, 100), 205 (12.26), 123 (13.07). Anal. Calcd for $C_{11}H_6NF_5$: C, 53.45; H, 2.45; N, 5.67; F, 38.43. Found: C, 53.25; H, 2.42; N, 5.50; F, 38.41.

2-(2,3,4,5,6-Pentafluorophenyl)pyrrole (11aa) and 3-(2,3,4,5,6-Pentafluorophenyl)pyrrole (11ab). **11aa**: mp 79–81 °C; IR 3450, 1560, 1450, 1250, 1120, 985, 875, and 790 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 8.67 (1 H, w), 6.24 (1 H, m), 6.62 (1 H, m), 7.01 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 62.4 (2 F, d), 82.4 (1 F, t), 88.2 (2 F, t); MS 234 (M^+ + 1, 21.88), 233 (M^+, 100), 205 (30.64), 187 (28.61), 116 (10.68). Anal. Calcd for $C_{10}H_4NF_5$: C, 51.51; H, 1.73; N, 6.01; F, 40.75. Found: C, 51.26; H, 1.71; N, 5.89; F, 40.49. **11ab**: mp 94 °C; IR 3500, 1560, 1450, 1400, 1295, 1085, 995, and 875 cm^{-1}; ^{1}H-NMR (acetone-d_6) δ 8.69 (1 H, w), 6.40 (2 H, m), 7.04 (1 H, m); ^{19}F-NMR (acetone-d_6) δ 64.2 (2 F, d), 79.1 (1 F, t), 88.0 (2 F, t); MS 234 (M^+ + 1, 34.5), 233 (M^+, 100). Anal. Calcd for $C_{10}H_4NF_5$: C, 51.51; H, 1.73; N, 6.01; F, 40.75. Found: C, 51.19; H, 1.47; N, 5.92; F, 40.79.

2,5-Dimethyl-3-(pentafluorophenyl)pyrrole (11c): mp 104 °C; IR 3450, 2900, 1535, 1515, 1490, 1410, 1320, 1135, 1055, 985, 840, and 780 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.15 (3 H, s), 2.26 (3 H, s), 5.91 (1 H, s), 7.86 (1 H, s); ^{19}F-NMR ($CDCl_3$) δ 64.1 (2 F, d), 81.7 (2 F, t), 86.3 (2 F, t); MS 261 (M^+, 100), 246 (9.74). Anal. Calcd for $C_{12}H_8NF_5$: C, 55.17; H, 3.09; N, 5.36; F, 36.37. Found: C, 55.27; H, 3.28; N, 5.21; F, 36.06.

2-(Pentafluorophenyl)indole (13aa) and 3-(Pentafluorophenyl)indole (13ab). **13aa**: mp 125–128 °C; IR 3450, 1555, 1500, 1490, 1340, 1330, 1230, 1155, 1065, 1010, 980, 975, and 800 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.08–7.48 (4 H, m), 7.65 (1 H, m), 8.80 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 64.7 (2 F, d), 77.8 (1 F, t), 84.2 (2 F, t); MS 282 (M^+ + 1, 15.23), 283 (M^+, 100), 255 (5.23), 142 (12.42), 90 (18.63), 69 (7.46). **13ab**: mp 138–140 °C; IR 3350, 1620, 1545, 1485, 1410, 1335, 1320, 1235, 1095, 980, 840, and 805 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.12–7.40 (4 H, m), 8.40 (1 H, s), 8.49 (1 H, s); ^{19}F-NMR ($CDCl_3$) δ 62.9 (2 F, d), 80.4 (1 F, t), 85.5 (2 F, t); MS 284 (M^+ + 1, 16.54), 283 (M^+, 100), 255 (12.04), 237 (19.71), 143 (10.04), 142 (12.59), 107 (17.95), 57 (33.88), 43 (78.91). Anal. Calcd for $C_{14}H_6NF_5$: C, 59.37; H, 2.14; N, 4.95; F, 33.54. Found: C, 59.37; H, 1.98; N, 4.84; F, 33.42.

3-Methyl-2-(pentafluorophenyl)indole (13b): mp 124–126 °C IR 3450, 1515, 1495, 1360, 1330, 1240, 1170, 1145, 1075, 1045, and 990 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.26 (3 H, s), 7.10–7.39 (3 H,

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m), 7.64 (1 H, d), 8.09 (1 H, s); ^{19}F-NMR ($CDCl_3$) δ 62.0 (2 F, d), 76.3 (1 F, t), 84.0 (2 F, t); MS 297 (M^+, 100), 296 (11.48), 276 (10.14), 130 (21.47). Anal. Calcd for $C_{15}H_8NF_5$: C, 60.61; H, 2.72; N, 4.71; F, 31.96. Found: C, 60.45; H, 2.56; N, 4.78; F, 31.78.

Typical Procedure for the Reaction of 1 with Phenols. 1b (2.32 g, 5 mmol), **14a** (1.41 g, 15 mmol), and acetonitrile (10 mL) were added to a Pyrex flask. Under N_2 atmosphere, the solution was exposed, with stirring, to a medium-pressure mercury lamp (450 W) for 20 h. The mixture was concentrated in vacuo. The oily residue was subject to column chromatography on silica gel using petroleum ether–ether (5:1) as eluent, giving **2-(pentafluorophenyl)phenol (15aa)** (0.49 g, 38%) and **4-(pentafluorophenyl)phenol (15ab)** (0.42 g, 32%). **15aa**: mp 32 °C; IR 3550, 1600, 1520, 1250, 1225, 1055, 980 and 855 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.62–6.95 (4 H, m), 8.15 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 64.0 (2 F, d), 81.9 (1 F, t), 88.5 (2 F, t); MS 261 (M^+ + 1, 10.75), 260 (M^+, 100), 241 (14.15), 231 (13.74), 213 (15.47), 182 (8.45). **15ab**: mp 208–10 °C; IR 3340, 1605, 1490, 1265, 1245, 985, and 820 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 6.75 (2 H, d, J = 8.5 Hz), 7.15 (2 H, d, J = 8.8 Hz), 8.05 (1 H, w); ^{19}F-NMR ($CDCl_3$) 64.8 (2 F, d), 81.8 (1 H, t), 88.5 (2 F, t); MS 261 (M^+ + 1, 20.43), 260 (M^+, 100), 241 (8.41), 231 (6.03), 45 (28.67), 44 (36.38).

2-(Pentafluorophenyl)-4-methylphenol (15ba) and 3-(Pentafluorophenyl)-4-methylphenol (15bb). 15ba: mp 58 °C; IR 3350, 2840, 1605, 1530, 1490, 1400, 1320, 1240, 1125, 1060, 985, and 885 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.75 (3 H, s), 6.25–6.62 (3 H, m), 8.65 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 64.4 (2 F, d), 81.8 (1 F, t), 88.5 (2 F, t); MS 275 (M^+ + 1, 15.24), 274 (M^+, 100), 255 (10.19), 198 (12.94). Anal. Calcd for $C_{13}H_7OF_5$: C, 56.62; H, 2.60; F, 34.90. Found: C, 56.34; H, 2.49; F, 34.98. **15bb**: mp 86 °C; IR 3350, 1660, 1610, 1580, 1510, 1490, 1270, 1230, 1160, 1120, 1055, and 995 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.73 (3 H, s), 6.23–6.53 (3 H, m), 8.19 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 65.4 (2 F, d), 81.3 (1 H, t), 87.5 (2 F, t); MS 275 (M^+ + 1, 24.18), 274 (M^+, 100), 255 (22.76), 107 (13.18). Anal. Calcd for $C_{13}H_7OF_5$: C, 56.62; H, 2.60; F, 34.90. Found: C, 56.24; H, 2.32; F, 35.03.

2-(Pentafluorophenyl)-4-chlorophenol (15ca) and 3-(Pentafluorophenyl)-4-chlorophenol (15cb). 15ca: IR 3400, 1515, 1495, 1300, 1260, 1220, 1185, 1100, 1065, 990, 945, and 875 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.25–6.75 (3 H, m), 9.13 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 64.0 (2 F, d), 80.5 (1 F, t), 87.9 (2 F, t); MS 297 (M^+, 5.52), 296 (M^+ + 1, 23.47), 294 (M^+, 100), 261 (12.73), 260 (15.51), 231 (21.40), 200 (11.98), 193 (10.62). Anal. Calcd for $C_{12}H_4OClF_5$: C, 48.92; H, 1.37; Cl, 12.03; F, 32.25. Found: C, 48.78; H, 1.02; Cl, 11.79; F, 32.01. **15cb**: mp 89 °C; IR 3450, 1605, 1545, 1500, 1280, 1145, 1025, 985, and 820 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.30–6.82 (3 H, m), 8.75 (1 H, w); ^{19}F-NMR ($CDCl_3$) δ 64.8 (2 F, d), 80.7 (1 F, t), 87.8 (2 F, t); MS 298 (M^+ + 1, 4.87), 297 (M^+, 10.62), 296 (M^+ + 1, 24.04), 295 (M^+, 70.30), 262 (33.21), 260 (100), 43 (43.26). Anal. Calcd for $C_{12}H_4OClF_5$: C, 48.92; H, 1.37; Cl, 12.03; F, 32.25. Found: C, 48.67; H, 1.21; Cl, 12.00; F, 32.01.

2-(Pentafluorophenyl)-4-nitrophenol (15d): mp 100–102 °C; IR 330, 1605, 1585, 1490, 1340, 1280, 1200, 1160, 1105, 985, 860, and 720 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.5 (1 H, w), 6.23 (1 H, dd, J = 9.5, 3.0 Hz), 7.39 (2 H, m); ^{19}F-NMR ($CDCl_3$) δ 64.2 (2 F, d), 79.6 (1 F, t), 87.4 (2 F, t); MS 305 (M^+, 21.54), 231 (10.08), 211 (13.51), 183 (13.11), 140 (16.10), 139 (Ar^+ + 1, 100), 123 (10.41), 109 (53.94), 93 (25.10), 65 (83.95). Anal. Calcd for $C_{12}H_4NO_3F_5$: C, 47.21; H, 1.36; N, 4.59; F, 31.12. Found: C, 47.00; H, 1.39; N, 4.55; F, 30.95.

The reaction of hydroquinone **16** and **1** was carried out similarly. **2,5-Dihydroxyl-2′,3′,4′,5′,6′-pentafluorobiphenyl (17)** was obtained in 55% yield: mp 178–180 °C. ^{1}H-NMR (acetone-d_6) δ 6.40–7.02 (3 H, m), 7.40 (1 H, s), 8.00 (1 H, s); ^{19}F-NMR (acetone-d_6) δ 65.0 (2 F, d), 80.1 (1 F, t), 87.2 (2 F, t). Anal. Calcd for $C_{12}H_5O_2F_5$: C, 52.19; H, 1.83; F, 34.40. Found: C, 52.00; H, 1.39; F, 34.09.

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