4-Nitrophenyltriflate and 4-Nitrophenylnonaflate as New Perfluoroalkanesulfonyl Transfer Agents: Experimental and Computational Studies

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Nucleophilic displacement at the sp^3 carbon of an alkyl perfluoroalkanesulfonate[1] has found numerous applications in organic synthesis. The discovery of transition-metal-catalyzed cross-coupling reactions[2] of aryl and vinyl triflates with different organometallic reagents as well as with nitrogen- and oxygen-centered nucleophiles[3] has broadened considerably the application scope of triflates as these reactions deal with the sp^2 carbon of triflates. Aryl triflates are usually prepared by treatment of the corresponding phenols with triflic anhydride in the presence of a base such as pyridine and triethylamine.[4] Other reagents, such as imidazole triflate,[5] *N*-phenyltriflimide,[6] and very recently *N*-(2-pyridyl)triflimide,[7] have been developed by the groups of Effenberger, McMurry, and Comins, respectively, for the purpose of regioselective synthesis of enol triflates from ketones. Recent applications of aryl triflate and enol triflate in complex natural product synthesis can be found in Evans's landmark synthesis of vancomycin[8] and Nicolaou's approach[9] toward the total synthesis of CP molecules.

In connection with our ongoing research in the field of nucleophilic aromatic substitution reactions (S_NAr),[10] we had the occasion to study the reaction of *o*- and *p*-nitro-substituted phenyl triflate and nonaflate with phenols. We wish to report in this paper that 4-nitrophenyl triflate (**1**) and 4-nitrophenyl nonaflate (**2**) are efficient perfluoroalkanesulfonyl transfer agents under very mild conditions.[11,12]

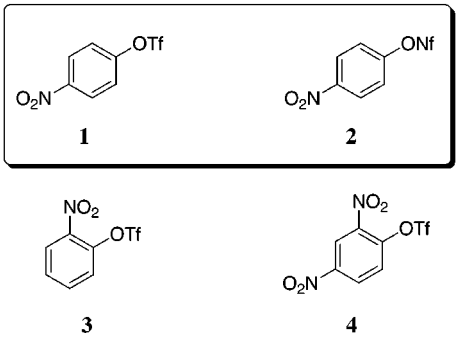

Figure 1.

The known 4-nitrophenyl triflate (**1**), 2-nitrophenyl triflate (**3**) and 2,4-dinitrophenyl triflate (**4**)[1] (Figure 1) were prepared in high yields by treating the corresponding phenol with triflic anhydride under standard conditions. We first examined the reaction of 4-*tert*-butylphenol (**5**) with reagents **1**, **3**, and **4** (Table 1). It was found that reaction of **1** or **3** with **5** in DMF at room temperature in the presence of 2 equiv of K_2CO_3 gave an excellent yield of 4-*tert*-butylphenyl triflate, together with the regeneration of the corresponding nitrophenol. Control experiments showed that **1** is more reactive than **3** as trifluoromethanesulfonyl transfer agent. Biaryl ether resulting from the S_NAr reaction was not detected from these experiments. While the reaction proceeded in acetonitrile (entry b), the time required for completion was lengthened significantly in agreement with the ionic mechanism. A different reactivity profile was, however, observed for the 2,4-dinitrophenyl triflate (**4**). In this case, exclusive S_NAr reaction took place to give the coupling product (biaryl ether **7**, entry d) in analogy with Hamilton's observation using 2,6-dinitrophenyltosylate.[13] To test the generality of this new triflate transfer reaction, other substrates were examined employing potassium carbonate in DMF as standard conditions using **1** as triflating agent. The results, depicted in Table 1, showed that both electron-rich and -poor aryl phenols could be triflated in good to excellent yields. Naphthol (**12**) and heteroaromatic compounds such as 2-hydroxy-6-methyl pyridine (**14**) could also be transformed into the corresponding triflate under identical conditions. The regenerated 4-nitrophenol can be removed by washing the reaction mixture with aqueous NaOH solution or more efficiently by filtration through a short pad of basic aluminum column.

Another important feature of the present method is its chemoselectivity. The aliphatic hydroxyl function was inert under our reaction conditions, and consequently, phenol can be selectively triflated in the presence of alcohol (Table 1, entries i−k), which was difficult to realize under classic conditions (e.g., triflic anhydride, Et_3N).

Very recently, it has been demonstrated that aryl nonaflates effectively enter into the field of palladium-

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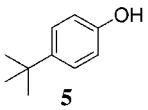
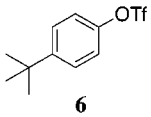
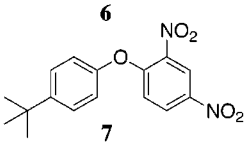
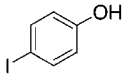
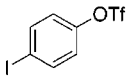
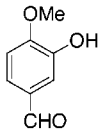
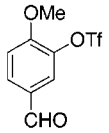
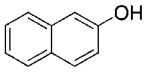
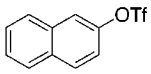
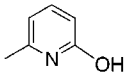
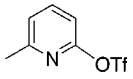
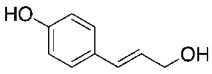
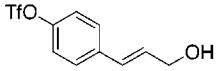
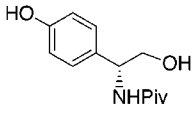
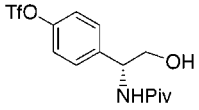
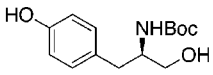
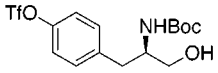
Table 1. Preparation of Aryl Triflates Using Nitrophenyl Triflates as Triflating Agents

Entry	Phenols	Conditions[a]	Product	Yield, %[b]
a	 **5**	K_2CO_3, DMF, **1**, 4h	 **6**	83
b	**5**	CsF, MeCN, **1**, 22h,	**6**	88
c	**5**	K_2CO_3, DMF, **3**, 10h	**6**	89
d	**5**	K_2CO_3, DMF, **4**, 2h	 **7**	91
e	 **8**	K_2CO_3, DMF, **1**, 1.5h	 **9**	90
f	 **10**	K_2CO_3, DMF, **1**, 2h	 **11**	92
g	 **12**	K_2CO_3, DMF, **1**, 1h	 **13**	92
h	 **14**	K_2CO_3, DMF, **1**, 4h	 **15**	75
i	 **16**	K_2CO_3, DMF, **1**, 0.5h	 **17**	81
j	 **18**	K_2CO_3, DMF, **1**, 2h	 **19**	60
k	 **20**	K_2CO_3, DMF, **1**, 2h	 **21**	64

[a] All reactions were performed on 0.5−1 mmol scale at room temperature; [b] Isolated yield

catalyzed cross-coupling reactions.[14] In fact, aryl nonaflates displayed a higher reactivity compared to the corresponding aryl triflates in its reaction with arylzinc derivatives and with diphenylphosphine−borane complex. We thus prepared the crystalline 4-nitrophenyl nonaflate **2** by reaction of 4-nitrophenol with nonafluorobutanesulfonic fluoride[15] and examined its reactivity profile toward phenol. As shown in Scheme 1, it turned out that compound **2** is slightly more prone to S_NAr (C−O cleavage) reaction compared to triflate **1** and that the ratio of C−O cleavage vs S−O cleavage depends on the base used. When K_2CO_3 and Cs_2CO_3 were used as base, S_NAr coupling product **23** was obtained in 10% and 28% yield, respectively. However, with cesium fluoride as base, nonafluorobutanesulfonyl transfer reaction took place exclusively at the expense of S_NAr reaction. Under optimized conditions (CsF, DMF, rt), 4-*tert*-butylphenyl nonaflate **22** was obtained in essentially quantitative yield. Nonaflates of other phenol prepared in this way were listed in Scheme 1. As is seen, the isolated yield of desired products was in general excellent.

It was known that nucleophilic reaction of nitrophenyl sulfonate gave rise to either C−O or S−O cleavage depending on the polarizability of the nucleophiles.[16] However, the corresponding nitrophenyl triflates were known to be less prone to undergo *S−O* cleavage and gave instead a high yield of S_NAr products when diethyl

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(15) (a) Niederprüm, H.; Voss, P.; Beyl, V. *Liebigs Ann. Chem.* **1973**, 20−32. (b) Subramanian, L. R.; Bentz, H.; Hanack, M. *Synthesis* **1973**, 293−294.

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Scheme 1

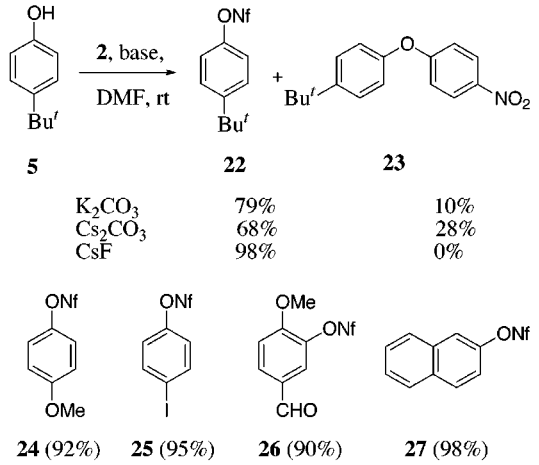


Table 2

	compd **1**		compd **3**		compd **4**	
	C	S	C	S	C	S
E(LUMO+1)[a]	−2.22		−1.96		−2.61	
1s	+0.03	+0.01	+0.04	+0.01	+0.03	+0.01
2px	+0.03	+0.23	+0.04	+0.31	+0.03	−0.28
2py	−0.05	+0.44	−0.05	+0.32	−0.04	+0.29
2pz	−0.30	−0.29	−0.33	−0.33	−0.40	−0.33
E(LUMO)[a]	−4.12		−3.86		−4.37	
1s	−0.03	−0.34	−0.03	−0.33	−0.03	−0.32
2px	−0.04	−0.16	−0.03	−0.26	−0.03	−0.26
2py	+0.06	+0.17	+0.06	+0.04	+0.05	+0.03
2pz	+0.02	+0.25	+0.04	+0.20	+0.07	+0.19
E(HOMO)[a]	−10.73		−10.46		−11.05	
l_C, l_S[b]	0.05	1.31	0.09	1.30	0.15	1.29
l_S/l_C	26.2		14.4		8.6	
O−N$_{ortho}$−C−C[c] (deg)			7		7	
O−N$_{para}$−C−C[c] (deg)	0				0	

[a] eV. [b] Electron density. [c] Dihedral angle.

malonate[17] and secondary amines[18] were used as nucleophiles. In an isolated example, the reaction of a phenol with aryl triflate was observed to give the biaryl ether as a side product.[17b,c] To rationalize the observed experimental results, we have undertaken the calculation of frontier molecular orbital energy levels and the atomic charges of **1**, **3**, **4**, and **5** at the RHF AM1 level[19] with mixed parameters (C, N, O, F, and H, AM1; S, MNDO) using MOPAC program (version 5.0).[20]

Frontier orbital energies and corresponding coefficients of **1**, **3**, and **4** and those of aniline, phenol, 4-*tert*-butylphenol **5**, and 4-*tert*-butylphenoxide were listed in Tables 2 and 3, respectively.

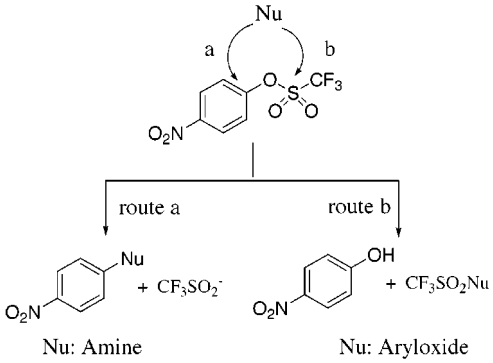
The relative disposition of the frontier orbitals of reagents **1**, **3**, and **4** (Table 2) and that of nucleophiles (Table 3) suggests that the reactions are predominantly controlled by LUMO of the nitrophenyl triflates and HOMO of the nucleophile on the basis of their narrower LUMO−HOMO gap. On the other hand, data shown in Table 3 revealed that the HOMO energy of aniline

Table 3

	PhNH$_2$	PhOH	*p*-^{t}BuPhOH	*p*-^{t}BuPhO$^-$
E(LUMO)[a]	0.64	0.39	0.46	5.53
E(HOMO)[b]	−8.52	−9.11	−8.90	−2.81
l_N or l_O	−0.33	−0.25	−0.25	−0.52

[a] eV. [b] Electron density.

Scheme 2. Dual Reactivities of 4-Nitrophenyl Triflate



(HOMO = −8.52 eV) is higher than that of phenol (HOMO = −9.11 eV) and 4-*tert*-butylphenol (HOMO = −8.90 eV) but considerably lower than that of 4-*tert*-butylphenoxide (HOMO = −2.81 eV), which explained their reactivity difference.

A priori, steric as well as field effect should favor the nucleophilic attack on carbon rather than on sulfur atom and the retarding effect of a CF_3 group on the reactivity of halides in the S_N2 reaction[21] is indeed well established. The different regioselectivity exhibited by soft nucleophiles (aniline and other secondary amines) and hard nucleophiles (phenoxide) could tentatively be explained as follows. First, from the above calculation (Table 2), it is seen that the positive charge was largely located on the sulfur atom rather than on the carbon atom (polarity index[22] $P = l_S/l_C = 26.2$ for **1**). Thus, under charge control,[24] a low polarizable nucleophile such as phenoxide (hard nucleophile)[23] attacks preferentially the sulfur atom leading to the observed products (Scheme 2, path b). Second, while the LUMO of compound **1** correspond to the orbitals of triflate group, the LUMO + 1 correspond to the π system of the aromatic ring, which is conjugated with the triflate group. The coefficient of the *pz* orbital of C-1 is equivalent to that of sulfur atom. Since the reaction of a soft nucleophile tends to imply a late transition state with strong mutual interaction between two reactants, attack of nitrogen on the sulfur atom would be disfavored under orbital control[24] because of important steric interaction between the entering nitrogen substituents (hydrogen or alkyl) and the triflate group.

It is seen that the LUMO energy of **1** is lower than that of **3** ($\Delta E = 0.26$ eV) and that the *o*-nitro group in **3** deviated from the plane of the aromatic ring [dihedral angle (O−N−C−C): 7° in minimized structure of **3**] probably due to the steric congestion. This led to the

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(24) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223−234.

conclusion that the charge stabilization effect of the intermediate should be less favored in **3** than in **1**, which is indeed in accord with the higher reactivity of **1** as a trifluoro methanesulfonyl transfer agent. On the other hand, charge analysis of 2,4-dinitrophenyl triflate (**4**) reveals that the positive charge on the sulfur atom is still greater than that on the carbon atom. However, the polarity index is decreased ($P = l_S/l_C = 8.6$ for **4**) and the *pz* orbital coefficient of C-1 carbon is greater than that of sulfur. It is known that S_NAr (C−O bond scission) reactions have especially high Hammett ρ values (+4 to +5) and, consequently, are very sensitive to electronic effect.[25] The presence of the second strong electron-withdrawing nitro group on the aromatic ring thus switched the attack of nucleophile on carbon atom, and the S_NAr pathway became predominant in the reaction of **4** with phenol (Table 1, entry d).

In conclusion, we have shown that 4-nitrophenyl triflate (**1**) as well as 4-nitrophenyl nonaflate **2** are excellent perfluoroalkanesufonyl transfer agents. The crystalline reagents **1** and **2** are not hygroscopic and appear to be indefinitely stable. From the viewpoint of atom economy,[26] compound **1** is superior to *N*-phenyltriflimide[6] and *N*-(2-pyridyl)triflimide[7] where one of the two trifluoromethanesulfonyl groups was wasted.

Experimental Section

General procedures and methods for characterization are described elewhere.[27] Melting points are uncorrected.

4-Nitrophenyl Triflate 1. To a cooled (−10 °C) solution of 4-nitrophenol (1.38 g, 9.92 mmol) and Et_3N (4.17 mL, 29.73 mmol) in CH_2Cl_2 (20 mL) was added triflic anhydride (2.5 mL, 14.87 mmol). After being stirred at −10 °C for 20 min, the reaction mixture was diluted with CH_2Cl_2 (20 mL), and the organic phase was washed with aqueous $NaHCO_3$ solution, water, and brine successively. Purification of the crude reaction mixture by flash chromatography (SiO_2, eluent: EtOAc/heptane 1/5) afforded product **1** (2.5 g, 93.0%) as a white solid: mp 52−53 °C (lit.[5] mp 52−53 °C); IR ($CHCl_3$) ν 1623, 1539, 1490, 1434, 1349 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.49 (d, J = 9.3 Hz, 2H), 8.38 (d, J = 9.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 118.8 (q, J = 318.2 Hz), 122.6, 126.1, 147.1, 153.2; CIMS (*m*/*z*) 272 $(M + H)^+$. Anal. Calcd for $C_7H_4F_3NO_5S$: C, 31.00; H, 1.49; N, 5.17. Found: C, 31.27; H, 1.72; N, 5.01.

2-Nitrophenyl Triflate 3. Following the same procedure, compound **2**[18] was obtained in 80% yield as pale yellow oil: ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 (br d, J = 8.0 Hz, 1H), 7.60 (br t, J = 8.0 Hz, 1H), 7.77 (dt, J = 1.6, 8.0 Hz, 1H), 8.19 (dd, J = 1.6, 8.0 Hz, 1H); CIMS *m*/*z* 272 $(M + H)^+$.

2,4-Nitrophenyl Triflate 4. Following the same procedure, compound **3** was obtained in 80% yield as a yellow solid: mp 51−52 °C (lit.[28] mp 50−51 °C); ^1H NMR (250 MHz, $CDCl_3$) δ 7.75 (d, J = 9.0 Hz, 1H), 8.65 (d, J = 2.7, 9.0 Hz, 1H), 9.04 (d, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 118.6 (q, J = 318.4 Hz), 122.6, 125.8, 129.8, 145.3, 146.7; CIMS (*m*/*z*) 317 (M + H).

Typical Experimental Procedure Using 1 as Trifluoromethanesulfonyl Transfer Reagent. To a solution of phenol (1.0 mmol) in DMF (10 mL) were added 4-nitrophenyltriflate (1.0 mmol) and K_2CO_3 (2.0 mmol) at room temperature. The reaction solution became yellow due to the generation of 4-nitrophenol. At the end of the reaction (followed by TLC), the yellow solution was diluted with H_2O (10 mL) and extracted with EtOAc. The combined organic phases were washed with 1 N NaOH and brine, dried (Na_2SO_4), and evaporated. The residue (contaminated with less than 10% of 4-nitrophenol) was filtered through a short pad of silica gel to afford the desired triflated compound.

4-*tert*-Butylphenyl triflate 6: colorless oil;[29] ^1H NMR (200 MHz, $CDCl_3$) δ 1.66 (s, 9H), 7.22 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H). Anal. Calcd for $C_{11}H_{13}F_3O_3S$: C, 46.81; H, 4.64. Found: C, 46.93; H, 4.62.

4-Iodophenyl triflate 9: colorless oil;[30] ^1H NMR (200 MHz, $CDCl_3$) δ 7.04 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H); EIMS (*m*/*z*) 372 $(M^{\bullet+})$.

5-Formyl-2-methoxyphenyl triflate 11: colorless oil;[31] IR ($CHCl_3$) ν 1701, 1609, 1518, 1427, 1286 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.19 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 1.9 Hz, 1H), 7.90 (dd, J = 1.9, 8.6 Hz, 1H), 9.90 (s, 1H); CIMS (*m*/*z*) 285 $(M + H)^+$.

2-Naphthyl triflate 13: mp 30−31 °C (lit.[6b] mp = 31−32 °C); IR ($CHCl_3$) ν 1631, 1600, 1513, 1463, 1425 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.38 (dd, J = 2.5, 9.0 Hz, 1H), 7.56−7.60 (m, 2H), 7.76 (d, J = 2.5 Hz, 1H), 7.86−7.91 (m, 2H), 7.93 (d, J = 9.0 Hz, 1H); CIMS (*m*/*z*) 277 $(M + H)^+$.

2-Trifluoromethanesulfonyloxy-6-methylpyridine 15: mp 164−165 °C; IR ($CHCl_3$) ν 1675, 1613, 1569, 1425 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 2.57 (s, 3H), 6.99 (d, J = 7.8 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.77 (t, J = 7.8 Hz, 1H); CIMS (*m*/*z*) 242 $(M + H)^+$.

Trifluoromethanesulfonic acid 4-(3-hydroxy-propenyl)-phenyl ester 17: IR ($CHCl_3$) ν 3613, 3445, 3030, 2931, 2875, 1504, 1427, 1258 cm^{-1}; ^1H NMR (250 MHz, acetone-d_6) δ 4.02 (t, J = 5.5 Hz, 1H, OH), 4.27 (dt, J = 1.7, 5.5 Hz, 2H), 6.51 (dt, J = 4.9, 16.0 Hz, 1H), 6.70 (dt, J = 1.7, 16.0 Hz, 1H), 7.40 (d, J = 8.9 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 62.5, 117.2 (q, J = 317.8 Hz), 122.1, 127.4, 128.6, 133.5, 138.8, 149.1; EIMS (*m*/*z*) 282 $(M^{\bullet+})$.

L-Trifluoromethanesulfonic acid 4-[1-(2,2-dimethylpropionylamino)-2-hydroxyethyl]phenyl ester 19: mp 73−74 °C; $[\alpha]_D = -40°$ (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν 1656, 1500, 1425 cm^{-1}; ^1H NMR (250 MHz, acetone-d_6) δ 1.20 (s, 9H), 3.82 (m, 2H), 4.19 (t, J = 5.8 Hz, 1H, OH), 5.05 (m, 1H), 7.18 (m, 1H, NH), 7.39 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 27.8, 39.2, 55.6, 65.6, 118.5 (q, J = 318.0 Hz), 121.8, 129.9, 143.7, 149.3, 178.1; EIMS (*m*/*z*) 351 $(M - H_2O)^+$.

L-Trifluoromethanesulfonic acid 4-(2-*tert*-butoxycarbonylamino-3-hydroxypropyl)phenyl ester 21: mp 94−95 °C; $[\alpha]_D = +21°$ (*c* 0.3, $CHCl_3$); IR ($CHCl_3$) ν 1708, 1497, 1427, 1370 cm^{-1}; ^1H NMR (250 MHz, acetone-d_6) δ 1.33 (s, 9H), 2.82 (dd, J = 8.5, 13.6 Hz, 1H), 3.03 (dd, J = 5.6, 13.6 Hz, 1H), 3.49−3.60 (m, 2H), 3.83 (m, 1H), 3.97 (t, J = 5.5 Hz, 1H, OH), 5.85 (d, J = 7.9 Hz, 1H, NH), 7.35 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H); ^{13}C NMR (acetone-d_6) δ 28.3, 37.2, 54.5, 64.1, 78.5, 118;5 (q, J = 318.0 Hz), 121.6, 132.0, 141.2, 148.8, 156.1; EIMS (*m*/*z*) 368 $(M^{\bullet} - CH_2OH)^+$, 343 $(M - C_4H_8)^+$, 326 $(M - O^tBu)^+$.

Biaryl ether 7: mp 107−108 °C (lit.[32] mp 108.5−110 °C); IR ($CHCl_3$) ν 1613, 1594, 1544, 1506, 1481 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.36 (s, 9H), 7.05 (d, J = 9.2 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 8.31 (dd, J = 2.6, 9.2 Hz, 1H), 8.85 (d, J = 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.0, 35.3, 118.9, 120.7, 122.7, 128.2, 129.3, 139.9, 142.0, 150.5, 151.6, 157.0; EIMS (*m*/*z*) 317 $(M + H)^+$.

4-Nitrophenyl Nonaflate 2. A solution of 4-nitrophenol (1.39 g, 10 mmol), triethylamine (2.08 mL, 15.0 mmol), and nonafluorobutanesulfonic fluoride (2.20 mL, 12.0 mmol) in CH_2Cl_2 was stirred at room temperature for 12 h. The reaction mixture was then diluted with water and was basified with aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and brine, dried (Na_2SO_4), and evaporated to dryness. Purification by flash chromatography (SiO_2, Et_2O/heptane = 1/20) gave product **2** (3.80 g, 90%) as a white solid: mp 70 °C; IR ($CHCl_3$) ν 1620, 1591, 1535, 1487,

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1433, 1243, 1147 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.50 (d, J = 9.2 Hz, 2H), 8.38 (d, J = 9.2 Hz, 2H); CIMS (m/z) 422 $(M + H)^+$. Anal. Calcd for $C_{10}H_4F_9O_5S$: C, 28.52; H, 0.96; N, 3.32. Found: C, 28.56; H, 0.85; N, 3.29.

Typical Experimental Procedure Using 2 as Nonafluorobutanesulfonyl Transfer Reagent. The same procedure described for the triflate transfer reaction was used except that CsF was employed as the base. The product was purified by column chromatography on basic aluminum.

4-*tert*-Butylphenyl nonaflate 22: colorless oil; IR ($CHCl_3$) ν 1503, 1423, 1353, 1243 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.34 (s, 9H), 7.21 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H); CIMS (m/z) 432 (M^+).

4-Methoxyphenyl nonaflate 24: colorless oil; IR ($CHCl_3$) ν 1596, 1502, 1424, 1352, 1242 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.92 (d, J = 9.1 Hz, 2H), 7.22 (d, J = 9.1 Hz, 2H); CIMS (m/z) 407 $(M + H)^+$.

4-Iodophenyl nonaflate 25: colorless oil;[14] IR ($CHCl_3$) ν 1478, 1427, 1353, 1243 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 7.04 (d, J = 8.9 Hz, 2H), 7.79 (d, J = 8.9 Hz, 2H); CIMS (m/z) 502 (M^+).

5-Formyl-2-methoxyphenyl nonaflate 26: colorless oil; IR ($CHCl_3$) ν 1698, 1610, 1513, 1429, 1286, 1242 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.19 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 1.9 Hz, 1H), 7.90 (dd, J = 1.9, 8.5 Hz, 1H), 9.90 (s, 1H); CIMS (m/z) 435 $(M + H)^+$.

2-Naphthyl nonaflate 27: colorless oil;[14] IR ($CHCl_3$) ν 1601, 1511, 1424, 1352, 1242 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.40 (dd, J = 2.5, 9.0 Hz, 1H), 7.54−7.65 (m, 2H); 7.78 (d, J = 2.5 Hz, 1H), 7.85−7.91 (m, 2H), 7.93 (d, J = 9.0 Hz, 1H); CIMS (m/z) 427 $(M + H)^+$.

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