Palladium-Catalyzed Cross-Coupling Reactions with Aryl Nonaflates: A Practical Alternative to Aryl Triflates

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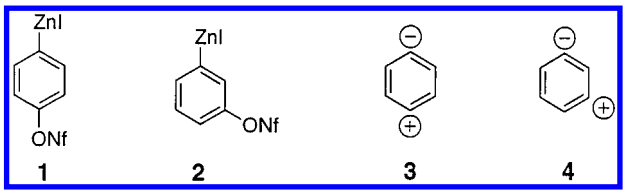
Introduction

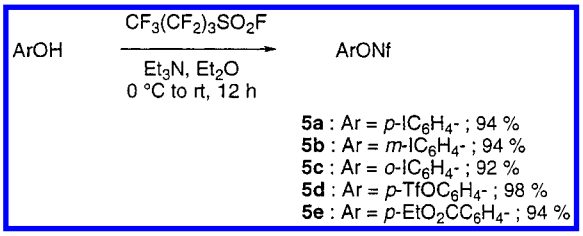
Cross-coupling reactions with aryl triflates ($ArOSO_2CF_3$) have been extensively used in synthesis.[1,2] The electron-withdrawing ability of the CF_3SO_2 group seems to be essential for a rapid insertion of palladium(0) to the C−O bond of the aryl triflate. Due to the moderate reactivity of aryl triflates and the high cost of the triflate functionality, aryl fluorosulfonates have been proposed as an alternative to triflates.[2] These sulfonates display similar reactivities compared to aryl triflates and give excellent results in various cross-coupling reactions. However, the not broadly commercialized fluorosulfonate anhydride ($(FSO_2)_2O$; bp = 50 °C) has a comparable toxicity to phosgene[3] and should be handled with care. Alternatively, aryl fluoroalkanesulfonates ($ArOSO_2(CF_2)_nCF_3$) are easily prepared using commercially available fluoroalkanesulfonic anhydrides or halides.[4] Especially attractive are aryl nonaflates (ArONf = $ArOSO_2(CF_2)_3CF_3$) which are readily prepared[5] and are stable to flash column chromatography. Herein, we wish to show their utility in palladium-catalyzed cross-coupling reactions and their use for the preparation of new polyfunctional arylzinc reagents such as **1** and **2** which are new multicoupling reagents.[6]



1 **2** **3** **4**

These zinc reagents possess both an electrophilic (C−ONf bond) and a nucleophilic (carbon−zinc bond) function and give a selective access to various polyfunctional terphenyls by using palladium(0)-catalyzed cross-coupling reactions. Respectively, the new reagents **1** and **2** are synthetic equivalents of the synthons **3** and **4**.

Scheme 1



Results and Discussion

Aryl nonaflates **5** are readily prepared by the reaction of phenols with commercially available $CF_3(CF_2)_3SO_2F$ (1.5 equiv)[5] in the presence of triethylamine (1.5 equiv) in ether at 0 °C to rt. The conversion is complete after a reaction time of 12 h affording the pure aryl nonaflates **5a**−**e** in 92−98% yield (Scheme 1).

The palladium-catalyzed cross-coupling reaction[7] of the aryl nonaflate **5e** with 3-(trifluoromethyl)phenylzinc bromide[8] in the presence of palladium bis(dibenzylideneacetone)[9] ($Pd(dba)_2$; 1 mol %) and bis(diphenylphosphino)ferrocene[10] (dppf; 1 mol %, 60 °C, 5 h) furnishes 4-(ethoxycarbonyl)-3′-(trifluoromethyl)biphenyl (**6a**) in 90% yield. Compared to the corresponding aryl triflates, aryl nonaflates display a slightly higher reactivity. Thus, the competitive reaction of an equimolar mixture of the aryl nonaflate **5e** and the corresponding triflate (ethyl (4-triflyloxy)benzoate) with 4-chlorophenylzinc bromide (2 mol % $Pd(dba)_2$, 2 mol % dppf, 55 °C, 8 h) shows that the nonaflate reacts ca. 1.4 times faster than the triflate. A selective reaction of the iodoaryl nonaflates **5a**−**c** is possible using $Pd(dba)_2$ (0.5−1 mol %) and tri-*o*-furylphosphine[11] (tfp; 1−2 mol %) leading to the cross-coupling products **6b**−**g** under very mild conditions (25 °C, 0.25−5 h) and in excellent yields (88−96%; Scheme 2 and Table 1). Compared to similar cross-coupling reactions performed with iodoaryl triflates,[7e] cleaner reactions and higher yields are obtained with the iodoaryl nonaflates **5a**−**c**.

(1) For an excellent review, see: (a) Ritter, K. *Synthesis* **1993**, 735. (b) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

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(3) Muetterties, E. L.; Coffman, D. D. *J. Am. Chem. Soc.* **1958**, *80*, 5914.

(4) For the use of triflates and aryl fluoroalkanesulfonates in Heck reactions, see: (a) Chen, Q.-Y.; Yang, Z.-Y. *Tetrahedron Lett.* **1986**, *27*, 1171. (b) de Meijere, A.; Meyer, F. E. *Angew. Chem.* **1994**, *106*, 2473. (c) Bräse, S.; de Meijere, A. In *Palladium-Catalyzed Coupling of Organyl Halides to Alkenes − The Heck Reaction*; Stang, P. J., Diederich, F., Eds.; Wiley−VCH: Weinheim, 1997. (d) Webel, M.; Reissig, H.-U. *Synlett* **1997**, 1141.

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(10) (a) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (b) Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 4449. (c) Hayashi, T.; Fujiwa, T.; Okamoto, Y.; Katsuro, Y.; Kumada, M. *Synthesis* **1981**, 1001. (d) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915. (e) Hayashi, T.; Konishi, M.; Yokota, K.; Kumada, M. *Chem. Lett.* **1980**, *6*, 767. (f) Hayashi, T.; Konishi, M.; Yokota, K.-I.; Kumada, M. *J. Organomet. Chem.* **1985**, *285*, 359. (g) The phosphine dppf is conveniently prepared in high yield by using the procedure of Brandsma: de Lang, R.-J.; van Soolingen, J.; Verkruijsse, H. D.; Brandsma, L. *Synth. Commun.* **1995**, *25*, 2989.

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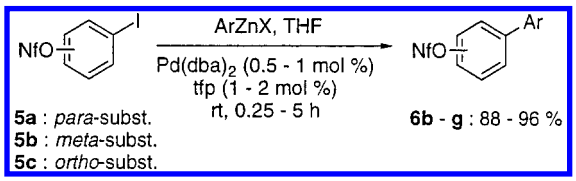
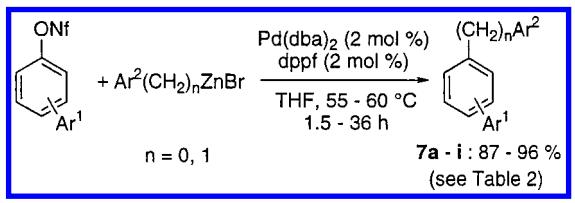
Scheme 2



Scheme 3



The biphenyl nonaflates **6c**−**g** can be employed in a second step to react with a different arylzinc bromide or benzylzinc bromide[12] using now a reaction temperature of 55−60 °C and dppf as phosphine ligand. Under these conditions, the nonaflate function is smoothly substituted leading to the polyfunctional aromatic compounds **7a**−**i** in 87−96% isolated yields (55−60 °C, 1.5−36 h; Scheme 3 and Table 2).

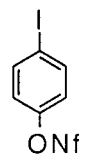
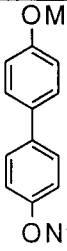
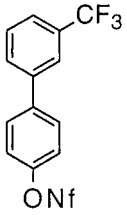
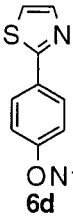
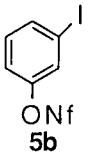
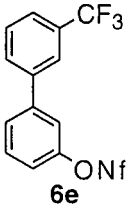
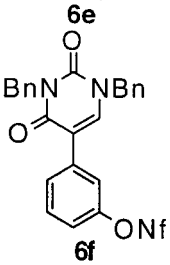
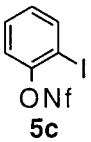
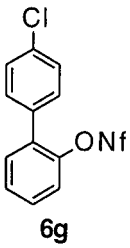
The representative examples contained in Table 2 show that ortho-, meta-, and para-substituted aryl nonaflates undergo the cross-coupling reaction equally well with uniformly high yields. Various functional groups can be present either in the organozinc reagent or in the aryl or heteroaryl nonaflate. Most coupling reactions are complete within 20 h at 60 °C; however, ortho-substituted aryl nonaflates require longer reaction times (36 h).

In the following, we wish to report the preparation of new arylzinc reagents bearing an electrophilic nonaflate function. Aryl iodides can be converted to nucleophilic reagents by the insertion of zinc dust leading to arylzinc iodides.[13] Whereas iodophenyl triflates react with zinc dust[13] to the corresponding zinc reagent with modest yield, the iodoaryl nonaflates **5a**,**b** undergo a clean insertion of zinc dust previously activated[14] with 1,2-dibromoethane and Me_3SiCl in *N*,*N*-dimethylacetamide (DMAC) at 45 °C (7 h) leading to the desired zinc reagents **1** and **2** in ca. 80% yield as estimated by iodolysis experiments (GC analysis). These new organozincs undergo smooth cross-coupling reactions with various functionalized aryl iodides in the presence of $Pd(dba)_2$ (1−2 mol %) and tfp (2−4 mol %) leading to the polyfunctional biphenyl nonaflates **8** and **9** in 83−86% yield (Scheme 4).

Interestingly, aryl nonaflates are also excellent substrates for the performance of Stille and Suzuki cross-coupling reactions. Thus, the treatment of the nonaflate **5e** with the boronic acid **10** or the arylstannane **11** provides, under typical conditions for Suzuki[15] or Stille[16] coupling, the expected products **12** and **13** in 82−89% yield (Scheme 5).

In summary, we have demonstrated that readily available aryl nonaflates are convenient substrates for the performance of palladium-catalyzed cross-coupling reactions with organozinc halides. New arylzinc reagents such as **1** and **2** bearing an electrophilic nonaflate function have also been prepared and used for the selective formation of cross-coupling products. The efficient preparation and purification of aryl nonaflates as well as their very clean palladium-catalyzed cross-coupling with organozincs and other organometallics

Table 1. Biphenyl Nonaflates 6b−g Obtained by Palladium-Catalyzed Cross-Coupling Reactions between Arylzinc Reagents and Iodophenyl Nonaflates 5a−c

aryl iodide **5**	RZnX (R)	product **6**	yield (%)[a]
 **5a**	*p*-$MeOC_6H_4$	 **6b**	92
5a	*m*-$CF_3C_6H_4$	 **6c**	92
5a	thiazol-2-yl	 **6d**	94
 **5b**	*m*-$CF_3C_6H_4$	 **6e**	91
5b	(N,N'-dibenzyl)-uracil-5-yl	 **6f**	96
 **5c**	*p*-ClC_6H_4	 **6g**	88

[a] Isolated yield of analytically pure product.

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(13) Knochel, P.; Singer, R. D. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 2117.
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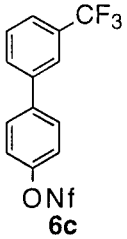
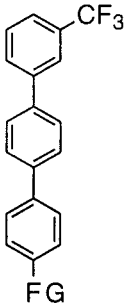
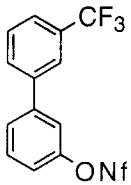
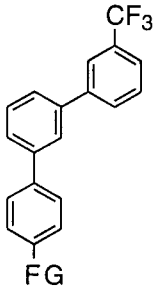
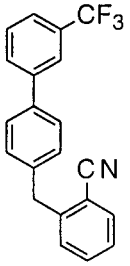
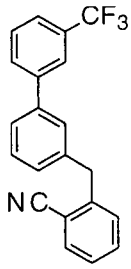
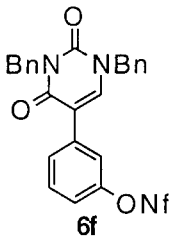
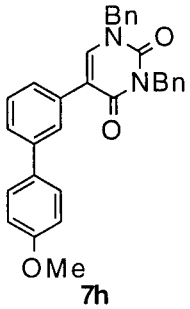
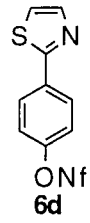
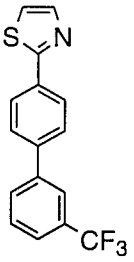
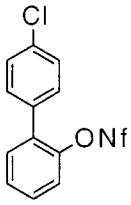
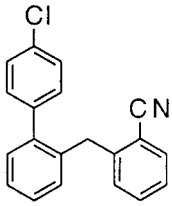
Table 2. Terphenyls 7a–I Obtained by Palladium-catalyzed Cross-Coupling Reactions between Aryl- or Benzylzinc Reagents and Functionalized Biphenyl Nonaflates 6c–g

aryl nonaflate	RZnX (R)	product 7	yield (%)[a]	aryl nonaflate	RZnX (R)	product 7	yield (%)[a]
 **6c**				 **6e**			
6c	*p*-ClC_6H_4	**7a** : FG = Cl	90	**6e**	*p*-ClC_6H_4	**7e** : FG = Cl	96
6c	*p*-NCC_6H_4	**7b** : FG = CN	94	**6e**	*p*-NCC_6H_4	**7f** : FG = CN	89
6c	*o*-$NCC_6H_4CH_2$	 **7c**	93	**6e**	*o*-$NCC_6H_4CH_2$	 **7g**	87
				 **6f**	*p*-$MeOC_6H_4$	 **7h**	92
 **6d**	*m*-$CF_3C_6H_4$	 **7d**	91	 **6g**	*o*-$NCC_6H_4CH_2$	 **7i**	89

[a] Isolated yield of analytically pure product.

should make these phenol derivatives an excellent alternative to aryl triflates.

Experimental Section

General. THF and DMAC were dried over sodium and CaH_2, respectively, and distilled prior to use. Commercially available starting materials were used without further purification. Melting points are uncorrected.

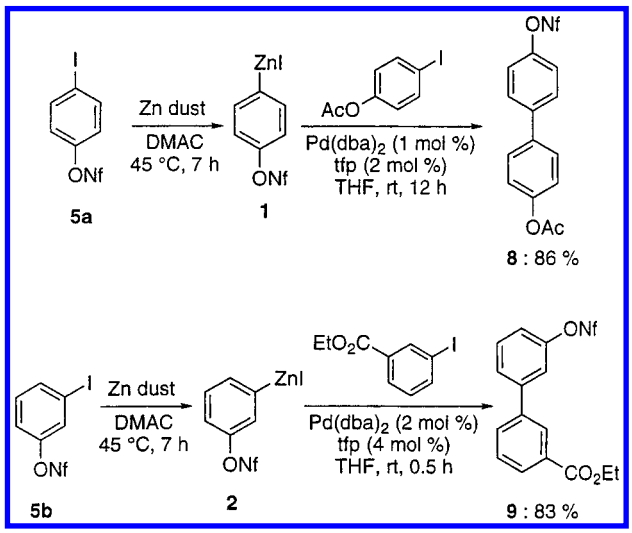
Starting Materials. The arylzinc reagents were prepared from the corresponding aryl iodides or bromides via halogen–lithium exchange followed by transmetalation according to a literature procedure.[8] Respectively, 2-cyanobenzylzinc bromide,[12] thiazol-2-ylzinc bromide,[17] and *N*,*N*′-dibenzyluracil-5-ylzinc iodide[17] were prepared from the corresponding halides by zinc insertion. All these preparation methods afforded THF/hexane or THF solutions (ca. 0.8 M) which were directly used for the cross-coupling reactions.

Typical Procedure A: Zinc Insertion into a Nonaflate-Functionalized Aryl Iodide. Preparation of 4-[(Nonafluorobutanesulfonyl)oxy]phenylzinc Iodide (1). A dried and argon-flushed 25-mL three-necked flask with a dropping funnel and a thermometer was charged with zinc dust (1.95 g, 30 mmol), DMAC (2 mL), and 1,2-dibromoethane (570 mg, 3.0 mmol). The mixture was heated twice for 3 min to ca. 80 °C with the aid of a heat gun. After the mixture cooled to rt, chlorotrimethylsilane (0.45 mL, 3.6 mmol) was added, and the mixture was again heated to ca. 80 °C as above. The dropping funnel was charged with the nonaflate **5a** (6.03 g, 12 mmol) in DMAC (8 mL). After dropwise addition at 40–43 °C, the mixture was heated at 45 °C for 7 h resulting in a ready-to-use solution of **1** (10 mmol, ca. 83% yield, 0.85 M solution in DMAC as estimated by GC analysis of a hydrolyzed and an iodolized aliquot).

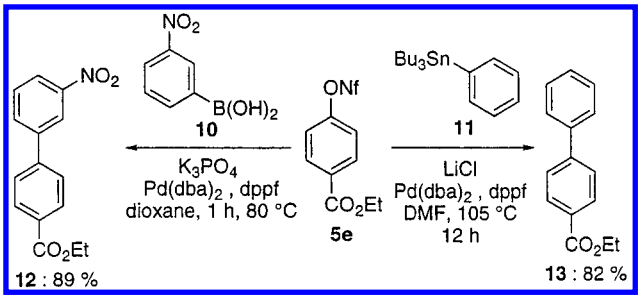
3-[(Nonafluorobutanesulfonyl)oxy]phenylzinc Iodide (2). This was prepared according to typical procedure A starting from

(17) Bhanu Prasad, A. S.; Stevenson, T. M.; Citineni, J. R.; Nyzam, V.; Knochel, P. *Tetrahedron* **1997**, *53*, 7237.

Scheme 4



Scheme 5



zinc dust (1.95 g, 30 mmol), 1,2-dibromoethane (570 mg, 3.0 mmol), chlorotrimethylsilane (0.45 mL, 3.6 mmol), and nonaflate **5b** affording **2** (9.6 mmol, ca. 80% yield, 0.82 M in DMAC as estimated by GC analysis of a hydrolyzed and an iodolized aliquot).

The nonaflates **5** were prepared according to a literature procedure.[5]

4-Iodophenyl Nonaflate (5a). Starting from 4-iodophenol (8.64 g, 39.3 mmol), nonafluorobutanesulfonic fluoride (10.60 mL, 58.9 mmol), and triethylamine (8.25 mL, 58.9 mmol), the product **5a** was isolated after purification by chromatography (pentane) as a colorless liquid (18.6 g, 94%). IR (neat): 3072 (w), 3030 (w), 1478 (s), 1430 (s), 1241 (s), 1204 (s), 1181 (s), 1146 (s), 1009 (m), 890 (s), 828 (m), 731 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.77 (d, J = 11.7 Hz, 2H), 7.04 (d, J = 11.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 139.5, 123.3, 119.5−106.0 (m), 93.1. MS (EI): 502 (42), 219 (100), 191 (19), 92 (39), 64 (38). Anal. Calcd for $C_{10}H_4F_9IO_3S$: C, 23.92; H, 0.80. Found: C, 23.93; H, 0.86.

3-Iodophenyl Nonaflate (5b). Starting from 3-iodophenol (11.0 g, 50 mmol), nonafluorobutanesulfonic fluoride (13.5 mL, 75 mmol), and triethylamine (10.5 mL, 75 mmol), the product **5b** was isolated after purification by chromatography (pentane) as a colorless liquid (23.6 g, 94%). IR (neat): 3068 (w), 1587 (m), 1574 (m), 1464 (m), 1431 (s), 1240 (s), 1204 (s), 1146 (s), 1035 (m), 895 (s), 785 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, J = 8.2 Hz, 1H), 7.61 (m, 1H), 7.29−7.12 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 137.6, 131.4, 130.4, 120.8, 119.5−106.2 (m), 93.8. ^{19}F NMR (188 MHz, $CDCl_3$): δ −81.2, −109.3, −121.4, −126.4. MS (EI): 502 (55), 438 (18), 219 (44), 203 (24), 191 (26), 92 (100), 69 (37), 64 (33). Anal. Calcd for $C_{10}H_4F_9IO_3S$: C, 23.92; H, 0.80. Found: C, 23.90; H, 0.80.

2-Iodophenyl Nonaflate (5c). Starting from 2-iodophenol (11.0 g, 50 mmol), nonafluorobutanesulfonic fluoride (13.5 mL, 75 mmol), and triethylamine (10.5 mL, 75 mmol), the product **5c** was isolated after purification by chromatography (pentane) as a colorless liquid (23.1 g, 92%). IR (neat): 3071 (w), 1572 (w), 1463 (s), 1430 (s), 1354 (s), 1238 (s), 1205 (s), 1144 (s), 1036 (s), 1022 (s), 890 (s), 769 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.6, 140.9, 130.3, 129.6, 122.1, 120−105 (m), 89.3. ^{19}F NMR (188 MHz, $CDCl_3$): δ −81.4, −109.7, −121.3, −126.5. MS (EI): 502 (59), 219 (100), 191 (23), 92 (93), 69 (29), 64 (35). Anal. Calcd for $C_{10}H_4F_9IO_3S$: C, 23.92; H, 0.80. Found: C, 23.98; H, 1.08.

4-[(Trifluoromethanesulfonyl)oxy]phenyl Nonaflate (5d). Starting from 4-[(trifluoromethanesulfonyl)oxy]phenol (1.95 g, 8.0 mmol), nonafluorobutanesulfonic fluoride (2.16 mL, 12 mmol), and triethylamine (1.68 mL, 12 mmol), the product **5d** was isolated after purification by flash chromatography (pentane/ether, 97:3) as a white solid (4.11 g, 98%), mp 40−41 °C. IR (KBr): 3123 (w), 1638 (m), 1616 (m), 1494 (m), 1426 (s), 1413 (s), 1250 (s), 1228 (s), 1143 (s), 906 (s), 619 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 4H). ^{13}C NMR (75 MHz): δ 148.7, 148.5, 123.5, 118.7 (quart, J = 321 Hz), 118−108 (m). ^{19}F NMR (188 MHz, $CDCl_3$): δ −73.4, −81.4, −109.3, −121.5, −126.5. MS (EI): 524 (14), 327 (15), 241 (29), 177 (27), 149 (13), 69 (100). Anal. Calcd for $C_{11}H_4F_{12}O_6S_2$: C, 25.20; H, 0.77. Found: C, 25.38; H, 0.80.

Ethyl 4-[(Nonafluorobutanesulfonyl)oxy]benzoate (5e). Starting from ethyl 4-hydroxybenzoate (3.32 g, 20 mmol), nonafluorobutanesulfonic fluoride (5.4 mL, 30 mmol), and triethylamine (4.2 mL, 30 mmol), the product **5e** was isolated after purification by flash chromatography (pentane/ether, 95:5) as a colorless liquid (8.36 g, 93%). IR (neat): 3077 (w), 2988 (w), 1727 (s), 1602 (m), 1498 (m), 1431 (s), 1279 (s), 1241 (s), 1205 (s), 1146 (s), 1018 (m), 894 (s), 861 (m), 774 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.13 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 4.38 (quart, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 164.9, 152.7, 131.8, 130.7, 121.3, 120−108 (m), 61.5, 14.1. ^{19}F NMR (188 MHz): δ −81.7, −109.6, −121.8, −126.8. MS (EI): 448 (29), 420 (47), 403 (100), 356 (41), 339 (71), 165 (53), 109 (69), 92 (56), 69 (57). HRMS: calcd for $C_{13}H_9F_9O_5S$, 448.0026; found, 448.0027.

Typical Procedure B: Cross-Coupling of an Aryl Nonaflate with an Arylzinc Halide in the Presence of a Palladium(0) Catalyst. Preparation of 4-(Ethoxycarbonyl)-3′-(trifluoromethyl)biphenyl (6a). A dried and argon-flushed 10-mL two-necked flask was charged with palladium bis(dibenzylideneacetone)[9] (5.8 mg, 0.01 mmol), bis(diphenylphosphino)ferrocene[10] (5.5 mg, 0.01 mmol), and THF (1 mL). The resulting solution was stirred for 10 min followed by the addition of ethyl 4-[(nonafluorobutanesulfonyl)oxy]benzoate (**5e**; 448 mg, 1 mmol). After the mixture stirred for 5 min, 3-(trifluoromethyl)phenylzinc bromide (2.0 mL, 1.47 mmol, 0.74 M in THF) was added, and the mixture was heated to 60 °C for 5 h. After usual aqueous workup the crude product was purified by flash chromatography (pentane/ether, 95:5) yielding **6a** as a white solid (265 mg, 90%), mp 78 °C. IR (KBr): 3072 (w), 2984 (m), 1706 (s), 1611 (m), 1492 (m), 1441 (m), 1337 (s), 1310 (m), 1160 (m), 1128 (m), 1078 (m), 772 (s), 707 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 2H), 7.86 (s, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.66−7.63 (m, 3H), 7.57 (t, J = 7.7 Hz, 1H), 4.41 (quart, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 143.9, 140.9, 131.4 (quart, J = 32.5 Hz), 130.5, 130.2, 129.4, 127.1, 124.7 (quart, J = 3.7 Hz), 124.1 (quart, J = 272.4 Hz), 124.0 (quart, J = 3.8 Hz), 61.1, 14.3. MS (EI): 294 (47), 249 (100), 201 (11), 152 (16). HRMS: calcd for $C_{16}H_{13}F_3O_2$, 294.0866; found, 294.0868.

4-Methoxy-4′-[(nonafluorobutanesulfonyl)oxy]biphenyl (6b). This was prepared according to typical procedure B starting from iodide **5a** (502 mg, 1 mmol), $Pd(dba)_2$ (5.8 mg, 0.01 mmol), tfp (4.6 mg, 0.02 mmol), and 4-methoxyphenylzinc bromide (1.20 mL, 1.15 mmol, 0.96 M in THF). Reaction time: 1.5 h at rt. After purification by flash chromatography (pentane/ether, 98:2), the product **6b** was obtained as a white solid (443.7 mg, 92%), mp 77−78 °C. IR (KBr): 3071 (w), 1638 (m), 1611 (m), 1495 (m), 1431 (m), 1355 (m), 1295 (m), 1238 (s), 1205 (s), 1148 (m), 1138 (m), 1038 (s), 892 (s), 824 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.60 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.32 (d, J = 9.0 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8, 148.8, 141.3, 131.8, 128.3, 119−105 (m), 128.3, 128.3, 121.6, 114.5, 55.3. MS (EI): 482 (35), 199 (100). HRMS: calcd for $C_{17}H_{11}F_9O_4S$, 482.0216; found, 482.0234.

4-[(Nonafluorobutanesulfonyl)oxy]-3′-(trifluoromethyl)-biphenyl (6c). This was prepared according to typical procedure B starting from iodide **5a** (3.01 g, 6 mmol), $Pd(dba)_2$ (35 mg, 0.06 mmol), tfp (28 mg, 0.12 mmol), and 3-(trifluoromethyl)phenylzinc bromide (10.1 mL, 7.2 mmol, 0.71 M in THF). Reaction time: 15 min at rt. After purification by flash chromatography (pentane/ether, 98:2), the product **6c** was obtained as a colorless oil (2.91 g, 92%). IR (neat): 3078 (w), 1510 (m), 1486 (m), 1430 (s), 1337 (s), 1242 (s), 1206 (s), 1146 (s), 1038 (m), 892 (s), 802 (s), 702 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.68−7.56 (m, 4H), 7.40 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 140.2, 140.2, 131.6 (quart, J = 32.5 Hz), 130.5, 129.6, 129.0, 124.8 (quart, J = 3.8 Hz), 124.1 (quart, J = 272 Hz), 124.0 (quart, J = 3.8 Hz), 122.0, 119−105 (m). MS (EI): 520 (19), 237 (100), 209 (23), 28 (32). Anal. Calcd for $C_{17}H_8F_{12}O_3S$: C, 39.24; H, 1.55. Found: C, 39.24; H, 1.65.

4-(Thiazol-2-yl)phenyl Nonaflate (6d). This was prepared according to typical procedure B starting from iodide **5a** (3.01 g, 6.0 mmol), $Pd(dba)_2$ (35 mg, 0.06 mmol), tfp (28 mg, 0.12 mmol), and thiazol-2-ylzinc bromide (6.3 mL, 7.7 mmol, 1.22 M in THF). Reaction time: 5 h at rt. After purification by flash chromatography (pentane/ether, 95:5 to 90:10 gradient), the product **6d** was obtained as a pale yellow solid (2.58 g, 94%), mp 50 °C. IR (KBr): 3089 (w), 3038 (w), 2849 (w), 1510 (m), 1479 (m), 1431 (s), 2251 (s), 1202 (s), 1146 (s), 896 (s), 846 (s), 726 (s), 630 (s), 588 (s), 523 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 3.2 Hz, 1H), 7.38−7.35 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 150.6, 144.2, 133.9, 128.4, 122.0, 119.8, 119−105 (m). ^{19}F NMR (188 MHz, $CDCl_3$): δ −81.5, −109.6, −121.8, −126.8. MS (EI): 459 (30), 176 (100), 148 (18), 69 (10), 58 (16), 28 (24). Anal. Calcd for $C_{13}H_6F_9NO_3S_2$: C, 34.00; H, 1.32; N, 3.05. Found: C, 34.21; H, 1.32; N, 3.03.

3-[(Nonafluorobutanesulfonyl)oxy]-3′-(trifluoromethyl)-biphenyl (6e). This was prepared according to typical procedure B starting from iodide **5b** (4.0 g, 7.97 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), tfp (18 mg, 0.08 mmol), and 3-(trifluoromethyl)phenylzinc bromide (11.3 mL, 8.02 mmol, 0.71 M in THF). Reaction time: 15 min at rt. After purification by flash chromatography (pentane/ether, 98:2), the product **6e** was obtained as a colorless oil (3.77 g, 91%). IR (neat): 3077 (w), 1611 (m), 1429 (s), 1337 (s), 1242 (s), 1205 (s), 1134 (s), 922 (m), 791 (m), 699 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.64−7.51 (m, 4H), 7.38−7.32 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.4, 142.6, 140.0, 131.8 (quart, J = 32.6 Hz), 130.9, 130.6, 129.7, 127.2, 125.1 (quart, J = 3.7 Hz), 124.1 (quart, J = 274.3 Hz), 124.0 (quart, J = 3.8 Hz), 121−105 (m), 120.7, 120.2. MS (EI): 520 (45), 456 (15), 209 (100), 69 (25), 28 (10). HRMS: calcd for $C_{17}H_8F_{12}O_3S$, 520.0000; found, 520.0002.

3-(*N*,*N*′-Dibenzyluracil-5-yl)phenyl Nonaflate (6f). This was made according to the preparation of **6a** starting from iodide **5b** (1.0 g, 2 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), tfp (8 mg, 0.04 mmol), and *N*,*N*′-dibenzyluracil-5-ylzinc iodide[17] (3.6 mL, 2.5 mmol, 0.70 M in DMAC). Reaction time: 1.5 h at rt. After purification by flash chromatography (pentane/ethyl acetate, 85:15), the product **6f** was obtained as a white foam (1.29 g, 96%). IR (neat): 3067 (m), 3037 (m), 2963 (w), 1713 (s), 1651 (s), 1611 (m), 1495 (m), 1456 (s), 1354 (m), 1252 (s), 1148 (s), 1033 (m), 920 (s), 734 (s), 698 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.57−7.55 (m, 3H), 7.46−7.17 (m, 12H), 5.24 (s, 2H), 4.96 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.3, 150.9, 149.5, 140.4, 136.5, 135.4, 135.0, 129.8, 128.9, 128.4, 128.3, 127.8, 127.7, 127.6, 121.1, 120.1, 119−105 (m), 112.5, 52.4, 44.9. ^{19}F NMR (188 MHz, $CDCl_3$): δ −81.2, −109.4, −121.3, −126.3. MS (EI): 666 (31), 91 (100). HRMS: calcd for $C_{28}H_{19}F_9N_2O_5S$, 666.0875; found, 666.0871.

4-Chloro-2′-[(nonafluorobutanesulfonyl)oxy]biphenyl (6g). This was prepared according to typical procedure B starting from iodide **5c** (3.50 g, 6.97 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), tfp (18 mg, 0.08 mmol), and 4-chlorophenylzinc bromide (11.4 mL, 8.8 mmol, 0.77 M in THF). Reaction time: 5 h at rt. After purification by flash chromatography (pentane/ether, 95:5), the product **6g** was obtained as a colorless oil (2.99 g, 88%). IR (neat): 3069 (w), 1475 (m), 1426 (s), 1240 (s), 1202 (s), 1144 (s), 890 (m), 831 (m), 775 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.47−7.40 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.9, 134.6, 134.2, 131.8, 130.7, 129.4, 128.7, 128.6, 125.2 (quart, J = 295 Hz), 122.1. MS (EI): 486 (44), 203 (79), 168 (100), 139 (21), 69 (16). Anal. Calcd for $C_{16}H_8ClF_9O_3S$: C, 39.48; H, 1.66. Found: C, 39.41; H, 1.67.

1-Chloro-3″-(trifluoromethyl)-4,1′:4′,1″-terphenyl (7a). This was prepared according to typical procedure B starting from nonaflate **6c** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 4-chlorophenylzinc bromide (1.43 mL, 1.1 mmol). Reaction time: 1.5 h at 60 °C. After purification by flash chromatography (pentane/ethyl acetate, 97:3), the product **7a** was obtained as a white solid (300 mg, 90%), mp 111−113 °C. IR (KBr): 1638 (m), 1616 (m), 1481 (m), 1341 (s), 1187 (s), 1126 (s), 1099 (s), 1074 (m), 804 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.72−7.57 (m, 8H), 7.46 (d, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.2, 139.5, 138.8, 138.7, 133.7, 131.2 (quart, J = 32.1 Hz), 130.2, 129.3, 129.0, 128.2, 127.5, 127.4, 124.2 (quart, J = 272.4 Hz), 124.1 (quart, J = 3.8 Hz), 123.7 (quart, J = 3.8 Hz). MS (EI): 334 (30), 332 (100), 166 (11). HRMS: calcd for $C_{19}H_{12}ClF_3$, 332.0574; found, 332.0580.

1-Cyano-3″-(trifluoromethyl)-4,1′:4′,1″-terphenyl (7b). This was prepared according to typical procedure B starting from nonaflate **6c** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 4-cyanophenylzinc bromide (3.4 mL, 1.8 mmol, 0.55 M in THF). Reaction time: 5 h at 60 °C. After purification by flash chromatography (pentane/ether, 95:5 to 90:10 gradient), the product **7b** was obtained as a white solid (305 mg, 94%), mp 96 °C. IR (KBr): 3069 (w), 2921 (w), 2223 (s), 1604 (m), 1484 (m), 1335 (s), 1268 (s), 1162 (s), 1128 (s), 1075 (s), 823 (s), 802 (s), 701 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.82 (d, J = 7.4 Hz, 1H), 7.79−7.57 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 141.0, 140.0, 138.8, 132.7, 131.4 (quart, J = 32.3 Hz), 130.3, 129.4, 127.9, 127.8, 127.6, 124.3 (quart, J = 4.3 Hz), 124.1 (quart, J = 272.2 Hz), 123.8 (quart, J = 4.3 Hz), 118.8, 111.2. MS (EI): 323 (100), 161 (10). HRMS: calcd for $C_{20}H_{12}F_3N$, 323.0924; found, 323.0922.

4-(2-Cyanobenzyl)-3′-(trifluoromethyl)biphenyl (7c). This was prepared according to typical procedure B starting from nonaflate **6c** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 2-cyanobenzylzinc bromide (3.90 mL, 3 mmol, 0.77 M in THF). Reaction time: 24 h at 60 °C. After purification by flash chromatography (pentane/ether, 95:5), the product **7c** was obtained as a colorless oil (314 mg, 93%). IR (neat): 3032 (m), 2226 (m), 1599 (w), 1487 (m), 1445 (m), 1337 (s), 1263 (s), 1165 (s), 1125 (s), 793 (s), 762 (s), 702 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.56−7.50 (m, 10H), 4.27 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 141.4, 138.7, 137.9, 132.9, 132.8, 130.5 (quart, J = 33.9 Hz), 130.1, 130.0, 129.5, 129.2, 127.3, 126.9, 124.2 (quart, J = 272.4 Hz), 123.7 (quart, J = 3.7 Hz), 123.5 (quart, J = 3.8 Hz), 118.0, 112.5, 39.6. MS (EI): 337 (100), 116 (92). HRMS: calcd for $C_{21}H_{14}F_3N$, 337.1077; found, 337.1079.

4-(Thiazol-2-yl)-3′-(trifluoromethyl)biphenyl (7d). This was prepared according to typical procedure B starting from nonaflate **6d** (459 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 3-(trifluoromethyl)phenylzinc bromide (3.9 mL, 2.8 mmol, 0.71 M in THF). Reaction time: 5 h at 55 °C. After purification by flash chromatography (pentane/ethyl acetate, 95:5), the product **7d** was obtained as a white solid (278 mg, 91%), mp 120 °C. IR (KBr): 3234 (w), 1638 (m), 1616 (m), 1337 (s), 1264 (m), 1110 (s), 801 (m). ^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.3 Hz, 2H), 7.90−7.88 (m, 2H), 7.78 (d, J = 7.7 Hz, 1H), 7.67−7.62 (m, 3H), 7.55 (t, J = 7.9 Hz, 1H), 7.34 (d, J = 3.0 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.5, 143.8, 140.9, 140.8, 133.1, 131.2 (quart, J = 32.2 Hz), 130.2, 129.3, 127.5, 127.0, 124.3 (quart, J = 3.5 Hz), 124.1 (quart, J = 272.3 Hz), 123.6 (quart, J = 4.0 Hz), 119.0. MS (EI): 305 (100), 58 (94). Anal. Calcd for $C_{16}H_{10}F_3NS$: C, 62.94; H, 3.28; N, 4.59. Found: C, 62.92; H, 2.98; N, 4.42.

1-Chloro-3″-(trifluoromethyl)-4,1′:3′,1″-terphenyl (7e). This was prepared according to typical procedure B starting from nonaflate **6e** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 4-chlorophenylzinc bromide (1.55 mL, 1.2 mmol, 0.77 M in THF). Reaction time: 3 h at 60 °C. After purification by flash chromatography (pentane/ether, 97:3), the product **7e** was obtained as a colorless oil. IR (neat):

3038 (m), 1604 (m), 1493 (m), 1480 (m), 1338 (s), 1165 (s), 1126 (s), 788 (s), 702 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.78 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.65−7.52 (m, 6H), 7.47 (d, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.8, 140.9, 140.5, 139.3, 133.8, 131.3 (quart, J = 32.4 Hz), 130.5, 129.6, 129.3, 129.0, 128.5, 126.7, 126.5, 125.9, 124.2 (quart, J = 272.9 Hz), 124.2 (quart, J = 3.7 Hz), 124.0 (quart, J = 3.7 Hz). MS (EI): 332 (100). Anal. Calcd for $C_{19}H_{12}ClF_3$: C, 68.58; H, 3.63. Found: C, 68.35; H, 3.76.

1-Cyano-3″-(trifluoromethyl)-4,1′:3′,1″-terphenyl (7f). This was prepared according to typical procedure B starting from nonaflate **6e** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 4-cyanophenylzinc bromide (3 mL, 1.65 mmol, 0.55 M in THF). Reaction time: 12 h at 60 °C. After purification by flash chromatography (pentane/ether, 95:5 to 88:12 gradient), the product **7f** was obtained as a pale yellow solid (288 mg, 89%), mp 79−81 °C. IR (KBr): 3052 (w), 2230 (m), 1638 (m), 1607 (m), 1510 (m), 1483 (m), 1341 (s), 1241 (m), 1161 (s), 1122 (s), 1076 (m), 800 (s), 703 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.82 (d, J = 7.7 Hz, 1H), 7.78 (s, 1H), 7.73 (s, 4H), 7.68−7.56 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 141.5, 140.7, 140.1, 132.7, 131.3 (quart, J = 32.3 Hz), 130.5, 129.8, 129.4, 127.8, 127.5, 126.8, 126.1, 124.4 (quart, J = 3.7 Hz), 124.2 (quart, J = 272.2 Hz), 124.0 (quart, J = 3.7 Hz), 118.8, 111.3. MS (EI): 323 (100), 161 (10). Anal. Calcd for $C_{20}H_{12}F_3N$: C, 74.30; H, 3.74; N, 4.33. Found: C, 74.17; H, 3.79; N, 4.35.

3-(2-Cyanobenzyl)-3′-(trifluoromethyl)biphenyl (7g). This was prepared according to typical procedure B starting from nonaflate **6e** (520 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 2-cyanobenzylzinc bromide (4.0 mL, 2.2 mmol, 0.55 M in THF). Reaction time: 20 h at 60 °C. After purification by flash chromatography (pentane/ether, 95:5 to 90:10 gradient), the product **7g** was obtained as a pale yellow oil (293 mg, 87%). IR (neat): 3065 (m), 2224 (s), 1600 (m), 1486 (m), 1444 (m), 1337 (s), 1267 (m), 1165 (s), 1125 (s), 1075 (m), 762 (m), 703 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.78 (d, J = 7.7 Hz, 1H), 7.70−7.30 (m, 10H), 4.33 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4, 141.6, 140.1, 139.6, 132.9, 132.8, 130.0 (quart, J = 32.1 Hz), 130.4, 129.9, 129.3, 129.2, 128.5, 127.7, 126.9, 125.5, 124.1 (quart, J = 272.3 Hz), 124.0−123.7 (m), 118.1, 112.5, 40.1. MS (EI): 337 (100). HRMS: calcd for $C_{21}H_{14}F_3N$, 337.1081; found, 337.1079.

3-(*N*,*N*′-Dibenzyluracil-5-yl)-4′-methoxybiphenyl (7h). This was prepared according to typical procedure B starting from nonaflate **6f** (890 mg, 1.3 mmol), $Pd(dba)_2$ (15 mg, 0.03 mmol), dppf (14 mg, 0.03 mmol), and 4-methoxyphenylzinc bromide (2.8 mL, 2.0 mmol, 0.71 M in THF). Reaction time: 4 h at 60 °C. After purification by flash chromatography (pentane/ethyl acetate, 80:20), the product **7h** was obtained as a white solid (582 mg, 92%), mp 145 °C. IR (KBr): 3069 (w), 1708 (s), 1650 (s), 1515 (m), 1482 (m), 1451 (s), 1364 (m), 1250 (s), 1237 (s), 1177 (m), 1022 (m), 804 (m), 728 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.50 (d, J = 7.3 Hz, 2H), 7.56−7.48 (m, 3H), 7.40−7.31 (m, 11H), 6.98 (d, J = 8.8 Hz, 2H), 5.27 (s, 2H), 4.97 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 159.1, 151.2, 140.9, 139.5, 136.8, 135.3, 133.2, 129.1, 129.0, 128.6, 128.3, 128.3, 128.1, 127.9, 127.5, 126.7, 126.5, 126.2, 114.8, 114.1, 55.2, 52.3, 44.8. MS (EI): 474 (100), 91 (71). HRMS: calcd for $C_{31}H_{26}N_2O_3$, 474.1939; found, 474.1943.

4-Chloro-2′-(2-cyanobenzyl)biphenyl (7i). This was prepared according to typical procedure B starting from nonaflate **6g** (487 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), and 2-cyanobenzylzinc bromide (4.0 mL, 2.4 mmol, 0.60 M in THF). Reaction time: 36 h at 60 °C. After purification by flash chromatography (pentane/ether, 95:5), the product **7i** was obtained as a colorless oil (270 mg, 89%). IR (neat): 3064 (m), 2225 (s), 1599 (m), 1478 (s), 1447 (m), 1090 (s), 1007 (m), 834 (m), 760 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (dd, J = 7.7, 1.4 Hz, 1H), 7.42 (dt, J = 7.6, 1.4 Hz, 1H), 7.37−7.21 (m, 5H), 7.19−7.12 (m, 3H), 6.96 (d, J = 7.9 Hz, 1H), 4.18 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 141.3, 139.7, 136.1, 133.3, 132.8, 132.7, 130.5, 130.3, 130.0, 128.5, 127.0, 126.7, 117.8, 112.7, 37.6. MS (EI): 305 (34), 303 (100), 268 (18), 267 (33), 266 (11), 165 (15), 133 (14). HRMS: calcd for $C_{20}H_{14}ClN$, 303.0818; found, 303.0815.

4-Acetoxy-4′-[(nonafluorobutanesulfonyl)oxy]biphenyl (8). This was prepared according to typical procedure B starting from 4-iodophenyl acetate (524 mg, 2 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), tfp (9 mg, 0.04 mmol), and arylzinc iodide **1** (3.53 mL, 3.0 mmol, ca. 0.85 M in DMAC). Reaction time: 12 h at rt. After purification by flash chromatography (pentane/ether, 95:5), the product **8** was obtained as a white solid (877 mg, 86%), mp 70 °C. IR (KBr): 3045 (m), 2980 (m), 1763 (m), 1637 (s), 1493 (m), 1227 (s), 1204 (s), 1144 (m), 701 (m), 687 (m), 660 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.6 Hz, 2H),7.36 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 150.7, 149.2, 140.7, 137.0, 128.8, 128.2, 122.1, 121.6, 119−105 (m), 21.0. MS (EI): 510 (5), 467 (25), 185 (100), 157 (15), 43 (25). Anal. Calcd for $C_{18}H_{11}F_9O_5S$: C, 42.36; H, 2.17. Found: C, 42.60; H, 2.21.

3-(Ethoxycarbonyl)-3′-[(nonafluorobutanesulfonyl)oxy]-biphenyl (9). This was prepared according to typical procedure B starting from ethyl 3-iodobenzoate (828 mg, 3 mmol), $Pd(dba)_2$ (36 mg, 0.06 mmol), tfp (27 mg, 0.12 mmol), and arylzinc iodide **2** (4.39 mL, 3.6 mmol, ca. 0.82 M in DMAC). Reaction time: 0.5 h at rt. After purification by flash chromatography (pentane/ether, 90:10), the product **9** was obtained as a colorless oil (1.30 g, 83%). IR (neat): 3065 (m), 2980 (m), 1720 (s), 1611 (m), 1574 (m), 1427 (s), 1298 (s), 1242 (s), 1202 (s), 1145 (s), 933 (s), 881 (s), 797 (s), 754 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.51−7.33 (m, 4H), 7.15 (d, J = 8.2 Hz, 1H), 4.27 (quart, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 166.2, 150.3, 142.9, 139.2, 131.4, 130.7, 129.3, 129.1, 128.2, 127.1, 120.3, 120.1, 119−105 (m), 61.3, 14.2. ^{19}F NMR (188 MHz, $CDCl_3$): δ −81.2, −109.5, −121.4, −126.4. MS (EI): 524 (100), 479 (30), 213 (74), 196 (27), 139 (22), 69 (20). Anal. Calcd for $C_{19}H_{13}F_9O_5S$: C, 43.52. H, 2.50. Found: C, 43.50; H, 2.49.

4-(Ethoxycarbonyl)-3′-nitrobiphenyl (12). This was made according to a literature procedure[15] starting from nonaflate **5e** (448 mg, 1 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), dppf (11 mg, 0.02 mmol), $K_3PO_4 \cdot 3H_2O$ (400 mg, 1.5 mmol), and boronic acid **10** (184 mg, 1.1 mmol). Reaction time: 1 h at 80 °C in dioxane. After recrystallization from MeOH, the product **12** was obtained as a white solid (241 mg, 89%), mp 112−114 °C (lit.[18] mp 113−115 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 8.45 (t, J = 2.0 Hz, 1H), 8.25−8.21 (m, 1H), 8.15 (dt, J = 8.7, 2.0 Hz, 2H), 7.96−7.91 (m, 1H), 7.69−7.64 (m, 3H), 4.41 (quart, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 148.7, 142.7, 141.6, 133.0, 130.5, 130.3, 129.9, 127.0, 122.7, 122.0, 61.1, 14.3. MS (EI): 271 (39), 243 (27), 226 (100), 152 (29).

4-(Ethoxycarbonyl)biphenyl (13). This was made according to a literature procedure[16] starting from nonaflate **5e** (448 mg, 1 mmol), $Pd(dba)_2$ (24 mg, 0.04 mmol), dppf (44 mg, 0.08 mmol), LiCl (240 mg, 6 mmol), and phenyltributyltin (**11**) (404 mg, 1.1 mmol). Reaction time: 12 h at 105 °C in DMF. After purification by flash chromatography (pentane/ether, 90:10), the product **13** was obtained as a white solid (185 mg, 82%), mp 48−49 °C (lit.[18] mp 49.2−49.6 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, J = 8.4 Hz, 2H), 7.69−7.63 (m, 4H), 7.48−7.40 (m, 3H), 4.43 (quart, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 145.4, 139.9, 130.0, 129.2, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3. MS (EI): 226 (100), 181 (80), 152 (47).

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **5a**−**e**, **6a**−**g**, **7a**−**i**, **8**, **9**, **12**, and **13** and ^{19}F NMR spectra of compounds **5d**, **6f**, and **9** (53 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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