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Palladium-Catalyzed Amination of Aryl Nonaflates

Kevin W. Anderson, Maria Mendez-Perez, Julian Priego, and Stephen L. Buchwald*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

sbuchwal@mit.edu

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The first detailed study of the palladium-catalyzed amination of aryl nonaflates is reported. Use of ligands **2**−**4** and **6** allows for the catalytic amination of electron-rich and -neutral aryl nonaflates with both primary and secondary amines. With use of Xantphos **5**, the catalytic amination of a variety of functionalized aryl nonaflates resulted in excellent yields of anilines; even 2-carboxymethyl aryl nonaflate is effectively coupled with a primary alkylamine. Moderate yields were obtained when coupling halo-aryl nonaflates with a variety of amines, where in most cases the aryl nonaflate reacted in preference to the aryl halide. Overall, aryl nonaflates are an effective alternative to triflates in palladium-catalyzed C−N bond-forming processes due to their increased stability under the reaction conditions.

Introduction

The palladium-catalyzed amination of aryl/heteroaryl halides has become an efficient and useful process for the preparation of various functionalized anilines.[1] The scope of this method was enhanced through the use of aryl triflates as compatible substrates due to the wide commercial availability of phenols.[2] While aryl triflates have worked well in many cases, base-promoted nucleophilic cleavage of the triflate moiety can occur with competitive rates that often lower the yields of desired product. Significant improvement was made through the use of weaker bases (e.g., Cs_2CO_3, K_3PO_4) or by slow addition of the aryl triflate; however, this protocol is not always successful or practical.[2] An attractive alternative to triflates are aryl nonaflates (ArONf = $ArOSO_2(CF_2)_3CF_3$), which can be readily prepared from the corresponding phenol and are stable to chromatography and storage at room temperature.[3−5] Aryl nonaflates have been shown to have reactivity similar to aryl triflates in cross-coupling reactions (Suzuki-Miyuara,[6] Negishi,[7] phosphonation,[8] reduction,[9] organosilanol coupling[10]) and are more stable toward hydrolysis.[11] Further, alkenyl nonaflates have also shown utility in cross-coupling reactions.[12] However, to our knowledge, no detailed study of the palladium-catalyzed amination reactions of aryl nonaflates has been reported.[13,14] Herein we report a detailed study of the palladium-catalyzed amination of aryl nonaflates. In addition, we describe several examples for the selective amination of halo aryl nonaflates.

Results and Discussion

Catalytic Amination of Electron-Rich and -Neutral Aryl Nonaflates. Initial attempts to couple aryl nonaflates with amines by using a catalyst system

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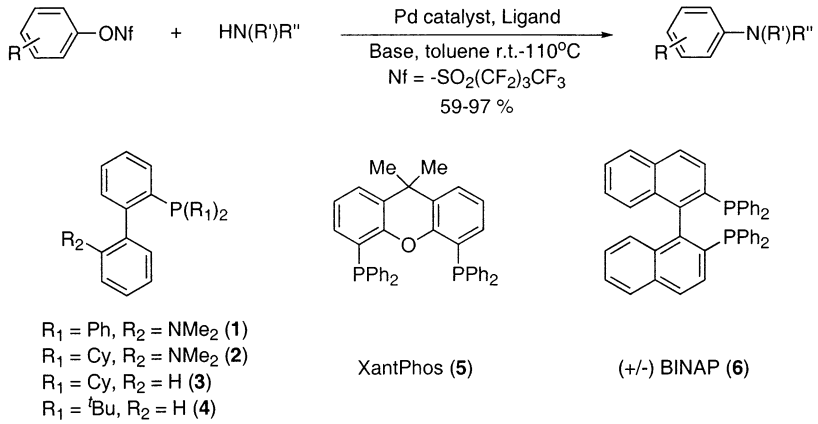
SCHEME 1



comprised of Pd_2dba_3, biphenyl phosphine ligand **1** and K_3PO_4 in toluene, THF, or DME at 80 °C (Scheme 1) gave little or none of the desired products. Increasing the reaction temperature to 105 °C led to the successful coupling of morpholine with aryl nonaflates. When primary alkylamines and aromatic amines were used, however, the reaction failed. To our delight, using the more electron rich, commercially available ligand **2** provided a catalyst system that proved to be effective in the amination of the majority of electron-rich or -neutral aryl nonaflates that were investigated (Table 1). Toluene proved to be the ideal solvent whereas use of more polar and coordinating solvents (e.g., THF or DME) gave much lower yields. Even sterically hindered aryl nonaflates gave excellent yields when utilizing this catalyst system (Table 1, entries 9−11). The ammonia equivalent benzophenone imine[15] proved to be an effective coupling partner when BINAP was used in place of **2** (Table 1, entry 11).

Room-Temperature Catalytic Amination of Aryl Nonaflates. The room-temperature catalytic amination of neutral and electron-rich aryl nonaflates was accomplished with use of **4** and NaO*t*-Bu as the base (Table 2). In some instances electron-rich aryl nonaflates could not be successfully coupled with primary alkylamines at elevated temperatures (nonaflate cleavage to the corresponding phenol occurred) with **2**; however, the room-temperature amination with **4** proceeded in good yields (Table 2, entries 6 and 7). Attempts to utilize electron-deficient aryl nonaflates at room temperature were unsuccessful; base-promoted nonaflate cleavage predominated. The use of weaker bases for reactions carried out at room temperature was unsuccessful; full recovery of the starting aryl nonaflate was realized.

Catalytic Amination of Electron-Deficient Aryl Nonaflates. Electron-deficient aryl nonaflates proved to be viable amination substrates at higher temperatures when the bidentate ligand Xantphos **5**[16] with K_3PO_4 was used as the base, whereas the use of **2** was ineffective (Table 3). In some cases it was necessary to increase the ligand/Pd ratio from 1/1 to 2/1 to maximize the yields (Table 3, entries 1and 3). With **5**, the coupling of 4-carboxymethylphenyl nonaflate and morpholine gave a 94% yield of the desired product (Table 3, entry 3), whereas under the same reaction conditions, the use of **2** gave a 54% yield. The reaction of this same nonaflate with aniline could be achieved with either **2** or **5** with comparable results. With **5**, 2-carboxymethyl nonaflate could be combined with *n*-hexylamine in excellent yield (Table 3, entry 5). This is in contrast with our results with the corresponding triflate, in which low yields were generally obtained.[2c] However, we are unaware of any reports in which the same transformation with a primary alkylamine can be carried out with a 2-halobenzoic acid ester.

With **5**, aryl nonaflates containing nitro and nitrile groups coupled efficiently with various amines, whereas with 4-acetylphenyl nonaflate, only the reaction with aniline was successful (Table 3, entry 11). We believe this is consistent with the notion that triflate/nonaflate cleavage is due to *the combination of the base and amine*, as well as that nonaflates are more stable toward cleavage. In Pd-catalyzed C−N bond-forming processes in general, reactions of anilines are more tolerant of functional groups than those with primary alkylamines.

Catalytic Amination of Halo-Aryl Nonaflates. We were also interested in determining whether the chemoselective Pd-catalyzed amination of substrates bearing both nonaflate and halide groups could be affected. To this end, we examined reactions of aryl nonaflates bearing either chlorine or bromine substituents (Table 4). In many cases, selective substitution of the nonaflate moiety could be achieved in moderate to good yields with use of either **2** or BINAP (**6**).[17] The use of other chelating phosphines such as Xantphos **5**, DPEphos, or dppf proved to be totally ineffective for these substrates.[18,19] While

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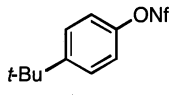
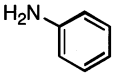
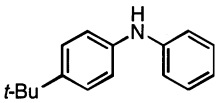
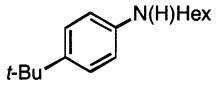
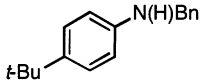
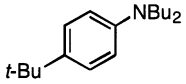
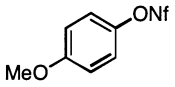
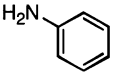
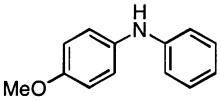
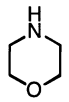
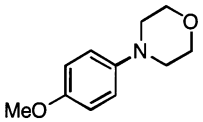
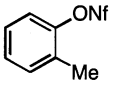
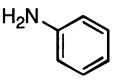
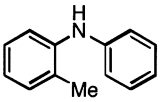
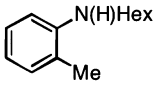
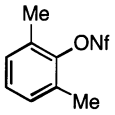
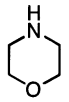
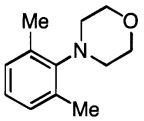
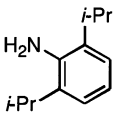
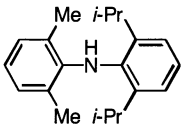
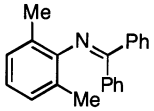
(17) Surprisingly, reactions of 4-bromophenyl nonaflate with either morpholine or aniline in the presence of **2** and K_3PO_4 as the base led preferentially to amination at bromine along with the diamination products. No reaction was observed with *n*-hexylamine.

(18) DPEphos = bis[2-(diphenylphosphino)phenyl] ether; dppf = 1,1′-bis(diphenylphosphino)ferrocene.

TABLE 1. Palladium-Catalyzed Amination of Unactivated Aryl Nonaflates[a]

Entry	Nonaflate	Amine	Product	Ligand	Yield (%)[b]
1				**2**	93
2		H_2NHex		**2**	78[c,d]
3		H_2NBn		**4**	82[d,e]
4		$HNBu_2$		**3**	86[d,e]
5				**2**	97
6				**2**	80[f]
7				**2**	86[c]
8		H_2NHex		**2**	84[c]
9				**2**	80
10				**2**	89[f]
11				**6**	97[g]

[a] Reaction conditions: 1.0 equiv of aryl nonaflate, 1.2 equiv of amine, 1.4 equiv of NaO*t*-Bu, Pd_2dba_3 (1 mol %), cat. ligand (L/Pd = 1/1), toluene (1.5−3.0 mL/mmol of nonaflate), 105 °C, 12−18 h. [b] Yields represent isolated yields of compounds estimated to be ≥95% pure as judged by ^{1}H NMR, GC analysis, and combustion analysis. [c] K_3PO_4 used instead of NaO*t*-Bu. [d] $Pd(OAc)_2$ used in place of Pd_2dba_3. [e] Reaction was run at 80 °C. [f] 2 mol % of Pd_2dba_3 used. [g] Best results were obtained when 4 Å molecular sieves were included in the reaction mixture.

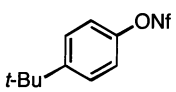
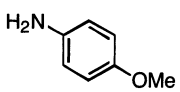
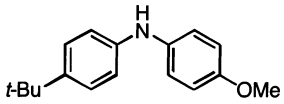
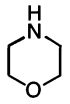
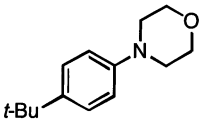
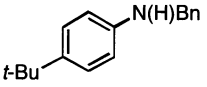
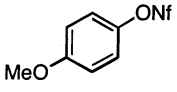
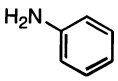
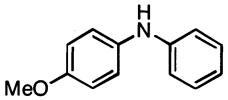
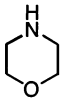
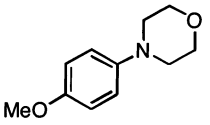
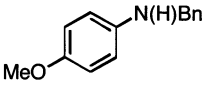
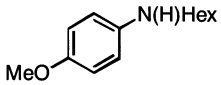
with some nonaflate/amine combinations K_3PO_4 was an effective base, in most cases employing NaO*t*-Bu was necessary to achieve full conversion and faster reaction times.[20] However, the use of NaO*t*-Bu generally led to higher degrees of nonaflate cleavage. This was particularly problematic for reactions involving bromo nonaflates and/or alkylamines, in which a considerable amount of products resulting from reduction or substitution of both the halide and nonaflate occurred.[21] All attempts to minimize these side reactions were met with little success. This included the use of Cs_2CO_3 in THF, the slow addition of NaO*t*-Am, which led to incomplete conversion of aryl nonaflate, as well as employing KO*t*-Bu or LiO*t*-Bu, which gave none of the desired product. Lowering the reaction temperature to 80 °C resulted in slight improvements in yield. Using $Pd(OAc)_2$ as an alternative palladium source resulted in lower reaction rates and selectivity in all cases. The addition of various halides (LiCl, LiBr, NaBr, KBr, NaF) or the use of higher catalyst loadings was either ineffective or produced deleterious effects.[22,23] Addition of LiI or various quantities of coordinating solvents (e.g., DMF or NMP) led to complete inhibition of the catalyst activity.

(19) This is the same behavior observed with the corresponding aryl triflate (see ref 2e).

(20) Most reactions with K_3PO_4 as base did not proceed beyond 65% conversion.

(21) Cleavage of the nonaflate was observed in the presence of amine and alkoxide in the absence of Pd. This side reaction had also been observed with the corresponding triflates (see ref 2f).

TABLE 2. Room-Temperature Catalytic Amination of Aryl Nonaflates[a]

Entry	Nonaflate	Amine	Product	Yield (%)[b]
1				87[c]
2				93
3		H_2NBn		88
4				91[c]
5				85
6		H_2NBn		85
7		H_2NHex		82

[a] Reaction conditions: 1.0 equiv of aryl nonaflate, 1.2 equiv of amine, 1.4 equiv of NaO*t*-Bu, $Pd(OAc)_2$ (1 mol %), cat. ligand **4** (L/Pd = 2/1), toluene (1.5−3.0 mL/mmol of nonaflate), rt, 18−24 h. [b] Yields represent isolated yields of compounds estimated to be ≥95% pure as judged by ^{1}H NMR, GC analysis, and combustion analysis. [c] Pd_2dba_3 used in place of $Pd(OAc)_2$.

As shown in Table 4, chloro nonaflates proved to be the best substrates in this class, resulting in chemoselective amination of the nonaflate moiety in reasonable yields with use of **2** or BINAP **6** (entries 1−6).[24] Bromo nonaflates proved to be more challenging substrates resulting in much lower yields.

In all but one instance, the selective substitution of the nonaflate was observed. Interestingly when **4** was used, aniline was selectively substituted for the bromide in preference to the nonaflate (Table 4, entry 8).[22a,25]

In conclusion we have described the first detailed study of the Pd-catalyzed amination of a variety of aryl nonaflates. This work complements the existing methodology for amination of aryl triflates, particularly for substrates bearing electron-withdrawing substituents, and in some cases allows the selective reaction of halo nonaflate substrates.

Experimental Details

Reagents. $Pd(OAc)_2$, Pd_2dba_3, and ligands **1**−**6** were purchased from Strem Chemical Co. and used without further purification. NaO*t*-Bu was stored under nitrogen in a Vacuum Atmosphere glovebox. Small portions (1−2 g) were removed from the glovebox in glass vials, stored in the air in desiccators filled with anhydrous calcium sulfate, and weighed in the air. Toluene, THF, and dichloromethane were purchased from J. T. Baker in CYCLE-TAINER solvent delivery kegs, which were vigorously purged with argon for 2 h, and further purified by passing the solvent through two packed columns of neutral alumina and copper(II) oxide under argon pressure. All other reagents were purchased from commercial sources and used without further purification.

Analytical Methods. All reactions were carried out under an argon atmosphere in oven-dried glassware. IR spectra were obtained by placing neat samples directly on the DiComp probe of an ASI REACTIR in situ IR instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian XL 300, Varian XL 500, or Bruker 400 MHz instruments with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Yield refers to isolated yields of compounds greater than 95% purity as determined by capillary gas chromatography (GC), and proton nuclear magnetic resonance spectroscopy (^{1}H NMR) analysis. Yields for the preparation of starting materials (nonaflates) refer to

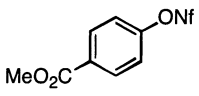
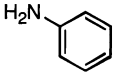
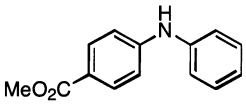
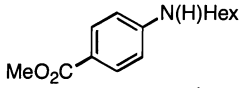
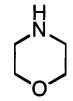
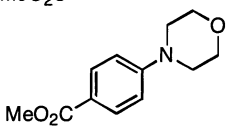
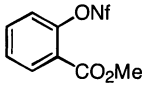
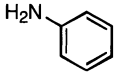
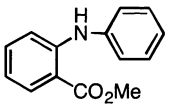
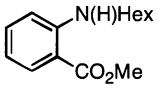
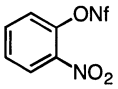
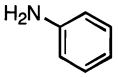
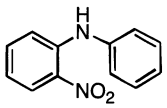
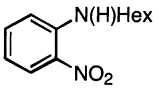
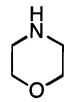
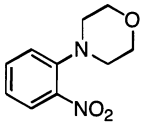
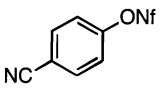
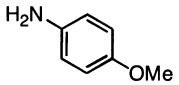
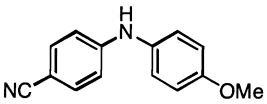
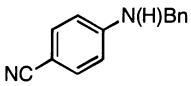
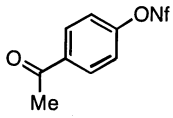
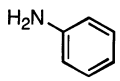
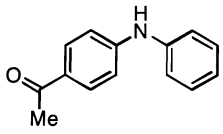
(22) These halide additives are often necessary to obtain high yields of coupled products with aryl triflates in Stille reactions: (a) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (b) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434 and references therein.

(23) It has been reported that the addition of halides inhibits the amination of aryl halides: (a) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609. (b) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.

(24) In these reactions only trace amounts of phenol or diamination products were detected by GC analysis.

(25) For recent Pd-catalyzed reactions where an aryl halide (Br, Cl) reacts in preference to an aryl triflate, see: (a) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343. (b) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (c) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.

TABLE 3. Palladium-Catalyzed Amination of Functionalized Aryl Nonaflates[a]

Entry	Nonaflate	Amine	Product	Ligand	Yield (%)[b]
1				**5**	92[c]
2		H_2NHex		**2**	81
3				**5**	94[c,d]
4				**5**	91
5		H_2NHex		**5**	93
6				**5**	97
7		H_2NHex		**5**	83
8				**5**	85
9				**5**	94
10		H_2NBn		**5**	88[e]
11				**5**	97

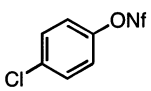
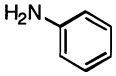
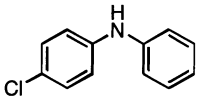
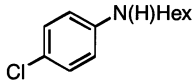
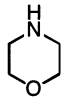
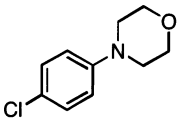
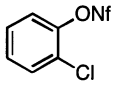
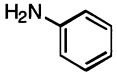
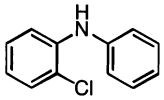
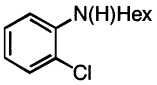
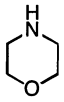
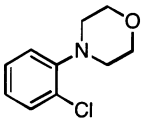
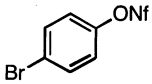
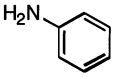
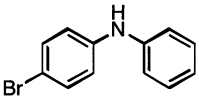
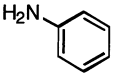
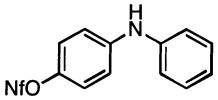
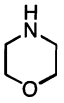
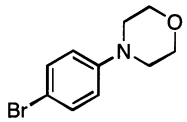
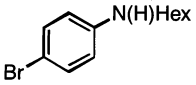
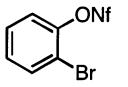
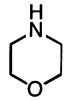
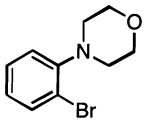
[a] Reaction conditions: 1.0 equiv of aryl nonaflate, 1.2 equiv of amine, 1.4 equiv of K_3PO_4, Pd_2dba_3 (1 mol %), cat. ligand (L/Pd = 1/1), toluene (1.5 mL/mmol of nonaflate), 105 °C, 24 h. [b] Yields represent isolated yields of compounds estimated to be ≥95% pure as judged by ^1H NMR, GC analysis, and combustion analysis. [c] L/Pd = 2/1. [d] 2 mol % of Pd_2dba_3 used. [e] 5.0 equiv of amine used.

a single experiment whereas those reported in Tables 1−4 are an average of two or more runs. The procedures described in this section are representative, thus, the yields may differ slightly from those given in Tables 1−4. ^1H NMR and melting points (where applicable) of all known compounds were taken. All new nonaflates and new amines were further characterized by elemental analysis except for *N*-[4-(nonafluorobutanesulfonyl)oxy]-phenyl-aniline (Table 4, entry 8), for which a HRMS was obtained.

General Procedure for the Synthesis of Nonaflates (Method 1). A round-bottom flask was charged with diethyl ether (4 mL/mmol of phenol) and NaH (1.3 equiv). The flask was cooled to 0 °C and a solution of phenol (1 equiv) in diethyl ether (0.5 mL/mmol) was slowly added. After 15 min, nonafluorobutanesulfonic fluoride (1.4 equiv) was added dropwise and the solution was allowed to warm to room temperature and stirred for 12 h. To the reaction mixture was added water (30 mL) and diethyl ether (50 mL) and the organic layer was separated. The aqueous layer was extracted twice with diethyl ether (2 × 10 mL) and the combined organic extracts were washed with aqueous NaOH (5%) and brine (20 mL), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel (eluting with ethyl acetate/hexane mixtures).

General Procedure for the Synthesis of Nonaflates (Method 2). A solution of phenol (1.0 equiv), cat. DMAP (0.05 equiv), and *i*-Pr_2NEt (1.2 equiv, 2.60 mL, 15.5 mmol) in dichloromethane (20 mL) was cooled to 0 °C in an ice bath and nonafluorobutanesulfonic fluoride (1.1 equiv) was added dropwise. The solution was allowed to warm to room temperature and stirred for 12 h after which the solution was poured into water (20 mL/mmol of phenol). The organic layer was extracted with dichloromethane, washed with brine, dried over

TABLE 4. Palladium-Catalyzed Amination of Halo-Aryl Nonaflates[a]

Entry	Nonaflate	Amine	Product	Ligand	Yield (%)[b]
1				**2**	88[c]
2		H_2NHex		**2**	63
3				**6**	77
4				**2**	87[c,e,f]
5		H_2NHex		**6**	69
6				**6**	85[c,d]
7				**6**	59
8				**4**	68[g]
9				**6**	79
10		H_2NHex		**6**	63
11				**6**	66

[a] Reaction conditions: 1.0 equiv of aryl nonaflate, 1.2 equiv of amine, 1.4 equiv of NaO*t*-Bu, Pd_2dba_3 (1 mol %), cat. ligand (L/Pd = 1/1), toluene (1.5 mL/mmol of nonaflate), 80−105 °C, 18−24 h. [b] Yields represent isolated yields of compounds estimated to be ≥95% pure as judged by ^{1}H NMR, GC analysis, and combustion analysis. [c] K_3PO_4 used instead of NaO*t*-Bu. [d] Reaction took 39 h. [e] L/Pd = 2/1. [f] Reaction carried out at 60 °C. [g] Reaction complete in 3 h.

anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes mixtures).

4-(*tert*-Butylphenyl) Nonaflate. With Method 1, 4-*tert*-butyl-phenol (1.50 g, 10.0 mmol), sodium hydride (520 mg, 13.0 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60 mL, 20.0 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with pentanes) to give the title compound as a colorless oil (3.6 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.9 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 147.7, 127.2, 120.7, 109.9−118.3 (m, 4C), 34.7, 31.2. IR (neat, cm^{-1}) 2967, 1503, 1427, 1243, 1205, 1144, 896. Anal. Calcd for $C_{14}H_{13}F_9O_3S$: C, 38.90; H, 3.03. Found: C, 39.13; H, 3.01.

4-(Methoxyphenyl) Nonaflate.[26] With Method 1, 4-methoxyphenol (1.241 g, 10.10 mmol), sodium hydride (525 mg, 13.1 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60 mL, 20.2 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a colorless oil (3.2 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21−7.25 (m, 2H), 6.98−7.05 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 143.3, 122.4, 114.8, 109.4−118.3 (m, 4C), 55.7.

2-(Methylphenyl) Nonaflate.[26] With Method 1, 2-methylphenol (1.092 g, 10.10 mmol), sodium hydride (525 mg, 13.1 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60

(26) Subramanian, L. R.; Garcia Martinez, A.; Herrero Fernandez, A.; Martinez Alvarez, R. *Synthesis* **1984**, 481.

mL, 20.2 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with pentanes) to give the title compound as a colorless oil (2.5 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.29 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 132.2, 131.0, 128.3, 127.7, 121.3, 109.4−118.3 (m, 4C), 16.4.

2,6-(Dimethylphenyl) Nonaflate. With Method 2, 2,6-dimethylphenol (1.899 g, 15.55 mmol), *i*-Pr_2NEt (3.25 mL, 18.7 mmol), nonafluorobutanesulfonic fluoride (3.07 mL, 17.1 mmol), DMAP (95 mg, 0.70 mmol), and dichloromethane (25 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:9) to give the title compound as a colorless oil (3.7 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.12 (m, 3H), 2.4 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 131.9, 130.2, 128.3, 109.3−118.4 (m, 4C), 17.4. IR (neat, cm^{-1}) 1475, 1406, 1353, 1202, 1144, 1079, 1034, 887, 776. Anal. Calcd for $C_{12}H_9F_9O_3S$: C, 35.65; H, 2.24. Found: C, 35.68; H, 2.23.

Methyl 4-[(Nonafluorobutanesulfonyl)oxy] Benzoate. With Method 1, methyl (4-hydroxy) benzoate (1.520 g, 10.00 mmol), sodium hydride (520 mg, 13.0 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60 mL, 20.0 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a colorless oil (3.6 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, J = 9.2, 1.2 Hz, 2H), 6.92 (dd, J = 9.2, 1.2 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 143.3, 122.4, 114.8−118.3 (m, 3C), 115.0, 109.7 (m), 55.8. IR (neat, cm^{-1}) 1732, 1601, 1434, 1285, 1203, 1145, 893. Anal. Calcd for $C_{12}H_7F_9O_5S$: C, 33.19; H, 1.62. Found: C, 33.40; H, 1.61.

Methyl 2-[(Nonafluorobutanesulfonyl)oxy] Benzoate. With Method 1, methyl (2-hydroxy) benzoate (1.30 mL, 10.0 mmol), sodium hydride (520 mg, 13.0 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60 mL, 20.0 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a white solid (3.2 g, 74%), mp 40−42 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 7.7 Hz, 1H), 7.64 (ddd, J = 8.2, 7.4, 1.9 Hz, 1H), 7.40 (td, J = 7.4, 1.1 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 148.5, 134.3, 132.7, 128.4, 124.6, 122.8, 107.9−118.2 (m, 4C), 52.6. IR (neat, cm^{-1}) 1732, 1606, 1430, 1240, 1190, 1135, 895. Anal. Calcd for $C_{12}H_7F_9O_5S$: C, 33.19; H, 1.62. Found: C, 33.20; H, 1.60.

2-(Nitrophenyl) Nonaflate. With Method 2, 2-nitrophenol (1.30 g, 10.0 mmol), *i*-Pr_2NEt (2.10 mL, 12.0 mmol), nonafluorobutanesulfonic fluoride (1.90 mL, 11.0 mmol), DMAP (60 mg, 0.50 mmol), and dichloromethane (20 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:6) to give the title compound as a white solid (2.7 g, 64%), mp 33−35 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0, 1.7 Hz, 1H), 7.67 (ddd, J = 8.2, 7.4, 1.9 Hz, 1H), 7.60 (td, J = 7.7, 1.4 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 135.2, 129.2, 126.7, 124.2, 109.0−118.4 (m, 4C), 99.3. IR (neat, cm^{-1}) 2921, 1601, 1538, 1434, 1235, 1200, 1142. Anal. Calcd for $C_{10}H_4F_9O_5NS$: C, 28.52; H, 0.96. Found: C, 28.49; H, 0.97.

4-(Nonafluorobutanesulfonyl)-benzonitrile. With Method 2, 4-cyanophenol (1.852 g, 15.55 mmol), *i*-Pr_2NEt (3.25 mL, 18.7 mmol), nonafluorobutanesulfonic fluoride (3.07 mL, 17.1 mmol), DMAP (95 mg, 0.70 mmol), and dichloromethane (25 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1.5:8.5) to give the title compound as a white solid (5.5 g, 88%), mp 111−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 134.7, 122.8, 117.3, 113.1, 109.2−18.7 (m, 4C). IR (neat, cm^{-1}) 2235, 1599, 1498, 1430, 1237, 1202, 1146, 889, 847. Anal. Calcd for $C_{11}H_4F_9O_3NS$: C, 32.93; H, 1.00. Found: C, 33.09; H, 1.00.

4-(Acetylphenyl) Nonaflate. With Method 2, 4-acetylphenol (1.36 g, 10.0 mmol), *i*-Pr_2NEt (2.10 mL, 12.0 mmol), nonafluorobutanesulfonic fluoride (1.90 mL, 11.0 mmol), DMAP (60 mg, 0.50 mmol), and dichloromethane (20 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:4) to give the title compound as a white solid (3.9 g, 92%), mp 38−40 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 152.7, 136.7, 130.6, 121.6, 96.7−118.1 (m, 4C), 26.7. IR (neat, cm^{-1}) 1694, 1594, 1422, 1356, 1265, 1203. Anal. Calcd for $C_{10}H_7F_9O_4S$: C, 34.46; H, 1.69. Found: C, 34.36; H, 1.70.

4-Chlorophenyl Nonaflate.[26] With Method 1, 4-chlorophenol (1.285 g, 10.00 mmol), sodium hydride (520 mg, 13.0 mmol, 60% dispersion), nonafluorobutanesulfonic fluoride (3.60 mL, 20.0 mmol), and diethyl ether (40 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:4) to give the title compound as a colorless oil (3.0 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 9.1 Hz, 2H), 7.23 (d, J = 9.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 134.3, 130.4, 122.7, 108.5−118.2 (m, 4C).

2-Chlorophenyl Nonaflate. With Method 2, 2-chlorophenol (1.29 g, 10.0 mmol), *i*-Pr_2NEt (2.10 mL, 12.0 mmol), nonafluorobutanesulfonic fluoride (1.90 mL, 11.0 mmol), DMAP (60 mg, 0.50 mmol), and dichloromethane (20 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a colorless oil (3.9 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51−7.55 (m, 3H), 7.31−7.38 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 131.3, 129.2, 128.3, 127.5, 123.0, 107.7−118.2 (m, 4C). IR (neat, cm^{-1}) 1430, 1240, 1203, 1144, 890, 768. Anal. Calcd for $C_{10}H_4F_9O_3SCl$: C, 29.25; H, 0.98. Found: C, 29.05; H, 0.98.

4-Bromophenyl Nonaflate. With Method 2, 4-bromophenol (2.238 g, 12.94 mmol), *i*-Pr_2NEt (2.70 mL, 15.5 mmol), nonafluorobutanesulfonic fluoride (2.60 mL, 14.2 mmol), DMAP (79 mg, 0.60 mmol), and dichloromethane (25 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a colorless oil (5.6 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, J = 9.1 Hz, 2H), 7.59 (d, J = 9.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 133.3, 123.0, 121.9, 103.3−118.5 (m, 4C). IR (neat, cm^{-1}) 1481, 1430, 1240, 1204, 1146, 890. Anal. Calcd for $C_{10}H_4F_9O_3SBr$: C, 26.39; H, 0.89. Found: C, 26.19; H, 0.97.

2-Bromophenyl Nonaflate. With Method 2, 2-bromophenol (2.238 g, 12.94 mmol), *i*-Pr_2NEt (2.70 mL, 15.5 mmol), nonafluorobutanesulfonic fluoride (2.60 mL, 14.2 mmol), DMAP (79 mg, 0.60 mmol), and dichloromethane (25 mL) were used. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexanes, 1:10) to give the title compound as a colorless oil (5.7 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.54 (m, 1H), 7.25−7.37 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 134.5, 129.5, 129.1, 122.9, 107.7−118.2 (m, 4C). IR (neat, cm^{-1}) 2926, 1431, 1240, 1202, 1144, 1033, 890. Anal. Calcd for $C_{10}H_4F_9O_3SBr$: C, 26.39; H, 0.89. Found: C, 26.61; H, 0.89.

General Procedure for Catalytic Amination of Aryl Nonaflates. An oven-dried resealable Schlenk flask was charged with Pd_2dba_3 (1 mol %, 2 mol % of Pd) or $Pd(OAc)_2$ (2 mol % of Pd), ligand (2−4 mol %), and base (1.4 equiv). The flask was evacuated and backfilled with argon; this sequence was repeated two additional times. The flask was capped with a rubber septum and toluene (1.5 mL/mmol of nonaflate), the nonaflate (1.0 equiv), and the amine (1.2 equiv.) were added through the septum via syringe (aryl nonaflates or amines that were solids at room temperature were added prior to addition of the base). The septum was replaced with a Teflon screwcap,

the flask was sealed, and the mixture was allowed to stir at room temperature or heated in an oil bath (80 or 105 °C) with stirring until the starting nonaflate had been completely consumed as judged by GC analysis. The mixture was cooled to room temperature, diluted with diethyl ether (20 mL), filtered through Celite, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane mixtures).

***N*-(4-*tert*-Butylphenyl)-aniline (Table 1, entry 1).**[27] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (432 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **2** (7.8 mg, 0.020 mmol), aniline (0.109 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (3 mL) was heated at 105 °C for 12 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (210 mg, 93%), mp 65−66 °C (lit.[27] mp 67 °C).

***N*-(4-*tert*-Butylphenyl)-*n*-hexylamine (Table 1, entry 2).**[28] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (432 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **2** (15.6 mg, 0.0400 mmol), *n*-hexylamine (0.159 mL, 1.20 mmol), and K_3PO_4 (297 mg, 1.40 mmol) in toluene (3 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (183 mg, 78%).

Benzyl-(4-*tert*-butylphenyl)-amine (Table 1, entry 3).[2a] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (216 mg, 0.500 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), ligand **4** (3.0 mg, 0.010 mmol), benzylamine (0.065 mL, 0.60 mmol), and NaO*t*-Bu (67 mg, 0.700 mmol) in toluene (1 mL) was heated at 80 °C for 21 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a colorless oil (94 mg, 78%).

Dibutyl-(4-*tert*-butylphenyl)-amine (Table 1, entry 4).[29] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (216 mg, 0.500 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), ligand **3** (3.5 mg, 0.010 mmol), di-*n*-butylamine (0.101 mL, 0.600 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (1 mL) was heated at 80 °C for 19 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:19) to give the title compound as a colorless oil (105 mg, 81%).

(4-Methoxyphenyl)-phenyl-amine (Table 1, entry 5).[30] With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (203 mg, 0.500 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), ligand **2** (4.0 mg, 0.010 mmol), aniline (0.054 mL, 0.60 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (1.5 mL) was heated at 105 °C for 20 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a white solid (96 mg, 98%), mp 99−101 °C (lit.[30] mp 98−100 °C).

4-(4-Methoxyphenyl)-morpholine (Table 1, entry 6).[31] With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (203 mg, 0.500 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), ligand **2** (8.0 mg, 0.020 mmol), morpholine (0.052 mL, 0.60 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (0.75 mL) was heated at 105 °C for 20 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:4) to give the title compound as a white solid (76 mg, 80%), mp 72 °C (lit.[31] mp 73.3 °C).

Phenyl-*o*-tolyl-amine (Table 1, entry 7).[30] With the general procedure, a solution of 2-(methylphenyl) nonaflate (200 mg, 0.510 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), ligand **2** (4.0 mg, 0.010 mmol), aniline (0.056 mL, 0.60 mmol), and K_3PO_4 (151 mg, 0.710 mmol) in toluene (1.5 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (81 mg, 86%), mp 37 °C (lit.[30] mp 38 °C).

Hexyl-*o*-tolyl-amine (Table 1, entry 8).[32] With the general procedure, a solution of 2-(methylphenyl) nonaflate (200 mg, 0.510 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), ligand **2** (4.0 mg, 0.010 mmol), *n*-hexylamine (0.081 mL, 0.60 mmol), and K_3PO_4 (151 mg, 0.710 mmol) in toluene (1.5 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a yellow oil (82 mg, 84%).

4-(2,6-Dimethylphenyl)-morpholine (Table 1, entry 9).[2a] With the general procedure, a solution of 2,6-(dimethylphenyl) nonaflate (202 mg, 0.500 mmol), Pd_2dba_3 (4.6 mg, 0.0050 mmol), ligand **2** (4.0 mg, 0.010 mmol), morpholine (0.053 mL, 0.60 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (1.5 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a light brown solid (76 mg, 80%), mp 86 °C (lit.[2a] mp 86−87 °C).

(2,6-Diisopropylphenyl)-(2,6-dimethyl-phenyl)-amine (Table 1, entry 10).[2a] With the general procedure, a solution of 2,6-(dimethylphenyl) nonaflate (202 mg, 0.500 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **2** (8.0 mg, 0.020 mmol), 2,6-diisopropyl aniline (0.113 mL, 0.600 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (1.0 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (130 mg, 93%).

Benzhydrylidene-(2,6-dimethylphenyl)-amine (Table 1, entry 11).[33] With the general procedure, a solution of 2,6-(dimethylphenyl) nonaflate (300 mg, 0.740 mmol), Pd_2dba_3 (6.8 mg, 0.0074 mmol), ligand **6** (18.5 mg, 0.0296 mmol), freshly distilled benzophenone imine (0.149 mL, 0.897 mmol), and NaO*t*-Bu (99 mg, 1.0 mmol) in toluene (2.5 mL) was heated at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:19) to give the title compound as a yellow oil (206 mg, 97%).

(4-*tert*-Butylphenyl)-(4-methoxy-phenyl)-amine (Table 2, entry 1).[2a] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (432 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **4** (7.5 mg, 0.025 mmol), 4-methoxy aniline (148 mg, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (3 mL) was stirred at room temperature for 28 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (222 mg, 87%), mp 80−81 °C (lit.[2a] mp 80−82 °C).

4-(4-*tert*-Butylphenyl)-morpholine (Table 2, entry 2).[2a] With the general procedure, a solution of 4-(*tert*-butylphenyl) nonaflate (432 mg, 1.00 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), ligand **4** (6.0 mg, 0.020 mmol), morpholine (0.106 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (1.5 mL) was stirred at room temperature for 24 h (usually formed a gel within 1 h). The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (198 mg, 90%), mp 58 °C (lit.[2a] mp 59 °C).

Benzyl-(4-*tert*-butylphenyl)-amine (Table 2, entry 3).[2a] With the general procedure, a solution of 4-(*tert*-butylphenyl)

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nonaflate (216 mg, 0.500 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), ligand **4** (3.0 mg, 0.010 mmol), benzylamine (0.065 mL, 0.60 mmol), and NaO*t*-Bu (67 mg, 0.70 mmol) in toluene (0.7 mL) was stirred at room temperature for 21 h (usually formed a gel within 1 h). The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a colorless oil (105 mg, 88%).

(4-Methoxyphenyl)-phenyl-amine (Table 2, entry 4).[30] With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (406 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **2** (6.0 mg, 0.020 mmol), aniline (0.109 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (1.5 mL) was stirred at room temperature (usually formed a gel within 1 h) for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a white solid (182 mg, 92%), mp 100 °C (lit.[30] mp 98−100 °C).

4-(4-Methoxy-phenyl)-morpholine (Table 2, entry 5).[31] With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (406 mg, 1.00 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), ligand **2** (6.0 mg, 0.020 mmol), morpholine (0.106 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (1.5 mL) was stirred at room temperature (usually formed a gel within 1 h) for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 3:7) to give the title compound as a white solid (170 mg, 88%), mp 71−72 °C (lit.[31] mp 73.3 °C).

Benzyl-(4-methoxyphenyl)-amine (Table 2, entry 6).[34] With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (406 mg, 1.00 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), ligand **2** (6.0 mg, 0.020 mmol), benzylamine (0.131 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (1.5 mL) was stirred at room temperature (usually formed a gel within 1 h) for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a colorless oil (181 mg, 85%).

***N*-(4-Methoxyphenyl)-*n*-hexylamine (Table 2, entry 7).** With the general procedure, a solution of 4-(methoxyphenyl) nonaflate (406 mg, 1.00 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), ligand **2** (6.0 mg, 0.020 mmol), *n*-hexylamine (0.159 mL, 1.20 mmol), and NaO*t*-Bu (135 mg, 1.40 mmol) in toluene (1.5 mL) was stirred at room temperature (usually formed a gel within 1 h) for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:9) to give the title compound as a colorless oil (174 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 8.9 Hz), 3.79 (s, 3H), 3.36 (br s, 1H), 3.10 (t, J = 7.2 Hz, 2H), 1.64 (m, J = 7.7 Hz, 2H), 1.47−1.37 (m, 6H), 0.97 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 142.9, 114.9, 114.0, 55.8, 45.1, 31.8, 29.7, 27.0, 22.8, 14.2. IR (neat, cm^{-1}) 3393, 1619, 1514, 1294, 1236, 1179, 1040, 818. Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21. Found: C, 75.58; H, 10.25.

***N*-(4-Methoxycarbonylphenyl)-aniline (Table 3, entry 1).** With the general procedure, a solution of methyl 4-[(nonafluorobutanesulfonyl)oxy] benzoate (200 mg, 0.480 mmol), Pd_2dba_3 (4.2 mg, 0.0046 mmol), ligand **5** (11.0 mg, 0.0180 mmol), aniline (0.051 mL, 0.55 mmol), and K_3PO_4 (137 mg, 0.640 mmol) in toluene (1.5 mL) was stirred at 105 °C for 15 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:3) to give the title compound as a pale yellow solid (92 mg, 89%), mp 108−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dt, J = 8.8, 2.5 Hz, 2H), 7.33 (tt, J = 7.5, 1.6 Hz, 2H), 7.18 (d, J = 7.4 Hz, 2H), 7.05 (t, J = 7.2 Hz, 1H), 6.97 (dt, J = 8.8, 2.5 Hz, 2H), 6.10 (br s, 1H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 147.9, 140.7, 131.3, 129.4, 122.9, 120.9, 120.3, 114.4, 51.7. IR (neat, cm^{-1}) 3343, 1695, 1592, 1280, 1170, 1109, 747. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77. Found: C, 73.93; H, 5.92.

***N*-(4-Methoxycarbonylphenyl)-*n*-hexylamine (Table 3, entry 2).**[2a] With the general procedure, a solution of methyl 4-[(nonafluorobutanesulfonyl)oxy] benzoate (200 mg, 0.480 mmol), Pd_2dba_3 (4.2 mg, 0.0046 mmol), ligand **2** (3.6 mg, 0.0092 mmol), *n*-hexylamine (0.073 mL, 0.55 mmol), and K_3PO_4 (138 mg, 0.650 mmol) in toluene (0.9 mL) was stirred at 105 °C for 16 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (86 mg, 79%), mp 93−94 °C (lit.[2a] mp 93−94 °C).

***N*-(4-Methoxycarbonylphenyl)-morpholine (Table 3, entry 3).**[35] With the general procedure, a solution of methyl 4-[(nonafluorobutanesulfonyl)oxy] benzoate (200 mg, 0.480 mmol), Pd_2dba_3 (4.2 mg, 0.0046 mmol), ligand **5** (10.6 mg, 0.0184 mmol), morpholine (0.049 mL, 0.55 mmol), and K_3PO_4 (137 mg, 0.640 mmol) in toluene (1.5 mL) was stirred at 105 °C for 16 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:2) to give the title compound as a white solid (96 mg, 94%), mp 154−156 °C (lit.[35] mp 152−154 °C).

***N*-(2-Methoxycarbonylphenyl)-aniline (Table 3, entry 4).**[36] With the general procedure, a solution of methyl 2-[(nonafluorobutanesulfonyl)oxy] benzoate (200 mg, 0.480 mmol), Pd_2dba_3 (4.2 mg, 0.0046 mmol), ligand **5** (5.3 mg, 0.0092 mmol), aniline (0.051 mL, 0.55 mmol), and K_3PO_4 (137 mg, 0.640 mmol) in toluene (1.5 mL) was stirred at 105 °C for 14 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a pale yellow solid (95 mg, 91%), mp 52−54 °C (lit.[36] mp 54−56 °C).

***N*-(2-Methoxycarbonylphenyl)-*n*-hexylamine (Table 3, entry 5).** With the general procedure, a solution of methyl 2-[(nonafluorobutanesulfonyl)oxy] benzoate (200 mg, 0.480 mmol), Pd_2dba_3 (4.2 mg, 0.0046 mmol), ligand **5** (5.3 mg, 0.0092 mmol), *n*-hexylamine (0.073 mL, 0.55 mmol), and K_3PO_4 (137 mg, 0.640 mmol) in toluene (1.5 mL) was stirred at 105 °C for 15 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:20) to give the title compound as a colorless oil (100 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.9, 1.7 Hz, 1H), 7.69 (br s, 1H), 7.35 (m, 1H), 6.68 (d, J = 7.7 Hz, 1H), 6.57 (t, J = 7.2 Hz, 1H), 3.86 (br s, 3H), 3.19 (t, J = 6.9 Hz, 2H), 1.65−1.75 (m, 2H), 1.31−1.49 (m, 6H), 0.52 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 151.1, 134.5, 131.5, 114.0, 111.1, 109.4, 51.4, 42.9, 31.7, 29.2, 26.9, 22.7, 14.2. IR (neat, cm^{-1}) 3365, 1686, 1581, 1518, 1450, 1259, 1169, 749. Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.46; H, 8.99. Found: C, 71.26; H, 9.03.

***N*-(2-Nitrophenyl)-aniline (Table 3, entry 6).** With the general procedure, a solution of 2-(nitrophenyl) nonaflate (200 mg, 0.470 mmol), Pd_2dba_3 (4.3 mg, 0.0047 mmol), ligand **5** (5.4 mg, 0.0094 mmol), aniline (0.052 mL, 0.56 mmol), and K_3PO_4 (140 mg, 0.660 mmol) in toluene (1.8 mL) was stirred at 105 °C for 13 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:6) to give the title compound as a orange oil (98 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.49 (br s, 1H), 8.20 (dd, J = 8.5, 1.6 Hz, 1H), 7.34−7.44 (m, 3H), 7.21−7.33 (m, 4H), 6.74−6.79 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 138.5, 135.6, 133.0, 129.6, 126.5, 125.5, 124.2, 117.4, 115.9. IR (neat, cm^{-1}) 3352, 3063, 1614, 1573, 1504, 1348, 1263, 1148, 741. Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71. Found: C, 67.52; H, 4.71.

***N*-(2-Nitrophenyl)-*n*-hexylamine (Table 3, entry 7).** With the general procedure, a solution of 2-(nitrophenyl) nonaflate (200 mg, 0.470 mmol), Pd_2dba_3 (4.3 mg, 0.0047

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mmol), ligand **5** (5.4 mg, 0.0094 mmol), *n*-hexylamine (0.075 mL, 0.56 mmol), and K_3PO_4 (140 mg, 0.660 mmol) in toluene (1.8 mL) was stirred at 105 °C for 13 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a bright orange oil (86 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, J = 8.8 Hz, 1H), 8.10 (br s, 1H), 7.38−7.45 (m, 1H), 6.84 (d, J = 8.8 Hz, 1H), 5.59−6.64 (m, 1H), 3.29 (t, J = 7.1 Hz, 2H), 1.68−1.78 (m, 2H), 1.25−1.49 (m, 6H), 0.75−0.93 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 136.2, 131.7, 126.9, 115.0, 113.8, 43.0, 31.5, 28.9, 26.3, 22.5, 14.0. IR (neat, cm^{-1}) 3381, 1618, 1510, 1350, 1260, 1156, 1038. Anal. Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16. Found: C, 65.07; H, 8.20.

***N*-(2-Nitrophenyl)-morpholine (Table 3, entry 8).** With the general procedure, a solution of 2-(nitrophenyl) nonaflate (200 mg, 0.470 mmol), Pd_2dba_3 (4.3 mg, 0.0047 mmol), ligand **5** (5.4 mg, 0.0094 mmol), morpholine (0.049 mL, 0.56 mmol), and K_3PO_4 (140 mg, 0.660 mmol) in toluene (1.8 mL) was stirred at 105 °C for 13 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:4) to give the title compound as a bright yellow oil (83 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (dt, J = 7.9, 1.2 Hz, 1H), 7.50 (d, J = 6.4 Hz, 1H), 7.16 (d, J = 7.4 Hz, 1H), 7.09 (t, J = 6.1 Hz, 1H), 3.85 (t, J = 4.6 Hz, 4H), 3.06 (t, J = 4.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 143.3, 133.6, 125.9, 122.3, 120.8, 66.8, 52.1. IR (neat, cm^{-1}) 2961, 2856,1605, 1520, 1344, 1115, 936, 754. Anal. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.68; H, 5.81. Found: C, 57.59; H, 5.84.

4-(4-Methoxyphenylamino)-benzonitrile (Table 3, entry 9).[37] With the general procedure, a solution of 4-(nonafluorobutanesulfonyl)-benzonitrile (401 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **5** (11.6 mg, 0.0200 mmol), *p*-anisidine (148 mg, 1.20 mmol), and K_3PO_4 (297 mg, 1.40 mmol) in toluene (3 mL) was stirred at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 3:7) to give the title compound as a light yellow solid (206 mg, 92%), mp 100 °C (lit.[37] mp 99−100 °C).

4-Benzylamino-benzonitrile (Table 3, entry 10).[38] With the general procedure, a solution of 4-(nonafluorobutanesulfonyl)-benzonitrile (401 mg, 1.00 mmol), Pd_2dba_3 (9.2 mg, 0.010 mmol), ligand **5** (11.6 mg, 0.0200 mmol), benzylamine (0.327 mL, 3.00 mmol), and K_3PO_4 (297 mg, 1.40 mmol) in THF (4 mL) was stirred at 65 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:4) to give the title compound as a light yellow solid (185 mg, 88%), mp 66 °C (lit.[38] mp 65 °C).

***N*-(4-Acetylphenyl)-aniline (Table 3, entry 11).**[39] With the general procedure, a solution of 4-(acetylphenyl) nonaflate (200 mg, 0.470 mmol), Pd_2dba_3 (4.4 mg, 0.0048 mmol), ligand **5** (5.5 mg, 0.0096 mmol), aniline (0.053 mL, 0.57 mmol), and K_3PO_4 (143 mg, 0.670 mmol) in toluene (0.75 mL) was stirred at 105 °C for 14 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:6) to give the title compound as a yellow solid (92 mg, 91%), mp 104−105 °C (lit.[39] mp 106 °C).

***N*-(4-Chlorophenyl)-aniline (Table 4, entry 1).**[40] With the general procedure, a solution of 4-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (4.5 mg, 0.0049 mmol), ligand **2** (3.4 mg, 0.0097 mmol), aniline (0.054 mL, 0.59 mmol), and K_3PO_4 (146 mg, 0.690 mmol) in toluene (1.5 mL) was stirred at 105 °C for 13 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:4) to give the title compound as a yellow solid (95 mg, 95%), mp 72−74 °C (lit.[40] mp 74 °C).

***N*-(4-Chlorophenyl)-*n*-hexylamine (Table 4, entry 2).**[40] With the general procedure, a solution of 4-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (4.5 mg, 0.0049 mmol), ligand **2** (3.9 mg, 0.0010 mmol), *n*-hexylamine (0.078 mL, 0.60 mmol), and NaO*t*-Bu (66 mg, 0.680 mmol) in toluene (1.5 mL) was stirred at 105 °C for 16 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (60 mg, 59%).

***N*-(4-Chlorophenyl)-morpholine (Table 4, entry 3).**[41] With the general procedure, a solution of 4-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (9.0 mg, 0.0098 mmol), ligand **6** (24.0 mg, 0.0392 mmol), morpholine (0.052 mL, 0.59 mmol), and K_3PO_4 (146 mg, 0.690 mmol) in toluene (1.5 mL) was stirred at 105 °C for 21 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a pale yellow solid (66 mg, 68%), mp 69−70 °C (lit.[41] mp 71−72 °C).

***N*-(2-Chlorophenyl)-aniline (Table 4, entry 4).** With the general procedure, a solution of 2-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (4.5 mg, 0.0049 mmol), ligand **2** (8.0 mg, 0.020 mmol), aniline (0.054 mL, 0.59 mmol), and K_3PO_4 (146 mg, 0.690 mmol) in toluene (1.5 mL) was stirred at 60 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:6) to give the title compound as a colorless oil (82 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02−7.35 (m, 8H), 6.75−6.99 (m, 1H), 6.08 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 140.2, 129.4, 127.4, 122.6, 121.5, 120.3, 120.1, 115.5. IR (neat, cm^{-1}) 3401, 1587, 1503, 1311, 1090, 750. Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95. Found: C, 70.83; H, 4.98.

***N*-(2-Chlorophenyl)-*n*-hexylamine (Table 4, entry 5).** With the general procedure, a solution of 2-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (4.5 mg, 0.0049 mmol), ligand **6** (12.3 mg, 0.0200 mmol), *n*-hexylamine (0.078 mL, 0.60 mmol), and NaO*t*-Bu (66 mg, 0.70 mmol) in toluene (1.5 mL) was stirred at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (78 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09−7.25 (m, 2H), 6.57−6.65 (m, 2H), 4.25 (br s, 1H), 3.14 (t, J = 7.0 Hz, 2H), 1.61−1.69 (m, 2H), 1.00−1.44 (m, 6H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.9, 127.7, 116.7, 111.0, 43.7, 31.7, 29.3, 26.9, 22.7, 14.1. IR (neat, cm^{-1}) 3421, 2927, 2856, 1599, 1514, 1328, 1033, 739. Anal. Calcd for $C_{12}H_{18}ClN$: C, 68.07; H, 8.57. Found: C, 68.15; H, 8.60.

***N*-(2-Chlorophenyl)-morpholine (Table 4, entry 6).**[42] With the general procedure, a solution of 2-(chlorophenyl) nonaflate (200 mg, 0.490 mmol), Pd_2dba_3 (4.5 mg, 0.0049 mmol), ligand **6** (12.3 mg, 0.0200 mmol), morpholine (0.052 mL, 0.59 mmol), and K_3PO_4 (146 mg, 0.690 mmol) in toluene (1.5 mL) was stirred at 105 °C for 40 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (96 mg, 78%).

***N*-(4-Bromophenyl)-aniline (Table 4, entry 7).**[40] With the general procedure, a solution of 4-(bromophenyl) nonaflate (200 mg, 0.440 mmol), Pd_2dba_3 (4.0 mg, 0.0046 mmol), ligand **6** (12.3 mg, 0.0200 mmol), aniline (0.048 mL, 0.53 mmol), and NaO*t*-Bu (60 mg, 0.62 mmol) in toluene (1.5 mL) was stirred at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a tan solid (53 mg, 49%), mp 87−89 °C (lit.[40] mp 88 °C).

***N*-[4-(Nonafluorobutanesulfonyl)oxy]-phenyl-aniline (Table 4, entry 8).** With the general procedure, a solution of 4-(bromophenyl) nonaflate (200 mg, 0.440 mmol), Pd_2dba_3 (8.0

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mg, 0.0088 mmol), ligand **4** (5.2 mg, 0.0176 mmol), aniline (0.048 mL, 0.53 mmol), and NaO*t*-Bu (60 mg, 0.62 mmol) in toluene (2.0 mL) was stirred at 80 °C for 15 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:4) to give the title compound as a yellow oil (102 mg, 50%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31−7.34 (m, 2H), 6.99−7.29 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 142.7, 141.5, 129.4, 122.4, 122.3, 119.2, 117.2. IR (neat, cm^{-1}) 3419, 3060, 1593, 1504, 1422, 1350, 1240, 1144, 1035, 1010, 890, 751. HRMS (EI) calculated for $C_{16}H_{10}NF_9O_3S$ 467.2038, found 467.2039.

***N*-(4-Bromophenyl)-morpholine (Table 4, entry 9).**[43] With the general procedure, a solution of 4-(bromophenyl) nonaflate (200 mg, 0.440 mmol), Pd_2dba_3 (4.0 mg, 0.0044 mmol), ligand **6** (5.6 mg, 0.009 mmol), morpholine (0.046 mL, 0.53 mmol), and NaO*t*-Bu (60 mg, 0.62 mmol) in toluene (1.5 mL) was stirred at 105 °C for 12 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a white solid (79 mg, 75%), mp 111−112 °C (lit.[43] mp 112−113 °C).

***N*-(4-Bromophenyl)-*n*-hexylamine (Table 4, entry 10).**[43] With the general procedure, a solution of 4-(bromophenyl) nonaflate (200 mg, 0.440 mmol), Pd_2dba_3 (4.0 mg, 0.0044 mmol), ligand **6** (5.6 mg, 0.009 mmol), *n*-hexylamine (0.070 mL, 0.53 mmol), and NaO*t*-Bu (60 mg, 0.62 mmol) in toluene (1.5 mL) was stirred at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:6) to give the title compound as a colorless oil (48 mg, 52%).

***N*-(2-Bromophenyl)-morpholine (Table 4, entry 11).**[44] With the general procedure, a solution of 2-(bromophenyl) nonaflate (200 mg, 0.440 mmol), Pd_2dba_3 (4.0 mg, 0.0044 mmol), ligand **6** (11.0 mg, 0.0176 mmol), morpholine (0.047 mL, 0.53 mmol), and NaO*t*-Bu (60 mg, 0.62 mmol) in toluene (2.0 mL) was stirred at 105 °C for 24 h. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane, 1:10) to give the title compound as a colorless oil (84 mg, 78%).

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