Synthesis of Unsymmetrical Biaryls by Palladium-Catalyzed Cross Coupling Reactions of Arenes with Tetrabutylammonium Triphenyldifluorosilicate, a Hypervalent Silicon Reagent§

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Palladium-catalyzed cross coupling of arenes with tetrabutylammonium triphenyldifluorosilicate, a hypervalent silicon reagent, to give unsymmetrical biaryls is reported. The Pd(0)-catalyzed process proceeds in good yield with aryl iodides, most aryl triflates, and electron-deficient aryl bromides.

Introduction

Stoichiometric or catalytic palladium cross coupling reactions have been used extensively in the formation of C−C bonds.[1] The Stille and Suzuki couplings are the two methodologies most often utilized because of the high yields obtained as well as the high degree of stereoselectivity that is observed.[1−3] A major inadequacy of the Stille coupling technology is a requirement of a large excess of toxic tin reagents to achieve high yields. In addition, the toxic tin byproducts are problematic to remove.[4] The Suzuki coupling has largely supplanted the Stille method due to its generality, although it too has limitations with regard to synthesis and stability of reagents.[5]

Hypervalent silicon species have played an increased role in Pd(0)-catalyzed cross coupling strategies.[6−9] In contrast to the tin reagents traditionally used in Stille-type cross coupling reactions, silicon reagents are less expensive and less toxic, and their byproducts are easier to remove.[2e,7] Previous studies by our group and others have demonstrated that treatment of a tetravalent arylsiloxane, arylchlorosilane, or arylfluorosilane with an anionic salt results in formation of a hypervalent silicon species in situ, which, in turn, undergoes Pd(0)-catalyzed couplings.[6,7,9] A hypervalent silicon species has been postulated to be the reactive intermediate in these processes. Recently, we reported that tetrabutylammonium triphenyldifluorosilicate (TBAT) can serve as a phenylating agent in highly stereoselective Pd(0)-catalyzed cross coupling reactions with allylic esters.[7a] In this paper we report that TBAT can serve as an effective transmetallation reagent in Pd(0)-catalyzed cross coupling reactions with aryl iodides, some aryl triflates, and electron-deficient aryl bromides.

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§ Dedicated to Duilio Argoni on the occasion of his 70th birthday.

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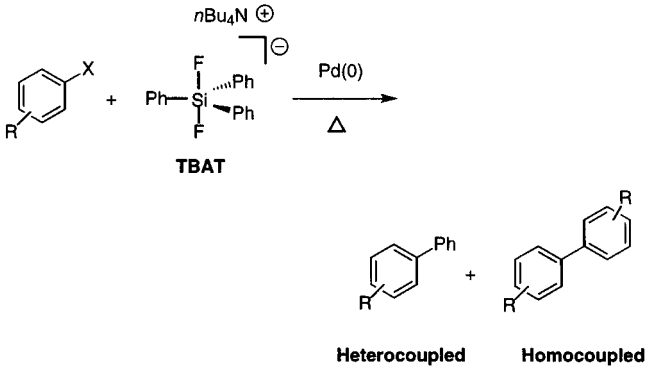
Table 1. Results of Cross Coupling Reactions Using TBAT[a]

Entry	R	X	Catalyst	Solvent	TBAT (eq.)	Time (h)	Yield (%)[b] Hetero	Homo
1	4-Ac	I	APC	DMF	5	5	86	14
2	4-Ac	I	$Pd(dba)_2$	DMF	5	4.5	87	13
3	4-Ac	I	APC	DMF	2	21	100	0
4	4-Ac[c]	I	APC	DMF	2	25.5	90	0
5	4-Ac	I	$Pd(dba)_2$	DMF	2	4.6	96	4
6a	4-Ac	I	APC	THF	2	22	84	16
6b	4-Ac	I	APC	THF	2	6	79	21
7	4-Ac	I	$Pd(dba)_2$	THF	2	19	76	24
8	4-Ac	I	$Pd(dba)_2$	dioxane	2	6	83	17
9	4-Ac[d]	I	$Pd(dba)_2$	THF	1	27.5	80	20
10	4-Ac	I	APC	DMF	1.2	23	93	0
11	4-OMe	I	APC	DMF	3	19	97	0
12	4-OMe	I	$Pd(dba)_2$	THF	2	2.5	88	0
13	4-Me	I	APC	DMF	1.4	4	86	4
14	4-Me	I	$Pd(dba)_2$	THF	2	25.5	64	17
15	3-Me	I	APC	DMF	1.4	24	97	3
16	3-Me	I	$Pd(dba)_2$	THF	2	26.5	68	10
17	2-Me	I	APC	DMF	1.4	4	93	2
18	2-Me	I	$Pd(dba)_2$	THF	2	5	90	0
19	4-Ac	Br	APC	DMF	2	21	62	8
20	4-Ac	Br	$Pd(dba)_2$	THF	2	5	90	0
21	4-Ac	Cl	APC	DMF	2	nr	0	0
22	4-OMe	Br	APC	DMF	2	nr	0	0
23	4-OMe	Cl	APC	DMF	2	nr	0	0
24	4-Me	Br	APC	DMF	2	nr	0	0
25	4-Me	Cl	APC	DMF	2	nr	0	0
26	4-Me	OTf	$Pd(dba)_2$	THF	2	nr	0	0
27	H	OTf	$Pd(dba)_2$	THF	2	nr	0	0
28	4-NO_2	OTf	$Pd(dba)_2$	THF	2	2.5	73	0
29	4-Ac	OTf	$Pd(dba)_2$	THF	2	18.5	73	0
30	4-COOMe	OTf	$Pd(dba)_2$	THF	2	19	90	0
31			$Pd(dba)_2$	THF	2	25.5	71	0

a: Reaction conditions: 10 mol% $Pd(dba)_2$ or 10 mol% APC (allyl palladium chloride dimer). Reactions were degassed by freeze-pump-thaw cycle prior to heating. Solvent and reaction conditions as noted in Table entries.
b: Isolated yield.
c: 20 mol% PPh_3 added.
d: Yield based on recovered starting material.

Scheme 1



Results and Discussion

The general reaction is shown in Scheme 1, and the results are summarized in Table 1. Initial optimization studies utilized 4′-iodoacetophenone as the aryl substrate. Couplings performed with 5 equiv of TBAT and 20 mol % allyl palladium chloride dimer (APC) in DMF gave 86% of the heterocoupled product, 4-acetylbiphenyl, and 14% of the homocoupled product, 4,4′-diacetylbiphenyl (Table 1, entry 1). Reducing the amount of TBAT to 2 equiv (entry 3) gave a quantitative yield of heterocoupled product. Further reducing the amount to 1.2 equiv also gave exclusively the heterocoupled product, but the yield was marginally lower (93% vs 100%, entry 10). Subsequent studies of the coupling reaction were performed with 2 equiv of TBAT to obtain a maximum yield of the heterocoupled product.

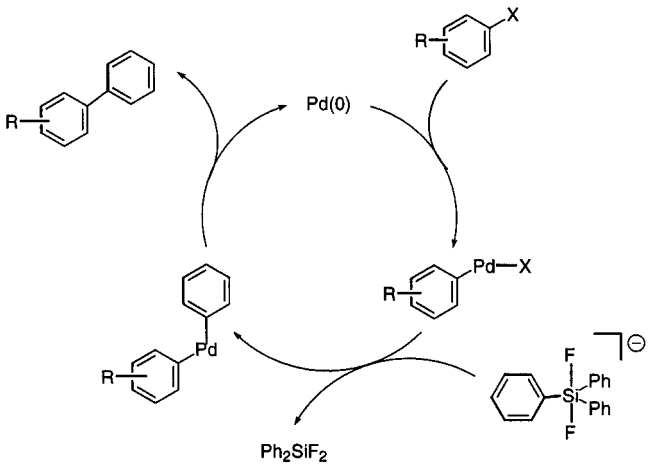
Several palladium catalysts were also investigated. Allylpalladium chloride dimer (APC) is a more reactive catalyst than bis(dibenzylideneacetone)palladium ($Pd(dba)_2$), but APC is particularly air sensitive. Substituting $Pd(dba)_2$ for APC (entry 1 vs 2) did not have a significant effect on either the yield or the product distribution. In entry 5, where 2 equiv of TBAT and $Pd(dba)_2$ are used, there is more homocoupled product formed (4%) than when APC is used (0%, entry 3), but the difference is insignificant.

As was noted in the earlier study of allylic esters,[7a] the presence of phosphines has no appreciable effect on the yield of biaryls. When an equimolar amount of triphenylphosphine to APC was included (entry 4), there was only a 10% decrease in heterocoupled product formed and no homocoupled product was observed. This indicates that the reaction tolerates the presence of phosphine.[2e,7a]

Solvents were also evaluated to determine optimum conditions. Dimethylformamide (DMF) was used initially because it is the typical solvent employed in Stille couplings.[2e] Switching to tetrahydrofuran (THF) resulted in an increase in homocoupled product (entries 6a and 6b). However, changing both the catalyst from APC to $Pd(dba)_2$ and the solvent from DMF to THF gave the most unsatisfactory results (entry 7). If $Pd(dba)_2$ is used as the catalyst, dioxane can be substituted for THF (entry 8) and this lowers the amount of homocoupled product formed. On the basis of these preliminary studies (entries 1−10), it was concluded that 2 equiv of TBAT, APC, or $Pd(dba)_2$ in DMF was the optimum reaction conditions for the cross coupling reactions.

Under the optimized reaction conditions, 4-iodoanisole (entry 11) gave almost a quantitative yield of heterocoupled product and no homocoupled product. Altering catalysts and solvents reduced the yield of heterocoupled

Scheme 2



adduct slightly (entry 12). Substrates such as 2-, 3-, and 4-iodotoluene gave the best results when APC and DMF were used (entries 17, 15, and 13, respectively). This demonstrated that the position of the substituent did not affect the yield of homocoupled product.

Since the cross coupling worked well with aryl iodides, extension to aryl bromides and chlorides was studied. Using the electron-deficient 4-bromoacetophenone surprisingly gave better results with $Pd(dba)_2$ and THF (entries 19 and 20). When 4-bromoanisole (entry 22) or 4-bromotoluene (entry 24) was employed, only starting material was isolated. Attempts to couple aryl chlorides were not successful either; 4-chloroacetophenone (entry 21), 4-chloroanisole (entry 23), or 4-chlorotoluene (entry 25) gave only starting material under standard conditions. This has been a general trend seen in these cross coupling reactions.[5]

The presumed mechanism in these reactions is depicted in Scheme 2.[1d,2a−c] The first step involves the oxidative addition of the aryl halide to Pd(0) to form an aryl palladium halide complex. Next, an R group is transferred from the silicate reagent to Pd. The last step is reductive elimination to generate the transmetallation product and regeneration of the Pd(0) catalyst. In the case of the aryl bromides and chlorides, it has been proposed that the lack of reaction is the result of ineffective oxidative addition to palladium since starting material is recovered.[1d,2a−c] Recently, several solutions to activation of chloro derivatives have been reported.[10]

Since TBAT appeared to be an effective phenylating agent, an experiment was performed to determine if TBAT could deliver all three phenyl groups when excess TBAF was included. The experiment used 1 equiv of 4-iodoanisole, 1 equiv of TBAT, and 3 equiv of TBAF. Three equivalents of TBAF are required to make the silicon byproducts hypervalent again after each of the phenyl transfers so that another phenyl group can be transferred. The catalyst used was $Pd(dba)_2$, and THF was the solvent employed. Results indicated that 34% of the starting material was isolated and 5% biphenyl (from homocoupling of TBAT), 45% heterocoupled product, and 16% of the homocoupled product formed. These results indicate that TBAT delivered approximately 1.25 phenyl groups.

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Since aryl iodides are expensive and often difficult to synthesize, aryl triflates were investigated as substrates because of the ease of preparation from cheap, readily available phenols.[11] Using 4-tolyl trifluoromethanesulfonate (entry 26) or 4-phenyl trifluoromethanesulfonate (entry 27) gave only starting material. Again, this problem was attributed to the lack of oxidative addition to Pd(0). Strongly electron-deficient 4-nitrophenyl trifluoromethanesulfonate gave exclusively heterocoupled product 4-nitrobiphenyl (entry 28, 73%). Results were also successful with 4-acetylphenyl (entry 29, 73%) and 4-carbomethoxyphenyl (entry 30, 90%) triflate. It was also found that 1-naphthyl trifluoromethanesulfonate gave exclusively heterocoupled product (entry 31) in a 71% yield.

Conclusion

In summary, the hypervalent silicate complex TBAT has been shown to be a highly effective transmetallation reagent for the Pd(0)-catalyzed cross coupling of aryl iodides and triflates and electron-deficient aryl bromides. The reaction is tolerant to changes in the Pd catalyst as well as the presence of an equimolar amount of phosphine to catalyst. Changes in solvent used in the reaction can also be tolerated at the expense of formation of slightly more homocoupled product. Cross coupling reactions of hypervalent silicon compounds expanded to transfer substituted aryl groups in addition to phenyl will be reported in due course.

Experimental Section

General. All ^1H and ^{13}C NMR spectra were recorded on a 400 MHz instrument in $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in parts per million (δ) downfield from TMS. Coupling constants (J values are given in hertz (Hz)) and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), and m (multiplet). IR absorbances are reported in reciprocal centimeters (cm^{-1}). Gas chromatography was performed on a Hewlett-Packard 5890 GC equipped with a flame ionization detector using a 25 m methyl silicone column.

Tetrahydrofuran (THF) and dioxane were distilled from sodium/benzophenone ketyl. Dimethylformamide (DMF) was distilled from molecular sieves. Glassware used in the reactions was dried overnight in an oven at 120 °C. All reactions were performed under an atmosphere of nitrogen unless noted otherwise.

Allyl palladium chloride dimer, triflic anhydride, and all aryl iodides, bromides, chlorides, and phenols were purchased from Aldrich and used as received. Bis(dibenzylideneacetone)-palladium ($Pd(dba)_2$) was purchased from Acros. Triphenylphosphine (PPh_3) was purchased from Aldrich and recrystallized from pentane prior to use.

Tetrabutylammonium triphenyldifluorosilicate (TBAT) was prepared according to the literature procedure[7c] and is commercially available. All compounds were determined to be >95% pure by GC and ^1H NMR spectroscopy unless otherwise noted.

General Procedure for the Cross Coupling Reactions Utilizing Aryl Iodides, Bromides, and Chlorides (Entries 1−20). Entry 1: 4-Acetylbiphenyl. To a solution of 0.101 g (0.410 mmol) of 4′-iodoacetophenone and 1.113 g (2.062 mmol) of TBAT in 10 mL of DMF was added 12 mg (0.033 mmol) of allyl palladium chloride dimer. The reaction mixture was degassed to remove oxygen via one freeze−pump−thaw cycle. The red-brown mixture was heated at 95 °C for 5 h. The resulting brown mixture was quenched by the addition of 50

(11) Ritter, K. *Synthesis* **1993**, 735−762.

mL of H_2O; the aqueous layer was then extracted with 4 × 50 mL of Et_2O, and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (25 mm, 17 cm, 0−10% EtOAc/hexane) gave 70 mg (86%) of 4-acetylbiphenyl as a yellow solid and 7 mg (14%) of 4,4′-diacetylbiphenyl, the homocoupled product. Recrystallization from absolute EtOH yielded pale yellow needles: TLC R_f = 0.29 (10% EtOAc/hexane); mp 119−119.5 °C (lit. mp 119−120 °C (EtOH));[2f] IR (CCl_4) 3081 (w), 3038 (w), 3000 (w), 2931 (m), 2850 (w), 1691 (m), 1569 (s), 1538 (s); ^{1}H NMR δ 2.63 (s, 3H), 7.38 (t, J = 7.3, 1H), 7.46 (t, J = 7.4, 2H), 7.61 (d, J = 7.2, 2H), 7.67 (A of AB quartet, J_{AB} = 8.4, 2H), 8.02 (B of AB quartet, J_{AB} = 8.4, 2H); ^{13}C NMR δ 26.6, 127.2, 128.2, 128.9, 135.9, 139.9, 145.8, 197.7; LRMS (EI) 197 ((M + 1), 10), 196 ((M$^+$), 59), 181 (100), 153 (35), 152 (41); HRMS (EI) calcd for $C_{14}H_{12}O$ 196.0888 (M$^+$);, found 196.0883. The IR and ^{1}H NMR are identical to the spectral data found in ref 2f.

Entry 11, 4-Methoxybiphenyl: TLC R_f = 0.46 (10% EtOAc/hexane); mp 83.5−85.5 °C (lit. mp 90 °C (EtOH));[12] IR (CCl_4) 3081 (w), 3047 (w), 3006 (w), 2931 (w), 2856 (w), 2838 (w), 1563 (s), 1512 (s); ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.95−6.97 (m, 2H), 7.40 (t, J = 7.7, 2H), 7.50−7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 55.4, 114.2, 126.6, 126.7, 128.2, 128.7, 135.2; LRMS 185 ((M + 1), 15), 184 ((M$^+$), 100), 169 (39), 141 (35), 115 (21); HRMS (EI) calcd for $C_{13}H_{12}O$ 184.0888 (M$^+$),; found 184.0885. The ^{1}H NMR, ^{13}C NMR, and LRMS are identical to the spectral data found in ref 13.

Entry 13, 4-Methylbiphenyl: TLC R_f = 0.47 (10% Et_2O/pentane); mp 44.5−46.5 °C (lit. mp 49 °C (EtOH));[14] IR (CCl_4) 3081 (w), 3063 (w), 3038 (w), 2925 (w), 2863 (w), 1556 (s), 1531 (s); ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 7.23 (m, 2H), 7.30 (t, J = 7.6, 1H), 7.41 (t, J = 7.6, 2H), 7.48 (d, J = 8.1, 2H), 7.58 (d, J = 7.3, 2H); ^{13}C NMR ($CDCl_3$) δ 21.1, 127.0, 128.7, 129.5, 137.0, 138.4, 141.2; LRMS 169 ((M + 1), 19), 168 ((M$^+$), 100), 167 (63), 165 (24), 149 (52), 90 (21); HRMS (EI) calcd for $C_{13}H_{12}$ 168.0939 (M$^+$), found 168.0945. The IR and ^{1}H NMR are identical to the spectral data found in ref 14.

Entry 15, 3-Methylbiphenyl: TLC R_f = 0.47 (10% Et_2O/pentane); IR (CCl_4) 3093 (w), 3069 (s), 3031 (s), 2969 (m), 2931 (s), 2869 (w), 1600 (s), 1575 (s), 1531 (m); ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 7.23−7.28 (m, 4H), 7.32−7.35 (m, 3H), 7.39−7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.8, 126.1, 127.1, 127.6, 128.4, 129.1, 129.5, 130.1, 130.6; LRMS 169 ((M + 1), 17), 168 ((M$^+$), 100), 167 (54), 165 (23), 152 (21); HRMS (EI) calcd for $C_{13}H_{12}$ 168.0939 (M$^+$), found 168.0941. The IR and ^{1}H NMR are identical to the spectral data found in ref 14.

Entry 17, 2-Methylbiphenyl: TLC R_f = 0.59 (10% Et_2O/pentane); IR (CCl_4) 3063 (m), 3025 (m), 2963 (w), 2925 (m), 2869 (w), 1600 (s), 1550 (s); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H), 7.22−7.44 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 21.9, 124.6, 127.5, 128.3, 129.0, 138.7, 141.6; LRMS 169 ((M + 1), 20), 168 ((M$^+$), 100), 167 (85), 165 (41), 153 (34), 152 (28); HRMS (EI) calcd for $C_{13}H_{12}$ 168.0939 (M$^+$), found 168.0937. The IR, ^{1}H NMR, and HRMS are identical to the spectral data found in ref 15.

General Procedure for the Preparation of Triflates To Be Used in Cross Coupling Reactions (Entries 26−31). The triflates were prepared using a modification of a procedure in *Synthesis*.[11]

4-Tolyl Trifluoromethanesulfonate. To a 0 °C solution of 1.002 g (9.27 mmol) of *p*-cresol in 5.3 mL of pyridine was added 2.37 mL (14.09 mmol) of triflic anhydride. The reaction turned brownish-yellow upon addition of the triflic anhydride. The reaction was stirred at room temperature for 1.75 h. The resulting mixture was quenched by the addition of 30 mL of H_2O; the aqueous layer was then extracted with 2 × 30 mL of Et_2O, and the combined organic layers were washed with 30 mL of 10% HCl and 30 mL of saturated NaCl and then dried over $MgSO_4$ and concentrated in vacuo. This yielded 2.131 g (96%) of a yellow oil that was 96% pure by GC. Purification of the residue by column chromatography (15 mm, 19 cm, 25% Et_2O/pentane) gave 1.956 g (88%) of a colorless oil: TLC R_f = 0.75 (25% Et_2O/pentane); IR (CCl_4) 3050 (w), 2988 (w), 2938 (w), 2869 (w), 1600 (m), 1556 (m), 1506 (s); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 7.14 (A of AB quartet, J_{AB} = 8.6, 2H), 7.22 (B of AB quartet, J_{AB} = 8.6, 2H); ^{13}C NMR ($CDCl_3$) δ 20.7, 118.8 (q, J_{C-F} = 320), 121.0, 130.7, 138.5, 147.6; LRMS 241 ((M + 1), 4), 240 ((M$^+$), 43), 107 (100), 77 (46); HRMS (EI) calcd for $C_8H_7O_3F_3S$ (M$^+$) 240.0068, found 240.0061. The IR and ^{1}H NMR are identical to the spectral data found in ref 16, and the LRMS is identical to data found in ref 17. Elemental analysis data can be found in ref 16.

Phenyl Trifluoromethanesulfonate: TLC R_f = 0.53 (10% EtOAc/hexane); IR (CCl_4) 3066 (w), 1602, 1488 (m), 1427 (s), 1248 (m), 1225 (m), 1206 (m), 1173 (m), 1145 (s); ^{1}H NMR ($CDCl_3$) δ 7.25−7.27 (m, 2H), 7.38−7.40 (m, 1H), 7.43−7.45 (m, 2H). The IR and ^{1}H NMR are identical to the spectral data found in ref 18. Additional spectral information (^{13}C, ^{19}F, and GC/MS data) can be found in ref 19.

4-Nitrophenyl Trifluoromethanesulfonate: TLC R_f = 0.37 (25% Et_2O/hexane); mp 50.5−52 °C (lit. mp 53−54 °C);[20] IR (CCl_4) 3119 (w), 3087 (w), 3006 (w), 1717 (s), 1620 (m), 1488 (m), 1436 (s), 1348 (s); ^{1}H NMR ($CDCl_3$) δ 7.45−7.48 (m, 2H), 8.34−8.37 (m, 2H); ^{13}C NMR ($CDCl_3$) 118.6 (q, J_{C-F} = 321), 122.5, 126.0, 147.2, 153.1. The IR and ^{1}H NMR are identical to the spectral data found in ref 20. Reference 20 also contains HRMS data. IR and ^{1}H NMR data can also be found in ref 2f. LRMS data can be found in ref 17.

4-Acetylphenyl Trifluoromethanesulfonate: TLC R_f = 0.38 (25% Et_2O/hexane); IR (CCl_4) 3107 (w), 3070 (w), 3009 (w), 1649 (s), 1600 (m); ^{1}H NMR ($CDCl_3$) δ 2.61 (s, 3H), 7.36 (A of AB quartet, J_{AB} = 8.8, 2H), 8.04 (B of AB quartet, J_{AB} = 8.8, 2H); ^{13}C NMR ($CDCl_3$) δ 26.3, 118.6 (q, J_{C-F} = 321), 121.4, 130.4, 136.8, 152.3, 195.9. The IR and ^{1}H NMR are identical to spectral data found in ref 2f. Elemental analysis results are available in ref 2f.

4-Carbomethoxyphenyl Trifluoromethanesulfonate: TLC R_f = 0.35 (10% EtOAc/hexane); IR (CCl_4) 3000 (w), 2954 (m), 2845 (w), 1924 (w), 1732 (s), 1604 (m), 1499 (m), 1430 (s), 1412 (s), 1284 (s); ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H), 7.33 (m, 2H), 8.13 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 52.4, 118.7 (q, J_{C-F} = 320), 121.4, 130.4, 131.8, 152.5, 165.4; LRMS 285 ((M + 1), 8), 284 ((M$^+$), 76), 253 (100), 189 (89), 123 (28), 95 (33), 70 (32); HRMS (EI) calcd for $C_9H_7O_5F_3S$ (M$^+$) 283.9966, found 283.9965. The ^{1}H NMR is identical to spectral data found in ref 21.

1-Naphthyl Trifluoromethanesulfonate: TLC R_f = 0.51 (10% EtOAc/hexane); IR (CCl_4) 3062 (m); 1602 (m), 1508 (m), 1418 (s), 1388 (s), 1231 (m), 1201 (m), 1145 (s), 1071 (m), 1030 (m), 901 (s); ^{1}H NMR ($CDCl_3$) δ 7.44−7.50 (m, 2H), 7.57−7.65 (m, 2H), 7.85−7.92 (m, 2H), 8.07 (d, J = 8.2, 1H). The IR and ^{1}H NMR are identical to spectral data found in ref 2c. Elemental analysis results can also be found in ref 2f. ^{13}C NMR, LRMS, and elemental analysis results can also be found in ref 22.

Cross Coupling Reactions (Entries 28−31). Entry 28, 4-Nitrobiphenyl: TLC R_f = 0.56; mp 111.5−112 °C (lit. mp 113−115 °C (MeOH));[23] IR (CCl_4) 3067 (w), 3034 (w), 1604 (m),

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1521 (w),1347 (s); ^{1}H NMR (CDCl3) δ 7.47−7.49 (m, 3H), 7.61 (d, J = 7.2, 2H), 7.72 (A of AB quartet, J_{AB} = 8.7, 2H), 8.29 (B of AB quartet, J_{AB} = 8.7, 2H). The ^{1}H NMR is identical to spectral data found in ref 23. Additional spectral information (^{13}C NMR and MS data) can be found in ref 23.

Entry 30, 4-Carbomethoxybiphenyl: TLC R_f = 0.37; mp 108−108.5 °C (lit. mp 116−117 (hexane/EtOAc));[24] IR (CCl_4) 3033 (w), 2952 (w), 1728 (m), 1560 (s), 1279 (s); ^{1}H NMR ($CDCl_3$) δ 3.92 (s, 3H), 7.30−7.40 (m, 1H), 7.40−7.50 (m, 2H), 7.60−7.66 (m, 4H), 8.09 (d, J = 8.3, 2H). The IR and ^{1}H NMR are identical to spectral data found in ref 24. LRMS data can also be found in ref 24. ^{13}C NMR data can be found in ref 25.

Entry 31, 1-Phenylnaphthylene: TLC R_f = 0.54; mp 191−199 °C; IR (CCl_4) 3071 (w), 3058 (w), 2986 (w), 1569 (s), 1533 (s), 1252 (s), 1217 (s), 1118 (s), 1006 (s), 834 (s); ^{1}H NMR ($CDCl_3$) δ 7.21−7.25 (m, 2H), 7.33−7.35 (m, 4H), 7.43−7.46 (m, 6H); GC/MS 205 ((M+1), 13), 204 ((M^+), 92), 203 (100), 202 (56), 101 (66). The IR and LRMS data are identical to spectral data found in ref 26. Additional spectral information (^{13}C NMR, LRMS, and elemental analysis) can also be found in ref 22.

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