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Steric and Electronic Effects Influencing β-Aryl Elimination in the Pd-catalyzed Carbon−Carbon Single Bond Activation of Triarylmethanols

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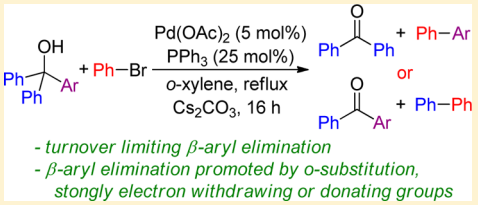
Supporting Information

ABSTRACT: An analysis of the palladium-catalyzed activation of carbon−carbon single bonds within triarylmethanols has led to a greater understanding of factors influencing the β-aryl elimination process responsible for C−C bond cleavage. A series of competition reactions were utilized to determine that β-aryl elimination of aryl substituents containing *ortho*-substitution proceeds with significant preference to unsubstituted phenyl rings. Further experiments indicate that substrates containing either strongly donating or withdrawing substituents are cleaved from triarylmethanols more readily than relatively neutral species.

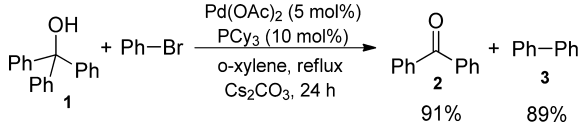


Despite the ubiquity of carbon−carbon single bonds in virtually every aspect of organic chemistry, methods for their controlled activation and functionalization remain largely unrealized.[1−3] Efforts to date rely upon the use of privileged substrates, such as those containing strained rings[4−6] or with structures that enforce proximity of the metal to the targeted C−C bond.[7−9] Although the challenges are significant, limited successes have been achieved,[10−14] and the promise of general and synthetically meaningful carbon−carbon bond activation has the potential to greatly influence the means through which complex molecules are synthesized.[15−20]

It is our belief that an increased understanding of the process of carbon−carbon bond activation will assist in the rational extension of known reactivity as well as the development of new methodologies. Just as reactions utilizing carbon−carbon single bond activation remain quite scarce, there have been very few examples of mechanistic investigations of these transformations within the context of a transition metal-catalyzed process.[21−23] As it is currently understood, single bond activation occurs via one of two general methods: oxidative addition or β-elimination. Our group has previously investigated a rhodium-catalyzed system shown to proceed via oxidative addition,[24,25] and for comparative purposes, we initiated an investigation of the palladium-catalyzed β-aryl elimination of triarylmethanols, first reported by Miura and coworkers (Scheme 1).[26−29] Herein we describe our efforts to provide insight into the process of β-aryl elimination and the factors that influence the course of this transformation.

Congruent with our focus on the nature of the carbon−carbon activation process was an interest in the reaction in the context of catalysis. At the onset of this study, several reaction sequences were envisioned as potential catalytic cycles for this palladium-catalyzed process. Although the oxidation states and the order of the elementary transformations are not immediately obvious, the fundamental steps of aryl bromide oxidative addition, β-aryl elimination from a palladium alkoxide, and reductive elimination to form biphenyl are all clearly involved in this process. Due to complications arising from the standard reaction conditions, particularly the heterogeneous nature of the reaction mixture, a traditional kinetic study proved intractable. Instead, a series of alternative mechanistic investigations, primarily via competition reactions, were utilized to develop a greater understanding of the nature of the carbon−carbon bond activation step while simultaneously providing insight into the overall catalytic cycle.

Scheme 1



Our investigations began with an examination of the influence of aryl halide on the reaction. Two aryl halides, each present in a 1.2:1 excess to triphenylmethanol, were reacted under otherwise standard conditions: $Pd(OAc)_2$ (5 mol %), PPh_3 (20 mol %) and Cs_2CO_3 (3 equiv) in refluxing *o*-xylene. After 16 h, the reaction mixture was analyzed by GC/MS to determine the relative ratio of the two possible biaryl species. The reaction of 3,5-bis(trifluoromethyl)-1-bromobenzene occurred in greater than 5:1 selectivity versus 4-trifluoromethylbromobenzene, which in turn reacted with greater than 50:1 selectivity over unsubstituted bromobenzene. The series of aryl bromides and their respective reactivity is provided in Scheme 2. These results illustrate that electron deficient aryl halides undergo reaction with preference to their electron rich counterparts. This trend is similar to the behavior

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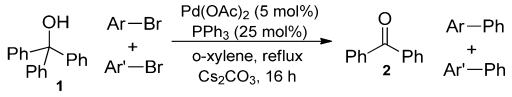
Scheme 2



Relative incorporation of aryls into biphenyl:

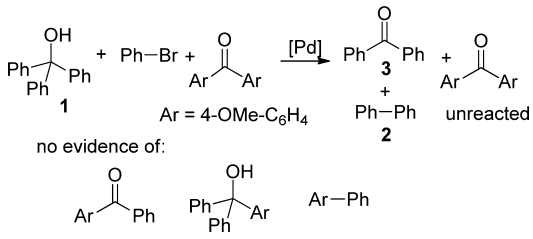
$3,5\text{-}(CF_3)_2C_6H_3 > 4\text{-}CF_3C_6H_4 > 3\text{-}OMeC_6H_4 > 2\text{-}OMeC_6H_4 > Ph > 4\text{-}OMeC_6H_4$

of these species in oxidative addition,[30,31] suggesting that this fundamental transformation either limits the catalyst turnover or reaches equilibrium prior to the turnover limiting step of catalysis.[32]

A similar experiment was performed with an equimolar ratio of *p*-trianisylmethanol (1.0 equiv) and triphenylmethanol (1.0 equiv) in the presence of 1.2 equiv of bromobenzene under otherwise standard reaction conditions. Analysis of the product mixture at approximately 50% conversion revealed a 2.7:1 ratio of methoxybiphenyl to biphenyl. The differentiation between the two species, which was also observed with other similar competition reactions (*vide infra*), suggests that the cleavage of the carbon−carbon bond occurs during, or prior to, the turnover limiting step of catalysis.

In order to probe the reversibility of carbon−carbon bond activation, a reaction was performed under standard reaction conditions with the addition of exogenous 4,4′-dimethoxybenzophenone. The observation of methoxy-containing triarylmethanol or biphenyl species would provide evidence for reversibility of the *β*-aryl elimination. After 16 h under otherwise standard reaction conditions, benzophenone and biphenyl were observed, but no sign of mixed methoxy-containing species were observed (Scheme 3). These results

Scheme 3. Probe of *β*-Aryl Elimination Reversibility

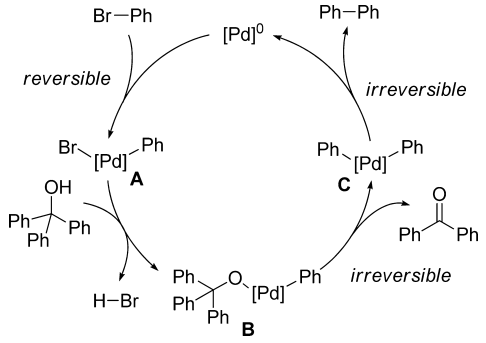


suggest that *β*-aryl elimination is either an irreversible process or that the resulting diaryl palladium complex is not sufficiently stable to allow ketone exchange and insertion prior to further reductive elimination. In a similar fashion, the exposure of a substituted biphenyl to standard reaction conditions leads to no evidence of carbon−carbon bond cleavage, suggesting that reductive elimination is irreversible.

The results from the above experiments are most consistent with a reaction sequence that begins with reversible oxidative addition of the palladium(0) species with the aryl bromide to form intermediate **A** (Scheme 4). Following ligand exchange, irreversible *β*-aryl elimination generates benzophenone and palladium diaryl species **C**, which in turn undergoes reductive elimination to generate biphenyl. Because reductive elimination to form sp^2−sp^2 carbon−carbon bonds typically occurs rapidly, particularly under the high temperatures utilized in this study, it is assumed that this step occurs rapidly relative to *β*-aryl elimination.[33−37]

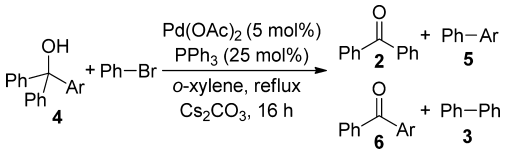
With a schematic representation of the catalytic cycle in hand, we turned our attention to the primary goal of this study,

Scheme 4. Proposed Catalytic Cycle



the determination of factors that influence the process of carbon−carbon bond activation. To gain further insight on the *β*-aryl elimination, a series of aryldiphenylmethanols were prepared and subjected to palladium catalysis under standard conditions.[38] Upon reaction, several products can be formed: activation of the carbon-aryl bond ultimately leads to benzophenone (**2**) and a substituted biphenyl (**5**), whereas activation of the carbon-phenyl bond leads to biphenyl (**3**) and substituted benzophenone (**6**) (Scheme 5). These reactions

Scheme 5. Intramolecular Competition Reactions for Examining Process of *β*-Aryl Elimination



were quenched after 16 h and the relative propensity of aryl cleavage versus phenyl cleavage was determined via GC/MS analysis of the resulting product mixtures. The influence of sterics upon *β*-aryl elimination was immediately apparent, as aryl groups with *ortho*-substitution of any kind demonstrate a dramatic propensity to cleave preferentially to the unsubstituted phenyl ring (Table 1, entries 1−3). The extent of this significant selectivity ranges from 29:1 for methyl substitution to 114:1 for chloride substitution.[39,40] While this effect is most pronounced for species with Lewis basic *ortho*-substitution, the significant selectivity observed with methyl substitution suggests a purely steric contribution. X-ray structural data from a bis(triethylphosphine)rhodium-triarylalkoxide complex, an analogue of proposed intermediate **B** in Scheme 4, illustrates a strong interaction between the metal center and a *β*-aryl group prior to *β*-elimination.[40] This coordination event serves to orient the aryl ring in a parallel fashion to the phosphine ligands while slightly lengthening the carbon−carbon bond destined for cleavage. In the presence of aryldiphenylmethanols, coordination of the *β*-aryl group with *ortho*-substitution may effectively minimize interaction of the *ortho*-group with the phosphine ligands as well as the other phenyl rings, thus promoting selective cleavage.

In contrast to the steric effects, variation of the electronic nature of the aryl rings resulted in only a subtle influence on selectivity of *β*-aryl elimination (Table 1). A series of substituents, varying from electron deficient 3,5-bis(trifluoromethyl)phenyl to electron rich 4-dimethylaminophenyl were prepared and subjected to the reaction conditions.[41] The observed selectivity was significantly attenuated relative to

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Table 1. Intramolecular Competition Reactions Utilizing Aryldiphenylmethanol Substrates

entry[a]	Ar	starting material 4	product ketone 6[b]	transfer ratio Ar:Ph[c,d]
1	2-Cl−C_6H_4	**4a**	**6a**	114 ± 13:1[e]
2	2-OMe−C_6H_4	**4b**	**6b**	50 ± 5:1
3	2-Me−C_6H_4	**4c**	**6c**	29 ± 2:1
4	3-Me−C_6H_4	**4d**	**6d**	0.9 ± 0.1:1
5	3-OMe−C_6H_4	**4e**	**6e**	1.0 ± 0.1:1
6	4-Me−C_6H_4	**4f**	**6f**	1.2 ± 0.3:1
7	4-NMe_2−C_6H_4	**4g**	**6g**	2.9 ± 0.2:1
8	4-CF_3−C_6H_4	**4h**	**6h**	3.0 ± 0.5:1
9	4-Cl−C_6H_4	**4i**	**6i**	2.6 ± 0.1:1
10	4-OMe−C_6H_4	**4j**	**6j**	3.0 ± 0.3:1
11	3,5-$(CF_3)_2$−C_6H_3	**4k**	**6k**	6.0 ± 0.4:1
12	3,4,5-$(OMe)_3$−C_6H_2	**4l**	**6l**	3.0 ± 0.2:1

[a]Reactions performed in refluxing *o*-xylene with [**4**] = 0.167 M, [Ph-Br] = 0.40 M, [$Pd(OAc)_2$] = 8.3 mM, [PPh_3] = 0.043 M, [Cs_2CO_3] = 0.22 M for 16 h. [b]Formed in addition to unsubstituted benzophenone. [c]Determined by GC/MS analysis of three trials. The error represents the standard deviation. [d]Values account for 2:1 ratio of Ph:Ar substituents in **4**. [e]Determined by analysis of two trials.

that observed for compounds containing *ortho* substitution, peaking with the bis(trifluoromethyl)-substituted substrate **4k** in which the aryl group is transferred with 6:1 selectivity over the phenyl ring. Compounds with electronically neutral substitutions (entries 4−6) result in nearly statistical aryl transfer. While there is a general selectivity for cleavage of the more electron deficient aryl ring relative to more neutral species, electron rich aryl rings are also cleaved more readily than neutral substituents, up to 3:1 with the *para*-methoxy substituted aryl (entry 10), with no clear correlation between the electronic character of the aryl substituents and corresponding migratory aptitude.[42] This deviation from linearity suggests that selectivity is not purely governed by electronic factors and may be affected by Lewis acid−Lewis base interactions between these triarylmethanol substrates and other reaction components or variations in C−C bond length of the substrates.

To minimize the effect of coordination events and other unforeseen variables upon the selectivity of aryl group transfer, a similar set of competition reactions was performed using a series of fluorine substituted aryldiphenylmethanol substrates. Results from these experiments are provided in Table 2. As with previous examples, the significant influence of the *ortho* substitution is readily apparent, with the further observation that this effect appears to be cumulative with the incorporation of a second fluorine substitution (entries 1 and 6). Specifically, the selectivity of the C−C activation of *ortho*-fluorinated compounds is attributed to stabilization of the intermediate Pd-aryl species in analogy to that observed for related rhodium-aryl species. Calculations have quantified this stabilization to be approximately 5.5 kcal/mol for each *ortho* C−F bond versus the unsubstituted phenyl ring.[43,44] Beyond *ortho*-substitution, the results contained in the remainder of Table 2 clearly demonstrate that more electronic deficient aryl rings more readily undergo *β*-aryl elimination and subsequent coupling than do relatively more electron rich species.

The selectivity of *β*-aryl elimination from aryldiphenylmethanols was also examined with aryl halides other than

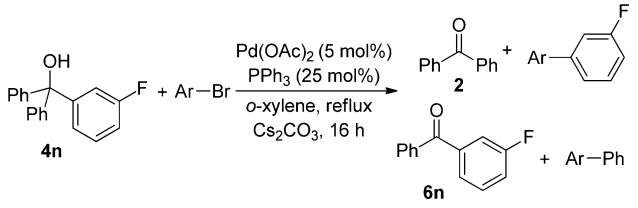
Table 2. Intramolecular Competition Reactions Utilizing Fluorinated Aryldiphenylmethanol Substrates

entry[a]	Ar	starting material 4	product ketone 6[b]	transfer ratio Ar:Ph[c,d]
1	2-F−C_6H_4	**4m**	**6m**	76 ± 2:1
2	3-F−C_6H_4	**4n**	**6n**	4.0 ± 1.1:1
3	4-F−C_6H_4	**4o**	**6o**	3.5 ± 1.1:1
4	2,5-F_2−C_6H_3	**4p**	**6p**	190 ± 33:1
5	3,4-F_2−C_6H_3	**4q**	**6q**	8.1 ± 1.4:1
6	2,6-F_2−C_6H_3	**4r**	**6r**	240 ± 30:1
7	3,5-F_2−C_6H_3	**4s**	**6s**	11 ± 1:1
8	3,4,5-F_3−C_6H_2	**4t**	**6t**	>500 ± 10:1
9	C_6F_5	**4u**	**6u**	>500 ± 10:1

[a]Reactions performed in refluxing *o*-xylene with [**4**] = 0.167 M, [Ph-Br] = 0.40 M, [$Pd(OAc)_2$] = 8.3 mM, [PPh_3] = 0.043 M, [Cs_2CO_3] = 0.22 M for 16 h. [b]Formed in addition to unsubstituted benzophenone. [c]Determined by GC/MS analysis of three trials. The error represents the standard deviation. [d]Values account for 2:1 ratio of Ph:Ar substituents in **4**.

bromobenzene (Scheme 6). As shown in Table 2, entry 2, 3-fluoro-substituted substrate **4n** undergoes reaction and

Scheme 6. Effects of Aryl Bromide Electronics on Selectivity



coupling with bromobenzene with cleavage of the fluorinated aryl ring favored by a 4:1 ratio. The use of 4-trifluoromethyl-1-bromobenzene, however, resulted in a 1.2:1 product distribution of **6n** and **2**, indicating a reversal of selectivity as this ratio of aryl to phenyl cleavage drops to 0.6:1. This ratio further decreases to 0.2:1 with 3,5-bis(trifluoromethyl)-1-bromobenzene. These results clearly indicate that the aryl bromide interacts with the palladium catalyst prior to *β*-aryl elimination with the triarylmethanol substrate, lending further support for the proposed catalytic cycle, and also demonstrates that the electronic character of the metal center and its ligands significantly influence the selectivity of the carbon−carbon bond activation.[45]

This work has provided insight into the catalytic cycle of this palladium-catalyzed transformation, suggesting that the turnover limiting *β*-aryl elimination process follows reversible aryl bromide oxidative addition. Results from these intramolecular competition reactions indicate that *ortho*-substituted triarylmethanol substrates have a significant propensity to undergo *β*-aryl elimination and significantly electron deficient or electron rich species undergo C−C cleavage more readily than neutral substituents. These results present a potential strategy for the generation of palladium-aryl species with sterically hindered *ortho*-substitution and promise a means of utilizing these difficult substituents in coupling processes.

EXPERIMENTAL SECTION

General Methods. Unless otherwise indicated, all reactions were carried out under an atmosphere of nitrogen or argon in oven-dried

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glassware with magnetic stirring. Solvents, including toluene, tetrahydrofuran, and diethyl ether were purged with argon and passed through two columns of neutral alumina or molecular sieves. Starting materials are commercially available and used with further purification. Substituted aryldiphenylmethanol substrates (**4**) were commercially available or prepared via Grignard reaction of the corresponding benzophenone (*vide infra*). Those that are not previously reported are fully characterized. $Pd(OAc)_2$ was obtained commercially and utilized without further purification. ^1H and ^{13}C spectra were obtained using standard acquisition parameters and referenced to TMS. ^{19}F NMR spectra were obtained using standard acquisition parameters and referenced to an external standard of fluorobenzene. All HRMS measurements were made using ESI with TOF detection.

General Procedure for Formation of Aryldiphenylmethanols. This procedure will be illustrated with a specific example. 2,5-Difluorobenzophenone (0.90 g, 4.1 mmol) was added to an oven-dried 50 mL round-bottom flask containing a stir bar, sealed with a septum and evacuated and refilled with N_2 (3×). Via syringe, 15 mL of anhydrous THF was added. Phenylmagnesium bromide (3 M solution in THF, 1.7 mL, 5.1 mmol) was added dropwise via syringe over ∼15 min. The reaction was allowed to stir overnight, at which point it was quenched with 30 mL of 1H HCl (aq). The mixture was extracted with Et_2O (3× 20 mL) and the combined organic layers were washed with sat. $NaHCO_3$ (aq), H_2O, and brine, then dried over $MgSO_4$ and concentrated. The resulting crude solid was recrystallized from hexanes to form the product as a white crystalline solid in 68% yield (0.83 g, 2.8 mmol).

Procedure for Intermolecular Competition Experiments Using Two Aryl Bromides. This procedure will be illustrated with a specific example. Prior to reaction setup, Cs_2CO_3 was dried for at least 3 h under high vacuum at 125 °C. Dried Cs_2CO_3 (1.3 equiv, 220 mg, 0.67 mmol), triphenylmethanol (1 equiv, 130 mg, 0.5 mmol), PPh_3(25 mol %, 34.5 mg, 0.13 mmol), and $Pd(OAc)_2$(5 mol %, 6.0 mg, 0.025 mmol) were combined in a 250 mL round-bottom flask. A condenser was attached to the flask and a rubber septum added to the top of the condenser. The condenser/round-bottom flask system was evacuated and refilled with argon (4×). To this flask, 3 mL of anhydrous *o*-xylene and bromobenzene (1.2 equiv, 65 μL, 0.6 mmol) and 4-trifluoromethyl-1-bromobenzene (1.2 equiv, 84 μL, 0.6 mmol) were added via syringe. The flask was heated in an oil bath with a temperature of 150 °C. After 16 h the reaction was removed from the oil bath, cooled to room temperature and quenched with 10 mL of 2 M HCl (aq). Following extraction with Et_2O (2× 10 mL), the organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Analysis was carried out via GC/MS.

Procedure for Intermolecular Competition Experiments Using Two Triarylmethanols. This procedure will be illustrated with a specific example. Prior to the reaction, Cs_2CO_3 was dried for at least 3 h under high vacuum at 125 °C. Dried Cs_2CO_3 (1.3 equiv, 220 mg, 0.67 mmol), triphenylmethanol (1 equiv, 130 mg, 0.5 mmol), tri(*p*-anisyl)methanol (1 equiv, 175 mg, 0.5 mmol), PPh_3(25 mol %, 34.5 mg, 0.13 mmol), and $Pd(OAc)_2$(5 mol %, 6.0 mg, 0.025 mmol) were combined in a 250 mL round-bottom flask. A condenser was attached to the flask and a rubber septum added to the top of the condenser. The condenser/round-bottom flask system was evacuated and refilled with argon (4×). To this flask, 3 mL of anhydrous *o*-xylene and bromobenzene (1.2 equiv, 130 μL, 1.2 mmol) were added via syringe. The flask was heated in an oil bath with a temperature of 150 °C. After 16 h (prior to complete consumption of either triarylmethanol) the reaction was removed from the oil bath, cooled to room temperature and quenched with 10 mL of 2 M HCl (aq). Following extraction with Et_2O (2× 10 mL), the organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Analysis was carried out via GC/MS.

General Procedure for Intramolecular Competition Experiments. This procedure will be illustrated with a specific example. Prior to the reaction, Cs_2CO_3 was dried for at least 3 h under high vacuum at 125 °C. Dried Cs_2CO_3 (1.3 equiv, 220 mg, 0.67 mmol), (2,6-difluorophenyl)diphenylmethanol (1 equiv, 148 mg, 0.5 mmol), PPh_3(25 mol %, 34.5 mg, 0.13 mmol), and $Pd(OAc)_2$(5 mol %, 6.0 mg, 0.025 mmol) were combined in a 250 mL round-bottom flask. A condenser was attached to the flask and a rubber septum added to the top of the condenser. The condenser/round-bottom flask system was evacuated and refilled with argon (4×). To this flask, 3 mL of anhydrous *o*-xylene and bromobenzene (2.5 equiv, 130 μL, 1.2 mmol) were added via syringe. The flask was heated in an oil bath with a temperature of 150 °C. After 16 h the reaction was removed from the oil bath, cooled to room temperature and quenched with 10 mL of 2 M HCl (aq). Following extraction with Et_2O (2× 10 mL), the organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. Analysis was carried out via GC/MS and assignments were made by comparison to commercially available standards.

*(2,5-Difluorophenyl)diphenylmethanol (**4p**).* Product is a white crystalline solid (816 mg, 2.8 mmol, 68%): Recrystallized from hexane. mp = 82−85 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (mult, 6H), 7.33−7.26 (mult, 4H), 7.09−6.97 (mult, 2H), 6.61(ddd, *J* = 10, 6, 3 Hz, 1H), 3.48 (d, *J* = 9 Hz, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 158.1 (dd, $^1J_{CF}$ = 243, $^3J_{CF}$ = 2 Hz), 156.6 (dd, $^1J_{CF}$ = 243, $^3J_{CF}$ = 2 Hz), 144.8, 136.1 (dd, *J* = 12, 7 Hz), 128.2, 127.8, 127.4, 117.0 (dd, *J* = 26, 4 Hz), 116.6 (dd, *J* = 24, 10 Hz), 116.3 (dd, 24, 10 Hz), 80.6. ^{19}F (363 MHz, $CDCl_3$) δ −116.4 (d, *J* = 21 Hz), −118.5 (d, *J* = 21 Hz). IR (diamond atr) 3450, 1482, 1445, 1241, 755, 695 cm^{-1}. HRMS (ESI, TOF) for $C_{19}H_{15}F_2O^+$, calcd 297.1085. Found 297.1096.

*(3,4-Difluorophenyl)diphenylmethanol (**4q**).* Product is a white crystalline solid (486 mg, 1.6 mmol, 40%): Crystallized from hexane. mp = 82−85 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.29 (multi, 5H), 7.28−7.21 (mult, 5H), 7.18 (ddd, *J* = 19, 8, 2 Hz, 1H), 7.08 (q, *J* = 9 Hz, 1H); 7.03−6.97 (mult, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 149.8 (dd, *J* = 248, 13 Hz), 149.3 (dd, *J* = 248, 13 Hz), 146.1, 143.9 (t, *J* = 4 Hz), 128.2, 127.7, 127.6, 124.0 (dd, *J* = 6, 3 Hz), 117.2 (d, *J* = 19 Hz). 116.4 (d, *J* = 19 Hz), 81.4 (d, *J* = 2 Hz). ^{19}F (363 MHz, $CDCl_3$) δ −138.0 (d, *J* = 21 Hz), −140.4 (d, *J* = 21 Hz). IR (diamond atr) 3460, 3061, 3027, 1512, 1445, 1278, 1110, 752 cm^{-1}. HRMS (ESI, TOF) for $C_{19}H_{14}F_2ONa^+$, calcd 319.0885. Found 319.0905.

*(2,6-Difluorophenyl)diphenylmethanol (**4r**).* Product is a white crystalline solid (814 mg, 2.7 mmol, 67%): Crystallized from hexane. mp =124−126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.25 (mult, 11H), 6.84 (dd, *J* = 9.8, 8.5 Hz, 2H), 3.89 (t, *J* = 7.5 Hz, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 160.7 (dd, *J* = 249, 7 Hz), 145.5, 129.5 (t, *J* = 12 Hz), 127.9, 127.7, 127.1, 123.2 (t, *J* = 12 Hz), 112.7 (mult), 80.4. ^{19}F (363 MHz, $CDCl_3$) δ −107.0. IR (diamond ATR) 3609, 3404, 1619, 1447, 1390, 764, 676 cm^{-1}. HRMS (ESI, TOF) for $C_{19}H_{14}F_2ONa^+$, calcd 319.0885. Found 319.0868.

*(3,5-Difluorophenyl)diphenylmethanol (**4s**).* Product is a white crystalline solid (1032 mg, 3.5 mmol, 85%): Recrystallized from hexane. mp = 82−85 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.28 (mult, 6H), 7.25−7.21 (mult, 4H), 6.89−6.82 (mult, 2H), 6.69 (tt, *J* = 9, 2 Hz, 1H), 2.76 (s, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 162.58 (dd, *J* = 248, 13 Hz), 150.8 (t, *J* = 8 Hz), 145.7, 128.2, 127.8, 127.7, 111.0 (mult), 102.6 (t, *J* = 25 Hz), 81.6 (t, *J* = 2 Hz). ^{19}F (363 MHz, $CDCl_3$) δ −110.1. IR (NaCl) 3579, 3467, 3058, 3024, 1622, 1599, 1444, 1295, 1156 cm^{-1}. HRMS (ESI, TOF) for $C_{19}H_{15}F_2O^+$, calcd 297.1085. Found 297.1071.

*(3,4,5-Trifluorophenyl)diphenylmethanol (**4t**).* Product is a white crystalline solid (515 mg, 1.6 mmol, 41%): Crystallized from hexane. mp = 72−74 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.27 (mult, 6H), 7.23−7.18 (mult, 4H), 6.96 (dd, *J* = 9, 7 Hz, 2H), 2.74 (s, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ 150.5 (ddd, *J* = 249, 10, 4 Hz), 145.5, 143.1 (dt, *J* = 6, 6 Hz), 138.7 (dt, *J* = 254, 18 Hz), 128.3, 127.9, 127.7, 112.2 (mult), 81.3. ^{19}F (363 MHz, $CDCl_3$) δ −134.6 (d, *J* = 22 Hz), −162.6 (t, *J* = 22 Hz). IR (diamond ATR) 3450.0, 1620.2, 1520.8, 1433.2, 1340.1, 1000.4, 856.5, 696.4 cm^{-1}. HRMS (ESI, TOF) for $C_{19}H_{14}F_3O^+$, calcd 315.0991. Found 315.0982.

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■ ASSOCIATED CONTENT

Supporting Information

Complete results for aryl bromide competition reactions and characterization material for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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