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Nickel-catalyzed intramolecular C–H arylation using aryl pivalates as electrophiles

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ABSTRACT

This paper describes a method for nickel catalyzed intramolecular C–H arylation using aryl pivalates as electrophiles. The transformation is efficient for the synthesis of diverse electronically and sterically differentiated dibenzofurans. Additionally, the method could be expanded toward the synthesis of carbazoles. Preliminary mechanistic studies of the transformation are also described.

1. Introduction

Carbon–carbon bonds are critical to the skeleton of many classes of valuable chemical compounds including fuels, pharmaceuticals, agrochemicals, conjugated materials, and commodity chemicals.[1] Consequently, the development of atom economical, cost-effective, and environmentally friendly methods for the construction of C–C bonds from hydrocarbon precursors is very desirable. Over the past decade numerous examples of Pd-, Ru-, Rh- and Ir-catalyzed intra- and intermolecular direct arylations of sp^2 and sp^3 C–H bonds using aryl halides or Ar–[M] (M=B, Sn, Si) have been developed.[2] Although these represent significant advances, they are limited by the use of costly noble metal catalysts. In contrast the utilization of inexpensive, earth-abundant first row transition metals (e.g., Fe,[3] Co,[4] Ni,[5] and Cu[6]) as catalysts for general, mild, and efficient C–H arylations remains challenging. In particular there have been only a few sporadic reports on the Ni-catalyzed C–H arylation of unactivated arenes.[5g,h] Furthermore, several disadvantages are associated with the use of aryl halides, the most commonly employed electrophiles in currently known transition metal-catalyzed direct arylations. Recently, there has been an increasing demand for the use of inexpensive phenolic electrophiles (e.g., tosylates, mesylates, carbamates, pivalates, etc.) in place of aryl halides.[7–9] This is because phenols are far more naturally abundant than aryl halides, and are readily commercially available. Furthermore, phenolic electrophiles bearing diverse substitutions can be easily accessed because the C–OR group serves as a versatile handle for the installation of additional functional groups using electrophilic aromatic substitution and directed *ortho*-lithiation strategies.[10]

Despite the advantages associated with the use of inexpensive phenolic electrophiles and earth-abundant first row transition metal catalysts, there have been only a few reports on C–H arylation using this combination of catalysts and electrophiles.[11] Two examples of Ni-catalyzed C–H arylation of heteroarenes using C–O electrophiles have been reported.[12] However, to date no examples of Ni-catalyzed C–H arylation of simple arenes using C–O electrophiles have been described. Arguably, the development of such methodology has been hindered by a dearth of understanding of the mechanism of C–H activation at nickel centers. Herein, we disclose the development of a Ni-catalyzed method for the intramolecular C–H arylation using pivalate electrophiles. Preliminary efforts to probe the mechanism of this transformation are also described.

2. Results and discussion

2.1. Optimization

Our initial studies have focused on the investigation of an intramolecular arylation of diaryl ether substrates to provide

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dibenzofurans (Scheme 1). This system was attractive for study because the electronics and sterics on both aryl rings can be modulated, thereby allowing systematic evaluation of these effects on the Ni-catalyzed C–H arylation. We expect that the resulting insights into the requirements for C–H activation at nickel centers, could contribute to the subsequent development of more broadly applicable Ni-catalyzed direct arylations.

Scheme 1. Proposed Ni-catalyzed intramolecular C–H arylation.

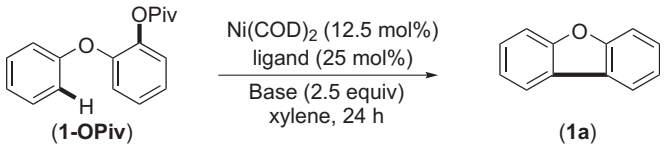
The development of the proposed Ni-catalyzed intramolecular C–H arylation began with the identification of conditions to effect the intramolecular arylation of pivalate **1-OPiv** using $Ni(COD)_2$ in combination with a phosphine ligand and a stoichiometric base (Table 1). Evaluation of a number of ligands revealed that the use of 1,2-bis(dicyclohexylphosphino)ethane (dcype) led to product **1a** in modest yield (41%) after 24 h at 140 °C (entry 1). Complete conversion of **1-OPiv** was achieved by increasing the temperature to 160 °C to afford the product in 74% yield as determined by gas chromatographic analysis of the crude reaction mixture (entry 2). The remaining mass balance of the reaction is accounted for by significant substrate protodeoxygenation under the reaction conditions to yield the diphenyl ether (21%). The use of ligands analogous to dcype either led to no product or afforded **1a** in significantly diminished yields (entries 3–5). Additionally, the use of other ligands (e.g., XPhos, RuPhos, and SPhos) that have been successfully employed for Pd-catalyzed C–H arylation using sulfonate electrophiles were also inefficient in this transformation (entries 6–8).[8e,h]

While a number of bases including K_3PO_4 and KOAc led to significant quantities of the product, carbonate bases generally afforded **1a** in higher yields (entries 2 and 9–12). Finally, polar solvents, such as *N*,*N*-dimethylacetamide (DMA) led to poor yields (5%) of the product, in part due to significant hydrolysis of **1-OPiv** (entry 13). Notably, catalysis does not proceed in the absence of ligand, Cs_2CO_3 or $Ni(COD)_2$ (entries 14–16). As such, the optimal conditions for the conversion of **1-OPiv** to **1a** involves the use of $Ni(COD)_2$ (12.5 mol %), dcype (25 mol %), Cs_2CO_3 (2.5 equiv), and xylene at 160 °C (entry 2).

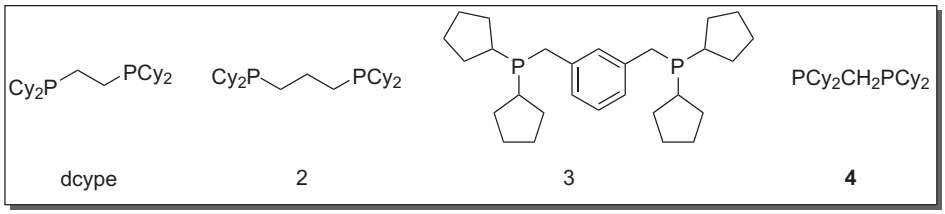
2.2. Substrate scope

We next examined the generality of this transformation with respect to varied substitution patterns on the aryl ring undergoing C–H functionalization. As shown in Table 2, dibenzofuran products are obtained in modest to good yields and the ratio of the desired product to that of the protodeoxygenated substrate (A:B) was similar in most cases (~3:1).[13] Substrates containing benzylic methyl groups (entries 2 and 7) as well as aryl halides (entry 4) effectively participated in these reactions.[14] The method is compatible with electron-donating (entries 3 and 5) and electron-withdrawing substituents (entry 6). Substrates, such as **5-OPiv**, **6-OPiv**, and **8-OPiv** bear two different aromatic C–H bonds that could undergo arylation (entries 5, 6, and 8). While products **5a** and **6a** form via functionalization of the less sterically hindered C–H bond,

Table 1
Optimization of the intramolecular C–H arylation

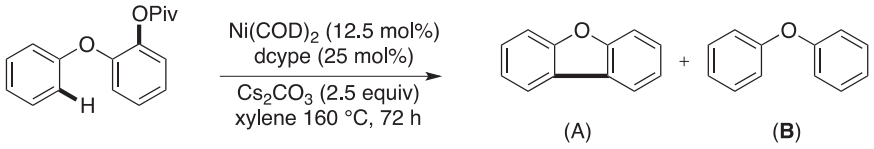


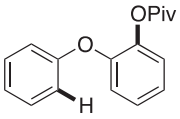
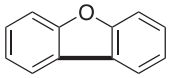
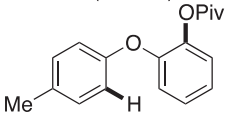
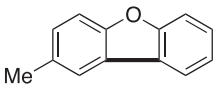
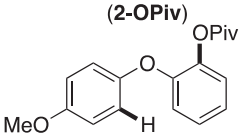
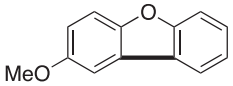
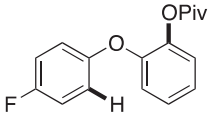
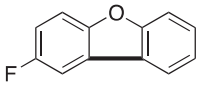
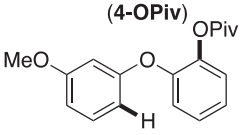
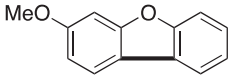
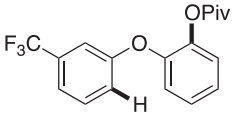
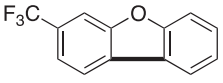
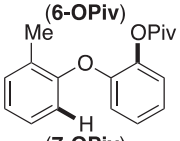
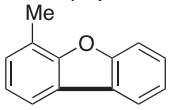
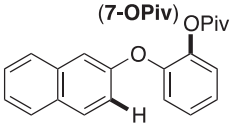
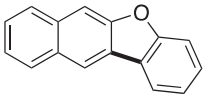
Entry	Ligand	Base	Temp (°C)	GC yield[a,b]
1	dcype	Cs_2CO_3	140	41%
2	dcype	Cs_2CO_3	160	74%
3	2	Cs_2CO_3	160	0%
4	3	Cs_2CO_3	160	0%
5	4	Cs_2CO_3	160	2%
6	XPhos	Cs_2CO_3	160	0%
7	RuPhos	Cs_2CO_3	160	0%
8	SPhos	Cs_2CO_3	160	2%
9	dcype	Rb_2CO_3	160	58%
10	dcype	K_2CO_3	160	54%
11	dcype	K_3PO_4	160	41%
12	dcype	KOAc	160	18%
13[c]	dcype	Cs_2CO_3	160	5%
14	dcype	None	160	0%
15[d]	dcype	Cs_2CO_3	160	0%
16	None	Cs_2CO_3	160	0%



[a] General conditions: **1-OPiv** (1 equiv), $Ni(COD)_2$ (0.125 equiv), dcype (0.25 equiv), base (2.5 equiv), xylene (0.125 M in **1-OPiv**), 24 h.
[b] Calibrated GC yields against hexadecane as the internal standard.
[c] General conditions with DMA as solvent.
[d] General conditions with no $Ni(COD)_2$.

Table 2
Scope of Ni-catalyzed C–H arylation



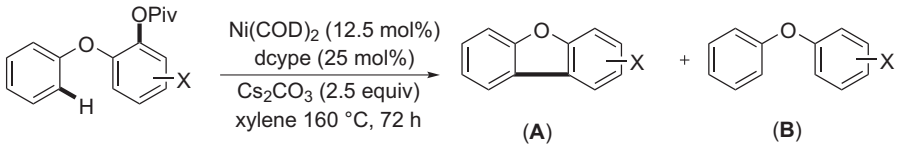
Entry	Substrate	Product	Isolated Yield[a] (GC yield)[b]	A:B[c]
1	 (**1-OPiv**)	 (**1a**)	66% (71%)	3.6:1
2	 (**2-OPiv**)	 (**2a**)	74% (81%)	3.9:1
3	 (**3-OPiv**)	 (**3a**)	75% (75%)	4.3:1
4	 (**4-OPiv**)	 (**4a**)	67% (76%)	4.4:1
5	 (**5-OPiv**)	 (**5a**)	77% (74%)	3.8:1
6	 (**6-OPiv**)	 (**6a**)	62% (64%)	3.3:1
7	 (**7-OPiv**)	 (**7a**)	67% (69%)	2.7:1
8[d]	 (**8-OPiv**)	 (**8a**)	65% (68%)	2.9:1

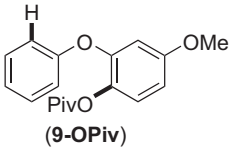
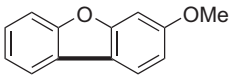
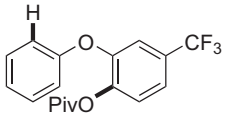
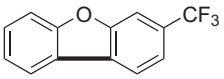
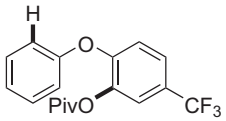
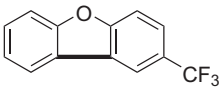
[a] Substrate (1 equiv), $Ni(COD)_2$ (0.125 equiv), dcype (0.25 equiv), Cs_2CO_3 (2.5 equiv), xylene, 160 °C.
[b] Calibrated GC yields of the desired products (**A**) against hexadecane as the internal standard.
[c] Ratio of product (**A**) to protodeoxygenated substrate (**B**) determined by GC analysis of the crude reaction mixture.
[d] Obtained as a 2.9:1 mixture of isomers favoring **8a**.

a 2.9:1 mixture of isomers was obtained from the reaction of naphthyl substrate **8-OPiv**. The steric-dictated selectivities observed for the reaction of pivalates **5-OPiv** and **6-OPiv** are consistent with those previously documented for known Pd-catalyzed C–H arylation reactions.[15] Interestingly, however, the selectivity for the reaction of the naphthyl substrate **8-OPiv** is opposite to that observed for similar Pd-catalyzed intramolecular C–H arylations.[15,8i] The selectivity for the reaction of **8-OPiv** suggests that Ni-catalyzed C–H functionalizations might allow for a complementary scope of C–C bond constructions than similar Pd-catalyzed transformations.

In contrast to the minimal effect of substituents on the ring undergoing C–H functionalization (vide supra), the electronic nature of the pivalate-bearing ring had a strong influence on the efficiency of these reactions (Table 3). The electron rich pivalate substrate **9-OPiv** led to the desired product in moderate yield (entry 1) accompanied by significant protodeoxygenation. Significantly diminished yields of the product were observed with

Table 3
Effect of substitution on the pivalate-bearing ring

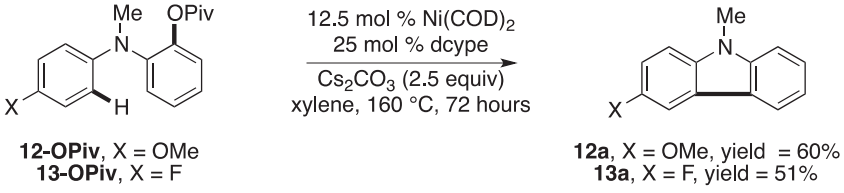


Entry	Substrate	Product	Isolated yield[a] (GC yield)[b]	A:B[c]
1	 (**9-OPiv**)	 (**5a**)	55% (48%)[b]	1.5:1
2	 (**10-OPiv**)	 (**6a**)	8%[b]	1:1.8
3	 (**11-OPiv**)	 (**11a**)	35% (37%)[b,d]	3.4:1

[a] Substrate (1 equiv), $Ni(COD)_2$ (0.125 equiv), dcype (0.25 equiv), Cs_2CO_3 (2.5 equiv), xylene, 160 °C, 72 h.
[b] Calibrated GC yields of the desired products (**A**) against hexadecane as the internal standard.
[c] Ratio of product (**A**) to protodeoxygenated substrate (**B**) determined by GC analysis of the crude reaction mixture.
[d] Reaction time is 24 h because yields did not increase over longer times.

substrates **10-OPiv** and **11-OPiv**, each bearing a trifluoromethyl group on the pivalate-bearing ring (entries 2 and 3). Notably the low yield of **11a** is due to significant hydrolysis of the pivalate group in **11-OPiv** under the reaction conditions.

The Ni-catalyzed intramolecular arylations are not limited to the synthesis of dibenzofurans and could be expanded toward the synthesis of carbazoles. For example, the reaction of substrates **12-OPiv** and **13-OPiv** led to products **12a** and **13a** in modest yields (Scheme 2).[16]



Scheme 2. Carbazole synthesis via Ni-catalyzed intramolecular C–H arylation.

2.3. Mechanistic studies

Having explored a preliminary scope of the Ni-catalyzed intramolecular C–H arylations, we next desired to gain insight into the C–H activation step. These studies began by examining the efficiency of the reaction using varied C–O electrophiles. As shown in Fig. 1, the use of the carbamate substrate **1-OCONEt$_2$** led to **1a** in somewhat lower yield (40%) than observed using **1-OPiv** (74%) over 24 h. The yield for the reaction of **1-OCONEt$_2$** did not increase over longer reaction times. The tosylate and benzoate substrates **1-OTs** and **1-OBz** also led to **1a** in significantly diminished yields. Finally, the electron rich and the electron deficient benzoates **1-OCO**(*p*-**OMeC$_6$H$_4$**) and **1-OCO**(*p*-**CF$_3$C$_6$H$_4$**) performed even more poorly than **1-OBz**. As such, under our current optimized conditions, aryl pivalates are the most effective electrophiles for the Ni-catalyzed intramolecular C–H arylation. Since the oxidative addition of Ni(0) into C–OPiv, C–OCONEt$_2$ and C–OTs bonds using the $Ni(COD)_2$/dcype catalyst system is known,[12a] the superior reactivity of **1-OPiv** and **1-OCONEt$_2$** in our system may be due to the possibility of carboxylate (or carbamate) assisted intramolecular deprotonation in the C–H activation step of these transformations.

Additionally, the difference in reactivity between **1-OPiv** and **1-OBz** suggests that the nature of the carboxylate is important for the efficiency of these transformations.

Next, we desired to gain insight into the mechanism of the C–H activation step. As such, we determined the kinetic isotope effect for the C–H arylations using the monodeuterated substrate **1-OPiv**-*d*. As shown in Scheme 3, the reaction of **1-OPiv**-*d* led to products **1a**-*d* and **1a** in a 2.8:1 ratio as determined by ^{1}H NMR spectroscopic analysis of the isolated product. The observed intramolecular primary K.I.E of 2.8 is close to the isotope effects documented for related Pd-catalyzed intramolecular arylations (K.I.E≈3.5) that proceed via a concerted-metalation–deprotonation (CMD) pathway.[17,18a]

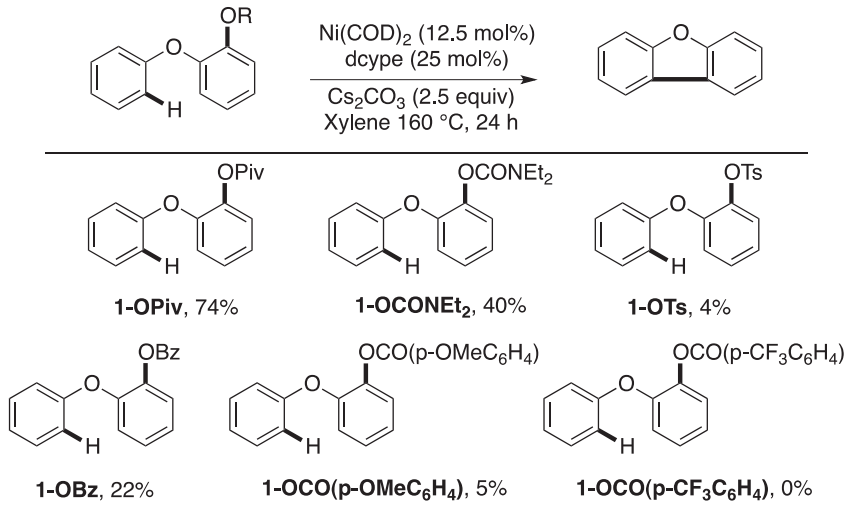
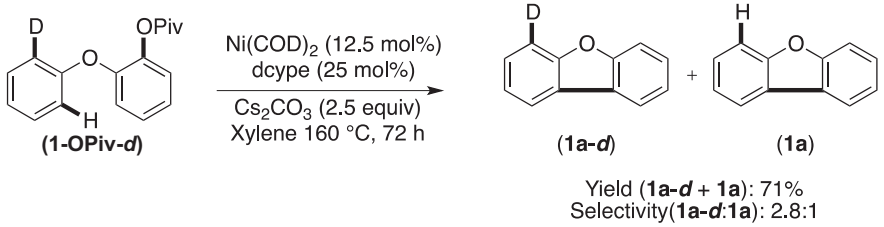


Fig. 1. Evaluation of varied C–O electrophiles.



Scheme 3. Determination of the intramolecular kinetic isotope effect.

3. Conclusion

In summary, this paper describes the development of a nickel-catalyzed intramolecular C–H arylation of arenes using pivalate electrophiles. The transformation can be applied to a number of electronically- and sterically-differentiated diaryl ether substrates to afford dibenzofurans. Furthermore, this methodology can be applied toward the synthesis of carbazoles from diaryl amines. Preliminary mechanistic studies have been conducted to understand the nature of the C–H activation step at nickel centers. Although further investigations are needed, these studies suggest that the efficiency of the arylations is significantly impacted by the nature of the C–OR group in the substrates. Additionally the observed K.I.E are similar to those reported for analogous Pd-catalyzed intramolecular C–H arylations that are believed to proceed via CMD-type C–H activation steps. Ongoing studies will focus on the development of second-generation catalyst systems to allow for an increased substrate scope and milder reaction conditions.

4. Experimental

4.1. General

All Ni-catalyzed reactions were performed with magnetic stirring in scintillation vials sealed with Teflon coated thermoset caps. Reaction product solutions and chromatography fractions were concentrated by rotary evaporation and then at ca. 10 mtorr (vacuum pump). Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and thin layer chromatography was performed on Analtech TLC plates pre-coated with silica gel 60 F_{254}.

4.2. Materials

Rubidium carbonate, pivaloyl chloride, carbamoyl chloride, 4-methoxybenzoyl chloride, 4-trifluoromethylbenzoyl chloride, and 1,2-bis(dicyclohexylphosphino)ethane (dcype) were obtained from Aldrich and used as received. Anhydrous potassium phosphate tribasic and anhydrous potassium acetate were obtained from Acros organics and used as received. Anhydrous cesium carbonate was obtained from Acros organics and further dried at 100 °C under high vacuum for 5–8 h prior to use. Anhydrous xylene and anhydrous *N*,*N*-dimethylacetamide were obtained from Aldrich and used as received. Other solvents were obtained from Fisher Chemical or VWR Chemical and used without further purification.

4.3. Instrumentation

NMR spectra were obtained on a Bruker 400 (399.96 MHz for ^{1}H; 100.57 MHz for ^{13}C) spectrometer. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet of doublets (td), triplet (t), multiplet (m), and broad resonance (br). IR spectra were obtained on a Thermo scientific Nicolet iS5 iD5 ATR spectrometer. Melting points were obtained on a Thomas Hoover melting point apparatus.

4.4. Synthesis and characterization of substrates

*4.4.1. 2-Phenoxyphenyl pivalate (**1-OPiv**).* 2-Phenoxyphenol (**1-OH**)[8i,19a] (500 mg, 2.69 mmol, 1.0 equiv) and DMAP (32.8 mg, 0.27 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (9.3 mL), Et_3N (326 mg, 3.22 mmol, 1.2 equiv), and pivaloyl chloride (389 mg, 3.22 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on

a silica gel column using 97/3 hexanes/EtOAc (R_f=0.30 in 97% hexanes/3% ethyl acetate). The product **1-OPiv** was obtained as white solid (537 mg, 74% yield); mp=62.5 °C. [Note: the product was further recrystallized using petroleum ether prior to using it for catalysis.] ^{1}H NMR ($CDCl_3$): δ 7.30 (t, J=8.0 Hz, 2H), 7.23–7.14 (multiple peaks, 3H), 7.09–7.04 (multiple peaks, 2H), 6.97–6.93 (multiple peaks, 2H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 176.4, 157.3, 147.8, 142.7, 129.5, 126.7, 124.3, 123.7, 122.8, 121.1, 117.4, 39.0, 27.0. IR (neat): 2971, 1749, 1586, 1490, 1479, 1459, 1253, 1205, 1182, 1112, 1068, 881, 796, 742, 692 cm^{-1}. HRMS calcd for $C_{17}H_{18}O_3Na$ 293.1154; found: 293.1139.

*4.4.2. A solution of alcohol **1-OH**[8i,19b]* (500 mg, 2.69 mmol, 1.0 equiv) in THF (7.0 mL) was added dropwise to a solution of NaH (77.3 mg, 3.22 mmol, 1.2 equiv) in THF (1.8 mL) at 0 °C. The resulting mixture was allowed to stir at room temperature for 10 min after which a solution of *N*,*N*-diethyl carbamoyl chloride (437 mg, 3.22 mmol, 1.2 equiv) in THF (2.9 mL) was added to it at 0 °C. The resulting solution was allowed to warm to room temperature and stirred at room temperature for 15 h. The reaction mixture was then quenched with H_2O (1.0 mL) at 0 °C and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with 1.0 M aqueous KOH solution (1×20 mL), H_2O (1×20 mL), and brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 90/10 hexanes/EtOAc (R_f=0.24 in 90% hexanes/10% ethyl acetate). The product **1-OCONEt$_2$** was obtained as a clear viscous oil (471 mg, 61% yield). ^{1}H NMR ($CDCl_3$): δ 7.32–7.26 (multiple peaks, 3H), 7.21–7.14 (multiple peaks, 2H), 7.08–7.03 (multiple peaks, 2H), 6.98 (d, J=8.1 Hz, 2H), 3.30 (q, J=7.2 Hz, 2H), 3.19 (q, J=7.2 Hz, 2H), 1.11 (t, J=7.2 Hz, 3H), 1.06 (t, J=7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.6, 153.4, 147.9, 143.1, 129.4, 126.1, 124.3, 124.2, 122.6, 121.2, 117.3, 42.2, 41.7, 13.8, 13.2. IR (neat): 2975, 1717, 1587, 1488, 1472, 1417, 1254, 1204, 1184, 1104, 1074, 879, 783, 745, 690 cm^{-1}. HRMS calcd for $C_{17}H_{19}O_3NNa^+$ 308.1263; found: 308.1271.

*4.4.3. Alcohol **1-OH**[8i,19b]* (500 mg, 2.69 mmol, 1.0 equiv) and DMAP (32.8 mg, 0.27 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (9.2 mL), Et_3N (326 mg, 3.22 mmol, 1.2 equiv), and benzoyl chloride (453 mg, 3.22 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 12 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.26 in 97% hexanes/3% ethyl acetate). The product **1-OBz** was obtained as a clear viscous oil (380 mg, 49% yield). ^{1}H NMR ($CDCl_3$): δ 8.06 (d, J=8.1 Hz, 2H), 7.60 (t, J=7.5 Hz, 1H), 7.45 (t, J=7.8 Hz, 2H), 7.34–7.19 (multiple peaks, 5H), 7.11–7.06 (multiple peaks, 2H), 7.02 (d, J=8.4 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.5, 157.2, 148.5, 142.1, 133.4, 130.2, 129.6, 129.1, 128.4, 126.9, 124.1, 123.8, 123.2, 120.6, 118.2. IR (neat): 3065, 1740, 1586, 1487, 1451, 1249, 1202, 1173, 1103, 1077, 1057, 1023, 880, 794, 748, 703, 690 cm^{-1}. HRMS calcd for $C_{19}H_{14}O_3Na^+$ 313.0841; found: 313.0837.

*4.4.4. Alcohol **1-OH**[8i,19a]* (500 mg, 2.69 mmol, 1.0 equiv) and DMAP (32.8 mg, 0.27 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (9.3 mL), Et_3N (326 mg, 3.22 mmol, 1.2 equiv), and 4-methoxybenzoyl chloride (550 mg, 3.22 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 95/5 hexanes/EtOAc (R_f=0.16 in 95% hexanes/5% ethyl acetate). The product **1-OCO(p-OMeC$_6$H$_4$)** was obtained as white solid (667 mg, 78% yield); mp=81–82 °C. ^{1}H NMR ($CDCl_3$): δ 7.99 (d, J=8.8 Hz, 2H), 7.32–7.18 (multiple peaks, 5H), 7.10–7.04 (multiple peaks, 2H), 7.00 (d, J=8.6 Hz, 2H), 6.91 (d, J=8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.2, 163.8, 157.3, 148.5, 142.3, 132.3, 129.5, 126.8, 124.1, 124.0, 123.1, 121.4, 120.7, 118.1, 113.6, 55.4. IR (neat): 3066, 3019, 2975, 2844, 1727, 1602, 1586, 1576, 1508, 1487, 1269, 1248, 1206, 1164, 1103, 1058, 1021, 880, 854, 786, 752, 691 cm^{-1}. HRMS calcd for $C_{20}H_{16}O_4Na^+$ 343.0946; found: 343.0929.

*4.4.5. Alcohol **1-OH**[8i,19a]* (500 mg, 2.69 mmol, 1.0 equiv) and DMAP (32.8 mg, 0.27 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (9.3 mL), Et_3N (326 mg, 3.22 mmol, 1.2 equiv), and 4-trifluoromethylbenzoyl chloride (672 mg, 3.22 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 96/4 hexanes/EtOAc (R_f=0.26 in 96% hexanes/4% ethyl acetate). The product **1-OCO(p-CF$_3$C$_6$H$_4$)** was obtained as a clear viscous oil (402 mg, 42% yield). ^{1}H NMR ($CDCl_3$): δ 8.15 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.2 Hz, 2H), 7.34–7.20 (multiple peaks, 5H), 7.12–7.06 (multiple peaks, 2H), 7.00 (d, J=8.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.3, 157.0, 148.4, 141.8, 134.9 ($^2J_{C-F}$=32 Hz), 132.3, 130.6, 129.7, 127.3, 125.4 ($^3J_{C-F}$=3.4 Hz), 124.2, 123.6, 123.5 ($^3J_{C-F}$=271 Hz), 123.4, 120.7, 118.1. IR (neat): 3069, 1745, 1587, 1488, 1411, 1323, 1254, 1203, 1175, 1127, 1104, 1069, 1016, 881, 860, 768, 746, 689 cm^{-1}. HRMS calcd for $C_{20}H_{13}O_3F_3Na^+$ 381.0714; found: 381.0709.

*4.4.6. 2-(p-Tolyloxy)phenyl pivalate (**2-OPiv**).* 2-(*p*-Tolyloxy)phenol (**2-OH**)[8i,19a] (500 mg, 2.50 mmol, 1.0 equiv) and DMAP (30.5 mg, 0.25 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (8.6 mL), Et_3N (303 mg, 3.00 mmol, 1.2 equiv), and pivaloyl chloride (361 mg, 3.00 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with H_2O (1×20 mL) and satd aq NH_4Cl (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.24 in 97% hexanes/3% ethyl acetate). The product **2-OPiv** was obtained as white solid (537 mg, 76% yield); mp=73–74 °C. ^{1}H NMR ($CDCl_3$): δ 7.20–7.11 (multiple peaks, 5H), 7.00 (d, J=7.8 Hz, 1H), 6.88 (d, J=8.2 Hz, 2H), 2.33 (s, 3H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 176.4, 154.9, 148.5, 142.4, 132.5, 130.0, 126.6, 123.8, 123.6, 120.3, 117.8, 39.0, 27.0, 20.6. IR (neat): 3038, 1751, 1593, 1505, 1491, 1457, 1253, 1208, 1177, 1164, 1113, 1103, 1034, 1014, 883, 835, 756, 741 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_3Na^+$ 307.1310; found: 307.1305.

*4.4.7. 2-(4-Methoxyphenoxy)phenyl pivalate (**3-OPiv**).* 2-(4-Methoxyphenoxy)phenol (**3-OH**)[8i,19a] (348 mg, 1.61 mmol, 1.0 equiv) and DMAP (19.7 mg, 0.16 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2

(5.6 mL), Et_3N (196 mg, 1.93 mmol, 1.2 equiv), and pivaloyl chloride (194 mg, 1.61 mmol, 1.0 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.22 in 97% hexanes/3% ethyl acetate). The product **3-OPiv** was obtained as a white solid (241 mg, 50% yield); mp=84–87 °C. ^1H NMR ($CDCl_3$): δ 7.18–7.07 (multiple peaks, 3H), 6.95–6.92 (multiple peaks, 3H), 6.86 (d, J=8.8 Hz, 2H), 3.80 (s, 3H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.6, 155.6, 150.6, 149.2, 142.0, 126.6, 123.5, 123.4, 119.48, 119.46, 114.7, 55.7, 39.0, 27.1. IR (thin film, CH_2Cl_2): 2972, 1756, 1504, 1492, 1456, 1258, 1240, 1201, 1180, 1105, 1034, 881, 830, 757 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_4Na^+$ 323.1259; found: 323.1253.

*4.4.8. 2-(4-Fluorophenoxy)phenyl pivalate (**4-OPiv**).* 2-(4-Fluorophenoxy)phenol (**4-OH**)[8i,19a] (600 mg, 2.94 mmol, 1.0 equiv) and DMAP (35.9 mg, 0.29 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (10.1 mL), Et_3N (357 mg, 3.53 mmol, 1.2 equiv), and pivaloyl chloride (354 mg, 2.94 mmol, 1.0 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.20 in 97% hexanes/3% ethyl acetate). The product **4-OPiv** was obtained as white solid (448 mg, 53% yield); mp=79 °C. ^1H NMR ($CDCl_3$): δ 7.22–7.15 (multiple peaks, 3H), 7.02–6.98 (multiple peaks, 3H), 6.95–6.91 (multiple peaks, 2H), 1.26 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4, 158.6 ($^1J_{C-F}$=240 Hz), 153.1, 148.3, 142.4, 126.8, 124.3, 123.7, 120.4, 119.0 ($^3J_{C-F}$=8.1 Hz), 116.1 ($^2J_{C-F}$=23 Hz), 39.0, 27.0. IR (neat): 3074, 2971, 1742, 1502, 1492, 1458, 1260, 1223, 1195, 1119, 1105, 1088, 885, 853, 834, 813, 788, 756, 746 cm^{-1}. HRMS calcd for $C_{17}H_{17}FO_3Na^+$ 311.1059; found: 311.1051.

*4.4.9. 2-(3-Methoxyphenoxy)phenyl pivalate (**5-OPiv**).* 2-(3-Methoxyphenoxy)phenol (**5-OH**)[8i,19a] (435 mg, 2.01 mmol, 1.0 equiv) and DMAP (24.6 mg, 0.20 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (6.9 mL), Et_3N (245 mg, 2.42 mmol, 1.2 equiv), and pivaloyl chloride (291 mg, 2.42 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.18 in 97% hexanes/3% ethyl acetate). The product **5-OPiv** was obtained as a clear viscous oil (325 mg, 54% yield). ^1H NMR ($CDCl_3$): δ 7.24–7.15 (multiple peaks, 4H), 7.08 (d, J=7.7 Hz, 1H), 6.63 (d, J=8.0 Hz, 1H), 6.56–6.53 (multiple peaks, 2H), 3.77 (s, 3H), 1.24 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.3, 160.8, 158.5, 147.6, 142.7, 130.0, 126.7, 124.5, 123.7, 121.2, 109.6, 108.6, 103.4, 55.3, 39.0, 27.0. IR (neat): 2972, 1753, 1588, 1486, 1453, 1264, 1245, 1182, 1137, 1101, 1034, 953, 844, 756, 736, 686 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_4Na^+$ 323.1259; found: 323.1248.

*4.4.10. 2-(3-Trifluoromethylphenoxy)phenyl pivalate (**6-OPiv**).* 2-(3-Trifluoromethylphenoxy)phenol (**6-OH**)[8i,19a] (500 mg, 1.97 mmol, 1.0 equiv) and DMAP (24.0 mg, 0.19 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (6.8 mL), Et_3N (239 mg, 2.36 mmol, 1.2 equiv), and pivaloyl chloride (237 mg, 1.97 mmol, 1.0 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.16 in 97% hexanes/3% ethyl acetate). The product **6-OPiv** was obtained as a clear viscous oil (325 mg, 49% yield). ^1H NMR ($CDCl_3$): δ 7.41 (t, J=8.1 Hz, 1H), 7.32 (d, J=7.8 Hz, 1H), 7.28–7.18 (multiple peaks, 4H), 7.11–7.08 (multiple peaks, 2H), 1.18 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.2, 157.7, 146.7, 142.8, 132.1 ($^2J_{C-F}$=32 Hz), 130.2, 127.0, 125.4, 124.1, 123.7 ($^1J_{C-F}$=271 Hz), 121.6, 120.1, 119.4 ($^3J_{C-F}$=3.8 Hz), 114.0 ($^3J_{C-F}$=4.0 Hz), 39.0, 26.9. IR (neat): 2976, 1756, 1591, 1491, 1449, 1325, 1283, 1254, 1203, 1169, 1125, 1100, 1063, 1029, 918, 890, 792, 764, 742, 697, 655 cm^{-1}. HRMS calcd for $C_{18}H_{17}F_3O_3Na^+$ 361.1027; found: 361.1018.

*4.4.11. 2-(o-Tolyloxy)phenyl pivalate (**7-OPiv**).* 2-(*p*-Tolyloxy)phenol (**7-OH**)[8i,19a] (500 mg, 2.50 mmol, 1.0 equiv) and DMAP (30.5 mg, 0.25 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (8.6 mL), Et_3N (303 mg, 3.00 mmol, 1.2 equiv), and pivaloyl chloride (361 mg, 3.00 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with H_2O (1×20 mL) and satd aq NH_4Cl (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.41 in 97% hexanes/3% ethyl acetate). The product **7-OPiv** was obtained as a clear viscous oil after drying under high vacuum at 55 °C (366 mg, 52% yield). ^1H NMR ($CDCl_3$): δ 7.24 (d, J=7.4 Hz, 1H), 7.18–7.08 (multiple peaks, 4H), 7.04 (t, J=7.5 Hz, 1H), 6.86–6.81 (multiple peaks, 2H), 2.27 (s, 3H), 1.27 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4, 154.6, 148.6, 141.7, 131.2, 128.9, 127.0, 126.6, 123.6, 123.5, 123.2, 118.8, 117.9, 39.0, 27.0, 16.0. IR (neat): 2973, 1756, 1585, 1490, 1455, 1252, 1221, 1183, 1102, 1029, 883, 794, 741, 710 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_3Na^+$ 307.1310; found: 307.1294.

*4.4.12. 2-(Naphthalene-2-yloxy)phenyl pivalate (**8-OPiv**).* 2-(2-Naphthalen-2-yloxy)phenol (**8-OH**)[8i,19a] (600 mg, 2.54 mmol, 1.0 equiv) and DMAP (31.0 mg, 0.25 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (8.8 mL), Et_3N (308 mg, 3.05 mmol, 1.2 equiv), and pivaloyl chloride (367 mg, 3.05 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.17 in 97% hexanes/3% ethyl acetate). The product **8-OPiv** was obtained as white solid after drying under high vacuum at 55 °C (697 mg, 86% yield); mp=57–58 °C. ^1H NMR ($CDCl_3$): δ 7.82 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.0 Hz, 1H), 7.48–7.39 (multiple peaks, 2H), 7.28–7.20 (multiple peaks, 5H), 7.13–7.10 (m, 1H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4, 155.1, 147.8, 142.8, 134.2, 130.0, 129.7, 127.6, 127.0, 126.8, 126.5, 124.5, 123.8, 121.2, 119.0, 112.4, 39.0, 27.0 (Two peaks in the carbon spectrum are coincidentally overlapping.). IR (neat): 2970, 2869, 1744, 1596, 1509, 1492, 1479, 1466, 1457, 1251, 1211, 1180, 1109, 1033,

964, 911, 885, 867, 822, 756, 742 cm^{-1}. HRMS calcd for $C_{21}H_{20}O_3Na^+$ 343.1310; found: 343.1299.

*4.4.13. 4-Methoxy-2-phenoxyphenyl pivalate (**9-OPiv**).* 4-Methoxy-2-phenoxyphenol (**9-OH**)[8i,19a] (455 mg, 2.10 mmol, 1.0 equiv) and DMAP (25.7 mg, 0.21 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (7.3 mL), Et_3N (256 mg, 2.53 mmol, 1.2 equiv), and pivaloyl chloride (254 mg, 2.10 mmol, 1.00 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 95/5 hexanes/EtOAc (R_f=0.11 in 95% hexanes/5% ethyl acetate). The product **9-OPiv** was obtained as a clear viscous oil (198 mg, 31% yield). [Note: the yield is approximate because the starting alcohol was impure.] ^1H NMR ($CDCl_3$): δ 7.31 (t, J=7.9 Hz, 2H), 7.09–7.04 (multiple peaks, 2H), 6.97 (d, J=8.2 Hz, 2H), 6.70 (dd, J=8.8, 2.9 Hz, 1H), 6.60 (d, J=3.0 Hz, 1H), 3.76 (s, 3H), 1.20 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.7, 158.0, 157.1, 148.2, 136.1, 129.6, 123.8, 122.9, 117.5, 109.3, 106.9, 55.6, 38.9, 27.0. IR (neat): 2972, 1752, 1588, 1503, 1489, 1256, 1212, 1195, 1152, 1106, 1032, 958, 838, 756, 690 cm^{-1}. HRMS calcd for $C_{18}H_{20}O_4Na^+$ 323.1259; found: 323.1252.

*4.4.14. 2-Phenoxy-4-(trifluoromethyl)phenyl pivalate (**10-OPiv**).* 2-Phenoxy-4-(trifluoromethyl)phenol (**10-OH**)[8i,19a] (243 mg, 0.96 mmol, 1.0 equiv) and DMAP (11.7 mg, 0.10 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (3.3 mL), Et_3N (116 mg, 1.15 mmol, 1.2 equiv), and pivaloyl chloride (138 mg, 1.15 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.26 in 97% hexanes/3% ethyl acetate). The product **10-OPiv** was obtained as a clear viscous oil (213 mg, 66% yield). ^1H NMR ($CDCl_3$): δ 7.42 (d, J=8.6 Hz, 1H), 7.35 (t, J=7.9 Hz, 2H), 7.27 (dd, J=10, 2.3 Hz, 2H), 7.14 (t, J=7.4 Hz, 1H), 6.99 (d, J=8.0 Hz, 2H), 1.25 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.0, 156.3, 148.6, 145.1, 129.9, 129.1 ($^2J_{C-F}$=33 Hz), 124.3, 123.9, 123.4 ($^1J_{C-F}$=271 Hz), 121.0 ($^3J_{C-F}$=4.0 Hz), 118.0, 117.4 ($^3J_{C-F}$=3.4 Hz), 39.2, 26.9. IR (thin film, $CDCl_3$): 2976, 1761, 1589, 1511, 1491, 1425, 1330, 1265, 1249, 1206, 1168, 1119, 1100, 1066, 930, 888 cm^{-1}. HRMS calcd for $C_{18}H_{17}F_3O_3Na^+$ 361.1027; found: 361.1017.

*4.4.15. 2-Phenoxy-5-(trifluoromethyl)phenyl pivalate (**11-OPiv**).* 2-Phenoxy-5-(trifluoromethyl)phenol **11-OH**[8i,19a] (500 mg, 1.97 mmol, 1.0 equiv) and DMAP (24.0 mg, 0.19 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (2.9 mL), Et_3N (239 mg, 2.36 mmol, 1.2 equiv), and pivaloyl chloride (249 mg, 2.07 mmol, 1.05 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL) and brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.23 in 95% hexanes/5% ethyl acetate). The product **11-OPiv** was obtained as a clear viscous oil (533 mg, 80% yield). ^1H NMR ($CDCl_3$): δ 7.46–7.41 (multiple peaks, 2H), 7.37 (t, J=7.9 Hz, 2H), 7.17 (t, J=7.4 Hz, 1H), 7.05–6.99 (multiple peaks, 3H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.1, 155.9, 151.7, 142.0, 129.9, 125.8 ($^2J_{C-F}$=33 Hz), 124.2, 123.9 ($^3J_{C-F}$=3.8 Hz), 123.6 ($^1J_{C-F}$=271 Hz), 121.3 ($^3J_{C-F}$=3.8 Hz), 119.4, 118.8, 39.1, 27.0. IR (neat): 2976, 1760, 1591, 1511, 1458, 1430, 1327, 1269, 1200, 1183, 1166, 1119, 1094, 1066, 1027, 903, 851, 825, 794, 748, 691 cm^{-1}. HRMS calcd for $C_{18}H_{17}F_3O_3Na^+$ 361.1027; found: 361.1016.

*4.4.16. 2-((4-Methoxyphenyl)(methyl)amino)phenyl pivalate (**12-OPiv**).* 2-((4-Methoxylphenyl)(methyl)amino)phenol (**12-OH**)[8i,19a] (500 mg, 2.18 mmol, 1.0 equiv) and DMAP (30.7 mg, 0.25 mmol, 0.12 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (3.7 mL), Et_3N (305 mg, 3.01 mmol, 1.4 equiv), and pivaloyl chloride (363 mg, 3.01 mmol, 1.4 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 95/5 hexanes/EtOAc (R_f=0.21 in 95% hexanes/5% ethyl acetate). The product **12-OPiv** was obtained as a clear yellow oil (471 mg, 69% yield). ^1H NMR ($CDCl_3$): δ 7.25–7.18 (multiple peaks, 3H), 7.08 (d, J=8.2 Hz, 1H), 6.78 (dt, J=9.0, 3.0 Hz, 2H), 6.65 (dt, J=9.0, 3.0 Hz, 2H), 3.76 (s, 3H), 3.20 (s, 3H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4, 152.6, 147.3, 143.2, 141.5, 127.7, 127.0, 125.6, 123.4, 116.0, 114.3, 55.7, 40.1, 38.9, 26.9. IR (neat): 2971, 2933, 2905, 2872, 2831, 1748, 1508, 1495, 1463, 1452, 1239, 1106, 1035, 819, 779, 756, 735 cm^{-1}. HRMS calcd for $C_{19}H_{23}NO_3Na^+$ 336.1576; found: 336.1569.

*4.4.17. 2-((4-Fluorophenyl)(methyl)amino)phenyl pivalate (**13-OPiv**).* 2-((4-Fluorolphenyl)(methyl)amino)phenol (**13-OH**) (500 mg, 2.30 mmol, 1.0 equiv) and DMAP (28.1 mg, 0.23 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (3.4 mL), Et_3N (279 mg, 2.76 mmol, 1.2 equiv), and pivaloyl chloride (291 mg, 2.42 mmol, 1.05 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with satd aq NH_4Cl (3×20 mL) and brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel column using 95/5 hexanes/EtOAc (R_f=0.34 in 95% hexanes/5% ethyl acetate). The product **13-OPiv** was obtained as white solid (536 mg, 77% yield); mp=56.5–57.5 °C. ^1H NMR ($CDCl_3$): δ 7.30–7.23 (multiple peaks, 3H), 7.12–7.10 (m, 1H), 6.92–6.85 (multiple peaks, 2H), 6.60–6.55 (multiple peaks, 2H), 3.20 (s, 3H), 1.11 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4, 156.2 ($^1J_{C-F}$=235 Hz), 147.7, 145.1, 140.8, 128.4, 127.2, 126.4, 123.6, 115.1 ($^2J_{C-F}$=22 Hz), 114.9 ($^3J_{C-F}$=7.4 Hz), 39.9, 38.9, 26.9. IR (neat): 2978, 1742, 1505, 1497, 1476, 1453, 1349, 1283, 1256, 1216, 1196, 1111, 1067, 1033, 899, 818, 789, 759, 735, 577, 559 cm^{-1}. HRMS calcd for $C_{18}H_{20}FNO_2Na^+$ 324.1376; found: 324.1369.

*4.4.18. Alcohol **1-OH**-d* (465 mg, 2.48 mmol, 1.0 equiv) and DMAP (30.3 mg, 0.25 mmol, 0.1 equiv) were added to a schlenk flask, which was then put under N_2 atmosphere using a manifold. CH_2Cl_2 (3.7 mL), Et_3N (302 mg, 2.98 mmol, 1.2 equiv), and pivaloyl chloride (359 mg, 2.98 mmol, 1.2 equiv) were added to the flask sequentially. The resulting mixture was allowed to stir at room temperature for 15 h. The reaction mixture was then diluted with 20 mL H_2O and 20 mL CH_2Cl_2 and transferred to a separatory funnel. The aqueous and organic layers were separated and the organic layer was extracted with brine (1×20 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated, and chromatographed on a silica gel

column using 97/3 hexanes/EtOAc (R_f=0.30 in 97% hexanes/3% ethyl acetate). The product **1-OPiv**-*d* was obtained as white solid. [Note: the product was further recrystallized using petroleum ether prior to using it for catalysis] (300 mg, 44.5% yield); mp=62.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.33–7.28 (multiple peaks, 2H), 7.23–7.14 (multiple peaks, 3H), 7.09–7.03 (multiple peaks, 2H), 6.94 (d, J=8.3 Hz, 1H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 176.4, 157.3, 147.8, 142.7, 129.5, 126.7, 124.3, 123.7, 122.8, 121.1, 117.4, 39.0, 27.0. IR (neat): 2972, 1749, 1582, 1493, 1477, 1458, 1252, 1205, 1182, 1111, 1036, 1028, 884, 796, 745 cm^{-1}. HRMS calcd for $C_{17}H_{17}DO_3Na^+$ 294.1154; found: 294.1207.

4.5. C–H arylation of aryl pivalates

*4.5.1. General procedure (**A**) for C–H arylations with solid substrates.* To an oven dried 20 mL scintillation vial containing a magnetic stir bar was added $Ni(COD)_2$, dcype, Cs_2CO_3, substrate, and xylene in the glove box. The vial was sealed with a Teflon lined cap, taken out of the glove box, and the reaction mixture was allowed to stir at the 160 °C for 72 h. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

*4.5.2. General procedure (**B**) for C–H arylations with liquid substrates.* To an oven dried 20 mL scintillation vial containing a magnetic stir bar was added $Ni(COD)_2$, dcype, and Cs_2CO_3 in the glove box. A solution of substrate in xylene was added to this mixture. The vial was sealed with a Teflon lined cap, taken out of the glove box, and the reaction mixture was allowed to stir at 160 °C for 72 h. The reaction mixture was cooled to room temperature and filtered through a 1.5 inch plug of silica gel, eluting with Et_2O (100 mL). The filtrate was concentrated and chromatographed on a silica gel column to afford the product.

*4.5.2.1. Dibenzo[b,d]furan (**1a**), Table 2, entry 1.* Following general procedure **A**, pivalate **1-OPiv** (135 mg, 0.500 mmol, 1.0 equiv), $Ni(COD)_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.79 in 98% hexanes/2% ethyl acetate) yielded product **1a** as a 4.9:1 mixture of product **1a** and the protodeoxygenated substrate[20] (55.1 mg, 66% yield). ^{1}H NMR ($CDCl_3$): δ 8.00 (d, J=7.6 Hz, 2H), 7.63 (d, J=8.2 Hz, 2H), 7.50 (t, J=7.8 Hz, 2H), 7.39 (t, J=7.8 Hz, 2H). The spectroscopic data is consistent with that reported in the literature.[8i,21,14a]

*4.5.2.2. 2-Methyldibenzo[b,d]furan (**2a**), Table 2, entry 2.* Following general procedure **A**, pivalate **2-OPiv** (142.2 mg, 0.500 mmol, 1.0 equiv), $Ni(COD)_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.58 in 98% hexanes/2% ethyl acetate) yielded product **2a** as a 25:1 mixture of product **2a** and the protodeoxygenated substrate.[22] The yield of the desired product **2a** was 74% (67.5 mg). ^{1}H NMR ($CDCl_3$): δ 7.94 (dd, J=7.6, 0.6 Hz, 1H), 7.77 (t, J=0.7 Hz, 1H), 7.57 (d, J=8.2 Hz, 1H), 7.50–7.44 (multiple peaks, 2H), 7.34 (td, J=7.6, 0.9 Hz, 1H), 7.28 (dd, J=8.8, 1.7 Hz, 1H), 2.54 (s, 3H). The spectroscopic data is consistent with that reported in the literature.[8i,21,14a]

*4.5.2.3. 2-Methoxydibenzo[b,d]furan (**3a**), Table 2, entry 3.* Following general procedure **A**, pivalate **3-OPiv** (150.2 mg, 0.500 mmol, 1.0 equiv), $Ni(COD)_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.30 in 98% hexanes/2% ethyl acetate) yielded product **3a** as a 4:1 mixture of product **3a** and the protodeoxygenated substrate.[20] The yield of the desired product was 75% (74.2 mg). ^{1}H NMR ($CDCl_3$): δ 7.94 (d, J=7.7 Hz, 1H), 7.57 (d, J=8.2 Hz, 1H), 7.50–7.44 (multiple peaks, 3H), 7.35 (t, J=7.5 Hz, 1H), 7.07 (dd, J=8.9, 2.6 Hz, 1H), 3.93 (s, 3H). The spectroscopic data is consistent with that reported in the literature.[8i,21,14a]

*4.5.2.4. 2-Fluorodibenzo[b,d]furan (**4a**), Table 2, entry 4.* Following general procedure **A**, pivalate **4-OPiv** (144.2 mg, 0.500 mmol, 1.0 equiv), $Ni(COD)_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.62 in 98% hexanes/2% ethyl acetate) yielded product **4a** as a 3.8:1 mixture of product **4a** and the protodeoxygenated substrate.[22] The yield of the desired product was 67% (62.8 mg). ^{1}H NMR ($CDCl_3$): δ 7.92 (d, J=7.7 Hz, 1H), 7.65–7.56 (multiple peaks, 2H), 7.54–7.48 (multiple peaks, 2H), 7.37 (t, J=7.5 Hz, 1H), 7.19 (td, J=9.0, 2.6 Hz, 1H). The spectroscopic data is consistent with that reported in the literature.[8i,21,14a]

*4.5.2.5. 3-Methoxydibenzo[b,d]furan (**5a**), Table 2, entry 5.* Following general procedure **B**, pivalate **5-OPiv** (150.2 mg, 0.500 mmol, 1.0 equiv), $Ni(COD)_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 97/3 hexanes/EtOAc (R_f=0.37 in 97% hexanes/3% ethyl acetate) yielded product **5a** as a 4.2:1 mixture of product **5a** and the protodeoxygenated substrate.[20] The yield of the desired product **5a** was 77% (76.0 mg). ^{1}H NMR ($CDCl_3$): δ 7.88 (d, J=7.4 Hz, 1H), 7.83 (d, J=8.5 Hz, 1H), 7.56 (d, J=8.1 Hz, 1H), 7.41 (t, J=7.7 Hz, 1H), 7.34 (t, J=7.4 Hz, 1H), 7.12 (d, J=2.1 Hz, 1H), 6.97 (dd, J=8.5, 2.2 Hz, 1H), 3.92 (s, 3H). The spectroscopic data is consistent with that reported in the literature.[8i,14b]

*4.5.2.6. 3-(Trifluoromethyl)dibenzo[b,d]furan (**6a**), Table 2, entry 6.* Following general procedure **B**, pivalate **6-OPiv** (120 mg, 0.355 mmol, 1.0 equiv), $Ni(COD)_2$ (12.2 mg, 0.044 mmol, 0.125 equiv), dcype (37.4 mg, 0.089 mmol, 0.25 equiv), Cs_2CO_3 (289 mg, 0.89 mmol, 2.5 equiv), and xylene (2.8 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.55 in 98% hexanes/2% ethyl acetate) yielded product **6a** as a 5.3:1 mixture of product **6a** and the protodeoxygenated substrate.[20] The yield of the desired product was 62% (51.9 mg). ^{1}H NMR ($CDCl_3$): δ 8.03 (d, J=8.1 Hz, 1H), 8.00 (d, J=7.8 Hz, 1H), 7.84 (s, 1H), 7.65–7.60 (multiple peaks, 2H), 7.55 (td, J=7.8, 1.2 Hz, 1H), 7.41 (t, J=7.5 Hz, 1H). The spectroscopic data is consistent with that reported in the literature.[8i,14b]

*4.5.2.7. 4-Methyldibenzo[b,d]furan (**7a**) Table 2, entry 7.* Following general procedure **B**, pivalate **7-OPiv** (100 mg, 0.352 mmol, 1.0 equiv), $Ni(COD)_2$ (12.1 mg, 0.044 mmol, 0.125 equiv), dcype (37.2 mg, 0.088 mmol, 0.25 equiv), Cs_2CO_3 (286 mg, 0.879 mmol, 2.5 equiv), and xylene (2.8 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.64 in 98% hexanes/2% ethyl acetate) yielded product **7a** as a 2.7:1 mixture of product **6a** and the protodeoxygenated substrate.[23] The yield of the desired product **7a** was 67% (42.9 mg). ^{1}H NMR ($CDCl_3$): δ 7.98 (d,

J=7.5 Hz, 1H), 7.82 (dd, J=6.5, 2.3 Hz, 1H), 7.64 (d, J=7.9 Hz, 1H), 7.49 (td, J=7.8, 1.1 Hz, 1H), 7.37 (t, J=7.5 Hz, 1H), 7.32–7.26 (multiple peaks, 2H), 2.66 (s, 3H). The spectroscopic data is consistent with that reported in the literature.[8i,21,14a]

*4.5.2.8. Naphtho[2,3-b]benzofuran (**8a**) Table 2, entry 8.* Following general procedure **A**, pivalate **8-OPiv** (100 mg, 0.312 mmol, 1.0 equiv), Ni(COD)$_2$ (10.7 mg, 0.039 mmol, 0.125 equiv), dcype (33.0 mg, 0.078 mmol, 0.25 equiv), Cs_2CO_3 (254 mg, 0.780 mmol, 2.5 equiv), and xylene (2.5 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. The ratio of **8a**:**8b** was determined by GC analysis of the crude reaction mixture and was determined to be 2.9:1. Chromatography on a silica gel column using 98/2 hexanes/DCM yielded product as a mixture of **8a** and **8b**.[24] The yield of the desired product (**8a**+**8b**) was 65% (44.2 mg).

Major isomer (**8a**): ^{1}H NMR ($CDCl_3$): δ 8.43 (br s, 1H), 8.12–8.02 (multiple peaks, 2H), 7.99 (d, J=8.5 Hz, 1H), 7.94 (br s, 1H), 7.63–7.46 (multiple peaks, 4H), 7.39 (t, J=7.3 Hz, 1H). The spectroscopic data is consistent with that reported in the literature.[25]

Minor isomer (**8b**): ^{1}H NMR ($CDCl_3$): δ 8.65 (d, J=7.9 Hz, 1H), 8.42 (dd, J=7.0, 1.7 Hz, 1H), 8.05 (d, J=8.0 Hz, 1H), 7.95 (d, J=8.7 Hz, 1H), 7.79 (d, J=8.9 Hz, 1H), 7.77–7.70 (multiple peaks, 2H), 7.57 (t, J=7.6 Hz, 1H), 7.53–7.49 (multiple peaks, 2H).

*4.5.2.9. 3-Methoxydibenzo[b,d]furan (**5a**), Table 3, entry 1.* Following general procedure **B**, pivalate **9-OPiv** (150 mg, 0.500 mmol, 1.0 equiv), Ni(COD)$_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.79 in 98% hexanes/2% ethyl acetate) yielded product **5a** as a 1.7:1 mixture of product **5a** and the protodeoxygenated substrate (54.3 mg, 55% yield).[20] ^{1}H NMR ($CDCl_3$): δ 7.88 (d, J=7.4 Hz, 1H), 7.83 (d, J=8.5 Hz, 1H), 7.56 (d, J=8.1 Hz, 1H), 7.41 (t, J=7.7 Hz, 1H), 7.34 (t, J=7.4 Hz, 1H), 7.12 (d, J=2.1 Hz, 1H), 6.97 (dd, J=8.5, 2.2 Hz, 1H), 3.92 (s, 3H). The spectroscopic data of the product was identical to that isolated from the reaction of pivalate **5-OPiv**.

*4.5.2.10. 3-(Trifluoromethyl)dibenzo[b,d]furan (**6a**) Table 3, entry 2.* Following general procedure **B**, pivalate **10-OPiv** (169 mg, 0.500 mmol, 1.0 equiv), Ni(COD)$_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. The yield of the desired product was determined to be 8% from the GC analysis of the crude reaction mixture against hexadecane as the internal standard.

*4.5.2.11. 2-(Trifluoromethyl)dibenzo[b,d]furan (**11a**), Table 3, entry 3.* Following general procedure **B**, pivalate **11-OPiv** (169 mg, 0.500 mmol, 1.0 equiv), Ni(COD)$_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 24 h. The yield of the desired product was determined to be 37% from the GC analysis of the crude reaction mixture against hexadecane as the internal standard. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.51 in 98% hexanes/2% ethyl acetate) yielded product as a 4.0:1 mixture of product **11a** and the protodeoxygenated substrate[25] (41.2 mg, 35% yield). ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 1H), 8.00 (d, J=7.9 Hz, 1H), 7.74 (d, J=8.6 Hz, 1H), 7.67 (d, J=8.6 Hz, 1H), 7.63 (d, J=8.2 Hz, 1H), 7.57–7.52 (m, 1H), 7.42 (t, J=7.6 Hz, 1H). The spectroscopic data of the product was identical to that reported in the literature.[26]

*4.5.2.12. 3-Methoxy-9-methyl-9H-carbazole (**12a**), Scheme 3.* Following general procedure **B**, pivalate **12-OPiv** (142 mg, 0.453 mmol, 1.0 equiv), Ni(COD)$_2$ (17.2 mg, 0.062 mmol, 0.136 equiv), dcype (52.8 mg, 0.125 mmol, 0.28 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.8 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 96/4 hexanes/EtOAc (R_f=0.18 in 96% hexanes/4% ethyl acetate) yielded product **12a** as a white solid (57.1 mg, 60% yield).[20] ^{1}H NMR ($CDCl_3$): δ 8.11 (d, J=7.8 Hz, 1H), 7.64 (d, J=2.5 Hz, 1H), 7.51 (d, J=7.8 Hz, 1H), 7.40 (d, J=8.2 Hz, 1H), 7.32 (d, J=8.8 Hz, 1H), 7.25 (t, J=7.4 Hz, 1H), 7.18 (dd, J=8.8, 2.5 Hz, 1H), 3.98 (s, 3H), 3.83 (s, 3H). The spectroscopic data is consistent with that reported in the literature.[8i]

*4.5.2.13. 3-Fluoro-9-methyl-9H-carbazole (**13a**), Scheme 2.* Following general procedure **B**, pivalate **13-OPiv** (151 mg, 0.500 mmol, 1.0 equiv), Ni(COD)$_2$ (17.2 mg, 0.063 mmol, 0.125 equiv), dcype (52.8 mg, 0.125 mmol, 0.25 equiv), Cs_2CO_3 (407 mg, 1.25 mmol, 2.5 equiv), and xylene (4.0 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.18 in 98% hexanes/2% ethyl acetate) yielded product **13a** as a white solid (51.0 mg, 51% yield).[23] ^{1}H NMR ($CDCl_3$): δ 8.06 (d, J=7.8 Hz, 1H), 7.77 (dd, J=8.9, 2.5 Hz, 1H), 7.52 (t, J=7.7 Hz, 1H), 7.41 (d, J=8.2 Hz, 1H), 7.33–7.21 (multiple peaks, 3H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.2 ($^1J_{C-F}$=234 Hz), 141.8, 137.4, 126.2, 123.1 ($^3J_{C-F}$=9.7 Hz), 122.3 ($^3J_{C-F}$=4.1 Hz), 120.5, 118.8, 113.3 ($^2J_{C-F}$=25 Hz), 108.9 ($^3J_{C-F}$=9.3 Hz), 108.7, 106.0 ($^2J_{C-F}$=24 Hz), 29.2. HRMS [EI] calcd for $C_{13}H_{10}FN$ 199.0797; found: 199.0807.

4.5.2.14. Scheme 3. Following general procedure **A**, pivalate **1-OPiv-*d*** (100 mg, 0.366 mmol, 1.0 equiv), Ni(COD)$_2$ (12.7 mg, 0.046 mmol, 0.125 equiv), dcype (38.6 mg, 0.091 mmol, 0.25 equiv), Cs_2CO_3 (298 mg, 0.91 mmol, 2.5 equiv), and xylene (2.9 mL) were combined in a 20 mL scintillation vial. The reaction mixture was allowed to stir at 160 °C for 72 h. Chromatography on a silica gel column using 98/2 hexanes/EtOAc (R_f=0.79 in 98% hexanes/2% ethyl acetate) yielded product as a 3.4:1 mixture of product **1a**-*d* (and **1a**) and the protodeoxygenated substrate (44.0 mg, 71% yield) °C. ^{1}H NMR ($CDCl_3$): δ 8.00 (dd, J=7.6, 1.4 Hz, 2H), 7.62 (d, J=8.4 Hz, 1.26H), 7.52–7.48 (multiple peaks, 2H), 7.38 (t, J=7.5 Hz, 2H). The ratio of **1a**-*d*:**1a** was determined to be 2.8:1 based on the analysis of ^{1}H NMR spectroscopic data. The spectroscopic data is consistent with that reported in the literature.[14]

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