Note

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Chromium-Catalyzed Regioselective Kumada Arylative Cross-Coupling of C(aryl)–O Bonds with a Traceless Activation Strategy

Fei Fan, Jinghua Tang, Meiming Luo,* and Xiaoming Zeng*

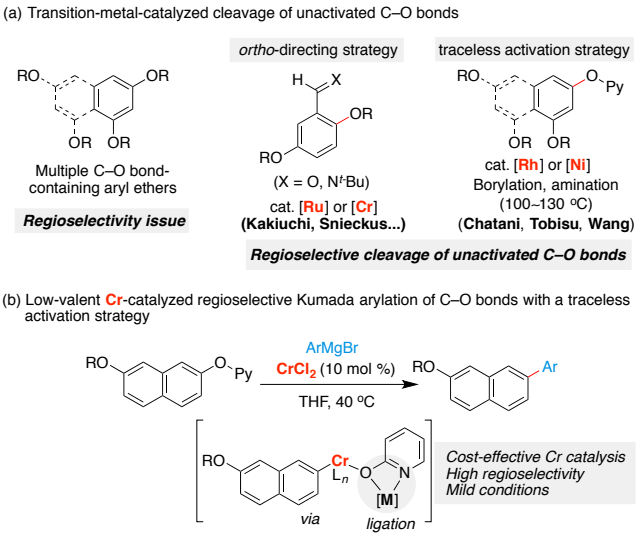
Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

ABSTRACT: We report here the chromium-catalyzed regioselective Kumada arylative cross-coupling of C(aryl)–O bonds at ambient temperature. By using a simple and low-cost chromium(II) chloride salt as precatalyst, accompanied by a 2-pyridyl ligation, the catalytic cleavage and arylative coupling of C(aryl)–O bonds was achieved with a traceless activation strategy, allowing for overcoming the regioselectivity obstacle when several C–O bonds are coexisted in the Kumada coupling system.

Selective cleavage and transformation of unactivated C(aryl)–O bonds by transition metal catalysis are of high synthetic interest because these bonds are common in organic chemistry.[1–7] Among compounds containing C(aryl)–O bonds, phenol and derivatives are naturally abundant and usually non-toxic precursors compared with their halide counterparts, which generally derived from oxygen-rich lignocellulosic plant biomass.[8] Transition metal catalysis using phenol derivatives as building blocks provides an ecologically strategy to the construction of aromatic feedstock chemicals.[9–27] However, regioselectivity in the transformation of phenol derivatives still remains a prominent issue when several C(aryl)–O bonds are coexisted in the reaction system (Scheme 1a).[28] A pioneering work by Kakiuchi and Chatani demonstrated that introduction of a carbonyl ligation auxiliary enabled achieving the *ortho*-selective cleavage and transformation of unactivated C(aryl)–O bonds with ruthenium catalysis.[29–32] Analogous *ortho*-chelation activation strategy has been described by Snieckus[33–35] and Zeng[36,37] to develop Ru or Cr-catalyzed cross-coupling reactions, which were able to retain the related *ortho*-functionality in the coupling products after the coupling of C(aryl)–O bonds. In contrast, methodology that enables the selective cleavage of a regiospecific C(aryl)–O bond without the ligation assistance of *ortho*-auxiliary has not rarely been studied for molecule construction.

Recently, the use of earth-abundant, inexpensive first-row transition metals such as nickel, iron and cobalt to replace precious metal catalysts in developing cost-effective synthetic strategies has attracted much attention.[38–42] To functionalization of C(aryl)–O bonds, nickel usually shows unique ability in catalytic cleavage of these unactivated chemical bonds.[2–5] By contrast, the reactivity of other first-row transition metals in the cleavage of C(aryl)–O bonds have not been widely explored.[39] Interestingly, by the use of aryl 2-pyridyl ethers combined with rhodium or nickel catalysis, Chatani and Tobisu achieved the site-selective borylation of C(aryl)–O bonds, and the competitive transformation of *ortho*-C–H bonds did not occur (Scheme 1a).[43,44] While it was found that

Scheme 1. Transition-Metal-Catalyzed Regioselective Transformation of C(aryl)–O Bonds



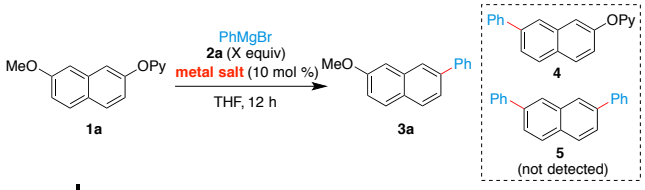
the reduction and amination of 2-pyridyl ethers can be promoted by nickel catalysis.[45,46] Along with our interest in probing the catalytic activity of group 6 metal chromium,[47–50] we questioned whether it's possible to adopt 2-pyridyl as a traceless auxiliary to assist chromium in cleavage of the phenolic C(aryl)–O bonds, while keeping other C(aryl)–O bonds in the reaction system intact to achieve the selective transformation of C–O bonds. Herein, we report a regioselective Kumada arylative cross-coupling of C(aryl)–O bonds that was catalyzed by chromium with a traceless activation strategy, the formation of fundamentally important biaryl motifs (Scheme 1b).[51–56] This reaction was promoted by a simple and low-cost chromium(II) chloride salt without the need of additional ligand or *ortho*-ligation auxiliary.

Based on our previous studies, the formation of low-valent chromium species by the reduction of $CrCl_2$ with arylmagnesium bromide can be considered.[36,56] To probe the reactivity

of chromium in the selective cleavage of C(aryl)–O bonds, 7-methoxy-containing naphthyl 2-pyridyl ether derivative (**1a**) was choose to treat with phenyl Grignard reagent (Table 1). We were pleased to find that the Kumada arylative coupling occurred, giving 2-methoxy-7-phenylnaphthalene (**3a**) in 60% yield by regioselective cleavage of the C(aryl)–OPy bond (entry 2). It was noteworthy that the C(aryl)–O bond at C7 position and *ortho*-C–H bond were retained in the reaction. Without chromium salt, the cross-coupling did not take place (entry 1). Other chromium salts such as $CrCl_3$ and $Cr(acac)_3$ led to inferior results in the transformation (entries 3 and 4). However, the coupling reaction did not proceed by use of $Cr(CO)_6$ (entry 5). Interestingly, other first-row transition metal salts of $FeCl_2$ and $NiCl_2$ also possess the capability to promote the Kumada coupling of C(aryl)–O bond, albeit giving low conversion (entries 6 and 7). However, Lewis acid of aluminium salt ($AlCl_3$) completely inhibited the coupling reaction (entry 8). Good result was obtained when increasing the amount of phenyl Grignard reagent to 3 equivalent at elevated temperature (entry 11).

Having the optimal reaction conditions in hand, the scope of aryl 2-pyridyl ether derivatives was examined. As shown in Scheme 2, the incorporation of oxygen-containing scaffolds such as alkoxy, phenoxy and siloxy groups into the scaffolds of aryl 2-pyridyl ether motifs did not affect the regioselectivity of Cr-catalyzed arylative cross-coupling. Only the C(aryl)–OPy bonds were cleaved and coupled with phenylmagnesium bromide to form the compounds **3b**–**3g** in preparatively useful yields. The coupling using 7-hydroxyl-substituted naphthyl 2-pyridyl ether occurred effectively, leading to the phenylated naphthol compound **3h** in 80% yield. Functionalities of alkenyl and amino groups can be well compatible with the reaction system (**3k** and **3l**). In addition to naphthyl 2-pyridyl ethers, the C(aryl)–O bond on the scaffold of polycyclic aromatic hydrocarbon coupled with phenyl Grignard smoothly, providing access to the coupling product **3m** in excellent yield. In addition, the imino group on aryl 2-pyridyl ether derivative can be tolerated by the reaction system, offering a methodology to the synthesis of terphenyl carbaldehyde compound after work up with acid (**3n**). The C–O bonds on the scaffolds of *N*-heterocycles were amenable to the coupling reaction, albeit forming the phenylated quinolone and pyridine derivatives in low yields (**3o** and **3p**).

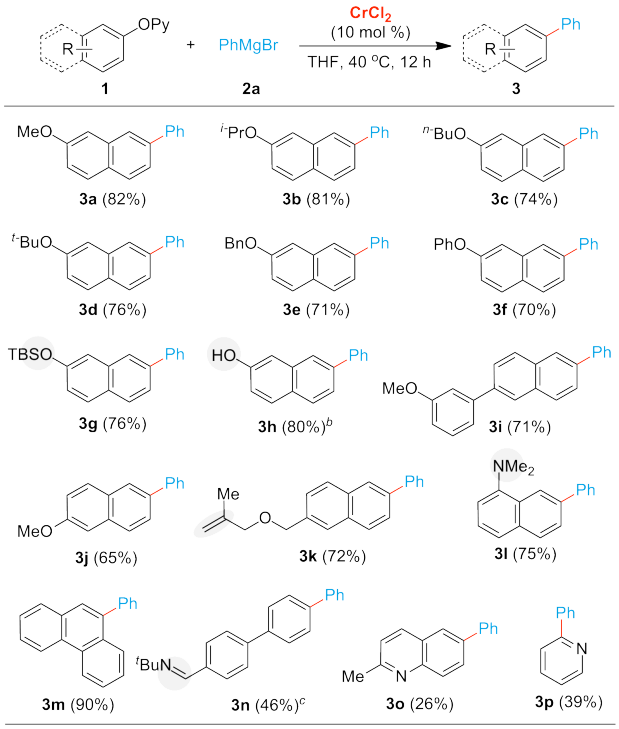
Table 1. Optimization Reaction Conditions[a]



entry	metal salt	2a (equiv)	T (°C)	yield (3a)
1	–	2	rt	nd[b]
2	$CrCl_2$	2	rt	60%
3	$CrCl_3$	2	rt	26%
4	$Cr(acac)_3$	2	rt	10%
5	$Cr(CO)_6$	2	rt	nd[b]
6	$FeCl_2$	2	rt	11%
7	$NiCl_2$	2	rt	5%
8	$AlCl_3$	2	rt	nd[b]
9	$MgCl_2$	2	rt	nd[b]
10	$CrCl_2$	2	40	71%
11	$CrCl_2$	3	40	82%
12	$CrCl_2$	4	40	80%

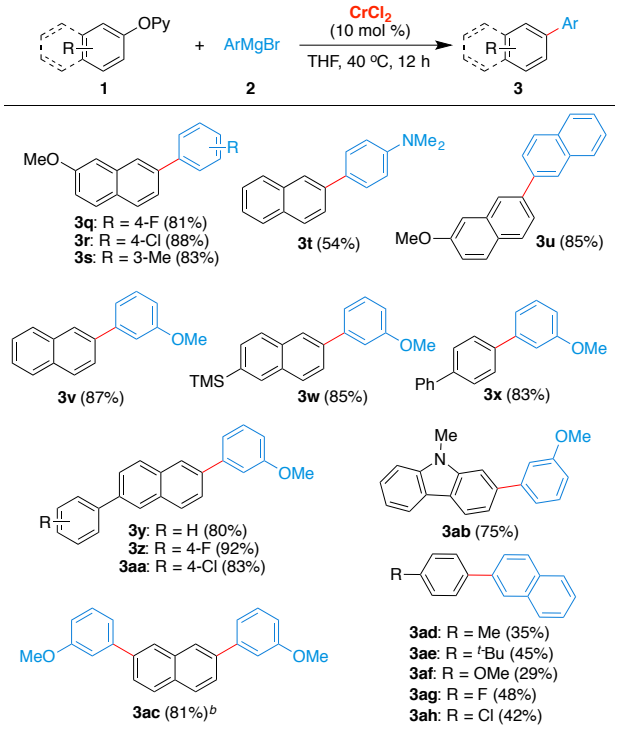
[a]Reactions were conducted on a 0.3 mmol scale. Isolated yields are given. [b]Not detected. The purities of metal salts: $CrCl_2$ (99.99%), $CrCl_3$ (99.99%), $Cr(acac)_3$ (97%) and $FeCl_2$ (98%).

Scheme 2. Chromium-Catalyzed Selective Kumada Arylative Coupling of C(aryl)–N Bonds in Aryl 2-Pyridyl Ethers[a]



[a]Conditions: **1** (0.3 mmol), **2a** (0.9 mmol), $CrCl_2$ (0.03 mmol), 40 °C, 12 h. Isolated yields were given. [b]PhMgBr (1.2 mmol). [c]Isolated as an aldehyde after aqueous workup.

Scheme 3. Chromium-Catalyzed Regioselective Cleavage of C(aryl)–O Bonds[a]



[a]Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), $CrCl_2$ (0.03 mmol), 40 °C, 12 h. Isolated yields are given. [b]2,7-Bis(pyridin-2-yloxy)naphthalene was used.

The Kumada coupling using phenyl Grignard reagents that contain substituents such as alkyl, fluoride, chloride and amino occurred smoothly, providing access to the arylated compounds **3q**–**3t** in moderate to good yields (Scheme 3). 2-Naphthylmagnesium bromide can be used as partner to regioselective couple with C(aryl)–O bond of aryl 2-pyridyl ether (**3u**). Notably, the incorporation of methoxy group into the motif of phenylmagnesium bromide did not affect the selectivity of C(aryl)–O bond in aryl 2-pyridyl ethers, leading to the desired products **3v**–**3aa** with retaining the C–OMe bond. Moreover, this Cr-catalyzed coupling strategy can be used to construct 2-(3-methoxyphenyl)-9-methyl-9*H*-carbazole motif at ambient temperature (**3ab**). Interestingly, the two C(aryl)–OPy bonds on the scaffold of naphthalene were synchronously cleaved and coupled with aryl Grignard to form bis-functionalized naphthalene derivative **3ac** in 81% yield. Notably, phenol-derived 2-pyridyl ethers also provided the desired products **3ad-3ah** in relatively low yields.

It was found that the C(aryl)–OPy bond in the scaffold of biologically active estrone derivative was regioselective phenylated, allowing for retaining other C–O bonds in the resulting product (Figure 1). Notably, the two different C(aryl)–O bonds in the motif of naphthalene were sequential functionalized by coupling with arylmagnesium bromide with Cr and Ni catalysis, respectively. It provides a route to the synthesis of conjugated diaryl-bearing naphthalene derivative **6**.[57] Moreover, the chromium-catalyzed reaction between C(aryl)–OPy with phenylmagnesium bromide is scalable, and can be performed on gram-scale without loss of the efficiency (Figure 1).

Having these results with chromium catalysis, the preliminary mechanistic studies were next performed. It was noted that the Kumada coupling with naphthyl 3-pyridyl ether cannot proceed with Cr catalysis (Scheme 4, eq 1). Meanwhile, the reaction by the use of (naphthalen-2-yloxy)methylpyridine (**8**) did not give the coupling product **3ai** with recovery of starting material (Scheme 4, eq 2). These indicate that a ligation of *N*,*O* scaffolds with metal can be considered for achieving the Cr-catalyzed coupling of C(aryl)–O bond. To probe the possibility that the in-situ formed reactive Cr species is responsible for the Kumada coupling, $CrCl_2$ was initially treated with PhMgBr, and then naphthyl 2-pyridyl ether (**1b**) with another aryl Grignard of (4-methoxyphenyl)magnesium bromide (**2b**) was putted into the reaction system. When the use of 0.1 equiv of $CrCl_2$ and

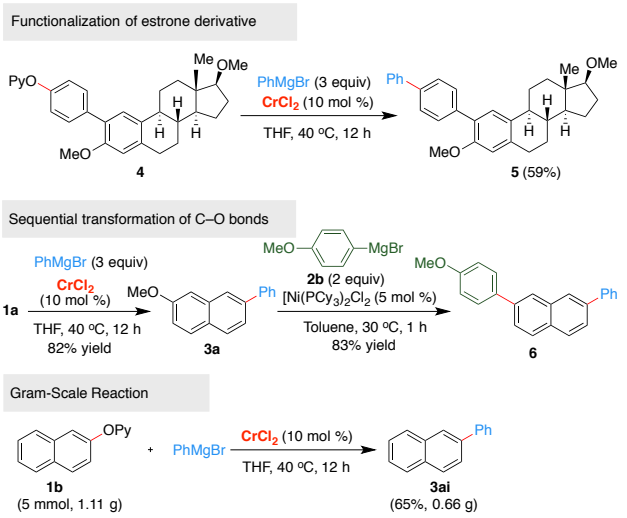
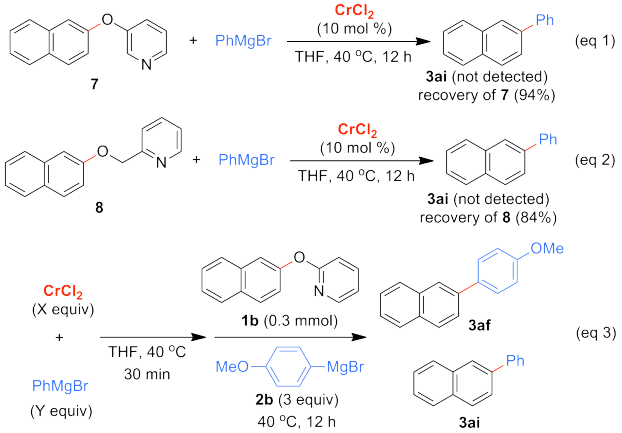


Figure 1. The application of the Cr-catalyzed regioselective cross-coupling of C(aryl)–O bonds.

Scheme 4. Preliminary Mechanistic Studies



X	Y	Yield (**3af**)[a]	Yield (**3ai**)[a]
0.1	0.2	78%	nd[b]
0.1	0.3	76%	trace
0.1	0.5	70%	9%
0.5	1.0	71%	trace

[a]Isolated yield. [b]Not detected by GC/MS analysis

0.2 equiv of PhMgBr, the related coupling product of C(aryl)–O bond with phenyl Grignard reagent was not detected (Scheme 4, eq 3). Interestingly, increasing the amount of phenyl Grignard was able to form its coupling product with C(aryl)–O bond. Phenyl Grignard reagent might be initially consumed by the reduction of the $CrCl_2$ salt in forming reactive low-valent Cr species in situ, which could promote the cross-coupling of C(aryl)–O bond.[58]

In summary, we have developed a mild and regioselective chromium catalysis for the arylative Kumada cross-coupling of C(aryl)–O bonds. This reaction was enabled by the use of a low-cost chromium(II) chloride as the precatalyst, regioselective providing access to fundamentally valuable biaryl motifs at ambient temperature. A reactive Cr species that was formed in-situ by reaction of $CrCl_2$ with aryl Grignard is likely to responsibility for the cleavage of C(aryl)–O bond under the ligation assistance of 2-pyridyl. This reaction presents a Cr-catalyzed traceless activation strategy for Kumada coupling in tackling the regioselectivity issue, and shows that Cr possesses good reactivity in the catalytic cleavage of unactivated C–O bonds, which is usually dominated by nickel catalysis. Studies on the application of cost-effective chromium catalysis in synthetic chemistry are under way.

EXPERIMENTAL SECTION

General Methods. All reactions dealing with air- or moisture-seneitive compounds were carried out in a flame-dried, scaled schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel chromatography was performed on silica gel 60N (spherical and neutral, 140-325 mesh) as described by Still. NMR spectra were measured on a BrukerAV-400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas-beta and other commercial suppliers and used as received. Solvents were dried over sodium (for THF and ether) by refluxing for overnight and freshly distilled prior to use. Metallic magnesium turnings (>99.99%) were purchased from Adamas-beta. $CrCl_2$ (99.99%), $CrCl_3$ (99.99%), $Cr(acac)_3$ (97%), $AlCl_3$ (99.9%), $MgCl_2$ (99.9%), $NiCl_2$ and $FeCl_2$ (>98%) were purchased from Aldrich Inc. and used as received.

General Procedure for the Preparation of Aryl 2-Pyridyl Ethers.[43] An oven-dried flask was charged with phenol (10 mmol), K_3PO_4 (4.3 g, 20 mmol), CuI (0.19 g, 1 mmol), and picolinic acid (0.25 g, 2 mmol). After the flask was evacuated and back-filled with N_2, DMSO (20 mL) and 2-bromopyridine (1.9 g, 12 mmol) were added, and then the mixture was heated at 100 °C for 24 h. EtOAc (10 mL) and H_2O (10 mL) were added and the mixture was filtered through a Celite pad. The organic layer was separated and the aqueous layer was extracted twice with EtOAc (20 mL). The combined organic layers were washed with H_2O (20 mL), dried over anhydrous Na_2SO_4, and filtered through a pad of silica gel. The filtrate was concentrated and the residue was purified by column chromatography using PE/EA as eluent.

2-((7-Methoxynaphthalen-2-yl)oxy)pyridine ***(1a).*** white solid (2.3 g, 92%); TLC, R_f = 0.25 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.22 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.72–7.68 (m, 2H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.12–7.08 (m, 2H), 7.03–6.70 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 158.1, 152.5, 147.8, 139.4, 135.6, 129.4, 129.3, 126.4, 118.8, 118.5, 118.0, 116.5, 111.6, 105.5, 55.3.

2-((7-Isopropoxynaphthalen-2-yl)oxy)pyridine ***(1b).*** white solid (2.5 g, 90%); TLC, R_f = 0.23 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.22 (m, 1H), 7.79–7.67 (m, 3H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09–7.07 (m, 2H), 7.01–7.00 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.71–4.65 (m, 1H), 1.39 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 156.3, 152.4, 147.9, 139.4, 135.6, 129.3, 129.28, 126.3, 119.0, 118.7, 118.5, 116.4, 111.6, 69.8, 22.0.

2-((7-Butoxynaphthalen-2-yl)oxy)pyridine ***(1c).*** white solid (2.7 g, 91%); TLC, R_f = 0.20 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.22 (m, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.74–7.67 (m, 2H), 7.45 (s, 1H), 7.16–7.07 (m, 3H), 7.02–7.00 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.05 (t, *J* = 7.2 Hz, 2H), 1.87–1.80 (m, 2H), 1.59–1.49 (m, 2H), 1.03–0.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 157.7, 152.5, 147.9, 139.4, 135.7, 129.4, 129.2, 118.7, 118.5, 118.3, 116.5, 111.6, 106.3, 67.7, 31.3, 19.3, 13.9.

2-((7-(Tert-butoxy)naphthalen-2-yl)oxy)pyridine ***(1d).*** white solid (2.6 g, 90%); TLC, R_f = 0.30 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.21 (m, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.75–7.68 (m, 2H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.02–6.96 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 153.8, 152.1, 147.8, 139.4, 135.1, 129.2, 128.5, 127.8, 124.2, 119.9, 119.3, 118.5, 116.8, 111.6, 79.0, 28.9.

2-((7-(Benzyloxy)naphthalen-2-yl)oxy)pyridine ***(1e).*** white solid (3.1 g, 94%); TLC, R_f = 0.33 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.23 (m, 1H), 7.82–7.75 (m, 2H), 7.72–7.68 (m, 1H), 7.50–7.47 (m, 3H), 7.44–7.40 (m, 2H), 7.37–7.35 (m, 1H), 7.22–7.16 (m, 3H), 7.03–7.00 (m, 1H), 6.95 (dd, *J* = 8.8, 0.8 Hz, 1H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 157.3, 152.5, 147.8, 139.4, 136.8, 135.5, 129.4, 129.3, 128.6, 127.5, 126.5, 118.9, 118.5, 118.3, 116.5, 111.6, 106.9, 70.0.

2-((7-Phenoxynaphthalen-2-yl)oxy)pyridine ***(1f).*** white solid (3.0 g, 95%); TLC, R_f = 0.30 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.20 (m, 1H), 7.82 (t, *J* = 8.0 Hz, 2H), 7.73–7.68 (m, 1H), 7.43–7.35 (m, 3H), 7.24–7.21 (m, 3H), 7.16–7.13 (m, 1H), 7.09–7.07 (m, 2H), 7.03–7.00 (m, 1H), 6.96 (dd, *J* = 8.4, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 157.0, 155.8, 152.6, 147.8, 139.5, 135.4, 129.8, 129.7, 129.5, 127.6, 123.5, 120.1, 119.2, 119.1, 118.6, 116.7, 113.6, 111.8.

2-((7-((Tert-butyldimethylsilyl)oxy)naphthalen-2-yl)oxy)pyridine ***(1g).*** brown oil (3.1 g, 89%); TLC, R_f = 0.26 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.75–7.67 (m, 2H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.19–7.16 (m, 2H), 7.05 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.02–6.96 (m, 2H), 1.05 (s, 9H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 154.0, 152.3, 147.8, 139.3, 135.6, 129.3, 129.2, 126.7, 121.3, 119.1, 118.4, 116.2, 114.6, 111.6, 25.7, 18.2, –4.4.

7-(Pyridin-2-yloxy)naphthalen-2-ol ***(1h).*** white solid (2.0 g, 85%); TLC, R_f = 0.30 (PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 8.15 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.87–7.75 (m, 3H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.13–7.02 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.9, 152.1, 147.5, 140.1, 135.6, 129.3, 125.1, 119.0, 118.1, 117.9, 115.6, 111.5, 108.4.

2-((6-(3-Methoxyphenyl)naphthalen-2-yl)oxy)pyridine ***(1i).*** white solid (2.9 g, 88%); TLC, R_f = 0.35 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.23 (m, 1H), 8.06 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.74–7.70 (m, 2H), 7.61 (s, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.36–7.31 (m, 2H), 7.27–7.26 (m, 1H), 7.05–6.94 (m, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 160.0, 152.0, 147.8, 142.5, 139.5, 137.8, 133.5, 131.1, 129.8, 127.9, 126.1, 125.7, 121.8, 119.8, 118.6, 117.2, 113.1, 112.7, 111.6, 55.3.

2-((6-Methoxynaphthalen-2-yl)oxy)pyridine ***(1j).*** white solid (2.4 g, 96%); TLC, R_f = 0.22 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.67–7.66 (m, 2H), 7.53 (s, 1H), 7.30–7.27 (m, 1H), 7.18–7.16 (m, 2H), 7.01–6.98 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 157.2, 150.0, 147.7, 139.3, 132.0, 129.5, 128.8, 128.3, 121.8, 119.2, 118.3, 117.6, 111.3, 105.9, 55.3.

2-((6-(((2-Methylallyl)oxy)methyl)naphthalen-2-yl)oxy)pyridine ***(1k).*** white solid (2.6 g, 87%); TLC, R_f = 0.34 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.77 (t, *J* = 8.8 Hz, 2H), 7.70–7.68 (m, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.03–7.00 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 4.66 (s, 2H), 3.98 (s, 2H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 151.8, 147.7, 142.1, 139.4, 135.2, 133.7, 130.7, 129.5, 127.6, 126.3, 126.2, 121.5, 118.5, 117.3, 112.3, 111.6, 73.9, 71.8, 19.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_2$ 306.1489; Found 306.1483.

N,N-Dimethyl-7-(pyridin-2-yloxy)naphthalen-1-amine ***(1l).*** white solid (2.3 g, 88%); TLC, R_f = 0.27 (PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.21 (m, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.69–7.66 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.32–7.29 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.01–6.93 (m, 2H), 2.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 151.4, 150.6, 147.8, 139.3, 132.3, 130.0, 129.9, 125.1, 122.7, 121.1, 118.4, 114.5, 111.4, 45.1.

2-(Phenanthren-9-yloxy)pyridine ***(1m).*** white solid (2.4 g, 90%); TLC, R_f = 0.30 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.24–8.22 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72–7.68 (m, 2H), 7.66–7.58 (m, 3H), 7.51 (s, 1H), 7.03–7.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 148.5, 148.0, 139.5, 132.0, 131.8, 128.6, 128.2, 127.3, 127.1, 126.9, 126.7, 126.0, 122.9, 122.8, 122.6, 118.6, 116.2, 111.1.

2-Methyl-N-((4'-(pyridin-2-yloxy)-[1,1'-biphenyl]-4-yl)methylene)propan-2-amine ***(1n).*** white solid (3.2 g, 98%); TLC, R_f = 0.30 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.23–8.22 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.73–7.69 (m, 1H), 7.67–7.62 (m, 4H), 7.25–7.21 (m, 2H), 7.03–6.70 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 154.7, 153.8, 147.7, 142.2, 139.5, 137.0, 136.0, 128.4, 128.3, 127.1, 125.5, 118.5, 111.7, 57.3, 29.7.

2-Methyl-6-(pyridin-2-yloxy)quinolone ***(1o).*** white solid (1.9 g, 80%); TLC, R_f = 0.25 (PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–9.16 (m, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.73–7.69 (m, 1H), 7.49–7.47 (m, 2H), 7.27–7.25 (m, 1H), 7.03–7.00 (m, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 158.2, 151.4, 147.7, 145.4, 139.6, 135.7, 130.3, 127.1, 124.7, 122.3, 118.8, 116.9, 111.8, 25.2.

2,2'-Oxydipyridine ***(known compounds 1, known 1p).***[59] slight oil (1.2 g, 70%); TLC, R_f = 0.35 (PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 2.8, 0.8 Hz, 2H), 7.77–7.72 (m, 2H), 7.11–7.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.0, 139.5, 119.9, 113.9.

2-(Naphthalen-2-yloxy)pyridine ***(1t).*** white solid (2.1 g, 96%); TLC, R_f = 0.33 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.22 (m, 1H), 7.91–7.85 (m, 2H), 7.81–7.79 (m, 1H), 7.73–7.68 (m, 1H), 7.60–7.58 (m, 1H), 7.51–7.47 (m, 2H), 7.35–7.30 (m, 1H), 7.03–6.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 151.8, 147.8, 139.4, 134.3, 131.0, 129.6, 127.5, 126.4, 125.2, 121.4, 118.6, 117.4, 111.6.

2-((6-(Trimethylsilyl)naphthalen-2-yl)oxy)pyridine ***(1w).*** white solid (2.7 g, 91%); TLC, R_f = 0.35 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.22 (m, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.89–7.87 (m, 1H), 7.82–7.76 (m, 1H), 7.72–7.67 (m, 1H), 7.62–7.59 (m, 1H), 7.55 (s, 1H), 7.33–7.30 (m, 1H), 7.03–7.00 (m, 1H), 6.97–6.94 (m, 1H), 0.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 152.2, 147.9, 139.4, 137.1, 134.4, 133.6, 130.5, 130.4, 129.8, 126.5, 121.3, 118.6, 117.2, 111.6, –1.1.

2-([1,1'-Biphenyl]-4-yloxy)pyridine ***(1x).*** white solid (2.3 g, 94%); TLC, R_f = 0.23 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.24 (m, 1H), 7.73–7.69 (m, 1H), 7.65–7.60 (m, 4H), 7.47–7.43 (m, 2H), 7.37–7.34 (m, 1H), 7.27–7.22 (m, 2H), 7.03–7.00 (m, 1H), 6.96 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 153.6, 147.7, 140.6, 139.4, 137.7, 128.7, 128.4, 127.1, 127.0, 121.4, 118.5, 111.7.

2-((6-Phenylnaphthalen-2-yl)oxy)pyridine ***(1y).*** white solid (2.7 g, 92%); TLC, R_f = 0.40 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.25 (m, 1H), 8.07 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.79–7.70 (m, 4H), 7.62 (s, 1H), 7.53–7.49 (m, 2H), 7.42–7.35 (m, 2H), 7.05–6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 152.0, 147.8, 141.0, 139.4, 137.9, 133.4, 131.2, 129.9, 128.8, 127.3, 126.1, 125.6, 121.8, 118.6, 117.2, 111.6.

2-((6-(4-Fluorophenyl)naphthalen-2-yl)oxy)pyridine ***(1z).*** white solid (2.8 g, 89%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.0 Hz, 1H), 8.00 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.74–7.65 (m, 4H), 7.60 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.05–6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.3 (d,

J = 245.0 Hz), 152.0, 147.8, 139.5, 137.1 (d, *J* = 3.0 Hz), 136.9, 133.3, 131.1, 129.8, 128.8 (d, *J* = 8.0 Hz), 128.0, 125.9, 125.5, 122.0, 118.6, 117.2, 115.6 (d, *J* = 21.0 Hz), 111.7.

2-((6-(4-Chlorophenyl)naphthalen-2-yl)oxy)pyridine ***(1aa).*** white solid (3.0 g, 90%); TLC, R_f = 0.35 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.23 (m, 1H), 8.01 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.74–7.68 (m, 2H), 7.65–7.60 (m, 3H), 7.47–7.44 (m, 2H), 7.37–7.34 (m, 1H), 7.05–6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 152.1, 147.8, 139.4, 136.6, 133.5, 133.4, 131.1, 129.0, 128.5, 128.1, 125.7, 125.6, 122.0, 118.7, 117.2, 111.7.

9-Methyl-2-(pyridin-2-yloxy)-9H-carbazole ***(1ab).*** white solid (2.2 g, 82%); TLC, R_f = 0.30 (PE/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.25 (m, 1H), 8.11–8.03 (m, 2H), 7.72–7.68 (m, 1H), 7.47–7.45 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.28–7.24 (m, 1H), 7.21–7.16 (m, 1H), 7.06–7.00 (m, 2H), 6.95 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.8, 147.9, 141.4, 139.3, 125.2, 122.6, 121.1, 119.9, 119.89, 119.1, 118.2, 112.8, 111.3, 108.3, 101.4, 29.1.

2,7-Bis(pyridin-2-yloxy)naphthalene ***(1ac).*** white solid (2.5 g, 80%); TLC, R_f = 0.33 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.21 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.70–7.67 (m, 2H), 7.51 (s, 2H), 7.28–7.25 (m, 2H), 7.02–6.99 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 152.5, 147.8, 139.5, 135.3, 129.6, 128.5, 120.7, 118.7, 117.1, 111.6.

2-(p-tolyloxy)pyridine ***(1ad).*** colorless oil (1.7 g, 91%); TLC, R_f = 0.32 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.68–7.64 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.98–6.95 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 151.7, 147.7, 139.2, 134.2, 130.1, 121.0, 118.1, 111.2, 20.8.

2-(4-(Tert-butyl)phenoxy)pyridine ***(1ae).*** white solid (2.0 g, 90%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.20 (m, 1H), 7.69–7.64 (m, 1H), 7.42–7.39 (m, 2H), 7.09–7.05 (m, 2H), 6.99–6.96 (m, 1H), 6.88 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 151.7, 147.8, 147.3, 139.3, 126.6, 120.5, 118.2, 111.4, 34.4, 31.5.

2-(4-Methoxyphenoxy)pyridine ***(1af).*** colorless oil (1.8 g, 92%); TLC, R_f = 0.32 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.18 (m, 1H), 7.67–7.63 (m, 1H), 7.10–7.06 (m, 2H), 6.97–6.91 (m, 3H), 6.86 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 156.5, 147.7, 147.4, 139.2, 122.3, 118.0, 114.7, 111.0, 55.5.

2-(4-Fluorophenoxy)pyridine ***(1ag)****.* colorless oil (1.7 g, 93%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.17 (m, 1H), 7.71–7.66 (m, 1H), 7.12–7.06 (m, 4H), 7.00–6.97 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 158.3 (d, *J* = 242.5 Hz), 149.8 (d, *J* = 2.9 Hz), 147.6, 139.4, 122.7 (d, *J* = 8.6 Hz), 118.5, 116.1 (d, *J* = 24.0 Hz), 111.4.

2-(4-chlorophenoxy)pyridine ***(1ah).*** colorless oil (1.9 g, 92%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.72–7.67 (m, 1H), 7.36 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.11-7.08 (m, 2H), 7.02-6.99 (m, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3, 152.6, 147.6, 139.5, 129.8, 129.6, 122.5, 118.7, 111.6.

2-(4-((8R,9S,13S,14S,17S)-3,17-Dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)phenoxy)pyridine ***(4).*** White solid (1.48 g, 80%); TLC, R_f = 0.34 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 4.4 Hz 1H), 7.71–7.67 (m, 1H), 7.57–7.54 (m, 2H), 7.28 (s, 1H), 7.16 (m, 2H), 6.99 (t, *J* = 6.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 3.80 (s, 3H), 3.40 (s, 3H), 3.32 (t, *J* = 8.0 Hz, 1H), 2.91 (d, *J* = 5.2 Hz, 2H), 2.35–2.23 (m, 2H), 2.06 (d, *J* = 10.8 Hz, 2H), 1.92 (d, *J* = 9.6 Hz, 1H), 1.71 (d, *J* = 9.6 Hz, 1H), 1.57–1.48 (m, 3H), 1.46–1.36 (m, 3H), 1.28–1.21 (m, 1H), 0.82 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 154.3, 152.9, 147.8, 139.3, 137.1, 135.2, 132.6, 130.8, 128.1, 127.4, 120.5, 118.4, 111.5, 90.7, 57.9, 55.5, 50.2, 43.9, 43.2, 38.6, 38.0, 29.8, 27.8, 27.3, 26.5, 23.0, 11.5; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{31}H_{36}NO_3$ 470.2690; Found 470.2683.

General Procedure for Cr-Catalyzed Regioselective Arylative Kumada Cross-Couplings of Aryl 2-Pyridyl Ethers. In a dried Schlenk tube were placed aryl 2-pyridyl ether (0.3 mmol) and $CrCl_2$ (3.7 mg, 0.03 mmol), then a freshly distilled THF (0.5 ml) was added by a syringe under atmosphere of nitrogen. After stirring at room temperature for 5 min, aromatic Grignard reagent (0.9 ml, 1.0 M in THF, 0.9 mmol) was dropwise added, and the mixture was stirred at 40 °C for 12 h. After quenched with saturated aqueous solution of NH_4Cl (1 mL), the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired coupling product.

2-Methoxy-7-phenylnaphthalene ***(known compounds 2, known 3a).***[60] white solid (58 mg, 82%); TLC, R_f = 0.40 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.78–7.72 (m, 3H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 2.4 Hz, 1H) 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.3, 138.9, 134.9, 129.1, 128.1, 127.4, 127.3, 124.6, 123.4, 118.6, 105.8, 55.3; GC-MS (EI): $[M^+]$ Calcd for $C_{17}H_{14}O$ 234.10; Found 234.11.

2-Isopropoxy-7-phenylnaphthalene ***(3b).*** slight yellow oil (64 mg, 81%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 0.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.80–7.74 (m, 3H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53–7.49 (m, 2H), 7.43–7.39 (m, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.78–4.72 (m, 1H), 1.45 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 141.1, 138.9, 134.9, 129.0, 128.8, 128.0, 127.4, 127.2, 124.5, 123.2, 119.8, 108.6, 69.3, 21.9; IR(neat) 2974, 2927, 1625, 1606, 1458, 1363, 1207, 1116, 977, 841, 746, 693 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}O$ 263.1430; Found 263.1436.

2-Butoxy-7-phenylnaphthalene ***(3c).*** slight yellow oil (62 mg, 74%); TLC, R_f = 0.38 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.2 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.79–7.74 (m, 3H), 7.61 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53–7.49 (m, 2H), 7.43–7.38 (m, 1H), 7.22–7.18 (m, 2H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.92–1.83 (m, 2H), 1.64–1.53 (m, 2H), 1.03 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 141.3, 139.0, 134.9, 129.0, 128.8, 128.1, 128.0, 127.4, 127.2, 124.7, 123.2, 119.1, 106.8, 67.7, 31.3, 19.3, 13.9; IR(neat) 2955, 2870, 1626, 1459, 1211, 1175, 1123, 1004, 896, 840, 753, 698 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O$ 277.1587; Found 277.1586.

2-(Tert-butoxy)-7-phenylnaphthalene ***(3d).*** slight yellow oil (63 mg, 76%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.2 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.77–7.75 (m, 2H), 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.53–7.50 (m, 3H), 7.43–7.39 (m, 1H), 7.22 (dd, *J* = 8.8, 2.0 Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.1, 138.7, 134.4, 129.4, 128.8, 128.3, 128.0, 127.4, 127.3, 125.1, 125.05, 124.3, 120.0, 79.0, 28.9; IR(neat) 2981, 1627, 1457, 1363, 1158, 1142, 963, 906, 843, 752, 695 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O$ 277.1587; Found 277.1583.

2-(Benzyloxy)-7-phenylnaphthalene ***(3e).*** white solid (66 mg, 71%); m.p. = 125–127 °C; TLC, R_f = 0.30 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.72–7.69 (m, 2H), 7.61–7.58 (m, 1H), 7.50–7.42 (m, 4H), 7.41–7.34 (m, 4H), 7.27–7.21 (m, 2H), 5.18 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 141.2, 139.1, 136.8, 134.7, 129.2, 128.8, 128.6, 128.2, 128.1, 128.0, 127.5, 127.4, 127.3, 124.8, 123.5, 119.1, 107.5, 70.0; IR(neat) 2924, 1625, 1454, 1373, 1207, 1173, 1127, 1007, 885, 755, 697 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1426.

2-Phenoxy-7-phenylnaphthalene ***(3f).*** white solid (62 mg, 70%); m.p. = 105–108 °C; TLC, R_f = 0.33 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 3H), 7.74–7.69 (m, 3H), 7.52–7.48 (m, 2H), 7.43–7.39 (m, 4H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.20–7.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 155.6, 140.9, 139.2, 134.5, 129.8, 129.6, 129.3, 128.8, 128.2, 127.4, 127.38, 125.0, 124.4, 123.5, 120.0, 119.2, 114.2; IR(neat) 2923, 2852, 1585, 1486, 1218, 1166, 964, 910, 848, 757, 696, 689 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}O$ 297.1274; Found 297.1279.

Tert-butyldimethyl((7-phenylnaphthalen-2-yl)oxy)silane ***(3g).*** slight yellow oil (76 mg, 76%); TLC, R_f = 0.33 (PE/EtOAc = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 1.2 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.79–7.74 (m, 3H), 7.63 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53–7.49 (m, 2H), 7.43–7.39 (m, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.12 (dd, *J* = 8.8, 1.6 Hz, 1H), 1.09 (s, 9H), 0.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 141.2, 138.8, 134.9, 129.1, 128.8, 128.4, 128.1, 127.4, 127.3, 124.6, 123.4, 122.2, 115.0, 25.4, 18.3, –4.3; IR(neat): 2928, 2857, 1629, 1459, 1368, 1240, 1169, 971, 836, 763, 752, 696 cm^{-1}; HRMS(ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}OSi$ 335.1826; Found 335.1828.

7-Phenylnaphthalen-2-ol ***(known compounds 3, known 3h).***[61] white solid (53 mg, 80%); TLC, R_f = 0.30 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.59 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.2, 139.2, 134.9, 129.7, 128.8, 128.1, 127.4, 127.36, 124.3, 123.4, 117.7, 109.8; GC-MS (EI): $[M^+]$ Calcd for $C_{16}H_{12}O$ 220.09; Found 220.08.

2-(3-Methoxyphenyl)-6-phenylnaphthalene ***(3i).*** white solid (66 mg, 71%); m.p. = 113–115 °C; TLC, R_f = 0.34 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.97 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.81–7.75 (m, 4H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.45–7.39 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.4, 141.0, 138.6, 138.4, 132.9, 132.8, 129.9, 128.9, 128.7, 128.67, 127.4, 126.0, 125.6, 125.5, 119.9, 113.1, 112.8, 55.3; IR(neat) 2955, 2835, 1576, 1485, 1433, 1296, 1205, 1029, 871, 789, 755,695 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1435.

2-Methoxy-6-phenylnaphthalene ***(known compounds 4, known 3j).***[62] white solid (46 mg, 65%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.6 Hz, 1H), 7.84–7.80 (m, 2H), 7.75–7.72 (m, 3H), 7.51–7.48 (m, 2H), 7.40–7.36 (m, 1H), 7.21–7.18 (m, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 141.2, 136.3, 133.7, 129.6, 129.1, 128.8, 127.2, 127.19, 127.0, 126.0, 125.6, 119.1, 105.5, 54.8; GC-MS (EI): $[M^+]$ Calcd for $C_{17}H_{14}O$ 234.10; Found 234.12.

2-(((2-Methylallyl)oxy)methyl)-6-phenylnaphthalene ***(3k).*** slight yellow oil (63 mg, 72%); TLC, R_f = 0.34 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.93–7.90 (m, 2H), 7.84 (s, 1H), 7.81–7.73 (m, 3H), 7.54–7.49 (m, 3H), 7.38 (t, *J* = 7.2 Hz, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 4.68 (d, *J* = 5.2 Hz, 2H), 4.01 (s, 2H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 141.0, 138.5, 136.0, 133.2, 132.4, 128.8, 128.4, 128.36, 127.4, 127.3, 126.2, 126.1, 125.8, 125.6, 112.4, 74.1, 71.9, 19.6; IR(neat) 2697, 2913, 2849, 1657, 1446, 1353, 1138, 1123, 889, 825, 752, 691 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{20}ONa$ 311.1406; Found 311.1404.

N,N-Dimethyl-7-phenylnaphthalen-1-amine ***(3l).*** white solid (56 mg, 75%). m.p. = 77–79 °C; TLC, R_f = 0.28 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (t, *J* = 0.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.82–7.76 (m, 3H), 7.64–7.53 (m, 3H), 7.48–7.40 (m, 2H), 7.17–7.15 (m, 1H), 2.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 141.6, 137.8, 133.9, 128.9, 128.86, 128.8, 127.5, 127.1, 125.9, 125.3, 122.5, 122.2, 114.3, 45.2; IR(neat) 2942, 2823, 1596, 1493, 1449, 1373, 1179, 1037, 932, 838, 751, 694 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}N$ 248.1434; Found 248.1432.

9-Phenylphenanthrene ***(known compounds 5, known 3m).***[63] white solid (69 mg, 90%); TLC, R_f = 0.36 (PE/EtOAc = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.4 Hz, 1H), 8.81 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 1H), 8.01–7.99 (m, 1H), 7.83–7.82 (m, 1H), 7.79–7.58 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.7, 131.5, 131.1, 130.5, 130.0, 129.9, 128.6, 128.3, 127.5, 127.3, 126.9, 126.8, 126.5, 126.4, 126.39, 122.9, 122.5; GC-MS (EI): $[M^+]$ Calcd for $C_{20}H_{14}$ 254.11; Found 254.10.

[1,1':4',1''-Terphenyl]-4-carbaldehyde ***(3n).*** white solid (36 mg, 46%); m.p. = 201–203 °C; TLC, R_f = 0.25 (PE/EtOAc = 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.73 (s, 4H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 146.6, 141.3, 140.3, 138.5, 135.2, 130.3, 128.9, 127.7, 127.69, 127.6, 127.5, 127.0; IR(neat) 2833, 2741, 1700, 1600, 1482, 1204, 1172, 1003, 818, 724, 686 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{14}ONa$ 281.0937; Found 281.0937.

2-Methyl-6-phenylquinoline ***(known compounds 6, known 3o).***[64] yellow solid (17 mg, 26%); TLC, R_f = 0.34 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.08 (m, 2H), 7.96–7.94 (m, 2H), 7.73–7.71 (m, 2H), 7.51–7.47 (m, 2H), 7.41–7.37 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 147.3, 140.5, 138.4, 136.3, 129.1, 129.0, 128.9, 127.5, 127.4, 126.6, 125.2, 122.4, 25.5; GC-MS (EI): $[M^+]$ Calcd for $C_{16}H_{13}N$ 219.10; Found 219.11.

2-Phenylpyridine ***(known compounds 7, known 3p).***[65] slight yellow oil (18 mg, 39%); TLC, R_f = 0.30 (PE/EtOAc = 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71–8.69 (m, 1H), 8.01–7.98 (m, 2H), 7.75–7.72 (m, 2H), 7.50–7.46 (m, 2H), 7.44–7.40 (m, 1H), 7.24–7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.7, 139.3, 136.7, 128.9, 128.7, 126.9, 122.1, 120.5; GC-MS (EI): [M^+] Calcd for $C_{11}H_9N$ 155.07; Found 155.10.

2-(4-Fluorophenyl)-7-methoxynaphthalene ***(3q).*** slight yellow solid (61 mg, 81%); m.p. = 97–98 °C; TLC, R_f = 0.28 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70–7.65 (m, 2H), 7.55 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.21–7.16 (m, 4H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 245.0 Hz), 157.9, 138.0, 137.3 (d, *J* = 3.0 Hz), 134.8, 129.1, 128.8 (d, *J* = 8.0 Hz), 128.2, 128.0, 124.5, 123.1, 118.8, 115.5 (d, *J* = 21.0 Hz), 105.9, 55.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ –115.6; IR(neat) 2966, 2933, 1629, 1572, 1504, 1423, 1263, 1172, 1030, 897, 815, 734 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{17}H_{13}FONa$ 275.0843; Found 275.0847.

2-(4-Chlorophenyl)-7-methoxynaphthalene ***(3r).*** slight yellow solid (71 mg, 88%); m.p. = 69–71 °C; TLC, R_f = 0.28 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.19–7.15 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 139.7, 137.8, 134.8, 133.4, 129.1, 128.9, 128.6, 128.3, 128.2, 124.7, 123.0, 119.0, 106.0, 55.3; IR(neat) 2966, 1627, 1515, 1492, 1420, 1241, 1171, 1094, 1027, 834, 778, 758 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{17}H_{14}ClO$ 269.0728; Found 269.0728.

2-Methoxy-7-(m-tolyl)naphthalene ***(3s).*** slight oil (62 mg, 83% yield); TLC, R_f = 0.26 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.4 Hz, 1H), 7.93–7.90 (m, 1H), 7.87–7.83 (m, 1H), 7.72–7.65 (m, 3H), 7.50–7.46 (m, 1H), 7.33–7.27 (m, 3H), 4.01 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.2, 139.1, 138.3, 134.8, 129.1, 128.7, 128.1, 128.0, 124.6, 124.5, 123.3, 118.6, 105.9, 55.1, 21.5; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{18}H_{16}ONa$ 271.1093; Found 271.1089.

N,N-Dimethyl-4-(naphthalen-2-yl)aniline ***(known compounds 8, known 3t).***[66] white solid (40 mg, 54%); TLC, R_f = 0.31 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.2 Hz, 1H), 7.90–7.84 (m, 3H), 7.75 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.69–7.65 (m, 2H), 7.51–7.43 (m, 2H), 6.88–6.86 (m, 2H), 3.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 138.5, 133.9, 132.0, 128.9, 128.2, 127.93, 127.9, 127.6, 126.0, 125.3, 125.2, 124.2, 112.8, 40.3; GC-MS (EI): [M^+] Calcd for $C_{18}H_{17}N$ 247.14; Found 247.13.

7-Methoxy-2,2'-binaphthalene ***(3u).*** white solid (73 mg, 85%); TLC, R_f = 0.32 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.05 (s, 1H), 7.94–7.84 (m, 5H), 7.77–7.70 (m, 2H), 7.52–7.46 (m, 2H), 7.21 (s, 1H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 138.9, 138.6, 134.9, 133.7, 132.6, 129.1, 128.4, 128.23, 128.20, 128.18, 127.6, 126.3, 126.1, 125.9, 125.7, 125.1, 123.5, 118.8, 106.1, 55.2; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{21}H_{17}O$ 285.1274; Found: 285.1272.

2-(3-Methoxyphenyl)naphthalene ***(known compounds 9, known 3v).***[67] white solid (61 mg, 87%); TLC, R_f = 0.29 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.95–7.89 (m, 3H), 7.78–7.76 (m, 1H), 7.53–7.51 (m, 2H), 7.45–7.42 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30–7.27 (m, 1H), 6.98–6.96 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.6, 138.4, 133.6, 132.7, 129.9, 128.4, 128.2, 127.6, 126.3, 126.0, 125.9, 125.6, 119.9, 113.1, 112.7, 55.3; GC-MS (EI): [M^+] Calcd for $C_{17}H_{14}O$ 234.10; Found 234.09.

(6-(3-Methoxyphenyl)naphthalen-2-yl)trimethylsilane ***(3w).*** slight oil (78 mg, 85%); TLC, R_f = 0.33 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.95–7.90 (m, 2H), 7.77 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.92 (s, 3H), 0.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.6, 138.7, 138.1, 133.8, 133.4, 132.1, 130.3, 129.8, 128.5, 127.2, 125.6, 125.57, 119.9, 113.1, 112.7, 55.4, -1.1; IR(neat) 2954, 1607, 1465, 1436, 1251, 1212, 1084, 1053, 819, 776, 751, 693 cm^{-1}; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for $C_{20}H_{22}OSiNa$ 329.1332; Found 329.1329.

3-Methoxy-1,1':4',1''-terphenyl ***(known compounds 10, known 3x).***[68] white solid (65 mg, 83%); TLC, R_f = 0.35 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.66 (m, 6H), 7.50–7.46 (m, 2H), 7.42–7.36 (m, 2H), 7.27–7.25 (m, 1H), 7.21–7.20 (m, 1H), 6.95–6.93 (m, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.2, 140.7, 140.3, 140.0, 129.8, 128.8, 127.5, 127.46, 127.4, 127.0, 119.5, 112.7, 55.2; GC-MS (EI): [M^+] Calcd for $C_{19}H_{16}O$ 260.12; Found 260.11.

2-(3-Methoxyphenyl)-6-phenylnaphthalene ***(3y).*** white solid (75 mg, 80%); m.p. = 113–115 °C; TLC, R_f = 0.31 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 2H), 7.97 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.81–7.75 (m, 4H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.45–7.39 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 1.6 Hz, 1H), 6.95 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.4, 141.0, 138.6, 138.4, 132.9, 132.8, 129.9, 128.9, 128.7, 128.67, 127.4, 126.0, 125.6, 125.5, 119.9, 113.1, 112.8, 55.3; IR(neat) 2955, 2835, 1576, 1485, 1433, 1296, 1205, 1029, 871, 789, 755,695 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1435.

2-(4-Fluorophenyl)-6-(3-methoxyphenyl)naphthalene ***(3z).*** white solid (91 mg, 92%); m.p. = 153–155 °C; TLC, R_f = 0.31 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.01 (s, 1H), 7.97 (d, *J* = 3.6 Hz, 1H), 7.94 (d, *J* = 4.0 Hz, 1H), 7.78 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.74–7.67 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.30–7.29 (m, 1H), 7.22–7.16 (m, 2H), 6.97–6.95 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 245.0 Hz), 160.1, 142.5, 138.5, 137.6, 137.1 (d, *J* = 3.0 Hz), 132.9, 132.7, 129.9, 128.9, 128.8 (d, *J* = 3.0 Hz), 128.6, 126.1, 125.8, 125.6, 125.3, 119.9, 115.6 (d, *J* = 21.0 Hz), 113.1, 112.8, 55.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ = -115.4; IR(neat) 2932, 2837, 1578, 1488, 1436, 1292, 1207, 1056, 839, 808, 791, 688 cm^{-1}; HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{23}H_{18}FO$ 329.1336; Found 329.1334.

2-(4-Chlorophenyl)-6-(3-methoxyphenyl)naphthalene ***(3aa).*** white solid (86 mg, 83%); m.p. = 158–160 °C; TLC, R_f = 0.32 (PE/EtOAc = 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 (s, 1H), 7.98–7.94 (m, 2H), 7.80–7.65 (m, 4H), 7.53–7.45 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 2.0 Hz, 1H), 6.97–6.95 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 142.4, 139.4, 138.7, 137.4, 133.5, 132.9, 132.86, 129.9, 129.0, 128.9, 128.7, 128.6, 127.4, 126.2, 125.6, 125.56, 125.4, 119.9, 113.1, 112.8, 55.3; IR(neat) 3027, 2927, 1600, 1485, 1432, 1294, 1229, 1171, 1091, 1033, 1010, 875, 776,

670 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}ClO$ 345.1041; Found 345.1035.

2-(3-Methoxyphenyl)-9-methyl-9H-carbazole ***(3ab).*** white solid (65 mg, 75%); m.p. = 85–86 °C; TLC, R_f = 0.25 (PE/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (t, *J* = 8.0 Hz, 2H), 7.61 (s, 1H), 7.54–7.50 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.32–7.28 (m, 2H), 6.97–6.95 (m, 1H), 3.93 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 143.7, 141.5, 141.4, 138.9, 129.7, 125.7, 122.5, 122.1, 120.4, 120.3, 120.1, 119.0, 118.6, 113.4, 112.3, 108.4, 107.0, 55.3, 29.0; IR(neat) 2923, 1604, 1561, 1419, 1316, 1205, 1174, 1050, 1032, 889, 724, 696 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}NO$ 288.1383; Found 288.1378.

2,7-Bis(3-methoxyphenyl)naphthalene ***(3ac).*** white solid (83 mg, 81%); m.p. = 90–91 °C; TLC, R_f = 0.34 (PE/EtOAc = 20:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.45–7.41 (m, 2H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.29 (s, 2H), 6.97–6.95 (m, 2H), 3.92 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 142.2, 138.7, 133.6, 131.7, 129.6, 128.3, 126.1, 125.7, 119.8, 113.1, 112.8, 55.2; IR(neat) 2929, 1603, 1578, 1487, 1423, 1289, 1204, 1169, 1029, 841, 778, 966 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}O_2Na$ 363.1356; Found 363.1360.

2-(p-tolyl)naphthalene ***(known compounds 11, known 3ad).***[69] white solid (23 mg, 35%); TLC, R_f = 0.40 (PE/EtOAc = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.94–7.88 (m, 3H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 6.4 Hz, 2H), 7.54-7.48 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.2, 137.1, 133.7, 132.5, 129.6, 128.3, 128.1, 127.6, 127.2, 126.2, 125.7, 125.5, 125.4, 21.1; GC-MS (EI): $[M^+]$ Calcd for $C_{17}H_{14}$ 218.11; Found 218.08.

2-(4-(Tert-butyl)phenyl)naphthalene ***(known compounds 12, known 3ae).***[69] white solid (35 mg, 45%); TLC, R_f = 0.26 (PE/EtOAc = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.93–7.87 (m, 3H), 7.76 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.71–7.68 (m, 2H), 7.55–7.46 (m, 4H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 138.4, 138.2, 133.7, 132.5, 128.3, 128.1, 127.6, 127.0, 126.2, 125.8, 125.75, 125.6, 125.5, 34.6, 31.4; GC-MS (EI): $[M^+]$ Calcd for $C_{20}H_{20}$ 260.16; Found 260.15.

2-(4-Methoxyphenyl)naphthalene ***(known compounds 13, known 3af).***[69] white solid (20 mg, 29%); TLC, R_f = 0.33 (PE/EtOAc = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92–7.86 (m, 3H), 7.73 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.53–7.46 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.4; GC-MS (EI): $[M^+]$ Calcd for $C_{17}H_{14}O$ 234.10; Found 234.12.

2-(4-Fluorophenyl)naphthalene ***(known compounds 14, known 3ag).***[70] white solid (32 mg, 48%); TLC, R_f = 0.38 (PE/EtOAc = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.94–7.88 (m, 3H), 7.72–7.67 (m, 3H), 7.54–7.51 (m, 2H), 7.21–7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 245.0 Hz), 137.5, 137.2 (d, *J* = 3.0 Hz), 133.6, 132.4, 128.9 (d, *J* = 8.0 Hz), 128.5, 128.1, 127.6, 126.4, 126.0, 125.6, 125.4, 115.6 (d, *J* = 21.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ –115.4; GC-MS (EI): $[M^+]$ Calcd for $C_{16}H_{11}F$ 222.08; Found 222.10.

2-(4-chlorophenyl)naphthalene ***(known compounds 15, known 3ah).***[69] white solid (30 mg, 42%); TLC, R_f = 0.29 (PE/EtOAc = 100:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.94–7.88 (m, 3H), 7.72-7.65 (m, 3H), 7.54-7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 137.2, 133.6, 133.4, 132.7, 129.0, 128.6, 128.2, 127.6, 126.4, 126.1, 125.7, 125.2; GC-MS (EI): $[M^+]$ Calcd for $C_{16}H_{11}Cl$ 238.05; Found 238.02.

Application of the Cr-Catalyzed Arylative Kumada Coupling. (1) Functionalization of Estrone Derivative: The general procedure was applied to 2-(4-((8R,9S,13S,14S,17S)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)phenoxy)pyridine (141 mg, 0.3 mmol) and phenylmagnesium bromide (0.9 mL, 1.0 M in THF, 0.9 mmol). The crude product was purified by column chromatography on silica gel (EtOAc/PE = 1/10) to afford the title compound. *(8R,9S,13S,14S,17S)-2-([1,1'-Biphenyl]-4-yl)-3,17-dimethoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene* ***(5).*** white solid (80 mg, 59%); m.p. = 172–174 °C; TLC, R_f = 0.26 (PE/EtOAc = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67–7.46 (m, 6H), 7.50–7.46 (m, 2H), 7.40–7.32 (m, 2H), 6.75 (d, *J* = 1.2 Hz, 1H), 3.84 (d, *J* = 2.8 Hz, 3H), 3.41 (d, *J* = 3.6 Hz, 3H), 3.38–3.33 (m, 1H), 2.96–2.94 (m, 2H), 2.39–2.26 (m, 2H), 2.10–2.07 (m, 2H), 1.97–1.94 (m, 1H), 1.78–1.71 (m, 1H), 1.64–1.43 (m, 6H), 1.30–1.23 (m, 1H), 0.84 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 141.1, 139.5, 137.8, 137.3, 132.6, 129.9, 128.7, 128.0, 127.6, 127.1, 126.7, 111.5, 90.7, 57.9, 55.6, 50.2, 43.9, 43.2, 38.6, 38.0, 29.8, 27.7, 27.2, 26.5, 23.0, 11.5; IR(neat) 2921, 2850, 1498, 1483, 1448, 1390, 1225, 1130, 1101, 1047, 837, 771,698 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{36}O_2Na$ 475.2608; Found 475.2614. (2) Sequential Transformation of C–O Bonds: In a dried Schlenk tube were placed 3a (47 mg, 0.2 mmol) and $[Ni(PCy_3)_2Cl_2]$ (7 mg, 0.01 mmol), then a freshly distilled toluene (0.5 mL) was added by a syringe under atmosphere of nitrogen. After stirring at room temperature for 5 min, (4-methoxyphenyl)magnesium bromide (0.4 mL, 1.0 M in THF, 0.4 mmol) was dropwise added, and the mixture was stirred at 30 °C for 1 h. After quenched with saturated aqueous solution of NH_4Cl (1 mL), the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc/PE = 1/50) to afford the desired coupling product. *2-(4-Methoxyphenyl)-7-phenylnaphthalene* ***(6).*** slight oil (63 mg, 83%); TLC, R_f = 0.36 (PE/EtOAc = 50:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.07 (s, 1H), 7.95–7.91 (m, 2H), 7.78–7.72 (m, 4H), 7.717–7.69 (m, 2H), 7.54–7.50 (m, 2H), 7.43–7.41 (m, 1H), 7.07–7.04 (m, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 141.1, 138.9, 138.6, 134.0, 133.6, 131.5, 128.8, 128.4, 128.1, 128.08, 127.4, 127.36, 125.9, 125.5, 125.4, 125.3, 114.3, 55.4; IR(neat) 2956, 1604, 1506, 1463, 1292, 1246, 1182, 1038, 902, 833, 760, 699 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O$ 311.1430; Found 311.1425.

Preliminary Mechanistic Studies. Probing the Catalytic Activity of Low-Valent Cr Species that was Formed in-Situ in the Cleavage of C(aryl)–O Bond: In a dried Schlenk tube were placed $CrCl_2$ (4–18 mg, 0.03–0.15 mmol), a freshly distilled THF (0.5 mL) was added by a syringe under atmosphere of nitrogen. After stirring at room temperature for 5 min, phenylmagnesium bromide (0.06–0.3 mL, 1.0 M in THF, 0.06–0.3 mmol) was dropwise added, after stirring at 40 °C for 30 min, the mixture was added 2-(naphthalen-2-yloxy)pyridine (67 mg, 0.3 mmol) and (4-methoxyphenyl)magnesium bromide

(0.9 mL, 1.0 M in THF, 0.9 mmol) stirred at 40 °C for 12 h. After quenched with saturated aqueous solution of NH_4Cl (1 mL), the mixture was extracted three times with ethyl acetate. The organic phases were collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography to afford the desired coupling product. *2-Phenylnaphthalene **(known compounds 16, known 3ai).**[70]* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.97–7.89 (m, 3H), 7.81–7.76 (m, 3H), 7.57–7.52 (m, 4H), 7.45–7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.5, 133.7, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6; GC-MS (EI): [M^+] Calcd for $C_{16}H_{12}$ 204.09; Found 204.10.

Kinetic Studies. (1) Procedure for determining the order in $CrCl_2$: Aryl 2-Pyridyl ether **1a** (0.500 mmol) and different amounts of $CrCl_2$ (0.0125, 0.025, 0.0375, 0.05, 0.075 mmol) were placed in a Schlenk tube, followed by addition of n-tridecane (0.25 mmol, an internal standard for GC analysis) and freshly distilled THF (0.5 mL). After stirring the mixture for 5 min, phenylmagnesium bromide **2a** (1.5 mmol, 1 M in THF) was dropwise added by syringe in one minute at 40 °C. Periodic aliquots (30 μL) were removed by a syringe and quenched by an aqueous solution of NH_4Cl (3 N, 0.5 mL) for another 5 min. The resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of **3a**. (2) Procedure for determining the order in PhMgBr **2a:** Aryl 2-Pyridyl ether **1a** (0.500 mmol) and $CrCl_2$ (0.05 mmol) were placed in a Schlenk tube, followed by addition of n-tridecane (0.25 mmol, an internal standard for GC analysis) and freshly distilled THF (1.25-0 mL, keeping the concentration of **1a** at 0.25 M). After stirring the mixture for 5 min, phenylmagnesium bromide **2a** (0.75, 1.0, 1.25, 1.5, 1.75, 2.0 mmol, 1 M in THF) was dropwise added by syringe in one minute at 40 °C. Periodic aliquots (30 μL) were removed by a syringe and quenched by an aqueous solution of NH_4Cl (3 N, 0.5 mL) for another 5 min. The resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of **3a**. (3) Procedure for determining the order in Aryl 2-Pyridyl ether **1a:** Different amounts of Aryl 2-Pyridyl ether **1a** (0.25, 0.50, 0.75, 1.00, 1.25, 1.50 mmol) and different amounts of $CrCl_2$ (0.05 mmol) were placed in a Schlenk tube, followed by addition of n-tridecane (0.25 mmol, an internal standard for GC analysis) and freshly distilled THF (0.5 mL). After stirring the mixture for 5 min, phenylmagnesium bromide **2a** (1.5 mmol, 1 M in THF) was dropwise added by syringe in one minute at 40 °C. Periodic aliquots (30 μL) were removed by a syringe and quenched by an aqueous solution of NH_4Cl (3 N, 0.5 mL) for another 5 min. The resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as internal standard. The concentrations of the products were plotted to yield the initial rates for the formation of **3a**.

ASSOCIATED CONTENT

Supporting Information. ^{1}H, ^{13}C and ^{19}F NMR spectra and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mails: zengxiaoming@scu.edu.cn (X.Z)
luomm@scu.edu.cn (M.L.)

Notes

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REFERENCES

(1) Anctil, E. J.; Snieckus, V. in *Metal Catalyzed Cross-Coupling Reactions* Vol. 1, eds De Meijere, A.; Diederich, F., Wiley-VCH, 2004.

(2) Tobisu, M.; Chatani, N. Cross-couplings using aryl ethers via C–O bond activation enabled by nickel catalysts. *Acc. Chem. Res.* **2015**, *48*, 1717–1726.

(3) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. Exploration of new C–O electrophiles in cross-coupling reactions. *Acc. Chem. Res.* **2010**, *43*, 1486–1495.

(4) Cornella, J.; Zarate, C.; Martin, R. Metal-catalyzed activation of ethers *via* C–O bond cleavage: a new strategy for molecular diversity. *Chem. Soc. Rev.* **2014**, *43*, 8081–8097.

(5) Selected examples of cross-coupling reactions using pyridyl ether as leaving group: (a) Li, X.; Zhang, J.; Geng, Y.; Jin, Z. Nickel-Catalyzed Suzuki–Miyaura Coupling of Heteroaryl Ethers with Arylboronic Acids. *J. Org. Chem.* **2013**, *78*, 5078–5084. (b) Heravi, M. M.; Panahi, F.; Iranpoor, N. Nickel-Catalyzed Deoxycyanation of Activated Phenols via Cyanurate Intermediates with $Zn(CN)_2$: A Route to Aryl Nitriles. *Org. Lett.* **2018**, *20*,2753–2756. (c) Wang, L.; Wang, Y.; Shen, J.; Chen, Q.; He, M. Y. Nickel-catalyzed cyanation of phenol derivatives activated by 2,4,6-trichloro-1,3,5-triazine. *Org. Biomol. Chem.* **2018**, *16*, 4816–4820. (d) Li, J.; Wang, Z. X. Nickel-Catalyzed Transformation of Aryl 2-Pyridyl Ethers via Cleavage of the Carbon–Oxygen Bond: Synthesis of Mono-α-arylated- Ketones. *Synthesis* **2018**, *50*, 3217-3223.

(6) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A.-M.; Garg, N. K.; Percec, V. Nickel-catalyzed cross-couplings involving carbon–oxygen bonds. *Chem. Rev.* **2011**, *111*, 1346–1416.

(7) Yamaguchi, J.; Muto, K.; Itami, K. Recent progress in nickel-catalyzed biaryl coupling. *Eur. J. Org. Chem.* **2013**, 19–30.

(8) Sergeev, A. G.; Hartwig, J. F. Selective, nickel-catalyzed hydrogenolysis of aryl ethers. *Science* **2011**, *332*, 439–443.

(9) Tobisu, M.; Shimasaki, T.; Chatani, N. Nickel-catalyzed cross-coupling of aryl methyl ethers with aryl boronic esters. *Angew. Chem., Int. Ed.* **2008**, *47*, 4866–4869.

(10) Yu, D.-G.; Shi, Z.-J. Mutual activation: Suzuki–Miyaura coupling through direct cleavage of the sp^2 C–O bond of naphtholate. *Angew. Chem., Int. Ed.* **2011**, *50*, 7097–7100.

(11) Álvarez-Bercedo, P.; Martin, R. Ni-catalyzed reduction of inert C–O bonds: a new strategy for using aryl ethers as easily removable directing groups. *J. Am. Chem. Soc.* **2010**, *132*, 17352–17353.

(12) Tobisu, M.; Takahira, T.; Ohtsuki, A.; Chatani, N. Rhodium-catalyzed borylation of aryl and alkenyl pivalates through the cleavage of carbon–oxygen bonds. *Chem. Lett.* **2015**, *44*, 366–368.

(13) Tobisu, M.; Yasutome, A.; Kinuta, H.; Nakamura, K.; Chatani, N. 1,3-Dicyclohexylimidazol-2-ylidene as a superior ligand for the nickel-catalyzed cross-couplings of aryl and benzyl methyl ethers with organoboron reagents. *Org. Lett.* **2014**, *16*, 5572–5575.

(14) Tobisu, M.; Takahira, T.; Morioka, T.; Chatani, N. Nickel-catalyzed alkylative cross-coupling of anisoles with Grignard reagents via C–O bond activation. *J. Am. Chem. Soc.* **2016**, *138*, 6711–6714.

(15) Leiendecker, M.; Hsiao, C.-C.; Guo, L.; Alandini, N.; Rueping, M. Metal-catalyzed dealkoxylative C_{aryl}–C_{sp^3} cross-coupling—replacement of aromatic methoxy groups of aryl ethers by employing a functionalized nucleophile. *Angew. Chem., Int. Ed.* **2014**, *53*, 12912–12915.

(16) Tobisu, M.; Takahira, T.; Chatani, N. Nickel-catalyzed cross-coupling of anisoles with alkyl Grignard reagents via C–O bond cleavage. *Org. Lett.* **2015**, *17*, 4352–4355.

(17) Zarate, C.; Nakajima, M.; Martin, R. A mild and ligand-free Ni-catalyzed silylation via C–OMe cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 1191–1197.

(18) Li, B.-J.; Xu, L.; Wu, Z.-H.; Guan, B.-T.; Sun, C.-L.; Wang, B.-Q.; Shi, Z.-J. Cross-coupling of alkenyl/aryl carboxylates with Grignard reagent via Fe-catalyzed C–O bond activation. *J. Am. Chem. Soc.* **2009**, *131*, 14656–14657.

(19) Zarate, C.; Manzano, R.; Martin, R. *Ipso*-borylation of aryl ethers via Ni-catalyzed C–OMe cleavage. *J. Am. Chem. Soc.* **2015**, *137*, 6754–6757.

(20) Wang, Y.; Wu, S.-B.; Shi, W.-J.; Shi, Z.-J. C–O/C–H coupling of polyfluoroarenes with aryl carbamates by cooperative Ni/Cu catalysis. *Org. Lett.* **2016**, *18*, 2548–2551.

(21) Tobisu, M.; Takahira, T.; Ohtsuki, A.; Chatani, N. Nickel-catalyzed alkynylation of anisoles via C–O bond cleavage. *Org. Lett.* **2015**, *17*, 680–683.

(22) Cornella, J.; Gómez-Bengoa, E.; Martin, R. Combined experimental and theoretical study on the reductive cleavage of inert C–O bonds with silanes: ruling out a classical Ni(0)/Ni(II) catalytic couple and evidence for Ni(I) intermediates. *J. Am. Chem. Soc.* **2013**, *135*, 1997–2009.

(23) Schwarzer, M. C.; Konno, R.; Hojo, T.; Ohtsuki, A.; Nakamura, K.; Yasutome, A.; Takahashi, H.; Shimasaki, T.; Tobisu, M.; Chatani, N.; Mori, S. Combined theoretical and experimental studies of nickel-catalyzed cross-coupling of methoxyarenes with arylboronic esters via C–O bond cleavage. *J. Am. Chem. Soc.* **2017**, *139*, 10347–10358.

(24) Saper, N. I.; Hartwig, J. F. Mechanistic investigations of the hydrogenolysis of diaryl ethers catalyzed by nickel complexes of *N*-heterocyclic carbene ligands. *J. Am. Chem. Soc.* **2017**, *139*, 17667–17676.

(25) Correa, A.; Martin, R. Ni-catalyzed direct reductive amidation via C–O bond cleavage. *J. Am. Chem. Soc.* **2014**, *136*, 7253–7256.

(26) Chatupheeraphat, A.; Liao, H.-H.; Srimontree, W.; Guo, L.; Minenkov, Y.; Poater, A.; Cavallo, L.; Rueping, M. Ligand-controlled chemoselective C(acyl)–O bond vs C(aryl)–C Bond activation of aromatic esters in nickel catalyzed $C(sp^2)$–$C(sp^3)$ cross-couplings. *J. Am. Chem. Soc.* **2018**, *140*, 3724–3735.

(27) Saito, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. Nickel-catalyzed boron insertion into the C2–O bond of benzofurans. *J. Am. Chem. Soc.* **2016** *138*, 15315–15318.

(28) Dankwardt, J. W. Nickel-catalyzed cross-coupling of aryl Grignard reagents with aromatic alkyl ethers: an efficient synthesis of unsymmetrical biaryls. *Angew. Chem., Int. Ed.* **2004**, *43*, 2428–2432.

(29) Kakiuchi, F.; Usui, M.; Ueno, S.; Chatani, N.; Murai, S. Ruthenium-catalyzed functionalization of aryl carbon–oxygen bonds in aromatic ethers with organoboron compounds. *J. Am. Chem. Soc.* **2004**, *126*, 2706–2707.

(30) Ueno, S.; Mizushima, E.; Chatani, N.; Kakiuchi, F. Direct observation of the oxidative addition of the aryl carbon–oxygen bond to a ruthenium complex and consideration of the relative reactivity between aryl carbon–oxygen and aryl carbon–hydrogen bonds. *J. Am. Chem. Soc.* **2006**, *128*, 16516–16517.

(31) Kondo, H.; Kochi, T.; Kakiuchi, F. Selective monoarylation of aromatic ketones and esters via cleavage of aromatic carbon–heteroatom bonds by trialkylphosphine ruthenium catalysts. *Org. Lett.* **2017**, *19*, 794–797.

(32) Kondo, H.; Akiba, N.; Kochi, T.; Kakiuchi, F. Ruthenium-catalyzed monoalkenylation of aromatic ketones by cleavage of carbon–heteroatom bonds with unconventional chemoselectivity. *Angew. Chem., Int. Ed.* **2015**, *54*, 9293–9297.

(33) Zhao, Y.; Snieckus, V. Beyond directed *ortho* metalation: Ru-catalyzed C_{Ar}–O activation/cross-coupling reaction by amide chelation. *J. Am. Chem. Soc.* **2014**, *136*, 11224–11227.

(34) Zhao, Y.; Snieckus, V. Beyond directed *ortho* metalation: ruthenium-catalyzed amide-directed C_{Ar}–OMe activation/cross-coupling reaction of naphthamides with aryl boronates. *Org. Lett.* **2015** *17*, 4674–4677.

(35) Zhao, Y.; Snieckus, V. Amide-directed Ru-catalyzed hydrodemethoxylation of *ortho*-methoxy-benzamides and -naphthamides: a DoM reaction counterpart. *Org. Lett.* **2018**, *20*, 2826–2830.

(36) Cong, X.; Tang, H.; Zeng, X. Regio- and chemoselective Kumada–Tamao–Corriu reaction of aryl alkyl ethers catalyzed by chromium under mild conditions. *J. Am. Chem. Soc.* **2015**, *137*, 14367–14372.

(37) Tang, J.; Luo, M.; Zeng, X. Chromium-catalyzed, regioselective cross-coupling of C–O bonds by using organic bromides as reactants. *Synlett* **2017**, *28*, 2577–2580.

(38) Choi, J.; Fu, G. C. Transition metal–catalyzed alkyl-alkyl bond formation: another dimension in cross-coupling chemistry. *Science* **2017**, *356*, eaaf7230.

(39) Su, B.; Cao, Z.-C.; Shi, Z.-J. Exploration of earth-abundant transition metals (Fe, Co, and Ni) as catalysts in unreactive chemical bond activations. *Acc. Chem. Res.* **2015**, *48*, 886–896.

(40) Nakamura, E.; Sato, K. Managing the scarcity of chemical elements. *Nat. Mater.* **2011**, *10*, 158–161.

(41) Gao, K.; Yoshikai, N. Low-valent cobalt catalysis: new opportunities for C–H functionalization. *Acc. Chem. Res.* **2014**, *47*, 1208–1219.

(42) Tasker, S. Z., Standley, E. A.; Jamison, T. F. Recent advances in homogeneous nickel catalysis. *Nature* **2014**, *509*, 299–309.

(43) Kinuta, H.; Tobisu, M.; Chatani, N. Rhodium-catalyzed borylation of aryl 2-pyridyl ethers through cleavage of the carbon–oxygen bond: borylative removal of the directing group. *J. Am. Chem. Soc.* **2015**, *137*, 1593–1600.

(44) Tobisu, M.; Zhao, J.; Kinuta, H.; Furukawa, T.; Igarashi, T.; Chatani, N. Nickel-catalyzed borylation of aryl and benzyl 2-pyridyl ethers: a method for converting a robust *ortho*-directing group. *Adv. Synth. Catal.* **2016**, 358, 2417–2421.

(45) Li, J.; Wang, Z.-X. Nickel-catalyzed amination of aryl 2-pyridyl ethers via cleavage of the carbon–oxygen bond. *Org. Lett.* **2017** *19*, 3723–3726.

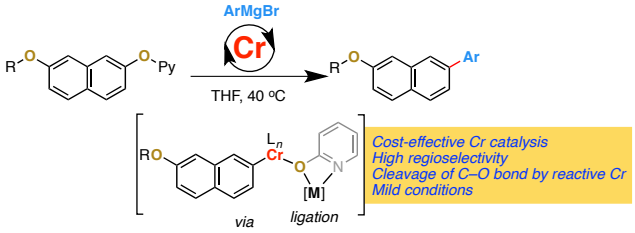
(46) Li, J.; Wang, Z.-X. Nickel-catalyzed C–O bond reduction of aryl and benzyl 2-pyridyl ethers. *Chem. Commun.* **2018**, *54*, 2138–2141.

(47) Fürstner, A. Carbon–carbon bond formations involving organochromium(III) reagents. *Chem. Rev.* **1999**, *99*, 991–1046.

(48) Muzart, J. Chromium-catalyzed oxidations in organic synthesis. *Chem. Rev.* **1992**, *92*, 113–140.

(49) Hargaden, G. C.; Guiry, P. J. The development of the asymmetric Nozaki–Hiyama–Kishi reaction. *Adv. Synth. Catal.* **2007**, *349*, 2407–2424.

(50) Zeng, X.; Cong, X. Chromium-catalyzed transformations with Grignard reagents–new opportunities for cross-coupling reactions. *Org. Chem. Front.* **2015**, *2*, 69–72.
(51) Murakami, K.; Ohmiya, H.; Yorimitsu, H.; Oshima, K. Chromium-catalyzed arylmagnesiation of alkynes. *Org. Lett.* **2007**, *9*, 1569–1571.
(52) Yan, J.; Yoshikai, N. Phenanthrene synthesis via chromium-catalyzed annulation of 2-biaryl Grignard reagents and alkynes. *Org. Lett.* **2017**, *19*, 6630–6633.
(53) Yan, J.; Yoshikai, N. Chromium-catalyzed migratory arylmagnesiation of unactivated alkynes. *Org. Chem. Front.* **2017**, *4*, 1972–1975.
(54) Kuzmina, O. M.; Knochel, P. Room-temperature chromium(II)-catalyzed direct arylation of pyridines, aryl oxazolines, and imines using arylmagnesium reagents. *Org. Lett.* **2014**, *16*, 5208–5211.
(55) Steib, A. K.; Kuzmina, O. M.; Fernandez, S.; Flubacher, D.; Knochel, P. Efficient chromium(II)-catalyzed cross-coupling reactions between C_{sp^2} centers. *J. Am. Chem. Soc.* **2013**, *135*, 15346–15349.
(56) Cong, X.; Fan, F.; Ma, P.; Luo, M.; Chen, H.; Zeng, X. Low-valent, high-spin chromium-catalyzed cleavage of aromatic carbon–nitrogen bonds at room temperature: a combined experimental and theoretical study. *J. Am. Chem. Soc.* **2017**, *139*, 15182–15190.
(57) Zhao, F.; Yu, D.-G.; Zhu, R.-Y.; Xi, Z.; Shi, Z.-J. Cross-Coupling of aryl / alkenyl silyl ethers with Grignard reagents through nickel-catalyzed C-O bond activation. *Chem. Lett.* **2011**, *40*, 1001-1003.
(58) Albahily, K.; Shaikh, Y.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Gorelsky, S. I. Vinyl oxidative coupling as a synthetic route to catalytically active monovalent chromium. *J. Am. Chem. Soc.* **2011**, *133*, 6388–6395.
(59) Tlili, A.; Monnier, F.; Taillefer, M. Selective One-Pot Access to Symmetrical or Unsymmetrical Diaryl Ethers by Copper-Catalyzed Double Arylation of a Simple Oxygen Source. *Chem. Eur. J.* **2010**, *16*, 12299–12302.
(60) Niimi, K.; Kang, M. J.; Miyazaki, E.; Osaka, I.; Takimiya, K. General Synthesis of Dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) Derivatives. *Org. Lett.* **2011**, *13*, 3430–3433.
(61) Chen, Y. –H.; Cheng, D. -J.; Zhang, J.; Wang, Y.; Liu, X. –Y.; Tan, B. Atroposelective Synthesis of Axially Chiral Biaryldiols via Organocatalytic Arylation of 2-Naphthols. *J. Am. Chem. Soc.* **2015**, *137*, 15062–15065.
(62) Serrano, J. L.; Perez, J.; García, L.; Sanchez. G.; García, J.; Lozano, P.; Zende, V.; Kapdi, A. N-Heterocyclic-Carbene Complexes Readily Prepared from Di-μ-hydroxopalladacycles Catalyze the Suzuki Arylation of 9-Bromophenanthrene. *Organmetallics* **2015**, *34*, 522–533.
(63) Li, J.; Zhang, J.; Yang, H.; Jing, G. Assembly of Diversely Substituted Quinolines via Aerobic Oxidative Aromatization from Simple Alcohols and Anilines. *J. Org. Chem.* **2017**, *82*, 3284–3290.
(64) Karmi, B.; Mansouri, F.; Vali, H. A highly water-dispersible/magnetically separable palladium catalyst based on a Fe_3O_4@SiO_2 anchored TEG-imidazolium ionic liquid for the Suzuki–Miyaura coupling reaction in water. *Green Chem.* **2014**, *16*, 2587–2596.
(65) Yang, B.; Wang, Z.-X. Transition-Metal-Free Cross-Coupling of Aryl and Heteroaryl Thiols with Arylzinc Reagents. *Org. Lett.* **2017**, *19*, 6220–6223.
(66) Zhao, C.-W.; Ma, J.-P.; Liu, Q.-K.; Yu, Y.; Wang, P.; Li, Y.-A.; Wang, K.; Dong, Y.-B. A self-assembled Pd_6L_8 nanoball for Suzuki–Miyaura coupling reactions in both homogeneous and heterogeneous formats. *Green Chem.* **2013**, *15*, 3150–3154.
(67) Jin, M.-Y.; Yoshikai, N. Cobalt–Xantphos-Catalyzed, LiCl-Mediated Preparation of Arylzinc Reagents from Aryl Iodides, Bromides, and Chlorides. *J. Org. Chem.* **2011**, *76*, 1972–1978.
(68) Cao, Z.-C.; Luo, Q.-Y.; Shi, Z.-J. Practical Cross-Coupling between O-Based Electrophiles and Aryl Bromides via Ni Catalysis. *Org. Lett.* **2016**, *18*, 5978–5981.
(69) Wang, Z.-Y.; Chen, G.-Q.; Shao, L.-X. N-Heterocyclic Carbene–Palladium(II)–1-Methylimidazole Complex-Catalyzed Suzuki–Miyaura Coupling of Aryl Sulfonates with Arylboronic Acids. *J. Org. Chem.* **2012**, *77*, 6608–6614.
(70) Yu, D.-G.; Li, B.-J.; Zheng, S.-F.; Guan, B.-T.; Wang, B.-Q.; Shi, Z.-J. *Angew. Chem., Int.* Ed. **2010**, *49*, 4566 –4570.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Cost-effective Cr catalysis
High regioselectivity
Cleavage of C–O bond by reactive Cr
Mild conditions