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Article

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Nickel-Catalyzed Cyanation of Phenol Derivatives with $Zn(CN)_2$ Involving C-O Bond Cleavage

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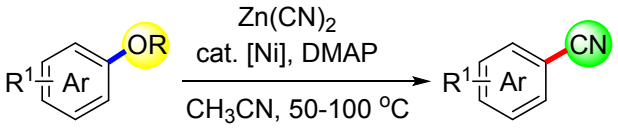


R = Ms, SO_2F, Tf, Ts, SO_2NMe_2 41 examples, up to 94% yield

- *less toxic cyanide source*
- *Ni^{II} complex as the precatalyst*
- *high efficiency, mild reaction conditions*
- *extendable to vinyl sulfonates*

Abstract: An efficient nickel-catalyzed cyanation of aryl sulfonates, fluorosulfonates or sulfamates with $Zn(CN)_2$ has been developed, which provides a facile access to the nitrile products in generally good to excellent yields. The reaction is accomplished by using Ni^{II} complex as the precatalyst and DMAP as the additive. The method also displays wide functional group compatibility, for example, keto, methoxy,

N,*N*-dimethylamino, cyano, ester or pyridyl groups are well tolerated during the reaction process.

INTRODUCTION

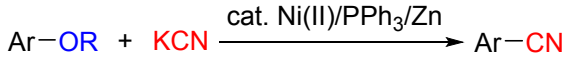
Aromatic nitriles are highly important intermediates, which not only serve as efficient building blocks for a variety of synthetic transformations,[1] but also are present in a large number of pharmaceuticals, agrochemicals, bioactive natural products and functional materials.[2] Traditionally, aryl nitriles were prepared through the Rosenmund-von Braun reaction[3] or the Sandmeyer reaction[4]. However, these reactions have some limitations such as the use of aryl diazonium salts, high temperature and limited substrate scope. Transition metals such as Pd[5]- or Ni[6]-catalyzed cross-coupling reactions of aryl halides with cyanide sources have become one of the most promising approaches to access aryl nitriles. Despite much progress in this area, the development of efficient and practical methods for the synthesis of aryl nitriles utilizing low-cost, more available and green reagents in transformations are still highly desired. Compared with aryl halides, phenol-derived electrophiles are more attractive for cross-coupling reactions since these compounds are naturally abundant or can be readily prepared from easily-available aromatic substrates.[7] In addition, no hazardous halogen-containing waste is generated by using these electrophiles. However, due to the higher C-O bond strength relative to C-Cl, C-Br, and C-I bond, the use of phenol derivatives as

electrophilic coupling partners in the cross-coupling reactions is highly challengeable. Although several practical methods for the synthesis of aryl nitriles from phenol derivatives have been developed using palladium catalyst,[8] the earth-abundant nickel catalyzed cyanation of C-O electrophiles have less been developed.[9] It was not until 1989 that the first metal-catalyzed cyanation of aryl triflates with KCN was reported by Widdowson et al. catalyzed by $Ni^0(PPh_3)_4$ formed in situ by reduction of $(PPh_3)_2NiBr_2$ with Zn under highly concentrated conditions ($\geqslant 2$ M).[9a] Soon after, Takagi et al. reported a similar catalyst system for nickel-catalyzed cyanation of aryl triflates.[9b] Since then, only very limited examples utilizing phenol derivatives as electrophiles have been reported. In 1995, Percec et al. reported that cyanation of less reactive aryl mesylates could be achieved by nickel-catalyzed reaction with KCN. In one example, they observed that a moderate yield (46% GC yield) of benzonitrile could be obtained using $Zn(CN)_2$ as the cyanide source and NaBr as an additive.[9c] In 2016, Itami and Yamaguchi reported that aryl pivalates or carbamates could be cyanated by aminoacetonitrile catalyzed by nickel complex bearing an unique diphosphine ligand such as dcype or dcypt.[9d] However, high reaction temperature of 150 ^oC was required in these reactions. Recently, we reported an efficient nickel-catalyzed cyanation of hetero(aryl) chlorides with less toxic $Zn(CN)_2$ using DMAP as the additive.[10] Inspired by this work, in this paper, we report Ni-catalyzed cyanation of phenol derivatives with $Zn(CN)_2$ for the synthesis of aryl nitriles by C-O bond cleavage. These reactions were

carried out at temperatures ranging from 50 to 100 °C, allowing the cyanation of aryl sulfonates, fluorosulfonates or sulfamates to the corresponding nitriles (Scheme 1). Under these conditions, vinyl sulfonates could also be cyanated by $Zn(CN)_2$. During our work going on, Morandi reported a nickel-catalyzed cyanation of aryl triflates or aryl chlorides using butyronitrile as the cyanating reagent in the presence of Lewis acid.[11] More recently, Heravi and Panahi reported that phenols activated by 2,4,6-trichloro-1,3,5-triazine (TCT) could be cyanated by $Zn(CN)_2$.[12] However, these reactions utilized highly unstable $Ni(COD)_2$ as the catalyst.

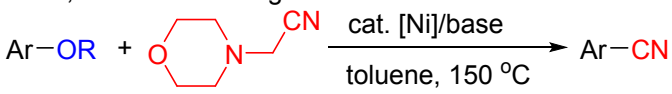
Scheme 1. Nickel-catalyzed Cyanation of Phenol Derivatives

Widdowson et al. and Takagi et al. (**1989**), Percec et al. (**1995**)



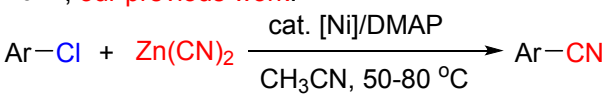
R = Tf, Ms

2016, Itami and Yamaguchi et al.

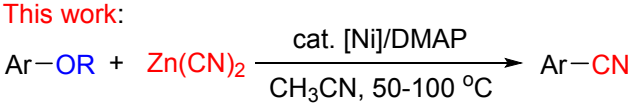


R = Piv, $C(O)NMe_2$, Ts, Ms, Tf, OSO_2NMe_2, $OP(O)(OEt)_3$

2017, our previous work:

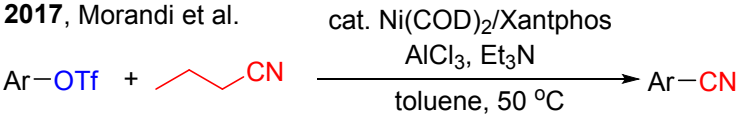


This work:

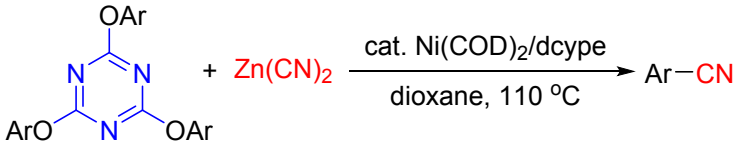


R = Ms,SO_2F, Tf, Ts, SO_2NMe_2

2017, Morandi et al.



2018, Heravi and Panahi et al.

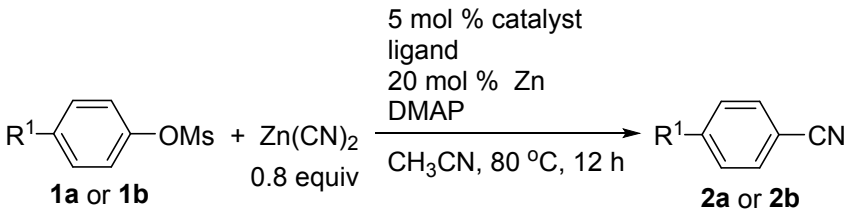


RESULTS AND DISCUSSION

We first investigated the nickel-catalyzed cyanation of 4-acetylphenyl methanesulfonate **1a** bearing an electron-withdrawing group with $Zn(CN)_2$ under our previous conditions for cyanation of aryl halides.[10] To our delight, the desired 4-acetylbenzonitrile **2a** was obtained in a high yield of 81% (Table 1, entry 1). However, when we applied this reaction condition for the cyanation of less reactive 4-methoxyphenyl methanesulfonate **1b** bearing an electron-donating group, only 19%

of the corresponding product **2b** was obtained, possibly due to its lower reactivity towards oxidative addition in the catalytic cycle (entry 2). In order to find out more general reaction conditions that could be compatible with a wide range of the functional groups, we continued to explore the reaction conditions using **1a** as the reaction partner. We first investigated the effects of ligands using $NiBr_2$(DME) as a catalyst in the presence of 1.5 equiv of DMAP. Monodentate ligands such as PMe_2Ph or $PMePh_2$ provided **2a** in good to high yields of 76-90% (entries 3-4), while PPh_3, which has been shown to be an active ligand in Ni-catalyzed cyanation of aryl triflates with KCN,[9a-b] afforded the product in only 26% yield (entry 5). The use of PCy_3 resulted in only trace amount of the desired product (entry 6). Further optimizations revealed that bidentate ligands such as dppf and DPEphos were also highly effective for this reaction (entries 7-8), while Xantphos with a large bite angle (β = 111°) resulted in erosion in yield (entry 9). The best result was obtained using dppb as the ligand (entry 10). Reducing the amount of DMAP to 1.0 equiv or

Table 1. Optimization of the Reaction Conditions



1a or **1b** **2a** or **2b**

R^1 = COMe (**1a**); R^1 = OMe (**1b**)

entry	substrate	catalyst	ligand (mol %)	DMAP (equiv)	yield (%)[a]
1	**1a**	$NiCl_2•6H_2O$	dppf (6)	1	81
2	**1b**	$NiCl_2•6H_2O$	dppf (6)	1	19
3	**1a**	$NiBr_2$(DME)	PMe_2Ph (12)	1.5	76
4	**1a**	$NiBr_2$(DME)	$PMePh_2$ (12)	1.5	90
5	**1a**	$NiBr_2$(DME)	PPh_3 (12)	1.5	26
6	**1a**	$NiBr_2$(DME)	PCy_3 (12)	1.5	5
7	**1a**	$NiBr_2$(DME)	dppf (6)	1.5	87
8	**1a**	$NiBr_2$(DME)	DPEphos (6)	1.5	87
9	**1a**	$NiBr_2$(DME)	Xantphos (6)	1.5	35
10	**1a**	$NiBr_2$(DME)	dppb (6)	1.5	94
11	**1a**	$NiBr_2$(DME)	dppb (6)	1	87
12[b]	**1a**	$NiBr_2$(DME)	dppb (6)	1.5	86
13	**1a**	$NiCl_2$(DME)	dppb (6)	1.5	93
14	**1a**	$NiCl_2•6H_2O$	dppb (6)	1.5	89
15	**1a**	$Ni(acac)_2$	dppb (6)	1.5	(-97)
16	**1a**	$NiBr_2$(DME)	dppb (6)	0	19 (-73)
17	**1a**	-	dppb (6)	1.5	(-98)
18	**1a**	$NiBr_2$(DME)	-	1.5	(-97)
19[c]	**1a**	$NiBr_2$(DME)	dppb (6)	1.5	(-98)
20	**1b**	$NiBr_2$(DME)	dppb (6)	1.5	61
21[d]	**1b**	$NiBr_2$(DME)	dppb (12)	1.5	80
22[e]	**1a**	$NiBr_2$(DME)	dppb (6)	1.5	0 (-66)

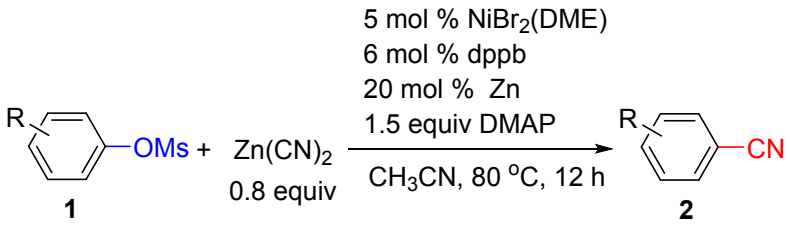
[a]The yields of the recovered **1a** are shown in the parentheses. [b]60 °C. [c]In the absence of Zn. [d]10 mol % $NiBr_2$(DME), 12 mol % dppb, 40 mol % Zn and 1.5 equiv DMAP were used. [e]1.2 equiv TMSCN was used instead of 0.8 equiv $Zn(CN)_2$.

lowering the reaction temperature to 60 °C led to a slightly drop in the yield of **2a** (entries 11-12). $NiCl_2$(DME) or $NiCl_2 \cdot 6H_2O$ also catalyzed the desired transformation efficiently (entries 13-14). However, $Ni(acac)_2$ failed to give the desired nitrile (entry 15). In the absence of DMAP, **2a** was formed in 19% yield (entry 16). The results indictaed that DMAP played a crucial role. And DMAP may have the effect on the activation of $Zn(CN)_2$ by forming of a DMAP-$Zn(CN)_2$ complex, which facilitates the transmetalation, or acts as a co-ligand.[10] Control experiments indicated that the reaction could not proceed in the absence of the nickel catalyst, a ligand or zinc (entries 17-19). Under the conditions shown in entry 10, the use of less reactive substrate **1b** gave **2b** in 61% yield (entry 20). To our delight, the yield of **2b** could be improved to 80% by doubling the amounts of $NiBr_2$(DME), dppb and Zn (entry 21). It was noted that no desired nitrile was observed using other cyanide source such as TMSCN under the conditions shown in entry 10.

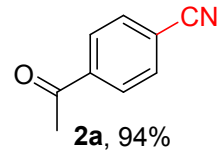
Next, we concentrated on the examination of the substrate scope of this Ni-catalyzed cyanation reaction under the conditions shown in Table 1, entry 10. In some cases, higher catalyst loading was employed in order to improve the product yields. To our delight, a wide range of electron-donating and electron-withdrawing

groups could be accommodated in this reaction (Scheme 2). We first investigated the electronic effect of the substituents on the aryl moiety of the aryl mesylates. For

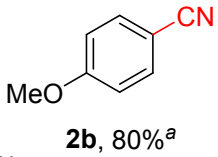
Scheme 2. Scope of the Ni-Catalyzed Cyanation of Aryl Mesylates with $Zn(CN)_2$



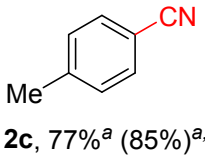
For aryl or heteroaryl mesylates



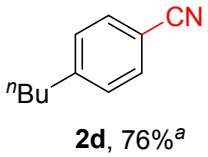
2a, 94%
10 mmol scale, 92%



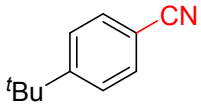
2b, 80%[a]



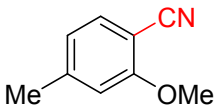
2c, 77%[a] (85%)[a,b]



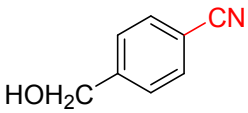
2d, 76%[a]



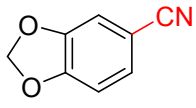
2e, 64%[a,c]



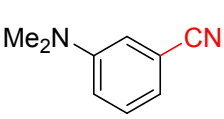
2f, 64%[a]



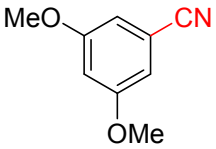
2g, 73%



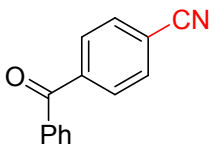
2h, 94%



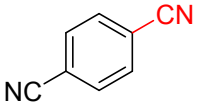
2i, 87%



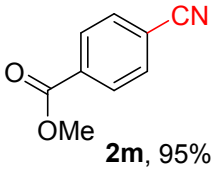
2j, 86%



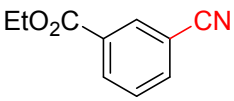
2k, 63% (84%)[d]



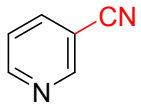
2l, 88%



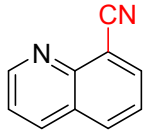
2m, 95%



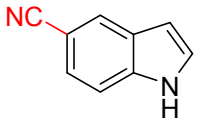
2n, 93%



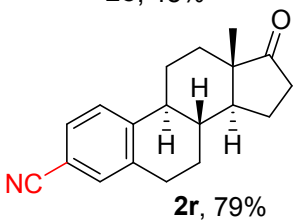
2o, 48%



2p, 73%[a]

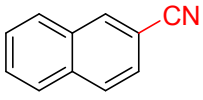


2q, 66%[a]

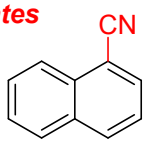


2r, 79%

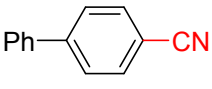
For naphthyl or biaryl mesylates



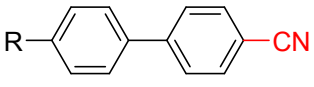
2s, 94%[e]



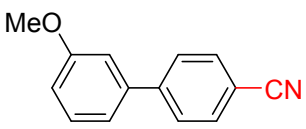
2t, 89%[e]



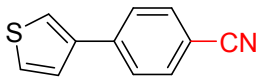
2u, 93%



R = Me, **2v**, 85%
R = F, **2w**, 77%
R = CN, **2x**, 86%



2y, 91%



2z, 86%

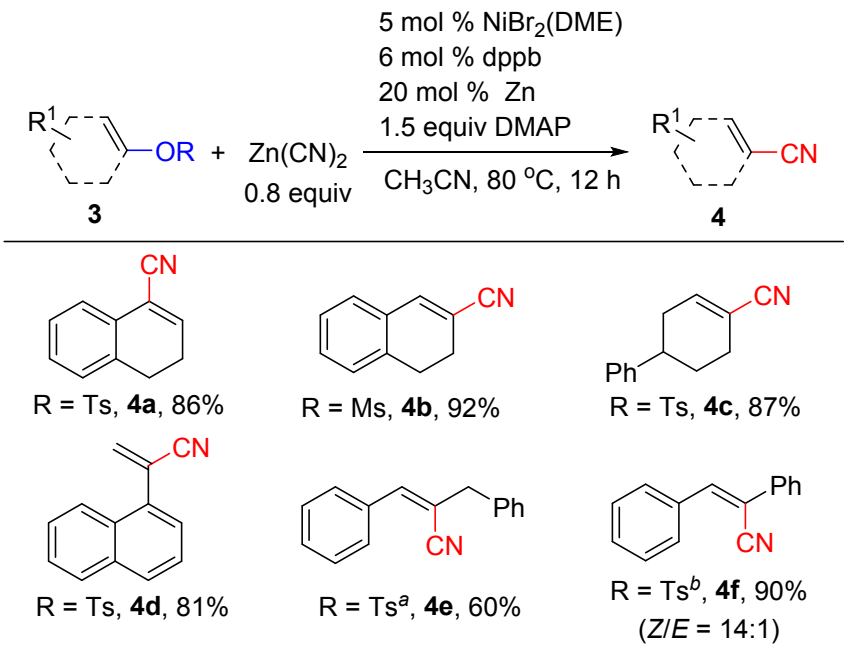
[a]10 mol % $NiBr_2$(DME), 12 mol % dppb, 40 mol % Zn and 1.5 equiv DMAP were used. [b]NMR yield. [c]100 °C. [d]12 mol % $PMePh_2$ was used instead of dppb. [e]50 °C.

example, *para*-methyl substituted aryl mesylate transformed to the nitriles **2c** in 85% NMR yield (due to the low boiling point of this product, a NMR yield of **2c** was provided). When the *para*-substituent was a larger ^{n}Bu group, a similar yield of **2d** was obtained (76%). The presence of a bulky ^{t}Bu group at the *para*-position was cyanated smoothly, although higher catalyst loading and temperature were needed (**2e**). Other functional groups such as 2-methoxy-4-methyl, *p*-CH_2OH or methylenedioxy groups could also be well tolerated, and the corresponding products **2f-2h** were obtained in moderate to high yields. Aryl mesylate bearing an *N*,*N*-dimethylamino group was compatible to provide **2i** in 87% yield. Substrate with two *m*-methoxy groups showed a high reactivity for this reaction (**2j**). The presence of a benzoyl group on the aryl ring resulted in moderate yield (63%) of the desired nitrile **2k** under the standard conditions. Remarkably, using a monodentate phosphine ligand $PMePh_2$ instead of dppb improved the yield of **2k** to 84%. Other electron-withdrawing groups such as cyano and ester groups were well tolerated (**2l-2n**). Heterocyclic substrates such as pyridyl or quinolyl-substituted mesylates were also suitable (**2o** and **2p**). Unprotected indole substrate was also compatible in the reaction (**2q**). Estrone derivative underwent the cyanation smoothly to give the corresponding nitrile **2r** in 79% yield. Naphthyl sulfonates, which were proved to be more efficient electrophiles than phenyl sulfonates in Ni-catalyzed cross-coupling via C-O bond activation,[13] coupled with $Zn(CN)_2$ cleanly at 50 ^{o}C to afford **2s** and **2t** in high yields. The reaction could be applied to

biaryl systems. A wide variety of functional groups such as methyl (**2v**), fluoride (**2w**), cyano (**2x**), methoxy (**2y**), and 3-thienyl (**2z**) on the aryl rings were well tolerated. To demonstrate the practicality of this method, a gram-scale synthesis of **2a** was conducted under the standard reaction conditions, and it was found that **2a** was obtained in an excellent yield of 92%.

α,β-Unsaturated nitriles serve as important building blocks and also are present in natural products and pharmaceutical agents.[2a,14] The above results encouraged us to investigate the cyanation of enol derivatives with $Zn(CN)_2$ (Scheme 3). To our delight, the expected cross-coupling took place smoothly. For example, enol substrates prepared from α- or β-tetralone derivatives were converted to nitriles **4a** and **4b** in 86% and 92% yields, respectively. Vinyl tosylate bearing a cyclohexene ring converted efficiently to **4c**. Linear vinyl tosylate **3d** coupled with $Zn(CN)_2$ well

Scheme 3. Ni-Catalyzed Cyanation of Enol Derivatives with $Zn(CN)_2$

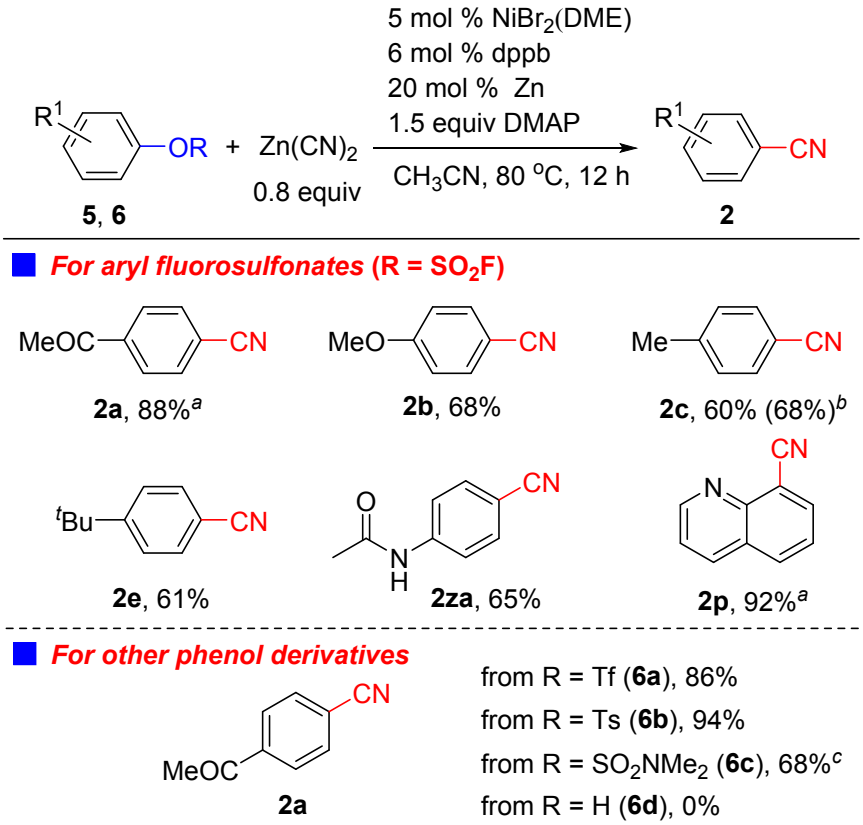


[a]*Z*-**3e** was used. [b]*Z*-**3f** was used.

to afford **4d** in 81% yield. Moreover, when stereodefined (*Z*)-**3e** was used as the substrate, the corresponding product (*Z*)-**4e** was formed as the major product. In the case of (*Z*)-**3f**, the product **4f** was obtained as a mixture of *Z*/*E* isomers in a ratio of 14:1, indicating a slight double bond isomerization occurred during the process.

The reactivity of other electrophiles with different protection groups was also investigated (Scheme 4). Aryl fluorosulfonates, which can be easily prepared from phenol and sulfuryl fluoride in the presence of a base,[15] have been utilized as an

Scheme 4. Scope of the Ni-Catalyzed Cyanation of Phenol Derivatives with $Zn(CN)_2$



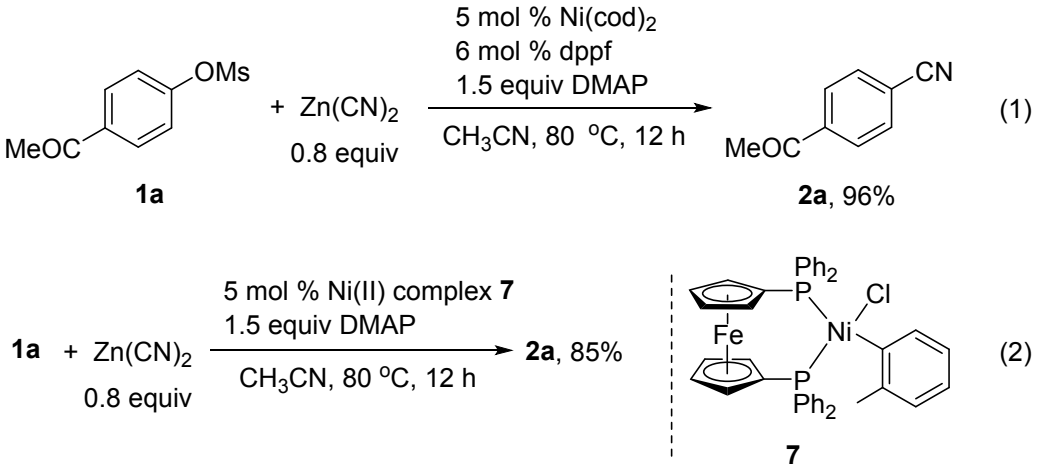
[a]5 mol % $NiBr_2$(DME), 6 mol % dppb, 20 mol % Zn in DMF. [b]NMR yield. [c]10 mol % $NiBr_2$(DME), 12 mol % dppb, 40 mol % Zn and 1.5 equiv DMAP in CH_3CN at 100 °C.

inexpensive alternative to aryl halides in the cross-coupling reactions.[16] Until now, examples of cyanation reactions of aryl fluorosulfonates under transition-metal-catalyzed conditions are scarce.[8g] Here we found that aryl fluorosulfonates **5** could be successfully converted into the nitriles in moderate to excellent yields under mild reaction conditions. When the 4-acetylphenyl sulfurofluoridate was used, the desired product **2a** was obtained in 88% yield in the absence of DMAP. Aryl fluorosulfonates bearing electron-donating group such as methoxy, methyl, ^{t}Bu and amide substituents underwent cyanation smoothly (**2b-2c**, **2e**,

2za). Heterocyclic substrate such as quinolyl-substituted fluorosulfonate was also compatible (**2p**). Excellent product yields were also achieved using 4-acetylphenyl triflate **6a** and tosylate **6b** as the substrates. Aryl sulfamate **6c** was also a suitable coupling partner. Unfortunately, unprotected phenol **6d** was not suitable for this reaction.

Finally, the catalytic systems without using the reducing agent of Zn were

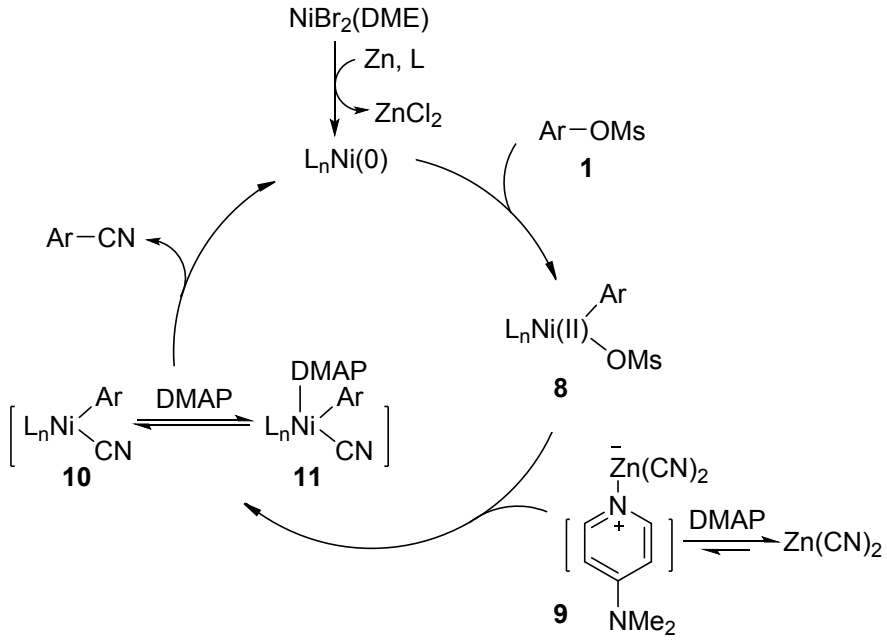
Scheme 5. Ni-Catalyzed Cyanation without Using Reducing Agent



examined. It was found that $Ni(COD)_2$ could catalyze the cyanation reaction of **1a** with a high yield (Scheme 5, eq 1). When pre-prepared air-stable Ni(II) complex [(dppf)Ni(II)(Cl)(*o*-MeC_6H_4)] **7** was used as the catalyst, **2a** could also be formed in 85% yield (Scheme 5, eq 2). These results indicated the involvement of a catalytically active Ni(0) species in the reaction.

We propose the following reaction mechanism for this reaction, which is similar to that of metal-catalyzed cyanation reactions of aryl halides with metal cyanides (Scheme 6). The first step involves the formation of Ni(0) species by reduction of Ni(II) complex with Zn. This is followd by oxidative addition of aryl mesylate to Ni(0) to give an arylnickel(II) intermediate **8**. Transmetalation of **8** with $Zn(CN)_2$ in the presence of DMAP as a promotor occurs to give complex **10**. This process is possibly accelerated through the formation of "ate" complex **9** with enhanced

Scheme 6. Possible Reaction Mechanism



solubility and reactivity. Reductive elimination of **10** delivers the target nitriles. It is possible that DMAP may ligate with Ni in complex **11** to facilitate the reductive elimination by forcing the aryl and cyanide groups into closer proximity. The

analogous bimolecular attack leading to a five-coordinate intermediate involved in reductive elimination of benzonitrile from (cyano)phenylnickel(II) complex has been reported.[17]

CONCLUSION

In summary, we have developed an efficient methodology for the conversion of phenol derivatives to aryl nitriles by using $NiBr_2$(DME)/dppb/Zn/DMAP as the catalyst system and $Zn(CN)_2$ as the cyanating reagent. Aryl mesylates, fluorosulfonates, triflates, tosylates, sulfamates as well as vinyl sulfonates all coupled well with $Zn(CN)_2$. The reaction also displays wide functional group compitability, for example, keto, methoxy, *N*,*N*-dimethylamino, cyano, ester or pyridyl groups were well tolerated during the reaction. This method is also highly useful to pharmaceutical chemists for the drug discovery and development. Further extensions of the electrophiles to other phenol derivatives for cyanation reactions are in progress.

EXPERIMENTAL SECTION

General Methods. Unless noted, all reactions were carried out using standard Schlenk technique under an argon atmosphere or a dry box technique under a nitrogen atmosphere. Tetrahydrofuran was distilled from sodium and benzophenone. MeCN was dried using Innovative Technology Solvent Purifier. *N*,*N*-Dimethylformamide was distilled from calcium

hydride. *o*-Tolylmagnesium chloride (1.0 M solution in THF) was purchased from J&K Chemical Company. $Zn(CN)_2$ was purchased from Alfa Aesar. Zinc powder (99.9% metals basis, -100 mesh) was purchased from Alfa Aesar. Before using, zinc flake was stirred with 1 M HCl aqueous solution, filtered and washed thoroughly with water, acetone and diethyl ether and dried under vacuum. $NiBr_2$(DME) and $NiCl_2$(DME) were purchased from Sigma-Aldrich. $NiCl_2 \cdot 6H_2O$ was purchased from Alfa Aesar. $Ni(COD)_2$ and $Ni(acac)_2$ was purchased from Strem Chemicals Inc. [(dppf)Ni(II)(Cl)(*o*-MeC_6H_4)] **7** was synthesized according to published methods.[10] Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ or d_6-DMSO (containing 0.03% TMS) solutions on Varian or Agilent XL-400 MHz spectrometer. ^1H NMR spectra was recorded with tetramethylsilane (0.00 ppm) or solvent residual peak ($CDCl_3$: 7.26 ppm; d_6-DMSO: 2.50 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (77.00 ppm) or d_6-DMSO (39.52 ppm) as internal reference. High-resolution mass spectra were obtained by using Waters Micromass GCT Premier, Agilent Technologies 6224 TOF LC/MS, or Thermo Fisher Scientific LTQ FT Ultra mass spectrometers. The IR spectra were measured on a ThermoFisher Nicolet FT-IR spectrometer. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer.

Aryl mesylates **1a-1f, 1h-1u** were synthesized according to the published methods.[18] For the characterization of new aryl mesylate substrates, see following:

4-Butylphenyl methanesulfonate (1d). Ten mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1) afforded the title product in 98% yield (2.24 g) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.32-1.38 (m, 2H), 1.55-1.63 (m, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 3.11 (s, 3H), 7.17-7.26 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.8, 22.2, 33.4, 34.9, 37.1, 121.6, 129.8, 142.3, 147.2. IR (neat): 3029, 2957, 2932, 2860, 1503, 1365, 1330, 1197, 1173, 1147, 1113, 1018, 968, 865, 841, 814, 776, 740, 681cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{11}H_{20}NO_3S$, 246.1158; found 246.1157.

2-Methoxy-4-methylphenyl methanesulfonate (1f). Five mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 4/1/1) afforded the title product in 94% yield (1.013 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H), 3.14 (s, 3H), 3.86 (s, 3H), 6.74-6.77 (m, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.3, 37.9, 55.8, 113.6, 121.4, 123.9, 136.0, 138.5, 150.8. IR (neat): 3037, 3013, 2933, 2843, 1602, 1505, 1473, 1415, 1356, 1290, 1196, 1174, 1145, 1110, 1035, 966, 850, 812, 786, 684 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_9H_{16}NO_4S$, 234.0795; found 234.0792.

Synthesis of 4-(hydroxymethyl)phenyl methanesulfonate (1g): To a solution of 4-hydroxybenzaldehyde (1.22 g, 10 mmol) in ethyl acetate (30.0 mL) at 0 °C was added

triethylamine (2.8 mL, 20 mmol) followed by MsCl (1.0 mL, 13 mol). After addition of MsCl, the ice-water bath was removed and the resulting thick slurry was vigorously stirred for 1 h. To the slurry was then added water. The two-phase mixture was separated and extracted with ethyl acetate. The organic layer was washed with water, brine and dried over anhydrous $MgSO_4$. The mixture was filtered and the solvent was evaporated under the reduced pressure. The residue was dissolved in MeOH (20.0 mL) and DCM (20.0 mL), then $NaBH_4$ (491.8 mg, 13.0 mmol) was added to the solution. The reaction mixture was then stirred at room temperature overnight before adding a saturated NH_4Cl solution. Then the mixture was extracted with dichloromethane, washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 1/1/1) to afford the title product in 94% yield (1.899 g) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.56 (brs, 1H), 3.11 (s, 3H), 4.65 (s, 2H), 7.24 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 37.2, 64.0, 121.9, 128.3, 140.3, 148.2. IR (neat): 3561, 3383, 3024, 2938, 2871, 1603, 1504, 1412, 1358, 1196, 1170, 1144, 1015, 969, 865, 838, 812, 773, 678 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_8H_{14}NO_4S$, 220.0638; found 220.0637.

Synthesis of aryl mesylates 1v-1z

Typical procedure for the synthesis of 1v:

A mixture of 4-iodophenol (1.76 g, 8 mmol), *p*-tolylboronic acid (1.31 g, 9.6 mmol), 1.5

mol% Pd/$CaCO_3$ (5% Pd/$CaCO_3$, 255 mg, 0.12 mmol), K_2CO_3 (2.21 g, 16 mmol), ethanol (16 mL) and distilled water (16 mL) were stirred at 50 °C in air for 7 h. The mixture was cooled down to room temperature and filtered over a celite pad. The mixture was added to brine and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$ and filtered. The organic solvent was removed under vacuum, and the product was isolated by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) followed by recrystallization from dichloromethane/hexane afforded 4'-Methyl-[1,1'-biphenyl]-4-ol in 71% yield (1.04 g) as a white solid.

To a solution of 4'-Methyl-[1,1'-biphenyl]-4-ol (921.2 mg, 5 mmol) in ethyl acetate (15.0 mL) at 0 °C was added Et_3N (1.4 mL, 10 mmol) followed by MsCl (0.5 mL, 6.5 mmol). After addition of MsCl, the ice-water bath was removed and the resulting thick slurry was vigorously stirred for 1 h. To the slurry was then added water. The two-phase mixture was separated and extracted with ethyl acetate. The organic layer was washed with water, brine and dried over anhydrous $MgSO_4$. The mixture was filtered through a silica gel and the solvent was evaporated under the reduced pressure, and the residue was recrystallized from dichloromethane/hexane afforded the product **1v** in 89% yield (1.1649 g) as a white solid.

4'-Methyl-[1,1'-biphenyl]-4-yl methanesulfonate (1v). M.p.: 148.6-149.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.15 (s, 3H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 21.0,

37.3, 122.2, 126.9, 128.4, 129.6, 136.8, 137.6, 140.5, 148.3. IR (neat): 3039, 3026, 2944, 1611, 1491, 1360, 1334, 1173, 1151, 973, 964, 867, 852, 811, 788, 720, 655 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{14}H_{18}NO_3S$, 280.1002; found 280.0998.

4'-Fluoro-[1,1'-biphenyl]-4-yl methanesulfonate (1w). 4'-fluoro-[1,1'-biphenyl]-4-ol was synthesized according to the general procedure from 4-iodophenol and (4-fluorophenyl)boronic acid. Compound **1w** was synthesized according to the general procedure from 4'-fluoro-[1,1'-biphenyl]-4-ol (941.0 mg, 5 mmol), ethyl acetate (15 mL), Et_3N (1.4 mL, 10 mmol), MsCl (0.5 mL, 6.5 mmol). The mixture was stirred at room temperature for 1 h. Recrystallization from dichloromethane/hexane afforded the title product in 95% yield (1.27 g) as a white solid. M.p.: 120.8-122.2 ℃. ^1H NMR (400 MHz, DMSO-d_6): δ 3.43 (s, 3H), 7.27-7.31 (m, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.69-7.75 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 37.4, 115.8 ($^2J_{C\text{-}F}$ = 21.3 Hz), 122.7, 128.3, 128.8 ($^3J_{C\text{-}F}$ = 7.5 Hz), 135.4 ($^4J_{C\text{-}F}$ = 3.8 Hz), 138.3, 148.6, 162.1 ($^1J_{C\text{-}F}$ = 242.9 Hz). IR (neat): 3062, 3029, 2944, 1735, 1599, 1491, 1370, 1336, 1254, 1210, 1182, 1157, 1115, 1016, 1006, 968, 945, 864, 825, 789, 739, 719, 653 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{13}H_{15}FNO_3S$, 284.0751; found 284.0750.

4'-Cyano-[1,1'-biphenyl]-4-yl methanesulfonate (1x). 4'-hydroxy-[1,1'-biphenyl]-4-carb-onitrile was synthesized according to the general procedure from 4-iodophenol and

(4-cyanophenyl)boronic acid. Compound **1x** was synthesized according to the general procedure from 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (976.1 mg, 5 mmol), ethyl acetate (20 mL), Et_3N (1.4 mL, 10 mmol), MsCl (0.5 mL, 6.5 mmol). The mixture was stirred at room temperature for 1 h. Recrystallization from dichloromethane/hexane afforded the title product in 90% yield (1.23 g) as a white solid. ^1H NMR (400 MHz, DMSO-d_6): δ 3.44 (s, 3H), 7.49 (d, J = 7.6 Hz, 2H), 7.85-7.89 (m, 4H), 7.93 (d, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): 37.5, 110.4, 118.8, 123.0, 127.7, 128.9, 132.9, 137.4, 143.3, 149.5. The spectroscopic data are in agreement with that previously reported.[19]

3'-Methoxy-[1,1'-biphenyl]-4-yl methanesulfonate (1y). 3'-methoxy-[1,1'-biphenyl]-4-ol was synthesized according to the general procedure from 4-iodophenol and (3-methoxyphenyl)boronic acid. Compound **1y** was synthesized according to the general procedure from 3'-methoxy-[1,1'-biphenyl]-4-ol (1.00 g, 5 mmol), ethyl acetate (15 mL), Et_3N (1.4 mL, 10 mmol), MsCl (0.5 mL, 6.5 mmol). The mixture was stirred at room temperature for 1 h. Recrystallization from dichloromethane/hexane afforded the title product in 95% yield (1.32 g) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 3.16 (s, 3H), 3.86 (s, 3H), 6.91 (d, J = 8.4 Hz, 1H), 7.07 (s, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.33-7.38 (m, 3H), 7.59-7.61 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 37.3, 55,2, 112.9, 113.0, 119.5, 122.2, 128.7, 129.9, 140.4, 141.1, 148.6, 159.9. IR (neat): 2962, 2938, 2838, 1608, 1576, 1482, 1356, 1333, 1299, 1215, 1171, 1147, 1056, 972, 963, 862, 838, 793, 735, 721, 696 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$

calcd for $C_{14}H_{18}NO_4S$, 296.0951; found 296.0948.

4-(Thiophen-3-yl)phenyl methanesulfonate (1z). 4-(thiophen-3-yl)phenol was synthesized according to the general procedure from 4-iodophenol and thiophen-3-ylboronic acid. Compound **1z** was synthesized according to the general procedure from 4-(thiophen-3-yl)phenol (881.2 mg, 5 mmol), ethyl acetate (15 mL), Et_3N (1.4 mL, 10 mmol), MsCl (0.5 mL, 6.5 mmol). The mixture was stirred at room temperature for 1 h. Recrystallization from dichloromethane/hexane afforded the title product in 84% yield (1.07 g) as a white solid. M.p.: 160.8-162.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.41 (s, 3H), 7.40 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 3.6 Hz, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.91 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): 37.4, 121.7, 122.7, 126.2, 127.4, 127.6, 134.3, 140.1, 148.1. IR (neat): 3096, 3037, 3024, 2941, 1600, 1530, 1495, 1372, 1327, 1203, 1182, 1155, 1107, 1012, 970, 863, 850, 819, 792, 781, 729, 705 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{11}H_{14}NO_3S_2$, 272.0410; found 272.0410.

Nickel-catalyzed cyanation of aryl mesylates 1 with $Zn(CN)_2$:

Typical procedure for the synthesis of 2a:

The reaction was conducted in an oven-dried screw-cap vial (volume: 12 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP

(91.6 mg, 0.75 mmol), 4-acetylphenyl methanesulfonate **1a** (107.1 mg, 0.5 mmol), CH_3CN (5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 °C. After stirring for 12 h, the mixture was cooled down to room temperature. Then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1) to afford **2a** in 94% yield (67.9 mg) as a white solid.

4-Acetylbenzonitrile (2a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3H), 7.80 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 26.6, 116.1, 117.8, 128.5, 132.3, 139.7, 196.4. The spectroscopic data are in agreement with that previously reported.[10]

4-Methoxybenzonitrile (2b). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-methoxyphenyl methanesulfonate (101.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded the title product in 80% yield (53.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.4, 103.7, 114.6, 119.1, 133.8, 162.7.

The spectroscopic data are in agreement with that previously reported.[20]

4-Methylbenzonitrile (2c). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), *p*-tolyl methanesulfonate (93.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 30/1/1) afforded the title product in 77% yield (45.2 mg) as a colorless oil. Due to the lower boiling point of this product, the NMR yield of **2c** (85%) was also determined. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.7, 109.1, 119.0, 129.7, 131.9, 143.6. The spectroscopic data are in agreement with that previously reported.[21]

4-Butylbenzonitrile (2d). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-butylphenyl methanesulfonate (114.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 90/3/1) afforded the title product in 76% yield (60.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.30-1.39 (m, 2H), 1.56-1.64 (m, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 22.1, 32.9, 35.7, 109.3, 119.1,

129.1, 131.9, 148.5. The spectroscopic data are in agreement with that previously reported.[10]

4-(*tert*-Butyl)benzonitrile (2e). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-(*tert*-butyl)phenyl methanesulfonate (114.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 100 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 64% yield (50.6 mg) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 7.49 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 30.8, 35.2, 109.2, 119.1, 126.1, 131.9, 156.6. The spectroscopic data are in agreement with that previously reported.[10]

2-Methoxy-4-methylbenzonitrile (2f). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 2-methoxy-4-methylphenyl methanesulfonate (108.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 15/1/1) afforded the title product in 64% yield (47.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.91 (s, 3H), 6.78 (s, 1H), 6.81 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.2, 55.8, 98.6, 112.0, 116.8, 121.5, 133.2, 145.7, 161.1. IR (neat): 3074, 3019, 2951, 2921, 2849, 2217, 1608, 1572, 1503, 1466, 1409, 1380, 1302, 1286, 1272,

1200, 1164, 1123, 1033, 929, 864, 813, 741, 728 cm^{-1}. HRMS (ESI): m/z $[M]^+$ calcd for C_9H_9NO, 147.0684; found 147.0690.

4-(Hydroxymethyl)benzonitrile (2g). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol)， 4-(hydroxymethyl)phenyl methanesulfonate (101.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) afforded the title product in 73% yield (48.8 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.91 (brs, 1H), 4.74 (s, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 63.8, 110.6, 118.8, 126.9, 132.1, 146.4. The spectroscopic data are in agreement with that previously reported.[5d]

Benzo[*d*][1,3]dioxole-5-carbonitrile (2h). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), benzo[*d*][1,3]dioxol-5-yl methanesulfonate (108.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded the title product in 94% yield (69.5 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 6.08 (s, 2H), 6.87 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 7.20 (d, J = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz,

$CDCl_3$): δ 102.1, 104.7, 109.0, 111.2, 118.7, 128.0, 147.9, 151.4. The spectroscopic data are in agreement with that previously reported.[22]

3-(Dimethylamino)benzonitrile (2i). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 3-(dimethylamino)phenyl methanesulfonate (107.6 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) afforded the title product in 87% yield (63.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 (s, 6H), 6.86-6.88 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 39.9, 112.5, 114.5, 116.1, 119.1, 119.7, 129.6, 150.0. The spectroscopic data are in agreement with that previously reported.[9d]

3,5-Dimethoxybenzonitrile (2j). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 3,5-dimethoxyphenyl methanesulfonate (116.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the title product in 86% yield (69.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 6H), 6.65 (s, 1H), 6.75 (d, *J* = 0.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.5, 105.4, 109.7, 113.2, 118.6, 160.8.

The spectroscopic data are in agreement with that previously reported.[22]

4-Benzoylbenzonitrile (2k). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-benzoylphenyl methanesulfonate (138.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the title product in 63% yield (65.5 mg) as a white solid. When uisng $PMePh_2$ (12.0 mg, 0.06 mmol) as the ligand, purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the title product in 84% yield (87.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (t, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.78-7.80 (m, 4H), 7.87 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 115.4, 117.9, 128.5, 129.9, 130.0, 132.0, 133.1, 136.1, 141.0, 194.8. The spectroscopic data are in agreement with that previously reported.[20]

Terephthalonitrile (2l). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-cyanophenyl methanesulfonate (98.6 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate/ dichloromethane = 15/1/10) afforded the title product in 88% yield (56.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 4H). ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$): δ 116.7, 117.0, 132.7. The spectroscopic data are in agreement with that previously reported.[22]

Methyl 4-cyanobenzoate (2m). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), methyl 4-((methylsulfonyl)oxy)benzoate (115.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded the title product in 95% yield (76.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 (s, 3H), 7.76 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 52.6, 116.2, 117.8, 129.9, 132.1, 133.7, 165.2. The spectroscopic data are in agreement with that previously reported.[21]

Ethyl 3-cyanobenzoate (2n). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), ethyl 3-((methylsulfonyl)oxy)benzoate (122.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded the title product in 93% yield (81.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (t, J = 7.0 Hz, 3H), 4.43 (q, J = 7.2 Hz, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.33 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 61.6, 112.7, 117.8, 129.3, 131.6, 133.0,

133.5, 135.7, 164.4. The spectroscopic data are in agreement with that previously reported.[23]

Nicotinonitrile (2o). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), pyridin-3-yl methanesulfonate (86.6 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1) afforded the title product in 48% yield (24.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.0, 4.8 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 8.84 (d, J = 4.4 Hz, 1H), 8.91 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 110.0, 116.4, 123.6, 139.2, 152.4, 152.9. The spectroscopic data are in agreement with that previously reported.[22]

Quinoline-8-carbonitrile (2p). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), quinolin-8-yl methanesulfonate (111.6 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/ dichloromethane = 5/1/1) afforded the title product in 73% yield (56.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J = 8.2, 4.0 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 8.09-8.13 (m, 2H), 8.27 (d, J = 8.4 Hz, 1H), 9.08 (d, J = 4.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 112.7, 117.1, 122.6, 125.7, 127.9, 132.8, 135.3, 136.4,

147.2, 152.3. The spectroscopic data are in agreement with that previously reported.[24]

1*H*-Indole-5-carbonitrile (2q). $NiBr_2$(DME) (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 1*H*-indol-5-yl methanesulfonate (105.6 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 ^oC for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/ dichloromethane = 6/1/1) afforded the title product in 65% yield (46.5 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 6.61(s, 1H), 7.34 (t, *J* = 2.8 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.97(s, 1H), 9.03(brs, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 102.1, 103.0, 112.1, 121.0, 124.5, 126.2, 126.6, 127.5, 137.5. The spectroscopic data are in agreement with that previously reported.[10]

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3-carbonitrile (2r). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl methanesulfonate (174.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 ^oC for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7/1) afforded the title product in 79% yield (110.1 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 0.92 (s, 3H), 1.43-1.70 (m, 6H),

1.97-2.01 (m, 1H), 2.05-2.18 (m, 3H), 2.31-2.44 (m, 2H), 2.52 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.92-2.96 (m, 2H), 7.38-7.43 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 13.6, 21.4, 25.3, 25.8, 28.8, 31.3, 35.6, 37.4, 44.4, 47.7, 50.3, 109.4, 119.0, 126.1, 129.2, 132.4, 137.8, 145.3, 220.1. The spectroscopic data are in agreement with that previously reported.[9d]

2-Naphthonitrile (2s). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), naphthalen-2-yl methanesulfonate (111.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 50 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 94% yield (71.8 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.63 (m, 3H), 7.80-7.85 (m, 3H), 8.14 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 109.1, 119.1, 126.1, 127.4, 127.8, 128.2, 128.8, 129.0, 132.0, 133.9, 134.4. The spectroscopic data are in agreement with that previously reported.[10]

1-Naphthonitrile (2t). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), naphthalen-1-yl methanesulfonate (111.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 50 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 89% yield (68.1 mg) as a

colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, *J* = 7.8 Hz, 1H), 7.56-7.60 (m, 1H), 7.64 (td, *J* = 7.6, 1.2 Hz, 1H), 7.84-7.88 (m, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 109.9, 117.7, 124.7, 124.9, 127.4, 128.4, 128.5, 132.1, 132.4, 132.7, 133.1. The spectroscopic data are in agreement with that previously reported.[25]

[1,1'-Biphenyl]-4-carbonitrile (2u). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), [1,1'-biphenyl]-4-yl methanesulfonate (124.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 93% yield (83.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.42 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.63-7.69 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 110.7, 118.8, 127.0, 127.5, 128.5, 129.0, 132.4, 138.9, 145.4. The spectroscopic data are in agreement with that previously reported.[20]

4'-Methyl-[1,1'-biphenyl]-4-carbonitrile (2v). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4'-methyl-[1,1'-biphenyl]-4-yl methanesulfonate (131.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title

product in 85% yield (82.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.26 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.61-7.67 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.0, 110.3, 118.9, 126.9, 127.3, 129.7, 132.4, 136.04, 138.6, 145.4. The spectroscopic data are in agreement with that previously reported.[26]

4'-Fluoro-[1,1'-biphenyl]-4-carbonitrile (2w). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4'-fluoro-[1,1'-biphenyl]-4-yl methanesulfonate (133.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 77% yield (75.7 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.18 (m, 2H), 7.54-7.57 (m, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 110.8, 116.0 ($^2J_{C\text{-}F}$ = 21.3 Hz), 118.7, 127.5, 128.9 ($^3J_{C\text{-}F}$ = 8.4 Hz), 132.5, 135.2 ($^4J_{C\text{-}F}$ = 3.0 Hz), 144.5, 163.1 ($^1J_{C\text{-}F}$ = 248.2 Hz). The spectroscopic data are in agreement with that previously reported.[27]

[1,1'-Biphenyl]-4,4'-dicarbonitrile (2x). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4'-cyano-[1,1'-biphenyl]-4-yl methanesulfonate (136.7 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column

chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 20/2/3) afforded the title product in 86% yield (88.0 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 4H), 7.79 (d, *J* = 8.0 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 112.3, 118.4, 127.9, 132.8, 143.4. The spectroscopic data are in agreement with that previously reported.[28]

3'-Methoxy-[1,1'-biphenyl]-4-carbonitrile (2y). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 3'-methoxy-[1,1'-biphenyl]-4-yl methanesulfonate (139.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 91% yield (95.5 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.95 (ddd, *J* = 8.4, 2.4, 0.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.14 (ddd, *J* = 7.4, 1.8, 0.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.62-7.68 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 55.2, 110.8, 112.9, 113.7, 118.8, 119.4, 127.6, 130.0, 132.4, 140.4, 145.3, 160.0. The spectroscopic data are in agreement with that previously reported.[29]

4-(Thiophen-3-yl)benzonitrile (2z). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-(thiophen-3-yl)phenyl methanesulfonate (127.2 mg, 0.5 mmol) and CH_3CN (5 mL)

were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 86% yield (79.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.38 (m, 1H), 7.40-7.42 (m, 1H), 7.54-7.55 (m, 1H), 7.61-7.66 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 110.2, 118.8, 122.5, 125.7, 126.6, 127.0, 132.5, 139.7, 140.1. The spectroscopic data are in agreement with that previously reported.[30]

Synthesis of vinyl sulfonates 3.

3,4-Dihydronaphthalen-1-yl 4-methylbenzenesulfonate (3a). In a round-bottomed flask under magnetic stirring and argon atmosphere was added 3,4-dihydronaphthalen-1(2*H*)-one (1.17 g, 8 mmol) and THF (30 mL). The reaction mixture was cooled to -20 °C, potassium bis(trimethylsilyl)amide (17.6 mL, 8.8 mmol, 0.5 M in toluene) was added in one portion. The solution was stirred at -20 °C to 0 °C for 1 h. *p*-Toluenesulfonic anhydride (2.87 g, 8.8 mmol) was added in one portion at 0 °C. The resulting solution was stirred at room temperature for 14 h, and finally quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1) followed by Recrystallization from ethyl acetate/hexane to afford the title product in 51% yield (1.2149 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33-2.39 (m, 2H), 2.41 (s, 3H), 2.75 (t, J = 8.4 Hz, 2H), 5.72 (t, J = 4.8

Hz, 1H), 7.06-7.14 (m, 3H), 7.22 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 21.5, 22.1, 26.9, 116.9, 121.6, 126.2, 127.2, 128.1, 128.2, 129.5, 129.7, 132.8, 136.0, 145.1, 145.4. The spectroscopic data are in agreement with that previously reported.[31]

3,4-Dihydronaphthalen-2-yl methanesulfonate (3b). In a round-bottomed flask under magnetic stirring and argon atmosphere was added 3,4-dihydronaphthalen-2(1*H*)-one (1.46 g, 10 mmol) and THF (20 mL). The reaction mixture was cooled to -20 °C. Sodium *tert*-butoxide (1.06 g, 11 mmol) was added in one portion. The solution was stirred at -5 °C for 1 h and then at room temperature for 30 min. The solution was cooled to -15 °C. Mesyl anhydride (1.92 g, 11 mmol) was added in one portion. The resulting solution was stirred at -15 to -5 °C for 1.5 h and quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the title product in 35% yield (786.1 mg) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (t, J = 8.4 Hz, 2H), 3.01 (t, J = 8.4 Hz, 2H), 3.16 (s, 3H), 6.43 (s, 1H), 7.03-7.05 (m, 1H), 7.12-7.17 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 26.7, 28.5, 37.7, 116.6, 116.7, 126.7, 127.4, 127.7, 132.0, 133.0, 149.6. The spectroscopic data are in agreement with that previously reported.[32]

1,2,3,6-Tetrahydro-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (3c). In a round-bottomed flask under magnetic stirring and argon atmosphere was added 4-phenylcyclohexan-1-one (1.39 g, 8 mmol) and THF (30 mL). The reaction mixture was cooled to -15 °C. Potassium bis(trimethylsilyl)amide (17.6 mL, 8.8 mmol, 0.5 M in toluene) was added in one portion. The solution was stirred at -15 °C for 1 h. *p*-Toluenesulfonic anhydride (2.87 g, 8.8 mmol) was added in one portion at -15 °C. The resulting solution was stirred at -15 °C for 0.5 h, then allowed to reach room temperature and stir for 14 h, and finally quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 15/1) followed by recrystallization from dichloromethane/hexane to afford the title product in 32% yield (841.6 mg) as a white solid. M.p.: 100.8-101.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-1.87 (m, 1H), 1.93-1.96 (m, 1H), 2.16-2.22 (m, 2H), 2.27-2.33 (m, 2H), 2.47 (s, 3H), 2.71-2.76 (m, 1H), 5.45 (d, J = 2.8 Hz, 1H), 7.17-7.23 (m, 3H), 7.26-7.32 (m, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.7, 27.8, 29.6, 31.6, 38.9, 116.6, 126.3, 126.7, 128.2, 128.4, 129.7, 133.5, 144.9, 145.2, 147.9. IR (neat): 3060, 3029, 2920, 2892, 2840, 1735, 1681, 1593, 1493, 1371, 1290, 1190, 1174, 1081, 1036, 891, 853, 815, 763, 743, 696, 688, 675 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{19}H_{24}NO_3S$, 346.1471; found 346.1466.

1-(Naphthalen-1-yl)vinyl 4-methylbenzenesulfonate (3d). In a round-bottomed flask under magnetic stirring and argon atmosphere was added 1-(naphthalen-1-yl)ethan-1-one (1.36 g, 8 mmol) and THF (24 mL). The reaction mixture was cooled to -20 °C. A solution of ^{t}BuOK (1.27 g, 11.2 mmol) in THF (11 mL) was added dropwise over 10 min. The solution was stirred at 0 °C for 1.5 h and then the solution was cooled to -20 °C. *p*-Toluenesulfonic anhydride (3.13 g, 9.6 mmol) was added in one portion. The resulting solution was stirred at -20 °C for 1 h, 0 °C for 6 h, then allowed to reach room temperature and stir for 12 h and quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title product in 68% yield (1.77 g) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 5.25 (d, J = 1.6 Hz, 1H), 5.53 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.28-7.32 (t, J = 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.41-7.45 (m, 4H), 7.71-7.75 (m, 2H), 8.00-8.02 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.4, 108.9, 124.6, 125.3, 125.9, 126.6, 127.9, 127.9, 128.0, 128.8, 129.8, 130.4, 131.4, 132.8, 133.2, 144.4, 152.9. IR (neat): 3117, 3052, 2944, 1655, 1590, 1505, 1451, 1364, 1234, 1190, 1171, 1125, 1089, 922, 900, 851, 798, 777, 731, 682, 655 cm^{-1}. HRMS (ESI): m/z $[M+NH_4]^+$ calcd for $C_{19}H_{20}NO_3S$, 342.1158; found 342.1151.

(*Z*)-1,3-Diphenylprop-1-en-2-yl 4-methylbenzenesulfonate (3e). In a round-bottomed flask

under magnetic stirring and argon atmosphere was added 1,3-diphenylpropan-2-one (2.10 g, 10 mmol) and THF (30 mL). The reaction mixture was cooled to -20 °C. A solution of ^{t}BuOK (1.23 g, 11 mmol) in THF (11 mL) was added dropwise over 10 min. The mixture was then warmed up to 0 °C, stirred for 1.5 h and cooled to -20 °C. *p*-Toluenesulfonic anhydride (3.59 g, 11 mmol) was added to the solution and the mixture was stirred for 1 h at -20 °C, then warmed up to 0 °C, stirred for 5 h. The mixture was quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) followed by recrystallization from ethyl acetate/hexane to afford the title product in 58% yield (2.10 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.81 (s, 2H), 5.81 (s, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.10-7.12 (m, 3H), 7.14-7.16 (m, 2H), 7.23-7.26 (m, 3H), 7.29-7.33 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.5, 41.1, 120.2, 126.8, 127.2, 127.9, 128.0, 128.5, 128.8, 129.1, 129.2, 132.9, 133.0, 136.5, 144.8, 147.9. The spectroscopic data are in agreement with that previously reported.[33]

(*Z*)-3,4-Dihydronaphthalen-2-yl methanesulfonate (3f). In a round-bottomed flask under magnetic stirring and argon atmosphere was added 1,2-diphenylethan-1-one (1.57 g, 8 mmol) and THF (30 mL). The reaction mixture was cooled to -20 °C. A solution of ^{t}BuOK (1.08 g, 9.6 mmol) in THF (10 mL) was added dropwise over 10 min. The mixture was then warmed

to -5 °C stirred for 1 h and then at room temperature for 30 min. The reaction mixture was cooled to -15 °C. *p*-Toluenesulfonic anhydride (3.13 g, 9.6 mmol) was added in one portion. The resulting solution was stirred at -15 °C to -5 °C for 1 h and then at 0 °C for 3 h. quenched with aq. $NaHCO_3$. The aqueous phase was further extracted with ethyl acetate and the combined organic phase was washed with water, brine, dried on Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25/1 to petroleum ether/ethyl acetate/dichloromethane = 15/1/1) afforded the title product in 51% yield (1.42 g) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 6.48 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 7.18-7.24 (m, 3H), 7.27-7.29 (m, 3H), 7.43-7.45 (m, 3H), 7.48-7.50 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.5, 120.0, 126.2, 127.7, 128.1, 128.2, 128.7, 129.0, 129.2, 133.1, 133.2, 135.2, 144.7, 146.3. The spectroscopic data are in agreement with that previously reported.[33]

Nickel-catalyzed cyanation of vinyl sulfonates 3 with $Zn(CN)_2$

Typical procedure for the synthesis of 4a:

The reaction was conducted in an oven-dried screw-cap vial (volume: 12 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 3,4-dihydronaphthalen-1-yl 4-methylbenzenesulfonate (150.2 mg, 0.5 mmol), CH_3CN (5 mL) were added sequentially to a screw-cap vial. The vial cap was then

securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 °C. After stirring for 12 h, the mixture was cooled down to room temperature. Then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the title product in 86% yield (67.1 mg) as a colorless oil.

3,4-Dihydronaphthalene-1-carbonitrile (4a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (dt, *J* =12.8, 3.8 Hz, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 4.8 Hz, 1H), 7.13-7.14 (m, 1H), 7.22-7.28 (m, 2H), 7.42-7.44 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.5, 25.9, 114.2, 117.0, 124.5, 127.0, 127.8, 128.5, 129.0, 134.0, 143.8. The spectroscopic data are in agreement with that previously reported.[34]

3,4-Dihydronaphthalene-2-carbonitrile (4b). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 3,4-dihydronaphthalen-2-yl methanesulfonate (112.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 8 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the title product in 92% yield (71.6 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.50 (t, *J* = 8.4 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H), 7.11-7.15 (m, 3H), 7.19-7.29 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ 24.4, 26.4, 109.4, 119.5, 126.9, 127.8, 130.1, 130.9, 135.2, 141.5. The spectroscopic data are in agreement with that previously reported.[9d]

1,2,3,6-Tetrahydro-[1,1'-biphenyl]-4-carbonitrile (4c). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (164.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) afforded the title product in 87% yield (80.1 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.71-1.82 (m, 1H), 1.97-2.01 (m, 1H), 2.22-2.31 (m, 3H), 2.43-2.49 (m, 1H), 2.75-2.82 (m, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 7.17-7.23 (m, 3H), 7.31 (t, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 27.0, 28.4, 33.3, 38.1, 112.1, 119.3, 126.4, 126.5, 128.5, 144.4, 144.8. IR (neat): 3027, 2922, 2883, 2855, 2211, 1634, 1493, 1453, 1431, 1418, 1161, 1127, 1029, 944, 923, 910, 831, 767, 702 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_{13}N$, 183.1048; found 183.1049.

2-(Naphthalen-1-yl)acrylonitrile (4d). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 1-(naphthalen-1-yl)vinyl 4-methylbenzenesulfonate (162.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column

chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) afforded the title product in 81% yield (72.2 mg) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.12 (s, 1H), 6.38 (s, 1H), 7.42-7.43 (m, 2H), 7.48-7.57 (m, 2H), 7.84-7.86 (m, 2H), 8.09 (d, *J* = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 118.3, 122.0, 124.1, 125.1, 126.4, 126.9, 127.0, 128.6, 130.0, 130.1, 131.6, 133.5, 134.6. The spectroscopic data are in agreement with that previously reported.[35]

(*Z*)-2-Benzyl-3-phenylacrylonitrile (4e). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), (*Z*)-1,3-diphenylprop-1-en-2-yl 4-methylbenzenesulfonate (182.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) afforded the title product in 60% yield (66.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 2H), 6.94 (s, 1H), 7.25-7.28 (m, 3H), 7.32-7.39 (m, 5H), 7.69-7.71 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 42.0, 110.6, 118.6, 127.2, 128.6, 128.7, 128.78, 128.80, 130.0, 133.4, 136.3, 144.0. The spectroscopic data are in agreement with that previously reported.[36]

2,3-Diphenylacrylonitrile (4f). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), (*Z*)-1,2-diphenylvinyl 4-methylbenzenesulfonatee (175.2 mg, 0.5 mmol) and CH_3CN

(5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40/1) afforded the title product in 90%(*Z*/*E* = 14:1) yield (92.3 mg) as a white solid. **(*Z*)-2,3-diphenylacrylonitrile**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.44 (m, 6H), 7.48 (s, 1H), 7.64 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.85 (dd, *J* = 8.0, 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 111.4, 117.9, 125.8, 128.8, 128.9, 129.0, 129.1, 130.4, 133.5, 134.2, 142.1. Partial NMR of **(*E*)-2,3-diphenylacrylonitrile**: ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.10-7.12 (m, 2H), 7.18-7.24 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 128.4, 128.7, 129.6, 129.7, 144.0. The spectroscopic data are in agreement with that previously reported.[37]

Synthesis of 5 and 6. Aryl fluorosulfonates **5a-5d**[16a], **5e**[38], **5f**[16a] were synthesized according to published methods. Aryl triflate **6a**[39], aryl tosylate **6b**[18] and aryl sulfamate **6c**[40] were synthesized according to published methods. For the characterization of new aryl fluorosulfonate substrates, see following:

4-Acetylphenyl sulfurofluoridate (**5a**). Ten mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) afforded the title product in 95% yield (2.08 g) as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (s, 3H), 7.46 (d, *J* = 8.8 Hz, 2H), 8.07-8.11 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 26.6, 121.1, 130.7, 137.0, 152.7, 196.1. IR (neat): 3110, 3071, 1689, 1593, 1497, 1450, 1410, 1359, 1261, 1232, 1180, 1142, 1104, 1015, 909, 846, 813, 779, 682 cm^{-1}. HRMS (EI): m/z $[M]^+$ calcd for $C_8H_7O_4FS$,

218.0049; found 218.0045.

Ni-catalyzed cyanation of phenol derivatives 5 or 6 with $Zn(CN)_2$

Synthesis of 2a and 2p from aryl fluorosulfonates 5: Typical procedure for the synthesis of 2a:

The reaction was conducted in an oven-dried screw-cap vial (volume: 12 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), 4-acetylphenyl sulfurofluoridate (109.1 mg, 0.5 mmol), DMF (5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 °C. After stirring for 12 h, the mixture was cooled down to room temperature, then the reaction mixture was filtered through a short pad of silica gel and washed with diethyl ether. H_2O was added and the layers were separated. the aqueous layer was extracted with Et_2O. The combined organic layers were washed with H_2O and brine. The combined aqueous layers were further extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1) afforded the title product **2a** in 88% yield (64.1 mg) as a white solid.

Quinoline-8-carbonitrile (2p). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), quinolin-8-yl sulfurofluoridate (113.7 mg, 0.5 mmol) and DMF (5 mL) were stirred at 80 °C for 12 h. The mixture was cooled down to room temperature, then the reaction mixture was filtered through a short pad of silica gel and washed with DCM. H_2O was added and the layers were separated.

the aqueous layer was extracted with DCM. The combined organic layers were washed with H_2O and brine. The combined aqueous layers were further extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/ dichloromethane = 10/1/3) afforded the title product in 92% yield (70.7 mg) as a white solid.

Synthesis of 2b-2c, 2e and 2za from aryl fluorosulfonates 5 and Synthesis of 2a from phenol derivatives 6

Typical procedure for the synthesis of 2b:

The reaction was conducted in an oven-dried screw-cap vial (volume: 12 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-methoxyphenyl sulfurofluoridate (103.1 mg, 0.5 mmol) and CH_3CN (5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 ^oC. After stirring for 12 h, the mixture was cooled down to room temperature, then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1) afforded the title

product **2b** in 68% yield (45.5 mg) as a white solid.

4-Methylbenzonitrile (2c). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), *p*-tolyl sulfurofluoridate (95.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 60% yield (35.2 mg) as a colorless oil. Due to the lower boiling point of this product, the NMR yield of **2c** (68%) was also determined.

4-(*tert*-Butyl)benzonitrile (2e). $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-(*tert*-butyl)phenyl sulfurofluoridate (116.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by preparative TLC on silica gel (eluent: petroleum ether/ethyl acetate = 30/1) afforded the title product in 61% yield (48.8 mg) as a colorless oil.

***N*-(4-Cyanophenyl)acetamide (2za).** $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-acetamidophenyl sulfurofluoridate (116.6 mg, 0.5 mmol) and CH_3CN (5 mL) were

stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate/dichloromethane = 2/1/2) afforded the title product in 65% yield (52.4 mg) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.08 (s, 3H), 7.72-7.76 (m, 4H), 10.36 (brs, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 24.2, 104.7, 118.9, 119.1, 133.2, 143.5, 169.2. The spectroscopic data are in agreement with that previously reported.[41]

Synthesis of 4-acetylbenzonitrile (2a) from 4-acetylphenyl trifluoromethanesulfonate. $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-acetylphenyl trifluoromethanesulfonate (134.1 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1) afforded the title product in 86% yield (62.6 mg) as a white solid.

Synthesis of 4-acetylbenzonitrile (2a) from 4-acetylphenyl 4-methylbenzenesulfonate. $NiBr_2$(DME) (7.7 mg, 0.025 mmol), dppb (12.8 mg, 0.03 mmol), Zinc (6.5 mg, 0.1 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-acetylphenyl 4-methylbenzenesulfonate (145.2 mg, 0.5 mmol) and CH_3CN (5 mL) were stirred at 80 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent:

petroleum ether/ethyl acetate = 6/1) afforded the title product in 94% yield (68.4 mg) as a white solid.

Synthesis of 4-acetylbenzonitrile (2a) from 4-acetylphenyl dimethylsulfamate. $NiBr_2$·DME (15.4 mg, 0.05 mmol), dppb (25.6 mg, 0.06 mmol), Zn (13.1 mg, 0.2 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-acetylphenyl dimethylsulfamate (121.6 mg, 0.5 mmol) and CH_3CN (5 mL) (5 mL) were stirred at 100 °C for 12 h. Purification of the crude product by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 6/1) afforded the title product in 68% yield (49.2 mg) as a white solid.

Gram scale study

A Schlenk tube was dried under vacuum using a heat gun, and evacuated and back-filled with argon for several times. Then $NiBr_2$(DME) (154.3 mg, 0.5 mmol), dppb (255.8 mg, 0.6 mmol), Zn (130.8 mg, 2.0 mmol), $Zn(CN)_2$ (939.4 mg, 8.0 mmol), DMAP (1.8326 g, 15.0 mmol) and 4-acetylphenyl methanesulfonate (2.1424 g, 10.0 mmol) were added under argon. The tube was evacuated and refilled with argon for three times, and then acetonitrile (100.0 mL) was added via syringe. The Schlenk tube was immersed into an oil bath preheated at 80 °C. After stirring for 12 h, the mixture was cooled down to room temperature. Then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate.

The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 6:1) to afford **1a** in 92% yield (1.34 g) as a white solid.

Mechanistic studies

$Ni(COD)_2$-catalyzed cyanation of 4-acetylphenyl methanesulfonate (1a).

The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, $Ni(COD)_2$ (6.9 mg, 0.025 mmol), dppf (16.6 mg, 0.03 mmol) and CH_3CN (5 mL). The solution was stirred at room temperature for 10 min. Then $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol) and 4-acetylphenyl methanesulfonate **1a** (107.1 mg, 0.5 mmol) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 ^oC. After stirring for 12 h, the mixture was cooled down to room temperature. Then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **2a** in 96% yield (69.4 mg) as a white solid.

Nickel-catalyzed cyanation of 4-acetylphenyl methanesulfonate (1a) using Ni-complex 7 as the precatalyst.

The reaction was conducted in an oven-dried screw-cap vial (volume: 8 mL) equipped with a magnetic stir bar. In a nitrogen-filled glove box, Ni-complex **7** (18.5 mg, 0.025 mmol), $Zn(CN)_2$ (47.0 mg, 0.4 mmol), DMAP (91.6 mg, 0.75 mmol), 4-acetylphenyl methanesulfonate **1a** (107.1 mg, 0.5 mmol), CH_3CN (5 mL) were added sequentially to a screw-cap vial. The vial cap was then securely fitted and taken outside the glove box. The vial was immersed into an oil bath preheated at 80 °C. After stirring for 12 h, the mixture was cooled down to room temperature. Then the reaction mixture was filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford **2a** in 85% yield (61.8 mg) as a white solid.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Spectroscopic data (PDF).

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Notes

The authors declare no competing financial interest.

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