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COMMUNICATION

Enhanced Activity of Bulky N-Heterocylic Carbenes in Nickel–NHC Catalyzed Kumada–Corriu Cross-Coupling of Aryl Tosylates

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Over the last decades, advances in Ni catalysis have expanded the chemical reactivity of cross-coupling reactions and led to the discovery of catalytic systems that are now widely applied in industrial and academic research. Herein, we report the cross-coupling of aryl tosylates by Ni–NHC catalysis using bulky N-heterocyclic carbene ligands. A notable feature of this operationally-simple method is the combination of 'fluoride effect' to minimize homocoupling and bulky NHC ligands, such as IPr* and IPr*^{MeO}, that enhance the activity of Ni in cross-coupling and prevent hydrolysis of sensitive oxygen electrophiles. A broad range of aryl and heteroaryl tosylates underwent cross-coupling with high efficiency. The finding that easily accessible, bulky NHCs with flexible $CHPh_2$ wingtips enhance the reactivity in Ni–NHC cross-coupling represents a powerful approach for catalysis.

Cross-coupling reactions have had a major impact on chemical synthesis and catalysis, enabling molecule synthesis and discovery in diverse fields of science and technology.[1] Although the majority of cross-coupling research has been focused on palladium, advances in nickel catalysis[2] have expanded the chemical reactivity of cross-coupling reactions and led to the discovery of catalytic systems that are now widely applied in industrial research.[3] In particular, nickel is considered as highly attractive metal from the industrial standpoint owing to the increasing price, toxicity and uncertain long-term supply of palladium. However, in contrast to palladium–NHCs,[1,2] studies on ligand design in cross-coupling with nickel–NHC catalysts have received significantly less attention.[4]

In this context, since the first isolation by Arduengo in 1991,[5] N-heterocyclic carbenes (NHCs) have represented a tremendously popular class of ligands for catalysis.[6] The combination of strong σ-donation[7] with distinct umbrella-type steric shape of N-Ar wingtips,[8] facilitating oxidative addition and reductive elimination,[9] have rendered NHCs ligands of choice in many cross-coupling reactions. However, despite the success of Pd–NHC systems, with many catalysts now commercially available and routinely utilized in cross-coupling reaction discovery, Ni–NHC systems are underdeveloped.[1–4] Notably, despite the utility of phenolic C–O electrophiles in cross-coupling reactions as orthogonal and inexpensive alternatives to aryl halides,[10,11] there are no examples of Ni–NHC systems for the cross-coupling of bench-stable C–O electrophiles.

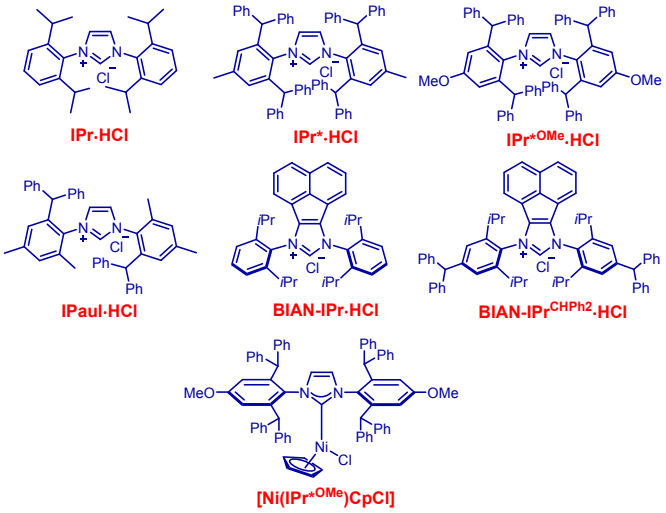

Fig. 1 Structures of NHC Ligands.

Studies by Nakamura established the utility of metal fluorides in cross-coupling of aryl halides through the formation of high-valent metalate complexes.[10b,c] Crucial to this reactivity is ancillary ligand design. Based on our experience in NHC ligand development,[12] we proposed that nickel–NHCs could be an ideal system for the cross-coupling of bench-stable phenolic C–O electrophiles. In particular, we proposed that the synergistic merger of N-Ar wingtip stabilization of the NHC ligand with flexible $CHPh_2$ wingtips with nickel fluoride would disfavour

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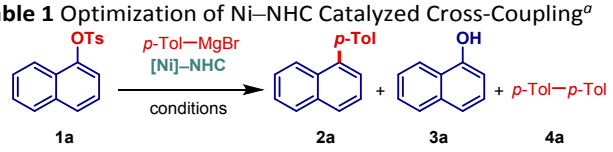
†Electronic Supplementary Information (ESI) available: Experimental details and characterization data. See DOI: 10.1039/x0xx00000x

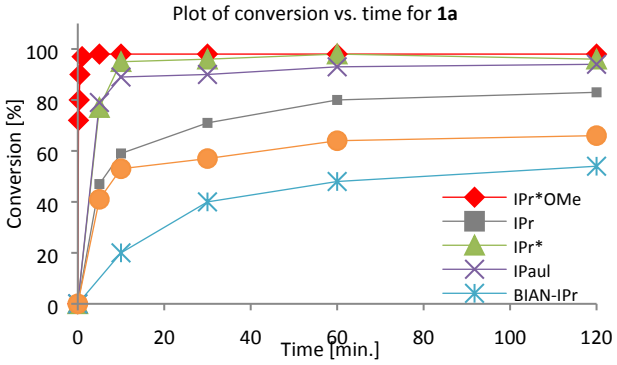
Table 1 Optimization of Ni–NHC Catalyzed Cross-Coupling[a]



entry[a]	catalyst	ligand	ligand (equiv)	yield **2a/3a/4a** (%)[b]
1	NiF_2	IPr*^{OMe}·HCl	0.2	98/2/6
2	NiF_2	IPr*·HCl	0.2	98/0/8
3	NiF_2	IPaul·HCl	0.2	93/7/13
4	NiF_2	BIAN-IPr·HCl	0.2	57/35/33
5	NiF_2	BIAN-IPr^{CHPh2}·HCl	0.2	69/27/34
6	NiF_2	IPr·HCl	0.2	92/7/3
7[c]	NiF_2	IPr*^{OMe}·HCl	0.1	98/0/6
8[c]	NiF_2	IPr·HCl	0.1	79/11/8
9	$Ni(acac)_2$	IPr*^{OMe}·HCl	0.2	89/11/34
10	$NiCl_2·6H_2O$	IPr*^{OMe}·HCl	0.2	87/13/21
11	NiF_2	-	-	46/41/46
12[d]	NiF_2	IPr*^{OMe}·HCl	0.2	52/3/32
13[e]	[Ni(IPr*^{OMe})CpCl]	-	-	89/11/53
14[e]	Ni(IPr*^{OMe})CpCl]	IPr*^{OMe}·HCl	0.2	>98/0/0
15	NiF_2	IPr*^{OMe}·HCl	0.1	98/2/13
16	NiF_2	IPr*^{OMe}·HCl	0.4	99/1/13

[a]Conditions: **1a** (0.25 mmol), [Ni] (10 mol%), THF (0.19 M), *p*-TolMgBr (3.0 equiv, 1.0 M, THF), 66 °C, 20 h. [b]Determined by ^{1}H NMR. [c][Ni] (5 mol%). [d]*p*-TolMgBr (1.5 equiv, 1.0 M, THF). [e][Ni(IPr*^{OMe})CpCl] (10 mol%).

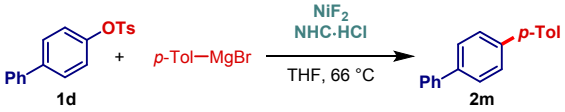
Fig. 2 Kinetic profiles. **1a** (naphthalen-1-yl *p*-toluenesulfonate). Conditions: *p*-TolMgBr (3.0 equiv), [Ni] (10 mol%), ligand (20 mol%), THF (0.19 M), 66 °C.



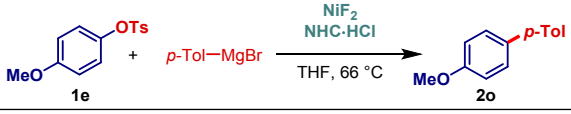
homocoupling and hydrolysis, which represent two major side reactions that have thus far limited the development of cross-couplings of bench-stable C–O electrophiles using Ni–NHCs.[2d]

With this hypothesis in hand, we first examined the cross-coupling of 1-Np-OTs with *p*-Tol-MgBr (Table 1). Structures of NHC ligands selected for our study are presented in Fig. 1. After extensive optimization we identified conditions involving NiF_2 (10 mol%) as a catalyst in the presence of IPr*^{MeO}HCl (20 mol%) as a ligand in THF at 66 °C using a rapid addition of p-TolMgBr (3 equiv), which delivered the desired product in 98% yield with minimal amounts of hydrolysis and homocoupling side products (entry 1). Several points regarding optimization are worth noting: (1) Examination of other sterically-demanding ligands in the IPr* series, namely IPr* (entry 2) and IPaul (entry 3) revealed that these two ligands are also highly effective in the coupling; (2) Examination of BIAN NHCs with acenaphthoimidazolylidene scaffold that brings N-Ar wingtips closer to the metal center

Table 2 Optimization of Ni–NHC Catalyzed Cross-Coupling of Neutral and Electronically-Deactivated Electrophiles[a]



entry[a]	ligand	ligand (equiv)	yield (%)[b]
1	IPr·HCl	0.2	26
2	IPr*·HCl	0.2	81
3	IPr*^{OMe}·HCl	0.2	92
4	IPaul·HCl	0.2	73



5	IPr·HCl	0.2	16
6	IPr*·HCl	0.2	46
7	IPr*^{OMe}·HCl	0.2	77
8	IPaul·HCl	0.2	56

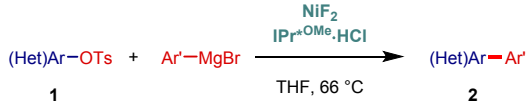
[a]Conditions: **1** (0.25 mmol), [Ni] (10 mol%), THF (0.19 M), *p*-TolMgBr (3.0 equiv, 1.0 M in THF), 66 °C, 20 h, *p*-TolMgBr added dropwise over 1-2 s. [b]Determined by ^{1}H NMR.

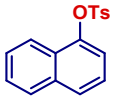
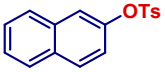
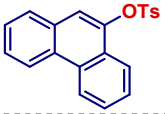
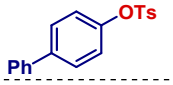
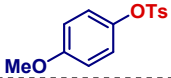
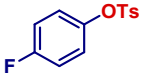
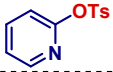
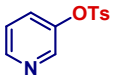
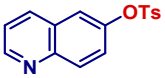
through buttressing effect of the naphthyl C1–H bond (entry 4), including remote para substitution that stabilizes the N-Ar wingtip from rotation (entry 5), revealed that these ligands are less effective in the cross-coupling; (3) the classical imidazol-2-ylidene IPr performed well in the cross-coupling of the activated 1-Np-OTs substrate (entry 6); however, (i) this ligand completely fails in the reactions of neutral and deactivated substrates (Table 2, *vide infra*), and (ii) is much less effective than the bulky IPr*^{MeO} (Table 1, entries 7-8); (4) The choice of nickel salt is critical for the coupling as other Ni precursors, such as $Ni(acac)_2$ (entry 9) and $NiCl_2·6H_2O$ (entry 10) gave substantially lower selectivity in the coupling (cf. hetero/homocoupling), consistent with the stabilizing role of fluoride; (5) the NHC ligand is required for the efficient coupling as inefficient reaction is observed in its absence (entry 11); (6) The use of less than 3 equivalents of nucleophile leads to a significant decrease in reaction yield (entry 12); (7) We also tested well-defined [Ni(IPr*^{MeO})CpCl] complex with cyclopentadienyl throw-away ligand, which gave promising levels of efficiency in the coupling (entries 13-14); (8) Finally, experiments aimed at determining Ni:NHC ratio revealed that 1:1 ratio suffices for the efficient coupling (entries 15-16).

In general, the coupling efficiency can be correlated with the steric demand of the NHC ligand as determined by the % buried volume (%V_{bur}) in linear NHC–Ag–Cl complexes, IPr*^{MeO}: 54.0%, IPr*: 53.5%; IPaul: 43.3% (*syn* conformation); IPr: 43.8%.[13] It should be noted that IPaul features rotatable N-Ar wingtips, with *anti* conformation close in steric demand to IPr*.

To gain further insight into the reaction, kinetic studies were performed (Fig. 2). As shown, kinetic profiling studies revealed that IPr*^{MeO} (red diamonds) is superior to IPr* (green triangles) and IPaul (purple crosses) with these three ligands showing significant enhancement of reactivity compared to IPr (grey squares) and BIAN-IPr^{CHPH2} (orange circles), with BIAN-IPr (blue squares) showing the poorest performance.

Table 3 Scope of Ni–NHC Catalyzed Cross-Coupling[a]

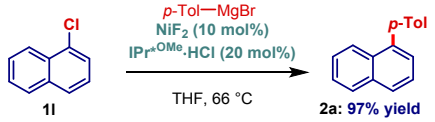


entry[a]	substrate	Ar'	2	yield (%)[b]
1		Ar' = *p*-Tolyl	**2a**	98
2[c]		Ar' = *o*-Tolyl	**2b**	96
3		Ar' = Ph	**2c**	94
4		Ar' = 4-OMe-Ph	**2d**	98
5		Ar' = 4-F-Ph	**2e**	98
6[d]		Ar' = 2-Np	**2f**	98
7		Ar' = *p*-Tolyl	**2g**	88
8		Ar' = Ph	**2h**	90
9		Ar' = 4-OMe-Ph	**2i**	98
10		Ar' = 4-F-Ph	**2j**	81
11		Ar' = *p*-Tolyl	**2k**	>98
12		Ar' = 4-OMe-Ph	**2l**	>98
13		Ar' = *p*-Tolyl	**2m**	92
14		Ar' = Ph	**2n**	>98
15		Ar' = *p*-Tolyl	**2o**	77
16		Ar' = Ph	**2p**	77
17		Ar' = *p*-Tolyl	**2q**	93
18		Ar' = *p*-Tolyl	**2r**	65
19		Ar' = 4-OMe-Ph	**2s**	72
20		Ar' = *p*-Tolyl	**2t**	67
21[c]		Ar' = *o*-Tolyl	**2u**	56
22		Ar' = 4-F-Ph	**2v**	89
23		Ar' = Ph	**2x**	50
24		Ar' = 4-OMe-Ph	**2y**	55

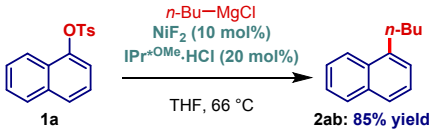
[a]Conditions: **1** (0.25 mmol), [Ni] (10 mol%), IPr*^{OMe}·HCl (20 mol%); THF (0.19 M), *p*-TolMgBr (3.0 equiv, 1.0 M in THF), *p*-TolMgBr added dropwise over 1-2 s. [b]Determined by ^{1}H NMR. [c]*o*-Tolyl-MgBr (2.0 M in Et_2O). [d]2-NpMgBr (0.5 M in Et_2O).

To further investigate the catalytic reactivity of sterically-demanding NHC ligands, we conducted comparative study using neutral (4-Ph-C_6H_4-OTs) and electronically-deactivated (4-MeO-C_6H_4-OTs) substrates (Table 2). In particular, the latter substrate is especially challenging for the C–O cross-coupling with very few ligand systems capable of its selective activation. Remarkably, we found that IPr*^{MeO} is much superior to IPr in the cross-coupling of both substrates, offering practical levels of efficiency for the first time in Ni–NHC-catalyzed cross-coupling of bench-stable C–O electrophiles. The order of ligand efficiency is as follows: IPr*^{MeO} > IPr* ≈ IPaul >> IPr, consistent with the steric demand of the ortho-$CHPh_2$ wingtips and electronic donation of the NHC ligand (TEP, Tolman electronic parameter, ν_{CO} IPr*^{MeO} = 2051.1 cm^{-1}; ν_{CO} IPr* = 2052.7 cm^{-1}).[14] The electronic effect is most likely the major contributor to the reactivity of IPr*^{MeO} vs. IPr*.[13,14]

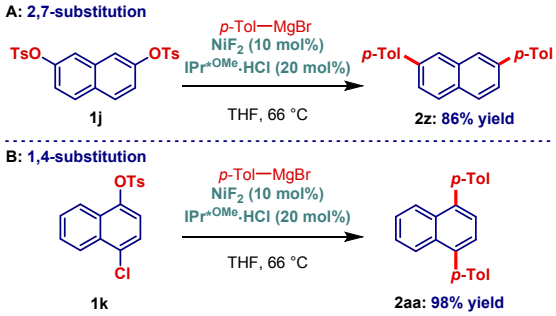
Scheme 1 Ni–NHC Catalyzed Cross-Coupling of Aryl Chlorides



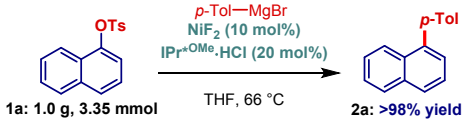
Scheme 2 Ni–NHC Catalyzed C(sp^2)–C(sp^3) Cross-Coupling



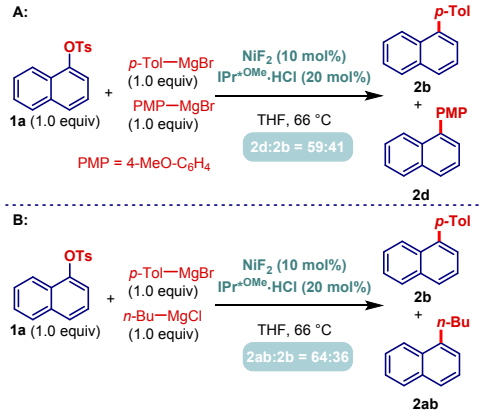
Scheme 3 Double Ni–NHC Catalyzed Cross-Coupling



Scheme 4 Gram Scale Cross-Coupling



Scheme 5 Preliminary Studies to Establish the Selectivity of Ni–NHC Cross-Coupling Reactions



With the optimized conditions in hand, the scope of the cross-coupling using the newly identified NiF_2/IPr*^{MeO} system was next investigated (Table 3). As shown, the catalytic system is general and accommodates a variety of aryl and heteroaryl toluenosulfonates and aryl Grignard reagents. As such, naphthyl and phenanthrenyl electrophiles cross-coupled with electronically- and sterically-diverse aryl Grignards (including *o*-substituted Grignards) to give polycyclic biaryls in excellent yields (entries 1-12). The system is compatible with electronically-neutral (entries 13-14), electron-rich (entries 15-16) and electron-deficient (entry 17) electrophiles. The cleavage of C–OMe and C–F groups was not observed under these conditions despite the capacity of the related Ni systems to activate ethers and fluorides. Notably, heteroaryl electrophiles

are also compatible, including conjugated and unconjugated 2-pyridyl (entries 18-19) and 3-pyridyl (entries 20-23) as well as quinolinyl (entry 24) eletrophiles. The biaryl products of these couplings are important scaffolds in medicinal chemistry research.[15]

Considering the high activity of the catalytic system, we were interested to test its activity in cross-coupling of aryl chlorides. Pleasingly, model 1-Np-Cl substrate was cross-coupled in 97% yield (Scheme 1). We conducted intermolecular competition studies to establish the facility of OTs:Cl activation by NiF_2/IPr*^{MeO}. The coupling of aryl chlorides is inherently favored over aryl tosylates, consistent with the ease of oxidative addition (Cl>OTs, Cl:OTs = 70:30, 1-NpCl:1-Np-OTs) (not shown).

Furthermore, preliminary studies indicate that the cross-coupling of challenging alkyl nucleophiles that are prone to β-hydride elimination is feasible (Scheme 2). We note however that preliminary studies using demanding 3° nucleophiles were unsuccessful, suggesting that a different ligand system might be required to accommodate *t*-Bu organometallics.

Moreover, the present catalytic system enables multiple cross-couplings, exploiting the synthetic presence of polyphenols and halophenols (Scheme 3). These reactions lead to the formation of terphenyls, which have broad applications in functional materials.[16]

Scalability of the cross-coupling has been assessed (Scheme 4). Pleasingly, the reaction could be readily performed on a gram scale, attesting to the scalability of the protocol.

Finally, preliminary selectivity studies have been conducted (Scheme 5). (1) Intermolecular competition experiments between aryl Grignard reagents establish that electron-rich nucleophiles are preferred (*p*-MeO:*p*-Me = 59:41, Scheme 5A). (2) Alkyl nucleophiles couple preferentially (*n*-Bu:*p*-Tol = 64:36) (Scheme 5B). Based on previous mechanistic studies, Ni-NHC complexes are formed in situ under the reaction conditions with Grignard reagents. A mechanism involving a higher-valent heteroleptic metalate species, [Ar(NHC)Ni(II)F_2]MgBr, as the intermediate has been proposed.[10b,c]

In conclusion, this study identified a combination of bulky N-heterocyclic carbene ligands with nickel fluoride as a highly reactive catalyst for the cross-coupling of challenging bench-stable C–O electrophiles. This catalyst system prevents the major side reactions, leading to high selectivity and enabling for the first time to use versatile Ni–NHC catalysis for the cross-coupling of aryl tosylates. A broad range of aryl and heteroaryl tosylates underwent coupling with high efficiency. The NHC ligand design strategies incorporating bulky and flexible $CHPh_2$ wingtips open up new possibilities in nickel catalysis using NHC ligands. Future work focused on the development of well-defined Ni–NHC systems, including structural and mechanistic studies, and expansion of substrate scope is underway and will be reported in due course.

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