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COMMUNICATION

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C(sp²)–C(sp²) and C(sp²)–C(sp³) nickel-catalyzed Kumada–Corriu and Buchwald–Hartwig cross-coupling of aryl sulfamates enabled by sterically-demanding, electron-rich IPr*^OMe *N*-heterocyclic carbenes

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Nickel-catalyzed cross-coupling reactions are among the most powerful tools in organic synthesis owing to the low cost, natural abundance and high activity of versatile nickel catalysts. However, there is a scarcity of efficient Ni-catalyzed systems for the cross-coupling of bench-stable, readily accessible and orthogonal C–O electrophiles. Herein, we report the cross-coupling of aryl sulfamates enabled by sterically-demanding and electron-rich *N*-heterocyclic carbenes. The study identified sulfamates as the most reactive C–O electrophiles enabled by a combination of IPr*^OMe bearing sterically-demanding *ortho*-diphenyl wingtip substitution and NiF_2 exploiting the fluoride effect. The system enables efficient C(sp²)–C(sp²) and C(sp²)–C(sp³) cross-coupling avoiding hydrolysis, homocoupling and unselective C–O and S–N cleavages, providing a powerful platform for the orthogonal use of C–O electrophiles. The system is also applicable to Buchwald–Hartwig amination. The broad access to electron-rich, sterically-demanding *N*-heterocyclic carbenes combined with the high reactivity of aryl sulfamates furnishes a commanding avenue for the development of Ni-catalyzed processes in academic and industrial research.

As highlighted by the 2010 Nobel Prize,[1] transition-metal-catalyzed cross-coupling reactions represent a critical method for the construction of carbon–carbon and carbon–heteroatom bonds in organic synthesis and catalysis with broad ranging applications in every aspect of chemical science, including pharmaceuticals, agrochemicals, and advanced materials.[2] The importance of cross-coupling processes stems from the fact that, in particular, C(sp²)–C(sp²), C(sp²)–C(sp³) and C(sp²)–N disconnections are not possible using other established or alternative methods.[3] In general, as emphasized by the 2010 Nobel Prize, palladium-based catalysts have dominated the field of cross-coupling research.[1,2a,4] This has resulted in the development of a plethora of ligands and catalytic systems specific to palladium that enable broad generality and utility of the palladium catalytic platform. However, owing to the limited resources of palladium and impending supply shortage, the use of naturally abundant 3d nickel has received major attention.[5] The pioneering studies by Dankwardt,[6] Snieckus,[7] Garg,[8] Shi,[9] Chatani[10] and others[11] have shown that Ni catalysts are effective for the traditionally-challenging cross-coupling of C–O electrophiles owing to the lower electronegativity and higher redox potential of nickel compared with palladium.[12] However, in contrast to palladium, there is a scarcity of efficient Ni-catalyzed systems that would enable to expand the scope of cross-coupling partners and provide an efficient platform for the deployment of practical phenol-derived electrophiles as alternatives to aryl halides.[5a]

In this context, aryl sulfamates have emerged as highly valuable electrophiles for carbon–carbon bond formation.[7b,8b,13] Aryl sulfamates are easily accessible by modular methods, are significantly stable to various reaction conditions, including traditional cross-couplings and feature an inherent directing group ability in both directed *ortho*-metallations and C–H functionalizations.[7c] Crucially, the C–O bond in aryl sulfamates is considerably more robust than in other related phenolic electrophiles, including triflates, tosylates and carbamates. While aryl sulfamates can be categorized as ideal and highly desirable electrophiles for cross-coupling, the strong $C–OS(O)_2NR_2$ bond presents a major challenge as a kinetic barrier to oxidative addition necessitating the development of highly tailored ligands.[14]

In our previous studies we have been focused on *N*-heterocyclic carbenes (*N*-heterocyclic carbene = NHC) as enabling ligands for transition-metal-catalysis.[15] *N*-Heterocyclic carbenes feature strong σ-donation[16] of the carbenic center together with high steric demand and

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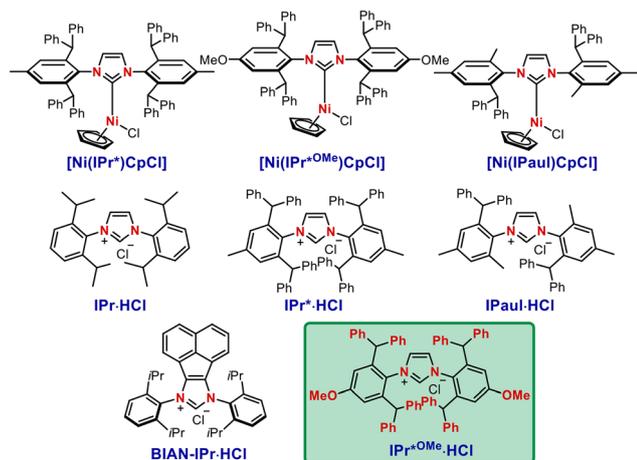
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Fig. 1 Structures of NHC ligands and [Ni–NHC] complexes.

variable flexibility of *N*-aromatic wingtip,[17] permitting for highly efficient catalysis of the elementary steps of cross-coupling cycle.[18] Further, the large steric-demand of select *N*-heterocyclic carbene ligands is highly beneficial for suppressing β-hydride elimination and undesired homocoupling side processes.[19] However, compared with palladium catalysis, where many classes of different NHC ligands have been secured, the establishment of efficient Ni–NHC systems has been significantly underdeveloped.[3,5] Taking inspiration from the studies by Snieckus,[7] Nicasio,[11a] Chatani[10] and others[6,8,9,11b–f] on nickel catalysis and cognizant of the work by Nakamura[20] on the utility of metal fluorides in the formation of high-valent metalate complexes preventing homocoupling,[15a] herein we report the nickel-catalyzed cross-coupling of aryl sulfamates enabled by

sterically-demanding and electron-rich *N*-heterocyclic carbenes (Fig. 1). The study identified sulfamates as the most reactive C–O electrophiles enabled by a combination of IPr*[OMe] bearing sterically-demanding *ortho*-diphenyl wingtip substitution and NiF$_2$ exploiting the fluoride effect. The system enables efficient C(sp^2)–C(sp^2) and C(sp^2)–C(sp^3) cross-coupling avoiding hydrolysis, homocoupling and unselective C–O and S–N cleavages, providing a powerful platform for the orthogonal use of C–O electrophiles. The system is also applicable to Buchwald–Hartwig amination.[21] Overall, the broad access to electron-rich, sterically-demanding *N*-heterocyclic carbenes combined with the high reactivity of aryl sulfamates furnishes a commanding avenue for the development of Ni-catalyzed cross-coupling processes in academic and industrial research.

Our study commenced with the examination of the cross-coupling of electronically-deactivated 4-anisolyl electrophile (4-MeO-C$_6$H$_4$-OSO$_2$NMe$_2$) with 4-Tol-MgBr under a variety of conditions (Table 1). We established that a combination of NiF$_2$ (10 mol%) and IPr*[OMe]·HCl (20 mol%) in THF at 66 °C permits for the cross-coupling in a quantitative yield in the absence of any further additives within 30 min reaction time (Table 1, entry 1). The reaction was fully selective with respect to the alternative C–OMe bond, the cleavage of the alternative S–O bond as well as deaminative S–N cleavage, all processes known to occur with Ni-catalyzed systems.[14a] This high selectivity was further confirmed by experiments with respect to the reaction time, temperature (see SI) and stoichiometry (Table 1, entries 2–5), demonstrating exquisite chemoselectivity under the developed conditions. Next, we comprehensively evaluated the effect of different NHC ligands (Table 1, entries 6–9).

Table 1 Optimization of Ni–NHC catalyzed cross-coupling[a]

Entry[a]	Catalyst	Ligand	Ligand (equiv.)	Time	Yield **2a** (%)[b]
1	NiF$_2$	IPr*[OMe]·HCl	0.2	30 min	98
2[c]	NiF$_2$	IPr*[OMe]·HCl	0.1	30 min	86
3[c]	NiF$_2$	IPr*[OMe]·HCl	0.05	30 min	27
4[c]	NiF$_2$	IPr*[OMe]·HCl	0.025	30 min	34
5[d]	NiF$_2$	IPr*[OMe]·HCl	0.2	30 min	8
6	NiF$_2$	IPr*·HCl	0.2	30 min	98
7	NiF$_2$	IPaul·HCl	0.2	30 min	32
8	NiF$_2$	IPr·HCl	0.2	30 min	0
9	NiF$_2$	BIAN-IPr·HCl	0.2	30 min	0
10	NiF$_2$	—	—	30 min	0
11	[Ni(IPr*[OMe])CpCl]	—	—	30 min	82
12	[Ni(IPr*)CpCl]	—	—	30 min	77
13	[Ni(IPaul)CpCl]	—	—	30 min	78
14	[Ni(IPr*[OMe])CpCl]	IPr*[OMe]·HCl	0.2	30 min	92
15	Ni(acac)$_2$	IPr*[OMe]·HCl	0.2	30 min	85
16	NiCl$_2$·6H$_2$O	IPr*[OMe]·HCl	0.2	30 min	14
17	Ni(COD)$_2$	IPr*[OMe]·HCl	0.2	30 min	82

[a] Conditions: **1a** (0.25 mmol), [Ni] (10 mol%), THF (0.19 M), *p*-TolylMgBr (2.0 equiv., 1.0 M in THF), 66 °C, *p*-TolylMgBr added dropwise over 1–2 s. [b] Determined by ^{1}H NMR. [c] [Ni] (5 mol%). [d] [Ni] (0.5 mol%).

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As such, sterically-demanding but less electron-rich IPr* is also effective in promoting the desired cross-coupling; however, it is less efficient requiring longer reaction time to reach the desired conversions (Table 1, entry 6 and SI). Its sterically-adjustable counterpart, IPaul, gives a noticeable decrease in yield (Table 1, entry 7), however, we note that this ligand is still effective under longer reaction time regimen (see SI). Most interestingly, the classic IPr and the more sterically-demanding BIAN–IPr featuring the buttressing acenaphthoimidazolylidene scaffold are ineffective (Table 1, entries 8–9), demonstrating the key role of steric *ortho*-diphenyl wingtip substitution on the reactivity. As expected, *N*-heterocyclic carbene ligand is absolutely required for the cross-coupling with no reaction observed in its absence (Table 1, entry 10). We also evaluated well-defined Ni(II)–NHC complexes based on the established cyclopentadienyl ancillary ligand (Table 1, entries 11–14). Interestingly, the well-defined [Ni(IPr*^{OMe})CpCl], [Ni(IPr*)CpCl], and [Ni(IPaul)CpCl] complexes can also be used for the cross-coupling with a yield slightly lower than the *in situ* prepared complexes. These results suggest the importance of activation to the catalytically active Ni(0)–NHC and excess of ligand for the desired cross-coupling. Finally, studies with different Ni sources, such as Ni(acac)$_2$, NiCl$_2$ and Ni(cod)$_2$ (Table 1, entries 15–17), resulted in lower yields, consistent with the key role of NiF$_2$ for this class of cross-couplings. It should also be noted that the use of bench-stable Ni(II)–NHC complexes is preferred, because *in situ* generation of Ni(0)–NHCs may reduce the effective concentration of Ni–NHC in the early stages of the reaction. Furthermore, Ni(0) sources such as Ni(cod)$_2$ are known to exist in equilibrium with Grignard reagents with COD dissociation, leading to
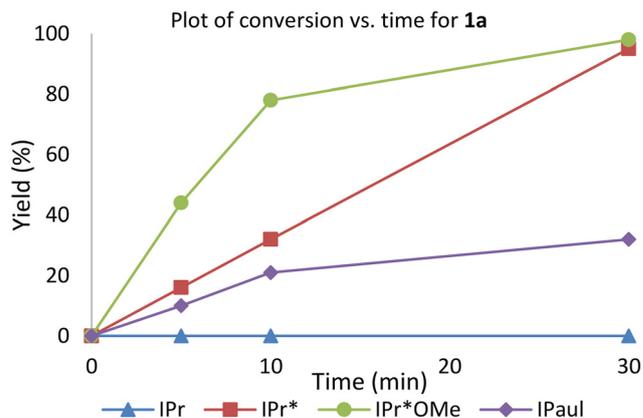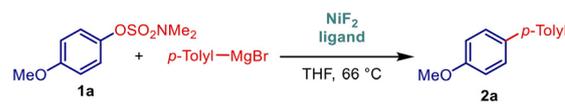

Fig. 3 Kinetic profiles. Conditions: **1a** (0.25 mmol), *p*-TolylMgBr (2.0 equiv., 1.0 M in THF), [Ni] (10 mol%), ligand (20 mol%), THF (0.19 M), 66 °C.

competitive reactions,[22] whereas NiF$_2$/IPr*^{OMe} benefits from direct activation under Grignard conditions and consistently provides optimal reactivity.

Next, kinetic studies were conducted to investigate the effect of the C–O leaving group (Fig. 2). Unexpectedly, in the series of OTf, OTs, OCONEt$_2$, OSO$_2$NMe$_2$, the most challenging sulfamate featuring the strongest C–O bond was found the most reactive. Probably the main difference between sulfamates and the usually most reactive triflate electrophiles is the lower stability of triflates under the reaction conditions. Aryl sulfamates may also benefit from stabilizing nitrogen coordination to nickel, which lowers the
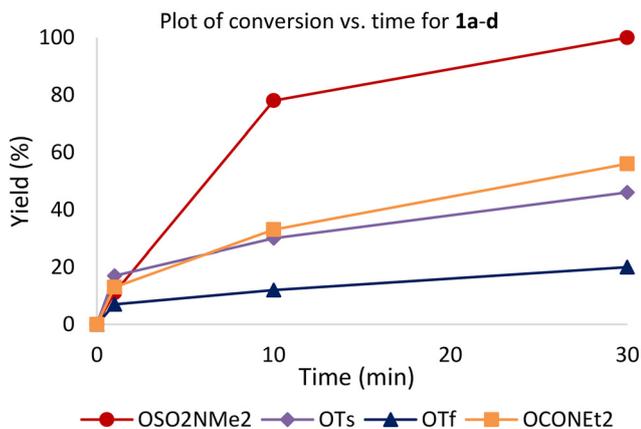

Fig. 2 Kinetic profiles. Conditions: **1** (0.25 mmol), *p*-TolylMgBr (2.0 equiv., 1.0 M in THF), [Ni] (10 mol%), ligand (20 mol%), THF (0.19 M), 66 °C.
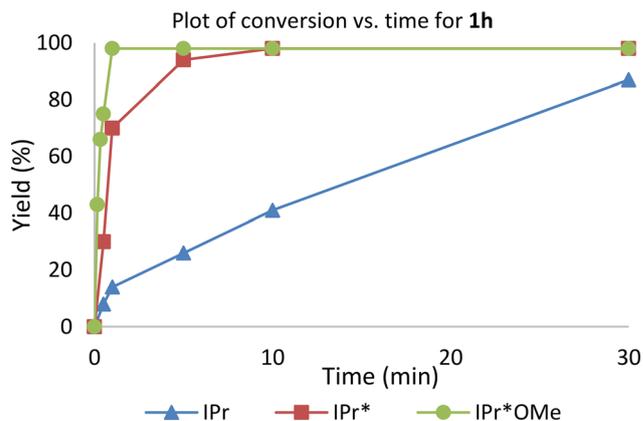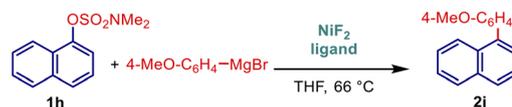

Fig. 4 Kinetic profiles. Conditions: **1h** (0.25 mmol), 4-OMe-PhMgBr (2.0 equiv., 1.0 M in THF), [Ni] (10 mol%), ligand (20 mol%), THF (0.19 M), 66 °C.

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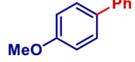*Catal. Sci. Technol.*, 2025, **15**, 6651–6659 | **6653**

Table 2 Scope of Ni–NHC-catalyzed cross-coupling reactions[a]

$$(Het)Ar\!-\!OSO_2NMe_2 \; + \; R\!-\!MgX \xrightarrow[\text{THF, 66 °C}]{\substack{NiF_2 \\ IPr^{*OMe}.HCl}} (Het)Ar\!-\!R$$

Entry[a]	Substrate	R-MgX	Time	2	Product	Yield (%)
1	MeO-C6H4-OSO2NMe2	p-TolylMgBr	30 min	2a	MeO-C6H4-p-Tolyl	98
2		4-F-C6H4MgBr	30 min	2b	MeO-C6H4-4-F-C6H4	98
3		PhMgBr	30 min	2c	MeO-C6H4-Ph	94
4	Ph-C6H4-OSO2NMe2	p-TolylMgBr	30 min	2d	Ph-C6H4-p-Tolyl	86
5		PhMgBr	30 min	2e	Ph-C6H4-Ph	69
6	F-C6H4-OSO2NMe2	p-TolylMgBr	30 min	2f	F-C6H4-p-Tolyl	90
7		4-MeO-C6H4MgBr	30 min	2b	F-C6H4-4-OMe-C6H4	77
8		PhMgBr	30 min	2g	F-C6H4-Ph	77
9	Ph-OSO2NMe2	p-TolylMgBr	30 min	2h	Ph-p-Tolyl	98
10		4-MeO-C6H4MgBr	30 min	2c	Ph-4-OMe-C6H4	98
11	Naphthyl-1-OSO2NMe2	p-TolylMgBr	30 min	2i	Naphthyl-p-Tolyl	98
12		4-MeO-C6H4MgBr	30 min	2j	Naphthyl-4-OMe-C6H4	98
13		PhMgBr	30 min	2k	Naphthyl-Ph	96
14[b]		o-TolylMgBr	30 min	2l	Naphthyl-o-Tolyl	78
15		2-ThienylMgBr	21 h	2m	Naphthyl-2-Thienyl	53
16	Naphthyl-2-OSO2NMe2	p-TolylMgBr	30 min	2n	Naphthyl-p-Tolyl	91
17		4-MeO-C6H4MgBr	30 min	2o	Naphthyl-4-OMe-C6H4	92
18		PhMgBr	30 min	2p	Naphthyl-Ph	86
19	Pyridyl-2-OSO2NMe2	p-TolylMgBr	3 h	2q	Pyridyl-p-Tolyl	67
20		4-MeO-C6H4MgBr	3 h	2r	Pyridyl-4-OMe-C6H4	74
21		PhMgBr	3 h	2s	Pyridyl-Ph	98
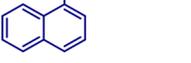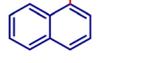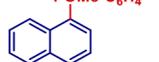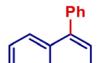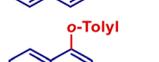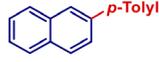
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Table 2 (continued)

$$(Het)Ar\!-\!OSO_2NMe_2 \ + \ R\!-\!MgX \ \xrightarrow[\text{THF, 66 °C}]{\text{NiF}_2 \atop \text{IPr*}^{OMe}\cdot\text{HCl}} \ (Het)Ar\!-\!R$$

Entry[a]	Substrate	R-MgX	Time	2	Product	Yield (%)
22	3-pyridyl-OSO₂NMe₂	p-TolylMgBr	3 h	2t	3-(p-Tolyl)pyridine	61
23	6-quinolinyl-OSO₂NMe₂	PhMgBr	30 min	2u	6-Ph-quinoline	75

[a] Conditions: **1** (0.25 mmol), [Ni] (10 mol%), IPr*OMe·HCl (20 mol%); THF (0.19 M), RMgX (2.0 equiv., 1.0 M in THF), 66 °C, RMgX added dropwise over 1–2 s. [b] o-Tolyl-MgBr (2.0 M in Et₂O).

barrier for oxidative addition.[23] Undoubtedly, the high reactivity of bench-stable aryl sulfamates is very beneficial from the practical standpoint.

Kinetic studies were also performed to gain insight into the effect of NHC ligands (Fig. 3 and 4). In the cross-coupling of the electronically-deactivated 4-MeO-C₆H₄-OSO₂NMe₂ with 4-Tol-MgBr, IPr*[MeO] outperformed its electronically less σ-donating IPr* and less sterically-demanding IPaul, while the reactivity of IPr was negligible (Fig. 3). Further, in the reactivity of activated 1-naphthyl electrophile, IPr*[MeO] was still the most reactive catalyst, closely followed by IPr*, while IPr was again the least effective catalyst. These studies together with the optimization results clearly indicate the combined effect of strong σ-donation and high steric demand on the reactivity in this cross-coupling.

With the optimized conditions in hand, the scope of this C(sp²)–C(sp²) cross-coupling was next investigated (Table 2). In general, the scope of the reaction is very broad and encompasses various aryl sulfamates featuring electron donating (Table 2, entries 1–3), biaryl (Table 2, entries 4–5), electron-withdrawing (Table 2, entries 6–8), unsubstituted (Table 1, entries 9–10), sterically-hindered 1-naphthlyl (Table 2, entries 11–15), conjugated 2-naphthyl (Table 2, entries 16–18), heterocyclic 2- and 3-pyridyl (Table 2, entries 19–22) and quinolinyl (Table 2, entry 23) electrophiles using neutral (Table 2, entry 3), electron-deficient (Table 2, entry 2), electron-rich (Table 2, entry 7) and heterocyclic (Table 2, entry 15) organometallic reagents.

In light of the unexpectedly high reactivity of the present NiF₂/IPr*[MeO] system in the cross-coupling with aryl

Table 3 Ni–NHC-catalyzed C(sp)²–C(sp)³ cross-coupling reactions[a]

$$1\text{-naphthyl-OSO}_2NMe_2 \ + \ Alkyl\!-\!MgX \ \xrightarrow[\text{THF, 66 °C}]{\text{NiF}_2 \atop \text{IPr*}^{OMe}\cdot\text{HCl}} \ 1\text{-Alkyl-naphthalene}$$

Entry[a]	Ligand	R-MgX	Time	2	Product	Yield (%)
1[b]	IPr*[OMe]·HCl	MeMgCl	30 min	2v	1-Me-naphthalene	96
2[c]	IPr*[OMe]·HCl	n-BuMgCl	30 min	2w	1-n-Bu-naphthalene	96
3[c]	IPr*·HCl					88
4[c]	IPr·HCl					34
5[c]	IPr*[OMe]·HCl	n-HexMgCl	30 min	2x	1-n-Hex-naphthalene	92
6[d]	IPr*[OMe]·HCl	c-HexMgCl	30 min	2y	1-c-Hex-naphthalene	97
7	IPr*[OMe]·HCl	C₁₄H₂₉MgCl	30 min	2z	1-C₁₄H₂₉-naphthalene	81

[a] Conditions: **1h** (0.25 mmol), [Ni] (10 mol%), IPr*OMe·HCl (20 mol%); THF (0.19 M), RMgX (2.0 equiv., 1.0 M in THF), 66 °C, RMgX added dropwise over 1–2 s. [b] Me-MgCl (3.0 M in THF). [c] R-MgCl (2 M in THF). [d] c-HexMgBr (1 M in 2-MeTHF).

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Table 4 Double Ni–NHC-catalyzed cross-coupling reactions[a]

Entry[a]	Substrate	R-MgX	Time	2	Product	Yield (%)
1	Me₂NO₂SO–naphthalene–OSO₂NMe₂	p-TolylMgBr	1 h	2aa	p-Tolyl–naphthalene–p-Tolyl	98
2		n-BuMgCl	1 h	2ab	n-Bu–naphthalene–n-Bu	59
3	naphthalene-1,5-diyl bis(OSO₂NMe₂)	p-TolylMgBr	1 h	2ac	1,5-di-p-Tolylnaphthalene	88
4	naphthalene substrate	p-TolylMgBr	1 h	2ad	p-Tolyl naphthalene	81
5	naphthalene substrate	p-TolylMgBr	1 h	2ae	p-Tolyl naphthalene	75
6	benzene-1,3-diyl bis(OSO₂NMe₂)	p-TolylMgBr	1 h	2af	1,3-di-p-Tolylbenzene	58

[a] Conditions: **1** (0.25 mmol), [Ni] (10 mol%), IPr*^{OMe}·HCl (20 mol%), p-TolylMgBr (4 equiv., 1.0 M in THF), 66 °C, RMgX added dropwise over 1–2 s.

organometallics, we were also keen on investigating the significantly more challenging C(sp²)–C(sp³) cross-coupling (Table 3). In general, alkylative cross-couplings of C–O electrophiles are prone to β-hydride elimination, homocoupling and protodemetalation pathways. We were delighted to find that the present system is also highly efficient in the cross-coupling of alkyl organometallics (Table 3, entries 1–7). Interestingly, IPr*^{MeO} again outperforms IPr* and IPr (Table 3, entries 2–4), indicating a generality of the catalyst system.

We also evaluated the highly challenging cross-coupling of bis-C–O electrophiles (Table 4). The NiF₂/IPr*^{MeO} catalytic system enables double C(sp²)–C(sp²) cross-coupling of variously substituted naphthyl electrophiles (Table 4, entries 1, 3–5) and is also feasible for double C(sp²)–C(sp³) cross-coupling (Table 4, entry 2) and double C–O cross-coupling of unactivated electrophiles (Table 4, entry 6), affording terphenyl and dialkylaryl products that have broad application in advanced materials and liquid crystals.
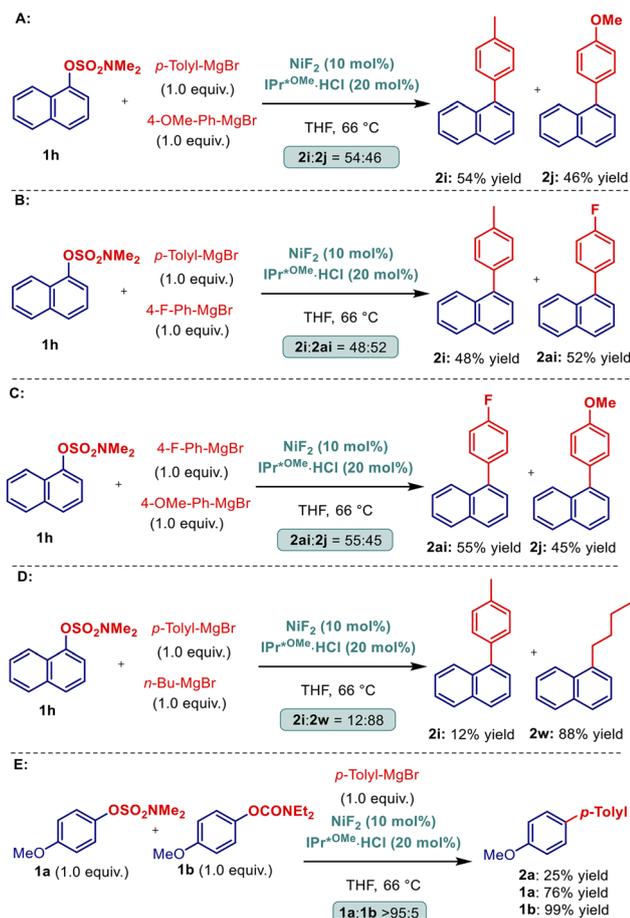
Preliminary mechanistic experiments were conducted to gain insight into the selectivity of the cross-coupling (Schemes 1 and 2). First, intermolecular competition experiments between aryl Grignard reagents established that electron-deficient nucleophiles are preferred in the C(sp²)–C(sp²) cross-coupling (p-Me : p-MeO = 54 : 46, Scheme 1A; p-F : p-Me = 52 : 48, Scheme 1B; p-F : p-MeO = 55 : 45, Scheme 1C), consistent with reductive elimination as a kinetically relevant step. Second, further competition experiments indicated that alkyl nucleophiles cross-couple preferentially (n-Bu : p-Tol =

88 : 12) (Scheme 1D). Furthermore, competition experiments between unactivated aryl sulfamates and aryl carbamates indicated full selectivity for the sulfamate cross-coupling (OSO₂NMe₂ : OCONMe₂ > 95 : 5). This synthetically useful selectivity is consistent with the kinetic experiments (Fig. 2) and is characteristic to the Ni–IPr*^{MeO} catalyst system, while other catalysts typically cannot distinguish between sulfamate and carbamate electrophiles. Finally, isomerization experiments using i-PrMgCl indicated that β-hydride elimination occurs at a rate similar to the cross-coupling (linear : branched = 58 : 48, Scheme 2).

Importantly, scalability experiments demonstrated that the reaction can be readily performed on a gram scale without any modification of the reaction conditions, affording the desired product in 96% yield (Scheme 3).

Furthermore, this approach of C–O cross-coupling can be exploited in the sequential orthogonal cross-couplings using the same Ni–NHC reagent system (Scheme 4). Thus, the C–Br cross-coupling of 6-bromo-2-naphthol afforded the first cross-coupling in the presence of the unprotected hydroxyl group, which was followed by C–O protection with sulfamoyl chloride and C–O cross-coupling in 50% yield.

Finally, although our focus was on establishing an Ni–NHC system for C–O/C–C sulfamate cross-coupling, we are cognizant of the tremendous importance of Buchwald–Hartwig amination methods in pharmaceutical industry and the extreme scarcity of Ni-catalyzed amination methods of C–O electrophiles. Our preliminary studies indicate that the present Ni–IPr*^{MeO} system is also capable of the C–O/C–N Buchwald–Hartwig amination

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Scheme 1 Selectivity studies of Ni–NHC cross-coupling reactions. (A) *p*-Me *vs.* *p*-MeO, (B) *p*-F *vs.* *p*-Me, (C) *p*-F *vs.* *p*-MeO, (D) *n*-Bu *vs.* *p*-Tol, (E) OSO$_2$NMe$_2$ *vs.* OCONMe$_2$.
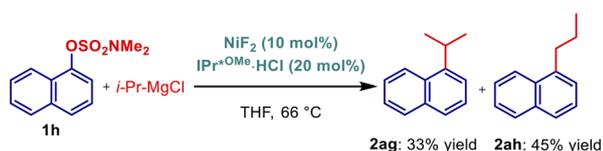
Scheme 2 Ni–NHC-catalyzed cross-coupling/isomerization.
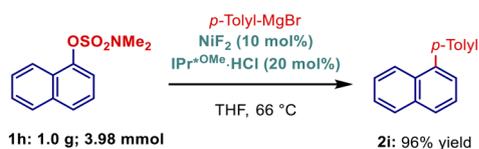
Scheme 3 Gram scale cross-coupling.

of unactivated sulfamates. The order of reactivity (IPr*^{MeO} > IPr* >> IPr) mirrors the findings from the C–O/C–C cross-coupling, indicating a generality of this catalyst system (Scheme 5A). Furthermore, the reaction with sulfamate **1a** (Scheme 5B) unequivocally confirmed that under our conditions the reaction proceeds *via* C–O bond cleavage, without any C–B bond cleavage product.
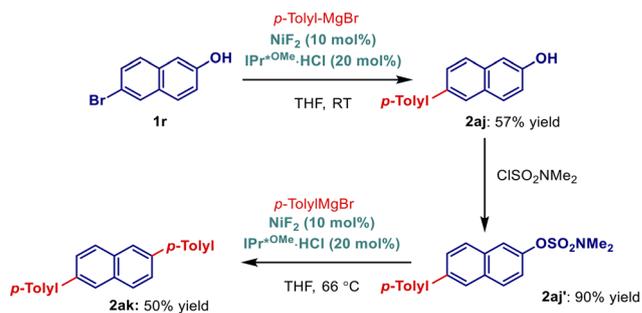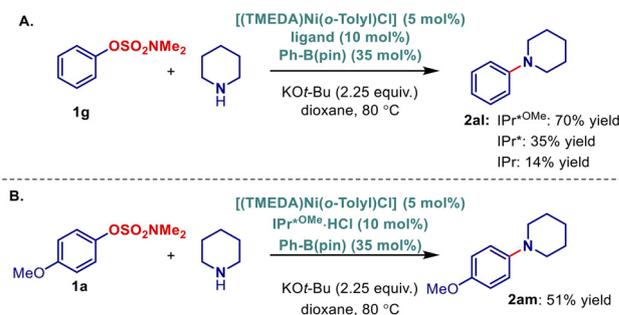

Scheme 4 Sequential cross-coupling *via* Ni–NHC-catalyzed C(sp^2)–C(sp^2) C–O activation.

Scheme 5 Ni–NHC catalyzed Buchald–Hartwig amination: (A) using Ph–OSO$_2$NMe$_2$, (B) using MeO–Ph–OSO$_2$NMe$_2$.

In summary, although C–O electrophiles represent a powerful orthogonal class of substrates for cross-coupling reactions, there is a shortage of efficient Ni-catalyzed systems for the cross-coupling of bench-stable, readily accessible and orthogonal C–O electrophiles. In this manuscript, we have reported the C(sp^2)–C(sp^2) and C(sp^2)–C(sp^3) Kumada–Coriu and Buchwald–Hartwig cross-coupling of aryl sulfamates enabled by sterically-demanding and electron-rich *N*-heterocyclic carbenes. Crucially, this study identified sulfamates as the most reactive C–O electrophiles enabled by a combination of sterically-demanding IPr*^{OMe} featuring *ortho*-diphenyl wingtip substitution. Comparative and kinetic studies demonstrate that electron-rich, sterically-demanding *N*-heterocyclic carbenes show high reactivity for the challenging C–O cross-coupling obviating common issues, such as hydrolysis, homocoupling and unselective C–O and S–N cleavages. The generality of the catalyst system has been demonstrated by the range of C(sp^2)–C(sp^2) and C(sp^2)–C(sp^3) C–O/C–C cross-couplings as well as by the C–O/C–N amination, where IPr*^{OMe} outperforms less electron-donating and less sterically-demanding carbenes. The broad availability to NHC ligands with *ortho*-diphenyl wingtip substitution represents an attractive entryway for the development of Ni-catalyzed cross-coupling processes for academic and industrial research.

Conflicts of interest

There are no conflicts to declare.

Data availability

Acknowledgements

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