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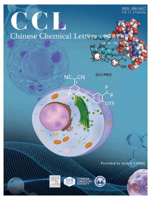

Fluoride-promoted Ni-catalyzed cyanation of C–O bond using CO_2 and NH_3

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ABSTRACT

The selective conversion of CO_2 and NH_3 into valuable nitriles presents significant potential for CO_2 utilization. In this study, we exploited the synergistic interplay between silicon and fluoride to augment the nickel-catalyzed reductive cyanation of aryl pseudohalides containing silyl groups, utilizing CO_2 and NH_3 as the CN source. Our methodology exhibited exceptional compatibility with diverse functional groups, such as alcohols, ketones, ethers, esters, nitriles, olefins, pyridines, and quinolines, among others, as demonstrated by the successful synthesis of 58 different nitriles. Notably, we achieved high yields in the preparation of bifunctionalized molecules, including intermediates for perampanel, derived from *o*-silylaryl triflates, which are well-known as aryne precursors. Remarkably, no degradation of substrates or formation of aryne intermediates were observed. Mechanistic studies imply that the formation of pentacoordinated silyl isocyanate intermediates is crucial for the key C–C coupling step and the presence of vicinal silyl group in the substrate is beneficial to further make this step kinetically favorable.

Carbon dioxide (CO_2) is an attractive C1 source for the construction of fine chemicals and valuable drug products. The catalytic C–C coupling with CO_2 has currently received considerable attention from the scientific community [1–4]. However, the activation and utilization of CO_2 are still problematic due to its inherent thermodynamic stability and/or kinetic inertness. Many transition metals based catalytic systems have been developed for selective CO_2 transformation [5–12].

On the other hand, nitriles are key synthons used in the synthesis of aldehydes, ketones, carboxylic acids, alcohols, amides, amines, and heterocycles [13–15]. In the past decades, preparation of cyano-containing compounds using transition metal catalysts developed rapidly. And the direct employment of metal/metalloid-bound cyanides or the *in situ* generation of cyanide ion, such as KCN [16–18], $Zn(CN)_2$ [19–21], TMSCN [22,23], acetone cyanohydrin [24,25], is often involved. Higher activity was demonstrated by these cyanide reagents. Nonetheless, catalyst deactivation was usually observed because of the fast liberation of cyanide ligands, causing a limited substrate scope [26–28].

In this regard, the general cyanation of aryl triflates is rarely investigated [29] while phenol analogues exist extensively in bulk chemicals, natural products and pharmaceuticals. In 2010, Kwong *et al.* [30] reported palladium-catalyzed cyanation of aryl mesylates. Here, only very limited examples were suitable for utilizing $K_4[Fe(CN)_6]$ due to the heterogeneous nature of the reaction mixture. To address these concerns, Morandi [31] employed butyronitrile as a cyanide (CN) source to achieve nickel-catalyzed cyanation of aryl triflates. And different non-metallic cyano-group sources including acetonitrile, 2-methyl-2-phenylmalononitrile (MPMN) and morpholinoacetonitrile [32–35] were then utilized in transition metal catalyzed cyanation reaction of phenol analogues (Scheme 1a).

Meanwhile, peculiar fluoride effect has already been proved critical on the carboxylation with CO_2 [36,37], seeming mainly to stabilize intermediates. Based on the above reports and the continuation of our interest on the catalytic cyanation using CO_2 [38,39], we report here the cyanation of C–O bonds with CO_2 and NH_3 starting from the investigation of fluoride effect (Scheme 1b).

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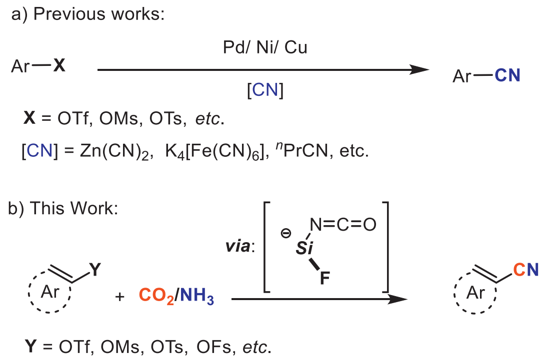
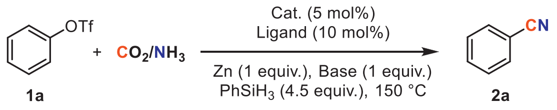


Scheme 1. Catalytic cyanations of C(sp^2)–O bond with different cyano sources.

Table 1
Optimization of reaction conditions.[a]



Entry	Cat.	Ligand	Base	Yield (%)[b]
1	$NiBr_2$	Triphos	None	n.d.
2	$NiBr_2$	Triphos	KF	24
3	NiF_2	Triphos	KF	61
4	$PdCl_2$	Triphos	KF	31
5	$CoCl_2$	Triphos	KF	trace
6	NiF_2	dppe	KF	79
7	NiF_2	dppp	KF	68
8	NiF_2	PPh_3	KF	73
9	NiF_2	P(*p*-F-Ph)$_3$	KF	92
10	NiF_2	P(*p*-F-Ph)$_3$	NaF	71

Triphos: bis(2-diphenylphosphinoethyl)phenylphosphine, dppe: 1,2-bis(diphenylphosphino)ethane, dppp: 1,3-bis(diphenylphosphino)propane, P(*p*-F-Ph)$_3$: tris(*p*-fluorophenyl)phosphine, $PhSiH_3$: phenylsilane, NMP: 1-methy-2-pyroidinone.

[a] Reaction conditions: **1a** (0.1 mmol), NMP (0.5 mL), CO_2/NH_3 (4/6 mL) in 10 mL sealed tube, 8 h.

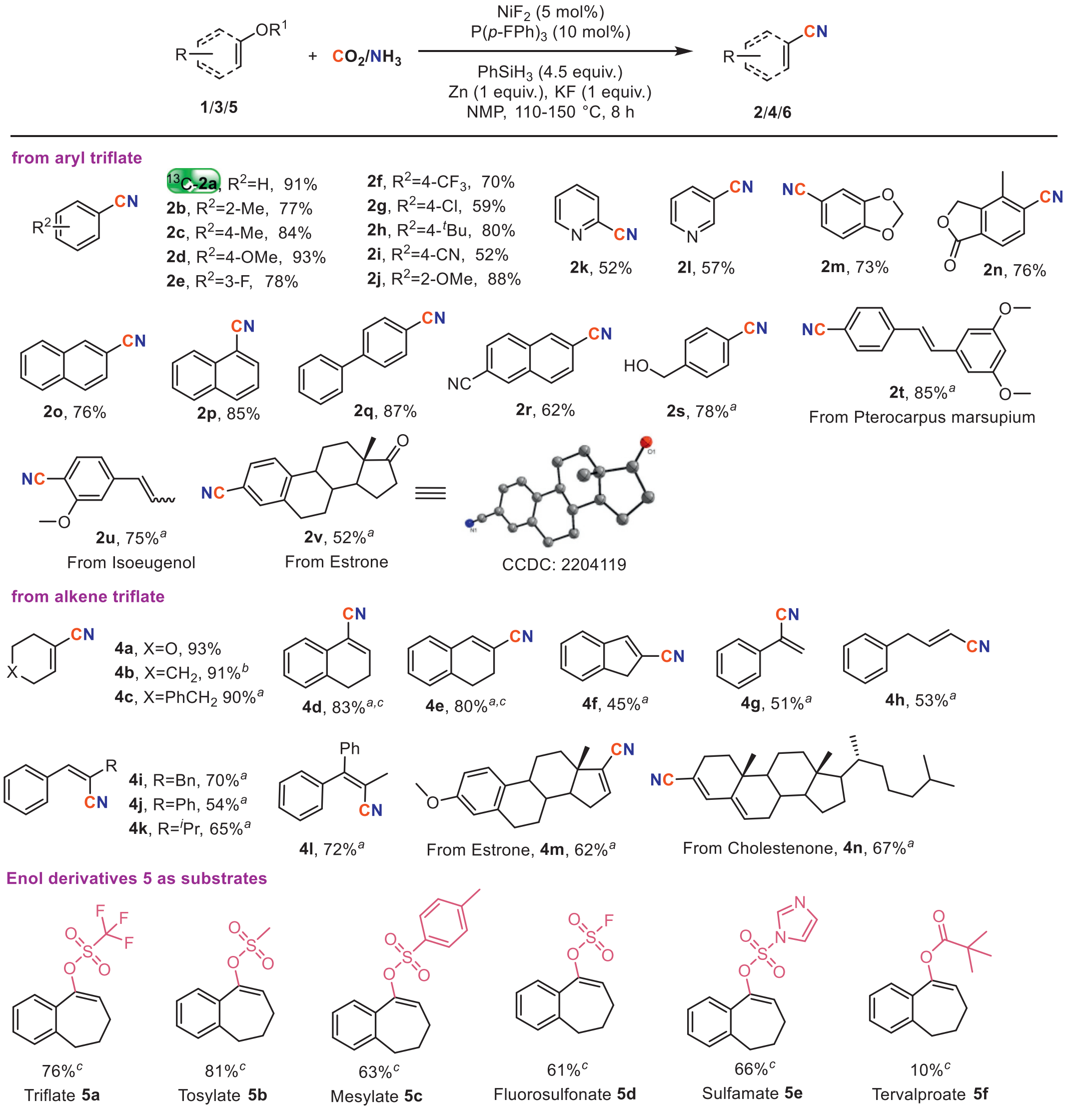
[b] GC yields using *n*-dodecane as the internal standard.

Phenyl trifluoromethanesulfonate **1a** was chosen as the model substrate to investigate catalytic cyanation with CO_2 and NH_3 (Table 1). Firstly, KF was demonstrated exceptional efficacy in this transformation since the target product **2a** was not detected without F source. And 24% yield of **2a** could be obtained when KF was added (entry 2). Various metal catalysts were then examined (entries 2–5). NiF_2 was the optimal choice, likely due to favorable C–O bond insertion facilitated by the small anion radius of fluorine. Surprisingly, evaluation of ligands indicated that simple PPh_3 provided an almost comparable yield of 73% compared to bidentate or multidentate ligands (entries 6–8). It was recognized that electron-deficient phosphine ligands exhibited somewhat distinctive effects on the C–C coupling reaction [40–44]. And a similar phenomenon was noted in our system. Tris(*p*-fluorophenyl)phosphine (P(*p*-F-Ph)$_3$) was found to be superior to other ligands, yielding **2a** with 92% yield (entry 9). And a modest yield was obtained when NaF was used instead of KF (entry 10).

Based on the encouraging results mentioned above, the versatility and applicability of this system were further investigated under the optimized conditions, as depicted in Scheme 2. An array of substrates bearing electron-donating groups (alkyl, OMe, naphthyl) as well as electron-withdrawing groups (F, Cl, CF_3, CN) underwent the cyanation reaction smoothly. ^{13}C-labeled nitrile ^{13}C-**2a** was conveniently obtained with $^{13}CO_2$ (91% yield). And triflates incorporating a series of different heterocyclic patterns, including benzodioxole, phthalide, and pyridine were tested and the products **2k**-**2n** were isolated with high yields. In addition, the cyanation of polycyclic compounds **1o**-**1p** took place as expected, affording the corresponding arylnitriles with satisfactory yields (76%–85%). It is noteworthy that alcohol group was also tolerated under the system, providing the desired nitrile **2s** in 78% yields. We then proceeded to assess the applicability in modifying bioactive intermediates. Specifically, cyanation of pterocarpus marsupium derivative **1t** provided (*E*)-4-(3,5-dimethoxystyryl)benzonitrile **2t** in excellent yield (85%). Isoeugenol derivative was successfully cyanated to produce **2u** in good yield (75%). And the functionalized nitrile **2v** could be readily prepared from estrone derivative, with 52% isolated yield attained.

Vinyl triflates were found compatible, allowing access to important synthon α,β-unsaturated nitriles. A series of substrates exhibiting different electronic properties reacted delicately to furnish desired products **4a**-**4n** in moderate to excellent yields (45%–93%). For example, oxyheterocyclohexene triflate **3a** was converted to **4a** in 93% yield. Cyanated cyclohexene ring products **4b** and **4c** were both obtained with high yields. Cycloalkenes triflates **3d**-**3f** resulted in similarly acceptable yields (45%–83%). Cyanation of external olefin **3g** gave medium yield (51%). When linear vinyl triflate **3h** was used as the substrate, cyanated product **4h** was formed as the major product. It was found that sterically hindered substituent on α-position of the C–O bond gave rise to relatively low yields **4i**-**4k**. And the reaction also occurred smoothly when trisubstituted alkene substrate was employed, providing cyanation product **4l** in decent yield (72%). Moreover, derivatives **3m**-**3n** from steroid hormones estrone and cholestenone were successfully cyanated, resulting in corresponding nitriles **4m** and **4n** with yields of 62% and 67%, respectively. These results not only highlighted the preferable performance of the catalytic system in accomplishing cyanation but also demonstrated the generality of this vinyl triflates cyanation reaction. Furthermore, the cyanation of other enol derivatives **5a**-**5f** with different *o*-protecting groups were investigated under the optimized conditions. It was found that alcohols substituted with OTf (**5a**), OMs (**5b**), OTs (**5c**) as well as OFs (**5d**) underwent the cyanation reaction smoothly. In addition, vinyl imidazole sulfonate **5e** was a suitable coupling partner. And, vinyl trimethylacetate **5f** was also be compatible with this catalytic system, albeit with a low yield of 10%.

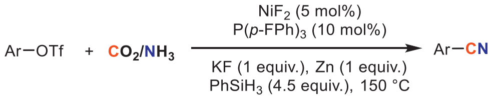
Control experiments were devised and conducted to gain insight into this transformation. In the presence of Et_3SiH, no nitrile product **2a** was observed while triethylsilyl isocyanate could be detected by GCMS (Scheme 3a and Fig. S3 in Supporting information). So, the formation of active silyl isocyanates were considered as the possible intermediate in this reaction [45]. In addition, the use of amidate metal as the reaction intermediate has been extensively investigated, particularly in the synthesis and conversion of amides [46–51]. In our prior research, we observed that amides could be efficiently converted to nitriles using HBpin [52]. Consequently, we hypothesized that the coupling and deoxygenation processes involving isocyanate could potentially be achieved through synergistic silane/nickel catalysis mediated by amidate metal intermediates. *N*-Silyl benzamides were prepared as substrates to test the feasibility of this proposal (Scheme 3b). No cyanated product was detected with nickel and ligand only (Scheme 3b, entry 1). And benzonitrile was formed in modest yield in the presence of cesium salt (entries 2 and 3). These results indicated that the alkali metal promoted the deoxygenation of amide and F^- served as the accelerator *via* Si-F interaction. Surprisingly, the yield of benzonitrile can reach 60% under similar standard conditions (entry 4). In contrast, no benzonitrile was formed under the same conditions when Si in N-silyl benzamides was replaced by C (Scheme 3b, entries 5–8). These results imply that the cyanation through an *in situ* formation and transformation of silyl amide moiety is feasible.



Scheme 2. Reaction conditions: substrate (0.1 mmol), CO_2/NH_3 (4/6 mL) in 10 mL sealed tube, NMP (0.5 mL) at 150 °C for 8 h. Isolated yield. [a] dppe instead of P(p-F-Ph)$_3$. [b] NMR yield with 1,1,2,2-tetrachloroethane as internal standard. [c] 110 °C.

Given the importance of Si-containing nitriles, we then turned attention to exploring cyanation of the substrates with silyl group on the basis of our discovery. *o*-Silylaryl triflates, recognized as Kobayashi's precursor, have been extensively employed in aryne chemistry due to their ready availability and facile generation of arynes through fluoride-induced 1,2-elimination [53,54]. Therefore, we propose precise control of chemoselectivity through the fluorine-silicon chelation with *o*-silylaryl triflate. To our delight, nitrile product **8a** was formed in 81% yield under standard conditions (Scheme 4a). Then, cyanation of **7a** without silane was conducted. No desired product was detected despite the high conversion while arylamines were the main byproducts, which indicated the formation of arynes from **7a** due to the activation of fluoride. And hydrosilanes might play an important role in this system, as they could not only act as reduction reagents but also serve as accelerating agents by promoting the cleavage of C–OTf bond basing on the high fluorophilicity [55–59]. Thus, aryl triflates with silyl substituent were also tolerant.

Table 2
Control experiments for F-Si interaction.[a]

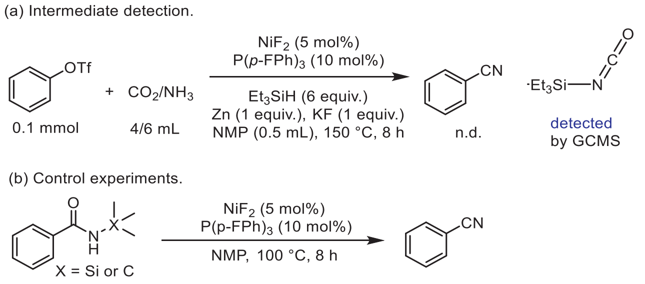


Entry	Deviation from optimal conditions	Yield (%)[b]	
		8a	2a
1	None	81	92
2	No KF	n.d.	47
3	KI instead of KF	8	56
4	ZnF_2 instead of KF	47	68
5	$NiCl_2$ instead of NiF_2	29	35
6	$NiCl_2$ instead of NiF, no KF	n.d.	n.d.

[a] Reaction conditions: Substrate (0.1 mmol), NMP (0.5 mL), CO_2/NH_3 (4/6 mL) in 10 mL sealed tube, 8 h.

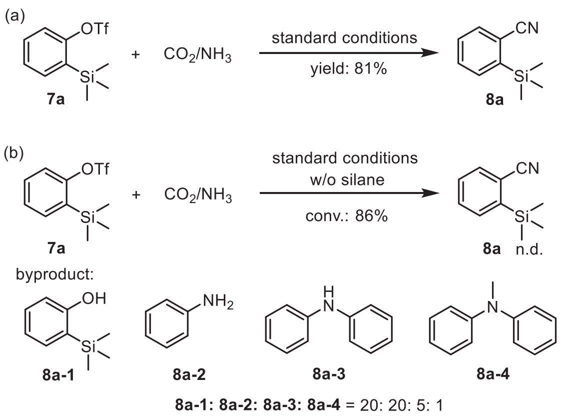
[b] GC yields using *n*-dodecane as the internal standard.

To demonstrate the key role of Si–F interaction, a series of control experiments were conducted (Table 2). When **7a** used as the substrate, desired product **8a** was not detected under otherwise identical conditions but without KF (entry 2). Only 8% yield was obtained with KI instead of KF while ZnF_2 delivering **8a** in 47% yield (entries 3 and 4). And $NiCl_2$ instead of NiF_2 as the catalyst yields the cyanation product in obviously reduced yield. No prod-



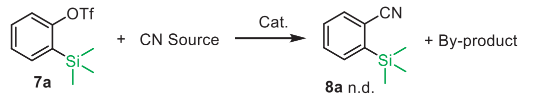
Entry	X	Condition	Yield (%)
1	Si	None	n.d.
2	Si	Cs_2CO_3 (1 equiv.)	7
3	Si	CsF (1 equiv.)	33
4	Si	$PhSiH_3$ (3 equiv.), Zn (1 equiv.), KF (1 equiv.)	60
5	C	None	n.d.
6	C	Cs_2CO_3 (1 equiv.)	n.d.
7	C	CsF (1 equiv.)	n.d.
8	C	$PhSiH_3$ (3 equiv.), Zn (1 equiv.), KF (1 equiv.)	n.d.

Scheme 3. Mechanistic probe for the reaction. (a) Intermediate detection. (b) Control experiments. Reaction scale (0.1 mmol), NMP (0.5 mL).



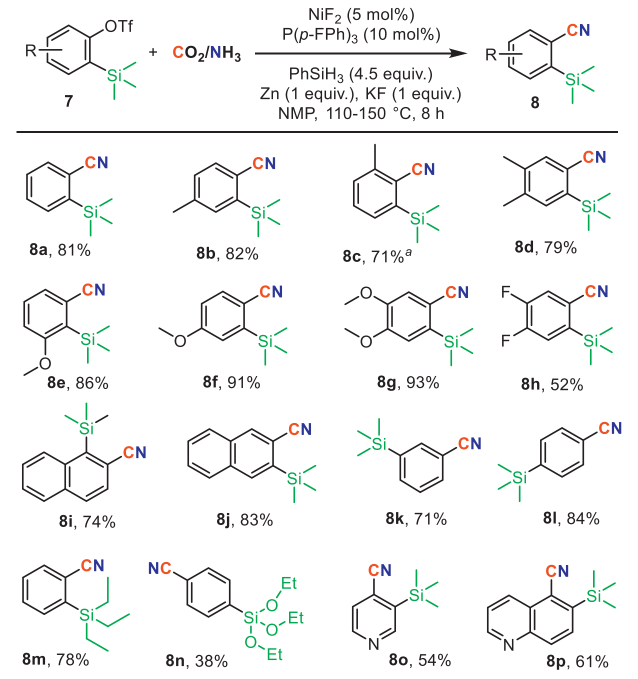
Scheme 4. Cyanidation of *o*-silylaryl triflate **7a**.

Table 3
Results by using the conditions of the reported systems.^{a}



Entry	CN Source	By-product	Ref.
1	Morpholinoacetonitrile (2.0 equiv.)	Phenol	[32]
2	Butyronitrile (2.0 equiv.)	Phenol	[31]
3	$Zn(CN)_2$ (0.8 equiv.)	*o*-(Trimethylsilyl)-phenol	[60]
4	4-Cyanopyridine noxide (1.3 equiv.)	–	[61]
5	MeCN (solvent)	Phenol	[35]
6	MPMN (1 equiv.)	–	[34]

[a] Reaction conditions followed the corresponding reference and GC yields using *n*-dodecane as the internal standard.



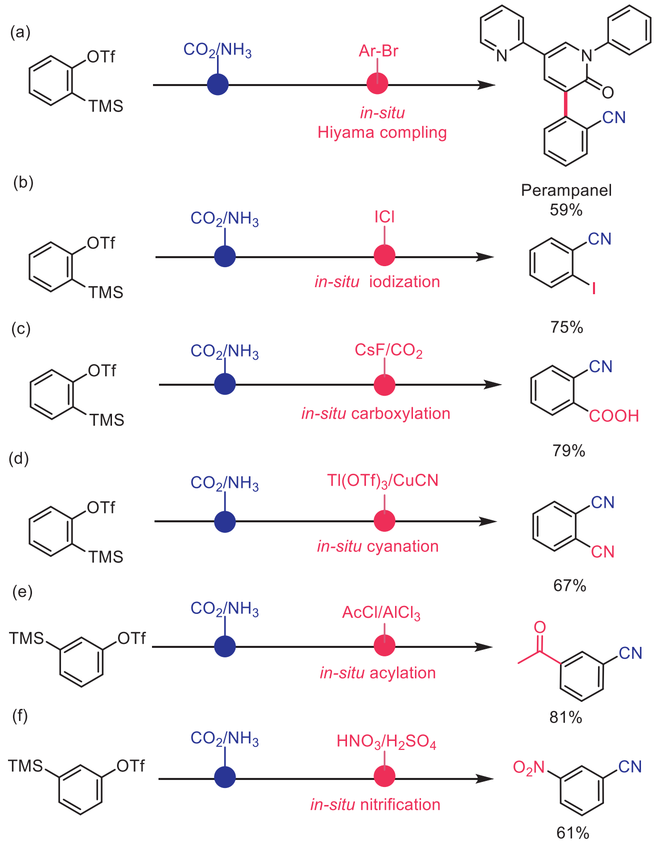
Scheme 5. Reaction conditions: substrate (0.1 mmol), CO_2/NH_3 (4/6 mL) in 10 mL sealed tube, NMP (0.5 mL) at 150 °C for 8 h. Isolated yield. ^{a} dppe instead of P(*p*-F-Ph)$_3$.

uct was detected without F source (entry 6). These results revealed that fluoride plays a crucial role in the reaction pathway. Similar results were observed when **1a** was used as the substrate. Standard conditions resulted in a satisfactory reaction with 92% yield. Visibly lower yield of **2a** was detected without KF. And ZnF_2 furnished **2a** in an acceptable yield (entry 4, 68%) while $NiCl_2$ was less reactive (entry 5, 35%). No target product was detected without F source as well (entry 6). These results implied that Si–F interaction also has a promoting effect on the cyanation for substrates.

A series of comparative experiments were then conducted using other established Ni-catalyzed cyanation systems utilizing various cyano sources (Table 3). The optimized reaction conditions reported in the literature were directly employed without alteration. None of these previously known catalytic systems yielded the desired cyanation product, underscoring the distinct advantages of our approach. Partial breakage of the C–Si bond in the substrate occurred due to hydrodesilylation during the reaction process. Additionally, phenol was occasionally detected due to the hydrolysis of triflates.

We further explored the scope of this cyanation reaction with a variety of silylaryl triflate (Scheme 5). Gratifyingly, a variety of aryne precursors bearing diverse substituents were well tolerated, yielding the corresponding products **8a**-**8p** with moderate to good yields. Functional groups such as ethers **7e**-**7g**, fluorides **7h**, and naphthalene **7i**-**7j** were compatible. Substrates bearing TMS groups at the *meta*- or *para*-position of the C–O bond **7k**-**7l** were also amenable to this transformation, affording the respective nitriles **8k** and **8l** in good yields. Aryl triflates with triethylsilyl **7m** and triethylsiloxy groups **7n** resulted in moderate yields, with benzonitrile detected as the main by-product derived from hydrodesilylation. Heterocycle-containing substrates such as pyridine **7o** and quinolone **7p** also exhibited favorable reactivity, providing heteroaryl nitriles in comparable yields.

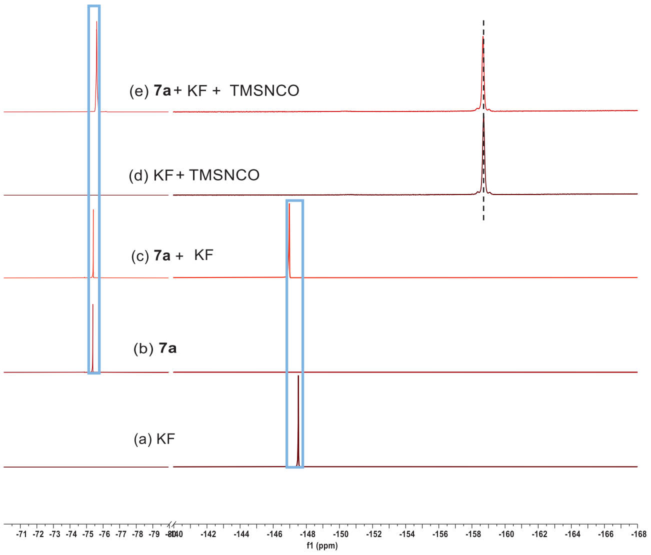
Since organosilicon compounds have been found to be versatile motif in organic synthesis and materials science, this catalytic system provides a good opportunity for fortifying the cyano-containing products. Perampanel (brand name: Fycompa), which is the first noncompetitive AMPA (α-amino-3-hydroxy-5-methyl-4-isoxazole-propionic acid) receptor antagonist authorized by FDA [62–64], could be conveniently obtained *via* Pd-catalyzed Hiyama reaction [65–67] with a synthetically useful yield (Scheme 6a). Then sequential cyanation and iodination was realized by adding iodine monochloride [68,69], affording 75% yield of 2-cyanophenyliodobenzene (Scheme 6b). The optimized conditions of carboxylation reported in the literature were applied without



Scheme 6. Synthetic utility. Conditions: (a) CuF_2 (10 mol%), $Pd_2(dba)_3$ (1.0 mol%), tris(2,4,6-trimethoxyphenyl)phosphine (4.0 mol%), CsF (1.2 equiv.) DMI, 120 °C, 17 h. (b) ICl (2.2 equiv.), $CHCl_3$, reflux, 6 h. (c) CsF (1 equiv.), CO_2 (1 atm.), DMF, 60 °C, 1 h. (d) $Tl(OTf)_3$ (1.1 equiv.), CuCN (4 equiv.), MeCN, reflux, 17 h. (e) AcCl (2 equiv.), $AlCl_3$ (2 equiv.), CS_2, room temperature, 7 h. (f) HNO_3, H_2SO_4, 0 °C to room temperature.

modification [70–72]. And, satisfactory selectivity for benzoic acid was achieved (Scheme 6c). In addition, phthalonitrile could also be obtained with modest yield (67%) by using the reported method (Scheme 6d) [73–75]. Furthermore, well known acylation or nitration methods could be employed directly, and the corresponding products were attained with acceptable yields (81% and 61% respectively).

To elucidate the Si-F interaction modes in this transformation, a series of ^{19}F NMR experiments were conducted (Scheme 7). All chemical shifts were recorded at 298 K in methanol unless otherwise specified. Notably, the chemical shift value of KF shifted significantly upfield upon addition of TMS-NCO (trimethylsilylisocyanate) (Schemes 7a and d). This outcome indicates the presence of a bonding-like effect between the fluorine (in KF) and silicon (in TMS-NCO), which was further supported by the ^{29}Si NMR spectra of TMS-NCO (Figs. S7a and d in Supporting information, downfield). HRMS of the mixture of TMS-NCO and KF was carried out at room temperature, and a peak at $m/z = 134.0434$ was observed and assigned to their adduct. A slight downfield peak of KF was observed (Schemes 7a–c) when exposed to substrate **7a**, attributed to a static inductive effect. Furthermore, when **7a**, KF, and TMS-NCO were combined, both KF and **7a** exhibited upfield shifts in chemical shift (Scheme 7e), accompanied by a notable downfield shift in the ^{29}Si NMR spectrum of TMS-NCO (Fig. S7e in Supporting information). These shifts in chemical shift values suggest the emergence of a bonding-like effect between the fluorine (in KF) and silicon (in TMS-NCO) through transient pentacoordinated silicon anion species, while the interaction between fluorine (in KF) and silicon (in **7a**) is likely governed by a spatial electrostatic effect.

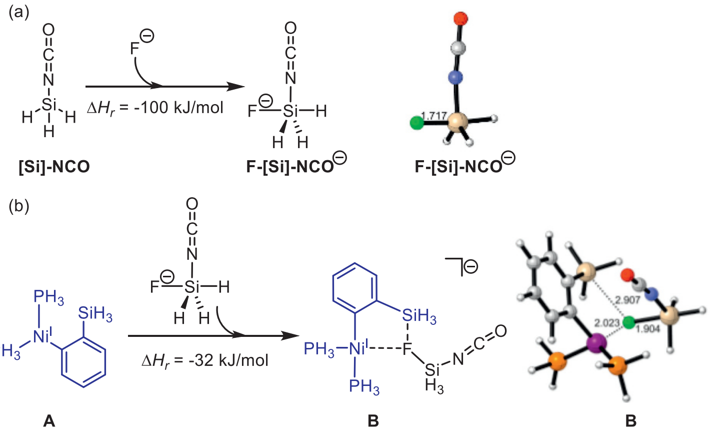


Scheme 7. ^{19}F NMR experiments.

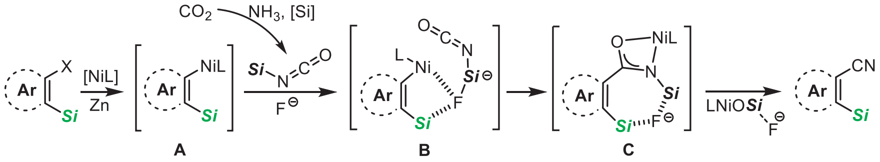
Besides, DFT calculations were carried out to understand the important promotion effect of F-Si interaction in this work (Scheme 8). As a simplification, we used PH_3 and SiH_3 to model the $P(p\text{-F-Ph})_3$ ligand and $SiMe_3$ group, respectively. The optimized 3D structure was displayed by CYLview program. Scheme 8a shows that the reaction between F^- and silyl isocyanate, forming a pentacoordinate Si adduct, has a reaction enthalpy of −100 kJ/mol, indicating that F^- effectively stabilizes the highly reactive silyl isocyanate species. Furthermore, the interaction of pentacoordinate anionic silyl isocyanate F-[Si]-NCO^- with Ni complex of **A** to form complex **B** has a reaction enthalpy of −32 kJ/mol, highlighting the strong electrostatic interactions between F^- and Ni as well as the SiH_3 of **A** with the F–Ni and F–Si distance of 2.023 and 2.907 Å, respectively (Scheme 8b).

Based on both experimental results and literature reports [76], the reaction pathway for *o*-silylaryl triflate is proposed, as illustrated in Scheme 9. Initially, nucleophilic Ni(I) species **A** is formed in the presence of zinc powder and silane (refer to Supporting information). Simultaneously, the fluoro-silicon adduct is produced through the capture of *in-situ* generated silyl isocyanate from CO_2 and NH_3 by fluoride, owing to its robust affinity. This adduct is subsequently attracted by the intrinsic silyl group in species **A**, leading to the formation of five membered ring species **B**. Then, the nickel-carbon insertion process, involving an intramolecular-like nucleophilic attack, occurs readily. Consequently, amidate nickel species **C** is formed, accompanied by changes in the bonding strength between F and Si. Further transformation leads to the desired product through a conceivable silyl N-to-O migration, releasing the fluoride-attached nickel silanoxy.

In summary, we have developed an innovative approach for the nickel-catalyzed reductive cyanation of aryl pseudohalides, utilizing CO_2 and NH_3 as the carbon and nitrogen sources, respectively. This system exhibits a wide substrate scope with excellent tolerance to various functional groups. We successfully implemented selective relay bifunctionalization of silyl-containing compounds, including aryne precursors. The F-Si interactions might play dual roles: 1) formation of the penta-coordinated fluoro-silicon adduct through the capture of *in-situ* generated silyl isocyanate by fluoride; 2) for substrates with vicinal silyl group, further making coupling step kinetically favorable due to the inherent affinity between F and Si. Through a carefully crafted Si–F–Si interaction model, we achieved excellent chemo-selectivity by modulating the strength of the F-Si bond. Furthermore, the practical utility of this catalytic



Scheme 8. (a) The reaction between F^- and silyl isocyanate with formation of F-[Si]-NCO. (b) The interaction of complex **A** and F-[Si]-NCO^-.



Scheme 9. Proposed reaction pathway for *o*-silylaryl triflate.

system was demonstrated through the modification of biologically active compounds.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yang Li: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation. **Yanan Dong:** Writing – original draft, Funding acquisition, Validation, Supervision, Investigation, Conceptualization. **Zhihong Wei:** Writing – original draft, Supervision, Software. **Changzeng Yan:** Supervision, Resources, Project administration. **Zhen Li:** Data curation, Writing – review & editing. **Lin He:** Resources, Project administration, Funding acquisition. **Yuehui Li:** Writing – original draft, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110206.

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