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Redox Neutral Radical-Relay Cobalt Catalysis toward C−H Fluorination and Amination

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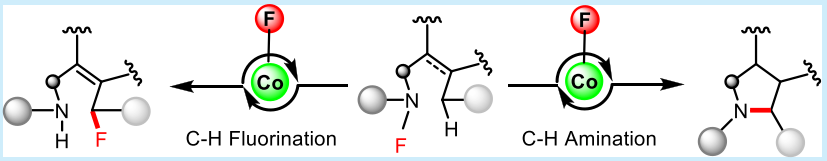


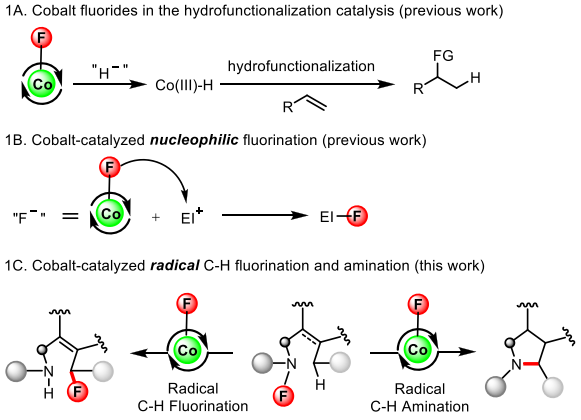
ABSTRACT: A redox neutral radical-relay cobalt-catalyzed intramolecular C−H fluorination of *N*-fluoroamides featuring the in situ formed cobalt fluorides as the latent radical fluorinating agents is reported. Moreover, the reactivity of such a cobalt catalysis could be diverted from C−H fluorination to amination by engineering substrates' conformational flexibility. Preliminary mechanistic studies (UV−vis spectroscopy, cyclic voltammetry studies and DFT calculations, etc.) support the reaction proceeding a redox neutral radical-relay mechanism.

The incorporation of fluorine atoms into organic molecules is of great significance due to the unique properties of fluorine element in life[1,2] (including pharmaceuticals and agrochemicals) and material sciences.[3] In this contest, recent advances of selective fluorine incorporation[4] including nucleophilic fluorination,[5] electrophilic fluorination,[6] and radical fluorination[7] have dramatically enriched the synthetic chemists' tools for challenging carbon−fluorine bond formation. Despite those advances, complementarily mild and selective late-stage fluorination[8] methods are still highly demanding.

Among structurally diverse metal fluorides, organometallic cobalt fluorides[9] have drawn considerable attention of chemists recently. Though bearing a fluorine atom, such complexes are most frequently employed in the hydrofunctionalization of olefins[10] serving as nonfluorinating agents (Scheme 1A). Typical synthetic route to those complexes requires a *N*-fluoropyridinium salt as oxidant. Once formed, such species are poised to undergo a facile reduction with silane generating formal Co^{III}−H species,[11] which are capable to facilitate the hydrogen atom addition across alkenes followed either by a radical trapping,[12] an oxidation to carbocation readily for downstream nucleophilic addition[13] or a cross-coupling[14] to their corresponding hydrofunctionalized products.

The adoption of organometallic cobalt fluorides as the latent fluorinating agents is much less explored.[9a] Notable advances of using cobalt fluorides as nucleophilic fluorinating agents have been comprehensively investigated by Doyle and co-workers in the enantioselective nucleophilic ring opening of epoxides[15] and aziridines[16] (Scheme 1B). Moreover, Baker and co-workers have successfully employed the in situ generated cobalt fluorides in the acyl chloride/fluoride metathesis.[17] The use of cobalt fluorides as the radical fluorinating source, however, is elusive thus seldomly reported[18] despite the analogously rich precedents of organometallic fluorides including Mn,[19] Ag,[20] Cu,[21] Fe,[22] and so on.[23]

Scheme 1. Organometallic Cobalt Fluorides in Catalysis



Herein, we explore the organometallic cobalt fluorides as latent radical fluorinating agents in the late-stage intramolecular fluorination (Scheme 1C, left). This protocol allows highly selective fluorine-atom incorporation forming the valuable functionalized benzylic fluorides[24] under mild conditions. Interestingly, engineering of substrate's conforma-

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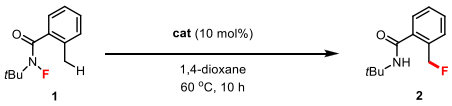
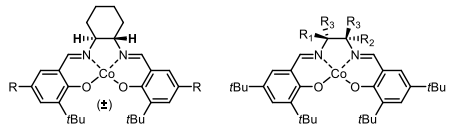
tional flexibility diverts the reaction pathway from C−H fluorination to amination delivering another biologically important pyrrolidine scaffold (Scheme 1C, right). Preliminary mechanistic studies (including UV−vis spectroscopy, cyclic voltammetry studies and DFT calculations) support the in situ generated organometallic cobalt fluorides being key intermediates in such a redox neutral radical-relay mechanism.

N-tert-Butyl fluoroamides, prepared and employed by Cook and co-workers pioneeringly in the iron-catalyzed C−H fluorination,[25] exhibit much higher air, moisture, and thermal stability compared with their haloamide analogues.[26] Since then, *N*-fluoroamides have been intensively investigated in the Cu-catalyzed C−H functionalization.[27] However, in those transformations they only served as latent amidyl radicals leaving the precious fluorine element to byproducts. We anticipate the use of proper cobalt catalyst would take the advantage of *N*-fluoroamides not only as amidyl radicals but also fluorine surrogates in a redox neutral radical-relay manner. Indeed, we found 10 mol % of Jacobsen Co(salen) complex **3**[28] in 1,4-dioxane as solvent at 60 °C efficiently catalyzed the intramolecular fluorine-relay of fluoroamide **1** forming C−H fluorinated product **2** (92% NMR yield and 93% isolated yield, entry 1, Table 1). A control experiment in the absence of

Table 1. Reaction Conditions Optimization



entry	cat.	yield[b] (%)
1	3	92 (93)[c]
2		<5
3[d]	3	78
4[e]	3	21
5	4	60
6	5	75
7	6	<5
8	7	48
9	8	54
10	9	70

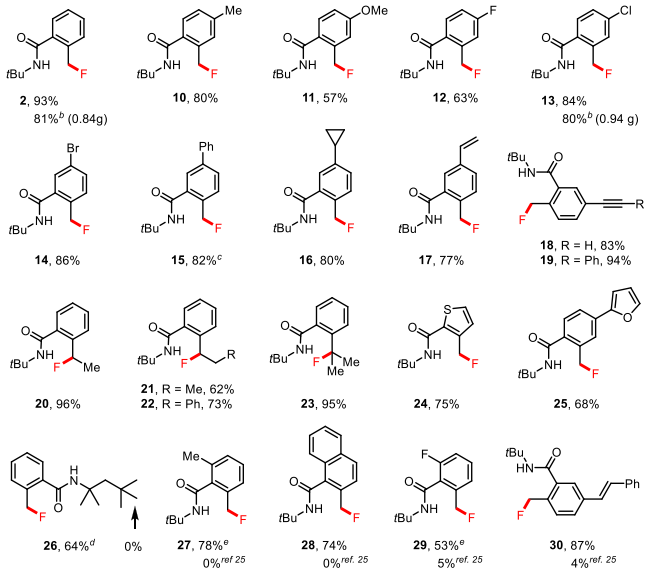


[a]Reaction conditions: **1** (0.2 mmol, 1 equiv), **3** (0.02 mmol, 10 mol %), 1,4-dioxane (*c* 0.05M), 60 °C, 10 h. [b]Yield determined by ^{19}F NMR analysis using trifluoromethoxyl benzene as the internal standard. [c]Isolated yield. [d]5 mol % of **3**. [e]1 mol % of **3**.

cobalt showed no conversion (entry 2), while reducing catalyst loading to 5 mol % (or 1 mol %) significantly depressed the reaction yields to 78% (or 21%), suggesting a radical chain process is not likely (entries 3, 4). Co^{III}(salen)-Cl **4** was also able to catalyze such a fluorine-relay event albeit in a diminished yield (entry 5). Steric and electronic properties of substituents at the salen scaffold were also evaluated showing the Co(salen) complex **3** with highest catalytic efficiency (entries 6−10).

With the optimal conditions in hand, we then evaluated the scope and limitation of this protocol (Scheme 2). Substrates

Scheme 2. Substrate Scope of the Co-catalyzed C−H Fluorination



[a]Reaction conditions: fluoroamide (0.2 mmol, 1 equiv), **3** (0.02 mmol, 10 mol %), 1,4-dioxane (c 0.05M), 60 °C, 10 h unless otherwise noted. Yield of purified product. [b]Gram-scale reaction, 48 h. [c]3 h. [d]Dichloromethane as solvent. [e]20 mol % of **3** used.

with electron-donating (**10**, **11**) or -withdrawing (**12**−**15**) substituents all proceeded smoothly (57−86%). This reaction could also be performed in a gram-scale manner in good yields (81% for **2** and 80% for **13**, respectively). Cyclopropane (**16**), alkene (**17**) and alkyne (**18**, **19**) functionalities were all well tolerated. It is worthy of note that severe polymerization of the styrene moiety in the preparation of **17**, a significant side reaction in Fe-catalyzed C−H fluorination,[25] was not observed under current conditions. Besides primary C−H bonds, secondary (**20**−**22**) and tertiary (**23**) C−H bonds could also be efficiently fluorinated. Heterocycle incorporated substrates including thiophene (**24**) and furan (**25**) were proved to be good candidates for this fluorine-relay process, too. When there were competing C−H bonds available, the 1,5-HAT (hydrogen-atom transfer) and sequential fluorination selectively occurred at the activated benzylic C−H position (**26**). To be noted, our protocol is capable to provide facile entries to challenging fluorinated compounds (**27**−**30**) previously unsuccessful in the iron catalysis[25] (53−87%). It is worth noting that though most substrates in Scheme 2 underwent the desired transformation smoothly, an appreciable amount of the defluorinated amide formation was observed for compounds **27**−**29**. In addition, a multitude of functionalities (including primary alcohol, epoxide, nitrile, aldehyde, ethyl cinnamate, quinoline, etc.) were also highly compatible with this protocol but not carboxylic acid, primary amine or indole as evaluated by Glorius' robustness screen method (see the Supporting Information for details).[29]

To shed light on the mechanism of this Co-catalyzed fluorine-relay reaction, several mechanistic experiments were then carried out. The facile redox character of Co^{II}(salen) **3** [E(Co$^{III/II}$) = +125 mV vs Ag/AgCl] would allow it easily being oxidized by fluoroamide **1** (E_p = −880 mV, N−F BDE ≈ 63 kcal mol^{-1}),[30] which is consistent with the observation of color change from orange of Co(salen) **3** in MeCN to deep brown rapidly upon addition of fluoroamide **1**. Cyclic

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voltammetry studies indicated the mixture of Co(salen) **3** and fluoroamide **1** generated a species ($E_{1/2}$ = +80 mV, red trace) with similar cyclic voltammetry behavior of Co^{III}(salen)-Cl ($E_{1/2}$ = +110 mV, purple trace, Figure 1A).[31] The generation

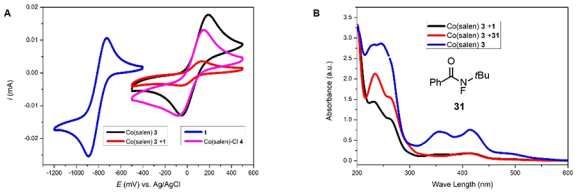
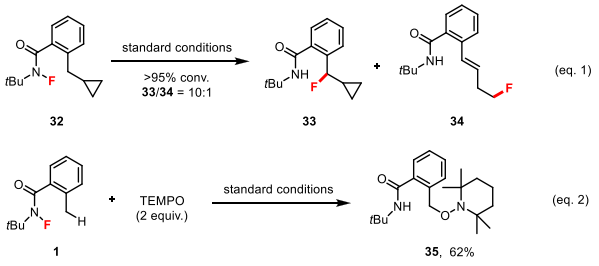


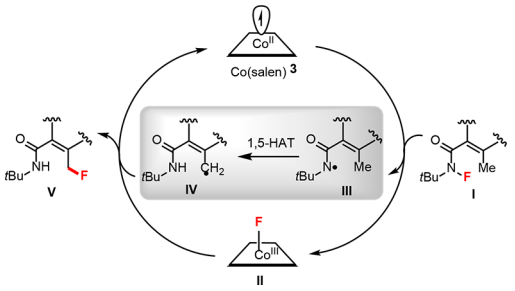
Figure 1. (A) Cyclic voltammogram in DMF with nBu$_4$NBF$_4$ (0.1 M) as electrolyte: (a) fluoroamide **1** (12.5 mM), blue; (b) Co(salen) **3** (2.5 mM), black; (c) mixture of Co(salen) **3** (2.5 mM) and fluoroamide **1** (12.5 mM), red; (d) Co(salen)-Cl **4** (2.5 mM), purple. Scan rate: 100 mV/s. (B) UV−vis absorbance of: (a) Co(salen) **3** (5 mM) in MeCN, blue; (b) mixture of Co(salen) **3** (5 mM) and fluoroamide **1** (5.5 mM), black; (c) mixture of Co(salen) **3** (5 mM) and fluoroamide **31** (5.5 mM), red.

of such a species was further evident by the UV−vis spectroscopy studies as the characteristic absorption bands at 420 and 360 nm of Co(salen) **3** disappeared while new peaks at 234 and 264 nm showed up upon addition of fluoroamide **1** or **31**, which again is analogously to that of Co^{III}(salen)-Cl (Figure 1B).[32] Therefore, We tentatively assigned the new species to be Co^{III}(salen)-F.[15,16] Additionally, radical rearrangement experiment of the *ortho*-cyclopropylmethyl fluoroamide **32** proceed smoothly delivering the unopened (**33**) and opened (**34**) fluorides in 10:1 ratio (eq 1). The preference of unopened fluoride versus opened one is surprising and it is probably because benzyl stabilization increases the lifetime of the short-live radical intermediate.[25,27a] Radical inhibition test using TEMPO completely shut down the reactivity and the corresponding nitroxyl radical adduct **35** was isolated in 62% yield (eq 2). Both experiments strongly support the existence of radical intermediates in this cobalt catalyzed C−H fluorination.



On the basis of the preliminary mechanistic information gained, a redox neutral radical-relay mechanism is proposed (Scheme 3). The unpaired electron in the d_{z^2} orbital of the square-planar Co^{II}(salen) **3** (spin density on Co ≈ 1.0) initially interacts with the low-lying LUMO of the fluoroamide **I** presumably via an inner-sphere SET (single-electron transfer) mechanism generating the organometallic cobalt fluoride species **II** and an amidyl radical **III**. Subsequent 1,5-HAT transfers the spin density from nitrogen (**III**) to benzylic carbon center (**IV**). Following the persistent radical effect,[33] fluorine radical rebound from the persistent cobalt fluoride **II** (at least comparable to the time scale of UV−vis spectroscopy and cyclic voltammetry) to the transient carbon-center radical **IV** furnishes the fluorinated product **V** while regenerating the Co(salen) **3** to close the catalytic cycle. This proposed

Scheme 3. Proposed Mechanism



mechanism was further substantiated by DFT calculations (vide infra).

DFT calculations were performed at the level of (U)B3LYP theory and the relative Gibbs free energies for possible reaction pathways of the cobalt-catalyzed C−H fluorination are depicted in Figure 2. The two para *t*-Bu groups in Co(salen) **3** were simplified to H and only one enantiomer, i.e., (*S*,*S*)-**3**-**H**, was used in the calculation. Accordingly, fluoroamide **1** initially interacts with Co(salen) **3**-**H** to generate the cobalt fluoride species **A** and an amidyl radical **B** via **TS1** with a predicted energy barrier of 10.3 kcal mol^{-1}. Subsequently, **B** undergoes 1,5-HAT reaction via **TS2** (8.5 kcal mol^{-1}) to give a benzyl radical **C**, from which C−H fluorinated product **2** can be obtained in two possible pathways. In path A, **C** abstracts the F atom from another equiv of **1** generating product **2** and a new amidyl **B** with an energy barrier of 14.9 kcal mol^{-1}, whereas fluorine radical rebound from cobalt fluoride **A** to **C** is almost barrier-free (1.7 kcal mol^{-1}, path B). Though both routes are principally feasible according to the calculations, path B featuring cobalt fluoride **A** as the radical fluorinating agent is more favorable. This conclusion is further supported by the observation of much lower yield with 1 mol % of catalyst and moderate asymmetric induction when using the enantiomerically pure Co complex. Consistent with the calculations, the kinetic-isotope-effect (KIE) analysis also supports the 1,5-HAT or prior event being the rate-limiting-step (see the Supporting Information for more details).[25,27a]

Unlike the unified Fe-catalyzed C−H fluorination,[25,34] this redox neutral radical-relay cobalt catalysis was found to be surprisingly sensitive to the conformational flexibility of substrates. For instance, starting from the corresponding conformationally flexible *N*-fluoroamide only intramolecular amination[27c,35] product **36** could be obtained in 64% yield other than the anticipated fluorinated one. Thus, diverse biologically important pyrrolidines could be conveniently prepared accordingly (Scheme 4). The intramolecular amination of geminal disubstituted substrates generally proceeded in good yields (**37**−**42**, 62−91%) consistent with Thorpe−Ingold effect.[36] Besides substrates underwent benzylic C−H amination, those without benzylic but with primary (**39**−**41**) or secondary C−H (**42**, **43**) bonds available for the 1,5-HAT also proceeded smoothly. In sharp contrast, the analogous reaction using Cu catalysis was only limited to substrates at the benzylic positions.[27c] Distinct from the C−H fluorination mentioned previously, *N*-fluorosulfonamide with competing C−H bonds available for the 1,5-HAT preferred the flexible primary C−H bond (**44**) other than the activated benzylic one.[27d] However, this protocol was not the choice of piperidine preparation as both pyrrolidine (**45**) and piperidine (**46**) were obtained unselectively. A more detailed mechanistic

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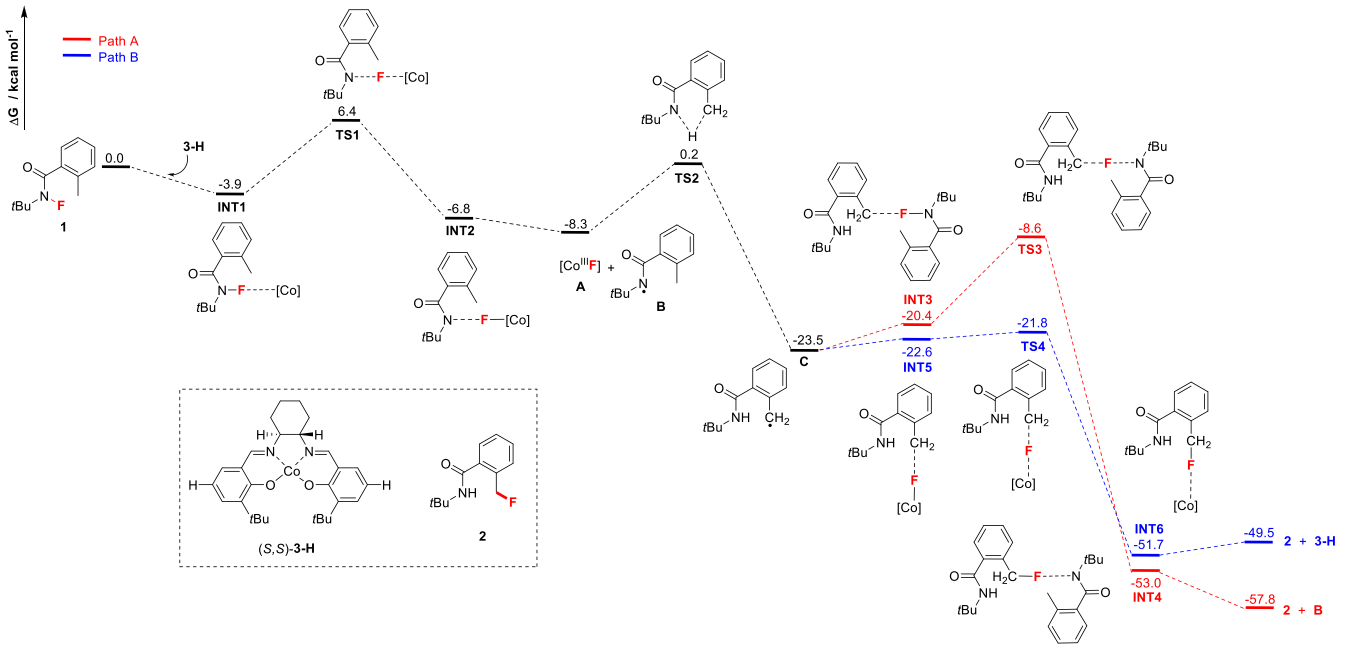
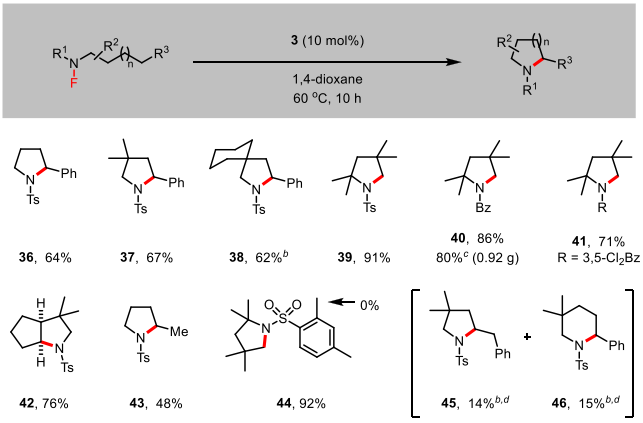


Figure 2. Relative Gibbs free energies (in kcal mol^{-1}) for possible reaction pathways of the Co-catalyzed C−H fluorination (see the Supporting Information for more computational details).

Scheme 4. Substrate Scope of the Co-catalyzed C−H Amination



[a]Reaction conditions: fluoroamide or fluorosulfonamide (0.2 mmol, 1 equiv), **3** (0.02 mmol, 10 mol %), 1,4-dioxane (c 0.05M), 60 °C, 10 h unless otherwise noted. Yield of purified product. [b]Dichloromethane as solvent. [c]Gram-scale reaction, 48 h. [d]20 mol % of **3** used.

investigation is still needed to elucidate the origin of formation of pyrrolidines.[37]

In conclusion, we have shown that the redox neutral radical-relay cobalt catalysis provides facile entries to biologically important fluorinated compounds. Preliminary mechanistic investigations revealed the in situ formed cobalt fluorides being the key species in such a radical-relay fluorination. In addition, it was found the conformational flexibility of substrates (*N*-fluoroamides or *N*-fluorosulfonamides) diverts the reaction pathway toward C−H fluorination or C−H amination reaction, respectively. More detailed mechanism investigations and applications of this protocol in the late-stage fluorination including asymmetric fluorine transfer[38] are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01072.

Experimental procedures and characterization data for all compounds and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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