ORGANIC CHEMISTRY

Reductive deaminative cross-coupling of alkyl bistriflimides enabled by electrocatalysis

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We present a versatile nickel-electrocatalytic deaminative cross-coupling platform for the efficient construction of C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) bonds from readily available alkyl bistriflimides. This methodology involves the assembly of two leaving groups on alkyl amines to form alkyl bistriflimides, followed by their effective coupling with a wide range of alkyl halides, alkyl pseudohalides, aryl halides, and alkenyl halides under electrochemical reductive conditions. Moreover, the successful application of electrochemical reductive relay cross-coupling and transition metal–free cross-electrophile coupling further demonstrates the versatility of alkyl bistriflimides as valuable building blocks in organic synthesis. Combined control experiments and density functional theory calculations provide insights into the reaction pathway and the crucial role of iodide in the catalytic process.

INTRODUCTION

Electrochemically cross-electrophile coupling (e-XEC) protocols have garnered notable attention for their ability to construct complex carbon scaffolds from generally readily available electrophiles (*1–5*). Compared to the cross-electrophile coupling (XEC) strategies, e-XEC uses renewable and easily accessible electricity to replace traditional redox reagents, promoting more sustainable chemical production (*6–14*). In the past decade, e-XEC strategies have been used to construct C–C (*14*) and C–X (*15–18*) bonds, thereby enriching the compound library. Among these efficient methodologies, the construction of C(sp^3)–C(sp^3) bonds is in high demand in contemporary organic synthesis (*19–25*). Recent advances include the Baran group's nickel-electrocatalytic doubly decarboxylative coupling for C(sp^3)–C(sp^3) bond formation using redox-active esters derived from aliphatic acids (*26, 27*), the Qiu group's C(sp^3)–C(sp^3) cross-coupling of unactivated alkyl halides under similar catalytic conditions (*28*), and the Lin group's e-XEC of different alkyl halides (Fig. 1A) (*29*). However, there is a notable lack of focus on C(sp^3)–C(sp^3) e-XEC efforts in deaminative coupling (Fig. 1A) (*30, 31*).

While approaches to constructing C(sp^3)-centered molecules have primarily used aliphatic alcohols (*32–35*) and carboxylic acids (*36–39*) as precursors, amines have been less frequently used as cross-coupling partners (*40–42*). Strategies for deaminative cross-coupling reactions include conversion of amines to pyridinium salts (*30, 43–61*) and use of redox-active imines (Fig. 1B) (*62–65*). However, these methods produce neutral molecule by-products that may be captured by radicals, reducing reaction efficiency (*66*). Inspired by seminal reports from the 1980s concerning bis-sulfonyl amide ion moieties (*67, 68*), we propose, using trifluoromethanesulfonic anhydride as an activating agent, to form the C–NTf$_2$ structure (*69*). This approach could facilitate the deamination process of alkyl bistriflimides to form alkyl radicals by single electron reduction, due to the excellent leaving ability of NTf$_2$. To date, the use of alkyl bistriflimides in cross-coupling reactions, particularly those involving double deamination, has not been reported. We present a versatile nickel-electrocatalytic deaminative cross-coupling platform that enables the efficient construction of C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) bonds from readily available alkyl bistriflimides (Fig. 1C).

RESULTS

We initiated the assessment of nickel-electrocatalytic double deaminative reaction using alkyl bistriflimides **1** and **2** as model substrates to develop the e-XEC (Table 1). The optimal reaction conditions were identified as follows: Nickel(II) bromide ethylene glycol dimethyl ether complex (NiBr$_2$·dme) as the catalyst, di(1-pyrazolyl) pyridine **L3** as the ligand, and NaI as the supporting electrolyte under a constant current (5 mA) in *N,N'*-dimethylformamide (DMF) with iron plate and Ni foam as electrodes. The reaction was conducted for 6 hours at room temperature, achieving a maximum yield of 70% for the cross-coupling product **3** (entry 1). Other electrode combinations decreased the efficiency or suppressed the transformation (entry 2) (*70*). The application of alternative electrolytes also diminished the yield (entry 3). Similar outcomes were obtained by changing the electric current to 2.5 or 10 mA (entries 4 and 5). Control experiments revealed that the reaction cannot proceed in the absence of the electricity or catalyst (entries 6 and 7).

The role of the ligand was further investigated. As shown in Fig. 2A, using bipyridine **L1** (**bpy**) or terpyridine **L2** (**tpy**) as the ligand led to the formation of homocoupling product **3-2** of two alkyl bistriflimides, along with protonation product **3-1** and low efficiency for heterocoupling product **3**. **L4** gave a lower yield, with only 36% of the heterocoupling product. We then expanded this platform for C(sp^3)–C(sp^3) bond construction. Cross-coupling products were obtained in 55 to 78% yields, as demonstrated with alkyl bistriflimides, alkyl Katritzky salts, redox-active esters, and alkyl iodides, encompassing both long-chain (**5** to **7**, **12**, and **13**) and cyclic structures (**8** to **11**). These results demonstrate that this electrochemical synthesis platform can use a diverse array of radical precursors from various sources to facilitate C(sp^3)–C(sp^3) bond formation. Moreover, alkyl bistriflimides in electrochemical reactions not only act as radical precursors but also undergo a pathway involving a sequence of electrochemical-chemical-electrochemical-chemical steps (*29, 71*).

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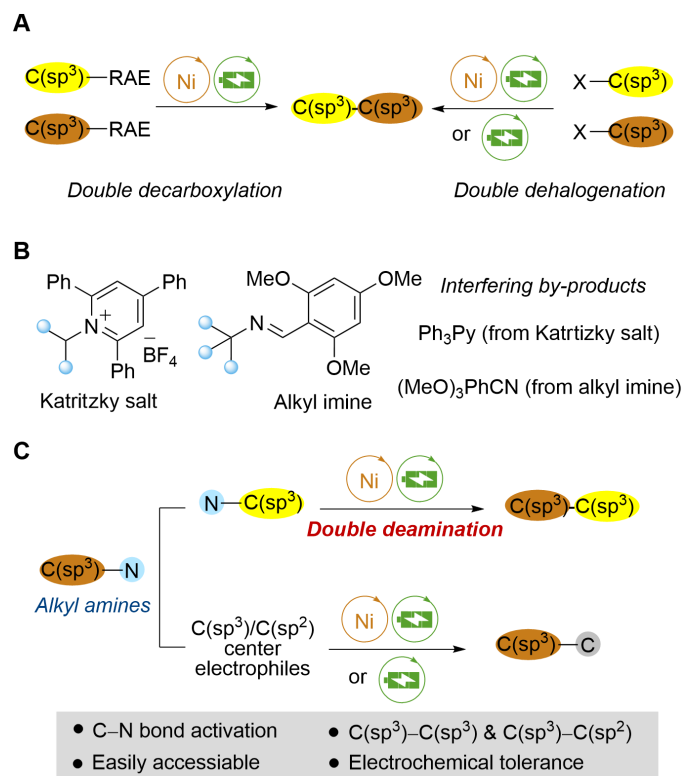*Corresponding author. Email: hongorg@kaist.ac.kr (S.H.); yiwang@nju.edu.cn (Y.W.)

Fig. 1. Strategies for deaminative C(sp³)–C bond construction. (**A**) Electrocatalytic C(sp³)–C(sp³) cross-coupling. (**B**) Strategies of deaminative cross-coupling. (**C**) Deaminative cross-coupling of alkyl bistriflimides (this work). RAE, redox active ester.

Using tetrabutylammonium bromide (TBAB) as the electrolyte, Mg as the sacrificial anode, carbon as the cathode, non-anhydrous THF as the solvent, and a constant current of 5.0 mA under ambient conditions, we successfully used the e-XEC to synthesize a diverse array

of coupling products, demonstrating compatibility with various functional groups, including alkyl chlorides, ethers, and fluorides from alkyl bistriflimides and α-haloboronate esters (**14** to **17**) as well as benzyl chloride (**18**). It is noteworthy that the activation method using pyridinium salts is ineffective for obtaining the desired products. These methods highlight the unique advantages of alkyl bistriflimides in the electrochemical construction of C(sp³)–C(sp³) bonds, demonstrating their versatility in being modified to suit different reaction conditions.

To further prove the applicability of this electrochemical deamination method, we subsequently evaluated the scope of (hetero)aryl halides to construct the C(sp³)–C(sp²) bonds. As shown in Fig. 3, electron-rich and electron-deficient aryl halides could be converted to the corresponding product in high efficiency. Functional groups such as chlorine (**19**), cyano (**20**), methoxy (**21**), and ketone (**22**) afforded the desired products in 50 to 78% yields. Aldehyde (**23**), amide (**24**), boronic acid pinacol ester (Bpin) (**25**), and Boc-amide (**27**) on the *para* position of the benzene ring were tolerated; in particular, the Bpin group provides opportunities for further diversification. The benzyl alcohol group is also compatible but less efficient (**26**). Allyloxa (**29**) on the *ortho* position of the benzene ring could be tolerated here. Heterocycles including pyridine (**28**), quinoline (**30** and **31**), benzothiophenyl (**32**), and benzofuran (**33**) could be converted to the corresponding products in 42 to 83% yields. This nickel-electrocatalytic deaminative arylation reaction appears to be a general protocol for heterocycles such as *N*-alkylpyrazoles and azaindoles (**35** and **36**, 37 and 42% yield, respectively) (*72*). Unprotected indole motifs exhibited compatibility within this reaction, as evidenced by the efficient coupling of 5-iodoindole, yielding **37** in 68% yield. Probenecid (**39**), menthol (**40**), and dehydroabietylamine (**41**) were successfully alkylated, yielding the desired products in 52 to 83% yields. Notably, the coupling electrophile in this C(sp³)–C(sp²) construction reaction can be extended to alkenyl bromo/triflate coupling partners, yielding the products with moderate efficiency (**38** and **42** to **45**). To broaden the method's applicability, we further investigated electrochemical

Table 1. Optimization of the cross-coupling reaction involving double deamination. Reaction condition: **1** (0.3 mmol), **2** (0.9 mmol), [Ni] (0.045 mmol), ligand (0.045 mmol), NaI (0.5 M), DMA (3 ml), Ar atmosphere, and rt. Detected by gas chromatography with dodecane as the internal standard. NFE, nickel foam electrode; n.d., not detected.

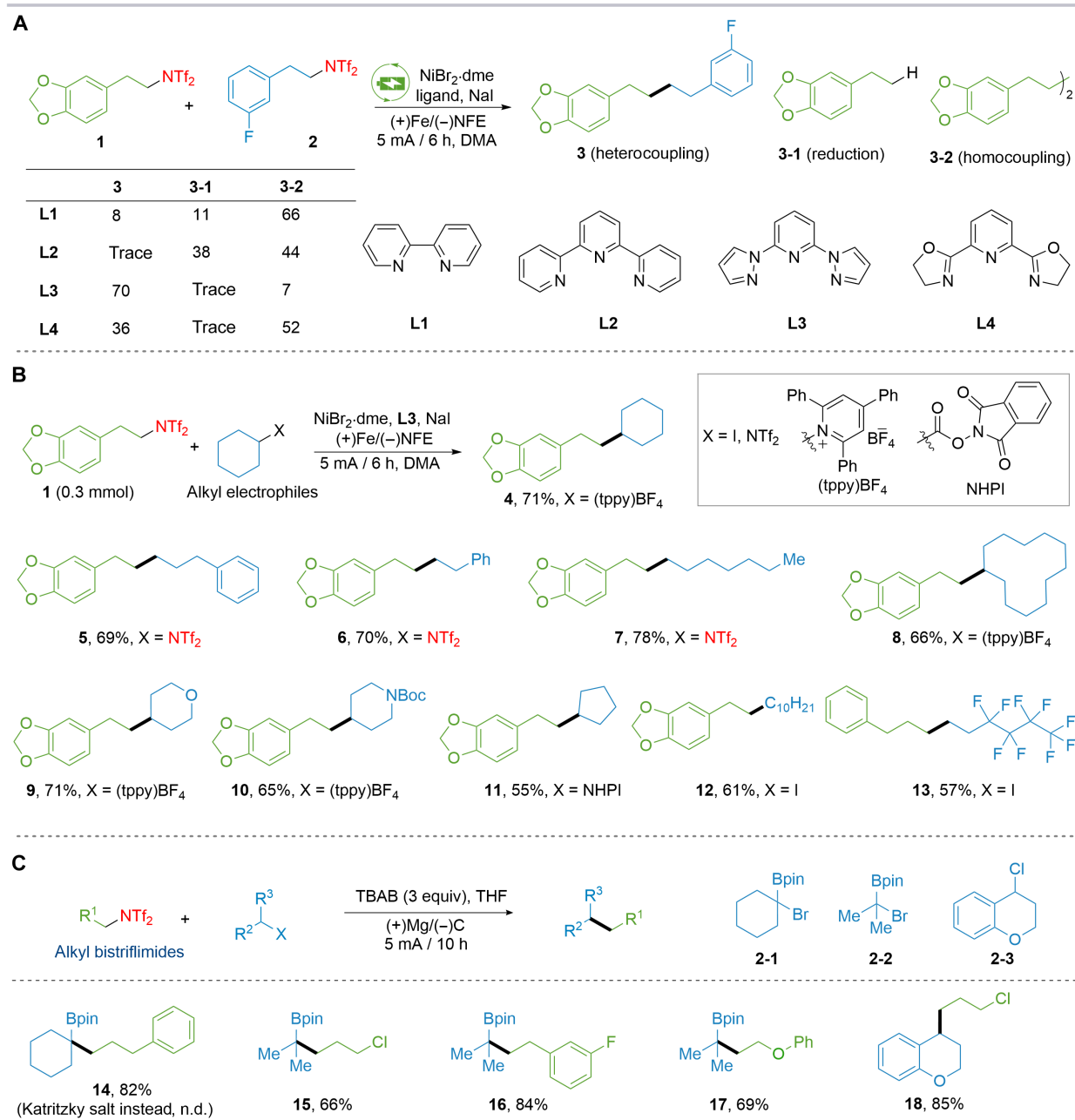| Entry	Variation from the standard conditions	Yield [%]
1	None	74 (70)*
2	(+)C/(−)NFE, 2.5 equiv of B₂pin₂ or Et₃N	n.d.
3	TBAB or TBAI or NaBr	33–62
4	2.5 mA/12 h	54
5	10 mA/3 h	65
6	No electricity	n.d.
7	W/o NiBr₂ dme	Trace

*Isolated yield.

Fig. 2. Effect of ligand and scope of various alkyl electrophiles. Yields of isolated products unless otherwise specified. (**A**) Ligand effect in C(sp³)-C(sp³) formation. NFE, nickel foam electrode; h, hours. (**B**) Scope of C(sp³)-C(sp³) formation. (**C**) Electrochemically driven cross-electrophile coupling of alkyl bistriflimides and alkyl halides. n.d., not detected; tppy, 2,4,6-triphenylpyridine.

reductive relay cross-coupling of alkyl bistriflimides to aryl halides (*73*, *74*). Using ligand **L5**, TBAB as the electrolyte, and dimethylamine (DMA) as the solvent, the electrochemical coupling between alkyl bistriflimides and aryl bromides yielded 1,1-diarylalkanes in 65 to 80% yields, with good functional group compatibility and regioselectivity (**46** to **50**). Next, we examined the scope with respect to the alkyl bistriflimides, as illustrated in Fig. 4. Alkyl bistriflimides bearing a heterocyclic or halogen-containing aromatic ring reacted smoothly to afford the products (**51** to **56**) in moderate to good yields (49 to 96%). For alkyl amine substrates, long carbon chains

(**57**), and with various functional groups like chloro (**58**), fluoro (**59**), ether (**60**, **63**, and **64**), thiomethyl (**61**), and ester (**62**), were well tolerated under standard reaction conditions, yielding the products in good yields. Other alkyl bistriflimides, such as those derived from cyclic olefin (**66**), silyl ether (**67**), and oleylamine (**68**), were readily applicable in this reaction. The bistriflimide derived from a disiloxane structure also performed well in this catalytic system, producing the desired product with a 63% yield (**69**). For secondary alkylamines, straightforward modifications to the leaving group enabled successful deaminative arylation under
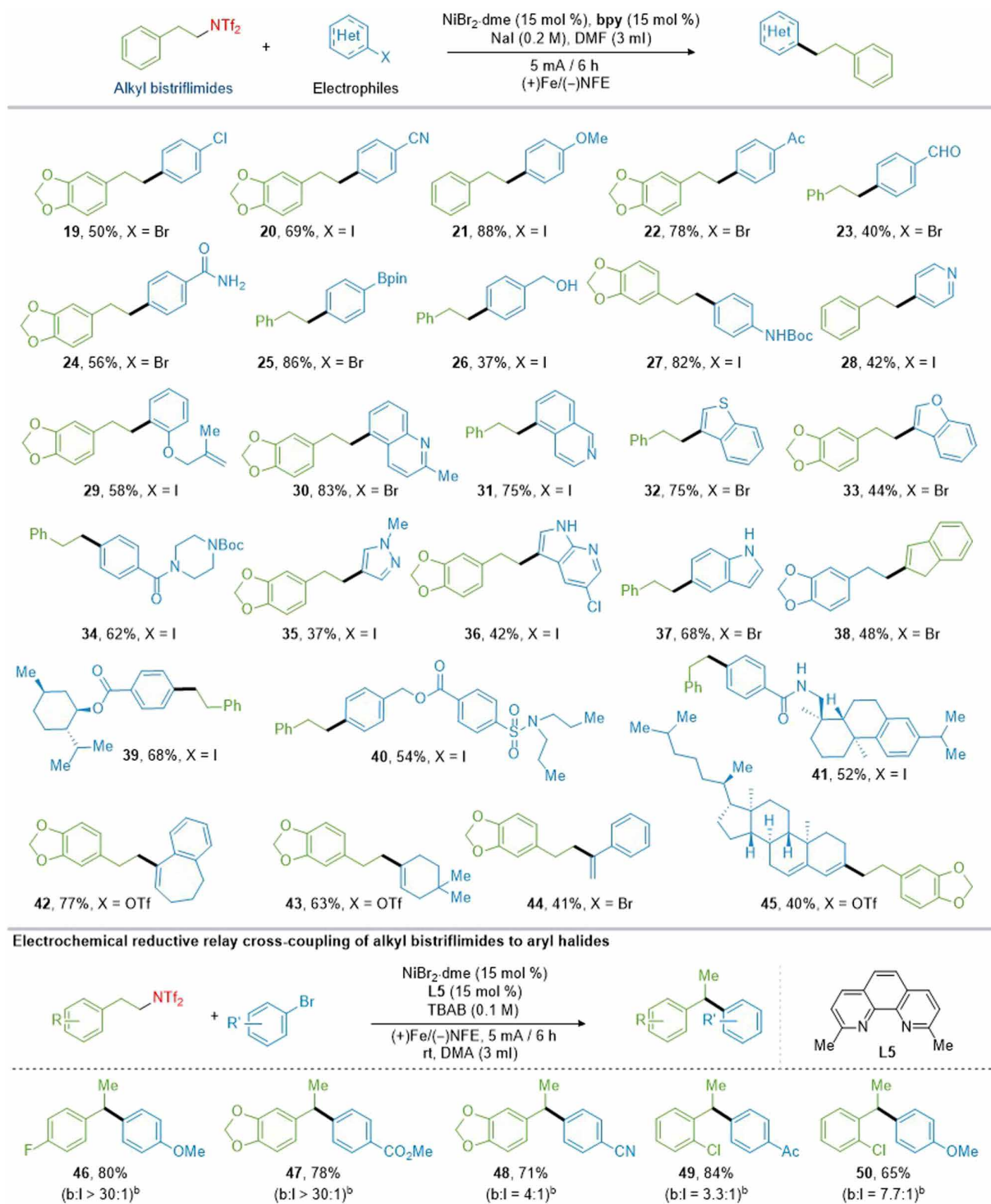
Fig. 3. Reaction scope of the electrophiles. Yields of isolated products unless otherwise specified. [b]The ratio of branched-to-linear products (b:l) was determined by ^{1}H NMR. rt, room temperature.
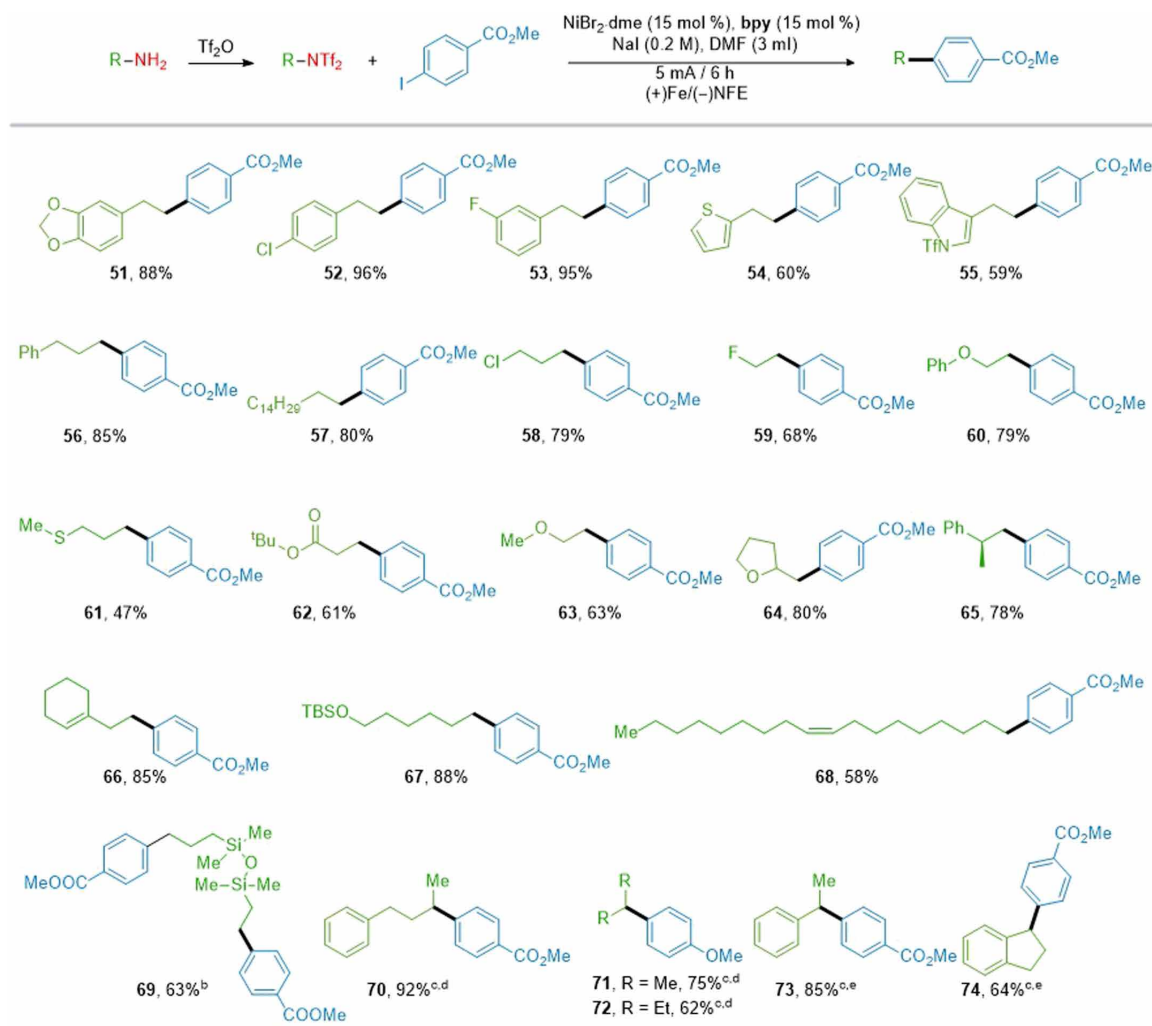
Fig. 4. Reaction scope of alkyl bistriflimides. Yields of isolated products unless otherwise specified. [b]Methyl 4-iodobenzoate (2.5 equiv). [c]NiBr₂·dme (0.03 mmol), dtbpy (0.03 mmol), NaI (0.3 mmol), and Mn (0.6 mmol), 60°C, in DMF (1 ml) under Ar atmosphere for 6 hours. [d]3,5-Difluorobenzenesulfonyl chloride instead of Tf₂O. [e]TsCl instead of Tf₂O.

manganese powder reduction conditions. However, under electrochemical conditions, the disubstituted structure exhibited minimal reactivity, resulting in its conversion to a monosubstituted configuration (**70** to **74**).

To elucidate the mechanism, a series of controlled experiments was conducted. The intermediate (**1-1**) rapidly underwent equimolar conversion with alkyl bistriflimide **1** and sodium iodide in DMF within 5 min, showcasing a highly efficient protocol for arylation reactions. The role of NaI was investigated by systematically examining its concentration and corresponding impact on yields (see fig. S2 in the Supplementary Materials for more details). Productivity was found to be linearly related to the content of NaI. Even in the absence of NaI, a substantial product yield was obtained, suggesting that the iodide generated from aryl iodide during the reaction likely plays a central role in enabling the catalytic cycle.

Next, a series of control experiments with the nickel catalyst was performed to elucidate the mechanism in the construction of C(sp³)–C(sp³) bonds. The cross-coupling product was obtained with a 61% yield when Ni(0) was used as a catalyst (see the Supplementary Materials

for more details). This result suggests that, under the standard conditions, Ni(0) might be produced from the electroreduction of Ni(II), subsequently enabling the reduction of the substrates. To validate this hypothesis, we conducted control experiments using equimolar amounts of nickel(0) and nickel(II) complexes in the absence of current (Fig. 5B). The efficiency of coupling product formation increased with higher amounts of nickel(0), whereas the use of an equivalent amount of only nickel(II) resulted in no reaction. Premixing nickel(0) and nickel(II) in a 1:1 ratio provided only a 6% product yield. This low yield suggests the formation of a Ni(I)-Br species, which was confirmed by electron paramagnetic resonance (EPR). These findings highlight that the formation of nickel(0) in the initial stage of the reaction mechanism plays a crucial role. In addition, in the cyclic voltammetry (CV) experiments, incorporating NaI and bistriflimide **1** into the current nickel catalytic system revealed a distinct current peak corresponding to Ni(I) (see fig. S1 in the Supplementary Materials), indicating the capability of Ni(0) to reduce iodide **1-1**. Radical trapping experiments also suggest that the electrochemical reaction may proceed through a radical pathway
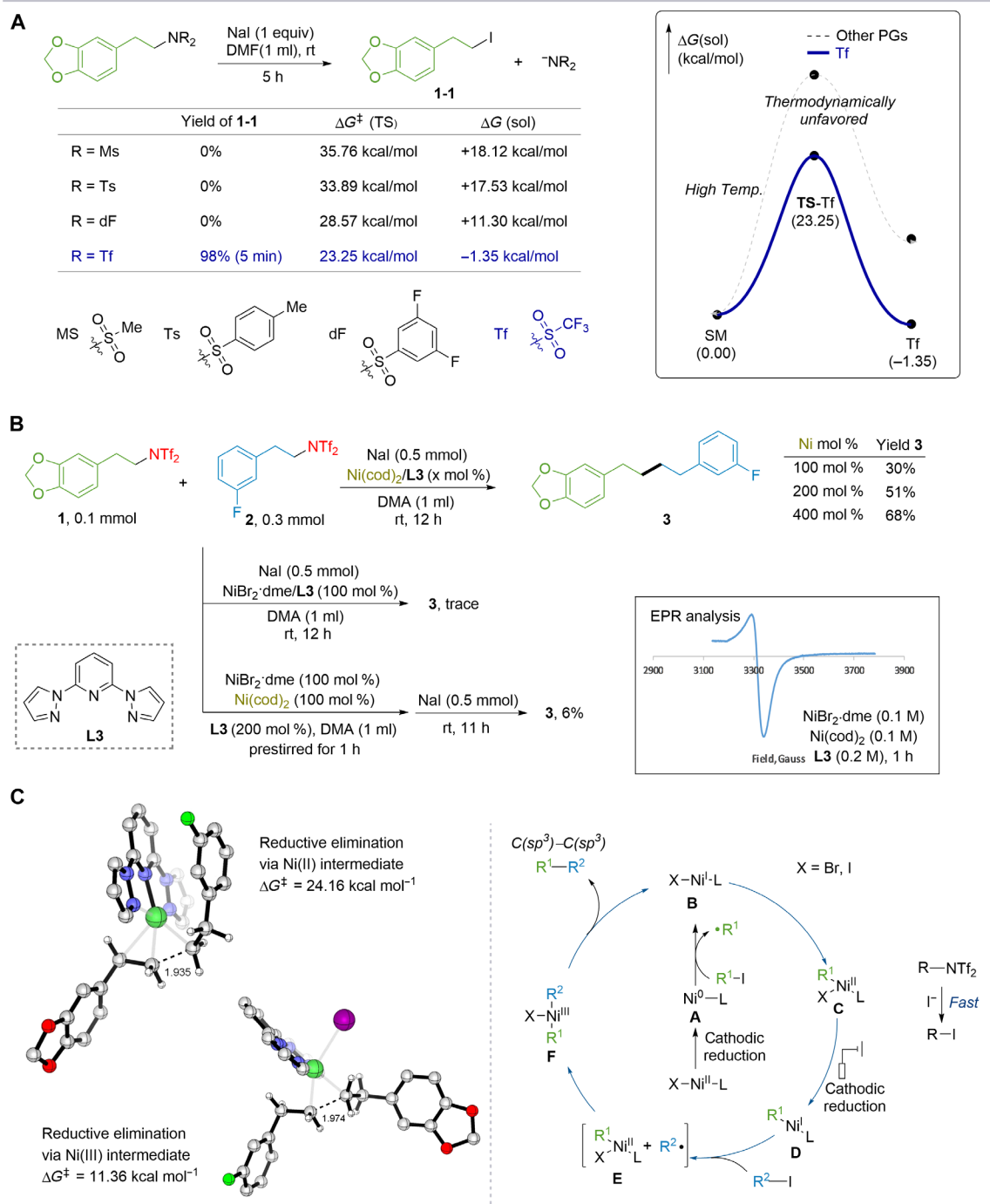
Fig. 5. Effect of leaving groups and DFT calculations. (**A**) Effect of leaving groups. (**B**) Control experiments of [Ni] without using electricity. (**C**) DFT-calculated free energy barrier of the reductive elimination step and proposed mechanism. Ts, Tosyl; sol, solvent; PGs, protective groups; cod, 1,5-cyclooctadiene.

(see fig. S3 in the Supplementary Materials for more details). However, we cannot exclude the possibility that Ni(I)-Br species reduces the substrate to generate an alkyl radical (75).

Further density functional theory (DFT) calculations were performed to elucidate the reaction mechanism. We used quantum chemical methods at the M06-D3/6-311G(d,p)//B3LYP-D3/6-31G** level of theory (Fig. 5). Experimental results revealed that triflate is the only

feasible functional group, as indicated by the outcomes of the S_N2 reaction (Fig. 5A). For other functional groups, the calculated transition energies were notably high, and these groups were predicted to undergo thermodynamically unfavorable endothermic processes (see fig. S15 in the Supplementary Materials for more details). In contrast, triflate was found to proceed through an exothermic reaction, consistent with our experimental findings. Furthermore, increasing the temperature to 60°C

enabled reactions with other leaving groups, enhancing the reliability of our computational results. Next, we calculated the free energy barrier for the reductive elimination step, considering the two possible oxidation states for Ni (see fig. S17 in the Supplementary Materials for more details). The calculations for both Ni(II) and Ni(III) oxidation states indicated that reductive elimination via dialkyl-Ni(III) complexes is preferred by 12.9 kcal mol^{-1} (Fig. 5C). On the basis of these results and DFT calculations, we proposed a Ni(I–III) catalytic cycle as the plausible mechanism for this nickel-electrocatalyzed cross-coupling reaction. In this mechanism, alkyl bistriflimides react rapidly via an S_N2 mechanism to generate alkyl iodide intermediates in the presence of iodide within the system. Concurrently, electroreduction of Ni(II) provides low-valent Ni(0) species **A**. This Ni(0) species then reduces alkyl halides, generating alkyl radicals and Ni(I) species **B**. Species **B** engages in radical addition processes to deliver Ni(II) species **C**. This Ni(II) species **C** is electrochemically reduced to Ni(I) species **D** (*76, 77*). The alkyl Ni(I) species **D** then reacts with an additional halide substrate, forming Ni(III) species **F**. Last, the reaction advances through a reductive elimination step, yielding the desired product. However, based on the literature (*28*), we cannot exclude the potential involvement of species **B** in a sequence of consecutive radical addition and reductive elimination processes that ultimately lead to the formation of the cross-coupled products; in addition, the mechanism involving Ni(I) species **B** in the radical generation process cannot be excluded either (see figs. S10 and S11 in the Supplementary Materials). The mechanisms of other reaction products are discussed in the Supplementary Materials.

DISCUSSION

In conclusion, we have developed a powerful and versatile nickel-electrocatalytic deaminative cross-coupling methodology that enables efficient construction of C(sp^3)–C(sp^3) and C(sp^3)–C(sp^2) bonds from readily available alkyl bistriflimides. The key to this approach is the straightforward assembly of leaving groups on alkyl amines to form alkyl bistriflimides, which can then be effectively coupled with a wide range of partners under mild electrochemical reductive conditions. The successful application of electrochemical reductive relay cross-coupling and transition metal–free e-XEC further underscores the versatility of alkyl bistriflimides as valuable building blocks in organic synthesis. The broad substrate scope, functional group tolerance, and mild reaction conditions demonstrate the practicality and utility of this methodology. Mechanistic studies, including control experiments and DFT calculations, have provided insights into the reaction pathway and highlighted the crucial role of the iodine anion in the catalytic process. This work not only expands the toolbox for C–C bond formation but also offers a sustainable approach to using amine-derived precursors in organic synthesis.

MATERIALS AND METHODS

General procedure 1 for the e-XEC reaction of alkyl bistriflimides with C(sp^3) electrophiles using electrocatalysis

In a glove box, NaI (90.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1 equiv), alkyl electrophiles (0.9 mmol, 3 equiv), NiBr$_2$·dme (13.8 mg, 0.03 mmol, 15 mol %), **L5** (9.4 mg, 0.02 mmol, 15 mol %), and dried DMA (3.0 ml) were added into the flame-dried undivided ElectraSyn vial (5 ml) equipped with a stir bar. The resulting suspension was prestirred for about 1 min to dissolve the electrolyte (if the substrate was solid, it would be added to the vial before adding the solvent; if

the substrate was sticky oil, it would be added as a solution in DMA). After the reaction is completed, the mixture was transferred to a separatory funnel. Then, H$_2$O (20 ml) was added and the mixture was extracted three times with ethyl acetate (EtOAc) (20 ml). The combined organic layer was washed with 1.0 M NaOH (20 ml), brine (20 ml), and H$_2$O (20 ml). The organic layer was dried with anhydrous Na$_2$SO$_4$ and then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or Preparative Thin-Layer Chromatography (PTLC) using petroleum ether/EtOAc as the eluent.

General procedure 2 for the e-XEC reaction with alkyl bistriflimides

In a glove box, TBAB (483.0 mg, 1.5 mmol, 3 equiv) and dried THF (2.5 ml) were added into the flame-dried undivided ElectraSyn vial (5 ml) equipped with a stir bar. The resulting suspension was prestirred for about 1 min to dissolve the electrolyte (if the substrate was solid, it would be added to the vial before adding the solvent; if the substrate was sticky oil, it would be added as a solution in THF). Then, the substrate with an anion-stabilizing group (0.5 mmol, 1 equiv) and alkyl bistriflimides (1.5 mmol, 3 equiv) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then it was brought out of the glove box. Prestirring the resulting mixture for 2 min, and then the reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 10 hours. After the reaction is completed, the mixture was transferred to a separatory funnel, and electrodes were washed with EtOAc. Then, the crude mixture was further diluted with Et$_2$O (if there were too much floc., filter it by Celite). The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General procedure 3 for the e-XEC reaction of alkyl bistriflimides with C(sp^2) electrophiles using electrocatalysis

In a glove box, NaI (90.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1.5 equiv), electrophiles (0.2 mmol, 1 equiv), NiBr$_2$·dme (9.2 mg, 0.03 mmol, 15 mol %), bpy (4.7 mg, 0.02 mmol, 15 mol %), and dried DMF (3.0 ml) were added into the flame-dried undivided ElectraSyn vial (5 ml) equipped with a stir bar. The resulting suspension was prestirred for about 1 min to dissolve the electrolyte (if the substrate was solid, it would be added to the vial before adding the solvent; if the substrate was sticky oil, it would be added as a solution in DMF). After the reaction is completed, the mixture was transferred to a separatory funnel. Then, H$_2$O (20 ml) was added and the mixture was extracted three times with EtOAc (20 ml). The combined organic layer was washed with 1.0 M NaOH (20 ml), brine (20 ml), and H$_2$O (20 ml). The organic layer was dried with anhydrous Na$_2$SO$_4$ and then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as the eluent.

General procedure 4 for the electrochemical reductive relay cross-coupling of alkyl bistriflimides to aryl halides

In a glove box, TBAB (290.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1.5 equiv), aryl bromide (0.2 mmol, 1 equiv), NiBr$_2$·dme (9.2 mg, 0.03 mmol, 15 mol %), ligand (0.02 mmol, 15 mol %), and

dried DMA (3.0 ml) were added into the flame-dried undivided ElectraSyn vial (5 ml) equipped with a stir bar. The resulting suspension was prestirred for about 1 min to dissolve the electrolyte (if the substrate was solid, it would be added to the vial before adding the solvent; if the substrate was sticky oil, it would be added as a solution in DMA). After the reaction is completed, the mixture was transferred to a separatory funnel. Then, H_2O (20 ml) was added and the mixture was extracted three times with EtOAc (20 ml). The combined organic layer was washed with 1.0 M NaOH (20 ml), brine (20 ml), and H_2O (20 ml). The organic layer was dried with anhydrous Na_2SO_4 and then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as the eluent.

General procedure 5 for the XEC reaction of alkyl bistriflimides with C(sp^2) electrophiles using metal reductant Mn

In a glove box, a dry 8-ml vial equipped with a Teflon-coated magnetic stir bar was charged with electrophiles (0.2 mmol, 1 equiv, if solid), alkyl bistriflimides (0.3 mmol, 1.5 equiv, if solid), NiBr$_2$·dme (9.2 mg, 0.03 mmol, 15 mol %), 4,4′-di-tert-butyl-2,2′-dipyridyl (dtbpy) (8.0 mg, 0.03 mmol, 15 mol %), NaI (45.0 mg, 0.3 mmol, 1.5 equiv), and Mn (33 mg, 0.6 mmol, 2.5 equiv). Anhydrous and degassed DMF (1.0 ml), electrophiles (0.2 mmol, 1 equiv, if liquid), and alkyl bistriflimides (0.3 mmol, 1.5 equiv, if liquid) were added via a syringe. The vial was capped and sealed with Parafilm. The reaction mixture was stirred for 6 hours at 60°C. After the reaction is completed, the mixture was transferred to a separatory funnel. Then, H_2O (20 ml) was added and the mixture was extracted three times with EtOAc (20 ml). The combined organic layer was washed with 1.0 M NaOH (20 ml), brine (20 ml), and H_2O (20 ml). The organic layer was dried with anhydrous Na_2SO_4 and then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as the eluent.

Supplementary Materials

This PDF file includes:
Supplementary Text
Tables S1 to S7
Figs. S1 to S17
References

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