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Reductive coupling of benzyl oxalates with highly functionalized alkyl bromides by nickel catalysis†

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Coupling reactions involving non-sulfonated C–O electrophiles provide a promising method for forming C–C bonds, but the incorporation of functionalized or secondary alkyl groups remains a challenge due to the requirement for well-defined alkylmetal species. In this study, we report a reductive nickel-catalyzed cross-coupling of benzyl oxalates with alkyl bromides, using oxalate as a new leaving group. A broad range of highly functionalized alkyl units (such as functional groups: alkyl chloride, alcohol, aldehyde, amine, amide, boronate ester, ether, ester, heterocycle, phosphonate, strained ring) were efficiently incorporated at the benzylic position. The utility of this synthetic method was further demonstrated by late-stage modification of complex bioactive compounds. Preliminary mechanistic experiments revealed that a radical process might be involved in the reaction.

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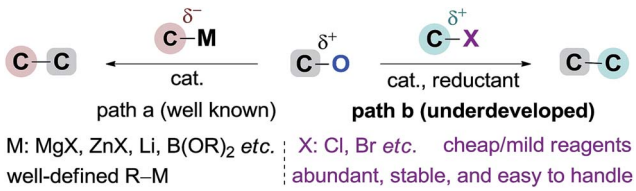
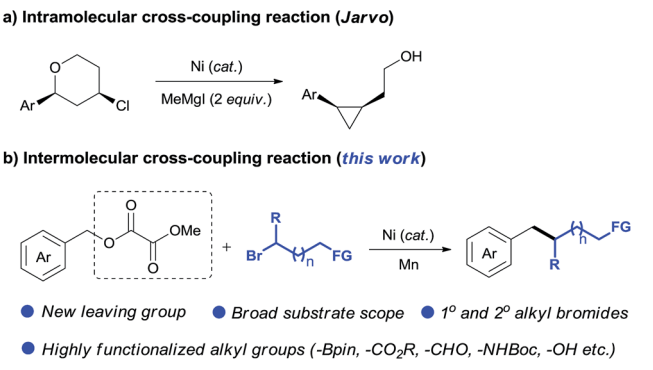
Introduction

Transition metal-catalyzed cross-coupling reactions have become one of the most important tools in organic synthesis.[1] Recent efforts have been focused on the use of non-sulfonated C–O electrophiles (*e.g.*, carboxylates, ethers) as coupling partners *versus* organic halides.[2] Their advantages involve low toxicity, low cost and ready availability, and abundant C–O bonds in a wide range of natural and artificial compounds. The high activation barrier for C–O cleavage and selectivity challenge in the presence of multiple C–O bonds[3] mean that their coupling reactions have been realized only recently by using organometallic species (*e.g.*, Grignards, organozincs, and boronic acids) as coupling partners (Scheme 1, path (a)).[2] In contrast to the major advances achieved in the field of arylation reactions,[4] the development of alkylation reactions has proved more difficult.[5] To date, only a few elegant studies have demonstrated the Csp^3–Csp^3 coupling of relatively unreactive C–O electrophiles. The incorporation of functionalized or secondary alkyl groups remains a particular challenge,[6] which can partially be ascribed to the low availability and high reactivity profiles of alkylmetal reagents. The development of protocols using electrophiles instead of organometallic reagents to couple with C–O electrophiles may provide a solution to these problems, offering a unique opportunity to discover new reactivities within this field (Scheme 1, path (b)).[7]

The reductive cross-coupling of two electrophiles has emerged as an increasingly popular approach for constructing the C–C bond.[8] One of the major challenges in this field is to expand the scope of electrophiles. Encouraged by the pioneer work of Weix,[8e] the groups of Martin, Jarvo, Shi, Molander, and Shu have launched a program to disclose the potential of nickel-catalyzed reductive cross-coupling of relatively unreactive C–O electrophiles.[7d–l] Notably Jarvo's group has disclosed intramolecular Csp^3–Csp^3 coupling of benzyl ethers with alkyl



Scheme 1 Catalytic cross-coupling reactions *via* C–O bond cleavage.



Scheme 2 Reductive Csp^3–Csp^3 cross-coupling reactions *via* benzylic C–O bond cleavage.

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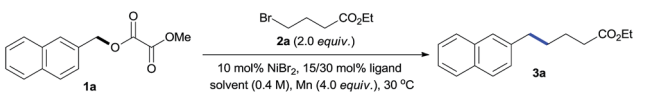
halides (Scheme 2a).[7k] However, intermolecular Csp^3–Csp^3 coupling is still unresolved because of difficulty and complexity with controlling selectivity for the cross-product.[9] Herein, we demonstrate the use of oxalate[10] as a leaving group to allow an intermolecular Csp^3–Csp^3 coupling between benzyl carboxylates and alkyl bromides (Scheme 2b). This method accomplishes the incorporation of a wide range of highly functionalized alkyl groups at the benzylic position and tolerates both primary and secondary alkyl bromides. Our study demonstrates this method is an attractive alternative for the alkylation of benzylic derivatives using alkyl nucleophiles.[6,11]

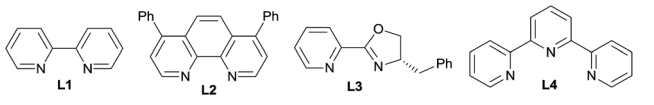
Results and discussion

We started our investigations by exploring the reaction of oxalate **1a** with alkyl bromide **2a** (Table 1, see Table S1 and S2† for more details). Initial experiments revealed that reactions under the conditions of $NiBr_2$ (10 mol%), Mn (4.0 equiv.) in DMF using nitrogen ligands gave no or low yields of the desired product **3a** (entries 1–4), along with large amounts of $ArCH_3$ (2-methylnaphthalene) and $ArCH_2$–OH (2-naphthalenemethanol) side products. A review of the literature revealed that phosphine ligands were mostly ineffective for reductive cross-coupling reactions.[8] However, the use of PPh_3 gave **3a** with an unexpected 34% yield (entry 5), encouraging us to study the electronic and steric effects of the ligands. We found that P(4-$CF_3Ph)_3$ was the most effective (entries 6–9). Screening of solvents revealed that DMSO was crucial to increasing reaction efficiency, as it significantly inhibited formation of the $ArCH_2$–OH side product (entries 9–13). No reaction was observed in the absence of the Ni catalyst or Mn reductant (entries 14–15). Due to the solubility problem, reactions using non-polar alkyl bromides for the preparation of **3b–3e** and **3y–3aa** were sluggish in DMSO. Thus, the conditions of entry 13 using DMSO/DMF (1 : 1) were used as standard conditions under which the gram-scale reaction of **1a** gave **3a** with 82% yield.

Table 1 Nickel-catalyzed reductive coupling of **1a** with **2a**[a]



Entry	Ligand	Solvent	Yield (%)
1	**L1**	DMF	20
2	**L2**	DMF	18
3	**L3**	DMF	32
4	**L4**	DMF	0
5	PPh_3	DMF	34
6	P(4-MePh)$_3$	DMF	16
7	P(2-MePh)$_3$	DMF	0
8	P(4-FPh)$_3$	DMF	50
9	P(4-CF_3Ph)$_3$	DMF	58
10	P(4-CF_3Ph)$_3$	DMA	52
11	P(4-CF_3Ph)$_3$	DMSO	73 (79)[b]
12	P(4-CF_3Ph)$_3$	DMSO/DMA 1 : 1	68 (73)[b]
13	P(4-CF_3Ph)$_3$	DMSO/DMF 1 : 1	70 (75)[b], (82)[c]
14[d]	P(4-CF_3Ph)$_3$	DMSO/DMF 1 : 1	0
15[e]	P(4-CF_3Ph)$_3$	DMSO/DMF 1 : 1	0

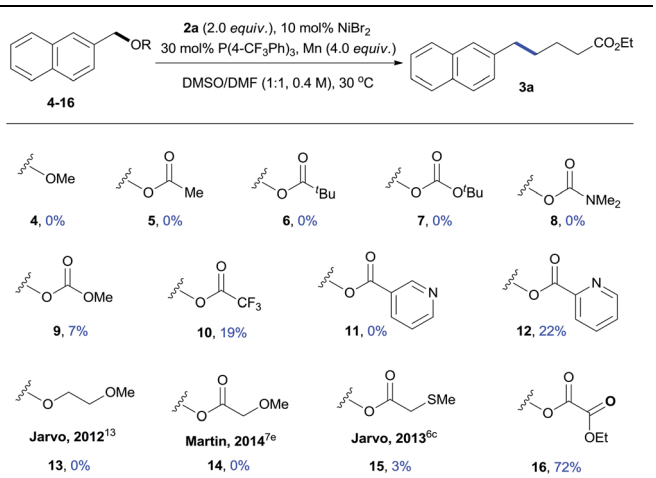


[a] Substrates **1a** (0.2 mmol), monodentate ligand (30 mol%), or bidentate ligand (15 mol%) were used and reacted for 24 h; yields were determined by ^{1}H NMR using anisole as an internal standard. [b] Yields are isolated yields. [c] **1a** (4 mmol, 0.976 g) was used; isolated yield. [d] No Ni catalyst. [e] No Mn.

The effects of various leaving groups were then studied (Table 2). Simple benzyl ether (**4**) was unreactive. While carboxylates were more reactive than methyl ether, reactions of commonly used carboxylates gave no or very low yields of the desired product (**5–9**). In these cases, most starting materials of **4–9** remained unchanged. By increasing the leaving ability of carboxylate,[12] a full conversion of trifluoroacetate **10** was observed, affording **3a** with 19% yield along with large amounts of $ArCH_2$–CH_2Ar (30%), $ArCH_2$–OH (15%), and $ArCH_3$ (11%) side products. While 3-pyridyl ester **11** was totally unreactive under standard conditions, the reaction of 2-pyridyl ester **12** gave **3a** with 22% yield. This result indicated that use of the bidentate leaving group was beneficial to this reaction,[13] prompting us to examine the effects of several others. Ether **13** and acetate **14** were found to be unreactive, even though they were active leaving groups for the benzylic C–O cleavage.[7e,13] The use of a stronger coordinating group, 2-(methylthio)acetate (**15**), led to trace amounts of **3a**. The reaction of ethyl oxalate **16** gave a comparable result to that of methyl oxalate **1a**, affording **3a** with 72% NMR yield.[14]

We subsequently focused on examining the generality of this protocol. The incorporation of functionalized alkyl units is important in the synthesis of complex molecules. The use of functionalized alkylmetal reagents is severely restricted because of limited availability and high reactivity profiles of the reagent

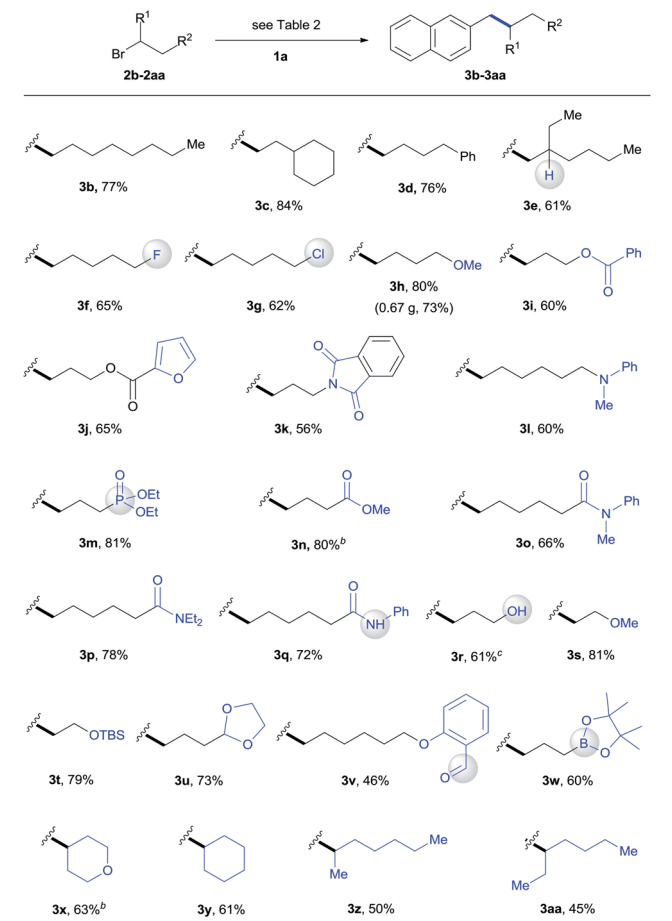
Table 2 Evaluation of leaving groups[a]



[a] Substrates **4–16** (0.2 mmol) were used and reacted for 24 h; yields were determined by ^{1}H NMR using anisole as an internal standard.

itself.[5b] The use of alkyl halides would circumvent these problems. In this work, both simple long-chain alkyl substrates (**3b–3d**) and a wide range of functionalized alkyl bromides coupled with **1a** efficiently under standard conditions (Table 3). The incorporation of β-substituted alkyl unit represents a challenge due to the fast β-H elimination of alkylmetal intermediates.[6e] Product **3e** was formed in a moderate yield under our conditions. The reaction was highly chemoselective for functionalization of the C–Br bond over C–F (**3f**) and C–Cl (**3g**) bonds. Moreover, a gamut of functionalities such as methyl and silyl ethers (**3h**, **3s**, **3t**), esters (**3i**, **3j**, **3n**), heterocycle (**3j**), tertiary amides (**3k**, **3o**, **3p**), amine (**3l**), phosphonate (**3m**), acidic amide (**3q**), alcohol (**3r**), aldehyde (**3v**), and boronate ester (**3w**) were accommodated. Although the direct coupling of aldehyde substrate (**3v**) was less effective, the use of alkyl bromides bearing protected aldehyde function gave a good yield of product **3u**. The reaction was selective for functionalization of the C–Br bond, leaving the nucleophilic C–B bond for additional transformation (**3w**). Furthermore, the scope of this alkylation protocol could be extended to secondary alkyl bromides to give cyclic (**3x**, **3y**) and acyclic (**3z**, **3aa**) products. The reaction could be scaled up to gram-scale and produced **3h** with 73% yield.

Table 3 Scope of alkyl bromides[a]

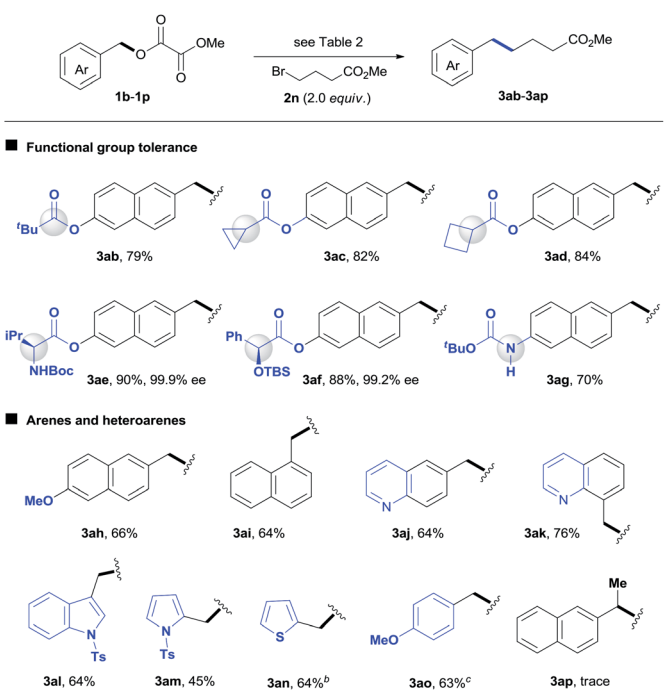


[a] Reactions for 24 h, isolated yields, average of two experiments. [b] Solvent: DMSO. [c] Catalyst: 20 mol% $NiBr_2$.

A wide range of benzyl oxalates coupled with functionalized alkyl bromide **2n** efficiently under standard conditions (Table 4). The reaction was highly chemoselective for alkylation of benzyl esters, leaving a number of aryl esters intact (**3ab–3af**).[2] Functional units such as strained rings, amino acid and α-oxy acid derivatives, as well as acidic carbamates were tolerated under reductive conditions (**3ac–3ag**). No erosion in enantioselectivity was found en route to either **3ae** or **3af**. The reaction of 1-naphthyl oxalate (**3ai**) gave a comparable result to that for **3ah**. Nitrogen and sulfur heterocycles are prevalent in pharmaceuticals but always represent a challenge for metal catalysis. The expected products **3aj–3an** were formed with moderate yields under standard conditions. Unfortunately, our method did not allow the coupling reaction of secondary benzyl electrophiles (**3ap**).

To date, most Ni-catalyzed cross-coupling reactions *via* inert C–O bond cleavage are limited to substrates with π-extended systems like naphthalene.[2] One possible explanation is that, unlike a regular arene, the π-extended system can be coordinated to Ni(0) efficiently,[15] because the binding complex might retain a certain aromaticity and might still be partially stable.[7e] Indeed, under standard conditions the reaction of a regular benzyl oxalate only gave trace amounts of product **3ao**. The vast majority of substrate was converted to benzyl alcohol. This prompted us to study the reaction conditions again. Finally, we found that by changing the ligand to dppb and using $MgBr_2$ (1.5 equiv.) and 3-CF_3-Py (5 mol%) as additives, the reaction

Table 4 Scope of benzyl oxalates[a]



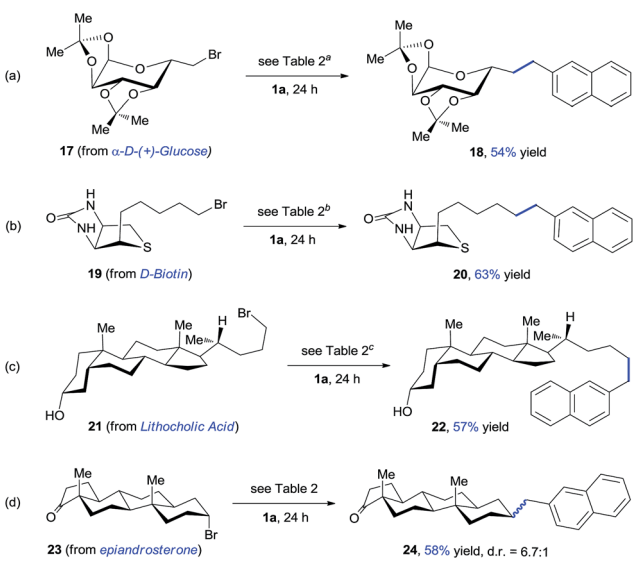
[a] Reactions for 24 h, isolated yields, average of two experiments. [b] Reaction at 45 °C. [c] Conditions: 10 mol% $NiBr_2$(diglyme), 20 mol% dppb, 5 mol% 3-CF_3-Py, $MgBr_2$ (1.5 equiv.), Mn (4.0 equiv.), DMSO/CH_3CN (4 : 1, 0.4 M), 45 °C, 36 h.

afforded a useful 63% yield of **3ao**. Although the role of additives is unclear, the use of $MgBr_2$ significantly improved selectivity for **3ao** over benzyl alcohol, and the addition of 3-CF_3-Py inhibited the formation of benzyl dimer.

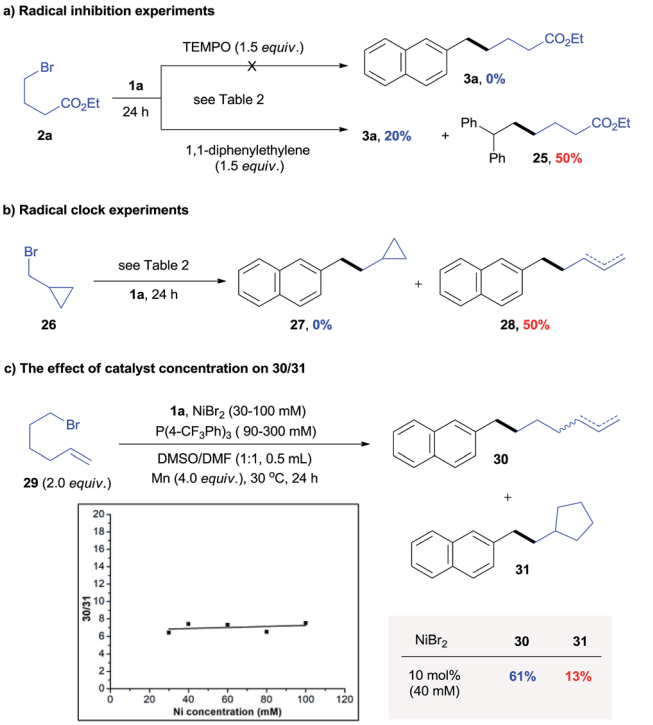
The late-stage modification of complex molecules provides a promising approach to altering the pharmacological profiles of natural products. To further demonstrate the synthetic utility of our method, we studied the alkylation reactions of several complex bioactive compounds (Scheme 3). The reaction of α-D-(+)-glucose derivate **17** with oxalate **1a** gave product **18** with 54% yield. The presence of highly coordinative thioether and amide groups makes functionalization of D-biotin a challenge for metal catalysis. The expected product **20** was formed with 63% yield under standard conditions. Lithocholic acid derivate **21** selectively coupled with oxalate **1a**, leaving a free alcohol group intact. In addition, this approach allows for incorporation of a naphthyl group at the secondary alkyl carbon, affording **24** with moderate yield.

Use of the optically pure alkyl bromide **23** gave **24** with a dr of 6.7 : 1, indicating a potential radical mechanism (Scheme 3d). The reaction of **1a** and **2a** was significantly inhibited in the presence of a radical scavenger such as TEMPO and 1,1-diphenylethylene (Scheme 4a). The radical trapping product **25** was obtained with 50% NMR yield. Further, radical clock experiments revealed that the reaction of cyclopropylmethyl bromide **26** only produced the ring opening product **28** (Scheme 4b), which is consistent with the process of rearrangement of the cyclopropylmethyl radical to the homoallyl radical.[16] These results suggest the presence of a C-centered radical in the reaction pathway.

To verify a potential radical chain mechanism, the effect of catalyst concentrations on products of reaction **1a** with 6-bromo-1-hexene **29** was then studied (Scheme 4c).[17] Under higher catalyst concentrations, the C-centered radical was more



Scheme 3 Late-stage modification of biologically active molecules. [a]Oxalate **1a** (2.0 equiv.), 20 mol% $NiBr_2$, 45 °C. [b]20 mol% $NiBr_2$, 45 °C. [c]20 mol% $NiBr_2$.



Scheme 4 Mechanistic studies.

easily trapped by catalysts before cyclization.[17] We expected that if a radical chain mechanism was to apply, the ratio of unrearranged to rearranged products (**30**/**31**) would increase with increasing catalyst concentration. However, our result in Scheme 4c shows that **30**/**31** was not dependent upon catalyst concentrations. This result indicates that the oxidative addition of the alkyl halide appears to occur *via* a non-chain process.[18]

Conclusions

In summary, we have demonstrated a nickel-catalyzed cross-coupling of benzyl carboxylate with alkyl bromide by using oxalate as a leaving group. This study suggests that the reductive cross-coupling of electrophiles might be the foundation for new discoveries in the field of metal-catalyzed cleavages of the C–O bond. This method's excellent functional group compatibility suggests that it can be a powerful alternative to established protocols using alkyl nucleophiles for the alkylation of benzylic derivatives. Further mechanistic investigation and extension to other electrophiles are ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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14 At present, the reasons for the success of the oxalate is still not clear. We tentatively suggested that both the high leaving ability (pK_a: oxalic acid 1.27, CF_3CO_2H 0.52, CH_3CO_2H 4.76) and bidentate nature of oxalate might be important for the reaction.

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