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Formation of allylated quaternary carbon centers *via* C–O/C–O bond fragmentation of oxalates and allyl carbonates†

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Disclosed herein emphasizes Fe-promoted cross-electrophile allylation of tertiary alkyl oxalates with allyl carbonates that generates all C(sp^3)–quaternary centers. The reaction involves fragmentation of tertiary alkyl oxalate C–O bonds to give tertiary alkyl radical intermediates, addition of the radicals to less hindered alkene terminals, and subsequent cleavage of the allyl C–O bonds. Allylation with 2-aryl substituted allyl carbonates was mediated by Zn/$MgCl_2$, and Fe is used to promote the radical addition efficiency. By introduction of activated alkenes, a three-component radical cascade reaction took place.

Transition metal-catalyzed cross-electrophile coupling of alkyl electrophiles has emerged as an important research area of interest in the field of cross-coupling chemistry.[1] The exploitation of nickel and cobalt catalysts in particular has enabled a range of useful transformations. The scope of alkyl electrophiles has been largely expanded from the initial alkyl halides. Among them, the engagement of carboxylate modified with NHP and alkyl pyrylium (Katritzky salts) and benzyl ammonium salts was noted, which featured radical decarboxylation and deamination processes.[2,3] By contrast, reductive coupling of readily accessible unactivated alkyl alcohols and their derivatives remains a formidable challenge.[4–8] Recently we have discovered that a combination of Zn and $MgCl_2$ triggered Barton C–O bond radical scission of unsymmetrical tertiary alkyl oxalates, enabling efficient generation of unactivated tertiary alkyl radicals.[9] Such a reduction process is attributed to the coordination of $MgCl_2$ with the oxalates which lowered the LUMO of the carbonyl groups, thus allowing the single electron reduction of the carbonyl to take place. The process is further promoted in the presence of a Ni catalyst, permitting reductive coupling with aryl halides to afford arylated all carbon quaternary centers.[9] Encouraged by these results, we investigated whether reductive coupling of tertiary alkyl oxalates with allyl carbonates is feasible, which would involve two C–O bonds as the coupling partners, and lead to the construction of all C(sp^3)–quaternary centers. To our knowledge, formation of C–C bonds *via* the reaction of unactivated tertiary alkyl oxalates with a different C–O bond partner remains unexplored.

On the other hand, all (sp^3) quaternary carbon centers are an important class of structural motifs widely found in natural products and bioactive compounds.[10–14] To access these congested structural units, coupling of tertiary alkyl–MgX (X = halides) with alkyl halides has shown considerable success under Cu and Co-catalyzed conditions.[11,12] Alternatively, the coupling of tertiary alkyl halides with allylic metallic nucleophiles (*e.g.*, Zn and Mg) has also been revealed.[13] To avoid the pre-preparation of organometallic reagents, we have developed the Ni-catalyzed reductive coupling of tertiary alkyl halides with allyl carbonates, allowing facile access to allylated quaternary centers.[14] However, the allylation was limited to less hindered geminal dimethyl-derived tertiary alkyl halides or special adamantyl bromide (in a Co-catalyzed case),[15] wherein addition of the alkyl radicals to the Ni centers within η^1- and η^3-Ni-allyl intermediates was proposed (Scheme 1).[14]

Herein we depict an unusual Fe-promoted reductive coupling of tertiary alkyl oxalates with allyl carbonates/acetates affording all C(sp^3) quaternary carbon centers up to moderately high yields. This approach offers a valuable alternative to the concurrent allylation methods: (1) the use of earth-abundant Fe as a promoter for reductive allylation has not been reported; (2) unlike the Ni-catalyzed allylation, the present method is suitable for more hindered tertiary alkyl oxalates; (3) a unique mechanism involving double C–O bond fragmentation was proposed, which is rare in radical addition chemistry; and (4) the use of alcohol derivatives as the coupling partners is beneficial as compared to that of less accessible halides.

We set out to examine the reaction of di-*tert*-butyl oxalate **1a** with methyl(2-phenylallyl)carbonate **2a**. It was noted that the previously developed Ni-allylation method for tertiary halides proved to be ineffective for oxalates (Scheme S11, ESI†).[14,16] After extensive experiments, we identified that the optimized

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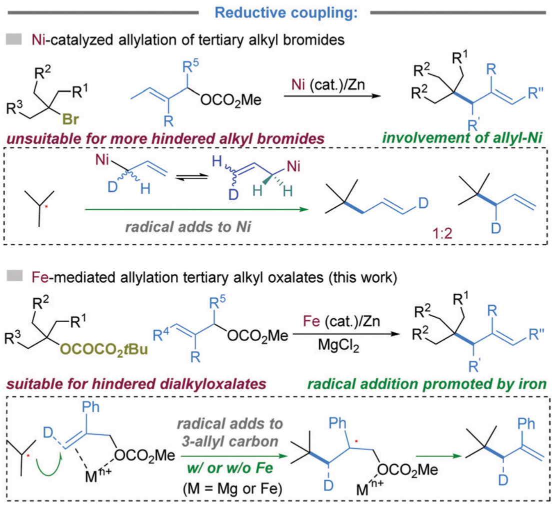
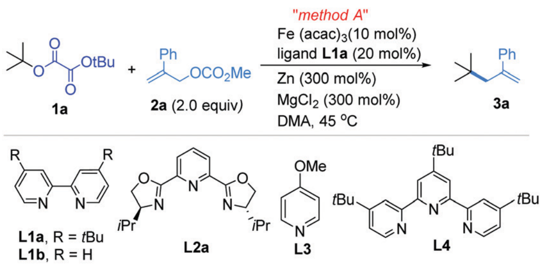


Scheme 1 Construction of allylated quaternary carbon centers *via* Ni and Fe-mediated reductive coupling conditions (the proposed mechanism in boxes).

conditions (method A) comprised the use of *N*,*N*-dimethylacetamide (DMA) as solvent, Fe(acac)$_3$ (10 mol%) as a promoter, dtBBipy **L1a** (20 mol%) as a ligand, Zn powder (3.0 equiv.) as a reductant and MgCl$_2$ (3.0 equiv.) as an additive.[16] The reaction went to completion after 8 h at 45 °C, furnishing **3a** in 84% yield (Table 1, entry 1). Control experiments showed that without Fe salt and a ligand, **3a** was still obtained in 38% yield (entries 2 and 3). When MgCl$_2$ or Zn was omitted, no reaction occurred (entries 4 and 5). By contrast, the use of *tert*-butyl bromide to replace **1a** generated **3a** in ~10% yield (entry 6). Other ligands and metal catalysts proved to be less effective (entries 7–12). Reduction of Fe(acac)$_3$ and ligand loading to half afforded **3a** in 64% yield (entry 13). Operation of the reaction at 25 °C gave **3a** in 62% yield. Replacement of Zn with TDAE offered a trace amount of **3a** (Table S5, ESI†).

Table 1 Optimization for the coupling of di-*t*Bu-oxalate **1a** with methyl(2-phenylallyl)carbonate **2a**[a]



Entry	Variation from method A	Yield[b] (%)
1	None	84[c]
2	w/o Fe(acac)$_3$	41
3	w/o Fe(acac)$_3$ and w/o dtBBipy	38
4	w/o MgCl$_2$	ND
5	w/o Zn	ND
6	*tert*-Butyl bromide instead of **1a**	~10
7	**L1b** instead of **L1a**	61
8	**L2a** instead of **L1a**	58
9	**L3** instead of **L1a**	69
10	**L4** instead of **L1a**	60
11	Ni(acac)$_2$ instead of Fe(acac)$_3$	Trace
12	Co(acac)$_2$ instead of Fe(acac)$_3$	36
13	5 mol% Fe(acac)$_3$, 10 mol% dtBBipy	64
14	25 °C	62

[a] Method A: **1** (0.15 mmol), **2a** (0.3 mmol), Fe(acac)$_3$ (10 mol%), ligand (20 mol%), MgCl$_2$ (300 mol%), Zn (300 mol%), DMA (1.0 mL), 45 °C. [b] NMR yield using 2,5-dimethylfuran as the internal reference. [c] Isolated yield.

With method A (Table 1, entry 1), we evaluated the scope of unsymmetrical tertiary alkyl oxalates containing a *t*-butyl group and a more sterically hindered *t*-alkyl group with respect to *t*-butyl by reacting with allyl carbonate **2a** (Fig. 1). Tertiary oxalates containing geminal dimethyl groups generally gave good results, as exemplified by **3–20**, including those bearing long-aliphatic chains derived from palmitate, laurate and oleate (*e.g.*, **9–11**). For oxalates arising from naturally occurring (−)-alpha-terpineol, lithocholic and cholic acids, and tetrahydro linalool, up to moderately high yields were obtained for **17–19** and **22.** The suitability of the present method for sterically more hindered tertiary oxalates than the geminal dimethyl ones is noteworthy. As such, **21–23** were obtained in preparatively useful yields. It should be noted that the bromo analogs of these substrates were incompetent under our previous Ni-catalyzed allylation conditions,[14] indicating the unique reactivity of oxalates using an Fe-promoted reductive allylation method. The oxalates arising from

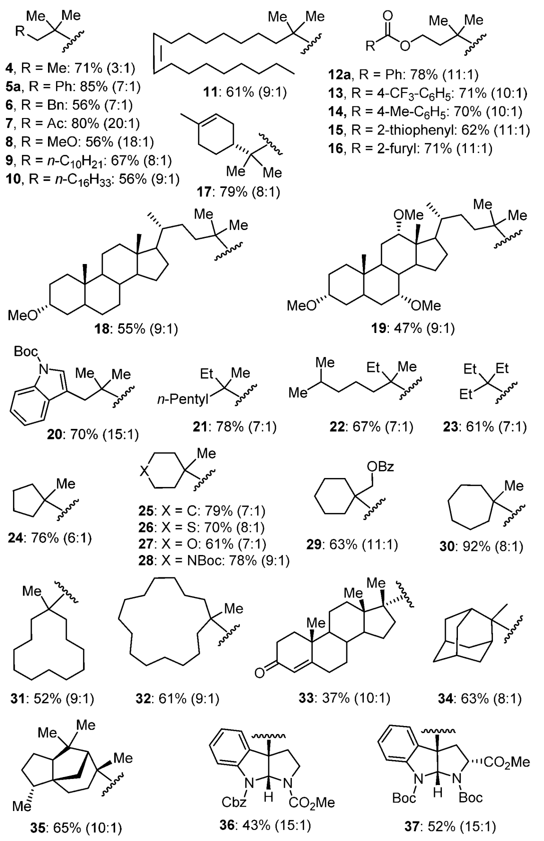


Fig. 1 Scope of oxalates using method A (Table 1, entry 1). Ratio in parentheses refers to that of products arising from a more hindered tertiary group to a *t*-butyl one.

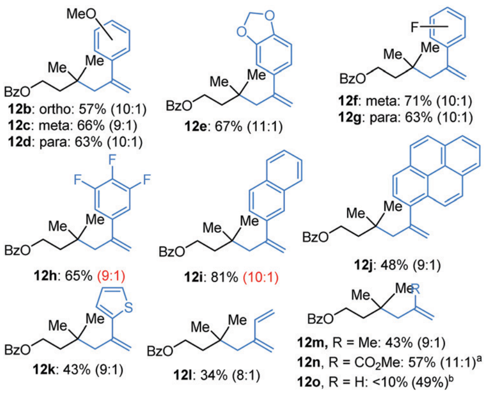


Fig. 2 Scope of allyl carbonates using method A. (a) Methyl 2-(((*tert*-butoxycarbonyl)oxy)methyl)acrylate was used. (b) FePc (10%) and **L4** (10%) were used. Ratio in parentheses refers to that of products arising from a more hindered tertiary group to a *t*-butyl one.

hydroxyl groups present on 5-, 6-, 7-, 12- and 15-memebered rings furnished the allylated products in good to high yields, as exemplified by **24–32**. In these cases, the heterocyclic compounds were found to be compatible (*e.g.*, **26–28**). Moderate yields for **33–37** were obtained for more complex oxalates derived from testosterone, 2-adamantanol, (+)-cedrol, and cyclotryptamine derivatives respectively. The reaction was suitable on a gram scale. The coupling of the (2-phenyl) allyl carbonate with the oxalate **1b** on a 5.0 mmol scale delivered **12a** in 67% yield, wherein ∼14% of oxalate was recovered.[16] The ratio of **12a** to **3a** was determined to be ∼10 : 1 which is lower than 11 : 1 for a 0.15 mmol scale reaction (Schemes S5 and S6, ESI†), indicating high chemoselectivity for the unsymmetrical oxalate.[16]

The reaction protocol also displayed good compatibility across a range of allylic carbonates (Fig. 2). For instance, using oxalate (**1b**) derived from 3-hydroxy-3-methylbutyl benzoate as the coupling partner, 2-aryl-substituted allyl products bearing methoxy phenyl (**12b–d**), 1,3-benzodioxole (**12e**), fluorinated phenyl (**12f–h**), 2-naphthyl (**12i**), pyrenyl and thiophenyl (**12j–k**) all furnished the coupling products in moderate yields. Low to moderate yields were detected for 2-vinyl, -methyl and -ester decorated allylic partners, as manifested by the examples of **12l–n**. By contrast, the unsubstituted allyl carbonate generated **12o** in a poor yield, which was boosted to 49% using FePc/**L4** as a promoter.[16] Finally, the coupling of di-*tert*-butyl oxalate with 1- and 3-phenyl substituted allylic carbonates indicated both that reactions were not satisfactory. While 3-phenyl allylic carbonate gave a trace amount of (*E*)-(4,4-dimethylpent-1-en-1-yl)benzene, the 1-phenyl substituted substrate resulted in the same product in 35% yield (Scheme S4, ESI†).[16] Both reactions generated a substantial amount of *tert*-butanol as the major byproduct.[16]

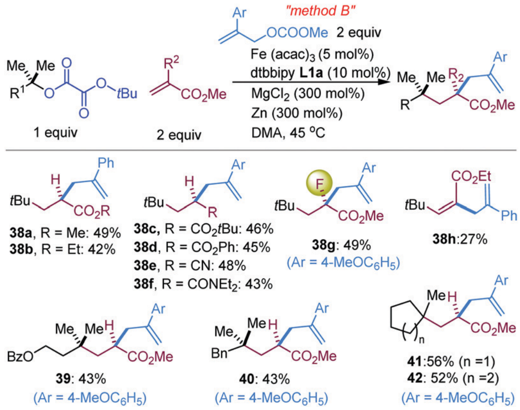
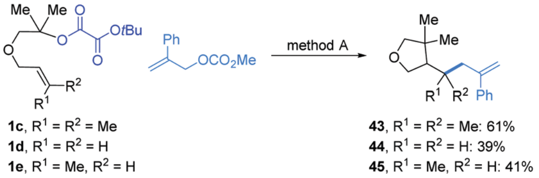


Fig. 3 Three component reaction (method B): oxalate (0.3 mmol), acrylate (0.6 mmol), allyl carbonate (0.6 mmol), Fe (acac)$_3$ (5%), **L1a** (10%), MgCl$_2$ (300%), Zn (300%), DMA (1.0 mL), 45 °C.

To further explore the utility of this allylation strategy, we sought to integrate the allylation approach into three-component reactions (Fig. 3).[17] When methyl acrylate was introduced, we were pleased to isolate a three-component product **38a** in 49% yield (method B, Fig. 3). Screening of a range of activated alkenes indicated that acrylates decorated with different alkyl groups, acrylonitrile, *N*,*N*-diethylacrylamide and methyl 2-fluoroacrylate, on the ester moieties were effective as evidenced by the formation of **38b–g**. An unexpected discovery was the capability of methyl propiolate that generated conjugated trisubstituted alkene **38h** in 27% yield. Other tertiary alkyl oxalates present on open-chain and cyclic rings were also efficient, as exemplified by **39–42**. A competing product arising from *tert*-butyl addition was negligible based on the reaction of **1b**, acrylate and **2a** (Scheme S8, ESI†).[16]

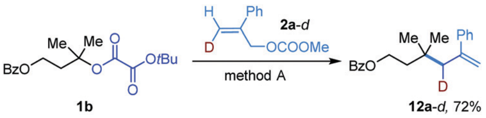
In line with our previous evidence that alkyl oxalates underwent radical process,[9] we performed radical cyclization experiments using allyl-tethered oxalates **1c–1e** to react with methyl-(2-phenylallyl)carbonate with method A. The cyclization products **43–45** were obtained in moderate yields (eqn (1)), supporting the fact that radicals were involved in the allylation event.[9]



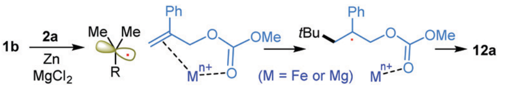
(1)

To gain further insight into the reaction details, treatment of **1b** with (*Z*)-methyl(2-phenylallyl-3-*d*)carbonate **2a**-*d* with method A furnished the mono-deuterated product **12a**-*d* in 72% yield (eqn (2)). This result is in sharp contrast to our previous Ni-catalyzed allylation tertiary alkyl bromides, wherein a mixture of 1- or 3-deuterated allylic products with a ratio of 1 : 2 was observed (Scheme S12, ESI†). Thus, we reason that formation of π-allyl-Fe and its equilibria with η^1-allyl-Fe is unlikely. This notion is in accordance with the fact that with the removal of Fe and the ligand, the yield for **3a** was 38%, indicating that allylation is a radical addition and allyl C–O bond cleavage process (Table 1, entry 3). We inferred that coordination of MgCl$_2$ with allyl carbonate may play a key role in the allyl C–O bond fragmentation (eqn (3)). Complexation of MgCl$_2$ with **2a** was confirmed by ^{1}H NMR spectral analysis of a mixture of the two species in DMSO-d$_6$ wherein appreciable changes in chemical shifts for **2a** were observed upon addition of 1.5 equiv. of MgCl$_2$ (Fig. S3, ESI†). Similarly, low valent Fe(I) or Fe(II) may function in the same way as

Mg^{2+} so as to promote the reaction efficiency.[18] The result of addition of a tertiary alkyl radical to 1-phenyl substituted allyl carbonate (35% yield, Scheme S4, ESI†) further supports the mechanistic proposal in eqn (2) that may involve a possible SN2′-type process.



(2)



(3)

In summary, a new allylation protocol that afforded all C(sp^3) quaternary centers has been developed. The mild Fe-promoted conditions are suitable for a wide set of unactivated tertiary alkyl oxalates and allylic carbonates decorated with different substituents. $MgCl_2$ not only serves as a Lewis-acid to promote reduction of C–O bonds of oxalates to generate tertiary alkyl radicals as described previously, but also plays a key role in allyl C–O bond cleavage.

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Conflicts of interest

There are no conflicts to declare.

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