Multicomponent Reactions

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Titanocene(III)-Catalyzed Three-Component Reaction of Secondary Amides, Aldehydes, and Electrophilic Alkenes

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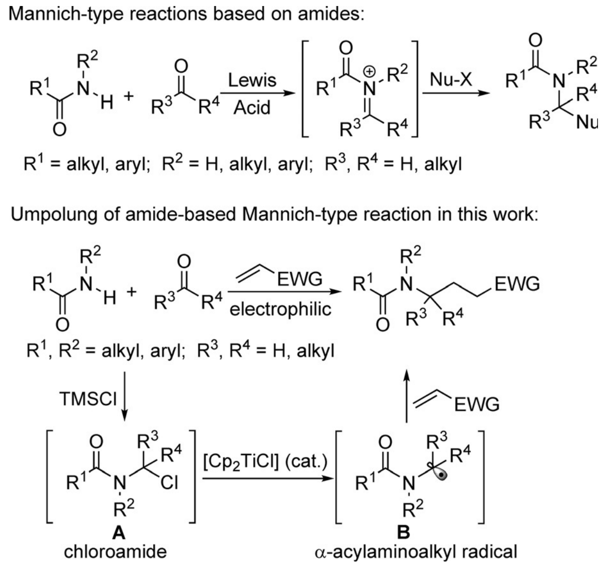
Abstract: *An umpolung Mannich-type reaction of secondary amides, aliphatic aldehydes, and electrophilic alkenes has been disclosed. This reaction features the one-pot formation of C–N and C–C bonds by a titanocene-catalyzed radical coupling of the condensation products, from secondary amides and aldehydes, with electrophilic alkenes. N-substituted γ-amido-acid derivatives and γ-amido ketones can be efficiently prepared by the current method. Extension to the reaction between ketoamides and electrophilic alkenes allows rapid assembly of piperidine skeletons with α-amino quaternary carbon centers. Its synthetic utility has been demonstrated by a facile construction of the tricyclic core of marine alkaloids such as cylindricine C and polycitorol A.*

The three-component reaction[1] of an amine, an aldehyde, and a ketone, known as the Mannich reaction,[2] is the most widely utilized chemical transformation for the tandem construction of C–N and C–C bonds. In recent years, similar three-component reactions using amides, instead of amines, as a component have been reported, and can be viewed as an amide-based Mannich-type reaction.[3] In the Mannich-type reactions, the addition of C-nucleophiles to N-acyliminium ions are generally involved. The resulting α-amidoalkylation products[4] are versatile synthetic intermediates for the synthesis of various nitrogen-containing natural products and bioactive compounds.[5]

Our group has long been interested in the development of C–C bond-formation methodologies based on the radical cross-coupling of α-acylaminoalkyl radicals,[6] which are generated by single-electron transfer (SET) reduction from N-acyliminium ions.[7] We recently reported a titanocene-catalyzed[8] radical umpolung cross-coupling reaction[9] of hemiaminals with electrophilic alkenes to give α-amidoalkylated derivatives.[10] In this reaction, chloroamide **A** was proposed to act as the precursor of α-acylaminoalkyl radical **B**. Since **A** could also be formed by the reaction of amides with aldehydes in the presence of TMSCl,[11] the three-component reaction of secondary amides, aldehydes, and electrophilic alkenes, which involves the addition of **B** to electrophilic alkenes, was thus envisaged as an umpolung of the Mannich-type reaction to construct C–N and C–C bonds in one pot (Scheme 1). To the best of our knowledge, such a three-component reaction has never been reported. Herein, we report the results of our investigations on this reaction. The extension of the methodology to the reaction of ketoamides with electrophilic alkenes to build piperidine skeletons with α-amino quaternary carbon centers, and its application in the synthesis of the tricyclic core of marine alkaloids are also included.



Scheme 1. Umpolung of Mannich-type reaction of secondary amides, aldehydes, and electrophilic alkenes. Cp = cyclopentadienyl, EWG = electron-withdrawing group, TMS = trimethylsilyl.

The three-component reaction of the carbamate **1**, paraformaldehyde, and ethyl acrylate was chosen as the model study (Table 1). After extensive trials (see Table S1 in the Supporting Information), optimized reaction conditions were established: condensation of an amide (1.0 mmol) with $(CH_2O)_n$ (1.6 mmol) in anhydrous CH_2Cl_2 (4.0 mL) in the presence of TMSCl (3.0 mmol) under an argon atmosphere at room temperature for 2 hours. Then coupling of the resulting mixture with electrophilic alkenes (2.0 mmol) in a green suspension of Sm (3.0 mmol),[12] [Cp_2TiCl] (0.1 mmol), and $Et_3N{\cdot}HCl$ (3.0 mmol)[13] in THF (4.0 mL), for additional 6 hours. Under the optimized reaction conditions, the desired cross-coupling product **2a** was obtained in 73 % yield, along with the byproduct **3** in 13 % yield. Other acrylates could also undergo this one-pot reaction with **1** and paraformaldehyde

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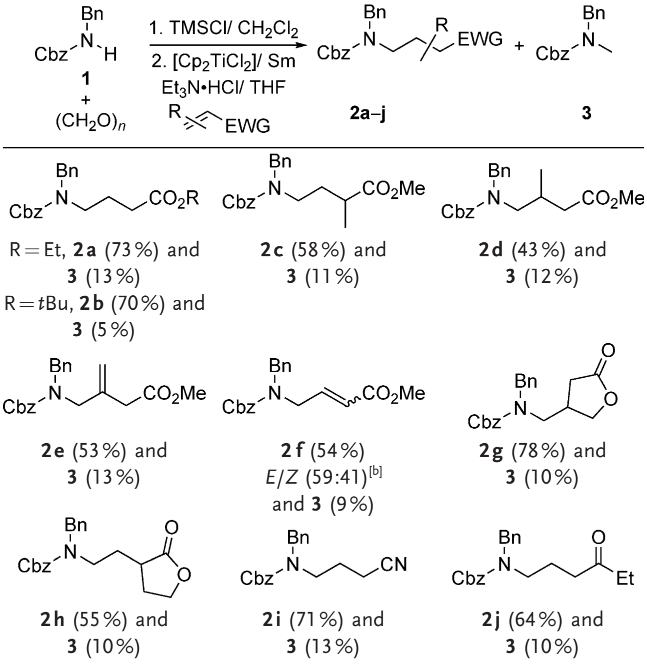
Table 1: The scope of electrophilic alkenes of the umpolung of the Mannich-type reaction.[a]



1 + $(CH_2O)_n$ → **2a–j** + **3**

R = Et, **2a** (73 %) and **3** (13 %)
R = *t*Bu, **2b** (70 %) and **3** (5 %)

2c (58 %) and **3** (11 %)

2d (43 %) and **3** (12 %)

2e (53 %) and **3** (13 %)

2f (54 %) *E*/*Z* (59:41)[b] and **3** (9 %)

2g (78 %) and **3** (10 %)

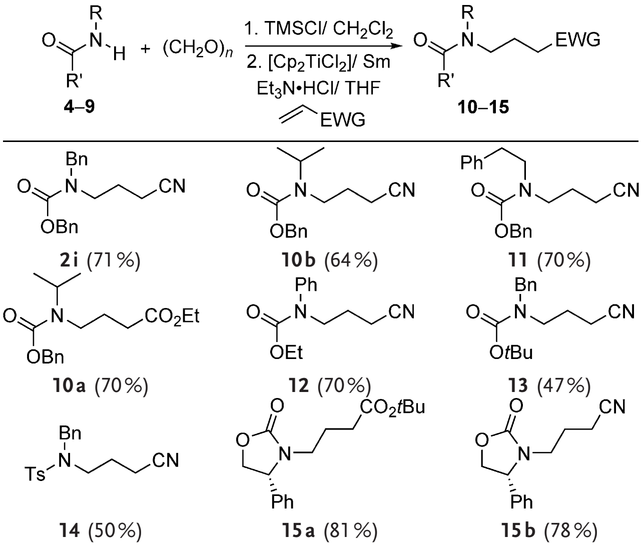
2h (55 %) and **3** (10 %)

2i (71 %) and **3** (13 %)

2j (64 %) and **3** (10 %)

[a] Standard reaction conditions: 1.0 mmol of amide **1**, 1.6 mmol of $(CH_2O)_n$, 3.0 mmol of TMSCl, 4.0 mL of anhydrous CH_2Cl_2, 2.0 mmol of electrophilic alkenes, 3.0 mmol of Sm, 0.1 mmol of $[Cp_2TiCl_2]$ and 3.0 mmol of $Et_3N{\cdot}HCl$, 4.0 mL of THF. Yields of products isolated after chromatographic separation are given within parentheses. [b] Determined upon isolation of the products. Cbz = benzyloxycarbonyl, THF = tetrahydrofuran.

Table 2: The scope of secondary amides of the umpolung of the Mannich-type reaction.[a]



4–9 + $(CH_2O)_n$ → **10–15**

2i (71 %)

10b (64 %)

11 (70 %)

10a (70 %)

12 (70 %)

13 (47 %)

14 (50 %)

15a (81 %)

15b (78 %)

[a] Under standard reaction conditions as detailed in Table 1. Yield of the product isolated after chromatographic separation is given within parentheses. Ts = 4-toluenesulfonyl.

to give the corresponding coupling products **2b–d** in moderate to good yields. Ethyl buta-2,3-dienoate and methyl propiolate were also applicable to produce the cross-coupling products in moderate yields (**2e** and **2f**). In addition, both the *endo*- and *exo*-cyclic α,β-unsaturated lactones could also participate in this one-pot reaction in good to moderate yields (**2g** and **2h**). Besides α,β-unsaturated esters, α,β-unsaturated nitriles and ketones, were all well tolerated under the standard reaction conditions (**2i** and **2j**).

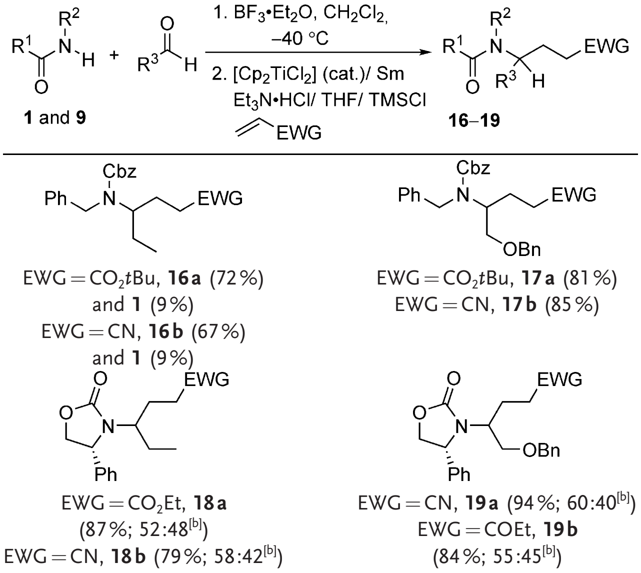
We next investigated a wide array of secondary amides (Table 2). Various R substituents on the nitrogen atoms of the carbamates seemed to have little influence on the reaction outcome. The coupling of Cbz-protected carbamates (**1**, **4** and **5**) with paraformaldehyde and acrylonitrile gave the desired products in comparable yields (**2i**, **10b**, and **11**). The acyl protecting groups, in contrast, strongly affected the reactions. Moderate to good yields (**2i**, **10–12**) were obtained with N-Cbz carbamates (**1**, **4**, and **5**) and the Eoc-protected carbamate **6**, while low yields (**13** and **14**) were observed with the N-Boc carbamate **7** and N-Ts amide **8**. The low yields in the latter cases might be caused by the decreased nucleophilicity of **7** and **8**, as a lot of the starting amides were recovered. In addition, when the chiral oxazolidone **9** was used as the secondary amides, the desired α-amidoalkylated products were obtained in satisfactory yields (**15a** and **15b**).

The scope with respect to the aldehydes was subsequently explored. Unfortunately, under the standard reaction conditions, only a small amount of the desired products were obtained, along with a lot of recovered amide substrates, when aldehydes other than paraformaldehyde were used. To our delight, when $BF_3{\cdot}Et_2O$ was added (see Scheme S1), the condensation of amides (**1** and **9**) with aldehydes [propanal or 2-(benzyloxy)acetaldehyde] at −40 °C for 2 hours, followed by the coupling with electrophilic alkenes in the presence of $Et_3N{\cdot}HCl$/TMSCl led to the desired coupling products in 67 % to 94 % yields (Table 3). Higher yields were obtained with 2-(benzyloxy)acetaldehyde (**17** and **19**) than with propanal (**16** and **18**), thus suggesting a strong influence of the electrophilicity of aldehydes. Notably, low diastereoselectivities (**18** and **19**) were obtained even though the optically pure amide **9** was used. Aromatic aldehydes and ketones, however, could not produce the desired products.

This three-component reaction was expanded further to ketoamides (Table 4). By using the same reaction conditions as in Table 3, the ketoamides **20–23** (for preparation, see the Supporting Information) were treated with $BF_3{\cdot}Et_2O$ and the resulting mixture was then subjected to titanocene-catalyzed coupling with the electrophilic alkenes in the presence of TMSCl and $Et_3N{\cdot}HCl$. To our delight, the N-Boc piperidines **24** and **25**, having α-amino quaternary carbon center, were obtained in excellent yields (92–96 %). Apart from N-Boc carbamates, N-benzyl amides were also applicable, thus providing the piperidin-2-ones **26** and **27** in moderate to good yields.

To demonstrate the synthetic utility of our methodology, a concise synthesis of the tricyclic lactam **34** was carried out (Scheme 2). The lactam **34** is the core skeleton of cylindricine C (**28**)[14] and polycitorol A (**29**),[15] two tricyclic marine alkaloids with a perhydropyrrolo[1,2-*j*]quinoline ring system. The treatment of the commercially available 2-oxo-1-cyclohexanepropionitrile (**30**) with lithium aluminum hydride (LAH) in refluxing THF, followed by an acidic aqueous (HCl, 3 M) work-up, afforded the corresponding aminoalcohol

Table 3: The scope of aldehydes of the umpolung of the Mannich-type reaction.[a]



EWG = CO_2tBu, **16a** (72 %) and **1** (9 %)
EWG = CN, **16b** (67 %) and **1** (9 %)

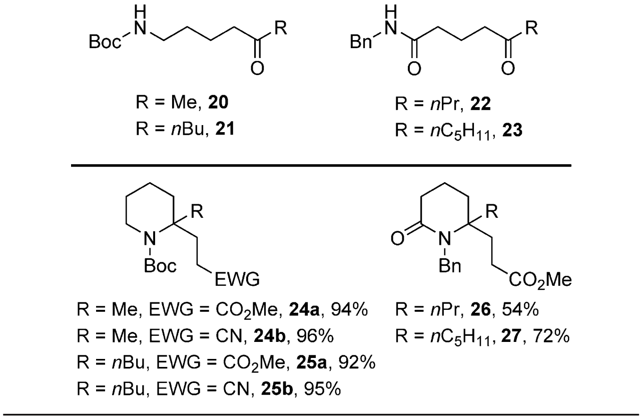
EWG = CO_2tBu, **17a** (81 %)
EWG = CN, **17b** (85 %)

EWG = CO_2Et, **18a** (87 %; 52:48[b])
EWG = CN, **18b** (79 %; 58:42[b])

EWG = CN, **19a** (94 %; 60:40[b])
EWG = COEt, **19b** (84 %; 55:45[b])

[a] Reaction conditions: an amide (1.0 mmol) with an aldehyde (1.6 mmol) in anhydrous CH_2Cl_2 (4.0 mL) in the presence of $BF_3 \cdot Et_2O$ (1.0 mmol) at −40 °C for 2 h. The resulting mixture with electrophilic alkenes (2.0 mmol) was added to a green suspension of Sm (3.0 mmol), $[Cp_2TiCl_2]$ (0.1 mmol), $Et_3N \cdot HCl$ (3.0 mmol), and TMSCl (3.0 mmol) in THF (4.0 mL) at RT for an additional 6 h. Yields of products isolated after chromatographic separation are given within parentheses. [b] The d.r. values were determined by integration of the peaks in the ^1H NMR spectrum (see the Supporting Information).

Table 4: The construction of α-amino quaternary carbon centers from ketoamides with electrophilic alkenes.[a]



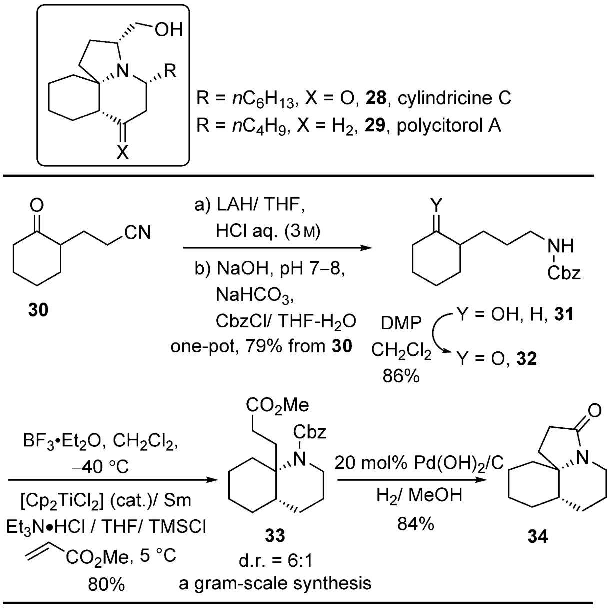
R = Me, **20**
R = *n*Bu, **21**

R = *n*Pr, **22**
R = nC_5H_{11}, **23**

R = Me, EWG = CO_2Me, **24a**, 94%
R = Me, EWG = CN, **24b**, 96%
R = *n*Bu, EWG = CO_2Me, **25a**, 92%
R = *n*Bu, EWG = CN, **25b**, 95%

R = *n*Pr, **26**, 54%
R = nC_5H_{11}, **27**, 72%

[a] A ketoamide (1.0 mmol) under the reaction conditions as detailed in Table 3. Yield is that of the product isolated after chromatographic separation. Boc = *tert*-butoxycarbonyl.



Scheme 2. Concise construction of the tricyclic core of marine alkaloids.

hydrochloride salt. After careful neutralization, by solid NaOH, to pH 7–8, solid $NaHCO_3$ and a solution of CbzCl in THF were added successively to furnish the N-Cbz aminoalcohol **31** in 79 % yield in one pot. Oxidation of **31** by Dess–Martin periodinane (DMP) gave the ketoamide **32** in 86 % yield. By using a modified sequence, **32** was treated by $BF_3 \cdot Et_2O$ in CH_2Cl_2 at −40 °C, and then coupled with methyl acrylate under the titanocene-cataylzed conditions at 5 °C for 8 hours to afford the substituted octahydroquinoline (1-azadecalin) **33** in 80 % yield with 6:1 diastereoselectivity. Notably, a large-scale synthesis of **33** (1.73 g, 4.81 mmol) can be performed efficiently without a decrease in either the yield or diastereoselectivity. Removal of the Cbz protecting group of **33** in the presence of 20 % $Pd(OH)_2/C$ under an atmosphere of H_2 afforded the *cis*-tricyclic lactam **34** in 84 % yield, along with the uncyclized *trans*-amine in 16 % yield. The ^1H and ^{13}C NMR spectra of **34** were consistent with literature data,[16b,c] and thus confirmed the *cis*-1-azadecalin configuration of **34**. The core skeleton of tricyclic the marine alkaloids **28** and **29** was thus synthesized in only five steps with an overall yield of 39 %.

In conclusion, a three-component reaction of secondary amides, aliphatic aldehydes, and electrophilic alkenes has been developed. The reaction can be regarded as the umpolung of the amide-based Mannich-type reaction, which features a titanocene-catalyzed radical coupling of electrophilic alkenes with the condensation products from secondary amides and aldehydes to construct C–N and C–C bonds in one pot. Extension of the method to ketoamides to furnish piperidine skeletons with α-amino quaternary carbon centers has been achieved in satisfactory yields. The synthetic value of this methodology has been demonstrated by a concise construction of the tricyclic lactam **34**, the core of cylindricine C (**28**) and polycitorol A (**29**). Notably, these reactions can produce cyclic tertiary amides which recently have been used in C–C bond formation to give α-alkylated amines directly, and been applied for the synthesis of alkaloids.[17] Further studies on the mechanism and the application of this method to synthesize those marine alkaloids are in progress.

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