Lewis Acid Catalyzed [3+2] Coupling of Quinone Monoacetals or Quinone Imine Ketals with Vinylcarbamates

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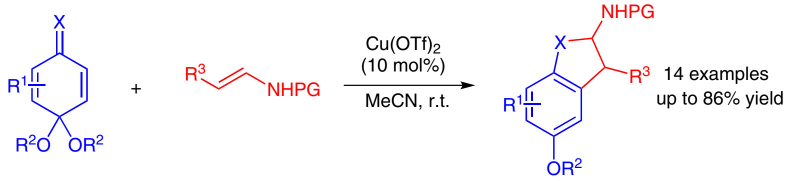

R^1 = H, Me, Et, *t*-Bu, CH=CH–CH=CH
R^2 = Me, Et
R^3 = H, Me
PG = Cbz, Boc

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Abstract A mild and concise [3+2] coupling of quinone monoacetals or quinone imine ketals with vinylcarbamates promoted by Lewis acid was realized. Various 2-carbamate-2,3-dihydrobenzofurans and 2-carbamate-indolines have been prepared in moderate to good yields.

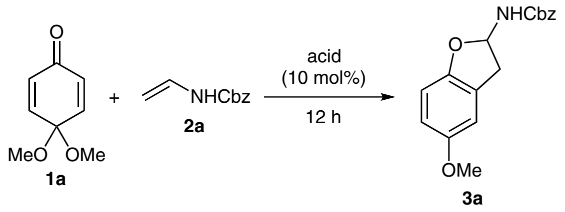
Key words [3+2] coupling, Lewis acid, synthesis, 2-carbamate-2,3-dihydrobenzofurans, 2-carbamate-indolines

2,3-Dihydrobenzofurans are important motifs widely existing in numerous biologically active natural products and pharmaceuticals.[1,2] Consequently, construction of 2,3-dihydrobenzofurans have attracted considerable attention and many efficient strategies for the synthesis of these valuable substances have been developed.[3–5]

Quinone derivatives are versatile electrophiles which have been employed in reactions with a wide variety of nucleophiles to generate structurally diverse compounds.[5,6] For example, quinone derivatives were frequently employed in [3+2] coupling with alkene nucleophiles to give various 2,3-dihydrobenzofurans.[5] Although significant progress has been made in the synthesis of 2,3-dihydrobenzofurans via [3+2] coupling of quinone derivatives with alkene nucleophiles, up to now, systematic research of coupling of quinone derivatives with enecarbamates has not been reported yet. Herein, we describe the Lewis acid promoted [3+2] coupling[7] of quinone monoacetals or quinone imine ketals with benzyl vinylcarbamate by which various 2-carbamate-2,3-dihydrobenzofurans and 2-carbamate-indolines have been prepared in moderate to good yields.

First, several acids were tested in promoting [3+2] coupling of quinone monoacetal **1a** with benzyl vinylcarbamate **2a** in toluene at room temperature. As can be seen in Table 1, only trace of the product was obtained with iron(III) chloride and nickel(II) chloride (Table 1, entries 1 and 2). Aluminium chloride and tin(IV) chloride provided low yields of the product (Table 1, entries 3 and 4). Zinc trifluoromethanesulfonate [Zn(OTf)$_2$] delivered obviously better yields (Table 1, entry 5). When copper trifluoromethanesulfonate [Cu(OTf)$_2$] was employed, good yield was obtained (Table 1, entry 6). Meanwhile, pentafluorobenzoic acid led to lower yield (Table 1, entry 7). Thus Cu(OTf)$_2$ was

Table 1 [3+2] Coupling of 4,4-Dimethoxy-cyclohexa-2,5-dienone (**1a**) with Benzyl Vinylcarbamate (**2a**) Promoted by Acids[a]



Entry	Cat.	Solvent	Temp (°C)	Yield (%)[b]
1	$FeCl_3$	toluene	r.t.	trace
2	$NiCl_2$	toluene	r.t.	trace
3	$AlCl_3$	toluene	r.t.	28
4	$SnCl_4$	toluene	r.t.	30
5	$Zn(OTf)_2$	toluene	r.t.	65
6	$Cu(OTf)_2$	toluene	r.t.	80
7	$C_6F_5CO_2H$	toluene	r.t.	70
8	$Cu(OTf)_2$	toluene	0	trace
9	$Cu(OTf)_2$	CH_2Cl_2	r.t.	67
10	$Cu(OTf)_2$	MeCN	r.t.	84
11	$Cu(OTf)_2$	THF	r.t.	trace
12	$Cu(OTf)_2$	MeCN	50	80

[a] Unless otherwise specified, the reactions were carried out with 0.30 mmol of **1a**, 0.20 mmol of **2**, and 0.02 mmol of Lewis acid in 2 mL of solvent for 12 h.
[b] Isolated yield based on **2**.

determined as the optimal catalyst and employed in the following investigations. Afterwards, the reaction was conducted at 0 °C, however, it was very difficult for the reaction to proceed at that lower temperature (Table 1, entry 8). Subsequent screening of the solvents revealed that acetonitrile was the most favorable solvent in the reaction (Table 2, entry 10). In order to further improve the yield, we tried to perform the reaction at 50 °C, however, lower yield was obtained due to the decomposition of the substrates at higher temperature (Table 1, entry 12).

Having established the optimal reaction conditions, the scope of the reaction was examined. The results are summarized in Table 2. Generally, quinone monoacetals bearing various substituents were tolerable in the reaction with benzyl vinylcarbamate (**2a**) to generate the corresponding 2-carbamate-2,3-dihydrobenzofurans **3a**–**k** in moderate to good yields. Additionally, reaction of *tert*-butyl vinylcarbamate (**2b**) with quinone monoacetal **1a** also provided good yield of the product (Table 2, entry 11). However, no product was detected with the reaction of (*E*)-*tert*-butyl prop-1-enylcarbamate (**2c**, Table 2, entry 12). Finally, quinone imine ketals **1k** and **1l** were also subjected to the reaction with **2a**, and 2-carbamate-indolines **3m** and **3n** were obtained in good yields (Table 2, entries 13 and 14).

Table 2 [3+2] Coupling of Quinone Monoacetals or Quinone Imine Ketals **1a–l** with Benzyl Vinylcarbamate **2** Promoted by Cu(OTf)$_2$[a]

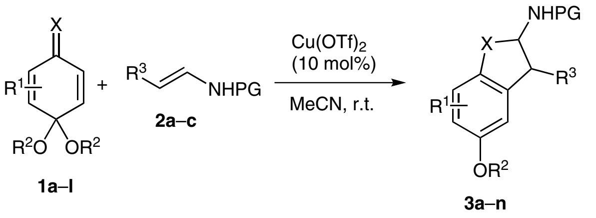


Table 2 (continued)

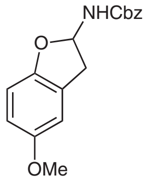
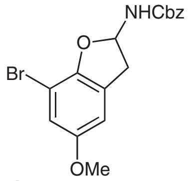
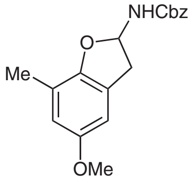
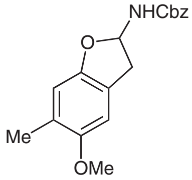
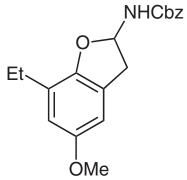
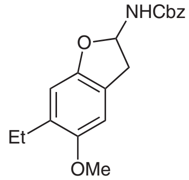
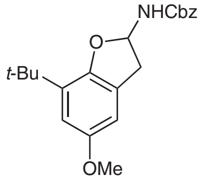
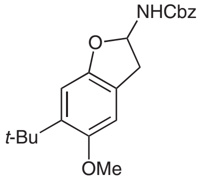
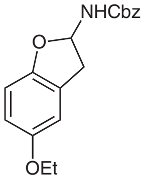
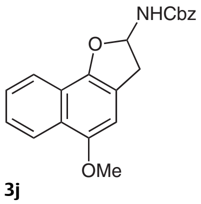
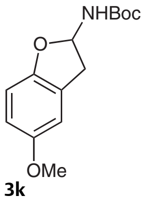
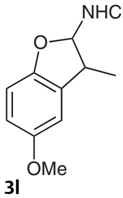
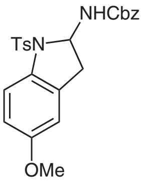
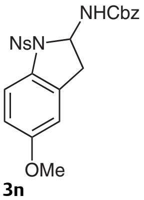
Entry	3[8]	Time (h)	Yield (%)[b]
1	 **3a**[9]	12	84
2	 **3b**	12	82
3	 **3c**	24	50
4	 **3d**	12	74
5	 **3e**	24	52
6	 **3f**	24	54
7	 **3g**	24	62
8	 **3h**	24	81
9	 **3i**	12	81

Table 2 (continued)

Entry	3[a]	Time (h)	Yield (%)[b]
10	 **3j**	24	77
11	 **3k**	24	84
12	 **3l**	24	n.d.
13	 **3m**	12	86
14	 **3n**	12	80

[a] Unless otherwise specified, the reactions were carried out with 0.20 mmol of **1**, 0.30 mmol of **2**, and 0.02 mmol of $Cu(OTf)_2$ in 2 mL of MeCN for 24 h.

[b] Isolated yield based on **1**.

In summary, we have developed a Lewis acid promoted [3+2] coupling of quinone monoacetals or quinone imine ketals with vinylcarbamates. This transformation enables the straightforward and mild synthesis of various 2-carbamate-2,3-dihydrobenzofurans and 2-carbamate-indolines in moderate to good yields.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380723.

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(8) **General Experimental Procedure for the [3+2] Coupling of Quinone Monoacetals or Quinone Imine Ketals 1 with Vinylcarbamates 2**

Quinone monoacetal or quinone imine ketal **1** (0.30 mmol) and vinylcarbamate **2** (0.20 mmol) were added to a flame-dried vial equipped with a magnetic stirring bar. Then MeCN (2 mL) was added to dissolve the mixture. Afterwards Cu(OTf)$_2$ (10.8 mg, 0.02 mmol) was introduced in the solution. The reaction mixture was stirred at 25 °C for 12 h. Then the solvent was evaporated, and the residue was subjected to chromatography (silica gel; hexane–EtOAc, 20:1 to 10:1) to afford the desired product **3**.

(9) **Benzyl (5-Methoxy-2,3-dihydrobenzofuran-2-yl)carbamate (3a)**
Yield 84%, 0.050 g; white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.35 (m, 5 H), 6.65–6.74 (m, 3 H), 6.26 (br s, 1 H), 5.75 (d, J = 8.8 Hz, 1 H), 5.08–5.18 (m, 2 H), 3.74 (s, 3 H), 3.49 (dd, J_1 = 8.3 Hz, J_2 = 16.4 Hz, 1 H), 2.89 (dd, J_1 = 16.5 Hz, J_2 = 4.5 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.3, 154.3, 151.8, 135.8, 128.5, 128.3, 128.2, 125.2, 113.3, 110.9, 109.8, 85.3, 67.2, 55.9, 36.1. ESI-HRMS: m/z calcd for $C_{17}H_{17}NO_4Na^+$ $[M + Na]^+$: 322.1047; found: 322.1055.