

Preparation of Furo[3,2-*c*]coumarins from 3-Cinnamoyl-4-hydroxy-2*H*-chromen-2-ones and Acyl Chlorides: A Bu₃P-Mediated C-Acylation/Cyclization Sequence**

Chia-Jui Lee, Cheng-Che Tsai, Shao-Hao Hong, Geng-Hua Chang, Mei-Chun Yang, Lennart Möhlmann, and Wenwei Lin*

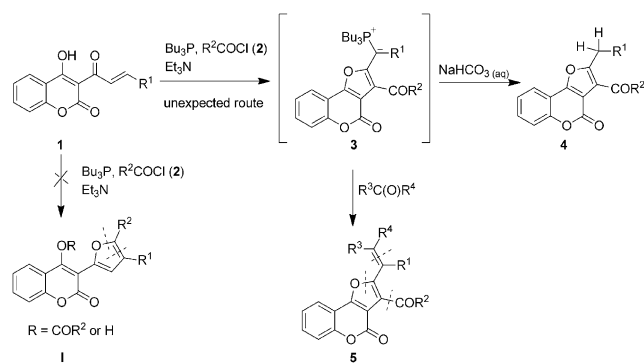
Abstract: A Bu₃P-mediated cyclization reaction of 3-cinnamoyl-4-hydroxy-2*H*-chromen-2-ones through electrophilic addition of acyl chlorides towards the synthesis of highly functionalized furo[3,2-*c*]coumarins bearing a phosphorus ylide moiety is described. These unprecedented cyclization reaction proceeds under mild reaction conditions within short reaction times (1 min to 1 h), and can be further applied in the synthesis of alkenyl-substituted furo[3,2-*c*]coumarins by the treatment with carbonyl electrophiles under basic conditions.

Given their frequent appearance in drugs and natural products, the efficient construction of highly functionalized furans and furo[3,2-*c*]coumarins is a major challenge in organic synthesis.^[1] Tremendous work has been done within this field of chemistry, and thus various transition-metal-catalyzed cyclization reactions are well established.^[2] As cheap and metal-free alternatives, phosphine-triggered reactions have recently attracted great interest.^[3] Previously we demonstrated that multifunctionalized furan derivatives were afforded simply by treating Michael acceptors, such as α,β-unsaturated carbonyl compounds, with tributylphosphine in the presence of acyl chlorides using an intramolecular Wittig reaction as the key step.^[3d–g] Based on this discovery, we were interested in the extension of this method to the application of coumarin derivatives, such as **1**, as Michael acceptors, which is proposed to give access to 3-furyl-4-hydroxycoumarin derivatives (**I**; Scheme 1).

Following our previously established protocol using 3-cinnamoyl-4-hydroxy-2*H*-chromen-2-ones **1** and acyl chlorides **2** as substrates in the presence of Et₃N as base, the expected adducts **I** could not be obtained (Scheme 1). Instead, the phosphorus ylides **3** were determined to be the major products. Remarkably, these ylide intermediates showed good reactivity for undergoing additional transformations in a one-pot approach: addition of a saturated NaHCO₃ solution directly led to the dephosphorated com-

pounds **4**, whereas the treatment with carbonyl electrophiles afforded the corresponding Wittig products **5**.

A screening of the reaction conditions was pursued using the coumarin derivative **1a** and benzoyl chloride (**2a**) as model substrates (Table 1). Initially, THF was used as the solvent and Bu₃P as the nucleophile. After 3.5 hours, the reaction was quenched by saturated NaHCO₃(aq), and the desired product **4aa** was obtained in 39% yield (NMR; entry 1). When other solvents such as CH₂Cl₂ and toluene were used, **4aa** was provided in 33–35% yields (entries 2 and 3). To our delight, the reaction proceeded more effectively in MeCN to afford **4aa** in 59% yield (entry 4). After further optimization of the reaction conditions (2.8 equiv of **2a** and 3.4 equiv of Et₃N), the adduct **4aa** could be furnished in 82% isolated yield within 1 hour (entries 4–6).^[4] In addition, different phosphine sources, such as *i*Bu₃P, Cy₃P, MePh₂P, EtPh₂P, and (OEt)₃P, as well as DABCO, were examined (entries 7–12). Presumably because of the lower nucleophilicity, only *i*Bu₃P could successfully promote the reaction to provide **4aa**, albeit with low yield (entry 7).^[5] Therefore, the



Scheme 1. Unexpected formation of the products **4** and **5** by treating **1** with Bu₃P, acyl chlorides **2**, and Et₃N.

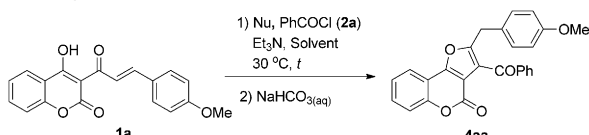
use of MeCN as solvent, 1.1 equivalents of Bu₃P, 2.8 equivalents of acyl chloride, and 3.4 equivalents of Et₃N were selected as the optimal reaction conditions.^[6]

With the optimized reaction conditions in hand, the substrate scope of this novel cyclization was investigated (Table 2). A wide range of aryl-substituted acyl chlorides was screened, and good to excellent results could be achieved within short reaction times (entries 1–8). Heteroaryl-substituted (entries 9 and 10) as well as aliphatic acyl chlorides (entries 11 and 12) were also employed successfully for this

[*] C.-J. Lee, C.-C. Tsai, S.-H. Hong, G.-H. Chang, M.-C. Yang, Dr. L. Möhlmann, Prof. Dr. W. Lin
Department of Chemistry, National Taiwan Normal University
88, Sec. 4, Tingchow Road, Taipei 11677 (Taiwan, R.O.C.)
E-mail: wenweilin@ntnu.edu.tw

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Table 1: Optimization of reaction conditions.^[a]


Entry	Solvent	Nu	2 a (equiv)	Et ₃ N (equiv)	t [h]	Yield [%] ^[b]
1	THF	Bu ₃ P	2.2	2.3	3.5	39
2	toluene	Bu ₃ P	2.2	2.3	3.5	35
3	CH ₂ Cl ₂	Bu ₃ P	2.2	2.3	3.5	33
4	MeCN	Bu ₃ P	2.2	2.3	3.5	59
5	MeCN	Bu ₃ P	2.8	3.4	1	82 ^[c]
6	MeCN	Bu ₃ P	1.3	1.5	1	26
7	MeCN	iBu ₃ P	2.8	3.4	1 (12)	25 (31)
8	MeCN	Cy ₃ P	2.8	3.4	1 (12)	0 (0)
9	MeCN	MePh ₂ P	2.8	3.4	1 (12)	2 (3)
10	MeCN	EtPh ₂ P	2.8	3.4	1 (12)	1 (2)
11	MeCN	(OEt) ₃ P	2.8	3.4	1 (12)	0 (0)
12	MeCN	DABCO	2.8	3.4	1 (12)	0 (0)

[a] Reaction conditions: Step 1: 0.2 mmol of **1a** and 1.1 equiv of the nucleophile (Nu) were utilized in dry solvent (1 mL) under N₂ atmosphere. Step 2: Saturated NaHCO₃(aq) (3 mL) was added and stirred for additional 30 min. [b] Yield determined by NMR analysis of the crude reaction mixture using CHPh₃ as an internal standard. Values within parentheses represent the yield of the product after a reaction time of 12 hours. [c] Yield of isolated product. DABCO = 1,4-diazabicyclo-[2.2.2]octane, THF = tetrahydrofuran.

protocol, albeit in slightly reduced yields. Furthermore, different coumarin derivatives (**1a**, **1c**, and **1d**) have been examined with various acyl chlorides **2**. Delightfully, under the given reaction conditions, the corresponding products **4** were provided in moderate to excellent yields (entries 13–24).

Further transformation of the phosphorus ylide **3** was realized through intermolecular Wittig reactions.^[8] In the presence of additional carbonyl electrophiles (**6**), the corresponding adducts **5** and **5'** could be furnished in one-pot reactions (Table 3). Moderate to excellent yields of **5** and **5'** were obtained using ethyl glyoxylate (**6a**) and ninhydrin (**6b**), respectively, as trapping reagents.

A control experiment was carried out to demonstrate the existence of the phosphorus zwitterion **A-d** as the key intermediate for the generation of **4da** (Scheme 2). The zwitterionic adduct **A-d** resulting from **1d** and Bu₃P was afforded in 91 % isolated yield, and characterized by X-ray analysis.^[7] It is worth mentioning that, compared to the work of Kwon and co-workers, we also did not observe any intramolecular electrostatic interaction in the zwitterion **A-d**.^[7,9] After treatment of **A-d** with benzoyl chloride (**2a**) in the presence of Et₃N, and subsequent quenching with saturated NaHCO₃(aq), the product **4da** was furnished in 70 % yield.

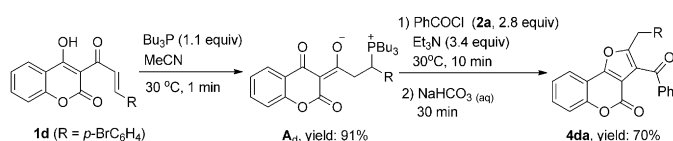
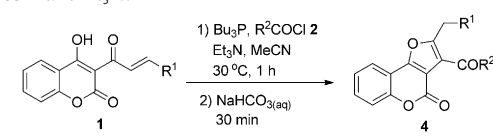

Scheme 2. Confirmation of the phosphorus zwitterion **A-d** as the reaction intermediate in the control experiment.

Table 2: Synthesis of furo[3,2-c]coumarin derivatives **4** from **1**, Bu₃P, acyl chlorides **2** and Et₃N.^[a]


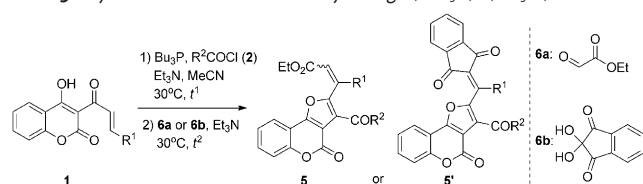
Entry	R ¹	R ²	Yield [%] ^[b]
1	Ph (1b)	Ph (2a)	86 (4ba) ^[c]
2	Ph	<i>p</i> -MeOC ₆ H ₄ (2b)	83 (4bb)
3	Ph	<i>p</i> -NO ₂ C ₆ H ₄ (2c)	77 (4bc)
4	Ph	<i>p</i> -ClC ₆ H ₄ (2d)	79 (4bd)
5	Ph	<i>m</i> -ClC ₆ H ₄ (2e)	94 (4be)
6	Ph	<i>o</i> -ClC ₆ H ₄ (2f)	85 (4bf)
7	Ph	<i>p</i> -BrC ₆ H ₄ (2g)	80 (4bg)
8	Ph	<i>o</i> -BrC ₆ H ₄ (2h)	82 (4bh)
9	Ph	2-thienyl (2i)	40 (4bi)
10	Ph	2-furyl (2j)	33 (4bj)
11	Ph	Cy (2k)	74 (4bk)
12	Ph	<i>i</i> Pr (2l)	49 ^[d] (4bl)
13	<i>p</i> -MeOC ₆ H ₄ (1a)	Ph (2a)	82 (4aa)
14	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄ (2b)	81 (4ab)
15	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -NO ₂ C ₆ H ₄ (2c)	92 (4ac)
16	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -ClC ₆ H ₄ (2d)	86 (4ad)
17	<i>p</i> -MeOC ₆ H ₄	<i>m</i> -ClC ₆ H ₄ (2e)	90 (4ae)
18	<i>p</i> -MeOC ₆ H ₄	<i>o</i> -ClC ₆ H ₄ (2f)	60 (4af)
19	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -BrC ₆ H ₄ (2g)	83 (4ag)
20	<i>p</i> -MeC ₆ H ₄ (1c)	<i>p</i> -MeOC ₆ H ₄ (2b)	52 (4cb)
21	<i>p</i> -MeC ₆ H ₄	<i>p</i> -ClC ₆ H ₄ (2d)	82 (4cd)
22	<i>p</i> -MeC ₆ H ₄	<i>p</i> -BrC ₆ H ₄ (2g)	79 (4cg)
23	<i>p</i> -MeC ₆ H ₄	Cy (2k)	54 (4ck)
24	<i>p</i> -BrC ₆ H ₄ (1d)	Ph (2a)	74 ^[e] (4da)

[a] Reaction conditions: Step 1: **1** (0.2 mmol), Bu₃P (1.1 equiv), **2** (2.8 equiv), and Et₃N (3.4 equiv) in dry MeCN (1 mL) were stirred for 1 h under N₂ atmosphere. Step 2: Saturated NaHCO₃(aq) (3 mL) was added and stirred for additional 30 min. [b] Yield of isolated product. [c] The structure of **4ba** was determined by X-ray analysis.^[7] [d] Reaction time: 3 h. [e] Reaction time: 10 min.

As presented in Tables 1–3, 2.8 equivalents of acyl chloride **2** was necessary to obtain reasonable yields of **4**, although only one acyl group is incorporated into the product.^[4] To understand the exact function of **2**, additional investigations were carried out (Scheme 3). The substrate **1b** was treated with 1.1 equivalents of Bu₃P and 0.9 equivalents of benzoyl chloride (**2a**) [Eq. (1)]. After 10 minutes, 1.8 equivalents of 4-nitrobenzoyl chloride (**2c**) and Et₃N (3.4 equiv) were added, and the reaction mixture was stirred for another hour. By quenching with NaHCO₃(aq), ¹H NMR analysis of the crude reaction mixture revealed that only trace amounts of the benzoyl-substituted product **4ba** was formed. Instead, **4bc** could be identified as the major product. The other control experiment with reversed addition sequence of **2a** and **2c** showed comparable results with contrary product ratio [Eq. (2)].

Based on these results, we propose a plausible reaction mechanism (Scheme 4). First, the phosphorus zwitterion **A** is formed by Michael addition of Bu₃P to **1**. The zwitterionic intermediate **A** then undergoes acylation with **2** (RCOCl) to provide the intermediate **B**. Under basic conditions, the elimination reaction of **B** takes place, thus leading to the formation of the corresponding allene intermediate **C**.^[10]

Table 3: Synthesis of either **5** or **5'** by using **1**, Bu₃P, **2**, Et₃N, and **6**.^[a]



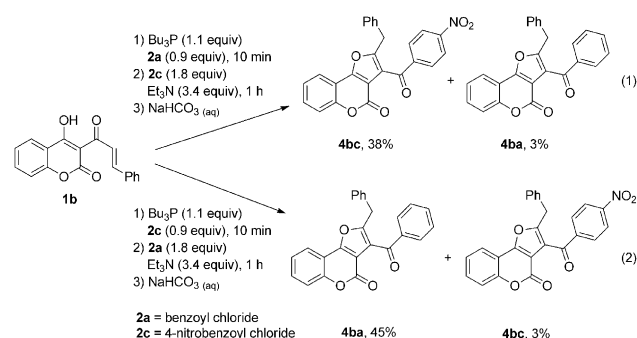
Entry	R ¹	R ²	t ¹ [min]	t ² [h]	Yield [%] ^[b]
1	<i>p</i> -MeOC ₆ H ₄	Ph	60	1	88 (3.7:1) ^[c] (5 aa)
2	Ph	<i>p</i> -ClC ₆ H ₄	60	1	91 (3.5:1) ^[c] (5 bd)
3	<i>p</i> -NO ₂ C ₆ H ₄	Ph	10	0.5	75 (3.2:1) ^[c] (5 ea)
4	<i>p</i> -MeC ₆ H ₄	Ph	60	1	77 (3.6:1) ^[c] (5 ca)
5	<i>p</i> -BrC ₆ H ₄	Ph	10	0.5	75 (3.0:1) ^[c] (5 da) ^[d]
6	<i>p</i> -MeOC ₆ H ₄	Ph	30	1	86 (5'aa) ^[d]
7	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	30	1.5	41 (5'ab)
8	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -BrC ₆ H ₄	30	3	78 (5'ag)
9	Ph	<i>p</i> -MeOC ₆ H ₄	30	5	61 (5'bb)
10	Ph	Ph	30	1	84 (5'ba)
11	Ph	<i>p</i> -NO ₂ C ₆ H ₄	30	5	75 (5'bc)
12	Ph	<i>p</i> -ClC ₆ H ₄	30	1	90 (5'bd)
13	Ph	<i>i</i> Pr	30	1	45 (5'bl)
14	<i>p</i> -MeC ₆ H ₄	Ph	30	3	88 (5'ca)
15	<i>p</i> -BrC ₆ H ₄	Ph	10	0.5	71 (5'da)
16	<i>p</i> -NO ₂ C ₆ H ₄	Ph	5	0.5	66 (5'ea)
17	<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	5	1	48 (5'eb)
18	<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -ClC ₆ H ₄	1	1	74 (5'ed)
19	<i>p</i> -NO ₂ C ₆ H ₄	<i>i</i> Pr	5	1	34 (5'el)

[a] Reaction conditions: Step 1: **1** (0.2 mmol), Bu₃P (1.1 equiv), **2** (2.8 equiv), and Et₃N (3.0 equiv) were stirred in dry MeCN (1 mL) under N₂ atmosphere. Step 2: Et₃N (1.0 equiv) and **6** (1.3 equiv) were added to the reaction mixture. [b] Yield of the isolated product. [c] The isomeric ratio of **5** (Z/E). [d] The structures of **5 da** and **5'aa** were determined by X-ray analysis.^[7]

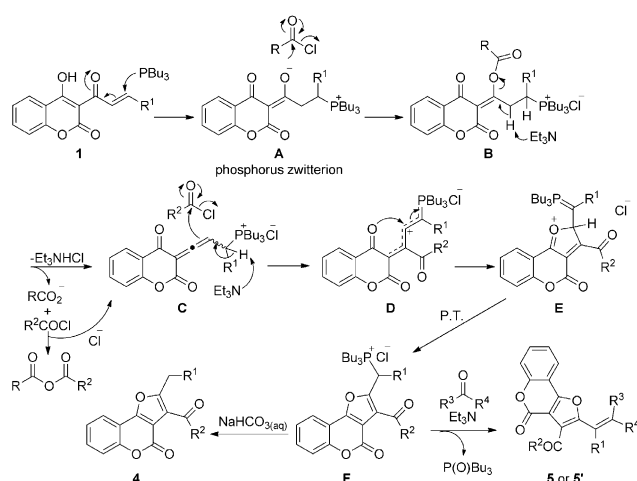
Because of their instability and high reactivity we were not able to isolate **B** and **C**. However, their appearance could be verified by in situ ESI-HRMS analysis of the reaction mixture.^[11] The intermediate **C** then undergoes C-acylation with **2** (R²COCl), thus furnishing the corresponding phosphonium chloride **D**. Thereafter, the intramolecular cyclization of **D** proceeds to afford **E**, which further isomerizes to generate the ylide precursor **F**.^[12] The phosphonium chloride **F** can be activated in the presence of Et₃N to react with a carbonyl electrophile (**6**), thus giving either the corresponding adduct **5** or **5'**.

With regard to the proposed reaction mechanism, we anticipated that this protocol is not only limited to coumarin derivatives but also could be extended to a more versatile substrate scope. Hence, in our preliminary study, the acyclic compound **7** was examined under the given reaction conditions (Scheme 5). Without further optimization, moderate yields of **8a** and **8b** could be achieved after 1 hour, thus demonstrating the generality of this novel phosphine-triggered reaction.

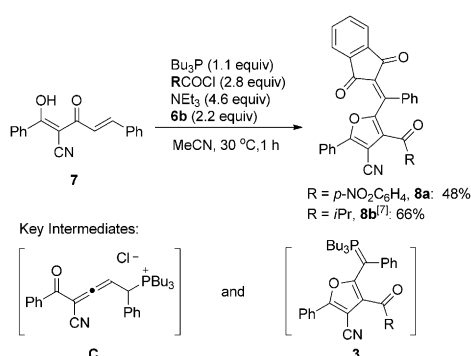
In summary, we have developed a novel phosphine-promoted C-acylation/cyclization reaction of **1**, **2**, and Bu₃P in the presence of Et₃N to access to the phosphorus ylides **3** under very mild reaction conditions. The in situ generated ylide intermediates **3** can efficiently react with carbonyl electrophiles **6** or be quenched with saturated NaHCO_{3(aq)},



Scheme 3. Control experiments: elucidating the roles of acyl chlorides **2** in the reaction mechanism. Reaction conditions: Step 1: The reaction of **1b** (0.2 mmol) and all the indicated reagents were carried out in dry MeCN (1 mL) at 30°C under N₂ atmosphere. Step 2: Saturated NaHCO_{3(aq)} (3 mL) was added and stirred for additional 30 min.



Scheme 4. Proposed mechanism for the Bu₃P-mediated cyclization reaction.



Scheme 5. Preliminary results for the synthesis of **8a,b** by using our one-pot approach.

thus furnishing either the corresponding furo[3,2-*c*]coumarin derivatives **5**, **5'**, or **4**, respectively, in moderate to excellent yields. Furthermore, the substrate scope can be further extended to the acyclic precursor **7** according to our developed concept. A plausible reaction mechanism is also proposed and supported by control experiments. Further

investigations on this chemistry are currently ongoing in our laboratory.

Experimental Section

Typical procedure for the preparation of **4**: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1** (0.2 mmol), dry MeCN (1 mL), Bu₃P (1.1 equiv), acyl chloride **2** (2.8 equiv), and Et₃N (3.4 equiv). The reaction mixture was stirred for 1 h at 30 °C. Then the reaction was quenched by sat. NaHCO₃ solution (3 mL), stirred for an additional 30 min, and extracted with EtOAc (3 × 20 mL). Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide **4**.

Typical procedure for the preparation of **5** or **5'**: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1** (0.2 mmol), dry MeCN (1 mL), Bu₃P (1.1 equiv), acyl chloride **2** (2.8 equiv), and Et₃N (3.4 equiv). The reaction mixture was stirred at 30 °C until **1** was fully consumed. Then Et₃N (1.2 equiv) and either ethyl glyoxalate (**6a**) or ninhydrin (**6b**; 1.3 equiv) were added, and the resulting reaction mixture was stirred until the reaction was completed. Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide either **5** or **5'**.

Typical procedure for the preparation of **8**: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **7** (0.2 mmol), dry MeCN (1 mL), Bu₃P (1.1 equiv), the acyl chloride **2** (2.8 equiv), Et₃N (4.6 equiv), and ninhydrin (**6b**; 2.2 equiv, dissolved in 2 mL MeCN). The reaction mixture was stirred for 1 h at 30 °C. Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide **8**.

Keywords: acylation · cyclizations · heterocycles · ylides · zwitterion

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- [11] For the details of ESI-HRMS results, please see the Supporting Information.
- [12] The original phosphonium salt **F** with chloride as the counterion is too unstable to be identified. We therefore quenched the reaction by HBF₄ to afford the more stable intermediate **F** (R¹ = *p*-MeOC₆H₄, R² = Ph) with BF₄[−] as the counterion, which was confirmed by NMR and HRMS analysis. For the experimental details, please see the Supporting Information.

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