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Tunable Phosphine-Triggered Cascade Reactions of MBH Derivatives and 3-Acyl-2*H*-chromen-2-ones: Highly Selective Synthesis of Diverse Chromenones

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Diverse chromenones were synthesized through tunable phosphine-mediated cascade reactions between 3-acyl-2*H*-chromen-2-ones and Morita–Baylis–Hillman (MBH) derivatives. With different phosphine loadings and reaction temperatures, MBH derivatives act either as C_1 or C_3 synthons for the construction of potential biologically active 3-dihydrofuran-fused chromen-2-ones, 4-allyl-3-acyl-chromen-2-ones, or 6*H*-benzo[*c*]chromen-6-ones. This method has the advantages of mild conditions, simple workup, and wide substrate scope, which make it powerful for the synthesis of diverse chromenone derivatives.

Introduction

Chromenone derivatives receive continuing attention due to their versatile pharmaceutical activities[1] as, for example, anticancer,[1a,1b] antimicrobial,[1c,1d] and antiinflammatory[1e] agents, selective human dopamine D4 antagonists,[1f] lipid peroxidation agents,[1g] and aromatase,[1i] monoamine oxidase,[1j] and acetylcholinesterase inhibitors.[1k,1l] Recently, nucleophilic phosphine-catalyzed organic reactions in the construction of complicated cyclic compounds or natural product skeletons have attracted the interest of organic chemists.[2] Phosphine-catalyzed cascade annulation processes involving allenoates or Morita–Baylis–Hillman (MBH) derivatives have been well documented.[3] Tunable organic reactions for selective synthesis of different products from the same starting materials represent a great and challenging goal for organic chemists.[4] Most such reactions involve transition-metal catalysts,[5] however, and only a few tunable phosphine-catalyzed domino reactions have been reported,[6] although during the preparation of this manuscript Huang and co-workers reported tunable phosphine-mediated domino reactions between MBH carbonates and β,γ-unsaturated α-keto esters.[6b] In that context, when catalytic amounts of phosphines were used, MBH carbonates acted as C_1 synthons and 2,3-dihydrofurans were obtained, whereas when stoichiometric amounts of phosphines were used, MBH derivatives acted C_3 synthons and biaryls were obtained (Scheme 1A).

In 2012 we reported a catalyst-based controllable procedure that permitted selection between [4+2] or [3+2] cycloadditions between 3-acyl-2*H*-chromen-2-ones and ethyl buta-2,3-dienoate (Scheme 1, B) catalyzed either by DABCO or by Bu_3P, in which ethyl buta-2,3-dienoate served as a C_2 or a C_3 synthon, respectively.[6c] Because of their convenient availability and versatile reactivity patterns, MBH derivatives have been used as 1,3-zwitterionic C_3 or C_1 synthons in phosphine-mediated [3+*n*] and [1+*n*] annulations[7] or applied in the synthesis of natural products.[8] As part of our ongoing interest in developing concise, convenient, and environmentally benign methods for the synthesis of important biologically active heterocycles, we now wish to report highly selective phosphine-triggered cascade annulations between MBH derivatives and 3-acyl-2*H*-chromen-2-ones (Scheme 1, C) to afford structurally diverse chromenone derivatives.

Results and Discussion

We began our study by treating MBH carbonate **2a** (Table 1) and 3-benzoylchromen-2-one (**1a**) with 10 mol-% PPh_3 at room temperature. To our delight, the reaction proceeded smoothly and gave [4+1] annulation product **3a** (73%) and allylation product **4a** (5%) after 16 h (Table 1, Entry 1). The more strongly nucleophilic PPh_2Me and $PPhEt_2$ and the bifunctional phosphine LBBA-1 [3′-(diphenylphosphanyl)biphenyl-2-ol], however, were less effective than Ph_3P, whereas tributyl phosphine was ineffective (Table 1, Entries 2–5). The effects of solvents on the [4+1] annulation were then investigated (Table 1, Entries 6–12): THF proved best. Neither raising nor lowering of the reaction temperature resulted in higher yields of **3a** (Table 1,

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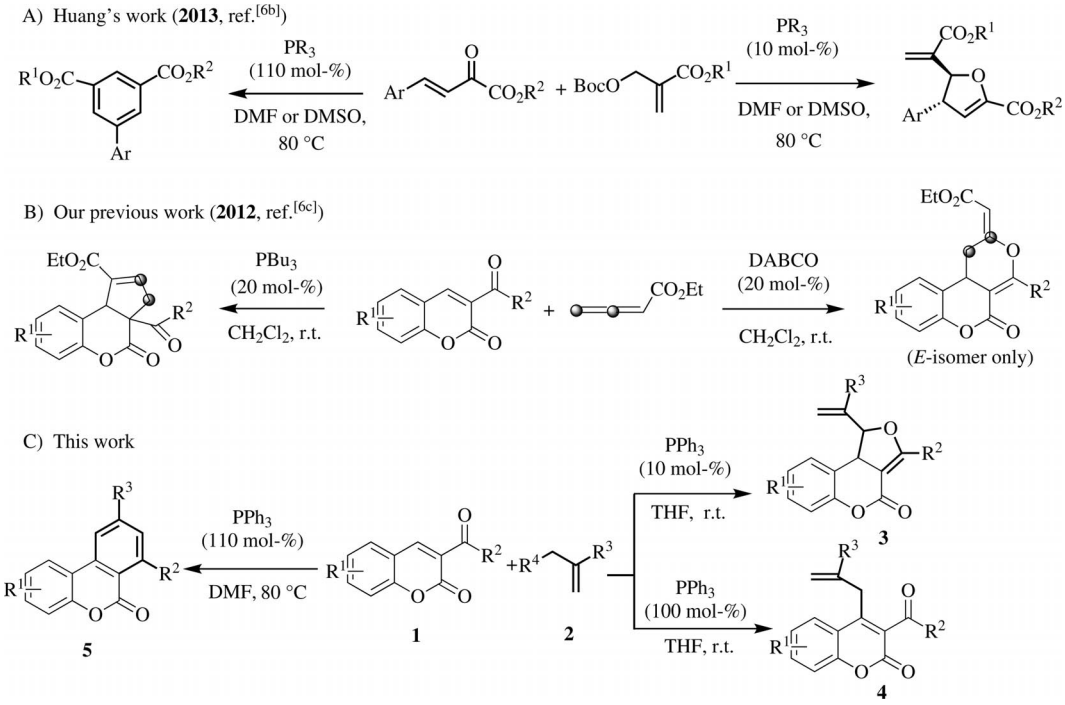


Scheme 1. Tunable phosphine-catalyzed cascade reactions.

Entries 14 and 15). Interestingly, though, increasing the PPh_3 loading resulted in an improvement in the yield of allylation product **4a** and a reduction in the yield of **3a** (Table 1, Entries 13 and 16): when 1.0 equiv. of PPh_3 was used, **4a** was obtained in 78% yield (Table 1, Entry 16).

From the above results, the yields of **3a** and **4a** showed a high dependence on PPh_3 loading, so we examined the relationships between PPh_3 loading (10–100 mol-%) and the yields of **3a** or **4a**. The results show that the yield of **4a** varies in proportion to the phosphine loading whereas the yield of **3a** demonstrates an opposite trend (Figure 1). The optimal reaction conditions for the selective synthesis of **3a** are therefore: **1a** (0.5 mmol), **2a** (0.75 mmol), PPh_3 (10 mol-%) in THF (5 mL) under N_2 at room temperature. The optimal conditions for **4a** are similar to those for **3a** except for the different PPh_3 loading (1.0 equiv.).

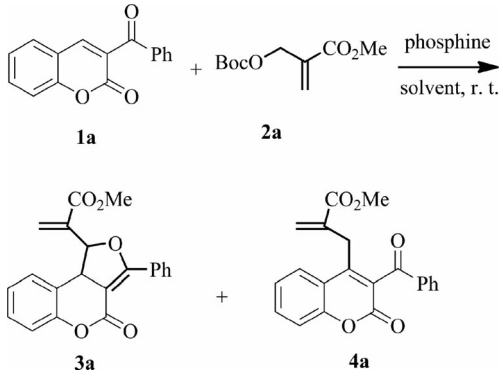
During our optimization of the conditions for the synthesis of **4a**, when the reaction mixture was stirred in the presence of PPh_3 (1.0 equiv.) under air at 40 °C, **4a** (72%) and the unexpected 6*H*-benzo[*c*]chromen-6-one **5a** (Table 2, 8%) were obtained. We wondered whether the product distribution between **4a** and **5a** could be controlled by choosing different conditions. In order to optimize the reaction conditions for selective synthesis of **5a**, the effects of the nucleophilicities of phosphines on the formation of **5a** were explored (Table 2, Entries 1–4); the results indicated that PPh_3 was the most effective catalyst. Secondly, the effects of solvents on the benzannulation reaction were also explored (Table 2, Entries 4–10): when CH_3CN, DMSO, or DMF were used **5a** could be obtained in good yields, with DMF giving the best results. Furthermore, the benzannulation reaction benefitted from higher temperatures (Table 2, Entries 4, 11–14). Finally, the amount of PPh_3 also affected the yield of **5a** (Table 2, Entries 4, 15–16), with 1.1 equiv. of PPh_3 giving the best result.

In addition, as shown in Figure 1, the relationship between the yield of **5a** and different phosphine loadings (10–120 mol-%) was also examined.

With the optimized conditions to hand, a variety of substrates **1** and **2** were examined in the [4+1] annulation reaction. As shown in Table 3, the desired products **3** were obtained in moderate to excellent yields and only trace amounts of allylation products **4** (yields <5%) we observed, irrespective of the electronic and steric properties of the aryl substituents R^1 and R^2 and the position(s) of R^1. The results showed that substrates **1** with electron-rich R^1 substituents were more suitable for [4+1] annulations. Moreover, this reaction had a good tolerance for 3-(furylcarbonyl)-2*H*-chromen-2-one, albeit with a slight lower yield and the need for a prolonged reaction time (Table 3, Entry 14). When R^1 was a strongly electron-withdrawing nitro group, however, only a trace amount of **3** was observed (Table 3, Entry 13), and when 3-acetyl-2*H*-chromen-2-one was used the product mixture became complex (Table 3, Entry 15). With regard to different MBH derivatives **2**, both *tert*-butyl (2-methoxycarbonylallyl) carbonate and methyl 2-(bromomethyl)-acrylate were suitable candidates for the [4+1] annulations (Table 3, Entries 18–19), but, when *tert*-butyl (2-cyanoallyl) carbonate was used, only a trace of product was detected (Table 3, Entry 17).

Next, the substrate scope of the cascade allylation reaction catalyzed by PPh_3 (1.0 equiv.) was also examined (Table 4). The results indicated that the scope of substrates for the allylation was similar to that of the [4+1] annulation.

Table 1. Optimization of conditions for the selective synthesis of **3a** or **4a**.[a]



Entry	Phosphine	Solvent	*t* [h]	Yield [%][b]	
				3a	**4a**
1	PPh_3	THF	16	73	5
2	PBu_3	THF	16	0	0
3	PPh_2Me	THF	16	54	6
4	$PPhEt_2$	THF	16	29	trace
5[c]	LBBA-1	THF	24	46	trace
6	PPh_3	toluene	18	41	<5
7	PPh_3	CH_3CN	16	52	trace
8	PPh_3	CH_2Cl_2	16	50	<5
9	PPh_3	ethanol	24	20	7
10	PPh_3	$CHCl_3$	18	51	<5
11	PPh_3	1,4-dioxane	18	56	<5
12	PPh_3	DMF	17	38	trace
13[d]	PPh_3	THF	12	68	12
14[e]	PPh_3	THF	24	45	trace
15[f]	PPh_3	THF	12	64	8
16[g]	PPh_3	THF	5	trace	78

[a] Unless otherwise noted, the reaction conditions were: **1a** (0.5 mmol), **2a** (0.75 mmol), phosphine (0.05 mmol) in solvent (5.0 mL) under N_2 at room temperature. [b] Isolated yields based on **1a**. [c] LBBA-1 is 3′-(diphenylphosphinyl)biphenyl-2-ol. [d] Ph_3P (20 mol-%) was used. [e] Stirred at 0 °C. [f] Stirred at 40 °C. [g] Ph_3P (1.0 equiv.) was used.

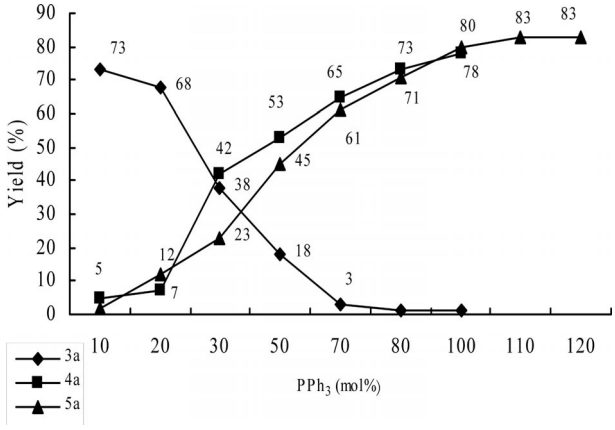
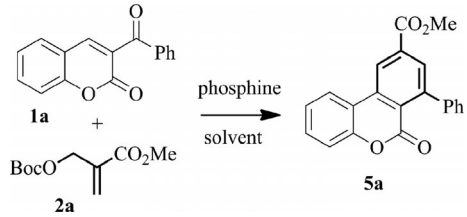


Figure 1. The effects of phosphine loading on the yields of **3a**, **4a**, and **5a**.

Firstly, the desired products **4** were formed in moderate to excellent yields (Table 4, Entries 1–7), irrespective of the electronic and steric properties and position(s) of the aryl substituents R^1. Acetyl (2-methoxycarbonylallyl) carbonate was also a suitable candidate substrate (Table 4, Entry 10). With the substrate bearing a nitro substituent or with 3-acetyl-2*H*-chromen-2-one, however, only traces of **4** were observed (Table 4, Entries 8 and 9).

Table 2. Optimization of the benzannulation for the synthesis of **5a**.[a]



Entry	Phosphine	Solvent	Temp. [°C]	*t* [h]	Yield [%][b]
1	PBu_3	DMF	80	4	0
2	PPh_2Me	DMF	80	4	41
3	$PPhEt_2$	DMF	80	4	62
4	PPh_3	DMF	80	4	83
5	PPh_3	THF	80	4	46
6	PPh_3	1,4-dioxane	80	6	34
7	PPh_3	CH_3CN	80	6	78
8	PPh_3	ethanol	80	4	36
9	PPh_3	toluene	80	4	59
10	PPh_3	DMSO	80	4	80
11	PPh_3	DMF	room temp.	8	45
13	PPh_3	DMF	60	4	68
14	PPh_3	DMF	120	4	78
15[c]	PPh_3	DMF	80	4	73
16[d]	PPh_3	DMF	80	4	80

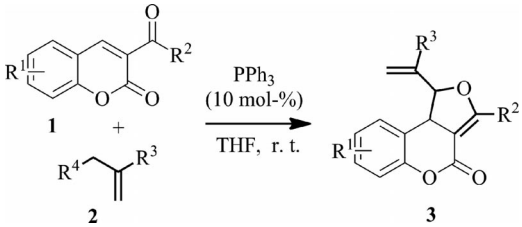
[a] Unless otherwise noted, the reaction conditions are: a mixture of **1a** (0.5 mmol), **2a** (0.75 mmol), and phosphine (0.55 mmol) in a solvent (5.0 mL) was stirred under air at 80 °C. [b] Isolated yields based on **1a**. [c] 0.4 mmol Ph_3P was used. [d] 0.6 mmol Ph_3P was used.

As shown in Table 5, a series of 3-acyl-2*H*-chromen-2-ones were effective candidates for the benzannulation reactions (Table 5, Entries 1–10), irrespective of the electronic and steric properties and position(s) of the aryl substituents R^1. It is worth noting that in this case when R^1 was a strongly electron-withdrawing nitro group, **5g** could be obtained in 83% yield (Table 5, Entry 7). However, when 3-acetyl-2*H*-chromen-2-one was used, the product mixture became complex (Table 5, Entry 11).

In addition, control experiments were performed to investigate the mechanism and to explain how the different phosphine loadings influenced the selection of the final products **3**, **4**, and **5**. Both compound **3a** and compound **4a** could indeed be transformed into **5a** under air in the presence of PPh_3 (1.1 equiv.) at 80 °C (Scheme 2). Compound **3a** could be converted into **4a** in the presence of a stoichiometric amount of PPh_3, in 23% yield (Scheme 2). The transformation of **4a** into **3a** in the presence of a catalytic amount of phosphine was difficult, however. These results revealed that the product distribution of the cascade reaction could be controlled by choosing a different phosphine loading and suitable reaction conditions.

A plausible reaction mechanism based on our experimental results and the related literature[6b] has been pro-

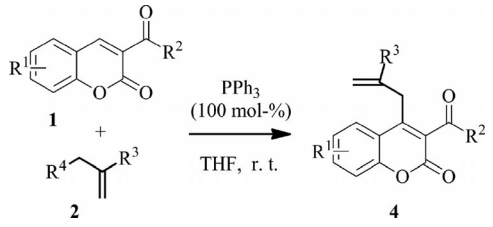
Table 3. Substrate scope of phosphine-mediated [4+1] annulation domino reactions.[a]



Entry	R^1	R^2	R^3	R^4	*t* [h]	Yield [%][b]
1	H	Ph	CO_2Me	BocO	16	73 (**3a**)
2	6-Cl	Ph	CO_2Me	BocO	16	61 (**3b**)
3	6-F	Ph	CO_2Me	BocO	18	60 (**3c**)
4	H	4-ClC_6H_4	CO_2Me	BocO	18	64 (**3d**)
5	H	4-BrC_6H_4	CO_2Me	BocO	24	62 (**3e**)
6	H	4-$MeOC_6H_4$	CO_2Me	BocO	24	66 (**3f**)
7	6-MeO	Ph	CO_2Me	BocO	24	74 (**3g**)
8	6-*tert*-butyl	Ph	CO_2Me	BocO	18	82 (**3h**)
9	6-MeO	Ph	CO_2Et	BocO	24	77 (**3i**)
10	7-CH_3	Ph	CO_2Me	BocO	18	80 (**3j**)
11	7,8-CH_3	Ph	CO_2Me	BocO	18	72 (**3k**)
12	6-EtO_2C	Ph	CO_2Me	BocO	18	61 (**3l**)
13	6-NO_2	Ph	CO_2Me	BocO	16	trace
14	H	2-furyl	CO_2Me	BocO	24	45 (**3m**)
15	H	CH_3	CO_2Me	BocO	16	complex
16	H	1-naphthyl	CO_2Me	BocO	18	84 (**3n**)
17	H	Ph	CN	BocO	16	trace
18[c]	H	Ph	CO_2Me	Br	20	70 (**3a**)
19[c]	H	Ph	CO_2Me	AcO	20	72 (**3a**)

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), and PPh_3 (0.05 mmol) in THF (5.0 mL) were stirred under N_2 at room temperature. [b] Isolated yields based on **1**. [c] K_2CO_3 (0.75 mmol, 103 mg) was added.

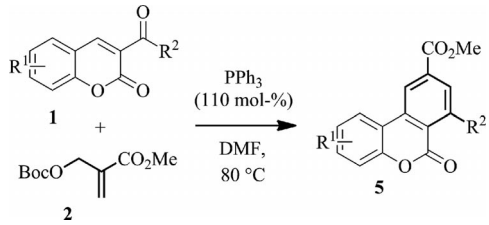
Table 4. Substrate scope of phosphine-mediated allylation of 3-acyl-2*H*-chromen-2-ones and MBH carbonates.[a]



Entry	R^1	R^2	R^3	R^4	*t* [h]	Yield [%][b]
1	H	Ph	CO_2Me	BocO	6	78 (**4a**)
2	6,8-Cl_2	Ph	CO_2Me	BocO	6	61 (**4b**)
3	6-*tert*-butyl	Ph	CO_2Me	BocO	6	81 (**4c**)
4	7,8-CH_3	Ph	CO_2Me	BocO	12	65 (**4d**)
5	6-EtO_2C	Ph	CO_2Me	BocO	5	83 (**4e**)
6	6-EtO_2C	Ph	CO_2Et	BocO	5	85 (**4f**)
7	H	1-naphthyl	CO_2Me	BocO	8	80 (**4 g**)
8	6-NO_2	Ph	CO_2Me	BocO	8	trace
9	H	CH_3	CO_2Me	BocO	8	trace
10	H	Ph	CO_2Me	AcO	6	70 (**4a**)

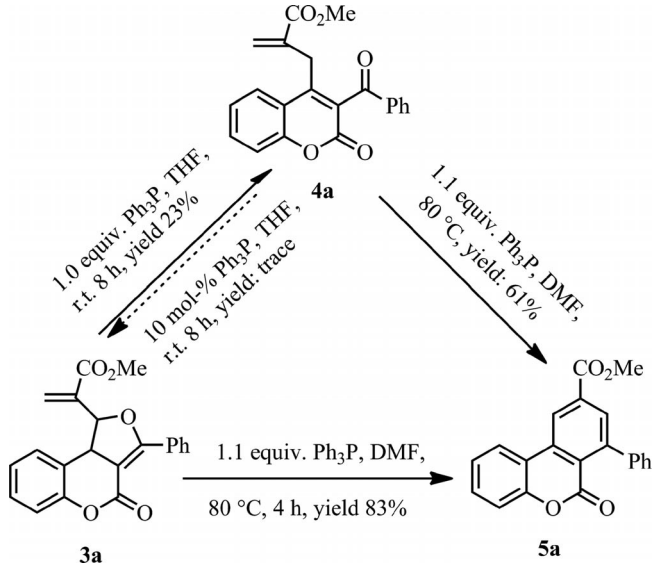
[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), and PPh_3 (0.5 mmol) in THF (5.0 mL) were stirred under N_2 at room temperature. [b] Isolated yields based on **1**.

Table 5. Substrate scope of phosphine-mediated benzannulation domino reactions for the construction of 6*H*-benzo[*c*]chromen-6-ones.[a]



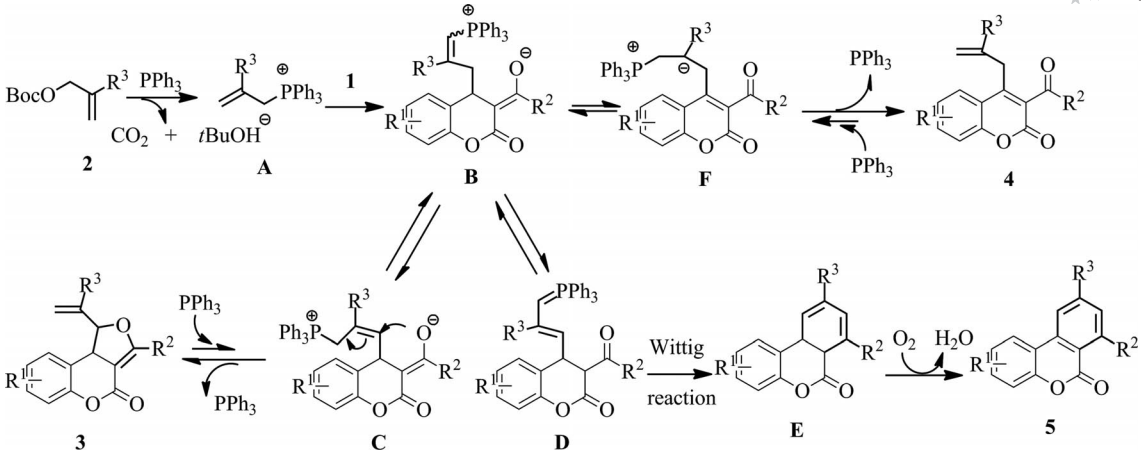
Entry	R^1	R^2	*t* [h]	Yield [%][b]
1	H	Ph	4	83 (**5a**)
2	6-F	Ph	3	90 (**5b**)
3	6-*tert*-butyl	Ph	4	82 (**5c**)
4	7,8-$(CH_3)_2$	Ph	8	75 (**5d**)
5	H	4-BrC_6H_4	5	87 (**5e**)
6	6-EtO_2C	Ph	4	86 (**5f**)
7	6-NO_2	Ph	3.5	83 (**5g**)
8	H	2-furyl	6	78 (**5h**)
9	H	1-naphthyl	4	71 (**5i**)
10	naphthylethyl	Ph	6	74 (**5j**)
11	H	CH_3	4	complex

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), and PPh_3 (0.55 mmol) in DMF (5.0 mL) were stirred under air at 80 °C. [b] Isolated yields based on **1**.



Scheme 2. The mutual transformation relationships of **3a**, **4a**, and **5a**.

posed (Scheme 3). Firstly, allylic phosphorus ylides **A** could be formed through a process of addition/elimination and subsequent deprotonation. Michael addition of the resultant ylides **A** to 3-acyl-2*H*-chromen-2-ones **1** would generate **B** by a favored γ-carbon attack pattern, which could transform variously into **C**, **D**, or **F** through proton transfer processes. Intermediates **C** could then undergo reversible intramolecular oxygen anion Michael addition to yield the kinetically favored products **3** with the release of PPh_3. Compounds **5** could be formed through intramolecular Wittig reaction of **D**, followed by an oxidative aromatization process. Meanwhile, the allylation products **4** could be gener-



Scheme 3. Plausible mechanism for the tunable phosphine-catalyzed cascade reactions.

ated from **F** through elimination in the presence of a stoichiometric amount of phosphine.

The different phosphine loadings and reaction conditions governed the transformation of **3** as well as the formation of **5** and **4**. Higher temperatures, O_2, and a suitable solvent (DMF) are beneficial to the formation of **5**, whereas room temperature, absence of O_2, and a suitable solvent (THF) are better for the formation of **4**. In brief, the reaction conditions (temperature and solvent) and different phosphine loadings determined the pathway of the tunable phosphine-mediated cascade reactions.

Conclusions

In summary, we have developed a tunable phosphine-mediated cascade reaction process based on 3-acyl-chromen-2-ones **1** and MBH derivatives **2**. Under different phosphine loading conditions and reaction temperatures, MBH derivatives act as C_1 or C_3 synthons for selective construction of potential biologically active 2,3-dihydrofuran-fused chromen-2-ones, 4-allyl-3-acyl-chromen-2-ones, and 6*H*-benzo[*c*]chromen-6-ones. This method has the advantages of mild conditions, simple workup, and wide substrate scope, which make it powerful for the synthesis of diverse chromenones.

Experimental Section

General Procedure for the Synthesis of 2,3-Dihydrofuran-Fused Chromene-2-ones 3: A mixture of a 3-acyl-2*H*-chromen-2-one **1** (0.5 mmol), a MBH derivative **2** (0.75 mmol), and PPh_3 (0.05 mmol) in anhydrous THF (5.0 mL) was stirred at room temperature under N_2. After the reaction was complete (monitoring by TLC), the workup involved the addition of water (5 mL), extraction with ethyl acetate (3 × 10 mL), and drying over anhydrous Na_2SO_4. After the solvent had been removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc 10–20:1) to afford the appropriate compound **3**.

Methyl 2-(4-Oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]chromen-1-yl)acrylate (3a): Yield 73%. White solid, m.p. 80–81 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.2 Hz, 2 H), 7.46 (ddd, J = 20.4, 14.9, 7.8 Hz, 4 H), 7.27 (dd, J = 15.6, 7.8 Hz, 1 H), 7.18 (t, J = 7.5 Hz, 1 H), 7.11 (d, J = 7.8 Hz, 1 H), 6.57 (s, 1 H), 6.12 (s, 1 H), 5.86 (d, J = 8.6 Hz, 1 H), 4.62 (d, J = 8.6 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.22, 164.91, 160.82, 151.19, 138.39, 131.75, 129.27, 128.40, 128.04, 127.98, 127.73, 125.03, 124.50, 124.45, 116.89, 97.13, 84.28, 52.23, 47.42 ppm. MS (EI, 70 eV): *m*/*z* (%) = 348 (6.4) $[M]^+$, 346 (42), 330 (12), 287 (47), 262 (60), 105 (100), 77 (48). $C_{21}H_{16}O_5$ (348.35): calcd. C 72.41, H 4.63; found C 72.29, H 4.50.

Methyl 2-(6-Chloro-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3b): Yield 61%. White solid, m.p. 126–127 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.8 Hz, 2 H), 7.50 (dd, J = 15.0, 7.2 Hz, 2 H), 7.44 (t, J = 7.6 Hz, 2 H), 7.27–7.21 (m, 1 H), 7.04 (d, J = 8.6 Hz, 1 H), 6.57 (s, 1 H), 6.12 (s, 1 H), 5.82 (d, J = 8.3 Hz, 1 H), 4.58 (d, J = 8.3 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.44, 165.10, 160.27, 149.81, 138.12, 131.98, 129.53, 129.32, 128.39, 128.06, 128.02, 127.53, 126.80, 124.76, 118.27, 96.28, 83.97, 52.31, 47.55 ppm. MS (EI, 70 eV): *m*/*z* (%) = 382 (6.4) $[M]^+$, 323 (7.3), 297 (34), 296 (56), 205 (5.6), 105 (100), 77 (32). $C_{21}H_{15}ClO_5$ (382.80): calcd. C 65.89, H 3.95; found C 65.97, H 3.72.

Methyl 2-(6-Fluoro-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3c): Yield 60%. White solid, m.p. 84–85 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, J = 7.6 Hz, 2 H), 7.49 (t, J = 7.3 Hz, 1 H), 7.43 (t, J = 7.6 Hz, 2 H), 7.24 (dd, J = 9.0, 2.4 Hz, 1 H), 7.05 (dd, J = 8.9, 5.4 Hz, 1 H), 6.96 (td, J = 9.0, 3.0 Hz, 1 H), 6.56 (s, 1 H), 6.11 (s, 1 H), 5.80 (d, J = 8.3 Hz, 1 H), 4.57 (d, J = 8.3 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.18, 160.54, 159.13 (d, J = 242.3 Hz), 147.29 (d, J = 2.2 Hz), 138.22, 131.92, 129.29, 128.06, 127.83, 127.59, 126.83 (d, J = 7.6 Hz), 118.22, 115.09, 114.86, 111.65 (d, J = 22.4 Hz), 96.41, 83.93, 52.29, 47.84 ppm. MS (EI, 70 eV): *m*/*z* (%) = 366 (5.5) $[M]^+$, 348 (10), 305 (9.3), 281 (37), 280 (50), 105 (100), 77 (41). $C_{21}H_{15}FO_5$ (366.34): calcd. C 68.85, H 4.13; found C 69.03, H 4.26.

Methyl 2-[3-(4-Chlorophenyl)-4-oxo-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl]acrylate (3d): Yield 64%. White solid, m.p. 107–108 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, J = 9.0 Hz, 2 H), 7.42 (dd, J = 14.4, 7.8 Hz, 3 H), 7.29 (t, J = 7.7 Hz, 1 H), 7.19 (t, J = 7.8 Hz, 1 H), 7.12 (d, J = 8.1 Hz, 1 H), 6.58 (s, 1 H), 6.12 (s, 1 H), 5.84 (d, J = 8.8 Hz, 1 H), 4.64 (d, J = 8.8 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.20, 163.70, 160.77, 151.19, 138.31, 137.90, 130.76, 128.56, 128.36, 128.27, 126.23, 124.84, 124.61, 124.54, 117.01, 97.74, 84.60, 52.32,

47.40 ppm. MS (EI, 70 eV): *m*/*z* (%) = 382 (10) $[M]^+$, 323 (11), 297 (51), 271 (11), 205 (13),139 (100), 111 (28). $C_{21}H_{15}ClO_5$ (382.80): calcd. C 65.89, H 3.95; found C 65.61, H 4.00.

Methyl 2-[3-(4-Bromophenyl)-4-oxo-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl]acrylate (3e): Yield 62%. White solid, m.p. 126–128 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.5 Hz, 2 H), 7.57 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 7.2 Hz, 1 H), 7.29 (t, *J* = 7.7 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 7.12 (d, *J* = 8.1 Hz, 1 H), 6.58 (s, 1 H), 6.11 (s, 1 H), 5.84 (d, *J* = 8.8 Hz, 1 H), 4.63 (d, *J* = 8.8 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.19, 163.75, 160.76, 151.18, 138.31, 131.34, 130.89, 128.57, 128.28, 126.67, 126.53, 124.82, 124.62, 124.54, 117.03, 97.87, 84.62, 52.33, 47.44 ppm. MS (EI, 70 eV): *m*/*z* (%) = 426 (6.0) $[M]^+$, 367 (10.0), 342 (43), 271 (11), 182 (100), 154 (27), 115 (10). $C_{21}H_{15}BrO_5$ (427.25): calcd. C 59.04, H 3.54; found C 58.89, H 3.39.

Methyl 2-[3-(4-Methoxyphenyl)-4-oxo-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl]acrylate (3f): Yield 66%. White solid, m.p. 122–123 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 9.0 Hz, 2 H), 7.42 (d, *J* = 7.8 Hz, 1 H), 7.26 (t, *J* = 7.8 Hz, 1 H), 7.16 (t, *J* = 7.2 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 1 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.57 (s, 1 H), 6.11 (s, 1 H), 5.80 (d, *J* = 8.8 Hz, 1 H), 4.61 (d, *J* = 8.8 Hz, 1 H), 3.85 (s, 3 H), 3.84 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.29, 165.15, 162.30, 161.12, 151.35, 138.56, 131.42, 128.34, 128.13, 125.10, 124.47, 124.36, 120.29, 116.88, 113.35, 95.22, 84.04, 55.28, 52.23, 47.27 ppm. MS (EI, 70 eV): *m*/*z* (%) = 378 (3.0) $[M]^+$, 360 (3.6), 317 (6.0), 292 (25), 221 (6.0), 135 (100), 77 (9). $C_{22}H_{18}O_6$ (378.38): calcd. C 69.83, H 4.79; found C 69.96, H 4.51.

Methyl 2-(6-Methoxy-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3g): Yield 74%. White solid, m.p. 106–108 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.8 Hz, 2 H), 7.49 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.07–7.01 (m, 2 H), 6.80 (d, *J* = 8.9 Hz, 1 H), 6.56 (s, 1 H), 6.12 (s, 1 H), 5.84 (d, *J* = 8.4 Hz, 1 H), 4.58 (d, *J* = 8.4 Hz, 1 H), 3.86 (s, 3 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.22, 164.71, 161.11, 156.21, 145.12, 138.53, 131.71, 129.27, 127.99, 127.84, 127.79, 126.01, 117.56, 112.94, 110.23, 97.19, 84.08, 55.58, 52.26, 47.95 ppm. MS (EI, 70 eV): *m*/*z* (%) = 378 (14) $[M]^+$, 360 (4.7), 319 (11), 292 (37), 232 (7.2), 105 (100), 77 (31). $C_{22}H_{18}O_6$ (378.38): calcd. C 69.83, H 4.79; found C 69.67, H 4.88.

Methyl 2-[6-(*tert*-Butyl)-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl]acrylate (3h): Yield 82%. White solid, m.p. 128–130 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.9 Hz, 2 H), 7.48 (d, *J* = 11.0 Hz, 2 H), 7.43 (t, *J* = 7.5 Hz,2 H), 7.29 (d, *J* = 8.5 Hz, 1 H), 7.04 (d, *J* = 8.5 Hz, 1 H), 6.58 (s, 1 H), 6.13 (s, 1 H), 5.90 (d, *J* = 8.4 Hz, 1 H), 4.60 (d, *J* = 8.4 Hz, 1 H), 3.87 (s, 3 H), 1.34 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.19, 164.78, 161.04, 148.99, 147.46, 138.91, 131.68, 129.30, 127.98, 127.85, 125.33, 124.21, 121.43, 116.35, 97.45, 84.31, 52.26, 48.07, 34.53, 31.41, 31.31 ppm. MS (EI, 70 eV): *m*/*z* (%) = 404 (10) $[M]^+$, 347 (11), 318 (34), 303 (20), 287 (19), 105 (100), 77 (30). $C_{25}H_{24}O_5$ (404.46): calcd. C 74.24, H 5.98; found C 74.32, H 6.11.

Ethyl 2-(6-Methoxy-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3i): Yield 77%. White solid, m.p. 142–143 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 7.8 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.03 (dd, *J* = 4.8, 1.2 Hz, 2 H), 6.78 (dd, *J* = 9.0, 2.2 Hz, 1 H), 6.55 (s, 1 H), 6.09 (s, 1 H), 5.83 (d, *J* = 8.5 Hz, 1 H), 4.59 (d, *J* = 8.5 Hz, 1 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 3.81 (s, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.82, 161.17, 156.24, 145.18, 138.88, 131.74, 129.30, 128.03, 127.98, 127.87, 127.69, 126.12, 117.60, 112.87, 110.40, 97.23, 84.26, 61.36, 55.63, 47.97, 14.13 ppm. MS (EI, 70 eV): *m*/*z* (%) = 392 (11.0) $[M]^+$, 374 (5.6), 317 (13), 292 (48), 287 (8.9), 105 (100), 77 (34). $C_{23}H_{20}O_6$ (392.41): calcd. C 70.40, H 5.14; found C 70.53, H 5.24.

Methyl 2-(7-Methyl-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3j): Yield 80%. White solid, m.p. 61–62 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.5 Hz, 2 H), 7.48 (t, *J* = 7.3 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 7.31 (d, *J* = 7.8 Hz, 1 H), 6.98 (d, *J* = 7.8 Hz, 1 H), 6.92 (s, 1 H), 6.55 (s, 1 H), 6.11 (s, 1 H), 5.81 (d, *J* = 8.6 Hz, 1 H), 4.57 (d, *J* = 8.6 Hz, 1 H), 3.85 (s, 3 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.22, 164.72, 160.96, 151.06, 138.63, 138.45, 131.66, 129.26, 129.20, 127.94, 127.81, 125.13, 124.20, 121.94, 117.28, 97.43, 84.46, 52.17, 47.16, 20.99 ppm. MS (EI, 70 eV): *m*/*z* (%) = 362 (8.1) $[M]^+$, 360 (21), 344 (11), 301 (20), 276 (71), 105 (100), 77 (42). $C_{22}H_{18}O_5$ (362.38): calcd. C 72.92, H 5.01; found C 79.80, H 4.87.

Methyl 2-(7,8-Dimethyl-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]-chromen-1-yl)acrylate (3k): Yield 72%. White solid, m.p. 111–113 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 7.7 Hz, 2 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 2 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 6.98 (d, *J* = 7.8 Hz, 1 H), 6.54 (s, 1 H), 6.10 (s, 1 H), 5.83 (d, *J* = 8.3 Hz, 1 H), 4.55 (d, *J* = 8.3 Hz, 1 H), 3.85 (s, 3 H), 2.28 (s, 3 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.28, 164.22, 161.23, 149.34, 138.68, 137.38, 131.61, 129.17, 128.00, 127.92, 127.68, 125.34, 124.92, 122.55, 120.94, 97.67, 84.30, 52.20, 47.78, 19.89, 12.06 ppm. MS (EI, 70 eV): *m*/*z* (%) = 376 (8.6) $[M]^+$, 347 (7.4), 318 (32), 287 (17), 243 (5.6), 105 (100), 77 (34). $C_{23}H_{20}O_5$ (376.41): calcd. C 73.39, H 5.36; found C 73.31, H 5.33.

Ethyl 1-(3-Methoxy-3-oxoprop-1-en-2-yl)-4-oxo-3-phenyl-1,9b-dihydro-4*H*-furo[3,4-*c*]chromene-8-carboxylate (3l): Yield 61%. White solid, m.p. 131–133 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.20–8.17 (m, 3 H), 7.98 (d, *J* = 7.8 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.15 (d, *J* = 8.4 Hz, 1 H), 6.61 (s, 1 H), 6.15 (s, 1 H), 5.90 (d, *J* = 8.6 Hz, 1 H), 4.66 (d, *J* = 8.6 Hz, 1 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 3.88 (s, 3 H), 1.41 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.88, 165.63, 164.99, 159.96, 154.63, 138.25, 132.05, 130.17, 129.42, 128.40, 128.09, 127.56, 126.64, 126.47, 125.20, 117.01, 96.25, 84.54, 61.10, 52.30, 47.28, 14.26 ppm. MS (EI, 70 eV): *m*/*z* (%) = 420 (3.0) $[M]^+$, 418 (6.0), 373 (11), 346 (35), 187 (15), 105 (100), 77 (42). $C_{21}H_{15}FO_5$ (366.34): calcd. C 68.57, H 4.80; found C 68.60, H 4.71.

Methyl 2-[3-(Furan-2-yl)-4-oxo-1,9b-dihydro-4*H*-furo[3,4-*c*]chromen-1-yl]acrylate (3m): Yield 45%, Pale yellow solid, m.p. 65–66 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 3.6 Hz, 1 H), 7.58 (s, 1 H), 7.33 (d, *J* = 7.8 Hz, 1 H), 7.27 (t, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.12 (d, *J* = 7.8 Hz, 1 H), 6.63 (s, 1 H), 6.60–6.56 (m, 1 H), 6.21 (s, 1 H), 5.80 (d, *J* = 9.6 Hz, 1 H), 4.70 (d, *J* = 9.6 Hz, 1 H), 3.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.99, 159.91, 155.21, 151.32, 145.39, 142.39, 137.86, 129.50, 128.46, 124.44, 124.34, 119.73, 117.01, 112.41, 95.43, 86.48, 52.18, 46.04, 29.52 ppm. MS (EI, 70 eV): *m*/*z* (%) = 338 (16) $[M]^+$, 336 (24), 320 (81), 277 (27), 148 (20), 139 (30), 95 (100). $C_{19}H_{14}O_6$ (338.32): calcd. C 67.45, H 4.17; found C 67.63, H 4.25.

Methyl 2-[3-(Naphthalen-1-yl)-4-oxo-1,9b-dihydro-1*H*-furo[3,4-*c*]-chromen-1-yl]acrylate (3n): Yield 84%. White solid, m.p. 188–189 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 7.8 Hz, 1 H), 7.95–7.93 (m, 2 H), 7.84 (d, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 7.8 Hz, 1 H), 7.50–7.45 (m, 2 H), 7.41 (d, *J* = 7.2 Hz, 1 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 7.11 (d, *J* = 7.8 Hz, 1 H), 6.59 (s, 1 H), 6.17 (s, 1 H), 5.96 (d, *J* = 9.0 Hz, 1 H), 4.80 (d, *J* = 9.0 Hz, 1 H), 3.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.08, 165.09, 159.69, 151.49, 138.14, 133.24, 131.66, 130.78, 130.11, 129.12, 128.59, 128.36, 126.78, 126.07, 125.16, 125.08,

124.84, 124.66, 124.55, 124.48, 117.24, 100.45, 86.98, 52.22, 46.00 ppm. MS (EI, 70 eV): *m*/*z* (%) = 398 (4.2) $[M]^+$, 380 (8.7), 337 (8.3), 312 (99), 255 (21), 155 (100), 127 (83). $C_{25}H_{18}O_5$ (398.41): calcd. C 75.37, H 4.55; found C 75.32, H 4.64.

General Procedure for the Synthesis of 4-Allyl-3-acyl-2*H*-chromen-2-ones 4: The procedure was similar to that used for compounds **3**, except for the different PPh_3 loading (1.0 equiv., 0.5 mmol).

Methyl 2-[(3-Benzoyl-2-oxo-2*H*-chromen-4-yl)methyl]acrylate (4a): Yield 78%. White solid, m.p. 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.2 Hz, 2 H), 7.63–7.57 (m, 3 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 6.29 (s, 1 H), 5.55 (s, 1 H), 3.77 (s, 3 H), 3.74 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.44, 166.39, 158.57, 153.47, 150.41, 135.79, 135.22, 134.34, 132.61, 129.32, 128.85, 128.23, 127.64, 125.89, 124.82, 118.18, 117.33, 52.33, 30.64 ppm. MS (EI, 70 eV): *m*/*z* (%) = 348 (4.0) $[M]^+$, 330 (32), 289 (13), 262 (100), 239 (12), 105 (79), 77 (60). $C_{21}H_{16}O_5$ (348.35): calcd. C 72.41, H 4.63; found C 72.33, H 4.51.

Methyl 2-[(3-Benzoyl-6,8-dichloro-2-oxo-2*H*-chromen-4-yl)methyl]-acrylate (4b): Yield 61%. White solid, m.p. 151–152 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.2 Hz, 2 H), 7.64 (dd, *J* = 12.0, 1.8 Hz, 2 H), 7.48 (dd, *J* = 12.6, 7.8 Hz, 3 H), 6.31 (s, 1 H), 5.56 (s, 1 H), 3.78 (s, 3 H), 3.69 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.47, 166.12, 156.85, 149.09, 147.81, 135.19, 134.69, 134.61, 132.49, 129.98, 129.30, 129.08, 128.93, 128.65, 123.91, 123.20, 120.36, 52.46, 30.72 ppm. MS (EI, 70 eV): *m*/*z* (%) = 416 (2.6) $[M]^+$, 398 (10), 357 (7.4), 331 (36), 330 (27), 105 (100), 77 (58). $C_{21}H_{14}Cl_2O_5$ (417.24): calcd. C 60.45, H 3.38; found C 60.58, H 3.34.

Methyl 2-{[3-Benzoyl-6-(*tert*-butyl)-2-oxo-2*H*-chromen-4-yl]methyl}acrylate (4c): Yield 81%. White solid, m.p. 139–141 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.8 Hz, 2 H), 7.62 (dd, *J* = 18.0, 9.0 Hz, 2 H), 7.56 (s, 1 H), 7.48 (t, *J* = 7.8 Hz, 2 H), 7.35 (d, *J* = 9.0 Hz, 1 H), 6.33 (s, 1 H), 5.69 (s, 1 H), 3.79 (s, 3 H), 3.76 (s, 2 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.75, 166.54, 158.90, 151.48, 151.15, 147.90, 135.94, 135.37, 134.26, 130.22, 129.31, 128.82, 128.63, 127.16, 122.16, 117.41, 116.80, 52.36, 34.66, 31.17, 30.26 ppm. MS (EI, 70 eV): *m*/*z* (%) = 404 (8) $[M]^+$, 386 (17), 371 (10), 318 (41), 303 (21), 105 (100), 77 (38). $C_{25}H_{24}O_5$ (404.46): calcd. C 74.24, H 5.98; found C 74.31, H 5.87.

Methyl 2-[(3-Benzoyl-7,8-dimethyl-2-oxo-2*H*-chromen-4-yl)methyl]-acrylate (4d): Yield 65%. White solid, m.p. 165–166 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 7.2 Hz, 2 H), 7.61 (t, *J* = 7.2 Hz, 1 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 6.28 (s, 1 H), 5.52 (s, 1 H), 3.76 (s, 3 H), 3.71 (s, 2 H), 2.42 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.87, 166.45, 158.98, 151.70, 150.95, 142.62, 136.00, 135.52, 134.16, 129.32, 128.76, 127.98, 126.18, 126.07, 125.05, 122.63, 115.89, 52.26, 30.67, 20.36, 11.58 ppm. MS (EI, 70 eV): *m*/*z* (%) = 376 (10) $[M]^+$, 358 (36), 317 (19), 290 (100), 267 (18), 105 (83), 77 (41). $C_{23}H_{20}O_5$ (376.41): calcd. C 73.39, H 5.36; found C 79.22, H 5.25.

Ethyl 3-Benzoyl-4-[2-(methoxycarbonyl)allyl]-2-oxo-2*H*-chromene-6-carboxylate (4e): Yield 83%. White solid, m.p. 111–112 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.32 (s, 1 H), 8.26 (d, *J* = 8.5 Hz, 1 H), 7.91 (d, *J* = 7.8 Hz, 2 H), 7.63 (t, *J* = 6.6 Hz, 1 H), 7.50–7.45 (m, 3 H), 6.30 (s, 1 H), 5.57 (s, 1 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 2 H), 3.77 (s, 3 H), 1.42 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.99, 166.15, 164.88, 157.96, 156.10, 150.41, 135.64, 135.11, 134.48, 133.35, 129.30, 128.90, 128.57, 128.08, 127.97, 127.25, 118.15, 117.51, 61.52, 52.33, 30.60, 14.20 ppm. MS (EI, 70 eV): *m*/*z* (%) = 420 (4.6) $[M]^+$, 346 (46), 334 (49), 306 (10), 287 (21), 105 (100), 77 (78). $C_{24}H_{20}O_7$ (420.42): calcd. C 68.57, H 4.80; found C 68.42, H 4.66.

Ethyl 3-Benzoyl-4-[2-(ethoxycarbonyl)allyl]-2-oxo-2*H*-chromene-6-carboxylate (4f): Yield 85%. White solid, m.p. 139–140 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 1.8 Hz, 1 H), 8.26 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.91 (d, *J* = 7.2 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.50–7.45 (m, 3 H), 6.29 (s, 1 H), 5.55 (s, 1 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H), 1.28 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.00, 165.63, 164.84, 157.93, 156.06, 150.56, 135.63, 135.35, 134.41, 133.30, 129.26, 128.85, 128.26, 127.97, 127.20, 118.15, 117.45, 61.45, 61.34, 30.50, 14.15, 14.00 ppm. MS (EI, 70 eV): *m*/*z* (%) = 434 (3.0) $[M]^+$, 388 (10), 360 (28), 334 (36), 287 (25), 105 (100), 77 (52). $C_{25}H_{22}O_7$ (434.44): calcd. C 69.12, H 5.10; found C 69.01, H 5.08.

Methyl 2-{[3-(1-Naphthoyl)-2-oxo-2*H*-chromen-4-yl]methyl}acrylate (4g): Yield 80%. White solid, m.p. 126–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (d, *J* = 8.4 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.91 (t, *J* = 6.8 Hz, 2 H), 7.68 (t, *J* = 7.6 Hz, 1 H), 7.61–7.55 (m, 3 H), 7.42 (dd, *J* = 13.6, 8.0 Hz, 2 H), 7.30 (dd, *J* = 16.0, 7.6 Hz, 1 H), 6.31 (s, 1 H), 5.60 (s, 1 H), 3.83 (s, 2 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.18, 166.26, 158.62, 153.35, 149.90, 135.33, 135.04, 133.98, 132.48, 132.32, 132.20, 130.60, 128.86, 128.46, 128.06, 126.70, 125.90, 125.87, 125.86, 124.73, 124.16, 118.22, 117.17, 52.19, 30.67 ppm. MS (EI, 70 eV): *m*/*z* (%) = 398 (10) $[M]^+$, 380 (6.8), 339 (80), 312 (56), 169 (20), 155 (44), 127 (100). $C_{25}H_{18}O_5$ (398.41): calcd. C 75.37, H 4.55; found C 75.40, H 4.39.

General Procedure for the Synthesis of 6*H*-Benzo[*c*]chromen-6-ones 5: A mixture of a 3-acyl-2*H*-chromen-2-one **1** (0.5 mmol), an allylic carbonate **2** (0.75 mmol), and PPh_3 (0.55 mmol) in DMF (5.0 mL) was stirred at 80 °C under air. After the reaction was complete, the workup involved the addition of water (5 mL), extraction with CH_2Cl_2 (3 × 10 mL), and drying over anhydrous Na_2SO_4. After the solvent had been removed under reduced pressure, the crude product was purified by flash column chromatography on silica gel (petroleum ether/CH_2Cl_2 1:3–4) to afford **5**.

9-(Methoxycarbonyl)-7-phenyl-6*H*-benzo[*c*]chromen-6-one (5a): Yield 83%. White solid, m.p. 211–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75 (s, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 8.00 (s, 1 H), 7.51–7.39 (m, 4 H), 7.32 (dd, *J* = 14.8, 7.8 Hz, 4 H), 3.98 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.47, 158.38, 151.34, 147.16, 140.97, 136.29, 134.06, 132.15, 130.92, 128.07, 127.80, 127.50, 124.41, 123.25, 122.29, 121.38, 117.43, 117.31, 52.72 ppm. MS (EI, 70 eV): *m*/*z* (%) = 330 (60) $[M]^+$, 329 (100), 299 (3.7), 271 (9.0), 215 (14), 135 (16), 94 (10). $C_{21}H_{14}O_4$ (330.34): calcd. C 76.35, H 4.27; found C 76.39, H 4.43.

2-Fluoro-9-(methoxycarbonyl)-7-phenyl-6*H*-benzo[*c*]chromen-6-one (5b): Yield 90%. White solid, m.p. 208–210 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 8.07 (s, 1 H), 7.84 (d, *J* = 9.0 Hz, 1 H), 7.45 (d, *J* = 7.2 Hz, 3 H), 7.32 (dd, *J* = 12.6, 7.2 Hz, 3 H), 7.22 (t, *J* = 7.8 Hz, 1 H), 4.01 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.34, 159.15 (d, *J* = 242.0 Hz), 158.09, 147.50 (d, *J* = 3.4 Hz), 140.75, 135.49, 134.32, 132.91, 128.08, 127.89, 127.66, 122.50, 121.41, 118.97 (d, *J* = 8.2 Hz), 118.69 (d, *J* = 8.2 Hz), 118.32 (d, *J* = 23.8 Hz), 109.44, 109.19, 52.84 ppm. MS (EI, 70 eV): *m*/*z* (%) = 348 (64) $[M]^+$, 347 (100), 289 (8.0), 260 (11), 233 (13), 157 (6), 115 (7.0). $C_{21}H_{13}FO_4$ (348.33): calcd. C 72.41, H 3.76; found C 72.60, H 3.56.

2-(*tert*-Butyl)-9-(methoxycarbonyl)-7-phenyl-6*H*-benzo[*c*]chromen-6-one (5c): Yield 82%. White solid, m.p. 227–228 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1 H), 8.14 (s, 1 H), 8.01 (s, 1 H), 7.56 (d, J = 7.2 Hz, 1 H), 7.33 (dd, J = 44.8, 20.5 Hz, 6 H), 4.01 (s, 3 H), 1.44 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.72, 158.67, 149.39, 147.45, 147.23, 141.17, 136.74, 134.02, 131.95, 128.59, 128.06, 127.81, 127.45, 122.13, 121.52, 119.41, 116.94, 116.64, 52.76, 34.73, 31.42 ppm. MS (EI, 70 eV): *m*/*z* (%) = 386 (40) $[M]^+$, 371 (100), 343 (4.6), 283 (5.1), 185 (8.8), 171 (39). $C_{25}H_{22}O_4$ (386.45): calcd. C 77.70, H 5.74; found C 77.62, H 5.83.

9-(Methoxycarbonyl)-3,4-dimethyl-7-phenyl-6*H*-benzo[*c*]chromen-6-one (5d): Yield 75%. White solid, m.p. 237–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 7.95 (s, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.43 (q, J = 5.2 Hz, 3 H), 7.37–7.31 (m, 2 H), 7.09 (d, J = 8.0 Hz, 1 H), 3.97 (s, 3 H), 2.35 (s, 3 H), 2.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.64, 158.74, 149.48, 146.91, 141.14, 140.34, 136.94, 133.90, 131.39, 128.13, 127.75, 127.40, 125.69, 124.78, 122.23, 120.68, 119.92, 114.95, 52.66, 20.11, 11.50 ppm. MS (EI, 70 eV): *m*/*z* (%) = 358 (72) $[M]^+$, 357 (100), 299 (5.8), 255 (7.9), 228 (6.0), 163 (7.5), 148 (11). $C_{23}H_{18}O_4$ (358.39): calcd. C 77.08, H 5.06; found C 77.25, H 4.95.

7-(4-Bromophenyl)-9-(methoxycarbonyl)-6*H*-benzo[*c*]chromen-6-one (5e): Yield 87%. White solid, m.p. 249–250 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1 H), 8.18 (d, J = 6.8 Hz, 1 H), 7.98 (s, 1 H), 7.54 (dd, J = 21.2, 6.8 Hz, 3 H), 7.36 (dd, J = 15.6, 6.8 Hz, 2 H), 7.21 (d, J = 6.4 Hz, 2 H), 4.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.46, 158.54, 151.42, 145.96, 139.96, 136.60, 134.35, 132.04, 131.19, 131.06, 129.87, 124.63, 123.39, 122.80, 121.92, 121.40, 117.48, 117.44, 52.88 ppm. MS (EI, 70 eV): *m*/*z* (%) = 408 (84) $[M]^+$, 409 (100) $[M + 1]^+$, 407 (99), 270 (28), 213 (46), 164 (21), 135 (53), 93 (19). $C_{21}H_{13}BrO_4$ (409.24): calcd. C 61.63, H 3.20; found C 61.49, H 3.05.

2-(Ethoxycarbonyl)-9-(methoxycarbonyl)-7-phenyl-6*H*-benzo[*c*]-chromen-6-one (5f): Yield 86%. White solid, m.p. 206–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (s, 1 H), 8.16 (d, J = 8.4 Hz, 1 H), 8.06 (s, 1 H), 7.44 (d, J = 1.4 Hz, 3 H), 7.34 (dd, J = 15.2, 8.4 Hz, 3 H), 4.47 (q, J = 7.2 Hz, 2 H), 4.03 (s, 3 H), 1.47 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.37, 157.76, 154.21, 147.38, 140.66, 135.65, 134.49, 132.78, 131.86, 128.07, 127.89, 127.67, 126.82, 125.45, 122.54, 121.29, 117.50, 61.47, 52.85, 14.34 ppm. MS (EI, 70 eV): *m*/*z* (%) = 402 (100) $[M]^+$, 401 (98), 373 (27), 357 (28), 213 (20), 178 (22), 106 (16). $C_{24}H_{18}O_6$ (402.40): calcd. C 71.64, H 4.51; found C 76.80, H 4.33.

9-(Methoxycarbonyl)-2-nitro-7-phenyl-6*H*-benzo[*c*]chromen-6-one (5g): Yield 83%. White solid, m.p. > 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$/CF_3CO_2D): δ = 9.31 (s, 1 H), 9.10 (s, 1 H), 8.50 (d, J = 8.8 Hz, 1 H), 8.29 (s, 1 H), 7.61 (d, J = 9.2 Hz, 1 H), 7.52–7.45 (m, 3 H), 7.43–7.36 (m, 2 H), 4.21 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ = 168.33, 161.17, 155.00, 149.32, 145.13, 140.07, 135.85, 135.41, 134.50, 128.69, 128.61, 128.27, 126.66, 123.48, 121.34, 120.56, 119.35, 119.05, 54.18 ppm. MS (EI, 70 eV): *m*/*z* (%) = 375 (84) $[M]^+$, 374 (100), 328 (23), 270 (9.0), 213 (22), 134 (9.3), 106 (21). $C_{21}H_{13}NO_6$ (375.34): calcd. C 67.20, H 3.49, N 3.73; found C 67.07, H 3.32, N 3.91.

7-(Furan-2-yl)-9-(methoxycarbonyl)-6*H*-benzo[*c*]chromen-6-one (5h): Yield 78%. White solid, m.p. 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.21 (s, 1 H), 8.04 (d, J = 7.6 Hz, 1 H), 7.59 (s, 1 H), 7.46 (t, J = 7.5 Hz, 1 H), 7.29 (t, J = 9.2 Hz, 2 H), 6.78 (d, J = 2.7 Hz, 1 H), 6.57 (s, 1 H), 3.99 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$/CF_3CO_2D): δ = 168.57, 163.01, 151.12, 150.84, 138.03, 136.23, 135.03, 134.94, 132.26, 131.93, 126.19, 123.71, 123.46, 120.35, 117.66, 117.42, 111.69, 111.57, 54.12 ppm. MS (EI, 70 eV): *m*/*z* (%) = 320 (100) $[M]^+$, 319 (7.8), 292 (17), 260 (12), 233 (28), 205 (35), 176 (30), 88 (26). $C_{19}H_{12}O_5$ (320.30): calcd. C 71.25, H 3.78; found C 71.00, H 3.81.

9-(Methoxycarbonyl)-7-(naphthalen-1-yl)-6*H*-benzo[*c*]chromen-6-one (5i): Yield 71%. White solid, m.p. 236–237 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.20 (d, J = 7.8 Hz, 1 H), 8.09 (s, 1 H), 7.91 (d, J = 6.7 Hz, 2 H), 7.54 (t, J = 7.2 Hz, 1 H), 7.50–7.41 (m, 2 H), 7.33 (dd, J = 12.0, 7.8 Hz, 4 H), 7.28 (d, J = 8.4 Hz, 1 H), 3.94 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.55, 157.86, 151.46, 145.36, 139.07, 136.25, 134.47, 133.17, 132.63, 131.63, 131.02, 128.32, 127.90, 126.06, 125.64, 125.14, 125.03, 124.96, 124.49, 123.33, 123.06, 122.85, 117.49, 117.44, 52.73 ppm. MS (EI, 70 eV): *m*/*z* (%) = 380 (100) $[M]^+$, 363 (56), 321 (18), 263 (19), 160 (21), 131 (43), 118 (14). $C_{25}H_{16}O_4$ (380.40): calcd. C 78.94, H 4.24; found C 79.03, H 4.15.

7-(Methoxycarbonyl)-5-phenyl-4*H*-benzo[d]naphtha[1,2-*b*]pyran-4-one (5j): Yield 74%. White solid, m.p. 219–221 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.25 (s, 1 H), 8.73 (d, J = 8.4 Hz, 1 H), 8.07 (s, 1 H), 7.94 (dd, J = 11.4, 8.4 Hz, 2 H), 7.72 (t, J = 8.4 Hz, 1 H), 7.57 (t, J = 7.2 Hz, 1 H), 7.50–7.42 (m, 4 H), 7.39 (d, J = 7.8 Hz, 2 H), 4.01 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.76, 158.58, 150.10, 146.82, 140.90, 136.84, 133.56, 132.09, 131.43, 131.30, 129.30, 129.24, 128.38, 128.14, 127.86, 127.64, 127.04, 125.38, 124.57, 122.63, 116.92, 112.25, 52.80 ppm. MS (EI, 70 eV): *m*/*z* (%) = 380 (100) $[M]^+$, 379 (41), 321 (14), 292 (15), 263 (22), 182 (15), 131 (19). $C_{25}H_{16}O_4$ (380.40): calcd. C 78.94, H 4.24; found C 78.87, H 4.30.

General Procedure for the Effect of Phosphine Loading on the 3a/4a Ratio: The general procedure for the investigation of the effect of phosphine loading (PPh_3 ranging from 0.1 to 1.0 equiv.) on the **3a**/**4a** ratio was similar to the procedure used for the synthesis of products **3** and the results are summarized in Figure 1.

General Procedure for the Effect of Phosphine Loading on the Yield of 5a: The general procedure for the investigation of the effect of phosphine loading (PPh_3 ranging from 0.1 to 1.2 equiv.) on the yield of **5a** was similar to the procedure used for synthesis of products **5**. The results are summarized in Figure 1.

Supporting Information (see footnote on the first page of this article): General Remarks, General Procedure of control experiments and copies of ^{1}H and ^{13}C NMR spectra of all new products **3**, **4**, and **5**.

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