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PAPER

DABCO and Bu_3P catalyzed [4 + 2] and [3 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones and ethyl 2,3-butadienoate†

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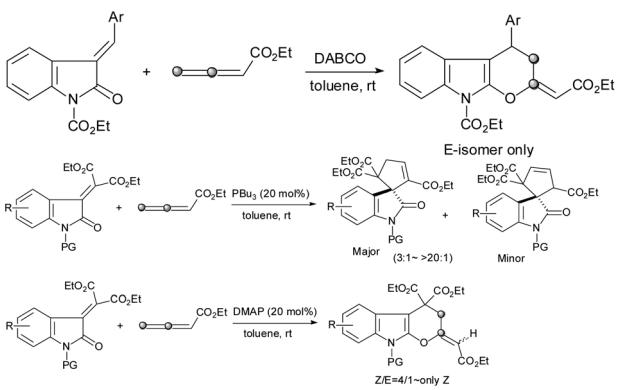
DABCO-catalyzed [4 + 2] and Bu_3P-catalyzed [3 + 2] cycloadditions between 3-acyl-2*H*-chromen-ones and ethyl 2,3-butadienoate were developed for the synthesis of dihydropyran-fused and cyclopenten-fused chromen-2-ones with high regio- and stereo-selectivities, respectively. The synthetic procedures have the advantages of mild reaction conditions, convenient handling and good atom economy as well as a wide substrate scope, which make this method useful for the synthesis of potentially biologically active dihydropyran-fused and cyclopenten-fused chromen-2-ones derivatives. Possible reaction mechanisms have also been proposed on the basis of previous literature and our investigation.

Introduction

Chromen-2-one (coumarin) derivatives have exhibited a wide range of biological activities and have received more and more attention. Some of them are used as anti-cancer agents,[1a,b] antimicrobial agents,[1c,d] antiinflammatory agents,[1e] selective human dopamine D4 antagonists,[1f] lipid peroxidation inhibitors,[1g] DNA-PK inhibitors,[1h] aromatase inhibitors,[1i] inhibitors of monoamine oxidases,[1j] and dual inhibitors of acetylcholinesterase and monoamine oxidase[1k,l] *etc.* Recently, organocatalysts such as tertiary phosphine and tertiary amine have catalyzed cycloadditions of allenoates, constructing complicated cyclic compounds or natural product skeletons, and have received more and more attention by organic chemists.[2] Lu *et al.*'s [3 + 2] cycloaddition of allenoate catalyzed by tertiary phosphine, in which allenoate usually acts as the three-carbon unit, sometimes as the two-carbon one, is well documented.[3] On the other hand, [4 + 2] annulation of allenoates with imine,[4] activated olefins[5] or trifluoromethyl ketones[6] have also been investigated well. In 2003, Miller and Evans reported the amine-catalyzed Baylis–Hillman reaction of allenic esters with α,β-unsaturated carbonyls,[7] however, the [4 + 2] cycloadditions of allenoates used as the two-carbon unit with α,β-unsaturated carbonyls were firstly reported in 2011.[8] Despite these prominent works, due to its divergent reactivity modes, and the regio- and stereo-selectivities of cycloadditions of allenoates with α,β-unsaturated carbonyls, further development of the tertiary phosphine and amine catalyzed cycloaddition of allenoates with different α,β-unsaturated carbonyl substrates to obtain novel potentially biologically active heterocycle skeletons remains in high demand. During the preparation of the manuscript, Shi *et al.* (ref. 8*a*, *Org. Lett.*, 2011, **13**, 1142) and Wang *et al.* (ref. 8*b*, *Org. lett.*, 2011, **13**, 1138) reported the cycloadditions of allenoate and isatin derived electron deficient olefins (Scheme 1). In Shi's work, the [4 + 2] cycloaddition products catalyzed by DMAP are mainly in the *Z*-configuration (*Z* : *E* = 4 : 1 ~ only *Z*), whereas three tautomers of [4 + 2] cycloadducts are generated when the reaction was catalyzed by DABCO. Secondly, there are two spiro tautomers in the [3 + 2] cycloadditions catalyzed by Bu_3P. Herein, we wish to report DABCO and Bu_3P catalyzed [4 + 2] and [3 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones and ethyl 2,3-butadienoate to access potentially biologically active dihydropyran-fused and cyclopenten-fused chromen-2-one derivatives with high regio- and stereo-selectivity (*E*-configuration only, Scheme 2).



Scheme 1 Previous work by Wang[8b] and Shi.[8a]

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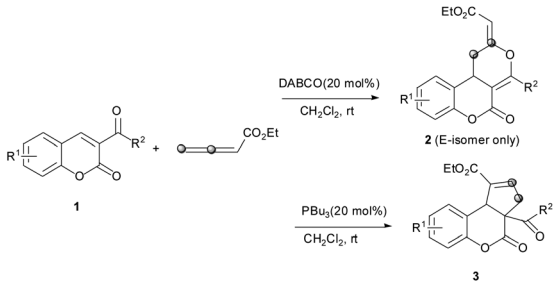


Scheme 2 DABCO and Bu_3P catalyzed [4 + 2] and [3 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones with 2,3-butadienoate.

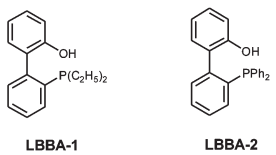


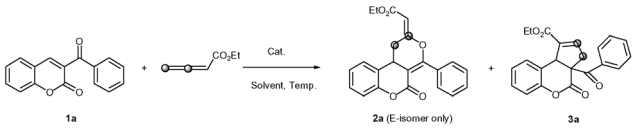
Fig. 1 Structural of bifunctional phosphine catalysts LBBA1 and LBBA2.

Results and discussion

We began the cycloaddition study by utilizing simple substrate **1a** and 2,3-butadienoate as the substrates in order to optimize the reaction conditions. The initial screening was arranged with 20 mol% of tertiary phosphine or amine as the catalyst and THF (2.5 mL) as the solvent at room temperature with the results summarized in Table 1. To our delight, the reaction proceeded smoothly and gave [3 + 2] cycloaddition products **3a** in 60–85% yield in the presence of various tertiary phosphines as the catalysts at room temperature (Table 1, entries 1–4); Bu_3P was the most effective catalyst (85% yield, Table 1, entry 2). Whereas with the tertiary amines as the catalyst, [4 + 2] cycloadduct **2a** was obtained (Table 1, entries 5–7). DABCO was the most effective catalyst (86% yield, entry 6) and DBU failed to initiate the reaction (entry 7). Investigations on the effects of various solvents on the reaction indicated that many common solvents were suitable (Table 1, entries 8–17), among which moderately polar CH_2Cl_2 was the best one for both [3 + 2] and [4 + 2] cycloadditions (entry 8, entry 14). Subsequently, the effects of reaction temperatures were examined using 20 mol% Bu_3P or DABCO in CH_2Cl_2 (0.2 M) as a control. The efficiency was weakened slightly when the reaction was conducted at low temperature (0 °C, entry 18, entry 20) or under reflux (entry 19 and entry 21). Thus, the optimized reaction conditions were established as follows: 20 mol% Bu_3P or DABCO as the catalysts, with the ratio of **1** and allenoate as 1 : 1.2, CH_2Cl_2 (0.2 M) as the solvent and stirring at room temperature.

With the optimized conditions in hand, we next explored the scope of the 3-acyl-2*H*-chromen-one substrates with different substituents on the benzene rings (Table 2 and Table 3). It was found that a range of substituents in the 3-acyl-2*H*-chromen-ones were accommodated to afford the corresponding cycloadducts in moderate to excellent yields with high regio- and stereo-selectivities, no matter whether they had electron-withdrawing or electron-donating substituents on the aromatic ring at different

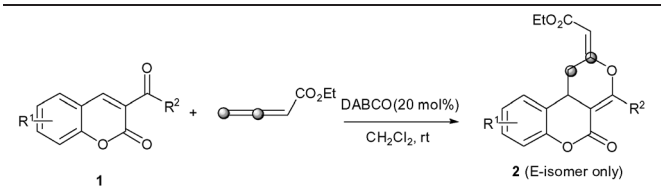
Table 1 Optimization of conditions



Entry[a]	Cata.	Solvent	Time/h	Yield[b] (%) 2a	3a
1	Ph_3P	THF	24		60
2	Bu_3P	THF	6		85
3	LBBA1 (Fig. 1)	THF	8		76
4	LBBA2 (Fig. 1)	THF	8		72
5	DMAP	THF	5	75	
6	DABCO	THF	4	86	
7	DBU	THF	24	Trace	
8	DABCO	CH_2Cl_2	4	92	
9	DABCO	CH_3OH	8	78	
10	DABCO	$CHCl_3$	6	80	
11	DABCO	MeCN	24	60	
12	DABCO	Toluene	6	65	
13	Bu_3P	MeCN	12		65
14	Bu_3P	CH_2Cl_2	4		90
15	Bu_3P	CH_3OH	6		75
16	Bu_3P	Toluene	6		72
17	Bu_3P	$CHCl_3$	6		81
18[c]	DABCO	CH_2Cl_2	8	78	
19[d]	DABCO	CH_2Cl_2	4	80	
20[c]	Bu_3P	CH_2Cl_2	8		82
21[d]	Bu_3P	CH_2Cl_2	4		72

[a] All the reactions were carried out on 0.5 mmol scale with the catalyst (20 mol%) in solvent (0.2 M) at room temperature unless otherwise noted, with the ratio of **1a** : allenoate as 1 : 1.2. [b] Isolated yields. [c] Reaction temperature at 0 °C. [d] Under reflux.

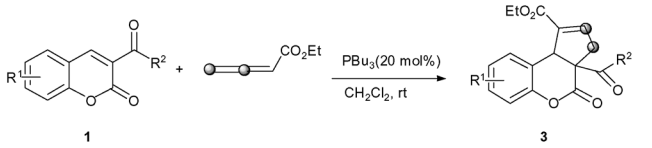
Table 2 Substrate scope of [4 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones with ethyl 2,3-butadienoate catalyzed by DABCO



Entry	Compd.	R^1	R^2	Time/h	M. p./°C	Yield[a,b] (%)
1	**2a**	H	C_6H_5	4	125.2–126.0	92
2	**2b**	6-Br	C_6H_5	4	151.7–153.3	85
3	**2c**	6-Cl	C_6H_5	4	158.8–161.4	79
4	**2d**	6-F	C_6H_5	3	130.2–132.0	86
5	**2e**	6,8-Cl_2	C_6H_5	4	89.2–90.6	80
6	**2f**	7-CF_3	C_6H_5	3	115.0–116.8	92
7	**2g**	6-CH_3	C_6H_5	3	144.0–145.4	94
8	**2h**	7-CH_3	C_6H_5	3	124.0–126.0	95
9	**2i**	6-CH_3O	C_6H_5	4	156.6–158.4	88
10	**2j**	H	CH_3	4	110.0–111.2	87
11	**2k**	H	4-CH_3-C_6H_4	4	197.0–198.4	86
12	**2l**	H	4-Cl-C_6H_4	3	139.0–140.2	89

[a] Isolated yield of product. [b] Stereo-configuration was determined by ^1H NMR and X-ray diffraction analysis of a crystal of **2b** (CCDC: 889494†).

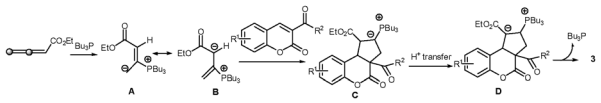
Table 3 Substrate scope of [3 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones with ethyl 2,3-butadienoate catalyzed by Bu_3P



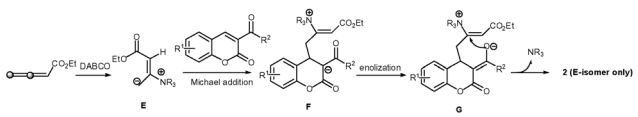
Entry	Compd.	R^1	R^2	Time/h	M. p./°C	Yield (%)[a,b]
1	**3a**	H	C_6H_5	4	123.0–124.4	90
2	**3b**	6-Br	C_6H_5	4	130.1–132.0	91
3	**3c**	6-Cl	C_6H_5	4	127.0–128.5	94
4	**3d**	6-F	C_6H_5	6	102.2–104.0	72
5	**3e**	6,8-Cl_2	C_6H_5	6	128.0–129.8	75
6	**3f**	6-CH_3	C_6H_5	4	103.0–104.2	85
7	**3g**	7-CH_3	C_6H_5	4	164.6–166.0	92
8	**3h**	6-CH_3O	C_6H_5	4	118.0–119.0	86
9	**3i**	H	4-CH_3-C_6H_4	4	106.0–107.0	86
10	**3j**	H	4-Cl-C_6H_4	4	110.4–111.3	89

[a] Isolated yield of product. [b] Regio-selectivity was determined by ^1H NMR and X-ray diffraction analysis of a crystal of **3j** (CCDC: 889495†).

1. A possible [3+2] cycloaddition catalyzed by Bu_3P pathway:



2. A possible [4+2] cycloaddition catalyzed by DABCO pathway:



Scheme 3 Possible mechanisms suggested for the [4 + 2] and [3 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones with ethyl 2,3-butadienoate catalyzed by DABCO and Bu_3P, respectively.

positions. Varying the different acyl group in the 3-position (R^2 = methyl or substituted phenyl groups) of the 2*H*-chromen-ones also gave satisfactory results.

The structures and configurations of the [4 + 2] and [3 + 2] cycloadducts **2** and **3** were assigned *via* ^{1}H-NMR, ^{13}C-NMR, MS, elemental analysis and further confirmed by single crystal X-ray diffraction analysis (see the ESI†).

Based on our system and the reported literature, possible mechanisms are suggested as shown in Scheme 3. The reactions proceed through different cycloaddition modes in the presence of tertiary phosphine and amine catalysts, respectively. In the case of the PBu_3-catalyzed [3 + 2] cycloaddition reaction, Bu_3P attacks the β-carbon of 2,3-butadienoate to give intermediate **A**, which can isomerize to the more stable intermediate **B**, because both the phosphonium salt and ester group can stabilize the β-carbanion of **B**. So, compound **B** acts as a 1,3 dipole for the [3 + 2] cycloaddition with activated olefins **1**, which follows by 1,2-proton transfer and Bu_3P release, producing the [3 + 2] cycloadduct **3**. As for the [4 + 2] cycloaddition pathway catalyzed by DABCO, reaction with 2,3-butadienoate generates zwitterionic **E**, in which the γ-position carbanion attacks the β-carbon of enones **1** to give *Z* configuration of **F**, avoiding the interaction of the ester group with the 3-position acyl one. **F** converted to the enolate form **G**, in which the oxygen anion of enolate **G** undergoes molecular nucleophilic substitution with the β-carbon of the α,β-unsaturated ester moiety which is followed by the release of DABCO, generating the [4 + 2] cycloadduct **2**.

Conclusions

In summary, we have developed novel highly regio- and stereoselective [3 + 2] and [4 + 2] cycloadditions of 3-acyl-2*H*-chromen-ones with ethyl 2,3-butadienoate catalyzed by Bu_3P and DABCO, respectively, to access potentially biologically active dihydropyran-fused and cyclopenten-fused chromen-2-one derivatives in moderate to excellent yields. The synthetic procedures have the advantages of mild reaction conditions, convenient handling and high atom economy as well as wide substrate scopes. Possible mechanisms have been proposed based on the reported literature and our investigation.

Experimental

General

All the reactions are conducted under a dry N_2 atmosphere. All the solvents and reagents are commercially available and used as received with the following exceptions. THF, toluene and dioxane were distilled from sodium/benzophenone. Dichloromethane, chloroform and acetonitrile were distilled from calcium hydride. Ethanol was distilled form Mg turnings. Substituted salicylaldehydes and ethyl substituted benzoyl (acetyl) acetates were prepared according to the literature,[9,10] whereas LBBA 1, LBBA 2 and ethyl 2,3-butadienoate were synthesized according to the reported methods,[11,12] respectively. Melting points were determined with a WRS-1B digital melting point apparatus, and the thermometer was uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury PLUS 400 or a Varian Mercury PLUS 600 spectrometer in chloroform-d. Chemical shift in parts per million (δ ppm) from an internal standard [tetramethylsilane (TMS) or chloroform ($CHCl_3$)], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C NMR chemical shifts are reported in ppm from $CDCl_3$ (taken as 77.0 ppm). The mass spectra were obtained on a Finnigan TRACEMS 2000 spectrometer using the EI method or an Applied Biosystems API 2000 LC/MS/MS (ESI-MS) spectrometer. Elemental analyses were performed with an Elementar Vario EL#xX_CYR_-HEX_428; CHNSO elemental analyzer. X-ray diffraction analysis was carried out with a Bruker APEX-II CCD X-ray diffraction instrument.

General procedure for the synthesis of 3-acyl-2*H*-chromen-ones 1.[13] To a dry 50 mL flask were added substituted salicylaldehyde (8 mmol), ethyl substituted benzoyl (acetyl) acetates

(8 mmol), piperidine (0.25 mL), several drops of glacial acetic acid and anhydrous acetonitrile (20 mL). The solution was stirred under reflux for 0.5–1 h until the reaction completed (monitored by TLC). The mixture was poured into iced water (50 mL), filtered and recrystallized with anhydrous ethanol. **1** was obtained as colorless crystals or light yellow solid in 55–82% yield.

Preparation of 3-benzoyl-chromen-2-one (1a).[13a] Yellow solid, yield 85%, m. p. 149.7–151.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.09 (s, 1H), 7.89 (d, J = 9.6 Hz, 2H), 7.60–7.67 (m, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.2 Hz, 1H);^{13}C NMR (150 MHz, $CDCl_3$): δ 191.6, 158.3, 154.7, 145.3, 136.1, 133.7, 133.6, 129.5, 129.2, 128.5, 126.9, 124.9, 118.1, 116.8.

Preparation of 3-benzoyl-6-bromo-chromen-2-one (1b).[13a] Colorless solid, yield 62%, m. p. 171.2–172.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.99 (s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.59–7.65 (m, 3H), 7.50 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 9.2 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 157.7, 153.4, 143.7, 136.2, 135.8, 134.0, 131.2, 129.5, 128.6, 128.0, 119.6, 118.6, 117.5.

Preparation of 3-benzoyl-6-chloro-chromen-2-one (1c).[13a] White solid, yield 68%, m. p. 161.0–162.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.99 (s, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 9.2 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 157.7, 153.0, 143.8, 135.8, 134.0, 133.4, 130.2, 129.5, 128.6, 128.2, 119.1, 118.3.

Preparation of 3-benzoyl-6-fluoro-chromen-2-one (1d).[13a] White solid, yield 65%, m. p. 157.9–158.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.00 (s, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.37–7.42 (m, 2H), 7.28 (dd, J = 7.2 Hz, J = 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 191.2, 159.9, 157.6 (d, J = 75 Hz), 150.8.7, 144.0, 135.8, 133.9, 129.3, 128.6, 127.9, 121.1, 120.6, 118.2, 114.2 (d, J = 45 Hz).

Preparation of 3-benzoyl-6,8-dichloro-chromen-2-one (1e).[13b] White solid, yield 60%, m. p. 185.4–186.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.96 (s, 1H), 7.87 (d, J = 7.2 Hz, 2H), 7.69 (s, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 156.7, 149.0, 143.3, 135.6, 134.2, 133.3, 130.1, 129.6, 128.9, 128.7, 126.7, 122.9, 120.0.

Preparation of 3-benzoyl-7-(trifluoromethyl)-chromen-2-one (1f). White solid, yield 58%, m. p. 179.9–181.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.09 (s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.60–7.67 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 157.4, 154.2, 143.5, 135.7, 134.6, 134.2, 129.9, 129.6, 129.3, 128.7, 124.3, 121.5, 120.6, 114.3; ESI-MS: m/z = 319 $[M + H]^+$, 341 $[M + Na]^+$. Anal. calcd for $C_{17}H_9F_3O_3$: C, 64.16; H, 2.85. Found: C, 64.01; H, 2.66.

Preparation of 3-benzoyl-6-methyl-chromen-2-one (1g).[13a] Light yellow solid, yield 78%, m. p. 157.7–158.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.03 (s, 1H), 7.88 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.45–7.50 (m, 3H), 7.38 (s, 1H), 7.30 (d, J = 8.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 158.6, 154.9, 145.7, 145.5, 136.3, 133.6, 129.5, 128.9, 128.6, 126.2, 125.5, 116.9, 115.7, 22.0.

Preparation of 3-benzoyl-7-methyl-chromen-2-one (1h).[13a] Light yellow solid, yield 80%, m. p. 157.6–158.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.08 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.67 (t, J = 6.8 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 158.9, 153.1, 145.7, 136.5, 135.0, 134.0, 129.8, 129.1, 128.8, 127.0, 118.1, 116.8, 21.0.

Preparation of 3-benzoyl-6-methoxy-chromen-2-one (1i).[13a] Light yellow solid, yield 85%, m. p. 144.0–145.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.05 (s, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.01 (s, 1H), 3.87 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8, 158.6, 156.4, 149.2, 145.2, 136.2, 133.8, 129.5, 128.6, 127.2, 121.7, 118.4, 117.9, 110.6, 55.9.

Preparation of 3-acetyl-chromen-2-one (1j).[13c] Light yellow solid, yield 80%, m. p. 99.7–101.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 8.52 (s, 1H), 7.67 (t, J = 4.8 Hz, 2H), 7.34–7.39 (m, 2H), 2.74 (s, 3H), 3.87 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 159.0, 155.2, 147.4, 134.3, 130.2, 124.9, 124.4, 118.3, 116.6, 30.5.

Preparation of 3-(4-methylbenzoyl)-chromen-2-one (1k).[13d] Light yellow solid, yield 83%, m. p. 170.0–171.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.04 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.58–7.63 (m, 2H), 7.32–7.40 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1, 158.4, 154.6, 144.9, 144.8, 133.6, 133.4, 129.7, 129.2, 129.1, 127.1, 124.9, 118.1, 116.8, 21.7.

Preparation of 3-(4-chlorobenzoyl)-chromen-2-one (1l). White solid, yield 72%, m. p. 198.0–200.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.13 (s, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.61–7.67 (m, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.35–7.43 (m, 2H); ESI-MS: m/z = 285 $[M + H]^+$, 307 $[M + Na]^+$. Anal. calcd for $C_{16}H_9ClO_3$: C, 67.50; H, 3.19. Found: C, 67.63; H, 3.27.

General procedure for the preparation of 2. To a solution of 3-acyl-2*H*-chromen-one **1** (0.5 mmol) and ethyl 2,3-butadienoate (67.2 mg, 0.6 mmol) in CH_2Cl_2 (2.5 mL) was added DABCO (11.2 mg, 20 mol %) under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 3–4 h till the reaction completed (monitored by TLC). After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60–120 mesh) column using 10 : 1 petroleum ether–ethyl acetate solvent mixture as eluent to afford **2** as colorless or light yellow solid in 79–95% yield.

Preparation of (*E*) ethyl (5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2a). Light yellow solid, yield 92%, m. p. 125.2–126.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.50 (d, J = 7.8 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 3H), 7.33 (t, J = 7.2 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 5.84 (s, 1H), 4.88 (dd, J =

6.0 Hz, J = 15. 0Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 4.01 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.51 (t, J = 13.2 Hz, 1H), 1.33 (t, J = 7.8 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.5, 162.2, 161.5, 150.6, 132.9, 130.7, 129.0, 128.8, 128.1, 125.6, 124.8, 122.6, 117.1, 102.3, 101.1, 60.4, 30.1, 25.6, 14.2; EI-MS (70 eV): m/z = 362 (M^+, 10.2), 289 (47.7), 247 (16.5), 221 (26.0), 173 (25.6), 144 (14.7), 129 (13.1), 150 (100), 77 (74.5), 44 (52.0). Anal. calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.83; H, 4.94.

Preparation of (*E*) ethyl (9-bromo-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2b). Light yellow solid, yield 85%, m. p. 151.7–153.3 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.54 (s, 1H), 7.49 (t, J = 7.8 Hz, 3H), 7.42 (dd, J = 7.2 Hz, J = 15.6 Hz, 3H), 6.97 (d, J = 8.4 Hz, 1H), 5.86 (s, 1H), 4.84 (dd, J = 6.0 Hz, J = 14. 4 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.00 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.51 (t, J = 12.6 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 162.9, 160.9, 149.7, 132.7, 132.0, 130.8, 128.8, 128.6, 128.1, 127.4, 124.7, 118.8, 117.4, 102.7, 100.1, 60.5, 30.1, 25.5, 14.2; EI-MS (70 eV): m/z = 441 (M + 1, 3.0), 440 (M^+, 3.2), 369 (13.9), 367 (11.8), 341 (10.0), 251 (9.7), 202 (7.0), 189 (10.0), 129 (10.5), 105 (100), 77 (67.5), 44 (16). Anal. calcd for $C_{22}H_{17}BrO_5$: C, 59.88; H, 3.88. Found: C, 59.64; H,3.97.

Preparation of (*E*) ethyl (9-chloro-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2c). Light yellow solid, yield 79%, m. p. 158.8–160.4 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.49 (t, J = 7.8 Hz, 3H), 7.42 (t, J = 7.2 Hz, 3H), 7.29 (d, J = 9.0 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 5.86 (s, 1H), 4.85 (dd, J = 5.4 Hz, J = 14. 4 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.99 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.51 (t, J = 13.2 Hz, 1H), 1.34 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 162.9, 162.8, 160.9, 149.2, 132.7, 130.8, 130.0, 129.0, 128.8, 128.1, 125.7, 124.3, 118.4, 102.7, 100.1, 60.5, 30.2, 25.5, 14.2; EI-MS (70 eV): m/z = 396 (M^+, 7.7), 324 (9.5), 323 (28.7), 322 (12.8), 296 (10.6), 295 (11.4), 281 (8.5), 255 (10.6), 207 (11.5), 178 (10.8), 129 (16.0), 105 (100), 77 (62.2), 44 (38). Anal. calcd for $C_{22}H_{17}ClO_5$: C, 66.59; H, 4.32. Found: C, 66.70; H, 4.17.

Preparation of (*E*) ethyl (9-fluoro-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2d). Light yellow solid, yield 86%, m. p. 130.2–132.0 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.47–7.51 (m, 3H), 7.42 (t, J = 7.8 Hz, 2H), 7.15 (d, J = 6.6 Hz, 1H), 7.01–7.08 (m, 2H), 5.86 (s, 1H), 4.81 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.24 (q, J = 7.8 Hz, 2H), 3.99 (dd, J = 6.0 Hz, J = 12.6 Hz, 1H), 2.51 (t, J = 13.8 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 162.8 (d, J = 25.1 Hz), 160.6, 146.7, 132.7, 130.8, 128.9, 128.1, 124.3, 118.4, 115.8, 115.6, 112.6, 112.3, 102.6, 100.2, 60.5, 30.3, 25.5, 14.2; EI-MS (70 eV): m/z = 380 (M^+, 4.5), 303 (45.9), 276 (27.0), 261 (10.4), 221 (9.0), 173 (27.0), 155 (10.6), 144 (19.9), 120 (14.4), 119 (100), 91 (62.0), 65 (12.5), 44 (31.3). Anal. calcd for $C_{22}H_{17}FO_5$: C, 69.47; H, 4.50. Found: C, 69.60; H, 4.67.

Preparation of (*E*) ethyl (7,9-dichloro-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2e). Light yellow solid, yield 80%, m. p. 89.2–90.6 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.53 (s, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 3H), 7.32 (s, 1H), 5.88 (s, 1H), 4.82 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.00 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.54 (t, J = 13.8 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 163.4, 162.5, 159.5, 132.3, 131.0, 129.9, 129.7, 129.5, 128.9, 128.2, 125.7, 124.1, 122.9, 103.0, 99.2, 60.6, 30.6, 25.3, 14.2; EI-MS (70 eV): m/z = 432 (M + 2, 1.5), 430 (M^+, 1.9), 333 (6.2), 331 (11.0), 106 (9.8), 105 (100), 77 (56.1), 51 (9.8), 44 (19.5). Anal. calcd for $C_{22}H_{16}Cl_2O_5$: C, 61.27; H, 3.74. Found: C, 61.08; H, 3.63.

Preparation of (*E*) ethyl (5-oxo-4-phenyl-8-trifluoromethyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2f). Light yellow solid, yield 92%, m. p. 115.0–116.8 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.55 (d, J = 7.8 Hz, 1H), 7.47–7.51 (m, 4H), 7.43 (t, J = 7.2 Hz, 2H), 7.35 (s, 1H), 5.87 (s, 1H), 4.90 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 4.05 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.55 (t, J = 12.6 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 163.1, 162.7, 160.6, 157.9, 150.8, 132.6, 130.9, 128.8, 128.2, 126.6, 126.4, 125.8, 121.3, 114.4, 102.8, 99.8, 60.5, 30.3, 25.4, 14.2; EI-MS (70 eV): m/z = 430 (M^+, 9.3), 357 (20.9), 356 (14.8), 315 (9.8), 289 (11.2), 241 (19.1), 221 (9.5), 212 (11.9), 149 (8.4), 129 (8.5), 106 (10.2), 105 (100), 77 (62.5), 44 (34.8). Anal. calcd for $C_{23}H_{17}F_3O_5$: C, 64.19; H, 3.98. Found: C, 64.33; H, 4.07.

Preparation of (*E*) ethyl (9-methyl-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2g). Light yellow solid, yield 94%, m. p. 144.0–145.4 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.50 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.21 (s, 1H), 7.12 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 5.84 (s, 1H), 4.88 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 3.97 (dd, J = 6.0 Hz, J = 12.0 Hz, 1H), 2.50 (t, J = 13.2 Hz, 1H), 2.37 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 163.7, 162.1, 148.4, 134.5, 133.0, 130.6, 129.5, 128.8, 128.1, 126.0, 125.8, 122.1, 116.7, 102.1, 101.4, 60.4, 30.0, 25.8, 20.8, 14.2; EI-MS (70 eV): m/z = 376 (M^+, 7.4), 303 (13.3), 277 (18.7), 249 (6.3), 187 (6.7), 127 (6.7), 105 (100), 77 (56.3), 44 (17.8). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.17; H, 5.22.

Preparation of (*E*) ethyl (8-methyl-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2h). Light yellow solid, yield 95%, m. p. 124.0–126.0 °C;^{1}H NMR (600 MHz, $CDCl_3$), δ 7.49 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.91 (s, 1H), 5.83 (s, 1H), 4.86 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.96 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 2.46 (t, J = 13.2 Hz, 1H), 2.37 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 163.7, 162.0, 161.7, 150.4, 139.3, 133.0, 130.6, 128.9, 128.1, 125.5, 125.4, 119.5, 117.4, 102.1, 101.5, 60.4, 29.9, 25.9, 21.0, 14.2; EI-MS (70 eV): m/z = 376 (M^+, 9.2), 331 (5.9), 304 (12.3), 303 (43.2), 302 (21.6), 277 (12.4), 275 (14.2), 261 (15.3), 235 (14.6), 221 (14.6), 187 (27.5), 185 (7.9), 158 (8.2), 129 (20.0), 115 (11.0), 105 (100), 91 (12.6), 77 (74.6), 44

(41.6). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.53; H, 5.31.

Preparation of (*E*) ethyl (9-methoxy-5-oxo-4-phenyl-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2i). White solid, yield 88%, m. p. 156.6–158.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.50 (d, J = 6.6 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.03 (d, J = 9.0 Hz, 1H), 6.93 (s, 1H), 6.85 (dd, J = 1.8 Hz, J = 8.4 Hz, 1H), 5.84 (s, 1H), 4.81 (dd, J = 6.0 Hz, J = 15.0 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.97 (dd, J = 5.4 Hz, J = 12.0 Hz, 1H), 3.84 (s, 3H), 2.53 (t, J = 12.6 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.4, 162.0, 161.8, 156.6, 144.5, 132.9, 130.6, 128.9, 128.1, 123.6, 117.8, 114.0, 110.9, 102.3, 101.1, 60.4, 55.8, 30.4, 25.6, 14.2; EI-MS (70 eV): m/z = 392 (M^+, 12.7), 319 (36.5), 291 (14.4), 277 (13.7), 251 (7.2), 203 (6.5), 189 (6.5), 129 (12.5), 105 (100), 77 (52.6). Anal. calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.17; H, 5.05.

Preparation of (*E*) ethyl (4-methyl-5-oxo-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2j). Light yellow solid, yield 87%, m. p. 110.0–111.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.36 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 5.73 (s, 1H), 4.80 (dd, J = 5.4 Hz, J = 15.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.86 (d, J = 11.4 Hz, 1H), 2.47 (s, 3H), 2.35 (t, J = 15.0 Hz, 1H), 1.33 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 164.4, 163.8, 161.8, 150.4, 134.5, 128.8, 125.8, 124.6, 121.9, 116.9, 101.1, 51.4, 29.1, 26.3, 19.8, 14.2; EI-MS (70 eV): m/z = 300 (M^+, 14.4), 271 (11.5), 255 (14.5), 254 (10.1), 253 (17.0), 228 (16.6), 227 (100), 226 (16.5), 199 (16.2), 189 (24.5), 173 (90.4), 144 (17.0), 128 (13.5), 115 (24.0), 91 (8.5), 89 (16.3), 67 (24.2), 44 (15.1). Anal. calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.16; H, 5.19.

Preparation of (*E*) ethyl (5-oxo-4-(*p*-tolyl)-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2k). White solid, yield 86%, m. p. 197.0–198.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.40 (d, J = 7.6 Hz, 3H), 7.32 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 8.0 Hz, 3H), 7.08 (d, J = 8.0 Hz, 1H), 5.83 (s, 1H), 4.85 (dd, J = 5.2 Hz, J = 11.4 Hz, 1H), 4.23 (q, J = 7.6 Hz, 2H), 3.98 (dd, J = 5.2 Hz, J = 12.0 Hz, 1H), 2.49 (t, J = 14.0 Hz, 1H), 2.41 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 163.6, 162.3, 161.7, 150.7, 141.1, 129.9, 128.9, 125.6, 124.7, 122.8, 117.0, 102.1, 100.6, 60.3, 30.2, 25.7, 21.5, 14.3; EI-MS (70 eV): m/z = 376 (M^+, 9.5), 307 (41.0), 279 (13.3), 265 (11.5), 239 (21.8), 237 (9.0), 220 (6.9), 191 (15.8), 162 (16.6), 129 (15.5), 106 (7.4), 105 (100), 77 (64.7), 44 (46.5). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.17; H, 5.44.

Preparation of (*E*) ethyl (4-(4-chlorophenyl)-5-oxo-1,10b-dihydro-5*H*-pyrano[3,4-*c*]chromen-2-ylidene) acetate (2l). White solid, yield 89%, m. p. 139.0–140.2 °C;^{1}H NMR (400 MHz, $CDCl_3$), δ 7.31–7.46 (m, 6H), 7.21 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 5.83 (s, 1H), 4.86 (dd, J = 5.6 Hz, J = 14. 4 Hz, 1H), 4.24 (q, J = 6.8 Hz, 2H), 3.99 (dd, J = 5.6 Hz, J = 12.0 Hz, 1H), 2.51 (t, J = 14.4 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 163.2, 161.3, 160.9, 150.5, 136.8, 131.3, 130.3, 129.0, 128.4, 125.6, 124.8, 122.4, 117.1, 102.5, 101.6, 60.4, 30.1, 25.6, 14.2; EI-MS (70 eV): m/z = 396 (M^+, 8.2), 351 (5.7), 325 (20.0), 324 (16.2), 323 (55.4), 322 (14.7), 296 (11.9), 295 (9.6), 285 (8.2), 284 (7.9), 281 (10.8), 255 (15.4), 249 (13.1), 221 (13.0), 202 (11.5), 189 (10.2), 173 (41.1), 163 (10.9), 144 (20.5), 141 (37.0), 139 (100), 111 (54.8), 89 (9.8), 75 (13.6), 44 (36.2). Anal. calcd for $C_{22}H_{17}ClO_5$: C, 66.59; H, 4.32. Found: C, 66.47; H, 4.20.

General procedure for the preparation of 3. To a flame-dried Schlenk flask equipped with a magnetic bar was added 3-acyl-2*H*-chromen-one **1** (0.5 mmol, 1.0 equiv), Bu_3P (20.2 mg, 0.1 mmol, 20 mol%) and dry CH_2Cl_2 (2 mL) under an argon atmosphere at room temperature. Then 2,3-butadienoate (67.2 mg, 0.6 mmol) in CH_2Cl_2 (0.5 mL) was added slowly and the resulting mixture was stirred at room temperature for 4–6 h until the reaction completed (monitored by TLC). After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60–120 mesh) column using 4 : 1 hexane–ethyl acetate solvent mixture as eluent to afford **3** as white or light yellow solid in 72–94% yield.

Preparation of 3a-benzoyl-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3a). White solid, yield 90%, m. p. 123.0–124.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$), δ 7.83 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.19 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 4.91 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.77 (dd, J = 2.4 Hz, J = 18.6 Hz, 1H), 3.14 (d, J = 18.0 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 167.1, 164.2, 149.3, 142.8, 136.8, 133.6, 132.8, 129.6, 129.2, 128.9, 125.6, 119.2, 117.4, 61.1, 48.6, 48.5, 41.1, 14.2; EI-MS (70 eV): m/z = 362 (M^+, 5.6), 271 (75.9), 225 (19.9), 198 (17.3), 105 (100), 77 (47.8). Anal. calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 73.01; H, 5.15.

Preparation of 3a-benzoyl-8-bromo-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3b). Light yellow solid, yield 91%, m. p. 130.1–132.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, J = 6.8 Hz, 3H), 7.56 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 3H), 7.02 (d, J = 8.4 Hz, 1H), 6.97 (s, 1H), 4.88 (s, 1H), 4.24 (q, J = 7.2 Hz, 2H), 3.73 (dd, J = 2.0 Hz, J = 18.4 Hz, 1H), 3.20 (d, J = 18.4 Hz, 1H), 1.32 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 166.5, 163.8, 148.4, 143.1, 136.2, 133.7, 132.7, 132.3, 129.2, 128.9, 127.7, 121.2, 119.0, 118.0, 61.2, 61.1, 48.5, 41.1, 14.1; EI-MS (70 eV): m/z = 441 (M + 1, 7.8), 422 (6.8), 337 (10.4), 335 (11.9), 270 (10.1), 213 (14.4), 211 (8.4), 126 (6.9), 106 (15.2), 105 (100), 77 (43.5), 65 (7.2), 44 (17.3). Anal. calcd for $C_{22}H_{17}BrO_5$: C, 59.88; H, 3.88. Found: C, 59.97; H, 3.70.

Preparation of 3a-benzoyl-8-chloro-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3c). Light yellow solid, yield 94%, m. p. 127.0–128.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, J = 8.0 Hz, 2H), 7.67 (s, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.96 (s, 1H), 4.88 (s, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.73 (dd, J = 2.8 Hz, J = 17.6 Hz, 1H), 3.20 (d, J = 18.4 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 166.6, 163.8, 147.9, 143.1, 136.2, 133.7,

132.7, 130.5, 129.7, 129.3, 129.2, 128.9, 120.8, 118.6, 61.2, 61.0, 48.5, 41.1, 14.1; EI-MS (70 eV): *m/z* = 397 (M + 1, 10.5), 378 (9.0), 305 (8.7), 293 (11.6), 291 (23.7), 245 (12.1), 203 (9.5), 202 (72.2), 171 (16.0), 170 (13.8), 155 (9.8), 121 (9.9), 115 (28.8), 114 (98.1), 105 (100), 91 (14.2), 77 (57.8). Anal. calcd for $C_{22}H_{17}ClO_5$: C, 66.59; H, 4.32. Found: C, 66.43; H, 4.25.

Preparation of 3a-benzoyl-8-fluoro-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3d). Light yellow solid, yield 72%, m. p. 102.2–104.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, J = 8.0 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.40–7.45 (m, 3H), 7.12 (dd, J = 4.8 Hz, J = 9.2 Hz, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.97 (s, 1H), 4.87 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.77 (dd, J = 2.0 Hz, J = 18.4 Hz, 1H), 3.16 (d, J = 18.0 Hz, 1H), 1.30 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 166.8, 164.0, 160.7, 158.3, 145.3, 143.1, 136.3, 133.7, 132.7, 129.1 (d, J = 24 Hz), 127.7 (d, J = 37 Hz), 120.8 (d, J = 8 Hz), 118.7 (d, J = 8 Hz), 116.2 (q, J = 16 Hz), 61.2, 60.5, 48.7, 41.1, 14.1; EI-MS (70 eV): *m/z* = 380 (M^+, 4.3), 362 (10.6), 317 (10.9), 289 (13.1), 275 (46.9), 229 (20.9), 202 (9.3), 173 (5.7), 146 (5.6), 105 (100), 91 (8.5), 77 (47.1), 44 (36.8). Anal. calcd for $C_{22}H_{17}FO_5$: C, 69.47; H, 4.50. Found: C, 69.28; H, 4.41.

Preparation of 3a-benzoyl-6,8-dichloro-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3e). White solid, yield 75%, m. p. 128.0–129.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.84 (d, J = 7.6 Hz, 2H), 7.60 (s, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 4.0 Hz, 1H), 6.95 (s, 1H), 4.90 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.65 (dd, J = 2.8 Hz, J = 17.2 Hz, 1H), 3.36 (d, J = 18.4 Hz, 1H), 1.30 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 165.6, 163.7, 144.3, 143.1, 135.9, 133.9, 132.9, 130.1, 129.8, 129.3, 129.0, 128.5, 122.8, 122.3, 61.8, 61.3, 49.0, 41.2, 14.1; EI-MS (70 eV): *m/z* = 430 (M^+, 1.0), 327 (11.2), 325 (17.9), 281 (4.2), 279 (4.3), 106 (7.8), 105 (100), 77 (35.2), 44 (5.1). Anal. calcd for $C_{22}H_{16}Cl_2O_5$: C, 61.27; H, 3.74. Found: C, 61.39; H, 3.87.

Preparation of 3a-benzoyl-8-methyl-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3f). Light yellow solid, yield 85%, m. p. 103.0–104.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.83 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 8.4 Hz, 3H), 7.13 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.94 (s, 1H), 4.86 (s, 1H), 4.23 (q, J = 6.0 Hz, 2H), 3.77 (dd, J = 2.8 Hz, J = 18.4 Hz, 1H), 3.11 (d, J = 18.0 Hz, 1H), 2.32 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 167.3, 164.2, 147.2, 142.8, 136.9, 135.2, 133.5, 132.7, 129.8, 129.6, 129.2, 128.8, 118.7, 117.1, 61.0, 60.8, 48.5, 40.9, 20.9, 14.1; EI-MS (70 eV): *m/z* = 376 (M^+, 4.2), 358 (4.4), 271 (42.0), 257 (15.3), 225 (19.8), 197 (3.8), 141 (5.3), 115 (9.2), 105 (100), 77 (39.8), 44 (9.6). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.53; H, 5.49.

Preparation of 3a-benzoyl-7-methyl-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3g). Light yellow solid, yield 92%, m. p. 164.6–166.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, J = 7.2 Hz, 2H), 7.49–7.56 (m, 2H), 7.42 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 4.86 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.77 (dd, J = 2.8 Hz, J = 18.0 Hz, 1H), 3.11 (d, J = 18.4 Hz, 1H), 2.32 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 167.4, 164.2, 142.6, 139.6, 136.9, 133.5, 132.7, 129.1, 128.8, 127.9, 127.5, 126.5, 117.6, 116.0, 61.0, 60.8, 48.4, 41.0, 21.0, 14.1; EI-MS (70 eV): *m/z* = 376 (M^+, 2.3), 257 (65.4), 243 (12.3), 211 (20.7), 184 (14.3), 128 (7.5), 105 (100), 77 (53.2), 44 (9.0). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.27; H, 5.50.

Preparation of 3a-benzoyl-8-methoxy-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3h). Light yellow solid, yield 86%, m. p. 118.0–119.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.82 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.20 (s, 1H), 7.09 (d, J = 8.8 Hz, 1H), 6.96 (s, 1H), 6.88 (dd, J = 3.2 Hz, J = 9.2 Hz, 1H), 4.86 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 3.81 (dd, J = 3.2 Hz, J = 18.4 Hz, 1H), 3.76 (s, 3H), 3.07 (d, J = 18.4 Hz, 1H), 1.29 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 167.3, 164.3, 156.9, 143.0, 136.7, 133.5, 132.6, 129.2, 128.9, 119.8, 118.3, 115.4, 113.3, 61.1, 60.3, 55.6, 48.8, 41.0, 14.2; EI-MS (70 eV): *m/z* = 392 (M^+, 2.0), 287 (47.4), 241 (30.4), 213 (11.0), 186 (3.6), 115 (6.6), 105 (100), 77 (50.6), 43 (7.8). Anal. calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.55; H, 5.23.

Preparation of 3a-(4-methylbenzoyl)-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3i). White solid, yield 86%, m. p. 106.0–107.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.73 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.13–7.23 (m, 4H), 6.94 (s, 1H), 4.90 (s, 1H), 4.21 (q, J = 6.8 Hz, 2H), 3.77 (dd, J = 2.0 Hz, J = 18.0 Hz, 1H), 3.12 (d, J = 18.4 Hz, 1H), 2.37 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 167.2, 164.2, 149.3, 144.6, 142.8, 136.8, 130.2, 129.6, 129.3, 129.2, 125.5, 119.3, 117.3, 61.0, 60.8, 48.7, 41.0, 21.6, 14.1; EI-MS (70 eV): *m/z* = 377 (M + 1, 1.8), 257 (67.0), 243 (12.1), 211 (17.3), 184 (12.8), 127 (5.6), 119 (100), 91 (48.5), 77 (12.5), 44 (19.8). Anal. calcd for $C_{23}H_{20}O_5$: C, 73.39; H, 5.36. Found: C, 73.51; H, 5.20.

Preparation of 3a-(4-chlorobenzoyl)-1-(ethoxycarbonyl)-3a,9b-dihydro-3*H*-cyclopenta[*c*]chromen-4-one (3j). White solid, yield 89%, m. p. 110.4–111.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.70 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 4.78 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.65 (dd, J = 2.4 Hz, J = 18.0 Hz, 1H), 3.08 (d, J = 18.4 Hz, 1H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0, 167.0, 164.1, 149.2, 142.6, 140.1, 136.8, 131.2, 130.6, 129.6, 129.3, 129.2, 125.6, 119.0, 117.4, 61.2, 61.1, 48.5, 41.0, 14.1; EI-MS (70 eV): *m/z* = 396 (M^+, 1.2), 257 (79.0), 211 (23.3), 184 (16.8), 155 (7.4), 141 (32.0), 139 (100), 111 (43.6), 77 (4.8), 75 (8.6), 44 (7.5). Anal. calcd for $C_{22}H_{17}ClO_5$: C, 66.59; H, 4.32. Found: C, 66.48; H, 4.17.

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Notes and references

1 (*a*) Z.-Y. Cai, Y. Yang, X.-H. Liu and X.-B. Qi, *Lett. Drug Des. Discovery*, 2010, **7**, 640; (*b*) Y. Dong, K. Nakagawa-Goto, C.-Y. Lai, S. L. Morris-Natschke, K. F. Bastow and K.-H. Lee, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 4085; (*c*) A. M. Vijesh, M. Arun, A. M. Isloor, V. Prabhu, S. Ahmad and S. Malladi, *Eur. J. Med. Chem.*, 2010, **45**, 5460; (*d*) M. Mladenović, N. Vuković, N. Nićiforović, S. Sukdolak and S. Slavica Solujić, *Molecules*, 2009, **14**, 1495; (*e*) C. A. Kontogiorgis and D. J. Hadjipavlou-Litina, *J. Med. Chem.*, 2005, **48**, 6400; (*f*) S. R. Kesten, T. G. Heffner, S. J. Johnson, T. A. Pugsley, J. L. Wright and L. D. Wise, *J. Med. Chem.*, 1999, **42**, 3718; (*g*) T. Symeonidis, M. Chamilos, D. J. Hadjipavlou-Litina, M. Kallitsakis and K. E. Litinas, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 1139; (*h*) I. R. Hardcastle, X. Cockcroft, N. J. Curtin, M. D. El-Murr, J. J. J. Leahy, M. Stockley, B. T. Golding, L. Rigoreau, C. Richardson, G. C. M. Smith and R. J. Griffin, *J. Med. Chem.*, 2005, **48**, 7829; (*i*) F. Leonetti, A. Favia, A. Rao, R. Aliano, A. Paluszcak, R. W. Hartmann and A. Carotti, *J. Med. Chem.*, 2004, **47**, 6792; (*j*) C. Gnerre, M. Catto, F. Leonetti, P. Weber, P.-A. Carrupt, C. Altomare, A. Carotti and B. Testa, *J. Med. Chem.*, 2000, **43**, 4747; (*k*) Q. Shen, Q. Peng, J. Shao, X. Liu, Z. Huang, X. Pu, L. Ma, Y.-M. Li, A. S. C. Chan and L. Gu, *Eur. J. Med. Chem.*, 2005, **40**, 1307; (*l*) C. Brühlmann, F. Ooms, P.-A. Carrupt, B. Testa, M. Catto, F. Leonetti, C. Altomare and A. Carotti, *J. Med. Chem.*, 2001, **44**, 3195.

2 For reviews, see: (*a*) X. Lu, C. Zhang and Z. Xu, *Acc. Chem. Res.*, 2001, **34**, 535; (*b*) B. J. Cowen and J. S. Miller, *Chem. Soc. Rev.*, 2009, **38**, 3102; (*c*) S. Ma, *Acc. Chem. Res.*, 2009, **42**, 1679.

3 For selected phosphine catalyzed [3 + 2] cycloadditions of allenoates, see: (*a*) C. Zhang and X. Lu, *J. Org. Chem.*, 1995, **60**, 2906; (*b*) Y. S. Du, X. Y. Lu and Y. H. Yu, *J. Org. Chem.*, 2002, **67**, 8901; (*c*) Y. Du, X. Lu and C. Zhang, *Angew. Chem., Int. Ed.*, 2003, **42**, 1035; (*d*) Y. Du, J. Feng and X. Lu, *Org. Lett.*, 2005, **7**, 1987; (*e*) M. Yang, X. Zhang and X. Lu, *Org. Lett.*, 2007, **9**, 5131; (*f*) S. Zheng and X. Lu, *Org. Lett.*, 2008, **10**, 4481; (*g*) Z. Lu, S. Zheng, X. Zhang and X. Lu, *Org. Lett.*, 2008, **10**, 3267; (*h*) X. Yu and X. Lu, *Org. Lett.*, 2009, **11**, 4366; (*i*) S. Zheng and X. Lu, *Org. Lett.*, 2009, **11**, 3978; (*j*) T. Dudding, O. Kwon and E. Mercier, *Org. Lett.*, 2006, **8**, 3643; (*k*) B. J. Cowen and S. J. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 10988; (*l*) Y. Z. Xia, Y. Liang, Y. Y. Chen, M. Wang, L. Jiao, F. Huang, S. Liu, Y. H. Li and Z. X. Yu, *J. Am. Chem. Soc.*, 2007, **129**, 3470; (*m*) Y. Q. Fang and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2008, **130**, 5660; (*n*) S. Xu, L. Zhou, R. Ma, H. Song and Z. He, *Chem.–Eur. J.*, 2009, **15**, 8698; (*o*) X.-Y. Guan, Y. Wei and M. Shi, *Org. Lett.*, 2010, **12**, 5024; (*p*) N. Pinto, P. Retailleau, A. Voituriez and A. Marinetti, *Chem. Commun.*, 2011, **47**, 1015; (*q*) H. Xiao, Z. Chai, C. W. Zheng, Y. Q. Yang, W. Liu, J. K. Zhang and G. Zhao, *Angew. Chem., Int. Ed.*, 2010, **49**, 4467.

4 (*a*) X. F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.*, 2003, **125**, 4716; (*b*) R. P. Wurz and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 12234; (*c*) X. Meng, Y. Huang, H. Zhao, P. Xie, J. Ma and R. Chen, *Org. Lett.*, 2009, **11**, 991; (*d*) Y. S. Tran and O. Kwon, *Org. Lett.*, 2005, **7**, 4289; (*e*) Y.-W. Sun, X.-Y. Guan and M. Shi, *Org. Lett.*, 2010, **12**, 5664; (*f*) Y.-L. Shi and M. Shi, *Org. Lett.*, 2005, **7**, 3057.

5 (*a*) Y. S. Tran and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 12632; (*b*) S. Castellano, H. D. G. Fiji, S. S. Kinderman, M. Watanabe, P. de Leon, F. Tamanoi and O. Kwon, *J. Am. Chem. Soc.*, 2007, **129**, 5843; (*c*) R. P. Wurz and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 12234; (*d*) X.-F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.*, 2003, **125**, 4716; (*e*) X.-F. Zh, A.-P. Schaffner, R. C. Li and O. Kwon, *Org. Lett.*, 2005, **7**, 2977.

6 T. Wang and S. Ye, *Org. Lett.*, 2010, **12**, 4168.

7 C. A. Evans and S. J. Miller, *J. Am. Chem. Soc.*, 2003, **125**, 12394.

8 (*a*) X.-C. Zhang, S.-H. Cao, Y. Wei and M. Shi, *Org. Lett.*, 2011, **13**, 1142; (*b*) X.-Y. Chen, M.-W. Wen, S. Ye and Z.-X. Wang, *Org. Lett.*, 2011, **13**, 1138; (*c*) X. Wang, T. Fang and X. Tong, *Angew. Chem., Int. Ed.*, 2011, **50**, 5361; (*d*) K. D. Ashtekar, R. J. Staples and B. Borhan, *Org. Lett.*, 2011, **13**, 5732.

9 For synthetic routes to substituted salicylaldehyde, see: S. Bhatt and S. K. Nayak, *Tetrahedron Lett.*, 2009, **50**, 5823.

10 Y. Zhu, X. Zou, F. Hu, C. Yao, B. Liu and H. Yang, *J. Agric. Food Chem.*, 2005, **53**, 9566.

11 X. Meng, Y. Huang and Y. Chen, *Org. Lett.*, 2009, **11**, 137.

12 (*a*) J. C. Anderson, R. j. Cubbon and J. D. Harling, *Tetrahedron: Asymmetry*, 2001, **12**, 923; (*b*) H. Jansch, S. Kannenberg and G. Boche, *Eur. J. Org. Chem.*, 2001, 2923.

13 For the synthesis of 3-acyl-2*H*-chromen-ones, see: (*a*) D. Secci, S. Carradori, A. Bolasco, P. Chimenti, M. Yáñez, F. Ortuso and S. Alcaro, *Eur. J. Med. Chem.*, 2011, **46**, 4846; (*b*) Y.-J. Jang, S. Syu, Y.-J. Chen, M.-C. Yang and W. Lin, *Org. Biomol. Chem.*, 2012, **10**, 843; (*c*) L. V. Frolova, I. Malik, P. Y. Uglinskii, S. Rogelj, A. Kornienko and I. V. Magedov, *Tetrahedron Lett.*, 2011, **52**, 6643; (*d*) S.-J. Wang, H.-W. Zheng, M. Zhang and Y.-K. Jing, *Chin. J. Med. Chem.*, 2009, **19**, 321.

