Michael Addition–Lactonization Reaction of Electron-Deficient Alkynes with *N*-(Diphenylmethylene)glycinates: An Efficient Synthesis of 3-Amino-2-pyrone Derivatives

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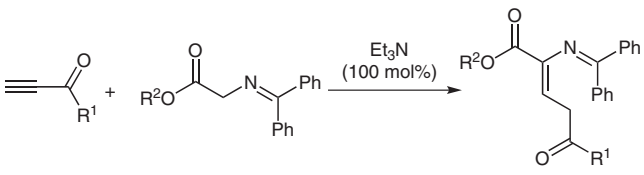
Abstract: A mild and efficient process for the synthesis of 3-amino-2-pyrone derivatives has been developed. This approach is based on the Michael addition of *N*-(diphenylmethylene)glycinates to various alkynyl ketones, followed by lactonization using 10 mol% sodium hydroxide as catalyst. Aromatic and aliphatic alkynyl ketones were converted into the corresponding 3-amino-2-pyrone derivatives in moderate to high yields. When methyl propiolate was submitted to the reaction, α,β-dehydroamino acids were formed in good yields.

Key words: 3-amino-2-pyrone derivatives, alkynyl ketones, Michael addition, lactonization, synthesis

2-Pyrones are found in numerous natural products[1] and exhibit a wide range of biological activities; such compounds possess anti-HIV,[2] telomerase inhibition,[3] antimicrobial,[4] antifungal,[5] cardiotonic,[6] pheromonal,[7] androgen-like,[8] and phytotoxic[9] properties. 2-Pyrones are also versatile synthetic building blocks due to the existence of a six-membered cyclic unsaturated ester.[10] Thus, many ways have been developed for the synthesis of 2-pyrones either through traditional approaches[11] or by transition-metal catalyzed procedures.[7,12] Recently, 2-pyrones were synthesized via electron-deficient allenes with acetates or aldehydes substituted with electron-withdrawing groups, in the presence of either potassium carbonate[13] or phosphine[14] catalyst. Despite the plethora of these synthetic processes, there is a general lack of simple procedures with which to synthesize 3-amino-2-pyrone derivatives from simple and readily available starting materials.



Scheme 1

Recently, Xue reported an efficient synthesis of α,β-dehydroamino acid derivatives from the reaction of acetylenic ketones with *N*-(diphenylmethylene)glycinates (Scheme 1).[15] The reaction proceeded effectively with both aliphatic and aromatic acetylenic ketones, in the presence of triethylamine at –10 °C, to gave the corresponding α,β-dehydroamino acid derivatives in good yields. When 1-phenylhex-2-yn-1-one and methyl propiolate were tested under the above reaction conditions, no product was found. Due to the importance of α,β-dehydroamino acid derivatives, we re-examined the reaction using sodium hydroxide as base, in place of triethylamine, to catalyze the reaction of 1-phenylhex-2-yn-1-one (**1a**) with *N*-(diphenylmethylene)glycinate **2a**. We were surprised to find that, under these conditions, the 3-amino-2-pyrone derivative **3a** was obtained (Scheme 2). Here, we wish to report a one-step, sodium hydroxide catalyzed synthesis of 3-amino-2-pyrone derivatives from simple and readily available starting materials: alkynyl ketones and *N*-(diphenylmethylene)glycinate.

Table 1 Reactions of 1-Phenylhex-2-yn-1-one (**1a**) with *N*-(Diphenylmethylene)glycinate **2a** under Various Conditions

Entry	Base (mol%)	Solvent	Temp (°C)	Time (h)	Yield of **3a** (%)[a]
1	Cs_2CO_3 (50)	CH_2Cl_2	r.t.	120	36
2	Et_3N (50)	CH_2Cl_2	r.t.	120	0
3	Ph_3P (50)	CH_2Cl_2	r.t.	120	0
4	KOH (50)	CH_2Cl_2	r.t.	16	76
5	NaOH (50)	CH_2Cl_2	r.t.	24	83
6	NaOH (100)	CH_2Cl_2	r.t.	6	84
7	NaOH (10)	CH_2Cl_2	r.t.	48	81
8	NaOH (10)	CH_2Cl_2	0	72	trace
9	NaOH (10)	CH_2Cl_2	40	2	86
10	NaOH (10)	acetone	55	40 min	70
11	NaOH (10)	toluene	60	40 min	68
12	NaOH (10)	EtOAc	60	3	51
13	NaOH (10)	THF	60	1	69
14	NaOH (10)	Et_2O	35	50 min	89

[a] Yield after purification by silica gel column chromatography.

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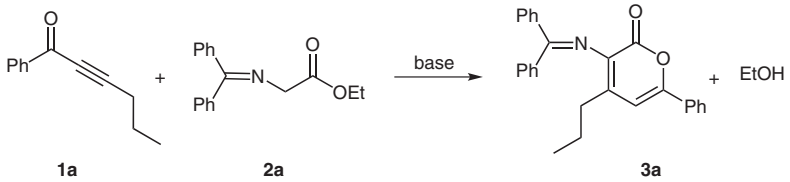
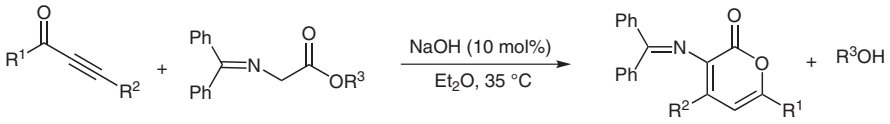


Scheme 2

We started our studies with the reaction of 1-phenylhex-2-yn-1-one (**1a**) with *N*-(diphenylmethylene)glycinate (**2a**) in the presence of cesium carbonate (50 mol%) in dichloromethane at room temperature for five days. To our surprise, 3-(diphenylmethyleneamino)-6-phenyl-4-propyl-2*H*-pyran-2-one (**3a**) was isolated from the reaction mixture. This compound was satisfactorily characterized by NMR and MS analysis. This metal-free base-catalyzed process thus generates a 3-amino-2-pyrone derivative that is difficult to construct using other methods. This prompted us to explore the feasibility of constructing 3-amino-2-pyrone derivatives using readily available alkynyl ketones and *N*-(diphenylmethylene)glycinates. To this end, we then carried out the reaction under various conditions in order to optimize the catalyst and reaction conditions; the results are shown in Table 1. It was found that the nature of the base was critical to the success of the reaction (Table 1, entries 1–4). Among the catalysts tested, sodium hydroxide was found to be the best choice. The amount of sodium hydroxide employed had a significance effect on the reaction rate, but no obvious effect on the yield (Table 1, entries 4–6). The effect of higher temperatures was found to be beneficial not only to the reaction rate but also for the yield of **3a** (Table 1, entries 6–8). When the reaction was carried out at 0 °C, only trace amounts of product were obtained even after a prolonged reaction time (72 h). The choice of solvent also had an effect on the reaction; performing the reactions in acetone, toluene, ethyl acetate or tetrahydrofuran afforded the target product in good yields. It was interesting to observe that, when the same reaction was performed in diethyl ether at 35 °C, compound **3a** was obtained in excellent yield after 50 minutes. Thus, the optimal reaction conditions for this reaction were determined to be: 10 mol% sodium hydroxide as base catalyst in diethyl ether at 35 °C.

Table 2 Reaction of Acetylenic Ketones **1** with *N*-(Diphenylmethylene)glycinates **2**



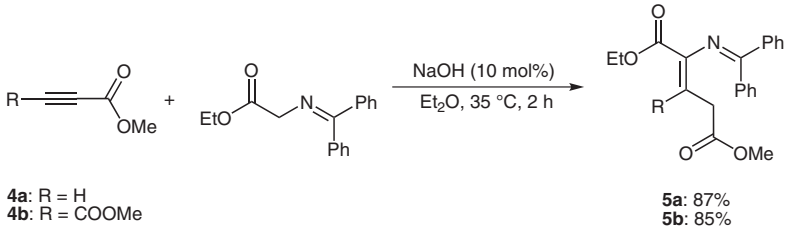
Entry	R^1	R^2	R^3	Time (min)	Product	Yield (%)[a]
1	Ph	Pr	Et	50	**3a**	89
2	Ph	Pr	Me	30	**3a**	91
3	Ph	Pr	*t*-Bu	60	**3a**	68
4	4-FC_6H_4	Pent	Et	30	**3b**	86
5	4-ClC_6H_4	Pr	Et	70	**3c**	90
6	4-BrC_6H_4	Pr	Et	60	**3d**	92
7	4-$O_2NC_6H_4$	Pr	Et	120	**3e**	94
8	4-$F_3CC_6H_4$	Pr	Et	30	**3f**	92
9	2-$F_3CC_6H_4$	Pr	Et	30	**3g**	90
10	4-MeC_6H_4	Pr	Et	100	**3h**	92
11	4-$MeOC_6H_4$	Pr	Et	70	**3i**	96
12	1-naphthyl	Pr	Et	70	**3j**	81
13	Pr	Pr	Et	30	**3k**	65
14	CH_2CH_2Ph	Pr	Et	30	**3l**	62

[a] Yield after purification by silica gel column chromatography.

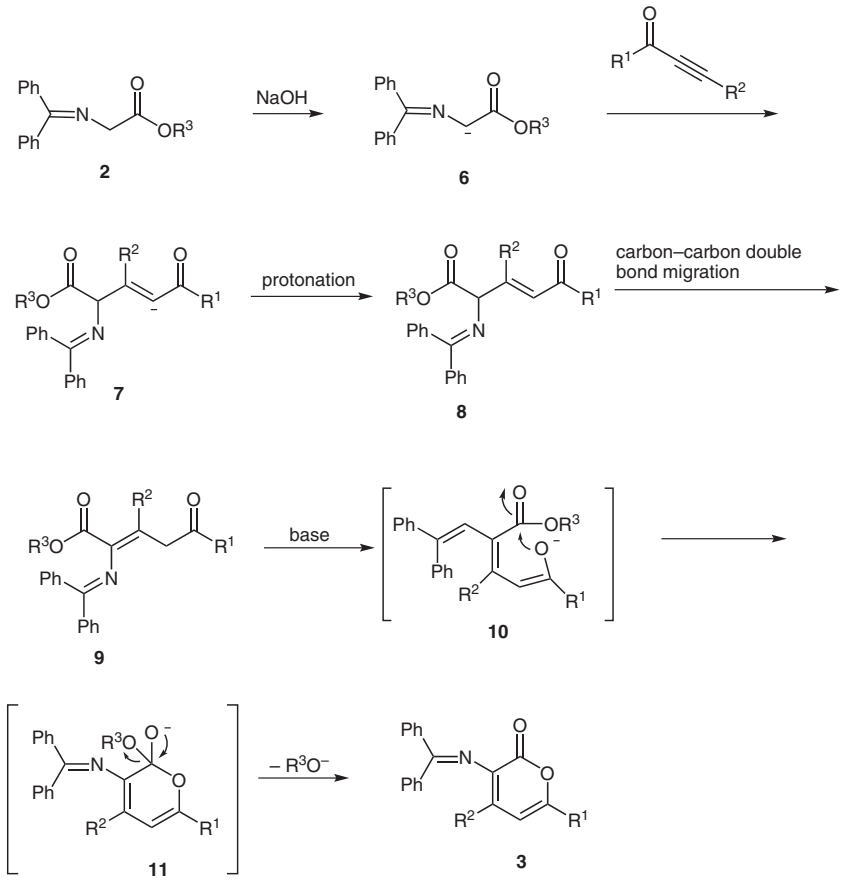
With these results in hand, several derivatives of glycine esters were synthesized and tested under the reaction conditions (Table 2). Methyl and ethyl glycine derivatives gave the expected products in similar yields, whereas the corresponding bulky *tert*-butyl ester afforded the desired product **3a** in lower yield. A variety of electron-deficient alkynes were then submitted to the reaction; these results are summarized in Table 2. It was observed that all of the reactions proceeded smoothly under the optimized conditions, to afford the corresponding products with moderate to excellent yields. The results show the scope of the reaction with respect to a range of aromatic and aliphatic alkyne ketones. Aromatic alkyne ketones show higher reactivity in the reaction than the aliphatic alkyne ketones. The substituents on the phenyl ring of the aromatic acetylenic ketones have no obvious effect on the yields of the reactions. For example, the reaction of 1-(4-chlorophenyl)hex-2-yn-1-one or 1-(4-methoxyphenyl)hex-2-yn-1-one, under the conditions described, gave the corresponding products **3c** and **3j** in 90% and 96% yields, respectively.

When methyl propiolate[16] and dimethyl but-2-ynedioate were submitted to the reaction conditions, the reaction proceeded smoothly at 35 °C in two hours to afford the corresponding α,β-dehydroamino acids in good yields (Scheme 3).

A plausible mechanism to account for the formation of the 3-amino-2-pyrone derivatives **3** is presented in Scheme 4 as follows:[17] Sodium hydroxide deprotonates the active methylene proton of the benzophenone Schiff base derivative of glycine ester **2** to generate intermediate **6**. The intermediate **6** then undergoes conjugate addition to the electron-deficient alkyne to give **7**, followed by proton transfer to give compound **8**. The intermediate **8** would undergo carbon–carbon double bond migration and the



Scheme 3



Scheme 4 Possible mechanism for the formation of 3-amino-2-pyrone derivatives **3**

subsequent cyclization would give the product 3-amino-2-pyrone derivatives **3**.

In summary, we have developed an efficient methodology for the synthesis of 3-amino-2-pyrone derivatives **3** from simple and commercially available starting materials. High yields of α,β-dehydroamino acids were obtained when ethyl propynoate and dimethyl but-2-ynedioate were submitted to the reaction. Efforts are currently underway in our laboratories to reveal the biological activities of 3-amino-2-pyrone derivatives **3** and to develop their synthetic applications.

All reactions were performed in anhydrous solvents under an argon atmosphere. THF, Et_2O, and toluene were distilled from K and Na metal, respectively. CH_2Cl_2, EtOAc and acetone were distilled from CaH_2. PE refers to petroleum ether (boiling range 60–90 °C). Acetylenic ketones[18] and *N*-(diphenylmethylene)glycinates[19] were prepared following known procedures. Methyl propiolate and dimethyl but-2-ynedioate are commercially available. Reaction progress was monitored using thin layer chromatography (TLC) on precoated Merck silica gel Kiese gel 60 F_{254} plates; the spots were visualized under UV light (254 nm). Flash chromatography was conducted with silica gel 230–400 mesh. The IR spectra were measured on a Jasco FT/IR-430 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Bruker Avance 300 spectrometer. Chemical shifts (δ, ppm) were determined with TMS as the internal reference; *J* values are given in Hz. GC-MS spectra were obtained on a Fisons 8000 Trio instrument at an ionization potential of 70 eV. High-resolution mass spectra (HRMS) were recorded on a Shimadzu LC-IT-TOF/MS instrument.

Reaction of 1-Phenylhex-2-yn-1-one (1) with *N*-(Diphenylmethylene)glycinate 2; General Procedure

A mixture of the benzophenone Schiff base derivative of glycine ethyl ester (0.2 mmol), alkynyl ketone (0.3 mmol), and NaOH (0.02 mmol) in Et_2O (2 mL) under argon, was heated to 35 °C with stirring. When the reaction was complete (monitored by TLC), the solvent was evaporated and the crude product was purified by flash chromatography on silica gel (PE–EtOAc, 10:1→5:1), to afford the corresponding pure product.

3-(Diphenylmethyleneamino)-6-phenyl-4-propyl-2*H*-pyran-2-one (3a)

Yellow oil.

IR (KBr): 2924, 1707, 1633, 1504, 1447, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 4 H), 7.49–7.25 (m, 11 H), 6.51 (s, 1 H), 2.38 (t, *J* = 7.8 Hz, 2 H), 1.62–1.59 (m, 2 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.2, 157.5, 154.0, 140.4, 138.6, 137.1, 133.7, 131.6, 131.2, 129.8, 129.7, 129.3, 128.8, 128.2, 128.1, 127.9, 124.9, 103.6, 33.1, 20.9, 14.1.

MS (70 eV): *m*/*z* = 393 [M$^+$].

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{27}H_{23}NO_2$: 393.1729; found: 393.1732.

3-(Diphenylmethyleneamino)-6-(4-fluorophenyl)-4-pentyl-2*H*-pyran-2-one (3b)

Yellow oil.

IR (KBr): 2928, 1711, 1635, 1508, 1446, 835, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.67 (m, 4 H), 7.48–7.24 (m, 8 H), 7.24–7.03 (m, 2 H), 2.37 (t, *J* = 6.9 Hz, 2 H), 1.58–1.51 (m, 2 H), 1.34–1.24 (m, 4 H), 0.91 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 165.3, 157.5, 153.2, 140.6, 138.7, 137.2, 133.5, 131.3, 129.8, 129.4, 128.2, 128.1, 128.0, 127.9, 127.1, 116.1, 103.4, 31.8, 31.2, 29.8, 27.3, 22.6, 14.0.

MS (70 eV): *m*/*z* = 439 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{29}H_{26}FNO_2$: 440.2020; found: 440.2021.

6-(4-Chlorophenyl)-3-(diphenylmethyleneamino)-4-propyl-2*H*-pyran-2-one (3c)

Yellow oil.

IR (KBr): 2930, 1710, 1634, 1575, 1446, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.5 Hz, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.50–7.24 (m, 10 H), 6.46 (s, 1 H), 2.37 (t, *J* = 7.5 Hz, 2 H), 1.64–1.52 (m, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 157.3, 152.9, 140.3, 138.6, 137.1, 135.7, 133.9, 131.3, 130.2, 130.1, 129.8, 129.4, 129.0, 128.2, 127.9, 126.2, 103.9, 33.2, 20.9, 14.2.

MS (70 eV): *m*/*z* = 427 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}ClNO_2$: 428.1412; found: 428.1414.

6-(4-Bromophenyl)-3-(diphenylmethyleneamino)-4-propyl-2*H*-pyran-2-one (3d)

Yellow oil.

IR (KBr): 2916, 1708, 1634, 1568, 1486, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.5 Hz, 2 H), 7.59 (d, *J* = 8.7 Hz, 2 H), 7.51 (d, *J* = 8.4 Hz, 2 H), 7.46–7.24 (m, 8 H), 6.47 (s, 1 H), 2.37 (t, *J* = 7.5 Hz, 2 H), 1.64–1.50 (m, 2 H), 1.00 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 157.2, 152.9, 140.2, 138.6, 137.1, 134.0, 132.0, 131.8, 131.3, 130.6, 129.8, 129.4, 128.2, 127.9, 126.3, 124.0, 103.9, 33.1, 20.9, 14.2.

MS (70 eV): *m*/*z* = 473 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}BrNO_2$: 472.0907; found: 472.0901.

3-(Diphenylmethyleneamino)-6-(4-nitrophenyl)-4-propyl-2*H*-pyran-2-one (3e)

Yellow oil.

IR (KBr): 2930, 1711, 1637, 1595, 1518, 1446, 694 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 9.0 Hz, 2 H), 7.87 (d, *J* = 9.0 Hz, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.58–7.24 (m, 8 H), 6.65 (s, 1 H), 2.41 (t, *J* = 7.2 Hz, 2 H), 1.64–1.57 (m, 2 H), 1.02 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5, 156.8, 151.0, 147.9, 139.5, 138.3, 137.3, 135.4, 131.5, 129.5, 128.2, 127.8, 125.4, 124.1, 106.6, 33.1, 20.9, 14.1.

MS (70 eV): *m*/*z* = 438 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}N_2O_4$: 439.1652; found: 439.1658.

3-(Diphenylmethyleneamino)-4-propyl-6-[4-(trifluoromethyl)phenyl]-2*H*-pyran-2-one (3f)

Yellow oil.

IR (KBr): 2962, 1712, 1637, 1614, 1577, 1446, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.86 (m, 4 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.49–7.24 (m, 8 H), 6.57 (s, 1 H), 2.39 (t, *J* = 7.5 Hz, 2 H), 1.63–1.54 (m, 2 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.5, 157.1, 152.2, 139.9, 138.5, 137.1, 134.9, 131.5, 130.1, 129.9, 129.5, 129.0, 128.2, 127.9, 125.9, 125.8, 125.1, 105.2, 33.2, 20.9, 14.2.

MS (70 eV): *m*/*z* = 461 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{22}F_3NO_2$: 462.1675; found: 462.1674.

3-(Diphenylmethyleneamino)-4-propyl-6-[2-(trifluoromethyl)phenyl]-2*H*-pyran-2-one (3g)
Yellow oil.

IR (KBr): 2962, 1714, 1643, 1577, 1447, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.2 Hz, 2 H), 7.71 (d, *J* = 7.5 Hz, 2 H), 7.55–7.24 (m, 10 H), 6.18 (s, 1 H), 2.36 (t, *J* = 7.5 Hz, 2 H), 1.59–1.52 (m, 2 H), 0.98 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 157.4, 152.4, 139.6, 138.6, 136.9, 134.3, 131.7, 131.3, 131.0, 129.8, 129.7, 129.4, 128.2, 128.1, 128.0, 126.8, 126.4, 125.8, 108.4, 32.9, 20.7, 14.0.

MS (70 eV): *m*/*z* = 461 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{22}F_3NO_2$: 462.1675; found: 462.1672.

3-(Diphenylmethyleneamino)-4-propyl-6-*p*-tolyl-2*H*-pyran-2-one (3h)
Yellow oil.

IR (KBr): 2961, 1708, 1633, 1596, 1574, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.2 Hz, 2 H), 7.62 (d, *J* = 8.1 Hz, 2 H), 7.50–7.27 (m, 8 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 6.45 (s, 1 H), 2.37–2.32 (m, 5 H), 1.62–1.54 (m, 2 H), 1.00 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.1, 156.5, 153.2, 139.5, 138.9, 137.6, 132.2, 130.1, 128.7, 128.2, 127.8, 127.0, 126.9, 126.8, 123.7, 101.8, 32.1, 20.3, 19.8, 13.1.

MS (70 eV): *m*/*z* = 407 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}NO_2$: 408.1958; found: 408.1958.

3-(Diphenylmethyleneamino)-6-(4-methoxyphenyl)-4-propyl-2*H*-pyran-2-one (3i)
Yellow oil.

IR (KBr): 2932, 1705, 1633, 1607, 1575, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.2 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 7.51–7.28 (m, 8 H), 6.92 (d, *J* = 8.7 Hz, 2 H), 6.39 (s, 1 H), 3.84 (s, 3 H), 2.38 (t, *J* = 7.5 Hz, 2 H), 1.66–1.52 (m, 2 H), 1.01 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.1, 160.9, 157.6, 154.3, 141.0, 138.8, 137.2, 132.7, 131.2, 129.7, 129.3, 129,1, 128.1, 127.9, 126.5, 124.4, 114.2, 102.1, 55.4, 33.2, 20.9, 14.2.

MS (70 eV): *m*/*z* = 423 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}NO_3$: 424.1907; found: 424.1905.

3-(Diphenylmethyleneamino)-6-(naphthalen-1-yl)-4-propyl-2*H*-pyran-2-one (3j)
Yellow oil.

IR (KBr): 2929, 1709, 1636, 1595, 1575, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.07 (m, 1 H), 7.90–7.83 (m, 4 H), 7.63–7.61 (m, 1 H), 7.55–7.65 (m, 11 H), 6.37 (s, 1 H), 2.45 (t, *J* = 7.5 Hz, 2 H), 1.66–1.59 (m, 2 H), 1.04 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.4, 158.0, 155.2, 140.3, 137.2, 133.8, 131.3, 130.5, 130.4, 129.8, 129.4, 128.6, 128.3, 128.2, 128.0, 127.4, 127.1, 126.9, 126.2, 125.1, 125.0, 108.8, 104.1, 33.2, 20.9, 14.2.

MS (70 eV): *m*/*z* = 443 [M$^+$].

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{31}H_{25}NO_2$: 444.1958; found: 444.1956.

3-(Diphenylmethyleneamino)-4,6-dipropyl-2*H*-pyran-2-one (3k)
Yellow oil.

IR (KBr): 2932, 1712, 1645, 696 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.2 Hz, 2 H), 7.46–7.24 (m, 8 H), 5.76 (s, 1 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 2.26 (t, *J* = 7.5 Hz, 2 H), 1.63–1.54 (m, 4 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 0.90 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 157.7, 157.5, 139.1, 137.6, 136.0, 131.3, 130.0, 128.6, 128.1, 127.0, 126.9, 126.8, 103.7, 34.0, 31.7, 19.6, 19.2, 13.0, 12.2.

MS (70 eV): *m*/*z* = 359 [M$^+$].

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{24}H_{25}NO_2$: 359.1885; found: 359.1883.

3-(Diphenylmethyleneamino)-6-phenethyl-4-propyl-2*H*-pyran-2-one (3l)
Yellow oil.

IR (KBr): 2930, 1704, 1648, 1600, 1556, 699 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.2 Hz, 2 H), 7.49–7.31 (m, 6 H), 7.25–7.14 (m, 5 H), 7.05 (d, *J* = 7.8 Hz, 2 H), 5.61 (s, 1 H), 2.90 (t, *J* = 7.5 Hz, 2 H), 2.67 (t, *J* = 7.5 Hz, 2 H), 2.20 (t, *J* = 7.5 Hz, 2 H), 1.47–1.37 (m, 2 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.3, 158.5, 157.4, 140.3, 140.1, 138.8, 137.2, 132.6, 131.2, 129.7, 128.5, 128.3, 128.2, 128.0, 127.9, 126.3, 105.6, 35.4, 33.4, 32.8, 20.7, 14.1.

MS (70 eV): *m*/*z* = 421 [M$^+$].

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{29}H_{27}NO_2$: 421.2042; found: 421.2039.

(*Z*)-1-Ethyl 5-Methyl 2-(Diphenylmethyleneamino)pent-2-enedioate (5a)[16]
Pale-yellow oil.

IR (KBr): 2961, 1735, 1717, 1262, 1097, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.2 Hz, 2 H), 7.35–7.23 (m, 6 H), 7.09–7.01 (m, 2 H), 6.11 (d, *J* = 7.2 Hz, 1 H), 3.93 (q, *J* = 6.9 Hz, 2 H), 3.53 (s, 3 H), 3.03 (d, *J* = 6.9 Hz, 2 H), 1.04 (t, *J* = 7.2 Hz, 3 H).

MS (70 eV): *m*/*z* = 351 [M$^+$].

HRMS (ESI): *m*/*z* [M$^+$] calcd for $C_{21}H_{21}NO_4$: 351.1471; found: 351.1473.

(*Z*)-1-Ethyl 2,3-Dimethyl 1-(Diphenylmethyleneamino)prop-1-ene-1,2,3-tricarboxylate (5b)
Pale-yellow oil.

IR (KBr): 2951, 1737, 1720, 1272, 1089, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.2 Hz, 2 H), 7.48–7.37 (m, 8 H), 4.01 (q, *J* = 6.9 Hz, 2 H), 3.67 (s, 3 H), 3.56 (s, 3 H), 3.27 (s, 2 H), 1.16 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.7, 170.7, 166.8, 165.3, 150.4, 131.1, 129.7, 128.3, 128.2, 111.5, 61.8, 52.1, 52.0, 33.1, 13.8.

MS (70 eV): *m*/*z* = 409 [M$^+$].

HRMS (ESI): *m/z* [M$^+$] calcd for $C_{23}H_{23}NO_6$: 409.1525; found: 409.1523.

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