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Consecutive Alkynylation–Michael Addition–Cyclocondensation (AMAC) Multicomponent Syntheses of α-Pyrones and α-Pyridones

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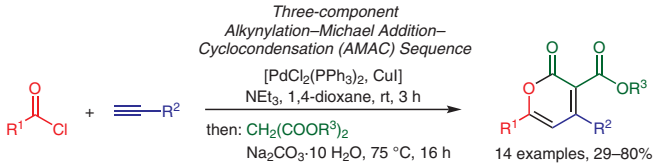

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Abstract A novel consecutive three-component synthesis of α-pyrones is based upon an alkynylation–Michael addition–cyclocondensation (AMAC) sequence, starting from (hetero)aroyl chloride and terminal alkyne to furnish the alkynone which reacts with malonates to give the α-pyrones in moderate to very good yields. By concatenating ammonolysis of the α-pyrones, an alkynylation–Michael addition–cyclocondensation–ammonolysis (AMACA) synthesis of α-pyridones can be conceived. α-Pyridone products with and without ester functionality are obtained in moderate yields.

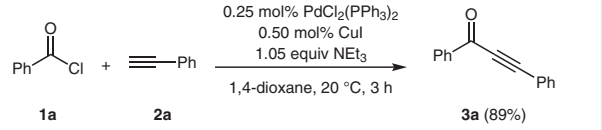
Key words multicomponent reactions, C–C coupling, cyclocondensation, alkynes, heterocycles, palladium

α-Pyrones, six-membered unsaturated lactones,[1] are key motifs in many natural products, which have been isolated from various animals, plants, marine organisms, bacteria, fungi and insects. These natural products exhibit a wide range of biological activities, including antifungal, cytotoxic, neurotoxic and phytotoxic properties.[2] α-Pyrones display similar reactivity as aromatics,[3] dienes[4] and enones,[5] and as a consequence they have received considerable interest in the synthesis of polysubstituted arenes via [4+2]/retro-[4+2] sequences.[4b,6] Therefore, they have become interesting building blocks for the synthesis of key intermediates in organic and medicinal chemistry.[2a,7] Amongst various syntheses of α-pyrones, quite a number of transition-metal-catalyzed routes have been developed. Palladium-catalyzed methodologies employing alkynes as key components were introduced by Larock,[8] Burton[9] and Negishi.[10] Also starting from alkynes, Miura[11] and co-workers reported a rhodium-catalyzed oxidative coupling reaction of substituted acrylic acids with alkynes and alkenes, and Ackermann[12] introduced a ruthenium-catalyzed synthesis towards α-pyrones. Furthermore, the addition of β-keto esters to 1,2-allenyl ketones[13] or alkynones[14] has become a general access to α-pyrones. Also, the 1,4-addition of malonates to alkynones was studied by Kohler[15] and Barat.[16]

Interestingly, α-pyrones easily react with nucleophiles. For instance, with ammonia or primary amines as nucleophiles, they are readily transformed into α-pyridones.[17] α-Pyridones are isosteres of α-pyrones containing an amide moiety. Like α-pyrones, α-pyridones are structural motifs in various biologically active natural products, and some of them find application as anticancer,[18] antibacterial[19] and antiviral agents.[20] Many synthetic routes to α-pyridones have been reported, including copper(II)-catalyzed [3+2+1] annulations of 2-aminopyridines and β-enamino esters,[21] Michael addition–cyclocondensation of acetamides and α,β-unsaturated ketones,[22] nucleophilic addition of malonic esters to alkynyl imines,[23] and rhodium- and ruthenium-catalyzed oxidative coupling of alkynes and acrylamides.[24]

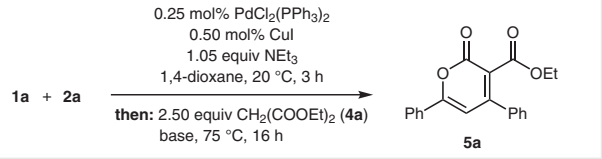
Alkynones can be formed by catalytic alkynylation of acid chlorides with terminal alkynes.[25] Due to their enhanced Michael reactivity, alkynones constitute key intermediates in consecutive multicomponent syntheses of heterocycles.[26] In our group, we have developed several multicomponent syntheses with alkynones as key intermediates for the synthesis of six-membered heterocycles, for example pyrimidines[27] and 5-acylpyridin-2(1*H*)-ones.[28] Therefore, a base-mediated addition of malonate to the *in situ* generated alkynone could well evolve into a novel multicomponent synthesis of α-pyrones. Furthermore, their immediate transformation into α-pyridones appears even more rewarding. Herein, we report the consecutive alkynylation–Michael addition–cyclocondensation (AMAC) multicomponent syntheses of α-pyrones and α-pyridones initiated by catalytic alkynylation and subsequent reaction with malonates, and also with amines.

The consecutive three-component synthesis of α-pyrones commenced with Sonogashira coupling between acid chloride **1** and terminal alkyne **2**. Deviating from our standard alkynone synthesis,[25] we could considerably lower the catalyst loading to 0.25 mol% $PdCl_2(PPh_3)_2$ and 0.50 mol% CuI, as shown for the model reaction of benzoyl chloride (**1a**) and phenylacetylene (**2a**), which upon stirring in 1,4-dioxane at 20 °C for 3 hours furnished alkynone **3a** in 89% isolated yield (Scheme 1).



Scheme 1 Synthesis of 1,3-diphenylprop-2-yn-1-one (**3a**)

With these optimized conditions for the alkynylation step, the second Michael addition–cyclocondensation step was directly probed *en route*, i.e. without isolation of the alkynone (Scheme 2, Table 1). Therefore, directly after full conversion into the alkynone **3a**, diethyl malonate (**4a**) and bases were added to the reaction mixture. Although for the direct transformation of alkynone to α-pyrone, sodium ethoxide has been reported to be effective,[15,16] this base did not work in a one-pot fashion. Only decreasing the amount of sodium ethoxide to 2.50 equivalents led to a minor formation of α-pyrone **5a** (Table 1, entries 1–4).



Scheme 2 Model reaction for optimization of the consecutive three-component synthesis of α-pyrone **5a**

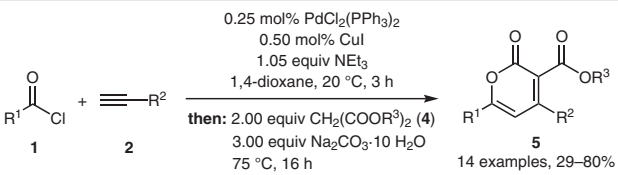
Sodium hydroxide and sodium acetate as bases only gave traces of α-pyrone **5a** or did not lead to any product formation at all (Table 1, entries 5 and 6). The addition of 8.00 equivalents of $Na_2CO_3 \cdot 10\ H_2O$ at least led to the formation of the desired product in 35% yield (Table 1, entry 7). Lowering the amount of $Na_2CO_3 \cdot 10\ H_2O$ to 3.00 equivalents enhanced the yield of compound **5a** considerably (Table 1, entries 8, 9 and 11). Further lowering, however, resulted in a drop in yield (Table 1, entry 13). The necessity for the presence of certain water was underlined by using anhydrous sodium carbonate, which only gave 2% yield (Table 1, entry 10), while further addition of water to 3.00 equivalents of $Na_2CO_3 \cdot 10\ H_2O$ led to a reduced yield of 64% (Table 1, entry 12 vs entry 11). The amount of malonate could be reduced to 2.00 equivalents (Table 1, entry 14), while further lowering resulted in a drop in yield (Table 1, entry 15).

Table 1 Optimization of the Michael Addition–Cyclocondensation Step in the Consecutive Three-Component Synthesis of α-Pyrone **5a**[a]

Entry	Base ([equiv])	Additive ([equiv])	Compound **5a** (isolated yield)[b]
1	NaOEt (8.00)	–	no conversion
2	NaOEt (4.00)	–	no conversion
3	NaOEt (2.50)	–	15%
4[c]	NaOEt (8.00)	–	8%
5	NaOH (8.00)	–	traces
6	NaOAc (8.00)	–	no conversion
7	$Na_2CO_3 \cdot 10\ H_2O$ (8.00)	–	35%
8	$Na_2CO_3 \cdot 10\ H_2O$ (5.00)	–	64%
9	$Na_2CO_3 \cdot 10\ H_2O$ (4.00)	–	75%
10	Na_2CO_3 (4.00)	–	2%
11	$Na_2CO_3 \cdot 10\ H_2O$ (3.00)	–	81%
12	$Na_2CO_3 \cdot 10\ H_2O$ (3.00)	H_2O (15.0)	64%
13	$Na_2CO_3 \cdot 10\ H_2O$ (2.50)	–	74%
14[d]	$Na_2CO_3 \cdot 10\ H_2O$ (3.00)	–	78%
15[e]	$Na_2CO_3 \cdot 10\ H_2O$ (3.00)	–	64%

[a] All reactions were carried out on a 2.00 mmol scale (c_0(**1a**) = 1.1 M, c_0(**2a**) = 1.0 M).
[b] All yields refer to isolated and purified products.
[c] Diethyl malonate (**4a**) (8.00 equiv).
[d] Diethyl malonate (**4a**) (2.00 equiv).
[e] Diethyl malonate (**4a**) (1.50 equiv).

With the optimized conditions for the three-component synthesis in hand, a variety of different acid chlorides **1**, terminal alkynes **2** and malonates **4** were employed (Scheme 3). The one-pot synthesis was performed to give 14 examples of α-pyrones **5** in moderate to very good isolated yields (Table 2). The structures of the α-pyrones **5** were unambiguously assigned by ^1H and ^{13}C NMR and IR spectroscopy, as well as by mass spectrometry. In addition, the constitution was unambiguously corroborated for compound **5i** by NOESY, HSQC and HMBC NMR spectra. Electron-donating and electron-withdrawing groups, as well as heterocyclic substituents (**5h**, **i**), could uneventfully be introduced at the 4- and 6-position of the α-pyrone core by the alkynylation–Michael addition–cyclocondensation sequence.



Scheme 3 Consecutive three-component alkynylation–Michael addition–cyclocondensation (AMAC) synthesis of α-pyrones **5** from acid chlorides **1**, terminal alkynes **2** and dialkyl malonates **4**

Table 2 Consecutive Three-Component Alkynylation–Michael Addition–Cyclocondensation (AMAC) Synthesis of α-Pyrones **5**[a]

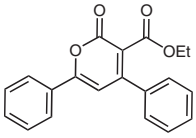
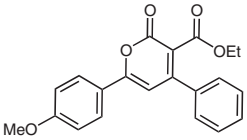
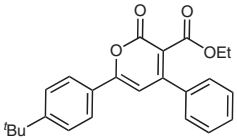
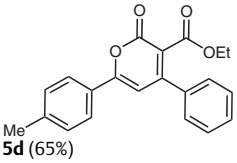
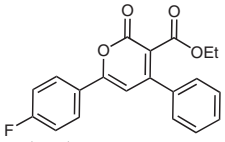
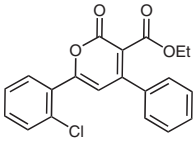
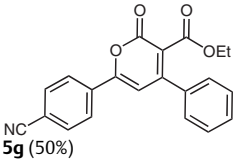
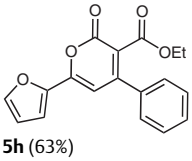
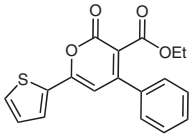
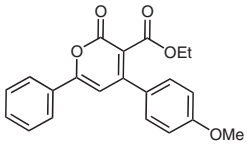
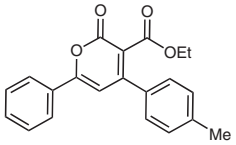
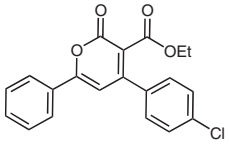
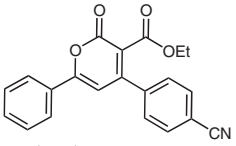
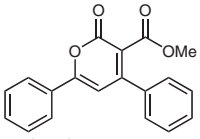
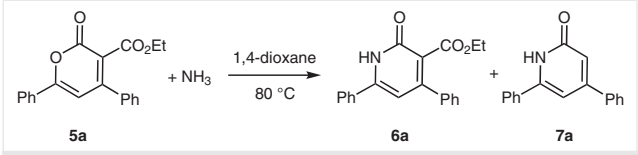
Entry	Acid chloride **1**	Terminal alkyne **2**	Dialkyl malonate **4**	α-Pyrone **5**[b]
1	R^1 = Ph (**1a**)	R^2 = Ph (**2a**)	R^3 = Et (**4a**)	 **5a** (78%)
2	R^1 = 4-$MeOC_6H_4$ (**1b**)	**2a**	**4a**	 **5b** (29%)
3	R^1 = 4-$^tBuC_6H_4$ (**1c**)	**2a**	**4a**	 **5c** (58%)
4	R^1 = 4-MeC_6H_4 (**1d**)	**2a**	**4a**	 **5d** (65%)
5	R^1 = 4-FC_6H_4 (**1e**)	**2a**	**4a**	 **5e** (75%)
6	R^1 = 2-ClC_6H_4 (**1f**)	**2a**	**4a**	 **5f** (80%)
7	R^1 = 4-NCC_6H_4 (**1g**)	**2a**	**4a**	 **5g** (50%)
8	R^1 = 2-furyl (**1h**)	**2a**	**4a**	 **5h** (63%)

Table 2 (continued)

Entry	Acid chloride **1**	Terminal alkyne **2**	Dialkyl malonate **4**	α-Pyrone **5**[b]
9	R^1 = 2-thienyl (**1i**)	**2a**	**4a**	 **5i** (64%)
10	**1a**	R^2 = 4-$MeOC_6H_4$ (**2b**)	**4a**	 **5j** (65%)
11	**1a**	R^2 = 4-MeC_6H_4 (**2c**)	**4a**	 **5k** (54%)
12	**1a**	R^2 = 4-ClC_6H_4 (**2d**)	**4a**	 **5l** (43%)
13	**1a**	R^2 = 4-NCC_6H_4 (**2e**)	**4a**	 **5m** (37%)
14	**1a**	**2a**	R^3 = Me (**4b**)	 **5n** (52%)

[a] All reactions were carried out on a 2.00 mmol scale (c_0(**1**) = 1.1 M, c_0(**2**) = 1.0 M, c_0(**4**) = 2.0 M).
[b] All yields refer to isolated and purified products.

The consecutive three-component synthesis of α-pyrones **5** can be extended to a four-component synthesis of α-pyridones by *in situ* reaction with ammonia. However, two α-pyridone derivatives are formed, one with and one without the ester substituent.[29] Starting from ethyl 2-oxo-4,6-diphenyl-2*H*-pyran-3-carboxylate (**5a**), we also observed the formation of two α-pyridones, **6a** and **7a** (Scheme 4, Table 3). Besides the expected ester-substituted α-pyridone **6a** (21%), the α-pyridone **7a** devoid of an ester function could be isolated in 70% yield (Table 3, entry 1). Neither a longer reaction time (Table 3, entry 2) nor an increased amount of ammonia solution (Table 3, entry 3) significantly changed the product ratio or the yield.



5a 6a 7a

Scheme 4 Model reaction for optimization of the transformation of α-pyrone **5a** into α-pyridones **6a** and **7a**

Table 3 Optimization of the Synthesis of Ethyl 2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carboxylate (**6a**) and 4,6-Diphenylpyridin-2(1*H*)-one (**7a**) from Ethyl 2-Oxo-4,6-diphenyl-2*H*-pyran-3-carboxylate (**5a**)[a]

Entry	25% Aqueous ammonia solution (equiv)	Time (h)	α-Pyridone **6a**[b]	α-Pyridone **7a**[b]
1	64.0	0.5	21%	70%
2	64.0	3	23%	70%
3	128	0.5	23%	63%

[a] All reactions were carried out on a 1.00 mmol scale (c_0(**5a**) = 1.0 M).
[b] All yields refer to isolated and purified products.

Next, the formation of α-pyrone **5a** was concatenated with ammonolysis to give α-pyridones **6a** and **7a** in an alkynylation–Michael addition–cyclocondensation–ammonolysis (AMACA) sequence. Indeed, after the addition of aqueous ammonia and reaction at 90 °C for 3 hours, α-pyridones **6a** and **7a** were isolated in a combined yield of 67% (Table 4, entry 1). Increasing the reaction time to 4 hours only slightly increased the yield of both α-pyridones (Table 4, entry 2), but a further increase in the reaction time did not increase the yield (Table 4, entry 3). Using less ammonia solution led to a prolonged reaction time of 24 hours and a decreased overall yield (Table 4, entry 4). The use of ammonia solution in 1,4-dioxane instead of the aqueous solution also led to a prolonged reaction time and isolated yields of 40–50% (Table 4, entries 5 and 6).

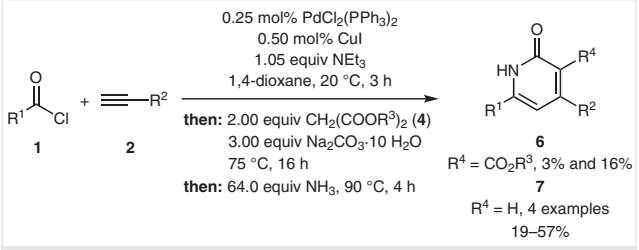
Table 4 Optimization of the Ammonolysis Step in the Consecutive Four-Component Alkynylation–Michael Addition–Cyclocondensation–Ammonolysis (AMACA) Synthesis of Ethyl 2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carboxylate (**6a**) and 4,6-Diphenylpyridin-2(1*H*)-one (**7a**) in a One-Pot Fashion[a]

Entry	25% Aqueous ammonia solution (equiv)	Time (h)	α-Pyridone **6a**[b]	α-Pyridone **7a**[b]
1	64.0	3	12%	55%
2	64.0	4	16%	57%
3	64.0	5	15%	55%
4	6.40	24	4%	24%
5	1.50[c]	24	10%	30%
6	3.00[c]	24	20%	30%

[a] All reactions were carried out on a 1.00 mmol scale (c_0(**1a**) = 1.1 M, c_0(**2a**) = 1.0 M, c_0(**4a**) = 2.0 M, c_0(Na_2CO_3·10 H_2O) = 3.0 M).
[b] All yields refer to isolated and purified products.
[c] Employed as a 0.5 M solution in 1,4-dioxane.

We also tried to cleave the ester group by addition of concentrated sulfuric acid, aiming to obtain only α-pyridone **7a** at the end of the sequence. However, no changes in the yield and ratio of **6a** and **7a** were detected. Therefore, we reasoned that the ester cleavage rather occurs as a consequence of ring opening by ammonolysis.

With the optimized reaction conditions in hand, two examples of α-pyridones **6** and four examples of **7** were synthesized, in low to moderate yields (Scheme 5, Table 5), thereby extending the one-pot process by an additional step to an alkynylation–Michael addition–cyclocondensation–ammonolysis sequence. Interestingly, both electron-rich and electron-deficient substituted aroyl chlorides and arylacetylenes only furnished the ester-cleaved products **7b–d** (Table 5, entries 2, 3 and 5). However, the strongly electron-withdrawing 4-cyanophenyl substituent at position R^1 does not allow ammonolysis and, therefore, only α-pyrone **5g** was isolated (Table 5, entry 4). All this can be accounted for by a crucial influence of the electron density distribution in α-pyrone **5** and, thereby, modulation of its electrophilicity.

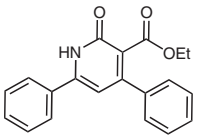
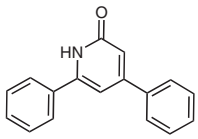
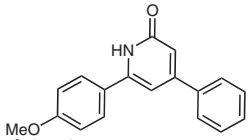
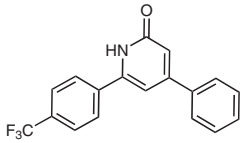
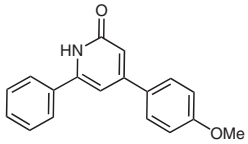
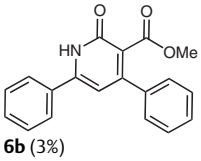
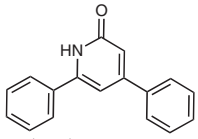


Scheme 5 Consecutive four-component alkynylation–Michael addition–cyclocondensation–ammonolysis (AMACA) synthesis of α-pyridones **6** and **7** from acid chlorides **1**, terminal alkynes **2**, dialkyl malonates **4** and ammonia

Based upon an alkynylation–Michael addition–cyclocondensation (AMAC) sequence by way of a consecutive three-component reaction, we have developed a novel one-pot synthesis of α-pyrones. Furthermore, upon concatenation of an ammonolysis, a four-component synthesis of α-pyridones could be realized. This alkynylation–Michael addition–cyclocondensation–ammonolysis (AMACA) sequence interestingly gives α-pyridones, however predominantly the products without esters as a consequence of cleavage. The dense presence of diene and lactone functionalities is predestined for further concatenations of elementary processes. Studies directed to enhance the molecular diversity and structural complexity based upon AMAC sequences are currently underway.

All reactions were performed in dried Schlenk tubes under a nitrogen atmosphere. TLC was used to monitor the reaction progress qualitatively, using silica gel coated aluminum foil. For detection, UV light of wavelengths 254 and 366 nm was employed. Commercially available chemicals were used as received without any further purification. ^{1}H, ^{13}C and DEPT NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 300 MHz (Bruker Avance III 300) or 600 MHz (Bruker Avance III 600) NMR spectrometer. Chemical shifts are referenced to the internal solvent signal: $CDCl_3$ (^{1}H, δ 7.26; ^{13}C, δ 77.2), DMSO-d_6 (^{1}H, δ 2.50; ^{13}C, δ 39.5). Multiplicities are stated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (*J*) are given in hertz. The assignment of primary (CH_3), secondary (CH_2), tertiary (CH) and qua-

Table 5 Consecutive Four-Component Alkynylation–Michael Addition–Cyclocondensation–Ammonolysis (AMACA) Synthesis of α-Pyridones **6** and **7**[a]

Entry	Acid chloride **1**	Terminal alkyne **2**	Dialkyl malonate **4**	α-Pyridone **6**[b]	α-Pyridone **7**[b]
1	R^1 = Ph (**1a**)	R^2 = Ph (**2a**)	R^3 = Et (**4a**)	 **6a** (16%)	 **7a** (57%)
2	R^1 = 4-$MeOC_6H_4$ (**1b**)	**2a**	**4a**	–	 **7b** (19%)
3	R^1 = 4-$F_3CC_6H_4$ (**1j**)	**2a**	**4a**	–	 **7c** (30%)
4	R^1 = 4-NCC_6H_4 (**1g**)	**2a**	**4a**	–	–[c]
5	**1a**	R^2 = 4-$MeOC_6H_4$ (**2b**)	**4a**	–	 **7d** (24%)
6	**1a**	**2a**	R^3 = Me (**4b**)	 **6b** (3%)	 **7a** (31%)

[a] All reactions were carried out on a 2.00 mmol scale (c_0(**1**) = 1.1 M, c_0(**2**) = 1.0 M, c_0(**4**) = 2.0 M).
[b] All yields refer to isolated and purified products.
[c] Compound **5g** (13%) was isolated instead.

ternary (C_{quat}) carbon nuclei was made by using DEPT-135 spectra. Mass spectroscopic measurements were conducted on a quadrupole (EI) analyzer (TSQ 7000, Finnigan MAT). IR spectra were measured using the ATR technique (Shimadzu IRAffinity-1). The intensities of the IR bands are abbreviated as w (weak), m (medium), s (strong) and vs (very strong). Elemental analyses were carried out on a Perkin Elmer Series II Analyzer 2400 in the microanalytical laboratory of the Pharmazeutisches Institut of the Heinrich-Heine-Universität Düsseldorf. Uncorrected melting points and were determined with a Reichert Thermovar melting point microscope (heating unit: PeakTech 6000A DC Power Supply; thermometry: Norma D2400 (digital)).

2-Oxo-2*H*-pyran-3-carboxylates 5; General Procedure (GP 1)

$PdCl_2(PPh_3)_2$ (3.50 mg, 5.00 µmol, 0.25 mol%) and CuI (1.90 mg, 10.0 µmol, 0.50 mol%) were placed in a dry Schlenk tube under a nitrogen atmosphere and anhydrous 1,4-dioxane (2.00 mL) was added. An acid chloride **1** (2.20 mmol), a terminal alkyne **2** (2.00 mmol) and NEt_3 (212 mg, 2.10 mmol) were added and the mixture was stirred at 20 °C for 3 h until complete conversion (monitored by TLC). Afterwards, Na_2CO_3·10 H_2O (1.72 g, 6.00 mmol) and diethyl malonate (**4a**) (640 mg, 4.00 mmol) were added and stirring at 75 °C was continued for 16 h. After the addition of brine (2.00 mL), the solution was extracted with CH_2Cl_2 (3 × 50.0 mL). The combined organic layers were dried (anhydrous $MgSO_4$) and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (*n*-hexane–EtOAc, 20:1 → 10:1).

Ethyl 2-Oxo-4,6-diphenyl-2*H*-pyran-3-carboxylate (5a)

According to GP1 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and phenylacetylene (**2a**) (209 mg, 2.00 mmol), **5a** (519 mg, 1.62 mmol, 78%) was obtained as a colorless solid; mp 112 °C.

IR (ATR): 3061 (w), 3005 (w), 2984 (w), 2938 (w), 1728 (m), 1715 (w), 1674 (m), 1622 (m), 1578 (w), 1530 (s), 1495 (m), 1466 (w), 1451 (m), 1439 (w), 1379 (m), 1258 (m), 1188 (w), 1121 (s), 1092 (m), 1080 (m), 1053 (w), 1024 (s), 995 (w), 949 (w), 939 (w), 845 (w), 835 (w), 762 (s), 750 (m), 710 (s), 689 (s), 667 (w), 637 (m) cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.1 Hz, 3 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 6.78 (s, 1 H), 7.40–7.56 (m, 8 H), 7.82–7.94 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.9 (CH_2), 103.6 (CH), 116.8 (C_{quat}), 126.1 (CH), 127.3 (CH), 129.0 (CH), 129.2 (CH), 130.3 (CH), 130.9 (C_{quat}), 131.7 (CH), 136.5 (C_{quat}), 155.5 (C_{quat}), 159.5 (C_{quat}), 160.7 (C_{quat}), 164.9 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 320 ([M]$^+$, 43), 292 ([M – C_2H_6]$^+$, 63), 276 ([M – CO_2]$^+$, 5), 275 ([M – C_2H_5O]$^+$, 23), 247 ([M – $C_3H_5O_2$]$^+$, 11), 220 (100), 191 ([M – $C_5H_5O_4$]$^+$, 34), 165 ([M – $C_{12}H_9$]$^+$, 7), 129 ([M – $C_{15}H_{11}$]$^+$, 3), 77 ([M – $C_{14}H_{11}O_4$]$^+$, 24).

Anal. Calcd for $C_{20}H_{16}O_4$ (320.3): C, 74.99; H, 5.03. Found: C, 75.14; H, 5.23.

Ethyl 6-(4-Methoxyphenyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5b)

According to GP1 using 4-methoxybenzoyl chloride (**1b**) (344 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5b** (199 mg, 0.570 mmol, 29%) was obtained as a yellow solid; mp 99–100 °C.

IR (ATR): 3011 (w), 2980 (w), 2940 (w), 2901 (w), 2845 (w), 1728 (s), 1688 (s), 1618 (m), 1605 (m), 1576 (w), 1530 (m), 1504 (vs), 1445 (m), 1425 (m), 1381 (w), 1369 (w), 1300 (m), 1260 (s), 1240 (m), 1182 (s), 1119 (m), 1090 (m), 1078 (m), 1057 (m), 1026 (s), 1001 (m), 949 (w), 928 (w), 856 (m), 827 (s), 814 (m), 768 (s), 748 (m), 700 (m), 652 (m) cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.1 Hz, 3 H), 3.87 (s, 3 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 6.66 (s, 1 H), 6.92–7.01 (m, 2 H), 7.41–7.50 (m, 5 H), 7.79–7.87 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 55.7 (CH_3), 61.8 (CH_2), 102.2 (CH), 114.6 (CH), 115.4 (C_{quat}), 123.4 (C_{quat}), 127.3 (CH), 128.0 (CH), 128.9 (CH), 130.1 (CH), 136.9 (C_{quat}), 156.1 (C_{quat}), 159.6 (C_{quat}), 161.0 (C_{quat}), 162.5 (C_{quat}), 165.1 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 351 ([M + H]$^+$, 23), 350 ([M]$^+$, 99), 323 (21), 322 ([M – CO]$^+$, 100), 305 ([M – C_2H_5O]$^+$, 26), 294 ([M – C_3H_4O]$^+$, 18), 277 ([M – $C_3H_5O_2$]$^+$, 11), 251 (20), 250 ([M – $C_4H_4O_3$]$^+$, 96), 221 ([M – $C_5H_5O_4$]$^+$, 30), 178 (15), 152 (15), 135 ([M – $C_{13}H_{11}O_3$]$^+$, 81), 77 ([M – $C_{15}H_{13}O_5$]$^+$, 16).

Anal. Calcd for $C_{21}H_{18}O_5$ (350.1): C, 71.99; H, 5.18. Found: C, 72.07; H, 5.27.

Ethyl 6-(4-*tert*-Butylphenyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5c)

According to GP1 using 4-*tert*-butylbenzoyl chloride (**1c**) (439 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5c** (437 mg, 1.16 mmol, 58%) was obtained as a yellow resin.

IR (ATR): 3088 (w), 3061 (w), 3030 (w), 2963 (w), 2905 (w), 2870 (w), 1709 (vs), 1622 (m), 1578 (w), 1530 (s), 1512 (s), 1464 (w), 1445 (w), 1414 (w), 1377 (m), 1346 (w), 1260 (s), 1200 (w), 1186 (m), 1117 (s), 1078 (w), 1047 (m), 1022 (m), 1015 (m), 945 (w), 827 (m), 787 (w), 768 (s), 743 (m), 698 (s), 640 (m), 613 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.1 Hz, 3 H), 1.35 (s, 9 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 6.74 (s, 1 H), 7.43–7.52 (m, 7 H), 7.78–7.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 31.2 (CH_3), 35.2 (C_{quat}), 61.9 (CH_2), 103.1 (CH), 116.3 (C_{quat}), 126.0 (CH), 126.2 (CH), 127.4 (CH), 128.1 (C_{quat}), 129.0 (CH), 130.2 (CH), 136.7 (C_{quat}), 155.5 (C_{quat}), 155.8 (C_{quat}), 159.6 (C_{quat}), 161.1 (C_{quat}), 165.0 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 377 ([M + H]$^+$, 11), 376 ([M]$^+$, 43), 349 (15), 348 ([M – CO]$^+$, 57), 334 (25), 333 ([M – C_2H_3O]$^+$, 100), 331 ([M – C_2H_5O]$^+$, 14), 291 (16), 276 ([M – $C_4H_6O_3$]$^+$, 10), 161 ([M – $C_{13}H_{11}O_3$]$^+$, 28), 144 (10), 77 ([M – $C_{18}H_{19}O_4$]$^+$, 3), 57 ([M – $C_{20}H_{15}O_4$]$^+$, 7).

Anal. Calcd for $C_{24}H_{24}O_4$ (376.2): C, 76.51; H, 6.93. Found: C, 76.32; H, 6.64.

Ethyl 2-Oxo-4-phenyl-6-(*p*-tolyl)-2*H*-pyran-3-carboxylate (5d)

According to GP1 using 4-methylbenzoyl chloride (**1d**) (347 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5d** (453 mg, 1.30 mmol, 65%) was obtained as a yellow solid; mp 80–89 °C.

IR (ATR): 3055 (w), 2980 (w), 2864 (w), 2729 (w), 2359 (w), 1730 (m), 1691 (m), 1622 (m), 1580 (w), 1530 (s), 1510 (m), 1462 (w), 1443 (w), 1414 (w), 1375 (m), 1260 (m), 1244 (m), 1190 (m), 1115 (m), 1107 (m), 1018 (m), 1001 (w), 949 (w), 928 (w), 851 (w), 820 (s), 766 (s), 746 (m), 700 (s), 650 (w), 637 (m), 617 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.1 Hz, 3 H), 2.41 (s, 3 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 6.73 (s, 1 H), 7.23–7.32 (m, 2 H), 7.42–7.50 (m, 5 H), 7.74–7.81 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 21.7 (CH_3), 61.8 (CH_2), 103.0 (CH), 116.2 (C_{quat}), 126.1 (CH), 127.3 (CH), 128.1 (C_{quat}), 129.0 (CH), 129.9 (CH), 130.2 (CH), 136.7 (C_{quat}), 142.4 (C_{quat}), 155.8 (C_{quat}), 159.6 (C_{quat}), 161.0 (C_{quat}), 165.0 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 335 ([M + H]$^+$, 12), 334 ([M]$^+$, 51), 307 (16), 306 ([M – CO]$^+$, 71), 289 ([M – C_2H_5O]$^+$, 23), 278 ([M – C_3H_4O]$^+$, 13), 261 ([M – $C_3H_5O_2$]$^+$, 10), 235 (19), 234 ([M – $C_4H_4O_3$]$^+$, 100), 205 ([M – $C_5H_5O_4$]$^+$, 26), 119 ([M – $C_{13}H_{11}O_3$]$^+$, 44), 91 ([M – $C_{14}H_{11}O_4$]$^+$, 24), 77 ([M – $C_{15}H_{13}O_4$]$^+$, 4).

Anal. Calcd for $C_{21}H_{18}O_4$ (334.1): C, 75.43; H, 5.43. Found: C, 75.17; H, 5.72.

Ethyl 6-(4-Fluorophenyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5e)

According to GP1 using 4-fluorobenzoyl chloride (**1e**) (355 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5e** (509 mg, 1.50 mmol, 75%) was obtained as a yellow solid; mp 143 °C.

IR (ATR): 3152 (w), 3094 (w), 3057 (w), 2988 (w), 2967 (w), 2899 (w), 1730 (m), 1688 (s), 1624 (m), 1599 (w), 1578 (w), 1533 (m), 1506 (s), 1464 (w), 1443 (w), 1418 (m), 1379 (m), 1301 (w), 1260 (m), 1233 (m), 1163 (m), 1121 (m), 1092 (m), 1078 (m), 1053 (w), 1024 (m), 1011 (m), 999 (m), 949 (m), 930 (m), 835 (s), 814 (w), 797 (w), 785 (w), 768 (vs), 748 (m), 702 (s), 631 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.1 Hz, 3 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 6.71 (s, 1 H), 7.14–7.19 (m, 2 H), 7.43–7.49 (m, 5 H), 7.84–7.90 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.9 (CH_2), 103.4 (CH), 116.3 (CH), 116.6 (d, *J* = 2.0 Hz, C_{quat}), 127.2 (d, *J* = 3.3 Hz, C_{quat}), 127.3 (CH), 128.4 (d, *J* = 8.8 Hz, CH), 129.0 (CH), 130.3 (CH), 136.4 (C_{quat}), 155.6 (C_{quat}), 159.3 (C_{quat}), 159.5 (C_{quat}), 164.76 (d, *J* = 254 Hz, C_{quat}), 164.82 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 339 ([M + H]$^+$, 12), 338 ([M]$^+$, 49), 311 (15), 310 ([M – C_2H_4]$^+$, 72), 293 ([M – C_2H_5O]$^+$, 29), 282 ([M – C_3H_4O]$^+$, 15), 265 ([M – $C_3H_5O_2$]$^+$, 15), 239 (19), 238 ([M – $C_4H_4O_3$]$^+$, 100), 210 (11), 209 (33), 207 ([M - $C_5H_7O_4$]$^+$, 15), 123 ([M – $C_{13}H_{11}O_3$]$^+$, 59), 95 ([M – $C_{14}H_{11}O_4$]$^+$, 25), 77 ([M – $C_{14}H_{10}FO_4$]$^+$, 3).

Anal. Calcd for $C_{20}H_{15}FO_4$ (338.3): C, 71.00; H, 4.47. Found: C, 70.94; H, 4.56.

Ethyl 6-(2-Chlorophenyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5f)

According to GP1 using 2-chlorobenzoyl chloride (**1f**) (400 mg, 2.22 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5f** (568 mg, 1.60 mmol, 80%) was obtained as an orange solid; mp 94–98 °C.

IR (ATR): 3073 (w), 2984 (w), 2936 (w), 2868 (w), 2849 (w), 2355 (w), 1738 (s), 1699 (s), 1674 (w), 1632 (m), 1616 (w), 1589 (w), 1545 (m), 1493 (w), 1470 (w), 1441 (w), 1377 (m), 1348 (w), 1271 (m), 1250 (m), 1192 (m), 1180 (w), 1121 (m), 1111 (m), 1099 (w), 1072 (w), 1020 (m), 999 (w), 980 (w), 949 (w), 922 (w), 849 (w), 841 (m), 827 (w), 766 (vs), 748 (m), 700 (vs), 685 (w), 654 (w), 638 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.1 Hz, 3 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 6.89 (s, 1 H), 7.34–7.53 (m, 8 H), 7.65–7.80 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 62.1 (CH_2), 109.4 (CH), 117.7 (C_{quat}), 127.4 (CH), 127.5 (CH), 129.1 (CH), 130.5 (CH), 130.6 (C_{quat}), 130.9 (CH), 131.1 (CH), 131.9 (CH), 132.5 (C_{quat}), 136.1 (C_{quat}), 154.6 (C_{quat}), 158.3 (C_{quat}), 159.5 (C_{quat}), 164.8 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 356 ([M(^{37}Cl)]$^+$, 14), 354 ([M(^{35}Cl)]$^+$, 38), 328 ([M(^{37}Cl) – C_2H_4]$^+$, 28), 326 ([M(^{35}Cl) – C_2H_4]$^+$, 77), 311 ([M(^{37}Cl) – C_2H_5O]$^+$, 11), 309 ([M(^{35}Cl) – C_2H_5O]$^+$, 30), 300 ([M(^{37}Cl) – C_3H_4O]$^+$, 4), 298 ([M(^{35}Cl) – C_3H_4O]$^+$, 13), 283 ([M(^{37}Cl) – $C_3H_5O_2$]$^+$, 6), 281 ([M(^{35}Cl) – $C_3H_5O_2$]$^+$, 18), 256 ([M(^{37}Cl) – $C_4H_4O_3$]$^+$, 34), 254 ([M(^{35}Cl) – $C_4H_4O_3$]$^+$, 100), 227 ([M(^{37}Cl) – $C_5H_5O_4$]$^+$, 8), 225 ([M(^{35}Cl) – $C_5H_5O_4$]$^+$, 24), 191 (16), 189 (29), 141 ([M(^{37}Cl) – $C_7H_4ClO_4$]$^+$, 16), 139 ([M(^{35}Cl) – $C_7H_4ClO_4$]$^+$, 47), 111 ([M(^{35}Cl) – $C_{14}H_{11}O_4$]$^+$, 19), 77 ([M – $C_{14}H_{10}ClO_4$]$^+$, 3).

Anal. Calcd for $C_{20}H_{15}ClO_4$ (354.1): C, 67.71; H, 4.26. Found: C, 67.88; H, 4.34.

Ethyl 6-(4-Cyanophenyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5g)

According to GP1 using 4-cyanobenzoyl chloride (**1g**) (374 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol) and after washing with hot ethanol (4.00 mL), **5g** (344 mg, 1.00 mmol, 50%) was obtained as a yellow solid; mp 150–159 °C.

IR (ATR): 3103 (w), 3084 (w), 2957 (w), 2857 (w), 2226 (w), 1730 (m), 1692 (s), 1624 (m), 1607 (w), 1533 (m), 1503 (m), 1412 (m), 1373 (m), 1346 (w), 1287 (w), 1273 (w), 1248 (m), 1198 (m), 1111 (m), 1080 (m), 1063 (m), 1016 (m), 999 (w), 843 (s), 829 (m), 768 (s), 748 (m), 700 (s), 613 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, *J* = 7.1 Hz, 3 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 6.87 (s, 1 H), 7.42–7.55 (m, 5 H), 7.73–8.02 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 62.1 (CH_2), 105.0 (CH), 114.8 (C_{quat}), 118.0 (C_{quat}), 118.5 (C_{quat}), 126.5 (CH), 127.3 (CH), 129.2 (CH), 130.6 (CH), 132.9 (CH), 134.7 (C_{quat}), 135.9 (C_{quat}), 154.7 (C_{quat}), 158.0 (C_{quat}), 158.7 (C_{quat}), 164.4 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 345 ([M]$^+$, 7), 317 ([M – CO]$^+$, 14), 272 ([M – $C_3H_5O_2$]$^+$, 4), 245 ([M – $C_4H_4O_3$]$^+$, 24), 216 ([M – $C_5H_5O_4$]$^+$, 6), 130 ([M – $C_{13}H_{11}O_3$]$^+$, 14), 113 (11), 102 ([M – $C_{14}H_{11}O_4$]$^+$, 7), 77 ([M – $C_{15}H_{10}NO_4$]$^+$, 2), 71 (15), 70 (11), 57 (20), 43 (13).

Anal. Calcd for $C_{21}H_{15}NO_4$ (345.1): C, 73.04; H, 4.38; N, 4.06. Found: C, 73.05; H, 4.68; N, 3.87.

Ethyl 6-(Furan-2-yl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (5h)

According to GP1 using furan-2-carbonyl chloride (**1h**) (295 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5h** (392 mg, 1.26 mmol, 63%) was obtained as a yellow solid; mp 111–121 °C.

IR (ATR): 3146 (w), 3117 (w), 3003 (w), 2978 (w), 2963 (w), 2934 (w), 2897 (w), 2870 (w), 1724 (m), 1705 (s), 1628 (m), 1580 (w), 1562 (w), 1518 (m), 1491 (w), 1476 (m), 1464 (m), 1443 (w), 1404 (w), 1371 (m), 1346 (w), 1300 (w), 1265 (m), 1240 (m), 1231 (m), 1188 (m), 1163 (w), 1109 (s), 1080 (m), 1063 (m), 1018 (m), 1001 (m), 953 (w), 925 (w), 883 (m), 827 (m), 785 (s), 766 (s), 737 (m), 700 (s), 665 (w), 648 (w), 629 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.1 Hz, 3 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 6.58 (dd, *J* = 3.6, 1.8 Hz, 1 H), 6.69 (s, 1 H), 7.09–7.13 (m, 1 H), 7.45 (d, *J* = 2.4 Hz, 5 H), 7.54 (dd, *J* = 1.8, 0.8 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.9 (CH_2), 101.8 (CH), 112.9 (CH), 113.6 (CH), 116.1 (C_{quat}), 127.3 (CH), 129.0 (CH), 130.3 (CH), 136.4 (C_{quat}), 145.7 (CH), 146.2 (C_{quat}), 152.4 (C_{quat}), 155.8 (C_{quat}), 158.7 (C_{quat}), 164.9 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 311 ([M + H]$^+$, 18), 310 ([M]$^+$, 88), 283 (19), 282 ([M – CO]$^+$, 94), 265 ([M – C_2H_5O]$^+$, 36), 254 (20), 237 ([M – $C_3H_5O_2$]$^+$, 12), 211 (15), 210 ([M – $C_4H_4O_3$]$^+$, 100), 197 ([M – $C_5H_5O_3$]$^+$, 14), 181 ([M – $C_5H_5O_4$]$^+$, 31), 153 (14), 152 (31), 95 ([M – $C_{13}H_{11}O_3$]$^+$, 54), 77 ([M – $C_{12}H_9O_5$]$^+$, 5), 67 ([M – $C_{14}H_{11}O_4$]$^+$, 2).

Anal. Calcd for $C_{18}H_{14}O_5$ (310.1): C, 69.67; H, 4.55. Found: C, 69.65; H, 4.76.

Ethyl 2-Oxo-4-phenyl-6-(thien-2-yl)-2*H*-pyran-3-carboxylate (5i)

According to GP1 using 2-thenoyl chloride (**1i**) (329 mg, 2.20 mmol) and phenylacetylene (**2a**) (206 mg, 2.00 mmol), **5i** (416 mg, 1.27 mmol, 64%) was obtained as a yellow solid; mp 90–97 °C.

IR (ATR): 3115 (w), 3090 (w), 2976 (w), 2953 (w), 1709 (s), 1614 (m), 1578 (w), 1526 (m), 1514 (m), 1506 (m), 1489 (m), 1441 (m), 1425 (m), 1377 (m), 1335 (w), 1298 (w), 1256 (m), 1238 (m), 1182 (m), 1107 (s), 1076 (m), 1061 (w), 1032 (m), 1013 (m), 922 (w), 860 (m), 849 (m), 818 (m), 804 (w), 768 (m), 735 (vs), 698 (s), 681 (w), 660 (w), 648 (m), 613 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.1 Hz, 3 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 6.59 (s, 1 H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1 H), 7.40–7.49 (m, 5 H), 7.52 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.69 (dd, *J* = 3.8, 1.2 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (CH_3), 61.9 (CH_2), 102.6 (CH), 115.9 (C_{quat}), 127.3 (CH), 128.75 (CH), 128.77 (CH), 129.0 (CH), 130.3 (CH), 134.6 (C_{quat}), 136.5 (C_{quat}), 155.9 (C_{quat}), 156.4 (C_{quat}), 158.8 (C_{quat}), 164.8 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 327 ([M + H]$^+$, 17), 326 ([M]$^+$, 80), 299 (18), 298 ([M – CO]$^+$, 87), 281 ([M – C_2H_5O]$^+$, 32), 270 ([M – C_3H_5O]$^+$, 17), 253 ([M – $C_3H_5O_2$]$^+$, 10), 241 ([M – $C_4H_5O_2$]$^+$, 10), 227 (17), 226 ([M – $C_4H_4O_3$]$^+$, 100), 198 (11), 197 ([M – $C_5H_5O_4$]$^+$, 40), 111 ([M – $C_{13}H_{11}O_3$]$^+$, 63), 83 ([M – $C_{14}H_{11}O_4$]$^+$, 6), 77 ([M – $C_{12}H_9O_4S$]$^+$, 3).

Anal. Calcd for $C_{18}H_{14}O_4S$ (326.1): C, 76.57; H, 6.93. Found: C, 76.32; H, 6.64.

Ethyl 4-(4-Methoxyphenyl)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (5j)

According to GP1 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and 1-ethynyl-4-methoxybenzene (**2b**) (264 mg, 2.00 mmol), **5j** (455 mg, 1.30 mmol, 65%) was obtained as a yellow solid; mp 101–108 °C.

IR (ATR): 2980 (w), 2972 (w), 2930 (w), 2901 (w), 2841 (w), 1749 (w), 1705 (vs), 1622 (m), 1605 (m), 1576 (w), 1533 (s), 1510 (m), 1493 (m), 1441 (m), 1393 (m), 1381 (m), 1350 (w), 1296 (m), 1258 (s), 1246 (m), 1196 (m), 1179 (m), 1123 (m), 1113 (s), 1092 (m), 1074 (m), 1038 (s), 1018 (m), 964 (w), 943 (w), 824 (m), 797 (m), 768 (s), 748 (w), 689 (s), 677 (w), 648 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, *J* = 7.1 Hz, 3 H), 3.86 (s, 3 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 6.77 (s, 1 H), 6.93–7.01 (m, 2 H), 7.40–7.52 (m, 5 H), 7.83–7.92 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 55.6 (CH_3), 61.9 (CH_2), 103.6 (CH), 114.5 (CH), 116.0 (C_{quat}), 126.1 (CH), 128.5 (C_{quat}), 129.2 (CH), 131.0 (CH), 131.5 (C_{quat}), 154.8 (C_{quat}), 159.7 (C_{quat}), 160.4 (C_{quat}), 161.5 (C_{quat}), 165.4 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 350 ([M]$^+$, 38), 323 (20), 322 ([M – C_2H_4]$^+$, 85), 305 ([M – C_2H_5O]$^+$, 22), 294 ([M – C_3H_4O]$^+$, 14), 277 ([M – $C_3H_5O_2$]$^+$, 13), 251 (19), 250 ([M – $C_4H_4O_3$]$^+$, 100), 221 ([M – $C_5H_5O_4$]$^+$, 20), 178 (11), 135 (10), 105 ([M – $C_{14}H_{13}O_4$]$^+$, 43), 77 ([M – $C_{15}H_{13}O_5$]$^+$, 25).

Anal. Calcd for $C_{21}H_{18}O_5$ (350.1): C, 71.99; H, 5.18. Found: C, 71.96; H, 5.25.

Ethyl 2-Oxo-6-phenyl-4-(*p*-tolyl)-2*H*-pyran-3-carboxylate (5k)

According to GP1 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and 1-ethynyl-4-methylbenzene (**2c**) (260 mg, 2.00 mmol), **5k** (359 mg, 1.07 mmol, 54%) was obtained as a yellow solid; mp 116–120 °C.

IR (ATR): 3030 (w), 3003 (w), 2982 (w), 2953 (w), 2934 (w), 2926 (w), 2864 (w), 1730 (s), 1690 (s), 1618 (m), 1609 (m), 1568 (w), 1526 (m), 1512 (m), 1495 (m), 1470 (w), 1449 (m), 1441 (w), 1375 (m), 1348 (m), 1294 (w), 1252 (m), 1215 (w), 1186 (m), 1113 (m), 1099 (m), 1051 (w), 1016 (m), 1001 (m), 982 (w), 945 (w), 922 (w), 837 (w), 818 (m), 785 (m), 766 (vs), 746 (m), 687 (s), 673 (w), 646 (m), 602 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.1 Hz, 3 H), 2.42 (s, 3 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 6.77 (s, 1 H), 7.24–7.30 (m, 2 H), 7.34–7.40 (m, 2 H), 7.42–7.54 (m, 3 H), 7.82–7.92 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 21.5 (CH_3), 61.9 (CH_2), 103.7 (CH), 116.5 (C_{quat}), 126.1 (CH), 127.4 (CH), 129.2 (CH), 129.7 (CH), 131.0 (CH), 131.6 (C_{quat}), 133.6 (C_{quat}), 140.8 (C_{quat}), 155.4 (C_{quat}), 159.6 (C_{quat}), 160.5 (C_{quat}), 165.2 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 335 ([M + H]$^+$, 10), 334 ([M]$^+$, 43), 307 (16), 306 ([M – CO]$^+$, 72), 289 ([M – C_2H_5O]$^+$, 25), 278 ([M – C_3H_4O]$^+$, 12), 261 ([M – $C_3H_5O_2$]$^+$, 10), 235 (20), 234 ([M – $C_4H_4O_3$]$^+$, 100), 205 ([M – $C_5H_5O_4$]$^+$, 21), 105 ([M – $C_{14}H_{13}O_3$]$^+$, 33), 91 ([M – $C_{14}H_{11}O_4$]$^+$, 2), 77 ([M – $C_{15}H_{13}O_4$]$^+$, 22).

Anal. Calcd for $C_{21}H_{18}O_4$ (334.1): C, 75.43; H, 5.43. Found: C, 75.18; H, 5.58.

Ethyl 4-(4-Chlorophenyl)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (5l)

According to GP1 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and 1-chloro-4-ethynylbenzene (**2d**) (273 mg, 2.00 mmol), **5l** (302 mg, 0.850 mmol, 43%) was obtained as a yellow solid; mp 95–100 °C.

IR (ATR): 2978 (m), 2936 (w), 2901 (m), 2824 (w), 2336 (w), 2313 (w), 1732 (s), 1717 (m), 1694 (m), 1616 (m), 1593 (w), 1568 (w), 1558 (w), 1522 (m), 1491 (m), 1443 (m), 1402 (m), 1393 (w), 1379 (m), 1350 (w), 1325 (w), 1294 (w), 1256 (m), 1186 (m), 1125 (m), 1107 (m), 1090 (vs), 1078 (m), 1049 (m), 1015 (s), 1001 (m), 951 (w), 860 (w), 829 (m), 768 (s), 746 (w), 710 (w), 691 (s), 644 (w), 629 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 3 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 6.72 (s, 1 H), 7.38–7.53 (m, 7 H), 7.83–7.91 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 62.1 (CH_2), 103.2 (CH), 116.9 (C_{quat}), 126.2 (CH), 128.8 (CH), 129.3 (CH), 129.3 (CH), 130.7 (C_{quat}), 131.8 (CH), 134.9 (C_{quat}), 136.6 (C_{quat}), 154.2 (C_{quat}), 159.2 (C_{quat}), 161.0 (C_{quat}), 164.7 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 356 ([M(^{37}Cl)]$^+$, 15), 354 ([M(^{35}Cl)]$^+$, 41), 328 ([M(^{37}Cl) – C_2H_4]$^+$, 25), 326 ([M(^{35}Cl) – C_2H_4]$^+$, 71), 311 ([M(^{37}Cl) – C_2H_4O]$^+$, 10), 309 ([M(^{35}Cl) – C_2H_5O]$^+$, 25), 300 ([M(^{37}Cl) – C_3H_4O]$^+$, 5), 298 ([M(^{35}Cl) – C_3H_5O]$^+$, 16), 283 ([M(^{37}Cl) – $C_3H_5O_2$]$^+$, 7), 281 ([M(^{35}Cl) – $C_3H_5O_2$]$^+$, 13), 256 ([M(^{37}Cl) – $C_4H_4O_3$]$^+$, 33), 254 ([M(^{35}Cl) – $C_4H_4O_3$]$^+$, 100), 227 ([M(^{37}Cl) – $C_5H_5O_4$]$^+$, 7), 225 ([M(^{35}Cl) – $C_5H_5O_4$]$^+$, 21), 191 (12), 189 (24), 105 ([M – $C_{13}H_{10}O_3Cl$]$^+$, 59), 77 ([M – $C_{14}H_{10}ClO_4$]$^+$, 33).

Anal. Calcd for $C_{20}H_{15}ClO_4$ (354.1): C, 67.71; H, 4.26. Found: C, 67.45; H, 4.47.

Ethyl 4-(4-Cyanophenyl)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (5m)

According to GP1 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and 1-cyano-4-ethynylbenzene (**2e**) (260 mg, 2.00 mmol) and after washing with hot ethanol (6.00 mL), **5m** (250 mg, 0.730 mmol, 37%) was obtained as a yellow solid; mp 100–119 °C.

IR (ATR): 2986 (w), 2972 (w), 2943 (w), 2922 (w), 2901 (w), 2230 (w), 1740 (vs), 1705 (s), 1626 (m), 1607 (w), 1558 (w), 1533 (m), 1506 (w), 1495 (w), 1449 (w), 1381 (w), 1350 (w), 1263 (m), 1242 (m), 1179 (w), 1125 (m), 1113 (m), 1078 (m), 1051 (m), 1016 (s), 1001 (m), 949 (w), 868 (w), 854 (m), 833 (m), 806 (w), 783 (m), 772 (s), 760 (m), 731 (w), 692 (s), 652 cm^{-1} (w).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.1 Hz, 3 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 6.70 (s, 1 H), 7.40–7.73 (m, 5 H), 7.73–7.80 (m, 2 H), 7.83–7.90 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 62.2 (CH_2), 102.7 (CH), 114.0 (C_{quat}), 117.2 (C_{quat}), 118.0 (C_{quat}), 126.2 (CH), 128.2 (CH), 129.3 (CH), 130.5 (C_{quat}), 132.1 (CH), 132.7 (CH), 141.0 (C_{quat}), 153.8 (C_{quat}), 158.7 (C_{quat}), 161.7 (C_{quat}), 164.1 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 346 ([M + H]$^+$, 11), 345 ([M]$^+$, 47), 317 ([M – CO]$^+$, 83), 300 ([M – C_2H_5O]$^+$, 26), 289 ([M – C_3H_4O]$^+$, 24), 272 ([M – $C_3H_5O_2$]$^+$, 15), 261 (17), 260 (38), 245 ([M – $C_4H_4O_3$]$^+$, 100), 217 (13), 216 ([M – $C_5H_5O_4$]$^+$, 31), 214 (12), 105 ([M – $C_{14}H_{10}NO_3$]$^+$, 78), 77 ([M – $C_{15}H_{10}NO_4$]$^+$, 38).

Anal. Calcd for $C_{21}H_{15}NO_4$ (345.1): C, 73.04; H, 4.38; N, 4.06. Found: C, 73.18; H, 4.51; N, 4.21.

Methyl 2-Oxo-4,6-diphenyl-2*H*-pyran-3-carboxylate (5n)

In a deviation from GP1, using benzoyl chloride (**1a**) (312 mg, 2.20 mmol), phenylacetylene (**2a**) (209 mg, 2.00 mmol) and dimethyl malonate (**4b**) (528 mg, 4.00 mmol), **5n** (316 mg, 1.03 mmol, 52%) was obtained as a colorless solid; mp 124–126 °C.

IR (ATR): 3098 (w), 3065 (w), 2997 (w), 2990 (w), 2949 (w), 2901 (w), 2887 (w), 1732 (s), 1694 (s), 1674 (m), 1624 (m), 1578 (m), 1530 (s), 1495 (m), 1443 (m), 1431 (m), 1381 (m), 1352 (m), 1323 (w), 1290 (w), 1263 (m), 1246 (m), 1196 (m), 1161 (w), 1123 (m), 1101 (w), 1078 (m), 1055 (m), 1020 (s), 1001 (m), 962 (w), 920 (m), 837 (m), 804 (m), 762 (s), 748 (m), 704 (s), 687 (s), 667 (m), 635 (m), 613 cm^{-1} (m).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.69 (d, *J* = 1.3 Hz, 3 H), 6.79 (s, 1 H), 7.43–7.53 (m, 8 H), 7.85–7.91 (m, 2 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 52.7 (CH_3), 103.6 (CH), 116.4 (C_{quat}), 126.2 (CH), 127.3 (CH), 129.1 (CH), 129.2 (CH), 130.4 (CH), 130.8 (C_{quat}), 131.7 (CH), 136.4 (C_{quat}), 155.7 (C_{quat}), 159.4 (C_{quat}), 160.8 (C_{quat}), 165.5 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 307 ([M + H]$^+$, 9), 306 ([M]$^+$, 41), 279 (21), 278 ([M – CO]$^+$, 100), 275 ([M – CH_3O]$^+$, 18), 247 ([M – $C_2H_3O_2$]$^+$, 35), 220 (47), 191 ([M – $C_4H_3O_4$]$^+$, 28), 189 (14), 105 ([M – $C_{12}H_9O_3$]$^+$, 37), 77 ([M – $C_{13}H_9O_4$]$^+$, 26).

Anal. Calcd for $C_{19}H_{14}O_4$ (306.1): C, 74.50; H, 4.61. Found: C, 74.41; H, 4.71.

2-Oxo-1,2-dihydropyridine-3-carboxylates 6 and Pyridin-2(1*H*)-ones 7; General Procedure (GP 2)

$PdCl_2(PPh_3)_2$ (3.50 mg, 5.00 µmol, 0.25 mol%) and CuI (1.90 mg, 10.0 µmol, 0.50 mol%) were placed in a dry Schlenk tube under a nitrogen atmosphere and anhydrous 1,4-dioxane (2.00 mL) was added. An acid chloride **1** (2.20 mmol), a terminal alkyne **2** (2.00 mmol) and NEt_3 (212 mg, 2.10 mmol) were added and the mixture was stirred at 20 °C for 3 h until complete conversion (monitored by TLC). Subsequently, $Na_2CO_3{\cdot}10\ H_2O$ (1.72 g, 6.00 mmol) and diethyl malonate (**4a**) (640 mg, 4.00 mmol) were added and stirring at 75 °C was continued for 16 h. Aqueous ammonia (25 wt %, 2.40 mL, 128 mmol) was added and the mixture was stirred at 90 °C for 4 h. After the addition of brine (2.00 mL), the solution was extracted with CH_2Cl_2 (3 × 50.0 mL). The combined organic layers were dried (anhydrous $MgSO_4$) and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel (*n*-hexane–acetone, 3:1).

Ethyl 2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carboxylate (6a)

According to GP2 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and phenylacetylene (**2a**) (209 mg, 2.00 mmol), **6a** (103 mg, 0.320 mmol, 16%) was obtained as a colorless solid; mp 200 °C.

IR (ATR): 3130 (w), 3057 (w), 3032 (w), 2914 (w), 2895 (w), 2849 (w), 2795 (w), 2702 (w), 2687 (w), 1721 (m), 1614 (s), 1597 (m), 1574 (m), 1559 (s), 1541 (w), 1501 (w), 1474 (w), 1441 (w), 1292 (w), 1252 (m), 1227 (w), 1138 (w), 1111 (m), 1061 (m), 1001 (w), 918 (w), 858 (w), 850 (w), 779 (w), 760 (s), 692 (s), 667 (m), 652 (w), 637 (w), 608 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.1 Hz, 3 H), 4.15 (q, *J* = 7.1 Hz, 2 H), 6.63 (s, 1 H), 7.43 (m, 3 H), 7.48 (s, 5 H), 7.83–7.86 (m, 2 H), 12.77 (br s, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.9 (CH_3), 61.4 (CH_2), 107.2 (CH), 127.2 (CH), 127.7 (CH), 128.7 (CH), 129.2 (CH), 129.3 (CH), 130.7 (CH), 133.1 (C_{quat}), 138.4 (C_{quat}), 148.2 (C_{quat}), 153.5 (C_{quat}), 162.71 (C_{quat}), 162.74 (C_{quat}), 166.6 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 320 ([M + H]$^+$, 23), 319 ([M]$^+$, 100), 275 (15), 274 ([M – C_2H_5O]$^+$, 65), 273 (10), 248 (11), 247 (61), 246 ([M – $C_3H_5O_2$]$^+$, 26), 245 (89), 224 (19), 219 (12), 218 (10), 217 ([M – C_8H_6]$^+$, 42), 216 (19), 202 (16), 189 ([M – $C_5H_8NO_3$]$^+$, 12), 105 (17), 77 ([M – $C_{14}H_{12}NO_3$]$^+$, 15).

Anal. Calcd for $C_{20}H_{17}NO_3$ (319.1): C, 75.22; H, 5.37; N, 4.39. Found: C, 75.18; H, 5.39; N, 4.37.

4,6-Diphenylpyridin-2(1*H*)-one (7a)

According to GP2 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and phenylacetylene (**2a**) (209 mg, 2.00 mmol), **7a** (280 mg, 1.13 mmol, 57%) was obtained as a colorless solid; mp 206 °C.

IR (ATR): 3138 (w), 3075 (w), 2920 (w), 2849 (w), 2826 (w), 2758 (w), 2727 (w), 2671 (w), 1645 (s), 1634 (s), 1609 (s), 1597 (s), 1574 (s), 1531 (w), 1504 (s), 1470 (w), 1452 (m), 1431 (w), 1402 (w), 1281 (w), 1231 (w), 1155 (w), 991 (m), 924 (w), 876 (w), 858 (m), 843 (m), 820 (w), 752 (s), 719 (m), 677 (s), 665 (m), 652 (m), 621 cm^{-1} (w).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.75–6.80 (m, 2 H), 7.43–7.51 (m, 4 H), 7.51–7.56 (m, 2 H), 7.63–7.67 (m, 2 H), 7.80–7.84 (m, 2 H), 12.62 (s, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 105.1 (CH), 115.3 (CH), 127.0 (CH), 127.1 (CH), 129.1 (CH), 129.3 (CH), 129.6 (CH), 130.3 (CH), 133.8 (C_{quat}), 138.3 (C_{quat}), 147.0 (C_{quat}), 153.9 (C_{quat}), 165.7 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 247 ([M]$^+$, 100), 219 ([M – CO]$^+$, 13), 199 (25), 183 (16), 152 (30), 121 (22), 105 (31), 77 ([M – $C_{11}H_8NO$]$^+$, 29).

Anal. Calcd for $C_{17}H_{13}NO$ (247.1): C, 82.57; H, 5.30; N, 5.66. Found: C, 82.34; H, 5.30; N, 5.51.

6-(4-Methoxyphenyl)-4-phenylpyridin-2(1*H*)-one (7b)

According to GP2 using 4-methoxybenzoyl chloride (**1b**) (344 mg, 2.20 mmol) and phenylacetylene (**2a**) (209 mg, 2.00 mmol), **7b** (104 mg, 0.370 mmol, 19%) was obtained as a colorless solid; mp 250–253 °C.

IR (ATR): 3078 (w), 2999 (w), 2938 (w), 2911 (w), 2899 (w), 2837 (w), 2710 (w), 1632 (s), 1605 (s), 1570 (m), 1530 (m), 1508 (s), 1499 (m), 1456 (m), 1439 (m), 1422 (m), 1402 (w), 1358 (w), 1293 (w), 1250 (s), 1119 (w), 1107 (w), 1078 (w), 1059 (w), 1030 (m), 1018 (w), 989 (m), 978 (m), 943 (m), 910 (m), 853 (m), 820 (s), 797 (m), 770 (s), 704 (m), 644 (m), 615 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.82 (s, 3 H), 6.57 (s, 1 H), 6.90 (s, 1 H), 6.99–7.09 (m, 2 H), 7.44–7.56 (m, 3 H), 7.77–7.82 (m, 2 H), 7.83–7.90 (m, 2 H), 11.65 (s, 1 H).

^{13}C NMR (151 MHz, DMSO-d_6): δ = 55.0 (CH_3), 103.4 (CH), 111.1 (CH), 113.9 (CH), 126.4 (CH), 126.9 (C_{quat}), 127.9 (CH), 128.5 (CH), 128.8 (CH), 137.5 (C_{quat}), 148.2 (C_{quat}), 151.5 (C_{quat}), 160.2 (C_{quat}), 163.2 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 278 ([M + H]$^+$, 20), 277 ([M]$^+$, 100), 276 ([M – H]$^+$, 20), 249 ([M – CO]$^+$, 17), 235 ([M – CNO]$^+$, 7), 234 ([M – CHNO]$^+$, 39), 206 (8), 204 ([M – $C_2H_3NO_2$]$^+$, 9), 178 (8).

Anal. Calcd for $C_{18}H_{15}NO_2$ (277.1): C, 77.96; H, 5.45; N, 5.05. Found: C, 77.73; H, 5.43; N, 4.92.

4-Phenyl-6-(4-(trifluoromethyl)phenyl)pyridin-2(1*H*)-one (7c)

According to GP2 using 4-(trifluoromethyl)benzoyl chloride (**1j**) (468 mg, 2.20 mmol) and phenylacetylene (**2a**) (209 mg, 2.00 mmol), **7c** (191 mg, 0.610 mmol, 30%) was obtained as a colorless solid; mp 260–262 °C.

IR (ATR): 3125 (w), 3082 (w), 3022 (w), 2886 (w), 2847 (w), 2802 (w), 2749 (w), 2708 (w), 2648 (w), 2525 (w), 1819 (w), 1630 (s), 1601 (s), 1574 (m), 1530 (m), 1516 (w), 1462 (m), 1422 (w), 1395 (w), 1321 (m), 1314 (m), 1287 (w), 1265 (w), 1240 (w), 1190 (w), 1159 (m), 1124 (s), 1113 (s), 1067 (s), 1057 (m), 1018 (m), 991 (m), 976 (m), 945 (w), 918 (m), 868 (m), 824 (s), 764 (s), 733 (w), 694 (s), 681 (m), 669 (w), 623 (m), 606 cm^{-1} (m).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.75–6.82 (m, 1 H), 7.30 (s, 1 H), 7.46–7.56 (m, 3 H), 7.81–7.89 (m, 4 H), 8.19 (d, *J* = 8.0 Hz, 2 H), 11.63 (s, 1 H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 106.4 (CH), 116.0 (CH), 123.9 (dq, *J* = 272.9 Hz, C_{quat}), 126.4 (q, *J* = 3.8 Hz, CH), 127.1 (CH), 127.4 (CH), 129.3 (CH), 130.0 (CH), 130.8 (dq, *J* = 392.4 Hz, C_{quat}), 137.1 (C_{quat}), 137.7 (C_{quat}), 145.5 (C_{quat}), 154.3 (C_{quat}), 165.4 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 315 ([M]$^+$, 100), 314 ([M – H]$^+$, 39), 287 ([M – CO]$^+$, 60), 217 (10), 115 ([M – $C_9H_5F_3NO$]$^+$, 16).

Anal. Calcd for $C_{18}H_{12}F_3NO$ (315.1): C, 65.12; H, 4.16; N, 3.62. Found: C, 65.42; H, 4.46; N, 3.39.

4-(4-Methoxyphenyl)-6-phenylpyridin-2(1*H*)-one (7d)

According to GP2 using benzoyl chloride (**1a**) (312 mg, 2.20 mmol) and 1-ethynyl-4-methoxybenzene (**2b**) (264 mg, 2.00 mmol), **7d** (131 mg, 0.470 mmol, 24%) was obtained as a colorless solid; mp 197–220 °C.

IR (ATR): 3086 (w), 2955 (w), 2909 (w), 2835 (w), 1636 (s), 1609 (m), 1578 (m), 1530 (m), 1516 (m), 1498 (m), 1464 (m), 1439 (m), 1422 (w), 1400 (w), 1362 (w), 1296 (m), 1250 (m), 1236 (m), 1171 (m), 1096 (w), 1028 (m), 991 (m), 935 (w), 914 (w), 903 (m), 853 (m), 829 (s), 812 (m), 773 (m), 760 (s), 731 (w), 683 (m), 673 (m), 650 (m), 638 (m), 617 cm^{-1} (m).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.82 (s, 3 H), 6.60 (s, 1 H), 6.96 (s, 1 H), 7.00–7.12 (m, 2 H), 7.38–7.57 (m, 3 H), 7.74–7.81 (m, 2 H), 7.84–7.91 (m, 2 H), 11.61 (s, 1 H).

^{13}C NMR (151 MHz, DMSO-d_6): δ = 55.0 (CH_3), 104.2 (CH), 110.8 (CH), 114.6 (CH), 126.5 (CH), 127.8 (CH), 128.2 (CH), 129.0 (CH), 129.4 (C_{quat}), 134.7 (C_{quat}), 148.3 (C_{quat}), 150.9 (C_{quat}), 160.1 (C_{quat}), 163.3 (C_{quat}).

EI-MS (70 eV): *m*/*z* (%) = 278 ([M + H]$^+$, 20), 277 ([M]$^+$, 100), 276 ([M – H]$^+$, 45), 249 ([M – CO]$^+$, 20), 234 ([M – CHNO]$^+$, 38), 233 ([M – CH_2NO]$^+$, 8), 206 (11), 204 ([M – $C_2H_3NO_2$]$^+$, 8), 178 (9).

Anal. Calcd for $C_{18}H_{15}NO_2$ (277.1): C, 77.96; H, 5.45; N, 5.05. Found: C, 77.66; H, 5.55; N, 4.92.

Methyl 2-Oxo-4,6-diphenyl-1,2-dihydropyridine-3-carboxylate (6b) and 4,6-Diphenylpyridin-2(1*H*)-one (7a)

In a deviation from GP2, using benzoyl chloride (**1a**) (313 mg, 2.20 mmol), phenylacetylene (**2a**) (209 mg, 2.00 mmol) and dimethyl malonate (**4b**) (539 mg, 4.00 mmol), a mixture of **6b** (18.0 mg, 60 µmol, 3%) and **7a** (156 mg, 63 µmol, 31%) was obtained as a colorless solid.

Data Below is on mixture.

IR (ATR): 3142 (w), 3053 (w), 3030 (w), 2916 (w), 2853 (w), 2359 (w), 2332 (w), 1726 (m), 1620 (s), 1608 (s), 1595 (s), 1574 (m), 1531 (m), 1497 (m), 1470 (w), 1449 (m), 1393 (w), 1265 (m), 1254 (m), 1229 (m), 1188 (w), 1140 (w), 1115 (m), 1065 (m), 995 (m), 926 (w), 855 (w), 833 (w), 806 (w), 791 (w), 758 (s), 704 (m), 689 (s), 667 (m), 635 cm^{-1} (w).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.59 (s, 3 H), 6.65 (s, 1 H), 6.71 (s, 1 H), 7.00 (s, 1 H), 7.47–7.53 (m, 14 H), 7.79–7.91 (m, 6 H), 12.05 (s, 2 H).

EI-MS (70 eV): *m*/*z* (%) = 305 ([M (**6b**)]$^+$, 100), 274 ([M – OCH_3]$^+$, 76), 247 ([M – $C_2H_3O_2$]$^+$, 26), 246 ([M (**7a**)]$^+$, 246 ([M – $C_2H_3O_2$]$^+$, 16), 245 ([M – $C_2H_4O_2$]$^+$, 69), 217 ([M – $C_3H_4O_3$]$^+$, 37), 216 ([M – $C_3H_5O_3$]$^+$, 18), 202 ([M – $C_3H_5NO_3$]$^+$, 15), 94 (13).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}NO_3$ (**6b**): 306.1130; found: 306.1128; *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{14}NO$ (**7a**): 248.1075; found: 248.1072.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610129.

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