Synthesis H. Yassine et al. Paper

Synthesis of New Dialkyl 2,2′-[Carbonyl*bis*(azanediyl)]dibenzoates via Curtius Rearrangement

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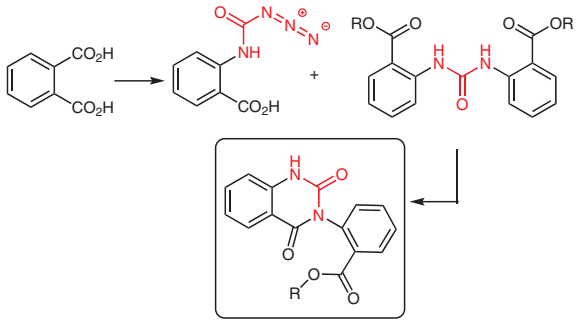


Received: 27.08.2020
Accepted after revision: 19.11.2020
Published online: 11.01.2021
DOI: 10.1055/s-0040-1706643; Art ID: ss-2020-z0458-op

Abstract The 2-(alkylcarbonyl)benzoic acids obtained by esterification of phthalic anhydride are converted into azide derivatives: alkyl 2-[(azidocarbonyl)amino]benzoates and to ureas: dialkyl 2,2′-[carbonyl-*bis*(azanediyl)]dibenzoates. These transformations were carried out using classical Curtius rearrangement conditions in the presence of diphenylphosphoryl azide (DPPA) in a basic medium, followed by hydrolysis. Subsequently, a final condensation reaction of these urea derivatives enabled us to obtain, for the first time, the new alkyl derivatives, alkyl 2-[2,4-dioxo-1,2-dihydroquinazolin-3(4*H*)-yl]benzoates. All the new compounds obtained in satisfactory yields were characterized by ^{1}H and ^{13}C NMR, and by X-ray crystallographic analysis.

Key words phthalic anhydride, Curtius rearrangement, azide, acyl azide, urea

Acyl azides and urea derivatives are widely used as important reaction intermediates in organic synthesis, and especially in pharmaceuticals, dyes, and agrochemicals.[1,2] Urea function exists in a large number of biologically active compounds such as VEGFR inhibitors (*Sorafenib*, ABT-869, *Lenvatinib*, PD173074)[3] and PKI-587, which is a potent kinase inhibitor and an anticancer agent (Figure 1).[4] These compounds are obtained by the reaction of azide anion with acid chlorides or anhydrides.[5] Easy thermal rearrangement transforms these into isocyanates[6] that are useful for the preparation of amides, amines, carbodiimides, urea, and urethanes.[7–10]

The direct conversion of carboxylic acids into acyl azides is generally accomplished using acid activators such as thionyl chloride in dimethylformamide ($SOCl_2$/DMF) or cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) in the presence of *N*-methylmorpholine. According to the literature, triphosgene with triethylamine also converts various aryl acids and alkyl carboxylic acids into the corresponding acyl azides.[11]

In addition, diphenylphosphoryl azide (DPPA) directly converts carboxylic acid derivatives into acyl azides.[5] On the other hand, urea derivatives are generally prepared by condensation of amines with isocyanates[2] or the reaction of these amines with triphosgene.[11] Other alternative methods for the preparation of ureas, cited in the literature, involve a stepwise addition sequence of amines to carbonyldiimidazole,[12] or by an exchange process catalyzed by zirconium(IV), starting from carbonates and dialkyl carbamates.[13] Aromatic and aliphatic amines undergo oxidative carbonylation with carbon monoxide catalyzed by transition metals to afford ureas.[14,15]

In this work, we were interested in the synthesis of symmetric and non-symmetric urea derivatives from the corresponding isocyanates through Curtius rearrangement,[16] by using DPPA as an activator for the reaction.

A work carried out by Sabitha et al.[17] describes the opening of the phthalic anhydride ring, catalyzed by different Lewis acids such as $BF_3{\cdot}OEt_2$ in a polar and protic solvent such as ethanol or methanol in excellent yields. Furthermore, Yamada et al.[18] recently described the opening of

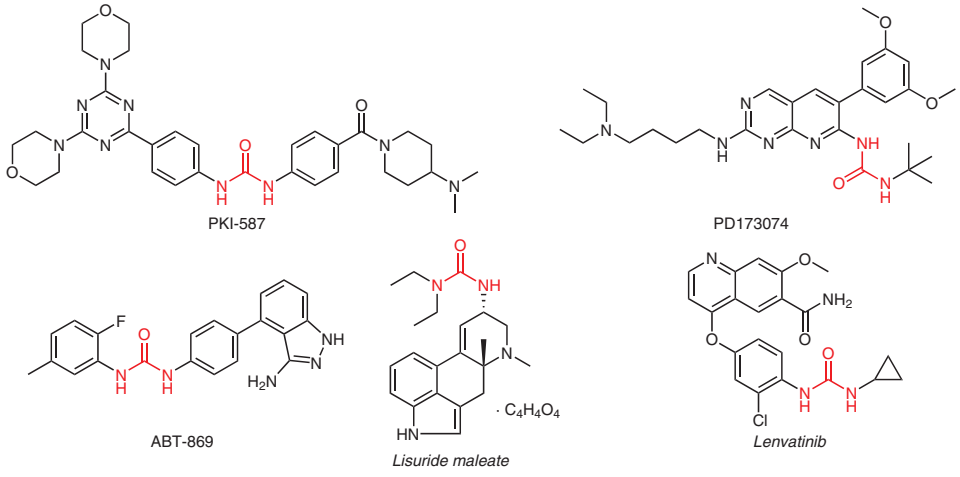


Figure 1 Examples of bioactive compounds containing urea function

anhydrides with asymmetric esterification catalyzed this time by a chiral phosphoric acid. Applying this methodology, esters were obtained with yields ranging from 8% to 95%, depending on the anhydrides used and the reaction time.

At first, we screened the esterification of the phthalic anhydride (**1**) with different alcohols giving two compounds, acid ester 2-(methoxycarbonyl)benzoic acid (**2a**) and phthalic acid (**3**) in different yields (Table 1).

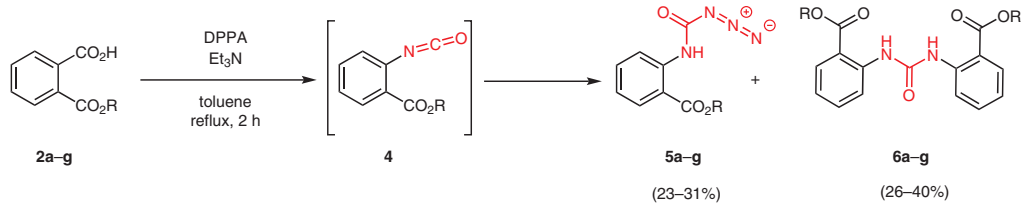
Next, the **2a–g** monoesters were then treated with DPPA as a source of azide in the presence of triethylamine in toluene, however, the expected isocyanates **4** were not isolated. Surprisingly and for our interest a mixture of two compounds **5** and **6** was formed in average yields of 31% and 40%, respectively (Scheme 1). The structures of both the products were confirmed by X-ray crystallography (vide infra). Based on these experimental results, we generalized this method to synthesize different symmetrical urea derivatives in a single step from carboxylic acids **2a–g** (Scheme 1).

The first tests of the reaction to determine the best conditions were tried on 2-(butoxycarbonyl)benzoic acid (**2e**). The reaction was carried out in toluene at reflux with 1.5 equivalents of DPPA, but under these conditions almost 64% of the starting material were recovered after purification by column chromatography (Table 2, entry 1). Increasing the equivalent number of DPPA to 2, the acid reacted completely and only urea and acyl azide were obtained in an overall yield of around 57% (entry 2).

This moderate yield can be attributed to the low stability of the intermediate isocyanate. Taking into account the previous results, it was decided to carry out the reaction at room temperature for 24 hours, using equimolar amount of DPPA with triethylamine in toluene. However, after treatment and purification, it was observed that there was no significant difference in the results (Table 2, entry 3).

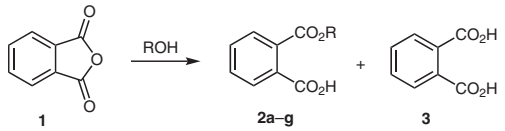
To prevent the formation of acyl azide, 2-(butoxycarbonyl)benzoic acid (**2e**) was treated with toluene in the presence of water (toluene/H_2O) by heating at reflux for 2 hours. With these modifications, practically the same yields of **5e** and **6e** were obtained (Table 2, entry 4).

However, in order to know the stability of acyl azide, and according to the protocol described above, the reaction was conducted at reflux for almost 29 hours or longer. Thus, the presence of phthalic acid (**3**) from the hydrolysis of ester **2** was observed together with urea **6** and acyl azide **5** (Table 2, entry 5).



Scheme 1 Reaction of phthalic acid monoesters

Table 1 Esterification of Phthalic Anhydride with Different Alcohols



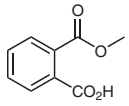
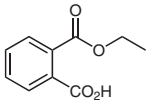
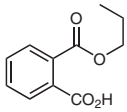
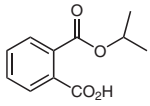
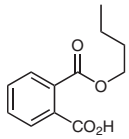
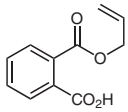
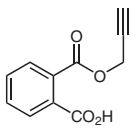
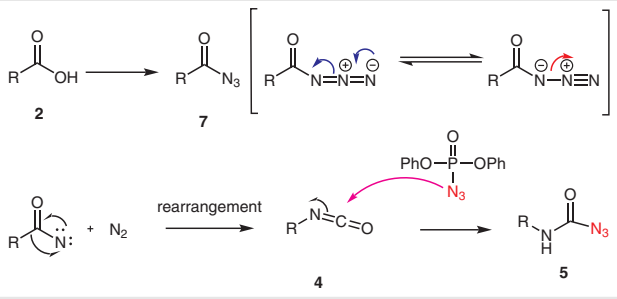
Entry	Solvent	Temp (°C)	Product 2	Yield (%) of 2 and 3	
				2	3
1	MeOH	reflux	 **2a**	57	30
2	EtOH	reflux	 **2b**	53	32
3	1-propanol	reflux	 **2c**	57	31
4	2-propanol	reflux	 **2d**	54	30
5	butanol	reflux	 **2e**	58	33
6	allylic alcohol	reflux	 **2f**	41	38
7	propargylic alcohol	reflux	 **2g**	39	40

Table 2 Optimization of Reaction from **2e**

Entry	DPPA (equiv)	Solvent	Time (h)	Temp	Yield (%)		
					5e	**6e**	**3**
1	1.5	toluene	24	reflux	14	22	–
2	2	toluene	2	reflux	31	26	–
3	2	toluene	24	rt	30	26	–
4	2	toluene/H_2O	2	reflux	30	23	–
5	2	toluene	29	reflux	30	25	10

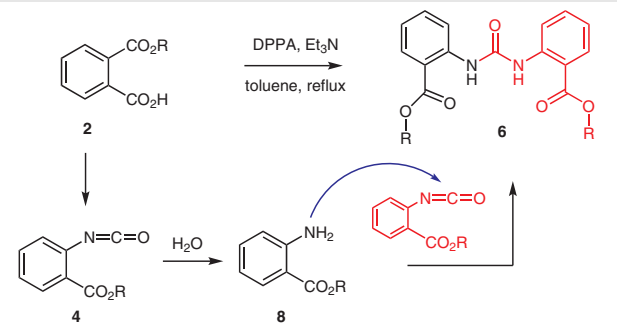
The yields were slightly improved but it was not possible to selectively obtain ureas. Subsequently, we generalized this method to synthesize symmetric urea derivatives in a single step, using simple conditions with an equimolar amount of DPPA and triethylamine at reflux (Table 3).

A plausible mechanism for the formation of compounds **5** is illustrated in Scheme 2. Acyl azide **7** is obtained from carboxylic acid **2** in the presence of DPPA, followed by Curtius rearrangement to give isocyanate **4**. The DPPA attacks the carbonyl of the isocyanate to form the alkylcarbamoyl azide **5**.



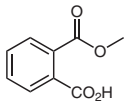
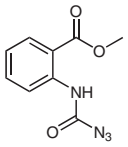
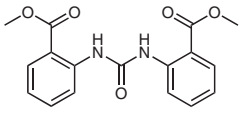
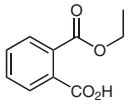
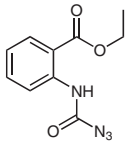
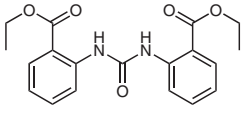
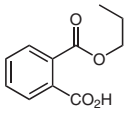
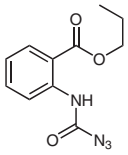
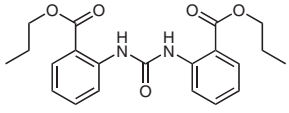
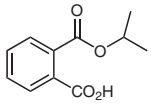
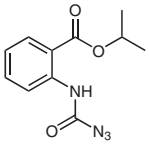
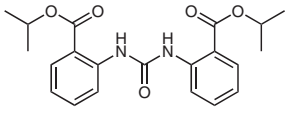
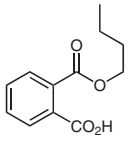
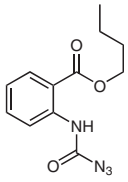
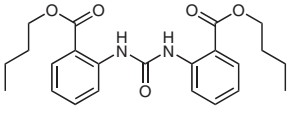
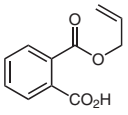
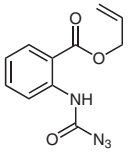
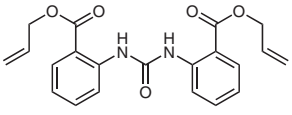
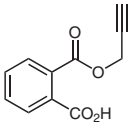
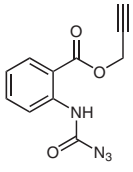
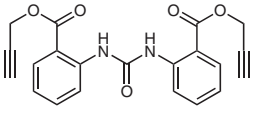
Scheme 2 Proposed mechanism to form azide derivatives **5**

The proposed mechanism for urea **6** is shown in Scheme **3**. The first step involves both the formation of isocyanate **4**, and the hydrolysis of this isocyanate with water, present in the reaction medium, to obtain the aniline **8**. Addition of the amine to the carbonyl of the isocyanate results in the formation of the urea derivative **6**.



Scheme 3 Proposed mechanism to form urea **6**

Table 3 Synthesis of Acyl Azide and Urea Derivatives via Curtius Rearrangement

Entry	Substrate	Product 5	Product 6	Yield (%) 5	Yield (%) 6
1		 **5a**	 **6a**	23	40
2		 **5b**	 **6b**	28	30
3		 **5c**	 **6c**	23	34
4		 **5d**	 **6d**	28	30
5		 **5e**	 **6e**	31	26
6		 **5f**	 **6f**	28	35
7		 **5g**	 **6g**	28	50

The synthesized products were characterized by NMR spectral data. In addition, the structures of products **5b**, **5e**, and **6a** were confirmed by X-ray crystallographic analysis of the obtained single crystals (Figure 2).[19–21]

These results underline the importance of continuing our investigation to study and develop the synthesis and re-

activity of these symmetrical ureas. In this context, based on our research work on the synthesis of nitrogenous heterocyclic compounds, we report here a convenient synthesis of novel derivatives of alkyl 2-[2,4-dioxo-1,2-dihydroquinazolin-3(4*H*)-yl]benzoates.

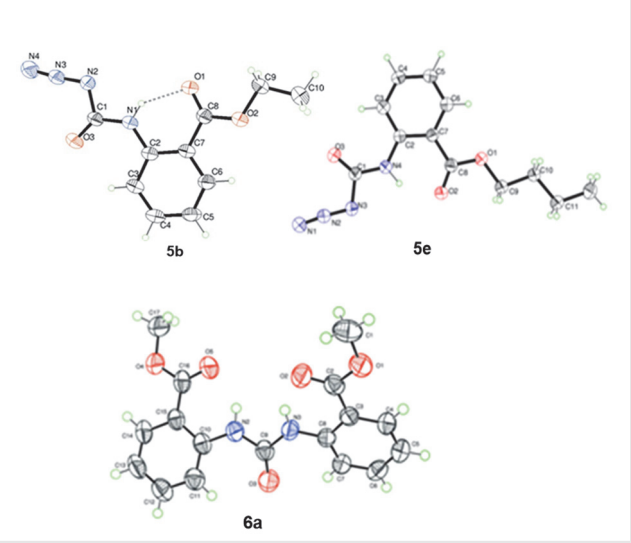
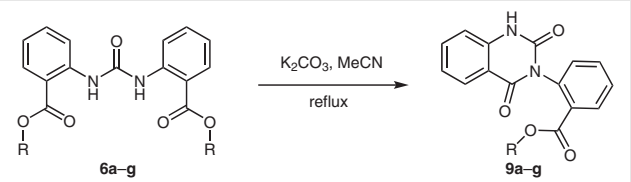


Figure 2 ORTEP plot of ethyl 2-[(azidocarbonyl)amino]benzoate (**5b**), butyl 2-[(azidocarbonyl)amino]benzoate (**5e**), and dimethyl 2,2′-[carbonyl*bis*(azanediyl)]dibenzoate (**6a**)

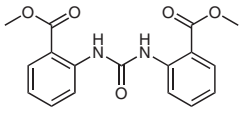
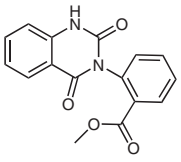
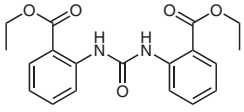
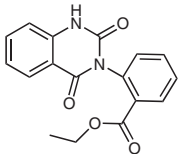
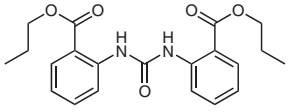
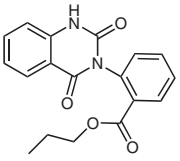
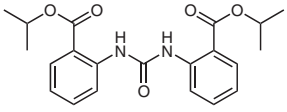
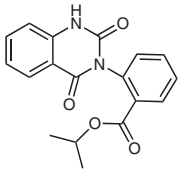
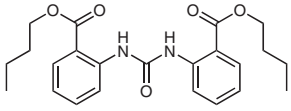
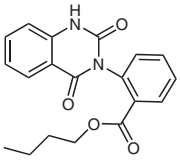
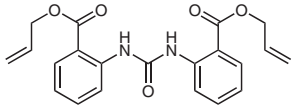
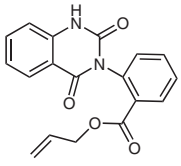
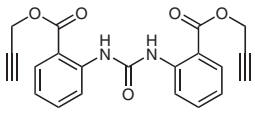
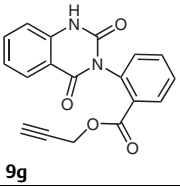
The preparation of trisubstituted indoles by cyclization of the diarylurea derivatives when refluxed in acetonitrile in the presence of potassium carbonate has been reported by Balci et al.[22] In this work, the application of these conditions to dialkyl 2,2′-[carbonylbis(azanediyl)]dibenzoates **6a–g** previously prepared, leads to the alkyl 2-(2,4-dioxo-1,2-dihydroquinazolin-3(4*H*)-yl)benzoates **9a–g** (Scheme 4). In this case, the symmetrical urea benzoates give rise to novel quinazolin-2,4-diones **9a–g** by intramolecular cyclization, forming a six-membered ring, while ureas that bind to 2-phenylacetic esters, described by Balci et al.[22] lead to indole derivatives due to having the longest substituent.



Scheme 4 Cyclization reaction of **6a–g** to **9a–g** (yields 80–96%)

The results obtained in the formation of quinazolin-2,4-diones show that although urea bound to methyl benzoate **6a** is the one with the highest yield (Table 4, entry 1), the other ureas **6b–g** (Table 4, entries 2–7) show little difference in reactivity under the conditions tested (Table 4).

Table 4 Synthesis of Alkyl 2-[2,4-Dioxo-1,2-dihydroquinazolin-3(4*H*)-yl]benzoates **9a–g**

Entry	Substrate	Product 9	Yield (%)
1		 **9a**	96
2		 **9b**	89
3		 **9c**	94
4		 **9d**	80
5		 **9e**	87
6		 **9f**	95
7		 **9g**	87

In summary, we have succeeded in synthesizing a new series of dialkyl 2,2′-[carbonyl*bis*(azanediyl)]dibenzoates **6a–g** and 2-[(azidocarbonyl)amino]benzoates **5a–g** in a single step and using only the carboxylic acid in presence of DPPA. The dialkyl 2,2′-[carbonyl*bis*(azanediyl)]dibenzoates synthesized were converted by lactamization into new alkyl2-[2,4-dioxo-1,2-dihydroquinazolin-3(4*H*)-yl]benzoates **9a–g** in good yields. The preparation of single crystal of compounds **5b**, **5e**, and **6a** allowed the confirmation of their structures by X-ray diffraction.

Melting points were obtained on an MFB-595010M Gallenkamp apparatus in open capillary tubes and are corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 (300 and 75.5 MHz) or Varian Gemini-400 (400 and 100.6 MHz) spectrometers using $CDCl_3$ or acetone-d_6 as solvent with TMS as internal standard. Other ^{1}H NMR spectra and heterocorrelation ^{1}H-^{13}C (HMQC and HMBC) experiments were recorded on a Varian VXR-500 (500 MHz) spectrometer. Mass spectra were recorded on a Helwett-Packard 5988-A spectrometer. Column chromatography was performed with silica gel (E. Merck, 70–230 mesh). Reactions were monitored by TLC using 0.25 mm silica gel F-254 (E. Merck). Microanalysis was determined on a Carlo Erba-1106 analyzer. All reagents were of commercial quality or were purified before use. Organic solvents were of analytical grade or were purified by standard procedures. Commercial products were obtained from Sigma-Aldrich. Elemental analysis was used to ascertained purity of >95% for all compounds of this work for which biological activities were determined.

Alkoxycarbonyl Benzoic Acids 2a–g; General Procedure

A solution of phthalic anhydride (**1**; 20.27 mmol) in the respective alcohol (10 mL) was stirred at reflux temperature until complete consumption of the starting material as determined by TLC analysis (1 h). Then, the solvent was evaporated under vacuo and the crude product was purified by silica gel column chromatography (EtOAc/hexane 3:7).

(Methoxycarbonyl)benzoic Acid (2a)

White solid; yield: 2 g (57%, 11.48 mmol); mp 82–84 °C (Lit.[23] mp 82–84 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.41 (s, 1 H, OH), 8.13 (d, *J* = 8.1 Hz, 1 H, ArH), 7.63 (t, *J* = 7.8 Hz, 1 H, ArH), 7.36 (t, *J* = 7.8 Hz, 1 H, ArH), 7.14 (d, *J* = 8.1 Hz, 1 H, ArH), 2.35 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 170.1, 169.8, 151.2, 134.9, 132.5, 126.2, 124.0, 122.1, 21.0.

2-(Ethoxycarbonyl)benzoic Acid (2b)

Colorless oil; yield: 2.1 g (54%, 10.82 mmol).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.53 (s, 1 H, OH), 7.77–7.52 (m, 4 H, ArH), 4.25 (q, *J* = 7.2 Hz, 2 H, CH_2), 1.24 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 168.0, 133.0, 132.5, 131.6, 131.4, 129.2, 128.6, 61.5, 14.7.

2-(Propoxycarbonyl)benzoic Acid (2c)[23]

Colorless oil; yield: 2.43 g (58%, 11.67 mmol).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.37 (s, 1 H, OH), 7.78–7.51 (m, 4 H, ArH), 4.15 (t, *J* = 6.3 Hz, 2 H, OCH_2), 1.72–1.56 (m, 2 H, CH_2), 0.89 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.6, 168.0, 133.0, 132.7, 131.5, 131.3, 129.2, 128.6, 67.1, 21.7, 10.7.

2-(Isopropoxycarbonyl)benzoic Acid (2d)[23]

White solid; yield: 1.35 g (54%, 6.48 mmol); mp 79–81 °C (Lit.[23] mp 78–80 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.18 (s, 1 H, OH), 7.75–7.55 (m, 4 H, ArH), 5.15-4.9 (m, 1 H), 1.25 [d, *J* = 6.3 Hz, 6 H, $CH(CH_3)_2$].

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 167.5, 133.2, 132.5, 131.6, 131.2, 129.1, 128.6, 69.1, 21.7.

2-(Butoxycarbonyl)benzoic Acid (2e)

White solid; yield: 2.61 g (58%, 11.75 mmol); mp 82–84 °C (Lit.[23] mp 82–84 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.56 (s, 1 H, OH), 7.77–7.51 (m, 4 H, ArH), 4.18 (t, *J* = 6.3 Hz, 2 H, OCH_2), 1.63–1.52 (m, 2 H, CH_2), 1.42–1.28 (m, 2 H, CH_2), 0.86 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 168.0, 133.0, 132.6, 131.6, 131.3, 129.2, 128.6, 65.3, 30.4, 19.1, 13.9.

2-[(Allyloxy)carbonyl]benzoic Acid (2f)

Colorless oil; yield: 1.7 g (41%, 8.27 mmol).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 12.24 (s, 1 H, OH), 7.80–7.55 (m, 4 H, ArH), 6.05–5.90 (m, 1 H, CH=), 5.39 (d, *J* = 17.2 Hz, 1 H, CH), 5.25 (d, *J* = 14.7 Hz, 1 H, CH), 4.75 (s, 2 H, CH_2).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 167.7, 133.3, 131.7, 131.5, 131.3, 129.3, 128.9, 128.7, 118.6, 66.1.

2-[(Prop-2-yn-1-yloxy)carbonyl]benzoic Acid (2g)

White solid; yield: 1.61 g (39%, 7.9 mmol); mp 167–169 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 13.30 (s, 1 H, OH), 7.85–7.55 (m, 4 H, ArH), 4.90 (d, *J* = 2.4 Hz, 2 H, CH_2), 3.62 (t, *J* = 2.4 Hz, 1 H, CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.2, 167.3, 132.4, 132.0, 131.9, 131.8, 129.4, 128.7, 78.6 (2 C), 53.4.

Alkyl 2-[(Azidocarbonyl)amino]benzoates 5a–g; General Procedure

To a solution of 2-(alkoxycarbonyl)benzoic acid **2** (0.45 mmol) in toluene (15 mL) were added DPPA (0.90 mmol) and Et_3N (0.90 mmol), and the resulting mixture was stirred at reflux for 2 h. After cooling, the solvent and Et_3N were removed under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc/hexane 1:9).

Methyl 2-[(Azidocarbonyl)amino]benzoate (5a)

Blue crystalline solid; yield: 23 mg (23%, 0.10 mmol); mp 74–76 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.81 (s, 1 H, NH), 8.48 (d, *J* = 8.4 Hz, 1 H, ArH), 8.03 (d, *J* = 8.1 Hz, 1 H, ArH), 7.56 (t, *J* = 8.4 Hz, 1 H, ArH), 7.11 (t, *J* = 8.1 Hz, 1 H, ArH), 3.92 (s, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.4, 154.4, 140.6, 134.7, 130.9, 122.8, 119.5, 115.2, 52.4.

HRMS (ESI): *m*/*z* [M + 1] calcd for $C_9H_9N_4O_3$: 221.06; found: 221.06.

Ethyl 2-[(Azidocarbonyl)amino]benzoate (5b)

Blue crystalline solid; yield: 29 mg (28%, 0.13 mmol); mp 64–66 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.89 (s, 1 H, NH), 8.51 (d, *J* = 8.5 Hz, 1 H, ArH), 8.05 (d, *J* = 8.0 Hz, 1 H, ArH), 7.58 (t, *J* = 8.5 Hz, 1 H, ArH), 7.13 (t, *J* = 8.0 Hz, 1 H, ArH), 4.40 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.43 (t, *J* = 7.1 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 154.4, 140.6, 134.6, 130.0, 122.1, 119.5, 115.5, 61.6, 14.1.

HMRS (ESI): *m*/*z* [M + 1] calcd for $C_{10}H_{11}N_4O_3$: 235.08; found: 235.08.

Propyl 2-[(Azidocarbonyl)amino]benzoate (5c)

Blue oil; yield: 26 mg (23%, 0.11 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.85 (s, 1 H, NH), 8.47 (d, *J* = 8.4 Hz, 1 H, ArH), 8.03 (d, *J* = 8.1 Hz, 1 H, ArH), 7.53 (t, *J* = 8.1 Hz, 1 H, ArH), 7.09 (t, *J* = 8.4 Hz, 1 H, ArH), 4.26 (t, *J* = 6.6 Hz, 2 H, OCH_2), 1.88–1.72 (m, 2 H, CH_2), 1.02 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 154.3, 140.6, 134.5, 130.8, 122.8, 119.5, 115.5, 67.1, 21.9, 14.1.

HRMS (ESI): *m*/*z* [M + 1] calcd for $C_{11}H_{13}N_4O_3$: 249.09; found: 249.09.

Isopropyl 2-[(Azidocarbonyl)amino]benzoate (5d)

Purple oil; yield: 26 mg (28%, 0.11 mmol).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.91 (s, 1 H, NH), 8.48 (d, *J* = 8.4 Hz, 1 H, ArH), 8.03 (d, *J* = 7.8 Hz, 1 H, ArH), 7.54 (t, *J* = 8.4 Hz, 1 H, ArH), 7.10 (t, *J* = 7.8 Hz, 1 H, ArH), 5.31–5.18 (m, 1 H), 1.40 [d, *J* = 6.3 Hz, 6 H, $CH(CH_3)_2$].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 154.3, 140.4, 134.4, 130.9, 122.7, 119.5, 115.9, 69.4, 21,8.

HRMS (ESI): *m*/*z* [M + 1] calcd for $C_{11}H_{13}N_4O_3$: 249.09; found: 249.09.

Butyl 2-[(Azidocarbonyl)amino]benzoate (5e)

Purple crystalline solid; yield: 37 mg (31%, 0.14 mmol); mp 44–46 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.86 (s, 1 H, NH), 8.48 (d, *J* = 8.3 Hz, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.55 (t, *J* = 8.3 Hz, 1 H, ArH), 7.11 (t, *J* = 8.0 Hz, 1 H, ArH), 4.30 (t, *J* = 6.5 Hz, 2 H, OCH_2), 1.82–1.68 (m, 2 H, CH_2), 1.58–1.48 (m, 2 H, CH_2), 0.98 (t, *J* = 7.3 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 154.4, 140.5, 134.5, 130.8, 122.8, 119.5, 115.5, 65.4, 30.5, 19.2, 13.7.

HRMS (ESI): *m*/*z* [M + 1] calcd for $C_{12}H_{15}N_4O_3$: 263.11; found: 263.11.

Allyl 2-[(Azidocarbonyl)amino]benzoate (5f)

Blue solid; yield: 31 mg (28%, 0.12 mmol); mp 46–48 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (s, 1 H, NH), 8.41 (d, *J* = 8 Hz, 1 H, ArH), 8.01 (d, *J* = 8 Hz, 1 H, ArH), 7.50 (t, *J* = 8 Hz, 1 H, ArH), 7.04 (t, *J* = 8 Hz, 1 H, ArH), 6.04–5.89 (m, 1 H), 5.35 (d, *J* = 16 Hz, 1 H), 5.25 (d, *J* = 14.7 Hz, 1 H, CH), 4.75 (d, *J* = 4 Hz, 2 H, CH_2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.7, 154.5, 140.8, 134.9, 131.6, 131.0, 123.0, 119.7, 119.1, 115.9, 69.4.

HRMS (ESI): *m*/*z* [M + 1] calcd for $C_{11}H_{11}N_4O_3$: 247.08; found: 247.08.

Prop-2-yn-1-yl 2-[(Azidocarbonyl)amino]benzoate (5g)

White solid; yield: 31 mg (28%, 0.13 mmol); mp 88–90 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.64 (s, 1 H, NH), 8.50 (d, *J* = 8 Hz, 1 H, ArH), 8.08 (d, *J* = 8 Hz, 1 H, ArH), 7.50 (t, *J* = 7.1 Hz, 1 H, ArH), 7.13 (d, *J* = 7.1 Hz, 1 H, ArH), 4.92 (d, *J* = 2.4 Hz, 2 H, CH_2), 2.55 (t, *J* = 2.4 Hz, 1 H, CH).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 167.3, 154.6, 141.0, 135.3, 131.3, 123.1, 119.7, 114.6, 75.7 (2 C), 53.0.

Dialkyl 2,2′-[Carbonylbis(azanediyl)]dibenzoates 6a–g; General Procedure

A mixture of 2-(alkoxycarbonyl)benzoic acid **2** (0.45 mmol), DPPA (0.90 mmol), and Et_3N (0.90 mmol) in toluene was stirred during 2 h at reflux temperature. After cooling, the solvent and Et_3N were removed under reduced pressure. The obtained residue was purified by silica gel column chromatography (EtOAc/hexane 1:9).

Dimethyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6a)

Yellow solid; yield: 59 mg (40%, 0.17 mmol); mp 138–140 °C (hexane) (Lit.[24] mp 142–144 °C).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.25 (s, 2 H, NH), 8.09 (d, *J* = 8.4 Hz, 2 H, ArH), 7.86 (d, *J* = 8.1 Hz, 2 H, ArH), 7.56 (t, *J* = 8.4 Hz, 2 H, ArH), 7.10 (t, *J* = 8.1 Hz, 2 H, ArH), 3.84 (s, 6 H, 2 × OCH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.2, 152.4, 141.0, 134.2, 130.9, 122.5, 121.2, 117.8, 52.7.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{17}N_2O_5$: 329.1137; found: 329.1133.

Diethyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6b)

Blanc solid; yield: 48 mg (30%, 0.13 mmol); mp 96–98 °C (EtOAc).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.81 (s, 2 H, NH), 8.54 (d, *J* = 8.7 Hz, 2 H, ArH), 8.04 (d, *J* = 8.1 Hz, 2 H, ArH), 7.52 (t, *J* = 8.7 Hz, 2 H, ArH), 7.01 (t, *J* = 8.1 Hz, 2 H, ArH), 4.48–4.35 (q, *J* = 6.9 Hz, 4 H, CH_2), 1.42 (t, *J* = 6.9 Hz, 6 H, 2 × CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 152.1, 142.6, 134.4, 130.8, 121.1, 119.6, 114.6, 61.3, 14.2.

HMRS (ESI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}N_2O_5$: 356.14; found: 357.14.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{21}N_2O_5$: 357.1450; found: 357.1449.

Dipropyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6c)

White solid; yield: 59 mg (34%, 0.15 mmol); mp 82–84 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.82 (s, 2 H, NH), 8.54 (d, *J* = 8.4 Hz, 2 H, ArH), 8.04 (d, *J* = 8.1 Hz, 2 H, ArH), 7.52 (t, *J* = 8.4 Hz, 2 H, ArH), 7.01 (t, *J* = 8.1 Hz, 1 H, ArH), 4.32 (t, *J* = 6.6 Hz, 4 H, OCH_2), 1.91–1.72 (m, 4 H, CH_2), 1.05 (t, *J* = 7.2 Hz, 6 H, 2 × CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 168.5, 152.1, 142.6, 134.4, 130.7, 121.1, 119.6, 114.6, 66.9, 22.0, 10.5.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{25}N_2O_5$: 385.1763; found: 385.1766.

Diisopropyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6d)

White solid; yield: 52 mg (30%, 0.14 mmol); mp 88–90 °C (hexane).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.82 (s, 2 H, NH), 8.54 (d, *J* = 8.4 Hz, 2 H, ArH), 8.04 (d, *J* = 8.1 Hz, 2 H, ArH), 7.52 (t, *J* = 8.4 Hz, 2 H, ArH), 7.01 (t, *J* = 8.1 Hz, 2 H, ArH), 5.41–5.18 (m, 2 H), 1.4 [d, *J* = 7.2 Hz, 6 H, 2 × $CH(CH_3)_2$].

^{13}C NMR (75 MHz, DMSO-d_6): δ = 167.9, 152.1, 142.6, 134.2, 130.8, 121.1, 121.1, 119.6, 115.0, 68.9, 21.9.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{25}N_2O_5$: 385.1763; found: 385.1764.

Dibutyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6e)

White solid; yield: 55 mg (30%, 0.13 mmol); mp 88–90 °C (hexane).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 10.82 (s, 2 H, NH), 8.54 (d, *J* = 8.4 Hz, 2 H, ArH), 8.04 (d, *J* = 8.1 Hz, 2 H, ArH), 7.52 (t, *J* = 8.4 Hz, 2 H, ArH), 7.01 (t, *J* = 8.1 Hz, 2 H, ArH), 4.36 (t, *J* = 6.6 Hz, 4 H, CH_2), 1.54–1.55 (m, 4 H, CH_2), 1.43–1.58 (m, 4 H, CH_2), 0.99 (t, *J* = 7.5 Hz, 6 H, CH_3).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 167.9, 152.1, 142.6, 134.2, 130.8, 121.1, 121.1, 119.6, 115.0, 68.9, 21.9.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{23}H_{29}N_2O_5$: 413.2076; found: 413.2074.

Diallyl 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6f)

Beige solid; yield: 60 mg (35%, 0.16 mmol); mp 85–87 °C (hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.75 (s, 2 H, NH), 8.55 (d, *J* = 8 Hz, 2 H, ArH), 8.07 (d, *J* =12 Hz, 2 H, ArH), 7.54 (t, *J* = 8 Hz, 1 H, ArH), 7.03 (t, *J* = 12 Hz, 2 H, ArH), 6.03–5.89 (m, 2 H), 5.43 (d, *J* = 16 Hz, 2 H), 5.32 (d, *J* = 4 Hz, 2 H, 2 × CH), 4.86 (d, *J* = 4 Hz, 4 H, 2 × CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 152.1, 142.8, 134.7, 131.9, 131.0, 121.4, 119.8, 118.8, 114.4, 65.9.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{21}N_2O_5$: 381.1450; found: 381.1455.

Di(prop-2-yn-1-yl) 2,2′-[Carbonylbis(azanediyl)]dibenzoate (6g)

Beige solid; yield: 85 mg (50%, 0.22 mmol); mp 178–180 °C (hexane).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.1 (s, 2 H, NH), 8.07 (d, *J* = 8 Hz, 2 H, ArH), 7.89 (d, *J* = 8 Hz, 2 H, ArH), 7.60 (t, *J* = 8 Hz, 2 H, ArH), 7.15 (t, *J* = 8 Hz, 2 H, ArH), 4.95 (d, *J* =2.4 Hz, 4 H, 2 × CH_2), 3.60 (t, *J* = 2.4 Hz, 2 H, 2 × CH).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.3, 166.3, 152.0, 140.5, 134.0, 130.4, 122.2, 121.2, 117.2, 78.1, 78.1, 59.7.

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{17}N_2O_5$: 377.1137; found: 377.1141.

Alkyl 2-[2,4-Dioxo-1,2-dihydroquinazolin-3(4*H*)-yl]benzoates 9a–g; General Procedure

To a solution of the respective 2,2′-[carbonylbis(azanediyl)]dimethyldibenzoate **6** (0.37 mmol) in MeCN (10 mL) at reflux was added an excess of K_2CO_3 (8 equiv). After stirring for 2 h, the excess of K_2CO_3 was removed by filtration and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using a mixture of EtOAc/hexane (6:4).

Methyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9a)

White solid; yield: 85 mg (96%, 0.29 mmol); mp 275–277 °C (EtOAc).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.13 (s, 1 H, NH), 8.23 (d, *J* = 8 Hz, 1 H, ArH), 8.14 (d, *J* = 8 Hz, 1 H, ArH), 7.72 (t, *J* = 8 Hz, 1 H, ArH), 7.51–7.63 (m, 2 H, ArH), 7.37 (d, *J* = 8 Hz, 1 H, ArH), 7.23 (t, *J* = 4 Hz, 1 H, ArH), 7.01 (d, *J* = 8 Hz, 1 H, ArH), 3.74 (s, 3 H, CH_3).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{13}N_2O_4$: 297.0875; found: 297.0872.

Ethyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9b)

White solid; yield: 88 mg (89%, 0.28 mmol); mp 268–270 °C (EtOAc).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.85 (s, 1 H, NH), 8.25 (d, *J* = 8 Hz, 1 H, Ar-H), 8.13 (d, *J* = 8 Hz, 1 H, ArH), 7.72 (t, *J* = 8 Hz, 1 H, ArH), 7.52–7.60 (m, 2 H, ArH), 7.37 (d, *J* = 8 Hz, 1 H, ArH), 7.22 (t, *J* = 4 Hz, 1 H, ArH), 6.94 (d, *J* = 8 Hz, 1 H, ArH), 4.10–4.22 (m, 2 H, CH_2), 1.11 (t, *J* = 8 Hz 3 H, CH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.6 (COO), 162.8 (C=O), 151.8 (C=O), 138.9 (C), 135.4 (C), 135.2 (CH), 133.5 (CH), 132.1 (CH), 130.6 (CH), 129.2 (CH), 128.5 (C), 128.3 (CH), 123.4 (CH), 115.4 (CH), 114.8 (C), 61.3 (OCH_2), 13.8 (CH_3).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{15}N_2O_4$: 311.1032; found: 311.1029.

Propyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9c)

White solid; yield: 79 mg (94%, 0.24 mmol); mp 260–262 °C (hexane).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.82 (s, 1 H, NH), 8.25 (d, *J* = 8 Hz, 1 H, ArH), 8.13 (d, *J* = 8 Hz, 1 H, ArH), 7.72 (t, *J* = 8 Hz, 1 H, ArH), 7.53–7.62 (m, 2 H, ArH), 7.37 (d, *J* = 8 Hz, 1 H, ArH), 7.22 (t, *J* = 8 Hz, 1 H, ArH), 6.94 (d, *J* = 8 Hz, 1 H, ArH), 4.07 (t, *J* = 8 Hz, 2 H, OCH_2), 1.46–1.58 (m, 2 H, CH_2), 0.84 (t, *J* = 8 Hz, 3 H, CH_3).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{17}N_2O_4$: 325.1188; found: 325.1191.

Isopropyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9d)

White solid; yield: 67 mg (80%, 0.21 mmol); mp 238–240 °C (hexane).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.68 (s, 1 H, NH), 8.24 (d, *J* = 8 Hz, 1 H, ArH), 8.14 (d, *J* = 8 Hz, 1 H, ArH), 7.71 (t, *J* = 8 Hz, 1 H, ArH), 7.58 (t, *J* = 8 Hz, 2 H, ArH), 7.30 (d, *J* = 8 Hz, 1 H, ArH), 7.23 (t, *J* = 8 Hz, 1 H, ArH), 6.95 (d, *J* = 8 Hz, 1 H, ArH), 4.10–4.22 (m, 1 H, CH), 1.10 (d, *J* = 8 Hz, 6 H, 2 × CH_3).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{17}N_2O_4$: 325.1188; found: 325.1189.

Butyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9e)

White solid; yield: 70 mg (87%, 0.20 mmol); mp 230–232 °C (hexane).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.60 (s, 1 H, NH), 8.04 (d, *J* = 7.8 Hz, 1 H, ArH), 7.92 (d, *J* = 9 Hz, 1 H, ArH), 7.66–7.76 (m, 2 H, ArH), 7.59 (t, *J* = 9 Hz, 1 H, ArH), 7.45 (d, *J* = 7.8 Hz, 1 H, ArH), 7.22 (t, *J* = 7.8 Hz, 2 H, ArH), 4.03 (t, *J* = 6.3 Hz, 2 H, OCH_2), 1.10–1.36 (m, 4 H, 2 × CH_2), 0.67 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 165.0 (COO), 162.7 (C=O), 150.5 (C=O), 140.3 (C), 136.1 (C), 135.8 (CH), 133.9 (CH), 131.6 (CH), 131.5 (CH), 129.3 (CH), 128.7 (C), 128.0 (CH), 123.0 (CH), 115.7 (CH), 114.7 (C), 65.1 (OCH_2), 30.4 (CH_2), 19.1 (CH_2), 13.9 (CH_3).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{19}N_2O_4$: 339.1345; found: 339.1342.

Allyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9f)

White solid; yield: 79 mg (95%, 0.24 mmol); mp 236–238 °C (EtOAc).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.53 (s, 1 H, NH), 8.26 (d, *J* = 8 Hz, 1 H, ArH), 8.13 (d, *J* = 8 Hz, 1 H, ArH), 7.73 (t, *J* = 8 Hz, 1 H, ArH), 7.54–7.63 (m, 2 H, ArH), 7.38 (d, *J* = 8 Hz, 1 H, ArH), 7.23 (t, *J* = 8 Hz, 1 H, ArH), 6.94 (d, *J* = 8 Hz, 1 H, ArH), 5.83–5.70 (m, 2 H), 5.21 (d, *J* = 16 Hz, 1 H, =CH), 5.07 (d, *J* = 8 Hz, 1 H, =CH), 4.60 (d, *J* = 4 Hz, 2 H, CH_2).

^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 164.2 (COO),162.8 (C=O), 151.8 (C=O), 139.0 (C), 135.6 (C), 135.2 (CH), 133.7 (CH), 132.1 (CH), 131.4 (CH), 130.7 (CH), 129.2 (C), 128.5 (CH), 128.0 (CH), 123.3 (CH), 118.9 (C), 115.4 (=CH_2), 114.8 (C), 65.6 (CH_2).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{15}N_2O_4$: 323.1032; found: 321.1022.

Propargyl 2-[2,4-Dioxo-1,2-dihydroquinazoline-3(4*H*)-yl]benzoate (9g)

White solid; yield: 72 mg (87%, 0.23 mmol); mp 254–256 °C (EtOAc).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.18 (s, 1 H, NH), 8.27 (d, *J* = 8 Hz, 1 H, ArH), 8.14 (d, *J* = 8 Hz, 1 H, ArH), 7.74 (t, *J* = 8 Hz, 1 H, ArH), 7.56–7.61 (m, 2 H, ArH), 7.38 (d, *J* = 8 Hz, 1 H, ArH), 7.24 (t, *J* = 8 Hz, 1 H, ArH), 6.99 (d, *J* = 8 Hz, 1 H, ArH), 4.73 (d, *J* = 8 Hz, 2 H, CH_2), 2.25 (t, *J* = 4 Hz, 1 H, CH).

^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 163.8 (COO), 162.7 (C=O), 151.8 (C=O), 139.0 (C), 135.6 (C), 135.2 (CH), 134.1 (CH), 132.2 (CH), 130.70 (CH), 129.3 (CH), 128.6 (C), 127.4 (CH), 123.4 (CH), 115.4 (CH), 114.9 (C), 75.9 (C, CH), 52.8 (CH_2).

HMRS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{13}N_2O_4$: 321.0875; found: 321.0879.

Funding Information

The authors are greatly thankful to the National Centre for Scientific and Technical Research (CNRST) of Morocco and the University of Sultan Moulay Slimane, Beni-Mellal, Morocco for financial support.

Acknowledgment

The authors thank Prof. El Mostafa Ketatni (Laboratory of Applied Spectro-Chemistry and Environment, University Sultan Moulay Slimane, Faculty of Science and Technology, PO Box 523, Beni-Mellal, Morocco) for the X-ray measurements.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1706643.

References

(1) Akhlaghinia, B.; Saadabad, H. R. *Can. J. Chem.* **2013**, *91*, 181.
(2) (a) Kulkarni, A. R.; Garai, S.; Thakur, G. A. *J. Org. Chem.* **2017**, *82*, 992. (b) Koziara, A.; Zawadzki, S.; Zwierzak, A. *Synthesis* **1979**, 527. (c) Gajda, T.; Koziara, A.; Zawadzki, S.; Zwierzak, A. *Synthesis* **1979**, 549. (d) Gajda, T.; Zwierzak, A. *Synthesis* **1981**, 1005.
(3) Musumeci, F.; Radi, M.; Brullo, C.; Schenone, S. *J. Med. Chem.* **2012**, *55*, 10797.
(4) Shapiro, G. I.; Bell-McGuinn, K. M.; Molina, J. R.; Bendell, J.; Spicer, J.; Kwak, E. L.; Pandya, S. S.; Millham, R.; Borzillo, G.; Pierce, K. J.; Han, L. X.; Houk, B. E.; Gallo, J. D.; Alsina, M.; Brana, I.; Tabernero, J. *Clin. Cancer Res.* **2015**, *21*, 1888.
(5) Katritzky, A. R.; Widyan, K.; Kirichenko, K. *J. Org. Chem.* **2007**, *72*, 5802.
(6) Gumaste, V. K.; Bhawal, B. M.; Deshmukh, A. R. A. S. *Tetrahedron Lett.* **2002**, *43*, 1345.
(7) Bandgar, B. P.; Pandit, S. S. *Tetrahedron Lett.* **2002**, *43*, 3413.
(8) Narendra, N.; Lamani, R. S.; Sureshbabu, V. V. *Tetrahedron Lett.* **2010**, *51*, 3002.
(9) Kim, J. G.; Jang, D. O. *Synlett* **2008**, 2072.
(10) Nowrouzi, N.; Jonaghani, M. Z. *Chin. Chem. Lett.* **2012**, *23*, 442.
(11) (a) Bigi, F.; Maggi, R.; Sartori, G. *Green Chem.* **2000**, *2*, 140. (b) Sureshbabu, V. V.; Lalithamba, H. S.; Narendra, N.; Hemantha, H. P. *Org. Biomol. Chem.* **2010**, *8*, 835.
(12) (a) Padiya, K. J.; Gavade, S.; Kardile, B.; Tiwari, M.; Bajare, S.; Mane, M.; Gaware, V.; Varghese, S.; Harel, D.; Kurhade, S. *Org. Lett.* **2012**, *14*, 2814. (b) Dube, P.; Nathel, N. F. F.; Vetelino, M.; Couturier, M.; Aboussafy, C. L.; Pichette, S.; Jorgensen, M. L.; Hardink, M. *Org. Lett.* **2009**, *11*, 5622. (c) Bertrand, M. B.; Wolfe, J. P. *Tetrahedron* **2005**, *61*, 6447.
(13) Han, C.; Porco, J. A. *Org. Lett.* **2007**, *9*, 1517.
(14) (a) McCusker, J. E.; Main, A. D.; Johnson, K. S.; Grasso, C. A.; McElwee-White, L. *J. Org. Chem.* **2000**, *65*, 5216. (b) Zhao, J.; Li, Z. Y.; Yan, S. H.; Xu, S. Y.; Wang, M. A.; Fu, B.; Zhang, Z. H. *Org. Lett.* **2016**, *18*, 1736.
(15) (a) Vinogradova, E. V.; Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 11132. (b) Guan, Z. H.; Lei, H.; Chen, M.; Ren, Z. H.; Bai, Y. J.; Wang, Y. Y. *Adv. Synth. Catal.* **2012**, *354*, 489. (c) Kim, S. H.; Hong, S. H. *Org. Lett.* **2016**, *18*, 212.
(16) Hayashi, K.; Choshi, T.; Chikaraishi, K.; Oda, A.; Yoshinaga, R.; Hatae, N.; Ishikura, M.; Hibino, S. *Tetrahedron* **2012**, *68*, 4274.
(17) Sabitha, G.; Srividya, R.; Yadav, J. S. *Tetrahedron Lett.* **1999**, *55*, 4015.
(18) Yamada, K. I.; Oonishi, A.; Kuroda, Y.; Harada, S.; Kiyma, H.; Yamaoka, Y.; Takasu, K. *Tetrahedron Lett.* **2016**, *57*, 4098.
(19) Yassine, H.; Khouili, M.; ElAmmari, L.; Saadi, M.; Ketatni, E. M. *Acta Crystallogr. Ser. E* **2015**, *71*, o297.
(20) Ethyl 2-[(azidocarbonyl)amino]benzoate: Yassine, H.; Khouili, M.; Hafid, A.; Mentre, O.; Ketatni, E. M. *IUCrData* **2016**, *1*, x161155.
(21) Butyl 2-[(azidocarbonyl)amino]benzoate: Yassine, H.; Khouili, M.; Hafid, A.; Mentre, O.; Ketatni, E. M. *IUCrData* **2016**, *1*, 161454.
(22) Doğan, S. D.; Demirpolat, E.; Aycan, M. B. Y.; Balci, M. *Tetrahedron* **2015**, *71*, 252.
(23) Shi, J.; Zhao, T.; Niwayama, S. *Tetrahedron* **2018**, *74*, 6815.
(24) Peet, N. P. *J. Heterocycl. Chem.* **1987**, *24*, 223.