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NBS-Mediated Oxygen Transfer Reaction of Carbonyl in Ester: Efficient Synthesis of Benzil-*o*-carboxylate Derivative From *o*-Alkynylbenzoate

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Abstract. A neighbouring ester group-participated diketonization of *o*-alkynylbenzoate is described here for the synthesis of benzil-*o*-carboxylate. Application of the resulting benzil-*o*-carboxylate in the synthesis of quinoxalines is also reached from *o*-alkynylbenzoate in an one-pot fashion. This diketonization proceeds smoothly with a high regioselectivity under mild conditions. Importantly, neighbouring group plays an important role in diketonization. A plausible mechanism suggests that a bromo-incoporated isocoumarin cation is described as an intermediate, and the whole process is constituted by NBS-mediated electrophilic 6-*endo* annulation and oxygen transfer reaction through NBS-mediated oxidative ring-opening. Water serves as a nucleophile of ring-opening.

Keywords:NBS;Electrophilic Bromocyclization; *o*-alkynylbenzoate; Oxidative Ring-opening; Metal-free

o-Alkynylbenzoate was a kind of powerful dual-functional building blocks.[1-7] Traditionally, this type of substrates was always employed to construct isocoumarin derivatives through a 6-*endo* cyclization due to its easy accessibility of the starting materials.To date, three well-recognized strategies, which were accordingly concluded as electrophile-mediated 6-*endo* cyclization,[1,5,6]Bronsted acid/Lewis acid-promoted 6-*endo* cyclization[2-3] and transitional-metal-catalyzed 6-*endo* cyclization,[4] enabled the synthesis of various isocoumarins under mild conditions with high efficiency and regioselectivity. As one of electrophilic cyclization, 6-*endo* halocyclization was initially investigated by Oliver and Gandour,[5] and was further developed in perpetuity by Larock and other groups (Scheme 1a).[6] Among these achievements, Br_2, I_2, and ICl *etc*. were recognized as efficient electrophiles to trigger 6-*endo* halocyclization to form 4-haloisocoumarins, a versatile handle for further structural elaboration. However, the above established reactions were basically carried out in organic solvent. Therefore, we would like to develop a 6-*endo* cyclization of *o*-alkynylbenzoate in water or co-solvent of water and organic solvent.

Our initial trials intended to use water as solvent to realize 6-*endo* bromocyclization of methyl *o*-phenylalkynylbenzoate **1** in the presence of NBS (*N*-bromosuccinimide) at room temperature (Scheme 1b). To our surprise, this projected transformation just provided a trace amount of the desired 4-bromoisocoumarin **4**, with a recovery of most parts of starting material **1**. A distinctive compound benzil-*o*-carboxylate **3** was pleased to be observed in a promising isolated yield (17% yield). We reasoned that the synthesis of benzil-*o*-carboxylate **3** was probably ascribed to a catalyst and metal-free diketonization of triple bond in *o*-phenylalkynylbenzoate **1**.

According to the findings from Liu and co-workers,[8] a gold catalyst/Selectfluor system enabled the diketonization of *o*-alkynylbenzoate for the synthesis of benzil-*o*-carboxylate. Mechanism investigation suggested that neighboring ester group served as a directing group to assist difluorohydration of triple bond in *o*-alkynylbenzoate. The difluorohydrative product was *in situ* hydrolyzed into benzil-*o*-carboxylate. However, 2-alkynylheteroaryl carboxylate and 2-alkylethynylbenzoate did not give the desired products. As we know, the success of Liu's work resorted to the use of the gold catalyst. However, our above observation was metal-free, probably indicating a distinctive mechanism to explain the

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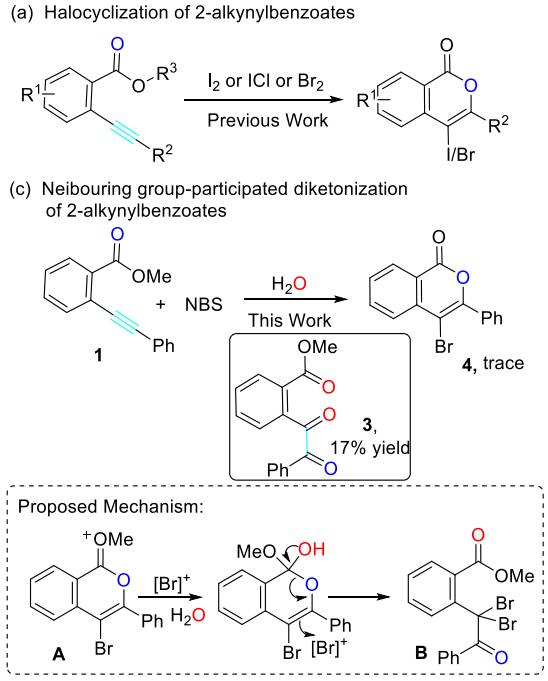
synthesis of benzil-*o*-carboxylate, a versatile synthon[9].

Additionally, I_2 or ICl-mediated diketonization of triple bond in *o*-alkynylbenzaldehyde was already witnessed by Srinivasan and co-workers for the synthesis of tricarbonyl compounds.[10] In the reaction, a neighboring aldehyde group-participated 6-*endo* cyclization and water-attacked oxidative ring opening were involved. Here oxygen in aldehyde carbonyl of *o*-alkynylbenzaldehyde already transferred into triple bond to produce one of keto carbonyl. However, I_2 or ICl/water reaction system was not compatible for diketonization of *o*-alkynylbenzoate for the synthesis of benzil-*o*-carboxylate.

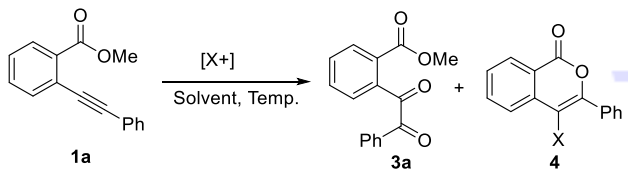
Inspired by what mention above, it seemed that it was highly desirable to optimize the reaction presented in Scheme 1b. It was believed that the procedure in Scheme 1b represented a metal-free diketonization of *o*-alkynylbenzoate, which served as a supplement of the previous works.[8,10,11] In the process, a plausible mechanism involving oxygen transfer of carbonyl in ester was proposed[11].As illustrated in Scheme 1b, the above diketonization went through a NBS-mediated 6-*endo* cyclization with the formation of bromo-incorporated isocoumarin cation **A**, followed by water-based nucleophilic addition and oxidative ring-opening. The resulting dibromohydrative intermediate **B** was *in situ* hydrolyzed into benzil-*o*-carboxylate. It was noteworthy that oxygen of ester carbonyl in starting material transferred into triple bond to form one of keto carbonyl group.



Scheme 1. Proposed route for the synthesis of benzil-*o*-carboxylate

Initial trials were focused on finding efficient electrophile to promote the above oxygen transfer reaction of ester carbonyl. As presented in Table 1, NBS was the best choice among I_2, Br_2, NIS and NCS (entries 1-7, Table 1). Pleasingly, treating the model reaction of **1a** with 2.1 NBS in a co-solvent (DCE:H_2O, v/v = 1:1) at room temperature provided benzil-*o*-carboxylate **3a** in moderate yield (46% yield) as well as 4-bromoisocoumarin **4** in 11% yield (entry 7, Table 1), with recovery of the starting material **1a**. Consequently, increase of reaction temperature was then explored with a wish to improve reaction efficiency. As expected, the desired benzil-o-carboxylate **3a** was afforded in 71% yield as well as the formation of 4-bromoisocoumarin **4** in 12% yield when the model reaction was performed at 50 °C (entry 8, Table 1). Further increase of reaction temperature was favorable for improving reaction efficiency and chem-selectivity. When the model reaction was conducted at 80 °C, the desired benzil-o-carboxylat **3a** was produced in 90% yield and the side product 4-bromoisocoumarin **4** was reduced into 5% yield (entry 9, Table 1). Subsequently, solvent effect was also examined accordingly. From screening results, it seemed that water was essential for this oxygen transfer reaction. A blank reaction using DCE as a solvent uniquely offered 4-bromoisocoumarin **4** in 65% yield (entry 13, Table 1). Other co-solvents including MeCN:H_2O, DMF:H_2O, and THF:H_2O gave inferior yields and chem-selectivity (entries 10-12, Table 1). Changing ratio between DCE and H_2O from 5:1 to 1:5 indicated that DCE:H_2O (1:1, v/v) was the best choice (entries 14-15, Table 1).

Table 1. Initial studies for the reaction of neibouring group-participated dibromohydration of 2-alkynylbenzoate.



Entry	[X⁺] (2.1 equiv)	Solvent	Temp (°C)	Yield (**3a**, %)[a]	Yield (**4**, %)[a]
1	NBS	H_2O	rt	17	trace
2	I_2	H_2O	rt	0	22
3	I_2	MeCN:H_2O (1:1, v/v)	rt	0	47
4	Br_2	H_2O	rt	0	trace
5	NBS	DCE : H_2O (1:1, v/v)	rt	46	11
6	NIS	DCE : H_2O (1:1, v/v)	rt	41	14
7	NCS	DCE : H_2O (1:1, v/v)	rt	37	9
8	NBS	DCE : H_2O (1:1, v/v)	50	71	12
9	**NBS**	**DCE : H_2O (1:1, v/v)**	**80**	**90**	**5**
10	NBS	MeCN : H_2O (1:1, v/v)	80	79	14

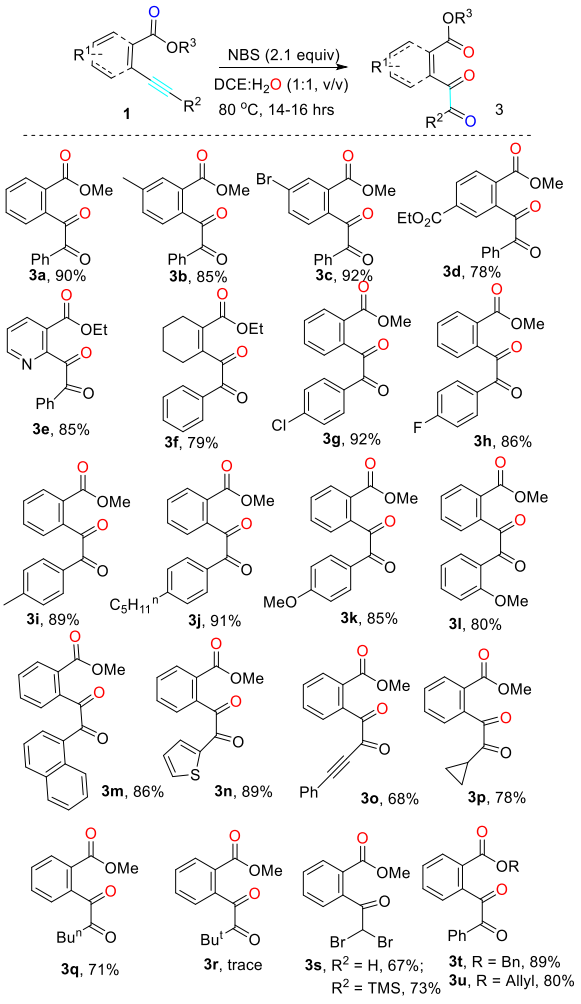
11	NBS	DMF : H_2O (1:1, v/v)	80	trace	35
12	NBS	THF : H_2O (1:1, v/v)	80	85	10
13	NBS	DCE	80	trace	65
14	NBS	DCE : H_2O (5:1, v/v)	80	52	30
15	NBS	DCE : H_2O (1:5, v/v)	80	64	25

[a]Isolated yield based on 2-alkynylbenzoate **1a**. [b]Standard conditions: 2-alknylbenzoate **1a** (0.2 mmol), NBS (2.1 equiv), solvent (2 mL). DCE = 1, 2-dichloroethane; NIS = *N*-iodosuccinimide; NCS = *N*-chlorosuccinimide.

With the optimized conditions (entry 9, Table 1) in hand, we then explored the generality of our method. The results were illustrated in Scheme 2. From the results, an array of benzil-*o*-carboxylates **3** were achieved accordingly. For example, the reactions using substrates **1b-1d** with methyl, bromo, and ester group attached on R^1 site provided the corresponding products **3b-3d** in good to excellent yields. Particularly, Interestingly, *o*-alkynylnicotinate **1e** was an efficient reaction partner, leading to the desired product **3e** in 85% yield. Furthermore, *o*-alkynylcyclohex-1-ene-1-carboxylate **1f** was compatible for the reaction, with the formation of the product **3f** in 79% yield. Interestingly, by the previous pathway the substrates (such as **3e** and **3f**) did not produced the corresponding benzil-*o*-carboxylate.[8]

Subsequently, we explored the influence of the R^2 substituent. From the results, it seemed that the reactions using the substrates with aryl or heteroaryl on R^2 were more favorable than these of the substrates with alkyl. For instance, under standard conditions the reactions of methyl 2-(naphthalen-1-ylethynyl)benzoate and methyl 2-(thiophen-2-ylethynyl)benzoate gave rise to benzil-*o*-carboxylate **3m** and **3n** in 86% and 89% yields, respectively, while the reaction of methyl 2-(cyclopropylethynyl)benzoate produced **3p** in 78% yield. The alkyl-connected benzil-*o*-carboxylates (such as **3p** and **3q**) were not achieved by the previous procedure[8]. Additionally, electronic effect of aryl substituent on R^2 made slight impact on the reactions' outcomes. 4-chlorophenyl, 4-fluorophenyl, 4-methylphenyl, and 4-pentylphenyl-connected substrates provided the corresponding benzil-*o*-carboxylates **3g-3j** in similar yields. Effect of steric hinderance on R^2 substituent was also detected. Interestingly, the steric hinderance of R^2 substituent did not make significant impact on the reactions' yields. For example, the reactions of the substrates with 4-methoxylphenyl and 2-methoxylphenyl offered the corresponding products **3k** and **3l** in similar yields. Interestingly, methyl 2-(phenylbuta-1,3-diyn-1-yl)benzoate was effective under standard conditions, producing phenylethynyl-linked benzil-*o*-carboxylate **3o** in 68% yield. This result was supportive for the fact that neighboring ester group was required in this diketonization for the synthesis of benzil-*o*-carboxylate. The dibromo function survived under standard conditions when methyl 2-ethynylbenzoate and methyl 2-(trimethylsilyl)ethynylbenzoate were employed as the starting materials, releasing methyl 2-(2,2-dibromoacetyl)benzoate **3s** in moderate yields. It was noteworthy that oxygen of carbonyl ester in starting materials was transferred into the internal carbon of triple bond to form a new keto carbonyl. This was probably attributed to a *5-exo-dig* cyclization[6a,12] and water-attacked oxidative ring-opening. In light of the above results, it was believed that diketonization of *o*-alknylbenzoate developed here represented a supplementary for Liu's work since we expanded the diketonization of the substrates failed in Liu's work.

Scheme2. Generation of benzil-o-carboxylate **3** through neighboring ester participated reaction of *o*-alkynylbenzoate **1**[a]

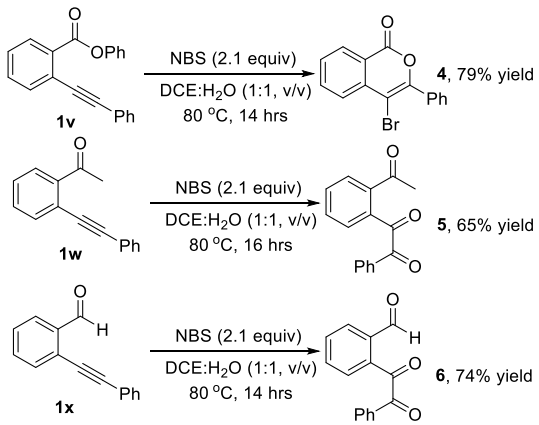


[a]Based on 2-alkynylbenzoate **1**;[b] Standard Conditions: **1** (0.2 mmol), NBS (2.1 equiv), DCE:H_2O (v/v = 1:1, 2 mL), 80 °C, 14-16 hrs.

Various benzoates were also tested. Benzyl benzoate and allylic benzoate were efficient

reaction partners, leading to the corresponding benzil-*o*-carboxylates **3t** and **3u** in good yields. However, we found that the reaction of phenyl 2-phenylethynylbenzoate **1v** did not product benzil-*o*-carboxylate, but a 4-bromoisocoumarin **4** in 79% yield (Scheme 3), probably due to relatively less instability of phenyl-connected 4-bromoisocoumarin cation intermediate.

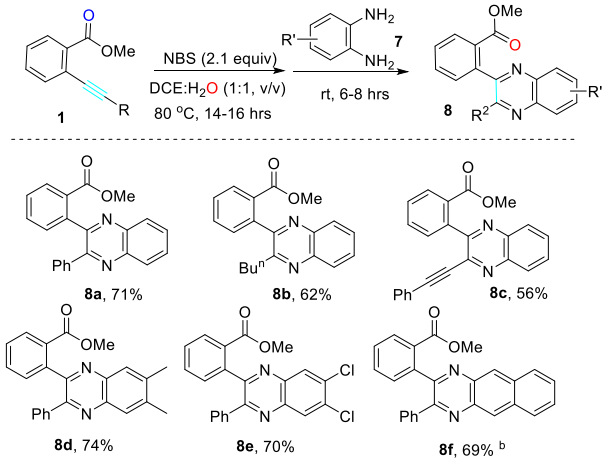
Scheme 3. Effect on different neighboring groups [a]



[a] Based on 2-alkynylbenzoate **1**.

By altering neighboring group to aldehyde and ketone group, the neighboring carbonyl group-participated diketonization of triple bonds took place with the formation of tricarbonyl compound **5** and **6** in moderate to good yields (Scheme 3).[9] However, the reaction of 2-alkynylbenzoic acid did not the desired benzil-o-carboxylic acid (data not shown in Scheme 3).

Scheme 4. The reaction of benzil-*o*-carboxylate with 1,2-diamine[a]

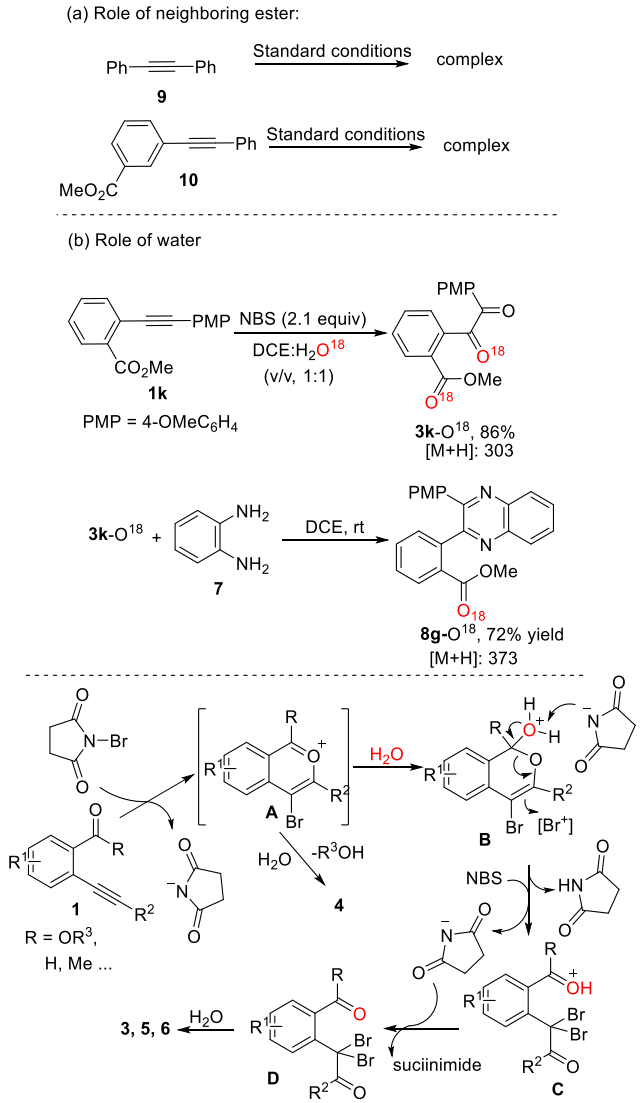


[a] Based on 2-alkynylbenzoate **1**; [b] Condensation was conducted at 50 °C

Additionally, application of the resulting benzil-*o*-carboxylate **3** in organic synthesis was then explored. Considering importance of quinoxaline core in organic, medicine and material chemistry[13],we explored condensation of benzil-*o*-carboxylate with 1,2-diamine **7**. To reduce reaction cost, we envisioned that the quinoxalines **8** could be achieved in an one-pot fashion from *o*-alkynylbenzoate **1**, avoiding isolation of benzil-*o*-carboxylate **3** intermediate. To our delight, this one-pot procedure worked well by adding 1.2 equiv 1,2-diamine **7** after completion of diketonization of *o*-alkynylbenzoate **1**. The condensation of *in situ* generated benzil-*o*-carboxylate with 1,2-diamine **7** proceeded smoothly without any catalyst at room temperature. As shown in Scheme 4, a number of *o*-alkynylbenzoate **1** and 1,2-diamine **7** could be compatible for the condensation, delivering an array of quinoxalines **8** in moderate to good yields. To understand the reaction, several control experiments were carried out (Scheme 5). Firstly, we would like to identify the role of neighboring ester group. The reactions using the substrate without neighboring ester group and the substrate with *meta* ester group were then ran. Disappointingly, either the reaction of **9** or the reaction of **10** did not give the corresponding diketone compounds, and the both reactions became complex under standard conditions (Scheme 5a). Secondly, we wanted to identify the role of water. Therefore, the reaction of 2-(4-methoxylphenyl)ethynylbenzoate **1k** in DCE:H_2O^{18} (v/v, 1:1) was carried out. The reaction provided benzil-o-carboxylate **3k**-O^{18} in 86% yield. Electrospray ionization mass spectroscopic analysis of the product **3k**-O^{18} showed a strong signal at [M+H] = 303, suggesting two equivalent H_2O^{18} being incorporated into **3k**. To clarify exact site of oxygen-18, the condensation of **3k**-O^{18} with benzene-1,2-diamine was conducted. The reaction offered the desired quinoxaline **8g** in 72% yield. Electrospray ionization mass spectroscopic analysis showed the product **8g** contained one oxygen-18, whose [M+H] was equal to 373 (Scheme 5b). The above information implied that two equivalent water were installed into diketonization of *o*-alkynylbenzoate. One of them was incorporated into ester group of benzil-*o*-carboxylate, and the other was installed into triple bond to form one of carbonyl group in benzil-*o*-carboxylate.

In light of the above results, a plausible mechanism was proposed in Scheme 2. As illustrated in Scheme 2, this reaction went through a NBS-promoted electrophilic annulation and water-attacked oxygen transfer reaction. In the process, bromo-incorporated isocoumarin cation **A**, generated from NBS-mediated 6-*endo-dig* annulation, was postulated as a key intermediate. Two possibility probably happened to the intermediate **A.** First of them was removal of an alcohol to afford isocoumarin **4**. Otherwise, water served as a nucleophile to attack ester cation in intermediate **A** to form an intermediate **B**. The intermediate **B** was readily converted into dibromohydrative product **C** through NBS-mediated oxidative ring-opening.[14] It was noteworthy that oxygen in ester group was transferred into triple bond

to form a carbonyl. The resulting dibromohydrative product **C** was hydrolyzed into the final benzil-*o*-carboxylate **3**. Therefore, two keto carbonyl in final product were derived from different sources. One of them was from ester by oxygen transfer reaction, and another came from water by hydrolysis.



Scheme 5. Control experiments and possible mechanism.

In conclusion, we have developed a neighbouring ester group-participated metal-free diketonization of *o*-alkynylbenzoate for the synthesis of benzil-*o*-carboxylate. Application of the resulting benzil-*o*-carboxylate in the synthesis of quinoxalines was also accomplished in an one-pot fashion. This diketonization proceeded smoothly with a high regioselectivity under mild conditions. Importantly, neighbouring group played an important role in diketonization. Mechanism studies suggested that a bromo-incoporated isocoumarin cation was described as an intermediate and the whole process was constituted by NBS-mediated electrophilic 6-*endo* annulation and oxygen transfer reaction through NBS-mediated oxidative ring-opening. Water served as a nucleophile of ring-opening.

Experimental Section

General procedure for the synthesis of compound 3. 2-alkynylbenzoate**1**(0.2 mmol), NBS (2.1 equiv) were added to a test tube, and then co-solvent DCE:H_2O (v/v =1:1, 2 mL) was added. The mixture was stirred at 80 °C for 14-16 h. After completion of reaction as indicated by TLC, the mixture was filtrated and the resulting filtrate was dried by Na_2SO_4. Then filtration again, evaporation of the solvent and purification by flash column chromatograph provided the desired product **3**. The final products **5** and **6** were also synthesized according to the above procedure.

General procedure for the synthesis of compound 8. 2-alkynylbenzoate**1**(0.2 mmol), NBS (2.1 equiv) were added to a test tube, and then co-solvent DCE:H_2O (v/v =1:1, 2 mL) was added. The mixture was stirred at 80 °C for 14-16 h. After completion of reaction as indicated by TLC, aryl-1,2-diamine **7** (0.2 mmol) was added. The mixture was stirred at room temperature for 6-8 h. After completion of reaction as indicated by TLC,the mixture was filtrated and the resulting filtrate was dried by Na_2SO_4. Then filtration again, evaporation of the solvent and purification by flash column chromatograph provided the desired product **8**.

Methyl 2-(2-oxo-2-phenylacetyl)benzoate (**3a**)[8a](yellow powder, 48.3 mg, 90%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.11 (m, 1H), 8.10 – 7.96 (m, 1H), 7.79 – 7.59 (m, 4H), 7.59 – 7.45 (m, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.64, 188.98, 166.86, 138.73, 133.92, 133.10, 132.95, 131.64, 130.80, 130.09, 129.71, 129.49, 128.46, 52.75.

Methyl 5-methyl-2-(2-*oxo*-2-phenylacetyl)benzoate (**3b**) (Light yellow liquid, 48.0 mg, 85%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 2H), 7.80 (s, 1H), 7.70 – 7.59 (m, 2H), 7.57 – 7.44 (m, 3H), 3.63 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.51, 189.34, 167.03, 142.67, 135.32, 133.84, 133.48, 133.04, 130.69, 130.38, 130.32, 129.87, 128.42, 52.58, 21.44; HRMS (ESI) calcd for $C_{17}H_{15}O_4^+$: 283.0965 (M^++H), found: 283.0973

Methyl 5-bromo-2-(2-oxo-2-phenylacetyl)benzoate (**3c**) (Light yellow liquid, 63.9 mg, 92%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.12 (m, 3H), 7.97 – 7.75 (m, 1H), 7.71 – 7.61 (m, 1H), 7.59 – 7.50 (m, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.57, 188.68, 165.63, 137.35, 136.04, 134.05, 132.73, 132.68, 131.55, 131.13, 130.76, 128.47, 126.17, 53.01; HRMS (ESI) calcd for $C_{16}H_{12}BrO_4^+$: 346.9913 (M^++H), found: 346.9914

Dimethyl 2-(2-oxo-2-phenylacetyl)terephthalate (**3d**) (Light yellow liquid, 50.9 mg, 78%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 1.5 Hz, 1H), 8.28 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.22 – 8.19 (m, 2H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.62 (m, 1H), 7.60 – 7.52 (m, 2H), 3.97 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.49, 188.61, 166.16, 165.28, 139.02, 134.26, 134.08, 132.96, 132.73, 132.40, 131.04, 130.80, 129.82, 128.49, 53.03, 52.71; HRMS (ESI) calcd for $C_{18}H_{15}O_6^+$: 327.0863 (M^++H), found: 327.0863

Ethyl 2-(2-oxo-2-phenylacetyl)nicotinate (**3e**) (Light yellow liquid, 48.2 mg, 85%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.78 (m, 1H), 8.13 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.33 (m, 2H), 7.25 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.28, 165.19, 155.88, 150.90, 139.55, 132.51, 132.02, 130.59, 127.88, 124.71, 124.23, 62.25, 13.96; HRMS (ESI) calcd for $C_{16}H_{14}NO_4^+$: 284.0917 (M^++H), found: 284.0921

Ethyl 2-(2-oxo-2-phenylacetyl)cyclohex-1-enecarboxylate (**3f**) (Light yellow liquid, 45.2 mg, 79%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.63 – 7.58 (m, 1H), 7.53 – 7.45 (m, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.50 – 2.36 (m, 4H), 1.80– 1.70 (m, 4H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.60, 188.79, 167.34, 149.44, 133.66, 132.97, 131.21, 130.81, 128.27, 61.40, 28.74, 24.58, 21.40, 21.26, 14.00; HRMS (ESI) calcd for $C_{17}H_{19}O_4^+$: 287.1278 (M^++H), found: 287.1280

Methyl 2-(2-(4-chlorophenyl)-2-oxoacetyl)benzoate (**3g**) (Light yellow liquid, 55.7 mg, 92%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.58 (m, 3H), 7.51 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.48, 187.71, 166.89, 140.35, 138.81, 133.18, 132.16, 131.61, 131.42, 129.97, 129.66, 129.32, 128.79, 52.80; HRMS (ESI) calcd for $C_{16}H_{12}ClO_4^+$: 303.0419 (M^++H), found: 303.0420

Methyl 2-(2-(4-fluorophenyl)-2-oxoacetyl)benzoate (**3h**) (Light yellow liquid, 49.2 mg, 86%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.17 (m, 2H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.53 (m, 3H), 7.26 – 7.14 (m, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.66, 187.41, 166.90, 166.19 (d, *J* = 254.9 Hz), 138.90, 133.59 (d, *J* = 9.5 Hz), 133.18, 131.60, 129.98, 129.67, 129.42 (d, *J* = 3.0 Hz), 129.34, 115.70 (d, *J* = 21.8 Hz), 52.80; HRMS (ESI) calcd for $C_{16}H_{12}FO_4^+$: 287.0714 (M^++H), found: 287.0709

Methyl 2-(2-oxo-2-(p-tolyl)acetyl)benzoate (**3i**) (Light yellow liquid, 50.2 mg, 89%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 4.1 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.65 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.80, 188.72, 166.83, 145.01, 138.74, 132.99, 131.57, 130.89, 130.44, 130.09, 129.67, 129.57, 129.23, 52.69, 21.92; HRMS (ESI) calcd for $C_{17}H_{15}O_4^+$: 283.0965 (M^++H), found: 283.0969

Methyl 2-(2-oxo-2-(4-pentylphenyl)acetyl)benzoate (**3j**) (Light yellow liquid, 61.6 mg, 91%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.69-7.68 (m, 2H), 7.66 – 7.55 (m, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 3.65 (s, 3H), 2.70 (t, *J* = 7.8 Hz, 2H), 1.76 – 1.58 (m, 2H), 1.41 – 1.30 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.83, 188.76, 166.85, 149.91, 138.75, 132.97, 131.55, 130.91, 130.61, 130.08, 129.66, 129.59, 128.59, 52.68, 36.20, 31.49, 30.74, 22.53, 14.04; HRMS (ESI) calcd for $C_{21}H_{23}O_4^+$: 339.1591 (M^++H), found: 339.1590

Methyl 2-(2-(4-methoxyphenyl)-2-oxoacetyl)benzoate (**3k**) (Light yellow liquid, 48.9 mg, 82%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.16 (m, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.67 – 7.51 (m, 1H), 7.08 – 6.96 (m, 2H), 3.91 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.05, 187.69, 166.82, 164.23, 138.85, 133.19, 132.87, 131.45, 130.02, 129.60, 125.93, 113.82, 55.52, 52.62. HRMS (ESI) calcd for $C_{17}H_{15}O_5^+$: 299.0914 (M^++H), found: 299.0916

Methyl 2-(2-(2-methoxyphenyl)-2-oxoacetyl)benzoate (**3l**) (Light yellow liquid, 47.7 mg, 80%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.96 (m, 1H), 7.82 – 7.72 (m, 2H), 7.71 – 7.49 (m, 3H), 7.20 – 7.07 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.83, 191.25, 168.29, 160.05, 135.68, 134.02, 132.39, 132.35, 131.44, 131.26, 130.76, 129.09, 123.53, 121.00, 112.17, 55.81, 52.59; HRMS (ESI) calcd for $C_{17}H_{15}O_5^+$: 299.0914 (M^++H), found: 299.0916

Methyl 2-(2-(naphthalen-1-yl)-2-oxoacetyl)benzoate (**3m**) (yellow liquid, 54.8 mg, 86%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 7.3 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.85 – 7.39 (m, 6H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.74, 190.99, 167.10, 138.72, 134.53, 134.35, 133.92, 132.89, 131.57, 131.46, 130.22, 130.09, 129.54, 128.73, 128.62, 128.41, 126.39, 125.37, 124.42, 52.78; HRMS (ESI) calcd for $C_{20}H_{15}O_4^+$: 319.0965 (M^++H), found: 319.0966

Methyl 2-(2-oxo-2-(thiophen-2-yl)acetyl)benzoate (**3n**) (Light yellow liquid, 48.8 mg, 89%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.26 (m, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.82-7.80 (m, 1H), 7.73 – 7.58 (m, 3H), 7.31 – 7.19 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.30, 180.35, 166.60, 138.48, 138.12, 136.76, 136.33, 133.00, 131.36, 129.66, 129.55, 129.38, 128.47, 52.63; HRMS (ESI) calcd for $C_{14}H_{11}O_4S^+$: 275.0373 (M^++H), found: 275.0374

Methyl 2-(2-oxo-4-phenylbut-3-ynoyl)benzoate (**3o**) (yellow liquid, 39.7 mg, 68%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.77 – 7.59 (m, 4H), 7.58 – 7.47 (m, 2H), 7.46 – 7.38 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.34, 174.85, 166.55, 137.68, 133.79, 133.29, 131.46, 129.62, 129.13, 128.67, 119.54, 98.21, 86.30, 52.96; HRMS (ESI) calcd for $C_{18}H_{13}O_4^+$: 293.0808 (M^++H), found: 293.0810

Methyl 2-(2-cyclopropyl-2-oxoacetyl)benzoate (**3p**)[8a](yellow liquid, 36.2 mg, 78%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.61 – 7.55 (m, 1H), 7.54 – 7.49 (m, 1H), 3.86 (s, 3H), 2.93 (s, 1H), 1.20 – 1.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.49, 193.34, 166.80, 138.41, 133.05, 131.05, 129.60, 129.35, 128.89, 52.72, 16.06, 13.19.

Methyl 2-(2-oxohexanoyl)benzoate (**3q**) (Light yellow liquid, 35.3 mg, 71%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.61 – 7.54 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.47 – 1.37 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.18, 194.08, 167.07, 138.74, 133.12, 131.01, 129.39, 129.29, 128.91, 52.77, 36.09, 24.99, 22.25, 13.87; HRMS (ESI) calcd for $C_{14}H_{17}O_4^+$: 249.1121 (M^++H), found: 249.1126

Methyl 2-(2,2-dibromoacetyl)benzoate (**3s**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.61 – 7.52 (m, 2H), 6.36 (s, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.81, 166.15, 137.82, 133.08, 130.70, 130.39, 130.25, 127.39, 53.21, 44.24. HRMS (ESI) calcd for $C_{10}H_9Br_2O_3^+$: 334.8913 (M^++H), found: 334.8915

Benzyl 2-(2-oxo-2-phenylacetyl)benzoate (**3t**) (yellow liquid, 61.3 mg, 89%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 2H), 8.07 – 8.00 (m, 1H), 7.72 – 7.59 (m, 4H), 7.58 – 7.49 (m, 2H), 7.38 – 7.27 (m, 5H), 5.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.69, 189.03, 166.46, 139.03, 135.06, 133.80, 133.09, 133.07, 131.52, 130.82, 130.05, 129.66, 129.62, 128.55, 128.41, 128.36, 128.25, 67.55; HRMS (ESI) calcd for $C_{22}H_{17}O_4^+$: 345.1121 (M^++H), found: 345.1128

Allyl 2-(2-oxo-2-phenylacetyl)benzoate (**3u**) (yellow liquid, 47.1 mg, 80%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.15 (m, 2H), 8.07 – 8.00 (m, 1H), 7.77 – 7.60 (m, 4H), 7.59 – 7.47 (m, 2H), 5.94 – 5.78 (m, 1H), 5.30 – 5.16 (m, 2H), 4.64 – 4.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.67, 189.01, 166.24, 138.97, 133.84, 133.10, 133.06, 131.55, 131.29, 130.83, 130.07, 129.67, 129.58, 128.38, 118.96, 66.44; HRMS (ESI) calcd for $C_{18}H_{15}O_4^+$: 295.0965 (M^++H), found: 295.0973

4-bromo-3-phenyl-1H-isochromen-1-one (**4**)[6d] (White powder, 47.6 mg, 79%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.83 – 7.77 (m, 2H), 7.64 – 7.57 (m, 1H), 7.53 – 7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.14, 151.81, 136.60, 135.46, 132.76, 130.18, 129.79, 129.66, 129.16, 128.10, 126.65, 120.57, 101.37.

1-(2-acetylphenyl)-2-phenylethane-1,2-dione (**5**)[10] (Light yellow liquid, 32.8 mg, 65%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.17 (m, 2H), 7.94 – 7.89 (m, 1H), 7.76 – 7.61 (m, 4H), 7.58 – 7.51 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.97, 194.03, 189.27, 138.55, 137.04, 133.89, 133.48, 133.22, 131.43, 130.84, 130.33, 129.30, 128.41, 26.60.

2-(2-oxo-2-phenylacetyl)benzaldehyde (**6**)[10] (Light yellow liquid, 35.3 mg, 74%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 7.96 – 7.89 (m, 1H), 7.80 – 7.69 (m, 3H), 7.69 – 7.63 (m, 1H), 7.61 – 7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.43, 192.47, 189.46, 137.05, 135.81, 134.40, 134.23, 132.94, 132.42, 132.41, 130.82, 130.65, 128.58.

Methyl 2-(2-phenylquinoxalin-3-yl)benzoate (**8a**) (yellow brown solid, 48.3 mg, 71%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.11 (m, 2H), 7.86-7.84 (m, 1H), 7.82 – 7.74 (m, 2H), 7.66 – 7.54 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.34 – 7.20 (m, 3H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.87, 154.43, 153.76, 141.32, 140.82, 140.74, 138.25, 132.38, 131.20, 130.33, 130.16, 129.94, 129.79, 129.71, 129.33, 129.08, 128.79, 128.77, 127.99, 52.10; HRMS (ESI) calcd for $C_{22}H_{17}N_2O_2^+$: 341.1285 (M^++H), found: 341.1280

Methyl 2-(3-butylquinoxalin-2-yl)benzoate (**8b**) (yellow brown solid, 39.7 mg, 62%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.78 – 7.65 (m, 3H), 7.62 – 7.54 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 3.60 (s, 3H), 2.95 – 2.57 (m, 2H), 1.72 – 1.60 (m, 2H), 1.27 – 1.18 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.54, 156.54, 155.99, 141.33, 140.73, 140.20, 132.72, 130.78, 130.19, 129.40, 129.14, 128.96, 128.91, 128.89, 128.64, 52.16, 35.47, 30.45, 22.53, 13.77; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_2^+$: 321.1598 (M^++H), found: 321.1595

Methyl 2-(3-(phenylethynyl)quinoxalin-2-yl)benzoate (**8c**) (yellow brown solid, 40.8 mg, 56%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.08 (m, 3H), 7.85 – 7.70 (m, 3H), 7.69 – 7.60 (m, 2H), 7.40 – 7.27 (m, 5H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.04, 157.02, 140.89, 140.28, 139.38, 139.26, 132.59, 132.14, 131.01, 130.46, 130.36, 130.22, 130.09, 129.54, 129.38, 129.21, 128.94, 128.35, 121.32, 95.03, 87.15, 52.23; HRMS (ESI) calcd for $C_{24}H_{17}N_2O_2^+$: 365.1285 (M^++H), found: 365.1290

Methyl 2-(6,7-dimethyl-2-phenylquinoxalin-3-yl)benzoate (**8d**) (yellow brown solid, 54.5 mg, 74%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.89 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.47 – 7.36 (m, 3H), 7.31 – 7.20 (m, 3H), 3.48 (s, 3H), 2.51 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.01, 153.30, 152.72, 140.93, 140.43, 140.43, 140.26, 139.77, 138.53, 132.17, 131.23, 130.51, 130.12, 129.69, 128.53, 128.52, 128.35, 128.14, 127.94, 52.04, 20.45; HRMS (ESI) calcd for $C_{24}H_{21}N_2O_2^+$: 369.1598 (M^++H), found:369.1601

Methyl 2-(6,7-dichloro-3-phenylquinoxalin-2-yl)benzoate (**8e**) (Brick red solid, 57.1 mg, 70%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.25 (s, 1H), 7.87-7.85 (m, 1H), 7.63-7.56 (m, 1H), 7.56-7.47 (m, 2H), 7.38-7.31 (m, 2H), 7.26-7.24 (m, 3H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.65, 155.69, 154.86, 140.23, 140.10, 139.56, 137.58, 134.32, 134.12, 132.51, 131.00, 130.23, 130.20, 129.95, 129.74, 129.69, 129.23, 128.05, 52.18; HRMS (ESI) calcd for $C_{22}H_{15}Cl_2N_2O_2^+$: 409.0505 (M^++H), found: 409.0510
Methyl 2-(3-phenylbenzo[g]quinoxalin-2-yl)benzoate (**8f**) (Brick red solid, 53.8 mg,)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.72 (s, 1H),8.11-8.10 (m, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.67-7.66 (m, 2H), 7.56-7.47 (m, 2H), 7.47-7.45 (m, 3H), 7.28-7.25 (m, 3H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

166.78, 155.43, 154.48, 140.93, 138.32, 137.61, 134.02, 133.87, 132.52, 131.11, 130.32, 129.73, 128.98, 128.92, 128.51, 127.97, 127.69, 127.48, 126.72, 126.69, 52.12; HRMS (ESI) calcd for $C_{26}H_{19}N_2O_2^+$: 391.1441 (M^++H), found:391.1441

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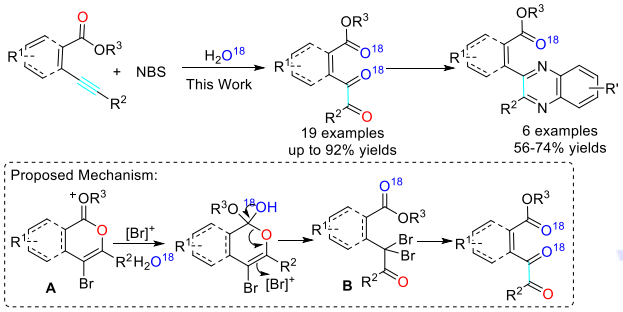
UPDATE

NBS-Mediated Oxygen Transfer Reaction of Carbonyl in Ester: Efficient Synthesis of Benzil-*o*-carboxylate Derivative From *o*-Alkynylbenzoate



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