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Substituent Effect in the Synthesis of α,α-Dibromoketones, 1,2-Dibromalkenes, and 1,2-Diketones from the Reaction of Alkynes and Dibromoisocyanuric Acid

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Abstract. Internal alkynes reacted with dibromoisocyanuric acid/H_2O to afford α,α-dibromoketone and 1,2-diketone derivatives. Diarylalkynes with activating groups provided 1,2-diketone derivatives as the major products, whereas diarylalkynes with a non-activating group or alkylarylalkynes gave α,α-dibromoketone derivatives as the major products. In addition, diarylalkynes with deactivating groups provided 1,2-dibromoalkenes. The reaction was conducted at room temperature and showed good yields in most cases. Reaction pathways have been proposed on the basis of experimental observations and density functional theory (DFT) calculations.
Keywords: α,α-dibromoketones, 1,2-dibromoalkene, 1,2-diketone, alkyne, DFT calculation

Introduction

Alkynes are one of the most efficient starting materials as a result of their versatility in transformations and their usefulness as building blocks in the preparation of bioactive and functional materials. Many efficient synthetic methods using an alkyne as a starting material have been developed.[1] Among them, α,α-dibromoketones have been generally prepared through the dibromohydration of alkynes. The method has been developed to allow potassium bromide,[2] 1,3-dibromo-5,5-dimethylhydantoin,[3] and *N*,*N*-dibromo-*p*-toluenesulfonamide[4] to be employed as bromine sources in the presence of water for the preparation of α,α-dibromoketones. However, these reactions showed few examples of the formation of 2,2-dibromo-1,2-diarylethanones. Fu and coworkers reported that a mixture of α,α-dibromoketones and 1,2-diketones was formed in the reaction of alkynes and *N*-bromosuccinimide/H_2O.[5]

1,2-Diketones have attracted interest from organic chemists because they can be readily transformed into useful building blocks such as heterocyclic compounds.[6] A number of methods to synthesize 1,2-diketones have been developed from the reactions of alkynes. Metal-free synthetic methods for 1,2-diketones have been accomplished by using iodine,[7] photo-induced aerobic oxidation,[8] mercury salts,[9] water/SO_3,[10] *N*-iodosuccinimide/dimethyl sulfoxide (DMSO),[5] and oxone.[11]

1,2-Dibromoalkene derivatives have been used as coupling partners for the synthesis of conjugated functional materials, such as field effect transistors. They can be generally prepared through the bromination of alkynes with reagents like NaBr–$NaBrO_3$,[12] HBr/$NaNO_2$,[13] $KHSO_5$/NaBr,[14] tetrabutylammonium tribromide,[15] and tridecylmethylphosphonium tribromide.[16]

Previously, we reported the synthesis of 2,2-dichloro-1,2-diarylethanones from the reaction of diarylalkynes and trichloroisocyanuric acid (TCCA), and we provided a number of examples.[17] We also showed that these compounds could be prepared from aryl bromides and propiolic acid via sequential Pd-catalyzed decarboxylative coupling and chlorination. In addition, alkynoic acid reacted with TCCA to give trichloroacetophenone derivatives.[18] To expand the scope of this type of reaction, we attempted to employ dibromoisocyanuric acid (DBCA) as a brominating reagent. We also developed the selective synthesis of tribromovinyl and tribromomethyl ketone groups by the reaction of alkynoic acids and DBCA.[19] During studies of the reaction with DBCA and diarylalkynes, we found that three different products were generated, viz. α,α-dibromoketones, 1,2-diketones, and 1,2-dibromoalkenes. The obtained products are highly dependent on the substituent on the aryl ring of the

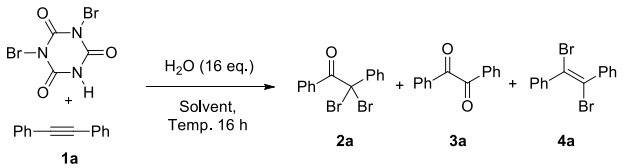
10.1002/adsc.201801535

alkyne. Herein, we report our studies of the synthesis of these three different products from the reaction of diarylalkynes with DBCA/H_2O.

Results and Discussion

To study the formation of dibrominated products, diphenylacetylene was chosen as a model substrate. DBCA was allowed to react with diphenylacetylene in the presence of H_2O (16.0 eq.). The results are summarized in Table 1. As expected, the reaction in CH_3CN gave α,α-dibromoketone **2a** in 80% yield. In addition, 1,2-diketone **3a**, which is benzil, was also found in 5% yield (entry 1). When the reaction was conducted in DMF or NMP, **2a** was formed as the major product; however, the yields of product were lower than those obtained in CH_3CN (entries 2 and 3). No **2a** was found when the reaction was carried out in DMSO and toluene; in these cases, small amounts of 1,2-dibromoalkene **4a** were found (entries 4 and 5). When the reaction temperature was increased to 50 °C or 75 °C, the yields of **3a** increased to 15% and 25%, respectively (entries 6 and 7). We then decided to increase the amount of DBCA to 2 equivalents. The reaction at 25 °C gave **3a** in 38% yield (entry 8). When this reaction was allowed to proceed at 75 °C, the yield of **3a** was increased to 65% (entry 9).

Table 1. Optimized conditions for the reaction with diphenylacetylene and DBCA/H_2O.[a]



Entry	DBCA (eq.)	Temp. (°C)	Solvent	Yield (%)[b]		
				2a	**3a**	**4a**
1	1.0	25	CH_3CN	80	5	ND
2	1.0	25	DMF	64	4	ND
3	1.0	25	NMP	52	8	6
4	1.0	25	DMSO	ND	ND	5
5	1.0	25	Toluene	ND	ND	4
6	1.0	50	CH_3CN	69	15	ND
7	1.0	75	CH_3CN	60	25	ND
8	2.0	25	CH_3CN	ND	38	ND
9	2.0	75	CH_3CN	ND	65	ND
10[c]	1.0	25	CH_3CN	72	4	ND
11	1.0	25	H_2O	45	ND	ND

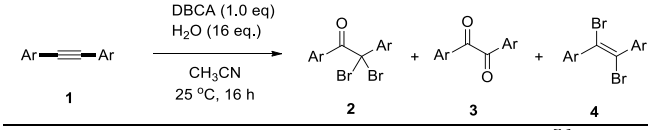
[a] Reaction conditions: **1a** (0.5 mmol), DBCA (0.5 mmol or 1 mmol), and H_2O (8.0 mmol) were mixed in the solvent (1.5 mL) for 16 h. DMF = *N*,*N*-dimethylformamide; NMP = *N*-methylpyrrolidine; DMSO = dimethylsulfoxide. [b] Determined by gas chromatography and ^1H NMR spectroscopy. ND = not detected. [c] H_2O (12.0 eq.) was used.

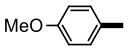
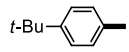
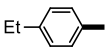
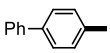
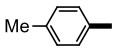
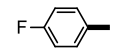
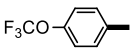
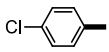
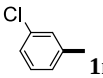
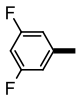
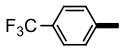
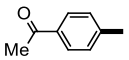
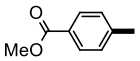
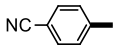
When the amount of water was decreased to 12.0 equivalents, the yield of **2a** decreased to 72% (entry 10). The reaction at water provided **2a** with 45% yield (entry 11). Based on these results, we found that the α,α-dibromoketone can be obtained from the reaction with 1 equivalent of DBCA at 25 °C and the 1,2-diketone can be obtained from the reaction with 2 equivalents of DBCA at 75 °C. It is noteworthy that unsatisfactory results were obtained when other conditions such as Br_2/H_2O, HBr/H_2O_2 and $NaBrO_3/NaBr/H_2SO_4$ were employed instead of DBCA. (See Supporting Information Table S1)

Next, we studied the effects of the diarylalkyne substituents in the reaction with DBCA/H_2O, as shown in Table 2. Diphenylacetylene provided **2a** and **3a** with 80% and 5% yields, respectively (entry 1). However, the 4-methoxy-, 4-*tert*-butyl-, and 4-ethyl-substituted diphenylacetylenes gave only 1,2-diketones **3b**, **3c**, and **3d**, in 45%, 92%, and 89% yields, respectively (entries 2–4). In addition, the reaction with the 1,1'-biphenyl- and 1-naphthyl-substituted diarylalkynes also provided only 1,2-diketones **3e** and **3f**, in 82% and 65% yields, respectively (entries 5 and 6). In the case of the tolyl-substituted diarylalkynes, the *para*-substituted one produced **3g** with 75% yield, and the *meta*-substituted one provided **3h** as the major product with **2h** as a minor product; however, the *ortho*-substituted one afforded α,α-dibromoketone **2i** as the major product with **3i** as a minor product (entries 7–9). 4-Fluoro-substituted diphenylalkyne gave **3j** and **2j** with 45% and 20% yields, respectively (entry 10). 4-Trifluoromethoxy- and 4-chloro-substituted diphenylalkynes gave α,α-dibromoketones **2k** and **2l** as the major products (entries 11 and 12). In the reaction with the 3-chloro-, 3,5-difluoro-, and 4-trifluoromethyl-substituted diphenylalkynes, the α,α-dibromoketones were still the major products; however, the 1,2-dibromoalkenes **4m**, **4n**, and **4o** were also formed, in 29%, 30%, and 35% yields, respectively (entries 13–15). 4-Acetyl-substituted diphenylalkyne provided **2p** as the major product; interestingly, 1,2-dibromalkene **4p** was also formed in 20% yield (entry 16). 4-Methyl ester and 4-cyano-substituted diphenylalkynes gave only 1,2 dibromoalkenes **4q** and **4r**, in 55% and 65% yields, respectively (entries 17 and 18). 2- and 3-Pyridinyl-substituted diarylalkynes provided only 1,2-dibromoalkenes **4s** and **4t** in good yields (entries 19 and 20). When 1,2-di(thiophen-2-yl)ethyne was treated with DBCA/water, it did not give any desired product. However, the mixture of (*E*) and (*Z*)-1,2-dibromo-1,2-bis(5-bromothiophen-2-yl)ethenes were found with 40% yield (entry 21).

10.1002/adsc.201801535

Table 2. Reaction with diarylalkynes and DBCA/H_2O.[a]

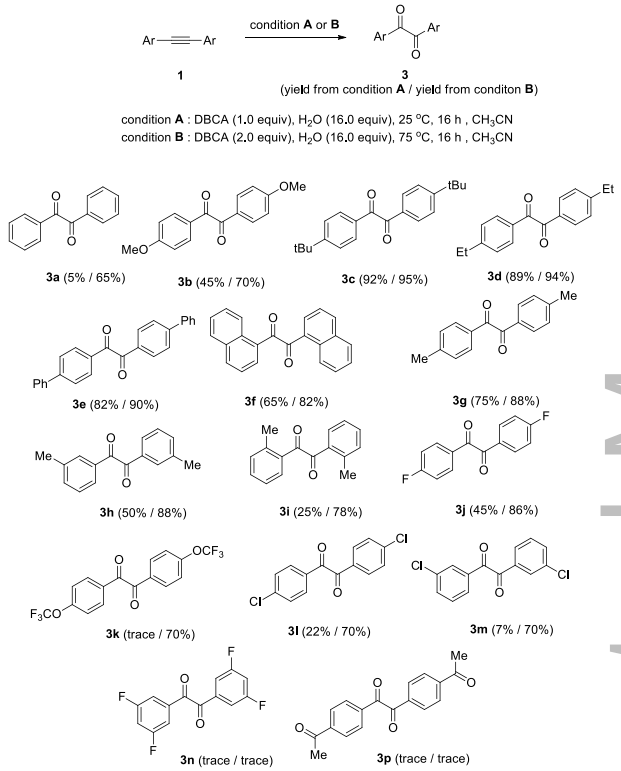


Entry	Ar	Product: Yield (%)[b]		
1	 **1a**	**2a**: 80	**3a**: 5	**4a**: trace
2	 **1b**	**2b**: ND	**3b**: 45	**4b**: ND
3	 **1c**	**2c**: ND	**3c**: 92	**4c**: ND
4	 **1d**	**2d**: ND	**3d**: 89	**4d**: ND
5	 **1e**	**2e**: ND	**3e**: 82	**4e**: ND
6	 **1f**	**2f** : ND	**3f**: 65	**4f**: ND
7	 **1g**	**2g**: trace	**3g**: 75	**4g**: trace
8	 **1h**	**2h**: 35	**3h**: 50	**4h**: ND
9	 **1i**	**2i**: 45	**3i**: 25	**4i**: ND
10	 **1j**	**2j**: 20	**3j**: 45	**4j**: ND
11	 **1k**	**2k**: 61	**3k**: ND	**4k**: ND
12	 **1l**	**2l**: 55	**3l**: 22	**4l**: trace
13	 **1m**	**2m**: 52	**3m**: 7	**4m**: 29[c]
14	 **1n**	**2n**: 40	**3n**:trace	**4n**: 30
15	 **1o**	**2o**: 40	**3o**: ND	**4o**: 35
16	 **1p**	**2p**: 54	**3p**: ND	**4p**: 20
17	 **1q**	ND	ND	**4q**: 55
18	 **1r**	ND	ND	**4r**: 65
19	 **1s**	ND	ND	**4s**: 63
20	 **1t**	ND	ND	**4t**: 71
21	 **1u**	ND	ND	ND

[a] Reaction conditions: **1** (1.5 mmol), DBCA (1.5 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN at 25 °C for 16 h. [b] Isolated yield. [c] The mixture of *E* and *Z* isomers (ratio is 3:1). ND = not detected.

Based on these results, we found that the following substituents on the phenyl groups of diarylalkynes afforded the corresponding dibromoketones: 2-methyl, 3-methyl, 4-fluoro, 4-trifluoromethyl, 4-chloro, 3-chloro, 2,4-difluoro, trifluoromethyl, and acetyl groups. However, diarylalkynes bearing highly activating groups, such as 4-methoxy, 4-alkyl, 4-phenyl- and naphthyl substituents, afforded only 1,2-diketone products. In the case of diarylalkynes with deactivating groups, such as ester, cyano, and pyridine substituents, the 1,2-dibromoalkenes were formed as the major products.

Scheme 1. Synthesis of 1,2-diketones from diarylalkynes.[a]



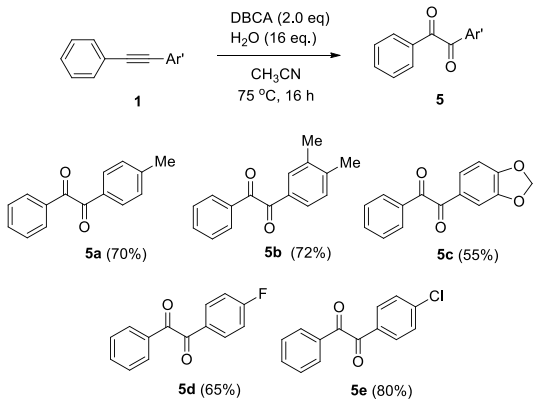
[a] Reaction conditions **A**: **1** (1.5 mmol), DBCA (1.5 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN at 75 °C for 16 h. Reaction conditions **B**: **1** (1.5 mmol), DBCA (3.0 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN at 75 °C for 16 h.

In order to obtain 1,2-diketone derivatives from diarylalkynes, we employed 2.0 equivalents of DBCA for the reaction with symmetrical diarylalkynes. The results are summarized in Scheme 1. We employed two different conditions: Conditions **A** refer to the reaction performed in the presence of 1 equivalent of DBCA at 25 °C, and conditions **B** refer to the use of 2 equivalents of DBCA at 75 °C. In all cases, the yields of 1,2-diketone derivatives were higher under conditions **B** than those under condition **A**. Methyl-

substituted diarylalkynes gave good yields; in particular, the *ortho*-substituted alkyne produced a much higher yield under conditions **B** than that under conditions **A**. Diarylalkynes such as **1j**, **1k**, **1l**, and **1m**, which showed low yields for the formation of 1,2-diketones under conditions **A**, afforded the corresponding 1,2-diketones with good yields under conditions **B**. However, unfortunately, in case of diarylalkynes with difluoro or acetyl groups, such as **1n** and **1p**, no 1,2-diketone products were obtained under conditions **B**. It is noteworthy that only symmetrical diarylalkynes which did not provide the 1,2-dibromoalkene in Table 2 except **1m** afforded the 1,2-diketone. From these results, we found that the formation of 1,2-diketone might highly dependent on the function group of substituent.

To expand this methodology, unsymmetrically substituted diarylalkynes were also allowed to react with 2 equivalents of DBCA in the presence of H_2O. As shown in Scheme 2, most cases showed good yields in the formation of 1,2-diketones.

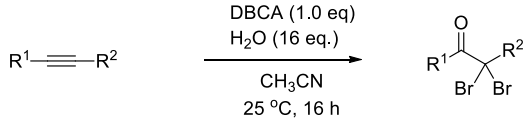
Scheme 2. Synthesis of 1,2-diketones from unsymmetrically substituted diarylalkynes.[a]



[a] Reaction conditions: **1** (1.5 mmol), DBCA (3.0 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN at 75 °C for 16 h.

When alkyl-substituted alkynes, such as hept-1-yn-1-ylbenzene and pent-1-yn-1-ylbenzene were employed under conditions **A**, α,α-dibromoketones **7a** and **7b** were predominantly formed. No 1,2-diketone products were formed, even under conditions **B**. Additional discussion about possible reason of regioselectivities of α,α-dibromoketones for alkyl-substituted arylalkynes, such as **7a** and **7b**, was added in Supporting Information (Table S4). We also found that dialkyl-substituted alkynes, such as 5-decyne, 4-octyne and 3-hexyne afforded the corresponding α,α-dibromoketones **7c, 7d** and **7e** with good yields.

Scheme 3. Reaction with alkyl-substituted alkynes and DBCA/H_2O.[a]



6a: R^1 = *n*-Pentyl, R^2 = Ph
6b: R^1 = *n*-Propyl, R^2 = Ph
6c: R^1, R^2 = *n*-Butyl
6d: R^1, R^2= *n*-Propyl
6e: R^1, R^2= Ethyl

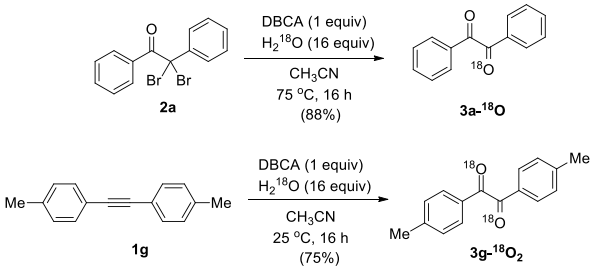
7a: R^1 = *n*-Pentyl, R^2 = Ph (72%)
7b: R^1 = *n*-Propyl, R^2 = Ph (65%)
7c: R^1, R^2 = *n*-Butyl (79%)
7d: R^1, R^2= *n*-Propyl (77%)
7e: R^1, R^2= Ethyl (76%)

[a] Reaction conditions: **6** (1.5 mmol), DBCA (1.5 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN at 25 °C for 16 h.

When phenylacetylene and 1,4-diphenylbuta-1,3-diyne were treated under condition A, phenylacetylene afforded $PhCOCHBr_2$ with 65% yield[3] and 1,4-diphenylbuta-1,3-diyne provided the (Z)-2,3-dibromo-1,4-diphenylbut-2-ene-1,4-dione along with its (E)-isomer (42% yield, (Z)/(E) = 7.7/1).[20]

It was found in a previous report that the oxygen atom of the ketone in the α,α-dichloroketone products came from H_2O. Therefore, we studied the reaction pathway and the oxygen source for the diketones. To accomplish our goals, we employed $H_2{}^{18}O$, instead of $H_2{}^{16}O$. The α,α-dibromoketone **2a** was treated with $H_2{}^{18}O$ at 75 °C to give 1,2-diketone **3a**-^{18}O, which has one oxygen-18 atom and a molecular mass of 212.0719; this mass corresponds to $C_{14}H_{10}{}^{16}O{}^{18}O$ (m/z calculated for $[M]^+$: 212.0723). The reaction with 1,2-di-*para*-tolylethyne (**1 g**) and $H_2{}^{18}O$ showed the mass peak for **3g**-$^{18}O_2$ bearing two oxygen-18 atoms; a molecular mass of 242.1073 was observed, which corresponds to $C_{16}H_{14}{}^{18}O_2$ (m/z calculated for $[M]^+$: 242.1079). From these results, we found that all of the oxygen atoms of the ketones come from the H_2O. In addition, the α,α-dibromoketone might be an intermediate for the formation of 1,2-diketones.

Scheme 4. Reaction with $H_2{}^{18}O$.

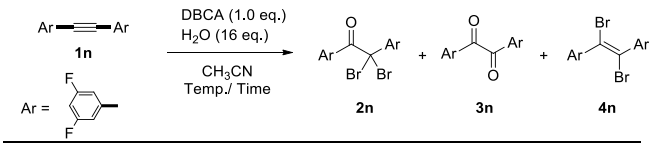


Next, we studied different reactivities in the formation of α,α-dibromoketones and 1,2-dibromoalkenes. Diarylalkyne **1n** was chosen and subjected to different reaction temperatures. The

10.1002/adsc.201801535

results are summarized in Table 3. When the reaction was conducted at 0 ° C, only 1,2-dibromoalkene **4n** was formed, with 20% yield, after 3 h; **4n** was still the major product even after 16 h. When the reaction temperature was increased to 50 °C and 80 °C, α,α-dibromoketone **2n** was the major product at 3 h and 16 h. In addition, 1,2-diketone **3n** was also found at the high reaction temperatures, although the yield was very low.

Table 3. Temperature control.[a]

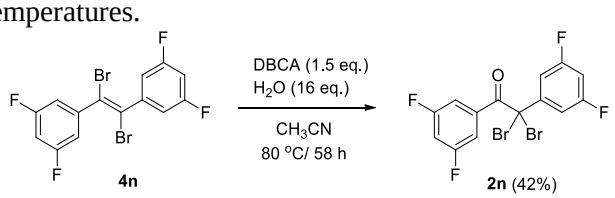


Entry	Temp. (°C)	Time (h)	Yield (%)		
			2n	**3n**	**4n**
1	0	3	ND	ND	20
2	0	16	10	ND	25
3	50	3	30	4	30
4	50	16	49	5	42
5	80	3	44	5	41
6	80	16	52	5	45

[a] Reaction conditions: **1n** (1.5 mmol), DBCA (1.5 mmol), and H_2O (24.0 mmol) were mixed in CH_3CN.

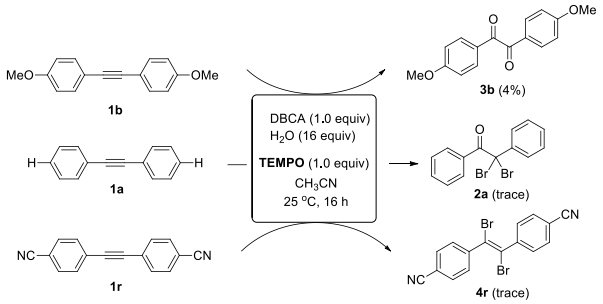
In addition, it was found that α,α-dibromoketone **2n** was formed with 42% yield when 1,2-dibromoalkene **4n** was treated with DBCA/H_2O at 80 °C for 58 h. Based on these results, we suggest that the formation of 1,2-dibromoalkenes might be favored at low temperatures and the formation of α,α-dibromoketone might be favored at high temperatures.

Scheme 5. Reaction of **4n** with DBCA/H_2O at high temperatures.



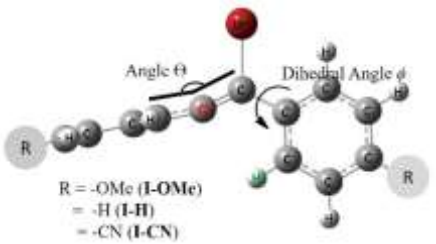
To study the reaction pathway, we chose three substrates and treated them with DBCA/H_2O in the presence of a radical scavenger. Diaryl alkyne **1b**, with methoxy substituents, was chosen as a representative substrate with an activating group because diketone **3b** was formed as the major product. Diaryl alkyne **1r**, with nitrile substituents, was chosen as a representative substrate with a deactivating group because dibromoalkene **4r** was formed as the major product. Diphenyl acetylene (**1a**) was chosen as a representative substrate that provides α,α-dibromoketone **2a** as the major product. As a radical scavenger, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was chosen. As shown in Scheme 6, the desired products were formed with very low yields when the reactions were conducted in the presence of TEMPO. These results support the idea that a radical pathway might be predominant in all cases.

Scheme 6. Reactions with TEMPO



In order to shed light on the reason for the substituent effect yielding different major products, density functional theory (DFT) calculations were carried out for the three representative substrates (**1b**, **1a**, and **1r**). As mentioned and proved by the TEMPO experiments, a radical reaction pathway might be predominant. Thus, we supposed that vinyl bromide radical intermediates might first be generated by the adduction of a Br radical in all reactions, regardless of the type of substituent. By scrutinizing the calculated optimized geometries and their molecular energies for these radical intermediates, we realized that two geometrical variables, i.e., angle Θ and dihedral angle ϕ, can determine the total molecular energy for the vinyl bromide radical intermediates (Scheme 7).

Scheme 7. Schematic representation of angle Θ and dihedral angle ϕ for the vinyl bromide radical intermediates (**I-OMe**, **I-H**, and **I-CN**, with R = OMe, H, and CN, respectively).[a]

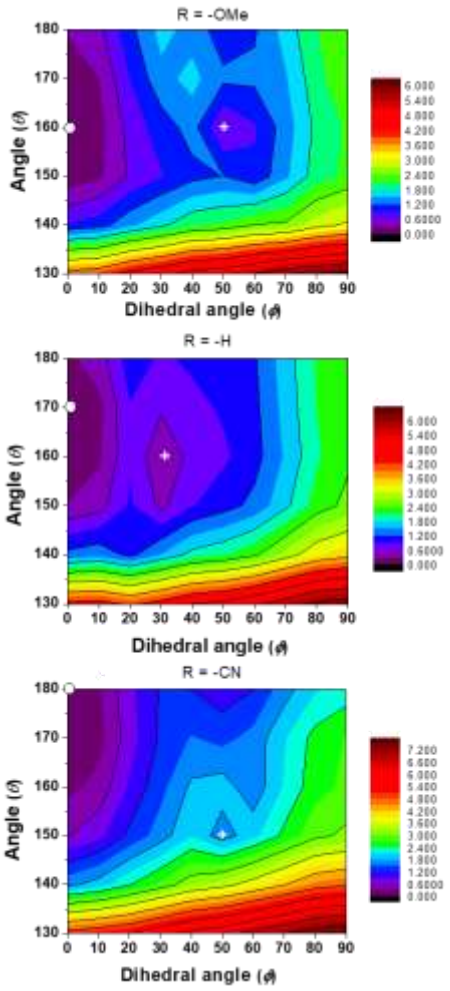


[a] The carbon atom denoted by the red C* can react with a Br radical (•Br) or hydroxyl radical (•OH) in the next reaction step. The hydrogen atom denoted by H# might cause steric hindrance in subsequent radical reactions.

The two-dimensional potential energy surfaces (2D-PES) of the three representative vinyl bromide radical intermediates (**I-OMe**, **I-H**, and **I-CN**)

according to angles Θ and dihedral angles ϕ are depicted in Figure 1.

Figure 1. 2D-PES according to angles Θ and dihedral angles ϕ for three representative vinyl bromide radical intermediates (**I-OMe**, **I-H**, **and I-CN**).[a]



[a] The global minimums and noticeable local minimums are denoted by white circles and white crosses, respectively. The unit of energy scale is kcal/mol.

It was found that the global minimums of **I-OMe**, **I-H**, and **I-CN** have different angles, i.e., 160°, 170°, and 180°, respectively, as denoted by the white circles in Figure 1. It is reasonable that smaller angles Θ of C* atoms, near 120°, might have better reactivity, based on the concept of sp^2 hybridization. This would be in line with changes of the reactivity of these radical intermediates depending on the types of substitution, such as activating groups (OMe) and deactivating groups (CN), on the basis of the H group, just by considering angle Θ for the global minimums. On the other hand, the dihedral angles ϕ of the global minimums are expected to be similar at around 0°. This indicates that energetically the C* atom and H# atom of the benzene ring (shown in Scheme 7) tend to be located on the same plane. Therefore, it is possible that the H# atom would become a substantial steric factor disturbing adduction of another radical to the C* atom of the vinyl bromide radical intermediate in the next reaction step, especially for global minimums.

We then postulated that a hydroxyl radical (•OH) or bromine radical (•Br) will competitively react with the vinyl bromide radical intermediates to form the next intermediate or final product. From scan calculations, along with the different lengths depicted in Figure S1 in the Supporting Information, it was found that the optimized bond lengths between vinyl bromide radical intermediates and •OH are shorter than those with •Br by 0.53 Å. Thus, adduction of •OH requires closer approach to the C* atoms of vinyl bromide radical intermediates than that of •Br. Herein, we propose that the H# atom can cause more significant steric hindrance for the deeper approach of •OH than that of •Br to the vinyl bromide radical intermediates. Therefore, it is probable that adduction of •Br might be favorable because of the steric factor resulting from the H# atom. This kind of reaction pathway might be connected to the formation of 1,2-dibromoalkene **4r** as the major product for **I-CN**.

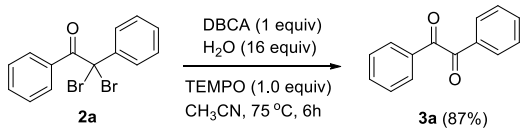
To explain how other major products, such as the α,α-diketone of **I-OMe** and α,α-dibromoketone of **I-H** were obtained in our synthesis, we tried to search the singularity of **I-CN** in comparison with **I-OMe** and **I-H**. Interestingly, it was found that **I-OMe** and **I-H** have considerably stable local minimums, with a dihedral angle ϕ larger than 0°, as denoted by the white crosses in Figure 1. By using a (ϕ, Θ) notation, these points can be marked as (50°, 160°) and (30°, 160°) for **I-OMe** and **I-H**, respectively. Those local minimums are energetically higher than each of the global minimums by 0.60 kcal/mol and 0.36 kcal/mol, respectively, and can be thermodynamically accessible at room temperature. As the dihedral angle ϕ becomes larger, the steric hindrance of the H# atom would be effectively reduced by distortion of the benzene ring, and approach of •OH to the C* atom then becomes much easier. In this context, it may be reasonable to suppose that such considerably stable local minimums for **I-OMe** and **I-H** might contribute to open up a new reaction pathway for adduction of •OH. We also assumed that the O atom of •OH will be a source of O atoms for final products such as 1,2-diketone for **I-OMe** and α,α-dibromoketone for **I-H**. The details of the overall reaction mechanism are discussed in the last paragraph.

By contrast, **I-CN** also has a local minimum point of (50°, 160°), depicted in Figure 1. However, this local minimum is energetically much higher than its global minimum (by 1.63 kcal/mol), which indicates a thermodynamically small population of this local minimum state at room temperature. Consequently, the reaction pathway for adduction of •OH might be blocked for **I-CN** relative to that with **I-OMe** and **I-H**.

The driving force of •OH adductions can be explained by the calculated binding energies. (see Table S3 in the Supporting Information.) For all three representative cases (**I-OMe**, **I-H**, and **I-CN**), the binding energies of •OH are higher than those of •Br by around 18 kcal/mol. This indicates that adduction of •OH would be favorable from the thermodynamic aspect. The data in Table 3 might provide evidence that the population of products related with the adduction of •OH, such as 1,2-diketone and α,α-dibromoketone, may be steadily increased under thermodynamic control.

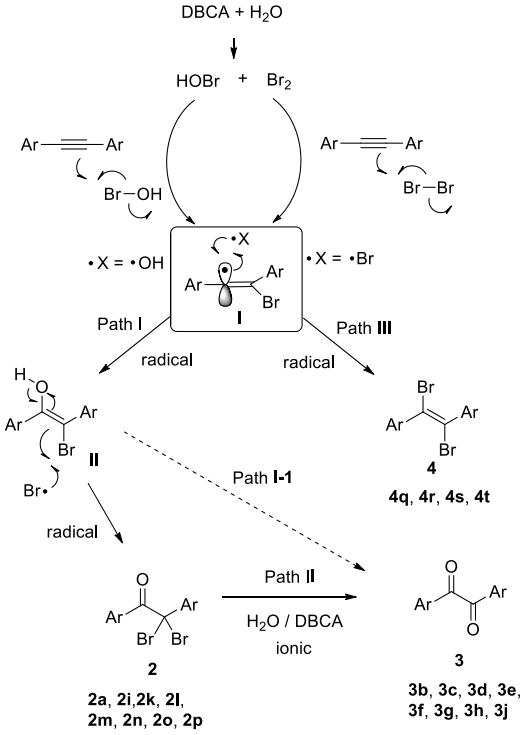
However, we found that the reaction pathway from **2a** to **3a** might be an ionic pathway because **3a** was formed in 87% yield even in the presence of TEMPO.

Scheme 8. Reaction of **2a** with TEMPO for the formation of **3a**.



Finally, we suggest the possible overall reaction pathway. It is known that HOBr is generated rapidly from the reaction of DBCA and H_2O. In addition, we demonstrated that Br_2 was also generated from the reaction of DBCA and H_2O in our previous report on the formation of tribromovinyl derivatives. Based on previous results and our control experiment results, we suggest that the reaction pathways are highly dependent on the substituents of the aryl groups in the diarylalkynes. We propose the reaction pathway shown in Scheme 9. The diarylalkynes react with HOBr or Br_2 to give vinyl bromide radical (**I**) as an intermediate. The intermediate then reacts with hydroxide radical to give 1,2-diaryl-2-bromoethenol (**II**) and this is followed by further bromination to afford α,α-dibromoketone **2** through radical pathway. However, diarylalkynes bearing activating functional groups, such as methoxy or alkyl groups, further react with H_2O in the presence of DBCA to afford 1,2-diketone **3** (**Path II**)[21] through ionic pathway. We do not rule out the direct pathway (**Path I-1**) for the formation of 1,2-diketones. Regarding substituente effect on the selectivity of mjor products between α,α-dibromoketone **2** and 1,2-diketone **3**, we simply supposed that an activating functional group might induce considerable stabilization to the adjacent ketone moiety, because a ketone is one of electron withdrawing groups whereas an activating functional group is one of electron donating groups. By extending this concept, we proposed that diarylalkynes bearing activating groups might afford 1,2-diketone **3** due to its higher thermodynamic stability compared with a non-activating group case. The DFT calculation results shown in Scheme S1 and Table S5 in Supporting Information can support our assumption by comparing the realtive stabilities of **2** (or **3**) for two representative diarylalkynes with an activating group (OMe) and a non-activating group (H). In the case of diarylalkynes bearing deactivating groups, such as pyridinyl, ester, and cyano groups, intermediate I reacts with bromo radical to give 1,2-dibromoalkene **4**. Although we have proposed the radical pathway in this mechanism, we do not rule out an ionic pathway.

Scheme 9. Proposed reaction pathways.



Conclusion

In summary, we studied the reaction of diarylalkynes with DBCA/H_2O. We found that DBCA works as both oxidant and bromide source and reacts with arylalkynes in the presence of water to provide three different products, namely α,α-dibromoketones, 1,2-diketones, and 1,2-dibromoalkenes. We have proposed vinyl bromide radical (**I**) as a key intermediate, and the reaction pathways are highly dependent on the substituents of the aryl groups in the diarylalkynes. DFT calculations for three representative vinyl bromide radicals also revealed that the most favorable reaction pathway between adductions of •OH and •Br might be changeable according to the type of substituent. It was found that the oxygen atoms of ketones in the products come from water, on the basis of experiments with $H_2{}^{18}O$. The reaction conditions are mild and showed good yields in most cases. In addition, 1,2-diketone derivatives were obtained with high yields when

conditions **B** (2 equivalents of DBCA, 75 °C) were employed. In particular, unsymmetrically substituted alkynes were also successfully converted into 1,2-diketone derivatives

Experimental Section

General Experimental Procedure (**Conditions A**)

Diarylalkyne (or alkyl-substituted alkyne) (1.5 mmol, 1.0 equiv), dibromoisocyanuric acid (430 mg, 1.5 mmol, 1.0 equiv), and water (432 mg, 24.0 mmol, 16.0 equiv) were added to acetonitrile (5.0 mL) in a 20-mL screw cap vial, which was then closed tightly. The solution was stirred at 25 °C for 16 h. The resulting mixture was placed in a separating funnel, water and 10% sodium thiosulphate were added, and the mixture was extracted with EtOAc. The separated organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the EtOAc under vacuum, the crude product was purified by column chromatography on a silica gel column with n-hexane/ethyl acetate as the eluent to obtain the desired product.

General Experimental Procedure (**Conditions B**)

Diarylalkyne (1.5 mmol, 1.0 equiv), dibromoisocyanuric acid (860 mg, 3.0 mmol, 2.0 equiv), and water (432 mg, 24.0 mmol, 16.0 equiv) were added to acetonitrile (7.0 mL) in a 20-mL screw cap vial, which was then closed tightly. The solution was stirred at 75 °C for 16 h. The resulting mixture was placed in a separating funnel, water and 10% sodium thiosulphate were added, and the mixture was extracted with EtOAc. The separated organic layer was washed with water and dried over anhydrous $MgSO_4$. After removal of the EtOAc under vacuum, the crude product was purified by column chromatography on a silica gel column with n-hexane/ethyl acetate as the eluent to obtain the desired product.

2,2-Dibromo-1,2-diphenylethanone (2a) [5]

1,2-Diphenylethyne (267 mg, 1.5 mmol) afforded **2a** (424 mg, 1.2 mmol, 80% yield); white solid, mp 109.5-110.2 °C (lit. 112-113 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dt, *J* = 8.7, 1.5 Hz, 2H), 7.64 (m, 2H), 7.43 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.37 (m, 2H), 7.33 (m, 1H) 7.26 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.1, 140.9, 133.1, 131.4, 130.7, 129.6, 128.9, 128.0, 126.6, 69.5; MS (EI) *m/z* = 351 (M^+).

2,2-Dibromo-1,2-di-*m*-tolylethanone (2h)

1,2-Di-*m*-tolylethyne (309 mg, 1.5 mmol) afforded **2h** (200 mg, 0.52 mmol, 35% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, *J* = 1.7 Hz, 1H), 7.47 (dd, *J* = 2.1, 1.5 Hz, 1H), 7.41 (ddd, *J* = 7.9, 1.1, 0.6 Hz, 1H), 7.38 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1H), 7.25 (m, 1H), 7.24 (m, 1H), 7.14 (dt, *J* = 7.5, 0.6 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.4, 140.8, 138.8, 137.9, 133.8, 131.8, 130.8, 130.4, 128.7, 128.5, 127.6, 127.1, 123.7, 70.0, 21.4, 21.3; HRMS (FD) m/z calcd for $C_{16}H_{14}Br_2O$ (M^+): 379.9412, found: 379.9409.

2,2-Dibromo-1,2-di-*o*-tolylethanone (2i)

1,2-Di-*o*-tolylethyne (309 mg, 1.5 mmol) afforded **2i** (257 mg, 0.67 mmol, 45% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.34 (td, *J* = 7.7, 1.0 Hz, 1H), 7.29 (td, *J* = 7.4, 1.4, 1H), 7.26 (m, 1H), 7.25 (m, 1H), 7.07 (dd, *J* = 7.2, 0.6 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.81 (m, 1H), 2.60 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.5, 141.5, 138.3, 135.1, 132.3, 132.2, 131.8, 131.0, 130.0, 129.1 (2C), 126.9, 124.5, 75.2, 22.1, 21.1; HRMS (FD) m/z calcd for $C_{16}H_{14}Br_2O$ (M^+): 379.9411, found: 379.9420.

2,2-Dibromo-1,2-bis(4-fluorophenyl)ethanone (2j)

1,2-Bis(4-fluorophenyl)ethyne (321 mg, 1.5 mmol) afforded **2j** (117 mg, 0.3 mmol, 20% yield); white solid, mp 75.1-76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.63 (m, 2H), 7.07 (m, 2H), 6.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 165.4 (d, J_{C-F} = 258.3 Hz), 162.9 (d, J_{C-F} = 253.2 Hz), 136.9 (d, J_{C-F} = 3.7 Hz), 134.3 (d, J_{C-F} = 10.0 Hz), 128.8 (d, J_{C-F} = 8.8 Hz), 126.6 (d, J_{C-F} = 2.5 Hz), 116.0 (d, J_{C-F} = 22.6 Hz), 115.4 (d, J_{C-F} = 21.4 Hz), 67.6; HRMS (FD) m/z calcd for $C_{14}H_8Br_2F_2O$ (M^+): 387.8910, found: 387.8914.

2,2-Dibromo-1,2-bis(4-(trifluoromethoxy)phenyl)ethanone (2k)

1,2-Bis(4-(trifluoromethoxy)phenyl)ethyne (519 mg, 1.5 mmol) afforded **2k** (477 mg, 0.91 mmol, 61% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.69 (m, 2H), 7.24 (m, 2H), 7.14 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 152.5 (d, J_{C-F} = 1.26 Hz), 149.8 (d, J_{C-F} = 1.26 Hz), 139.0, 133.5, 128.6, 128.5, 120.9 (d, J_{C-F} = 1.26 Hz), 120.2 (d, J_{C-F} = 259.5 Hz), 120.1 (d, J_{C-F} = 260.8 Hz), 119.6 (d, J_{C-F} = 1.26 Hz), 66.7; HRMS (FD) m/z calcd for $C_{16}H_8Br_2F_6O_3$ (M^+): 519.8744, found: 519.8744.

2,2-Dibromo-1,2-bis(4-chlorophenyl)ethanone (2l)

1,2-Bis(4-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **2l** (348 mg, 0.82 mmol, 55% yield); pale yellow solid; mp 99-100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.56 (dd, *J* = 8.8, 2.1 Hz, 2H), 7.36 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.28 (dd, *J* = 8.9, 2.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.7, 140.0, 139.3, 135.9, 132.8, 129.2, 128.7, 128.5, 128.1, 67.3; HRMS (FD) m/z calcd for $C_{14}H_8Br_2Cl_2O$ (M^+): 419.8313, found: 419.8320.

2,2-Dibromo-1,2-bis(3-chlorophenyl)ethanone (2m)

1,2-Bis(3-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **2m** (329 mg, 0.78 mmol, 52% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.74 (td, *J* = 2.0, 0.5 Hz, 1H), 7.54 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.45 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 7.42

(ddd, *J* = 7.4, 2.0, 1.5 Hz, 1H), 7.35 (m, 1H), 7.31 (m, 1H), 7.22 (td, *J* = 8.0, 0.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 142.1, 135.1, 134.5, 133.3, 132.1, 131.2, 130.2, 130.0, 129.4, 129.3, 127.1, 124.8, 66.5; HRMS (FD) m/z calcd for $C_{14}H_8Br_2Cl_2O$ (M^+): 419.8319, found: 419.8310.

2,2-Dibromo-1,2-bis(3,5-difluorophenyl)ethanone (2n)

1,2-Bis(3,5-difluorophenyl)ethyne (375 mg, 1.5 mmol) afforded **2n** (255 mg, 0.6 mmol, 40% yield); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.18 (m, 2H), 6.97 (tt, *J* = 8.3, 2.3 Hz, 1H), 6.86 (tt, *J* = 8.4, 2.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.2 (t, J_{C-F} = 2.52 Hz), 163.5 (dd, J_{C-F} = 252, 12.6 Hz), 161.5 (dd, J_{C-F} = 252, 12.6 Hz), 143.4 (t, J_{C-F} = 8.8 Hz), 133.1 (t, J_{C-F} = 8.8 Hz), 114.2 (dd, J_{C-F} = 21.2, 7.5 Hz), 110.6 (dd, J_{C-F} = 21.4, 7.5 Hz), 109.2 (t, J_{C-F} = 25.2 Hz), 105.7 (t, J_{C-F} = 25.2 Hz), 64.4; MS (EI) *m/z* = 423 (M^+); Anal. Calcd. for $C_{14}H_6Br_2F_4O$: C, 39.47; H, 1.42. Found : C, 39.12; H, 1.67.

2,2-Dibromo-1,2-bis(4-(trifluoromethyl)phenyl)ethanone (2o)

1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (471 mg, 1.5 mmol) afforded **2o** (294 mg, 0.6 mmol, 40% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 143.8, 134.6 (q, J_{C-F} = 32.7 Hz), 133.5, 131.9 (q, J_{C-F} = 32.7 Hz), 131.6, 127.3, 126.1 (q, J_{C-F} = 3.78 Hz), 125.3 (q, J_{C-F} = 3.78 Hz), 123.2 (q, J_{C-F} = 273 Hz), 123.1 (q, J_{C-F} = 273 Hz), 66.2 MS (EI) *m/z* = 489 (M^++2); Anal. Calcd. for $C_{16}H_8Br_2F_6O$: C, 39.22; H, 1.65. Found : C, 39.42; H, 1.55.

1,1'-((2,2-Dibromoacetyl)bis(4,1-phenylene))diethanone (2p)

1,1'-(Ethyne-1,2-diylbis(4,1-phenylene))diethanone (393 mg, 1.5 mmol) afforded **2p** (354 mg, 0.81 mmol, 54% yield); white solid, mp 103.3-104.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dt, *J* = 8.8, 2.1 Hz, 2H), 7.85 (m, 2H), 7.84 (m, 2H), 7.74 (dt, *J* = 8.8, 2.1 Hz, 2H), 2.62 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 196.7, 185.1, 144.6, 140.0, 137.7, 134.0, 131.5, 128.9, 127.8, 127.1, 67.1, 26.8, 26.7; HRMS (FD) m/z calcd for $C_{18}H_{14}Br_2O_3$ (M+): 435.9310, found: 435.9306.

Benzil (3a) [22]

Condition A : 1,2-Diphenylethyne (267 mg, 1.5 mmol) afforded **3a** (15 mg, 0.07 mmol, 5% yield). **Condition B** : : 1,2-Diphenylethyne (267 mg, 1.5 mmol) afforded **3a** (189 mg, 0.9 mmol, 65% yield); yellow solid, mp 95-96 °C (lit. 95-96 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 4H), 7.66 (tt, *J* = 7.5, 1.3 Hz, 2H), 7.51 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 134.8, 132.9, 129.8, 129.0; MS (EI) *m/z* = 210 (M^+).

1,2-Bis(4-methoxyphenyl)ethane-1,2-dione (3b) [23]

Condition A : 1,2-Bis(4-methoxyphenyl)ethyne (357 mg, 1.5 mmol) afforded **3b** (182 mg, 0.67 mmol, 45% yield). **Condition B** : 1,2-Bis(4-methoxyphenyl)ethyne (357 mg, 1.5 mmol) afforded **3b** (283 mg, 1.05 mmol, 70% yield); yellow solid, mp 120-121 °C (lit. 121-122 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (m, 4H), 6.96 (m, 4H), 3.88 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 164.8, 132.3, 126.3, 114.2, 55.6; MS (EI) *m/z* = 270 (M^+).

1,2-Bis(4-(*tert*-butyl)phenyl)ethane-1,2-dione (3c) [24]

Condition A : 1,2-Bis(4-(tert-butyl)phenyl)ethyne (435 mg, 1.5 mmol) afforded **3c** (444 mg, 1.38 mmol, 92% yield). **Condition B** : 1,2-Bis(4-(tert-butyl)phenyl)ethyne (405 mg, 1.5 mmol) afforded **3c** (459 mg, 1.42 mmol, 95% yield); yellow solid, mp 99-100 °C (lit. 101-102 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (m, 4H), 7.51 (m, 4H), 1.34 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 158.8, 130.5, 129.8, 125.9, 35.3, 30.9; MS (EI) *m/z* = 322 (M^+).

1,2-Bis(4-ethylphenyl)ethane-1,2-dione (3d) [22]

Condition A : 1,2-Bis(4-ethylphenyl)ethyne (351 mg, 1.5 mmol) afforded **3d** (355 mg, 1.33 mmol, 89% yield). **Condition B** : 1,2-Bis(4-ethylphenyl)ethyne (351 mg, 1.5 mmol) afforded **3d** (375 mg, 1.41 mmol, 94% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.5, 1.9 Hz, 4H), 7.32 (ddd, *J* = 8.0, 1.9, 1.4 Hz, 4H), 2.70 (q, *J* = 7.6 Hz, 4H), 1.25 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 152.1, 130.8, 130.1, 128.5, 29.1, 15.0; MS (EI) *m/z* = 266 (M^+).

1,2-Di([1,1'-biphenyl]-4-yl)ethane-1,2-dione (3e) [25]

Condition A : 1,2-Di([1,1'-biphenyl]-4-yl)ethyne afforded (495 mg, 1.5 mmol) **3e** (445 mg, 1.23 mmol, 82% yield). **Condition B** : 1,2-Di([1,1'-biphenyl]-4-yl)ethyne afforded (495 mg, 1.5 mmol) **3e** (489 mg, 1.35 mmol, 90% yield); yellow solid, mp 132.5-133.8 °C (lit. 131-132 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (m, 4H), 7.75 (m, 4H), 7.64 (m, 4H), 7.49 (m, 4H), 7.43 (tt, *J* = 7.4, 1.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 147.6, 139.5, 131.7, 130.5, 129.0, 128.6, 127.6, 127.3; MS (EI) *m/z* = 362 (M^+).

1,2-Di(naphthalen-1-yl)ethane-1,2-dione (3f) [25]

Condition A : 1,2-Di(naphthalen-1-yl)ethyne (417 mg, 1.5 mmol) afforded **3f** (302 mg, 0.97 mmol, 65% yield). **Condition B** : 1,2-Di(naphthalen-1-yl)ethyne (417 mg, 1.5 mmol) afforded **3f** (381 mg, 1.23 mmol, 82% yield); orange solid, mp 190-190.5 °C (lit. 190-191 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.35 (dd, *J* = 8.6, 0.9 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 8.02 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.96 (dt, *J* = 8.2, 0.7 Hz, 2H), 7.76 (ddd, *J* = 8.5, 6.9, 1.2 Hz, 2H), 7.64 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 2H), 7.50 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 135.8, 135.0, 134.1, 131.1, 129.4, 128.9, 128.7, 127.0, 126.0, 124.4; MS (EI) *m/z* = 310 (M^+).

1,2-Di-*p*-tolylethane-1,2-dione (3g) [26]
Condition A : 1,2-Di-*p*-tolylethyne (309 mg, 1.5 mmol) afforded **3g** (268 mg, 1.12 mmol, 75% yield). **Condition B** : 1,2-Di-*p*-tolylethyne (309 mg, 1.5 mmol) afforded **3g** (314 mg, 1.32 mmol, 88% yield); white solid, mp 94-96 °C (lit. 100-102 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.1, 1.8 Hz, 4H), 7.30 (m, 4H), 2.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 146.0, 130.6, 130.0, 129.6, 21.9; MS (EI) *m/z* = 238 (M^+).

1,2-Di-*m*-tolylethane-1,2-dione (3h) [22]
Condition A : 1,2-Di-*m*-tolylethyne (309 mg, 1.5 mmol) afforded **3h** (178 mg, 0.75 mmol, 50% yield). **Condition B** : 1,2-Di-*m*-tolylethyne (309 mg, 1.5 mmol) afforded **3h** (314 mg, 1.32 mmol, 88% yield); yellow solid, mp 93.9-95.8 °C (lit. 97-99 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.76 (m, 2H), 7.47 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.9, 138.9, 135.7, 132.9, 130.2, 128.8, 127.2, 21.2; MS (EI) *m/z* = 238 (M^+).

1,2-Di-*o*-tolylethane-1,2-dione (3i) [27]
Condition A : 1,2-Di-*o*-tolylethyne (309 mg, 1.5 mmol) afforded **3i** (89 mg, 0.37 mmol, 25% yield). **Condition B** : 1,2-Di-*o*-tolylethyne (309 mg, 1.5 mmol) afforded **3i** (278 mg, 1.17 mmol, 78% yield); yellow crystal, mp 82-84 °C (lit. 88-89 °C, 89-91 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.49 (td, *J* = 7.6, 1.4 Hz, 2H), 7.34 (m, 2H), 7.29 (m, 2H), 2.70 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 141.5, 133.6, 133.0, 132.5, 131.7, 126.0, 21.9; MS (EI) *m/z* = 238 (M^+).

1,2-Bis(4-fluorophenyl)ethane-1,2-dione (3j) [28]
Condition A : 1,2-Bis(4-fluorophenyl)ethyne (321 mg, 1.5 mmol) afforded **3j** (166 mg, 0.67 mmol, 45% yield). **Condition B** : 1,2-Bis(4-fluorophenyl)ethyne (321 mg, 1.5 mmol) afforded **3j** (317 mg, 1.29 mmol, 86% yield); yellow solid, mp 117-117.2 °C (lit. 118-119 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (m, 4H), 7.20 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 166.8 (d, J_{C-F} = 259.5 Hz), 132.7 (d, J_{C-F} = 10.0 Hz), 129.3 (d, J_{C-F} = 2.5 Hz), 116.4 (d, J_{C-F} = 22.6 Hz); MS (EI) *m/z* = 246 (M^+).

1,2-Bis(4-(trifluoromethoxy)phenyl)ethane-1,2-dione (3k) [29]
Condition B : 1,2-Bis(4-(trifluoromethoxy)phenyl)ethyne (915 mg, 1.5 mmol) afforded **3k** (397 mg, 1.05 mmol, 70% yield); yellow solid, mp 107-108 °C (lit. 108 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 9.0, 4.7 Hz, 4H), 7.35 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 154.0 (d, J_{C-F} = 1.2 Hz), 132.1, 130.8, 120.7 (d, J_{C-F} = 1.2 Hz), 120.2 (q, J_{C-F} = 260.8 Hz); MS (EI) *m/z* = 378 (M^+).

1,2-Bis(4-chlorophenyl)ethane-1,2-dione (3l) [30]
Condition A : 1,2-Bis(4-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **3l** (92 mg, 0.33 mmol, 22% yield). **Condition B** : 1,2-Bis(4-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **3l** (293 mg, 1.05 mmol, 70% yield); yellow solid, mp 195.8-196 °C (lit. 194-196 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.8, 4.3 Hz, 4H), 7.50 (dd, *J* = 8.8, 4.3 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 141.8, 131.2, 131.1, 129.5; MS (EI) *m/z* = 277 (M^+).

1,2-Bis(3-chlorophenyl)ethane-1,2-dione (3m) [31]
Condition A : 1,2-Bis(3-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **3m** (29 mg, 0.10 mmol, 7% yield). **Condition B** : 1,2-Bis(4-chlorophenyl)ethyne (370 mg, 1.5 mmol) afforded **3m** (293 mg, 1.05 mmol, 70% yield); yellow solid, mp 116-117 °C (lit. 114-115 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 2.1, 1.6, 0.4 Hz, 2H), 7.83 (ddd, *J* = 7.8, 1.6, 1.1 Hz, 2H), 7.64 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 2H), 7.47 (td, *J* = 7.9, 0.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 135.5, 135.0, 134.1, 130.4, 129.6, 128.1; MS (EI) *m/z* = 277 (M^+).

***(E)*-1,2-Dibromo-1,2-bis(3,5-difluorophenyl)ethane (4n)**
1,2-Bis(3,5-difluorophenyl)ethyne (375 mg, 1.5 mmol) afforded **4n** (184 mg, 0.45 mmol, 30% yield); white solid, mp 158.8-160 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (m, 4H), 6.85 (tt, *J* = 8.8, 2.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6 (dd, J_{C-F} = 250.7, 12.6 Hz), 142.6 (t, J_{C-F} = 10.0 Hz), 116.7 (t, J_{C-F} = 2.5 Hz), 112.2 (dd, J_{C-F} = 20.1, 6.3 Hz), 104.8 (t, J_{C-F} = 25.2 Hz); HRMS (FD) m/z calcd for $C_{14}H_6Br_2F_4$ (M^+): 407.8772, found: 407.8768.

***(E)*-1,2-Dibromo-1,2-bis(4-(trifluoromethyl)phenyl)ethane (4o)**
1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (471 mg, 1.5 mmol) afforded **4o** (248 mg, 0.52 mmol, 35% yield); white solid, mp 183-184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (m, 4H), 7.65 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6 (d, J_{C-F} = 1.26 Hz), 131.1 (q, J_{C-F} = 32.7 Hz), 129.5, 125.5 (q, J_{C-F} = 3.78 Hz), 123.7 (q, J_{C-F} = 273.4 Hz), 117.5; HRMS (FD) m/z calcd for $C_{16}H_8Br_2F_6$ (M^+): 471.8897, found: 471.8894.

***(E)*-1,1'-((1,2-Dibromoethene-1,2-diyl)bis(4,1-phenylene))diethanone (4p)**
1,1'-(Ethyne-1,2-diylbis(4,1-phenylene))diethanone (393 mg, 1.5 mmol) afforded **4p** (126 mg, 0.3 mmol, 20% yield); white solid, mp 195.9-196.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 8.6, 1.9, 1.7 Hz, 4H), 7.64 (ddd, *J* = 8.6, 1.9, 1.7 Hz, 4H), 2.65 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 144.6, 137.2, 129.3, 128.5, 117.6, 26.7; HRMS (FD) m/z calcd for $C_{18}H_{14}Br_2O_2$ (M^+): 419.9360, found: 419.9371.

***(E)*-Dimethyl-4,4'-(1,2-dibromoethene-1,2-diyl)dibenzoate (4q)**
Dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (441 mg, 1.5 mmol) afforded **4q** (374 mg, 0.82 mmol, 55% yield); white solid, mp 178.8-180.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 8.6, 2.0, 1.7 Hz, 4H), 7.63 (ddd, *J* = 8.6, 2.0, 1.7 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 144.5, 130.5, 129.7, 129.1,

117.6, 52.3; HRMS (FD) m/z calcd for $C_{18}H_{14}Br_2O_4$ (M^+): 451.9259, found: 451.9256.

***(E)*-4,4'-(1,2-Dibromoethene-1,2-diyl)dibenzonitrile (4r)**
4,4'-(Ethyne-1,2-diyl)dibenzonitrile (342 mg, 1.5 mmol) afforded **4r** (378 mg, 0.97 mmol, 65% yield); white solid, mp 218-219 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (ddd, *J* = 8.6, 2.0, 1.5 Hz, 4H), 7.63 (ddd, *J* = 8.6, 2.0, 1.5 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 132.3, 129.8, 118.0, 117.3, 113.0; HRMS (FD) m/z calcd for $C_{16}H_8Br_2N_2$ (M^+): 385.9055, found: 385.9043.

***(E)*-1,2-Dibromo-1,2-di(pyridin-2-yl)ethane (4s)**
1,2-Di(pyridin-2-yl)ethyne (270 mg, 1.5 mmol) afforded **4s** (321 mg, 0.94 mmol, 63% yield); white solid, mp 177-178 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 7.80 (td, *J* = 7.7, 1.8 Hz, 2H), 7.64 (dt, *J* = 7.8, 1.1 Hz, 2H), 7.31 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9, 149.7, 136.7, 124.4, 123.7, 118.4; HRMS (FD) m/z calcd for $C_{12}H_8Br_2N_2$ (M^+): 385.9055, found: 385.9052.

***(E)*-1,2-Dibromo-1,2-di(pyridin-3-yl)ethane (4t)**
1,2-Di(pyridin-3-yl)ethyne (270 mg, 1.5 mmol) afforded **4t** (362 mg, 1.06 mmol, 71% yield); white solid, mp 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 1.6 Hz, 2H), 8.63 (dd, *J* = 4.6, 1.0 Hz, 2H), 7.85 (dt, *J* = 7.9, 2.0 Hz, 2H), 7.39 (dd, *J* = 7.9, 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 149.8, 136.5, 136.4, 123.2, 116.5; HRMS (FD) m/z calcd for $C_{12}H_8Br_2N_2$ (M^+): 337.9054, found: 337.9050.

1-Phenyl-2-(*p*-tolyl)ethane-1,2-dione (5a) [7c]
1-Methyl-4-(phenylethynyl)benzene (288 mg, 1.5 mmol) afforded **5a** (235 mg, 1.05 mmol, 70% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97(m, 2H), 7.86 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.65 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.51(m, 2H), 7.31 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.7, 194.2, 146.2, 134.7, 133.1, 130.5, 130.0, 129.8, 129.7, 128.9, 21.9; MS (EI) *m/z* = 224 (M^+).

1-(3,4-Dimethylphenyl)-2-phenylethane-1,2-dione (5b) [7c]
1,2-Dimethyl-4-(phenylethynyl)benzene (309 mg, 1.5 mmol) afforded **5b** (257 mg, 1.08 mmol, 72% yield); pale yellow solid; mp: 61-62 °C (lit. 63 °C);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 8.5, 1.5 Hz, 2H), 7.73 (s, 1H), 7.69 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (m, 1H), 7.49 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 194.6, 145.0, 137.6, 134.7,133.2, 130.9, 130.7, 130.3, 129.9, 128.9, 127.7, 20.3, 19.7; MS (EI) *m/z* = 238 (M^+).

1-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenylethane-1,2-dione (5c) [32]
5-(Phenylethynyl)benzo[*d*][1,3]dioxole (333 mg, 1.5 mmol) afforded **5c** (209 mg, 0.82 mmol, 55% yield); yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 8.5, 1.4 Hz, 2H), 7.65 (m, 1H), 7.51 (m, 2H), 7.48 (m, 2H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.08 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 192.8, 153.4, 148.6, 134.7, 133.0, 129.9, 128.9, 127.9, 127.8, 108.4, 108.3, 102.2; MS (EI) *m/z* = 254 (M^+).

1-(4-Fluorophenyl)-2-phenylethane-1,2-dione (5d) [32]
1-Fluoro-4-(phenylethynyl)benzene (294 mg, 1.5 mmol) afforded **5d** (222 mg, 0.97 mmol, 65% yield); pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (ddt, *J* = 8.9, 5.3, 2.1 Hz, 2H), 7.98 (m, 2H), 7.67 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.53 (m, 2H), 7.20 (ddt, *J* = 9.0, 7.4, 2.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.0, 192.7, 166.7 (d, J_{C-F} = 259.5 Hz), 135.0, 132.8, 132.7 (d, J_{C-F} = 10.0 Hz), 129.9, 129.4 (d, J_{C-F} = 3.78 Hz), 129.0, 116.4 (d, J_{C-F} = 22.6 Hz); MS (EI) *m/z* = 228 (M^+).

1-(4-Chlorophenyl)-2-phenylethane-1,2-dione (5e) [7c]
1-Chloro-4-(phenylethynyl)benzene (319 mg, 1.5 mmol) afforded **5e** (293 mg, 1.2 mmol, 80% yield); yellow solid; mp 70-72 °C (lit. 70 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.93 (m, 2H), 7.68 (m, 1H), 7.53 (m, 2H), 7.50 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 193.0, 141.6, 135.0, 132.7, 131.3, 131.2, 129.9, 129.4, 129.0; MS (EI) *m/z* = 244 (M^+).

1,1-Dibromo-1-phenylheptan-2-one (7a)
Hept-1-yn-1-ylbenzene (258 mg, 1.5 mmol) afforded **7a** (375 mg, 1.08 mmol, 72% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (m, 2H), 7.56 (tt, *J* = 7.4, 1.2, 1H), 7.45 (m, 2H), 2.66 (m, 2H), 1.72 (m, 2H), 1.41 (m, 2H), 1.38 (m, 2H), 0.92 (t, *J* = 7.1, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6, 133.1, 132.6, 131.0, 127.8, 66.9, 46.7, 31.1, 27.0, 22.4, 13.9; HRMS (FD) m/z calcd for $C_{13}H_{16}Br_2O$ (M^+): 345.9568, found: 345.9572.

1,1-Dibromo-1-phenylpentan-2-one (7b)
Pent-1-yn-1-ylbenzene (216 mg, 1.5 mmol) afforded **7b** (312 mg, 0.97 mmol, 65% yield); pale yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (m, 2H), 7.56 (tt, *J* = 7.4, 1.2, 1H), 7.45 (m, 2H), 2.65 (m, 2H), 1.76 (m, 2H), 1.05 (t, *J* = 7.4, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.5, 133.1, 132.6, 131.0, 127.8, 66.6, 48.7, 20.8, 13.5; HRMS (FD) m/z calcd for $C_{11}H_{12}Br_2O$ (M^+): 317.9255, found: 317.9264.

6,6-Dibromodecan-5-one (7c)
Dec-5-yne (207 mg, 1.5 mmol) afforded **7c** (371 mg, 1.18 mmol, 79% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.09 (m, 2H), 2.46 (m, 2H), 1.68 (m, 2H), 1.62 (m, 2H), 1.47 – 1.35 (m, 4H), 0.96 (td, *J* = 7.3, 2.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.2, 71.9, 44.6, 36.1, 29.7, 27.5, 22.2, 22.1, 13.9, 13.9; HRMS (FD) m/z calcd for $C_{10}H_{18}Br_2O$ (M^+): 314.9724, found: 314.9726.

5,5-Dibromooctan-4-one (7d)
Oct-4-yne (165 mg, 1.5 mmol) afforded **7d** (329 mg, 1.15 m
mol, 77% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.05 (t, *J* = 7.3 Hz, 2H), 2.41 (m, 2H), 1.71 (m, 2H), 1.64 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.0, 71.6, 46.7, 38.1, 21.0, 18.8, 13.5, 13.5; HRMS (FD) m/z calcd for $C_8H_{14}Br_2O$ (M^+): 283.9411, found: 283.9411.

4,4-Dibromohexan-3-one (7e)
Hex-3-yne (123 mg, 1.5 mmol) afforded 7e (294 mg, 1.14 mmol, 76% yield); colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.09 (q, *J* = 7.3 Hz, 2H), 2.46 (q, *J* = 7.1 Hz, 2H), 1.16 (td, *J* = 7.2, 3.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.9, 72.8, 38.2, 29.8, 11.9, 9.7; HRMS (FD) m/z calcd for $C_6H_{10}Br_2O$ (M^+): 255.9098, found: 255.9098.

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[21] When **2a** was treated with bromine reagents in water, it was found that NBS converted **2a** to **3a** (See Supporting Information Table S2)

10.1002/adsc.201801535

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FULL PAPER

Substituent Effect in the Synthesis of α,α-Dibromoketones, 1,2-Dibromalkene, and 1,2-Diketones from the Reaction of Alkynes and Dibromoisocyanuric Acid

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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