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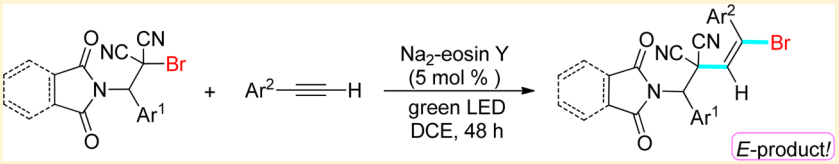
Visible-Light-Initiated Na_2-Eosin Y Catalyzed Highly Regio- and Stereoselective Difunctionalization of Alkynes with Alkyl Bromides

Kuai Wang, Ling-Guo Meng,* and Lei Wang*

Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, People's Republic of China

Supporting Information



ABSTRACT: A highly regioselective and stereoselective addition of alkyl bromides (amino-brominated aromatic *β,β*-dicyanoalkenes) to arylacetylenes by photoredox catalysis was developed. This difunctionalization of arylacetylenes was accomplished under ambient and metal-free conditions to produce alkenyl bromides in high efficiency with a wide range of group tolerance.

INTRODUCTION

One-step addition to an unsaturated C−C bond can provide an efficient platform to construct complex organic molecules from simple alkenes or alkynes as building blocks.[1] Among these transformations, simultaneous addition of a C(sp^3)−X (X = halogens) bond to alkynes has been proven to be an effective protocol for the synthesis of alkenyl halides, which are valuable intermediates in diverse of transition-metal-catalyzed cross-coupling reactions. In the reported works, various additions of C−X to alkynes for the preparation of vinyl halides were usually conducted in the presence of transition-metal salts, such as Pd,[2] Fe,[3] Cu,[4] Zn,[5] etc. as catalysts.[6] On the other hand, forming C(sp^2)−X and C(sp^2)−C bonds via additions of C(sp^3)−X to alkynes could also proceed in an organo-catalytic system.[7]

Recently, visible-light photoredox catalysis was proven to be a powerful and environmental tool to initiate a variety of organic reactions,[8] including cyclizations,[9] C−H functionalizations,[10] and decarboxylative coupling reactions.[11] It is well-known that C(sp^3)−X has a distinctive reactivity in photocatalyzed reactions. Cleavage of C−X generally occurred under photocatalysis, and functionalized molecules were obtained from easily available starting materials.[8a] However, a halide atom was not presented in the final products in the most cases.[12] Although a few reports on the additions of C−X to alkenes provided alkyl halides (Scheme 1, eq 1),[13] the addition of C−X to alkynes was rare.[13a,14]

Amino-brominated aromatic *β,β*-dicyanoalkene is a new reactant and is attractive for potential utilization in organic transformations. We found that it could exhibit good photochemical activity and react with alkyne (Scheme 1, eq 2), giving alkenyl bromide with high regio- and stereoselectivity (only *E*-product). Compared with the reported additions of C−X to alkynes, regardless whether in a metallo- or organo-system, most of them cannot be stereoselectively controlled and a mixture of *E*- and *Z*-isomers was obtained. Herein, we describe a photoredox catalytic stereoselective addition of functionalized alkyl bromides to alkynes to generate the corresponding vinyl bromides in *E*-isomers, forming C(sp^2)−X and C(sp^2)−C bonds simultaneously via cleavage of the C−Br bond followed by their addition to a C−C triple bond.

RESULTS AND DISCUSSION

At first, the reaction was carried out with 2-bromo-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**1a**) to phenylacetylene (**2a**) as model substrates, and the results are shown in Table 1. The model reaction was conducted at room temperature and air atmosphere in CH_3CN for 48 h in the presence of Na_2-eosin Y as a photoredox catalyst under light bulb irradiation, and the desired addition product **3aa** was obtained in 29% yield. This transformation was almost halted without visible light or photocatalyst, as demonstrated in comparison experiments (Table 1, entries 1−3). Then, different solvents, such as DCE, C_6H_6, CCl_4, THF, EtOH, H_2O, CCl_3, and EtOAc, were examined, and DCE was the best one (Table 1, entries 4−11). With other polar solvents, such as DMF or DMSO, much lower yields were obtained (Table 1, entries 12 and 13). With the utilization of other photoredox catalysts including eosin Y, rose bengal, methylene blue, rhodamine B, and $[Ru(bpy)_3]Cl_2·6H_2O$, the reaction also occurred but with slightly less efficiency (Table 1, entries 14−18). When the model reaction was performed under green LED (530−535 nm) irradiation, a 65% yield of **3aa** was obtained, and a lower yield of **3aa** was observed under blue LED (450−455 nm) irradiation (Table 1, entries 19 and 20). Further, only a trace amount of desired product was observed when the reaction was

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Scheme 1. Visible-Light-Induced Different Difunctionalization Reactions

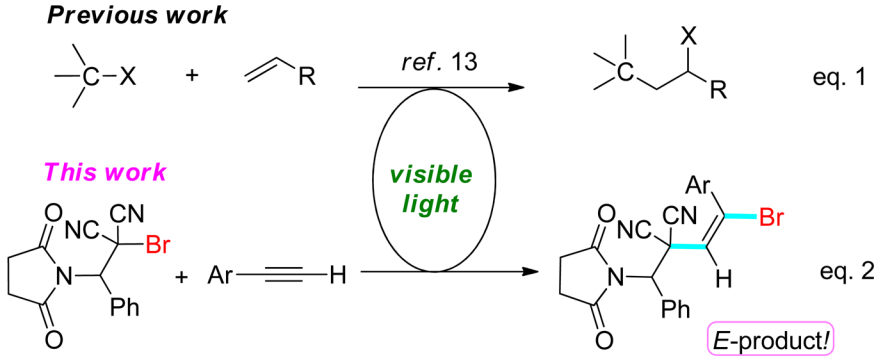
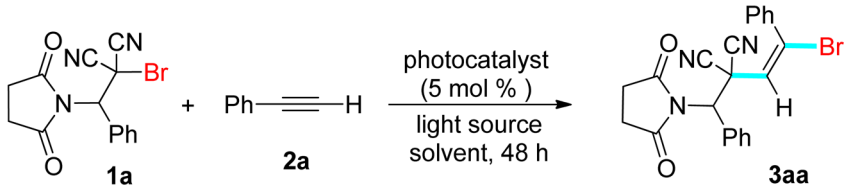


Table 1. Optimization of the Reaction Conditions[a]



entry	photocatalyst	light source	solvent	yield[b] (%)
1	Na_2-eosin Y	15 W light bulb	CH_3CN	29
2	Na_2-eosin Y		CH_3CN	<5
3		15 W light bulb	CH_3CN	<5
4	Na_2-eosin Y	15 W light bulb	DCE	62
5	Na_2-eosin Y	15 W light bulb	C_6H_6	47
6	Na_2-eosin Y	15 W light bulb	CCl_4	45
7	Na_2-eosin Y	15 W light bulb	THF	40
8	Na_2-eosin Y	15 W light bulb	EtOH	35
9	Na_2-eosin Y	15 W light bulb	H_2O	32
10	Na_2-eosin Y	15 W light bulb	$CHCl_3$	27
11	Na_2-eosin Y	15 W light bulb	EtOAc	23
12	Na_2-eosin Y	15 W light bulb	DMF	<5
13	Na_2-eosin Y	15 W light bulb	DMSO	<5
14	eosin Y	15 W light bulb	DCE	55
15	rose bengal	15 W light bulb	DCE	53
16	methylene blue	15 W light bulb	DCE	46
17	rhodamine B	15 W light bulb	DCE	43
18	$[Ru(bpy)_3]Cl_2{\cdot}6H_2O$	15 W light bulb	DCE	34
19	Na_2-eosin Y	green LED	DCE	65
20	Na_2-eosin Y	blue LED	DCE	17
21	Na_2-eosin Y	red LED	DCE	<5
22	Na_2-eosin Y	yellow LED	DCE	<5

[a]Reaction conditions: **1a** (0.40 mmol), **2a** (0.80 mmol), photocatalyst (0.02 mmol), light source, solvent (2.0 mL), rt, 48 h. [b]Isolated yield.

stirred under red or yellow light irradiation (Table 1, entries 21 and 22).

With the optimized reaction conditions in hand, a variety of arylacetylenes were chosen as substrates, aimed at investigating the reaction scope. Moderate to good yields of the desired products with excellent stereoselectivity were obtained regardless of whether electron-rich or electron-poor groups were on the aromatic rings of alkynes, as shown in Scheme 2. Compared with the formation of **3aa**−**ag**, alkynes with an electron-rich group on the aromatic ring gave a better yield than an electron-poor group on the aromatic ring. The substrates with an electron-donating group (MeO, Me, or Pr) on the phenyl rings reacted with **1a** to afford desired addition products **3ab**−**ad** in good yields. Alkynes with an electron-withdrawing group, such as F, Cl, or Br, on the phenyl rings generated the corresponding products **3ae**−**ag** in 55−64% yields. However, when we used NO_2-substituted substrate in the reaction, only a trace amount of desired product **3ah** was detected. When *N*-phthalimidyl was used instead of *N*-succinimidyl in substrate **1**, the reactions also proceeded well, providing the corresponding adducts **3ba**−**bg** in a range of 60−77% yields. A similar substitution effect was observed in the formation of **3ba**−**bg**. Only a trace amount of desired product was formed when 1-pentyne was used as the substrate. Furthermore, the reaction failed when internal alkyne was used in the reaction. The configuration of the double bond in the addition product was determined by NOESY analysis of compound **3bg** (see the Supporting Information for details).

To further evaluate the scope of this reaction, reactions with different amino-brominated aromatic *β*,*β*-dicyanoalkenes were

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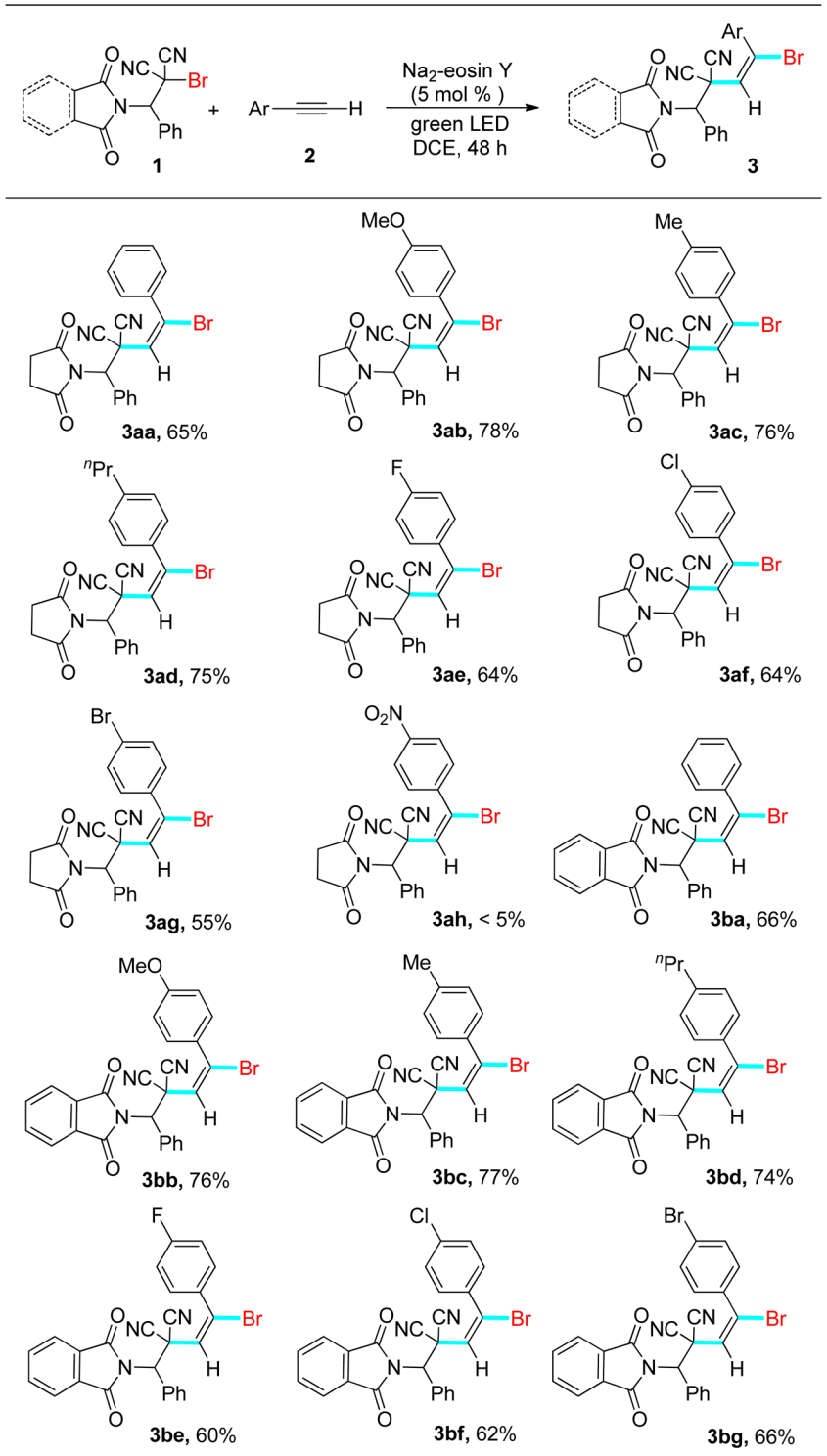
Scheme 2. Scope of Alkynes in the Reactions[a,b]



[a]Reaction conditions: **1** (0.40 mmol), **2** (0.80 mmol), Na_2-eosin Y (0.02 mmol), green LED, DCE (2.0 mL), rt, 48 h. [b]Isolated yield.

examined, and the results are shown in Scheme 3. Substrates **1** with an electron-rich or electron-poor group on the phenyl rings were compatible with the reaction conditions, and no obvious substitution effect was observed (**3cc**, **3ec**, **3hc**−**jc**). When *meta*-substituted substrates **1** were involved in the reaction, the corresponding products (**3dc** and **3fc**) were obtained in 73 and 78% yields, respectively. The *ortho*-substituted phenyl group was used for the reaction, and no obvious steric effect was observed (**3gc** vs **3ec** and **3fc**). Further, use of substrate **1** with a bulk group, such as 3,4,5-trimethoxyphenyl and 1,1′-biphenyl, could also be converted to corresponding products **3kc** and **3lc** in 41 and 65% yields, respectively. However, only a trace amount of desired adduct product was observed when 2-chloro-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile was reacted with phenylacetylene under the standard conditions.

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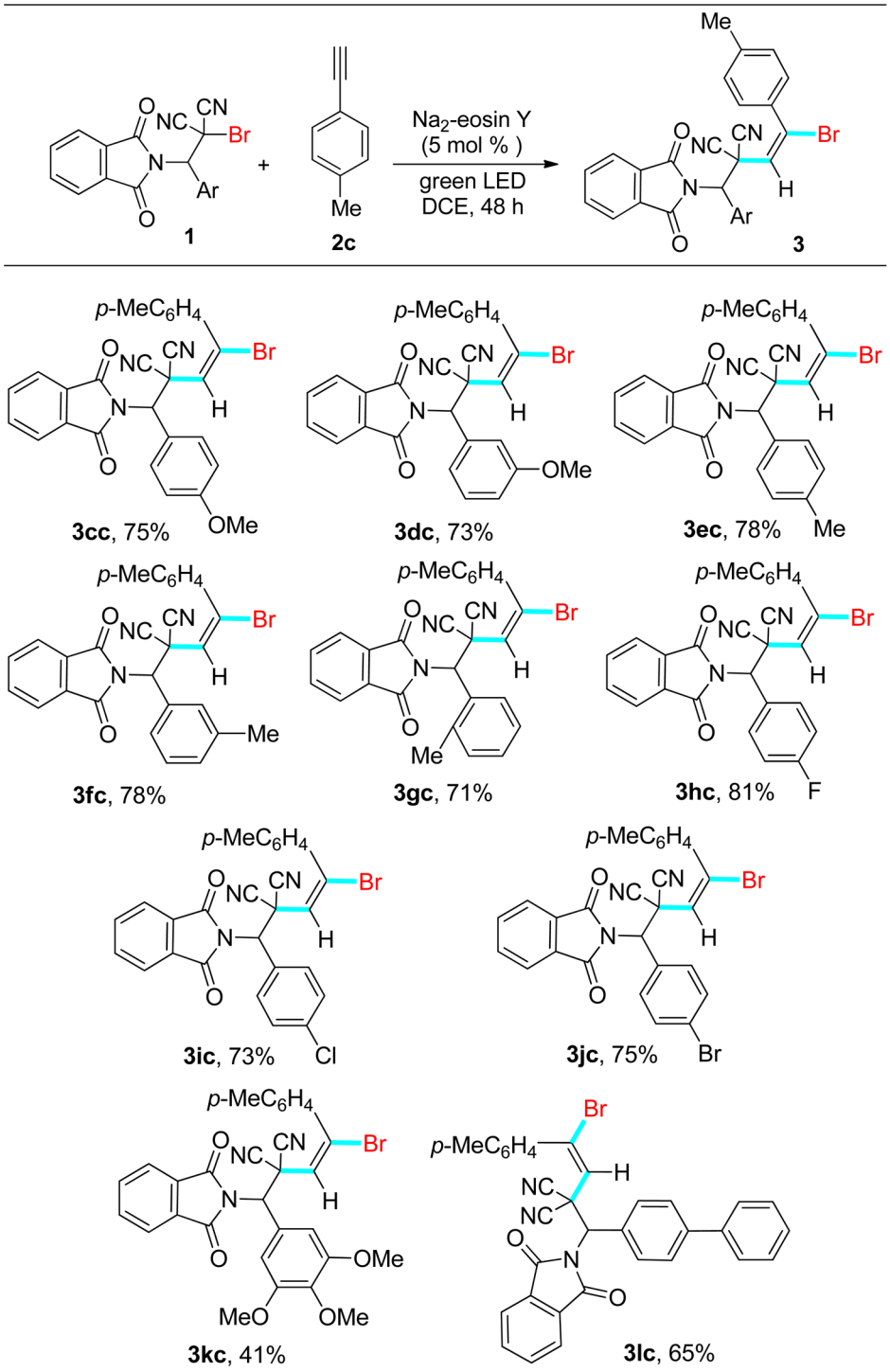
Scheme 3. Scope of Aminobrominated Aromatic *β,β*-Dicyanoalkenes[a,b]



[a]Reaction conditions: **1** (0.40 mmol), **2c** (0.80 mmol), Na_2-eosin Y (0.02 mmol), green LED, DCE (2.0 mL), rt, 48 h. [b]Isolated yield.

Finally, a one-pot reaction of *N*-bromosuccinimide (NBS) or *N*-bromophthalimide (NBP), 2,2-dicyanostyrene (**5**), and terminal aromatic alkyne (**2**) was carried out under standard reaction conditions, providing the corresponding addition products in lower yields with high stereoselectivity, as shown in Table 2.

On the basis of the above observation and a previous report,[13b] a proposed mechanism is depicted in Scheme 4. Photoexcitation of Na_2-eosin Y by visible light provides [Na_2-eosin Y]*, which is then oxidatively quenched by **1a** to produce [Na_2-eosin Y]$^+$ and a radical intermediate **A**. This radical **A** then undergoes a regioselective addition to alkyne to form **B**. It should be noted that the final product **3aa** can be obtained from **B** via two possible pathways. First, intermediate **B** reacts with **1a** by a radical chain transfer to give product **3aa** along with the regeneration of radical **A**. Alternatively, oxidation of the intermediate **B** produces vinyl carbocation **C**, which reacts with the produced bromine anion to provide the final product

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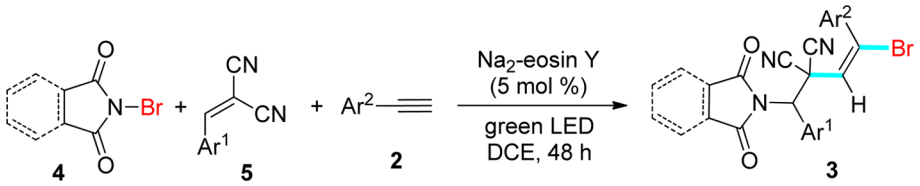
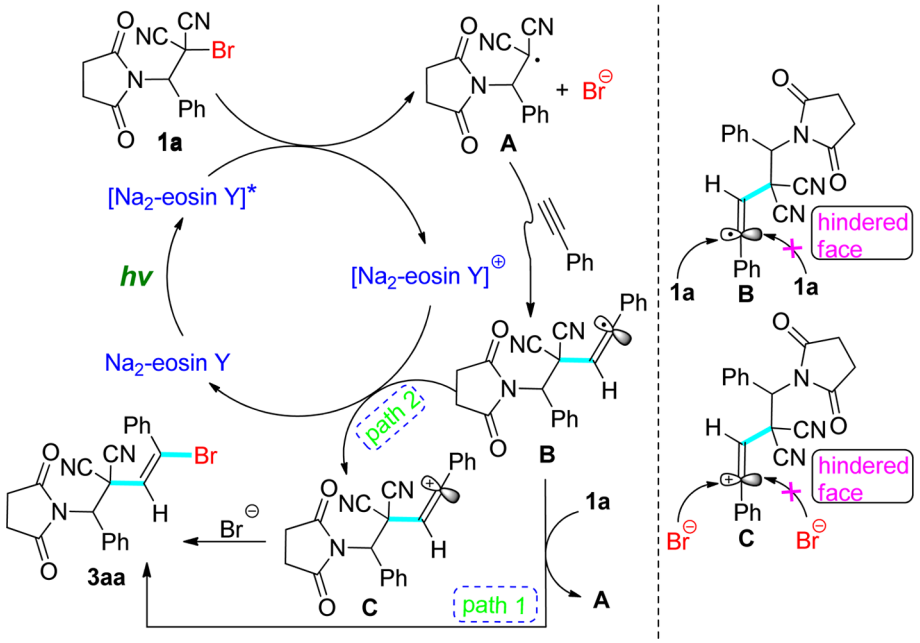
Table 2. One-Pot Reactions[a]



entry	4	Ar^1 of 5	Ar^2 of 2	yield[b] (%)
1	NBS	Ph	Ph	**3aa**, 38
2	NBS	Ph	*p*-MeC_6H_4	**3ac**, 35
3	NBS	Ph	*p*-ClC_6H_4	**3af**, 25
4	NBP	Ph	*p*-$MeOC_6H_4$	**3bb**, 40
5	NBP	*p*-MeC_6H_4	*p*-MeC_6H_4	**3ec**, 32
6	NBP	*p*-ClC_6H_4	*p*-MeC_6H_4	**3ic**, 36

[a]Reaction conditions: NBS or NBP (0.50 mmol), dicyanostyrene (**5**, 0.40 mmol), alkyne (**2**, 0.80 mmol), Na_2-eosin Y (0.02 mmol), green LED, DCE (2.0 mL), rt, 48 h. [b]Isolated yield.

Scheme 4. Proposed Mechanism



3aa. Either with path 1 or path 2, the double bond in the final product is in the *E*-configuration, which may be ascribed to steric hindrance.[15]

In order to further understand the mechanism of the intriguing processes, several control experiments were performed, as shown in Scheme 5. When a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was added to the reaction of **1a** and **2c**, formation of the desired product **3ac** was inhibited. *N*-Iodosuccinimide (NIS) or KI was added to the reaction, affording a mixture of **3ac** and **3ac′** with different molar ratios (**3ac**/**3ac′** = 6:1 for NIS; **3ac**/**3ac′** = 10:1 for KI; see the Supporting Information for details). It should be implied that path 1 would give priority to path 2 during the formation of the final product.[13a,b]

CONCLUSION

In conclusion, we have developed a highly stereoselective and regioselective addition of amino-brominated aromatic *β*,*β*-dicyanoalkenes to alkynes by photoredox catalysis. The results indicated that the formation of (*E*)-alkenyl bromides is through the direct difunctionalization of C≡C bonds under metal-free conditions. This reaction provides a simple route to a bifunctional structure motif in atom-economy and high efficiency with a wide range of group tolerance. Further investigation of other applications for photocatalysts in organic synthesis is still in progress.

EXPERIMENTAL SECTION

General Information. All reactions were conducted in clean glassware with magnetic stirring. Chromatographic purification was performed on silica gel (100−200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254}, which was detected by fluorescence. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with a 400 MHz NMR spectrometer with $CDCl_3$ as solvent and recorded in parts per million relative to an internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: *δ*, chemical shift; coupling constants (*J* are given in hertz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). High-resolution mass spectra were obtained by using an

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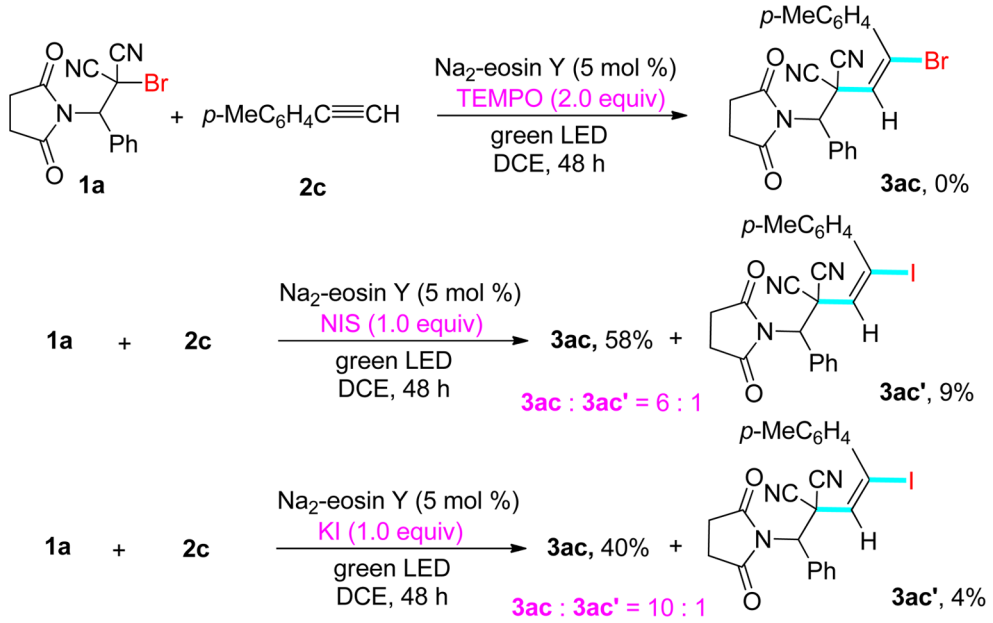
Scheme 5. Control Experiments



ion trap mass spectrometer. Melting points were determined on a digital melting point apparatus, and temperatures were uncorrected.

General Procedure for Difunctionalization of a C≡C Bond. To a stirred solution of amino-brominated aromatic *β,β*-dicyanoalkene (0.40 mmol) with alkyne (0.80 mmol) in 2.0 mL of DCE was added Na_2-eosin Y (0.02 mmol). The reaction mixture was stirred in the presence of green LED (530−535 nm) at room temperature for 48 h. Then the solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel to give the pure product.

*(E)-2-(2-Bromo-2-phenylvinyl)-2-((2,5-dioxopyrrolidin-1-yl)-(phenyl)methyl)malononitrile (**3aa**).* Following the general procedure, the product was isolated as a white solid: 112.5 mg (65%); mp = 186−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (d, *J* = 7.2 Hz, 2H), 7.46−7.37 (m, 8H), 6.19 (s, 1H), 5.59 (s, 1H), 2.78 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.0, 135.7, 131.7, 131.2, 130.6, 130.4, 129.8, 129.3, 128.7, 128.3, 121.0, 112.2, 111.2, 60.9, 40.6, 27.8; HRMS (ESI) calcd for $C_{22}H_{16}BrN_3O_2Na$ (M + Na)$^+$ 456.0324; found 456.0318.

*(E)-2-(2-Bromo-2-(4-methoxyphenyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**3ab**).* Following the general procedure, the product was isolated as a white solid: 144.5 mg (78%); mp = 133−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.71 (d, *J* = 7.2 Hz, 2H), 7.46−7.44 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.13 (s, 1H), 5.58 (s, 1H), 3.82 (s, 3H), 2.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 161.3, 132.3, 131.4, 130.5, 130.2, 129.9, 129.4, 128.0, 120.6, 114.2, 112.5, 111.4, 61.0, 55.3, 40.7, 28.0; HRMS (ESI) calcd for $C_{23}H_{18}BrN_3O_3Na$ (M + Na)$^+$ 486.0429; found 486.0421.

*(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)-(phenyl)methyl)malononitrile (**3ac**).* Following the general procedure, the product was isolated as a white solid: 135.9 mg (76%); mp = 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (d, *J* = 7.2 Hz, 2H), 7.45−7.44 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.16 (s, 1H), 5.58 (s, 1H), 2.78 (s, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.0, 141.0, 132.9, 132.2, 131.3, 130.4, 129.8, 129.3, 129.3, 128.3, 120.6, 112.3, 111.3, 60.9, 40.6, 27.8, 21.4; HRMS (ESI) calcd for $C_{23}H_{18}BrN_3O_2Na$ (M + Na)$^+$ 470.0480; found 470.0472.

*(E)-2-(2-Bromo-2-(4-propylphenyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**3ad**).* Following the general procedure, the product was isolated as a pale yellow oil: 142.5 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (d, *J* = 7.2 Hz, 2H), 7.45−7.43 (m, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 5.58 (s, 1H), 2.77 (s, 4H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.68−1.59 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.0, 145.7, 133.1, 132.2, 131.3, 130.4, 129.8, 129.2, 128.7, 128.2, 120.6, 112.3, 111.2, 60.9, 40.6, 37.7, 27.8, 24.0, 13.5; HRMS (ESI) calcd for $C_{25}H_{22}BrN_3O_2Na$ (M + Na)$^+$ 498.0793; found 498.0785.

*(E)-2-(2-Bromo-2-(4-fluorophenyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**3ae**).* Following the general procedure, the product was isolated as a white solid: 115.5 mg (64%); mp = 190−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.70 (d, *J* = 7.2 Hz, 2H), 7.47−7.45 (m, 3H), 7.37 (dd, *J* = 5.2, 8.0 Hz, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.21 (s, 1H), 5.58 (s, 1H), 2.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 164.9 (d, *J* = 250.8 Hz), 131.8 (d, *J* = 3.5 Hz), 131.2, 130.7, 130.6 (d, *J* = 8.8 Hz), 130.5, 129.8, 129.3, 121.6, 116.1 (d, *J* = 22.0 Hz), 112.1, 111.2, 60.8, 40.6, 27.8; HRMS (ESI) calcd for $C_{22}H_{15}BrFN_3O_2Na$ (M + Na)$^+$ 474.0229; found 474.0221.

*(E)-2-(2-Bromo-2-(4-chlorophenyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**3af**).* Following the general procedure, the product was isolated as a white solid: 119.6 mg (64%); mp = 128−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.69 (d, *J* = 7.2 Hz, 2H), 7.48−7.43 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.22 (s, 1H), 5.58 (s, 1H), 2.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 136.7, 134.1, 131.1, 130.5, 130.4, 129.8, 129.7, 129.3, 129.0, 121.7, 112.0, 111.2, 60.8, 40.6, 27.9; HRMS (ESI) calcd for $C_{22}H_{15}BrClN_3O_2Na$ (M + Na)$^+$ 489.9934; found 489.9925.

*(E)-2-(2-Bromo-2-(4-bromophenyl)vinyl)-2-((2,5-dioxopyrrolidin-1-yl)(phenyl)methyl)malononitrile (**3ag**).* Following the general procedure, the product was isolated as a white solid: 112.5 mg (55%); mp = 135−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.71 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.48−7.47 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.23 (s, 1H), 5.59 (s, 1H), 2.82 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 176.1, 134.6, 132.1, 131.2, 130.6, 130.5, 129.9, 129.9, 129.4, 125.2, 121.7, 112.1, 111.3, 60.9, 40.7, 28.0; HRMS (ESI) calcd for $C_{22}H_{15}Br_2N_3O_2Na$ (M + Na)$^+$ 533.9429; found 533.9421.

*(E)-2-(2-Bromo-2-phenylvinyl)-2-((1,3-dioxoisoindolin-2-yl)-(phenyl)methyl)malononitrile (**3ba**).* Following the general procedure, the product was isolated as a white solid: 126.9 mg (66%); mp = 153−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90−7.88 (m, 2H), 7.77−7.75 (m, 4H), 7.44−7.42 (m, 8H), 6.34 (s, 1H), 5.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.1, 135.8, 134.8, 132.0, 131.7, 130.9, 130.6, 130.2, 129.6, 129.2, 128.7, 128.3, 124.1, 121,0, 112.2, 111.4, 60.4, 41.1; HRMS (ESI) calcd for $C_{26}H_{16}BrN_3O_2Na$ (M + Na)$^+$ 504.0324; found 504.0336.

*(E)-2-(2-Bromo-2-(4-methoxyphenyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3bb**).* Following the general procedure, the product was isolated as a white solid: 155.4 mg (76%); mp = 141−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.89−7.87 (m, 2H), 7.76−7.75 (m, 4H), 7.43 (s, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.93

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J. Org. Chem. 2016, 81, 7080−7087

(d, J = 8.4 Hz, 2H), 6.29 (s, 1H), 5.83 (s, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.1, 134.8, 132.5, 131.8, 130.9, 130.2, 130.1, 129.6, 129.2, 128.0, 124.1, 120.5, 114.1, 112.4, 111.6, 60.4, 55.2, 41.1; HRMS (ESI) calcd for $C_{27}H_{18}BrN_3O_3Na$ $(M + Na)^+$ 534.0429; found 534.0421.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3bc**). Following the general procedure, the product was isolated as a white solid: 152.5 mg (77%); mp = 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.87 (m, 2H), 7.76−7.74 (m, 4H), 7.44−7.43 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.30 (s, 1H), 5.83 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 141.0, 134.8, 133.0, 132.5, 131.8, 130.9, 130.2, 129.6, 129.4, 129.2, 128.3, 124.1, 120.7, 112.3, 111.6, 60.5, 41.1, 21.4; HRMS (ESI) calcd for $C_{27}H_{18}BrN_3O_2Na$ $(M + Na)^+$ 518.0480; found 518.0496.

(E)-2-(2-Bromo-2-(4-propylphenyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3bd**). Following the general procedure, the product was isolated as a white solid: 154.9 mg (74%); mp = 176−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 2H), 7.75−7.74 (m, 4H), 7.44 (s, 3H), 7.34 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.29 (s, 1H), 5.82 (s, 1H), 2.62 (t, J = 7.2 Hz, 2H), 1.67−1.58 (m, 2H), 091 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.7, 134.8, 133.2, 132.5, 131.8, 130.9, 130.1, 129.6, 129.2 128.8, 128.3, 124.0, 120,6, 112.3, 111.5, 60.4, 41.1, 37.7, 24.0, 13.5; HRMS (ESI) calcd for $C_{29}H_{22}BrN_3O_2Na$ $(M + Na)^+$ 546.0793; found 546.0785.

(E)-2-(2-Bromo-2-(4-fluorophenyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3be**). Following the general procedure, the product was isolated as a white solid: 119.8 mg (60%); mp = 185−187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2H), 7.78−7.74 (m, 4H), 7.45 (s, 3H), 7.40 (dd, J = 5.2, 8.0 Hz, 2H), 7.13 (t, J = 8.4 Hz, 2H), 6.35 (s, 1H), 5.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.9 (d, J = 250.7 Hz), 134.9, 131.9 (d, J = 3.5 Hz), 131.6, 130.9, 130.9, 130.6 (d, J = 8.8 Hz), 130.3, 129.6, 129.2, 124.1, 121,6, 116.1 (d, J = 22.0 Hz), 112.2, 111.5, 60.4, 41.0; HRMS (ESI) calcd for $C_{26}H_{15}BrFN_3O_2Na$ $(M + Na)^+$ 522.0229; found 522.0220.

(E)-2-(2-Bromo-2-(4-chlorophenyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3bf**). Following the general procedure, the product was isolated as a white solid: 127.8 mg (62%); mp = 180−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.90 (m, 2H), 7.79−7.74 (m, 4H), 7.47−7.46 (m, 3H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 6.36 (s, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 136.7, 134.9, 134.1, 131.6, 130.9, 130.6, 130.3, 129.7, 129.6, 129.3, 129.0, 124.1, 121,6, 112.1, 111.4, 60.4, 41.0; HRMS (ESI) calcd for $C_{26}H_{15}BrClN_3O_2Na$ $(M + Na)^+$ 537.9934; found 537.9925.

(E)-2-(2-Bromo-2-(4-bromophenyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(phenyl)methyl)malononitrile (**3bg**). Following the general procedure, the product was isolated as a white solid: 147.6 mg (66%); mp = 192−193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2H), 7.78−7.74 (m, 4H), 7.56 (d, J = 8.0 Hz, 2H), 7.45 (s, 3H), 7.25−7.24 (m, 2H), 6.36 (s, 1H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 134.9, 134.6, 132.0, 131.6, 130.9, 130.6, 130.3, 129.9, 129.6, 129.3, 125.1, 124.1, 121.6, 112.1, 111.4, 60.4, 41.0; HRMS (ESI) calcd for $C_{26}H_{15}Br_2N_3O_2Na$ $(M + Na)^+$ 581.9424; found 581.9436.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(4-methoxyphenyl)methyl)malononitrile (**3cc**). Following the general procedure, the product was isolated as a white solid: 157.6 mg (75%); mp = 157−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2H), 7.78−7.76 (m, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 5.80 (s, 1H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.9, 141.0, 134.9, 133.1, 132.4, 131.3, 131.0, 129.5, 128.4, 124.1, 123.7, 120.9, 114.5, 112.6, 111.7, 60.3, 55.3, 41.4, 21.5; HRMS (ESI) calcd for $C_{28}H_{20}BrN_3O_3Na$ $(M + Na)^+$ 548.0568; found 548.0577.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(3-methoxyphenyl)methyl)malononitrile (**3dc**). Following the general procedure, the product was isolated as a white solid: 153.4 mg (73%); mp = 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.90 (m, 2H), 7.79−7.77 (m, 2H), 7.40−7.24 (m, 7H), 7.00 (d, J = 8.0 Hz, 1H), 6.33 (s, 1H), 5.82 (s, 1H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 160.0, 141.0, 134.9, 133.1, 133.0, 132.5, 131.0, 130.3, 129.5, 128.4, 124.2, 121.9, 120.8, 116.1, 115.1, 112.5, 111.6, 60.5, 55.4, 41.1, 21.5; HRMS (ESI) calcd for $C_{28}H_{20}BrN_3O_3Na$ $(M + Na)^+$ 548.0568; found 548.0599.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(p-tolyl)methyl)malononitrile (**3ec**). Following the general procedure, the product was isolated as a white solid: 158.9 mg (78%); mp = 178−180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.86 (m, 2H), 7.74−7.72 (m, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.22 (s, 4H), 6.30 (s, 1H), 5.80 (s, 1H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 141.0, 140.5, 134.9, 133.1, 132,4, 131.1, 130.0, 129.7, 129.5, 128.9, 128.4, 124.1, 121,0, 112.6, 111.8, 60.5, 41.3, 21.5, 21.2; HRMS (ESI) calcd for $C_{28}H_{20}BrN_3O_2Na$ $(M + Na)^+$ 532.0637; found 532.0627.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(m-tolyl)methyl)malononitrile (**3fc**). Following the general procedure, the product was isolated as a white solid: 158.9 mg (78%); mp = 165−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.73 (s, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.32−7.30 (m, 3H), 7.23 (s, 3H), 6.31 (s, 1H), 5.79 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 141.0, 139.2, 134.9, 133.1, 132.4, 131.8, 131.1, 130.3, 129.5, 129.2, 128.4, 126.8, 124.1, 120.9, 112.5, 111.7, 60.6, 41.2, 21.5, 21.5; HRMS (ESI) calcd for $C_{28}H_{20}BrN_3O_2Na$ $(M + Na)^+$ 532.0637; found 532.0628.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(o-tolyl)methyl)malononitrile (**3gc**). Following the general procedure, the product was isolated as a white solid: 144.6 mg (71%); mp = 163−165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22−8.20 (m, 1H), 7.84−7.83 (m, 2H), 7.71 (s, 2H), 7.30−7.29 (m, 4H), 7.22−7.21 (m, 3H), 6.25 (s, 1H), 6.13 (s, 1H), 2.50 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 141.1, 137.3, 134.9, 133.1, 132.5, 131.4, 131.0, 130.8, 130.1, 129.5, 128.4, 127.0, 124.1, 120.8, 112.5, 111.9, 55.9, 41.3, 21.5, 20.0; HRMS (ESI) calcd for $C_{28}H_{20}BrN_3O_2Na$ $(M + Na)^+$ 532.0637; found 532.0628.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)(4-fluorophenyl)methyl)malononitrile (**3hc**). Following the general procedure, the product was isolated as a white solid: 166.3 mg (81%); mp = 170−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.89 (m, 2H), 7.79−7.77 (m, 4H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 6.27 (s, 1H), 5.83 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 164.8 (d, J = 249.7 Hz), 141.2, 135.0, 133.0, 132.9, 132.0 (d, J = 8.6 Hz), 130.9, 129.5, 128.4, 127.9 (d, J = 3.5 Hz), 124.2, 120.5, 116.5 (d, J = 21.7 Hz), 112.3, 111.6, 59.9, 41.3 (d, J = 0.7 Hz), 21.5; HRMS (ESI) calcd for $C_{27}H_{17}BrFN_3O_2Na$ $(M + Na)^+$ 536.0386; found 536.0377.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((4-chlorophenyl)(1,3-dioxoisoindolin-2-yl)methyl)malononitrile (**3ic**). Following the general procedure, the product was isolated as a white solid: 154.5 mg (73%); mp = 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 2H), 7.77−7.75 (m, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 7.6 Hz, 2H), 6.27 (s, 1H), 5.82 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 141.2, 136.5, 135.1, 133.0, 133.0, 131.2, 130.9, 130.4, 129.5, 129.5, 128.4, 124.3, 120.4, 112.3, 111.5, 59.9, 41.2, 21.5; HRMS (ESI) calcd for $C_{27}H_{17}BrClN_3O_2Na$ $(M + Na)^+$ 552.0090; found 552.0084.

(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((4-bromophenyl)(1,3-dioxoisoindolin-2-yl)methyl)malononitrile (**3jc**). Following the general procedure, the product was isolated as a white solid: 171.9 mg (75%); mp = 183−186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2H), 7.79−7.77 (m, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 5.78 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 141.2, 135.0, 133.0, 132.9, 132.5, 131.4, 130.9, 130.8, 129.5, 128.3, 124.9, 124.3, 120.3, 112.2, 111.5, 60.0, 41.1, 21.5; HRMS (ESI) calcd for $C_{27}H_{17}Br_2N_3O_2Na$ $(M + Na)^+$ 595.9585; found 595.9557.

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J. Org. Chem. 2016, 81, 7080−7087

*(E)-2-(2-Bromo-2-(p-tolyl)vinyl)-2-((1,3-dioxoisoindolin-2-yl)-(3,4,5-trimethoxyphenyl)methyl)malononitrile (**3kc**).* Following the general procedure, the product was isolated as a white solid: 95.9 mg (41%); mp = 158−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2H), 7.78−7.76 (m, 2H), 730 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.09 (s, 2H), 6.30 (s, 1H), 5.73 (s, 1H), 3.89 (s, 6H), 3.87 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 153.5, 141.1, 139.5, 135.0, 133.0, 132.4, 130.9, 129.4, 128.4, 126.8, 124.2, 120.7, 112.6, 111.5, 107.5, 60.9, 60.8, 56.3, 41.4, 21.5; HRMS (ESI) calcd for $C_{30}H_{24}BrN_3O_5Na$ $(M + Na)^+$ 608.0797; found 608.0787.

*(E)-2-([1,1′-Biphenyl]-4-yl(1,3-dioxoisoindolin-2-yl)methyl)-2-(2-bromo-2-(p-tolyl)vinyl)malononitrile (**3lc**).* Following the general procedure, the product was isolated as a white solid: 148.5 mg (65%); mp = 171−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.82 (m, 4H), 7.74−7.73 (m, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.36−7.32 (m, 3H), 7.23 (d, J = 8.0 Hz, 2H), 6.36 (s, 1H), 5.89 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 143.1, 141.1, 139.7, 135.0, 133.1, 132.7, 131.1, 130.7, 130.3, 129.5, 129.0, 128.5, 128.0, 127.9, 127.1, 124.2, 120.8, 112.6, 111.8, 60.4, 41.3, 21.6; HRMS (ESI) calcd for $C_{33}H_{22}BrN_3O_2Na$ $(M + Na)^+$ 594.0793; found 594.0782.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00973.

Copies of NMR spectra for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: milig@126.com.

*E-mail: leiwang@chnu.edu.cn. Phone: +86-561-380-2069. Fax: +86-561-309-0518.

Notes

The authors declare no competing financial interest.

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