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# Metal-Free Radical Haloazidation of Benzene-Tethered 1,7-Enynes Leading to Polyfunctionalized 3,4-Dihydroquinolin-2(1*H*)-ones

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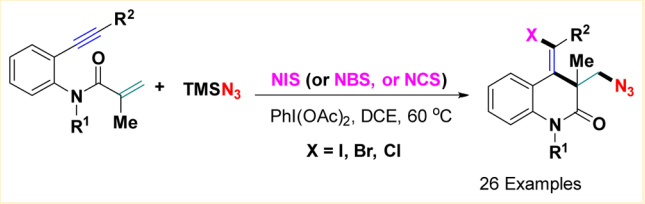
Supporting Information

**ABSTRACT:** A new cascade three-component haloazidation of benzene-tethered 1,7-enynes for the formation of biologically interesting azidylated 3,4-dihydroquinolin-2(1*H*)-ones has been achieved under mild and metal-free conditions using $TMSN_3$ as a $N_3$ source and NIS (or NBS or NCS) as a halogen source. The reaction pathway involves in situ-generated azidyl radical-triggered $\alpha,\beta$-conjugated addition/6-exo-dig cyclization/radical coupling sequence, resulting in successive multiple bond-forming events, including carbon−nitrogen, carbon−carbon, and carbon−halogen bonds to rapidly construct complex heterocyclic molecules. Furthermore, the resulting products would be useful building blocks in the discovery of lead compounds and other biologically interesting $N_3$-containing heterocycles.

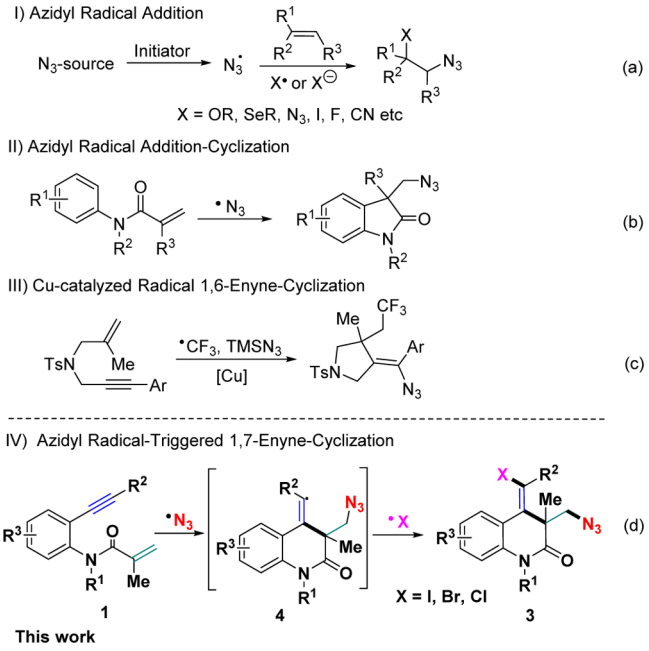



## INTRODUCTION

Owing to their special structural motifs and unique reactivity, organic azides serve as highly powerful and valuable building blocks for the collection of nitrogen-containing molecules.[1] Moreover, the applications of organic azides have expanded extensively in biology, supramolecular chemistry, and materials sciences.[2] Additionally, because of their significant biological activity, highly reactive azido functionalities have been used to design and synthesize lead compounds for drug discovery.[3] In the past few decades, substantial efforts have been paid to pave the pathways to access this important class of compounds, which made them more powerful and applicable.[4] Generally, strategies for organic azide syntheses can be classified into three types, that is, traditional $S_N2$ reactions of alkyl halides,[5] metal-catalyzed cross coupling,[6] and recent azidation of alkenes or alkynes.[7] Among them, the last provides a straightforward and atom economic protocol for organic azide syntheses with good functional group compatibility, especially well-developed azidyl radical addition to unsaturated systems using $TMSN_3$, $NaN_3$, or $IN_3$ as the $N_3$ source[8] (Scheme 1a) and thus has attracted considerable attention. For example, Antonchick et al. reported a direct radical azidoarylation of alkenes for the construction of azidylated 2-oxindoles using $PhI(OCOCF_3)_2$ (PIFA) as an oxidant (Scheme 1b).[9] Despite these significant advances, the discovery of a practical, general, and site-specific protocol under mild conditions is still highly desired but full of challenges.

On one hand, oxidative radical 1,n-enyne-cyclizations have become a useful platform for rapidly accessing a large number of complex cyclic compounds.[10] In addition to atom-economy, annulation efficiency, and high functional group compatibility, these reactions could avoid the prefunctionalization of reaction

**Scheme 1. Profiling Applications of Azidation**

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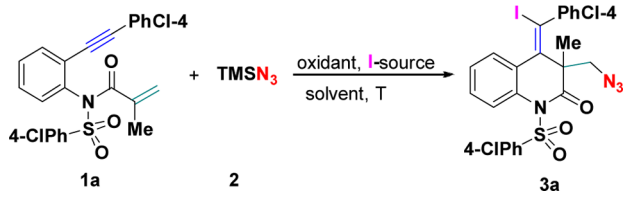
substrates or the use of expensive transition metals. Recently, our group[11] and others[12] have focused great effort on developing radical 1,n-enyne-cyclizations for the assembly of complicated carbocyclic and heterocyclic frameworks with chemical and pharmaceutical interest. For instance, Liang and co-workers reported copper-catalyzed trifluoromethyl radicals-involved 1,6-enyne-cyclization to synthesize azidylated pyrrolidine derivatives (Scheme 1c).[12g] However, to the best of our knowledge, azide radicals triggered 1,7-enyne-cyclization involving C−halogen bond formation has rarely been reported partly because of difficult control of different radicals in a one-pot operation during the long process and its poor selectivity of the radical addition toward alkenyl and alkynyl groups. Thus, metal-free regioselective radical 1,7-enyne-addition cyclization remains a formidable challenge. Specifically, our group developed the addition of various C-center radicals to *N*-tethered 1,7-enynes **1**, which involved the participation of a vinyl intermediate **4** followed by H-abstraction and radical coupling to afford spiro-substituted cyclopenta[c]-quinolones.[11b] We hypothesized that under suitable oxidative conditions, azidyl radicals could be preferentially engaged in activated alkenyl addition of *N*-tethered 1,7-enynes **1** to give vinyl radical intermediates **4**, which would be captured by adequate radical partners, thereby expanding these radical synthetic strategies to create new heterocyclic molecules. Herein, we report a new azidyl radical triggered 1,7-enyne-cyclization, which was trapped by halogen radicals to form a variety of densely functionalized 3,4-dihydroquinolin-2(1*H*)-ones with unprecedented substitution patterns[13] (Scheme 1d). This methodology allows two different radicals in a one-pot manner and shows a broad substrate scope to access cycloaddition products through a highly regioselective haloazidation of 1,7-enynes. Thus, this protocol demonstrates great potential in subsequent transformations in organic synthesis.

## RESULTS AND DISCUSSION

To test the possibility of our envisioned method, commercially available $TMSN_3$ was selected as a radical $N_3$ source due to $TMSN_3$ being easily converted into azidyl radicals in the presence of *N*-iodosuccinimide (NIS).[14] We initially chose 1,7-enynes **1a** as a model substrate to react with 2.0 equiv of $TMSN_3$ in the presence of NIS (2.0 equiv) in DCE at 60 °C. Much to our delight, the reaction proceeded to give access to the desired iodoazidation product **3a**, albeit with a low yield (36%). Encouraged by this result, we planned to employ different solvents and iodine sources to search for the optimal reaction conditions. The results are summarized in Table 1. It is found that solvent effect imposed an important impact on the reaction efficiency. Several other aprotic solvents, such as ethanol (EtOH), dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl-formamide (DMF), and acetonitrile ($CH_3CN$), were utilized, and only a trace amount of product **3a** was observed in all of these solvents (entries 2−5). In another case of ethyl acetate, the reaction stumbled and proved to be far less effective than DCE (entry 1 vs entry 6). In an attempt to enhance the yield further, different iodine sources, such as molecular iodine ($I_2$), tetrabutylammonium iodide (TBAI), and KI, were investigated. A slightly lower yield (32%) was obtained in the presence of 2.0 equiv of $I_2$ (entry 7). However, the use of TBAI or KI completely compressed the reaction process, which may be caused by the lack of oxidants (entries 8 and 9). Next, we attempted to use organic oxidants to improve the reaction

**Table 1. Optimization of Reaction Conditions for Forming Product 3a**[a]




1a 2 3a

| entry | oxidant (equiv) | I-source (equiv) | solvent | *t* (°C) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | | NIS (2.0) | DCE | 60 | 36% |
| 2 | | NIS (2.0) | EtOH | 60 | trace |
| 3 | | NIS (2.0) | DMSO | 60 | trace |
| 4 | | NIS (2.0) | DMF | 60 | trace |
| 5 | | NIS (2.0) | $CH_3CN$ | 60 | trace |
| 6 | | NIS (2.0) | EA | 60 | 24% |
| 7 | | $I_2$ (2.0) | DCE | 60 | 32% |
| 8 | | TBAI (2.0) | DCE | 60 | ND[c] |
| 9 | | KI (2.0) | DCE | 60 | ND[c] |
| 10 | PIDA (2.0) | NIS (2.0) | DCE | 60 | 41% |
| 11 | PIFA (2.0) | NIS (2.0) | DCE | 60 | 22% |
| 12 | TBHP (2.0) | NIS (2.0) | DCE | 60 | trace |
| 13 | TBPB (2.0) | NIS (2.0) | DCE | 60 | trace |
| 14 | BPO (2.0) | NIS (2.0) | DCE | 60 | trace |
| 15 | $H_2O_2$ (2.0) | NIS (2.0) | DCE | 60 | 31% |
| 16 | PIDA (3.0) | NIS (2.0) | DCE | 60 | 43% |
| 17 | PIDA (1.0) | NIS (2.0) | DCE | 60 | 31% |
| 18 | PIDA (2.0) | NIS (1.0) | DCE | 60 | 22% |
| 19 | PIDA (2.0) | NIS (3.0) | DCE | 60 | 45% |
| 20 | PIDA (2.0) | NIS (4.0) | DCE | 60 | 44% |
| 21 | PIDA (2.0) | NIS (3.0) | DCE | 60 | 21%[d] |
| 22 | PIDA (2.0) | NIS (3.0) | DCE | 60 | 55%[e] |
| 23 | PIDA (2.0) | NIS (3.0) | DCE | 60 | 55%[f] |
| 24 | PIDA (2.0) | NIS (3.0) | DCE | rt | 33%[e] |
| 25 | PIDA (2.0) | NIS (3.0) | DCE | 40 | 41%[e] |
| 26 | PIDA (2.0) | NIS (3.0) | DCE | 80 | 43%[e] |
| 27 | PIDA (2.0) | | DCE | 60 | NR[e,g] |

[a]Reaction conditions: 1,7-enynes **1a** (0.2 mmol), **2** (0.4 mmol), oxidant, and I-source in solvent (2.0 mL). [b]Isolated yield of product **3a** based on 1,7-enynes **1** by column chromatography. [c]Not detected (ND). [d]Ratio of **1a**:**2** of 1:1. [e]Ratio of **1a**:**2** of 1:4. [f]Ratio of **1a**:**2** of 1:5. [g]No reaction (NR).

efficiency. The screening of organic oxidants (2.0 equiv) revealed that, compared with phenyliodine bis(trifluoroacetate) (PIFA), *tert*-butyl hydroperoxide (TBHP, 70% in water), *tert*-butyl peroxybenzoate (TBPB), benzoyl peroxide (BPO), and hydrogen peroxide ($H_2O_2$) (entries 11−15), phenyliodine diacetate (PIDA) gave the best outcome in this radical addition-cyclization, delivering 41% yield of **3a** (entry 10). Our next endeavor to change other reaction parameters was attempted to improve the reaction efficiency, including loading of PIDA (1.0 to 3.0 equiv) and NIS (1.0 to 3.0 equiv), substrate ratio, and reaction temperature (entries 16−26). After careful optimization, we found that adjusting the dosage of NIS to 3.0 equiv and substrate ratio to 1:4 (**1a**:**2**) in the presence of 2.0 equiv of PIDA in DCE at 60 °C further facilitated the reaction process and afforded 55% yield of **3a** (entry 22). Without NIS, the reaction did not proceed (entry 27).

With the optimized reaction conditions in hand, we set out to examine the scope of iodoazidation with the use of differently substituted *N*-tethered 1,7-enynes **1**, $TMSN_3$, and NIS in the presence of PIDA (Scheme 2). Upon repeating the



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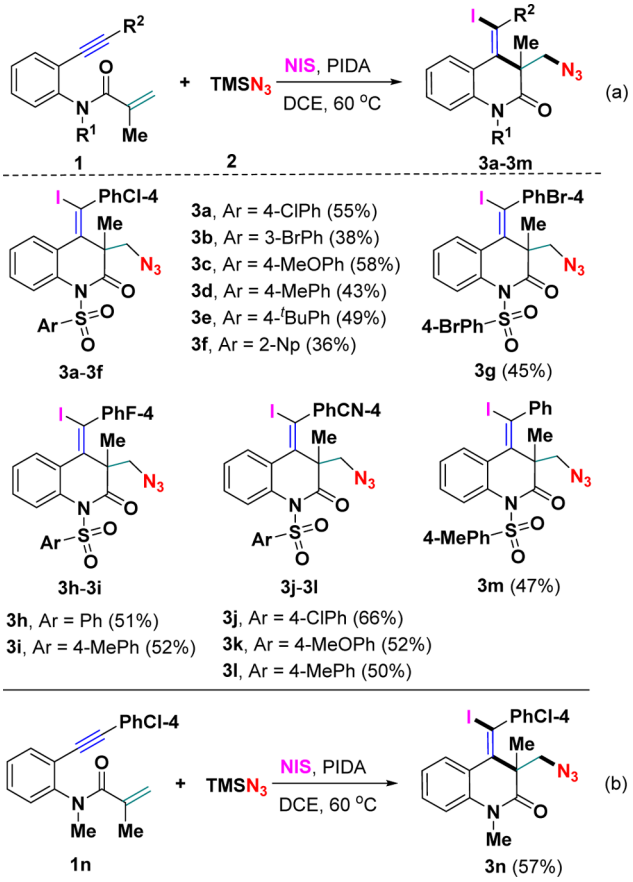
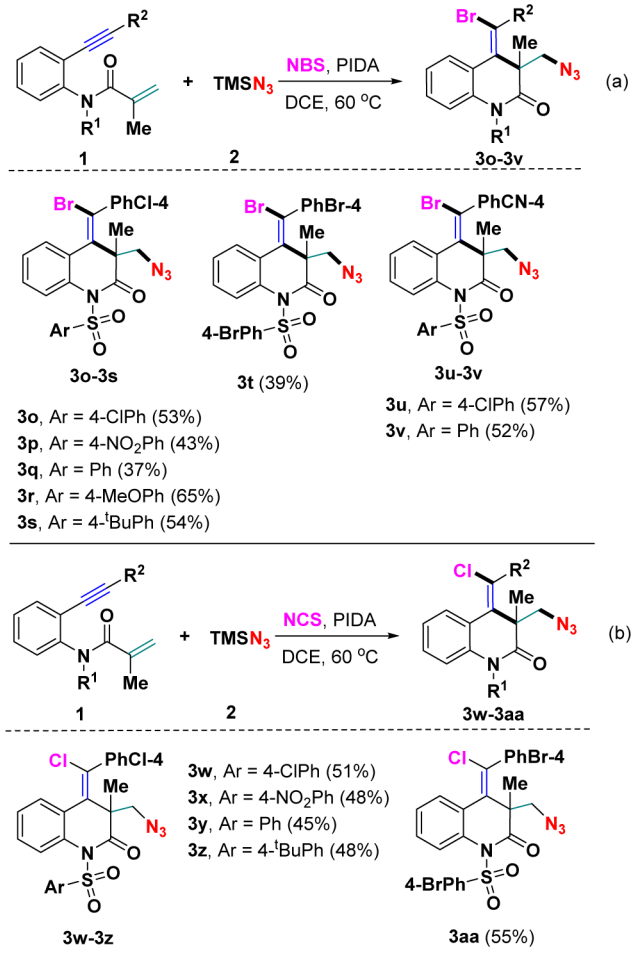
**Scheme 2. Three-Component Iodoazidation of 1,7-Enynes**[a]




[a]Reaction conditions: all reactions were performed with **1** (0.2 mmol), **2** (0.8 mmol), NIS (0.6 mmol), PIDA (0.4 mmol), and DCE (2.0 mL) at 60 °C under air conditions for 12 h. Isolated yield is based on **1**.

**Scheme 3. Three-Component Bromo- and Chloroazidation of 1,7-Enynes**[a]




[a]Reaction conditions: all reactions were performed with **1** (0.2 mmol), **2** (0.8 mmol), NBS (or NCS, 0.6 mmol), PIDA (0.4 mmol), and DCE (2.0 mL) at 60 °C under air conditions for 12 h. Isolated yield is based on **1**.

reaction with $TMSN_3$ **2** and NIS, substrates **1** with different functional groups on the aromatic ring of both the alkynyl ($R^2$) and sulfonyl ($R^1$) moieties all work well, efficiently transforming into the corresponding poly-functionalized 3,4-dihydroquinolin-2(1*H*)-ones **3** in acceptable yields. With a 4-chlorophenyl group on the alkynyl ($R^2$) motif, the variant of substituents on the arylsulfonyl moiety, including Cl, Br, MeO, Me, and *t*-Bu, were successful engaged in these transformations under the above conditions. When the 2-naphthalenyl (2-Np) counterpart was employed as a reaction partner, a significant drop in the yields was obtained (36%), which may be caused by its relatively strong steric hindrance. Functional groups like bromide, fluoride, and cyano at the para-position of the aromatic alkyne moiety were well-tolerated in the azidyl radical-initiated addition cyclization (Scheme 2a). Alternatively, *N*-methylbenzene-tethered 1,7-enynes **1n** was successfully converted to the corresponding *N*-methyl 3,4-dihydroquinolin-2(1*H*)-ones **3n** in 57% yield (Scheme 2b).

In light of these results, we decided to evaluate the possibility of domino bromoazidation of these benzene-tethered 1,7-enynes by exchanging NIS for *N*-bromosuccinimide (NBS). As we had expected, this radical strategy tolerates various benzene-tethered 1,7-enynes, leading to the formation of structurally diverse 3,4-dihydroquinolin-2(1*H*)-ones **3o**−**3v** in synthetically useful yields (Scheme 3). The presence of electron-donating substituents (methoxy, *t*-butyl) at the para-position of the benzenesulfonyl protection group ($R^1$) on the amine anchor seemed to improve the efficiency of the reaction, as the corresponding products **3r** and **3s** could be isolated in slightly higher yields. The reaction can be extended to different functional groups, such as chloride, bromide, and cyano on the arylalkynyl unit, with the realization of cascade bromoazidation of 1,7-enynes. On the basis of our success with bromoazidation of 1,7-enynes, we attempted to further broaden this addition−cyclization of 1,7-enynes to their chloroazidation reactions with $TMSN_3$ using *N*-chlorosuccinimide (NCS) as a chlorine source. Satisfyingly, different substituted 1,7-enynes did not hamper this reaction process. With the presence of NCS, reactions of substrates **1** involving an arylsulfonyl moiety attached by both electron-poor and -donating groups with $TMSN_3$ all worked well, delivering the corresponding chloroazidation products **3w**−**3aa** with yields ranging from 45 to 55%. In current haloazidation cascades, the halogen atom was introduced into the exocyclic vinyl unit, offering an opportunity for further elaboration. Additionally, as mentioned above, azido compounds are very useful building blocks in organic synthesis, which can be further utilized for other transformations. Note that this is the first reported procedure for the three-component synthesis of these new densely functionalized 3,4-



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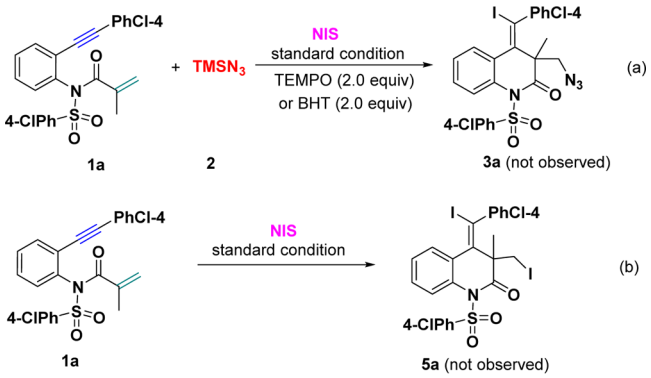
dihydroquinolin-2(1*H*)-ones through a metal-free azide radical triggered 1,7-enyne cyclization.

The resulting 3,4-dihydroquinolin-2(1*H*)-ones **3** were fully characterized by their NMR spectroscopy and HRMS. Furthermore, in the case of compound **3a**, its structure was unambiguously determined by X-ray diffraction (see the Supporting Information)

For gaining insight into the mechanism, several control experiments were conducted. The reaction of 1,7-enynes **1a** with $TMSN_3$ and NIS in the presence of 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylhydroxytoluene (BHT) was carried out (Scheme 4a), but no expected

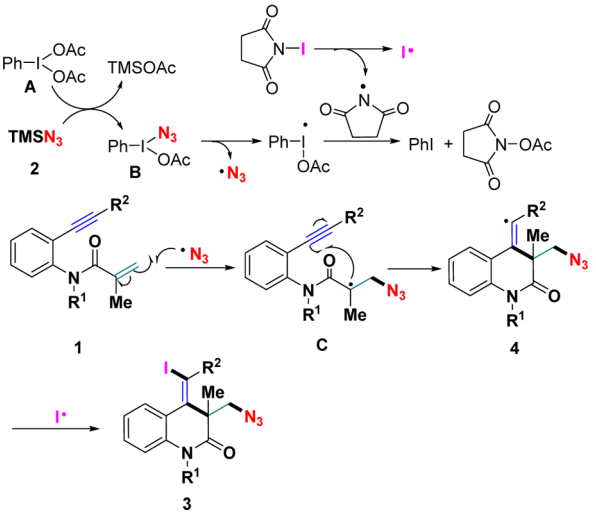
**Scheme 4. Control Experiments**




product **3a** was observed with the starting material **1a** remaining, suggesting that a radical addition mechanism was involved in this transformation. Next, without $TMSN_3$, treatment of **1a** and 3.0 equiv of NIS under standard conditions failed to yield diiodinated 3,4-dihydroquinolin-2(1*H*)-ones **5a** (Scheme 4b), confirming that azide radical, generated in situ from $TMSN_3$, triggered *α,β*-conjugated addition/*6-exo-dig* cyclization to form a vinyl radical intermediate, which was trapped by the iodine radical. Therefore, azidylation occurred prior to the iodination step.

On the basis of the controlled experiments and literature survey,[8,9] we propose a plausible mechanism for the formation of products **3** as depicted in Scheme 5. A ligand exchange between $PhI(OAc)_2$ and $TMSN_3$ would give intermediate **B**.

**Scheme 5. Proposed Mechanism for Forming Products 3**




Intermediate **B** is converted into an azide radical by thermal homolytic cleavage due to the weak I−N bond. Similar to this homolysis, NIS generates a pyrrolidine-2,5-dione radical and iodine radical. The azide radical attacks activated alkenyl moiety of 1,7-enynes **1** to give radical **C** trapped by the alkynyl motif through *6-exo-dig* cyclization to yield vinyl radical intermediate **4**. With the presence of iodine radicals, intermediate **4** is transformed to final 3,4-dihydroquinolin-2(1*H*)-ones **3** by radical coupling.

In conclusion, we have established a new three-component haloazidation/*6-exo-dig* cyclization of 1,7-enynes under mild and metal-free reaction conditions leading to biologically interesting 3,4-dihydroquinolin-2(1*H*)-ones. A significant feature of the developed process is cascade-type formation of successive C−N, C−C, and C−halogen bonds initiated by the addition of an azidyl radical. This reaction enables sequential radical addition/*6-exo-dig* cyclization/radical coupling process and represents a new strategy for the construction of nitrogen-containing compounds. Currently, experiments toward further mechanistic studies are underway in our laboratory.

## EXPERIMENTAL SECTION

**General Information.** All one-pot reactions were carried out in a 25 mL Schlenk tube equipped with a magnetic stir bar under air. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO-$d_6$ on a 400 MHz instrument with TMS as internal standard. Chemical shifts ($\delta$) were reported in ppm with respect to TMS. Data are represented as follows: chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J, Hz), and integration; HRMS analyses were carried out using a TOF-MS instrument with an ESI source. X-ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer.

**General Procedure for the Synthesis of 3.** *Example for the Synthesis of 3a.* 1,7-Enynes **1a** (0.2 mmol, 94 mg), azidotrimethylsilane **2** (4.0 equiv, 0.8 mmol, 92 mg), and phenyliodine diacetate (PIDA, 2.0 equiv, 0.4 mmol, 128 mg) were introduced in a 25 mL Schlenk tube. *N*-Iodosuccinimide (3.0 equiv, 0.6 mmol, 135 mg) and 1,2-dichloroethane (2 mL) were then successively added, and the mixture was stirred at 60 °C for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired product **3a**.

*3-(Azidomethyl)-4-((4-chlorophenyl)iodomethylene)-1-((4-chlorophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3a**).* White solid, 71 mg, 55% yield; mp 167−168 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 8.4 Hz, 2H), 7.81 (d, $J$ = 7.2 Hz, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 2H), 7.59−7.52 (m, 1H), 7.50−7.43 (m, 1H), 7.33−7.28 (m, 1H), 7.24 (d, $J$ = 6.8 Hz, 2H), 6.48 (d, $J$ = 7.6 Hz, 1H), 3.04−2.85 (m, 2H), 0.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 143.2, 141.0, 137.9, 136.9, 134.7, 134.6, 133.1, 131.0, 130.5, 129.9, 129.2, 128.6, 128.2, 127.2, 124.9, 57.2, 56.2, 21.1; IR (KBr, $\nu$, cm$^{-1}$) 3093, 2997, 2110, 1724, 1580, 1454, 1378, 835, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Cl_2IN_4O_3S$ [M + Na]$^+$ 660.9341, found 660.9340.

*3-(Azidomethyl)-1-((3-bromophenyl)sulfonyl)-4-((4-chlorophenyl)iodomethylene)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3b**).* White solid, 52 mg, 38% yield; mp 157−158 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.16 (d, $J$ = 8.4 Hz, 1H), 7.98 (d, $J$ = 7.6 Hz, 1H), 7.89 (d, $J$ = 7.6 Hz, 1H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.61−7.43 (m, 4H), 7.32−7.28 (m, 1H), 7.24 (d, $J$ = 8.4 Hz, 1H), 6.62 (d, $J$ = 8.4 Hz, 1H), 3.02−2.88 (m, 2H), 0.77 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.7, 143.3, 140.4, 137.8, 137.2, 134.6, 131.1, 130.3, 129.9, 129.2, 128.9, 128.5, 128.2, 127.7, 127.2, 124.6, 122.9, 57.1, 56.2, 21.1; IR (KBr, $\nu$, cm$^{-1}$) 3102, 2999, 2103, 1722, 1624, 1453, 1380, 834, 761; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}BrClIN_4O_3S$ [M + Na]$^+$ 704.8836, found 704.8837.



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*3-(Azidomethyl)-4-((4-chlorophenyl)iodomethylene)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3c**).* White solid, 74 mg, 58%; mp 165−166 °C; $^1$H NMR (400 MHz, DMSO) $\delta$ 7.86 (d, $J$ = 8.8 Hz, 2H), 7.76 (d, $J$ = 7.6 Hz, 1H), 7.65 (d, $J$ = 8.0 Hz, 1H), 7.62−7.55 (m, 1H), 7.54−7.48 (m, 1H), 7.44 (d, $J$ = 8.0 Hz, 1H), 7.37 (d, $J$ = 8.0 Hz, 1H), 7.33−7.21 (m, 3H), 6.60 (d, $J$ = 7.6 Hz, 1H), 3.94 (s, 3H), 3.12−2.92 (m, 2H), 0.61 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.5, 164.2, 143.4, 138.2, 134.5, 133.4, 131.3, 130.8, 129.7, 129.2, 128.6, 128.3, 128.2, 126.9, 124.9, 114.0, 102.1, 57.3, 56.2, 55.9, 21.1; IR (KBr, $\nu$, cm$^{-1}$) 2993, 2947, 2108, 1709, 1593, 1453, 1368, 833, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{20}ClIN_4O_4S$ $[M + Na]^+$ 656.9836, found 656.9832.

*3-(Azidomethyl)-4-((4-chlorophenyl)iodomethylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1H)-one (**3d**).* White solid, 54 mg, 43%; mp 183−184 °C; 1H NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.82−7.73 (m, 2H), 7.60−7.50 (m, 1H), 7.45 (d, $J$ = 8.0 Hz, 3H), 7.31−7.28 (m, 1H), 7.23 (d, $J$ = 7.6 Hz, 1H), 7.16 (d, $J$ = 8.0 Hz, 1H), 6.42 (d, $J$ = 7.2 Hz, 1H), 3.00−2.87 (m, 2H), 2.54 (s, 3H), 0.73 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 145.3, 143.4, 138.1, 135.7, 134.6, 133.4, 130.9, 129.8, 129.5, 129.2, 129.0, 128.5, 128.3, 126.9, 124.9, 102.2, 57.3, 56.2, 21.8, 21.1; IR (KBr, $\nu$, cm$^{-1}$) 3030, 2981, 2100, 1749, 1624, 1453, 1373, 837, 763; HRMS (ESI) $m/z$ calcd for $C_{25}H_{20}ClIN_4O_3S$ $[M + Na]^+$ 640.9887, found 640.9879.

*3-(Azidomethyl)-1-((4-(tert-butyl)phenyl)sulfonyl)-4-((4-chlorophenyl)iodomethylene)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3e**).* White solid, 65 mg, 49% yield; mp 196−197 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.94 (d, $J$ = 8.4 Hz, 2H), 7.82−7.73 (m, 2H), 7.66 (d, $J$ = 8.4 Hz, 2H), 7.59−7.52 (m, 1H), 7.50−7.43 (m, 1H), 7.32−7.27 (m, 1H), 7.25−7.20 (m, 1H), 7.12−7.07 (m, 1H), 6.44−6.37 (m, 1H), 3.02−2.88 (m, 2H), 1.43 (s, 9H), 0.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.5, 158.2, 143.4, 138.1, 135.5, 134.6, 133.4, 130.8, 129.8, 129.2, 128.8, 128.4, 128.2, 127.0, 125.9, 125.0, 102.1, 57.3, 56.2, 35.4, 31.1, 21.0; IR (KBr, $\nu$, cm$^{-1}$) 3032, 2957, 2102, 1724, 1593, 1458, 1369, 1351, 837, 61; HRMS (TOF-ESI) $m/z$ calcd for $C_{28}H_{26}ClIN_4O_3S$ $[M + Na]^+$ 683.0357, found 683.0360.

*3-(Azidomethyl)-4-((4-chlorophenyl)iodomethylene)-3-methyl-1-(naphthalen-2-ylsulfonyl)-3,4-dihydroquinolin-2(1H)-one (**3f**).* White solid, 47 mg, 36% yield; mp 163−164 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.70−8.59 (m, 1H), 8.14 (d, $J$ = 8.0 Hz, 1H), 8.12−8.06 (m, 1H), 8.05−7.98 (m, 1H), 7.96−7.92(m, 1H), 7.84−7.76 (m, 3H), 7.74−7.67 (m, 1H), 7.61−7.53 (m, 1H), 7.52−7.45 (m, 1H), 7.25−7.18 (m, 1H), 7.18−7.12 (m, 1H), 6.75−6.68(m, 1H), 5.85−5.78 (m, 1H), 2.99−2.88 (m, 2H), 0.62 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 143.1, 137.9, 135.5, 135.3, 134.6, 134.2, 133.4, 131.8, 130.9, 129.9, 129.8, 128.9, 128.3, 128.1, 128.0, 127.9, 127.0, 125.1, 123.4, 57.3, 56.1, 21.0; IR (KBr, $\nu$, cm$^{-1}$) 3039, 2998, 2102, 1720, 1623, 1451, 1376, 826, 775; HRMS (TOF-ESI) $m/z$ calcd for $C_{28}H_{20}ClIN_4O_3S$ $[M + Na]^+$ 676.9887, found 676.9882.

*3-(Azidomethyl)-4-((4-bromophenyl)iodomethylene)-1-((4-bromophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3g**).* White solid, 66 mg, 45% yield; mp 179−180 °C; $^1$H NMR (400 MHz, DMSO) $\delta$ 8.00 (d, $J$ = 8.4 Hz, 2H), 7.85 (d, $J$ = 8.4 Hz, 2H), 7.77 (d, $J$ = 7.6 Hz, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.62−7.47 (m, 4H), 7.32−7.20 (m, 1H), 6.56−6.39 (m, 1H), 3.18−2.90 (m, 2H), 0.63 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 143.6, 137.8, 137.4, 134.7, 133.0, 132.2, 131.6, 131.2, 130.5, 129.9, 129.3, 128.7, 127.2, 125.0, 122.7, 102.7, 57.1, 56.3, 21.1; IR (KBr, $\nu$, cm$^{-1}$) 3094, 3003, 2098, 1721, 1571, 1452, 1376, 820, 747; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Br_2IN_4O_3S$ $[M + Na]^+$ 750.8310, found 750.8307.

*3-(Azidomethyl)-4-((4-fluorophenyl)iodomethylene)-3-methyl-1-(phenylsulfonyl)-3,4-dihydroquinolin-2(1H)-one (**3h**).* White solid, 60 mg, 51% yield; mp 178−179 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 7.6 Hz, 2H), 7.84−7.70 (m, 4H), 7.68−7.60 (m, 2H), 7.56−7.48 (m, 1H), 7.48−7.41 (m, 1H), 7.01−6.93 (m, 1H), 6.90−6.82(m, 1H), 6.46 (s, 1H), 2.98−2.86 (m, 2H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 162.3 (d, $J_{CF}$ = 248.5 Hz), 140.94 (d, $J_{CF}$ = 3.2 Hz), 138.7, 137.9, 134.7, 134.0, 133.3, 131.0, 129.75 (d, $J_{CF}$ = 6.6 Hz), 129.1, 128.9, 127.0, 124.8, 115.33 (d, $J_{CF}$ = 22.2 Hz), 115.0, 114.8, 57.2, 56.2, 20.9; IR (KBr, $\nu$, cm$^{-1}$) 3067, 2952, 2102, 1596, 1448, 1374, 835, 575; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{18}FIN_4O_3S$ $[M + Na]^+$ 611.0026, found 611.0020.

*3-(Azidomethyl)-4-((4-fluorophenyl)iodomethylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1H)-one (**3i**).* White solid, 63 mg, 52% yield; mp 176−178 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.83−7.73 (m, 2H), 7.57−7.51 (m, 1H), 7.45 (d, $J$ = 8.0 Hz, 3H), 7.27−7.21 (m, 1H), 7.04−6.97 (m, 1H), 6.91−6.84 (m, 1H), 6.51−6.43 (m, 1H), 3.00−2.87(m, 2H), 2.54 (s, 3H), 0.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.6, 162.2 (d, $J_{CF}$ = 248.5 Hz), 145.3, 141.0 (d, $J_{CF}$ = 3.3 Hz), 138.0, 135.7, 134.7, 133.3, 131.0, 129.8 (d, $J_{CF}$ = 9.6 Hz), 129.0, 126.9, 124.9, 115.24 (d, $J_{CF}$ = 21.9 Hz), 115.1, 114.9, 102.7, 57.3, 56.2, 21.8, 21.0; IR (KBr, $\nu$, cm$^{-1}$) 3062, 2953, 2103, 1718, 1596, 1451, 1373, 830, 746; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{20}FIN_4O_3S$ $[M + Na]^+$ 625.0183, found 625.0174.

*4-((3-(Azidomethyl)-1-((4-chlorophenyl)sulfonyl)-3-methyl-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)iodomethyl)benzonitrile (**3j**).* White solid, 84 mg, 66% yield; mp 156−157 °C; $^1$H NMR (400 MHz, DMSO) $\delta$ 7.95 (d, $J$ = 8.4 Hz, 2H), 7.85 (d, $J$ = 8.4 Hz, 3H), 7.80 (d, $J$ = 7.6 Hz, 2H), 7.68 (d, $J$ = 7.6 Hz, 1H), 7.64−7.58 (m, 1H), 7.57−7.51 (m, 1H), 7.48 (d, $J$ = 7.6 Hz, 1H), 6.80 (d, $J$ = 8.0 Hz, 1H), 3.13−2.96 (m, 2H), 0.61 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.4, 149.0, 141.1, 138.8, 136.8, 134.1, 133.1, 132.0, 130.9, 130.5, 130.2, 129.2, 128.6, 127.3, 124.9, 118.0, 112.3, 100.6, 57.1, 56.4, 21.2; IR (KBr, $\nu$, cm$^{-1}$) 3091, 2995, 2224, 2110, 1716, 1596, 1454, 1381, 826, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{17}ClIN_5O_3S$ $[M + Na]^+$ 651.9683, found 651.9680.

*4-((3-(Azidomethyl)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)iodomethyl)benzonitrile (**3k**).* White solid, 66 mg, 52% yield; mp 172−173 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.97 (d, $J$ = 8.8 Hz, 2H), 7.83−7.74 (m, 2H), 7.63 (d, $J$ = 7.6 Hz, 1H), 7.58−7.52 (m, 1H), 7.51−7.38 (m, 3H), 7.10 (d, $J$ = 8.8 Hz, 2H), 6.68 (d, $J$ = 8.0 Hz, 1H), 3.96 (s, 3H), 3.01−2.88 (m, 2H), 0.70 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.3, 164.2, 149.3, 139.1, 134.0, 133.4, 131.7, 131.4, 130.6, 130.0, 129.7, 128.6, 126.9, 124.9, 118.0, 114.0, 112.2, 100.1, 57.2, 56.3, 56.0, 21.3; IR (KBr, $\nu$, cm$^{-1}$) 3066, 2998, 2225, 2103, 1711, 1596, 1452, 1370, 830, 751; HRMS (TOF-ESI) $m/z$ calcd for $C_{26}H_{20}IN_5O_4S$ $[M + Na]^+$ 648.0178, found 648.0177.

*4-((3-(Azidomethyl)-3-methyl-2-oxo-1-tosyl-2,3-dihydroquinolin-4(1H)-ylidene)iodomethyl)benzonitrile (**3l**).* White solid, 61 mg, 50% yield; mp 173−174 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.82−7.75 (m, 2H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.60−7.52 (m, 1H), 7.50−7.43 (m, 4H), 7.41 (d, $J$ = 8.0 Hz, 1H), 6.60 (d, $J$ = 8.0 Hz, 1H), 3.00−2.89 (m, 2H), 2.55 (s, 3H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.3, 149.3, 145.4, 139.0, 135.7, 134.1, 133.4, 131.7, 130.7, 130.0, 129.5, 129.0, 128.0, 127.0, 124.9, 118.0, 112.2, 100.2, 57.2, 56.3, 21.8, 21.2; IR (KBr, $\nu$, cm$^{-1}$) 3067, 2952, 2225, 2101, 1709, 1596, 1452, 1368, 830, 751; HRMS (TOF-ESI) $m/z$ calcd for $C_{26}H_{20}IN_5O_3S$ $[M + Na]^+$ 632.0229, found 632.0223.

*3-(Azidomethyl)-4-(iodo(phenyl)methylene)-3-methyl-1-tosyl-3,4-dihydroquinolin-2(1H)-one (**3m**).* White solid, 55 mg, 47% yield; mp 184−185 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 8.0 Hz, 2H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.57−7.50 (m, 1H), 7.46 (d, $J$ = 8.0 Hz, 4H), 7.27−7.20 (m, 2H), 7.19−7.13 (m, 1H), 6.48 (d, $J$ = 7.2 Hz, 1H), 3.00−2.86 (m, 2H), 2.54 (s, 3H), 0.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.8, 145.3, 145.0, 137.1, 135.7, 134.8, 133.4, 131.0, 129.6, 129.5, 129.0, 128.4, 127.9, 127.1, 126.9, 124.9, 104.2, 57.3, 56.2, 21.8, 20.7; IR (KBr, $\nu$, cm$^{-1}$) 3058, 2951, 2102, 1716, 1596, 1449, 1372, 832, 758; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{21}IN_4O_3S$ $[M + Na]^+$ 607.0277, found 607.0268.

*3-(Azidomethyl)-4-((4-chlorophenyl)iodomethylene)-1,3-dimethyl-3,4-dihydroquinolin-2(1H)-one (**3n**).* Yellow oil, 55 mg, 57%; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95 (m, 1H), 7.47−7.42 (m, 1H), 7.41−7.36 (m, 2H), 7.36−7.31 (m, 2H), 7.22−7.17 (m, 1H), 7.07−7.02 (m, 1H), 3.41 (s, 3H), 3.34 (d, $J$ = 10.4 Hz, 1H), 2.97 (d, $J$ = 12.0 Hz, 1H), 1.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.0, 144.8, 139.7, 138.4, 134.2, 132.1, 130.3, 129.8, 129.5, 128.3, 128.0, 123.0, 114.4, 57.1, 52.9, 30.9, 21.3; IR (KBr, $\nu$, cm$^{-1}$) 3077, 2929, 2093, 1671, 1597, 1470, 1349, 832, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{19}H_{16}ClIN_4O$ $[M + Na]^+$ 500.9950, found 500.9954.

*3-(Azidomethyl)-4-(bromo(4-chlorophenyl)methylene)-1-((4-chlorophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one (**3o**).* White solid, 63 mg, 53% yield; mp 176−177 °C; $^1$H NMR (400



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MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$ = 8.4 Hz, 2H), 7.83 (d, $J$ = 7.2 Hz, 1H), 7.76−7.70 (m, 1H), 7.63−7.59 (m, 2H), 7.57−7.50 (m, 1H), 7.49−7.41 (m, 1H), 7.38−7.27 (m, 3H), 6.57 (s, 1H), 3.07−2.87 (m, 2H), 0.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.0, 139.0, 136.9, 135.2, 133.0, 132.8, 131.4, 130.8, 130.4, 130.2, 129.6, 129.3, 129.1, 128.7, 128.4, 127.2, 124.8, 56.7, 56.1, 21.0; IR (KBr, $\nu$, $cm^{-1}$) 3100, 3007, 2951, 2102, 1716, 1583, 1452, 1377, 826, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}BrCl_2N_4O_3S$ [M + Na]$^+$ 612.9479, found 612.9484.

*3-(Azidomethyl)-4-(bromo(4-chlorophenyl)methylene)-3-methyl-1-((4-nitrophenyl)sulfonyl)-3,4-dihydroquinolin-2(1H)-one* ***(3p)***. White solid, 52 mg, 43% yield; mp 175−176 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48−8.42 (m, 2H), 8.22 (d, $J$ = 8.8 Hz, 2H), 7.91−7.85 (m, 1H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.60−7.52 (m, 1H), 7.48 (d, $J$ = 6.4 Hz, 1H), 7.36−7.32 (m, 1H), 7.29−7.22 (m, 2H), 6.68 (s, 1H), 3.11−2.89 (m, 2H), 0.76 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 150.9, 144.1, 138.9, 135.5, 132.7, 132.5, 131.2, 130.3, 130.2, 129.9, 129.4, 128.5, 127.4, 124.2, 124.0, 56.5, 56.1, 20.9; IR (KBr, $\nu$, $cm^{-1}$) 3104, 3066, 2870, 2109, 1718, 1599, 1530, 1453, 1383; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}BrClN_5O_5S$ [M + Na]$^+$ 623.9720, found 623.9714.

*3-(Azidomethyl)-4-(bromo(4-chlorophenyl)methylene)-3-methyl-1-(phenylsulfonyl)-3,4-dihydroquinolin-2(1H)-one* ***(3q)***. White solid, 41 mg, 37% yield; mp 179−181 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.01 (d, $J$ = 7.6 Hz, 2H), 7.83 (d, $J$ = 7.6 Hz, 1H), 7.80−7.71 (m, 2H), 7.67−7.61 (m, 2H), 7.57−7.50 (m, 1H), 7.49−7.41 (m, 1H), 7.35−7.27 (m, 2H), 7.23 (s, 1H), 6.52 (s, 1H), 3.06−2.89(m, 2H), 0.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 139.1, 138.7, 135.1, 134.1, 133.3, 132.9, 131.4, 130.7, 130.2, 129.6, 129.5, 128.9, 128.8, 128.6, 128.3, 127.0, 124.7, 56.7, 56.1, 20.9; IR (KBr, $\nu$, $cm^{-1}$) 3069, 2984, 2098, 1701, 1597, 1449, 1358, 830, 752; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{18}BrClN_4O_3S$ [M + Na]$^+$ 578.9869, found 578.9870.

*3-(Azidomethyl)-4-(bromo(4-chlorophenyl)methylene)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3r)***. White solid, 77 mg, 65% yield; mp 175−176 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.95 (d, $J$ = 8.8 Hz, 2H), 7.82 (d, $J$ = 7.6 Hz, 1H), 7.78−7.72 (m, 1H), 7.55−7.48 (m, 1H), 7.43 (d, $J$ = 7.2 Hz, 1H), 7.37−7.28 (m, 2H), 7.24 (s, 1H), 7.09−7.07 (m, 1H), 7.07−7.05 (m, 1H), 6.61 (s, 1H), 3.94 (s, 3H), 3.06−2.85 (m, 2H), 0.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 139.2, 135.1, 133.4, 133.1, 131.3, 130.6, 130.2, 129.8, 129.5, 128.5, 128.3, 126.8, 124.7, 114.0, 56.8, 56.1, 55.9, 21.0; IR (KBr, $\nu$, $cm^{-1}$) 3115, 2951, 2105, 1705, 1593, 1451, 1361, 835, 753; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{20}BrClN_4O_4S$ [M + Na]$^+$ 608.9975, found 608.9980.

*3-(Azidomethyl)-4-(bromo(4-chlorophenyl)methylene)-1-((4-(tert-butyl)phenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3s)***. White solid, 66 mg, 54% yield; mp 199−200 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.92 (d, $J$ = 8.8 Hz, 2H), 7.82 (d, $J$ = 7.6 Hz, 1H), 7.79−7.75 (m, 1H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.57−7.50 (m, 1H), 7.45 (d, $J$ = 6.8 Hz, 1H), 7.35−7.24 (m, 2H), 7.16 (s, 1H), 6.53 (s, 1H), 3.08−2.85 (m, 2H), 1.41 (s, 9H), 0.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.2, 139.2, 135.6, 135.0, 133.4, 133.1, 131.4, 130.6, 130.2, 129.5, 129.3, 128.7, 128.3, 126.9, 125.9, 124.9, 123.9, 56.8, 56.1, 35.4, 31.1, 20.9; IR (KBr, $\nu$, $cm^{-1}$) 2957, 2871, 2104, 1718, 1592, 1453, 1397, 1366, 830, 756; HRMS (ESI) $m/z$ calcd for $C_{28}H_{26}BrClN_4O_3S$ [M + Na]$^+$ 635.0495, found 635.0504.

*3-(Azidomethyl)-4-(bromo(4-bromophenyl)methylene)-1-((4-bromophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3t)***. White solid, 53 mg, 39% yield; mp 183 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.89−7.81 (m, 3H), 7.80−7.75 (m, 2H), 7.74−7.71 (m, 1H), 7.57−7.50 (m, 2H), 7.49−7.45 (m, 2H), 7.29−7.19 (m, 1H), 6.49 (s, 1H), 3.06−2.85(m, 2H), 0.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.9, 139.4, 137.4, 133.0, 132.8, 132.1, 131.7, 131.4, 131.4, 130.8, 130.4, 129.6, 129.1, 127.2, 124.9, 123.4, 56.7, 56.2, 21.1; IR (KBr, $\nu$, $cm^{-1}$) 3090, 3005, 2097, 1713, 1570, 1455, 1374, 833, 742; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Br_3N_4O_3S$ [M + Na]$^+$ 702.8449, found 702.8447.

*4-((3-(Azidomethyl)-1-((4-chlorophenyl)sulfonyl)-3-methyl-2-oxo-2,3-dihydroquinolin-4(1H)-ylidene)bromomethyl)benzonitrile* ***(3u)***. White solid, 67 mg, 57% yield; mp 155−156 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96 (d, $J$ = 8.4 Hz, 2H), 7.83 (d, $J$ = 7.6 Hz, 1H), 7.74 (d, $J$ = 8.4 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.62 (d, $J$ = 8.8 Hz, 3H), 7.59−7.53 (m, 1H), 7.48 (d, $J$ = 6.8 Hz, 2H), 6.77 (s, 1H), 3.05−2.90 (m, 2H), 0.71 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 168.7, 145.0, 141.1, 136.9, 133.8, 133.1, 132.0, 130.9, 130.7, 130.4, 129.9, 129.6, 129.2, 127.3, 124.7, 122.5, 117.9, 112.9, 56.6, 56.2, 21.1; IR (KBr, $\nu$, $cm^{-1}$) 3067, 2998, 2225, 2102, 1710, 1598, 1452, 1372, 831, 755; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{17}BrClN_5O_3S$ [M + Na]$^+$ 603.9822, found 603.9827.

*4-((3-(Azidomethyl)-3-methyl-2-oxo-1-(phenylsulfonyl)-2,3-dihydroquinolin-4(1H)-ylidene)bromomethyl)benzonitrile* ***(3v)***. White solid, 57 mg, 52% yield; mp 141−142 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.02 (d, $J$ = 7.6 Hz, 2H), 7.83 (d, $J$ = 7.6 Hz, 1H), 7.80−7.74 (m, 3H), 7.66−7.62 (m, 3H), 7.59−7.52 (m, 2H), 7.49−7.44 (m, 1H), 6.72 (s, 1H), 3.06−2.90 (m, 2H), 0.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 145.1, 138.7, 134.1, 133.9, 133.3, 132.4, 131.9, 130.8, 130.6, 129.9, 129.7, 129.6, 128.9, 127.1, 124.7, 117.9, 112.8, 56.7, 56.0, 21.1; IR (KBr, $\nu$, $cm^{-1}$) 3067, 2999, 2224, 2100, 1713, 1598, 1450, 1372, 830, 756; HRMS (TOF-ESI) $m/z$ calcd for $C_{25}H_{18}BrN_5O_3S$ [M + Na]$^+$ 570.0211, found 570.0215.

*3-(Azidomethyl)-4-(chloro(4-chlorophenyl)methylene)-1-((4-chlorophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3w)***. White solid, 56 mg, 51% yield; mp 189 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.96−7.92 (m, 2H), 7.85−7.81(m, 1H), 7.75−7.71 (m, 1H), 7.62−7.57 (m, 2H), 7.55−7.50 (m, 1H), 7.47−7.42 (m, 1H), 7.38−7.28 (m, 2H), 7.27−7.13 (m, 1H), 6.76 (s, 1H), 3.13−2.87 (m, 2H), 0.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.0, 137.1, 137.0, 135.5, 133.1, 130.6, 130.5, 130.3, 129.6, 129.5, 129.4, 129.1, 128.7, 128.5, 127.1, 124.5, 56.1, 54.9, 21.3; IR (KBr, $\nu$, $cm^{-1}$) 3088, 2949, 2105, 1708, 1587, 1452, 1361, 826, 759; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Cl_3N_4O_3S$ [M + Na]$^+$ 568.9985, found 568.9976.

*3-(Azidomethyl)-4-(chloro(4-chlorophenyl)methylene)-3-methyl-1-((4-nitrophenyl)sulfonyl)-3,4-dihydroquinolin-2(1H)-one* ***(3x)***. White solid, 54 mg, 48% yield; mp 182−183 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47−8.40 (m, 2H), 8.25−8.18 (m, 2H), 7.90−7.84 (m, 1H), 7.76−7.70 (m, 1H), 7.57−7.52 (m, 1H), 7.50−7.43 (m, 1H), 7.40−7.35 (m, 1H), 7.33−7.23 (m, 2H), 6.87 (s, 1H), 3.21−2.87 (m, 2H), 0.84 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 150.9, 144.2, 137.0, 135.7, 132.7, 131.1, 130.7, 130.2, 130.0, 129.7, 129.6, 129.2, 128.7, 128.6, 127.3, 124.0, 55.8, 55.0, 21.4; IR (KBr, $\nu$, $cm^{-1}$) 3105, 2866, 2098, 1715, 1603, 1530, 1456, 1380, 836, 740; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Cl_2N_5O_5S$ [M + Na]$^+$ 580.0225, found 580.0222.

*3-(Azidomethyl)-4-(chloro(4-chlorophenyl)methylene)-3-methyl-1-(phenylsulfonyl)-3,4-dihydroquinolin-2(1H)-one* ***(3y)***. White solid, 46 mg, 45% yield; mp 188−189 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.03−7.98 (m, 2H), 7.86−7.81 (m, 1H), 7.80−7.71(m, 2H), 7.65−7.58(m, 2H), 7.56−7.50 (m, 1H), 7.48−7.41 (m, 1H), 7.37−7.32 (m, 1H), 7.29−7.17 (m, 2H), 6.72 (s, 1H), 3.15−2.87 (m, 2H), 0.79 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 138.7, 137.2, 135.4, 134.1, 133.3, 130.5, 130.4, 129.7, 129.4, 128.9, 128.8, 128.5, 128.4, 127.0, 124.5, 56.2, 54.9, 21.2; IR (KBr, $\nu$, $cm^{-1}$) 3065, 2998, 2093, 1710, 1596, 1449, 1366, 845, 753; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{18}Cl_2N_4O_3S$ [M + Na]$^+$ 535.0374, found 535.0363.

*3-(Azidomethyl)-1-((4-(tert-butyl)phenyl)sulfonyl)-4-(chloro(4-chlorophenyl)methylene)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3z)***. White solid, 55 mg, 48% yield; mp 188−189 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.91 (d, $J$ = 8.8 Hz, 2H), 7.84−7.80 (m, 1H), 7.79−7.75 (m, 1H), 7.64−7.58 (m, 2H), 7.55−7.49 (m, 1H), 7.47−7.41 (m, 1H), 7.37−7.25 (m, 2H), 7.22 (d, $J$ = 7.6 Hz, 1H), 6.71 (s, 1H), 3.15−2.85 (m, 2H), 1.40 (s, 9H), 0.78 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 158.2, 137.3, 135.7, 135.3, 133.5, 130.6, 130.4, 129.6, 129.4, 128.7, 128.4, 126.9, 125.9, 124.6, 56.3, 55.0, 35.4, 31.1, 21.2; IR (KBr, $\nu$, $cm^{-1}$) 2957, 2871, 2104, 1719, 1592, 1453, 1398, 1365, 831, 756; HRMS (TOF-ESI) $m/z$ calcd for $C_{28}H_{26}C_{l2}N_4O_3S$ [M + Na]$^+$ 591.1000, found 591.1008.

*3-(Azidomethyl)-4-((4-bromophenyl)chloromethylene)-1-((4-bromophenyl)sulfonyl)-3-methyl-3,4-dihydroquinolin-2(1H)-one* ***(3aa)***. White solid, 70 mg, 55% yield; mp 180−182 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.86 (d, $J$ = 2 Hz, 1H), 7.86−7.82 (m, 2H), 7.81 (d, $J$ = 1.6 Hz, 1H), 7.78−7.76 (m, 1H), 7.76−7.73(m, 1H), 7.72 (d, $J$ = 1.2 Hz, 1H), 7.55−7.52 (m, 1H), 7.52−7.49 (m, 1H), 7.49−7.46 (m, 1H),


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7.44 (d, $J$ = 8.0 Hz, 1H), 6.67 (s, 1H), 3.10- 2.90 (m, 2H), 0.80 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 169.7, 137.5, 133.1, 132.1, 131.7, 131.4, 130.7, 130.6, 130.4, 130.3, 129.8, 129.6, 129.5, 129.4, 127.1, 124.6, 123.7, 56.1, 55.0, 21.2; IR (KBr, $\nu$, cm$^{-1}$) 3092, 2954, 2097, 1713, 1570, 1455, 1373, 834, 743; HRMS (TOF-ESI) $m/z$ calcd for $C_{24}H_{17}Br_2ClN_4O_3S$ $[M + Na]^+$ 658.8954, found 658.8958.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02655.

$^1$H and $^{13}$C NMR spectra for all pure products (PDF)
X-ray crystal data (CIF) for **3a** (CIF)

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### Notes

The authors declare no competing financial interest.

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