

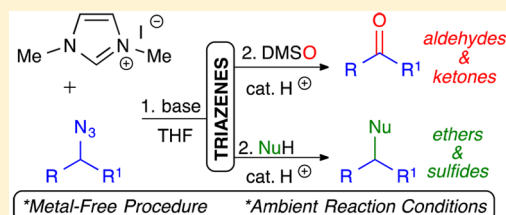
π -Conjugated Triazenes: Intermediates That Undergo Oxidation and Substitution Reactions

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S Supporting Information

ABSTRACT: Novel reactivity for π -conjugated triazenes is herein reported. This observed and unprecedented triazene reactivity gave access to oxidation and substitution reactions. These transformations include successful synthesis of aldehydes, ketones, ethers, and sulfides from readily available organic azides via π -conjugated triazene intermediates. Notably, the afforded adducts were obtained in good yields, at room temperature, and in the absence of added metal catalysts.



INTRODUCTION

Molecules that improve access to synthetic targets, so-called “versatile molecules”, have played an important role throughout the history of chemistry. It is well-known that allenylsilanes,¹ arylsulfonium salts,² hypervalent iodine,³ dimethyl sulfoxide,⁴ dimethylformamide,⁵ and organic azides⁶ are examples of molecules that can be derivatized through various pathways. In addition, their general usefulness reflects the fact that these molecules can also function as reagents, intermediates, or catalysts for many transformations. Among these versatile molecules, organic azides are perhaps the most widely used compounds as exemplified in click chemistry,⁷ syntheses of natural products,⁸ heterocycles,⁹ Staudinger reaction,¹⁰ and nitrene precursors.¹¹ Recently, we observed that π -conjugated triazenes, synthesized from azides and *N*-heterocyclic carbenes (NHCs),¹² provide potentially valuable new intermediates for use in organic syntheses.¹³ Initially, we investigated the thermal stability of these π -conjugated triazenes. It was observed that these triazenes were stable at 60 °C for 2 h. However, when these same triazenes were heated at 120 °C some byproducts (unknown at the time) were observed for a couple of triazenes (e.g., 1).¹² Later identification of these byproducts revealed them to be an iminoimidazole (e.g., 2) and a carbonyl compound (e.g., 3) (Figure 1).

Identification of these byproducts has led to the current report, which documents the exceptional reactivity of π -conjugated triazenes, results that now suggest inclusion of these compounds in the list of “versatile molecules”. Specifically, this paper reports an unprecedented, simple, two-

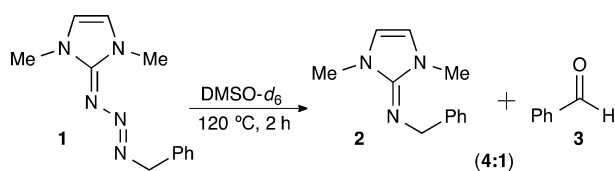


Figure 1. Initial observation.

step protocol that commences from readily available organic azides to provide syntheses of aldehydes, ketones, ethers, and sulfides via π -conjugated triazene intermediates. Furthermore, the method is compatible with a wide-range of nucleophiles, including oxygen, and sulfur nucleophiles, as achieved under mild reaction conditions. This adds to the previously known reactivity of π -conjugated triazenes: nitrogen extrusion and selective *N*-methylation.¹⁴

RESULTS AND DISCUSSION

To help optimize reaction conditions, triazene 4 was synthesized (Table 1). This selection was based on the consideration that triazene 4 produces benzophenone 6 instead

Table 1. Optimization of Reaction Conditions^a

entry	acid	temp (°C)	time (h)	ratio 5/6 ^b	yield of 6 ^c (%)
1	none	120	2	4:1	20
2	none	120	12	4:1	21
3	PdCl ₂	120	2	1:1	43
4	ZnCl ₂	120	2	1:3	58
5	CuSO ₄	120	2	1:3	62
6	SnCl ₄	rt	5	1:4	72
7	TsOH	rt	0.5	1:9	89
8	TFA	rt	0.5	1:2	39

^aReactions were carried out with triazene 4 (0.2 mmol, 103 mg, 1.0 equiv) and the corresponding acid (0.1 mmol, 0.5 equiv) in 1.0 mL of DMSO. ^bRatios calculated using ¹H NMR. ^cIsolated yields (average of two to three runs) by silica gel flash chromatography.

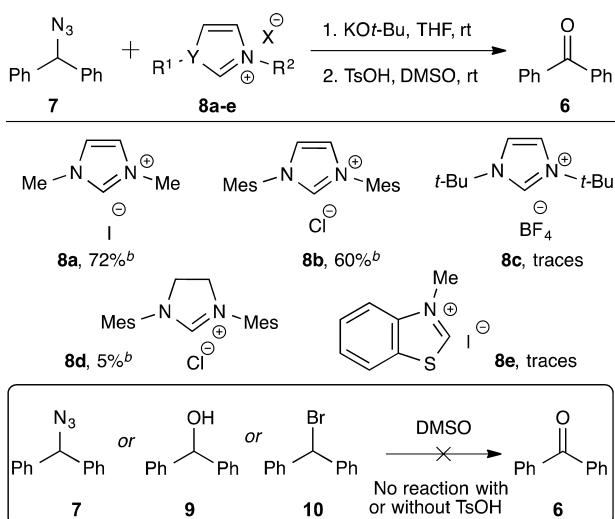
Received: November 9, 2016

Published: January 13, 2017

of the volatile benzaldehyde **3**, thus easing isolation. Heating of triazene **4** at 120 °C for 2 h in DMSO, without any additive, afforded benzophenone **6** in 20% yield (entry 1). Increasing the reaction time did not improve the reaction yield (entry 2), indicating that the triazene is the reacting substrate and not the iminoimidazole byproduct **5**, which remains intact after 12 h of heating. Based on this observation, to activate further triazene **4**, we screened several Lewis and Brønsted acids (entries 3–8), and it was clearly established that the stronger the Lewis acid the higher the yield. In fact, SnCl₄ furnished the product in 72% yield even at room temperature (entry 6). Nonetheless, among all screened Lewis and Brønsted acids, TsOH afforded the product with the highest yield (89%) at room temperature, as achieved in only 30 min (entry 7). Based on this result, we decided to use TsOH for further investigations.

Having optimized conditions for the conversion of a π -conjugated triazene to a carbonyl compound, we next investigated the scope of converting benzhydryl azide **7** to benzophenone **6** in a two-step, one-pot protocol (Table 2), this

Table 2. Optimization of NHC Precursors^a



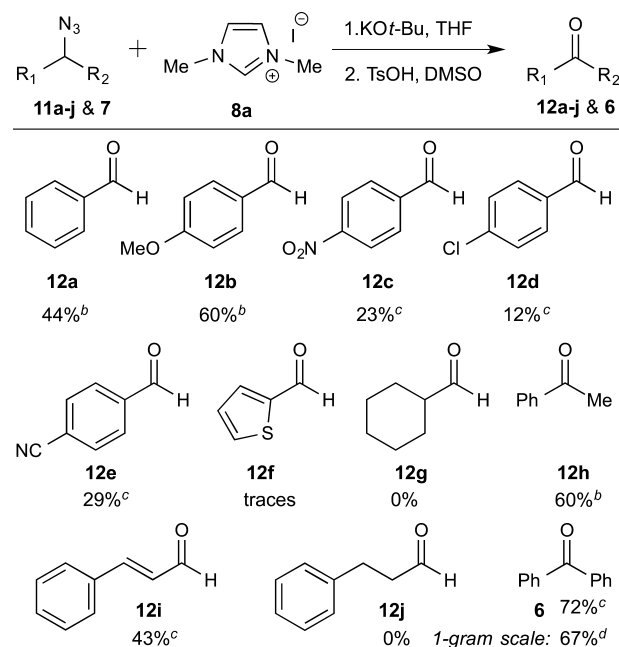
^aReactions were carried out with benzhydryl azide **7** (0.2 mmol, 42 mg, 1.0 equiv), the corresponding NHC precursor **8a–e** (0.3 mmol, 1.5 equiv), KO-*t*-Bu (0.3 mmol, 34 mg, 1.5 equiv), in 1.0 mL of THF for 12 h. Then, the volatiles were removed under reduced pressure. Followed by addition of 1.0 mL of DMSO and TsOH (0.1 mmol, 17 mg, 0.5 equiv) and stirred at rt for 30 min. ^bIsolated yields (average of two to three runs) by silica gel flash chromatography.

to demonstrate a net conversion of organic azides into carbonyl compounds via a triazene intermediate. Examining the new reactivity, in a two-step, one-pot procedure, presented two challenges. First, the formation of the triazene intermediate is dependent on the NHC precursor used (e.g., **8c**, **8d**, and **8e** did not provide a significant yield of their respective triazene intermediate). Second, the TsOH–DMSO-catalyzed oxidation, in the second step, is affected by steric effects of the triazene intermediate (e.g., **8b** is more sterically hindered than **8a**). This size difference makes **8b** more stable and, therefore, less responsive to Brønsted acid activation. In contrast, **8a** produces a less sterically hindered or more reactive triazene intermediate, which afforded benzophenone **6** in 72% yield after two-step, one-pot reaction versus a 60% yield using **8b**. Thus, these results establish 1,3-dimethylimidazolium iodide **8a** as the best NHC precursor, among those tested, to accomplish this

unprecedented transformation. Furthermore, azide **7**, alcohol **9**, and alkyl bromide **10** counterparts were reacted under the same reaction conditions, with or without the Brønsted acid, and no reaction was observed for any of the substrates at rt. This indicating the activation is due to the triazene (Table 2, bottom).¹⁵

With the optimal conditions for the two-step, one-pot procedure in hand, we subsequently explored the scope of this new transformation (Table 3) by surveying the reactivity of

Table 3. Scope of the Oxidation Reaction^a



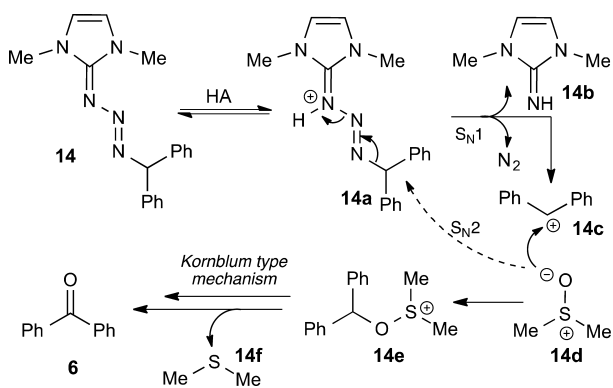
^aReactions were carried out with dimethylimidazolium iodide **8a** (0.75 mmol, 168 mg, 1.5 equiv), KO-*t*-Bu (0.75 mmol, 84 mg, 1.5 equiv), and the corresponding azide **11a–i** and **7** (0.5 mmol, 1.0 equiv) in 1.0 mL of THF for 12 h. The volatiles were then removed under reduced pressure. This was followed by addition of 1.0 mL of DMSO and TsOH (0.25 mmol, 48 mg, 0.5 equiv) and stirred at rt for 30 min. ^bYields calculated using ¹H NMR with DMF as internal standard. ^cIsolated yields (average of two to three runs) by silica gel flash chromatography. ^dIsolated yield for 1 g scale reaction.

freshly prepared organic azides (**11a–j** and **7**) and 1,3-dimethylimidazolium iodide **8a** using KO-*t*-Bu and THF, at room temperature. All reactions were terminated after 12 h (the standard time for triazene formation) for comparison purposes, although starting materials were still present. THF was then removed under reduced pressure, and a catalytic amount of TsOH (50 mol %) in DMSO was added to the reaction mixture. The reaction mixture was quenched after only 30 min, and the product was isolated using silica gel flash chromatography. From this study, it was observed that secondary azides afford their products in higher yields (e.g., **6** and **12h** were obtained in 72% and 60% yield, respectively). The system is also efficient for the allylic azide **11i**, affording *trans*-cinnamaldehyde **12i** in moderate yield (43%). Two classes of primary azides were investigated: benzylic azides and aliphatic azides. Unfortunately, aliphatic azides proved to be unreactive toward our reaction conditions and did not create the expected aldehyde products (e.g., **12g** and **12j**). Nonetheless, the other class of primary azides (benzylic) exhibited high sensitivity to electronic effects. The electron-rich 4-methoxybenzaldehyde

12b was obtained in a good yield (60%), whereas benzaldehyde 12c was obtained in a moderate yield (44%), and the electron-poor 4-nitrobenzaldehyde 12c was obtained in relatively small yield (23%). Finally, several heterocycles containing a benzylic azide were investigated (not shown), including 2-(azidomethyl)thiophene 11f, but unfortunately, only traces of thiophene-2-carbaldehyde 12f were observed. This presumably indicates Brønsted acid protonation of the heterocycle itself instead of activation of a nitrogen atom on the triazene moiety, leading to unknown decomposition pathways. Overall, although the yields are modest, it is worth noting that this is a two-step, one-pot procedure and represents the net conversion of an azide to a carbonyl compound under mild reaction conditions, in other words, an unprecedented transformation.

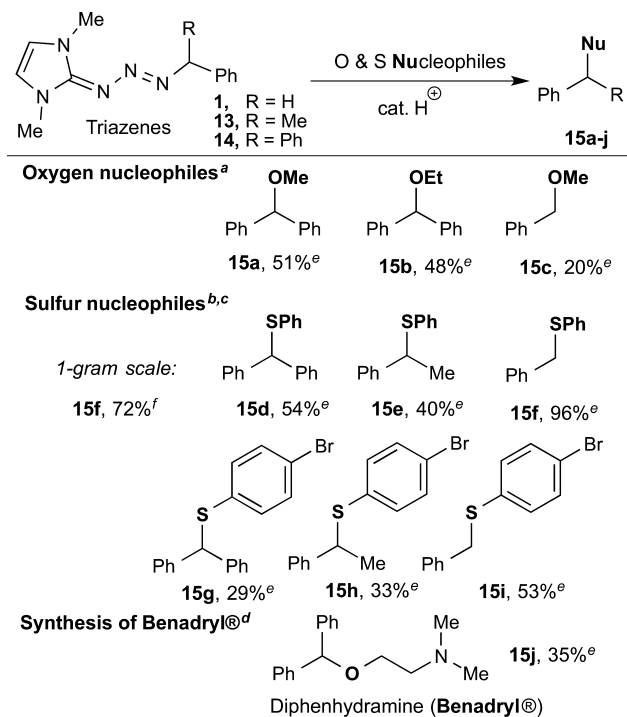
In order to elucidate further the mechanistic details of this novel transformation, we turned our attention to the data obtained during the azide survey (Table 3), the reagents employed (TsOH and DMSO), and the detection of dimethyl sulfide 14f as a byproduct. From Table 2, it is clear that secondary azides are the best substrates, followed by allylic azides, benzylic azides, and finally primary aliphatic azides (which do not work). Based on this information, we propose a S_N1 mechanism where triazene 14 is first activated by TsOH followed by fast triazene disintegration into three fragments. These fragments are nitrogen gas (bubbles observed), iminoimidazole 14b, and carbocation 14c. After carbocation 14c is released, DMSO quickly traps it, forming the alkoxyulfonium intermediate 14e. Finally, 14e undergoes a Kornblum-type mechanism,^{16,17} which releases dimethyl sulfide 14f (observed) and the expected benzophenone 6. An alternative, less likely, mechanism is the direct attack of DMSO to protonated triazene 14a (S_N2). However, the data from Table 2 suggest that substrates that produce more stable carbocations (secondary azides) generated higher yields, supporting the proposed S_N1 mechanism (Scheme 1).

Scheme 1. Proposed Mechanism (Acidic Conditions)



Considering the proposed Scheme 1 mechanism, it was hypothesized that nucleophiles, other than DMSO, could attack the protonated triazene intermediate 14a. If so, this would allow access to a variety of organic compounds from common triazene intermediates. To test this hypothesis, we synthesized triazenes 1, 13, and 14 and subjected them to reaction conditions described in Table 4 in the presence of oxygen and sulfur nucleophiles. Since DMSO can no longer be the reaction's solvent, a brief solvent screening was performed using catalytic TsOH and 50 equiv of methanol as nucleophile. Unfortunately, low yields were observed with other solvents

Table 4. Scope of Substitution Reactions



^aReactions were carried out with triazene 1 or 14 (0.3 mmol, 1.0 equiv) and 5% PhSH in 0.5 mL of the corresponding alcohol (methanol or ethanol) at 55 °C for 4 h. ^bReactions were carried out with its respective triazene 1, 13, or 14 (0.3 mmol, 1.0 equiv) in 0.3 mL of thiophenol at rt for 1 h. ^cReactions were carried out with its respective triazene 1, 13, or 14 (0.3 mmol, 1.0 equiv) and 4-bromothiophenol (0.6 mmol, 76 mg, 2.0 equiv) in 0.5 mL of THF at rt for 1 h. ^dReaction was carried out with triazene 14 (0.3 mmol, 92 mg, 1.0 equiv) and TsOH (0.15 mmol, 29 mg, 0.5 equiv) in 0.5 mL of (dimethylamino)ethanol at 60 °C for 36 h. ^eIsolated yields (average of two to three runs) by silica gel flash chromatography. ^fIsolated yield for 1 g scale reaction.

(e.g., DMF, acetone, THF, EtOAc, and CH_2Cl_2). However, very surprisingly, when thiophenol was investigated as nucleophile, we observed an excellent yield (96%) of sulfide 15f without an external Brønsted acid (Table 4). This result indicates that thiophenol can serve as both nucleophile and Brønsted acid. In addition, two more sulfides derived from thiophenol were also synthesized and afforded the desired products 15d and 15e in 54% and 40% yield, respectively (Table 4). To our gratification, using 4-bromothiophenol as nucleophile in THF also afforded the sulfide adducts 15g (from 14), 15h (from 13), and 15i (from 1) in 29%, 33%, and 53% yield, respectively.

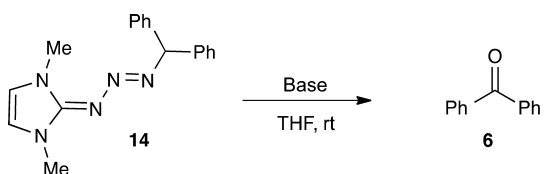
Encouraged by these results, and because ethers and their corresponding derivatives are valuable synthetic intermediates,¹⁸ we next explored the compatibility of the thiophenol-mediated nucleophilic substitution using oxygen-containing nucleophiles. We were pleased to discover that our approach is viable for use with nucleophiles other than thiols. For example, good results were obtained with methanol and ethanol, using only 5 mol % of thiophenol as Brønsted acid. Triazene 14 afforded ethers 15a and 15b in 51% and 48% yield, respectively, while triazene 1 gave benzylmethyl ether 15c in 20% yield. The low yield of 15c is apparently due to the higher activation energy required to liberate its benzylic carbocation intermediate (Table 4).

To further demonstrate the synthetic utility and practicality of this transformation, we applied our methodology to the synthesis of the antihistaminic drug diphenhydramine (**15j**, Benadryl),¹⁹ depicted on the bottom of Table 4. The synthesis of **15j** was accomplished using triazene **14** and 2-(dimethylamino)ethanol, as nucleophile, at 60 °C for 36 h, with a modest 35% yield. The lower yield obtained in this case is the result of incomplete reaction due to the nature of the starting material (very polar oxygen nucleophile); extended reaction times will likely provide increased yields.

Overall, the data in Tables 3 and 4 provide strong certification for the unusually wide scope inherent in our approach. These preliminary results clearly establish that this method can be used to prepare selectively substituted ketones and aldehydes, structural motifs present in a plethora of important compounds as illustrated with the above-noted synthesis of the ethercontaining drug Benadryl. The notable feature of our new carbonyl synthesis is the use of *acidic* conditions to accomplish the oxidation (Scheme 1) instead of the well-known *basic* conditions used for the reported DMSO oxidations (e.g., Kornblum^{16,17} and Swern^{20–22}). This method thus enables the synthesis of ketones and aldehydes from azides under acidic media, a current limitation of the Kornblum and Swern oxidations.^{23,24}

During the synthesis of triazene **14** with a small excess of base (1.5 equiv of KO-*t*-Bu), trace amounts of benzophenone **6** were observed, indicating that an oxidation of benzhydryl azide **7** was occurring (Table 5). In order to interpret the mechanism of this reaction, a comprehensive set of experiments was performed as follows: Triazene **14** was subjected to an excess of different bases (20.0 equiv) and stirred at room temperature for 3 h. From this study, it was found that organic bases such as

Table 5. Oxidation Reaction under Basic Conditions^a



entry	substrate	base	atmosphere	time (h)	yield of 6 ^c (%)
1 ^b	14	none	argon	3	0
2	14	DBU	O ₂ /air	3	0
3	14	CsCO ₃	O ₂ /air	3	55
4	14	KO- <i>t</i> -Bu	O ₂ /air	3	56
5	14	NaH	O ₂ /air	3	58
6 ^b	14	NaH	argon	3	57
7 ^c	8a + 7	NaH	O ₂ /air	3	50
8 ^{b,d}	7	NaH	argon	3	0
9 ^d	7	NaH	O ₂ /air	3	0

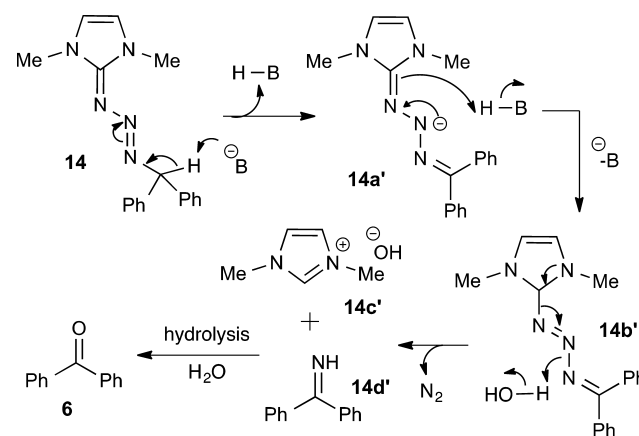
^aReactions were carried out with triazene **14** (0.3 mmol, 93 mg, 1.0 equiv) and the corresponding base (6 mmol, 144 mg, 20 equiv) in THF (3 mL) with stirring at rt for 3 h. ^bReactions carried out under argon atmosphere. ^cReactions were carried out with dimethylimidazolium iodide **8a** (0.3 mmol, 67 mg, 1.5 equiv), KO-*t*-Bu (0.3 mmol, 34 mg, 1.5 equiv), and benzhydryl azide **7** (0.2 mmol, 42 mg, 1.0 equiv) in 1.0 mL of THF for 12 h followed by addition of NaH (4 mmol, 96 mg, 20 equiv) and stirring at rt for 3 h. ^dReactions were carried out with benzhydryl azide **7** (0.3 mmol, 63 mg, 1 equiv) and NaH (6 mmol, 144 mg, 20 equiv) in THF (3 mL) stirred at rt for 3 h. ^eIsolated yields (average of two to three runs) by silica gel flash chromatography.

DBU did not promote this oxidation (entry 2). On the other hand, CsCO₃, KO-*t*-Bu, and NaH provided the adduct **6** in 55%, 56%, and 58% yield, respectively (entries 3–5). Since these reactions were performed under an air atmosphere and oxygen is known to promote alcohol oxidations under basic conditions,²⁵ we carried out an oxygen-free reaction by purging THF with argon and stirring the reaction mixture under an argon atmosphere (entry 6). Surprisingly, the yield was comparable under both argon (57%) and air (58%), and the absence of base did not produce benzophenone **6** (entry 1).

Subsequently, we performed a two-step, one-pot procedure, without the isolation of triazene **14** from NHC precursor **8a** and benzhydryl azide **7**, under basic conditions (entry 7). This also provided benzophenone **6** in similar yield (50%), supporting the power of using a one-pot procedure. Finally, to eliminate the possible background reaction during the in situ formation of triazene **14**, benzhydryl azide **7** was also subjected to 20 equiv of sodium hydride, in both air and argon atmosphere, resulting in no reaction, as expected (Table 5, entries 8 and 9), indicating that triazene **14** is the reactive species.

In an effort to extend the scope of this transformation using basic conditions, all azide precursors of aldehydes and ketones from Table 3 were screened. Unfortunately, only benzophenone **6** was observed in 50% yield (Table 5, entry 7) and 4-cyanobenzaldehyde **12e** in less than 10% yield. We propose that product formation, under basic conditions, undergoes a polar mechanism (Scheme 2). First, a benzylic deprotonation

Scheme 2. Proposed Mechanism (Basic Conditions)



takes place to form triazene anion **14a'**, followed by a selective protonation to form intermediate **14b'**. Thereafter, **14b'** decomposes to NHC **14c'** and imine **14d'** (observed), with nitrogen extrusion providing the driving force. Finally, hydrolysis of the imine produces benzophenone **6**. However, it should be noted that a radical mechanism is also plausible. Additional studies are required to either refute or support this hypothesis.

In conclusion, we have documented, for the first time, a new versatile molecule, i.e., π -conjugated triazene, capable of undergoing both oxidation and substitution reactions, under mild reaction conditions. The transformations described above establish the use of organic azides as useful synthetic scaffolds for the synthesis of aldehydes, ketones, ethers, and sulfides compounds via π -conjugated triazene intermediates. In general, the produced adducts were observed in moderate to excellent yields, under mild reaction conditions. In addition, sulfur

nucleophiles were better than oxygen nucleophiles. Overall, this unprecedented methodology not only broadens the application of traditional organic azides but also additionally provides direct disconnections for rapidly building organic frameworks, an important consideration in many synthetic studies.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in oven-dried glassware with magnetic stirring. All NHC precursors were commercially obtained and used as received with the exception of **8a**, which was synthesized using a known procedure.¹² Solvents were dried and degassed from a solvent purification system. Heating was accomplished by oil bath. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230–400 mesh). TLC visualization was accompanied by UV light and KMnO₄ and iodine stains. The removal of volatile solvent was accomplished using a rotary evaporator attached to a dry diaphragm pump (10–15 mmHg) followed by pumping to a constant weight with an oil pump (<300 mTorr). ¹H NMR spectra were recorded at 500 and 300 MHz and are reported relative to CDCl₃ (δ 7.25). ¹H NMR coupling constants (*J*) are reported in hertz (Hz), and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Proton-decoupled ¹³C NMR spectra were recorded at 125 and 75 MHz and reported relative to CDCl₃ (δ 77). IR experiments were recorded with neat samples on an instrument fitted with a diamond ATR sample plate. High-resolution (HR) mass spectra were recorded using an ESI-TOF instrument.

General Procedure for the Synthesis of Azides. Method A. Following a previously reported procedure,²⁶ the corresponding halide (1 equiv) was dissolved in DMF (0.5 M). Sodium azide (1.2 equiv) was then added, and the resulting mixture was stirred at 80 °C for 4 h. Then the mixture was allowed to cool to room temperature, and water was added. Two extractions were then performed with Et₂O, and the organic layer was washed with brine dried over Na₂SO₄ and evaporated under reduced pressure to yield products **11a,b,d,e,g,h,j**.

Method B. Following a previously reported procedure,²⁷ *p*-nitrobenzyl chloride (1 mmol), sodium azide (1.2 mmol), and 30 mL of DMSO were added to a light-shielded reaction flask. The mixture was then stirred at room temperature for 1 h. Then, 30 mL of water was added. The mixture was extracted with ethyl acetate (3 × 15 mL), and the organic layer was washed with brine (2 × 15 mL), dried over Na₂SO₄, and evaporated under reduced pressure to yield **11c**.

Method C. Following a previously reported procedure,²⁸ to a vigorously stirred solution of NaI (4 mmol) and furfuryl alcohol (2 mmol) in 2 mL of acetonitrile under argon was added methanesulfonic acid (4 mmol) at room temperature. The reaction mixture was stirred for 15 min. Then, anhydrous aluminum chloride (0.2 mmol) and sodium azide (6 mmol) were added, and the reaction mixture was heated to reflux and stirred for 5 h. Then the mixture was allowed to cool to room temperature and quenched with water. Three extractions were then performed with Et₂O, and the organic layer was washed with 10% sodium sulfate solution, dried over Na₂SO₄, and evaporated under reduced pressure to yield crude products. The crude products were purified by column chromatography on silica gel using hexanes as the mobile phase to yield product **11f**.

(Azidomethylene)dibenzene (7): known compound;²⁶ colorless liquid (146 mg, 70% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.46–7.36 (m, 10H), 5.79 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8, 128.9, 128.3, 127.6, 68.7.

(Azidomethyl)benzene (11a): known compound;²⁶ colorless liquid (109 mg, 82% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.49–7.39 (m, 5H), 4.37 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 135.6, 129.0, 128.5, 128.4, 54.9.

1-(Azidomethyl)-4-methoxybenzene (11b): known compound; colorless liquid (98 mg, 60% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.26 (s, 2H), 3.80 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.8, 129.9, 127.6, 114.3, 55.3, 54.5.

1-(Azidomethyl)-4-nitrobenzene (11c): known compound;²⁷ colorless liquid (98 mg, 55% yield); ¹H NMR (500 MHz, CDCl₃) δ 8.21 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 4.49 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 147.8, 142.9, 128.7, 124.1, 53.8.

1-(Azidomethyl)-4-chlorobenzene (11d): known compound;²⁹ colorless liquid (144 mg, 86% yield); ¹H NMR (300 MHz, CDCl₃) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.31 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 134.3, 134.1, 129.7, 129.1, 54.1.

4-(Azidomethyl)benzotrile (11e): known compound;²⁶ colorless liquid (123 mg, 78% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.9, 132.7, 128.6, 118.6, 112.2, 54.1.

2-(Azidomethyl)thiophene (11f): known compound;²⁸ colorless liquid (60 mg, 43% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.33 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.06 (d, *J* = 3.4 Hz 1H), 7.03–7.01 (m, 1H), 4.49 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 137.4, 127.5, 127.3, 126.6, 49.2.

(Azidomethyl)cyclohexane (11g): known compound;³⁰ colorless liquid (84 mg, 60% yield); ¹H NMR (500 MHz, CDCl₃) δ 3.08 (d, *J* = 6.3 Hz, 2H), 1.76–1.70 (m, 4H), 1.57–1.48 (s, 1H), 1.28–1.09 (m 3H), 0.98–0.90 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 58.1, 38.1, 30.7, 26.3, 25.8.

2-Azidoethylbenzene (11h): known compound;²⁶ colorless liquid (130 mg, 88% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.45–7.36 (m, 5H), 4.66 (q, *J* = 6.9 Hz, 1H), 1.58 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 128.9, 128.3, 126.6, 61.3, 21.7.

trans-Cinnamyl azide (11i): known compound.³¹ To a solution of allylbenzene in 20 mL of CHCl₃ was added Br₂ at 0 °C. The mixture was stirred at 0 °C for 10 min, and then the solvent was evaporated at reduced pressure to afford the crude dibromide intermediate. This intermediate was dissolved in 20 mL of DMSO, and NaN₃ (12 mmol) and DBU (20 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. Then water was added, and the mixture was extracted with ethyl acetate (3 × 10 mL), the organic layer was dried over Na₂SO₄, and the solvent was evaporated at reduced pressure to afford the crude product. This crude product was purified by column chromatography using hexanes/ethyl acetate (9:1) as mobile phase to afford compound **11i** as a colorless liquid (107 mg, 67% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.48–7.26 (m, 5H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.94 (d, *J* = 6.3 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 136.1, 134.7, 128.8, 128.3, 126.8, 122.5, 53.1.

(3-Azidopropyl)benzene (11j): known compound;³⁰ colorless liquid (137 mg, 85% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.40–7.26 (m, 5H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 1.98 (dt, *J* = 7.5, 6.9 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 128.7, 128.6, 126.3, 50.8, 32.9, 30.6.

General Procedure for the Synthesis of Triazenes. Following our previously reported procedure,¹² to a suspension of the corresponding NHC precursor (1.5 mmol) in THF (20 mL) was added the respective azide (1 mmol) and the mixture was allowed to stir for 5 min. KO-*t*-Bu (1.5 mmol) was added to the mixture and allowed to stir at room temperature for 12 h. To the resulting mixture was added 5 mL of hexanes, and the solids were filtered through Celite. The volatiles were evaporated under reduced pressure to afford an oily product. This crude product was washed with hexanes (3 × 20 mL) and dried under reduced pressure, which afforded solid products **1**, **4**, **13**, and **14**.

(E)-1-Benzyl-3-(1,3-dimethylimidazol-2-ylidene)triazene (1): known compound;¹² strong orange solid (211 mg, 92% yield); ¹H NMR (500 MHz, CDCl₃) δ 7.34 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.30 (s, 2H), 4.83 (s, 2H), 3.52 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 152.7, 139.1, 129.0, 128.2, 126.6, 115.7, 65.3, 35.5.

(E)-1-Benzhydryl-3-(1,3-dimesitylimidazol-2-ylidene)triazene (4): pale orange solid (370 mg, 72% yield); IR (neat) ν 3173, 1541, 1489, 1409, 1232, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.20–7.05 (m, 10 H), 6.87 (s, 4 H), 6.44 (s, 2 H), 4.64 (s, 1 H), 2.31 (s, 6 H), 2.11 (s, 12 H); ¹³C NMR (75 MHz, CDCl₃) δ 152.5, 143.3, 138.3,

135.6, 134.5, 128.9, 128.3, 127.9, 126.3, 116.2, 21.2, 18.2; HRMS (ESI) m/z 514.2965, calcd for $C_{34}H_{36}N_5$ $[M + H]^+$ 514.2963.

(*E*)-1-(1-Phenylethyl)-3-(1,3-dimethylimidazol-2-ylidene)triazene (**13**): brown oil (124 mg, 51% yield); IR (neat) ν 3114, 1660, 1559, 1502, 1418, 1243, 701 cm^{-1} ; 1H NMR (300 MHz, CD_3OD) δ 7.33–7.24 (m, 4H), 7.19–7.16 (m, 1H), 6.62 (s, 2H) 4.69 (q, $J = 6.9$ Hz, 1H), 3.46 (s, 6H) 1.53 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ 152.2, 144.4, 128.0, 127.0, 126.5, 116.4, 68.1, 34.4, 20.7; HRMS (ESI) m/z 244.1550, calcd for $C_{13}H_{18}N_5$ $[M + H]^+$ 244.1555.

(*E*)-1-Benzhydryl-3-(1,3-dimethylimidazol-2-ylidene)triazene (**14**): orange solid (168 mg, 55% yield); IR (neat) ν 3119, 2099, 1555, 1492, 1403, 1260, 694 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, $J = 7.2$ Hz, 4H), 7.30–7.20 (m, 4H), 7.19–7.11 (m, 2H), 6.24 (s, 2H), 5.76 (s, 1H), 3.45 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 143.6, 128.5, 128.3, 126.6, 115.9, 35.6; HRMS (ESI) m/z 306.1713, calcd for $C_{18}H_{20}N_5$ $[M + H]^+$ 306.1708.

N-Benzyl-1,3-dimethyl-1,3-dihydro-2H-imidazol-2-imine (**2**): 1H NMR (500 MHz, $DMSO-d_6$) δ 7.28–7.27 (m, 4 H, Ph-H), 7.20–7.18 (m, 1 H, Ph-H), 6.52 (s, 2 H, NCH), 4.45 (s, 2 H, Ph- CH_2), 3.15 (s, 6 H, N- CH_3); HRMS (ESI, N_2) m/z calcd for $C_{12}H_{15}N_3$ $[M + H]^+$ 202.1339, found 202.1328.

General Procedure for Oxidation Reactions. Dimethylimidazolium iodide (0.75 mmol) and KO-*t*-Bu (0.75 mmol) were suspended in THF (1.0 mL) and stirred under argon at room temperature for 15 min. To this suspension was added the corresponding azide (0.5 mmol), and the suspension was stirred at room temperature for 12 h. The volatiles were then removed under reduced pressure. This was followed by addition of DMSO (1.0 mL) and TsOH (0.25 mmol) and stirred at room temperature for 30 min. The crude mixture was then purified using column chromatography with silica gel and hexanes/ethyl acetate (9:1) as mobile phase to afford products **6** and **12a–i**.

Benzophenone (6): known compound;³² colorless liquid (66 mg, 72% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.81–7.78 (m, 4H), 7.59–7.54 (m, 2H), 7.49–7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 137.7, 132.6, 130.2, 128.4; 1 g scale (547 mg, 67% yield).

Benzaldehyde (12a): known compound;³³ colorless liquid (23 mg, 44% yield); 1H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.71–7.67 (m, 2H), 7.45–7.25 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 136.4, 134.5, 129.7, 129.0.

4-Methoxybenzaldehyde (12b): known compound;³⁴ colorless liquid (41 mg, 60% yield); 1H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.74 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 164.7, 132.0, 130.0, 114.4, 55.6.

4-Nitrobenzaldehyde (12c): known compound;³⁴ pale yellow solid (17 mg, 23% yield); 1H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H), 8.34 (d, $J = 8.6$ Hz, 2H), 8.05 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 151.2, 140.1, 130.6, 124.4.

4-Chlorobenzaldehyde (12d): known compound;³⁴ white solid (8 mg, 12% yield); 1H NMR (300 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.63 (d, $J = 8.6$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 140.6, 134.7, 130.8, 129.3.

4-Formylbenzotrile (12e): known compound;³⁵ white solid (19 mg, 29% yield); 1H NMR (300 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.96 (d, $J = 8.3$ Hz, 2H), 7.81 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 138.8, 133.0, 130.0, 117.9, 117.6.

Acetophenone (12h): known compound;³³ colorless liquid (36 mg, 60% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, $J = 7.2$ Hz, 2H), 7.47–7.45 (m, 1H), 7.37–7.32 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.0, 137.1, 133.1, 128.6, 128.3, 26.6.

trans-Cinnamaldehyde (12i): known compound;³⁶ yellow oil. (28 mg, 43% yield); 1H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, $J = 7.9$ Hz, 1H), 7.47–7.44 (m, 2H), 7.38–7.30 (m, 4H), 6.64–6.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 152.9, 134.1, 131.4, 129.2, 128.6, 128.5.

General Procedure for the Synthesis of Ethers. The corresponding triazene (0.3 mmol) was dissolved in 0.5 mL of the respective alcohol (methanol for **15a** and **15c** or ethanol for **15b**), PhSH (0.015 mmol) was added, and the mixture was stirred at 55 °C for 4 h. The volatiles were then removed under reduced pressure, and

the crude mixture was purified using column chromatography with silica gel and hexanes/ethyl acetate (9:1) as mobile phase to afford products **15a–c**.

(*Methoxymethylene*)dibenzene (**15a**): known compound;³⁷ colorless oil (30 mg, 51% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.29 (m, 10H), 5.30 (s, 1H), 3.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 128.6, 127.6, 127.1, 85.6, 57.2.

(*Ethoxymethylene*)dibenzene (**15b**): known compound;³⁸ colorless oil (31 mg, 48% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.43–7.28 (m, 10H), 5.41 (s, 1H), 3.57 (q, $J = 6.9$ Hz, 2H) 1.32 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 128.5, 127.5, 127.1, 83.6, 64.7, 15.5.

(*Methoxymethylene*)benzene (**15c**): known compound;³⁹ colorless oil (7 mg, 20% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.32 (m, 5H), 4.50 (s, 2H), 3.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 128.6, 127.9, 127.8, 74.8, 58.2.

General Procedure for the Synthesis of Thiophenol Derivatives. The respective triazene (0.3 mmol) was dissolved in thiophenol (0.3 mL) and stirred at room temperature for 1 h. Then ethyl acetate (15 mL) was added to the mixture, which was then washed with 10% NaOH solution (3 \times 10 mL). The organic layer was dried over Na_2SO_4 , and the volatiles were removed under reduced pressure. The crude mixture was then purified using column chromatography with silica gel and hexanes/dichloromethane (1:1) as mobile phase to afford products **15d–f**.

Benzhydryl(phenyl)sulfane (15d): known compound;⁴⁰ white solid (45 mg, 54% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.23 (m, 15H), 5.58 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 136.2, 130.6, 128.8, 128.7, 128.5, 127.4, 126.7, 57.5.

Phenyl(1-phenylethyl)sulfane (15e): pale yellow oil⁴¹ (26 mg, 40% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.30 (m, 10H), 4.48 (q, $J = 6.9$ Hz, 1H), 1.76 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 135.4, 132.7, 129.0, 128.7, 127.5, 127.4, 127.3, 48.2, 22.6.

Benzyl(phenyl)sulfane (15f): known compound;⁴² white solid (58 mg, 96% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.37–7.21 (m, 10H), 4.16 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 136.5, 129.9, 129.0, 128.6, 127.3, 126.5, 39.1; 1 g scale (629 mg, 71% yield).

General Procedure for the Synthesis of 4-Bromothiophenol Derivatives. The respective triazene (0.3 mmol) and 4-bromothiophenol (0.6 mmol) were dissolved in THF (0.5 mL), and the mixture was stirred at room temperature for 1 h. The volatiles were then removed under reduced pressure, and ethyl acetate (15 mL) was added. The solution was washed with 10% NaOH solution (3 \times 10 mL). The organic layer was dried over Na_2SO_4 , and the volatiles were removed under reduced pressure. The crude mixture was then purified using column chromatography with silica gel and hexanes/dichloromethane (1:1) as mobile phase to afford products **15g–i**.

Benzhydryl(4-bromophenyl)sulfane (15g): white solid. (31 mg, 29% yield); mp 98–100 °C; IR (neat) ν 3076, 1561, 1489, 694 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.40 (m, 4H), 7.34–7.21 (m, 8H), 7.11–7.07 (m, 2H), 5.52 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 135.3, 132.1, 131.9, 128.8, 128.5, 127.6, 120.8, 57.6; HRMS (ESI) m/z 355.0151, calcd for $C_{19}H_{16}BrS$ $[M + H]^+$ 355.0156.

(4-Bromophenyl)(1-phenylethyl)sulfane (15h): colorless oil. (29 mg, 33% yield); IR (neat) ν , 3085, 1570, 1470, 697 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, $J = 2.1$ Hz, 4H), 7.43–7.31 (m, 5H), 5.09 (q, $J = 6.9$ Hz, 1H), 1.85 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 134.3, 134.1, 131.9, 128.6, 127.4, 127.3, 121.4, 48.2, 22.3; HRMS (ESI) m/z 290.9838, calcd for $C_{14}H_{12}BrS$ $[M - H]^+$ 290.9840.

Benzyl(4-bromophenyl)sulfane (15i): known compound;⁴³ white solid (44 mg, 53% yield); 1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, $J = 8.6$ Hz, 2H), 7.30–7.26 (m, 5H), 7.15 (d, $J = 8.6$ Hz, 2H), 4.09 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 135.5, 132.0, 131.6, 128.9, 128.7, 127.4, 120.4, 39.2.

Diphenylhydramine (15j). Triazene **14** (0.3 mmol) and TsOH (0.15 mmol) were dissolved in (dimethylamino)ethanol (0.5 mL) and stirred at 60 °C for 36 h. The crude mixture was then purified using column chromatography with silica gel and ethyl acetate/methanol (9:1) as mobile phase to afford product **15j** as a colorless oil (27 mg,

35% yield): IR (neat) ν 3061, 2941, 1492, 1452, 1102, 696 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.46–7.28 (m, 10H), 5.46 (s, 1H), 3.67 (t, J = 5.8 Hz, 2H), 2.71 (t, J = 5.8 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.4, 128.6, 127.6, 127.2, 84.2, 67.6, 59.1, 46.2; HRMS (ESI) m/z 256.1696, calcd for $\text{C}_{17}\text{H}_{22}\text{NO}$ [$\text{M} + \text{H}$] $^+$ 256.1700.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02705.

Additional studies and ^1H and ^{13}C NMR spectra of each compound (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The University of Texas at Arlington and the Research Enhancement Program supported this work. We also recognize Dr. Xiaojun Hung and Jonathan Lefton (UTA) for their assistance in the synthesis of some azides and NMR analysis. In addition, we acknowledge the Shimadzu Center for MS data collection and NSF grants (CHE-0234811 and CHE-0840509) for additional instrumentation.

■ REFERENCES

- (1) For select examples, see: (a) Swain, S. P. *Synlett* **2014**, 25, 2085–2086. (b) Felzmann, W.; Castagnolo, D.; Rosenbeiger, D.; Mulzer, J. *J. Org. Chem.* **2007**, 72, 2182.
- (2) Cowper, P.; Jin, Y.; Turton, M. D.; Kociok-Köhn, G.; Lewis, S. E. *Angew. Chem., Int. Ed.* **2016**, 55, 2564–2568 and references therein.
- (3) For select examples, see: (a) Storr, T. E.; Greaney, M. F. *Org. Lett.* **2013**, 15, 1410–1413. (b) Charpentier, J.; Früh, N.; Togni, A. *Chem. Rev.* **2015**, 115, 650–682. (c) Jia, Z.; Gálvez, E.; Sebastián, R. M.; Pleixats, R.; Álvarez-Larena, Á.; Martín, E.; Vallribera, A.; Shafir, A. *Angew. Chem., Int. Ed.* **2014**, 53, 11298–11301.
- (4) For select examples, see: (a) Mal, K.; Kaur, A.; Haque, F.; Das, I. *J. Org. Chem.* **2015**, 80, 6400–6410. (b) Chen, J.-Y.; Chen, X.-L.; Li, X.; Qu, L.-B.; Zhang, Q.; Duan, L.-K.; Xia, Y.-Y.; Chen, X.; Sun, K.; Liu, Z.-D.; Zhao, Y.-F. *Eur. J. Org. Chem.* **2015**, 2015, 314–319. (c) Diao, T.; Pun, D.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, 135, 8205–8212. (d) Sharma, P.; Rohilla, S.; Jain, N. *J. Org. Chem.* **2015**, 80, 4116–4122. (e) Jiang, T.; Quan, X.; Zhu, C.; Andersson, P. G.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2016**, 55, 5824–5828.
- (5) For select examples, see: (a) Li, Y.; Xue, D.; Lu, W.; Wang, C.; Liu, Z.-T.; Xiao, J. *Org. Lett.* **2014**, 16, 66–69. (b) Wu, X.; Zhao, Y.; Ge, H. *J. Am. Chem. Soc.* **2015**, 137, 4924–4927. (c) Ding, S.; Jiao, N. *Angew. Chem., Int. Ed.* **2012**, 51, 9226–9237 and references cited therein. (d) Wang, Z.; Chang, S. *Org. Lett.* **2013**, 15, 1990–1993.
- (6) For select examples, see: (a) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, 44, 5188–5240 and references cited therein. (b) Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, 88, 297–368.
- (7) (a) Coady, D. J.; Khramov, D. M.; Norris, B. C.; Tennyson, A. G.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2009**, 48, 5187–5190. (b) Huang, D.; Zhao, P.; Astruc, D. *Coord. Chem. Rev.* **2014**, 272, 145–165. (c) Risse, J.; Scopelliti, R.; Severin, K. *Organometallics* **2011**, 30, 3412–3418. (d) Kacprzak, K.; Skiera, I.; Piasecka, M.; Paryzek, Z. *Chem. Rev.* **2016**, 116, 5689–5743. (e) Thirumurugan, P.; Matosiuk, D.; Jozwiak, K. *Chem. Rev.* **2013**, 113, 4905–4979. (f) Tiwari, V. K.;

Mishra, B. B.; Mishra, K. B.; Mishra, N.; Singh, A. S.; Chen, X. *Chem. Rev.* **2016**, 116, 3086–3240.

- (8) (a) Tanimoto, H.; Kakiuchi, K. *Nat. Prod. Commun.* **2013**, 8, 1021–1034. (b) Adam, G.; Andriblax, J.; Plat, M. *Tetrahedron Lett.* **1981**, 22, 3181–3184.
- (9) (a) Hu, B.; DiMugno, S. G. *Org. Biomol. Chem.* **2015**, 13, 3844–3855. (b) Hickey, D. M. B.; MacKenzie, A. R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 921–926. (c) Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, 73, 2435–2437. (d) Cramer, S. A.; Jenkins, D. M. *J. Am. Chem. Soc.* **2011**, 133, 19342–19345.
- (10) (a) Myers, E. L.; Raines, R. T. *Angew. Chem., Int. Ed.* **2009**, 48, 2359–2363. (b) van Kalker, H. A.; Bruins, J. J.; Rutjes, F. P. J. T.; van Delft, F. L. *Adv. Synth. Catal.* **2012**, 354, 1417–1421. (c) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, 2, 635–646.
- (11) (a) Dequierez, G.; Pons, V.; Dauban, P. *Angew. Chem., Int. Ed.* **2012**, 51, 7384–7395. (b) Koga, G.; Anselme, J. P. *J. Org. Chem.* **1970**, 35, 960–964.
- (12) Patil, S.; White, K.; Bugarin, A. *Tetrahedron Lett.* **2014**, 55, 4826–4829.
- (13) Patil, S.; Bugarin, A. *Eur. J. Org. Chem.* **2016**, 2016, 860–870.
- (14) (a) Khramov, D. M.; Bielawski, C. W. *Chem. Commun.* **2005**, 4958–4960. (b) Tennyson, A. G.; Moorhead, E. J.; Bielawski, C. W. *Eur. J. Org. Chem.* **2010**, 2010, 6277–6282. (c) Jishkariani, D.; Hall, C. D.; Demircan, A.; Tomlin, B. J.; Steel, P. J.; Katritzky, A. R. *J. Org. Chem.* **2013**, 78, 3349–3354.
- (15) Alagiri, K.; Prabhu, K. R. *Tetrahedron* **2011**, 67, 8544–8551.
- (16) Kornblum, N.; Jones, W. J.; Anderson, G. J. *J. Am. Chem. Soc.* **1959**, 81, 4113–4114.
- (17) Kornblum, N.; Powers, J. W.; Anderson, G. J.; Jones, W. J.; Larson, H. O.; Levand, O.; Weaver, W. M. *J. Am. Chem. Soc.* **1957**, 79, 6562–6562.
- (18) Bull, J. A.; Croft, R. A.; Davis, O. A.; Doran, R.; Morgan, K. F. *Chem. Rev.* **2016**, 116, 12150–12233.
- (19) Gutmann, B.; Cantillo, D.; Kappe, C. O. *Angew. Chem., Int. Ed.* **2015**, 54, 6688–6728.
- (20) Sharma, A. K.; Ku, T.; Dawson, A. D.; Swern, D. *J. Org. Chem.* **1975**, 40, 2758–2764.
- (21) Sharma, A. K.; Swern, D. *Tetrahedron Lett.* **1974**, 15, 1503–1506.
- (22) Omura, K.; Sharma, A. K.; Swern, D. *J. Org. Chem.* **1976**, 41, 957–962.
- (23) Arterburn, J. B. *Tetrahedron* **2001**, 57, 9765–9788.
- (24) Epstein, W. W.; Sweat, F. W. *Chem. Rev.* **1967**, 67, 247–260.
- (25) (a) Joo, C.; Kang, S.; Kim, S. M.; Han, H.; Yang, J. W. *Tetrahedron Lett.* **2010**, 51, 6006–6007. (b) Wang, X.; Wang, D. Z. *Tetrahedron* **2011**, 67, 3406–3411.
- (26) Colombano, G.; Albani, C.; Ottonello, G.; Ribeiro, A.; Scarpelli, R.; Tarozzo, G.; Daglian, J.; Jung, K.; Piomelli, D.; Bandiera, T. *ChemMedChem* **2015**, 10, 380–395.
- (27) Yang, S.; Li, X.; Hu, F.; Li, Y.; Yang, Y.; Yan, J.; Kuang, C.; Yang, Q. *J. Med. Chem.* **2013**, 56, 8321–8331.
- (28) Kamal, A.; Ramesh, G.; Laxman, N. *Synth. Commun.* **2001**, 31, 827–833.
- (29) Elson, K. E.; Jenkins, I. D.; Loughlin, W. A. *Org. Biomol. Chem.* **2003**, 1, 2958–2965.
- (30) Suzuki, T.; Ota, Y.; Kasuya, Y.; Mutsuga, M.; Kawamura, Y.; Tsumoto, H.; Nakagawa, H.; Finn, M. G.; Miyata, N. *Angew. Chem., Int. Ed.* **2010**, 49, 6817–6820.
- (31) Alonso, F.; Moglie, Y.; Radivoy, G.; Yus, M. *Eur. J. Org. Chem.* **2010**, 2010, 1875–1884.
- (32) Jeon, K. O.; Jun, J. H.; Yu, J. S.; Lee, C. K. *J. Heterocycl. Chem.* **2003**, 40, 763–771.
- (33) Abraham, R. J.; Mobli, M.; Smith, R. J. *Magn. Reson. Chem.* **2003**, 41, 26–36.
- (34) Iinuma, M.; Moriyama, K.; Togo, H. *Tetrahedron* **2013**, 69, 2961–2970.
- (35) Kornblum, N.; Fifolt, M. J. *Tetrahedron* **1989**, 45, 1311–1322.
- (36) Jiang, N.; Ragauskas, A. J. *Org. Lett.* **2005**, 7, 3689–3692.

- (37) Phan, T. B.; Nolte, C.; Kobayashi, S.; Ofial, A. R.; Mayr, H. *J. Am. Chem. Soc.* **2009**, *131*, 11392–11401.
- (38) Davis, P. J.; Harris, L.; Karim, A.; Thompson, A. L.; Gilpin, M.; Moloney, M. G.; Pound, M. J.; Thompson, C. *Tetrahedron Lett.* **2011**, *52*, 1553–1556.
- (39) Tsai, C.; Sung, R.; Zhuang, B.; Sung, K. *Tetrahedron* **2010**, *66*, 6869–6872.
- (40) Shirakawa, S.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 311–314.
- (41) Yadav, L. D. S.; Kapoor, R. *Synth. Commun.* **2010**, *41*, 100–112.
- (42) Itoh, T.; Mase, T. *Org. Lett.* **2004**, *6*, 4587–4590.
- (43) Ham, J.; Yang, I.; Kang, H. *J. Org. Chem.* **2004**, *69*, 3236–3239.