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

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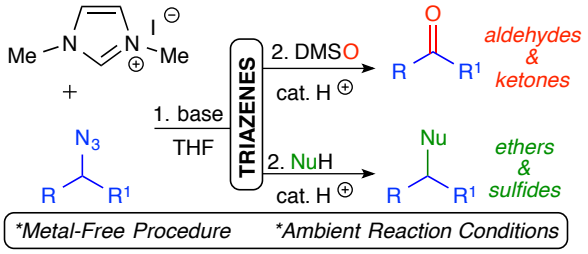
Supporting Information Placeholder



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] dimethylsulfoxide,[4] dimethylformamide,[5] and organic azides[6] 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 ºC for 2 hours. However, when these same triazenes were heated at 120 ºC 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).

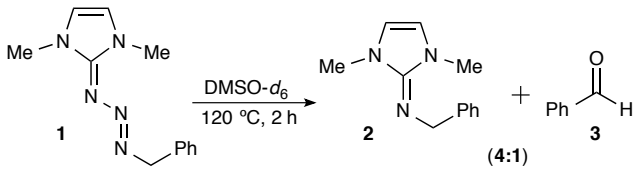
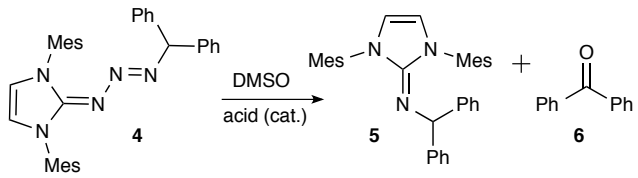


Figure 1. Initial observation.

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 communication reports an unprecedented simple two-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 me-

Table 1. Optimization of Reaction Conditions[a]



entry	acid	temp (ºC)	time (h)	ratio (5:6)[b]	yield 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

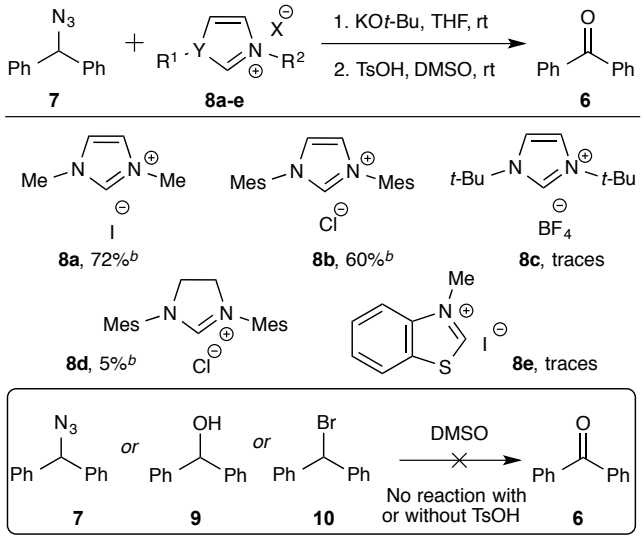
[a]Reactions were carried out with triazene 4 (0.2 mmol, 103 mg, 1.0 equiv.) and the corresponding acid (0.1 mmol, 0.5 equiv.) in 1.0 mL of DMSO. [b]Ratios calculated using ^{1}H NMR. [c]Isolated yields (average of 2-3 runs) by silica gel flash chromatography.

thod 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 of the volatile benzaldehyde **3**, thus easing isolation. Heating of triazene **4** at 120 ºC for 2 hours 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 by-product **5**, which remains intact after 12 hours 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, $SnCl_4$ 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.

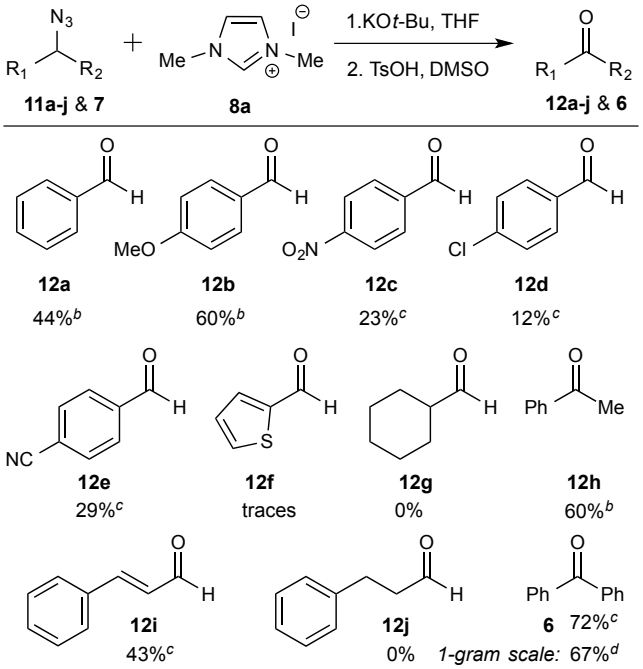
Table 2. Optimization of NHC Precursors[a]



[a]Reactions 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. [b] Isolated yields (average of 2-3 runs) by silica gel flash chromatography.

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 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 of 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 steric hindered than **8a**). This size difference makes **8b** more stable, therefore less responsive to Brønsted acid activation. In contrast, **8a** produces a less steric 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]

Table 3. Scope of the Oxidation Reaction[a]

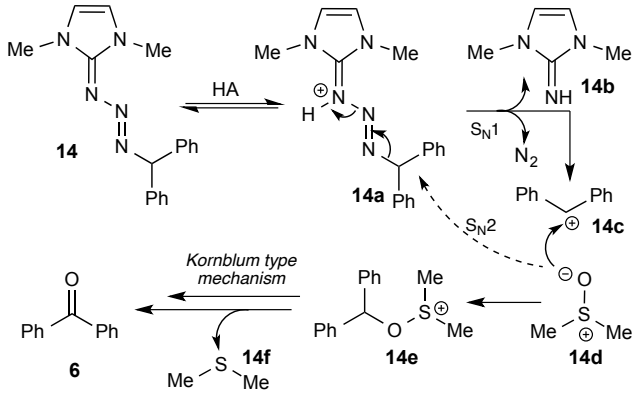


[a]Reactions were carried out with dimethylimidazolium iodide **8a** (0.75 mmol, 168 mg, 1.5 equiv.), KO*t*-Bu (0.75 mmol, 84 mg, 1.5 equiv.), and the corresponding azide **11a-i** & **7** (0.5 mmol, 1.0 equiv.) in 1.0 mL of THF for 12 h. The volatiles were then removed under reduced pressure. This was 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. [b]Yields calculated using ^{1}H NMR with DMF as internal standard. [c]Isolated yields (average of 2-3 runs) by silica gel flash chromatography. [d]Isolated yield for 1-gram scale reaction.

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 freshly prepared organic azides (**11a-j** & **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 towards our reaction conditions and did not create the expected aldehydes products (e.g., **12g** and **12j**). Nonetheless, the other class of primary azides (benzylic) exhibited high sensitivity to electronic effects. The electron-rich 4-methoxy-benzaldehyde **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.

Scheme 1. Proposed Mechanism (acidic conditions)

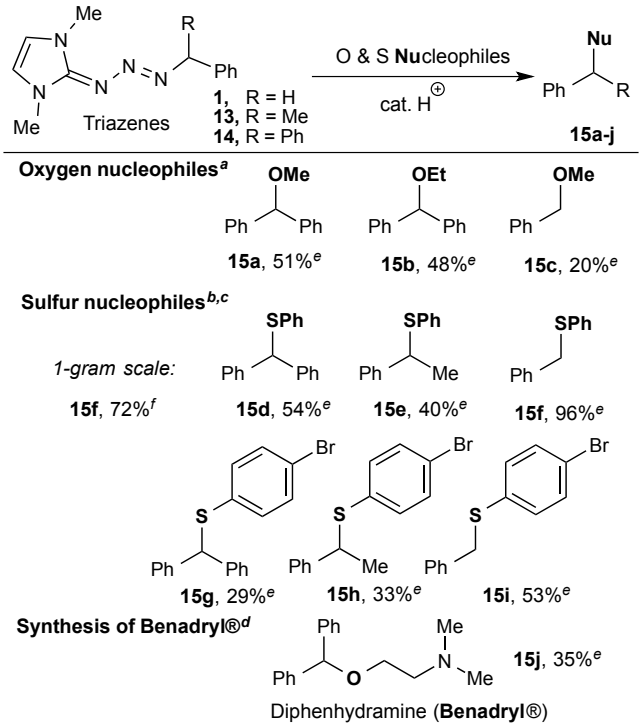


In order to elucidate further the mechanistic details of this novel transformation, we turned our attention to the data obtained during the azide survey (Table 3), the reagents employed (TsOH and DMSO), and the detection of dimethyl sulfide **14f** as a byproduct. From Table 2, it is clear that secondary 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 alkoxysulfonium intermediate **14e**. Finally, **14e** undergoes a Kornblum type mechanism,[16,17] which release 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).

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 cannot 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 (e.g., DMF, acetone, THF, EtOAc, and CH_2Cl_2). However, very surprisingly, when investigating thiophenol 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 derivated 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 benzyl carbocation intermediate (Table 4).

Table 4. Scope of Substitution Reactions



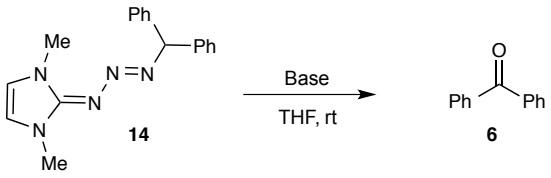
[a]Reactions were carried out with triazene **1** or **14** (0.3 mmol, 1.0 equiv.), and 5% PhSH in 0.5 mL of the corresponding alcohol (methanol or ethanol) at 55 °C for 4 h. [b]Reactions were carried out with its respective triazene **1**, **13**, or **14** (0.3 mmol, 1.0 equiv.) in 0.3 mL of thiophenol at rt for 1 h. [c]Reactions 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. [d]Reaction 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 dimethylaminoethanol at 60 °C for 36 h. [e]Isolated yields (average of 2-3 runs) by silica gel flash chromatography. [f]Isolated yield for 1-gram scale reaction.

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 ºC 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 & 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 ether containing 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[20,21,22]). 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]

Table 5. Oxidation Reaction Under Basic Conditions[a]



entry	substrate	base	atmosphere	time (h)	yield 6 (%)[e]
1	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*t*-Bu	O_2/air	3	56
5	14	NaH	O_2/air	3	58
6	14	NaH	Argon	3	57
7[c]	8a + 7	NaH	O_2/air	3	50
8[d]	7	NaH	Argon	3	0
9[d]	7	NaH	O_2/air	3	0

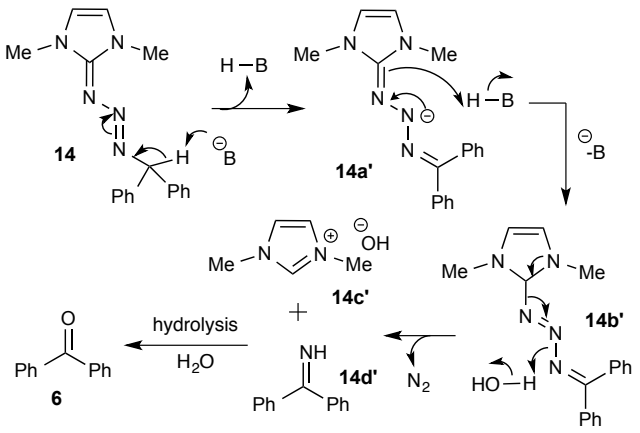
[a]Reactions were carried out with triazene 14 (0.3 mmol, 93 mg, 1.0 equiv.) and the corresponding base (6 mmol, 144 mg, 20 equiv.) in THF (3 mL) stirring at rt for 3 h. [b]Reactions carried out under Argon atmosphere. [c]Reactions were carried out with dimethylimidazolium iodide 8a (0.3 mmol, 67 mg, 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 3h. [d]Reactions 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 3h. [e]Isolated yields (average of 2-3 runs) by silica gel flash chromatography.

While synthesizing 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 DBU did not promote this oxidation (entry 2). On the other hand, $CsCO_3$, KO*t*-Bu, and NaH provided the adduct **6** in 55%, 56%, and 58% yield, respectively (entries 3 to 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%) vs air (58%), and 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 specie.

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 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.

Scheme 2. Proposed Mechanism (basic conditions)



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. Also, sulfur nucleophiles were better than oxygen nucleophiles. Overall, this unprecedented methodology not only broadens the application of traditional organic azides, but it 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 with UV light and $KMnO_4$ and iodine stains. The removal of volatile solvent was accomplished using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). ^{1}H NMR spectra were recorded at 500 MHz and 300 MHz, and are reported relative to $CDCl_3$ (δ 7.25). ^{1}H 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 ^{13}C NMR spectra were recorded at 125 MHz and 75 MHz and reported relative to $CDCl_3$ (δ 77) IR experiments were recorded with neat samples on an instrument fitted with 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 Et_2O, the organic layer was washed with brine dried over Na_2SO_4 and evaporated under reduced pressure to yield products **11a**, **11b**, **11d**, **11e**, **11g**, **11h**, and **11j**.

Method B. Following a previously reported procedure,[27] *p*-nitro benzyl 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 were added. The mixture was extracted with ethyl acetate (3 x 15 mL), the organic layer was washed with brine (2 x 15 mL), dried over Na_2SO_4, 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 minutes. 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 Et_2O, the organic layer was washed with 10% sodium sulfate solution, dried over Na_2SO_4 and evaporated under reduced pressure to yield crude products. The crude products were purified by column chromatography on silica gel, using hexanes as mobile phase yielding product **11f**.

(Azidomethylene)dibenzene (7). Known compound.[26] Colorless liquid. (146 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.36- (m, 10H), 5.79 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 128.9, 128.3, 127.6, 68.7.

*(Azidomethyl)benzene (**11a**).* Known compound.[26] Colorless liquid. (109 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.39 (m, 5H), 4.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 129.0, 128.5, 128.4, 54.9.

*1-(azidomethyl)-4-methoxybenzene (**11b**).* Known compound.[26] Colorless liquid. (98 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 9.2, 2.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 4.49 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 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). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.31 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 134.1, 129.7, 129.1, 54.1.

*4-(azidomethyl)benzonitrile (**11e**).* Known compound.[26] Colorless liquid. (123 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.43 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 127.5, 127.3, 126.6, 49.2.

*(Azidomethyl)cyclohexane (**11g**).* Known compound.[30] Colorless liquid. (84 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) δ 58.1, 38.1, 30.7, 26.3, 25.8.

*2-azidoethylbenzene (**11h**).* Known compound.[26] Colorless liquid. (130 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.36 (m, 5H), 4.66 (q, *J* = 6.9 Hz, 1H), 1.58 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $CHCl_3$, Br_2 was added at 0 °C. The mixture was stirred at 0 °C for 10 min, then the solvent was evaporated at reduced pressure to afford the crude dibromide intermediate. This intermediate was dissolved in 20 mL of DMSO and NaN_3 (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 x 10 mL), the organic layer was dried over Na_2SO_4 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 left stirring for 5 min. KO*t*-Bu (1.5 mmol) was added to the mixture and left stirring a room temperature for 12 h. To the resulting mixture 5 mL of hexanes were added 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 x 20 mL) and dried under reduce 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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}; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (75 MHz, $CDCl_3$) 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}; ^{1}H 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}; ^{1}H 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**)*: ^{1}H 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 the corresponding azide was added (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). ^{1}H 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-Gram scale: (547 mg, 67% yield).

*Benzaldehyde (**12a**)*. Known compound.[33] Colorless liquid. (23 mg, 44% yield). ^{1}H 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). ^{1}H 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). ^{1}H 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). ^{1}H 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-formylbenzonitrile (**12e**)*. Known compound.[35] White solid. (19 mg, 29% yield). ^{1}H 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). ^{1}H 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). ^{1}H 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**) and 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). ^{1}H 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). ^{1}H 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). ^{1}H 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 x 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). ^{1}H 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 oil.[41] (26 mg, 40% yield). ^{1}H 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). ^{1}H 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-Gram 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 x 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}; ^{1}H 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}; ^{1}H 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). ^{1}H 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.

*Diphenhydramine (**15j**)*. Triazene **14** (0.3 mmol) and TsOH (0.15 mmol) were dissolved in dimethylaminoethanol (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 colorless oil. (27 mg, 35% yield). IR (neat) ν 3061, 2941, 1492, 1452, 1102, 696 cm^{-1}; ^{1}H 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 $C_{17}H_{22}NO$ $[M+H]^+$ 256.1700.

ASSOCIATED CONTENT

Supporting Information

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

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

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Notes

The authors declare no competing financial interest.

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