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Article

Selective Azidooxygenation of Alkenes Enabled by Photo-induced Radical Transfer Using Aryl-λ^3-azidoiodane Species

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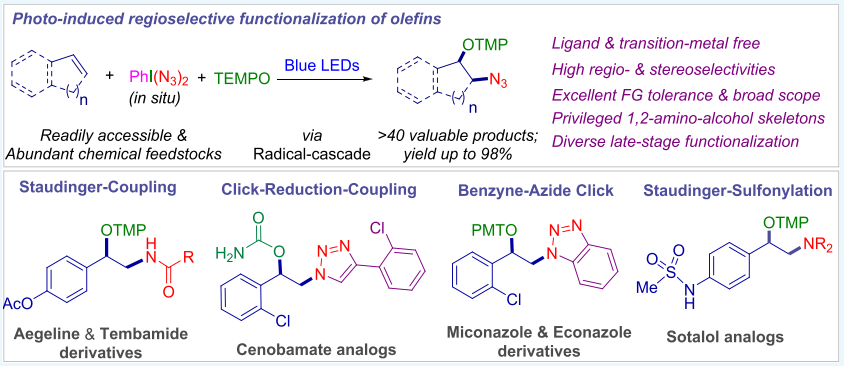


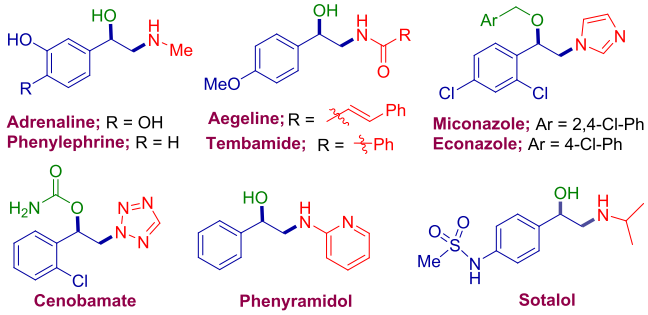
ABSTRACT: The photolytic radical-induced vicinal azidooxygenation of synthetically important and diverse functionalized substrates including unactivated alkenes is reported. The photoredox-catalyst/additive-free protocol enables intermolecular oxyazidation by simultaneously incorporating two new functionalities; *C*−*O* and *C*−*N* across the *C*═*C* double bond in a selective manner. Mechanistic investigations reveal the intermediacy of the azidyl radical facilitated *via* the photolysis of λ^3-azidoiodane species and cascade proceeding to generate an active carbon-centered radical. The late-stage transformations of azido- and oxy-moieties were amply highlighted by assembling high-value drug analogs and bioactive skeletons.

INTRODUCTION

The nitrogen functionalities frequently present in small molecules are of outmost importance as pharmacological probes for studying protein interactions in biological systems.[1] The azidation of an olefin moiety has gained substantial attention owing to the diverse applications of azides as versatile precursors to prevalent nitrogen-based natural products and bioactive molecules.[2] Concurrently, azido-compounds have shown diverse synthetic utilities in robust and efficacious chemical reactions[3−5] as well as in chemical biology[6] and drug discovery.[7] Over the decade, the stereoselective difunctionalization of alkenes,[8] especially the renaissance of azidooxygenation,[9] has been proven as a powerful chemical tool for installing the nitrogen and oxygen functionalities on a *C*═*C* π bond *en route* to pivotal 1,2-amino-alcohol building blocks.[10] In addition to the well-appreciated role as chelating agents, chiral auxiliaries, and privileged ligands in asymmetric syntheses and material sciences, the vicinal amino-alcohol structural motif is of profound relevance in various pharmaceuticals, agrochemicals, biologically active natural products, and several FDA-approved drugs[11] (Scheme 1).

Conceptually, the azidooxygenation of olefins involves a radical or oxidative pathway employing an electrophilic azide source, leading to the intrinsic carbon-centered radical (**A**). The latter may be rapidly trapped by an extrinsic radical donor or get oxidized to nascent cationic species (**B**) *via* SET (single-electron transfer) and subsequently coupled with a nucleophile to achieve azido-functionalization (Scheme 2a).[9] Recent

Scheme 1. Representative Drugs and Natural Bioactive Compounds



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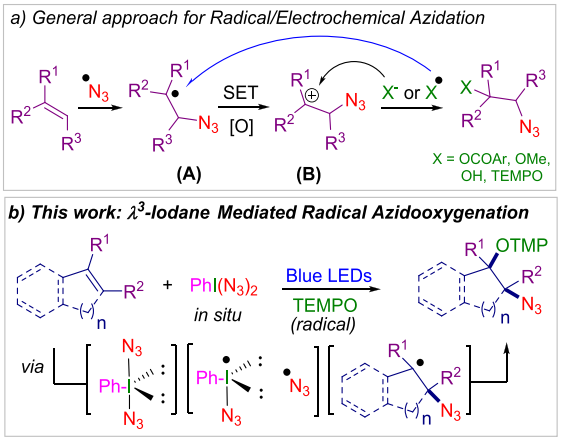
Scheme 2. Previous Approaches and Our Rationalization for Photochemical Radical-Induced Olefin Azidooxygenation Using λ^3-Azidoiodane Species



advances in hypervalent iodine chemistry led to the rapid development of versatile and synthetically advantageous applications emphasizing environmentally benign and promising alternatives to toxic metal salts.[12] Besides exhibiting remarkable ionic reactivity, the hypervalent iodines, particularly trivalent I(III) species (λ^3-iodanes), have been efficiently utilized as radical precursors in enormous radical transformations.[12,13]

Cyclic λ^3-iodanes such as the Zhdankin reagent (azidobenziodoxolone or IBA-N_3) have emerged as reliable sources of highly electrophilic azidyl radicals.[13] The azidooxygenation employing IBA-N_3 and single electron reductant TEMPONa salt as aminoxyl radical has been first investigated by Zhang and Studer.[9a] On the other hand, Siu *et al.* have achieved the electrochemical azidation *via* an orderly radical addition on alkene emanating from azido ($TMSN_3$) and aminooxy species (TEMPO radical).[9b] Lu *et al.* have demonstrated another intriguing application of hypervalent species by exploiting the dual reactivity of the Zhdankin reagent in direct oxyazidation of vinyl arenes.[9c] Meanwhile, Fumagalli *et al.* developed a visible-light-controlled azidation of styrenes using the Zhdankin reagent as the azidating source in the presence of a photoredox Cu-catalyst.[9d] Most recently, Kösel and coworkers have investigated the hypervalent-based solid phase reagent for radical azidation facilitated *via* the photochemical homolytic cleavage of I−N_3 (iodine azide).[9e]

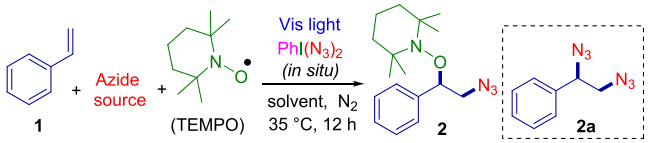
Despite the significant insights, radical-promoted functionalization is scarcely investigated and aims to discover new chemical transformations to understand rather superficial mechanistic outcomes.[14] Apparently, the stereoselective azidooxygenation of unactivated alkene is particularly challenging owing to the innate high reactivity and indistinguishable stability of radicals or intermediate species. The recent progress in visible-light-stimulated organic transformations made a notable impact as sustainable alternative approaches to toxic metal complexes and expensive ligands.[15] In this context, we previously have demonstrated the visible-light-accelerated vicinal diazidation of the *C*=*C* π bond with the sulfonium bis(acetoxy)iodate (I) complex $Me_3SI(OAc)_2$ under a metal-free protocol.[16a] The unprecedented reactivity of trimethylsulfonium [bis(azido)iodate(I)] species was further investigated to realize the photoswitchable regiodivergent selective azidation of alkenes without any precious photoredox-catalyst or ligands.[16b]

Inspired by these precedents and augmented with our previous studies,[16] herein we propose a visible-light-promoted approach for the radical azidooxygenation of olefinic moiety with [bis(azido)iodo(III)]arene ($PhI(N_3)_2$) under additive-free conditions (Scheme 2b). It is attributed to the fact that the "hypervalent I−N_3 bond" in λ^3-azidoiodane species is significantly longer lifetime and highly polarized, which is eventually capable of generating the requisite radicals under mild visible-light irradiation.[17] We further reasoned that the electrophilic azidyl radical instigated from hypervalent species could be selectively trapped by the *C*=*C* π system and the sequential quenching of stabilized carbon-radical adding aminooxy radical (TEMPO•) would ensure the vicinal azidooxygenation.[16a,b]

RESULTS AND DISCUSSION

To realize our hypothesis, the photo-induced transformation of styrene (**1**) as the model substrate was performed with $PhI(N_3)_2$ generated *in situ* by employing $PhI(OAc)_2/NaN_3$ and TEMPO• as the aminoxyl nucleophile (Table 1). Initial optimization revealed the feasibility of azidooxygenation allowing an orderly radical cascade to afford the azido-functionalized product **2** in 40% yield employing MeCN as the solvent and CFL (27 W) as the source of visible light (Table 1, entry 1). A modest increment in the conversion was observed

Table 1. Investigations on λ^3-Iodane Promoted Radical Azidation of Styrene[a]



entry	solvent/azide source	light source	yield (%)[b]
1	MeCN/NaN_3	CFL (27 W)	40
2	toluene/NaN_3	CFL (27 W)	52
3	DMF/NaN_3	CFL (27 W)	48
4	AcOH/NaN_3	CFL (27 W)	trace
5	toluene/$TMSN_3$	CFL (27 W)	65
6	DMF/$TMSN_3$	CFL (27 W)	63
7	DCE/$TMSN_3$	CFL (27 W)	66
8	DCM/$TMSN_3$	CFL (27 W)	70
9	DCM/$TMSN_3$	white LEDs (7 W)	72
10	DCM/$TMSN_3$	green LEDs (7 W)	75
11	**DCM/$TMSN_3$**	**blue LEDs (7 W)**	**92**
12	DCM/$TMSN_3$	ultra-sonication	68
13[c]	DCM/$TMSN_3$	dark	38 (60)
14[d]	DCM/$TMSN_3$	blue LEDs (7 W)	52
15[e]	DCM/$TMSN_3$	blue LEDs (7 W)	**2a**; 22
16[e]	DCM/$TMSN_3$	blue LEDs (7 W)	**2a**; 65[f]

[a]Reaction conditions: **1** (1.0 mmol, 1.0 equiv), $PhI(OAc)_2$ (1.1 equiv), $TMSN_3$ or NaN_3 (2.5 equiv), TEMPO (1.2 equiv), and solvent (2 mL) stirred at 35 °C for 12 h and irradiated with a CFL (27 W) or LEDs (7 W), unless otherwise noted. [b]The isolated and unoptimized yield after chromatography. [c]The reaction was conducted in a dark room. Parenthesis refers to the yields under normal daylight. [d]The reaction was performed with $PhI(OTFA)_2$ (1.1 equiv). [e]The reaction was performed without TEMPO. [f]The reaction was performed with $PhI(OAc)_2$ (2.2 equiv) and $TMSN_3$ (4.4 equiv) at 0−15 °C for 4 h.

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when the reaction was performed in toluene or DMF, i.e., 52 and 48% yields, respectively (entries 2 and 3). On the other hand, using acetic acid as the solvent led to a poor transformation providing a complex mixture of undesired byproducts with traces of oxyazide (entry 4). However, switching the azide source to $TMSN_3$ resulted in a considerable enhancement in radical-enabled transformation to obtain the desired product **2** in decent yield (entries 5 and 6).

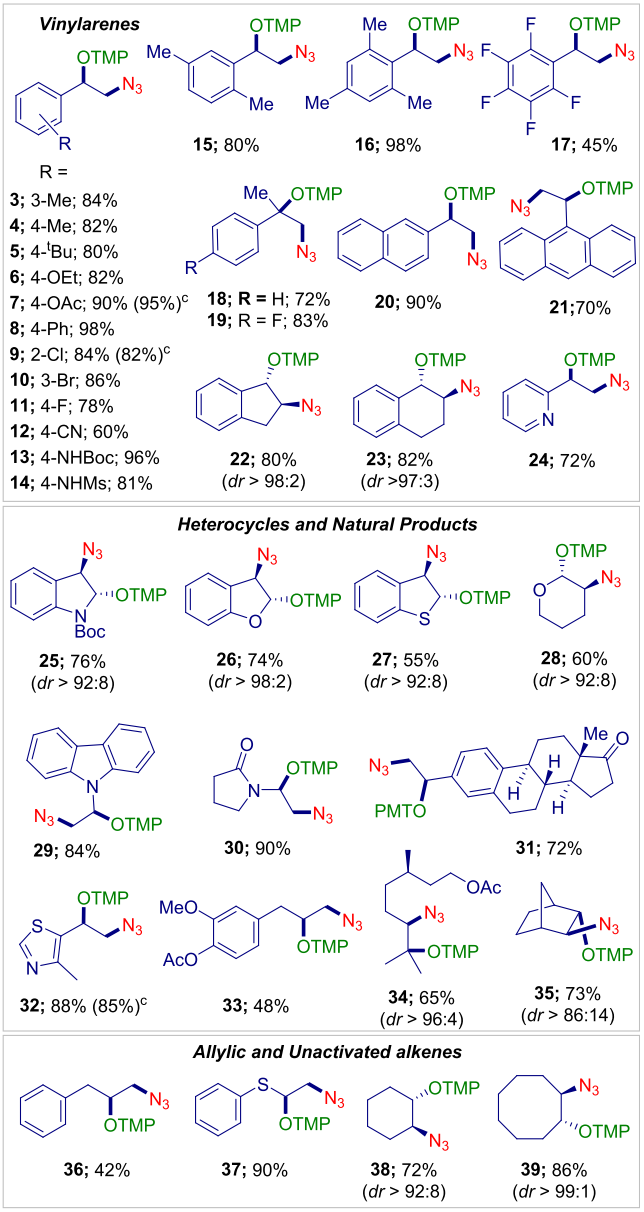
Subsequently, the oxyazidation of **1** with the aforementioned reagent system employing DCE or DCM as the solvent proceeded with better efficiency, furnishing **2** in 66 and 70% yield, respectively (entry 7 and 8). Notably, employing $TMSN_3$ to access I(III)-N_3 under ambient conditions is advantageous as a relatively safer and reliable alternative to toxic I−N_3 and eliminates "azidophobia" condition as well.[18] We further investigated the effect of modulated light sources, for instance, visible LEDs (light-emitting diodes), on radical-induced olefin azidooxygenation. We observed a noticeable improvement in the conversion when the experiment was performed with 7 W white (λ_{max} ∼ 380−740 nm) or green (λ_{max} ∼ 535 nm) LEDs (Table 1, entries 9 and 10). Lastly, using blue LEDs (λ_{max} ∼ 460 nm) established the optimum protocol facilitating the smooth transformation to obtain the desired oxyazide **2** in 92% yield (entry 11).

Of note, CFL and LEDs are operationally safer and economical visible light sources with a more tolerant lower energy. Conducting the reaction under ultrasonication (40 ± 3 kHz) or without light (in the dark) and normal daylight led to a comparable or diminished conversion (entries 12 and 13). However, employing [bis(trifluoroacetoxy)iodo]benzene PhI-$(OTFA)_2$ with $TMSN_3$ accomplished the photo-induced oxyazidation with a decent yield (entry 14). The carbon-radical instigated in photo-induced azidation could be terminated by adding another azidyl radical directly enabling the corresponding 1,2-diazide **2a**[16a] albeit with a lower efficiency (entry 15). Nevertheless, the conceptually envisaged radical diazidation[19] could be obtained in moderate conversion by increasing the amount of $PhI(OAc)_2$ (2.2 equiv) and $TMSN_3$ (4.4 equiv) (entry 16). Notably, the vicinal diazides represent potential precursors to 1,2-diamine, a prevalent structural moiety endowed with prominent drug candidacy and pharmaceutical actions.[20]

With these results, we next aimed to investigate the substrate scope for metal-free azidooxygenation under identified optimal conditions. As illustrated in Table 2, a broad variety of readily accessible styrenes comprising structurally and electronically diverse substituents were evaluated to access the corresponding oxyazides **3**−**14** in good-to-excellent yields ranging from 60 to 98%. The aryl substrates including various electron-donating (3-Me, 4-Me, and 4-*tert*-Bu), electron-rich (4-OEt, 4-OAc, and 4-Ph), and diversely substituted halogens (2-Cl, 3-Br, and 4-F) were well tolerated (Table 2). Other susceptible yet synthetically important functionalities, for instance, −CN, −NHBoc, or −NHMs, were well preserved under the visible-light process. Also, di-(2,5-Me) and trisubstituted (2,4,6-Me) styrenes were reacted smoothly, affording the corresponding oxyazides **15** (80%) and **16** (98%). Noteworthily, a highly and sterically functionalized 2,3,4,5,6-pentafluorostyrene restrained the standard reaction, furnishing the desired product **17** in a moderate yield.

Subsequently, the radical azidooxygenation of α-methyl styrenes can be achieved to access the oxyazides **18** and **19**

Table 2. Scope for the Visible-Light-Mediated Radical Azidooxygenation[a,b]



[a]Reaction conditions: olefins (1.0 equiv), $PhI(OAc)_2$ (1.1 equiv), $TMSN_3$ (2.5 equiv), TEMPO (1.2 equiv), and DCM (2 mL) stirred at 35 °C for 3−12 h and irradiated with blue LEDs (7 W). The *dr* values were examined by ^{1}H NMR spectroscopic analysis of the isolated compound and are given in parenthesis. [b]The isolated and unoptimized yields. [c]Reactions were performed at the gram-scale.[21]

exclusively[21] with no discrepancy in regioselectivity (Table 2). Then, polycyclic arenes such as naphthalene and anthracene were found to be compatible with the λ^3-azidoiodane-mediated method, affording the corresponding azidooxygenated products **20** and **21** in good efficiency. It is pertinent to mention that vinylarenes comprising the internal π system such as indene and 1,2-dihydronaphthalene underwent stereoselective addition of *amino-oxy* radical species on the C=C bond resulting in *trans*-products **22** and **23** with high *dr*. Of the note, the heteroarene comprising 2-vinylpyridine participated effectively, affording the *N,O*-functionalized product **24** in

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72% yield under blue-light irradiation and further accentuating the synthetic versatility of the developed protocol.

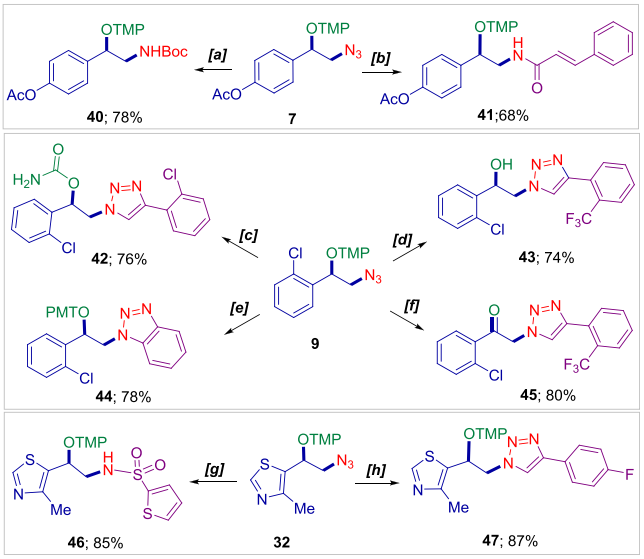
Encouraged by these seminal results, we next examined the applicability of electron-rich heterocycles to access the various functionalizations and complementary structural diversity (Table 2). Pleasingly, the radical cascade azidooxygenation of biologically relevant scaffolds including indole, benzofuran, and thiophene was performed successfully, allowing the facile transfer of azidyl and aminooxy groups to obtain the dearomatized derivatives **25**−**27** in complete regio- and diastereoselectivity. Notably, the observed reversed-regiochemical outcome was consistent and may be attributed to an enhanced stabilization of SOMO at *C*-2 (*vs* benzylic centered radical at *C*-3) effectively by a characteristic 3 e$^-$ bonding interaction (−$\ddot{X}$−$\dot{C}$−) with the adjacent electron donor (unshared lone pairs of the hetero-atom).

In contrast, hetero-vinyl substrates including enol-ether (1,2-dihydropyran) or enamines (*N*-vinyl carbazole and *N*-vinyl pyrrolidone) were reacted efficiently under light-induced radical addition enabling the *β*-azido products **28**−**30** with standard regioselectivity[21] (Table 2). Likewise, privileged pharmaceutical motifs comprising estrone, thiazoline, eugenol and acyclic terpenoid citronellol, or a bicyclic norbornene bearing unactivated olefinic moiety were proved to be favorable substrates furnishing the corresponding azidooxygenated compounds **31**−**35** with high selectivity. To further ameliorate the proposed radical-enabled functionalization of the unactivated *π*-system, an allylic double bond in phenylpropene, a light-sensitive phenylvinylsulfide, and an endocyclic unsaturated system (cyclohexene and cyclooctene) were rewardingly transformed into their respective products **36**−**39** with favored selectivities. The scability of the optimized protocol was further highlighted with the radical oxiazidation of 4-acetoxy styrene, 2-chloro-styrene, and 4-methyl-5-vinylthiazole to obtain the corresponding oxyazides **7** (2.238 g, 95%), **9** (3.917 g, 82%), and **32** (3.60 g, 85%), respectively.[21]

Considering the growing impetus and modular synthetic versatility of oxyazides, we next pursued the late-stage functionalization into relevant drug analogues and natural bioactive products (Scheme 3). Thus, the Staudinger reaction employing oxyazide **7** following *N*-Boc protection in a one-pot process conveniently afforded the masked *β*-aminoalcohol motif **40** in 78% yield. A direct amide-coupling of activated cinnamic acid and aminooxy derived from **7** has been depicted to access aegeline analog **41**, a natural product that exhibits antibacterial and antihyperglycemic activities.[22] Then, cenobamate[23] drug analog **42** was successfully assembled by employing sequential transformation of oxyazide **9**. Enthusiastically, a set of diverse and potentially active[24] pharmaceutical ingredients embedding benzimidazole or triazole hetereocycles (**43**−**45**) was rapidly synthesized from azido-derivative **9**. Additionally, a facile Staudinger reduction−sulfonylation and a CuAAC click coupling of azidooxy **32** were readily performed to obtain the thiazoline−triazole hybrid drug-like molecules (**46**−**47**).

To gain in-depth insights into photo-induced radical transformation, several control experiments were conducted (Scheme 4). Preliminarily, a radical clock reaction of diallyl ether (**1a**) under blue LEDs consistently resulted in the monooxyazide **48** (46%) with traces of the diene rearranged cyclized adduct, plausibly attributed to a radical ring-closure pathway.[9b] Furthermore, *trans*-*β*-Me-styrene (**1b**) was subjected to λ^3-azidoiodane to afford a mixture of diastereomeric *syn*/*anti***49** (*dr*; 5:1, 82%).

Scheme 3. Late-Stage Diverse Transformations of the Oxyazide Functional Group into Biologically Relevant Scaffolds



[a](i) PPh_3 (1.5 equiv), H_2O (3.0 equiv), THF, 50 °C, 15 h; (ii) Boc_2O (3.0 equiv), 0 °C to RT, 12 h. [b](i) Reduction using PPh_3/H_2O; (ii) cinnamic acid (1.0 equiv), EDC·HCl (1.0 equiv), HOBt (1.2 equiv), DIPEA (2.5 equiv), DMF (4 mL), 0 °C to RT, 24 h. [c](i) 2-Cl phenylacetylene (1.2 equiv), CuI (1.5 equiv), DIPEA (3.0 equiv), MeCN (3 mL), RT, 4 h; (ii) nano Zn (6.0 equiv) in $AcOH/H_2O$ (2:6 mL), RT, 16 h; and (iii) CDI (1.2 equiv) in DCM (5 mL), NH_4OH (excess), RT, 4 h. [d](i) 2-CF_3 phenylacetylene (1.2 equiv), CuI (1.5 equiv), DIPEA (3.0 equiv), MeCN (3 mL), RT, 4 h and (ii) nano Zn (6.0 equiv) in $AcOH/H_2O$ (2:6 mL), RT, 12 h. [e]2-(Trimethylsilyl)-phenyl trifluoromethanesulfonate (1.2 equiv), CsF (2.0 equiv), MeCN (3 mL), 70 °C, 16 h. [f]2-CF_3 phenylacetylene (1.2 equiv), CuI (1.5 equiv), DIPEA (3.0 equiv), MeCN (3 mL), RT, 4 h and (ii) mCPBA (1.3 equiv) in DCM (4 mL), RT, 16 h. [g](i) Reduction using PPh_3/H_2O; (ii) 2-thiophenesulfonyl chloride (1.2 equiv), DCM (2 mL), 0 °C to RT, 16 h. [h]4-F phenylacetylene (1.2 equiv), $CuSO_4$ (cat.), sodium ascorbate (cat.), ^{t}BuOH/H_2O (2:1 mL), RT, 4 h.

Indeed, the radical clock azidooxygenation of (*E*) or (*Z*)-stilbene (**1c**, **1d**) unambiguously afforded the identical diastereoisomeric oxyazides **50** and *vic*-diazide **51**, albeit with varied yields and *dr* values (Scheme 4). The stereochemical outcome is consistent with our previous studies[16b] and evidently confirms the non-stereospecific addition of *N*/*O* species on the benzylic-radical intermediate in a two-step radical process. Subsequently, a spin trapping experiment employing 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical scavenger resulted in quenching the azidooxygenation while producing azidyl spin adduct **52** in 52% isolated yield and another spin adduct (4-azido-*cyclo*-hexanedienone) as traces, revealing the subsistence of free azidyl in operative radical transformation.

Based on the literature precedents and key observations from aforementioned experiments, a speculative rationalization for radical azidooxygenation is postulated. As elucidated in Scheme 4, $PhI(OAc)_2$ and $TMSN_3$ could rapidly participate in ligand exchange to enable the active λ^3-azidoiodane radical precursor. The photolytic cleavage of the I−N_3 hypervalent bond in the putative transient species generated *in situ* would

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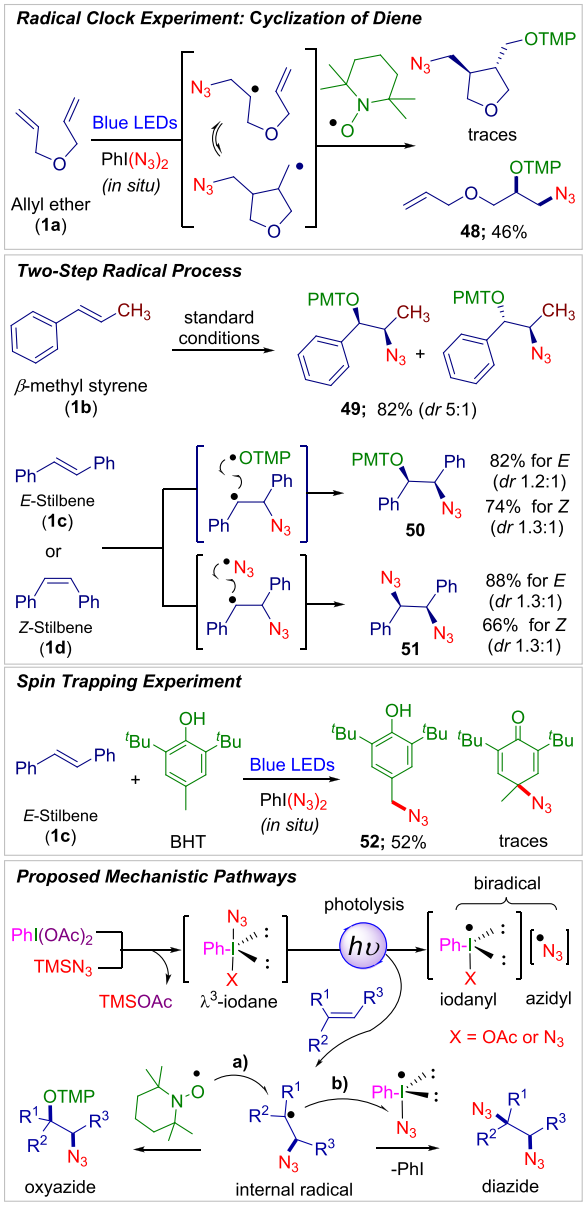
Scheme 4. Control Experiments to Probe the Mechanistic Hypothesis for λ^3-Iodane-Mediated Photolytic Radical Azidooxygenation



likely facilitate the initiation of requisite azidyl (and iodanyl) radicals.[17] The pertinent electrophilic nature of the azidyl radical toward an electron-rich moiety, the *C*=*C* π bond, would distinctly produce the penultimate internal carbon radical.

Successively trapping the resultant *C*-centered intermediate by an extrinsic radical donor (TEMPO•) would eventually lead to the formation of the target azidooxygenated product with the preferred regioselectivity (pathway a). In the absence of radical scavengers, the incipient β-azido alkyl-radical could lastly bond with another azido-radical that was instigated from imperative azidoiodane to access the corresponding *vic*-diazide (pathway b).

With no discrepancy, ^{1}H NMR studies revealed the presence of characteristic resonances of TMSOAc and PhI,[21] which plausibly promoted by dissipating of azidoiodane or proportionate with respective species. The proposed mechanism is sufficiently validated and correlated by further spectroscopic data analyses using IR absorption experiments.[17d,21]

CONCLUSIONS

In summary, we have advanced the most intriguing implication of the λ^3-azidoiodane reagent to illustrate the possibility of photo-induced selective induction of hetero-atoms on olefins. The developed radical oxyazidation is amenable to a diverse array of substrates including vinylarenes, allylic or unactivated alkenes, heterocycles, and natural products bearing synthetically useful functionalities. Noteworthily, the diverse skeletons generated through azidooxygenation represent essential building blocks that offer potential late-stage modifications in various chemical transformations *en route* to biologically valuable scaffolds and drug analogs. The preliminary yet key mechanistic observations on the distinct reactivity of λ^3-azidoiodane species in the intermolecular functionalization of olefin rendered this discovery highly desirable. The ameliorated protocol impressively highlights the prospect of pertinent radical-cascade processes for investigating the new transformations to aid in expanding the chemical diversity and drug discovery paradigm.

EXPERIMENTAL SECTION

General Synthesis Information. Moisture and air-sensitive reactions were performed in flame-dried round-bottom flasks or glass tubes, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via a nitrogen-flushed syringe. Experiments were monitored by thin layer chromatography (TLC). Melting points were obtained in open capillary tubes using a micro melting point apparatus and were uncorrected. Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of the solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg). Analytical TLC was performed using Whatman 250 μm aluminum-backed UV F254 precoated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for the visualization of UV active materials. Staining with *p*-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization. Proton and carbon nuclear magnetic resonance spectra (^{1}H, ^{13}C NMR) were recorded on Avance 300, 400, or 500 MHz and ECS 4000 MHz (JEOL) NMR spectrometers. The proton resonances are annotated as follows: chemical shift (δ) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad), coupling constant (*J*, Hz), and number of protons for a given resonance indicated by *n*H. The chemical shifts of ^{13}C NMR are reported in ppm relative to the central line of the triplet at δ 77.00 ppm for $CDCl_3$. IR spectra were recorded on a PerkinElmer FT-IR spectrometer, and wave numbers of maximum absorption peaks are presented in cm^{-1}. Mass analyses (ESI-MS) and HRMS were performed on a Xevo G2-S QTTOF (Waters, USA) spectrometer. A blue LED apparatus (7 W ribbon λ_{max} ~ 460 nm) equipped with a magnetic stirrer and chiller was used as the light source.

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General Procedure for Radical Azidooxygenation. An oven-dried, 10 mL glass tube was equipped with a magnetic stir bar, a rubber septum, and a threaded Teflon cap. A nitrogen-filled balloon was fitted through the septum to sustain a nitrogen atmosphere. To this vessel was added a solution of alkene (1.0 equiv) in DCM (2 mL) *via* a syringe followed by the sequential addition of $TMSN_3$ (2.5 equiv), TEMPO (1.2 equiv), and $PhI(OAc)_2$ (1.1 equiv) at room temperature (25 °C). The reaction mixture was then purged with nitrogen (gas) for another 5 min with the aid of an exit needle on the septum. A stirring rate was established at 900 rpm. The reaction tube was irradiated with visible light, a common 7 W blue LED ribbon ($\lambda_{max} \sim 460$ nm), under stirring. The distance between the light source and the reaction flask was maintained at approximately 3−4 cm, resulting in the temperature increasing up to 35 °C. The tube was then submerged in an insulated bath to maintain the temperature. For safety reasons, the reaction was carried out behind an anti-blast shield. The reaction was stirred until the complete consumption of the starting material, typically for 6−12 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL) and saturated aqueous sodium thiosulfate (2 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography (using gradient eluent of hexanes/EtOAc) to obtain the desired oxyazides **2**−**39** or **48**−**50**.

The Statement Concerning Safety Issues. Organic azides are potentially explosive compounds, and appropriate safety protocols[2b] should be observed as they decompose with a slight input of energy from external sources such as light, heat, pressure, etc. During the utilization and preparation of compounds containing azides, we generally follow the equation as below: the ratio of carbon (C), oxygen (O), and nitrogen (N) atoms in the molecule. It is noted that this equation takes into account all nitrogen atoms in the organic azide and not just those in the azido group; n (C) + n (O)/n (N) ≥ 3, where n = number of atoms. All organic azides prepared in this work satisfied the above equation, and they are relatively stable at room temperature and can be stored at lower temperatures for several months. In addition, we have never experienced a safety problem with these experiments.

*1-(2-Azido-1-phenylethoxy)-2,2,6,6-tetramethylpiperidine (**2**).* Following the general procedure, a preformed solution of styrene **1** (104 mg, 1.0 mmol, 1.0 equiv) in DCM (2 mL) was treated with $TMSN_3$ (328 μL, 287 mg, 2.5 mmol, 2.5 equiv) followed by TEMPO (187 mg, 1.2 mmol, 1.2 equiv) and $PhI(OAc)_2$ (354 mg, 1.1 mmol, 1.1 equiv) at room temperature (25 °C). The mixture was stirred under a nitrogen atmosphere and irradiated with visible light (7 W blue LED). Following the usual workup and purification by silica gel column chromatography using hexanes as the eluent, the desired compound **2** was obtained as a pale-yellow oil (278 mg, 0.92 mmol, 92%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.16 (m, 5H), 4.73 (dd, J = 6.8, 4.7 Hz, 1H), 3.61 (dd, J = 12.3, 4.6 Hz, 1H), 3.52 (dd, J = 12.2, 6.9 Hz, 1H), 1.40 (s, 3H), 1.31−1.15 (m, 6H), 1.11 (s, 3H), 0.95 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 128.1, 127.8, 127.5, 84.9, 60.0, 55.2, 40.3, 34.3, 33.9, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

Representative Procedure for Radical Diazidation. A preformed solution of styrene **1** (104 mg, 1.0 mmol, 1.0 equiv) in DCM (2 mL) was treated with $TMSN_3$ (582 μL, 506 mg, 4.4 mmol, 4.4 equiv) followed by $PhI(OAc)_2$ (708 mg, 2.2 mmol, 2.2 equiv) at room temperature (25 °C). The mixture was stirred under a nitrogen atmosphere and irradiated with visible light (7 W blue LED) at 0−15 °C. For safety reasons, the reaction was carried out behind an anti-blast shield. The reaction was stirred until the consumption of the starting material, typically for 4 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL) and saturated aqueous sodium thiosulfate (2 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography using hexanes as the eluent to afford the diazide **2a** as a pale-yellow oil (141 mg, 0.75 mmol, 75%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.26 (m, 5H), 4.66 (dd, J = 8.3, 5.0 Hz, 1H), 3.49 (dd, J = 12.7, 8.3 Hz, 1H), 3.43 (dd, J = 12.7, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 129.0, 128.9, 126.9, 65.4, 55.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16a]

*1-(2-Azido-1-(m-tolyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**3**).* Following the general azidooxygenation procedure using 1-methyl-3-vinylbenzene (90 mg, 0.762 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a colorless oil (202 mg, 0.640 mmol, 84%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.4 Hz, 1H), 7.12 (dd, J = 16.6, 7.9 Hz, 3H), 4.78 (dd, J = 6.7, 4.8 Hz, 1H), 3.73 (dd, J = 12.3, 4.6 Hz, 1H), 3.63 (dd, J = 12.2, 6.9 Hz, 1H), 2.36 (s, 3H), 1.36 (d, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 137.6, 128.5, 128.1, 128.0, 124.5, 84.8, 59.9, 55.2, 40.3, 34.3, 34.0, 21.4, 20.6, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

*1-(2-Azido-1-(m-tolyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**4**).* Following the general azidooxygenation procedure using 1-methyl-3-vinylbenzene (90 mg, 0.762 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a pale-yellow semi-solid (197 mg, 0.624 mmol, 82%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.4 Hz, 1H), 7.12 (dd, J = 16.6, 7.9 Hz, 3H), 4.78 (dd, J = 6.7, 4.8 Hz, 1H), 3.73 (dd, J = 12.3, 4.6 Hz, 1H), 3.63 (dd, J = 12.2, 6.9 Hz, 1H), 2.35 (s, 3H), 1.49−1.38 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.03 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.4, 128.8, 128.7, 84.6, 60.0, 55.2, 40.3, 34.3, 34.0, 21.2, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

*1-(2-Azido-1-(4-(tert-butyl)phenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**5**).* Following the general azidooxygenation procedure using 1-(*tert*-butyl)-4-vinylbenzene (90 mg, 0.562 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a pale-yellow semi-solid (161 mg, 0.449 mmol, 80%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 4.81 (dd, J = 6.7, 4.8 Hz, 1H), 3.76 (dd, J = 12.2, 4.7 Hz, 1H), 3.62 (dd, J = 12.2, 6.9

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Hz, 1H), 1.50−1.33 (m, 6H), 1.31 (s, 12H), 1.19 (s, 3H), 1.05 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 137.4, 127.1, 125.0, 84.4, 60.0, 55.1, 40.4, 34.5, 34.3, 33.9, 31.3, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,9,9e]

*1-(2-Azido-1-(4-ethoxyphenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**6**).* Following the general azidooxygenation procedure using 1-ethoxy-4-vinylbenzene (100 mg, 0.675 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (191 mg, 0.553 mmol, 82%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 9.5, 2.2 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.69 (dd, J = 7.0, 4.9 Hz, 1H), 4.00−3.91 (m, 2H), 3.66 (dd, J = 12.2, 4.9 Hz, 1H), 3.51 (dd, J = 12.2, 7.1 Hz, 1H), 1.52−1.27 (m, 9H), 1.24 (s, 3H), 1.11 (s, 3H), 0.95 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 132.6, 128.8, 114.0, 84.3, 63.3, 60.0, 55.2, 40.3, 34.3, 34.1, 20.3, 17.1, 14.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*4-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxyethyl)-phenyl acetate (**7**).* Following the general azidooxygenation procedure using 4-acetoxy styrene (94 mg, 0.582 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (188 mg, 0.523 mmol, 90%). Rf (10% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 4.83 (m, 1H), 3.73 (dd, J = 12.3, 4.7 Hz, 1H), 3.63 (dd, J = 12.3, 6.7 Hz, 1H), 2.28 (s, 3H), 1.49−1.37 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.03 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 150.1, 138.0, 128.4, 121.1, 84.1, 65.0, 59.9, 54.9, 41.8, 40.2, 34.2, 33.9, 23.2, 22.9, 21.0, 20.2, 16.9, 13.9, 10.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a]

*1-(1-([1,1′-Biphenyl]-4-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (**8**).* Following the general azidooxygenation procedure using 4-vinyl-1,1′-biphenyl (100 mg, 0.555 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (205 mg, 0.543 mmol, 98%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, J = 8.1 Hz, 4H), 7.42 (t, J = 7.9 Hz, 4H), 7.32 (t, J = 7.3 Hz, 1H), 4.88 (dd, J = 6.5, 4.8 Hz, 1H), 3.77 (dd, J = 12.3, 4.6 Hz, 1H), 3.68 (dd, J = 12.3, 6.8 Hz, 1H), 1.51−1.38 (m, 6H), 1.34 (s, 3H), 1.21 (s, 3H), 1.06 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 140.6, 139.6, 128.7, 127.9, 127.2, 127.0, 126.8, 84.6, 60.0, 55.1, 40.4, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

*1-(2-Azido-1-(2-chlorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**9**).* Following the general azidooxygenation procedure using 1-chloro-3-vinylbenzene (110 mg, 0.797 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (225 mg, 0.669 mmol, 84%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.24−7.20 (m, 1H), 5.34 (dd, J = 4.9, 3.4 Hz, 1H), 3.96 (dd, J = 12.8, 5.2 Hz, 1H), 3.55 (dd, J = 12.8, 3.2 Hz, 1H), 1.62−1.39 (m, 6H), 1.35 (s, 3H), 1.20 (s, 3H), 1.04 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 131.6, 129.2, 129.0, 128.5, 126.6, 82.0, 60.2, 59.5, 53.4, 40.2, 34.5, 33.0, 20.1, 16.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(2-Azido-1-(3-bromophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**10**).* Following the general azidooxygenation procedure using 1-bromo-3-vinylbenzene (140 mg, 0.769 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (251 mg, 0.661 mmol, 86%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.42 (dd, J = 7.8, 0.6 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 4.78 (dd, J = 6.5, 4.8 Hz, 1H), 3.70 (dd, J = 12.4, 4.6 Hz, 1H), 3.64 (dd, J = 12.4, 6.7 Hz, 1H), 1.58−1.34 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 130.9, 130.5, 129.7, 126.1, 122.3, 84.3, 60.0, 54.9, 40.3, 34.3, 34.0, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(2-Azido-1-(4-fluorophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**11**).* Following the general azidooxygenation procedure using 1-fluoro-4-vinylbenzene (100 mg, 0.819 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (204 mg, 0.638 mmol, 78%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 2H), 7.04 (t, J = 8.7 Hz, 2H), 4.81 (dd, J = 6.9, 4.7 Hz, 1H), 3.72 (dd, J = 12.3, 4.7 Hz, 1H), 3.61 (dd, J = 12.3, 7.0 Hz, 1H), 1.64−1.35 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H), 1.02 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.31 (d,$^1J_{C\text{-}F}$ = 246.1 Hz), 136.42 (d,$^4J_{C\text{-}F}$ = 3.0 Hz), 129.11 (d,$^3J_{C\text{-}F}$ = 8.2 Hz), 115.02 (d,$^2J_{C\text{-}F}$ = 21.2 Hz), 84.1, 60.0, 55.0, 40.3, 34.3, 34.0, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

*4-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-ethyl)benzonitrile (**12**).* Following the general azidooxygenation procedure using 1-cyano-4-vinylbenzene (110 mg, 0.853 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (167 mg, 0.511 mmol, 60%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 4.89 (dd, J = 6.1, 4.7 Hz, 1H), 3.77−3.66 (m, 2H), 1.50−1.40 (m, 6H), 1.32 (s, 3H), 1.19 (s, 3H), 1.04 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 131.7, 127.9, 118.4, 111.3, 84.2, 59.9, 59.8, 40.0, 34.1, 33.7, 20.0, 16.7, 16.6; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a]

*tert-Butyl(4-(2-azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)carbamate (**13**).* Following the general azidooxygenation procedure using *tert*-butyl (4-vinylphenyl)-carbamate (125 mg, 0.392 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a white solid (157 mg, 0.376 mmol, 96%). Rf (10% EtOAc/hexane) 0.5; Mp: 102−104 °C; IR (film): 3320, 2983, 2942, 2103, 1729, 1598, 1535, 1456, 1414, 1366, 1319, 1231, 1155, 1051, 1006, 922, 844, 821, 770, 663, 553 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 6.58 (s, 1H), 4.77 (dd, J = 6.5, 5.1 Hz, 1H), 3.71 (dd, J = 12.3, 4.7 Hz, 1H), 3.60 (dd, J = 12.2, 6.9 Hz, 1H), 1.51 (s, 9H), 1.45−1.32 (m, 9H), 1.18 (s, 3H), 1.02 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 137.9, 135.1, 128.2, 118.0, 84.4, 84.3, 65.2, 60.0, 55.1,

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41.8, 40.3, 34.3, 34.1, 28.2, 23.2, 23.0, 20.2, 17.0, 14.0, 11.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{22}H_{35}N_5O_3]^+$: 418.2813; found: 418.2814.

*N-(4-Vinylphenyl)methanesulfonamide (**14A**).* A 50 mL round-bottom flask was dried and charged with 4-amino styrene (300 mg, 2.556 mmol, 1 equiv), dissolved in DCM (2 mL), and treated with $MeSO_2Cl$ (217 μL, 320 mg, 2.811 mmol, 1.1 equiv) followed by TEA (533 μL, 387 mg, 30.834 mmol, 1.5 equiv) at 0 °C. The mixture was stirred under a nitrogen atmosphere until the completion of the starting material, typically for 2 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), quenched with 10 N HCl (5 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the mixture, which was used for the next reaction without further purification. It is worth mentioning that several attempts with mesylchloride in TEA always yielded mixtures containing variable proportions of *N*-monomesyl and dimesyl compounds.

TBAF (1.0 M solution in THF, 1.3 mL, 4.36 mmol) was added to a solution of mixture in THF (5 mL) at room temperature and stirred for 2 days. The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated NH_4Cl (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the title compound **14A** as a white solid (352 mg, 1.789 mmol, 70%). Rf (30% EtOAc/hexane) 0.5; Mp: 97−99 °C; IR (film): 3236, 3014, 2928, 2852, 2464, 2300, 2092, 1908, 1813, 1742, 1607, 1506, 1446, 1391, 1312, 1224, 1138, 983, 899, 832, 773, 641, 571, 517, 478 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.5 Hz, 2H), 7.18 (s, 1H), 7.14 (d, J = 8.6 Hz, 2H), 6.59 (dd, J = 17.6, 10.9 Hz, 1H), 5.62 (d, J = 17.6 Hz, 1H), 5.16 (d, J = 10.9 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 135.6, 134.8, 127.4, 120.8, 111.9, 39.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_9H_{11}NO_2S]^+$: 198.0583; found: 198.0585.

*N-(4-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-ethyl)phenyl)methanesulfonamide (**14**).* Following the general azidooxygenation procedure using **14A***N*-(4-vinylphenyl)-methanesulfonamide (200 mg, 0.506 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a transparent semi-solid (162 mg, 0.409 mmol, 81%). Rf 30% EtOAc/hexane) 0.5; IR (film): 3259, 2930, 2098, 1737, 1614, 1512, 1461, 1324, 1260, 1148, 1064, 1025, 969, 917, 823, 764, 646, 521 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.03 (s, 1H), 4.69 (dd, J = 8.2, 4.1 Hz, 1H), 4.05−3.90 (m, 2H), 3.00 (d, J = 4.4 Hz, 3H), 1.45 (d, J = 3.3 Hz, 4H), 1.25 (s, 2H), 1.17 (s,3H), 1.13 (d, J = 3.6 Hz, 6H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 134.2, 128.4, 120.5, 80.2, 64.1, 60.1, 60.0, 59.9, 39.6, 39.5, 39.3, 32.9, 20.0, 19.9, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{18}H_{29}N_5O_3S]^+$: 396.2064; found: 396.2062.

*1-(2-Azido-1-(2,5-dimethylphenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (**15**).* Following the general azidooxygenation procedure using 1,4-dimethyl-2-vinylbenzene (90 mg, 0.681 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a pale-yellow semi-solid (180 mg, 0.547 mmol, 80%). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.02−6.97 (m, 2H), 5.05 (t, J = 5.7 Hz, 1H), 3.72−3.65 (m, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 1.50−1.39 (m, 6H), 1.34 (s, 3H), 1.20 (s, 3H), 1.02 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 135.0, 131.7, 129.9, 128.0, 127.9, 81.6, 59.9, 59.7, 54.6, 40.2, 34.2, 33.2, 21.0, 20.2, 20.1, 19.0, 16.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(2-Azido-1-mesitylethoxy)-2,2,6,6-tetramethylpiperidine (**16**).* Following the general azidooxygenation procedure using 1,3,5-trimethyl-2-vinylbenzene (90 mg, 0.616 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a colorless semi-solid (208 mg, 0.604 mmol, 98%). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 6.78 (s, 1H), 5.23 (dd, J = 8.9, 5.2 Hz, 1H), 3.88 (dd, J = 12.0, 5.1 Hz, 1H), 3.70 (dd, J = 11.9, 8.9 Hz, 1H), 2.49 (s, 3H), 2.33 (s, 3H), 2.24 (s, 3H), 1.66−1.35 (m, 6H), 1.34−1.29 (m, 3H), 1.16 (s, 3H), 0.99 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 136.9, 130.6, 128.6, 82.3, 61.8, 59.6, 59.4, 54.0, 53.1, 40.2, 40.1, 34.1, 33.1, 20.6, 16.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(Azido(perfluorophenyl)methoxy)-2,2,6,6-tetramethylpiperidine (**17**).* Following the general azidooxygenation procedure using 2,3,4,5,6-pentafluorostyrene (96 mg, 0.496 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (88 mg, 0.223 mmol, 45%). Rf (10% EtOAc/hexane) 0.5; IR (film): 2934, 2103, 1739, 1652, 1521, 1420, 1377,1362, 1306, 1259, 1210, 1130, 1089, 1025, 1008, 966, 929, 887, 800, 742, 714 cm-1; ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (dd, J = 8.0, 6.4 Hz, 1H), 3.98 (dd, J = 12.3, 6.2 Hz, 1H), 3.67 (dd, J = 12.3, 8.2 Hz, 1H), 1.62−1.35 (m, 6H), 1.33 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H), 0.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4 (dm, $^3J_{C\text{-}F}$ = 249.5 Hz), 141.0 (dm, $^1J_{C\text{-}F}$ = 255.5 Hz), 137.5 (dm, $^2J_{C\text{-}F}$ = 253 Hz) 114.0 (m), 76.6, 60.6, 59.8, 52.6, 40.3, 40.2, 33.9, 33.3, 20.1, 20.0, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{17}H_{21}F_5N_4O]^+$: 393.1708; found: 393.1704.

*1-((1-Azido-2-phenylpropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**18**).* Following the general azidooxygenation procedure using prop-1-en-2-ylbenzene (91 mg, 0.875 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (199 mg, 0.630 mmol, 72%). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51−7.46 (m, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 3.62 (d, J = 11.8 Hz, 1H), 3.44 (d, J = 11.8 Hz, 1H), 1.73 (s, 3H), 1.59−1.34 (m, 6H), 1.20 (s, 3H), 1.20 (s, 3H), 1.04 (s, 3H), 0.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 127.6, 126.9, 126.1, 81.4, 62.0, 59.6, 59.4, 40.7, 40.5, 34.0, 33.0, 20.5, 20.4, 19.1, 16.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a]

*1-((1-Azido-2-(4-fluorophenyl)propan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**19**).* Following the general azidooxygenation procedure using 1-fluoro-4-(prop-1-en-2-yl)benzene (101 mg, 0.742 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (206 mg, 0.616 mmol, 83%). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 8.8, 5.4 Hz, 2H), 7.03 (t, J = 8.7 Hz, 2H), 3.59 (d, J = 11.8 Hz, 1H), 3.43 (d, J = 11.8 Hz, 1H), 1.71 (s, 3H), 1.58−1.36 (m, 6H), 1.19 (s, 3H), 1.19 (s, 3H), 1.03 (s, 3H), 0.49 (s,

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3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 160.5, 41.5, 127.9 (d,$^2J_{C\text{-}F}$ = 7.8 Hz), 114.6, 114.5 (d,$^1J_{C\text{-}F}$ = 21.1 Hz), 81.2, 62.1, 59.7, 59.5, 40.8, 40.6, 34.1, 33.2, 20.5 (d,$^3J_{C\text{-}F}$ = 2.6 Hz), 19.4, 16.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(2-Azido-1-(naphthalen-2-yl)ethoxy)-2,2,6,6-tetramethylpiperidine (**20**).* Following the general azidooxygenation procedure using 2-vinylnaphthalene (100 mg, 0.649 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a pale-yellow solid (205 mg, 0.584 mmol, 90%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, J = 7.5, 3.0 Hz, 3H), 7.78 (s, 1H), 7.49 (dd, J = 8.5, 1.2 Hz, 1H), 7.48−7.44 (m, 2H), 4.98 (dd, J = 6.7, 4.8 Hz, 1H), 3.80 (dd, J = 12.4, 4.6 Hz, 1H), 3.73 (dd, J = 12.3, 6.9 Hz, 1H), 1.51−1.31 (m, 9H), 1.23 (s, 3H), 1.04 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 133.0, 132.9, 127.9, 127.8, 127.7, 126.7, 125.9, 125.8, 125.1, 85.1, 60.0, 55.1, 40.3, 34.3, 34.1, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,e]

*1-(1-(Anthracen-9-yl)-2-azidoethoxy)-2,2,6,6-tetramethylpiperidine (**21**).* Following the general azidooxygenation procedure using 9-vinylanthracene (100 mg, 0.490 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a brown solid (137 mg, 0.343 mmol, 70%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.48−7.41 (m, 2H), 6.32 (dd, J = 9.1, 4.0 Hz, 1H), 4.72 (t, J = 9.5 Hz, 1H), 4.12 (dd, J = 10.0, 4.1 Hz, 1H), 1.48−1.36 (m, 9H), 1.23 (s, 3H), 1.08 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.7, 129.4, 129.0, 127. 5, 124.8, 79.2, 61.0, 60.0, 59.8, 39.6, 39.5, 33.0, 32.9, 21.0, 20.0, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-((2-Azido-2,3-dihydro-1H-inden-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (**22**).* Following the general azidooxygenation procedure using indene (100 mg, 0.862 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (216 mg, 0.689 mmol, 80%, *dr* > 98:02). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.1 Hz, 1H), 7.23 (ddd, J = 24.1, 12.0, 4.2 Hz, 3H), 5.33 (d, J = 4.1 Hz, 1H), 4.39 (dt, J = 7.2, 4.8 Hz, 1H), 3.34 (dd, J = 16.2, 7.2 Hz, 1H), 2.86 (dd, J = 16.2, 5.2 Hz, 1H), 1.60−1.36 (m, 6H), 1.29 (s, 3H), 1.19 (s, 3H), 1.10 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 140.0, 128.8, 126.6, 126.5, 124.5, 90.1, 66.5, 60.6, 59.8, 40.1, 36.5, 34.2, 33.6, 20.4, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,e]

*1-(((1S,2S)-2-Azido-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (**23**).* Following the general azidooxygenation procedure using 1,2-dihydronaphthalene (99 mg, 0.761 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (238 mg, 0.624 mmol, 82%, *dr* > 97:03). Rf (10% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.5 Hz, 1H), 7.25−7.18 (m, 1H), 7.16−7.06 (m, 2H), 4.78 (d, J = 2.5 Hz, 1H), 4.27 (dd, J = 6.9, 3.2 Hz, 1H), 2.90−2.76 (m, 2H), 2.31−2.28 (m, 1H), 1.97 (dtd, J = 9.4, 6.3, 3.2 Hz, 1H), 1.53−1.33 (m, 9H), 1.14 (s, 3H), 0.97 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 133.3, 133.0, 128.2, 128.1, 124.9, 78.6, 60.6, 59.4, 58.3, 40.2, 40.0, 34.4, 33.0, 24.0, 22.3, 20.5, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,e]

*2-(2-Azido-1-((2,2,6,6-tetramethylpipridin-1-yl)oxy)ethyl)-pyridine (**24**).* Following the general azidooxygenation procedure using 2-vinyl pyridine (102 mg, 0.971 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (212 mg, 0.699 mmol, 72%). Rf (10% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63−8.55 (m, 1H), 7.70 (td, J = 7.7, 1.7 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.21 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 5.00 (t, J = 4.9 Hz, 1H), 3.93 (dd, J = 12.7, 5.4 Hz, 1H), 3.82 (dd, J = 12.7, 4.4 Hz, 1H), 1.54−1.36 (m, 9H), 1.22 (s, 3H), 1.09 (s, 3H), 0.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 148.9, 136.1, 123.4, 122.6, 85.6, 60.0, 53.5, 41.9, 40.3, 34.2, 33.3, 23.3, 23.0, 20.3, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9b]

*tert-Butyl-3-azido-2-((2,2,6,6-tetramethylpiperidin-1-yl)-oxy)-2,3-dihydro-1H-indene-1-carboxylate (**25**).* Following the general azidooxygenation procedure using *N*-Boc-indole (214 mg, 0.986 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (311 mg, 0.749 mmol, 76%, *dr* > 92:08). Rf (10% EtOAc/hexane) 0.5; IR (film): 2975, 2932, 2104, 1720, 1607, 1481, 1380, 1314, 1296, 1254, 1095, 1160, 1144, 1043, 1017, 987, 937, 907, 852, 792, 749, 711, 596, 570, 492, 469, 419 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.43 (d, J = 7.3 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.27 (s, 1H), 4.95 (s, 1H), 1.60 (s, 9H), 1.50−1.32 (m, 6H), 1.14 (s, 9H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 142.3, 130.4, 127.8, 126.8, 125.8, 124.1, 123.0, 122.6, 120.9, 115.5, 115.1, 107.2, 85.3, 82.4, 78.0, 60.8, 59.9, 40.2, 34.5, 33.5, 28.2, 20.6, 20.4, 17.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{22}H_{33}N_5O_3]^+$: 416.2656; found: 416.2655.

*1-((3-Azido-2,3-dihydrobenzofuran-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**26**).* Following the general azidooxygenation procedure using benzofuran (93 mg, 0.792 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (243 mg, 0.586 mmol, 74%, *dr* > 92:08). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.4 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.01−6.90 (m, 2H), 6.14 (s, 1H), 5.13 (s, 1H), 1.58−1.30 (m, 6H), 1.21 (s, 3H), 1.09 (s, 3H), 1.07 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 130.7, 127.6, 124.7, 121.3, 110.5, 96.0, 87.0, 60.2, 59.9, 40.0, 39.9, 33.9, 33.4, 20.2, 16.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a,b]

*1-((3-Azido-2,3-dihydrobenzo[b]thiophen-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**27**).* Following the general azidooxygenation procedure using benzothiophene (87 mg, 0.649 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (119 mg, 0.357 mmol, 55%, *dr* > 92:08). Rf (4% EtOAc/hexane) 0.5; IR (film): 2926, 2854, 2098, 1739, 1589, 1452, 1375, 1258, 1234, 1091, 1025, 956, 903, 864, 798, 748, 712, 623, 550, 451 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 1H), 7.28−7.20 (m, 2H), 7.09 (dd, J = 10.5, 4.0 Hz, 1H), 5.53 (s, 1H), 5.32 (s, 1H), 1.61−1.47 (m, 6H), 1.28 (s, 3H), 1.08 (d, J = 7.7 Hz, 6H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 136.3, 130.3, 128.3, 124.6,

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122.6, 91.6, 73.1, 60.6, 60.4, 40.3, 40.2, 34.1, 33.6, 22.6, 20.5, 17.1, 14.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{17}H_{24}N_4OS]^+$: 333.1744; found: 333.1746.

*1-((3-Azidotetrahydro-2H-pyran-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**28**).* Following the general azidooxygenation procedure using 3,4-dihydro-2*H*-pyran (108 mg, 1.29 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (218 mg, 0.774 mmol, 60%, *dr* > 92:08). Rf (10% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (d, J = 5.2 Hz, 1H), 4.02−3.82 (m, 1H), 3.59−3.43 (m, 2H), 2.16−2.00 (m, 1H), 1.75 (dtd, J = 13.9, 6.9, 3.7 Hz, 1H), 1.67−1.45 (m, 6H), 1.30−1.16 (m, 14H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.1, 62.9, 59.3, 40.1, 39.8, 33.7, 33.1, 26.5, 22.3, 20.4, 19.9, 16.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a]

*9-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-ethyl)-9H-carbazole (**29**).* Following the general azidooxygenation procedure using 9-vinyl-9*H*-carbazole (100 mg, 0.521 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (171 mg, 0.437 mmol, 84%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.56 (d, J = 93.4 Hz, 4H), 7.24 (s, 2H), 6.20 (dd, J = 8.9, 4.8 Hz, 1H), 4.14 (dd, J = 12.7, 9.0 Hz, 1H), 3.99 (dd, J = 12.8, 4.8 Hz, 1H), 1.48 (d, J = 28.6 Hz, 6H), 1.26 (s, 6H), 0.97 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.1, 125.8, 125.5, 120.4, 120.1, 119.7, 119.4, 112.4, 108.9, 89.3, 60.9, 59.5, 50.6, 40.2, 40.1, 33.6, 31.6, 20.1, 19.9, 16.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a]

*1-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-ethyl)pyrrolidi-2-one (**30**).* Following the general azidooxygenation procedure using 1-vinylpyrrolidin-2-one (89 mg, 1.050 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (292 mg, 0.945 mmol, 90%). Rf (20% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (dd, J = 8.3, 4.8 Hz, 1H), 3.64−3.52 (m, 3H), 3.46 (dd, J = 12.4, 4.5 Hz, 1H), 2.40 (ddd, J = 10.0, 8.9, 5.7 Hz, 2H), 2.12−1.96 (m, 2H), 1.58−1.35 (m, 6H), 1.25 (s, 3H), 1.10 (s, 3H), 1.06 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 99.7, 84.3, 60.5, 59.1, 59.0, 49.7, 42.7, 39.9, 39.9, 33.3, 32.6, 31.1, 20.1, 19.7, 17.5, 16.7; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9b]

*(8R,9S,13S,14S)-3-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-13-methyl 6,7,8,9,11,12,13,14,15,16-Decahydro-17H-cyclopenta[a]phenanthren-17-one (**31A**).* 3-Vinylestrone: First step: A 100 mL round-bottom flask was dried and charged with estrone (200 mg, 0.740 mmol, 1.0 equiv), DCM (10 mL), and Et_3N (205 μL, 150 mg, 1.481 mmol, 2.0 equiv). The mixture was cooled to 0 °C, and Tf_2O (149 μL, 251 mg, 0.888 mmol, 1.2 equiv) was added over 3 min dropwise. The mixture was allowed to warm to room temperature and stirred at room temperature under nitrogen for 3 h. The resulting brown mixture was diluted with DCM and washed with sat. NH_4Cl, and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified with column chromatography to afford 3-(trifluoromethanesulfonyl) estrone as a white solid (250 mg, 0.621 mmol, 84%). Second step: A 100 mL two-neck round-bottom flask was charged with 3-(trifluoromethanesulfonyl) estrone (200 mg, 0.497 mmol, 1.0 equiv), potassium vinyl trifluoroborate (65 mg, 0.497 mmol, 1.0 equiv), and $PdCl_2$ (2 mg, 0.009 mmol, 0.02 equiv), and the round-bottom flask was brought into a N_2-filled glove box. PPh_3 (8 mg, 0.029 mmol, 0.06 equiv), Cs_2CO_3 (485 mg, 1.492 mmol, 3.0 equiv), and THF (1.8 mL) were added, and the round-bottom flask was sealed. H_2O (0.2 mL) was added, the reaction mixture was degassed using nitrogen, and the mixture was stirred at 85 °C for 24 h. The resulting dark brown mixture was allowed to cool to room temperature, diluted with DCM, and washed with H_2O. The aqueous layer was extracted with DCM (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, and the filtrate was concentrated. The crude was purified with column chromatography to afford 3-vinylestrone as a white solid (171 mg, 0.357 mmol, 72%). Rf (30% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.24 (m, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.14 (s, 1H), 6.66 (dd, J = 17.6, 10.9 Hz, 1H), 5.70 (d, J = 17.6 Hz, 1H), 5.19 (d, J = 10.9 Hz, 1H), 2.92 (dd, J = 8.7, 3.9 Hz, 2H), 2.51 (dd, J = 18.7, 8.7 Hz, 1H), 2.42 (dt, J = 8.9, 3.5 Hz, 1H), 2.29 (dd, J = 13.6, 7.0 Hz, 1H), 2.16 (dd, J = 18.4, 9.4 Hz, 1H), 2.11−1.93 (m, 3H), 1.68−1.39 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 139.4, 136.5, 135.2, 126.8, 125.5, 123.6, 113.2, 50.5, 47.955, 44.4, 38.1, 35.8, 31.6, 29.3, 26.5, 25.7, 21.6, 13.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*(8R,9S,13S,14S)-3-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-13-methyl 6,7,8,9,11,12,13,14,15,16-Decahydro-17H-cyclopenta[a]phenanthren-17-one (**31**).* Following the general radical azidooxygenation procedure using **31A** 3-vinylestrone (100 mg, 0.357 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a white solid (103 mg, 0.257 mmol, 72%). Rf (20% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 4.70 (dd, J = 6.8, 4.5 Hz, 1H), 3.75−3.65 (m, 1H), 3.57 (dd, J = 12.2, 7.0 Hz, 1H), 2.86 (dd, J = 7.8, 3.1 Hz, 2H), 2.44 (dd, J = 18.7, 8.7 Hz, 1H), 2.39−2.32 (m, 1H), 2.24 (td, J = 11.0, 3.3 Hz, 1H), 2.13−1.87 (m, 4H), 1.60−1.32 (m, 12H), 1.25 (s, 3H), 1.12 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 137.8, 136.1, 136.0, 127.9, 127.8, 125.0, 124.8, 124.6, 84.4, 84.3, 60.1, 59.9, 55.1, 50.5, 47.9, 44.3, 40.3, 38.0, 35.7, 34.3, 34.1, 31.5, 29.6, 29.3, 26.5, 25.6, 25.5, 21.5, 20.3, 17.0, 13.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*5-(2-Azido-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-ethyl)-4-methylthiazole (**32**).* Following the general azidooxygenation procedure using 4-methyl-5-vinylthiazole (109 mg, 0.872 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a yellow oil (247 mg, 0.767 mmol, 88%). Rf (20% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 5.23 (t, J = 5.5 Hz, 1H), 3.67 (d, J = 5.5 Hz, 2H), 2.51 (s, 3H), 1.53−1.30 (m, 9H), 1.17 (s, 3H), 1.01 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 150.9, 131.2, 78.0, 60.4, 60.0, 55.2, 40.3, 34.1, 32.9, 20.1, 17.0, 15.8; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*4-(3-Azido-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-propyl)-2-methoxyphenyl Acetate (**33**).* Following the general azidooxygenation procedure using eugenyl acetate (100 mg,

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0.485 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (93 mg, 0.232 mmol, 48%). Rf (10% EtOAc/hexane) 0.5; IR (film): 2932, 2098, 1765, 1603, 1565, 1509, 1463, 1419, 1264, 1195, 1152, 1123, 1036, 1011, 939, 903, 825, 718, 670, 634, 601, 556, 515, 469, 420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 8.0 Hz, 1H), 6.81 (s, 1H), 6.75 (dd, J = 8.0 Hz, 1.8 Hz, 1H), 4.11 (dd, J = 8.8, 4.6 Hz, 1H), 3.79 (s, 3H), 3.33 (d, J = 4.5 Hz, 2H), 3.22 (dd, J = 13.3, 5.0 Hz, 1H), 2.74 (dd, J = 13.3, 8.6 Hz, 1H), 2.28 (s, 3H), 1.46 (d, J = 6.6 Hz, 6H), 1.19−1.11 (m, 9H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 150.6, 138.0, 137.2, 122.4, 121.5, 113.6, 82.0, 60.0, 59.9, 55.7, 52.2, 40.2, 40.1, 37.1, 34.1, 34.1, 20.5, 20.4, 20.3, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{21}H_{32}N_4O_4]^+$: 405.2496; found: 405.2496.

*(3R)-6-Azido-3,7-dimethyl-7-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)octyl Acetate (**34**).* Following the general azidooxygenation procedure using citronellyl acetate (100 mg, 0.505 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a pale-yellow oil (129 mg, 0.328 mmol, 65%, *dr* > 96:04). Rf (10% EtOAc/hexane) 0.5; IR (film): 2931, 2095, 1741, 1460, 1364, 1322, 1231, 1181, 1134, 1033, 958, 912, 878, 801, 715, 642, 606, 555 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.18−4.05 (m, 2H), 3.46 (dd, J = 14.4, 5.3 Hz, 1H), 2.04 (s, 3H), 1.58 (dd, J = 15.2, 8.6 Hz, 3H), 1.46 (d, J = 12.2 Hz, 6H), 1.34 (s, 3H), 1.32−1.23 (m, 3H), 1.19 (d, J = 7.9 Hz, 3H), 1.13 (s, 3H), 1.10 (d, J = 1.8 Hz, 10H), 0.95 (dd, J = 6.3, 2.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 81.7, 81.6, 72.4, 72.2, 62.7, 59.4, 59.2, 40.8, 35.3, 35.2, 34.9, 34.8, 34.4, 29.8, 29.6, 26.8, 26.6, 23.4, 23.3, 22.7, 22.6, 20.9, 20.5, 19.4, 19.3, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{21}H_{40}N_4O_3]^+$: 397.3173; found: 397.3170.

*1-(((1S,2R,3S,4R)-3-Azidobicyclo[2.2.1]heptan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**35**).* Following the general azidooxygenation procedure using norbornene (100 mg, 1.063 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a colorless oil (227 mg, 0.776 mmol, 73%, *dr* > 86:14). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 3.99 (d, J = 6.8 Hz, 1H), 3.95 (s, 1H), 3.26 (t, J = 2.5 Hz, 1H), 3.18 (d, J = 6.7 Hz, 1H), 2.70 (s, 1H), 2.58 (s, 1H), 2.35 (s, 1H), 2.29 (d, J = 4.6 Hz, 1H), 1.85 (ddd, J = 9.0, 8.2, 4.6 Hz, 1H), 1.79 (d, J = 10.4 Hz, 1H), 1.69−1.58 (m, 2H), 1.54 (d, J = 10.5 Hz, 2H), 1.52−1.41 (m, 12H), 1.40−1.28 (m, 6H), 1.28−1.19 (m, 12H), 1.14 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 92.7, 90.0, 70.6, 66.7, 59.8, 59.3, 42.0, 41.8, 40.6, 40.2, 40.1, 39.8, 34.5, 34.0, 33.8, 33.2, 26.8, 26.5, 24.5, 20.3, 20.2, 20.1, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,e]

*1-((1-Azido-3-phenylpropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidine (**36**).* Following the general azidooxygenation procedure using allyl benzene (112 mg, 0.949 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (126 mg, 0.398 mmol, 42%). Rf (4% EtOAc/hexane) 0.5; IR (film): 2927, 2097, 1739, 1603, 1494, 1453, 1375, 1361, 1259, 1232, 1216, 1183, 1132, 1080, 1029, 956, 939, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.6 Hz, 3H), 4.07 (dq, J = 9.1, 4.5 Hz, 1H), 3.30−3.18 (m, 3H), 2.71−2.62 (m, 1H), 1.50−1.30 (m, 6H), 1.12 (s, 3H), 1.09 (s, 6H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 129.5, 128.3, 126.1, 82.4, 60.1, 59.9, 52.4, 40.3, 40.2, 37.3, 34.3, 34.1, 29.6, 20.5, 20.3, 17.1, 16.9; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{18}H_{28}N_4O]^+$: 317.2336; found: 317.2334.

*1-(2-Azido-1-(phenylthio)ethoxy)-2,2,6,6-tetramethylpiperidine (**37**).* Following the general azidooxygenation procedure using phenyl(vinyl)sulfane (100 mg, 0.735 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (221 mg, 0.661 mmol, 90%). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.0, 1.4 Hz, 2H), 7.34−7.23 (m, 3H), 5.31 (t, J = 6.0 Hz, 1H), 3.70 (dd, J = 12.8, 5.8 Hz, 1H), 3.46 (dd, J = 12.8, 6.2 Hz, 1H), 1.58−1.46 (m, 6H), 1.31 (s, 3H), 1.19 (s, 3H), 1.15 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 133.1, 128.8, 127.5, 91.9, 60.8, 60.1, 53.7, 40.3, 34.6, 33.8, 20.6, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(((1R,2R)-2-Azidocyclohexyl)oxy)-2,2,6,6-tetramethylpiperidine (**38**).* Following the general azidooxygenation procedure using cyclohexene (123 mg, 1. 503 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (303 mg, 1.082 mmol, 72%, *dr* > 92:08). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 3.65 (ddd, J = 10.2, 8.5, 4.0 Hz, 1H), 3.29−3.19 (m, 1H), 2.33−2.23 (m, 1H), 1.92−1.81 (m, 1H), 1.67−1.53 (m, 3H), 1.38 (t, J = 11.7 Hz, 4H), 1.19−1.01 (m, 17H); 3.72 (ddd, J = 10.3, 8.7, 3.9 Hz, 1H), 3.33 (ddd, J = 10.4, 8.6, 4.5 Hz, 1H), 2.40−2.29 (m, 1H), 1.99−1.88 (m, 1H), 1.76−1.00 (m, 24H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.8, 64.9, 61.7, 61.4, 40.5, 40.3, 34.5, 34.3, 31.0, 30.7, 24.1, 23.7, 20.5, 17.3; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a,b]

*1-((2-Azidocyclooctyl)oxy)-2,2,6,6-tetramethylpiperidine (**39**).* Following the general azidooxygenation procedure using *cis*-cyclooctene (118 mg, 1.074 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a dark-yellow oil (284 mg, 0.924 mmol, 86%, *dr* > 92:08). Rf (4% EtOAc/hexane) 0.5; ^1H NMR (400 MHz, $CDCl_3$) δ 4.11 (t, J = 8.7 Hz, 1H), 3.56−3.48 (m, 1H), 2.75 (ddd, J = 9.5, 5.5, 3.1 Hz, 1H), 1.90 (ddd, J = 11.9, 9.1, 5.8 Hz, 1H), 1.86−1.77 (m, 1H), 1.77−1.54 (m, 6H), 1.54−1.36 (m, 6H), 1.36−1.27 (m, 3H), 1.23 (s, 3H), 1.16 (s, 3H), 1.08 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.1, 67.8, 60.3, 59.1, 40.5, 40.1, 34.5, 33.4, 28.1, 27.4, 27.0, 26.1, 25.1, 22.3, 21.0, 20.9, 17.3; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9b]

Derivatization of Oxyazides. *4-(2-((tert-Butoxycarbonyl)amino)-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl Acetate (**40**).* A preformed solution of PPh_3 (191 mg, 0.729 mmol, 1.5 equiv) and H_2O (34 μL, 2.431 mmol, 5 equiv) in THF (5 mL) was treated with compound **7** (175 mg, 0.486 mmol, 1.0 equiv, prepared by oxyazidation of 4-acetoxy styrene) at 50 °C. The reaction was stirred until the complete conversion of the starting material as observed by TLC. Subsequently, a solution of di-*tert*-butyl dicarbonate (Boc anhydride) (333 μL, 1.458 mmol, 318 mg, 3.0 equiv) in THF (2 mL) was added to the above reaction mixture dropwise at 0 °C to rt. The resulting mixture was then stirred until amine intermediates were fully consumed (monitored by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with

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EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography using hexane/EtOAc (from 10:1 to 2:1) as the eluent to afford the protected amine **40** as a white solid (164 mg, 0.379 mmol, 78%). Rf (20% EtOAc/hexane) 0.5; Mp: 110−112 °C; IR (film): 3743, 3055, 2928, 2321, 1969, 1900, 1757, 1680, 1580, 1438, 1310, 1183, 1116, 995, 853, 750, 720, 695, 532, 451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 4.84 (d, J = 5.4 Hz, 2H), 3.84−3.75 (m, 1H), 3.35 (dd, J = 13.3, 6.4 Hz, 1H), 2.29 (s, 3H), 1.51 (d, J = 12.1 Hz, 3H), 1.39 (s, 9H), 1.34 (s, 6H), 1.17 (s, 3H), 1.03 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 155.6, 149.9, 138.5, 128.3, 121.1, 83.7, 78.9, 60.0, 59.9, 45.2, 40.3, 33.9, 28.2, 21.0, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{24}H_{38}N_2O_5]^+$: 434.2781; found: 434.2779.

*4-(2-Cinnamamido-1-((2,2,6,6-tetramethylpiperidin-1-yl)-oxy)ethyl)phenyl Acetate (**41**).* A preformed solution of PPh_3 (191 mg, 0.729 mmol, 1.5 equiv) and H_2O (34 μL, 2.431 mmol, 5.0 equiv) in THF (5 mL) was treated with compound **7** (175 mg, 0.486 mmol, 1.0 equiv, prepared by oxyazidation of 4-acetoxy styrene) at 50 °C. The reaction was stirred until the complete conversion of the starting material as observed by TLC. The reaction mixture was concentrated *in vacuo* and kept on high vacuum for an hour. A preformed solution of cinnamic acid (56 mg, 0.379 mmol, 1.0 equiv) in DMF (3 mL) and EDC·HCl (73 mg, 0.379 mmol, 1.0 equiv) was added at 0 °C followed by HOBt (51 mg, 0.379 mmol, 1.0 equiv), and the reaction mixture was stirred for 1 h. To the abovementioned crude reaction mixture, amine was added in *N*,*N*-DIPEA (203 μL, 153 mg, 1.137 mmol, 3 equiv), and the reaction was continuously stirred at room temperature until the complete conversion of the starting material, typically for 24 h (as observed by TLC).[10a] The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the amide **41** as a transparent semi-solid (119 mg, 0.258 mmol, 68%). Rf (40% EtOAc/hexane) 0.5; IR (film): 3283, 2929, 1757, 1451, 1757, 1660, 1619, 1541, 1505, 1364, 1198, 1130, 979, 913, 846, 761, 711, 546, 486, 414 cm^{-1}; ^1H NMR (400 MHz,) δ 7.57 (d, J = 15.6 Hz, 1H), 7.46 (d, J = 1.1 Hz, 2H), 7.34 (dd, J = 7.6, 2.8 Hz, 5H), 7.06 (d, J = 8.1 Hz, 2H), 6.51 (s, 1H), 6.29 (d, J = 15.6 Hz, 1H), 4.98 (t, J = 6.4 Hz, 1H), 4.05−3.97 (m, 1H), 3.69−3.61 (m, 1H), 2.28 (d, J = 0.5 Hz, 3H), 1.55−1.27 (m, 9H), 1.21 (d, J = 21.3 Hz, 3H), 1.06 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 165.5, 150.1, 140.9, 138.3, 134.8, 129.6, 128.7, 128.3, 127.7, 121.4, 120.7, 83.0, 60.4, 60.1, 45.0, 40.5, 34.2, 33.7, 21.1, 20.5, 20.3, 17.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{28}H_{36}N_2O_4]^+$: 465.2745; found: 465.2747.

*1-(1-(2-Chlorophenyl)-2(4-(2-chlorophenyl)-1H-1,2,3-triazol-1-yl)ethoxy)-2,2,6,6-tetramethylpiperidine (**42A**).* To a preformed solution of compound **9** (303 mg, 300 μL, 1.859 mmol, 1.0 equiv, prepared by oxyazidation of 2-chloro styrene) and 1-ethynyl-2-chlorobenzene (303 mg, 270 μL 2.231 mmol, 1.2 equiv) in MeCN (5 mL) were added CuI (530 mg, 2.7885 mmol, 1.5 equiv) and *N*,*N*-DIPEA (970 μL 5.577 mmol, 719 mg, 3.0 equiv). The reaction mixture was stirred at room temperature for 3 h until the complete conversion of the starting material as observed by TLC.[16a,d] The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the triazole **42A** as a white solid (772 mg, 1.635 mmol, 88%). Rf (15% EtOAc/hexane) 0.5; Mp: 90−92 °C; IR (film): 3171, 3075, 2958, 2925, 2863, 1793, 1461, 1442, 1360, 1259, 1233, 1190, 1085, 1053, 1021, 978, 967, 917, 882, 803, 752, 722, 711, 673 cm^{-1}; ^1H NMR (400 MHz) δ 8.09 (dd, J = 7.8, 1.7 Hz, 1H), 7.85 (s, 1H), 7.35−7.30 (m, 1H), 7.27−7.15 (m, 4H), 7.12−7.04 (m, 3H), 5.61−5.55 (m, 1H), 4.98 (dd, J = 14.1, 3.8 Hz, 1H), 4.87 (dd, J = 14.1, 5.9 Hz, 1H), 3.47 (d, J = 5.1 Hz, 1H), 1.51−1.39 (m, 7H), 1.21 (d, J = 3.7 Hz, 4H), 0.96 (s, 3H), 0.85−0.79 (m, 4H), 0.71 (s, 3H); ^{13}C NMR (101 MHz) δ 143.5, 137.2, 132.1, 131.1, 130.0, 129.8, 129.4, 129.3, 129.0, 128.8, 127.0, 126.9, 124.1, 65.2, 53.2, 41.9, 40.5, 30.1, 29.7, 29.1, 23.3, 23.1, 17.0, 14.1, 11.1; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{25}H_{30}Cl_2N_4O]^+$: 473.1869; found: 473.1868.

*1-(2-Chlorophenyl)-2-(4-(2-chlorophenyl)-1H-1,2,3-triazol-1-yl)ethan-1-ol (**42B**).* To a solution of compound **42A** (772 mg, 1.635 mmol, 1.0 equiv) in AcOH/H_2O (2:6 mL) (1:3) was added nano zinc (647 mg, 9.81 mmol, 6.0 equiv). The reaction mixture was stirred at room temperature for 16 h until the complete conversion of the starting material as observed by TLC.[9a] The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the **42B** as a white solid (435 mg, 1.308 mmol, 80%). Rf (20% EtOAc/hexane) 0.5; Mp: 150−152 °C; IR (film): 3352, 3182, 3068, 2090, 1750, 1469, 1435, 1350, 1314, 1261, 1236, 1208, 1180, 1162, 1126, 1031, 978, 953, 896, 806, 750, 727, 613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.04 (dd, J = 7.8, 1.5 Hz, 1H), 7.52 (d, J = 7.0 Hz, 1H), 7.33−7.29 (m, 2H), 7.26−7.14 (m, 4H), 5.60−5.54 (m, 1H), 4.73 (dd, J = 14.0, 2.7 Hz, 1H), 4.38 (dd, J = 14.0, 8.1 Hz, 1H), 3.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.3, 131.6, 131.2, 130.1, 129.6, 129.5, 129.4, 129.0, 128.9, 127.4, 127.1, 124.6, 69.8, 55.6; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{16}H_{13}Cl_2N_3O]^+$: 335.0508; found 335.0639.

*1-(2-Chlorophenyl)-2-(4-(2-chlorophenyl)-1H-1,2,3-triazol-1-yl)ethyl Carbamate (**42**).* To a solution of compound **42B** (435 mg, 1.308 mmol, 1.0 equiv) in DCM (4 mL) was added 1,1′-carbonyl diimidazole (96 mg, 1.569 mmol, 1.2 equiv), and the reaction mixture was stirred at room temperature for 4 h. To the reaction mixture, excess NH_4OH (15 mL) was added and stirred for 4 h.[23a,b] The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the **42** as a white solid (373 mg, 0.994 mmol, 76%). Rf (50% EtOAc/hexane) 0.5; Mp: 182−184 °C; IR (film): 3369, 3327, 3270, 3192, 3129, 3065, 2927, 2853, 2116, 1731, 1619, 1530, 1448,1428, 1377, 1325, 1268, 1231, 1208, 1160, 1130, 1086, 1045, 949, 891, 754, 726, 566 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 7.45−

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7.40 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.26 (dd, J = 15.0, 6.7 Hz, 4H), 6.46 (dd, J = 6.3, 2.9 Hz, 1H), 5.04−4.87 (m, 3H), 4.78 (dd, J = 14.3, 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 144.0, 134.0, 131.7, 131.2, 130.1, 129.9, 129.9, 129.8, 129.1, 129.0, 127.4, 127.1, 127.0, 124.0, 71.6, 52.9; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{17}H_{14}Cl_2N_4O]^+$: 378.2320; found 378.2322.

*1-(1-(2-Chlorophenyl)-2-(4-(2-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)ethoxy)-2,2,6,6-tetramethylpiperidine (**43A**).* To a preformed solution of compound **9** (150 mg, 0.446 mmol, 1.0 equiv, prepared by oxyazidation of 2-chloro styrene) and 2-(trifluoromethyl)phenyl acetylene (75 μL, 0.535 mmol, 91 mg, 1.2 equiv) in MeCN (3 mL) were added CuI (127 mg, 0.669 mmol, 1.5 equiv) and *N*,*N*-DIPEA (233 μL, 173 mg, 0.1338 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 4 h until the complete conversion of the starting material as observed by TLC.[16b,d] The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the triazole **43A** as a pale-yellow solid (189 mg, 0.374 mmol, 84%). Rf (20% EtOAc/hexane) 0.5; Mp: 88−90 °C; IR (film): 3065, 2973, 2941, 1995, 1739, 1608, 1527, 1437, 1362, 1315, 1195, 1105, 1034, 908, 757, 646, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.60 (s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 7.24−7.18 (m, 1H), 7.11−7.02 (m, 3H), 5.59 (t, J = 4.3 Hz, 1H), 4.99 (dd, J = 14.2, 3.7 Hz, 1H), 4.88 (dd, J = 14.1, 5.5 Hz, 1H), 1.61−1.32 (m, 9H), 1.18 (s, 3H), 0.98 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 137.0, 131.9, 131.8, 131.7, 129.7, 129.3, 129.0, 128.5, 128.0, 126.8, 126.0, 125.9, 123.7, 123.6, 82.4, 60.5, 59.8, 53.1, 40.5, 34.9, 33.1, 20.5, 17.0; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{26}H_{30}ClF_3N_4O]^+$: 507.2133; found 507.2133.

*1-(1-(2-Chlorophenyl)-2-(4-(2-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)ethan-1-ol (**43**).* To a solution of compound **43A** (189 mg, 0.374 mmol, 1.0 equiv) in AcOH/H_2O (2:6 mL) (1:3) was added nano zinc (148 mg, 2.244 mmol, 6.0 equiv), and the reaction mixture was stirred at room temperature for 12 h.[9a] After the completion of the reaction, the reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the **43** as a white solid (101 mg, 0.276 mmol, 74%). Rf (20% EtOAc/hexane) 0.5; Mp: 99−101 °C; IR (film): 3288, 3160, 2966, 2927, 2852, 1729, 1637, 1612, 1580, 1491, 1436, 1316, 1295, 1174, 1122, 1106, 1089, 1077,1059, 1047, 1032, 769, 752, 703, 596, 546 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.72 (m, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.42 (ddd, J = 17.4, 9.7, 5.3 Hz, 2H), 7.31−7.25 (m, 1H), 7.22−7.13 (m, 2H), 5.51 (d, J = 5.5 Hz, 1H), 4.71 (dd, J = 14.0, 2.8 Hz, 1H), 4.44 (dd, J = 14.1, 7.5 Hz, 1H), 3.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.9, 137.3, 131.9, 131.6, 131.52, 129.5, 129.4, 129.3, 129.2, 128.3, 127.3, 127.2, 127.1, 69.5, 69.4, 55.4; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{17}H_{13}ClF_3N_3O]^+$: 368.0772; found 368.0773.

*1-(2-(2-Chlorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-1H benzo[d][1,2,3]triazole (**44**).* To a preformed solution of compound **9** (130 mg, 0.387 mmol, 1.0 equiv, prepared by oxyazidation of 2-chlorostyrene) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (113 μL, 138 mg, 0.464 mmol, 1.2 equiv) in MeCN (2.0 mL) was added CsF (118 mg, 0.774 mmol, 2.0 equiv), and the reaction mixture was stirred at 70 °C for 16 h.[16b] After cooling to ambient temperature, the reaction was quenched with NH_4Cl (aq.), extracted with EtOAc (3 × 30 mL), dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel chromatography to afford the desired product **44** as a yellow solid (124 mg, 0.301 mmol, 78%). Rf (10% EtOAc/hexane) 0.5; Mp: 113−115 °C; IR (film): 3068, 3015, 2966, 2927, 2866, 2856, 1732, 1612, 1495, 1470, 1452, 1438, 1406, 1374, 1360, 1346, 1307, 1268, 1219, 1194, 1156, 1130, 1089, 1059, 1040, 1020, 955, 804, 750, 730, 714, 552 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88−7.80 (m, 1H), 7.11 (dd, J = 3.7, 1.2 Hz, 3H), 6.98 (d, J = 2.5 Hz, 3H), 6.79 (d, J = 4.6 Hz, 1H), 5.62 (s, 1H), 5.25 (dd, J = 14.1, 4.6 Hz, 1H), 4.92 (dd, J = 14.0, 7.6 Hz, 1H), 1.37 (m, 9H), 1.12 (s, 3H), 0.94 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 137.8, 133.5, 132.5, 129.0, 128.8, 126.7, 126.6, 123.2, 119.4, 108.8, 60.0, 51.5, 40.3, 16.9; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{23}H_{29}ClN_4O]^+$: 412.2103; found 413.2101.

*1-(2-Chlorophenyl)-2-(4-(2-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)ethan-1-one (**45**).* A solution of compound **43A** (189 mg, 0.374 mmol, 1.0 equiv) and mCPBA (84 mg, 0.486 mmol, 1.3 equiv 70−75% in H_2O) in DCM (5 mL) was stirred at room temperature for 16 h.[9a] The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the triazole **45** as a pale-yellow oil (109 mg, 0.299 mmol, 80%). Rf (20% EtOAc/hexane) 0.5; IR (film): 3157, 3075, 2927, 2849, 1715, 1612, 1591, 1470, 1438, 1357, 1313, 1279, 1226, 1172, 1121, 1107, 1050, 1034, 978, 857, 755, 644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 1H), 7.95 (s, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.72−7.68 (m, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.53−7.46 (m, 3H), 7.41 (ddd, J = 7.8, 5.2, 3.3 Hz, 1H), 5.91 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 144.6, 135.3, 133.6, 132.0, 131.8, 131.7, 131.0, 130.4, 128.4, 127.5, 126.1, 126.0, 124.7, 58.4; HRMS (ESI) m/z $[M + H]^+$ calculated for $[C_{17}H_{11}ClF_3N_3O]^+$: 366.0616; found 366.0617.

*N-(2-(4-Methylthiazol-5-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)thiophene-2-sulfonamide (**46**).* A preformed solution of PPh_3 (178 mg, 0.681 mmol, 2.2 equiv) and H_2O (28 μL, 1.547 mmol, 5.0 equiv) in THF (5 mL) was treated with compound **32** (100 mg, 0.309 mmol, 1.0 equiv, prepared by oxyazidation of 4-methyl-5-vinylthiazole) at 0 °C. The reaction was stirred at room temperature until the complete conversion of the starting material as observed by TLC. The reaction mixture was concentrated *in vacuo*, and the crude amine was added to a preformed solution of thiophene-2-sulfonyl chloride (67 mg, 0.371, 1.2 equiv) in DCM dropwise at 0 °C followed by Et_3N (64 μL, 47 mg, 0.464, 1.5 equiv). The resulting mixture was then stirred until amine intermediate was fully consumed (monitored by TLC). The reaction mixture was diluted with CH_2Cl_2 (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with DCM (30 × 3 mL). The combined organic layers were washed with a

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brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography to afford the sulfonamide **46** as a white solid (116 mg, 0.262 mmol, 85%). Rf (30% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.65−7.53 (m, 2H), 7.14−7.04 (m, 1H), 6.07 (s, 1H), 5.36 (t, J = 6.1 Hz, 1H), 3.71−3.57 (m, 1H), 3.38−3.24 (m, 1H), 2.42 (s, 3H), 1.46 (d, J = 12.3 Hz, 6H), 1.17 (s, 3H), 1.09 (s, 3H), 1.02 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.2, 140.7, 131.9, 131.8, 130.3, 127.3, 60.7, 60.1, 48.5, 40.2, 40.0, 33.2, 20.3, 20.2, 16.9, 15.5, 14.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*5-(2-(4-(4-Fluorophenyl)-1H-1,2,3-triazol-1-yl)-1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)-4-methylthiazole (**47**).* To a preformed solution of compound **32** (100 mg, 0.309 mmol, 1.0 equiv, prepared by oxyazidation of 4-methyl-5-vinylthiazole) and 1-ethynyl-4-fluorobenzene (42 μL, 0.371 mmol, 44 mg, 1.2 equiv) in ^{t}BuOH/H_2O (2:1 mL) (2:1) were added $CuSO_4$ (10 mg, 0.619 mmol, 0.2 equiv) and sodium ascorbate (24 mg, 0.123 mmol, 0.4 equiv), and the reaction mixture was stirred at room temperature for 3 h until completion of the starting material (monitored by TLC). The reaction mixture was diluted with EtOAc (10 mL), quenched with saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column to afford the triazole **47** as a white solid (119 mg, 0.268 mmol, 87%). Rf (40% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.70 (d, J = 13.9 Hz, 2H), 7.38 (s, 1H), 7.09 (d, J = 17.3 Hz, 2H), 5.57 (dd, J = 7.5, 5.8 Hz, 1H), 5.22 (dd, J = 13.5, 5.6 Hz, 1H), 4.49 (dd, J = 13.5, 7.8 Hz, 1H), 2.17 (s, 3H), 1.56−1.38 (m, 6H), 1.13 (s, 3H), 1.05 (s, 3H), 0.89 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 161.4, 151.9, 151.7, 146.8, 130.2, 127.5, 127.4, 126.6, 120.4, 115.90, 115.7, 78.2, 60.4, 54.7, 40.4, 37.2, 34.2, 33.1, 31.9, 30.1, 30.0, 29.3, 22.7, 20.4, 17.0, 15.2, 14.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

Mechanistic Studies. *1-((1-(Allyloxy)-3-azidopropan-2-yl)oxy)-2,2,6,6-tetramethtlpiperidine (**48**).* Following the general azidooxygenation procedure using allyl ether **1a** (104 mg, 0.769 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a semi-solid (105 mg, 0.353 mmol, 46%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, J = 22.7, 10.7, 5.6 Hz, 1H), 5.27 (dd, J = 17.2, 1.6 Hz, 1H), 5.17 (d, J = 10.4 Hz, 1H), 4.07 (dt, J = 8.8, 4.4 Hz, 1H), 4.00−3.92 (m, 2H), 3.71 (dd, J = 9.6, 3.9 Hz, 1H), 3.59−3.46 (m, 3H), 1.63−1.45 (m, 6H), 1.19 (s, 3H), 1.15 (s, 6H), 1.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 116.9, 80.1, 72.2, 68.3, 60.3, 59.8, 51.7, 40.3, 34.2, 33.6, 29.7, 20.3, 17.1; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

*1-(2-Azido-1-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (**49**).* Following the general azidooxygenation procedure using (*E*)-prop-1-en-1-ylbenzene **1b** (91 mg, 0.771 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound as a yellow oil (200 mg, 0.632 mmol, 82%). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.24 (m, 10H), 4.74 (d, J = 6.1 Hz, 1H), 4.61 (d, J = 3.2 Hz, 1H), 4.44 (qd, J = 6.8, 3.3 Hz, 1H), 4.16−4.10 (m, 1H), 1.63−1.28 (m, 18H), 1.25 (d, J = 3.6 Hz, 3H), 1.23 (s, 3H), 1.07 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 14.5 Hz, 6H), 0.95 (d, J = 6.9 Hz, 3H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 137.9, 128.9, 128.6, 127.5, 127.4, 90.2, 87.8, 59.9, 59.2, 58.6, 40.4, 34.5, 34.0, 20.1, 17.0, 13.9; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[9a,e,16b]

*1-((1R,2R)-2-Azido-1,2-diphenylethoxy)-2,2,6,6-tetramethylpiperidine (**50**).* Following the general azidooxygenation procedure using *trans*-stilbene **1c** (114 mg, 0.633 mmol) and purification by silica gel column chromatography, eluting with hexanes afforded the title compound (*dr* = 1.2:1) as a semi-solid (196 mg, 0.519 mmol, 82%). Rf (4% EtOAc/hexane) 0.5. The azidooxygenation reaction of *cis*-stilbene **1d** (101 mg, 0.561 mmol) gave **50** as a semi-solid (157 mg, 0.415 mmol, 74%) with *dr* = 1.3:1. Rf (4% EtOAc/hexane) 0.5; ***syn-isomer;*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.15 (m, 6H), 7.15−7.09 (m, 6H), 6.99 (dd, J = 6.3, 2.8 Hz, 4H), 6.94 (d, J = 6.0 Hz, 4H), 5.61 (d, J = 3.4 Hz, 1H), 5.10 (d, J = 8.0 Hz, 1H), 5.00 (d, J = 8.0 Hz, 1H), 4.88 (d, J = 3.4 Hz, 1H), 1.71−1.22 (m, 24H), 1.05 (t, J = 16.6 Hz, 6H), 0.61 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.8, 136.7, 136.4, 129.2, 128.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.0, 126.9, 126.8, 126.6, 99.5, 91.2, 88.7, 68.9, 67.6, 59.8, 40.6, 40.3, 34.8, 33.8, 19.9, 16.8; ***anti-isomer;*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.17 (m, 6H), 7.16−7.10 (m, 6H), 7.00 (dd, J = 6.4, 2.7 Hz, 4H), 6.94 (d, J = 6.7 Hz, 4H), 5.62 (d, J = 3.4 Hz, 1H), 5.11 (d, J = 8.0 Hz, 1H), 5.00 (d, J = 8.0 Hz, 1H), 4.88 (d, J = 3.5 Hz, 1H), 1.77−1.16 (m, 27H), 1.06 (s, 3H), 0.60 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.1, 137.0, 136.7, 129.5, 129.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.3, 127.2, 127.1, 126.9, 91.4, 89.0, 69.2, 67.9, 60.1, 40.8, 40.6, 35.1, 34.1, 20.2, 17.0; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b,9a,b]

*1,2-Diazido-1,2-diphenylethane (**51**).* A preformed solution of *trans*-stilbene **1c** (114 mg, 0.633 mmol, 1 equiv) in DCM (2 mL) was treated with $TMSN_3$ (366 μL, 320 mg, 2.785 mmol, 4.4 equiv) followed by $PhI(OAc)_2$ (448 mg, 1.392 mmol, 2.2 equiv) at room temperature (25 °C). The mixture was stirred under a nitrogen atmosphere and irradiated with visible light (7 W blue LED) at 0−15 °C. For safety reasons, the reaction was carried out behind an anti-blast shield. The reaction was stirred until the completion of the starting material, typically for 4 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), quenched with saturated aqueous sodium thiosulfate (2 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography using hexanes as the eluent to afford the title compound **51** as a semi-solid (134 mg, 0.510 mmol, 88%). The diazidation reaction of *cis*-stilbene **1d** (101 mg, 0.561 mmol) gave **51** as a yellow oil (134 mg, 0.510 mmol, 66%, *dr* 1.3:1). Rf (4% EtOAc/hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, J = 4.7, 1.7 Hz, 4H),7.21−7.12 (m,10H) 7.03−6.95 (m, 6H), 4.69 (s, 1H), 4.54 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 129.9, 129.0, 128.9, 128.7, 128.6, 128.5, 127.9, 127.6, 70.8, 69.6; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16a]

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*4-(Azidomethyl)-2,6-di-tert-butylphenol (**52**).* A preformed solution of $PhI(OAc)_2$ (197 mg, 0.611 mmol, 1.1 equiv), $TMSN_3$ (159 mg, 182 μL, 1.388 mmol, 2.5 equiv), 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (104 mg, 0.666 mmol, 1.2 equiv), and BHT (244 mg, 1.110 mmol, 2.0 equiv) in DCM (5 mL) was treated with *trans*-stilbene (**1c**) (100 mg, 0.555 mmol, 1.0 equiv) at room temperature. The mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W blue LED). The distance between the light source and the reaction flask was approximately 3−4 cm, resulting in the temperature increasing up to 35 °C. For safety reasons, the reaction was carried out behind an anti-blast shield. The reaction was stirred until the completion of the starting material, typically for 15 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), quenched with saturated $NaHCO_3$ (5 mL) and saturated aqueous sodium thiosulfate (2 mL), and extracted with DCM (3 × 30 mL). The combined organic layers were washed with a brine solution, dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and purified by silica gel column chromatography using hexanes as the eluent to afford the compound **52** as a pale-yellow oil (75 mg, 0.288 mmol, 52%). Rf (100% Hexane) 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 5.27 (s, 1H), 4.25 (s, 2H), 1.45 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 136.2, 126.1, 125.2, 55.4, 30.2; the overall spectroscopic data are in complete agreement with assigned structures and consistent with the literature.[16b]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03991.

General synthetic information, detailed experimental procedure, and characterization data of the products and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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