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Taming Chlorine Azide: Access to 1,2-Azidochlorides from Alkenes

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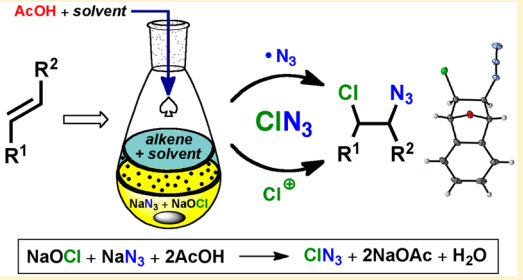
Supporting Information

ABSTRACT: The in situ preparation and trapping of chlorine azide provided a versatile one-pot method for the azidochlorination of alkenes. Gaseous ClN_3 generated from sodium azide, hypochlorite, and acetic acid can be explosive if isolation is attempted. Instead, we generated the reagent in biphasic media in the presence of olefinic compounds dissolved in the organic layer or evenly emulsified throughout the solution in the absence of organic solvent. Under these conditions, ClN_3 is created slowly and trapped immediately at the aqueous−organic interface. The resulting safe and reliable procedure provided 1,2-azidochloride derivatives of a variety of substrates, with evidence for both polar and radical mechanisms. Minor impurities characterized in the product mixtures indicated the presence of alternative reaction pathways deriving primarily from radical intermediates.



INTRODUCTION

Since their initial discovery [in 1900 (IN_3),[1] 1908 (ClN_3),[2] 1925 (BrN_3),[3] and 1942 (FN_3)[4,5]], halogen azides have been regarded as challenging compounds to work with due to their extreme chemical reactivity, volatility, and potential toxicity. However, the extraordinarily useful nature of halogen and azide substituents in organic chemistry has engendered some exploration of XN_3 reactivity through the years. Figure 1 summarizes most of the known examples of the reactions of halogen azides or their equivalents and analogues with alkenes, with particular attention to the methods by which these reactive compounds were generated.

Iodine azide was first synthesized from AgN_3 and I_2,[1] and methods associated with its preparation and reactivity[6] are the most abundant in the literature. Hassner and co-workers[7−18] made significant contributions to the understanding of the mechanism of halogen azide addition to alkenes, and his original procedures for the formation of IN_3 (from ICl + NaN_3[19−30] or I_2 + NaN_3[31−34]) became popular among those disposed to use the reagent for synthetic purposes. Several alternatives soon followed, including those with thallium (TlN_3) or stannous (Bu_3SnN_3) reagents as the source of azide ion,[35−37] but these and other methods[38] did not find widespread application. Barluenga et al. found a way to perform azido-iodination of terpenes using IPy_2BF_4−$TMSN_3$,[39,40] leading to several modified protocols employing more familiar oxidants (hypervalent iodine,[41] periodate,[42] oxone,[43] and cerium(VI)[44,45]). In many of these cases, anti-Markovnikov products were found, in contrast to earlier reports of the opposite regiochemistry. Kirsching developed several clever ways to ameliorate the dangers of IN_3, first by creating a nonexplosive polymer-bound form [of general formula $R_4NI(N_3)_2$],[46−48] and then by making stable iodine(III)-based precursors [Et_4NX−$PhI(OAc)_2$−NaN_3, X = I, Br] capable of promoting azidohalogenation of alkenes.[49]

Consistent with the higher oxidation potential of bromine, the published chemistry of *bromine azide* is less extensive than that of iodine azide. BrN_3 was first synthesized from Br_2 gas and solid NaN_3,[3] which was modified by Hassner [Br_2−HCl−NaN_3][10,13,18] into a somewhat hazardous procedure that nevertheless achieved some subsequent use.[50−52] Other approaches have involved the in situ generation of toxic and explosive hydrazoic acid [NXS−HN_3, X = I, Br];[53,54] the use of Br_2 solution in the presence of sodium azide under neutral or basic conditions[55,56] avoids that particular hazard, albeit with diminished yields and the formation of other side products. The accessibility and versatility of the technique reported by Krief in 1974 [NBS−NaN_3][57,58] was noted by several groups,[59−63] and other recently published protocols still rely on NBS as the most common bromine source [NBS−$TMSN_3$].[64] A few variations of this reaction conducted in the presence of catalytic amounts of various metal triflates augmented the regio- and stereoselectivity of BrN_3 addition to organic substrates,[65,66] including the asymmetric azidobromination of α,β-unsaturated carbonyl compounds.[67] Lastly, several sources of Br^+ (such as $TsNBr_2$[68] and $PhNMe_3Br_3$[69]) have been used with trimethylsilylazide ($TMSN_3$) in fast and efficient reactions yielding vicinal bromoazides under catalyst-free conditions.

While all halogen azides are highly explosive, their stability is believed to ascend in the following order: FN_3 < IN_3 < BrN_3 < ClN_3.[70] A solution of *chlorine azide* in organic solvents can be stored for several days at room temperature,[2,70] although we do not recommend this. From its discovery in 1908 through 1965,

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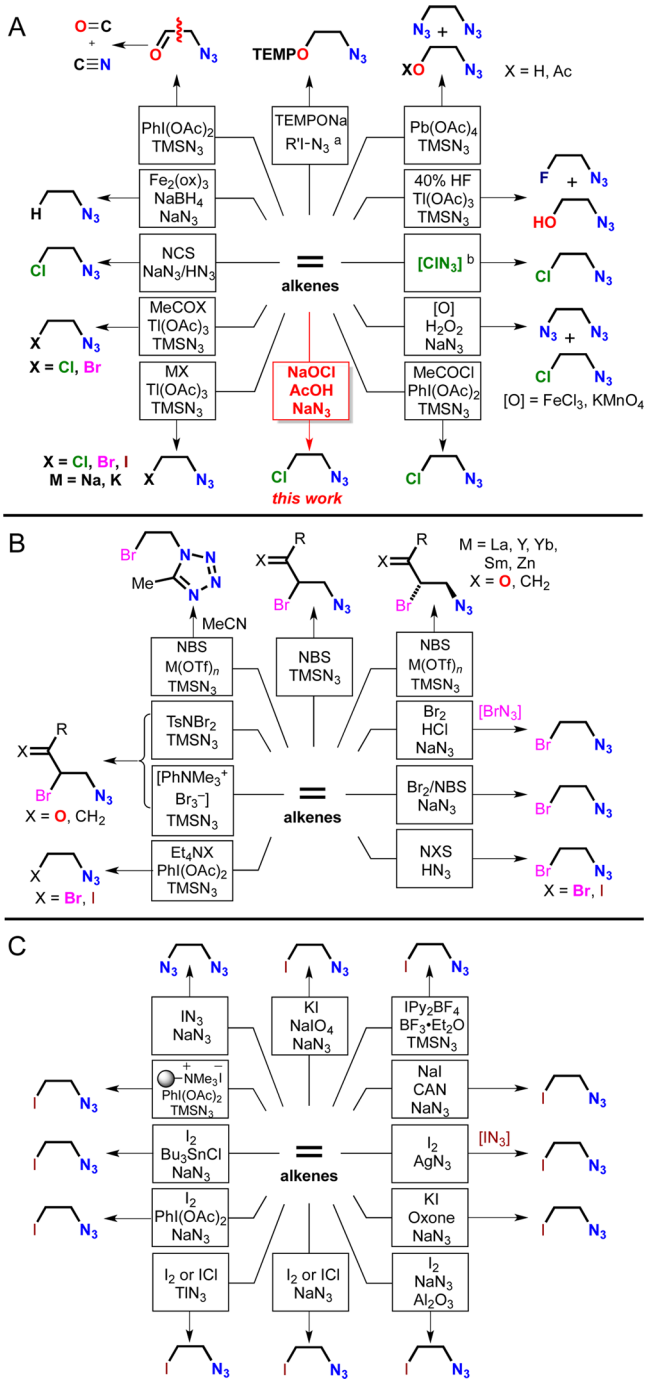


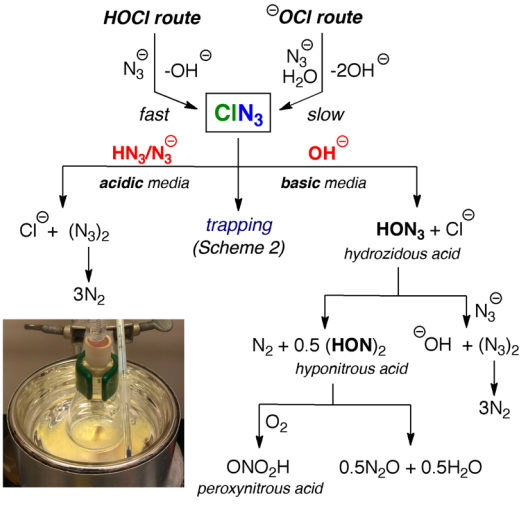
Figure 1. Published methods for the formation of vicinal azidohalogenides from alkenes. (A) 1,2-Azidochlorides (formal addition of ClN_3); (B) 1,2-azidobromides (formal addition of BrN_3); (C) 1,2-azidoiodides (formal addition of IN_3). Notes: (a) R′I−N_3 = 1-azido-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (azidoiodine(III)). (b) ClN_3 obtained from [AgN_3 + Cl_2], [HN_3 + HClO], or [NaN_3 + Cl_2].

only several examples of the formation of ClN_3 [from HClO−HN_3,[2] Cl_2−AgN_3,[71,72] and Cl_2−NaN_3[73]] were described; none were generally adopted by synthetic chemists. But some interesting reports then began to appear, such as the method by Minisci and co-workers [$FeCl_3$−H_2O_2−NaN_3][74] in which either two azido groups (related to $Pb(OAc)_4$−$TMSN_3$)[75,76] or an azido group and a chlorine atom were added to an unsaturated substrate via a radical mechanism. Zbiral reported several protocols based on thallium(III) acetate: [MX−$Tl(OAc)_3$−$TMSN_3$, X = Cl, Br, I][77] and [MeCOX−$Tl(OAc)_3$−$TMSN_3$, X = Cl, Br].[78] In this case, the substitution of a chlorine (or other halogen) source with 40% HF yielded 1,2-azido-fluorides—the only transformation of this kind to our knowledge. Furthermore, Zbiral also reported a competitive azidochlorinating reagent $PhI(Cl)(N_3)$ obtained from phenyliodosodiacetate [MeCOCl−$PhI(OAc)_2$−$TMSN_3$].[79] The reaction outcome based on this reagent system differs considerably from ClN_3-based protocols, including the potential for alkyne cleavage if there action is performed in the absence of a chlorine source.[80] It is assumed that the reaction occurs via azidonium ion formation.

Many of the protocols described above lack selectivity, are low-yielding, or require toxic or exotic reagents. In a search for a facile and cost-effective technique, we anticipated that *N*-chlorosuccinamide (NCS)-based reactions could be a dependable option. We were surprised to find only several examples reported thus far,[81−83] including a number of recent reports of azidooxygenation or hydroazidation, rather than chloroazidation, of alkenes.[84,85] We therefore turned to the original Raschig conditions, acidification of aqueous sodium azide and sodium hypochlorite with acetic acid,[2] and describe here a convenient and safe one-pot method and a survey of its application to an initial panel of various types of alkenes.

Mechanisms of Chlorine Azide Formation and Degradation. The formation of chlorine azide likely occurs by azide attack on the hypochlorite bond. It is therefore fastest at pH 4−6, where significant concentrations of N_3^- and HOCl exist (Scheme 1).[86] ClN_3 is soluble in both aqueous and

Scheme 1. Formation and Decomposition of Chlorine Azide in Aqueous Solution



organic media,[70] giving the solution a characteristic yellow color. It is quite stable in aqueous solution at room temperature but can be eliminated from the system either via explosive decomposition (initiated by heat, for example),[87] by reaction with excess azide or hydroxide in solution, or by productive addition to unsaturated compounds (Scheme 2). Under acidic conditions, the formation of $(N_3)_2$ and its immediate rearrangement to $3N_2$ can be explosively rapid, and is likely the source of some of the danger associated with this chemistry. Basic hydrolysis of ClN_3 is relatively slow but can be significant; hydrozidous acid is believed to be the first intermediate, leading either to the formation of nitrogen gas via $(N_3)_2$ or hyponitrous

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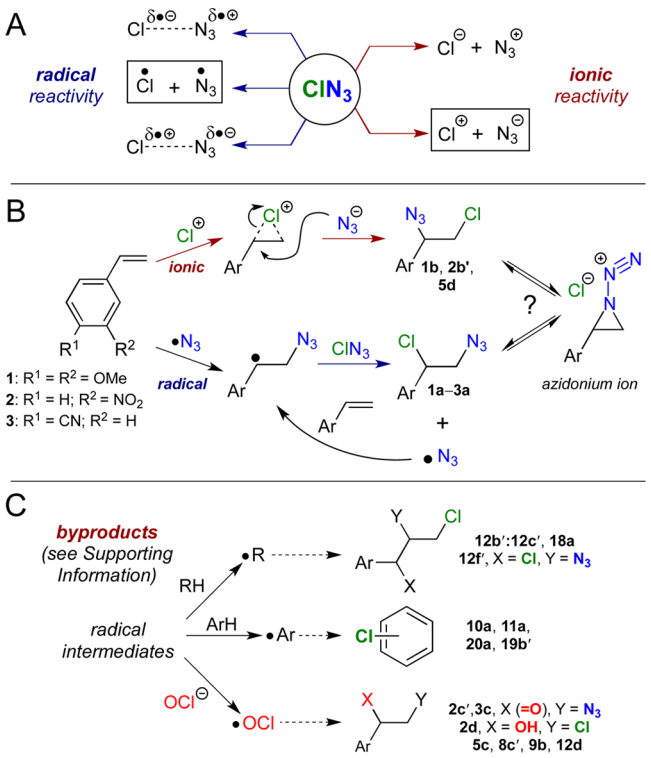
Scheme 2. General Mechanisms of Reactivity of ClN_3 with Alkenes[a]



[a](A) Fragmentation pathways for ClN_3. (B) Formation of 1,2-azidochlorides. (C) Formation of byproducts.

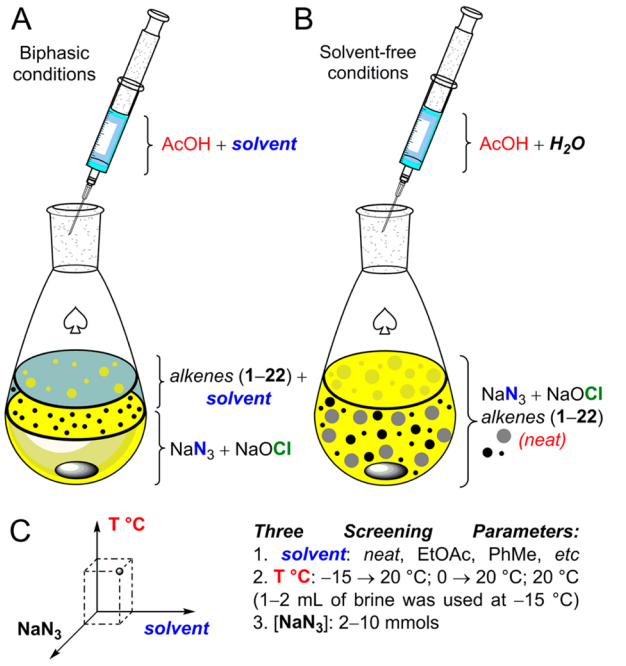


Figure 2. Reaction setup for the formation of 1,2-azidochlorides. (A) Biphasic conditions in which the olefinic substrate is dissolved in an organic phase. (B) Solvent-free conditions in which the liquid olefinic substrate is added without organic solvent. Both conditions involve vigorous magnetic stirring. (C) Reaction parameters varied in preliminary optimization studies.

acid (HON═NOH). The latter species either undergoes rearrangement to nitrous oxide (N_2O) or reaction with dissolved oxygen, producing peroxynitrous acid (ONO_2H)[86] (Scheme 1).

RESULTS AND DISCUSSION

NaN_3 and NaOCl (4.0–4.99% hypochlorite) can be combined in dilute aqueous solution without apparent reaction for periods of at least several hours. Chlorine azide formation can be initiated by the addition of a weak acid such as acetic acid. The balanced stoichiometry of this overall transformation is shown in eq 1. The ClN_3 thus produced is a gas and can be isolated by transfer out of the reaction flask with a gentle stream of nitrogen, bubbled into an organic solvent placed in a receiving flask. While we performed this procedure a number of times, it proved to be occasionally explosive, and we strongly discourage its practice. Instead, we developed a safe procedure to generate ClN_3 in small quantities in situ and in the presence of an alkene with which it can immediately react, as shown in Figure 2.

$$NaOCl + NaN_3 + 2AcOH \rightarrow ClN_3 + 2NaOAc + H_2O \quad (1)$$

Two variants of the procedure were routinely used. In a biphasic protocol (Figure 2A), an aqueous solution of sodium azide and sodium hypochlorite was kept either at room temperature (20 °C) or was cooled to −15 °C. (A small amount of brine was added to ensure that the solution at −15 °C would not freeze, but the mixture often remained in the liquid state without added salt.) The alkene of interest (0.5–1.0 mmol) was dissolved in an organic solvent of lower density than water (toluene, ether, ethyl acetate), and this solution was introduced into the reaction flask. The resulting mixture was then vigorously stirred, chlorine azide generation was initiated by the dropwise addition of acetic acid to the open or vented flask (typically 1–2 equiv with respect to azide), and ClN_3 was rapidly consumed in situ by the alkene. The amount and rate of evolution of ClN_3 can be controlled by the amount of acetic acid added. In most cases, NaN_3 was used in excess (2–10 mmol), and the amounts of acetic acid (4–15 mmol) and sodium hypochlorite (1–2 mmol) were varied. Approximate concentrations were as follows: NaN_3, 0.6–2 mM in the aqueous phase; NaOCl, 0.4–0.6 mM in the aqueous phase; AcOH, 0.5–2 mM in the combined phases after addition is complete; alkene, 0.1–0.5 mM in the organic phase. In an alternative "solvent-free" biphasic procedure (Figure 2B), no organic solvent was used. Here, the liquid alkene was distributed as an emulsion in the rapidly stirred mixture, performing the same trapping function during the reaction. Water-misicible cosolvents (acetonitrile, THF) can be used, but provided sluggish reactions and poor yields in the few cases tested. Each organic substrate required the determination of a partially optimized set of conditions, varying three key parameters (Figure 2C and Supporting Information): the nature of the solvent, the reaction temperature, and the amount of sodium azide. ***Caution!*** *Even though these conditions diminish the hazards of chlorine azide substantially, it is still necessary to use common sense and care. Furthermore, acidic conditions with azide ion are always to be used with caution and avoided in workup, since HN_3 is highly volatile, toxic, and explosive. Therefore, the reaction should be performed only in a well-ventilated fume hood behind a protective shield or hood sash, and workup should avoid the use of acid, especially when a large excess of NaN_3 is left after the reaction is complete.*

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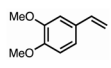
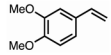
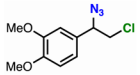
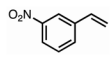
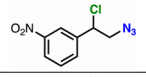
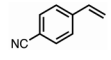
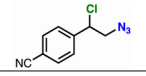
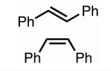
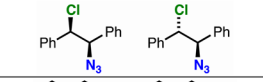
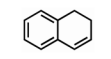
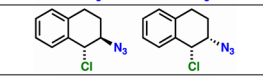
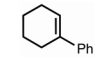
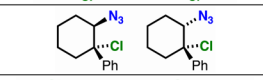
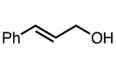
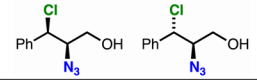
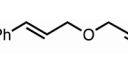
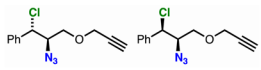
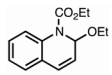
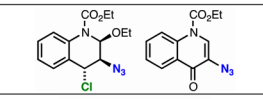
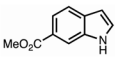
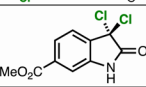
Table 1. Vicinal Azidochlorination of Aromatic Alkenes

Entry	Conditions[a]	Alkene		Product		Ratio Yield (%)[b]
1	A	**1**		**1a**+**1b**		1.3:1 [c]
2	B,C,F	**1**		**1b**		85%
3	A	**2**		**2a**		97% (+ **2b'**, **2c'**, **2d**) [d]
4	A	**3**		**3a**		83% (+ **3c**) [d]
5	E	**4** or **4'**		**4a**+**4b**		≈1:1.5 86%
6	A,B,F	**5**		**5a**, **5b**		67%, 26% (+ **5c**) [d]
7	B,D,F	**6**		**6a**, **6b**		61%, 8%
8	A,B,E	**7**		**7a**+**7b**		≈1.1:2 71%
9	A	**8**		**8a**+**8b**		≈1:1.8 82% (+ **8c**) [d]
10	A,B,E	**9**		**9a**, **9b**		67%, 32%
11	E	**10**		**10a**		89%
12	A	**11**		**11a**		91%

[a]Experimental conditions: A = PhMe, 20 °C; B = PhMe, −15 °C; C = solvent-free, 20 °C; D = solvent-free, −15 °C; E = EtOAc, 20 °C; F = EtOAc, −15 °C. When multiple procedures are listed, the underlined procedure is the one for which the yield is reported, but all gave comparable results. [b]Yields refer to isolated products (or their isolated diastereomeric mixtures), except where noted otherwise. [c]Analysis of crude reaction mixture by NMR. [d]See Supporting Information.

The pioneering studies of Alfred Hassner and co-workers established that heterolytic cleavage dominates the chemistry of IN_3, such that it reacts predominantly as a source of I^+, but BrN_3 and ClN_3 can be directed along ionic (heterolytic) or radical (homolytic) pathways by changing the reaction conditions.[12,17] Polar solvents favor ionic addition for styrenyl substrates, while nonpolar solvents and the absence of molecular oxygen were reported to promote radical formation.[12,17] A continuum of reactivity is likely, with polar components to a radical pathway, and, in principle, the participation of either chloronium or azidonium cations in ionic reactions (Scheme 2A). For the purposes of this introductory report, however, we restrict our mechanistic discussion to the possibilities of Cl^+/N_3^- or $\bullet Cl/\bullet N_3$ described by Hassner. Thus, ionic reactions are expected to produce regioisomers derived from azide capture of the most stable cationic intermediate(s); for styrenes, this places azide at the benzylic position (Scheme 2B). Radical reactions are expected to proceed by addition of $\bullet N_3$ to give the most stable carbon radical, which captures ClN_3 to continue the chain, giving benzylic chlorides from styrenes (Scheme 2B, termination steps not shown). Some byproducts derived from radical pathways were also expected and observed (Scheme 2C).

Substrate Scope and Limitations. Table 1 summarizes a preliminary survey of the vicinal azidochlorination of aromatic alkenes. Most of the substrates (**1**−**6**, entries 1−7) underwent anti-Markovnikov type addition, in agreement with Hassner's observation that a radical pathway is favored for these substrates. 3,4-Dimethoxystyrene (**1**) (entry 1) provided an exception, presumably because the electron-rich nature of the aromatic ring favored the formation of a cationic benzylic intermediate. Only at room temperature in toluene was the radical pathway competitive. The stereochemistry of 1,2-addition to styrene derivatives was not well controlled, consistent with the expected stability of the putative benzylic radical intermediate. Thus, both *cis*- and *trans*-stilbene (**4** and **4′**) gave the same nearly equimolar mixture of erythro and threo isomers in excellent yield, although this transformation required a larger excess of sodium azide and higher temperature to reach completion than for most substrates. (A significant amount of unreacted starting material **4** was isolated at lower temperatures.) Similarly, 1,2-dihydronaphthalene (**5**) and 1-phenyl-1-cyclohexene (**6**) also gave stereochemical mixtures, with a modest preference for *anti*-addition (entries 6 and 7). Hydroxyl (entry 8) and terminal alkyne (entry 9) functional groups were well tolerated. Substrate **9** showed the *α*-

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ethoxycarbamate moiety to remain intact, with the *anti,syn*-isomer **9a** isolated as the major product. The azido-carbonyl derivative **9b** was also obtained by a mechanism that we have not investigated. In contrast, electron-rich nitrogen heterocycles underwent chlorination rather than chloroazidation under all conditions tested. Methylindole-6-carboxylate (**10**) was converted to the corresponding 3,3-dichlorolactam **10a** in excellent yield, implicating hypochlorite as an oxidant as well as a source of chloride radical. Similarly, 7-azaindole (**11**) gave only 3-chloro-1*H*-pyrollo[2,3-*b*]pyridine (**11a**). Indoles are well-known to undergo chlorination with hypochlorite,[88−90] although oxidation at the 2-position, as observed for **10**, is rare.[91−93] In some cases (substrates **2**, **5**, and **8**), other oxidation products were isolated and characterized, reflecting the pathways shown in Scheme 2C. These results are provided in Supporting Information, since only small amounts of these byproducts were formed.

The X-ray structures of a representative azidochloride (**13a**), an unusual byproduct azide (**9b**) and a product of radical chlorination (**10a**) are shown in Figure 3. In general, however,

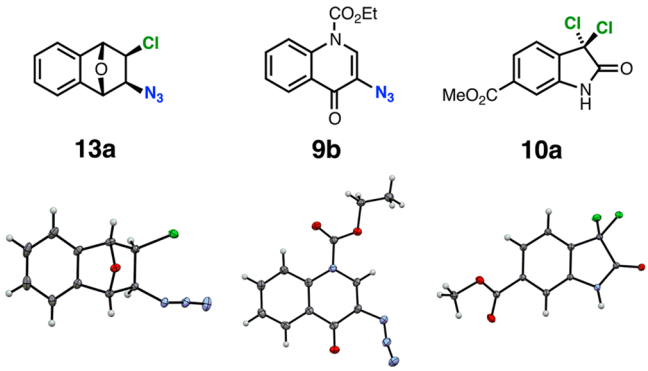

Figure 3. ORTEP representations of X-ray crystallographic analyses of an azidochloride and two byproducts, each from a different alkene.

the structures and stereochemical assignments of the products were established by conversion of the isolated azides to the corresponding 1,2,3-triazoles by thermal reaction with dimethylacetylenedicarboxylate (DMAD). This allowed for bond connectivities to be established by two-dimensional NMR techniques, and for five cases, by crystallization and X-ray analysis. Complete details of all structural assignments are given in the Experimental Section and Supporting Information.

Table 2 shows the results of ClN_3 reactions with unsaturated aliphatic olefins. A radical pathway was indicated by the formation of the secondary chloride from 4-allylanisole (**12**, entry 1). In this case, radical-derived byproducts were observed with substantial variation in identity and relative amounts as the solvent, temperature, reagent stoichiometry, and NaOCl concentration were changed (see Supporting Information). Switching to the solvent-free protocol at room temperature addressed this complication, giving **12a** in a consistent and efficient manner. This procedure (at 20 or −15 °C) proved to be superior for substrates which remained liquid under the reaction conditions (Table 1, entries 2, 7; Table 2, entries 1, 4). In these cases, the interface between the aqueous medium where ClN_3 is generated and the substrate is much different (droplet size, reactant density and interfacial organization, etc.) than when the substrate is dissolved in a hydrophobic solvent. It is therefore not surprising that the reaction proceeds differently under these two conditions, although we are not yet able to explain exactly why the formation of side products is suppressed.

As before, a two-step mechanism with attack on a radical (or ionic) intermediate seemed to determine the stereochemistry of 1,2-addition. *anti*-Chloroazides predominated for cycloheptene and cholesterol (**15** and **17**, entries 4 and 7); no stereoselectivity was observed for *trans*-1,4-butenediol (**16**, entry 5); and *syn*-endo products were modestly favored from bridged bicyclic substrates **13** and **14** (entries 2 and 3). Studies of the reaction of **13** with variation of solvent and the addition of a radical trapping agent, described in Supporting Information, support the assignment of a primarily radical pathway using this substrate. The isopropenyl group of (*S*)-(+)-carvone (**18**) participated in dual reactivity depending on the reaction conditions (entries 8, 9). At low temperatures in EtOAc as the organic solvent, only allylic chlorination (**18a**) was observed, whereas reaction in the less polar toluene at room temperature gave rise to the azidochloride **18b** in modest yield (23%), which could be increased to 42% with the use of a higher concentration of NaN_3 in the aqueous phase. In both cases, a significant amount of starting material **18** remained in the mixture; all other attempts to drive the reaction to completion resulted in the formation of more **18a** as a byproduct.

The existence of radical chlorination as an alternative reaction was further demonstrated by the fate of three other substrates. Anthracene (**19**, entry 10) gave both 9-azido (**19a**) and 9-azido-10-chloro (**19b**) derivatives; one possible pathway is shown in Scheme 3. The expected addition of azide radical to C-9 followed by trapping with ClN_3 provides intermediate **19c**, with the observed products deriving from either base-mediated chloride elimination or oxidative aromatization. (Interestingly, phenanthrene was completely resistant to the biphasic reaction conditions.) *N*-Allylaniline (**20**, entry 11) underwent radical chlorination of the aromatic ring at −15 °C, leaving the pendant olefin untouched. Complex mixtures of products were formed at warmer temperatures; comparable outcomes were observed for colchicine and other aromatic compounds with electron-rich aromatic rings (not shown). Lastly, 2′-aminoethylcyclohexene (**21**, entry 12) was converted to a single product tentatively assigned as structure **21a**, which after chromatographic purification possessed the pungent bleach-like odor characteristic of *N*-chloramines.

While clean azidochlorination of olefins requires that the substrate contain neither electron-rich aromatic rings nor unfunctionalized amines, the alkene also must not be too electron-deficient. This is indicated by the lack of reactivity at the enone moiety of substrate **18** and of the resistance of *trans*-4-phenyl-3-buten-2-one (benzylideneacetone) to reaction with ClN_3 under standard biphasic conditions (not shown). Remarkably, the diacetate of allylic diol **16** was also completely unreactive (Table 2, entry 6). The addition of Lewis acids [$Y(OTf)_3$, $Sc(OTf)_3$], iodobenzene (PhI), iodosobenzene (PhIO), and diacetyliodobenzene [$PhI(OAc)_2$] failed to promote reaction in this case, returning starting material **16-(OAc)$_2$** in each case after prolonged exposure. Similarly, the introduction of a nitrogen into each ring of stilbene (*trans*-1,2-di(4-pyridyl)ethylene) gave an unreactive substrate.

Early in our studies, we used solutions of ClN_3 isolated in organic solvent by the procedure mentioned at the beginning of the Results section. In these cases, several additional substrates were found to react cleanly, although the stereo- and regiochemical outcomes were not firmly established (Supporting Information Table S7). These substrates included several

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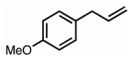
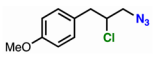
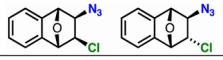
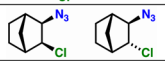
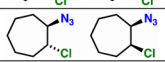
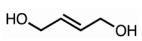
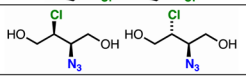
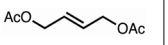
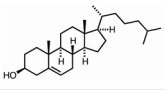
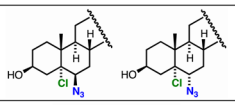
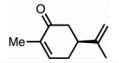
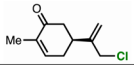
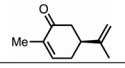
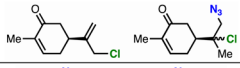
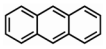
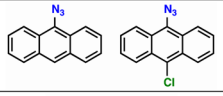
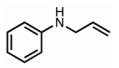
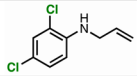
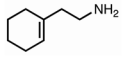
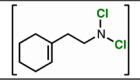
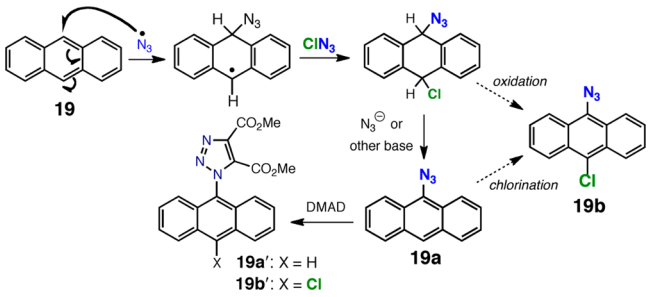
Table 2. Vicinal Azidochlorination of Aliphatic Alkenes

Entry	Conditions[a]	Alkene		Product		Ratio Yield (%)[b]
1	A,C	**12**		**12a**		94% (+ **12b'**, **12c'**, **12d**, **12e'**, **12f'**) [c]
2	A,B,E,F	**13**		**13a**, **13b**		64%, 27%
3	A[d]	**14**		**14a**+**14b**		≈2:1 95%
4	C	**15**		**15a**, **15b**		98%, trace
5	A	**16**		**16a**+**16b**		≈1:1 94%
6	A	**16-(OAc)$_2$**			no reaction	
7	A	**17**		**17a**, **17b**		47%, 8%
8	F	**18**		**18a**		65% [e]
9	A[f]	**18**		**18a**, **18b**		16%, 42% (+ 42% **18**)
10	A	**19**		**19a**, **19b**		66%, 18%
11	B	**20**		**20a**		67%
12	A	**21**		**21a**		73%

[a]Experimental conditions: A = PhMe, 20 °C; B = PhMe, −15 °C; C = solvent-free, 20 °C; D = solvent-free, −15 °C; E = EtOAc, 20 °C; F = EtOAc, −15 °C. When multiple procedures are listed, the underlined procedure is the one for which the yield is reported, but all gave comparable results. [b]Yields refer to isolated products (or their isolated diastereomeric mixtures). [c]See Supporting Information. [d]Diethyl ether (Et_2O) was used instead of toluene. [e]A trace amount of the azidochloride, **18b**, was observed in the product mixture. [f]A larger excess of NaN_3 than usual (18 vs 10 equiv) was used.

Scheme 3. Vicinal Azidochlorination of Anthracene Showing a Potential Pathway for the Formation of 19a and 19b



allyl ethers, an allyl ester, and a glycal vinyl ether. Ester and epoxide groups were found to be undisturbed, while a *tert*-butyldiphenylsilyl ether did not survive.

Several recent reports have appeared of azide modification of graphene,[94] carbon surfaces,[95] and fullerene,[96] most using gas-phase reactions of iodine azide. Akhmetov and co-workers[96] employed several methodologies developed previously[65,67] to prepare new 1-halo-2-azidofullerenes which were characterized by NMR, IR, and MALDI-TOF. None of these reported examples were based on vicinal azidochlorination. We were encouraged to find that solutions of C_{60} in chlorobenzene or toluene[97] reacted with ClN_3 under our standard conditions to give an azide-containing fullerene derivative in good yield (Supporting Information); further characterization of this transformation and those involving related substrates are in progress.

■ CONCLUSIONS

We describe here a simple, reliable, inexpensive, and safe method for the generation of ClN_3 and its use for the preparation of 1,2-azidochlorides from olefins. Its success relies on the slow generation and rapid capture of ClN_3, both of which are enabled by the use of biphasic reaction conditions, preventing the buildup of the explosive oxidant. Aryl, alcohol, alkyne, ester, and ether functional groups are well tolerated; others will be tested in due course. The method is not presently applicable to molecules containing electron-rich aromatic rings or free amines, which undergo radical chlorination faster than chloroazidation. 1,2-Azidochlorides are expected to be a very useful class of organic compounds suitable for further derivatization by a variety of processes, including 1,3-dipolar cycloaddition, S_N2 or anchimerically assisted substitution, reduction, aziridine and azirine formation, elimination, etc. While we focused on small organic molecules here, including a natural product and a fullerene, we believe these methods (or

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variations thereof) will be equally useful for the functionalization of polymeric materials and surfaces.

EXPERIMENTAL SECTION

Representative and detailed procedures for azidochlorination of olefins are described below; the largest scale employed for these procedures was 2 mmol of alkene.

(A). General Biphasic Procedure. Sodium azide (150 mg, 2.31 mmol) was added to a mixture of aqueous sodium hypochlorite (4.00−4.99% obtained from Sigma-Aldrich, 3.5 mL, 2.06 mmol) and 2 mL of an organic solvent (PhMe, EtOAc, or Et_2O, unless otherwise stated). The mixture was stirred briefly to dissolve the NaN_3. An organic substrate (**13**) (88 mg, 0.61 mmol) was added to the resulting heterogeneous mixture, allowed to dissolve in the organic media, and the resulting biphasic mixture was either kept at room temperature (20 °C) or cooled to −15 °C. With continuous vigorous magnetic stirring, a solution of glacial acetic acid (0.25 mL, 4.37 mmol) in 2 mL of the organic solvent was added in dropwise fashion with a syringe over a period of 15 min to 1 h. After the addition was complete, the mixture was stirred at 20 °C for an additional 30 min to 2 h (or, if initially carried out at −15 °C, the reaction was allowed to warm to room temperature over a period of 30 min to 2 h).

(B). General Solvent-Free Procedure. Sodium azide (350 mg, 5.38 mmol) was dissolved in aqueous sodium hypochlorite (4.00−4.99% obtained from Sigma-Aldrich, 4 mL, 2.36 mmol) immediately prior to use, and the resulting solution was cooled to −15 °C if desired. An organic substrate (**5**) (as a neat liquid, 0.1 mL, 0.63 mmol) was added to the resulting aqueous solution, which was either kept at room temperature (20 °C) or cooled to −15 °C. A solution of glacial acetic acid (0.26 mL, 4.54 mmol) in 2 mL of water was added dropwise with a syringe over the period of 15 min to 1 h to the vigorously stirred mixture. After the addition was complete, the resulting reaction mixture was stirred at 20 °C for an additional 30 min to 2 h (or allowed to warm to room temperature over a period of 30 min to 2 h if it had been initially cooled).

(C). Workup. For each of the above procedures, the completed reaction (monitored by TLC) was quenched by the slow addition of saturated aq. $NaHCO_3$ (5 mL) at 20 °C, during which the evolution of CO_2 ceased, followed by stirring for 5−10 min. The biphasic mixture was extracted with EtOAc (3 × 5 mL), the combined organic layers were dried over anhydrous $MgSO_4$, the resulting solution was concentrated by rotary evaporation, and the crude product was purified by flash chromatography or preparative thin-layer chromatography (silica gel, hexanes/EtOAc).

(D). Important Notes. (1) The solvent-free conditions should be used only if the alkene remains in the liquid state throughout the process (in other words, does not freeze if the reaction is cooled; true here for compounds **1**−**3**, **5**, **6**, **8**, **12**, **15**, **16**, **18**, **20**, **21**). (2) Brine can be added if the reaction is performed at −15 °C to prevent the aqueous medium (solution of NaOCl, NaN_3, and AcOH) from solidifying. (3) ***Caution!*** *Even though these conditions diminish the hazards of chlorine azide substantially, it is still necessary to use common sense and care. The addition of glacial acetic acid is an exothermic reaction accompanied by rapid gas evolution (ClN_3, and possibly N_2, Cl_2, HN_3). It is important to add the acetic acid solution slowly (dropwise), and to make sure the flask is open or vented to relieve pressure. Furthermore, acidic conditions with azide ion are always to be used with caution and avoided in workup, since HN_3 is highly volatile, toxic, and explosive. Therefore, the reaction should be performed only in a well-ventilated fume hood behind a protective shield or hood sash, and workup should avoid the use of acid, especially when a large excess of NaN_3 is left after the reaction is complete.* (4) The procedures described here were optimized using only the 4.00−4.99% solution of sodium hypochlorite available from Sigma-Aldrich. Higher concentrations of sodium hypochlorite were not exhaustively tested, but preliminary experiments showed a greater propensity for runaway reactions at higher active concentrations of NaOCl. (5) Remaining unreacted chlorine azide and any HN_3 ion were neutralized and quenched by the added saturated sodium bicarbonate solution,[86] and (like diazomethane) by letting the mixture stir open to air in the fume hood to allow ClN_3 to evaporate.

(E). Structure Elucidation. Since the chemical shifts of protons attached to C−N_3 and C−Cl centers are very similar, the determination of the 1,2-azidochloride regio- and stereochemistry requires some care. We employed the convenient and reliable thermal [3 + 2] cycloaddition of organic azides with an excess of dimethylacetylene dicarboxylate (DMAD)[99] to make the corresponding 1,2,3-triazoles of many of the compounds reported above (Tables S8 and S9), and characterized these products extensively by 1D and 2D NMR techniques and X-ray crystallographic analysis (Figures S2 and S3). Further details can be found in Supporting Information.

(F). Reactions and Characterization Data. *4-(2-Azido-1-chloroethyl)-1,2-dimethoxybenzene (**1a**).* Compound **1a** was obtained as a crude mixture together with **1b** (**1a**:**1b** ≈ 1.3:1 ratio based on the NMR spectroscopic analysis) from 0.1 mL of 3,4-dimethoxystyrene (**1**) (0.675 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; 0.5 h). **1a**: R_f = 0.23 (silica gel, hexanes/EtOAc 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.94−6.81 (m, 3H), 4.92 (dd, $J \approx$ 6.9, 6.9 Hz, 1H; in DMSO-d_6, apparent t or dd, J = 8.0, 5.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.74 (dd, J = 12.9, 7.5 Hz, 1H), 3.67 (dd, J = 12.9, 6.4 Hz, 1H).

*Dimethyl 1-(2-chloro-2-(3,4-dimethoxyphenyl)ethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**1a′**).* Compound **1a′** was isolated in 25% yield (64 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 163 mg (0.674 mmol) of **1a**:**1b** mixture (**1b′** was isolated in 13% yield, 33 mg) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **1a′**: R_f = 0.33 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} 2956, 1737, 1727, 1514, 1462, 1263, 1221, 1141, 1024, 729 = cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.84 (d, J = 2.0 Hz, 1H), 6.82−6.80 (m, 1H), 6.76 (d, J = 8.2 Hz, 1H), 5.28 (dd, J = 6.6, 8.1 Hz, 1H), 5.16 (dd, J = 13.9, 8.2 Hz, 1H), 5.04 (dd, J = 13.9, 6.6 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.4, 159.1, 150.1, 149.5, 139.9, 130.6, 128.9, 120.2, 111.2, 110.1, 60.6, 56.3, 56.17, 56.16, 53.6, 53.0; HRMS (ESI-TOF) calcd for $C_{16}H_{18}ClN_3O_6$ [M + Na^+] 406.0782, found 406.0806.

*4-(1-Azido-2-chloroethyl)-1,2-dimethoxybenzene (**1b**).* Compound **1b** was obtained in 85% yield (138 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 0.1 mL of 3,4-dimethoxystyrene (**1**) (0.675 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; neat; 20 °C; 2 h). Alternatively, **1b** can be obtained quantitatively (∼163 mg) after FCC (silica gel, hexanes/EtOAc = 10:1) from 0.1 mL of 3,4-dimethoxystyrene (**1**) (0.675 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (with or without 1.0 mL of brine) (procedure I; PhMe or EtOAc; −15 °C → 20 °C; 2 h). **1b**: R_f = 0.30 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3000−2800, **2102**, 1514, **1262**, 1138, 1023, 763, 715 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.86 (m, 2H), 6.80 (m, 1H), 4.66 (dd, J = 7.3, 6.3 Hz, 1H or dd, J = 8.1, 5.4 Hz, 1H in DMSO-d_6), 3.88 (s, 3H), 3.86 (s, 3H), 3.66 (d, J = 1.4 Hz, 1H), 3.64 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.7, 149.5, 129.0, 119.7, 111.3, 109.8, 67.0, 56.1, 56.0, 47.7; HRMS (ESI-TOF) calcd for $C_{10}H_{12}ClN_3O_2$ [M + Na^+] 264.0516, found 264.0495.

*Dimethyl 1-(2-chloro-1-(3,4-dimethoxyphenyl)ethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**1b′**).* Compound **1b′** was isolated in 90% yield (286 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 200 mg of **1b** (0.828 mmol) and 0.2 mL of DMAD (1.63 mmol) (procedure II; C_6H_6; 65 °C; 14 h). **1b′**: R_f = 0.10 (silica gel, hexanes/EtOAc 5:1) or 0.60 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 2956, 1737, 1728, 1515, 1450, 1263, 1214, 1142, 1024, 727 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.95−6.93 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.18 (dd, J = 10.2, 4.9 Hz, 1H), 4.63 (dd, J = 11.6, 10.3 Hz, 1H), 4.04 (dd, J = 11.7, 4.9 Hz, 1H), 3.91 (s, 3H) overlaps with 3.91 (s, 3H), 3.81 (s, 3H) overlaps with 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.6, 159.0, 150.1, 149.5, 140.3, 130.3, 127.6, 120.5, 111.3, 110.3, 66.1, 56.11, 56.06, 53.6, 52.9, 45.5; HRMS (ESI-TOF) calcd for $C_{16}H_{18}ClN_3O_6$ [M + H^+] 384.0962, found 384.0960; [M + Na^+] 406.0782, found 406.0779.

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*1-(2-Azido-1-chloroethyl)-3-nitrobenzene (**2a**).* Compound **2a** was obtained in 97% yield (206 mg) after FCC (silica gel, hexanes/EtOAc = 5:1) from 0.15 mL of 3-nitrostyrene (**2**) (1.08 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; from 0.5 to 1 h). **2a**: R_f = 0.35 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = **2104**, 1530, 1350, 1310, **1260**, 731, 687 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.29 (t, J = 2.0 Hz, 1H), 8.22 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 7.75 (ddd, J = 7.7, 1.3, 1.3 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 5.03 (t, J = 6.7 Hz, 1H or dd, J = 7.4, 5.7 Hz, 1H in DMSO-d_6), 3.82 (dd, J = 13.0, 6.8 Hz, 1H), 3.73 (dd, J = 13.0, 6.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.7, 140.4, 133.6, 130.2, 124.3, 122.7, 59.6, 57.8.

*Dimethyl 1-(2-chloro-2-(3-nitrophenyl)ethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**2a′**).* Compound **2a′** was isolated in 78% yield (127 mg) (together with 13% of **2b′**, 21 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 100 mg of **2a** (0.441 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **2a′**: R_f = 0.15 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2956, 1737, 1726, 1530, 1350, 1219, 1061, 732, 683 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.28 (t, J = 2.0 Hz, 1H), 8.20 (ddd, J = 8.2, 2.2, 1.0 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 5.49 (dd, J = 8.4, 6.2 Hz, 1H), 5.19 (dd, J = 14.1, 8.4 Hz, 1H), 5.08 (dd, J = 14.1, 6.2 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.3, 159.0, 148.7, 140.3, 138.9, 133.5, 130.4, 130.2, 124.6, 122.6, 58.8, 56.1, 53.8, 53.0; HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClN_4O_6$ [M + H^+] 369.0601, found 369.0605; [M + Na^+] 391.0421, found 391.0417.

*Dimethyl 1-(2-chloro-1-(3-nitrophenyl)ethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**2b′**).* Compound **2b′** was isolated in 13% yield (21 mg) (together with 78% of **2a′**, 127 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 100 mg of **2a** (0.441 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **2b′**: R_f = 0.24 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 2956, 1737, 1727, 1530, 1351, 1282, 1221, 727 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.34 (t, J = 2.0 Hz, 1H), 8.23 (ddd, J = 8.3, 2.2, 1.0 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 6.42 (dd, J = 9.4, 5.7 Hz, 1H), 4.63 (dd, J = 11.7, 9.5 Hz, 1H), 4.18 (dd, J = 11.6, 5.7 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.1, 158.5, 148.4, 140.4, 136.8, 133.5, 130.3, 129.7, 124.5, 122.9, 64.7, 53.5, 52.8, 44.7; HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClN_4O_6$ [M + H^+] 369.0601, found 369.0597; [M + Na^+] 391.0421, found 391.0415.

*Dimethyl 1-(2-(3-nitrophenyl)-2-oxoethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**2c′**).* Compound **2c′** was isolated in 56% yield (34 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 36 mg of **2c** (0.175 mmol, small amounts 0−24% usually formed at 0 °C in PhMe) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 21 h). **2c′**: R_f = 0.35 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 2956, 1737−1712, 1531, 1352, 1278, 1223, 1064, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.80 (t, J = 1.8 Hz, 1H), 8.51 (d, J = 8.1 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 6.21 (s, 2H), 3.97 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 188.0, 160.5, 159.1, 148.8, 140.6, 135.1, 133.8, 130.8, 130.1, 129.0, 123.2, 56.7, 53.7, 53.1; HRMS (ESI-TOF) calcd for $C_{14}H_{12}N_4O_7$ [M + H^+] 349.0784, found 349.0781; [M + Na^+] 371.0604, found 371.0600.

*2-Chloro-1-(3-nitrophenyl)ethan-1-ol (**2d**).* Compound **2d** was obtained in 57% yield (82 mg) (together with **2a**) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 0.1 mL of 3-nitrostyrene (**2**) (0.717 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; EtOAc; −15 °C → 20 °C; 1.5 h). **2d**: R_f = 0.15 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3425 (broad), 1524, 1519, 1346, 1068, 729, 676 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.27 (t, J = 2.0 Hz, 1H), 8.16 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 5.02 (m, 1H), 3.78 (dd, J = 11.4, 3.6 Hz, 1H), 3.65 (dd, J = 11.4, 8.1 Hz, 1H), 2.89 (br s, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.6, 142.2, 132.4, 129.9, 123.5, 121.4, 73.1, 50.5; HRMS (ESI-TOF) calcd for $C_8H_8ClNO_3$ [M + H^+] 202.0270, found 202.0287.

*4-(2-Azido-1-chloroethyl)benzonitrile (**3a**).* Compound **3a** was obtained in 83% yield (141 mg) after FCC (silica gel, hexanes/EtOAc = 10:1 → 5:1) from 0.1 mL of 4-cyanostyrene (**3**) (0.774 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; 1.5 h). **3a**: R_f = 0.45 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2230, **2104**, 1307, **1258**, 836, 559 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 4.97 (t, J = 6.6 Hz, 1H), 3.76 (dd, J = 12.9, 6.9 Hz, 1H), 3.67 (dd, J = 13.0, 6.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 143.2, 132.8, 128.3, 118.3, 113.1, 59.9, 57.6; HRMS (ESI-TOF) calcd for $C_9H_7ClN_4$ [M + H^+] 207.0437, found 207.0401.

*Dimethyl 1-(2-chloro-2-(4-cyanophenyl)ethyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**3a′**).* Compound **3a′** was isolated in 42% yield (81 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 114 mg of **3a** (0.552 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **3a′**: R_f = 0.27 (silica gel, hexanes/EtOAc 2:1); IR (film) ν_{max} = 2956, 2231, 1737, 1726, 1221, 1062, 825, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.64 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 5.40 (dd, J = 8.4, 6.1 Hz, 1H), 5.14 (dd, J = 14.0, 8.4 Hz, 1H), 5.02 (dd, J = 14.0, 6.2 Hz, 1H), 3.92 (s, 3H) overlaps with 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.3, 158.9, 141.7, 140.2, 133.0, 130.1, 128.3, 118.1, 113.6, 59.1, 56.0, 53.7, 53.0; HRMS (ESI-TOF) calcd for $C_{15}H_{13}ClN_4O_4$ [M + H^+] 349.0704, found 349.0702; [M + Na^+] 371.0523, found 371.0520.

*4-(2-Azidoacetyl)benzonitrile (**3c**).* Compound **3c** was obtained in 27% yield (41 mg) (together with 71 mg of **3a**, 42%) after FCC (silica gel, hexanes/EtOAc = 10:1 → 5:1) from 0.1 mL of 4-cyanostyrene (**3**) (0.774 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; EtOAc; −15 °C → 20 °C; 3 h). **3c**: R_f = 0.36 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2232, **2105**, 1694, **1217**, 833 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 4.55 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 192.4, 137.5, 133.0, 128.7, 117.8, 117.7, 55.3; HRMS (ESI-TOF) calcd for $C_9H_6N_4O$ [M + Na^+] 209.0439, found 209.0408.

*Mixture of syn- and anti-1-Azido-2-chloroethane-1,2-diyl)-dibenzene (**4a:4b**).* Compounds **4a:4b** were obtained as a mixture of diastereomers in 86% yield (123 mg) after FCC (silica gel, hexanes/EtOAc = 20:1 → 15:1) from 100 mg of *trans*-stilbene (**4**) (0.555 mmol), 400 mg of NaN_3 (6.15 mmol), 3.0 mL of NaOCl solution (1.77 mmol), 0.85 mL of AcOH (14.8 mmol), and 1.0 mL of brine (procedure I; EtOAc; 20 °C; 3 h). **4a:4b**: R_f = 0.51 (silica gel, hexanes/EtOAc 15:1 or 20:1); IR (film) ν_{max} = 3032, **2101**, **1254**, 727, 693 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.39−7.35 (m), 7.27 (m), 7.23−7.20 (m), 7.16 (m), 7.07 (m), 5.00 (d, J = 7.8 Hz, 1H) overlaps with 5.00 (d, J = 8.6 Hz, 1H), 4.95 (d, J = 7.8 Hz, 1H), 4.88 (d, J = 8.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.7, 137.6, 136.4, 136.2, 129.14, 129.12, 128.9, 128.82, 128.79, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 72.5, 71.6, 67.0, 64.9.

*(1R,2R)-2-Azido-1-chloro-1,2,3,4-tetrahydronaphthalene + Enantiomer (**5a**).* Compound **5a** was obtained in 67% yield (107 mg) (together with 26% of **5b** (42 mg); and ∼10% of **5c** (∼14 mg)) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 1,2-dihydronaphthalene (5) (0.766 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 3 h). **5a**: R_f = 0.80 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2937, 2093, 1259, 739 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.43 (m, 1H), 7.22 (m, 2H), 7.10 (m, 1H), 5.04 (d, J = 5.3 Hz, 1H), 4.12 (ddd, J = 7.6, 5.3, 2.9 Hz, 1H), 2.97−2.84 (m, 2H), 2.39 (dddd, J = 13.9, 8.6, 5.9, 2.8 Hz, 1H), 1.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 135.5, 133.5, 130.7, 129.0, 128.8, 126.9, 63.4, 59.5, 25.5, 24.4; HRMS (ESI-TOF) calcd for $C_{10}H_{10}ClN_3$ [M + H^+] 208.0642, found 208.0627.

*anti-Dimethyl-1-chloro-1,2,3,4-tetrahydronaphthalen-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**5a′**).* Compound **5a′** was isolated in 75% yield (167 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 132 mg of **5a** (0.636 mmol) and 0.2 mL of DMAD (1.63 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **5a′**: R_f = 0.22 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2954, 1737, 1731, 1453, 1286,

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1223, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.59 (m, 1H), 7.25 (m, 2H), 7.14 (m, 1H), 5.77 (d, J = 9.4 Hz, 1H), 5.33 (ddd, J = 12.1, 9.4, 3.4 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 3.16 (ddd, J = 17.1, 12.0, 5.3 Hz, 1H), 3.02 (ddd, J = 17.1, 5.0, 3.1 Hz, 1H), 2.64 (dddd, J = 13.2, 12.1, 12.1, 5.2 Hz, 1H), 2.46 (dddd, J = 13.2, 5.3, 3.2, 3.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7, 159.5, 139.6, 135.4, 134.0, 131.5, 129.8, 128.7 overlaps with 128.7, 127.2, 64.7, 61.8, 53.8, 52.9, 29.7, 28.7; HRMS (ESI-TOF) calcd for $C_{16}H_{16}ClN_3O_4$ [M + H^+] 350.0908, found 350.0906; [M + Na^+] 372.0728, found 372.0725.

*(1R,2S)-2-Azido-1-chloro-1,2,3,4-tetrahydronaphthalene + Enantiomer (**5b**).* Compound **5b** was obtained in 26% yield (42 mg) (together with 67% of **5a** (107 mg); and ∼10% of **5c** (∼14 mg)) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 1,2-dihydronaphthalene (**5**) (0.766 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 3 h). **5b**: R_f = 0.72 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2939, **2094**, **1258**, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (d, J = 7.5 Hz, 1H), 7.24−7.19 (m, 2H), 7.12 (d, J = 7.5 Hz, 1H), 5.26 (dd, J = 3.4, 1.3 Hz, 1H), 3.90 (ddd, J = 11.8, 3.4, 3.4 Hz, 1H), 3.08 (ddd, J = 17.5, 6.3, 2.7 Hz, 1H), 2.93 (ddd, J = 17.5, 11.2, 6.4 Hz, 1H), 2.39 (dddd, J = 13.0, 11.5, 11.5, 6.3 Hz, 1H), 2.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 134.8, 134.6, 130.5, 129.3, 129.2, 126.9, 61.8, 60.2, 27.8, 22.6.

*syn-Dimethyl-1-chloro-1,2,3,4-tetrahydronaphthalen-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**5b′**).* Compound **5b′** was isolated in 48% yield (40 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 49 mg of **5b** (0.236 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **5b′**: R_f = 0.20 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2923, 2853, 1742, 1737, 1726, 1450, 1220, 1062, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.32 (d, J = 7.8 Hz, 1H), 7.29 (ddd, J = 7.4, 7.4, 1.5 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 5.54 (dd, J = 3.3, 1.4 Hz, 1H), 5.39 (ddd, J = 12.4, 3.2, 3.2 Hz, 1H), 3.97 (s, 6H), 3.23−3.14 (m, 2H), 3.06 (m, 1H), 2.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.9, 159.6, 140.9, 134.7, 134.1, 130.9, 129.63, 129.57, 129.4, 127.1, 61.4, 60.0, 53.8, 53.0, 28.8, 22.4; HRMS (ESI-TOF) calcd for $C_{16}H_{16}ClN_3O_4$ [M + H^+] 350.0908, found 350.0910; [M + Na^+] 372.0728, found 372.0724. **5d′**: HRMS (ESI-TOF) calcd for $C_{16}H_{16}ClN_3O_4$ [M + H^+] 350.0908, found 350.0907; [M + Na^+] 372.0728, found 372.0726.

*2-Azido-3,4-dihydronaphthalen-1(2H)-one (**5c**).* Compound **5c** was obtained in 10% yield (14 mg) (together with 67% of **5a** (107 mg); and 26% of **5b** (42 mg)) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 1,2-dihydronaphthalene (**5**) (0.766 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 3 h). **5c**: R_f = 0.50 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2933, **2100**, 1692, 1682, 1601, **1264**, 1228, 745 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.05 (dd, J = 7.8, 1.2 Hz, 1H), 7.50 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 4.21 (dd, J = 12.1, 4.7 Hz, 1H), 3.06 (dd, J = 7.8, 4.5 Hz, 2H), 2.36 (dddd, J = 13.3, 4.5, 4.5, 4.5 Hz, 1H), 2.16−2.08 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 194.0, 143.6, 134.4, 131.3, 128.9, 128.2, 127.3, 64.5, 29.6, 27.8; HRMS (ESI-TOF) calcd for $C_{10}H_9N_3O$ [M + Na^+] 210.0643, found 210.0638.

*((1S,2R)-2-Azido-1-chlorocyclohexyl)benzene + Enantiomer (**6a**).* Compound **6a** was obtained in 61% yield (91 mg) (together with 8% of **6b**, 12 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 1-phenyl-1-cyclohexene (**6**) (0.628 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; neat; −15 °C → 20 °C; 2 h). **6a**: R_f = 0.80 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2939, 2866, **2101**, 1446, **1267**, 751, 694, 658 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.58 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 4.22 (m, 1H), 2.53 (ddd, J = 13.9, 12.4, 4.1 Hz, 1H), 2.38 (dddd, J = 14.3, 13.0, 4.6, 2.9 Hz, 1H), 2.22 (ddddd, J = 13.9, 3.3, 3.3, 1.5, 1.5 Hz, 1H), 1.95 (m, 1H), 1.89 (m, 1H), 1.76 (m, 1H), 1.60 (m, 1H) overlaps with 1.55 (dddd, J = 13.2, 13.2, 4.0, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 143.6, 128.7, 128.5, 126.8, 73.1, 67.4, 32.4, 27.0, 21.5, 19.4; HRMS (ESI-TOF) calcd for $C_{12}H_{14}ClN_3$ [M + H^+] 236.0955, found 236.0961.

*Dimethyl 1-((1R,2S)-2-chloro-2-phenylcyclohexyl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**6a′**).* Compound **6a′** was isolated in 56% yield (18 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 20 mg of **6a** (0.085 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 17 h). **6a′**: R_f = 0.20 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2952, 1737, 1727, 1446, 1278, 1214, 753, 735, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.28 (m, 2H), 7.16−7.10 (m, 3H), 5.62 (ddd, J = 4.8, 2.4, 2.4 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.30 (m, 1H), 2.71 (m, 1H), 2.24 (m, 1H), 2.19−2.08 (m, 2H), 2.02 (m, 1H), 1.96 (m, 1H), 1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 159.3, 141.5, 138.5, 131.2, 128.6, 128.4, 126.3, 73.6, 64.1, 53.5, 52.7, 33.0, 27.6, 21.4, 19.1; HRMS (ESI-TOF) calcd for $C_{18}H_{20}ClN_3O_4$ [M + H^+] 378.1215, found 378.1219; [M + Na^+] 400.1035, found 400.1035.

*((1S,2S)-2-Azido-1-chlorocyclohexyl)benzene + Enantiomer (**6b**).* Compound **6b** was obtained as a mixture of **6b** plus two other unidentified products in 8% yield (12 mg) (together with 61% of **6a**, 91 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 1-phenyl-1-cyclohexene (**6**) (0.628 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; neat; −15 °C → 20 °C; 2 h). **6b**: R_f = 0.70 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2942, 2865, **2100**, 1446, **1262**, 751, 694 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$ − *a mixture of three products*) δ = 7.68 (m, 2H), 7.61 (m, 2H), 7.53−7.26 (m, 11H), 4.88 (m, 1H), 4.49 (m, 1H), 4.28 (dd, J = 10.9, 4.8 Hz, 1H), 3.77 (dd, J = 11.2, 4.3 Hz, 1H), 2.55 (m, 1H), 2.34 (m, 1H), 2.24−2.08 (m, 7H), 2.05−1.86 (m, 8H), 1.70−1.64 (m, 4H), 1.50−1.40 (m, 2H); HRMS (ESI-TOF) calcd for $C_{12}H_{14}ClN_3$ [M + H^+] 236.0955, found 236.0966.

*Dimethyl 1-((1S,2S)-2-chloro-2-phenylcyclohexyl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**6b′**).* Compound **6b′** was isolated in 62% yield (52 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 52 mg of **6b** (0.221 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **6b′**: R_f = 0.17 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 2951, 1737, 1726, 1445, 1285, 1214, 1061, 734, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.22−7.16 (m, 3H), 7.19−7.14 (m, 2H), 5.19 (dd, J = 12.0, 3.5 Hz, 1H), 3.86 (s, 3H), 3.52 (s, 3H), 3.01 (m, 1H), 2.55 (ddd, J = 14.1, 12.4, 3.9 Hz, 1H), 2.29 (m, 1H), 2.17 (ddddd, J = 13.1, 13.1, 13.1, 3.7, 3.7 Hz, 1H) overlaps with 2.09 (m, 2H), 1.84 (m, 1H), 1.61 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7, 159.2, 140.9, 138.5, 131.3, 128.6, 128.4, 126.9, 76.3, 67.4, 53.1, 52.7, 40.2, 29.1, 25.3 21.6; HRMS (ESI-TOF) calcd for $C_{18}H_{20}ClN_3O_4$ [M + H^+] 378.1221, found 378.1226; [M + Na^+] 400.1040, found 400.1037.

*Mixture of syn- and anti-2-Azido-3-chloro-3-phenylpropan-1-ol (**7a**:**7b**).* Compounds **7a**:**7b** were obtained as an inseparable mixture in 71% yield (112 mg) after PTLC (silica gel, hexanes/EtOAc = 5:1) from 100 mg of cinnamyl alcohol (**7**) (0.745 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), 0.26 mL of AcOH (4.54 mmol), and 1.0 mL of brine (procedure I; PhMe; 20 °C; 1 h). Alternatively, **7a**:**7b** can be obtained (together with 35% of other region-isomers; 78% combined yield) from 100 mg of **7** (0.745 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 2.5 h). **7a**:**7b**: R_f = 0.28 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3363 (broad), **2102**, **1265**, 1057, 733, 697, 550 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.45−7.32 (m, 10H), 5.01 (d, J = 7.8 Hz, 1H), 4.93 (d, J = 8.2 Hz, 1H), 3.96−3.83 (m, 4H), 3.61 (dd, J = 11.6, 3.8 Hz, 1H), 3.40 (dd, J = 11.5, 6.2 Hz, 1H), 2.05 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.9, 137.8, 129.4, 129.3, 129.12, 129.06, 128.2, 127.7, 69.8, 69.0, 63.8, 63.0, 62.9, 60.7.

*Mixture of syn- and anti-2-Azido-3-chloro-3-phenylpropyl acetate (**7a′**:**7b′**).* A mixture of **7a**:**7b** (110 mg, 0.520 mmol) and Et_3N (0.2 mL, 1.43 mmol) in 5 mL of dry DCM was treated with acetyl chloride (0.07 mL, 0.984 mmol) at 0 °C for 0.5 h. Excess DCM was removed in vacuo. After FCC (silica gel, hexanes/EtOAc = 5:1) 78% of pure **7a′**:**7b′** (103 mg) was isolated. **7a′**:**7b′**: R_f = 0.55 (silica

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gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = **2106**, 1753−1732, **1221**, 1044, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43−7.32 (m, 10H), 4.92 (d, J = 7.1 Hz, 1H), 4.88 (d, J = 7.9 Hz, 1H), 4.43 (dd, J = 11.7, 3.4 Hz, 1H), 4.25 (dd, J = 11.7, 6.9 Hz, 1H), 4.15 (dd, J = 11.5, 3.7 Hz, 1H), 4.04 (ddd, J = 7.9, 6.9, 3.4 Hz, 1H) overlaps with 4.01 (ddd, J = 7.2, 7.2, 3.6 Hz, 1H), 3.91 (dd, J = 11.5, 7.2 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.6, 170.5, 137.4, 137.3, 129.49, 129.47, 129.2, 129.1, 128.1, 127.6, 66.3, 65.7, 64.3, 64.2, 63.0, 60.9, 20.9, 20.8; HRMS (ESI-TOF) calcd for $C_{11}H_{12}ClN_3O_2$ [M + Na$^+$] 276.0515, found 276.0550.

*Mixture of syn- and anti-Dimethyl-3-acetoxy-1-chloro-1-phenylpropan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**7a″:7b″**).* Compounds **7a″:7b″** were isolated in 57% yield (89 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 100 mg of **7a′:7b′** (0.394 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **7a″:7b″**: R_f = 0.15 (silica gel, hexanes/EtOAc 5:1) or 0.68 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 1753−1728, 1453, 1214, 1077, 1047, 731, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45−7.34 (m, 5H), 7.18 (m, 5H), 5.73 (ddd, J = 10.2, 8.1, 4.4 Hz, 1H), 5.65 (ddd, J = 10.2, 9.0, 3.3 Hz, 1H), 5.50 (d, J = 10.2 Hz, 1H), 5.43 (d, J = 10.2 Hz, 1H), 5.16 (dd, J = 11.8, 3.3 Hz, 1H), 4.72 (dd, J = 11.8, 9.1 Hz, 1H), 4.34−4.25 (m, 2H), 3.99 (s, 3H), 3.97 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 1.95 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.3, 170.2, 160.6, 160.2, 159.2, 158.8, 139.7, 139.3, 136.4, 136.1, 132.1, 131.4, 130.2, 129.62, 129.58, 129.0, 127.7, 127.5, 65.1, 64.6, 63.8, 63.3, 62.0, 59.8, 53.8, 53.6, 53.0, 52.9, 20.7, 20.6; HRMS (ESI-TOF) calcd for $C_{17}H_{18}ClN_3O_6$ [M + H$^+$] 396.0962, found 396.0976; [M + Na$^+$] 418.0782, found 418.0778.

*(E)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (**8**).* Cinnamyl alcohol (7) (0.5 g, 3.73 mmol) was dissolved in dry THF (15 mL). The resulting solution was cooled to 0 °C. Sodium hydride (134 mg, 5.58 mmol, prewashed separately from 60% in mineral oil) was added in portions over the period of 5 min, the reaction was stirred for additional 20 min at 0 °C after which propargyl bromide (0.72 mL, 6.68 mmol, 80% solution in toluene) was added dropwise. After the reaction was completed (monitored by TLC, 0 °C → 20 °C; 3 h) it was slowly quenched with sat. aq. NH_4Cl (10 mL). The biphasic mixture was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. FCC (silica gel, hexanes/EtOAc = 10:1 → 5:1) yielded 76% (0.49 g) of **8** as a colorless oil. **8**: R_f = 0.75 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3290, 3026, 2851, 1356, 1116, 1073, 965, 736, 691, 669, 632 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (m, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 16.0 Hz, 1H), 6.26 (ddd, J = 16.0, 6.2, 6.2 Hz, 1H), 4.23 (dd, J = 6.2, 1.4 Hz, 2H), 4.19 (d, J = 2.4 Hz, 2H), 2.45 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 136.7, 133.6, 128.8, 128.0, 126.8, 125.2, 79.9, 74.7, 70.4, 57.2; HRMS (ESI-TOF) calcd for $C_{12}H_{12}O$ [M + H$^+$] 173.0966, found 173.0949.

*Mixture of syn- and anti-2-Azido-1-chloro-3-(prop-2-yn-1-yloxy)-propyl)benzene (**8a:8b**).* Compounds **8a:8b** were obtained in 82% yield (119 mg) (together with 5% of **8c**, 7 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of **8** (0.581 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; 0.5 h). **8a:8b**: R_f = 0.60−0.70 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3295, 2916, **2105**, **1267**, 1094, 732, 697, 639, 528 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.48−7.31 (m, 10H), 5.04 (d, J = 6.9 Hz, 1H), 4.99 (d, J = 7.8 Hz, 1H), 4.21 (t, J = 2.6 Hz, 2H), 4.12 (d, J = 2.4 Hz, 2H), 3.97 (m, 1H), 3.87 (m, 1H), 3.82−3.76 (m, 2H), 3.65 (dd, J = 9.9, 4.1 Hz, 1H), 3.42 (dd, J = 9.9, 5.9 Hz, 1H), 2.46 (t, J = 2.4 Hz, 1H), 2.40 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.0, 137.6, 129.23, 129.15, 129.0, 128.9, 128.2, 127.8, 79.0, 78.9, 75.47, 75.46, 69.6, 69.5, 67.0, 66.4, 63.0, 60.9, 58.9, 58.8. **8a:8b** (one of the diastereomers): R_f = 0.62 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3294, 2916, **2104**, **1270**, 1109, 744, 699, 649 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43−7.33 (m, 5H), 5.04 (d, J = 6.9 Hz, 1H), 4.12 (d, J = 2.4 Hz, 2H), 3.86 (d, J = 6.8, 5.8, 4.2 Hz, 1H), 3.65 (dd, J = 9.9, 4.1 Hz, 1H), 3.42 (dd, J = 9.9, 5.8 Hz, 1H), 2.39 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.0, 129.2, 129.0, 127.8, 78.9, 75.5, 69.7, 67.1, 63.0, 58.9.

*Mixture of syn- and anti-Dimethyl-1-chloro-1-phenyl-3-(prop-2-yn-1-yloxy)propan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**8a′:8b′**).* Compounds **8a′:8b′** were isolated in 52% yield (41 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 50 mg of **8a:8b** (0.200 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 18 h). **8a′:8b′**: R_f = 0.18 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3286, 2954, 1737, 1727, 1453, 1275, 1217, 1099, 699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43−7.33 (m, 5H), 7.22−7.18 (m, 5H), 5.72 (m, 1H) overlaps with 5.69 (m, 1H), 5.53 (d, J = 9.9 Hz, 1H), 5.45 (d, J = 10.0 Hz, 1H), 4.45 (dd, J = 10.1, 3.5 Hz, 1H), 4.27 (dd, J = 10.1, 9.0 Hz, 1H), 4.09 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.91 (m, 2H), 3.89 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.60 (dd, J = 10.1, 3.8 Hz, 1H), 2.42 (t, J = 2.4 Hz, 1H), 2.27 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7, 160.4, 159.3, 159.0, 139.8, 139.3, 137.0, 136.4, 132.1, 131.7, 129.8, 129.5, 129.4, 129.3, 128.9, 128.7, 127.74, 127.69, 78.6, 78.3, 75.62, 75.58, 69.6, 68.9, 61.7, 59.9, 58.7, 58.6, 53.6, 53.5, 52.9, 52.8; HRMS (ESI-TOF) calcd for $C_{18}H_{18}ClN_3O_5$ [M + H$^+$] 392.1013, found 392.1036; [M + Na$^+$] 414.0833, found 414.0832.

*2-Azido-1-phenyl-3-(prop-2-yn-1-yloxy)propan-1-one (**8c**).* Compound **8c** was obtained (together with 98 mg of **8a:8b**, 68%) in 10% yield (13 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of **8** (0.581 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; EtOAc; 20 °C; 1 h). **8c**: R_f = 0.44 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3293, 2916, 2849, **2102**, 1702−1682, **1270**, 1228, 1104, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, J = 7.3 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 4.84 (dd, J = 6.9, 4.3 Hz, 1H), 4.20 (d, J = 2.4 Hz, 1H), 4.18 (d, J = 2.4 Hz, 1H), 4.04 (dd, J = 10.2, 4.3 Hz, 1H), 3.94 (dd, J = 10.2, 6.9 Hz, 1H), 2.41 (t, J = 2.4 Hz, 1H).

*Dimethyl 1-(1-oxo-1-phenyl-3-(prop-2-yn-1-yloxy)propan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**8c′**).* Compound **8c′** was isolated in 48% yield (10 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 13 mg of **8c** (0.057 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 17 h). **8c′**: R_f = 0.11 (silica gel, hexanes/EtOAc 5:1) or 0.50 (silica gel, hexanes/EtOAc 2:1); IR (film) ν_{max} = 3283, 2955, 1737−1698, 1450, 1285, 1215, 1102, 692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 6.71 (dd, J = 9.0, 4.0 Hz, 1H), 4.39 (dd, J = 10.6, 4.0 Hz, 1H), 4.32 (dd, J = 10.6, 9.0 Hz, 1H), 4.14 (dd, J = 16.0, 2.4 Hz, 1H), 4.07 (dd, J = 16.0, 2.4 Hz, 1H), 3.94 (s, 3H) overlaps with 3.94 (s, 3H), 2.38 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 190.9, 160.6, 159.6, 140.0, 134.5, 134.4, 131.0, 129.3, 128.8, 78.6, 75.6, 68.4, 64.9, 58.9, 53.7, 53.0.

*Ethyl (2S,3R,4R)-3-azido-4-chloro-2-ethoxy-3,4-dihydroquinoline-1(2H)-carboxylate + Enantiomer (**9a**).* Compound **9a** was obtained in 67% yield (97 mg) (together with 32% of 9b, 37 mg) after PTLC (silica gel, hexanes/EtOAc = 5:1) from 110 mg of 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) (9) (0.445 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 3 h). **9a**: R_f = 0.68 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2980, 2106, 1712, 1311, 1274, 1080, 1046 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 (d, J = 7.7 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.25 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 5.69 (d, J = 3.8 Hz, 1H), 4.79 (d, J = 9.2 Hz, 1H), 4.32−4.17 (m, 2H), 3.78 (dd, J = 9.1, 3.8 Hz, 1H), 3.73−3.62 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.6, 134.7, 128.8, 128.7, 126.9, 126.2, 125.8, 86.1, 72.1, 64.3, 62.8, 57.8, 15.1, 14.5; HRMS (ESI-TOF) calcd for $C_{14}H_{17}ClN_4O_3$ [M + Na$^+$] 347.0886, found 347.0886.

*Dimethyl 1-((2S,3R,4R)-4-chloro-2-ethoxy-1-(ethoxycarbonyl)-1,2,3,4-tetrahydroquinolin-3-yl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**9a′**).* Compound **9a′** was isolated in 61% yield (125 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 142 mg of **9a** (0.437 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **9a′**: R_f = 0.18 (silica gel, hexanes/EtOAc 5:1)

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or 0.37 (silica gel, hexanes/EtOAc 3:1); IR (film) ν_{max} = 2954, 1737, 1731, 1453, 1286, 1223, 1069, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.64 (t, J = 7.8 Hz, 1H), 7.42−7.37 (m, 2H), 7.30 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 6.16 (d, J = 4.4 Hz, 1H), 5.49 (d, J = 10.8 Hz, 1H), 5.16 (dd, J = 10.8, 4.4 Hz, 1H), 4.30−4.16 (m, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.64 (dddd, J = 9.6, 7.1, 7.1, 7.1 Hz, 1H), 3.84 (dddd, J = 9.6, 7.1, 7.1, 7.1 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.4, 158.8, 154.4, 139.7, 134.9, 132.1, 129.1, 128.8, 126.6, 126.3, 126.2, 86.4, 71.6, 64.3, 63.1, 57.0, 53.8, 52.9, 14.9, 14.5; HRMS (ESI-TOF) calcd for $C_{20}H_{23}ClN_4O_7$ [M + H^+] 467.1333, found 467.1334; [M + Na^+] 489.1153, found 489.1150.

*Ethyl 3-azido-4-oxoquinoline-1(4H)-carboxylate (**9b**).* Compound **9b** was obtained in 32% yield (37 mg) (together with 67% of **9a**, 97 mg) after PTLC (silica gel, hexanes/EtOAc = 5:1) from 110 mg of 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) (**9**) (0.445 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; −15 °C → 20 °C; 3 h). **9b**: R_f = 0.55 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2982, **2122**, 1759, 1630, 1327, **1275**, 1212, 1189, 1032, 765 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.68 (d, J = 8.9 Hz, 1H), 8.37 (dd, J = 8.1, 1.7 Hz, 1H), 8.19 (s, 1H), 7.68 (ddd, J = 8.9, 7.1, 1.8 Hz, 1H), 7.45 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 175.0, 151.2, 137.8, 133.3, 127.2, 126.6, 125.8, 125.2, 123.6, 120.1, 65.7, 14.4; HRMS (ESI-TOF) calcd for $C_{12}H_{10}N_4O_3$ [M + H^+] 259.0831, found 259.0822; [M + Na^+] 281.0650, found 281.0642.

*Dimethyl 1-(1-(ethoxycarbonyl)-4-oxo-1,4-dihydroquinolin-3-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**9b′**).* Compound **9b′** was isolated in 39% yield (14 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 23 mg of **9b** (0.089 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 18 h). **9b′**: R_f = 0.08 (silica gel, hexanes/EtOAc 5:1) or 0.19 (silica gel, hexanes/EtOAc 2:1); IR (film) ν_{max} = 1760−1728, 1656−1644, 1475−1453, 1279, 1206, 1026, 865, 764, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.03 (s, 1H), 8.74 (d, J = 8.9 Hz, 1H), 8.42 (dd, J = 8.0, 1.7 Hz, 1H), 7.78 (ddd, J = 8.9, 7.1, 1.7 Hz, 1H), 7.52 (ddd, J = 8.0, 7.1, 0.9 Hz, 1H), 4.59 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.92 (s, 3H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.6, 160.3, 159.1, 150.6, 139.0, 138.1, 136.1, 134.3, 133.4, 127.4, 126.7, 126.3, 120.9, 120.4, 66.5, 53.8, 53.0, 14.4; HRMS (ESI-TOF) calcd for $C_{18}H_{16}N_4O_7$ [M + H^+] 401.1098, found 401.1091; [M + Na^+] 423.0917, found 423.0915.

*Methyl 3,3-dichloro-2-oxoindoline-6-carboxylate (**10a**).* Compound **10a** was obtained in 89% yield (159 mg) after FCC (silica gel, hexanes/EtOAc = 5:1) from 120 mg of methylindole-6-carboxylate (**10**) (0.685 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; EtOAc; 20 °C; 1.5 h). **10a**: R_f = 0.25 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3214, 1747, 1715, 1450, 1278, 1221, 1090, 768, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 9.09 (br s, 1H), 7.87 (dd, J = 7.9, 1.5 Hz, 1H), 7.69−7.67 (m, 2H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.7, 165.9, 138.3, 134.0, 133.8, 126.1, 125.3, 112.4, 73.9, 52.9; HRMS (ESI-TOF) calcd for $C_{10}H_7Cl_2NO_3$ [M + H^+] 259.9881, found 259.9877.

*3-Chloro-1H-pyrrolo[2,3-b]pyridine (**11a**).* Compound **11a** was obtained in 91% yield (118 mg) after FCC (silica gel, hexanes/EtOAc = 1:1) from 100 mg of 7-azaindole (**11**) (0.846 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; 0.5 h). **11a**: R_f = 0.29 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 3077−2821 (br), 1590, 1414, 1291, 1001, 787, 761, 662 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ = 8.24 (dd, J = 4.8, 1.5 Hz, 1H), 7.94 (dd, J = 7.9, 1.5 Hz, 1H), 7.39 (s, 1H), 7.15 (dd, J = 7.9, 4.8 Hz, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ = 147.6, 144.5, 127.9, 123.8, 119.7, 117.2, 104.8.

*1-(3-Azido-2-chloropropyl)-4-methoxybenzene (**12a**).* Compound **12a** was obtained in 87% yield (128 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of 4-allylanisole (**12**) (0.651 mmol), 500 mg of NaN_3 (7.69 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; neat; 20 °C; 1 h). Alternatively, **12a** can be obtained in 94% yield (138 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1 → 10:1) from 0.1 mL of 4-allylanisole (**12**) (0.651 mmol), 500 mg of NaN_3 (7.69 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.35 mL of AcOH (6.11 mmol) (procedure I; PhMe; at room temperature or 0 °C → 20 °C; 5 h). NOTE: Larger amounts of NaOCl, older reagents, EtOAc, lower temperature, lack of the excess of NaN_3 usually cause the formation of other side products (see **12b′** and **12c′**). **12a**: R_f = 0.65 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2957, 2837, **2100**, 1611, 1513, 1302, **1246**, 1178, 1032, 833, 543 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.12 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 4.13 (dddd, J = 7.0, 7.0, 6.0, 4.7 Hz, 1H), 3.78 (s, 3H), 3.50 (dd, J = 13.0, 4.6 Hz, 1H), 3.44 (dd, J = 13.0, 6.0 Hz, 1H), 3.06 (dd, J = 14.2, 7.0 Hz, 1H), 3.00 (dd, J = 14.2, 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.9, 130.6, 128.7, 114.2, 61.4, 56.0, 55.4, 40.9; HRMS (ESI-TOF) calcd for $C_{10}H_{12}ClN_3O$ [M + Na^+] 248.0566, found 248.0558.

*Dimethyl 1-(2-chloro-3-(4-methoxyphenyl)propyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**12a′**).* Compound **12a′** was isolated in 72% yield (162 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 138 mg of **12a** (0.611 mmol) and 0.25 mL of DMAD (2.03 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **12a′**: R_f = 0.10 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2955, 1737, 1728, 1514, 1462, 1221, 1178, 1062, 1033, 824, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.14 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.89−4.80 (m, 2H), 4.48 (dddd, J = 7.9, 7.1, 7.1, 4.8 Hz, 1H), 3.94 (s, 3H) overlaps with 3.94 (s, 3H), 3.76 (s, 3H), 3.05 (d, J = 1.6 Hz, 1H), 3.04 (d, J = 2.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 159.2, 159.1, 139.9, 131.1, 130.6, 127.8, 114.3, 60.5, 55.4, 54.7, 53.7, 52.9, 41.3; HRMS (ESI-TOF) calcd for $C_{16}H_{18}ClN_3O_5$ [M + H^+] 368.1013, found 368.1038; [M + Na^+] 390.0832, found 390.0833.

*Mixture of syn- and anti-Dimethyl-1,3-dichloro-1-(4-methoxyphenyl)propan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**12b′**) plus syn- and anti-Dimethyl-2,3-dichloro-1-(4-methoxyphenyl)propyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**12c′**).* Compounds **12b′**:**12c′** were isolated in various yields after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from various amounts of **12a** (crude mixture obtained at −15 °C and in EtOAc) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **12b′**:**12c′**: R_f = 0.20 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2956, 1737, 1728, 1514, 1453, 1281, 1256, 1226, 1180, 1154, 1058, 1031, 825 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.55 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H) overlaps with 6.87 (d, J = 8.8 Hz, 2H), 6.34 (d, J = 10.1 Hz, 1H) overlaps with 6.32 (d, J = 9.4 Hz, 1H), 5.37 (m, 1H), 5.29 (ddd, J = 9.8, 3.6, 3.1 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H) overlaps with 3.93 (s, 3H), 3.84 (dd, J = 12.7, 3.0 Hz, 1H), 3.79 (dd, J = 12.5, 2.8 Hz, 1H), 3.78 (s, 3H) overlaps with 3.77 (s, 3H), 3.61 (dd, J = 12.7, 3.7 Hz, 1H), 3.51 (dd, J = 12.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 161.0, 160.8, 160.6, 160.5, 159.0, 158.8, 140.24, 140.15, 130.1, 130.0, 129.1, 129.0, 126.6, 125.6, 114.9, 114.5, 67.3, 65.0, 61.6, 60.5, 55.6, 55.5, 53.8, 53.7, 53.1, 53.0, 47.2, 46.9; HRMS (ESI-TOF) calcd for $C_{16}H_{17}Cl_2N_3O_5$ [M + H^+] 402.0623, found 402.0621; [M + Na^+] 424.0442, found 424.0439.

*1-Chloro-3-(4-methoxyphenyl)propan-2-ol (**12d**).* Compound **12d** was obtained in 24% yield (32 mg) (together with 66% of **12a** (97 mg) and other side-products (see **12b′** and **12c′**) usually formed at −15 °C) after FCC (silica gel, hexanes/EtOAc = 20:1 → 5:1) from 0.1 mL of 4-allylanisole (**12**) (0.651 mmol), 300 mg of NaN_3 (4.61 mmol), 8.0 mL of NaOCl solution (4.72 mmol), and 0.52 mL of AcOH (9.08 mmol) (procedure I; EtOAc; −15 °C; 2.5 h). **12d**: R_f = 0.20 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3410 (broad), 2955−2836, 1513, 1246, 1178, 1034, 810 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.18 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 4.03 (dddd, J = 6.5, 6.5, 6.5, 3.8 Hz, 1H), 3.82 (s, 3H), 3.64 (dd, J = 11.1, 3.9 Hz, 1H), 3.52 (d, J = 11.1, 6.2 Hz, 1H), 2.86 (d, J = 6.6 Hz, 2H), 2.12 (br s, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 158.7, 130.5, 129.1, 114.3, 72.5, 55.5, 49.4, 39.9.

*Dimethyl 1-(2-chloro-3-phenylpropyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**12e′**).* Compound **12e′** was isolated in 42% yield (29

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mg) (together with 17% of **12f′**, 13 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 40 mg of **12e** (0.204 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **12e′**: R_f = 0.15 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2955, 1737, 1728, 1454, 1273, 1217, 1145, 1061, 825, 737, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.32 (m, 2H), 7.27 (m, 1H), 7.23 (m, 2H), 4.91−4.83 (m, 2H), 4.54 (dddd, J = 7.2, 7.2, 7.2, 5.3 Hz, 1H), 3.95 (s, 3H) overlaps with 3.95 (s, 3H), 3.15−3.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 159.2, 140.0, 135.9, 131.2, 129.5, 129.0, 127.7, 60.2, 54.9, 53.7, 53.0, 42.2; HRMS (ESI-TOF) calcd for $C_{15}H_{16}ClN_3O_4$ [M + H^+] 338.0907, found 338.0945; [M + Na^+] 360.0727, found 360.0725.

*Mixture of syn- and anti-Dimethyl-1,3-dichloro-1-phenylpropan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**12f′**).* Compound **12f′** was isolated in 17% yield (13 mg) (together with 42% of **12e′**, 29 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 40 mg of **12e** (0.204 mmol, crude mixture) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **12f′**: R_f = 0.25 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2955, 1742, 1737, 1731, 1454, 1281, 1228, 1076, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.47 (m, 4H), 7.27−7.21 (m, 6H), 5.89 (ddd, J = 9.9, 9.9, 3.7 Hz, 1H), 5.80 (ddd, J = 10.2, 10.2, 3.3 Hz, 1H), 5.50 (d, J = 9.8 Hz, 1H), 5.43 (d, J = 10.0 Hz, 1H), 4.57 (dd, J = 11.8, 3.3 Hz, 1H), 4.39 (d, J = 11.7, 10.3 Hz, 1H), 4.03 (m, 1H) overlaps with 4.03 (s, 3H) overlaps with 4.03 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 3.61 (d, J = 11.8, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7, 160.2, 159.2, 158.6, 140.1, 139.6, 136.4, 135.9, 131.9, 131.4, 130.3, 129.8, 129.7, 129.0, 127.7, 127.6, 67.3, 67.1, 62.6, 61.5, 53.7, 53.6, 53.1, 52.9, 44.5, 43.7; HRMS (ESI-TOF) calcd for $C_{15}H_{15}Cl_2N_3O_4$ [M + H^+] 372.0517, found 372.0525; [M + Na^+] 394.0338, found 394.0334.

*(1R,2R,3R,4S)-2-Azido-3-chloro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene + Enantiomer (**13a**).* Compound **13a** was obtained in 64% yield (86 mg) (together with 27% of **13b**, 36 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 88 mg of 1,4-epoxy-1,4-dihydronaphthalene (**13**) (0.610 mmol), 350 mg of NaN_3 (5.38 mmol), 2.5 mL of NaOCl solution (1.47 mmol), and 0.85 mL of AcOH (14.8 mmol) (with or without 1.0 mL of brine) (procedure I; PhMe; −15 °C → 20 °C; 3 h). Alternatively, **13a** can be obtained in 56% yield (75 mg) (together with 24% of **13b**, 32 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 88 mg of 1,4-epoxy-1,4-dihydronaphthalene (**13**) (0.610 mmol), 150 mg of NaN_3 (2.31 mmol), 3.5 mL of NaOCl solution (2.06 mmol), and 0.25 mL of AcOH (4.37 mmol) (procedure I; PhMe; −15 °C → 20 °C; 1 h). **13a**: R_f = 0.45 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3013, **2100**, **1257**, 1230, 917, 847, 769, 756, 715, 646, 626, 551, 528 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.31 (m, 2H), 7.23 (m, 2H), 5.38 (s, 2H), 4.26 (d, J = 6.2 Hz, 1H), 3.62 (d, J = 6.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 142.8, 142.2, 128.6, 128.5, 120.73, 120.65, 86.7, 84.2, 63.3, 62.8; HRMS (ESI-TOF) calcd for $C_{10}H_8ClN_3O$ [M + Na^+] 244.0253, found 244.0246.

*(1R,2R,3S,4S)-2-Azido-3-chloro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene + Enantiomer (**13b**).* Compound **13b** was obtained in 27% yield (36 mg) (together with 64% of **13a**, 86 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 88 mg of 1,4-epoxy-1,4-dihydronaphthalene (**13**) (0.610 mmol), 350 mg of NaN_3 (5.38 mmol), 2.5 mL of NaOCl solution (1.47 mmol), and 0.85 mL of AcOH (14.8 mmol) (with or without 1.0 mL of brine) (procedure I; PhMe; −15 °C → 20 °C; 3 h). Alternatively, **13b** can be obtained in 24% yield (32 mg) (together with 56% of **13a**, 75 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 88 mg of 1,4-epoxy-1,4-dihydronaphthalene (**13**) (0.610 mmol), 150 mg of NaN_3 (2.31 mmol), 3.5 mL of NaOCl solution (2.06 mmol), and 0.25 mL of AcOH (4.37 mmol) (procedure I; PhMe; −15 °C → 20 °C; 1 h). **13b**: R_f = 0.60 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2916, **2093**, **1240**, 952, 937, 859, 849, 835, 785, 754, 637, 585, 543 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.40 (m, 1H), 7.34 (m, 1H), 7.28 (m, 2H), 5.41 (d, J = 4.7 Hz, 1H), 5.33 (s, 1H), 4.29 (ddd, J = 4.7, 2.3, 0.5 Hz, 1H), 3.42 (d, J = 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 141.7, 141.5, 128.4, 127.9, 123.4, 120.2, 84.9, 82.2, 70.7, 58.5.

*Dimethyl 1-((1R,2R,3S,4S)-3-chloro-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**13b′**).* Compound **13b′** was isolated in 65% yield (29 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 27 mg of **13b** (0.122 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **13b′**: R_f = 0.05 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 1737, 1726, 1450, 1282, 1220, 1155, 1067, 912, 853, 839, 765, 732, 630, 584 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.47 (m, 2H), 7.33 (m, 2H), 5.57 (d, J = 4.8 Hz, 1H), 5.52 (s, 1H), 5.38 (dd, J = 4.8, 3.1 Hz, 1H), 4.82 (d, J = 3.1 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 159.3, 141.5, 141.3, 140.9, 130.7, 128.7, 128.3, 123.6, 120.5, 85.5, 82.5, 71.8, 56.3, 53.9, 53.0; HRMS (ESI-TOF) calcd for $C_{16}H_{14}ClN_3O_5$ [M + H^+] 364.0700, found 364.0709; [M + Na^+] 386.0520, found 386.0516.

*Mixture of (1S,2R,3S,4R)-2-Azido-3-chlorobicyclo[2.2.1]heptane + Enantiomer (**14a**) and (1S,2R,3R,4R)-2-Azido-3-chlorobicyclo-[2.2.1]heptane + Enantiomer (**14b**).* Compounds **14a**:**14b** (a mixture of diastereomers) were obtained in 95% yield (225 mg) from 130 mg of bicyclo[2.2.1]hept-2-ene (**14**) (1.38 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; Et_2O; 20 °C; 1 h). The product was extracted with Et_2O and used without further purification. **14a**:**14b**: IR (film) ν_{max} = 2967, 2877, 2098, 1335, 1311, 1252, 947, 810, 769, 644, 553 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.05 (dd, J = 6.5, 1.9 Hz, 1H), 3.89 (m, 1H), 3.58 (dd, J = 6.5, 1.5 Hz, 1H), 3.38 (t, J = 2.7 Hz, 1H), 2.48−2.38 (m, 2H), 2.33 (m, 1H), 2.29 (d, J = 4.9 Hz, 1H), 1.90 (m, 1H), 1.69−1.54 (m, 4H), 1.46−1.39 (m, 2H), 1.35−1.17 (m, 5H).

*Dimethyl 1-((1S,2R,3S,4R)-3-chlorobicyclo[2.2.1]heptan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**14a′**).* Compound **14a′** was isolated in 45% yield (165 mg) (together with 19% of **14b′**, 70 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 200 mg of **14a**:**14b** (1.17 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **14a′**: R_f = 0.18 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2955, 1737−1726, 1450, 1286, 1216, 1066, 947−764, 730, 684 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.89 (dd, J = 6.8, 1.1 Hz, 1H), 4.27 (dd, J = 6.8, 1.7 Hz, 1H), 3.91 (s, 3H) overlaps with 3.91 (s, 3H), 3.21 (m, 1H), 2.52 (m, 1H), 2.43 (m, J_1 = 10.8 Hz, 1H), 1.80−1.67 (m, 2H), 1.48 (m, J_1 = 10.8 Hz, 1H), 1.37−1.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.9, 159.3, 140.0, 130.1, 67.5, 65.2, 53.4, 52.8, 46.4, 41.6, 35.6, 27.7, 26.4; HRMS (ESI-TOF) calcd for $C_{13}H_{16}ClN_3O_4$ [M + H^+] 314.0907, found 314.0944; [M + Na^+] 336.0728, found 336.0726.

*Dimethyl 1-((1S,2R,3R,4R)-3-chlorobicyclo[2.2.1]heptan-2-yl)-1H-1,2,3-triazole-4,5-dicarboxylate + Enantiomer (**14b′**).* Compound **14b′** was isolated in 19% yield (70 mg) (together with 45% of **14a′**, 165 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 200 mg of **14a**:**14b** (1.17 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **14b′**: R_f = 0.29 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2956, 1737, 1728, 1450, 1285, 1213, 1069, 948, 825−732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.89 (ddd, J = 4.2, 4.2, 1.5 Hz, 1H), 4.58 (dd, J = 4.2, 2.1 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 2.62 (m, 1H), 2.50 (d, J = 4.5 Hz, 1H), 2.19 (m, J_1 = 10.9 Hz, 1H), 2.00 (m, 1H), 1.75 (dddd, J = 12.3, 12.3, 4.7, 4.7 Hz, 1H), 1.57 (dddd, J = 12.8, 4.3, 4.3, 1.8 Hz, 1H), 1.54−1.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.6, 159.2, 140.1, 130.7, 72.6, 64.8, 53.7, 52.9, 45.3, 43.8, 35.8, 27.9, 21.4; HRMS (ESI-TOF) calcd for $C_{13}H_{16}ClN_3O_4$ [M + H^+] 314.0907, found 314.0958; [M + Na^+] 336.0728, found 336.0724.

*anti-1-Azido-2-chlorocycloheptane (**15a**) with Trace Amount of syn-1-Azido-2-chlorocycloheptane (**15b**).* Compound **15a** (with trace amount of **15b**) was obtained in 98% yield (219 mg) from 0.15 mL of cycloheptene (**15**) (1.285 mmol), 350 mg of NaN_3 (5.38 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; neat; 20 °C; 1 h). The product was used without further purification. **15a**: IR (film) ν_{max} = 2933, 2862, **2093**, 1461−1445, **1258**, 954, 876, 724 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 3.93 (ddd, J = 8.1, 8.1, 3.5 Hz, 1H), 3.64 (ddd, J = 8.6, 8.1, 3.2 Hz, 1H), 2.09 (m, 1H), 1.99−1.91 (m, 2H), 1.79−1.65 (m, 3H), 1.59−1.48 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 70.6, 66.4, 35.0, 30.9, 27.6, 23.6, 23.4.

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*anti-Dimethyl-2-chlorocycloheptyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**15a′**).* Compound **15a′** was isolated in 55% yield (149 mg) (together with 13% of **15b′**, 36 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 150 mg of **15a** (0.864 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **15a′**: R_f = 0.30 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2939, 1737, 1728, 1461, 1453, 1278, 1211, 1179, 1151, 1062, 825, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.98 (ddd, J = 9.7, 9.7, 3.2 Hz, 1H), 4.60 (ddd, J = 9.7, 8.4, 3.8 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.29−2.18 (m, 2H), 2.08−2.00 (m, 2H), 1.94 (m, 1H), 1.81 (m, 1H), 1.71−1.55 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7, 159.6, 139.1, 130.8, 69.5, 65.1, 53.6, 52.8, 35.6, 32.9, 27.3, 24.6, 23.3; HRMS (ESI-TOF) calcd for $C_{13}H_{18}ClN_3O_4$ [M + H^+] 316.1064, found 316.1092; [M + Na^+] 338.0883, found 338.0881.

*syn-Dimethyl-2-chlorocycloheptyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**15b′**).* Compound **15b′** was isolated in 13% yield (36 mg) (together with 55% of **15a′**, 149 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1) from 150 mg of **15a** (0.864 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **15b′**: R_f = 0.18 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2937, 1742, 1737, 1726, 1450, 1346, 1279, 1214, 1179, 1063, 825 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.23 (ddd, J = 10.4, 4.9, 2.9 Hz, 1H), 4.48 (ddd, J = 7.5, 2.9, 2.9 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 2.68 (dddd, J = 14.3, 10.2, 10.2, 4.0 Hz, 1H), 2.33−2.23 (m, 2H), 2.03 (dddd, J = 15.1, 9.3, 3.1, 3.1 Hz, 1H), 1.95−1.87 (m, 2H), 1.77−1.53 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 161.0, 159.8, 140.0, 130.1, 65.1, 64.1, 53.7, 52.9, 34.5, 29.6, 27.1, 24.17, 24.16; HRMS (ESI-TOF) calcd for $C_{13}H_{18}ClN_3O_4$ [M + H^+] 316.1064, found 316.1095; [M + Na^+] 338.0883, found 338.0886.

*syn- and anti-2-Azido-3-chlorobutane-1,4-diol (**16a**).* Compounds **16a**:**16b** were obtained as a mixture of diastereomers in 94% yield (189 mg) from 0.1 mL of *cis*-2-butene-1,4-diol (**16**) (1.22 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (procedure I; PhMe; 20 °C; 1.5 h). The product was used without further purification. **16a**:**16b**: R_f = 0.19 (silica gel, hexanes/EtOAc 2:1); IR (film) ν_{max} = 3338 (broad), 2942, 2104, 1259, 1034, 550 cm^{-1}.

*(3S,5R,6R,8S,9S,10R,13R,14S,17R)-6-Azido-5-chloro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (**17a**).* Compound **17a** was obtained in 47% yield (148 mg) (together with 8% of **17b**, 26 mg) after PTLC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 261 mg of cholesterol (**17**) (0.675 mmol), 400 mg of NaN_3 (6.15 mmol), 2.5 mL of NaOCl solution (1.47 mmol), 0.85 mL of AcOH (14.8 mmol), and 1.0 mL of brine (procedure I; PhMe; 20 °C; 2.5 h). **17a**: R_f = 0.51 (silica gel, hexanes/EtOAc 3:1) or 0.15 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3331 (broad), 2943, 2868, **2100**, 1467, 1381, **1267**, 1038, 905, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.28 (dddd, J = 10.8, 10.8, 5.4, 5.4 Hz, 1H), 3.80 (dd, J = 3.8, 2.3 Hz, 1H), 2.29 (dd, J = 13.4, 10.4 Hz, 1H), 2.07−1.95 (m, 3H), 1.88 (m, 1H), 1.82 (m, 1H), 1.71 (ddd, J = 14.5, 4.2, 2.3 Hz, 1H), 1.66−1.44 (m, 8H), 1.40−1.23 (m, 6H), 1.21 (s, 3H), 1.18−1.04 (m, 7H), 0.97 (m, 1H), 0.88 (d, J = 6.6 Hz, 3H), 0.85 (d, J = 2.3 Hz, 3H), 0.83 (d, J = 2.3 Hz, 3H), 0.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 83.9, 67.8, 67.1, 56.3, 55.7, 46.1, 42.9, 42.3, 40.4, 39.9, 39.7, 36.4, 36.0, 33.8, 31.2, 31.1, 30.6, 28.4, 28.2, 24.2, 24.0, 23.0, 22.8, 21.4, 18.9, 18.1, 12.4.

*Dimethyl 1-((3S,5R,6R,8S,9S,10R,13R,14S,17R)-5-chloro-3-hydroxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-6-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**17a′**).* Compound **17a′** was isolated in 47% yield (30 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 2:1 → 1:1) from 49 mg of **17a** (0.106 mmol) and 0.2 mL of DMAD (1.63 mmol) (procedure II; C_6H_6; 65 °C; 16 h). **17a′**: R_f = 0.10 (silica gel, hexanes/EtOAc 5:1) or 0.50 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 3424 (broad), 1737−1731, 1450, 1267, 1228, 1063, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.31 (dd, J = 5.6, 0.9 Hz, 1H), 4.25 (dddd, J = 10.8, 10.8, 5.3, 5.3 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 2.48 (m, 1H), 2.38 (ddd, J = 14.6, 12.7, 6.4 Hz, 1H), 2.10−1.99 (m, 3H), 1.82 (m, 2H), 1.67 (m, 2H), 1.55−1.43 (m, 5H), 1.40−1.05 (m, 11H) overlaps with 1.23 (s, 3H), 0.98 (s, 3H) overlaps with 0.97 (m, 1H), 0.89 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 2.1 Hz, 3H), 0.83 (d, J = 2.1 Hz, 3H), 0.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.6, 160.4, 139.1, 132.7, 83.5, 67.6, 64.0, 56.4, 56.3, 53.9, 52.9, 46.1, 43.1, 41.3, 40.6, 40.0, 39.7, 36.4, 36.0, 34.6, 32.5, 31.5, 30.4, 28.5, 28.2, 24.1, 24.0, 23.0, 22.8, 21.6, 18.9, 17.7, 12.6; HRMS (ESI-TOF) calcd for $C_{33}H_{52}ClN_3O_5$ [M + H^+] 606.3674, found 606.3666; [M + Na^+] 628.3494, found 628.3485.

*(3S,5R,6S,8S,9S,10R,13R,14S,17R)-6-Azido-5-chloro-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-ol (**17b**).* Compound **17b** was obtained in 8% yield (26 mg) (together with 47% of **17a**, 148 mg) after PTLC (silica gel, hexanes/EtOAc = 5:1 → 3:1) from 261 mg of cholesterol (**17**) (0.675 mmol), 400 mg of NaN_3 (6.15 mmol), 2.5 mL of NaOCl solution (1.47 mmol), 0.85 mL of AcOH (14.8 mmol), and 1.0 mL of brine (procedure I; PhMe; 20 °C; 2.5 h). **17b**: R_f = 0.43 (silica gel, hexanes/EtOAc 3:1) or 0.06 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 3348 (broad), 2936, 2867, **2097**, 1467−1445, 1382−1366, **1240**, 1059−1028, 907, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 4.22 (dddd, J = 10.8, 10.8, 5.3, 5.3 Hz, 1H), 3.43 (dd, J = 11.4, 5.0 Hz, 1H), 2.53 (ddd, J = 13.7, 5.1, 1.8 Hz, 1H), 1.97 (m, 1H), 1.89−1.65 (m, 7H), 1.63−1.45 (m, 6H), 1.41 (m, 1H), 1.37−1.27 (m, 3H), 1.26−1.08 (m, 9H), 1.07 (s, 3H), 0.97 (m, 1H), 0.88 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 2.4 Hz, 3H), 0.83 (d, J = 2.4 Hz, 3H), 0.63 (s, 3H).

*Dimethyl 1-((3S,5R,6S,8S,9S,10R,13R,14S,17R)-5-chloro-3-hydroxy-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-6-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**17b′**).* Compound **17b′** was isolated in 68% yield (23 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 26 mg of **17b** (0.056 mmol) and 0.1 mL of DMAD (0.813 mmol) (procedure II; C_6H_6; 65 °C; 15 h). **17b′**: R_f = 0.04 (silica gel, hexanes/EtOAc 5:1) or 0.25 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 3340 (broad), 2950, 2868, 1742−1728, 1450, 1279, 1223, 1066, 735 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 5.48 (dd, J = 12.5, 3.7 Hz, 1H), 4.08 (dddd, J = 10.8, 10.8, 5.2, 5.2 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 2.70 (q, J = 12.5 Hz, 1H), 2.00 (m, 1H), 1.87−1.79 (m, 4H), 1.77−1.64 (m, 3H), 1.60−1.45 (m, 6H), 1.39−1.19 (m, 8H) overlaps with 1.24 (s, 3H), 1.15−0.95 (m, 6H), 0.88 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 2.5 Hz, 3H), 0.83 (d, J = 2.5 Hz, 3H), 0.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 161.1, 160.0, 140.0, 130.6, 82.6, 67.0, 62.7, 56.2, 55.4, 53.7, 53.0, 46.0, 43.0, 42.5, 40.4, 39.8, 39.7, 36.3, 36.0, 35.1, 32.8, 32.2, 29.9, 28.3, 28.2, 24.1, 24.0, 23.0, 22.8, 21.7, 18.8, 16.9, 12.4; HRMS (ESI-TOF) calcd for $C_{33}H_{52}ClN_3O_5$ [M + H^+] 606.3674, found 606.3664; [M + Na^+] 628.3494, found 628.3482.

*((S)-5-(3-Chloroprop-1-en-2-yl)-2-methylcyclohex-2-en-1-one (**18a**).* Compound **18a** was obtained in 65% yield (77 mg) (together with trace amount of **18b** and **18**) after PTLC (silica gel, hexanes/EtOAc = 10:1) from 0.1 mL of (*S*)-(+)-carvone (**18**) (0.639 mmol), 350 mg of NaN_3 (5.38 mmol), 2.5 mL of NaOCl solution (1.47 mmol), and 0.85 mL of AcOH (14.8 mmol), and 1.0 mL of brine (procedure I; EtOAc; −15 °C → 20 °C; 0.5 h). **18a**: R_f = 0.37 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2923, 1677−1667, 1366, 1253, 1108, 902, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.73 (m, 1H), 5.24 (s, 1H), 5.04 (s, 1H), 4.07 (m, 2H), 2.96 (m, 1H), 2.64 (ddd, J = 16.1, 3.7, 1.3 Hz, 1H), 2.54 (m, 1H), 2.37 (dd, J = 16.1, 13.1 Hz, 1H) overlaps with 2.30 (m, 1H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 199.1, 146.8, 144.2, 135.9, 115.4, 47.2, 43.3, 38.1, 31.6, 15.9; HRMS (ESI-TOF) calcd for $C_{10}H_{13}ClO$ [M + H^+] 185.0733, found 185.0732; [M + Na^+] 207.0552, found 207.0551.

*(S)-5-((R)-1-Azido-2-chloropropan-2-yl)-2-methylcyclohex-2-en-1-one + (S)-5-((S)-1-Azido-2-chloropropan-2-yl)-2-methylcyclohex-2-en-1-one (**18b**).* Compound **18b** was obtained as a diastereomeric mixture in 42% yield (60 mg) (together with 16% of **18a** (19 mg) and 42% of **18** (42 mg)) after FCC (silica gel, hexanes/EtOAc = 10:1) from 0.1 mL of (*S*)-(+)-carvone (**18**) (0.639 mmol), 770 mg of NaN_3 (11.8 mmol), 4.0 mL of NaOCl solution (2.36 mmol), 0.28 mL of AcOH (4.89 mmol), and 1.0 mL of brine (procedure I; PhMe; 20 °C; 1.5 h). **18b**: R_f = 0.25 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2924, **2100**, 1677−1666, 1450, 1383, 1367, 1294, **1256**, 1108, 905 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 6.71 (m, 1H), 3.55 (dd, J = 18.1, 12.8 Hz, 1H − *one diastereomer*) overlaps with 3.53 (dd, J = 16.6, 12.8 Hz, 1H − *another diastereomer*), 2.59 (m, 1H), 2.50−2.31 (m, 4H), 1.75 (m, 3H), 1.56 (s, 1.5H − *one diastereomer*) overlaps with

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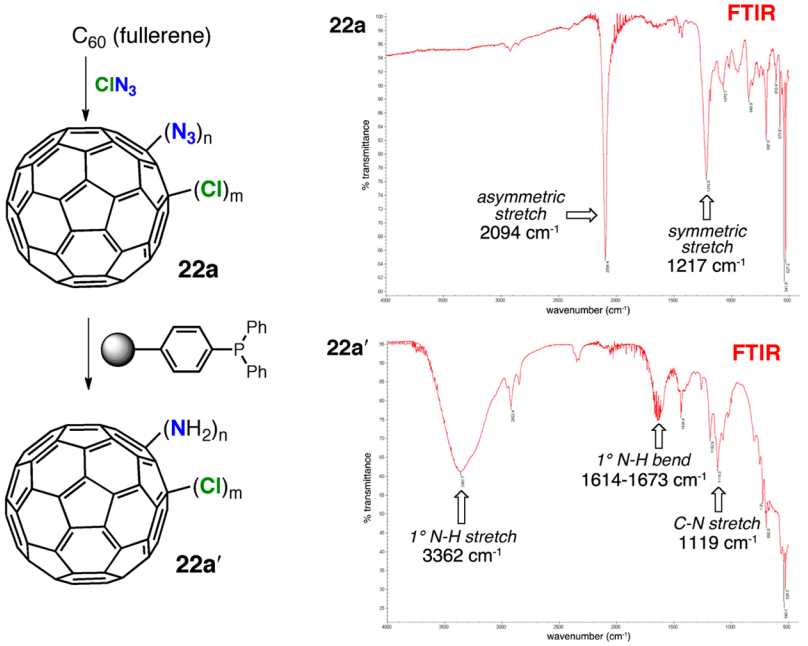
Scheme 4. FTIR Spectra of Azidochloro-Fullerene (22a) and Aminochloro-Fullerene (22a′)[a]



[a]The number of azide and chloride groups introduced to the fullerene structure was not established.

1.55 (s, 1.5H − *another diastereomer*); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 198.59, 198.57, 144.0, 143.8, 135.7, 135.6, 73.46, 73.45, 60.1, 60.0, 42.83, 42.79, 39.5, 39.4, 27.42, 27.35, 25.93, 25.90, 15.72, 15.71; HRMS (ESI-TOF) calcd for $C_{10}H_{14}ClN_3O$ [M + Na^+] 250.0723, found 250.0713.

Dimethyl 1-((R)-2-chloro-2-((S)-4-methyl-5-oxocyclohex-3-en-1-yl)propyl)-1H-1,2,3-triazole-4,5-dicarboxylate + Diastereomer (**18b′**).* Compound **18b′** was isolated in 78% yield (42 mg) after FCC (silica gel, hexanes/EtOAc = 5:1 → 1:1) from 33 mg of **18b** (0.145 mmol) and 0.15 mL of DMAD (1.22 mmol) (procedure II; C_6H_6; 65 °C; 17 h). **18b′**: R_f = 0.07 (silica gel, hexanes/EtOAc 5:1) or 0.45 (silica gel, hexanes/EtOAc 1:1); IR (film) ν_{max} = 2955, 1737–1728, 1673, 1434, 1352, 1279, 1226, 1112, 1062, 825, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.73 (m, 1H), 5.08 (d, J = 14.4 Hz, 0.5H − *one diastereomer*) overlaps with 5.07 (d, J = 14.4 Hz, 0.5H − *another diastereomer*), 4.81 (d, J = 14.4 Hz, 0.5H − *one diastereomer*) overlaps with 4.80 (d, J = 14.4 Hz, 0.5H − *another diastereomer*), 3.96 (s, 1.5H − *one diastereomer*) overlaps with 3.96 (s, 1.5H − *another diastereomer*), 3.94 (s, 1.5H − *one diastereomer*) overlaps with 3.94 (s, 1.5H − *another diastereomer*), 2.75 (m, 1H), 2.66 (m, 1H), 2.49–2.33 (m, 3H), 1.76 (m, 3H), 1.50 (s, 1.5H − *one diastereomer*), 1.47 (s, 1.5H − *another diastereomer*); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 197.9, 197.7, 160.36, 160.35, 159.7, 159.6, 143.6, 143.3, 139.52, 139.46, 136.0, 135.8, 132.3, 132.1, 72.71, 72.69, 56.88, 56.82, 53.79, 53.78, 52.95, 52.93, 44.1 (2 overlapping peaks), 39.7, 39.5, 27.61, 27.58, 25.6, 25.5, 15.68, 15.67; HRMS (ESI-TOF) calcd for $C_{16}H_{20}ClN_3O_5$ [M + H^+] 370.1169, found 370.1169; [M + Na^+] 392.0989, found 392.0976.

*9-Azidoanthracene (**19a**).* Compound **19a** was obtained in 66% yield (81 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 100 mg of anthracene (**19**) (0.561 mmol), 350 mg of NaN_3 (5.38 mmol), 2.5 mL of NaOCl solution (1.47 mmol), and 0.7 mL of AcOH (12.2 mmol) (with or without 1.0 mL of brine) (procedure I; PhMe; 20 °C; 0.5 h). **19a**: R_f = 0.78 (silica gel, hexanes/EtOAc 20:1); IR (film) ν_{max} = 3049, **2097**, 1347, 1282, **1242**, 1002, 883, 837, 730, 718, 541 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.35 (dddd, J = 8.8, 0.9, 0.9, 0.9 Hz, 2H), 8.28 (s, 1H), 7.98 (d, J = 8.5 Hz, 2H), 7.55 (ddd, J = 8.7, 6.6, 1.2 Hz, 2H), 7.49 (ddd, J = 8.3, 6.6, 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 132.0, 130.9, 128.9, 126.5, 125.8, 125.7, 125.4, 122.7.

*Dimethyl 1-(anthracen-9-yl)-1H-1,2,3-triazole-4,5-dicarboxylate (**19a′**).* Compound **19a′** was isolated in 82% yield (149 mg) (together with trace amount of **19b′**, ∼ 18%) after FCC (silica gel, hexanes/EtOAc = 20:1 → 5:1 → 2:1) from 110 mg of **19a** (0.502 mmol) and 0.2 mL of DMAD (1.63 mmol) (procedure II; C_6H_6; 65 °C; 17 h). **19a′**: R_f = 0.41 (silica gel, hexanes/EtOAc 5:1); IR (film) ν_{max} = 2953, 1737–1731, 1445, 1315, 1289, 1224, 1136, 1064, 908, 733 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.65 (s, 1H), 8.05 (m, 2H), 7.52–7.47 (m, 4H), 7.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 158.4, 139.1, 135.3, 131.1, 131.0, 128.9, 128.7, 128.59, 128.57, 126.2, 121.6, 53.5, 53.1; HRMS (ESI-TOF) calcd for $C_{20}H_{15}N_3O_4$ [M + H^+] 362.1140, found 362.1142; [M + Na^+] 384.0960, found 384.0955. Dimethyl 1-(10-chloroanthracen-9-yl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (**19b′**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.58 (ddd, J = 8.9, 0.9, 0.9 Hz, 2H), 7.63 (ddd, J = 8.9, 6.6, 1.1 Hz, 2H), 7.53 (ddd, J = 8.8, 6.6, 1.1 Hz, 2H), 7.15 (ddd, J = 8.8, 0.9, 0.9 Hz, 2H), 4.07 (s, 3H), 3.52 (s, 3H); HRMS (ESI-TOF) calcd for $C_{20}H_{14}ClN_3O_4$ [M + H^+] 396.0751, found 396.0747; [M + Na^+] 418.0570, found 418.0565.

*N-Allyl-2,4-dichloroaniline (**20a**).* Compound **20a** was obtained in 67% yield (100 mg) after PTLC (silica gel, hexanes/EtOAc = 20:1) from 0.1 mL of *N*-allylaniline (**20**) (0.737 mmol), 150 mg of NaN_3 (2.31 mmol), 4.0 mL of NaOCl solution (2.36 mmol), and 0.26 mL of AcOH (4.54 mmol) (with or without 1.0 mL of brine) (procedure I; PhMe; −15 °C → 20 °C; 1 h). **20a**: R_f = 0.75 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 3424, 3100–2800 (weak), 1598, 1510, 1503, 1321, 923, 800 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.24 (d, J = 2.5 Hz, 1H), 7.07 (dd, J = 8.8, 2.4 Hz, 1H), 6.54 (d, J = 8.8 Hz, 1H), 5.91 (dddd, J = 17.1, 10.3, 5.2, 5.2 Hz, 1H), 5.26 (dddd, J = 17.1, 1.6, 1.6, 1.6 Hz, 1H), 5.18 (dddd, J = 10.3, 1.5, 1.5, 1.5 Hz, 1H), 4.45 (br s, NH), 3.80 (ddd, J = 5.2, 1.6, 1.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 142.7, 134.5, 128.9, 127.9, 121.5, 119.6, 116.9, 112.3, 46.3; HRMS (ESI-TOF) calcd for $C_9H_9Cl_2N$ [M + H^+] 202.0190, found 202.0174; [M + Na^+] 224.0009, found 224.0005.

*N,N-Dichloro-2-(cyclohex-1-en-1-yl)ethan-1-amine (**21a**).* Proposed compound **21a** was obtained in 73% yield (102 mg) after PTLC (silica gel, hexanes/EtOAc = 10:1 → 5:1) from 0.1 mL of 2-(cyclohexen-1-yl)ethylamine (**21**) (0.717 mmol), 350 mg of NaN_3 (5.38 mmol), 2.5 mL of NaOCl solution (1.47 mmol), 0.7 mL of AcOH (12.2 mmol), and 1.0 mL of brine (procedure I; PhMe; 20 °C; 0.5 h). **21a**: R_f = 0.79 (silica gel, hexanes/EtOAc 10:1); IR (film) ν_{max} = 2924, 2857, 2834, 1446, 1439, 1435, 1136, 919, 910, 802, 694, 641,

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576 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.47 (m, 1H), 3.67 (m, 2H), 2.35 (t, J = 7.5 Hz, 2H), 1.97 (m, 2H), 1.91 (m, 2H), 1.63−1.58 (m, 2H), 1.56−1.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 133.3, 124.1, 74.9, 37.0, 28.8, 25.5, 23.0, 22.4.

C_{60} Derivatives. The fullerene C_{60} was subjected to general procedure I in either chlorobenzene or toluene solvent, resulting in the complete consumption of starting material and the isolation of a product (or mixture of products) with good mass recovery (Scheme 4). The presence of the azide group in the product was confirmed by IR spectroscopy (strong asymmetric stretch at 2094 cm^{-1}, weaker symmetric stretching band at 1217 cm^{-1}),[98] and by reduction with polymer-bound triphenylphosphine to give the amine derivative **22a′**. The presence of chloride has not been verified, so structures **22a** and **22a′** are speculative at present.

*Azido-chloro-fullerene (**22a**).* Product **22a** was obtained in 22 mg yield as a crude mixture from 20 mg of fullerene (**22**) (0.028 mmol), 500 mg of NaN_3 (7.69 mmol), 8.0 mL of NaOCl solution (4.72 mmol), and 0.52 mL of AcOH (9.08 mmol) (procedure I; PhMe or PhCl; 20 °C; 1 h). **22a**: IR (film) ν_{max} = **2094**, **1217** cm^{-1}.

*Amino-chloro-fullerene (**22a′**).* Product **22a′** was isolated from 20 mg of **22a** and 100 mg of polymer-bound triphenylphosphine (3 mmol/g, 200−400 mesh) (procedure II; C_6H_6/THF/H_2O; 65 °C; 16 h). **22a′**: IR (film) ν_{max} = 3362 (broad), 1673−1614, 1119, 722−693 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

Tables summarizing optimization experiments, details of X-ray crystallographic analyses (including CIF files), NMR and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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