Triazene-Activated Donor-Acceptor Cyclopropanes: Ring-Opening and (3+2) Annulation Reactions

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Supporting Information Placeholder

ABSTRACT: Donor-acceptor cyclopropanes substituted with 3,3-dialkyltriazenyl groups are described herein. The strong electron-donating character of the triazene renders the cyclopropanes highly reactive, allowing for catalyst-free ring-opening reactions with methanol and tetracyanoethylene under mild conditions. The triazene-substituted cyclopropanes could also be used as substrates in Lewis acid catalyzed (3+2) annulations with silyl enol ethers.

Cyclopropanes substituted with both electron-withdrawing and electron-donating groups in vicinal position display a high reactivity, which can be accentuated by using catalysts.^{1,2} Typically, catalytic activation is achieved by coordination of a Lewis or Brønsted acid to the acceptor group.² The acid facilitates heterolytic C-C bond cleavage of the strained ring, allowing for reactions with electrophiles or nucleophiles, as well as cycloaddition and rearrangement reactions (Scheme 1a). Alternatively, formyl-acceptor groups can be activated by amine catalysts via iminium formation.³ The catalytic activation of donor-acceptor (D-A) cyclopropanes via interaction of the donor group with Lewis bases is less common.⁴ Examples of isolable D-A cyclopropanes, which are able to undergo ring-opening reactions without external catalysts, remain scarce.⁵ The paucity of such cyclopropanes is related to the difficulty of finding donor/acceptor pairs, which provide the right amount of activation, while insuring sufficient stability of the three-membered ring. Indeed, too much activation can result in spontaneous rearrangement of cyclopropanes into larger 5-membered heterocycles.⁶

A good balance between stability and reactivity has traditionally been realized with carbon and oxygen-based donor groups, whereas nitrogen-based substituents were less investigated, despite their synthetic relevance.² To address this limitation, the Waser group has introduced phthalimide-, succinimide- and nucleobase-substituted cyclopropanes (Scheme 1b).^{2c,7} In this work we introduce 3,3-dialkyltriazenes as new nitrogen-based donors. We

show that triazenes provide an exceptional activation of the cyclopropane ring, allowing for ring-opening and expansion reactions under mild conditions.

Scheme 1. Reactivity of D-A Cyclopropanes (A) and Nitrogen-Based Donor Groups (B).²⁻⁷

a) Reactivity of D-A cyclopropanes

b) D-A Cyclopropanes with nitrogen donor groups

Over the last five years, we have studied the chemistry of 1-alkynyl triazenes.⁸ These investigations have revealed that the triazene group is a very good electron donor, enabling an electrophilic attack to the triple bond. In view of these results, we were interested to explore if triazenes could be

used as donors in D-A cyclopropanes to expand the range of useful nitrogen substituents.

A common procedure for the synthesis of diester-substituted cyclopropanes is the Rh-catalyzed cyclopropanation of olefins with diazomalonates.⁹ This approach could be implemented for the synthesis of cyclopropanes bearing triazene groups. The required vinyl triazenes starting materials **1a–1e** were accessed by coupling of vinyl Grignard reagents with nitrous oxide and lithium amides,^{8g,10} or by hydrogenation of alkynyl triazenes.¹¹

Cyclopropane **2a** could then be prepared by reaction of (*E*)-3,3-dicyclohexyl-1-vinyltriazene-1-ene (**1a**) with dimethyl diazomalonate (1.2 equiv.) in the presence of commercially available Rh₂(esp)₂ (0.2 mol %) as catalyst (Scheme 2). The desired product was obtained in good yield, and the procedure was further optimized to gram scale with an isolated yield of 87%. Compound **2a** is a colorless crystalline solid, and its structure could be confirmed by single crystal X-ray diffraction. Using this optimized procedure, we could prepare cyclopropanes **2b–2e** having additional phenyl, 4-anisyl, 2-thienyl or cyclopropyl groups in C3 position from the corresponding *cis*-1,2-disubstituted vinyl triazenes **1b–1e**. The isolated yields of **2b–2e** varied from 52% to 65%. According to the ¹H NMR spectra, the *cis* stereochemistry is conserved in the products.

Scheme 2. Synthesis of D-A Cyclopropanes with Triazene Groups.^a

^a Reaction conditions: vinyl triazene (1 equiv.), diazomalonate (1.2 equiv.), Rh₂(esp)₂ (0.2–0.5 mol %), DCM (0.1 M), 0 °C – RT.

The ¹³C NMR spectrum of cyclopropane **2a** in CDCl₃ shows a chemical shift for the C2 atom next to the triazene group at 55.6 ppm. Calculation of ¹³C NMR chemical shifts for DFT-optimized structures of **2a** gave a similar value.¹² For comparison, the corresponding values for 'standard' D-A

cyclopropanes having aryl, cyclopropyl, or phthalimidyl donor groups lie in the range of 31–35 ppm, and cyclopropanes with poor donor groups such as *n*-butyl and hydrogen show a C2 signal at 24 ppm and 17 ppm, respectively (Figure 1a).¹³ The strongly shifted C2 signal of **2a** was a first indication for the pronounced electronic effect of the triazene group.

Figure 1. ¹³C NMR Chemical Shifts of Different D-A Cyclopropanes (a) and (b) Relative Stability of Carbocations (ΔG^{298} (kcal·mol⁻¹)).^a

Figure 1. ¹³C NMR Chemical Shifts of Different D-A Cyclopropanes (a) and (b) Relative Stability of Carbocations (ΔG^{298} (kcal·mol⁻¹)). The reference values were taken from the literature (ref. 13). All spectra were measured in CDCl₃. The calculations for the carbocations were performed on Mo6-2X/6-311+G(d,p) level.

Further evidence for the strong electron-donating properties of the triazene group were obtained by calculating the relative stability of carbocations **A** and **B** (Figure 1b). This approach, which was developed by Werz,¹⁴ allows comparing the donor capabilities of different substituents. As a reference, we used the *p*-methoxyphenyl group, which is known to be one of the strongest donors amongst the reported stable D-A cyclopropanes, both from a thermodynamic¹⁴ as well as a kinetic¹⁵ point of view. The calculations on Mo6-2X/6-311+G(d,p) level showed that carbocation **A** is 19 kcal·mol⁻¹ more stable than **B**. Accordingly, the triazene group was expected to provide a very strong activation of the cyclopropane ring.

Diverse reactivity studies with these new cyclopropanes **2** were then carried out. When **2a** was dissolved in methanol, the ring-opened adduct **3a** (Scheme 3) could be isolated in quantitative yield after heating to 60 °C for 2 h, followed by evaporation of the solvent. The structure of **3a** could be confirmed by X-ray crystallography. Analogously, reaction of methanol with cyclopropanes **2b–2e** gave the addition products **3b–3e** in quantitative yields as a mixture of two diastereoisomers (ratio: ~ 1:1). In all cases, the bond between the triazene and the diester was broken, showing again that it was a better donor than a (hetero)arene or a

cyclopropyl group. Preliminary mechanistic investigations indicate that methanol addition proceeds with participation of the ester group: more details are given in the Supporting Information.

For comparison, we have attempted reactions with methanol using three literature-known D-A cyclopropanes (donor = *p*-methoxyphenyl, *N*-phthalimide, or *O*-acetate). No reaction was observed, even after prolonged (24 h) heating at 60 °C. These results underline the unique donor properties of the triazene group.

Scheme 3. Methanol Addition Reactions.

Scheme 4. (3+2) Annulation with TCNE.^a

^a Reaction conditions: **2a** (1 equiv.), TCNE (1.2 equiv.), acetone (0.1 M), 40 °C, 12 h.

Next, we have explored the reactivity of **2a** towards electrophiles. Ring-opening of D-A cyclopropanes with electrophiles is generally more challenging.² Cyclopropane **2a** reacted with tetracyanoethylene (TCNE) in a formal (3+2)

cycloaddition reaction, in the absence of any external catalyst, to give the highly functionalized cyclopentane **4a** in 65% yield (Scheme 4).¹⁶ Similarly, we were able to prepare the addition products **4d** and **4e**, albeit with reduced yields of 40% and 46%, respectively. The cyclopentanes **4d** and **4e** were isolated as mixtures of diastereoisomers, with prevalence of the *trans* isomer ($\text{dr} = 2:1$). As for the reactions with methanol, we found that D-A cyclopropanes with *p*-methoxyphenyl or *N*-phthalimide donor groups did not react with TCNE under these conditions.

After having established catalyst-free reactions with methanol and TCNE, we turned our attention to less reactive reaction partners, which require activation of the acceptor group by a catalyst. A priori, it was not clear if cyclopropanes bearing triazene groups could be activated by Lewis or Brønsted acids, because the triazene groups are known to be acid-sensitive.¹⁷

As a benchmark reaction, we have examined the addition of silyl enol ethers to cyclopropane **2a**. For D-A cyclopropanes with N-donor groups, this reaction is known to occur with a Lewis acid catalyst such as SnCl_4 .⁷ Screening of different LA catalysts and reaction conditions revealed that hafnium triflate¹⁸ can catalyze the desired reaction between **2a** and silyl enol ethers at $-40\text{ }^{\circ}\text{C}$ (see SI for details).

Scheme 5. (3+2) Annulation with Silyl Enol Ethers.^a

^a Reaction conditions: **2a** (1 equiv.), enol ether (1.2 equiv.), Hf(OTf)_4 (10 mol %), DCM (0.1 M), $-40\text{ }^{\circ}\text{C}$, 20 h. * After recrystallization from MeOH.

Using the optimized reaction conditions, we have tested different acetophenone-based silyl enol ethers (**5a-5c**, Scheme 5). Bulky TBDPS and TIPS groups allowed isolation

of the cyclopentanes **6a** and **6b** in good yields with a dr of 4:1. Recrystallization of **6a** from methanol improved the dr to 16:1. Analysis of **6a** by NOESY NMR spectroscopy revealed that the major diastereoisomer has a *trans* configuration of the triazene and the OSiR₃ group. The same selectivity had been observed for reactions with *N*-phthalimide D-A cyclopropanes.^{7a} Utilization of a silyl enol ether with a less bulky TMS group (**5c**) gave cyclopentane **6c** in lower yield (57%) and a dr of 2.6:1. Next, we tested silyl enol ethers with different aryl groups. Electron-withdrawing 4-fluorophenyl and electron-donating 4-anisyl led to the formation of **6d** and **6e** in 54% and 88% yield, respectively. Interestingly, the dr of the products was only slightly influenced by the electronic properties of the aryl groups. On the other hand, using a substrate with a bulky 1-naphthyl substituent gave **6f** almost exclusively as one diastereoisomer (dr > 20:1) in 49% yield. Cyclopentane **6f** was additionally characterized by single crystal X-ray diffraction.

In conclusion, we report the first synthesis of D-A cyclopropanes substituted with dialkyltriazene groups by a simple Rh-catalyzed reaction of vinyl triazenes with dimethyl diazomalonate. The triazene group was found to provide an exceptionally strong activation of the cyclopropane ring, allowing for catalyst-free reactions with methanol and TCNE. Combined with the good stability of the new cyclopropanes, this type of reactivity is unique, as evidenced by the fact that 'standard' D-A cyclopropanes with 4-methoxyphenyl or *N*-phthalimide donor groups do not react under these conditions. The usefulness of the new triazenyl cyclopropanes was further highlighted by their compatibility with Lewis acid catalysts in a (3+2) cycloaddition with silyl enol ethers, which delivered highly-functionalized cyclopentanes. Taken together, our findings highlight the potential of the triazene group in activating cyclopropane ring systems. The results are also relevant from the more general perspective of triazene chemistry. So far, most investigations about triazenes have focused on 1-aryl triazenes,¹⁸ with studies about 1-vinyl^{11,20} and 1-alkynyl triazenes⁸ as recent additions. There are very few reports about 1-alkyl triazenes, and no examples of alkyl triazenes with additional functional groups.²¹ The D-A cyclopropane chemistry described above offers a means to prepare structurally and functionally complex alkyl triazenes. Further reactivity studies are ongoing in our laboratories.

ASSOCIATED CONTENT

Supporting Information

Experimental details and analytical data of the new compounds (PDF). Crystallographic data for compounds **2a**, **3a**, **4a** and **6f** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Recent reviews on cyclopropane chemistry: (a) Liu, J.; Liu, R.; Wei, Y.; Shi, M. Recent Developments in Cyclopropane Cycloaddition Reactions. *Trends in Chemistry* **2019**, *1*, 779–793. (b) Rassadin, V. A.; Six, Y. Ring-Opening, Cycloaddition and Rearrangement Reactions of Nitrogen-Substituted Cyclopropane Derivatives. *Tetrahedron* **2016**, *72*, 4701–4757. (c) Rubin, M.; Rubina, M.; Gevorgyan, V. Transition Metal Chemistry of Cyclopropenes and Cyclopropanes. *Chem. Rev.* **2007**, *107*, 3117–3179.
- (2) Reviews on D-A cyclopropanes: (a) Werz, D. B.; Biju, A. T. Uncovering the Neglected Similarities of Arynes and Donor-Acceptor Cyclopropanes. *Angew. Chem. Int. Ed.* **2020**, *59*, 3385–3398. (b) Singh, P.; Varshnaya, R. K.; Dey, R.; Banerjee, P. Donor-Acceptor Cyclopropanes as an Expedient Building Block Towards the Construction of Nitrogen-Containing Molecules: An Update. *Adv. Synth. Catal.* **2020**, *362*, 1447–1484. (c) Tomilov, Yu. V.; Menchikov, L. G.; Novikov, R. A.; Ivanova, O. A.; Trushkov, I. V. Methods for the Synthesis of Donor-Acceptor Cyclopropanes. *Russ. Chem. Rev.* **2018**, *87*, 201–250. (d) Grover, H. K.; Emmett, M. R.; Kerr, M. A. Carbocycles from Donor-Acceptor Cyclopropanes. *Org. Biomol. Chem.* **2015**, *13*, 655–671. (e) de Nanteuil, F.; De Simone, F.; Frei, R.; Benfatti, F.; Serrano, E.; Waser, J. Cyclization and Annulation Reactions of Nitrogen-Substituted Cyclopropanes and Cyclobutanes. *Chem. Commun.* **2014**, *50*, 10912–10928. (f) Schneider, T. F.; Kaschel, J.; Werz, D. B. A New Golden Age for Donor-Acceptor Cyclopropanes. *Angew. Chem. Int. Ed.* **2014**, *53*, 5504–5523. (g) De Simone, F.; Waser, J. Cyclization and Cycloaddition Reactions of Cyclopropyl Carbonyls and Imines. *Synthesis* **2009**, 3353–3374. (h) Yu, M.; Pagenkopf, B. L. Recent Advances in Donor-Acceptor (DA) Cyclopropanes. *Tetrahedron* **2005**, *61*, 321–347. (i) Reissig, H.-U.; Zimmer, R. Donor-Acceptor-Substituted Cyclopropane Derivatives and Their Application in Organic Synthesis. *Chem. Rev.* **2003**, *103*, 1151–1196.
- (3) (a) Wallbaum, J.; Garve, L. K. B.; Jones, P. G.; Werz, D. B. Ring-Opening Regio-, Diastereo-, and Enantioselective 1,3-Chlorochalcogenation of Cyclopropyl Carbaldehydes. *Chem. Eur. J.* **2016**, *22*, 18756–18759. (b) Sparr, C.; Gilmour, R. Cyclopropyl Iminium Activation: Reactivity Umpolung in Enantioselective Organocatalytic Reaction Design. *Angew. Chem. Int. Ed.* **2011**, *50*, 8391–8395.
- (4) (a) Blom, J.; Vidal-Albalat, A.; Jørgensen, J.; Barløse, C. L.; Jessen, K. S.; Iversen, M. V.; Jørgensen, K. A. Directing the Activation of Donor-Acceptor Cyclopropanes Towards Stereoselective 1,3-Dipolar Cycloaddition Reactions by Brønsted Base Catalysis. *Angew. Chem. Int. Ed.* **2017**, *56*, 11831–11835. (b) Sanchez-Diez, E.; Vesga, D. L.; Reyes, E.; Uria, U.; Carrillo, L.; Vicario, J. L. Organocatalytically Generated Donor-Acceptor Cyclopropanes in Domino Reactions. One-Step Enantioselective Synthesis of Pyrrolo[1,2-*a*]quinolones. *Org. Lett.* **2016**, *18*, 1270–1273. (c) Halskov, K. S.; Kniep, F.; Lauridsen, V. H.; Iversen, E. H.; Donslund, B. S.; Jørgensen, K. A. Organocatalytic Enamine-Activation of Cyclopropanes for Highly Stereoselective Formation of Cyclobutanes. *J. Am. Chem. Soc.* **2015**, *137*, 1685–1691. (d) Dickmeiss, G.; De Sio, V.; Udmark, J.; Poulsen, T. B.; Marcos, V.; Jørgensen, K. A. Organocatalytic Asymmetric Desymmetrization-Fragmentation of Cyclic Ketones. *Angew. Chem. Int. Ed.* **2009**, *48*, 6650–6653. (e) Corey, E. J.; Wollenberg, R. H. Total Synthesis of (±)-Brefeldin A. *Tetrahedron Lett.* **1976**, *17*, 4705–4708.
- (5) (a) Graziano, M. L.; Iesce, M. R.; Cermola, F.; Caputo, G.; De Lorenzo F. Ring-Opening Reactions of Cyclopropanes. Part 7. Selenenylation and Cyanoselenenylation of Ethyl 2,2-Dimethoxycyclopropanecarboxylates. *J. Chem. Soc., Perkin Trans. 1* **2002**, 664–

668. (b) Graziano, L.; Iesce, R.; Cermola, F.; Cimminello, G. Ring-Opening Reactions of Cyclopropanes. Part 4. Reactivity of trans-Ethyl 2,2-Dimethoxycyclopropane-1-carboxylates towards Dimethylacetylene-dicarboxylate. A New Route to Functionalized Cyclopent-2-enones. *J. Chem. Res.* **1992**, 4–5. (c) Graziano, M.; Chiossi, S. Ring-Opening Reactions of Cyclopropanes. Part 3. Cycloaddition of Ethyl 2,2-Dimethoxycyclopropane-1-carboxylates to Tetracyanoethylene. *J. Chem. Res.* **1989**, 44–45. (d) Abdallah, H.; Gree, R.; Carrie, R. Synthèse et Réactivité d'Oxycyclopropanes Electrophiles. *Tetrahedron* **1985**, 41, 4339–4346. (e) Ohkata, K.; Tamaru, A.; Nagai, T.; Hanafusa, T. Reaction of a Highly Spiro-activated Cyclopropane with Pyridines. A Novel Intramolecular Charge Transfer Interaction of the Product. *J. Chem. Soc., Perkin Trans. 2* **1982**, 499–503. (f) Internally activated hemimalonate cyclopropanes: Emmet, M. R.; Kerr, M. A. Nucleophilic Ring Opening of Cyclopropane Hemimalonates Using Internal Brønsted Acid Activation. *Org. Lett.* **2011**, 13, 4180–4183.
- (6) (a) Schmidt, C. D.; Kaschel, J.; Schneider, T. F.; Kratzert, D.; Stalke, D.; Werz, D. B. Donor-Substituted Nitrocyclopropanes: Immediate Ring-Enlargement to Cyclic Nitronates. *Org. Lett.* **2013**, 15, 6098–6101. (b) Jiang, Y.; Khong, V. Z. Y.; Lourdasamy, E.; Park, C.-M. Synthesis of 2-Aminofurans and 2-Unsubstituted Furans via carbenoid-Mediated [3 + 2] Cycloaddition. *Chem. Commun.* **2012**, 48, 3133–3135. (c) Wurz, R. P.; Charette, A. B. Doubly Activated Cyclopropanes as Synthetic Precursors for the Preparation of 4-Nitro- and 4-Cyano-dihydropyrroles and Pyrroles. *Org. Lett.* **2005**, 7, 2313–2316.
- (7) (a) Racine, S.; de Nanteuil, F.; Serrano, E.; Waser, J., Synthesis of (Carbo)nucleoside Analogues by [3+2] Annulation of Aminocyclopropanes. *Angew. Chem., Int. Ed.* **2014**, 53, 8484–8487. (b) de Nanteuil, F.; Serrano, E.; Perrotta, D.; Waser, J., Dynamic Kinetic Asymmetric [3+2] Annulation Reactions of Aminocyclopropanes. *J. Am. Chem. Soc.* **2014**, 136, 6239–6242. (c) Nanteuil, F.; Waser, J., Catalytic [3+2] Annulation of Aminocyclopropanes for the Enantiospecific Synthesis of Cyclopentylamines. *Angew. Chem. Int. Ed.* **2011**, 50, 12075–12079.
- (8) (a) Tan, J.-F.; Bormann, C. T.; Severin, K.; Cramer, N. Alkynyl Triazenes as Fluoroalkyne Surrogates: Regioselective Access to 4-Fluoro-2-pyridones by a Rh(III)-Catalyzed C–H Activation–Lossen Rearrangement–Wallach Reaction. *ACS Catal.* **2020**, 10, 3790–3796. (b) Tan, J.-F.; Bormann, C. T.; Chadwick, F. M.; Severin, K.; Cramer, N. Divergent Synthesis of Densely Substituted Arenes and Pyridines via Cyclotrimerization Reactions of Alkynyl Triazenes. *J. Am. Chem. Soc.* **2019**, 141, 10372–10383. (c) Wezeman, T.; Scopelliti, R.; Fadaei Tirani, F.; Severin, K. Synthesis of Heteroaryl Triazenes via Rh(III)-catalyzed Annulation Reactions with Alkynyl Triazenes. *Adv. Synth. Catal.* **2019**, 361, 1383–1388. (d) Kossler, D.; Perrin, F.; Suleymanov, A. A.; Kiefer, G.; Scopelliti, R.; Severin, K.; Cramer, N. Divergent Asymmetric Synthesis of Polycyclic Compounds via Vinyl Triazenes. *Angew. Chem. Int. Ed.* **2017**, 56, 11490–11493. (e) Jeanbourquin, L. N.; Scopelliti, R.; Fadaei Tirani, F.; Severin, K. Synthesis and Reactivity of 1-Allenyltriazenes. *Org. Lett.* **2017**, 19, 2070–2073. (f) Perrin, F.; Kiefer, G.; Jeanbourquin, L.; Racine, S.; Perrotta, D.; Waser, J.; Scopelliti, R.; Severin, K. 1-Alkynyltriazenes as Functional Analogues of Ynamides. *Angew. Chem. Int. Ed.* **2015**, 54, 13393–13396. (g) Kiefer, G.; Riedel, T.; Dyson, P. J.; Scopelliti, R.; Severin, K. Synthesis of Triazenes with Nitrous Oxide. *Angew. Chem. Int. Ed.* **2015**, 54, 302–305.
- (9) González-Bobes, F.; Fenster, M. D. B.; Kiau, S.; Kolla, L.; Kolotuchin, S.; Soumeillant, M. Rhodium-Catalyzed Cyclopropanation of Alkenes with Dimethyl Diazomalonate. *Adv. Synth. Catal.* **2008**, 350, 813–816.
- (10) For the use of N₂O in synthetic chemistry, see: Severin, K. Synthetic Chemistry with Nitrous Oxide. *Chem. Soc. Rev.* **2015**, 44, 6375–6386.
- (11) Suleymanov, A. A.; Scopelliti, R.; Fadaei-Tirani, F.; Severin, K. Synthesis of Vinyl Triazenes by Palladium-Catalyzed Addition Reactions to Alkynyl Triazenes. *Adv. Synth. Catal.* **2018**, 360, 4178–4183.
- (12) (a) The Gaussian 16 program was used. M. Frisch, et al., Gaussian 16, Revision A.03; Gaussian, Inc.: Wallingford, CT, **2016**. (b) For detailed description, see the Supporting Information.
- (13) See SI for extended table of examples with references.
- (14) Kreft, A.; Jones, P. G.; Werz, D. B. The Cyclopropyl Group as a Neglected Donor in Donor–Acceptor Cyclopropane Chemistry. *Org. Lett.* **2018**, 20, 2059–2062.
- (15) Kreft, A.; Lucht, A.; Grunenberg, J.; Jones, P. G.; Werz, D. B. Kinetic Studies of Donor–Acceptor Cyclopropanes: The Influence of Structural and Electronic Properties on the Reactivity. *Angew. Chem. Int. Ed.* **2019**, 58, 1955–1959.
- (16) For reaction of cyclopropanes with TCNE, see: (a) see refs 5a–5b. (b) Park, Y. S.; Beak, P. Lithiation-Substitutions of N-Boc N-alkyl Cyclopropylamines. *Tetrahedron* **1996**, 52, 12333–12350. (c) Oku, A.; Abe, M.; Iwamoto, M. Electron Transfer Profile of Cyclopropanone Acetals in the Nonirradiated Reaction with Tetracyanoethylene, Chloranil, and Dicyanodichlorobenzoquinone. *J. Org. Chem.* **1994**, 59, 7445–7452. (d) Wiering, P. G.; Steinberg, H. Cycloaddition of Cyclopropanone Acetals to Tetracyanoethylene. *J. Org. Chem.* **1981**, 46, 1663–1666.
- (17) Landman, I. R.; Suleymanov, A. A.; Fadaei-Tirani, F.; Scopelliti, R.; Chadwick, F. M.; Severin, K. Brønsted and Lewis Acid Adducts of Triazenes. *Dalton Trans.* **2020**, 49, 2317–2322.
- (18) For the activation of D-A cyclopropanes by Hf(OTf)₄, see: (a) Racine, S.; Hegedüs, B.; Scopelliti, R.; Waser, J., Divergent Reactivity of Thioalkynes in Lewis Acid Catalyzed Annulations with Donor–Acceptor Cyclopropanes. *Chem. Eur. J.* **2016**, 22, 11997–12001. (b) Pohlhaus, P. D.; Sanders, S. D.; Parsons, A. T.; Li, W.; Johnson, J. S. Scope and Mechanism for Lewis Acid-Catalyzed Cycloadditions of Aldehydes and Donor–Acceptor Cyclopropanes: Evidence for a Stereospecific Intimate Ion Pair Pathway. *J. Am. Chem. Soc.* **2008**, 130, 8642–4650.
- (19) (a) Dong, W.; Chen, Z.; Xu, J.; Miao, M.; Ren, H. Synthesis of Benzo-Fused Cyclic Compounds via Intramolecular Cyclization of Aryltriazenes. *Synlett* **2016**, 27, 1318–1334. (b) Zhang, Y.; Cao, D.; Liu, W.; Hu, H.; Zhang, X.; Liu, C. Recent Applications of Aryltriazenes in Organic Synthesis via C–N/N–N Bond Cleavage. *Curr. Org. Chem.* **2015**, 19, 151–178. (c) Kölmel, D. K.; Jung, N.; Bräse, S. Azides – Diazonium Ions – Triazenes: Versatile Nitrogen-rich Functional Groups. *Austr. J. Chem.* **2014**, 67, 328–336. (d) Kimball, D. B.; Haley, M. M. Triazenes: A Versatile Tool in Organic Synthesis. *Angew. Chem. Int. Ed.* **2002**, 41, 3338–3351.
- (20) (a) Suleymanov, A. A.; Doll, M.; Ruggi, A.; Scopelliti, R.; Fadaei-Tirani, F.; Severin, K. Synthesis of Tetraarylethene Lumino- gens by C–H Vinylation of Aromatic Compounds with Triazenes. *Angew. Chem. Int. Ed.* **2020**, 59, DOI: 10.1002/anie.201908755. (b) Suleymanov, A. A.; Scopelliti, R.; Fadaei Tirani, F.; Severin, K. One-Pot Synthesis of Trisubstituted Triazenes from Grignard Reagents and Organic Azides. *Org. Lett.* **2018**, 20, 3323–3326.
- (21) (a) Smith, R. H.; Michejda, C. J. Synthesis of Triazenes: Efficient Preparation of the Simplest Di- and Trialkyltriazenes and a Novel 3-Acyl-1,3-dialkyltriazene. *Synthesis* **1983**, 476–477. (b) Sieh, D. H.; Michejda, C. J. Acid-Catalyzed Decomposition of Trialkyltriazenes: Protected Alkyldiazonium Ions. *J. Am. Chem. Soc.* **1981**, 103, 442–445. (c) Sieh, D. H.; Wilbur, D. J.; Michejda, C. J. Preparation of Trialkyltriazenes. A Comparison of the Nitrogen–Nitrogen Bond Rotation in Trialkyltriazenes and Aryldialkyltriazenes by Variable Temperature Carbon-13 NMR. *J. Am. Chem. Soc.* **1980**, 102, 3883–3887.

Supporting Information

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1. Materials and methods

All *reactions* were carried out in oven dried glassware under an atmosphere of dry nitrogen or nitrous oxide (purity: 99.999%, Messer Schweiz AG), unless stated otherwise. For flash chromatography for analysis, HPLC grade *solvents* were used. Dry THF, Et₂O, CH₃CN, toluene, hexane and CH₂Cl₂ were dried by passage over activated alumina under nitrogen atmosphere using solvent purification system. All *chemicals* were purchased from commercial suppliers and used as such unless stated otherwise. *TLC* was performed on Merck silica gel 60 F254 TLC glass plates or aluminium oxide plates were visualized with UV light, permanganate stain, CAN stain or *p*-anisaldehyde stain. *Melting points* were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. *NMR* spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in CDCl₃, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm (¹H) and 77.16 ppm (¹³C) as standard. *Infrared spectra* were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm⁻¹ (w = weak, m = medium, s = strong, sh = shoulder). *High resolution mass* spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL. Electrospray-ionisation HRMS data were acquired on a Q-ToF Ultima mass spectrometer (Waters) or a Q-ToF 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionisation (APPI) HRMS measurements were done on a LTQ-Orbitrap Elite instrument (ThermoFisher) operated in the positive ionization mode. *Column chromatography* was carried out employing silica gel 230–460 mesh (100 g) deactivated by adding dichloromethane containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying at room temperature under oil pump vacuum overnight.

2. Synthesis of vinyl triazenes

*Safety note: N₂O-lithium amide intermediate generated in the synthesis of **1a** poses a risk of explosion, so a protective blast shield is recommended during the synthesis.*

Following the reported procedure,¹ a Schlenk flask was charged with lithium dicyclohexylamide (1.9 g, 10 mmol, 1.0 equiv.) dissolved in THF (24 mL). The resulting solution was stirred vigorously under N₂O (1 atm) for 1 h at room temperature. A white precipitate formed. The N₂O atmosphere was then replaced by an atmosphere of dry N₂ and vinyl magnesium bromide (15 mL, 1 M in THF, 15 mmol, 1.5 equiv.) was added resulting in the formation of a yellow solution. The solution was stirred for 2 h at 50 °C (oil bath heating). The mixture was then cooled down to room temperature and quenched with water (35 mL), extracted with ethyl acetate (3 x 35 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, the crude product was purified by flash chromatography with a gradient of hexane to hexane/ethyl acetate (5%) as eluent. Compound **1a** was obtained as a white solid. Yield = 1.7 g (73%).

¹H NMR (400 MHz, CDCl₃) δ 7.16 (dd, *J* = 15.5, 7.8 Hz, 1H, CH_{olef}), 5.17 (d, *J* = 15.5 Hz, 1H, CH), 5.00–4.82 (m (br), 1H, CH), 4.76 (d, *J* = 8.1 Hz, 1H, CH_{olef}), 3.53–3.22 (m (br), 1H, CH), 1.84–1.64 (m, 12H, 6 x CH₂), 1.49–1.25 (s, 6H, 3 x CH₂), 1.19–1.07 (d, 2H, CH₂); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 149.2, 104.5, 56.9, 53.5, 34.1, 29.9, 26.2, 25.7, 25.4. The characterization data corresponded to the reported values.¹

*Triazenes **1b-1f** were prepared following the reported procedure by hydrogenation of corresponding 1-alkynyl triazenes.²*

3. Synthesis of silyl enol ethers

General Procedure 1 (GP1):

Following a slightly modified procedure.³ A flame-dried 50 mL round bottom flask was charged with the ketone (2.8 mmol, 1.0 equiv.) and THF (12 mL) under N₂. The reaction mixture was cooled to −78 °C and KHMDS (6.7 mL, 0.5M in toluene, 3.4 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was then stirred for 1 h at room temperature. The reaction mixture was cooled again to −78 °C and the corresponding silyl chloride (3.4 mmol, 1.2 equiv.) was added dropwise. The reaction mixture was then stirred at room temperature for 6 h. The reaction was quenched by adding 2.0 mL of a saturated solution of NaHCO₃ and extracted with Et₂O. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane) to give the title compound.

General Procedure 2 (GP2):

Following a slightly modified procedure.⁴ In a 100 mL flame-dried round-bottom flask equipped with a stirring bar and filled with THF (20 mL), acetophenone (1.0 equiv.) and Et₃N (1.8 equiv.) were added. The solution was stirred at room temperature for 15 min before cooling down to 0 °C. Triisopropylsilyl-trifluoromethanesulfonate (1.2 equiv.) was added *via* a syringe slowly over 2 min at 0 °C. The resulting mixture was stirred under N₂ atmosphere at 0 °C for 24 h. The reaction was then quenched by saturated NaHCO₃ solution (20 mL) and diluted with cooled CH₂Cl₂ (10 mL). The organic layer was washed with cooled saturated NaHCO₃ solution twice, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane) to give the title compound.

tert-butyldiphenyl((1-phenylvinyl)oxy)silane

5a

Following GP1, starting from acetophenone (0.36 g, 2.8 mmol), compound **5a** was obtained as a white solid. Yield = 0.82 g (82%).

¹H NMR (400 MHz, CDCl₃) δ 7.79–7.72 (m, 6H, *ArH*), 7.43–7.30 (m, 9H, *ArH*), 4.75 (d, *J* = 1.5 Hz, 1H, *CH*₂), 4.02 (d, *J* = 1.5 Hz, 1H, *CH*₂), 1.10 (s, 9H, TBDPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 137.5, 135.5, 134.8, 132.4, 129.8, 128.24, 128.20, 127.7, 125.2, 92.2, 26.6, 19.5. The characterization data corresponded to the reported values.⁵

triisopropyl((1-phenylvinyl)oxy)silane

5b

Following GP2, starting from acetophenone (0.580 g, 4.82 mmol), compound **5b** was obtained as a colorless oil. Yield = 1.3 g (93%).

¹H NMR (400 MHz, CDCl₃) δ 7.69–7.65 (m, 2 H, *ArH*), 7.38–7.29 (m, 3 H, *ArH*), 4.85 (d, 1 H, *J* = 1.8 Hz, *CH*₂), 4.41 (d, 1 H, *J* = 1.8 Hz, *CH*₂), 1.39–1.27 (m, 3 H, SiCH(CH₃)₂), 1.19–1.13 (m, 18 H, TIPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 156.2, 138.0, 128.2, 128.1, 125.4, 90.0, 18.2, 12.9. The characterization data corresponded to the reported values.⁴

trimethyl((1-phenylvinyl)oxy)silane

5c

Following GP1, starting from acetophenone (0.36 g, 2.8 mmol), compound **5c** was obtained as a colorless oil. Yield = 0.31 g (58%).

¹H NMR (400 MHz, CDCl₃) δ 7.10–7.39 (m, 5H, ArH), 4.91 (d, *J* = 1.7 Hz, 1H, C=CH₂), 4.43 (d, *J* = 1.7 Hz, 1H, C=CH₂), 0.27 (s, 9H, TMS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 157.7, 136.5, 128.6, 125.9, 125.3, 91.1, 0.17. The characterization data corresponded to the reported values.⁶

tert-butyl((1-(4-fluorophenyl)vinyl)oxy)diphenylsilane

5d

Following GP1, starting from 4-fluoroacetophenone (0.39 g, 2.8 mmol), compound **5d** was obtained as a white solid. Yield = 0.76 g (71%).

R_f 0.24 (Pentane); **Mp** 58–60 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.77 (dt, *J* = 6.7, 1.6 Hz, 4H, ArH), 7.74–7.68 (m, 2H, ArH), 7.47–7.37 (m, 6H, ArH), 7.06 (t, *J* = 8.7 Hz, 2H, ArH), 4.67 (d, *J* = 2.4 Hz, 1H, CH₂), 4.01 (d, *J* = 2.4 Hz, 1H, CH₂), 1.10 (s, 9H, TBDPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 162.9 (d, *J* = 247.4 Hz), 154.4, 135.6, 134.9, 133.8 (d, *J* = 3.2 Hz), 132.4, 130.0, 127.9, 127.1 (d, *J* = 8.1 Hz), 115.1 (d, *J* = 21.6 Hz), 92.0 (d, *J* = 1.7 Hz), 26.7, 19.6; **¹⁹F NMR** (376 MHz, CDCl₃) δ -113.96; **IR** 3072 (w), 2954 (w), 2932 (w), 2858 (w), 1621 (m), 1604 (w), 1505 (m), 1427 (w), 1310 (m), 1220 (m), 1154 (w), 1114 (s), 1098 (m), 1018 (m), 1003 (m), 845 (m), 821 (s), 768 (s), 744 (m); **HRMS** (APCI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₄H₂₆FOSi⁺ 377.1731; Found 377.1723.

tert-butyl((1-(4-methoxyphenyl)vinyl)oxy)diphenylsilane

5e

Following GP1, starting from 4-methoxyacetophenone (0.42 g, 2.8 mmol), compound **5e** was obtained as a yellowish oil. Yield = 1.0 g (94%).

Rf 0.1 (Pentane); **¹H NMR** (400 MHz, CDCl₃) δ 7.81–7.76 (m, 4H, *ArH*), 7.72–7.67 (m, 2H, *ArH*), 7.47–7.36 (m, 6H, *ArH*), 6.95–6.88 (m, 2H, *ArH*), 4.64 (d, *J* = 2.2 Hz, 1H, *CH*₂), 3.93 (d, *J* = 2.3 Hz, 1H, *CH*₂), 3.85 (s, 3H, OCH₃), 1.10 (s, 9H, TBDPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 159.8, 154.9, 135.6, 132.6, 130.3, 129.9, 127.8, 126.6, 113.6, 90.6, 55.4, 26.7, 19.6; **IR** 3074 (w), 2959 (w), 2931 (w), 2856 (w), 1608 (m), 1509 (m), 1313 (m), 1291 (s), 1247 (s), 1172 (m), 1110 (s), 1031 (m), 1003 (m), 820 (m), 764 (s); **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₂₉O₂Si⁺ 389.1931; Found 389.1930.

tert-butyl((1-(naphthalen-1-yl)vinyl)oxy)diphenylsilane

5f

Following GP1, starting from 1-acetonaphthone (0.48 g, 2.8 mmol), compound **5f** was obtained as a white solid. Yield = 1.1 g (96%).

Rf 0.25 (Pentane); **Mp** 43–45 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.48–8.37 (m, 1H, *ArH*), 7.89–7.76 (m, 6H, *ArH*), 7.55–7.35 (m, 10H, *ArH*), 4.52 (d, *J* = 1.5 Hz, 1H, *CH*₂), 4.46 (d, *J* = 1.4 Hz, 1H, *CH*₂), 1.02 (s, 9H, TBDPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 156.6, 137.2, 135.8, 133.8, 132.8, 131.0, 129.9, 128.6, 128.2, 127.7, 126.6, 126.2, 126.0, 125.7, 125.1, 97.9, 26.7, 19.5; **IR**

3071 (w), 2950 (w), 2929 (w), 2856 (w), 1625 (w), 1611 (w), 1470 (w), 1427 (m), 1287 (m), 1248 (m), 1199 (m), 1141 (m), 1111 (m), 1017 (s), 997 (m), 854 (w), 838 (m), 825 (m), 806 (m), 777 (s), 742 (s); **HRMS** (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₂₈H₂₉OSi⁺ 409.1982; Found 409.1979.

4. Synthesis of D-A cyclopropanes

dimethyl (*E*)-2-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopropane-1,1-dicarboxylate

2a

To a solution of (*E*)-3,3-dicyclohexyl-1-vinyltriaz-1-ene (**1a**) (1.4 g, 6.0 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{esp})_2$ (9.0 mg, 0.0118 mmol, 0.2 mol%) in 14 mL of DCM at 0 °C, was added dropwise a solution of dimethyl 2-diazomalonate (1.1 g, 7.2 mmol, 1.2 equiv.) in 8 mL of DCM. The resulting mixture was allowed to slowly warm to room temperature and was stirred overnight. The solvent was removed under vacuum, and the residue was purified by column chromatography using pentane/EtOAc (10:1) to give compound **2a** as a colorless solid. Yield = 1.9 g (87%).

Single crystals suitable for X-ray analysis were obtained from an oily non-solidified batch of 2a upon storage at – 20 °C (freezer).

Rf 0.67 (5:1 Pentane/EtOAc); **Mp** 62–64 °C; **¹H NMR** (400 MHz, CDCl_3) δ 4.44–4.25 (br m, 1H, $\text{CH}_{(\text{cyclohexyl})}$), 4.09–4.05 (m, 1H, $\text{NCH}_{(\text{cyclopropyl})}$), 3.72 (s, 3H, CO_2CH_3), 3.69 (s, 3H, CO_2CH_3), 3.43–3.24 (br m, 1H, $\text{CH}_{(\text{cyclohexyl})}$), 2.15–2.12 (m, 1H, $\text{CH}_{(\text{cyclopropyl})}$), 1.80–1.78 (m, 1H, $\text{CH}_{(\text{cyclopropyl})}$), 1.76–1.61 (m, 11H, $\text{CH}_2_{(\text{cyclohexyl})}$), 1.33–1.10 (m, 9H, $\text{CH}_2_{(\text{cyclohexyl})}$); **¹³C {¹H} NMR** (101 MHz, CDCl_3) δ 170.2, 167.5, 55.6, 52.7, 52.4, 36.0, 34.0, 29.8, 26.2, 25.8, 21.0; **IR** 2921 (m), 2854 (m), 1722 (s), 1448 (s), 1330 (s), 1274 (s), 1201 (s), 1128 (s), 887 (m); **HRMS** (ESI-TOF): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{32}\text{N}_3\text{O}_4^+$ 366.2393; Found 366.2396.

dimethyl (2*S*,3*S*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-phenylcyclopropane-1,1-dicarboxylate
2b

Cyclopropane **2b** was prepared following the procedure for **2a** using **1b** (115 mg, 0.5 mmol), dimethyl 2-diazomalonate (95 mg, 0.6 mmol) and Rh₂(esp)₂ (2 mg, 0.05 mmol). Yield (colorless oil) = 140 mg (64%).

¹H NMR (400 MHz, CDCl₃) δ 7.27–7.21 (m, 5H), 4.81–4.37 (br m, 1H) 4.64 (d, *J* = 6.6 Hz, 1H), 4.22–3.58 (br m, 1H), 3.79 (d, *J* = 6.6 Hz, 1H), 3.74 (s, 3H), 3.44 (s, 3H), 1.34–1.10 (br m, 12H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 167.5, 167.1, 134.6, 129.0, 128.3, 127.3, 57.6, 52.7, 52.3, 47.5 (br), 46.4, 44.6, 36.5, 22.9 (br), 19.9 (br). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₂₈N₃O₄⁺ 362.2074; Found 362.2076.

dimethyl (2*S*,3*S*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate
2c

Cyclopropane **2c** was prepared following the procedure for **2a** using **1c** (130 mg, 0.5 mmol), dimethyl 2-diazomalonate (119 mg, 0.75 mmol) and Rh₂(esp)₂ (2 mg, 0.05 mol). Yield (colorless oil) = 86 mg (44%).

¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.80–4.40 (br m, 1H), 4.59 (d, *J* = 6.5 Hz, 1H), 4.10–3.60 (br m, 1H), 3.78 (s, 3H), 3.75–3.73 (m, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 1.20 (s, 12H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 167.6, 167.1, 158.8, 130.0, 126.4, 113.7, 57.7, 55.3, 52.6, 52.4, 49.2 (br), 46.4 (br), 44.5, 36.0, 23.4 (br), 19.5 (br). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₃₀N₃O₅⁺ 392.2180; Found 392.2163.

dimethyl (2*S*,3*R*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-3-(thiophen-3-yl)cyclopropane-1,1-dicarboxylate
2d

Cyclopropane **2d** was prepared following the procedure for **2a** using **1d** (118 mg, 0.5 mmol), dimethyl 2-diazomalonate (119 mg, 0.75 mmol) and Rh₂(esp)₂ (2 mg, 0.05 mol). Yield (pale-yellow oil) = 119 mg (65%).

¹H NMR (400 MHz, CDCl₃) δ 7.23–7.21 (m, 1H), 7.14–7.13 (m, 1H), 7.02–7.01 (m, 1H), 4.80–4.38 (br m, 1H), 4.55 (d, *J* = 6.5 Hz, 1H), 4.01–3.50 (br m, 1H), 3.73 (s, 3H), 3.69 (d, *J* = 6.4 Hz, 1H), 3.51 (s, 3H), 1.38–1.01 (br m, 12H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 167.3, 167.1, 135.1, 128.3, 125.2, 122.9, 58.4, 52.7, 52.5, 48.8 (br), 46.3 (br), 44.5, 31.9, 23.3 (br), 18.9 (br). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₆N₃O₄S⁺ 368.1639; Found 368.1637.

dimethyl (1*S*,3*S*)-3-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-[1,1'-bi(cyclopropane)]-2,2-dicarboxylate
2e

Cyclopropane **2e** was prepared following the procedure for **2a** using **1e** (103 mg, 0.53 mmol), dimethyl 2-diazomalonate (125 mg, 0.8 mmol) and Rh₂(esp)₂ (2 mg, 0.05 mol). Yield (colorless oil) = 85 mg (52%). Compound **2e** solidified upon storage at –20 °C.

¹H NMR (400 MHz, CDCl₃) δ 4.57–3.50 (br m, 2H), 4.13 (d, *J* = 6.3 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.14 (t, *J* = 6.9 Hz, 1H), 1.30–1.06 (br m, 12H), 0.81–0.73 (m, 1H), 0.60–0.40 (m, 3H), 0.34–0.28 (m, 1H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 168.6, 167.8, 59.3, 52.5, 52.4, 47.1 (br, iPr), 42.2, 36.6, 20.6 (br, iPr), 7.6, 5.3, 4.2. **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₂₈N₃O₄⁺ 326.2074; Found 326.2060.

5. Alcohol addition reactions

General Procedure 3 (GP3).

An oven-dried vial was charged with the cyclopropane **2** and MeOH (0.3 M). The reaction mixture was stirred at 60 °C in an aluminum heating block for 2 h. The solvent was removed under reduced pressure to give the desired compound in analytically pure form.

dimethyl (E)-2-(2-(3,3-dicyclohexyltriaz-1-en-1-yl)-2-methoxyethyl)malonate

3a

Following GP3, compound **3a** was obtained from **2a** (110 mg, 0.3 mmol) as a white solid (118 mg, 99% yield).

Single crystals of 3a suitable for X-ray analysis were obtained from saturated MeOH solution at 4 °C (fridge).

Rf 0.45 (Pentane/EtOAc 10:2); **Mp** 42–44 °C; **¹H NMR** (400 MHz, CDCl₃) δ 4.71 (br m, 1H, NCH_{cyclohexyl}), 4.36 (dd, *J* = 6.9, 5.4 Hz, 1H, NCHO), 3.73 (s, 3H, CO₂CH₃), 3.72 (s, 3H, CO₂CH₃), 3.58 (t, *J* = 7.3 Hz, 1H, (CO₂CH₃)₂CH), 3.35 (br m, 1H, NCH_{cyclohexyl}), 3.17 (s, 3H, OCH₃), 2.39 (dt, *J* = 14.4, 7.3 Hz, 1H, CH₂), 2.23 (ddd, *J* = 14.0, 7.0, 5.4 Hz, 1H, CH₂), 1.83–1.13 (m, 20H, CH_{2(cyclohexyl)}); **¹³C {¹H} NMR** (101 MHz, CDCl₃) 170.1, 170.0, 96.8, 55.4, 52.6, 52.5, 48.0, 34.2, 29.8, 26.0, 25.7; **IR** 2927 (s), 2854 (m), 1750 (s), 1725 (s), 1435 (s), 1331 (m), 1312 (m), 1269 (s), 1192 (s), 1142 (s), 1111 (s), 1068 (s), 1007 (m), 980 (m), 941 (m), 891 (m), 844 (m); **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₃₆N₃O₅⁺ 398.2649; Found 398.2659.

dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-phenylethyl)malonate
3b

Following GP3, compound **3b** was obtained from **2b** (20 mg, 0.045 mmol) as a colorless oil (20 mg, 96% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.22–7.08 (m, 2x5H), 4.92–4.75 (br m, 2x1H), 4.67 (t, *J* = 3.9 Hz, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 4.17 (d, *J* = 10.7 Hz, 1H), 3.96 (m, 2x1H), 3.83 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.77–3.55 (br m, 2x1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.45 (s, 3H), 3.39 (s, 3H), 3.17 (s, 3H), 3.17 (s, 3H), 1.18–0.81 (br m, 2x12H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 169.0, 168.95, 168.64, 168.62, 138.20, 138.13, 129.84, 129.81, 127.98, 127.87, 126.80, 126.75, 100.9, 99.4, 55.93, 55.71, 55.52, 54.2, 52.7, 52.5, 52.3, 52.3, 50.7, 50.6, 47.8 (br), 45.3 (br), 23.3 (br), 19.3 (br). **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₃₂N₃O₅⁺ 394.2336; Found 394.2333.

dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-(4-methoxyphenyl)ethyl)malonate
3c

Following GP3, compound **3c** was obtained from **2c** (39 mg, 0.1 mmol) as a colorless oil (40 mg, 95% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.17–7.09 (m, 2x2H), 6.79–6.68 (m, 2x2H), 4.97–4.74 (br m, 2x1H), 4.63 (d, *J* = 5.7 Hz, 1H), 4.57 (d, *J* = 4.9 Hz, 1H), 4.12 (d, *J* = 10.6 Hz, 1H), 3.92–3.89 (m, 2H), 3.78–3.76 (m, 1H), 3.75–3.72 (m, 4x3H), 3.80–3.58 (br m, 2x1H), 3.47 (s, 3H), 3.42 (s, 3H), 3.17 (s, 2x3H), 1.25–0.85 (br m, 2x12H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 169.1, 169.00, 168.7, 158.42, 158.38, 130.84, 130.81, 130.26, 130.12, 113.43, 113.33, 100.8, 99.4, 55.90, 55.70,

55.5, 55.29, 55.25, 54.3, 52.6, 52.5, 52.3, 49.8, 47.8 (br), 45.4 (br), 23.3 (br), 19.4 (br). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{21}H_{34}N_3O_6^+$ 424.2442; Found 424.2423.

dimethyl (*E*)-2-(2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxy-1-(thiophen-3-yl)ethyl)malonate

3d

Following GP3, compound **3d** was obtained from **2d** (39 mg, 0.1 mmol) as pale yellow oil (40 mg, 95% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, $J = 4.8, 3.1$ Hz, 1H), 7.12 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.06–7.01 (m, 3H), 6.96 (dd, $J = 4.9, 1.3$ Hz, 1H), 4.93–4.77 (br m, 2x1H), 4.68 (d, $J = 7.6$ Hz, 1H), 4.59 (d, $J = 4.8$ Hz, 1H), 4.13–4.06 (m, 2H), 4.00–3.88 (m, 2H), 3.78–3.68 (br m, 2x1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.52 (s, 3H), 3.46 (s, 3H), 3.19 (s, 3H), 3.18 (s, 3H), 1.21–0.89 (br m, 2x12H). **^{13}C { 1H } NMR** (101 MHz, $CDCl_3$) δ 169.00, 168.94, 168.8, 168.7, 138.4, 138.3, 129.1, 128.8, 124.4, 124.2, 123.4, 123.1, 100.2, 98.8, 55.9, 55.7, 55.0, 54.2, 52.7, 52.5, 52.38, 52.36, 47.4 (br), 46.0, 45.8, 44.8 (br), 23.8 (br), 19.2 (br). **HRMS** (ESI/QTOF) m/z : $[M + H]^+$ Calcd for $C_{18}H_{30}N_3O_5S^+$ 400.1901; Found 400.1887.

dimethyl (*E*)-2-(1-cyclopropyl-2-(3,3-diisopropyltriaz-1-en-1-yl)-2-methoxyethyl)malonate

3e

Following GP3, compound **3e** was obtained from **2e** (10 mg, 0.03 mmol) as a colorless oil (10 mg, 93% yield).

1H NMR (400 MHz, $CDCl_3$) δ 5.10–4.92 (br m, 2x1H), 4.51 (d, $J = 6.7$ Hz, 1H), 4.45 (d, $J = 3.8$ Hz, 1H), 3.95 (d, $J = 7.8$ Hz, 1H), 3.90–3.66 (br m, 2x1H), 3.86 (d, $J = 6.8$ Hz, 1H), 3.72 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.16 (s, 3H), 3.15 (s, 3H), 1.91–1.76 (m, 2x1H), 1.19 (br m, 2x12H), 0.94–0.69 (m, 2H), 0.54–0.29 (m, 4H), 0.26–0.01 (m, 4H). **^{13}C { 1H } NMR** (101 MHz,

CDCl₃) δ 170.1, 169.9, 169.8, 169.7, 100.8, 100.0, 55.61, 55.56, 52.8, 52.6, 52.4, 52.2, 52.1, 49.1, 48.8, 47.6 (br), 44.9 (br), 23.6 (br), 19.5 (br), 10.4, 9.8, 5.0, 4.3, 3.7. **HRMS** (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₁₇H₃₂N₃O₅⁺ 358.2336; Found 358.2321.

5.1. Mechanistic study of alcohol addition: deuterium labeling experiment

Cyclopropane **2a** (ca. 10 mg) was dissolved in CD_3OD (0.5 mL) and heated at 60 °C for 2 h. The solvent was removed under reduced pressure, and the product was analyzed by NMR spectroscopy. The mass spectrum (ESI-MS) of the product shows a peak corresponding to **2a**+ CD_3OD + H^+ .

Figure 5.1. ^1H NMR (400 MHz, CDCl_3) spectra of **3a** (top) and **3a-1** + **3a-2** (bottom).

Figure 5.2. ^{13}C NMR (100 MHz, CDCl_3) spectra of **3a** (top) and **3a-1** + **3a-2** (bottom).

Figure 5.3. ^2H NMR (400 MHz, CHCl_3) spectrum of **3a-1** + **3a-2**.

6. (3+2) cycloaddition with TCNE

General Procedure 4 (GP4).

A solution of tetracyanoethylene (1.25–2.00 equiv.) in acetone (0.25 M) was added to a stirred solution of a cyclopropane **2** (1.00 equiv.) in acetone (1.00 M) at room temperature. The mixture was then closed with a cap and heated to 40 °C in an aluminum heating block overnight. The solvent was removed under reduced pressure, and the residue was extracted several times with pentane. Evaporation of pentane afforded the desired product in analytically pure form.

dimethyl (*E*)-2,2,3,3-tetracyano-4-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopentane-1,1-dicarboxylate
4a

Following GP4, product **4a** was obtained from **2a** (46.0 mg, 0.126 mmol) and TCNE (32.0 mg, 0.25 mmol) as a colorless solid. Yield = 40 mg (65%).

Single crystals of 4a suitable for X-ray analysis were obtained from saturated hexane solution at –20 °C (freezer).

¹H NMR (400 MHz, CDCl₃) δ 4.81 (t, *J* = 7.8 Hz, 1H), 4.69–4.62 (m, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.48–3.40 (m, 1H), 3.21 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.95 (dd, *J* = 14.9, 7.9 Hz, 1H), 1.89–1.09 (m, 22 H). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 165.2, 164.8, 110.9, 109.8, 109.4, 108.7, 73.2, 66.4, 58.3, 56.4, 55.2, 54.9, 51.6, 48.7, 36.3, 34.9, 33.7, 29.5, 29.3, 26.2, 26.1, 25.8, 25.74, 25.70, 25.4. **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₂₅H₃₂N₇O₄⁺ 494.2510; Found 494.2488.

dimethyl (*E*)-2,2,3,3-tetracyano-4-(3,3-diisopropyltriaz-1-en-1-yl)-5-(thiophen-3-yl)cyclopentane-1,1-dicarboxylate

4d trans:cis = 2:1

Following GP4, product **4d** was obtained from **2d** (63.0 mg, 0.170 mmol) and TCNE (28.0 mg, 0.21 mmol) as a yellow solid. Yield = 33 mg (40%).

¹H NMR (400 MHz, CDCl₃) δ 7.28–7.24 (m, 4H_{trans} + 1H_{cis}), 7.21–7.19 (m, 1H_{cis}), 7.06–7.01 (m, 2H_{trans} + 1H_{cis}), 5.15 (d, *J* = 9.5 Hz, 1H_{cis}), 5.13 (d, *J* = 11.6 Hz, 2x1H_{trans}), 5.00 (d, *J* = 9.5 Hz, 1H_{cis}), 4.91–4.84 (m, 2x1H_{trans} + 1H_{cis}), 4.55 (d, *J* = 11.6 Hz, 2x1H_{trans}), 3.98 (s, 3H_{cis}), 3.96 (s, 2x3H_{trans}), 3.87–3.77 (m, 2x1H_{trans} + 1H_{cis}), 3.66 (s, 2x3H_{trans}), 3.42 (s, 3H_{cis}), 1.29–1.04 (m, 2x12H_{trans} + 12H_{cis}). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 165.7, 164.5, 132.30, 130.25, 127.7, 127.6, 126.0, 125.7, 124.9, 112.0, 111.6, 110.3, 109.8, 109.6, 109.1, 109.0, 75.2, 70.7, 55.2, 54.8, 54.5, 54.0, 49.6, 49.5, 49.1, 48.9, 48.1, 47.6, 47.5, 23.4, 23.21, 23.17, 19.2, 19.0, 18.81, 18.75. **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₅N₇NaO₄S⁺ 518.1581; Found 518.1556.

dimethyl (*E*)-2,2,3,3-tetracyano-5-cyclopropyl-4-(3,3-diisopropyltriaz-1-en-1-yl)cyclopentane-1,1-dicarboxylate

4e trans:cis = 2:1

Following GP4, product **4e** was obtained from **2e** (18.0 mg, 0.055 mmol) and TCNE (14.0 mg, 0.11 mmol) as a colorless solid. Yield = 11 mg (46%).

¹H NMR (400 MHz, CDCl₃) δ 4.99 (p, *J* = 6.8 Hz, 2x1H_{trans}), 4.90 (p, *J* = 6.9 Hz, 1H_{cis}), 4.75 (d, *J* = 8.3 Hz, 1H_{cis}), 4.65 (d, *J* = 9.4 Hz, 2x1H_{trans}), 3.98–3.95 (m, 2x1H_{trans} + 1H_{cis}), 3.97 (m, 3H_{cis} + 2x3H_{trans}), 3.96 (s, 2x3H_{trans}), 3.90 (s, 3H_{cis}), 2.79 (t, *J* = 9.2 Hz, 2x1H_{trans}), 2.70 (dd, *J* = 11.0, 8.3 Hz, 1H_{cis}), 1.35–1.17 (m, 2x12H_{trans} + 12H_{cis}), 0.98–0.46 (m, 7H_{cyclopropyl}) 0.26–0.20 (m, 2H_{cyclopropyl}), 0.16–0.11 (m, 1H_{cyclopropyl}). **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 165.51, 165.45, 164.7, 164.3, 111.5, 110.0, 109.8, 109.6, 109.4, 109.1, 76.3, 70.5, 70.4, 55.0, 54.8, 54.4, 53.8, 53.4, 52.1, 50.4, 49.8, 49.7, 49.6, 49.1, 47.6, 47.4, 23.7, 23.5, 23.3, 23.3, 19.3, 19.2, 19.1, 19.0, 11.2, 9.0, 5.9, 5.7, 4.2, 3.2, 1.2. **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₈N₇O₄⁺ 454.2197; Found 454.2211.

7. (3+2) cycloaddition reaction with silyl enol ethers

Table S7.1. Optimization of Lewis acid with **5a** at room temperature.

Entry ^[a]	LA	Yield ^[b]	Ratio 6a/8 ^[c]	d.r. ^[c]
1	none	NR		
2	Yb(OTf) ₃	23%	33:67	3.5:1
3	FeCl ₃ -Al ₂ O ₃	15%	91:9	3:1
4	In(OTf) ₃	47%	ND	4:1
5	Hf(OTf)₄	50%	91:9	3:1
6	Sc(OTf) ₃	55%	67:33	3:1

[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at RT. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ¹H NMR of the crude reaction mixture.

Table S7.2. Optimization of Lewis acid with **5a** at $-78\text{ }^{\circ}\text{C}$.

Entry ^[a]	LA	Yield ^[b]	Ratio 6a/8 ^[c]	d.r. ^[c]
1	In(OTf) ₃	<5%	ND	ND
2	Sc(OTf) ₃	<5%	ND	ND
3	Hf(OTf) ₄	40%	>20:1	4.4:1

[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at $-78\text{ }^{\circ}\text{C}$. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ^1H NMR of the crude reaction mixture.

Table S7.3. Temperature optimization with **5a** and Hf(OTf)₄.

Entry ^[a]	Temp	Yield ^[b]	Ratio 6a/8 ^[c]	d.r. ^[c]
1	$-78\text{ }^{\circ}\text{C}$	40%	>20:1	4.4:1
2	$-40\text{ }^{\circ}\text{C}$	84%	>20:1	4.3:1
3	$-20\text{ }^{\circ}\text{C}$	66%	>20:1	3.5:1
4	$0\text{ }^{\circ}\text{C}$	62%	>20:1	3.8:1

[a] Reaction conditions: 0.05 mmol of **2a**, 0.06 mmol of **5a**, 0.005 mmol of LA in DCM (0.05 M) at $-78\text{ }^{\circ}\text{C}$. [b] NMR yields determined for **6a** using 3,4,5-trichloropyridine as internal standard. [c] Determined by ^1H NMR of the crude reaction mixture.

General Procedure 5 (GP5):

An oven-dried flask sealed with a septum was charged in the glovebox with Hf(OTf)_4 (23 mg, 0.030 mmol, 0.1 equiv.) and 3.0 mL of dry DCM. The solution was cooled down to $-40\text{ }^\circ\text{C}$. A solution of the silyl enol ether (0.36 mmol, 1.2 equiv.) in 1.5 mL of dry DCM was then added, followed by a solution of (*E*)-dimethyl 2-(3,3-dicyclohexyltriaz-1-en-1-yl)cyclopropane-1,1-dicarboxylate (**2a**) (0.11 g, 0.30 mmol, 1.0 equiv.) in 1.5 mL of dry DCM. The reaction mixture was stirred at $-40\text{ }^\circ\text{C}$ for 20 h, and then filtered through a short plug of basic alumina eluting with EtOAc. The filtrate was evaporated under reduced pressure. The crude mixture was purified by column chromatography (pentane/EtOAc, 30:1) to give the desired product.

dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenylcyclopentane-1,1-dicarboxylate

6a

Following GP5, compound **6a** was obtained as an inseparable mixture of diastereoisomers (4:1) as a white foam (166 mg, 0.229 mmol, 77% yield). A recrystallization from MeOH gave a d.r. of 16:1 in favor of the *trans* product.

This procedure was carried out in 1 mmol scale using the same general procedure (GP5) with the reagent and solvent loadings multiplied accordingly. The product 6a was isolated in 55% yield (400 mg, 0.55 mmol).

Rf 0.64 (pentane/EtOAc 10:1);

Major diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (ddd, *J* = 8.1, 2.6, 1.3 Hz, 2H, Ar*H*), 7.45 (dt, *J* = 8.1, 1.6 Hz, 3H, Ar*H*), 7.38 (ddt, *J* = 14.9, 7.0, 1.5 Hz, 1H, Ar*H*), 7.33–7.27 (m, 1H, Ar*H*), 7.25–7.10 (m, 5H, Ar*H*), 7.03 (tq, *J* = 7.0, 1.5 Hz, 1H, Ar*H*), 6.99–6.93 (m, 2H, Ar*H*), 4.30 (qd, *J* = 8.4, 6.7 Hz, 1H, CHN_{cyclopentane}), 3.96–3.88 (br m, 1H, NCH_{cyclohexyl}), 3.86 (s, 3H, OCH₃), 3.42 (s, 3H, OCH₃), 2.85–2.75 (m, 2H, (CO₂Me)₂CCH₂ and OCCH₂), 2.75–2.66 (m, 1H, NCH_{cyclohexyl}), 2.55 (dd, *J* = 13.8, 6.7 Hz, 1H, OCCH₂), 2.37–2.28 (m, 1H, (CO₂Me)₂CCH₂), 1.84–1.60 (m, 10H, CH₂ cyclohexyl), 1.54–1.40 (m, 3H, CH₂ cyclohexyl), 1.38–1.26 (m, 3H, CH₂ cyclohexyl), 1.21–1.10 (m, 3H, CH₂ cyclohexyl), 1.04 (s, 9H, TBDPS), 0.92–0.80 (m, 1H, CH₂ cyclohexyl);

¹³C {¹H} NMR (101 MHz, CDCl₃) δ 170.9, 170.3, 143.0, 136.7, 136.3, 134.8, 134.2, 129.3, 129.0, 128.7, 127.3, 127.1, 126.9, 126.8, 89.5, 70.7, 64.9, 55.1, 52.5, 51.8, 46.2, 45.7, 40.1, 32.1, 27.5, 26.4, 26.3, 25.9, 19.8;

Minor diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (ddd, *J* = 8.1, 2.6, 1.3 Hz, 2H, Ar*H*), 7.45 (dt, *J* = 8.1, 1.6 Hz, 3H, Ar*H*), 7.38 (ddt, *J* = 14.9, 7.0, 1.5 Hz, 1H, Ar*H*), 7.33–7.27 (m, 1H, Ar*H*), 7.25–7.10 (m, 5H, Ar*H*), 7.03 (tq, *J* = 7.0, 1.5 Hz, 1H, Ar*H*), 6.99–6.93 (m, 2H, Ar*H*), 4.17 (p, *J* = 8.2 Hz, 1H, CHN_{cyclopentane}), 3.99 (m, 1H, NCH_{cyclohexyl}), 3.83 (s, 3H, OCH₃), 3.47 (s, 3H, OCH₃), 2.98 (dd, *J* = 13.8, 8.6 Hz, 1H, (CO₂Me)₂CCH₂), 2.85–2.75 (m, 1H, OCCH₂), 2.75–2.66 (m, 1H, NCH_{cyclohexyl}), 2.48 (dd, *J* = 13.8, 7.7 Hz, 1H, (CO₂Me)₂CCH₂), 2.37–2.28 (m, 1H, OCCH₂), 1.84–1.60 (m, 10H, CH₂ cyclohexyl), 1.54–1.40 (m, 3H, CH₂ cyclohexyl), 1.38–1.26 (m, 3H, CH₂ cyclohexyl), 1.21–1.10 (m, 3H, CH₂ cyclohexyl), 1.04 (s, 9H, TBDPS), 0.92–0.80 (m, 1H, CH₂ cyclohexyl); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 170.9, 169.8, 143.1, 136.8, 136.2, 134.6, 134.5, 129.3, 128.9, 128.3, 127.3, 127.1, 127.0, 126.8, 89.5, 70.5, 65.5, 55.1, 52.3, 52.2, 47.1, 40.9, 32.1, 24.6, 23.9, 23.1, 19.8, 14.3, 14.2; **IR:** 2981 (m), 2944 (m), 2860 (m), 1734 (m), 1454 (w), 1258 (m), 1136 (s), 846 (w); **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M+H]⁺ Calcd for C₄₃H₅₈N₃O₅Si⁺ 724.4140; Found 724.4163.

dimethyl (2*R*,4*R*)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenyl-2-((triisopropylsilyl)oxy)cyclopentane-1,1-dicarboxylate
6b

Following GP5, compound **6b** was obtained as an inseparable mixture of diastereoisomers (4:1) as a colorless oil (146 mg, 0.228 mmol, 76% yield).

Rf 0.60 (pentane/EtOAc 10:1);

Major diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.89–7.85 (m, 2H, *ArH*), 7.25–7.19 (m, 3H, *ArH*), 4.42 (td, *J* = 8.6, 7.3 Hz, 1H, *CHN*_{cyclopentane}), 4.07–3.87 (br m, 2H, *NCH*_{cyclohexyl}), 3.78 (s, 3H, *OCH*₃), 3.40 (s, 3H, *OCH*₃), 2.85 (dd, *J* = 7.9, 2.3 Hz, 2H, (CO₂Me)₂CCH₂), 2.72 (dd, *J* = 14.0, 8.4 Hz, 1H, OCCH₂), 2.42–2.33 (m, 1H, OCCH₂), 1.84–1.01 (m, 20H, CH₂ cyclohexyl), 0.96 (m, 21H, TIPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 171.0, 170.3, 144.2, 128.4, 127.7, 127.1, 88.1, 70.9, 65.2, 52.4, 51.8, 46.2, 39.7, 32.2, 31.9, 26.3, 25.9, 18.3, 13.7;

Minor diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.70–7.66 (m, 2H, *ArH*), 7.25–7.19 (m, 3H, *ArH*), 4.38–4.29 (m, 1H, *CHN*_{cyclopentane}), 4.07–3.87 (br m, 2H, *NCH*_{cyclohexyl}), 3.74 (s, 3H, *OCH*₃), 3.43 (s, 3H, *OCH*₃), 3.31–3.20 (m, 1H, (CO₂Me)₂CCH₂), 3.00 (dd, *J* = 13.6, 9.5 Hz, 1H, OCCH₂), 2.57 (dd, *J* = 14.8, 6.4 Hz, 1H, (CO₂Me)₂CCH₂), 2.46–2.40 (m, 1H, OCCH₂), 1.84–1.01 (m, 20H, CH₂ cyclohexyl), 0.96 (m, 21H, TIPS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 170.8, 169.4, 143.2, 128.5, 127.5, 126.9, 88.3, 71.6, 65.7, 52.1, 52.0, 46.8, 40.6, 32.2, 31.9, 26.4, 25.9, 18.5, 13.8; **IR** 2930 (s), 2861 (m), 1731 (s), 1455 (s), 1255 (s), 1186 (s), 1135 (s), 1015 (m), 884 (s), 753 (s), 698 (s), 673 (s); **HRMS** (ESI-TOF): *m/z* [M+H]⁺ calcd for C₃₆H₆₀N₃O₅Si⁺ 642.4297; Found 642.4302.

dimethyl (2*R*,4*R*)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-phenyl-2-((trimethylsilyl)oxy)cyclopentane-1,1-dicarboxylate
6c

Following GP5, compound **6c** was obtained as an inseparable mixture of diastereoisomers (2.6:1) as a white foam (95 mg, 0.17 mmol, 57% yield).

Rf 0.41 (pentane/EtOAc 20:1);

Major diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.82–7.76 (2H, m, *ArH*), 7.36–7.26 (3H, m, *ArH*), 4.45 (1H, p, *J* = 8.3 Hz, *CHN*_{cyclopentane}), 3.97 (2H, m, *NCH*_{cyclohexyl}), 3.84 (3H, s, *OCH*₃), 3.43 (3H, s, *OCH*₃), 2.98 (dd, *J* = 13.4, 8.6 Hz, 2H, (CO₂Me)₂CCH₂ and OCCH₂), 2.66–2.58 (m, 1H, (CO₂Me)₂CCH₂), 2.42 (dd, *J* = 13.9, 8.4 Hz, 1H, OCCH₂), 1.90–1.14 (m, 20H, CH₂ cyclohexyl), 0.00 (s, 9H, TMS); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 171.1, 170.2, 143.6, 128.1, 127.5, 127.1, 88.0, 70.8, 65.7, 65.6, 52.1, 51.8, 46.1, 39.9, 32.1, 26.3, 26.3, 25.9, 22.4, 1.8;

Minor diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.65–7.62 (m, 2H, *ArH*), 7.36–7.26 (m, 3H, *ArH*), 4.45 (p, *J* = 8.3 Hz, 1H, *CHN*_{cyclopentane}), 3.97 (m, 2H, *NCH*_{cyclohexyl}), 3.74 (s, 3H, *OCH*₃), 3.54 (s, 3H, *OCH*₃), 3.33 (dd, *J* = 15.0, 10.6 Hz, 1H, (CO₂Me)₂CCH₂), 3.03 (m, 1H, OCCH₂), 2.65 (m, 1H, (CO₂Me)₂CCH₂), 2.53–2.45 (m, 1H, OCCH₂), 1.90–1.14 (m, 20H, CH₂ cyclohexyl), 0.12 (s, 9H); **¹³C {¹H} NMR** (101 MHz, CDCl₃) δ 170.8, 169.7, 142.4, 128.3, 127.3, 126.9, 88.5, 72.2, 65.6, 52.1, 51.7, 46.1, 40.9, 32.1, 29.8, 26.3, 26.3, 25.9, 22.4, 2.2; **IR** 2924 (m), 2850 (w), 1734 (s), 1449 (m), 1249 (s), 1182 (m), 1134 (s), 1082 (m), 891 (m), 839 (s), 754 (m), 700 (s); **HRMS** (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₃₀H₄₈N₃O₅Si⁺ 558.3358; Found 558.3365.

dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(4-fluorophenyl)cyclopentane-1,1-dicarboxylate

6d

Following GP5, compound **6d** was obtained as an inseparable mixture of diastereoisomers (4:1) as a white foam (121 mg, 0.163 mmol, 54% yield).

Rf 0.7 (pentane/EtOAc 10:1);

The signal of $NCH_{\text{cyclohexyl}}$ was overlapping with other signals and could not be properly attributed.

Major diastereoisomer: ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.49 (m, 2H, ArH), 7.49–7.44 (m, 4H, ArH), 7.38–7.27 (m, 2H, ArH), 7.20 (q, J = 8.0 Hz, 4H, ArH), 6.62 (q, J = 9.2, 8.8 Hz, 2H, ArH), 4.38–4.27 (m, 1H, $CHN_{\text{cyclopentane}}$), 3.86 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.81 (ddd, J = 16.6, 14.1, 8.7 Hz, 2H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$ and OCCH_2), 2.49 (ddd, J = 18.7, 13.7, 7.1 Hz, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 2.30 (dd, J = 14.1, 7.9 Hz, 1H, OCCH_2), 1.84–1.10 (m, 20H, $\text{CH}_2_{\text{cyclohexyl}}$), 1.05 (s, 9H, TBDPS); ^{13}C { ^1H } NMR (101 MHz, CDCl_3) δ 170.6, 170.0, 163.1, 160.6, 136.4, 136.1, 130.4, 130.3, 129.3, 129.0, 127.0, 126.9, 113.3, 113.1, 88.8, 70.4, 64.7, 54.9, 52.4, 51.7, 45.7, 39.9, 31.9, 27.3, 27.2, 26.2, 26.1, 25.7, 19.6; ^{19}F NMR (376 MHz, CDCl_3) δ -116.03;

Minor diastereoisomer: ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.49 (m, 2H, ArH), 7.49–7.44 (m, 4H, ArH), 7.38–7.27 (m, 2H, ArH), 7.20 (q, J = 8.0 Hz, 4H, ArH), 6.62 (q, J = 9.2, 8.8 Hz, 2H, ArH), 4.15 (p, J = 8.2 Hz, 1H, $CHN_{\text{cyclopentane}}$), 3.84 (s, 1H, OCH_3), 3.48 (s, 1H, OCH_3), 3.03 (dd, J = 13.8, 9.0 Hz, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 2.81 (ddd, J = 16.6, 14.1, 8.7 Hz, 1H, OCCH_2), 2.68 (dd, J = 14.7, 9.5 Hz, 1H, OCCH_2), 2.49 (ddd, J = 18.7, 13.7, 7.1 Hz, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 1.84–1.10 (m, 20H, $\text{CH}_2_{\text{cyclohexyl}}$), 1.03 (s, 9H, TBDPS); ^{13}C { ^1H } NMR (101 MHz, CDCl_3) δ 170.7, 169.5, 163.0, 160.6, 138.8, 138.8, 136.6, 136.0, 134.3, 134.1, 133.9, 130.1, 130.1, 128.9, 126.7, 113.5,

113.3, 88.7, 70.4, 65.2, 54.9, 52.2, 52.0, 47.0, 46.2, 40.8, 31.9, 27.3, 26.1, 25.7, 19.6; **¹⁹F NMR** (376 MHz, CDCl₃) δ -116.01; **IR** 2931 (m), 2855 (w), 1737 (s), 1513 (m), 1454 (m), 1427 (m), 1253 (m), 1134 (m), 1102 (s), 824 (m), 741 (m), 703 (s); **HRMS** (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₄₃H₅₇FN₃O₅Si⁺ 742.4046; Found 742.4048.

dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(4-methoxyphenyl)cyclopentane-1,1-dicarboxylate

6e

Following GP5, compound **6e** was obtained as an inseparable mixture of diastereoisomers (4.9:1) as a white foam (198 mg, 0.262 mmol, 88% yield).

Rf 0.5 (pentane/EtOAc 10:1);

The signal of NCH_{cyclohexyl} was overlapping with other signals and could not be properly attributed.

Major diastereoisomer: **¹H NMR** (400 MHz, CDCl₃) δ 7.49–7.43 (m, 6H, ArH), 7.34–7.27 (m, 2H, ArH), 7.20 (q, *J* = 7.7 Hz, 4H, ArH), 6.50–6.45 (m, 2H, ArH), 4.28 (p, *J* = 8.0 Hz, 1H, CHN_{cyclopentane}), 3.85 (s, 3H, OCH₃), 3.71 (s, 3H, ArOCH₃), 3.44 (s, 3H, OCH₃), 2.84 (dd, *J* = 14.1, 8.5 Hz, 1H, (CO₂Me)₂CCH₂), 2.73 (dd, *J* = 13.8, 8.7 Hz, 1H, OCCH₂), 2.58–2.49 (m, 1H, OCCH₂), 2.31 (dd, *J* = 14.1, 7.8 Hz, 1H, (CO₂Me)₂CCH₂), 1.83–1.08 (m, 20H, CH₂ cyclohexyl), 1.04 (s, 9H, TBDPS); **¹³C NMR** {**¹H**} (101 MHz, CDCl₃) δ 171.0, 170.3, 158.6, 136.6, 136.3, 135.3, 134.8, 134.3, 129.9, 129.3, 129.0, 127.1, 126.9, 112.0, 89.2, 70.6, 64.9, 55.1, 52.5, 51.8, 46.4, 45.7, 40.1, 32.1, 27.4, 26.3, 26.3, 25.9, 19.7;

Minor diastereoisomer: ^1H NMR (400 MHz, CDCl_3) δ 7.55–7.51 (m, 2H, ArH), 7.43–7.39 (m, 2H, ArH), 7.34–7.26 (m, 4H, ArH), 7.20 (q, $J = 7.7$ Hz, 4H, ArH), 6.51–6.47 (m, 2H, ArH), 4.15 (p, $J = 8.1$ Hz, 1H, $\text{CHN}_{\text{cyclopentane}}$), 3.82 (s, 3H, OCH_3), 3.69 (s, 3H, ArOCH_3), 3.49 (s, 3H, OCH_3), 2.99 (dd, $J = 13.8, 8.6$ Hz, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 2.78 (d, $J = 6.7$ Hz, 1H, OCCH_2), 2.69–2.63 (m, 1H, OCCH_2), 2.49–2.43 (m, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 1.84–1.06 (m, 20H, $\text{CH}_2_{\text{cyclohexyl}}$), 1.01 (s, 9H, TBDPS); ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 171.0, 169.9, 158.6, 136.8, 136.2, 135.4, 134.7, 134.5, 129.9, 129.6, 128.8, 127.0, 126.7, 112.2, 89.2, 70.6, 65.4, 55.2, 52.2, 52.1, 47.1, 40.9, 32.1, 27.4, 26.3, 26.3, 25.9, 19.7; IR 2931 (m), 2856 (w), 1735 (m), 1514 (m), 1453 (m), 1252 (s), 1186 (m), 1106 (s), 1031 (m), 820 (m), 740 (m), 703 (s); HRMS (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{44}\text{H}_{60}\text{N}_3\text{O}_6\text{Si}^+$ 754.4246; Found 754.4229.

dimethyl (2*R*,4*R*)-2-((*tert*-butyldiphenylsilyl)oxy)-4-((*E*)-3,3-dicyclohexyltriaz-1-en-1-yl)-2-(naphthalen-1-yl)cyclopentane-1,1-dicarboxylate

6f

Following GP5, compound **6f** was obtained as a single diastereoisomer as a white foam (115 mg, 0.149 mmol, 49% yield). Product was recrystallized from MeOH at -20 °C. *Recrystallized product contained single crystals suitable for X-ray analysis of 6f.*

Rf 0.63 (pentane/EtOAc 10:1); ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 8.8$ Hz, 1H, ArH), 7.74 (d, $J = 7.6$ Hz, 1H, ArH), 7.70–7.57 (m, 4H, ArH), 7.30 (d, $J = 8.1$ Hz, 2H, ArH), 7.17 (ddt, $J = 23.8, 16.3, 7.4$ Hz, 6H, ArH), 6.95 (t, $J = 7.4$ Hz, 2H, ArH), 3.97–3.78 (br m, 2H, $\text{NCH}_{\text{cyclohexyl}}$), 3.72 (t, $J = 6.2$ Hz, 1H, $\text{CHN}_{\text{cyclopentane}}$), 3.63 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.05 (dt, $J = 13.2, 6.5$ Hz, 2H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$ and OCCH_2), 2.90 (dd, $J = 14.3, 9.1$ Hz, 1H, OCCH_2), 2.43 (dd, $J = 13.7, 5.2$ Hz, 1H, $(\text{CO}_2\text{Me})_2\text{CCH}_2$), 1.85–1.04 (m, 20H, $\text{CH}_2_{\text{cyclohexyl}}$), 0.96 (s, 9H, TBDPS); ^{13}C

¹H NMR (101 MHz, CDCl₃) δ 170.6, 170.5, 138.0, 136.6, 136.0, 134.8, 134.2, 133.9, 132.2, 129.3, 129.2, 128.8, 128.5, 128.1, 127.1, 126.6, 124.6, 124.2, 124.1, 93.0, 63.5, 55.0, 54.7, 52.5, 51.7, 46.9, 41.9, 32.1, 29.8, 27.9, 26.3, 25.9, 20.1; **IR** 2927 (m), 2854 (w), 1730 (s), 1455 (m), 1430 (m), 1255 (m), 1191 (m), 1104 (s), 1074 (m), 1027 (m), 963 (m), 778 (m), 741 (m); **HRMS** (ESI/QTOF) m/z: [M + H]⁺ Calcd for C₄₇H₆₀N₃O₅Si⁺ 774.4297; Found 774.4278.

8. Computational details

All quantum chemical calculations were carried out using the Gaussian16 package.⁷ The molecular structure optimizations were performed using the M06-2X functional⁸ along with the 6-311+G(d,p) basis set for all elements.⁹ Stationary points were verified as minima by subsequent frequency calculations (Number of imaginary frequencies (NIMAG): 0).

NMR chemical shift computations were performed using the GIAO method as implemented in Gaussian 16 and the M06-L functional along with the 6-311(2d,p) basis set for molecular structure obtained at the M06-2X/6-311+G(d,p) level of theory.^{10, 11}

Table S5.1. Calculated absolute energies, E(SCF), and free enthalpies at 298 K, G^{298} , for compounds of interest.

Compound	Method/basis set	E(SCF) [a.u.]	NIMAG ZPVE [kJ mol ⁻¹]	G^{298} [a.u.]
2a	M06-2X/6-311+G(d,p)	-1207.62880	0, 1313	-1207.18664
Carbocation A	M06-2X/6-311+G(d,p)	-1097.82201	0, 1418	-1097.34144
Carbocation B	M06-2X/6-311+G(d,p)	-1097.79210	0, 1417	-1097.31200

Figure S5.1. Calculated differences in Gibbs energy at 298 K, ΔG^{298} for carbocation **A** and carbocation **B** (in kcal·mol⁻¹, at M06-2X/6-311+G(d,p) level).

Figure S5.2. Calculated ¹³C NMR chemical shifts of **2a** (at GIAO/M06L/6-311G(2d,p)//M06-2X/6-311+G(d,p) level).

Figure S5.3. Optimized structure of **2a** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

Figure S5.4. Optimized structure of carbocation **A** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

Figure S5.5. Optimized structure of carbocation **B** at M06-2X/6-311+G(d,p) level. Color code: blue, nitrogen; gray, carbon; white: hydrogen; red: oxygen.

Cartesian Coordinates of Computed Structures

2a, M06-2X/6-311+G(d,p)

O	2.89125315	2.07587532	-0.62044255
C	2.73376799	1.00999757	-0.09251096
O	2.39448232	0.85974696	1.19329384
C	2.85732116	-0.32307117	-0.77398255
C	2.31464285	2.07116688	1.94438875
C	1.56133793	-0.92132695	-1.31712580
C	2.57756719	-0.37520298	-2.25582905
C	3.85534320	-1.30229217	-0.26414789
H	1.99011268	1.78107469	2.94053792
H	1.59837724	2.75506348	1.48812064
H	3.29260358	2.55257131	1.98375632
N	0.40477603	-0.11947504	-1.07789092
H	1.46049662	-1.99721630	-1.21737783

H	2.36215202	0.58434210	-2.70779960
H	3.16247275	-1.08155680	-2.82876290
O	3.92620767	-2.44443866	-0.63715022
O	4.69786293	-0.75813643	0.61992180
N	-0.59919821	-0.81425652	-0.81935772
C	5.69949747	-1.63959441	1.13190681
N	-1.73147223	-0.15277225	-0.60509096
H	6.32425858	-2.01304487	0.32049392
H	5.23368522	-2.48278945	1.64187857
H	6.28577210	-1.04539340	1.82730299
C	-1.72534491	1.31123806	-0.52607091
C	-2.79343646	-0.97984825	-0.02066358
H	-0.99158676	1.62885800	-1.27177245
C	-1.24889002	1.81782359	0.84056590
C	-3.06594350	1.93982431	-0.90373171
H	-3.62454314	-0.30003126	0.18284850
C	-3.27959047	-2.03686854	-1.01545084
C	-2.37185221	-1.62885508	1.30355364
H	-1.98589822	1.53126807	1.60200827
H	-0.30153243	1.33364848	1.09366755
C	-1.10412771	3.34141257	0.81130347
C	-2.91397484	3.46444214	-0.95229126
H	-3.83319855	1.69604354	-0.16077954
H	-3.40216884	1.54783568	-1.86788964
H	-2.43423251	-2.68602462	-1.26663469
H	-3.59574561	-1.54246881	-1.93810023
C	-4.41902487	-2.86667231	-0.41966175
C	-3.51776036	-2.45207243	1.89613102
H	-1.51188285	-2.27772082	1.10774770
H	-2.04244622	-0.85686383	2.00460860

H	-0.31316797	3.60789980	0.09901402
H	-0.78950185	3.71187757	1.79122212
C	-2.41510184	4.01079699	0.38860034
H	-2.20136749	3.73176852	-1.74088472
H	-3.86899534	3.92513386	-1.21701060
H	-5.28686706	-2.21819456	-0.24525313
H	-4.73595852	-3.63054403	-1.13410126
C	-4.00280388	-3.51117105	0.90415780
H	-4.35287487	-1.78640152	2.14846983
H	-3.19574050	-2.92080283	2.82947161
H	-2.28550651	5.09447513	0.32951757
H	-3.17618666	3.82266780	1.15590129
H	-3.19195292	-4.22508349	0.71713070
H	-4.83552401	-4.07760290	1.32921402

Carbocation **A**, M06-2X/6-311+G(d,p)

C	2.63980582	-2.90295930	-0.23422568
C	0.86219500	-1.44180457	0.72646198
C	1.57849448	-2.72258686	0.88560990
N	-0.41504505	-1.40892859	0.53640973
H	1.43391493	-0.51023051	0.74645278
H	0.86939492	-3.55032714	0.90146882
H	2.10394418	-2.68297300	1.84747908
N	-0.82172152	-0.10973884	0.40876523
N	-2.03133852	0.05142433	0.18879882
C	-3.04620969	-1.03750803	0.04336373
C	-2.46585681	1.47804137	0.05976955
H	-2.50465070	-1.96672386	0.20191140
C	-3.61494827	-1.01991709	-1.38001291
C	-4.12923907	-0.89401413	1.11787107

H	-3.53115406	1.43029365	-0.16647980
C	-2.26093450	2.21276216	1.38630307
C	-1.73338044	2.15868250	-1.09797814
H	-4.10884297	-0.06386475	-1.58310822
H	-2.80360115	-1.13737177	-2.10328063
C	-4.63679049	-2.15407765	-1.51876626
C	-5.14319611	-2.03182010	0.94977592
H	-4.64760772	0.06516389	1.01709703
H	-3.67219791	-0.92494699	2.11041216
H	-1.19430763	2.19630882	1.63150609
H	-2.79906856	1.69687881	2.18650295
C	-2.74422946	3.65894660	1.24381857
C	-2.22301457	3.60434162	-1.22441203
H	-0.65921114	2.14467728	-0.89001849
H	-1.90512929	1.60399622	-2.02491557
H	-4.12416554	-3.11681858	-1.41653998
H	-5.06380613	-2.12784824	-2.52279934
C	-5.73538342	-2.04250519	-0.46039321
H	-4.64924785	-2.98914649	1.14880335
H	-5.92998401	-1.92036786	1.69784768
H	-3.82673449	3.66590140	1.07122224
H	-2.57296009	4.18744760	2.18329556
C	-2.03598303	4.36756565	0.08795817
H	-3.28303325	3.60764983	-1.50371019
H	-1.68315106	4.09523596	-2.03607927
H	-6.43895278	-2.87040073	-0.56374729
H	-6.30550883	-1.12037626	-0.62285310
H	-0.96618032	4.44649535	0.31207454
H	-2.41423769	5.38624566	-0.01441850
H	2.12841866	-3.01085490	-1.19349258

H	3.15547279	-3.84514790	-0.03788990
C	3.62152538	-1.75880826	-0.29408101
C	4.62119415	-1.62476407	0.66389543
C	3.52842532	-0.77966304	-1.28910792
C	5.50931313	-0.55135090	0.64807045
H	4.72941791	-2.37909822	1.43789163
C	4.39900422	0.29529706	-1.32129194
H	2.77213399	-0.87158855	-2.06329161
C	5.39754073	0.41842160	-0.34931853
H	6.28131627	-0.49013037	1.40281879
H	4.34189876	1.04865945	-2.09718711
O	6.20126530	1.49702826	-0.46296977
C	7.26376252	1.63832265	0.46321178
H	6.88439397	1.73935906	1.48425354
H	7.94893111	0.78789147	0.40555545
H	7.78853923	2.54687512	0.18002835

Carbocation **B**, M06-2X/6-311+G(d,p)

C	2.84929086	1.23388434	-0.82356579
C	0.93510306	0.33215405	0.43454885
C	1.58375642	0.52647072	-0.99605360
N	-0.31449425	-0.37257553	0.27519442
H	1.61462057	-0.28146971	1.02970114
H	0.88029707	1.11529070	-1.58480141
H	1.69186487	-0.46450316	-1.43689602
N	-1.27231940	0.44452751	0.21593508
N	-2.47445971	-0.02951620	0.06249777
C	-2.78092540	-1.46824498	0.00265967
C	-3.54884298	0.97716295	0.07488963
H	-1.81421346	-1.97208978	-0.02204880

C	-3.54326893	-1.82249100	-1.27777997
C	-3.53207440	-1.92166029	1.25926143
H	-4.47928360	0.40935663	-0.00795444
C	-3.58429054	1.75648196	1.39183353
C	-3.45141260	1.91538977	-1.12967784
H	-4.49529648	-1.28048817	-1.31298990
H	-2.95888861	-1.50929813	-2.14743029
C	-3.82728632	-3.32693215	-1.32443696
C	-3.82256325	-3.42353741	1.19498167
H	-4.47913376	-1.37412481	1.33987212
H	-2.93723563	-1.67652344	2.14356414
H	-2.63155047	2.28372919	1.50771586
H	-3.67568561	1.05628804	2.22735795
C	-4.73774055	2.76255061	1.38950618
C	-4.60192717	2.92491750	-1.12265183
H	-2.49287799	2.44351281	-1.07703468
H	-3.45335702	1.32542825	-2.05098935
H	-2.87804369	-3.87190959	-1.38811404
H	-4.39114740	-3.56728818	-2.22847444
C	-4.58896406	-3.78404615	-0.07888711
H	-2.87483532	-3.97435879	1.21511966
H	-4.38444514	-3.72896216	2.08039352
H	-5.69138228	2.22251247	1.34788099
H	-4.73774682	3.32696776	2.32465307
C	-4.64158032	3.70832594	0.19084713
H	-5.55150057	2.39214140	-1.25369687
H	-4.50398945	3.60426477	-1.97244116
H	-4.76774282	-4.86081278	-0.12009638
H	-5.57253817	-3.29964568	-0.05884762
H	-3.72962350	4.31079455	0.27958639

H	-5.48324305	4.40456581	0.18993666
H	2.81085094	2.32218162	-0.85073059
C	4.07256868	0.67075448	-0.51752489
C	4.26842119	-0.74667854	-0.40844756
C	5.19395000	1.52641371	-0.28665517
C	5.48733000	-1.25468054	-0.08914269
H	3.43542466	-1.41836524	-0.57745517
C	6.42693532	1.02686736	0.02656519
H	5.05348415	2.59918820	-0.36522881
C	6.58642664	-0.37735830	0.12970706
H	5.66596552	-2.31819456	0.00346961
H	7.26115759	1.69308338	0.19438316
O	7.71723815	-0.96455918	0.42380351
C	8.90161743	-0.19065735	0.66302431
H	9.67868633	-0.91685645	0.87817070
H	9.16067091	0.38313662	-0.22779895
H	8.75336641	0.46555520	1.52171767
H	0.80124153	1.30579610	0.91567974

9. Crystallographic data

Bragg-intensities of **2a**, **3a** and **4a** were collected at 140(1) K using Cu $K\alpha$ radiation. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used. The dataset was reduced and corrected for absorption, with the help of a set of faces enclosing the crystal as snugly as possible, with *CrysAlis^{Pro}*.¹² The diffraction data of compound **6f** were measured at low temperature [120(2) K] using Mo $K\alpha$ radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by EvalCCD¹³ and then corrected for absorption.¹⁴

The solution and refinements were performed by the latest available version of *ShelXT*¹⁵ and *ShelXL*.¹⁶ All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the “riding” model in which each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups). For compound **2a**, the major problems found during the refinement of the crystal structure dealt with the disorder of the -COOMe moiety. It was treated by the splitting method and some restraints (SADI and SIMU cards) were applied to bond distances and to the adp's, in order to obtain acceptable values. In the structure **3a**, some moieties are disordered over two orientations each, found in difference maps. These were anisotropically refined by imposing distance and similarity restraints (SADI and SIMU) on the least-squares refinement yielding site occupancies of 0.9298(14)/0.0702(14). In the case of compound **4a** some restraints (ISOR and RIGU cards) were used for the displacement parameters of some atoms. Finally, compound **6f** displayed clear disorder for the -N(cyclohexyl)₂; the substituent was refined by splitting it and by applying restraints (DFIX, SADI, DANG, SIMU) in order to get reasonable adp's and geometric parameters.

Crystallographic and refinement data are summarized in **Table S9.1**. Crystallographic data have been deposited with the CCDC and correspond to the following codes: **2a** (1995416), **3a** (1995157), **4a** (1995417) and **6f** (1995418). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk).

Figure S9.1. X-ray structures of **2a**, **3a**, **4a** and **6f** (hydrogen atoms are omitted for clarity, probability level 50%).

Table S9.1. Crystallographic and refinement data for **2a**, **3a**, **4a** and **6f**.

Compound	2a	3a	4a	6f
Formula	C ₁₉ H ₃₁ N ₃ O ₄	C ₂₀ H ₃₅ N ₃ O ₅	C ₂₅ H ₃₁ N ₇ O ₄	C ₄₇ H ₅₉ N ₃ O ₅ Si
<i>D</i> _{calc.} / g cm ⁻³	1.229	1.214	1.235	1.192
μ /mm ⁻¹	0.702	0.710	0.708	0.103
Formula Weight	365.47	397.51	493.57	774.06
Colour	clear pale yellow	clear colourless	clear pale colourless	colourless
Shape	irregular	prism	plate	prism
Size/mm ³	0.871x0.377x0.346	0.72x0.55x0.14	0.42x0.08x0.06	0.382x0.278x0.072
<i>T</i> /K	140.00(10)	140.00(10)	140.00(10)	120(2)
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	14.2084(3)	8.7504(2)	43.268(5)	16.9645(15)
<i>b</i> /Å	9.04241(18)	8.8246(2)	6.7588(6)	14.2356(18)
<i>c</i> /Å	15.5363(3)	16.0455(4)	40.361(3)	18.3540(19)
α /°	90	82.937(2)	90	90
β /°	98.371(2)	82.375(2)	115.909(11)	103.404(10)
γ /°	90	62.604(3)	90	90
<i>V</i> /Å ³	1974.81(8)	1087.63(6)	10616.6(19)	4311.8(8)
<i>Z</i>	4	2	16	4
<i>Z'</i>	1	1	2	1
Wavelength/Å	1.54184	1.54184	1.54184	0.71073
Radiation type	CuK α	CuK α	Cu K α	Mo K α
θ_{min} /°	5.677	5.577	3.991	1.473
θ_{max} /°	75.460	76.101	66.597	24.997
Measured Refl.	13869	9387	34567	42887
Independent Refl.	4032	4471	9322	7573
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3714	4372	3615	5490
<i>R</i> _{int}	0.0244	0.0131	0.1226	0.0465
Parameters	377	350	653	628
Restraints	112	181	612	450
Largest Peak/e Å ⁻³	0.263	0.446	0.576	1.167
Deepest Hole/e Å ⁻³	-0.194	-0.212	-0.239	-0.535
GooF	1.038	1.120	0.840	1.077
<i>wR</i> ₂ (all data)	0.0955	0.1239	0.2326	0.2139
<i>wR</i> ₂	0.0926	0.1234	0.1938	0.1879
<i>R</i> ₁ (all data)	0.0395	0.0494	0.1564	0.1197
<i>R</i> ₁	0.0361	0.0487	0.0738	0.0833
CCDC code	1995416	1995157	1995417	1995418

10. ¹³C NMR of reported D-A cyclopropanes

D-A cyclopropane	C2 (ppm)	C1 (ppm)	Reference
16.5	27.7	<i>Org. Biomol. Chem.</i> 2018 , 16, 9472-9476 (600 MHz, CDCl ₃)
23.5	34.5	<i>J. Org. Chem.</i> 2009 , 470 (300 MHz, CDCl ₃)
31.8	34.1	<i>J. Am. Chem. Soc.</i> 2006 , 128, 5600-5601 (400 MHz, CDCl ₃)
32.4	37.1	<i>Chem. Eur. J.</i> 2018 , 24, 6062- 6066 (500 MHz, CDCl ₃)
32.2	37.1	<i>Chem. Eur. J.</i> 2018 , 24, 6062- 6066 (500 MHz, CDCl ₃)
32.8	37.2	<i>Eur. J. Org. Chem.</i> 2019 , 5475–5485 (500 MHz, CDCl ₃)
32.2	36.6	<i>Eur. J. Org. Chem.</i> 2019 , 5475–5485 (500 MHz, CDCl ₃)
31.5	35.8	<i>Chem. Eur. J.</i> 2018 , 24, 6062- 6066 (500 MHz, CDCl ₃)
34.9	33.1	<i>Chem. Eur. J.</i> 2018 , 24, 6062- 6066 (500 MHz, CDCl ₃)
55.6	36.0	This work

11. NMR spectra

¹H NMR (400 MHz, CDCl₃) spectrum of **2a**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **2a**.

^1H NMR (400 MHz, CDCl_3) spectrum of **2b**.

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) spectrum of **2b**.

¹H NMR (400 MHz, CDCl₃) spectrum of **2c**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **2c**.

¹H NMR (400 MHz, CDCl₃) spectrum of **2e**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **2e**.

¹H NMR (400 MHz, CDCl₃) spectrum of **3a**.

¹³C{¹H} NMR (101 MHz, CDCl₃) spectrum of **3a**.

¹H NMR (400 MHz, CDCl₃) spectrum of **3c**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **3c**.

¹H NMR (400 MHz, CDCl₃) spectrum of **3d**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **3d**.

¹H NMR (400 MHz, CDCl₃) spectrum of **3e**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **3e**.

¹H NMR (400 MHz, CDCl₃) spectrum of **4a**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **4a**.

¹H NMR (400 MHz, CDCl₃) spectrum of **4d**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **4d**.

¹H NMR (400 MHz, CDCl₃) spectrum of **4e**.

¹H-¹H COSY NMR (400 MHz, CDCl₃) spectrum of **4e**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **4e**.

¹H NMR (400 MHz, CDCl₃) spectrum of **6a**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **6a**.

¹H NMR (400 MHz, CDCl₃) spectrum of **6c**.

¹³C {¹H} NMR (101 MHz, CDCl₃) spectrum of **6c**.

^1H NMR (400 MHz, CDCl_3) spectrum of **6f**.

^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) spectrum of **6f**.

12. References

- 1 Kiefer, G.; Riedel, T.; Dyson, P. J.; Scopelliti, R.; Severin, K. Synthesis of Triazenes with Nitrous Oxide. *Angew. Chem. Int. Ed.* **2015**, *54*, 302–305.
- 2 Suleymanov, A. A.; Scopelliti, R.; Fadaei-Tirani, F.; Severin, K. Synthesis of Vinyl Triazenes by Palladium-Catalyzed Addition Reactions to Alkynyl Triazenes. *Adv. Synth. Catal.* **2018**, *360*, 4178–4183.
- 3 de Nanteuil, F.; Waser, J. Catalytic [3+2] Annulation of Aminocyclopropanes for the Enantiospecific Synthesis of Cyclopentylamines. *Angew. Chem. Int. Ed.* **2011**, *50*, 12075–12079.
- 4 Zhao, J.-F.; Tan, B.-H.; Loh, T.-P. In(iii)-pybox complex catalyzed enantioselective Mukaiyama aldol reactions between polymeric or hydrated glyoxylates and enolsilanes derived from aryl ketones. *Chem Sci* **2011**, *2*, 349–352.
- 5 Ventura, D. L.; Li, Z.; Coleman, M. G.; Davies, H. M. L. Intermolecular C–H functionalization versus cyclopropanation of electron rich 1,1-disubstituted and trisubstituted alkenes. *Tetrahedron* **2009**, *65*, 3052–3061.
- 6 Aggarwal, V. K.; Sheldon, C. G.; Macdonald, G. J.; Martin, W. P. A New Method for the Preparation of Silyl Enol Ethers from Carbonyl Compounds and (Trimethylsilyl)diazomethane in a Regiospecific and Highly Stereoselective Manner. *J. Am. Chem. Soc.* **2002**, *124*, 10300–10301.
- 7 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J. Gaussian16, Revision A. 03, Inc., Wallingford CT, **2016**.

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- 8 Zhao, Y.; Schultz, N. E.; Truhlar, D. G. Design of Density Functionals by Combining the Method of Constraint Satisfaction with Parametrization for Thermochemistry, Thermochemical Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* **2006**, *2*, 364–382.
- 9 (a) McLean, A. D.; Chandler, G. S. Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, Z=11–18. *J. Chem. Phys.* **1980**, *72*, 5639–5648. (b) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- 10 Zhao, Y.; Truhlar, D. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- 11 Deng, W. Cheeseman, J. R. Frisch, M. J. Calculation of Nuclear Spin–Spin Coupling Constants of Molecules with First and Second Row Atoms in Study of Basis Set Dependence. *J. Chem. Theory and Comput.* **2006**, *2*, 1028–1037.
- 12 *CrysAlis^{Pro}*, Rigaku Oxford Diffraction, release 1.171.40.68a, 2019.
- 13 Duisenberg, A. J. M. ; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220–229.
- 14 Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
- 15 *SHELXT* - Integrated space-group and crystal-structure determination, Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.
- 16 *SHELXL* - Crystal structure refinement, Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.