RESEARCH ARTICLE

Check for updates

Scope and mechanistic insight into the chemistry of cyanocarbenes derived from alkynyl triazenes by UV irradiation†

Melina Maag, [ID] [a] Linus Bjarne Dittmer, [ID] [b] Elena Michel,[a]
Alexandra V. Mackenroth, [ID] [a] Martin C. Dietl, [ID] [a] Frank Rominger,[a]
Matthias Rudolph,[a] Andreas Dreuw [ID] [b] and A. Stephen K. Hashmi [ID] *[a,c]

Herein we disclose a systematic evaluation of the scope and limitations for the use of alkynyl triazenes for the synthesis of cyano-substituted cyclopropanes and cyclopropenes. The method is based on the formation of a cyanocarbene by cleavage of the N1–N2 bond of the alkynyl triazene precursor under UV light, which then reacts with a styrene or alkyne to form the respective products, making this a simple approach avoiding metals typically used in related reactions of organic azides. Different substituents on the triazene moiety, N-terminus and styrene/alkyne were investigated concerning their influence on the yield and diastereoselectivity with respect to the resulting cyclopropanes. The study showed that electron-rich aryl substituents at the alkynyl triazenes enable a good diastereomeric excess favouring the anti-diastereomer. Accompanying computational studies revealed that this diastereomeric preference can be qualitatively predicted from the relative stability of the singlet and triplet states of the cyanocarbene, as well as the dispersive attraction between the carbene and the olefin.

Introduction

Since the middle of the last century, triazenes have attracted significant interest within the scientific community regarding their use in organic synthesis,[1] coordination chemistry[2] and medicine.[3] These findings were all based on alkyl or aryl triazenes and only recently have alkynyl triazenes received some attention. In 2015, Severin *et al.* discovered an elegant synthetic access towards this novel class of triazenes. Compared to conventional triazenes, these compounds exhibit a distinct reactivity.[4] Their synthetic route involved the incorporation of nitrous gas for the construction of the triazene moiety, giving access to a vast variety of different alkynyl triazenes (Scheme 1).[4] This wide range of synthesizable triazenes already enabled fruitful contributions to organic synthesis

which were based on metal or Lewis acid catalysis.[5] Subsequently, Hashmi *et al.* investigated their reactivity under UV light irradiation, revealing the potential to use alkynyl triazenes as cyanocarbene precursors, which enabled access to nitrile-functionalized products like hydrazones without the need for common cyanating agents of any kind (Scheme 1).[6] Initial trapping experiments with alkenes and alkynes were also conducted, however, additional insight into the reactivity, synthetic utility and state of the intermediate species is still needed. The formation of hydrazones was consistently identified as a side product in all photolyses of triazenes. Furthermore, the zwitterion generated from the photolysis was observed to undergo recombination (see Scheme 1).[6]

[a]*Organisch-Chemisches Institut (OCI), Heidelberg University,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. E-mail: hashmi@hashmi.de*
[b]*Interdisziplinäres Zentrum für Wissenschaftliches Rechnen (IWR),
Heidelberg University, Im Neuenheimer Feld 205, 60120 Heidelberg, Germany.
E-mail: dreuw@uni-heidelberg.de*
[c]*Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah,
21589, Saudi Arabia*
†Electronic supplementary information (ESI) available: Experimental procedures, analytical data and spectra. CCDC 2384415 and 2384416. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4qo02023e

Scheme 1 Synthetic route to alkynyl triazenes using nitrous oxide by Severin *et al.*,[4] subsequent photolysis to the cyanocarbene and transformations to the nitrile-substituted products by Hashmi *et al*[6].

2180 | *Org. Chem. Front.*, 2025, **12**, 2180–2186

This journal is © the Partner Organisations 2025

Results and discussion

In this study, we further extend the knowledge on the reactivity of cyanocarbenes generated from alkynyl triazenes under UV light irradiation. First, the scope and limitations of the reaction with styrene derivatives, which are known to be effective trapping reagents for carbenes, was investigated. In addition, since two different diastereomers can be formed in this reaction (Scheme 2), the diastereoselectivity might serve as a probe to investigate the reactivity and nature of the generated carbene.[7]
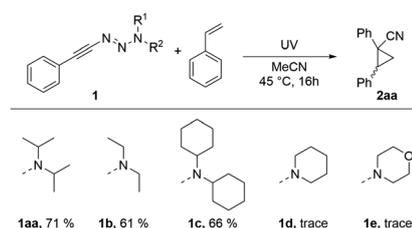
Related reactions using alternative cyanocarbene precursors have been studied before, including reactions of rhodium carbenoids, derived from diazo compounds,[7a] and reactions of hypervalent iodonium alkynyl triflates (HIATs) with azides[8] (Scheme 3). The rhodium-catalyzed reactions by Davies *et al.* produce cyclopropanes with high diastereoselectivity and enantioselectivity of 83–90% ee, but have the drawback of depending on the rather expensive $[Rh_2(S\text{-}PTAD)_4]$ catalyst.[7a] A metal-free alternative applying HIATs by Croatt *et al.* circumvents this problem, however it yields cyclopropanes with no diastereoselectivity and in low yields of 18–61%.[8] This work aims at improving the yield and diastereoselectivity by employing alkynyl triazenes under UV light and their photolysis, a metal-free protocol. Additionally, it was anticipated that this approach will provide further insight into the reactivity and spin state of the carbene.

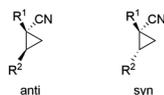The reaction of alkynyl triazenes with olefins offers three points of variation that can impact diastereoselectivity and yield: the substituents at the N-terminus, the olefin, and the triazene-bound aryl moiety.

First, we studied the effects of different substituents at the N-terminus of the triazene on the yield and diastereoselectivity of the cyclopropanes. As shown in Scheme 4, the best yield of 71% was achieved by using isopropyl-substituents **1aa** whereas diethyl- **1b** or dicyclohexyl-substituents **1c** gave slightly lower yields of 61% and 66%. If the N-atom was incorporated in the ring such as in **1d** and **1c**, the product was only detected in trace amounts. The different functionalization of the N-terminus showed no influence on the diastereoselectivity. Therefore, in the following investigations, diisopropyl triazenes **1aa** were employed. This choice was made as the reactant for the corresponding alkynyl triazene synthesis, lithium diisopropylamide (LDA), is commercially available and consequently easily accessible.
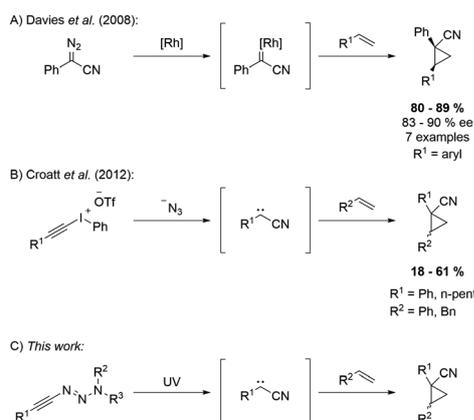
Since different substituents at the N-terminus showed no influence on the diastereoselectivity, the focus was shifted to variations of the olefin (Scheme 5). Interestingly, only reactions with styrenes were observed while alkyl-substituted olefines

Scheme 2 Anti- and syn-diastereomers of nitrile-substituted cyclopropanes as possible products.

Scheme 3 (A) Rhodium-catalyzed syntheses of cyclopropanes;[7a] (B) syntheses of cyclopropanes with HIATs;[8] (C) UV light-mediated photolysis of alkynyl triazenes.

Scheme 4 Screening of the reaction to cyclopropanes with triazenes with different N-terminal substitutions. 200 μmol triazene in a degassed 1 : 1 mixture of styrene : MeCN (0.8 mL).
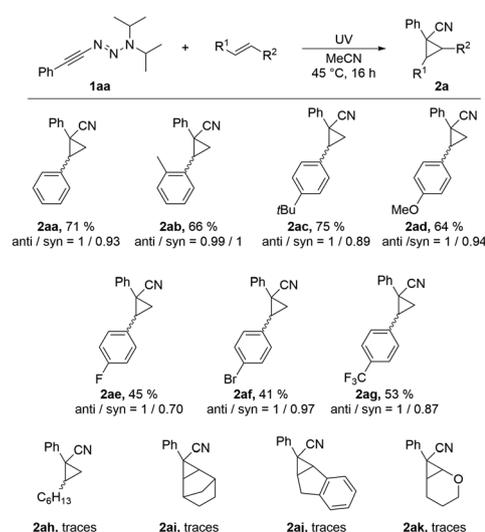
Scheme 5 Synthesis of cyclopropanes **2a** with different olefins. 200 μmol triazene in a degassed 1 : 1 mixture of styrene : MeCN (0.8 mL). Yield obtained after purification. Diastereomeric ratio determined by ^{1}H NMR.

gave the product in trace amounts, which is in line with observations by Davies *et al.* and Croatt *et al.*[7a,8] Moreover, stilbenes showed no reactions to cyclopropanes. Reactions with styrene derivatives yielded cyclopropanes **2a** in yields ranging from 41% to 71%. Compared to electron-poor styrenes, electron-rich styrenes resulted in higher yields of 64% to 71%. Regarding their diastereoselectivity, the anti-diastereomer exhibited a slight diastereomeric excess of 2% to 10%, favouring the anti-diastereomer in cyclopropanes **2aa**, **2ac**, **2ad**, **2ae**, **2af** and **2ag**, whereas cyclopropane **2ab** showed no diastereomeric excess. Compared to Croatt *et al.*,[8] who achieved yields ranging from 18–61%, the yield could be improved to 41–71%, featuring a wider range of synthesised cyclopropanes. The recombination of the N2–N3 fragment with the cyanocarbene leads to the formation of hydrazone as a side product (see Scheme 1), which consequently reduces the yield of all synthesized cyclopropanes and cyclopropenes.

The investigated olefins exhibited a significant impact on the yield but not on the diastereoselectivity. Consequently, the influence of the triazene-bound aryl moiety was studied by reacting different alkynyl triazenes **1aa–1ak** with styrene (Scheme 6). As expected, no reaction was observed with an alkyl substituent, which was already noted in the UV-mediated hydrazone synthesis by Hashmi *et al.*[6] Aryl substituents, on the other hand, gave yields in the range of 46% to 85%. The triazene-bound aryl moiety is therefore crucial for the excitation of the triazene and its subsequent photolysis. Interestingly, triazenes with electron-rich aryl substituents produced cyclopropanes with a diastereomeric excess ranging from 76% to 94% with the major diastereomer being the anti-diastereomer. This was confirmed by crystallographic data of
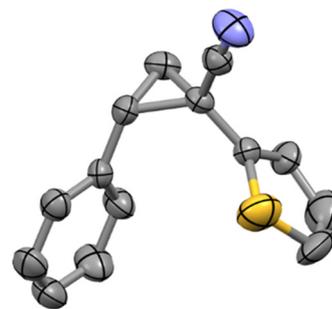

Fig. 1 Molecular structure of **2bc** in the solid state (thermal ellipsoids are shown at a 50% probability). The carbon atoms are shown in grey, nitrogen blue and sulfur yellow.[9]

2bc (Fig. 1) and by comparison with NMR data (Table s1, see ESI†). In contrast, triazenes with electron-poor and neutral substituents showed a lower diastereomeric excess of 2% to 40% while still favouring the anti-diastereomer.

In addition to crystallographic data of **2bc** (Fig. 1), a comparison of the ^{1}H NMR peaks of the H-atom indicated in Table s1 (see ESI†) of various literature-known diastereoselective nitrile-substituted cyclopropane compounds was performed. The cyclopropane bound H-atom of the anti-diastereomer possesses the characteristic peak of a doublet of a doublet or pseudo triplet at 3.10 to 3.20 ppm, whereas the syn-diastereomer has a characteristic pseudo triplet peak at 2.75 to 2.85 ppm (Scheme 7). This comparison confirmed the major diastereomer of compounds **2ba**, **2bb**, **2bc**, and **2bd** to be the anti-diastereomer.

To get further insight into the dependence of the diastereomeric preference on the electronic structure of the alkyne substituent, computational studies of the mechanism of the cyclopropanation were performed (computational details can be found in the ESI†). We investigated a potential concerted mechanism *via* the singlet carbene and a stepwise mechanism
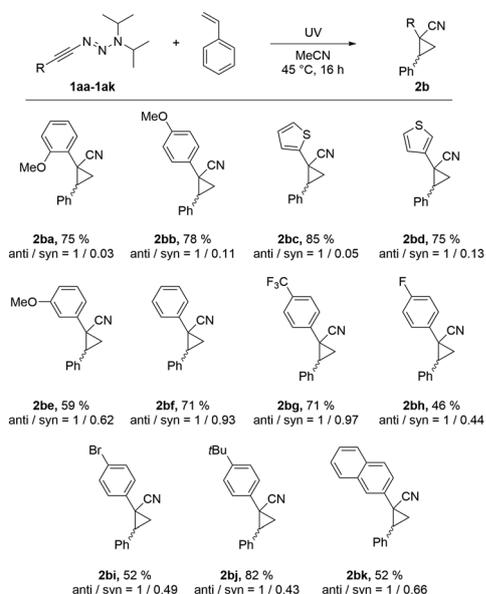
Scheme 6 Synthesis of cyclopropanes **2b** with different alkynyl triazenes. 200 μmol triazene in a 1:1 mixture degassed styrene : MeCN (0.8 mL). Yield obtained after purification. Diastereomeric ratio determined by ^{1}H NMR.
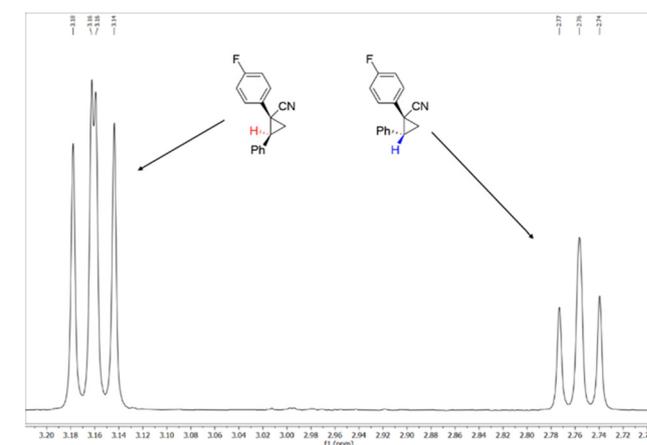
Scheme 7 Example of characteristic ^{1}H NMR peaks of compound **2bh** of the cyclopropane bound H-atom used to distinguish the syn- and anti-diastereomer.

2182 | *Org. Chem. Front.*, 2025, **12**, 2180–2186

This journal is © the Partner Organisations 2025

via the triplet carbene (both mechanistic alternatives presented in Scheme 8). Taking the cycloaddition of the cyanocarbene of alkynyl triazene **1aa** and styrene as a model system, we determined that the addition to the anti-diastereomer proceeds without a barrier, while addition to the syn-diastereomer occurs with a barrier of approximately 1.75 kcal mol^{-1}. We note that the computational method used within this study tends to underestimate barrier heights by 0.5–2.5 kcal mol^{-1},[10] therefore this value can be interpreted as a lower estimate of the real barrier. The reason for this kinetic selectivity of diastereomers is the lack of effective dispersion interaction during formation of the syn-diastereomer, as the two aromatic rings are more distant than in the anti diastereomer. Therefore, singlet cyanocarbenes react with olefins to form overwhelmingly anti-cyclopropanes.

Since triplet carbenes commonly react as electrophiles,[11] we investigated the reaction pathway of nucleophilic attack by the olefin. It was determined that formation of a triplet biradical species possesses a barrier of 1.73 kcal mol^{-1}. To balance dispersive attraction between the aromatic substituents, steric repulsion, as well as the Fermi repulsion of the radicals, the aromatic planes of this biradical are oriented at a relative angle of 69.3°, which is illustrated in Scheme 8. This orientation is close enough to perpendicular that solvent collisions and thermal fluctuations can cause the molecule to cyclize into either the syn- or the anti-diastereomer. Since these processes are completely isotropic, neither isomer is statistically preferred if the attraction between the aromatic rings is weak. Introduction of dispersive groups, such as *tert*-butyl or trifluoromethyl groups, increases the barrier of rotation and thus slightly favours formation of the anti-diastereomer. Notably, the intermediate must first undergo an intersystem crossing to cyclize, which is a fast process in solution. We thus conclude that triplet carbenes react with olefins to form an approximate 1 : 1 ratio of both diastereomers, where the exact ratio depends on the dispersive interactions of olefin and carbene substituents.

These observations allow for a straightforward determination of the diastereomeric preference of each cyanocarbene: As the cyano group stabilizes the carbene sufficiently for solvent or light-mediated intersystem crossing to take place,[12] we can assume the carbene spin states to be in chemical equilibrium. Furthermore, we may view all cyclopropanation steps as irreversible and neglect the reaction of singlet carbene to the syn-diastereomer. This mechanistic simplification is possible despite its small barrier, because it is directly in competition with the barrierless formation of the anti-diastereomer. Lastly, we presume the formation of the biradical species to be the rate-determining step in the reaction of the triplet carbene with an olefin.

With these assumptions we can predict the two central determining factors to be the equilibrium between the singlet–triplet carbene as well as the relative rates of cyclization for each diastereomer from the biradical mechanism. The former is physically determined from the adiabatic singlet–triplet gap of the carbene, which in turn is influenced by the electronic properties of the carbene substituents. Mesomeric, electron-withdrawing substituents on the aromatic ring as well as the cyano group strongly stabilise the triplet state, favouring a triplet ground state and thus the biradical mechanism. With increasing electron richness of the aromatic ring, however, the triplet state gets destabilized, and the singlet mechanism becomes energetically viable. We want to highlight the example of **2bc**, where the singlet is 3.04 kcal mol^{-1} more stable than the triplet, which thus causes the observed high diastereomeric excess.

The relative rates of formation of each diastereomer from the biradical species are mostly determined by the geometry of the biradical species and the required energy for rotation of the aryl planes. If the aromatic substituents show comparably strong dispersive attraction, the angle between the aromatic planes decreases and the barrier for rotation increases. Therefore, aromatic substituents with strong dispersive interactions slightly favour the formation of the anti-diastereomer. This can especially be seen in **2bg**, **2ac** and **2ag**. We note that these dispersive forces are nonetheless relatively weak and are thus only able to exert measurable, but minor influence on the diastereomeric ratio.

Finally, the synthesis of a cyclopropane *via* an intramolecular reaction of **3a** and **3b** was evaluated (Scheme 9). The respective en-yne was synthesized according to a literature procedure by Echavarren *et al.*[13] and the triazene was synthesized based on the alkynyl triazene synthesis by Severin *et al.*[4] The structure of the cyclopropane was confirmed by crystallographic data. Interestingly, in contrast to the previously conducted intermolecular reactions (Scheme 5), only substituted olefins reacted to form the desired cyclopropane **4a** in high yield.

In the next step, the UV light-mediated cyclopropenation using alkynyl triazenes with alkynes was studied (Scheme 10).
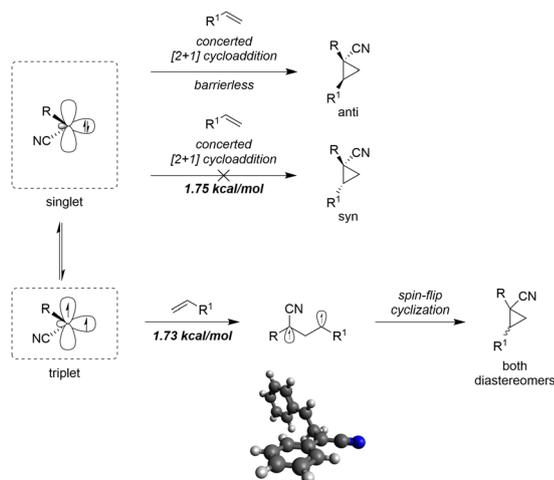

Scheme 8 Mechanism of cyclopropanation. Intersystem crossing and cyclization in the triplet mechanism are assumed to be much faster than the nucleophilic attack of the olefin. The 3D structure shown depicts the minimum potential energy geometry for the triplet biradical.

This journal is © the Partner Organisations 2025

Org. Chem. Front., 2025, **12**, 2180–2186 | **2183**
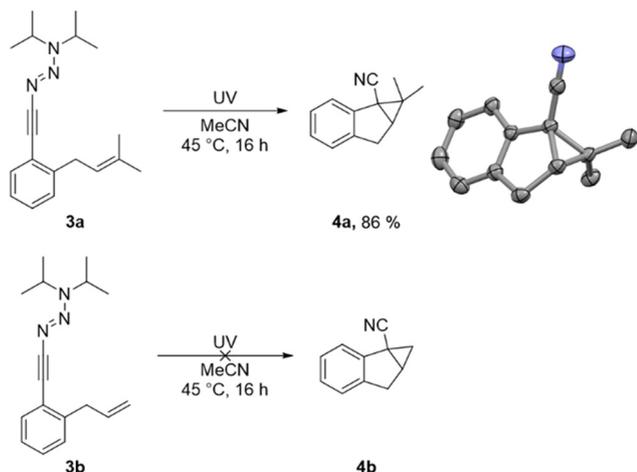
Scheme 9 Synthesis of **4a** *via* intramolecular cyclopropanation. 200 μmol triazene in degassed MeCN (0.8 mL). Yield obtained after purification. Molecular structure of **4a** in the solid state (thermal ellipsoids are shown at a 50% probability). The carbon atoms are shown in grey, nitrogen in blue.[9]
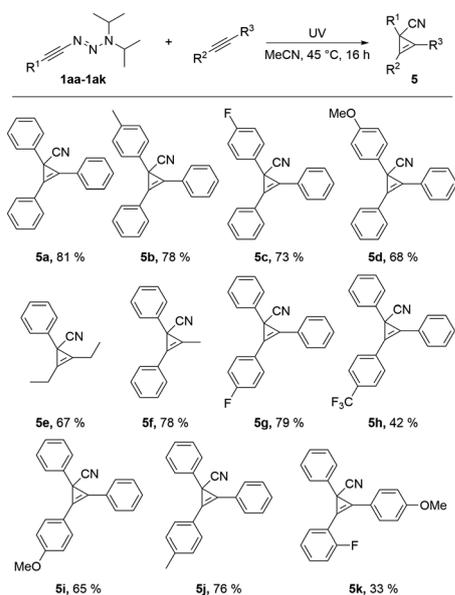
Scheme 10 Synthesis of cyclopropenes **5** with different alkynes and triazenes. 200 μmol triazene and 5.00 eq. alkyne in degassed MeCN (0.8 mL). Yields obtained after purification.

Triazenes and alkynes were varied to give a wide range of nitrile-substituted cyclopropenes **5**. Both aryl and alkyl groups were successfully utilized, yielding the desired products in good yields of 33% to 81%. Interestingly, alkyl groups at the alkyne were well tolerated, in contrast to the cyclopropanation reaction, where only styrenes were successfully employed. Furthermore, only tolanes were reactive, while cyclopropenes from terminal alkynes could not be synthesized. This contrasts with the cyclopropanation reaction, where stilbene showed no reaction.

Conclusion

In this work, we explored the use of cyanocarbenes formed by UV photolysis of alkynyl triazenes with styrenes or alkynes to form cyclopropanes and cyclopropenes. We studied the effect of the used olefins and triazenes on the yield and diastereoselectivity of the resulting cyclopropanes. Our findings indicate that electron-rich aryl substituents on the alkynyl triazenes significantly increase the diastereomeric excess favouring the anti-diastereomer over the syn-diastereomer, which in combination with the easy synthesis of the starting alkynyl triazenes delivers an attractive metal free alternative towards cyano-substituted cyclopropanes. These findings led us to further investigate the reactivity of the cyanocarbene precursor *via* computational methods. We confirmed that the presence of an electron-rich aromatic moiety is the central determining factor for good diastereomeric ratios, as it stabilizes the singlet state of the cyanocarbene relative to its triplet state. This causes the reaction to proceed primarily *via* a concerted [2 + 1] cycloaddition mechanism, which strongly favours the anti-diastereomer. We additionally found that dispersive attraction between the olefin and cyanocarbene play a minor role in determining the diastereomeric ratio, as strong dispersive interaction slightly favours the formation of the anti-diastereomer as well. Besides we could demonstrate that this approach is also feasible for metal-free cyclopropenations in moderate to good yields.

Data availability

The authors declare that all the data used for this manuscript can be found in its ESI.† The single crystal structures used in this manuscript have been assigned the CCDC numbers 2384415–2384416.

Conflicts of interest

There are no conflicts to declare.

References

1 (*a*) K. Nicolaou, C. N. Boddy, H. Li, A. E. Koumbis, R. Hughes, S. Natarajan, N. F. Jain, J. M. Ramanjulu, S. Bräse and M. E. Solomon, Total Synthesis of Vancomycin —Part 2: Retrosynthetic Analysis, Synthesis of Amino Acid Building Blocks and Strategy Evaluations, *Chem. – Eur. J.*, 1999, **5**, 2602–2621; (*b*) S. Bräse, S. Dahmen and M. Pfefferkorn, Solid-phase synthesis of urea and amide libraries using the T2 triazene linker, *J. Comb. Chem.*, 2000, **2**, 710–715; (*c*) L. Jones, J. S. Schumm and J. M. Tour, Rapid Solution and Solid Phase Syntheses of Oligo(1,4-phenylene ethynylene)s with Thioester Termini: Molecular Scale Wires with Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support, *J. Org. Chem.*,

2184 | *Org. Chem. Front.*, 2025, **12**, 2180–2186

This journal is © the Partner Organisations 2025

1997, **62**, 1388–1410; (d) J. S. Moore, Shape-persistent molecular architectures of nanoscale dimension, *Acc. Chem. Res.*, 1997, **30**, 402–413; (e) W. Wirschun, M. Winkler, K. Lutz and J. C. Jochims, 1, 3-Diaza-2-azoniaallene salts: cycloadditions to alkynes, carbodiimides and cyanamides, *J. Chem. Soc.*, 1998, 1755–1762.

2 (a) C. Verma, A. Thakur, R. Ganjoo, S. Sharma, H. Assad, A. Kumar, M. Quraishi and A. Alfantazi, Coordination bonding and corrosion inhibition potential of nitrogen-rich heterocycles: Azoles and triazines as specific examples, *Coord. Chem. Rev.*, 2023, **488**, 215177; (b) G. Albertin, S. Antoniutti, M. Bedin, J. Castro and S. Garcia-Fontán, Chemistry of azoethenes and azoethynes. I. Synthesis of phenylazoethynylbenzene and its derivatives, *Inorg. Chem.*, 2006, **45**, 3816–3825; (c) D. Wang, J. Unold, M. Bubrin, I. Elser, W. Frey, W. Kaim, G. Xu and M. R. Buchmeiser, Ruthenium–Triazene Complexes as Latent Catalysts for UV-Induced ROMP, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5462–5468; (d) W. Knoth, Triazene complexes of Group VIII metals, *Inorg. Chem.*, 1973, **12**, 38–44.

3 (a) A. P. Francisco, E. Mendes, A. R. Santos and M. J. Perry, Anticancer triazenes: from bioprecursors to hybrid molecules, *Curr. Pharm. Des.*, 2019, **25**, 1623–1642; (b) P. Ravula, H. B. Vamaraju, M. Paturi, S. Bodige, K. C. Gulipalli and J. N. Sharath Chandra, Design, synthesis, and docking studies of novel dimethyl triazene incorporated thiazolyl pyrazolines for anticancer activity, *J. Heterocycl. Chem.*, 2018, **55**, 1313–1323; (c) E. Carvalho, J. Iley, M. d. J. Perry and E. Rosa, Triazene drug metabolites: Part 15. Synthesis and plasma hydrolysis of anticancer triazenes containing amino acid carriers, *Pharm. Res.*, 1998, **15**, 931–935.

4 (a) G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti and K. Severin, Synthesis of triazenes with nitrous oxide, *Angew. Chem., Int. Ed.*, 2015, **54**, 302–305; (b) G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti and K. Severin, Synthese von Triazenen mit Distickstoffmonoxid, *Angew. Chem.*, 2015, **127**, 306–310.

5 (a) J.-F. Tan, C. T. Bormann, F. G. Perrin, F. M. Chadwick, K. Severin and N. Cramer, Divergent synthesis of densely substituted arenes and pyridines via cyclotrimerization reactions of alkynyl triazenes, *J. Am. Chem. Soc.*, 2019, **141**, 10372–10383; (b) T. Wezeman, R. Scopelliti, F. F. Tirani and K. Severin, Synthesis of Heteroaryl Triazenes via Rh(III)–catalyzed Annulation Reactions with Alkynyl Triazenes, *Adv. Synth. Catal.*, 2019, **361**, 1383–1388; (c) C. T. Bormann, F. Fadaei-Tirani, R. Scopelliti and K. Severin, Synthesis of bicyclic vinyl triazenes by Ficini-type reactions, *Org. Biomol. Chem.*, 2021, **19**, 8113–8117; (d) L. Zeng, Z. Lai, C. Zhang, H. Xie and S. Cui, Directing-group-enabled cycloaddition of azides and alkynes toward functionalized triazoles, *Org. Lett.*, 2020, **22**, 2220–2224; (e) S. Lv, H. Zhou, X. Yu, Y. Xu, H. Zhu, M. Wang, H. Liu, Z. Dai, G. Sun and X. Gong, Lewis base-catalyzed intermolecular triazene alkyne cycloaddition for late-stage functionalization and scaffold diversification, *Commun. Chem.*, 2019, **2**, 69.

6 (a) E. Michel, F. F. Grieser, A. V. Mackenroth, M. Schukin, P. Krämer, S. Tahir, F. Rominger, M. Rudolph and A. S. K. Hashmi, Lichtinduzierte, metallfreie Erzeugung von Cyanocarbenen aus Alkinyltriazenen für die Synthese von Nitrilderivaten, *Angew. Chem.*, 2023, **135**, e202309274; (b) E. Michel, F. F. Grieser, A. V. Mackenroth, M. Schukin, P. Krämer, S. Tahir, F. Rominger, M. Rudolph and A. S. K. Hashmi, Light-Induced Metal-Free Generation of Cyanocarbenes from Alkynyl Triazenes for the Synthesis of Nitrile Derivatives, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309274.

7 (a) J. R. Denton, K. Cheng and H. M. Davies, Stereoselective construction of nitrile-substituted cyclopropanes, *Chem. Commun.*, 2008, 1238–1240; (b) J. M. Fraile, J. I. García, V. Martínez-Merino, J. A. Mayoral and L. Salvatella, Theoretical (DFT) insights into the mechanism of copper-catalyzed cyclopropanation reactions. Implications for enantioselective catalysis, *J. Am. Chem. Soc.*, 2001, **123**, 7616–7625; (c) D. T. Nowlan, T. M. Gregg, H. M. Davies and D. A. Singleton, Isotope effects and the nature of selectivity in rhodium-catalyzed cyclopropanations, *J. Am. Chem. Soc.*, 2003, **125**, 15902–15911; (d) T. Ikeno, I. Iwakura, S. Yabushita and T. Yamada, Theoretical analysis of the reaction pathway and the effect of the axial ligand for 3-oxobutylideneaminatocobalt(II)-catalyzed cyclopropanation, *Org. Lett.*, 2002, **4**, 517–520; (e) T. Ikeno, I. Iwakura and T. Yamada, Highly Enantioselective Cyclopropanation of Styrenes and Diazoacetates Catalyzed by 3-Oxobutylideneaminatocobalt(II) Complexes, Part 2. Semiempirical Analysis of Diastereo and Enantioselectivities, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 2151–2160.

8 (a) I. D. Hyatt and M. P. Croatt, Reactions of hypervalent iodonium alkynyl triflates with azides: generation of cyanocarbenes, *Angew. Chem.*, 2012, **124**, 7629–7632; (b) I. D. Hyatt and M. P. Croatt, Reactions of hypervalent iodonium alkynyl triflates with azides: generation of cyanocarbenes, *Angew. Chem., Int. Ed.*, 2012, **51**, 7511–7514.

9 Deposition numbers 2384415 (for **2bc**) and 2384416 (for **4a**)† contain the supplementary crystallographic data for this paper.

10 G. Santra, R. Calinsky and J. M. Martin, Benefits of range-separated hybrid and double-hybrid functionals for a large and diverse data set of reaction energies and barrier heights, *J. Phys. Chem.*, 2022, **126**, 5492–5505.

11 J. Clayden, N. Greeves and S. Warren, *Organic chemistry*, Oxford University Press, USA, 2012.

12 (a) P. Costa, T. Lohmiller, I. Trosien, A. Savitsky, W. Lubitz, M. Fernandez-Oliva, E. Sanchez-Garcia and W. Sander, Light and Temperature Control of the Spin State of Bis (p-methoxyphenyl) carbene: A Magnetically Bistable Carbene, *J. Am. Chem. Soc.*, 2016, **138**, 1622–1629; (b) C. Wentrup, Carbenes and nitrenes: recent developments in fundamental chemistry, *Angew. Chem., Int. Ed.*,

This journal is © the Partner Organisations 2025

Org. Chem. Front., 2025, **12**, 2180–2186 | **2185**

2018, **57**, 11508–11521; (*c*) C. Wentrup, Carbene und Nitrene: Aktuelle Entwicklungen in der Grundlagenchemie, *Angew. Chem.*, 2018, **130**, 11680–11693.

13 (*a*) I. Martín-Torres, G. Ogalla, J. M. Yang, A. Rinaldi and A. M. Echavarren, Enantioselective Alkoxycyclization of 1, 6–Enynes with Gold(ɪ)–Cavitands: Total Synthesis of Mafaicheenamine C, *Angew. Chem., Int. Ed.*, 2021, **60**, 9339–9344; (*b*) I. Martín-Torres, G. Ogalla, J. M. Yang, A. Rinaldi and A. M. Echavarren, Enantioselective Alkoxycyclization of 1, 6–Enynes with Gold(ɪ)–Cavitands: Total Synthesis of Mafaicheenamine C, *Angew. Chem.*, 2021, **133**, 9425–9430.

2186 | *Org. Chem. Front.*, 2025, **12**, 2180–2186

This journal is © the Partner Organisations 2025