ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2026, 62, 7808

Received 7th March 2026,
Accepted 23rd March 2026

DOI: 10.1039/d6cc01379a

rsc.li/chemcomm

Generation of mono(amino)carbenes from *N*-triftosyl amino hydrazonates with blue light

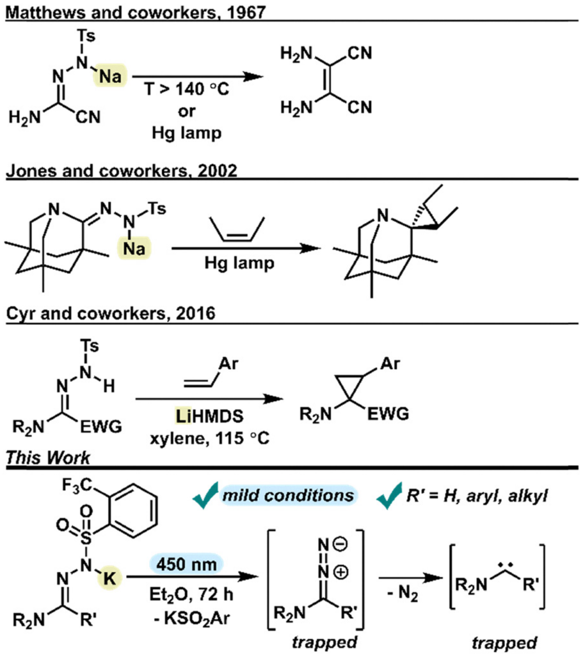
Patrick Yorkgitis, Mehdi Abdellaoui and Guy Bertrand *

Motivated by the lack of mild and general methods for accessing mono(amino)carbenes, we have developed an approach based on the photolysis of thermally stable *N*-triftosyl amino hydrazonates with blue light. No additives or catalysts are necessary. The resulting transient aminocarbenes can be trapped by [2+1] cycloaddition and σ-bond insertion reactions.

Free carbenes are valuable synthetic intermediates capable of facile [2+1] cycloadditions, σ-bond insertions, and other reactions.[1] Though electronically stabilized, mono(amino)-carbenes are still highly ambiphilic unlike most diaminocarbenes.[2,3] Through classical reactivity they can introduce amino groups, an important functionality in pharmaceuticals and materials.[4–8] However, mono(amino)carbenes remain underutilized as building blocks in comparison with aryl, alkyl,[9] keto-,[10] and halocarbenes.[11] This may be because the classical precursors to free carbenes – diazo compounds[12] and diazirines[13] – cannot be isolated with amino substituents and are explosive.[14–16] Consequently, generating mono(amino)carbenes under mild conditions is difficult. While synthetic equivalents are known, they require catalysts, (super)stoichiometric metallic reagents, and high temperatures.[17–22] Lastly, note that although stable mono(amino)carbenes have been known since 2001,[23] they have not found broad application as synthons due to the requirement for bulky substituents.

A particularly popular approach to generating aryl and alkyl diazo compounds uses *N*-sulfonyl hydrazonates.[9,24–35] In contrast, the generation of amino diazo compounds, and thus aminocarbenes, from *N*-sulfonyl amino hydrazonates has hardly been developed (Scheme 1). In 1967, Matthews and coworkers described the generation of (amino)(cyano)carbene, a push–pull carbene, *via* thermolysis or photolysis of an *N*-tosyl amino hydrazonate.[36] Later, Jones and coworkers generated a transient "twisted" aminocarbene *via* photolysis of an *N*-tosyl amino hydrazonate, whereas thermolysis was unproductive.[37] In the third and newest report to date, Cyr and coworkers further developed the thermolytic approach to prepare a variety of cyclopropylamines, but only push–pull motifs were accessible.[38] Given the limited substitution patterns accessible *via* these methods, all of which require harsh conditions, we endeavoured to develop a mild method for accessing structurally diverse mono(amino)carbenes.

Starting in 2018, Bi and coworkers have developed *N*-triftosyl hydrazonates (triftosyl = 2-(trifluoromethyl)benzenesulfonyl) which can generate alkyl and aryl diazo compounds at much lower temperatures than *N*-tosyl analogues.[39–42] We hypothesized that *N*-triftosyl hydrazonates with an amino substituent



Scheme 1 Prior reports on the generation of aminocarbenes from *N*-sulfonyl amino hydrazonates and this work.

UCSD-CNRS Joint Research Laboratory (IRL 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, USA. E-mail: gbertrand@ucsd.edu

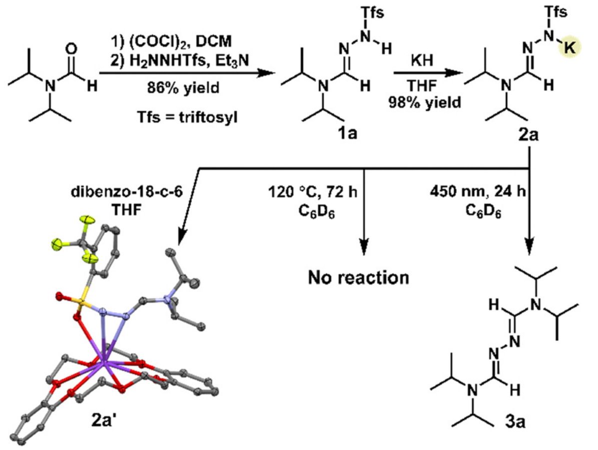
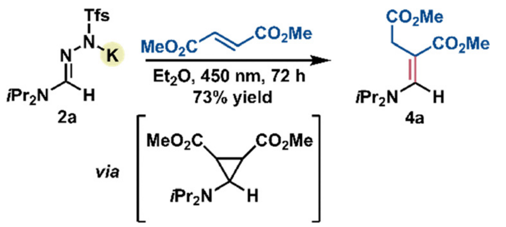


Fig. 1 Synthesis and reactivity of **2a**; solid-state structure of the crown ether adduct **2a**′ with thermal ellipsoids at 50% and hydrogens and solvent molecule removed for clarity.

should be accessible, and might also be thermally labile. To begin, we attempted to generate a very simple monosubstituted aminocarbene. Accordingly, from *N*,*N*-diisopropyl formamide we prepared *N*-triftosyl amino hydrazone **1a** (Fig. 1 and Fig. S2, SI). Deprotonation with KH gave **2a** as a yellow powder. In order to obtain single crystals and to confirm its identity, **2a** was treated with dibenzo-18-crown-6. Slow evaporation of a THF solution yielded the crystalline adduct **2a**′ which was characterized by single-crystal X-ray diffraction.

Heating a solution of **2a** in C_6D_6 at 120 °C gave no discernable reaction, even after 72 h. Noting the yellow color of **2a**, we considered that visible light photolysis might be efficient. The UV-Vis spectra of **2a** at different concentrations contain an absorption band which tails past 450 nm (Fig. S13, SI). A solution of **2a** in C_6D_6 was irradiated at 450 nm and azine **3a** was cleanly obtained. Azines are known to form *via* the addition of carbenes to diazo compounds.[43] Thus, the formation of **3a** suggests that photolysis of **2a** generates an amino diazo compound as well as the corresponding aminocarbene. To confirm the generation of the carbene, the photolysis was performed in the presence of dimethyl fumarate (Scheme 2). The cyclopropanation product was not observed, but rather the push–pull alkene **4a**, which was isolated in 73% yield. The latter likely results from the rearrangement of a donor–acceptor cyclopropane intermediate.[44] Similar rearrangements have been observed in the reaction of other mono(amino)carbenes with electron-poor alkenes.[4]

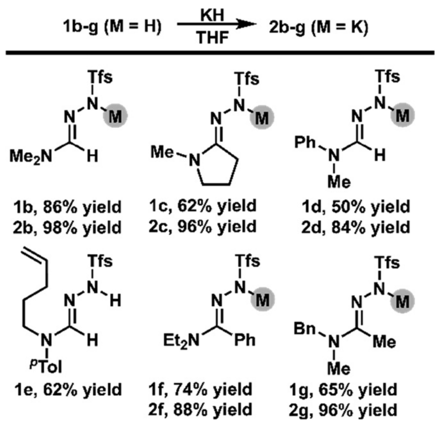


Scheme 2 Photolysis of **2a** in the presence of dimethyl fumarate. Reaction conditions: **2a** (0.5 mmol), dimethyl fumarate (0.5 mmol), Et_2O (10 mL), 450 nm (0.33 W × 4).

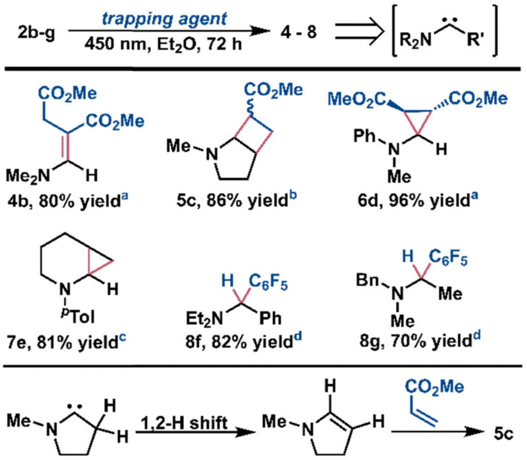
Having established that our photochemical approach allows for the generation and trapping of a transient aminocarbene, we explored the scope of accessible *N*-triftosyl amino hydrazonates (Scheme 3 and Fig. S2, S3, SI). **1b-g** were all prepared from secondary amides. Deprotonation with KH afforded the corresponding salts as yellow solids, all of which are thermally stable and exhibited no signs of decomposition upon storage at room temperature for over one year. Note, **2e** was not isolated, but generated *in situ* for the subsequent trapping reactions.

For each hydrazonate, successful carbene generation was evidenced by trapping reactions (Scheme 4). With **2b** and **2d** we used dimethyl fumarate as a trapping agent, whereas with **2c** we used methyl acrylate. With **2b**, we isolated the push–pull alkene **4b**, analogous to **4a**. For **2c**, bicyclic cyclobutane **5c** was obtained in 86% yield. Its formation can be explained *via* an initial intramolecular 1,2-hydride shift in the free carbene,[45] followed by a formal [2+2] cycloaddition of the resulting enamine to methyl acrylate.[46] Importantly, the *N*-aryl substituent in **2d** appeared to sufficiently stabilize the lone pair of the amino group to permit isolation of donor–acceptor cyclopropane **6d**.[44] Attempts to trap the aminocarbenes prepared from **2b–d** with less activated alkenes failed, possibly due to competitive azine formation or carbene dimerization. However, photolysis of **2e**, which features a tethered non-activated alkene, afforded bicyclic cyclopropane **7e** in 81% yield. This intramolecular cyclopropanation reaction is certainly of synthetic interest. For **2f** and **2g**, pentafluorobenzene proved to be a superior carbene trapping agent compared to electron poor alkenes, yielding the C–H σ-bond insertion products **8f** and **8g**, respectively.

We next investigated the origins of the observed photochemistry. The absorbance spectrum of **2a** shows a significant bathochromic shift in the lowest energy absorption band as compared to **1a**, which does not absorb at 450 nm (Fig. 2). This shift is consistent with the destabilization of the HOMO upon deprotonation. To gain insight into the electronic transition responsible for this band, we used simplified time-dependent density functional theory (sTD-DFT) calculations to efficiently



Scheme 3 Additional hydrazones and hydrazonate salts with isolated yields.



Scheme 4 Scope of trapping reactions with isolated yields. Reaction conditions: **2b-g** (0.5 mmol), Et_2O (10 mL), 450 nm (0.33 W × 4), ^{a}dimethyl fumarate (0.5 mmol, 1 eq.), ^{b}methyl acrylate (2.5 mmol, 5 eq.), ^{c}none, ^{d}pentafluorobenzene (5 mmol, 10 eq.). Carbene rearrangement leading to **5c**.

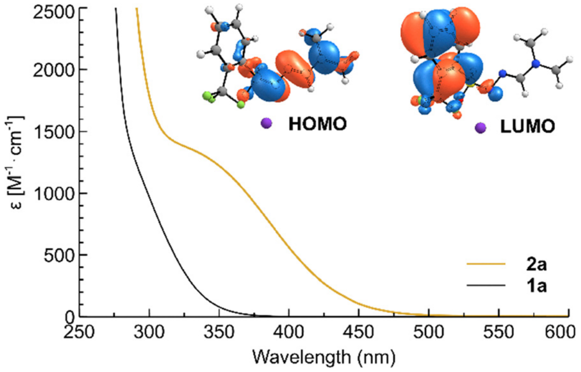


Fig. 2 UV-Vis spectra of **1a** and **2a** in THF (1 mM) at 25 °C; Calculated HOMO and LUMO isosurfaces for **2b** (inset).

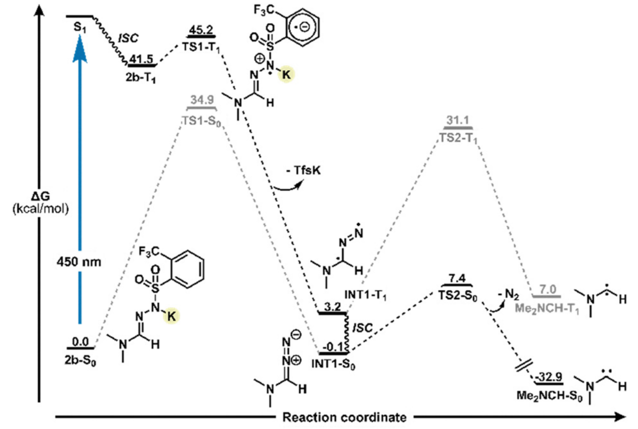


Fig. 3 Free energy profiles for carbene generation from **2b** along the S_0 and T_1 surfaces calculated at the ωB97x-V/def2-mTZVPP/SMD(Et_2O)//r^2SCAN-3c/CPCM(Et_2O) level of theory.

model the low-lying excited states of the structurally similar **1b** and **2b** (Fig. S18 and S21, SI).[47–50] For both, the $S_0 \rightarrow S_1$ transition produces a charge-transfer (CT) state primarily between a hydrazone π-orbital (HOMO) and a triftosyl π*-orbital (LUMO).[51] Note that Oschenfeld and coworkers recently showed that a similar CT state forms upon photoexcitation of alkyl *N*-tosyl hydrazonates.[52]

Finally, thermochemical calculations were used to better understand how the amino diazo compounds, and ultimately the free aminocarbenes, are formed after photoexcitation. CT states can undergo rapid intersystem crossing (ISC) from the S_1 state to a longer-lived T_1 state.[53] We thus reasoned that the photofragmentation of *N*-triftosyl amino hydrazonates may occur through the T_1 state. Accordingly, we modelled the generation of free aminocarbene **Me$_2$NCH** from **2b** along the S_0 and T_1 surfaces (Fig. 3).

From the ground state salt **2b-S$_0$**, the barrier to fragmentation *via* **TS1-S$_0$** is large ($\Delta G^\ddagger$ = 34.9 kcal mol^{-1}), corresponding with the thermal stability of **2a-g**. However, from the triplet **2b-T$_1$**, which is accessible *via* ISC from the photoexcited **S$_1$** state, sulfinate (**TfsK**) release proceeds over a small barrier ($\Delta G^\ddagger$ = 3.7 kcal mol^{-1}). This affords the intermediate amino diazo compound in the triplet state, **INT1-T$_1$**. Dediazotization *via* **TS2-T$_1$** occurs over a rather large barrier ($\Delta G^\ddagger$ = 27.9 kcal mol^{-1}) and is slightly endergonic (ΔG = +3.8 kcal mol^{-1}). In contrast, dediazotization in the singlet state *via* **TS2-S$_0$** occurs over a much smaller barrier ($\Delta G^\ddagger$ = 7.5 kcal mol^{-1}) and is highly exergonic (ΔG = −32.8 kcal mol^{-1}). Note, the intermediate amino diazo has a small adiabatic S_0-T_1 gap (3.3 kcal mol^{-1}; 0.14 eV). Therefore, ISC to the S_0 state may be relatively facile, permitting rapid release of N_2 from **INT1-S$_0$** to yield the singlet carbene **Me$_2$NCH-S$_0$**. While we did not model the formation of the diazo compound in the **S$_1$** state, such a process has been implicated in the photofragmentation of alkyl *N*-tosyl hydrazonates into diazo compounds.[52] Regardless of the state in which sulfinate release occurs, the fact that aminocarbenes strongly favor the S_0 state over the T_1 state (ΔE_{ST} = + 39.9 kcal mol^{-1} for **Me$_2$NCH**) may mitigate the direct formation of the triplet aminocarbene, **Me$_2$NCH-T$_1$**. Note, it has also been shown that the triplet state of stable singlet aminocarbenes can be accessed *via* photoexcitation of the free carbenes.[54]

To conclude, we have shown that mono(amino)carbenes are readily accessible from thermally robust potassium *N*-triftosyl amino hydrazonates. Unlike most prior approaches, our method does not require push–pull substitution, permitting access to monosubstituted, aryl, and alkyl aminocarbenes under blue light (450 nm) irradiation. We hope that the generality of this catalyst-free approach will facilitate the incorporation of mono(amino)carbene fragments into a variety of discrete molecules and materials. Investigations into the generation of other carbenes by our approach, as well as the synthetic possibilities presented by the intermediate amino diazo compounds, are ongoing. Further development of the intramolecular trapping reaction, as exemplified with **7e**, should provide access to various polycyclic motifs.

This work was supported by the NSF (CHE-2246948). This research was also supported in part by the W. M. Keck Foundation through computing resources at the W. M. Keck Laboratory for Integrated Biology. NMR measurements in this publication were supported in part by the Office of the Director of the National Institutes of Health under award number S10 OD032266.

Conflicts of interest

There are no conflicts to declare.

Data availability

All computational data underlying this study are openly available for download, free of charge, from the UC San Diego Library Digital Collections at DOI: https://doi.org/10.6075/J09P32M5.

Supplementary information (SI) is available. See DOI: https://doi.org/10.1039/d6cc01379a.

CCDC 2530033 contains the supplementary crystallographic data for this paper.[55]

References

1 *Reactive intermediate chemistry*, ed. R. A. Moss, M. Platz and M. Jones, Wiley-Interscience, Hoboken, N.J, 2004.
2 H. Kim and E. Lee, *Bull. Korean Chem. Soc.*, 2022, **43**, 1328–1341.
3 F. Vermersch, V. T. Wang, M. Abdellaoui, R. Jazzar and G. Bertrand, *Chem. Sci.*, 2024, **15**, 3707–3710.
4 D. Martin, Y. Canac, V. Lavallo and G. Bertrand, *J. Am. Chem. Soc.*, 2014, **136**, 5023–5030.
5 A. V. Zhukhovitskiy, M. G. Mavros, K. T. Queeney, T. Wu, T. Van Voorhis and J. A. Johnson, *J. Am. Chem. Soc.*, 2016, **138**, 8639–8652.
6 J. Lorkowski, P. Yorkgitis, F. Morvan, J. Morvan, N. Vanthuyne, T. Roisnel, M. Gembicky, G. Bertrand, M. Mauduit and R. Jazzar, *J. Am. Chem. Soc.*, 2025, **147**, 14777–14784.
7 P. Ertl, E. Altmann and J. M. McKenna, *J. Med. Chem.*, 2020, **63**, 8408–8418.
8 L. B. Hamdy, C. Goel, J. A. Rudd, A. R. Barron and E. Andreoli, *Mater. Adv.*, 2021, **2**, 5843–5880.
9 X. Zhang, P. Sivaguru, Y. Pan, N. Wang, W. Zhang and X. Bi, *Chem. Rev.*, 2025, **125**, 1049–1190.
10 N. R. Candeias, R. Paterna and P. M. P. Gois, *Chem. Rev.*, 2016, **116**, 2937–2981.
11 H.-M. To, O. Malets, M. Mazur, O. Mykhailenko, O. Kompaniiets and T. Ollevier, *Synthesis*, 2023, 263–271.
12 H. A. Khan, M. Szostak and C. Sivasankar, *Org. Biomol. Chem.*, 2026, **24**, 734–766.
13 D. Schnalzer, V. Savic, C. Cziegler, M. Schnürch and M. D. Mihovilovic, *Angew. Chem., Int. Ed.*, 2025, **65**, e14105.
14 R. A. Moss, D. Phillip Cox and H. Tomioka, *Tetrahedron Lett.*, 1984, **25**, 1023–1026.
15 J. S. Alford and H. M. L. Davies, *Org. Lett.*, 2012, **14**, 6020–6023.
16 S. P. Green, K. M. Wheelhouse, A. D. Payne, J. P. Hallett, P. W. Miller and J. A. Bull, *Org. Process Res. Dev.*, 2020, **24**, 67–84.
17 K. H. Dötz and J. Stendel, *Chem. Rev.*, 2009, **109**, 3227–3274.
18 H. Goto, R. Shiomi, T. Shimizu, T. Kochi and F. Kakiuchi, *Org. Lett.*, 2024, **26**, 10152–10157.
19 A. Ogawa, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe and N. Sonoda, *J. Am. Chem. Soc.*, 1992, **114**, 8729–8730.
20 T. Mitamura, A. Nomoto, M. Sonoda and A. Ogawa, *Tetrahedron*, 2008, **64**, 9983–9988.
21 J. Jiao, W. Yang and X. Wang, *J. Org. Chem.*, 2023, **88**, 594–601.
22 L. Chen, W. Zhou, J. Zhang, Y. Ding, M. Szostak and C. Liu, *Chem. Commun.*, 2024, **60**, 8454–8457.
23 S. Solé, H. Gornitzka, W. W. Schoeller, D. Bourissou and G. Bertrand, *Science*, 2001, **292**, 1901–1903.
24 W. Kirmse and K. H. Pook, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 594.
25 V. K. Aggarwal, E. Alonso, G. Hynd, K. M. Lydon, M. J. Palmer, M. Porcelloni and J. R. Studley, *Angew. Chem., Int. Ed.*, 2001, **40**, 1430–1433.
26 J. Barluenga, P. Moriel, C. Valdés and F. Aznar, *Angew. Chem., Int. Ed.*, 2007, **46**, 5587–5590.
27 X. Ning, T. Zhao, Y. Zhu, B. Liu, X. Yan and Y. Xia, *J. Am. Chem. Soc.*, 2025, **147**, 16773–16780.
28 Y. Xu, G. Lv, K. Yan, H. He, J. Li, Y. Luo, R. Lai, L. Hai and Y. Wu, *Chem. – Asian J.*, 2020, **15**, 1945–1947.
29 H. Wang, S. Wang, V. George, G. Llorente and B. König, *Angew. Chem., Int. Ed.*, 2022, **61**, e202211578.
30 Á. Valdés-Maqueda, L. López, M. Plaza and C. Valdés, *Chem. Sci.*, 2023, **14**, 13765–13775.
31 V. George and B. König, *Chem. Commun.*, 2023, **59**, 11835–11838.
32 Y. Zhang, Y. Li, S.-F. Ni, J.-P. Li, D. Xia, X. Han, J. Lin, J. Wang, S. Das and W.-D. Zhang, *Chem. Sci.*, 2023, **14**, 10411–10419.
33 Z. Zhang and V. Gevorgyan, *Chem. Rev.*, 2024, **124**, 7214–7261.
34 P. Yamini, A. Babbar and D. Yadagiri, *Org. Lett.*, 2024, **26**, 6035–6040.
35 W. Wang, Q. Zhang, M. Guo, M. Zhuo, W.-D. Zhang, Q. Wang and Y. Zhang, *Org. Biomol. Chem.*, 2025, **23**, 2935–2940.
36 R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss and C. N. Matthews, *J. Am. Chem. Soc.*, 1967, **89**, 5673–5676.
37 Q. Ye, I. V. Komarov, A. J. Kirby and M. Jones, *J. Org. Chem.*, 2002, **67**, 9288–9294.
38 P. Cyr, A. Côté-Raiche and S. M. Bronner, *Org. Lett.*, 2016, **18**, 6448–6451.
39 Z. Liu, K. R. Babu, F. Wang, Y. Yang and X. Bi, *Org. Chem. Front.*, 2018, **6**, 121–124.
40 Z. Liu, P. Sivaguru, G. Zanoni and X. Bi, *Acc. Chem. Res.*, 2022, **55**, 1763–1781.
41 X. Zhang, Q. Song, S. Liu, P. Sivaguru, Z. Liu, Y. Yang, Y. Ning, E. A. Anderson, G. de Ruiter and X. Bi, *Nat. Chem.*, 2025, **17**, 215–225.
42 Y. Ning, R. Wu, Y. Ning, Q. Song, J. Deng, Q. Jiao, P. Sivaguru, J. Mlynarski, G. de Ruiter, X. Hong and X. Bi, *Nat. Chem.*, 2026, **18**, 283–293.
43 S. S. Chourasiya, D. Kathuria, A. A. Wani and P. V. Bharatam, *Org. Biomol. Chem.*, 2019, **17**, 8486–8521.
44 T. F. Schneider, J. Kaschel and D. B. Werz, *Angew. Chem., Int. Ed.*, 2014, **53**, 5504–5523.
45 H. F. I. Schaefer, *Acc. Chem. Res.*, 1979, **12**, 288–296.
46 I. V. Efimov, D. I. Zhilyaev, L. N. Kulikova and L. G. Voskressensky, *Eur. J. Inorg. Chem.*, 2023, e202201450.
47 C. Bannwarth and S. Grimme, *Comput. Theor. Chem.*, 2014, **1040–1041**, 45–53.
48 S. Grimme, A. Hansen, S. Ehlert and J.-M. Mewes, *J. Chem. Phys.*, 2021, **154**, 064103.
49 F. Neese, *WIREs Comput. Mol. Sci.*, 2022, **12**, e1606.
50 P. Yorkgitis, M. Abdellaoui and G. Bertrand, UC San Diego Library Digital Collections, Data from: Generation of mono(amino)carbenes from *N*-triftosyl amino hydrazonates with blue light, 2026, DOI: 10.6075/J09P32M5.
51 T. Stein, L. Kronik and R. Baer, *J. Am. Chem. Soc.*, 2009, **131**, 2818–2820.
52 F. L. Pointner, J. Poll, E. K. Taskinen, V. George, T. Ruff, F. Rott, G. Mayer, N. Gessner, R.-J. Kutta, B. König, P. Nuernberger, C. Ochsenfeld and R. de Vivie-Riedle, *ChemistryEurope*, 2025, **3**, e202500133.
53 M. Amy Bryden and E. Zysman-Colman, *Chem. Soc. Rev.*, 2021, **50**, 7587–7680.
54 T. A. Perera, W. V. Taylor, M. B. Gildner, E. W. Reinheimer, S. Ito, A. Nelson, S. R. Yost and T. W. Hudnall, *Chem. Sci.*, 2023, **14**, 7867–7874.
55 CCDC 2530033: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2qxpzb.