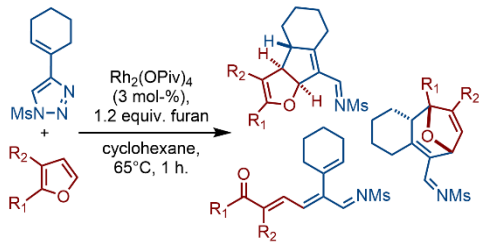
Unearthing the Subtleties of Rhodium(II)-Catalyzed Carbenoid Cycloadditions to Furans with a *N*-Sulfonyl-1,2,3-Triazole Probe

Christian J. Bettencourt,[a] Tanja Krainz,[a] Sharon Chow,[a] Brendan T. Parr,[b] William F. Tracy,[b] Paul V. Bernhardt,[a] Huw M. L. Davies,[b,*] and Craig M. Williams[a,*]

[a]School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia

[b]Emory University, Department of Chemistry, 1515 Dickey Drive, Atlanta Georgia, United States

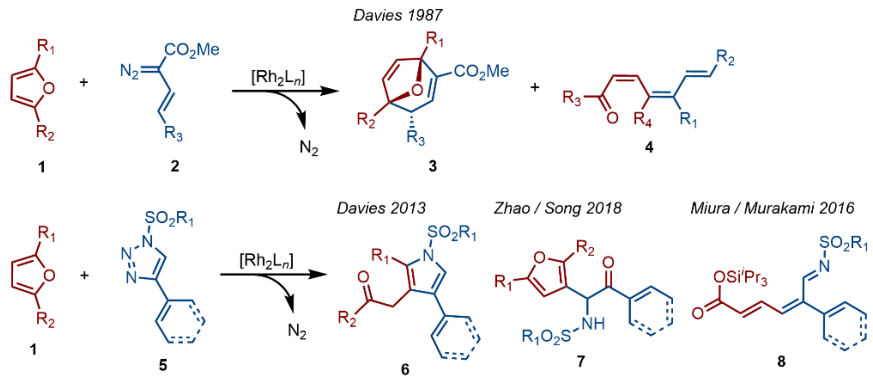
Supporting Information Placeholder



ABSTRACT: The rhodium(II)-catalyzed reaction of a model alkenyl-donor/acceptor *N*-sulfonyltriazole with a wide selection of furans is reported. This investigation unearthed a range of structurally diverse carbocyclic and ring opened products, in good to excellent yields. The products obtained are proposed to arise selectively via cyclopropanation or zwitterionic rearrangement pathways, which are highly dependent on both structural and electronic features of the furan substrate.

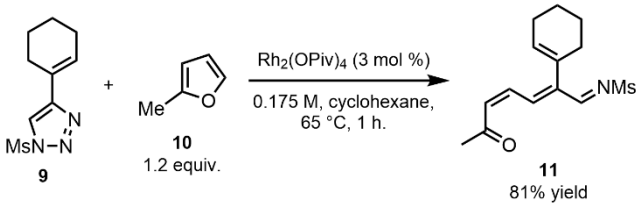
The use of vinylogous rhodium metallocarbenes as three-carbon synthons is a proven strategy for the synthesis of complex carbon ring systems via formal [4 + 3] and [3 + 2] cycloadditions.[1-8] An early example of this type of reactivity is the rhodium-catalyzed reaction of furans **1** with vinyldiazoacetates **2** to form [4+3] cycloadducts **3**, which often competes with furan ring opening to form **4** (Scheme 1). In recent years, considerable interest has been shown in accessing the carbenes from *N*-sulfonyl-1,2,3-triazoles, which act as masked diazo functions, alleviating the need to isolate the decomposition-prone alkenyl-diazo moiety.[9,10] Despite the high level of interest in *N*-sulfonyltriazole derived metallocarbene chemistry,[11-19] few methods have been reported of their utilization in cycloaddition reactions for the construction of carbocyclic systems.[10] One explanation for this observation is that donor/acceptor metallocarbenes derived from *N*-sulfonyltriazoles contain a nucleophilic sulfonyl imine, which often becomes incorporated into the reaction to form heterocycles. This is especially true for the reaction of *N*-sulfonyltriazoles **5** with furans **1**, which can generate products derived from sulfonyl imine participation (e.g., **6** and **7**) as well as furan ring opening to form the dienes **8**.[20-23] Therefore, a combination of competing reaction modes, from both the *N*-sulfonyltriazole and furan has caused the cycloaddition methodology for carbocycle construction to remain underdeveloped.[24] In order to build the utility of the reaction between *N*-sulfonyltriazoles and furans to generate carbocyclic products, we have conducted a systematic study to understand the controlling influences for the variety of potential products that can be formed.

Scheme 1. Reactions of vinylogous rhodium(II) carbenes with furans.



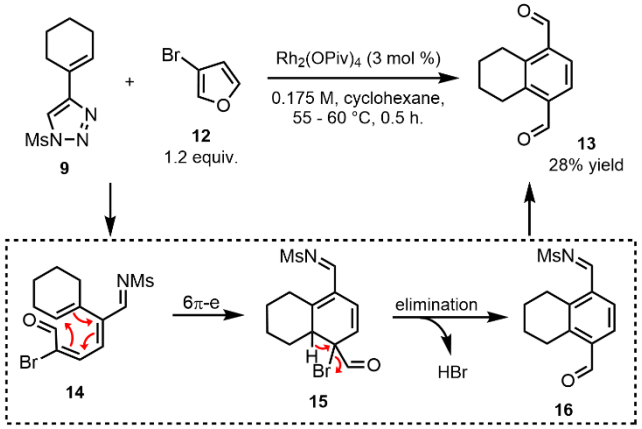
To address this issue, a study to understand the nuances of this reaction was undertaken using 4-(cyclohexenyl)-*N*-(mesyl)-1*H*-1,2,3-triazole (**9**) as a reaction probe (Scheme 2). Previous studies have tended to focus on electron-rich furans, but it was anticipated that carbocycle formation would be more likely to occur when electron-deficient furans were used. As a point of reference, the reaction with 2-methylfuran (**10**) was examined and this resulted in the clean formation of the ring-opened triene **11**. This type of product is considered to be formed by attack at C2 of the furan to form a zwitterionic intermediate, which then undergoes ring opening.[11]

Scheme 2. Generation of a triene is preferred from 2-methylfuran.



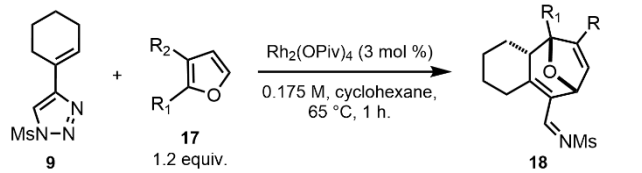
The next experiments examined electron-deficient furans. The reaction with 3-bromofuran (**12**) resulted in an unexpected outcome (Scheme 3). The reaction did not proceed smoothly, but the major product was the dialdehyde **13**, isolated in 28% yield. This product is also proposed to be derived from the initially formed triene **14**, which underwent a 6π electrocyclization to form **15**, followed by an elimination to form **16** and imine hydrolysis to form **13**.

Scheme 3. Unexpected dialdehyde from 3-bromofuran.



When the reaction was conducted with furans containing a strong electron-withdrawing group (**17a-c**), the chemistry was quite different (Scheme 4). In this case, the [4+3] cycloadducts **18a-c** were cleanly formed as single diastereomers in good yield. The [4+3] cycloadducts are established products from the reactions of vinylcarbenes with dienes and are considered to be generated by a cyclopropanation followed by a Cope rearrangement.[25-27]

Scheme 4. Electron-poor furans prefer carbocycle formation.



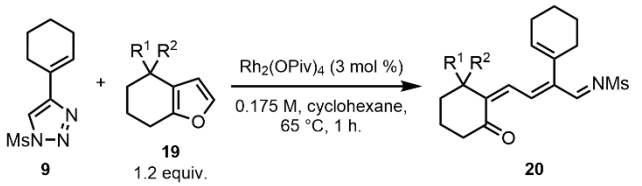
a: R_1 = H, R_2 = CO_2Et, 97% yield, d.r. > 20:1

b: R_1 = H, R_2 = Ac, 65% yield

c: R_1 = CO_2Me, R_2 = H, 82% yield

Having established a clear distinction between electron-rich and electron-deficient furans, the study was then extended to fused furan derivatives (Scheme 5). In the case of electron-rich fused furans **19a** and **19b**, trienes were the major product (**20a**,**b**). This would suggest that the reactions are proceeding through zwitterionic intermediates

Scheme 5. Reaction with electron rich fused furans

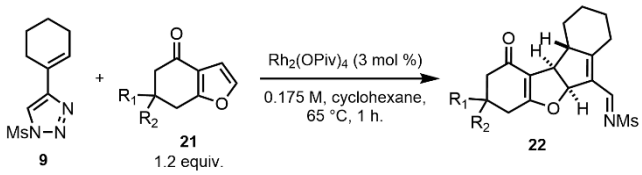


a: R_1= H, R_2 = OTBS, 69% yield

b: R_1, R_2 = OCH_2CH_2O, 70% yield

Extension of the chemistry to electron-deficient fused furans (i.e. **21**) resulted in the [3+2] cycloaddition product **22** in 53% yield (Scheme 6). Cyclopentene products related to **22**, have previously been accessed under rhodium catalysis from vinyl ethers with vinyldiazoacetates as the carbene source.[28,29] The formation of **22**, from an electron-deficient furan may suggest a different mechanism to the former, which involves partial zwitterion character, but ultimately results in cyclopentene synthesis.

Scheme 6. Reaction with electron deficient fused furans



a: R_1, R_2 = H, 53% yield

b: R_1, R_2 = Me, 62% yield

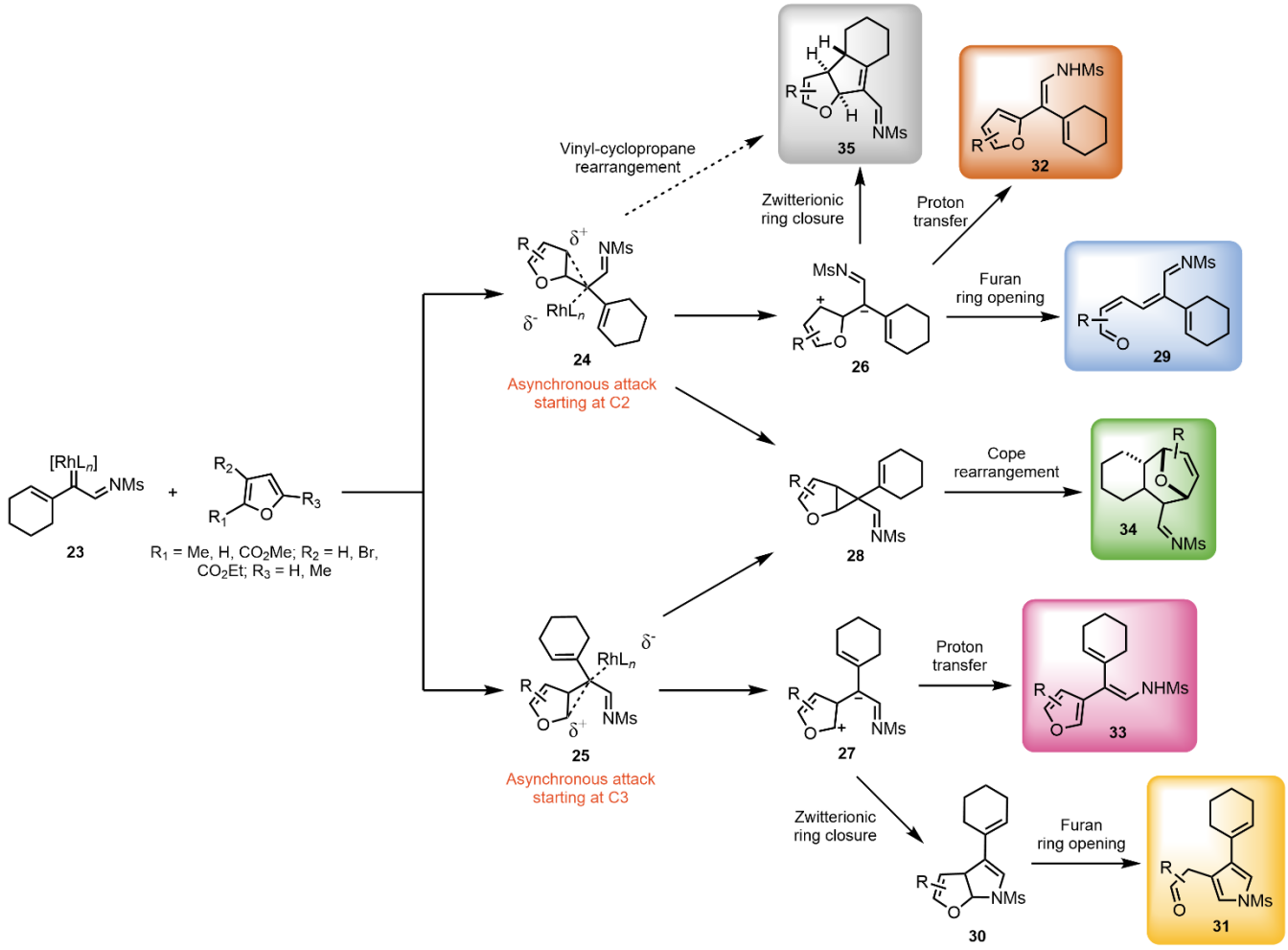
The formation of several distinct products from the reaction of the cyclohexyl iminocarbene with furans can be rationalized as shown in Scheme 7. Cyclopropanations of donor/acceptor carbenes like those of form **23** are considered to be a concerted, but highly asynchronous process as illustrated with the hypothetical transition states **24** and **25**. Depending on the functionality on the furan ring, the zwitterionic intermediates **25** and **26** can be preferentially formed instead of the cyclopropane **28**, leading to a variety of different products. Even though in principle, the zwitterionic intermediates could be generated from ring-opening of an initially formed furanocyclopropane, the preponderance of evidence suggests that they are formed in competition to cyclopropanation.[30] If electron-donating groups are present on the furan rings, the zwitterionic intermediates are strongly preferred, as this sufficiently stabilizes the build-up of positive charge on the furan ring. The asynchronous cyclopropanation can initiate at either the *alpha* or *beta* positions of the furan, which is governed by steric and electronic effects. The *alpha* position of the furan is generally preferred (**24**), because it is the position more prone to electrophilic attack, but when the furan is 2,5-disubstited then attack at the beta position is favored (**25**).[20] The side products could be derived from fully formed zwitterionic intermediates **26** and **27** or from rhodium-bound zwitterionic structure, analogous to **24** and **25**.

Previous studies on the reaction of *N*-sulfonyltriazoles with furans have tended to use either furan or alkylfurans as substrates, giving products derived from zwitterionic intermediates. In the case of

furan or 2-alkylfurans, the zwitterionic intermediate **26** is favored, and thus the ring-opened diene **29** is preferentially formed (Scheme 7). In the case of 2,5-disubstituted furans, the zwitterionic intermediate **27** is favored, which leads to the formation of the hemiaminal **30**, which then ring-opens to the pyrrole **31**.[20] Previous studies have also reported the formation of the formal aromatic substitution products related to **32** or **33**, which are likely formed by a proton transfer reaction from **26** or **27**.[31-33]

In the current study, furans with electron-withdrawing substituents have been used, which lead to other possible reaction outcomes, because the zwitterionic intermediates are not highly favored. The reaction with 3-carboethoxyfuran (**17a**) led to smooth formation of the [4+3] cycloadduct **18a**, by analogy to **34**. The reaction is highly diastereoselective because it proceeds by a cyclopropanation to form **28** followed by a Cope rearrangement, a well-established reaction for vinyldiazoacetates and *N*-sulfonyltriazoles.[7,10] In the case of furanocyclohexenone, the initial electrophilic attack occurs at the *alpha* position, leading to the formation of the [3+2] cycloadduct **35**. When the electron-withdrawing character of the furan is attenuated, then the diene **29** is produced. The formation of three types of products, **29**, **32** and **35**, derived from zwitterioinic intermediates involving initial attack at C2 is indicative that these products may not be derived from the fully formed zwitterionic intermediate **26**. Instead, the rhodium bound zwitterionic structure analogous to **24** may be involved, especially in the formation of **35**, which is observed in furan systems with electron-withdrawing groups that would not be ideally suited to stabilize the positive charge in **26**.

Scheme 7. Plausible mechanisms for the formation of the observed reaction product classes.

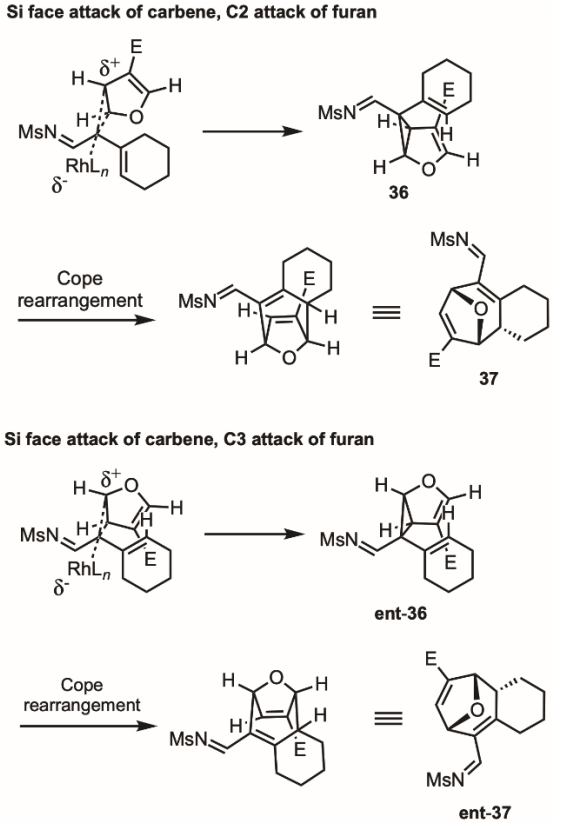


One of the more unexpected outcomes of this study is the clean formation of the [4+3] cycloadduct **18a** from the reaction with 3-carboethoxy furan (**17a**). From a steric and electronic perspective, initial attack at the C2 position of the furan would have been expected, but this typically results in side products derived from the zwitterionic intermediate such as the diene **29**. Either the ester group effectively limited charge build-up during the C2 attack, or C3 attack preferentially occurred. In order to study which process was occurring, the experimental design took advantage of the fact that initial C2- versus C3-attack would be expected to produce opposite asymmetric induction – as illustrated in Scheme 8. This effect has been previously observed in the reactions of aryl- and vinyldiazoacetates with furans.[5] Even though the chiral catalyst ensures only one face of the carbene is susceptible to attack (*Si* face in the model illustrated here), either enantiomer of the cyclopropane, **36** or **ent-36**, can be formed depending on the initial position of attack. The subsequent Cope rearrangement of the cyclopropane generates a specific enantiomer of [4+3] cycloadduct, **37** or **ent-37**.

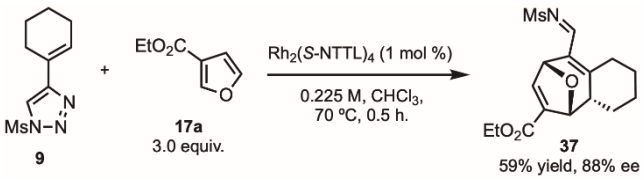
The most well-established chiral catalyst for enantioselective reactions of aryl *N*-sulfonyltriazoles is Rh_2(*S*-NTTL)$_4$, which routinely causes the *Si* face of the carbene to be preferentially attacked.[16,34,35] Therefore, the asymmetric induction generated in the reaction of

carboethoxyfuran **17a** with *N*-sulfonyltriazole **9** using Rh_2(*S*-NTTL)$_4$ was examined. The Rh_2(*S*-NTTL)$_4$-catalyzed reaction generated the [4+3] cycloadduct **37** in 59% yeld and 88% ee (Scheme 9). The absolute configuration of **37** was established by X-ray crystallography. This result is consistent with a reaction occurring at the *Si* face of the carbene with preferential attack occurring at the *alpha* position of the furan. Therefore, in this case, the electron withdrawing group on the furan disfavors the involvement of zwitterionic intermediates, leading to clean formation of the cyclopropane and subsequent Cope rearrangement to form **37**.

Scheme 8. Analysis of furan asymmetric induction.



Scheme 9. Rh_2(*S*-NTTL)4-induced asymmetric induction.



In conclusion, this study substantially expands and bridges historical work in the area of rhodium(II) metallocarbene transformations of furans, with the use of *N*-sulfonyl-1,2,3-triazole carbene precursors. The results demonstrate that multiple types of products can be formed, and the outcome is strongly dependent on the functionality of the furan. The cyclopropanation step is concerted asynchronous with a considerable build-up of zwitterionic character during the course of these reactions. If the functionality present favors the zwitterionic structure, then the cyclopropanation can be interrupted and side products can be formed. Different types of side product can be generated depending on whether the asynchronous cyclopropanation started at the *alpha*- or *beta*-position of the furan. These studies demonstrate the controlling factors in the reactions of furans with *N*-sulfonyltriazoles, which will enable the selection of appropriate substrates for predictable transformations.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Full synthetic procedures, X-ray crystallographic data, ^{1}H and ^{13}C NMR spectroscopic data, and HRMS reports (PDF).

Accession Codes

CCDC 2216763 (**13**), 2216762 (**20b**), 2216764 (**22**), and 2216761 (**37**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic DataCentre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 902 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Huw M. L. Davies – Department of Chemistry, Emory University, 440 Atwood Hall, 1515 Dickey Drive, Atlanta, GA 30322; orcid.org/0000-0001-6254-9398

Craig M. Williams – School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0002-3834-7398;
Email: c.williams3@uq.edu.au

Authors

Christian J. Bettencourt – School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0001-5855-9198

Tanja Krainz – School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0001-5335-9920

Sharon Chow – School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0001-8193-3504

Brendan T. Parr – Department of Chemistry, Emory University, 440 Atwood Hall, 1515 Dickey Drive, Atlanta, GA 30322; orcid.org/0000-0001-5774-8122

William F. Tracy – Department of Chemistry, Emory University, 440 Atwood Hall, 1515 Dickey Drive, Atlanta, GA 30322; orcid.org/0000-0003-1157-7684

Paul V. Bernhardt – School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Queensland 4072, Australia; orcid.org/0000-0001-6839-1763

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We thank the University of Queensland (UQ) and Emory University for financial support and the Australian Research Council for funding to C.M.W. (FT110100851 and DP180103004) and the National Science Foundation (CHE-1956154) for funding to HMLD. C.J.B. gratefully acknowledges the Australian Government and UQ for Research Training Program (RTP) and Tuition Fee Offset Scholarships.

REFERENCES

(1) Dong, K.; Zheng, H.; Su, Y.; Humeidi, A.; Arman, H.; Xu, X.; Doyle, M. P., Catalyst-directed divergent catalytic approaches to expand structural and functional scaffold diversity via metallo-enolcarbene intermediates. *ACS Catalysis* **2021**, *11*, 4712-4721.

(2) Schwartz, B. D.; Denton, J. R.; Davies, H. M. L.; Williams, C. M., Total Synthesis of (±)-vibsanin E. *Aust. J. Chem.* **2009**, *62*, 980-980.

(3. Schwartz, B. D.; Denton, J. R.; Lian, Y.; Davies, H. M. L.; Williams, C. M., Asymmetric [4 + 3] cycloadditions between vinylcarbenoids and dienes: Application to the total synthesis of the natural product (-)-5-epi-vibsanin E. *J. Am. Chem. Soc.* **2009**, *131*, 8329-8332.

(4) a) Chow, S.; Krainz, T.; Bernhardt, P. V.; Williams, C. M., En Route to D-Ring Inverted Phorbol Esters. *Org. Lett.* **2019**, *21*, 8761-8764; b) Chow, S.; Krainz, T.; Bettencourt, C. J.; Broit, N.; Ferguson, B.; Zhu, M.; Hull, K. G.; Pierens, G. K.; Bernhardt, P. V.; Parsons, P. G.; Romo, D.; Boyle, G. M.; Williams, C. M., Synthetic tigliane intermediates engage thiols to induce potent cell line selective anti-cancer activity. *Chem. Eur. J.* **2020**, *26*, 13372-13377.

(5) Krainz, T.; Chow, S.; Korica, N.; Bernhardt, P. V.; Boyle, G. M.; Parsons, P. G.; Davies, H. M. L. L.; Williams, C. M., Rhodium-catalyzed [4+3] cycloaddition to furans: Direct access to functionalized bicyclo[5.3.0]decane derivatives. *Eur. J. Org. Chem.* **2016**, *2016*, 41-44.

(6) Craig, R. A.; Smith, R. C.; Roizen, J. L.; Jones, A. C.; Virgil, S. C.; Stoltz, B. M., Development of a unified enantioselective, convergent synthetic approach toward the furanobutenolide-derived polycyclic norcembranoid diterpenes: Asymmetric formation of the polycyclic norditerpenoid varbocyclic core by tandem annulation cascade. *J. Org. Chem.* **2018**, *83*, 3467-3485.

(7) Spangler, J. E.; Lian, Y.; Raikar, S. N.; Davies, H. M. L., Synthesis of complex hexacyclic compounds via a tandem Rh(II)-catalyzed double-cyclopropanation/Cope rearrangement/Diels–Alder reaction. *Org. Lett.* **2014**, *16*, 4794-4797.

(8) Brummond, K. M.; Mao, S.; Shinde, S. N.; Johnston, P. J.; Day, B. W., Design and synthesis of a library of tetracyclic hydroazulenoisoindoles. *J. Comb. Chem.* **2009**, *11*, 486-494.

(9) Supurgibekov, M. B.; Zakharova, V. M.; Sieler, J.; Nikolaev, V. A., Stereochemistry and reactivity of F- and H-vinyldiazocarbonyl compounds and their phosphazines: synthesis of pyrazoles and pyridazines. *Tetrahedron Lett.* **2011**, *52*, 341-345.

(10) Parr, B. T.; Davies, H. M. L., Rhodium-catalyzed tandem cyclopropanation/cope rearrangement of 4-alkenyl-1-sulfonyl-1,2,3-triazoles with dienes. *Angew. Chem. Int. Ed.* **2013**, *52*, 10044-10047.

(11) Davies, H. M. L.; Alford, J. S., Reactions of metallocarbenes derived from N-sulfonyl-1,2,3-triazoles. *Chem. Soc. Rev.* **2014**, *43*, 5151-5162.

(12) Jiang, Y.; Sun, R.; Tang, X.-Y.; Shi, M., Recent advances in the synthesis of heterocycles and related substances based on α-imino rhodium carbene complexes derived from N-sulfonyl-1,2,3-triazoles. *Chem. – A Eur. J.* **2016**, *22*, 17910-17924.

(13) Wang, Y.; Lei, X.; Tang, Y., Rhodium-azavinylcarbene: A versatile synthon-enabling divergent synthesis of nitrogen heterocycles. *Synlett* **2015**, *26*, 2051-2059.

(14) Hockey, S. C.; Henderson, L. C., Rhodium(II) azavinyl carbenes and their recent application to organic synthesis. *Aust. J. Chem.* **2015**, *68*, 1796-1800.

(15) Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V., Rhodium-catalyzed transannulation of 1,2,3-triazoles with nitriles. *J. Am. Chem. Soc.* **2008**, *130*, 14972-14974.

(16) Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V., Rhodium-catalyzed enantioselective cyclopropanation of olefins with N-sulfonyl 1,2,3-triazoles. *J. Am. Chem. Soc.* **2009**, *131*, 18034-18035.

(17) Duan, S.; Zhang, W.; Hu, Y.; Xu, Z. F.; Li, C. Y., Synthesis of cyclopenta[b]indoles via a formal [3+2] cyclization of N-sulfonyl-1,2,3-triazoles and indoles. *Adv. Synth. Catal.* **2020**, *362*, 3570-3575.

(18) Tiuftiakov, N. Y.; Strelnikova, J. O.; Filippov, I. P.; Khaidarov, A. R.; Khlebnikov, A. F.; Bunev, A. S.; Novikov, M. S.; Rostovskii, N. V., Rhodium-catalyzed synthesis of 2-aroylpyrimidines via cascade heteropolyene rearrangement. *Org. Lett.* **2021**, *23*, 6998-7002.

(19) Patel, S. C.; Smith, M. W.; Mercer, J. A. M.; Suzuki, K.; Burns, N. Z., Enantioselective Cyclobutenylation of Olefins Using N-Sulfonyl-1,2,3-Triazoles as Vicinal Dicarbene Equivalents. *Org. Lett.* **2021**, *23*, 6530-6535.

(20) Parr, B. T.; Green, S. A.; Davies, H. M. L., Rhodium-catalyzed conversion of furans to highly functionalized pyrroles. *J. Am. Chem. Soc.* **2013**, *135*, 4716-4718.

(21) Makarov, A. S.; Uchuskin, M. G.; Hashmi, A. S. K., Intramolecular azavinyl carbene-triggered rearrangement of furans. *Chem. Sci.* **2019**, *10*, 8583-8588.

(22) Funakoshi, Y.; Miura, T.; Murakami, M., Synthesis of Penta-2,4-dien-1-imines and 1,2-Dihydropyridines by Rhodium-Catalyzed Reaction of N-Sulfonyl-1,2,3-triazoles with 2-(Siloxy)furans. *Org. Lett.* **2016**, *18*, 6284-6287.

(23) Mi, P.; Wang, H.; Zhao, R.; Song, J., Tandem O-H Insertion/[3,3]-Sigmatropic Rearrangement of Rhodium Carbenoids with 2-Furfuryl Alcohols: A Strategy To Access Polysubstituted Furans. *Eur. J. Org. Chem.* **2018**, *2018*, 759-762.

(24) Liu, Z.; Yang, Y.; Jiang, X.; Song, Q.; Zanoni, G.; Liu, S.; Bi, X., Dearomative [4 + 3] cycloaddition of furans with vinyl-N-triftosylhydrazones by silver catalysis: stereoselective access to oxa-bridged seven-membered bicycles. *Org. Chem. Front.* **2022**.

(25) Davies, H. M. L.; Clark, D. M.; Alligood, D. B.; Eiband, G. R., Mechanistic aspects of formal [3 + 4] cycloadditions between vinylcarbenoids and furans. *Tetrahedron* **1987**, *43*, 4265-4270.

(26) Davies, H. M. L.; Ahmed, G.; Churchill, M. R., Asymmetric synthesis of highly functionalized 8-oxabicyclo[3.2.1]octene derivatives. *J. Am. Chem. Soc.* **1996**, *118*, 10774-10782.

(27) Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. Tandem asymmetric cyclopropanation/Cope rearrangement. A highly diastereoselective and enantioselective method for the construction of 1,4-cycloheptadienes. *J. Am. Chem. Soc.* **1998**, *120*, 3326-3331.

(28) Wong, H. N. C.; Hon, M. Y.; Tse, C. W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. Use of cyclopropanes and their derivatives in organic synthesis. *Chem. Rev.* **1989**, 89, 165-198.

(29) Davies, H. M. L.; Xiang, B.; Kong, N.; Stafford, D. G. Catalytic asymmetric synthesis of highly functionalized cyclopentenes by a [3 + 2] cycloaddition. *J. Am. Chem. Soc.* **2001**, *123*, 7461-7462.

(30) Chuprakov, S.; Hwang, F. W.; Gevorgyan, V. Rh-catalyzed transannulation of pyridotriazoles with alkynes and nitriles. *Angew. Chem. Int. Ed.* **2007**, *46*, 4757-4759.

(31) Rajasekar, S.; Yadagiri, D.; Anbarasan, P. One-pot aminoethylation of indoles/pyrroles with alkynes and sulfonyl azides. *Chem. Eur. J.* **2015**, *21*, 17079-17084.

(32) Park, S.; Yong, W. S.; Kim, S.; Lee, P. H. Diastereoselective N-sulfonylaminoalkenylation of azulenes from terminal alkynes and azides via N-sulfonyl-1,2,3-triazoles. *Org. Lett.* **2014**, *16*, 4468-4471.

(33) Rajasekar, S.; Anbarasan, P. One-pot transannulation of N-sulfonyl-1,2,3-triazoles to dihydro-β-carbolines and dihydroisoquinolines via

rhodium-catalyzed C-H insertion-cum-base-mediated aza-Michael reaction. *J. Org. Chem.* **2019**, *84*, 7747-7761.

(34) Zibinsky, M.; Fokin, V. V. Sulfonyl-1,2,3-triazoles: Convenient synthones for heterocyclic compounds. *Angew. Chem.* **2013**, *125* (5), 1547-1550.

(35) DeAngelis, A.; Shurtleff, V. W.; Dmitrenko, O.; Fox, J. M. Rhodium(II)-catalyzed enantioselective C–H functionalization of indoles. *J. Am. Chem. Soc.* **2011**, *133* (6), 1650-1653.