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Synthesis and reactivity of 1-sulfonylcyclooctatriazoles†

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Strained eight-membered cyclic alkynes undergo rapid inverse electron demand cycloaddition with sulfonyl azides to give the corresponding 1-sulfonylcyclooctatriazoles in excellent yield. Treatment of these sulfonyltriazoles with a chiral rhodium(II) carboxylate catalyst prompted transannular C–H bond insertion in good yield and with excellent ee, or 1,2-H shift.

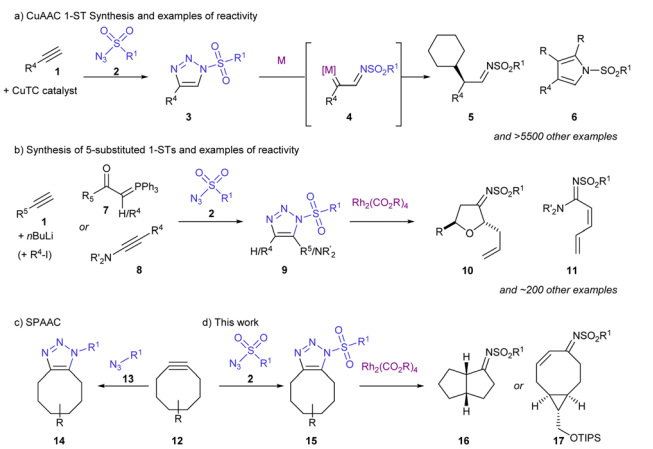
1-Sulfonyl-1,2,3-triazoles (1-STs) have emerged as valuable building blocks for organic synthesis.[1] The combination of nitrogen-rich heteroaromatic and electron-poor sulfonyl group means these compounds have on-demand access to powerful carbene reactivity. In the presence of a catalyst, typically a rhodium(II) carboxylate, the 1,2,3-triazole (**3**) undergoes denitrogenation to make a metal–carbene complex (**4**). The route to metal carbenes from 1-STs offers not only complementary reactivity to established carbene methodology but has allowed novel applications and this strategy has been applied to create value-added products, bioactive compounds and natural products. A small selection of 1-ST denitrogenation methodology includes (Scheme 1): functionalising C–H bonds with high yield and excellent selectivity (**5**),[2] heterocycle synthesis (**6**, **10**)[3] and 1,2-H shift (**11**).[4]

A key consideration in maximising the application of 1-ST methodology is facile access to these valuable heterocycles (Scheme 1). Most commonly, 1-STs with 4-substitution **3** are synthesised by Cu(I) thiophene carboxylate (CuTC) catalysed reaction between an alkyne and sulfonyl azide.[5] 5-Substituted and 1,4-disubstituted 1-STs **9** have also been synthesised but are less common. These 1-STs **9** can be accessed by anionic methods (using *n*BuLi),[6] Wittig-type reaction (*e.g.* with **7**),[7] or others[8] but these methods have drawbacks including limited applicability, low yield and poor atom economy. Using a reaction between an electronically matched azide and alkyne pair can also give an efficient route to triazoles. For sulfonyl azides **2**, which are very electron-poor, electron-rich alkynes (such as azoalkynes **8**) react very rapidly and selectively to form 1-STs.[4,9]

Increased rate of reaction is observed in the strain-promoted cycloaddition between azides **13** and cyclic alkynes **12** (SPAAC). This "explosive" reactivity was first noted by Blomquist and Liu[10] and characterised by Wittig and Krebs.[11] Later, Bertozzi realised this cycloaddition would by compatible *in vivo* and it has become a very popular technique for marking and imaging biological processes.[12] However, SPAAC has not been considered in the context of 1-ST synthesis.

Here, the cycloaddition between cyclic alkynes **12** and sulfonyl azides **2** is explored as a route to the less-exploited class of 4,5-disubstituted 1-ST and described computationally. The reactivity of two types of the resulting trisubstituted triazole products **15** has been developed into an enantioselective transannular C–H insertion (**16**) and 1,2-H shift (**17**) depending on the cyclic alkyne.

A range of sulfonyl azides **2** was considered in the cycloaddition with cyclooctyne **18** (Fig. 1). Cyclooctyne was readily prepared in



Scheme 1 Overview of sulfonyl triazole synthesis and examples of reactivity.

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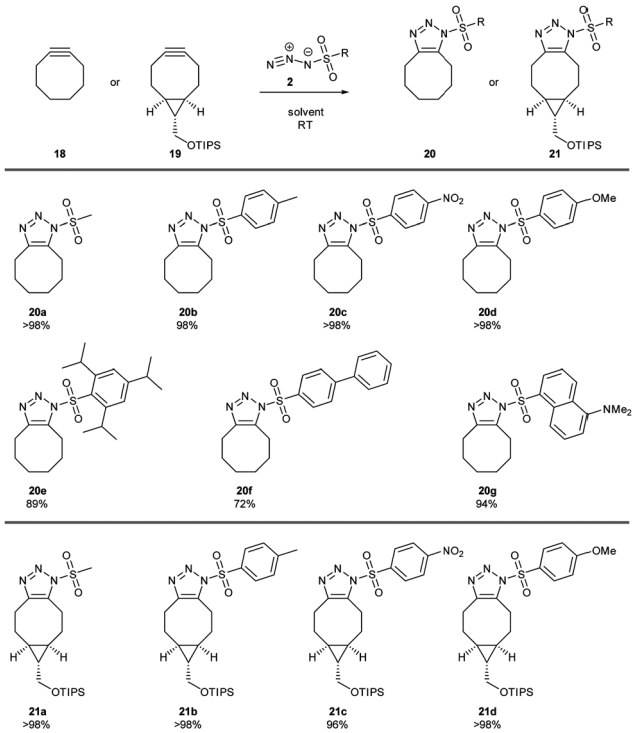
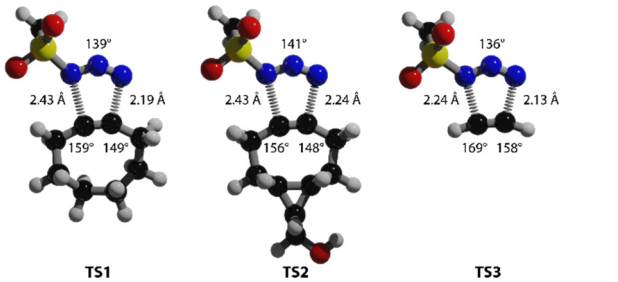


Fig. 1 Cycloaddition between MsN_3 **2** and cyclooctynes **18**, **19**. Isolated yield.

three steps from (*Z*)-cylcooctene[13] and it was an important consideration that cyclooctyne decomposes upon storage (over days under argon at −20 °C). An equimolar mixture of cyclooctyne **18** and sulfonyl azide **2** was stirred in dichloromethane and the cycloaddition was complete by 30 min. The cycloadduct 1-ST **20** could be isolated directly from the reaction or following facile purification. For operational convenience, cyclooctyne could also be used in excess to ensure complete conversion and any unreacted excess could be removed *in vacuo*. The reaction was quantitative to give methanesulfonyl **20a**, *p*-toluenesulfonyl **20b**, *p*-nitrobenzenesulfonyl **20c** and *p*-methoxybenzenesulfonyl **20d** triazoles, showing excellent tolerance for across a range of electron-rich to electron-poor sulfonyl azides. The process also gave a very high yield of the triazole with the bulky triisopropylbenzenesulfonyl group **20e** as well as polyaromatic sulfonyl triazoles with a *p*-biphenyl **20f** or dimethylaminonaphthyl **20g** substituent. Bicyclo[6.1.0]non-4-ynes (BCNs) are a popular class of cyclic alkyne, having a functional handle on the cyclopropyl ring, plus the bicyclic system brings an increase in reactivity through increased strain.[14] A silicon protected BCN **19** was prepared in short order. The more functionalised cyclooctyne **19** also gave excellent yields of triazole **21** when reacting with a selection of different alkyl and aryl sulfonyl azides **21a–d**.

The increased reactivity of cyclooctynes is attributed to the alkyne they contain being distorted from its ideal 180° angle. Bickelhaupt and Houk have formalised a distortion–interaction transition state theory for reactions[15] that is particularly suited to describe the reactions of strained molecules and has been applied to cyclooctynes.[16] In this model, the activation energy

Table 1 Transition structures for the cycloaddition between MsN_3 and cyclooctyne **TS1**, BCN **TS2** and acetylene **TS3**

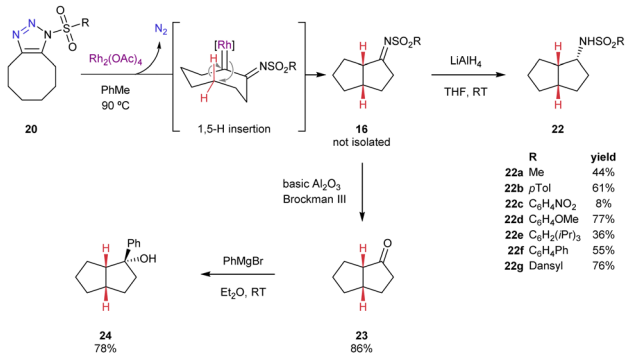


	TS1	TS2	TS3	
ΔE	8.4	7.1	16.1	kcal mol^{-1}
$\Delta E^{\ddagger}_{dist}$ (alkyne)	1.7	1.2	5.4	kcal mol^{-1}
$\Delta E^{\ddagger}_{dist}$ (azide)	17.7	16.0	21.6	kcal mol^{-1}
$\Delta E^{\ddagger}_{int}$	−11.0	−10.1	−10.9	kcal mol^{-1}
$\Delta G^{\ddagger}$	20.6	19.2	28.2	kcal mol^{-1}
$HOMO_{alkyne}$–$LUMO_{azide}$	10.5	10.6	12.1	eV
$HOMO_{azide}$–$LUMO_{alkyne}$	13.0	12.9	13.0	eV

Calculations at B3LYP/6-31g(d) except orbital energies at HF/6-311++G(2d,p)//B3LYP/6-31g(d). See ESI.

required for a reaction between molecules ($\Delta E^{\ddagger}$) is a combination of the energy required for the individual components to distort to their transition state geometries ($\Delta E^{\ddagger}_{dist}$) offset by stabilising orbital interactions between those two components ($\Delta E^{\ddagger}_{int} = \Delta E^{\ddagger} - \Delta E^{\ddagger}_{dist}$). The transition states for the cycloaddition between mesyl azide and each of cyclooctyne **TS1** BCN **TS2** and acetylene **TS3** were considered (Table 1) in the framework of Houk's previous work in this area.[16a] Calculations were performed on the PSI4 program:[17] geometry optimisation and thermochemistry analysis was performed using B3LYP/6-31G(d); and orbital energies were calculated using HF/6-311++G(2d,p) at the B3LYP/6-31g(d) geometries.

In each of the three transition structures, the cycloaddition was concerted, and asynchronous: with shorter C–N distances at the unsubstituted azide N3 terminus. The azide required significant distortion to reach its reacting geometry: the 175° ∠N–N–N bond angle in MsN_3 ground state[18] being reduced by over 35° in the three transition structures. This distortion corresponded to a 17.7, 16.0 and 21.6 kcal mol^{-1} increase in energy ($\Delta E^{\ddagger}_{dist}$) for the azide to attain these reactive geometries. For the cyclic alkynes, only a small deviation from the ground state[19] alkyne bond angles was required and the associated change in energy was small ($\Delta E^{\ddagger}_{dist}$ = 1.7 and 1.2 kcal mol^{-1}). In contrast, the 180° alkyne bond angles in acetylene were reduced considerably in its transition structure, with an associated $\Delta E^{\ddagger}_{dist}$ of 5.4 kcal mol^{-1}. The interaction energy, was very similar across the three reactions ($\Delta E^{\ddagger}_{int}$: −11.0, −8.7; −10.9 kcal mol^{-1}) suggesting that each of the three reactions has similar electrostatic, charge transfer and repulsion interactions. Overall, the $\Delta G^{\ddagger}$ for the cycloaddition of MsN_3 with the cyclic alkynes was significantly lower than calculated for acetylene and this analysis suggests that this is due to the strained alkyne being preorganised towards its transition state geometry.



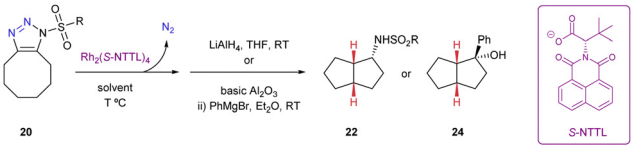
Scheme 2 Transannular C–H insertion reaction.

Examination of frontier molecular orbital energies revealed that for each of the transition structures, the $HOMO_{alkyne}$–$LUMO_{azide}$ gap was lower than the $HOMO_{azide}$–$LUMO_{alkyne}$ counterpart. This constitutes an inverse electron-demand (IED) mechanism:[16c] usually for SPAAC the dominant orbital interactions are between the azide HOMO and alkyne LUMO—that can be explained by the very electron withdrawing nature of the sulfonyl group.

As a novel class of 1-ST, the reactivity of the cyclooctatriazoles was probed (Scheme 2). The 1-ST **20b** derived from cyclooctyne and TsN_3 was treated with rhodium(II) acetate as catalyst in the presence of 2,5-dimethylfuran,[3c,i,j] styrene,[20] triethylsilane,[21] or benzonitrile,[22] all of which have been demonstrated to be excellent partners for transformations with 4-substituted sulfonyl triazoles. Once the starting material was consumed, THF and lithium aluminium hydride were added to convert any sulfonyl imine into the corresponding amide. In each case the same outcome was observed, a new product was formed that did not incorporate any reacting partner. Analysis by NMR revealed that the product was a [3.3.0]-bicyclic sulfonamide **22b** and that it had been formed with complete diastereocontrol (>20 : 1 dr by ^{1}H NMR). The eight-membered ring is well known to have close transannular interactions[23] so this reaction is proposed to involve 1,5-insertion of the rhodium carbene into the transannular C–H bond.[24,25] The same outcome was observed for all the different sulfonyl groups evaluated (**22a–g**). The stereochemistry was confirmed by comparison with known bicyclic sulfonamide **22b** that was accessed by anionic transannular aziridine opening and whose structure was validated by independent synthesis and crystallography.[26]

The generation of stereocentres prompted an investigation into creating an enantioselective variant of the reaction (Table 2 and ESI†). There are many chiral rhodium(II) carboxylate catalysts that have been demonstrated to impart good enantioselectivity using 1-STs. A brief screen showed that Rh_2(*S*-NTTL)$_4$ catalyst[27] was significantly more effective at controlling stereoselectivity in the reaction than Rh_2DOSP_4 or Rh_2PTAD_4. Interestingly, the selectivity was also complementary between these ligands. Lowering the temperature from 90 to 50 °C gave better enantioselectivity (29% ee) but at ambient temperature the reaction did not proceed. Varying the solvent gave another step towards enantioselectivity with toluene (68% ee) and perfluorobenzene (91% ee) giving further improvement. Finally, the sulfonyl group was considered. Enantiomeric excess was determined by HPLC analysis following $LiAlH_4$ reduction; or the intermediate sulfonyl imine was hydrolysed to the ketone **23** using basic Al_2O_3 and converted to the tertiary alcohol **24** by nucleophilic addition of PhMgBr (>20 : 1 dr by ^{1}H NMR, Scheme 2). Accessing known ketone **23**[28] allowed further confirmation of the absolute stereochemistry. The second workup was essential in cases where the sulfonamide enantiomers **22** could not be separated by HPLC or functionality was incompatible with $LiAlH_4$ reduction (*i.e.* Ns, R = *p*$NO_2C_6H_4$). Electron donating aromatic sulfonyl groups gave their bicyclic product in lower ee compared with electron withdrawing ones. The Ns group gave higher enantioselectivity and accelerated the reaction rate. Combining these outcomes: treating the *N*–Ns cyclooctatriazole product with Rh_2(*S*-NTTL)$_4$ in perfluorobenzene at 50 °C followed by the hydrolysis and Grignard addition resulted in clean conversion to the bicyclic product in 94% ee and with 78% yield over the two steps.

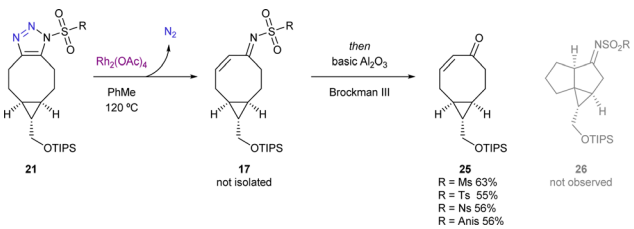
Table 2 Optimisation highlights for enantiomeric excess of transannular C–H insertion



Entry	R	Solvent	*T*	Workup	Yield (%)	ee (%)
1	*p*Tol	CH_2Cl_2	50	$LiAlH_4$	36	29
2	*p*Tol	PhMe	50	$LiAlH_4$	43	68
3	*p*Tol	**C_6F_6**	50	$LiAlH_4$	72	**91**
4	*p*$MeOC_6H_4$	PhMe	50	$LiAlH_4$	36	24
5	*p*$NO_2C_6H_4$	PhMe	50	Al_2O_3/PhMgBr	57	69
6	*p*$NO_2C_6H_4$	C_6F_6	50	Al_2O_3/PhMgBr	78	**94**

NTTL = 2-(1,3-dioxobenzo[*de*]isoquinolin-2-yl)-3,3-dimethyl-butanoate.

The reactivity of the novel *N*-sulfonylBCNs **21** was also investigated (Scheme 3). In the case of these 1-STs, there was no transannular reaction. Switching to much more forcing conditions was required to see any reaction, namely toluene as solvent, $Rh_2(OAc)_4$ as catalyst and 120 °C (sealed vial). At this temperature, the rhodium(II) complex catalysed a denitrogenation and 1,2-H shift to give an α,β-unsaturated intermediate **17**; that was hydrolysed to the corresponding ketone **25**. The same



Scheme 3 1,2-H Shift.

outcome was observed for a number of different sulfonyl group each of which delivered the enone in good yield. The 1,2-H shift is well-documented in metallocarbenes with an adjacent C–H bond, including those derived from 1-STs.[4] It is proposed that the difference in reactivity compared to the cyclooctyne derived 1-STs was that the resulting polycyclic product **26** would be highly strained.

In summary, strain-promoted inverse electron demand cycloaddition is an effective route to highly substituted 1-STs. These can undergo transannular C–H insertion with very high enantioselectivity or 1,2-H shift.

Conflicts of interest

There are no conflicts to declare.

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