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Enantioselective BIMP-catalysed [2,3]-Wittig rearrangements of oxindole-derived allylic and propargylic ethers

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The organocatalytic enantioselective [2,3]-Wittig rearrangement of a range of oxindole-derived allylic and propargylic ethers using bifunctional iminophosphorane (BIMP) organosuperbase catalysts has been investigated, generating 3-hydroxyoxindole derivatives in high stereoselectivity (>35 examples, up to 99 : 1 er). In the allylic ether series, substituent variation has a significant effect upon product diastereoselectivity, with excellent enantioselectivity observed in all cases. The incorporation of a C(3)-fluorine substituent leads to improved diastereoselectivity, giving products bearing a stereogenic tertiary fluoride, in up to 94 : 6 dr and 98 : 2 er. In the propargylic series, the [2,3]-rearrangement generates α-allenyl alcohols in excellent yield and enantioselectivity (up to 98% yield, 99 : 1 er) at 60 °C, with a range of substituents around the oxindole core, as well as alkyl and aryl-substitution at the alkyne functionality demonstrated. Functionalisation of the α-allenyl alcohol to spirocyclic oxindoles without loss of stereochemical integrity has also been demonstrated.

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Introduction

As an important subclass of [2,3]-sigmatropic rearrangements,[1–7] the anionic [2,3]-Wittig rearrangement of both allylic and propargylic ethers has attracted much synthetic attention due to its ability to rapidly construct complex stereodefined molecules with 100% atom economy (Fig. 1A).[8–13] Despite widespread applicability in organic synthesis,[8,9,13–25] catalytic enantioselective variants remain relatively understudied. In recent years approaches to the catalytic enantioselective [2,3]-Wittig rearrangement of allylic ethers have been disclosed by Denmark,[26] Gaunt,[27] Kanger,[28–31] Jacobsen,[32] and others[33,34] employing either organocatalysts or metal-based catalysts with promising results. As a representative example of these approaches, Kanger studied the [2,3]-rearrangement of cinnamyl substituted oxindole derived allylic ethers using a cinchona derived squaramide hydrogen-bonding catalyst (Fig. 1B). Although effective catalysis and excellent product enantioselectivity (up to 97 : 3 er for the major diastereoisomer) was observed, only moderate diastereoselectivity (from 52 : 48 to 70 : 30 dr) could be achieved, preferentially giving the *anti*-diastereoisomer **2**. Despite these encouraging precedents, only limited studies regarding the effect of varying the allylic substitution pattern (including (*E*)- and (*Z*)-configuration, incorporation of multiple substituents) upon both product diastereoselectivity and enantioselectivity within the catalytic enantioselective [2,3]-Wittig rearrangement have been established. Related enantioselective [2,3]-Wittig processes of propargylic ethers to deliver α-allenyl alcohols is also of significant interest.[19] The reduced reactivity of the propargylic substituent in such processes compared to the allylic counterpart is widely recognised, with the inclusion of an sp-hybridised carbon resulting in a significantly strained transition state.[35,36] To the best of our knowledge the only catalytic enantioselective [2,3]-Wittig rearrangement of propargylic ethers was elegantly documented by Feng and co-workers in 2018, catalysed by a chiral *N*,*N*′-dioxide/Ni^{II} complex. These reactions afforded functionalised allenes with excellent enantioselectivity but required the addition of stoichiometric base and long reaction times (up to 184 h) to reach completion (Fig. 1C).[37,38]

In previous work we have developed an organocatalytic enantioselective [1,2]-Wittig rearrangement of allylic ethers that employs the chiral bifunctional iminophosphorane (BIMP) superbase catalysts originally introduced by the Dixon group[39] and now widely exploited in a range of catalytic processes.[40–61] This transformation was shown to proceed *via* an initial enantioselective [2,3]-sigmatropic rearrangement, fol-

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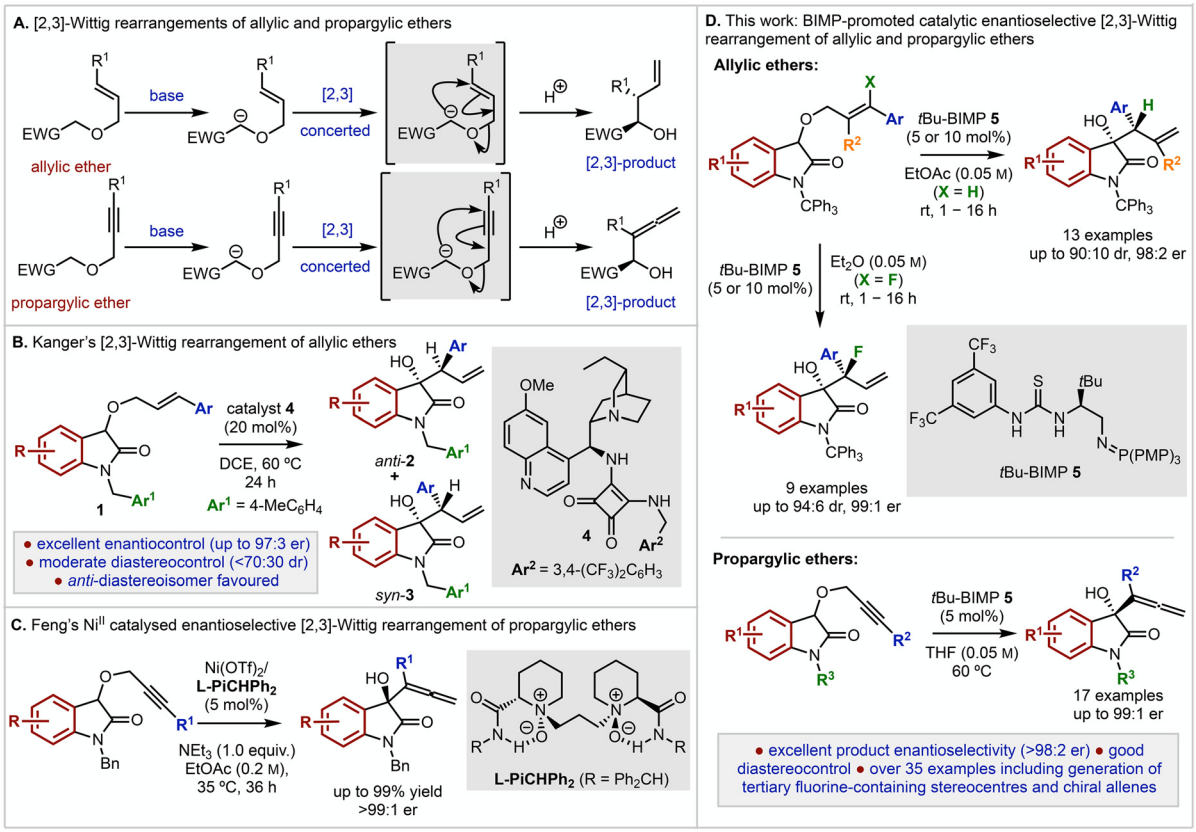


Fig. 1 Previous and current work on catalytic enantioselective [2,3]-Wittig rearrangements of allylic and propargylic ethers. PMP = $C_6H_4OCH_3$.

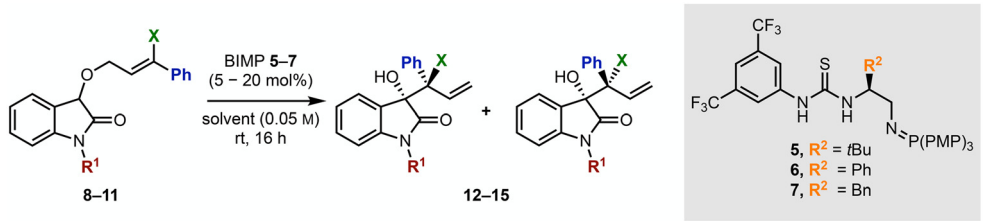
lowed by an *in situ* enantioretentive anionic fragmentation process (equivalent to a [1,3]-rearrangement), providing homoallylic alcohols with good to excellent yields and stereoselectivities.[62] Building upon this work, in this manuscript the scope and limitations of the [2,3]-Wittig rearrangement of oxindole-derived allylic and propargylic ethers using BIMP catalysts is explored. Optimisation in the allylic system with a C(3)-H substituent allows the preferential formation of the *syn*-diastereoisomer (complementary to Kanger's work), while the effect of altering the substituent pattern and configuration within the allylic ether functionality upon stereoselectivity has been sequentially investigated. The inclusion of a C(3)-F substituent within the allylic fragment leads to the selective formation of highly desirable tertiary fluorides with high diastereo- and enantiocontrol.[63–65] Furthermore, the [2,3]-Wittig rearrangement of oxindole-derived propargylic ethers is shown to proceed with high selectivity even at a reaction temperature of 60 °C, giving access to α-allenyl alcohols in excellent yield and enantioselectivity (up to 98% yield, 99 : 1 er) (Fig. 1D).

Results and discussion

Optimisation of the [2,3]-Wittig rearrangement of allylic ethers

Initial studies used cinnamyl ether **8** as a model system for reaction optimisation, with the effect of *N*-substitution and catalyst variation investigated using mesitylene as solvent (Table 1). Using *t*Bu-BIMP catalyst **5** (20 mol%), and consistent with the work of Kanger,[28] *N*-Me and *N*-Bn substitution gave preferential formation of the *anti*-diastereoisomer with moderate enantiocontrol (entries 1 and 2). Optimal diastereoselectivity and enantiocontrol was observed with *N*-trityl substitution, giving formation of the *syn*-diastereoisomer (70 : 30 dr) with excellent enantiocontrol (98 : 2 er, entry 3). Variation of the catalyst indicated that both Ph-BIMP **6** and Bn-BIMP **7** catalysts also led to effective rearrangement, giving products with slightly reduced diastereo- and enantiocontrol (entries 4 and 5). Screening of reaction solvents (see SI for full details) indicated that polar solvents such as DMF led to reduced conversion and stereocontrol (entry 6) while ethyl acetate and toluene were also effective (entries 7 and 8). In ethyl acetate the catalyst loading could be reduced to 10 mol% while maintaining stereocontrol (entry 9). The relative and absolute (3*S*,1′*S*)-configuration within the major diastereoisomer of **14** was confirmed by detritylation and comparison with known literature.[66] Similar trends in reactivity but noticeably improved levels of diastereocontrol were observed when a C(3)-F substituent was introduced within the cinnamyl ether (entries 10–12). Reaction in Et_2O proved most effective with the use of *t*Bu-BIMP catalyst **5** (5 mol%) giving the desired tertiary fluoride containing product **15** in 90% yield (91 : 9 dr, 98 : 2 er, entry 12).

Table 1 Variation of reaction conditions[a]



Entry[a]	X	R^1	Catalyst	Solvent	Product	Yield[b]/%	dr (*syn* : *anti*)[b]	er[c]
1	H	Me (**8**)	**5** (20 mol%)	Mesitylene	**12**	80	26 : 74	80 : 20/50 : 50
2	H	Bn (**9**)	**5** (20 mol%)	Mesitylene	**13**	>95	34 : 66	70 : 30/91 : 9
3	H	CPh_3 (**10**)	**5** (20 mol%)	Mesitylene	**14**	>95	70 : 30	98 : 2/97 : 3
4	H	CPh_3 (**10**)	**6** (20 mol%)	Mesitylene	**14**	95	66 : 34	97 : 3/93 : 7
5	H	CPh_3 (**10**)	**7** (20 mol%)	Mesitylene	**14**	>95	67 : 33	97 : 3/97 : 3
6	H	CPh_3 (**10**)	**5** (20 mol%)	DMF	**14**	40	60 : 40	84 : 16/82 : 18
7	H	CPh_3 (**10**)	**5** (20 mol%)	Toluene	**14**	>95	70 : 30	98 : 2/97 : 3
8	H	CPh_3 (**10**)	**5** (20 mol%)	EtOAc	**14**	>95	70 : 30	98 : 2/97 : 3
9	*H*	*CPh_3 (**10**)*	***5** (10 mol%)*	*EtOAc*	***14***	*>95 (97)*	*70 : 30*	*98 : 2/97 : 3*
10	F	CPh_3 (**11**)	**5** (5 mol%)	Mesitylene	**15**	>95	89 : 11	98 : 2
11	F	CPh_3 (**11**)	**5** (5 mol%)	*t*BuOMe	**15**	>95	85 : 15	97 : 3
12	*F*	*CPh_3 (**11**)*	***5** (5 mol%)*	*Et_2O*	***15***	*>95 (90)*	*91 : 9*	*98 : 2*

[a] Unless otherwise noted, the reaction was performed on a 0.05 mmol scale. [b] Determined by ^{1}H NMR analysis using 1,5-difluoro-2,4-dinitrobenzene as an internal standard (isolated yield in brackets). [c] Determined by HPLC analysis on a chiral stationary phase.

Scope and limitations. The scope and limitations of the [2,3]-Wittig rearrangement under the developed conditions were next explored (Fig. 2A). With X = H, the effect of (*E*)- and (*Z*)-olefin configuration was tested. Rearrangement of the (*E*)-configured ether **10** proceeded effectively to give **14** in high yield and stereoselectivity (97%, 70 : 30 dr, 98 : 2 er). However rearrangement of the (*Z*)-ether **16** proceeded slowly, giving **14** in 10% yield (>95 : 5 dr, 94 : 6 er), indicating this process is stereoselective but not stereospecific. With an (*E*)-cinnamyl unit the effect of substituent variation on the oxindole was probed. Halogenated (4-Cl and 6-B) as well as electron-donating (5-MeO) substituents were tolerated, affording **17–19** in high yields (74–87%) and uniformly excellent enantiocontrol (97 : 3–98 : 2 er) although with varying diastereoselectivity (54 : 46–75 : 25 dr). The effect of varying the C(3)-aryl substituent within the allylic framework was also tested, with the [2,3]-rearrangement products **20–26** all obtained with generally excellent yields (70–99%) and enantiocontrol (all >96 : 4 er). The inclusion of electron-donating (2-$MeOC_6H_4$), halogenated (4-FC_6H_4), electron-withdrawing (4-$F_3CC_6H_4$), extended aromatic (1-naphthyl; 2-naphthyl) as well as a heteroaromatic (3-thienyl) substituent was tolerated, with moderate to good diastereocontrol observed (up to 85 : 15 dr). Notably, 2-Me-3-Ph-disubstitution of the allylic fragment resulted in high diastereoselectivity (90 : 10 dr) in **27**, although 20 mol% catalyst loading was needed to promote high conversion. The inclusion of a C(3)-trifluoromethyl substituent was also tolerated, giving moderate conversion to **28** (33% yield, 68 : 32 dr, 97 : 3 er) at room temperature, but giving 70% yield upon heating at 100 °C resulting in poor diastereocontrol but high enantioselectivity (54 : 46 dr, 93 : 7 er).

The generality of the ability to generate products containing a tertiary fluoride stereocentre through the [2,3]-Wittig rearrangement was also investigated (Fig. 2B). The inclusion of halogenated (4-Cl, 5-F, and 6-Cl), electron-donating (5-MeO) and electron-withdrawing (5-O_2N) substituents were tolerated within the oxindole, giving the corresponding [2,3]-rearrangement products **29–33** bearing a stereogenic tertiary fluoride upon treatment with *t*Bu-BIMP **5** with excellent yields (up to 93%) and stereoselectivity (up to 94 : 6 dr, 99 : 1 er). Further investigation showed that electron-donating (4-MeC_6H_4, 4-$MeOC_6H_4$) and electron-withdrawing (4-$F_3CC_6H_4$)-substituted allylic ethers underwent [2,3]-rearrangement, giving tertiary fluorides **34–36** with excellent yields (up to 95%) and stereoselectivity (up to 94 : 6 dr, 98 : 2 er). The relative and absolute (3*S*,1′*R*)-configuration within the major diastereoisomer of **15** was unambiguously proven by X-ray crystallographic analysis, with all others assigned by analogy.

Optimisation of the [2,3]-Wittig rearrangement of propargylic ethers

In the propargylic ether series, initial optimisation used *N*-Bn substituted substrate **37** as a model substrate with *t*Bu-BIMP **5** as the catalyst in toluene at room temperature (Table 2). Treatment of **37** with 10 mol% *t*Bu-BIMP **5** in toluene gave the desired allenyl alcohol **39** in high yield and promising enantioselectivity (91% yield, 90 : 10 er, entry 1). Screening of alternative solvents (mesitylene, diethyl ether, THF and ethyl acetate) only marginally affected the product yield and enantioselectivity (entries 2–5) with THF giving optimal enantiocontrol (93 : 7 er). Having shown in previous work and in

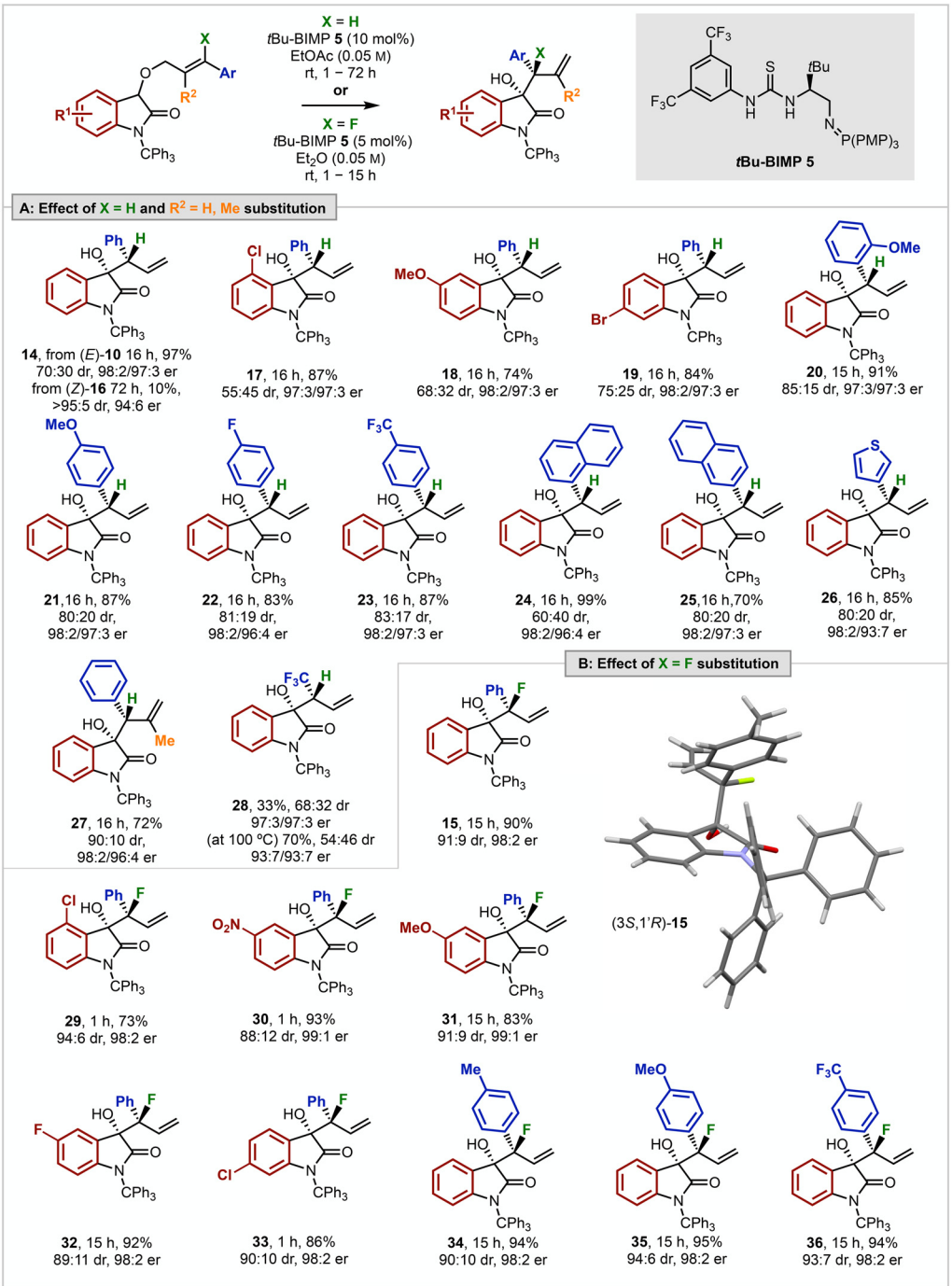
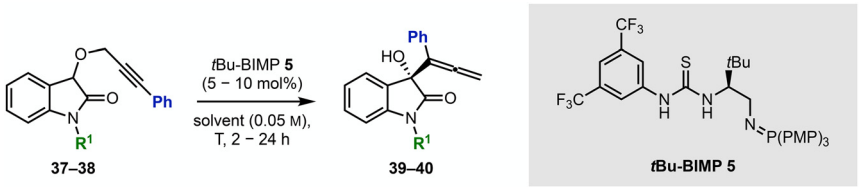


Fig. 2 Unless otherwise noted, the reaction was performed at 0.05 M concentration and on a 0.2 mmol scale. Reaction diastereoselectivity determined by ^{1}H NMR analysis of the crude reaction mixture using 1,5-difluoro-2,4-dinitrobenzene or 1,3,5-trimethoxybenzene as the internal standard; yields are isolated yields. Product enantioselectivity determined by HPLC analysis on a chiral stationary phase.

Table 1 that the *N*-substituent had a significant effect on enantioselectivity, the effect of introducing an *N*-trityl group was investigated. Although the yield significantly decreased to 30% in THF, the product enantioselectivity increased to 99 : 1 er (entry 6). Further optimisation of concentration, catalyst loading, and reaction temperature (entries 6–9) led to optimal conditions for [2,3]-Wittig rearrangement of propargylic ether **38** (60 °C, 5 mol% *t*Bu-BIMP catalyst **5**, 2 h reaction time) to obtain product **40** in 96% isolated yield and 98 : 2 er (entry 9). Similar results were obtained using either mesitylene or EtOAc as solvent. Given the availability of THF, as well as the short reaction time, THF was chosen as the best solvent for further investigations into the scope and limitations of the process.

Table 2 Optimisation of reaction conditions for propargylic ether [2,3]-Wittig rearrangement[a]



Entry[a]	R^1	Solvent	*T*/°C	Time/h	Product	Yield[b]/%	er[c]
1	Bn (**37**)	Toluene	rt	4	**39**	91	90 : 10
2	Bn (**37**)	Mesitylene	rt	4	**39**	91	91 : 9
3	Bn (**37**)	Et_2O	rt	4	**39**	95	91 : 9
4	Bn (**37**)	THF	rt	3	**39**	96	93 : 7
5	Bn (**37**)	EtOAc	rt	2	**39**	95	92 : 8
6	CPh_3 (**38**)	THF	rt	24	**40**	30	99 : 1
7[d]	CPh_3 (**38**)	THF	rt	24	**40**	33	99 : 1
8[d,e]	CPh_3 (**38**)	THF	rt	24	**40**	68	99 : 1
9[d,f]	*CPh_3 (**38**)*	*THF*	*60*	*2*	***40***	*97 (96)*	*98 : 2*
10[d,f]	CPh_3 (**38**)	EtOAc	60	4	**40**	94 (91)	98 : 2
11[d,f]	CPh_3 (**38**)	Mesitylene	60	2	**40**	98 (97)	98 : 2

[a] Unless otherwise noted, the reaction was performed with 0.05 mmol scale using the specified solvents and temperatures. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as the internal standard (isolated yield in brackets). [c] Determined by HPLC analysis on a chiral stationary phase. [d] With 0.10 M concentration. [e] With 15 mol% catalyst loading. [f] With 5 mol% catalyst loading at 60 °C.

Scope and limitations. With optimised conditions developed the scope of the [2,3]-Wittig rearrangement of propargylic ethers was examined (Fig. 3A). Incorporation of a chloro-substituent at the 4-, 5-, or 6-position on the oxindole ring system was readily accommodated, with excellent yields and enantioselectivity maintained in all cases (90–96% yield, 98 : 2 er, **41–43**). *N*-Tritylation of 7-chloroisatin was unsuccessful, hence the *N*-benzyl analogue was tested instead, giving 7-Cl **44** in 93% yield and 91 : 9 er; the slightly reduced enantioselectivity in this example is expected given the significant impact the *N*-substituent has on product enantiocontrol. Electron-withdrawing (5-O_2N) and electron-donating (5-MeO) substituents were also tolerated within the oxindole, furnishing the corresponding α-allenyl alcohols **45** and **46** in excellent yield and enantiocontrol (>98 : 2 er). Subsequent work varied the substitution on the propargylic framework (R^2). Incorporation of halogen (4-ClC_6H_4 and 3-BrC_6H_4), electron-donating (4-$MeOC_6H_4$) or electron-withdrawing (4-$MeO_2CC_6H_4$) substituents were all tolerated well, giving the target products **47–50** in excellent yields (88–98%) and enantioselectivity (97 : 3 to 98 : 2 er). In addition, the tolerance of the protocol towards steric bulk close to the electrophilic site of the alkyne was investigated by evaluating a substrate bearing a 2-Me substituent on the phenyl ring, as well as a 1-naphthyl-substituted derivative. In both cases, the reaction proceeded to give the corresponding products **51** and **52** in high yields and enantioselectivitiy although prolonged reaction times were required to reach full conversion. The rearrangement protocol also accommodates a heterocyclic 2-thienyl moiety at the alkyne, providing α-allenyl alcohol **53** in high yield and enantiopurity within 2 h (89% yield, 98.5 : 1.5 er). To further test this protocol, the R^2 substituent was changed from aryl to either a H- or Me-substituent, affording the corresponding [2,3]-rearrangement products **54** and **55** in good to excellent yields (68–80%) and enantioselectivity (>98 : 2 er). Cyclohexyl-substituted allenyl alcohol **56** was only obtained in a reduced 40% yield but still with excellent enantioselectivity (98 : 2 er). The absolute (*S*)-configuration within **40** was confirmed by comparison with known literature data.[37]

To illustrate the synthetic utility of this methodology, reaction scale-up and derivatisation of the α-allenyl alcohol products was investigated (Fig. 3B). The [2,3]-Wittig rearrangement reaction was carried out on a 1 mmol scale to afford almost quantitative yield (0.6 g) of the corresponding product **48** without any erosion of enantiopurity (98 : 2 er). Allenyl-species **48** was considered to be a potentially valuable building block for heterocycle formation, with derivatization generating spirocyclic oxindoles that are derivatives of bioactive and medicinally relevant compounds.[67–75] Spirocyclic oxindole **57** was obtained in excellent yield with complete retention of stereochemical integrity by treatment of allenyl alcohol **48** with silver nitrate. Subsequent detritylation with TFA and Et_3SiH delivered *N*-unprotected spirooxindole **58** in 97% yield (98 : 2 er). Furthermore, Pd^{II}-catalysed spirooxindole formation was coupled cross coupling with allyl bromide, affording product **59** in good yield (81%) and excellent enantioselectivity (98 : 2 er).[76]

Proposed mechanism and stereochemical model

A plausible simplified mechanism for these rearrangement processes is illustrated for the enantioselective [2,3]-rearrange-

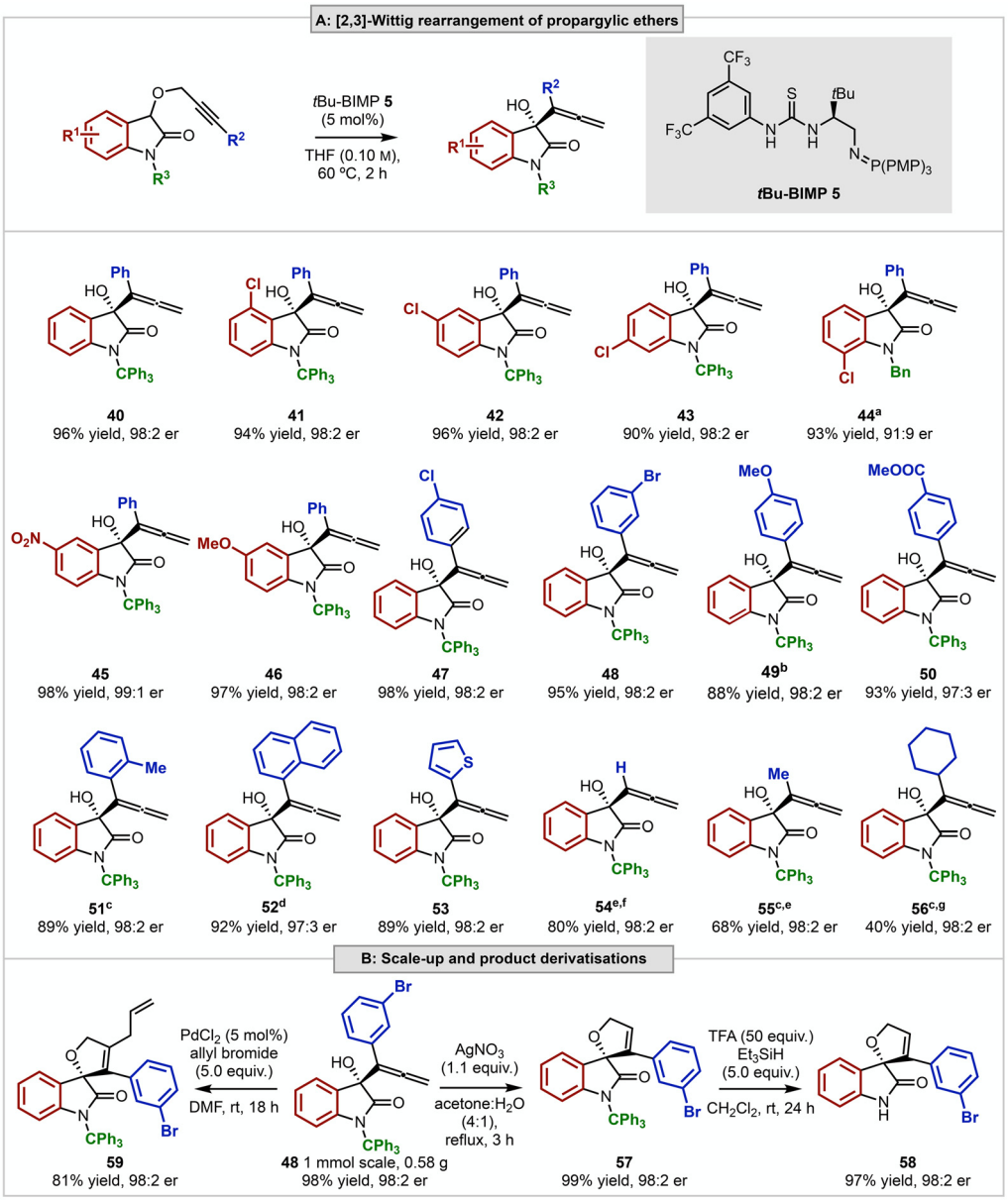


Fig. 3 All reactions were performed at 0.1 M concentration on a 0.1 mmol scale. Isolated yields are reported. The enantioselectivity was determined by HPLC analysis on a chiral stationary phase. [a] At 40 °C; [b] 3 h reaction time. [c] 24 h reaction time. [d] 8 h reaction time; [e] 0.2 M concentration. [f] 18 h reaction time. [g] 10 mol% catalyst loading.

ment of propargylic ether **I** (Fig. 4). Initial association of *t*Bu-BIMP to the oxindole carbonyl of the ether **I** (that was shown to be racemic throughout the reaction, see SI for further information) by hydrogen-bonding interactions is assumed prior to deprotonation of the propargylic ether-BIMP complex **II** to give intermediate **III**, with subsequent concerted [2,3]-sigmatropic rearrangement giving alkoxide **IV**. Subsequent protonation by [***t*Bu-BIMP**]H^+ gives the final [2,3]-rearrangement product **V** and releases the catalyst. The observed absolute configurations within the allene products, and relative and absolute configuration within the alkene products, is consistent with the transition state model developed within our previous collaborative computational analysis of the BIMP catalysed [2,3]-Wittig rearrangement of disubstituted allylic ethers.[62] Stereoselectivity in these processes is contingent upon multiple hydrogen-bonding interactions between the oxindole C═O and ether–O with the protonated BIMP catalyst, with sigmatropic rearrangement occurring preferentially from the *Re*-face of the anionic oxindole *anti* to the $P(PMP)_3$ substituent of the BIMP catalyst. An *exo*-conformation is favoured within the allylic-ether rearrangement, accounting for the observed major diastereoisomer.

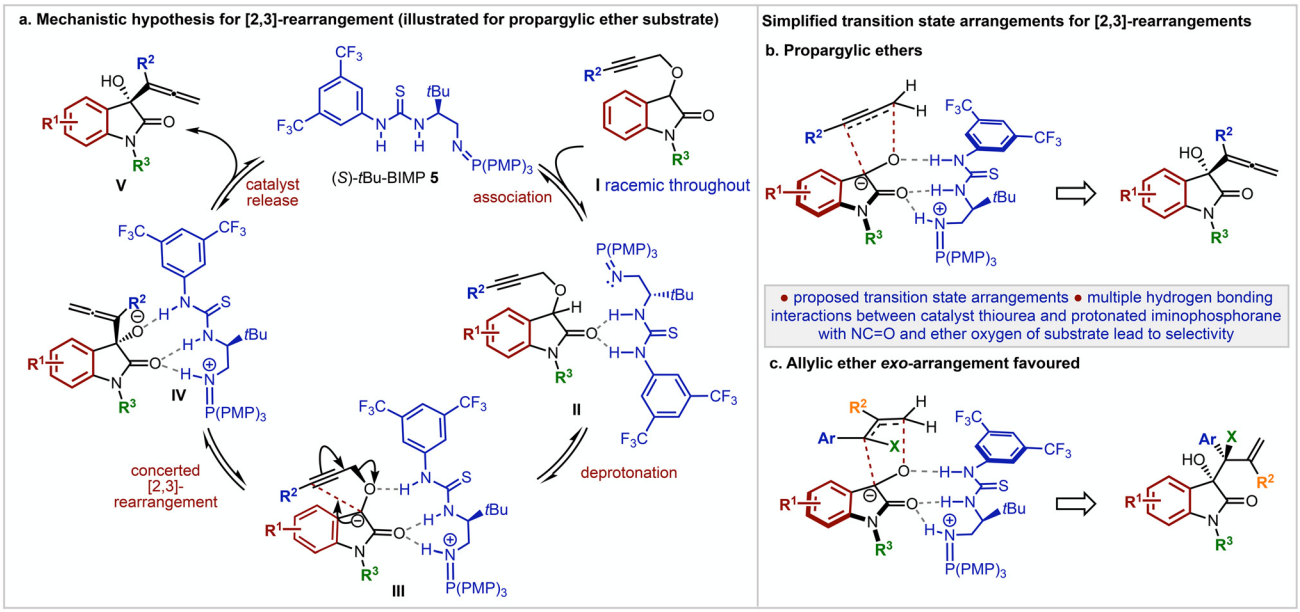


Fig. 4 Proposed mechanism and simplified stereochemical rationale.

Conclusion

In conclusion, a highly enantioselective [2,3]-Wittig rearrangement of oxindole-derived propargylic and allylic ethers using a bifunctional iminophosphorane (BIMP) organosuperbase catalyst has been developed. In the allylic series, the scope and limitations of this methodology has been extensively investigated, with the effect of substitution at C(2)- and C(3)-, (*E*)/(*Z*)-olefin configuration, and oxindole substitution investigated, giving products in up to 90 : 10 dr and >98 : 2 er. The incorporation of a C(3)-fluorine substituent leads to improved diastereoselectivity, giving products bearing a stereogenic tertiary fluoride, in up to 94 : 6 dr and 98 : 2 er. In the propargylic series, the [2,3]-rearrangement generates α-allenyl alcohols in generally excellent yield and enantioselectivity (up to 98% yield, 99 : 1 er) at 60 °C, with functionalisation of an α-allenyl alcohol to spirocyclic oxindoles without loss of stereochemical integrity demonstrated. Further studies concerning the generality and selectivity of related [2,3]- and other sigmatropic rearrangements are currently ongoing within this laboratory.

Author contributions

T. K. and A. D. S. conceived the project; T. K., J. O'Y., K. K. and A. D. S. designed the synthetic experiments; O. C., J. O'Y. and T. K. carried out all synthetic experimental studies and analyzed the reactions. D. B. C. and A. M. carried out single crystal X-ray analysis. T. K., K. K. and A. D. S. wrote the manuscript. All other correspondence should be addressed to A. D. S. and T. K.

Conflicts of interest

The authors declare no competing interests.

Data availability

All data that support the findings of this study are available within the article and its supplementary information (SI). Supplementary information: experimental procedures and characterization data.[77–103] See DOI: **https://doi.org/10.1039/d6qo00342g**.

The data underpinning this manuscript is available from the University of St Andrews Research Portal, Pure ID: 328159765, "Bifunctional Iminophosphorane-Catalysed Enantioselective [2,3]-Wittig Rearrangements of Oxindole-Derived Allylic and Propargylic Ethers" and can be accessed at **https://doi.org/10.17630/7f8b3d94-69e2-42f6-b3c7-18f414c42230**.

CCDC 2524416 ((3*S*,1′*R*)-**15**) contains the supplementary crystallographic data for this paper.[104]

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