Enantioselective synthesis of cyclopentenes by (2 + 3) cycloaddition via a 2-carbon phosphonium.**

*Antonia Seitz, Jeremy T. Maddigan-Wyatt, Jing Cao, Martin Breugst, David W. Lupton**

***Abstract**: Herein we report a catalytic enantioselective (2 + 3) cycloaddition in which a vinyl phosphonium intermediate serves as the 2-carbon component. The reaction involves an α–umpolung β–umpolung coupling sequence enabled by β–haloacrylates and chiral enantioenriched phosphepine catalysts. The reaction shows good generality providing access to an array of cyclopentenes, with mechanistic studies supporting stereospecific formation of the vinyl phosphonium intermediate which then undergoes annulation with turn over limiting catalyst elimination. Beyond defining a new approach to cyclopentenes these studies demonstrate that β–haloacrylates can replace ynoates in reaction designs that require exclusive umpolung coupling at the α– and β–positions.*

Cycloadditions define some of the most important synthetic approaches to cyclic structures. In the last three or so decades organophosphines have emerged as flexible cycloaddition catalysts allowing a broad, and often stereoselective, array of reactions.[1,2] Arguably the most recognizable are the (3 + n) cycloadditions between allenoates (i.e. **1**) and polarized π–systems (i.e. **2**) discovered by Lu.[3] Central to these reactions is phosphonium **3** which engages as a C_3-synthon to give various cyclic adducts (Fig. 1A).[4] While related annulations of other C_3-, C_4-, and higher synthons have received attention,[5-7] C_2-phosphonium **4** has been largely overlooked. Most commonly this species is accessed from ynoate **5** and allows α–umpolung couplings[8] or Michael additions[9,10] with to the best of our knowledge, cycloadditions only reported on two occasions (Fig. 1B). Specifically, in 2005 Yamamoto communicated the synthesis of pyrrole **7**,[11a] while more recently Sasai reported the preparation of racemic hydropyrrole **8**,[11b] along with a single low yielding enantioselective example. The paucity of (2 + n) cycloadditions is potentially attributable to the reactivity of ynoate **5**, the precursor to phosphonium **4**, which is both a potent Michael-acceptor[12a] and an acid[12b] (*vide infra*). Thus making a selective cycloaddition challenging.

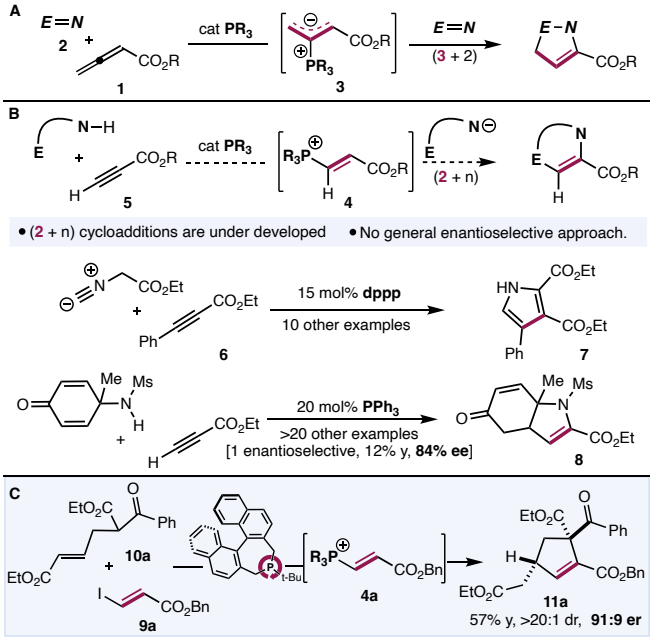


Figure 1. A) Phosphine catalyzed cycloadditions with allenoates. B) Proposed and previous studies on (2 + 3) cycloadditions via phosphonium **4**. C) Studies reported herein

As part of our interest in new enantioselective cycloadditions[13] we considered the potential for vinyl phosphonium **4** to enable a dual umpolung (2 + 3) cycloaddition approach to cyclopentenes (i.e. **11**). In addition to synthetic novelty such a process would provide a new approach to cyclopentenes with potential value in target synthesis. Herein we report the realization of this design with an enantioselective (2 + 3) cycloaddition between haloacrylates (i.e. **9a**) and bifunctional 1,3-dicarbonyls (i.e. **10a**) (Fig. 1C). Pivotal to the viability of this transformation is the use of haloacrylates (i.e. **9a**) rather than ynoate **5** as the vinyl phosphonium **4a** precursor. This avoids Michael additions,[9] allowing exclusive dual umpolung cycloaddition to occur. This design we believe has the potential to unlock the use of vinyl phosphoniums as a novel 2C-synthon for an array of cycloadditions.

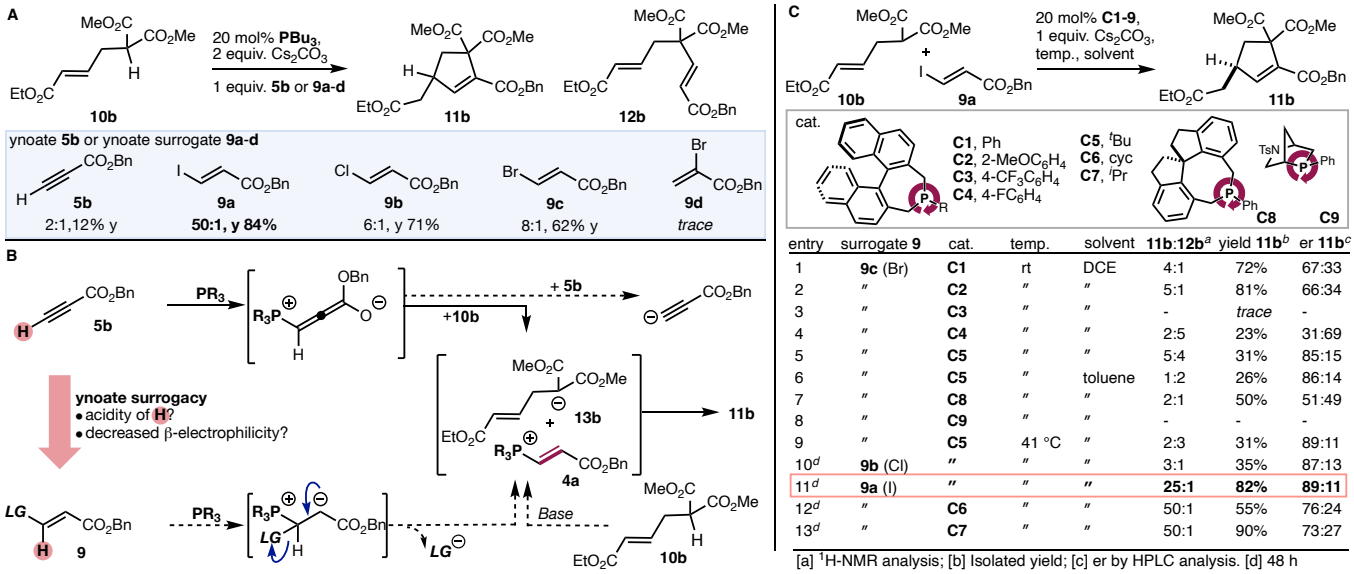
Our studies commenced by examining whether the proposed (2 + 3) annulation was indeed viable using ynoate **5b** and malonate **10b** (Fig. 2A). While successful, the reaction suffers from low yield and formation of the undesired Michael adduct **12b**.[9c] Mechanistically the intended reaction occurs by phosphine addition to ynoate **5b** to provide a ketenolate which then generates the targeted coupling partners **4b** and **13b** (Fig. 2B). Unfortunately, in addition to their desired α–umpolung coupling, Michael addition of enolate **13b** to ynoate **5b** can provide **12b**.[9c] Additionally the basicity of the ketenolate potentially allows undesired deprotonations thereby triggering decomposition and low yield.

[*] Ms. Antonia Seitz, Dr. Jeremy T. Maddigan Wyatt, Dr. Jing Cao, and Professor Dr. David W. Lupton*
School of Chemistry, Monash University
Clayton 3800, Victoria, AUSTRALIA
Fax: (+) 61 3 9905 4597
E-mail: david.lupton@monash.edu

Professor Dr. Martin Breugst
Institut für Chemie, Technische Universität Chemnitz
Straße der Nationen 62
09111 Chemnitz, GERMANY

[**] The authors thank the Australian Research Council through the Discovery (DP210103530) programs for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.



entry	surrogate **9**	cat.	temp.	solvent	**11b**:**12b**[a]	yield **11b**[b]	er **11b**[c]
1	**9c** (Br)	**C1**	rt	DCE	4:1	72%	67:33
2	〃	**C2**	〃	〃	5:1	81%	66:34
3	〃	**C3**	〃	〃	-	*trace*	-
4	〃	**C4**	〃	〃	2:5	23%	31:69
5	〃	**C5**	〃	〃	5:4	31%	85:15
6	〃	**C5**	〃	toluene	1:2	26%	86:14
7	〃	**C8**	〃	〃	2:1	50%	51:49
8	〃	**C9**	〃	〃	-	-	-
9	〃	**C5**	41 °C	〃	2:3	31%	89:11
10[d]	**9b** (Cl)	〃	〃	〃	3:1	35%	87:13
11[d]	**9a** (I)	〃	〃	〃	**25:1**	**82%**	**89:11**
12[d]	〃	**C6**	〃	〃	50:1	55%	76:24
13[d]	〃	**C7**	〃	〃	50:1	90%	73:27

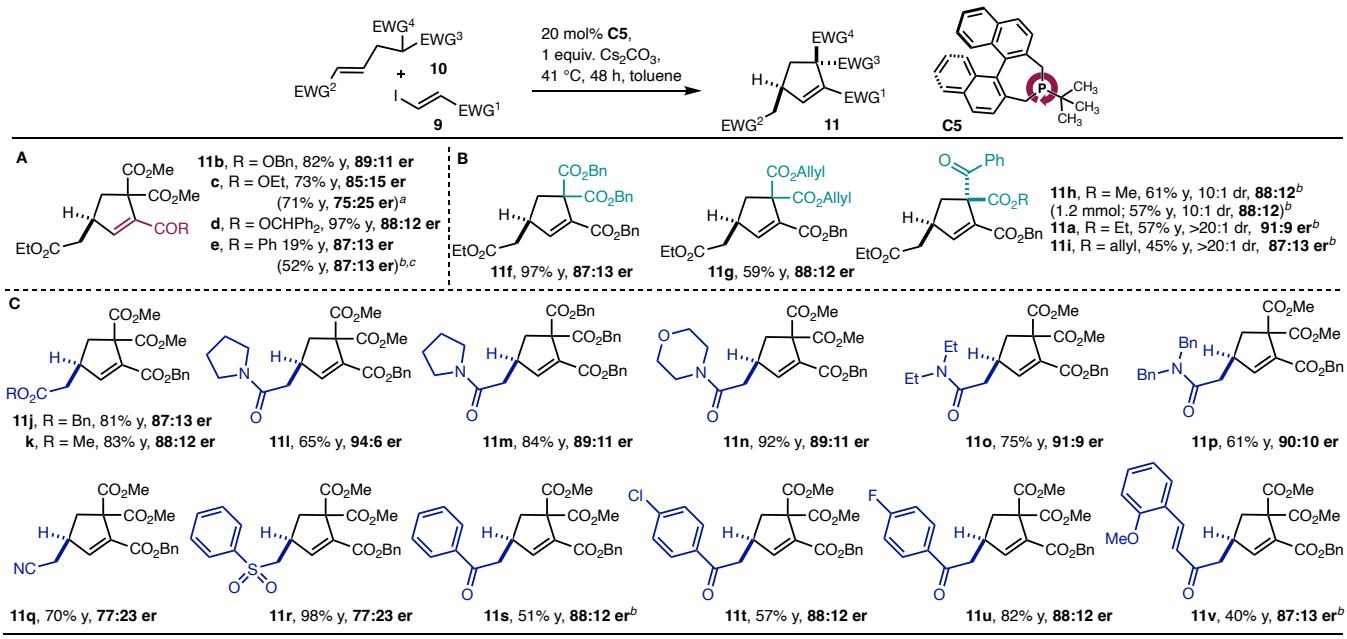
[a] ^{1}H-NMR analysis; [b] Isolated yield; [c] er by HPLC analysis. [d] 48 h

Figure 2. A) phosphine catalyzed (2 + 3) cycloaddition with ynoates and surrogates. B) Rationale behind ynoate surrogacy strategy. C) Selected optimization for the enantioselective synthesis of cyclopentene **11b**.

To address these shortcomings in the reaction design, we considered replacing the ynoate with an enoate bearing an α– or β–leaving group (Fig. 2A, **9a-d**). While β–haloenoates are unknown in phosphine organocatalysis they have been stoichiometrically coupled with triphenyl phosphine to give vinyl phosphonium species analogous to **4**.[14] We postulated that the haloenoates (i.e. **9**) should be both less electrophilic (particularly when β–substituted) and less acidic than ynoate **5b** thereby addressing the limitations previously identified (Fig. 2B). Pleasingly after screening α–, and β–haloenoates **9a-d** we found that β–iodo, chloro and bromoenoates (**9a-c**) all gave a high yield of cycloadduct **11b** (62 to 84%), with good selectivity for the cycloaddition over Michael addition (6:1 to 50:1) (Fig. 2A).

Studies into the enantioselective[15] (2 + 3) cycloaddition commenced by screening phosphepine catalysts **C1-C5** using malonate **10b** and β–bromoacrylate **9c**, a halide more easily handled than the preferred iodide. While most gave the expected product (Fig 2c, entries 1–5) only ^{t}Bu phosphepine **C5** gave the cyclopentene with significant enantioselectivity (85:15 er), although in low yield, and with low selectivity over the Michael adduct (Fig. 2C, entry 5). Changing the solvent to toluene increased the enantioselectivity slightly, while SITCP (**C8**) was viable (but not stereoselective), and *endo*-Kwon **C9** was not viable (Fig. 2C, entries 6–8). Raising the temperature improved the enantioselectivity and yield, while returning to β–iodoenoate **9a**, and extending the reaction time (48h), allowed an excellent yield of cyclopentene **11b** with good enantioselectivity (89:11 er) and only a trace of the β–coupled product **12b** (Fig. 2C, entry 11). Use of less encumbered catalysts (i.e. cyclohexyl **C6** and ^{i}propyl **C7**) gave similar yields but the enantioselectivity was diminished.

In general these conditions were compatible with a range of substrates giving cyclopentenes **11a-v** in good yield (>60%) and around 90:10 er (Fig. 3). All products were non-crystalline, thus absolute stereochemistry was determined by measured and computed CD spectra for cyclopentene **11b** (see SI). Specifically, scope studies commenced by examining alternate β–iodo α,β–unsaturated carbonyls (Fig. 3A). Increasing, or decreasing the bulk of the ester (i.e. **11c** or **11d**) had little impact on the reaction outcome, however the stereochemistry of the iodoenoate had a significant impact with *cis* iodoenoate ***cis*-9e** decreasing the enantiopurity of cyclopentene **11e** (75:25 cf 85:15 er from ***trans*-9e**) (*vide infra*). Ketone containing substrates were tolerated, with phenyl ketone **11e** formed in 52% yield and 87:13 er, although this required a slight elevation of reaction temperature and use of a bromoenone. The 1,3-dicarbonyl component of the 3-carbon coupling partner could be varied using symmetrical and non-symmetrical partners (Fig. 3B). Thus, the dibenzyl and diallyl malonate containing cyclopentenes **11f** and **11g** were prepared in 97 and 59% yield, and with 87:13 and 88:12 er respectively. In addition β–ketoester containing substrates provided cyclopentenes **11h**, **a** and **i** (87:13–91:9 er) and with ≥10:1diasteroselectivity. The coupling to provide **11h** was repeated on a 1.2 mmol scale without impacting the outcome. Finally, modifications to the Michael acceptor within **10** (Fig 3C) were examined starting with alternate esters, which gave cyclopentenes **11j** and **11k** with very similar yield and selectivity to the ethyl version. α,β–Unsaturated amides were well suited to the reaction with cyclopentenes **11l-p** formed with good enantioselectivity (87:13–93:7 er) and yield (61-92%). In contrast nitrile and phenyl sulfone substrates coupled well (to give **11q** and **r**) but selectivity was decreased (77:23 and 76:24 er respectively). Aryl ketones and styrenyl ketone substrates were smoothly reacted to give cyclopentenes (**11s-v**) in good yield and enantioselectivity (all >87:13 er).



[a] Formed using ***cis*-9f**; [b] Reaction performed at 60 °C; [c] Using the bromide version of **9**.

Figure 3. Scope of enantioselective (2 + 3) cycloaddition. A) Variation of haloacrylate **9**. B) Variation of 1,3-dicarbonyl in **10**. C) Variation of conjugate acceptor in **10**.

Derivatisations focused on addressing the 1,3-dicarbonyl functionality and the conjugate acceptor within the cyclopentene product **11** (Fig 4). To that end allylester **11i** was subjected to decarboxylative allylation to yield cyclopentene **14i**. While viable with dppe, and both enantiomers of Phox ligand,[16] the best diastereoselectivity, although low, was obtained using *S*-^{t}BuPhox giving a quantitative yield of **14i** as a 2:1 mix of diastereoisomers with 94:6 and 82:18 er. Starting with cyclopentene **11b** conjugate addition[17] of nitromethane gave a 6:1 ratio of cyclopentanes **15b** in good yield and with no erosion in enantiopurity.

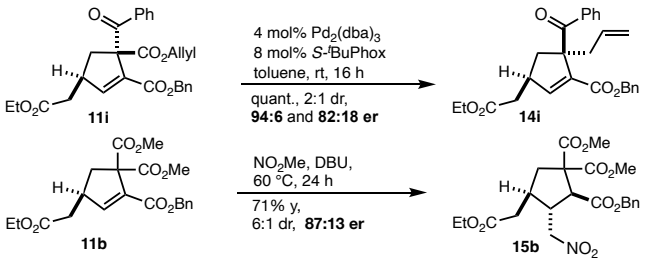


Figure 4. Derivatizations studies with cyclopentenes **11i** and **11b**.

The reaction mechanism was examined initially by considering whether the normal polarity coupling, as observed during optimization, occurs via vinyl phosphonium **4** or is a background reaction of iodide **9a**. This was examined through control experiments, with the absence of catalyst exclusively providing the normal polarity β–coupled product **12b** thereby demonstrating the viability of a background coupling pathway. Next we subjected deuterium labelled malonate **D-10b** to the (2 + 3) annulation providing cyclopentene **D-11b** with a slight decrease in yield and enantioselectivity compared to the protero version. Deuterium incorporation was found at positions correlating to the acidic C–H bonds α– to the ethyl ester and a putative phosphonium intermediate. While the former was expected the later suggests that the α–umpolung coupling leads to a long-lived species from which deuteration can occur (*vide infra*).

Finally, NMR monitoring experiments were conducted using both the *cis* and *trans* iodoenoates (***cis*-9a** and ***trans*-9a**). When ***trans*-9a** was exposed to catalyst **C5** in d_8-toluene the phosphine catalyst peak (at 29.1 ppm in the ^{31}P-NMR) gradually disappeared with no new signals observed, although an insoluble material formed which was isolated in 50% yield. This material, when dissolved in $CDCl_3$ was assigned as ***trans*-4a** with a ^{31}P-NMR signal at 57.6 ppm,[18a] and phosphorous decoupled ^{1}H-NMR spectroscopy revealing a coupling about the indicated hydrogens of 17.4 Hz.[18b] This material when resuspended in toluene and subjected to the standard reaction conditions provided cyclopentene **11b** in 93% yield and with good enantiopurity. When related experiments were performed with ***cis*-9a** a new signal was observed by ^{31}P-NMR (at 58.3 ppm in toluene). Switching to $CDCl_3$ revealed a 3:7 mixture of the previously characterized ***trans*-4a** (57.6 ppm) and the new phosphonium molecule (58.5 ppm). Incomplete conversion made analysis more challenging but from phosphorous decoupled ^{1}H-NMR analysis this species has a coupling of 8.5 Hz and was assigned as ***cis*-4a**. This species, albeit unpurified, was found to also give the cyclopentene **11b** although with decreased enantiopurity.

Taken together a plausible reaction mechanism commences with addition of phosphine **C5** to β–iodoacrylate **9a** to give enolate **16**, which following elimination gives ***trans*-4a**. This process is stereoretentive from the *trans*-iodide, but yields a *cis*:*trans* mixture using *cis*-iodoacrylates. Concurrent deprotonation of the malonate gives enolate **13b**, which undergoes α–umpolung coupling to establish the first new C–C bond and a stereogenic elements that is subsequently ablated. Intermediate **17** then undergoes β–umpolung cyclization to provide **18** before elimination of the catalyst delivers the cyclopentene **11b**. Based on deuteration studies, and the facile nature of 5-*exo*-trig cyclizations, we propose that catalyst elimination is likely turn-over limiting allowing the observed deuteration via phosphonium **18**.

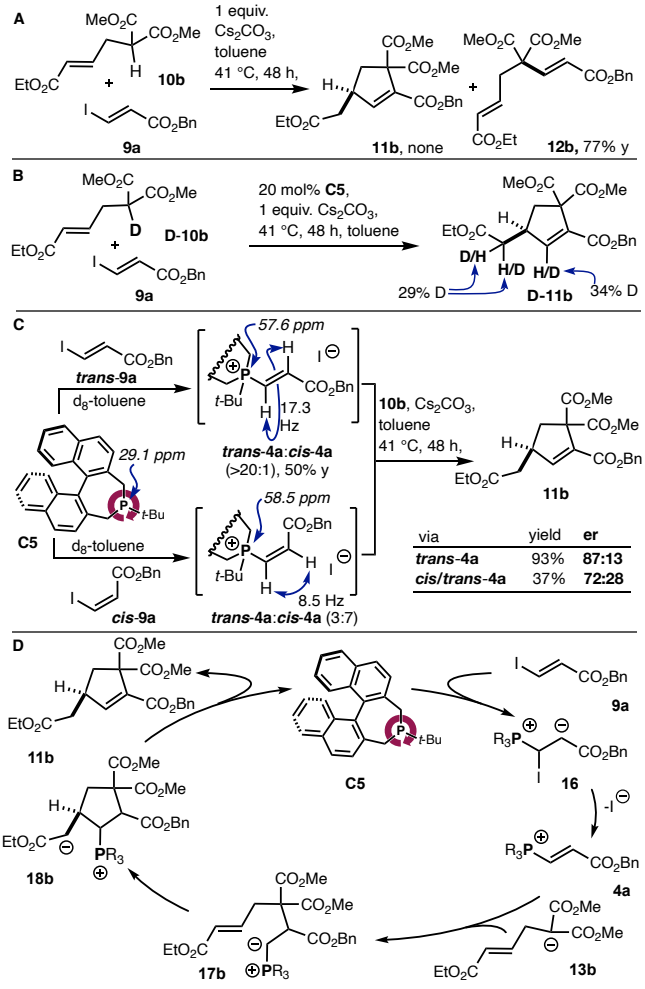


Figure 5. A) β–coupling is via iodide **9a**. B) Annulation of deuterated substrate **D-10b**. C) Monitoring studies. D) Plausible reaction mechanism

Enantioselective cycloadditions as catalyzed by phosphines have provided valuable new approaches to cyclic structures[1] and introduced new reactive intermediates to the community. Herein we report a new use for vinyl phosphoniums (i.e. **4**) allowing an enantioselective approach to cyclopentenes. Specifically, this was possible by using β–haloenoates (i.e. **9**) rather than ynoates (i.e. **5**). These substrates provide the vinyl phosphonium, while avoiding Michael additions. This has enabled the preparation of cyclopentenes bearing unusual substitution patterns due to the polarity inverted nature of both C–C bond forming events. Beyond providing a new enantioselective approach to cyclopentenes these studies pave the way for the discovery of other (2 + n) cycloadditions by using alternate bifunctional coupling partners

Keywords: Enantioselective catalysis • Organophosphines • (2 + 3) cycloaddition • umpolung • cyclopentenes •

[1] (a) *Organophosphines-Catalyzed Cycloaddition Reactions* Y. Wei, M. Shi in Organocatalytic Cycloadditions for Synthesis of Carbo- and Heterocycles, M. Shi, Y. Wei, M.-X Zhao, J. Zhang. © 2018 Wiley-VCH Verlag GmbH & Co. KGaA. **2018**; (b) Y. Long-Wu., J. Zhou, Y. Tang *Chem. Soc. Rev.* **2008**, *37*, 1140; (c) B. J. Cowen, S. J. Miller *Chem. Soc. Rev.* **2009**, *38*, 3102; (d) Y. C. Fan, O. Kwon *Chem. Commun.* **2013**, *49*, 11588; (e) Y. Wei, M. Shi *Chem. Rev.* **2013**, *113*, 6659; (f) Y. Wei, M. Shi *Chem. Asian J.* **2014**, *9*, 2720; (g) T. Wang, X. Han, F. Zhong, W. Yao, Y. Lu *Acc. Chem. Res.* **2016**, *49*, 1369–1378; (h) H. Zhang, R. Zhou *Eur. J. Org. Chem.* **2020**, 4098; (i) Y. Huang, J. Liao, W. Wang, H. Lei, Guo *Chem. Commun.* **2020**, *56*, 15235.

[2] For selected general reviews on phosphine catalysis: (a) H. Ni, W.-L. Chan, Y. Lu *Chem. Rev.* **2018**, *118*, 9344; (b) H. Guo, Y. C. Fan, Z. Sun, Y. Wu, O. Kwon *Chem. Rev.* **2018**, *118*, 10049; (c). E.-Q. Li, Y. Huang *Chem. Commun.* **2020**, *56*, 680; (d) C. Xie, A. J. Smaligo, X.-R. Song, O. Kwon *ACS Cent. Sci.* **2021**, *7*, 536-558.

[3] For pioneering studies see: (a) C. Zhang, X. Lu, *J. Org. Chem.* **1995**, *60*, 2906; (b) Z. Xu, X. Lu, *Tetrahedron Lett.* **1997**, *38*, 3461; (c) Z. Xu, X. Lu, *J. Org. Chem.* **1998**, *63*, 5031. For an account (d) X. Lu, C. Zhang, Z. Xu, *Acc. Chem. Res.* **2001**, *34*, 535.

[4] For a review and selected studies on allenoate cycloadditions see: (a) Y. Wei, M. Shi *Org. Chem. Front.* **2017**, *4*, 1876; (b) G.-L. Zhao, M. Shi *J. Org. Chem.* **2005**, *70*, 9975; (c) X.-F. Zhu, C. E. Henry, O. Kwon, *Tetrahedron* **2005**, 61, 6276; (d) L. Jean, A. Marinetti *Tetrahedron Lett.* **2006**, 47, 2141; (e) A. Scherer, J. A. Gladysz *Tetrahedron Lett.* **2006**, *47*, 6335; (f) Y.-Q. Fang, E. N. Jacobsen *J. Am. Chem. Soc.* **2008**, *130*, 5660; (g) M. Sampath, P.-Y. B. Lee, T.-P. Loh, *Chem. Sci.* **2011**, *2*, 1988; (h) X. Han, F. Zhong, Y. Wang, Y. Lu, *Angew. Chem. Int. Ed.* **2012**, 51, 7; (i) C. E. Henry, Q. Xu, Y. C. Fan, T. J. Martin, L. Belding, T. Dudding, O. Kwon *J. Am. Chem. Soc.* **2014**, *136*, 11890; (j) Z.-H. Cao, Y.-H. Wang, S. J. Kalita, U. Schneider, Y.-Y. Huang *Angew. Chem. Int. Ed.* **2020**, *59*, 1884; (k) D. Li, X. Zhang, W. Han, J. Jiao, Y. Tang, S. Xu *J. Org. Chem.* **2023**, *88*, 10212.

[5] For discovery and selected cycloadditions using Morita-Baylis Hillman adducts see: (a) Y. Du, X. Lu, C. Zhang *Angew. Chem. Int. Ed.* **2003**, *42*, 1035; (b) S. Zheng, X. Lu *Org. Lett.* **2008**, *10*, 4481; (c) L.-W. Ye, X.-L. Sun, Q.-G. Wang, Y. Tang *Angew. Chem. Int. Ed.* **2007**, *46*, 5951; (d) B. Tan, N. R. Candeias, C. F. Barbos *J. Am. Chem. Soc.* **2011**, *133,* 4672; (e) C. Wang, Y. Chen, J. Li, L. Zhou, B. Wang, Y. Xiao, H. Guo *Org. Lett.* **2019**, *21*, 7519.

[6] For C_4-sython cycloadditions using substituted allenoates see: (a) X.-F. Zhu, J. Lan, O. Kwon *J. Am. Chem. Soc.* **2003**, *127*, 4716; (b) Y. S. Tran, O. Kwon *J. Am. Chem. Soc.* **2007**, *129*, 12632; (c) R. P Wurz, G. C. Fu *J. Am. Chem. Soc.* **2005**, *127*, 12234: (d) R. Liu, Z. Qin, B. Fan, R. Li, R. Zhou, Z. He *J. Org. Chem.* **2019**, *84*, 12490; (e) M. Wu, Z. Han, H. Ni, N. Wang, K. Ding, Y. Lu, *Chem. Sci.* **2022**, *13*, 316; (f) Z. Gao, X. Zhou, L. Xie, X. Wang, S. Wang, H. Liu, H. Guo *J. Org. Chem.* **2024**, 10.1021/acs.joc.4c00564, using allenoate Morita-Baylis Hillman adducts see: (g) Q. Zhang, L. Yang, X. Tong *J. Am. Chem. Soc.* **2010**, *132*, 2550; (h) D. T. Ziegler, L. Riesgo, T. Ikeda, Y. Fujiwara, G. C. Fu *Angew. Chem. Int. Ed.* **2014**, *53*, 13183; (i) Y. Gu, P. Hu, X. Tong *J. Am. Chem. Soc.* **2015**, *137*, 6400; (j) B. R. Blank, I. P. Andrews, O. Kwon *ChemCatChem* **2020**, *12*, 4352; (k) X. Tang, C. Xiang A. Tan, W.-L. Chan, F. Zhang, W. Zheng, Y. Lu *ACS Catal.* **2021**, *11*, 1361, using other species see: (l) X.-N. Zhang, G.-Q. Chen, X.-Y. Tang, Y. Wie, M. Shi *Angew. Chem. Int. Ed.* **2014**, *53,* 10768.

[7] For *bis*-cycloadditions with vinyl allenoates see: (a) J. Feng, Y. Huang *Chem. Commun.* **2019**, *55*, 14011; (b) J. Feng, Y. Chen, W. Qin, Y. Huang *Org. Lett.* **2020**, *22*, 433; (c) X. Li, Y. Huang *Chem. Commun.* **2021**, *57*, 9934.

[8] For discovery and selected α–umpolung coupling see: (a) B. Trost, G. R. Dake *J. Am. Chem. Soc.* **1997**, *119*, 7595−7596; (b) M. Hanedanian, O. Loreau, F. Taran, C. Mioskowski *Tetrahedron Lett.* **2004**, *45*, 7035−7038; (c) D. Lecerclé, M. Sawicki, F. Taran *Org. Lett.* **2006**, *8*, 4283–4285; (d) L. Zhu, Y. Xiong, C. Li *J. Org. Chem.* **2015**, *80*, 628–633; (e) M. Raghu, J. Grover, S. S. V. Ramasastry *Chem.-Eur. J.* **2016**, *22*, 18316−18321; (f) K. Zhang, L. Cai, S. Hong, O. Kwon *Org. Lett.* **2019**, *21*, 5143–5146.

[9] For discover and selected normal polarity β–addition chemistry see: (a) J. Inanaga, Y. Baba, T. Hanamoto *Chem. Lett.* **1993**, *22*, 241−244; (b) M. Wende, R. Meier, J. A. Gladysz, *J. Am. Chem. Soc.* **2001**, *123*, 11490−11491; (c) R. B. Grossman, S. Comesse, R. M. Rasne, K. Hattori, M. N. Delong *J. Org. Chem.* **2003**, *68*, 871−874; (d) R. L. Stoddard, J. Luo, N. van der Wal, N. F. O'Rourke, J. E. Wulff, J. S. Mclndoe *New J. Chem.* **2014**, *38*, 5382−5390.

[10] For a β–radical addition see: J. Cao, A. Seitz, J. A. Forni, A. Polyzos, D. W. Lupton *Angew. Chem. Int. Ed.* **2023**, *62*, e202303869.

[11] (a) S. Kamijo, C. Kanazawa, Y. Yamamoto *J. Am. Chem. Soc.* **2005**, *127*, 9260; (b) K. Kishi, S. Takizawa, H. Sasai *ACS Catal.* **2018**, *8*, 5228.

[12 For electrophilicity parameters for electron-poor alkynes see: (a) R. J. Mayer, A. R. Ofial *Angew. Chem. Int. Ed.* **2019**, *58*, 17704. For acidity

see: (b) C. Laurence, R. Queignec *J. Chem. Soc. Perkin Trans. 2* **1992**, 1915.
[13] For representative examples towards carbocycles see: (a) L. Candish, C. M. Forsyth, D. W. Lupton *Angew. Chem. Int. Ed.* **2013***, 52*, 9149; (b) L. Candish, A. Levens, D. W. Lupton *J. Am. Chem. Soc.* **2014**, *136,* 14397; (c) A. Levens, A. Ametovski, D. W Lupton *Angew. Chem. Int. Ed.* **2016**, *55*, 16136; (d) R. M. Gillard, J. E. M. Fernando, D. W Lupton *Angew. Chem. Int. Ed.* **2018**, *57*, 4712; (e) X. B. Nguyen, Y. Nakano, N. Duggan, L. Scott, M. Breugst, D. W. Lupton *Angew. Chem. Int. Ed.* **2019**, *131*, 11607.
[14] G. Pattenden, B. J. Walker *J. Chem. Soc. C* **1969**, 531.
[15] For a review and selected examples of chiral phosphines for enantioselective organocatalysis see: (a) Y, Xiao, Z, Sun, H. Guo, O. Kwon *Beilstein J. Org. Chem.* **2014**, *10*, 2089; (b) S.-F. Zhu, Y. Yang, L.-X. Wang, B. Liu, Q.-L. Zhou *Org. Lett.* **2005**, *7*, 2333; (c) S. Gladiali, A. Dore, D. Fabbri, O. De Lucchi, M. Manassero *Tetrahedron Asymm.* **1994**, *5*, 511; (d) K. Junge, G. Oehme, A. Monsees, T. Riermeier, U. Dingerdissen, M. Beller *Tetrahedron Lett.* **2002**, *43*, 4977; (e) R. P. Wurz, G. C. Fu, *J. Am. Chem. Soc.* **2005**, *127*, 12234; (f) J. E. Wilson, G. C. Fu, *Angew. Chem. Int. Ed.* **2006**, *45*, 1426; (g) C. E. Henry, Q. Xu, Y. C. Fan, T. J. Martin, L. Belding, T. Dudding, O. Kwon *J. Am. Chem. Soc.* **2014**, *136*, 11890.
[16] For conditions for related carbocycles see: (a) C. J. Gartshore, D. W. Lupton *Angew. Chem. Int. Ed.* **2013***, 52*, 4113-4116, for reviews see: (b) J. D. Weaver, A. Recio III, A. J. Grenning, J. A. Tunge, *Chem. Rev.* **2011**, *111*, 1846.
[17] For conjugate additions with related cyclopentenes see: F. Sarabia, Q. Li, E. M. Ferriera *Angew. Chem. Int. Ed.* **2018***, 57*, 11015.
[18] (a) For phosphorous-NMR data of related phosphoniums see: A. C. Vetter, K. Nikitin, D. G. Gilheany *Chem. Commun.* **2018**, *54*, 5843-5846. For coupling constants in cis and trans vinyl phosphoniums see: (b) P. Majewski, E. Łukaszewicz *Collect. Czech. Chem. Commun.* **2011**, *76*,