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Expanding the Scope of Enantioselective FerroPHANE-Promoted [3+2] Annulations with α,β-Unsaturated Ketones

Nathalie Pinto,[a] Mathilde Neel,[a] Armen Panossian,[a] Pascal Retailleau,[a] Gilles Frison,[b] Arnaud Voituriez,[a] and Angela Marinetti*[a]

Abstract: The planar chiral 2-phospha[3]ferrocenophane **I** has been shown to be the first efficient nucleophilic organocatalyst for the enantioselective synthesis of cyclopentenylphosphonates, through [3+2] cyclizations between diethyl allenylphosphonate and α,β-unsaturated ketones. The same catalyst has also been applied to the highly enantioselective [3+2] cyclizations of allenic esters with dibenzylideneacetone and analogous bis-enones, leading to functionalised cyclopentenes with either monocyclic or spirocyclic structures (*ee* 84–95%). It has been shown that the residual enone functions in the resulting cyclopentenes can be involved in subsequent cyclization steps to afford unprecedented C_2-symmetric bis-cyclopentenylketones. In order to provide insight into the behaviour of FerroPHANE **I** as a chiral catalyst in [3+2] cyclisations, the energetically most favoured isomers of the key phosphine-allene adduct have been calculated by DFT methods. Factors likely to control the chiral induction process are highlighted.

Keywords: allenyl phosphonates · cyclization · enantioselectivity · organocatalysis · spiro compounds

Introduction

Phosphine organocatalysis is currently a rapidly expanding field affording an impressive number of new methods for the formation of carbon-carbon and carbon-heteroatom bonds from easily available starting materials.[1] It notably represents a privileged tool for the construction of cyclic compounds in single-step fashion through the use of simple allenes or alkynes and electron-poor olefins or imines as starting materials.[2] Surprisingly, however, the fascinating field of asymmetric phosphine organocatalysis is currently only at a very early stage of development.[3] It was only in the late 1990s that the first successful attempts directed towards this challenging target appeared in the literature, thanks to the pioneering work of Vedejs[4] and Zhang.[5] Since then, intensive efforts and some significant achievements have been made, by taking advantage of either known[6] or specifically designed chiral nucleophilic phosphines.[7]

Our recent contributions to the field of asymmetric phosphine organocatalysis have included the development of new applications of chiral phosphines,[8] as well as the design of planar chiral 2-phospha[3]ferrocenophanes as new cyclic scaffolds for phosphorus-based catalysts.[9] From these last studies, the trimethylsilyl-substituted, *P*-cyclohexyl-ferrocenophane **I** (called FerroPHANE) has been highlighted as a highly efficient promoter for enantioselective cyclizations of allenic esters and both unsaturated esters and ketones (Scheme 1).

Now, taking advantage of the excellent catalytic properties of the new phosphine **I**, we intend to expand the current range of organocatalytic enantioselective processes further. In this paper we report the most recent results of our investigations into the catalytic use of FerroPHANE **I** in [3+2] cyclizations, as well as the first attempts to elucidate the mechanism of chiral induction by DFT studies.

Results and Discussion

Enantioselective annulations on allenylphosphonates: The first catalytic application of FerroPHANE **I** that we would

[a] N. Pinto, M. Neel, Dr. A. Panossian, Dr. P. Retailleau, Dr. A. Voituriez, Dr. A. Marinetti
Centre de Recherche de Gif
Institut de Chimie des Substances Naturelles—CNRS UPR 2301
1, av. de la Terrasse, 91198 Gif-sur-Yvette Cedex (France)
Fax: (+33) 169-07-7247
E-mail: angela.marinetti@icsn.cnrs-gif.fr

[b] Dr. G. Frison
Laboratoire des Mécanismes Réactionnels—CNRS UMR 7651
Ecole Polytechnique, Département de Chimie
91128 Palaiseau Cedex (France)

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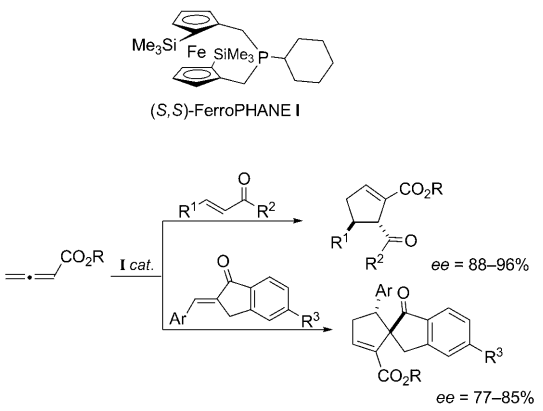


Scheme 1. Enantioselective [3+2] cyclizations promoted by FerroPHANE **I**.

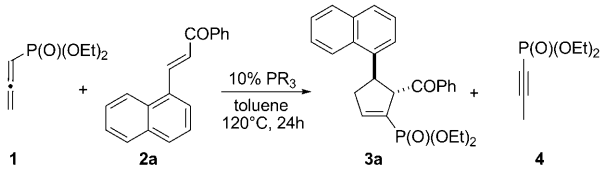
like to present here is its convenient use in [3+2] cyclizations on allenylphosphonates, leading to the highly enantioselective synthesis of functionalised cyclopentenylphosphonates.

The continuing search for synthetic approaches to phosphonates and phosphonic acids relates both to their involvement in synthetically important reactions and to their applications in medicine and other fields.[10] Common and suitable methods for the synthesis of phosphonates involve either formation of the carbon-phosphorus bond or modification of the carbon skeleton of a simple, easily available phosphonate to generate new species of increased complexity. So far only a few examples of phosphine-promoted organocatalytic transformations of phosphonates and other phosphorus-functionalised substrates have been reported,[11,12] and none of them has made use of allenylphosphonates as starting materials, despite the wide uses of the analogous allenic esters in organocatalysed reactions. Our initial investigations[8c] have shown that allenic phosphonates can serve as readily available[13] and inexpensive substrates for phosphine-promoted organocatalytic cyclization reactions. Attempts to perform enantioselective cyclizations through the use of chiral nucleophilic phosphines, such as (*S*)-*t*Bu-Binepine—one of the most prominent catalysts for enantioselective cyclization reactions[6a,b,8d]—were hampered, however, by the very low reactivity of allenylphosphonates, and the low conversion rates dramatically decreased the usefulness of these reactions. Gratifyingly, these limitations have been overcome by the use of FerroPHANE **I** as the catalyst.

In a first series of experiments, (*S,S*)-FerroPHANE **I** was used to promote cyclization reactions between diethyl propa-2,3-dienylphosphonate (**1**) and 3-(1-naphthyl)-1-phenylpropenone (**2a**). For purposes of comparison, (*S*)-*t*Bu-Binepine and some commercially available chiral phosphines were also evaluated. Representative results are given in Table 1.

BINAP, Me-DuPHOS, DIPAMP, Me-BPE and *t*Bu-Binepine converted **1** mainly into the isomeric propynylphosphonate **4**. With *t*Bu-Binepine an enantiomeric excess of 81% was measured, but the isolated yield of **3a** was very low, because alkyne **4** was also the major product in this case. Diop, PhanePhos and Et-FerroTANE did not afford active catalysts.

Table 1. Enantioselective [3+2] cyclizations between allenylphosphonate **1** and enone **2a**.

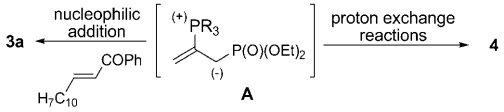


Entry	PR_3	**3a**/**4**	Yield of **3a** (conv.)[a]	*ee*[b]
1	(*R*)-BINAP	4:96	– (22)	n.d.
2	(*R*,*R*)-Me-DuPHOS	10:90	– (100)	n.d.
3	(*R*,*R*)-DIPAMP	19:81	– (74)	n.d.
4	(*S*)-Me-BPE	25:75	<10 (100)[c]	8
5	(*S*)-*t*Bu-Binepine	12:88	~10 (100)	81
6	(*S*,*S*)-FerroPHANE **I**	95:5	80 (100)	90
7	(*S*,*S*)-FerroPHANE **I**	95:5	49 (56)[d]	90
8	(*S*,*S*)-FerroPHANE **I**	82:18	30 (40)[e]	93

[a] For an allene/enone ratio of 1:2. [b] By chiral HPLC. [c] At a 30% catalyst loading. [d] At a 5 mol% catalyst loading. [e] Reaction performed at 100°C.

In relation to all other catalysts tested so far, FerroPHANE **I** displayed an excellent reactivity profile, affording the desired cyclopentene **3a** as the major product. The alkyne by-product **4** was formed in only <5% amount when optimised conditions were applied; these include the use of a twofold excess of enone **2a**, use of toluene as the solvent, a 0.3 M concentration of the reactants and heating at 120°C for 24 h (entry 6). Slightly lower **3a**/**4** ratios were obtained in reactions performed in toluene at 100°C (entry 8).

The high chemoselectivity of FerroPHANE in these reactions, in terms of the cyclopentene/alkyne ratio, has so far hardly been explained. From the mechanism postulated for analogous reactions with allenic esters,[2c,14] the first key step of the catalytic cycle leading to **3a** should be the addition of the nucleophilic phosphine to the allenic substrate **1** to give the zwitterionic intermediate **A** (Scheme 2). The isomeriza-



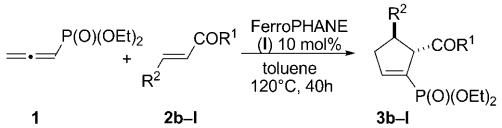
Scheme 2. Key intermediate for the phosphine-promoted transformations of allenylphosphonates.

tion process leading to the propynylphosphonate **4** might proceed via the same intermediate through intermolecular proton exchange reactions, in which **A** would behave as a strong base.[15,16] The high efficiency of FerroPHANE **I** in terms of product selectivity is therefore probably the result of an increased nucleophilicity of the intermediate phosphine-allene adduct, orienting the reaction course predominantly to the desired cyclization product **3a**.

FerroPHANE **I** also proved to be especially robust and enantioselective as a catalyst in this reaction: an enantiomeric excess as high as 90% was obtained, although prolonged heating at 120°C was required for the reaction to take place with good conversion rates and chemoselectivity (entry 6 in Table 1). A reduction in the catalyst loading to 5% decreases the conversion rate, although the same levels of enantioselectivity are retained (entry 7).

Further experiments to evaluate the scope of the above cyclization reactions were then conducted, by variation of the enone substrates **2** (Table 2). With enones **2b–l** the corresponding cyclopentenes **3** were obtained as the major isomers, with very high regio- and diastereoselectivities (only trace amounts of other isomers were observed). The cyclization reactions take place by attack of the allene γ-carbon on the enone in the Michael-type addition step. The *trans* stereochemistry of the enone is retained in the final product.

Table 2. Synthesis of cyclopentenylphosphonates **3** by FerroPHANE-catalysed annulations.



1 **2b–l** **3b–l**

Entry	R^1	R^2	Product	Yield [%]	*ee* [%]
1	Ph	Ph	**3b**	78	90
2	Ph	4-$MeOC_6H_4$	**3c**	80	91
3	Ph	4-$NO_2C_6H_4$	**3d**	68	86
4	Ph	2-naphthyl	**3e**	83	88
5	Ph	2-furyl	**3f**	77	91
6	Ph	3-quinolyl	**3g**	87	90
7	Ph	$C_5H_{11}C{\equiv}C$	**3h**	28	84
8	4-$MeOC_6H_4$	Ph	**3i**	73	90
9	4-$NO_2C_6H_4$	Ph	**3j**	60	84
10	2-furyl	Ph	**3k**	80	83
11	Me	Ph	**3l**	85	45

Conditions: allene/enone 1:2 ratio.

As shown in Table 2, the reactions can give good yields and enantiomeric excesses of over 86% for enones bearing substituted aryl or heteroaryl groups on the double bond (entries 1–6). The 1-heptynoyl-substituted enone **2h** displays lower reactivity, but the annulation reaction retains a good level of enantiocontrol, with an 84% *ee*. The reaction also tolerates substituted aryl groups as the carbonyl substituents (entries 8–10), whereas both conversion rates and enantioselectivity decrease when benzylidene acetone is used as the enone substrate (entry 11).

The results above highlight FerroPHANE **I** as the first synthetically useful phosphine catalyst for enantioselective annulations on allenylphosphonates. These reactions, taking place with excellent control over chemo-, regio- and stereoselectivity, open the way to the development of new families of cyclic enantioenriched vinylphosphonates, a well-known useful class of intermediates for organophosphorus chemistry and organic synthesis.[17]

Enantioselective annulations on bis-enones: [3+2] Cyclizations between allenoates and divinyl ketones were next considered as suitable applications for FerroPHANE **I**.

Phosphine-promoted [3+2] annulations between allenic esters and enones are widely documented as elegant and efficient protocols for carbon–carbon bond formation.[2h,k,q,6b,e] Nevertheless, the use of bis-enone substrates—that is, dibenzylidene acetone and analogues—has been barely mentioned in the literature. The only known examples of enantioselective cyclizations on cyclic or acyclic dienones have been reported by Fu, with use of *t*Bu-Binepine as the chiral promoter (four examples, with *ee* values of between 73 and 93%).[6b] With respect to simple enones, the peculiar advantage of these substrates is to give access to cyclopentenes that each contain a residual, potentially reactive enone function. An attractive target would therefore be first to build a cyclopentene ring through organocatalytic, enantioselective cyclizations and then to perform stereocontrolled transformations of the residual double bond. This strategy is typified here by a two-step sequence involving two successive organocatalysed cyclizations and FerroPHANE as the chiral auxiliary.

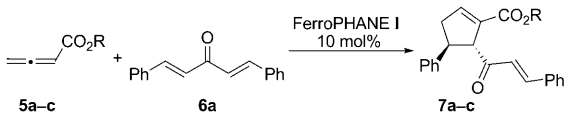
At the outset of our studies, investigations were carried out on cyclizations between buta-2,3-dienoates and dibenzylidene acetone (dba) as the model substrate, in the presence of FerroPHANE (Table 3). In principle, cyclizations between allenoates and α,β-unsaturated ketones might afford both the α-addition products (from attack of the allene α-carbon on the enone) and the γ-addition products: that is, 4-acyl-5-arylcyclopent-1-enecarboxylates and 5-acyl-4-arylcyclo-pent-1-enecarboxylates, respectively.[7d,14a] We had previously noticed that FerroPHANE **I** converts simple enones mainly into the γ-addition products.[9a] This is also the case with reactions involving dba and butadienoates **5a–c**, in which almost perfect regioselectivity in favour of **7** has been ascertained by NMR analysis of the crude reaction mixtures (>20:1 ratios of regioisomers[18]).

Several reactants and reaction parameters were screened in order to find optimal conditions with respect both to conversion rates and to enantioselectivity. The best solvent proved to be toluene, in which the expected cyclopentene **7a** was obtained in 90% yield and 92% *ee* (entry 3 vs. 1 and 2).[19] A reduction in the temperature to 0°C dramatically decreased the yield, but no significant increase in the enantioselectivity level was observed (93% *ee*, entry 4).

The replacement of ethyl buta-2,3-dienoate (**5a**) with three-atom synthons bearing bulkier ester groups—that is cyclohexyl (**5b**) or benzyl groups (**5c**)—led to cyclopentenes **7b** and **7c** with comparable enantiomeric excesses but in lower isolated yields (entries 5 and 6).

Because alkynes might represent more convenient starting materials than allenes, the possible use of ethyl but-2-ynoate was also checked. The reaction afforded the desired cyclopentene **7a**, but required a much higher reaction temperature (120°C, 80% yield after 24 h), with a concomitant decrease in the enantiomeric excess to 85% (entry 7).

Table 3. [3+2] Cyclizations between dibenzylideneacetone and buta-2,3-dienoates promoted by FerroPHANE **I**.



5a–c 6a 7a–c

	Subst.	R	Solvent	Conditions[a]	Prod.	Yield (conv.) [%]	*ee* [%][b]
1	**5a**	Et	CH_2Cl_2	RT, 16 h	**7a**	80 (100)	88
2	**5a**	Et	acetone	RT, 40 h	**7a**	26 (28)	90
3	**5a**	Et	toluene	RT, 24 h	**7a**	90 (100)	92
4	**5a**	Et	toluene	0 °C, 60 h	**7a**	13 (20)	93
5	**5b**	Cy	toluene	RT, 24 h	**7b**	28 (80)[c]	92
6	**5c**	Bn	toluene	RT, 24 h	**7c**	70 (100)	91
7	MeC≡CCO$_2$Et		toluene	120 °C, 24 h	**7a**	80 (100)	85

[a] Allene/enone ratio 2:1. [b] By HPLC. The configurations of the final products were assigned on the basis of the X-ray diffraction studies presented below. [c] Low yields are due to difficulties in separation of the final product from the starting enone.

After this optimization process, ethyl buta-2,3-dienoate was retained as the preferred reactant for further experiments with a range of enone substrates. The conditions of entry 3 in Table 3 were applied to reactions between **5a** and the acyclic and cyclic dienones **6d–h**, **8a–e** and **9** (Table 4).

The acyclic dienones **6d–h**, bearing substituted aryl and heteroaryl substituents, afforded cyclopentenes **7d–h** with good yields, high regioselectivities (>20:1 regioisomer ratios) and uniformly high enantiomeric excesses (92–95% *ee*). With dissymmetric substrates, the annulation reaction can take place on both olefinic functions. High product selectivity was observed when starting from the disymmetric enone **6g** bearing a phenyl and a 2,6-dichlorophenyl substituent (entry 4). Only cyclopentene **7g** (Ar^1 = Ph, Ar^2 = 2,6-dichlorophenyl) was isolated, because of the lower reactivity of the hindered *ortho*-dichlorophenyl-substituted double bond.[20] However, a mixture of two annulation products in a 1.7:1 ratio and in a combined yield of 87% was obtained from the reaction between enone **6h** and ethyl buta-2,3-dienoate (entry 5).

The five-membered cyclic enones **8a–d**, containing exocyclic double bonds, also undergo [3+2] annulations with ethyl buta-2,3-dienoate (**5a**) to afford spirocyclic products containing quaternary stereocentres (**10a–d**). The spirocyclopentanones **10a–d** were obtained in moderate to good yields and high enantiomeric excesses (84–92%, entries 6–9), although the electron-rich 4-methoxyphenyl-substituted enone **8e** failed to react under the given conditions (entry 10). The six-membered cyclic enone **9** afforded the expected annulation product **11** in 85% *ee* and 35% yield.

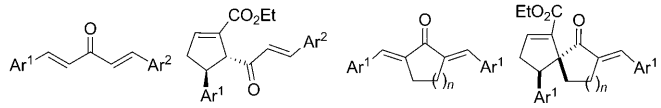
The above results demonstrate that, overall, FerroPHANE **I** performs as well as the previously used *t*Bu-Binepine catalyst[6b] in cyclizations on enones containing exocyclic double bonds and allows the scope of these cyclizations to be extended to a few additional substrates. These reactions represent a valuable strategy for the enantioselective construction of quaternary stereogenic centres at the crosspoints of spirocyclic derivatives.

With the cyclopentenes **7** now available with high regio- and enantioselectivities through the use of FerroPHANE as the catalyst, it seemed worthwhile to use them as substrates for subsequent reactions on the remaining enone function. With this in mind, we attempted a second phosphine-promoted cyclization with cyclopentene **7a** by treating this compound with an excess of ethyl buta-2,3-dienoate in the presence of achiral phosphines. PPh_3 was found to promote the desired cyclization reaction suitably at room temperature (Scheme 3). The product, isolated in 66% yield, consisted mainly (over 95%) of the bis-cyclopentenyl ketone **12a**. Minor amounts of other isomers were also observed in the crude reaction mixture. The stereochemistry of **12a** was established by single-crystal X-ray analysis. As shown by the ORTEP drawing in Figure 1, **12a** is the C_2-symmetric, chiral stereoisomer, with the C=O bond lying along the C_2 symmetry axis.

The good diastereoselectivities of reactions promoted by PPh_3 mean that effective stereochemical control of the second cyclization reaction is effected by the first formed cyclopentene unit.

Other enantiomerically enriched bis-cyclopentenyl ketones **12** could be accessed by the same two-step procedure: after the production of the cyclopentenyl ketones **7d–f** from

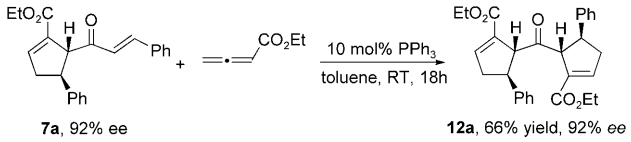
Table 4. [3+2] Cyclizations of dienones **6d–h**, **8a–e** and **9** with ethyl buta-2,3-dienoate (**5a**) promoted by (*S*,*S*)-FerroPHANE **I**: reactants and products.



6d–h 7d–h 8a–e: *n*=1, 9: *n*=2 10a–d: *n*=1, 11: *n*=2

Entry	Subst.	Ar^1	Ar^2	Product	Yield [%]	*ee* [%]
1	**6d**[a]	4-ClC_6H_4	4-ClC_6H_4	**7d**	67	92
2	**6e**[a]	4-MeC_6H_4	4-MeC_6H_4	**7e**	80	93
3	**6f**[a]	2-thienyl	2-thienyl	**7f**	60[b]	93
4	**6g**[a]	Ph	2,6-$Cl_2C_6H_3$	**7g**	55[b]	92
5	**6h**[a]	Ph	4-MeOC_6H_4	**7h+7h′**	55[c]/32	92/95
6	**8a**[d]	Ph		**10a**	84	85
7	**8b**[d]	4-ClC_6H_4		**10b**	90	87
8	**8c**[d]	4-BrC_6H_4		**10c**	85	92
9	**8d**[d]	2-furyl		**10d**	53	84
10	**8e**[d]	4-MeOC_6H_4		**10e**	<10	n.d.
11	**9**[d]	Ph		**11**	35	85

[a] Conditions: toluene, RT, 24 h, under argon, ethyl butadienoate/enone ratio 2:1, 0.3 M concentration of enone, FerroPHANE **I** 10 mol%. [b] Contains about 10% of a side product, presumably the α-addition product. [c] Ar^1 = Ph for the major regioisomer. [d] Reactions performed at 40 °C for 18 h. These substrates are poorly soluble in toluene at RT



Scheme 3. [3+2] annulation with the 5-cinnamoylcyclopentene (**7a**).

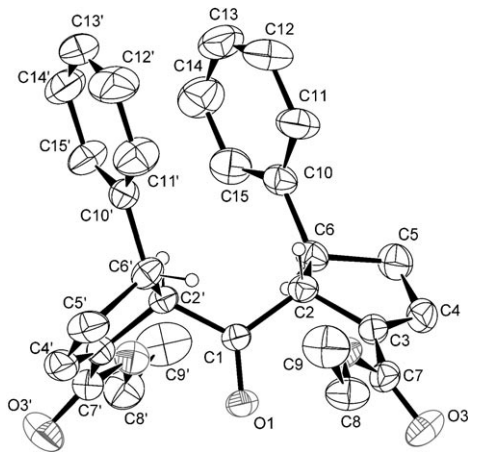
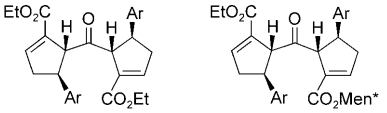


Figure 1. X-ray crystal structure of compound **12a**. Hydrogen atoms have been omitted for clarity.

the corresponding bis-enones **6** under FerroPHANE catalysis conditions, PPh_3 was used to promote the second cyclizations on the residual double bonds in compounds **7**. The expected compounds **12d–f** (Table 5) were isolated in about 50% yields as ~9:1 mixtures of isomers. The major isomers were fully characterised.

Table 5. Enantiomerically enriched bis(cyclopentenyl)ketones obtained through diastereoselective PPh_3-promoted cyclizations on the enone functions of compounds **7**.



12d–f

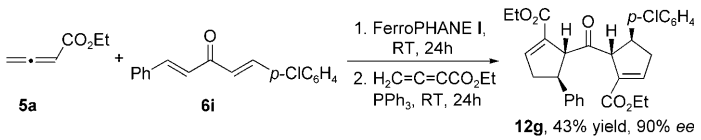
13

Entry	Substrate (*ee*)	Ar	Product[a]	Yield [%]
1	**7d** (92)	4-ClC_6H_4	**12d**	48
2	**7e** (93)	4-MeC_6H_4	**12e**	53
3	**7f** (93)	2-thienyl	**12f**	50
4	**7a** (92)	Ph	**13**[b]	58

[a] Conditions: $H_2C{=}C{=}CHCO_2Et$ (3 equiv), PPh_3 10 mol%, toluene, RT, 18 h. [b] $MeC{\equiv}CCO_2Men^*$ (3 equiv), PPh_3 10 mol%, toluene, RT, 24 h.

The dissymmetric bis-cyclopentenylketone **13** could also be obtained by treatment of **7a** with D-menthyl but-2-ynoate at room temperature, with PPh_3 (10 mol%) as the catalyst. Good diastereoselectivity was also observed in this case, with a d.r. of 90%. The double bonds in the spirocyclic enones **10a** and **11** failed to undergo cyclization with ethyl buta-2,3-dienoate in the presence of PPh_3, either under the above conditions or at higher temperature.

A "one-pot" process can be applied to these cyclizations, avoiding isolation of the intermediate cyclopentenes **7**, provided that total conversions of the starting bis-enones **6** into compounds **7** are achieved in the first FerroPHANE-catalysed annulations. Subsequent addition of PPh_3 to the reaction mixtures then allows the second annulation steps to be performed (Note: FerroPHANE itself does not promote the second cyclization steps at room temperature). This last procedure is especially convenient for unsymmetric enones, from which the first cyclization step takes place with low chemoselectivity. A representative example is the synthesis of compound **12g** (Scheme 4).



Scheme 4. One-pot synthesis of the unsymmetric bis(cyclopentenyl) ketone **12g**.

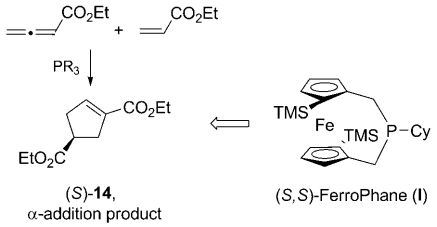
The above experiments simply reveal that the chiral cyclic moieties of **7** may effect efficient stereocontrol in reactions involving the enone functions. In the targeted organocatalytic cyclizations two additional stereogenic centres are generated with good diastereoselectivity. As an extension of this work, other relevant transformations of the same enone functions might be considered, with the aim of taking advantage of possible high levels of diastereocontrol.

As a very preliminary investigation, we performed the reduction of the carbonyl function of **7a** into the corresponding alcohol. Reductions either with $NaBH_4$ or with $NaBH_4$/$CeCl_3$ mixtures take place with a quite good diastereoselectivity (80:20 diastereomer ratio) and afford opposite epimers as the major products. Although they could not be made fully diastereoselective, these reductions suggest that some stereocontrol can be exerted by the chiral cyclopentenyl moiety of **7** in reactions other than the organocatalytic [3+2] cyclizations of Scheme 3.

In summary, the above results open promising perspectives for the stereoselective synthesis of variously functionalised chiral cyclopentenes. The synthetically challenging bis-cyclopentenyl ketones **12** are available through a simple two-step sequence involving a FerroPHANE-promoted organocatalytic process as the enantioselective step.

Sense of chiral induction and a tentative interpretation based on DFT studies: Both from our previous work and from the above studies, it appears that (*S*,*S*)-FerroPHANE **I** is an efficient and highly enantioselective catalyst for [3+2] annulations between electron-poor allenes (allenic esters or phosphonates) and olefinic double bonds activated by electron-withdrawing groups (acrylates, fumarates and various enones). The sense of chiral induction of FerroPHANE-promoted cyclizations has been established previously for the

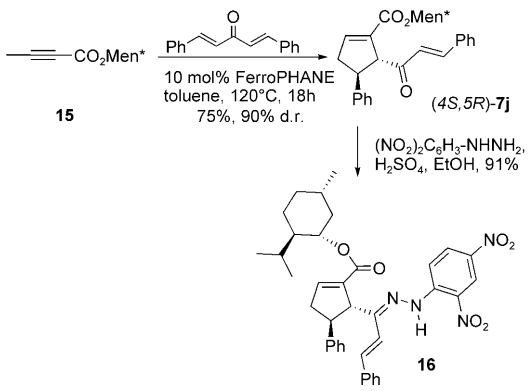
α-addition product **14** obtained from ethyl buta-2,3-dienoate and ethyl acrylate (Scheme 5). In this case, the *S*-configured FerroPHANE gives an *S*-configured cyclopentene **14**.



Scheme 5. Stereochemical course of the α-addition between ethyl buta-2,3-dienoate and ethyl acrylate.

With regard to the stereochemical outcomes of [3+2] annulations on enone derivatives that proceed by γ-addition, assignment has so far been achieved only for the cyclization product obtained from chalcone, based on $[\alpha]_D$ values by comparison with literature data.[6b,9b] In order to ascertain the stereochemical courses of the cyclization reactions involving bis-enones, as well as to confirm the previous assignments, we unambiguously determined the configuration of a representative γ-addition product through X-ray studies, as shown below.

(*S*,*S*)-FerroPHANE **I** was used to promote the [3+2] annulation between D-menthyl but-2-ynoate (**15**) and dba (Scheme 6). The reaction delivered the expected cyclopentene **7j** with a diastereomeric ratio of 95:5, in a phosphine-controlled process.[21] To obtain crystals suitable for X-ray diffraction studies, the cyclopentenylketone **7j** was converted into the corresponding hydrazone **16**.



Scheme 6. [3+2] cyclization between dba and D-menthyl but-2-ynoate (**15**).

The X-ray crystal structure of **16** (Figure 2) unambiguously shows that the major diastereomer obtained from the *S*,*S*-configured FerroPHANE has a 4*S*,5*R* configuration in the chiral cyclopentene ring.

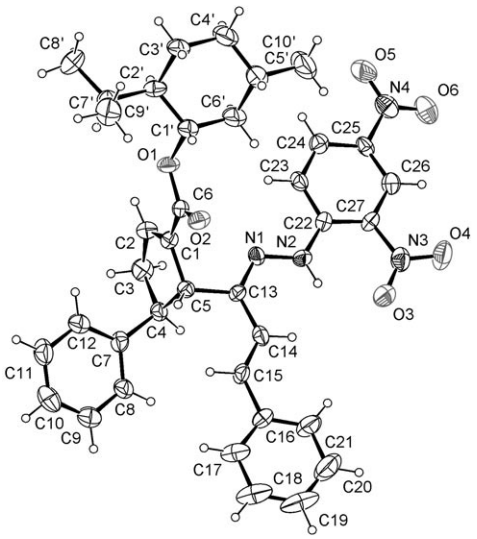
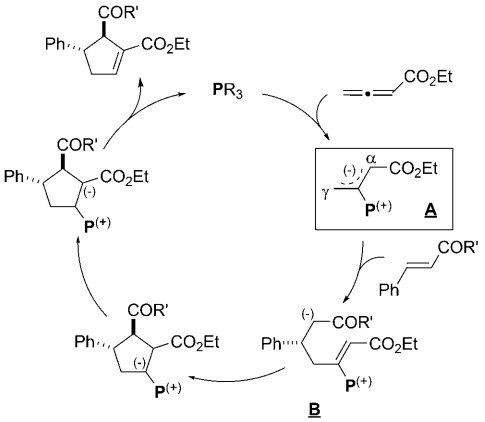


Figure 2. ORTEP drawing for compound **16**.

This assignment is fully consistent with the sense of chiral induction of (*S*,*S*)-FerroPHANE-promoted annulations on simple chalcones.

With the above assignment of configuration to hand, DFT analysis of some key reaction intermediates was envisioned with the aim of providing an explanation of the chiral induction process.

According to the widely accepted mechanistic proposal (Scheme 7),[14,22] the catalytic cycle of the above [3+2] annulations starts with the addition of the nucleophilic phosphine on the β-carbon atom of the allenic substrate to give the zwitterionic phosphonium salt **A**. The anionic allylic moiety of **A** may then add to an unsaturated electron-poor substrate through either its α- or its γ-carbon atom. Because γ-addition takes place selectively in the FerroPHANE-promoted annulations between allenes and enones, only the γ-adduct **B** is considered in Scheme 7.



Scheme 7. Postulated mechanism for phosphine-promoted [3+2] cyclizations between allenes and enones.

The zwitterionic intermediate **A** is likely to be a key intermediate, its three-dimensional arrangement potentially playing an essential role in the stereochemical control of the cyclization reaction.[23] On the basis of this working hypothesis, we focused our attention on this intermediate for P=(*S*,*S*)-FerroPHANE **I** as a key for understanding the catalytic behaviour of the chiral phosphine.

The geometric features of FerroPHANE **I**, of the simplified analogue **Ib** (in which the TMS and Cy groups have been substituted by a hydrogen atom and a methyl group, respectively) and their phosphine-allene adducts **A** were studied by quantum chemical calculations with the aid of the TURBOMOLE program and density functional methods (marij-BP86/def2-SVP level of calculation; see the Supporting Information for the calculated conformations and energy values). The resulting structural parameters for FerroPHANE **I** are in good agreement with the previously reported X-ray data (Figure 3).[9a]

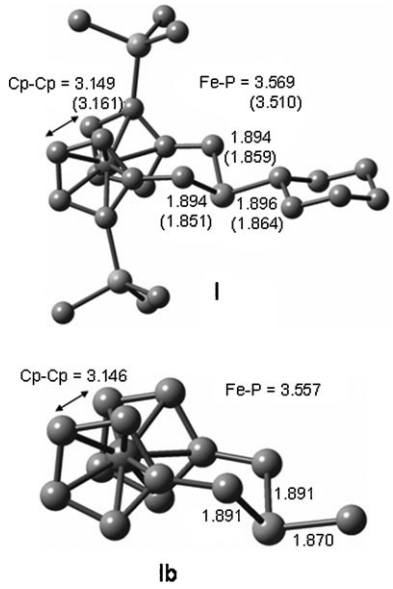


Figure 3. Optimized structures of phosphines **I** and **Ib** at the marij-BP86/def2-SVP level. Selected distances in Å (X-ray values in parentheses). An enlarged colour figure is given in the Supporting Information.

The corresponding phosphine-allene adduct **A** was constructed analogously, by starting from the calculated structure of FerroPHANE **I**. It was found that the most stable structure involves the enolate form of the ester function and a stabilizing dipolar $P^{+}\cdots O^{-}$ interaction (Figure 4). These results corroborate the previous findings of Dudding[14b] and Yu[14c] relating to the analogous PMe_3 adducts.[24] The phosphorus atom displays a distorted tetrahedral coordination, approaching a trigonal bipyramid geometry as a result of the $P^{+}\cdots O^{-}$ interaction. Energy minima were found for three isomeric forms in which the P···O bond lies along either the $P–C_{Cyclohexyl}$ axis (**A-1**) or the $P–C_{ferrocene}$ axes (**A-2** and **A-3**).

Isomer **A-3** was calculated to be the most stable form; steric hindrance between the TMS group and the ester function induces destabilization of **A-1** by $+20\ kJ\,mol^{-1}$ relative to **A-3**, whereas in **A-2** an energy difference of $+12\ kJ\,mol^{-1}$ is induced by the close proximity between the methylene group and the ferrocene scaffold. These main destabilising interactions are indicated in Figure 4 by black arrows. It should be noted here that structures **A-2** and **A-3** are epimeric forms in which the phosphorus centres display opposite configurations. They would have an enantiomeric relationship and would therefore be energetically equivalent for phosphines with achiral ferrocene scaffolds.

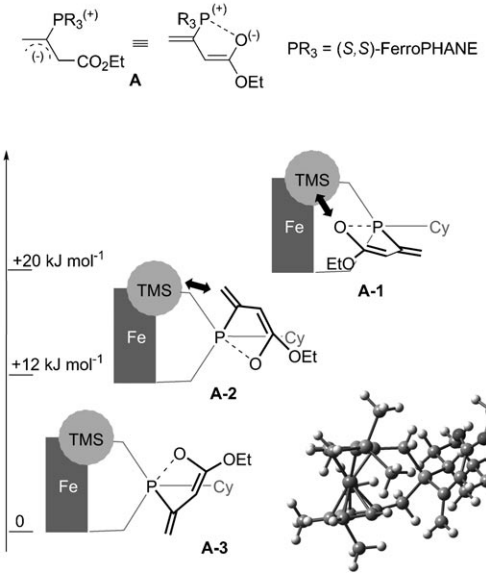
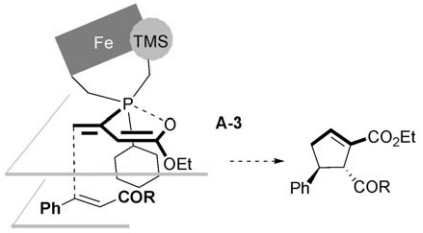


Figure 4. Optimised geometries of the zwitterionic intermediates **A** for PR_3=(*S*,*S*)-FerroPHANE.

With regard to the second step of the catalytic cycle, we may reasonably assume that the three isomeric intermediates **A** add to the enone with comparable reaction rates. If this is the case, the major stereoisomer of the final product should be formed from **A-3**. In this isomer, only one face of the unsaturated enolate—that is, the bottom face in Scheme 8—is reasonably accessible to the enone reactant, the upper face being hindered by the ferrocenyl-TMS group.



Scheme 8. Postulated approach of the enone to the zwitterionic intermediate **A-3**.

The enone might then approach the allene-phosphine adduct with either the Ph or the carbonyl group oriented toward the bulky phosphine. The preferred 4*S*,5*R*-configured product should then result from the approach shown in Scheme 8, which would allow the phenyl substituent to be in the less hindered region. The lower steric hindrance of the carbonyl function, relative to the aryl group, might account for this preferred orientation, but energetically favourable $P–O_{COR}$ interactions might also favour this approach.[14b]

In other words, according to the tentative model above, the planar chiral arrangement of the phosphine allows discrimination of the upper and bottom face of the allenoate (that is to say, it induces energy difference between **A-3** and **A-2**) and dictates attack of the olefin from the bottom face. The relative steric hindrance of the enone substituents then determines the sense of addition and the preferred configuration.

The same model might also account for the observed stereochemical outcome of the α-addition process shown in Scheme 5. In this case, the pathway leading to the major *S* enantiomer of **14** would involve approach of the olefin to the phosphine-allene adduct so as to minimise the destabilizing steric interactions between the phosphine and the acrylate ester group.

The above computations thus afford a reasonable heuristic model for the chiral discrimination operated by (*S*,*S*)-FerroPHANE **I**.

Conclusions

This work affords new evidence for the high efficiency of FerroPHANE **I** in the enantioselective [3+2] cyclizations of electron-poor allenes and enones. In particular, these reactions have been extended to allenic phosphonates and to dba derivatives. Unprecedented bis-cyclopentenyl scaffolds with four stereocentres have been created through sequences of two successive organocatalysed cyclizations.

A tentative interpretation of the chiral induction exerted by FerroPHANE **I** in the cyclization reactions involving allenic esters and enones has been afforded by modelling of the energetically most favoured isomers of the key phosphine-allene adduct.

Further applications of FerroPHANE **I** in organocatalytic processes are currently under study.

Experimental Section

General methods: All reactions were run under inert atmosphere (argon), by standard techniques for manipulation of air-sensitive compounds. All glassware was stored in the oven and/or was flame-dried prior to use. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2). All reagents and solvents were of commercial quality and were used without further purification. Flash column chromatography was performed with 40–63 mesh silica. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded with Brucker AV 500 or AV 300 spectrometers. IR spectra were recorded with a Perkin–Elmer FT-IR spectrophotometer. High-resolution mass spectra (HRMS-ESI) were obtained with LCT Waters equipment. Optical rotations were determined with a JASCO P-1010 polarimeter. HPLC was performed at a column temperature of 30 °C with a Waters 2695 Separations Module fitted with a diode array UV detector. Data are reported as follows: column type, eluent, flow rate, retention time. Substrates **2**, **6**, **8** and **9** were prepared by known procedures.[6b]

Representative procedure for the asymmetric [3+2] annulations of diethyl propa-1,2-dienylphosphonate with enones 2 (Tables 1 and 2)—synthesis of diethyl 5-benzoyl-4-(naphthalen-1-yl)cyclopent-1-enylphosphonate (3a, entry 6 in Table 1): Degassed toluene (0.5 mL) was added under argon to a mixture of enone **2a** (77 mg, 0.30 mmol), diethyl propa-1,2-dienylphosphonate (**1**, 26 mg, 0.15 mmol) and FerroPHANE **I** (7.1 mg, 0.015 mmol). The mixture was heated at 120 °C for 24 h in a sealed tube. The solvent and small amounts of the side product **4** were removed in vacuo. The final product was purified by flash chromatography on silica gel with an EtOAc/heptane 80:20 mixture ($R_f = 0.4$) Compound **3a** was obtained in 80% yield (52 mg) and 90% *ee*. $[\alpha]_D^{25} = +8$ ($c = 0.6$, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): *m*/*z*: calcd for $C_{26}H_{27}NaO_4P$ $[M+Na]^+$: 457.1545; found: 457.1540. The enantiomeric excess was measured by HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 285 nm, retention times: 89.3 min (minor) and 96.2 min (major).

Diethyl 5-benzoyl-4-phenylcyclopent-1-enylphosphonate (3b): Compound **3b** was obtained in 78% yield and 90% *ee* after purification with EtOAc/heptanes (70%, $R_f = 0.3$). $[\alpha]_D^{25} = +10$ ($c = 0.8$, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{25}NaO_4P$ $[M+Na]^+$: 407.1388; found: 407.1390; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (10%), 1 mL min^{-1}, 271 nm, retention times: 26.8 min (minor) and 32.3 min (major).

Diethyl 5-benzoyl-4-(4-methoxyphenyl)cyclopent-1-enylphosphonate (3c): Compound **3c** was obtained in 80% yield and 91% *ee* after purification on a silica gel column with EtOAc/heptanes (80%, $R_f = 0.2$). $[\alpha]_D^{25} = +20$ ($c = 1.2$, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): *m*/*z*: calcd for $C_{23}H_{27}NaO_5P$ $[M+Na]^+$: 437.1494; found: 437.1492; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 231 nm, retention times: 40.8 min (minor) and 52.3 min (major).

Diethyl 5-benzoyl-4-(4-nitrophenyl)cyclopent-1-enylphosphonate (3d): Compound **3d** was obtained in 68% yield and 86% *ee* after purification with EtOAc/heptanes (80%, $R_f = 0.2$). $[\alpha]_D^{25} = +2.5$ ($c = 0.5$, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{24}NNaO_6P$ $[M+Na]^+$: 452.1239; found: 452.1246; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 205 nm, retention times: 70.7 min (minor) and 85.5 min (major).

Diethyl 5-benzoyl-4-(naphthalen-2-yl)cyclopent-1-enylphosphonate (3e): Compound **3e** was obtained in 83% yield and 88% *ee* after column chromatography with EtOAc/heptanes (80%, $R_f = 0.25$); $[\alpha]_D^{25} = +41$ ($c = 0.3$, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.90$ (d, $J = 7.7$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.1$ Hz, 1H), 7.62 (s, 1H), 7.54 (t, $J = 7.3$ Hz, 1H), 7.50–7.45 (m, 2H), 7.45–7.35 (m, 3H), 7.08 (d, $J = 11.2$ Hz, 1H), 4.96 (br s, 1H), 4.10–3.95 (m, 4H), 3.95–3.90 (m, 1H), 3.40–3.30 (m, 1H), 2.82 (d, $J = 19.0$ Hz, 1H), 1.20 ppm (t, $J = 6.5$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.0$ (C), 150.8 (d, $J_{C,P} = 13.9$ Hz, CH), 142.3 (C), 136.7 (C), 133.6 (C), 133.4 (CH), 132.6 (C), 132.4 (d, $J_{C,P} = 191.4$ Hz, C), 129.1 (CH), 128.9 (2×CH), 128.6 (2×CH), 127.8 (CH), 127.7 (CH), 126.4 (CH), 125.9 (CH), 125.3 (CH), 125.0 (CH), 62.1 (d, $J_{C,P} = 5.1$ Hz, CH_2), 61.7 (d, $J_{C,P} = 5.9$ Hz, CH_2), 61.3 (d, $J_{C,P} = 12.8$ Hz, CH), 49.7 (d, $J_{C,P} = 10.5$ Hz, CH), 43.0 (d, $J_{C,P} = 19.2$ Hz, CH_2), 16.3 (d, $J_{C,P} = 6.4$ Hz, CH_3), 16.2 ppm (d, $J_{C,P} = 6.9$ Hz, CH_3); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 14.2$ ppm; IR: $\tilde{\nu}_{max} = 2982, 2355, 1662, 1590, 1573, 1449, 1332, 1207, 1023, 967, 852, 739$ cm^{-1}; HRMS (ESI): *m*/*z*: calcd for $C_{26}H_{27}NaO_4P$ $[M+Na]^+$: 457.1545; found: 457.1569; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 226 nm, retention times: 26.3 min (minor) and 39.6 min (major).

Diethyl 5-benzoyl-4-(furan-2-yl)cyclopent-1-enylphosphonate (3f): Compound **3f** was obtained in 77% yield and 91% *ee* after purification with EtOAc/heptanes (80%, R_f=0.2). $[\alpha]_D^{25}$=+67 (c=0.35, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): m/z: calcd for $C_{20}H_{23}NaO_5P$ $[M+Na]^+$: 397.1181; found: 397.1176; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 251 nm, retention times: 27.5 min (minor) and 31.0 min (major).

Diethyl 5-benzoyl-4-(quinolin-3-yl)cyclopent-1-enylphosphonate (3g): Compound **3g** was obtained in 87% yield and 90% *ee*. R_f=0.15 in EtOAc/heptanes (80%); $[\alpha]_D^{25}$=+180 (c=0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.79 (d, J=2.3 Hz, 1H), 8.1 Hz (d, J=8.5 Hz, 1H), 7.98–7.88 (m, 3H), 7.80–7.66 (m, 2H), 7.59–7.51 (m, 2H), 7.41 (t, J=8.1 Hz, 2H), 7.07 (dm, J=11.0 Hz, 1H), 4.96 (br s, 1H), 4.10–3.90 (m, 5H), 3.38 (dm, J=17.7 Hz, 1H), 2.81 (dm, J=18.4 Hz, 1H), 1.25–1.10 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=198.4, 149.4, 149.3 (d, $J_{C,P}$=14.2 Hz), 146.5, 136.5, 135.5, 132.6, 131.3 (d, $J_{C,P}$=193.0 Hz), 128.4, 128.3, 127.9, 127.8, 127.4, 127.1, 126.7, 126.1, 61.2 (d, $J_{C,P}$=5.3 Hz), 60.8 (d, $J_{C,P}$=6.0 Hz), 59.8 (d, $J_{C,P}$=13.2 Hz), 46.0 (d, $J_{C,P}$=10.5 Hz), 41.6 (d, $J_{C,P}$=20.2 Hz, C_3), 15.3 (d, $J_{C,P}$=6.5 Hz), 15.1 ppm (d, $J_{C,P}$=7.0 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ=13.6 ppm; IR: $\tilde{\nu}_{max}$=2928, 1678, 1596, 1579, 1493, 1447, 1244, 1048, 1024, 966, 838, 788, 752 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{25}H_{26}NNaO_4P$ $[M+Na]^+$: 458.1497; found: 458.1500; HPLC analysis: Daicel CHIRACEL IC column, EtOH/*n*-heptane (10%), 1 mL min^{-1}, 240 nm, retention times: 30.8 min (minor) and 36.9 min (major).

Diethyl 5-benzoyl-4-(hept-1-ynyl)cyclopent-1-enylphosphonate (3h): Compound **3h** was obtained in 28% yield and 84% *ee*. R_f=0.3 in EtOAc/heptanes (80%); $[\alpha]_D^{25}$=+86 (c=0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.12–8.06 (m, 1H), 7.64–7.46 (m, 4H), 6.88 (dm, J=10.8 Hz, 1H), 4.85 (s, 1H), 4.04–4.86 (m, 4H), 3.42–3.33 (m, 1H), 3.13–3.00 (m, 1H), 2.67 (dm, J=17.5, 1H), 2.14 (m, 1H),1.52–1.40 (m, 2H), 1.40–1.25 (m, 4H), 1.18 (m, 6H), 0.91–0.85 ppm (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=199.7, 150.0 (d, $J_{C,P}$=13.0 Hz), 137.3, 133.7, 131.8 (d, $J_{C,P}$=191.6 Hz), 129.0, 128.7, 82.6, 81.9, 62.1 (d, $J_{C,P}$=5.0 Hz), 61.8 (d, $J_{C,P}$=5.2 Hz), 60.5 (d, $J_{C,P}$=13.0 Hz), 42.1 (d, $J_{C,P}$=19.6 Hz), 35.3 (d, $J_{C,P}$=11.3 Hz), 31.2, 28.7, 22.3, 18.8, 16.2 (dd, $J_{C,P}$=6.2, 6.1 Hz), 14.1 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ=14.7 ppm; IR: $\tilde{\nu}_{max}$=2926, 2855, 1682, 1597, 1448, 1248, 1051, 1023, 969 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{23}H_{31}NaO_4P$ $[M+Na]^+$: 425.1858; found: 425.1852; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 248 nm, retention times: 16.6 min (minor) and 18.3 min (major).

Diethyl 5-(4-methoxybenzoyl)-4-phenylcyclopent-1-enylphosphonate (3i): Compound **3i** was obtained in 73% yield and 90% *ee*. R_f=0.23 in EtOAc/heptanes (80%); $[\alpha]_D^{25}$=+41 (c=0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.88 (d, J=8.8 Hz, 2H), 7.35–7.10 (m, 5H), 6.99 (dm, J=10.9 Hz, 1H), 6.88 (d, J=8.4 Hz, 2H), 4.81 (br s, 1H), 4.05–3.92 (m, 4H), 3.85 (s, 3H), 3.80–3.65 (m, 1H), 3.26 (dm, J=18.0 Hz, 1H), 2.70 (dm, J=18.0 Hz, 1H), 1.19 ppm (t, J=7.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=198.5, 163.8, 150.6 (d, $J_{C,P}$=13.8 Hz), 145.2, 133.4, 130.9, 130.6, 130.0 (d, $J_{C,P}$=170.0 Hz), 129.8, 127.0, 126.8, 113.8, 62.0 (d, $J_{C,P}$=5.4 Hz), 61.7 (d, $J_{C,P}$=6.4 Hz), 61.1 (d, $J_{C,P}$=12.7 Hz), 55.5, 49.7 (d, $J_{C,P}$=10.5 Hz), 42.9 (d, $J_{C,P}$=20.2 Hz), 16.3 (d, $J_{C,P}$=6.8 Hz), 16.2 ppm (d, $J_{C,P}$=6.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ=14.3 ppm; IR: $\tilde{\nu}_{max}$=2978, 1671, 1599, 1259, 1170, 1023, 967, 841, 700 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{23}H_{27}NaO_5P$ $[M+Na]^+$: 437.1494; found: 437.1480; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 210 nm, retention times: 43.7 min (minor) and 59.1 min (major).

Diethyl 5-(4-nitrobenzoyl)-4-phenylcyclopent-1-enylphosphonate (3j): Compound **3j** was obtained in 60% yield and 84% *ee*. R_f=0.15 in EtOAc/heptanes (80%); $[\alpha]_D^{25}$=+48 (c=0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.24 (d, J=8.5 Hz, 2H), 8.00 (d, J=8.5 Hz, 2H), 7.35–7.10 (m, 5H), 7.00 (d, J=11.0 Hz, 1H), 4.85 (br s, 1H), 4.05–3.90 (m, 4H), 3.75 (dt, J=9.3, 5.1 Hz, 1H), 3.30–3.20 (m, 1H), 2.77 (dm, J=18.5 Hz, 1H), 1.21 ppm (d, J=7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=207.5, 149.5, 143.6, 140.4, 128.7, 128.3, 127.0 (d, $J_{C,P}$=192.0 Hz), 126.1, 125.8, 122.8, 66.6, 61.2 (d, $J_{C,P}$=20.5 Hz), 48.9, 47.6, 41.8, 29.7, 15.5, 15.4 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ=13.7 ppm; IR: $\tilde{\nu}_{max}$=2926, 2854, 2361, 1726, 1688, 1602, 1524, 1344, 1246, 1208, 1021, 964, 832, 750, 699 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{22}H_{24}NNaO_6P$ $[M+Na]^+$ 452.1239; found: 452.1237; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 264 nm, retention times: 48.0 min (major) and 64.7 min (minor). Slow degradation of samples stored under argon at −20 °C has been observed.

Diethyl 5-(furan-2-carbonyl)-4-phenylcyclopent-1-enylphosphonate (3k): Compound **3k** was obtained in 80% yield and 83% *ee* after purification by column chromatography with EtOAc/heptanes (80%, R_f=0.17); $[\alpha]_D^{25}$=+37 (c=0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.39 (s, 1H), 7.15–6.95 (m, 5H), 6.95–6.90 (m, 1H), 6.80 (dm, J=11.0 Hz, 1H), 6.30–6.25 (m, 1H), 4.40–4.35 (m, 1H), 3.90–3.70 (m, 4H), 3.65–3.55 (m, 1H), 3.04 (dm, J=19.8, 1H), 2.51 (dm, J=18.4 Hz, 1H), 1.10–0.95 ppm (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ=188.2, 152.3, 150.9 (d, $J_{C,P}$=13.7 Hz), 147.2, 144.6, 131.4 (d, J=191.0 Hz), 128.8, 126.9, 126.7, 118.9, 112.3, 62.1 (d, $J_{C,P}$=4.8 Hz), 61.9 (d, $J_{C,P}$=13.2 Hz), 61.6 (d, $J_{C,P}$=5.7 Hz), 49.1 (d, $J_{C,P}$=10.3 Hz), 42.7 (d, $J_{C,P}$=19.6 Hz), 16.2 (d, $J_{C,P}$=6.9 Hz), 16.1 ppm (d, $J_{C,P}$=6.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ=14.2 ppm; IR: $\tilde{\nu}_{max}$=2926, 2359, 1672, 1566, 1465, 1393, 1245, 1023, 969, 763 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{20}H_{23}NaO_5P$ $[M+Na]^+$: 397.1181; found: 397.1187; HPLC analysis: Daicel CHIRACEL IC column, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 216 nm, retention times: 79.9 min (major) and 92.8 min (minor).

Diethyl 5-acetyl-4-phenylcyclopent-1-enylphosphonate (3l): Compound **3l** was obtained in 85% yield and 45% *ee* after column chromatography with EtOAc/heptanes (80%) as the eluent (R_f=0.3); $[\alpha]_D^{25}$=+72 (c=0.3, $CHCl_3$). NMR data for this compound have been reported in ref. [8c]. HRMS (ESI): m/z: calcd for $C_{17}H_{23}NaO_4P$ $[M+Na]^+$: 345.1232; found: 345.1241; HPLC analysis: Daicel CHIRACEL IC column, EtOH/*n*-heptane (20%), 1 mL min^{-1}, 210 nm, retention times: 9.0 min (minor) and 10.3 min (major).

Representative procedures for the asymmetric [3+2] annulations on enones 6, 8 and 9 (Tables 3 and 4 and Scheme 6)

a) Synthesis of the cyclopentenylcarboxylates 7

Ethyl (4*S*,5*R*,*E*)-5-cinnamoyl-4-phenylcyclopent-1-enylcarboxylate (7a, Table 3, entry 3): Ethyl buta-2,3-dienoate (35 μL, 0.3 mmol) was added to a mixture of dba (35 mg, 0.15 mmol) and FerroPHANE **I** (7.1 mg, 0.015 mmol) in degassed toluene (0.5 mL). The mixture was stirred at room temperature for 24 h. After evaporation of the solvent, the final product was purified by chromatography on silica gel with AcOEt/heptane (10%) as the eluent (R_f=0.25). Compound **7a** was obtained as a pale yellow solid, in 90% yield (47 mg) and 92% *ee*. $[\alpha]_D^{24}$=+190 (c=0.5, $CHCl_3$). NMR data for this compound have been reported in ref. [6b]. HRMS (ESI): m/z: calcd for $C_{23}H_{22}NaO_3$ $[M+Na]^+$: 369.1467; found: 369.1475; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 290 nm, retention times: 11.9 min (major) and 49.8 min (minor).

Cyclohexyl (4*S*,5*R*,*E*)-5-cinnamoyl-4-phenylcyclopent-1-enecarboxylate (7b): Compound **7b** was obtained in 28% yield and 92% *ee*, >20:1 regioselectivity, after chromatography (R_f=0.3 in EtOAc/heptanes 10%); $[\alpha]_D^{24}$=+105 (c=1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.30–7.00 (m, 11H), 6.85 (m, 1H), 6.55 (d, J=16.2 Hz, 1H), 4.60 (m, 1H), 4.17 (m, 1H), 3.40 (dt, J=9.0, 6.0 Hz, 1H), 2.96 (ddt, J=18.6, 9.0, 2.7 Hz, 1H), 2.53 (ddt, J=18.9, 6.0, 2.4 Hz, 1H), 1.70–1.00 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=200.2, 163.7, 144.9, 144.8, 144.0, 136.0, 134.7, 130.6, 129.0, 128.9, 128.5, 127.2, 127.1, 125.7, 73.0, 63.4, 48.9, 42.0, 31.6, 31.5, 25.7, 23.64, 23.61 ppm; IR: $\tilde{\nu}_{max}$=2932, 2856, 1704, 1607, 1448, 1330, 1240, 1090, 978, 752, 697 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{27}H_{28}NaO_3$ $[M+Na]^+$: 423.1936; found: 423.1936; HPLC analysis: Daicel CHIRACEL IC, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 290 nm, retention times: 14.9 min (major) and 38.9 min (minor).

Benzyl (4*S*,5*R*,*E*)-5-cinnamoyl-4-phenylcyclopent-1-enecarboxylate (7c): Compound **7c** was obtained in 70% yield and 91% *ee*, >25:1 regioselectivity, after purification by column chromatography with EtOAc/heptanes (10%, R_f=0.30); $[\alpha]_D^{24}$=+168 (c=1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.30–7.15 (m, 16H), 7.03 (m, 1H), 6.63 (d, J=15.9 Hz, 1H), 5.11 (d, J=12.6 Hz, 1H), 5.05 (d, J=12.6 Hz, 1H), 4.33 (m, 1H), 3.53 (dt, J=9.0, 6.0 Hz, 1H), 3.10 (ddt, J=19.2, 9.0, 2.4 Hz, 1H), 2.65 ppm

(ddt, $J=18.9$, 5.7, 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=200.0$, 164.0, 145.9, 144.8, 144.2, 135.9, 135.1, 134.6, 130.6, 129.0, 128.9, 128.6, 128.5, 128.2, 127.1, 125.6, 66.5, 63.3, 48.8, 42.0 ppm; IR: $\tilde{\nu}_{max}=3061$, 3028, 1710, 1658, 1605, 1574, 1494, 1449, 1329, 1090, 977 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{28}H_{24}NaO_3$ $[M+Na]^+$: 431.1623; found: 431.1631; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 206 nm, retention times: 18.0 min (minor) and 27.0 min (major).

Ethyl (4*S*,5*R*,*E*)-4-(4-chlorophenyl)-5-[3-(4-chlorophenyl)acryloyl]cyclopent-1-enecarboxylate (7d): Compound **7d** was obtained in 67% yield and 92% *ee*, >20:1 regioselectivity; R_f 0.13 in 30% Et_2O/heptanes; $[\alpha]_D^{24}=+247$ ($c=1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.30$–7.17 (m, 7H), 7.12–7.05 (m, 2H), 6.94 (m, 1H), 6.63 (d, $J=16.2$ Hz, 1H), 4.25–4.18 (m, 1H), 4.09 (dq, $J=7.2$, 2.1 Hz, 2H), 3.50 (dt, $J=9.0$, 6.0 Hz, 1H), 3.07 (ddt, $J=16.2$, 6.3, 2.4 Hz, 1H), 2.59 (ddt, $J=18.9$, 5.7, 2.4 Hz, 1H), 1.15 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=199.6$ (C), 164.1 (C), 145.0 (CH), 143.3 (C), 142.6 (CH), 136.7 (C), 135.4 (C), 133.0 (C), 132.9 (C), 129.7 (2×CH), 129.3 (2×CH), 129.2 (2×CH), 128.5 (2×CH), 125.8 (CH), 63.4 (CH), 60.8 (CH_2), 48.1 (CH), 41.9 (CH_2), 14.3 ppm (CH_3); HRMS (ESI): m/z: calcd for $C_{23}H_{20}Cl_2NaO_3$ $[M+Na]^+$: 437.0687; found: 437.0697; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 300 nm, retention times: 16.5 min (minor) and 21.4 min (major).

Ethyl (4*S*,5*R*,*E*)-4-*p*-tolyl-5-(3-*p*-tolylacryloyl)cyclopent-1-enecarboxylate (7e): Compound **7e** was obtained in 80% yield and 93% *ee*; >20:1 regioselectivity; $R_f=0.30$ (10% EtOAc/heptanes); $[\alpha]_D^{24}=+229$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.50$–7.35 (m, 3H), 7.30–7.25 (m, 6H), 7.16 (m, 1H), 6.82 (d, $J=16.2$ Hz, 1H), 4.46 (m, 1H), 4.28 (q, $J=6.9$ Hz, 2H), 3.68 (dt, $J=8.9$, 5.7 Hz, 1H), 3.30–3.20 (m, 1H), 2.85–2.75 (m, 1H), 2.47 (s, 3H), 2.46 (s, 3H), 1.35 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=200.3$, 164.3, 145.1, 144.1, 142.0, 141.1, 136.6, 135.5, 131.9, 129.7, 129.6, 128.5, 127.0, 124.8, 63.3, 60.7, 48.5, 42.0, 21.6, 21.2, 14.3 ppm; IR: $\tilde{\nu}_{max}=2979$, 1710, 1656, 1600, 1512, 1325, 1241, 1169, 1087, 978, 811, 750 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{25}H_{26}NaO_3$ $[M+Na]^+$: 397.1780; found: 397.1781; HPLC analysis: Daicel CHIRACEL IC, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 300 nm, retention times: 31.4 min (major) and 63.0 min (minor).

Ethyl (4*R*,5*S*,*E*)-4-(thiophen-2-yl)-5-[(*E*)-3-(thiophen-2-yl)acryloyl]cyclopent-1-enecarboxylate (7f): Compound **7f** was obtained in 60% yield and 93% *ee*, >20:1 regioselectivity; $R_f=0.3$ (EtOAc/heptanes 10%); $[\alpha]_D^{24}=+221$ ($c=1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.62$ (d, $J=15.6$ Hz, 1H), 7.38 (d, $J=5.1$ Hz, 1H), 7.23 (d, $J=3.6$ Hz, 1H), 7.16 (dd, $J=5.4$, 1.2 Hz, 1H), 7.08–6.98 (m, 2H), 6.91 (m, 1H), 6.85 (m, 1H), 6.64 (d, $J=15.9$ Hz, 1H), 4.33 (m, 1H), 4.16 (m, 2H), 3.96 (dt, $J=8.7$, 6.3 Hz, 1H), 3.18 (ddt, $J=18.6$, 8.7, 2.4 Hz, 1H), 2.76 (ddt, $J=18.6$, 6.3, 2.4 Hz, 1H), 1.23 ppm (t, $J=9.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=199.3$, 164.0, 147.8, 144.6, 140.1, 136.4, 135.5, 132.0, 129.2, 128.4, 127.0, 124.6, 124.3, 123.8, 63.6, 60.8, 44.3, 42.4, 14.3 ppm; IR: $\tilde{\nu}_{max}=2922$, 1708, 1589, 1367, 1243, 1091, 968, 699 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{19}H_{18}NaO_3S_2$ $[M+Na]^+$: 381.0595; found: 381.0594; HPLC analysis: Daicel CHIRACEL IC, *i*PrOH/*n*-heptane (20%), 1 mL min^{-1}, 320 nm, retention times: 23.7 min (major) and 45.1 min (minor).

Ethyl (4*S*,5*R*,*E*)-5-[3-(2,6-dichlorophenyl)acryloyl]-4-phenylcyclopent-1-enecarboxylate (7g): Compound **7g** was obtained in 55% yield and 92% *ee*, 9:1 regioselectivity; R_f 0.3 (EtOAc/heptanes 10%); $[\alpha]_D^{24}=+155$ ($c=1$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.53$ (d, $J=16.5$ Hz, 1H), 7.30–7.00 (m, 9H), 6.85 (d, $J=16.5$ Hz, 1H), 4.35–4.30 (m, 1H), 4.20–4.10 (m, 2H), 3.64 (dt, $J=9.0$, 6.0 Hz, 1H), 3.13 (ddt, $J=18.9$, 9.0, 2.4 Hz, 1H), 2.69 (ddt, $J=18.9$, 5.7, 2.4 Hz, 1H), 1.22 ppm (t, $J=7.2$ Hz, 3H); IR: $\tilde{\nu}_{max}=2980$, 1710, 1614, 1427, 1242, 1091, 975, 772, 755, 698 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{23}H_{20}Cl_2NaO_3$ $[M+Na]^+$: 437.0687; found: 437.0696; HPLC analysis: Daicel CHIRACEL IC, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 270 nm, retention times: 29.7 min (major) and 47.5 min (minor).

Entry 5 in Table 4: The two isomeric compounds **7h and 7h′** were obtained and characterised as pure samples after separation by column chromatography.

Ethyl (4*S*,5*R*,*E*)-5-cinnamoyl-4-(4-methoxyphenyl)cyclopent-1-enecarboxylate (7h′): Compound **7h′** was obtained in 32% yield and 95% *ee*, >25:1 regioselectivity; $R_f=0.20$ (Et_2O/heptanes 30%); $[\alpha]_D^{24}=+212$ ($c=1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.43$–7.33 (m, 6H), 7.16 (d, $J=8.7$ Hz, 2H), 7.04 (m, 1H), 6.86 (d, $J=8.7$ Hz, 2H), 6.74 (d, $J=15.9$ Hz, 1H), 4.34 (m, 1H), 4.17 (dq, $J=7.2$, 2.0 Hz, 2H), 3.80 (s, 3H), 3.56 (dt, $J=9.0$, 5.0 Hz, 1H), 3.14 (ddt, $J=19.0$, 9.0, 2.5 Hz, 1H), 2.68 (ddt, $J=19.0$, 6.0, 2.0 Hz, 1H), 1.24 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=200.2$, 164.2, 158.6, 145.0, 143.9, 136.9, 135.4, 134.6, 130.5, 128.9, 128.4, 128.1, 125.6, 114.3, 63.4, 60.6, 55.4, 48.1, 42.0, 14.2 ppm; IR: $\tilde{\nu}_{max}=2924$, 1705, 1650, 1512, 1243, 1170, 1101, 1033, 976, 829, 766, 698 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{24}H_{24}NaO_4$ $[M+Na]^+$: 399.1572; found: 399.1577; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (10%), 1 mL min^{-1}, 290 nm, retention times: 22.4 min (minor) and 29.5 min (major).

Ethyl (4*S*,5*R*,*E*)-5-[3-(4-methoxyphenyl)acryloyl]-4-phenylcyclopent-1-enecarboxylate (7h): Compound **7h** was obtained in 55% yield and 92% *ee*, >25:1 regioselectivity; $R_f=0.13$ (Et_2O/heptanes 30%); $[\alpha]_D^{24}=+222$ ($c=1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.38$–7.20 (m, 8H), 7.04 (m, 1H), 6.86 (dt, $J=9.0$, 2.1 Hz, 2H), 6.62 (d, $J=16.2$ Hz, 1H), 4.36 (m, 1H), 4.17 (dq, $J=7.2$, 1.8 Hz, 2H), 3.82 (s, 3H), 3.59 (dt, $J=9.0$, 5.7 Hz, 1H), 3.16 (ddt, $J=19.0$, 9.0, 2.7 Hz, 1H), 2.70 (ddt, $J=19.0$, 5.7, 2.4 Hz, 1H), 1.24 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=200.0$, 164.3, 161.6, 145.1, 144.9, 143.8, 135.4, 130.2, 128.9, 127.3, 127.1, 127.0, 123.4, 114.4, 63.2, 60.5, 55.4, 48.8, 41.9, 14.2 ppm; IR: $\tilde{\nu}_{max}=2933$, 1708, 1593, 1510, 1245, 1169, 1089, 1027, 827, 750, 700 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{24}H_{24}NaO_4$ $[M+Na]^+$: 399.1572; found: 399.1580; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 320 nm, retention times: 29.9 min (minor) and 42.5 min (major).

b) Synthesis of the spirocyclic enones 10

Ethyl (*E*)-7-benzylidene-6-oxo-4-phenylspiro[4.4]non-1-ene-1-carboxylate (10a, Table 4, entry 6): Ethyl buta-2,3-dienoate (35 μL, 34 mg, 0.3 mmol) was added to a mixture of enone **8a** (39 mg, 0.15 mmol) and Ferrophane **I** (7.1 mg, 0.015 mmol) in degassed toluene (0.5 mL). The mixture was stirred at 40°C for 18 h. After evaporation of the solvent, the final product was purified by chromatography on silica gel with AcOEt/heptane (10%) as the eluent (R_f 0.3). Compound **10a** was obtained in 84% yield (47 mg) and 85% *ee*. NMR data for this compound have been reported in ref. [6b]. HRMS (ESI): m/z: calcd for $C_{25}H_{24}NaO_3$ $[M+Na]^+$: 395.1623; found: 395.1634; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (10%), 1 mL min^{-1}, 295 nm, retention times: 7.0 min (major) and 15.3 min (minor).

Ethyl (*E*)-7-(4-chlorobenzylidene)-4-(4-chlorophenyl)-6-oxospiro[4.4]non-1-ene-1-carboxylate (10b): This compound was obtained in 90% yield and 87% *ee*, >20:1; R_f 0.30 (AcOEt/heptanes 10%); $[\alpha]_D^{24}=+127$ ($c=3.9$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.35$ (t, $J=2.7$ Hz, 1H), 7.32–7.24 (m, 4H), 7.16 (d, $J=8.7$ Hz, 2H), 7.04 (d, $J=8.7$ Hz, 2H), 6.99 (t, $J=2.7$ Hz, 1H), 4.06 (q, $J=7.2$ Hz, 2H), 3.82 (t, $J=9.0$ Hz, 1H), 2.80 (dd, $J=8.7$, 2.4 Hz, 2H), 2.75–2.60 (m, 1H), 2.05–1.85 (m, 2H), 1.78–1.65 (m, 1H), 1.15 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=210.3$ (C), 163.5 (C), 144.9 (CH), 140.6 (C), 137.4 (C), 136.8 (C), 135.4 (C), 134.2 (C), 133.3 (C), 132.0 (3×CH), 129.7 (2×CH), 129.0 (2×CH), 128.7 (2×CH), 64.4 (C), 60.8 (CH_2), 53.6 (CH), 36.7 (CH_2), 27.1 (CH_2), 26.8 (CH_2), 14.2 ppm (CH_3); IR: $\tilde{\nu}_{max}=2930$, 1702, 1621, 1490, 1369, 1244, 1231, 1177, 1087, 1012, 920, 822, 759 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{25}H_{22}Cl_2NaO_3$ $[M+Na]^+$: 463.0844; found: 463.0845; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (10%), 1 mL min^{-1}, 305 nm, retention times: 7.7 min (major) and 30.7 min (minor).

Ethyl (*E*)-7-(4-bromobenzylidene)-4-(4-bromophenyl)-6-oxospiro[4.4]non-1-ene-1-carboxylate (10c): This compound was obtained in 85% yield and 92% *ee*, 20:1 regioselectivity; $R_f=0.30$ (AcOEt/heptanes 10%); $[\alpha]_D^{24}=+116$ ($c=2.8$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.50$ (d, $J=8.5$ Hz, 2H), 7.45–7.38 (m, 3H), 7.29 (d, $J=8.5$ Hz, 2H), 7.10–7.05 (m, 3H), 4.14 (q, $J=7.0$ Hz, 2H), 3.89 (t, $J=9.0$ Hz, 1H), 2.92–2.85 (m, 2H), 2.75 (m, 1H), 2.10–1.95 (m, 2H), 1.85–1.75 (m, 1H), 1.23 ppm (t, $J=7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=210.2$, 163.5, 145.0,

140.6, 138.0, 137.0, 134.6, 132.2, 132.0, 131.7, 130.1, 123.8, 121.3, 64.3, 60.8, 53.7, 36.6, 27.1, 26.8, 14.2 ppm; IR: $\tilde{\nu}_{max}$ = 2938, 1698, 1621, 1486, 1243, 1231, 1177, 1072, 1006, 825, 813, 758 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{25}H_{22}Br_2NaO_3$ $[M+Na]^+$: 550.9833; found: 550.9830; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (10%), 1 mL min^{-1}, 305 nm, retention times: 8.3 min (major) and 29.0 min (minor).

Ethyl (*E*)-4-(furan-2-yl)-7-(furan-2-ylmethylene)-6-oxospiro[4.4]non-1-ene-1-carboxylate (10d): This compound was obtained in 53% yield and 84% *ee*, >20:1 regioselectivity; R_f 0.3 (5% AcOEt/toluene); $[\alpha]_D^{24}$ = +65 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 1.5 Hz, 1H), 7.33–7.23 (m, 2H), 6.99 (t, *J* = 2.4 Hz, 1H), 6.61 (d, *J* = 3.6 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.29 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.10 (d, *J* = 3.3 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.90 (t, *J* = 9.0 Hz, 1H), 2.95–2.75 (m, 3H), 2.10–1.95 (m, 3H), 1.20 ppm (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.6, 163.5, 153.7, 152.8, 144.9, 144.3, 142.0, 140.9, 134.2, 119.6, 116.0, 112.6, 110.5, 107.5, 64.4, 60.7, 47.7, 35.5, 27.2, 26.5, 14.2 ppm; IR: $\tilde{\nu}_{max}$ = 2360, 1707, 1620, 1476, 1236, 1181, 1092, 1019, 748 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{21}H_{20}NaO_5$ $[M+Na]^+$: 375.1208; found: 375.1204; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 300 nm, retention times: 9.9 min (major) and 25.5 min (minor).

Ethyl (*E*)-7-benzylidene-6-oxo-4-phenylspiro[4.5]dec-1-ene-1-carboxylate (11): This compound was obtained in 35% yield and 85% *ee*, 20:1 regioselectivity; R_f = 0.3 (AcOEt/heptanes 10%). $[\alpha]_D^{24}$ = +306 (*c* = 1.3, $CHCl_3$). NMR data for this compound have been reported in ref. [6b]. HRMS (ESI): *m/z*: calcd for $C_{26}H_{26}NaO_3$ $[M+Na]^+$: 409.1780; found: 409.1766; HPLC analysis: Daicel CHIRACEL OD, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 305 nm, retention times: 7.9 min (major) and 12.2 min (minor).

c) Synthesis of D-menthyl (4*S*,5*R*)-5-cinnamoyl-4-phenylcyclopent-1-enylcarboxylate (7j, Scheme 6): D-Menthyl but-2-ynoate (0.10 mg, 0.45 mmol) was added to a mixture of dba (35 mg, 0.15 mmol) and FerroPHANE **I** (7.1 mg, 0.015 mmol) in degassed toluene (0.5 mL). The mixture was stirred at 120 °C for 18 h. After evaporation of the solvent, the final product was purified by chromatography on silica gel with AcOEt/heptane (5%) as the eluent (R_f 0.3). Compound **7j** was obtained as a pale yellow solid in 75% yield (51 mg) and as a single regioisomer, in 90% *de*. R_f = 0.30 (EtOAc/heptanes 5%); $[\alpha]_D^{24}$ = +150 (*c* = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 11H), 6.96 (m, 1H), 6.66 (d, *J* = 15.9 Hz, 1H), 4.63 (td, *J* = 10.8, 4.5 Hz, 1H), 4.30 (m, 1H), 3.52 (dt, *J* = 9.0, 6.3 Hz, 1H), 3.08 (ddt, *J* = 18.9, 9.0, 2.7 Hz, 1H), 2.66 (ddt, *J* = 18.9, 6.0, 2.1 Hz, 1H), 1.95 (dm, *J* = 12.0 Hz, 1H), 1.80–1.70 (m, 1H), 1.63–1.48 (m, 2H), 1.45–1.30 (m, 1H), 1.30–1.15 (m, 1H), 1.00–0.70 (m, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.9 Hz, 3H), 0.65 ppm (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.1, 163.9, 144.8, 144.0, 135.9, 134.7, 130.6, 129.01, 128.96, 128.5, 127.2, 127.1, 125.6, 74.7, 63.4, 49.0, 47.2, 41.9, 41.0, 34.3, 31.5, 26.1, 23.3, 22.1, 21.0, 16.2 ppm; IR: $\tilde{\nu}_{max}$ = 2952, 2358, 1704, 1607, 1448, 1242, 1091, 980, 752, 698 cm^{-1}; HPLC analysis: Daicel CHIRACEL IA, EtOH/*n*-heptane (1%), 1 mL min^{-1}, 290 nm, retention times: 10.3 min (minor) and 43.6 min (major).

Representative procedure for the [3+2] annulations on cyclopentenylcarboxylates 7 (Scheme 3 and Table 5)

Synthesis of 12a: A mixture of cyclopentenylcarboxylate **7a** (52 mg, 0.15 mmol), ethyl buta-2,3-dienoate (52 μL, 50 mg, 0.45 mmol) and PPh_3 (4.0 mg, 10 mol%) in toluene was stirred under argon at RT for 24 h. The final product **12a** was purified by chromatography on silica gel with EtOAc/heptane (20%) as the eluent (R_f 0.4). Yield: 45 mg (66%). The final product displays the same enantiomeric excess as that of the starting cyclopentene **7a** (92% *ee*). $[\alpha]_D^{24}$ = +233 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.10 (m, 6H), 7.05–6.95 (m, 4H), 6.90 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 4H), 3.95–3.88 (m, 2H), 3.63 (dt, *J* = 9.3, 6.0 Hz, 2H), 3.03 (ddt, *J* = 18.6, 9.0, 2.7 Hz, 2H), 2.54 (ddt, *J* = 18.6, 5.7, 2.4 Hz, 2H), 1.29 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.0 (C), 164.4 (2C), 144.8 (2C), 144.6 (2×CH), 134.4 (2C), 128.8 (4×CH), 127.0 (4×CH), 126.7 (2×CH), 64.3 (2×CH), 60.6 (2×CH_2), 46.7 (2×CH), 42.2 (2×CH_2), 14.5 ppm (2×CH_3); IR: $\tilde{\nu}_{max}$ = 2980, 1699, 1326, 1241, 1196, 1088, 1029, 747, 698 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{29}H_{30}NaO_5$ $[M+Na]^+$: 481.1991; found: 481.1988; HPLC analysis: Daicel CHIRACEL IC, EtOH/*n*-heptane (10%), 1 mL min^{-1}, 230 nm, retention times: 7.5 min (major) and 30.8 min (minor).

Compound 12d: This compound was obtained in 48% yield and 93% *ee*; R_f = 0.4 (20% EtOAc/heptanes); $[\alpha]_D^{24}$ = +226 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 8.5 Hz, 4H), 6.96 (d, *J* = 8.5 Hz, 4H), 6.86 (m, 2H), 4.19 (q, *J* = 7.0 Hz, 4H), 3.79 (m, 2H), 3.57 (dt, *J* = 9.0, 6.5 Hz, 2H), 3.04 (ddt, *J* = 19.0, 9.0, 2.5 Hz, 2H), 2.51 (ddt, *J* = 19.0, 6.0, 2.5 Hz, 2H), 1.30 ppm (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.3, 164.3, 144.2, 143.4, 134.3, 132.7, 129.0, 128.4, 64.8, 60.7, 46.0, 42.3, 14.5 ppm; IR: $\tilde{\nu}_{max}$ = 2933, 1705, 1634, 1492, 1366, 1299, 1245, 1082, 1009, 818, 748 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{29}H_{28}Cl_2NaO_5$ $[M+Na]^+$: 549.1211; found: 549.1219; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (2%), 1 mL min^{-1}, 230 nm, retention times: 14.7 min (major) and 33.7 min (minor).

Compound 12e: This compound was obtained in 53% yield and 92% *ee*; R_f 0.4 (EtOAc/heptanes 20%); $[\alpha]_D^{24}$ = +227 (*c* = 0.93, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00–6.85 (m, 10H), 4.19 (q, *J* = 7.2 Hz, 4H), 3.89 (m, 2H), 3.57 (m, 2H), 2.98 (m, 2H), 2.52 (m, 2H), 2.31 (s, 6H), 1.29 ppm (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 208.1, 164.5, 144.5, 141.9, 136.1, 134.4, 129.4, 126.9, 64.3, 60.5, 46.3, 42.3, 21.2, 14.5 ppm; IR: $\tilde{\nu}_{max}$ = 2980, 2924, 1706, 1635, 1514, 1371, 1241, 1181, 1085, 1031, 811, 749 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{31}H_{34}NaO_5$ $[M+Na]^+$: 509.2304; found: 509.2296; HPLC analysis: Daicel CHIRACEL IC, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 205 nm, retention times: 8.9 min (major) and 36.9 min (minor).

Compound 12f: This compound was obtained in 50% yield and 93% *ee*; R_f = 0.4 (EtOAc/heptanes 20%); $[\alpha]_D^{24}$ = +236 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 4.5 Hz, 2H), 6.91 (s, 2H), 6.85 (t, *J* = 3.5 Hz, 2H), 6.81 (s, 2H), 4.18 (q, *J* = 7.0 Hz, 4H), 4.12 (m, 2H), 4.03 (m, 2H), 3.11 (dd, *J* = 18.5, 9.0 Hz, 2H), 2.67 (dt, *J* = 18.5, 2.5 Hz, 2H), 1.28 ppm (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 207.6, 164.2, 148.4, 144.2, 134.3, 126.8, 124.5, 123.9, 65.1, 60.7, 42.9, 42.3, 29.8, 14.4 ppm; IR: $\tilde{\nu}_{max}$ = 2978, 1705, 1634, 1368, 1250, 1078, 1029, 707 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{25}H_{26}NaO_5S_2$ $[M+Na]^+$: 493.1119; found: 493.1106; HPLC analysis: Daicel CHIRACEL IA, *i*PrOH/*n*-heptane (1%), 1 mL min^{-1}, 230 nm, retention times: 28.9 min (major) and 36.9 min (minor).

Compound 12g: This compound was obtained in 43% yield and 90% *ee*; R_f = 0.13 (30% Et_2O/heptanes); $[\alpha]_D^{24}$ = +191 (*c* = 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.13 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.05–6.99 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.90–6.85 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 4H), 3.84 (m, 2H), 3.58 (m, 2H), 3.03 (m, 2H), 2.55 (m, 2H), 1.29 ppm (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.6, 164.4, 164.3, 144.9, 144.5, 144.2, 143.3, 134.4, 134.2, 132.4, 129.0, 128.9, 128.4, 127.0, 126.8, 64.6, 64.5, 60.62, 60.59, 46.6, 46.0, 42.4, 42.2, 14.4 ppm; IR: $\tilde{\nu}_{max}$ = 2980, 1704, 1635, 1492, 1241, 1089, 1013, 972, 825, 750, 700 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{29}H_{29}ClNaO_5$ $[M+Na]^+$: 515.1601; found: 515.1594; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (5%), 1 mL min^{-1}, 250 nm, retention times: 8.2 min (major) and 15.6 min (minor).

Compound 13: This compound was obtained in 58% yield and 90% dr; R_f = 0.4 (EtOAc/heptanes 20%); $[\alpha]_D^{24}$ = +194 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.10 (m, 6H), 7.06–6.98 (m, 4H), 6.95–6.87 (m, 2H), 4.76 (dt, *J* = 10.8, 4.5 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.98–3.82 (m, 2H), 3.68–3.58 (m, 2H), 3.03 (ddt, *J* = 18.9, 9.3, 2.4 Hz, 2H), 2.60–2.48 (m, 2H), 2.14–2.02 (m, 1H), 2.00–1.88 (m, 1H), 1.75–1.60 (m, 3H), 1.60–0.75 ppm (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.6, 207.3, 164.3, 164.0, 145.1, 144.9, 144.8, 144.4, 134.8, 134.3, 128.8, 127.0, 126.9, 126.7, 74.4, 64.4, 64.2, 60.6, 47.4, 46.8, 46.3, 42.3, 42.1, 41.1, 34.6, 31.6, 26.5, 23.7, 22.2, 20.9, 16.6, 14.5 ppm; IR: $\tilde{\nu}_{max}$ = 2953, 2926, 1704, 1241, 1086, 962, 754, 697 cm^{-1}; HRMS (ESI): *m/z*: calcd for $C_{37}H_{44}NaO_5$ $[M+Na]^+$: 591.3086; found: 591.3087; HPLC analysis: Daicel CHIRACEL AD-H, *i*PrOH/*n*-heptane (1%), 1 mL min^{-1}, 230 nm, retention times: 17.8 min (major) and 23.0 min (minor).

Synthesis of 16: (2,4-Dinitrophenyl)hydrazine (26 mg, 0.13 mmol, 1.5 equiv) and H_2SO_4 (0.5 N, 87 μL, 0.5 equiv) were added to a solution of **7j** (40 mg, 0.087 mmol, 1.0 equiv) in ethanol (0.4 mL). The red heterogeneous mixture was heated at reflux for 2 h, and further (2,4-dinitrophe-

nyl)hydrazine (17 mg, 0.08 mmol, 0.5 equiv) was added. The mixture was heated at reflux until completion of the reaction. The orange mixture was concentrated and purified by column chromatography (heptane/Et_2O 8:2) to afford **16** (50 mg, 71%) as an orange solid (R_f=0.3); $[\alpha]_D^{24}$=+9 (c=1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ=11.56 (s, 1H), 9.14 (d, J=2.7 Hz, 1H), 8.31 (dd, J=9.6, 2.4 Hz, 1H), 7.87 (d, J=9.6 Hz, 1H), 7.03 (m, 1H), 7.00 (m, 10H), 6.96 (d, J=16.2 Hz, 1H), 6.67 (d, J=15.9 Hz, 1H), 4.68 (dt, J=10.8, 4.2 Hz, 1H), 4.46 (m, 1H), 3.48 (dt, J=9.0, 5.7 Hz, 1H), 3.19 (ddt, J=18.9, 9.0, 2.4 Hz, 1H), 2.76 (dm, J=18.9 Hz, 1H), 2.05–1.95 (m, 1H), 1.80–0.90 (m, 8H), 0.83 (d, J=6.6 Hz, 3H), 0.71 (d, J=6.9 Hz, 3H), 0.53 ppm (d, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=164.5, 156.7, 145.7, 145.0, 142.6, 141.2, 138.2, 136.8, 135.0, 130.3, 130.2, 129.5, 129.1, 127.7, 127.4, 127.2, 123.6, 116.8, 114.5, 74.4, 58.2, 51.5, 47.2, 42.1, 41.4, 34.2, 31.4, 26.1, 23.2, 22.1, 20.9, 16.2 ppm; IR: $\tilde{\nu}_{max}$=2920, 2850, 1703, 1613, 1589, 1515, 1500, 1425, 1329, 1306, 1262, 1092, 959, 741, 691 cm^{-1}; HRMS (ESI): m/z: calcd for $C_{37}H_{40}N_4NaO_6$ $[M+Na]^+$: 659.2846; found: 659.2836. X-ray quality crystals of **16** were obtained from a dichloromethane/heptane solution.

Computational methods: The phosphines **I** and **Ib** and the phosphine-allene adducts **A** were fully optimised without any symmetry constraints by the BP86 density functional method.[25] The Multipole Accelerated Resolution of Identity (MARI-J) approximation technique,[26] as implemented in Turbomole version 5.10,[27] was used to speed up the calculations. Basis sets of split valence quality, including polarization functions and labelled def2-SVP,[28] together with the associated auxiliary basis sets to fit Coulomb potentials,[29] were employed for all atoms. Further details, such as the complete list of coordinates and energies of the calculated species, are available in the Supporting Information.

X-ray data: Both structures were solved from single colourless crystals suitable for X-ray diffraction. Data collection was in each case carried out at 293(2) K on an Enraf–Nonius CCD diffractometer using MoKα radiation (λ=0.71070 Å) and equipped with a graphite monochromator. Complete data were measured according to a ϕ-and-ω-scan-strategy derived by the COLLECT[30] suite once the cell parameters had been estimated by DENZO[31] from a preliminary 10°–ϕ-scan.

Crystal parameters were later post-refined in SCALEPACK[31] and intensities were further converted to amplitudes and then scaled after Lorentz polarisation and absorption correction based on a multi-scan empirical approach within the same program. Structures were solved by direct methods (SIR97 and SHELXS-97, respectively)[32,33] and refined on F^2 by full-matrix, least-squares methods (SHELXL-97). All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were located from difference Fourier maps but refined as a riding model.

CCDC-738660 (**12a**) and 738661 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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