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Phosphine-catalyzed enantioselective [3 + 2] cycloadditions of γ -substituted allenates with β -perfluoroalkyl enones†

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The enantioselective construction of densely functionalized cyclopentene bearing contiguous three stereocenters has been a challenging task in organic synthesis. Herein, we present a phosphine-catalyzed highly regio-, diastereo- and enantioselective [3 + 2] cycloaddition of γ -substituted allenates with β -perfluoroalkyl enones, delivering a wide range of densely functionalized perfluoroalkylated cyclopentenes with three contiguous chiral stereocenters.

Introduction

Cyclopentenes (or cyclopentanes) are valuable skeletons found in several natural products and pharmaceuticals (Fig. 1).¹ Among existing methodologies for their preparation, phosphine-catalyzed [3 + 2] cycloaddition of allenates with electron-deficient olefins was first reported by Lu in 1995 as a powerful and straightforward strategy for the construction of functionalized cyclopentene rings.^{2,3} As a result of tremendous effort from numerous research groups, Lu's enantioselective [3 + 2] cycloaddition reaction of terminal allenates with electron-deficient olefins has been well established over the past years.⁴ However, asymmetric [3 + 2] cycloaddition reaction of γ -substituted allenates with electron-deficient olefins has been less explored despite the increase in stereochemical diversity of the cycloaddition products. In 2007, Miller's group first realized a unique "deracemization" reaction upon cycloaddition of chalcone with racemic γ -methyl allenates but requisite the use of a stoichiometric amount of chiral phosphine catalyst **A** (Scheme 1a).^{4c} Subsequently, Fu and co-workers have accomplished the cycloaddition reaction of racemic γ -substituted allenates with heteroatom-bearing olefins with the use of a catalytic amount of chiral phosphine **B**, furnishing a facile access to functionalized cyclopentenes with two adjacent stereo centers (Scheme 1b).⁵ Recently, Marinetti and coworkers have reported a highly enantioselective [3 + 2] cycloaddition of γ -substituted allenates with

benzylidenemalononitrile by utilizing chiral phosphahelicenes catalyst **C** (Scheme 1b).⁶

Despite this progress, the scope of γ -substituted allenates and electron-deficient olefin partner for enantioselective Lu's annulation is very limited, and the construction of cyclopentene derivatives with three contiguous chiral stereocenters has been a major challenge but a highly desirable task. Moreover, introduction of perfluoroalkylated, particularly trifluoromethylated, stereocenters into chiral compounds have garnered special attention in pharmaceutical and pesticide industry since the polarity, bioavailability, metabolic stability and other properties of the parent molecules could be influenced greatly by these perfluoroalkyl groups.⁷ During the course of our continuous interest in design, synthesis and application of novel chiral β -aminephosphines^{8,9} in asymmetric catalysis and the synthesis of enantio-enriched trifluoromethylated building blocks,^{8d,g} we envisaged that the challenging enantioselective [3 + 2] cycloadditions of γ -substituted allenates with β -perfluoroalkyl α,β -enones might be addressed by systematic screening of known phosphines or rational design of new catalysts (Scheme 1b). In

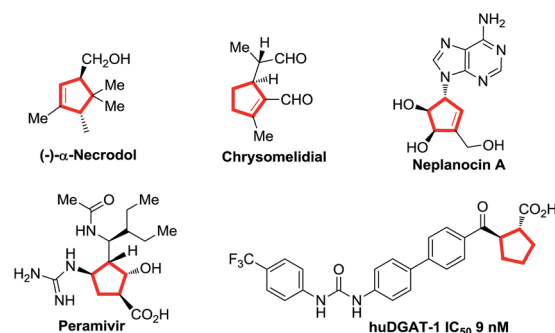
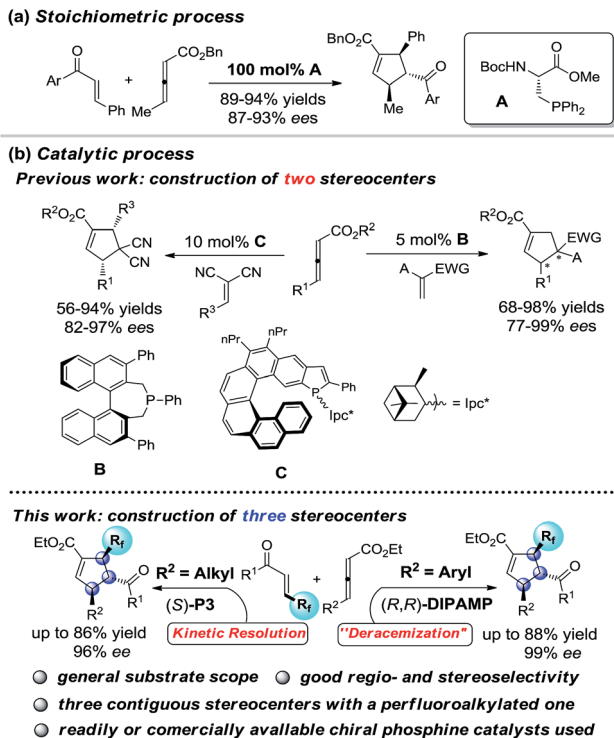


Fig. 1 Selected natural products and pharmaceuticals contain cyclopentene or cyclopentane rings.

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† Electronic supplementary information (ESI) available: Experimental details, analytical data, NMR spectra of products. CCDC 1503840 (3aa). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc01432e



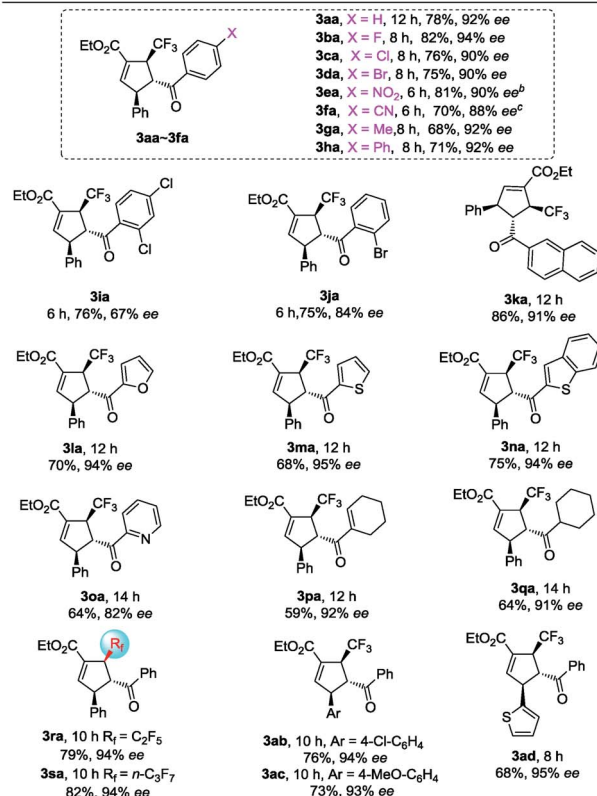
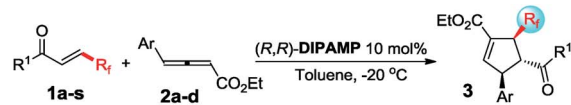


Scheme 1 [3 + 2] cycloaddition reaction of γ -substituted allenates and olefins.

the present study, we report our efforts in addressing this challenging reaction by identifying two phosphine catalysts, commercially available bisphosphine (*R,R*)-**DIPAMP** and novel multifunctional (*S*)-**P3** which have been developed in our group. Further control experiments have shown that the reaction under the catalysis of (*R,R*)-**DIPAMP** was a deracemization process, while the kinetic resolution reaction was observed under the multifunctional phosphine catalyst (Scheme 1).

Results and discussion

In order to validate the feasibility of the asymmetric [3 + 2] cycloaddition of γ -substituted allenates with β -perfluoroalkyl α,β -enones, allenate **2a** and enone **1a** were exposed to a range of commercially available chiral bisphosphine catalysts (Table 1). A small amount of the desired **3aa** was observed when (*S,S*)-**DIOP** or (*R,R*)-**Et-DUPHOS** was utilized as the catalyst (Table 1, entries 1 and 2). Interestingly, (*R,R*)-**Et-BPE** exhibited a promising level of reactivity with 64% yield and stereoselectivity with 39% ee (Table 1, entry 3). Fortunately, 86% yield of **3aa** with 89% ee was obtained using (*R,R*)-**DIPAMP** as a catalyst (Table 1, entry 4). It can be noted that multifunctional chiral phosphines (*S*)-**P1**–**P6** bearing hydrogen bond donors, such as amide and (thio) urea groups, could deliver higher chemical yield but with unacceptable enantioselectivity (Table 1, entries 5–10). Gratifyingly, the enantioselectivity was improved to 92%, albeit with a slightly lower yield when decreasing the reaction temperature from 25 °C to –20 °C (Table 1, entries 11–13). However, much lower reaction temperature was not beneficial for enantioselectivity and



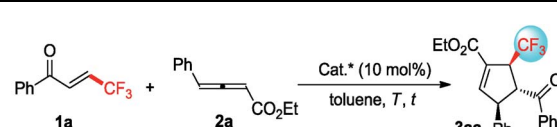
[a] Unless otherwise specified, all reactions were carried out with (*E*)-**1** (0.2 mmol), racemic **2** (0.3 mmol), (*R,R*)-**DIPAMP** (10 mol%) in toluene (2 mL) at –20 °C; isolated yield; d.r. and r.r. > 20:1. [b] r.r. = 8:1. [c] r.r. = 11:1.

Scheme 2 Enantioselective [3 + 2] cycloadditions of γ -aryl substituted allenates with β -perfluoro substituted enone^a.

reactivity (Table 1, entry 14). In addition, much lower yield and enantioselectivity was observed when (*Z*)-**1a** was utilized in the reaction, indicating that the configuration of enone also affected the reaction significantly (Table 1, entry 15). Further screening of solvents demonstrated that toluene was the best reaction medium for this transformation (see ESI† for details). Then, the optimized reaction conditions were identified: 10 mol% (*R,R*)-**DIPAMP** as the catalyst and toluene as the reaction medium at –20 °C.

Under optimal reaction conditions, we investigated the scope of the enantioselective [3 + 2] cycloaddition reaction (Scheme 2). Remarkably, a wide range of β -trifluoromethyl substituted enones containing different electron nature functional groups worked well with allenate **2a**, thereby resulting in a highly regioselective α -addition products **3ba–3ha** in good yields with 88–94% ee. However, the introduction of an *ortho* substituent, such as Cl and Br, to the phenyl ring of enone led to dramatic decrease in the enantioselectivity (**3ia** and **3ja**). To our delight, naphthyl- and heteroaryl-containing substrates **1k–1o**



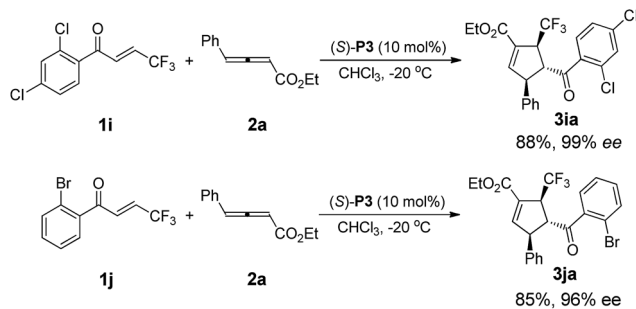
Table 1 Optimization of reaction conditions^a


Entry	Cat.	T (°C)	t (h)	Yield ^b (%)	ee ^c (%)
1	(<i>S,S</i>)-DIOP	25	12	<10	—
2	(<i>R,R</i>)-Et-Duphos	25	12	<10	—
3	(<i>R,R</i>)-Et-BPE	25	8	64	39
4	(<i>R,R</i>)-DIPAMP	25	6	81	89
5	(<i>S</i>)-P1	25	3	79	3
6	(<i>S</i>)-P2	25	3	85	14
7	(<i>S</i>)-P3	25	3	84	40
8	(<i>S</i>)-P4	25	3	86	21
9	(<i>S</i>)-P5	25	0.5	91	31
10	(<i>S</i>)-P6	25	0.5	88	38
11	(<i>R,R</i>)-DIPAMP	0	6	84	90
12	(<i>R,R</i>)-DIPAMP	-10	8	81	91
13	(<i>R,R</i>)-DIPAMP	-20	12	78	92
14	(<i>R,R</i>)-DIPAMP	-25	20	63	92
15 ^d	(<i>R,R</i>)-DIPAMP	-20	24	23	50

^a Unless otherwise specified, all reactions were carried out with (*E*)-**1a** (0.1 mmol), racemic **2a** (0.15 mmol) in toluene (1 mL). ^b Yield of isolated products; d.r. and r.r. > 20:1. ^c Determined by HPLC analysis. ^d (*Z*)-**1a** was used.

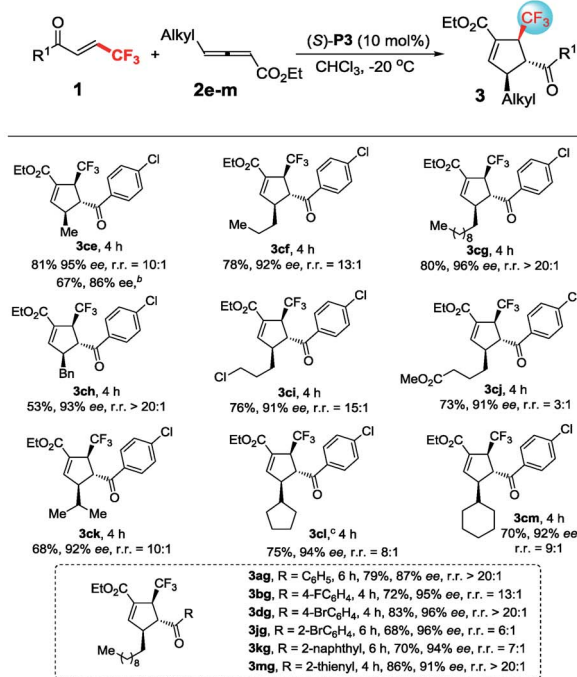
were also compatible, efficiently furnishing a set of trifluoromethylated cyclopentenes containing naphthyl- and heteroaryl frameworks **3ka–3oa**. In addition, the present protocol could be readily extended to the challenging synthesis of cyclohexenyl and cyclohexyl based trifluoromethyl enone **1p** and **1q**. It was noteworthy that both β -pentafluoroethyl and β -heptafluoropropyl enone were particularly effective in the present transformation, forming valuable perfluoroalkyl substituted cyclopentene **3ra** and **3sa** in good yields with 94% ee. Furthermore, γ -aryl allenates **2b–2d** with substituted aryl and heteroaryl groups were well applicable and formed corresponding products **3ab–3ad** with high regioselectivity and enantioselectivity. The absolute configuration of product **3aa** was confirmed by single-crystal X-ray diffraction analysis.¹⁰

After intensive screening of various chiral phosphine catalysts, it was found that multifunctional phosphine (*S*)-**P3** displayed good performance in the substrates with *ortho*-

Scheme 3 (*S*)-**P3** catalyzed enantioselective [3 + 2] cycloadditions of **1i** and **1j** with **2a**.

substituent, and the desired products **3ia** and **3ja** could be isolated in 85–88% yields with 96% and 99% ee, respectively (Scheme 3).

Unfortunately, the performance of (*R,R*)-**DIPAMP** in the cycloaddition of γ -alkyl substituted allenates was not as good as that in the cases of γ -aryl substituted allenates. For example, the reaction of **2e** with **1c** resulted in the formation of desired **3ce** in 67% yield but with only 86% ee. After further screening of a series of chiral phosphine catalysts, solvents and reaction temperature, it was found that (*S*)-**P3** was a privileged catalyst for cycloaddition of γ -alkyl allenates. In general, allenates **2e–2g** with different alkyl substituents at γ position participated

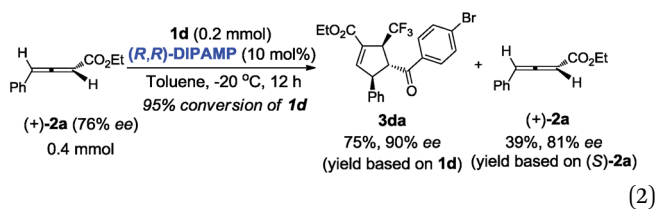
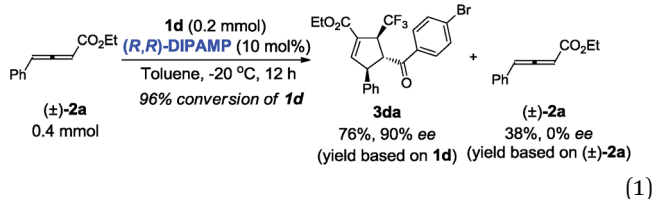


[a] Unless otherwise specified, all reactions were carried out with (*E*)-**1** (0.2 mmol), racemic **2** (0.44 mmol), (*S*)-**P3** (10 mol%) in CHCl₃ (2 mL) at -20 °C. [b] toluene, -20 °C, 10 h, (*R,R*)-**DIPAMP** (10 mol%). [c] the regioisomer of **3cl** was isolated and its structure was confirmed by 2D-NMR analysis.

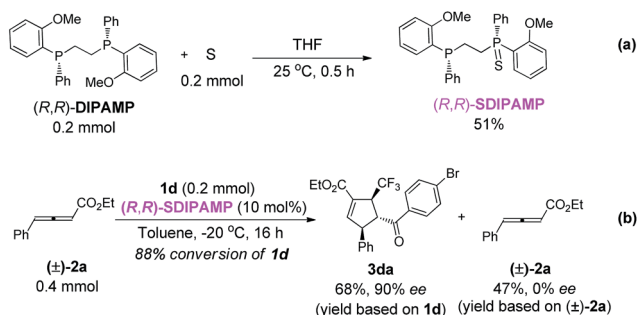
Scheme 4 Enantioselective [3 + 2] cycloadditions of γ -alkyl substituted allenates with β -perfluoro substituted enone^a.

in the annulation process with good regio- and enantioselectivity. In addition, diverse alkyl substituents such as benzyl, halogen and ester group were well tolerant, furnishing the corresponding cycloadducts **3ch–3ej** in moderate to good yields with high enantioselectivity. Furthermore, allenates with bulky substituents such as isopropyl, cyclopentyl and cyclohexyl at γ position worked well, thereby forming the desired **3ck–3cm** in good yields with 92–94% ee. Good to excellent regioselectivity and enantioselectivity were also obtained in the cycloaddition reactions of allenate **2g** with a wide range of β -trifluoromethyl substituted enones (Scheme 4).

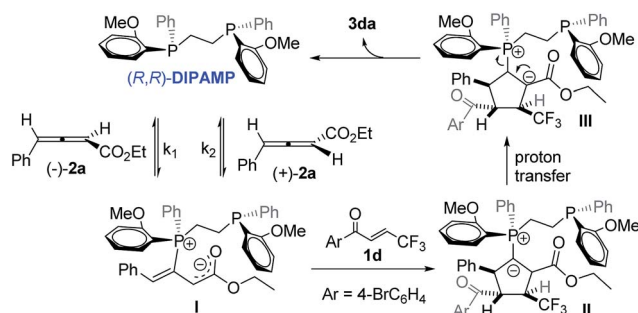
Next, we turned our attention to gain insight into catalytic process for the proposed [3 + 2] cycloaddition reaction. In case of (*R,R*)-DIPAMP catalysed cycloaddition of **1d** and racemic **2a**, the starting material **2a** was recovered in 38% yield (based on **2a**) with 0% ee (eqn (1)). Furthermore, when optically active allenates with bulky substituents such as isopropyl, cyclopentyl and cyclohexyl at γ position worked well, thereby forming the desired **3ck–3cm** in good yields with 92–94% ee. Good to excellent regioselectivity and enantioselectivity were also obtained in the cycloaddition reactions of allenate **2g** with a wide range of β -trifluoromethyl substituted enones (Scheme 4).



To examine both the phosphines in (*R,R*)-DIPAMP induce enantioselectivity independently or cooperatively, (*R,R*)-SDIPAMP that contained only one nucleophilic phosphine was synthesized and subjected to the reaction of **1d** and racemic **2a**



Scheme 5 Synthesis of (*R,R*)-SDIPAMP and its application in the asymmetric [3 + 2] cycloaddition of **2a** and **1d**.

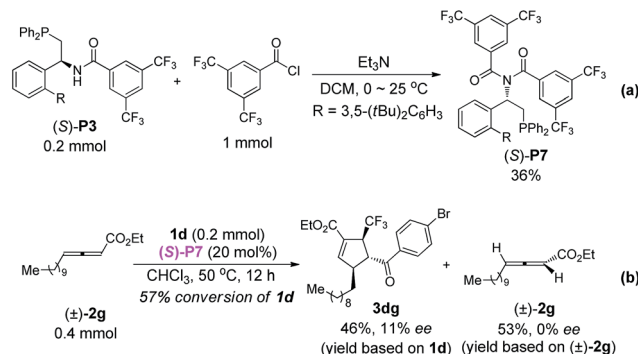


Scheme 6 Possible catalytic cycle for (*R,R*)-DIPAMP catalysed asymmetric [3 + 2] cycloaddition.

(Scheme 5). Although the reaction became slower, enantioselectivity of **3da** remained unchanged, demonstrating that both the phosphines in (*R,R*)-DIPAMP might induce enantioselectivity independently (Scheme 5b).

Based on the abovementioned results and earlier reports,¹¹ a plausible catalytic cycle for (*R,R*)-DIPAMP catalysed asymmetric [3 + 2] cycloaddition reaction of γ -aryl allenates with trifluoromethyl enones has been illustrated in Scheme 6. The zwitterionic intermediate **I** was formed through nucleophilic addition of (*R,R*)-DIPAMP to racemic **2a**. The deracemization process resulted from the same nucleophilic attack rate ($K_1 = K_2$) of (*R,R*)-DIPAMP to both the enantiomers of allenates **2a**. The subsequent [3 + 2] cycloaddition favoured α -addition to provide intermediate **II**, which then underwent proton transfer to provide intermediate **III**. Finally, (*R,R*)-DIPAMP and cyclopetene **3da** were released from intermediate **III**.

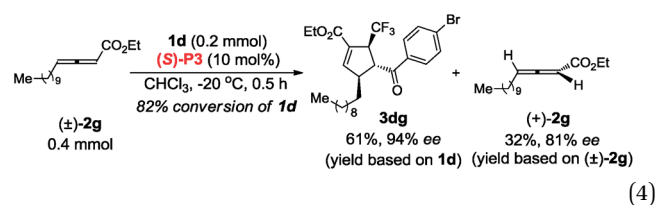
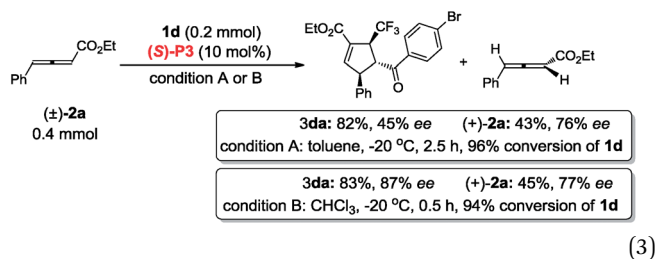
In contrast to (*R,R*)-DIPAMP, a kinetic resolution reaction takes place with multifunctional chiral phosphine (*S*)-P3 as the catalyst and (+)-**2a**¹² and (+)-**2g**¹³ is recovered in 76% ee (in toluene, 77% ee in CHCl_3) and 81% ee respectively (eqn (3) and (4)). In order to confirm the possible hydrogen-bonding interaction during the catalytic process, (*S*)-P7 without hydrogen-bond donor was synthesized and subjected to the cycloaddition reaction (Scheme 7). The conversion decreased dramatically under higher catalyst loading and higher reaction temperature. The ee value of the recovered **2g** also vanished (Scheme 7b). These results demonstrated that the hydrogen-



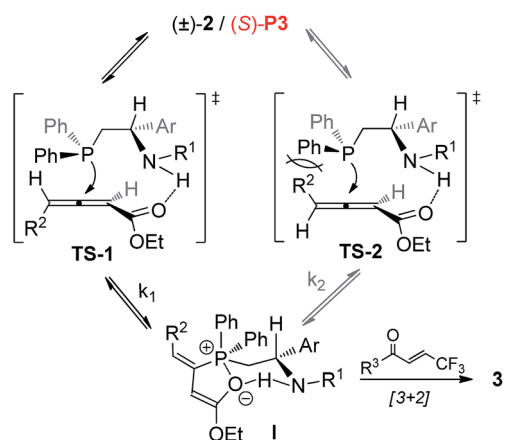
Scheme 7 Synthesis of (*S*)-P7 and its application in the asymmetric [3 + 2] cycloaddition of **2g** and **1d**.



bond donor in (*S*)-**P3** was crucial for enantioselective formation of cycloaddition product *via* kinetic resolution process.



On the basis of above control experiments and recent excellent mechanistic studies¹¹ on the [3 + 2] cycloaddition of allenates with electron-deficient olefins, a tentatively proposed catalytic cycle for (*S*)-**P3** catalysed asymmetric [3 + 2] cycloaddition reaction of racemic allenolate with trifluoromethyl enone is shown in Scheme 8. (–)-**2** might prefer a configuration that would facilitate hydrogen-bonding interactions of N–H and carbonyl group (Scheme 8, **TS-1**). On the other hand, the nucleophilic attack of (*S*)-**P3** with (+)-**2** might be suppressed by the steric interaction of the bulky *R*² group with the phenyl moiety (Scheme 8, **TS-2**). Accordingly, different nucleophilic attack rates (*K*₁ > *K*₂) of (*S*)-**P3** to both the enantiomers of allenates **2** contribute to the kinetic resolution process. It should be noted that further experimental and theoretical studies are required to gain insights into kinetic resolution process.



Scheme 8 Possible catalytic cycle for (*S*)-**P3** catalysed asymmetric [3 + 2] cycloaddition reaction of racemic allenolate with trifluoro-methyl enone.

Conclusions

In conclusion, we have developed a highly regio-, diastereo- and enantioselective [3 + 2] cycloaddition of γ -substituted allenates with β -perfluoroalkyl enones with (*R,R*)-**DIPAMP** or (*S*)-**P3** as a catalyst; it provides a facile access to a wide range of trifluoromethylated cyclopentenes with three contiguous chiral centers (up to 88% yield with 99% ee). In case of γ -aryl allenolate, commercially available chiral phosphine (*R,R*)-**DIPAMP** was identified as an efficient catalyst. In contrast, presently developed multifunctional phosphine (*S*)-**P3** has displayed high performance in the asymmetric cycloaddition of γ -alkyl allenates with trifluoromethyl enones. In addition, control experiments have demonstrated that under the catalysis of (*R,R*)-**DIPAMP**, racemic allenolate reacted with trifluoromethyl enone through a “deracemization” process, whereas a clearly kinetic resolution reaction takes place with multifunctional chiral phosphine (*S*)-**P3** as a catalyst due to the hydrogen-bonding interaction between catalyst and the allenolate. Efforts toward other transformations of allenolate under the catalysis of our developed catalysts **P1–P6** are currently underway and will be reported in due course.

Acknowledgements

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