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Phosphine-Catalyzed [3 + 2] Cycloaddition of 4,4-Dicyano-2-methylenebut-3-enoates with Benzyl Buta-2,3-dienoate and Penta-3,4-dien-2-one

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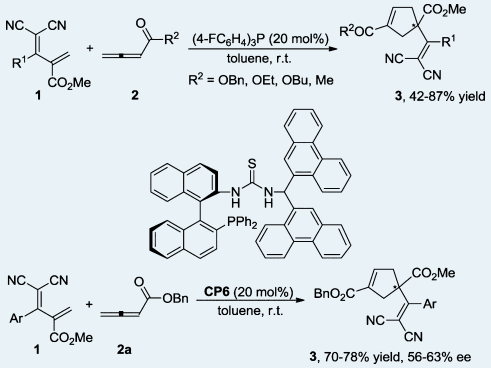
Supporting Information

ABSTRACT: 4,4-Dicyano-2-methylenebut-3-enoates are employed in the phosphine-catalyzed [3 + 2] cycloaddition with allenoates for the first time, affording regiospecific [3 + 2]-annulation products in moderate to good yields. The multifunctional chiral thiourea-phosphines having an axially chiral binaphthyl scaffold are effective catalysts for the asymmetric variant of this reaction, giving the α-regioisomers in good yields and moderate enantioselectivities.



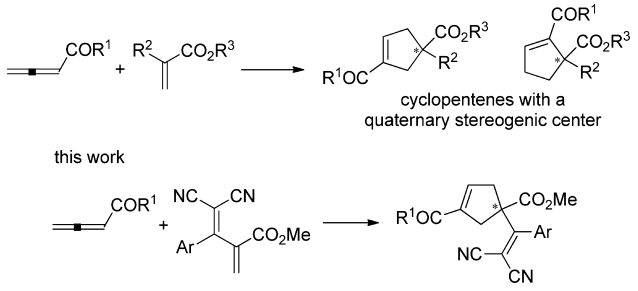
KEYWORDS: *allenoate, 4,4-dicyano-2-methylenebut-3-enoates, multifunctional chiral phosphines, [3 + 2] cycloaddition*

INTRODUCTION

Functionalized five-membered carbocycles as structural motifs are often found in natural products and medicinally important agents.[1,2] Among the known synthetic methods, phosphine-catalyzed [3 + 2] cycloaddition, developed by Lu in 1995,[3−8] is considered to be a powerful synthetic approach. Impressive progress in the phosphine-catalyzed [3 + 2] cycloaddition of allenoates with electron-deficient species such as olefins and imines has been made, thereby providing new pathways to functionalized five-membered carbo- and heterocycles.[9−36] Following Lu and Zhang's pioneering efforts,[3,9] further application of this annulations strategy to the total syntheses of natural products and the development of their asymmetric variants have also been important achievements.[7,37−44] Despite the above significant achievements, compared to the widespread applications of phosphine-catalyzed [3 + 2] annulations, the design and development of novel phosphine-mediated processes with regard to allenoates are still under-explored.

Five-membered carbocycles with a quaternary stereogenic center are interesting substructures often found in many natural products and bioactive molecules,[45−47] and we recently became interested in exploring organocatalytic methods to access highly functionalized cyclopentenes bearing one all-carbon quaternary stereogenic center.[48] It is known that phosphine-catalyzed [3 + 2] annulations between α-substituted acrylates and allenes may be utilized to construct such five-membered ring systems (Scheme 1). However, when the phosphine-catalyzed [3 + 2] cycloaddition of allenoates with electron-deficient olefins is concerned, α-substituted acrylates remain as elusive substrates.[9,49−51] Thus, the design and development of new phosphine-catalyzed [3 + 2] cycloaddition of allenoates with α-substituted acrylates is highly desirable. To the best of our knowledge, the direct application of α,α-dicyanoolefin-substituted acrylates in the phosphine-catalyzed [3 + 2] cycloaddition has not been reported before. Thus, it is highly desirable to develop a synthetic variant in which these acrylates can be used directly in such a cyclization.

Scheme 1. Phosphine-Catalyzed [3 + 2] Cycloaddition of Allenoates with α-Substituted Acrylates



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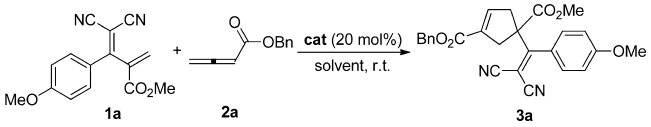
Herein we wish to report a novel [3 + 2] cycloaddition between α,α-dicyanoolefin-substituted acrylates with allenoates mediated by phosphine, providing a facile protocol to construct highly functionalized cyclopentenes bearing one all-carbon quaternary stereogenic center in good yields (Scheme 1). Moreover, the 4,4-dicyano-2-methylenebut-3-enoates as new α-substituted acrylates can be conveniently prepared from alkyl propiolates and α,α-dicyanoolefins.[52]

We began our investigation by using the [3 + 2] cycloaddition between 4,4-dicyano-2-methylenebut-3-enoate **1a** and benzyl allenoate **2a** as a model reaction (Table 1).

Table 1. Screening of Solvents and Catalysts.[a]



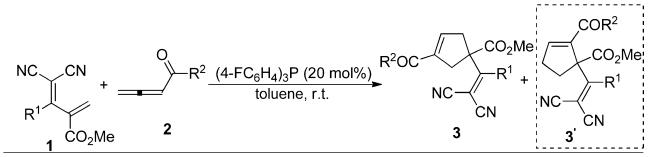
entry	solvent	catalyst	time (d)	yield (%)[b]
1	toluene	PPh_3	2	42
2	CH_2Cl_2	PPh_3	2	trace
3	Et_2O	PPh_3	2	trace
4	CH_3CN	PPh_3	2	trace
5	THF	PPh_3	2	trace
6	toluene	PPh_3	2	trace
7	toluene	PPh_2Me_2	2	trace
8	toluene	PPh_2Me	2	8
9	toluene	dppb	2	trace
10	toluene	DABCO	2	trace
11	toluene	$(4\text{-}CH_3OC_6H_4)_3P$	2	trace
12	toluene	$(4\text{-}FC_6H_4)_3P$	2	87
13	toluene	$(4\text{-}CF_3C_6H_4)_3P$	3	75
14[c]	toluene	$(4\text{-}FC_6H_4)_3P$	4	84

[a]Reactions were performed with **1a** (0.10 mmol) and **2a** (0.20 mmol) in the presence of 20 mol % of catalyst in solvent (2 mL) at room temperature. [b]Isolated yields. [c]10 mol % of catalyst was used.

We initially utilized 20 mol % of PPh_3 as catalyst and **1a** (1.0 equiv) and **2a** (2.0 equiv) as substrates to investigate the influence of solvents on this cycloaddition reaction. The results of these experiments are summarized in Table 1. It was found that toluene is the best solvent in this reaction, albeit giving the corresponding annulation product **3a** in only 42% yield within 2 days (Table 1, entries 1−5). The examination of other phosphines such as PBu_3, $PPhMe_2$, PPh_2Me, or dppb and 1,4-diazabicyclic-[2,2,2]-octane (DABCO) revealed that PPh_3 was the best catalyst for this reaction (Table 1, entries 6−10). Changing the nucleophilicity of triarylphosphine, we consecutively examined the catalysts $(4\text{-}CH_3OC_6H_4)_3P$, $(4\text{-}FC_6H_4)_3P$, and $(4\text{-}CF_3C_6H_4)_3P$ and identified that $(4\text{-}FC_6H_4)_3P$ was the most efficient catalyst, producing **3a** in 87% yield within 48 h (Table 1, entries 11−13). Reducing the employed amounts of $(4\text{-}FC_6H_4)_3P$ to 10 mol % also gave **3a** in 84% yield upon prolonging the reaction time to 4 days (Table 1, entry 14)

Having determined the optimal reaction conditions, we turned our attention to the substrate scope and limitations of this phosphine-catalyzed [3 + 2] cycloaddition of 4,4-dicyano-2-methylenebut-3-enoates with allenoates, and the results are summarized in Table 2. All reactions proceeded smoothly to give the corresponding products **3** in moderate to excellent yields under the optimal reaction conditions (Table 2). Using benzyl allenoate **2a** as substrate, we found that regardless of whether R^1 is an electron-rich or -deficient aromatic ring, the

Table 2. Substrate Scope for [3 + 2] Cycloaddition of 4,4-Dicyano-2-methylenebut-3-enoates with Allenoates.[a]



entry	R^1	R^2	time (d)	yield (%)[b]
1	**1b**, *o*-$MeOC_6H_4$	**2a**, OBn	2	**3b**, 47 (**3b′**, 39)[c]
2	**1c**, *m*-$MeOC_6H_4$	**2a**, OBn	2	**3c**, 84
3	**1d**, *p*-MeC_6H_4	**2a**, OBn	2	**3d**, 80
4	**1e**, *p*-FC_6H_4	**2a**, OBn	2	**3e**, 84
5	**1f**, *p*-ClC_6H_4	**2a**, OBn	2	**3f**, 80
6	**1g**, *m*-BrC_6H_4	**2a**, OBn	2	**3g**, 82
7	**1h**, *p*-BrC_6H_4	**2a**, OBn	2	**3h**, 76
8	**1i**, Ph	**2a**, OBn	2	**3i**, 80
9	**1j**, *p*-$CF_3C_6H_4$	**2a**, OBn	2	**3j**, 42
10	**1k**, furan-2-yl	**2a**, OBn	2	**3k**, 72
11	**1l**, naphtha-2-yl	**2a**, OBn	2	**3l**, 85
12	**1m**, 3,4,5-tri$MeOC_6H_2$	**2a**, OBn	2	**3m**, 84
13	**1a**, *p*-$MeOC_6H_4$	**2b**, OEt	2	**3n**, 82
14	**1a**, *p*-$MeOC_6H_4$	**2c**, O^{t}Bu	2	**3o**, 51
15	**1d**, *p*-MeC_6H_4	**2d**, Me	3	**3p**, 81
16	**1e**, *p*-FC_6H_4	**2d**, Me	2	**3q**, 86
17	**1f**, *p*-ClC_6H_4	**2d**, Me	2	**3r**, 80
18	**1g**, *m*-BrC_6H_4	**2d**, Me	2	**3s**, 78
19	**1k**, furan-2-yl	**2d**, Me	2	**3t**, 72
20	**1m**, 3,4,5-tri$MeOC_6H_2$	**2d**, Me	2	**3u**, 80

[a]Reactions were performed with **1** (0.10 mmol) and **2a** (0.20 mmol) in the presence of 20 mol % of $(4\text{-}FC_6H_4)_3P$ in toluene (2 mL) at room temperature. [b]Isolated yields. [c]Regioisomer of **3b** and **3b′**.

reactions proceeded smoothly to give the corresponding annulation products **3b**−**3j** in 42−86% yields, respectively (Table 2, entries 1−9). Only in the case of 4,4-dicyano-3-(ortho-methoxyphenyl)-2-methylenebut-3-enoate **1b** were two regioisomers **3b** and **3b′** formed in good total yields, perhaps because of the steric influence (Table 2, entry 1). When R^1 is a heteroaromatic group (R^1 = furan-2-yl) or a sterically more bulky 2-naphthalene moiety or a more substituted aromatic group (R^1 = 3,4,5-$(MeO)_3C_6H_2$), the reactions also proceeded efficiently to afford the corresponding products **3k**−**3m** in 72−85% yields (Table 2, entries 10−12). The reactions also worked well upon changing the ester groups in allenoates, providing the corresponding products **3n** and **3o** in 82% and 51% yields, respectively (Table 2, entries 13 and 14). Using penta-3,4-dien-2-one **2d** as substrate, whether R^1 is an electron-rich or -deficient aromatic ring or a heteroaromatic group (R^1 = furan-2-yl), the reactions also proceeded efficiently, affording the corresponding cycloadducts **3p**−**3u** in 72−86% yields, respectively (Table 2, entries 15−20). The relative configuration of **3p** has been assigned by X-ray diffraction. The ORTEP drawing is shown in Figure 1, and the CIF data are presented in the Supporting Information.

On the basis of our previous work on chiral phosphines as nucleophilic catalysts in asymmetric catalysis,[48,50,53−59] we next attempted to identify the best chiral phosphine catalyst and the optimal reaction conditions for the asymmetric version of this novel [3 + 2] cycloaddition between 4,4-dicyano-2-methylenebut-3-enoates and allenoates (Table 3 and the Supporting Information, Table SI-1). We initiated the study by

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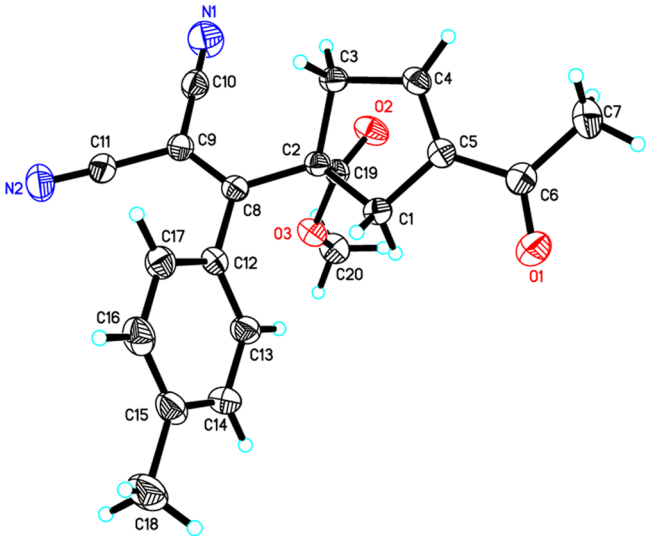
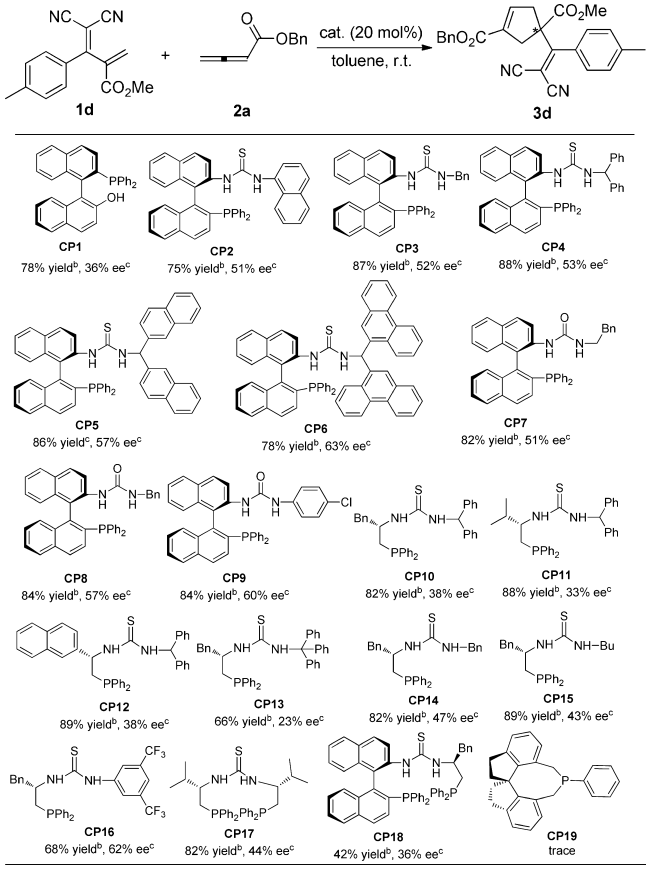


Figure 1. ORTEP drawing of **3p**.

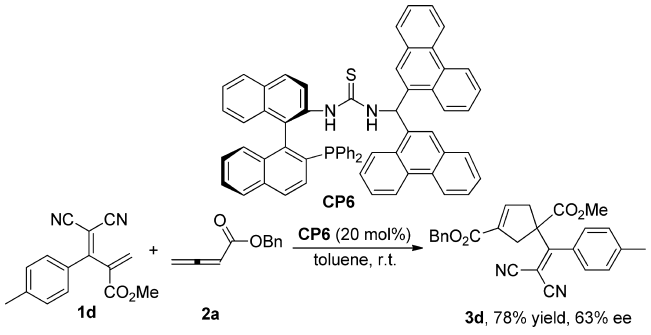
Table 3. Screening of Chiral Phosphine Catalysts for [3 + 2] Cycloaddition of 4,4-Dicyano-2-methylenebut-3-enoates with Allenoates.[a]



[a]Reactions were performed with **1d** (0.10 mmol) and **2a** (0.20 mmol) in the presence of 20 mol % of **CP** in toluene (2 mL) at room temperature. [b]Isolated yields. [c]Determined by HPLC analysis.

investigating the reaction between 4,4-dicyano-2-methylene-3-*p*-tolylbut-3-enoate **1d** and benzyl allenoate **2a** in the presence of chiral phosphine **CP1** (20 mol %) derived from axially chiral bi(2-naphthol) in toluene at room temperature for 2 days. To our delight, the desired annulation indeed took place, giving the corresponding product **3d** in 78% yield, albeit in only 36% ee (Table 3). Subsequently, we examined several multifunctional chiral thiourea-phosphines **CP2**-**CP4** having an axially chiral binaphthyl scaffold, and identified that **CP4** was the more efficient catalyst, producing **3d** in 88% yield along with 53% ee (Table 3). Gratifyingly, an improvement was realized using **CP5** and **CP6** through a slight structural modification of **CP4**, which could produce **3d** in better results. As a result, we found that **3d** could be obtained in 78% yield along with 63% ee using **CP6** as the catalyst (Table 3). Subsequently we also examined several multifunctional chiral urea-phosphine catalysts **CP7**−**CP9** having an axially chiral binaphthyl scaffold, revealing that they were not as efficient as that of **CP6**, affording **3d** in 82−84% yields with 51−60% ee values, respectively (Table 3). Moreover, various multifunctional thiourea-phosphines **CP10**−**CP18**, derived from amino acids, were also synthesized and subsequently examined in this asymmetric reaction under identical conditions, and the results indicated that they were also not as efficient as that of **CP6** (Table 3). Furthermore, the cycloaddition reaction even did not take place if using chiral phosphine **CP19** as the catalyst. On the basis of the above results, the best reaction conditions are shown in Scheme 2,

Scheme 2. Optimization of the Reaction Conditions for the Asymmetric [3 + 2] Cycloaddition Reaction.[a]



that is, using 20 mol % **CP6** as the catalyst and carrying out the reaction in toluene at room temperature for 2 days, giving **3d** in 78% yield along with 63% ee (for other chiral phosphine catalysts and optimization of the reaction conditions, please see the Supporting Information, Table SI-1).

Under the optimal reaction conditions, we also investigated the influence of the substrates **1** on this cycloaddition reaction. The results of these experiments revealed that using a sterically more bulky 2-naphthalene moiety-substituted **1l** or a more substituted aromatic group-substituted **1m** as substrate did not have significant influence on the ee value of the products, affording the corresponding products **3l** in 70% yield along with a 60% ee value and **3m** in 74% yield along with a 56% ee value, respectively (Scheme 3).

On the basis of the above experimental results and previous work on the phosphine-catalyzed [3 + 2] cycloaddition with allenoates,[3,23,24,29,60] a plausible reaction mechanism has been presented in Scheme 4. The reaction might be initiated with the formation of the phosphonium enolate intermediate **I** via the nucleophilic attack of the phosphine catalyst at the allene moiety. Then the subsequent nucleophilic attack of phosphonium enolate intermediate **I** on 4,4-dicyano-2-methylenebut-3-enoate **1** with its anionic allyl carbon atom results in intermediate **II**, which might keep an equilibrium with intermediate **II′**.[48] Intramolecular Michael addition of inter-

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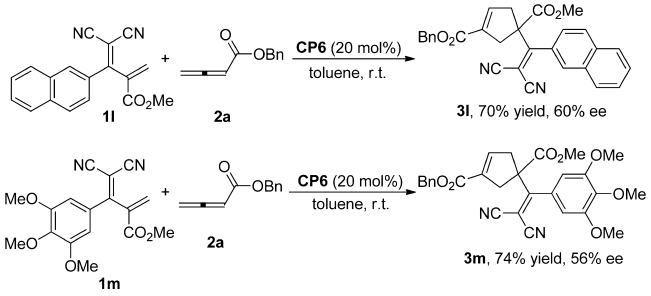
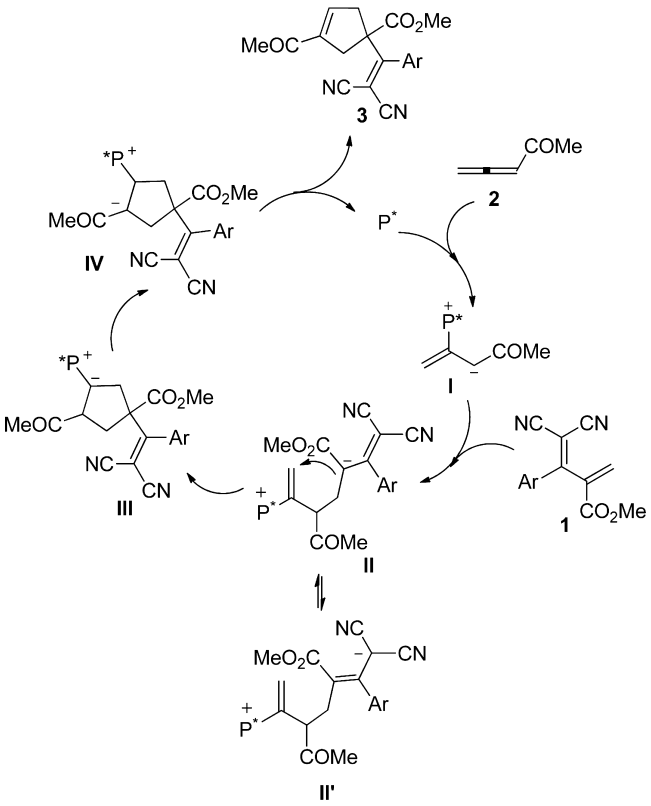
Scheme 3. Influence of Substrates 1 on This Asymmetric [3 + 2] Cycloaddition Reaction



Scheme 4. Plausible Reaction Mechanism



mediate **II** produces intermediate **III**, which isomerizes to intermediate **IV** through a proton transfer. Intermediate **IV** gives the desired highly functionalized cyclopentene **3** and regenerates the phosphine catalyst by the elimination of catalyst.

In conclusion, we have utilized 4,4-dicyano-2-methylenebut-3-enoates in phosphine-catalyzed [3 + 2] cycloaddition with allenoates for the first time, affording an efficient synthetic approach to highly functionalized cyclopentenes bearing one all-carbon quaternary stereogenic center in excellent regioselectivity and moderate to good yields. The asymmetric annulation reaction was promoted effectively by multifunctional chiral thiourea-phosphines having an axially chiral binaphthyl scaffold, giving the α-regioisomers in good yields and moderate enantioselectivities. This is also the first example in which α,α-dicyanoolefin-substituted acrylates are used directly in phosphine-catalyzed asymmetric [3 + 2] cycloaddition with allenoates. Further efforts are in progress toward the application of this new methodology to synthesize interesting bioactive compounds.

EXPERIMENTAL SECTION

General Procedure for Tris(4-fluorophenyl)phosphine Catalyzed [3 + 2] Cycloaddition of 4,4-Dicyano-2-methylenebut-3-enoates with Benzyl Buta-2,3-dienoate, Ethyl Buta-2,3-dienoate, *tert*-Butyl Buta-2,3-dienoate, and Penta-3,4-dien-2-one. *General Procedure.* To a solution of tris(4-fluorophenyl)phosphine (0.02 mmol) in toluene (1.0 mL) was added the corresponding benzyl buta-2,3-dienoate, ethyl buta-2,3-dienoate, *tert*-butyl buta-2,3-dienoate, or penta-3,4-dien-2-one (0.2 mmol). The reaction mixture was stirred at room temperature. To this resulting reaction mixture (1.0 mL) a solution of 4,4-dicyano-2-methylenebut-3-enoate (**1**) (0.1 mmol) was slowly added. The reaction mixture was stirred at room temperature until the reaction was complete (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the desired cyclic products **3**.

*1-(2,2-Dicyano-1-(4-methoxyphenyl)vinyl)cyclopent-3-ene-1,3-dicarboxylate (**3a**).* A colorless oil, 39 mg, 87% yield; IR (KBr): ν 2954, 2841, 2230, 1741, 1712, 1604, 1508, 1456, 1244, 1206, 1177, 1100, 1028, 836, 736, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.87−2.98 (m, 2H, CH_2), 3.46−3.59 (m, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.16 (s, 2H, CH_2), 6.65−6.66 (m, 1H, =CH), 6.97 (d, 2H, J = 8.8 Hz, ArH), 7.16 (d, 2H, J = 8.8 Hz, ArH), 7.33−7.39 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 43.1, 44.8, 53.9, 55.4, 59.3, 66.4, 88.9, 111.8, 112.5, 114.5, 127.2, 128.2, 128.3, 128.5, 128.6, 133.4, 135.5, 139.6, 161.5, 163.2, 172.1, 181.7; MS (ESI) m/z (%): 465.0 (100) [M+Na$^+$]; HRMS (ESI) Calcd. For $C_{26}H_{22}N_2O_5Na^{+1}$ (M+Na$^+$) requires 465.1426, Found: 465.1440.

General Procedure for Chiral Phosphines Catalyzed [3 + 2] Cycloaddition of 4,4-Dicyano-2-methylenebut-3-enoates with Benzyl Buta-2,3-dienoate, Ethyl Buta-2,3-dienoate, *tert*-Butyl Buta-2,3-dienoate, and Penta-3,4-dien-2-one. *General Procedure.* To a solution of chiral phosphines (0.02 mmol) in toluene (1.0 mL) was added the corresponding benzyl buta-2,3-dienoate, ethyl buta-2,3-dienoate, *tert*-butyl buta-2,3-dienoate, or penta-3,4-dien-2-one (0.2 mmol). The reaction mixture was stirred at room temperature. To this resulting reaction mixture (1.0 mL) a solution of 4,4-dicyano-2-methylenebut-3-enoate (**1**) (0.1 mmol) was slowly added. The reaction mixture was stirred at room temperature until the reaction was complete (monitoring by TLC). Then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to afford the desired cyclic products **3**.

*3-Ethyl 1-Methyl 1-(2,2-Dicyano-1-p-tolylvinyl)cyclopent-3-ene-1,3-dicarboxylate (**3d**).* A colorless solid, 34 mg, 80% yield; mp 53−54 °C; IR (KBr): ν 3032, 2954, 2231, 1743, 1713, 1644, 1455, 1433, 1347, 1242, 1205, 1178, 1100, 747, 735, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.40 (s, 3H, CH_3), 2.85−2.96 (m, 2H, CH_2), 3.44−3.56 (m, 2H, CH_2), 3.86 (s, 3H, OCH_3), 5.15 (s, 2H, CH_2), 6.64−6.65 (m, 1H, =CH), 7.07 (d, 2H, J = 8.0 Hz, ArH), 7.27 (d, 2H, J = 8.0 Hz, ArH), 7.31−7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.4, 43.1, 44.7, 53.8, 59.2, 66.3, 89.5, 111.6, 112.1, 126.4, 128.2, 128.3, 128.5, 129.8, 132.4, 133.5, 135.5, 139.6, 141.4, 163.2, 172.0, 182.2; MS (ESI) m/z (%): 449.1 (100) [M+Na$^+$]; HRMS (ESI) Calcd. For $C_{26}H_{22}N_2O_4Na^{1+}$ (M+Na$^+$)

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requires 449.1477, Found: 449.1480; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.5 mL/min; t_{minor} = 14.88 min, t_{major} = 16.19 min; ee % = 63%; $[\alpha]^{20}_{D}$ = −28.4 (c 1.50, CH_2Cl_2)].

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C NMR spectroscopic and analytic data of the compounds **3**, CIF data of **3p**, as well as the optimization of the reaction conditions for the asymmetric [3 + 2] cycloaddition reaction are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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