Stereochemical considerations on the stereoselective cyclopropanation reactions of 3-aryl-2-phosphonoacrylates induced by the (−)-8-phenylmenthyl† group as a chiral auxiliary

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The cyclopropanation of (−)-8-phenylmenthyl (*E*)-3-aryl-2-phosphonoacrylates *E*-**3a**–**d** with dimethyloxosulfonium methylide and diazomethane affords the corresponding *trans* cyclopropane derivatives as the major diastereomers with high diastereoselectivity. On the other hand, the cyclopropanation of (−)-8-phenylmenthyl (*Z*)-3-aryl-2-phosphonoacrylates *Z*-**3a**–**d** and (−)-menthyl derivative **4** gives mixtures of *cis* and *trans* cyclopropane derivatives with low diastereoselectivity. The high diastereoselectivity in the cyclopropanation of (*E*)-acrylates *E*-**3a**–**d** can be rationalized by considering the π–π interaction between the phenyl ring of the chiral auxiliary and the acrylate moiety in the s-*cis* conformer. The low selectivity in the cyclopropanation of (*Z*)-acrylates (*Z*-**3a**–**d** and **4**) can be attributed to a low-lying conformer with the acrylate moiety twisted out of conjugation.

Introduction

1-Aminocyclopropanecarboxylic acid derivatives have drawn widespread attention because of their biological activity[1] and potential use as conformationally restricted peptides.[2] Since transition-state analogues of a certain reaction catalyzed by an enzyme have been considered to be effective types of enzyme inhibitors for that specific enzyme reaction,[3] much effort has been directed toward the synthesis of cyclopropanephosphonic acid derivatives,[4,5] which can be considered to be transition-state analogues in the conversion of the carbonyl group to the tetrahedral hydroxide adduct in the hydrolysis reaction of acid derivatives of cyclopropanes.[6]

Recently, we have investigated asymmetric induction in the formation of cyclic compounds by using as the chiral auxiliary the (−)-8-phenylmenthyl group,[7] which has previously been applied with success in various types of asymmetric reactions.[8,9] Using this chiral auxiliary methodology, we have reported on the highly diastereoselective cyclopropanation reaction of sterically hindered (−)-8-phenylmenthyl (*E*)-3-aryl-2-phosphonoacrylates (**3a**–**d**) with dimethyloxosulfonium methylide and diazomethane.[10] This proved to be one of but a few successful uses of sterically hindered substrates in conjunction with this chiral auxiliary.[11] In this paper, we present a full account of the results with detailed stereochemical considerations on the stereoselectivity in the cyclopropanation reactions of the 3-aryl-2-phosphonoacrylates **3a**–**d** induced by the (−)-8-phenylmenthyl group.

Results and discussion

3-Aryl-2-phosphonoacrylates *E*-**3a**–**d**, *Z*-**3a**–**c** and **4** were each prepared from phosphonoacetates **1** and **2** and the corresponding aryl aldehydes with high geometrical selectivity by two separate methods which both utilize the titanium-mediated Knoevenagel condensation (Scheme 1).[12] The condensation reaction of **1** with aryl aldehydes in the presence of *N*-methyl-

† In this paper, menthyl refers to the menthan-3-yl radical.
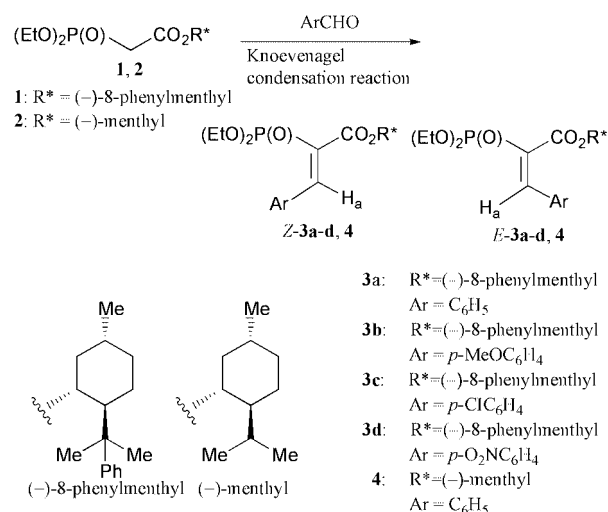
Scheme 1 *Reagents and conditions*: for *E*-**3a**–**d** and **4** (Method A): TiCl₄ (2 eq), *N*-methylmorpholine (NMM) (10 eq), THF; for *Z*-**3a**–**c** and **4** (Method B): Ti(O^iPr)₃Cl (2 eq), Et₃N (10 eq), THF.

morpholine–TiCl₄ at 0 °C gave Knoevenagel products **3a**–**d** and **4** having the thermodynamically more stable (*E*)-geometry (Table 1, entries 1–4, 9).[12b] The thermodynamically less stable (*Z*)-isomers **3a**–**c** and **4** were obtained by the reaction of **1** and **2** with aryl aldehydes in the presence of Ti(O^iPr)₃Cl–Et₃N at low temperature (−78 °C) (Table 1, entries 5–8, 10).[12a] The *E* and *Z* isomers could be separated by preparative TLC (PLC). The geometries were determined on the basis of the coupling constants $^3J_{HaP}$ in the ^1H NMR spectra and $^3J_{C(ipso),P}$ in the ^{13}C NMR spectra.[13]

The cyclopropanation of **3a**–**d** and **4** with dimethyloxosulfonium methylide was first examined (Scheme 2). Treatment of *E*- and *Z*-**3a**–**d** and *Z*-**4** with the ylide generated in DMSO with NaH at 25 °C gave mixtures of *cis*-I,II- and *trans*-I,II-**5a**–**d** and **6**, respectively. All four diastereomers of **3a**–**d** and **4** could be separated by HPLC. The *cis*/*trans* configurations were assigned by the coupling constant ($^3J_{CP}$) between the *ipso*-carbon of the

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Table 1 Knoevenagel reaction of phosphonoacetates **1** and **2** with aryl aldehydes

Entry	Substrate	ArCHO	Method[a]	Product	Yield (%)	E	:	Z[b]
1	**1**	PhCHO	A	**3a**	78	90	:	10
2	**1**	p-MeOC$_6$H$_4$CHO	A	**3b**	66	90	:	10
3	**1**	p-ClC$_6$H$_4$CHO	A	**3c**	65	90	:	10
4	**1**	p-O$_2$NC$_6$H$_4$CHO	A	**3d**	97	88	:	12
5	**1**	PhCHO	B	**3a**	86	8	:	92
6	**1**	PhCHO	B[c]	**3a**	96	43	:	57
7	**1**	p-MeOC$_6$H$_4$CHO	B	**3b**	80	8	:	92
8	**1**	p-ClC$_6$H$_4$CHO	B	**3c**	98	7	:	93
9	**2**	PhCHO	A	**4**	47	98	:	2
10	**2**	PhCHO	B	**4**	50	10	:	90

[a] Method A: TiCl$_4$, N-methylmorpholine (NMM), 0 °C, 3 h. Method B: Ti(O^{i}Pr)$_3$Cl, Et$_3$N, −78 °C, 6 h. [b] The ratios were determined by ^{1}H NMR of the crude products. [c] The reaction was conducted at 0 °C for 6 h.
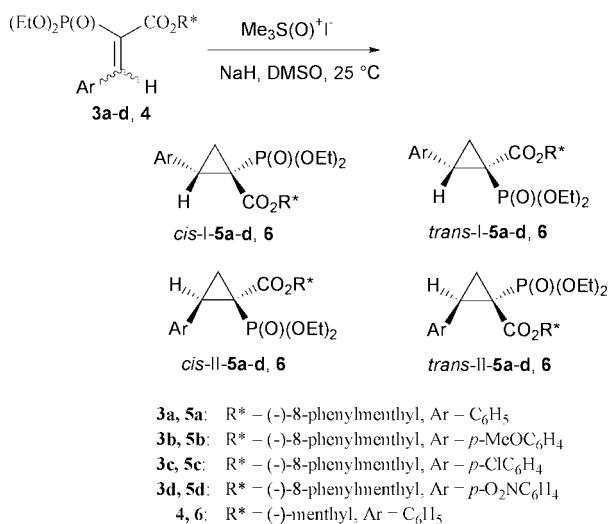
Scheme 2

aryl group and phosphorus. Those with coupling constants of $^3J_{CP} \approx 5$ Hz were assigned as *cis*, whereas those with $^3J_{CP} \approx 2$ Hz [13b–d] were assigned as *trans*. Of the two *cis*- and two *trans*-isomers, the one with a lower field proton signal for the cyclopropane hydrogen was arbitrarily designated I and the other II.

trans-II-**5b** turned out to be crystalline and was subjected to X-ray structural analysis. The absolute stereochemistry of *trans*-II-**5b** was determined to be 1S,2R as shown in Fig. 1,
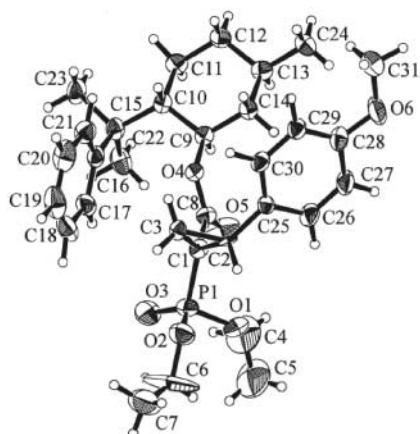
Fig. 1 ORTEP drawing of *trans*-II-**5b**.

based upon a comparison with the stereochemically defined 8-phenylmenthyl moiety. On the basis of the similarity of the NMR spectral data of *trans*-II-**5a–d**, the absolute configuration of the *trans*-II series of cyclopropane diastereomers was deter-

mined to be 1S,2R. Since the major *cis* diastereomer is expected to arise from the same Michael adduct intermediate as the major *trans* diastereomer (*vide infra*), differing only in the orientation of the following ring-closure step, the stereochemistry at the 2-position in the cyclopropane ring should be the same. Thus, the major *cis* product was assigned the *cis*-II configuration, as depicted in Scheme 4 (see below).

The reaction of (E)-3-aryl-2-phosphonoacrylates E-**3a–d** at 25 °C afforded preferentially the *trans*-isomers (Table 2, entries 1–4; *cis* : *trans* ≈ 1 : 2–3). The diastereoselectivity in the cyclopropanation was moderate (40–49% de) for the *cis*-isomers and but high (69–86% de) for the *trans*-isomers. The cyclopropanation of (Z)-3-aryl-2-phosphonoacrylates Z-**3a–d** and -**4** in DMSO at 25 °C gave a nearly equimolar mixture of the *cis* and *trans* cyclopropane derivatives (Table 2, entries 5–8; *cis* : *trans* ≈ 1 : 1). The diastereoselectivity in the reactions was low for both *cis*- and *trans*-products (5–58% de). As for the substituents in the aromatic ring, a clear trend could not be observed upon the selectivity of the cyclopropanation reaction using dimethyloxosulfonium methylide.

Next, the cyclopropanation of 3-aryl-2-phosphonoacrylates **3a–c** and **4** by reaction with excess of diazomethane followed by denitrogenation was examined (Scheme 3). Treatment of 3-aryl-2-phosphonoacrylates **3a–c** and **4** in Et$_2$O at 0 to 25 °C with
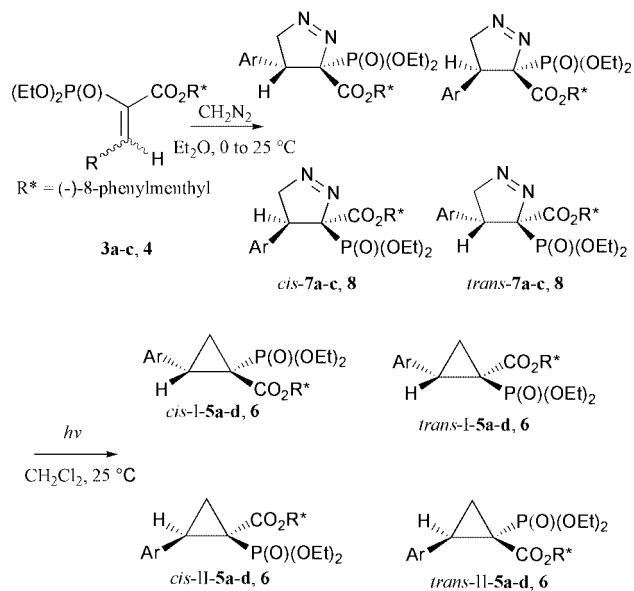

Scheme 3

Table 2 The cyclopropanation of **3a–d** and **4** with dimethyloxosulfonium methylide

Entry	Substrate	Product	Yield (%)	cis-I	:	cis-II	:	trans-I	:	trans-II	%de[a] cis	trans
1	*E*-**3a**	**5a**	72	2.1	:	5.7	:	1.0	:	13	46	86
2	*E*-**3b**	**5b**	96	1.8	:	5.2	:	1.0	:	11	49	83
3	*E*-**3c**	**5c**	93	1.7	:	4.0	:	1.0	:	9.1	40	80
4	*E*-**3d**	**5d**	97	0.5	:	1.3	:	1.0	:	5.4	44	69
5	*Z*-**3a**	**5a**	91	2.4	:	1.4	:	1.0	:	2.1	26	35
6	*Z*-**3b**	**5b**	97	2.1	:	1.4	:	1.0	:	2.1	20	35
7	*Z*-**3c**	**5c**	73	2.6	:	1.7	:	1.0	:	3.8	21	58
8	*Z*-**4**	**6**	83	1.2	:	1.1	:	1.1	:	1.0	4	5

[a] The ratios were determined by the integral values of cyclopropyl proton in ^{1}H NMR.

Table 3 The cyclopropanation of **3a–c** and **4** with CH$_2$N$_2$ *via* pyrazolines **7a–c** and **8**

Entry	Substrate	Pyrazoline	cis	:	trans	%de cis	trans	Cyclopropane	cis-I	:	cis-II	:	trans-I	:	trans-II[b]	%de[a] cis	trans	Yield (%)[c]
1	*E*-**3a**	**7a**	—	:	1.0	—	90	**5a**	0.3	:	0.3	:	1.0	:	14	0	87[e]	59
2	*E*-**3b**	**7b**	—	:	1.0	—	88	**5b**	0.5	:	0.5	:	1.0	:	14	0	87[e]	62
3	*E*-**3c**	**7c**	1.0	:	10[d]	43	80	**5c**	2.0	:	1.4	:	1.0	:	23	18[f]	92[f]	32
4	*E*-**4**	**8**	1.0	:	32[d]	12	4	**6**	1.0	:	1.6	:	10	:	16	23[f]	23[f]	69
5	*Z*-**3a**	**7a**	28	:	1.0[d]	25	>90	**5a**	3.7	:	11	:	1.0	:	4.8	50[f]	66[f]	28
6	*Z*-**3b**	**7b**	1.2	:	1.0[d]	40	76	**5b**	7.8	:	2.6	:	1.0	:	12	50[f]	85[f]	41
7	*Z*-**3c**	**7c**	2.8	:	1.0[d]	56	80	**5c**	12	:	4.1	:	1.0	:	7.7	50[f]	77[f]	48
8	*Z*-**4**	**8**	6.5	:	1.0[d]	10	6	**6**	5.4	:	6.7	:	1.0	:	1.4	11[f]	17[f]	49

[a] The %de was determined by integral values of ^{1}H NMR. [b] The ratios were determined by integral values of ^{1}H NMR. [c] The yields were calculated from **3a–c** and **4**. [d] The *cis* : *trans* ratio was determined by integral values of ^{31}P NMR. [e] The %de was determined by integral values of ^{1}H and ^{31}P NMR. [f] The %de was determined by integral values of ^{31}P NMR.
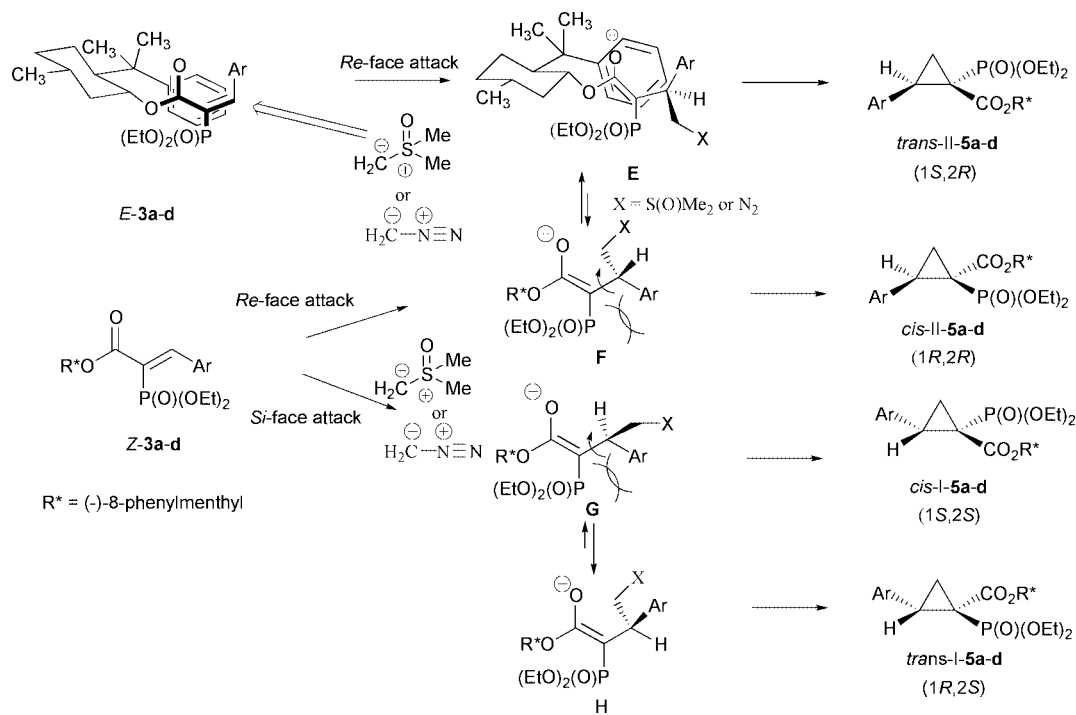
Scheme 4

diazomethane afforded mixtures of diastereomeric pyrazoline derivatives **7a–c** and **8**, respectively. The diastereomers of the pyrazolines **7a–c** and **8** could not be separated. The three proton signals for the pyrazoline ring were observed separately as multiplets. The *cis* and *trans* configurations of the pyrazoline derivatives **7a–c** and **8** were determined by the coupling constant ($^3J_{CP}$) in ^{13}C NMR spectra between the *ipso*-carbon of the aryl ring and phosphorus. Those of coupling constants

$^3J_{CP}$ = 10–13 Hz were assigned as *trans* and those of constants $^3J_{CP}$ = 2–8 Hz as *cis*.[13b–d]

The stereoselectivity in the formation of pyrazolines is summarized in Table 3. The ratios between the *trans*- and the *cis*-products were determined by integral values of NMR spectra. For entries 1 and 2, the ratios determined by ^{31}P NMR were in good agreement with those found by ^{1}H NMR. Thus, ratios for reactions that followed were all determined by ^{31}P NMR. The 1,3-dipolar addition reaction of *E*-**3a**–**c** with diazomethane proceeded to give the *trans* pyrazoline derivatives **7a**–**c** with high stereoselectivity (Table 3, entries 1–3). The selectivity between the two *trans*-diastereomers was also found to be high (80–90% de). The reaction of *Z*-**3a**–**c** with diazomethane gave the *cis* pyrazolines as the major diastereomers (Table 3, entries 5–7). However, the ratios of the geometric isomers (*cis* : *trans*) were generally lower than those for *E*-**3a**–**c** except for *Z*-**3a** where selectivity was exceptionally high. The diastereoselectivities were also lower compared with the reaction of *E*-**3a**–**c**, especially for the *cis*-products. For (−)-menthyl 3-phenyl-2-(diethoxyphosphonyl)acrylate **4**, the geometries of the substrates were highly retained in the products. Thus, the reaction of *E*-**4** with diazomethane gave the *trans* pyrazolines as the major diastereomers (Table 3, entry 4), while the treatment of *Z*-**4** with diazomethane gave the *cis* pyrazolines in preference (Table 3, entry 8). However, with regard to the face of the acrylate alkene moiety, the diastereoselectivities in the reactions of both isomers of **4** were very low.

Photolysis of the inseparable mixtures of pyrazolines **7a**–**c** and **8** gave cyclopropane derivatives **5a**–**c** and **6**, respectively, as shown in Table 3. The stereochemistry of the *trans* pyrazolines was retained to a high degree in the products, with essentially the same diastereomeric ratio in both the precursors and the products. Thus, the *trans* cyclopropane derivatives **5a**–**c** were obtained with high overall diastereoselectivity from *E*-**3a**–**c** *via* the corresponding pyrazolines (Table 3, entries 1–3). The major *trans*-products were found to have the same stereochemistry as those derived from the sulfonium ylides. In the reactions of *cis*-**7a**–**c**, there was an obvious decrease in the *cis* : *trans* ratios of the products (Table 3, entries 5–7). The conversion of pyrazolines **8** to the corresponding cyclopropane derivatives **6** was found to proceed with high retention of configuration (Table 3, entries 4,8), although the low facial selectivity was also carried over. A comparison between the results between substrates bearing the (−)-8-phenylmenthyl and the (−)-menthyl groups suggests that the phenyl group of the chiral auxiliary is critical for high facial selectivity.

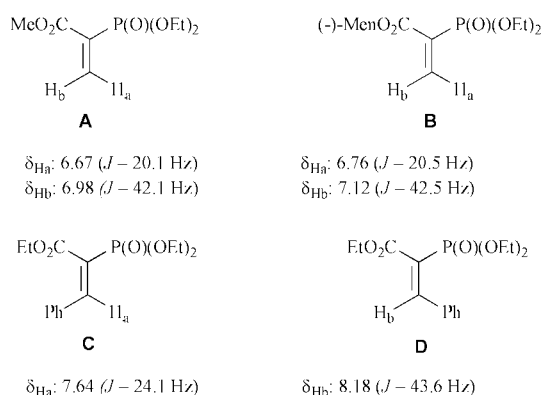Fig. 2 summarizes the reported ^{1}H NMR chemical-shift

A

δ_{Ha}: 6.67 (*J* − 20.1 Hz)
δ_{Hb}: 6.98 (*J* − 42.1 Hz)

B

δ_{Ha}: 6.76 (*J* − 20.5 Hz)
δ_{Hb}: 7.12 (*J* − 42.5 Hz)

C

δ_{Ha}: 7.64 (*J* − 24.1 Hz)

D

δ_{Hb}: 8.18 (*J* − 43.6 Hz)

Fig. 2 ^{1}H NMR chemical shifts of vinyl protons in various phosphonoacrylates.

values of vinylic protons in a few 3-unsubstituted and 3-phenyl-substituted 2-phosphonoacrylates.[5j] In the ^{1}H NMR spectra of methyl 2-(diethoxyphosphonyl)acrylate, the signal of the vinylic proton (H_b) positioned *trans* (*E*) to the phosphorus atom appears at lower magnetic field than that of the *cis* (*Z*)

counterpart (H_a) due to the magnetic anisotropic effect of the ester group (**A**). Placing a menthyl group in the place of the methyl group has no effect on the relative chemical shift (**B**). The introduction of a phenyl group in the 3-position leads to a lower field shift for both *trans* (*E*) (**D**, δ_{Hb} 8.18) and *cis* (*Z*) (**C**, δ_{Ha} 7.64) isomers. However, the difference in chemical shift is maintained between the two. A comparison of the chemical shifts of *E*- and *Z*-**4** with reported values (*E*: δ 7.63; *Z*: δ 8.14) show that those of **4** are of normal values. On the other hand, for (−)-8-phenylmenthyl 3-aryl-2-phosphonoacrylates **3a**–**d**, while the chemical shifts of the vinylic protons of *E*-**3a**–**d** (δ 7.55–7.67) were in the normal range, the vinylic proton of *Z*-**3a**–**d** (δ 6.94–7.28) appeared at higher magnetic field than that of **D** and *Z*-**4**. This distinct difference indicates that the vinylic protons of *Z*-**3a**–**d** are magnetically shielded by the phenyl ring of the chiral auxiliary, whereas those of the *E*-isomers are not. This implies that the stable conformation of *Z*-**3a**–**d** has the vinylic proton in question exceptionally close to the phenyl group of the chiral auxiliary.

In order to provide a rationale for the observed stereochemistry, conformers of model compounds *E*- and *Z*-**9** [(−)-8-phenylmenthyl 2-(dimethoxyphosphonyl)-3-phenylacrylate] were optimized by AM1[14] using the Hamiltonian implemented in MOPAC Ver. 6.0[15] (Fig. 3). Calculations on *E*-**9** gave rise to

E-**9**-s-*cis*: -234.82 kcal/mol

E-**9**-s-*trans*: -231.71 kcal/mol

Z-**9**-s-*cis*: -227.21 kcal/mol

Z-**9**-s-*trans*: -228.40 kcal/mol

I: -231.20 kcal/mol

$(MeO)_2P(O)$ CO_2R^*

H Ph

R* = (−)-8-phenylmenthyl

E- and *Z*-**9**
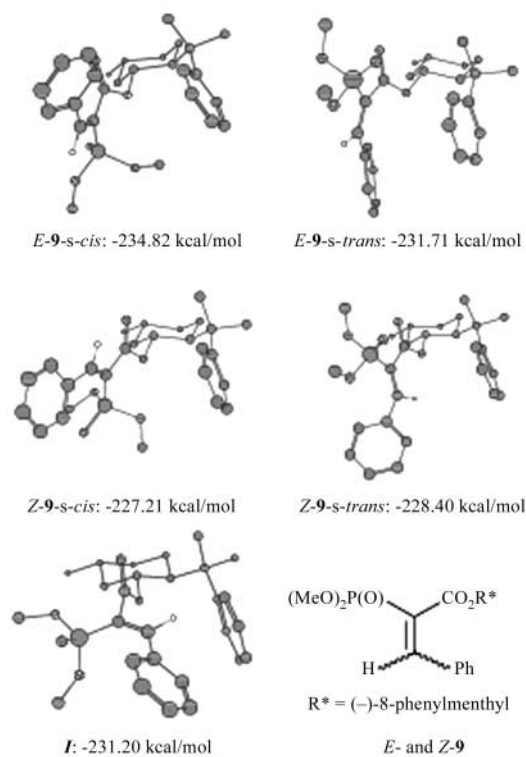
Fig. 3 AM1 Energies of s-*cis* and s-*trans* conformers of *E,Z*-**9**.

two stable conformations which correspond to the s-*cis* and s-*trans* conformers. Between these two, the s-*cis*-conformer was found to be more favourable than the s-*trans* one by 3.1 kcal mol^{-1}.‡ In the structural optimization of *Z*-**9**, calculations commenced from initial comformations of both s-*cis* and s-*trans*-conformers converged into the same structure (conformer **I**) in which the dihedral angle of the acrylate moiety is twisted to approximately 90°, in order to avoid unfavorable allylic interactions between the carbonyl oxygen and the 2-substituents. Although the value of 90° is probably overexaggerated due to an underestimation of conjugation, it is still a good indication that the phenyl group of the chiral auxiliary is not as involved as in the case of the *E*-isomers. As the ^{1}H NMR

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‡ 1 cal = 4.184 J.

spectrum indicated (*vide supra*), the vinylic proton is situated close to and above the phenyl ring of the chiral auxiliary. Such a distorted conformation is not possible for the corresponding *E*-isomers because repulsive edge-to-face interaction between the phenyl groups of the acrylate and chiral auxiliary moieties would result.

From the stable conformers deduced above, the observed differences in diastereoselectivity in the cyclopropanation between *E*- and *Z*-isomers can be explained as shown in Fig. 4 based
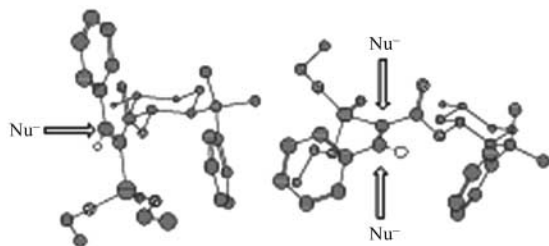

Fig. 4 Speculated direction of attack of cyclopropanation reagents to *E*- and *Z*-**3a**.

upon the assumption that selectivity at the 2-position is determined at the stage of Michael addition. For *E*-**3a**–**d**, the phenyl group of the chiral auxiliary is suitably positioned with possible π–π stacking interaction to block the depicted back face of the acrylate moiety.[16] This induces the reagents (dimethyloxosulfonium methylide and diazomethane) to approach from the *Re*-face of the more favorable s-*cis* conformation and results in high selectivity. On the other hand, for *Z*-**3a**–**d** there is little steric bias between the *Re*- and the *Si*-faces of the acrylate moiety and it is understandable that the cyclopropanation of *Z*-**3a**–**d** resulted in low diastereoselectivity.

Thus, the whole mechanistic scheme for the two reactions can be outlined as shown in Scheme 4. In the cyclopropanation using dimethyloxosulfonium methylide, the reaction with (*E*)-2-phosphonoacrylates *E*-**3a**–**d** preferentially give rise to intermediates **E** *via Re* face attack. Ring closure directly from this conformation gives rise to products *trans*-II-**5a**–**d**. Upon rotation of the C–C single bond (the original acrylic alkene double bond) in intermediates **E** and subsequent ring closure at intermediate **F**, *cis*-II-**5a**–**d** are formed. The fact that the ratio between *trans*-II and *cis*-II was only *ca.* 2 : 1 indicates that the ring-closure process is rather slow and allows ample time for conformational change to occur. Since it is difficult to imagine the nucleophile attacking from the side of the chiral auxiliary, the formation of the diastereomers due to *Si* face attack probably occurs in the s-*trans* conformation which was calculated not to be extremely different in energy compared with the s-*cis* conformation (*vide supra*). Thus, the selectivity with regards to facial attack on the acrylate moiety of *ca.* 4.5–6 : 1 [(*trans*-II + *cis*-II) : (*trans*-I + *cis*-I)] probably reflects the reactivity of the two conformers (s-*cis* and s-*trans*) of *E*-**3a**–**d**. As for *Z*-**3a**–**d**, the facial selectivity is practically 1 : 1 and in good agreement with predictions from AM1 calculations (*vide supra*). The fact that the ratios of *trans*-II : *cis*-II and *trans*-I : *cis*-I isomers do not differ by much between the series of *E*-**3a**–**d** and *Z*-**3a**–**d** indicates that these ratios are mainly governed by thermodynamic factors involving the corresponding pairs of intermediates **E**/**F** and **G**/**H**.

For the 1,3-dipolar addition reaction of diazomethane to phosphonoacrylates **3a**–**d** and **4**, the configuration of the major *trans*-product was found to have the same relative stereochemistry as that of the major products of the sulfonium ylide reactions. Therefore, the stereochemical implications from the AM1 calculations hold true here also. The incomplete stereospecificity in the reactions suggests that the reactions were stepwise. However, since the magnitude of isomer formation is lower compared with that in the sulfonium ylide reactions, the

subsequent pyrazoline-formation reactions can be considered to be fast reactions (Scheme 4). Here again, in order to avoid the large steric hindrance between the aryl group and the phosphonyl group, quite a significant amount of *trans*-product was formed in the reaction of the *Z*-substrates *via* bond rotation in the Michael adduct intermediates. As for the photolysis of the pyrazoline compounds to give the cyclopropane derivatives, the stereochemistry of the isomeric pyrazolines was retained to a high extent as is usual for such kinds of reaction which are presumed to involve singlet biradicals.

Conclusions

We have found that the cyclopropanation of (*E*)-3-aryl-2-phosphonoacrylates using the (−)-8-phenylmenthyl group as a chiral auxiliary gives the *trans* cyclopropane derivatives with high diastereoselectivity. The high diastereoselectivity can be attributed to the high π-face differentiation of the acrylate moiety by the face-to-face interaction with the phenyl ring of the chiral auxiliary in the s-*cis* conformer. On the other hand, the cyclopropanation of (−)-8-phenylmenthyl (*Z*)-3-aryl-2-phosphonoacrylates gave mixtures of *cis* and *trans* cyclopropane derivatives with low diastereoselectivity. The stable conformations of the phosphonoacrylates deduced from AM1 calculations served appropriately in explaining these observed stereochemical results.

Experimental

All reactions were carried out under N_2. THF and Et_2O were distilled after refluxing over Na–benzophenone prior to use. CH_2Cl_2, CCl_4 and DMSO were distilled over CaH_2 before use. NaH was used after washing with dry hexane. Silica gel $60F_{254}$ was used for PLC. NMR spectra were recorded on a JEOL GSX-270 or a JEOL JNM-LA500 instrument. Both ^{1}H NMR and ^{13}C NMR spectra were observed in $CDCl_3$ solutions with TMS as the internal reference. ^{31}P NMR spectra were observed in $CDCl_3$ solutions with 85% H_3PO_4 as the external reference. *J*-Values are given in Hz. MS spectra were recorded on a JEOL SX-102A instrument. FAB spectra were measured by using glycerol as the matrix. EI data were obtained by using 70 eV electrons. Optical rotations were recorded on a JASCO DIP-370 polarimeter, and [*a*]$_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. Petroleum ether refers to the fraction with distillation range 30–70 °C.

(−)-Menthyl 2-(diethoxyphosphonyl)acetate 2

The reaction conditions for the preparation of **1**[17] were followed using (−)-menthyl α-bromoacetate (5.8 g, 20.9 mmol) and P(OEt)$_3$ (6 cm³, 35 mmol). The residue was purified by bulb-to-bulb distillation (220 °C, 1 mmHg; 5.3 g, 92%) to give a colorless oil; δ_H (500 MHz) 0.76 (3 H, d, *J* 7.1, CH_3), 0.90 (3 H, d, *J* 4.0, CH_3), 0.91 (3 H, d, *J* 3.4, CH_3), 0.97–1.10 (2 H, m), 1.28–1.53 (3 H, m), 1.35 (6 H, t, *J* 7.1, OCH_2CH_3), 1.65–1.72 (2 H, m), 1.94–2.06 (2 H, m), 2.94 (2 H, d, *J* 2.9), 4.13–4.26 (4 H, m, OCH_2CH_3), 4.73 (1 H, td, *J* 4.2, 11.0, OCH).

(−)-8-Phenylmenthyl (*E*)-2-(diethoxyphosphonyl)-3-phenyl-acrylate *E*-3a

Titanium(IV) tetrachloride (0.06 cm³, 0.55 mmol) in CCl_4 (1.0 cm³) was added dropwise to THF (2.0 cm³) at 0 °C. The yellow titanium–THF complex was produced. To this solution were added benzaldehyde (0.03 cm³, 0.30 mmol) and **1** (99.3 mg, 0.24 mmol) in THF (2.0 cm³) at 0 °C. After 10 min, *N*-methylmorpholine (0.27 cm³, 2.46 mmol) was added to the solution and the reaction mixture was stirred for 3 h at 0 °C. The resulting mixture was diluted with Et_2O (10 cm³) and quenched with 1.0 M aq. HCl (15 cm³). The organic layer was extracted with Et_2O (3 × 20 cm³). The combined organic layers

were washed successively with water (2 × 20 cm³) and brine (2 × 20 cm³), dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by PLC (CHCl₃–petroleum ether = 10 : 1, 4 times) to produce E- and Z-**3a** [93.6 mg, 78%, E/Z = 90/10 (determined by ^{1}H NMR of crude product)] as a viscous colorless oil; $[a]_D^{25}$ +3.1 (c 0.89, CHCl₃); δ_H (270 MHz) 0.62–1.56 (6 H, m), 0.86 (3 H, d, J 6.4, CH₃), 1.16 (3 H, s, CH₃), 1.17 (3 H, s, CH₃), 1.37 (6 H, td, J 4.9, 6.8, OCH₂CH_3), 1.74–1.87 (1 H, m), 2.06–2.17 (1 H, m), 3.94–4.26 (4 H, m, OCH_2CH₃), 4.89 (1 H, td, J 3.9, 10.7, OCH), 7.04–7.20 (5 H, m), 7.32–7.42 (3 H, m), 7.46–7.53 (2 H, m), 7.64 (1 H, d, J 24.4, C$_\beta$H); δ_C (125 MHz) 16.1 (d, $^3J_{CP}$ 3.1, OCH₂CH₃), 16.2 (d, $^3J_{CP}$ 3.1, OCH₂CH₃), 21.6, 23.8, 27.2, 28.9, 31.2, 34.3, 39.9, 40.6, 50.5, 62.4 (d, $^2J_{CP}$ 5.2, OCH₂CH₃), 62.4 (d, $^2J_{CP}$ 5.2, OCH₂CH₃), 77.4 (OCH), 125.0, 125.1 (d, $^1J_{CP}$ 177.9, C$_\alpha$), 125.4 (×2), 127.8 (×2), 128.3 (×2), 129.4 (×2), 130.1, 133.9 [d, $^3J_{CP}$ 20.7, C($ipso$)], 148.2 (d, $^2J_{CP}$ 6.2, C$_\beta$), 150.6, 165.5 (d, $^2J_{CP}$ 12.4); δ_P (202 MHz) 16.5; HRMS m/z (FAB) 499.2589 (M$^+$H. C₂₉H₄₀O₅P requires m/z, 499.2613) (Calc. for C₂₉H₃₉O₅P: C, 69.86; H, 7.88. Found: C, 69.87; H, 7.70%).

(−)-8-Phenylmenthyl (E)-2-(diethoxyphosphonyl)-3-(4-methoxyphenyl)acrylate E-3b

The reaction conditions for the preparation of E-**3a** were followed using TiCl₄ (0.06 cm³, 0.55 mmol), p-anisaldehyde (0.04 cm³, 0.33 mmol), **1** (103.1 mg, 0.25 mmol) and N-methylmorpholine (NMM) (0.28 cm³, 2.55 mmol). Purification by PLC (CHCl₃–petroleum ether = 10 : 1, four times) gave E-**3b** [87.9 mg, 66%, E/Z = 90/10 (determined by ^{1}H NMR of crude product)]; $[a]_D^{25}$ −2.4 (c 3.6, CHCl₃); δ_H (500 MHz) 0.75 (1 H, m), 0.87 (3 H, d, J 6.1, CH₃), 0.82–1.01 (2 H, m), 1.20 (3 H, s), 1.21 (3 H, s), 1.29–1.34 (1 H, m), 1.36 (6 H, dt, J 9.7, 7.0, OCH₂CH_3), 1.43–1.56 (2 H, m), 1.82–1.89 (1 H, m), 2.12–2.18 (1 H, m), 3.84 (3 H, s, OCH₃), 3.91–4.21 (4 H, m), 4.93 (1 H, td, J 4.0, 10.7, OCH), 6.87–6.92 (2 H, m), 7.05–7.18 (5 H,

m), 7.49–7.59 (2 H, m), 7.55 (1 H, d, J 25.3 Hz); δ_C (125 MHz) 15.8 (d, $^3J_{CP}$ 5.1, OCH₂CH₃), 15.9 (d, $^3J_{CP}$ 7.6, OCH₂CH₃), 21.4, 23.8, 27.0, 28.6, 31.1, 34.2, 39.8, 40.6, 50.5, 55.2, 62.2 (d, $^2J_{CP}$ 4.7, OCH₂CH₃), 62.3 (d, $^2J_{CP}$ 5.7, OCH₂CH₃), 77.3 (OCH), 113.4, 114.1 (×2), 121.9 (d, $^1J_{CP}$ 180.9, C$_\alpha$), 125.4, 125.8 (×2), 126.7 [d, $^3J_{CP}$ 21.9, C($ipso$)], 128.2 (×2), 132.2 (×2), 148.7 (d, $^2J_{CP}$ 6.3, C$_\beta$), 150.9, 166.5 (d, $^2J_{CP}$ 12.5); δ_P (202 MHz) 16.3; HRMS m/z (EI) 528.2617 (M$^+$. C₃₀H₄₁O₆P requires M, 528.2641).

(−)-8-Phenylmenthyl (Z)-2-(diethoxyphosphonyl)-3-(4-methoxyphenyl)acrylate Z-3b

The reaction conditions for the preparation of Z-**3a** were followed using **1** (100.5 mg, 0.25 mmol), chlorotitanium triisopropoxide (0.12 cm³, 0.50 mmol), p-anisaldehyde (0.04 cm³, 0.33 mmol) and Et₃N (0.34 cm³, 2.42 mmol). Purification by PLC (CHCl₃–petroleum ether = 10 : 1, 4 times) gave Z-**3b** [104.6 mg, 80%, E/Z = 8/92 (determined by ^{1}H NMR of crude product)]; $[a]_D^{25}$ +6.5 (c 2.0, CHCl₃); δ_H (500 MHz) 0.88 (3 H, d, J 6.4, CH₃), 0.85–0.95 (1 H, m), 1.07 (1 H, dd, J 12.2, 23.5), 1.14 (6 H, dt, J 7.0, 11.6, OCH₂CH_3), 1.23 (3 H, s), 1.34 (3 H, s), 1.19–1.39 (1 H, m), 1.46–1.55 (1 H, m), 1.63–1.78 (2 H, m), 1.93–1.99 (1 H, m), 2.10–2.16 (1 H, m), 3.84 (3 H, s), 3.95–4.10 (4 H, m), 5.00 (1 H, td, J 4.6, 10.7, OCH), 6.88 (2 H, d, J 8.5), 6.94 (1 H, t, J 7.3), 7.16–7.32 (4 H, m), 7.28 (1 H, d, J 44.8, C$_\beta$H), 7.51 (2 H, d, J 8.8); δ_C (125 MHz) 16.0 (d, $^3J_{CP}$ 6.8, OCH₂CH₃), 16.1 (d, $^3J_{CP}$ 6.1, OCH₂CH₃), 21.8, 25.3, 26.7, 27.9, 31.4, 34.6, 39.7, 41.6, 50.5, 55.3, 62.3 (d, $^2J_{CP}$ 10.5, OCH₂CH₃), 62.4 (d, $^2J_{CP}$ 9.9, OCH₂CH₃), 75.6 (OCH), 113.2 (×2), 113.4, 125.1, 125.7 (d, $^1J_{CP}$ 160.9, C$_\alpha$), 125.4 (×2), 126.4 [d, $^3J_{CP}$ 8.1, C($ipso$)], 128.0 (×2), 132.9 (×2), 151.4, 153.4 (d, $^2J_{CP}$ 4.4, C$_\beta$), 161.4 (d, $^2J_{CP}$ 16.7); δ_P (202 MHz) 13.3; HRME m/z (EI) 528.2642 (M$^+$. C₃₀H₄₁O₆P requires M, 528.2641).

(−)-8-Phenylmenthyl (E)-3-(4-chlorophenyl)-2-(diethoxyphosphonyl)acrylate E-3c

The reaction conditions for the preparation of E-**3a** were followed using TiCl₄ (0.06 cm³, 0.55 mmol), 4-chlorobenzaldehyde (46.2 mg, 0.33 mmol), **1** (104.5 mg, 0.25 mmol) and NMM (0.29 cm³, 2.64 mmol). After usual work-up, purification by PLC (CHCl₃–petroleum ether = 10 : 1, 5 times) gave E-**3c** [87.6 mg, 65%, E/Z = 90/10 (determined by ^{1}H NMR of crude product)]; δ_H (500 MHz) 0.69–0.78 (1 H, m), 0.87 (3 H, d, J 6.7, CH₃), 0.82–0.97 (2 H, m), 1.16 (3 H, m), 1.18 (3 H, s), 1.28–1.34 (1 H, m), 1.37 (6 H, td, J 7.0, 9.5, OCH₂CH_3), 1.41–1.56 (2 H, m), 1.79–1.85 (1 H, m), 2.05–2.11 (1 H, m), 3.96–4.22 (4 H, m), 4.89 (1 H, td, J 4.3, 10.7, OCH), 7.07–7.19 (5 H, m), 7.33–7.37 (2 H, m), 7.41–7.44 (2 H, m), 7.57 (1 H, d, J 24.4, C$_\beta$H); δ_C (125 MHz) 16.2 (d, $^3J_{CP}$ 4.2, OCH₂CH₃), 16.3 (d, $^3J_{CP}$ 3.4, OCH₂CH₃), 21.7, 24.2, 27.2, 28.7, 31.3, 34.3, 40.0, 40.7, 50.6, 62.6 (d, $^2J_{CP}$ 4.8, OCH₂CH₃), 62.6 (d, $^2J_{CP}$ 6.6, OCH₂CH₃), 77.5 (OCH), 125.1, 125.5 (×2), 127.2 (d, $^1J_{CP}$ 171.6, C$_\alpha$), 127.9 (×2), 128.7 (×2), 130.8 (×2), 132.4 [d, $^3J_{CP}$ 20.8, C($ipso$)], 136.3, 146.9 (d, $^2J_{CP}$ 5.3, C$_\beta$), 150.7, 165.2 (d, $^2J_{CP}$ 12.4); δ_P (202 MHz) 14.9; HRMS m/z (EI) 532.2130 (M$^+$. C₂₉H₃₈ClO₅P requires M, 532.2145).

(−)-8-Phenylmenthyl (Z)-3-(4-chlorophenyl)-2-(diethoxyphosphonyl)acrylate Z-3c

The reaction conditions for the preparation of Z-**3a** were followed using **1** (114.3 mg, 0.28 mmol), chlorotitanium triisopropoxide (0.12 cm³, 0.50 mmol), 4-chlorobenzaldehyde (51.7 mg, 0.37 mmol) and Et₃N (0.40 cm³, 2.85 mmol). Purification by PLC (CHCl₃–petroleum ether = 10 : 1, 7 times) gave Z-**3c** [145.3 mg, 98%, E/Z = 7/93 (determined by ^{1}H NMR of crude product)]; δ_H (500 MHz) 0.89 (3 H, d, J 6.1, CH₃), 0.85–0.97 (1 H, m), 1.06 (1 H, dd, J 11.9, 23.5), 1.12 (6 H, t, J 7.0, OCH₂CH_3), 1.15–1.19 (1 H, m), 1.21 (3 H, s), 1.33 (3 H, s), 1.47–1.57 (1 H,

(−)-8-Phenylmenthyl (Z)-2-(diethoxyphosphonyl)-3-phenylacrylate Z-3a

To a solution of **1** (99.3 mg, 0.24 mmol) in THF (4.0 cm³) at −78 °C were added chlorotitanium triisopropoxide (0.12 cm³, 0.50 mmol) and benzaldehyde (0.03 cm³, 0.30 mmol), and the mixture was treated with Et₃N (0.34 cm³, 2.44 mmol) at −78 °C. The amine hydrochloride precipitated from the solution. The solution containing precipitates of the amine hydrochloride was allowed to warm slowly to room temperature over a period of 10 h. The resulting mixture was diluted with Et₂O (10 cm³) and quenched with 1.0 M aq. HCl (15 cm³). The organic layer was extracted with Et₂O (3 × 20 cm³). The combined organic layers were washed successively with water (2 × 20 cm³) and brine (2 × 20 cm³), and then dried over anhydrous MgSO₄. Removal of solvent left a residue, which was purified by PLC (CHCl₃–petroleum ether = 10 : 1, 4 times) to produce of E- and Z-**3a** [103.9 mg, 86%, E/Z = 8/92 (determined by ^{1}H NMR of crude product)] as a viscous colorless oil; δ_H (500 MHz) 0.84–1.20 (3 H, m), 0.89 (3 H, d, J 6.7, OCHCH_3), 1.08 (6 H, dt, J 7.0, 11.9, OCH₂CH_3), 1.23 (3 H, s, CH₃), 1.35 (3 H, s, CH₃), 1.46–1.57 (1 H, m), 1.64–1.71 (1 H, m), 1.73–1.80 (1 H, m), 1.93–2.00 (1 H, m), 2.11–2.20 (1 H, m), 3.88–4.07 (4 H, m, OCH₂CH₃), 5.01 (1 H, td, J 4.3, 10.7, OCH), 6.89–6.94 (1 H, m), 7.16–7.23 (2 H, m), 7.27–7.31 (3 H, m), 7.33–7.37 (3 H, m), 7.42–7.47 (2 H, m); δ_C (125 MHz) 15.8 (d, $^3J_{CP}$ 4.1, OCH₂CH₃), 15.9 (d, $^3J_{CP}$ 4.1, OCH₂CH₃), 21.7, 24.6, 26.6, 28.2, 31.2, 34.4, 39.5, 41.5, 50.3, 62.2 (d, $^2J_{CP}$ 6.2, OCH₂CH₃), 62.3 (d, $^2J_{CP}$ 6.2, OCH₂CH₃), 75.6 (OCH), 124.6 (d, $^1J_{CP}$ 209, C$_\alpha$), 125.0, 125.3 (×2), 127.5 (×2), 127.9 (×2), 129.6, 129.9 (×2), 134.2 [d, $^3J_{CP}$ 7.2, C($ipso$)], 151.3, 153.2 (d, $^2J_{CP}$ 4.1, C$_\beta$), 164.8 (d, $^2J_{CP}$ 12.4); δ_P (202 MHz) 12.1; HRMS m/z (EI) 498.2514 (M$^+$. C₂₉H₃₉O₅P requires M, 498.2535) (Calc. for C₂₉H₃₉O₅P: C, 69.86; H, 7.88. Found: C, 69.74; H, 8.01%).

m), 1.77–1.84 (1 H, m), 1.91–1.97 (1 H, m), 2.13–2.20 (1 H, m), 3.91–4.07 (4 H, m, OCH_2CH$_3$), 5.01 (1 H, td, J 4.6, 10.7, OCH), 6.87–6.92 (1 H, td, J 0.6, 7.3), 7.06 (1 H, d, J 43.9, C$_\beta$H), 7.14–7.21 (2 H, m), 7.26–7.41 (6 H, m); δ_C (125 MHz) 16.1 (d, $^3J_{CP}$ 7.1, OCH$_2$CH$_3$) (×2), 21.8, 24.2, 26.6, 28.8, 31.4, 34.5, 39.6, 41.6, 50.4, 62.5 (d, $^2J_{CP}$ 6.2, OCH$_2$CH$_3$), 62.5 (d, $^2J_{CP}$ 6.1, OCH$_2$CH$_3$), 75.8, 125.0, 125.4 (×2), 127.9 (×2), 128.0 (×2), 128.1 (d, $^1J_{CP}$ 146.7, C$_a$), 131.5 (×2), 132.7 [d, $^3J_{CP}$ 7.8, C($ipso$)], 135.9, 151.6, 151.8 (d, $^2J_{CP}$ 4.3, C$_\beta$), 164.7 (d, $^2J_{CP}$ 16.5); δ_P (202 MHz) 12.0; HRMS m/z (EI) 532.2147 (M$^+$. C$_{29}$H$_{38}$ClO$_5$P requires M, 532.2145).

(−)-8-Phenylmenthyl (E)-2-(diethoxyphosphonyl)-3-(4-nitrophenyl)acrylate E-3d

The reaction conditions for the preparation of E-3a were followed using TiCl$_4$ (0.31 cm^3, 2.83 mmol), p-nitrobenzaldehyde (259.1 mg, 1.71 mmol), 1 (577.0 mg, 1.41 mmol) and NMM (1.6 cm^3, 14.6 mmol). Purification by PLC (AcOEt–hexane = 1 : 1) gave E-3d (654.8 mg, 97%, E/Z = 88/12); δ_H (500 MHz) 0.70–0.81 (2 H, m), 0.85 (3 H, d, J 6.4, CH$_3$), 0.92 (1 H, ddd, J 3.4, 13.4, 26.2), 1.15 (6 H, d, J 1.5, OCH$_2$CH_3), 1.40 (6 H, td, J 7.0, 9.5), 1.31–1.49 (2 H, m), 1.49–1.56 (1 H, m), 1.75–1.82 (1 H, m), 1.99–2.05 (1 H, m), 4.03–4.26 (4 H, m, OCH_2CH$_3$), 4.87 (1 H, td, J 4.0, 10.7, OCH), 7.08–7.20 (5 H, m), 7.58 (2 H, d, J 8.8), 7.67 (1 H, d, J 24.1, C$_\beta$H), 8.20–8.25 (2 H, m).

(−)-8-Phenylmenthyl (Z)-2-(diethoxyphosphonyl)-3-(4-nitrophenyl)acrylate Z-3d.

δ_H (500 MHz) 0.90–1.01 (1 H, m), 0.91 (3 H, d, J 6.3, CH$_3$), 1.03–1.15 (1 H, m), 1.11 (3 H, t, J 7.1, OCH$_2$CH_3), 1.13 (3 H, t, J 7.2, OCH$_2$CH_3), 1.20 (3 H, s, CH$_3$), 1.34 (3 H, s, CH$_3$), 1.48–1.58 (2 H, m), 1.71–1.77 (1 H, m), 1.87–1.97 (2 H, m), 2.17–2.24 (1 H, m), 3.93–4.10 (4 H, m, OCH_2CH$_3$), 5.02 (1 H, td, J 4.4, 10.7, OCH), 6.83–6.87 (1 H, m), 6.94 (1 H, d, J 43.3, C$_\beta$H), 7.15–7.19 (2 H, m), 7.29–7.32 (2 H, m), 7.52 (2 H, d, J 8.4), 8.20 (2 H, d, J 8.4).

(−)-Menthyl (E)-2-(diethoxyphosphonyl)-3-phenylacrylate E-4

The reaction conditions for the preparation of E-3a were followed using TiCl$_4$ (0.33 cm^3, 3.01 mmol), benzaldehyde (0.2 cm^3, 1.97 mmol), 2 (499.1 mg, 1.49 mmol) and NMM (1.7 cm^3, 15.5 mmol). Purification by PLC (AcOEt–hexane = 1 : 1) gave E-4 [297.9 mg, 47%, E/Z = 98 : 2 (determined by ^{1}H NMR of crude product)]; $[a]_D^{25}$ −27.7 (c 1.7, CHCl$_3$); δ_H (500 MHz) 0.79–0.97 (2 H, m), 0.74 (3 H, d, J 6.3, CH$_3$), 0.81 (3 H, d, J 6.7, CH$_3$), 0.91 (3 H, d, J 6.4, CH$_3$), 1.00–1.15 (1 H, m), 1.36 (3 H, t, J 6.9, OCH$_2$CH_3), 1.37 (3 H, t, J 7.2, OCH$_2$CH_3), 1.44–1.56 (1 H, m), 1.62–1.71 (3 H, m), 1.80–1.87 (1 H, m), 2.08–2.13 (1 H, m), 4.13–4.22 (4 H, m, OCH_2CH$_3$), 4.83 (1 H, td, J 4.8, 10.8, OCH), 7.33–7.40 (2 H, m), 7.44–7.45 (3 H, m), 7.63 (1 H, d, J 24.4, C$_\beta$H); δ_C (125 MHz) 15.8. 16.1 (d, $^3J_{CP}$ 3.1, OCH$_2$CH$_3$), 16.2 (d, $^3J_{CP}$ 2.0, OCH$_2$CH$_3$), 20.8, 22.0, 22.9, 25.2, 31.4, 34.0, 40.2, 46.8, 62.5 (d, $^2J_{CP}$ 5.0, OCH$_2$CH$_3$), 62.6 (d, $^2J_{CP}$ 3.8, OCH$_2$CH$_3$), 76.0 (OCH), 125.1 (d, $^1J_{CP}$ 177.8, C$_a$), 128.5 (×2), 129.2 (×2), 130.2, 133.8 [d, $^3J_{CP}$ 20.0, C($ipso$)], 147.5 (d, $^2J_{CP}$ 7.1, C$_\beta$), 166.1 (d, $^2J_{CP}$ 12.6); δ_P (202 MHz) 14.9; HRMS m/z (EI) 422.2208 (M$^+$. C$_{23}$H$_{35}$O$_5$P requires M, 422.2222).

(−)-Menthyl (Z)-2-(diethoxyphosphonyl)-3-phenylacrylate Z-4

The reaction conditions for the preparation of Z-3a were followed using 2 (539.7 mg, 1.61 mmol), chlorotitanium triisopropoxide (0.75 cm^3, 3.14 mmol), benzaldehyde (0.17 cm^3, 1.67 mmol) and NMM (1.8 cm^3, 16.4 mmol). Purification by column chromatography (SiO$_2$; AcOEt–hexane = 1 : 1) gave Z-4 [340.4 mg, 50%, E/Z = 10 : 90 (determined by ^{1}H NMR of crude product)]; $[a]_D^{25}$ −52.6 (c 0.15, CHCl$_3$); δ_H (500 MHz) 0.60–1.60 (7 H, m), 0.80 (3 H, d, J 6.9, CH$_3$), 0.92 (3 H, d, J 4.8, CH$_3$), 0.93 (3 H, d, J 4.4, CH$_3$), 1.09 (3 H, t, J 7.2, OCH$_2$CH_3), 1.13 (3 H, t, J 6.9, OCH$_2$CH_3), 1.94–1.99 (1 H, m), 2.03–2.14 (1 H, m),

3.92–4.08 (4 H, m, OCH_2CH$_3$), 4.87 (1 H, td, J 4.6, 10.8, OCH), 7.35–7.47 (3 H, m), 7.60–7.67 (2 H, m), 8.14 (1 H, d, J 43.9, C$_\beta$H); δ_C (125 MHz) 15.9 (d, $^3J_{CP}$ 6.0, OCH$_2$CH$_3$), 16.0 (d, $^3J_{CP}$ 7.2, OCH$_2$CH$_3$), 16.1, 20.9, 22.0, 23.3, 26.0, 31.5, 34.2, 40.7, 47.1, 62.4 (d, $^2J_{CP}$ 6.4, OCH$_2$CH$_3$), 62.5 (d, $^2J_{CP}$ 5.3, OCH$_2$CH$_3$), 75.9 (OCH), 125.1 (d, $^1J_{CP}$ 187.4, C$_a$), 127.9 (×2), 130.0, 130.1 (×2), 134.1 [d, $^3J_{CP}$ 7.2, C($ipso$)], 153.7 (d, $^2J_{CP}$ 3.3, C$_\beta$), 166.0 (d, $^2J_{CP}$ 15.1); δ_P (202 MHz) 12.1; HRMS m/z (EI) 422.2221 (M$^+$. C$_{23}$H$_{35}$O$_5$P requires M, 422.2222).

General procedure of cyclopropanation using dimethyloxosulfonium methylide

A mixture of trimethyloxosulfonium iodide (39.2 mg, 0.18 mmol) and a 60% NaH dispersion (7.6 mg, 0.19 mmol) in DMSO (1.0 cm^3) was stirred at 25 °C for 30 minutes. When the evolution of gas ceased, a solution of E-3a (87.7 mg, 0.18 mmol) in DMSO (2.0 cm^3) was added via cannula to the freshly prepared ylide. The solution was stirred for 40 h at 25 °C. To the mixture was added water (10 cm^3), followed by extraction with Et$_2$O (3 × 20 cm^3). The organic fractions were combined, washed successively with several portions of water and brine, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure. Purification by PLC (hexane–EtOAc = 6 : 4, twice) and high performance liquid chromatography (HPLC) (WAKO Sil-100, hexane–^{i}PrOH = 10 : 1) provided the four cyclopropane derivatives 5a (64.6 mg, 72%) as colorless oils.

(−)-8-Phenylmenthyl cis-1-(diethoxyphosphonyl)-2-phenylcyclopropanecarboxylate cis-I-5a.

$[a]_D^{25}$ −25.0 (c 2.4, CHCl$_3$); δ_H (500 MHz) 0.75–0.90 (2 H, m), 0.87 (3 H, d, J 6.4, CH$_3$), 0.97–1.08 (1 H, m), 1.11 (3 H, t, J 7.1, OCH$_2$CH_3), 1.12 (3 H, t, J 7.0, OCH$_2$CH_3), 1.33 (3 H, s, CH$_3$), 1.43 (1 H, m), 1.46 (3 H, s, CH$_3$), 1.52–1.62 (3 H, m), 1.90–2.00 (3 H, m), 2.74 (1 H, q, J 8.9, H$_a$), 3.65–3.78 (3 H, m, OCH_2CH$_3$), 3.85–3.93 (1 H, m, OCH_2CH$_3$), 5.00 (1 H, td, J 4.6, 10.8, OCH), 7.18–7.34 (10 H, m); δ_C (125 MHz) 16.2 (d, $^3J_{CP}$ 5.3, OCH$_2$CH$_3$), 16.3 (d, $^3J_{CP}$ 3.8, OCH$_2$CH$_3$), 17.1 (d, $^2J_{CP}$ 2.0, CH$_b$), 21.7 (×2), 25.0, 27.0, 29.0, 29.1 (d, $^1J_{CP}$ 197.7), 31.2 (×2), 33.4 (d, $^2J_{CP}$ 2.0, CH$_a$), 34.4, 40.6, 41.7, 50.5, 61.6 (d, $^2J_{CP}$ 5.9, OCH_2CH$_3$), 62.6 (d, $^2J_{CP}$ 5.9, OCH_2CH$_3$), 75.8 (OCH), 125.4, 125.6, 127.3, 127.7 (×2), 128.1 (×2), 130.0, 134.7 [d, $^3J_{CP}$ 4.5, C($ipso$)], 150.8, 169.1 (d, $^2J_{CP}$ 8.6); δ_P (202 MHz) 21.5; HRMS m/z (EI) 512.2684 (M$^+$. C$_{30}$H$_{41}$O$_5$P requires M, 512.2692).

(−)-8-Phenylmenthyl cis-1-(diethoxyphosphonyl)-2-phenylcyclopropanecarboxylate cis-II-5a.

$[a]_D^{25}$ +36.2 (c 1.8, CHCl$_3$); δ_H (500 MHz) 0.75–0.90 (1 H, m), 0.88 (3 H, d, J 6.6, CH$_3$), 0.98–1.12 (1 H, m), 1.08 (3 H, t, J 7.1, OCH$_2$CH_3), 1.09 (3 H, t, J 7.0, OCH$_2$CH_3), 1.24–1.28 (1 H, m), 1.27 (3 H, s, CH$_3$), 1.38 (3 H, s, CH$_3$), 1.41–1.48 (2 H, m), 1.53–1.62 (2 H, m), 1.62–1.67 (1 H, m), 1.92–1.98 (1 H, m), 2.00–2.08 (1 H, m), 2.63 (1 H, q, J 8.2, H$_a$), 3.60–3.70 (1 H, m), 3.78–3.92 (3 H, m), 5.00 (1 H, td, J 4.6, 10.7, OCH), 7.40–7.80 (1 H, m), 7.19–7.34 (9 H, m); δ_C (125 MHz) 16.1 (d, $^3J_{CP}$ 3.7, OCH$_2$CH$_3$), 16.2 (d, $^3J_{CP}$ 1.8, OCH$_2$CH$_3$), 17.9 (d, $^2J_{CP}$ 2.1, CH$_b$), 21.8, 25.4, 27.1, 28.3, 28.9 (d, $^1J_{CP}$ 198.0), 31.4 (×2), 31.8 (d, $^2J_{CP}$ 3.9, CH$_a$), 34.4, 40.2, 41.8 (×2), 49.9, 61.7 (d, $^2J_{CP}$ 5.6, OCH_2CH$_3$), 62.1 (d, $^2J_{CP}$ 6.9, OCH_2CH$_3$), 76.4 (OCH), 125.4, 125.5. 127.0, 127.7 (×2), 128.1, 130.0 (×2), 135.3 [d, $^3J_{CP}$ 6.4, C($ipso$)], 150.8, 169.2 (d, $^2J_{CP}$ 9.6); δ_P (202 MHz) 21.2; HRMS m/z (EI) 512.2645 (M$^+$. C$_{30}$H$_{41}$O$_5$P requires M, 512.2692).

(−)-8-Phenylmenthyl $trans$-1-(diethoxyphosphonyl)-2-phenylcyclopropanecarboxylate $trans$-I-5a.

$[a]_D^{25}$ +10.4 (c 5.2, CHCl$_3$); δ_H (500 MHz) 0.37 (1 H, q, J 11.9), 0.47–0.60 (1 H, m), 0.58 (3 H, d, J 6.6, CH$_3$), 0.64–0.77 (2 H, m), 1.00–1.50 (2 H, m), 1.23 (3 H, s, CH$_3$), 1.34 (3 H, t, J 7.0, OCH$_2$CH_3), 1.34 (3 H, s, CH$_3$), 1.49 (3 H, t, J 7.1, OCH$_2$CH_3), 1.68–1.75 (1 H, m), 1.76–1.82 (1 H, m), 1.82–1.89 (1 H, m, H$_b$), 2.19–2.25 (1 H, m, H$_b$),

3.14 (1 H, m, H$_a$), 4.15–4.24 (2 H, m, OCH_2CH$_3$), 4.29–4.36 (2 H, m, OCH_2CH$_3$), 4.65 (1 H, dt, J 4.5, 10.5, OCH), 7.06–7.41 (10 H, m); δ_C (125 MHz) 14.9 (d, $^2J_{CP}$ 2.4, CH$_b$), 16.2 (d, $^3J_{CP}$ 7.1, OCH$_2$$CH_3$), 16.6 (d, $^3J_{CP}$ 7.2, OCH$_2$$CH_3$), 21.4, 22.7, 27.4, 29.3 (d, $^1J_{CP}$ 184.7), 30.8, 31.0, 31.5, 34.1, 40.5, 41.3, 50.1, 62.3 (d, $^2J_{CP}$ 4.5, OCH$_2$CH$_3$), 62.4 (d, $^2J_{CP}$ 3.6, OCH$_2$CH$_3$), 76.8 (OCH), 125.3, 125.9 (×2), 127.9 (×2), 128.1 (×2), 128.4, 129.4 (×2), 133.8 [d, $^3J_{CP}$ 1.8, C(*ipso*)], 150.1, 166.0 (d, $^2J_{CP}$ 6.3); δ_P (202 MHz) 23.4; HRMS *m/z* (EI) 512.2709 (M$^+$. $C_{30}H_{31}O_5P$ requires *M*, 512.2692).

(−)-8-Phenylmenthyl *trans*-1-(diethoxyphosphonyl)-2-phenyl-cyclopropanecarboxylate *trans*-II-5a. $[a]_D^{25}$ −2.0 (*c* 6.0, CHCl$_3$); δ_H (500 MHz) −0.04 (1H, q, J 13.1), 0.55–0.64 (2 H, m), 0.62 (3 H, d, J 6.8, CH$_3$), 0.78–0.88 (2 H, m), 1.00 (3 H, s, CH$_3$), 1.19 (3 H, s, CH$_3$), 1.35–1.45 (3 H, m), 1.39 (3 H, t, J 7.1, OCH$_2$CH_3), 1.44 (3 H, t, J 7.0, OCH$_2$CH_3), 1.52–1.58 (1 H, m), 1.70–1.76 (1 H, m), 2.98 (1 H, ddd, J 8.4, 8.4, 17.0, H$_a$), 4.24 (2 H, dq, J 7.2, 14.5, OCH_2CH$_3$), 4.31 (2 H, dq, J 7.2, 14.5, OCH_2CH$_3$), 4.53 (1 H, td, J 4.1, 10.8, OCH), 7.15–7.32 (10 H, m); δ_C (125 MHz) 15.6 (d, $^2J_{CP}$ 1.9, CH$_b$), 16.5 (d, $^3J_{CP}$ 6.7, OCH$_2$$CH_3$), 16.6 (d, $^3J_{CP}$ 6.7, OCH$_2$$CH_3$), 21.4 (×2), 26.0, 26.7, 26.9, 28.8 (d, $^1J_{CP}$ 191.0), 30.9 (d, $^2J_{CP}$ 17.2, CH$_a$), 34.3, 39.7, 40.0, 50.1, 62.5 (d, $^2J_{CP}$ 5.5, OCH$_2$CH$_3$), 62.7 (d, $^2J_{CP}$ 6.5, OCH$_2$CH$_3$), 75.7 (OCH), 125.2, 125.5 (×2), 127.4, 128.0 (×2), 128.2 (×2), 129.5 (×2), 134.6 [d, $^3J_{CP}$ 1.8, C(*ipso*)], 151.4, 166.1 (d, $^2J_{CP}$ 8.6); δ_P (202 MHz) 24.1; HRMS *m/z* (EI) 512.2698 (M$^+$. $C_{30}H_{41}O_5P$ requires *M*, 512.2692).

(−)-8-Phenylmenthyl *cis*-1-(diethoxyphosphonyl)-2-(4-meth-oxyphenyl)cyclopropanecarboxylate *cis*-I-5b. $[a]_D^{25}$ −15.9 (*c* 1.1, CHCl$_3$); δ_H (500 MHz) 0.74–0.87 (1 H, m), 0.86 (3 H, d, J 6.3, CH$_3$), 0.96–1.10 (2 H, m), 1.14 (3 H, t, J 7.0, OCH$_2$CH_3), 1.19 (3 H, t, J 7.0, OCH$_2$CH_3), 1.32 (3 H, s, CH$_3$), 1.40–1.48 (1 H, m), 1.41–1.46 (1 H, m), 1.45 (3 H, s, CH$_3$), 1.52–1.61 (2 H, m), 1.89–2.07 (3 H, m), 2.69 (1 H, m, H$_a$), 3.67–3.87 (3 H, m, OCH_2CH$_3$), 3.76 (3 H, s, OCH$_3$), 3.87–3.96 (1 H, m, OCH_2CH$_3$), 5.00 (1 H, td, J 4.2, 10.5, OCH), 6.89 (2 H, d, J 8.9), 7.17–7.28 (4 H, m), 7.29–7.34 (3 H, m); δ_C (125 MHz) 16.2 (d, $^3J_{CP}$ 2.6, OCH$_2$$CH_3$), 16.3 (d, $^3J_{CP}$ 2.2, OCH$_2$$CH_3$), 17.2 (CH$_b$), 21.7, 25.0, 27.0, 29.0, 29.1 (d, $^1J_{CP}$ 196.3), 31.3, 32.9 (d, $^2J_{CP}$ 3.3, CH$_a$), 34.4, 40.2, 41.6, 50.4, 55.2, 61.6 (d, $^2J_{CP}$ 4.7, OCH$_2$CH$_3$), 62.1 (d, $^2J_{CP}$ 8.1, OCH$_2$CH$_3$), 75.5 (OCH), 113.1 (×2), 125.3, 125.6 (×2), 126.6 [d, $^3J_{CP}$ 6.4, C(*ipso*)], 128.1 (×2), 131.0 (×2), 150.8, 158.8, 169.1 (d, $^2J_{CP}$ 8.7); δ_P (202 MHz) 21.5; HRMS *m/z* (EI) 542.2792 (M$^+$. $C_{31}H_{43}O_6P$ requires *M*, 542.2797).

(−)-8-Phenylmenthyl *cis*-1-(diethoxyphosphonyl)-2-(4-meth-oxyphenyl)cyclopropanecarboxylate *cis*-II-5b. $[a]_D^{25}$ +46.0 (*c* 0.84, CHCl$_3$); δ_H (500 MHz) 0.75–0.85 (1 H, m), 0.87 (3 H, d, J 6.6, CH$_3$), 0.97–1.16 (2 H, m), 1.13 (6 H, t, J 7.1, OCH$_2$CH_3), 1.25–1.36 (1 H, m), 1.27 (3 H, s, CH$_3$), 1.38 (3 H, s, CH$_3$), 1.41–1.48 (2 H, m), 1.52–1.59 (1 H, m), 1.65 (1 H, m, H$_b$), 1.94 (1 H, m, H$_b$), 2.00–2.07 (1 H, m), 2.58 (1 H, m, H$_a$), 3.67–3.76 (1 H, m, OCH_2CH$_3$), 3.78 (3 H, s, OCH$_3$), 3.80–3.87 (2 H, m, OCH_2CH$_3$), 3.88–3.94 (1 H, m, OCH_2CH$_3$), 4.98 (1 H, td, J 4.5, 10.6, OCH), 6.80 (2 H, d, J 9.0), 7.05–7.09 (1 H, m), 7.19–7.23 (2 H, m), 7.23–7.28 (2 H, m), 7.29–7.32 (2 H, m); δ_C (125 MHz) 16.2 (d, $^3J_{CP}$ 3.7, OCH$_2$$CH_3$), 16.3 (d, $^3J_{CP}$ 1.8, OCH$_2$$CH_3$), 18.0 (d, $^2J_{CP}$ 2.3, CH$_b$), 21.8, 25.4, 27.1, 28.4, 28.9 (d, $^1J_{CP}$ 198.9), 31.3, 31.4 (d, $^2J_{CP}$ 8.4, CH$_a$), 34.3, 40.2, 41.8, 49.8, 55.2, 61.6 (d, $^2J_{CP}$ 5.9, OCH$_2$CH$_3$), 62.1 (d, $^2J_{CP}$ 6.8, OCH$_2$CH$_3$), 76.3 (OCH), 113.2 (×2), 125.4, 125.5 (×2), 127.2 [d, $^3J_{CP}$ 5.0, C(*ipso*)], 128.1 (×2), 131.0 (×2), 150.8, 158.7, 169.2 (d, $^2J_{CP}$ 9.2); δ_P (202 MHz) 21.2; HRMS *m/z* (EI) 542.2809 (M$^+$. $C_{31}H_{43}O_6P$ requires *M*, 542.2797).

(−)-8-Phenylmenthyl *trans*-1-(diethoxyphosphonyl)-2-(4-meth-oxyphenyl)cyclopropanecarboxylate *trans*-I-5b. $[a]_D^{25}$ −51.8 (*c*

0.42, CHCl$_3$); δ_H (500 MHz) 0.38 (1 H, q, J 11.9), 0.48–0.58 (1 H, m), 0.59 (3 H, d, J 6.2, CH$_3$), 0.65–0.79 (2 H, m), 1.00–1.16 (2 H, m), 1.18–1.40 (1 H, m), 1.24 (3 H, s, CH$_3$), 1.33 (3 H, t, J 6.7, OCH$_2$CH_3), 1.35 (3 H, s, CH$_3$), 1.49 (3 H, t, J 6.9, OCH$_2$CH_3), 1.62 (1 H, m), 1.84 (1 H, m, H$_b$), 2.19 (1 H, m), 3.10 (1 H, m, H$_a$), 3.75 (3 H, OCH$_3$), 4.12—4.24 (2 H, m, OCH_2CH$_3$), 4.22–4.35 (2 H, m, OCH_2CH$_3$), 4.66 (1 H, dt, J 4.7, 10.5, OCH), 6.79–6.82 (2 H, m), 7.13–7.19 (3 H, m), 7.20–7.28 (4 H, m); δ_C (125 MHz) 15.1 (d, $^2J_{CP}$ 2.8, CH$_b$), 16.3 (d, $^3J_{CP}$ 7.8, OCH$_2$$CH_3$), 16.6 (d, $^3J_{CP}$ 7.2, OCH$_2$$CH_3$), 21.3, 22.7, 27.4, 29.3 (d, $^1J_{CP}$ 186.4), 30.4 (d, $^2J_{CP}$ 1.2, CH$_a$), 31.0, 31.5, 34.1, 40.5, 41.4, 50.1, 55.0, 62.3 (d, $^2J_{CP}$ 3.3, OCH$_2$CH$_3$), 62.4 (d, $^2J_{CP}$ 3.4, OCH$_2$CH$_3$), 76.8 (OCH), 113.5 (×2), 125.4, 125.6 [d, $^3J_{CP}$ 1.9, C(*ipso*)], 125.9 (×2), 127.9 (×2), 130.4 (×2), 150.0, 159.0, 166.2 (d, $^2J_{CP}$ 5.9); δ_P (202 MHz) 23.5; HRMS *m/z* (EI) 542.2798 (M$^+$. $C_{31}H_{43}O_6P$ requires *M*, 542.2797).

(−)-8-Phenylmenthyl *trans*-1-(diethoxyphosphonyl)-2-(4-meth-oxyphenyl)cyclopropanecarboxylate *trans*-II-5b. $[a]_D^{25}$ +11.4 (*c* 2.5, CHCl$_3$); δ_H (500 MHz) 0.0 (1 H, q, J 12.0), 0.56–0.64 (1 H, m), 0.63 (3 H, d, J 6.6, CH$_3$), 0.79–0.90 (1 H, m), 0.96–1.03 (1 H, m), 1.02 (3 H, s, CH$_3$), 1.12–1.22 (1 H, m), 1.21 (3 H, s, CH$_3$), 1.26–1.47 (3 H, m), 1.39 (3 H, t, J 7.0, OCH$_2$CH_3), 1.43 (3 H, t, J 7.1, OCH$_2$CH_3), 1.49–1.55 (1 H, m, H$_b$), 1.71–1.77 (1 H, m), 2.93 (1 H, m, H$_a$), 3.74 (3 H, s, OCH$_3$), 4.19–4.26 (2 H, m, OCH_2CH$_3$), 4.27–4.34 (2 H, m, OCH_2CH$_3$), 4.54 (1 H, td, J 4.2, 10.7, OCH), 6.76 (2 H, d, J 8.8), 7.08 (2 H, d, J 8.8), 7.14–7.19 (1 H, m), 7.20–7.23 (2 H, m), 7.27–7.32 (2 H, m); δ_C (125 MHz) 15.7 (d, $^2J_{CP}$ 1.6, CH$_b$), 16.4 (d, $^3J_{CP}$ 6.2, OCH$_2$$CH_3$), 16.5 (d, $^3J_{CP}$ 6.2, OCH$_2$$CH_3$), 21.4, 26.1, 26.6, 26.7, 28.6 (d, $^1J_{CP}$ 193.1), 30.2 (d, $^2J_{CP}$ 3.5, CH$_a$), 30.8, 34.3, 39.6, 40.0, 50.1, 55.0, 62.4 (d, $^2J_{CP}$ 6.2, OCH$_2$CH$_3$), 62.6 (d, $^2J_{CP}$ 6.0, OCH$_2$CH$_3$), 75.6 (OCH), 113.5 (×2), 125.1, 125.4 (×2), 126.5 [d, $^3J_{CP}$ 2.2, C(*ipso*)], 128.0 (×2), 130.5 (×2), 151.3, 159.0, 166.1; δ_P (202 MHz) 24.1; HRMS *m/z* (EI) 542.2778 (M$^+$. $C_{31}H_{43}O_6P$ requires *M*, 542.2797).

(−)-8-Phenylmenthyl *cis*-2-(4-chlorophenyl)-1-(diethoxyphos-phonyl)cyclopropanecarboxylate *cis*-I-5c. δ_H (500 MHz) 0.75–0.85 (1 H, m), 0.87 (3 H, d, J 6.4, CH$_3$), 0.97–1.08 (2 H, m), 1.14 (3 H, t, J 6.9, OCH$_2$CH_3), 1.19 (3 H, t, J 7.0, OCH$_2$CH_3), 1.31 (3 H, s, CH$_3$), 1.43 (3 H, s, CH$_3$), 1.45–1.60 (4 H, m), 1.87–1.94 (2 H, m), 1.95–2.01 (1 H, m), 2.65 (1 H, dd, J 9.0, 17.8, H$_a$), 3.70–3.78 (1 H, m, OCH_2CH$_3$), 3.78–3.85 (2 H, m, OCH_2CH$_3$), 3.90–3.99 (1 H, m, OCH_2CH$_3$), 5.01 (1 H, td, J 4.4, 10.7, OCH), 7.17–7.33 (9 H, m); δ_C (125 MHz) 15.9 (d, $^3J_{CP}$ 6.1, OCH$_2$$CH_3$), 16.0 (d, $^3J_{CP}$ 5.5, OCH$_2$$CH_3$), 16.7 (CH$_b$), 21.4, 25.0, 26.7, 28.2, 28.8 (d, $^1J_{CP}$ 196.9), 29.5, 31.0, 32.1 (d, $^2J_{CP}$ 2.5, CH$_a$), 34.1, 40.0, 41.4, 50.3, 61.7 (d, $^2J_{CP}$ 5.4, OCH$_2$CH$_3$), 62.2 (d, $^2J_{CP}$ 6.8, OCH$_2$CH$_3$), 75.8 (OCH), 125.7, 125.9 (×2), 128.1 (×2), 128.4 (×2), 131.7 (×2), 133.5, 133.6 [d, $^3J_{CP}$ 5.5, C(*ipso*)], 151.3, 169.4 (d, $^2J_{CP}$ 9.3); δ_P (202 MHz) 21.0; HRMS *m/z* (EI) 546.2300 (M$^+$. $C_{30}H_{40}ClO_5P$ requires *M*, 546.2302).

(−)-8-Phenylmenthyl *cis*-2-(4-chlorophenyl)-1-(diethoxyphos-phonyl)cyclopropanecarboxylate *cis*-II-5c. δ_H (500 MHz) 0.77–0.88 (1 H, m), 0.88 (3 H, d, J 6.5, CH$_3$), 0.99–1.15 (2 H, m), 1.11 (3 H, t, J 7.0, OCH$_2$CH_3), 1.12 (3 H, t, J 7.0, OCH$_2$CH_3), 1.25 (3 H, s, CH$_3$), 1.37 (3 H, s, CH$_3$), 1.39–1.63 (4 H, m), 1.82–1.96 (2 H, m), 2.00–2.10 (1 H, m), 2.42 (1 H, dd, J 8.9, 18.3, H$_a$), 3.70–3.80 (1 H, m, OCH_2CH$_3$), 3.80–3.96 (3 H, m, OCH_2CH$_3$), 4.98 (1 H, td, J 4.4, 10.8, OCH), 7.00–7.05 (1 H, m), 7.16–7.32 (8 H, m); δ_C (125 MHz) 15.8 (d, $^3J_{CP}$ 2.5, OCH$_2$$CH_3$), 15.9 (d, $^3J_{CP}$ 2.9, OCH$_2$$CH_3$), 17.6 (d, $^2J_{CP}$ 1.7, CH$_b$), 21.4, 25.8, 26.7, 27.2, 27.6, 28.4 (d, $^1J_{CP}$ 197.8), 30.8 (d, $^2J_{CP}$ 3.2, CH$_a$), 31.0, 34.1, 39.8, 41.5, 49.5, 61.7 (d, $^2J_{CP}$ 6.6, OCH$_2$CH$_3$), 61.7 (d, $^2J_{CP}$ 5.6, OCH$_2$CH$_3$), 76.4 (OCH), 125.6 (×2), 125.7, 128.0 (×2), 128.4 (×2), 131.6 (×2), 133.1, 134.3 [d, $^3J_{CP}$ 4.7, C(*ipso*)], 151.4, 169.5 (d, $^2J_{CP}$ 9.5); δ_P (202 MHz) 20.8; HRMS *m/z* (EI) 546.2310 (M$^+$. $C_{30}H_{40}ClO_5P$ requires *M*, 546.2302).

(−)-8-Phenylmenthyl **trans-2-(4-chlorophenyl)-1-(diethoxy-phosphonyl)-cyclopropanecarboxylate trans-I-5c.** $\delta_{\rm H}$ (500 MHz) 0.35–0.44 (1 H, m), 0.50–0.59 (1 H, m), 0.61–0.78 (2 H, m), 0.65 (3 H, J 6.4, CH$_3$), 1.04–1.47 (2 H, m), 1.25 (3 H, s, CH$_3$), 1.33 (3 H, t, J 6.9, OCH$_2$CH_3), 1.34 (3 H, s, CH$_3$), 1.49 (3 H, t, J 7.1, OCH$_2$CH_3), 1.69–1.77 (1 H, m), 1.83–1.91 (1 H, m), 1.83–1.90 (1 H, m, H$_b$), 2.15–2.21 (1 H, m, H$_b$), 3.09 (1 H, m, H$_a$), 4.14–4.26 (2 H, m, OCH_2CH$_3$), 4.27–4.34 (2 H, m, OCH_2CH$_3$), 4.67 (1 H, td, J 4.6, 10.5, OCH), 6.92–7.34 (9 H, m); $\delta_{\rm C}$ (125 MHz) 14.8 (d, $^2J_{\rm CP}$ 1.8, CH$_b$), 16.0 (d, $^3J_{\rm CP}$ 7.1, OCH$_2$CH$_3$), 16.2 (d, $^3J_{\rm CP}$ 7.7, OCH$_2$CH$_3$), 21.1, 22.4, 27.1, 29.1 (d, $^1J_{\rm CP}$ 196.2), 29.8 (d, $^2J_{\rm CP}$ 3.2, CH$_a$), 30.8, 31.2, 33.8, 40.3, 41.3, 49.9, 62.4 (d, $^2J_{\rm CP}$ 5.8, OCH$_2$CH$_3$), 62.5 (d, $^2J_{\rm CP}$ 7.1, OCH$_2$CH$_3$), 77.3 (OCH), 125.7, 126.2 (×2), 128.3 (×2), 128.6 (×2), 128.6 (×2), 131.0 (×2), 132.7 [d, $^3J_{\rm CP}$ 1.7, C(ipso)], 133.8, 150.4, 166.5 (d, $^2J_{\rm CP}$ 5.6); $\delta_{\rm P}$ (202 MHz) 23.0; HRMS m/z (EI) 546.2286 (M$^+$. C$_{30}$H$_{40}$Cl$_5$P requires M, 546.2302).

(−)-8-Phenylmenthyl **trans-2-(4-chlorophenyl)-1-(diethoxy-phosphoryl)cyclopropanecarboxylate trans-II-5c.** $\delta_{\rm H}$ (500 MHz) −0.08 (1 H, q, J 11.9), 0.58–0.67 (1 H, m), 0.68 (3 H, d, J 6.3), 0.81–0.91 (1 H, m), 0.93–0.99 (1 H, m), 1.01 (3 H, s, CH$_3$), 1.19 (3 H, s, CH$_3$), 1.28–1.34 (1 H, m, H$_b$), 1.37–1.55 (4 H, m), 1.39 (3 H, t, J 7.0, OCH$_2$CH_3), 1.43 (3 H, t, J 7.0, OCH$_2$CH_3), 1.71–1.78 (1 H, m), 2.90 (1 H, m, H$_a$), 4.20–4.27 (2 H, m, OCH_2CH$_3$), 4.27–4.34 (2 H, m, OCH_2CH$_3$), 4.54 (1 H, td, J 4.1, 10.8, OCH), 7.07–7.11 (2 H, m), 7.16–7.23 (5 H, m), 7.28–7.33 (2 H, m); $\delta_{\rm C}$ (125 MHz) 15.3 (d, $^2J_{\rm CP}$ 1.1, CH$_b$), 16.1 (d, $^3J_{\rm CP}$ 7.3, OCH$_2$CH$_3$), 16.2 (d, $^3J_{\rm CP}$ 6.9, OCH$_2$CH$_3$), 21.1, 26.0, 26.2, 26.4, 28.6 (d, $^1J_{\rm CP}$ 193.9), 29.7 (d, $^2J_{\rm CP}$ 2.7, CH$_a$), 30.6, 34.0, 39.3, 39.8, 49.9, 62.5 (d, $^2J_{\rm CP}$ 6.1, OCH$_2$CH$_3$), 62.7 (d, $^2J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 75.9 (OCH), 125.5, 125.7 (×2), 128.4 (×2), 128.6 (×2), 131.2 (×2), 133.5 [d, $^3J_{\rm CP}$ 1.5, C(ipso)], 133.7, 151.9, 166.5 (d, $^2J_{\rm CP}$ 8.9); $\delta_{\rm P}$ (202 MHz) 23.7; HRMS m/z (EI) 546.2310 (M$^+$. C$_{30}$H$_{40}$ClO$_5$P requires M, 546.2302).

(−)-8-Phenylmenthyl **cis-1-(diethoxyphosphoryl)-2-(4-nitro-phenyl)cyclopropanecarboxylate cis-I-5d.** $[a]_{\rm D}^{25}$ −49.8 (c 1.0, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) 0.74–0.90 (1 H, m), 0.88 (3 H, d, J 6.4, CH$_3$), 0.99–1.10 (2 H, m), 1.13 (3 H, t, J 7.2, OCH$_2$CH_3), 1.21 (3 H, t, J 7.1, OCH$_2$CH_3), 1.29 (3 H, s, CH$_3$), 1.42 (3 H, s, CH$_3$), 1.43–1.62 (4 H, m), 1.87–1.97 (2 H, m), 1.97–2.04 (1 H, m), 2.70 (1 H, m, H$_a$), 3.72–3.81 (1 H, m, OCH_2CH$_3$), 3.81–3.93 (2 H, m, OCH_2CH$_3$), 3.94–4.03 (1 H, m, OCH_2CH$_3$), 5.02 (1 H, td, J 4.3, 10.7, OCH), 7.18–7.23 (1 H, m), 7.29–7.34 (4 H, m), 7.45 (2 H, d, J 7.8), 8.11 (2 H, d, J 7.8); $\delta_{\rm C}$ (125 MHz) 15.8 (d, $^3J_{\rm CP}$ 6.4, OCH$_2$CH$_3$), 15.9 (d, $^3J_{\rm CP}$ 5.9, OCH$_2$CH$_3$), 16.7 (CH$_b$), 21.4, 25.6, 26.6, 27.5, 29.0 (d, $^1J_{\rm CP}$ 196.7), 31.0, 31.8 (d, $^2J_{\rm CP}$ 3.3, CH$_a$), 34.1, 39.8, 41.4, 50.2, 62.0 (d, $^2J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 62.3 (d, $^2J_{\rm CP}$ 6.8, OCH$_2$CH$_3$), 76.0 (OCH), 123.1 (×2), 125.7, 125.8 (×2), 128.5 (×2), 131.3 (×2), 143.0 [d, $^3J_{\rm CP}$ 5.6, C(ipso)], 147.5, 151.4, 168.8 (d, $^2J_{\rm CP}$ 7.7); $\delta_{\rm P}$ (202 MHz) 20.5; HRMS m/z (EI) 557.2534 (M$^+$. C$_{30}$H$_{40}$NO$_7$P requires M, 557.2542).

(−)-8-Phenylmenthyl **cis-1-(diethoxyphosphoryl)-2-(4-nitro-phenyl)cyclopropanecarboxylate cis-II-5d.** $[a]_{\rm D}^{25}$ +56.2 (c 2.2, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) 0.79–0.90 (1 H, m), 0.99–1.15 (2 H, m), 0.88 (3 H, d, J 6.4, CH$_3$), 1.11 (3 H, t, J 7.5, OCH$_2$CH_3), 1.12 (3 H, t, J 6.9, OCH$_2$CH_3), 1.22 (3 H, s, CH$_3$), 1.36 (3 H, s, CH$_3$), 1.41–1.52 (1 H, m), 1.56–1.64 (3 H, m), 1.88–1.95 (2 H, m), 2.05–2.12 (1 H, m), 2.36 (1 H, m, H$_a$), 3.77–3.99 (4 H, m, OCH_2CH$_3$), 4.98 (1 H, td, J 4.3, 10.7, OCH), 6.95–7.00 (1 H, m), 7.19–7.24 (2 H, m), 7.28–7.32 (2 H, m), 7.41 (2 H, d, J 8.6), 8.13 (2 H, d, J 8.6); $\delta_{\rm C}$ (125 MHz) 15.8 (d, $^3J_{\rm CP}$ 5.4, OCH$_2$CH$_3$), 15.9 (d, $^3J_{\rm CP}$ 5.5, OCH$_2$CH$_3$), 17.6 (d, $^2J_{\rm CP}$ 1.3, CH$_b$), 21.4, 25.7, 26.5, 26.3, 28.2 (d, $^1J_{\rm CP}$ 196.4), 30.2 (d, $^2J_{\rm CP}$ 3.8, CH$_a$), 31.0, 34.0, 39.6, 41.5, 49.3, 61.9 (d, $^2J_{\rm CP}$ 5.9, OCH$_2$CH$_3$), 62.3 (d, $^2J_{\rm CP}$ 6.6, OCH$_2$CH$_3$), 76.6 (OCH), 123.0 (×2), 125.5 (×2), 125.6, 128.2 (×2), 131.2 (×2), 143.8 [d, $^3J_{\rm CP}$ 6.1, C(ipso)], 147.3, 151.6,

169.0 (d, $^2J_{\rm CP}$ 9.1); $\delta_{\rm P}$ (202 MHz) 20.5; HRMS m/z (EI) 557.2534 (M$^+$. C$_{30}$H$_{40}$NO$_7$P requires M, 557.2542).

(−)-8-Phenylmenthyl trans-1-(diethoxyphosphoryl)-2-(4-nitro-phenyl)cyclopropanecarboxylate trans I-5d. $[a]_{\rm D}^{25}$ −64.0 (c 0.89, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) 0.43 (1 H, q, J 11.7), 0.50–0.61 (1 H, m), 0.55 (3 H, d, J 6.2, CH$_3$), 0.70–0.90 (2 H, m), 1.03–1.13 (1 H, m), 1.13–1.20 (1 H, m), 1.20–1.40 (1 H, m), 1.24 (3 H, s, CH$_3$), 1.34 (3 H, s, CH$_3$), 1.37 (3 H, t, J 7.1, OCH$_2$CH_3), 1.49 (3 H, t, J 7.1, OCH$_2$CH_3), 1.70–1.78 (1 H, m), 1.94 (1 H, m, H$_b$), 2.21 (1 H, m, H$_b$), 3.18 (1 H, m, H$_a$), 4.15–4.25 (2 H, m, OCH_2CH$_3$), 4.26–4.35 (2 H, m, OCH_2CH$_3$), 4.66 (1 H, td, J 4.7, 10.5, OCH), 7.14–7.18 (1 H, m), 7.23–7.30 (4 H, m), 7.41 (2 H, d, J 8.7), 8.16 (2 H, d, J 8.7); $\delta_{\rm C}$ (125 MHz) 15.8 (d, $^2J_{\rm CP}$ 3.4, CH$_b$), 16.4 (d, $^3J_{\rm CP}$ 5.8, OCH$_2$CH$_3$), 16.6 (d, $^3J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 21.3, 23.0, 27.3, 29.9 (d, $^1J_{\rm CP}$ 186.9), 30.2 (d, $^2J_{\rm CP}$ 1.7, CH$_a$), 30.9, 31.2, 33.9, 40.2, 41.6, 50.0, 62.6 (d, $^2J_{\rm CP}$ 6.1, OCH$_2$CH$_3$), 62.8 (d, $^2J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 77.2 (OCH), 123.2 (×2), 125.5, 125.8 (×2), 128.0 (×2), 130.3 (×2), 142.0 [d, $^3J_{\rm CP}$ 2.0, C(ipso)], 147.2, 149.8, 165.8 (d, $^2J_{\rm CP}$ 6.5); $\delta_{\rm P}$ (202 MHz) 22.3; HRMS m/z (EI) 557.2542 (M$^+$. C$_{30}$H$_{40}$NO$_7$P requires M, 557.2542).

(−)-8-Phenylmenthyl trans-1-(diethoxyphosphoryl)-2-(4-nitro-phenyl)cyclopropanecarboxylate trans II-5d. $[a]_{\rm D}^{25}$ +2.5 (c 6.6, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) −0.1 (1 H, q, J 11.8), 0.52–0.65 (1 H, m), 0.57 (3 H, d, J 6.6, CH$_3$), 0.80–0.90 (1 H, m), 0.92–1.01 (1 H, m), 0.98 (3 H, s, CH$_3$), 1.13–1.22 (1 H, m), 1.17 (3 H, s, CH$_3$), 1.32–1.38 (1 H, m), 1.39–1.51 (2 H, m), 1.41 (3 H, t, J 7.3, OCH$_2$CH_3), 1.44 (3 H, t, J 7.2, OCH$_2$CH_3), 1.59 (1 H, m, H$_b$), 1.72–1.79 (1 H, m), 2.99 (1 H, m, H$_a$), 4.21–4.27 (2 H, m, OCH_2CH$_3$), 4.27–4.35 (2 H, m, OCH_2CH$_3$), 4.56 (1 H, td, J 4.2, 10.9, OCH), 7.17–7.22 (3 H, m), 7.29–7.33 (2 H, m), 7.32 (2 H, d, J 8.5), 8.11 (2 H, d, J 8.5); $\delta_{\rm C}$ (125 MHz) 16.0 (d, $^2J_{\rm CP}$ 1.9, CH$_b$), 16.5 (d, $^3J_{\rm CP}$ 6.4, OCH$_2$CH$_3$), 16.6 (d, $^3J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 21.3, 26.1, 26.6, 26.7, 29.2 (d, $^1J_{\rm CP}$ 193.6), 30.0 (d, $^2J_{\rm CP}$ 2.9, CH$_a$), 30.8, 34.1, 39.5, 40.3, 50.1, 62.8 (d, $^2J_{\rm CP}$ 6.3, OCH$_2$CH$_3$), 63.0 (d, $^2J_{\rm CP}$ 6.1, OCH$_2$CH$_3$), 76.2 (OCH), 123.3 (×2), 125.3, 125.4 (×2), 128.2 (×2), 130.5 (×2), 142.5 [d, $^3J_{\rm CP}$ 1.9, C(ipso)], 147.3, 151.4, 165.6 (d, $^2J_{\rm CP}$ 8.6); $\delta_{\rm P}$ (202 MHz) 22.8; HRMS m/z (EI) 557.2554 (M$^+$. C$_{30}$H$_{40}$NO$_7$P requires M, 557.2542).

(−)-Menthyl cis-1-(diethoxyphosphoryl)-2-phenylcycloprop-anecarboxylate cis I-6. $[a]_{\rm D}^{25}$ +30.7 (c 0.26, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) 0.83 (3 H, d, J 6.9, CH$_3$), 0.92 (3 H, d, J 6.5, CH$_3$), 0.95 (3 H, d, J 6.9, CH$_3$), 0.86–0.92 (1 H, m), 1.01–1.10 (1 H, m), 1.08 (3 H, t, J 7.1, OCH$_2$CH_3), 1.11 (3 H, t, J 6.9, OCH$_2$CH_3), 1.42–1.55 (3 H, m), 1.67–1.74 (2 H, m), 1.94–2.00 (1 H, m), 2.02–2.16 (3 H, m), 2.92 (1 H, m, H$_a$), 3.62–3.80 (3 H, m, OCH_2CH$_3$), 3.82–3.91 (1 H, m, OCH_2CH$_3$), 4.78 (1H, td, J 4.2, 11.0, OCH), 7.20–7.26 (1 H, m), 7.26–7.31 (2 H, m), 7.33–7.37 (2 H, m); $\delta_{\rm C}$ (125 MHz) 15.8 (d, $^3J_{\rm CP}$ 4.7, OCH$_2$C H$_3$), 15.9 (d, $^3J_{\rm CP}$ 3.7, OCH$_2$C H$_3$), 16.0, 17.6 (d, $^2J_{\rm CP}$ 1.8, CH$_b$), 20.5, 21.6, 23.1, 25.9, 27.4, 30.0 (d, $^1J_{\rm CP}$ 197.9), 33.4 (d, $^2J_{\rm CP}$ 4.3, CH$_a$), 33.9, 40.4, 46.9, 61.5 (d, $^2J_{\rm CP}$ 5.9, OCH$_2$CH$_3$), 61.9 (d, $^2J_{\rm CP}$ 6.4, OCH$_2$CH$_3$), 75.8 (OCH), 127.5, 128.1 (×2), 130.3 (×2), 135.3 [d, $^3J_{\rm CP}$ 5.9, C(ipso)], 169.8 (d, $^2J_{\rm CP}$ 7.7); $\delta_{\rm P}$ (202 MHz) 21.0; HRMS m/z (EI) 436.2369 (M$^+$. C$_{24}$H$_{37}$O$_5$P requires M, 436.2379).

(−)-Menthyl cis-1-(diethoxyphosphoryl)-2-phenylcycloprop-anecarboxylate cis II-6. $[a]_{\rm D}^{25}$ −67.2 (c 0.38, CHCl$_3$); $\delta_{\rm H}$ (500 MHz) 0.77 (3 H, d, J 6.8, CH$_3$), 0.83–0.95 (1 H, m), 0.90 (3 H, d, J 7.0, CH$_3$), 0.93 (3 H, d, J 6.0, CH$_3$), 1.02–1.15 (1 H, m), 1.07 (3 H, t, J 7.1, OCH$_2$CH_3), 1.12 (3 H, t, J 7.1, OCH$_2$CH_3), 1.16–1.56 (3 H, m), 1.67–1.74 (2 H, m), 1.93–2.00 (1 H, m), 2.02–2.14 (3 H, m), 2.68 (1 H, m, H$_a$), 3.65 (3 H, m, OCH_2CH$_3$), 3.85–3.94 (1 H, m, OCH_2CH$_3$), 4.76 (1 H, td, J 4.0, 10.8, OCH), 7.20–7.31 (3 H, m), 7.34–7.38 (2 H, m); $\delta_{\rm C}$ (125 MHz) 15.4, 15.8 (d, $^2J_{\rm CP}$ 6.6, OCH$_2$CH$_3$), 15.9 (d, $^2J_{\rm CP}$ 6.8,

OCH$_2$CH$_3$), 17.7 (CH$_b$), 20.7, 21.7, 22.5, 25.2, 28.3 (d, $^1J_{CP}$ 196.6), 31.1, 33.3 (d, $^2J_{CP}$ 2.4, CH$_a$), 33.9, 40.5, 46.9, 61.7 (d, $^2J_{CP}$ 6.0, OCH$_2$CH$_3$, ×2), 75.8 (OCH), 127.5, 128.0 (×2), 130.3 (×2), 135.4 [d, $^3J_{CP}$ 4.9, C(*ipso*)], 170.3 (d, $^2J_{CP}$ 7.8); δ_P (202 MHz) 21.0; HRMS *m/z* (EI) 436.2377 (M$^+$. C$_{24}$H$_{37}$O$_5$P requires *M*, 436.2379).

(−)-Menthyl *trans*-1-(diethoxyphosphoryl)-2-phenylcyclopropanecarboxylate *trans*-I-6. $[a]_D^{25}$ +5.6 (*c* 0.41, CHCl$_3$); δ_H (500 MHz) 0.37 (3 H, d, *J* 6.9, CH$_3$), 0.62 (1 H, q, *J* 11.8), 0.73 (3 H, d, *J* 7.0, CH$_3$), 0.79 (3 H, d, *J* 6.5, CH$_3$), 0.82–0.92 (1 H, m), 1.14–1.21 (1 H, m), 1.23–1.45 (2 H, m), 1.35 (3 H, t, *J* 7.1, OCH$_2$CH_3), 1.41 (3 H, t, *J* 7.1, OCH$_2$CH_3), 1.51–1.61 (2 H, m), 1.62–1.70 (2 H, m), 1.87 (1 H, m, H$_b$), 2.19 (1 H, m, H$_b$), 3.06 (1 H, m, H$_a$), 4.15–4.22 (2 H, m, OCH_2CH$_3$), 4.23–4.30 (2 H, m, OCH_2CH$_3$), 4.37 (1 H, td, *J* 4.4, 10.9, OCH), 7.14–7.28 (5 H, m); δ_C (125 MHz) 15.4, 15.6 (d, $^2J_{CP}$ 2.8, CH$_b$), 16.0 (d, $^3J_{CP}$ 5.8, OCH$_2$CH$_3$), 16.1 (d, $^3J_{CP}$ 6.8, OCH$_2$CH$_3$), 20.4, 21.5, 22.6, 25.2, 29.0 (d, $^1J_{CP}$ 188.3), 30.4 (d, $^2J_{CP}$ 3.7, CH$_a$), 30.9, 33.8, 39.8, 46.5, 62.5 (d, $^2J_{CP}$ 7.8, OCH$_2$CH$_3$), 62.6 (d, $^2J_{CP}$ 3.6, OCH$_2$CH$_3$), 75.4 (OCH), 127.6, 128.5 (×2), 129.2 (×2), 134.8 [d, $^3J_{CP}$ 1.9, C(*ipso*)], 166.5 (d, $^2J_{CP}$ 7.8); δ_P (202 MHz) 23.5; HRMS *m/z* (EI) 436.2362 (M$^+$. C$_{24}$H$_{37}$O$_5$P requires *M*, 436.2379).

(−)-Menthyl *trans*-1-(diethoxyphosphoryl)-2-phenylcyclopropanecarboxylate *trans*-II-6. $[a]_D^{25}$ −44.8 (*c* 0.38, CHCl$_3$); δ_H (500 MHz) 0.36 (1 H, q, *J* 11.9), 0.62 (3 H, d, *J* 7.0, CH$_3$), 0.71 (3 H, d, *J* 8.7, CH$_3$), 0.83 (3 H, d, *J* 7.0, CH$_3$), 0.84–0.94 (1 H, m), 1.01–1.06 (1 H, m), 1.18–1.26 (2 H, m), 1.34 (3 H, t, *J* 14.0, OCH$_2$CH$_3$), 1.40 (3 H, t, *J* 13.9, OCH$_2$CH_3), 1.54–1.63 (3 H, m), 1.85 (1 H, m, H$_b$), 1.90–1.98 (1 H, m), 2.17 (1 H, m, H$_b$), 3.04 (1 H, m, H$_a$), 4.14–4.21 (2 H, m, OCH_2CH$_3$), 4.22–4.29 (2 H, m, OCH_2CH$_3$), 4.41 (1 H, td, *J* 4.4, 10.9, OCH), 7.14–7.29 (5 H, m); δ_C (125 MHz) 14.8 (d, $^2J_{CP}$ 1.6, CH$_b$), 15.0, 15.9 (d, $^3J_{CP}$ 6.5, OCH$_2$CH$_3$), 16.1 (d, $^3J_{CP}$ 6.6, OCH$_2$CH$_3$), 20.7, 21.4, 22.2, 24.5, 28.9 (d, $^1J_{CP}$ 185.2), 29.7 (d, $^2J_{CP}$ 2.6, CH$_a$), 30.8, 33.7, 39.8, 46.6, 62.3 (d, $^2J_{CP}$ 6.2, OCH$_2$CH$_3$), 62.4 (d, $^2J_{CP}$ 5.5, OCH$_2$CH$_3$), 75.5 (OCH), 127.6, 128.4 (×2), 129.2 (×2), 134.7 [d, $^3J_{CP}$ 3.1, C(*ipso*)], 166.6 (d, $^2J_{CP}$ 6.2); δ_P (202 MHz) 23.5; HRMS *m/z* (EI) 436.2379 (M$^+$. C$_{24}$H$_{37}$O$_5$P requires *M*, 436.2379).

General procedure of cyclopropanation using diazomethane

A solution of excess of diazomethane in Et$_2$O (generated from *N*-methyl-*N*-nitrosotoluene-*p*-sulfonamide) was added to a solution of mixed substrates **3a–c** and **4** at 0 °C. The light-protected resultant solution was stirred at 0 °C to ambient temperature for 24 h and the excess of diazomethane and solvent were removed under reduced pressure. A solution of the crude pyrazolines in CH$_2$Cl$_2$ was purged with N$_2$ in a quartz flask. The solution was irradiated with a low-pressure mercury lamp at 25 °C. For **5a–c**, the crude product was separated by PLC (hexane–EtOAc = 5 : 1, twice) to provide *trans*- and *cis*-**5a–c**. Purification with PLC (hexane–EtOAc = 6 : 4, twice) and HPLC (WAKO Sil-100; hexane–^{i}PrOH = 10 : 1) provided the four cyclopropane derivatives **5a–c** and **6** (28–69%), each as a colorless oil.

Pyrazoline 7a generated from the reaction of *E*-3a with CH$_2$N$_2$. δ_H (500 MHz) 0.22 (1 H, q, *J* 11.9), 0.47–0.57 (1 H, m), 0.59 (3 H, d, *J* 7.4, CH$_3$), 0.62–0.76 (2 H, m), 1.03–1.12 (2 H, m), 1.30 (3 H, s, CH$_3$), 1.36–1.42 (6 H, m, OCH$_2$CH_3), 1.52 (3 H, s, CH$_3$), 1.67–1.75 (2 H, m), 3.99 (1 H, ddd, *J* 2.8, 9.1, 18.3, H$_a$), 4.22–4.39 (4 H, m, OCH_2CH$_3$), 4.62 (1 H, td, *J* 4.0, 10.4, OCH), 4.91 (1 H, ddd, *J* 5.1, 9.1, 18.2, H$_b$), 5.19 (1 H, ddd, *J* 2.8, 4.2, 18.2, H$_b$), 7.00–7.03 (2 H, m), 7.12–7.30 (8 H, m); δ_C (125 MHz) 16.4 (d, $^3J_{cp}$ 5.5, OCH$_2$CH$_3$, ×2), 21.3, 22.2, 27.4, 30.9, 31.9, 34.1, 40.3, 43.9 (CH$_a$), 50.3, 53.4, 64.3 (d, $^2J_{CP}$ 8.1,

OCH$_2$CH$_3$), 64.4 (d, $^2J_{CP}$ 7.1, OCH$_2$CH$_3$), 78.0 (OCH), 84.6 (CH$_b$), 103.8 (d, $^1J_{CP}$ 103.8), 125.3, 125.9, 126.0 (×2), 127.9 (×2), 128.0 (×2), 128.7 (×2), 137.5 (d, $^2J_{CP}$ 12.9), 150.2, 164.8.

Pyrazoline 7a generated from the reaction of *Z*-3a with CH$_2$N$_2$. δ_H (500 MHz) 0.72–2.27 (17 H, m), 1.22 (s, CH$_3$), 1.30 (s, CH$_3$), 1.32 (s, CH$_3$), 1.40 (s, CH$_3$), 2.13–2.20 (m, major-H$_a$), 3.26–3.42 (1 H, m, OCH_2CH$_3$), 3.63–3.77 (m, OCH_2CH$_3$, minor-H$_a$), 4.05–4.23 (2 H, m, OCH_2CH$_3$), 4.69–4.78 (1 H, m, major-H$_b$), 4.83–4.97 (2 H, m, major-H$_b$, minor-H$_b$), 5.00–5.10 (1 H, m, minor-H$_b$), 5.22 (1 H, td, *J* 4.4, 10.8, OCH), 7.05–7.52 (10 H, m); δ_C (125 MHz) 15.1 (d, $^3J_{CP}$ 6.8, major-OCH$_2$CH$_3$), 15.4 (d, $^3J_{CP}$ 6.8, minor-OCH$_2$CH$_3$), 15.9 (d, $^3J_{CP}$ 5.9, major-OCH$_2$CH$_3$), 16.0 (d, $^3J_{CP}$ 6.7, minor-OCH$_2$CH$_3$), 21.3 (major), 21.4 (minor), 22.7 (major), 24.7 (minor), 26.2 (major), 27.0 (minor), 29.4 (minor), 29.5 (major), 31.0 (major), 31.1 (minor), 34.1 (major, minor), 39.4 (major), 40.1 (minor), 42.2 (major), 44.1 (minor), 50.1 (minor), 50.2 (major), 62.2 (d, $^2J_{CP}$ 7.7, major-OCH$_2$CH$_3$), 62.6 (d, $^2J_{CP}$ 6.6, minor-OCH$_2$CH$_3$), 63.9 (d, $^2J_{CP}$ 6.7, minor-OCH$_2$CH$_3$), 64.2 (d, $^2J_{CP}$ 6.3, major-OCH$_2$CH$_3$), 77.9 (major-OCH), 78.0 (minor-OCH), 81.6 (minor-CH$_b$), 81.8 (major-CH$_b$), 103.0 (d, $^1J_{CP}$ 139.9, major), 103.1 (d, $^1J_{CP}$ 140.5, minor), 125.2 (major), 125.6 (×2, major), 125.8 (minor), 126.1 (×2, minor), 127.6 (major), 127.7 (minor), 127.8 (×2, major), 128.1 (×2, minor), 128.3 (×2, minor), 128.7 (×2, major), 130.4 (×2, minor), 130.5 (×2, major), 134.2 [d, $^3J_{CP}$ 5.5, major-C(*ipso*)], 134.4 [d, $^3J_{CP}$ 4.7, minor-C(*ipso*)], 150.4 (minor), 152.4 (major), 165.3 (d, $^2J_{CP}$ 3.2, major), 167.1 (d, $^2J_{CP}$ 3.9, minor); δ_p (202 MHz) 11.8 (major), 12.4 (minor).

Pyrazoline 7b generated from the reaction of *E*-3b with CH$_2$N$_2$. *trans*-Major isomer: δ_H (500 MHz) 0.23 (1 H, q, *J* 11.9), 0.46–0.57 (1 H, m), 0.60 (3 H, d, *J* 6.4, CH$_3$), 0.65–0.90 (2 H, m), 1.00–1.15 (2 H, m), 1.31 (3 H, s, CH$_3$), 1.37 (3 H, t, *J* 7.2), 1.39 (3 H, t, *J* 7.1), 1.52 (3 H, s, CH$_3$), 1.64 (1 H, br s), 1.68–1.74 (1 H, m), 3.72 (3 H, s OCH$_3$), 3.96 (1 H, ddd, *J* 2.8, 8.8, 18.0, H$_a$), 4.20–4.38 (4 H, m, OCH_2CH$_3$), 4.64 (1 H, td, *J* 4.3, 10.6, OCH), 4.88 (1 H, ddd, *J* 5.4, 8.8, 17.9, H$_b$), 5.15 (1 H, ddd, *J* 2.8, 4.3, 17.9, H$_b$), 6.74–6.77 (2 H, m), 6.90–6.94 (2 H, m), 7.12–7.28 (6 H, m); δ_C (125 MHz) 16.0 (OCH$_2$CH$_3$), 16.1 (OCH$_2$CH$_3$), 21.0, 21.9, 27.2, 30.7, 31.7, 33.9, 40.2, 40.3, 43.1 (CH$_a$), 50.1, 54.9 (OCH$_3$), 64.2 (d, $^2J_{CP}$ 6.7, OCH$_2$CH$_3$), 64.3 (d, $^2J_{CP}$ 7.2, OCH$_2$CH$_3$), 77.8 (OCH), 84.5 (CH$_b$), 103.8 (d, $^1J_{CP}$ 145.9), 114.2 (×2), 125.6, 126.3 (×2), 128.3 (×2), 129.6, 130.1 (×2), 150.6, 159.6, 165.4; δ_p (202 MHz) 13.7 (minor), 14.9 (major).

Pyrazoline 7b generated from the reaction of *Z*-3b with CH$_2$N$_2$. *cis*-Isomers: δ_H (500 MHz) 0.23–2.08 (20 H, m), 3.35–3.44 (1 H, m, OCH_2CH$_3$), 3.72 (s, OCH$_3$), 3.78 (s, OCH$_3$), 3.96 (ddd, *J* 2.8, 8.8, 17.9, H$_a$), 4.39–4.02 (3 H, m, OCH_2CH$_3$), 4.61–4.73 (m, H$_b$), 4.77–4.92 (m, H$_b$), 5.02 (td, *J* 4.3, 10.6, OCH), 5.18 (td, *J* 4.3, 10.6, OCH), 6.74–7.42 (9 H, m); δ_C (125 MHz) 15.6 (d, $^3J_{CP}$ 7.1, OCH$_2$CH$_3$), 16.3 (d, $^3J_{CP}$ 6.1, OCH$_2$CH$_3$), 16.4 (d, $^3J_{CP}$ 6.0, OCH$_2$CH$_3$ ×2), 21.3, 21.7, 22.2, 23.4, 27.3, 27.5, 31.0, 31.3, 31.4, 31.9, 34.1, 34.4, 39.6, 40.4, 40.5, 41.8 (CH$_a$), 41.9 (CH$_a$), 50.3, 50.4, 55.0 (OCH$_3$), 55.3 (OCH$_3$), 64.4 (d, $^2J_{CP}$ 7.1, OCH$_2$CH$_3$), 64.3 (d, $^2J_{CP}$ 6.9, OCH$_2$CH$_3$), 64.1 (d, $^2J_{CP}$ 5.8, OCH$_2$CH$_3$), 62.3 (d, $^2J_{CP}$ 7.4, OCH$_2$CH$_3$), 77.8 (OCH), 77.9 (OCH), 81.9 (CH$_b$), 84.5 (CH$_b$), 102.3 (d, $^1J_{CP}$ 103.2), 102.8 (d, $^1J_{CP}$ 125.2), 112.9 (×2), 113.9 (×2), 125.0, 125.3, 125.8 (×2), 126.0 (×2), 127.9 (×2). 128.3 (×2), 128.9 [d, $^3J_{CP}$ 3.1, C(*ipso*)], 129.0 [d, $^3J_{CP}$ 2.4, C(*ipso*)], 131.1 (×2), 131.2 (×2), 150.1, 151.8, 159.0 (d, $^2J_{CP}$ 5.3), 164.8 (d, $^2J_{CP}$ 2.9); δ_p (202 MHz) 12.5 and 14.9.

Pyrazoline 7c generated from the reaction of *E*-3c with CH$_2$N$_2$. *trans*-Major isomer: δ_H (500 MHz) 0.23 (1 H, q, *J* 11.8), 0.50–0.58 (1 H, m), 0.65–0.75 (2 H, m), 0.67 (3 H, d, *J* 6.6, CH$_3$), 1.04–1.16 (2 H, m), 1.10 (3 H, s, CH$_3$), 1.31 (3 H, s, CH$_3$), 1.39

(6 H, t, J 6.9, OCH$_2$CH_3), 1.68–1.75 (2 H, m), 3.97 (1 H, ddd, J 3.0, 8.9, 14.9, H$_a$), 4.15–4.37 (4 H, m, OCH_2CH$_3$), 4.61–4.69 (1 H, m, OCH), 4.90 (1 H, ddd, J 5.5, 8.9, 17.8, H$_b$), 5.14 (1 H, ddd, J 3.0, 4.6, 17.8, H$_b$), 6.95 (2 H, d, J 8.8), 7.13–7.43 (7 H, m); δ_C (125 MHz) 16.0 (d, $^3J_{CP}$ 1.9, OCH$_2$CH_3). 16.1 (d, $^3J_{CP}$ 2.0, OCH$_2$CH_3), 21.2, 22.0, 27.2, 30.7, 31.6, 33.9, 39.2, 40.3, 43.1 (CH$_a$), 50.2, 64.3 (d,$^2J_{CP}$ 6.8, OCH_2CH$_3$), 64.5 (d, $^2J_{CP}$ 8.4, OCH_2CH$_3$), 78.2 (OCH), 84.3 (CH$_b$), 103.7 (d, $^1J_{CP}$ 146.8), 125.6, 125.8, 126.3 (×2), 128.3 (×2), 129.1 (×2), 130.3 (×2), 136.3 [d, $^3J_{CP}$ 10.7, C(ipso)], 150.5, 165.1; δ_P (202 MHz) 13.4 (minor) and 14.6 (major).

Pyrazoline 7c generated from the reaction of Z-3c with CH$_2$N$_2$. cis-Isomers; δ_H (500 MHz) 0.18–2.25 (24 H, m), 3.37–3.51 (m, H$_a$), 3.62–3.79 (m, OCH_2CH$_3$), 4.05–4.40 (m, OCH_2CH$_3$), 4.64–4.69 (m, H$_b$), 4.80–4.90 (m, H$_b$), 5.03–5.09 (m, minor-OCH), 5.20 (td, J 4.4, 10.9, major-OCH), 6.86–7.46 (9H, m); δ_C (125 MHz) 15.5 (d, $^3J_{CP}$ 7.3, OCH$_2$CH_3), 15.8 (d, $^3J_{CP}$ 6.5, OCH$_2$CH_3), 21.5 (minor), 21.6 (major), 22.3 (major), 22.6 (minor), 26.5 (major), 27.5 (minor), 30.2 (minor), 31.0 (major), 31.3 (major), 31.4 (minor), 34.1 (minor), 34.4 (major), 39.5 (major), 40.5 (minor), 41.7 (minor), 41.9 (major), 43.3 (major-H$_a$), 43.7 (minor-H$_a$), 50.3, 50.4, 64.2 (OCH_2CH$_3$), 64.4 (OCH_2CH$_3$), 78.1 (major-OCH), 78.2 (minor-OCH), 81.4 (minor-H$_b$), 81.8 (major-H$_b$), 103.6 (d, $^1J_{CP}$ 146.8), 124.9 (minor), 125.2 (major), 125.3 (major), 125.5 (minor), 125.8 (×2, minor), 126.0 (×2, major), 127.5 (×2, minor), 127.9 [d, $^3J_{CP}$ 7.7, major-C(ipso)], 128.0 [d, $^3J_{CP}$ 5.8, minor-C(ipso)], 128.4 (×2, major), 128.8 (×2, major), 130.0 (×2, minor), 131.5 (×2, minor), 131.6 (×2, major), 150.0 (major), 152.1 (minor), 164.4 (d, $^2J_{CP}$ 4.2, major), 164.6 (d, $^2J_{CP}$ 6.6, minor); δ_P (202 MHz) 12.5 (minor), 14.9 (major).

Pyrazoline 8 generated from the reaction of E-4 with CH$_2$N$_2$. trans-Isomers: δ_H (500 MHz) 0.22 (q, J 11.8, minor), 0.52–1.11 (4 H, m), 0.58 (d, J 6.8, major-CH$_3$), 0.63 (d, J 6.9, minor-CH$_3$), 0.71 (d, J 6.8, major-CH$_3$), 0.77 (d, J 6.3, minor-CH$_3$), 0.79 (d, J 7.3, major-CH$_3$), 0.85 (d, J 7.0, minor-CH$_3$),1.16–1.33 (3 H, m), 1.34–1.40 (6 H, m, OCH$_2$CH_3), 1.52–1.76 (3 H, m), 1.95–2.03 (m, major), 3.81–3.96 (1 H, m, H$_a$), 4.17–4.35 (4 H, m, OCH_2CH$_3$), 4.50 (1 H, td, J 4.3, 10.9, OCH), 4.90–4.99 (1 H, m, H$_b$), 5.03–5.11 (1 H, m, H$_b$), 6.89–6.93 (1 H, m), 6.94–6.98 (1 H, m), 7.17–7.24 (3 H, m); δ_C (125 MHz) 15.1 (major), 15.4 (minor), 15.9 (d, $^3J_{CP}$ 2.7, minor-OCH$_2$CH_3), 16.0 (d, $^3J_{CP}$ 2.9, major, minor-OCH$_2$CH_3), 16.1 (d, $^3J_{CP}$ 2.7, major-OCH$_2$CH_3), 20.5 (minor), 20.6 (major), 21.4 (major), 21.5 (minor), 22.1 (major), 22.5 (minor), 24.5 (minor), 24.9 (major), 30.8 (minor), 30.9 (major), 33.6 (minor), 33.7 (major), 38.8 (minor), 39.5 (major), 43.3 (minor), 43.4 (major), 46.2 (minor), 46.3 (major), 63.4 (d, $^2J_{CP}$ 7.8, major-OCH_2CH$_3$), 64.2 (d, $^2J_{CP}$ 6.4, major, mnior-OCH_2CH$_3$), 64.3 (d, $^2J_{CP}$ 7.3, minor-OCH_2CH$_3$), 76.3 (minor-OCH), 76.7 (major-OCH), 85.5 (minor-CH$_b$), 86.6 (major-CH$_b$), 104.1 (d, $^1J_{CP}$ 145.3, major), 104.3 (d, $^1J_{CP}$ 140.2, minor), 127.9 (minor), 128.0 (major), 128.3, 128.4, 128.9, 129.0, 138.5 [d, $^3J_{CP}$ 11.5, major-C(ipso)], 139.5 [d, $^3J_{CP}$ 11.2, minor-C(ipso)], 164.8 (d, $^2J_{CP}$ 4.0, major), 165.1 (d, $^2J_{CP}$ 2.2, minor); δ_P (202 MHz) 14.1 (major), 14.4 (minor).

Pyrazoline 8 generated from the reaction of Z-4 with CH$_2$N$_2$. cis-Isomers: δ_H (500 MHz) 0.75–1.25 (16 H, m), 2.21–2.30 (1 H, m), 2.46–2.62 (2 H, m), 2.64–2.79 (2 H, m), 2.93–3.21 (3 H, m), 3.30–3.45 (1 H, m, H$_a$), 3.64–3.79 (1 H, m, OCH_2CH$_3$), 3.82–3.95 (1 H, m, OCH_2CH$_3$), 4.00–5.18 (2 H, m, OCH_2CH$_3$), 4.70–5.15 (3 H, m, OCH, H$_b$), 7.25–7.65 (3 H, m), 7.81–7.95 (2 H, m); δ_C (125 MHz) 15.7 (major), 15.8 (d, $^3J_{CP}$ 1.9, minor-OCH$_2$CH_3), 15.9 (d, $^3J_{CP}$ 2.1, minor-OCH$_2$CH_3), 15.9 (minor), 16.2 (d, $^3J_{CP}$ 4.2, major-OCH$_2$CH_3), 16.3 (d, $^3J_{CP}$ 4.1, major-OCH$_2$CH_3), 20.8 (major), 20.9 (minor), 21.9 (major), 22.0 (minor), 22.8 (major), 23.1 (minor), 25.3 (major), 25.6 (minor), 31.4 (minor), 31.5 (major), 34.1 (major), 34.2 (minor), 40.4

(minor), 40.5 (major), 45.0 (major), 45.1 (minor), 46.9 (minor), 47.0 (major), 62.5 (d, $^2J_{CP}$ 7.3, major-OCH_2CH$_3$), 62.6 (d, $^2J_{CP}$ 8.1, minor-OCH_2CH$_3$), 63.8 (d, $^2J_{CP}$ 6.2, major-OCH_2CH$_3$), 63.9 (d, $^2J_{CP}$ 6.4, minor-OCH_2CH$_3$), 77.1 (minor-OCH), 77.2 (minor-OCH), 81.6 (major-H$_b$), 81.9 (minor-H$_b$), 102.7 (d, $^1J_{CP}$ 144.1, major), 102.9 (d, $^1J_{CP}$ 144.1, minor), 127.5, 127.8 (×2, major), 127.9 (×2, minor), 129.9 (×2, minor), 130.0 (×2, major), 133.9 [d, $^3J_{CP}$ 5.3, minor-C(ipso)], 134.2 [d, $^3J_{CP}$ 5.4, major-C(ipso)], 166.3 (d, $^2J_{CP}$ 2.6); δ_P (202 MHz) 11.9 (minor), 12.1 (major).

X-Ray structure determination

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC reference number 168719. See http://www.rsc.org/suppdata/p1/b1/b108925k/ for crystallographic files in .cif or other electronic format.

A crystal suitable for X-ray structure determination was mounted on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined by autoindexing several images in each data set separately with the DENZO program.[18] For each data set, rotation images were collected in 3° increments with a total rotation of 180° about φ (60 frames). Data were processed by using the SCALEPACK program.[18] The structures were solved by a direct method and refined by full-matrix least-squares methods with the TeXsan (Rigaku) program.[19]

Crystal data. Orthorhombic system, space group $P2_12_12_1$ (no. 19), $a = 9.4830(3)$, $b = 13.9840(4)$, $c = 23.2390(6)$ Å, $V = 3081.7(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.170$ g cm^{-3}, $F(000) = 2168$, $R = 0.0891$ ($R_w = 0.1566$) for 2650 reflections out of 4088 collected (344 parameters) with $I > 3\sigma(I)$. Goodness of fit = 1.582.

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