Stereoselective Michael Additions of Phosphorylated Allyl Carbanions − Synthesis of Functionalized Cyclopentylphosphonates and Phosphane Oxides[‡]

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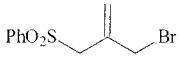
Dimethyl (2-chloromethyl-2-propenyl)phosphonate (**3b**) and (*tert*-butyl)[2-(chloromethyl)-2-propenyl](phenyl)phosphane oxide (**3d**) were prepared and their reactions with α,β-unsaturated esters **5a**–**c** and ketone **5d**, acting as phosphorylated trimethylenemethane equivalents by a [3+2] strategy, were investigated. With the use of LDA in the presence of DMPU, the Michael addition proceeded with high stereoselectivity and regioselectivity to afford methylenecyclopentyl-substituted dimethyl phosphonate or (*tert*-butyl)(phenyl)phosphane oxide derivatives **6a**–**d** and **14**(S_P). Compound **3d** reacted with **5a**–**b** and **5d** to give phosphorous diastereomers **10**(R_P) and **11**(S_P), **12**(R_P) and **13**(S_P), and **16**(R_P) and **17**(S_P), with complete stereoselectivity at the three stereogenic centers of the 5-methylenecyclopentanes, all possessing 1,2-*trans* and 2,3-*trans* stereochemistry. Formation of open-chain *syn* adduct **15** and of a 2,3-*cis*-disubstituted cyclopentane compound **18**(S_P) could also be achieved. The stereochemical features of all the products were ascertained by 1D and 2D NMR spectra.

Introduction

One of the important features of tertiary phosphane oxides in modern synthetic chemistry is that they can be used as precursors for the synthesis of phosphane ligands and as substrates in carbanion-stabilized reactions.[1−11] The impetus for the synthesis of these compounds has evolved over the years from the original intrinsic interest in the preparation of optically active *P*-chiral systems and their stereochemistry to the rapidly growing utility of such compounds in various actively developing fields.[12] Our previous studies of 2-(bromomethyl)allyl phenyl sulfone (**A**) in a [3+2] Michael-induced ring-closure (MIRC), leading stereoselectively and α-regioselectively to sulfone-substituted methylenecyclopentanes,[13] prompted us to study the so far unknown *P*-substituted allyl halides **3**. We wished to explore the [3+2] strategy for the synthesis of five-membered carbocycles from **3** because it offers the possibility of forming two carbon−carbon bonds under the same reaction conditions.[14,15] It was also of interest to determine the regiochemistry of Michael additions of *P*-allyl carbanions derived from **3,** in view of the fact that anions derived from the analogous sulfone had undergone additions through the α-carbon atom,[13] while Haynes et al.[16] have shown that the anions derived from allylic diphenylphosphane oxides react with Michael acceptors through the γ-carbon atom of the reagent.



A

We describe here the synthesis of allyl chlorides **3b** and **3d**, substituted with phosphonate and phosphane oxide moieties, and the reactions between their derived allyl carbanions and α,β-unsaturated esters **5a**−**c** and ketone **5d**, in an effort to achieve stereoselective formation of novel phosphorylated methylenecyclopentanes. The stereochemical and configurational assignments of all products are based on 1D and 2D NMR spectra.

Results and Discussion

1. Synthesis of Allylphosphorus Derivative Donors 3 for Michael Additions

The substrates **3**, required as Michael donors, were prepared by treatment of dimethyl phosphite (**2a**) and *tert*-butyl(phenyl)phosphane oxide (**2b**), respectively, with either methallyl chloride (**1a**) or dichloro olefin **1b** (Scheme 1). As starting material we first chose (*tert*-butyl)(phenyl)phosphane oxide (**2b**), which was treated with sodium hydride followed by dichloro olefin **1b** to afford **3d**, needed in the MIRC reaction with substrates **5**.

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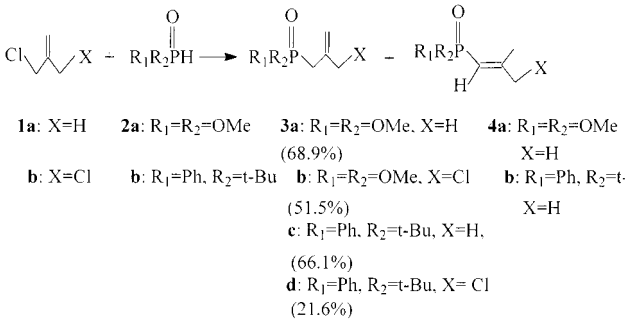
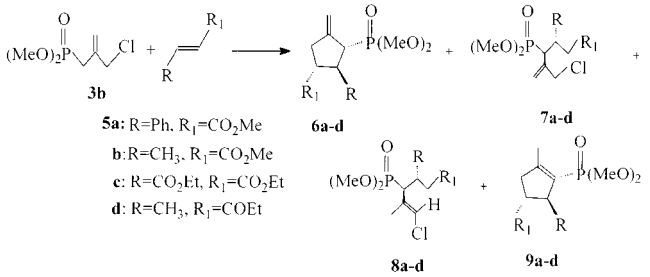


Scheme 1. Synthesis of allylphosphorous compounds **3**

The synthesis of phosphane oxide **3c** and phosphonates **3a** and **3b** was achieved in a similar manner (Scheme 1). When treatment of **2a** and **2b** with methallyl chloride (**1a**) was carried out at room temperature, compounds **3a** and **3c** were formed, respectively, together with significant amounts of rearranged isomers **4a** and **4b**. At 0 °C, no rearrangement product **4a** was found and only 5% of **4b** was present. There was no improvement at temperatures below 0 °C. In treatment of **2a** and **2b** with 2-chloromethallyl chloride (**1b**), no double bond rearrangement product of type **4** was found, but the yield of **3d** was still very low (Scheme 3).

2. Cyclopentanations with Dimethyl [2-(Chloromethyl)-2-propenyl]phosphonate (3b) as Donor

In order to investigate the feasibility and proper reaction conditions for a one-pot Michael addition−alkylation sequence to afford 5-membered, P-containing carbocycles, the reactions of chloroallyl dimethylphosphonate (**3b**) with (*E*)-α,β-unsaturated esters **5a**−**c** and with ketone **5d** were examined before the reactions of the related phosphane oxide **3d**. Though the reaction was initially unsuccessful, the phosphonylated methylenecyclopentanes **6** were ultimately obtained in a regioselective and stereoselective manner. Low-temperature (−95 to −78 °C) deprotonation of dimethyl allylphosphonate (**3b**) with LDA in THF, followed by addition of **5a**, afforded no Michael adduct. However, in the presence of *N*,*N*-dimethylpropylene urea (DMPU), quenching the reaction after 4 h, stereoselective MIRC was achieved to form *trans*,*trans* adduct **6a**, albeit in low yield (Table 1). The open-chain Michael adduct **8a** (4%) was also isolated, together with starting material (Scheme 2). The allylphosphonate **8a** is apparently the result of double-bond rearrangement of **7a**. An initial Michael adduct **7a** was not detected and **8a** failed to cyclize under reaction conditions. On the other hand, the open-chain adducts **7b** and **8b** were detected, in addition to the methylenecyclopentane **6b**, during addition of the lithio derivative of **3b** to methyl crotonate (**5b**). The yield of the inseparable mixture of Michael adducts **7b** and **8b** was only 5% (Table 1).



Scheme 2. Reaction between **3b** and Michael acceptors **5a**−**d**

The stereochemical assignments for the cyclopentanes and the open-chain adducts are based on ^{1}H NMR and ^{13}C NMR evidence and COSY, HMQC, and NOESY measurements. For instance, the main NOESY cross-peaks between protons for **6a** and **6b** are shown in Figure 1, and for **8a** in Figure 2 (note the special numbering of protons in the Figures). NOESY cross-peaks between the aromatic *ortho*-protons and H^2, as well as between the aromatic *ortho*-protons and H^4, indicate that **6a** possesses the *trans*,*trans* stereochemistry. Similarly, the stereochemistry of **6b** was obvious from NOESY cross-peaks between the methyl protons and H^2 and H^4. For the open-chain product **8a**, the *anti* stereochemistry between the phenyl and the chloropropene group was deduced from NOESY interactions between the vinylic CH_3 and the CH_2 protons, while the (*E*) stereochemistry of the double bond was obvious from C=CH to CH_2 interactions (Figure 2).

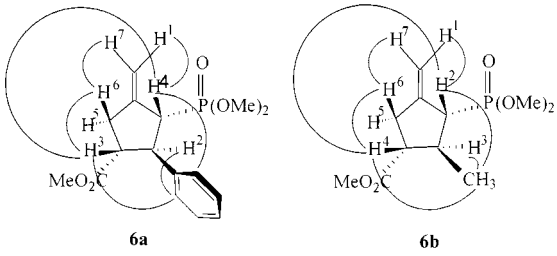
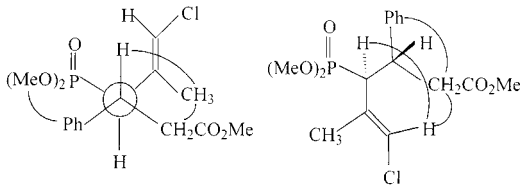


Figure 1. The main NOESY cross-peaks between protons for **6a** and **6b**

Under the above reaction conditions, the yield of conjugate addition of phosphonate **3b** to diethyl fumarate (**5c**) fol-

Table 1. Reaction between **3b** and Michael acceptors **5a**−**d**

Acceptor	Reaction conditions Temp. [°C]	Time [h]	Product, yield (%) **6**	**7**	**8**	**9**
5a	−95	4	45	−	4	−
5b	−95	4	45	< 5 (**7b** and **8b**)		−
5c	−78 to 50	3	26	−	−	−
5d	−78 to 2	6	60 (**6d**/**9d** = 10:1)	41		



8a

Figure 2. The main NOESY cross-peaks between protons for **8a**

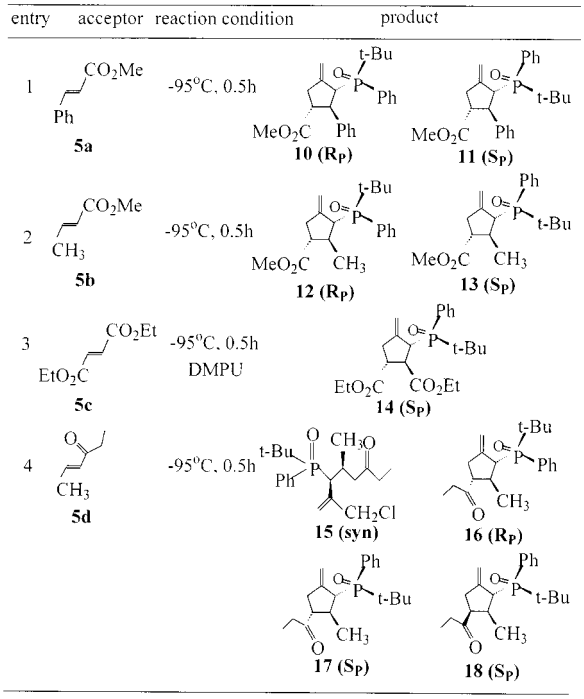
lowed by ring-closure was very poor (< 15%). A change of the reaction temperature from −95 to −78 °C and allowing the mixture to warm slowly from −78 to −50 °C over 3 h improved the yield somewhat (26%). A further increase in temperature, to −20 °C, resulted mainly in polymerization.

The lithio derivative of [2-(chloromethyl)allyl]phosphonate **3b** reacted with 4-hexen-3-one (**5d**) much more slowly than with the unsaturated esters. A stepwise increase in reaction temperature (from −78 to −68 °C) resulted in conjugate addition, to provide the open-chain adduct **7d** (41%). A further increase of temperature to −2 °C (over 6 h) resulted in cyclization to give **6d** and its olefin isomer product **9d** (60%, ratio **6d/9d** = 10:1). The stereochemistry of the cyclized products **6d** and **9d**, as well as of the open-chain product **7d**, was established by ^{1}H NMR and ^{13}C NMR evidence and COSY, HMQC, and NOESY measurements, in similar manner to that described for **6a**. These results are consistent with a Michael addition of the allylphosphonate carbanion to the unsaturated system **5a**−**d**, preferentially forming an *anti* product (see Figure 2 for **8a**), which undergoes base-induced ring-closure to the *trans*,*trans*-phosphonate-substituted methylenecyclopentanes **6a**−**d**. In the event, the slow addition to the unsaturated ketone **5d** permitted the isolation of the *anti* addition product **7d**, which indeed cyclized to the *trans*,*trans*-substituted methylenecyclopentane **6d** when the temperature was raised. The stereoselectivity of the *anti* Michael addition can be explained by Li cation chelation in the transition state by the oxygen atoms of the phosphonate group and the carbonyl groups.

3. Cyclopentanations with (*tert*-Butyl)[2-(chloromethyl)-2-propenyl](phenyl)phosphane Oxide (3d) as a Donor

(*tert*-Butyl)[2-(chloromethyl)allyl](phenyl)phosphane oxide **3d** reacted (as its lithio derivative) with (*E*)-α,β-unsaturated esters **5a**−**c** and unsaturated ketone **5d** in a similar manner to **3b**, affording cyclic products (Scheme 3 and Table 2). Some unchanged **3d** was also isolated. Unlike in the case of phosphonate carbanions, no DMPU was needed for these reactions to take place, except with diester **5c**.

All MIRC reactions occurred in a regioselective manner at the α-terminus of the (*tert*-butyl)(phenyl)phosphinoyl carbon atom of the allylic carbanion and were characterized by complete stereoselectivity at the three stereogenic centers (*trans*,*trans* in the resulting methylenecylopentane ring), except for the case of ketone **5d**, which produced a 3:1 mixture of *trans*,*trans* product **17** together with *trans*,*cis* product **18**. Because of the chiral center on P, a pair of diastereomers (racemic) was obtained in all cases, differing only in the configuration at P (S_p and R_p).



Scheme 3. Reaction between **3d** and Michael acceptors **5a**−**d**

Table 2. Yields of products in the reaction between **3d** and Michael acceptors **5a**−**d**

Acceptor	Product	Ratio	Total yield (%)
5a	**10** (R_p),**11** (S_p)	**10/11** (5:4)	39.9
5b	**12** (R_p), **13** (S_p)	**12/13** (5:2)	52.0
5c	**14** (S_p)		25.1
5d	**15** (*cis*)		38.5
	16 (R_p)		6.3
	17 (S_p), **18** (S_p)	**17/18** (3:1)	26.5

The adduct ratios in Table 2 were calculated from integrated ^{1}H NMR spectra of the products. The stereochemical and configurational assignments in the ring and in the side chain, about the chiral phosphorous element (Table 2), are based on ^{1}H NMR and ^{13}C NMR evidence and COSY, HMQC, and NOESY data. For instance, in both **10** and **12** (Figure 3), H^1, H^2, and the *tert*-butyl protons are spatially close and give rise to NOESY cross-peaks. No NOESY cross-peaks were found between the aromatic *ortho*-protons of the (*tert*-butyl)(phenyl)phosphinoyl group and the H^1 proton, while NOESY cross-peaks between the former protons and H^2 were observed, as well as with H^3, and with the *tert*-butyl protons. Some other observed NOESY cross-peaks are shown in Figure 3. It appears that the P chirality in **10** and **12** is of the (R_P) type.

According to their NOESY spectra, **11** and **13** have (S_P)-type stereochemical structures. Although no NOESY cross-peaks between the aromatic *ortho*-protons and the H^1 proton was observed in **13**, the NOESY cross-peaks between the *tert*-butyl protons and H^2, H^3, and the C-3 methyl group indicated that the *tert*-butyl group was remote from the H^1 proton. There were NOESY cross-peaks between

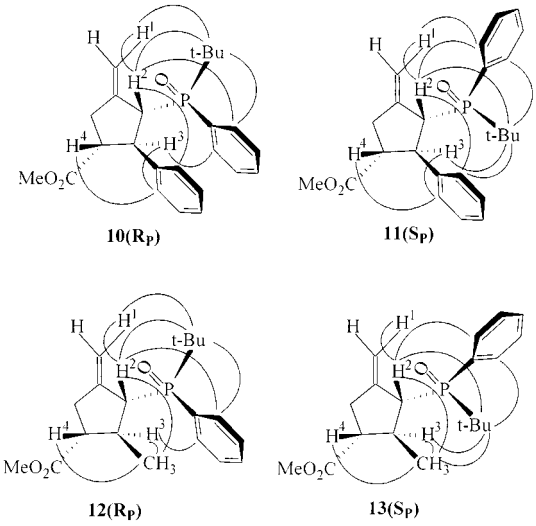


Figure 3. The main NOESY cross-peaks between protons for **10**, **11**, **12**, and **13**

the aromatic *ortho*-protons and H^2 and the *tert*-butyl group, suggesting that the phenyl group on P is closer in space to H^1 than the *tert*-butyl group is.

Treatment of the carbanion from allylphosphane oxide **3d** with diester **5c** in the presence of DMPU afforded a low yield (25%) of a single product **14**, the structure of which is analogous to that of **13**. Changing the reaction temperature did not improve the yield. The stereochemical assignments for the cyclopentane substituents are based on ^1H and ^{13}C NMR evidence and COSY, HMQC, and NOESY data. The observed NOESY proton cross-peaks are shown in Figure 4 (S_p type).

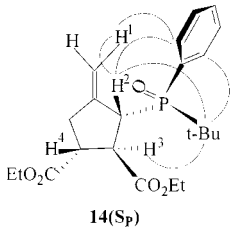


Figure 4. The main NOESY cross-peaks between protons for **14**

Unsaturated ketone **5d** was a poorer Michael acceptor for the phosphane oxide **3d** than the unsaturated esters **5a**−**c**; this was also observed with allylphosphonate **3b**. Low-temperature deprotonation of **3d** with LDA in THF, followed by addition of 4-hexen-3-one **5d** and quenching of the mixture after 0.5 h, resulted in the selective cyclization of the *anti* adducts to afford **16**, **17**, and **18** (Scheme 3), whereas the open-chain *syn* adduct **15** was left unchanged. The stereochemical assignments are based on spectroscopic data. For instance, the NOESY cross-peaks (Figure 5) observed between the *tert*-butyl protons and H^1 support structure **16**, while for **17** and **18** NOESY data indicate the *P*-phenyl group to be spatially close to H^1. Cross-peaks between the methyl group protons and H^4 were present in **16** and **17**, but were not found for **18**. Therefore, protons H^3 and H^4 are tentatively assigned as *cis* in **18**, but *trans* in **16** and **17**.

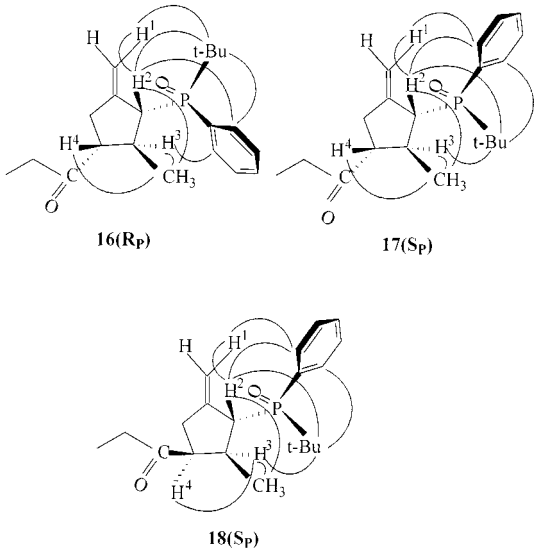


Figure 5. The main NOESY cross-peaks between protons for **16**, **17**, and **18**

The effectiveness of cyclopentanation of allylphosphorus derivatives **3** is not as good as that in the reaction of the analogous 2-(bromomethyl)allyl phenyl sulfone (**A**) with **5a**−**d**,[13] because the bulky groups bonded to the phosphorus atom hinder the Michael addition and in some cases the allylic carbanion also attacks through the γ-terminus. For instance, treatment of the chlorine-free methallylphosphane oxide **3c** with cinnamate **5a** under the same conditions as for **3d** resulted in addition through the α-terminus (**19**) as well as through the γ-terminus (**20**) in a ratio of 2:1 (Table 3).

Table 3. Reaction between **3a**−**c** and Michael acceptors **5a** and nitrostyrene

donor	reaction condition	product
3c	-95°C, 0.5h	**19** (68.3%) + **20** (30.8%)
3a	-95°C, 2h	**21** (81.7%)
3a	LDA -95°C,10min	**22** (69.1%)
3b	LDA,DMPU -95°C,10min	**23** (86.7%)

The highest yield and reaction rates in the reactions between **3a** and **3b** and **5a** was for addition product **21**, from **3a** (82%, 2 h) (Table 3), while from **3b** the yield was 49% after 4 h (for **6a** + **8a**, Table 1). The lower reactivity of the Cl-substituted allyl anion may be due to the higher electronegativity of chlorine, as well as to Li ion chelation by chlorine,[17] which reduces the carbanion reactivity.

Compounds **3a** and **3b** reacted with nitro olefin (*E*)-Ph−CH=CH−NO_2 only through the γ-terminus, to afford open-chain adducts (*E*+*Z*)-**22** and **23**, respectively, the major isomer possessing (*Z*) stereochemistry (Table 3). The change in regioselectivity may be due to the fact that the nitro group is not a good Li ion chelator.[18]

Conclusion

Allylphosphonate **3b** and allylphosphane oxide **3d**, incorporating allyl chloride moieties, and thus representing the first P-containing methylenemethane equivalents, have been prepared and their MIRC reactions with unsaturated esters and ketone **5a−d** examined. The Michael addition proceeded with high *anti* stereoselectivity and α-regioselectivity to form *P*-substituted methylenecyclopentanes. Methallylphosphonate **3a** and methallylphosphane oxide **3c** also gave *anti*-stereoselective Michael addition products, but attack from the γ-position was also observed, as was the case with a nitro olefin acceptor.

Experimental Section

General experimental techniques and analytical measurements were performed as previously described.[19] − Melting points are uncorrected. − High resolution mass spectra (DCI) were recorded at 60 eV. − ^{1}H and ^{13}C and 2D NMR spectra were taken with a Bruker AM 300 or Bruker AM 600 spectrometer. − (*tert*-Butyl)-(phenyl)phosphane oxide was prepared through a Grignard reaction.[20,21] Reactions were performed at −95 or −78 °C.

General Procedure for the Synthesis of Michael Addition Donors 3a−d (cf. Scheme 1): Dimethyl phosphite (for **3a** and **3b**, 5.0 mmol) or (*tert*-butyl)(phenyl)phosphane oxide (for **3c** and **3d**, 5.0 mmol) in 5 mL of THF was added dropwise at 0 °C to a suspension of sodium hydride (60% in dispersion in mineral oil, 5.0 mmol) in dry THF (5 mL). The addition was accompanied by formation of hydrogen and sodium dimethyl phosphite or sodium (*tert*-butyl)-(phenyl)phosphane oxide. After 5 min, 2-(chloromethyl)-1-propene (**1a**) (for **3a** and **3c**, 5.0 mmol) or 3-chloro-2-(chloromethyl)-1-propene (**1b**) (for **3b** and **3d**, 5.0 mmol) in THF (4 mL) was very slowly added dropwise to the mixture with stirring. The reaction mixture was then stirred for 3−4 h at 0 °C. Ice/water was added and the product was extracted with chloroform. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The products were purified by column chromatography on silica gel; the yields are indicated in Scheme 1.

Dimethyl (2-Methyl-2-propenyl)phosphonate (3a): Elution: acetone/petroleum ether (3:5). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.95 (dd, *J* = 3.0, 1.5 Hz, 1 H), 4.90 (d, *J* = 4.8 Hz, 1 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 2.64 (d, *J* = 1.0 Hz, 1 H), 2.57 (d, *J* = 1.0 Hz, 1 H), 1.89 (m, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 135.8, 115.5, 52.6, 52.5, 34.3, 23.4. − MS (DCI/CH_4): *m*/*z* (%) = 165 (100) [MH^+]. − HRMS (DCI) for $C_6H_{14}O_3P$ [MH^+]: calcd. 165.0681; found 165.0679.

Dimethyl [2-(Chloromethyl)-2-propenyl]phosphonate (3b): Elution: acetone/petroleum (1:2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.35 (dd, *J* = 5.1, 1.0 Hz, 1 H), 5.21 (dd, *J* = 5.4, 1.0 Hz, 1 H), 4.20 (dd, *J* = 2.2, 1.0 Hz, 2 H), 3.79 (s, 3 H), 3.75 (s, 3 H), 2.81 (d, *J* = 1.0 Hz, 1 H), 2.74 (d, *J* = 1.0 Hz, 1 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 135.7, 119.4, 52.8, 52.7, 48.0, 29.3. − MS (DCI/CH_4): *m*/*z* (%) = 163 (100), 199 (30) [MH^+]. − HRMS (DCI) for $C_6H_{13}O_3PCl$ [MH^+]: calcd. 199.0291; found 199.0295.

(*tert*-Butyl)(2-methyl-2-propenyl)(phenyl)phosphane Oxide (3c): Elution: acetone/ethyl acetate (1:1). − M.p. 91−93 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (m, 2 H), 7.49 (m, 3 H), 4.82 (m, 1 H), 4.75 (m, 1 H), 2.93 (m, ABX, 2 H), 1.81(s, 3 H), 1.15 (d, *J* = 14.4 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 136.7, 131.6, 130.9, 129.48, 127.5, 115.2, 32.9, 32.5, 24.1, 23.9. − MS (DCI/CH_4): *m*/*z* (%) = 125 (100), 180 (30), 236 (42). − HRMS (DCI) for $C_{14}H_{21}OP$: calcd. 236.1330; found 236.1330.

(*tert*-Butyl)(2-methyl-1-propenyl)(phenyl)phosphane Oxide (4b): Elution: acetone/ethyl acetate (1:1). Yield: 4.82%. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (m, 2 H), 7.47 (m, 3 H), 5.90 (dt, *J* = 25.8, 1.2 Hz, 1 H), 2.00 (t, *J* = 0.9 Hz, 3 H), 1.97 (dd, *J* = 2.4, 0.9 Hz, 3 H), 1.11 (d, *J* = 14.7 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.46, 131.55, 130.66, 127.51, 112.04, 32.32, 28.61, 23.60, 21.33. − MS (DCI/CH_4): *m*/*z* (%) = 180 (100), 236 (58). − HRMS (DCI) for $C_{14}H_{21}OP$: calcd. 236.1330; found 236.1350.

(*tert*-Butyl)[2-(chloromethyl)-2-propenyl](phenyl)phosphane Oxide (3d): Elution: acetone/petroleum ether (1:1). − M.p. 102−104 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (m, 2 H), 7.52 (m, 3 H), 5.20 (dd, *J* = 3.6, 0.6 Hz, 1 H), 4.98 (dd, *J* = 3.9, 0.6 Hz, 1 H), 4.31 (ddd, *J* = 11.7, 1.8, 1.2 Hz, 1 H), 3.96 (dd, *J* = 11.7, 0.9 Hz, 1 H), 3.08 (m, ABX, 2 H), 1.17 (d, *J* = 14.7 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 136.31, 131.58, 131.24, 128.83, 127.73, 119.26, 48.84, 32.89, 27.05, 23.93. − MS (DCI/CH_4): *m*/*z* (%) = 125 (28), 179 (24), 235 (100), 271 (9) [MH^+]. − HRMS (DCI) for $C_{14}H_{21}ClOP$ [MH^+]: calcd. 271.1019; found 271.0998.

Treatment of [2-(Chloromethyl)allyl]phosphonate 3b with (*E*)-α,β-Unsaturated Esters 5a−c and Ketone 5d (cf. Table 1). − **General Procedure:** A solution of **3b** (1.0 mmol, 199 mg) in THF (4.5 mL) was added dropwise at low temperature to a stirred solution of LDA, prepared at 0 °C from diisopropylamine (0.17 mL, 1.3 mmol) and *n*BuLi (0.781 mL, 1.24 mmol, 1.6 M solution in hexane) in THF (4 mL),. After 10 min, **5a−d** (1.0 mmol) in THF (2.3 mL) was added and stirring was continued for 5 min at the above temperature. DMPU (1.5 mL) in THF (3.0 mL) was then added dropwise and stirring was continued. After completion of the reaction (see Table 2), the reaction mixture was quenched with 20% aqueous AcOH, poured into water, and extracted with CH_2Cl_2. The extracts were washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated under reduced pressure. The products were purified by column chromatography on silica gel; the yields are indicated in Table 1.

Dimethyl (1*RS*,2*RS*,3*RS*)-[3-(Methoxycarbonyl)-5-methylene-2-phenylcyclopentyl]phosphonate (6a): Elution: ethyl acetate/petroleum ether (5:1). − ^{1}H NMR (600 MHz, [D_6]acetone): δ = 7.32 (m, 4 H), 7.23 (m, 1 H), 5.25 (dtt, *J* = 4.0, 2.5, 2.0 Hz, 1 H), 5.18 (dtt, *J* = 6.0, 2.5, 1.0 Hz, 1 H), 3.70 (ddd, *J* = 20.0, 10.5, 9.5 Hz, 1 H), 3.18 (ddq, *J* = 23.0, 9.5, 2.5 Hz, 1 H), 3.56 (d, *J* = 11.0 Hz, 3 H), 3.45 (d, *J* = 11.0 Hz, 3 H), 3.52 (s, 3 H), 2.98 (dddd, *J* =

12.5, 10.5, 6.5, 1.0 Hz, 1 H), 2.80 (dddt, *J* = 15.0, 6.5, 2.0, 1.0 Hz, 1 H), 2.70 (dddq, *J* = 15.0, 12.5, 4.5, 2.5 Hz, 1 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 174.01, 145.79, 142.91, 129.26, 128.64, 127.78, 110.73, 53.32, 53.17, 52.72, 51.85, 51.53, 48.63, 39.96. − MS (DCI/CH_4): *m*/*z* (%) = 265 (40), 293 (32), 325 (100) [MH^+]. − HRMS (DCI) for $C_{16}H_{22}O_5P$ [MH^+]: calcd. 325.1205; found 325.1224.

Dimethyl [1-Chloro-2-methyl-5-(methoxycarbonyl)-4-phenylpent-1-en-3-yl]phosphonate (8a): Elution: ethyl acetate/petroleum ether (5:1). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.29 (m, 4 H), 7.21 (m, 1 H), 6.17 (dq, *J* = 4.4, 1.4 Hz, 1 H), 3.70 (tdd, *J* = 10.8, 8.3, 4.1 Hz, 1 H), 3.53 (d, *J* = 10.7 Hz, 3 H), 3.48 (s, 3 H), 3.12 (d, *J* = 11.0 Hz, 3 H), 2.96 (dd, *J* = 21.5, 10.8 Hz, 1 H), 2.72 (dd, *J* = 15.5, 4.1 Hz, 1 H), 2.52 (dd, *J* = 15.5, 10.8 Hz, 1 H), 1.94 (dd, *J* = 2.6, 1.4 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.72, 140.57, 133.37, 128.45, 128.36, 127.28, 118.34, 52.85, 52.09, 51.58, 50.90, 40.98, 39.52, 16.13.

Dimethyl (1*RS*,2*SR*,3*RS*)-[3-(Methoxycarbonyl)-2-methyl-5-methylenecyclopentyl]phosphonate (6b): Elution: ethyl acetate/petroleum ether (5:1). − ^{1}H NMR (600 MHz, C_6D_6): δ = 5.38 (dtt, *J* = 4.0, 2.5, 2.0 Hz, 1 H), 5.01 (dtt, *J* = 6.0, 2.5, 1.0 Hz, 1 H), 3.43 (d, *J* = 11.0 Hz, 3 H), 3.42 (d, *J* = 10.5 Hz, 3 H), 3.33 (s, 3 H), 2.82 (dddq, *J* = 20.0, 10.5, 9.5, 6.5 Hz, 1 H), 2.77 (dddq, *J* = 15.0, 12.5, 4.5, 2.5 Hz, 1 H), 2.43 (dddt, *J* = 15.0, 7.0, 2.5, 1.0 Hz, 1 H), 2.39 (ddq, *J* = 23.5, 9.0, 2.5 Hz, 1 H), 2.19 (dddd, *J* = 12.5, 10.5, 6.5, 1.0 Hz, 1 H), 1.17 (d, *J* = 6.5 Hz, 3 H). − ^{13}C NMR (600 MHz, C_6D_6): δ = 173.73, 145.06, 110.74, 52.80, 52.36, 19.46. − MS (DCI/CH_4): *m*/*z* (%) = 231 (39), 263 (100) [MH^+]. − HRMS (DCI) for $C_{11}H_{20}O_5P$ [MH^+]: calcd. 263.1048; found 263.1063.

Dimethyl (1*RS*,2*RS*,3*RS*)-[2,3-Bis(ethoxycarbonyl)-5-methylenecyclopentyl]phosphonate (6c): Elution: ethyl acetate/petroleum ether (10:3). − ^{1}H NMR (600 MHz, C_6D_6): δ = 5.45 (dtt, *J* = 6.0, 3.0, 0.5 Hz, 1 H), 4.99 (dtt, *J* = 6.0, 3.5, 0.8 Hz, 1 H), 3.9−4.0 (m, 4 H), 3.77 (ddd, *J* = 19.0, 10.5, 9.0 Hz, 1 H), 3.59 (ddq, *J* = 23.5, 9.0, 2.5 Hz, 1 H), 3.44 (d, *J* = 10.5 Hz, 3 H), 3.40 (d, *J* = 10.5 Hz, 3 H), 2.98 (dddd, *J* = 12.0, 10.5, 7.0, 1.0 Hz, 1 H), 2.82 (dddq, *J* = 15.5, 12.0, 4.0, 2.5 Hz, 1 H), 2.47 (dddt, *J* = 15.5, 7.0, 2.0, 1.0 Hz, 1 H), 0.95 (t, *J* = 7.0 Hz, 3 H), 0.94 (t, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 172.18, 171.95, 142.08, 111.03, 60.82, 60.58, 53.0, 52.65, 48.50, 47.55, 42.76, 37.81, 13.69, 13.56. − MS (DCI/CH_4): *m*/*z* (%) = 187 (100), 215 (94), 260 (84), 334 (33). − HRMS (DCI) for $C_{14}H_{23}O_7P$: calcd. 334.1181; found 334.1197.

Dimethyl (1*RS*,2*SR*,3*RS*)-(2-Methyl-5-methylene-3-propanoylcyclopentyl)phosphonate (6d): Elution: ethyl acetate. − ^{1}H NMR (600 MHz, C_6D_6): δ = 5.34 (dtt, *J* = 4.0, 2.5, 2.0 Hz, 1 H), 5.00 (dtt,= 6.0, 2.5, 1.0 Hz, 1 H), 3.44 (d, *J* = 11.0 Hz, 3 H), 3.43 (d, *J* = 10.5 Hz, 3 H), 2.77 (dddq, *J* = 20.0, 10.0, 9.5, 6.5 Hz, 1 H), 2.42 (dddq, *J* = 15.0, 12.5, 4.5, 2.5 Hz, 1 H), 2.38 (ddq, *J* = 23.5, 9.5, 2.5 Hz, 1 H), 2.22 (dddt, *J* = 15.0, 6.5, 2.5, 1.0 Hz, 1 H), 2.09 (dddd, *J* = 12.5, 10.5, 6.5, 1.0 Hz, 1 H), 2.05 (dq, *J* = 18.0, 7.0 Hz, 1 H), 1.98 (dq, *J* = 18.0, 7.0 Hz, 1 H), 1.01 (d, *J* = 6.5 Hz, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (600 MHz, C_6D_6): δ = 209.88, 145.56, 110.39, 58.64, 52.76, 52.42, 47.86, 39.31, 39.14, 35.89, 19.59, 7.75. − MS (DCI/CH_4): *m*/*z* (%) = 93 (100), 203 (97), 261 (5.05) [MH^+]. − HRMS (DCI) for $C_{12}H_{22}O_4P$ [MH^+]: calcd. 261.1256; found 261.1287.

Dimethyl [2-(Chloromethyl)-4-methyl-6-oxo-1-octen-3-yl)phosphonate (7d, *anti*): Elution: ethyl acetate/petroleum ether (5:1). − ^{1}H NMR (300 MHz, [D_6]acetone): δ = 5.54 (d, *J* = 4.5 Hz, 1 H), 5.38 (d, *J* = 4.5 Hz, 1 H), 4.27 (t, *J* = 1.5 Hz, 2 H), 3.70 (d, *J* = 10.8 Hz, 3 H), 3.68 (d, *J* = 10.8 Hz, 3 H), 2.82 (dd, *J* = 17.0, 3.0 Hz, 1 H), 2.72 (dd, *J* = 21.5, 8.5 Hz, 1 H), 2.60 (m, 1 H), 2.47 (m, 2 H), 2.37 (dd, *J* = 17.0, 9.0 Hz, 1 H), 1.11 (d, *J* = 6.5 Hz, 3 H), 1.00 (d, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz): δ = 210.53, 139.91, 119.13, 53.38, 52.54, 49.37, 47.29, 45.13, 36.52, 29.76, 19.10, 7.68. − MS (DCI/CH_4): *m*/*z* (%) = 261 (100), 297 (64) [MH^+]. − HRMS (DCI) for $C_{12}H_{23}ClO_4P$ [MH^+]: calcd. 297.1023; found 297.1024.

Dimethyl (1*RS*,2*SR*,3*RS*)-(2,5-Dimethyl-3-propanoylcyclopentenyl)-phosphonate (9d): Elution: ethyl acetate. − ^{1}H NMR (600 MHz, C_6D_6): δ = 3.41 (d, *J* = 4.0 Hz, 3 H), 3.39 (d, *J* = 4.5 Hz, 3 H), 2.77 (dddq, *J* = 20.0, 10.0, 9.5, 6.5 Hz, 1 H), 2.46 (m, 1 H), 2.33 (m, 1 H), 2.09 (dddd, *J* = 12.0, 10.0, 6.5, 1.0 Hz, 1 H), 2.05 (dq, *J* = 18.0, 7.0 Hz, 1 H), 1.98 (m, 3 H), 1.97 (dq, *J* = 18.0, 7.0 Hz, 1 H), 1.19 (dd, *J* = 7.0, 0.5 Hz, 3 H), 0.90 (t, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (600 MHz, C_6D_6): δ = 208.81, 157.50, 56.61, 51.38, 51.23, 46.70, 41.58, 41.43, 34.37, 21.42, 16.32, 8.08.

Treatment of [2-(Chloromethyl)allyl]phosphane Oxide 3d with (*E*)-α,β-Unsaturated Esters 5a−c and Ketone 5d (cf. Scheme 3). − **General Procedure:** A solution of **3d** (1.0 mmol, 270.8 mg) in THF (4.5 mL) was added dropwise at −95 °C to a stirred solution of LDA, prepared at 0 °C from diisopropylamine (0.17 mL, 1.3 mmol) and *n*BuLi (0.781 mL, 1.24 mmol, 1.6 M solution in hexane) in THF (4 mL) of. After 10 min, (*E*)-α,β-unsaturated ester **5a−c** or ketone **5d** (1.0 mmol) in THF (2.3 mL) was added and stirring was continued for 30 min at the above temperature. After quenching (20% aqueous AcOH), the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated under reduced pressure. All the products were purified by column chromatography on silica gel; the yields are shown in Table 2.

(*tert*-Butyl)[(1*RS*,2*RS*,3*RS*)-3-(methoxycarbonyl)-5-methylene-2-phenylcyclopentyl](phenyl)phosphane Oxide [10(R_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (tt, *J* = 8.0, 2.0 Hz, 2 H), 7.43 (tq, *J* = 7.0, 1.0 Hz, 1 H), 7.28 (m, 2 H), 7.09 (m, 3 H), 6.73 (m, 2 H), 5.31 (tt, *J* = 3.0, 1.0 Hz, 1 H), 5.23 (dq, *J* = 6.0, 1.0 Hz, 1 H), 3.75 (ddd, *J* = 20, 8.4, 5.0 Hz, 1 H), 3.58 (s, 3 H), 3.41 (tq, *J* = 5.0, 1.0 Hz, 1 H), 3.12 (t of tm *J* = 16.0 Hz, 1 H), 2.86 (dt, *J* = 12.0, 7.5 Hz, 1 H), 2.73 (dd, *J* = 13.5, 7.0 Hz, 1 H), 1.19 (d, *J* = 14.0 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.32, 148.51, 144.43, 132.00, 131.15, 130.51, 128.35, 127.97, 127.14, 126.42, 111.04, 52.89, 51.80, 50.30, 48.37, 40.03, 34.84, 25.63.

(*tert*-Butyl)[(1*RS*,2*RS*,3*RS*)-3-(methoxycarbonyl)-5-methylene-2-phenylcyclopentyl](phenyl)phosphane Oxide [11(S_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (tt, *J* = 8.0, 2.0 Hz, 2 H), 7.50 (m, 1 H), 7.46 (ddd, *J* = 7.0, 3.0, 1.0 Hz, 2 H), 7.37 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.35 (tt, *J* = 7.0, 2.0 Hz, 2 H), 7.26 (tt, *J* = 7.0, 1.5 Hz, 1 H), 4.85 (dt, *J* = 15.0, 9.0 Hz, 1 H), 4.42 (ddd, *J* = 18.5, 8.5, 5.5 Hz, 1 H), 4.23 (dt, *J* = 15.0, 6.0 Hz, 1 H), 3.64 (s, 3 H), 3.46 (tq, *J* = 5.0, 1.0 Hz, 1 H), 2.88 (t of tm, *J* = 14.0 Hz, 1 H), 2.80 (ddd, *J* = 12.5, 8.5, 6.0 Hz, 1 H), 2.57 (dd, *J* = 12.5, 6.0 Hz, 1 H), 1.05 (d, *J* = 14.0 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.28, 147.27, 145.44, 132.17, 131.23, 130.65, 128.85, 127.83, 127.63, 126.98, 110.83, 54.59, 51.82, 49.20, 46.68, 40.31, 34.57, 25.75. − MS (DCI/CH_4): *m*/*z* (%) = 234 (46), 340 (55), 397 (100) [MH^+]. − HRMS (DCI) for $C_{24}H_{30}O_3P$ [MH^+]: calcd. 397.1932; found 397.1946.

(*tert*-Butyl)[(1*RS*,2*SR*,3*RS*)-3-(methoxycarbonyl)-2-methyl-5-methylenecyclopentyl](phenyl)phosphane Oxide [12(R_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76 (tt, *J* = 8.0,

1.0 Hz, 2 H), 7.51 (tq, *J* = 6.5, 1.0 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 3.0, 1.0 Hz, 2 H), 5.18 (td, *J* = 3.0, 1.0 Hz, 1 H), 5.12 (td, *J* = 3.0, 1.0 Hz, 3 H), 3.65 (s, 3 H), 3.01 (t of tm, *J* = 11.5 Hz, 1 H), 2.91 (t, *J* = 4.5 Hz, 1 H), 2.70 (m, 1 H), 2.52 (dd, *J* = 14, 7.0 Hz, 1 H), 2.30 (dt, *J* = 11.5, 7.0 Hz, 1 H), 1.22 (d, *J* = 14.0 Hz, 9 H), 0.91 (d, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.98, 147.86, 131.83, 131.21, 131.20, 128.06, 111.28, 51.76, 50.93, 49.29, 38.86, 37.80, 34.83, 22.57, 25.77.

(*tert*-Butyl)[(1*RS*,2*SR*,3*RS*)-3-(methoxycarbonyl)-5-methylene-2-methylcyclopentyl](phenyl)phosphane Oxide (13(S_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (tt, *J* = 8.5, 1.0 Hz, 2 H), 7.45 (tq, *J* = 7.0, 1.0 Hz, 1 H), 7.47 (ddd, *J* = 8.0, 3.0, 1.0 Hz, 2 H), 4.85 (dt, *J* = 5.0, 2.0 Hz, 1 H), 4.35 (dt, *J* = 4.5, 2.0 Hz, 1 H), 3.67 (s, 3 H), 3.13 (m, 1 H), 2.91 (t, *J* = 4.5 Hz, 1 H), 2.68 (m, 1 H), 2.40 (dd, *J* = 13.0, 7.0 Hz, 1 H), 2.35 (dt, *J* = 12.0, 7.0 Hz, 1 H), 1.36 (d, *J* = 7.0 Hz, 3 H), 1.23 (d, *J* = 14.0 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.90, 146.95, 132.39, 131.21, 130.44, 127.78, 111.16, 51.76, 51.59, 48.73, 39.68, 37.49, 34.84, 25.61, 21.91. − MS (DCI/CH_4): *m*/*z* (%) = 278 (12), 303 (16), 335 (100) [MH^+]. − HRMS (DCI) for $C_{19}H_{29}O_3P$ [MH^+]: calcd. 335.1776; found 335.1777.

(*tert*-Butyl)[(1*RS*,2*RS*,3*RS*)-2,3-bis(ethoxycarbonyl)-5-methylenecyclopentyl](phenyl)phosphane Oxide [14(S_P)]: The reaction conditions were as described earlier. After 5 min, diethyl fumarate was added, DMPU (1.5 mL) in THF (3.0 mL) was added dropwise, and stirring was continued for 30 min, followed by workup and chromatographic purification. Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (m, 2 H), 7.51 (m, 1 H), 7.46 (m, 2 H), 4.79 (m, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 4.20 (m, 1 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 4.14 (ddd, *J* = 12.5, 9.0, 5.5 Hz, 1 H), 3.75 (tt, *J* = 5.5, 1.0 Hz, 1 H), 2.97 (ddd, *J* = 12.5, 9.0, 7.0 Hz, 1 H), 2.75 (t of tm, *J* = 13.0 Hz, 1 H), 2.49 (dd, *J* = 13.5, 7.0 Hz, 1 H), 1.30 (t, *J* = 7.0 Hz, 3 H), 1.27 (t, *J* = 7.0 Hz, 3 H), 1.21 (d, *J* = 14.5 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.71, 172.46, 145.59, 132.33, 131.39, 130.05, 127.89, 111.71, 61.53, 60.96, 48.22, 46.95, 43.51, 39.87, 34.84, 25.46, 14.19. − MS (DCI/CH_4): *m*/*z* (%) = 407 (100) [MH^+]. − HRMS (DCI) for $C_{22}H_{32}O_5P$ [MH^+]: calcd. 407.1987; found 407.1985.

(*tert*-Butyl)[2-(chloromethyl)-4-methyl-6-oxo-1-octen-3-yl](phenyl)-phosphane Oxide (15, *cis*): Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (t, *J* = 9.0 Hz, 2 H), 7.48 (m, 1 H), 7.42 (m, 1 H), 5.56 (broad, 1 H), 5.36 (dd, *J* = 2.5, 1.0 Hz, 1 H), 3.82 (d, *J* = 13.4 Hz, 1 H), 3.73 (dd, *J* = 18.0, 1.0 Hz, 1 H), 3.71 (d, *J* = 13.4 Hz, 1 H), 3.17 (m, 1 H), 2.99 (ddd, *J* = 8.5, 3.5, 1.0 Hz, 1 H), 2.51 (dq, *J* = 17.5, 7.0 Hz, 1 H), 2.43 (dd, *J* = 18.0, 11.5 Hz, 1 H), 2.37 (dq, *J* = 17.5, 7.0 Hz, 1 H), 1.21 (d, *J* = 14.5 Hz, 9 H), 1.06 (t, *J* = 7.0 Hz, 3 H), 1.04 (d, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 210.48, 137.47, 131.45, 131.18, 131.15, 127.90, 121.91, 49.00, 45.47, 44.76, 36.77, 34.37, 29.11, 25.94, 20.89, 7.78. − MS (DCI/CH_4): *m*/*z* (%) = 182 (47), 333 (100), 369 (65) [MH^+]. − HRMS (DCI) for $C_{20}H_{31}ClO_2P$ [MH^+]: calcd. 369.1750; found 369.1722.

(*tert*-Butyl)[(1*RS*,2*SR*,3*RS*)-2-methyl-5-methylene-3-propanoyl-cyclopentyl](phenyl)phosphane Oxide [16(R_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (tt, *J* = 8.5, 1.5 Hz, 2 H), 7.54 (tq, *J* = 8.0, 1.5 Hz, 1 H), 7.49 (t of tm, *J* = 8.0 Hz, 2 H), 5.20 (dd, *J* = 3.5, 3.0 Hz, 1 H), 5.17 (t, *J* = 3.0 Hz, 1 H), 2.95 (t of tm, *J* = 4.5 Hz, 1 H), 2.90 (t of tm, *J* = 12.5 Hz, 1 H), 2.67 (dqd, *J* = 19.5, 7.0, 4.0 Hz, 1 H), 2.59 (dq, *J* = 18, 7.0 Hz, 1 H), 2.50 (bdd, *J* = 13.0, 7.5 Hz, 1 H), 2.46 (dq, *J* = 18.0, 7.0 Hz, 1 H), 2.31 (dt, *J* = 12.0, 7.5 Hz, 1 H), 1.25 (d, *J* = 14.5 Hz, 9 H), 1.01 (t, *J* = 7.0 Hz, 3 H), 0.89 (d, *J* = 6.5 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 210.95, 148.50, 131.90, 131.70, 128.33, 111.80, 59.15, 49.00, 39.28, 36.48, 35.02, 33.54, 25.57, 22.64, 7.74. − MS (DCI/CH_4): *m*/*z* (%) = 275 (40), 333 (100) [MH^+]. − HRMS (DCI) for $C_{20}H_{30}O_2P$ [MH^+]: calcd. 333.1983; found 333.1957.

(*tert*-Butyl)[(1*RS*,2*SR*,3*RS*)-2-methyl-5-methylene-3-propanoyl-cyclopentyl](phenyl)phosphane Oxide [17(S_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ =7.77 (m, 2 H), 7.50 (m, 1 H), 7.45 (m, 2 H), 4.83 (dt, *J* = 9.5, 2.0 Hz, 1 H), 4.34 (dt, *J* = 4.5, 1.5 Hz, 1 H), 3.17 (ddqd, *J* = 18.5, 8.0, 6.5, 5.0 Hz, 1 H), 2.89 (t of tm, *J* = 6.0 Hz, 1 H), 2.66 (t of tm, *J* = 14.0 Hz, 1 H), 2.55 (dq, *J* = 18.0, 7.0 Hz, 1 H), 2.43 (dq, *J* = 18.0, 7.0 Hz, 1 H), 2.39 (m, 1 H), 2.38 (m, 1 H), 1.29 (d, *J* = 6.5 Hz, 3 H), 1.24 (d, *J* = 14.0 Hz, 9 H), 1.03 (t, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 21.95, 146.54, 131.90, 130.59, 127.38, 110.76, 59.13, 48.33, 39.30, 35.64, 34.45, 33.42, 25.32, 21.62, 7.28.

(*tert*-Butyl)[(1*RS*,2*SR*,3*SR*)-2-methyl-5-methylene-3-propanoyl-cyclopentyl](phenyl)phosphane Oxide [18(S_P)]: Elution: ethyl acetate. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (m, 2 H), 7.50 (m, 1 H), 7.46 (m, 2 H), 4.90 (dq, *J* = 4.5, 2.0 Hz, 1 H), 4.44 (dq, *J* = 4.5, 1.5 Hz, 1 H), 3.64 (td, *J* = 10.0, 6.0 Hz, 1 H), 3.34 (dq, *J* = 11.0, 7.0 Hz, 1 H), 3.05 (d of dm, *J* = 7.0 Hz, 1 H), 2.77 (dddt, *J* = 15.0, 10.0, 4.5, 2.5 Hz, 1 H), 2.50 (dq, *J* = 18, 7.0 Hz, 1 H), 2.40 (dq, *J* = 18.0, 7.0 Hz, 1 H), 2.29 (m, 1 H), 1.26 (d, *J* = 14.0 Hz, 9 H), 1.05 (t, *J* = 7.0 Hz, 3 H), 0.89 (d, *J* = 7.0 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 21.93, 146.50, 131.60, 130.59, 127.74, 112.40, 53.20, 51.5, 38.0, 34.45, 33.00, 30.30, 23.95, 16.5, 7.30. − MS (DCI/CH_4): *m*/*z* (%) = 235 (17), 275 (10), 333 (100) [MH^+]. − HRMS (DCI) for $C_{20}H_{30}O_2P$ [MH^+]: calcd. 333.1983; found 333.1979.

Treatment of Phosphonate 3a or Phosphane Oxide 3c with Methyl Cinnamate (5a). − General Procedure: A solution of **3a** or **3c** (1.06 mmol) in THF (3.5 mL) was added dropwise at −95 °C to a stirred solution of LDA, prepared at 0 °C from diisopropylamine (0.13 mL, 0.99 mmol) and *n*BuLi (0.60 mL, 0.95 mmol, 1.6 M solution in hexane) in THF (4 mL). After 10 min, methyl cinnamate (**5a**) (0.75 mmol) in THF (2 mL) was added and stirring was continued at the above temperature. After completion of the reaction (see Table 3), the reaction mixture was quenched with 20% aqueous AcOH, poured into water and extracted with CH_2Cl_2. The extracts were washed successively with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated under reduced pressure. All the products were purified by column chromatography on silica gel; the yields are indicated in Table 3.

(*tert*-Butyl)[5-(methoxycarbonyl)-2-methyl-4-phenylpent-1-en-3-yl]-(phenyl)phosphane Oxide (19): Elution: acetone/petroleum ether (1:2). − M.p. 162−166 °C. − ^{1}H NMR (600 MHz, DMSO, 400 K): δ = 7.80 (m, 2 H), 7.53 (m, 3 H), 7.12 (m, 2 H), 7.07 (m, 1 H), 7.01 (m, 2 H), 5.30 (s, 1 H), 5.16 (s, 1 H), 3.46 (m, 1 H), 3.42 (dd, *J* = 16.0, 3.5 Hz, 1 H), 3.29 (s, 3 H), 3.18 (dd, *J* = 7.0, 5.0 Hz, 1 H), 2.79 (dd, *J* = 16.0, 12.0 Hz, 1 H), 1.71 (s, 3 H), 1.08 (d, *J* = 14.3 Hz, 9 H). − ^{13}C NMR (600 MHz, DMSO, 400 K): δ = 170.80, 141.0, 138.6, 131.2, 130.5, 130.2, 127.3, 127.1, 125.6, 118.6, 49.9, 47.6, 40.3, 34.45, 34.1, 24.86, 24.07. − MS (DCI/CH_4): *m*/*z* (%) = 235 (100), 399 (23) [MH^+]. − HRMS (DCI) for $C_{24}H_{32}O_3P$ [MH^+]: calcd. 399.2089; found 399.2046.

(*tert*-Butyl)[5-(methoxycarbonyl)-2-methyl-4-phenylpent-1-en-3-yl]-(phenyl)phosphane Oxide (20): Elution: acetone/petroleum ether (1:2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66−7.59 (m, 2 H), 7.45−7.38 (m, 3 H), 7.13−7.10 (m, 2 H), 7.00−6.90 (m, 3 H), 5.86 (d, *J* = 29.1 Hz, 1 H), 3.50 (s, 3 H), 3.40 (m, 1 H), 3.03 (ddd, *J* =

13.8, 8.6, 1.7 Hz, 1 H), 2.95 (ddd, J = 12.0, 7.8, 1.8 Hz, 1 H), 2.67 (m, ABX, 2 H), 1.93 (s, 3 H), 1.11 (d, J = 14.4 Hz, 9 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 172.55, 161.18, 142.54, 131.42, 130.52, 127.68, 127.45, 127.13, 125.85, 113.82, 50.88, 40.48, 39.79, 39.50, 32.44, 25.84, 23.74. − MS (DCI/CH_4): *m*/*z* (%) = 325 (100), 398 (23). − HRMS (DCI) for $C_{24}H_{31}O_3P$: calcd. 398.2011; found 398.2040.

Dimethyl [5-(Methoxycarbonyl)-2-methyl-4-phenylpent-1-en-3-yl]-phosphonate (21, *anti*): Elution: acetone/petroleum ether (3:5). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 4 H), 7.21 (m, 1 H), 5.14 (d, J = 1.2 Hz, 1 H), 5.12 (d, J = 1.2 Hz, 1 H), 3.68 (tdd, J = 11.2, 8.4, 3.7 Hz, 1 H), 3.53 (d, J = 10.7 Hz, 3 H), 3.13 (d, J = 10.9 Hz, 3 H), 3.46 (s, 3 H), 2.88 (dd, J = 21.1, 11.0 Hz, 1 H), 2.85 (dd, J = 15.5, 3.7 Hz, 1 H), 2.53 (ddd, J = 15.5 11.4, 0.8 Hz, 1 H), 1.88 (dt, J = 2.5, 1.2 Hz, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 172.08, 141.04, 139.70, 128.45, 128.17, 126.99, 117.06, 52.89, 51.90, 51.27, 51.39, 41.16, 39.33, 22.57. − MS (DCI/CH_4): *m*/*z* (%) = 163 (100) [MH^+], 295 (51), 327 (14). − HRMS (DCI) for $C_{16}H_{24}O_5P$ [MH^+]: calcd. 327.1361; found 327.1370.

Dimethyl [(*E*)- + (*Z*)-(2-Methyl-5-nitro-4-phenylpent-1-enyl]phosphonate (22): A solution of **3a** (2.0 mmol, 328.28 mg) in THF (7 mL) was added dropwise at −95 °C to a stirred solution of LDA, prepared at 0 °C from diisopropylamine (0.26 mL, 1.98 mmol) and *n*BuLi (1.2 mL, 1.9 mmol, 1.6 M solution in hexane) in THF (8 mL). After 10 min, (*E*)-β-nitrostyrene (1.8 mmol, 268.47 mg) in THF (4 mL) was added. Stirring was then continued for 5−10 min at the above temperature. After quenching (20% aqueous AcOH), the mixture was poured into water and extracted with CH_2Cl_2. The extracts were washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatographic purification [elution: acetone/petroleum ether (1:2)]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (m, 5 H), 5.4 (m, 1 H), 4.66 (m, 2 H), 3.75 (m, 1 H), 3.72 (d, J = 11 Hz, 3 H), 3.61 (d, J = 11 Hz, 3 H), 3.16 and 2.92 (m, 1 H), 1.90 (s br, 3 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.0, 129.0, 127.8, 127.7, 80.0, 52, 52.2, 42.5, 38.2, 25.6.

Dimethyl [(*E*)- + (*Z*)-2-(Chloromethyl)-5-nitro-4-phenylpent-1-enyl]-phosphonate (23): As described for **22**, using 20 mmol of **3b**. Chromatographic purification [elution: ethyl acetate/petroleum ether (4:1)], (*E*)/(*Z*) = 6.5:3.5. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 and 7.20 (m, 5 H), 5.80 and 5.39 (J = 13 Hz, 1 H), 4.70 and 4.6 (m, 2 H), 4.45 and 3.88 (m, 2 H), 3.77 and 3.66, 3.57 and 3.52 (d, J = 12 Hz, 6 H), 3.8 and 3.31 (m, 1 H), 2.99 and 2.77 (m, 2 H). − ^{13}C NMR (300 MHz, $CDCl_3$): δ = 155.8, 138.0, 129.2, 128.1, 127.6, 119.0 and 116.5, 80.0, 52.3, 47.5, 42.8 and 42.3, 39.0 and 34.8.

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