Use of Acyl Phosphonates as a Coupling Partner for Rhodium-Catalyzed [2+2+2] Cycloaddition: Unexpected Dependence of the Reactivity on Structures of α,ω-Diynes

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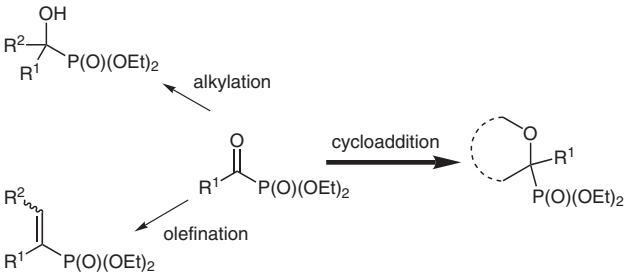
Abstract: A cationic rhodium(I)–H_8-BINAP complex catalyzes a [2+2+2] cycloaddition of 1,6- and 1,7-diynes with acyl phosphonates in high yields with high regioselectivity. Interestingly, the reactivity of α,ω-diynes toward acyl phosphonates is highly dependent on their own structures.

Key words: acylphosphonates, alkynes, cycloaddition, H_8-BINAP, rhodium

Catalytic [2+2+2] cycloadditions[1] of diynes with C(sp^2)-heteroatom multiple bonds such as aldehydes and ketones by using various transition-metal complexes as catalysts have been reported.[2–6] Recently, several groups have utilized rhodium-based catalysts for this transformation. Ojima and co-workers reported an intramolecular [2+2+2] cycloaddition of diynal in their study of a [2+2+2+1] cycloaddition with CO using $[Rh(cod)Cl]_2$ as a catalyst.[7] Kong and Krische reported a cationic rhodium(I)–BIPHEP [2,2′-bis(diphenylphosphino)-1,1′-biphenyl]-catalyzed carbonyl *Z*-dienylation via multicomponent reductive coupling of aldehydes and α-keto esters mediated by hydrogen in the presence of a catalytic amount of triphenylacetic acid, which involves carbonyl insertion into cationic rhodacyclopentadienes.[8,9] We have reported cationic rhodium(I)–H_8-BINAP-catalyzed [2+2+2] cycloadditions of 1,6-diynes with both activated and unactivated carbonyl compounds with alkynes.[10,11] On the other hand, we have recently determined that alkynylphosphonates are suitable substrates for cationic rhodium(I)–H_8-BINAP-catalyzed [2+2+2] cycloadditions.[12] Accordingly, we anticipated that acyl phosphonates, which are useful building blocks for the synthesis of functionalized phosphorus compounds via alkylation[13] or olefination,[14] would show high reactivity in cationic rhodium(I)–H_8-BINAP-catalyzed [2+2+2] cycloaddition (Scheme 1).[15,16] In this communication, we describe a cationic rhodium(I)–H_8-BINAP-catalyzed [2+2+2] cycloaddition of acyl phosphonates with 1,6-diynes leading to phosphonate-substituted dienones.



Scheme 1

We first investigated the reaction of tosylamide-linked 1,6-diyne **1a** with acetyl phosphonate **2a** in the presence of a cationic rhodium(I)–bisphosphine complex as a catalyst (Table 1). We were pleased to find that the reaction proceeded at room temperature to give the desired dienone **3aa** in moderate yield using 10 mol% of a $[Rh(cod)_2]BF_4$–BINAP complex (entry 1). Among the biarylbisphosphine ligands examined, the highest yield of **3aa** was obtained when H_8-BINAP was used as a ligand (entry 3). Non-biarylbisphosphine ligand dppb, which possesses a large bite angle, could be used, but the yield was very low (entry 4). After optimization of the reaction conditions, we determined that the reaction was completed within one hour and the use of two equivalents of **2a** further improved the yield of **3aa** (entry 5).

Thus, we explored the scope of this process with respect to both acyl phosphonates and α,ω-diynes (Table 2). Not only acetyl phosphonate (**2a**, entry 1) but also benzoyl phosphonate (**2b**, entry 2) could participate in this reaction. With respect to 1,6-diynes, not only symmetrical 1,6-diynes **1a** but also unsymmetrical 1,6-diynes **1b** and **1c** reacted with acyl phosphonates to give the corresponding dienones in good yields with perfect regioselectivity (entries 3 and 4). Interestingly, the reactivity of α,ω-diynes is highly dependent on their own structures. Terminal 1,6-diyne **1d** failed to react with **2b** due to the rapid homocyclotrimerization of **1d** (entry 5).[17] Tosylamide-linked internal 1,6-diyne **1a** smoothly reacted with **2b** (entry 2), while malonate- and dimethoxypropane-linked internal 1,6-diynes **1e** and **1f** failed to react with **2b**, and they remained unchanged (entries 6 and 7). In the case of 1,7-diynes, although internal 1,7-diyne **1g** failed to react with **2b** (entry 8), the reaction of terminal 1,7-diyne **1h** with

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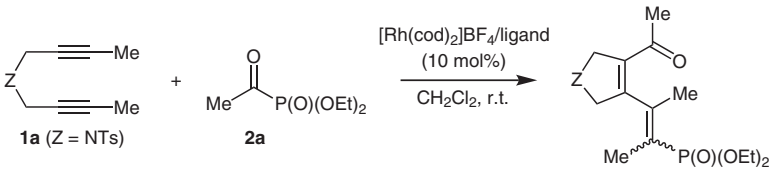
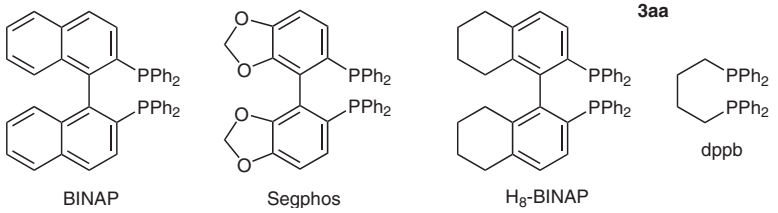
Table 1 Screening of Ligands for Rh-Catalyzed [2+2+2] Cycloaddition of 1,6-Diyne **1a** with Acetyl Phosphonate **2a**[a]

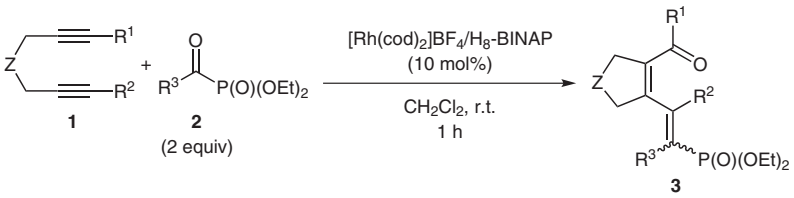




Entry	Ligand	**2a** (equiv)	Time (h)	Yield (%)[b]
1	BINAP	1.1	16	55
2	Segphos	1.1	16	67
3	H_8-BINAP	1.1	16	73
4	dppb	1.1	16	13
5	H_8-BINAP	2.0	1	84

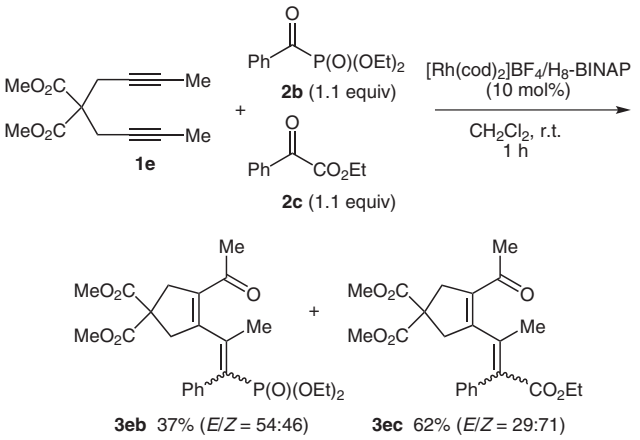
[a] $[Rh(cod)_2]BF_4$ (0.010 mmol), ligand (0.010 mmol), **1a** (0.10 mmol), **2a** (0.11 or 0.20 mmol), and CH_2Cl_2 (1.5 mL) were used.
[b] Isolated yield.

Table 2 $Rh(I)^+$–H_8-BINAP-Catalyzed [2+2+2] Cycloaddition of 1,6- and 1,7-Diynes **1** with Acyl Phosphonates **2**[a]



Entry	**1** (Z, R^1, R^2)	**2** (R^3)	**3**	Yield (%, *E*/*Z*)[b]
1	**1a** (NTs, Me, Me)	**2a** (Me)	**3aa**	84 (88:12)[c]
2	**1a** (NTs, Me, Me)	**2b** (Ph)	**3ab**	90 (40:60)
3	**1b** (NTs, Me, CO_2Me)	**2b** (Ph)	**3bb**	71 (59:41)[c]
4	**1c** (NTs, Me, H)	**2a** (Me)	**3ca**	78 (40:60)
5	**1d** (NTs, H, H)	**2b** (Ph)	**3db**	0 (–)[d]
6	**1e** [$C(CO_2Me)_2$, Me, Me]	**2b** (Ph)	**3eb**	0 (–)[e]
7	**1f** [$C(CH_2OMe)_2$, Me, Me]	**2b** (Ph)	**3fb**	0 (–)[e]
8	**1g** (CH_2CH_2, Me, Me)	**2b** (Ph)	**3gb**	0 (–)[e]
9	**1h** (CH_2CH_2, H, H)	**2a** (Me)	**3ha**	70 (60:40)
10	**1h** (CH_2CH_2, H, H)	**2b** (Ph)	**3hb**	76 (63:37)

[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-BINAP (0.020 mmol), **1a–h** (0.20 mmol), **2a**,**b** (0.40 mmol), and CH_2Cl_2 (1.5 mL) were used.
[b] Isolated yield.
[c] Isolated as a mixture of *E*/*Z* isomers.
[d] Homo-[2+2+2] cycloaddition of **1d** proceeded.
[e] Diynes **1** remained almost unchanged.

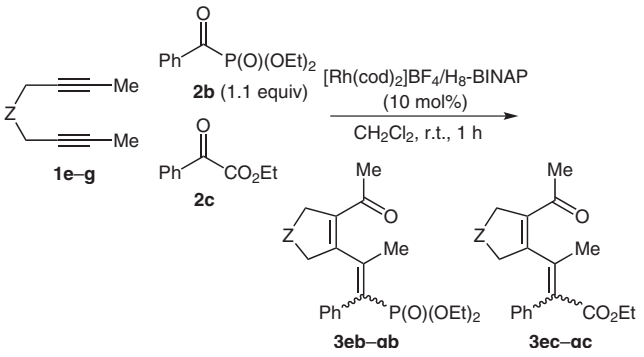


Scheme 2

acyl phosphonates proceeded in good yields (entries 9 and 10).[17]

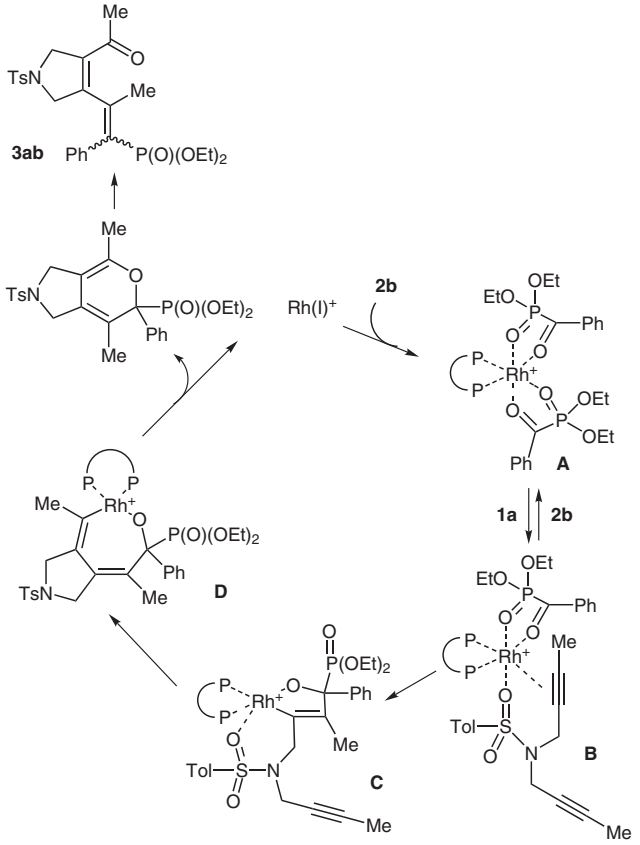
As we already demonstrated that keto esters are highly reactive coupling partners for cationic rhodium(I)–H_8-BINAP-catalyzed [2+2+2] cycloaddition with 1,6-diynes, a chemoselective [2+2+2] cycloaddition of **1e** with acyl phosphonate **2b** and keto ester **2c** was investigated in the presence of the cationic rhodium(I)–H_8-BINAP catalyst (Scheme 2). We anticipated that **1e** selectively reacts with **2c** leading to ester-substituted dienone **3ec**. Contrary to our expectation, **1e** reacted with both **2b** and **2c**.

Table 3 $Rh(I)^+$–H_8-BINAP-Catalyzed [2+2+2] Cycloaddition of 1,6-and 1,7-Diynes **1e**–**g** with Benzoyl Phosphonate (**2b**) in the Presence of Ethyl Phenylglyoxylate (**2c**)[a]



Entry	**1** (*Z*)	**2c** (equiv)	**3eb**–**gb** Yield (%, *E*/*Z*)[b]	**3ec**–**gc** Yield (%, *E*/*Z*)[b]
1	**1e** [Z = $C(CO_2Me)_2$]	0	0[c]	–
2	**1e** [Z = $C(CO_2Me)_2$]	0.2	74 (52:48)	19 (29:71)[d]
3	**1e** [Z = $C(CO_2Me)_2$]	1.1	37 (52:48)	62 (29:71)[d]
4	**1e** [Z = $C(CO_2Me)_2$]	2.0	5 (45:55)	76 (29:71)[d]
5	**1f** [Z = $C(CH_2OMe)_2$]	1.1	0[c]	0[c]
6	**1g** (Z = CH_2CH_2)	1.1	0[c]	0[c]

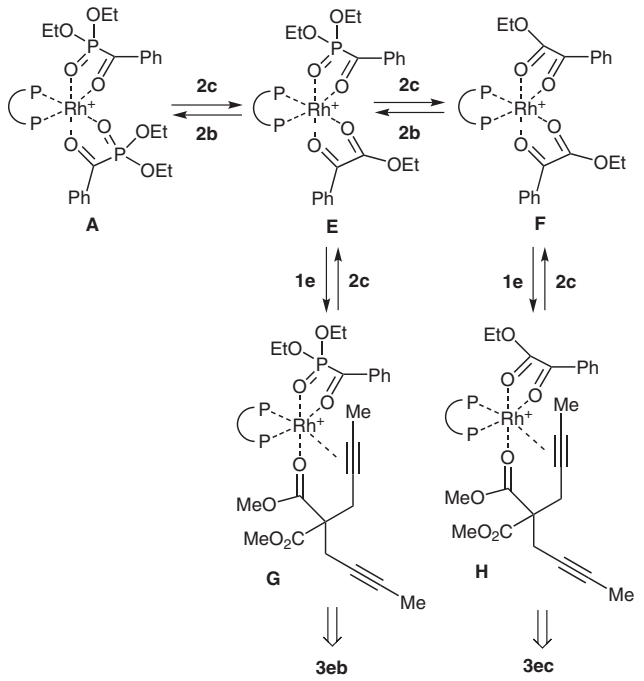
[a] $[Rh(cod)_2]BF_4$ (0.020 mmol), H_8-BINAP (0.020 mmol), **1e**–**g** (0.20 mmol), **2b** (0.22 mmol), **2c** (0–0.40 mmol), and CH_2Cl_2 (1.5 mL) were used.
[b] Isolated yield.
[c] Diynes **1** remained almost unchanged.
[d] Isolated as a mixture of *E*/*Z* isomers.



Scheme 3

Scheme 3 depicts a possible mechanism for the rhodium-catalyzed [2+2+2] cycloaddition of tosylamide-linked 1,6-diyne **1a** with benzoyl phosphonate **2b**. The reaction of **1a** and **2b** with rhodium generates an equilibrium mixture of intermediates **A** and **B** through the bidentate coordination of both **1a** and **2b**.[18] Intermediate **B** subsequently undergoes oxidative coupling leading to intermediate **C**. Insertion of another alkyne moiety of **1a** furnishes intermediate **D**. Reductive elimination of rhodium followed by electrocyclic ring opening furnishes dienone **3ab**. Indeed, a homo-[2+2+2] cycloaddition product of **1a** through a rhodacyclopentadiene intermediate was not observed in the reaction of **1a** and **2b**.

On the other hand, the equilibration of intermediates **A** and **E**–**H** may account for the results shown in Table 3 (Scheme 4).



Scheme 4

In the absence of keto ester **2c**, two molecules of benzoyl phosphonate **2b** coordinate to rhodium in a bidentate fashion to generate intermediate **A** due to higher coordination ability of **2b** than that of malonate-linked 1,6-diyne **1e**, which results in no conversion of **1e**. In the presence of **2c**, an equilibrium mixture of intermediates **A**, **E**, and **F** may be generated. Subsequent ligand exchange between **1e** and weakly coordinated **2c** may generate intermediates **G** and **H**, which furnish dienones **3eb** and **3ec**, respectively, depending on the amount of **2c**.[18] Dimethoxypropane-linked 1,6-diyne **1f** fails to react with both intermediates **E** and **F** presumably due to lower coordination ability of ether oxygen than that of ester carbonyl oxygen. Obviously, ligand exchange between ethylene-linked 1,7-diyne **1g** bearing no heteroatom in the linker and **2c** would be difficult to proceed.[17]

In conclusion, we have determined that a cationic rhodium(I)–H_8-BINAP complex catalyzes a [2+2+2] cycloaddition of 1,6- and 1,7-diynes with acyl phosphonates in high yields with high regioselectivity. Interestingly, the reactivity of α,ω-diynes toward acyl phosphonates is highly dependent on their own structures.[19]

Acknowledgment

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(17) In general, terminal alkynes are more reactive and coordinative toward rhodium than internal alkynes. Therefore, the reaction of terminal 1,6-diyne **1d** with **2b** results in the rapid homo-[2+2+2] cycloaddition of **1d** via a rhodacyclopentadiene intermediate. On the other hand, the formation of the rhodacyclopentadiene intermediate from terminal 1,7-diyne **1h** may be slower than that from terminal 1,6-diynes for steric reasons. Thus, the reaction of **1h** with **2b** may furnish the oxarhodacyclopentene intermediate. Insertion of another terminal alkyne moiety of **1h** followed by reductive elimination of rhodium furnishes the corresponding cross-[2+2+2] cycloaddition product **3hb** in good yield.

(18) Equilibrium coordination of the ester carbonyl oxygen vs. the alkyne moiety of a malonate-linked 1,6-diyne is proposed in the Ru-catalyzed [2+2+2] cycloaddition of alkynes, see: Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143.

(19) **Typical Procedure (Table 2, entry 1)**
Under an argon atmosphere, H_8-BINAP (12.6 mg, 0.02 mmol) and $[Rh(cod)_2]BF_4$ (8.1 mg, 0.02 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at r.t. for 5 min. Hydrogen was introduced to the resulting solution in a Schlenk tube. After stirring at r.t. for 1 h, the resulting solution was concentrated to dryness and dissolved in CH_2Cl_2 (0.5 mL). To this solution was added dropwise over 1 min a solution of diyne **1a** (55.1 mg, 0.20 mmol) and acyl phosphonate **2a** (72.1 mg, 0.40 mmol) in CH_2Cl_2 (1.0 mL) at r.t. The mixture was stirred at r.t. for 1 h. The resulting solution was concentrated and purified by a preparative TLC (hexane–EtOAc, 1:1), which furnished **3aa** (76.2 mg, 0.017 mmol, 84% yield) as a pale yellow oil.
Compound **3aa**: IR (neat): 3052, 2983, 2867, 1661, 1347, 1237, 1164, 1022, 671 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ (*E*-isomer) = 7.74–7.63 (m, 2 H), 7.33–7.21 (m, 2 H), 4.49–4.19 (m, 4 H), 3.97–3.73 (m, 4 H), 2.37 (s, 3 H), 2.10 (s, 3 H), 1.90–1.77 (m, 6 H), 1.16 (t, *J* = 7.2 Hz, 6 H); δ (*Z*-isomer) = 7.74–7.63 (m, 2 H), 7.33–7.21 (m, 2 H), 4.30–4.19 (m, 4 H), 4.12–3.97 (m, 4 H), 2.38 (s, 3 H), 2.10 (s, 3 H), 1.90–1.77 (m, 3 H), 1.58 (dd, *J* = 13.5, 1.5 Hz, 3 H), 1.28 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.9, 149.6, 149.4, 143.6, 142.8, 142.7, 133.9, 131.6, 129.9, 129.7, 127.4, 126.4, 124.0, 61.64, 61.56, 58.87, 58.86, 55.2, 28.3, 27.9, 21.4, 20.0, 19.8, 16.2, 16.11, 16.10, 15.9, 15.8. ^{31}P NMR (121 MHz, $CDCl_3$): δ (*E*-isomer) = 17.8; δ (*Z*-isomer) = 17.9. ESI-HRMS: *m/z* calcd for $C_{21}H_{30}NO_6PSNa$ $[M + Na]^+$: 478.1429; found: 478.1428.
Compound (*E*)-**3ab**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 8.4 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.16–7.00 (m, 3 H), 6.95–6.83 (m, 2 H), 4.12–3.87 (m, 8 H), 2.45 (s, 3 H), 2.29 (d, *J* = 3.3 Hz, 3 H), 2.17 (s, 3 H), 1.18 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3, 159.8, 148.7, 148.4, 147.6, 147.4, 143.7, 136.9, 133.1, 132.4, 131.8, 129.9, 128.22, 128.16, 127.91, 127.89, 127.62, 127.58, 127.3, 62.1, 62.0, 57.9, 54.8, 28.8, 21.5, 20.3, 20.2, 16.2, 16.1. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.5.
Compound (*Z*)-**3ab**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 2 H), 7.41–7.24 (m, 5 H), 7.17–7.09 (m, 2 H), 4.52 (s, 2 H), 4.51–4.28 (m, 2 H), 3.92–3.67 (m, 2 H), 3.78–3.52 (m, 2 H), 2.40 (s, 3 H), 2.32 (s, 3 H), 1.68 (d, *J* = 2.7 Hz, 3 H), 1.04 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.9, 148.7, 148.6, 145.3, 145.2, 143.7, 136.0, 135.9, 134.0, 133.5, 132.04, 132.03, 131.1, 129.8, 128.83, 128.77, 128.53, 128.51, 127.83, 127.80, 127.5, 62.14, 62.06, 59.0, 55.3, 28.7, 21.5, 21.4, 21.2, 16.1, 16.0. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.0.
Compound **3bb**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ (*E*-isomer) = 7.73 (d, *J* = 7.8 Hz, 2 H), 7.41–7.05 (m, 7 H), 4.60 (t, *J* = 4.2 Hz, 2 H), 4.37 (t, *J* = 4.2 Hz, 2 H), 3.91–3.77 (m, 2 H), 3.77–3.60 (m, 2 H), 3.36 (d, *J* = 0.9 Hz, 3H), 2.43 (s, 3 H), 2.38 (s, 3 H), 1.05 (t, *J* = 7.2 Hz, 6 H); δ (*Z*-isomer) = 7.57 (d, *J* = 7.5 Hz, 2 H), 7.41–7.05 (m, 5 H), 6.99 (d, *J* = 7.2 Hz, 2 H), 4.23 (t, *J* = 4.2 Hz, 2 H), 4.13–3.91 (m, 6 H), 3.82 (s, 3 H), 2.43 (s, 3 H), 2.22 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 193.7, 165.3, 164.8, 164.5, 143.7, 143.6, 141.0, 140.6, 140.5, 140.4, 140.3 138.7, 138.6, 138.5, 138.41, 138.38, 136.2, 136.0, 134.9, 134.8, 133.8, 133.7, 133.0, 129.8, 129.7, 128.6, 128.52, 128.49, 128.45, 128.22, 128.17, 127.9, 127.8, 127.6, 127.5, 127.4, 63.0, 62.9, 62.8, 59.88, 59.86, 59.3, 55.5, 55.3, 53.1, 52.5, 29.0, 28.8, 21.42, 21.38, 16.1, 16.0, 15.9. ^{31}P NMR (121 MHz, $CDCl_3$): δ (*E*-isomer) = 11.9; δ (*Z*-isomer) = 11.0.
Compound (*E*)-**3ca**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.29–7.16 (m, 1 H), 4.46–4.35 (m, 4 H), 4.18–4.03 (m, 4 H), 2.44 (s, 3 H), 2.21 (s, 3 H), 1.85 (dd, *J* = 15.0, 1.5 Hz, 3 H), 1.33 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.0, 144.2, 141.7, 141.3, 135.5, 134.8, 133.2, 133.1, 132.9, 132.5, 130.0, 127.5, 62.3, 62.2, 57.8, 55.0, 29.9, 21.5, 16.4, 16.3, 14.9, 14.8. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 19.3.
Compound (*Z*)-**3ca**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 6.77–6.54 (m, 1 H), 4.51–4.43 (m, 2 H), 4.37–4.29 (m, 2 H), 4.07–3.90 (m, 4 H), 2.42 (s, 3 H), 2.20 (s, 3 H), 2.04 (dd, *J* = 13.2, 1.8 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.1, 143.9, 143.8, 143.7, 134.2, 134.0, 133.9, 133.6, 133.48, 133.47, 131.9, 129.8, 127.6, 62.1, 62.0, 59.1, 59.0, 55.0, 29.8, 22.1, 22.0, 21.5, 16.3, 16.2. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 16.7.
Compound (*E*)-**3eb**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.15 (m, 3 H), 7.07–6.97 (m, 2 H), 4.12–3.91 (m, 4 H), 3.60 (s, 6 H), 3.10–3.02 (m, 2 H), 2.95 (s, 2 H), 2.35 (d, *J* = 3.3 Hz, 3 H), 2.18 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.4, 171.0, 152.0, 151.7, 151.6, 151.4, 137.4, 137.3, 133.8, 129.8, 128.8, 128.7, 127.8, 127.5, 127.3, 61.9, 61.8, 56.8, 53.0, 44.9, 40.8, 29.0, 20.2, 20.1, 16.2, 16.1. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 15.6.
Compound (*Z*)-**3eb**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 3 H), 7.22–7.16 (m, 2 H), 3.96–3.70 (m, 4 H), 3.74 (s, 6 H), 3.70–3.30 (m, 4 H), 2.33 (s, 3 H), 1.79 (d, *J* = 2.4 Hz, 3 H), 1.10 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.8 152.4, 152.2, 150.1, 150.0, 136.8, 136.6, 133.9, 130.5, 129.11, 129.05, 128.4, 128.0, 127.5, 127.4, 61.9, 61.8, 57.3, 53.0, 45.6, 41.0, 28.9, 21.1, 20.9, 16.1, 16.0. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.7.
Compound (*E*)-**3ha**: pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.66 (s, 1 H), 7.14–7.00 (m, 1 H), 4.20–3.95 (m, 4 H), 2.34–2.14 (m, 4 H), 1.77 (dd, *J* = 14.4, 1.8 Hz, 3 H),

1.75–1.59 (m, 4 H), 1.34 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.2, 154.0, 153.7, 140.9, 140.7, 135.6, 131.6, 129.2, 62.0, 61.9, 30.6, 21.7, 21.6, 21.2, 16.4, 16.3, 14.2, 14.1. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 20.3.
Compound (*Z*)-**3ha**: pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.79 (s, 1 H), 6.70–6.60 (m, 1 H), 4.12–3.92 (m, 4 H), 2.35–2.15 (m, 4 H), 2.04 (dd, *J* = 13.2, 1.8 Hz, 3 H), 1.74–1.56 (m, 4 H), 1.28 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.6, 155.6, 155.5, 141.0, 140.9, 135.1, 131.7, 129.3, 61.7, 61.6, 31.4, 21.8, 21.7, 21.6, 21.5, 21.1, 16.4, 16.3. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 17.6.
Compound (*E*)-**3hb**: pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 7.54 (d, *J* = 23.1 Hz, 1 H), 7.32–7.13 (m, 5 H), 4.18–3.99 (m, 4 H), 2.16–2.00 (m, 4 H), 1.57–1.41 (m, 4 H), 1.26 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.6, 153.3, 153.0, 142.4, 142.2, 137.3, 135.9, 135.0, 134.4, 134.3, 128.6, 128.5, 128.4, 128.20, 128.17, 62.5, 62.4, 30.92, 30.90, 21.7, 21.0, 16.3, 16.2. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 17.2.
Compound (*Z*)-**3hb**: pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 (s, 1 H), 7.45–7.31 (m, 5 H), 7.08–6.88 (m, 1 H), 4.08–3.83 (m, 4 H), 2.50–2.38 (m, 2 H), 2.34–2.21 (m, 2 H), 1.75–1.64 (m, 4 H), 1.18 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.4, 155.5, 155.4, 144.4, 144.3, 138.5, 138.4, 137.7, 135.3, 135.17, 135.15, 128.3, 128.12, 128.05, 62.1, 62.0, 31.24, 31.21, 21.9, 21.7, 21.1, 16.2, 16.1. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 15.1.