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Chiral ytterbium silylamide catalyzed enantioselective phospha-Michael addition of diethyl phosphite to chalcones

Guoyao Li, Lu Wang, Zhigang Yao, Fan Xu *

Key Laboratory of Organic Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

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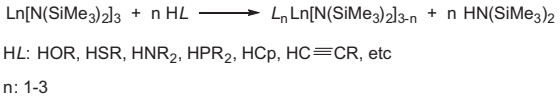
ABSTRACT

An efficient and enantioselective phospha-Michael addition of diethyl phosphite to chalcones has been established. In the presence of a catalytic amount of chiral lanthanide silylamide generated from $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ and salen, the reaction produced the target γ-oxophosphonates with high yields and enantioselectivity.

1. Introduction

Lanthanide silylamides, $Ln[N(SiMe_3)_2]_3$[1] and their chloride-bridged form $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$,[2] are regarded as a new type of catalyst that can function as a Lewis acid and a Brønsted base at the same time. A series of intermolecular and intramolecular reactions have been efficiently catalyzed by lanthanide silylamides and these include the Tishchenko reaction,[3] amidations,[4] monoadditions of terminal alkynes to nitriles,[5] coupling of isocyanides with terminal alkynes,[6] dimerization of terminal alkynes,[7] aldol condensations,[8] aza-Henry reactions,[9] guanylation of amines,[10] the Pudovik reaction,[11] phospha-Brook rearrangements,[12] and phospha-Michael additions.[13] Lanthanide silylamides are also highly active catalysts in versatile hydroelementation processes such as hydrosilylations,[14] hydroborations,[15] hydroaminations,[3b,16] hydrophosphinations,[17] and hydroalkoxylations.[18]

The most characteristic feature of lanthanide silylamides is that they can be used as precursors, because they easily react with Brønsted acidic compounds such as alcohols, phenols, cyclopentadienes, acetylenes, phosphanes, and thiols (Scheme 1). The rapid deprotonation of these substrates by $HN(SiMe_3)_2$ elimination may readily result in the generation of new Ln-X (X = O, S, P, N, C) bonds. It can therefore be assumed that if chiral Brønsted acidic ligands react with lanthanide silylamides, chiral lanthanide complexes can be prepared by the simple metathesis reaction between $Ln[N(SiMe_3)_2]_3$ and chiral ligands. To the best of our knowledge, a few chiral lanthanide silylamides have been synthesized and studied, however their use in asymmetric organic synthesis has received much less attention and reports concerning the development and application of chiral lanthanide silylamide-catalyzed asymmetric reactions are scarce. Marks[19] and Zi[20] evaluated chiral Ln catalysts generated from $Ln[N(SiMe_3)_2]_3$ and different chiral ligands, such as binaphthols and oxazolines, for the stereoselective intramolecular hydroamination/cyclization of aminoalkenes, respectively. Calter[21] achieved an efficient asymmetric synthesis of α-phenoxy-β-aryl-β-lactams in the presence of catalytic quantities of a silyl cinchona alkaloid and lanthanide silylamides. Therefore, due to the high activity of lanthanide silylamides presented in many reactions, the further development of chiral lanthanide silylamides and relevant processes of high efficiency and stereoselectivity for the asymmetric synthesis of valuable small molecule is a desirable and challenging goal.



Scheme 1. Metathesis reaction between lanthanide silylamides and Brønsted acidic compounds.

The formation of C—P bonds is one of the most important transformations in organic synthesis because of the tremendous importance of organophosphorus compounds in many different areas. Phospha-Michael addition,[22] the conjugate addition of P-nucleophiles to activated alkenes, is important in carbon—phosphorus bond formation because of its step-economy and atom-economy, and its catalysts, scope, and applications have been widely explored. Recently, to meet the growing demand for enantiomerically pure materials, the enantioselective phospha-Michael addition[23] has attracted considerable attention. Dialkyl phosphites,[24–28] diarylphosphines,[29,30] and dialkyl phosphine oxides[31–34] are used as

* Corresponding author. Tel.: +86 512 65880331; fax: +86 512 65880305.
E-mail address: xufan@suda.edu.cn (F. Xu).

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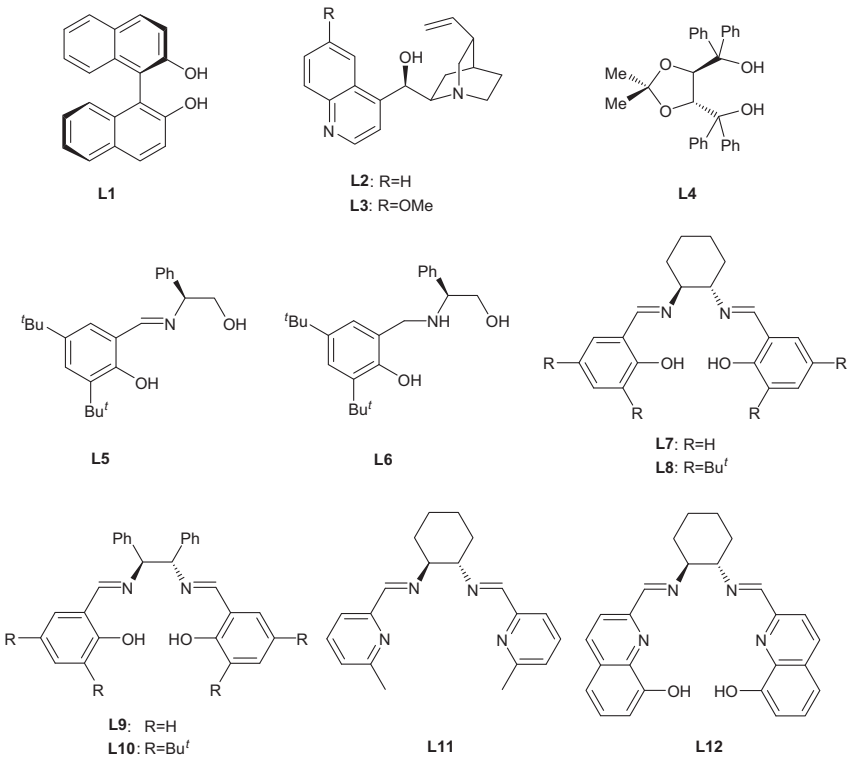
P-nucleophiles in this asymmetric addition. Considering the stability and smell of phosphorus reagents, dialkyl phosphite is the preferred choice and is also readily available. As for olefinic acceptors, reactions involving α,β-unsaturated ketones remain a challenge.[28–32] To date only one report[28] exists on the enantioselective phospha-Michael addition of a dialkyl phosphite to α,β-unsaturated ketones. This reaction was carried out in the presence of a dinuclear zinc catalyst to afford γ-oxophosphonates in high yields and with excellent enantioselectivities. Therefore, the development of efficient and catalytic processes to achieve this C—P bond-forming transformation and enable the enantioselective and atom economical synthesis of chiral phosphonates is still required. Herein, we report our recent results into the application of chiral lanthanide silylamides as catalysts for the asymmetric phospha-Michael addition of dialkyl phosphites to chalcones.

2. Results and discussion

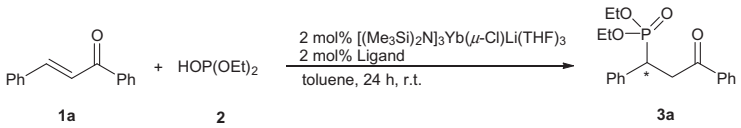
Initially, several chiral ligands (Scheme 2) were complexed in situ with $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, the tetracoordinate ytterbium silylamide, to catalyze the model reaction between chalcone **1a** and diethyl phosphite in dry toluene at room temperature; the results are shown in Table 1. We found that when (*R*)-BINOL, cinchonidine, quinine, and TADDOL **L1**–**L4** were used, the products were isolated in moderate yields but with no selectivity (Table 1, entries 1–4). A remarkable enhancement in enantioselectivity was achieved when the tridentate Schiff base **L5**, derived from L-phenylglycinol and 3,5-di-*tert*-butylsalicylaldehyde, was used (Table 1, entry 5). However, the hydrogenated Schiff base **L6** afforded a racemic product (Table 1, entry 6) although ligands **L5** and **L6** have the same absolute backbone configuration. Fortunately, the salen–Yb complexes that were formed in situ from $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ with different salens **L7**–**L10** showed great potential in this reaction. Product **3a** was thus obtained in moderate yields and with enhanced ee values (Table 1, entries 7–10). Table 1 indicates that the cyclohexanediamine-derived salens **L7**, **L8** were superior to the *o*-phenylenediamine-derived salens **L9**, **L10**, and the ligands with bulkier substituent groups such as *tert*-butyl provided better results. Complex **L7**-Yb afforded the product with 41% ee while **L8**-Yb afforded the product with the opposite configuration in 51% ee. Therefore, the steric hindrance of the R group of the salicylaldehyde moiety in the salen showed a complex effect on the enantioselectivity of the reaction. Additionally, the salen-like ligands **L11** and **L12** both afforded the product with no selectivity (Table 1, entries 11 and 12).

Next, a series of lanthanide silylamides were used to assess the influence of the central metal on the activity and selectivity (Table 2, entries 1–5). The results revealed that the lanthanide silylamides tested, besides that of Yb, all gave slightly increased yields with significantly diminished ee values. Considering the yield and the enantioselectivity, the **L8**-Yb complex was chosen for subsequent investigation. A further optimization of the reaction conditions, including catalyst loading and the molar ratio of lanthanide metal to ligand, was carried out and we found that a 10 mol % loading for both the catalyst and ligand was optimal (Table 2, entry 7). The reaction temperature was decreased to 0 °C with essentially no loss in yield; however, the enantioselectivity improved significantly (Table 2, entry 11). A survey of various solvents (Table 2, entries 11–17) revealed that toluene provided the product with comparatively good reactivity and enantioselectivity. When the chalcone/toluene solution was added slowly and evenly to the mixture of phosphite and catalyst within 2 h, an obvious increase in the enantiomeric excess from 73% to 89% was achieved and the yield also improved to 94% (Table 2, entry 18). A further decrease in temperature resulted in a reduction of the yield while the enantioselectivity was retained (Table 2, entry 19). Therefore, the optimal reaction conditions were identified as follows: 10 mol % $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, 10 mol % **L8**, 0.6 mmol diethyl phosphite, and 0.5 mmol chalcone in 2 mL toluene at 0 °C for 24 h.



Scheme 2. Chiral ligands **L1**–**L12**.

Table 1
Ligand screening for the asymmetric 1,4-addition of diethyl phosphite to chalcone[a]

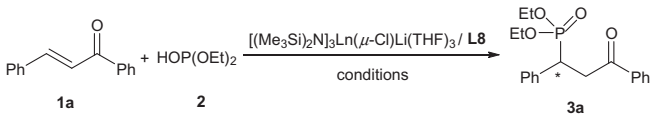


1a 2 3a

Entry	Ligand	Yield[b] (%)	ee[c] (%)
1	**L1**	52	0
2	**L2**	61	0
3	**L3**	71	0
4	**L4**	38	0
5	**L5**	29	−23
6	**L6**	43	0
7	**L7**	46	−41
8	**L8**	50	51
9	**L9**	45	9
10	**L10**	66	−37
11	**L11**	44	0
12	**L12**	56	0

[a] The reactions were carried out under argon by reacting chalcone (0.5 mmol), diethyl phosphite (0.6 mmol), 2 mol % $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$, and 2 mol % ligand in 2 mL of toluene at 25 °C for 24 h.
[b] Isolated yield.
[c] Determined by HPLC analysis.

Table 2
Condition screening for the asymmetric 1,4-addition of diethyl phosphite to chalcone[a]



1a 2 3a

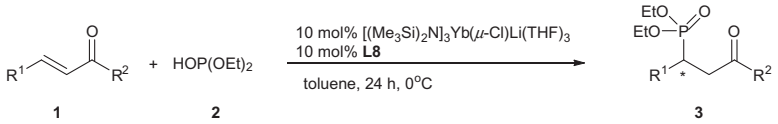
Entry	Ln	Catalyst loading (mol %)	Ligand loading (mol %)	Temp. (°C)	Solvent	Yield[b] (%)	ee[c] (%)
1	La	2	2	25	Toluene	62	5
2	Nd	2	2	25	Toluene	63	26
3	Sm	2	2	25	Toluene	60	36
4	Yb	2	2	25	Toluene	50	51
5	Y	2	2	25	Toluene	66	16
6	Yb	5	5	25	Toluene	88	57
7	Yb	10	10	25	Toluene	93	64
8	Yb	10	5	25	Toluene	87	47
9	Yb	10	15	25	Toluene	86	59
10	Yb	10	20	25	Toluene	84	47
11	Yb	10	10	0	Toluene	89	73
12	Yb	10	10	0	THF	81	63
13	Yb	10	10	0	CH_3CN	79	60
14	Yb	10	10	0	Et_2O	37	50
15	Yb	10	10	0	*n*-hexane	69	65
16	Yb	10	10	0	CH_2Cl_2	56	59
17	Yb	10	10	0	*m*-xylene	91	69
18[d]	Yb	10	10	0	Toluene	94	89
19[d]	Yb	10	10	−10	Toluene	86	89

[a] The reactions were carried out under argon by reacting chalcone (0.5 mmol) and diethyl phosphite (0.6 mmol) in 2 mL of solvent for 24 h.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] The chalcone/toluene solution was added slowly and evenly to a mixture of phosphite and catalyst within 2 h.

A series of substituted chalcones were examined under the optimized conditions, and the corresponding products were obtained in high yields and with high enantioselectivities (Table 3). The electronic properties of the aryls of chalcone had no obvious effect on the enantioselectivities of the products, while the steric hindrance was important with regard to the enantioselectivity. Chalcones with an *ortho*-substituted phenyl at the 3-position afforded the corresponding products with relatively higher ee values (Table 3, entries 8, 11–17). 3-Naphthyl substituted and 3-heteroaromatic chalcones all reacted smoothly with diethyl phosphite to give products with ee values higher than 90% (Table 3, entries 9 and 10). The absolute configuration of compound **3c** (Table 3, entry 3) was determined to be (*S*) by comparison with the literature data.[28] The other products were tentatively assigned by analogy.

Although the detailed reaction process remains unclear, a plausible mechanism is shown in Scheme 3. According to the properties of $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$, the initial step of this reaction involves an in situ protonolytic generation of the salen-Ln-$N(SiMe_3)_2$ complex **A**. Complex **A** reacts with diethyl phosphite to release the last $HN(SiMe_3)_2$ and forms intermediate **B**. As a

Table 3
Substrate scope for the asymmetric reactions of substituted chalcones with diethyl phosphite[a]



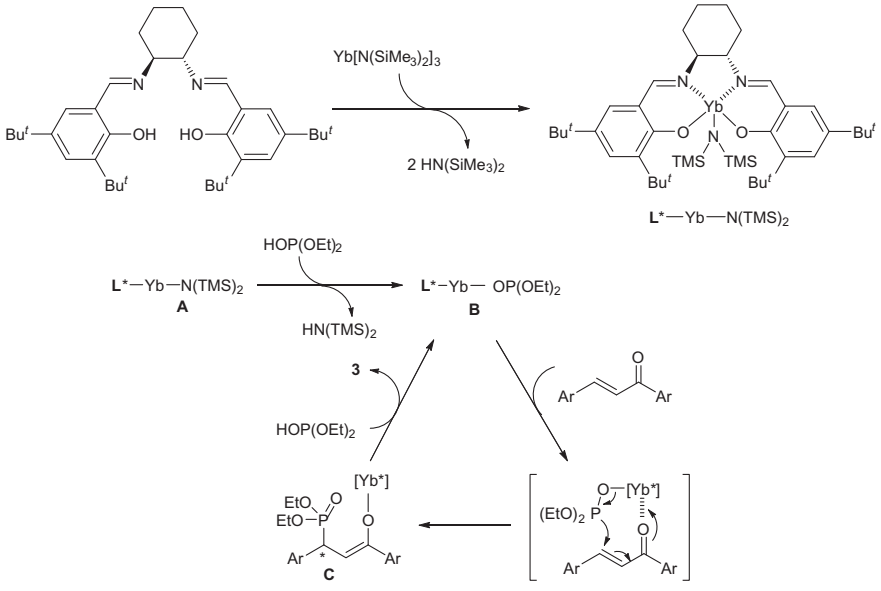
1 2 3

Entry	R^1	R^2	Product	Yield[b] (%)	ee[c] (%)
1	Ph	Ph	**3a**	94	89
2	Ph	4-ClC_6H_4	**3b**	87	88
3	Ph	4-$MeOC_6H_4$	**3c**	91	82(*S*)[d]
4	2-$MeOC_6H_4$	Ph	**3d**	80	82
5[e]	4-ClC_6H_4	Ph	**3e**	82	91
6[e]	4-BrC_6H_4	Ph	**3f**	82	90
7	4-MeC_6H_4	Ph	**3g**	88	86
8	2-MeC_6H_4	Ph	**3h**	84	94
9	1-naphthyl	Ph	**3i**	87	93
10	2-thienyl	Ph	**3j**	88	90
11	2-MeC_6H_4	4-ClC_6H_4	**3k**	89	93
12	2-MeC_6H_4	4-$MeOC_6H_4$	**3l**	86	91
13	2,6-$(Me)_2C_6H_3$	4-MeC_6H_4	**3m**	93	94
14	2,6-$(Me)_2C_6H_3$	4-FC_6H_4	**3n**	89	91
15	2,6-$(Me)_2C_6H_3$	4-ClC_6H_4	**3o**	87	94
16	2,6-$(Me)_2C_6H_3$	4-BrC_6H_4	**3p**	89	92
17	2,6-$(Me)_2C_6H_3$	4-$MeOC_6H_4$	**3q**	91	92

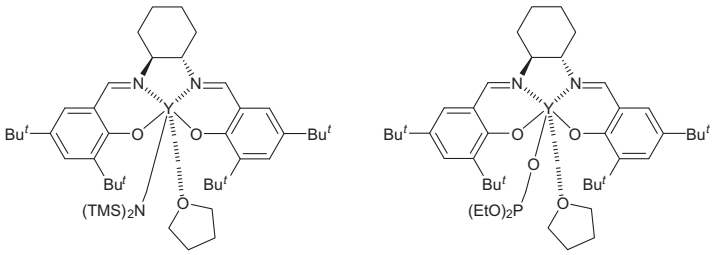
[a] The reactions were carried out under argon by reacting chalcone (0.5 mmol), diethyl phosphite (0.6 mmol), 10 mol % $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$, 10 mol % **L8** in 2 mL of toluene at 0 °C for 24 h.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] The absolute configuration was determined by chemical correlation with a known compound.
[e] 4 mL of toluene were used.

highly oxophilic Lewis acid, the central lanthanide atom of **B** can coordinate with the carbonyl group of the chalcone. Such a coordination may both activate the chalcone and lead to a close contact between the enone and the P-nucleophile. This simultaneously leads to a further face selective reaction in a chiral environment. γ-Oxophosphonate **3** is then released upon proton exchange between **C** and another phosphite, and catalyst **B** is regenerated.

For further insight into the chiral active species for the reaction, the **L8**-Y complex **4** was synthesized by treatment of **L8** with $[(Me_3Si)_2N]_3Y(\mu\text{-}Cl)Li(THF)_3$ in a molar ratio of 1:1 at room temperature in THF. Evaporation of the resulting yellow solution and crystallization from toluene and hexane gave a yellow powder, which was characterized by ^1H NMR spectroscopy. As expected, the spectrum showed that the central Y atom bonds to two aryloxide groups from salen and one silylamide, while one tetrahydrofuran molecule is also coordinated to the central metal, as shown in Scheme 4. Following the same procedure, the analogous **L8**–Yb complex was prepared as a yellow powder and evaluated as a catalyst for the model reaction between **1a** and **2**. A 93% yield and 85% ee value were obtained, which were similar to the results obtained for



Scheme 3. Proposed mechanism for the addition of diethyl phosphite to chalcone.



Scheme 4. Salen–Y complexes.

the in situ catalytic system. Next, complex **4** and diethyl phosphite were mixed in a molar ratio of 1:1 on an NMR-tube scale using C_6D_6 as the solvent. The ^{1}H NMR spectrum of the mixture showed that complex **5** (Scheme 4) was formed. The silylamide group bonding to the central metal in **4** was exchanged into a phosphite group, which is consistent with the hypothesis on the transformation of **A** to **B** in the proposed mechanism (Scheme 3). Bis(trimethylsilyl)amine [$HN(SiMe_3)_2$, 30 mol %], which is released in situ, was also used to verify whether it could act independently as a catalyst. No product was detected under the optimal reaction conditions.

3. Conclusion

We have successfully developed an asymmetric phospha-Michael addition of diethyl phosphite to chalcones. The chiral lanthanide silylamide, formed in situ from $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$ and salen, was found to be an efficient catalyst for the reaction and provided the target γ-oxophosphonates in high yields and enantioselectivities. The further development of chiral lanthanide silylamide compounds and their application as catalysts for asymmetric reactions are currently being investigated in our laboratory.

4. Experimental

4.1. General information

All manipulations were conducted under an atmosphere of dry argon with flame-dried glassware. $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$[2c-2e] were synthesized according to the literature method. Solvents were distilled before use from calcium hydride or sodium/benzophenone. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker AVANCEIII 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. HRMS data were obtained on a Micromass GCT instrument. IR spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer. The enantiomeric excess data were determined on an Agilent 1200 Series HPLC with Chiralpak AS-H, Chiralpak AD-H, Chiralcel OJ-H, and Chiralpak IA columns.

4.2. Typical procedure for the asymmetric phospha-Michael addition

A mixture of $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$ (45.5 mg, 0.05 mmol) and **L8** (27.3 mg, 0.05 mmol) in toluene (0.5 mL) was stirred at room temperature for 20 min. Next, a solution of diethyl phosphite (77 μL, 0.6 mmol) in toluene (0.5 mL) was added and stirred for 20 min. The mixture was then cooled to 0 °C, which was followed by the addition of a solution of chalcone **1a** (104.1 mg, 0.5 mmol) in toluene (1 mL) slowly and evenly within 2 h at 0 °C. The mixture was then stirred at this temperature for 24 h. Water was added, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 7:1 to 1:1) to give **3a** as a colorless oil.

4.3. Synthesis of compound 4

A mixture of $[(Me_3Si)_2N]_3Y(\mu\text{-Cl})Li(THF)_3$ (1.66 g, 2 mmol) and **L8** (1.09 g, 2 mmol) in THF (20 mL) was stirred at room temperature for 24 h. THF was then removed under reduced pressure, and compound **4** was obtained as a yellow powder in toluene and hexane mixed solvent at 0 °C. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm): 8.01 (s, 1H, N=C*H*), 7.77 (s, 1H, N=C*H*), 7.74 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.73 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.32 (d, *J* = 2.8 Hz, 1H, Ar*H*), 7.05 (d, *J* = 2.8 Hz, 1H, Ar*H*), 4.49–4.43 (m, 1H, N—C*H*), 3.81 (m, 4H, 2 × CH_2 (THF)), 2.31–2.25 (m, 1H, N—C*H*), 1.75 (s, 9H, *t*-Bu), 1.66 (s, 9H, *t*-Bu), 1.53–1.41 (m, 10H, 3 × CH_2 + 2 × CH_2 (THF)), 1.37 (s, 9H, *t*-Bu), 1.36 (s, 9H, *t*-Bu), 1.25–1.13 (m, 2H, CH_2), 0.31 (s, 18H, 2 × $Si(CH_3)_3$).

4.4. Characterization of compound 5

The reaction of compound **4** (33.6 mg, 0.0388 mmol) with $HOP(OEt)_2$ (5 μL, 0.0388 mmol) was performed using C_6D_6 (0.8 mL) as the solvent in a Teflon valve-sealed J-Young tube and the ^{1}H NMR spectrum of **5** was obtained using C_6D_6 as an internal reference. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm): 7.84 (s, 1H, N=C*H*), 7.74 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.70 (s, 1H, N=C*H*), 7.59 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.40 (d, *J* = 2.4 Hz, 1H, Ar*H*), 7.06 (d, *J* = 2.8 Hz, 1H, Ar*H*), 4.75–4.70 (m, 1H, N-C*H*), 4.19–4.04 (m, 2H, OCH_2), 3.98–3.85 (m, 2H, OCH_2), 3.59 (m, 4H, 2 × CH_2 (THF)), 2.25–2.19 (m, 1H, N-C*H*), 1.88 (s, 9H, *t*-Bu), 1.66 (s, 9H, *t*-Bu), 1.53 (s, 9H, *t*-Bu), 1.50–1.42 (m, 10H, 3 × CH_2 + 2 × CH_2 (THF)), 1.36 (s, 9H, *t*-Bu), 1.18–1.16 (m, 2H, CH_2), 1.10 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 0.89 (t, *J* = 7.2 Hz, 3H, CH_2CH_3).

5. Characterization of the products

5.1. (*S*)-Diethyl 3-oxo-1,3-diphenylpropylphosphonate[13] 3a

Colorless oil. 89% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 10.0 min, t_{minor} = 12.9 min). $[\alpha]_D^{29} = -33$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46–7.42 (m, 4H), 7.31–7.20 (m, 3H), 4.17–3.87 (m, 4H), 3.81–3.63 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H).

5.2. (*S*)-Diethyl 3-(4-chlorophenyl)-3-oxo-1-phenylpropylphosphonate[13] 3b

Colorless oil. 88% ee determined by HPLC on a Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min,

t_{minor} = 19.8 min, t_{major} = 23.5 min). $[\alpha]_D^{27}$ = −41 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.88 (d, *J* = 8.0 Hz, 2H), 7.42–7.40 (m, 4H), 7.32–7.21 (m, 3H), 4.10–3.85 (m, 4H), 3.76–3.60 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H).

5.3. (*S*)-Diethyl 3-(4-methoxyphenyl)-3-oxo-1-phenylpropylphosphonate[13] 3c

Colorless oil. 82% ee determined by HPLC on a Chiralcel OJ-H column (hexane/2-propanol = 92/8, flow rate = 1.0 mL/min, t_{minor} = 19.7 min, t_{major} = 24.5 min). $[\alpha]_D^{29}$ = −44 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.31–7.21 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.10–3.89 (m, 4H), 3.84 (s, 3H), 3.76–3.58 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H).

5.4. (*S*)-Diethyl 1-(2-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate[13] 3d

Colorless oil. 82% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 9.2 min, t_{minor} = 12.9 min). $[\alpha]_D^{29}$ = −40 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45–7.41 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.90–6.86 (m, 2H), 4.66–4.57 (m, 1H), 4.11–4.08 (m, 2H), 3.95–3.69 (m, 4H), 3.87 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H).

5.5. (*S*)-Diethyl 1-(4-chlorophenyl)-3-oxo-3-phenylpropylphosphonate[13] 3e

Colorless oil. 91% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{major} = 7.0 min, t_{minor} = 9.0 min). $[\alpha]_D^{29}$ = −46 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.47–7.26 (m, 6H), 4.14–4.05 (m, 2H), 3.99–3.89 (m, 2H), 3.83–3.61 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

5.6. (*S*)-Diethyl 1-(4-bromophenyl)-3-oxo-3-phenylpropylphosphonate[13] 3f

Colorless oil. 90% ee determined by HPLC on a Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 19.9 min, t_{minor} = 25.1 min). $[\alpha]_D^{26}$ = −43 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47–7.27 (m, 6H), 4.15–3.87 (m, 4H), 3.84–3.60 (m, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H).

5.7. (*S*)-Diethyl 3-oxo-3-phenyl-1-*p*-tolylpropylphosphonate[13] 3g

Colorless oil. 86% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, t_{major} = 10.5 min, t_{minor} = 14.9 min). $[\alpha]_D^{29}$ = −34 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 4.12–4.02 (m, 2H), 3.98–3.87 (m, 2H), 3.78–3.61 (m, 3H), 2.28 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

5.8. (*S*)-Diethyl 3-oxo-3-phenyl-1-*o*-tolylpropylphosphonate[13] 3h

Colorless oil. 94% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 5.3 min, t_{minor} = 7.6 min). $[\alpha]_D^{29}$ = −48 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.46–7.42 (m, 3H), 7.17–7.08 (m, 3H), 4.27–4.18 (m, 1H), 4.12–4.02 (m, 2H), 3.88–3.79 (m, 2H), 3.72–3.58 (m, 2H), 2.55 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H).

5.9. (*S*)-Diethyl 1-(naphthalen-1-yl)-3-oxo-3-phenylpropylphosphonate[13] 3i

Colorless oil. 93% ee determined by HPLC on a Chiralpak AD-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 18.0 min, t_{minor} = 22.1 min). $[\alpha]_D^{28}$ = −81 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.40 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75–7.43 (m, 8H), 4.94 (d, *J* = 22.4 Hz, 1H), 4.12–4.06 (m, 2H), 3.91 (dd, *J* = 10.4, 6.8 Hz, 2H), 3.78–3.68 (m, 1H), 3.42–3.36 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

5.10. (*S*)-Diethyl 3-oxo-3-phenyl-1-(thiophen-2-yl)propylphosphonate 3j

Colorless oil. 90% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 9.9 min, t_{minor} = 11.3 min). $[\alpha]_D^{28}$ = −25 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.96–7.94 (m, 2H), 7.58–7.54 (m, 1H), 7.47–7.43 (m, 2H), 7.16–7.15 (m, 1H), 7.09 (t, *J* = 3.2 Hz, 1H), 6.93–6.91 (m, 1H), 4.35–4.26 (m, 1H), 4.14–3.83 (m, 4H), 3.76–3.61 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.0 (d, *J* = 14.3 Hz), 138.1 (d, *J* = 8.3 Hz), 136.5, 133.5, 128.7, 128.2, 126.9, 126.8, 124.7 (d, *J* = 3.4 Hz), 63.2 (d, *J* = 6.8 Hz), 62.5 (d, *J* = 7.2 Hz), 40.4, 34.3 (d, *J* = 144.8 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 26.5. IR ν_{max}: 2982, 1689, 1597, 1393, 1249, 1028, 852, 789, 757, 692 cm^{-1}. HRMS (ESI): calcd for $C_{17}H_{21}NaO_4PS$ $[M+Na]^+$ 375.0790, found 375.0788.

5.11. (*S*)-Diethyl 3-(4-chlorophenyl)-3-oxo-1-*o*-tolylpropylphosphonate 3k

Colorless oil. 93% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 6.7 min, t_{minor} = 9.0 min). $[\alpha]_D^{29}$ = −64 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.87 (d, *J* = 8.4 Hz, 2H), 7.42–7.40 (m, 3H), 7.17–7.10 (m, 3H), 4.24–4.15 (m, 1H), 4.12–4.04 (m, 2H), 3.89–3.73 (m, 2H), 3.68–3.56 (m, 2H), 2.54 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.8 (d, *J* = 15.6 Hz), 139.2, 137.4 (d, *J* = 7.5 Hz), 134.4, 133.9 (d, *J* = 6.6 Hz), 130.1, 129.1, 128.5, 127.1 (d, *J* = 3.7 Hz), 126.7, 125.8, 62.6 (d, *J* = 6.8 Hz), 61.5 (d, *J* = 7.2 Hz), 39.2, 33.6 (d, *J* = 140.0 Hz), 19.8, 16.1 (d, *J* = 5.8 Hz), 15.8 (d, *J* = 5.4 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.0. IR ν_{max}: 2982, 1689, 1592, 1496, 1243, 1045, 1020, 860, 781, 740 cm^{-1}. HRMS (ESI): calcd for $C_{20}H_{24}ClNaO_4P$ $[M+Na]^+$ 417.0993, found 417.0991.

5.12. (*S*)-Diethyl 3-(4-methoxyphenyl)-3-oxo-1-*o*-tolylpropylphosphonate 3l

Colorless oil. 91% ee determined by HPLC on a Chiralpak AS-H column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{major} = 7.5 min, t_{minor} = 8.6 min). $[\alpha]_D^{29}$ = −63 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.93 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 6.4 Hz, 1H), 7.16–7.07 (m, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.27–4.18 (m, 1H), 4.10–4.02 (m, 2H), 3.85–3.74 (m, 5H), 3.65–3.57 (m, 2H), 2.55 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.9 (d, *J* = 15.5 Hz), 163.5, 137.7 (d, *J* = 7.0 Hz), 134.4 (d, *J* = 5.9 Hz), 130.3, 129.5, 127.5, 127.4, 126.9, 126.0, 113.6, 62.9 (d, *J* = 6.5 Hz), 61.8 (d, *J* = 6.8 Hz), 55.3, 39.1, 33.9 (d, *J* = 139.7 Hz), 20.1, 16.3 (d, *J* = 5.6 Hz), 16.1 (d, *J* = 5.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.6. IR ν_{max}: 2981, 1681, 1601, 1512, 1243, 1058, 1028, 838, 788, 769 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{27}NaO_5P$ $[M+Na]^+$ 413.1488, found 413.1490.

5.13. (*S*)-Diethyl 1-(2,6-dimethylphenyl)-3-oxo-3-*p*-tolylpropylphosphonate 3m

Colorless oil. 94% ee determined by HPLC on a Chiralpak IA column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{minor} = 4.6 min, t_{major} = 5.2 min). $[\alpha]_D^{28}$ = −58 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz,$CDCl_3$) δ (ppm): 7.86 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.02–6.96 (m, 3H), 4.70 (dt, *J* = 28.4, 6.0 Hz, 1H), 4.14–4.02 (m, 2H), 3.92–3.79 (m, 2H), 3.76–3.54 (m, 2H), 2.66 (s, 3H), 2.56 (s, 3H), 2.39 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 196.1 (d, *J* = 10.7 Hz), 144.0, 138.7 (d, *J* = 7.5 Hz), 137.7 (d, *J* = 4.4 Hz), 133.9, 133.0 (d, *J* = 5.6 Hz), 130.2, 129.3, 128.3, 128.1, 126.9, 62.8 (d, *J* = 6.9 Hz), 61.5 (d, *J* = 7.2 Hz), 38.0, 34.8 (d, *J* = 139.1 Hz), 21.8, 21.7, 21.6, 16.3 (d, *J* = 6.1 Hz), 16.0 (d, *J* = 5.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.7. IR ν_{max}: 2980, 1689, 1608, 1242, 1029, 798, 770 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{29}NaO_4P$ $[M+Na]^+$ 411.1696, found 411.1694.

5.14. (*S*)-Diethyl 1-(2,6-dimethylphenyl)-3-(4-fluorophenyl)-3-oxopropylphosphonate 3n

Colorless oil. 91% ee determined by HPLC on a Chiralpak IA column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{minor} = 4.6 min, t_{major} = 5.1 min). $[\alpha]_D^{29}$ = −46 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 7.03–6.98 (m, 3H), 4.67 (dt, *J* = 28.8, 6.0 Hz, 1H), 4.12–4.02 (m, 2H), 3.93–3.79 (m, 2H), 3.74–3.54 (m, 2H), 2.66 (s, 3H), 2.56 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.3 (d, *J* = 10.3 Hz), 165. 9 (d, *J* = 253.7 Hz), 138.9 (d, *J* = 7.7 Hz), 137.8 (d, *J* = 4.3 Hz), 133.1, 133.0, 130.8 (d, *J* = 9.2 Hz), 130.4, 128.5, 127.1, 115.9 (d, *J* = 21.7 Hz), 63.0 (d, *J* = 6.8 Hz), 61.7 (d, *J* = 7.2 Hz), 38.3, 34.1 (d, *J* = 139.2 Hz), 21.9, 21.8, 16.4 (d, *J* = 6.1 Hz), 16.1 (d, *J* = 5.9 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.4. IR ν_{max}: 2981, 1690, 1598, 1506, 1234, 1158, 1027, 841, 797, 769 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{27}FO_4P$ $[M+H]^+$ 393.1626, found 393.1626.

5.15. (*S*)-Diethyl 3-(4-chlorophenyl)-1-(2,6-dimethylphenyl)-3-oxopropylphosphonate 3o

Colorless oil. 94% ee determined by HPLC on a Chiralpak IA column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{minor} = 5.1 min, t_{major} = 5.9 min). $[\alpha]_D^{29}$ = −43 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.03–6.98 (m, 3H), 4.66 (dt, *J* = 28.8, 6.0 Hz, 1H), 4.12–4.03 (m, 2H), 3.92–3.81 (m, 2H), 3.73–3.56 (m, 2H), 2.65 (s, 3H), 2.55 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.6 (d, *J* = 10.8 Hz), 139.7, 138.8 (d, *J* = 7.5 Hz), 137.7 (d, *J* = 4.4 Hz), 134.7, 132.8 (d, *J* = 5.5 Hz), 130.3, 129.5, 129.0, 128.4, 127.1, 63.0 (d, *J* = 6.9 Hz), 61.7 (d, *J* = 7.3 Hz), 38.3, 33.9 (d, *J* = 139.2 Hz), 21.9, 21.8, 16.4 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 5.7 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.3. IR ν_{max}: 2980, 1690, 1590, 1475, 1242, 1093, 1029, 801, 771 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{26}ClNaO_4P$ $[M+Na]^+$ 431.1149, found 431.1150.

5.16. (*S*)-Diethyl 3-(4-bromophenyl)-1-(2,6-dimethylphenyl)-3-oxopropylphosphonate 3p

Colorless oil. 92% ee determined by HPLC on a Chiralpak IA column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{minor} = 5.3 min, t_{major} = 6.2 min). $[\alpha]_D^{27}$ = -49 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.03–6.98 (m, 3H), 4.65 (dt, *J* = 28.4, 6.0 Hz, 1H), 4.12–4.02 (m, 2H), 3.91–3.79 (m, 2H), 3.73–3.54 (m, 2H), 2.65 (s, 3H), 2.55 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.8 (d, *J* = 10.9 Hz), 138.8 (d, *J* = 7.7 Hz), 137.7 (d, *J* = 4.4 Hz), 135.2, 132.9 (d, *J* = 5.7 Hz), 132.0, 130.3 (d, *J* = 2.8 Hz), 129.6, 128.5, 128.4, 127.1, 63.0 (d, *J* = 6.8 Hz), 61.7 (d, *J* = 7.2 Hz), 38.3, 34.0 (d, *J* = 140.3 Hz), 21.9, 21.8, 16.4 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 5.8 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.3. IR ν_{max}: 2979, 1690, 1585, 1474, 1244, 1053, 1030, 799, 770 cm^{-1}. HRMS (ESI): calcd for $C_{21}H_{26}BrNaO_4P$ $[M+Na]^+$ 475.0644, found 475.0644.

5.17. (*S*)-Diethyl 1-(2,6-dimethylphenyl)-3-(4-methoxyphenyl)-3-oxopropylphosphonate 3q

Colorless oil. 92% ee determined by HPLC on a Chiralpak IA column (hexane/2-propanol = 90:10, flow rate = 1.0 mL/min, t_{minor} = 6.6 min, t_{major} = 7.8 min). $[\alpha]_D^{29}$ = −59 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.94 (d, *J* = 9.2 Hz, 2H), 7.01–6.96 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.70 (dt, *J* = 28.4, 6.0 Hz, 1H), 4.12–4.02 (m, 2H), 3.90–3.80 (m, 5H), 3.73–3.56 (m, 2H), 2.67 (d, *J* = 1.6 Hz, 3H), 2.57 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.1 (d, *J* = 10.7 Hz), 163.6, 138.8 (d, *J* = 7.5 Hz), 137.8 (d, *J* = 4.5 Hz), 133.2 (d, *J* = 5.5 Hz), 130.3, 130.2, 129.5, 128.3, 126.9, 113.8, 62.8 (d, *J* = 6.9 Hz), 61.6 (d, *J* = 7.2 Hz), 55.4, 37.9, 34.0 (d, *J* = 138.9 Hz), 21.9, 21.8, 16.3 (d, *J* = 6.0 Hz), 16.1 (d, *J* = 5.6 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 29.8. IR ν_{max}: 2980, 1681, 1602, 1512, 1242, 1054, 1030, 838, 798, 772 cm^{-1}. HRMS (ESI): calcd for $C_{22}H_{29}NaO_5P$ $[M+Na]^+$ 427.1645, found 427.1640.

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