Phosphine-Catalyzed [3+2] Cyclizations: Applications to the Enantioselective Synthesis of Cyclopentene-Fused Chromanones and Dihydroquinolinones

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Abstract: Phosphine-promoted [3+2] cyclizations of allenic esters or phosphonates with coumarin derivatives were used to synthesize functionalized bicyclo[4.3.0]chroman-2-ones. Analogous bicyclo[4.3.0]quinolinones were similarly prepared by a two-step strategy involving a phosphine-catalyzed [3+2] cyclization of diethyl propadienylphosphonate and 3-(2-nitrophenyl)acrylate as the key step. Enantiomerically enriched compounds, with enantiomeric excesses in the range 70–86%, were obtained by using (*S*,*S*)-FerroPHANE as the chiral catalyst for the cyclization step.

Key words: catalysis, cyclizations, heterocycles, stereoselective synthesis, chromanones

Cyclopentane-fused chromanones, dihydroquinolinones, and derived structures are structural features of many natural products and biologically active compounds. Some relevant examples, shown in Figure 1, include the hebertane sesquiterpene hebertenolide (**I**),[1] the estrogen receptor β agonist SERBA-1 (**II**),[2] (+)-meloscine (**III**),[3] and the nitric oxide synthase (NOS) inhibitors **IV**.[4]

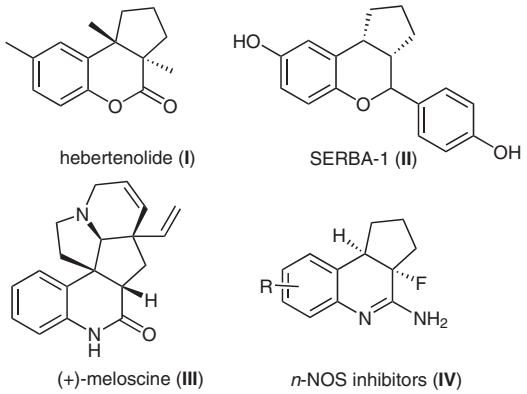
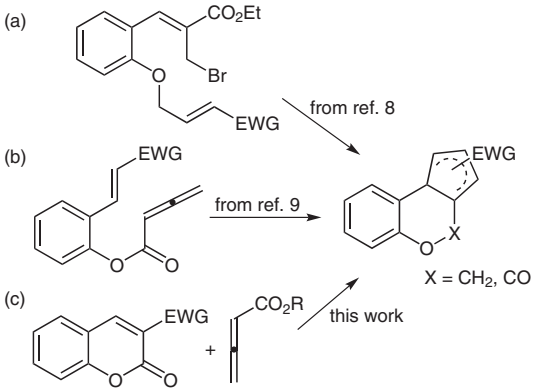


Figure 1 Natural products and biologically active compounds containing benzobicyclo[4.3.0] subunits derived from chromanones and dihydroquinolones

Construction of these [4.3.0] bicyclic scaffolds has been carried out mainly by cyclization methods in which chromen-2-ones[5,6] or quinolin-2-ones[7] served as the two-atom units. The olefinic bonds of these substrates underwent [3+2] cycloaddition reactions with cyclopropenones,[5] palladium-promoted cycloadditions with trimethylenemethane fragments,[6] or photochemical [2+2] annulations and ring-enlargement reactions.[7]

Bicyclic chromane and chromanone scaffolds have also been prepared by phosphine-catalyzed reactions by taking advantage of intramolecular annulation processes. These involve either ring-forming reactions combining an allylic and an olefinic function,[8] or intramolecular [3+2] cyclizations between an allene and an olefin function (Scheme 1).[9] Enantioselective variants have been developed only for the synthesis of bicyclic chromanes.[10]



Scheme 1 Strategies for building chromane-derived benzobicyclo[4.3.0] units with phosphine catalysis

As a complement to these established methods, we conceived a [3+2] cyclization strategy involving allenoates and either chromen-2-ones (Scheme 1, equation c) or quinolin-2-ones as the substrates in phosphine-promoted processes. We have examined enantioselective variants of these annulation reactions with the aim of preparing enantiomerically enriched bicyclic species. The main results of our studies are summarized below.

Our synthetic approach is based on the [3+2] cyclization between allenoates and electron-deficient olefins introduced by Zhang and Lu[11] which has been applied to a variety of functionalized substrates,[12] including cyclic alkenes as the two-carbon partners.[13] As a new variant on these reactions, we have investigated the use of coumarins and quinolin-2-ones as potentially suitable olefinic substrates. In preliminary experiments, mixtures of ethyl buta-2,3-dienoate and either ethyl 1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**) or ethyl 2-oxo-2*H*-

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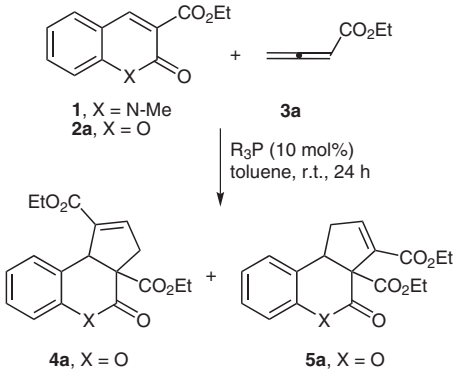
chromene-3-carboxylate (**2a**) were subjected to nucleophilic phosphine catalysis under the usual annulation conditions. With either triphenylphosphine or tributylphosphine as the catalyst, the dihydroquinoline derivative **1** failed to react at a 20% catalyst loading and a temperature of either 25 or 80 °C, whereas the substituted coumarin **2a** was efficiently converted into a mixture of the desired cycloadducts **4a** and **5a** at room temperature when triphenylphosphine was used as the catalyst (Table 1, entry 2).

Table 1 Phosphine-Promoted [3+2] Cyclizations of a 2-Oxo-2*H*-chromene and Attempted Cyclizations of a Quinoline Derivative



Entry	Substrate	Phosphine	**4a:5a**	Yield of **4a** (%)	ee (%)
1	**1**	Ph_3P or Bu_3P	–	–[a]	–
2	**2a**	Ph_3P	5:1	76	–
3	**2a**	(*S*)-*t*-Bu-Binepine	5:1	77	34
4	**2a**	(*S*,*S*)-FerroPHANE[b]	5:1	84	72

[a] Reactions performed at either r.t. or 80 °C with amounts of catalyst of up to 20 mol%.

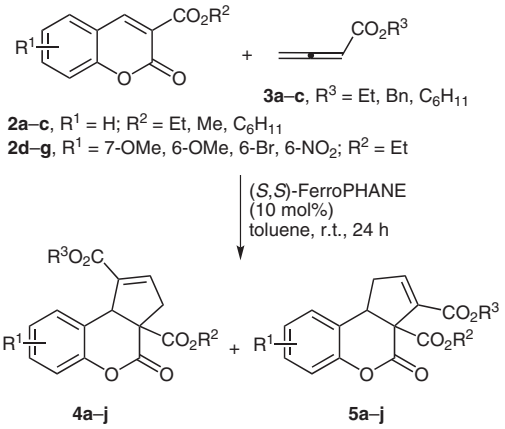
[b]

The reaction gave the so-called α-adduct **4a** as the major isomer (5:1 regioisomeric ratio); this was readily separated from the γ-adduct **5a** by column chromatography and isolated in pure form in 76% yield. The regiochemistry was unambiguously assigned by ^1H NMR. In the major product **4a**, the CH-proton at the ring junction (*9b*-CH) gives $^4J_{H-H}$ couplings of 2.7 and 1.2 Hz (δ = 4.64 ppm), whereas the same CH-proton of the γ-adduct **5a** displays $^3J_{H-H}$ couplings of 10.5 and 8.1 Hz (δ = 4.02 ppm). The observed regioselectivity is fully consistent with previous reports that prevalent or exclusive formation of α-adducts takes place for annulations of allenoates on cyclic alkenes.[13]

We then investigated enantioselective variants of the same reaction with either (*S*)-*t*-Bu-Binepine or (*S*,*S*)-FerroPHANE as the catalyst, since both these phosphines have been previously demonstrated to give high enantiocontrol in [3+2] cyclizations of this class.[14] In our experiments, these chiral catalysts afforded the desired cycloadducts in good yields and high regioselectivities. (*S*,*S*)-FerroPHANE also showed good levels of enantioselectivity (72% ee), whereas (*S*)-*t*-Bu-Binepine afforded an only moderate enantiomeric excess (34% ee). We therefore selected (*S*,*S*)-FerroPHANE as our preferred catalyst for further studies.

In an attempt to improve the selectivity of these cyclizations, we changed the ester functions in both the allene and the coumarin. With (*S*,*S*)-FerroPHANE as the catalyst, increasing the size of the allene R^2 group (entries 1–3, Table 2) had almost no effect on the regioselectivity, whereas the enantiomeric excess tended to decrease when a bulky cyclohexyl group was used (entry 3). On the other hand, only small modulations of the regioselectivity were observed on changing the steric bulk of the R^1 group of the coumarin esters **2** (entries 1,4, and 5). The enantiomeric excesses remained in the range 72–76%.

Table 2 (*S*,*S*)-FerroPHANE-Promoted Enantioselective [3+2] Cyclizations of 2-Oxo-2*H*-chromene-3-carboxylates



Entry	R^1	R^2	R^3	Products	**4:5** ratio	Yield of **4** (%)	ee (%)
1	H	Et	Et	**4a** + **5a**	5:1	84%	72%
2	H	Et	Bn	**4b** + **5b**	4:1	75%	76%[a]
3	H	Et	Cy	**4c** + **5c**	4:1	72%	53%
4	H	Me	Et	**4d** + **5d**	4:1	59%	76%
5	H	Cy	Et	**4e** + **5e**	4:1	61%	74%
6	H	Me	Bn	**4f** + **5f**	4:1	50%	72%
7	7-OMe	Et	Et	**4g** + **5g**[b]	4:1	45%	71%
8	8-OMe	Et	Et	**4h** + **5h**[b]	4:1	53%	71%
9	8-Br	Et	Et	**4i** + **5i**[b]	4:1	71%	64%
10	8-NO_2	Et	Et	**4j** + **5j**[b]	3:1	53%	71%

[a] The minor isomer **5b** was obtained in 54% ee.

[b] Reactions performed in toluene–CH_2Cl_2 (5:1).

The significant enantiomeric excesses attained in these cyclization reactions led us to examine the expansion of the scope of the method to coumarin derivatives with substituted aryl groups. As shown in entries 7–10 in Table 2, annulations on both electron-rich and electron-deficient substrates gave the desired products with comparable levels of enantioselectivity, with enantiomeric excesses peaking at about 71%.

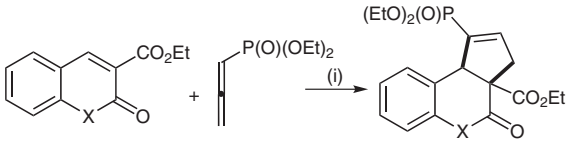
All the enantiomeric excesses discussed above were measured by chiral HPLC. Racemic samples of compounds **4b–j** were similarly obtained from cyclization reactions promoted by triphenylphosphine (20 mol%) under analogous conditions (yields: **4b**, 81%; **4c**, 60%; **4d**, 77%; **4e**, 71%; **4f**, 63%; **4g**, 63%; **4h**, 61%; **4i**, 59%; **4j**, 66%).

The minor γ-adducts **5** were isolated in pure form and characterized by means of NMR spectroscopy. Spectral data are reported in the experimental section for the representative compounds **5a** and **5b**.

As far as we know, these are the first examples of phosphine-promoted annulations leading to enantiomerically enriched coumarin derivatives. They produce highly functionalized benzo-fused bicyclo[4.3.0] scaffolds in synthetically useful yields and selectivities.

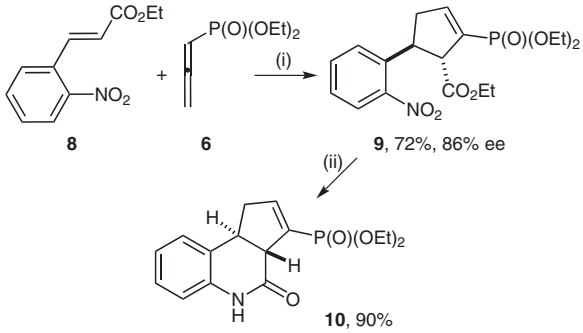
We therefore decided to further expand the scope of the method by using allenic phosphonates as the annulation partners. In previous studies, we have shown that diethyl propa-1,2-dien-1-ylphosphonate (**6**) and analogous propadienylphosphonates are suitable substrates for phosphine-promoted [3+2] cyclization reactions,[15,16] leading to new series of phosphonates with unusual molecular structures.

On the basis of these previous studies, we treated phosphonate **6** with ethyl 1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**) or ethyl 2-oxo-*2H*-chromene-3-carboxylate (**2a**) in the presence of (*S*,*S*)-FerroPHANE (10 mol%) in toluene at 110 °C. The coumarin derivative **2a** was converted into the expected bicyclic phosphonate **7** as the major product (6:1 isomers ratio), in 72% isolated yield and a 60% enantiomeric excess (Scheme 2).



Scheme 2 (*S*,*S*)-FerroPHANE-promoted enantioselective [3+2] cyclizations of diethyl propadienylphosphonate with ethyl 2-oxo-2*H*-chromene-3-carboxylate. *Reagents and conditions*: (i) (*S*,*S*)-FerroPHANE (10 mol%), toluene, 110 °C, 18 h.

The dihydroquinoline derivative **1** failed to react under analogous conditions. Nevertheless, the initial target of building cyclopentane-fused dihydroquinolinone moieties[17] could be attained by the alternative synthetic strategy shown in Scheme 3. This is a two-step approach involving an initial enantioselective (*S*,*S*)-FerroPHANE-promoted [3+2] annulation of the phosphonate **6** and the acrylate **8** as the key step. The nitro group serves as a precursor to an amino functionality that is involved in the final cyclization step.



Scheme 3 Enantioselective synthesis of a cyclopentane-fused dihydroquinolin-2-one by an (*S*,*S*)-FerroPHANE-promoted [3+2] cyclization. *Reagents and conditions*: (i) (*S*,*S*)-FerroPHANE (10 mol%), toluene, 110 °C, 18 h; (ii) Fe, AcOH, 80 °C, 90%.

With regard to the first step of this reaction sequence, it is worth noting that β-substituted olefins activated by a single ester group do not usually undergo phosphine-promoted [3+2] cyclizations with allenic esters or phosphonates, and that only β-unsubstituted acrylates[11,18] or olefins bearing two activating groups (e.g., fumarates, maleates,[11] or cyano esters[19]) are suitable as substrates for [3+2] cyclizations of this class. We were therefore pleased to observe that olefin **8**, in which the nitro group was expected to increase the electrophilic character, underwent the desired annulation reaction with phosphonate **6**. The desired cyclopentenyl phosphonate was obtained as a single isomer, i.e. the γ-adduct **9**, in good yield and 86% ee.

The second step of the reaction sequence shown in Scheme 3, reduction of the nitro group with iron dust and subsequent in situ cyclization, was performed under the usual conditions.[20] The targeted cyclopentene-fused dihydroquinolinone **10**, bearing a phosphonate function, was obtained in 65% cumulative yield and 86% ee.

In summary, we have demonstrated two synthetic approaches to cyclopentene-fused coumarin and quinoline derivatives based on phosphine-promoted [3+2] cyclizations. Benzo-fused bicyclo[4.3.0] scaffolds with unprecedented substitution schemes and functionalizations are available by these methods. Moreover, enantiomerically enriched compounds with enantiomeric excesses in the range 70–86% have been prepared by using (*S*,*S*)-FerroPHANE as the chiral phosphorus catalyst.

All reagents and solvents were of commercial quality and were used without further purification. NMR spectra (^{1}H, ^{13}C, and ^{31}P) were recorded on Bruker AV 500 or AV 300 spectrometers. Chemical shifts are reported in ppm relative to residual $CHCl_3$ as the internal standard (δ = 7.27 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR). IR spectra were recorded with a Perkin-Elmer Fourier-transform IR spectrophotometer on neat samples. High-resolution mass spectra (HRMS-ESI) were obtained on LCT Waters equipment. Optical rotations were determined with a JASCO P-1010 polarimeter. HPLC

was performed at a column temperature of 20 °C on a Waters 2695 Separations Module equipped with a diode array UV detector.

The coumarin-derived esters **2a–c** were prepared by esterification of 1-oxo-1*H*-isochromene-3-carboxylic acid under acidic conditions (H_2SO_4). Substrates **2d–g** were prepared according to the literature.[21] Ethyl 1-methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**1**) was prepared by alkylation of the ethyl 2-oxo-1,2-dihydroquinoline-3-carboxylate[22] with MeI in KOH/EtOH. Substrates **6**[23] and **8**[24] were prepared according to the literature methods.

Phosphine-Promoted [3+2]-Cyclization Reactions of Buta-2,3-dienoates 3 with 2-Oxo-2*H*-chromene-3-carboxylates 2; General Procedure

A mixture of buta-2,3-dienoate **3** (0.30 mmol), 2-oxo-2*H*-chromene-3-carboxylate **2** (0.15 mmol), and Ph_3P (7.8 mg, 0.030 mmol) or (*S*,*S*)-FerroPHANE (7.0 mg, 0.015 mmol) in degassed toluene (0.5 mL) was stirred under argon at r.t. for 24 h. The solvent was removed in vacuo, and the isomeric ratios of the crude products **4** and **5**c were determined by ^{1}H NMR spectroscopy. The final products were purified by column chromatography (silica gel, heptane–EtOAc), which also allowed efficient separation of the two regioisomers **4** and **5**.

Diethyl 4-Oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4a)

Orange oil; yield: 41 mg (84%); ee 72%; R_f = 0.33 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +67 (*c* 0.8, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 2% *i*-PrOH–heptane, 1 mL/min, 205 nm): t_R = 4.6 min (major), 5.1 min (minor).

IR: 2981, 1760, 1714, 1456, 1329, 1244, 1152, 1112, 1092, 759 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 7.7, 1.5 Hz, 1 H), 7.29 (dt, *J* = 7.8, 1.5 Hz, 1 H), 7.14 (dt, *J* = 7.8, 0.9 Hz, 1 H), 7.04 (dd, *J* = 8.1, 0.9 Hz, 1 H), 6.81 (m, 1 H), 4.64 (br s, 1 H), 4.20–4.05 (m, 4 H), 3.50 (ddd, *J* = 18.0, 2.8, 1.4 Hz, 1 H), 3.30 (dt, *J* = 18.0, 2.8 Hz, 1 H), 1.23 (t, *J* = 7.1 Hz, 3 H), 1.08 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 168.8 (C), 166.8 (C), 163.5 (C), 150.3 (C), 141.9 (CH), 135.5 (C), 131.5 (CH), 129.2 (CH), 124.4 (CH), 118.6 (C), 116.6 (CH), 62.6 (CH_2), 60.8 (CH_2), 59.3 (C), 50.3 (CH), 40.2 (CH_2), 14.2 (CH_3), 14.1 (CH_3).

HRMS (ESI+): *m/z* [M + Na]$^+$ calcd for $C_{18}H_{18}NaO_6$: 353.1001; found: 353.0994.

Diethyl 4-Oxo-1,9b-dihydrocyclopenta[*c*]chromene-3,3a(4*H*)-dicarboxylate (5a)

Orange oil; yield: 4 mg (8%); R_f = 0.17 (80% heptane–EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.05 (m, 5 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 4.15 (q, *J* = 7.2 Hz, 2 H), 4.02 (dd, *J* = 10.5, 8.1 Hz, 1 H), 3.03 (ddd, *J* = 17.7, 8.1, 3.0 Hz, 1 H), 2.48 (ddd, *J* = 17.7, 10.5, 1.5 Hz, 1 H), 1.26 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 168.9 (C), 166.9 (C), 163.6 (C), 150.7 (C), 145.5 (CH), 137.4 (C), 129.4 (CH), 128.6 (CH), 124.8 (CH), 120.8(C), 117.3 (CH), 62.7 (CH_2), 62.1 (C), 61.2 (CH_2), 48.2 (CH), 39.8 (CH_2), 14.2 (CH_3), 14.0 (CH_3).

1-Benzyl 3a-Ethyl 4-Oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4b)

Orange oil; yield: 44 mg (75%); 76% ee; R_f = 0.29 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +371 (*c* 0.4, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 2% *i*-PrOH–heptane, 1 mL/min, 206 nm): t_R = 12.3 min (major), 13.7 min (minor).

IR: 2982, 2361, 1760, 1722, 1456, 1330, 1250, 1155, 1114, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.40–7.25 (m, 6 H), 7.09 (dt, *J* = 7.2, 0.9 Hz 1 H), 7.06 (dd, *J* = 8.1, 0.9 Hz, 1 H), 6.88 (q, *J* ≈ 2.5 Hz, 1 H), 5.16 (d, *J* = 12.3 Hz, 1 H), 5.06 (d, *J* = 12.3 Hz, 1 H), 4.68 (br s, 1 H), 4.20–4.05 (m, 2 H), 3.52 (ddd, *J* = 18.0, 2.7, 1.2 Hz, 1 H), 3.32 (dt, *J* = 18.0, 2.7 Hz, 1 H), 1.09 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 168.8 (C), 166.8 (C), 163.2 (C), 150.2 (C), 142.6 (CH), 135.3 (C), 135.2 (C), 131.6 (CH), 129.2 (CH), 128.6 (CH × 2), 128.4 (CH × 2), 128.3 (CH), 124.4 (CH), 118.5 (C), 116.6 (CH), 66.6 (CH_2), 62.6 (CH_2), 59.3 (C), 50.3 (CH), 40.3 (CH_2), 13.7 (CH_3).

HRMS (ESI+): *m/z* [M + Na]$^+$ calcd for $C_{23}H_{20}NaO_6$: 415.1158; found: 415.1154.

3-Benzyl 3a-Ethyl 4-Oxo-1,9b-dihydrocyclopenta[*c*]chromene-3,3a(4*H*)-dicarboxylate (5b)

Colorless oil; yield: 9 mg (15%); R_f = 0.23 (80% heptane–EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45–7.05 (m, 10 H), 5.30 (d, *J* = 12.5 Hz, 1 H), 5.25 (d, *J* = 12.5 Hz, 1 H), 4.10–4.00 (m, 2 H), 3.98–3.90 (m, 1 H), 3.07 (ddd, *J* = 18.0, 8.0, 2.5 Hz, 1 H), 2.54 (dd, *J* = 18.0, 10.5 Hz, 1 H), 1.03 (t, *J* = 7.0 Hz, 3 H).

1-Cyclohexyl 3a-Ethyl 4-Oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4c)

Orange oil; yield: 41 mg (72%); 53% ee; R_f = 0.37 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +208 (*c* 0.4, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 2% *i*-PrOH–heptane, 1 mL/min, 205 nm): t_R = 4.3 min (major), 4.9 min (minor).

IR: 2937, 2859, 2361, 1764, 1737, 1712, 1456, 1336, 1248, 1153, 1114, 771 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.5, 1.2 Hz, 1 H), 7.30 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.16 (dt, *J* = 7.8, 1.5 Hz, 1 H), 7.05 (dd, *J* = 8.4, 1.2 Hz, 1 H), 6.81 (q, *J* = 2.7 Hz, 1 H), 4.80–4.70 (m, 1 H), 4.66 (br s, 1 H), 4.20–4.06 (m, 2 H), 3.51 (ddd, *J* = 17.8, 2.7, 1.5 Hz, 1 H), 3.31 (dt, *J* = 18.0, 2.7 Hz, 1 H), 1.88–1.78 (m, 2 H), 1.76–1.65 (m, 2 H), 1.64–1.15 (m, 6 H), 1.09 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.0 (C), 167.0 (C), 163.1 (C), 150.4 (C), 141.8 (CH), 136.1 (C), 131.7 (CH), 129.3 (CH), 124.5 (CH), 118.8 (C), 116.7 (CH), 73.5 (CH), 62.7 (CH_2), 59.5 (C), 50.4 (CH), 40.3 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 25.4 (CH_2), 23.9 (CH_2 × 2), 13.9 (CH_3).

HRMS (ESI+): *m/z* [M + Na]$^+$ calcd for $C_{22}H_{24}NaO_6$: 407.1471; found: 407.1476.

1-Ethyl 3a-Methyl 4-Oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4d)

Orange oil; yield: 28 mg (59%); 76% ee; R_f = 0.22 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +80 (*c* 1, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 0.5% *i*-PrOH–heptane, 1 mL/min, 205 nm): t_R = 10.7 min (major), 12.6 min (minor).

IR: 2981, 2358, 1763, 1741, 1715, 1458, 1329, 1252, 1153, 1111, 761 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (dd, *J* = 7.8, 1.5 Hz, 1 H), 7.31 (dt, *J* = 7.8, 1.8 Hz, 1 H), 7.16 (dt, *J* = 7.5, 1.2 Hz, 1 H), 7.05 (dd, *J* = 8.1, 0.9 Hz, 1 H), 6.82 (q, *J* = 2.7 Hz, 1 H), 4.70 (br s, 1 H), 4.25–4.05 (m, 2 H), 3.70 (s, 3 H), 3.52 (ddd, *J* = 18.0, 3.0, 1.5 Hz, 1 H), 3.32 (dt, *J* = 18.0, 2.4 Hz, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.5 (C), 166.6 (C), 163.4 (C), 150.1 (C), 141.8 (CH), 135.6 (C), 131.6 (CH), 129.3 (CH), 124.3 (CH), 118.4 (C), 116.7 (CH), 60.8 (CH_2), 59.3 (C), 53.6 (CH_3), 50.1 (CH), 40.6 (CH_2), 14.1 (CH_3).

HRMS (ESI+): *m/z* [M + Na]$^+$ calcd for $C_{17}H_{16}NaO_6$: 339.0845; found: 339.0841.

3a-Cyclohexyl 1-Ethyl 4-oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4e)

White solid; yield: 43 mg (61%); 74% ee; R_f = 0.46 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +70 (*c* 0.9, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 0.5% *i*-PrOH–heptane, 1 mL/min, 210 nm): t_R = 8.3 min (major), 10.3 min (minor).

IR: 2937, 2860, 1761, 1720, 1456, 1329, 1254, 1151, 1116, 1089, 759 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 7.5 Hz, 1 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.05 (d, *J* = 8.1 Hz, 1 H), 6.81 (q, *J* = 2.7 Hz, 1 H), 4.76 (m, 1 H), 4.58 (br s, 1 H), 4.20–4.05 (m, 2 H), 3.51 (ddd, *J* = 18.0, 2.7, 1.5 Hz, 1 H), 3.31 (dt, *J* = 18.0, 2.7 Hz, 1 H), 1.70–1.60 (m, 2 H), 1.55–1.20 (m, 8 H), 1.22 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 168.0 (C), 167.1 (C), 163.4 (C), 150.5 (C), 142.2 (CH), 135.2 (C), 131.8 (CH), 129.2 (CH), 124.3 (CH), 118.7 (C), 116.5 (CH), 74.7 (CH), 60.7 (CH_2), 59.6 (C), 50.7 (CH), 39.9 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 25.1 (CH_2), 22.4 (CH_2), 22.3 (CH_2), 14.1 (CH_3).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{22}H_{24}NaO_6$: 407.1471; found: 407.1467.

1-Benzyl 3a-Methyl 4-Oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4f)

White solid; yield: 28 mg (50%); 72% ee; R_f = 0.27 (80% heptane–EtOAc); $[\alpha]_D^{25}$ +63 (*c* 0.9, $CHCl_3$).

HPLC (Daicel CHIRACEL AD-H column, 0.5% *i*-PrOH–heptane, 1 mL/min, 238 nm): t_R = 8.5 min (major), 10.2 min (minor).

IR: 3033, 2955, 1760, 1738, 1714, 1456, 1330, 1252, 1154, 1114, 1086, 756 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 7.5, 1.7 Hz, 1 H), 7.40–7.26 (m, 6 H), 7.10 (t, *J* = 8.0 Hz, 1 H), 7.07 (d, *J* = 8.5 Hz, 1 H), 6.88 (q, *J* = 2.5 Hz, 1 H), 5.18 (d, *J* = 12.0 Hz, 1 H), 5.08 (d, *J* = 12.0 Hz, 1 H), 4.72 (br s, 1 H), 3.70 (s, 3 H), 3.54 (ddd, *J* = 18.0, 2.5, 1.5 Hz, 1 H), 3.34 (dt, *J* = 18.0, 2.5, 1 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.4 (C), 166.6 (C), 163.2 (C), 150.1 (C), 142.4 (CH), 135.3 (C × 2), 131.6 (CH), 129.3 (CH), 128.6 (CH × 2), 128.4 (CH), 128.3 (CH × 2), 124.5 (CH), 118.2 (C), 116.6 (CH), 66.6 (CH_2), 59.2 (C), 53.6 (CH_3), 50.1 (CH), 40.7 (CH_2).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{22}H_{18}NaO_6$: 401.1001; found: 401.0990.

Diethyl 7-Methoxy-4-oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4g)

Orange oil; yield: 24 mg (45%); 71% ee; R_f = 0.56 (70% heptane–EtOAc); $[\alpha]_D^{27}$ 72 (*c* 1.1, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 10% *i*-PrOH–heptane, 1 mL/min, 210 nm): t_R = 17.0 min (minor), 21.0 min (major).

IR: 2981, 2921, 2851, 1764, 1714, 1627, 1509, 1444, 1327, 1240, 1161, 1111, 1034 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.5 Hz, 1 H), 6.80 (q, *J* = 2.4 Hz, 1 H), 6.73 (dd, *J* = 8.5, 2.4 Hz, 1 H), 6.59 (d, *J* = 2.4 Hz, 1 H), 4.61 (br s, 1 H), 4.20–4.10 (m, 4 H), 3.81 (s, 3 H), 3.50 (d, *J* = 18 Hz, 1 H), 3.30 (dt, *J* = 18.0, 2.4 Hz, 1 H), 1.25 (t, *J* = 7.3 Hz, 3 H), 1.13 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.0 (C), 166.9 (C), 163.5 (C), 160.2 (C), 151.0 (C), 141.5 (CH), 135.8 (C), 132.2 (CH), 110.8 (CH), 110.4 (C), 101.6 (CH), 62.6 (CH_2), 60.7 (CH_2), 59.4 (C), 55.5 (CH_3), 49.9 (CH), 40.2 (CH_2), 14.1 (CH_3), 13.8 (CH_3).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{20}NaO_7$: 383.1107; found: 383.1100.

Diethyl 8-Methoxy-4-oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4h)

Yellow oil; yield: 28 mg (53%); 71% ee; R_f = 0.25 (70% heptane–EtOAc); $[\alpha]_D^{27}$ +73 (*c* 1.3, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 10% *i*-PrOH–heptane, 1 mL/min, 227 nm): t_R = 27.0 min (minor), 36.2 min (major).

IR: 2981, 2934, 1759, 1714, 1622, 1497, 1465, 1242, 1209, 1156, 1110, 1035 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 2.7 Hz, 1 H), 6.99 (d, *J* = 8.9 Hz, 1 H), 6.84 (dd, *J* = 8.9, 3.1 Hz, 1 H), 6.83 (t, *J* = 3.1 Hz, 1 H), 4.66 (br s, 1 H), 4.20–4.10 (m, 4 H), 3.82 (s, 3 H), 3.47 (d, *J* = 18.0 Hz, 1 H), 3.19 (dt, *J* = 18.0, 2.4 Hz, 1 H), 1.27 (t, *J* = 7.0 Hz, 3 H), 1.14 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.0 (C), 166.9 (C), 163.5 (C), 156.0 (C), 144.2 (C), 142.0 (CH), 135.7 (C), 119.4 (C), 117.3 (CH), 115.8 (CH), 115.0 (CH), 62.6 (CH_2), 60.8 (CH_2), 59.1 (C), 55.7 (CH_3), 50.4 (CH), 40.3 (CH_2), 14.1 (CH_3), 13.8 (CH_3).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{20}NaO_7$: 383.1107; found: 383.1092.

Diethyl 8-Bromo-4-oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4i)

Orange oil; yield: 44 mg (71%); 64% ee; R_f = 0.65 (70% heptane–EtOAc); $[\alpha]_D^{27}$ +104 (*c* 0.8, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 10% *i*-PrOH–heptane, 1 mL/min, 210 nm): t_R = 14.6 min (major), 16.0 min (minor).

IR: 2981, 1767, 1739, 1715, 1625, 1480, 1328, 1245, 1190, 1149, 1111, 1034 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 2.4 Hz, 1 H), 7.43 (dd, *J* = 8.7, 2.4 Hz, 1 H), 6.95 (d, *J* = 8.7 Hz, 1 H), 6.86 (q, *J* = 2.4 Hz, 1 H), 4.61 (br s, 1 H), 4.25–4.10 (m, 4 H), 3.53 (ddd, *J* = 18.1, 3.0, 1.5 Hz, 1 H), 3.31 (dt, *J* = 18.1, 2.6 Hz, 1 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 168.5 (C), 166.2 (C), 163.3 (C), 149.5 (C), 142.6 (CH), 135.1 (C), 134.5 (CH), 132.4 (CH), 120.7 (C), 118.4 (CH), 116.9 (C) 62.9 (CH_2), 61.1 (CH_2), 59.2 (C), 50.1 (CH_2), 40.3 (CH), 14.2 (CH_3), 13.9 (CH_3).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}BrNaO_6$: 431.0107; found: 431.0100.

Diethyl 8-Nitro-4-oxo-3,9b-dihydrocyclopenta[*c*]chromene-1,3a(4*H*)-dicarboxylate (4j)

White solid; yield: 30 mg (53%); 71% ee; R_f = 0.64 (70% heptane–EtOAc); $[\alpha]_D^{27}$ +104 (*c* 0.8, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 10% *i*-PrOH–heptane, 1 mL/min, 210 nm): t_R = 27.0 min (major), 40.7 min (minor).

IR: 2983, 2923, 2360, 1775, 1716, 1530, 1345, 1248, 1138, 1032, 840 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.56 (d, *J* = 2.4 Hz, 1 H), 8.22 (dd, *J* = 8.9, 2.7 Hz, 1 H), 7.21 (d, *J* = 8.9 Hz, 1 H), 6.92 (q, *J* = 2.7 Hz, 1 H), 4.73 (br s, 1 H), 4.20–4.10 (m, 4 H), 3.59 (dd, *J* = 18.0, 1.2 Hz, 1 H), 3.36 (dt, *J* = 18.0, 2.4 Hz, 1 H), 1.25 (t, *J* = 7.3 Hz, 3 H), 1.13 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.9 (C), 165.4 (C), 163.0 (C), 154.6 (C), 144.2 (C), 143.0 (CH), 134.5 (C), 128.2 (CH), 125.1 (C), 119.9 (C), 117.7 (CH), 63.2 (CH_2), 61.3 (CH_2), 59.1 (C), 50.2 (CH), 40.3 (CH_2), 14.2 (CH_3), 14.1 (CH_3).

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{17}NNaO_8$: 398.0852; found: 398.0847.

Phosphine-Promoted [3 + 2] Cyclization Reactions of Diethyl Propa-1,2-dien-1-ylphosphonate (6); General Procedure

A mixture of phosphonate **6** (0.30 mmol), carboxylate **2a** or acrylate **8** (0.15 mmol), and Ph_3P (7.8 mg, 0.030 mmol) or (*S*,*S*)-Ferro-PHANE (7.0 mg, 0.015 mmol) in degassed toluene (0.5 mL) was heated under argon at 110 °C for 24 h. The products were purified by column chromatography (silica gel, heptane–EtOAc gradient).

Ethyl 1-(Diethoxyphosphoryl)-4-oxo-1,9b-dihydrocyclopenta[*c*]chromene-3a(4*H*)-carboxylate (7)

Colorless oil; yield: 42 mg (72%); 60% ee; $[\alpha]_D^{25}$ +35.3 (*c* 1.0, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 20% EtOH–heptane, 1 mL/min, 210 nm): t_R = 11.0 min (minor), 12.3 min (major).

IR: 2984, 1763, 1736, 1493, 1458, 1243, 1149, 1019, 967, 757 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 7.5, 1.8 Hz, 1 H), 7.32 (dt, *J* = 7.8, 1.8 Hz, 1 H), 7.16 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.07 (dd, *J* = 7.8, 1.5 Hz, 1 H), 6.75 (dm, $J_{H\text{-}P}$ = 11.1 Hz, 1 H), 4.59 (br s, 1 H), 4.25–4.05 (m, 2 H), 3.95–3.72 (m, 4 H), 3.66 (dm, *J* = 17.7 Hz, 1 H), 3.29 (dm, *J* = 17.7 Hz, 1 H), 1.15 (t, *J* = 7.2 Hz, 3 H), 1.06 (t, *J* = 7.2 Hz, 3 H), 1.03 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7 (C), 167.0 (C), 150.8 (C), 146.8 (J_{CP} = 12.3 Hz, CH), 135.8 (C), 130.8 (CH), 129.6 (CH), 124.7 (CH), 118.6 (C), 116.6 (CH), 62.8 (CH_2), 62.1 ($J_{C,P}$ = 5.9 Hz, CH_2), 61.9 ($J_{C,P}$ = 5.8 Hz, CH_2), 60.5 ($J_{C,P}$ = 9.8 Hz, C), 52.4 ($J_{C,P}$ = 14.9 Hz, CH), 41.9 ($J_{C,P}$ = 18.2 Hz, CH_2), 16.2 ($J_{C,P}$ = 6.5 Hz, CH_3), 16.0 ($J_{C,P}$ = 6.2 Hz, CH_3), 13.9 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 11.6 ppm.

HRMS (ESI+): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{23}NaO_7P$: 417.1079; found: 417.1090.

Ethyl 2-(Diethoxyphosphoryl)-5-(2-nitrophenyl)cyclopent-2-ene-1-carboxylate (9)

Colorless oil; yield: 43 mg (72%); 86% ee; $[\alpha]_D^{25}$ +33.1 (*c* 1.0, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 20% EtOH–heptanes, 1 mL/min, 210 nm): t_R = 12.2 min (minor), 14.4 min (major).

IR: 2983, 2908, 1732, 1525, 1352, 1248, 1181, 1048, 1024, 963, 787, 748 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ = 7.81 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.55 (dt, *J* = 7.5, 1.2 Hz, 1 H), 7.42–7.32 (m, 2 H), 6.93 (dq, $J_{H\text{-}P}$ = 11.1 Hz, *J* = 2.1 Hz, 1 H), 4.30–4.00 (m, 7 H), 3.82 (m, J <3 Hz, 1 H), 3.34 (dddt, *J* = 18.6, 9.0, 4.5, 2.4 Hz, 1 H), 2.66 (dm, *J* = 18.6, <3 Hz, 1 H), 1.36–1.23 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 172.6 (C), 150.1 (J_{CP} = 16.0 Hz, CH), 149.3 (C), 138.9 (C), 133.5 (CH), 131.5 ($J_{C,P}$ = 192.3 Hz, C), 128.2 (CH), 128.0 (CH), 124.4 (CH), 62.3 ($J_{C,P}$ = 7.2 Hz, CH_2), 62.1 (J_{CP} = 6.6 Hz, CH_2), 61.4 (CH_2), 60.0 ($J_{C,P}$ = 12.4 Hz, CH), 43.2 ($J_{C,P}$ = 10.4 Hz, CH), 42.7 ($J_{C,P}$ = 20.2 Hz, CH_2), 16.5 ($J_{C,P}$ = 5.9 Hz, CH_3), 16.3 ($J_{C,P}$ = 7.2 Hz, CH_3), 14.2 (CH_3).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 13.3 ppm.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{24}NNaO_7P$: 420.1188; found: 420.1188.

Diethyl (4-Oxo-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinolin-3-yl)phosphonate (10)

Fe dust (1.0 mmol) was added to a soln of nitro derivative **9** (0.06 mmol) in AcOH (0.5 mL), and the mixture was heated at 80 °C for 3 h. The mixture was then cooled and filtered through Celite, which was washed with EtOAc. The combined organic phases were concentrated to give a crude mixture that was purified by column chromatography (5% MeOH–CH_2Cl_2).

Colorless oil; yield: 28 mg (90%); 86% ee; $[\alpha]_D^{25}$ –186 (*c* 0.3, $CHCl_3$).

HPLC (Daicel CHIRACEL IC column, 20% EtOH–heptanes, 1 mL/min, 240 nm): t_R = 25.2 min (minor), 35.4 min (major).

IR: 3426, 2924, 1736, 1491, 1345, 1185, 1041, 811 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) 8.35 (br s, 1 H), 7.23–7.14 (m, 2 H), 7.00 (t, *J* = 7.8 Hz, 1 H), 6.86 (d, *J* = 12.0 Hz, 1 H), 6.78 (d, *J* = 7.8 Hz, 1 H), 4.30–4.10 (m, 4 H), 3.98 (dm, *J* = 6.5 Hz, 1 H), 3.79 (q, *J* = 8.4 Hz, 1 H), 2.96 (dd, *J* = 16.9, 7.3 Hz, 1 H), 2.70–2.60 (m, 1 H), 1.43–1.25 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C), 149.1 (d, J_{CP} = 13.4 Hz, CH), 136.0 (C), 128.5 (CH), 128.1 (CH), 128.1 (C), 123.8 (C), 123.4 (CH), 115.7 (CH), 62.6 (d, $J_{C,P}$ = 6.6 Hz, CH_2), 62.3 (d, $J_{C,P}$ = 8.8 Hz, CH_2), 50.2 (d, $J_{C,P}$ = 9.8 Hz, CH), 42.9 (d, $J_{C,P}$ = 10.7 Hz, CH), 42.0 (d, $J_{C,P}$ = 18.8 Hz, CH_2), 16.6 (d, $J_{C,P}$ = 6.4 Hz, CH_3), 16.5 (d, $J_{C,P}$ = 7.5 Hz, CH_3).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 14.4 ppm.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{21}NO_4P$: 322.1208; found: 322.1200.

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