Asymmetric Carbon–Carbon Bond Formation γ to a Carbonyl Group: Phosphine-Catalyzed Addition of Nitromethane to Allenes

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SUPPORTING INFORMATION

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I. Preparation of Allenes

The yields have not been optimized.

Synthesis of Allenes (representative procedure): A 300-mL flask was charged with a phosphorane (14.5 g, 40.0 mmol), evacuated, and back-filled with argon. CH₂Cl₂ (200 mL) and Et₃N (6.1 mL, 40 mmol) were added via syringe, and the solution was cooled to −78 °C. The acid chloride (40.0 mmol) was then added dropwise via syringe over five min. The solution was allowed to warm to room temperature over 3-4 hours, and then the reaction was quenched by the addition of silica gel. After removal of the solvent on a rotary evaporator, the product (adsorbed on silica) was loaded onto a pre-packed column of silica gel and purified via flash chromatography (hexanes/ethyl acetate), which furnished the allene as an oil.

铑•n-PMTMeOME

(±)-N-Methoxy-N-methylhepta-2,3-dienamide. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and pentanoyl chloride via the
representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 40% yield).

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta \) 6.15 (quintet, \(J = 2.9\) Hz, 1H), 5.64 (q, \(J = 6.8\) Hz, 1H), 3.71 (s, 3H), 3.23 (s, 3H), 2.14-2.09 (m, 2H), 1.49 (sextet, \(J = 7.4\) Hz, 2H), 0.95 (t, \(J = 7.3\) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta \) 212.2, 166.1, 95.2, 86.3, 61.5, 32.6, 29.7, 22.2, 13.6.

IR (film) 3567, 3291, 3042, 2961, 2935, 2873, 2361, 2361, 2398, 1958, 1653, 1463, 1424, 1364 cm\(^{-1}\).

LRMS (ES+) calcd for C\(_9\)H\(_{16}\)NO\(_2\) (M+H\(^+\)) 170, found 170.

\(\text{O}^\bullet\text{N} \cdot \text{O}^\bullet\text{N} \cdot \text{Me}^\bullet\text{Me}^\bullet\text{O}^\bullet\text{Me}^\bullet\text{Me} \text{ (±)}\)

\(\text{Prepared from } \text{N}-\text{methoxy-N-methyl-2,3-dienamide.} \)

\(\text{Prepared from } \text{N}-\text{methoxy-N-methyl-2,3-dienamide.} \)

\(\text{Prepared from } \text{N}-\text{methoxy-N-methyl-2,3-dienamide.} \)
(±)-N-Methoxy-N,5-dimethylhexa-2,3-dienamide. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and isovaleroyl chloride via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 44% yield).

\[
\text{^1}{\text{H NMR (CDCl}_3\text{, 500 MHz) } \delta 6.20 (q, J = 3.1 Hz, 1H), 5.66 (t, J = 6.1 Hz, 1H), 3.71 (s, 3H), 3.23 (s, 3H), 2.52-2.42 (m, 1H), 1.08 (d, J = 6.7 Hz, 6H).}
\]

\[
\text{^13}{\text{C NMR (CDCl}_3\text{, 125 MHz) } \delta 211.1, 166.1, 102.6, 87.4, 61.8, 32.6, 27.7, 22.5, 22.3.}
\]

IR (film) 3291, 2963, 2937, 2871, 2361, 2339, 1957, 1653, 1465, 1384 cm\(^{-1}\).

LRMS (ES+) calcd for C\(_9\)H\(_{16}\)NO\(_2\) (M+H\(^+\)) 170, found 170.

(±)-8-(tert-Butyldimethylsilyloxy)-N-methoxy-N-methylocta-2,3-dienamide. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and 6-(tert-butyldimethylsilyloxy)hexanoyl chloride via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 10% yield).

\[
\text{\text{^1}{\text{H NMR (CDCl}_3\text{, 300 MHz) } \delta 6.09-6.06 (m, 1H), 5.57 (t, J = 6.7 Hz, 1H), 3.63 (s, 3H), 3.56-3.52 (m, 2H), 3.16 (s, 3H), 2.15-2.05 (m, 2H), 1.60-1.38 (m, 4H), 0.81 (s, 9H), -0.04 (s, 6H).}
\]

\[
\text{\text{^13}{\text{C NMR (CDCl}_3\text{, 125 MHz) } \delta 212.2, 166.1, 95.5, 86.5, 63.0, 61.8, 32.7, 32.3, 27.4, 26.1, 25.3, 18.5, -5.1.}
\]

IR (film) 3308, 2935, 2857, 2361, 2340, 1959, 1658, 1472 cm\(^{-1}\).

LRMS (ES+) calcd for C\(_{16}\)H\(_{32}\)NO\(_3\)Si (M+H\(^+\)) 314, found 314.

(±)-Methyl 8-(methoxy(methyl)amino)-8-oxoocta-5,6-dienoate. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and methyl adipoyl chloride via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 25% yield).

\[
\text{\text{^1}{\text{H NMR (CDCl}_3\text{, 500 MHz) } \delta 6.18 (quintet, J = 2.9 Hz, 1H), 5.63 (q, J = 6.7 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.23 (s, 3H), 2.39 (t, J = 7.4 Hz, 2H), 2.18 (qd, J = 7.1, 3.0 Hz, 2H), 1.80 (quintet, J = 7.4 Hz, 2H).}
\]

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 212.3, 173.9, 165.9, 94.7, 86.9, 61.9, 51.7, 33.3, 32.8, 27.1, 24.1.

IR (film) 3282, 2951, 2361, 2339, 1959, 1734, 1653, 1639, 1457 cm$^{-1}$.

LRMS (ES+) calcd for C$_{11}$H$_{18}$NO$_4$ (M$+H^+$) 228, found 228.

\[ \text{Me} \stackrel{N}{\longrightarrow} \text{O} \rightarrow \text{(CH}_2\text{)}_5\text{CO}_2\text{Me} \]

\[ \text{O} \cdot \text{(C}_\text{H}_2\text{)}_7 \text{Me} \・ \text{OMe} \]

(±)-Methyl 10-(methoxy(methyl)amino)-10-oxodeca-7,8-dienoate. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and methyl 8-chloro-8-oxooctanoate chloride\(^1\) via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 21% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) δ 6.18-6.14 (m, 1H), 5.52 (q, $J = 2.3$ Hz, 1H), 3.61 (s, 3H), 3.55 (s, 3H), 3.13 (s, 3H), 2.20 (t, $J = 7.4$ Hz, 2H), 2.06-2.01 (m, 2H), 1.56-1.49 (m, 2H), 1.42-1.35 (m, 2H), 1.31-1.24 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 212.2, 174.2, 166.0, 95.3, 86.5, 61.8, 51.5, 34.0, 32.7, 28.6, 28.5, 27.4, 24.8.

IR (film) 3288, 2937, 2859, 2361, 2338, 1958, 1734, 1653 cm$^{-1}$.

LRMS (ES+) calcd for C$_{13}$H$_{22}$NO$_4$ (M$+H^+$) 256, found 256.

\[ \text{Me} \stackrel{N}{\longrightarrow} \text{O} \rightarrow \text{(CH}_2\text{)}_5\text{CO}_2\text{Me} \]

(±)-N-Methoxy-N-methyltrideca-2,3,12-trienamide. Prepared from N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide and 10-undecenoyl chloride via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 39% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) δ 6.15 (quintet, $J = 2.9$ Hz, 1H), 5.80 (qt, $J = 10.3$, 6.7 Hz, 1H), 5.64 (q, $J = 6.9$ Hz, 1H), 4.98 (dq, $J = 17.1$, 1.6 Hz, 1H), 4.92 (dquintet, $J = 10.2$, 1.2 Hz, 1H), 3.71 (s, 3H), 3.24 (s, 3H), 2.13 (qd, $J = 7.0$, 3.0 Hz, 2H), 2.05-2.00 (m, 2H), 1.46 (quintet, $J = 6.4$ Hz, 2H), 1.40-1.27 (m, 8H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 212.3, 166.1, 139.4, 114.3, 95.7, 86.5, 61.9, 51.5, 34.0, 29.4, 29.3, 29.23, 29.21, 29.12, 29.10, 27.8.

IR (film) 3075, 2927, 2855, 2361, 2338, 1959, 1653, 1464, 1423, 1362 cm$^{-1}$.

LRMS (ES+) calcd for C$_{15}$H$_{26}$NO$_2$ (M$+H^+$) 252, found 252.

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(±)-(Z)-*N*-Methoxy-*N*-methylnonadeca-2,3,10-trienamide. Prepared from *N*-methoxy-*N*-methyl-2-(triphenylphosphoranylidene)acetamide and oleoyl chloride via the representative procedure (purification by flash chromatography: 25% EtOAc in hexanes; 55% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 6.15 (quintet, $J = 2.9$ Hz, 1H), 5.64 (q, $J = 6.9$ Hz, 1H), 5.37-5.30 (m, 2H), 3.71 (s, 3H), 3.24 (s, 3H), 2.16-2.11 (m, 2H), 2.02-1.99 (m, 4H), 1.50 (m, 2H), 1.37-1.22 (m, 18H), 0.88 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 212.3, 166.2, 130.1, 129.9, 95.6, 86.4, 61.8, 32.7, 32.1, 29.9, 29.8, 29.7, 29.53, 29.52, 29.2, 29.1, 29.0, 27.8, 27.4, 27.3, 22.9, 14.3.

IR (film) 3300, 3003, 2923, 2853, 2361, 2338, 1959, 1653, 1457, 1420, 1362 cm$^{-1}$.

LRMS (ES+) calcd for C$_{22}$H$_{40}$NO$_2$ (M$^+$H$^+$) 350, found 350.

(±)-*Methyl hepta*-2,3-dienoate [111425-91-5]. Prepared from methyl (triphenylphosphoranylidene)acetate and pentanoyl chloride via the representative procedure (purification by distillation; 71% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 5.59-5.52 (m, 2H), 3.68 (s, 3H), 2.10-2.05 (m, 2H), 1.48-1.41 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 212.6, 166.9, 95.4, 88.0, 52.1, 29.7, 22.1, 13.6.

IR (film) 2960, 2935, 2875, 2361, 2337, 1961, 1723, 1437, 1262 cm$^{-1}$.

LRMS (ES+) calcd for C$_8$H$_{13}$O$_2$ (M$^+$H$^+$) 141, found 141.

(±)-*tert-Butyl hepta*-2,3-dienoate [151860-31-0]. Prepared from (tert-butoxycarbonyl-methylene)triphenylphosphorane and pentanoyl chloride via the representative procedure (purification by flash chromatography: 5% EtOAc in hexanes; 38% yield).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 5.55 (q, $J = 6.9$ Hz, 1H), 5.47 (q, $J = 2.6$ Hz, 1H), 2.09-2.02 (m, 2H), 1.52-1.42 (m, 11H), 0.95 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 212.1, 165.8, 95.0, 89.9, 80.8, 29.8, 28.3, 22.2, 13.7.
IR (film) 3004, 2967, 2934, 2875, 2361, 2338, 1960, 1717, 1368, 1147 cm⁻¹.
LRMS (ES+) calcd for C₁₁H₁₉O₂ (M+H⁺) 183, found 183.

(±)-Diethyl octa-1,2-dienylphosphonate [344554-28-5]. Prepared according to a
literature procedure (purification by flash chromatography: 20 → 100% EtOAc in
hexanes; 75% yield).²

¹H NMR (CDCl₃, 500 MHz) δ 5.43 (sextet, J = 7.0 Hz, 1H), 5.29 (sextet, J = 3.4 Hz, 1H),
4.14-4.07 (m, 4H), 2.09 (quintet of doublets, J = 7.2, 3.4 Hz, 2H), 1.46-1.41 (m, 2H), 1.35-
1.29 (m, 10H), 1.33 (t, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz) δ 211.9, 92.4, 80.8, 79.2, 62.2, 31.2, 28.67, 28.64, 27.4, 22.5,
16.4, 14.1.

IR (film) 3482, 2980, 2958, 2872, 2859, 2360, 2338, 1955, 1258 cm⁻¹.
LRMS (ES+) calcd for C₁₂H₂₄O₃P (M+H⁺) 247, found 247.

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II. Phosphine-Catalyzed Asymmetric $\gamma$ Additions

**General Procedure.** In a glovebox, catalyst (S)-1 (29 mg, 0.075 mmol; 0.10 equiv) and phenol (7.0 mg, 0.075 mmol; 0.10 equiv) were added to an oven-dried 20-mL vial. These solids were dissolved in anhydrous dioxane (15 mL), and then nitromethane (225 $\mu$L, 4.15 mmol; 5.5 equiv) and the allene (0.75 mmol; 1.0 equiv) were added via syringe. The vial was capped and removed from the glovebox, and the reaction mixture was stirred at room temperature for 15 h. The solvent was then evaporated, and the product was purified by flash chromatography.

**Glovebox-free Procedure (Table 2, entry 2).** On a benchtop, catalyst (S)-1 (43.5 mg, 0.113 mmol; 0.15 equiv; with 10% (S)-1, a small amount of unreacted allene was observed after 15 h) and phenol (10.5 mg, 0.113 mmol; 0.15 equiv) were added to an oven-dried 20-mL vial. The vial was capped with a septum, and then it was evacuated and refilled with argon (three cycles). Next, anhydrous dioxane (15 mL), nitromethane (225 $\mu$L, 4.15 mmol; 5.5 equiv), and (±)-N-methoxy-N-methylhepta-2,3-dienamide (127 mg, 0.75 mmol; 1.0 equiv) were added in order via syringe through the septum. The reaction mixture was stirred at room temperature for 15 h. It was then concentrated and purified by flash chromatography (25% EtOAc in pentane), which afforded the desired product as a colorless oil (140 mg, 81% yield) with 93% ee.

(E)-N-Methoxy-N-4-dimethyl-5-nitropent-2-enamide (Table 2, entry 1). The compound was prepared according to the general procedure with (±)-N-methoxy-N-methylpenta-2,3-dienamide (106 mg, 0.75 mmol). After purification by flash chromatography (30% EtOAc in hexanes), the title compound was isolated as a colorless oil (144 mg, 95% yield) with 97% ee.

$[\alpha]_D^{22} = -45$ (c = 1.0, CHCl$_3$). HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 5.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 38.7 min (minor), 44.5 min (major).

The second run was performed with (R)-1. The product was isolated as a colorless oil (140 mg, 93% yield) with 97% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 6.73 (dd, $J = 15.4, 7.8$ Hz, 1H), 6.45 (d, $J = 15.4$ Hz, 1H), 4.37 (dd, $J = 12.2, 7.7$ Hz, 1H), 4.31 (dd, $J = 12.2, 7.0$ Hz, 1H), 3.63 (s, 3H), 3.18 (s, 3H), 3.24-3.15 (m, 1H), 1.15 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 165.9, 145.2, 120.6, 79.9, 62.0, 35.8, 32.4, 17.0.

IR (film) 3287, 2972, 2361, 2339, 1669, 1558 cm$^{-1}$.

LRMS (ES+) calcld for C$_8$H$_{15}$N$_2$O$_4$ (M+H$^+$) 203, found 203.
(E)-N-Methoxy-N-methyl-4-(nitromethyl)hept-2-enamide (Table 2, entry 2). The compound was prepared according to the general procedure with (±)-N-methoxy-N-methylhepta-2,3-dienamide (127 mg, 0.75 mmol). After purification by flash chromatography (30% EtOAc in hexanes), the title compound was isolated as a colorless oil (137 mg, 80% yield) with 93% ee.

\[ \alpha_d^{22} = -30 \ (c = 1.0, \text{CHCl}_3) \]. HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 5.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 24.5 min (major), 28.7 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (141 mg, 82% yield) with 93% ee.

\(^1\text{H NMR (CDCl}_3, 500 MHz)\) \( \delta 6.63 (d, J = 15.4, 9.1 \text{ Hz}, 1\text{H}), 6.44 (d, J = 15.4 \text{ Hz}, 1\text{H}), 4.38 (dd, J = 12.3, 5.9 \text{ Hz}, 1\text{H}), 4.30 (dd, J = 12.2, 8.9 \text{ Hz}, 1\text{H}), 3.61 (s, 3\text{H}), 3.17 (s, 3\text{H}), 3.09-3.01 (m, 1\text{H}), 1.46-1.17 (m, 4\text{H}), 0.85 (t, J = 7.2 \text{ Hz}, 3\text{H}).

\(^{13}\text{C NMR (CDCl}_3, 125 MHz)\) \( \delta 165.7, 144.2, 122.0, 79.1, 62.0, 41.3, 33.6, 32.4, 20.0, 13.9 \text{ cm}^{-1} \).

LRMS (ES+) calcd for C\(_{10}\)H\(_{19}\)N\(_2\)O\(_4\) (M+H\(^+\)) 231, found 231.

(E)-5-Cyclopentyl-N-methoxy-N-methyl-4-(nitromethyl)pent-2-enamide (Table 2, entry 3). The compound was prepared according to the general procedure with (±)-5-cyclopentyl-N-methoxy-N-methylpenta-2,3-dienamide (157 mg, 0.75 mmol). After purification by flash chromatography (30% EtOAc in hexanes), the title compound was isolated as a colorless oil (146 mg, 72% yield) with 87% ee.

\[ \alpha_d^{22} = -3.5 \ (c = 1.0, \text{CHCl}_3) \]. HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 3.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 33.7 min (major), 46.2 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (152 mg, 75% yield) with 86% ee.

\(^1\text{H NMR (CDCl}_3, 500 MHz)\) \( \delta 6.65 (d, J = 15.4, 9.4 \text{ Hz}, 1\text{H}), 6.47 (d, J = 15.4 \text{ Hz}, 1\text{H}), 4.38 (dd, J = 12.3, 5.8 \text{ Hz}, 1\text{H}), 4.30 (dd, J = 12.2, 9.0 \text{ Hz}, 1\text{H}), 3.63 (s, 3\text{H}), 3.18 (s, 3\text{H}), 3.13-3.04 (m, 1\text{H}), 1.75-1.70 (m, 3\text{H}), 1.58-1.36 (m, 6\text{H}), 1.05-1.00 (m, 2\text{H}).

\(^{13}\text{C NMR (CDCl}_3, 125 MHz)\) \( \delta 165.8, 144.4, 122.0, 79.4, 62.0, 41.0, 38.0, 37.4, 33.3, 32.1, 25.2 \).
IR (film) 2941, 2867, 2361, 2339, 1669, 1653, 1635, 1558 cm⁻¹.
LRMS (ES+) calcd for C₁₅H₂₃N₂O₄ (M+H⁺) 271, found 271.

(E)-N-Methoxy-N,5-dimethyl-4-(nitromethyl)hex-2-enamide (Table 2, entry 4). The compound was prepared according to the general procedure (except 15% catalyst was used) with (±)-N-methoxy-N,5-dimethylhexa-2,3-dienamide (127 mg, 0.75 mmol). After purification by flash chromatography (30% EtOAc in hexanes), the title compound was isolated as a colorless oil (102 mg, 60% yield) with 81% ee.

[α]D²² = −30 (c = 1.0, CHCl₃). HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 5.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 19.7 min (major), 24.0 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (108 mg, 63% yield) with 81% ee.

¹H NMR (CDCl₃, 500 MHz) δ 6.72 (dd, J = 15.4, 9.5 Hz, 1H), 6.44 (d, J = 15.4 Hz, 1H), 4.49 (dd, J = 12.2, 5.1 Hz, 1H), 4.35 (dd, J = 12.1, 9.8 Hz, 1H), 3.63 (s, 3H), 3.19 (s, 3H), 2.91 (septet, J = 5.4 Hz, 1H), 1.80 (sextet, J = 6.7 Hz, 1H), 0.92 (dd, J = 13.0, 6.7 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz) δ 165.6, 142.5, 122.8, 77.9, 62.0, 47.6, 32.4, 30.0, 20.5, 19.2.
IR (film) 2965, 2876, 2361, 2338, 1668, 1653, 1635, 1558, 1472, 1457 cm⁻¹.
LRMS (ES+) calcd for C₁₀H₁₉N₂O₄ (M+H⁺) 231, found 231.

(E)-8-(tert-Butyldimethylsilyloxy)-N-methoxy-N-methyl-4-(nitromethyl)oct-2-enamide (Table 2, entry 5). The compound was prepared according to the general procedure with (±)-8-(tert-butyldimethylsilyloxy)-N-methoxy-N-methylocta-2,3-dienamide (235 mg, 0.75 mmol). After purification by flash chromatography (25% EtOAc in hexanes), the title compound was isolated as a colorless oil (156 mg, 56% yield) with 92% ee.

[α]D²² = −19 (c = 1.0, CHCl₃). HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 5.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 16.6 min (major), 18.4 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (163 mg, 58% yield) with 92% ee.
$^1H$ NMR (CDCl$_3$, 500 MHz) δ 6.65 (dd, $J$ = 15.4, 9.1 Hz, 1H), 6.53 (d, $J$ = 15.4 Hz, 1H), 4.39 (dd, $J$ = 12.3, 6.0 Hz, 1H), 4.32 (dd, $J$ = 12.3, 9.0 Hz, 1H), 3.63 (s, 3H), 3.57-3.50 (m, 2H), 3.18 (s, 3H), 3.09-3.02 (m, 1H), 1.54-1.24 (m, 6H), 0.83 (s, 9H), −0.01 (s, 6H).

$^{13}C$ NMR (CDCl$_3$, 125 MHz) δ 165.6, 144.1, 122.1, 79.0, 62.9, 62.0, 41.6, 32.6, 31.4, 26.1, 23.3, 18.5, −5.1.

IR (film) 2933, 2858, 2361, 2339, 1668, 1653, 1635, 1557, 1380 cm$^{-1}$.

LRMS (ES+) calcd for C$_{17}$H$_{35}$N$_2$O$_5$Si (M+H$^+$) 375, found 375.

$\text{(E)-Methyl 8-(methoxy(methyl)amino)-5-(nitromethyl)-8-oxooct-6-enoate (Table 2, entry 6).}$ The compound was prepared according to the general procedure with (±)-methyl 8-(methoxy(methyl)amino)-8-oxoocta-5,6-dienoate (170 mg, 0.75 mmol). After purification by flash chromatography (15 → 50% EtOAc in hexanes), the title compound was isolated as a colorless oil (165 mg, 76% yield) with 94% ee.

$[\alpha]_{D}^{22} = -30$ (c = 1.0, CHCl$_3$). HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 5.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 59.9 min (major), 74.3 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (158 mg, 73% yield) with 92% ee.

$^1H$ NMR (CDCl$_3$, 500 MHz) δ 6.61 (dd, $J$ = 15.4, 9.1 Hz, 1H), 6.47 (d, $J$ = 15.5 Hz, 1H), 4.39 (dd, $J$ = 12.4, 6.0 Hz, 1H), 4.31 (dd, $J$ = 12.3, 8.8 Hz, 1H), 3.61 (s, 3H), 3.58 (s, 3H), 3.16 (s, 8H), 3.08-3.00 (m, 1H), 2.25 (t, $J$ = 6.9 Hz, 2H), 1.64-1.41 (m, 4H).

$^{13}C$ NMR (CDCl$_3$, 125 MHz) δ 173.5, 165.6, 143.5, 122.5, 78.8, 62.0, 51.8, 41.3, 33.6, 32.4, 30.8, 22.2.

IR (film) 2952, 2871, 2361, 2338, 1734, 1664, 1635, 1557 cm$^{-1}$.

LRMS (ES+) calcd for C$_{12}$H$_{21}$N$_2$O$_6$ (M+H$^+$) 289, found 289.

(E)-Methyl 10-(methoxy(methyl)amino)-7-(nitromethyl)-10-oxodec-8-enoate (Table 2, entry 7). The compound was prepared according to the general procedure with (±)-methyl 10-(methoxy(methyl)amino)-10-oxodeca-7,8-dienoate (191 mg, 0.75 mmol). After purification by flash chromatography (20 → 50% EtOAc in hexanes), the title compound was isolated as a colorless oil (195 mg, 82% yield) with 92% ee.
\[ [\alpha]_D^{22} = -26 \text{ (c = 1.0, CHCl}_3). \] HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 5.0\% i-PrOH in hexanes; 1.0 mL/min; retention times: 56.7 min (major), 63.5 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (193 mg, 82\% yield) with 92\% ee.

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 6.58 \text{ (dd, } J = 15.4, 9.1 \text{ Hz, 1H}), 6.40 \text{ (d, } J = 15.4 \text{ Hz, 1H}), 4.35 \text{ (dd, } J = 12.3, 5.9 \text{ Hz, 1H}), 4.28 \text{ (dd, } J = 12.3, 8.7 \text{ Hz, 1H}), 3.58 \text{ (s, 3H), 3.55 \text{ (s, 3H), 3.13 \text{ (s, 3H), 3.02-2.94 \text{ (m, 1H), 2.19 \text{ (t, } J = 7.4 \text{ Hz, 3H), 1.52-1.16 \text{ (m, 7H).}}}} \right.\)

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta 174.0, 165.7, 144.0, 122.1, 79.0, 61.9, 60.5, 41.4, 33.9, 32.3, 31.3, 28.9, 26.5, 24.7. \)

IR (film) 2938, 2861, 2361, 2339, 1734 cm\(^{-1}\).

LRMS (ES+) calcd for C\(_{14}\)H\(_{25}\)N\(_2\)O\(_6\) (M+H\(^+\)) 317, found 317.

(E)-N-Methoxy-N-methyl-4-(nitromethyl)trideca-2,12-dienamide (Table 2, entry 8).
The compound was prepared according to the general procedure with (±)-N-methoxy-N-methyltrideca-2,3,12-trienamide (189 mg, 0.75 mmol). After purification by flash chromatography (5 → 40\% EtOAc in hexanes), the title compound was isolated as a colorless oil (199 mg, 85\% yield) with 92\% ee.

\[ [\alpha]_D^{22} = -26 \text{ (c = 1.0, CHCl}_3). \] HPLC analysis of the product: Daicel CHIRALPAK AD-H column; 5.0\% i-PrOH in hexanes; 1.0 mL/min; retention times: 14.7 min (major), 18.0 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (190 mg, 81\% yield) with 92\% ee.

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 6.62 \text{ (dd, } J = 15.4, 9.1 \text{ Hz, 1H}), 6.43 \text{ (d, } J = 15.4 \text{ Hz, 1H), 5.71 \text{ (ddt, } J = 17.0, 10.2, 6.7 \text{ Hz, 1H), 4.93-4.83 \text{ (m, 2H), 4.37 \text{ (dd, } J = 12.3, 6.0 \text{ Hz, 1H), 4.29 \text{ (dd, } J = 12.1, 8.8 \text{ Hz, 1H), 3.60 \text{ (s, 3H), 3.16 \text{ (s, 3H), 3.06-2.98 \text{ (m, 1H), 1.97-1.93 \text{ (m, 2H), 1.48-1.14 \text{ (m, 12H)}}}} \right.\)

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta 165.7, 144.3, 139.2, 122.0, 114.4, 79.1, 61.9, 60.5, 41.5, 33.9, 31.6, 29.4, 29.1, 29.0, 26.8, 14.3.

IR (film) 3289, 3075, 2925, 2855, 2361, 2339, 1653 cm\(^{-1}\).

LRMS (ES+) calcd for C\(_{16}\)H\(_{29}\)N\(_2\)O\(_4\) (M+H\(^+\)) 313, found 313.
(2E,11Z)-N-Methoxy-N-methyl-4-(nitromethyl)icos-2,11-dienamide (Table 2, entry 9). The compound was prepared according to the general procedure with (±)-(Z)-N-methoxy-N-methylnonadeca-2,3,10-trienamide (262 mg, 0.75 mmol). After purification by flash chromatography (7 → 14% EtOAc in hexanes), the title compound was isolated as a colorless oil (257 mg, 83% yield) with 93% ee.

\[ [\alpha]_D^{22} = -24 \text{ (c = 1.0, CHCl}_3 \text{).} \]
HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 1.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 57.4 min (major), 64.0 min (minor).

The second run was performed with (R)-1. The product was isolated as a colorless oil (260 mg, 84% yield) with 93% ee.

\[ 1H \text{ NMR (CDCl}_3, 500 MHz) \delta 6.64 (dd, J = 15.4, 9.4 Hz, 1H), 6.47 (dd, J = 15.4 Hz, 1H), 5.31-5.20 (m, 2H), 4.38 (dd, J = 12.3, 6.0 Hz, 1H), 4.30 (dd, J = 12.1, 8.9 Hz, 1H), 3.61 (s, 3H), 3.17 (s, 3H), 3.08-2.98 (m, 1H), 2.00-1.88 (m, 4H), 1.48-1.10 (m, 22H), 0.81 (t, J = 6.5 Hz, 3H). \]

\[ 13C \text{ NMR (CDCl}_3, 125 MHz) \delta 165.8, 144.3, 143.0, 129.7, 122.0, 79.5, 79.1, 61.9, 41.5, 36.8, 32.4, 32.0, 31.6, 29.9, 29.8, 29.7, 29.5, 29.4, 29.2, 27.4, 27.3, 26.9, 22.9, 14.3. \]
IR (film) 3003, 2926, 2855, 2361, 2339, 1667, 1635, 1557, 1464 cm\(^{-1}\).
LRMS (ES+) calcd for C\(_{23}\)H\(_{43}\)N\(_2\)O\(_4\) (M+H\(^+\)) 411, found 411.

(E)-Methyl 4-(nitromethyl)hept-2-enoate (Table 3, entry 1). The compound was prepared according to the general procedure with (±)-methyl hepta-2,3-dienoate (105 mg, 0.75 mmol). After purification by flash chromatography (30% hexanes in CH\(_2\)Cl\(_2\)), the title compound was isolated as a colorless oil (109 mg, 72% yield) with 92% ee.

\[ [\alpha]_D^{22} = -32 \text{ (c = 1.0, CHCl}_3 \text{).} \]
HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 1.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 24.8 min (minor), 32.7 min (major).

The second run was performed with (R)-1. The product was isolated as a colorless oil (113 mg, 74% yield) with 93% ee.

\[ 1H \text{ NMR (CDCl}_3, 500 MHz) \delta 6.72 (dd, J = 15.6, 9.1 Hz, 1H), 5.90 (d, J = 15.7 Hz, 1H), 4.42 (dd, J = 12.3, 5.9 Hz, 1H), 3.85 (dd, J = 12.3, 8.7 Hz, 1H), 3.73 (s, 3H), 3.10-3.03 (m, 1H), 1.50-1.25 (m, 4H), 0.91 (t, J = 7.3 Hz, 3H). \]
(E)-tert-Butyl 4-(nitromethyl)hept-2-enoate (Table 3, entry 2). The compound was prepared according to the general procedure with (±)-tert-butyl hepta-2,3-dienoate (137 mg, 0.75 mmol). After purification by flash chromatography (10% EtOAc in hexanes), the title compound was isolated as a colorless oil (173 mg, 95% yield) with 90% ee.

\([\alpha]_D^{22} = -29\ (c = 1.0, \text{CHCl}_3).\) HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 1.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 13.6 min (minor), 17.4 min (major).

The second run was performed with (R)-1. The product was isolated as a colorless oil (168 mg, 93% yield) with 90% ee.

\(^1\text{H NMR (CDCl}_3, 500 \text{ MHz})\ \delta 6.56\ (dd, J = 15.6, 9.0 \text{ Hz}, 1\text{H}), 5.77\ (d, J = 15.6 \text{ Hz}, 1\text{H}), 4.37\ (dd, J = 12.3, 6.1 \text{ Hz}, 1\text{H}), 4.31\ (dd, J = 12.3, 8.5 \text{ Hz}, 1\text{H}), 3.04-2.96\ (m, 1\text{H}), 1.42-1.20\ (m, 13\text{H}), 0.86\ (t, J = 6.6 \text{ Hz}, 3\text{H}).\)

\(^{13}\text{C NMR (CDCl}_3, 125 \text{ MHz})\ \delta 165.1, 144.6, 126.1, 80.9, 78.9, 40.8, 33.5, 28.2, 20.0, 13.9.\)

IR (film) 2964, 2934, 2875, 2361, 2339, 1713, 1654, 1554, 1368, 1159 cm\(^{-1}\). LRMS (ES+) calcd for C\(_8\)H\(_{12}\)NO\(_4\) (M+H\(^+\)) 186, found 186.

(E)-Diethyl 3-(nitromethyl)oct-1-enylphosphonate (Table 3, entry 3). The compound was prepared according to the general procedure (except 3.0 equiv of phenol was used and the reaction mixture was heated at 60 °C) with (±)-diethyl octa-1,2-dienylphosphonate (185 mg, 0.75 mmol). After purification by flash chromatography (70% EtOAc in hexanes), the title compound was isolated as a colorless oil (203 mg, 89% yield) with 75% ee.

\([\alpha]_D^{22} = -18\ (c = 1.0, \text{CHCl}_3).\) HPLC analysis of the product: Daicel CHIRALPAK OD-H column; 2.0% i-PrOH in hexanes; 1.0 mL/min; retention times: 41.4 min (minor), 46.7 min (major).

The second run was performed with (R)-1. The product was isolated as a colorless oil (193 mg, 84% yield) with 72% ee.
$^1$H NMR (CDCl$_3$, 500 MHz) δ 6.45 (ddd, $J = 21.6, 17.1, 8.7$ Hz, 1H), 5.64 (dd, $J = 18.9, 17.1$ Hz, 1H), 4.35 (dd, $J = 12.2, 5.6$ Hz, 1H), 4.26 (dd, $J = 12.2, 9.0$ Hz, 1H), 4.01-3.87 (m, 4H), 2.96-2.89 (m, 1H), 1.42-1.30 (m, 2H), 1.28-1.11 (m, 12H), 0.77 (t, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 150.6, 121.7, 78.8, 62.0, 43.2, 43.0, 31.5, 31.1, 26.4, 22.5, 16.5, 16.4, 14.0.

IR (film) 2958, 2932, 2860, 2361, 2339, 1639, 1553, 1380, 1246 cm$^{-1}$.

LRMS (ES+) calcd for C$_{13}$H$_{27}$NO$_5$P (M+H$^+$) 308, found 308.
III. Determination of Absolute Stereochemistry

The stereochemistry of two of the γ-addition products was assigned by correlation with known compounds. The stereochemistry of the other products was assigned by analogy.

(S)-3-methyl-2-(nitromethyl)butanal:

(R)-tert-butyl 2-(hydroxymethyl)pentylcarbamate:

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Table 2, entry 9

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