Enantioselective Synthesis of Allenes by Catalytic Traceless Petasis Reactions

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1. General Information.

All $^1$H NMR and $^{13}$C NMR spectra were recorded using Varian Unity Plus 500 or 400 MHz spectrometer at ambient temperature in CDCl$_3$ (Cambridge Isotope Laboratories, Inc.). Chemical shifts in $^1$H NMR spectra are reported in parts per million from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: $\delta$ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (app = apparent, br = broad, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts in $^{13}$C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: $\delta$ 77.0 ppm). All $^{13}$C NMR spectra were recorded with complete proton decoupling. Chemical shifts in $^{19}$F NMR spectra are reported in parts per million using 0.05% $\alpha,\alpha,\alpha$-trifluorotoluene in...
deuterobenzene as the external standard. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. High-resolution mass spectra were obtained using a Waters Q-TOF mass spectrometer. LC-MS experiments were performed using an Agilent Single-Quad LC/MSD VL with single-quad low resolution (1 decimal place) capable of both ESI positive and negative modes using flow injection analysis. GC-MS experiments were performed using an Agilent GC-MS 6890N equipped with a MS detector up to 800 m/z. The ionization is electron impact (EI) and software is ChemStation. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as $\left[\alpha\right]_D^{\text{c},\text{solvent}}$ (concentration in grams/100 mL solvent). Chiral HPLC analysis was performed using an Agilent 1100 series HPLC System with a diode array detector. Chiral columns include Chiralcel® OD (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.), Chiralpak® AD-H (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.) and Chiralpak® IA-H (Chiral Technologies Inc., 25 cm × 4.6 mm I.D.). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Catalyst loadings were calculated with respect to the amount of boronates. All reactions were carried out in oven-dried glassware under an argon or nitrogen atmosphere unless otherwise noted. HPLC grade THF, dichloromethane, Et$_2$O and toluene were purchased from Fisher and VWR and were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology Inc.). Triethyl borate was distilled over CaH$_2$ before use in the preparation of alkynyl boronates. Mesitylene was dried by and stored with 3 Å molecular sieves beads. The previously reported chiral biphenol catalysts were prepared according to known literature procedures.$^1$ All other reagents were purchased from commercial suppliers and used without further purification.
2. Experimental Procedures
a. Synthesis of Hydrazides

2-Nitrobenzenesulfonylhydrazide (NBSH, 20) was synthesized according to the procedure reported by Myers and coworkers.²

\[
\begin{align*}
\text{Br} & \quad \text{SO}_2\text{Cl} \\
\text{Br} & \quad \text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O} \\
\end{align*}
\]

\[
\text{THF, } -30^\circ\text{C} \\
71\% \text{ yield}
\]

2,5-Dibromobenzenesulfonohydrazide (8)
Hydrazine monohydrate (6.1 mL, 125 mol, 2.5 eq) was added dropwise to a solution of 2,5-dibromobenzenesulfonyl chloride (16.7 g, 50 mmol, 1 eq) in THF (20 mL) at −30 °C under argon atmosphere. During the addition a white precipitate of hydrazine hydrochloride was deposited. After stirring at −30 °C for 1 h, EtOAc (30 mL, 23 °C) was added to the cold reaction solution and the mixture was washed repeatedly with ice-cold 10% aqueous sodium chloride solution (5 × 100 mL). The organic layer was dried over sodium sulfate at 0 °C and then was added slowly to a stirring solution of hexanes (500 ml) at 23 °C over 5 min. 2,5-Dibromobenzenesulfonohydrazide precipitated within 10 min as an off-white solid and was collected by vacuum filtration. The filter cake was washed with hexanes (2 × 20 mL, 23 °C) and then recrystallized by dichloromethane to afford an off-white crystal (11.7 g, 71% yield). The hydrazide was stored at −8 °C without exposure to light. Caution: During the reaction one equivalent of hydrazine hydrochloride was generated as a white precipitate. Stirring might be impeded and the rate of stirring should be adjusted. Hydrazine hydrochloride is extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion or inhalation. After the aqueous work-up it remained in the water layer, which should be disposed to a separate container as a hazardous waste.

\[
\begin{align*}
\text{1H NMR} \ (500 \text{ MHz, DMSO-}d_6) & \ 
\delta \ 8.80 \ (\text{br, 1H}, 8.04 \ (\text{d}, \ J = 2.4 \text{ Hz, 1H}), 7.79 – 7.68 \ (\text{m, 2H}), 4.43 \ (\text{br, 2H}). \\
\text{13C NMR} \ (126 \text{ MHz, DMSO-}d_6) & \ 
\delta \ 140.0, 137.5, 137.0, 134.4, 121.1, 119.2.
\end{align*}
\]

2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide (17)
Hydrazine monohydrate (6.1 mL, 125 mol, 2.5 eq) was added dropwise to a solution of 2-nitro-4-(trifluoromethyl)benzenesulfonyl chloride (14.5 g, 50 mmol, 1 eq) in THF (20 mL) at −30 °C under an argon atmosphere. During the addition a white precipitate of hydrazine hydrochloride was deposited. After stirring at −30 °C for 30 min, EtOAc (30 mL, 23 °C) was added to the cold reaction solution and the mixture was washed repeatedly with ice-cold 10% aqueous sodium chloride solution (5 × 100 mL). The organic layer was dried over sodium sulfate at 0 °C and then was added slowly to a stirring solution of hexanes (500 ml) at 23 °C over 5 min. 2-Nitro-4-(trifluoromethyl)benzenesulfonylhydrazide precipitated within 10 min as a yellow solid and was collected by vacuum filtration. The filter cake was washed with hexanes (2 × 20 mL, 23 °C) and then recrystallized by dichloromethane to afford a pale white solid (10.7 g, 75% yield).
hydrazide was stored at –8 °C without exposure to light.

*Caution:* During the reaction one equivalent of hydrazine hydrochloride was generated as a white precipitate. Stirring might be impeded and the rate of stirring should be adjusted. Hydrazine hydrochloride is extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion or inhalation. After the aqueous work-up it remained in the water layer, which should be disposed to a separate container as a hazardous waste.

\[ \text{1H NMR (500 MHz, Acetonitrile-d3) } \delta \text{ 8.26 (d, } J = 8.2 \text{ Hz, 1H), 8.22 (q, } J = 1.0 \text{ Hz, 1H), 8.13 (dq, } J = 8.3, 1.0 \text{ Hz, 1H), 7.15 (br, 1H), 2.74 (br, 2H).} \]

\[ \text{13C NMR (126 MHz, Acetonitrile-d3) } \delta \text{ 148.7, 135.0 (q, } J = 34.5 \text{ Hz), 133.9, 133.5, 129.3 (q, } J = 3.8 \text{ Hz), 122.5 (q, } J = 272.7 \text{ Hz), 122.3 (q, } J = 4.0 \text{ Hz).} \]

\[ \text{19F NMR (470 MHz, Acetonitrile-d3) } \delta \text{ –63.9.} \]

b. Synthesis of (S)-(CF₃)₄-BINOL (10)

(S)-3,3′-Diiodo-2,2′-bis(methoxymethoxy)-6,6′-bis(trifluoromethyl)-1,1′-binaphthalene (S10)

To a solution of (S)-2,2′-bis(methoxymethoxy)-6,6′-bis(trifluoromethyl)-1,1′-binaphthyl (3.17 g, 5.19 mmol) in dry THF (60 mL) was added a hexane-cyclohexane solution of s-BuLi (1.02 M, 20.8 mL, 21.2 mmol) at –78 °C under argon and the resulting mixture was stirred for 1 h at the same temperature. Iodine (7.92 g, 31.2 mmol) in dry THF (25 mL) was then added by a cannula and the reaction mixture was stirred for an additional 3 h at the same temperature. The reaction was quenched with water and diluted with EtOAc. The organic layer was separated and the aqueous layer was extracted with brine, and dried over anhydrous sodium sulfate. After filtration and concentration under reduced pressure, the crude product was purified by silica gel column chromatography (hexanes/EtOAc: 50/1) to afford (S)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-6,6′-bis(trifluoromethyl)-1,1′-binaphthalene as an amorphous oil in 65% yield.

\[ [\alpha]_{D}^{22} = +3.1 \text{ (c=1.1, CHCl}_3). \]

\[ \text{1H NMR (500 MHz, CDCl}_3 \delta 8.67 \text{ (s, 2H), 8.11 \text{ (s, 2H), 7.48 \text{ (d, } J = 8.9 \text{ Hz, 2H), 7.25 \text{ (d, } J = 8.9 \text{ Hz, 2H), 4.91} \text{ – 4.71 (m, 4H), 2.55 (s, 6H).} \]

\[ \text{13C NMR (126 MHz, CDCl}_3 \delta 154.5, 141.1, 134.9, 130.8, 127.9 \text{ (q, } J = 32.6 \text{ Hz), 127.5, 125.8, 125.0, 124.5 \text{ (q, } J = 4.5 \text{ Hz), 122.9 \text{ (q, } J = 3.2 \text{ Hz), 99.8, 94.2, 56.5.} \]

\[ \text{19F NMR (470 MHz, CDCl}_3 \delta 62.5. \]

ESI-MS found 762.9 (calculated for [C₂₆H₁₉F₆I₂O₄]⁺: 762.9)

IR (thin film, cm⁻¹): 3015, 2948, 2902, 2827, 1570, 1328, 1164, 1069, 957.
(S)-3,3',6,6'-Tetrakis(trifluoromethyl)-[1,1'-binaphthalene]-2,2'-diol (10)

A mixture of (S)-3,3'-diiodo-2,2'-bis(methoxymethoxy)-6,6'-bis(trifluoromethyl)-1,1'-binaphthalene (S10) (0.56 g, 1 mmol) and FSO$_2$CF$_2$CO$_2$Me (0.51 ml, 4 mmol), CuI (0.46 g, 2.4 mmol), HMPA (0.70 ml, 4 mmol) in NMP (20 mL) was stirred under argon atmosphere at 80 °C and monitored by TLC. When the starting material vanished, the reaction was cooled to room temperature and diluted with dichloromethane (50 mL). The solution was washed with water (3 X 100 mL), dried over sodium sulfate, and concentrated to afford a syrup. The crude product was then dissolved in THF/MeOH (1:1, 25 ml/ 25 ml) mixture. 1 gram of Amberlyst 15 was added and the mixture was heated to 50 °C for 3 h. The Amberlyst powder was filtered off and the filtrate was concentrated and subjected to column chromatography (hexanes/EtOAc: 50/1) to directly afford the deprotected product as a light yellow solid (45% yield over two steps).

$\alpha$$_D$$^{22}$ = +4.0 (c=1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.51 (s, 2H), 8.34 (s, 2H), 7.63 (d, $J$ = 9.0, 2H), 7.19 (d, $J$ = 9.0 Hz, 2H), 5.53 (s, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 151.1, 136.1, 131.4 (q, $J$ = 5.4 Hz), 127.9 (q, $J$ = 33.0 Hz), 127.4 (q, $J$ = 4.3 Hz), 126.7, 125.9 (q, $J$ = 3.0 Hz), 124.9, 124.4 (q, $J$ = 119.0 Hz), 122.2 (q, $J$ = 119.8 Hz), 120.4 (q, $J$ = 31.9 Hz), 112.3.

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -62.6, -62.7.

ESI-MS found 557.0 (calculated for [C$_{24}$H$_9$F$_{12}$O$_2$]$^-$: 557.0)

IR (thin film, cm$^{-1}$): 3549, 1639, 1467, 1338, 1144.
Table S1: Optimization of Asymmetric Petasis Alkynylations

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Hydrazide</th>
<th>Temperature/Time</th>
<th>Yield</th>
<th>e.r.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C1 (15 mol%)</td>
<td>20</td>
<td>0 °C /24 h</td>
<td>85%</td>
<td>86:14</td>
</tr>
<tr>
<td>2</td>
<td>C2 (15 mol%)</td>
<td>20</td>
<td>0 °C /24 h</td>
<td>20%</td>
<td>85:15</td>
</tr>
<tr>
<td>3</td>
<td>C3 (15 mol%)</td>
<td>20</td>
<td>0 °C /24 h</td>
<td>75%</td>
<td>70:30</td>
</tr>
<tr>
<td>4</td>
<td>19 (15 mol%)</td>
<td>20</td>
<td>0 °C /24 h</td>
<td>70%</td>
<td>73:27</td>
</tr>
<tr>
<td>5</td>
<td>10 (15 mol%)</td>
<td>20</td>
<td>0 °C /24 h</td>
<td>85%</td>
<td>87:13</td>
</tr>
<tr>
<td>6</td>
<td>C1 (15 mol%)</td>
<td>20</td>
<td>–10 °C /48 h</td>
<td>20%</td>
<td>88:12</td>
</tr>
<tr>
<td>7</td>
<td>10 (15 mol%)</td>
<td>20</td>
<td>–10 °C /48 h</td>
<td>50%</td>
<td>90:10</td>
</tr>
<tr>
<td>8</td>
<td>C1 (15 mol%)</td>
<td>8</td>
<td>0 °C /48 h</td>
<td>68%</td>
<td>88:12</td>
</tr>
<tr>
<td>9</td>
<td>C1 (15 mol%)</td>
<td>17</td>
<td>0 °C /24 h</td>
<td>83%</td>
<td>58:42</td>
</tr>
<tr>
<td>10</td>
<td>10 (15 mol%)</td>
<td>8</td>
<td>0 °C /48 h</td>
<td>83%</td>
<td>92:8</td>
</tr>
<tr>
<td>11</td>
<td>10 (10 mol%)</td>
<td>8</td>
<td>0 °C /48 h</td>
<td>85%</td>
<td>92:8</td>
</tr>
<tr>
<td>12</td>
<td>C4 (10 mol%)</td>
<td>8</td>
<td>0 °C /48 h</td>
<td>51%</td>
<td>85:15</td>
</tr>
<tr>
<td>13a</td>
<td>10 (10 mol%)</td>
<td>8</td>
<td>0 °C /48 h</td>
<td>85%</td>
<td>93:7</td>
</tr>
</tbody>
</table>

\(^a\) PhCH$_3$/Mesitylene=1:1
c. General Procedure for Synthesis of Acyclic Alkynyl Boronates

Acyclic alkynyl boronates were synthesized in a modified procedure based on the published method.\(^4\) To flask A charged with argon was added 25 mL diethyl ether and alkyne (15 mmol, 1 eq). Solution was cooled to \(-78 \, ^\circ\text{C}\) and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to \(-78 \, ^\circ\text{C}\) and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite\(^\circledR\) to flask C. The boronate solution in flask C was concentrated \textit{in vacuo} to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at \(-8 \, ^\circ\text{C}\). The boronates were allowed to be stored for up to 2 weeks and were used directly without further purification.

\[
\begin{align*}
\text{Diethyl (phenylethynyl)boronate (1a/14)}
\end{align*}
\]

To a flask A charged with argon was added diethyl ether (25 mL) and phenyl acetylene (1.65 ml, 15 mmol, 1 eq). Solution was cooled to \(-78 \, ^\circ\text{C}\) and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to \(-78 \, ^\circ\text{C}\) and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite\(^\circledR\) to flask C. The boronate solution in flask C was concentrated \textit{in vacuo} to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at \(-8 \, ^\circ\text{C}\). The toluene solution of diethyl (phenylethynyl)boronate (1a/14) was allowed to be stored for up to 2 weeks and used directly without further purifications.

\[\text{^1H NMR (500 MHz, CDCl}_3\text{)} \delta 7.54 - 7.47 (m, 2H), 7.37 - 7.29 (m, 3H), 4.09 (q, J = 7.1 Hz, 4H), 1.28 (t, J = 7.1 Hz, 6H).\]
**Diethyl ((4-methoxyphenyl)ethynyl)boronate (1b)**

To a flask A charged with argon was added 25 mL diethyl ether and 4-ethynylanisole (1.95 ml, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 mL dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 mL volume without exposure to the air, and made into a 1 M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl ((4-methoxyphenyl)ethynyl)boronate (1b) was allowed to be stored for up to 1 week and used directly without further purifications.

**1H NMR** (500 MHz, CDCl₃) δ 7.71 – 7.58 (m, 2H), 7.02 (d, J = 8.5, 2H), 4.39 – 4.25 (m, 4H), 3.92 (s, 3H), 1.52 (t, J = 7.6 Hz, 6H).

**Diethyl ((4-fluorophenyl)ethynyl)boronate (1c)**

To a flask A charged with argon was added 25 mL diethyl ether and 1-ethynyl-4-fluorobenzene (1.72 mL, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 mL dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 mL volume without exposure to the air, and made into a 1 M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl ((4-fluorophenyl)ethynyl)boronate (1c) was allowed to be stored for up to 2 weeks and used directly without further purifications.

**1H NMR** (500 MHz, CDCl₃) δ 7.78 – 7.58 (m, 2H), 7.18 (d, J = 7.4 Hz, 2H), 4.33 (q, J = 7.1 Hz, 4H), 1.51 (t, J = 7.1 Hz, 6H).
Diethyl ((2-(trifluoromethyl)phenyl)ethynyl)boronate (1d)

To a flask A charged with argon was added 25 mL diethyl ether and 1-ethynyl-2-trifluoromethylbenzene (2.09 mL, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl ((2-(trifluoromethyl)phenyl)ethynyl)boronate (1d) was allowed to be stored for up to 2 weeks and used directly without further purifications.

\[^1\text{H}\ \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta \ 7.86 - 7.70 \ (m, 2H), \ 7.64 - 7.54 \ (m, 1H), \ 7.53 \ (dd, J = 7.5, 7.5 \text{ Hz, 1H}), \ 4.29 \ (q, J = 7.0 \text{ Hz, 4H}), \ 1.42 \ (t, J = 7.0 \text{ Hz, 6H}).\]

Diethyl (thiophen-3-ylethynyl)boronate (1e)

To a flask A charged with argon was added 25 mL diethyl ether and 3-ethynylthiophene (1.48 ml, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl (thiophen-3-ylethynyl)boronate (1e) was allowed to be stored for up to 1 week and used directly without further purifications.

\[^1\text{H}\ \text{NMR} \ (500 \text{ MHz, CDCl}_3) \delta \ 7.75 - 7.60 \ (m, 2H), \ 7.64 - 7.54 \ (m, 1H), \ 7.53 \ (dd, J = 7.5, 7.5 \text{ Hz, 1H}), \ 4.29 \ (q, J = 7.1 \text{ Hz, 4H}), \ 1.39 \ (t, J = 7.1 \text{ Hz, 6H}).\]
Diethyl (naphthalen-2-ylethynyl)boronate (1f)
To a flask A charged with argon was added 25 mL diethyl ether and 2-ethynyl-naphthalene (2.13 mL, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl (naphthalen-2-ylethynyl)boronate (1f) was allowed to be stored for up to 1 week and used directly without further purifications.

^1H NMR (500 MHz, CDCl₃) δ 8.02 – 7.89 (m, 4H), 7.83 – 7.74 (m, 1H), 7.72 – 7.63 (m, 2H), 4.38 (q, J = 7.2 Hz, 4H), 1.54 (t, J = 7.2 Hz, 6H).

Diethyl (4-phenylbut-1-yn-1-yl)boronate (1g)
To a flask A charged with argon was added 25 mL diethyl ether and (3-butylnyl)benzene (1.95 g, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl (4-phenylbut-1-yn-1-yl)boronate (1g) was allowed to be stored for up to 2 weeks and used directly without further purifications.

^1H NMR (500 MHz, CDCl₃) δ 7.56 – 7.48 (m, 5H), 4.31 – 4.15 (m, 4H), 3.14 – 3.06 (m, 2H), 2.88 – 2.74 (m, 2H), 1.55 – 1.31 (m, 6H).
Diethyl (E)-(4-phenylbut-3-en-1-yn-1-yl)boronate (1h)

(E)-but-1-en-3-yn-1-ylbenzene (S6h) was synthesized according to disclosed procedure. To a flask A charged with argon was added 25 mL diethyl ether and (E)-but-1-en-3-yn-1-ylbenzene (1.92 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (E)-(4-phenylbut-3-en-1-yn-1-yl)boronate (1h) was allowed to be stored for up to 1 week and used directly without further purifications.

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.70 – 7.56 (m, 4H), 7.38 – 7.30 (m, 1H), 6.47 (d, $J = 16.2$ Hz, 1H), 6.37 (d, $J = 16.2$, 1H), 4.31 (q, $J = 7.2$ Hz, 4H), 1.48 (t, $J = 7.2$ Hz, 6H).

Diethyl (cyclohexylethynyl)boronate (1i)

To a flask A charged with argon was added 25 mL diethyl ether and cyclohexylacetylene (1.96 ml, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at –8 °C. The toluene solution of diethyl (cyclohexylethynyl)boronate (1i) was allowed to be stored for up to 2 weeks and used directly without further purifications.

$^1$H NMR (500 MHz, CDCl$_3$) δ 4.35 – 4.10 (m, 4H), 2.83 – 2.62 (m, 1H), 2.10 – 1.85 (m, 5H), 1.80 – 1.60 (m, 5H), 1.50 – 1.28 (m, 6H).
**Diethyl oct-1-yn-1-ylboronate (1j)**

To a flask A charged with argon was added 25 mL diethyl ether and 1-octyne (2.21 ml, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl oct-1-yn-1-ylboronate (1j) was allowed to be stored for up to 2 weeks and used directly without further purifications.

\[^{1}H\ NMR\ (500\ MHz,\ CDCl_{3})\ \delta\ 4.35 – 4.17\ (m,\ 4H),\ 1.87 – 1.72\ (m,\ 4H),\ 1.72 – 1.60\ (m,\ 4H),\ 1.53 – 1.39\ (m,\ 8H),\ 1.16\ (m,\ 3H)\].

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**Diethyl (3-(benzylxylo)prop-1-yn-1-yl)boronate (1k)**

To a flask A charged with argon was added 25 mL diethyl ether and propargyl benzyl ether (2.19 g, 15 mmol, 1 eq). Solution was cooled to −78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to −78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flame-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated *in vacuo* to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored in a sealed vial at −8 °C. The toluene solution of diethyl (3-(benzylxylo)prop-1-yn-1-yl)boronate (1k) was allowed to be stored for up to 2 weeks and used directly without further purifications.

\[^{1}H\ NMR\ (500\ MHz,\ CDCl_{3})\ \delta\ 7.64 – 7.53\ (m,\ 5H),\ 4.89 – 4.77\ (m,\ 2H),\ 4.48 – 4.34\ (m,\ 2H),\ 4.28\ (q,\ J = 7.2\ Hz,\ 4H),\ 1.55 – 1.35\ (m,\ 6H)\].
To a stirred solution of carbon tetrabromide (6.6 g, 20 mmol) in dichloromethane (100 mL) was added triphenylphosphine (7.9 g, 30 mmol) in dichloromethane (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, before a solution of 2-(5,5-dimethyl-1,3-dioxan-2-yl)acetaldehyde (1.6 g, 10 mmol) in anhydrous dichloromethane (5 mL) was added. The resulting mixture was stirred for 1 h at 0 °C before an addition of H₂O (40 mL) to partition the organic layer. The resulting mixture was extracted with dichloromethane (3 X 50 mL); the combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude mixture was dissolved in 5 ml dichloromethane and filtered through a silica gel column by hexane/ether (10:1, 500 ml) to afford 2-(3,3-dibromoallyl)-5,5-dimethyl-1,3-dioxane as a yellow solid, which was used in the next step without further purification.

To a stirred solution of 2-(3,3-dibromoallyl)-5,5-dimethyl-1,3-dioxane (3.1 g, 10 mmol) in THF (30 mL) was added nBuLi (15.6 mL, 1.6 M in hexane, 25 mmol) dropwise at –78 °C for 30 min. The resulting solution was stirred for 30 min at –78 °C, before it was quenched with aqueous sat. NH₄Cl (5 mL) at –78 °C. The aqueous layer was extracted with EtOAc (3 X 50 mL). The organic layer was washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was eluted through a silica column by hexanes/EtOAc (10:1) to afford compound 5,5-dimethyl-2-(prop-2-yn-1-yl)-1,3-dioxane (S11) (1.0 g, 65 % over two steps) as a colorless liquid.

**1H NMR** (500 MHz, C₆D₆) δ 4.35 (t, J = 5.1 Hz, 1H), 3.31 (d, J = 11.2, 2H), 3.02 (d, J = 10.7, 2H), 2.45 (dd, J = 5.1, 2.7 Hz, 2H), 1.83 (t, J = 2.7 Hz, 1H), 1.01 (s, 3H), 0.25 (s, 3H).

**13C NMR** (126 MHz, C₆D₆) δ 99.6, 79.2, 76.5, 70.1, 29.4, 25.5, 22.6, 21.1.

Diethyl (3-(5,5-dimethyl-1,3-dioxan-2-yl)prop-1-yn-1-yl)boronate (II)

To a flask A charged with argon was added 10 mL diethyl ether and 5,5-dimethyl-2-(prop-2-yn-1-yl)-1,3-dioxane (S11) (0.77 g, 5 mmol, 1 eq, vide infra). Solution was cooled to –78 °C and to it was added nBuLi (3.1 mL, 5 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 20 mL diethyl ether and freshly distilled triethyl borate (0.85 mL, 5 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (2.5 mL, 2 M solution sure-sealed in diethyl ether, 5 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 ml dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo
less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored
in a sealed vial at –8 °C. The toluene solution of diethyl (3-(5,5-dimethyl-1,3-dioxan-2-yl)prop-
yn-1-yl)boronate (1I) was allowed to be stored for up to 1 week and used directly without
further purifications.

\[ ^1H\text{ NMR} (500\text{ MHz, CDCl}_3) \delta 4.77 (t, J = 5.3\text{ Hz}, 1\text{H}), 4.30 – 4.15 (m, 4\text{H}), 3.87 – 3.73 (m, 2\text{H}),
3.61 (d, J = 10.8\text{ Hz}, 2\text{H}), 1.43 (ovrlp, 9\text{H}), 0.88 (s, 3\text{H}). \]

**Diethyl ((tert-butyldimethylsilyl)ethynyl)boronate (1m)**

To a flask A charged with argon was added 25 mL diethyl ether and (tert-butyldimethylsilyl)acetylene (2.80 g, 15 mmol, 1 eq). Solution was cooled to –78 °C and to it was added nBuLi (9.4 mL, 15 mmol, 1.6 M in hexane). Solution was allowed to stir at this temperature for 1 h. To a second flask B charged with argon was added 25 mL diethyl ether and freshly distilled triethyl borate (2.55 mL, 15 mmol). Solution was cooled to –78 °C and to flask B was added via cannula the solution of lithium-acetylene from flask A. Reaction was allowed to stir at the same temperature for 2 h, at which point to it was added anhydrous HCl (7.5 mL, 2 M solution sure-sealed in diethyl ether, 15 mmol). Reaction was removed from the dry ice-acetone bath and allowed to warm to room temperature for 1 h, during which time precipitate started to form. A third flask C was flamed-dried and to it was added 5 mL dry toluene. The crude boronate solution with precipitate from flask B was quickly filtered under nitrogen through an over-dried funnel and dry celite® to flask C. The boronate solution in flask C was concentrated in vacuo to less than 5 ml volume without exposure to the air, and made into a 1M solution in toluene stored
in a sealed vial at –8 °C. The toluene solution of diethyl ((tert-butyldimethylsilyl)ethynyl)boronate (1m) was allowed to be stored for up to 2 weeks and used directly without further purifications.

\[ ^1H\text{ NMR} (500\text{ MHz, CDCl}_3) \delta 4.24 (q, J = 7.6\text{ Hz}, 4\text{H}), 1.52 – 1.33 (m, 6\text{H}), 1.16 (s, 9\text{H}), 0.36 (s, 6\text{H}). \]

d. General Procedure for Racemic Petasis Alkynylation

2-Nitrobenzenesulfonohydrazide 20 (87 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Racemic BINOL catalyst (15 mg, 0.052 mmol) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was stirred for 5 min, at which moment to it was subjected the alkynyl boronate (0.52 mmol, stored as 1 M solution in toluene). The reaction was stirred at room temperature for 18 h. The racemic allenyl alcohol products were isolated directly by silica gel chromatography.
e. General Procedure for Asymmetric Petasis Alkynylations

\[
\begin{align*}
\text{8} & \quad + \quad \text{9} \\
\begin{array}{c}
\text{O} \quad \text{S} \\
\text{N} \quad \text{Br}
\end{array} & \quad \begin{array}{c}
\text{O} \quad \text{O} \\
\text{HO} \quad \text{HO}
\end{array} & \quad \begin{array}{c}
\text{HO} \\
\text{Br}
\end{array} \\
\text{N} \quad \text{H} & \quad \text{OEt} \quad \text{OEt} & \quad \text{R} \\
\text{R} \quad \text{R} & \quad \text{R} \\
\text{CF}_3 & \quad \text{CF}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{CF}_3 & \quad \text{CF}_3 & \quad \text{CF}_3
\end{align*}
\]

2,5-Dibromobenzenesulfonohydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF\(_3\))\(_4\)-BINOL catalyst 10 (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C for 10 min under argon, at which moment to it was subjected the alkynyl boronate (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 0 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H\(_2\)O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na\(_2\)SO\(_4\). Concentration under reduced pressure followed by flash column chromatography on silica gel afforded the desired compound.

f. Analytical Data for Allenyl Alcohols

(5)-4-Phenylbuta-2,3-dien-1-ol (6a)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1a (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil. **Yield:** 50 mg, 85%.
**e.r.:** 93:7.
\([\alpha]_D^{22} = +103.0 \ (c = 0.49, \text{CH}_3\text{CN})\). In lit:\(^7\) \([\alpha]_D^{22} = +105.9 \ (c = 0.49, \text{CH}_3\text{CN})\). The absolute stereochemistry was assigned as (S).
**HPLC Analysis,** tr major: 43.7 min., tr minor: 46.9 min., [Chiralpak® AD-H column, 24 cm × 4.6 mm I.D., Hexanes:iPrOH = 98:2, 0.5 mL/min, 250 nm].
All spectra were in agreement with reported data.\(^7\)
(S)-4-(4-Methoxyphenyl)buta-2,3-dien-1-ol (6b)

2,5-Dibromobenzenesulfonylhydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF₃)₄-BINOL catalyst 10 (58 mg, 0.104 mmol, 20 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to –10 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate 1b (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at –10 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H₂O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na₂SO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

**Yield:** 56 mg, 80%.

**e.r.:** 91:9.

\[ {\alpha}_D^{22} = +27.1 \text{ (c = 1.0, CHCl}_3 \text{).} \]

**HPLC Analysis,** tr major: 39.5 min., tr minor: 42.9 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1 mL/min, 250 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.⁸
(S)-4-(4-Fluorophenyl)buta-2,3-dien-1-ol (6c)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1c (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.
Yield: 51 mg, 78%.
e.r.: 93:7.
$[\alpha]_D^{22} = +53.8$ (c = 1.0, CHCl$_3$).

HPLC Analysis, tr major: 30.6 min., tr minor: 31.7 min., [Chiralpak®IA-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 0.8 mL/min, 254 nm].
The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data. 8

$\begin{aligned}
&\text{H NMR (500 MHz, CDCl$_3$) } \delta 7.65 – 7.59 (m, 2H), 7.47 (dd, J = 7.7, 7.7 Hz, 1H), 7.30 (dd, J = 7.7, 7.7 Hz, 1H), 6.69 (dddd, J = 6.0, 4.3, 2.0, 2.0 Hz, 1H), 5.84 (ddd, J = 6.1, 6.1, 6.0 Hz, 1H), 4.34 – 4.24 (m, 2H). \\
&\text{C NMR (126 MHz, CDCl$_3$) } \delta 205.5, 132.4 (q, ^4J_{C:F} = 1.3 Hz), 131.8, 128.7, 127.0, 126.2 (q, ^1J_{C:F} = 239.4 Hz), 126.8 (q, ^2J_{C:F} = 30.5 Hz), 126.0 (q, ^3J_{C:F} = 5.6 Hz), 95.9, 93.3 (q, ^4J_{C:F} = 2.7 Hz), 60.1 \\
&\text{F NMR (470 MHz, CDCl$_3$) } \delta –59.5. \\
&\text{HRMS found 215.0690 (calculated for } [\text{C}_11\text{H}_10\text{F}_3\text{O}]^+: 215.0684) \\
&\text{IR (thin film, cm}^{-1}\text{): 3377, 3082, 2940, 1955, 1731, 1495, 1316, 1162, 1121, 1060, 766.} \\
The absolute stereochemistry was assigned by analogy.
\end{aligned}$
(S)-4-(Thiophen-3-yl)buta-2,3-dien-1-ol (6e)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1e (0.52 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (6:1) to afford the pure product as a colorless oil.
**Yield:** 43 mg, 70%
**e.r.:** 92:8
\[\alpha\]_D^{22} = +116.4 (c = 1.0, CHCl_3).

**HPLC Analysis,** tr minor: 21.4 min., tr major: 23.9 min., [Chiralpak®IA-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1 mL/min, 254 nm].

**1H NMR** (500 MHz, CDCl_3) δ 7.27 (ddd, J = 5.1, 3.0, 0.6 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.07 (dd, J = 5.1, 1.2 Hz, 1H), 6.40 (ddd, J = 6.4, 3.0, 2.9 Hz, 1H), 5.73 (ddd, J = 6.4, 5.8, 5.8, 1H), 4.28 – 4.20 (m, 2H), 1.54 (t, J = 6.1 Hz, 1H).

**13C NMR** (126 MHz, CDCl_3) δ 204.5, 135.0, 126.2, 126.1, 121.3, 95.1, 91.8, 60.4.

**HRMS** found 153.0370 (calculated for [C_8H_9O_S]+: 153.0374)

**IR** (thin film, cm\(^{-1}\))**: 3381, 3104, 2926, 1952, 1435, 1333, 1234, 1015, 789.

The absolute stereochemistry was assigned by analogy.

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(S)-4-(Naphthalen-2-yl)buta-2,3-dien-1-ol (6f)
2,5-Dibromobenzenesulfonyldrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF_3)_4-BINOL catalyst 10 (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C for 10 min, at which moment it was subjected the alkynyl boronate 1f (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H_2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na_2SO_4. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

**Yield:** 67 mg, 85%
**e.r.:** 90:10.
\[\alpha\]_D^{22} = +116.8 (c = 1.0, CHCl_3).

**HPLC Analysis,** tr major: 40.5 min., tr minor: 47.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].

The absolute stereochemistry was assigned by analogy. All spectra agreed with reported data.
(S)-6-Phenylhexa-2,3-dien-1-ol (6g)
2,5-Dibromobenzenesulfonohydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF₃)₄-BINOL catalyst 10 (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate 1g (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H₂O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 × 5 ml). The combined organic layers were dried with Na₂SO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

Yield: 54 mg, 72%.

[α]ᵢᵈ₂² = +10.5 (c = 1.0, CHCl₃). In lit for (R)-6-phenylhexa-2,3-dien-1-ol: [α]ᵢᵈ₂⁰ = −38.7 (c = 1.05, CHCl₃, 96% ee).

HPLC Analysis, tr minor: 27.6 min., tr major: 44.8 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 0.8 mL/min, 210 nm]. All spectra were in agreement with reported data.

(S,E)-6-Phenylhexa-2,3,5-trien-1-ol (6h)
2,5-Dibromobenzenesulfonohydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and 3 Å oven-dried powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF₃)₄-BINOL catalyst 10 (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate 1h (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H₂O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 × 5 ml). The combined organic
layers were dried with Na$_2$SO$_4$. Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

**Yield:** 49 mg, 71%.

**e.r.:** 90:10.

$[\alpha]_D^{22} = +29.2$ (c = 1.0, CHCl$_3$).

**HPLC Analysis,** tr minor: 43.4 min., tr major: 54.0 min., [Chiralcel® OD column, 24 cm x 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].

The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.$^{10}$

\[
\text{(S)-4-Cyclohexylbuta-2,3-dien-1-ol (6i)}
\]

Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1i (0.52 mmol) according to the General Procedure, but for 72 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

**Yield:** 38 mg, 63%.

**e.r.:** 90:10.

$[\alpha]_D^{22} = +80.5$ (c = 1.0, CHCl$_3$). In lit.$^9$ $[\alpha]_D^{21} = +100.9$ (c = 1.04, CHCl$_3$, 99% ee).

**HPLC Analysis,** tr minor: 19.0 min., tr major: 19.8 min., [Chiralpak® IA column, 24 cm x 4.6 mm I.D., Hexanes: iPrOH = 99:1, 1.0 mL/min, 230 nm].

All spectra were in agreement with reported data.$^9$

\[
\text{(S)-Deca-2,3-dien-1-ol (6j)}
\]

Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1j (0.52 mmol) according to the General Procedure but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

**Yield:** 45 mg, 73%.

**e.r.:** 90:10.

$[\alpha]_D^{22} = +60.7$ (c = 1.0, CHCl$_3$). In lit for (R)-deca-2,3-dien-1-ol:$^{11}$ $[\alpha]_D^{20} = -72.5$ (c = 1.02, CHCl$_3$, 94% ee).

**HPLC Analysis,** tr minor: 18.3 min., tr major: 19.5 min., [Chiralpak® IA-H column, 24 cm x 4.6 mm I.D., Hexanes: iPrOH = 99:6:0.4, 1 mL/min, 210 nm].

All spectra were in agreement with reported data.$^{11}$
(S)-5-(Benzyloxy)penta-2,3-dien-1-ol (6k)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1k (0.52 mmol) according to the General Procedure but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.
**Yield:** 46 mg, 60%.
**e.r.:** 90:10.
\([\alpha]_D^{22} = +33.2 \text{ (c } 1.0, \text{ CHCl}_3\).**

**HPLC Analysis,** tr minor: 37.1 min., tr major: 39.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 99:1, 1.0 mL/min, 250 nm].
The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.

\[(S)-5-(\text{5,5-Dimethyl-1,3-dioxan-2-yl})\text{penta-2,3-dien-1-ol (6l)}\]
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1l (0.52 mmol) according to the General Procedure but for 72 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (10:1) to afford the pure product as a colorless oil.
**Yield:** 56 mg, 70%
**e.r.:** 85:15
\([\alpha]_D^{22} = -19.6 \text{ (c } 1.0, \text{ CHCl}_3\).**

**HPLC Analysis,** tr major: 13.0 min., tr minor: 13.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 97:3, 1.0 mL/min, 210 nm].

**1H NMR** (500 MHz, CDCl₃) δ 5.42 – 5.31 (m, 2H), 4.51 (dd, J = 4.8, 4.8 Hz, 1H), 4.13 – 4.07 (m, 2H), 3.61 (d, J = 11.0 Hz, 2H), 3.43 (d, J = 10.9 Hz, 2H), 2.39 – 2.35 (m, 2H), 2.19 (t, J = 5.9 Hz, 1H), 1.18 (s, 3H), 0.71 (s, 3H).

**13C NMR** (126 MHz, CDCl₃) δ 203.6, 100.8, 92.4, 89.2, 77.2, 77.1, 59.5, 34.4, 30.1, 22.9, 21.7.

**ESI-MS** found 199.1 (calculated for [C₁₁H₁₉O₃]⁺: 199.1)
**IR** (thin film, cm⁻¹): 3370, 2956, 2849, 1969, 1472, 1392, 1131, 1090, 1020.
The absolute stereochemistry was assigned by analogy.
(S)-4-(tert-Butyldimethylsilyl)buta-2,3-dien-1-ol (6m)

Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 1m (0.52 mmol) according to the General Procedure, but for 96 hours. The product was purified by flash column chromatography with elution by hexanes/EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 46 mg, 62%.
e.e.: 95:5.
\([\alpha]_{D}^{22} = +116.9 \text{ (c = 1.0, CHCl}_3\text{).}\)

HPLC Analysis, tr major: 14.9 min., tr minor: 16.8 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 99.6:0.4, 1.0 mL/min, 210 nm].
The absolute stereochemistry was assigned by analogy. All spectra were in agreement with reported data.\(^{12}\)

(S)-2-Methyl-4-phenylbuta-2,3-dien-1-ol (6n)

2,5-Dibromobenzenesulfonohydrazide 8 (132 mg, 0.4 mmol), hydroxyacetone (11) (30 mg, 0.4 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF\(_3\))\(_4\)-BINOL catalyst 10 (29 mg, 0.052 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to 0 °C under argon for 10 min, at which moment to it was subjected the alkynyl boronate 1a (0.52 mmol, 1 M solutions in toluene). The reaction was allowed to stir at 0 °C for 72 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and \(H_2O\) (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 x 5 ml). The combined organic layers were dried with Na\(_2\)SO\(_4\). Concentration under reduced pressure followed by flash column chromatography on silica gel with elution by hexanes/EtOAc (8:1) afforded the desired compound as a clear oil.

Yield: 58 mg, 91%.
e.e.: 90:10.
\([\alpha]_{D}^{22} = +9.8 \text{ (c = 1.0, CHCl}_3\text{).}\) In lit for (R)-2-methyl-4-phenylbuta-2,3-dien-1-ol:\(^{13}\) \([\alpha]_{D}^{20} = -10.9 \text{ (c = 0.5, CHCl}_3, 99% \text{ ee).}\)

HPLC Analysis, tr major: 14.3 min., tr minor: 15.7 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: EtOH = 98:2, 1.0 mL/min, 210 nm].
All spectra were in agreement with reported data.\(^{13}\)
g. General procedure for Synthesis of Cyclic Alkynyl Boronates

Cyclic alkynyl boronates were synthesized according to the modified procedure by Yamamoto.\textsuperscript{14} To a solution of the potassium trifluoro(phenylethynyl)borate (2.07 g, 10.0 mmol) and 2,2,7,7-tetramethyl-3,6-dioxo-2,7-disilaoctane\textsuperscript{15} (2.06 g, 10.0 mmol) in dry acetone (10 mL) was added chlorotrimethylsilane (2.17 g, 20.0 mmol) at room temperature, and the solution was stirred overnight. The precipitates were removed by filtration under N\textsubscript{2} atmosphere, and the filtrate was concentrated. The crude oil was purified by a quick neutral alumina column by hexanes and the resulting 2-(phenylethynyl)-1,3,2-dioxaborolane S1\textsubscript{a} solution was concentrated and stored as 1 M solution in toluene.

\textbf{1H NMR} (500 MHz, CDCl\textsubscript{3}) $\delta$ 7.57 – 7.50 (m, 2H), 7.41 – 7.34 (m, 1H), 7.36 – 7.29 (m, 2H), 4.32 (s, 4H).

\textbf{Potassium (S)-(1,4-dioxaspiro[4.5]decan-2-yl)ethynyl}trifluoroborate (S12)

The title trifluoroborate salt was synthesized according to the procedure reported by Thomson and coworkers.\textsuperscript{8} To a solution of (S)-2-ethynyl-1,4-dioxaspiro[4.5]decane\textsuperscript{16} (4.00 g, 24.1 mmol) in dry THF (75 mL) at −78 °C under N\textsubscript{2} atmosphere was added n-BuLi (13.75 mL, 24.1 mmol, 1.75 M in hexanes) dropwise over 10 minutes. After stirring at −78 °C for 1 h, triisopropyl borate (8.33 mL, 36.1 mmol) was quickly added by syringe. The reaction was maintained at −78 °C for 10 minutes, and removed from the bath and allowed to warm up to room temperature over 2 h. The reaction was then cooled to 0 °C and dry MeOH (25 mL) was then added by syringe, followed by a slurry of potassium hydrogen difluoride (KHF\textsubscript{2}) (11.28 g, 144.4 mmol) in H\textsubscript{2}O (60 mL + 2 x 5 mL rinses) via addition funnel. The reaction was then allowed to warm to room temperature over 1.5 h. The solvent was removed under reduced pressure, and the resulting suspension was allowed to dry over high vacuum overnight. The residual solids were broken up using a spatula and dissolved in 75 mL of acetone. The resulting mixture was placed on a rotary evaporator and rotated rapidly at atmospheric pressure with the bath set at 45 °C for 45 minutes. The mixture was decanted over Celite\textsuperscript{®} under vacuum, and the residual solids were once again taken up in 75 mL of acetone and the mixture was heated at 45 °C for 15 minutes. The mixture was filtered over Celite\textsuperscript{®}, washing with acetone. The filtrate was concentrated to ~ 10 mL, and Et\textsubscript{2}O (100 mL) was added, causing a gel to crash out. The flask was chilled in the freezer at −30 °C for 6 h, and the gel was collected by vacuum filtration using a medium gauge fritted filter, then further dried over high vacuum overnight to afford S12 (2.51 g, 9.22 mmol, 38%) as an off-white solid that contained minor impurities and cannot be further purified.

\textbf{mp (decomp) 327 °C}

$\alpha$\textsuperscript{23} = +268.5 (c = 0.94, CH\textsubscript{3}CN).
$^1$H NMR (500 MHz, DMSO-$d_6$) δ 4.58 (dd, J = 7.5, 6.1 Hz, 1H), 4.05 (dd, J = 7.5, 6.1 Hz, 1H), 3.60 (dd, J = 7.5, 7.5 Hz, 1H), 1.65 – 1.48 (m, 8H), 1.40 – 1.34 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO-$d_6$) (relaxation time $d_1 = 3$ seconds, increasing to $d_1 = 7$ seconds does not reveal clear signal for the second acetylenic carbon atom) δ 109.0, 69.2, 65.5, 35.6, 35.1, 24.6, 23.5.

$^{11}$B NMR (128.4 MHz, DMSO-$d_6$) δ –2.10.

$^{19}$F NMR (376.5 MHz, DMSO-$d_6$) δ –127.3.

ESI-HRMS found 233.1054 (calculated for C$_{10}$H$_{13}$BF$_3$O$_2$ [M – K$^-$]: 233.1075).

IR (thin film, cm$^{-1}$): 2935, 2861, 1449, 1365, 1345, 1279, 1236, 979.

(S)-2-((1,4-Dioxaspiro[4.5]decan-2-yl)ethynyl)-5,5-dimethyl-1,3-2-dioxaborinane (12)

To a flame-dried round bottom flask equipped with a stir bar was added potassium trifluoroborate S12 (1.00 g, 3.67 mmol) and dry acetone (3.70 mL). 1,3-Bis(trimethylsilyloxy)-2,2-dimethylpropane$^{17}$ (1.10 mL, 3.67 mmol) was then added quickly, followed by trimethyl silyl chloride (0.933 mL, 7.35 mmol). The reaction was allowed to stir at room temperature for 24 h, at which time it was filtered over a pad of neutral alumina, washing with hexanes. The filtrate was then concentrated to afford the title compound (0.762 g) with some impurities as a yellow oil. It was then stored as a 1M solution in toluene.

$^1$H NMR (500 MHz, CDCl$_3$) δ 4.71 (td, J = 6.3, 2.1 Hz, 1H), 4.17 (ddd, J = 8.0, 6.1, 0.6 Hz, 1H), 3.94 (dddd, J = 8.0, 6.2, 4.8, 0.6 Hz, 1H), 3.59 (d, J = 0.6 Hz, 3H), 3.50 (dd, J = 1.8, 0.6 Hz, 1H), 1.77 – 1.54 (m, 10 H), 0.95 (d, J = 0.6 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 111.2, 81.6, 73.7, 72.0, 69.8, 69.5, 64.9, 35.6, 35.4, 25.0, 23.9, 22.8, 22.6, 21.8.

$^{11}$B NMR (128.4 MHz, CDCl$_3$) δ 31.57.

h. General Procedure for Petasis Reactions Using Cyclic Alkynyl Boronates

2,5-Dibromobenzenesulfonylhydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF$_3$)$_4$-BINOL catalyst 10 (58 mg, 0.104 mmol, 20 mol%) was added and rinsed into the solution with tributyl borate (60 mg, 0.26 mmol) and dry toluene (0.48 mL). The mixture was cooled to
4 °C for 10 min, at which moment it was subjected 2-(phenylethynyl)-1,3,2-dioxaborolane S1a (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at 4 °C for 46 h and then quenched by 1 ml aqueous 10% NaOH solution and allowed to warm up to room temperature overnight. The reaction mixture was transferred to a separatory funnel using EtOAc (5 mL) and H2O (5 mL). The organic layer was collected and the aqueous layer was extracted by EtOAc (3 X 5 ml). The combined organic layers were dried with Na2SO4. Concentration under reduced pressure followed by flash column chromatography on silica gel afforded 6a in 91:9 e.r. and 65% yield.

(S)-4-((S)-1,4-Dioxaspiro[4.5]decan-2-yl)buta-2,3-dien-1-ol (6o)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 12 (0.52 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (19:1) to afford the pure product as a colorless oil. The single diastereomer can be isolated by the same chromatography conditions using silver-impregnated (AgNO3) silica gel.

Yield: 56 mg, 68%
[α]D24 = +35.8 (c = 2.0, CHCl3).
1H NMR (500 MHz, CDCl3) δ 5.48 (qd, J = 6.0, 1.6 Hz, 1H), 5.37 (tt, J = 6.1, 2.8 Hz, 1H), 4.59 (ddd, J = 6.4, 6.4, 1.6 Hz, 1H), 4.18 (dd, J = 6.0, 2.8, 2H), 4.12 (dd, J = 8.3, 6.1 Hz, 1H), 3.70 (dd, J = 8.2, 6.7 Hz, 1H), 1.75 – 1.53 (m, 11H), 1.48 – 1.32 (m, 2H).
13C NMR (126 MHz, CDCl3) δ 203.6, 110.2, 94.0, 94.0, 73.9, 73.8, 69.1, 60.2, 36.3, 35.3, 25.1, 23.9, 23.8.
HRMS (EI) found 210.1248 (calculated for C12H18O3: 210.1256.)
IR (thin film, cm⁻¹): 3399, 2934, 2861, 1966, 1448, 1366, 1279, 1162, 1096, 1018.

(R)-4-((S)-1,4-Dioxaspiro[4.5]decan-2-yl)buta-2,3-dien-1-ol (6p)
Prepared from glycolaldehyde dimer 9 (0.2 mmol) and the corresponding alkynyl boronate 12 (0.52 mmol) according to the General Procedure, using (R)-10 catalyst. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (19:1) to afford the pure product as a colorless oil. The single diastereomer can be isolated by the same chromatography conditions using silver-impregnated (AgNO3) silica gel.

Yield: 60 mg, 71%
[α]D24 = +16.5 (c = 1.3, CHCl3).
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.52 (qd, $J$ = 6.1, 1.5 Hz, 1H), 5.36 (tt, $J$ = 6.2, 2.9 Hz, 1H), 4.59 (ddd, $J$ = 6.3, 6.1, 1.2 Hz, 1H), 4.14 (dd, $J$ = 5.9, 2.8 Hz, 2H), 4.09 (dd, $J$ = 8.2, 6.1 Hz, 1H), 3.74 (dd, $J$ = 8.3, 6.3 Hz, 1H), 1.79 – 1.48 (m, 9H), 1.45 – 1.32 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.6, 110.3, 94.3, 93.8, 73.7, 73.7, 68.8, 60.1, 36.4, 35.3, 25.0, 23.9, 23.8.

h. Isolation of the Propargylic Intermediate 3a

2,5-Dibromobenzenesulfonohydrazide 8 (132 mg, 0.4 mmol), glycolaldehyde dimer 9 (24 mg, 0.2 mmol), and oven-dried 3 Å powdered molecular sieves (400 mg) were added to a 10 mL oven-dried reaction vial equipped with a magnet stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF$_3$)$_4$-BINOL catalyst 10 (29 mg, 0.104 mmol, 10 mol%) was added and rinsed into the solution with dry toluene (0.48 mL). The mixture was cooled to $-5$°C for 20 min, at which moment it was subjected alkynyl boronate 1a (0.52 mmol, 1 M solution in toluene). The reaction was allowed to stir at the same temperature for 48 h, at which moment the reaction mixture was subjected to flash column chromatography on silica gel using pentane/Et$_2$O (10:1 to 1:2) to afford allenol product 6a and intermediate 3a. 3a was condensed by a high-vac pump without allowing the temperature to exceed $10$°C.

$^1$H NMR (500 MHz, CDCl$_3$) 8.32 (s, 1H), 7.64 – 7.53 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 6.81 (s, 1H), 3.95 – 3.87 (m, 2H), 3.72 (par obsr, 1H), 2.82 (br, 1H).

Note: this compound is not stable and its spectra contain solvent peaks.

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.7, 137.4, 136.3, 135.6, 131.9, 129.0, 128.4, 122.1, 121.7, 118.2, 87.0, 83.7, 61.7, 54.7.

ESI-MS found 472.9, 474.9, 476.9 (calculated for 3a [C$_{16}$H$_{13}$Br$_2$N$_2$O$_3$S]$^+$: 474.9)
i. Synthesis of α-Hydroxy Lactones (S13)

(5)-2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-one (S13a)

To a flame-dried round bottom flask equipped with a stir bar was added S-(+)-mandelic acid (3.00 g, 19.7 mmol) and acetone (30 mL). 2,2-dimethoxypropane (7.19 g, 69.0 mmol) was then added, followed by p-toluenesulfonic acid (0.150 g, 0.789 mmol). The reaction was allowed to stir at room temperature for 14 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (40 mL) and transferred to a separatory funnel, where it was washed with 25 mL of sat. NaHCO₃ and 35 mL of brine. The organic layer was dried over MgSO₄ and concentrated to afford the title compound (3.60 g, 18.7 mmol, 95%) as a white solid that required no further purification. Spectral data matched those previously reported in the literature.18

1H NMR (500 MHz, CDCl₃) δ 7.48 – 7.35 (m, 5H), 5.39 (s, 1H), 1.73 (s, 3H), 1.68 (s, 3H).

(5)-5-Benzyl-2,2-dimethyl-1,3-dioxolan-4-one (S13b)

To a flame-dried round bottom flask equipped with a stir bar was added L-(−)-3-phenyllactic acid (3.00 g, 18.1 mmol) and acetone (30 mL). 2,2-dimethoxypropane (6.58 g, 63.2 mmol) was then added, followed by p-toluenesulfonic acid (0.137 g, 0.722 mmol). The reaction was allowed to stir at room temperature for 18 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (40 mL) and transferred to a separatory funnel, where it was washed with 25 mL of sat. NaHCO₃ and 25 mL of brine. The organic layer was dried over MgSO₄ and concentrated to afford the title compound (3.63 g, 17.6 mmol, 98%) as a clear and colorless liquid that solidified into a white solid upon refrigeration. Spectral data matched those previously reported in the literature.19

1H NMR (500 MHz, CDCl₃) δ 7.33 – 7.23 (m, 5H), 4.66 (dd, J = 6.6, 4.1 Hz, 1H), 3.20 (dd, J = 14.5, 4.1 Hz, 1H), 3.05 (dd, J = 14.5, 6.5 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H).

(5)-2,2,5-Trimethyl-1,3-dioxolan-4-one (S13c)

To a flame-dried round bottom flask equipped with a stir bar was added L-(+)–lactic acid (5.00 g, 55.5 mmol) and anhydrous benzene (35 mL). 2,2-dimethoxypropane (10.2 mL, 83.3 mmol) was then added, and the reaction was allowed to stir under reflux with a Dean-Stark apparatus for 4 h with azeotropic removal of methanol. The reaction was then concentrated to afford the title compound (4.05 g, 31.1 mmol, 56%) as a clear and colorless oil that required no further purification.
\([a]_D^{22} = +42.9 \text{ (c = 1.0, CHCl}_3\). \\
^1H\text{ NMR (400 MHz, CDCl}_3\) \(\delta 4.48 (q, J = 6.8 \text{ Hz, } 1\text{H}), 1.61 (s, 3\text{H}), 1.58 (s, 3\text{H}), 1.48 (d, J = 6.8 \text{ Hz, } 3\text{H}).\)

^13C\text{ NMR (126 MHz, CDCl}_3\) \(\delta 173.8, 110.3, 70.4, 27.4, 25.6, 17.4.\)

HRMS (ESI) found 131.0708. (Calculated for C_6H_{10}O_3 [M+H]^+ 131.0706.)

IR (neat, cm\(^{-1}\)): 2992, 2941, 2876, 1799, 1447, 1346, 1267, 1146, 1126, 1051, 935, 844.

(S)-5-Isopropyl-2,2-dimethyl-1,3-dioxlan-4-one (S13d)

To a flame-dried round bottom flask equipped with a stir bar was added (S)-(+)2-hydroxy-3-methyl-butyric acid (2.30 g, 19.5 mmol) and acetone (50 mL). 2,2-dimethoxypropane (7.10 g, 68.1 mmol) was then added, followed by p-toluenesulfonic acid (0.129 g, 0.677 mmol). The reaction was allowed to stir at room temperature for 18 h. The solvent was then evaporated under reduced pressure, and the residue was taken up in EtOAc (100 mL) and transferred to a separatory funnel, where it was washed with 50 mL of sat. NaHCO\(_3\) and 50 mL of brine. The organic layer was dried over MgSO\(_4\) and concentrated to afford the title compound (2.82 g, 17.8 mmol, 92%) as a pale yellow liquid. Spectral data matched those previously reported in the literature.\(^{19}\)

^1H\text{ NMR (400 MHz, CDCl}_3\) \(\delta 4.24 (d, J = 3.9 \text{ Hz, } 1\text{H}), 2.20 – 2.09 (m, 1\text{H}), 1.60 (s, 3\text{H}), 1.53 (s, 3\text{H}), 1.07 (d, J = 7.0 \text{ Hz, } 3\text{H}), 0.98 (d, J = 6.8 \text{ Hz, } 3\text{H}).\)

j. Synthesis of \(\alpha\)-Hydroxy Lactols (13)

(5S)-2,2-Dimethyl-5-phenyl-1,3-dioxlan-4-ol (13a)

To a flame-dried round bottom flask equipped with a stir bar was added the acetonide S13a (1.26 g, 6.57 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (10.95 mL, 10.95 mmol, 1.0 M in hexanes) was then added dropwise. The mixture was allowed to stir at –78°C for 50 minutes, at which time 15 mL of 1M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over MgSO\(_4\) and concentrated to afford the title compound (1.19 g, 6.13 mmol, 93%) as a clear and colorless oil that was directly used in the next step without further purification.

^1H\text{ NMR (500 MHz, CDCl}_3\) \(\delta 7.42 – 7.29 (m, 5\text{H}), 5.32 (t, J = 3.9 \text{ Hz, } 1\text{H}), 4.99 (d, J = 3.7 \text{ Hz, } 1\text{H}), 2.94 (br s, 1\text{H}), 1.64 (s, 3\text{H}), 1.59 (s, 3\text{H}), \) major diastereomer.
(5S)-5-Benzyl-2,2-dimethyl-1,3-dioxolane-4-ol (13b)
To a flame-dried round bottom flask equipped with a stir bar was added the acetonide S13b (1.50 g, 7.27 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (6.86 mL, 10.2 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at –78°C for 60 minutes, at which time 6 mL of 3M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over MgSO₄ and concentrated to afford the title compound (1.28 g, 6.15 mmol, 85%) as a clear and colorless oil that was directly used in the next step without further purification.

1H NMR (500 MHz, CDCl₃) δ 7.33 – 7.21 (m, 5H), 5.11 (dd, J = 4.0, 3.0 Hz, 1H), 4.28 (td, J = 6.7, 3.0 Hz, 1H), 3.04 (dd, J = 7.0, 1.2 Hz, 1H), 2.97 (dd, J = 14.0, 7.0 Hz, 1H), 2.89 (dd, J = 14.0, 6.5 Hz, 1H), 1.52 (s, 3H), 1.46 (s, 3H), major diastereomer.

(5S)-2,2,5-Trimethyl-1,3-dioxolane-4-ol (13c)
To a flame-dried round bottom flask equipped with a stir bar was added the acetonide S13c (0.335 g, 2.57 mmol) and anhydrous toluene (20 mL). The reaction was cooled to –78°C, and DIBAL (2.08 mL, 3.09 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at –78°C for 60 minutes, at which time 5 mL of anhydrous MeOH was added carefully to quench the reaction. The flask was allowed to warm to room temperature, and a saturated solution of Rochelle’s salt (10 mL) was then added, causing a gel to form immediately. This gel was filtered over Celite® to form a biphasic solution that was transferred to a separatory funnel with the aid of EtOAc (10 mL). The layers were separated, and the aq. Layer was extracted with 50 mL of EtOAc. The combined organic layers were washed with 50 mL of sat. NaHCO₃ followed by 50 mL of brine, then dried over MgSO₄ and concentrated to afford the title compound (68 mg, 0.51 mmol, 20%) that was directly used in the next step without further purification.

1H NMR (500 MHz, CDCl₃) δ 5.21 (t, J = 3.7 Hz, 1H), 3.72 (dd, J = 7.1, 3.4 Hz, 1H), 2.90 (br s, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 0.98 (d, J = 6.7 Hz, 3H), major diastereomer.
(5S)-5-Isopropyl-2,2-dimethyl-1,3-dioxolan-4-ol (13d)
To a flame-dried round bottom flask equipped with a stir bar was added the acetonide S\textsubscript{13d} (1.00 g, 6.32 mmol) and anhydrous toluene (20 mL). The reaction was cooled to \(-78^\circ\text{C}\), and DIBAL (5.05 mL, 7.59 mmol, 25 wt% in toluene) was then added dropwise. The mixture was allowed to stir at \(-78^\circ\text{C}\) for 60 minutes, at which time 15 mL of 1M HCl was added carefully to quench the reaction. The cooling bath was removed, and the flask was allowed to warm slowly to room temperature for 1h. After the clear formation of two layers, the mixture was transferred to a separatory funnel using EtOAc (25 mL) and water (10 mL). The layers were separated, and the aqueous layer was extracted with 3 x 25 mL of EtOAc. The combined organic layers were filtered through a pad of silica gel, washing with EtOAc, then were dried over MgSO\textsubscript{4} and concentrated to afford the title compound (0.785 g, 4.90 mmol, 78%) as a clear and colorless oil that was directly used in the next step without further purification.

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 5.11 (dd, \(J = 4.3, 3.5\) Hz, 1H), 4.14 (dqd, \(J = 19.2, 6.3, 3.4\) Hz, 1H), 2.73 (dd, \(J = 4.4, 0.9\) Hz, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.32 (d, \(J = 6.5\) Hz, 6H), major diastereoisomer.

**k. General Procedure for Diastereoselective Petasis Alkynylations**

![Chemical structure](image)

2,5-Dibromobenzenesulfonylazide 8 (132 mg, 0.4 mmol), \(\alpha\)-hydroxy lactol 13 (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (250 mg) were added to a 4 dram flame-dried reaction vial equipped with a magnetic stir bar. Dry mesitylene (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time (S)-(CF\textsubscript{3})\textsubscript{4}-BINOL catalyst 10 (44 mg, 0.078 mmol, 15 mol%) was added and rinsed into the solution with EtOAc (0.48 mL). The mixture was cooled to 0 °C for 10 min under nitrogen, at which time the alkynyl boronate 1a (0.52 mmol, 1 M solution in toluene) was added. The reaction was allowed to stir at 0 °C for 48 h and then quenched by 1 ml aqueous 10% NaOH solution. The reaction was then diluted with 5 mL Et\textsubscript{2}O and transferred to a separatory funnel with the aid of additional NaOH (5 mL). The layers were separated, and the aqueous layer was extracted with 3 x 5 mL Et\textsubscript{2}O. The combined organic layers were dried over MgSO\textsubscript{4} and concentrated under reduced pressure. Flash column chromatography on silica gel afforded the desired compound.
I. Analytical Data for Allenyl Alcohols

(1R, 3S)-1,4-Diphenylbuta-2,3-dien-1-ol (anti-15a)
Prepared from the corresponding α-hydroxy lactol 13a (0.4 mmol) and alkynyl boronate 1a (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (9:1) to afford the pure product as a pale yellow oil.

Yield: 80 mg, 90%.

\[ \alpha \] D\textsubscript{22} = +158.9 (c = 1.0, CHCl\textsubscript{3}). In lit: \[ \alpha \] D\textsubscript{22} = +168.6 (c = 1.0, CHCl\textsubscript{3}).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.42 – 7.37 (m, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.12 (m, 6H), 6.31 (dd, J = 6.4, 2.2 Hz, 1H), 5.81 (app t, J = 6.4 Hz, 1H), 5.31 (dd, J = 6.4, 2.3 Hz, 1H), 2.10 (br s, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 203.8, 142.8, 133.6, 128.7, 128.6, 127.9, 126.9, 126.0, 100.0, 97.9, 72.4.

All spectra were in agreement with reported data.\textsuperscript{20} Thus, the major diastereomer was assigned as anti-15a.

Carrying out the reaction under identical conditions with catalyst (R)-10 afforded the title compound (0.040 g, 0.17 mmol, 45%, 1.2 : 1 d.r.) as a pale yellow oil. The minor syn-15a isomer was not separable from its anti-15a isomer through chromatography. The following signals are discernible:

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 5.27 (dd, J = 6.4, 2.3 Hz, 1H)

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 203.5, 142.8, 133.6, 128.7, 128.6, 127.9, 126.9, 126.0, 100.0, 97.9, 72.4.

(2S, 4S)-1,5-Diphenylpenta-3,4-dien-2-ol (anti-15b)
Prepared from the corresponding α-hydroxy lactol 13b (0.4 mmol) and alkynyl boronate 1a (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.

Yield: 77 mg, 85%.

d.r.: 20:1.

\[ \alpha \] D\textsubscript{22} = -343.9 (c = 0.5, CHCl\textsubscript{3}).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta \) 7.36 – 7.10 (m, 8H), 7.08 – 7.05 (m, 2H), 6.26 (d, J = 6.4, 1.9 Hz, 1H), 5.69 (app t, J = 6.5 Hz, 1H), 4.53 (m, 1H), 3.02 (dd, J = 13.4, 7.0 Hz, 1H), 2.94 (dd, J = 13.4, 6.5 Hz, 1H), 1.86 (d, J = 4.1 Hz, 1H).

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \( \delta \) 204.0, 137.5, 133.6, 129.7, 128.6, 127.1, 126.8, 126.6, 98.6, 97.1,
The spectral data matched those of an authentic sample previously reported in the literature. Thus, the major diastereomer was assigned \textit{anti-15b}.

Carrying out the reaction under identical conditions with catalyst (\textit{R}-10 affording the title compound (0.044 g, 0.187 mmol, 47\%, 1.1 : 1 d.r.) as a clear and colorless oil. Partial separation of the minor \textit{syn-15b} isomer was possible under the chromatography conditions. The spectral data matched those of an authentic sample previously reported in the literature.\(^8\)

\begin{align*}
\text{\textbf{1H NMR}} & (500 \text{ MHz, CDCl}_3) \delta 7.31 (m, 2H); 7.26 (m, 5H), 7.19 (m, 1H), 7.12 (m, 2H), 6.29 (dd, J = 6.4, 2.9 Hz, 1H), 5.73 (app t, J = 5.8 Hz, 1H), 4.53 (m, 1H), 3.01 (dd, J = 13.6, 5.2 Hz, 1H), 2.91 (dd, J = 13.7, 6.9 Hz, 1H), 1.87 (d, J = 4.8 Hz, 1H).
\end{align*}

\begin{align*}
\text{\textbf{13C NMR}} & (126 \text{ MHz, CDCl}_3) \delta 203.1, 137.3, 133.6, 129.8, 128.6, 128.5, 127.2, 126.8, 126.6, 99.2, 98.0, 70.0, 43.8.
\end{align*}

\textbf{(2S,4S)-5-Phenylpenta-3,4-dien-2-ol (anti-15c)}

Prepared from the corresponding \textit{\alpha-hydroxy lactol 13c} (0.2 mmol) and alkynyl boronate 1a (0.26 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.

\begin{align*}
\text{Yield: } & 24.6 \text{ mg, 76\%.} \\
\text{d.r.: } & 6:1. \\
\alpha & = +70.7 (c = 0.15, \text{CHCl}_3).
\end{align*}

\begin{align*}
\text{\textbf{1H NMR}} & (500 \text{ MHz, C}_6\text{D}_6) \delta 7.51 – 7.48 (m, 1H), 7.22 (dd, J = 8.0, 1.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 – 6.93 (m, 2H), 6.14 (dd, J = 6.4, 2.5 Hz, 1H), 5.49 (app t, J = 6.0 Hz, 1H), 4.17 (app pd, J = 6.1, 2.4 Hz, 1H), 1.35 (br s, 1H), 1.15 (d, J = 6.3 Hz, 3H).
\end{align*}

\begin{align*}
\text{\textbf{13C NMR}} & (126 \text{ MHz, C}_6\text{D}_6) \delta 203.4, 129.6, 129.0, 127.4, 127.1, 101.5, 97.5, 23.8.
\end{align*}

This compound was previously reported in the literature.\(^{21}\)

Carrying out the reaction under identical conditions with catalyst (\textit{R}-10 afforded the title compound (12.2 mg, 0.076 mmol, 36\%, 1 : 1.4 d.r.) as a clear and colorless oil. Partial separation of the \textit{syn-15c} isomer was not possible under the chromatography conditions. The following peaks are discernible:

\begin{align*}
\text{\textbf{13C NMR}} & (125 \text{ MHz, C}_6\text{D}_6) \delta 203.5, 130.4, 128.9, 101.4, 97.6, 23.1.
\end{align*}

\textbf{(3S,5S)-2-Methyl-6-phenylhexa-4,5-dien-3-ol (anti-15d)}

Prepared from the corresponding \textit{\alpha-hydroxy lactol 13d} (0.4 mmol) and alkynyl boronate 1a (0.52 mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.

\begin{align*}
\text{Yield: } & 20.2 \text{ mg, 77\%.} \\
\text{d.r.: } & 6:1. \\
\alpha & = +70.7 (c = 0.15, \text{CHCl}_3).
\end{align*}

\begin{align*}
\text{\textbf{1H NMR}} & (500 \text{ MHz, C}_6\text{D}_6) \delta 7.51 – 7.48 (m, 1H), 7.22 (dd, J = 8.0, 1.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 – 6.93 (m, 2H), 6.14 (dd, J = 6.4, 2.5 Hz, 1H), 5.49 (app t, J = 6.0 Hz, 1H), 4.17 (app pd, J = 6.1, 2.4 Hz, 1H), 1.35 (br s, 1H), 1.15 (d, J = 6.3 Hz, 3H).
\end{align*}

\begin{align*}
\text{\textbf{13C NMR}} & (126 \text{ MHz, C}_6\text{D}_6) \delta 203.4, 129.6, 129.0, 127.4, 127.1, 101.5, 97.5, 23.8.
\end{align*}

This compound was previously reported in the literature.\(^{21}\)
mmol) according to the General Procedure. The product was purified by flash column chromatography with elution by hexanes/EtOAc (19:1) to afford the pure product as a clear and colorless oil.

**Yield:** 59 mg, 78%.

**d.r.:** 12:1.

$[\alpha]_D^{22} = +7.1$ (c = 0.25, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.33 – 7.30 (m, 4H), 7.22 (app h, J = 4.0 Hz, 1H), 6.34 (dd, J = 6.5, 2.7 Hz, 1H), 5.68 (app t, J = 6.1 Hz, 1H), 4.07 (td, J = 5.6, 2.7 Hz, 1H), 1.86 (dq, J = 13.0, 6.5, 6.1 Hz, 1H), 1.72 (br s, 1H), 1.01 (d, J = 6.8 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.5, 134.0, 128.7, 127.2, 126.8, 98.1, 97.6, 74.6, 34.3, 18.2, 17.7.

HRMS (ESI) found 188.1208 (calculated for C$_{13}$H$_{16}$O $[M]^+$: 188.1201).

IR (neat, cm$^{-1}$): 3410, 2961, 2926, 2873, 1951, 1598, 1459, 1386, 1261, 1168, 1027.

Carrying out the reaction under identical conditions with catalyst ($R$)-10 afforded the title compound (0.035 g, 0.187 mmol, 47%, 1.2 : 1 d.r.) as a clear and colorless oil. Partial separation of the minor *syn*-15d isomer was possible under the chromatography conditions.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31 – 7.29 (m, 4H), 7.22 (app h, J = 4.0 Hz, 1H), 6.32 (dd, J = 6.4, 2.1 Hz, 1H), 5.66 (app t, J = 6.4 Hz, 1H), 4.07 (td, J = 5.6, 2.7 Hz, 1H), 1.86 (dq, J = 13.0, 6.5, 6.1 Hz, 1H), 1.69 (br s, 1H), 1.02 (d, J = 6.8 Hz, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.0, 134.0, 128.7, 127.2, 126.8, 97.7, 97.0, 75.2, 34.2, 18.3, 17.9.

**HRMS (ESI)** found 216.1506 (calculated for C$_{15}$H$_{20}$O $[M]^+$: 216.1514).

**IR** (neat, cm$^{-1}$): 3384, 2959, 2929, 2873, 2858, 1952, 1598, 1496, 1460, 1377, 1216, 1081.

Carrying out the reaction under identical conditions with catalyst ($R$)-10 afforded the title...
compound (50 mg, 0.23 mmol, 58%, 9 : 1 d.r.) as a clear and colorless oil. Partial separation of the syn-15e isomer was not possible under the chromatography conditions. The following peaks are discernible:

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \] \( \delta \) 6.31 (app q, \( J = 3.0 \) Hz, 1H), 4.27 (ddt, \( J = 10.0, 6.4, 3.2 \) Hz, 1H); 

\[ ^13C \text{NMR (126 MHz, CDCl}_3 \] \( \delta \) 200.4, 135.1, 99.0, 68.5, 30.2, 29.1, 22.9, 21.2, 14.4.

**m. Synthesis of Ynals (18)**

Ynal 18a was purchased from Santa Cruz biotechnology and used as received. 18b, 18c, 18d, 18e, 18f, 18g, 18h, 18i, 18j, 18k, 18m, 18n were synthesized following the disclosed literature procedure. Hept-2-ynal in Table 4 was also synthesized in the same manner.

**n. Synthesis of 18l**

![Chemical structure of 18l](attachment:image.png)

Methyl phenyl(prop-2-yn-1-yl)carbamate (S18l)

To the solution of \( N \)-(prop-2-yn-1-yl)aniline (2.2 g, 17 mmol, 1.0 eq) in dichloromethane (35 ml) was added DIPEA (\( N,N \)-diisopropylethylamine) (4.4 ml, 1.5 eq) and methyl chloroformate (1.4 ml, 1.1 eq) at 0 °C. The reaction was allowed to warm up to room temperature and stir for overnight, after which moment the mixture was diluted with dichloromethane, washed with 1 M HCl solution and extracted with dichloromethane (3 X 100 ml). The combined organic layer was then washed with saturated NaHCO\(_3\) solution and brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated to give a residue, which was purified by flash chromatography with hexanes/EtOAc (10:1) to afford methyl phenyl(prop-2-yn-1-yl)carbamate (S18l) as a light yellow liquid in 90% yield (2.9 g).

\[ ^1H \text{NMR (500 MHz, CDCl}_3 \] \( \delta \) 7.40 – 7.28 (m, 4H), 7.30 – 7.22 (m, 1H), 4.39 (d, \( J = 2.5 \) Hz, 2H), 3.70 (s, 3H), 2.27 (t, \( J = 2.5 \) Hz, 1H).

\[ ^13C \text{NMR (126 MHz, CDCl}_3 \] \( \delta \) 155.5, 141.4, 129.0, 127.1, 126.7, 79.5, 72.3, 53.2, 40.2.

Methyl (4-oxobut-2-yn-1-yl)(phenyl)carbamate (18l)

Dry THF (25 ml) and methyl phenyl(prop-2-yn-1-yl)carbamate (S18l) (1.9 g, 10 mmol, 1.0 eq) were added to an oven dried nitrogen purged flask. The flask was cooled to \(-78 \) °C using a dry ice-acetone cold bath. Next, \( n \)-butyllithium (6.3 mL, 1.6 M in hexanes, 1.0 eq) was added dropwise to the flask and allowed to stir for 10 minutes at the same temperature. To the flask, dry
dimethylformamide (DMF) (1.5 mL, 2.0 eq) was then slowly added. The reaction temperature was allowed to warm to room temperature in 10 min. The reaction was then poured into a vigorously stirred biphasic solution prepared from a 10% aqueous solution of KH$_2$PO$_4$ (100 ml) and Et$_2$O (80 ml) at 0 °C. The organic layer was washed with water (2 X 100 ml). The combined aqueous layers were then extracted with Et$_2$O (200 ml). The combined organic layers were dried over MgSO$_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel using hexanes/EtOAc (8:1) to afford methyl (4-oxobut-2-yn-1-yl)(phenyl)carbamate (18l) in 45% yield (1.0 g) as a light yellow liquid.

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.18 (s, 1H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.34 – 7.24 (m, 3H), 4.61 (s, 2H), 3.73 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 176.3, 155.5, 140.9, 129.3, 127.5, 126.7, 92.0, 83.3, 53.5, 40.6.

**o. Synthesis of 18o**

(S)-3-(1,4-dioxaspiro[4.5]decan-2-yl)propiolaldehyde (18o)

To a solution of (S)-2-ethynyl-1-4-dioxaspiro[4.5]decan (1.00 g, 6.02 mmol, 1.0 eq) in dry THF (16.5 mL) at –40°C under N$_2$ atmosphere was added n-BuLi (2.4 mL, 6.02 mmol, 2.50 M in hexanes, 1.0 eq) dropwise over 3 minutes. The reaction was maintained at –40°C for 40 minutes, at which point N,N-dimethyl formamide (0.93 mL, 12.04 mmol, 2 eq) was added, and the reaction was allowed to stir at the same temperature for an additional 30 minutes. The solution was then poured into an Erlenmeyer flask containing a stirring mixture of KH$_2$PO$_4$ (0.90 g, 6.62 mmol, 1.1 eq), Et$_2$O (66 mL) and H$_2$O (66 mL) at 0°C. After stirring for 5 min at that temperature, the mixture was transferred to a separatory funnel with the aid of Et$_2$O and H$_2$O (10 mL each). The layers were separated, and the organic layer was washed with H$_2$O (30 mL), dried over anhydrous MgSO$_4$, and concentrated. The crude residue was purified by silica gel chromatography with hexanes/EtOAc (19:1) to afford the title compound (1.04 g, 5.35 mmol, 89%) as a pale yellow oil.

[$\alpha$]$_D^{22}$ = +48.5 (c = 1.1, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) δ 9.24 (d, $J = 0.7$ Hz, 1H), 4.89 (ddd, $J = 6.5, 5.4, 0.6$ Hz, 1H), 4.22 (dd, $J = 8.3, 6.6$ Hz, 1H), 4.05 (dd, $J = 8.3, 5.4$ Hz, 1H), 1.69 – 1.58 (m, 8H), 1.47 – 1.35 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 176.2, 112.0, 93.4, 83.9, 68.9, 64.7, 35.6, 35.1, 24.9, 23.8, 23.8.

ESI-HRMS found 194.0952 (calculated for [C$_{11}$H$_{14}$O$_3$]$^+$: 194.0943.)

IR (neat, cm$^{-1}$): 2935, 2861, 2262, 1713, 1449, 1366, 1333, 1160, 1094.
p. General Procedure for Racemic Allylation

2-Nitro-4-(trifluoromethyl)benzenesulfonylhydrazide 17 (114 mg, 0.4 mmol), ynal 18 (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. Racemic BINOL catalyst (17 mg, 0.06 mmol, 10 mol%), tert-butanol (89 mg, 1.2 mmol) and allylboronate 532 (76 mg, 0.6 mmol) was added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

q. General Procedure for Asymmetric Allylation

2-Nitro-4-(trifluoromethyl)benzenesulfonylhydrazide 17 (114 mg, 0.4 mmol), ynal 18 (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL oven dried reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (R)-Ph2-BINOL catalyst 19 (18 mg, 0.04 mmol, 7 mol%), tert-butanol (89 mg, 1.2 mmol) and allylboronate 5 (76 mg, 0.6 mmol) was added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.
General Procedure for Hydroboration/Oxidation

The allyl allene (0.3 mmol) was dissolved in dry THF (0.4 ml) under argon and cooled to 0 °C. 9-BBN (0.5 M in THF, 0.45 ml, 1.5 eq) was added dropwise to the reaction, and the reaction was allowed to warm up to room temperature naturally. After one hour, the reaction was cooled to 0 °C. 3 M NaOH solution (0.1 ml) was added slowly to the reaction, followed by dropwise addition of H₂O₂ (35% in water, 0.3 ml). The reaction was warmed to room temperature in 5 min. The reaction mixture was transferred to a separatory funnel using Et₂O (5 mL) and H₂O (5 mL). The organic layer was collected and the aqueous layer was extracted by Et₂O (3 X 5 ml). The combined organic layers were dried with Na₂SO₄. Concentration under reduced pressure followed by flash column chromatography on silica gel afforded the desired compound.

Analytical Data for Allyl Allenes

(R)-(Hexa-1,2,5-trien-1-yl)benzene (7a)
Prepared from the corresponding ynal 18a (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 52 mg, 83%
e.r.: 99:1
[α]D²² = −227.6 (c = 1.0, CHCl₃). Absolute stereochemistry as assigned by Lowe’s rule.
HPLC Analysis, tr major: 6.1 min., tr minor: 6.7 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes, 1 mL/min, 250 nm].
All spectra were in agreement with reported data.

(R)-1-(Hexa-1,2,5-trien-1-yl)-4-methoxybenzene (7b)
Prepared from the corresponding ynal 18b (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (50:1) to afford the pure product as a colorless oil.
Yield: 66 mg, 88%
e.r.: 98:2
[α]D²² = −248.7 (c = 1.0, CHCl₃).
HPLC Analysis, this compound was converted to the corresponding alcohol S7b following the hydroboration/oxidation procedure, tr major: 21.9 min., tr minor: 33.0 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 97:3, 1.0 mL/min, 254 nm].
**H NMR** (500 MHz, CDCl$_3$) δ 7.22 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 6.13 (ddd, $J = 6.0, 2.9, 2.9$ Hz, 1H), 5.97 – 5.85 (m, 1H), 5.56 (ddd, $J = 6.7, 6.7, 6.7$ Hz, 1H), 5.15 (ddd, $J = 17.1, 1.6, 1.6, 1.6$ Hz, 1H), 5.05 (ddd, $J = 10.2, 1.6, 1.5, 1.5$ Hz, 1H), 3.80 (s, 3H), 2.91 – 2.85 (m, 2H).

**13C NMR** (126 MHz, CDCl$_3$) δ 204.9, 158.6, 136.3, 127.7, 127.0, 115.5, 114.1, 94.4, 93.0, 55.3, 33.3.

**GCMS** found 186.1 (calculated for C$_{13}$H$_{14}$O: 186.1).

**IR** (thin film, cm$^{-1}$): 3072, 3005, 2935, 2836, 1608, 1511, 1303, 1172, 1035, 833.

**(R)-6-(4-Methoxyphenyl)-hexa-4,5-dien-1-ol (S7b)**

S7b was prepared following the general hydroboration/oxidation procedure in 0.2 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (5:1) to afford the pure product as a colorless oil.

**Yield:** 17 mg, 42%

**e.r.:** 98:2

[α]$_D^{22}$ = –66.0 (c = 1.0, CHCl$_3$).

**H NMR** (500 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 6.12 (ddd, $J = 6.3, 3.1, 3.1$ Hz, 1H), 5.58 (ddd, $J = 6.5, 6.5, 6.5$ Hz, 1H), 3.80 (s, 3H), 3.72 (t, $J = 6.5$ Hz, 2H), 2.21 (ddd, $J = 12.8, 6.5, 3.1, 1.7$ Hz, 2H), 1.76 (ddt, $J = 9.5, 7.8, 6.5$ Hz, 2H), 1.25 (br, 1H).

**13C NMR** (126 MHz, CDCl$_3$) δ 204.5, 127.6, 127.1, 114.1, 113.9, 94.5, 94.3, 62.4, 55.3, 31.9, 25.1.

**HRMS** found 205.1239 (calculated for [C$_{13}$H$_{17}$O$_2$]$^+$: 205.1229).

**IR** (thin film, cm$^{-1}$): 3412, 2989, 2934, 2875, 1605, 1511, 1303, 1172, 1034, 836.

**(R)-1-Fluoro-4-(hexa-1,2,5-trien-1-yl)benzene (7c)**

Prepared from the corresponding ynal 18c (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (200:1) to afford the pure product as a colorless oil.

**Yield:** 61 mg, 87%

**e.r.:** 99:1

[α]$_D^{22}$ = –246.6 (c = 1.0, CHCl$_3$).

**HPLC Analysis,** this compound was converted to the corresponding alcohol S7c following the hydroboration/oxidation procedure, tr major: 18.4 min., tr minor: 20.3 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 98:2, 1.0 mL/min, 254 nm].

**H NMR** (500 MHz, CDCl$_3$) δ 7.29 – 7.21 (m, 2H), 7.03 – 6.94 (m, 2H), 6.14 (ddd, $J = 6.2, 2.9, 2.9$ Hz, 1H), 5.90 (ddd, $J = 16.7, 10.2, 6.4, 6.4$ Hz, 1H), 5.59 (ddd, $J = 6.7, 6.7, 6.7$ Hz, 1H), 5.15 (ddd, $J = 17.0, 1.7, 1.7, 1.6$ Hz, 1H), 5.06 (ddd, $J = 10.2, 1.6, 1.5, 1.5$ Hz, 1H), 2.92 – 2.85 (m, 2H).
\[^{13}\text{C}\] NMR (126 MHz, CDCl\(_3\)) \(\delta\) 205.3 (d, \(J = 2.4\) Hz), 162.8, 160.8, 136.0, 130.7 (d, \(J = 3.3\) Hz), 128.0 (d, \(J = 7.8\) Hz), 115.6 (d, \(J = 19.4\) Hz), 115.5 (d, \(J = 21.7\) Hz), 93.7 (d, \(J = 84.3\) Hz), 33.1.

\[^{19}\text{F}\] NMR (470 MHz, CDCl\(_3\)) \(\delta\) –115.7 (ddd, \(J = 14.2, 9.1, 5.6\) Hz).

GCMS found 174.1 (calculated for C\(_{12}\)H\(_{11}\)F: 174.1)

IR (thin film, cm\(^{-1}\)): 3062, 2976, 2918, 1950, 1640, 1604, 1508, 1229, 1156, 837.

\((R)-6-(4-Fluorophenyl)-hexa-4,5-dien-1-ol (S7c)\)

S7c was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (4:1) to afford the pure product as a colorless oil.

Yield: 20 mg, 35%

\([\alpha]_{D}^{22} = -117.4\) (c = 1.0, CHCl\(_3\)).

\[^{1}\text{H}\] NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.25 – 7.21 (m, 2H), 7.01 – 6.95 (m, 2H), 6.12 (ddd, \(J = 6.5, 3.1, 3.1\) Hz, 1H), 5.61 (ddd, \(J = 6.6, 6.6, 6.6\) Hz, 1H), 3.76 – 3.67 (m, 2H), 2.22 (td, \(J = 7.2, 3.1\) Hz, 2H), 1.81 – 1.70 (m, 2H).

\[^{13}\text{C}\] NMR (126 MHz, CDCl\(_3\)) \(\delta\) 204.9, 162.8, 160.8, 130.8, 127.9 (d, \(J = 8.0\) Hz), 115.5 (d, \(J = 21.7\) Hz), 94.4 (d, \(J = 68.0\) Hz), 62.3, 31.8, 24.9.

\[^{19}\text{F}\] NMR (470 MHz, CDCl\(_3\)) \(\delta\) –115.8 (ddd, \(J = 13.9, 8.9, 5.5\) Hz).

ESI-MS found 175.1, 193.1 (calculated for [C\(_{12}\)H\(_{14}\)FO\]^+: 193.1)

IR (thin film, cm\(^{-1}\)): 3360, 3045, 2937, 1951, 1604, 1508, 1226, 1156, 840.

\((R)-1-(Hexa-1,2,5-trien-1-yl)-4-nitrobenzene (7d)\)

Prepared from the corresponding ynal 18d (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:1) to afford the pure product as a yellow oil.

Yield: 70 mg, 87%
e.r.: 98:2

\([\alpha]_{D}^{22} = -318.4\) (c = 1.0, CHCl\(_3\)).

HPLC Analysis, tr minor: 14.8 min., tr major: 16.3 min., [Chiralpak®IA column, 24 cm \times 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 230 nm].

\[^{1}\text{H}\] NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.15 (d, \(J = 8.3\) Hz, 2H), 7.40 (d, \(J = 8.3\) Hz, 2H), 6.26 – 6.20 (m, 1H), 5.89 (ddd, \(J = 16.7, 10.2, 6.4, 6.4\) Hz, 1H), 5.71 (ddd, \(J = 6.7, 6.7, 6.7\) Hz, 1H), 5.17 (ddd, \(J = 17.1, 1.5, 1.4, 1.4\) Hz, 1H), 5.09 (ddd, \(J = 10.1, 1.5, 1.4, 1.4\) Hz, 1H), 2.96 – 2.89 (m, 2H).

\[^{13}\text{C}\] NMR (126 MHz, CDCl\(_3\)) \(\delta\) 207.4, 146.4, 142.2, 135.4, 127.0, 124.0, 116.2, 94.2, 32.6.

GCMS found 201.1 (calculated for C\(_{12}\)H\(_{11}\)NO\(_{2}\): 201.1)

IR (thin film, cm\(^{-1}\)): 3078, 2979, 2843, 1949, 1640, 1595, 1516, 1494, 1342, 1110, 874.
(R)-1-Bromo-2-(hexa-1,2,5-trien-1-yl)benzene (7e)
Prepared from the corresponding ynal 18e (0.26 mmol) and allyl boronate 5 (0.4 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:1) to afford the pure product as a colorless oil.
Yield: 35 mg, 60%
e.r.: 99:1
[α]D 22 = −148.4 (c = 1.0, CHCl3).
HPLC Analysis, tr major: 7.4 min., tr minor: 9.3 min., [Chiralcel® OD column, 24 cm × 4.6 mm I.D., Hexanes, 1 mL/min, 254 nm],
1H NMR (500 MHz, CDCl3) δ 7.52 (dd, J = 8.0, 1.2 Hz, 1H), 7.46 (dd, J = 7.9, 1.7 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.04 (ddd, J = 8.0, 7.7, 1.7 Hz, 1H), 6.62 (ddd, J = 6.4, 2.9, 2.9 Hz, 1H), 5.91 (dddd, J = 16.9, 10.1, 6.4, 6.4 Hz, 1H), 5.63 (ddd, J = 6.7, 6.4, 6.4 Hz, 1H), 5.17 (dddd, J = 16.9, 1.7, 1.7, 1.6 Hz, 1H), 5.08 (dddd, J = 10.1, 1.6, 1.4, 1.4 Hz, 1H), 2.96 – 2.86 (m, 2H).
13C NMR (126 MHz, CDCl3) δ 206.5, 135.9, 134.2, 132.9, 128.3, 128.1, 127.4, 122.4, 115.8, 94.1, 93.3, 32.9.
GCMS found 234.1, 236.1 (calculated for C12H11Br: 234.0)
IR (thin film, cm−1): 3078, 2928, 1953, 1600, 1563, 1474, 1439, 1022, 917.

(R)-2-(Hexa-1,2,5-trien-1-yl)naphthalene (7f)
Prepared from the corresponding ynal 18f (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 73 mg, 89%
e.r.: 98:2
[α]D 22 = −236.4 (c = 1.0, CHCl3).
HPLC Analysis, tr major: 16.1 min., tr minor: 16.9 min., [Chiralpak® IA column, 24 cm × 4.6 mm I.D., Hexanes, 1.0 mL/min, 250 nm],
1H NMR (500 MHz, CDCl3) δ 7.82 – 7.74 (m, 3H), 7.66 (dd, J = 1.8, 0.9 Hz, 1H), 7.51 (dd, J = 8.5, 1.7 Hz, 1H), 7.49 – 7.39 (m, 2H), 6.36 (dd, J = 6.1, 2.9, 2.9 Hz, 1H), 5.95 (dddd, J = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.67 (dddd, J = 6.6, 6.6, 6.6 Hz, 1H), 5.20 (dddd, J = 17.1, 1.7, 1.7, 1.6 Hz, 1H), 5.09 (dddd, J = 10.1, 1.6, 1.5, 1.5 Hz, 1H), 2.98 – 2.91 (m, 2H).
13C NMR (126 MHz, CDCl3) δ 206.1, 136.1, 133.7, 132.6, 132.3, 128.2, 127.7, 127.7, 126.2, 125.5, 125.4, 124.6, 115.7, 95.4, 93.4, 33.2.
GCMS found 206.1 (calculated for C16H14: 206.1)
IR (thin film, cm−1): 3056, 2978, 1947, 1639, 1599, 1509, 895, 819, 754.
(R)-3-(Hexa-1,2,5-trien-1-yl)thiophene (7g)
Prepared from the corresponding ynal 18g (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
**Yield:** 56 mg, 87%
**e.r.:** 99:1
$[\alpha]_D^{22} = -267.4$ (c = 1.0, CHCl$_3$).

**HPLC Analysis,** this compound was converted to the corresponding alcohol S7g following the hydroboration/oxidation procedure, tr major: 44.6 min., tr minor: 50.0 min., [Chiralpak® AD-H column, 24 cm × 4.6 mm I.D., Hexanes: EtOH=99:1, 1.0 mL/min, 254 nm].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29 – 7.22 (m, 1H), 7.09 – 7.04 (m, 2H), 6.24 (ddd, $J$ = 6.1, 2.7, 2.7 Hz, 1H), 5.90 (ddd, $J$ = 16.6, 10.9, 6.5, 6.5 Hz, 1H), 5.52 (ddd, $J$ = 6.7, 6.7, 6.7 Hz, 1H), 5.15 (dd, $J$ = 17.2, 2.2 Hz, 1H), 5.06 (d, $J$ = 10.1 Hz, 1H), 2.91 – 2.84 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 205.8, 136.2, 136.1, 126.3, 125.8, 120.4, 115.6, 92.3, 89.6, 33.2.

**GCMS** found 162.1 (calculated for C$_{10}$H$_{10}$S: 162.1)
**IR** (thin film, cm$^{-1}$): 3079, 2978, 2911, 1952, 1791, 1639, 1435, 1258, 993, 787.

(R)-6-(Thiophen-3-yl)-hexa-4,5-dien-1-ol (S7g)
S7g was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (5:1) to afford the pure product as a colorless oil.
**Yield:** 32 mg, 59%
$[\alpha]_D^{22} = -183.7$ (c = 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 – 7.22 (m, 1H), 7.08 – 7.03 (m, 2H), 6.22 (ddd, $J$ = 6.3, 3.1, 3.1 Hz, 1H), 5.54 (ddd, $J$ = 6.5, 6.5, 6.5 Hz, 1H), 3.71 (t, $J$ = 6.5 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.80 – 1.70 (m, 2H), 1.39 (br, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 205.4, 136.2, 126.2, 125.8, 120.4, 93.6, 89.7, 62.3, 31.8, 25.0.

**ESI-MS** found 181.1 (calculated for [C$_{10}$H$_{13}$OS]$^+$: 181.1)
**IR** (thin film, cm$^{-1}$): 3463, 3056, 2944, 1951, 1057, 788.

(R)-3-(Hexa-1,2,5-trien-1-yl)pyridine (7h)
2-Nitro-4-(trifluoromethyl)benzenesulfonohydrazide 17 (114 mg, 0.4 mmol), 3-(pyridin-3-yl)propionaldehyde 18h (52 mg, 0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (0.5
mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (R)-Ph₂-BINOL catalyst 19 (36 mg, 0.08 mmol, 7 mol%), tert-butanol (89 mg, 1.2 mmol) and allylboronate 5 (152 mg, 1.2 mmol) was added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 24 h, at which time the crude mixture was chromatographed on silica gel with hexanes/EtOAc (50:1) to afford the pure product as a brown oil.

**Yield:** 17 mg, 27%

**e.r.:** 98:2

\[ [\alpha]_D^{22} = -222.4 \text{ (c = 1.0, CHCl}_3 \] .

**HPLC Analysis**, tr minor: 11.0 min., tr major: 11.5 min., [Chiralpak®IA-H column, 24 cm × 4.6 mm I.D., Hexanes:EtOH=99:1, 1 mL/min, 250 nm].

**H NMR** (500 MHz, CDCl₃) δ 8.51 (s, 1H), 8.41 (d, \( J = 4.6 \text{ Hz, 1H} \)), 7.58 (ddd, \( J = 7.9, 1.9, 1.9 \text{ Hz, 1H} \)), 7.21 (dd, \( J = 7.8, 4.8 \text{ Hz, 1H} \)), 6.14 (ddd, \( J = 6.1, 2.9, 2.9 \text{ Hz, 1H} \)), 5.89 (ddd, \( J = 16.7, 10.1, 6.4, 6.4 \text{ Hz, 1H} \)), 5.65 (ddd, \( J = 6.8, 6.8, 6.8 \text{ Hz, 1H} \)), 5.15 (ddd, \( J = 17.0, 1.6, 1.6, 1.5 \text{ Hz, 1H} \)), 5.07 (ddd, \( J = 10.1, 1.5, 1.4, 1.4 \text{ Hz, 1H} \)), 2.93 – 2.87 (m, 2H).

**C NMR** (126 MHz, CDCl₃) δ 206.0, 148.2, 147.9, 135.7, 133.4, 130.7, 123.4, 116.0, 93.9, 91.8, 32.8.

**HRMS** found 158.0979 (calculated for [C₁₁H₁₂N]⁺: 158.0970).

**IR** (thin film, cm⁻¹): 3057, 2982, 1951, 1640, 1571, 1481, 1431, 1025, 916, 810, 748.

(R)-(Hexa-1,2,5-trien-1-yl)dimethyl(phenyl)silane (7i)

Prepared from the corresponding ynal 18i (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

**Yield:** 62 mg, 73%

**e.r.:** 98:2

\[ [\alpha]_D^{22} = -50.0 \text{ (c = 1.0, CHCl}_3 \] .

**HPLC Analysis**, tr major: 9.9 min., tr minor: 10.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes, 0.5 mL/min, 254 nm].

**H NMR** (500 MHz, CDCl₃) δ 7.58 – 7.52 (m, 2H), 7.40 – 7.32 (m, 3H), 5.82 (ddd, \( J = 16.6, 10.1, 6.4, 6.4 \text{ Hz, 1H} \)), 5.13 – 5.03 (m, 2H), 5.00 (ddd, \( J = 10.1, 1.5, 1.5, 1.5 \text{ Hz, 1H} \)), 4.86 (ddd, \( J = 6.9, 6.9, 6.9 \text{ Hz, 1H} \)), 2.77 – 2.71 (m, 2H), 0.38 – 0.34 (m, 6H).

**C NMR** (126 MHz, CDCl₃) δ 211.1, 138.5, 136.9, 133.7, 129.1, 127.7, 115.0, 82.1, 81.5, 32.3, -2.2, -2.3.

**GCMS** found 214.1 (calculated for C₁₄H₁₈Si: 214.1).

**IR** (thin film, cm⁻¹): 3069, 3001, 2961, 2905, 1940, 1642, 1428, 1249, 1114, 816.
(R)-(((Hepta-2,3,6-trien-1-yl)oxy)methyl)benzene (7j)
Prepared from the corresponding ynal 18j (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (50:1) to afford the pure product as a colorless oil.
Yield: 72 mg, 90%
e.r.: 98:2
$[\alpha]_D^{22} = -58.6$ (c = 1.0, CHCl$_3$).

**HPLC Analysis**, tr major: 14.9 min., tr minor: 15.8 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 0.8 mL/min, 210 nm].

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 – 7.32 (m, 4H), 7.34 – 7.27 (m, 1H), 5.87 (dddd, $J$ = 16.6, 10.1, 6.4, 6.4 Hz, 1H), 5.35 – 5.21 (m, 2H), 5.12 (ddddd, $J$ = 17.1, 1.7, 1.7, 1.6 Hz, 1H), 5.06 (ddddd, $J$ = 10.1, 1.6, 1.5, 1.5 Hz, 1H), 4.55 (d, $J$ = 2.2 Hz, 2H), 4.13 – 4.02 (m, 2H), 2.84 – 2.79 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 205.4, 138.2, 136.2, 128.4, 127.8, 127.6, 115.5, 90.0, 88.9, 71.6, 68.4, 32.9.

GCMS found 200.1 (calculated for C$_{14}$H$_{16}$O: 200.1)

IR (thin film, cm$^{-1}$): 3064, 3030, 2978, 2857, 1964, 1640, 1496, 1454, 1351, 1095, 915, 736.

(R)-N-(Hepta-2,3,6-trien-1-yl)-N-methylaniline (7k)
Prepared from the corresponding ynal 18k (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure, but for 40 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:5) to afford the pure product as a brown oil.
Yield: 40 mg, 50%
e.r.: 99:1
$[\alpha]_D^{22} = +3.5$ (c = 1.0, CHCl$_3$).

**HPLC Analysis**, tr minor: 8.8 min., tr major: 9.2 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes, 1.0 mL/min, 254 nm].

$^1$H NMR (500 MHz, CDCl$_3$) δ 7.28 – 7.17 (m, 2H), 6.75 (d, $J$ = 8.2 Hz, 2H), 6.71 (t, $J$ = 7.3 Hz, 1H), 5.77 (ddddd, $J$ = 16.7, 10.1, 6.4, 6.4 Hz, 1H), 5.19 – 5.11 (m, 2H), 5.10 – 4.94 (m, 2H), 4.05 – 3.87 (m, 2H), 2.95 (s, 3H), 2.73 – 2.67 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 205.0, 149.1, 136.3, 129.0, 116.6, 115.3, 112.9, 90.4, 87.2, 51.9, 38.1, 33.1.

HRMS found 200.1433 (calculated for [C$_{14}$H$_{18}$N]$^+$: 200.1439)

IR (thin film, cm$^{-1}$): 3006, 2979, 2908, 1965, 1600, 1506, 1342, 748.
(R)-Methyl(hepta-2,3,6-trien-1-yl)(phenyl)carbamate (7l)

Prepared from the corresponding ynal 18l (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure, but for 40 hours. The crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:5) to afford the pure product as a colorless oil.

Yield: 83 mg, 85%
e.r.: 99:1
$[\alpha]_D^{22} = -23.2$ (c = 1.0, CHCl$_3$).

HPLC Analysis, tr major: 45.5 min., tr minor: 49.7 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

1H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 5.71 (dddd, $J = 16.9$, 10.1, 6.4, 6.4 Hz, 1H), 5.27 – 5.21 (m, 1H), 5.17 (dddd, $J = 6.6$, 6.6, 6.6, 2.6, 2.6 Hz, 1H), 5.02 (ddddd, $J = 16.9$, 1.7, 1.7, 1.6 Hz, 1H), 4.97 (ddddd, $J = 10.1$, 1.6, 1.5, 1.5 Hz, 1H), 4.33 (dddd, $J = 15.2$, 5.9, 2.8 Hz, 1H), 4.16 (ddd, $J = 15.2$, 6.5, 2.5 Hz, 1H), 2.68 – 2.63 (m, 2H).

13C NMR (126 MHz, CDCl$_3$) δ 204.9, 155.8, 136.1, 128.8, 126.9, 126.5, 115.4, 110.0, 91.0, 88.3, 52.9, 49.9, 32.9.

HRMS found 244.1338 (calculated for [C$_{15}$H$_{18}$NO$_2$]$^+$: 244.1331)

IR (thin film, cm$^{-1}$): 3292, 2958, 1700, 1596, 1497, 1446, 1381, 1280, 1218.

(R)-Octadeca-1,4,5-triene (7m)

Prepared from the corresponding ynal 18m (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 97 mg, 98%
e.r.: 98:2
$[\alpha]_D^{22} = -39.5$ (c = 1.0, CHCl$_3$).

HPLC Analysis, this compound was converted to the corresponding alcohol S7m following the hydroboration/oxidation procedure, tr minor: 28.3 min., tr major: 30.9 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

1H NMR (500 MHz, CDCl$_3$) δ 5.85 (dddd, $J = 16.7$, 10.5, 6.3, 6.3 Hz, 1H), 5.16 – 5.03 (m, 3H), 5.01 (ddd, $J = 10.3$, 1.7, 1.7 Hz, 1H), 2.77 – 2.71 (m, 2H), 2.02 – 1.92 (m, 2H), 1.43 – 1.36 (m, 2H), 1.36 – 1.18 (m, 18H), 0.88 (t, $J = 6.9$ Hz, 3H).

13C NMR (126 MHz, CDCl$_3$) δ 204.2, 136.8, 115.0, 91.4, 88.9, 33.5, 31.9, 29.7, 29.7, 29.5, 29.4, 29.1, 28.8, 22.7, 14.1.

GCMS found 248.3 (calculated for C$_{18}$H$_{32}$: 248.3)

IR (thin film, cm$^{-1}$): 3082, 2956, 2854, 1963, 1641, 1467, 1261, 991, 912, 870.
(R)-Octadeca-4,5-dien-1-ol (S7m)

S7m was prepared following the general hydroboration/oxidation procedure in 0.3 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:10) to afford the pure product as a colorless oil.

Yield: 58 mg, 72%

$[\alpha]_D^{22} = -41.2$ (c = 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.13 – 5.06 (m, 2H), 3.69 (dt, $J = 6.1$, 6.1 Hz, 2H), 2.11 – 2.04 (m, 2H), 2.02 – 1.91 (m, 2H), 1.69 (tt, $J = 6.9$, 6.9 Hz, 1H), 1.41 – 1.35 (m, 2H), 1.26 (m, 18H), 1.35 – 1.15 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.8, 91.6, 90.1, 62.4, 32.0, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 29.0, 25.2, 22.7, 14.1.

ESIMS found 267.3 (calculated for [C$_{18}$H$_{35}$O]$^+$: 267.3)

IR (thin film, cm$^{-1}$): 2952, 2924, 2854, 2200, 1964, 1467, 1059, 883.

(R)-(Hexa-1,2,5-trien-1-yl)cyclohexane (7n)

Prepared from the corresponding ynal 18n (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 40 mg, 62%

e.r.: 99:1

$[\alpha]_D^{22} = -57.0$ (c = 1.0, CHCl$_3$).

HPLC Analysis, this compound was converted to the corresponding alcohol S7n following the hydroboration/oxidation procedure, tr minor: 40.4 min., tr major: 53.8 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.84 (dddd, $J = 16.6$, 10.1, 6.4, 6.4 Hz, 1H), 5.16 – 5.03 (m, 3H), 5.00 (dddd, $J = 10.1$, 1.5, 1.5, 1.5 Hz, 1H), 2.78 – 2.68 (m, 2H), 2.00 – 1.90 (m, 1H), 1.74 – 1.57 (m, 4H), 1.33 – 1.06 (m, 6H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.1, 136.8, 115.0, 97.5, 89.8, 37.1, 33.6, 33.1, 33.0, 26.2, 26.0, 26.0.

GCMS found 162.1 (calculated for C$_{12}$H$_{18}$: 162.1)

IR (thin film, cm$^{-1}$): 3078, 2925, 2853, 1960, 1640, 1449, 1261, 992, 913, 761.
(R)-6-Cyclohexyl-hexa-4,5-dien-1-ol (S7n)
S7n was prepared following the general hydroboration/oxidation procedure in 0.25 mmol scale and the crude mixture was purified by flash column chromatography with hexanes/EtOAc (100:10) to afford the pure product as a colorless oil.

Yield: 27 mg, 59%

$[\alpha]_D^{22} = -37.6$ (c = 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.05 – 5.29 (m, 2H), 3.68 (tt, $J = 6.3, 2.9$ Hz, 2H), 2.06 (tdd, $J = 6.8, 5.4, 2.0$ Hz, 2H), 1.94 (m, 1H), 1.75 – 1.60 (m, 8H), 1.21 – 1.10 (m, 4H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 202.6, 97.6, 91.1, 62.4, 37.2, 33.1, 33.1, 32.0, 26.2, 26.0, 25.3.

ESIMS found 181.2 (calculated for $[\text{C}_{12}\text{H}_{21}\text{O}]^+$: 181.2)

IR (thin film, cm$^{-1}$): 2923, 2850, 1469, 1053.

(S)-2-((R)-Hexa-1,2-5-trien-1-yl)-1,4-dioxaspiro[4.5]decane (7o)
Prepared from the corresponding ynal 18o (0.4 mmol) and allyl boronate 5 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a pale yellow oil.

Yield: 70 mg, 79%
e.r.: 98:2

$[\alpha]_D^{22} = +69.0$ (c = 1.0, CHCl$_3$).

HPLC Analysis tr major: 4.25 min., tr minor: 6.69 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 99.0 : 1.0, 1.0 mL/min, 250 nm].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.81 (ddt, $J = 16.6, 10.1, 6.4$ Hz, 1H), 5.31 (qd, $J = 6.8, 1.4$ Hz, 1H), 5.21 (ddt, $J = 7.5, 6.0, 2.9$ Hz, 1H), 5.08 (dq, $J = 17.1, 1.7$ Hz, 1H), 5.03 (dq, $J = 10.1, 1.5$ Hz, 1H), 4.55 (ddt, $J = 7.4, 6.1, 1.4$ Hz, 1H), 4.09 (dd, $J = 8.2, 6.1$ Hz, 1H) 3.69 (dd, $J = 8.2, 7.0$ Hz, 1H), 2.76 (tdt, $J = 6.6, 2.9, 1.5$ Hz, 2H), 1.68 – 1.55 (m, 8H), 1.45 – 1.34 (m, 2H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 204.9, 135.9, 115.6, 110.0, 91.5, 91.4, 74.4, 69.3, 36.4, 35.4, 32.7, 25.1, 23.9, 23.9.

HRMS (EI) found 221.1467 (calculated for $\text{C}_{14}\text{H}_{20}\text{O}_2 [\text{M}+\text{H}]^+$ 221.1463)

IR (thin film, cm$^{-1}$): 2936, 2862, 2002, 1586, 1586, 1448, 1366, 1278, 1162, 1099, 1041.
t. General Procedure for Racemic Crotylations

2-Nitrobenzenesulfonohydrazide 20 (87 mg, 0.4 mmol), ynal 18 (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. Racemic Ph₂-BINOL catalyst 19 (18 mg, 0.04 mmol, 7 mol%), tert-butanol (89 mg, 1.2 mmol) and crotylboronate 21 or 22 (84 mg, 0.6 mmol) were added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to afford the desired product.

u. General Procedure for Asymmetric Crotylations

2-Nitrobenzenesulfonohydrazide 20 (87 mg, 0.4 mmol), ynal 18 (0.4 mmol), and oven-dried 3 Å powdered molecular sieves (200 mg) were added to a 10 mL reaction vial equipped with a magnet stir bar. Dichloromethane (1.0 mL) was added to the vial and the reaction mixture was stirred at room temperature for 2 h, at which time the reaction mixture was concentrated first by rotary evaporation and then by static pressure vacuum (2 – 10 Torr) for 10 min. (R)-Ph₂-BINOL catalyst 19 (18 mg, 0.04 mmol, 7 mol%), tert-butanol (89 mg, 1.2 mmol) and crotylboronate 21 or 22 (84 mg, 0.6 mmol) were added and rinsed into the solution with dry toluene (0.2 mL). The reaction was applied to sonication for 10 min to facilitate dissolution. The vial was sealed with a rubber septum and attached to a balloon filled with argon. The mixture was allowed to stir at room temperature for 48 h, at which time the crude mixture was chromatographed on silica gel to
afford the desired product.

v. Analytical Data for Crotyl Allenes

(R<sub>a</sub>, S)<sup>-</sup>(4-Methyl-hexa-1,2,5-trien-1-yl)benzene (23a)
Prepared from the corresponding ynal 18a (0.4 mmol) and crotyl boronate 21 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 53 mg, 78%
ed.r.: 98:2
d.r.: >20:1.

[α]<sub>D</sub><sup>22</sup> = −163.4 (c = 1.0, CHCl<sub>3</sub>).

HPLC Analysis, tr major: 6.2 min., tr minor: 6.6 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 800:1, 1.0 mL/min, 254 nm].

1<sup>H</sup> NMR (500 MHz, CDCl<sub>3</sub>) 6 7.33 – 7.31 (m, 4H), 7.23 – 7.17 (m, 1H), 6.23 (dd, J = 6.4, 2.9 Hz, 1H), 5.90 (ddd, J = 17.0, 10.2, 6.7 Hz, 1H), 5.62 (dd, J = 6.4, 6.3 Hz, 1H), 5.13 (ddd, J = 17.2, 1.5, 1.4 Hz, 1H), 5.03 (ddd, J = 10.2, 1.4, 1.3 Hz, 1H), 3.07 – 2.97 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H).

13<sup>C</sup> NMR (126 MHz, CDCl<sub>3</sub>) 6 204.3, 142.4, 134.9, 128.6, 126.8, 126.5, 113.3, 99.5, 96.0, 37.5, 19.8.

GCMS found 170.1 (calculated for C<sub>13</sub>H<sub>14</sub>: 170.1)

IR (thin film, cm<sup>-1</sup>): 3084, 3030, 2970, 2930, 1950, 1495, 1458, 915, 776.

(R<sub>a</sub>, R)<sup>-</sup>(4-Methyl-hexa-1,2,5-trien-1-yl)benzene (24a)
Prepared from the corresponding ynal 18a (0.4 mmol) and crotyl boronate 22 (0.6 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 36 mg, 53%
ed.r.: 98:2

[α]<sub>D</sub><sup>22</sup> = −120.8 (c = 1.0, CHCl<sub>3</sub>).

HPLC Analysis, tr major: 27.7 min., tr minor: 30.0 min., [Chiralcel®OD column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 800:1, 0.2 mL/min, 254 nm].

1<sup>H</sup> NMR (500 MHz, CDCl<sub>3</sub>) 6 7.35 – 7.28 (m, 4H), 7.24 – 7.18 (m, 1H), 6.23 (dd, J = 6.4, 2.8 Hz, 1H), 5.90 (ddd, J = 17.1, 10.2, 6.8 Hz, 1H), 5.62 (dd, J = 6.4, 6.3 Hz, 1H), 5.14 (ddd, J = 17.1, 1.5, 1.5 Hz, 1H), 5.03 (ddd, J = 10.2, 1.3, 1.3 Hz, 1H), 3.11 – 2.97 (m, 1H), 1.22 (d, J = 6.9 Hz, 3H).

13<sup>C</sup> NMR (126 MHz, CDCl<sub>3</sub>) 6 204.3, 142.4, 134.9, 128.6, 126.8, 126.5, 113.3, 99.5, 96.0, 37.5, 19.8.

GCMS found 170.1 (calculated for C<sub>13</sub>H<sub>14</sub>: 170.1)
IR (thin film, cm$^{-1}$): 3065, 3032, 2973, 1726, 1495, 1262, 919, 698.

(R$_{\alpha}$, S)-3-Methyl-deca-1,4,5-triene (23b)
Prepared from the corresponding ynal 36 (0.5 mmol) and crotyl boronate 21 (0.75 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.
Yield: 57 mg, 76%
e.r.: 99:1
[$\alpha$]$^D_{22} = +34.1$ (c = 1.0, CHCl$_3$).

HPLC Analysis, this compound was converted to the corresponding alcohol 23bS1 following the hydroboration/oxidation procedure, tr major: 28.3 min., tr minor: 33.7 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =800:1, 1.0 mL/min, 210 nm].

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.81 (ddd, $J = 17.1, 10.2, 6.8$ Hz, 1H), 5.18 (dddd, $J = 6.5, 6.5, 6.4, 2.9$ Hz, 1H), 5.10 (dddd, $J = 6.4, 6.2, 3.0, 3.0$ Hz, 1H), 5.04 (dddd, $J = 17.1, 1.7, 1.6$ Hz, 1H), 4.96 (dddd, $J = 10.2, 1.7, 1.1$ Hz, 1H), 2.90 – 2.78 (m, 1H), 2.00 (dt, $J = 7.4, 6.6, 3.0$ Hz, 2H), 1.45 – 1.30 (m, 4H), 1.11 (d, $J = 6.9$ Hz, 3H), 0.95 – 0.85 (m, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 202.9, 143.0, 112.6, 95.4, 92.5, 37.3, 31.3, 28.6, 22.2, 19.7, 13.9.

GCMS found 150.1 (calculated for C$_{11}$H$_{18}$: 150.1)

IR (thin film, cm$^{-1}$): 2960, 2872, 1683, 1590, 1456, 917, 875.

(R$_{\alpha}$, S)-3-Methyl-deca-4,5-dien-1-ol (23bS1)
The substrate was run in 0.2 mmol scale following the hydroboration/oxidation procedure and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.
Yield: 19 mg, 56%
[$\alpha$]$^D_{22} = -15.7$ (c = 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.12 (ddd, $J = 6.6, 6.6, 6.5, 2.5$ Hz, 1H), 5.04 (dddd, $J = 6.4, 6.3, 3.0, 3.0$ Hz, 1H), 3.70 (t, $J = 6.5$ Hz, 2H), 2.33 – 2.23 (m, 1H), 2.02 – 1.94 (m, 2H), 1.64 – 1.55 (m, 2H), 1.40 – 1.31 (m, 4H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 202.6, 96.4, 92.1, 61.2, 39.8, 31.3, 30.4, 28.7, 22.2, 20.7, 13.9.

HRMS found 169.1593 (calculated for [C$_{11}$H$_{21}$O]$: 169.1592$)

IR (thin film, cm$^{-1}$): 3370,2958, 2929, 2871, 1459, 1369, 1261. 1203, 1170, 1049, 874, 834, 755.
(R<sub>R</sub>, R)-3-Methyl-deca-1,4,5-triene (24b)
Prepared from the corresponding ynal 36 (1.0 mmol) and crotyl boronate 22 (1.5 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

Yield: 100 mg, 67%
e.r.: 99:1
[α]<sub>D</sub><sup>22</sup> = −124.4 (c = 1.0, CHCl<sub>3</sub>).

HPLC Analysis, this compound was converted to the corresponding alcohol 37 following the hydroboration/oxidation procedure, tr major: 32.3 min., tr minor: 39.7 min., [Chiralpak®AD-H column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH =99.9:0.1, 1.0 mL/min, 210 nm].

1H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.81 (ddd, <i>J</i> = 17.2, 10.2, 6.7 Hz, 1H), 5.17 (dddd, <i>J</i> = 6.5, 6.5, 6.5, 2.8 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.04 (dddd, <i>J</i> = 17.2, 1.7, 1.6 Hz, 1H), 4.96 (ddddd, <i>J</i> = 10.2, 1.7, 1.2 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.04 – 1.97 (m, 2H), 1.48 – 1.29 (m, 4H), 1.11 (d, <i>J</i> = 6.9 Hz, 3H), 0.91 (t, <i>J</i> = 7.2 Hz, 3H).

13C NMR (126 MHz, CDCl<sub>3</sub>) δ 202.9, 142.9, 112.6, 95.3, 92.5, 37.2, 31.3, 28.6, 22.1, 19.7, 13.9.

GCMS found 150.1 (calculated for C<sub>11</sub>H<sub>18</sub>: 150.1)
IR (thin film, cm<sup>-1</sup>): 2959, 2928, 2872, 1961, 1457, 1053.
w. Stereochemistry Determination of Crotyl Allenes

(Rα, S)-3-Methyldeca-4,5-dienoic acid (23bS2)

(Rα, S)-3-methyl-deca-4,5-dien-1-ol (23bS1) (73 mg, 0.4 mmol) was dissolved in 3 ml acetone and cooled to –20 °C. Jones reagent (2.5 equiv), prepared from CrO3 (100 mg, 1.0 mmol), concentrated H2SO4 (0.09 ml, 1.6 mmol), and water (0.4 ml), was added slowly to the reaction and the reaction was allowed to warm to 0 °C in 2 h before quenched by addition of 1 ml i-PrOH, and the mixture was filtered and concentrated down to 1 ml. The residue was then purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 39 mg, 53%

[a]D^22 = -50.9 (c = 1.0, CHCl3). In lit:35 its enantiomer (Sα, R)-3-methyldeca-4,5-dienoic acid [α]D^22 = +45 (c = 1.0, CHCl3).

1H NMR (500 MHz, CDCl3) δ 5.23 – 5.11 (m, 2H), 2.71 – 2.61 (m, 1H), 2.46 (dd, J = 15.6, 7.0 Hz, 1H), 2.30 (dd, J = 15.6, 7.4 Hz, 1H), 2.02 – 1.93 (m, 2H), 1.41 – 1.28 (m, 4H), 1.08 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H).

13C NMR (126 MHz, CDCl3) δ 202.4, 178.2, 95.5, 93.4, 40.9, 31.3, 29.7, 28.6, 22.2, 20.2, 13.9.

Analytical data for this compound matched that of the previously reported values and therefore confirmed the stereochemistry.

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(Rα, R)-3-Methyldeca-4,5-dienoic acid (38)

(Rα, R)- 3-Methyl-deca-4,5-dien-1-ol (37) (73 mg, 0.4 mmol) was dissolved in 3 ml acetone and cooled to 0 °C. Jones reagent (2.5 equiv), prepared from CrO3 (100 mg, 1.0 mmol), concentrated H2SO4 (0.09 ml, 1.6 mmol), and water (0.4 ml), was added slowly to the reaction and the reaction remained at the same temperature for 2 h before quenched by addition of 1 ml i-PrOH, and the mixture was filtered and concentrated down to 1 ml. The residue was then purified by flash column chromatography with hexanes:EtOAc (8:1) to afford the pure product as a colorless oil.

Yield: 41 mg, 56%

[a]D^22 = -80.5 (c = 1.34, CHCl3). In lit:35 [α]D^22 = -74.9 (c = 1.34, CHCl3).

1H NMR (500 MHz, CDCl3) δ 5.24 – 5.08 (m, 2H), 2.71 – 2.58 (m, 1H), 2.45 (dd, J = 15.6, 7.0 Hz, 1H), 2.29 (dd, J = 15.6, 7.4 Hz, 1H), 2.02 – 1.94 (m, 2H), 1.43 – 1.28 (m, 4H), 1.09 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H).

13C NMR (126 MHz, CDCl3) δ 202.4, 177.5, 95.5, 93.4, 40.8, 31.3, 29.8, 28.6, 22.2, 20.3, 13.9.

Analytical data for this compound matched that of the previously reported values and therefore confirmed the stereochemistry.
x. Cyclization of Enantioenriched Allenols

(R)-2-Phenyl-2,5-dihydrofuran (25)

(S)-4-Phenylbuta-2,3-dien-1-ol (6a) (44 mg, 0.3 mmol, 92:8 e.r.) was dissolved in 3 ml hot pentane. Silver nitrate on silica gel (51 mg, 10% wt, 0.1 eq) was added in and the reaction flask was wrapped with aluminum foil and allowed to stir for 26 hours at room temperature. After the allenol was consumed (as monitored by TLC), the reaction mixture was subjected directly to column chromatography on silica gel eluting with hexanes to afford the cyclized product 25 as a colorless oil.

Yield: 35 mg, 79%.

e.r.: 92:8.

\[\text{[\(\alpha\)}\]D22 = +111.8 (c = 0.42, CHCl3). In lit\textsuperscript{36}: [\(\alpha\)]D22 = +248 (c = 0.59, CHCl3, 93% ee).

HPLC Analysis, tr minor: 12.9 min., tr major: 17.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99.95:0.05, 1.0 mL/min, 210 nm].

All spectra were in agreement with reported data.\textsuperscript{37}

(S)-2-Phenethyl-2,5-dihydrofuran (26)

(S)-6-Phenylhexa-2,3-dien-1-ol (6g) (52 mg, 0.3 mmol, 92:8 e.r.) was dissolved in a mixture of acetone/water (1.2 ml/0.8 ml). Silver nitrate (10 mg, 0.2 eq) was added in and the reaction flask was wrapped with aluminum foil and allowed to stir for 48 hours at room temperature. After the allenol was consumed (as monitored by TLC), the solvent was removed under reduced pressure and the crude reaction mixture was subjected to column chromatography using hexanes to give cyclized product 26 as a colorless oil.

Yield: 35 mg, 67%.

e.r.: 92:8.

[\(\alpha\)]D22 = +74.6 (c = 1.0, CHCl3).

HPLC Analysis, tr minor: 11.5 min., tr major: 12.2 min., [Chiralpak®IA column, 24cm × 4.6 mm I.D., Hexanes: iPrOH = 99.9:0.1, 0.8 mL/min, 254 nm].

\(\text{H NMR (500 MHz, CDCl3)} \delta 7.35 – 7.23 (m, 2H), 7.24 – 7.09 (m, 3H), 5.91 (ddt, J = 6.0, 1.8, 1.8 Hz, 1H), 5.79 (dt, \text{dd} = 6.0, 2.4, 1.4 Hz, 1H), 4.90 – 4.83 (m, 1H), 4.76 – 4.57 (m, 2H), 2.78 – 2.61 (m, 2H), 1.95 – 1.79 (m, 2H).

\(\text{C NMR (126 MHz, CDCl3)} \delta 142.2, 129.5, 128.4, 128.3, 126.7, 125.7, 85.4, 75.1, 37.7, 31.5.

ESIMS found 175.1 (calculated for [C\textsubscript{12}H\textsubscript{15}O]: 175.1)

IR (thin film, cm\textsuperscript{-1}): 3081, 3061, 3027, 2924, 2848, 1603, 1496, 1454, 1354, 1079, 1018.

(2R, 5R)-2,5-Piphenyl-2,5-dihydrofuran (S19)

To a solution of AuCl\textsubscript{3} (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol (anti-15a) (33 mg, 0.15 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 4 h,
at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil.

**Yield:** 23 mg, 70%.

$[\alpha]_D^{22} = +382.2 \text{ (c = 0.48, CHCl}_3\text{).}$

$^1\text{H NMR (500 MHz, CDCl}_3\text{)}$ $\delta$ 7.30 – 7.23 (m, 7H), 7.20 – 7.05 (m, 3H), 5.93 (app d, $J = 2.4$ Hz, 4H).

$^{13}\text{C NMR (126 MHz, CDCl}_3\text{)}$ $\delta$ 141.5, 130.3, 128.6, 127.9, 126.5, 88.3.

**HRMS (ESI)** found 223.1116 (calculated for [C$_{16}$H$_{14}$O$+$ H]$^+$: 223.1123)

**IR** (thin film, cm$^{-1}$): 3084, 3062, 3029, 2922, 2851, 1601, 1493.

$^{(R)}$-2-((R)-2,5-Dihydrofuran-2-yl)-1,4-dioxaspiro[4.5]decane (27)

To a solution of AuCl$_3$ (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol 11o (30 mg, 0.14 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 2 h, at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil and a single diastereomer.

**Yield:** 19 mg, 64%.

$[\alpha]_D^{24} = +41.3 \text{ (c = 0.40, CH}_2\text{Cl}_2\text{).}$ In lit$^{38}$: $[\alpha]_D^{24} = +51 \text{ (c = 0.9, CH}_2\text{Cl}_2\text{).}$ All spectra were in agreement with reported data.$^{38}$

$^{(R)}$-2-((S)-2,5-Dihydrofuran-2-yl)-1,4-dioxaspiro[4.5]decane (28)

To a solution of AuCl$_3$ (0.6 mg, 0.0020 mmol) in THF (0.5 mL) in a flame-dried vial equipped with a magnetic stir bar was added a solution of the allenol 11p (30 mg, 0.14 mmol) in THF (1 mL) via cannula, followed by a 1 mL rinse. The reaction was allowed to stir at r.t. for 2 h, at which time TLC indicated full consumption of the starting material. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography with hexanes (39 : 1) to afford the title compound as a pale yellow oil and a single diastereomer.

**Yield:** 18 mg, 59%.

$[\alpha]_D^{24} = +26.1 \text{ (c = 0.40, CH}_2\text{Cl}_2\text{).}$ All spectra were in agreement with reported data.$^{38}$
(2S, 5R)-2-Benzyl-5-phenyl-2,5-dihydrofuran (29)

A solution of the allenol \textit{anti}-15b (0.046 g, 0.19 mmol) in THF (2.0 mL) was added by cannula to a solution of AuCl$_3$ (~0.6 mg, 0.002 mmol) in THF (0.5 mL). The reaction was allowed to stir at room temperature over 2h, at which time TLC indicated full consumption of the starting material. The reaction was then concentrated under reduced pressure, and the residue was purified by flash column chromatography with 0% → 2% EtOAc/Hexanes to afford the title compound as a clear and colorless oil.

**Yield:** (0.027 g, 0.16 mmol, 59%) as a clear oil.

All spectra were in agreement with reported data.

### y. Synthesis of Laballenic Acid

\[
\begin{array}{c}
\text{H}_3C \quad \text{H} \\
\end{array}
\]

(R)-Heptadeca-1,4,5-triene (31)

Prepared from the corresponding ynal 30 (2.0 mmol) and allyl boronate 5 (3.0 mmol) according to the General Procedure. The crude mixture was purified by flash column chromatography with hexanes to afford the pure product as a colorless oil.

**Yield:** 399 mg, 85%

e.r.: 99:1

\([\alpha]_D^{22} = -38.3 \ (c = 1.0, \text{CHCl}_3)\).

**HPLC Analysis,** this compound was converted to the corresponding alcohol (see below) following the hydroboration/oxidation procedure, \(t\) minor: 32.5 min., \(t\) major: 34.3 min., [Chiralpak®IA column, 24 cm × 4.6 mm I.D., Hexanes: iPrOH = 800:1, 1.0 mL/min, 210 nm].

**\textit{H} NMR** (500 MHz, CDCl$_3$) \(\delta\) 5.85 (dddd, \(J = 16.6, 10.1, 6.4, 6.4\) Hz, 1H), 5.16 – 5.04 (m, 3H), 5.01 (ddd, \(J = 10.1, 1.5, 1.5\) Hz, 1H), 2.80 – 2.71 (m, 2H), 2.03 – 1.92 (m, 2H), 1.46 – 1.35 (m, 2H), 1.35 – 1.19 (m, 16H), 0.89 (t, \(J = 6.9\) Hz, 3H).

**\textit{C} NMR** (126 MHz, CDCl$_3$) \(\delta\) 204.2, 136.8, 115.0, 91.5, 88.9, 33.5, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 29.1, 28.8, 22.7, 14.1.

**GCMS** found 234.2 (calculated for C$_{17}$H$_{30}$: 234.2)

**IR** (thin film, cm$^{-1}$): 2956, 2926, 2854.

(R)-Heptadeca-4,5-dien-1-ol (32)

The product was prepared on a 1.0 mmol scale following the general procedure for hydroboration/oxidation and the crude mixture was purified by flash column chromatography with hexanes:EtOAc (100:5) to afford the pure product as a colorless oil.
Yield: 189 mg, 75%
$[\alpha]_D^{22} = -43.7$ (c = 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) δ 5.13 – 5.07 (m, 2H), 3.74 – 3.62 (m, 2H), 2.12 – 2.03 (m, 2H), 2.01 – 1.93 (m, 2H), 1.69 (tt, $J = 7.3$, 6.5 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.33 – 1.21 (m, 16H), 0.91 – 0.85 (m, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 203.8, 91.6, 90.1, 62.4, 32.0, 31.9, 29.7, 29.7, 29.5, 29.3, 29.2, 29.1, 25.2, 22.7, 14.1.

ESIMS found 253.2 (calculated for [C$_{17}$H$_{33}$O]$^+$: 253.2)

IR (thin film, cm$^{-1}$): 3354, 2853, 1467, 1057, 930.

$^{1}$H NMR (500 MHz, CDCl$_3$) δ 5.14 (dddt, $J = 6.5$, 6.5, 6.4, 3.0 Hz, 1H), 5.05 (dddt, $J = 6.4$, 6.3, 6.3, 3.0 Hz, 1H), 2.39 (t, $J = 7.3$ Hz, 2H), 2.16 – 2.10 (m, 2H), 2.01 – 1.94 (m, 2H), 1.82 – 1.74 (m, 2H), 1.38 (q, $J = 7.3$ Hz, 2H), 1.34 – 1.20 (m, 16H), 0.88 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 204.1, 119.6, 92.3, 88.6, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.9, 27.6, 24.6, 22.7, 16.4, 14.1.

ESIMS found 262.2 (calculated for [C$_{18}$H$_{32}$N]$^+$: 262.2)

HRMS found 284.2364 (calculated for [C$_{18}$H$_{31}$NNa]$^+$: 284.2354)

IR (thin film, cm$^{-1}$): 2924, 2854, 2250, 1963, 1465, 880.

(R)-Octadeca-5,6-dienoic acid, laballenic acid (35)

(R)-Octadeca-5,6-dienoic acid 34 (115 mg, 0.44 mmol) was dissolved in EtOH (0.5 ml). To this solution was added a solution of NaOH (120 mg, 3 mmol) in H$_2$O (0.16 ml). The reaction mixture was stirred at 80 °C for 5 h. The reaction was acidified with HCl (2 M) to pH=1, and extracted with Et$_2$O (3 X 5 ml). The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated under vacuum. The crude mixture was purified by column chromatography with hexanes/EtOAc/AcOH (100:10:0.1) to afford the pure product as a colorless oil with acidic smell.

Yield: 107 mg, 87%
\[ [\alpha]_D^{22} = -45.0 \ (c = 1.0, \text{CHCl}_3). \] In lit: \[ [\alpha]_D^{29} = -42.7 \ (c = 0.96, \text{CHCl}_3). \]

\[ [\alpha]_D^{27} = -50.6 \ (c = 1.025, \text{CHCl}_3). \]

1H NMR (500 MHz, CDCl3) δ 5.14 – 5.00 (m, 2H), 2.41 (t, J = 7.5 Hz, 2H), 2.04 (qd, J = 7.0, 2.9 Hz, 2H), 1.97 (qd, J = 6.9, 2.9 Hz, 2H), 1.75 (tt, J = 7.3, 7.3 Hz, 2H), 1.38 (tt, J = 7.1, 7.1 Hz, 2H), 1.34 – 1.21 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H).

13C NMR (126 MHz, CDCl3) δ 204.0, 179.9, 91.6, 89.6, 33.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 29.1, 28.9, 28.2, 24.0, 22.7, 14.1.

ESIMS found 279.2 (calculated for [C18H31O2]-: 279.2)

HRMS found 279.2325 (calculated for [C18H31O2]-: 279.2324)

IR (thin film, cm\(^{-1}\)): 2923, 2854, 1710, 1457, 1254, 878.

All spectra were in agreement with reported data.\(^{39-40}\)

3. Summary of Absolute Stereochemistry Determination for Allenols and Allyl Allenes

The absolute stereochemistry of allenols was determined unambiguously by direct comparison of the optical rotations of 6a, 7, 6g, 6i, 6j, 11 6n, with those reported for the same compounds or their enantiomers.

The cyclized product 25 from 6a also matched the reported optical information.\(^{36}\)

The absolute stereochemistry of 23bS2 and 38 was confirmed by their NMR data and optical rotations compared to those that had been reported by Ma’s group.\(^{35}\) Therefore the absolute stereochemistry of crotol allenes was decisively determined.

The optical rotation of laballenic acid 35\(^{39-40}\) confirmed the absolute stereochemistry of the corresponding allyl allene precursor 31, and the absolute configuration of the remaining allyl allene products was determined by analogy.

The optical rotations of allenols and allyl allenes both match Lowe’s rules.\(^{33}\)
4. References

5. $^1$H and $^{13}$C NMR Spectra
17

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![Chemical Structure](image)

![NMR Spectrum](image)
6. HPLC Traces for Enantiomeric Excess Determination

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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

The compound shown is 6b, with the following molecular structure:

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\|     \|
CH3O    OH
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It appears to be a chemical compound with a benzene ring and a hydroxyl group (OH) bonded to a methyl group (CH3O).
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

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6c
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Totals: 5470.40137 94.65868

### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.388</td>
<td>BV</td>
<td>0.8341</td>
<td>1513.86182</td>
<td>27.94063</td>
<td>6.9265</td>
</tr>
<tr>
<td>2</td>
<td>45.705</td>
<td>VB</td>
<td>0.9033</td>
<td>2.03423e4</td>
<td>344.29584</td>
<td>93.0735</td>
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</tbody>
</table>

Totals: 2.18562e4 372.23647

---

**Chemical Structure:**

![Chemical Structure](image)
### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>-------</td>
<td>--------------</td>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>1</td>
<td>21.720 MM</td>
<td>0.4634</td>
<td>8912.11328</td>
<td>320.55563</td>
</tr>
<tr>
<td>2</td>
<td>24.288 MM</td>
<td>0.5168</td>
<td>8814.94434</td>
<td>284.26099</td>
</tr>
<tr>
<td><strong>Totals:</strong></td>
<td></td>
<td>1.77271e4</td>
<td>604.81662</td>
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</tr>
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### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>--------------------</td>
<td>-------</td>
<td>--------------</td>
<td>--------------</td>
<td>---------</td>
</tr>
<tr>
<td>1</td>
<td>21.396 MM</td>
<td>0.4464</td>
<td>1239.60657</td>
<td>46.28024</td>
</tr>
<tr>
<td>2</td>
<td>23.904 MM</td>
<td>0.5162</td>
<td>13764.907</td>
<td>444.45715</td>
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<tr>
<td><strong>Totals:</strong></td>
<td></td>
<td>1.50046e4</td>
<td>490.73739</td>
<td></td>
</tr>
<tr>
<td>#</td>
<td>RetTime [min]</td>
<td>Type</td>
<td>Width [min]</td>
<td>Area [mAU*s]</td>
</tr>
<tr>
<td>---</td>
<td>--------------</td>
<td>------</td>
<td>-------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1</td>
<td>40.188 VB</td>
<td>0.8526</td>
<td>4.64582e4</td>
<td>815.50146</td>
</tr>
<tr>
<td>2</td>
<td>46.776 VP</td>
<td>0.9386</td>
<td>4.63200e4</td>
<td>752.05536</td>
</tr>
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</table>

**Totals:** 9.27782e4 1567.55682

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.483 MM</td>
<td>0.8895</td>
<td>5456.49365</td>
<td>102.23568</td>
<td>90.2400</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>47.150 MM</td>
<td>0.9648</td>
<td>590.15155</td>
<td>10.19430</td>
<td>9.7600</td>
<td></td>
</tr>
</tbody>
</table>

**Totals:** 6046.64520 112.42998

**Signal 2: MWD1 B, Sig=254.16 Ref=360.100**

---

**6f**

---

**Signal 2: MWD1 B, Sig=254.16 Ref=360.100**
### Signal 3: MWD1 C, Sig=210.8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.586</td>
<td>0.8398</td>
<td>1.48552e4</td>
<td>294.81522</td>
<td>51.9704</td>
</tr>
<tr>
<td>2</td>
<td>45.160</td>
<td>1.2787</td>
<td>1.37288e4</td>
<td>178.94424</td>
<td>48.0296</td>
</tr>
</tbody>
</table>

**Totals:** 2.85839e4 473.75946

### Signal 3: MWD1 C, Sig=210.8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.595</td>
<td>0.7817</td>
<td>3616.99487</td>
<td>77.11399</td>
<td>8.0906</td>
</tr>
<tr>
<td>2</td>
<td>44.826</td>
<td>1.3273</td>
<td>4.10891e4</td>
<td>515.93872</td>
<td>91.9094</td>
</tr>
</tbody>
</table>

**Totals:** 4.47061e4 593.05271

---

![Diagram](image-url)
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th></th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42.449</td>
<td>BB</td>
<td>1.1259</td>
<td>7617.34766</td>
<td>101.0036</td>
<td>50.6764</td>
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<tr>
<td>2</td>
<td>52.680</td>
<td>BB</td>
<td>1.4192</td>
<td>7413.99902</td>
<td>78.1199</td>
<td>49.3236</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.50313e4   179.12346

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Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th></th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.438</td>
<td>MM</td>
<td>1.2537</td>
<td>105.0583</td>
<td>1.3966</td>
<td>10.0200</td>
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</tr>
<tr>
<td>2</td>
<td>53.981</td>
<td>MM</td>
<td>1.5653</td>
<td>943.43237</td>
<td>10.0454</td>
<td>89.9800</td>
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</tr>
</tbody>
</table>

Totals: 1048.49070   11.44204
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>[%]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17.50</td>
<td>2.00</td>
<td>494.06</td>
<td>34.30</td>
<td>4.80</td>
<td>9.60</td>
</tr>
<tr>
<td>2</td>
<td>18.75</td>
<td>2.00</td>
<td>139.27</td>
<td>34.30</td>
<td>9.60</td>
<td>19.20</td>
</tr>
<tr>
<td>Totals</td>
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<td></td>
<td>633.33</td>
<td>68.60</td>
<td>14.40</td>
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</table>

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>[%]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>19.01</td>
<td>2.00</td>
<td>55.70</td>
<td>5.70</td>
<td>10.00</td>
<td>19.00</td>
</tr>
<tr>
<td>2</td>
<td>19.83</td>
<td>2.00</td>
<td>1100.19</td>
<td>40.06</td>
<td>90.37</td>
<td>90.37</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>1155.89</td>
<td>45.76</td>
<td>90.37</td>
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</tr>
</tbody>
</table>

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>[%]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>19.01</td>
<td>2.00</td>
<td>55.70</td>
<td>5.70</td>
<td>10.00</td>
<td>19.00</td>
</tr>
<tr>
<td>2</td>
<td>19.83</td>
<td>2.00</td>
<td>1100.19</td>
<td>40.06</td>
<td>90.37</td>
<td>90.37</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>1155.89</td>
<td>45.76</td>
<td>90.37</td>
<td></td>
</tr>
</tbody>
</table>
**Signal 3: MWD1 C, Sig=210,8 Ref=360,100**

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MF</td>
<td>18.336</td>
<td>0.4368</td>
<td>3785.69141</td>
<td>144.43956</td>
<td>49.4461</td>
</tr>
<tr>
<td>2</td>
<td>FM</td>
<td>19.712</td>
<td>0.4830</td>
<td>3870.51025</td>
<td>133.54718</td>
<td>50.5539</td>
</tr>
</tbody>
</table>

Totals:  
Area: 7656.20166 | 277.98674

**Signal 3: MWD1 C, Sig=210,8 Ref=360,100**

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MF</td>
<td>18.348</td>
<td>0.4351</td>
<td>2369.49561</td>
<td>90.75724</td>
<td>9.9122</td>
</tr>
<tr>
<td>2</td>
<td>FM</td>
<td>19.511</td>
<td>0.5263</td>
<td>21535.3e4</td>
<td>681.97656</td>
<td>90.0878</td>
</tr>
</tbody>
</table>

Totals:  
Area: 2.39048e4 | 772.73380

---

![Diagram of compound 6j](image)
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.995</td>
<td>BV</td>
<td>0.7269</td>
<td>4664.57</td>
<td>94.66</td>
<td>49.64</td>
</tr>
<tr>
<td>2</td>
<td>39.363</td>
<td>VB</td>
<td>0.7895</td>
<td>4730.50</td>
<td>87.39</td>
<td>50.35</td>
</tr>
</tbody>
</table>

Totals : 9395.07 182.06

Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.125</td>
<td>BM</td>
<td>0.7558</td>
<td>441.55</td>
<td>9.74</td>
<td>10.02</td>
</tr>
<tr>
<td>2</td>
<td>39.213</td>
<td>MM</td>
<td>0.795</td>
<td>3966.54</td>
<td>72.78</td>
<td>89.98</td>
</tr>
</tbody>
</table>

Totals : 4408.09 82.52

Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.125</td>
<td>MM</td>
<td>0.555</td>
<td>441.55</td>
<td>9.73</td>
<td>10.02</td>
</tr>
<tr>
<td>2</td>
<td>39.213</td>
<td>MM</td>
<td>0.584</td>
<td>3966.54</td>
<td>72.77</td>
<td>89.98</td>
</tr>
</tbody>
</table>

Totals : 4408.09 82.52

6k
### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.865</td>
<td>PV</td>
<td>0.3912</td>
<td>934.88318</td>
<td>37.71471</td>
<td>49.9179</td>
</tr>
<tr>
<td>2</td>
<td>13.767</td>
<td>VV</td>
<td>0.4141</td>
<td>937.95966</td>
<td>35.05968</td>
<td>50.0821</td>
</tr>
</tbody>
</table>

**Totals:**

- \(\text{Area} = 1872.84283\) mAU*s
- \(\text{Area} = 72.77439\) %

### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.009</td>
<td>MF</td>
<td>0.4175</td>
<td>2627.55298</td>
<td>104.89553</td>
<td>85.2908</td>
</tr>
<tr>
<td>2</td>
<td>13.945</td>
<td>FM</td>
<td>0.4292</td>
<td>453.14676</td>
<td>17.59686</td>
<td>14.7092</td>
</tr>
</tbody>
</table>

**Totals:**

- \(\text{Area} = 3080.69974\) mAU*s
- \(\text{Area} = 122.49239\) %

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(12.865\) min
  - Type: PV
  - Width: \(0.3912\) min
  - Area: \(934.88318\) mAU*s
  - Height: \(37.71471\) mAU
  - Area [%]: \(49.9179\)

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.009\) min
  - Type: MF
  - Width: \(0.4175\) min
  - Area: \(2627.55298\) mAU*s
  - Height: \(104.89553\) mAU
  - Area [%]: \(85.2908\)

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.945\) min
  - Type: FM
  - Width: \(0.4292\) min
  - Area: \(453.14676\) mAU*s
  - Height: \(17.59686\) mAU
  - Area [%]: \(14.7092\)

---

**Chemical Structure:**

- **Chemical Structure:**
  - **6l**
  - **Chemical Structure:**
    - Me
    - O
    - O
    - H
    - H
  - **Chemical Structure:**
    - Olefin
  - **Chemical Structure:**
    - OH

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.009\) min
  - Type: MF
  - Width: \(0.4175\) min
  - Area: \(2627.55298\) mAU*s
  - Height: \(104.89553\) mAU
  - Area [%]: \(85.2908\)

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.945\) min
  - Type: FM
  - Width: \(0.4292\) min
  - Area: \(453.14676\) mAU*s
  - Height: \(17.59686\) mAU
  - Area [%]: \(14.7092\)

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.009\) min
  - Type: MF
  - Width: \(0.4175\) min
  - Area: \(2627.55298\) mAU*s
  - Height: \(104.89553\) mAU
  - Area [%]: \(85.2908\)

---

**Diagram:**

- **Signal 3: MWD1 C, Sig=210,8 Ref=360,100**
- **Diagram:**
  - Peak RetTime: \(13.945\) min
  - Type: FM
  - Width: \(0.4292\) min
  - Area: \(453.14676\) mAU*s
  - Height: \(17.59686\) mAU
  - Area [%]: \(14.7092\)
### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.449</td>
<td>MM</td>
<td>0.4552</td>
<td>2884.41772</td>
<td>105.60197</td>
<td>50.2031</td>
</tr>
<tr>
<td>2</td>
<td>17.403</td>
<td>MM</td>
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### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

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<tbody>
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<td>2.04740e4</td>
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Signal 3: MWD1 C, Sig=210,8 Ref=360,100

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<td>1.68211e4</td>
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Signal 3: MWD1 C, Sig=210,8 Ref=360,100

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<th>Area [%]</th>
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<td>3.79650e4</td>
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<td>2</td>
<td>15.693</td>
<td>MM</td>
<td>0.3535</td>
<td>4334.24658</td>
<td>204.35019</td>
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<td>4.22992e4</td>
<td>2009.08786</td>
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6n
### Signal 1: MWD1 A, Sig=250,100 Ref=360,100

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<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>6.257</td>
<td>VV</td>
<td>0.2115</td>
<td>1.26719e4</td>
<td>951.03210</td>
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<td>2</td>
<td>6.850</td>
<td>VB</td>
<td>0.2220</td>
<td>1.27616e4</td>
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### Signal 1: MWD1 A, Sig=250,100 Ref=360,100

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<tr>
<td>1</td>
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<td>MM</td>
<td>0.2224</td>
<td>1.43963e4</td>
<td>1078.87366</td>
<td>99.2730</td>
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<tr>
<td>2</td>
<td>6.706</td>
<td>MM</td>
<td>0.2043</td>
<td>1.05432e3</td>
<td>8.60119</td>
<td>0.7270</td>
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<td><strong>1.45017e4</strong></td>
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**7a**
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<tbody>
<tr>
<td>1</td>
<td>21.773</td>
<td>BB</td>
<td>0.6223</td>
<td>3592.5222</td>
<td>89.49754</td>
<td>50.0242</td>
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<tr>
<td>2</td>
<td>32.783</td>
<td>BB</td>
<td>0.9149</td>
<td>3589.04053</td>
<td>60.08356</td>
<td>49.9758</td>
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Totals: 7181.56274 149.58110

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

---

1 21.912 VB 0.6473 6562.77930 156.49417 98.3881
2 33.043 MM 1.0262 107.51844 1.74614 1.6119

Totals: 6670.29774 158.24032
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<th>Area %</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>18.725</td>
<td>BV</td>
<td>0.5064</td>
<td>764.85852</td>
<td>23.33280</td>
<td>50.1838</td>
</tr>
<tr>
<td>2</td>
<td>20.174</td>
<td>VB</td>
<td>0.5423</td>
<td>759.25659</td>
<td>21.69337</td>
<td>49.8162</td>
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</table>

Totals: 1524.11511 45.02617

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<table>
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<th>#</th>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>18.391</td>
<td>BB</td>
<td>0.5153</td>
<td>1.01933e4</td>
<td>307.01639</td>
<td>99.1788</td>
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<tr>
<td>2</td>
<td>20.308</td>
<td>BB</td>
<td>0.5158</td>
<td>8.40445</td>
<td>2.15095</td>
<td>0.8212</td>
</tr>
</tbody>
</table>

Totals: 1.02777e4 309.16734

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Signal 2: MWD1 B, Sig=254,16 Ref=360,100

**Diagram of Chemical Structure:**

S7c
Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.222</td>
<td>VV</td>
<td>0.3199</td>
<td>1.46301e4</td>
<td>561.6134</td>
<td>49.7165</td>
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<tr>
<td>2</td>
<td>16.080</td>
<td>VV</td>
<td>0.4940</td>
<td>1.44652e4</td>
<td>353.08664</td>
<td>49.7165</td>
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Totals: 2.90953e4 914.70004

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

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<tr>
<th>#</th>
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<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>14.808</td>
<td>MM</td>
<td>0.3344</td>
<td>105.754</td>
<td>5.27122</td>
<td>1.4140</td>
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<tr>
<td>2</td>
<td>16.320</td>
<td>VV</td>
<td>0.4909</td>
<td>7373.18750</td>
<td>206.31596</td>
<td>98.5860</td>
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</table>

Totals: 7478.94154 211.58718
### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>7.358</td>
<td>VB</td>
<td>0.2345</td>
<td>2268.17944</td>
<td>149.96297</td>
<td>50.3140</td>
</tr>
<tr>
<td>2</td>
<td>9.200</td>
<td>BB</td>
<td>0.2763</td>
<td>2239.86938</td>
<td>126.67419</td>
<td>49.6860</td>
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</table>

Totals: 4508.04883 276.63716

### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
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<tr>
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<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>7.379</td>
<td>VP</td>
<td>0.2477</td>
<td>1.39069e4</td>
<td>873.65680</td>
<td>99.4693</td>
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<td>2</td>
<td>9.273</td>
<td>BP</td>
<td>0.2707</td>
<td>74.19672</td>
<td>4.22903</td>
<td>0.5307</td>
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Totals: 1.39811e4 877.88583

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**Chemical Structure:**

![Chemical Structure](image)
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

<table>
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<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
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<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
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<tr>
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<td>MF</td>
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<td>6.14455e4</td>
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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

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<tbody>
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<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>%</td>
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</tr>
<tr>
<td>1</td>
<td>16.147</td>
<td>MF</td>
<td>0.4470</td>
<td>7124.74658</td>
<td>265.67194</td>
<td>98.7134</td>
</tr>
<tr>
<td>2</td>
<td>16.925</td>
<td>F</td>
<td>0.3361</td>
<td>92.85820</td>
<td>4.60466</td>
<td>1.2866</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td></td>
<td></td>
<td></td>
<td>7217.60478</td>
<td>270.27660</td>
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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

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<tr>
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<td>MF</td>
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<td>98.7134</td>
</tr>
<tr>
<td>2</td>
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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

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<thead>
<tr>
<th>Peak RetTime</th>
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<td>[mAU]</td>
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<tr>
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<td>16.925</td>
<td>F</td>
<td>0.3361</td>
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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
<table>
<thead>
<tr>
<th>#</th>
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<th>Type</th>
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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
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<tr>
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<td>1.0746</td>
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<td>BB</td>
<td>1.2408</td>
<td>9211.27930</td>
<td>112.31322</td>
<td>49.0725</td>
</tr>
</tbody>
</table>

**Totals:**
- Area: 1.87708 e4
- %: 240.12799

---

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

**S7g**

---

Peaks with retentions from 44.632 to 49.954 minutes, showing areas and percentage contributions.

**Totals:**
- Area: 2.13024 e4
- %: 293.68447

---

S142
<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<th>Area %</th>
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<tbody>
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<td>0.3721</td>
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<td>653.82581</td>
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Totals: 1252.33008 66.02874

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<th>Width [min]</th>
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Totals: 5248.06749 190.88926

Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Signal 2: MWD1 A, Sig=250,100 Ref=360,100

7h
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
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<th>Type</th>
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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<td>696.96429</td>
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<td>2</td>
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<td>701.50549</td>
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<td>50.1624</td>
</tr>
</tbody>
</table>

Totals: 1398.46979 61.75031

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.920</td>
<td>VV</td>
<td>0.3637</td>
<td>3677.83496</td>
<td>157.94389</td>
<td>98.0815</td>
</tr>
<tr>
<td>2</td>
<td>10.859</td>
<td>VB</td>
<td>0.3822</td>
<td>71.94074</td>
<td>2.30454</td>
<td>1.9185</td>
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</tbody>
</table>

Totals: 3749.77572 160.24843
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
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<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>14.435</td>
<td>MF</td>
<td>0.4298</td>
<td>5219.31787</td>
<td>202.38109</td>
<td>49.1914</td>
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<tr>
<td>2</td>
<td>15.299</td>
<td>FM</td>
<td>0.4627</td>
<td>5390.89844</td>
<td>194.17436</td>
<td>50.8086</td>
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<td>Totals:</td>
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<td></td>
<td></td>
<td>1.06102e4</td>
<td>396.55545</td>
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Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.907</td>
<td>MF</td>
<td>0.4493</td>
<td>1.83335e4</td>
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<td>15.759</td>
<td>FM</td>
<td>0.3634</td>
<td>251.26598</td>
<td>11.52379</td>
<td>1.3520</td>
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<tr>
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<td></td>
<td>1.85848e4</td>
<td>691.63927</td>
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</table>

MWD1 C, Sig=210,8 Ref=360,100 (YAO20\3.D)

Area: 5219.32

MWD1 C, Sig=210,8 Ref=360,100 (YAO20\8-88.D)

Area: 18333.5

MWD1 C, Sig=210,8 Ref=360,100 (YAO20\8-88.D)
### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>8.825</td>
<td>VV</td>
<td>0.2461</td>
<td>6892.05127</td>
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<tr>
<td>2</td>
<td>9.459</td>
<td>VB</td>
<td>0.2759</td>
<td>7138.33105</td>
<td>393.07870</td>
<td>50.8777</td>
</tr>
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</table>

**Totals:** 825.14746

### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
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<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>8.814</td>
<td>VV</td>
<td>0.1824</td>
<td>132.84184</td>
<td>11.53262</td>
<td>0.3823</td>
</tr>
<tr>
<td>2</td>
<td>9.187</td>
<td>VB</td>
<td>0.3317</td>
<td>3.46116e4</td>
<td>1542.96179</td>
<td>99.6177</td>
</tr>
</tbody>
</table>

**Totals:** 1554.49441

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**Chemical Structure:**

![Chemical Structure](image)
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
--- ------- ------- -------- -------
1 45.653 BV 1.2073 1.46786e4  177.04016  50.1230
2 48.827 VB 1.3625 1.46066e4  158.01196  49.8770
Totals : 2.92853e4 335.05212

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
--- ------- ------- -------- -------
1 45.547 BB 1.3380 2.47968e4  277.64362  99.5610
2 49.712 MM 1.2803 1.09.34953  1.42350  0.4390
Totals : 2.49062e4 335.05212

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
--- ------- ------- -------- -------
1 45.547 BB 1.3380 2.47968e4  277.64362  99.5610
2 49.712 MM 1.2803 1.09.34953  1.42350  0.4390
Totals : 2.49062e4 279.06711
<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>28.606</td>
<td>BP</td>
<td>0.7122</td>
<td>753.59131</td>
<td>13.60506</td>
<td>50.1497</td>
</tr>
<tr>
<td>2</td>
<td>31.300</td>
<td>VV</td>
<td>0.6875</td>
<td>749.09137</td>
<td>12.93819</td>
<td>49.8503</td>
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</table>

Totals: 1502.68268 26.54325

Signal 3: MWD1 C, Sig=210.8
Ref=360.100

<table>
<thead>
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<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>28.302</td>
<td>MM</td>
<td>1.0558</td>
<td>90.83733</td>
<td>1.43388</td>
<td>1.5843</td>
</tr>
<tr>
<td>2</td>
<td>30.948</td>
<td>VB</td>
<td>0.9454</td>
<td>564.261475</td>
<td>91.50510</td>
<td>98.4157</td>
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Totals: 5733.45207 92.93897
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<thead>
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<th>Height (mAU)</th>
<th>Area (%)</th>
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</thead>
<tbody>
<tr>
<td>41.073</td>
<td>BB</td>
<td>1.101</td>
<td>9302.50684</td>
<td>129.98210</td>
<td>50.0732</td>
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<tr>
<td>55.451</td>
<td>VB</td>
<td>1.411</td>
<td>9275.30566</td>
<td>92.23551</td>
<td>49.9268</td>
</tr>
</tbody>
</table>

Totals: $1.8578e+4$ mAU*s, $222.21761$ mAU

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area (mAU*s)</th>
<th>Height (mAU)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.424</td>
<td>VB</td>
<td>1.031</td>
<td>249.30116</td>
<td>2.83738</td>
<td>0.7788</td>
</tr>
<tr>
<td>53.796</td>
<td>BB</td>
<td>1.826</td>
<td>3.17606e4</td>
<td>234.44470</td>
<td>99.2212</td>
</tr>
</tbody>
</table>

Totals: $3.20099e+4$ mAU*s, $237.28209$ mAU

Signal 3: MWD1 C, Sig=210,8 Ref=360,100
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [mAU*s]</th>
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<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>4.670</td>
<td>MM</td>
<td>0.1120</td>
<td>389.2175</td>
<td>57.9370</td>
<td>50.6788</td>
</tr>
<tr>
<td>2</td>
<td>6.678</td>
<td>MM</td>
<td>0.1826</td>
<td>378.7915</td>
<td>78.2878</td>
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<td></td>
<td></td>
<td>768.0090</td>
<td>92.5142</td>
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Signal 1: MWD1 A, Sig=250,100 Ref=360,100

<table>
<thead>
<tr>
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<th>Type</th>
<th>Width [mAU*s]</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.249</td>
<td>MM</td>
<td>0.2976</td>
<td>8447.7949</td>
<td>473.1016</td>
<td>99.2555</td>
</tr>
<tr>
<td>2</td>
<td>6.669</td>
<td>MM</td>
<td>0.9822</td>
<td>63.3695</td>
<td>1.0753</td>
<td>0.7445</td>
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<tr>
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<td>8511.1644</td>
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S150
Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
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<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>6.167</td>
<td>MF</td>
<td>0.2403</td>
<td>2859.03613</td>
<td>198.30685</td>
<td>48.9020</td>
</tr>
<tr>
<td>2</td>
<td>6.609</td>
<td>FM</td>
<td>0.1582</td>
<td>66.97829</td>
<td>7.05811</td>
<td>0.8521</td>
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</table>

Totals: 5846.45581 383.05919

Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
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<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>6.159</td>
<td>MF</td>
<td>0.2429</td>
<td>7792.95996</td>
<td>534.67914</td>
<td>99.1479</td>
</tr>
<tr>
<td>2</td>
<td>6.600</td>
<td>FM</td>
<td>0.1582</td>
<td>66.97829</td>
<td>7.05811</td>
<td>0.8521</td>
</tr>
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</table>

Totals: 7859.93825 541.73725

---

23a

---
### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>%</td>
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<tr>
<td>1</td>
<td>26.983</td>
<td>BV</td>
<td>0.7082</td>
<td>3640.75757</td>
<td>75.28212</td>
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<tr>
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<td>29.081</td>
<td>VB</td>
<td>0.8073</td>
<td>3700.09692</td>
<td>65.07899</td>
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**Totals:** 7340.85449 140.36111

### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
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<tr>
<td>1</td>
<td>27.690</td>
<td>MF</td>
<td>0.8367</td>
<td>2.90638e4</td>
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<tr>
<td>2</td>
<td>29.756</td>
<td>FM</td>
<td>0.8905</td>
<td>354.86429</td>
<td>6.64148</td>
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</table>

**Totals:** 2.94186e4 585.55121
**Signal 3: MWD1 C, Sig=210,8 Ref=360,100**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>29.051</td>
<td>VV</td>
<td>1.0020</td>
<td>9274.04004</td>
<td>134.23459</td>
<td>50.3345</td>
</tr>
<tr>
<td>2</td>
<td>32.636</td>
<td>VB</td>
<td>1.1764</td>
<td>9150.77148</td>
<td>108.01012</td>
<td>49.6655</td>
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</tbody>
</table>

**Totals:** 1.84248e4 242.24471

**Signal 3: MWD1 C, Sig=210,8 Ref=360,100**

<table>
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<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
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<td>28.319</td>
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<td>1.5627</td>
<td>4.34380e4</td>
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<td>33.705</td>
<td>MM</td>
<td>1.2395</td>
<td>74.16568</td>
<td>108.01012</td>
<td>49.6655</td>
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**Totals:** 4.35121e4 464.28456

**23bS1**

![Graph of Signal 3: MWD1 C, Sig=210,8 Ref=360,100]
### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>32.817</td>
<td>VB</td>
<td>1.0170</td>
<td>6308.98682</td>
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<td>50.3866</td>
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<tr>
<td>2</td>
<td>40.385</td>
<td>BB</td>
<td>1.3166</td>
<td>6212.16943</td>
<td>64.56104</td>
<td>49.6134</td>
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</table>

**Totals:**
- Area: 1.25212e4 [mAU*s]
- Area %: 152.70578

---

### Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.260</td>
<td>MM</td>
<td>1.4188</td>
<td>1.68966e4</td>
<td>198.48203</td>
<td>99.6123</td>
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<tr>
<td>2</td>
<td>39.677</td>
<td>MM</td>
<td>0.9670</td>
<td>65.75671</td>
<td>1.13334</td>
<td>0.3877</td>
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</table>

**Totals:**
- Area: 1.69623e4 [mAU*s]
- Area %: 199.61536
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>13.094</td>
<td>VB</td>
<td>0.3188</td>
<td>9337.34863</td>
<td>444.97882</td>
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</tr>
<tr>
<td>2</td>
<td>17.492</td>
<td>VB</td>
<td>0.5446</td>
<td>9623.74023</td>
<td>252.50923</td>
<td>50.7552</td>
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</table>

Totals: 1.89611e4 697.48805

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

<table>
<thead>
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<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.903</td>
<td>MM</td>
<td>0.3132</td>
<td>230.10577</td>
<td>12.24614</td>
<td>7.7157</td>
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<tr>
<td>2</td>
<td>17.224</td>
<td>PB</td>
<td>0.4415</td>
<td>2752.19360</td>
<td>92.39245</td>
<td>92.2843</td>
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</table>

Totals: 2982.29938 104.63859
### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.792</td>
<td>BB</td>
<td>0.2996</td>
<td>311.73242</td>
<td>15.98258</td>
<td>50.4548</td>
</tr>
<tr>
<td>2</td>
<td>12.810</td>
<td>BB</td>
<td>0.3446</td>
<td>306.11273</td>
<td>13.49895</td>
<td>49.5452</td>
</tr>
</tbody>
</table>

**Totals:** 617.84515 29.48153

### Signal 2: MWD1 B, Sig=254,16 Ref=360,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.526</td>
<td>BB</td>
<td>0.2465</td>
<td>40.38449</td>
<td>2.52653</td>
<td>7.5520</td>
</tr>
<tr>
<td>2</td>
<td>12.229</td>
<td>MM</td>
<td>0.3876</td>
<td>494.36609</td>
<td>21.25785</td>
<td>92.4480</td>
</tr>
</tbody>
</table>

**Totals:** 534.75058 23.78438
Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th></th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.888</td>
<td>VV</td>
<td>0.7343</td>
<td>3128.99512</td>
<td>60.60584</td>
<td>51.1128</td>
</tr>
<tr>
<td>2</td>
<td>34.870</td>
<td>VB</td>
<td>0.8483</td>
<td>2992.74438</td>
<td>48.47647</td>
<td>48.8872</td>
</tr>
</tbody>
</table>

Totals: 6121.73950 109.08231

Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %

<table>
<thead>
<tr>
<th></th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.507</td>
<td>PV</td>
<td>0.8162</td>
<td>226.18513</td>
<td>3.25690</td>
<td>1.0226</td>
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<tr>
<td>2</td>
<td>34.345</td>
<td>VB</td>
<td>1.1085</td>
<td>2.18925e4</td>
<td>259.96841</td>
<td>98.9774</td>
</tr>
</tbody>
</table>

Totals: 2.21187e4 263.22532