

SUPPORTING INFORMATION

Cobalt-bisoxazoline Catalyzed Enantioselective Cross-Coupling of α -Bromo Esters with Alkenyl Grignard Reagents

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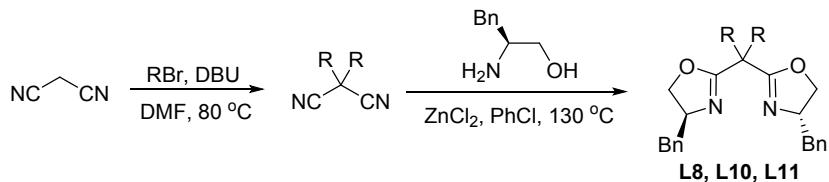
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1. General Information

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried following standard procedures and distilled before use. Alkenyl Grignard reagents and other commercial available reagents were purchased from Sigma Aldrich, Acros, or Alfa Aesar, and were used directly. Bisoxazoline ligands **L1–L11**¹, **L12**², **L13**³, **L14–L18**^{4–6} and α -bromo esters **1a–1v**, **4a–4m** and **10**^{1,2} were synthesized according to literature procedures. Racemic β,γ -unsaturated esters were prepared by repeating the similar procedures of the corresponding enantioenriched β,γ -unsaturated esters with racemic bisoxazoline ligand **L9**. ¹H and ¹³C NMR spectra were obtained from a Bruker DP-X300 MHz spectrometer, and chemical shifts (δ) were reported in ppm with internal tetramethylsilane (TMS) for ¹H NMR and the residual solvent signal of CDCl₃ for ¹³C NMR. High resolution mass spectrometry (HRMS) data were acquired using a Thermo Scientific Exactive Plus (EMR) with a quadrupole mass analyzer. GC-MS analysis was performed on a Varian 450GC-240MS mass spectrometer system with EI using a VF-5 capillary column (30m×0.25mm×0.25μm). Optical rotations were measured on a Rudolph Research Analytical AUTOPOL-IV polarimeter or a Perkin–Elmer PE-341 polarimeter. Enantiomeric excesses (ee) were determined by an Agilent 1200 HPLC system with a chiral column (Daicel Chiralcel OD-H, Daicel Chiralcel OJ-H, Daicel Chiralcel OX-H, Daicel Chiraldak AD-H, Phenomenex lux 5u Amylos-2, R&C OD) and *n*-hexane/isopropanol are the eluent.

2. Synthesis of the Ligands

Scheme S1. Synthesis of Ligand **L8**, **L10**, **L11**¹

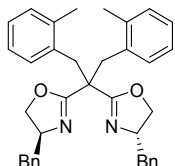


General Procedure 1.

To a stirring solution of malononitrile (3.30 g, 50 mmol) in dry DMF (130 mL) DBU (16.75 g, 110 mmol) was added at 0 °C. Alkyl bromide (110 mmol) was then added and the resulting mixture was stirring for 0.5 h at room temperature. After stirring for 8 h at 80 °C in an oil bath, the reaction mixture was cooled to room temperature. The reaction was quenched with water (100 mL) and diluted with CH₂Cl₂ (100 mL). Followed by the separation, the aqueous phase was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with saturated NaHCO₃ solution (150 mL) and brine (2 × 150 mL) sequentially, dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography to yield dialkylated malononitrile.

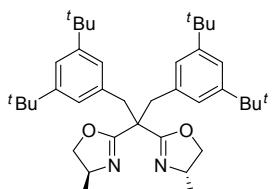
Dialkylated malononitrile (30 mmol) was dissolved in chlorobenzene (120 mL) at room temperature. Zinc chloride (12.27 g, 90 mmol) and (S)-2-amino-3-phenylpropan-1-ol (13.61 g, 90 mmol) were then added sequentially. The reaction mixture was heated to 130 °C in an oil bath and stirring for 24 h. After the reaction mixture was cooled to room temperature, ethylenediamine (45 mL) was added slowly. The resulting mixture

was stirred for another 3 h at room temperature and was diluted with water (150 mL) and CH_2Cl_2 (200 mL). Followed by the separation, the aqueous phase was extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were washed with saturated aqueous NaHCO_3 solution (150 mL) and brine (2×150 mL) sequentially, dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure, and the residue was purified by silica gel chromatography to afford the desired bisoxazoline ligand.



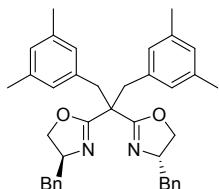
(4S,4'S)-2,2'-(1,3-di-*o*-Tolylpropane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (L8) (new compound)

Following the general procedure 1, the target product was synthesized from 2,2-bis(2-methylbenzyl)malononitrile (8.23 g, 30 mmol). The bisoxazoline **L8** was obtained as a colorless viscous liquid (11.05 g, 68% yield) after silica gel chromatography (petroleum ether/ethyl acetate 1:2). $[\alpha]_D^{20} = +7.71$ (c 2.65, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.41 – 7.18 (m, 18H), 4.48 – 4.32 (m, 2H), 4.11 – 4.08 (m, 2H), 3.88 – 3.85 (m, 2H), 3.55 (d, $J = 7.0$ Hz, 4H), 3.15 – 3.10 (m, 2H), 2.46 – 2.39 (m, 2H), 2.31 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.5, 138.1, 137.4, 135.8, 130.3, 129.8, 129.2, 128.5, 126.4, 126.4, 125.4, 71.9, 67.4, 47.9, 41.3, 36.2, 20.1. HRMS (ESI) m/z: Calcd for $\text{C}_{37}\text{H}_{39}\text{O}_2\text{N}_2$ [$\text{M}+\text{H}]^+$ 543.3006; Found 543.2996.



(4S,4'S)-2,2'-(1,3-Bis(3,5-di-*tert*-butylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (L10) (new compound)

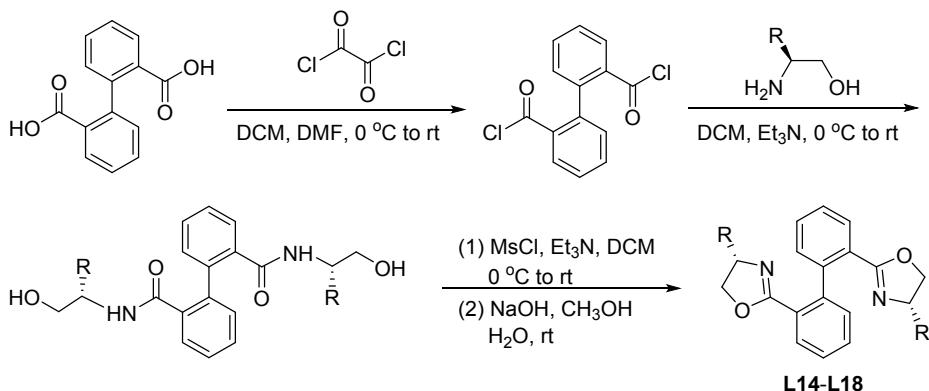
Following the general procedure 1, the target product was synthesized from 2,2-bis(3,5-di-*tert*-butylbenzyl)malononitrile (14.12 g, 30 mmol). The bisoxazoline **L10** was obtained as a white solid (12.86 g, 58% yield) after silica gel chromatography (petroleum ether/ethyl acetate 1:2). $[\alpha]_D^{20} = -12.35$ (c 1.81, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.32 – 7.22 (m, 12H), 7.19 – 7.11 (m, 4H), 4.30 – 4.26 (m, 2H), 4.17 – 4.11 (m, 2H), 3.95 – 3.86 (m, 2H), 3.55 (d, $J = 14.3$ Hz, 2H), 3.38 (d, $J = 14.4$ Hz, 2H), 3.00 (dd, $J = 13.9, 5.4$ Hz, 2H), 2.39 (dd, $J = 13.9, 9.0$ Hz, 2H), 1.34 (s, 36H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.2, 150.1, 138.2, 136.1, 129.1, 128.5, 126.3, 124.7, 120.6, 72.0, 67.4, 48.2, 41.8, 39.7, 34.8, 31.6. HRMS (ESI) m/z: Calcd for $\text{C}_{51}\text{H}_{67}\text{O}_2\text{N}_2$ [$\text{M}+\text{H}]^+$ 739.5197; Found 739.5302.



(4S,4'S)-2,2'-(1,3-Bis(3,5-dimethylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (L11) (new compound)

Following the general procedure 1, the target product was synthesized from 2,2-bis(3,5-dimethylbenzyl)malononitrile (9.07 g, 30 mmol). The bisoxazoline **L11** was obtained as a colorless viscous liquid (10.45 g, 61% yield) after silica gel chromatography (petroleum ether/ethyl acetate 1:2). $[\alpha]_D^{20} = +20.00$ (c 1.34, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.34 – 7.15 (m, 12H), 6.95 – 6.92 (m, 4H), 4.42 – 4.31 (m, 2H), 4.21 – 4.12 (m, 4H), 3.98 – 3.92 (m, 2H), 3.32 (s, 4H), 3.05 (dd, J = 13.6, 4.9 Hz, 2H), 2.35 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.0, 138.2, 137.2, 136.7, 129.1, 128.5, 128.5, 128.3, 126.4, 72.0, 67.5, 48.1, 41.7, 38.9, 21.4. HRMS (ESI) m/z: Calcd for $\text{C}_{39}\text{H}_{43}\text{O}_2\text{N}_2$ [M+H]⁺ 571.3319; Found 571.3315.

Scheme S2. Synthesis of Ligand **L14-L18**⁴⁻⁶



General Procedure 2.

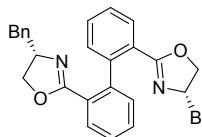
Under an argon atmosphere, to a solution of [1,1'-biphenyl]-2,2'-dicarboxylic acid (12.11 g, 50 mmol) in dry CH_2Cl_2 (100 mL) were added oxalyl chloride (31.66 g, 21.25 mL, 250 mmol) and DMF (0.1 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h, and the solvent was then removed under reduced pressure. The crude [1,1'-biphenyl]-2,2'-dicarbonyl dichloride was obtained as a light yellow solid.

The crude [1,1'-biphenyl]-2,2'-dicarbonyl dichloride was dissolved in dry CH_2Cl_2 (10 mL), and then was added to a stirred solution of amino alcohol (110 mmol) and Et_3N (25.30 g, 35.1 mL, 250 mmol) in CH_2Cl_2 (100 mL) at 0 °C. After the reaction mixture was stirring for 16 h at room temperature, it was quenched with water (100 mL) and diluted with CH_2Cl_2 (100 mL). The layers were separated, and aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with brine (3 × 150 mL), dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure to yield the desired bishydroxylamide.

After the desired bishydroxylamide was dissolved in dry CH_2Cl_2 (100 mL), Et_3N (250 mL) and methanesulfonyl chloride (14.32 g, 125 mmol) were then added slowly at 0 °C. The resulting mixture was stirring for 6 h, and the solvent was evaporated under reduced pressure to get the crude bismesylate as a yellow oil.

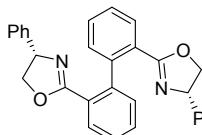
The crude bismesylate was dissolved in MeOH (250 mL), and NaOH (10 g, 250 mmol) in water (35 mL) was then added. The reaction mixture was stirring for 6 h at room temperature and diluted with CH_2Cl_2 (100 mL). The layers were separated, and aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL), and the combined organic layers were washed with brine (3 × 150 mL), dried over anhydrous Na_2SO_4 . The solvent

was evaporated under reduced pressure to yield the crude product, which was purified by silica gel chromatography to afford the corresponding bisoxazoline ligand.



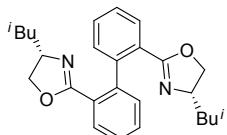
**2,2'-Bis((S)-4-benzyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (L14)
(CAS 282732-58-5)**

Following the general procedure 2, the target product was synthesized from (*S*)-2-amino-3-phenylpropan-1-ol (16.63 g, 110 mmol). The bisoxazoline **L14** was obtained as a colorless viscous liquid (11.81 g, 50% yield, dr = 2.3:1) after silica gel chromatography (petroleum ether/ethyl acetate 1:1). The dr was determined by ¹H NMR analysis of the methylene region on benzyl of **L14**, and the configuration of major diastereomer was assigned as (*S*, *aS*, *S*).⁵ [α]_D²⁰ = -108.59 (c 1.09, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.88 – 7.79 (m, 2H), 7.51 – 7.09 (m, 16H), 4.41 – 4.31 (m, 2H), 4.13 – 3.95 (m, 2H), 3.89 – 3.78 (m, 2H), 3.10 – 2.93 (m, 2H), 2.66 – 2.55 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (164.6) 164.5, (141.7) 141.4, 138.2, (130.2) 130.1, 129.9, 129.5, 129.3 (129.2), 129.1, 128.3 (127.8), 127.0, 126.3, 71.9, 67.9, (41.4) 41.2. HRMS (ESI) m/z: Calcd for C₃₂H₂₉N₂O₂ [M+H]⁺ 473.2229; Found 473.2232.



**2,2'-Bis((S)-4-phenyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl
(L15) (CAS 282732-57-4)**

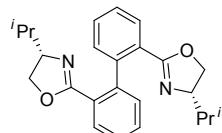
Following the general procedure 2, the target product was synthesized from (*S*)-2-amino-2-phenylethan-1-ol (15.09 g, 110 mmol). The bisoxazoline **L15** was obtained as a white solid (9.56 g, 43% yield, dr = 2.3:1) after silica gel chromatography (petroleum ether/ethyl acetate 1:1). The dr was determined by ¹H NMR analysis of the methylene region on oxazoline cycle of **L15**, and the configuration of major diastereomer was assigned as (*S*, *aS*, *S*).⁵ [α]_D²⁰ = -155.81 (c 0.83, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.94 – 7.89 (m, 2H), 7.39 – 7.10 (m, 16H), 5.24 – 5.12 (m, 2H), 4.47 – 4.36 (m, 2H), 3.95 – 3.79 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 165.9 (165.2), (142.4) 142.3, (141.8) 141.3, 130.3, 130.2 (129.9), 129.5, 128.5, 128.4, (127.7) 127.3, 127.2, 126.9, 75.0 (74.4), 69.8. HRMS (ESI) m/z: Calcd for C₃₀H₂₅N₂O₂ 445.1916; Found 445.1918.



**2,2'-Bis((S)-4-iso-butyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl
(L16) (CAS 1428785-62-9)**

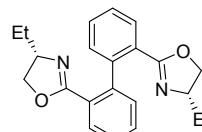
Following the general procedure 2, the target product was synthesized from (*S*)-2-amino-4-methylpentan-1-ol (12.89 g, 110 mmol). The bisoxazoline **L16** was obtained as a colorless viscous liquid (11.33 g, 56% yield, dr = 2.0:1) after silica gel chromatography (petroleum ether/ethyl acetate 1:1). The dr was determined by ¹H NMR analysis of the 3-H and 3'-H region on biphenyl backbone of **L16**, and the configuration of major diastereomer was assigned as (*S*, *aS*, *S*).⁵ [α]_D²⁰ = -135.7 (c 1.61, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.84 – 7.73 (m, 2H), 7.45 – 7.24 (m, 6H), 4.21

– 4.05 (m, 4H), 3.64 – 3.57 (m, 2H), 1.56 – 1.43 (m, 4H), 1.26 – 1.13 (m, 2H), 0.88 – 0.84 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 163.7, 129.9, (129.9) 129.7, 129.4, 129.0, 127.9, 126.8, 73.1, 64.9, 45.1, (25.3) 25.1, 22.8 (22.6), 22.4. HRMS (ESI) m/z: Calcd for $\text{C}_{26}\text{H}_{33}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}]^+$ 405.2542; Found 405.2542.



2,2'-Bis((S)-4-iso-propyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (L17) (CAS 190327-53-8)

Following the general procedure 2, the target product was synthesized from (*S*)-2-amino-3-methylbutan-1-ol (11.35 g, 110 mmol). The bisoxazoline **L17** was obtained as a colorless viscous liquid (8.85 g, 47% yield, dr = 2.7:1) after silica gel chromatography (petroleum ether/ethyl acetate 1:1). The dr was determined by ^1H NMR analysis of the 3-H and 3'-H region on biphenyl backbone of **L17**, and the configuration of major diastereomer was assigned as (*S*, *aS*, *S*).⁵ $[\alpha]_D^{20} = -174.40$ (*c* 1.00, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.86 – 7.77 (m, 2H), 7.47 – 7.20 (m, 6H), 4.14 – 3.69 (m, 6H), 1.73 – 1.62 (m, 2H), 0.86 – 0.77 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3) δ 164.0, 141.4, 130.1 (129.8), (129.4) 129.3, 129.1, 127.8, 126.9 (126.8), 72.6, 70.2, (32.7) 32.5, 18.8, (18.3) 18.1. HRMS (ESI) m/z: Calcd for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}]^+$ 377.2229; Found 377.2228.

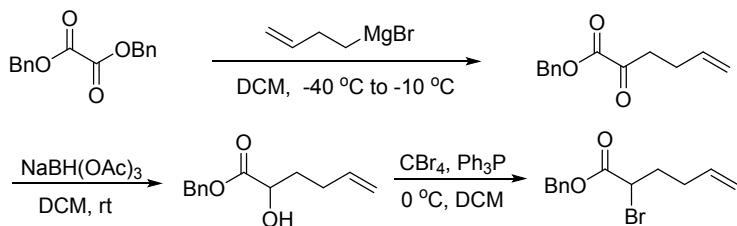


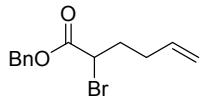
2,2'-Bis((S)-4-ethyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (L18) (new compound)

Following the general procedure 2, the target product was synthesized from (*S*)-2-aminobutan-1-ol (9.81 g, 110 mmol). The bisoxazoline **L18** was obtained as a white solid (6.62 g, 38% yield, dr = 2.1:1) after silica gel chromatography (petroleum ether/ethyl acetate 1:1). The dr was determined by ^1H NMR analysis of the 4-H, 5-H, 6-H and 4'-H, 5'-H, 6'-H region on biphenyl backbone of **L18**. $[\alpha]_D^{20} = -165.3$ (*c* 1.58, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.84 – 7.79 (m, 2H), 7.50 – 7.31 (m, 6H), 4.20 – 3.96 (m, 4H), 3.74 – 3.64 (m, 2H), 1.54 – 1.44 (m, 4H), 0.88 – 0.80 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 164.0, (141.5) 141.4, 130.0 (129.9), (129.6) 129.3, 129.1, 127.8, 126.8, 72.2, (67.9) 67.7, 28.2, (10.1) 9.8. HRMS (ESI) m/z: Calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}]^+$ 349.1916; Found 349.1916.

3. Synthesis of the Racemic α -Bromoester 4n

Scheme S3. Synthesis of the Racemic Benzyl 2-Bromohex-5-enoate





Benzyl 2-bromohex-5-enoate (4n) (new compound)^{1,7,8}

Under an argon atmosphere, to a mixture of magnesium turnings (0.72 g, 30 mmol) and I₂ (0.10 g, 0.4 mmol) in dry THF (20 mL) was added 1-bromo-3-butene (2.70 g, 20 mmol). The reaction was initiated by gently heating with a heat gun, and stirred vigorously at 70 °C in an oil bath for 2 h to get the but-3-en-1-ylmagnesium bromide solution (0.73 M in THF).

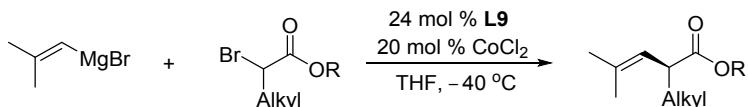
To a solution of dibenzyl oxalate (2.90 g, 10.7 mmol) in CH₂Cl₂ (80 mL), the Grignard solution (15 mL, 0.73 M in THF, 11.0 mmol) was added slowly at -40 °C. The reaction mixture was stirring for 0.5 h and warmed to -10 °C over 1 h. After stirring for another 1 h at -10 °C, the reaction was quenched with saturated aqueous NH₄Cl solution (20 mL). The layers were separated, and aqueous phase was extracted with Et₂O (3 × 30 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to yield the crude benzyl 2-oxohex-5-enoate as a pale yellow oil.

The crude benzyl 2-oxohex-5-enoate was dissolved in CH₂Cl₂ (40 mL), NaBH(OAc)₃ (3.43 g, 16.2 mmol) was then added. The reaction mixture was stirred for 10 h and quenched with saturated NaHCO₃ solution (20 mL) at room temperature. The layers were separated, and aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to yield the crude product. The crude product was purified by silica gel chromatography (EtOAc/n-hexane 1:5) to afford benzyl 2-hydroxyhex-5-enoate (1.10 g, 47% yield).

2-Hydroxyhex-5-enoate (1.10 g, 5.0 mmol) was dissolved in CH₂Cl₂ (15 mL), and was cooled to 0 °C. Ph₃P (4.22 g, 16.1 mmol) and CBr₄ (2.49 g, 7.5 mmol) were then added sequentially. After the reaction mixture was stirred for 3 h at 0 °C, it was concentrated under reduced pressure. n-Hexane was added to the residue and precipitated Ph₃PO. The resulting mixture was filtered, and filtrate was concentrated under reduced pressure to yield crude product. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 100:1) to give benzyl 2-bromohex-5-enoate **4n** (1.06 g, 75% yield) as a pale yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 7.39 – 7.33 (m, 5H), 5.73 (ddt, *J* = 11.1, 10.2, 6.4 Hz, 1H), 5.21 (s, 2H), 5.09 – 5.01 (m, 2H), 4.30 – 4.25 (m, 1H), 2.25 – 2.08 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 135.9, 135.2, 128.6, 128.5, 128.2, 116.5, 67.6, 45.2, 33.8, 31.1. HRMS (ESI) m/z: Calcd for C₁₃H₁₆O₂Br [M+H]⁺ 283.0328; Found 283.0333.

4. Enatioselective Kumada Cross-Coupling Reaction

Scheme S4. Enatioselective Kumada Cross-Coupling of Isobutenyl Magnesium Bromide

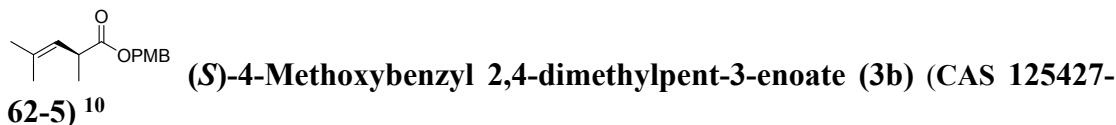


General Procedure 3.

Anhydrous CoCl_2 (6.5 mg, 0.05 mmol) was placed in a 50-mL Schlenk tube and heated at 80°C with a heating mantle for 2 h in vacuo. After being cooled to room temperature under an argon atmosphere, anhydrous THF (2 mL) and **L9** (37.6 mg, 0.06 mmol) in THF (1 mL) were added. The resulting mixture was stirred for 2 h at room temperature, and was cooled to -40°C . Racemic α -bromo ester (0.25 mmol) was added via syringe, and the suspension of (2-methylprop-1-en-1-yl) magnesium bromide **2a** (2.7 mL, 0.37 M in THF, 1 mmol) diluted in THF (5 mL) was then added dropwise over 2.5 h by injection pump. The reaction mixture was stirred for 5 h at -40°C , and quenched with saturated NH_4Cl solution (3 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography to provide corresponding enantioenriched β,γ -unsaturated ester.

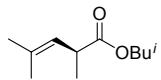


Following the general procedure 3, the target product was synthesized from benzyl 2-bromopropanoate **1a** (60.8 mg, 0.25 mmol). The product **3a** was obtained as a pale yellow oil (43.7 mg, 80% yield, 91% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +74.09$ (c 0.77, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 7.97$ min (*S*), minor $t_r = 8.83$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 87.37–7.31 (m, 5H), 5.20–5.16 (m, 1H), 5.12 (s, 2H), 3.39 (dq, $J = 9.2, 7.0$ Hz, 1H), 1.72 (d, $J = 1.2$ Hz, 3H), 1.66 (d, $J = 1.2$ Hz, 3H), 1.23 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.2, 136.3, 134.2, 128.5, 128.0, 127.8, 123.8, 66.0, 39.0, 25.6, 18.0, 17.9. HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}]^+$ 219.1380; Found 219.1378.



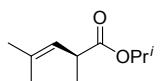
Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromopropanoate **1b** (68.3 mg, 0.25 mmol). The product **3b** was obtained as a pale yellow oil (37.2 mg, 60% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +67.88$ (c 1.73, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 22.64$ min (*S*), minor $t_r = 21.66$ min (*R*)).

¹H NMR (300 MHz, CDCl₃) δ 7.29 – 6.87 (m, 4H), 5.18 – 5.14 (m, 1H), 5.04 (s, 2H), 3.81 (s, 3H), 3.39 – 3.29 (m, 1H), 1.70 (s, 3H), 1.64 (s, 3H), 1.20 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.3, 159.5, 134.0, 129.7, 128.4, 123.8, 113.8, 65.9, 55.2, 39.0, 25.6, 18.0. HRMS (ESI) m/z: Calcd for C₁₅H₂₁O₃ [M+H]⁺ 249.1485; Found 249.1479.



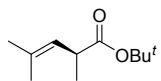
(S)-iso-Butyl 2,4-dimethylpent-3-enoate (3c) (new compound)

Following the general procedure 3, the target product was synthesized from isobutyl 2-bromopropanoate **1c** (52.3 mg, 0.25 mmol). The product **3c** was obtained as a pale yellow oil (28.6 mg, 62% yield, 85% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). [α]_D²⁰ = +54.67 (*c* 0.60, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 8.60 min (*S*), minor *t*_r = 8.28 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 5.16 – 5.12 (m, 1H), 3.84 (dd, *J* = 6.6, 3.9 Hz, 2H), 3.32 (dq, *J* = 9.2, 7.0 Hz, 1H), 1.94 – 1.87 (m, 1H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 175.5, 133.8, 124.1, 70.4, 39.1, 29.7, 27.8, 25.6, 19.0, 18.01, 17.99. HRMS (ESI) m/z: Calcd for C₁₁H₂₁O₂ [M+H]⁺ 185.1536; Found 185.1538.



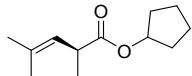
(S)-iso-Propyl 2,4-dimethylpent-3-enoate (3d) (CAS 108584-76-5)¹⁰

Following the general procedure 3, the target product was synthesized from isopropyl 2-bromopropanoate **1d** (48.8 mg, 0.25 mmol). The product **3d** was obtained as a pale yellow oil (30 mg, 70% yield, 91% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). [α]_D²⁰ = +10.24 (*c* 0.27, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 4.33 min (*S*), minor *t*_r = 4.19 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 5.17 – 5.13 (m, 1H), 4.96 (dd, *J* = 12.5, 6.3 Hz, 1H), 3.25 (dq, *J* = 9.0, 7.0 Hz, 1H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.25 – 1.16 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 175.1, 133.7, 124.1, 67.4, 39.2, 25.7, 21.8, 21.7, 18.2, 18.0. HRMS (ESI) m/z: Calcd for C₁₀H₁₉O₂ [M+H]⁺ 171.1380; Found 171.1388.



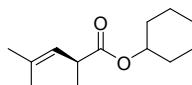
(S)-tert-Butyl 2,4-dimethylpent-3-enoate (3e) (CAS 125427-60-3)¹⁰

Following the general procedure 3, the target product was synthesized from *tert*-butyl 2-bromopropanoate **1e** (52.3 mg, 0.25 mmol). The product **3e** was obtained as a pale yellow oil (32.2 mg, 70% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). [α]_D²⁰ = +68.14 (*c* 0.39, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 5.48 min (*S*), minor *t*_r = 5.20 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 5.14 – 5.11 (m, 1H), 3.19 (dq, *J* = 13.9, 6.9 Hz, 1H), 1.71 (d, *J* = 1.1 Hz, 3H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.43 (s, 9H), 1.15 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.9, 133.4, 124.4, 79.9, 40.0, 28.1, 25.7, 18.1, 18.0. HRMS (ESI) m/z: Calcd for C₁₁H₂₁O₂ [M+H]⁺ 185.1536; Found 185.1530.



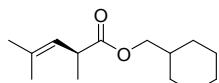
(S)-Cyclopentyl 2,4-dimethylpent-3-enoate (3f) (new compound)

Following the general procedure 3, the target product was synthesized from cyclopentyl 2-bromopropanoate **1f** (55.3 mg, 0.25 mmol). The product **3f** was obtained as a pale yellow oil (36.8 mg, 75% yield, 83% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +79.39$ (*c* 1.09, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major $t_r = 4.77$ min (*S*), minor $t_r = 4.51$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 5.14 – 5.09 (m, 2H), 3.31 – 3.18 (m, 1H), 1.70 – 1.58 (m, 14 H), 1.16 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.2, 133.8, 124.1, 76.8, 39.1, 32.6, 32.6, 25.6, 23.7, 23.7, 18.0, 17.9. HRMS (ESI) m/z: Calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$ 219.1356; Found 219.1366.



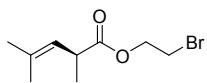
(S)-Cyclohexyl 2,4-dimethylpent-3-enoate (3g) (new compound)

Following the general procedure 3, the target product was synthesized from cyclohexyl 2-bromopropanoate **1g** (58.8 mg, 0.25 mmol). The product **3g** was obtained as a pale yellow oil (40.0 mg, 76% yield, 85% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +90.64$ (*c* 0.63, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major $t_r = 4.78$ min (*S*), minor $t_r = 4.32$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 5.17 – 5.12 (m, 1H), 4.73 (td, *J* = 8.5, 3.7 Hz, 1H), 3.27 (dq, *J* = 9.0, 7.0 Hz, 1H), 1.78 – 1.65 (m, 10H), 1.40 – 1.30 (m, 6H), 1.18 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.9, 133.7, 124.2, 72.1, 39.3, 31.5, 31.4, 25.6, 25.4, 23.5, 23.5, 18.0. HRMS (ESI) m/z: Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$ 233.1512; Found 233.1519.



(S)-Cyclohexylmethyl 2,4-dimethylpent-3-enoate (3h) (CAS 108584-81-2)¹¹

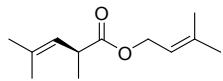
Following the general procedure 3, the target product was synthesized from cyclohexylmethyl 2-bromopropanoate **1h** (62.3 mg, 0.25 mmol). The product **3h** was obtained as a pale yellow oil (43.2 mg, 77% yield, 72% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +61.15$ (*c* 1.05, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major $t_r = 4.34$ min (*S*), minor $t_r = 4.15$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 5.16 – 5.12 (m, 1H), 3.86 (dd, *J* = 6.4, 2.5 Hz, 2H), 3.31 (dq, *J* = 9.2, 7.0 Hz, 1H), 1.72 – 1.63 (m, 14H), 1.25 – 1.18 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.5, 133.8, 124.1, 69.5, 39.1, 37.2, 29.6, 26.4, 25.7, 25.6, 18.0. HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Na} [\text{M}+\text{Na}]^+$ 247.1668; Found 247.1669.



(S)-2-Bromoethyl 2,4-dimethylpent-3-enoate (3i) (new compound)

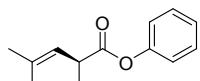
Following the general procedure 3, the target product was synthesized from 2-bromoethyl 2-bromopropanoate **1i** (65.0 mg, 0.25 mmol). The product **3i** was obtained as a pale yellow oil (42.9 mg, 73% yield, 85% ee) after silica gel chromatography

(petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +104.62$ (*c* 0.26, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 0.7 mL/min, 220 nm, major *t*_r = 6.48 min (*S*), minor *t*_r = 6.27 min (*R*)). ¹H NMR (400 MHz, CDCl₃) δ 5.14 – 5.12 (m, 1H), 4.36 (t, *J* = 6.1 Hz, 2H), 3.49 (t, *J* = 6.1 Hz, 2H), 3.37 – 3.33 (m, 1H), 1.71 (s, 3H), 1.67 (s, 3H), 1.21 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 175.0, 134.3, 123.7, 63.3, 38.8, 28.9, 25.7, 17.9. HRMS (ESI) m/z: Calcd for C₉H₁₆O₂Br [M+H]⁺ 235.0328; Found 235.0331.



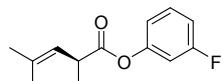
(*S*)-3-Methylbut-2-en-1-yl 2,4-dimethylpent-3-enoate (3j) (CAS 108584-82-3)¹¹

Following the general procedure 3, the target product was synthesized from 3-methylbut-2-en-1-yl 2-bromopropanoate **1j** (55.3 mg, 0.25 mmol). The product **3j** was obtained as a pale yellow oil (32 mg, 65% yield, 85% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +63.62$ (*c* 0.77, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 4.96 min (*S*), minor *t*_r = 4.71 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 5.35 – 5.29 (m, 1H), 5.18 – 5.14 (m, 1H), 4.55 (d, *J* = 7.1 Hz, 2H), 3.31 (dq, *J* = 9.1, 7.0 Hz, 1H), 1.75 – 1.64 (m, 12H), 1.19 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.6, 138.6, 133.8, 124.0, 118.8, 61.4, 39.1, 25.7, 25.7, 18.1, 18.0, 17.9. HRMS (ESI) m/z: Calcd for C₁₂H₂₁O₂ [M+H]⁺ 197.1536; Found 197.1539.



(*S*)-Phenyl 2,4-dimethylpent-3-enoate (3k) (new compound)

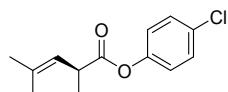
Following the general procedure 3, the target product was synthesized from phenyl 2-bromopropanoate **1k** (57.3 mg, 0.25 mmol). The product **3k** was obtained as a pale yellow oil (31.2 mg, 61% yield, 86% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +88.04$ (*c* 0.71, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 18.64 min (*S*), minor *t*_r = 15.48 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.04 (m, 5H), 5.30 – 5.24 (m, 1H), 3.61 – 3.46 (m, 1H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.75 (d, *J* = 1.2 Hz, 3H), 1.34 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 173.8, 151.0, 134.9, 129.3, 125.6, 123.3, 121.5, 39.2, 25.7, 18.1, 17.9. HRMS (ESI) m/z: Calcd for C₁₃H₁₇O₂ [M+H]⁺ 205.1223; Found 205.1222.



(*S*)-3-Fluorophenyl 2,4-dimethylpent-3-enoate (3l) (new compound)

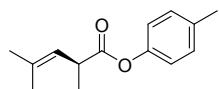
Following the general procedure 3, the target product was synthesized from 3-fluorophenyl 2-bromopropanoate **1l** (61.7 mg, 0.25 mmol). The product **3l** was obtained as a pale yellow oil (35.0 mg, 63% yield, 76% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +93.58$ (*c* 0.89, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 7.37 min (*S*), minor *t*_r = 6.14 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.36 – 7.26 (m, 1H), 6.95 – 6.82 (m, 2H), 5.25 – 5.21 (m, 1H), 3.55 (dq, *J* = 9.1, 6.9 Hz, 1H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 173.4, 162.9 (d, *J* = 245.8 Hz), 151.8

(d, $J = 10.8$ Hz), 135.2, 130.0 (d, $J = 9.3$ Hz), 123.0, 117.3 (d, $J = 3.2$ Hz), 112.6 (d, $J = 21.0$ Hz), 109.6 (d, $J = 24.1$ Hz), 39.1, 25.7, 18.1, 17.8. ^{19}F NMR (282 MHz, CDCl_3) $\delta -111.3$. HRMS (ESI) m/z: Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{F} [\text{M}+\text{H}]^+$ 223.1129; Found 223.1127.



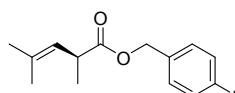
(S)-4-Chlorophenyl 2,4-dimethylpent-3-enoate (3m) (new compound)

Following the general procedure 3, the target product was synthesized from 4-chlorophenyl 2-bromopropanoate **1m** (65.9 mg, 0.25 mmol). The product **3m** was obtained as a pale yellow oil (35.2 mg, 59% yield, 81% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+97.35$ (c 1.71, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 8.20$ min (*S*), minor $t_r = 7.45$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.35 – 6.98 (m, 4H), 5.26 – 5.22 (m, 1H), 3.60 – 3.50 (m, 1H), 1.77 (d, $J = 1.2$ Hz, 3H), 1.74 (d, $J = 1.2$ Hz, 3H), 1.33 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 173.6, 149.4, 135.1, 131.0, 129.3, 123.0, 122.9, 39.1, 25.7, 18.1, 17.9. HRMS (ESI) m/z: Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Cl} [\text{M}+\text{H}]^+$ 239.0833; Found 239.0832.



(S)-*p*-Tolyl 2,4-dimethylpent-3-enoate (3n) (new compound)

Following the general procedure 3, the target product was synthesized from *p*-tolyl 2-bromopropanoate **1n** (60.8 mg, 0.25 mmol). The product **3n** was obtained as a pale yellow oil (39.8 mg, 73% yield, 87% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+114.07$ (c 1.82, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 16.27$ min (*S*), minor $t_r = 14.81$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.18 – 6.94 (m, 2H), 5.29 – 5.25 (m, 1H), 3.56 (dq, $J = 9.1, 7.0$ Hz, 1H), 2.34 (s, 3H), 1.78 (d, $J = 1.3$ Hz, 3H), 1.75 (d, $J = 1.3$ Hz, 3H), 1.35 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.0, 148.7, 135.2, 134.7, 129.8, 123.4, 121.1, 39.1, 25.7, 20.8, 18.1, 18.0. HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2 [\text{M}+\text{H}]^+$ 219.1380; Found 219.1381.



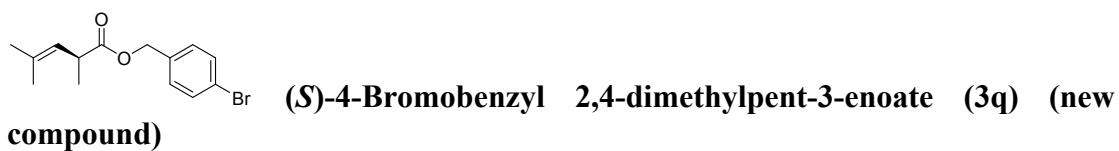
(S)-4-Fluorobenzyl 2,4-dimethylpent-3-enoate (3o) (CAS 125427-61-4)¹⁰

Following the general procedure 3, the target product was synthesized from 4-fluorobenzyl 2-bromopropanoate **1o** (65.3 mg, 0.25 mmol). The product **3o** was obtained as a pale yellow oil (41 mg, 69% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+56.35$ (c 2.3, CHCl_3). The ee was determined by HPLC with a Phenomenex lux 5u Amylos-2 (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 10.83$ min (*S*), minor $t_r = 11.36$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.28 (m, 2H), 7.06 – 7.00 (m, 2H), 5.17 – 5.13 (m, 1H), 5.07 (s, 2H), 3.36 (dq, $J = 9.2, 7.0$ Hz, 1H), 1.71 (d, $J = 1.2$ Hz, 3H), 1.64 (d, $J = 1.1$ Hz, 3H), 1.21 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.1, 162.5 (d, $J = 245.0$ Hz), 160.9, 134.2, 132.1 (d, $J = 3.2$ Hz), 132.1, 129.8 (d, $J = 8.2$ Hz), 123.7,

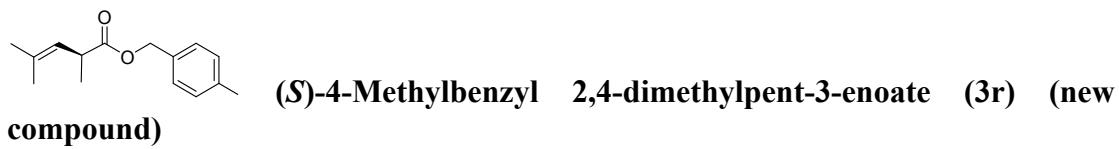
115.4 (d, $J = 21.4$ Hz), 65.3, 39.0, 25.6, 18.0, 17.9. ^{19}F NMR (282 MHz, DMSO) δ – 114.0. HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{F} [\text{M}+\text{H}]^+$ 237.1285; Found 237.1282.



Following the general procedure 3, the target product was synthesized from 4-(trifluoromethyl)benzyl 2-bromopropanoate **1p** (77.8 mg, 0.25 mmol). The product **3p** was obtained as a pale yellow oil (41.5 mg, 58% yield, 86% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+49.85$ (c 1.34, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OX column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 11.36$ min (*S*), minor $t_r = 13.35$ min (*R*)). ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 5.20 – 5.12 (m, 3H), 3.44 – 3.37 (m, 1H), 1.73 (s, 3H), 1.67 (s, 3H), 1.23 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.4, 140.3, 134.1, 130.1 (q, $J = 32.6$ Hz), 127.7, 125.4 (q, $J = 3.7$ Hz), 124.0 (q, $J = 270.4$ Hz), 123.5, 65.1, 38.9, 25.6, 18.2, 18.0. ^{19}F NMR (282 MHz, CDCl_3) δ – 62.6. HRMS (ESI) m/z: Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{F}_3 [\text{M}+\text{H}]^+$ 287.1253; Found 287.1249.

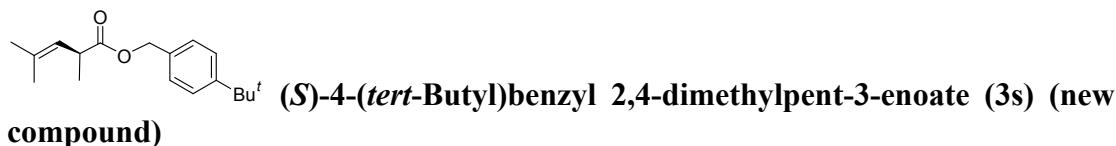


Following the general procedure 3, the target product was synthesized from 4-bromobenzyl 2-bromopropanoate **1q** (80.5 mg, 0.25 mmol). The product **3q** was obtained as a pale yellow oil (37.1 mg, 50% yield, 74% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+52.65$ (c 1.31, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major $t_r = 20.11$ min (*S*), minor $t_r = 18.10$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.49 – 7.19 (m, 4H), 5.19 – 5.05 (m, 3H), 3.37 (dq, $J = 14.3, 7.2$ Hz, 1H), 1.71 (s, 3H), 1.65 (s, 3H), 1.22 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.1, 135.3, 134.3, 131.6, 129.5, 128.8, 127.7, 124.7, 123.6, 65.2, 39.0, 25.6, 18.0, 17.9. HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Br} [\text{M}+\text{H}]^+$ 297.0485; Found 297.0484.

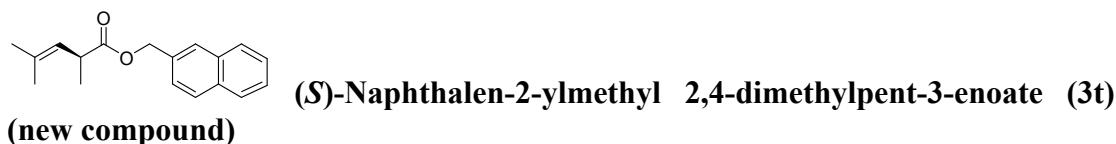


Following the general procedure 3, the target product was synthesized from 4-methylbenzyl 2-bromopropanoate **1r** (64.3 mg, 0.25 mmol). The product **3r** was obtained as a pale yellow oil (43.6 mg, 75% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+75.90$ (c 1.66, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 6.39$ min (*S*), minor $t_r = 8.16$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.26 – 7.15 (m, 4H), 5.19 – 5.15 (m, 1H), 5.07 (s, 2H), 3.37 (dq, $J = 9.2, 7.0$ Hz, 1H), 2.35 (s, 3H), 1.72 (d, $J = 1.2$ Hz, 3H), 1.65 (d, $J = 1.2$ Hz, 3H), 1.22 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.3, 137.8, 134.0, 133.3,

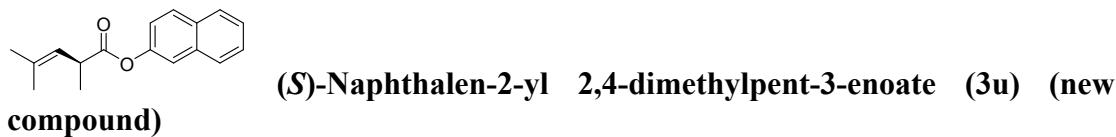
129.1, 128.0, 123.8, 66.0, 39.0, 25.6, 21.1, 18.01, 17.98. HRMS (ESI) m/z: Calcd for C₁₅H₂₀O₂ [M+H]⁺ 233.1536; Found 233.1535.



Following the general procedure 3, the target product was synthesized from 4-(*tert*-butyl)benzyl 2-bromopropanoate **1s** (74.8 mg, 0.25 mmol). The product **3s** was obtained as a pale yellow oil (45.3 mg, 66% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +56.18$ (*c* 2.41, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OX-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major t_r = 14.37 min (*S*), minor t_r = 13.91 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.26 (m, 4H), 5.24 – 5.17 (m, 1H), 5.09 (s, 2H), 3.38 (dq, *J* = 9.1, 7.0 Hz, 1H), 1.73 (d, *J* = 1.2 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H), 1.33 (s, 9H), 1.23 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.3, 151.0, 134.0, 133.3, 127.7, 125.4, 123.8, 65.9, 39.0, 34.5, 31.3, 25.6, 18.0. HRMS (ESI) m/z: Calcd for C₁₈H₂₇O₂ [M+H]⁺ 275.2006; Found 275.2005.

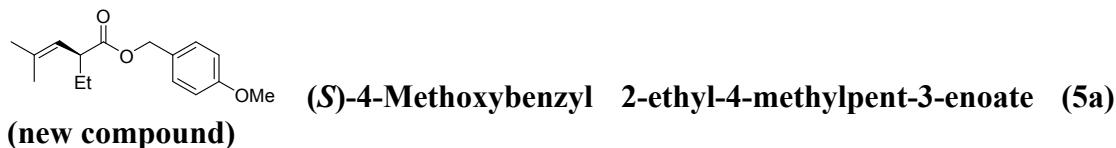


Following the general procedure 3, the target product was synthesized from naphthalen-2-yl 2-bromopropanoate **1t** (73.3 mg, 0.25 mmol). The product **3t** was obtained as a pale yellow oil (53.0 mg, 79% yield, 93% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +69.89$ (*c* 2.51, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (1% isopropanol in *n*-hexane, 1 mL/min, 254 nm, major t_r = 7.51 min (*S*), minor t_r = 7.22 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.86 – 7.81 (m, 4H), 7.53 – 7.43 (m, 3H), 5.29 (s, 2H), 5.24 – 5.20 (m, 1H), 3.44 (dq, *J* = 9.0, 7.0 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H), 1.27 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 175.2, 134.2, 133.7, 133.2, 133.0, 128.2, 127.9, 127.7, 126.9, 126.2, 126.1, 125.6, 123.8, 66.1, 39.0, 25.6, 18.0, 17.9. HRMS (ESI) m/z: Calcd for C₁₈H₂₁O₂ [M+H]⁺ 269.1536; Found 269.1528.

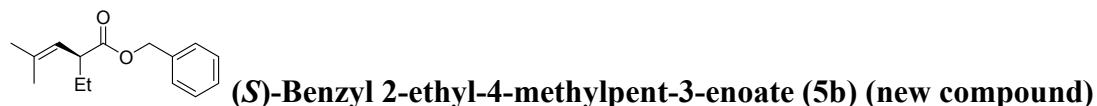


Following the general procedure 3, the target product was synthesized from naphthalen-2-yl 2-bromopropanoate **1u** (69.8 mg, 0.25 mmol). The product **3u** was obtained as a pale yellow oil (43.9 mg, 69% yield, 81% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +136.92$ (*c* 0.52, CHCl₃). The ee was determined by HPLC with a R&C OD column (1% isopropanol in *n*-hexane, 1 mL/min, 254 nm, major t_r = 5.53 min (*S*), minor t_r = 5.91 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.86 – 7.78 (m, 3H), 7.55 – 7.43 (m, 3H), 7.26 – 7.19 (m, 1H), 5.34 – 5.31 (m, 1H), 3.64 (dq, *J* = 9.0, 7.0 Hz, 1H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.79 (d, *J* = 1.3 Hz, 3H), 1.40 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.0, 148.6, 134.9,

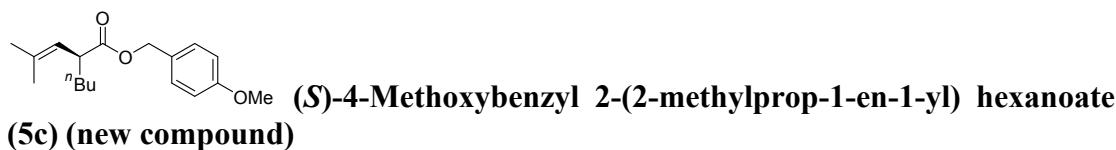
133.8, 131.4, 129.6, 127.7, 127.6, 126.5, 125.6, 123.3, 121.1, 118.4, 39.2, 25.7, 18.2, 18.0. HRMS (ESI) m/z: Calcd for C₁₇H₁₉O₂ [M+H]⁺ 255.1380; Found 255.1372.



Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromobutanoate **4a** (71.8 mg, 0.25 mmol). The product **5a** was obtained as a pale yellow oil (53.8 mg, 82% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +62.98$ (*c* 2.28, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 30.49 min (*S*), minor *t*_r = 25.03 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.29 – 6.86 (m, 4H), 5.15 – 5.11 (m, 1H), 5.04 (s, 2H), 3.80 (s, 3H), 3.16 (dt, *J* = 9.3, 7.3 Hz, 1H), 1.77 – 1.70 (m, 4H), 1.64 (d, *J* = 1.1 Hz, 3H), 1.53 – 1.48 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.8, 159.5, 134.8, 129.7, 128.4, 122.5, 113.8, 65.8, 55.2, 46.5, 26.2, 25.7, 18.2, 11.6. HRMS (ESI) m/z: Calcd for C₁₆H₂₃O₃ [M+H]⁺ 263.1645; Found 263.1635.

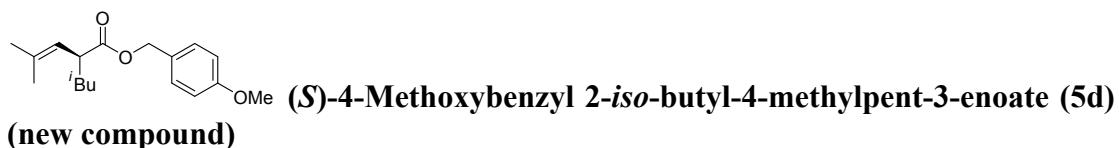


Following the general procedure 3, the target product was synthesized from benzyl 2-bromobutanoate **4b** (64.3 mg, 0.25 mmol). The product **5b** was obtained as a pale yellow oil (44.1 mg, 76% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +62.93$ (*c* 0.55, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (*n*-hexane, 0.5 mL/min, 220 nm, major *t*_r = 26.80 min (*S*), minor *t*_r = 26.24 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.36 – 7.31 (m, 5H), 5.17 – 5.12 (m, 3H), 3.20 (dt, *J* = 9.4, 7.3 Hz, 1H), 1.80 – 1.73 (m, 1H), 1.74 (d, *J* = 1.0 Hz, 3H), 1.66 (d, *J* = 1.1 Hz, 3H), 1.58 – 1.51 (m, 1H), 0.88 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.7, 136.3, 135.0, 128.4, 128.0, 127.9, 122.5, 65.9, 46.6, 26.2, 25.7, 18.2, 11.6. HRMS (ESI) m/z: Calcd for C₁₅H₂₁O₂ [M+H]⁺ 233.1536; Found 233.1531.



Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromohexanoate **4c** (78.8 mg, 0.25 mmol). The product **5c** was obtained as a pale yellow oil (53.7 mg, 74% yield, 91% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +49.21$ (*c* 2.37, CHCl₃). The ee was determined by HPLC with a Phenomenex lux 5u Amylos-2 column (*n*-hexane, 1 mL/min, 220 nm, major *t*_r = 50.93 min (*S*), minor *t*_r = 54.84 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.15 – 5.10 (m, 1H), 5.04 (s, 2H), 3.81 (s, 3H), 3.22 (dt, *J* = 9.4, 7.3 Hz, 1H), 1.72 – 1.64 (m, 4H), 1.63 (d, *J* = 1.2 Hz, 3H), 1.52 – 1.40 (m, 1H), 1.29 – 1.21 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.9, 159.5, 134.6, 129.7, 128.4, 122.8, 113.8,

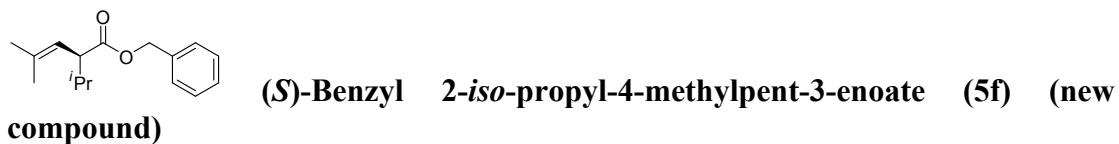
65.8, 55.2, 44.9, 32.7, 29.2, 25.7, 22.5, 18.2, 13.9. HRMS (ESI) m/z: Calcd for C₁₈H₂₇O₃ [M+H]⁺ 291.1955; Found 291.1954.



Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromo-4-methylpentanoate **4d** (78.8 mg, 0.25 mmol). The product **5d** was obtained as a pale yellow oil (45.0 mg, 62% yield, 86% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +44.19$ (*c* 2.23, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 12.75 min (*S*), minor *t*_r = 12.13 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.25 (m, 2H), 6.90 – 6.81 (m, 2H), 5.11 – 5.06 (m, 1H), 5.03 (d, 2H), 3.81 (s, 3H), 3.37 – 3.27 (m, 1H), 1.71 (d, *J* = 1.2 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.63 – 1.36 (m, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.9, 159.5, 134.5, 129.7, 128.4, 123.0, 113.8, 65.8, 55.2, 43.1, 41.9, 25.7, 25.7, 22.7, 22.3, 18.2. HRMS (ESI) m/z: Calcd for C₁₈H₂₇O₃ [M+H]⁺ 291.1955; Found 291.1947.

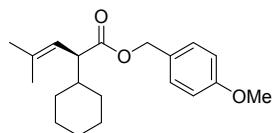


Following the general procedure 3, the target product was synthesized from benzyl 2-bromo-4-methylpentanoate **4e** (71.3 mg, 0.25 mmol). The product **5e** was obtained as a pale yellow oil (46.2 mg, 71% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +70.13$ (*c* 2.49, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 0.6 mL/min, 220 nm, major *t*_r = 12.34 min (*S*), minor *t*_r = 11.62 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.35 – 7.33 (m, 5H), 5.14 – 5.11 (m, 3H), 3.40 – 3.33 (m, 1H), 1.72 (d, *J* = 0.7 Hz, 3H), 1.67 (d, *J* = 1.0 Hz, 3H), 1.61 – 1.26 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.8, 136.3, 134.6, 128.4, 128.0, 127.8, 123.0, 66.0, 43.1, 41.9, 25.7, 25.7, 22.6, 22.3, 18.2. HRMS (ESI) m/z: Calcd for C₁₇H₂₅O₂ [M+H]⁺ 261.1849; Found 261.1848.



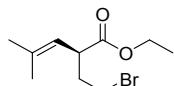
Following the general procedure 3, the target product was synthesized from benzyl 2-bromo-3-methylbutanoate **4f** (67.8 mg, 0.25 mmol). The product **5f** was obtained as a pale yellow oil (28.3 mg, 46% yield, 32% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +13.57$ (*c* 0.56, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 8.63 min (*S*), minor *t*_r = 7.99 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.34 (m, 5H), 5.20 – 5.07 (m, 3H), 3.01 – 2.95 (m, 1H), 2.01 – 1.90 (m, 1H), 1.74 (s, 3H), 1.64 (d, *J* = 1.1 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.3, 136.3, 135.4, 128.4,

128.0, 121.8, 65.9, 52.5, 31.5, 25.8, 20.7, 19.7, 18.3. HRMS (ESI) m/z: Calcd for C₁₆H₂₃O₂ [M+H]⁺ 247.1693; Found 247.1684.



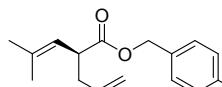
**(S)-4-Methoxybenzyl 2-cyclohexyl-4-methylpent-3-enoate (5g)
(new compound)**

Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromo-2-cyclohexylacetate **4g** (85.3 mg, 0.25 mmol). The product **5g** was obtained as a pale yellow oil (22.2 mg, 28 % yield, 32% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+11.58$ (*c* 0.76, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 0.1 mL/min, 220 nm, major t_r = 15.52 min (*S*), minor t_r = 14.58 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.27 (dd, *J* = 6.5, 2.2 Hz, 2H), 6.89 – 6.86 (m, 2H), 5.16 – 5.01 (m, 3H), 3.81 (s, 3H), 3.03 – 2.96 (m, 1H), 1.78 – 1.56 (m, 13H), 1.32 – 1.20 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 174.4, 159.5, 135.2, 129.8, 128.5, 121.8, 113.8, 65.7, 55.3, 51.6, 40.9, 31.2, 30.1, 26.3, 26.2, 26.1, 25.8, 18.3. HRMS (ESI) m/z: Calcd for C₂₀H₂₉O₃ [M+H]⁺ 317.2111; Found 317.2103.



(S)-Ethyl 2-(2-bromoethyl)-4-methylpent-3-enoate (5h) (new compound)

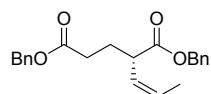
Following the general procedure 3, the target product was synthesized from ethyl 2,4-dibromobutanoate **4h** (68.5 mg, 0.25 mmol). The product **5h** was obtained as a pale yellow oil (32.4 mg, 52% yield, 73% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+63.16$ (*c* 0.76, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major t_r = 10.92 min (*S*), minor t_r = 10.56 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 5.05 – 5.01 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.43 – 3.32 (m, 3H), 2.27 – 2.00 (m, 2H), 1.74 (d, *J* = 1.2 Hz, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 173.9, 136.8, 120.9, 60.7, 43.3, 35.3, 31.0, 25.8, 18.4, 14.2. HRMS (ESI) m/z: Calcd for C₁₀H₁₈O₂Br [M+H]⁺ 249.0485; Found 249.0480.



(S)-4-Methoxybenzyl 2-allyl-4-methylpent-3-enoate (5i) (new compound)

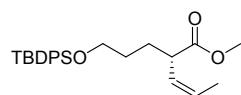
Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromopent-4-enoate **4i** (74.8 mg, 0.25 mmol). The product **5i** was obtained as a pale yellow oil (38.4 mg, 56% yield, 80% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+25.35$ (*c* 1.42, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 0.5 mL/min, 220 nm, major t_r = 17.74 min (*S*), minor t_r = 16.54 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.28 – 7.25 (m, 2H), 6.89 – 6.86 (m, 2H), 5.71 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.16 – 4.95 (m, 5H), 3.81 (s, 3H), 3.35 – 3.29 (m, 1H), 2.48 – 2.43 (m, 1H), 2.27 – 2.22 (m, 1H), 1.72 (d, *J* = 0.9 Hz, 3H), 1.64 (d, *J* = 1.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.1, 159.5, 135.3, 135.2, 129.8,

128.3, 121.9, 116.6, 113.9, 65.9, 55.2, 44.9, 37.1, 25.7, 18.3. HRMS (ESI) m/z: Calcd for C₁₇H₂₃O₃ [M+H]⁺ 275.1642; Found 275.1636.



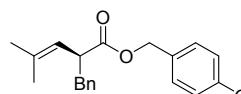
(S)-Dibenzyl 2-(2-methylprop-1-en-1-yl)pentanedioate (5j) (new compound)

Following the general procedure 3, the target product was synthesized from dibenzyl 2-bromopentanedioate **4j** (97.8 mg, 0.25 mmol). The product **5j** was obtained as a pale yellow oil (51.3 mg, 56% yield, 85% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +38.75$ (*c* 0.64, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 27.73 min (*S*), minor *t*_r = 25.46 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.31 (m, 10H), 5.12 – 5.09 (m, 5H), 3.35 (ddd, *J* = 9.6, 8.2, 6.6 Hz, 1H), 2.38 – 2.32 (m, 2H), 2.12 – 1.86 (m, 2H) 1.73 (d, *J* = 1.2 Hz, 3H), 1.62 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 173.9, 172.8, 136.2, 136.1, 135.9, 128.5, 128.4, 128.2, 128.0, 127.9, 121.4, 66.21, 66.17, 44.0, 31.6, 27.6, 25.7, 18.2. HRMS (ESI) m/z: Calcd for C₂₃H₂₇O₄ [M+H]⁺ 367.1904; Found 367.1895.



(S)-Methyl 2-(3-((tert-butyldiphenylsilyl)oxy)propyl)-4-methylpent-3-enoate (5k) (new compound)

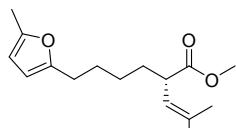
Following the general procedure 3, the target product was synthesized from methyl 2-bromo-5-((tert-butyldiphenylsilyl)oxy)pentanoate **4k** (112.4 mg, 0.25 mmol). The product **5k** was obtained as a pale yellow oil (69.0 mg, 65% yield, 66% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +20.37$ (*c* 1.43, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OD-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 9.88 min (*S*), minor *t*_r = 9.10 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.66 (m, 4H), 7.46 – 7.36 (m, 6H), 5.14 – 5.10 (m, 1H), 3.67 – 3.65 (m, 5H), 3.24 (dt, *J* = 9.5, 7.0 Hz, 1H), 1.74 – 1.53 (m, 10H), 1.07 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 175.3, 135.5, 134.8, 134.0, 129.5, 127.6, 122.6, 63.5, 51.5, 44.5, 30.1, 29.3, 26.8, 25.7, 19.2, 18.1. HRMS (ESI) m/z: Calcd for C₂₆H₃₆O₃NaSi [M+Na]⁺ 447.2326; Found 447.2309.



(S)-4-Methoxybenzyl 2-benzyl-4-methylpent-3-enoate (5l) (new compound)

Following the general procedure 3, the target product was synthesized from 4-methoxybenzyl 2-bromo-3-phenylpropanoate **4l** (87.3 mg, 0.25 mmol). The product **5l** was obtained as a pale yellow oil (42.2 mg, 52% yield, 88% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +47.22$ (*c* 1.75, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major *t*_r = 22.66 min (*S*), minor *t*_r = 33.28 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.26 – 7.12 (m, 7H), 6.87 – 6.84 (m, 2H), 5.24 – 5.19 (m, 1H), 5.00 (s, 2H), 3.81 (s, 3H), 3.58 – 3.49 (m, 1H), 3.06 (dd, *J* = 13.5, 7.9 Hz, 1H),

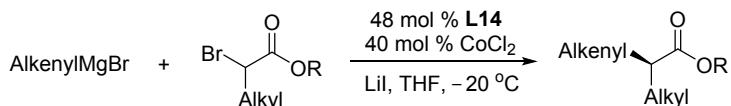
2.76 (dd, $J = 13.5, 7.2$ Hz, 1H), 1.70 (d, $J = 1.0$ Hz, 3H), 1.49 (d, $J = 1.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.1, 159.5, 139.0, 135.5, 129.8, 129.0, 128.2, 126.2, 121.8, 113.8, 65.9, 55.2, 47.1, 39.1, 25.6, 18.0. HRMS (ESI) m/z: Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_3$ [M+H]⁺ 325.1798; Found 325.1791.



(S)-Methyl 6-(5-methylfuran-2-yl)-2-(2-methylprop-1-en-1-yl)hexanoate (5m) (new compound)

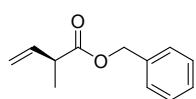
Following the general procedure 3, the target product was synthesized from methyl 2-bromo-6-(5-methylfuran-2-yl)hexanoate **4m** (72.3 mg, 0.25 mmol). The product **5m** was obtained as a brown oil (33.0 mg, 50% yield, 33% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +12.40$ (c 1.00, CHCl_3). The ee was determined by HPLC with a Daicel Chiralcel OX-H column (0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm, major $t_r = 25.31$ min (*S*), minor $t_r = 24.63$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 5.84 – 5.82 (m, 2H), 5.12 – 5.08 (m, 1H), 3.65 (s, 3H), 3.21 (dt, $J = 9.5, 7.3$ Hz, 1H), 2.57 – 2.52 (m, 2H), 2.24 (s, 3H), 1.76 – 1.73 (m, 1H), 1.72 (d, $J = 1.2$ Hz, 3H), 1.65 (d, $J = 1.3$ Hz, 3H), 1.50 – 1.22 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.4, 154.4, 150.1, 134.7, 122.7, 105.7, 105.2, 51.5, 44.7, 32.7, 28.0, 27.9, 26.6, 25.7, 18.1, 13.5. HRMS (ESI) m/z: Calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3$ [M+H]⁺ 265.1798; Found 265.1791.

Scheme S5 Enantioselective Kumada Cross-Coupling of Alkenyl Magnesium Bromide



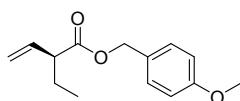
General Procedure 4.

Anhydrous CoCl_2 (13.0 mg, 0.1 mmol) and anhydrous LiI (26.8 mg, 0.2 mmol) were placed in a 50-mL Schlenk tube and heated at 80 °C with a heating mantle for 2 h in vacuo. After being cooled to room temperature under an argon atmosphere, anhydrous THF (2 mL) and **L14** (56.7 mg, 0.12 mmol) in THF (1 mL) were added. The resulting mixture was stirred for 2 h at room temperature, and was cooled to –20 °C. Racemic α -bromo ester (0.25 mmol) was added via syringe, and the suspension of alkenylmagnesium bromide (1.25 mmol) diluted in THF (5 mL) was then added dropwise over 2.5 h by injection pump. The reaction mixture was stirred for 24 h at –20 °C, and quenched with saturated NH_4Cl solution (3 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography to provide corresponding enantioenriched β,γ -unsaturated ester.



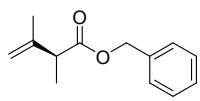
(S)-Benzyl 2-methylbut-3-enoate (6a) (CAS 1242024-69-6)¹³

Following the general procedure 4, the target product was synthesized from benzyl 2-bromopropanoate **1a** (60.8 mg, 0.25 mmol) and vinylmagnesium bromide **2b** (2.1 mL, 0.6 M in THF, 1.25 mmol). The product **6a** was obtained as a pale yellow oil (23.8 mg, 50% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +12.19$ (*c* 0.85, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t_r* = 21.17 min (*S*), minor *t_r* = 19.65 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.40 – 7.30 (m, 5H), 5.95 (ddd, *J* = 17.4, 10.2, 7.4 Hz, 1H), 5.19–5.18 (m, 1H), 5.14 (s, 2H), 5.13–5.10 (m, 1H), 3.21 (dd, *J* = 14.2, 7.1 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 135.2, 128.6, 128.5, 128.5, 128.2, 128.0, 116.0, 67.6, 40.0, 21.6. HRMS (ESI) m/z: Calcd for C₁₂H₁₅O₂ [M+H]⁺ 191.1067; Found 191.1061.



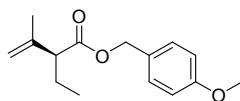
(*S*)-4-Methoxybenzyl 2-ethylbut-3-enoate (6b) (new compound)

Following the general procedure 4, the target product was synthesized from 4-methoxybenzyl 2-bromopropanoate **1b** (68.3 mg, 0.25 mmol) and vinylmagnesium bromide **2b** (2.1 mL, 0.6 M in THF, 1.25 mmol). The product **6b** was obtained as a pale yellow oil (26 mg, 44% yield, 86% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +21.37$ (*c* 0.97, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t_r* = 57.91 min (*S*), minor *t_r* = 44.07 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.31 – 6.87 (m, 4H), 5.88 – 5.78 (m, 1H), 5.15 – 4.94 (m, 4H), 3.81 (s, 3H), 2.98 – 2.90 (m, 1H), 1.82 – 1.75 (m, 1H), 1.62 – 1.53 (m, 1H), 0.88 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.0, 159.6, 135.9, 130.0, 129.9, 117.2, 113.9, 66.1, 55.3, 51.9, 25.4, 11.5. HRMS (ESI) m/z: Calcd for C₁₄H₁₉O₃ [M+H]⁺ 235.1329; Found 235.1324.



(*S*)-Benzyl 2,3-dimethylbut-3-enoate (6c) (new compound)

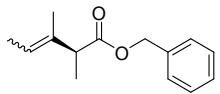
Following the general procedure 4, the target product was synthesized from benzyl 2-bromopropanoate **1a** (60.8 mg, 0.25 mmol) and prop-1-en-2-ylmagnesium bromide **2c** (4.0 mL, 0.31 M in THF, 1.25 mmol). The product **6c** was obtained as a pale yellow oil (29.1 mg, 57% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +23.84$ (*c* 0.97, CHCl₃). The ee was determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, major *t_r* = 17.73 min (*S*), minor *t_r* = 19.82 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.33 (m, 5H), 5.13 (s, 2H), 4.88 (d, *J* = 1.0 Hz, 2H), 3.21 (q, *J* = 7.0 Hz, 1H), 1.75 (d, *J* = 1.0 Hz, 3H), 1.30 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 174.1, 143.8, 136.1, 128.5, 128.1, 128.08, 128.04, 112.6, 66.3, 46.9, 20.4, 15.8. HRMS (ESI) m/z: Calcd for C₁₃H₁₇O₂ [M+H]⁺ 205.1223; Found 205.1222.



(*S*)-4-Methoxybenzyl 2-ethyl-3-methylbut-3-enoate (6d) (new compound)

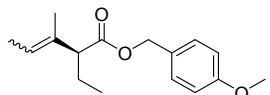
Following the general procedure 4, the target product was synthesized from 4-methoxybenzyl 2-bromopropanoate **1b** (68.3 mg, 0.25 mmol) and prop-1-en-2-ylmagnesium bromide **2c** (4.0 mL, 0.31 M in THF, 1.25 mmol). The product **6d** was

obtained as a pale yellow oil (33.5 mg, 54% yield, 91% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+20.73$ (*c* 1.64, CHCl_3). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (*n*-hexane, 1 mL/min, 220 nm, major $t_r = 31.18$ min (*S*), minor $t_r = 30.54$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 5.06 (s, 2H), 4.88 (dd, *J* = 4.1, 2.6 Hz, 2H), 3.80 (s, 3H), 2.95 (t, *J* = 7.6 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.70 (s, 3H), 1.66 – 1.58 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 173.6, 159.5, 142.3, 129.8, 128.3, 113.8, 113.7, 66.0, 55.2, 54.9, 23.3, 20.1, 11.9. HRMS (ESI) m/z: Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ [$\text{M}+\text{H}]^+$ 249.1485; Found 249.1482.



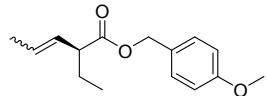
(*S*)-Benzyl 2,3-dimethylpent-3-enoate (6e) (new compound)

Following the general procedure 4, the target product was synthesized from benzyl 2-bromopropanoate **1a** (60.8 mg, 0.25 mmol) and 1-methyl-1-propenylmagnesium bromide **2d** (4 mL, 0.31 M in THF, 1.25 mmol). The product **6e** was obtained as a pale yellow oil (33.8 mg, 62% yield, *E/Z* = 76:24, *E*: 95% ee, *Z*: 78% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+50.74$ (*c* 1.17, CHCl_3). The *E/Z* and ee were determined by HPLC with a Daicel Chiralpak AD-H column (*n*-hexane, 1 mL/min, 220 nm, *E*: major $t_r = 27.75$ min (*S*), minor $t_r = 27.32$ min (*R*)); *Z*: major $t_r = 22.26$ min (*S*), minor $t_r = 24.37$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.36 – 7.26 (m, 5H), 5.43 – 5.29 (m, 1H), 5.12 (s, *J* = 1.2 Hz, 2H), 3.71 – 3.13 (m, 1H), 1.65 – 1.59 (m, 6H), 1.27 – 1.22 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 174.7 (174.4), 136.3, 134.28 (134.0), 128.5 (128.0), 127.93 (127.88), 122.0, 121.5, 66.1, 48.3 (40.2), 29.7 (19.4), 15.8 (14.7), 13.6 (13.4). HRMS (ESI) m/z: Calcd for $\text{C}_{14}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}]^+$ 219.1380; Found 219.1376.



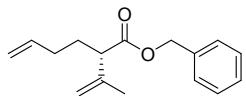
(*S*)-4-Methoxybenzyl 2-ethyl-3-methylpent-3-enoate (6f) (new compound)

Following the general procedure 4, the target product was synthesized from 4-methoxybenzyl 2-bromopropanoate **1b** (68.3 mg, 0.25 mmol) and 1-methyl-1-propenylmagnesium bromide **2d** (4 mL, 0.31 M in THF, 1.25 mmol). The product **6f** was obtained as a pale yellow oil (31.5 mg, 48% yield, *E/Z* = 54:46, *E*: 92% ee, *Z*: 44% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20}=+27.98$ (*c* 1.19, CHCl_3). The *E/Z* and ee were determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, *E*: major $t_r = 34.92$ min (*S*), minor $t_r = 31.38$ min (*R*)); *Z*: major $t_r = 43.06$ min (*S*), minor $t_r = 67.00$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 1H), 5.48 – 5.33 (m, 1H), 5.05 (s, 2H), 3.80 (s, 3H), 3.46 – 2.85 (m, 1H), 1.87 – 1.84 (m, 1H), 1.64 – 1.53 (m, 8H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ (174.2) 173.8, 159.4, (132.7) 132.4, (129.8) 129.7, 128.5, 123.3 (122.7), 113.8, 65.8, (56.3) 55.2, 47.7, (23.1) 22.4, 19.4, (13.4) 13.3, (11.9) 11.7. HRMS (ESI) m/z: Calcd for $\text{C}_{16}\text{H}_{23}\text{O}_3$ [$\text{M}+\text{H}]^+$ 263.1642; Found 263.1647.



(*S*)-4-Methoxybenzyl 2-ethylpent-3-enoate (6g**) (new compound)**

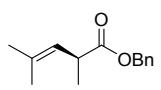
Following the general procedure 4, the target product was synthesized from 4-methoxybenzyl 2-bromopropanoate **1b** (68.3 mg, 0.25 mmol) and 1-propenylmagnesium bromide **2e** (3.1 mL, 0.4 M in THF, 1.25 mmol). The product **6g** was obtained as a pale yellow oil (31.7 mg, 51% yield, *E/Z* = 60:40, *E*: 94% ee, *Z*: 88% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +50.23$ (*c* 2.05, CHCl₃). The *E/Z* and ee were determined by HPLC with a Daicel Chiralcel OJ-H column (*n*-hexane, 1 mL/min, 220 nm, *E*: major *t_r* = 43.69 min (*S*), minor *t_r* = 33.39 min (*R*); *Z*: major *t_r* = 57.50 min (*S*), minor *t_r* = 53.87 min (*R*)). ¹H NMR (300 MHz, CDCl₃) δ 7.30 – 6.87 (m, 4H), 5.63 – 5.39 (m, 2H), 5.05 (s, 2H), 3.81 (s, 3H), 3.32 – 2.85 (m, 1H), 1.69 – 1.65 (m, 1H), 1.64 – 1.62 (m, 3H), 1.55 – 1.52 (m, 1H), 0.90 – 0.83 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ (174.5) 174.4, 159.5, (129.83) 129.77, 128.6 (128.3), 128.1 (128.0), 126.8, 113.9, 65.9, 55.2, (50.9) 45.3, 25.9 (25.8), 17.8, (11.6) 11.5. HRMS (ESI) m/z: Calcd for C₁₅H₂₁O₃ [M+H]⁺ 249.1485; Found 249.1481.



(*S*)-Benzyl 2-(prop-1-en-2-yl)hex-5-enoate (6h**) (new compound)**

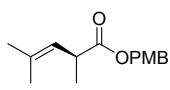
Following the general procedure 4, the target product was synthesized from benzyl 2-bromohex-5-enoate **4n** (70.8 mg, 0.25 mmol) and prop-1-en-2-ylmagnesium bromide **2c** (4.0 mL, 0.31 M in THF, 1.25 mmol). The product **6h** was obtained as a pale yellow oil (31.8 mg, 52% yield, 90% ee) after silica gel chromatography (petroleum ether/ethyl acetate 80:1). $[\alpha]_D^{20} = +20.00$ (*c* 1.24, CHCl₃). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (0.8% isopropanol in *n*-hexane, 1 mL/min, 254 nm, major *t_r* = 13.92 min (*S*), minor *t_r* = 15.20 min (*R*)). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 5H), 5.77 (ddt, *J* = 16.9, 10.2, 6.4 Hz, 1H), 5.13 (s, 2H), 5.02 – 4.90 (m, 4H), 3.11 (t, *J* = 7.5 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.73 (s, 3H), 1.70 – 1.60 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 142.2, 137.5, 135.9, 128.5, 128.1, 128.0, 115.3, 114.0, 66.4, 52.0, 31.7, 29.2, 20.1. HRMS (ESI) m/z: Calcd for C₁₆H₂₁O₂ [M+H]⁺ 245.1536; Found 245.1544.

5. Assignment of Absolute Configuration



(*S*)-Benzyl 2,4-dimethylpent-3-enoate (3a**)**

The optical rotation measured for **3a** [$[\alpha]_D^{20} = +74.09$ (*c* 0.77, CHCl₃); 91% ee] matched the literature data [$[\alpha]_D^{20} = +33.3$ (*c* 0.4, CH₂Cl₂); 37% ee] of (*S*)-**3a**,⁹ therefore the absolute configuration of **3a** was confirmed as (*S*).



(*S*)-4-Methoxybenzyl 2,4-dimethylpent-3-enoate (3b**)**

The optical rotation measured for **3b** [$[\alpha]_D^{20} = +67.88$ (*c* 1.73, CHCl₃); 90% ee] matched the literature data [$[\alpha]_D^{20} = +16.3$ (*c* 0.1, CH₂Cl₂); 20% ee] of (*S*)-**3b**,¹⁰

therefore the absolute configuration of **3b** was confirmed as (*S*).



The optical rotation measured for **3d** $[\alpha]_D^{20} = +10.24$ (*c* 0.27, CHCl₃); 91% ee] matched the literature data $[\alpha]_D^{20} = +16.8$ (*c* 1.0, CH₂Cl₂); 20% ee] of (*S*)-**3d**,⁹ therefore the absolute configuration of **3d** was confirmed as (*S*).



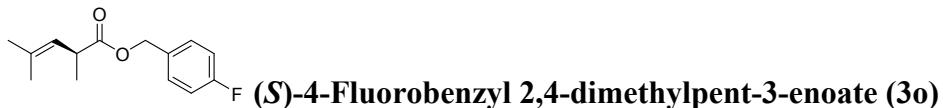
The optical rotation measured for **3e** $[\alpha]_D^{20} = +68.14$ (*c* 0.39, CHCl₃); 90% ee] matched the literature data $[\alpha]_D^{20} = +11.6$ (*c* 1.2, CH₂Cl₂); 17% ee] of (*S*)-**3e**,⁹ therefore the absolute configuration of **3e** was confirmed as (*S*).



The optical rotation measured for **3h** $[\alpha]_D^{20} = +61.15$ (*c* 1.05, CHCl₃); 72% ee] matched the literature data $[\alpha]_D^{20} = +17.8$ (*c* 0.4, CH₂Cl₂); 17% ee] of (*S*)-**3h**,⁹ therefore the absolute configuration of **3h** was confirmed as (*S*).



The optical rotation measured for **3j** $[\alpha]_D^{20} = +63.62$ (*c* 0.77, CHCl₃); 91% ee] matched the literature data $[\alpha]_D^{20} = +21.6$ (*c* 0.8, CH₂Cl₂); 21% ee] of (*S*)-**3j**,⁹ therefore the absolute configuration of **3j** was confirmed as (*S*).



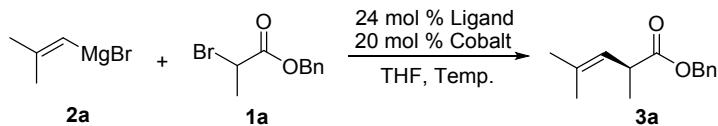
The optical rotation measured for **3o** $[\alpha]_D^{20} = +56.35$ (*c* 2.3, CHCl₃); 90% ee] matched the literature data $[\alpha]_D^{20} = +27.6$ (*c* 0.8, CH₂Cl₂); 21% ee] of (*S*)-**3o**,¹⁰ therefore the absolute configuration of **3o** was confirmed as (*S*).



The optical rotation measured for **6a** $[\alpha]_D^{20} = +12.19$ (*c* 0.85, CHCl₃); 90% ee] matched the literature data $[\alpha]_D^{20} = +19.0$ (*c* 1.0, CH₂Cl₂); 96% ee] of (*S*)-**6a**,¹³ therefore the absolute configuration of **6a** was confirmed as (*S*).

6. Effect of Reaction Parameters on the Enantioselective Kumada Cross-Coupling

Table S1. Effect of Reaction Parameters on the Enantioselective Kumada Cross-Coupling of **2a** with **1a**^a



Entry	Ligand	Cobalt	Solvent	Temp. (°C)	Yield (%) ^b	ee (%) ^c
1	L9	—	THF	-60	—	—
2	—	CoCl ₂	THF	-60	25 ^d	0
3	L9	CoI ₂	THF	-60	65	83
4	L9	CoBr ₂	THF	-60	62	81
5	L9	Co(dppe)Cl ₂	THF	-60	61	60
6	L9	Co(OAc) ₂	THF	-60	56	62
7	L9	Co(PPh ₃) ₂ Cl ₂	THF	-60	62	70
8	L9	Co(acac) ₃	THF	-60	40	42
9	L9	NiCl ₂ (glyme)	THF	-40	49	—
10	L9	CoCl ₂	THF	-30	79	88
11	L9	CoCl ₂	THF	-35	83	89
12	L9	CoCl ₂	THF	-40	80	91
13	L9	CoCl ₂	THF	-45	78	88
14	L9	CoCl ₂	THF	-50	68	86
15	L9	CoCl ₂	THF	-70	65	86
16	L9	CoCl ₂	THF	-80	40	70
17	L9	CoCl ₂	Et ₂ O	-40	46	83
18	L9	CoCl ₂	DME	-40	28	81
19	L9	CoCl ₂	Tol	-40	76	80
20 ^e	L9	CoCl ₂	THF	-40	73	82
21 ^f		CoCl ₂	THF	-60	51	80
22 ^f		CoCl ₂	THF	-60	53	69
23 ^f		CoCl ₂	THF	-60	45	65
24 ^f		CoCl ₂	THF	-60	50	72

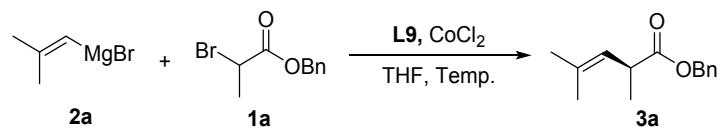
^aAll reactions were run for 5 h, and performed on 0.25 mmol scale. **2a** was diluted with THF to 5 mL and added slowly for 2.5 h. ^bIsolated yields after chromatographic purification.

^cDetermined by chiral HPLC on a Daicel Chiralcel OJ-H column. ^dDetermined by GC analysis.

^e**2a** was added in 5 min. ^fThe reactions were run for 4 h, and performed on 0.25 mmol scale.

2a was diluted with THF to 3 mL and added slowly for 2.5 h.

Table S2. Effect of Reaction Parameters on the Enantioselective Kumada Cross-Coupling of **2a** with **1a**^a

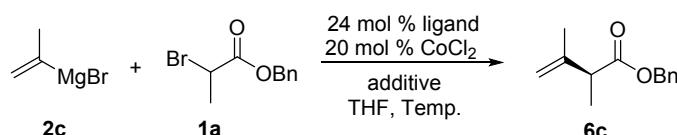


Entry	Catalyst (%)	Temp.(°C)	1a: 2a	THF (mL) ^d	Yield (%) ^b	Ee (%) ^c
1	10	-40	1:4	3	70	85
2	20	-40	1:4	3	80	91
3 ^e	20	-40	1:4	3	52	73
4	20	-60	1:2.5	3	26	81
5	20	-60	1:3	3	37	84
6	20	-60	1:3.5	3	49	85
7	20	-60	1:4	3	65	86
8	20	-60	1:4.5	3	63	85
9	20	-60	1:5	3	64	86
10	20	-60	1:4	1.5	65	83
11	20	-60	1:4	4	60	80
12	20	-60	1:4	6	62	79

^aAll reactions were run for 5 h, and performed on 0.25 mmol scale. **2a** was diluted with THF to 5 mL and added slowly for 2.5 h. ^bIsolated yields after chromatographic purification.

^cDetermined by chiral HPLC on a Daicel Chiralcel OJ-H column. ^dVolume of THF added to the mixture of CoCl₂ and ligand **L9**. ^e**2a** was not diluted.

Table S3. Effect of Parameters on the Enantioselective Kumada Cross-coupling of **1a** with **2c**^a

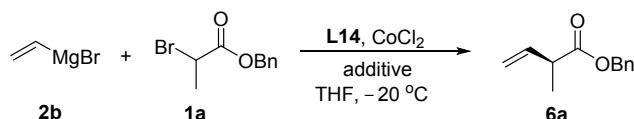


Entry	Ligand	Additive (% mmol)	Temp. (°C)	Yield (%) ^b	Ee (%) ^c
1	L9	20% HMTA	-20	44	53
2	L9	20% HMTA	-5	-	-
3	L9	20% HMTA	-15	43	53
4	L9	20% HMTA	-40	20	51
5	L1	20% HMTA	-20	45	68
6	L2	20% HMTA	-20	26	0
7	L3	20% HMTA	-20	23	65
8	L7	20% HMTA	-20	45	47
9	L12	20% HMTA	-20	47	60
10	L13	20% HMTA	-20	39	60
11	L14	20% HMTA	-20	40	72
12	L15	20% HMTA	-20	43	6
13	L16	20% HMTA	-20	41	50
14	L17	20% HMTA	-20	43	7

15	L18	20% HMTA	-20	39	45
16 ^d	L14	80% LiI	-20	57	90

^aAll reactions were run for 12 h, and performed on 0.25 mmol scale. **2c** was diluted with THF to 5 mL and added slowly for 2.5 h. ^bIsolated yields after chromatographic purification. ^cDetermined by chiral HPLC on a Daicel Chiralcel OJ-H column. ^d40% mmol CoCl₂ and 48% mmol **L14** were used, and the reaction was conducted for 24 h.

Table S4. Effect of Catalyst Loading and Additives on the Enantioselective Kumada Cross-coupling of **1a** with **2b**^a

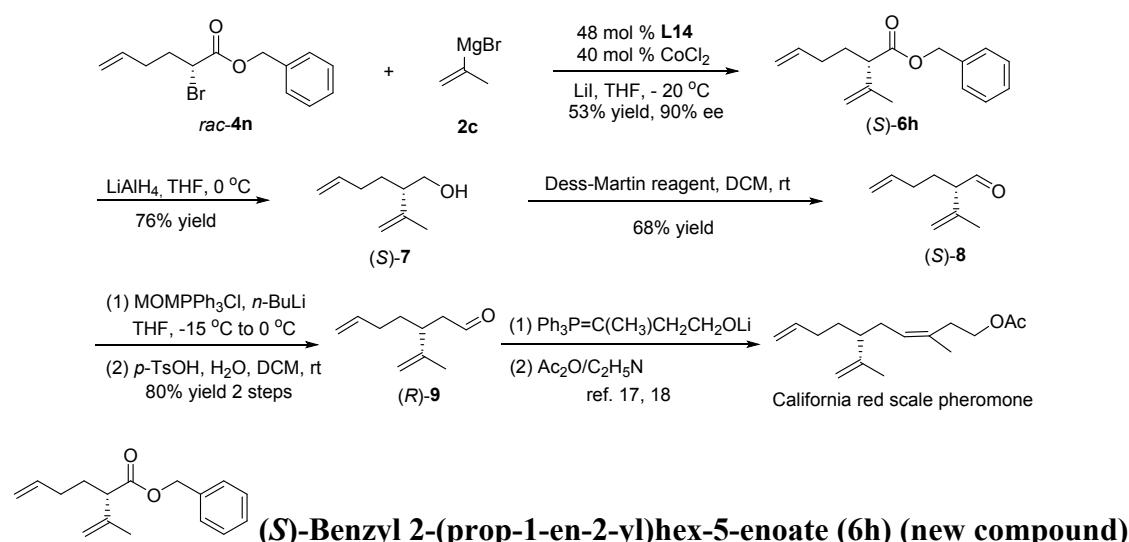


Entry	Catalyst loading (% mmol)	Additive (% mmol)	Yield (%) ^b	Ee (%) ^c
1	20	20% HMTA	20	84
2	20	20% HMTA, 40%TMEDA	20	-
3	20	120% HMTA	20	85
4	20	40% LiI	48	88
5	20	40% LiBr	21	88
6	20	40% LiCl	16	86
7	20	80% Ph ₃ P	14	86
8 ^d	40	80% LiI	50	90

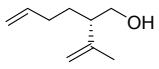
^aAll reactions were run for 12 h, and performed on 0.25 mmol scale. **2b** was diluted with THF to 5 mL and added slowly for 2.5 h. ^bIsolated yields after chromatographic purification. ^cDetermined by chiral HPLC on a Daicel Chiralcel OJ-H column. ^dThe reaction was conducted for 24 h.

7. Enantioselective Synthesis of California Red Scale Pheromone

Scheme S6. Enantioselective Synthesis of California Red Scale Pheromone

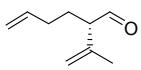


Anhydrous CoCl_2 (52.0 mg, 0.4 mmol) and anhydrous LiI (107.2 mg, 0.8 mmol) were placed in a 100-mL Schlenk tube and heated at 80 °C with a heating mantle for 2 h in vacuo. After being cooled to room temperature under an argon atmosphere, anhydrous THF (8 mL) and **L14** (226.8 mg, 0.48 mmol) in THF (4 mL) were added. The resulting mixture was stirred for 2 h at room temperature, and was cooled to –20 °C. Benzyl 2-bromohex-5-enoate (**4n**) (283.2 mg, 1.0 mmol) was added via syringe, and the suspension of prop-1-en-2-ylmagnesium bromide (**2c**) (8.0 mL, 0.31 M in THF, 5.0 mmol) diluted in THF (20 mL) was then added dropwise over 5 h by injection pump. The reaction mixture was stirred for 24 h at –20 °C, and quenched with saturated NH_4Cl solution (12 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 80:1) to provide diene ester (*S*)-**6h** (127.0 mg, 52% yield, 90% ee) as a pale yellow oil. $[\alpha]_D^{20} = +20.00$ (*c* 1.24, CHCl_3). The ee was determined by HPLC with a Daicel Chiralpak AD-H column (0.8% isopropanol in *n*-hexane, 1 mL/min, 254 nm, major $t_r = 13.92$ min (*S*), minor $t_r = 15.20$ min (*R*)). ^1H NMR (300 MHz, CDCl_3) δ 7.35 – 7.31 (m, 5H), 5.77 (ddt, *J* = 16.9, 10.2, 6.4 Hz, 1H), 5.13 (s, 2H), 5.03 – 4.89 (m, 4H), 3.11 (t, *J* = 7.4 Hz, 1H), 2.03 – 1.90 (m, 2H), 1.73 (s, 3H), 1.70 – 1.60 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 173.4, 142.1, 137.7, 136.1, 130.9, 128.8, 128.5, 128.1, 128.0, 115.3, 114.1, 66.3, 52.3, 31.4, 29.2, 20.2. HRMS (ESI) m/z: Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_2[\text{M}+\text{H}]^+$ 245.1536; Found 245.1544.



(*S*)-2-(Prop-1-en-2-yl)hex-5-en-1-ol (**7**) (new compound)¹⁴

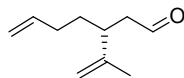
To a suspension of LiAlH_4 (7.2 mmol, 0.27 g) in THF (10 mL) was added diene ester (*S*)-**6h** (0.59 g, 2.4 mmol) at 0 °C under an argon atmosphere. The resulting mixture was stirred for 6 h at the same temperature. The reaction mixture was then quenched with a small piece of ice and diluted with Et_2O (10 mL), followed by filtering through a celite pad. The filtrate was dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure to give crude product. The crude product was purified by silica gel chromatography (petroleum ether /ethyl acetate 15:1) to afford diene alcohol (*S*)-**7** (0.26 g, 76% yield) as a pale yellow oil. $[\alpha]_D^{20} = -10.91$ (*c* 0.22, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03 – 4.84 (m, 4H), 3.56 – 3.48 (m, 2H), 2.31 – 2.29 (m, 1H), 2.07 – 1.96 (m, 2H), 1.71 – 1.64 (m, 4H), 1.47 – 1.36 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.8, 138.4, 114.7, 114.0, 64.0, 49.3, 31.3, 28.4, 18.7. HRMS (ESI) m/z: Calcd for $\text{C}_9\text{H}_{17}\text{O} [\text{M}+\text{H}]^+$ 141.1274; Found 141.1278.



(*S*)-2-(prop-1-en-2-yl)hex-5-enal (**8**) (new compound)¹⁵

To a solution of Dess-Martin reagent (0.94 g, 2.2 mmol,) in dry DCM (10 mL) was added diene alchol (*S*)-**7** (0.21 g, 1.5 mmol) at 0 °C under an argon atmosphere. The reaction mixture was warmed to room temperature and stirred for 3 h. After cooling to 0 °C, sodium bicarbonate solution (10 mL) and saturated sodium thiosulfate (20 mL) was added slowly. The organic layer was separated and the aqueous layer was extracted with DCM (3 × 30 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure at 0 °C to obtain crude product. The crude product was purified by silica gel chromatography (petroleum ether/DCM 10:1) and concentrated at 0 °C to afford diene aldehyde (*S*)-**8**

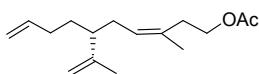
(0.14 g, 68% yield) as a pale yellow oil. $[\alpha]_D^{20} = +96.21$ (*c* 0.39, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 9.52 (d, *J* = 1.9 Hz, 1H), 5.78 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.10 – 4.91 (m, 4H), 3.02 – 2.93 (m, 1H), 2.29 – 2.20 (m, 5H), 2.10 – 2.03 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 201.2, 137.6, 125.8, 115.7, 115.5, 59.8, 31.0, 26.0, 20.9. HRMS (ESI) m/z: Calcd for C₉H₁₅O [M+H]⁺ 139.1117; Found 139.1121.



(*R*)-3-(Prop-1-en-2-yl)hept-6-enal (9) (CAS 67169-07-7)¹⁶

To a suspension of (methoxymethyl)triphenylphosphonium chloride (1.39 g, 4.0 mmol) in dry THF (10 mL) was added *n*-butyllithium (4.1 mmol, 2.4 M in *n*-hexane, 1.7 mL) at –15 °C. After stirring for 20 min, a solution of the diene aldehyde (*S*)-8 (0.080 g, 0.58 mmol) in dry THF (2 mL) was added slowly at the same temperature. The reaction mixture was stirred for 3 h at 0 °C, and quenched with water (5mL). Et₂O (20 mL) was added, and the layers were separated. The aqueous layer was extracted with Et₂O (3 × 30 mL). The combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure at 0 °C to obtain the crude enol ether.

The crude enol ether was dissolved in DCM (10 mL), and *p*-TsOH (0.69 g, 4.0 mmol) and water (0.1 mL) were then added at room temperature. The reaction mixture was stirred for 18 h at the same temperature, and quenched with saturated NaHCO₃ (5 mL) solution. The layers were separated, and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 0 °C to obtain the crude product. The crude product was purified by silica gel chromatography (petroleum ether/DCM 20:1) to give diene aldehyde (*R*)-9 (0.049 g, 80% yield 2 steps) as a colorless oil. $[\alpha]_D^{20} = +5.45$ (*c* 0.59, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 9.69 (t, *J* = 2.4 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.96 (m, 2H), 4.86 – 4.76 (m, 2H), 2.78 – 2.68 (m, 1H), 2.48 – 2.43 (m, 2H), 2.09 – 2.00 (m, 2H), 1.69 (s, 3H), 0.96 – 0.85 (m, 2H). ¹³C NMR (75 MHz, DMSO) δ 202.2, 145.6, 138.1, 114.9, 112.7, 47.4, 41.0, 31.1, 18.7. HRMS (ESI) m/z: Calcd for C₁₀H₁₇O [M+H]⁺ 153.1274; Found 153.1279.

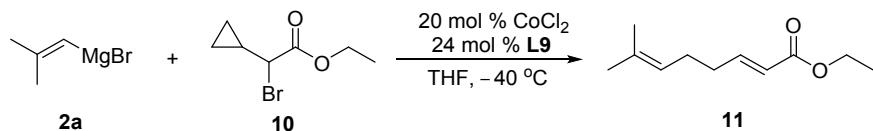


California red scale pheromone (CAS 67225-47-2)^{17,18}

According to the references 17 and 18, diene aldehyde (*R*)-9 can be reacted with 3-hydroxy-1-methylpropyltriphenylphosphonium lithium to afford triene alcohol, which can easily be converted to the target California red scale pheromone via acetylation with acetic anhydride.

8. Radical Clock Experiments

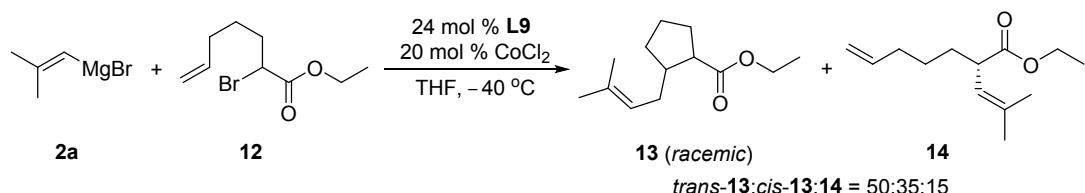
Scheme S7. Cobalt-catalyzed the Reaction of **10** with **2a**





Anhydrous CoCl_2 (6.5 mg, 0.05 mmol) was placed in a 50-mL Schlenk tube and heated at 80 °C with a heating mantle for 2 h in vacuo. After being cooled to room temperature under an argon atmosphere, anhydrous THF (2 mL) and **L9** (37.6 mg, 0.06 mmol) in THF (1 mL) were added. The resulting mixture was stirred for 2 h at room temperature, and was cooled to –40 °C. Ethyl 2-bromo-2-cyclopropylacetate **10** (51.8 mg, 0.25 mmol) was added via syringe, and the suspension of (2-methylprop-1-en-1-yl) magnesium bromide **2a** (2.7 mL, 0.37 M in THF, 1 mmol) diluted in THF (5 mL) was then added dropwise over 2.5 h by injection pump. The reaction mixture was stirred for 5 h at –40 °C, and quenched with saturated NH_4Cl solution (3 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 80:1) to provide **11** (23.2 mg, 51% yield) as a pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 6.96 (dt, $J = 15.6, 6.6$ Hz, 1H), 5.82 (dt, $J = 15.6, 1.4$ Hz, 1H), 5.12 – 5.08 (m, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 2.24 – 2.12 (m, 4H), 1.69 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 148.9, 132.7, 122.9, 121.4, 60.1, 32.4, 26.6, 25.6, 17.7, 14.3. HRMS (ESI) m/z: Calcd for $\text{C}_{11}\text{H}_{19}\text{O}_2$ [$\text{M}+\text{H}]^+$ 183.13850; Found 183.13849.

Scheme S8. Cobalt-catalyzed the Reaction of **12** with **2a**

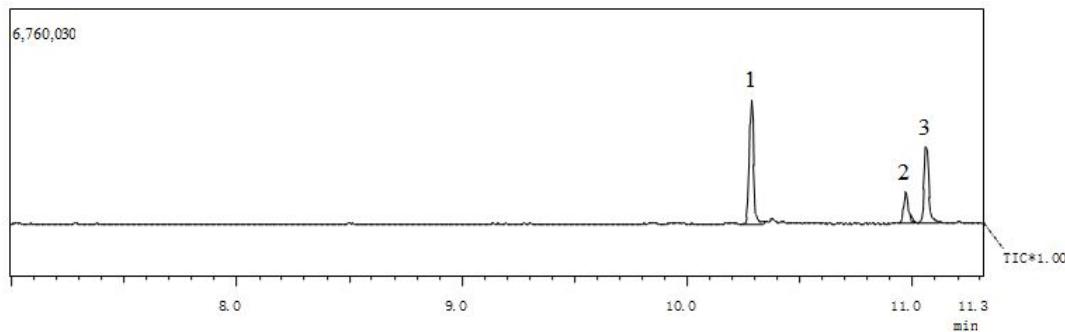


Anhydrous CoCl_2 (6.5 mg, 0.05 mmol) was placed in a 50-mL Schlenk tube and heated at 80 °C with a heating mantle for 2 h in vacuo. After being cooled to room temperature under an argon atmosphere, anhydrous THF (2 mL) and **L9** (37.6 mg, 0.06 mmol) in THF (1 mL) were added. The resulting mixture was stirred for 2 h at room temperature, and was cooled to –40 °C. Ethyl 2-bromohept-6-enoate **12** (58.8 mg, 0.25 mmol) was added via syringe, and the suspension of (2-methylprop-1-en-1-yl) magnesium bromide **2a** (2.7 mL, 0.37 M in THF, 1 mmol) diluted in THF (5 mL) was then added dropwise over 2.5 h by injection pump. The reaction mixture was stirred for 5 h at –40 °C, and quenched with saturated NH_4Cl solution (3 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give the crude product. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate 80:1) to afford the mixture of **13** and **14** (28.2 mg, 53% yield, $\text{trans-13:cis-13:14} = 50:35:15$) as a pale yellow oil. HRMS (ESI) m/z: Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_2$ [$\text{M}+\text{H}]^+$ 211.1698; Found 211.1697.

The ratio of trans-13 , cis-13 and **14** was determined by GC-Mass. GC-MS total ion chromatogram (TIC) of the mixture of trans-13 , cis-13 and **14** (Figure S1) shows relative retention times and ratio of **14** (peak 1), cis-13 (peak 2) and trans-13 (peak 3). Moreover, mass spectra are presented in Figure S2. Peak 1 is identified as (*S*)-methyl

2-(2-methylprop-1-en-1-yl)hept-6-enoate (**14**), which is the cross-coupling product. Peak 2 is identified as *cis*-ethyl 2-(3-methylbut-2-en-1-yl)cyclopentane-1-carboxylate (*cis*-**13**), and peak 3 is identified as *trans*-ethyl 2-(3-methylbut-2-en-1-yl)cyclopentane-1-carboxylate (*trans*-**13**).

Figure S1. GC-MS Total Ion Chromatogram (TIC) of the Mixture of *trans*-**13**, *cis*-**13** and **14**^a

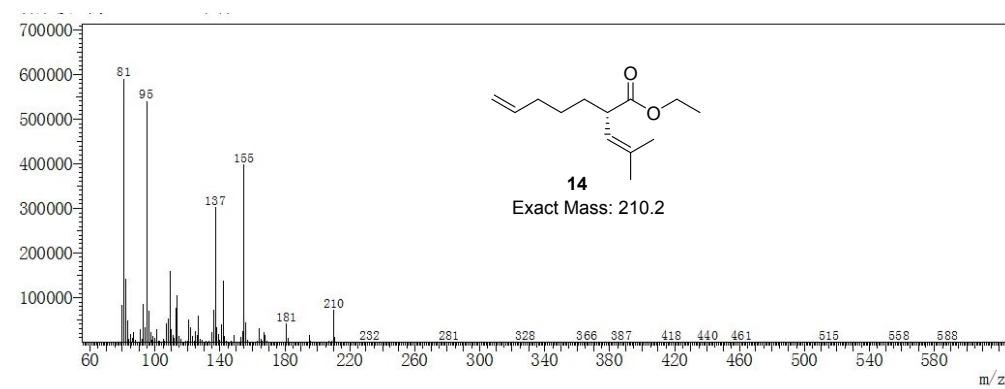


Peak	RetTime	Height	Area	Area (%)
1	10.285	3890409	4914912	50.16
2	10.972	994507	1448633	14.78
3	11.061 23	96692	3436285	35.06
Total		7281608	9799830	100

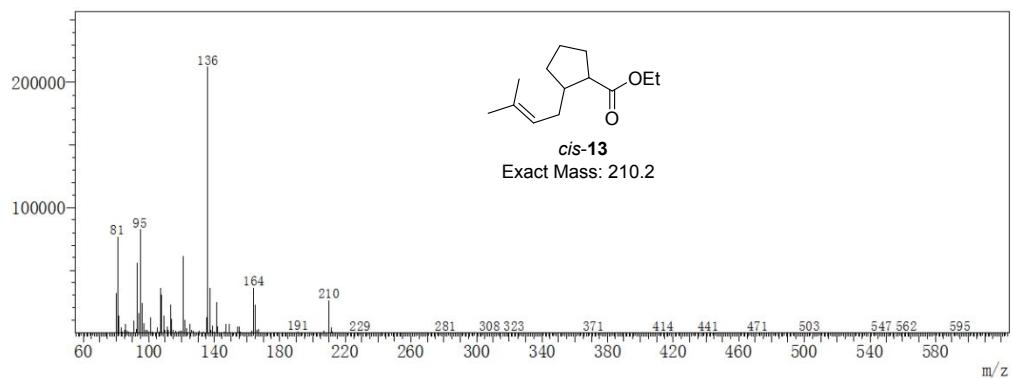
^aGC-MS analysis was carried out on a Varian 450 GC-240MS mass spectrometer system with EI using a VF-5 capillary column (30 m×0.25 mm×0.25 μm). The initial column temperature was 60 °C (for 4 min) and programmed to 280 °C with a rate of 20 deg/min, and the injector temperature was 250 °C. The carrier gas was Helium with a flow rate of 3 mL/min.

Figure S2. Mass spectra of compounds **14** (peak 1), *cis*-**13** (peak 2) and *trans*-**13** (peak 3)

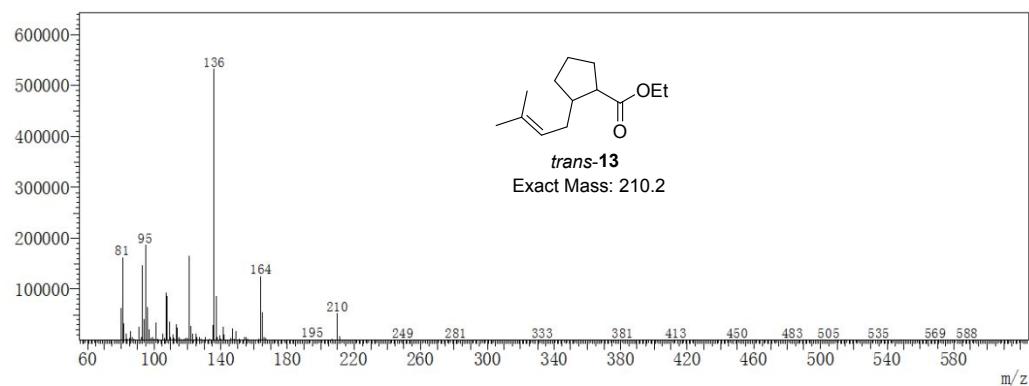
Peak 1 (*t*_r = 10.285 min)



Peak 2 ($t_r = 10.972$ min)



Peak 3 ($t_r = 11.061$ min)



9.¹H and ¹³C NMR Spectra of the Products

Figure S1. ¹H NMR Spectrum of (4S,4'S)-2,2'-(1,3-di-*o*-tolylpropane-2,2-diyl)bis(4-benzyl-4,5-dihydro-oxazole) (**L8**) (300 MHz, CDCl₃)

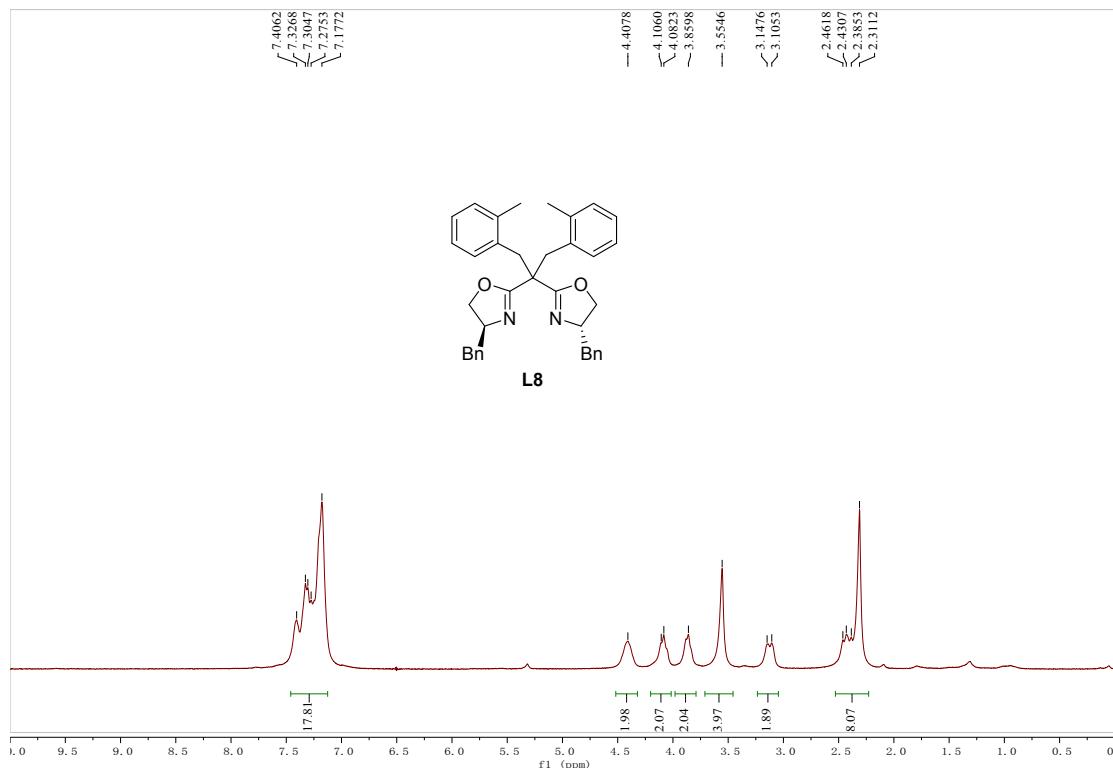


Figure S2. ¹³C NMR Spectrum of (4S,4'S)-2,2'-(1,3-di-*o*-tolylpropane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (**L8**) (75 MHz, CDCl₃)

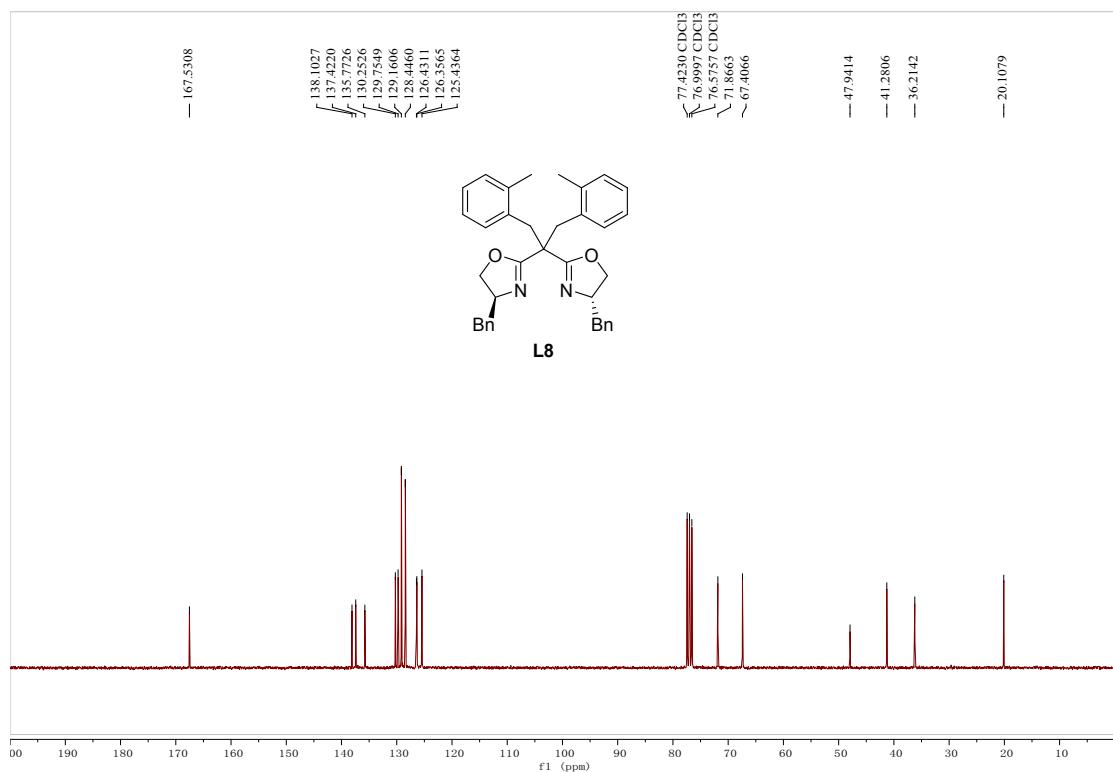


Figure S3. ^1H NMR Spectrum of (*4S,4'S*)-2,2'-(1,3-bis(3,5-di-*tert*-butylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (**L10**) (300 MHz, CDCl_3)

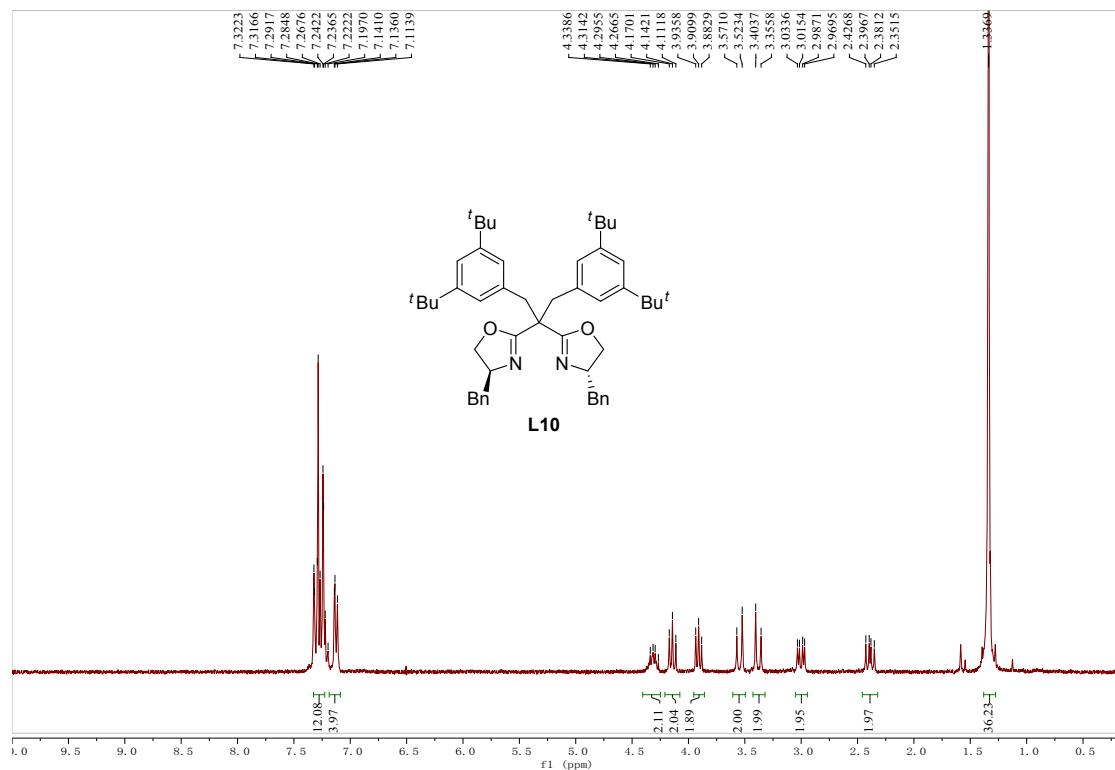


Figure S4. ^{13}C NMR Spectrum of (*4S,4'S*)-2,2'-(1,3-bis(3,5-di-*tert*-butylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (**L10**) (75 MHz, CDCl_3)

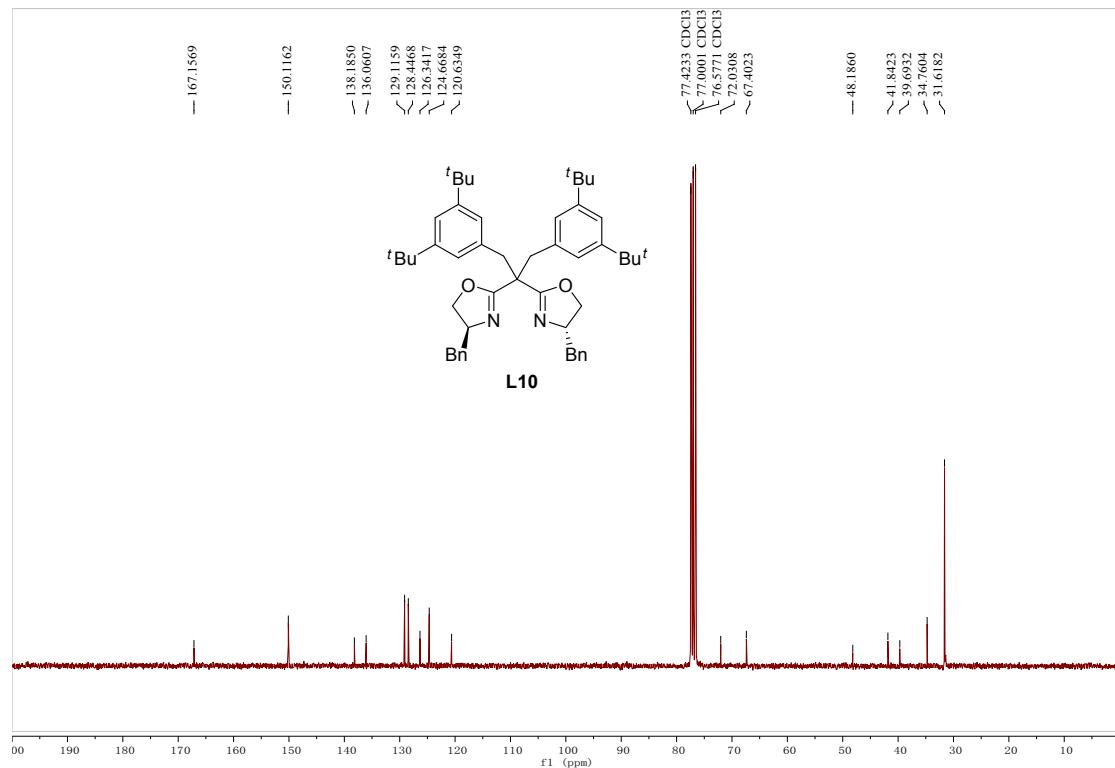


Figure S5. ^1H NMR Spectrum of ($4S,4'S$)-2,2'-(1,3-bis(3,5-dimethylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (**L11**) (300 MHz, CDCl_3)

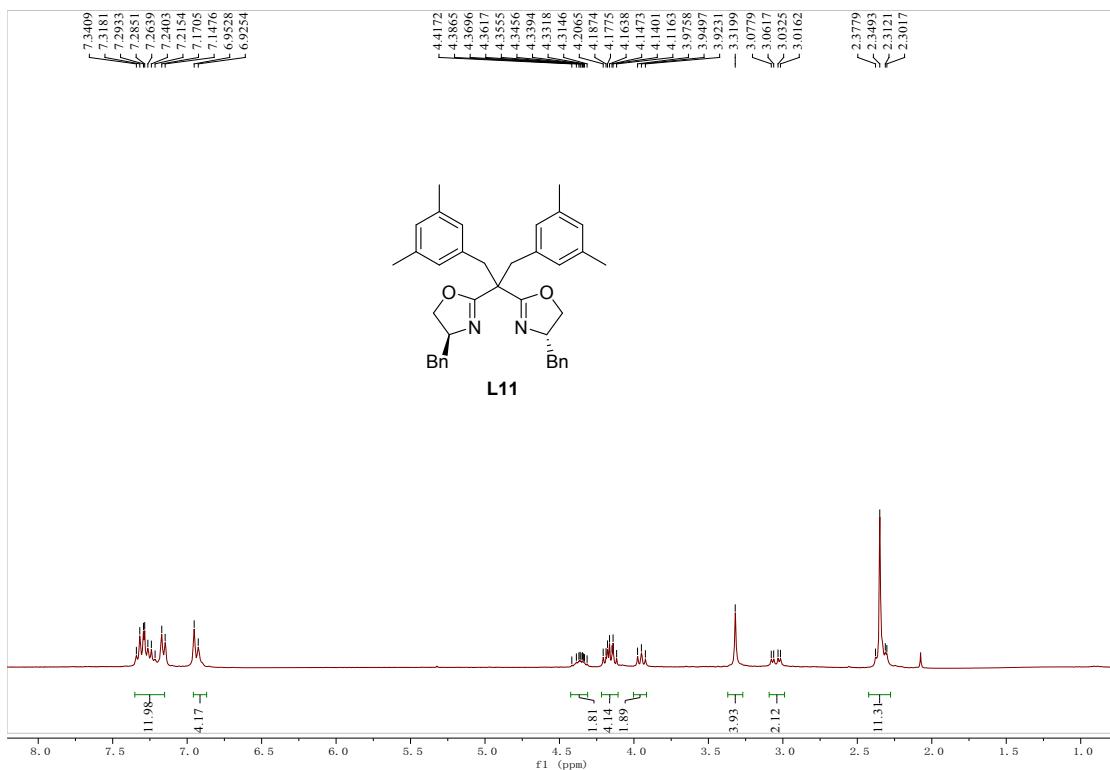


Figure S6. ^{13}C NMR Spectrum of ($4S,4'S$)-2,2'-(1,3-bis(3,5-dimethylphenyl)propane-2,2-diyl)bis(4-benzyl-4,5-dihydrooxazole) (**L11**) (75 MHz, CDCl_3)

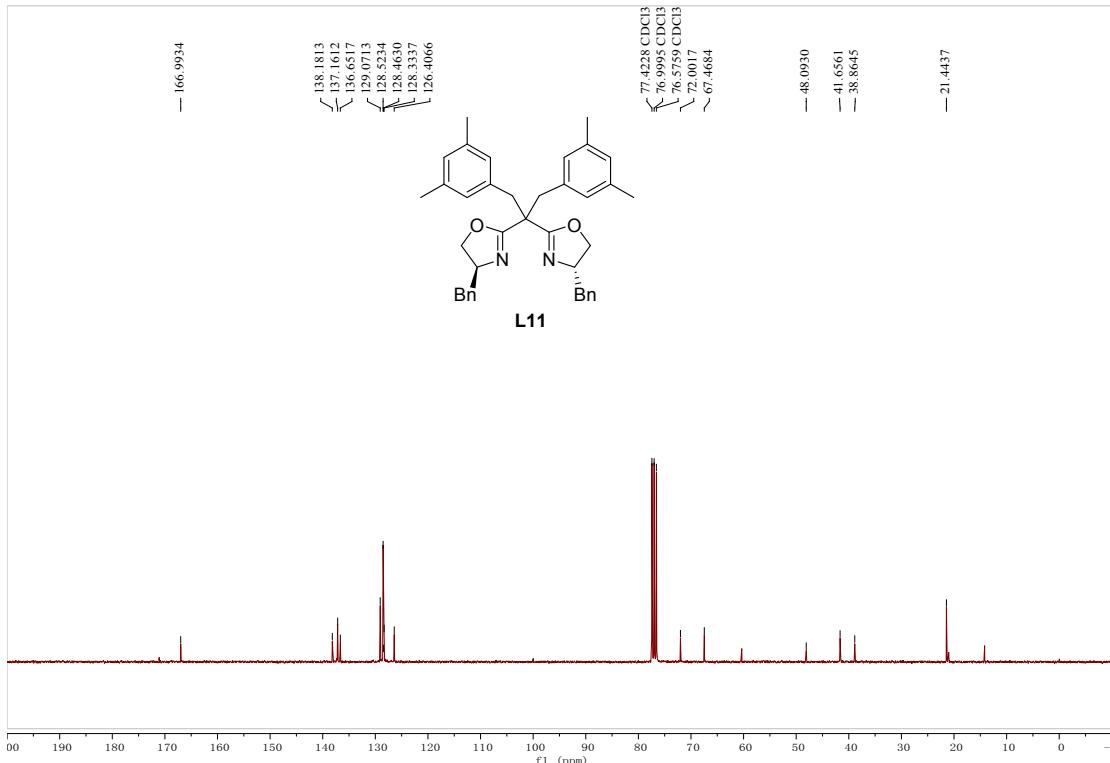


Figure S7. ^1H NMR Spectrum of 2,2'-bis((S)-4-benzyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L14**) (300 MHz, CDCl_3)

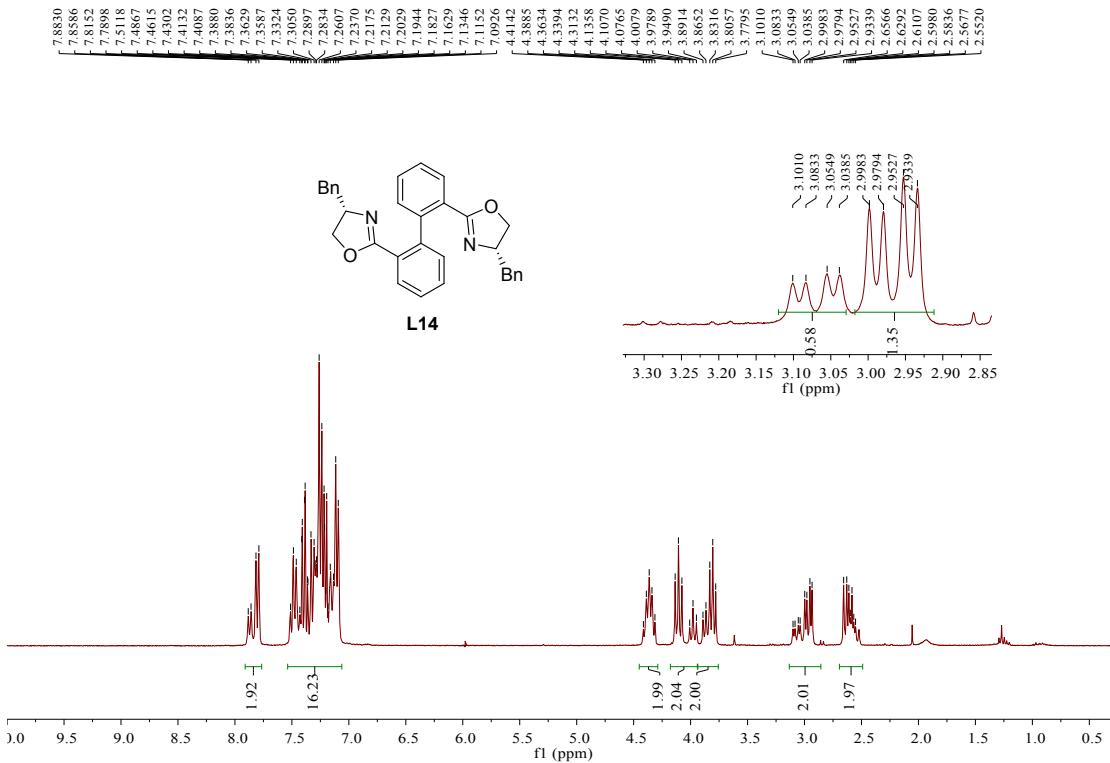


Figure S8. ^{13}C NMR Spectrum of 2,2'-bis((S)-4-benzyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L14**) (75 MHz, CDCl_3)

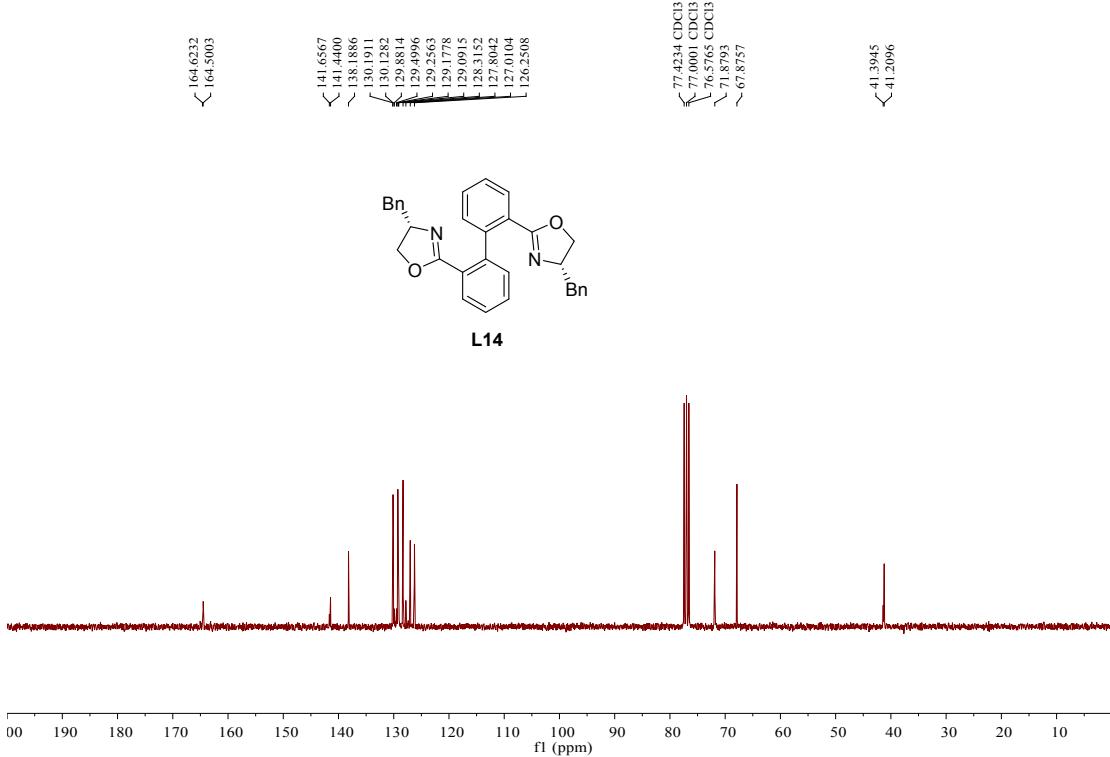


Figure S9. ^1H NMR Spectrum of 2,2'-bis((S)-4-phenyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L15**) (300 MHz, CDCl_3)

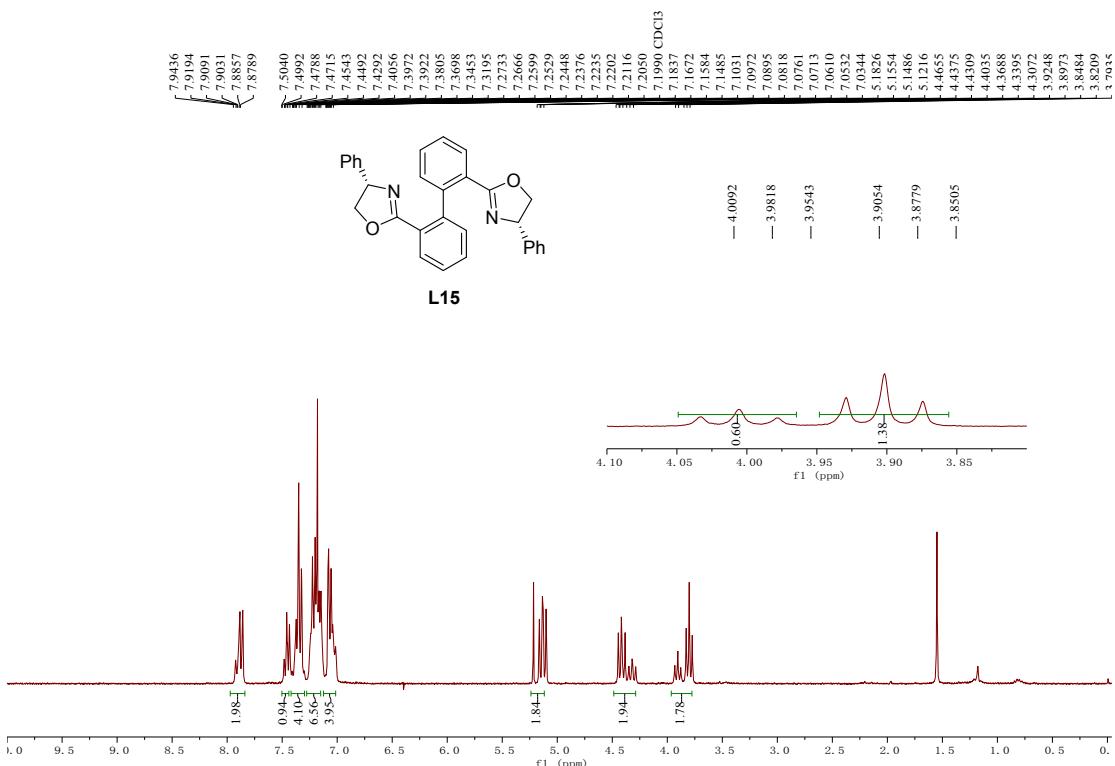


Figure S10. ^{13}C NMR Spectrum of 2,2'-bis((S)-4-phenyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L15**) (75 MHz, CDCl_3)

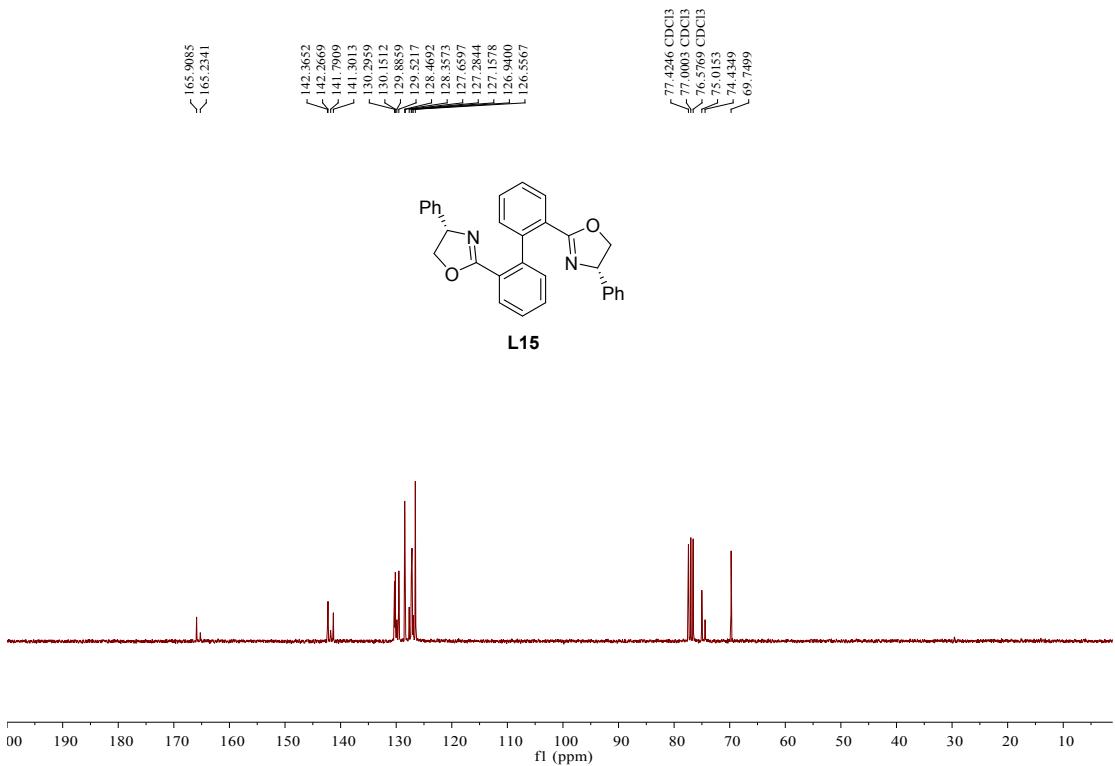


Figure S11. ^1H NMR Spectrum of 2,2'-bis((*S*)-4-*iso*-butyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L16**) (300 MHz, CDCl_3)

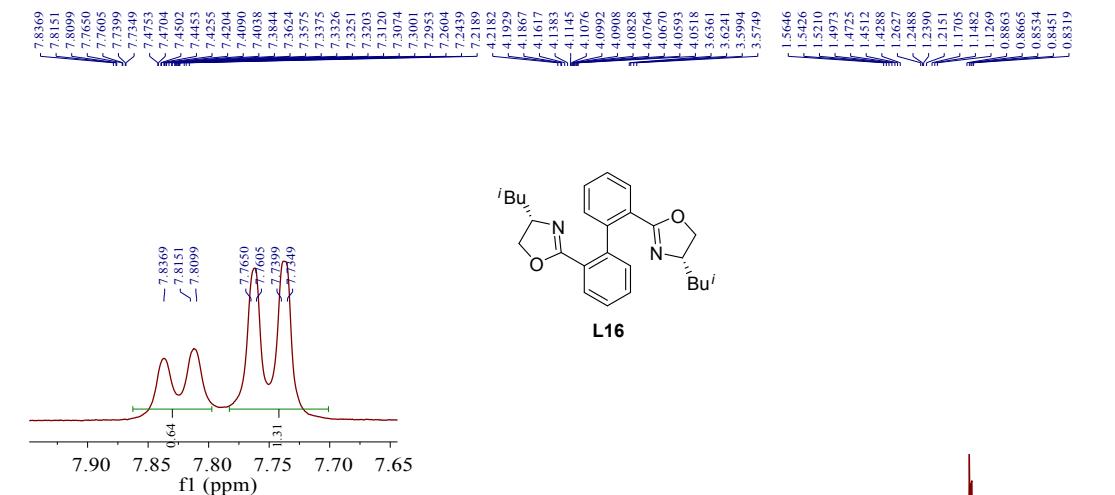


Figure S12. ^{13}C NMR Spectrum of 2,2'-bis((*S*)-4-isobutyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L16**) (75 MHz, CDCl_3).

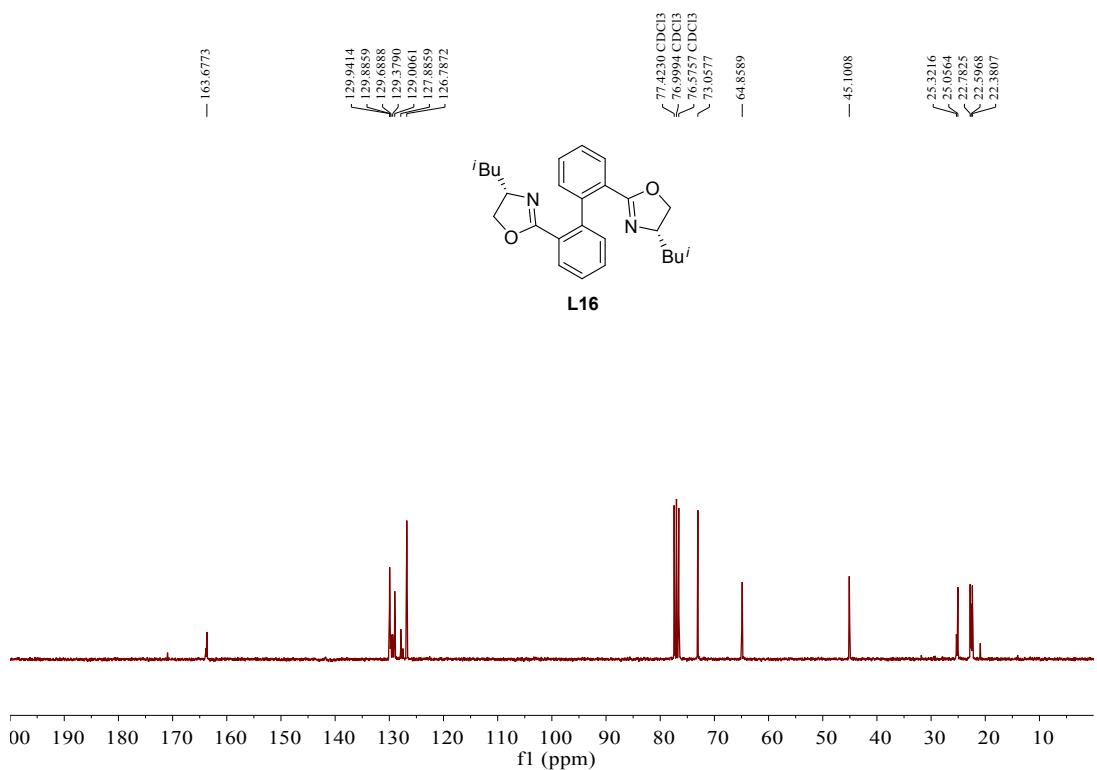


Figure S13. ^1H NMR Spectrum of 2,2'-bis((*S*)-4-*iso*-propyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L17**) (300 MHz, CDCl_3)

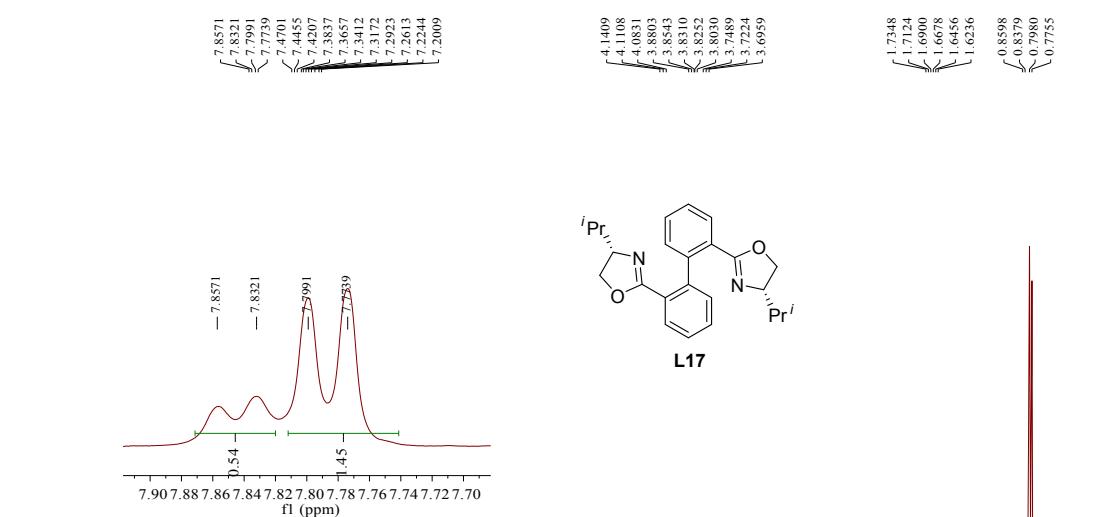


Figure S14. ^{13}C NMR Spectrum of 2,2'-bis((*S*)-4-*iso*-propyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L17**) (75 MHz, CDCl_3)

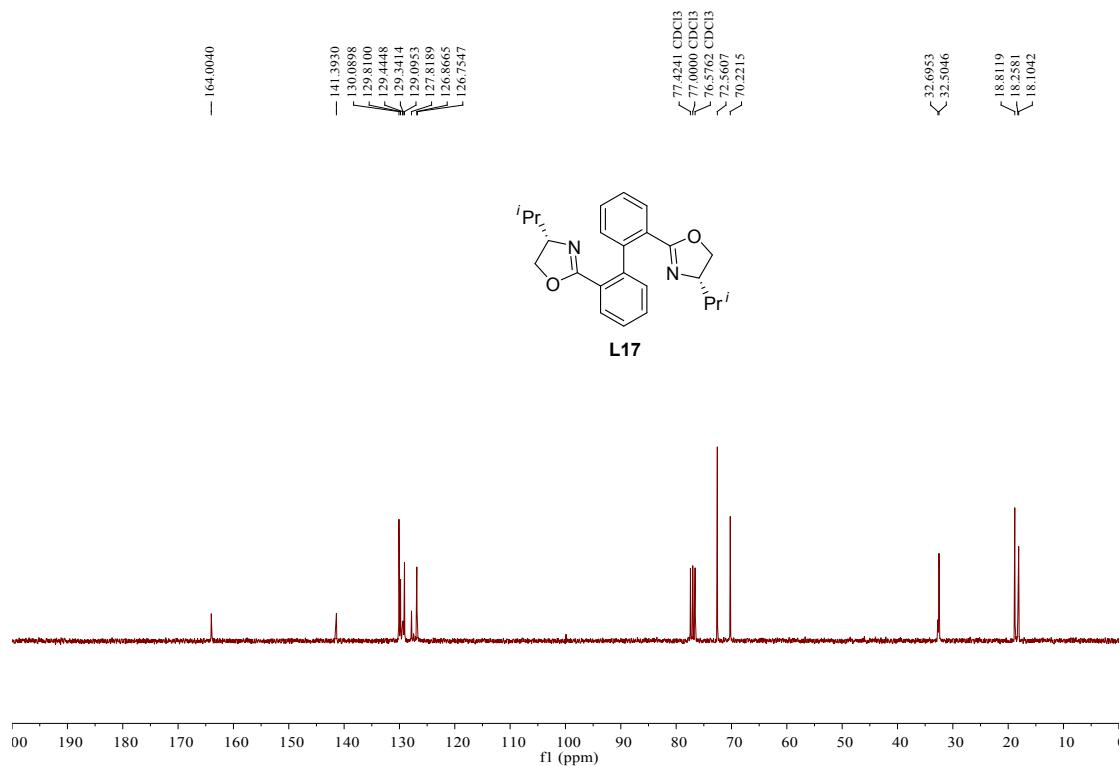


Figure S15. ^1H NMR Spectrum of 2,2'-bis((S)-4-ethyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L18**) (300 MHz, CDCl_3)

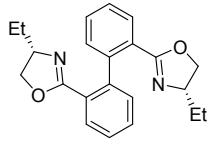
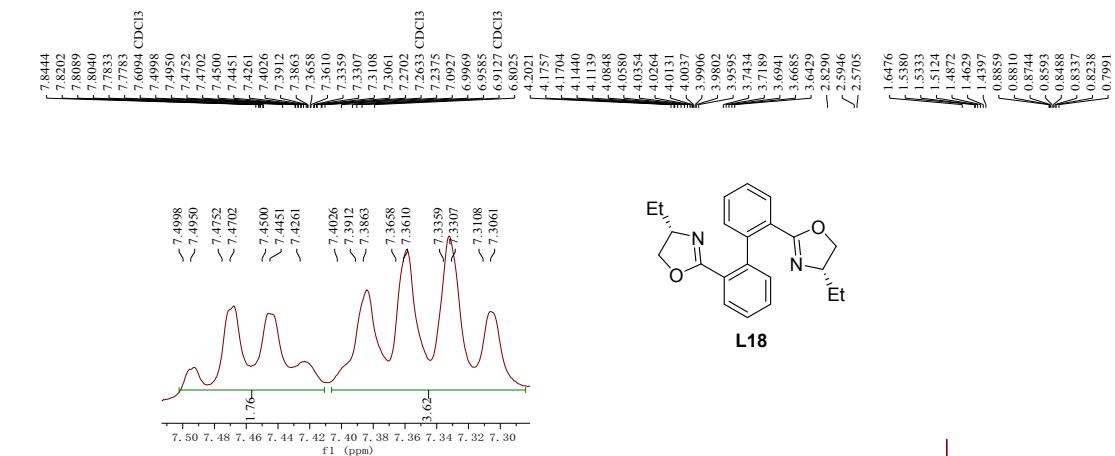


Figure S16. ^{13}C NMR Spectrum of 2,2'-bis((S)-4-ethyl-4,5-dihydrooxazol-2-yl)-1,1'-biphenyl (**L18**) (75 MHz, CDCl_3)

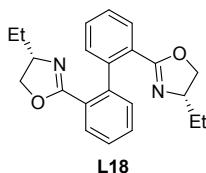
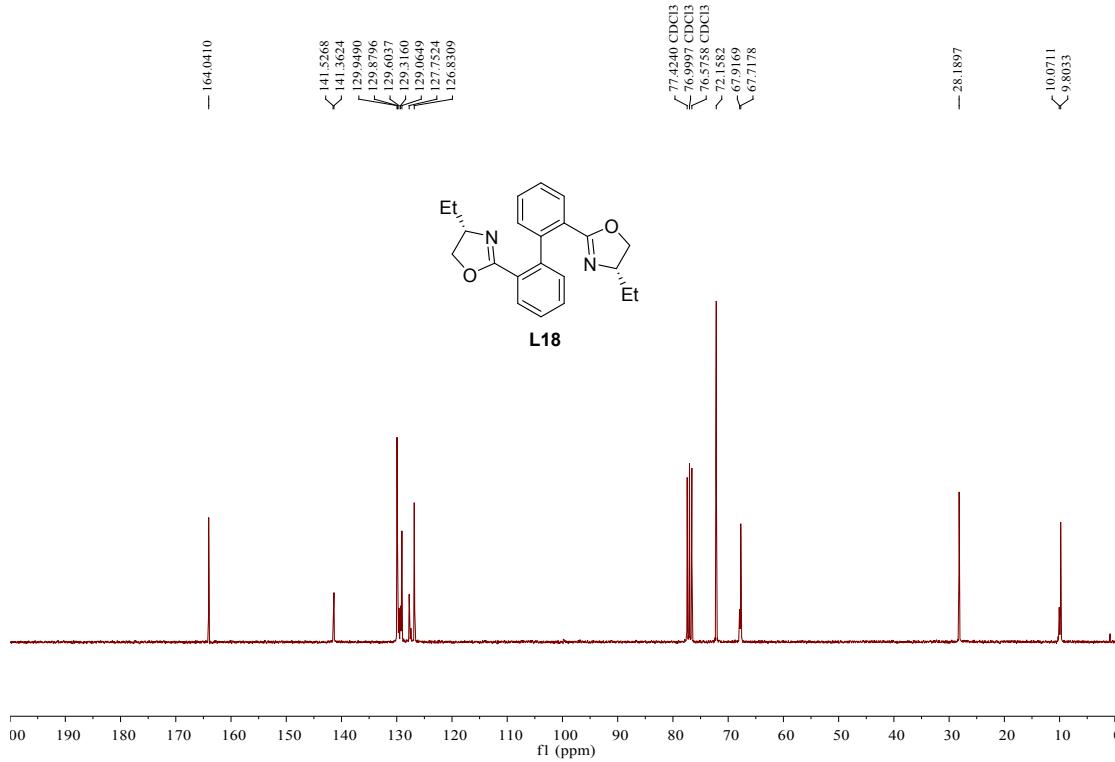


Figure S17. ^1H NMR Spectrum of benzyl 2-bromohex-5-enoate (**4n**) (300 MHz, CDCl_3)

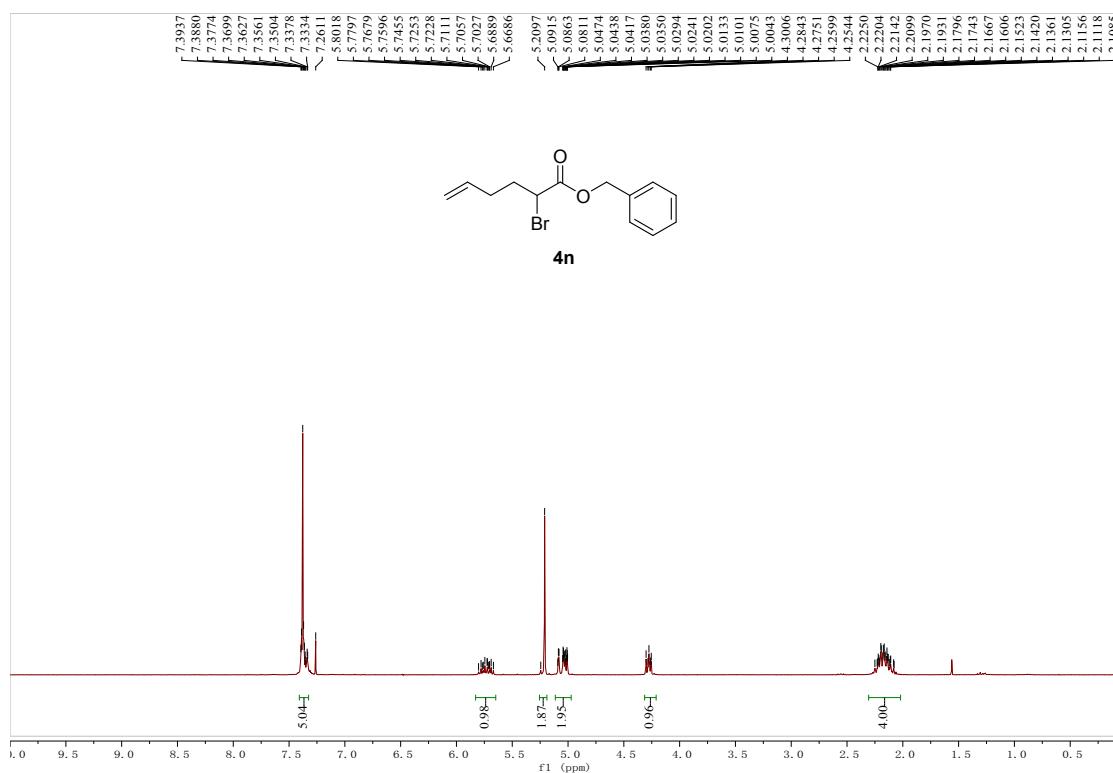


Figure S18. ^{13}C NMR Spectrum of benzyl 2-bromohex-5-enoate (**4n**) (75 MHz, CDCl_3)

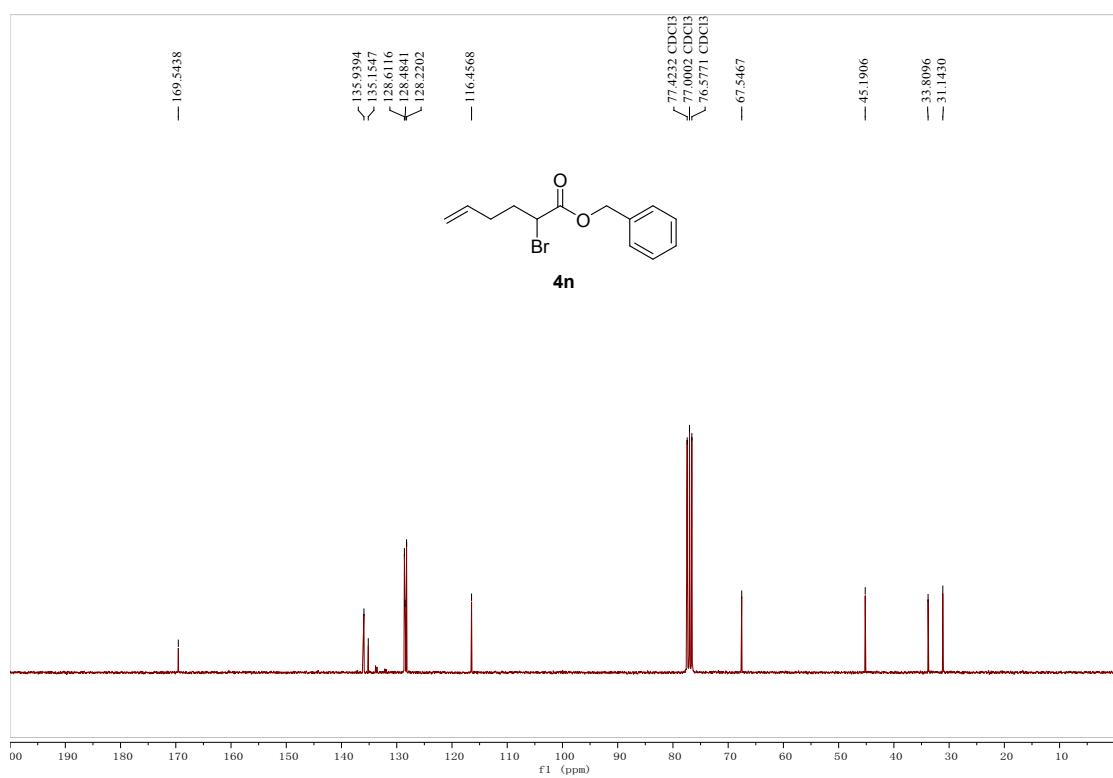


Figure S19. ^1H NMR Spectrum of (*S*)-benzyl 2,4-dimethylpent-3-enoate (**3a**) (300 MHz, CDCl_3)

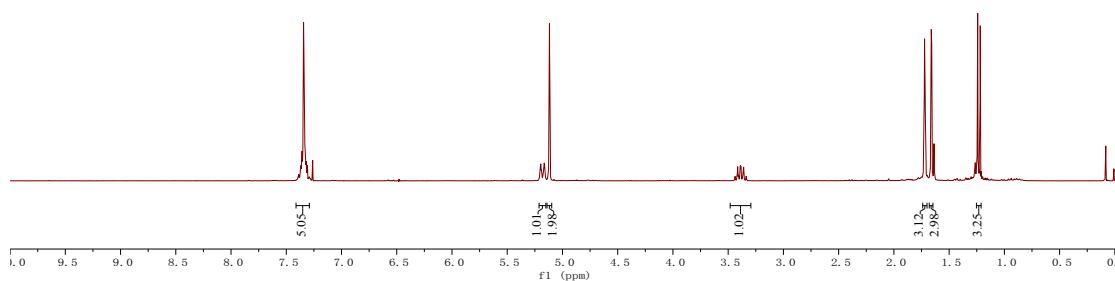
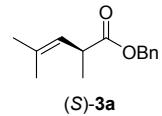


Figure S20. ^{13}C NMR Spectrum of (*S*)-benzyl 2,4-dimethylpent-3-enoate (**3a**) (75 MHz, CDCl_3)

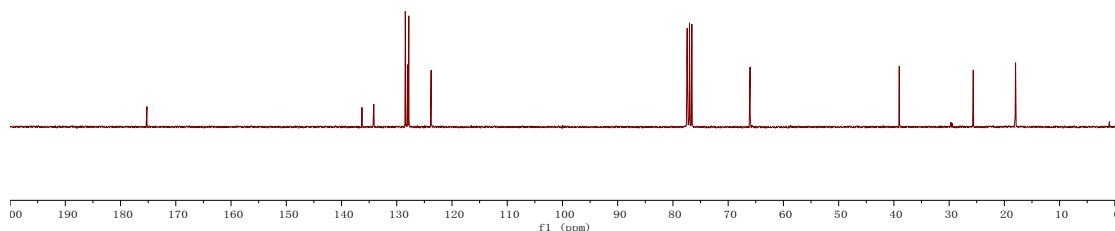
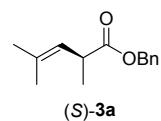


Figure S21. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2,4-dimethylpent-3-enoate (**3b**) (300 MHz, CDCl_3)

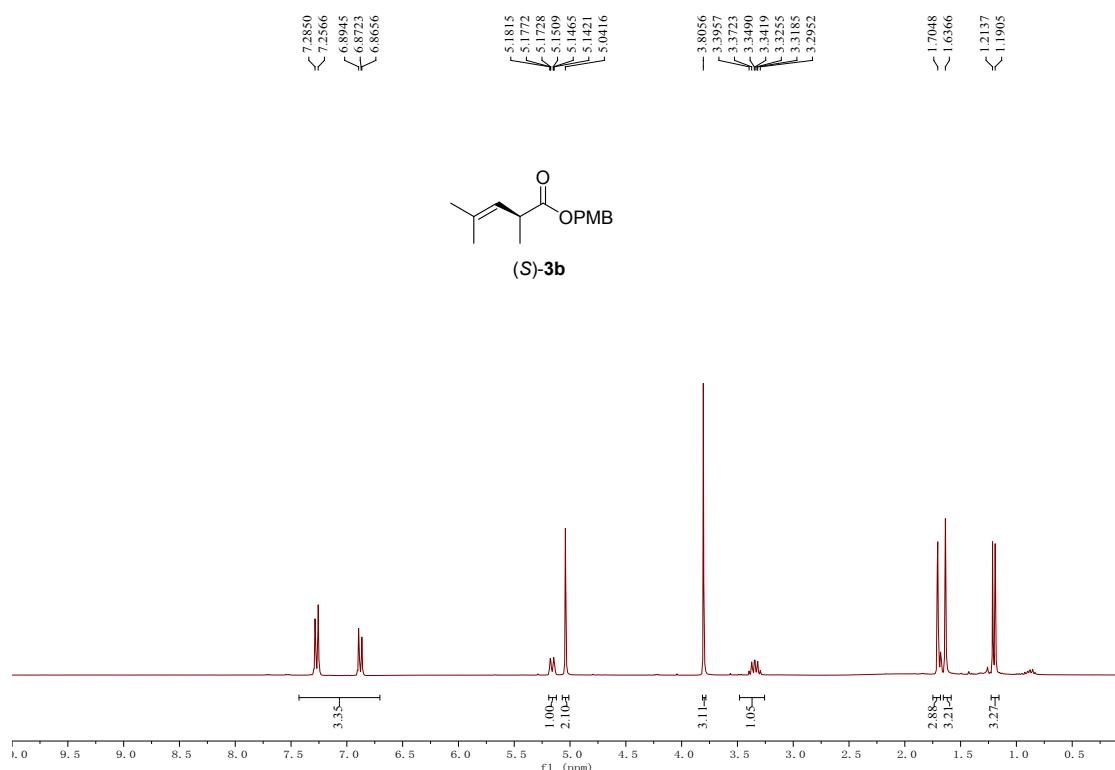


Figure S22. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2,4-dimethylpent-3-enoate (**3b**) (75 MHz, CDCl_3)

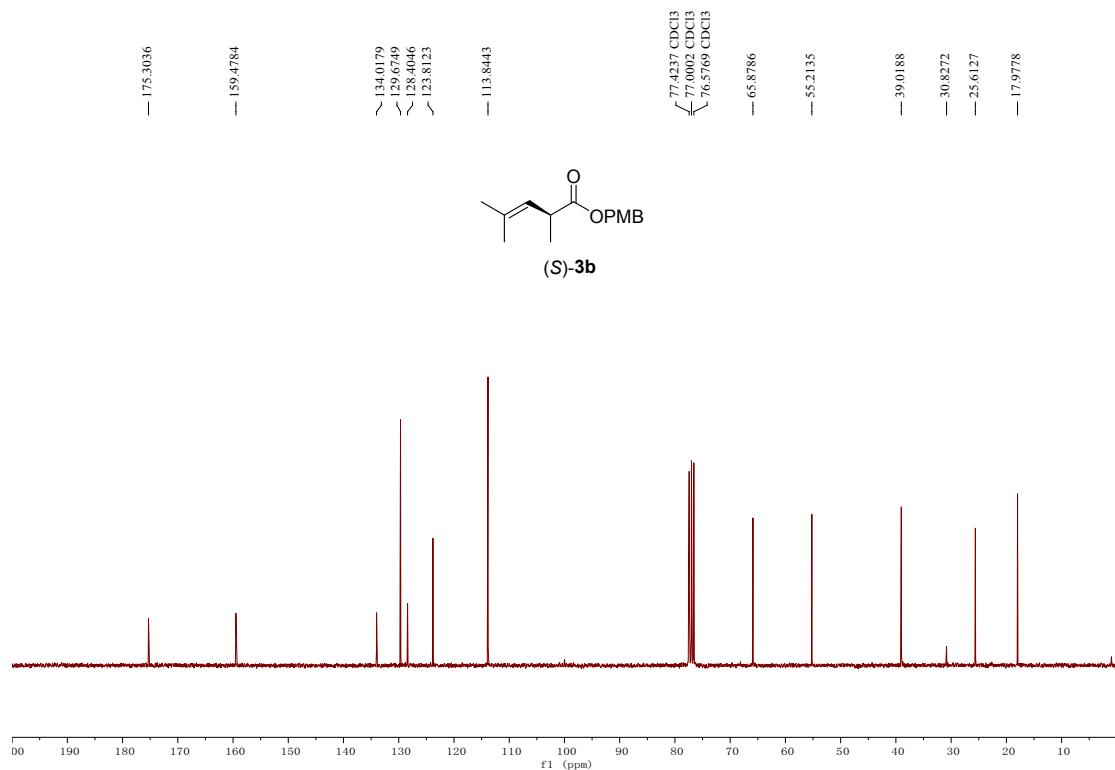


Figure S23. ^1H NMR Spectrum of (*S*)-*iso*-butyl 2,4-dimethylpent-3-enoate (**3c**) (300 MHz, CDCl_3)

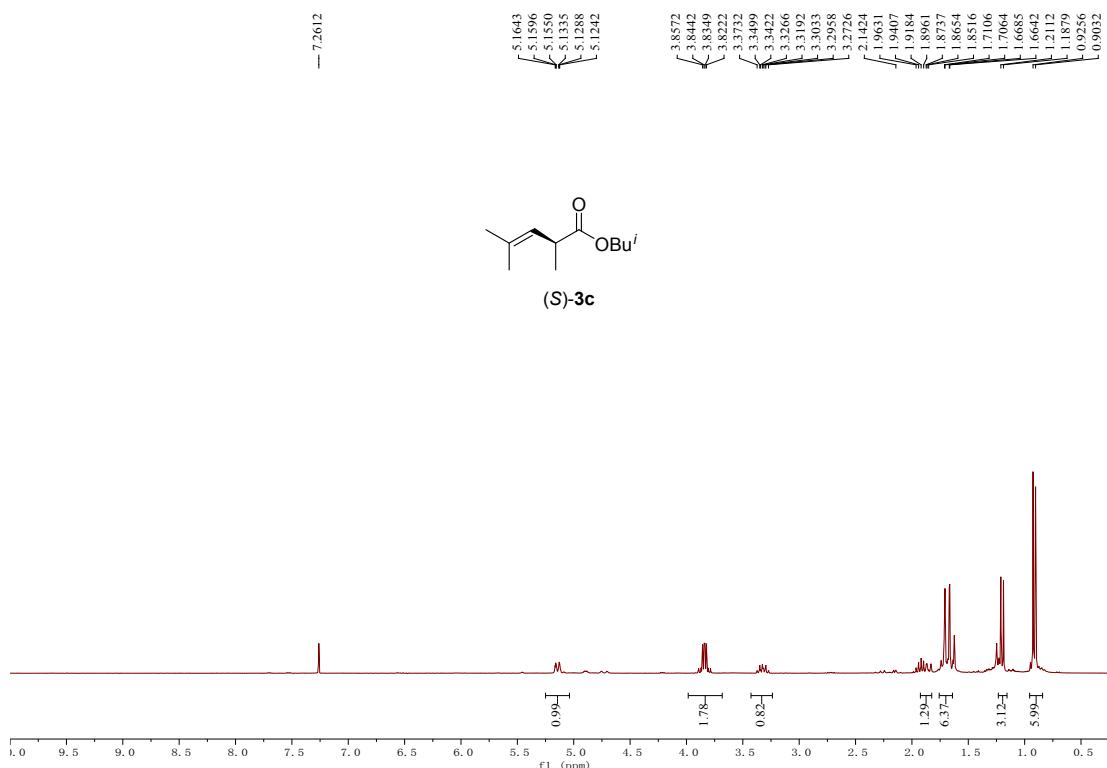


Figure S24. ^{13}C NMR Spectrum of (*S*)-*iso*-butyl 2,4-dimethylpent-3-enoate (**3c**) (75 MHz, CDCl_3)

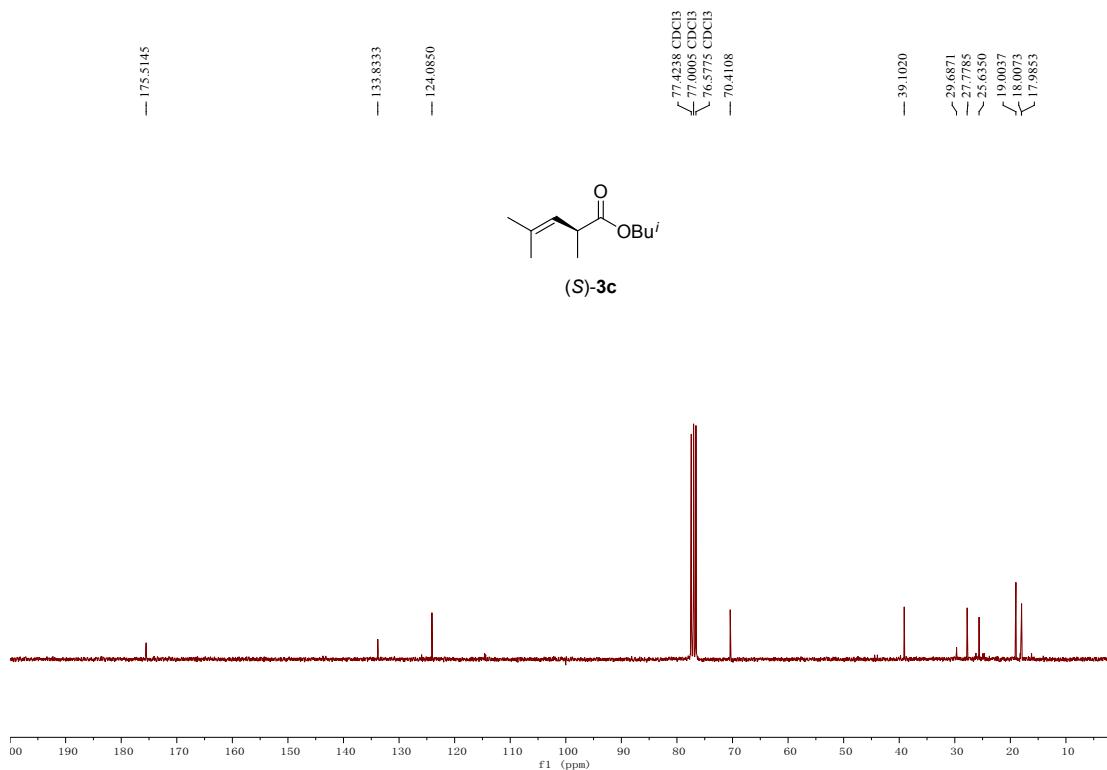


Figure S25. ^1H NMR Spectrum of (*S*)-*iso*-propyl 2,4-dimethylpent-3-enoate (**3d**) (300 MHz, CDCl_3)

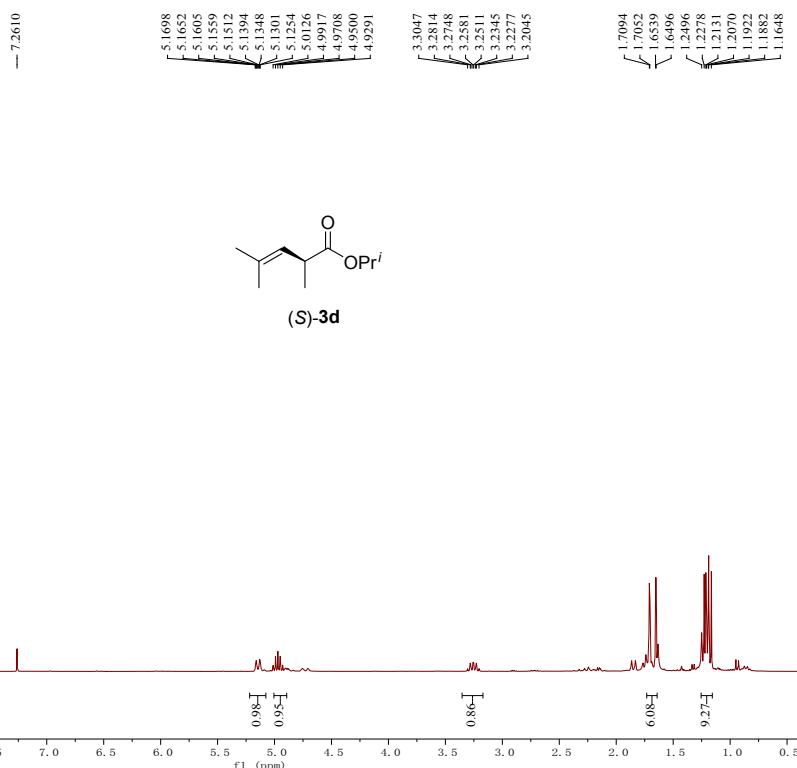


Figure S26. ^{13}C NMR Spectrum of (*S*)-*iso*-propyl 2,4-dimethylpent-3-enoate (**3d**) (75 MHz, CDCl_3)

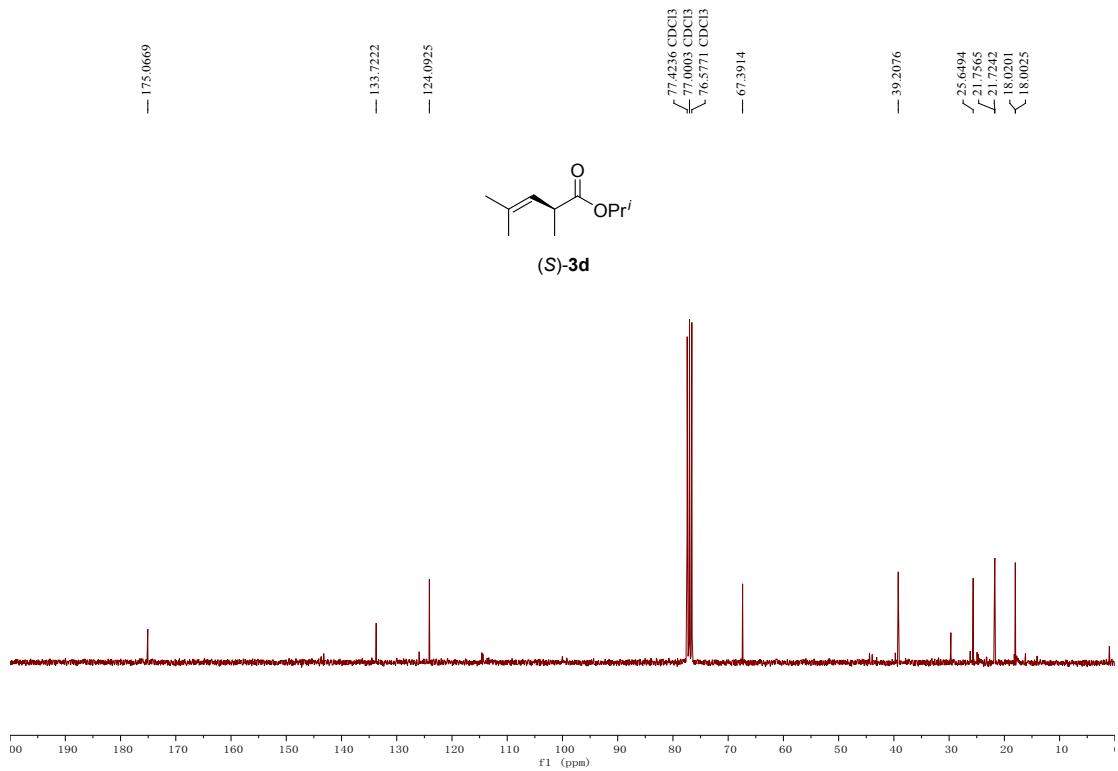


Figure S27. ^1H NMR Spectrum of (*S*)-*tert*-butyl 2,4-dimethylpent-3-enoate (**3e**) (300 MHz, CDCl_3)

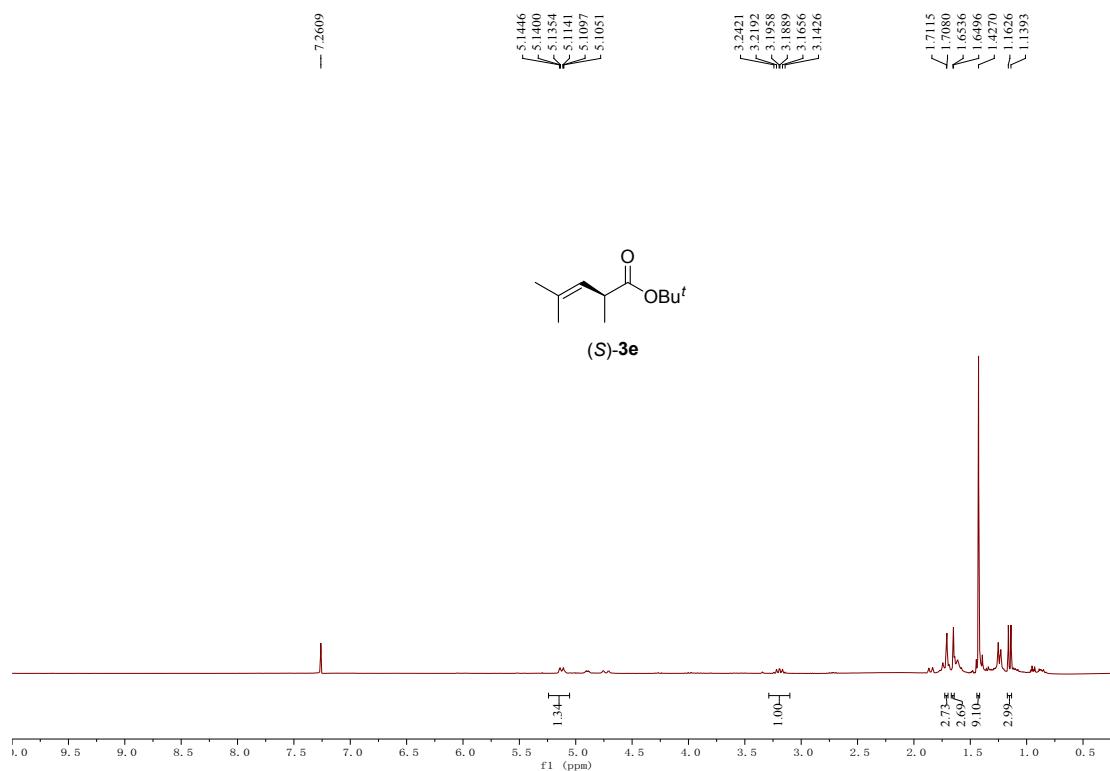


Figure S28. ^{13}C NMR Spectrum of (*S*)-*tert*-butyl 2,4-dimethylpent-3-enoate (**3e**) (75 MHz, CDCl_3)

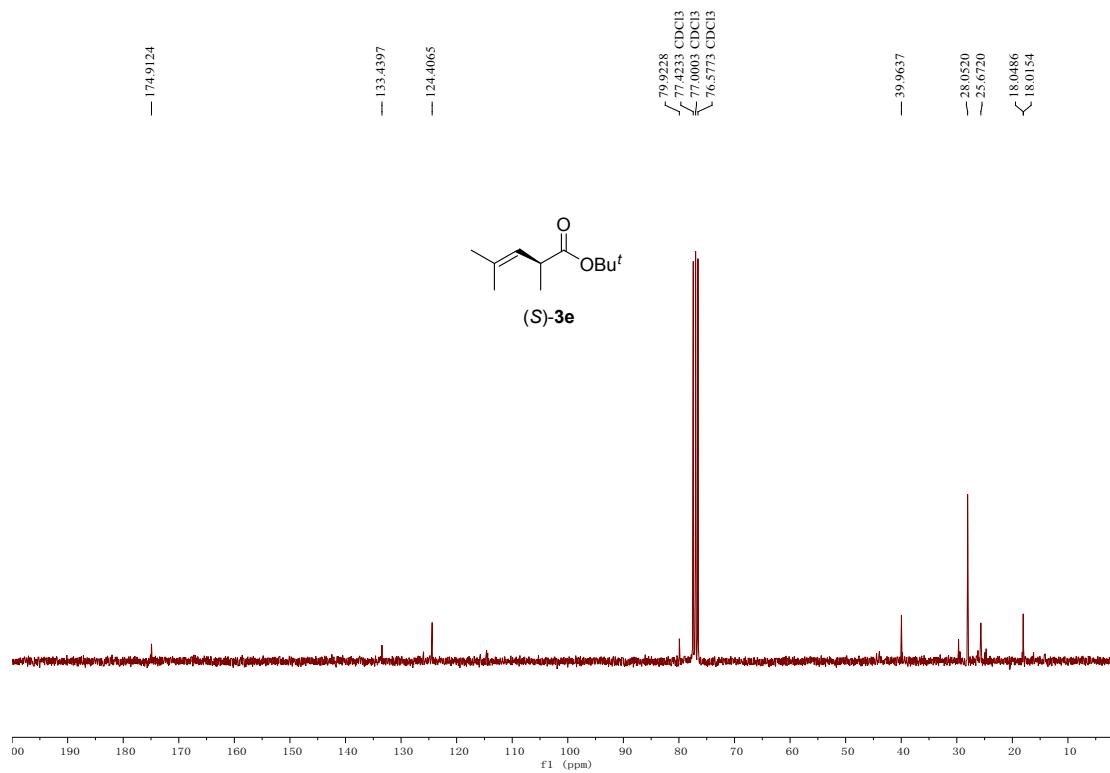


Figure S29. ^1H NMR Spectrum of (*S*)-cyclopentyl 2,4-dimethylpent-3-enoate (**3f**) (300 MHz, CDCl_3)

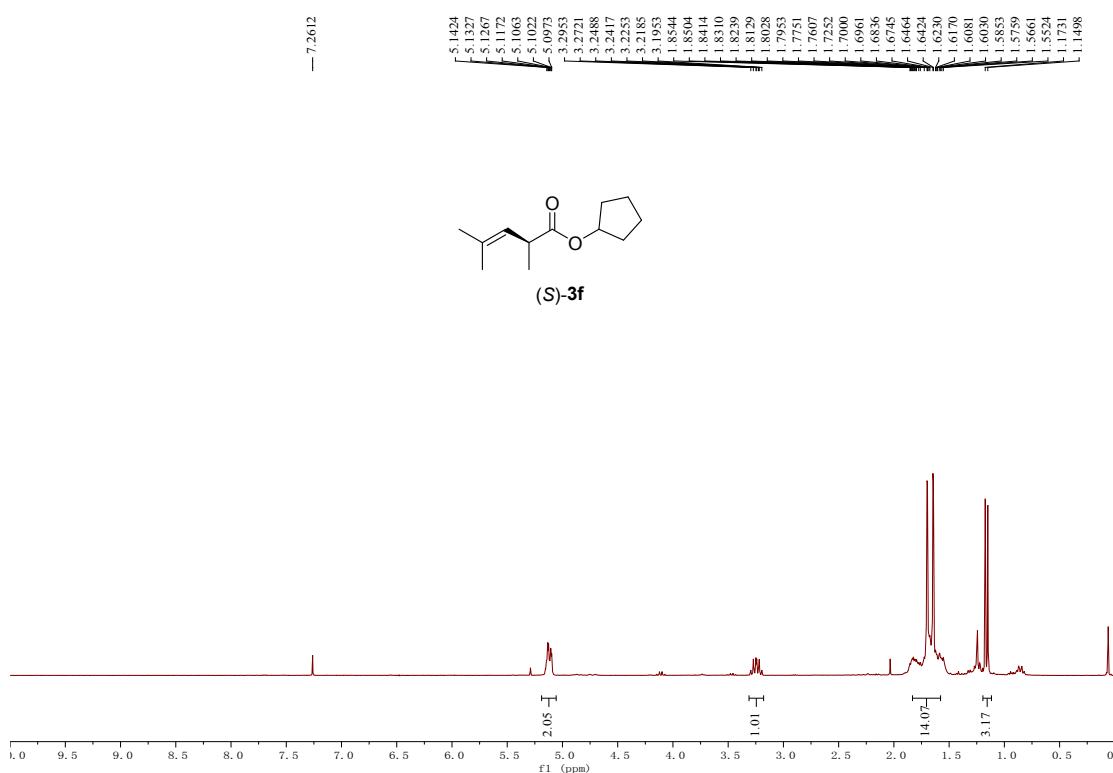


Figure S30. ^{13}C NMR Spectrum of (*S*)-cyclopentyl 2,4-dimethylpent-3-enoate (**3f**) (75 MHz, CDCl_3).

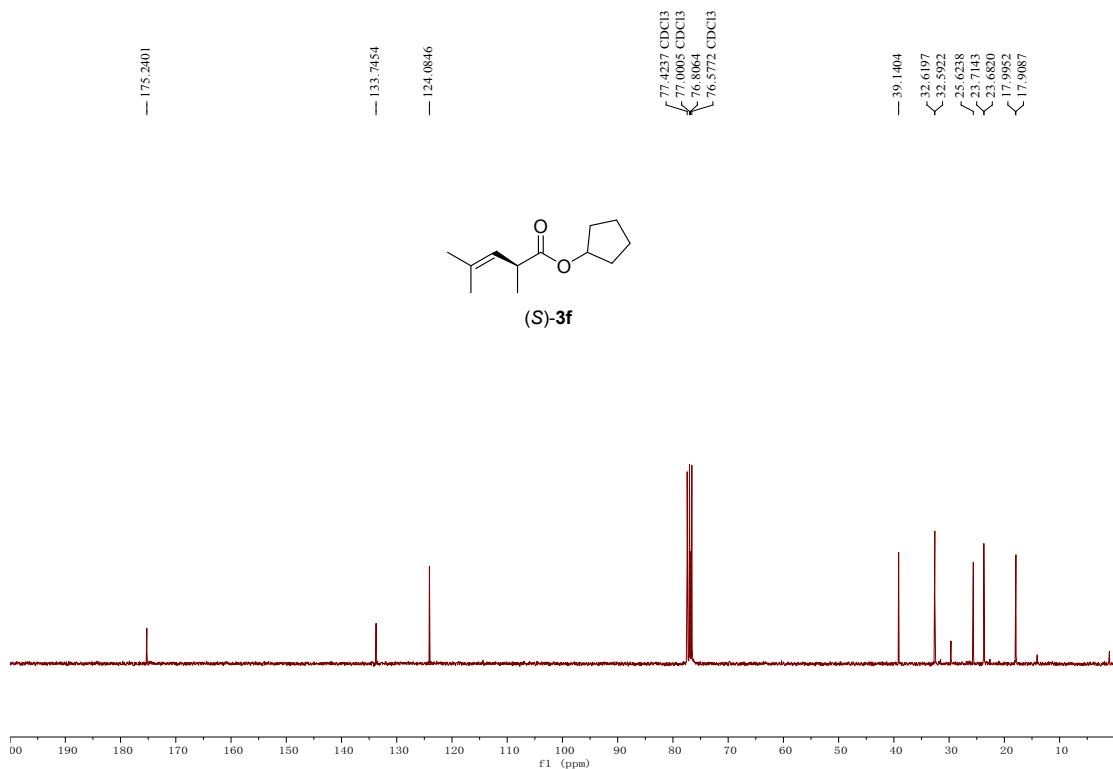


Figure S31. ^1H NMR Spectrum of (*S*)-cyclohexyl 2,4-dimethylpent-3-enoate (**3g**) (300 MHz, CDCl_3)

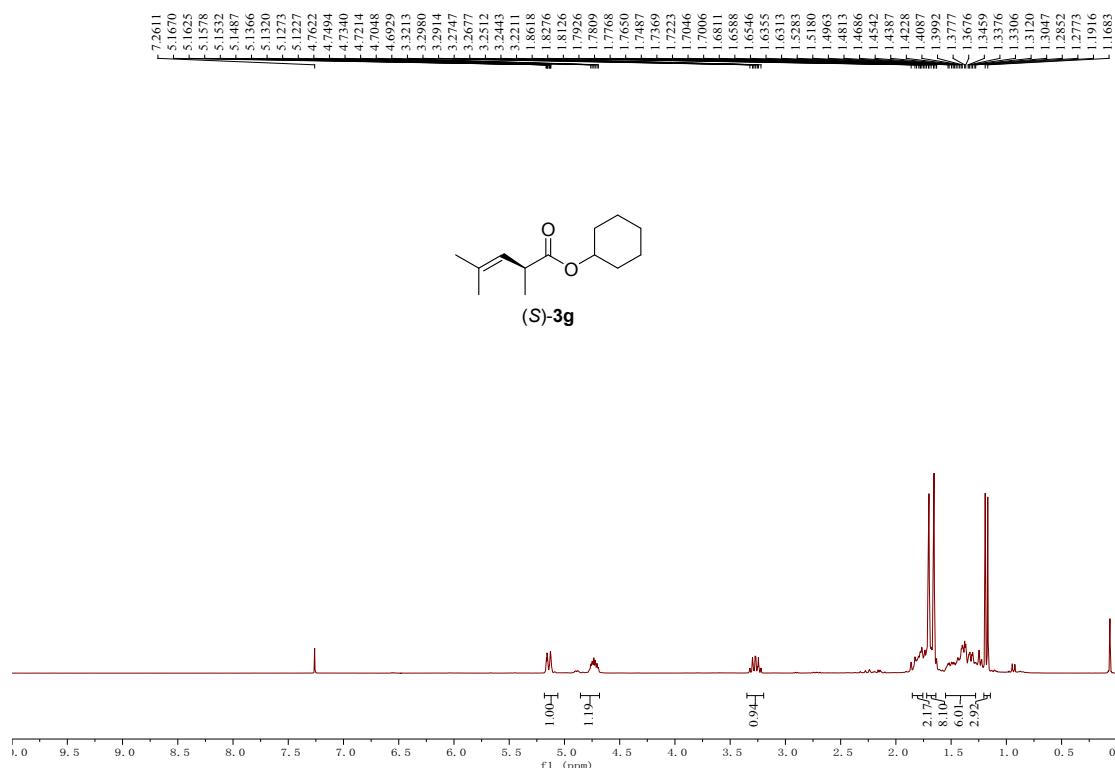


Figure S32. ^{13}C NMR Spectrum of (*S*)-cyclohexyl 2,4-dimethylpent-3-enoate (**3g**) (75 MHz, CDCl_3)

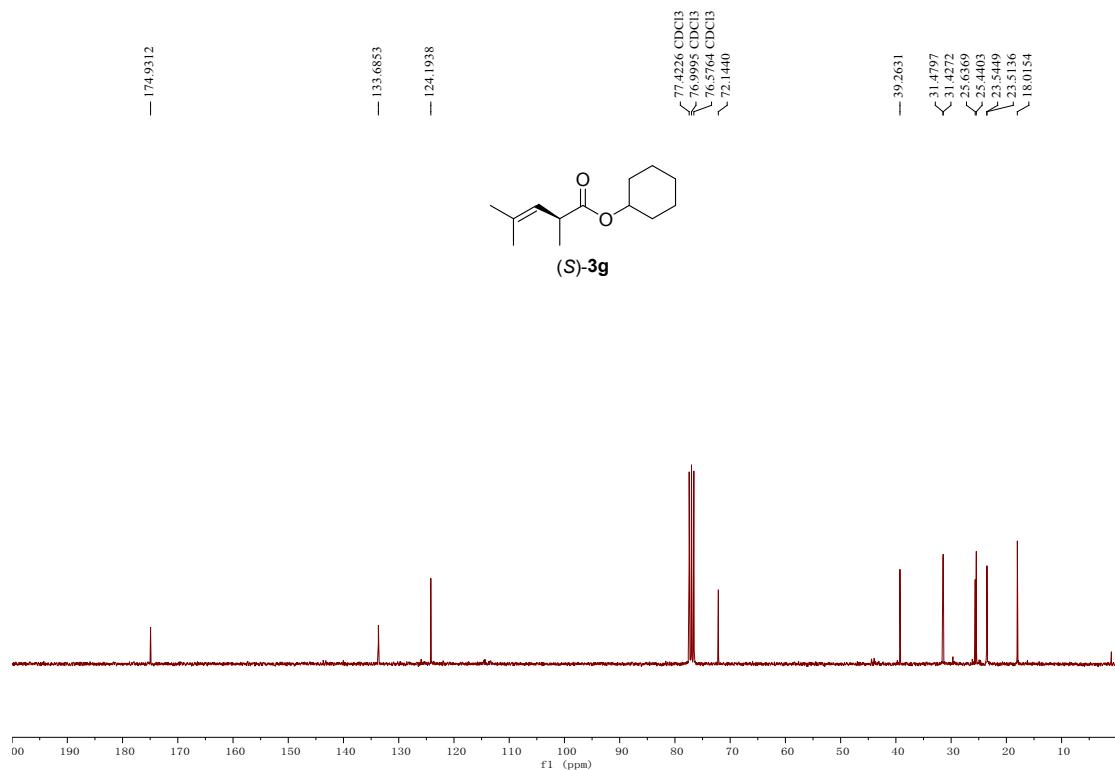


Figure S33. ^1H NMR Spectrum of (*S*)-cyclohexylmethyl 2,4-dimethylpent-3-enoate (**3h**) (300 MHz, CDCl_3)

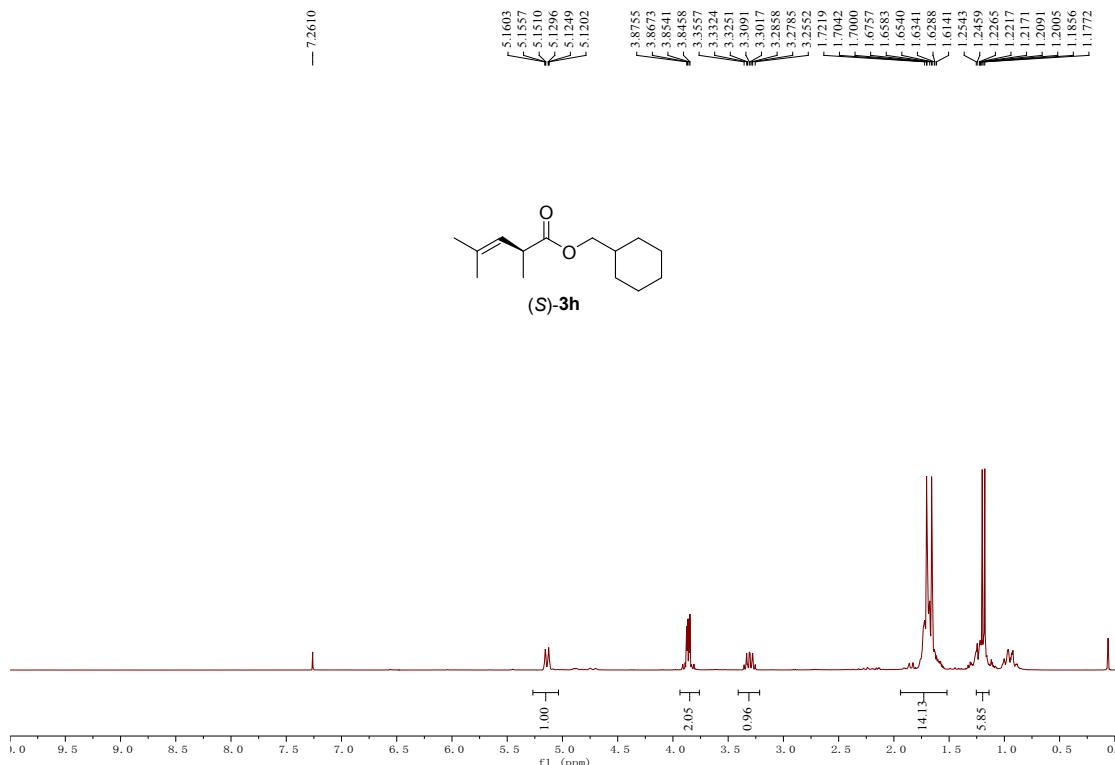


Figure S34. ^{13}C NMR Spectrum of (*S*)-cyclohexylmethyl 2,4-dimethylpent-3-enoate (**3h**) (75 MHz, CDCl_3)

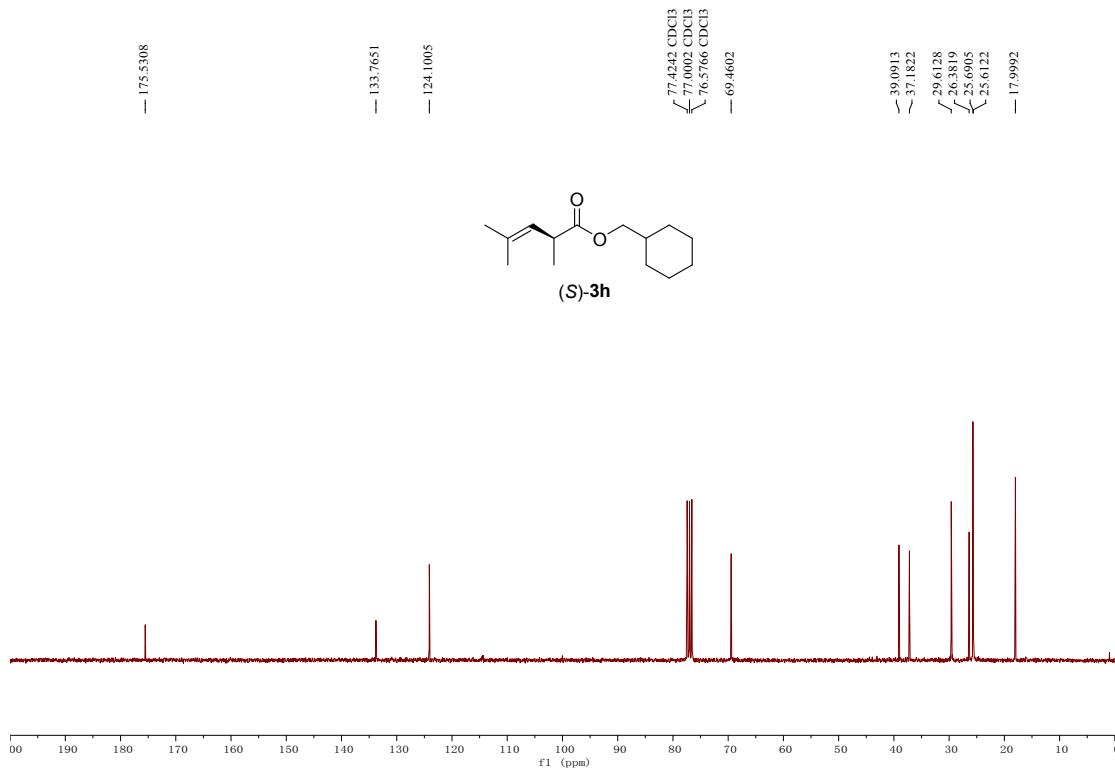


Figure S35. ^1H NMR Spectrum of (*S*)-2-bromoethyl 2,4-dimethylpent-3-enoate (**3i**) (400 MHz, CDCl_3)

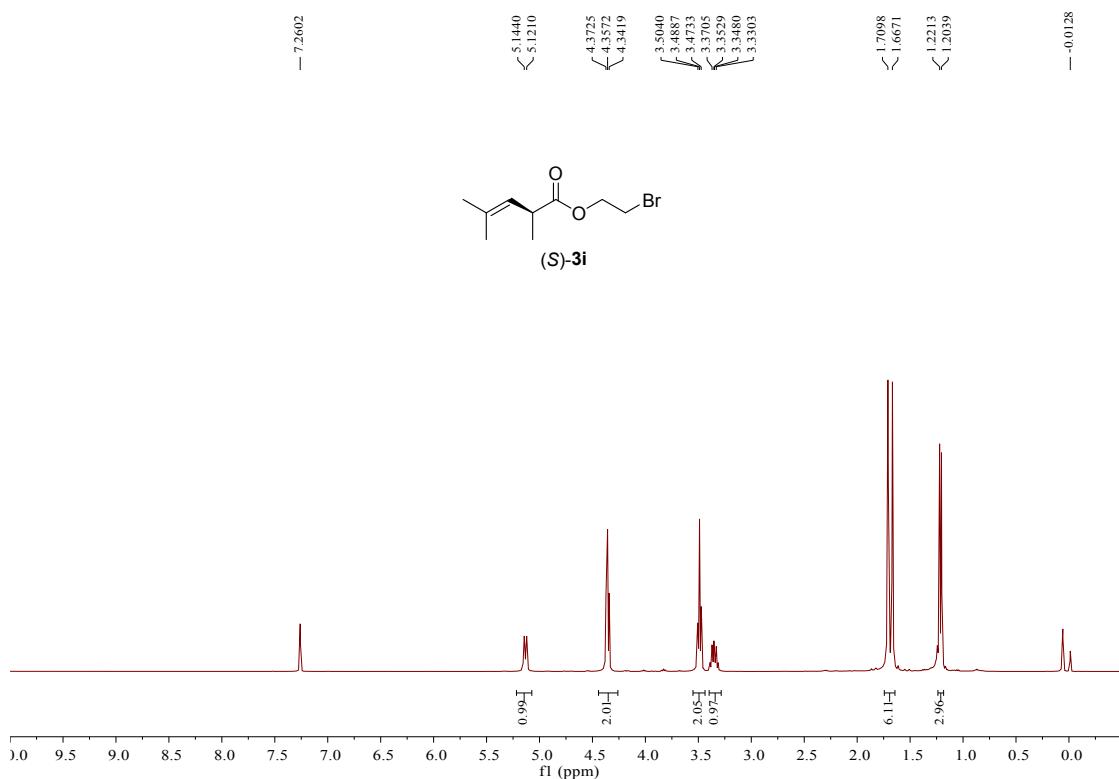


Figure S36. ^{13}C NMR Spectrum of (*S*)-2-bromoethyl 2,4-dimethylpent-3-enoate (**3i**) (100 MHz, CDCl_3)

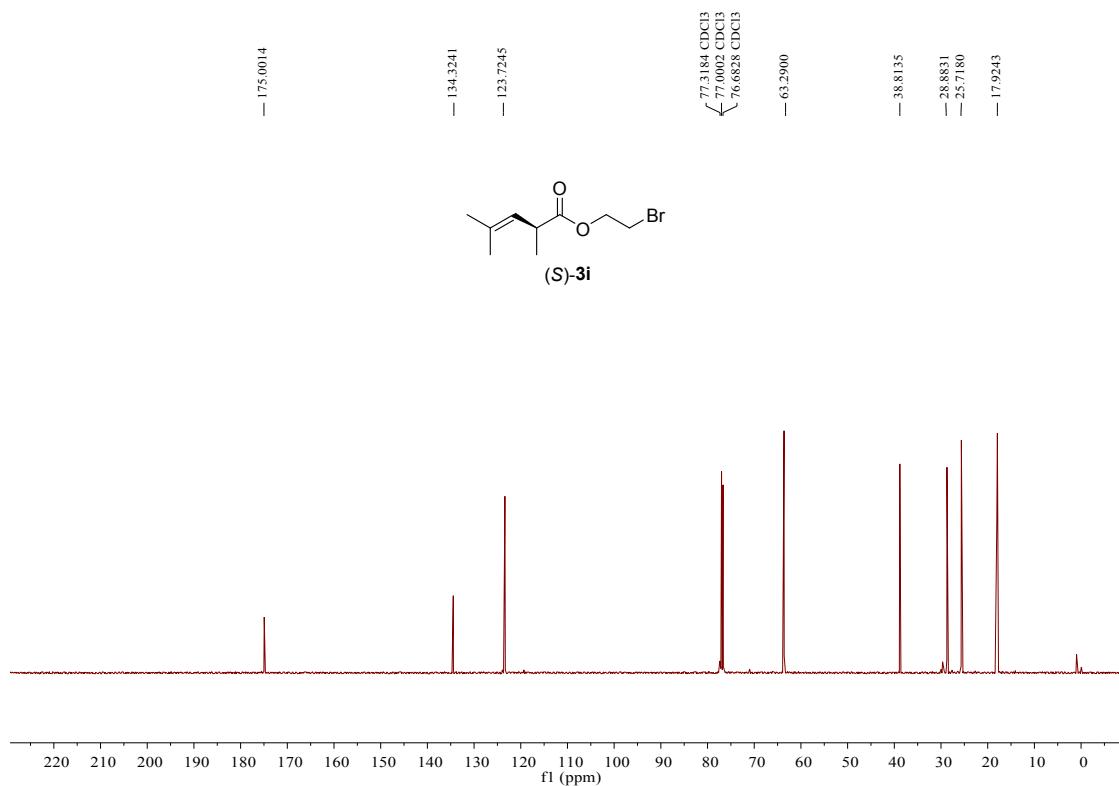


Figure S37. ^1H NMR Spectrum of (*S*)-3-methylbut-2-en-1-yl 2,4-dimethylpent-3-enoate (**3j**) (300 MHz, CDCl_3)

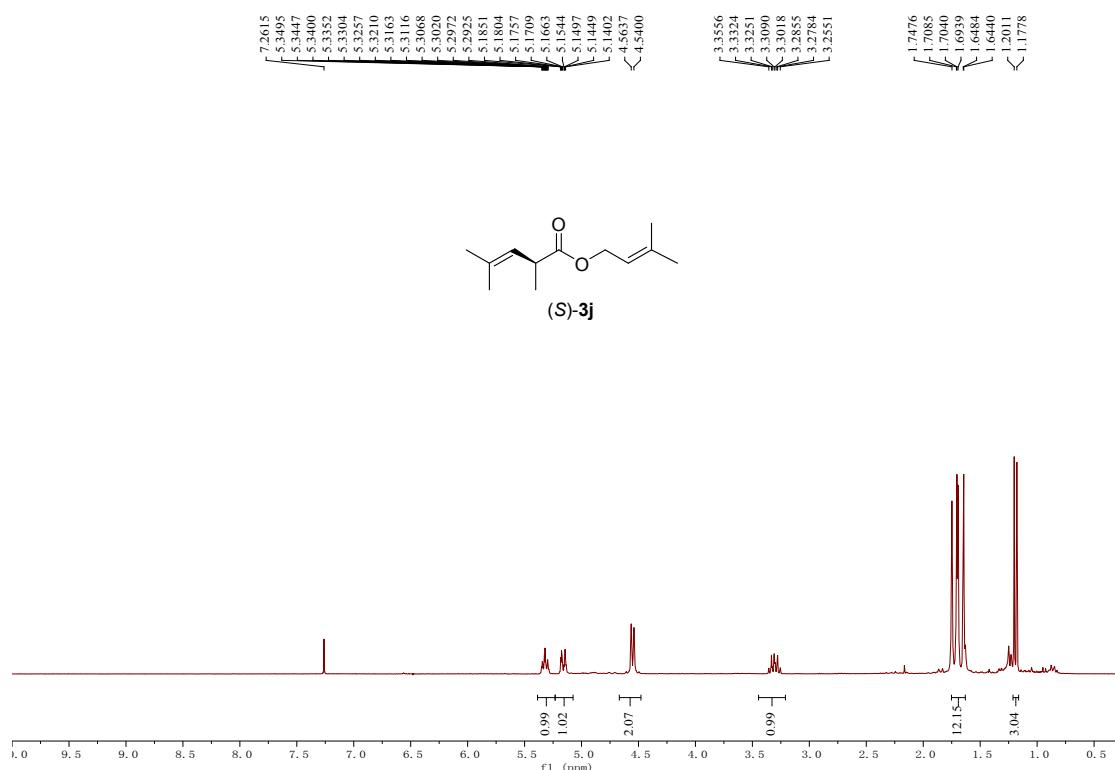


Figure S38. ^{13}C NMR Spectrum of (*S*)-3-methylbut-2-en-1-yl 2,4-dimethylpent-3-enoate (**3j**) (75 MHz, CDCl_3)

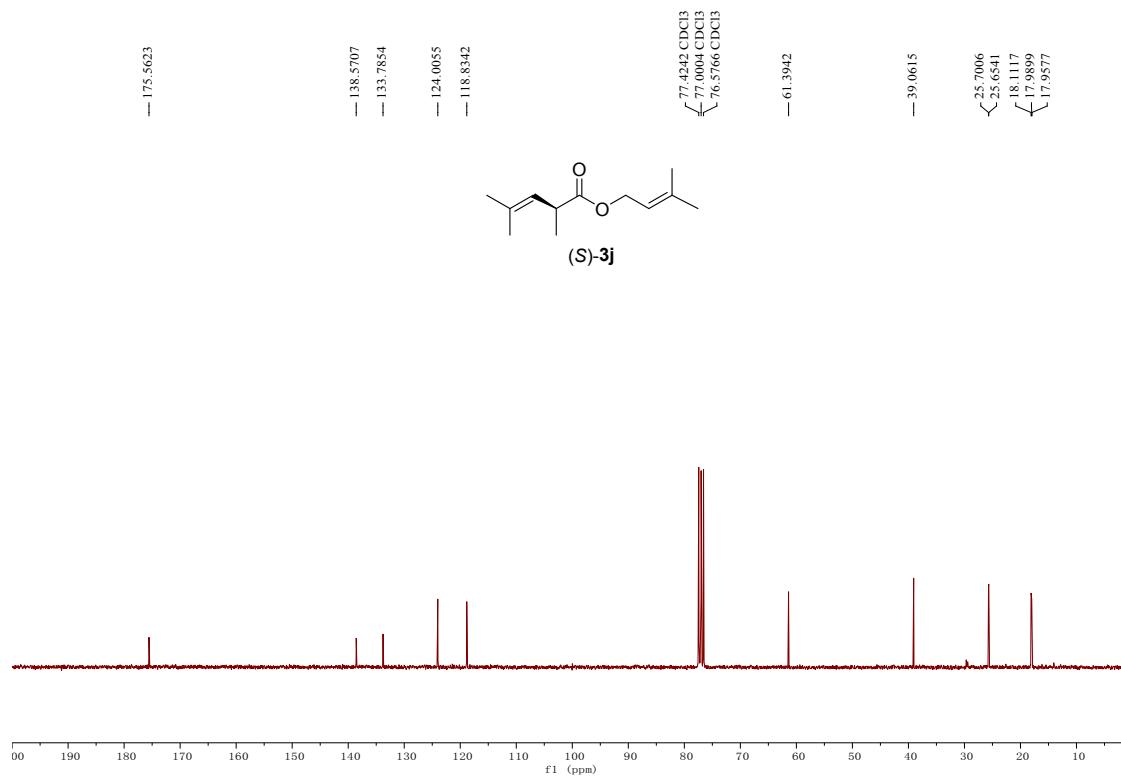


Figure S39. ^1H NMR Spectrum of (*S*)-phenyl 2,4-dimethylpent-3-enoate (**3k**) (300 MHz, CDCl_3)

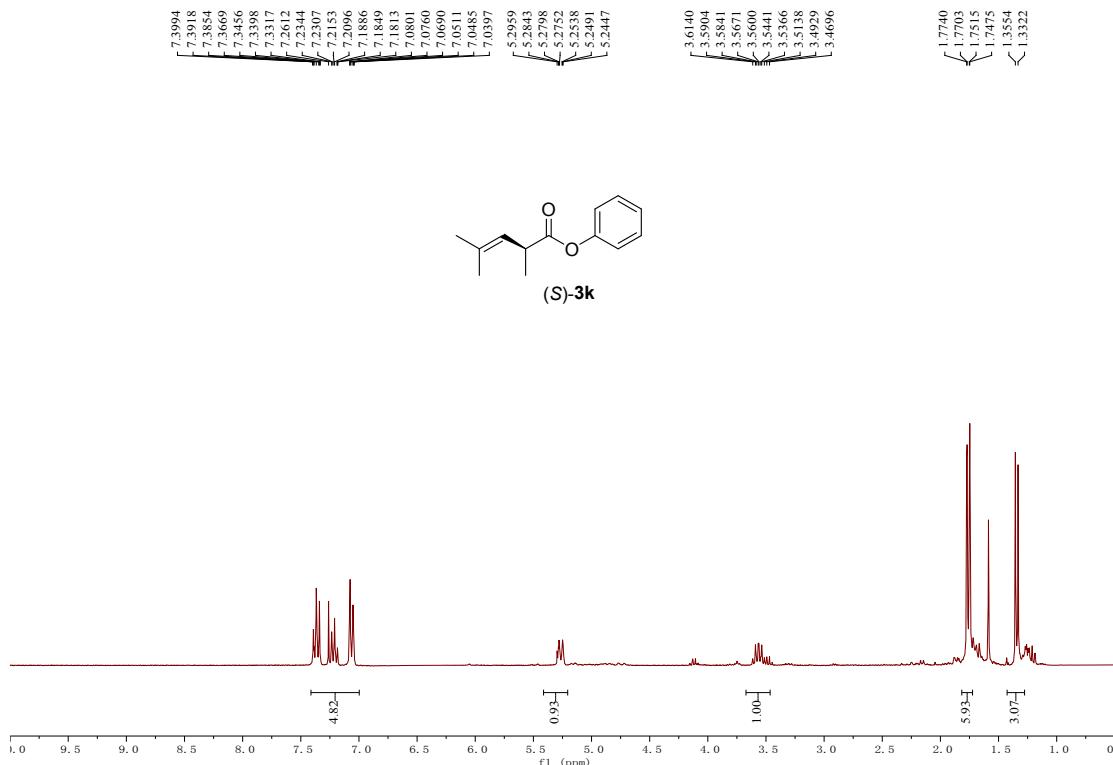


Figure S40. ^{13}C NMR Spectrum of (*S*)-phenyl 2,4-dimethylpent-3-enoate (**3k**) (75 MHz, CDCl_3)

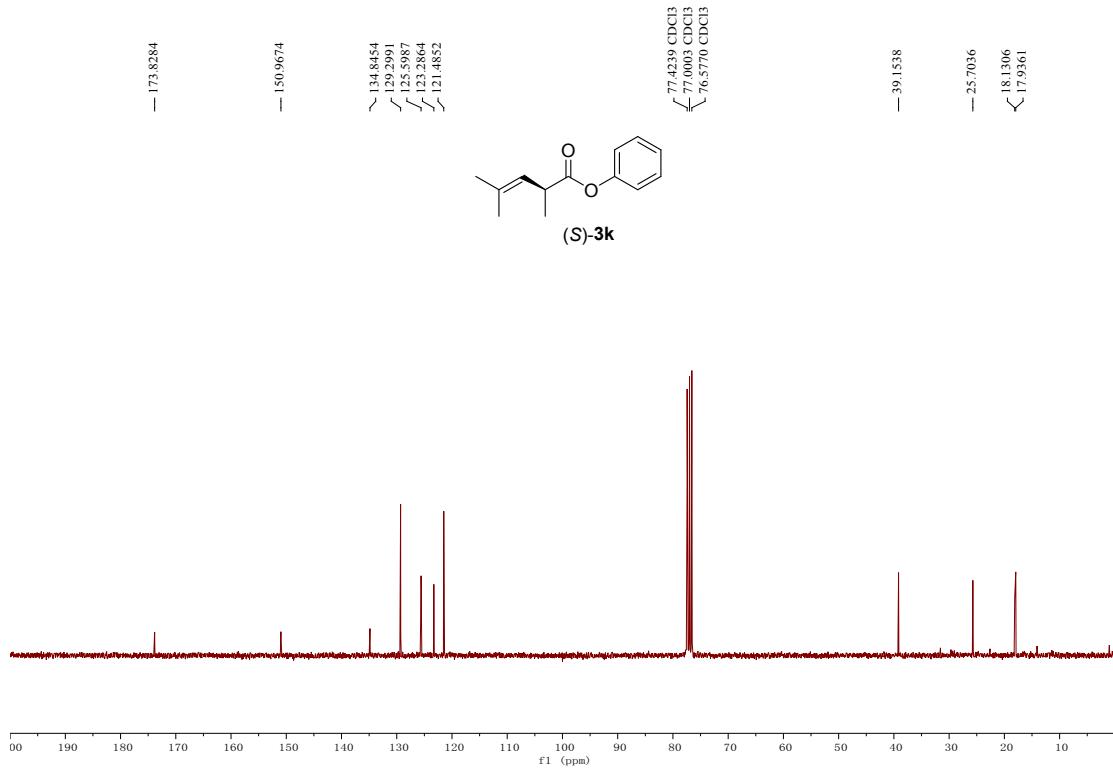


Figure S41. ^1H NMR Spectrum of (*S*)-3-fluorophenyl 2,4-dimethylpent-3-enoate (**3I**) (300 MHz, CDCl_3)

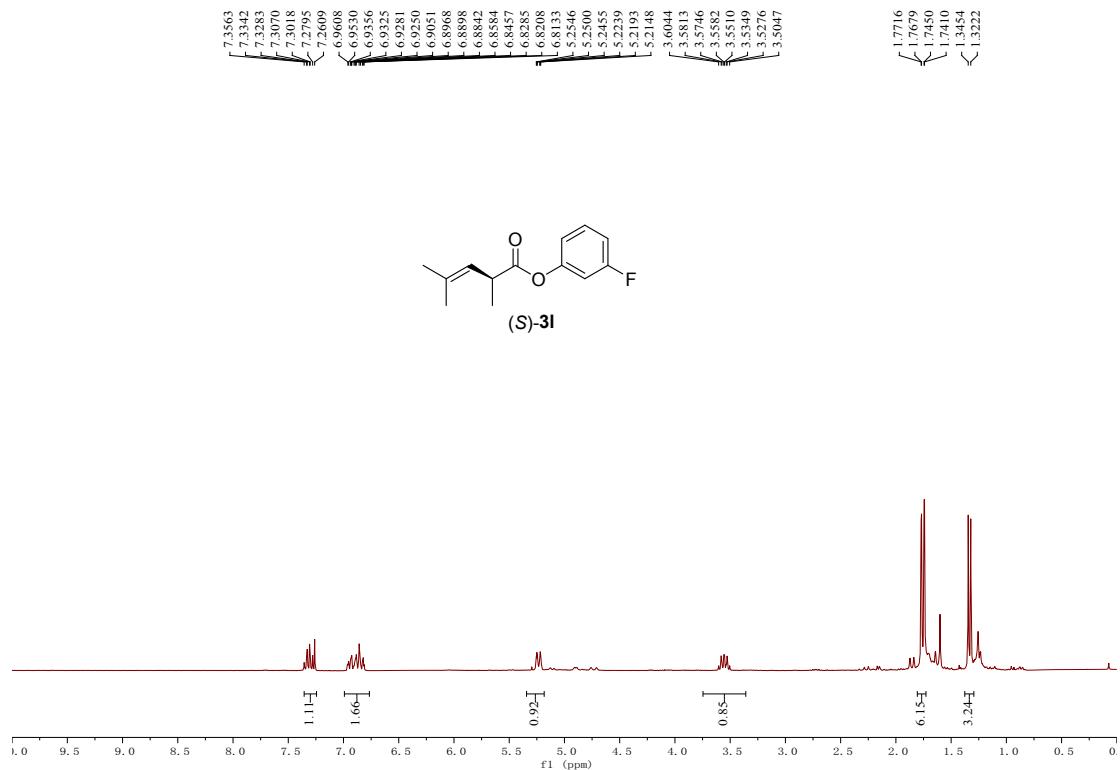


Figure S42. ^{13}C NMR Spectrum of (*S*)-3-fluorophenyl 2,4-dimethylpent-3-enoate (**3I**) (75 MHz, CDCl_3)

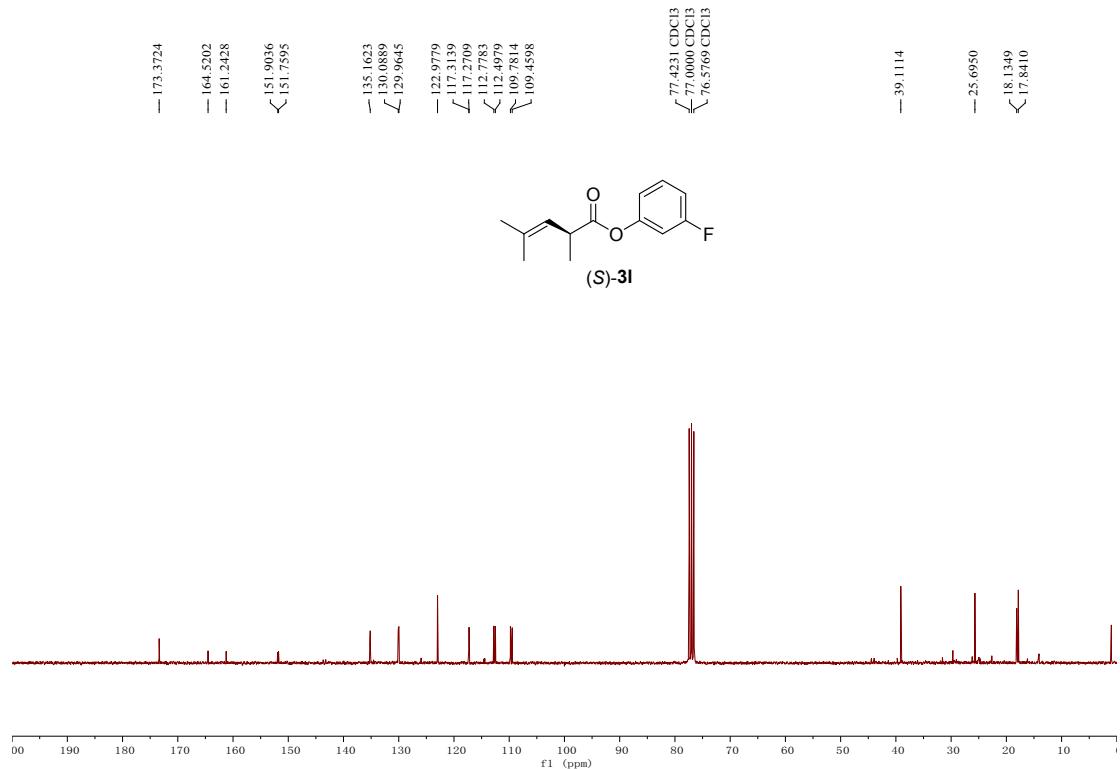


Figure S43. ^{19}F NMR Spectrum of (*S*)-3-fluorophenyl 2,4-dimethylpent-3-enoate (**3l**) (282MHz, CDCl_3)

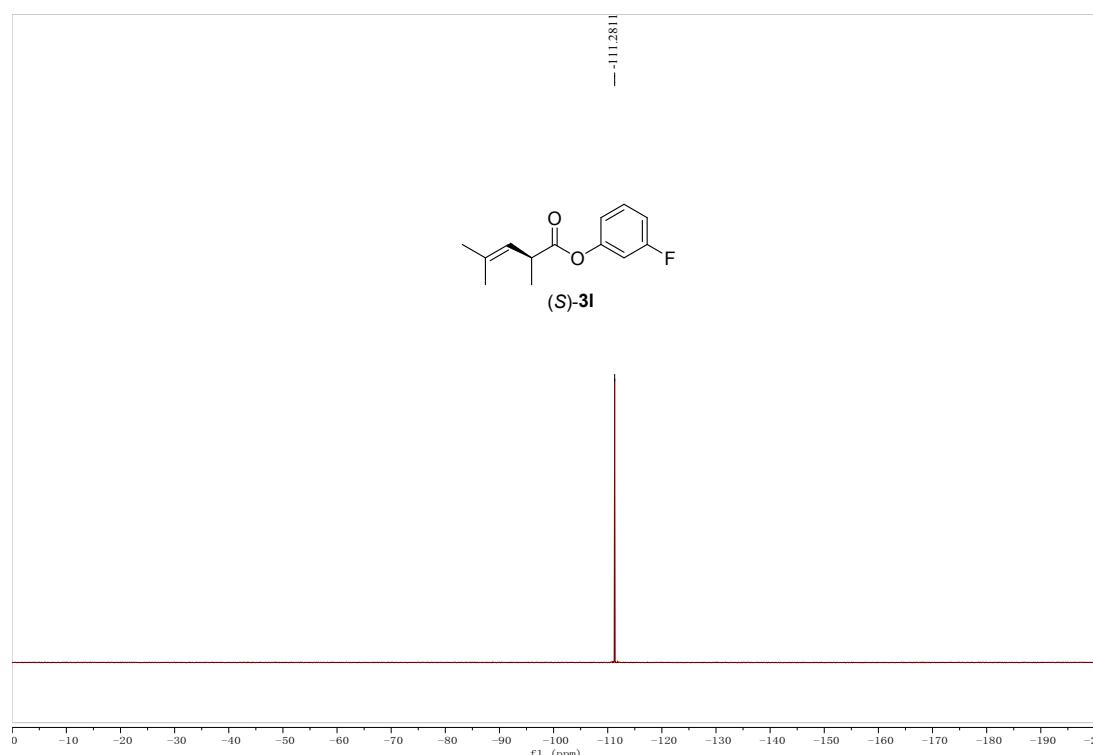


Figure S44. ^1H NMR Spectrum of (*S*)-4-chlorophenyl 2,4-dimethylpent-3-enoate (**3m**) (300 MHz, CDCl_3)

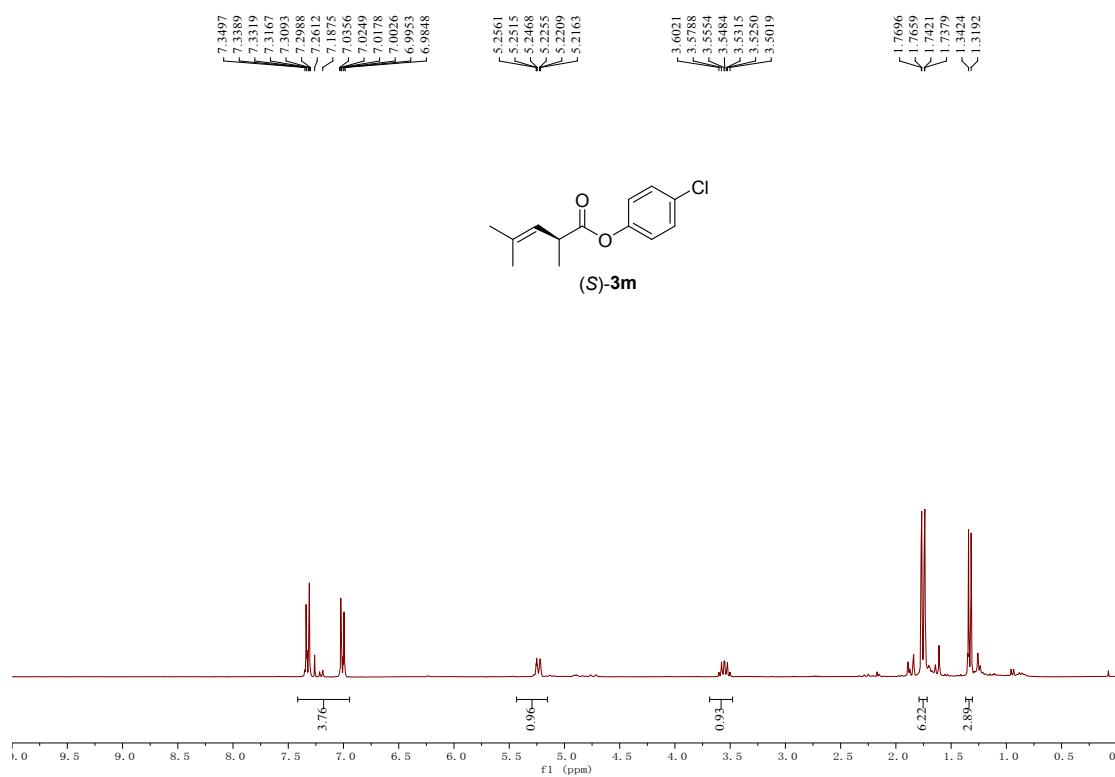


Figure S45. ^{13}C NMR Spectrum of (*S*)-4-chlorophenyl 2,4-dimethylpent-3-enoate (**3m**) (75 MHz, CDCl_3)

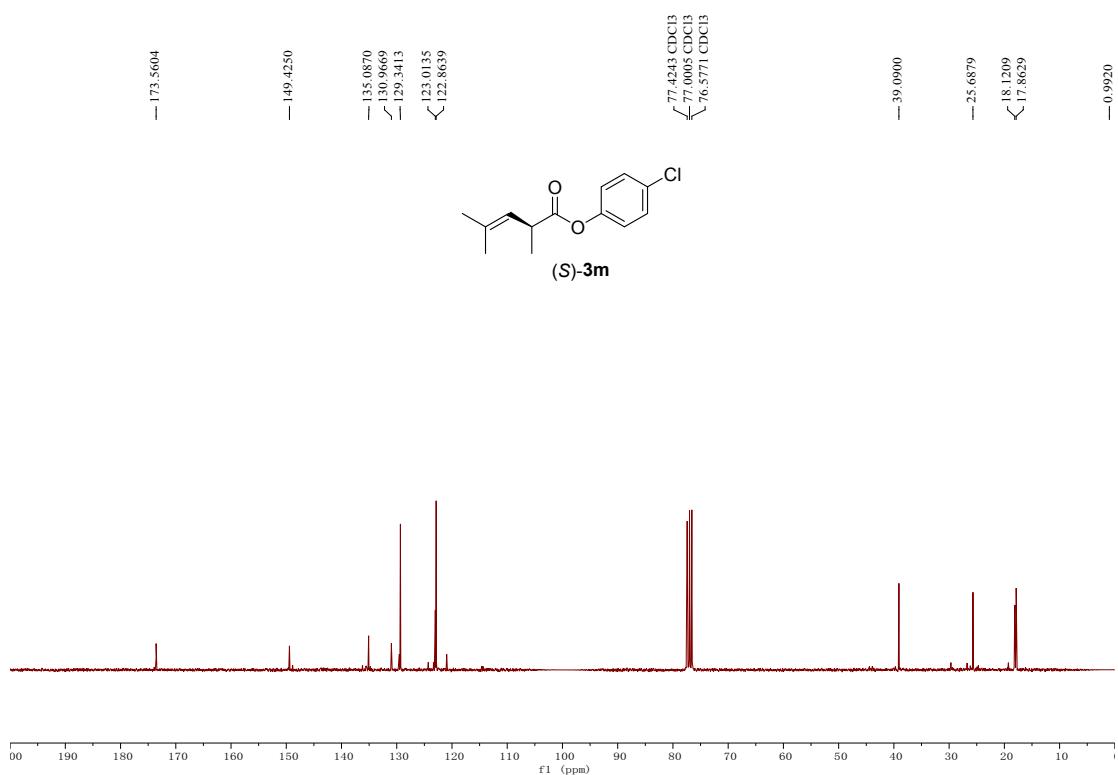


Figure S46. ^1H NMR Spectrum of (*S*)-*p*-tolyl 2,4-dimethylpent-3-enoate (**3n**) (300 MHz, CDCl_3)

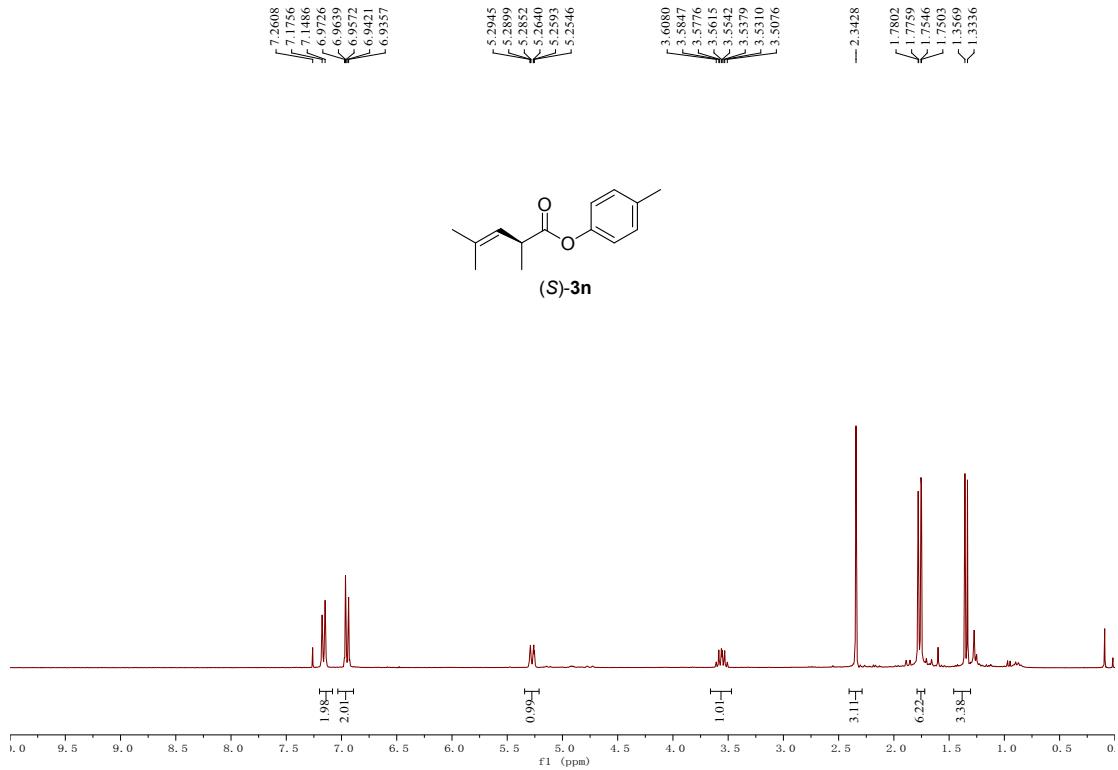


Figure S47. ^{13}C NMR Spectrum of (*S*)-*p*-tolyl 2,4-dimethylpent-3-enoate (**3n**) (75 MHz, CDCl_3)

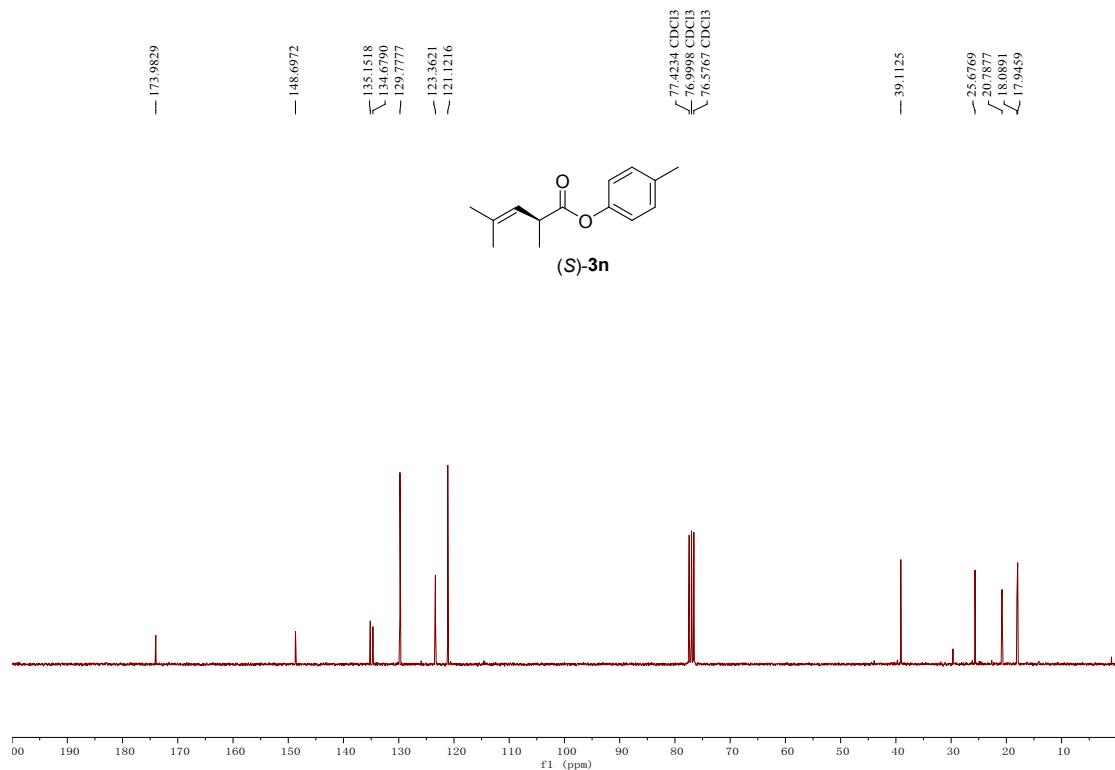


Figure S48. ^1H NMR Spectrum of (*S*)-4-fluorobenzyl (*S*)-2,4-dimethylpent-3-enoate (**3o**) (300 MHz, CDCl_3)

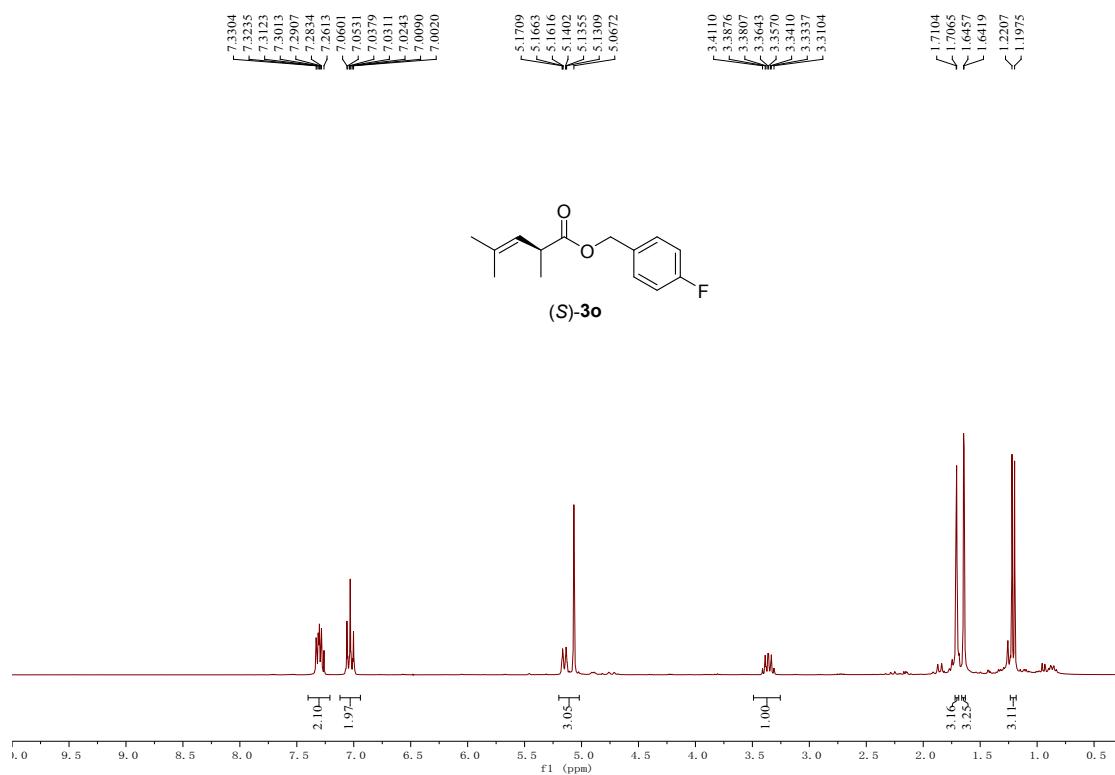


Figure S49. ^{13}C NMR Spectrum of (*S*)-4-fluorobenzyl (*S*)-2,4-dimethylpent-3-enoate (**3o**) (75 MHz, CDCl_3)

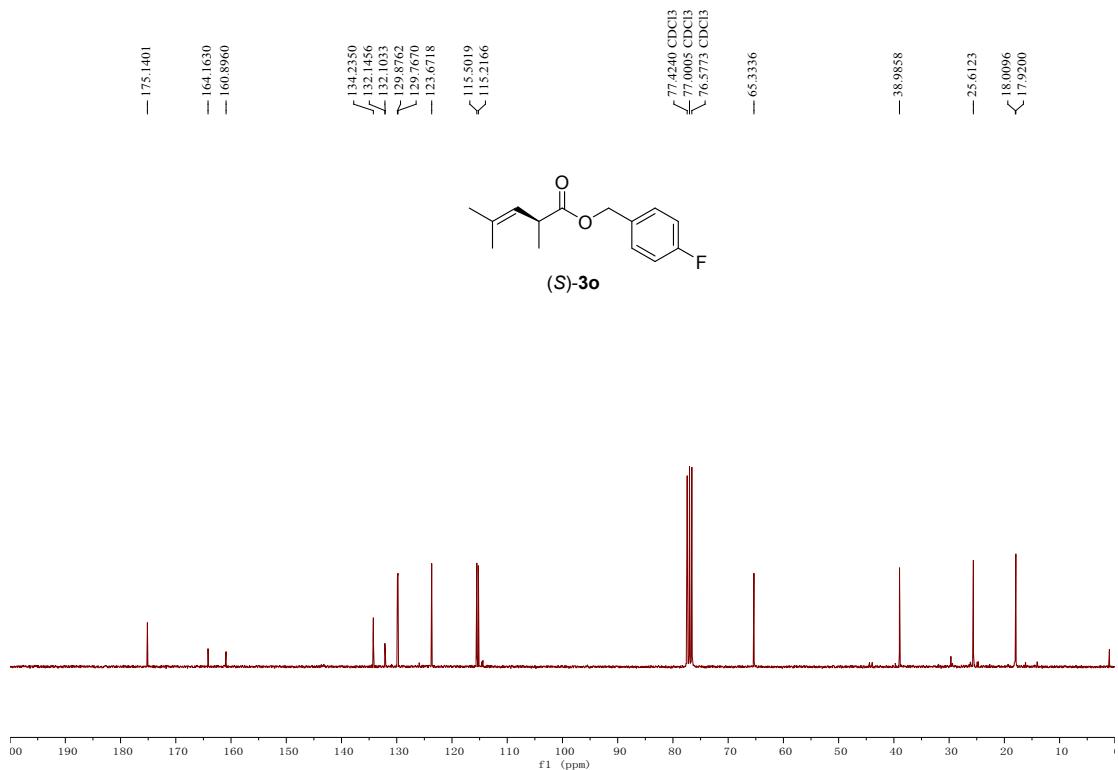


Figure S50. ^{19}F NMR Spectrum of (*S*)-4-fluorobenzyl (*S*)-2,4-dimethylpent-3-enoate (**3o**) (282MHz, CDCl_3)

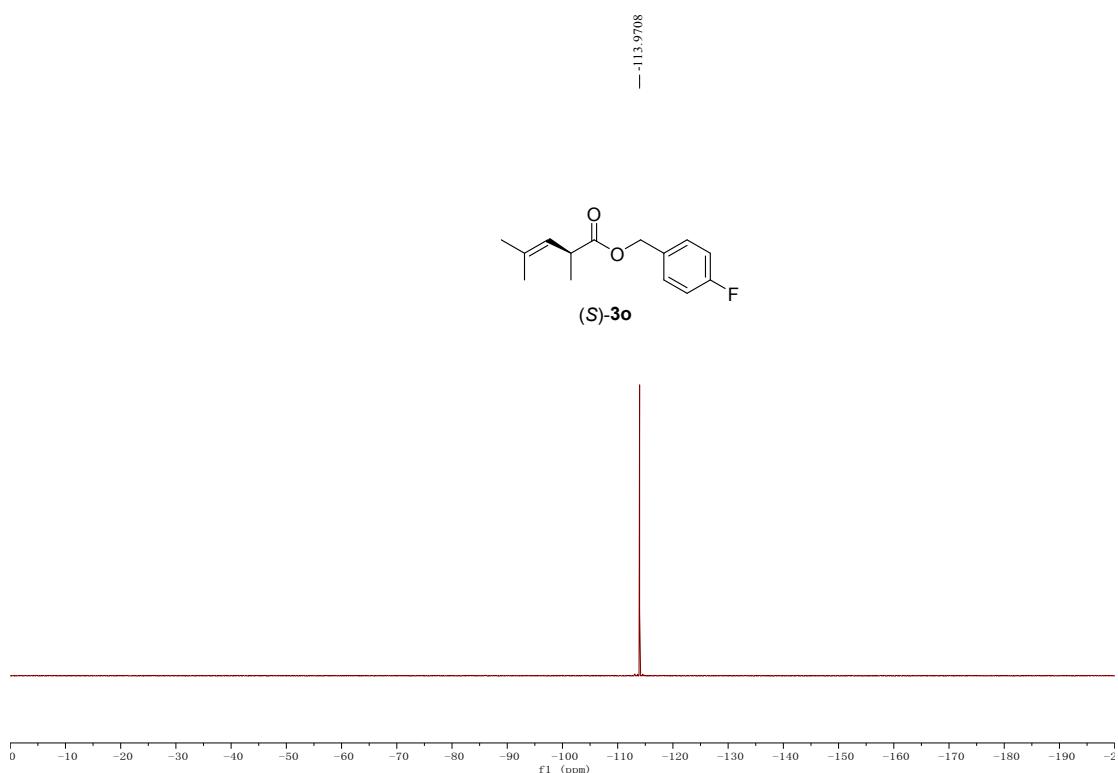


Figure S51. ^1H NMR Spectrum of (*S*)-4-(trifluoromethyl)benzyl 2,4-dimethylpent-3-enoate (**3p**) (400 MHz, CDCl_3)

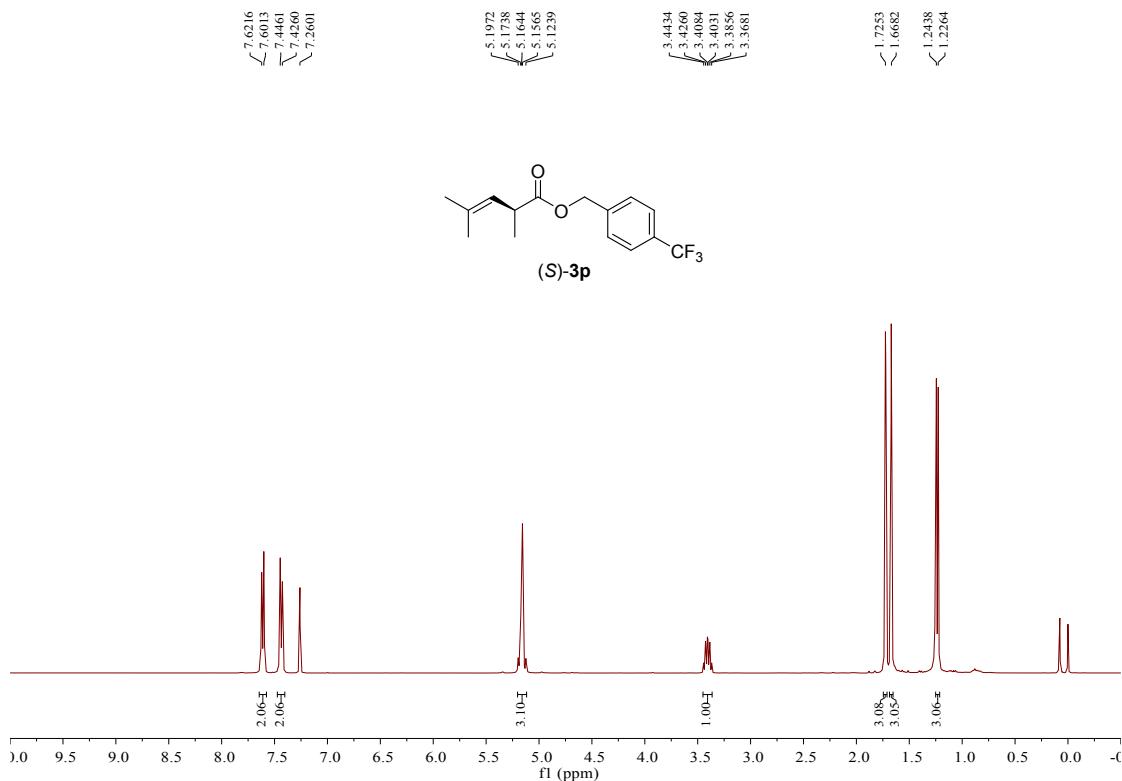


Figure S52. ^{13}C NMR Spectrum of (*S*)-4-(trifluoromethyl)benzyl 2,4-dimethylpent-3-enoate (**3p**) (100 MHz, CDCl_3)

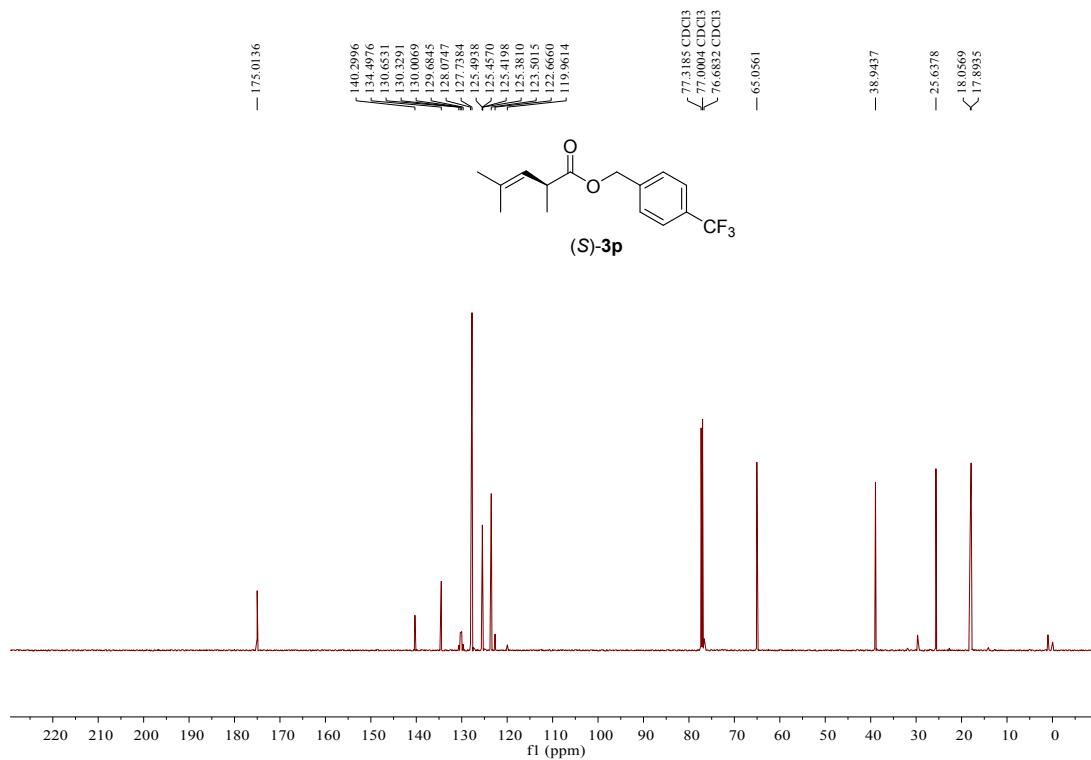


Figure S53. ^{19}F NMR Spectrum of (*S*)-4-(trifluoromethyl)benzyl 2,4-dimethylpent-3-enoate (**3p**) (282MHz, CDCl_3)

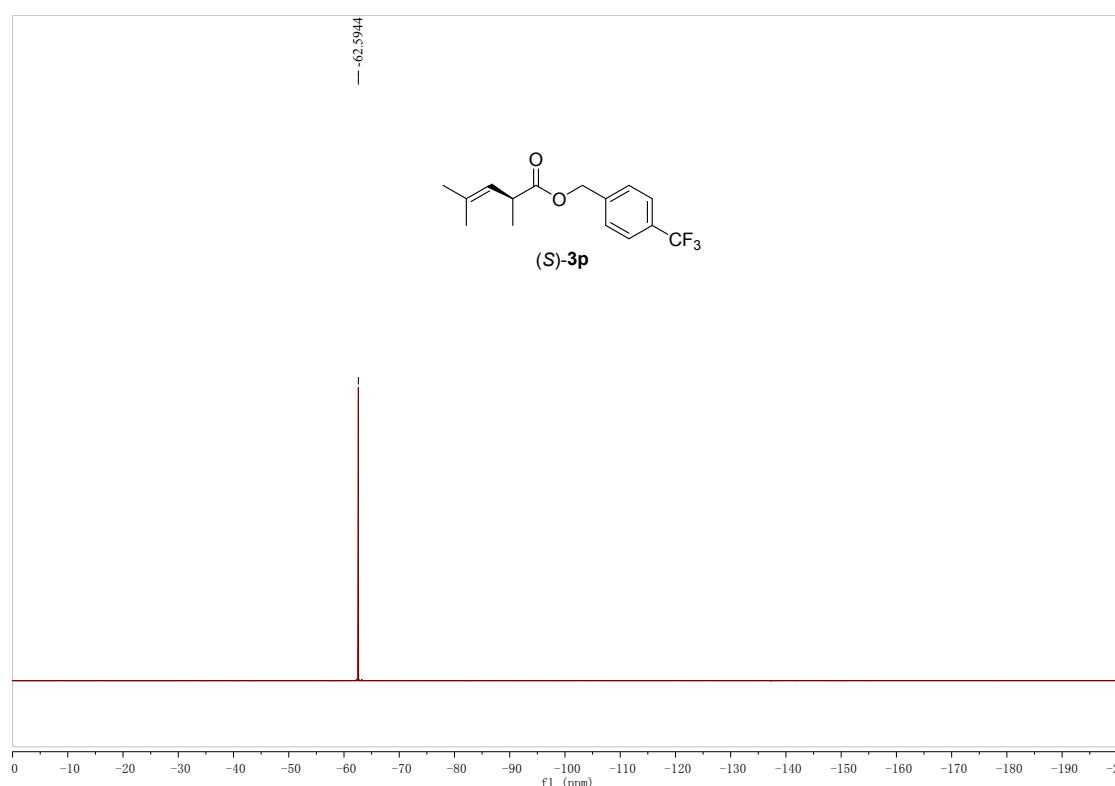


Figure S54. ^1H NMR Spectrum of (*S*)-4-bromobenzyl 2,4-dimethylpent-3-enoate (**3q**) (300 MHz, CDCl_3)

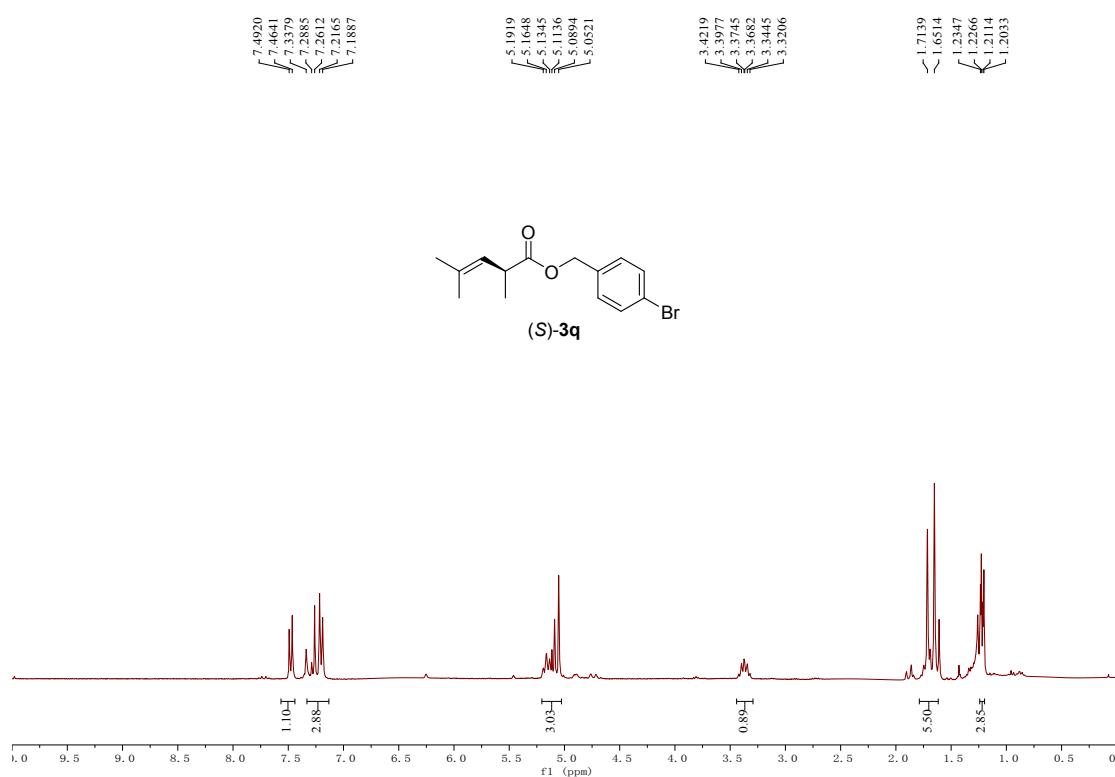


Figure S55. ^{13}C NMR Spectrum of (*S*)-4-bromobenzyl 2,4-dimethylpent-3-enoate (**3q**) (75 MHz, CDCl_3)

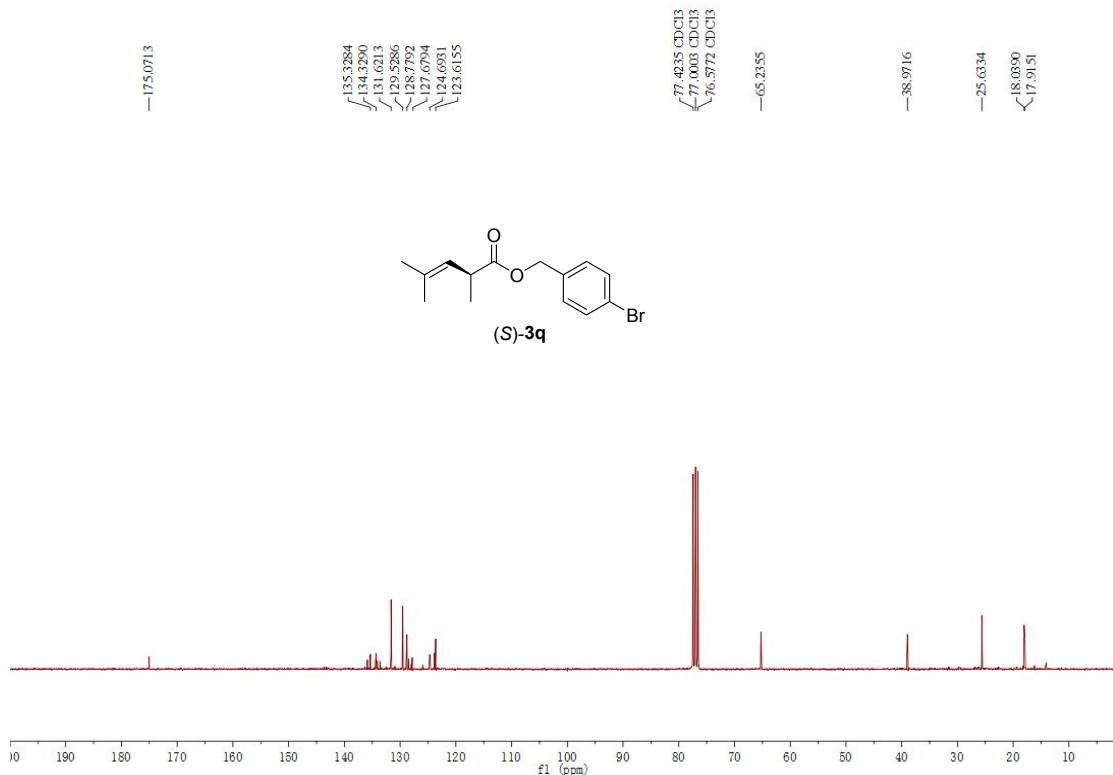


Figure S56. ^1H NMR Spectrum of (*S*)-4-methylbenzyl 2,4-dimethylpent-3-enoate (**3r**) (300 MHz, CDCl_3)

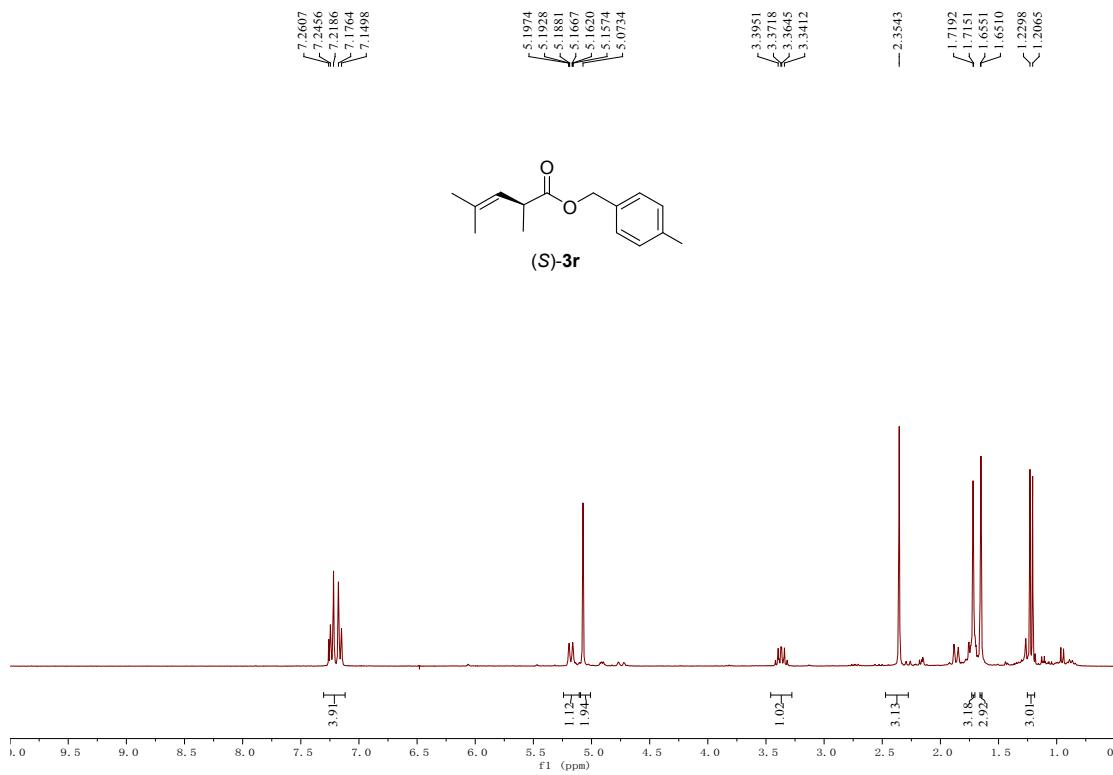


Figure S57. ^{13}C NMR Spectrum of (*S*)-4-methylbenzyl 2,4-dimethylpent-3-enoate (**3r**) (75 MHz, CDCl_3)

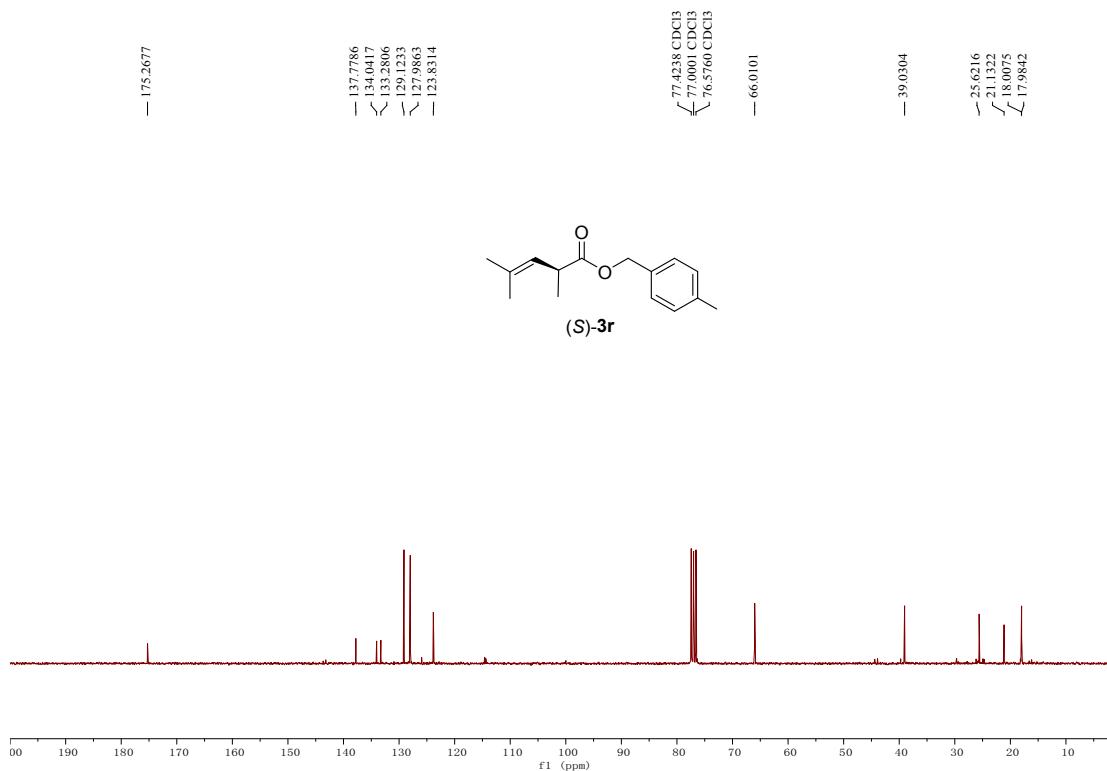


Figure S58. ^1H NMR Spectrum of (*S*)-4-(*tert*-butyl)benzyl 2,4-dimethylpent-3-enoate (**3s**) (300 MHz, CDCl_3)

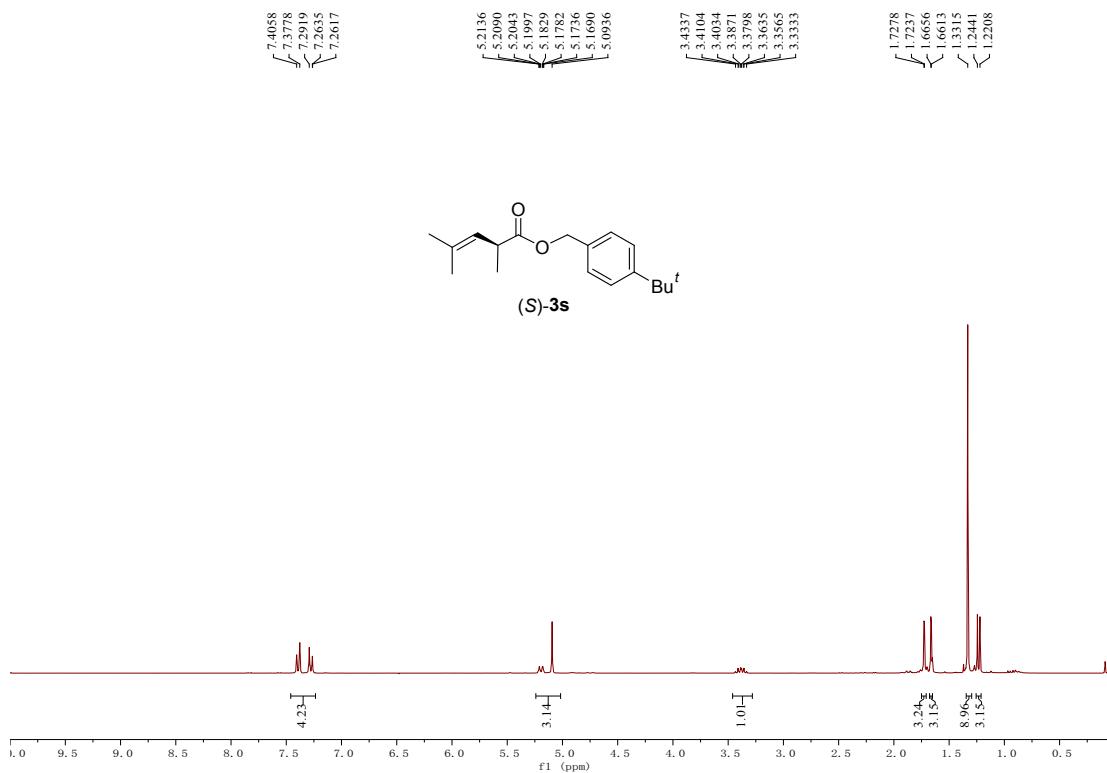


Figure S59. ^{13}C NMR Spectrum of (*S*)-4-(*tert*-butyl)benzyl 2,4-dimethylpent-3-enoate (**3s**) (75 MHz, CDCl_3)

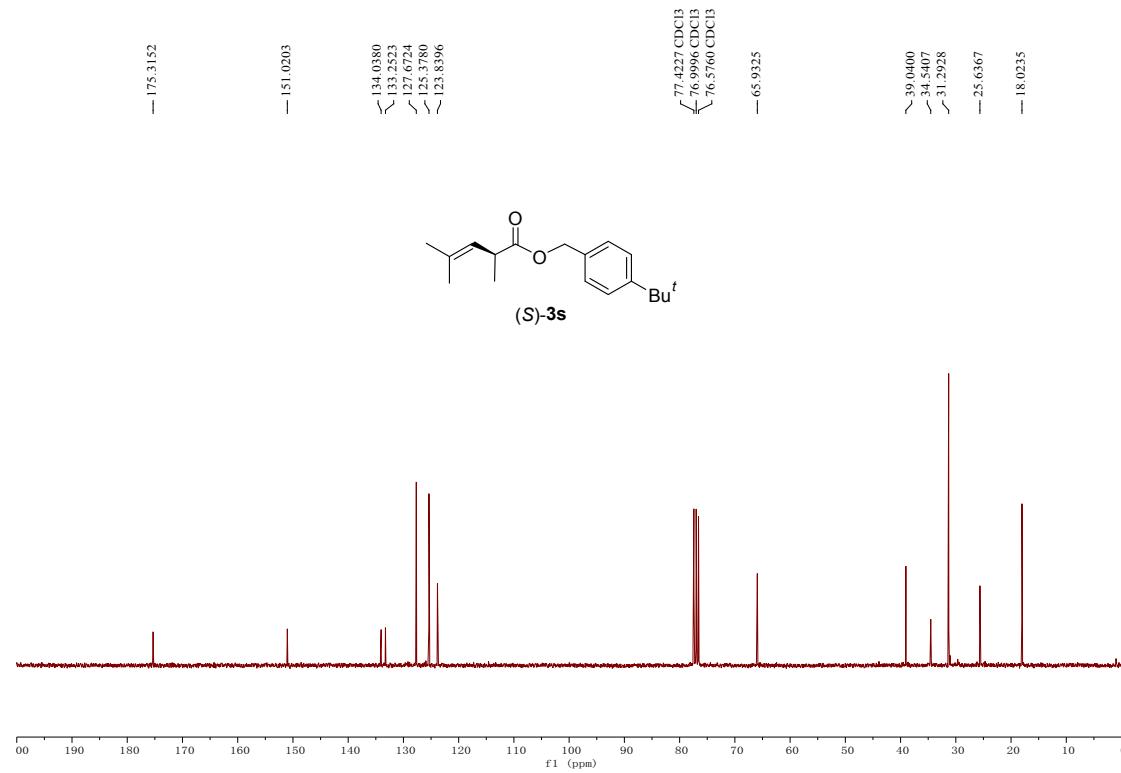


Figure S60. ^1H NMR Spectrum of (*S*)-naphthalen-2-ylmethyl 2,4-dimethylpent-3-enoate (**3t**) (300 MHz, CDCl_3)

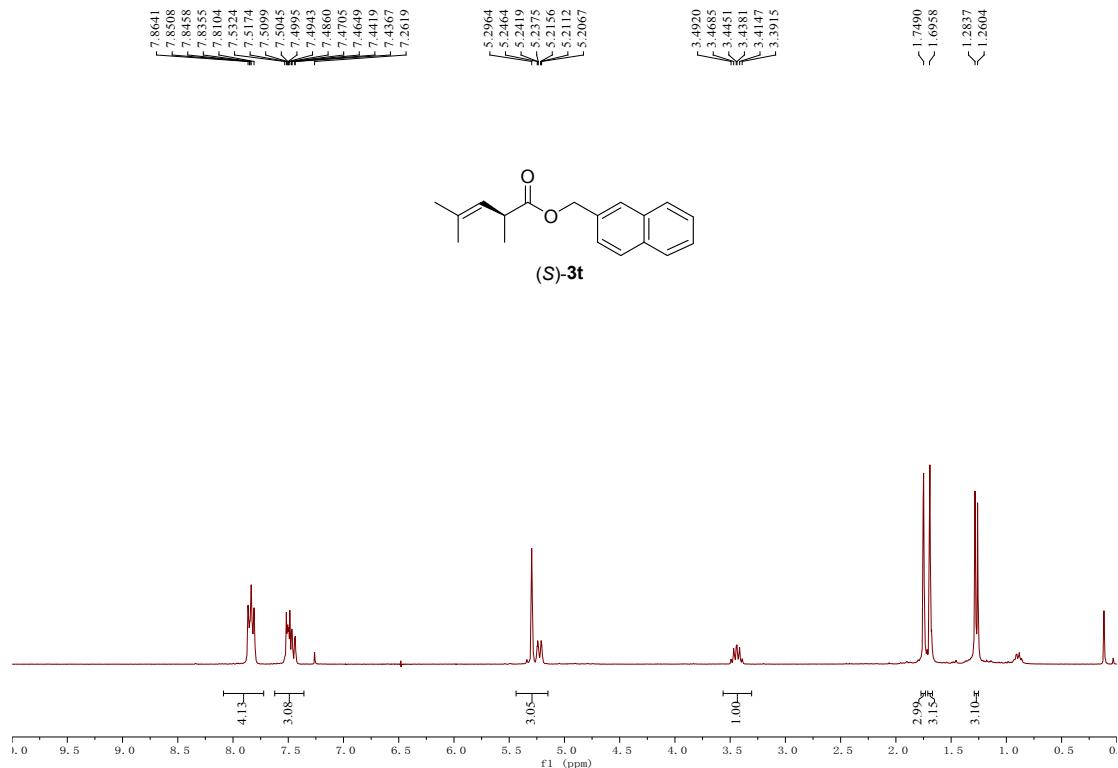


Figure S61. ^{13}C NMR Spectrum of (*S*)-naphthalen-2-ylmethyl 2,4-dimethylpent-3-enoate (**3t**) (75 MHz, CDCl_3)

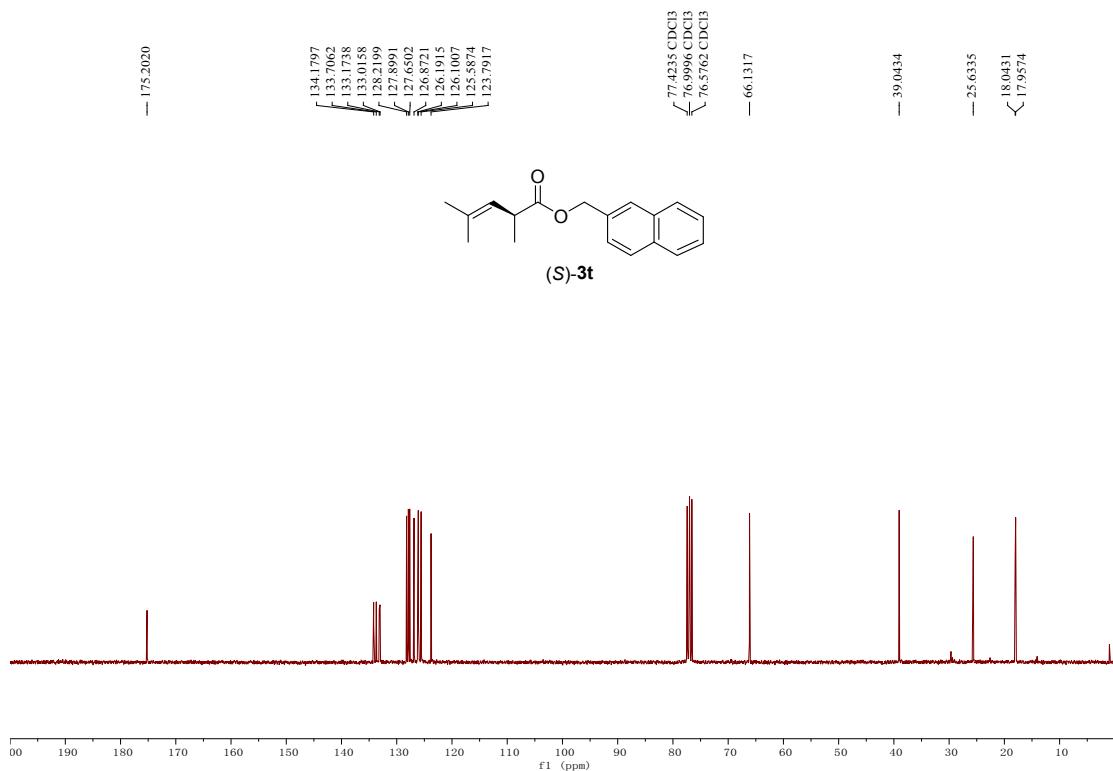


Figure S62. ^1H NMR Spectrum of (*S*)-naphthalen-2-yl 2,4-dimethylpent-3-enoate (**3u**) (300 MHz, CDCl_3)

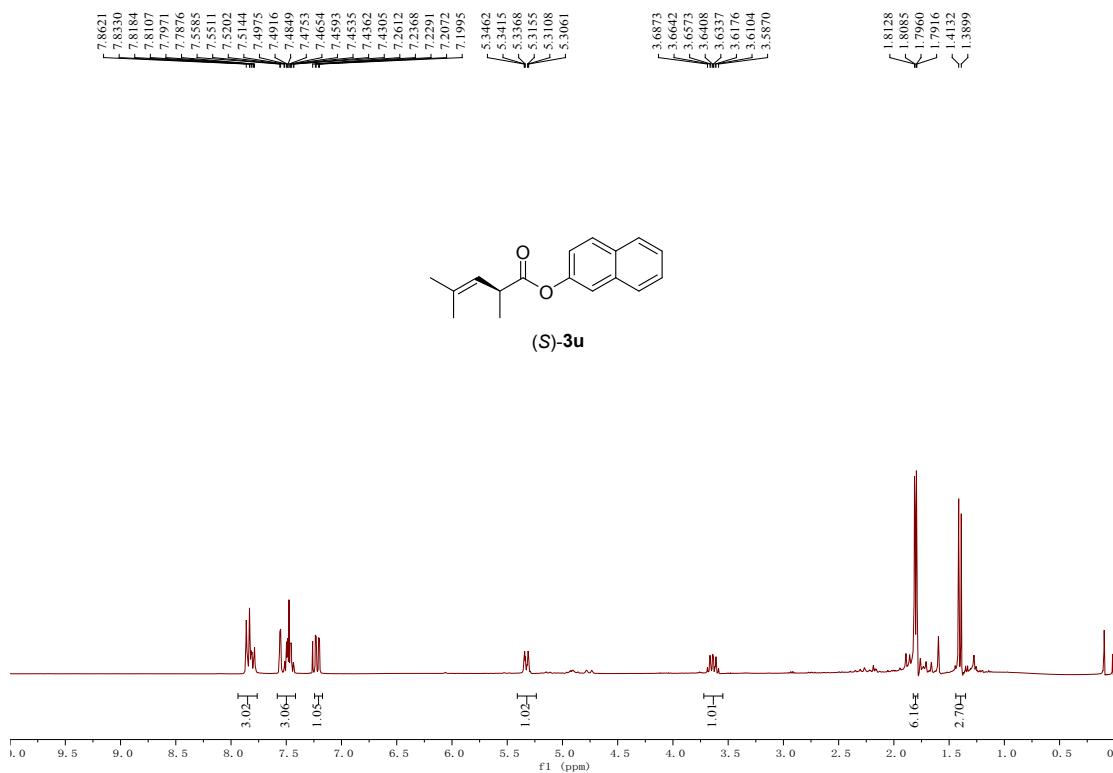


Figure S63. ^{13}C NMR Spectrum of (*S*)-naphthalen-2-yl 2,4-dimethylpent-3-enoate (**3u**) (75 MHz, CDCl_3)

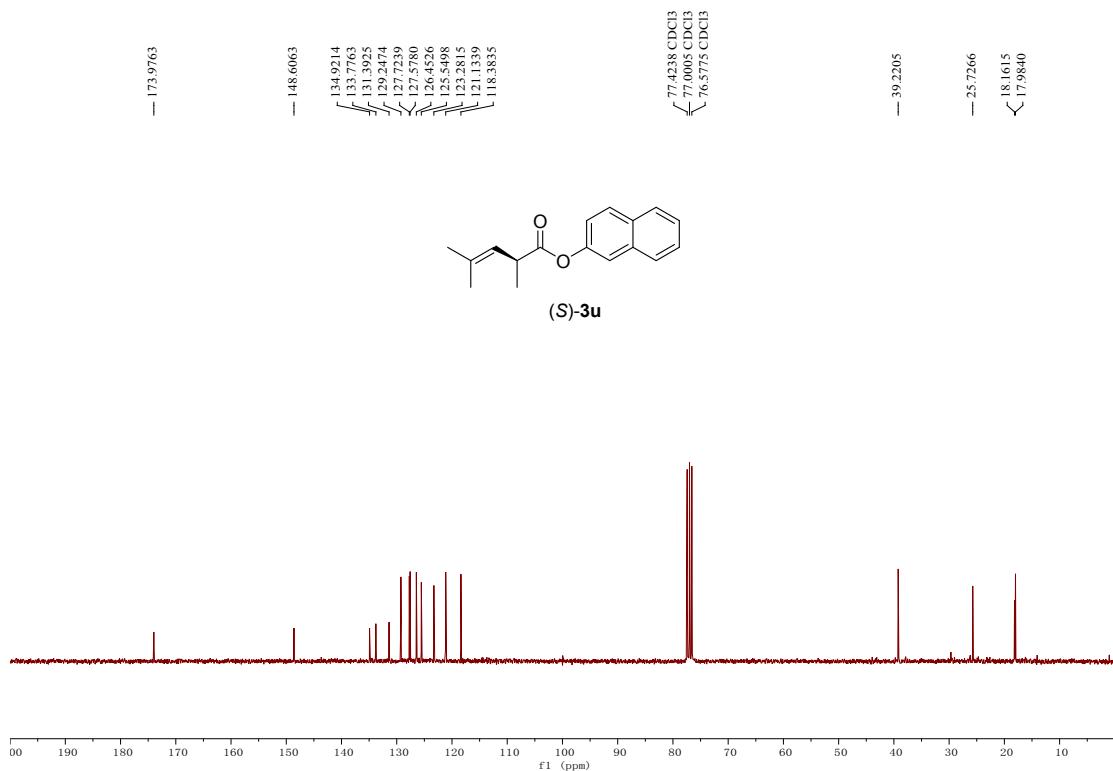


Figure S64. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-4-methylpent-3-enoate (**5a**) (300 MHz, CDCl_3)

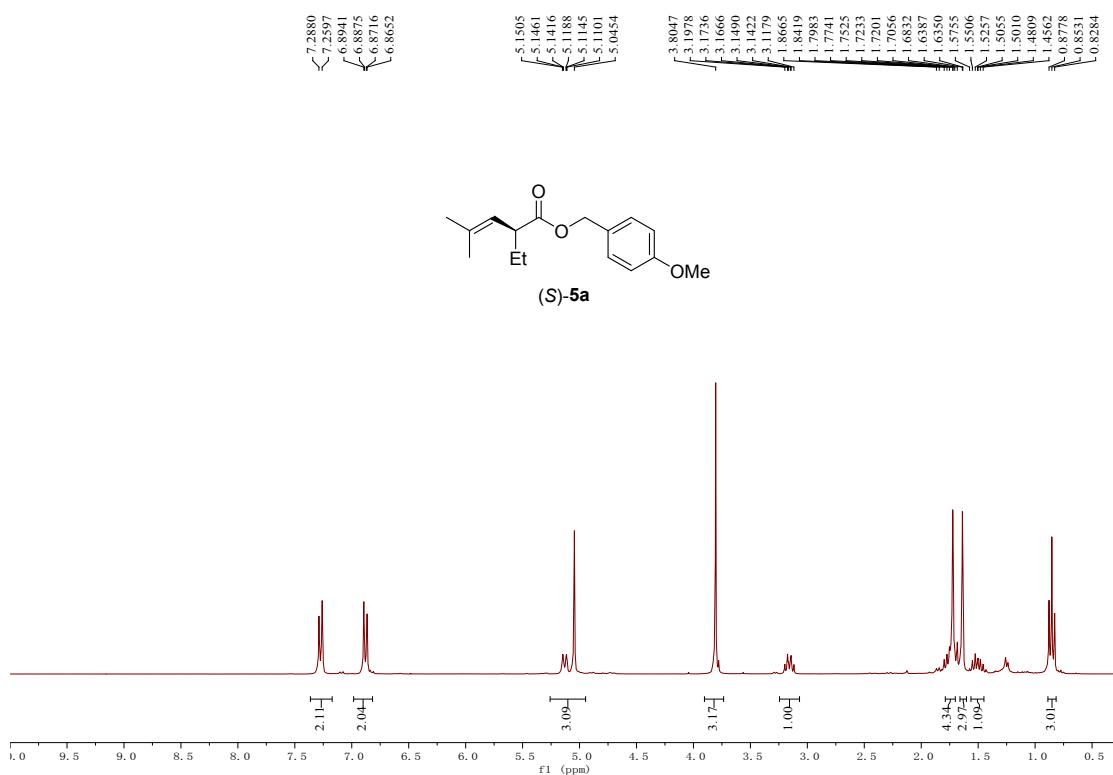


Figure S65. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-4-methylpent-3-enoate (**5a**) (75 MHz, CDCl_3)

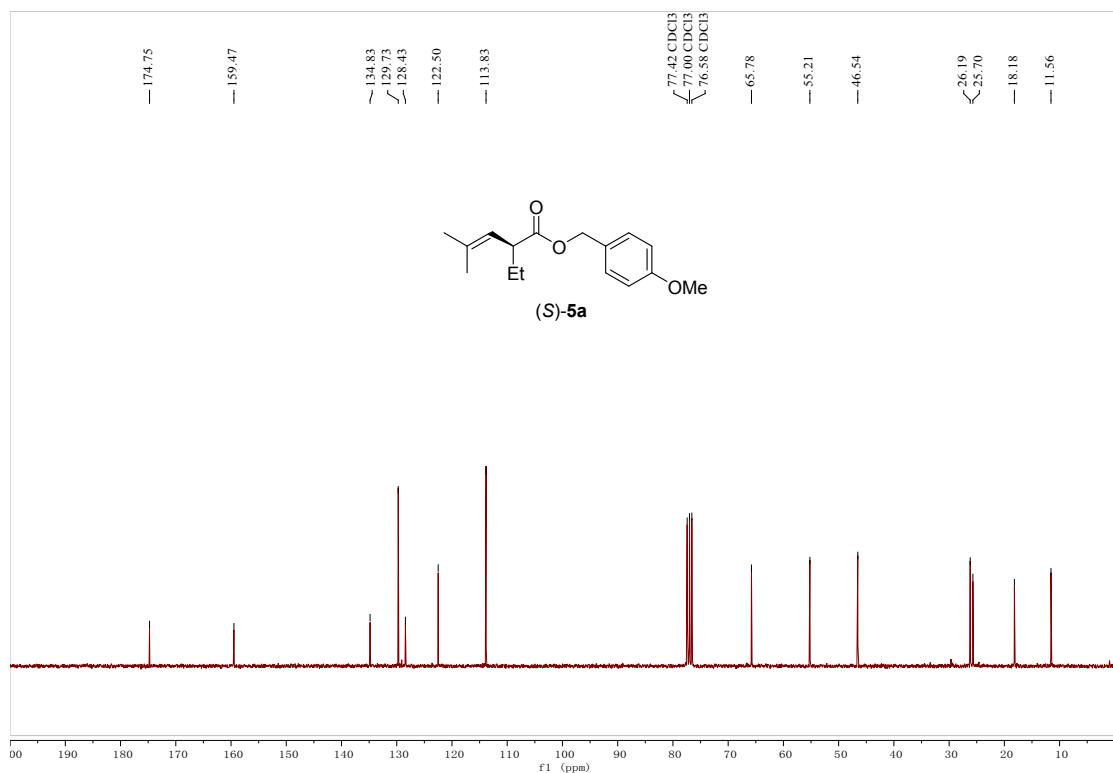


Figure S66. ^1H NMR Spectrum of (*S*)-benzyl 2-ethyl-4-methylpent-3-enoate (**5b**) (300 MHz, CDCl_3)

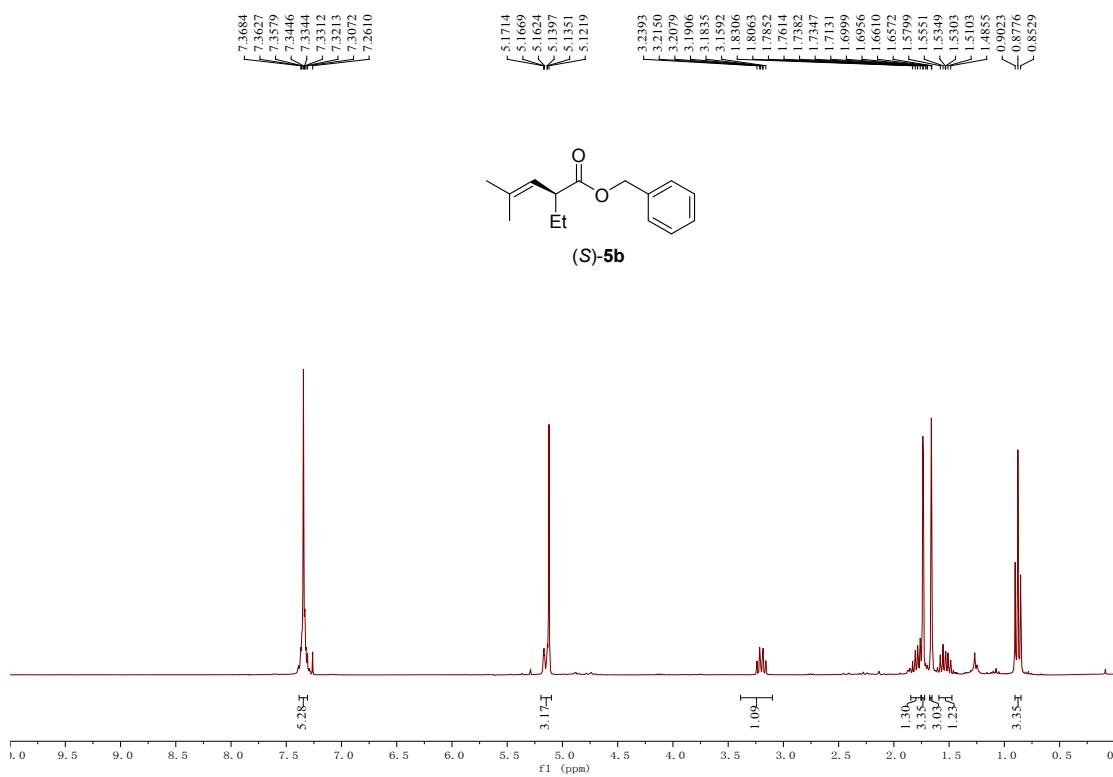


Figure S67. ^{13}C NMR Spectrum of (*S*)-benzyl 2-ethyl-4-methylpent-3-enoate (**5b**) (75 MHz, CDCl_3)

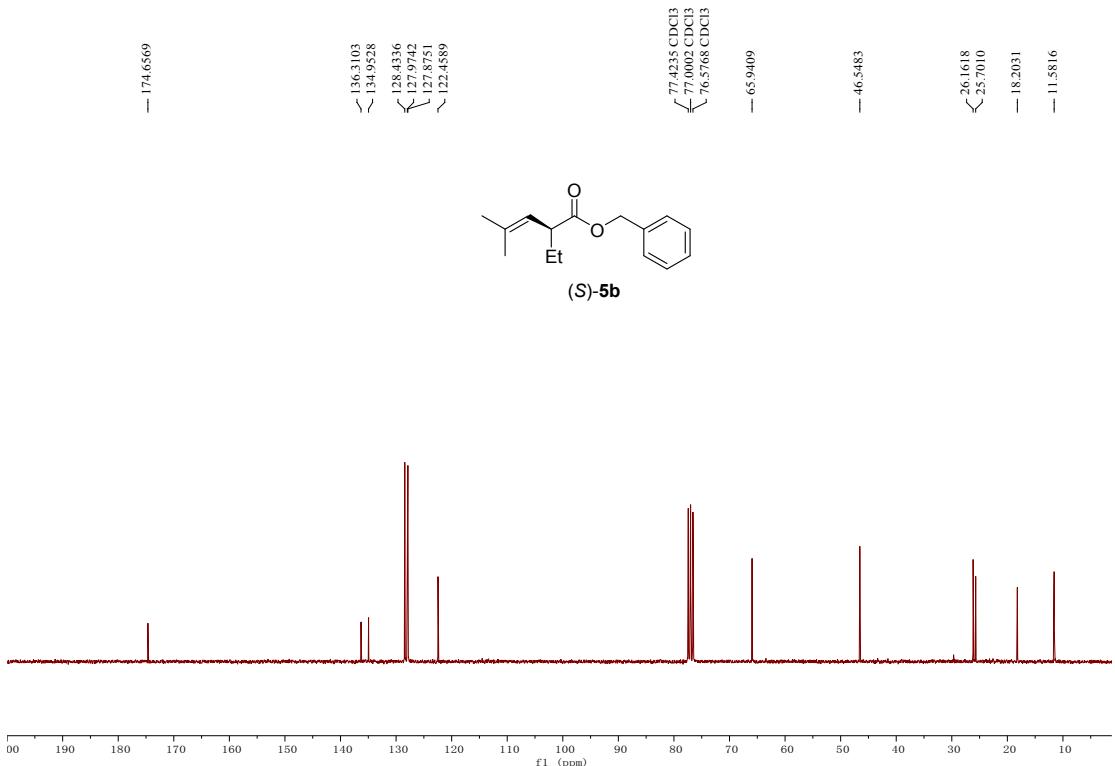


Figure S68. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-(2-methylprop-1-en-1-yl) hexanoate (**5c**) (300 MHz, CDCl_3)

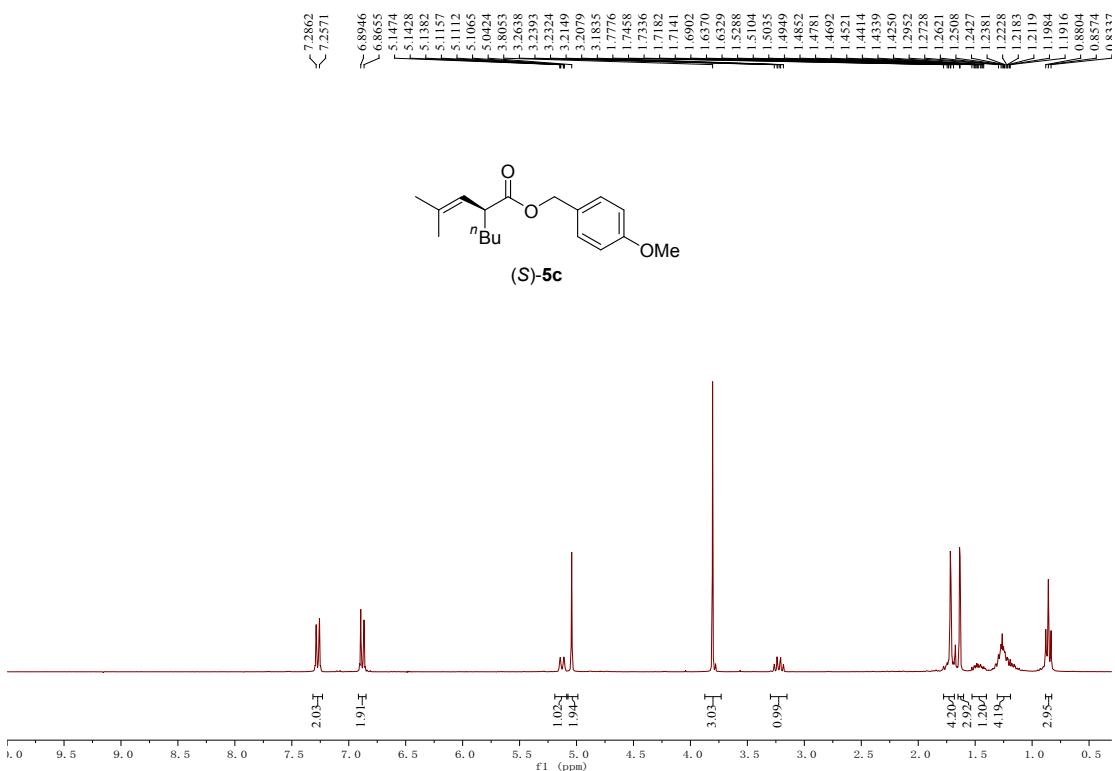


Figure S69. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-(2-methylprop-1-en-1-yl) hexanoate (**5c**) (75 MHz, CDCl_3)

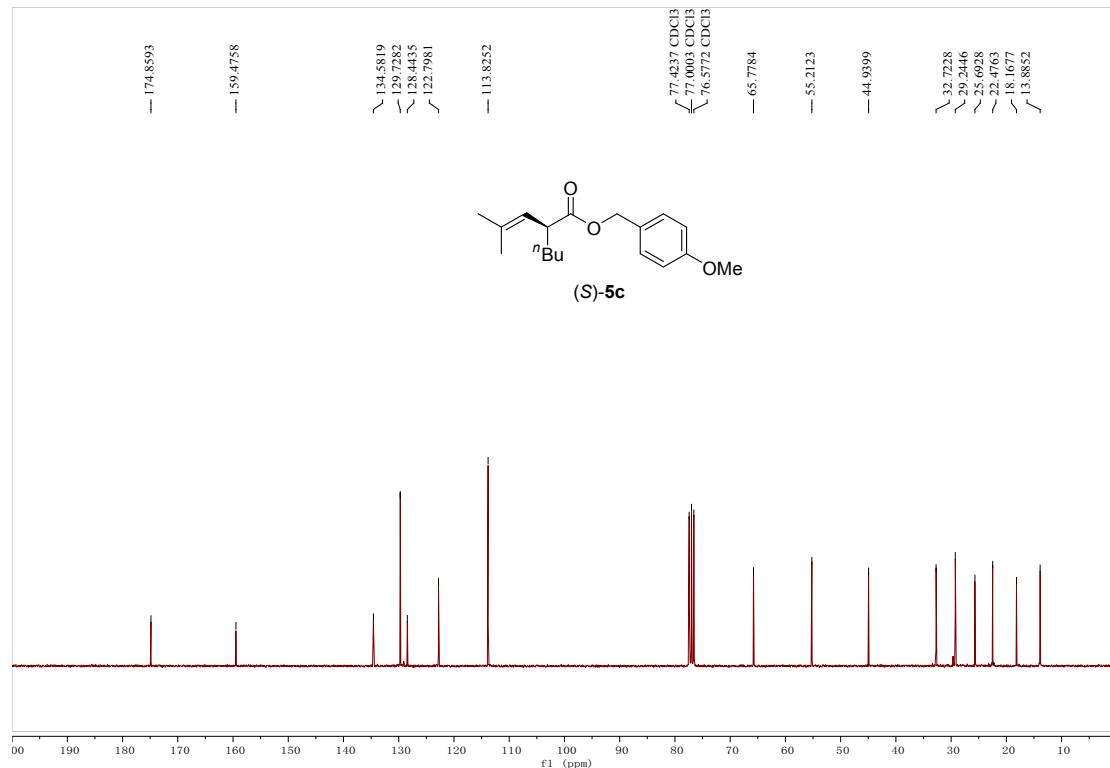


Figure S70. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5d**) (300 MHz, CDCl_3)

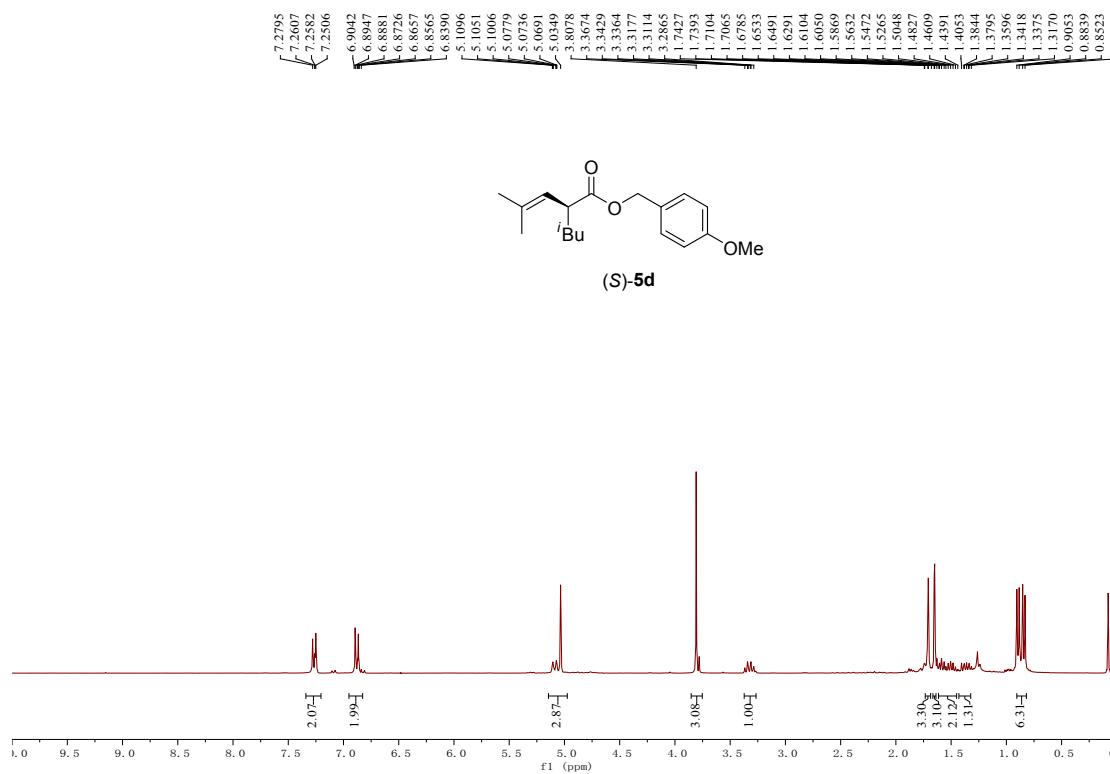


Figure S71. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5d**) (75 MHz, CDCl_3)

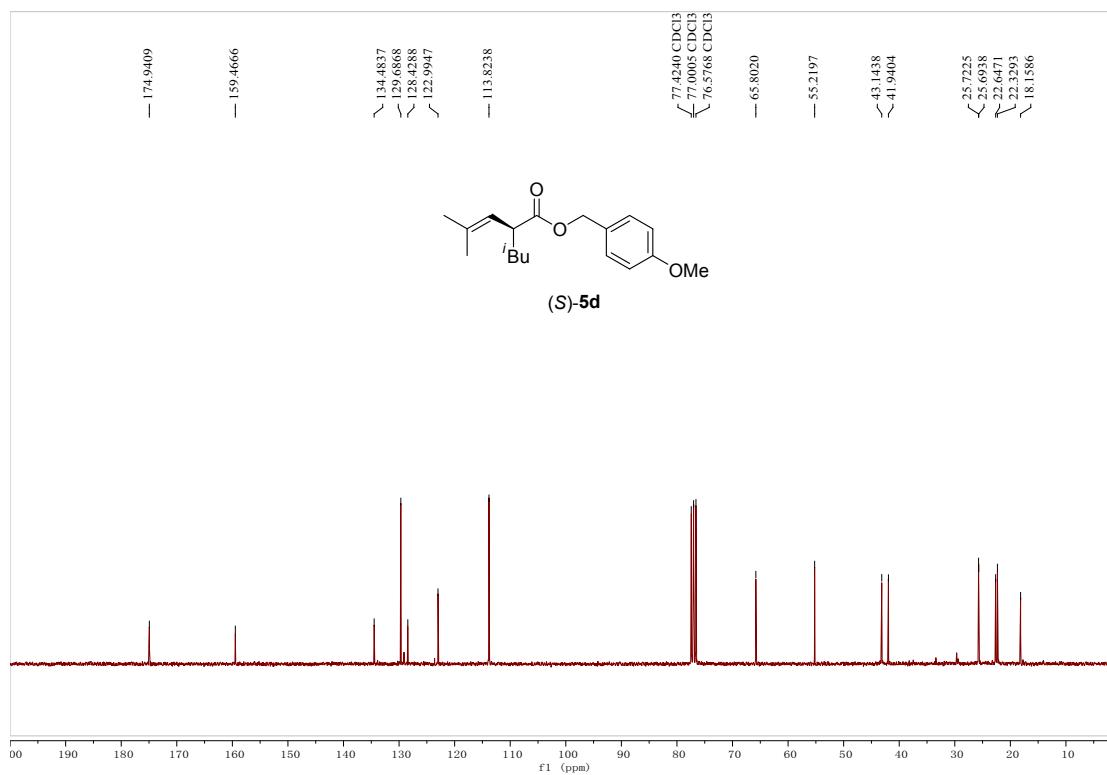


Figure S72. ^1H NMR Spectrum of (*S*)-benzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5e**) (300 MHz, CDCl_3)

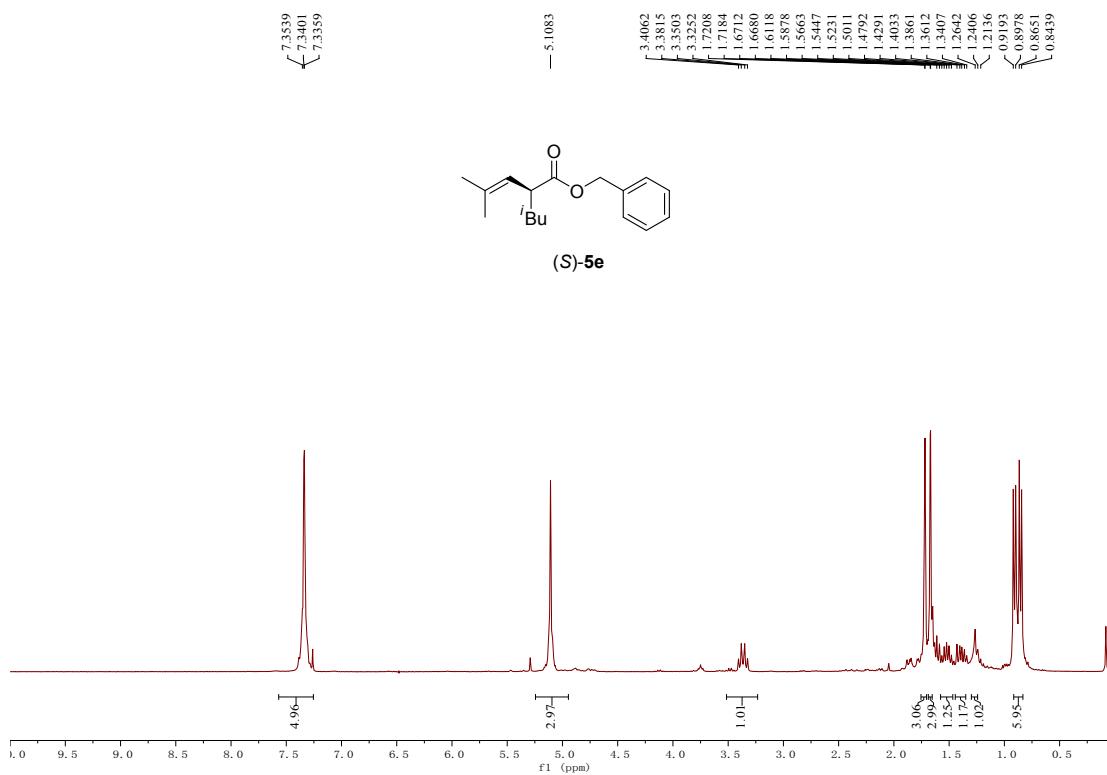


Figure S73. ^{13}C NMR Spectrum of (*S*)-benzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5e**) (75 MHz, CDCl_3)

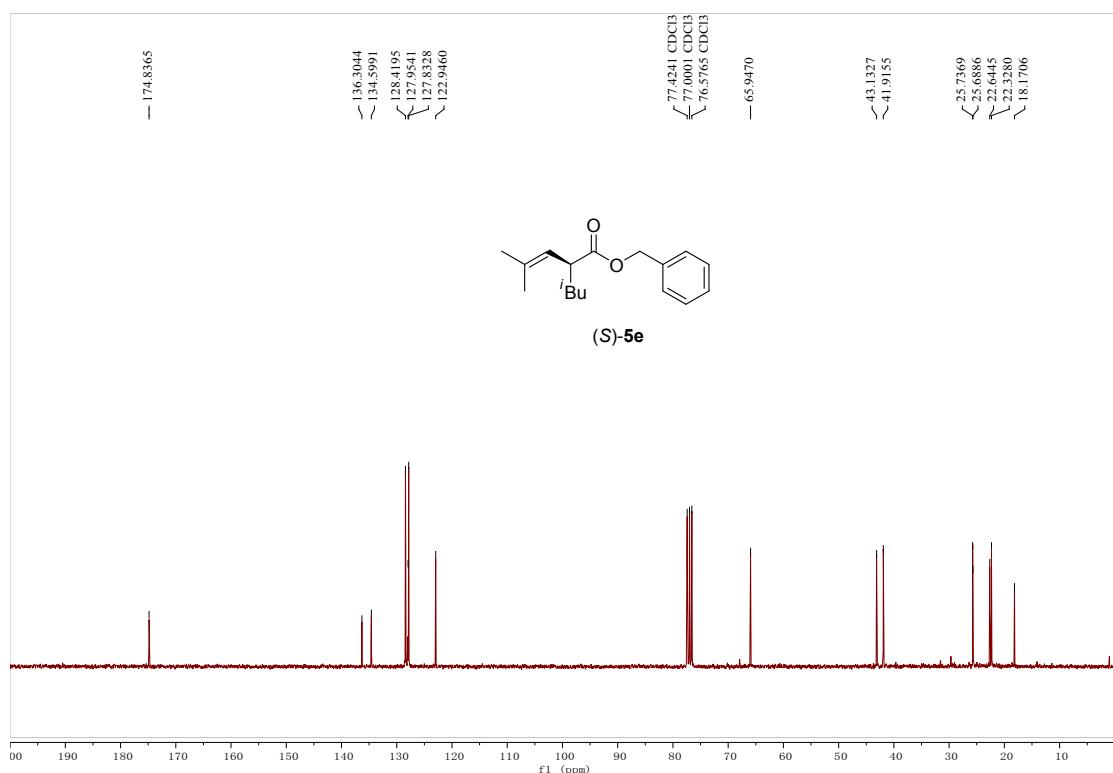


Figure S74. ^1H NMR Spectrum of (*S*)-benzyl 2-*iso*-propyl-4-methylpent-3-enoate (**5f**) (300 MHz, CDCl_3)

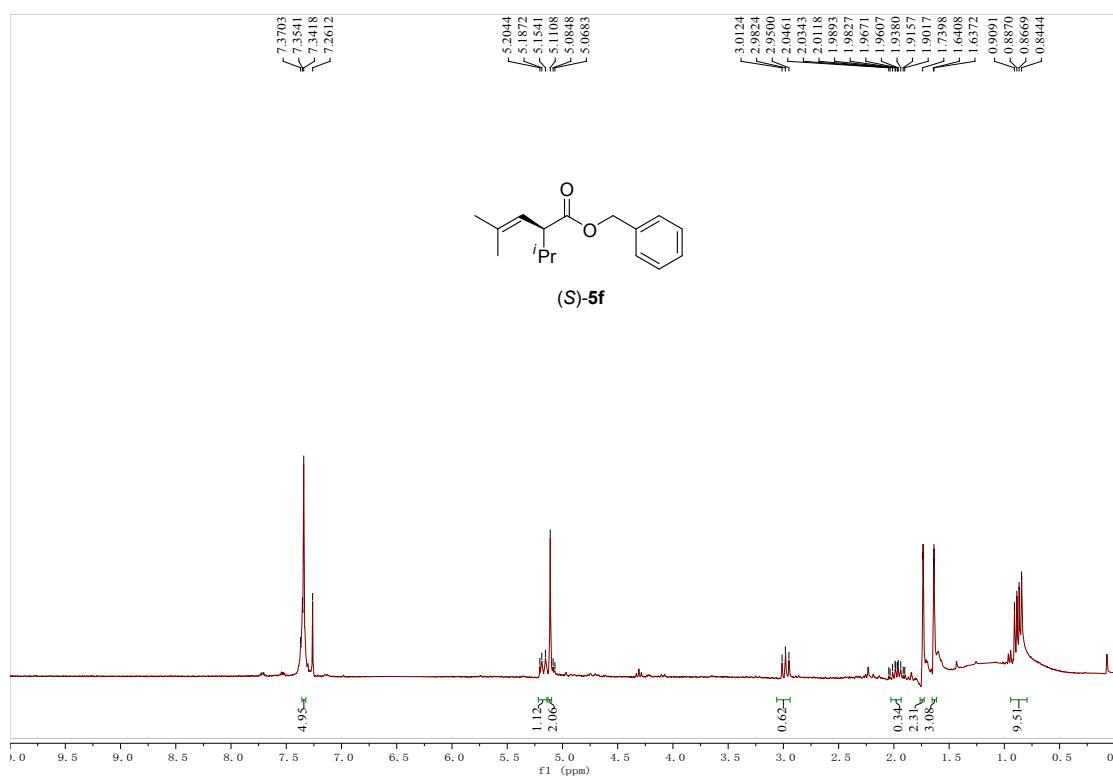


Figure S75. ^{13}C NMR Spectrum of (*S*)-benzyl 2-*iso*-propyl-4-methylpent-3-enoate (**5f**) (75 MHz, CDCl_3)

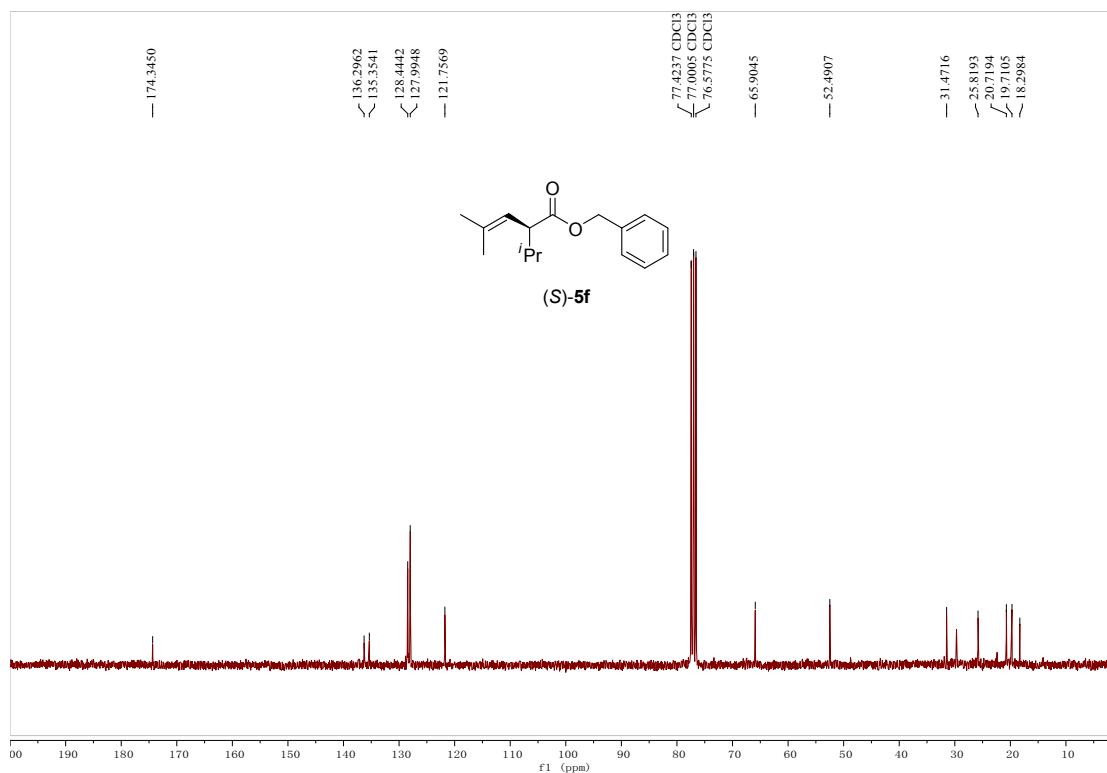


Figure S76. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-cyclohexyl-4-methylpent-3-enoate (**5g**) (300 MHz, CDCl_3)

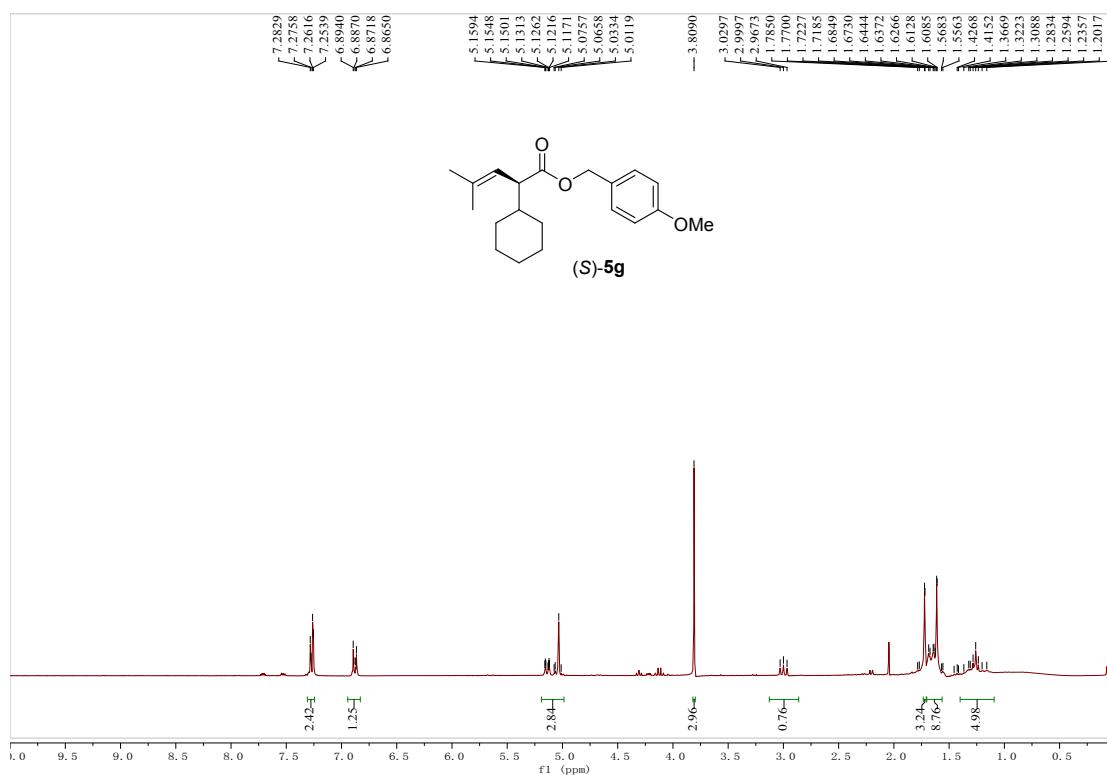


Figure S77. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-cyclohexyl-4-methylpent-3-enoate (**5g**) (75 MHz, CDCl_3)

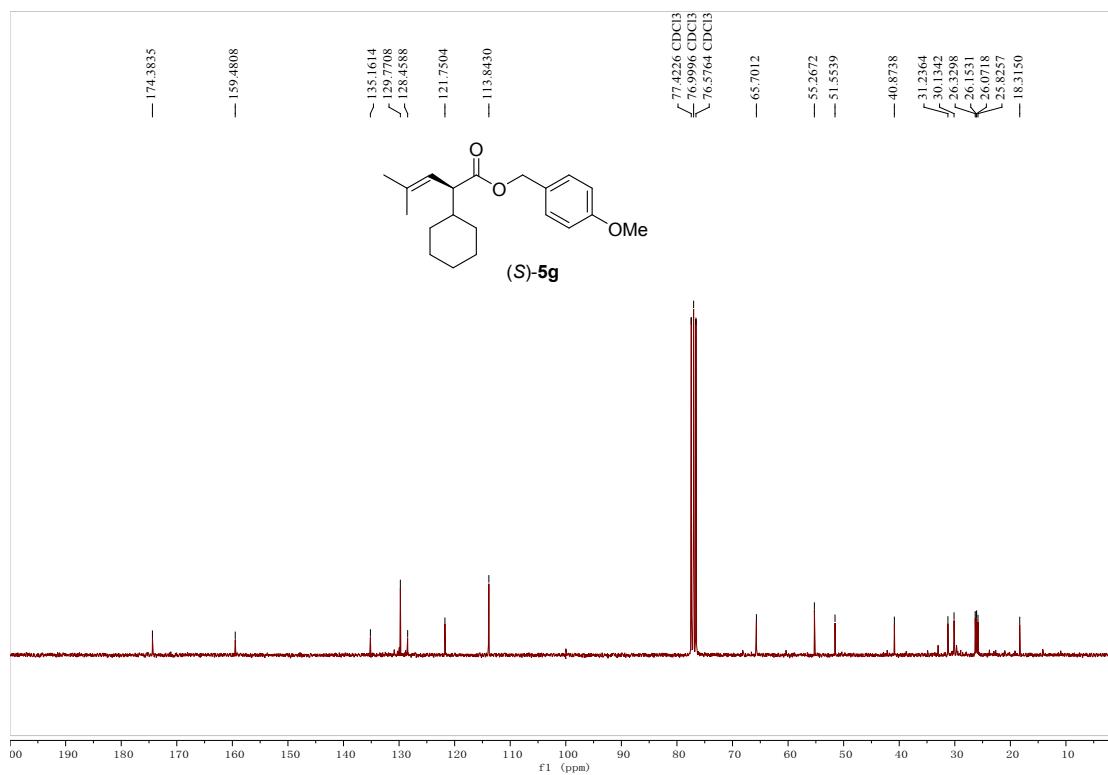


Figure S78. ^1H NMR Spectrum of (*S*)-ethyl 2-(2-bromoethyl)-4-methylpent-3-enoate (**5h**) (300 MHz, CDCl_3)

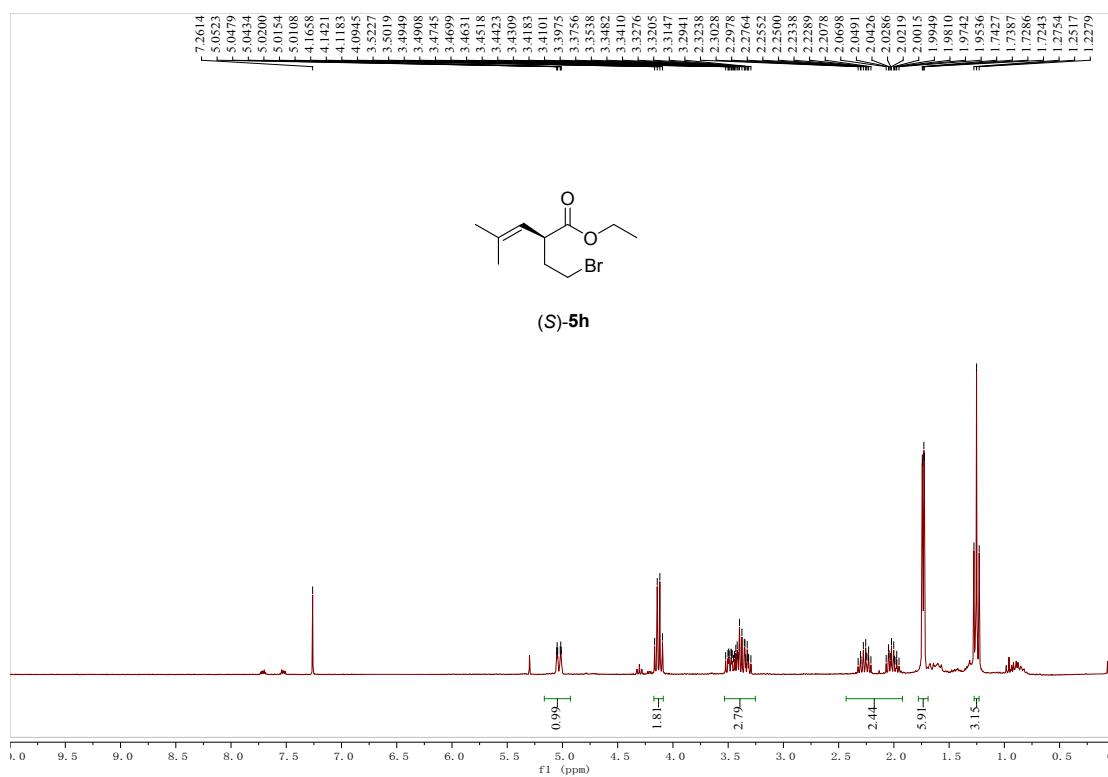


Figure S79. ^{13}C NMR Spectrum of (*S*)-ethyl 2-(2-bromoethyl)-4-methylpent-3-enoate (**5h**) (75 MHz, CDCl_3)

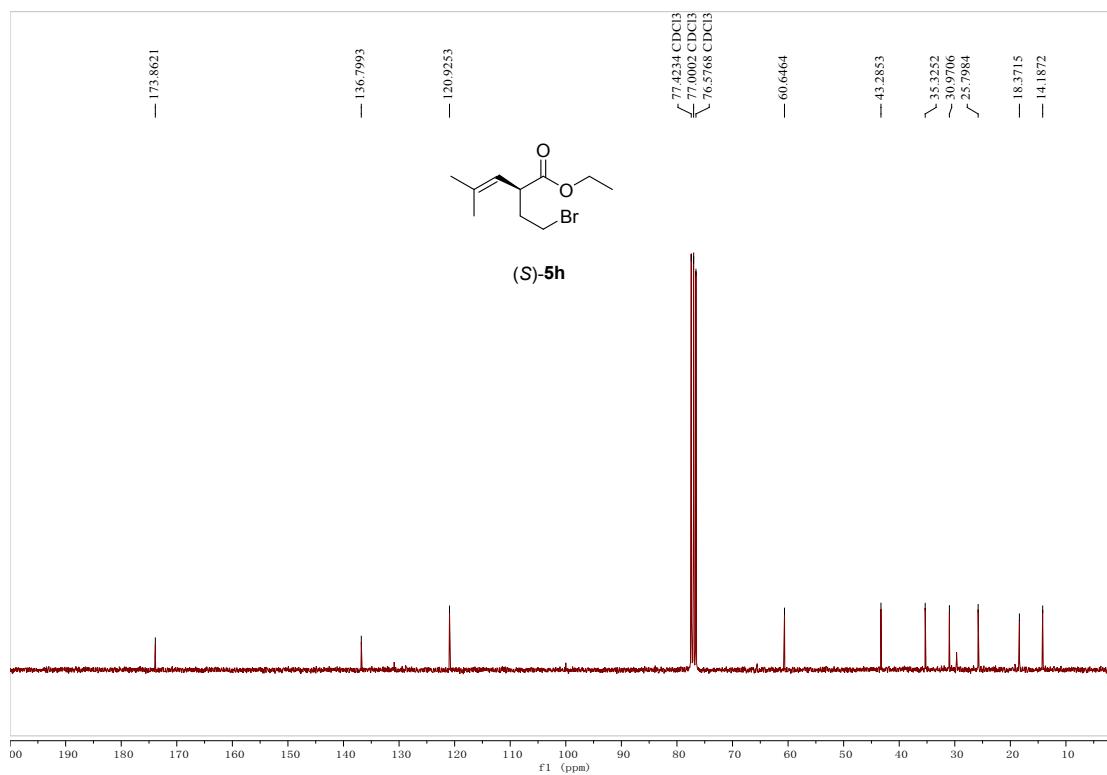


Figure S80. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-allyl-4-methylpent-3-enoate (**5i**) (300 MHz, CDCl_3)

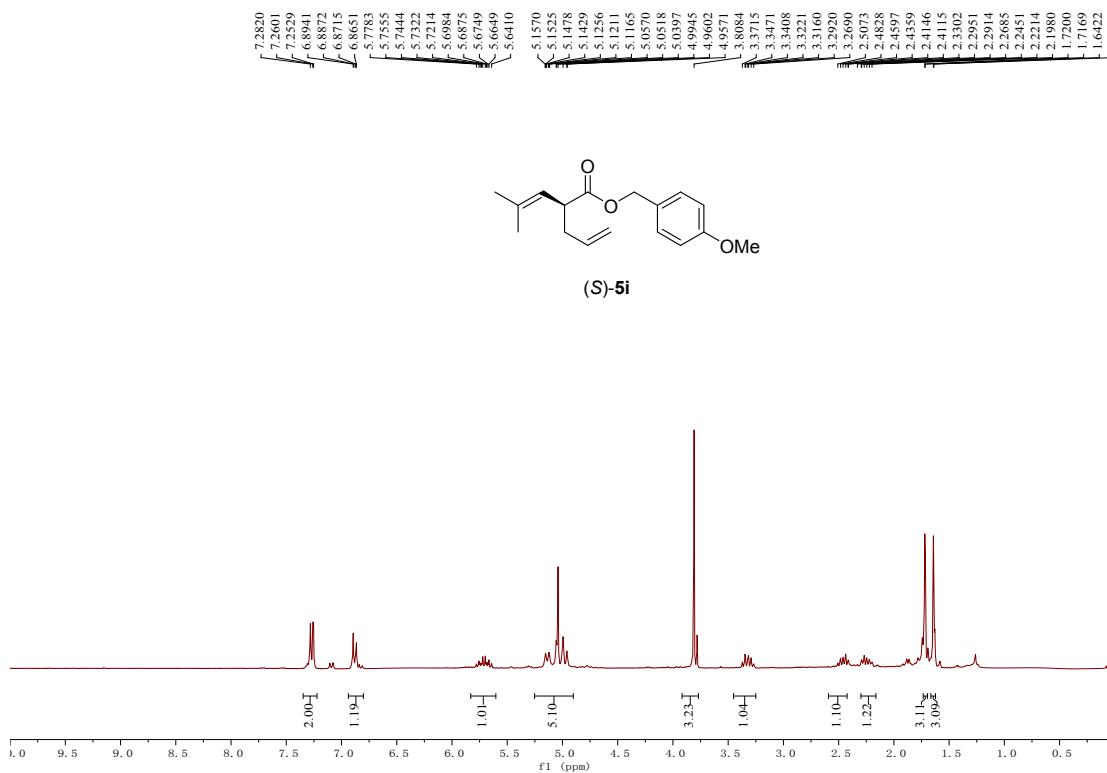


Figure S81. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-allyl-4-methylpent-3-enoate (**5i**) (75 MHz, CDCl_3)

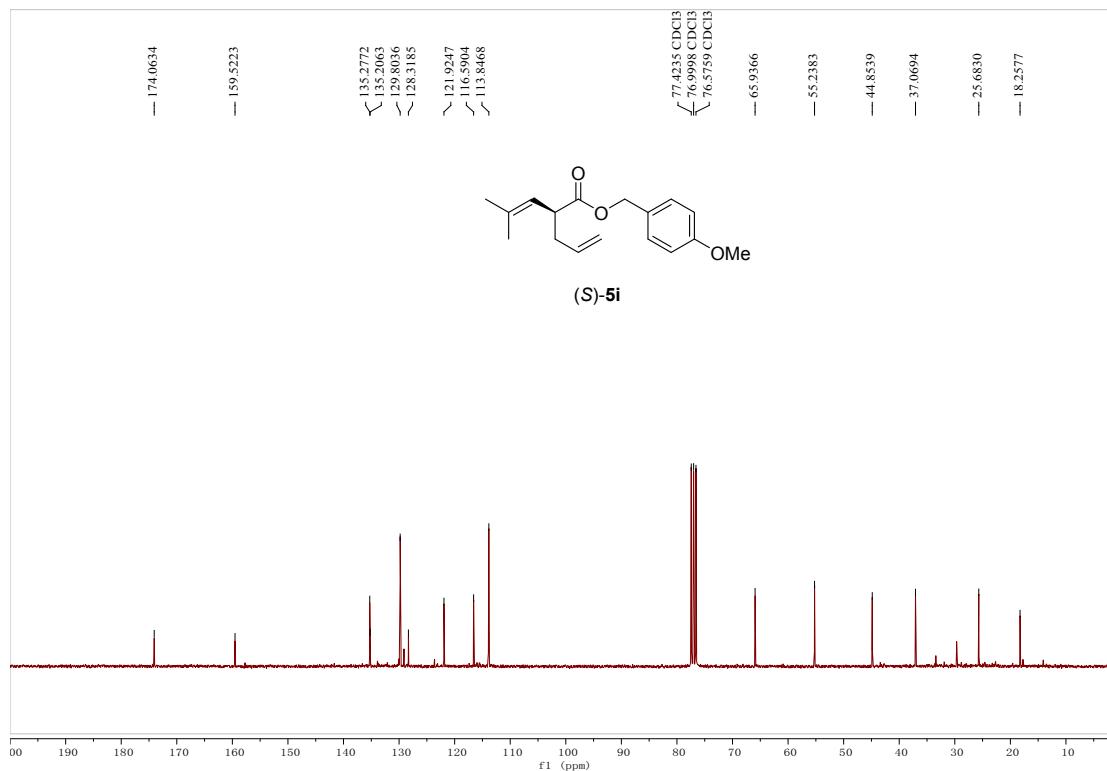


Figure S82. ^1H NMR Spectrum of (*S*)-dibenzyl 2-(2-methylprop-1-en-1-yl)pentanedioate (**5j**) (300 MHz, CDCl_3)

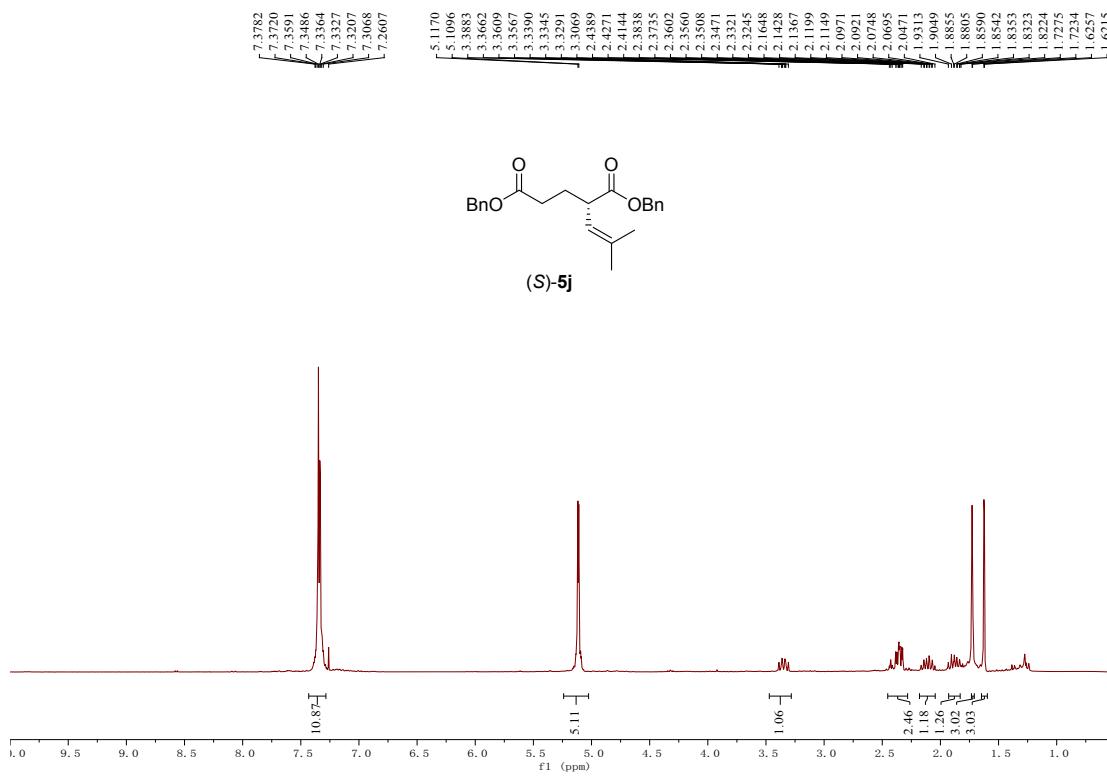


Figure S83. ^{13}C NMR Spectrum of (*S*)-dibenzyl 2-(2-methylprop-1-en-1-yl)pentanedioate (**5j**) (75 MHz, CDCl_3).

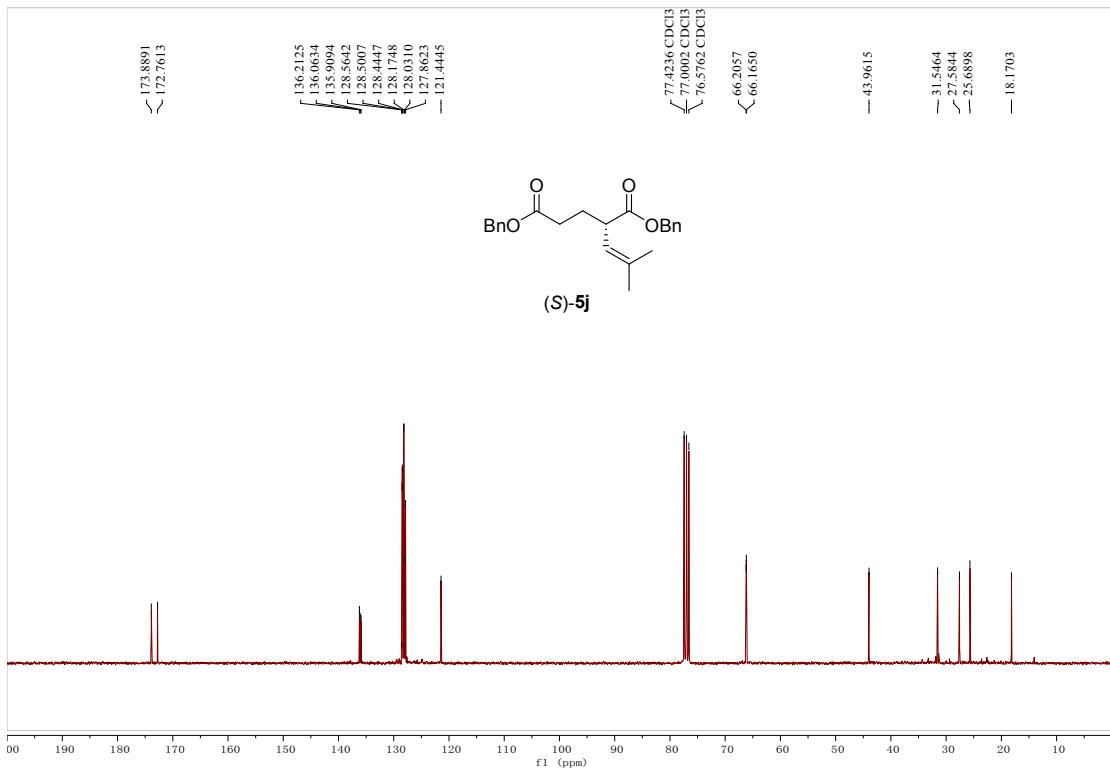


Figure S84. ^1H NMR Spectrum of (*S*)-methyl 2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4-methylpent-3-enoate (**5k**) (300 MHz, CDCl_3)

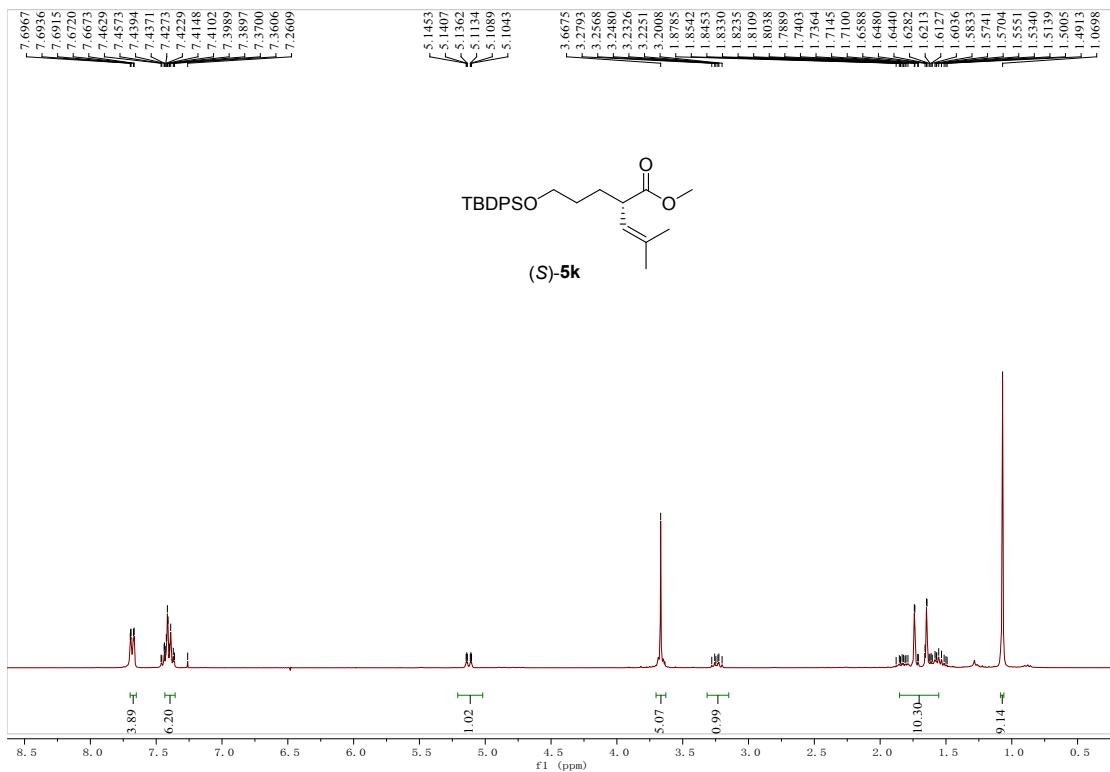


Figure S85. ^{13}C NMR Spectrum of (*S*)-methyl 2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4-methylpent-3-enoate (**5k**) (75 MHz, CDCl_3)

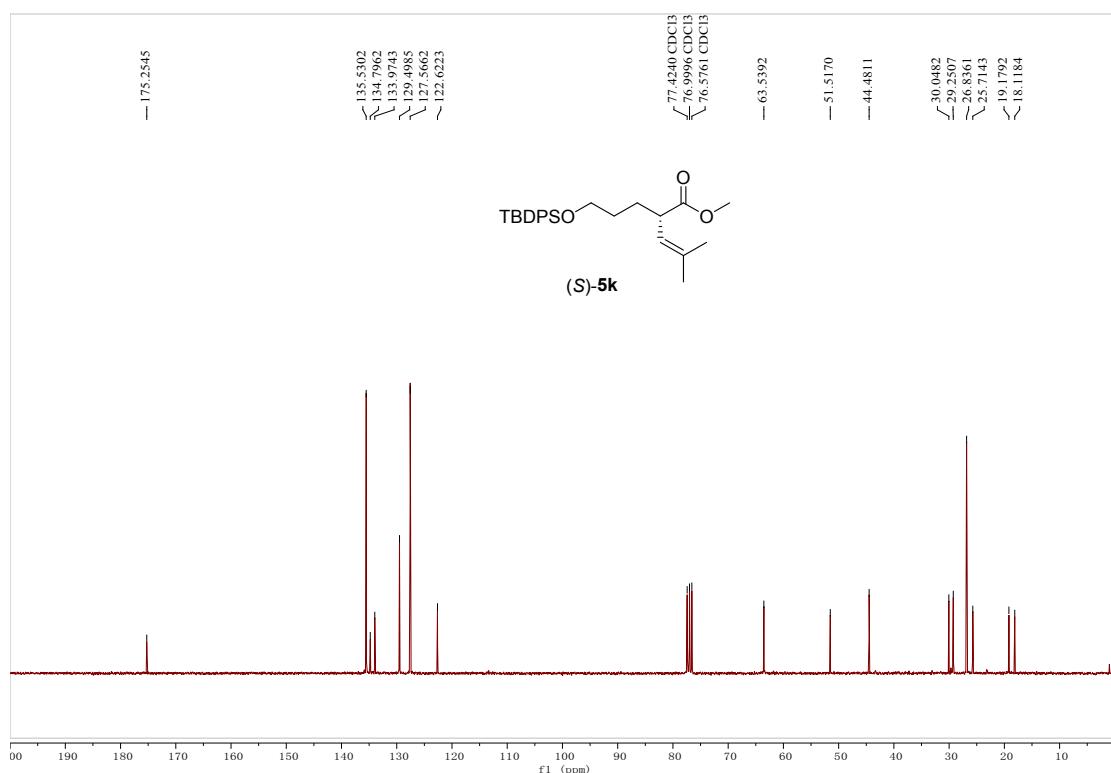


Figure S86. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-benzyl-4-methylpent-3-enoate (**5l**) (300 MHz, CDCl_3)

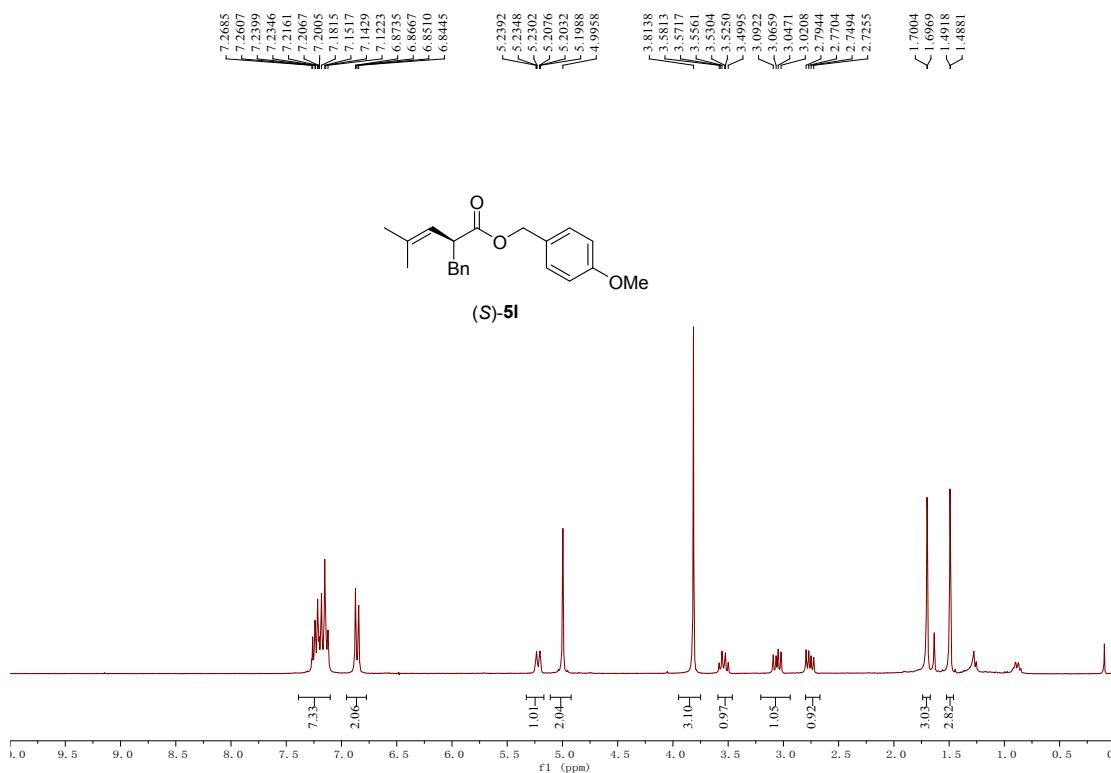


Figure S87. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-benzyl-4-methylpent-3-enoate (**5l**) (75 MHz, CDCl_3)

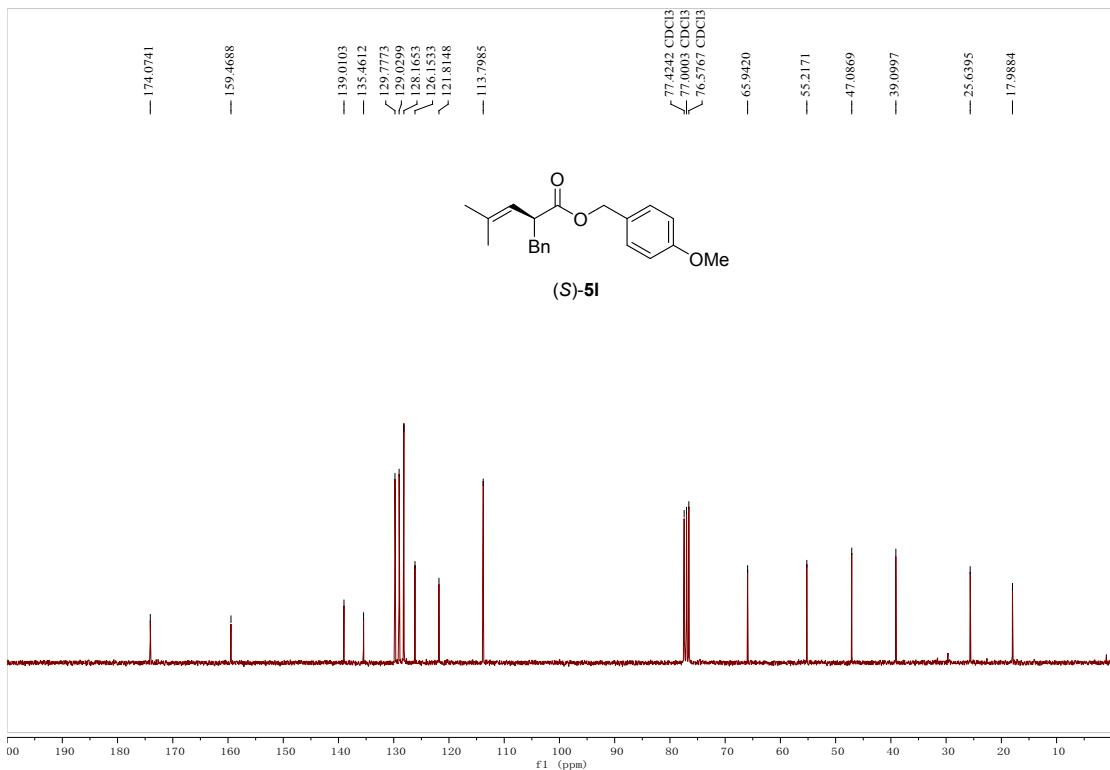


Figure S88. ^1H NMR Spectrum of (*S*)-methyl 6-(5-methylfuran-2-yl)-2-(2-methylprop-1-en-1-yl) hexanoate (**5m**) (300 MHz, CDCl_3)

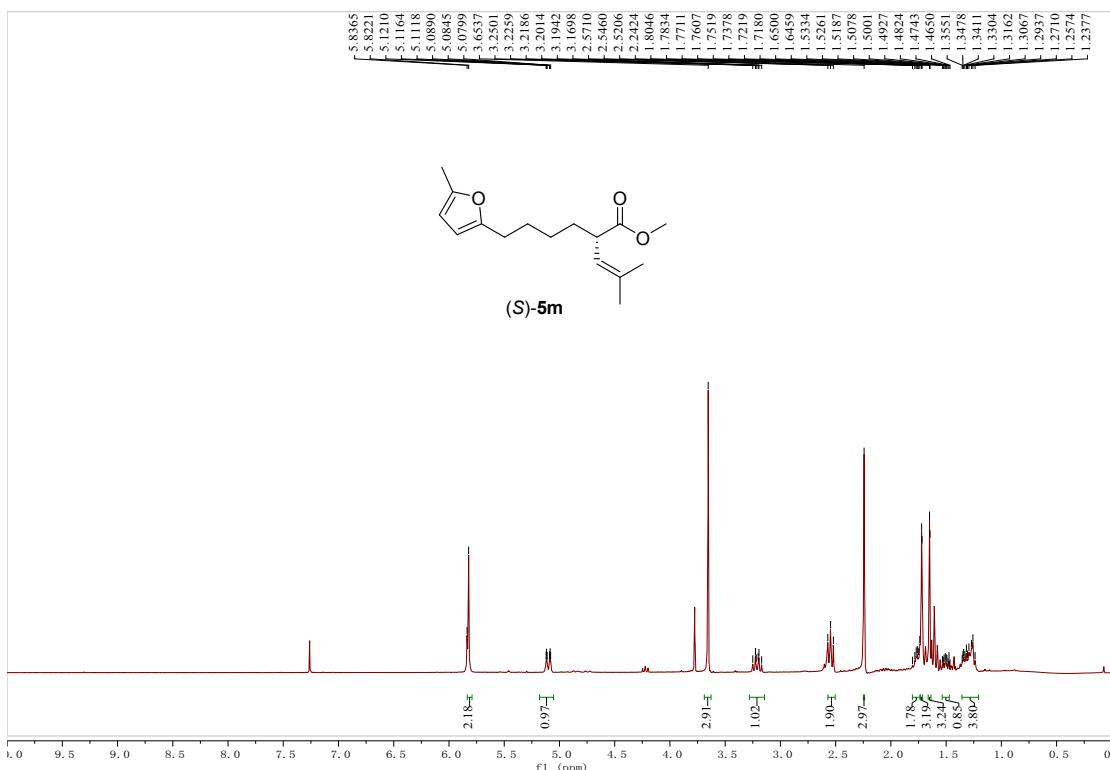


Figure S89. ^{13}C NMR Spectrum of (*S*)-methyl 6-(5-methylfuran-2-yl)-2-(2-methylprop-1-en-1-yl) hexanoate (**5m**) (75 MHz, CDCl_3)

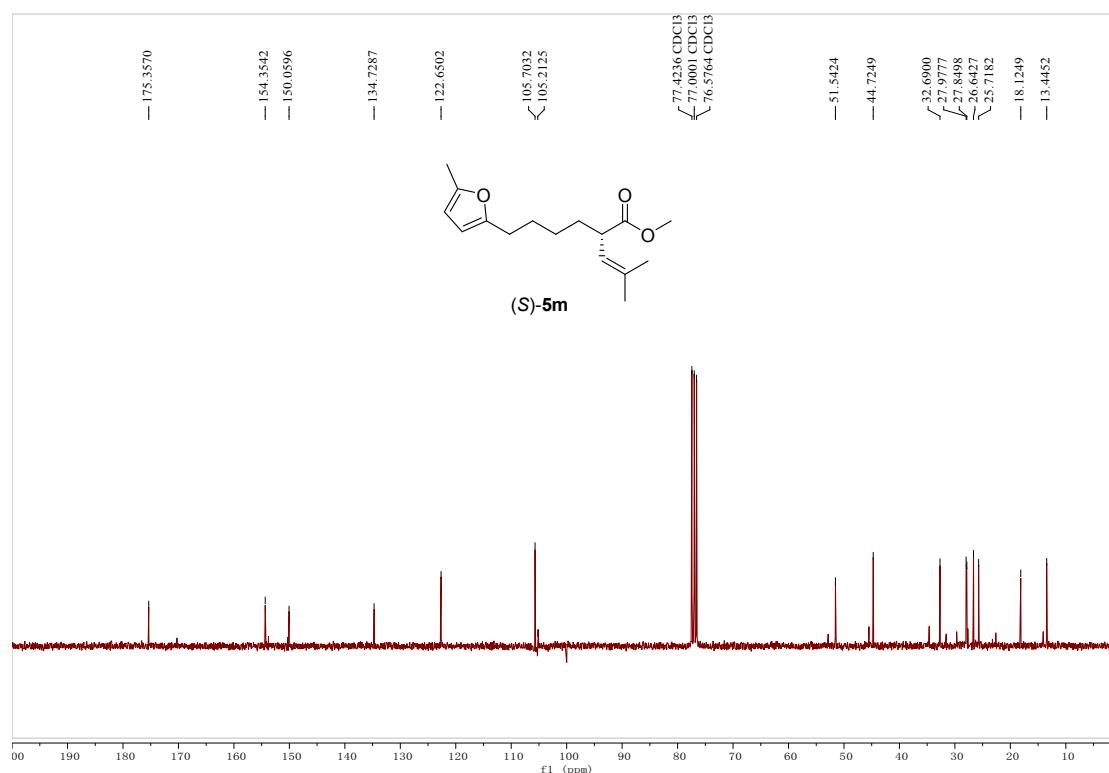


Figure S90. ^1H NMR Spectrum of (*S*)-benzyl 2-methylbut-3-enoate (**6a**) (300 MHz, CDCl_3)

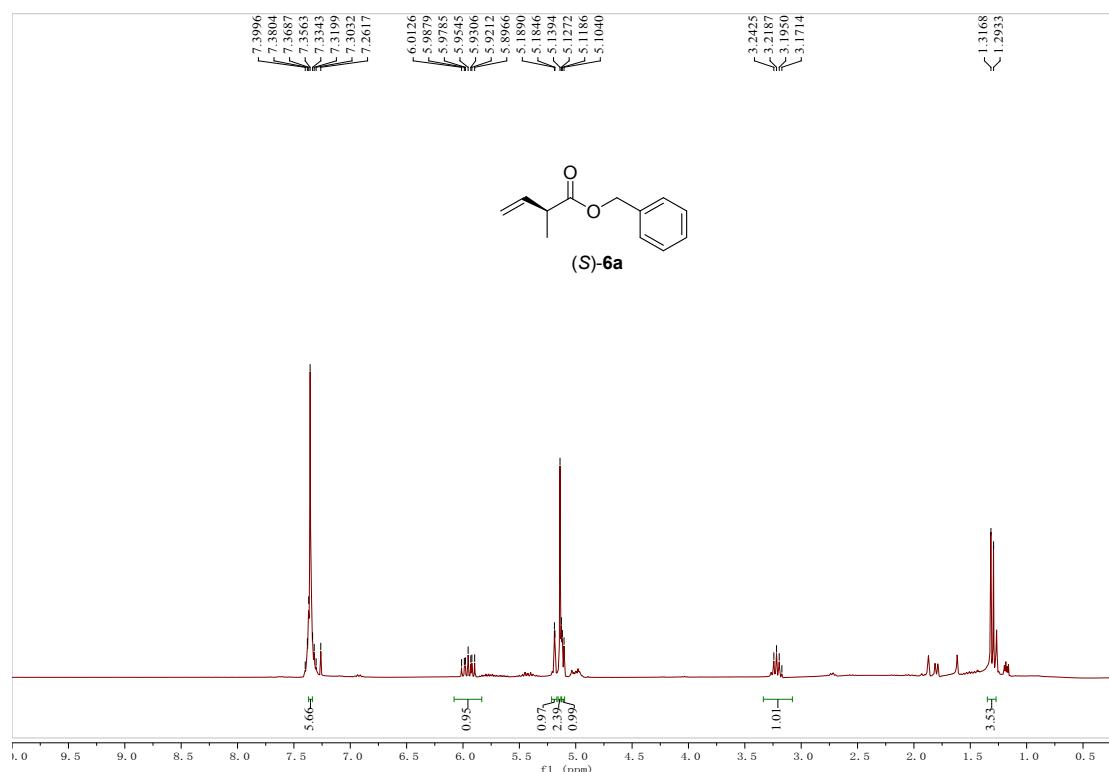


Figure S91. ^{13}C NMR Spectrum of (*S*)-benzyl 2-methylbut-3-enoate (**6a**) (75 MHz, CDCl_3)

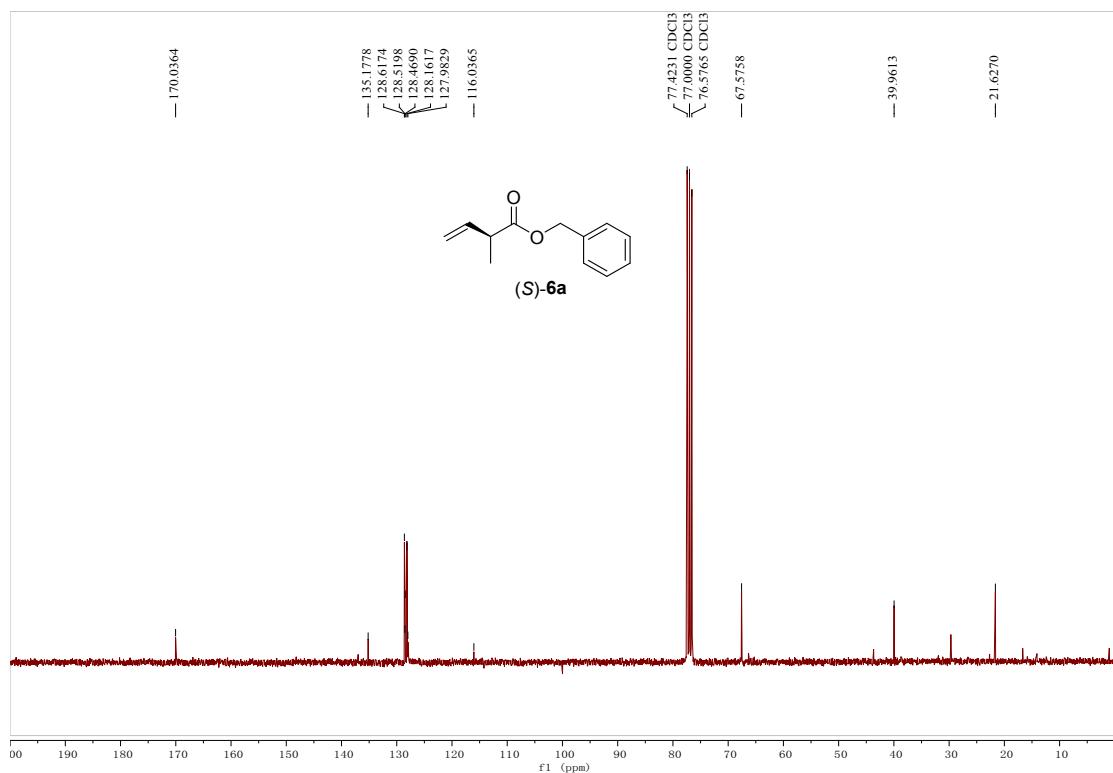


Figure S92. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethylbut-3-enoate (**6b**) (300 MHz, CDCl_3)

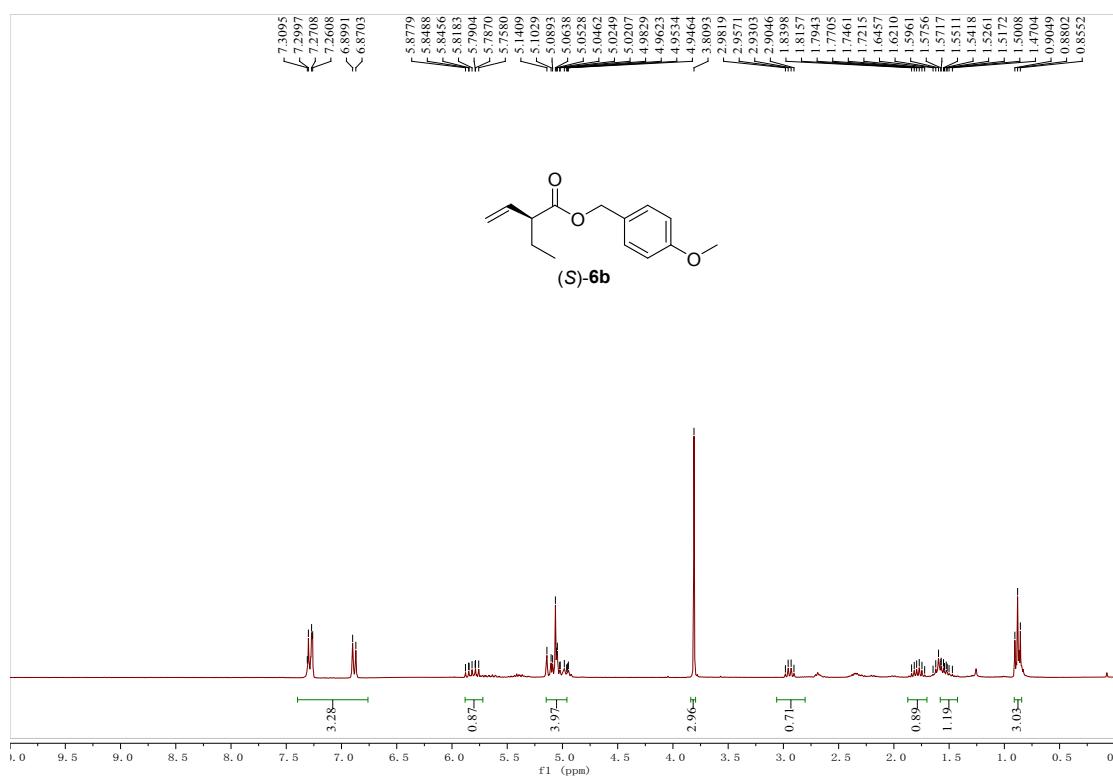


Figure S93. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethylbut-3-enoate (**6b**) (75 MHz, CDCl_3)

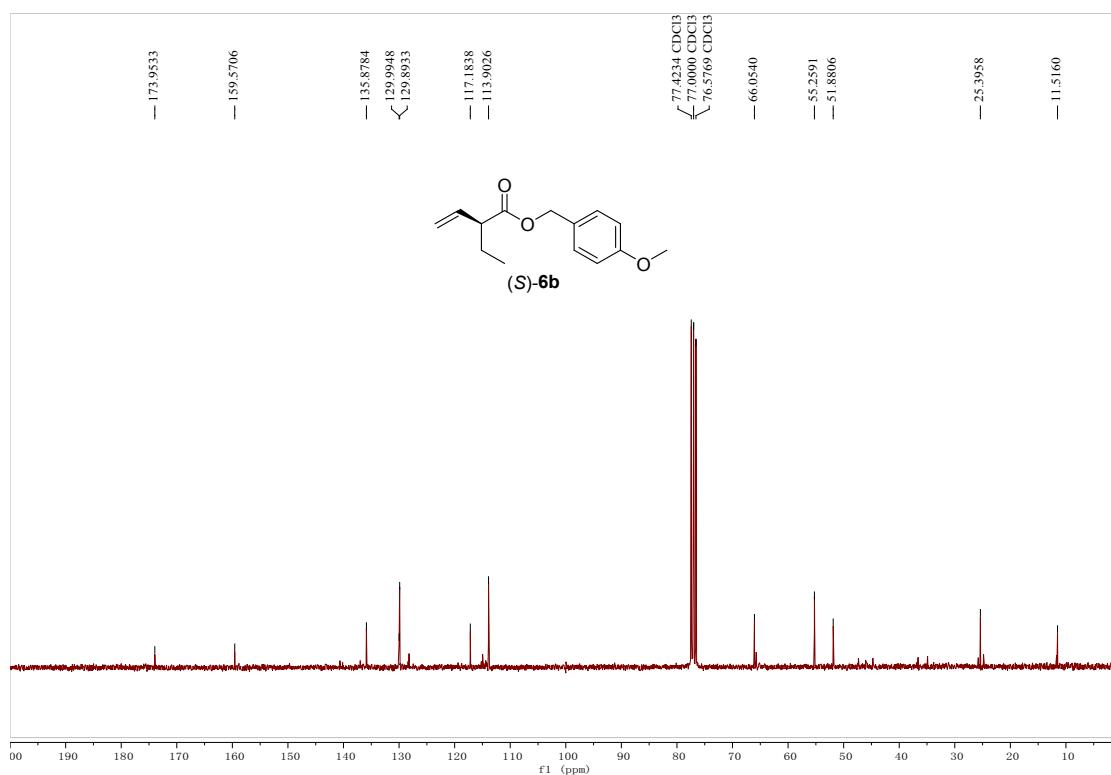


Figure S94. ^1H NMR Spectrum of (*S*)-benzyl 2,3-dimethylbut-3-enoate (**6c**) (300 MHz, CDCl_3)

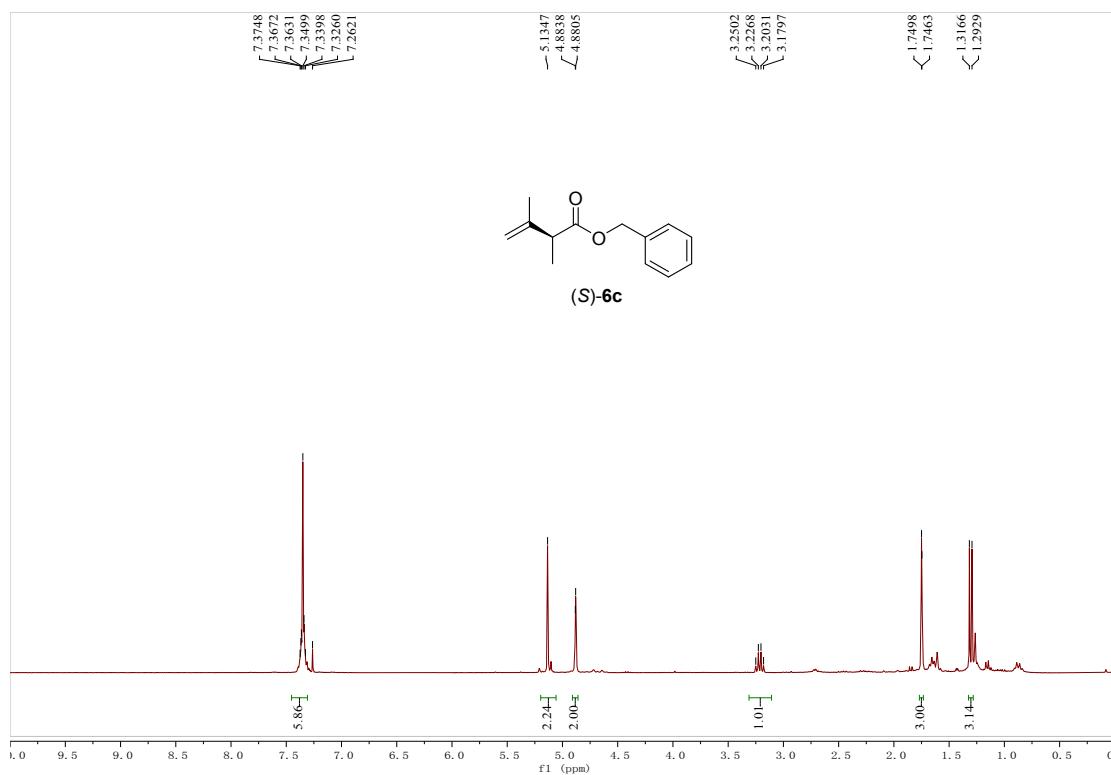


Figure S95. ^{13}C NMR Spectrum of (*S*)-benzyl 2,3-dimethylbut-3-enoate (**6c**) (75 MHz, CDCl_3)

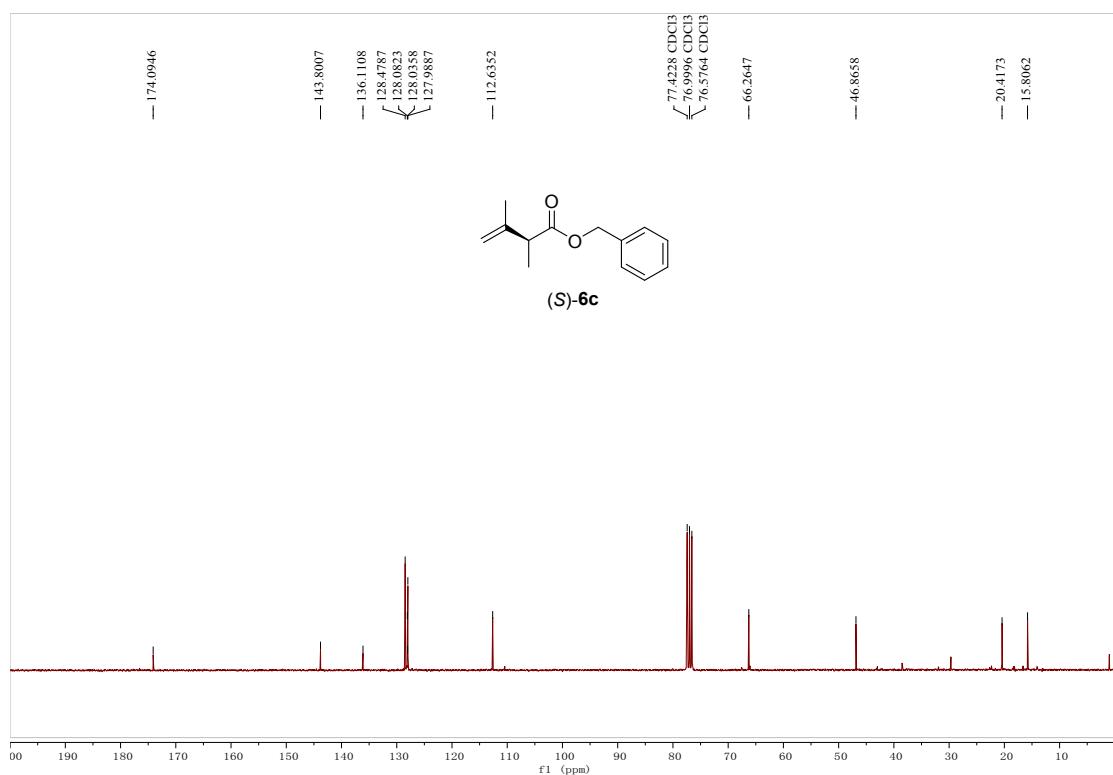


Figure S96. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-3-methylbut-3-enoate (**6d**) (300 MHz, CDCl_3)

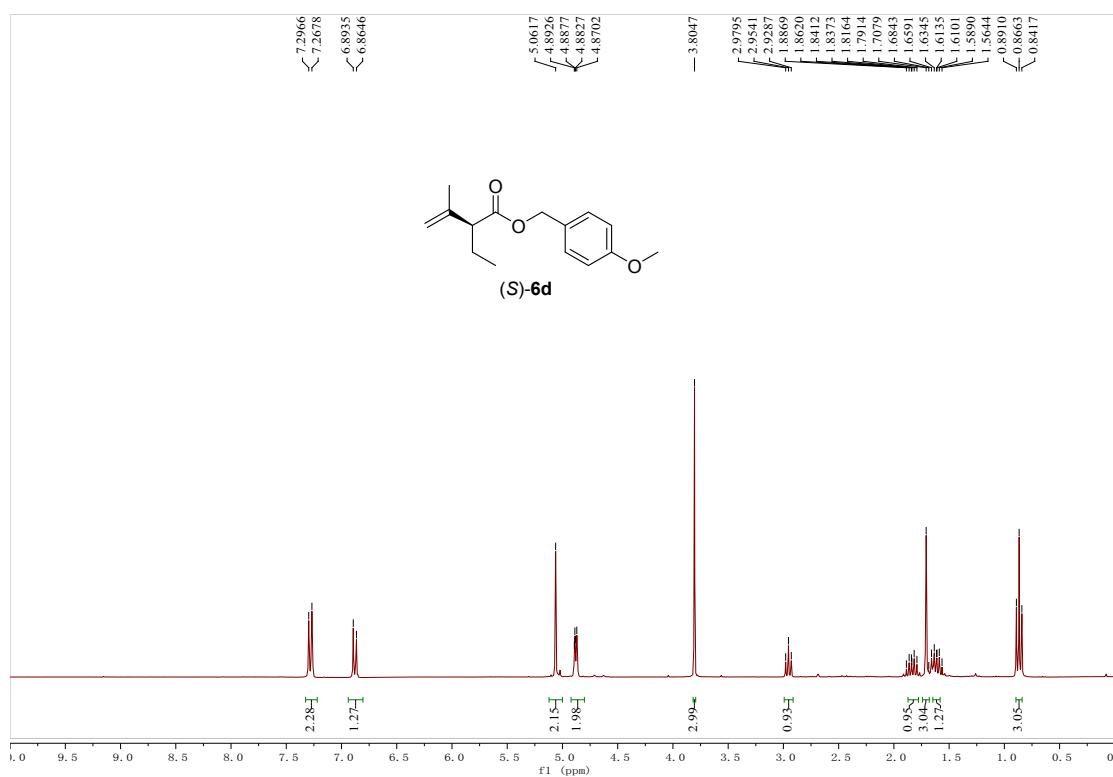


Figure S97. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-3-methylbut-3-enoate (**6d**) (75 MHz, CDCl_3)

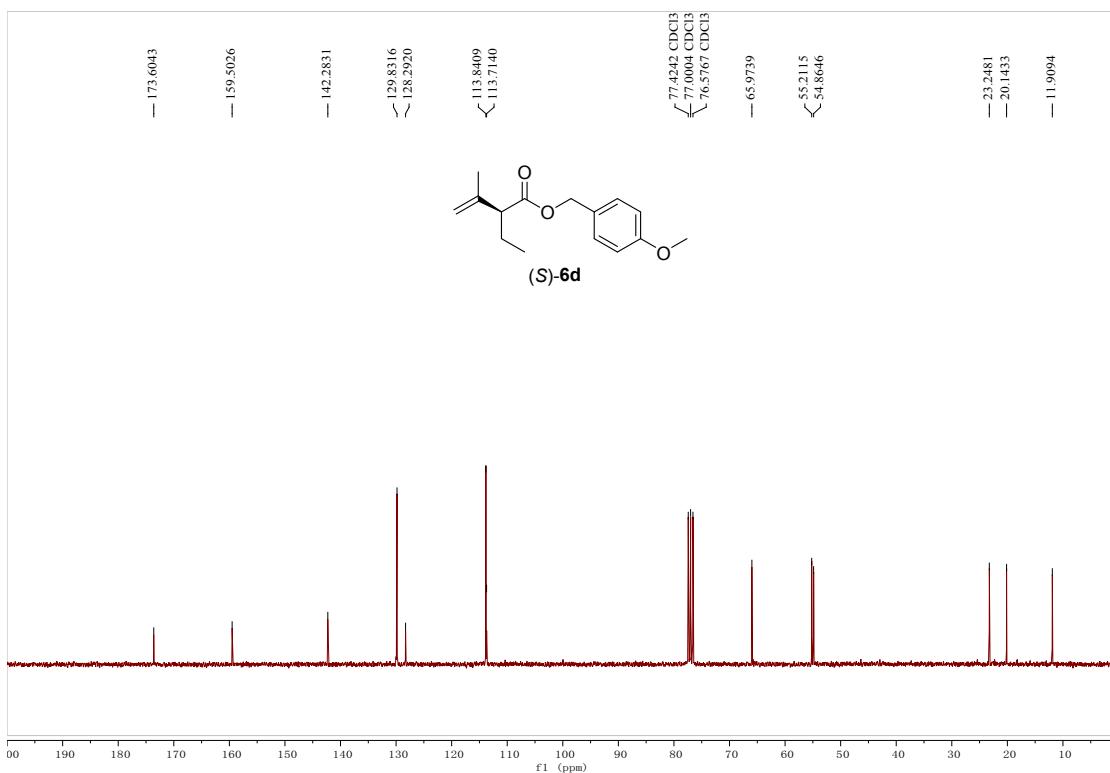


Figure S98. ^1H NMR Spectrum of (*S*)-benzyl 2,3-dimethylpent-3-enoate (**6e**) (300 MHz, CDCl_3)

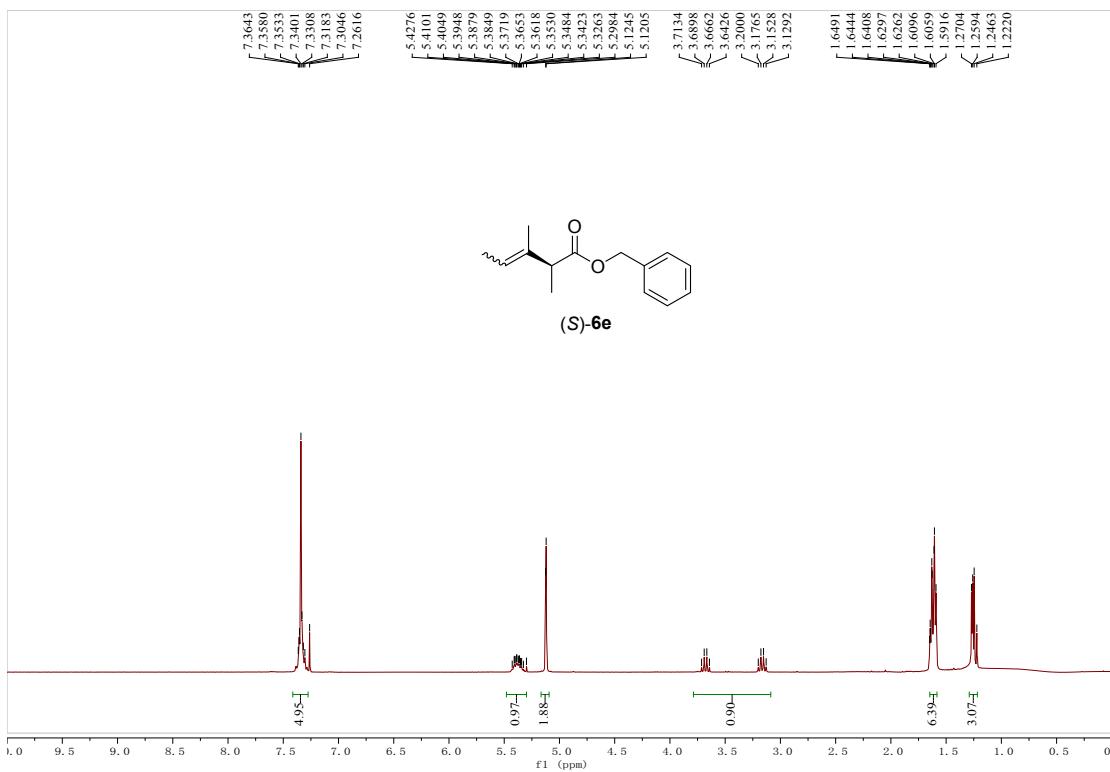


Figure S99. ^{13}C NMR Spectrum of (*S*)-benzyl 2,3-dimethylpent-3-enoate (**6e**) (75 MHz, CDCl_3)

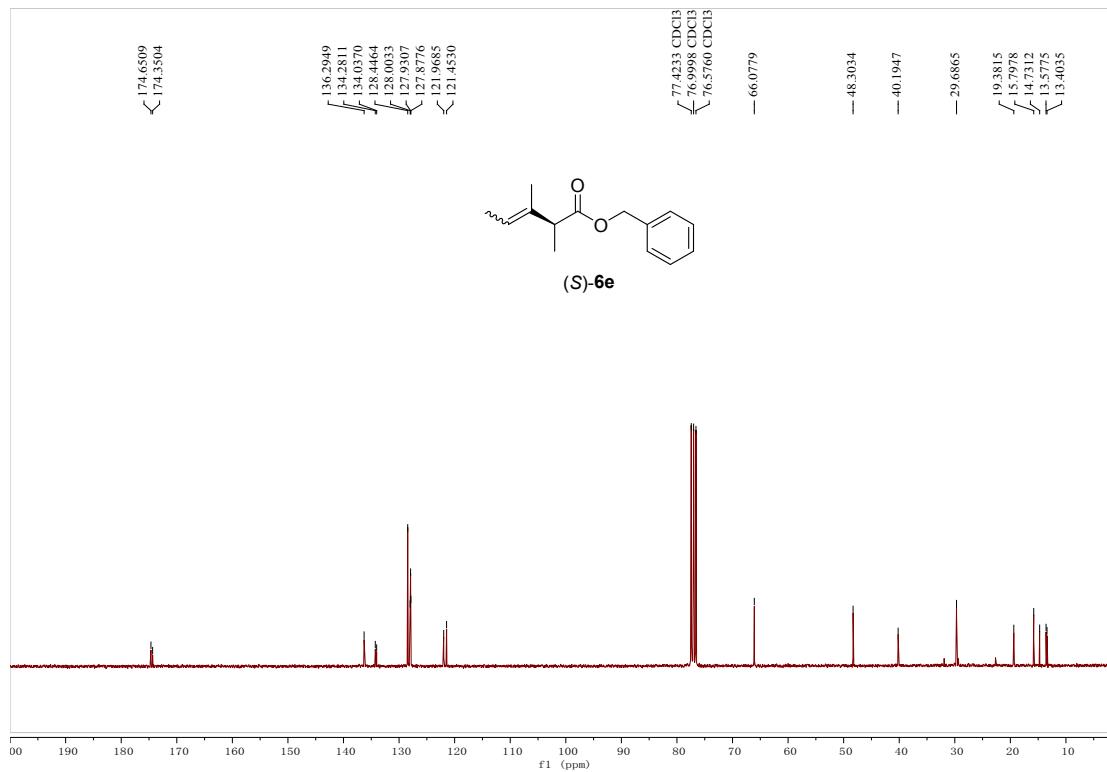


Figure S100. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-3-methylpent-3-enoate (**6f**) (300 MHz, CDCl_3)

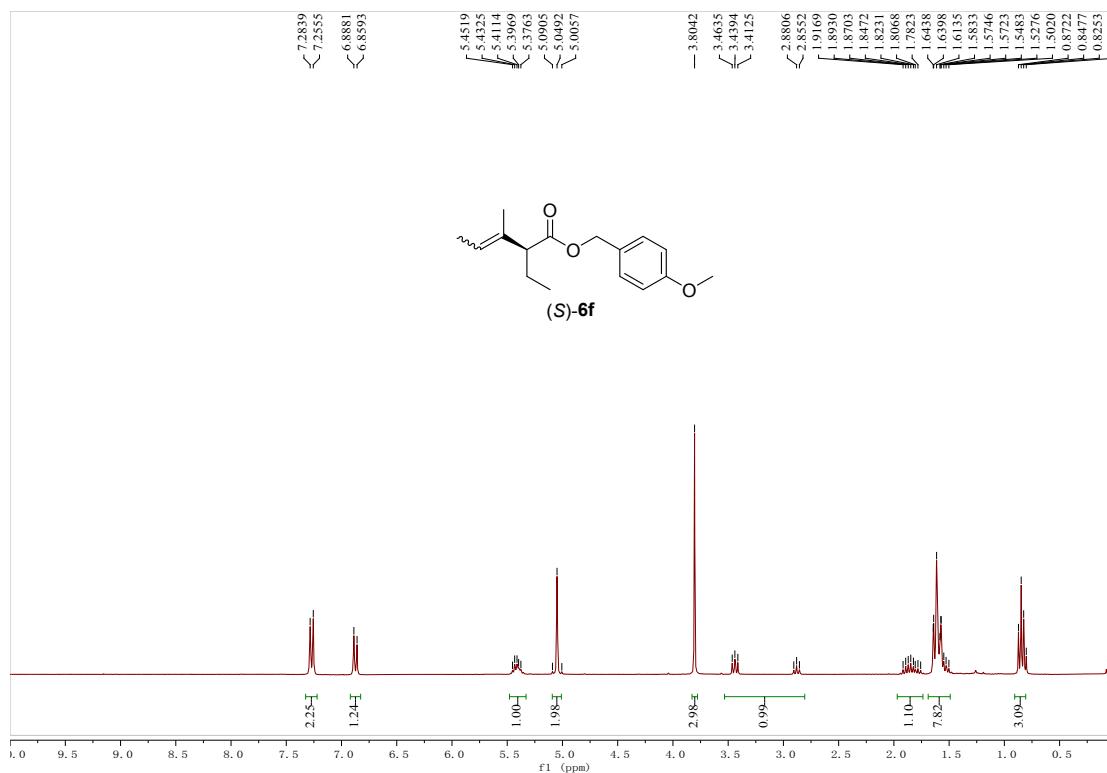


Figure S101. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethyl-3-methylpent-3-enoate (**6f**) (75 MHz, CDCl_3)

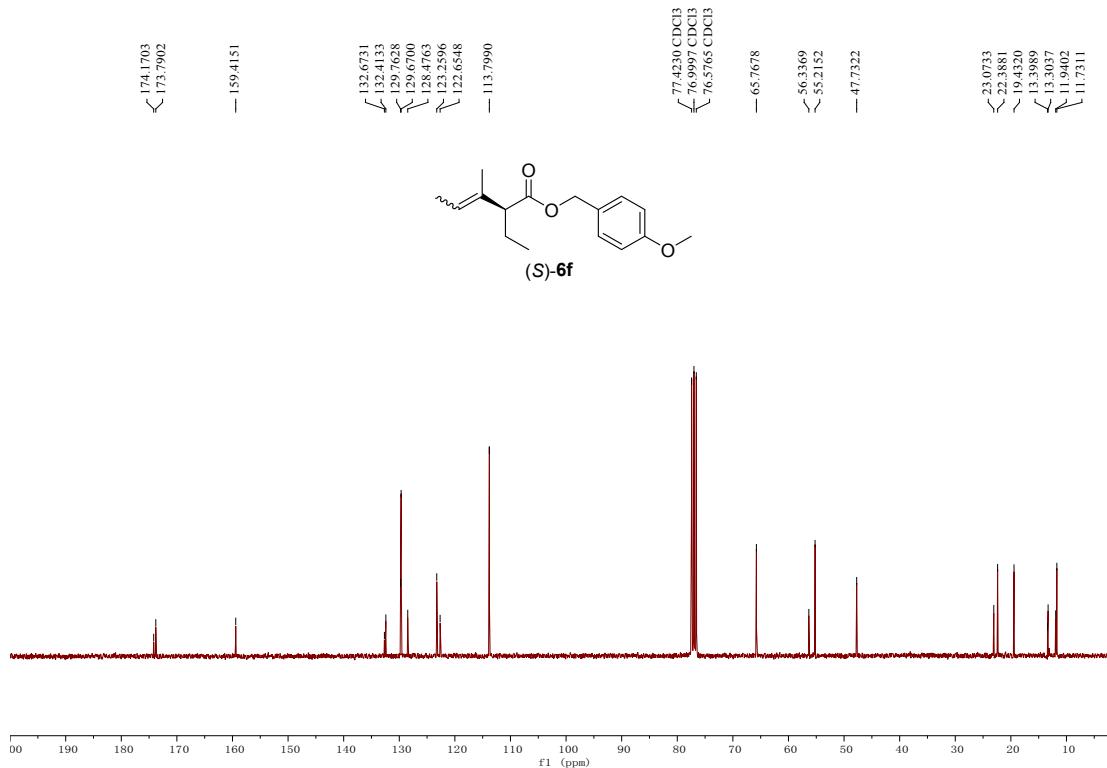


Figure S102. ^1H NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethylpent-3-enoate (**6g**) (300 MHz, CDCl_3)

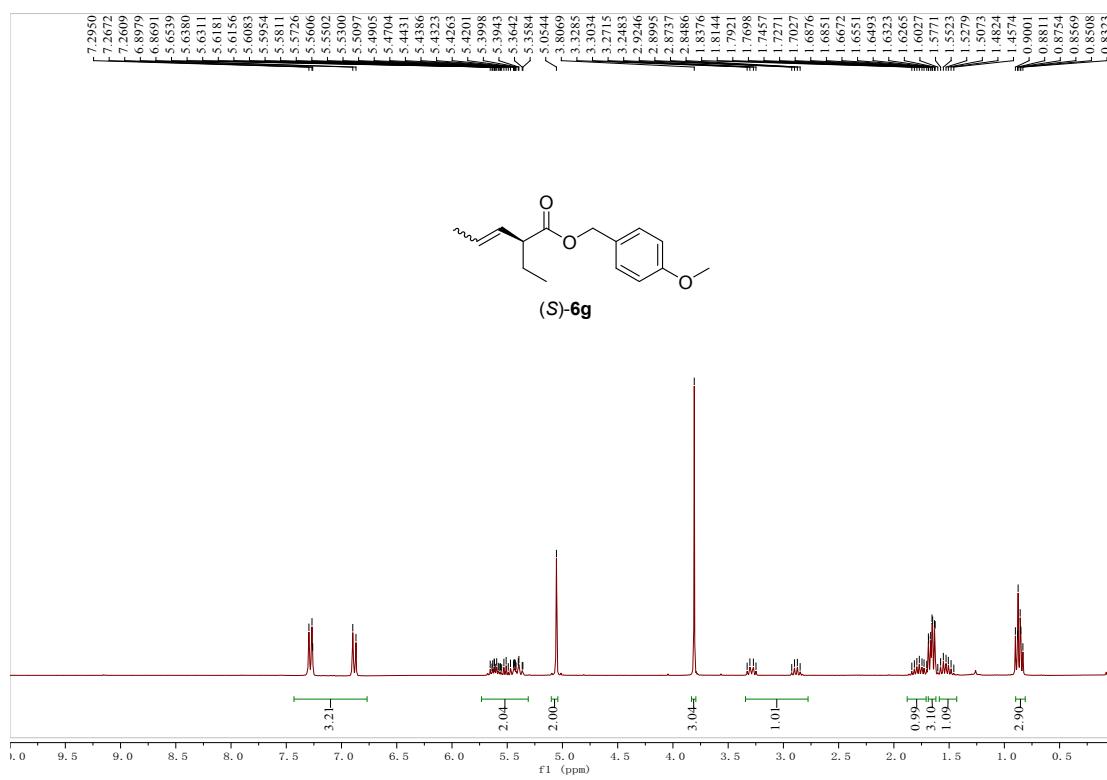


Figure S103. ^{13}C NMR Spectrum of (*S*)-4-methoxybenzyl 2-ethylpent-3-enoate (**6g**) (75 MHz, CDCl_3)

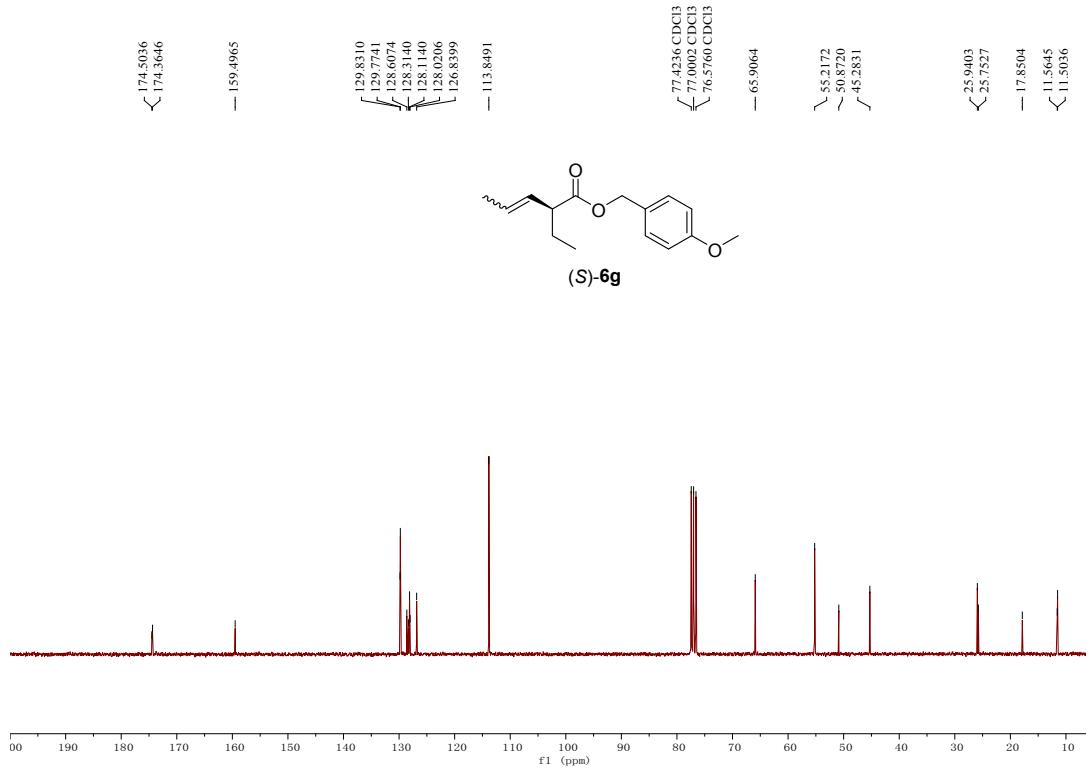


Figure S104. ^1H NMR Spectrum of (*S*)-benzyl 2-(prop-1-en-2-yl)hex-5-enoate (**6h**) (400 MHz, CDCl_3)

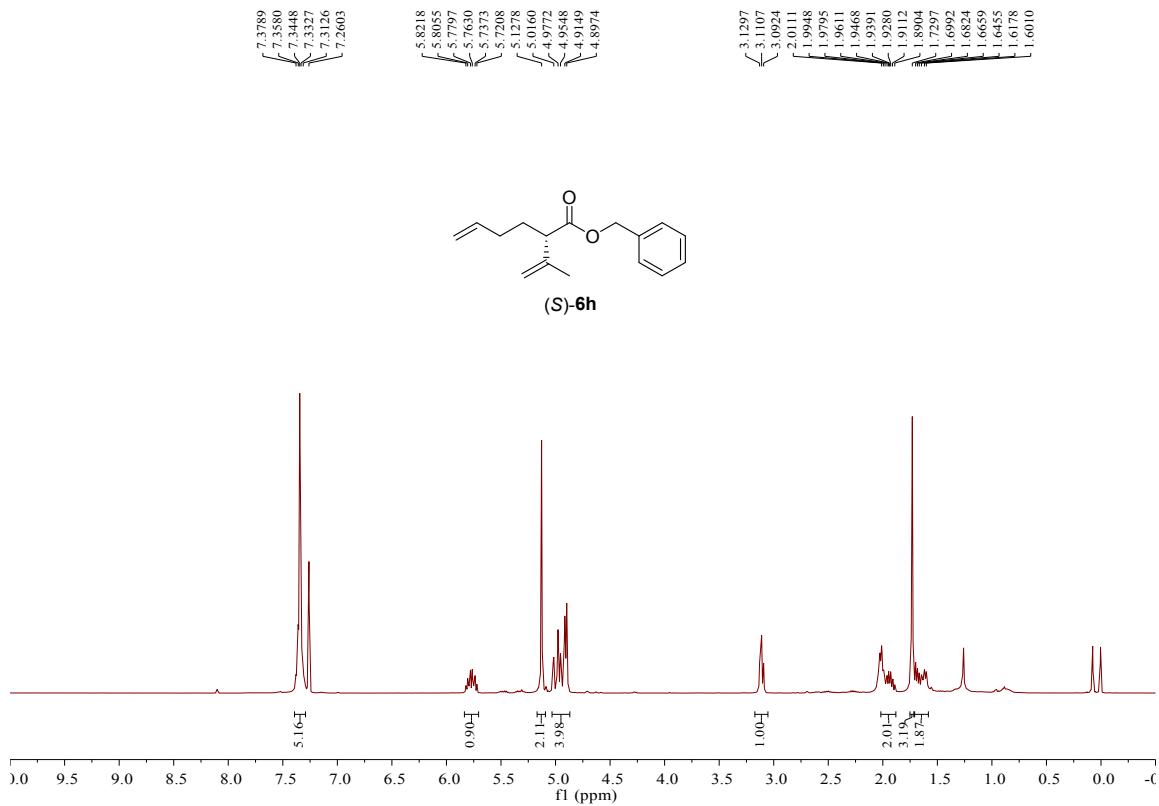


Figure S105. ^{13}C NMR Spectrum of (*S*)-benzyl 2-(prop-1-en-2-yl)hex-5-enoate (**6h**) (100 MHz, CDCl_3)

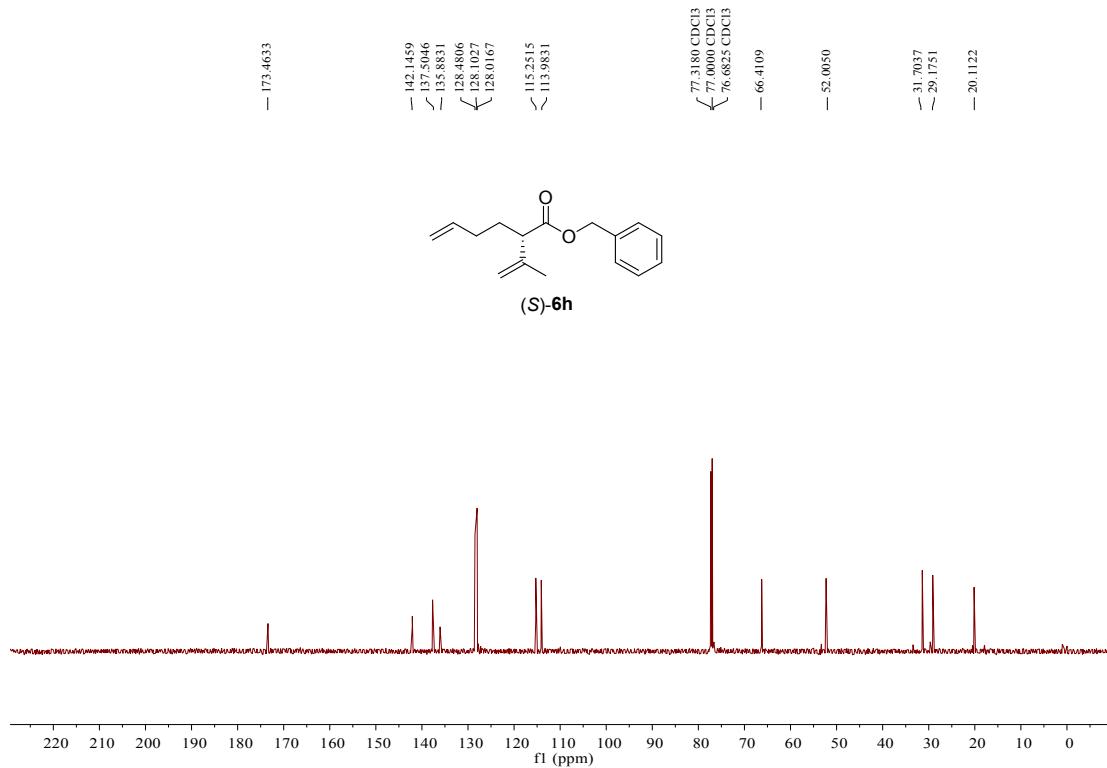


Figure S106. ^1H NMR Spectrum of (*S*)-2-(prop-1-en-2-yl)hex-5-en-1-ol (**7**) (300 MHz, CDCl_3)

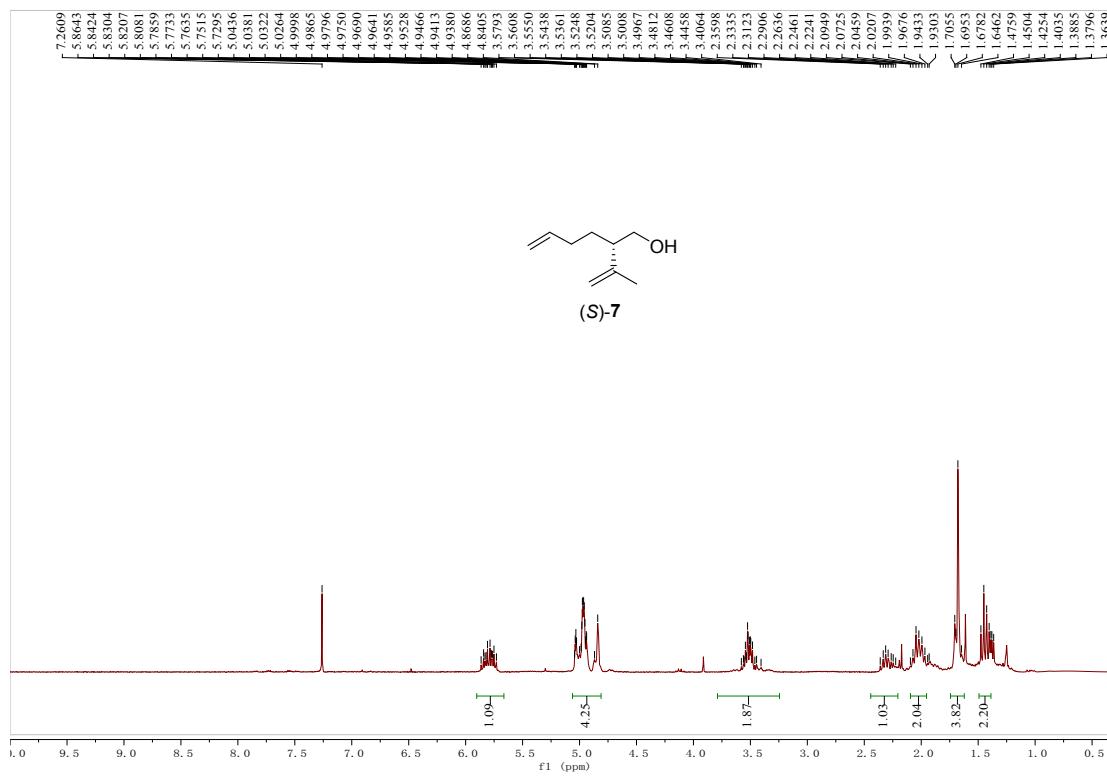


Figure S107. ^{13}C NMR Spectrum of (*S*)-2-(prop-1-en-2-yl)hex-5-en-1-ol (**7**) (75 MHz, CDCl_3)

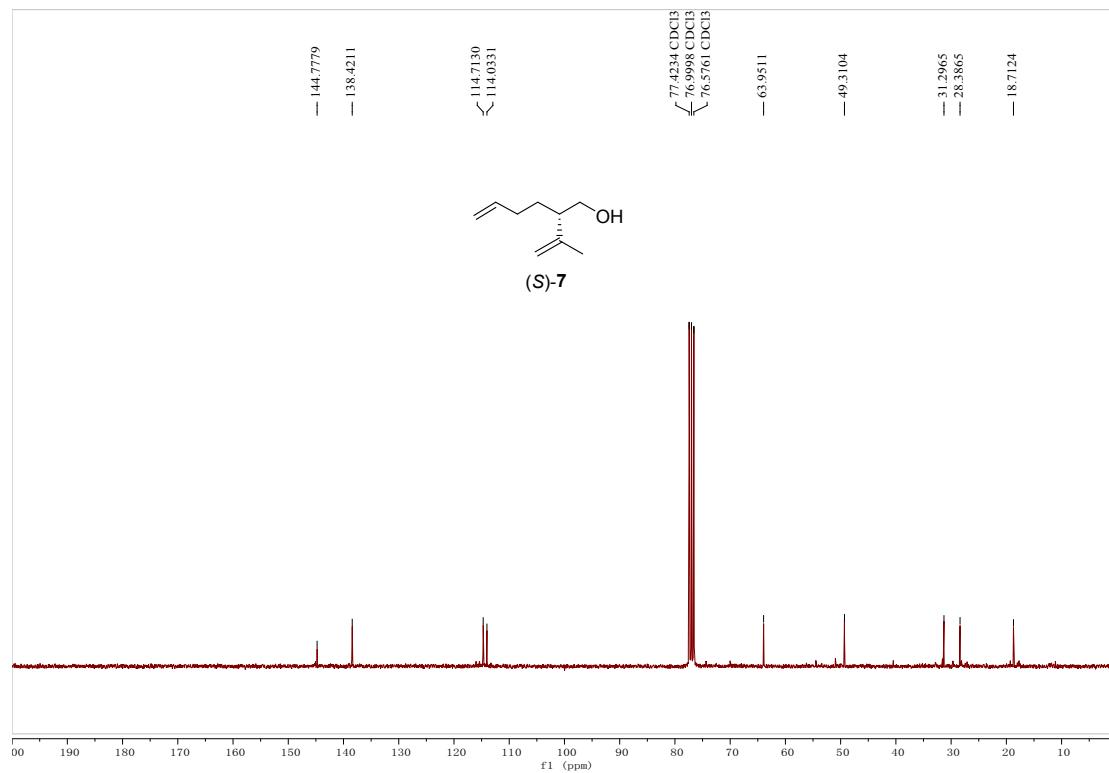


Figure S108. ^1H NMR Spectrum of (*S*)-2-(prop-1-en-2-yl)hex-5-enal (**8**) (300 MHz, CDCl_3)

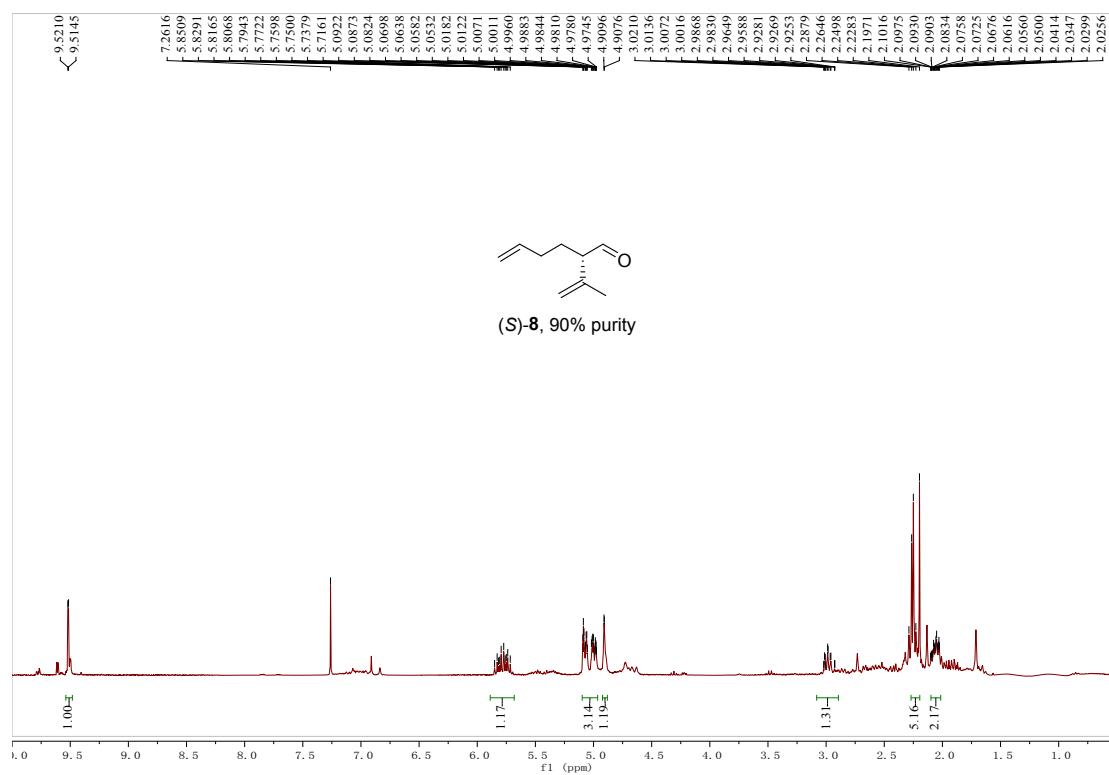


Figure S109. ^{13}C NMR Spectrum of (*S*)-2-(prop-1-en-2-yl)hex-5-enal (**8**) (75 MHz, CDCl_3)

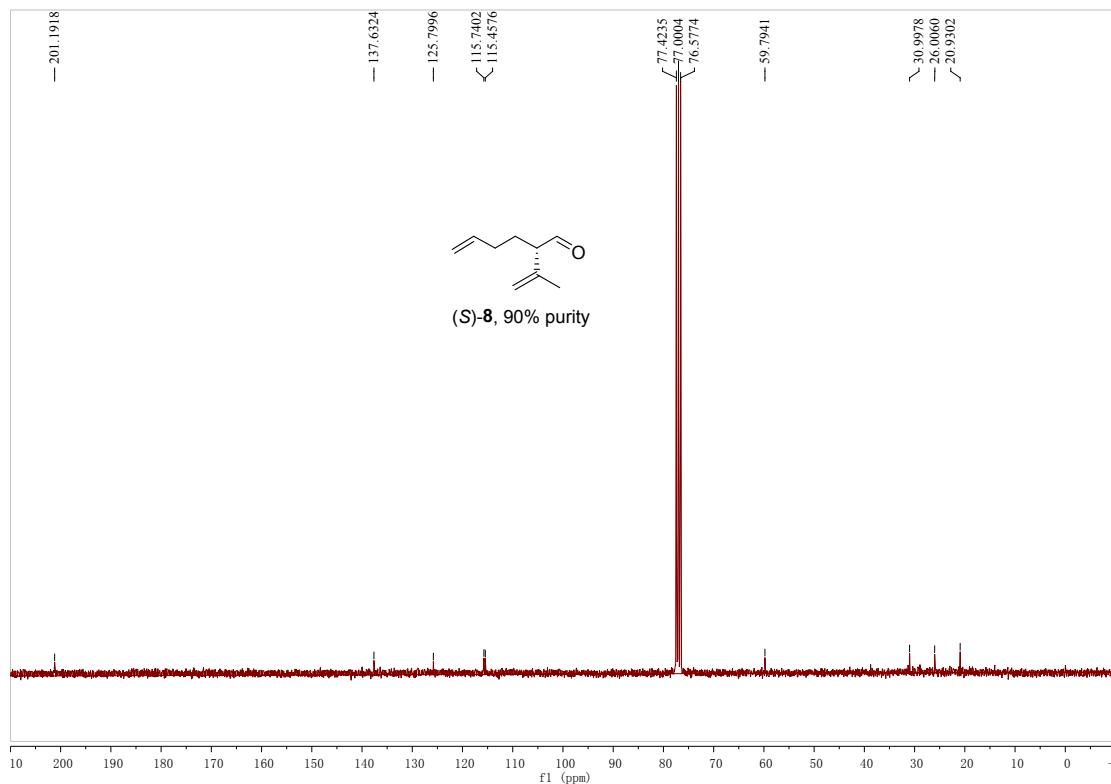


Figure S110. ^1H NMR Spectrum of (*R*)-3-(prop-1-en-2-yl)hept-6-enal (**9**) (300 MHz, CDCl_3)

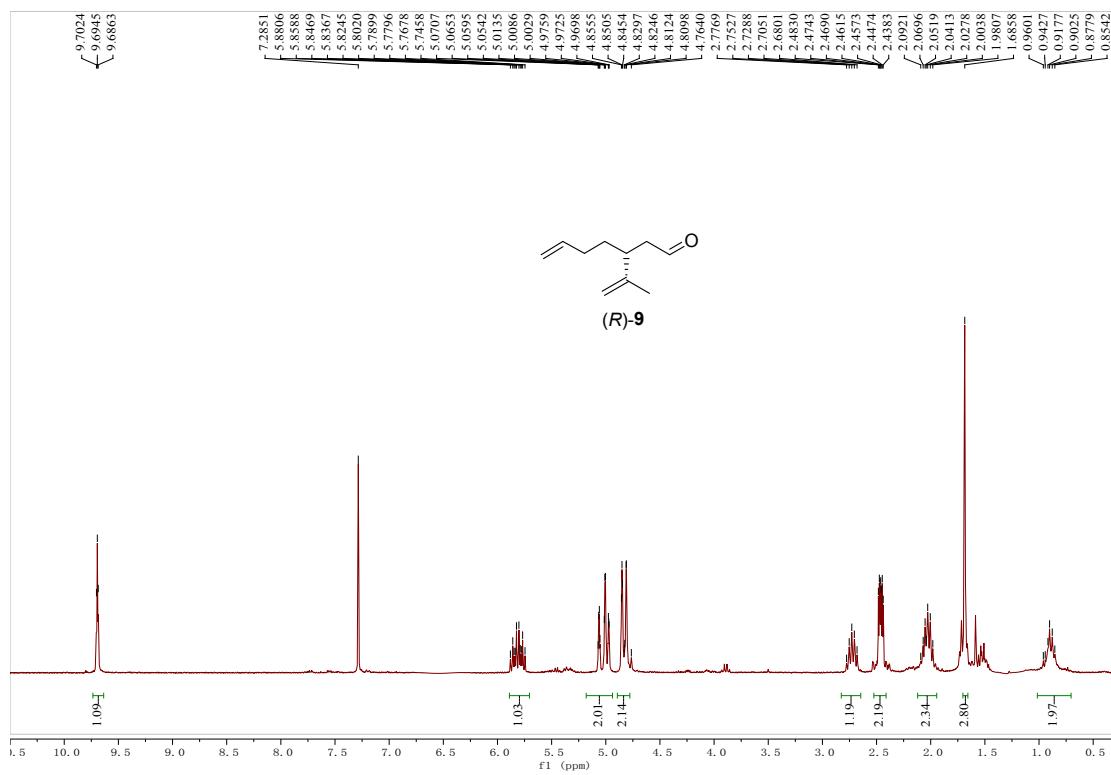


Figure S111. ^{13}C NMR Spectrum of (*R*)-3-(prop-1-en-2-yl)hept-6-enal (**9**) (75 MHz, CDCl_3)

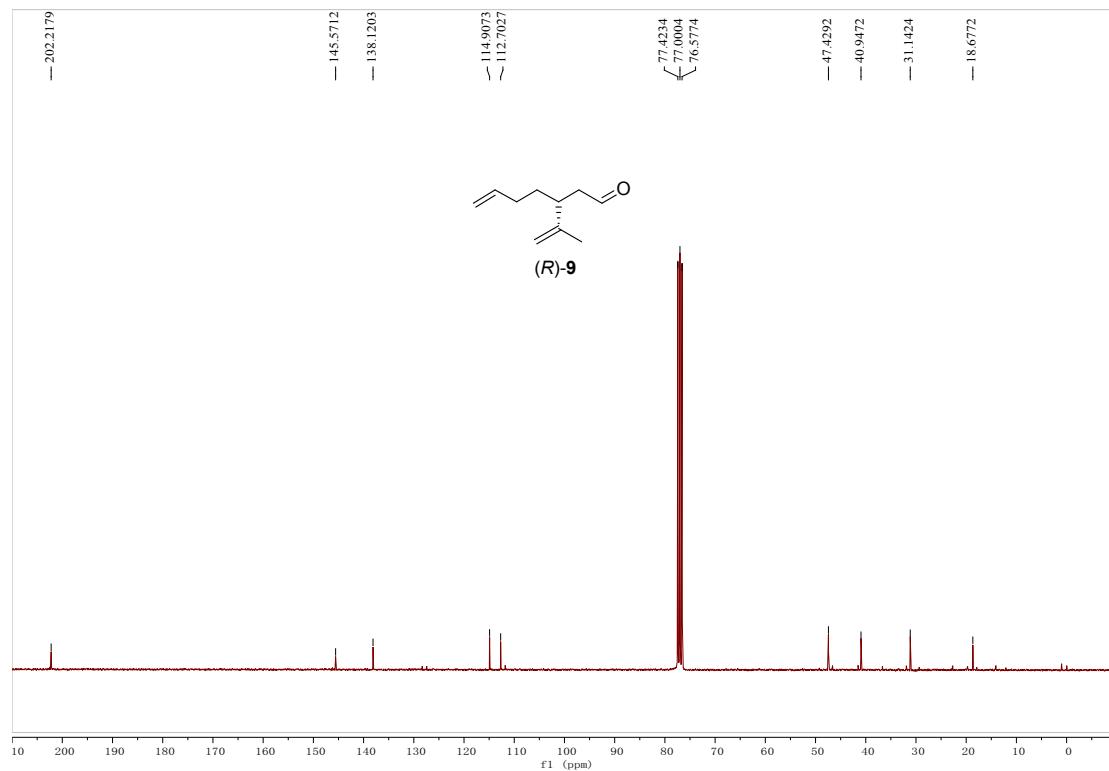


Figure S112. ^1H NMR Spectrum of (*E*)-ethyl 7-methylocta-2,6-dienoate (**11**) (300 MHz, CDCl_3)

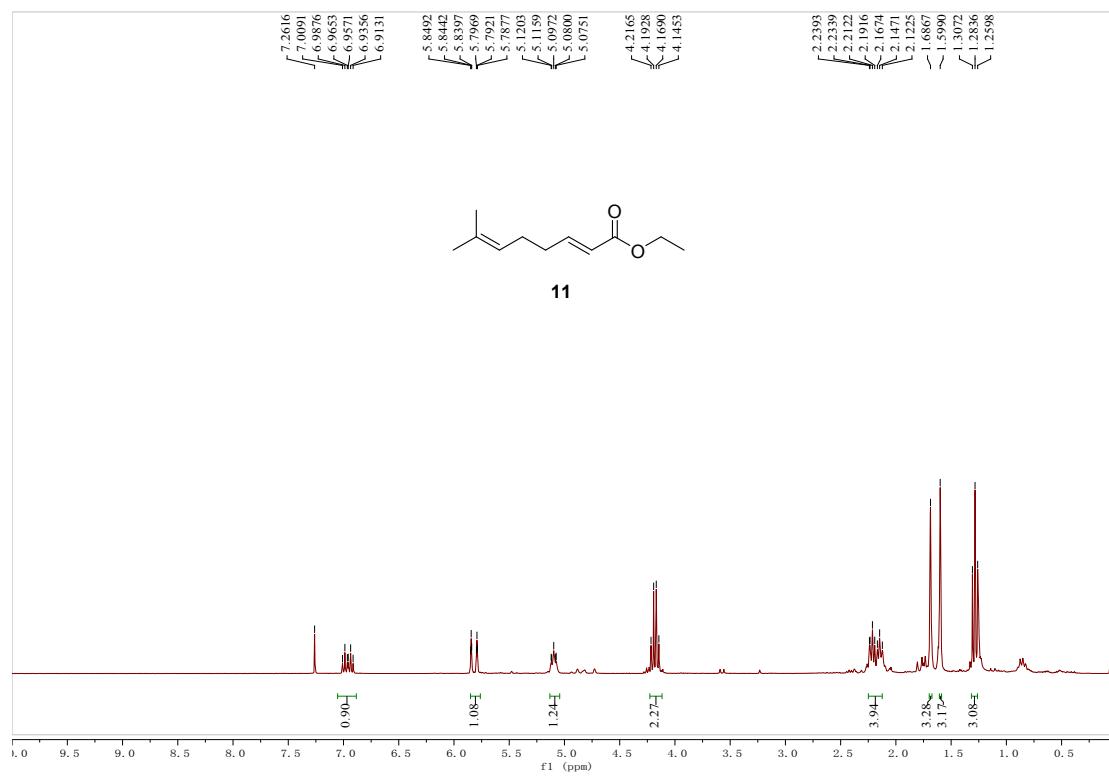
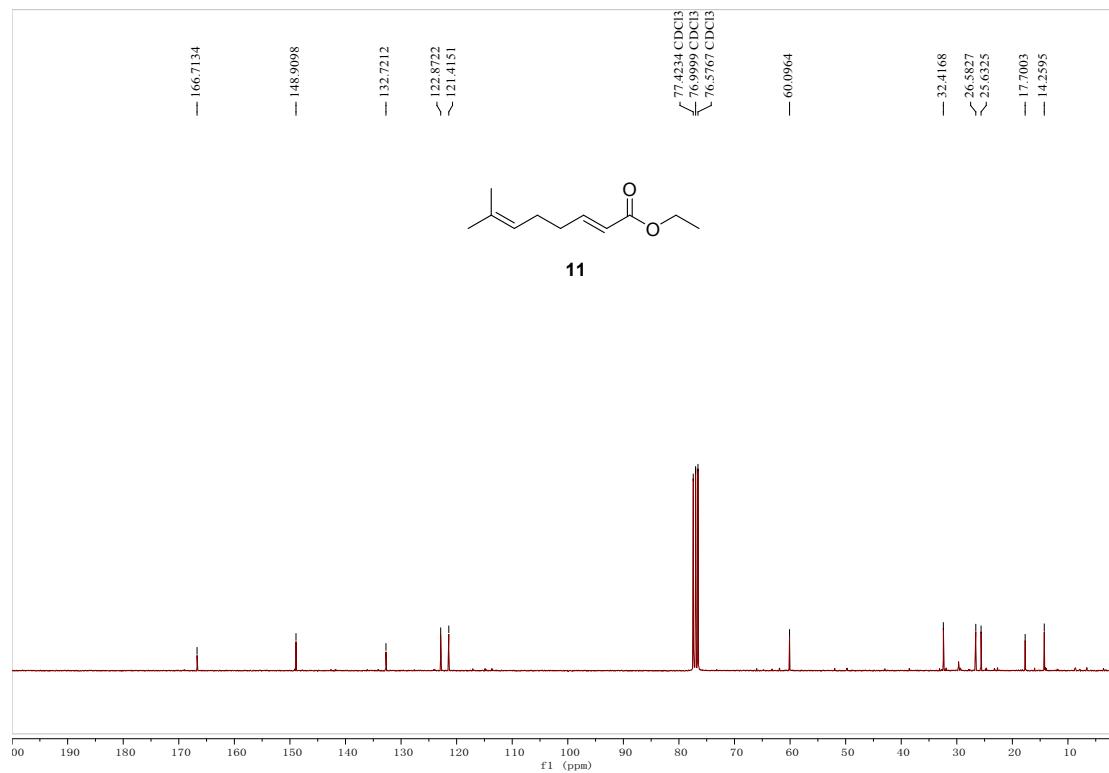
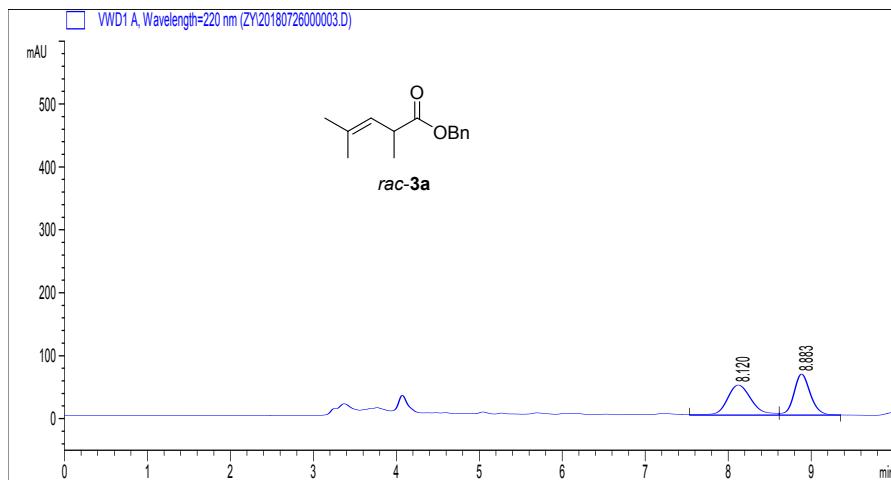


Figure S113. ^{13}C NMR Spectrum of (*E*)-ethyl 7-methylocta-2,6-dienoate (**11**) (75 MHz, CDCl_3)



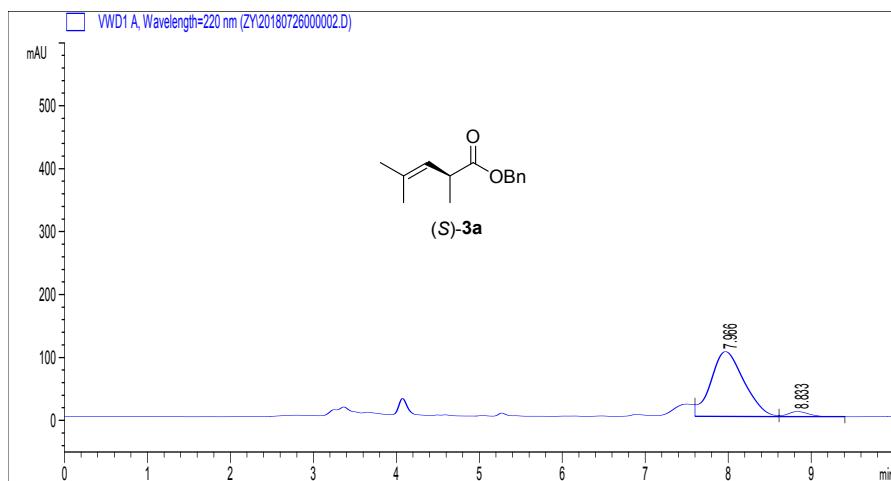
10. HPLC Chromatography of the Products

Figure S114. HPLC Chromatography of racemic benzyl 2,4-dimethylpent-3-enoate (**3a**) (Daicel Chiralcel OJ-H column, 0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



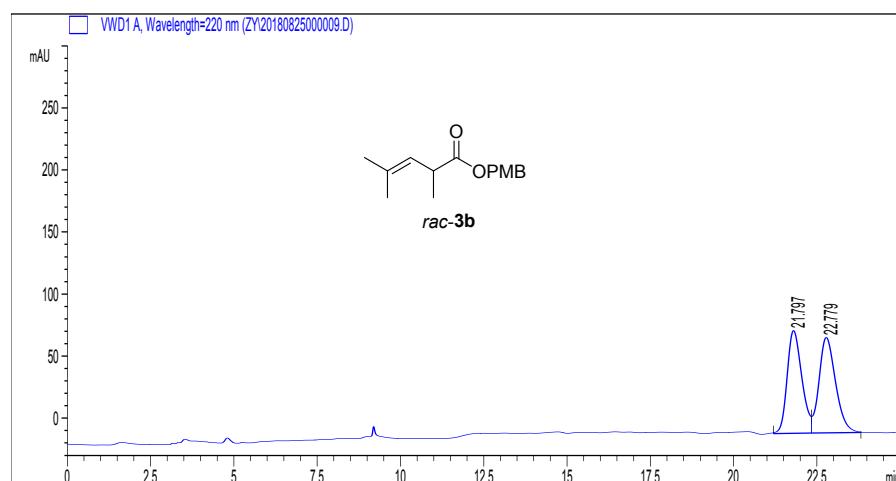
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	8.120	VV	0.3162	976.99017	47.96978	51.9853
2	8.883	VB	0.2105	902.36975	65.39768	48.0147
Totals:				1879.35992	113.36747	

Figure S115. HPLC Chromatography of (*S*)-benzyl 2-phenylpropanoate (**3a**) (Daicel Chiralcel OJ-H column, 0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



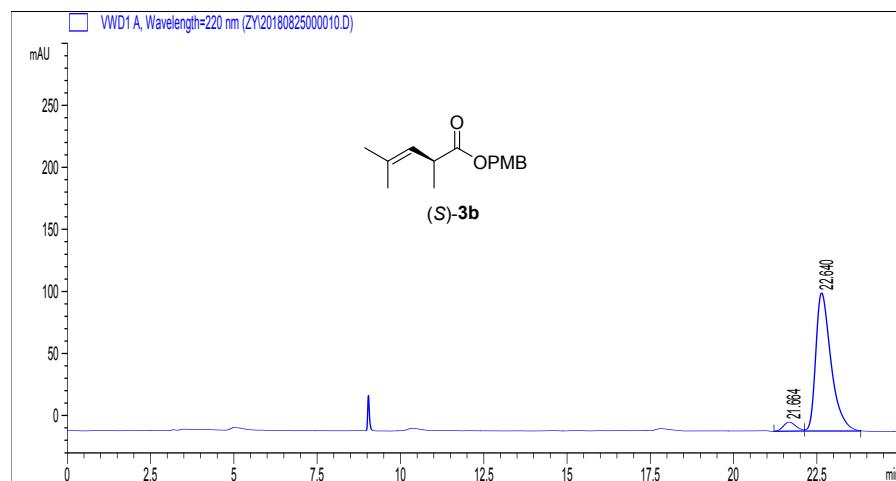
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	7.966	VV	0.4199	2865.93799	103.25255	95.2986
2	8.833	VB	0.2592	141.38631	8.26821	4.7014
Totals:				3007.32430	111.52075	

Figure S116. HPLC Chromatography of racemic 4-methoxybenzyl 2,4-dimethylpent-3-enoate (**3b**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



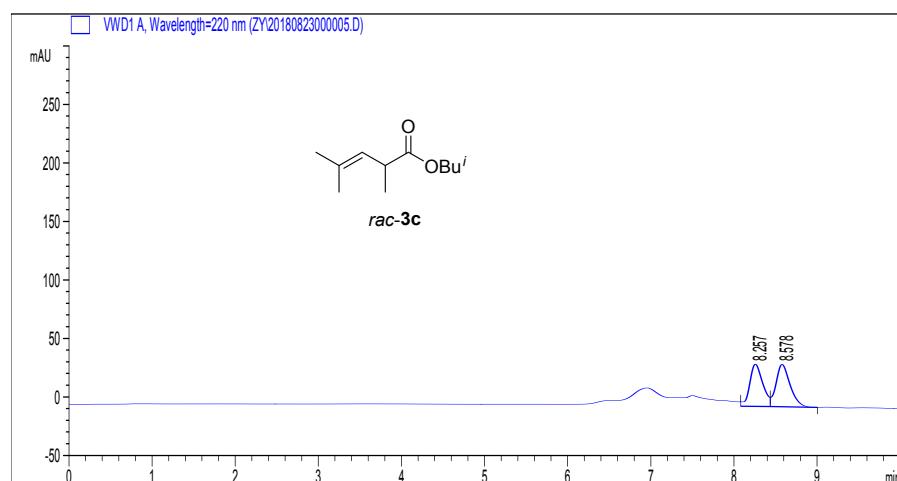
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	21.797	BV	0.4708	2538.13672	82.89212	48.7384
2	22.779	VB	0.5267	2669.53589	77.01931	51.2616
Totals:				5207.67261	159.91143	

Figure S117. HPLC Chromatography of (*S*)-4-methoxybenzyl 2,4-dimethylpent-3-enoate (**3b**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



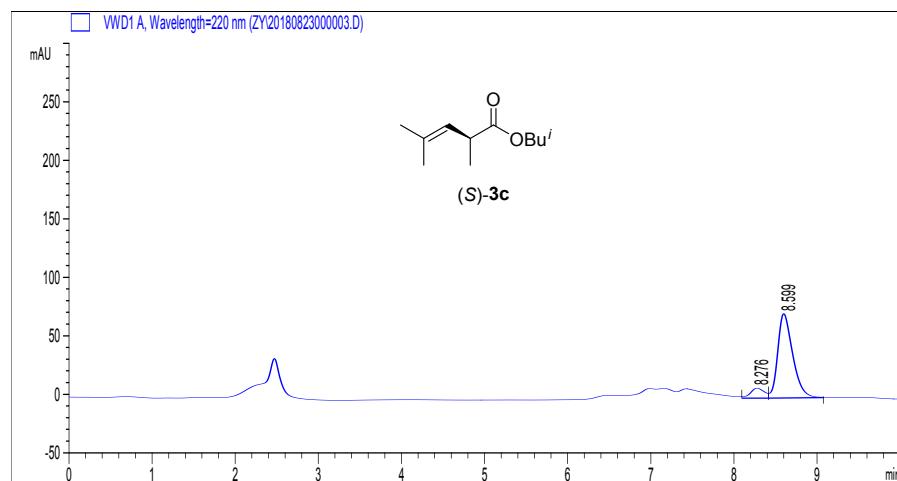
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	21.664	BV	0.4116	197.29198	7.39753	5.2549
2	22.640	VB	0.4827	3557.15991	111.55138	94.7451
Totals:				3754.45189	118.94890	

Figure S118. HPLC Chromatography of racemic *iso*-butyl 2,4-dimethylpent-3-enoate (**3c**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



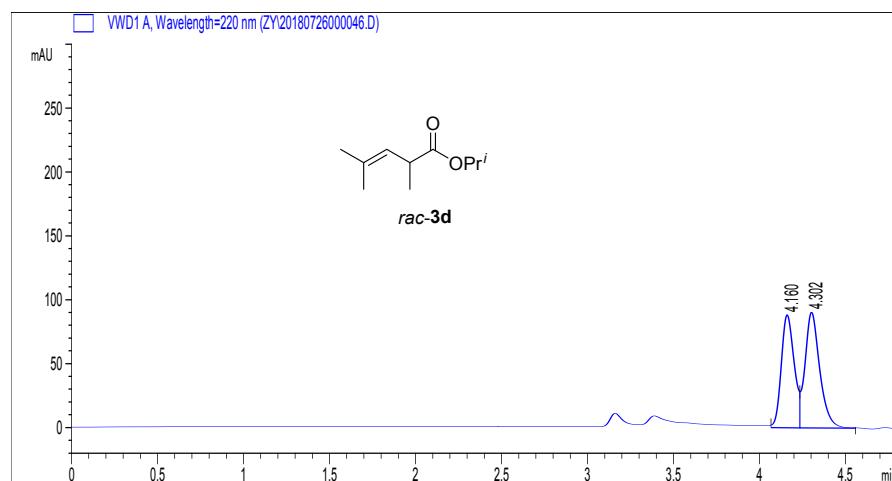
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	8.257	BV	0.1639	396.96436	36.32099	48.0559
2	8.578	VB	0.1768	429.08273	36.42344	51.9441
Totals:				826.04709	72.74443	

Figure S119. HPLC Chromatography of (*S*)-*iso*-butyl 2,4-dimethylpent-3-enoate (**3c**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



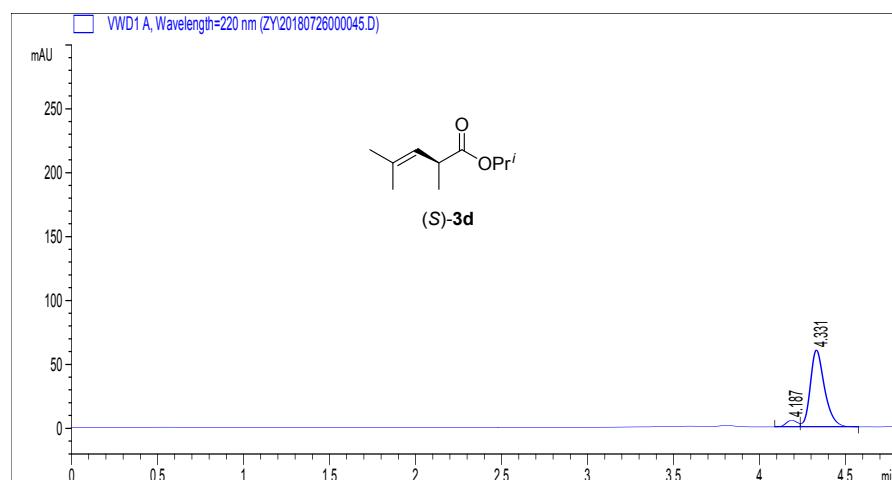
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	8.276	MM	0.1644	69.41195	7.03804	7.3940
2	8.598	MM	0.2055	869.35486	70.49699	92.6060
Totals:				938.76681	77.53503	

Figure S200. HPLC Chromatography of racemic *iso*-propyl 2,4-dimethylpent-3-enoate (**3d**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



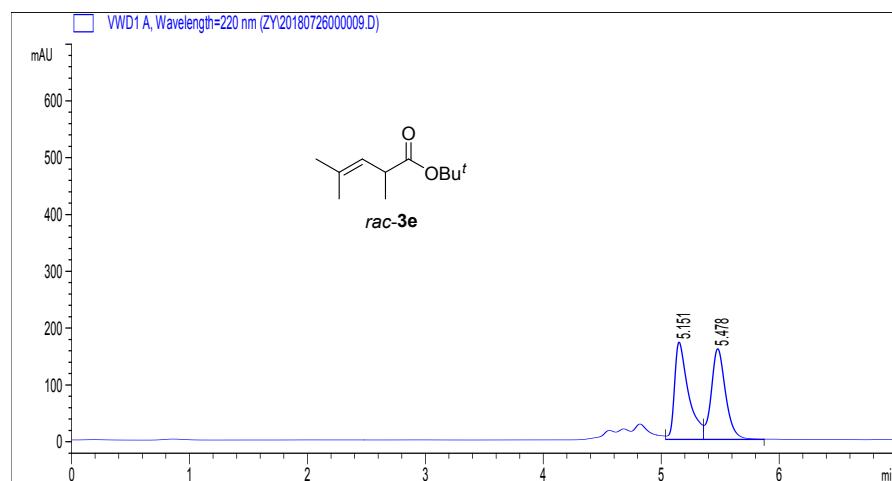
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.160	MF	0.0923	498.82864	90.03123	48.3744
2	4.302	FM	0.0969	532.35529	91.60358	51.6256
Totals :				1031.18393	181.63482	

Figure S201. HPLC Chromatography of (*S*)-*iso*-propyl 2,4-dimethylpent-3-enoate (**3d**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



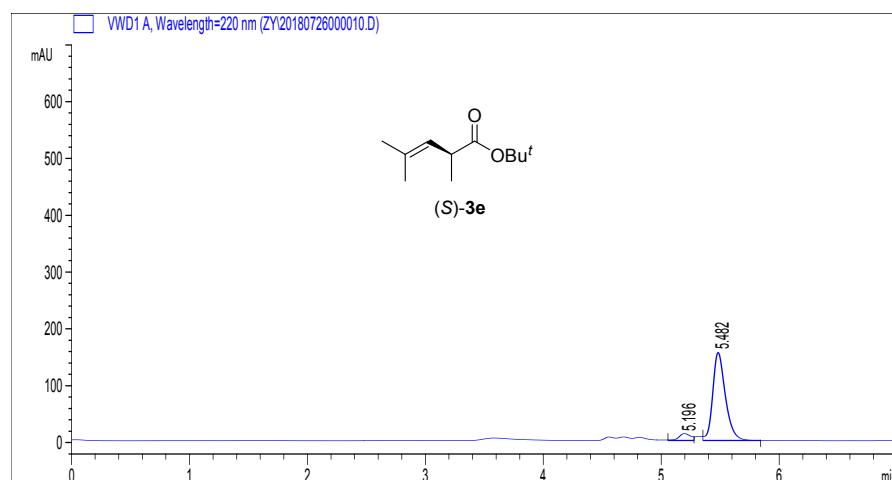
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.187	MM	0.0647	15.13485	3.89676	4.3902
2	4.330	MM	0.0935	329.60889	58.72643	95.6098
Totals:				344.74373	62.62319	

Figure S202. HPLC Chromatography of racemic *tert*-butyl 2,4-dimethylpent-3-enoate (**3e**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



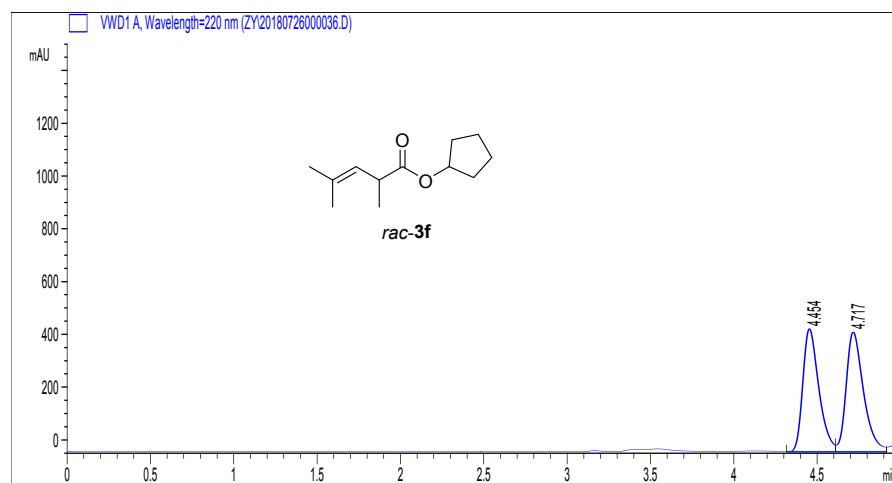
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	5.151	VV	0.1194	1416.90320	172.09431	51.1548
2	5.478	VB	0.1263	1352.93140	160.08701	48.8452
Totals:				2769.83459	332.18132	

Figure S203. HPLC Chromatography of (*S*)-*tert*-butyl 2,4-dimethylpent-3-enoate (**3e**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



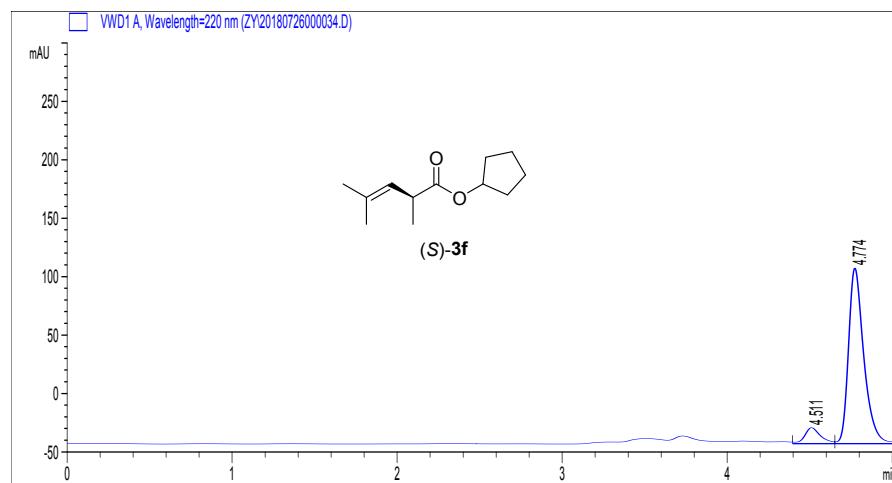
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	5.196	MM	0.1029	61.98684	10.04427	5.0810
2	5.482	VB	0.1133	1157.98206	155.08470	94.9190
Totals:				1219.96890	165.12897	

Figure S204. HPLC Chromatography of racemic cyclopentyl 2,4-dimethylpent-3-enoate (**3f**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



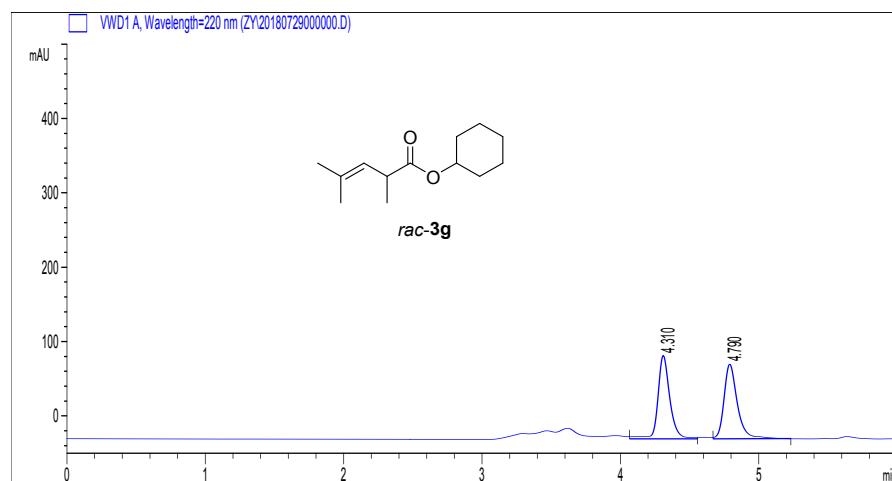
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.454	VV	0.1011	3111.70532	466.61646	48.7194
2	4.717	VV	0.1088	3275.29468	454.37253	51.2806
Totals:				6387.00000	920.98898	

Figure S205. HPLC Chromatography of (*S*)-cyclopentyl 2,4-dimethylpent-3-enoate (**3f**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



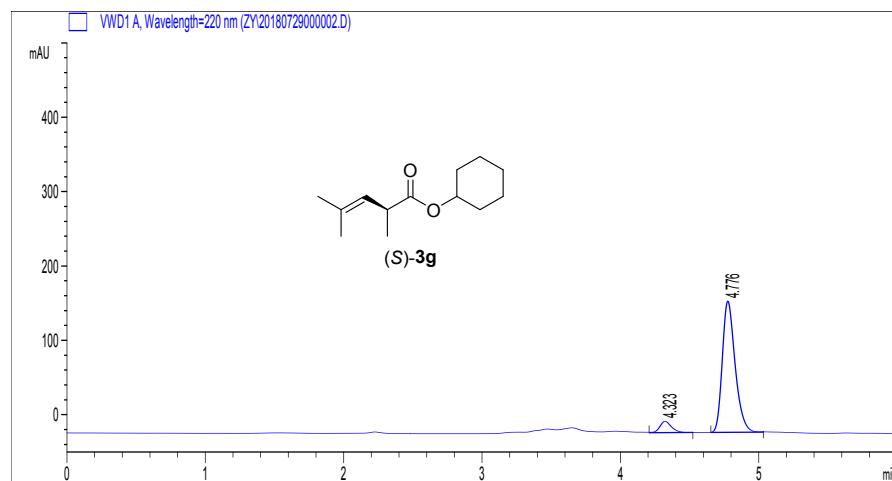
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.511	BV	0.0986	92.32779	13.77192	8.7369
2	4.774	VV	0.0981	964.43036	150.37050	91.2631
Totals:				1056.75815	164.14242	

Figure S206. HPLC Chromatography of racemic cyclohexyl 2,4-dimethylpent-3-enoate (**3g**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.310	VB	0.0911	681.80530	112.45009	50.1924
2	4.790	BB	0.1018	676.57874	100.60569	49.8076
Totals:				1358.38403	213.05578	

Figure S207. HPLC Chromatography of (*S*)-cyclohexyl 2,4-dimethylpent-3-enoate (**3g**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.323	VB	0.0897	91.28226	15.35780	7.4283
2	4.776	BB	0.0998	1137.56238	176.74908	92.5717
Totals:				1228.84464	192.10689	

Figure S208. HPLC Chromatography of racemic cyclohexylmethyl 2,4-dimethylpent-3-enoate (**3h**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

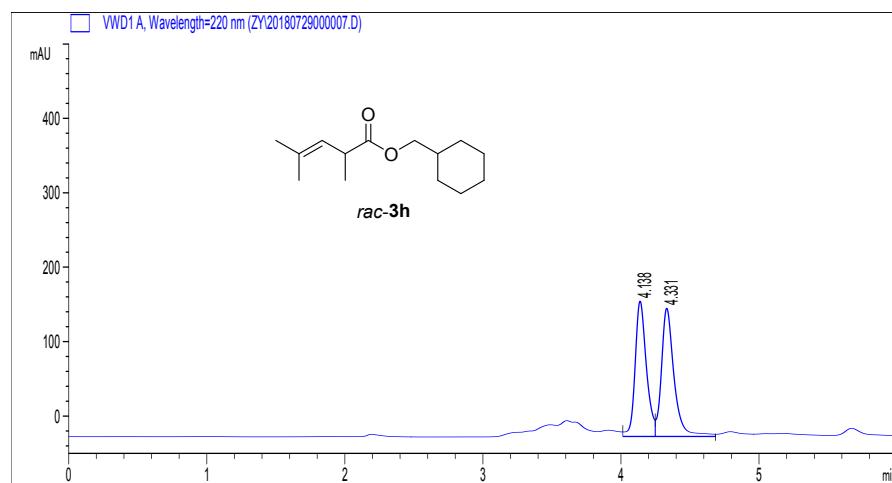


Figure S209. HPLC Chromatography of (*S*)-cyclohexylmethyl 2,4-dimethylpent-3-enoate (**3h**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

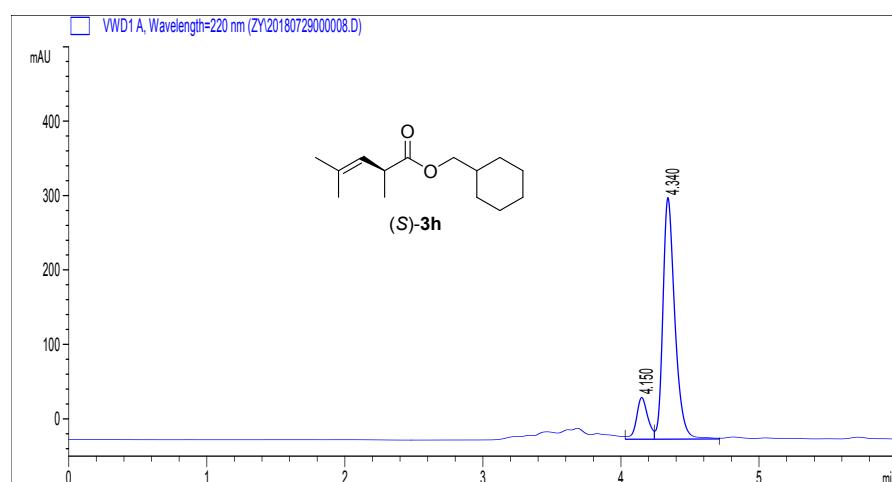
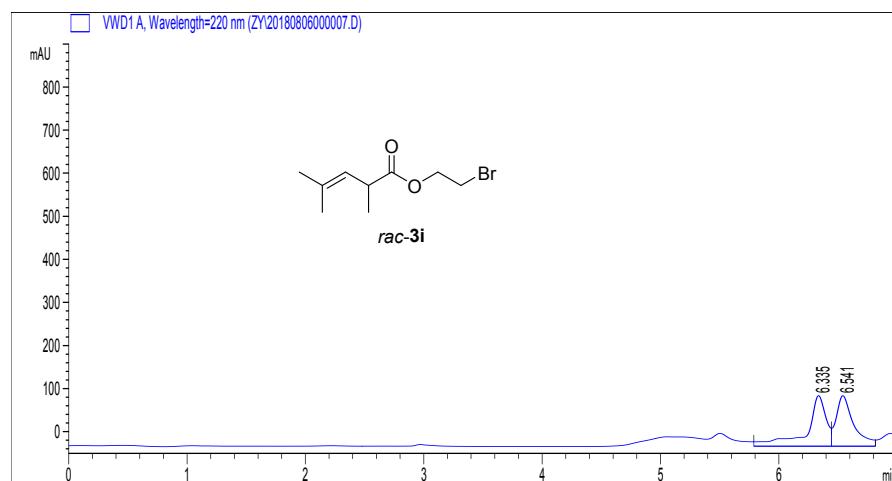
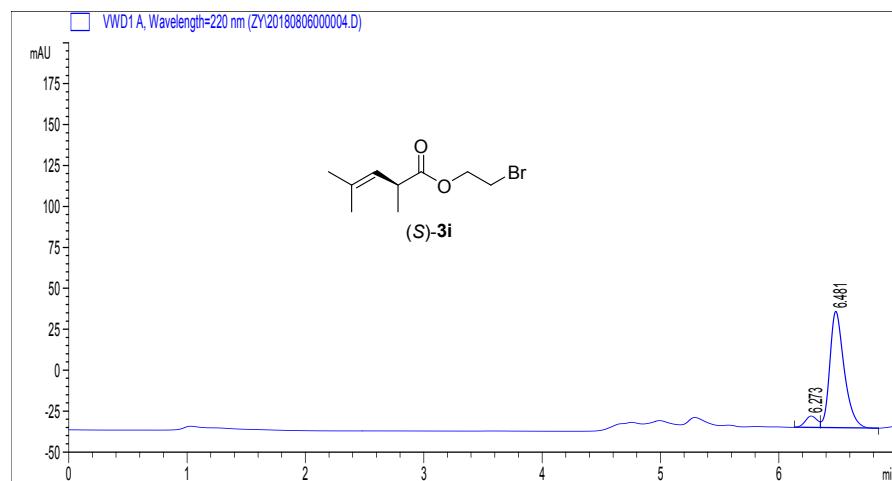


Figure S210. HPLC Chromatography of racemic 2-bromoethyl 2,4-dimethylpent-3-enoate (**3i**) (Daicel Chiralcel OJ-H column, *n*-hexane, 0.7mL/min, 220 nm)



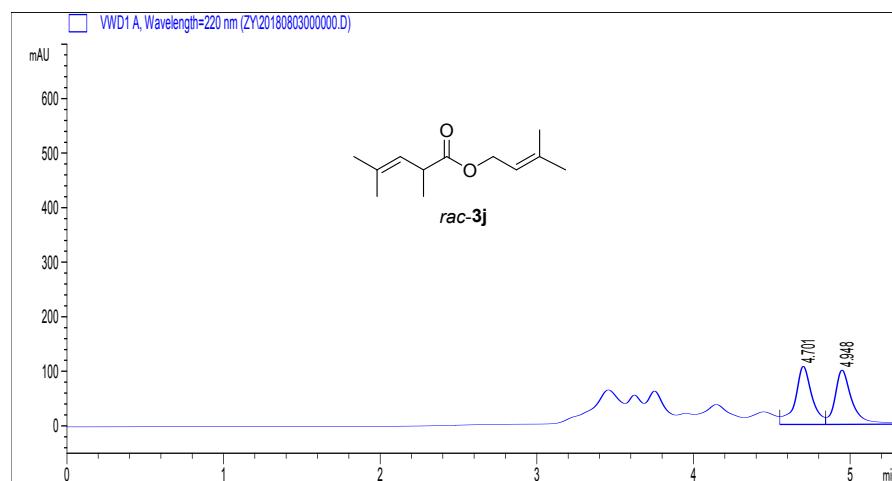
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	6.335	VV	0.1609	1363.50220	118.09920	53.0615
2	6.541	VV	0.1470	1206.16064	117.87498	46.9385
Totals :				2569.66284	235.97417	

Figure S211. HPLC Chromatography of (*S*)-2-bromoethyl 2,4-dimethylpent-3-enoate (**3i**) (Daicel Chiralcel OJ-H column, *n*-hexane, 0.7mL/min, 220 nm)



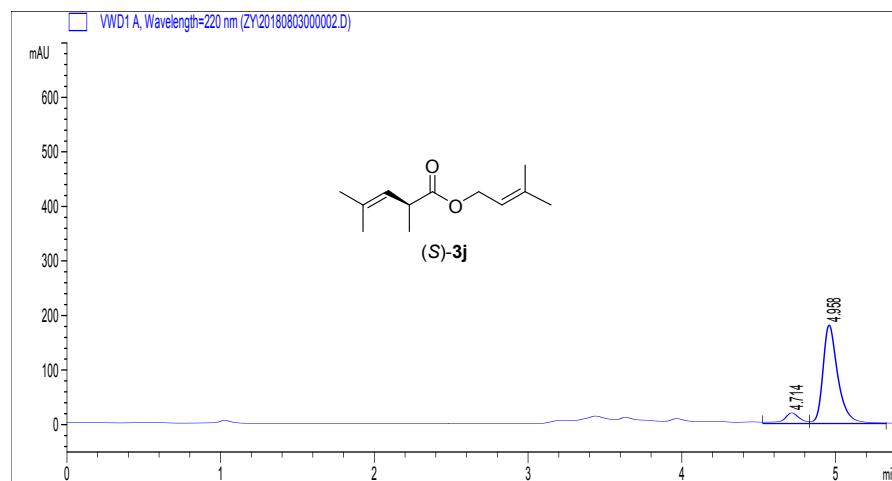
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	6.273	BV	0.1093	48.75711	6.96744	7.4967
2	6.481	VB	0.1277	601.62268	71.17770	92.5033
Totals :				650.37980	78.14513	

Figure S212. HPLC Chromatography of racemic 3-methylbut-2-en-1-yl 2,4-dimethylpent-3-enoate (**3j**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



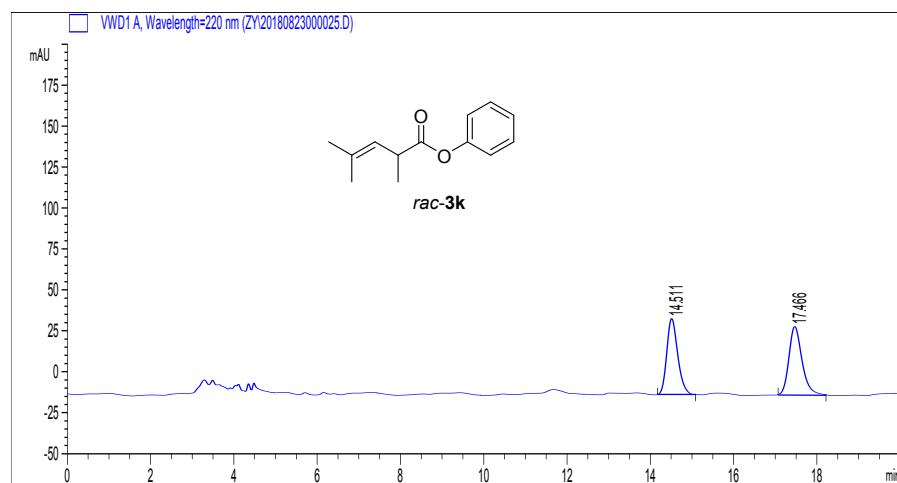
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.701	VV	0.1068	792.16608	107.00812	51.3404
2	4.948	VV	0.1110	750.80090	99.82353	48.6596
Totals:				1542.96698	206.83165	

Figure S213. HPLC Chromatography of (*S*)-3-methylbut-2-en-1-yl 2,4-dimethylpent-3-enoate (**3j**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



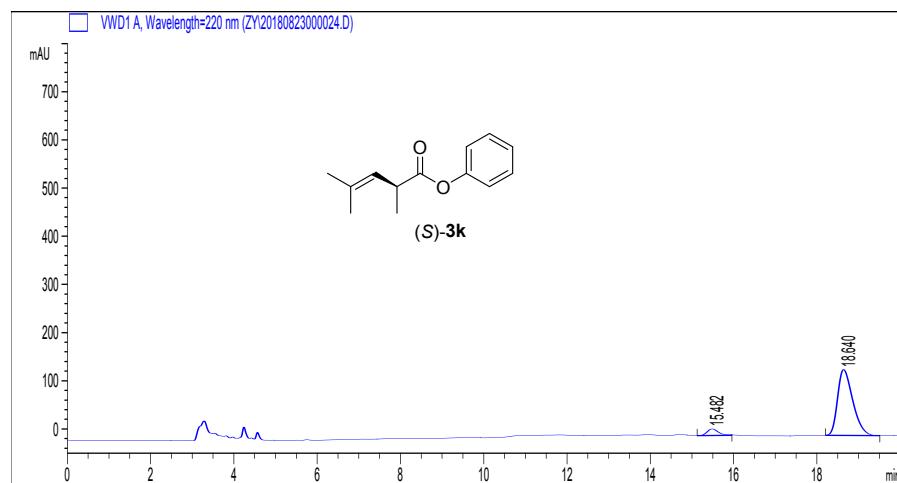
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	4.714	MM	0.0921	95.25379	17.23207	7.4603
2	4.957	MM	0.1096	1181.55212	179.69040	92.5397
Totals:				1276.80592	196.92247	

Figure S214. HPLC Chromatography of racemic phenyl 2,4-dimethylpent-3-enoate (**3k**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	14.511	BB	0.2800	847.06592	46.40076	47.8236
2	17.466	BB	0.3344	924.16248	41.91624	52.1764
Totals :				1771.22839	88.31700	

Figure S215. HPLC Chromatography of (*S*)-phenyl 2,4-dimethylpent-3-enoate (**3k**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	15.482	VB	0.2950	270.90387	13.95007	7.2375
2	18.640	BB	0.3891	3472.14087	136.89651	92.7625
Totals:				3743.04474	150.84659	

Figure S216. HPLC Chromatography of racemic 3-fluorophenyl 2,4-dimethylpent-3-enoate (**3I**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

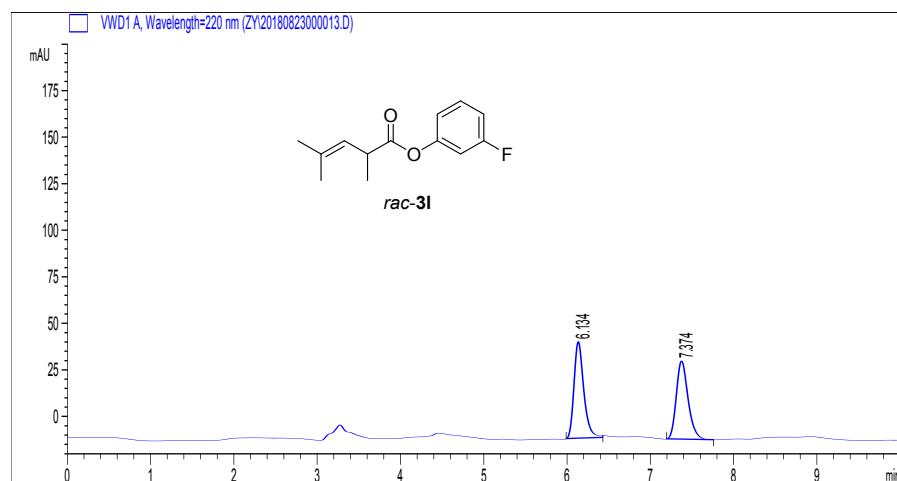


Figure S217. HPLC Chromatography of (*S*)-3-fluorophenyl 2,4-dimethylpent-3-enoate (**3I**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

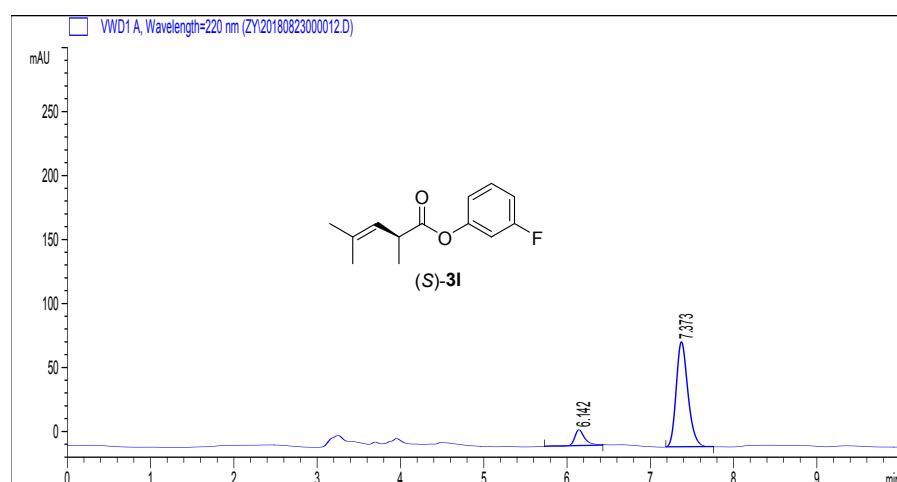


Figure S218. HPLC Chromatography of racemic 4-chlorophenyl 2,4-dimethylpent-3-enoate (**3m**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

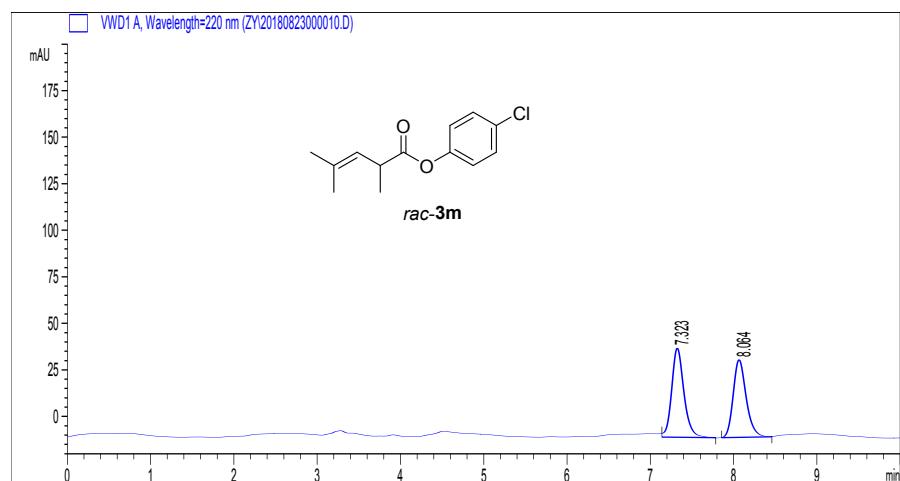


Figure S219. HPLC Chromatography of (*S*)-4-chlorophenyl 2,4-dimethylpent-3-enoate (**3m**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

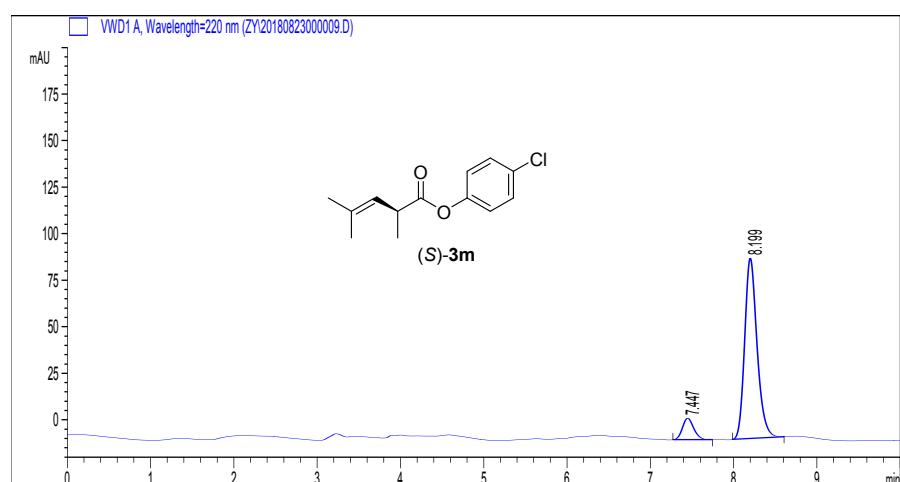


Figure S220. HPLC Chromatography of racemic *p*-tolyl 2,4-dimethylpent-3-enoate (**3n**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

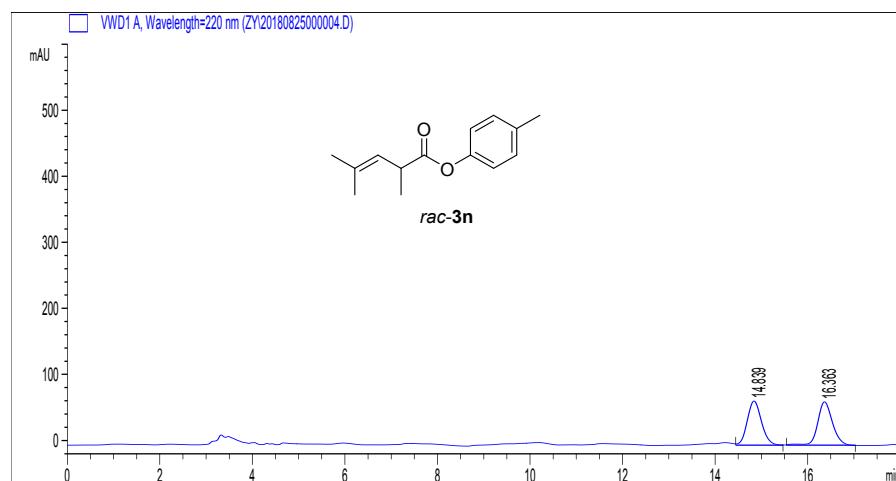


Figure S221. HPLC Chromatography of (*S*)-*p*-tolyl 2,4-dimethylpent-3-enoate (**3n**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

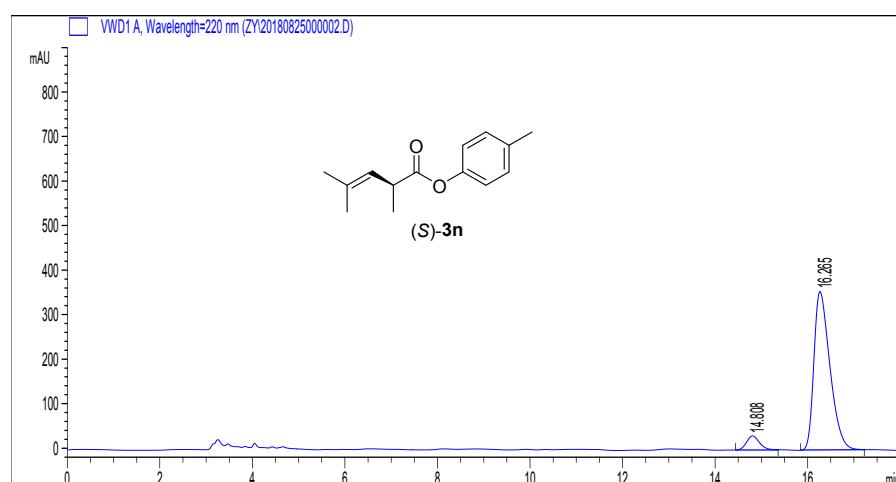
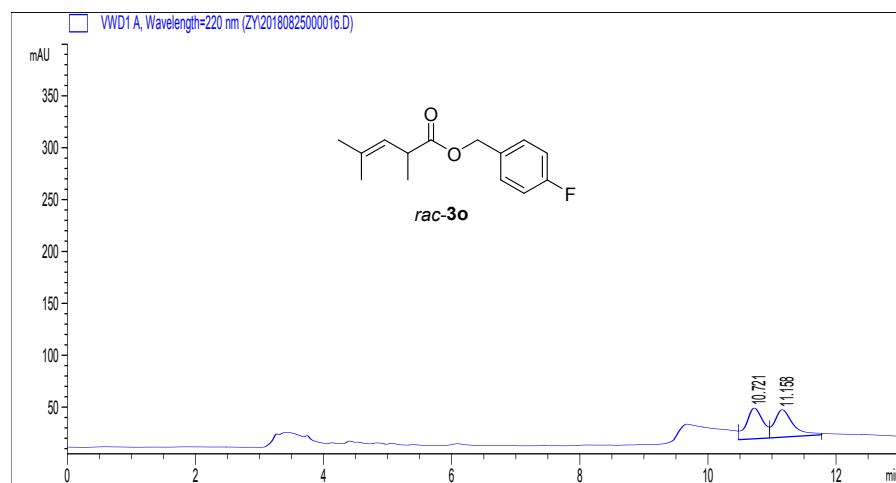
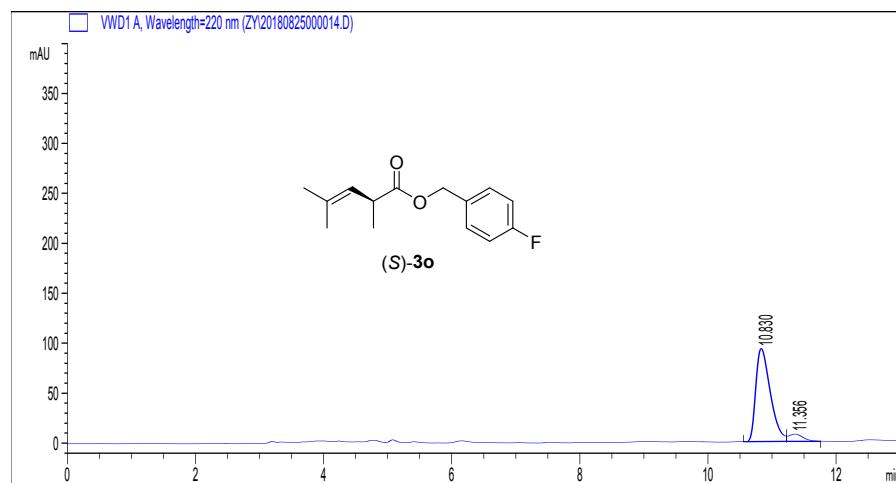


Figure S222. HPLC Chromatography of racemic 4-fluorobenzyl 2,4-dimethylpent-3-enoate (**3o**) (Phenomenex lux 5u Amylos-2, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	10.721	VV	0.2662	528.65894	29.65312	49.3616
2	11.158	VB	0.2996	542.33380	26.53480	50.6384
Totals:				1070.99274	56.18792	

Figure S223. HPLC Chromatography of (*S*)-4-fluorobenzyl 2,4-dimethylpent-3-enoate (**3o**) (Phenomenex lux 5u Amylos-2, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	10.830	MF	0.2704	1519.75562	93.68719	94.7336
2	11.357	FM	0.1865	84.48599	7.55147	5.2664
Totals:				1604.24161	101.23867	

Figure S224. HPLC Chromatography of racemic 4-(trifluoromethyl)benzyl 2,4-dimethylpent-3-enoate (**3p**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

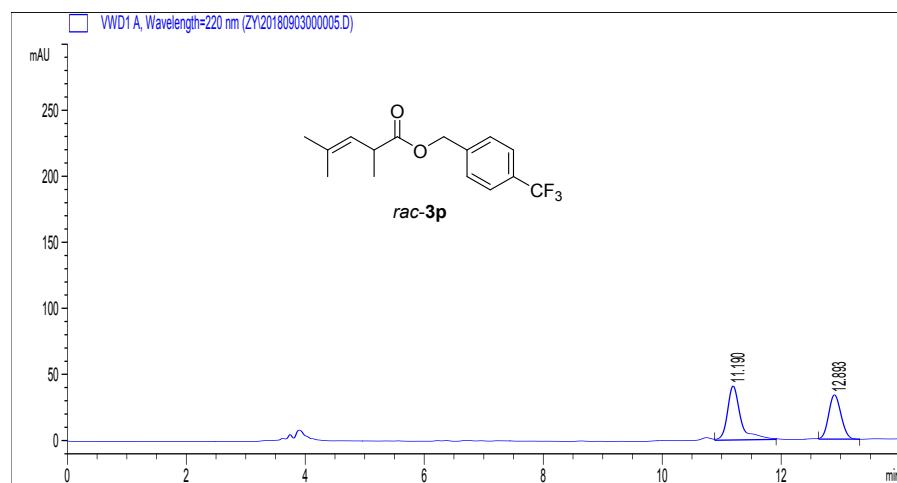


Figure S225. HPLC Chromatography of (*S*)-4-(trifluoromethyl)benzyl 2,4-dimethylpent-3-enoate (**3p**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

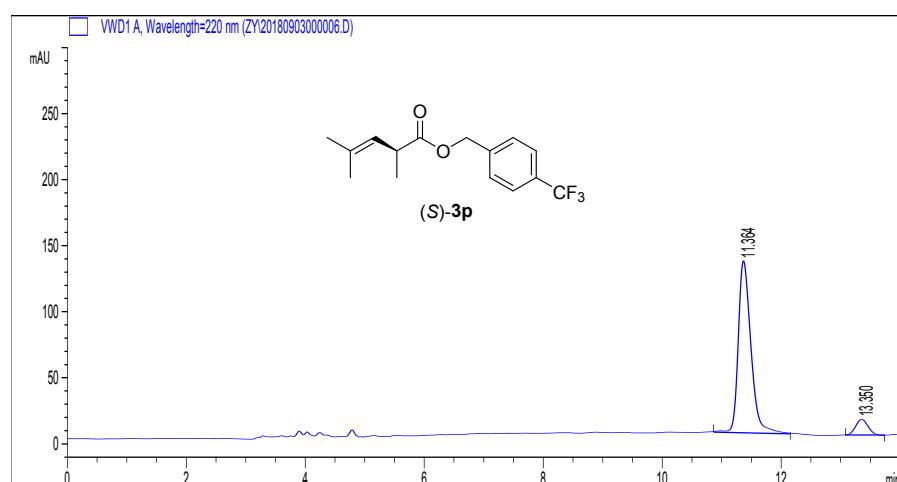
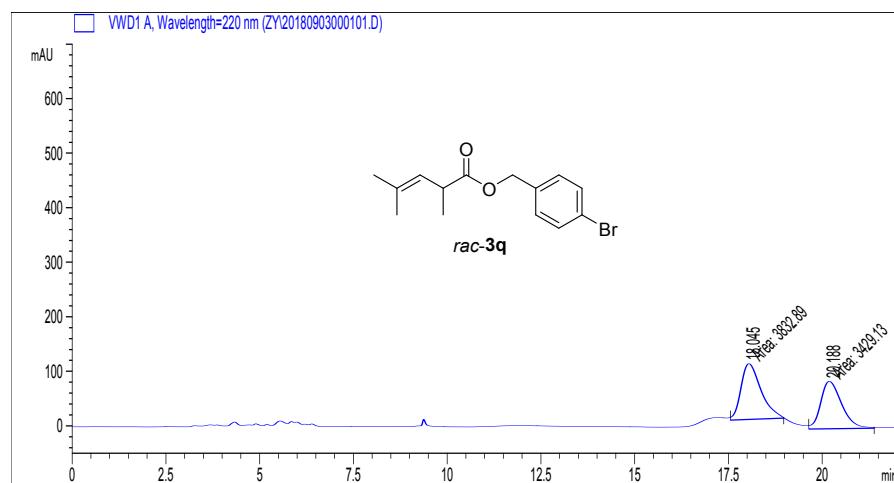
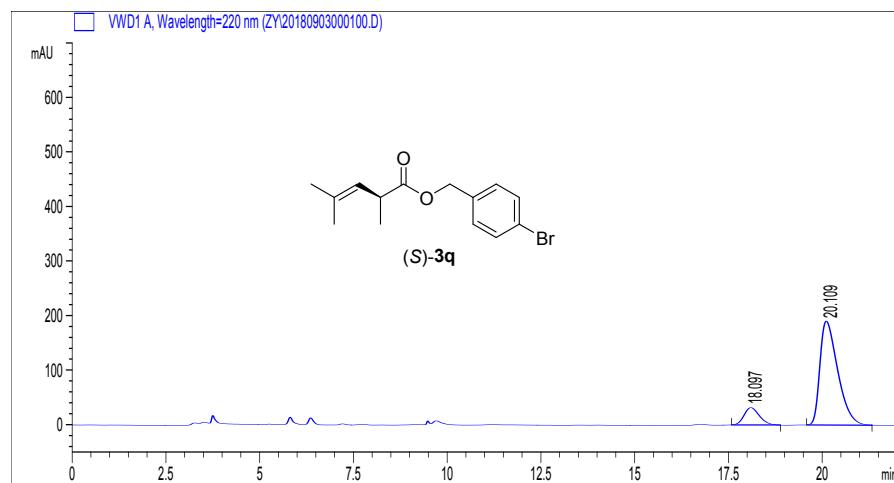


Figure S226. HPLC Chromatography of racemic 4-bromobenzyl 2,4-dimethylpent-3-enoate (**3q**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



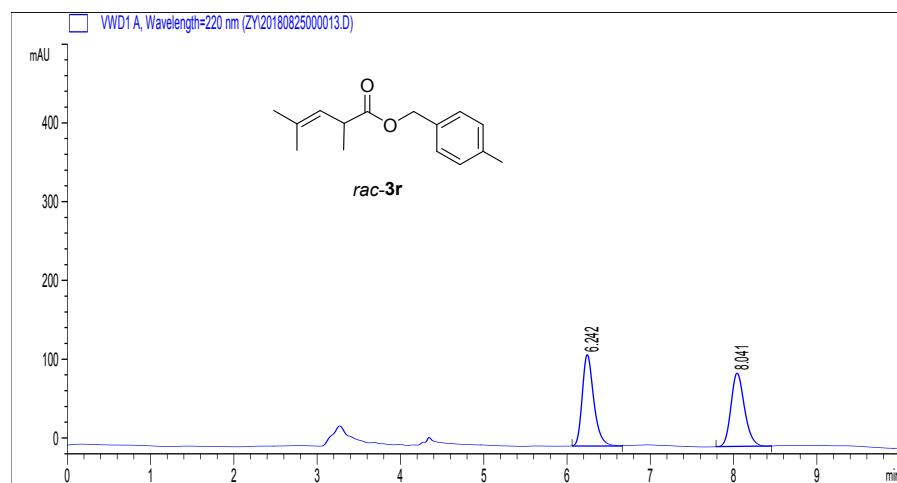
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	18.045	MM	0.6227	3832.89355	102.58493	52.7800
2	20.188	MM	0.6531	3429.12817	87.51350	47.2200
Totals:				7262.02173	190.0984	

Figure S227. HPLC Chromatography of (*S*)-4-bromobenzyl 2,4-dimethylpent-3-enoate (**3q**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



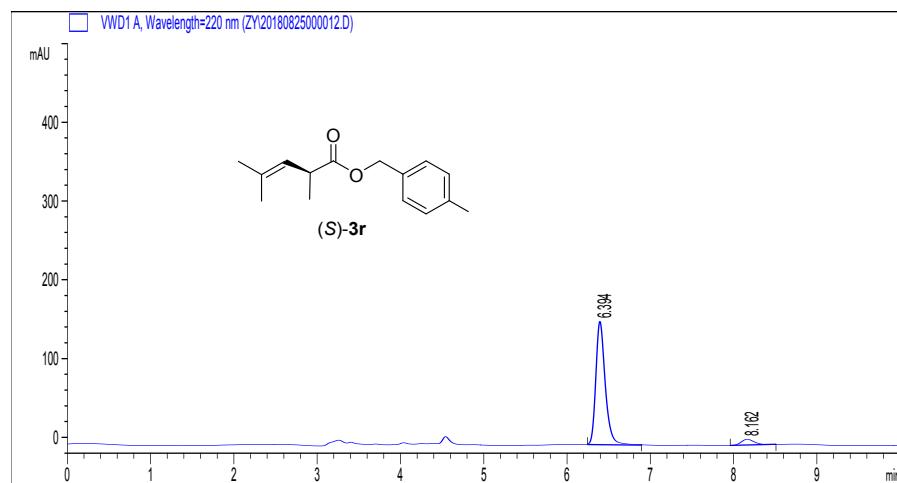
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	18.097	BB	0.4447	930.79749	32.22684	12.8672
2	20.109	BB	0.5078	6303.06494	190.74641	87.1328
Totals:				7233.86243	222.97326	

Figure S228. HPLC Chromatography of racemic 4-methylbenzyl 2,4-dimethylpent-3-enoate (**3r**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



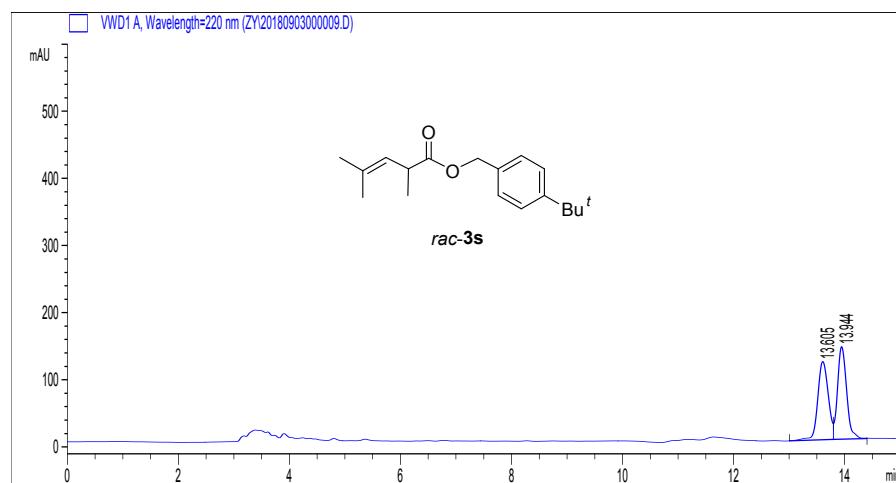
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	6.242	BB	0.1463	1123.61792	116.24437	51.4503
2	8.041	BB	0.1731	1060.27258	93.47292	48.5497
Totals:				2183.89050	209.71729	

Figure S229. HPLC Chromatography of (*S*)-4-methylbenzyl 2,4-dimethylpent-3-enoate (**3r**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



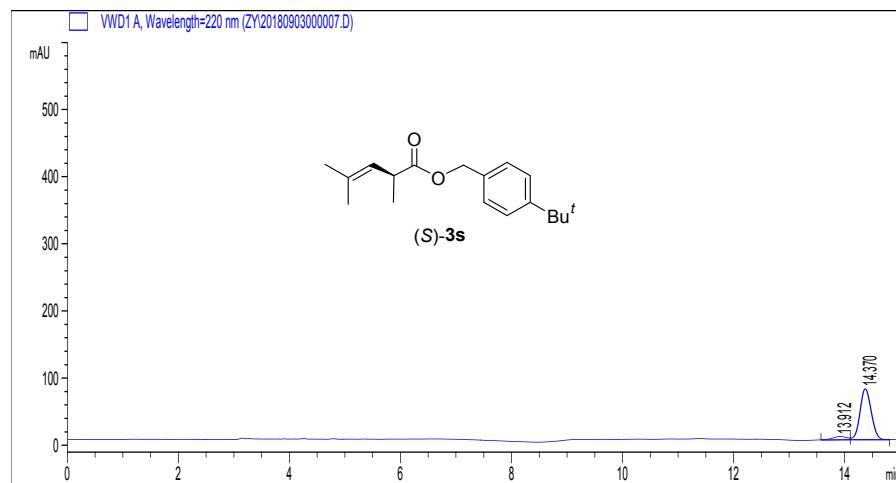
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	6.394	MM	0.1334	1257.32983	157.12898	94.9173
2	8.162	MM	0.1630	67.32800	6.88446	5.0827
Totals:				1324.65784	164.01344	

Figure S230. HPLC Chromatography of racemic 4-(*tert*-butyl)benzyl 2,4-dimethylpent-3-enoate (**3s**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	13.605	BV	0.2066	1544.49512	116.84493	49.3963
2	13.944	VB	0.1802	1582.24707	138.13553	50.6037
Totals:				3126.74219	254.98046	

Figure S231. HPLC Chromatography of (*S*)- 4-(*tert*-butyl)benzyl 2,4-dimethylpent-3-enoate (**3s**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	13.912	MM	0.2423	52.22727	3.59252	4.8896
2	14.369	MM	0.2273	1015.90918	74.48100	95.1104
Totals:				1068.13645	78.07352	

Figure S232. HPLC Chromatography of racemic naphthalen-2-ylmethyl 2,4-dimethylpent-3-enoate (**3t**) (Daicel Chiralcel OD-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 254 nm)

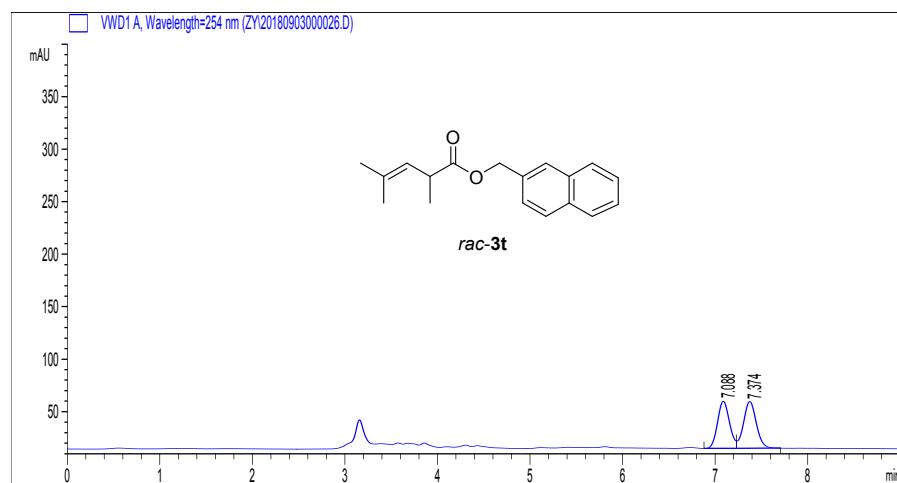


Figure S233. HPLC Chromatography of (*S*)-Naphthalen-2-ylmethyl 2,4-dimethylpent-3-enoate (**3t**) (Daicel Chiralcel OD-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 254 nm)

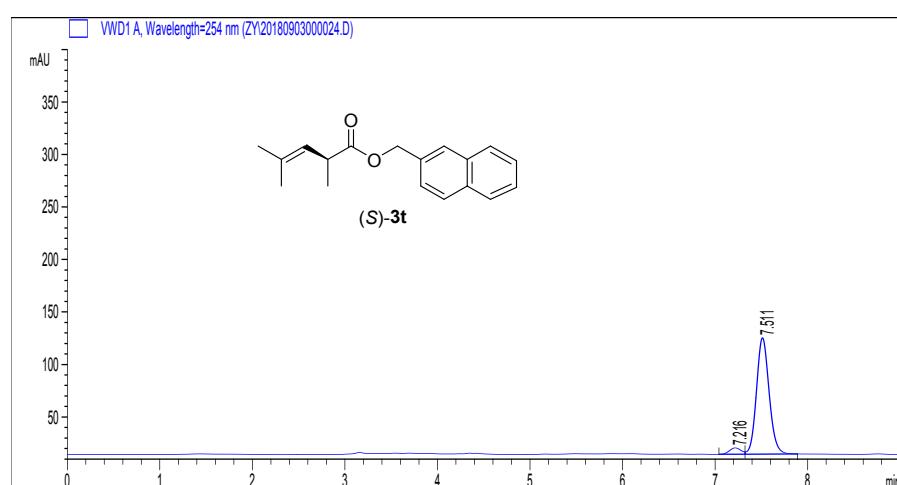
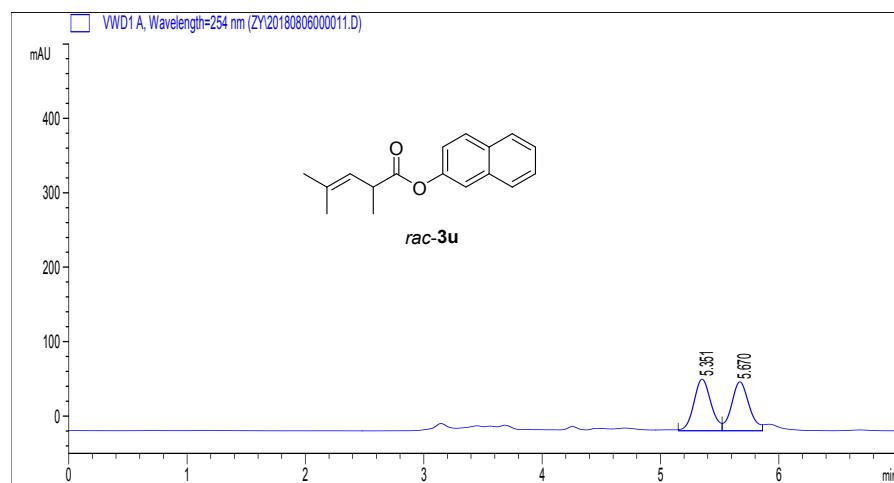
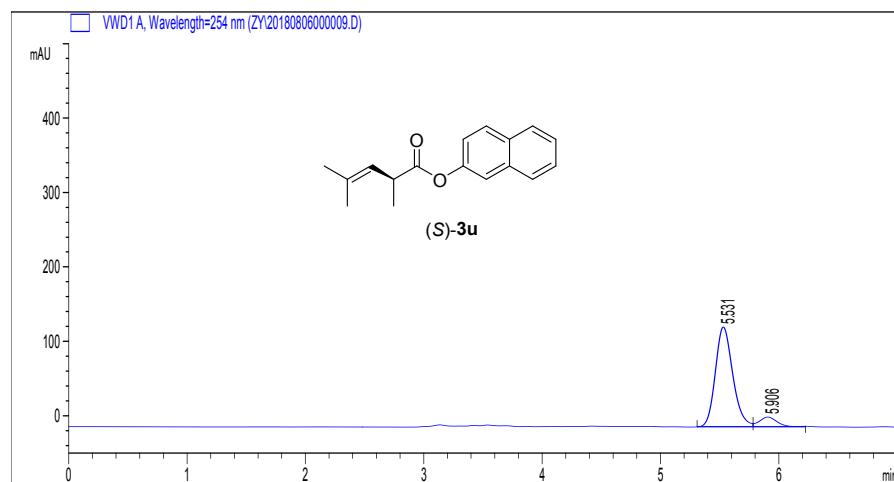


Figure S234. HPLC Chromatography of racemic naphthalen-2-yl 2,4-dimethylpent-3-enoate (**3u**) (R&C OD column, 1% isopropanol in *n*-hexane, 1 mL/min, 254 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	5.351	BV	0.1548	696.06342	69.43098	50.7968
2	5.670	VV	0.1572	674.22662	65.89436	49.2032
Totals:				1370.29004	135.32535	

Figure S235. HPLC Chromatography of (*S*)-naphthalen-2-yl 2,4-dimethylpent-3-enoate (**3u**) (R&C OD column, 1% isopropanol in *n*-hexane, 1 mL/min, 254 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	5.531	BV	0.1572	1373.05115	134.27669	90.5730
2	5.906	VB	0.1607	142.91035	13.26055	9.4270
Totals:				1515.96150	147.53724	

Figure S236. HPLC Chromatography of racemic 4-methoxybenzyl 2-ethyl-4-methylpent-3-enoate (**5a**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

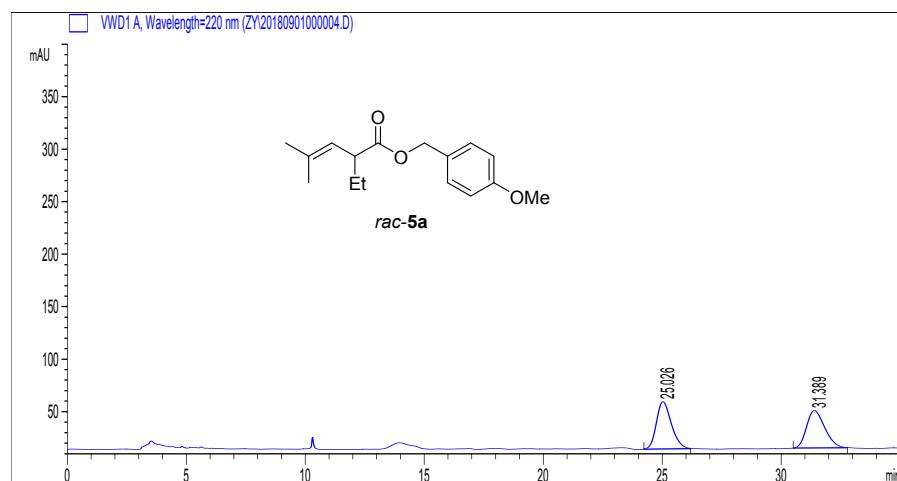


Figure S237. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-ethyl-4-methylpent-3-enoate (**5a**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

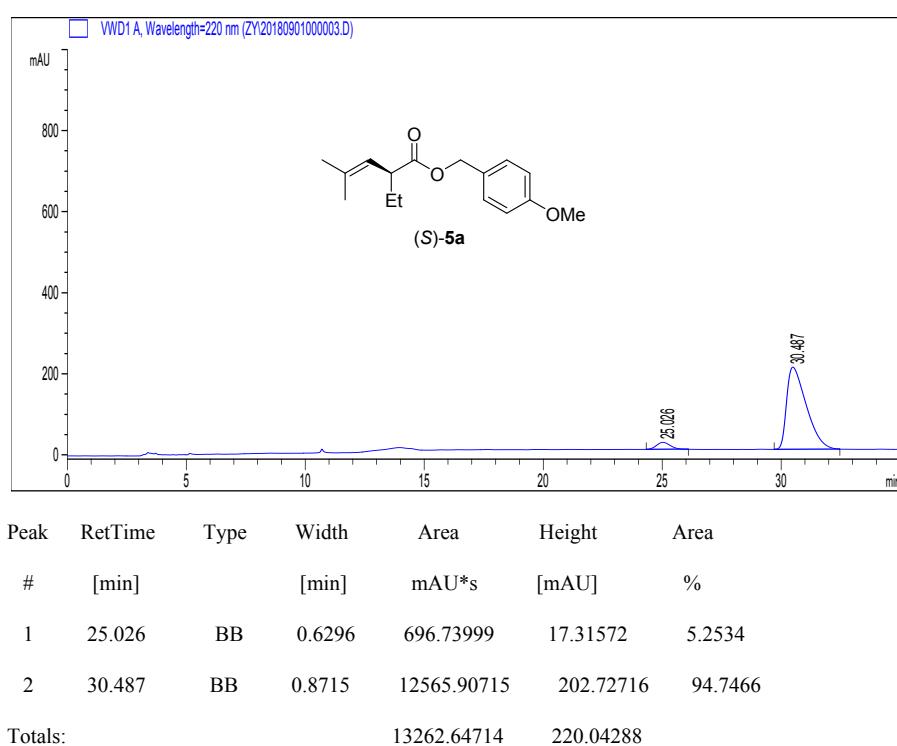
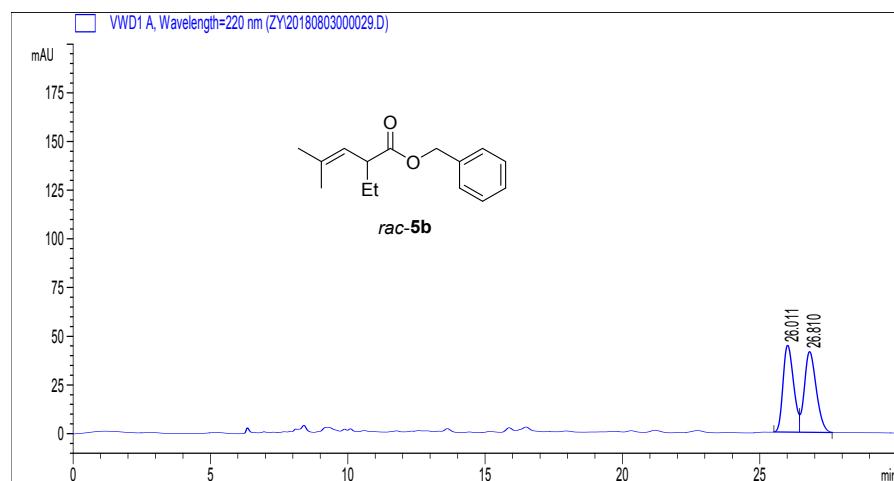
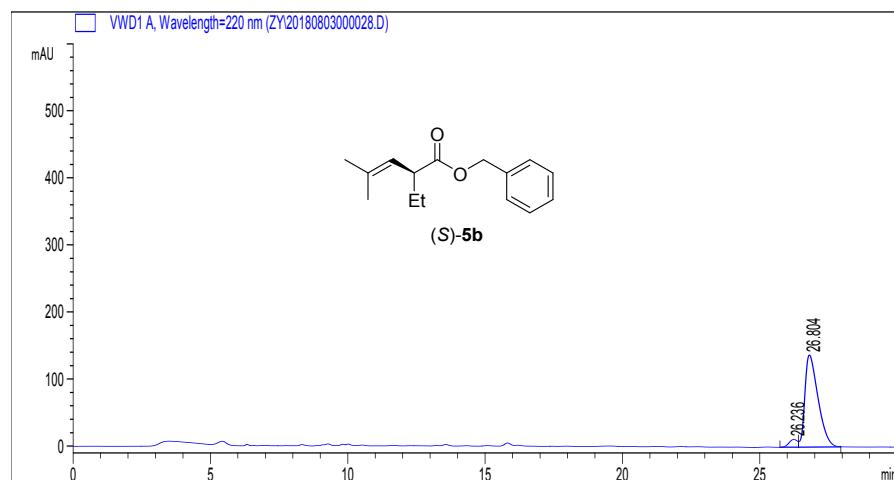


Figure S238. HPLC Chromatography of racemic benzyl 2-ethyl-4-methylpent-3-enoate (**5b**) (Daicel Chiralcel OD-H column, *n*-hexane, 0.5 mL/min, 220 nm)



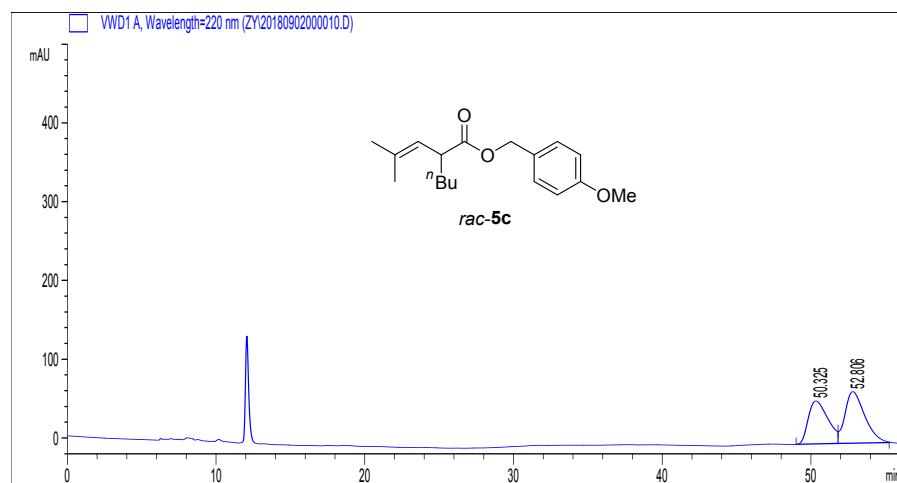
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	26.011	BV	0.4234	1199.43494	44.74531	48.9657
2	26.810	VB	0.4586	1250.10559	41.56466	51.0343
Totals:				2449.54053	86.30997	

Figure S239. HPLC Chromatography of (*S*)-benzyl 2-ethyl-4-methylpent-3-enoate (**5b**) (Daicel Chiralcel OD-H column, *n*-hexane, 0.5 mL/min, 220 nm)



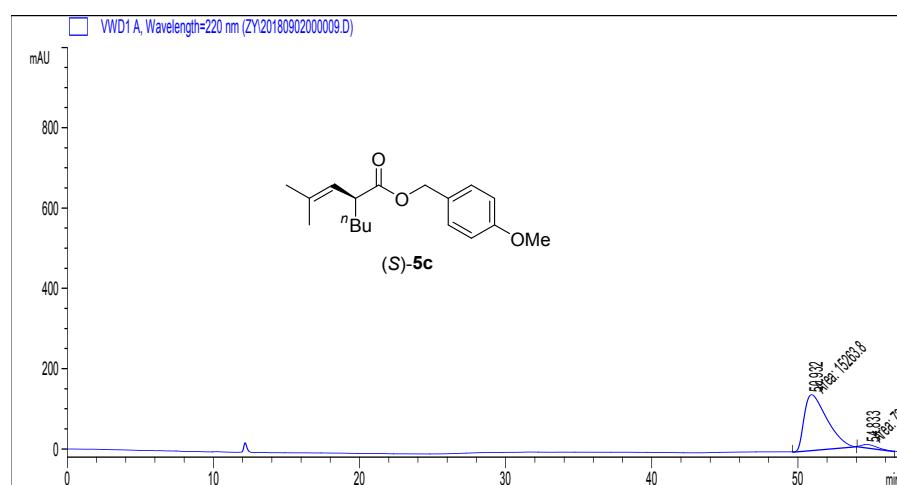
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	26.236	BV	0.3340	248.95374	11.63727	5.1479
2	26.804	VB	0.5082	4587.09814	137.65195	94.8521
Totals:				4836.05188	149.28922	

Figure S240. HPLC Chromatography of racemic 4-methoxybenzyl 2-(2-methylprop-1-en-1-yl) hexanoate (**5c**) (Phomenex lux 5u Amylos-2 column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	50.325	MF	1.7353	5953.15674	57.17678	49.1712
2	52.806	FM	1.5154	6153.85010	67.68169	50.8288
Totals:				12107.00684	124.85848	

Figure S241. HPLC Chromatography of (*S*)- 4-methoxybenzyl 2-(2-methylprop-1-en-1-yl) hexanoate (**5c**) (Phomenex lux 5u Amylos-2 column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	50.932	MM	1.8237	15391.10287	140.65747	95.7429
2	54.838	MM	1.2597	684.34802	9.05444	4.2571
Totals:				16075.45089	149.71191	

Figure S242. HPLC Chromatography of racemic 4-methoxybenzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5d**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

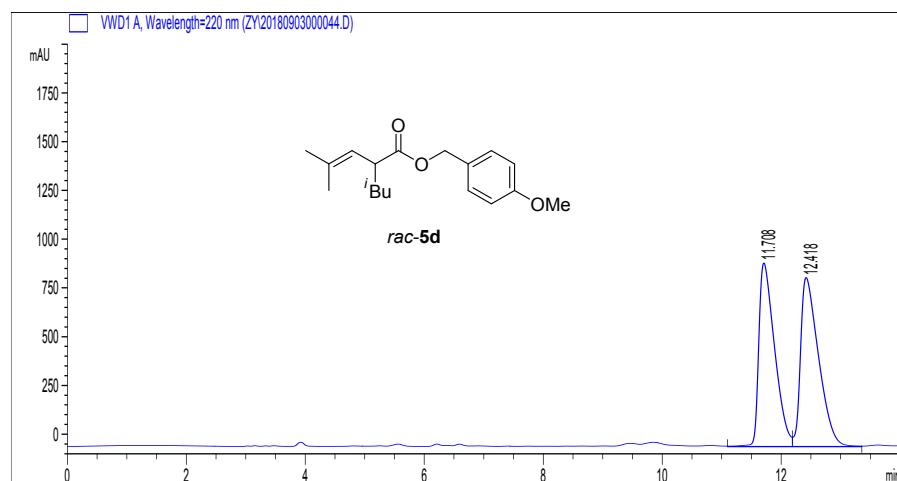


Figure S243. HPLC Chromatography of (*S*)- 4-methoxybenzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5d**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

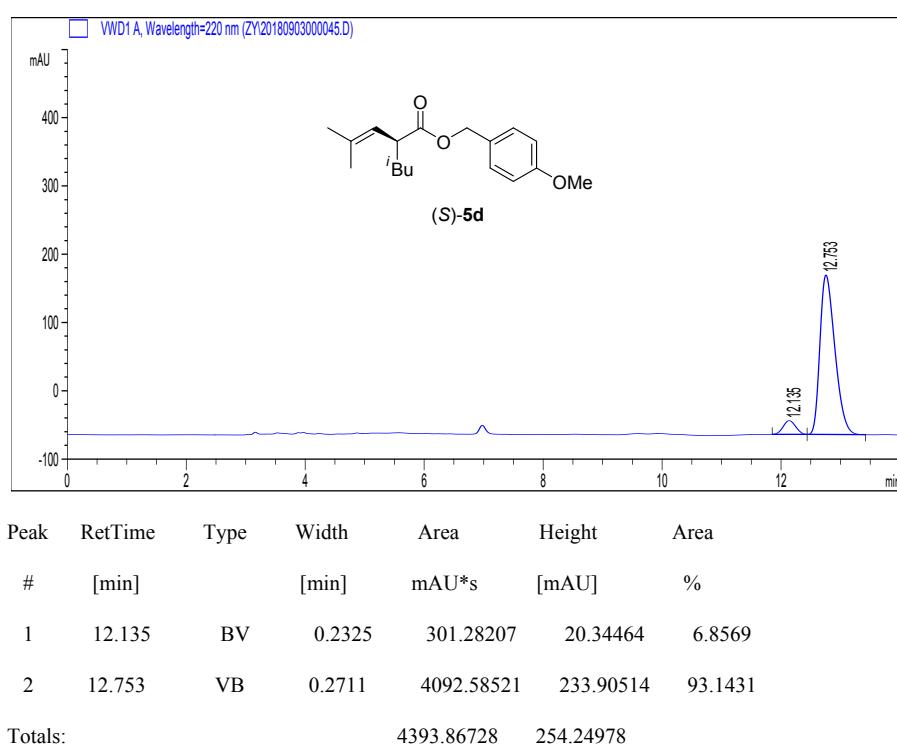
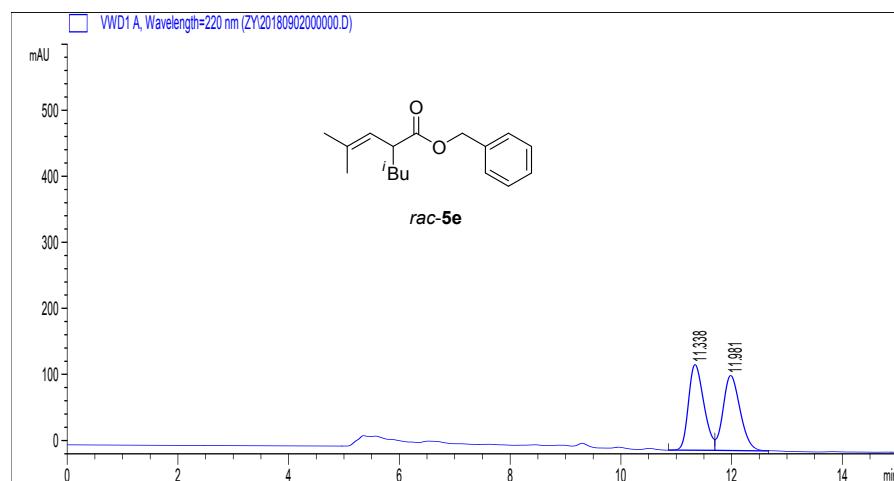
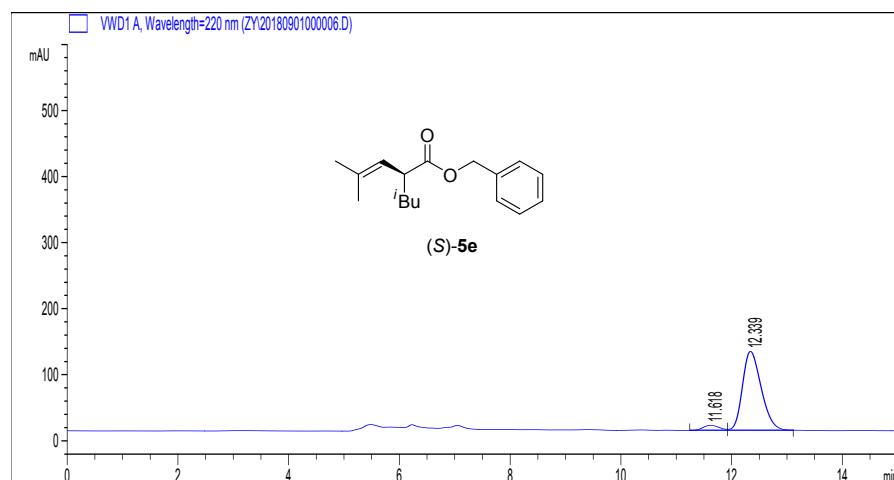


Figure S244. HPLC Chromatography of racemic benzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5e**) (Daicel Chiralcel OJ-H column, *n*-hexane, 0.6mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	11.338	VV	0.2993	2507.31372	129.96550	50.6036
2	11.981	VB	0.3322	2447.50146	113.91441	49.3964
Totals:				4954.81519	243.87991	

Figure S245. HPLC Chromatography of (*S*)-benzyl 2-*iso*-butyl-4-methylpent-3-enoate (**5e**) (Daicel Chiralcel OJ-H column, *n*-hexane, 0.6mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	11.618	BV	0.3195	159.85645	7.83710	5.3658
2	12.339	VB	0.3678	2819.29614	119.76895	94.6342
Totals:				2979.15259	127.60605	

Figure S246. HPLC Chromatography of racemic benzyl 2-*iso*-propyl-4-methylpent-3-enoate (**5f**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

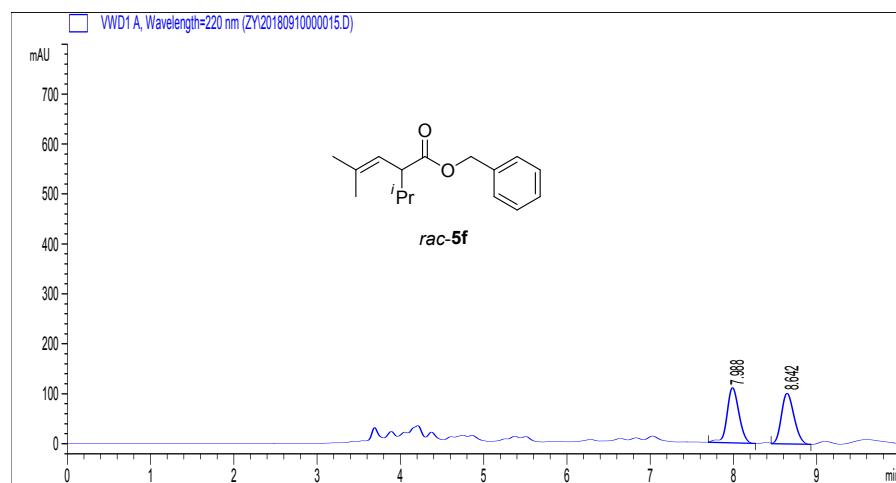


Figure S247. HPLC Chromatography of (*S*)-benzyl 2-*iso*-propyl-4-methylpent-3-enoate (**5f**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

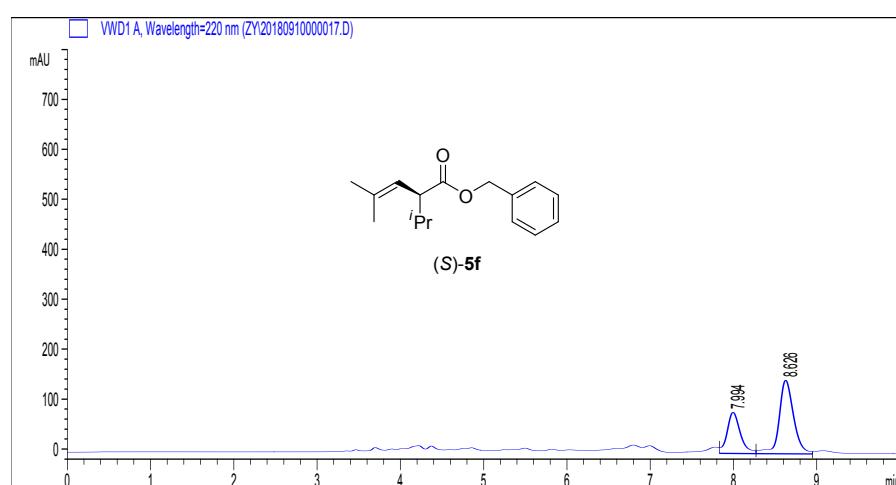
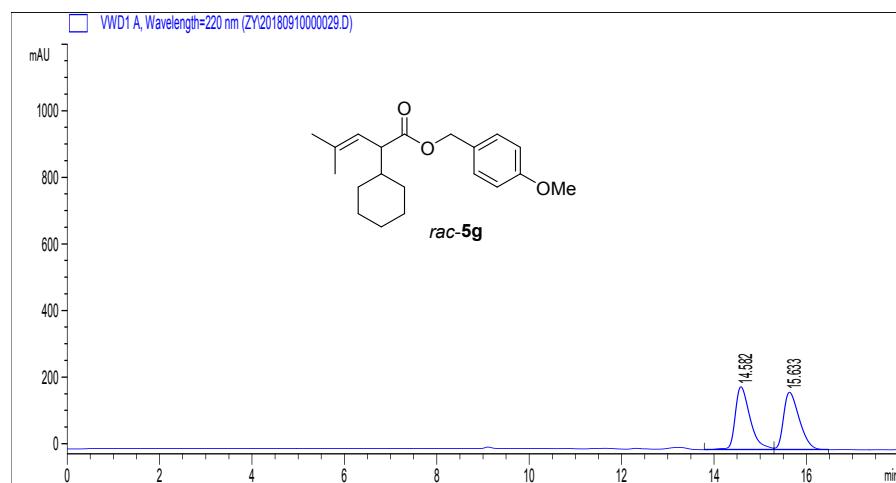
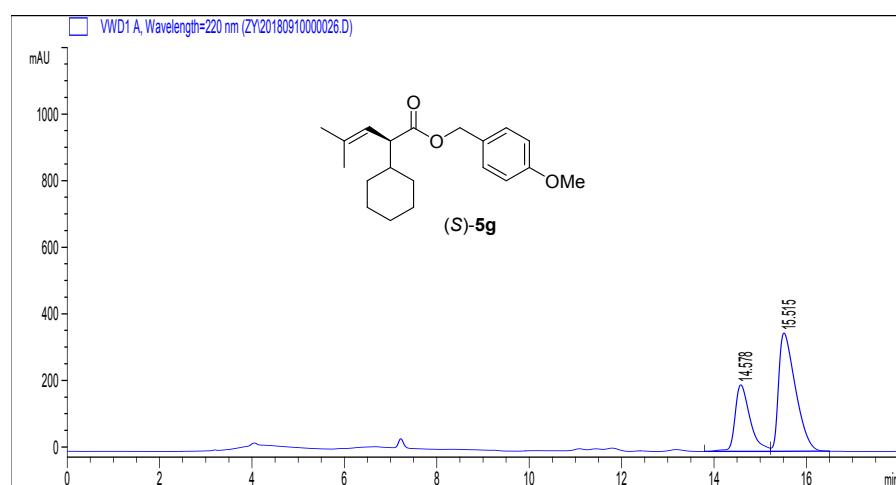


Figure S248. HPLC Chromatography of racemic 4-methoxybenzyl 2-cyclohexyl-4-methylpent-3-enoate (**5g**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	14.582	VV	0.3403	4238.68994	188.97357	50.9972
2	15.633	VB	0.3658	4072.92090	172.46031	49.0028
Totals:				8311.61084	361.43388	

Figure S249. HPLC Chromatography of (*S*)- 4-methoxybenzyl 2-cyclohexyl-4-methylpent-3-enoate (**5g**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	14.578	VV	0.3417	4512.79883	200.15343	33.3572
2	15.515	VB	0.3890	9015.89844	355.54150	66.6428
Totals:				13528.69727	555.69493	

Figure S250. HPLC Chromatography of racemic ethyl 2-(2-bromoethyl)-4-methylpent-3-enoate (**5h**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

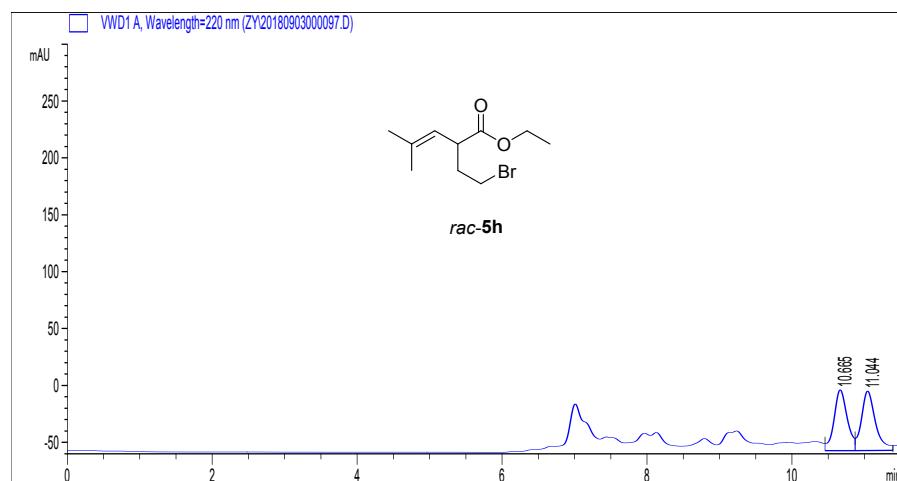


Figure S251. HPLC Chromatography of (*S*)-ethyl 2-(2-bromoethyl)-4-methylpent-3-enoate (**5h**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)

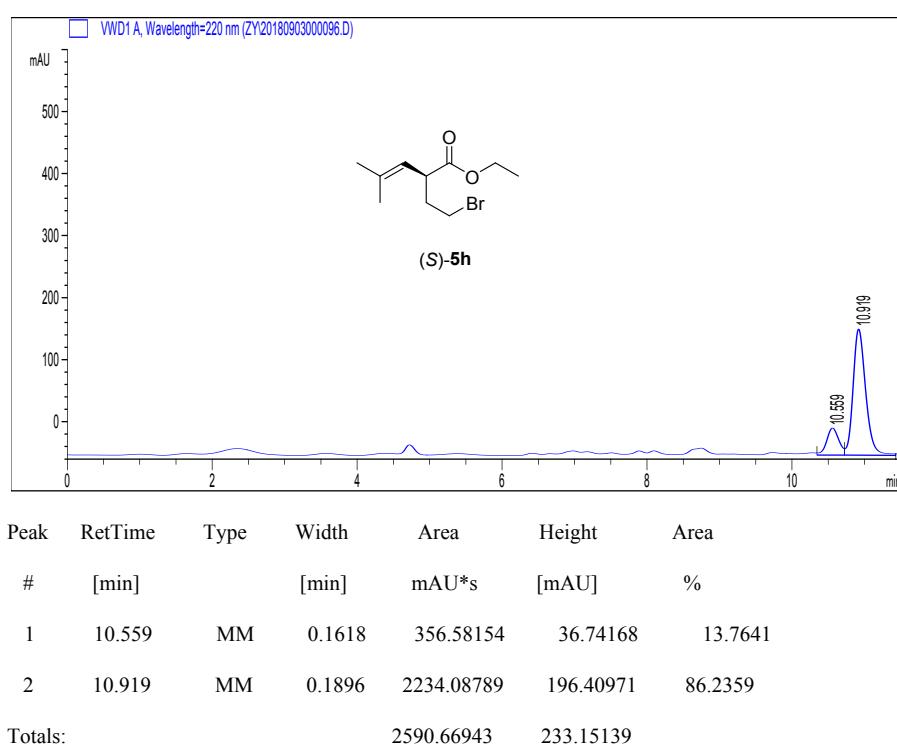
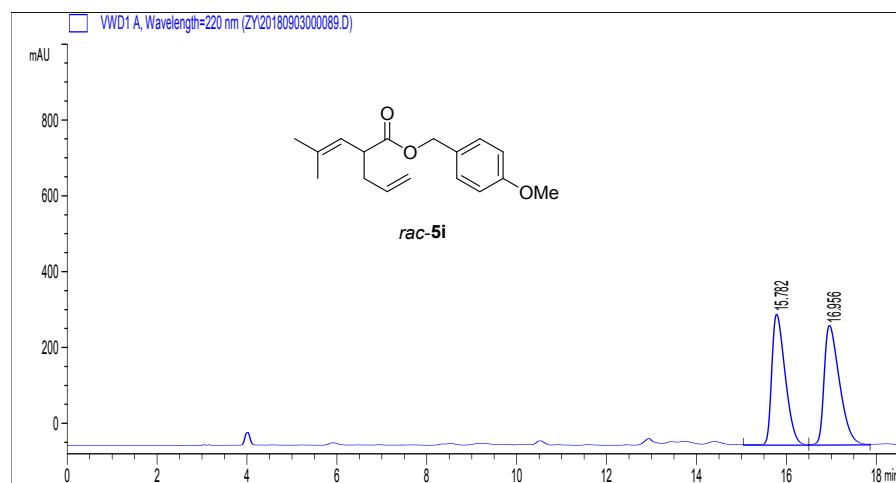
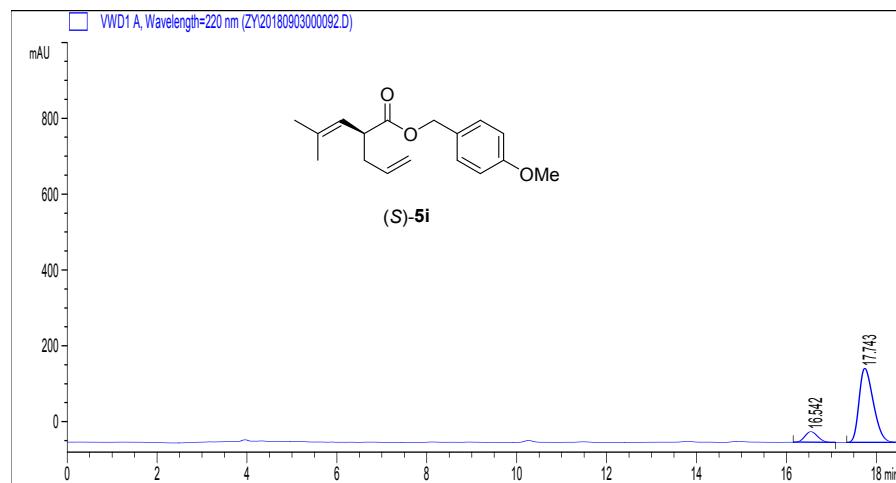


Figure S252. HPLC Chromatography of racemic 4-methoxybenzyl 2-allyl-4-methylpent-3-enoate (**5i**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 0.5 mL/min, 220 nm)



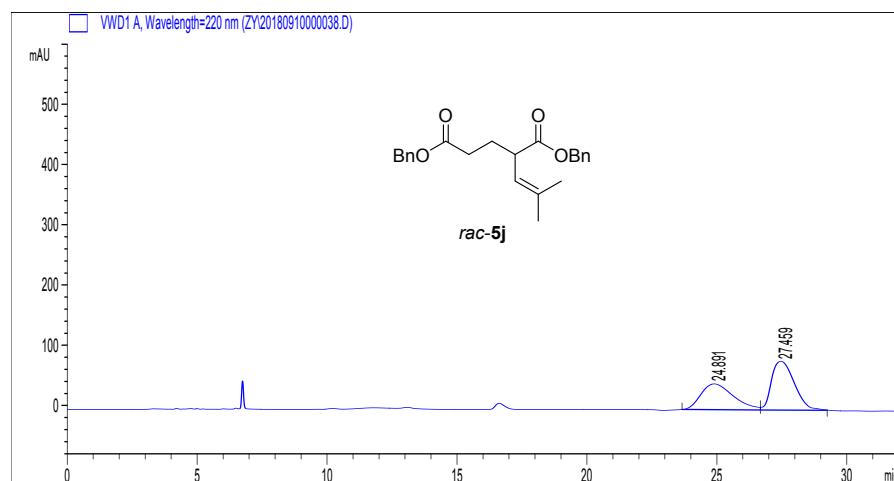
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	15.782	VV	0.3218	7202.65479	345.54477	48.8659
2	16.956	VB	0.3655	7536.96484	316.16705	51.1341
Totals:				14739.61963	661.71182	

Figure S253. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-allyl-4-methylpent-3-enoate (**5i**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 0.5 mL/min, 220 nm)



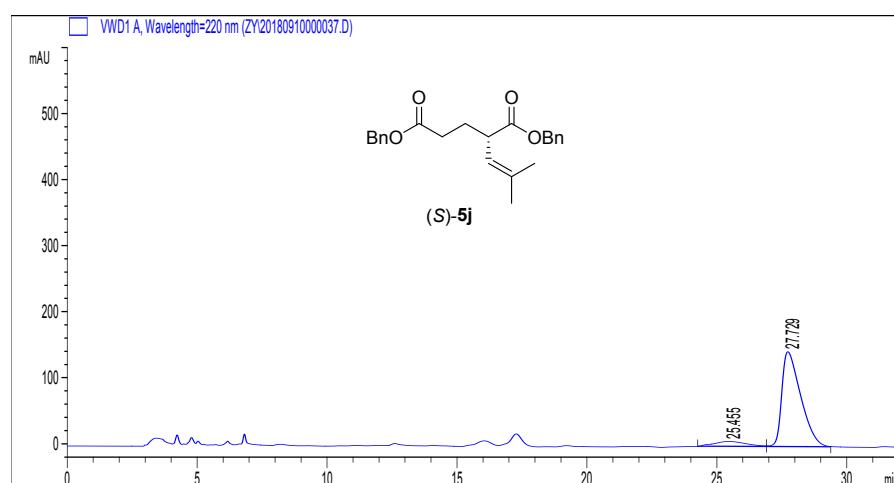
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	16.542	MM	0.3057	483.33386	26.34892	10.0678
2	17.743	BB	0.3418	4317.43262	195.71666	89.9322
Totals:				4800.76648	222.06558	

Figure S254. HPLC Chromatography of racemic dibenzyl 2-(2-methylprop-1-en-1-yl)pentanedioate (**5j**) (Daicel Chiralcel OD-H column, 0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



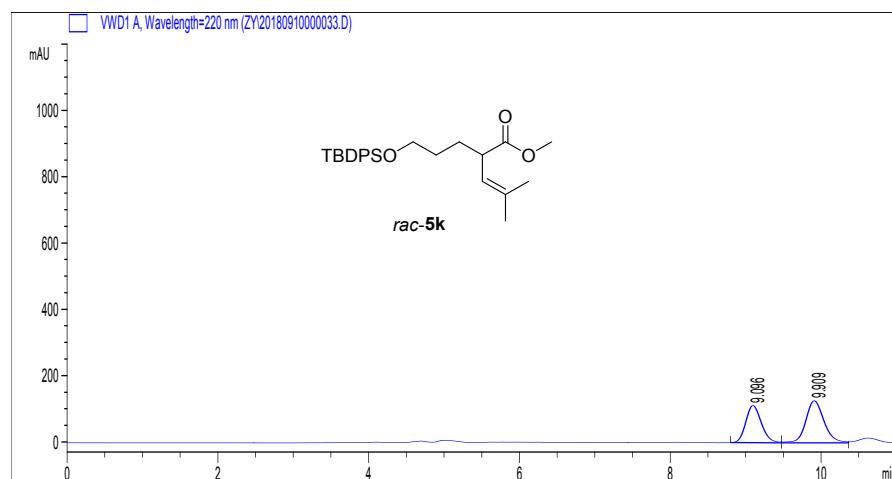
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	24.890	MM	1.4793	3843.01147	43.29823	49.6247
2	27.459	MM	0.8994	3901.13477	72.29410	50.3753
Totals:				7744.14624	115.59233	

Figure S255. HPLC Chromatography of (*S*)-dibenzyl 2-(2-methylprop-1-en-1-yl)pentanedioate (**5j**) (Daicel Chiralcel OD-H column, 0.5% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



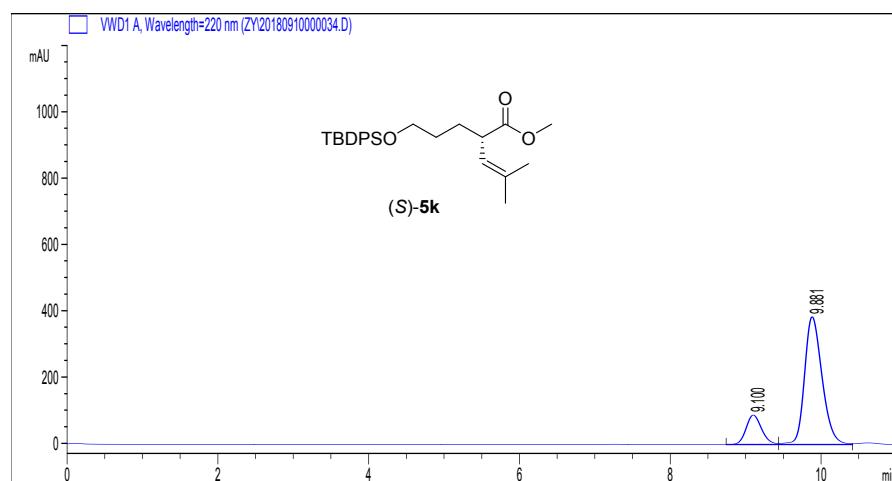
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	25.456	FM	1.3181	605.90002	7.66123	7.6975
2	27.729	VB	0.7569	7265.53076	143.80174	92.3025
Totals:				7871.43079	151.46297	

Figure S256. HPLC Chromatography of racemic methyl 2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4-methylpent-3-enoate (**5k**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



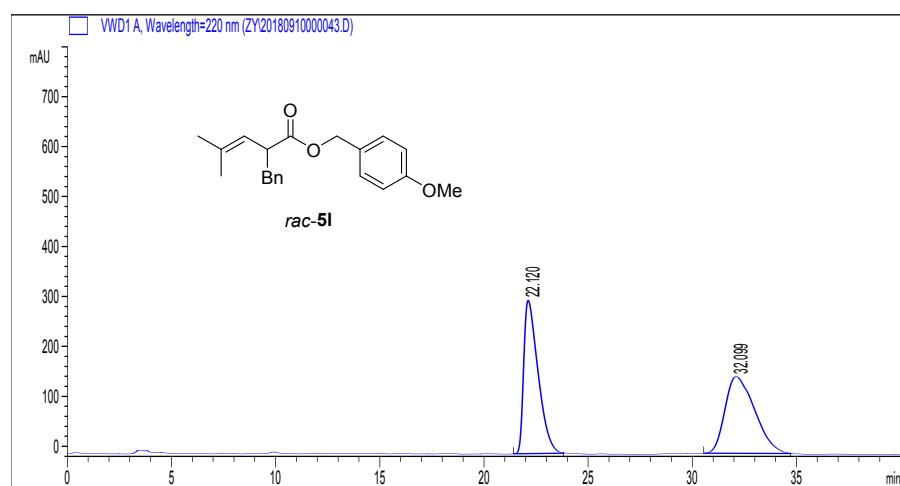
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	9.095	MM	0.2426	1647.03271	113.15827	47.5272
2	9.908	MM	0.2527	1818.41858	119.95554	52.4728
Totals:				3465.45129	233.11381	

Figure S257. HPLC Chromatography of (*S*)-Methyl 2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)-4-methylpent-3-enoate (**5k**) (Daicel Chiralcel OD-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



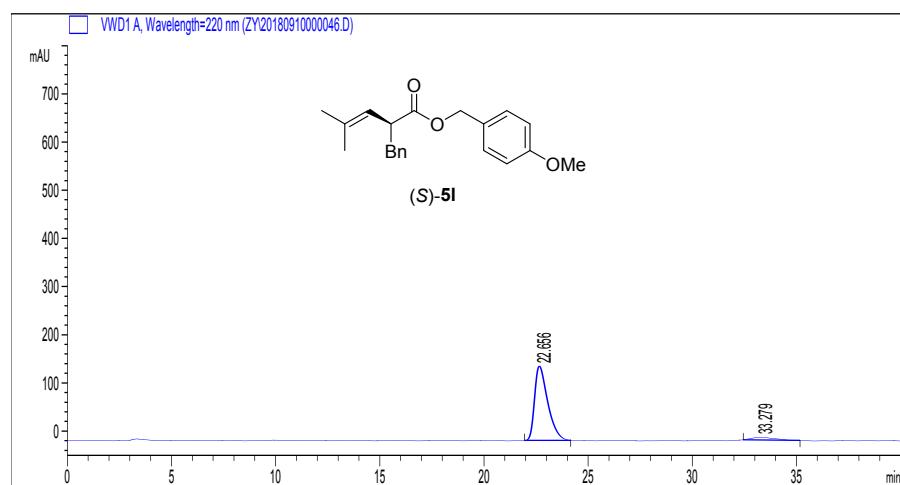
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	9.100	BV	0.2218	1281.86584	89.08168	17.0357
2	9.881	VV	0.2500	6242.72314	385.63971	82.9643
Totals:				7524.58899	474.72139	

Figure S258. HPLC Chromatography of racemic 4-methoxybenzyl 2-benzyl-4-methylpent-3-enoate (**5I**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



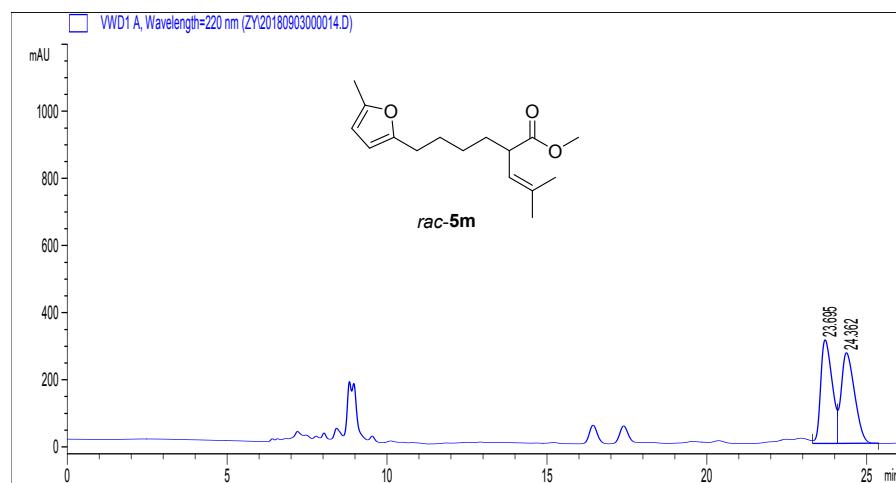
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	22.120	BB	0.7175	14725.02315	307.41165	49.0314
2	32.099	BB	1.4141	15306.79962	154.04263	50.9686
Totals:					30031.82277	461.45428

Figure S259. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-benzyl-4-methylpent-3-enoate (**5I**) (Daicel Chiralcel OJ-H column, 1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



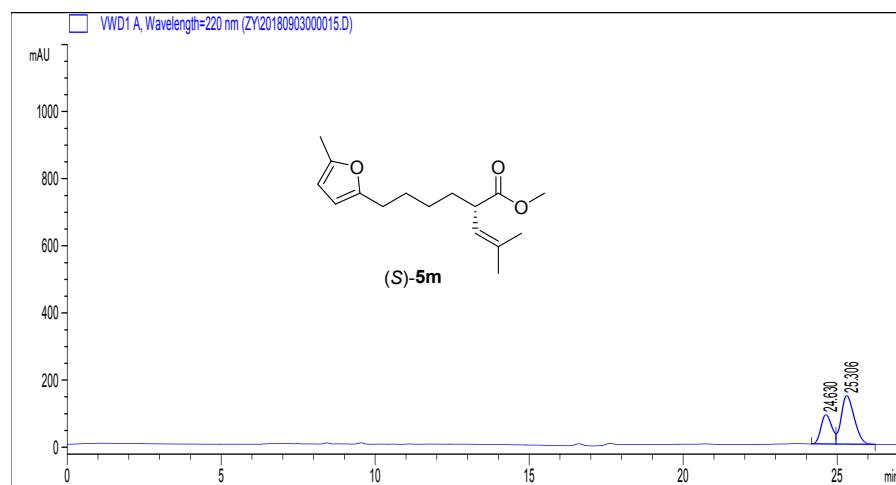
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	22.656	MM	0.7525	7027.41016	155.63943	93.8522
2	33.279	BB	1.0649	460.32828	5.87900	6.1478
Totals:					7487.73843	161.51844

Figure S260. HPLC Chromatography of racemic methyl 6-(5-methylfuran-2-yl)-2-(2-methylprop-1-en-1-yl)hexanoate (**5m**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



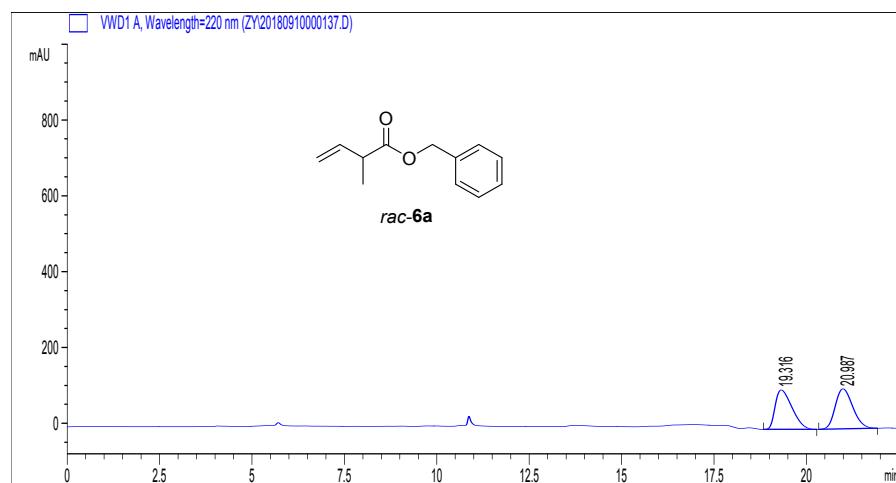
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	23.695	VV	0.3906	7721.15039	308.93335	49.4576
2	24.362	VB	0.4540	7890.49609	270.44315	50.5424
Totals:				15611.64648	579.37650	

Figure S261. HPLC Chromatography of (*S*)-methyl 6-(5-methylfuran-2-yl)-2-(2-methylprop-1-en-1-yl)hexanoate (**5m**) (Daicel Chiralcel OX-H column, 0.1% isopropanol in *n*-hexane, 1 mL/min, 220 nm)



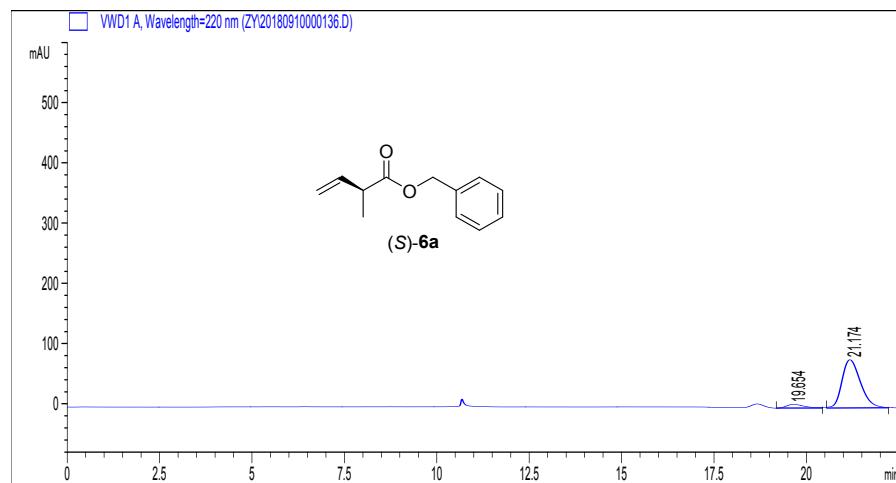
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	24.630	BV	0.3827	2147.50293	87.43151	33.4988
2	25.306	VB	0.4569	4263.17383	144.87750	66.5012
Totals:				6410.67676	232.30901	

Figure S262. HPLC Chromatography of racemic benzyl 2-methylbut-3-enoate (**6a**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



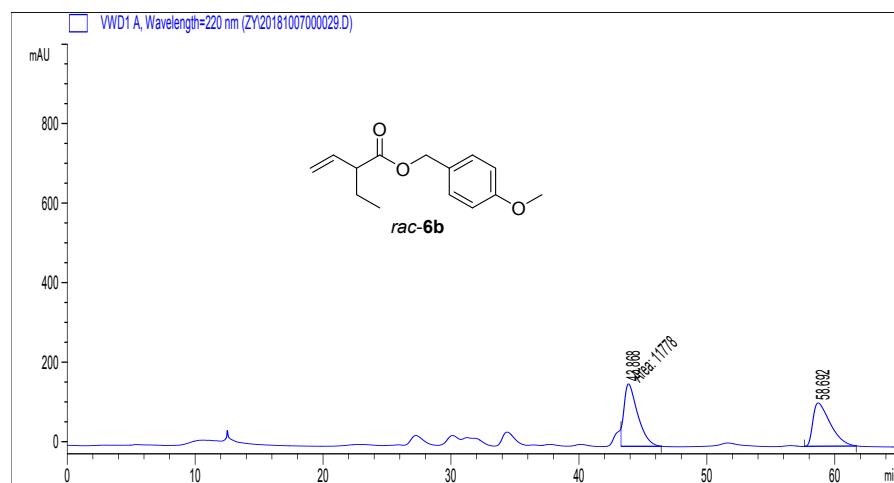
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	19.316	VB	0.4848	3299.75903	104.11175	48.5744
2	20.987	BB	0.5149	3493.44507	105.78862	51.4256
Totals:				6793.20410	209.90037	

Figure S263. HPLC Chromatography of (*S*)-benzyl 2-methylbut-3-enoate (**6a**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



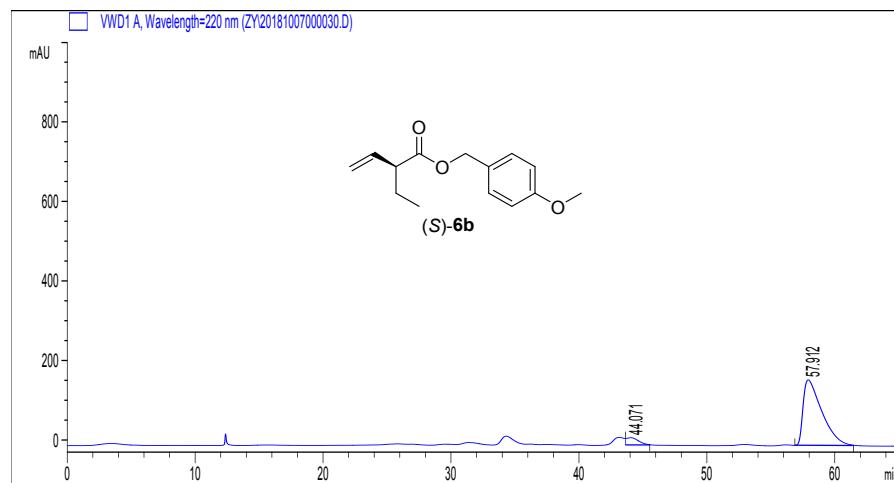
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	19.654	MM	0.4526	148.75249	5.47818	5.0685
2	21.174	BB	0.5356	2786.08472	80.05580	94.9315
Totals:				2934.83720	85.53398	

Figure S264. HPLC Chromatography of racemic 4-methoxybenzyl 2-ethylbut-3-enoate (**6b**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



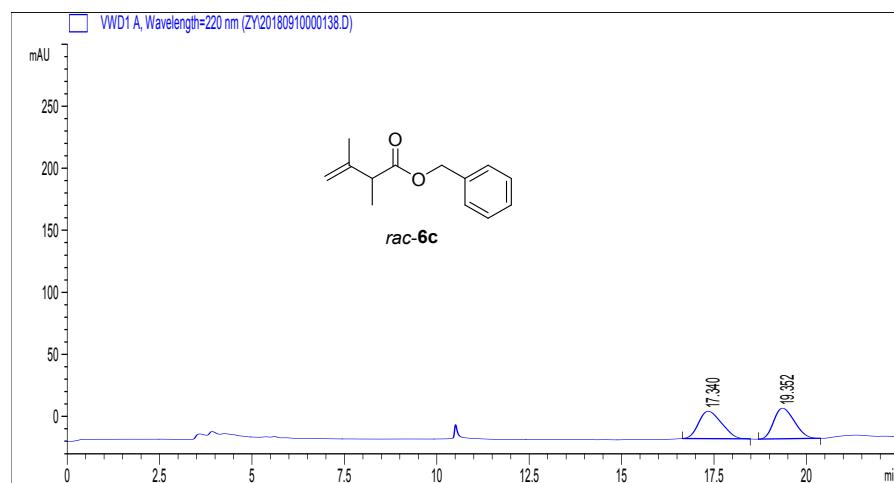
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	43.868	FM	1.2470	11777.97770	57.41600	53.2890
2	58.692	BB	1.3620	10324.10223	109.36593	46.7110
Totals:				22102.07923	266.78193	

Figure S265. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-ethylbut-3-enoate (**6b**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



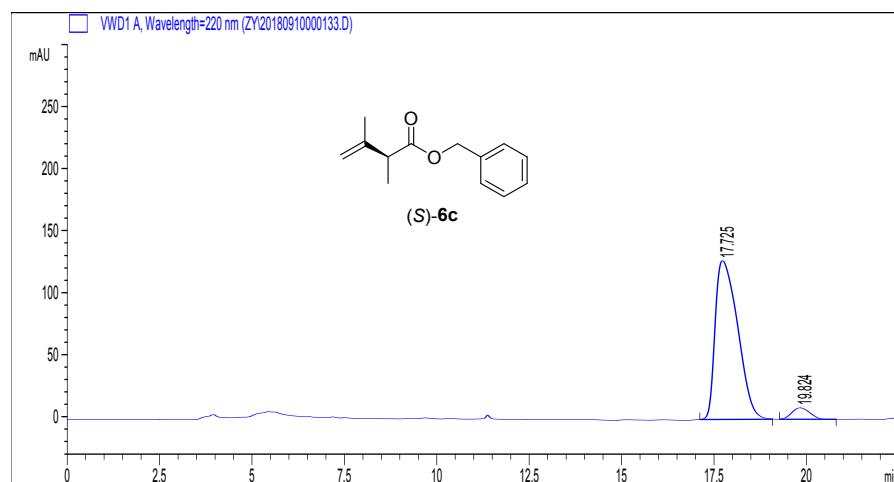
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	44.071	VB	0.9248	1217.51123	18.43579	6.7942
2	57.912	BB	1.4742	16702.35027	164.71242	93.2058
Totals:				17919.86149	183.14821	

Figure S266. HPLC Chromatography of racemic benzyl 2,3-dimethylbut-3-enoate (**6c**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



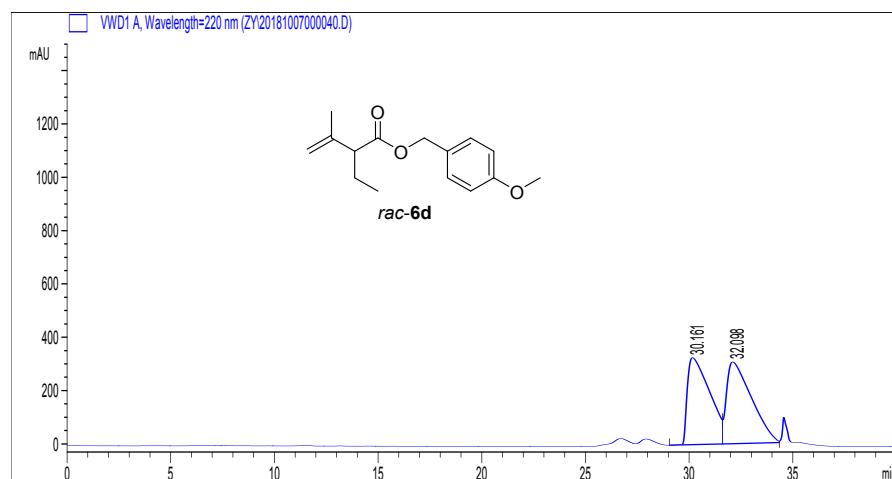
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	17.340	BB	0.6707	973.63293	22.31445	50.1709
2	19.352	BB	0.6016	967.00146	24.74300	49.8291
Totals:				1940.63440	47.05745	

Figure S267. HPLC Chromatography of (*S*)-benzyl 2,3-dimethylbut-3-enoate (**6c**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



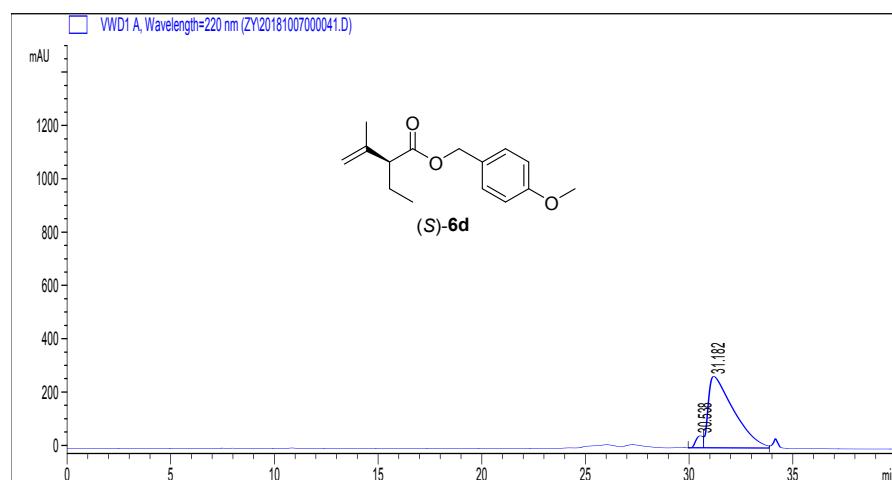
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	17.725	BB	0.6977	5438.32080	128.09698	95.0270
2	19.823	MM	0.5351	284.60254	8.86525	4.9730
Totals:				5722.92334	136.96223	

Figure S268. HPLC Chromatography of racemic 4-methoxybenzyl 2-ethyl-3-methylbut-3-enoate (**6d**) (Daicel Chiralpak AD-H column, *n*-hexane, 1 mL/min, 220 nm)



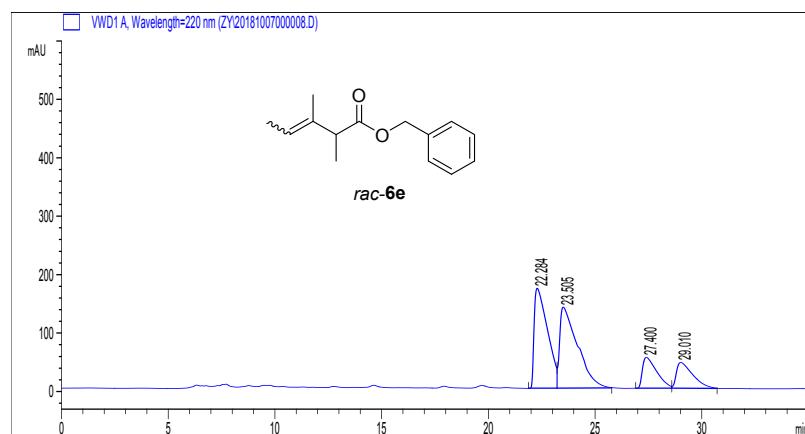
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	30.161	VV	1.0702	24290.80123	327.09973	48.5900
2	32.098	VV	1.1817	25700.55754	307.54965	51.4100
Totals:				49991.35878	634.64938	

Figure S269. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-ethyl-3-methylbut-3-enoate (**6d**) (Daicel Chiralpak AD-H column, *n*-hexane, 1 mL/min, 220 nm)



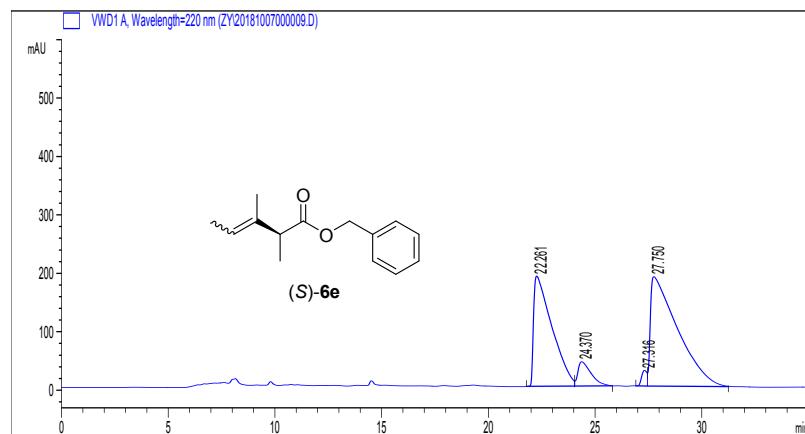
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	30.538	BV	0.3962	1102.72278	45.51405	4.5872
2	31.182	VV	1.2080	22936.40305	268.82831	95.4128
Totals:				24039.12583	314.34235	

Figure S270. HPLC Chromatography of racemic benzyl 2,3-dimethylpent-3-enoate (**6e**) (Daicel Chiraldpak AD-H column, *n*-hexane, 1 mL/min, 220 nm)



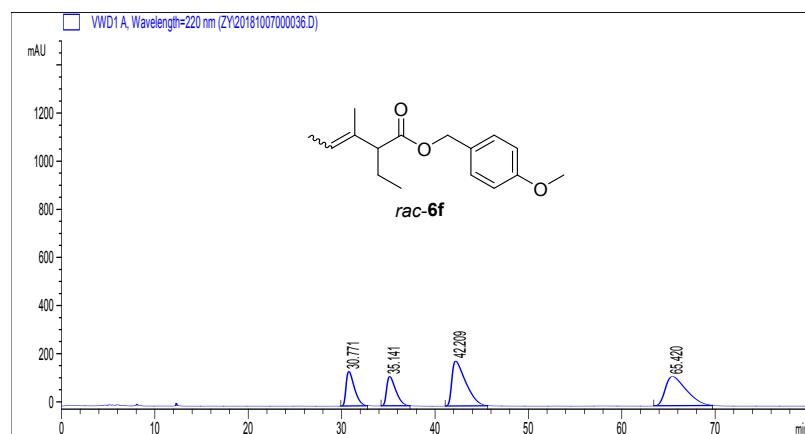
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	22.284	BV	0.6019	7470.10938	171.31602	36.5972
2	23.505	VB	0.7670	8091.61963	138.90578	39.6421
3	27.400	BV	0.6395	2470.11890	53.03603	12.1015
4	29.010	VB	0.7197	2379.85669	44.52562	11.6593
Totals:				20411.7046	407.78346	

Figure S271. HPLC Chromatography of (*S*)-benzyl 2,3-dimethylpent-3-enoate (**6e**) (Daicel Chiraldpak AD-H column, *n*-hexane, 1 mL/min, 220 nm)



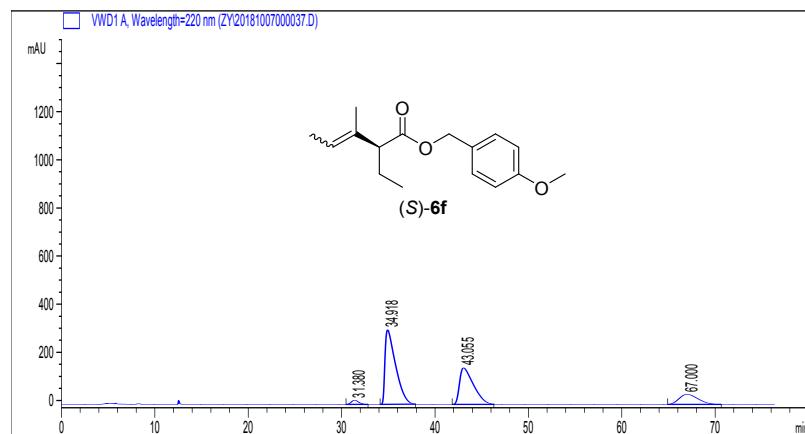
Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	22.261	BV	0.7696	12922.69810	189.06854	37.5178
2	24.370	VB	0.5941	1792.55005	41.74661	5.9554
3	27.316	BV	0.2713	455.39157	26.75895	1.5129
4	27.750	VB	1.1098	16558.91963	187.34387	55.0138
Totals:				31729.55935	444.91798	

Figure S272. HPLC Chromatography of racemic 4-methoxybenzyl 2-ethyl-3-methylpent-3-enoate (**6f**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	30.771	BB	0.9239	8877.04395	143.83244	15.9977
2	35.141	BB	1.0207	8345.99512	122.69231	15.0407
3	42.209	BB	1.4689	19201.11102	186.97548	34.6032
4	65.420	BB	2.2615	19065.27214	122.09193	34.3584
Totals:				55489.42142	575.59216	

Figure S273. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-ethyl-3-methylpent-3-enoate (**6f**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	mAU*s	[mAU]	%
1	31.380	BB	0.8475	996.86188	17.82748	2.0995
2	34.918	BB	1.1391	24540.09661	310.47168	51.6839
3	43.055	BB	1.4796	15829.54198	152.59233	33.3386
4	67.000	BB	2.0167	6114.61914	42.67437	12.8780
Totals:				47481.11961	523.56586	

Figure S274. HPLC Chromatography of racemic 4-methoxybenzyl 2-ethylpent-3-enoate (**6g**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

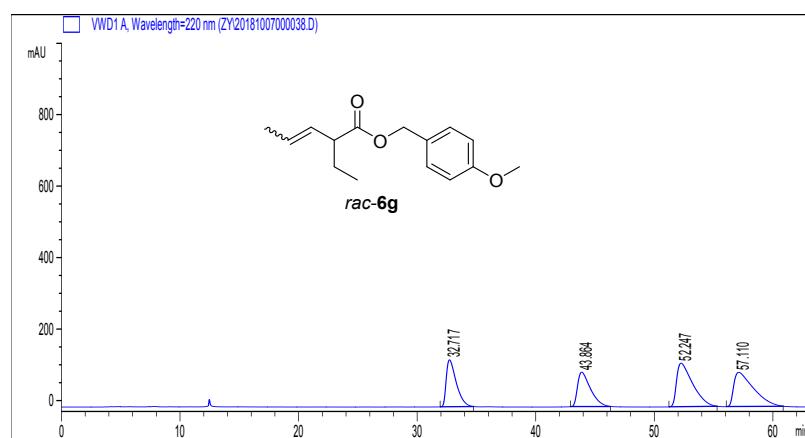


Figure S275. HPLC Chromatography of (*S*)-4-methoxybenzyl 2-ethylpent-3-enoate (**6g**) (Daicel Chiralcel OJ-H column, *n*-hexane, 1 mL/min, 220 nm)

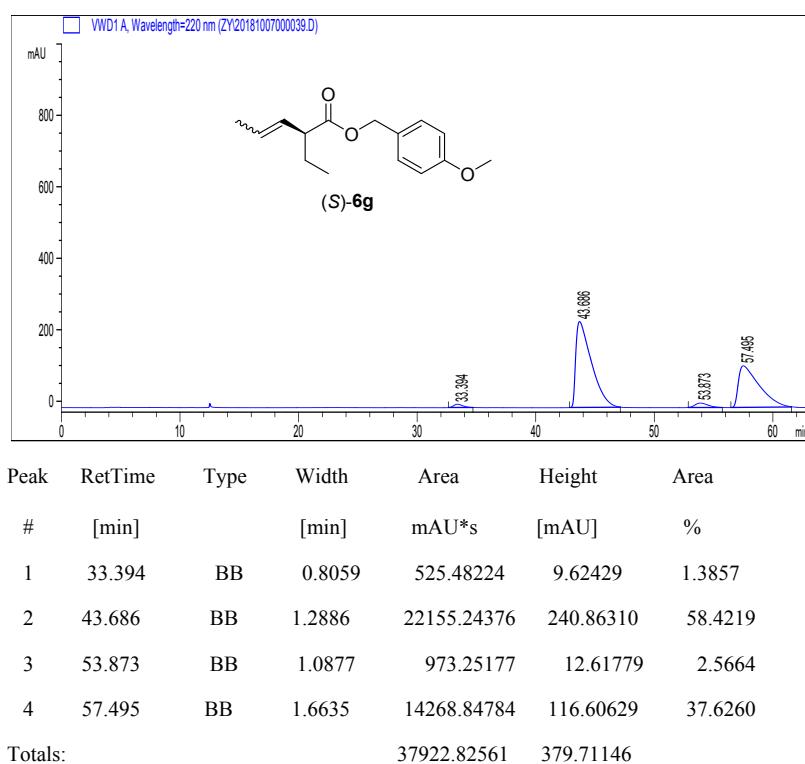


Figure S276. HPLC Chromatography of racemic benzyl 2-(prop-1-en-2-yl)hex-5-enoate (**6h**) (Daicel Chiralpak AD-H column, 0.8% isopropanol in *n*-hexane, 1 mL/min, 254 nm)

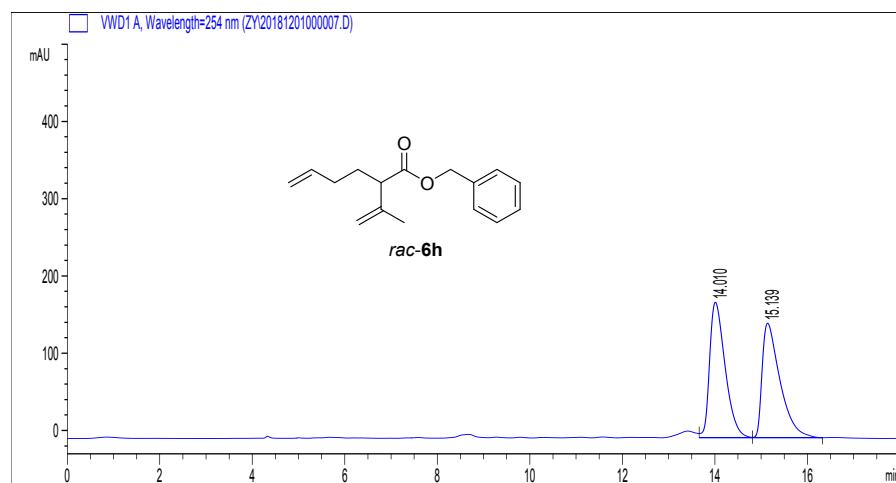
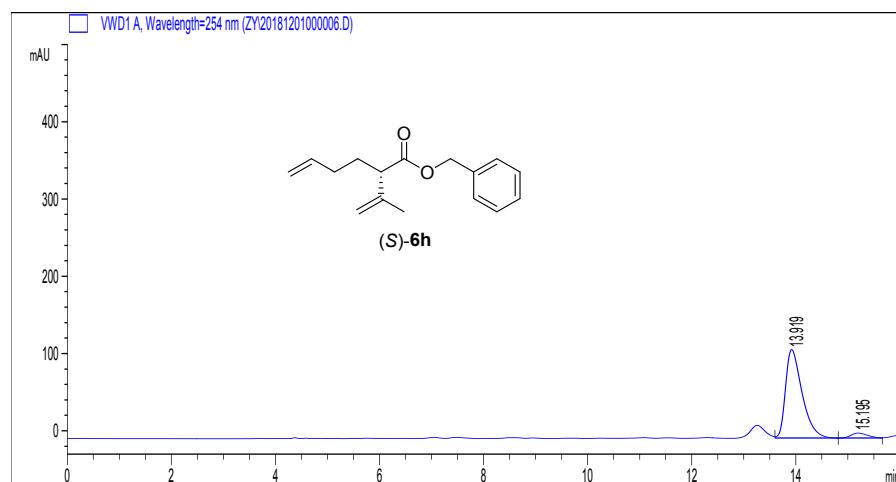


Figure S277. HPLC Chromatography of (*S*)-benzyl 2-(prop-1-en-2-yl)hex-5-enoate (**6h**) (Daicel Chiralpak AD-H column, 0.8% isopropanol in *n*-hexane, 1 mL/min, 254 nm)



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