Supporting Information

Enhanced *anti*-Diastereo- and Enantioselectivityin Alcohol Mediated Carbonyl Crotylation Using an Isolable Single Component Iridium Catalyst

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Table of Contents

General Experimental Methods --S2

Procedure for the Preparation of (*S*)-**I** ---S3

Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Carbonyl Crotylation from the Alcohol Oxidation Level --S4–S39

Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Carbonyl Crotylation from the Aldehyde Oxidation Level ---S40–S57

General Methods

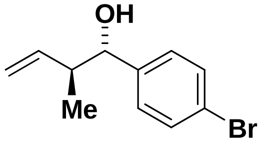
All reactions were run under an atmosphere of Argon. Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. Anhydrous solvents were transferred by an oven-dried syringe. Sealed tubes (13x100 mm) were dried in an oven overnight and cooled under a stream of nitrogen prior to use. Commercially available allyl acetate was purified by distillation prior to use. Cesium carbonate was used directly without further purification. Isopropanol was purified by distillation prior to use. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates. High-resolution mass spectra (HRMS) are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M or M-H) or a suitable fragment ion. ^{1}H Nuclear magnetic resonance spectra were recorded using a 400 MHz and spectrometer. Coupling constants are reported in Hertz (Hz). For $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CHCl_3$ δ_H (7.26 ppm). ^{13}C Nuclear magnetic resonance spectra were recorded using a 100 MHz spectrometer. For $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to residual $CDCl_3$ δ_C (77.0 ppm).

Preparation of (*S*)-I

To a mixture of [Ir(cod)Cl]$_2$ (87.3 mg, 0.13 mmol, 100 mol%), (*S*)-SEGPHOS (159 mg, 0.26 mmol, 200 mol%), Cs_2CO_3 (169 mg, 0.52 mmol, 400 mol%), 4-CN-3-NO_2BzOH (100 mg, 0.52 mmol, 400 mol%) and allyl acetate (65 mg, 0.65 mmol, 500 mol%) in a sealed tube under an atmosphere of N_2 was added THF (2.6 mL, 0.05 M). The reaction mixture was stirred for 30 minutes at ambient temperature and heated for 1.5 hours at 80 ^{o}C. Upon cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a celite plug, washed with CH_2Cl_2 (50 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography (SiO_2, 20% Et_2O/CH_2Cl_2) and concentrated *in vacuo*. The light yellow gum was dissolved in THF (3 mL). Rapid addition of hexanes (50 mL) to the stirred solution resulted in precipitation of a bright yellow powder, which was collected by gravity filtration. Removal of trace solvents *in vacuo* delivered (*S*)-**I** (228 mg, 0.221 mmol) in 85% yield.

Detailed Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Carbonyl Crotylation from the Alcohol Oxidation Level

(*1S,2S*)-1-(4-bromophenyl)-2-methylbut-3-en-1-ol



4a

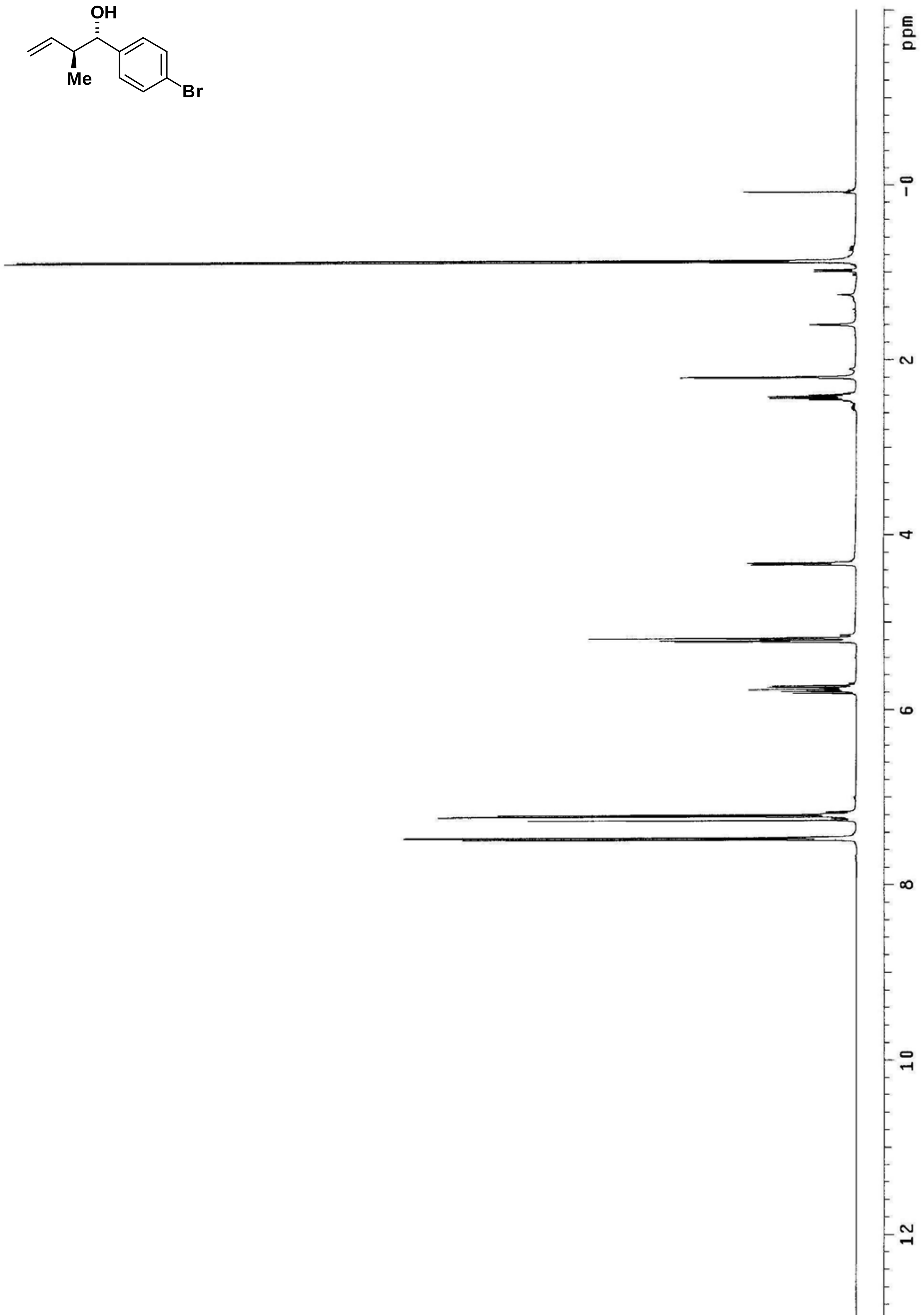
An oven-dried sealed tube under an atmosphere of N_2 was charged with (4-bromophenyl)methanol **2a** (37.4 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 °C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4a** (37.6 mg, 0.156 mmol) as a colorless oil in 78% yield (16:1 dr).

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.81-5.71 (m, 1H), 5.22-5.16 (m, 2H), 4.32 (d, *J* = 7.6 Hz, 1H), 2.45-2.37 (m, 1H), 2.20 (br s, 1H), 0.87 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ141.4, 140.1, 131.3, 128.6, 121.4, 117.3, 77.1, 46.4, 16.4.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 230 nm), t_{minor} = 27.9 min, t_{major} = 31.8 min; ee = 97%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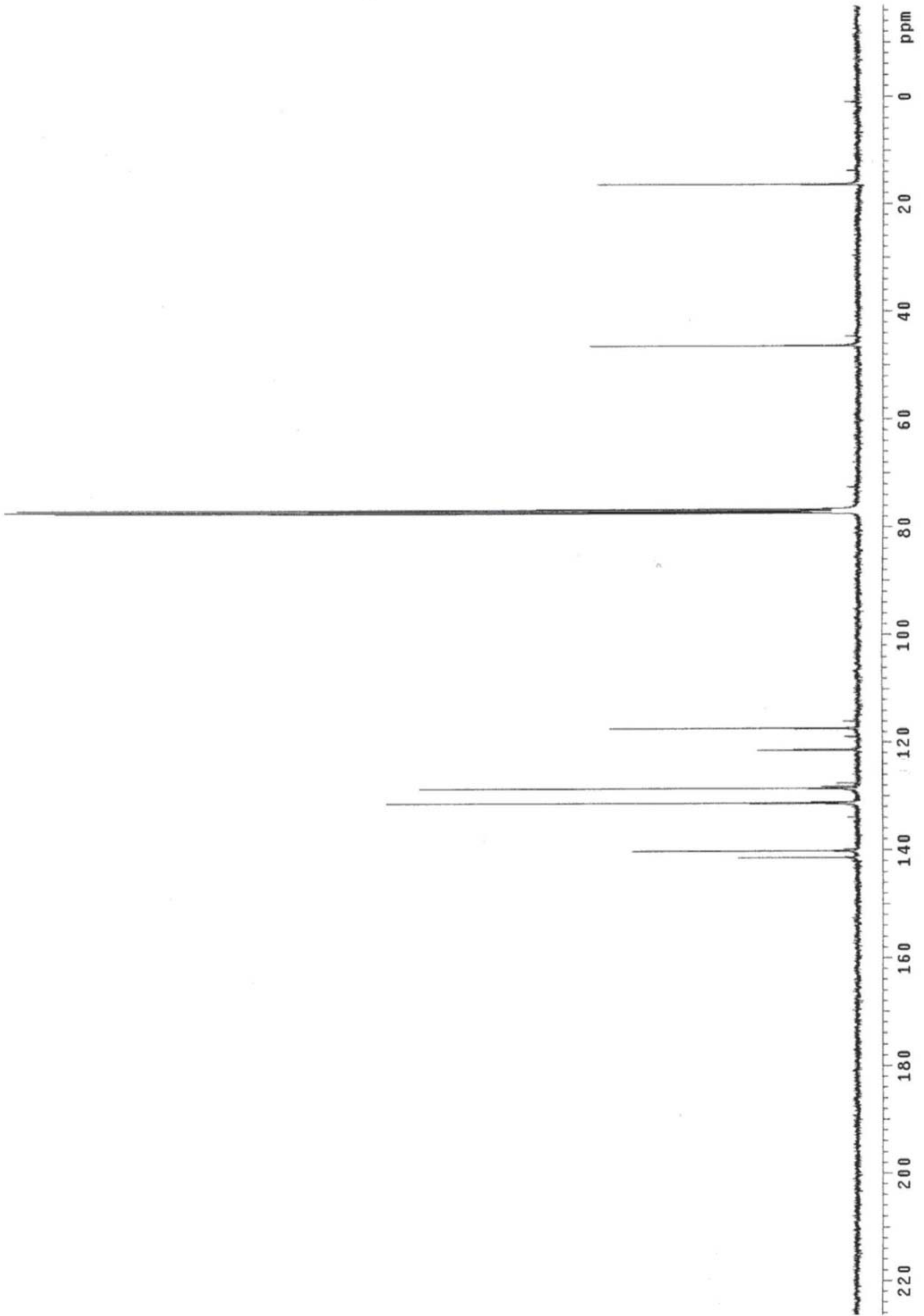
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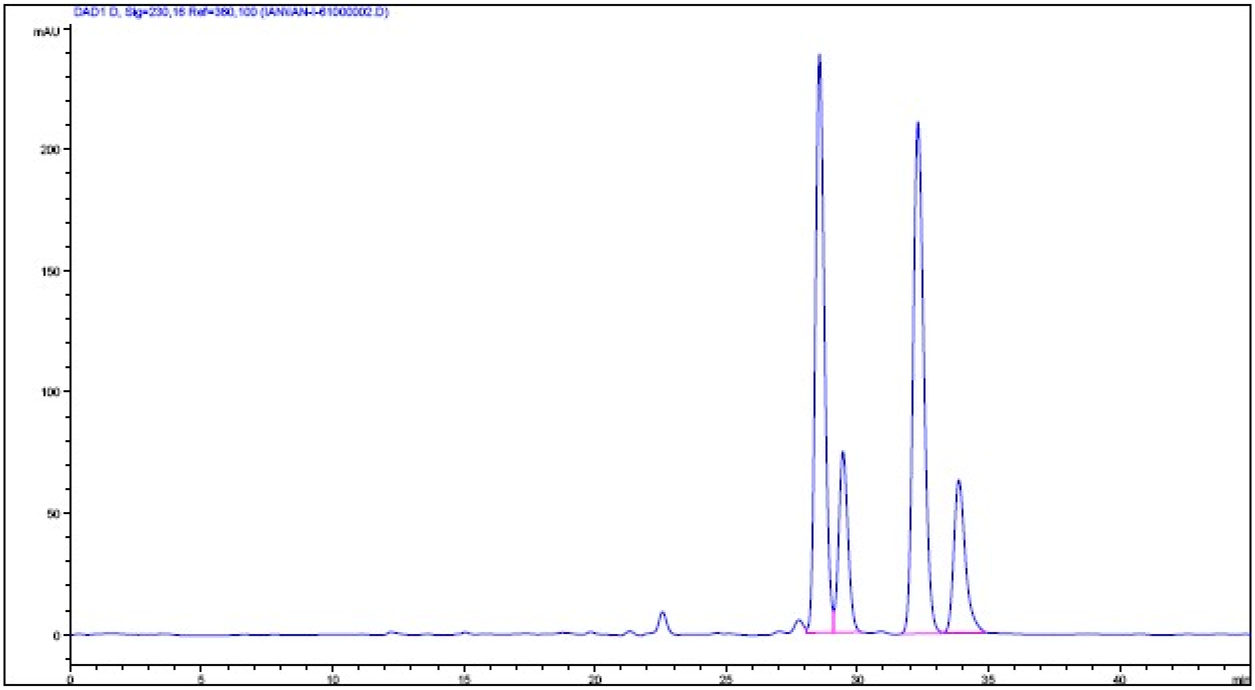

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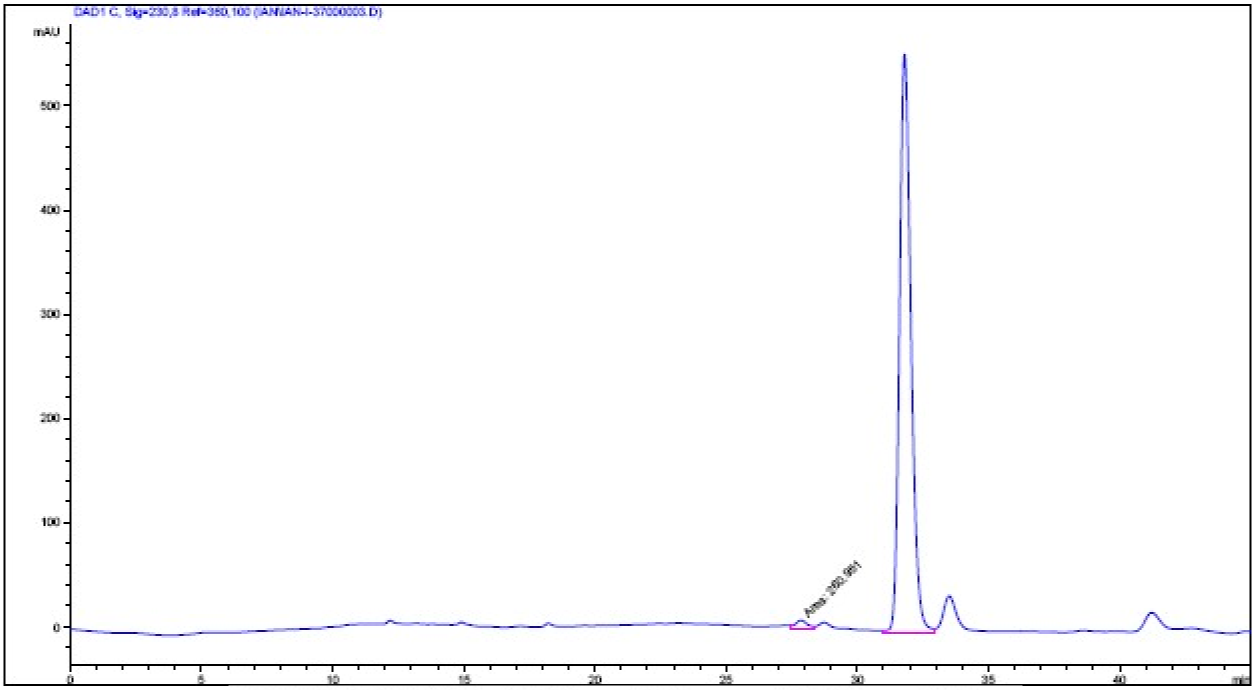

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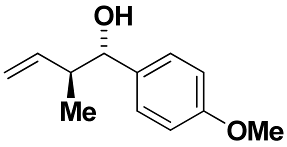
(*1S,2S*)-1-(4-methoxyphenyl)-2-methylbut-3-en-1-ol



4b

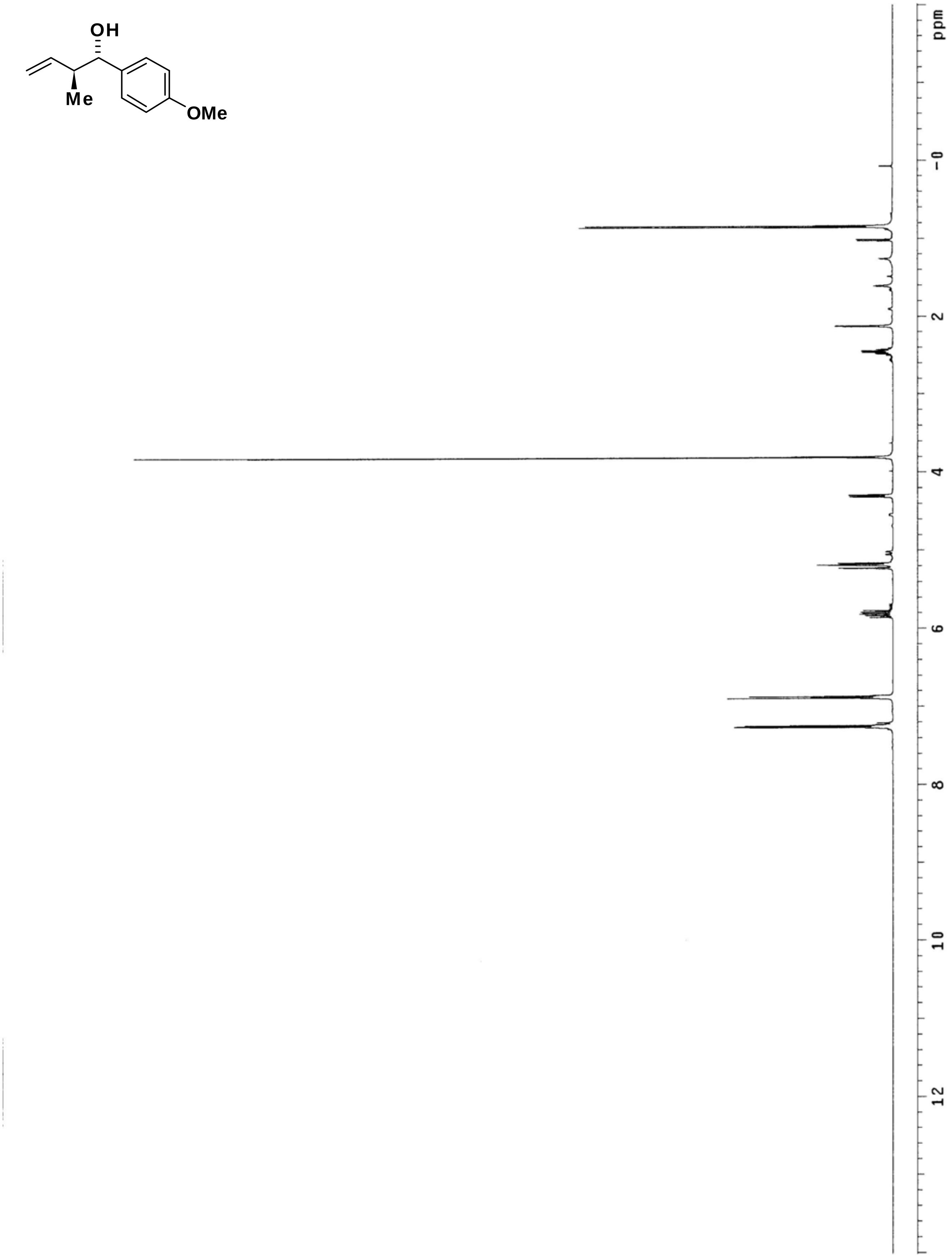
An oven-dried sealed tube under an atmosphere of N_2 was charged with (4-methoxyphenyl)methanol **2b** (27.6 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 °C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4b** (35.0 mg, 0.182 mmol) as a colorless oil in 91% yield (10:1 dr).

TLC (SiO_2): $R_f = 0.4$ (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.86-5.76 (m, 1H), 5.23-5.16 (m, 2H), 4.29 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.48-2.42 (m, 1H), 2.15 (br s, 1H), 0.83 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ159.3, 141.2, 134.8, 128.2, 117.0, 113.9, 77.7, 55.5, 46.7, 16.8.

HPLC: (Chiralpak AD-H/AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{minor} = 40.2 min, t_{major} = 47.6 min; ee = 95%.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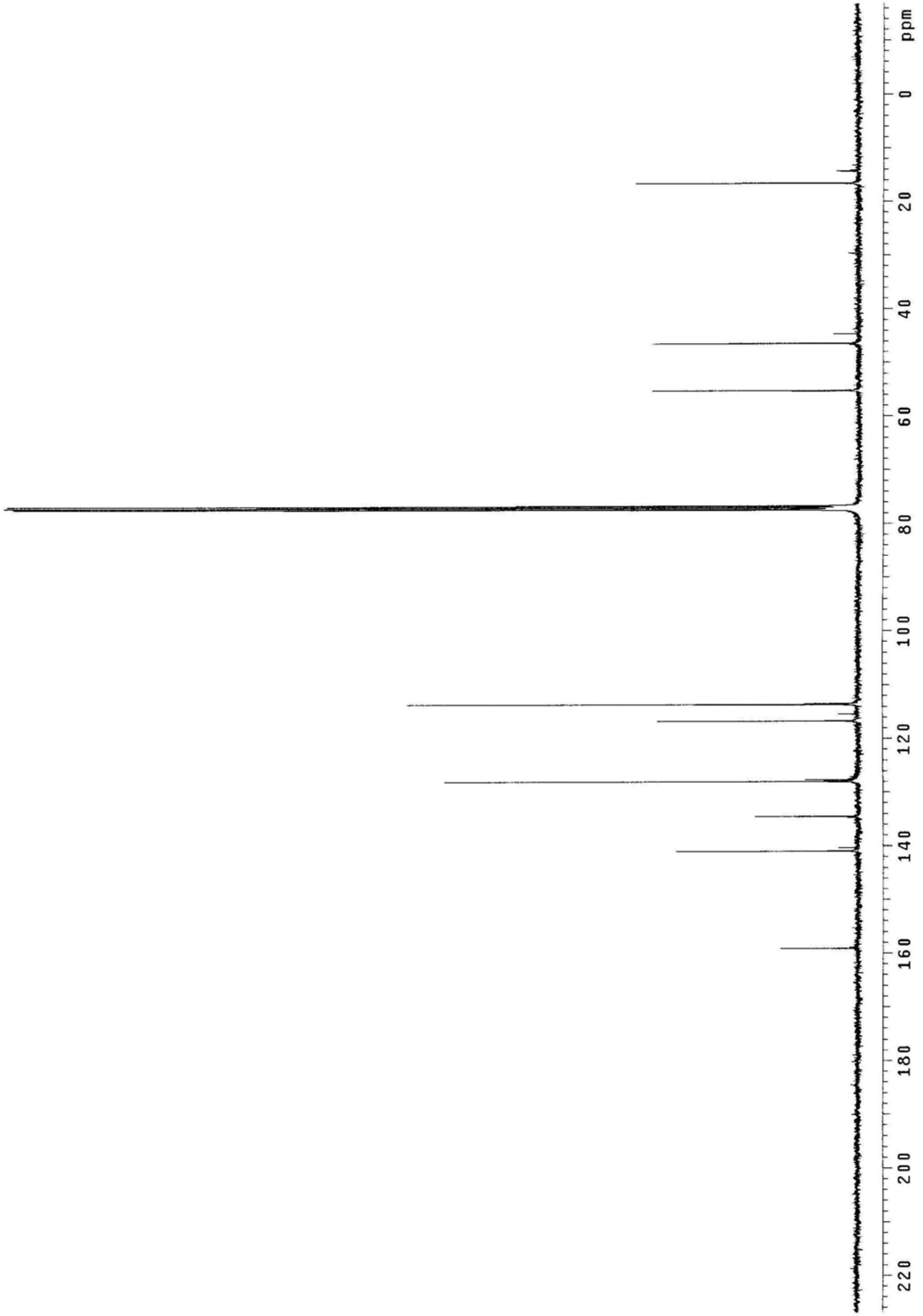
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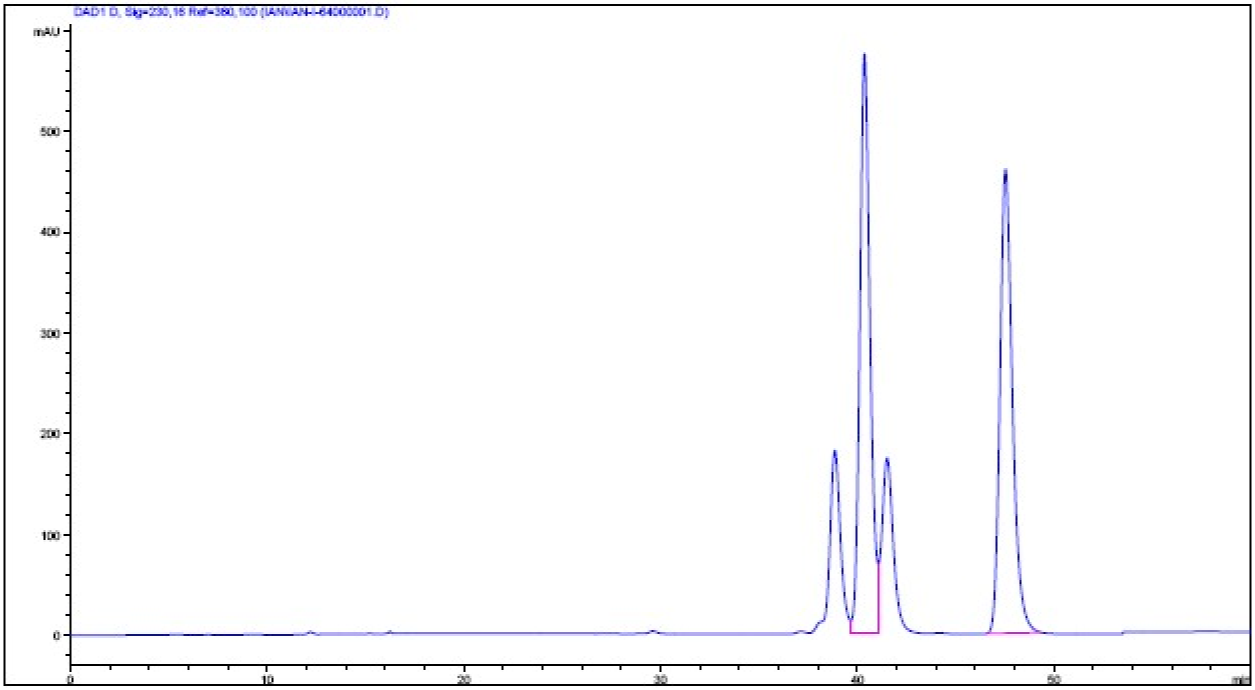

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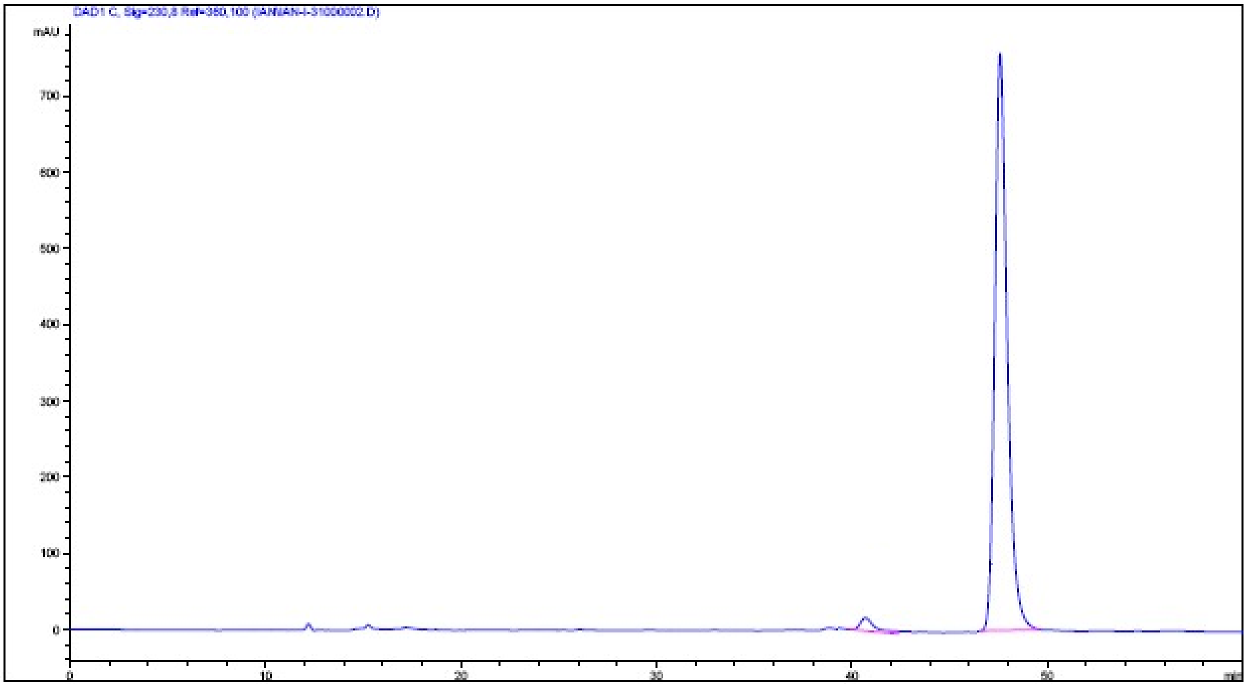

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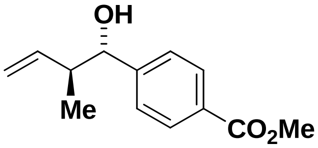
Methyl 4-((*1S,2S*)-1-hydroxy-2-methylbut-3-enyl)benzoate



4c

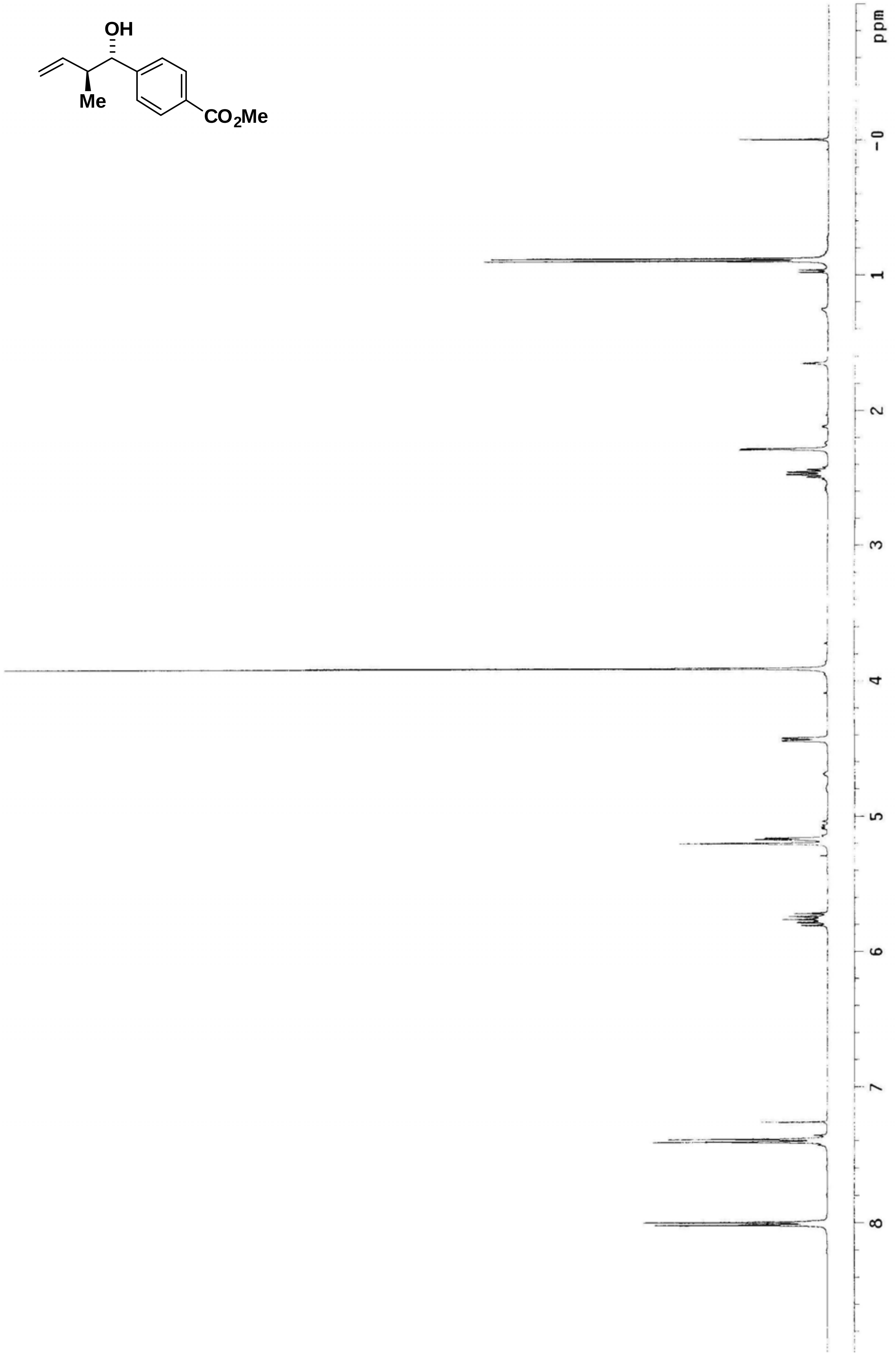
An oven-dried sealed tube under an atmosphere of N_2 was charged with methyl 4-(hydroxymethyl)benzoate **2c** (33.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 °C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4c** (34.4 mg, 0.156 mmol) as a colorless oil in 78% yield (11:1 dr).

TLC (SiO_2): $R_f = 0.4$ (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.79-5.69 (m, 1H), 5.17-5.12 (m, 2H), 4.40 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.49-2.36 (m, 2H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ167.2, 147.9, 140.1, 129.7, 129.6, 127.0, 117.5, 77.3, 52.3, 46.5, 16.6.

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 27.1 min, t_{major} = 32.3 min; ee = 98%.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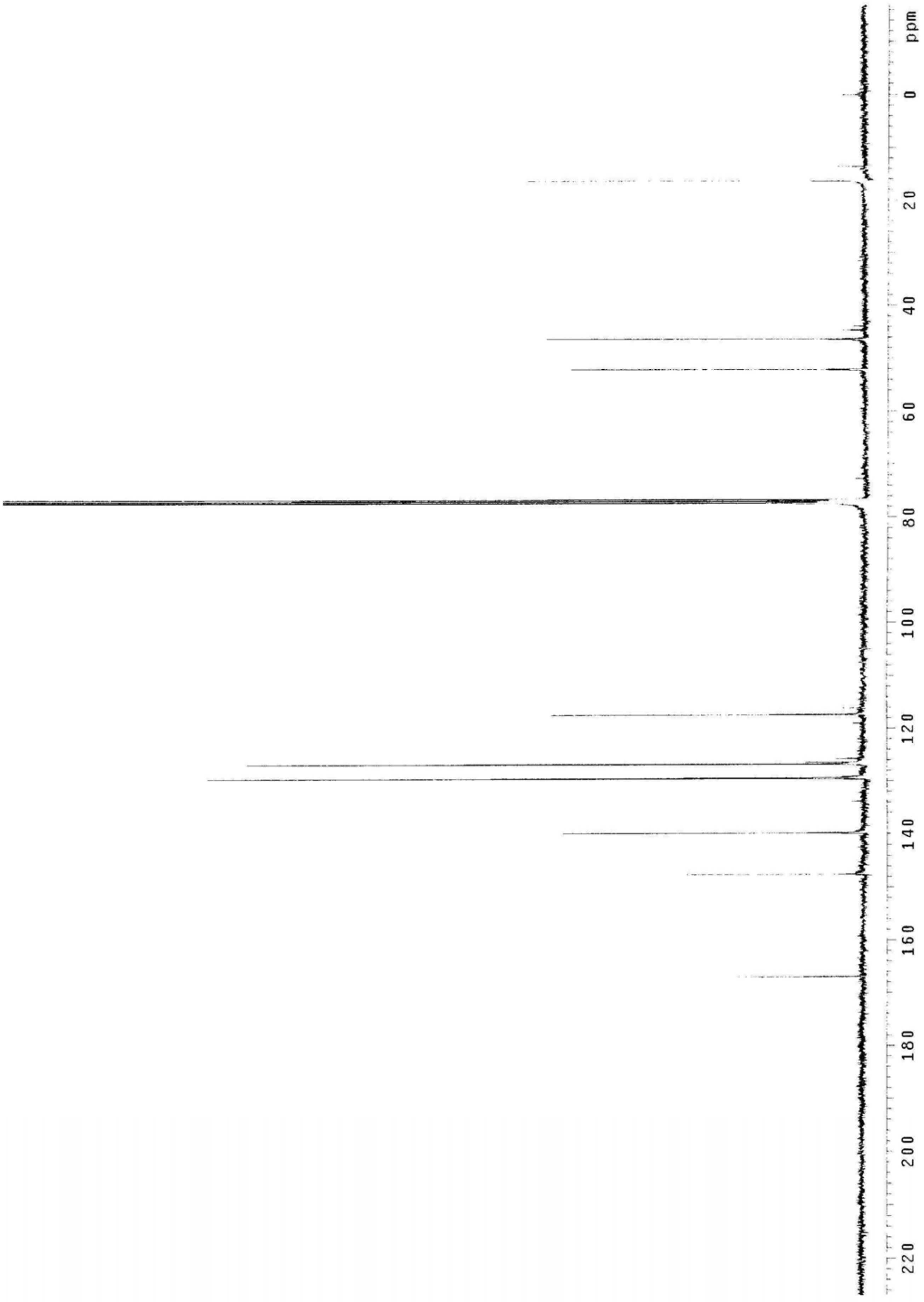
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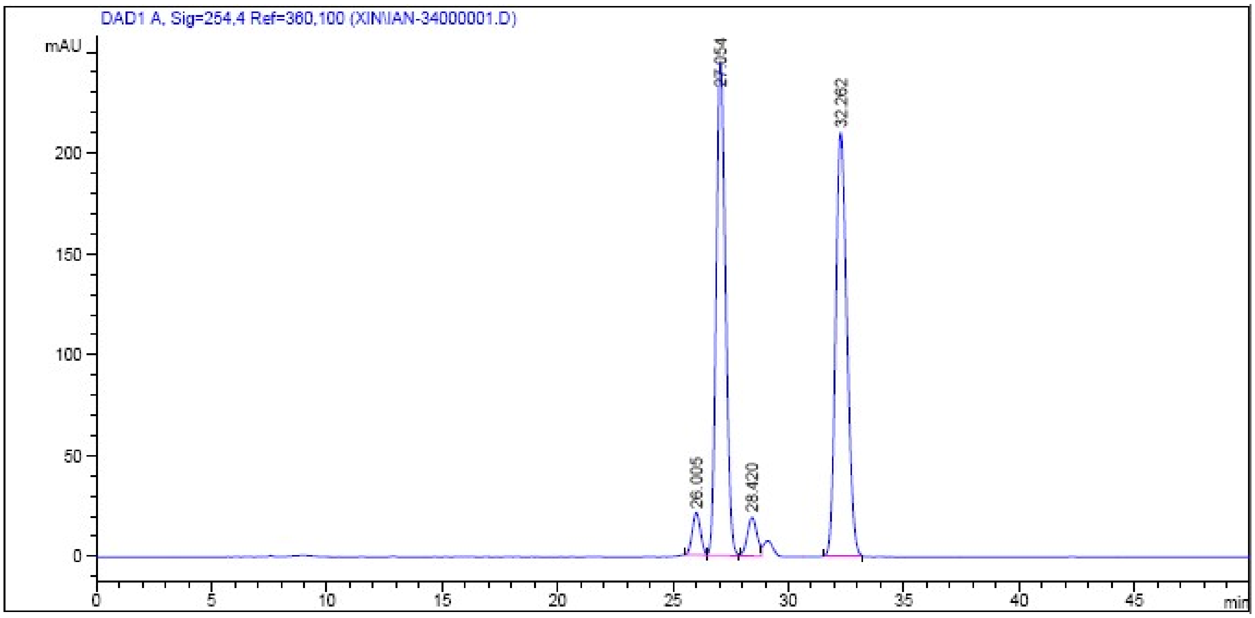

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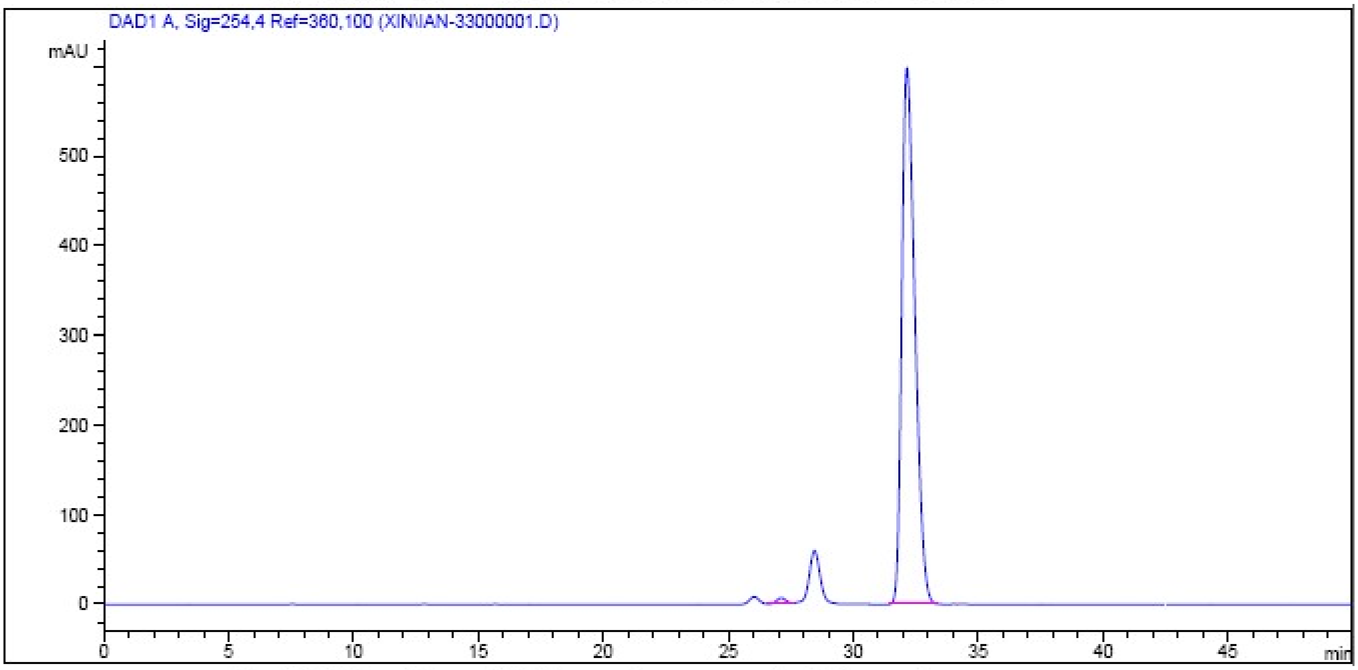

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   2  32.133 BB    0.5662 2.18716e4  598.67102  99.1221
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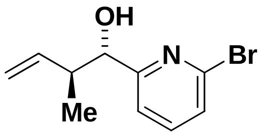
(*1S,2S*)-1-(6-bromopyridin-2-yl)-2-methylbut-3-en-1-ol



4d

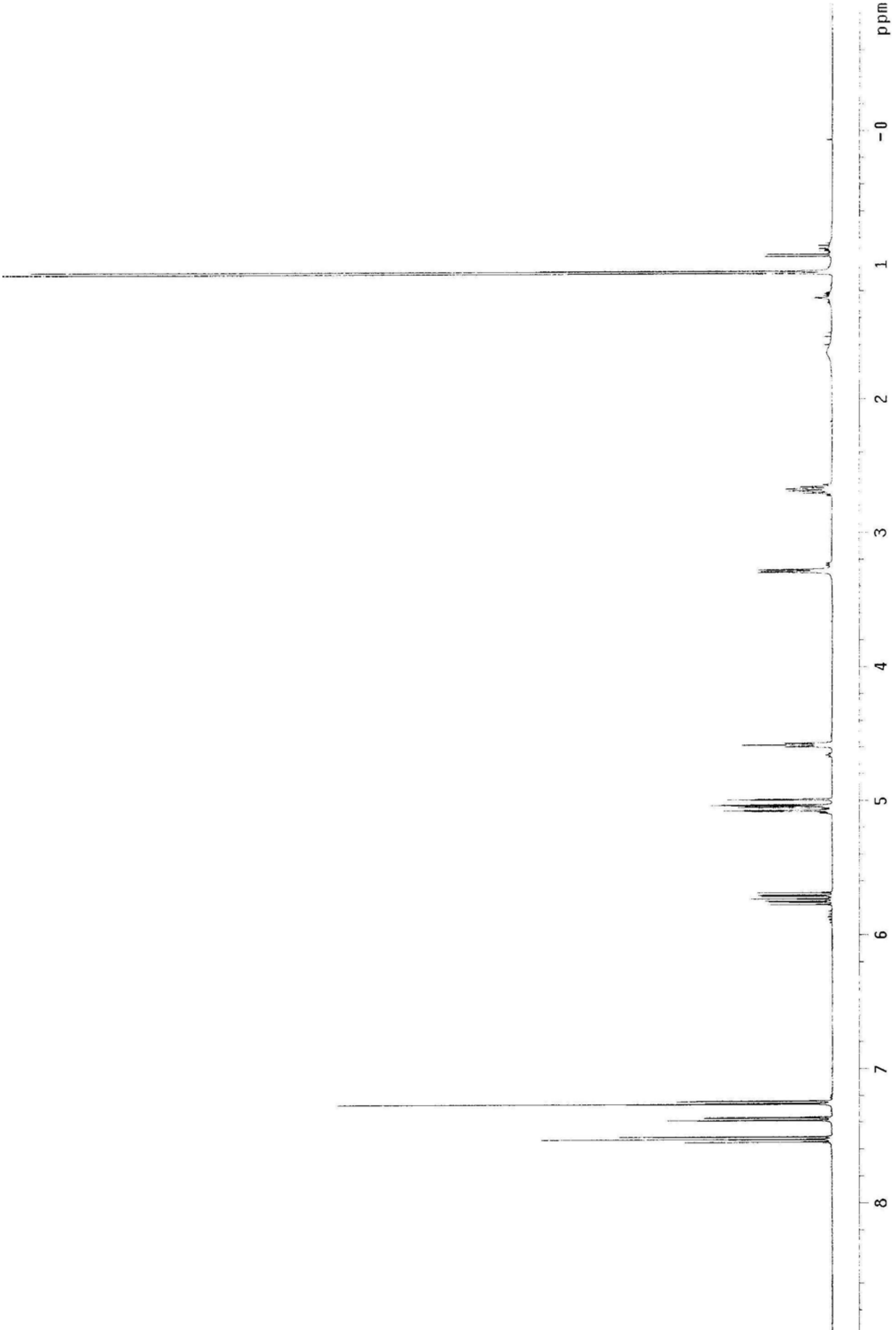
An oven-dried sealed tube under an atmosphere of N_2 was charged with (6-bromopyridin-2-yl)methanol **2d** (37.6 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4d** (24.2 mg, 0.100 mmol) as a colorless oil in 50% yield (14:1 dr).

TLC (SiO_2): $R_f = 0.3$ (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 5.73 (dt, *J* = 17.2, 10.4, 1H), 5.10-4.99 (m, 2H), 4.58 (t, *J* = 5.2 Hz, 1H), 3.28 (d, *J* = 6.0 Hz, 1H), 2.72-2.64 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 141.0, 138.7, 138.6, 126.7, 120.0, 116.5, 44.6, 16.1.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 210 nm), t_{major} = 12.1 min, t_{minor} = 16.8 min ; ee = 98%.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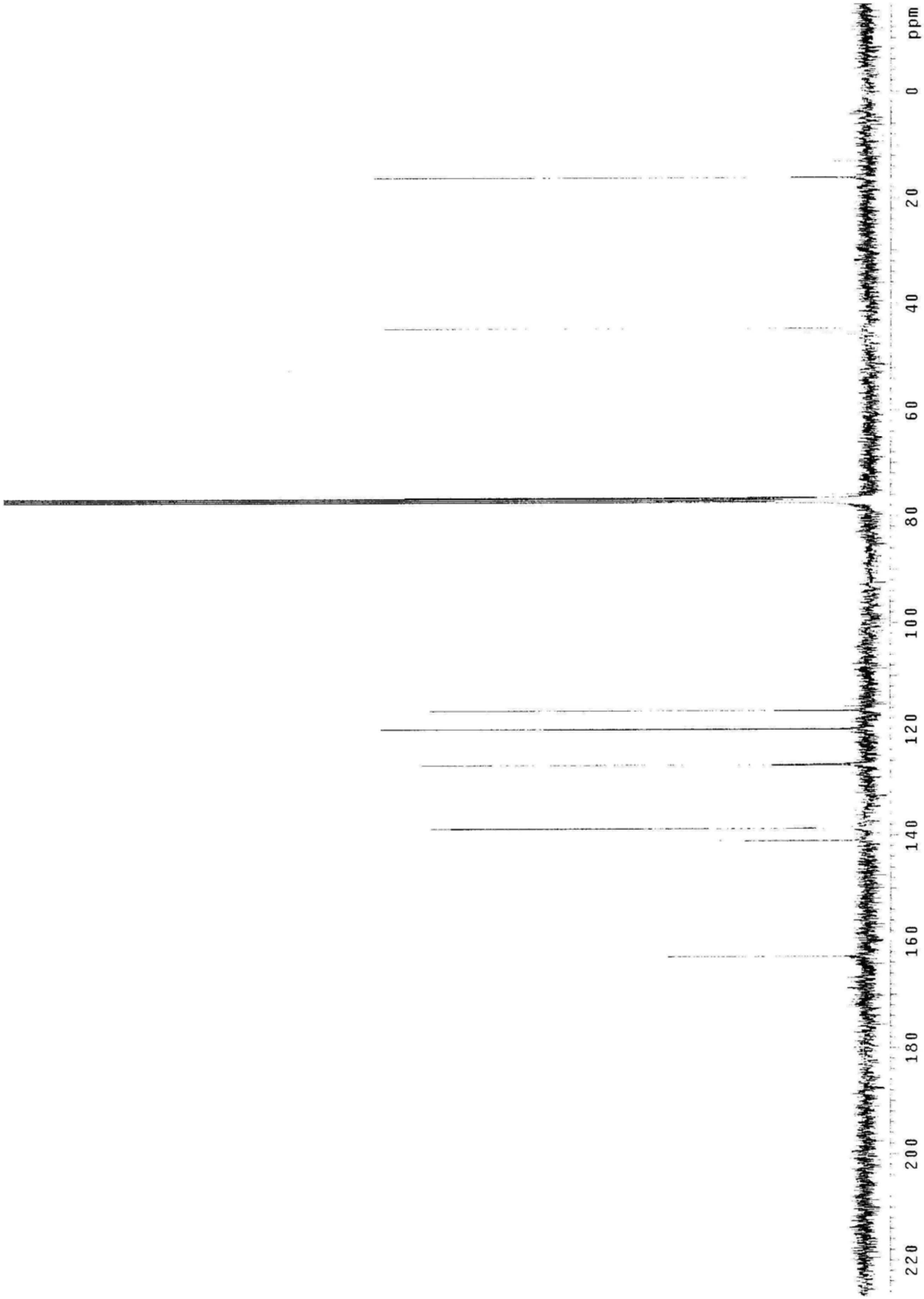
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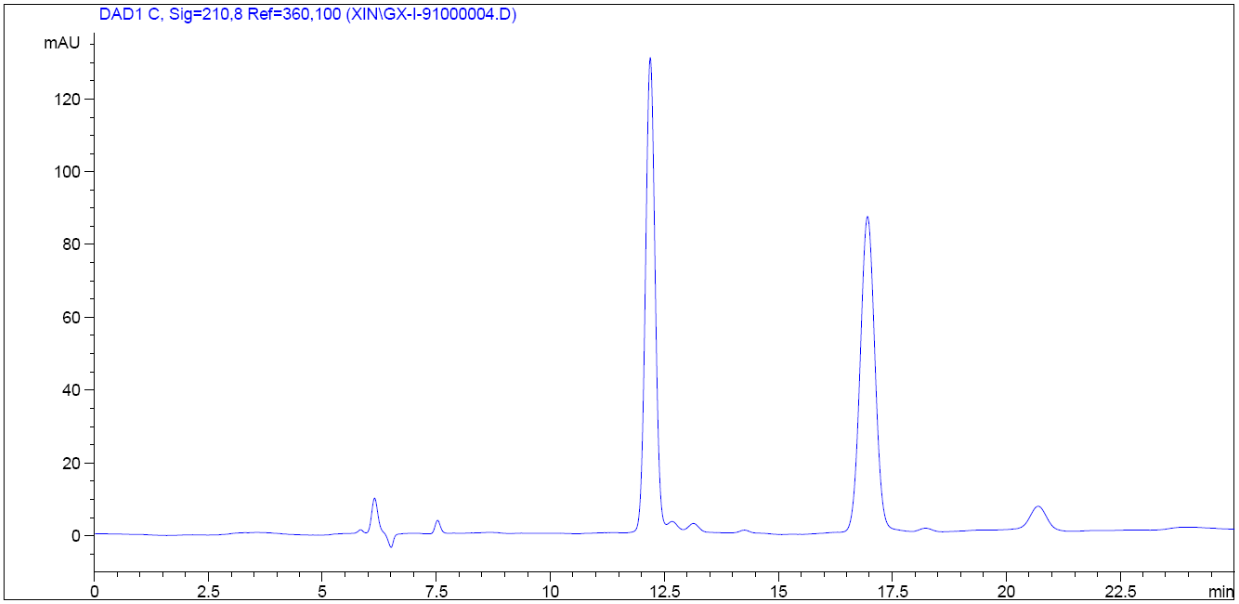

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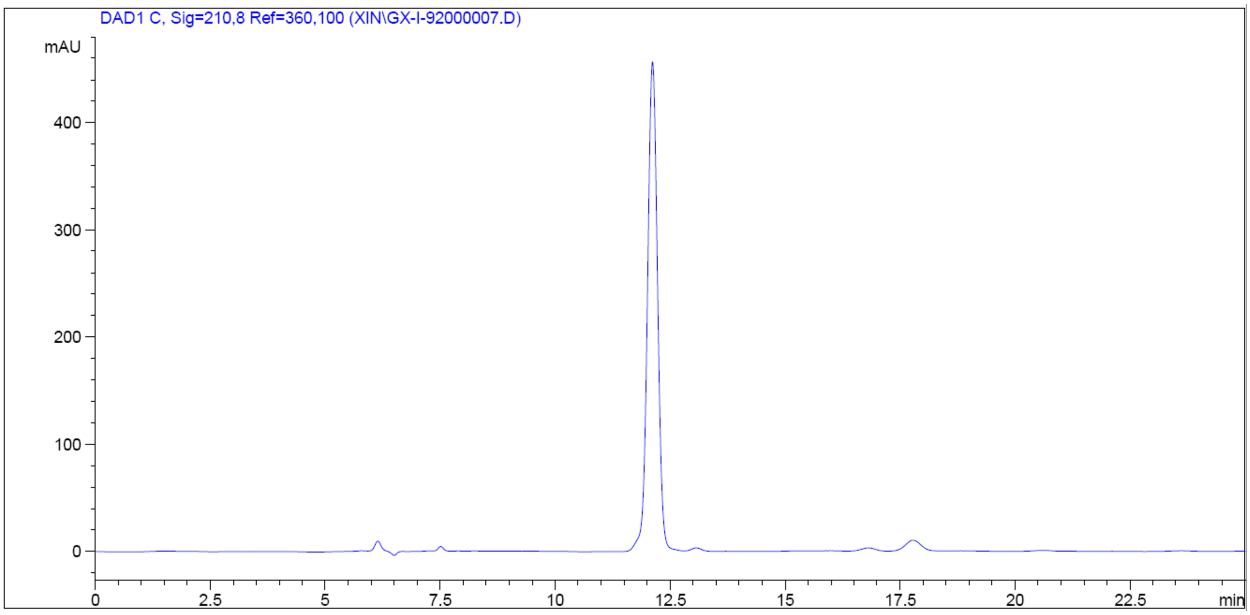

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  2  16.806 BB    0.2874   56.88535    2.89344   0.8132
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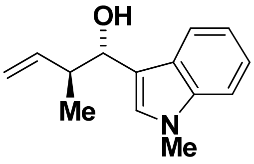
(*1S*,*2S*)-2-methyl-1-(1-methyl-1*H*-indol-3-yl)but-3-en-1-ol



4e

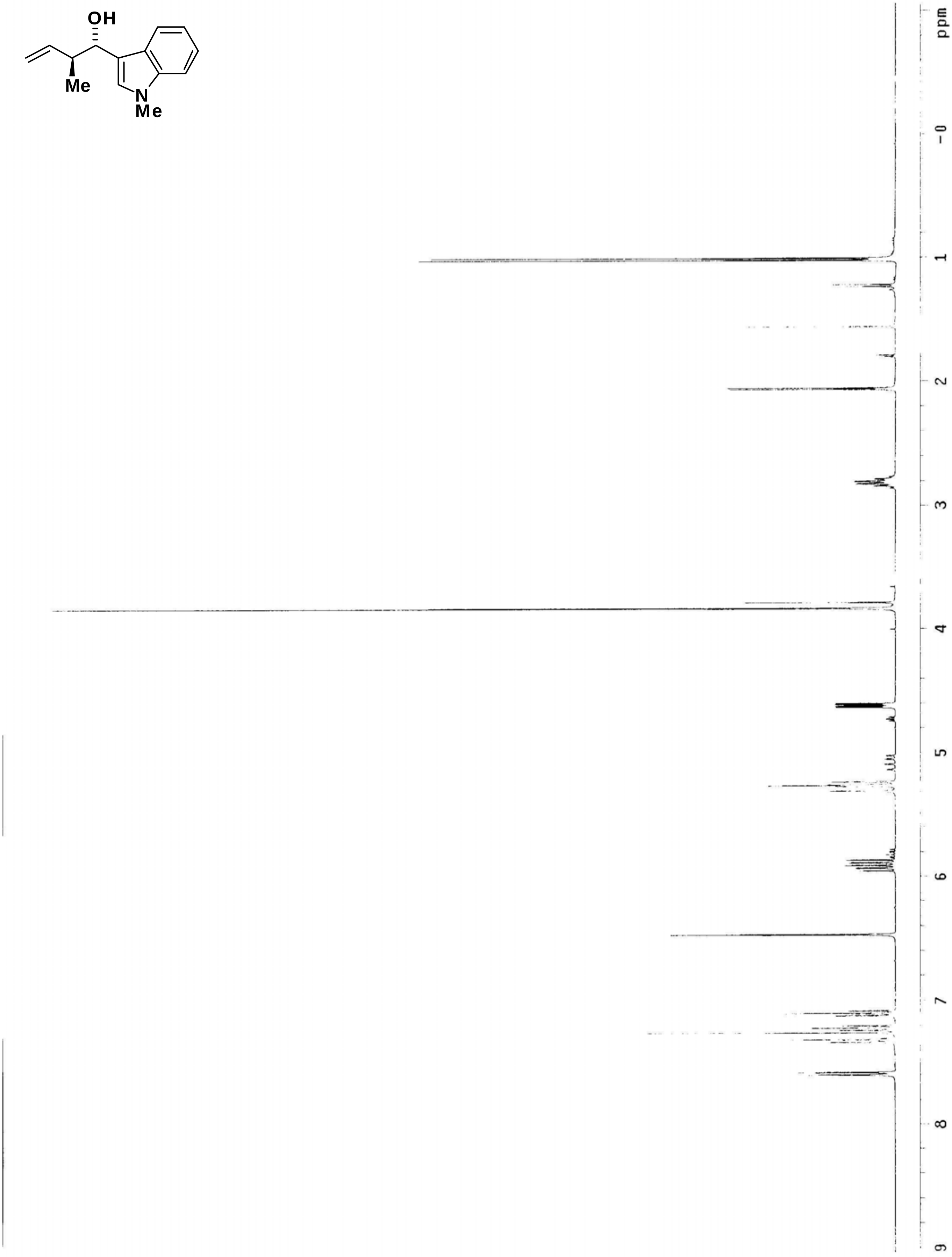
An oven-dried sealed tube under an atmosphere of N_2 was charged with (1-methyl-1*H*-indol-3-yl)methanol **2e** (32.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 °C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4e** (32.3 mg, 0.150 mmol) as a colorless oil in 75% yield (7:1 dr).

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 5.98-5.88 (m, 1H), 5.33-5.25 (m, 2H), 4.60 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.86-2.78 (m, 1H), 2.22 (br s, 1H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.3, 138.2, 127.5, 121.9, 120.9, 119.8, 117.4, 109.4, 100.8, 71.4, 44.3, 30.7, 17.5.

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 254 nm), t_{major} = 53.3 min, t_{minor} = 66.0 min; ee = 98%.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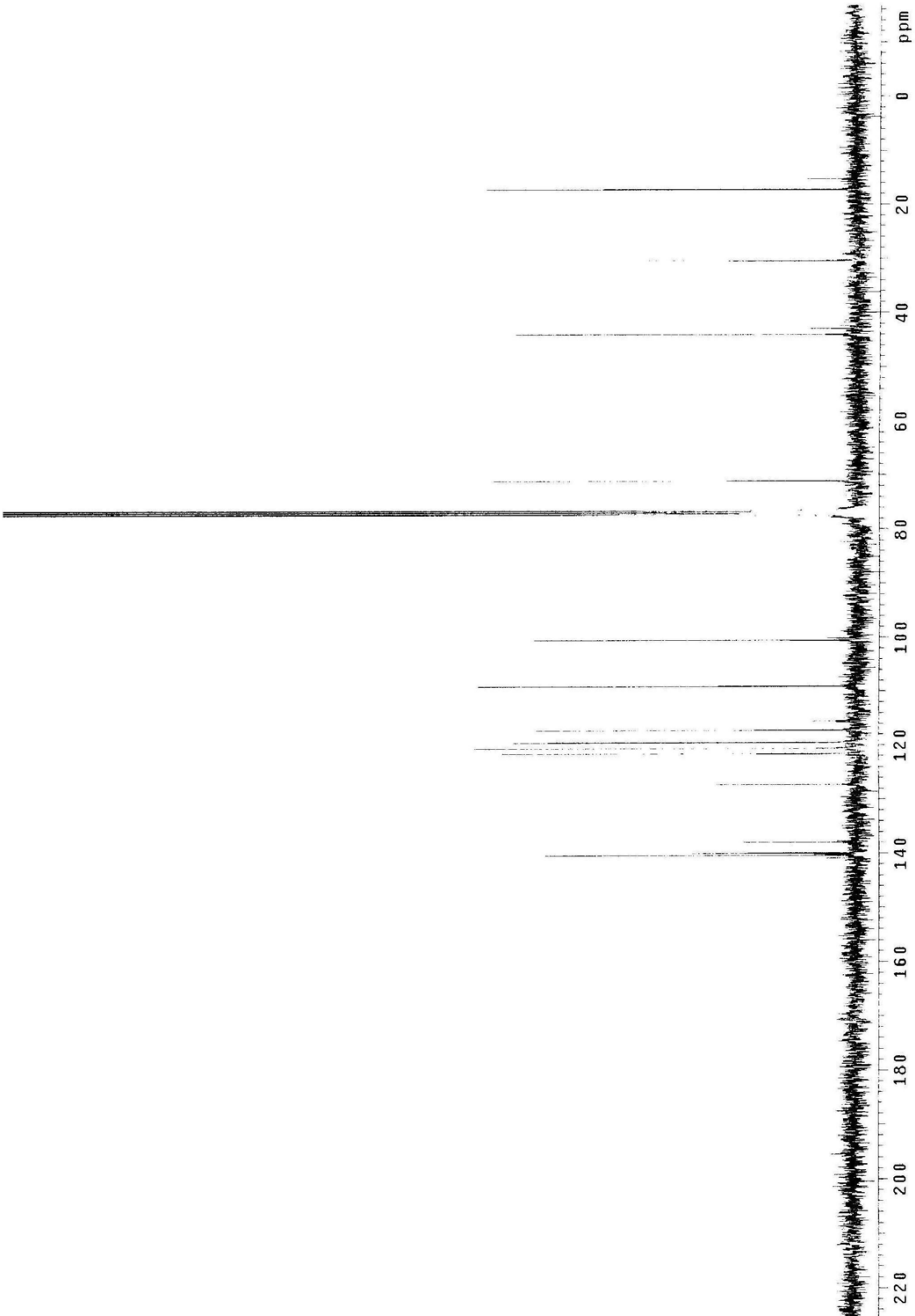
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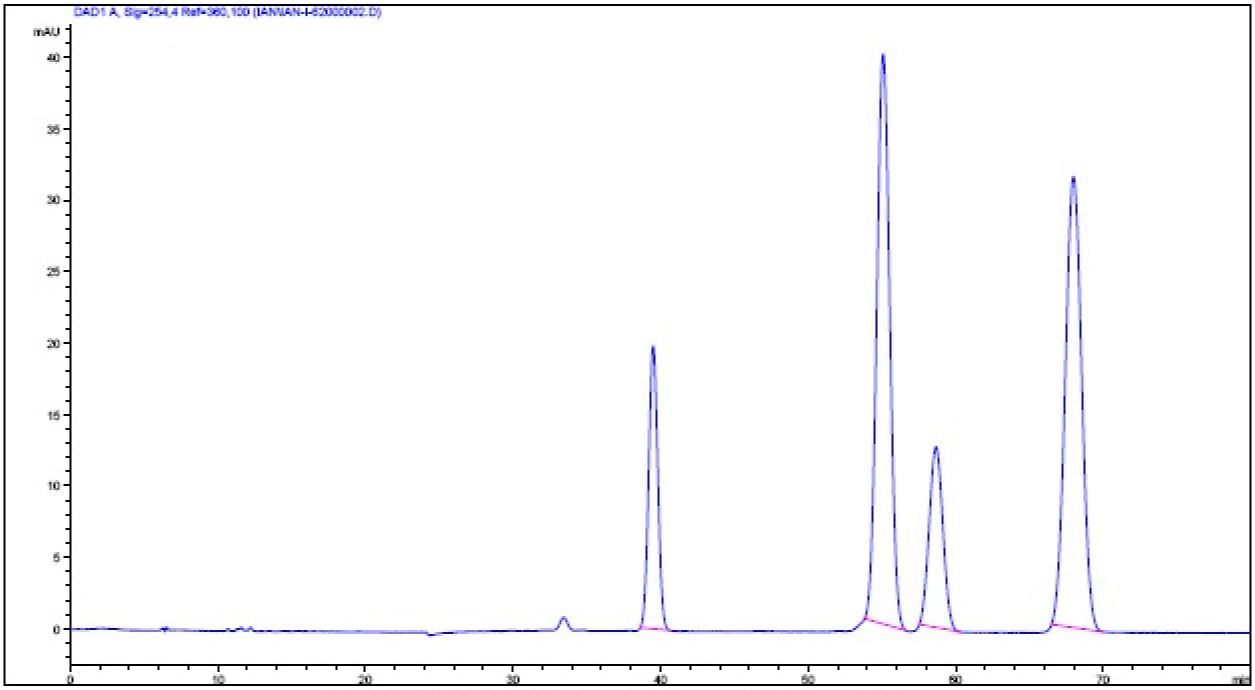

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   4  67.979 BB    1.0884 2437.29663   31.58078 37.2813
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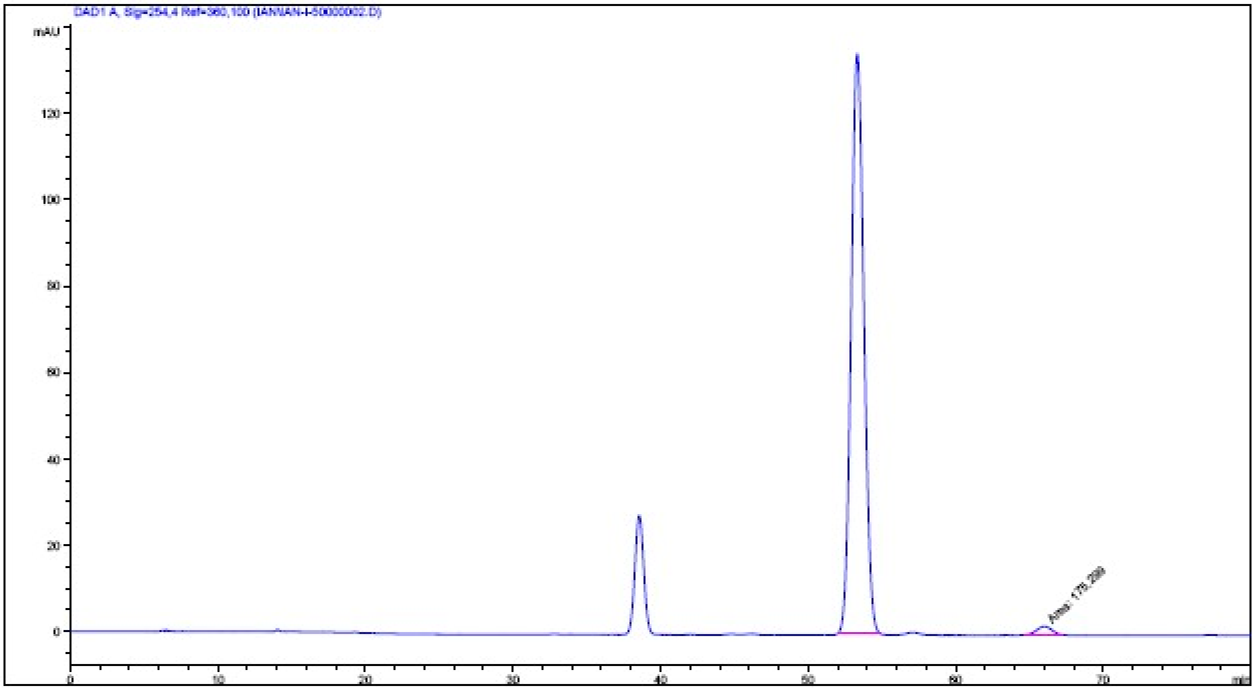

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   1  53.326 BB    0.9330 8082.24170  134.51173 98.8771
   2  66.037 MM    1.3160  175.29871    2.22011  1.1229
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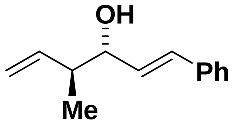
(*3R,4S,E*)-4-methyl-1-phenylhexa-1,5-dien-3-ol



4f

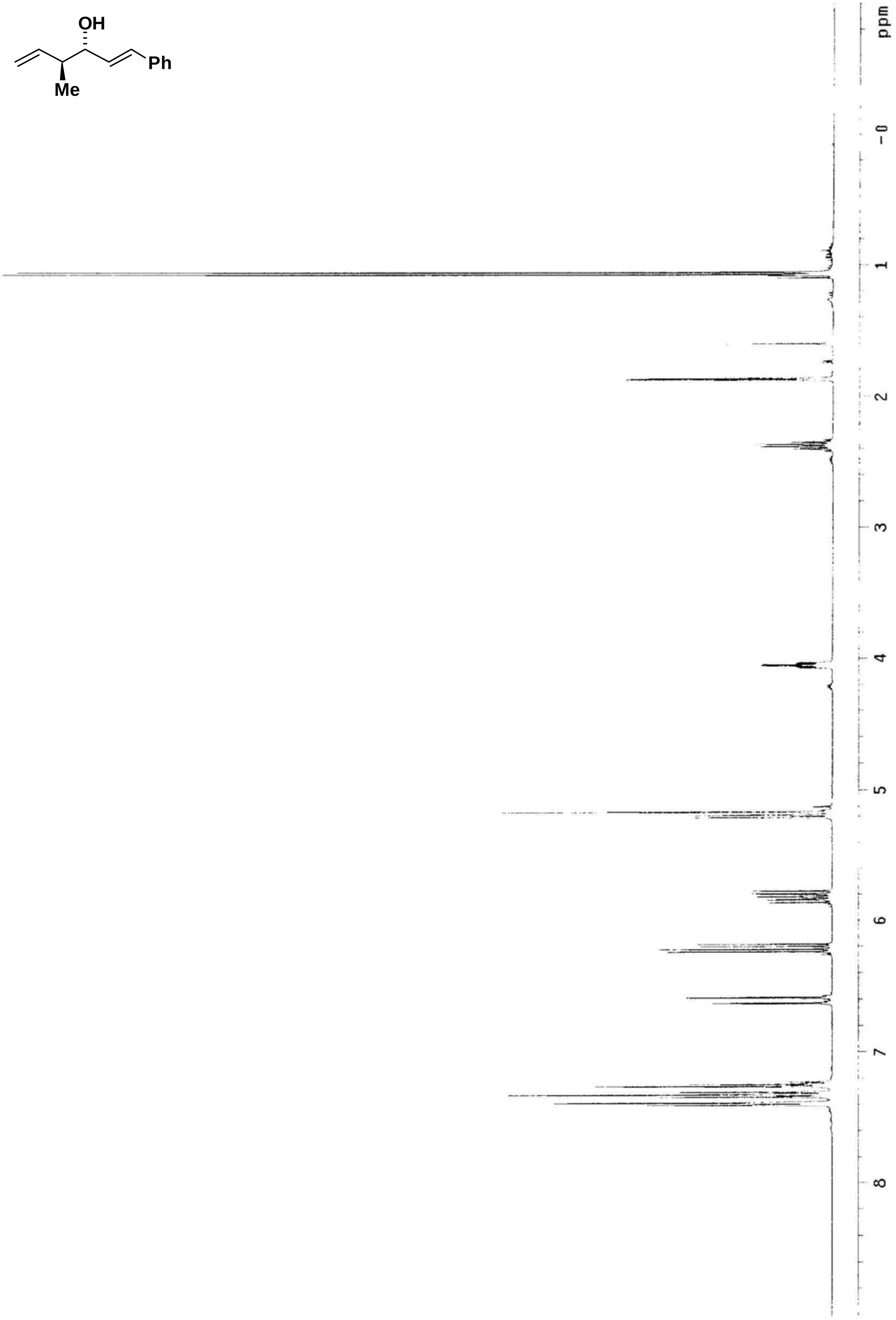
An oven-dried sealed tube under an atmosphere of N_2 was charged with *trans*-cinnamyl alcohol **2f** (26.8 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 70 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4f** (27.1 mg, 0.144 mmol) as a colorless oil in 72% yield (10:1 dr).

TLC (SiO_2): R_f = 0.3 (ethyl acetate:hexanes, 1:10).

^{1}H NMR (400 MHz, CDCl3): δ 7.41-7.23 (m, 5H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0, 7.2 Hz, 1H), 5.88-5.78 (m, 1H), 5.21-5.16 (m, 2H), 4.06 (t, *J* = 6.8 Hz, 1H), 2.41-2.35 (m, 1H), 1.99 (br s, 1H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl3): δ 140.4, 136.9, 132.0, 130.4, 128.8, 127.9, 126.8, 117.0, 76.4, 44.9, 16.3.

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 26.8 min, t_{major} = 31.5 min; ee = 93%.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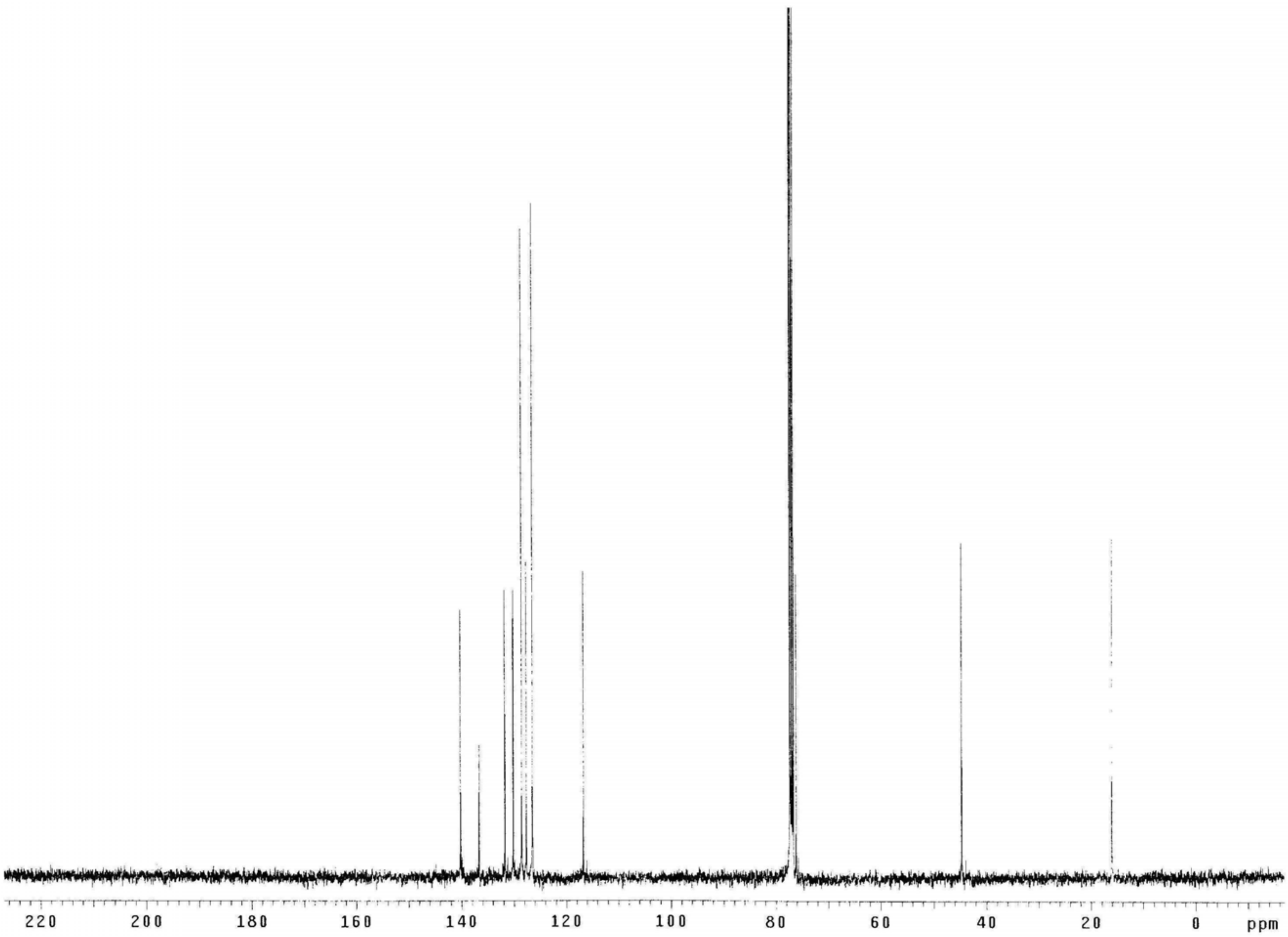
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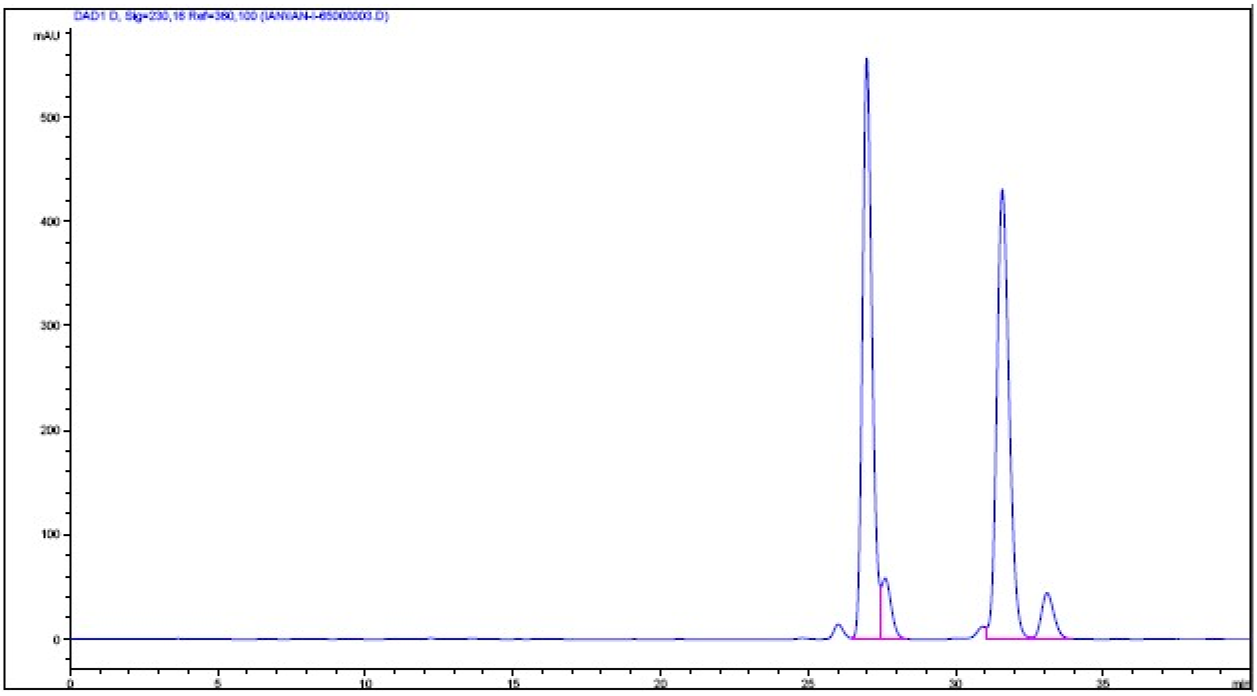

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   2  27.611 VB    0.3413 1330.46252   58.51318   4.7848
   3  31.580 VB    0.4475 1.25149e4   430.09030  45.0083
   4  33.097 BB    0.4564 1284.49683   43.77251   4.6195
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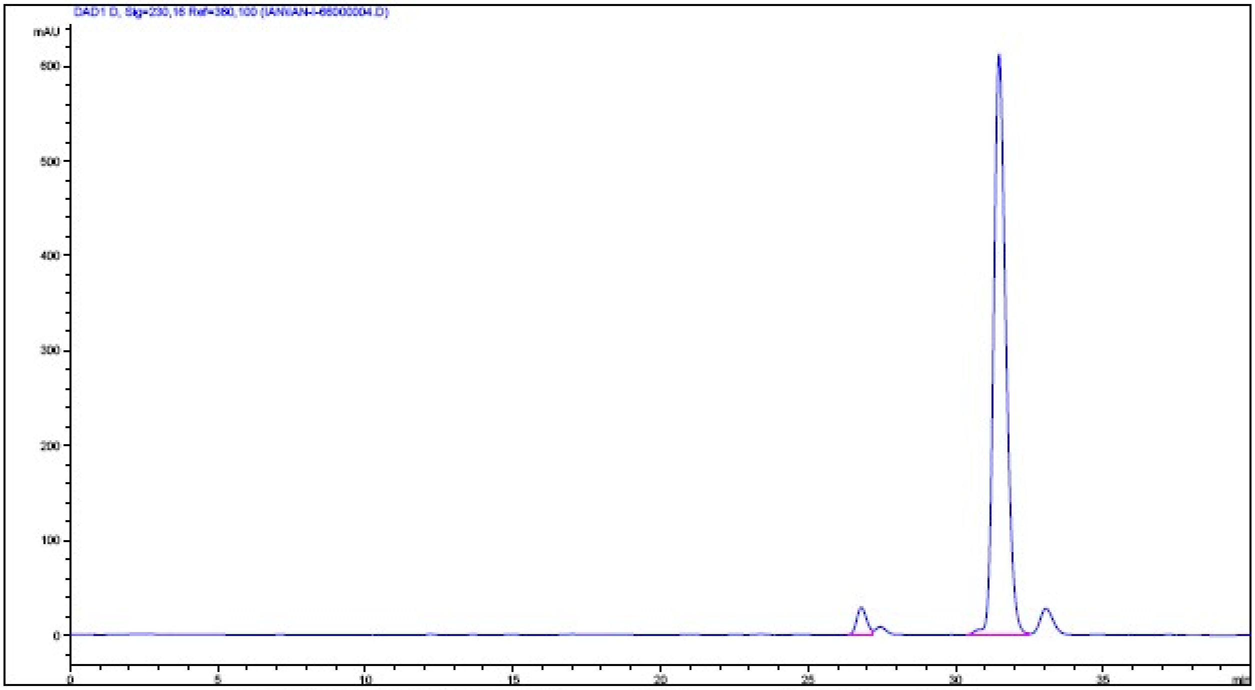

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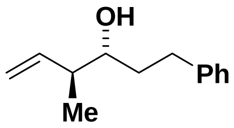
   1  26.797 BV    0.3670  682.55109   28.95984   3.7180
   2  31.467 BB    0.4385 1.76757e4   612.88232  96.2820
```

(*3R,4S*)-4-methyl-1-phenylhex-5-en-3-ol



4g

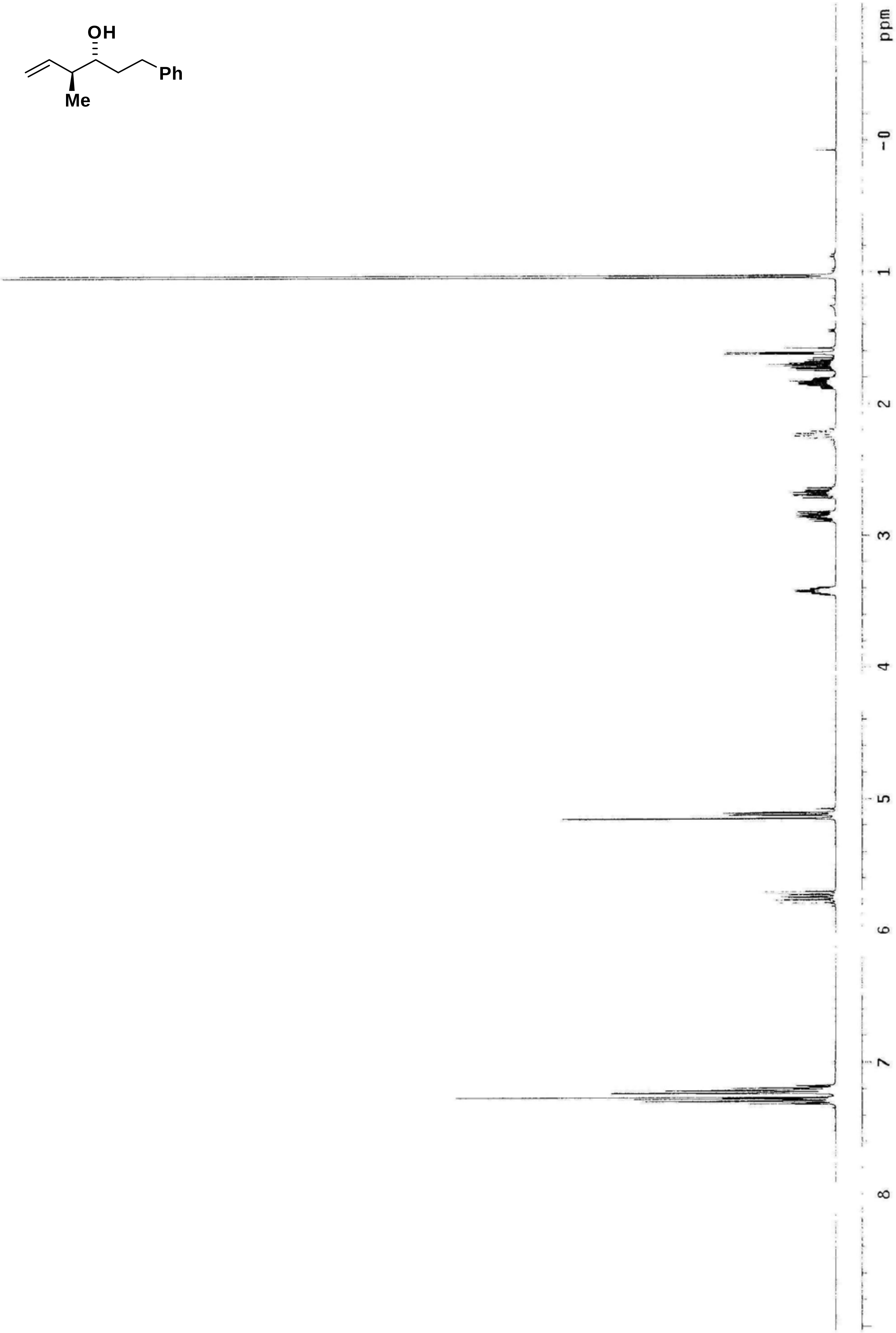
An oven-dried sealed tube under an atmosphere of N_2 was charged with 3-phenylpropan-1-ol **2g** (27.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4g** (27.0 mg, 0.142 mmol) as a colorless oil in 71% yield (>20:1 dr).

TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexanes, 1:5).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.17 (m, 5H), 5.80-5.70 (m, 1H), 5.15-5.10 (m, 2H), 3.43-3.40 (m, 1H), 2.89-2.81 (m, 1H), 2.72-2.64 (m, 1H), 2.26-2.20 (m, 1H), 1.89-1.80 (m, 1H), 1.75-1.62 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.4, 128.7, 128.6, 126.0, 116.8, 74.2, 44.6, 36.4, 32.4, 16.5.

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 254 nm), t_{minor} = 11.5 min, t_{major} = 18.7 min; ee = 99%.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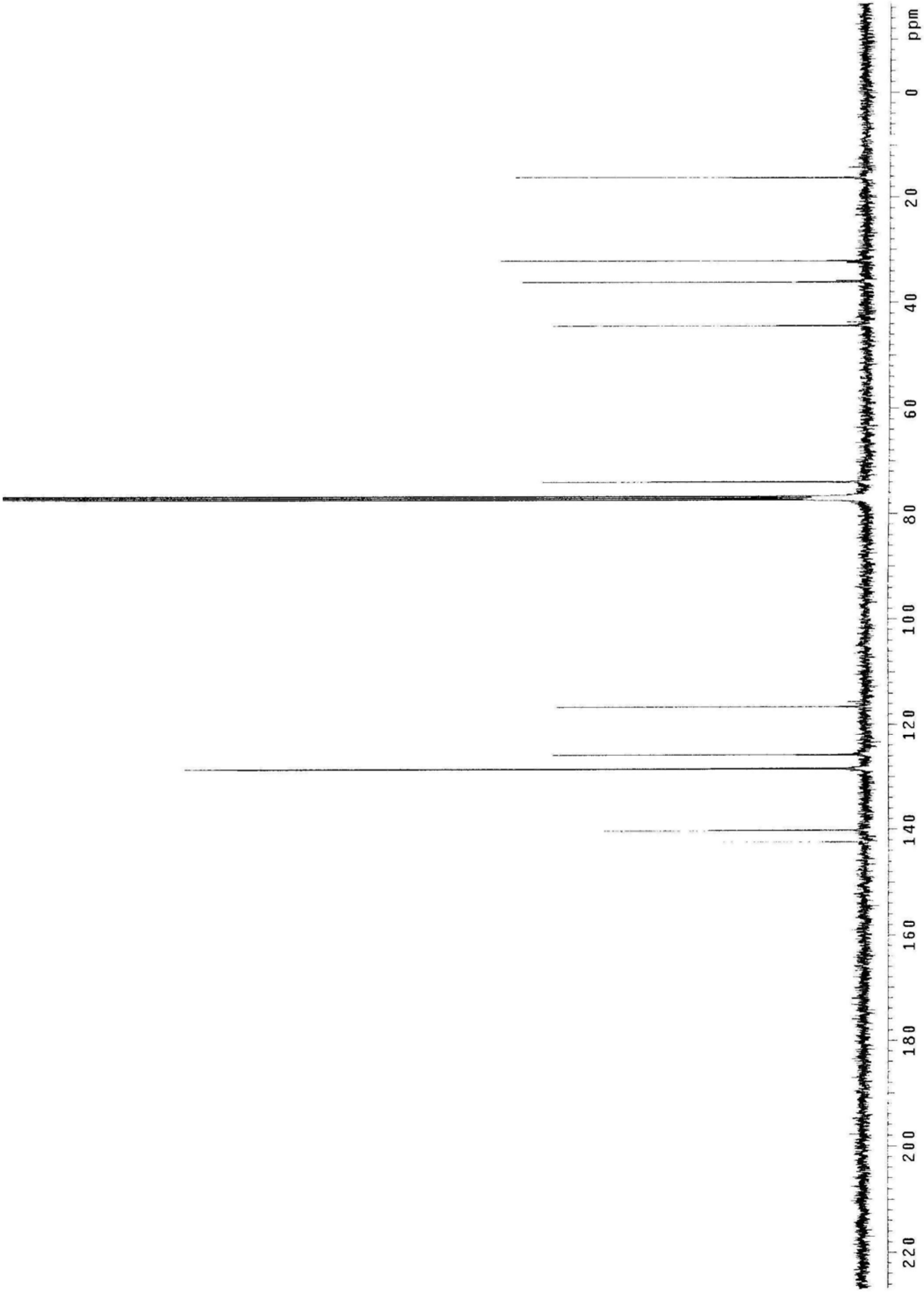
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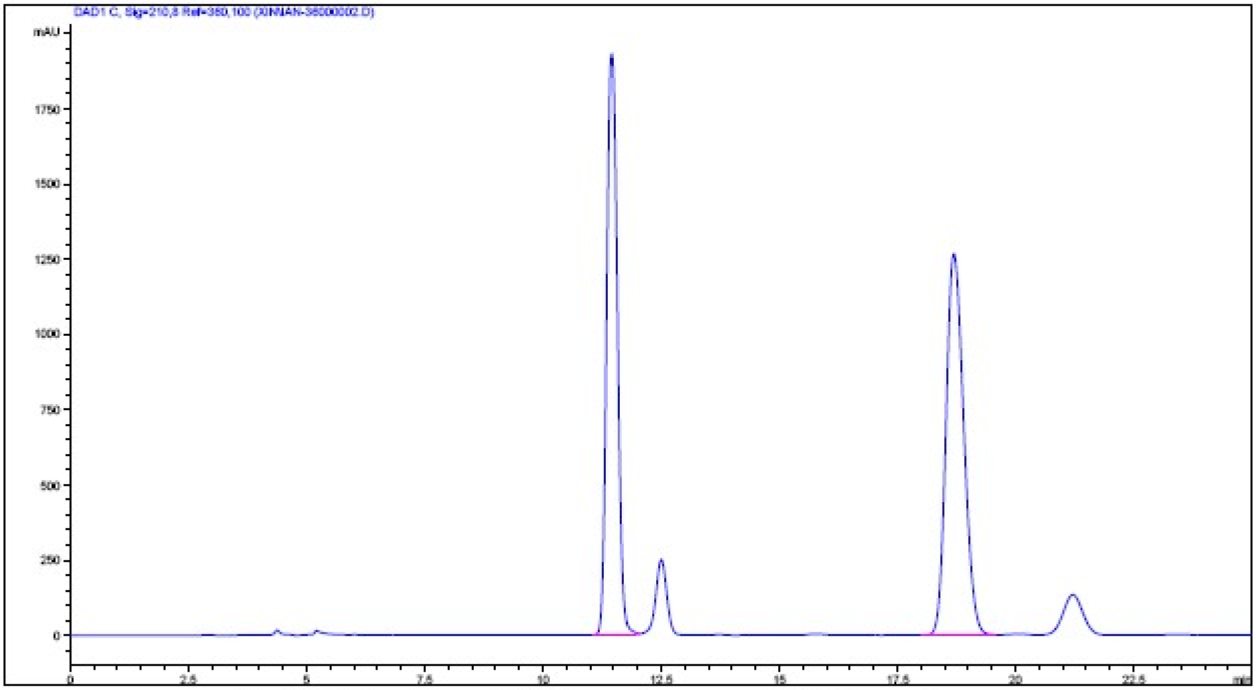

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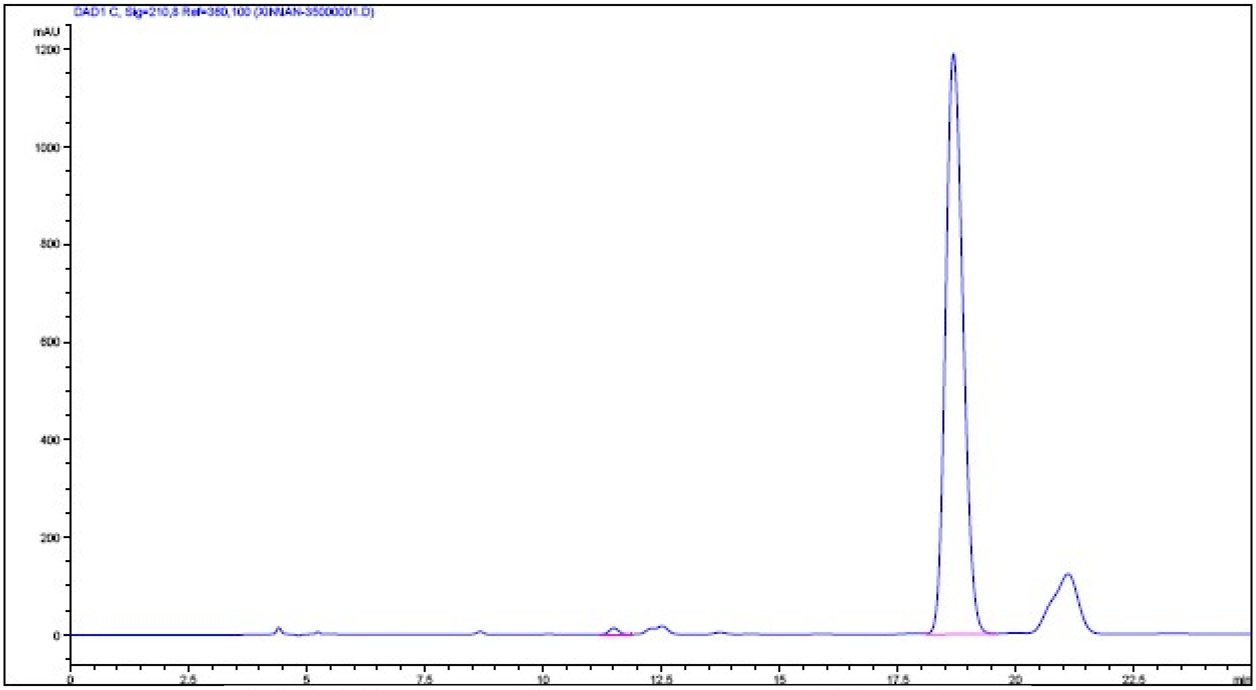

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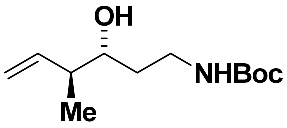
----|-------|----|-------|----------|----------|--------|
   1  11.503 BB     0.2170  179.06799   12.97591   0.5821
   2  18.685 BB     0.4019 3.05811e4 1189.62244  99.4179
```

tert-butyl (3R,4S)-3-hydroxy-4-methylhex-5-enylcarbamate



4h

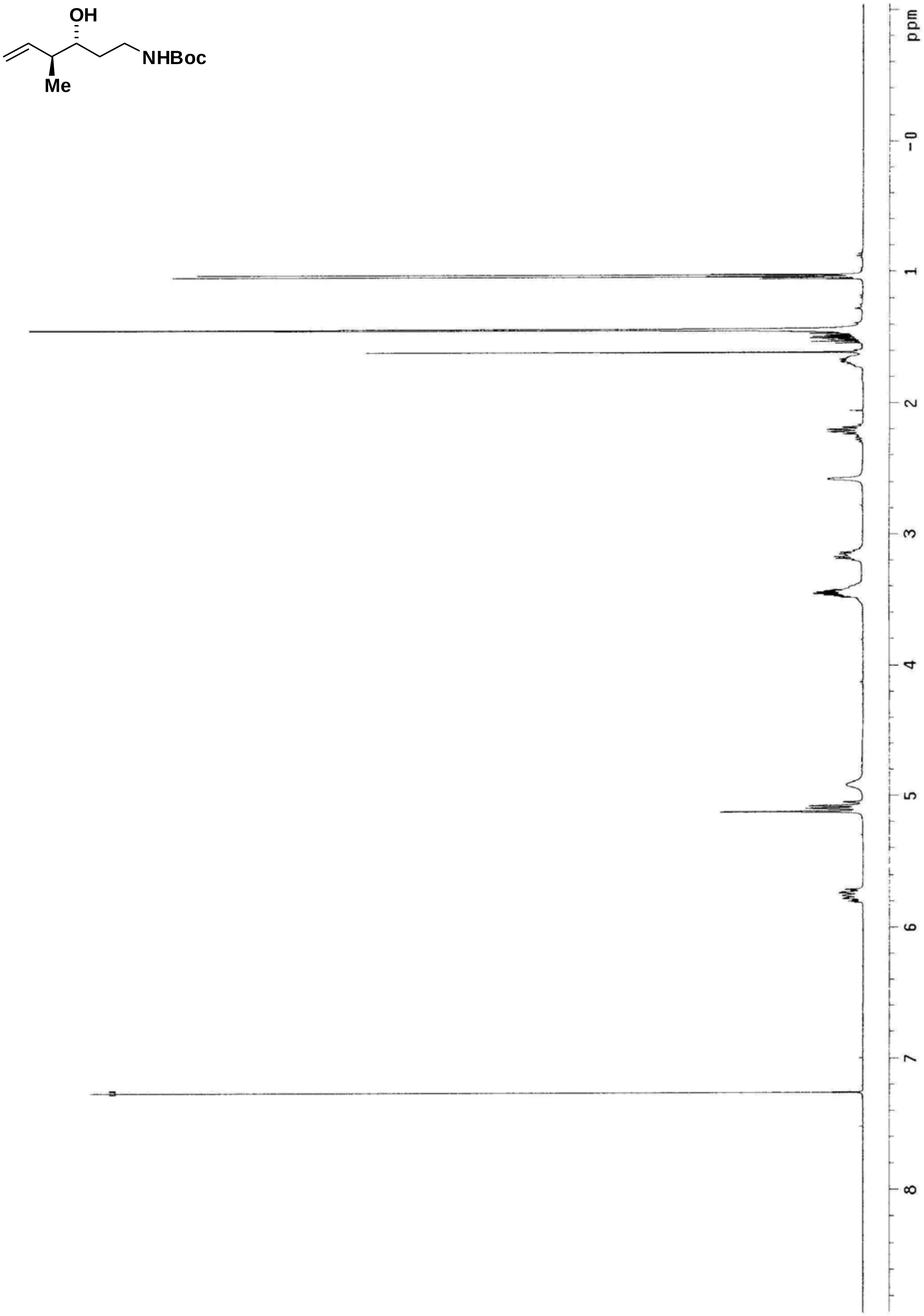
An oven-dried sealed tube under an atmosphere of N_2 was charged with *tert*-butyl 3-hydroxypropylcarbamate **2h** (35.0 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 70 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4h** (32.6 mg, 0.142 mmol) as a colorless oil in 71% yield (>20:1 dr).

TLC (SiO_2): R_f = 0.5 (ethyl acetate:hexanes, 1:3).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 (dtd, *J* = 17.2, 10.0, 0.4 Hz, 1H), 5.12-5.05 (m, 2H), 4.91 (br, 1H), 3.48-3.41 (m, 2H), 3.20-3.11 (m, 1H), 2.58 (d, *J* = 2.8 Hz, 1H), 2.30-2.17 (m, 1H), 1.72-1.64 (m, 1H), 1.54-1.45 (m, 1H), 1.44 (s, 9H), 1.03 (d, *J* = 6.8 Hz,3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 140.4, 116.1, 79.3, 72.6, 44.2, 37.7, 34.2, 28.4, 16.2.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product (Chiralcel OJ-H column, hexanes:*i*-PrOH = 98:2, 0.75 mL/min, 254 nm), t_{minor} = 24.4 min, t_{major} = 28.1 min; ee = 96%.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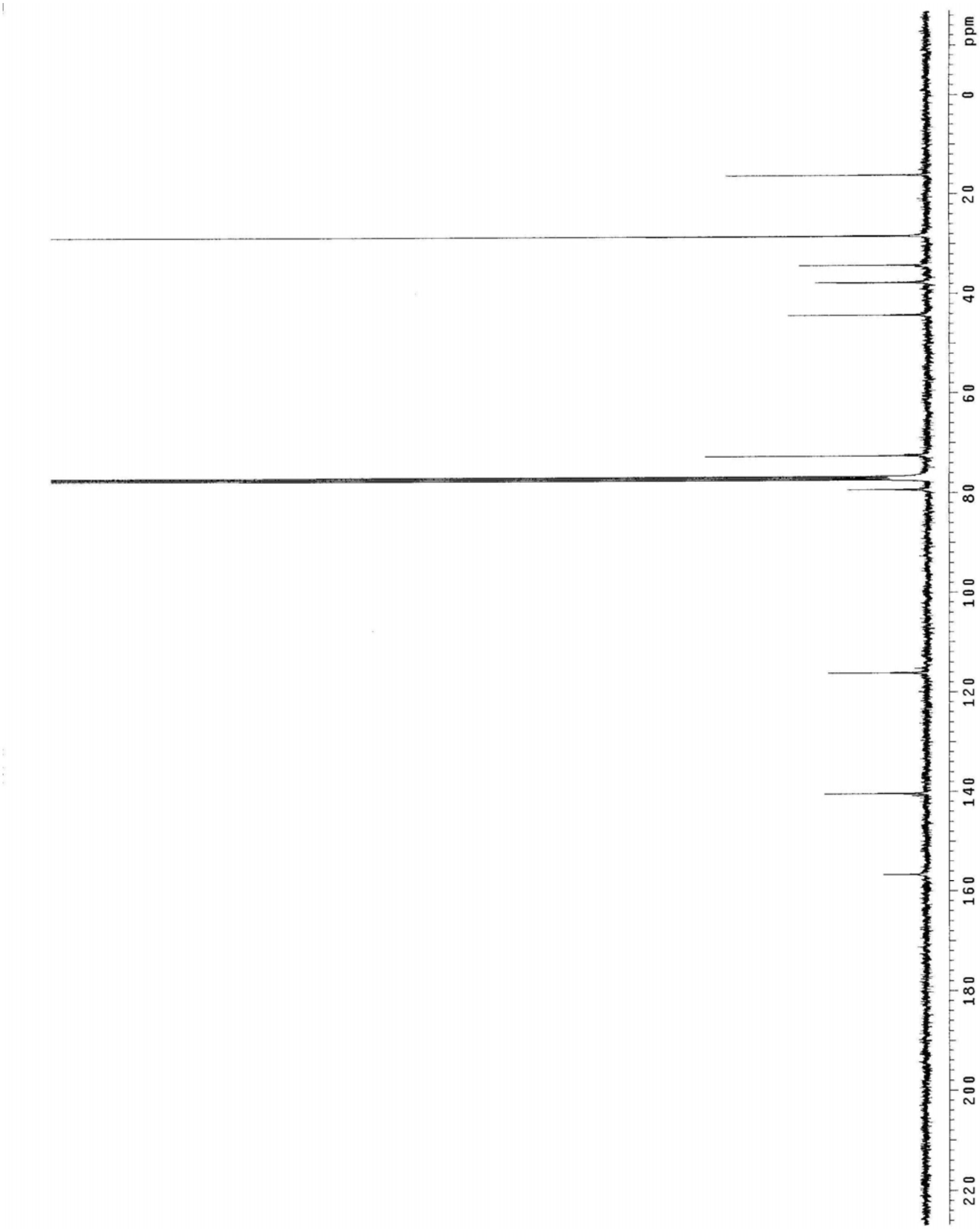
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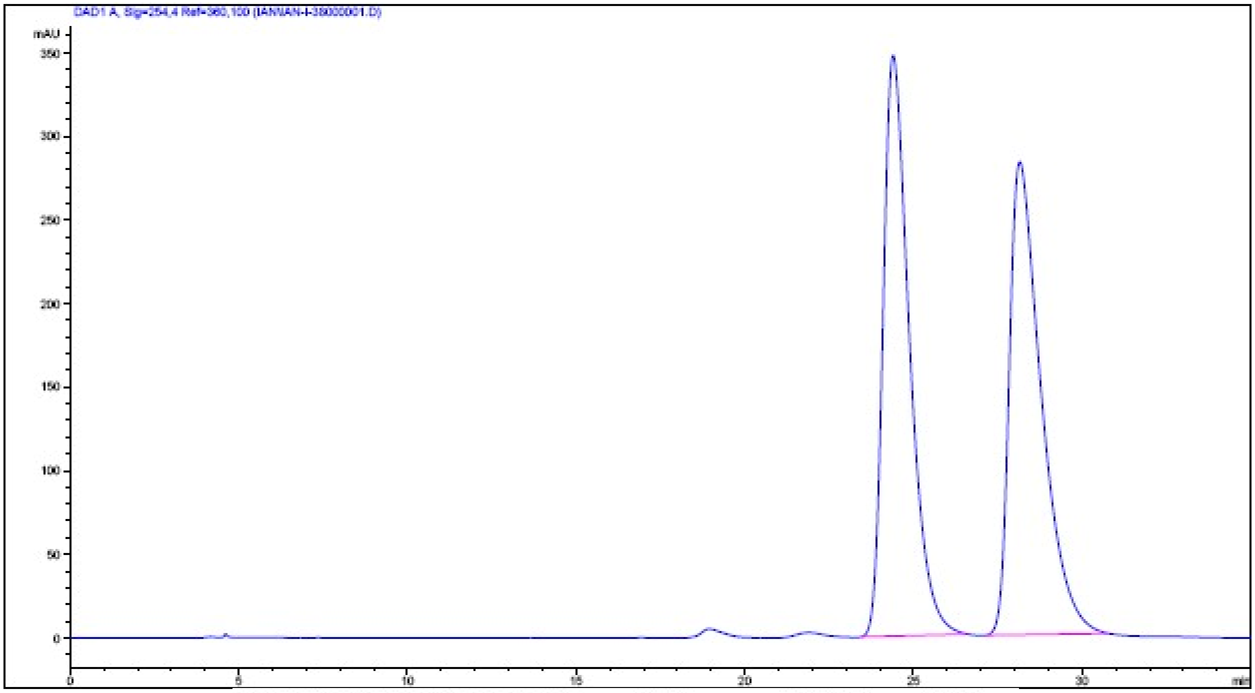

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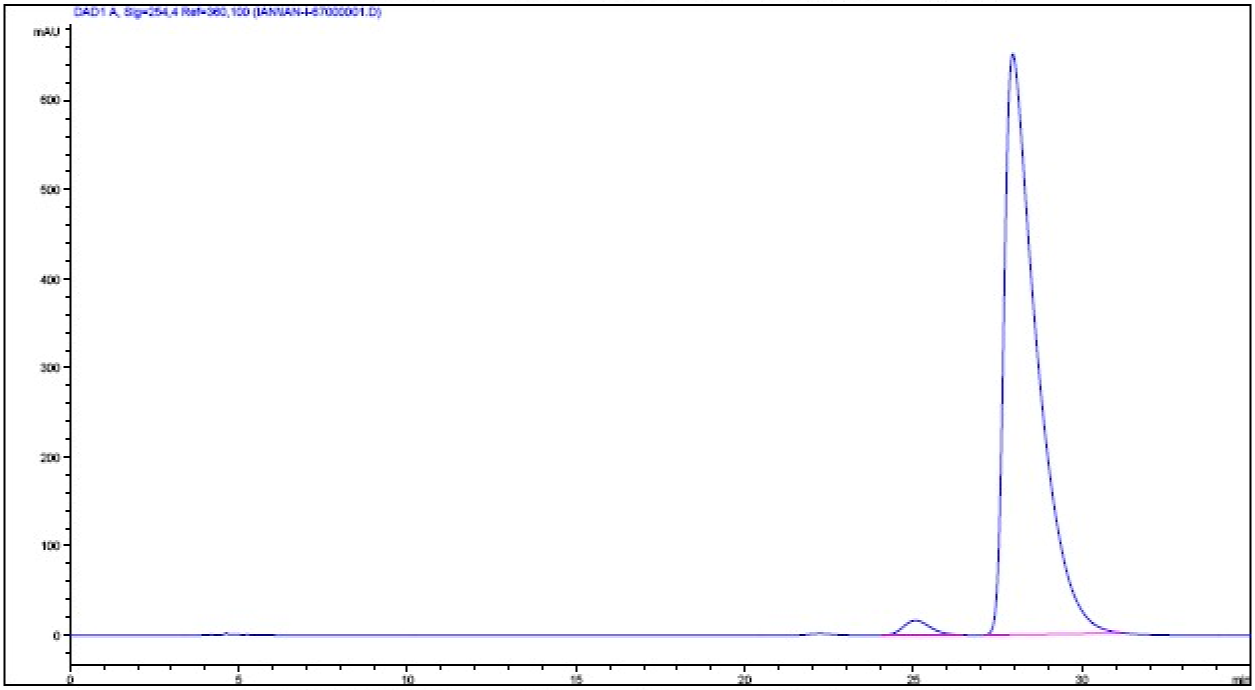

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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
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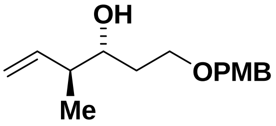
   1  25.055 BB    0.8165  947.26202   16.73059   2.1209
   2  27.941 BB    0.9663 4.37170e4  651.95068  97.8791
```

(*3R,4S*)-1-(4-methoxybenzyloxy)-4-methylhex-5-en-3-ol



4i

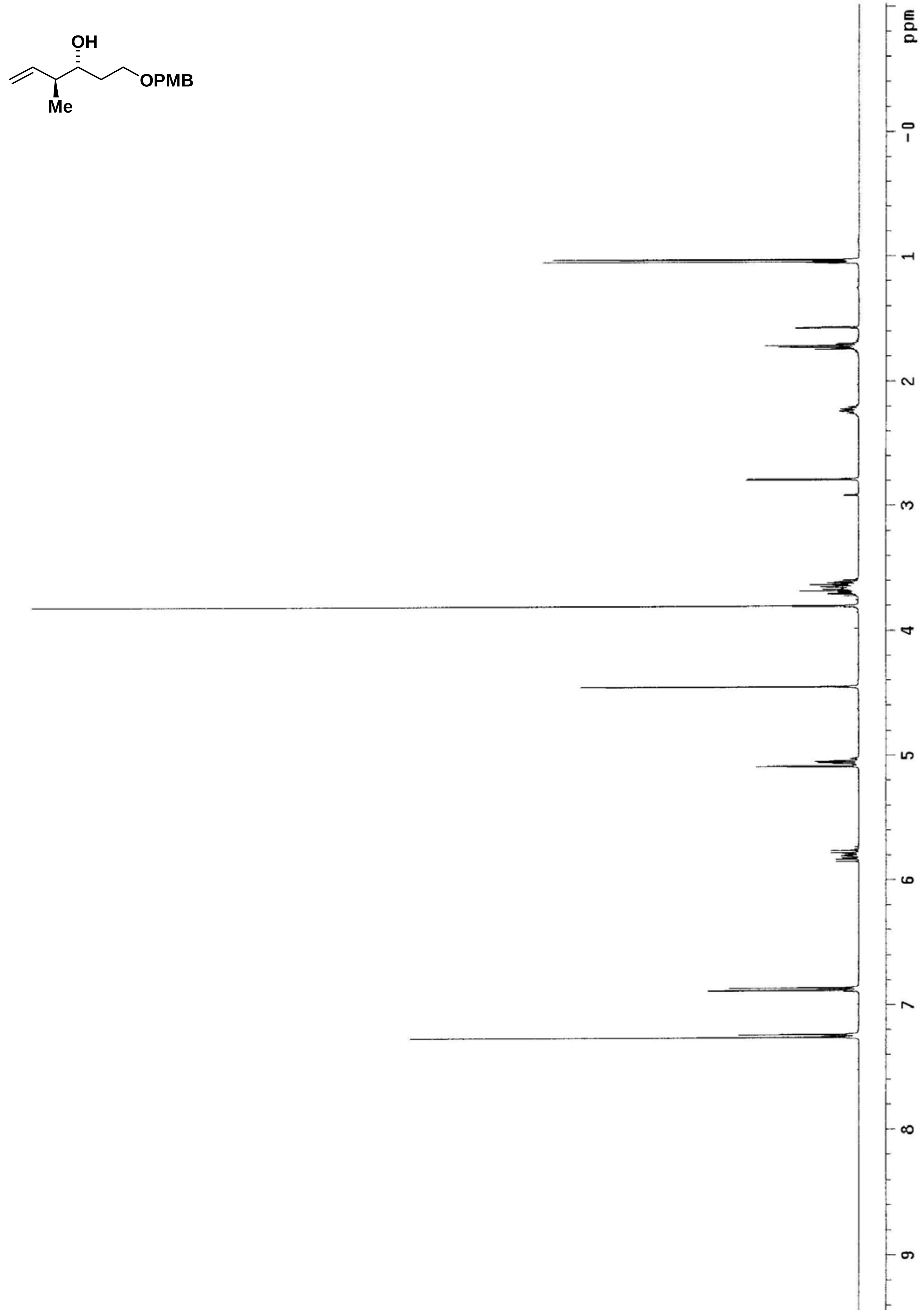
An oven-dried sealed tube under an atmosphere of N_2 was charged with 3-(4-methoxybenzyloxy)propan-1-ol **2i** (39.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 °C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4i** (38.1 mg, 0.152 mmol) as a colorless oil in 76% yield (15:1 dr).

TLC (SiO_2): $R_f = 0.5$ (ethyl acetate:hexanes, 1:4).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H), 6.90-6.86 (m, 2H), 5.80 (dt, *J* = 17.2, 10.0 Hz, 1H), 5.09-5.02 (m, 2H), 4.45 (s, 2H), 3.80 (s, 3H), 3.71-3.61 (m, 3H), 2.79 (d, *J* = 2.8, 1H), 2.23 (qt, *J* = 6.8, 0.8 Hz, 1H), 1.74-1.70 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 140.5, 130.1, 129.3, 115.4, 113.8, 74.3, 73.0, 68.9, 55.3, 44.0, 33.5, 15.8.

HPLC: Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 15.4 min, t_{major} = 17.9 min; ee = 97%.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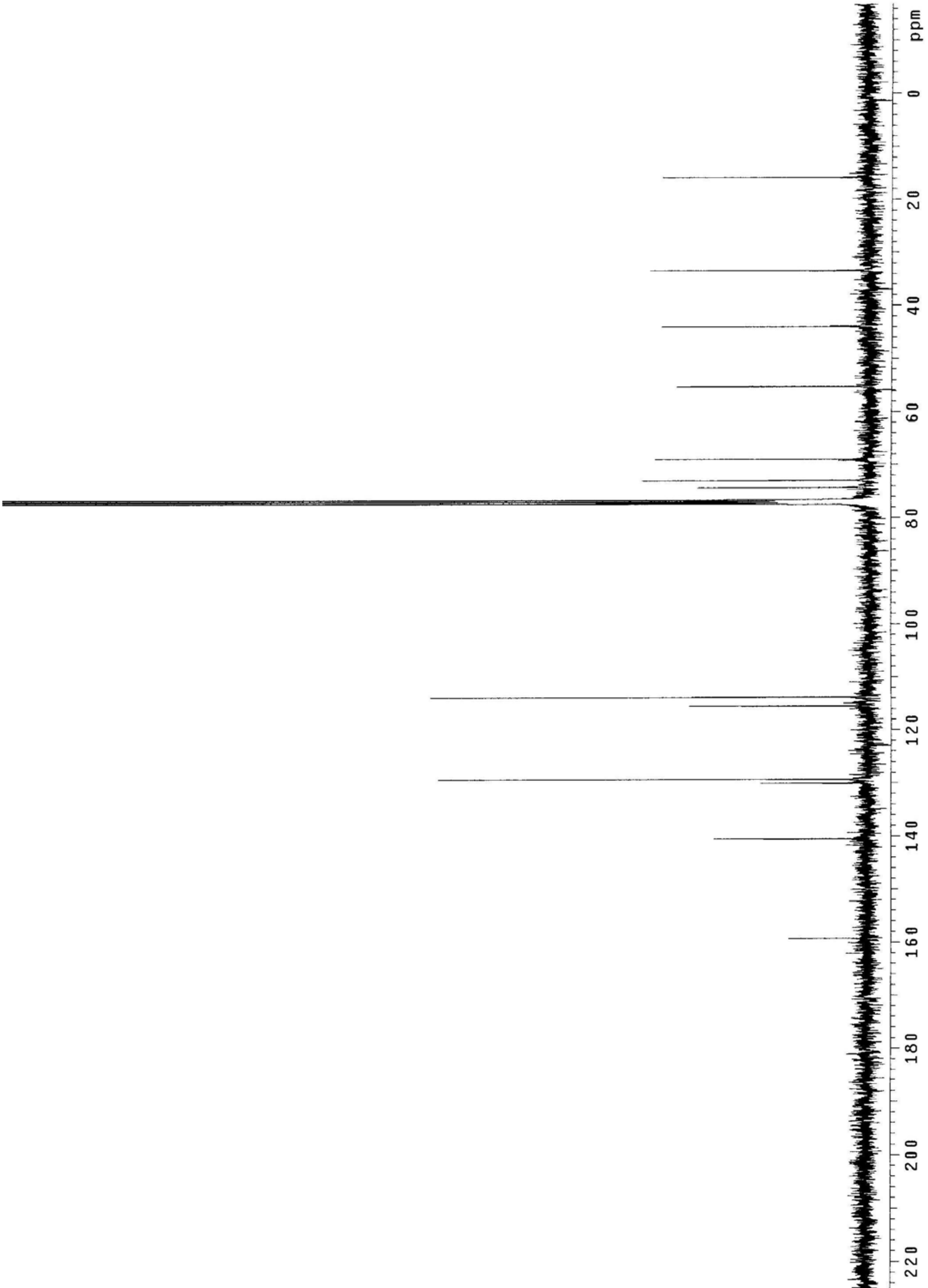
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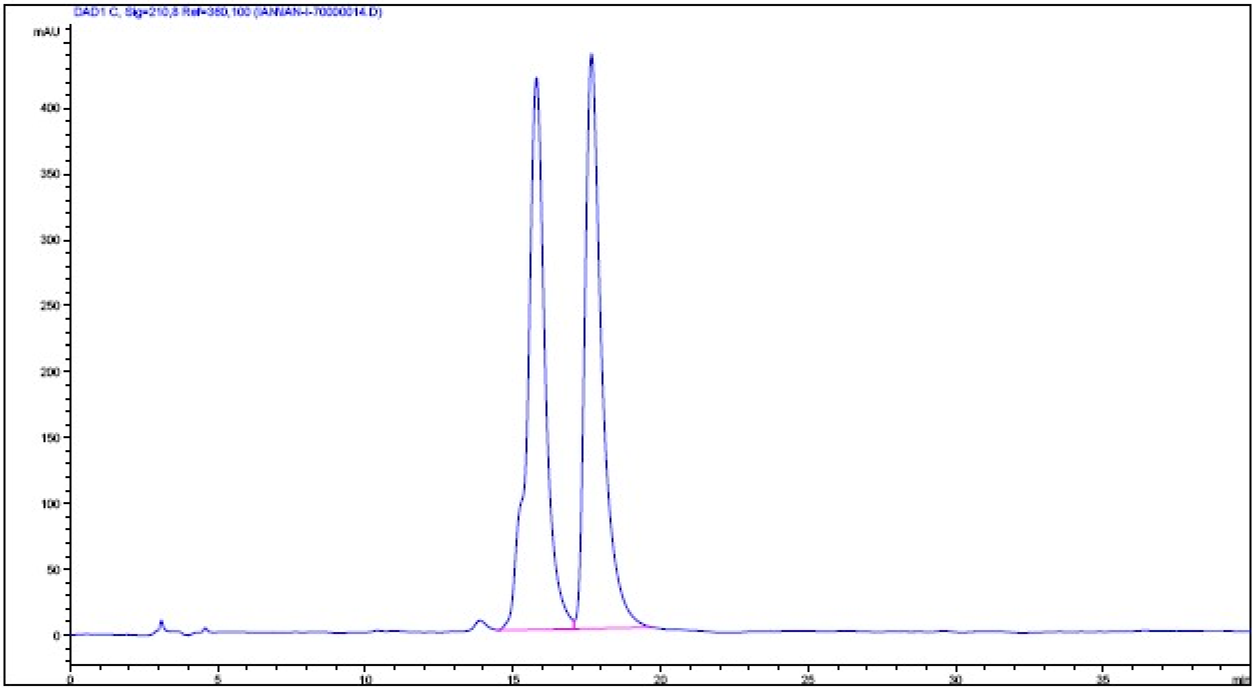

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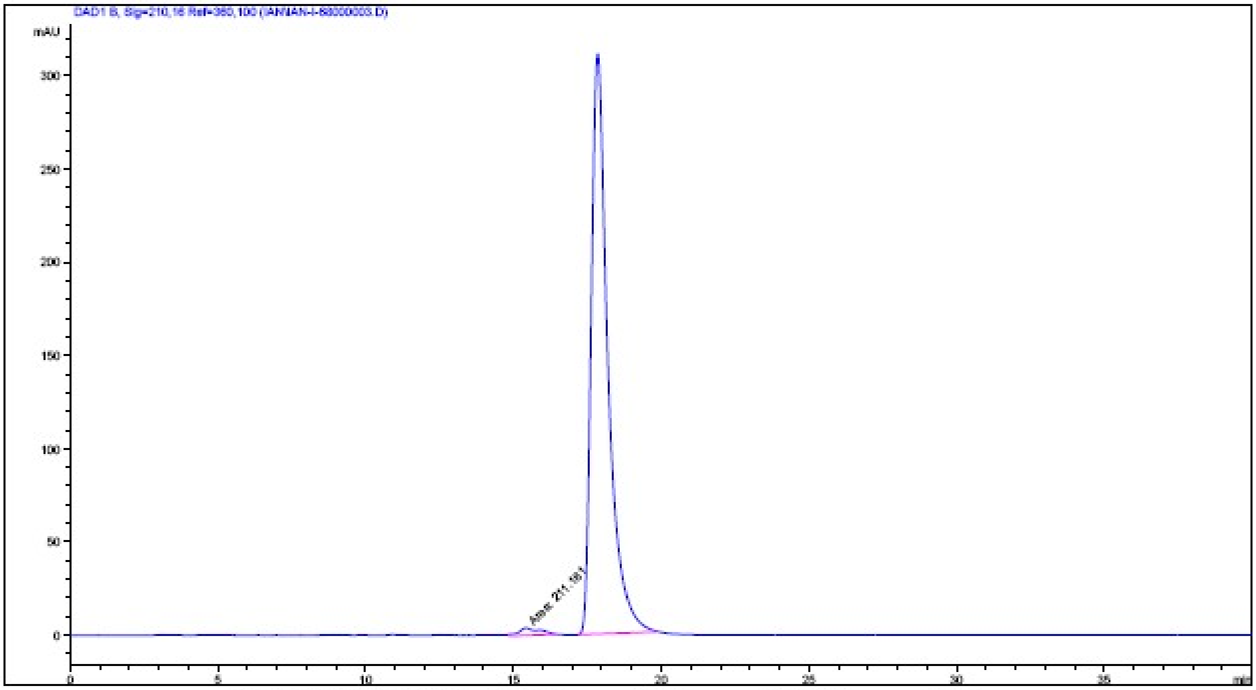

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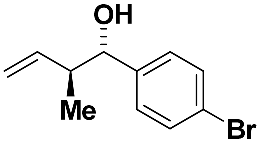
   2  17.859 BB     0.5847 1.21779e4  311.11398  98.2954
```

Detailed Procedure and Spectral Data for *anti*-Diastereo- and Enantioselective Carbonyl Crotylation from the Aldehyde Oxidation Level

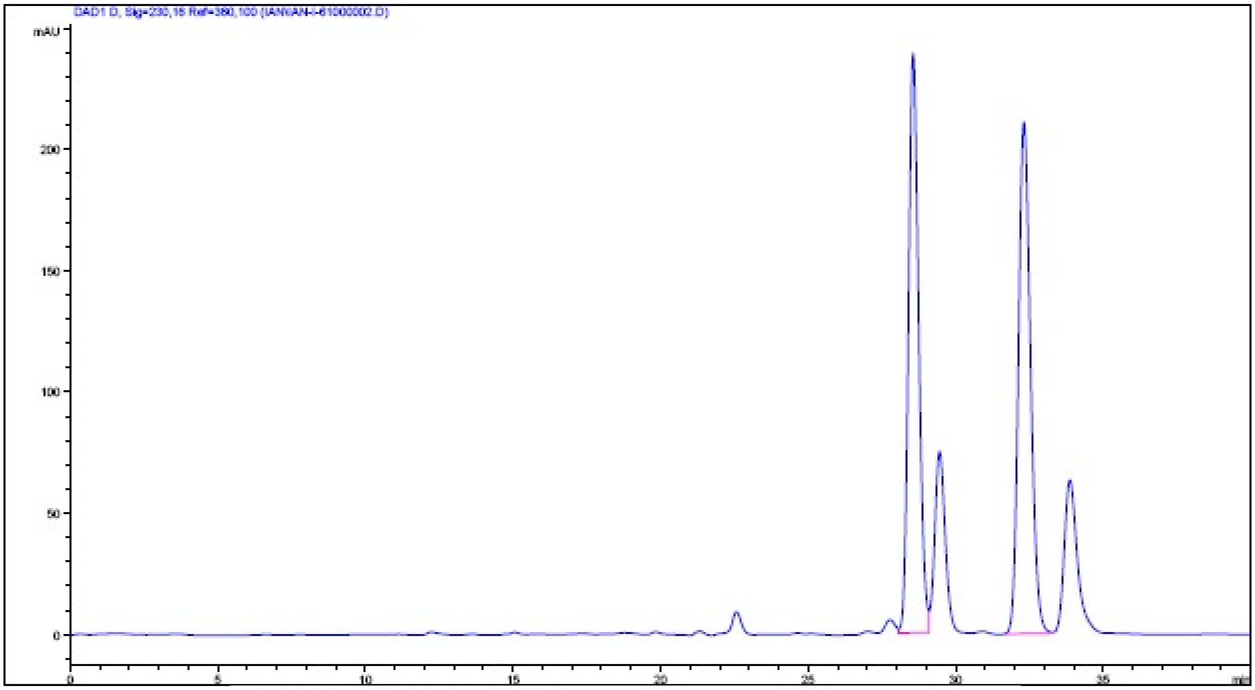
(*1S,2S*)-1-(4-bromophenyl)-2-methylbut-3-en-1-ol



4a

An oven-dried sealed tube under an atmosphere of N_2 was charged with 4-bromobenzaldehyde **3a** (37.0 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 µL, 0.4 mmol, 200 mol%), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4a** (39.5 mg, 0.164 mmol) as a colorless oil in 82% yield (17:1 dr).

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 230 nm), t_{minor} = 27.9 min, t_{major} = 31.8 min; ee = 98%



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   2  32.309 BB     0.4394 5992.81738  210.96976  51.1096
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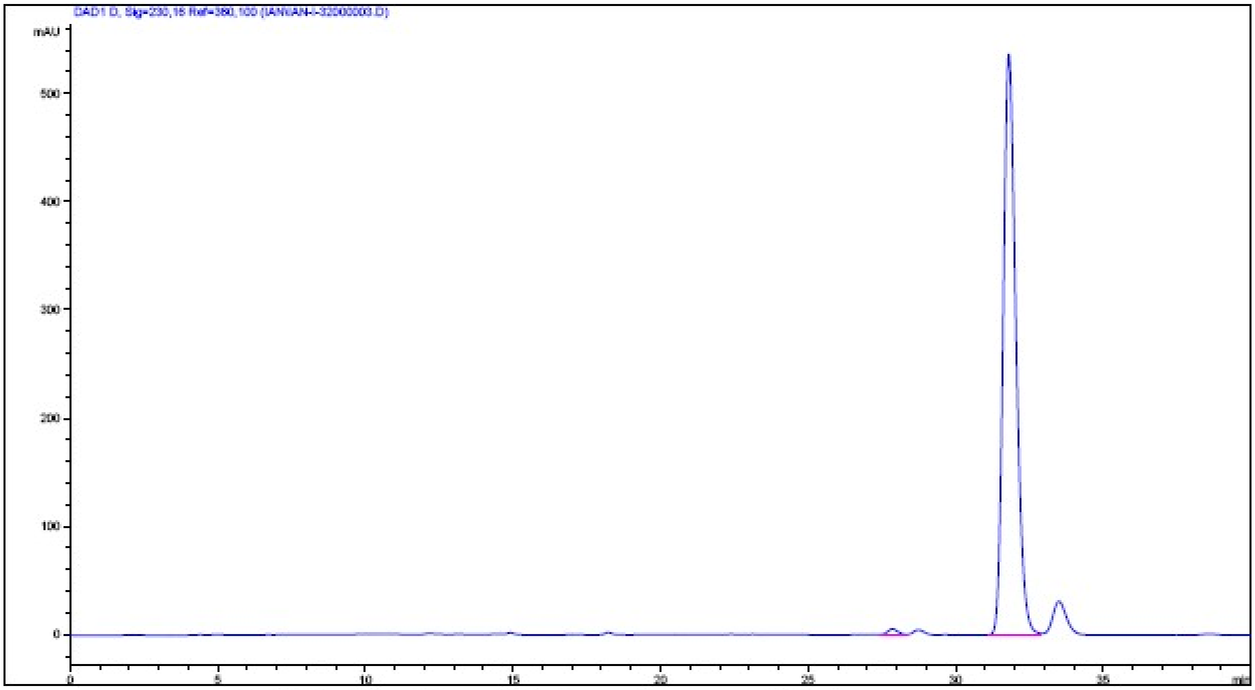

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  #   [min]         [min]   [mAU*s]     [mAU]       %
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   1  27.855 BV     0.3535  122.30916    5.25518   0.7588
   2  31.800 BB     0.4577 1.59964e4  536.71680  99.2412
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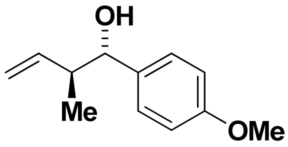
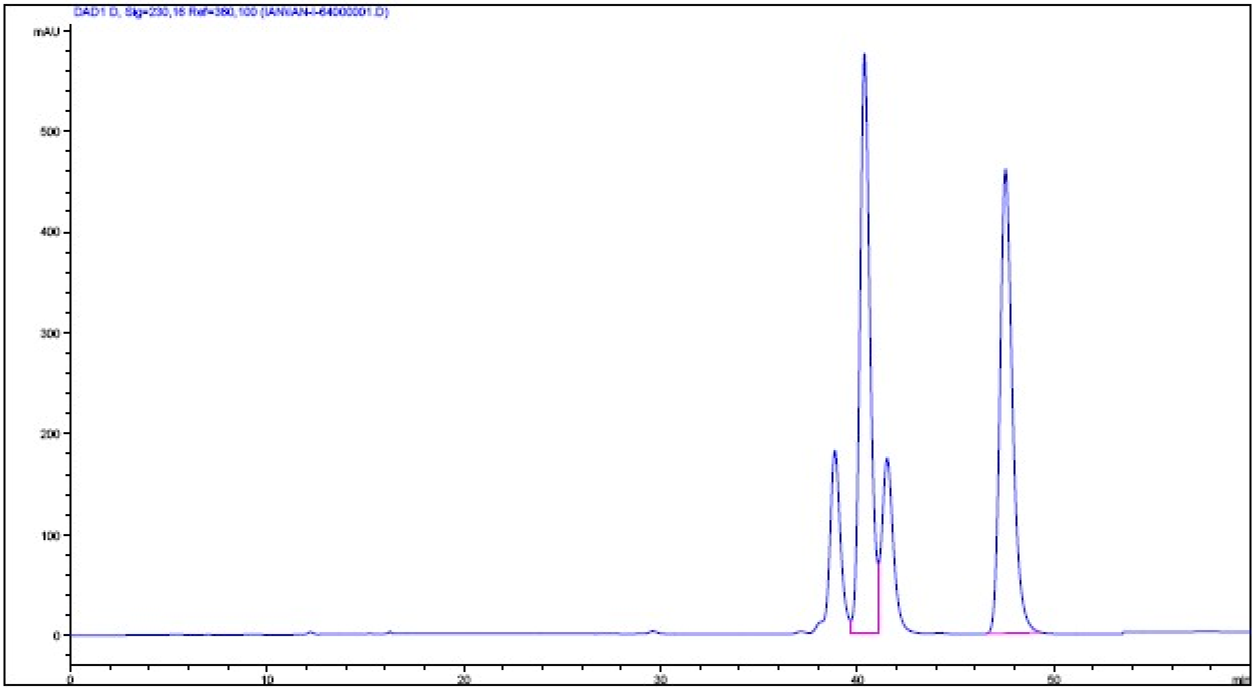
(*1S,2S*)-1-(4-methoxyphenyl)-2-methylbut-3-en-1-ol



4b

An oven-dried sealed tube under an atmosphere of N_2 was charged with 4-methoxybenzaldehyde **3b** (27.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 µL, 0.4 mmol, 200 mol%), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4b** (34.2 mg, 0.178 mmol) as a colorless oil in 89% yield (12:1 dr).

HPLC: (Chiralpak AD-H/AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 230 nm), t_{minor} = 40.2 min, t_{major} = 47.6 min; ee = 98%.



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   2  47.529 BB    0.6652 2.03343e4  460.43875  49.3994
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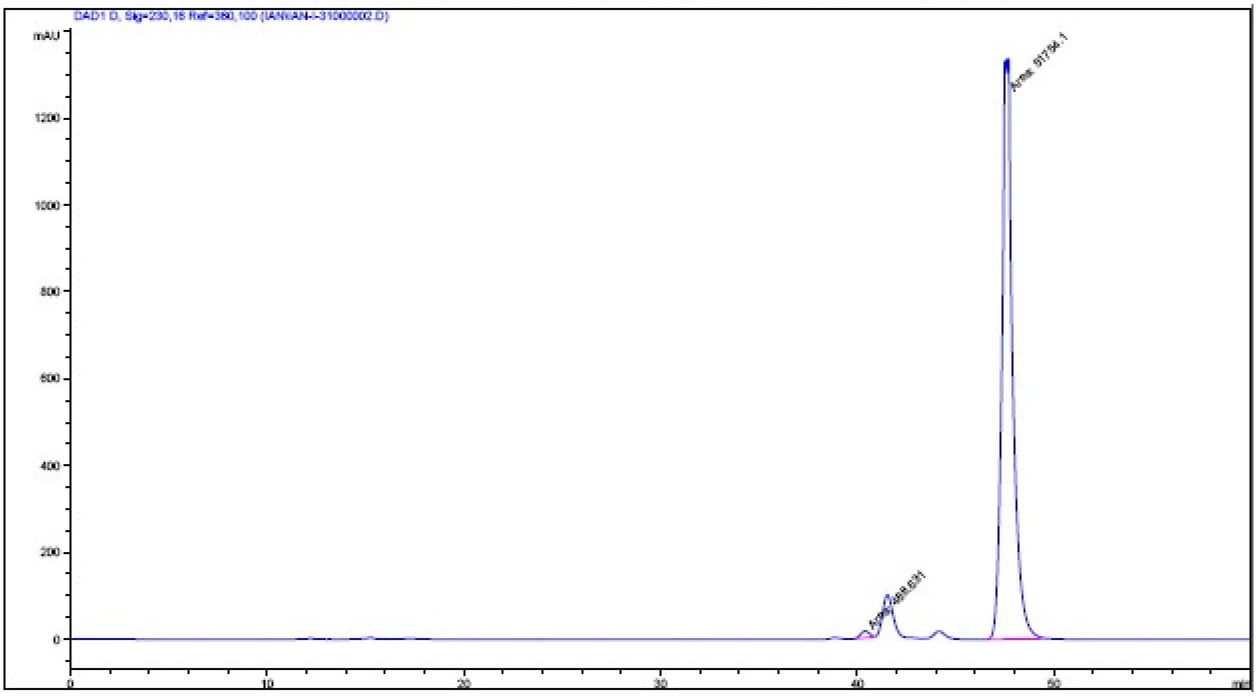

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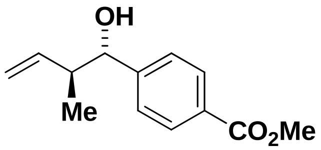
   2  47.622 MM    0.6438 5.17541e4 1339.86853  99.0647
```

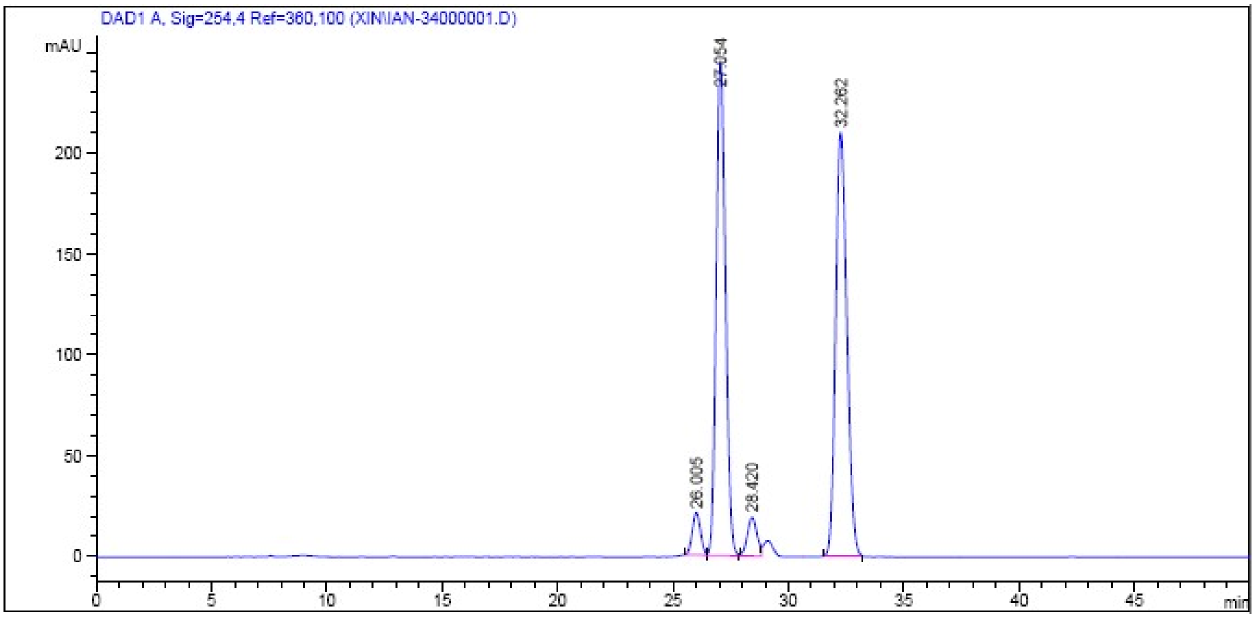
Methyl 4-((*1S,2S*)-1-hydroxy-2-methylbut-3-enyl)benzoate



4c

An oven-dried sealed tube under an atmosphere of N_2 was charged with methyl 4-formylbenzoate **3c** (32.8 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 μL, 0.4 mmol, 200 mol%), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4c** (35.7 mg, 0.162 mmol) as a colorless oil in 81% yield (11:1 dr).

HPLC: (Chiralpak AD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 254 nm), t_{minor} = 27.1 min, t_{major} = 32.3 min; ee = 98%.



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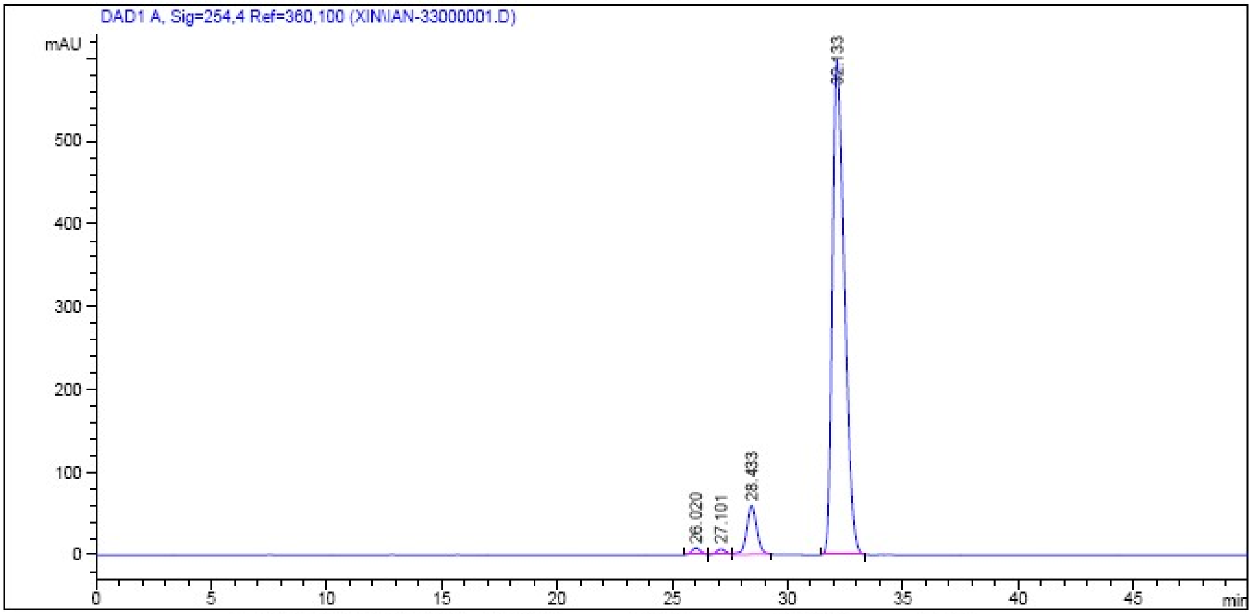
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.005 BV    0.3946  529.10156   20.95080   3.5067
   2  27.054 VB    0.4368 6857.31104  244.83498  45.4484
   3  28.420 BV    0.4493  565.99902   19.12413   3.7513
   4  32.262 BB    0.5267 7135.71631  209.86855  47.2936
```



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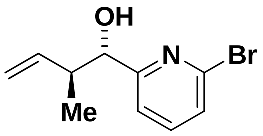
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.020 BV    0.4193  231.31941    8.50547   0.9585
   2  27.101 VV    0.4236  193.71434    6.98357   0.8027
   3  28.433 VB    0.4696 1836.16467   59.57385   7.6086
   4  32.133 BB    0.5662 2.18716e4   598.67102  90.6302
```

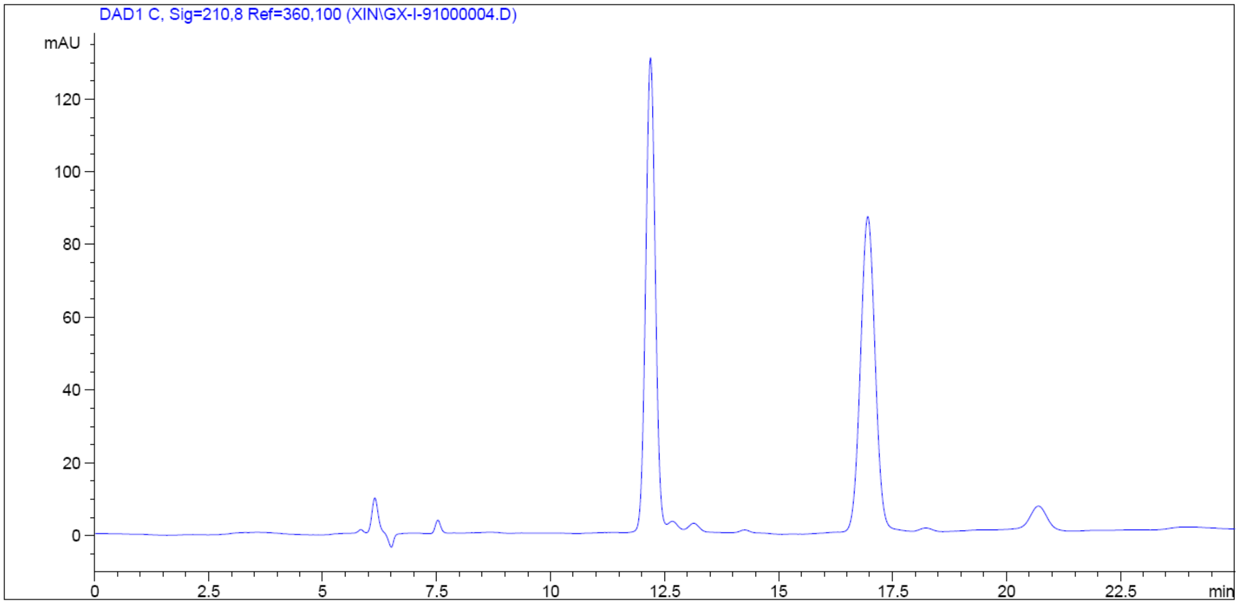
(*1S,2S*)-1-(6-bromopyridin-2-yl)-2-methylbut-3-en-1-ol



4d

An oven-dried sealed tube under an atmosphere of N_2 was charged with 6-bromopicolinaldehyde **3d** (37.2 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 µL, 0.4 mmol, 200 mol%), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4d** (36.3 mg, 0.150 mmol) as a colorless oil in 75% yield (>20:1 dr).

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.5 mL/min, 210 nm), t_{major} = 12.1 min, t_{minor} = 16.8 min ; ee = 97%.



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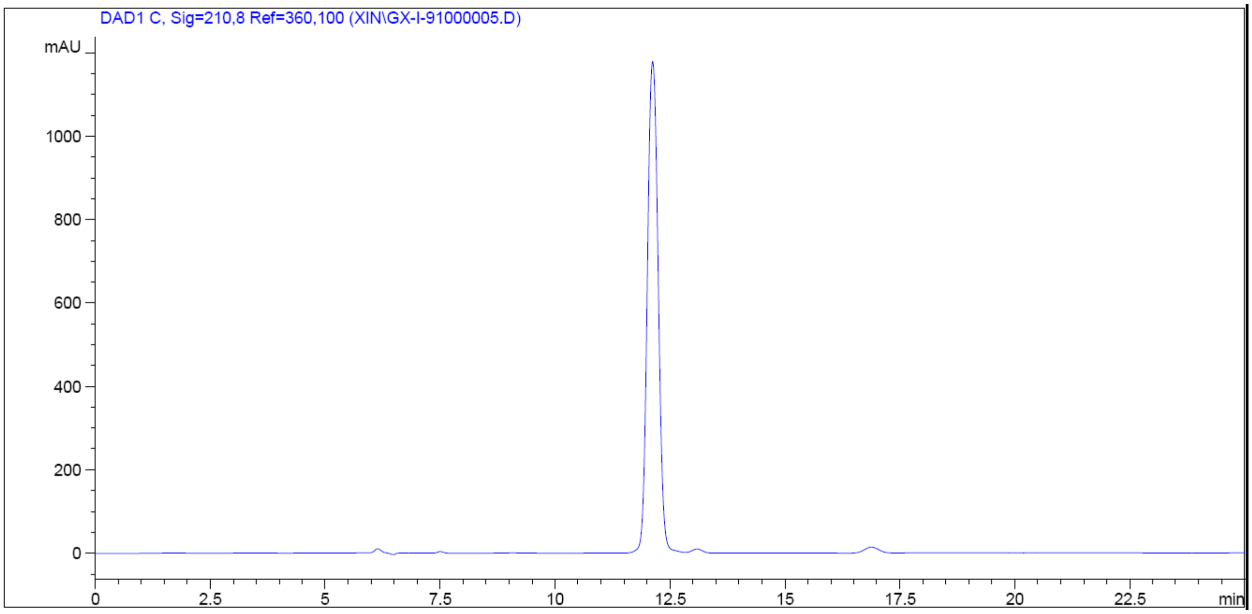
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  12.186 BV    0.2295 1919.80676  130.59860  49.8528
   2  16.951 BB    0.3462 1931.14453   86.57128  50.1472
```



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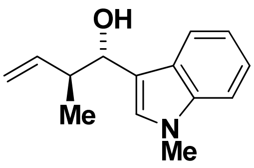
Peak RetTime Type  Width     Area      Height     Area
  #   [min]         [min]   [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  12.118 BB    0.2608 1.92732e4  1178.34497  98.4124
   2  16.880 BB    0.3391  310.91425   14.21759   1.5876
```

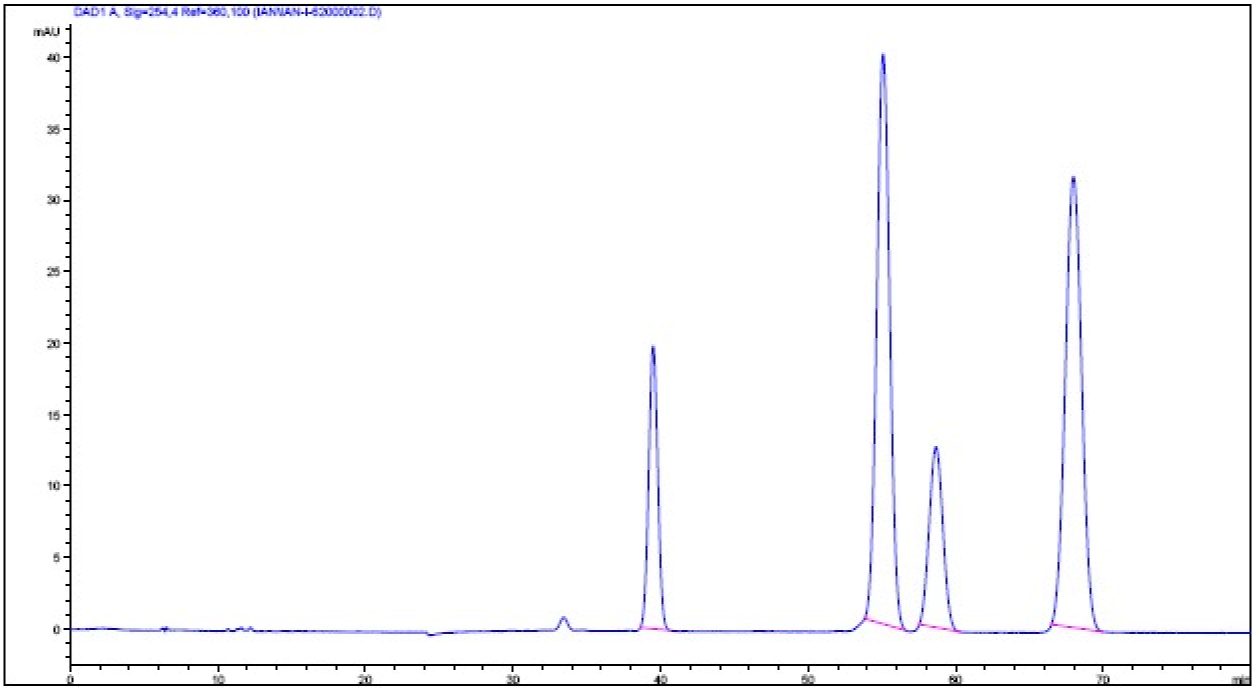
(*1S,2S*)-2-methyl-1-(1-methyl-1*H*-indol-3-yl)but-3-en-1-ol



4e

An oven-dried sealed tube under an atmosphere of N_2 was charged with 1-methyl-1*H*-indole-3-carbaldehyde **3e** (31.8 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 μL, 0.4 mmol, 200 mol%), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4e** (31.9 mg, 0.148 mmol) as a colorless oil in 75% yield (10:1 dr).

HPLC: (Chiralcel OJ-H column, hexanes:*i*-PrOH = 93:7, 0.5 mL/min, 254 nm), t_{major} = 53.3 min, t_{minor} = 66.0 min; ee = 98%.



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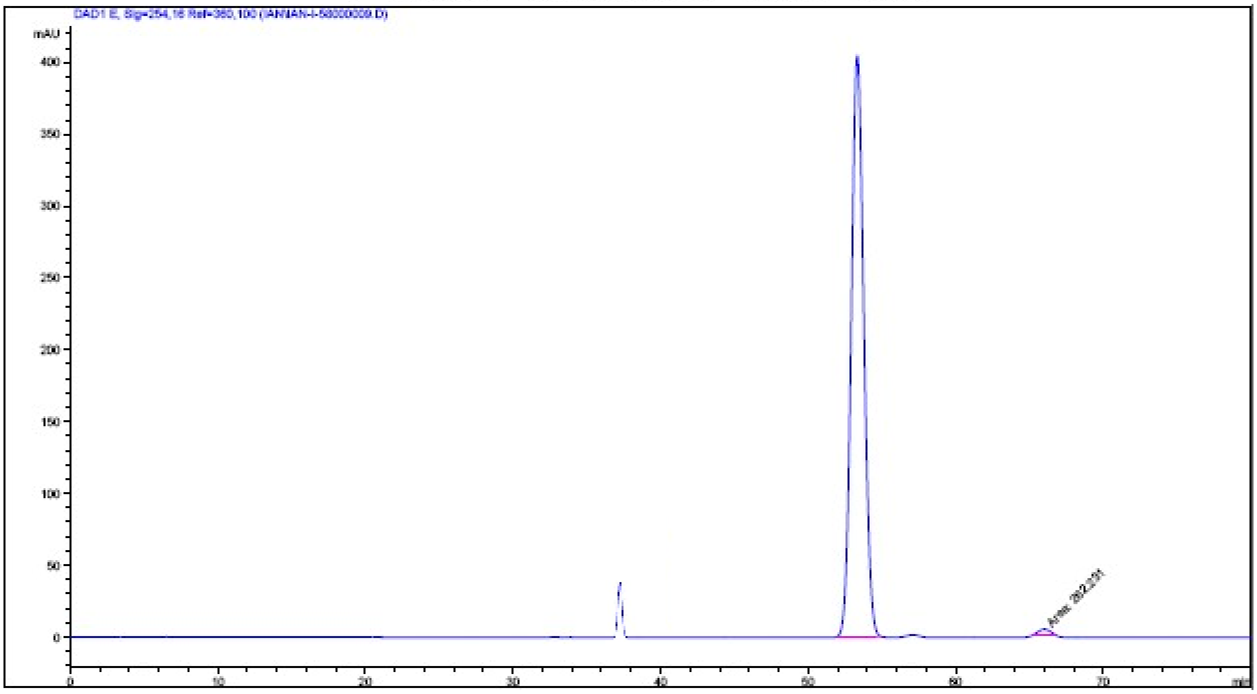
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  39.492 BB    0.6589  850.65906   19.81396  13.0118
   2  55.079 BB    0.9157 2436.11816   39.93385  37.2632
   3  58.665 BB    0.8004  813.51562   12.64772  12.4437
   4  67.979 BB    1.0884 2437.29663   31.58078  37.2813
```



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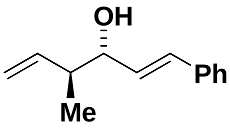
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  53.326 BB    0.9154 2.38488e4  404.75348  98.9124
   2  66.016 MM    0.9653  262.23096   4.52740   1.0876
```

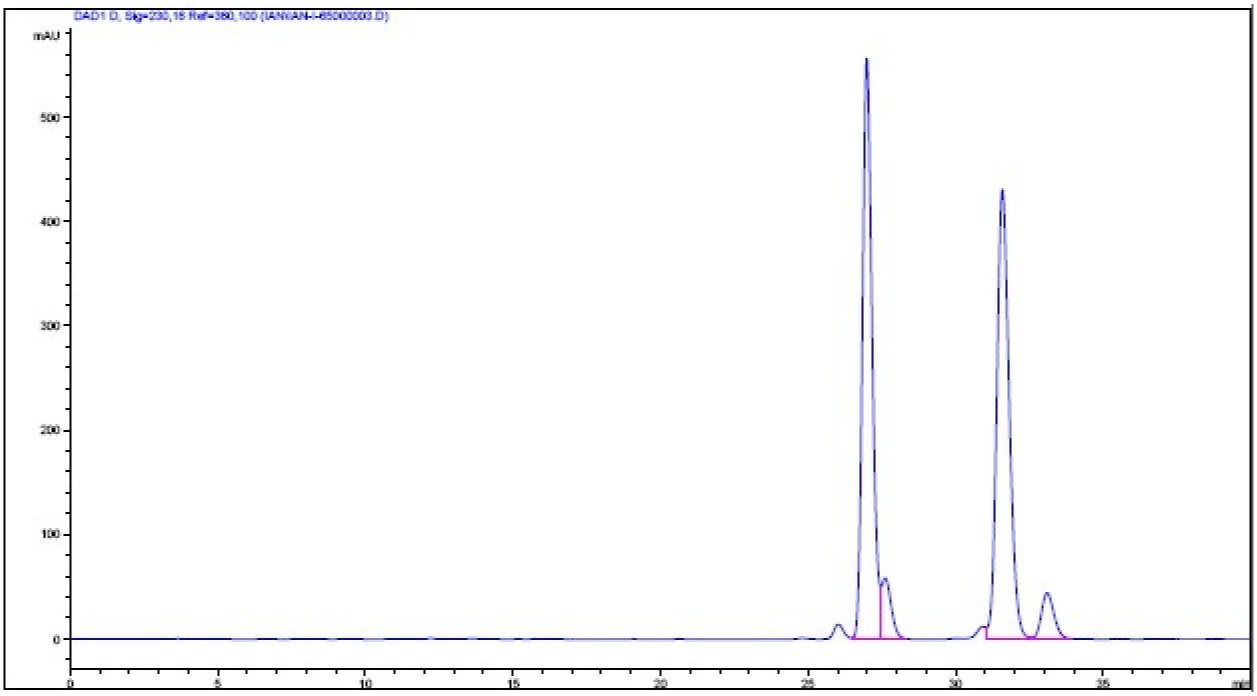
(*3R,4S,E*)-4-methyl-1-phenylhexa-1,5-dien-3-ol



4f

An oven-dried sealed tube under an atmosphere of N_2 was charged with *trans*-cinnamyl aldehyde **3f** (26.4 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 µL, 0.4 mmol, 200 mol%), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 70 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4f** (29.0 mg, 0.154 mmol) as a colorless oil in 77% yield (10:1 dr).

HPLC: (Chiralpak AS-H/AS-H column, hexanes:*i*-PrOH = 98:2, 0.5 mL/min, 254 nm), t_{minor} = 26.8 min, t_{major} = 31.5 min; ee = 98%.



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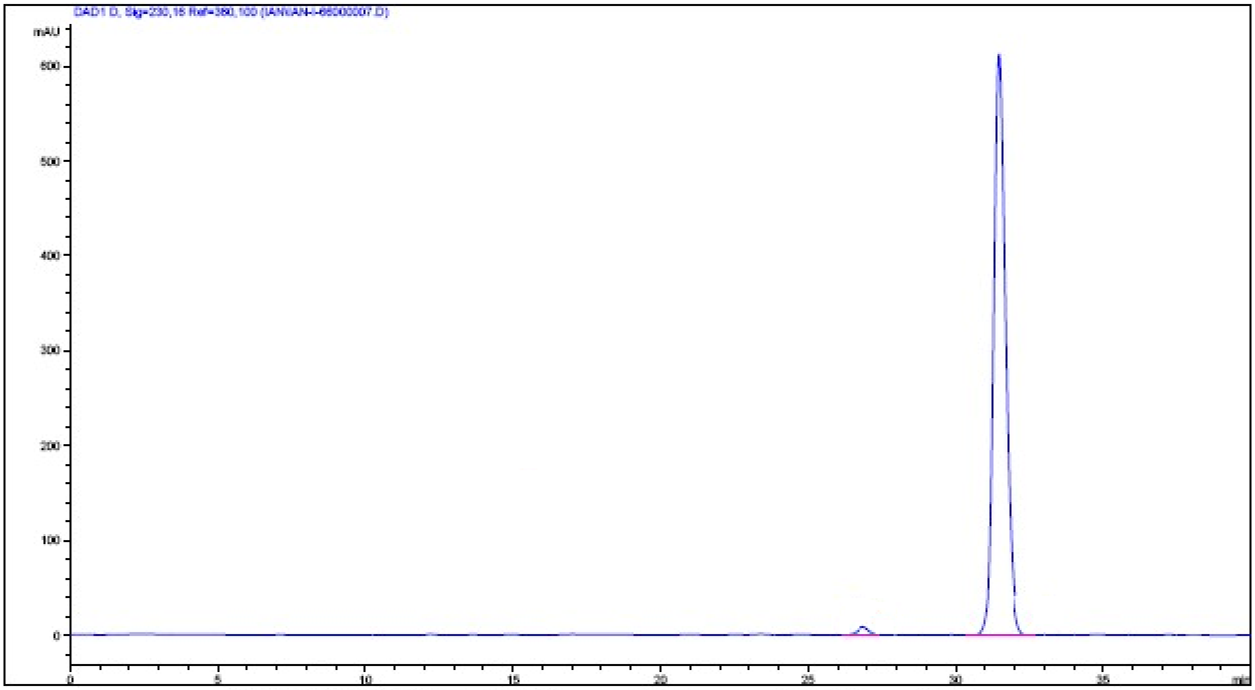
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  26.987 VV    0.3475 1.26759e4  557.10522  45.5873
   2  27.611 VB    0.3413 1330.46252   58.51318   4.7848
   3  31.580 VB    0.4475 1.25149e4  430.09030  45.0083
   4  33.097 BB    0.4564 1284.49683   43.77251   4.6195
```



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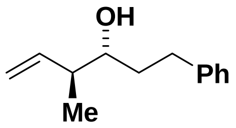
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  26.800 BV    0.3580  190.00429   10.05732   1.0683
   2  31.501 BB    0.4995 1.75957e4  610.08494  98.9317
```

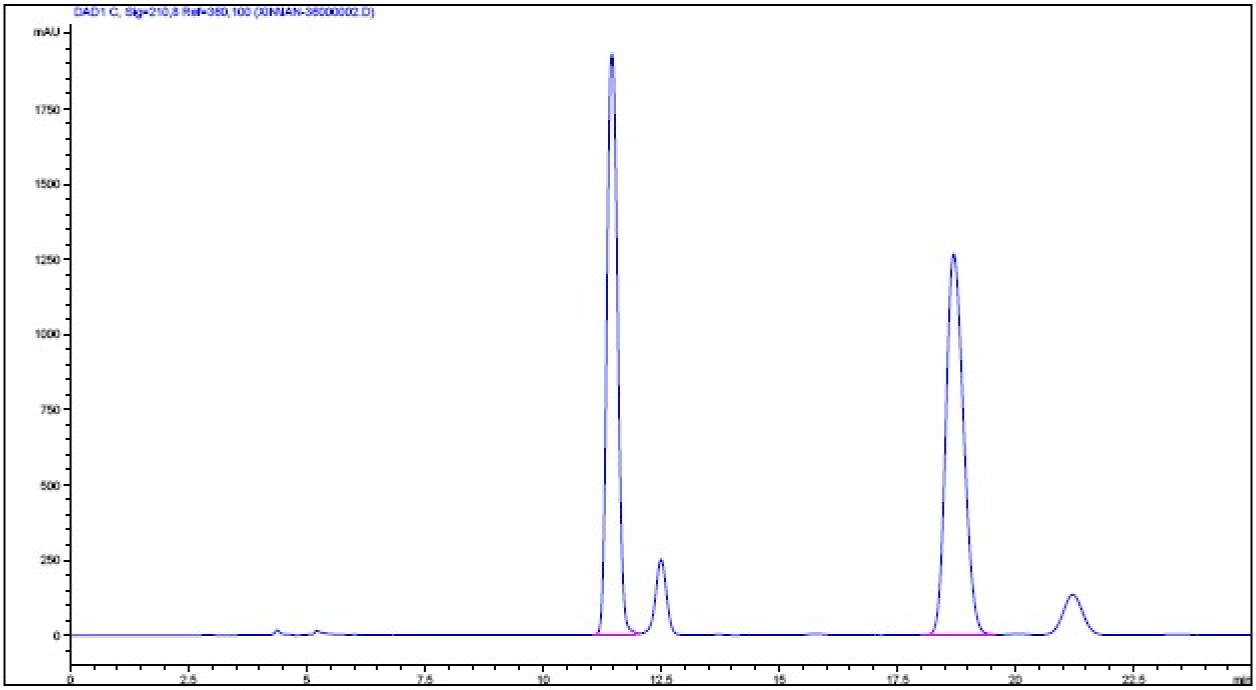
(*3R,4S*)-4-methyl-1-phenylhex-5-en-3-ol



4g

An oven-dried sealed tube under an atmosphere of N_2 was charged with 3-phenylpropanal **3g** (26.8 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 µL, 0.4 mmol, 200 mol%), and H_2O (18 µL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4g** (27.0 mg, 0.142 mmol) as a colorless oil in 71% yield (>20:1 dr).

HPLC: (Chiralcel OD-H column, hexanes:*i*-PrOH = 97:3, 0.7 mL/min, 254 nm), t_{minor} = 11.2 min, t_{major} = 17.4 min; ee = 98%.



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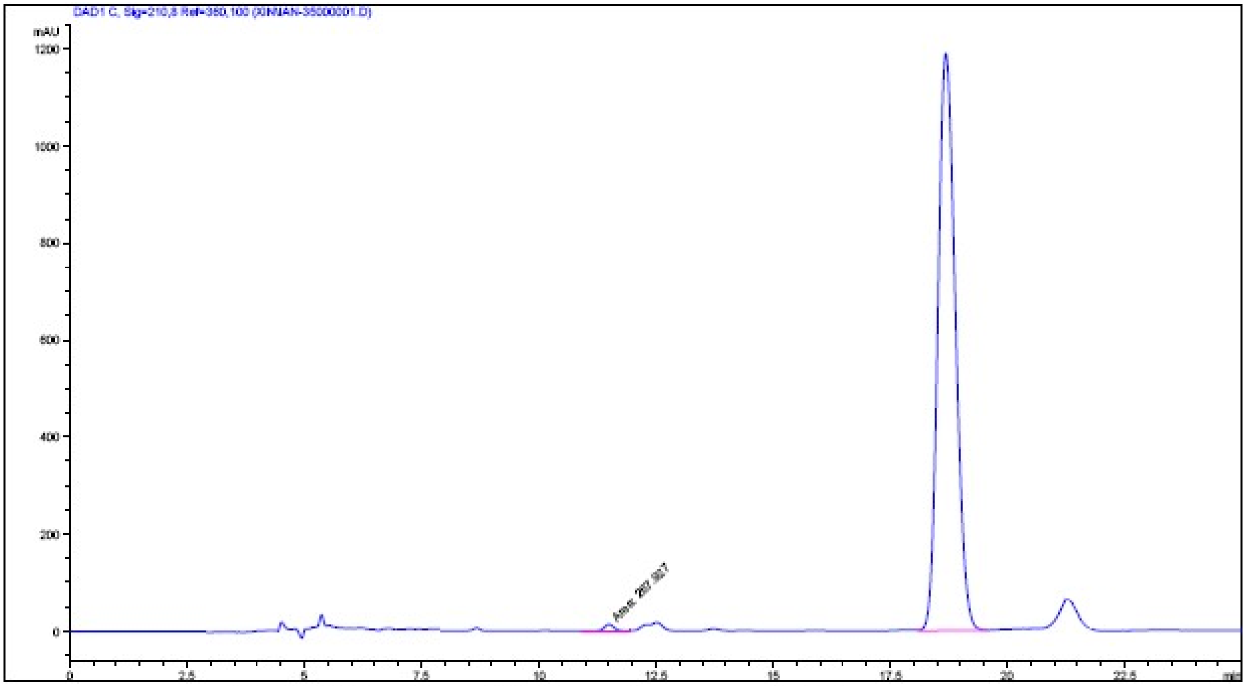
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.459 BV    0.2517 3.04228e4 1932.34814  47.9834
   2  18.694 VB    0.4076 3.29800e4 1267.50708  52.0166
```



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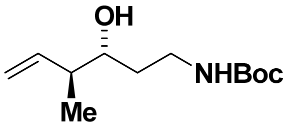
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.503 MM    0.3098  267.92664   14.41337   0.8685
   2  18.685 BB    0.4019 3.05811e4 1189.62244  99.1315
```

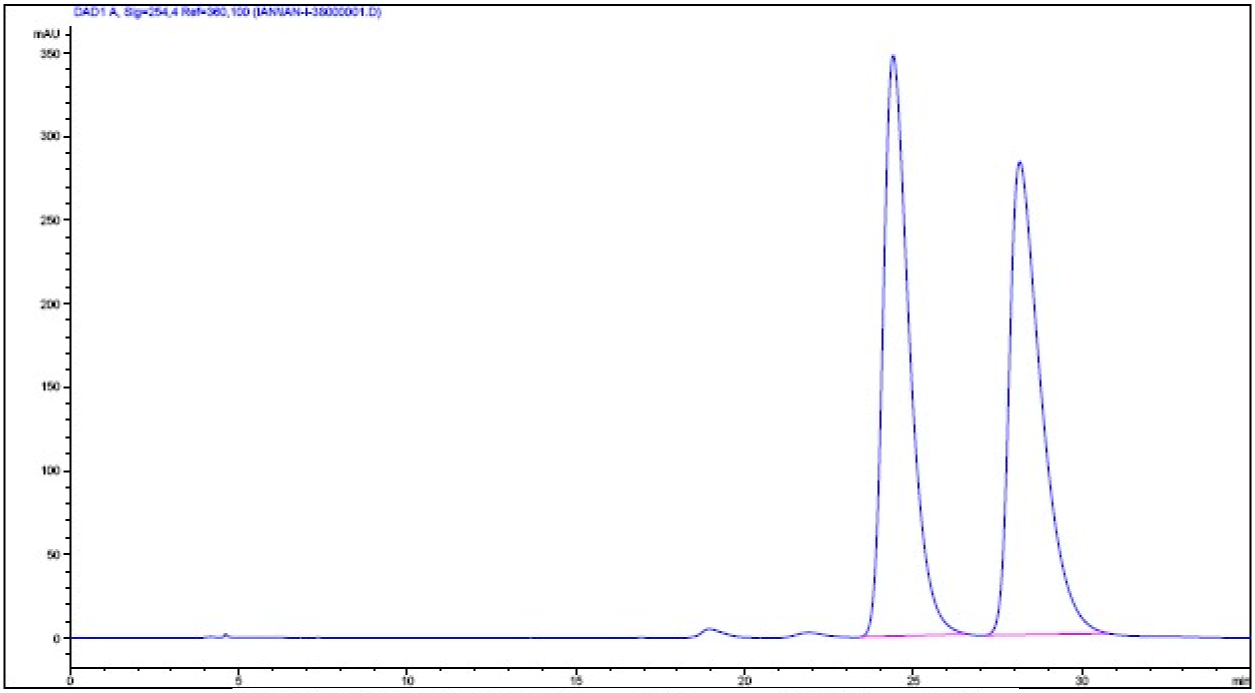
tert-butyl (_3R,4S_)-3-hydroxy-4-methylhex-5-enylcarbamate



4h

An oven-dried sealed tube under an atmosphere of N_2 was charged with _tert_-butyl 3-oxopropylcarbamate **3h** (34.6 mg, 0.20 mmol, 100 mol%), (_S_)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 μL, 0.4 mmol, 200 mol%), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 70 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated _in vacuo_. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4h** (30.3 mg, 0.142 mmol) as a colorless oil in 66% yield (>20:1 dr).

HPLC: Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product (Chiralcel OJ-H column, hexanes:_i_-PrOH = 98:2, 0.75 mL/min, 254 nm), t_{minor} = 24.4 min, t_{major} = 28.1 min; ee = 99%.



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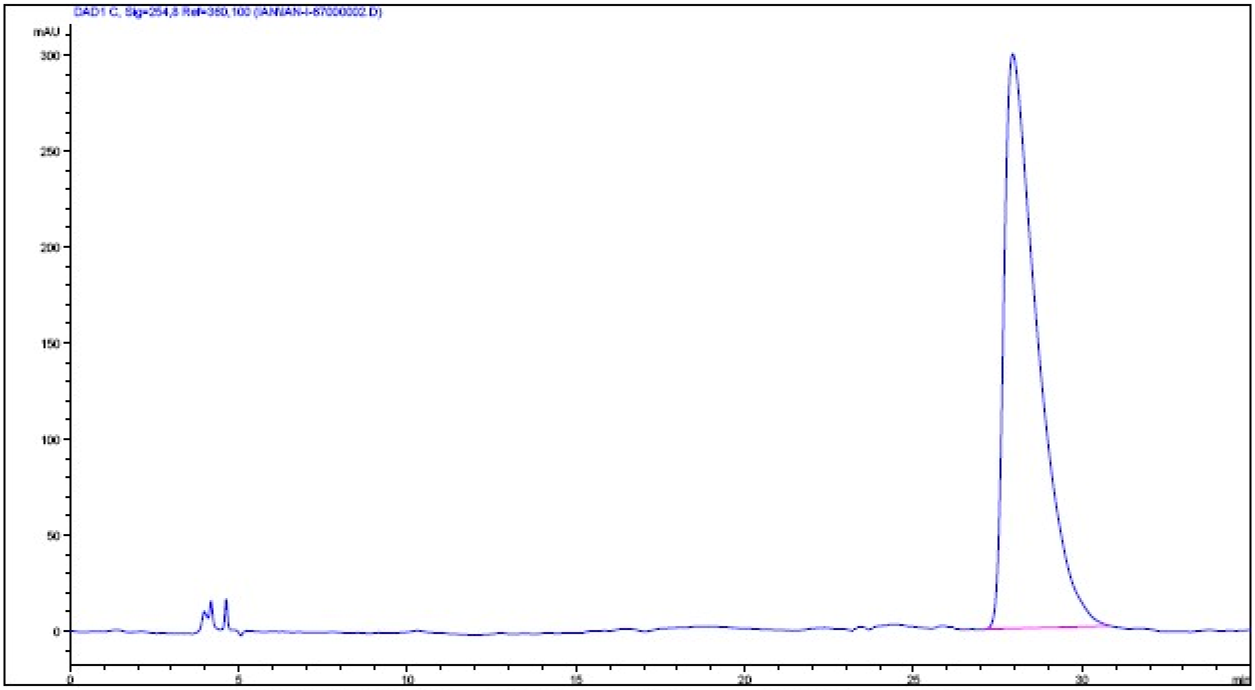
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.394 BB    0.8231 1.88485e4  347.35727  50.3245
   2  28.148 BB    0.9777 1.86054e4  282.74048  49.6755
```



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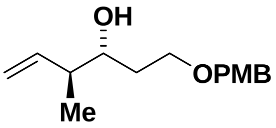
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|---------|
   1  27.941 BB    0.9825 2.07452e4  299.35754 100.0000
```

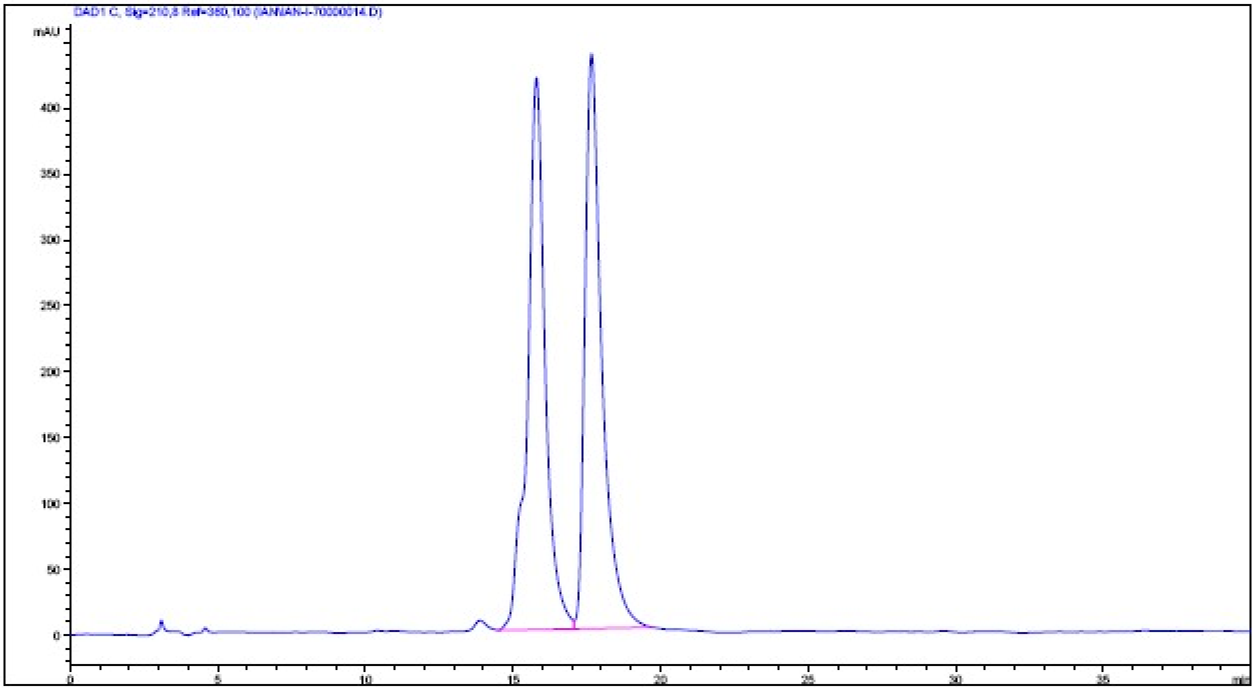
(*3R,4S*)-1-(4-methoxybenzyloxy)-4-methylhex-5-en-3-ol



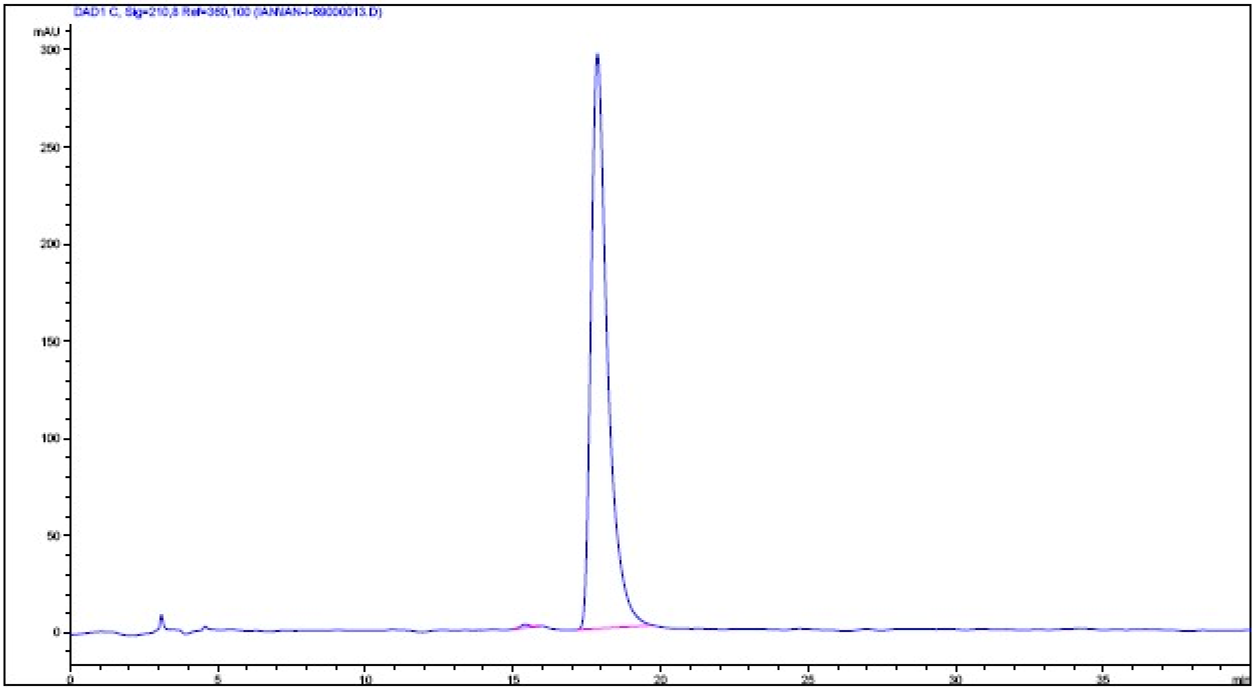
4i

An oven-dried sealed tube under an atmosphere of N_2 was charged with 3-(4-methoxybenzyloxy)propanal **3i** (38.8 mg, 0.20 mmol, 100 mol%), (*S*)-**I** (10.3 mg, 0.01 mmol, 5 mol%), K_3PO_4 (21.5 mg, 0.10 mmol, 50 mol%), THF (0.1 mL, 2.0 M), isopropanol (31 μL, 0.4 mmol, 200 mol%), and H_2O (18 μL, 1.0 mmol, 500 mol%). But-3-en-2-yl acetate **1** (45.6 mg, 0.40 mmol, 200 mol%) was added and the mixture was allowed to stir at ambient temperature for 0.5 hr, at which point the reaction vessel was placed in an oil bath at 60 ^{o}C and was allowed to stir for 48 hr. The reaction mixture was concentrated *in vacuo*. Purification of the residue by column chromatography (SiO_2; ethyl acetate: hexanes, 1:20 with 0.1% TEA) provided **4i** (38.1 mg, 0.152 mmol) as a colorless oil in 76% yield (>20:1 dr).

HPLC: Enantiomeric excess was determined by HPLC analysis of the 4-nitrobenzoate derivative of the product (Chiralcel AD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 15.4 min, t_{major} = 17.9 min; ee = 99%.



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.791 VV    0.6118 1.75273e4  419.21658  50.0536
  2  17.658 VB    0.5995 1.74898e4  436.47791  49.9464
```



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  15.420 BB    0.3205   42.41079    1.85682   0.3663
  2  17.859 BB    0.5810 1.15342e4  295.77335  99.6337
```