Accessing Both Retention and Inversion Pathways in Stereospecific, Nickel-Catalyzed Miyaura Borylations of Allylic Pivalates

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General Information

Reactions were performed in oven-dried vials with Teflon-lined caps or in oven-dried round-bottomed flasks unless otherwise noted. Flasks were fitted with rubber septa, and reactions were conducted under a positive pressure of N_2. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, 60Å) unless otherwise noted. Commercial reagents were purchased from Sigma Aldrich, Acros, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, or Cambridge Isotopes Laboratories and used as received with the following exceptions: Potassium phosphate and bis(pinacolato)diboron were purchased from Sigma Aldrich and immediately placed in a N_2-atmosphere glovebox for storage. Pivaloyl chloride was purchased from Acros and distilled before use. PhMe, CH_2Cl_2, MeCN, and THF were dried by passing through drying columns.[1] PhMe and MeCN were then degassed by sparging with N_2 and stored over activated 4Å MS in a N_2-atmosphere glovebox. Enantioenriched allylic alcohols are obtained via either CBS reduction of ketones or kinetic resolution of racemic allylic alcohols according to procedures reported in the literature.[2] Oven-dried potassium carbonate was added into $CDCl_3$ to remove trace amount of acid. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on both 400 MHz and 600 MHz spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.2). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra

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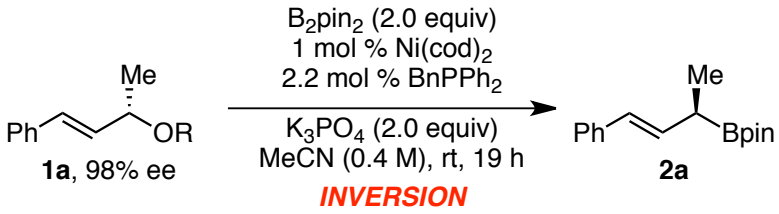
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs. R. H.: Rosen. R. K.: Timmers. F. J. *Organometallics* **1996**.
[2] CBS reduction of ketones, see: (a) Corey, E. J.; Bakshi, R. K. *Tetrahedron Lett.* **1990**, *31*, 611. (b) Corey, E. J.; Helal, C. J. *Tetrahedron Lett.* **1995**, *36*, 9153. Kinetic resolution of allylic alcohols, see: (c) Sasaki, M.; Ikemoto, H.; Kawahata, M.; Yamaguchi, K.; Takeda, K. *Chem. Eur. J.* **2009**, *15*, 4663.

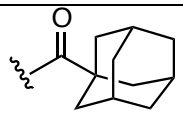
were obtained using FTIR spectrophotometers with material loaded onto a NaCl plate. The mass spectral data were obtained at the University of Delaware mass spectrometry facility. Optical rotations were measured using a 2.5 mL cell with a 0.1 dm path length. Melting points were taken on a Stuart SMP10 instrument.

Leaving Group Effects

The effect of various leaving groups was examined under stereoinvertive and stereoretentive conditions. Please note that these conditions are not the final optimized conditions.

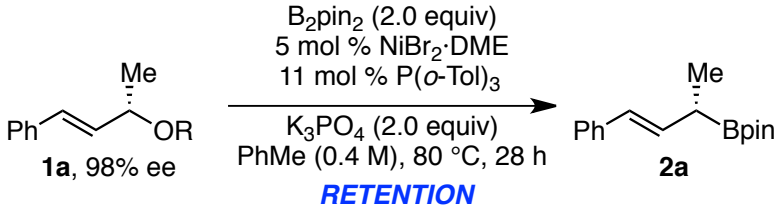
Table S1. Leaving Group Effects Under Inversion Conditions.

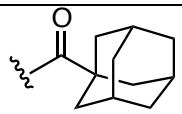


Entry	R	Conversion (%)[a]	Yield (%)[a]	ee (%)[b]
1	Piv	>99	88	95
2	Ac	56	53	95
3		88	69	92
4	Boc	86	44	95
5	$C(O)NMe_2$	>99	71	92
6	$C(O)C_6F_5$	38	13	80

[a] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b] ee's of the subsequent alcohol (**3a**), formed via oxidation with H_2O_2 and NaOH. Determined by HPLC analysis using a chiral stationary phase.

Table S2. Leaving Group Effects Under Retention Conditions.

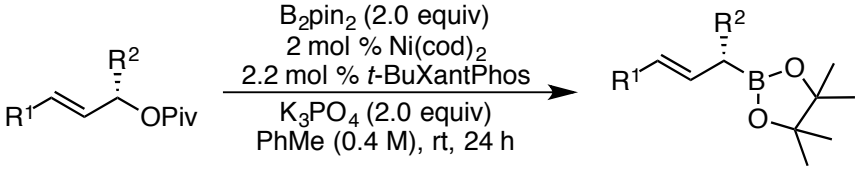


Entry	R	Conversion (%)[a]	Yield (%)[a]	ee (%)[b]
1	Piv	91	85	97
2	Ac	65	55	96
3		48	40	95
4	Boc	>99	71	72
5	$C(O)NMe_2$	>99	75	94
6	$C(O)C_6F_5$	36	26	46

[a] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [b] ee's of the subsequent alcohol (**3a**), formed via oxidation with H_2O_2 and NaOH. Determined by HPLC analysis using a chiral stationary phase.

Borylation of Allylic Pivalates

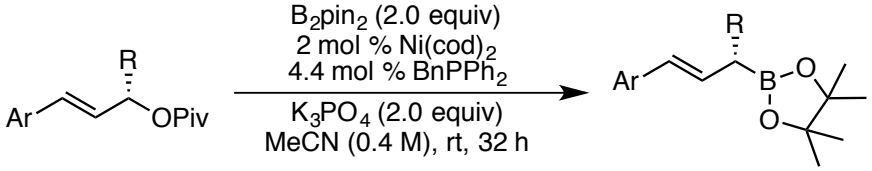
General Procedure A: Borylation with Retention of Configuration



In a N_2-atmosphere glovebox, $Ni(cod)_2$ (2.2 mg, 0.0080 mmol, 2 mol %), *t*-Bu-XantPhos (4.4 mg, 0.0088 mmol, 2.2 mol %) and K_3PO_4 (169.7 mg, 0.8 mmol, 2.0 equiv) were weighed into a 2-dram vial fitted with a magnetic stir bar. B_2pin_2 (203 mg, 0.80 mmol, 2.0 equiv) and allylic pivalate (0.40 mmol, 1.0 equiv) were added, followed by

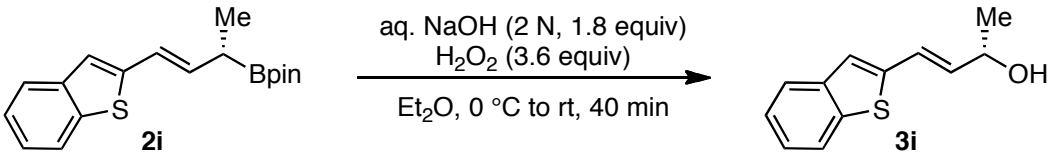
PhMe (1.0 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a plug of silica gel and Celite®, which was then rinsed with Et_2O (~ 15 mL). The filtrate was concentrated and then purified by silica gel chromatography to give the allylic boronate product. The α:γ ratios reported below are of isolated allylic boronates. The allylic boronate was then converted to the corresponding allylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure B: Borylation with Inversion of Configuration

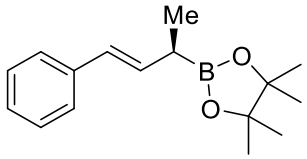


In a N_2-atmosphere glovebox, $Ni(cod)_2$ (2.2 mg, 0.0080 mmol, 2 mol %), $BnPPh_2$ (4.9 mg, 0.0176 mmol, 4.4 mol %) and K_3PO_4 (169.7 mg, 0.80 mmol, 2.0 equiv) were weighed into a 2-dram vial fitted with a magnetic stir bar. B_2pin_2 (203 mg, 0.80 mmol, 2.0 equiv) and allylic pivalate (0.40 mmol, 1.0 equiv) were added, followed by MeCN (1.0 mL, 0.4 M). The vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at room temperature for 32 h. The reaction mixture was then diluted with Et_2O (2.5 mL) and quickly filtered through a plug of silica gel and Celite®, which was then rinsed with Et_2O (~15 mL). The filtrate was concentrated and then purified by silica gel chromatography to give the allylic boronate product. The α:γ ratios reported below are of isolated allylic boronates. The allylic boronate was then converted to the corresponding allylic alcohol via oxidation (see General Procedure C below) to determine the enantiomeric excess (ee).

General Procedure C: Oxidation of Allylic Boronates to Allylic Alcohols for Determination of Enantiomeric Excess (ee).



A solution of (*S*,*E*)-2-(4-(benzothiophen-2-yl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-**2i**, 10 mg, 0.0318 mmol, 1.0 equiv) and Et_2O (0.08 mL, 0.4M) was cooled to 0 ˚C. Aqueous NaOH (2 N, 0.029 mL, 0.058 mmol, 1.8 equiv) was added, followed by H_2O_2 (0.013 mL, 0.116 mmol, 3.6 equiv). The mixture was stirred at 0 ˚C for 10 min and then at room temperature for an additional 30 min. The reaction mixture was diluted with H_2O, and extracted with Et_2O. The organic layer was dried ($MgSO_4$), filtered, and concentrated to give (*S*)-**3i** (6.45 mg, 99%) with sufficient purity for HPLC analysis using a chiral stationary phase without further purification. The oxidations of other boronates were performed with different amounts of starting material.

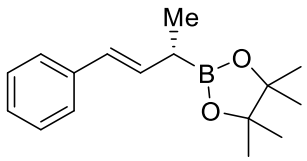


(*R*,*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)–2a). Prepared via General Procedure A using pivalate **1a** (prepared in 98% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2a** (run 1: 78.4 mg, α:γ=20:1, 76%; run 2: 77.2 mg, α:γ=20:1, 75%) as colorless oil. $[\alpha]_D^{24}$ = +15.9 (c 0.69, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.30 – 7.26 (m, 2H), 7.19 – 7.14 (m, 1H), 6.37 – 6.32 (m, 2H), 2.15 – 2.0 (m, 1H), 1.24 (s, 12H), 1.19 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 133.3, 128.4, 127.6, 126.5, 125.9, 83.3, 24.7, 24.6, 14.8;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (NaCl/thin film) 2977, 1457, 1379, 1352, 1322, 1143, 965, 750, 695 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{16}H_{22}BO_2$: 257.1713, found: 257.1734.

[3] In some cases, the allylic carbon is not observed due to quadrupolar broadening caused by ^{11}B.

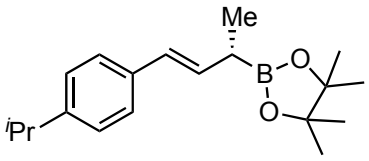
Boronate (*R*)-**2a** was oxidized to alcohol (*R*)-**3a** via General Procedure C. The enantiomeric excess was determined to be 97% (run 1: 96% ee; run 2: 97% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 15.323 min, t_R(minor) = 23.090 min. The spectral data of this alcohol matched that of alcohol **3a** as prepared via General Procedure E (see below).

The borylation of pivalate **1a** was also performed on 5-mmol scale, following General Procedure A. In a N_2-atmosphere glovebox, pivalate **1a** (116.1 mg, 5.0 mmol, 1.0 equiv), $Ni(cod)_2$ (27.5 mg, 0.10 mmol, 2 mol %), *t*-Bu-XantPhos (55 mg, 0.11 mmol, 2.2 mol %) and K_3PO_4 (2.12 g, 10 mmol, 2.0 equiv) were weighed into a heavy wall pressure vessel. B_2pin_2 (2.54 g, 10 mmol, 2.0 equiv) and pivalate **1a** (1.16 g, 5 mmol, 1.0 equiv) were added, followed by PhMe (12.5 mL, 0.4 M). The vessel was sealed, and removed from the glovebox. The mixture was stirred at room temperature for 24 h, then diluted with Et_2O (25 mL), and filtered through a plug of silica gel and Celite®. The filter cake was rinsed with Et_2O (50 mL). The filtrate was concentrated and then purified by silica gel chromatography (0−2% Et_2O/hexanes) to give the (*R*)-**2a** (938 mg, 73%, α:γ=20:1). Boronate (*R*)-**2a** was then oxidized to alcohol (*R*)-**3a** via General Procedure C. The enantiomeric excess was determined to be 93%.



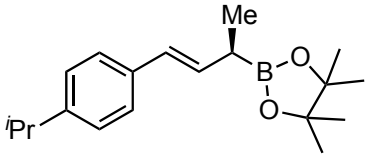
(*S*,*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-2a). Prepared via General Procedure B using pivalate **1a** (prepared in 98% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2a** (run 1: 88.2 mg, α:γ=7:1, 85%; run 2: 83.0 mg, α:γ=9:1, 80%) as colorless oil. $[\alpha]_D^{24}$ = −27.8 (c 0.72, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*S*)-**2a** was oxidized to alcohol (*S*)-**3a** via General Procedure C. The enantiomeric excess was determined to be 87% (run 1: 86% ee; run 2: 87% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.980 min, t_R(minor) = 15.249 min. The spectral data of this alcohol matched that of alcohol **3a** as prepared via General Procedure E (see below).



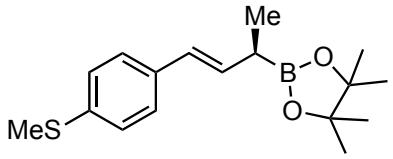
(*S*,*E*)-2-(4-(4-isopropylphenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-2b). Prepared via General Procedure A using pivalate **1b** (prepared in 92% ee). The crude mixture was purified by silica gel chromatography (0−4% Et_2O/hexanes) to give (*S*)-**2b** (run 1: 93.8 mg, 78%, α:γ>20:1; run 2: 96.8 mg, 81%, α:γ>20:1) as colorless oil. $[\alpha]_D^{24}$ = +6.0 (c 2.6, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.37 – 6.22 (m, 2H), 2.87 (h, *J* = 6.9 Hz, 1H), 2.04 (p, *J* = 7.2 Hz, 1H), 1.25 – 1.22 (m, 18H), 1.18 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 136.1, 132.5, 127.6, 126.6, 126.0, 83.4, 33.9, 24.9, 24.8, 24.1, 15.1;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (NaCl/thin film) 2961, 2872, 1653, 1558, 1507, 1457, 1379, 1325, 1143, 966, 855 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{19}H_{29}BO_2$: 300.2261, found: 300.2273.

Boronate (*S*)-**2b** was oxidized to alcohol (*S*)-**3b** via General Procedure C. The enantiomeric excess was determined to be 84% (run 1: 84% ee; run 2: 84% ee) by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 4% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 8.743 min, t_R(minor) = 9.345 min. The spectral data of this alcohol matched that of alcohol **3b** as prepared via General Procedure F (see below).



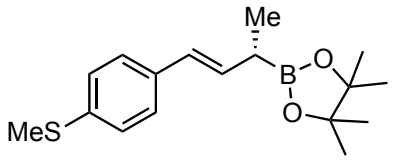
(*R*,*E*)-2-(4-(4-isopropylphenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2b). Prepared via General Procedure B using pivalate **1b** (prepared in 92% ee). The crude mixture was purified by silica gel chromatography (0−4% Et_2O/hexanes) to give (*R*)-**2b** (run 1: 90.1 mg, α:γ=10:1, 75%; run 2: 97.5 mg, 81%, α:γ=10:1) as a colorless oil. $[\alpha]_D^{24}$ = −12.4 (c 2.6, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*R*)-**2b** was oxidized to alcohol (*R*)-**3b** via General Procedure C. The enantiomeric excess was determined to be 84% (run 1: 84% ee; run 2: 83% ee) by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 4% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 9.363 min, t_R(minor) = 8.748 min. The spectral data of this alcohol matched that of alcohol **3b** as prepared via General Procedure F (see below).



(*R*,*E*)-4,4,5,5-tetramethyl-2-(4-(4-(methylthio)phenyl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)-2c). Prepared via General Procedure A using pivalate **1c** (prepared in 93% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2c** (run 1: 75.6 mg, α:γ=20:1, 62%; run 2: 78 mg, α:γ=15:1 64%) as pale yellow, waxy solid. $[\alpha]_D^{24}$ = +10.9 (c 2.84, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.17 (m, 2H), 6.33 – 6.26 (m, 2H), 2.47 (s, 3H), 2.08 – 2.01 (m, 1H), 1.24 (s, 12H), 1.18 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 135.7, 133.1, 127.2, 127.1, 126.5, 83.4, 24.9, 24.8, 16.4, 15.0;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2. FTIR (NaCl/thin film) 2976, 2924, 2871, 1652, 1558, 1493, 1373, 1321, 1143, 966 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{17}H_{25}BO_2S$: 304.1668, found: 304.1680.

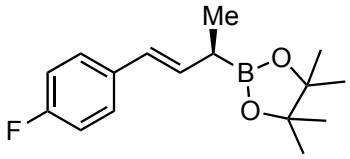
Boronate (*R*)-**2c** was oxidized to alcohol (*R*)-**3c** via General Procedure C. The enantiomeric excess was determined to be 88% (run 1: 88% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 13.108 min, t_R(minor) = 15.130 min. The spectral data of this alcohol matched that of alcohol **3c** as prepared via General Procedure F (see below).



(*S*,*E*)-4,4,5,5-tetramethyl-2-(4-(4-(methylthio)phenyl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-2c). Prepared via General Procedure B using pivalate **1c** (prepared in

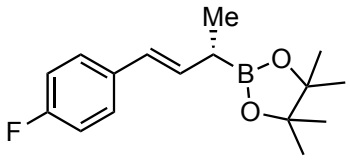
93% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2c** (run 1: 76.8 mg, α:γ=6:1, 63%; run 2: 70.7 mg, α:γ=7:1, 58%) as pale yellow, waxy solid. $[\alpha]_D^{24} = -10.4$ (c 2.30, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*S*)-**2c** was oxidized to alcohol (*S*)-**3c** via General Procedure C. The enantiomeric excess was determined to be 86% (run 1: 87% ee; run 2: 84% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 15.145 min, t_R(minor) = 13.127 min. The spectral data of this alcohol matched that of alcohol **3c** as prepared via General Procedure F (see below).



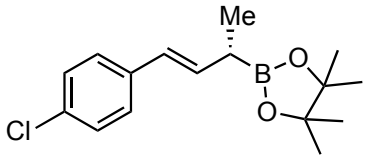
(*R*,*E*)-2-(4-(4-fluorophenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2d). Prepared via General Procedure A using pivalate **1d** (prepared in 97% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2d** (run 1: 77.5 mg, 70%, α:γ=20:1; run 2: 88.8 mg, α:γ>20:1, 80%) as pale yellow oil. $[\alpha]_D^{24} = +7.4$ (c 2.4, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 6.99 – 6.94 (m, 2H), 6.31 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.9, 7.3 Hz, 1H), 2.07 –2.01 (m, 1H), 1.24 (s, 12H), 1.18 (d, J = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.8 (d, $J_{C–F}$ = 245.1 Hz), 134.6 (d, $J_{C–F}$ = 3.2 Hz), 133.2 (d, $J_{C–F}$ = 2.2 Hz, olefin carbon), 127.4 (d, $J_{C–F}$ = 7.8 Hz), 126.6, 115.3 (d, $J_{C–F}$ = 21.3 Hz), 83.5, 24.87, 24.81, 15.0;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.1; FTIR (NaCl/thin film) 2979, 2923, 1652, 159, 1507, 1456, 1373, 1226, 1145, 982, 851, 699 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{16}H_{22}BFO_2$: 276.1697, found: 276.1674.

Boronate (*R*)-**2d** was oxidized to alcohol (*R*)-**3d** via General Procedure C. The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.7 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 29.973 min, t_R(minor) = 28.727 min. The spectral data of this alcohol matched that of alcohol **3d** as prepared via General Procedure E (see below).



(*S*,*E*)-2-(4-(4-fluorophenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*(S)*-2d). Prepared via General Procedure B using pivalate **1d** (prepared in 97% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2d** (run 1: 82.2 mg, α:γ=7:1, 74%; run 2: 70.7 mg, α:γ=6:1, 67%) as pale yellow oil. $[\alpha]_D^{24} = -8.5$ (c 2.35, $CHCl_3$). The spectral data of this compound matches that described above.

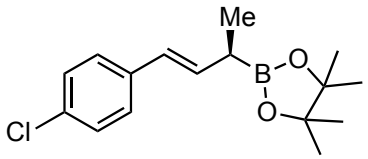
Boronate (*S*)-**2d** was oxidized to alcohol (*S*)-**3d** via General Procedure C. The enantiomeric excess was determined to be 89% (run 1: 89% ee; run 2: 88% ee) by chiral HPLC analysis (CHIRALPAK IA, 0.7 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 28.547 min, t_R(minor) = 29.818 min. The spectral data of this alcohol matched that of alcohol **3d** as prepared via General Procedure E (see below).



(*S*,*E*)-2-(4-(4-chlorophenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*(S)*-2e). Prepared via General Procedure A using pivalate **1e** (prepared in 96% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2e** (run 1: 78 mg, 67%, α:γ>20:1; run 2: 75.6 mg, α:γ>20:1, 65%) as pale yellow, waxy solid. $[\alpha]_D^{24} = -5.9$ (c 2.52, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.25 – 7.21 (m, 2H), 6.35 – 6.26 (m, 2H), 2.08 – 2.02 (m, 1H) 1.24 (s, 12H), 1.18 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 134.3, 132.1, 128.6, 127.2, 126.6, 83.5, 24.9, 24.8, 14.9;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.1; FTIR (NaCl/thin film) 2978, 2931, 2874, 1653, 1490, 1373, 1324, 1143, 1090, 854, 807 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{16}H_{22}BClO_2$: 292.1401, found: 292.1376.

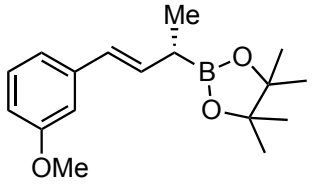
Boronate (*S*)-**2e** was oxidized to alcohol (*S*)-**3e** via General Procedure C. The enantiomeric excess was determined to be 87% (run 1: 88% ee; run 2: 86% ee) by chiral

HPLC analysis (CHIRALPAK IA, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.413 min, t_R(minor) = 25.711 min. The spectral data of this alcohol matched that of alcohol **3e** as prepared via General Procedure E (see below).



(*R*,*E*)-2-(4-(4-chlorophenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2e). Prepared via General Procedure B using pivalate **1e** (prepared in 97% ee) except with 5 mol% $Ni(cod)_2$ and 11 mol % $BnPPh_2$ for 29 h. The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2e** (run 1: 60.7 mg, α:γ=8:1, 52%; run 2: 59 mg, α:γ=5:1, 50%) as pale yellow oil. $[\alpha]_D^{24}$ = +6.7 (c 1.92, $CHCl_3$). The spectral data of this compound matches that described above.

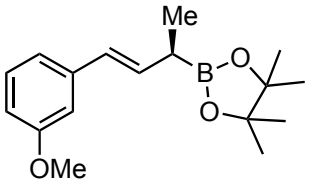
Boronate (*R*)-**2e** was oxidized to alcohol (*R*)-**3e** via General Procedure C. The enantiomeric excess was determined to be 82% (run 1: 82% ee; run 2: 81% ee) by chiral HPLC analysis (CHIRALPAK IA, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 25.679 min, t_R(minor) = 22.319 min. The spectral data of this alcohol matched that of alcohol **3e** as prepared via General Procedure E (see below).



(S,E)-2-(4-(3-methoxyphenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((S)-2f). Prepared via General Procedure A using pivalate **1f** (prepared in 98% ee). The crude mixture was purified by silica gel chromatography (2−5% Et_2O/hexanes) to give (*S*)-**2f** (run 1: 76.1 mg, 66%, α:γ=14:1; run 2: 81 mg, α:γ=13:1, 70%) as a colorless oil. $[\alpha]_D^{24}$ = +8.5 (c 1.63, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.88 (m, 1H), 6.73 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.38 – 6.29 (m, 2H), 3.81 (s, 3H), 2.08 – 2.02 (m, 1H), 1.24 (s, 12H), 1.19 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.9, 139.9, 133.8, 129.5, 127.7, 118.8, 112.3, 111.3, 83.4, 55.3,

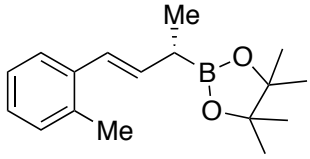
24.9, 24.8, 15.0;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.1; FTIR (NaCl/thin film) 2977, 1653, 1558, 1506, 1456, 1147, 980, 668 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{17}H_{25}BO_3$: 288.1897, found: 288.1915.

Boronate (*S*)-**2f** was oxidized to alcohol (*S*)-**3f** via General Procedure C. The enantiomeric excess was determined to be 95% (run 1: 95% ee; run 2: 94% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 17.987 min, t_R(minor) = 20.193 min. The spectral data of this alcohol matched that of alcohol **3f** as prepared via General Procedure F (see below).



(*R*,*E*)-2-(4-(3-methoxyphenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2f). Prepared via General Procedure B using pivalate **1f** (prepared in 98% ee). The crude mixture was purified by silica gel chromatography (2−5% Et_2O/hexanes) to give (*R*)-**2f** (run 1: 82.7 mg, α:γ=6:1, 72%; run 2: 78 mg, α:γ=6:1, 68%) as a colorless oil. $[\alpha]_D^{24} = -5.3$ (c 2.05, $CHCl_3$). The spectral data of this compound matches that described above.

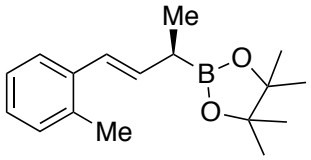
Boronate (*R*)-**2f** was oxidized to alcohol (*R*)-**3f** via General Procedure C. The enantiomeric excess was determined to be 90% (run 1: 90% ee; run 2: 89% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 5% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 20.030 min, t_R(minor) = 17.856 min. The spectral data of this alcohol matched that of alcohol **3f** as prepared via General Procedure F (see below).



(*S*,*E*)-4,4,5,5-Tetramethyl-2-(4-(o-tolyl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-2g). Prepared via General Procedure A using pivalate **1g** (prepared in 94% ee), except with 5 mol % $Ni(cod)_2$ and 5.5 mol % *t*-BuXantPhos. The crude mixture was purified by silica

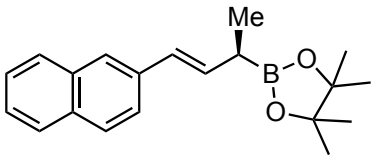
gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2g** (run 1: 80.4 mg, α:γ=10:1, 74%; run 2: 77.4 mg, α:γ=15:1, 71%) as a colorless oil. $[\alpha]_D^{24}$ = +18.2 (c 0.95, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.4 Hz, 1H), 7.06 – 7.02 (m, 3H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.12 (dd, *J* = 15.7, 7.7 Hz, 1H), 2.25 (s, 3H), 2.07 – 1.95 (m, 1H), 1.18 (s, 12H), 1.13 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.4, 134.8, 134.7, 130.1, 126.5, 125.9, 125.5, 125.4, 83.2, 27.2, 24.74, 24.70, 19.9, 15.0; ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3; FTIR (NaCl/thin film) 2976, 1457, 1321, 1143, 966, 749 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{17}H_{24}BO_2$: 271.1869, found: 271.1873.

Boronate (*S*)-**2g** was oxidized to alcohol (*S*)-**3g** via General Procedure C. The enantiomeric excess was determined to be 93% (run 1: 93% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 16.057 min, t_R(minor) = 24.458 min. The spectral data of this alcohol matched that of alcohol **3g** as prepared via General Procedure F (see below).



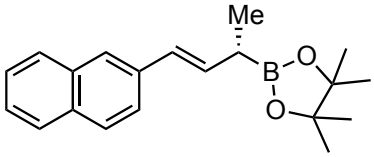
(*R*,*E*)-4,4,5,5-Tetramethyl-2-(4-(o-tolyl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)-2g). Prepared via General Procedure B using pivalate **1g** (prepared in 94% ee) except using 5 mol % $Ni(cod)_2$ and 11 mol % $BnPPh_2$. The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2g** (run 1: 83.4 mg, α:γ=10:1, 78%; run 2: 80.2 mg, α:γ=13:1, 75%) as a colorless oil. $[\alpha]_D^{24}$ = −22.6 (c 0.83, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*R*)-**2g** was oxidized to alcohol (*R*)-**3g** via General Procedure C. The enantiomeric excess was determined to be 84% (run 1: 83% ee; run 2: 84% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 24.786 min, t_R(minor) = 16.280 min. The spectral data of this alcohol matched that of alcohol **3g** as prepared via General Procedure F (see below).



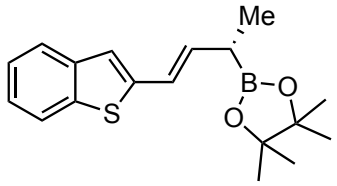
(*R*,*E*)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)-2h). Prepared via General Procedure A using pivalate **1h** (prepared in 97% ee). The crude mixture was purified by silica gel chromatography (0−3% Et_2O/hexanes) to give (*R*)-**2h** (run 1: 108.5 mg, 88%, α:γ>20:1; run 2: 99.7 mg, α:γ>20:1, 81%) as off-white solid (mp 78−81°C). $[\alpha]_D^{24}$ = +10.8 (c 1.58, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 3H), 7.67 (s, 1H), 7.59 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.45 – 7.37 (m, 2H), 6.55 – 6.44 (m, 2H), 2.16 – 2.10 (m, 1H), 1.26 (s, 12H), 1.24 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.9, 134.0, 133.9, 132.7, 128.0, 127.93, 127.91, 127.7, 126.2, 125.4, 125.2, 123.9, 83.5, 24.9, 24.8, 15.0;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3; FTIR (NaCl/thin film) 2980, 2920, 1683, 1635, 1558, 1506, 1456, 1142, 667 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{20}H_{25}BO_2$: 308.1948, found: 308.1947.

Boronate (*R*)-**2h** was oxidized to alcohol (*R*)-**3h** via General Procedure C. The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 21.293 min, t_R(minor) = 23.576 min. The spectral data of this alcohol matched that of alcohol **3h** as prepared via General Procedure E (see below).



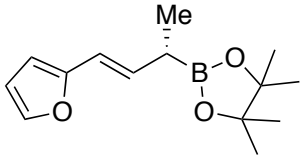
(*S*,*E*)-4,4,5,5-tetramethyl-2-(4-(naphthalen-2-yl)but-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-2h). Prepared via General Procedure B using pivalate **1h** (prepared in 97% ee). The crude mixture was purified by silica gel chromatography (0−3% Et_2O/hexanes) to give (*S*)-**2h** (run 1: 64.1 mg, α:γ=9:1, 52%; run 2: 67.8 mg, α:γ=7:1, 55%) as off-white solid (mp 78−81°C). $[\alpha]_D^{24}$ = −9.1 (c 3.08, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*S*)-**2h** was oxidized to alcohol (*S*)-**3h** via General Procedure C. The enantiomeric excess was determined to be 88% (run 1: 88% ee; run 2: 87% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 23.494 min, t_R(minor) = 21.244 min. The spectral data of this alcohol matched that of alcohol **3h** as prepared via General Procedure E (see below).



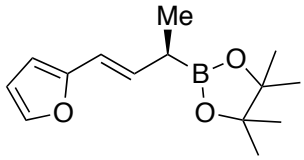
(*S*,*E*)-2-(4-(benzothiophen-2-yl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-2i). Prepared via General Procedure A using pivalate **1i** (prepared in 70% ee) except on a 0.30 mmol scale. The crude mixture was purified by silica gel chromatography (0−4% Et_2O/hexanes) to give (*S*)-**2i** (60 mg, 64%, α:γ>20:1) as a pale yellow, waxy solid. $[\alpha]_D^{24}$ = +10.7 (c 1.9, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.03 (s, 1H), 6.61 – 6.55 (m, 1H), 6.29 (dd, *J* = 15.6, 7.6 Hz, 1H), 2.11 – 2.06 (m, 1H), 1.25 (s, 12H), 1.21 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.0, 140.5, 138.6, 136.5, 124.3, 124.2, 123.2, 122.2, 121.9, 120.8, 83.6, 24.9, 24.8, 14.7;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.2; FTIR (NaCl/thin film) 2978, 1652, 1558, 1457, 1373, 1144, 981, 851 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{18}H_{24}BO_2S$: 315.1590, found: 315.1591.

Boronate (*S*)-**2i** was oxidized to alcohol (*S*)-**3i** via General Procedure C. The enantiomeric excess was determined to be 68% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 21.095 min, t_R(minor) = 23.755 min. The spectral data of this alcohol matched that of alcohol **3i** as prepared via General Procedure F (see below).



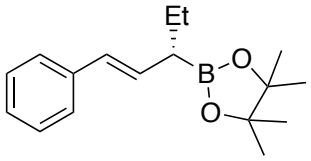
(*S*,*E*)-2-(4-(Furan-2-yl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-2j). Prepared via General Procedure A using pivalate **1j** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2j** (run 1: 39.1 mg, α:γ > 20:1, 39%; run 2: 48.7 mg, α:γ > 20:1, 48%) as colorless oil. $[\alpha]_D^{24}$ = +24.0 (c 0.71, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 1H), 6.33 – 6.26 (m, 2H), 6.18 (dd, *J* = 16.0, 1.4 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.24 (s, 12H), 1.17 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.8, 140.9, 132.4, 116.5, 111.0, 105.4, 83.3, 24.7, 24.7, 14.6;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.3; FTIR (NaCl/thin film) 2977, 1457, 1373, 1351, 1323, 1143, 1011, 964, 728 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{14}H_{21}BO_3$: 248.1584, found: 248.1577.

Boronate (*S*)-**2j** was oxidized to alcohol (*S*)-**3j** via General Procedure C. The enantiomeric excess was determined to be 92% (run 1: 91% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALCEL OD–H, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.253 min, t_R(minor) = 25.273 min. The spectral data of this alcohol matched that of alcohol **3j** as prepared via General Procedure F (see below).



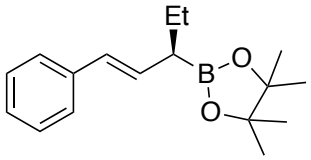
(*R*,*E*)-2-(4-(Furan-2-yl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2j). Prepared via General Procedure B using pivalate **1j** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2j** (run 1: 29.2 mg, α:γ=11:1, 30%; run 2: 31.6 mg, α:γ=14:1, 31%) as a colorless oil. $[\alpha]_D^{24}$ = −26.8 (c 0.6, $CHCl_3$). The spectral data of this compound matches that described above.

Boronate (*R*)-**2j** was oxidized to alcohol (*R*)-**3j** via General Procedure C. The enantiomeric excess was determined to be 77% (run 1: 77% ee; run 2: 76% ee) by chiral HPLC analysis (CHIRALCEL OD–H, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 24.874 min, t_R(minor) = 22.002 min. The spectral data of this alcohol matched that of alcohol **3j** as prepared via General Procedure F (see below).



(*S*,*E*)-4,4,5,5-Tetramethyl-2-(1-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane ((*S*)-2k). Prepared via General Procedure A using pivalate **1k** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2k** (run 1: 94.0 mg, α:γ=10:1, 86%; run 2: 93.6 mg, α:γ=8:1, 86%) as colorless oil. $[\alpha]_D^{24}$ = +26.8 (c 0.87, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 2H), 7.29 – 7.27 (m, 2H), 7.18 – 7.15 (m, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.8, 9.0 Hz, 1H), 1.93 – 1.89 (m, 1H), 1.72 – 1.65 (m, 1H), 1.58 – 1.51 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 131.9, 129.1, 128.4, 126.5, 125.9, 83.2, 24.8, 24.6, 24.0, 13.7;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.0; FTIR (NaCl/thin film) 2977, 1371, 1321, 1143, 967, 749, 694 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{17}H_{25}BO_2$: 272.1948, found: 272.1924.

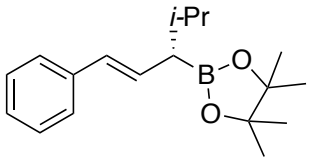
Boronate (*S*)-**2k** was oxidized to alcohol (*S*)-**3k** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 98% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 17.361 min, t_R(minor) = 28.554 min. The spectral data of this alcohol matched that of alcohol **3k** as prepared via General Procedure F (see below).



(*R*,*E*)-4,4,5,5-Tetramethyl-2-(1-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane ((*R*)-2k). Prepared via General Procedure B using pivalate **1k** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2k** (run 1: 95.0 mg, α:γ=8:1, 87%; run 2: 93.9 mg, α:γ=8:1, 86%) as colorless oil. $[\alpha]_D^{24}$ = −22.1 (c 0.95, $CHCl_3$). The spectral data of this compound matches that described above.

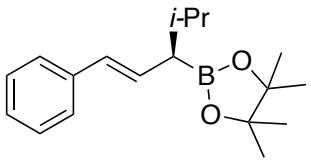
Boronate (*R*)-**2k** was oxidized to alcohol (*R*)-**3k** via General Procedure C. The enantiomeric excess was determined to be 91% (run 1: 91% ee; run 2: 90% ee) by chiral

HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 28.625 min, t_R(minor) = 17.498 min. The spectral data of this alcohol matched that of alcohol **3k** as prepared via General Procedure F (see below).



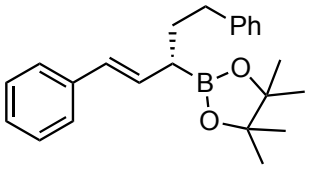
(*S*,*E*)-4,4,5,5-Tetramethyl-2-(4-methyl-1-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane ((*S*)-2l). Prepared via General Procedure A using pivalate **1l** (prepared in 99% ee), except using 5 mol % $Ni(cod)_2$ and 5.5 mol % *t*-BuXantPhos at 40 °C. The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2l** (run 1: 89.8 mg, α:γ=2:1, 78%; run 2: 91.0 mg, α:γ=2:1, 79%) as colorless oil. $[\alpha]_D^{24}$ = +15.7 (c 0.36, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$, α-isomer) δ 7.35 – 7.34 (m, 2H), 7.29 – 7.27 (m, 2H), 7.18 – 7.17 (m, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.19 (dd, *J* = 15.8, 9.9 Hz, 1H), 1.95 – 1.93 (m, 1H), 1.74 (t, *J* = 9.3 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.00 – 0.97 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$, α and γ mixture) δ 142.3, 138.3, 131.1, 130.0, 128.42, 128.37, 128.3, 128.2, 126.7, 126.5, 125.9, 125.2, 83.4, 83.2, 31.2, 30.0, 24.74, 24.66, 24.5, 22.7, 22.6, 22.1; ^{11}B NMR (193 MHz, $CDCl_3$) δ 32.6; FTIR (NaCl/thin film) 2977, 1371, 1320, 1142, 970, 853, 750, 695 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{18}H_{27}BO_2$: 286.2104, found: 286.2131.

Boronate (*S*)-**2l** was oxidized to alcohol (*S*)-**3l** via General Procedure C. The enantiomeric excess was determined to be 98% (run 1: 97% ee; run 2: 98% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 14.739 min, t_R(minor) = 22.980 min. The spectral data of this alcohol matched that of alcohol **3l** as prepared via the General Procedure F (see below).



(*R*,*E*)-4,4,5,5-Tetramethyl-2-(4-methyl-1-phenylpent-1-en-3-yl)-1,3,2-dioxaborolane ((*R*)-2l). Prepared via General Procedure B using pivalate **1l** (prepared in 99% ee), except using 5 mol % $Ni(cod)_2$ and 11 mol % *t*-BuXantPhos at 40 °C. The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2l** (run 1: 94.0 mg, α:γ=3:2, 83%; run 2: 91.7 mg, α:γ=7:5, 81%) as colorless oil. $[\alpha]_D^{24} = -11.6$ (c 0.9, $CHCl_3$). The spectral data of this compound matches that described above.

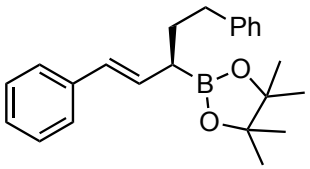
Boronate (*R*)-**2l** was oxidized to alcohol (*R*)-**3l** via General Procedure C. The enantiomeric excess was determined to be 80% (run 1: 79% ee; run 2: 80% ee) by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 22.643 min, t_R(minor) = 14.374 min. The spectral data of this alcohol matched that of alcohol **3l** General Procedure F (see below).



(*S*,*E*)-2-(1,5-diphenylpent-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-2m). Prepared via General Procedure A using pivalate **1m** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2f** (run 1: 104.7 mg, 75%, α:γ=14:1; run 2: 109.2 mg, α:γ=14:1, 78%) as a white solid (mp 87−90 °C). $[\alpha]_D^{24} = -20.4$ (c 4.4, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.31 – 7.26 (m, 4H), 7.21 – 7.16 (m, 4H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.64 – 2.56 (m, 1H), 2.09 – 2.01 (m, 1H), 2.00 – 1.92 (m, 1H), 1.89 – 1.78 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 138.3, 131.6, 129.7, 128.7, 128.6, 128.4, 126.8, 126.1, 125.8, 83.5, 35.6, 32.8, 24.9, 24.8;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 32.9; FTIR (NaCl/thin film) 3024, 2977, 2928, 1653, 1495, 1456, 1370, 1323, 1142, 967, 750 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{23}H_{29}BO_2$: 348.2261, found: 348.2287.

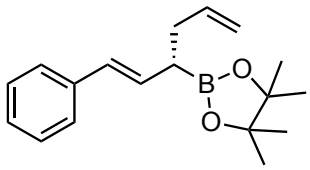
Boronate (*S*)-**2m** was oxidized to alcohol (*S*)-**3m** via General Procedure C. The enantiomeric excess was determined to be 96% (run 1: 96% ee; run 2: 95% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major)

= 22.971 min, t_R(minor) = 27.376 min. The spectral data of this alcohol matched that of alcohol **3m** as prepared via General Procedure F (see below).



(*R*,*E*)-2-(1,5-diphenylpent-1-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*R*)-2m). Prepared via General Procedure B using pivalate **1m** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2m** (run 1: 107.6 mg, α:γ=14:1, 77%; run 2: 112.3 mg, α:γ=12:1, 81%) as a white solid (mp 87−90 °C). $[\alpha]_D^{24}$ = +20.7 (c 3.46, $CHCl_3$). The spectral data of this compound matches that described above.

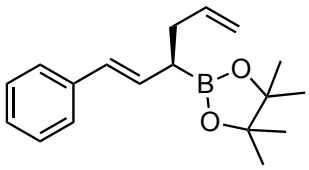
Boronate (*R*)-**2m** was oxidized to alcohol (*R*)-**3m** via General Procedure C. The enantiomeric excess was determined to be 92% (run 1: 92% ee; run 2: 92% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 27.197 min, t_R(minor) = 22.849 min. The spectral data of this alcohol matched that of alcohol **3m** as prepared via General Procedure F (see below).



(*S*,*E*)-4,4,5,5-tetramethyl-2-(1-phenylhexa-1,5-dien-3-yl)-1,3,2-dioxaborolane ((*S*)-2n). Prepared via General Procedure A using pivalate **1n** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2n** (run 1: 100 mg, α:γ>20:1, 88%; run 2: 91.4 mg, α:γ=18:1, 80%) as a pale yellow solid (mp 57−60 °C). $[\alpha]_D^{24}$ = −2.8 (c 3.19, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.29 − 7.25 (m, 2H), 7.19 – 7.15 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 8.7 Hz, 1H), 5.90 – 5.82 (m, 1H), 5.09 – 5.04 (m, 1H), 4.97 (dd, *J* = 10.2, 1.9 Hz, 1H), 2.45 − 2.37 (m, 1H), 2.34 – 2.27 (m, 1H), 2.12 − 2.07 (m, 1H), 1.242 (s, 6H), 1.236 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 138.1, 131.2, 129.4, 128.5, 126.7, 126.1,

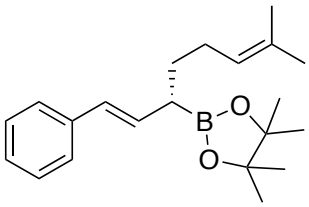
115.3, 83.5, 35.2, 24.9, 24.8;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 32.8; FTIR (NaCl/thin film) 3024, 2977, 2928, 1653, 1495, 1456, 1370, 1323, 1142, 967, 750 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{23}H_{29}BO_2$: 348.2261, found: 348.2287.

Boronate (*S*)-**2n** was oxidized to alcohol (*S*)-**3n** via General Procedure C. The enantiomeric excess was determined to be 77% (run 1: 75% ee; run 2: 79% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 15.203 min, t_R(minor) = 17.382 min. The spectral data of this alcohol matched that of alcohol **3n** as prepared via General Procedure F (see below).



(*R*,*E*)-4,4,5,5-tetramethyl-2-(1-phenylhexa-1,5-dien-3-yl)-1,3,2-dioxaborolane ((*R*)-2n). Prepared via General Procedure B using pivalate **1n** (prepared in 99% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2n** (run 1: 81.5 mg, α:γ=16:1, 72%; run 2: 80.5 mg, α:γ=20:1, 71%) as a white solid (mp 57−60 °C). $[\alpha]_D^{24}$ = +13.6 (c 2.6, $CHCl_3$). The spectral data of this compound matches that described above.

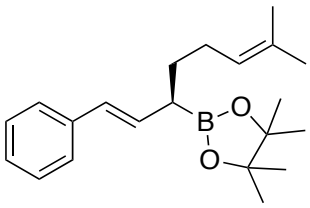
Boronate (*R*)-**2n** was oxidized to alcohol (*R*)-**3n** via General Procedure C. The enantiomeric excess was determined to be 88% (run 1: 89% ee; run 2: 87% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 2% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 17.361 min, t_R(minor) = 15.181 min. The spectral data of this alcohol matched that of alcohol **3n** as prepared via General Procedure F (see below).



(*S*,*E*)-4,4,5,5-Tetramethyl-2-(7-methyl-1-phenylocta-1,6-dien-3-yl)-1,3,2-dioxaborolane ((*S*)-2o). Prepared via General Procedure A using pivalate **1o** (prepared in 78% ee). The crude mixture was purified by silica gel chromatography (0−2%

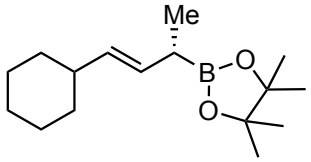
Et_2O/hexanes) to give (*S*)-**2o** (run 1: 122.8 mg, α:γ=10:1, 94%; run 2: 119.9 mg, α:γ=10:1, 92%) as colorless oil. $[\alpha]_D^{24}$ = +21.2 (c 1.18, MeOH): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.33 (m, 2H), 7.29 – 7.27 (m, 2H), 7.18 – 7.15 (m, 1H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.9, 9.0 Hz, 1H), 5.14 – 5.12 (m, 1H), 2.05 – 1.98 (m, 3H), 1.68 (s, 3H), 1.67 – 1.64 (m, 1H), 1.59 (s, 3H), 1.57 – 1.53 (m, 1H), 1.244 (s, 6H), 1.240 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 131.8, 131.6, 129.1, 128.4, 126.5, 125.9, 124.5, 83.2, 30.9, 27.6, 25.7, 24.8, 24.6, 17.7;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1; FTIR (NaCl/thin film) 2977, 2927, 1448, 1371, 1321, 1143, 966, 854, 750, 695 cm^{-1}; HRMS (LIFDI) [M]+ calculated for $C_{21}H_{31}BO_2$: 326.2417, found: 326.2429.

Boronate (*S*)-**2o** was oxidized to alcohol (*S*)-**3o** via General Procedure C. The enantiomeric excess was determined to be 76% (run 1: 76% ee; run 2: 76% ee) by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 10.883 min, t_R(minor) = 13.071 min. The spectral data of this alcohol matched that of alcohol **3o** as prepared via General Procedure F (see below).



(*R*,*E*)-4,4,5,5-Tetramethyl-2-(7-methyl-1-phenylocta-1,6-dien-3-yl)-1,3,2-dioxaborolane ((*R*)-2o). Prepared via General Procedure B using pivalate **1o** (prepared in 78% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2o** (run 1: 109.3 mg, α:γ=10:1, 84%; run 2: 102.4 mg, α:γ=10:1, 78%) as colorless oil. $[\alpha]_D^{24}$ = −17.0 (c 1.0, $CHCl_3$). The spectral data of this compound matches that described above.

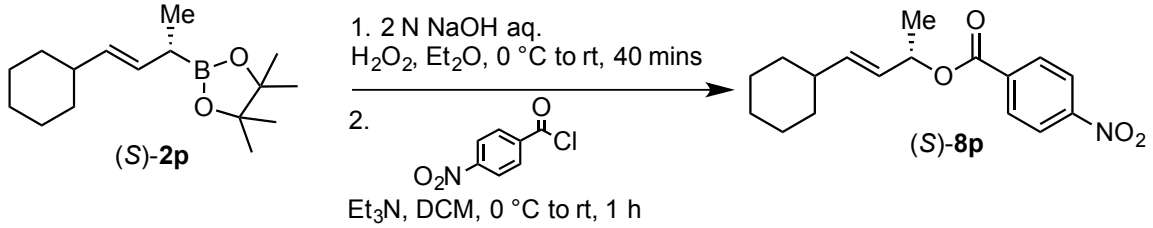
Boronate (*R*)-**2o** was oxidized to alcohol (*R*)-**3o** via General Procedure C. The enantiomeric excess was determined to be 70% (run 1: 71% ee; run 2: 69% ee) by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 13.055 min, t_R(minor) = 10.880 min. The spectral data of this alcohol matches that of alcohol **3o** as prepared via General Procedure F (see below).



(*S*,*E*)-2-(4-cyclohexylbut-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((*S*)-2p). Prepared via General Procedure A using pivalate **1p** (prepared in 99% ee) except using 5 mol % $Ni(cod)_2$ and 5.5 mol % *t*-BuXantPhos at 40 °C for 24 h. The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*S*)-**2p** (run 1: 96 mg, 91%; run 2: 94 mg, 89%) as a colorless oil. The α:γ ratio was determined after oxidation to alcohol (*S*)-**3p** (see below). $[\alpha]_D^{24}$ = −4.5 (c 2.2, $CHCl_3$): ^{1}H NMR (600 MHz, $C(O)(CD_3)_2$) δ 5.43 (ddd, *J* = 15.7, 7.4, 1.2 Hz, 1H), 5.28 (ddd, *J* = 15.6, 6.9, 1.4 Hz, 1H), 1.89 (dt, *J* = 11.2, 3.9 Hz, 1H), 1.72 – 1.65 (m, 4H), 1.62 – 1.60 (m, 1H), 1.31 – 1.22 (m, 3H), 1.20 (s, 12H), 1.15 – 1.01 (m, 3H), 1.00 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $C(O)(CD_3)_2$) δ 134.8, 131.1, 83.8, 41.9, 34.4, 27.1, 26.9, 25.2, 25.1, 15.8;[3] ^{11}B NMR (193 MHz, $C(O)(CD_3)_2$) δ 33.4; FTIR (NaCl/thin film) 2977, 924, 2851, 1378, 1353, 1144, 965 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{16}H_{30}BO_2$: 265.2339, found: 265.2344.

Boronate (*S*)-**2p** was oxidized to alcohol (*S*)-**3p** via General Procedure C to determine the α:γ ratio (run 1: α:γ=14:1; run 2: α:γ=12:1).

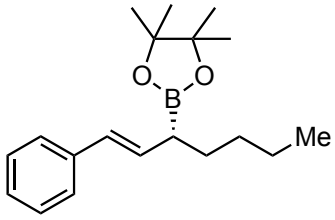
The enantiomeric excess of (*S*)-**2p** was determined by conversion first to alcohol (*S*)-**3p** and then to ester (*S*)-**8p**, as described below. The use of *p*-nitrobenzoate (*S*)-**8p** has been previously described to determine the ee of alcohol **3p**.[4]



Boronate (*S*)-**2p** (33.4 mg, 0.126 mmol, 1.0 equiv) was oxidized to alcohol (*S*)-**3p** via General Procedure C in quantitative yield. The obtained alcohol (*S*)-**3p** was dissolved in CH_2Cl_2 (1 mL) and treated with Et_3N (35 μL, 0.252 mmol, 2.0 equiv) and 4-

[4] Ye, J.; Zhao, J.; Xu, J.; Mao, Y.; Zhang, Y. J. *Chem. Commun.* **2013**, *49*, 9761.

nitrobenzoyl chloride (28 mg, 0.15 mmol, 1.2 equiv) at 0 °C. The solution was allowed to stir at rt for an additional 1h. The reaction was quenched with H_2O (2 mL), and the product was extracted with CH_2Cl_2 (2 x 1 mL). The organic layers were washed with sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The crude mixture was purified via silica gel chromatography (3−5% Et_2O/hexanes) to afford ester (*S*)-**8p** as a sticky yellow oil (33.2 mg, 87%). The enantiomeric excess of (*S*)-**8p** was determined to be 91% (run 1: 92% ee; run 2: 90% ee) by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 1% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 14.953 min, t_R(minor) = 17.280 min. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 8.16 – 8.10 (m, 2H), 5.72 – 5.65 (m, 1H), 5.54 – 5.49 (m, 1H), 5.47 – 5.43 (m, 1H), 1.95 – 1.85 (m, 1H), 1.70 – 1.60 (m, 4H), 1.60 – 1.55 (m, 1H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.25 – 1.13 (m, 2H), 1.13 – 0.90 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 150.4, 140.0, 136.3, 130.7, 126.3, 123.4, 73.4, 40.2, 32.60, 32.56, 26.1, 26.0, 25.9, 20.5.

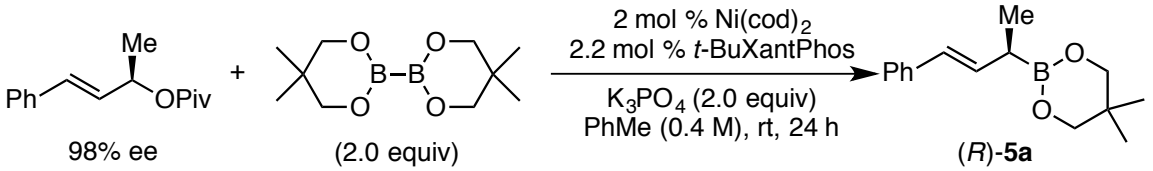


(*R*,*E*)-4,4,5,5-tetramethyl-2-(1-phenylhept-1-en-3-yl)-1,3,2-dioxaborolane ((*R*)-2r). Prepared via General Procedure B using pivalate **1r** (prepared in 94% ee). The crude mixture was purified by silica gel chromatography (0−2% Et_2O/hexanes) to give (*R*)-**2r** (102.2 mg, α:γ=9:1, 85%) as a colorless oil. $[\alpha]_D^{24}$ = +6.9 (c 2.6, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 9.1 Hz, 1H), 1.97 (q, *J* = 8.0 Hz, 1H), 1.64 (ddt, *J* = 13.1, 9.6, 6.4 Hz, 1H), 1.51 (td, *J* = 8.1, 3.4 Hz, 1H), 1.39 – 1.25 (m, 4H), 1.243 (s, 6H), 1.239 (s, 6H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 132.3, 129.1, 128.5, 126.6, 126.0, 83.4, 31.6, 30.7, 24.9, 24.8, 22.9, 14.2;[3] ^{11}B NMR (193 MHz, $CDCl_3$) δ 33.0; FTIR (NaCl/thin film) 2929, 1652, 1558, 1456, 1373, 1143, 967, 852 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{19}H_{29}BO_2$: 301.2339, found: 301.2336.

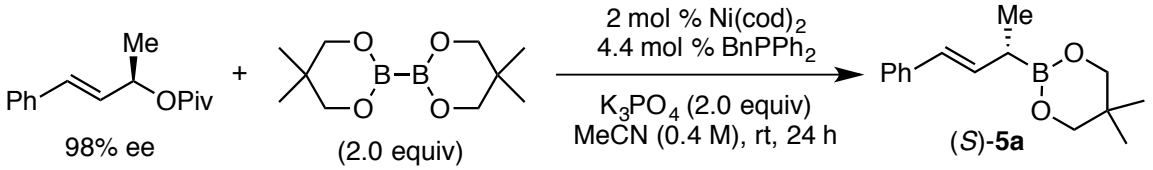
Boronate (*R*)-**2r** was oxidized to alcohol (*R*)-**3r** via General Procedure C. The enantiomeric excess was determined to be 70% by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 12.018 min, t_R(minor) = 19.733 min. The spectral data of this alcohol matched that of alcohol **3r** reported in the literature.[5]

Use of Other Diboron Reagents

Bis(neopentyl glycolato)diboron



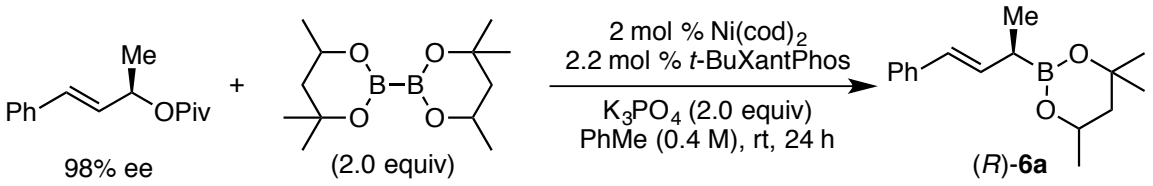
Retention Conditions: (*R*)-**5a** was prepared on 0.2-mmol scale following General Procedure A, except using bis(neopentyl glycolato)diboron (90.4 mg, 0.4 mmol, 2.0 equiv). Because (*R*)-**5a** was unstable to silica gel chromatography, the yield (77%, α:γ=18:1) was determined via ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.5 equiv) as internal standard. The enantiomeric excess (ee) was determined to be 93% after oxidation following General Procedure C.



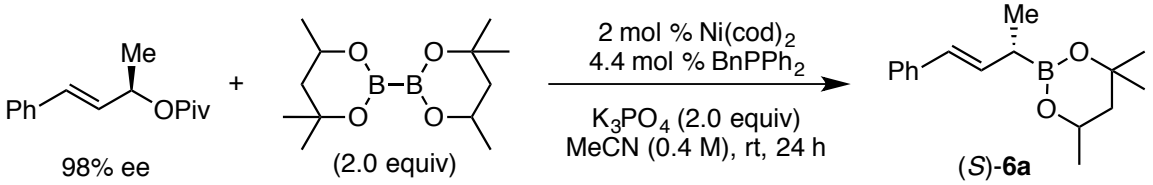
Inversion Conditions: (*S*)-**5a** was prepared on 0.2-mmol scale following General Procedure B except using bis(neopentyl glycolato)diboron (90.4 mg, 0.4 mmol, 2.0 equiv). Because (*S*)-**5a** was unstable to silica gel chromatography, the yield (95%, α:γ=5:1) was determined via ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.5 equiv) as internal standard. The enantiomeric excess (ee) was determined to be 81% after oxidation following General Procedure C.

[5] Stevens, B.D.; Bungard, C.J.; Nelson, S. *J. Org. Chem*. **2006**, *71*, 6397.

Bis(hexylene glycolato)diboron

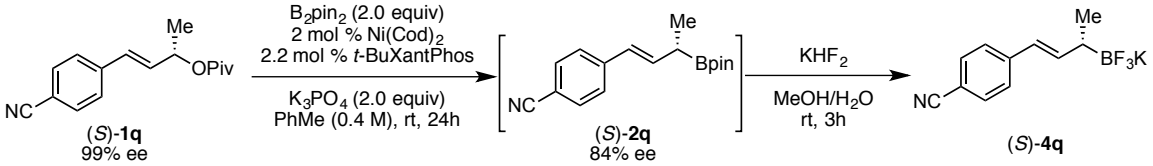


Retention Conditions: (*R*)-**6a** was prepared on 0.2-mmol scale following General Procedure A except using bis(hexylene glycolato)diboron (101.6 mg, 0.4 mmol, 2.0 equiv). Because (*R*)-**6a** was unstable to silica gel chromatography, the yield (81%, α:γ=11:1) was determined via ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.5 equiv) as internal standard. The enantiomeric excess (ee) was determined to be 90% after oxidation following General Procedure C.



Inversion Conditions: (*S*)-**6a** was prepared on 0.2-mmol scale following General Procedure B except using bis(hexylene glycolato)diboron (101.6 mg, 0.4 mmol, 2.0 equiv). Because (*S*)-**6a** was unstable to silica gel chromatography, the yield (20%, α:γ<10:1) was determined via ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol, 0.5 equiv) as internal standard. The enantiomeric excess (ee) was determined to be 85% after oxidation following General Procedure C.

Preparation of Potassium Trifluoroborate Salt 4q



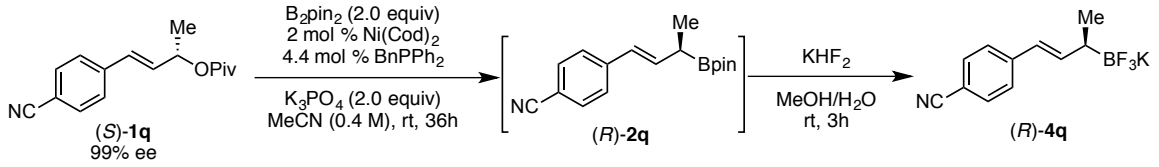
(*S*,*E*)-4,4,5,5-Tetramethyl-2-(4-(4-cyanophenyl)-but-3-en-2-yl)-1,3,2-dioxaborolane ((*S*)-4q). *Retention Conditions*: (*S*)-**4q** was prepared using General

Procedure A using pivalate (*S*)-**1q** (108.5 mg, 0.4 mmol, prepared in 99% ee). Since (*S*)-**2q** was not stable on silica gel, the crude mixture was directly used in next step.

To a solution of crude boronate (*S*)-**2q** in methanol (3 mL) was added aq. KHF_2 (0.27 M, 3 mL, 0.8 mmol). The resulting mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated, washed with Et_2O/hexane (v/v = 1:10, 10 mL). Then the solid residue was extracted with acetone (10 mL) and filtered. The filtrate was concentrated to afford potassium trifluorobrate salt (*S*)-**4q** (run 1: 88.5 mg, α:γ>20:1, 84%, run 2: 87.0 mg, α:γ>20:1, 83%) as a white solid (m.p 131–133 °C). $[\alpha]_D^{24}$ = +11.6 (c 1.7, MeOH); ^{1}H NMR (600 MHz, CD_3CN) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.84 (dd, *J* = 16.0, 7.2 Hz, 1H), 6.16 (dd, *J* = 16.0, 1.6 Hz, 1H), 1.43 – 1.41 (m, 1H), 1.00 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, CD_3CN) δ 148.8, 145.8, 133.2, 126.4, 121.7, 120.3, 108.5, 14.7;[3] ^{19}F NMR (565 MHz, CD_3CN) δ –145.5; ^{11}B NMR (193 MHz, CD_3CN) δ 3.98 (q, *J* = 60.1 Hz); FTIR (NaCl/thin film) 2976, 1854, 1599, 1181, 695.

Trifluoroborate salt (*S*)-**4q** was oxidized to alcohol (*S*)-**3q** via a literature procedure.[6] The enantiomeric excess was determined to be 81% (run 1: 81% ee; run 2: 81% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 20.539 min, t_R(minor) = 18.421 min. The spectral data of this alcohol matched that of alcohol **3q** reported in the literature.[4]

In a separate experiment, crude boronate (*S*)-**2q** was oxidized to alcohol (*S*)-**3q** via General Procedure C. The enantiomeric excess was determined to be 84% by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 20.638 min, t_R(minor) = 18.477 min.

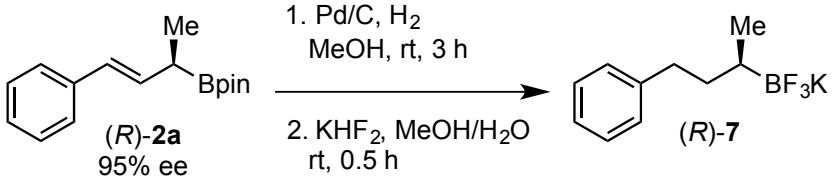


[6] Molander, G. A.; Cavalcanti, L. N. *J. Org. Chem.* **2011**, *76*, 623.

(*R*,*E*)-4,4,5,5-Tetramethyl-2-4-(4-cyanophenyl)-but-3-en-2-yl)-1,3,2-dioxaborolane ((*R*)-4q). *Inversion Conditions*: (*R*)-**4q** was prepared via General Procedure B using pivalate **(S)-1q** (108.5 mg, 0.4 mmol, prepared in 99% ee). The crude mixture was used directly in the next step. To a solution of crude boronate (*R*)-**2q** in methanol (3 mL) was added aq. KHF_2 (0.27 M, 3 mL, 0.8 mmol). The resulting mixture was stirred for 3 h at room temperature. The reaction mixture was concentrated, washed with Et_2O/hexane (v/v = 1:10, 10 mL). Then the solid residue was extracted with acetone (10 mL), and the filtered extract was concentrated to afford trifluorobrate salt (*R*)-**4q** (run 1: 86.0 mg, α:γ>20:1, 83%, run 2: 88.1 mg, α:γ>20:1, 83%) as a white solid (mp 130–133 °C). $[\alpha]_D^{24}$ = –8.2 (0.97, MeOH). The spectral data of this compound matched that described above.

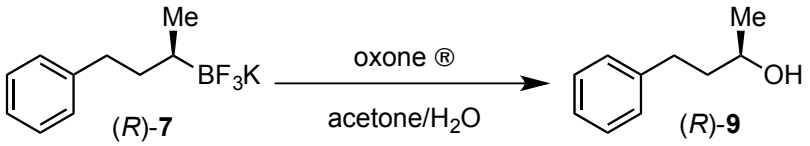
Trifluoroborate salt (*R*)-**4q** was oxidized to alcohol (*R*)-**3q** via a literature procedure.[6] The enantiomeric excess was determined to be 78% (run 1: 77% ee; run 2: 79% ee) by chiral HPLC analysis (CHIRALPAK IA, 1.0 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 18.626 min, t_R(minor) = 20.767 min. The spectral data of this alcohol matched that of alcohol **3q** prepared above.

Preparation of Potassium Trifluoroborate Salt (*R*)-7



In an oven-dried, round-bottomed flask, (*R*)-**2a** (163 mg, 0.63 mmol, 1.0 equiv), Pd/C (10% w, 34 mg, 0.0315 mmol, 0.05 equiv), and MeOH (3.1 mL, 0.2 M) were combined at room temperature. The flask was evacuated and refilled with H_2 three times. Under a H_2 balloon, the reaction mixture was stirred at room temperature for 3 h, after which analysis by ^{1}H NMR of the crude material showed full conversion. The solids were removed via filtration through a plug of Celite®. The filtrate was concentrated to give pale yellow oil (154.3 mg, 94%), which was dissolved in MeOH (0.4 mL) and slowly added to a solution of KHF_2 (166.3 mg, 2.13 mmol) in degassed H_2O (0.8 mL) at room

temperature. The mixture was allowed to stir at room temperature for 30 min, and then concentrated under vacuum. The residue was extracted with acetone (3 x 5 mL), and solid particles were removed via filtration through a plug of Celite®. The filtrate was then concentrated, titrated with hexanes (3 x 5 mL), and dried under vacuum to give (*R*)-**7** as white solid (122 mg, 86%). The spectral data of this compound matched that reported in the literature.[7] The enantiomeric excess was determined after oxidation (below).

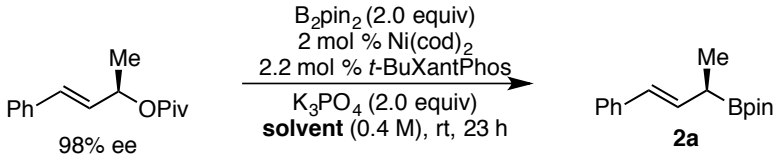


The procedure was adapted from that reported in the literature.[8] In a round-bottomed flask was placed (*R*)-**7** (15 mg, 0.0623 mmol, 1.0 equiv) and acetone (0.2 mL). The solution was cooled to 0 °C, and then a solution of oxone® (0.2 N in H_2O, 0.33 mL, 0.066 mmol, 1.05 equiv) was added. The mixture was stirred at 0 °C for 5 min, and then stirred at room temperature for another 10 min. The reaction was quenched with HCl (1 N). The product was extracted with Et_2O (5 mL). The organic layer was concentrated to give alcohol (*R*)-**9** (8.6 mg, 92%) as a pale yellow oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA, 1 mL/min, 1% *i*-PrOH/hexanes, λ=210 nm); t_R(major) = 29.035 min, t_R(minor) = 27.460 min. The spectral data of this compound match those reported in the literature.[9]

[7] Li, L.; Zhao, S.B.; Joshi-Pangu, A.; Diane, M.; Biscoe, M. *J. Am. Soc. Chem.*; **2014**, *136*, 14027.
[8] Molander, G.; Siddiqui, S.Z.; Fleury-Brégeot, N. *Org. Synth.* **2013**, *90*, 153.
[9] Cheng, Y.N.; Wu, H.L.; Wu, P.Y.; Shen, Y.Y.; Uang, B.J. *Chem. Asian J.* **2012**, *7*, 2921.

Mechanistic Experiments

Solvent Effect



The borylation of pivalate **1a** was performed using General Procedure A, except on a 0.2-mmol scale and using the solvents indicated in Table S3. The reaction mixture was diluted with Et_2O and filtered through a plug of silica gel, which was then rinsed with additional Et_2O. After concentration of the filtrate, 1,3,5-trimethoxybenzene was added as an internal standard. The yield and α:γ ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Boronate **2a** was then oxidized to alcohol **3a** via General Procedure C, and the ee of alcohol **3a** was determined via HPLC analysis using a chiral stationary phase.

Table S3. Effect of solvent on stereospecificity.[a]

entry	Solvents	E_T^N[b]	ε_r[c]	$(\varepsilon_r-1)/(2\varepsilon_r+1)$[d]	yield(%)[e]	α:γ[f]	ee(%)[g]	er[h]	log(er)
1	Hexanes	0.009	1.88	0.1848	92	>20:1	97	65.67	1.82
2	Benzene	0.111	2.27	0.2292	99	>20:1	95	21.22	1.33
3	PhMe	0.099	2.38	0.2396	96	>20:1	91	39.00	1.59
4	EtOAc	0.228	6.02	0.385	94	>20:1	92	15.67	1.19
5	THF	0.207	7.58	0.472	94	>20:1	88	24.00	1.38
6	CH_2Cl_2	0.309	8.93	0.4205	24	>20:1	39	2.28	0.36
7	DMF	0.386	36.71	0.4798	60	>20:1	26	1.70	0.23
8	MeCN	0.46	35.94	0.4794	72	>20:1	−85	0.08	−0.19

[a] Conditions: pivalate **1a** (0.2 mmol, 1 equiv), $Ni(cod)_2$ (2 mol%), *t*-BuXantPhos (2.2 mol %), K_3PO_4 (2 equiv), solvent (1 mL, 0.4 M), rt, 24 h. [b] Empirical polarity parameter. [c] Relative permittivity value. [d] Kirkwood function. [e] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [f] Determined by ^{1}H NMR analysis of crude mixture. [g] Determined by HPLC analysis using a chiral stationary phase of the subsequent alcohol (**3a**), formed via General Procedure C. A negative number indicates that the opposite major enantiomer is formed (stereoinversion). [h] er = ratio of enantiomers (*R*/*S*).

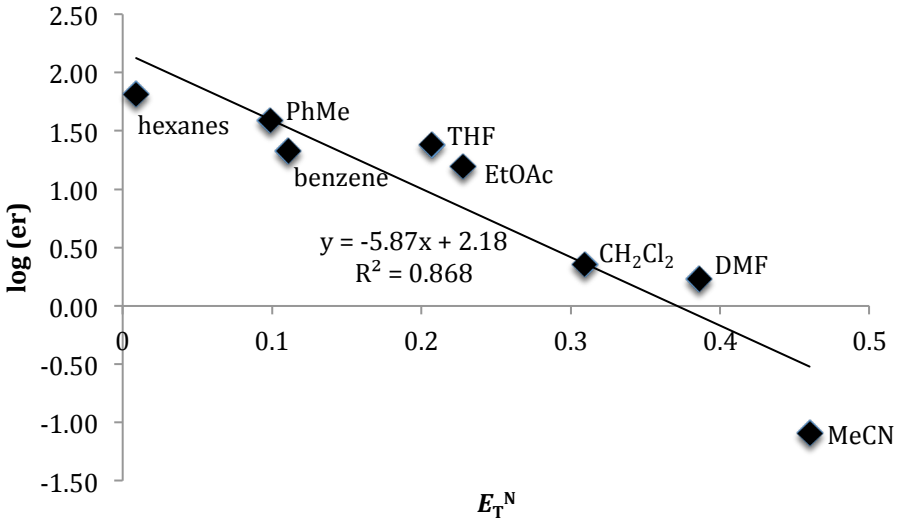


Figure S1. Plot of log(er) vs. E_T^N.

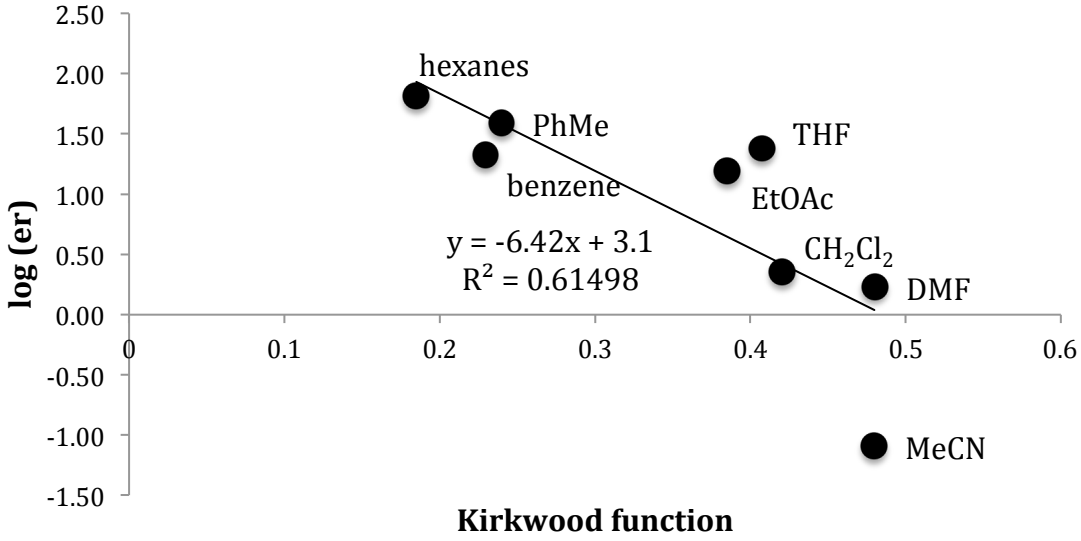
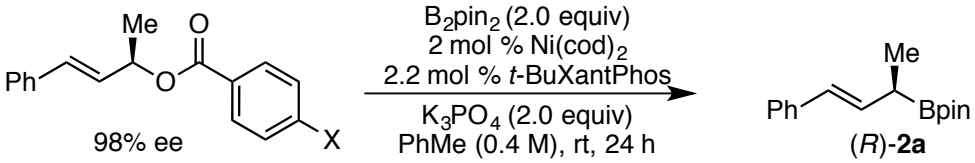


Figure S2. Plot of log(er) vs. the Kirkwood function.

$$\text{Kirkwood function} = \frac{(\varepsilon_r - 1)}{(2\varepsilon_r + 1)}$$

Leaving Group Effect: Hammett Correlation



The borylation of the benzoates was performed using General Procedure A, except on a 0.2-mmol scale and using the benzoates indicated in Table S4. The reaction mixture was diluted with Et_2O and filtered through a plug of silica gel, which was then rinsed with additional Et_2O. After concentration of the filtrate, 1,3,5-trimethoxybenzene was added as an internal standard. The yield and α:γ ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Boronate **2a** was then oxidized to alcohol **3a** via General Procedure C, and the ee of alcohol **3a** was determined via HPLC analysis using a chiral stationary phase.

Table S4. Hammett correlation between carboxylate and enantiomeric ratio.[a]

entry	X	σ	yield(%)[b]	α:γ[c]	ee(%)[d]	er[e]	log(er)
1	OMe	-0.268	76	>20:1	82.7	10.55	1.023
2	H	0	85	>20:1	81.2	9.68	0.986
3	F	0.062	50	>20:1	85.2	12.54	1.098
4	OCF_3	0.35	86	>20:1	38.0	2.23	0.348
5	CF_3	0.54	80	>20:1	41.2	2.4	0.38

[a] Conditions: Benzoate (0.2 mmol, 1.0 equiv), $Ni(cod)_2$ (2 mol %), *t*-BuXantPhos (2.2 mol %), K_3PO_4 (2.0 equiv), PhMe (1.0 mL, 0.4 M), rt, 24 h. [b] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^{1}H NMR analysis of crude mixture. [d] Determined by HPLC analysis using a chiral stationary phase of the subsequent alcohol (**3a**), formed via General Procedure C. [e] er = ratio of enantiomers (*R*/*S*).

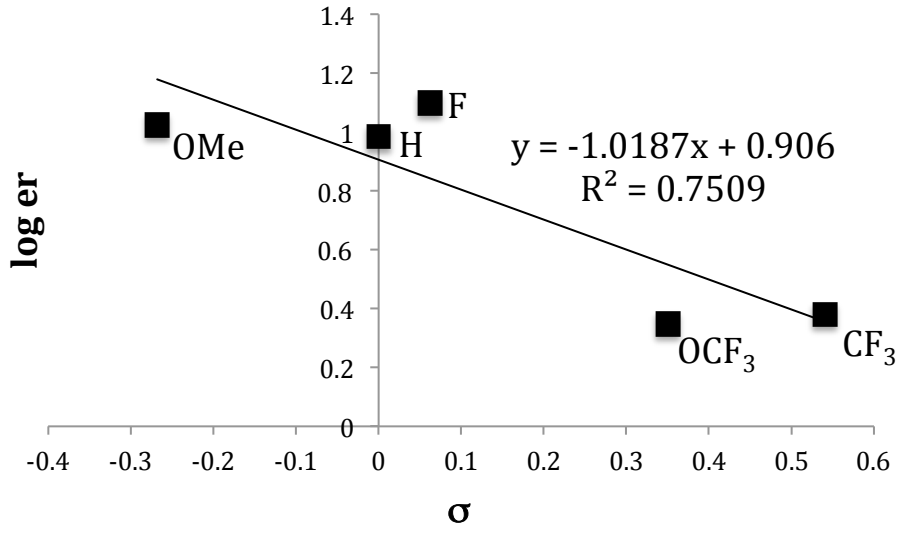
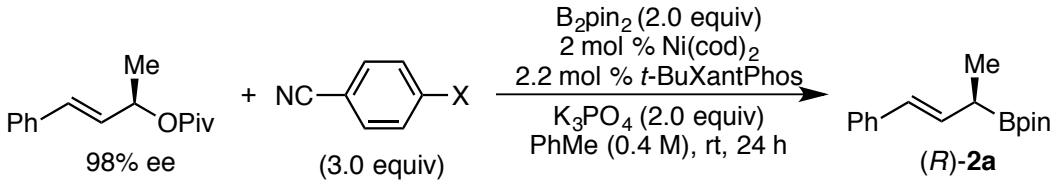


Figure S3. Hammett correlation between carboxylate and enantiomeric ratio.

Addition of Benzonitriles: Hammett Correlation



The borylation of pivalate **1a** was performed using General Procedure A, except on a 0.2-mmol scale and with the addition of the benzonitriles (3.0 equiv) listed in Table S5. Solid nitriles were added along with the other solid reagents. Liquid nitriles were added last, after the solvent. The reaction mixture was diluted with Et_2O and filtered through a plug of silica gel, which was then rinsed with additional Et_2O. After concentration of the filtrate, 1,3,5-trimethoxybenzene was added as an internal standard. The yield and α:γ ratio was determined by ^1H NMR analysis of the crude reaction mixture. Boronate **2a** was then oxidized to alcohol **3a** via General Procedure C, and the ee of alcohol **3a** was determined via HPLC analysis using a chiral stationary phase.

Table S5. Hammett correlation between benzonitriles and enantiomeric ratio.[a]

entry	X	σ	yield(%)[b]	α:γ[c]	ee(%)[d]	er[e]	log(er)
1	H	0	79	11:1	33.4	2	0.301
2	F	0.062	84	11:1	37.7	2.21	0.344
3	CH_3	-0.17	65	11:1	15.1	1.36	0.134
4	Cl	0.227	82	11:1	55.4	3.48	0.542
5	CF_3	0.54	89	11:1	70.5	5.78	0.762

[a] Conditions: pivalate **1a** (0.2 mmol, 1 equiv), $Ni(cod)_2$ (2 mol%), *t*-BuXantPhos (2.2 mol %), K_3PO_4 (2 equiv), nitrile (3 equiv), PhMe (1 mL, 0.4 M), rt, 24 h. [b] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard. [c] Determined by ^1H NMR analysis of crude mixture. [d] Determined by HPLC analysis using a chiral stationary phase of the subsequent alcohol (**3a**), formed via General Procedure C. A negative number indicates that the opposite major enantiomer is formed (stereoinversion). [e] er = ratio of enantiomers (*R*/*S*).

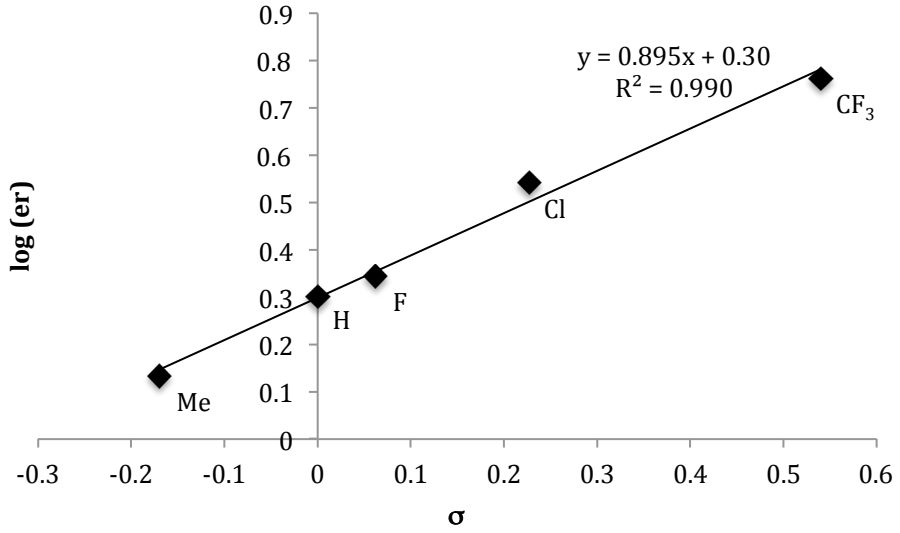
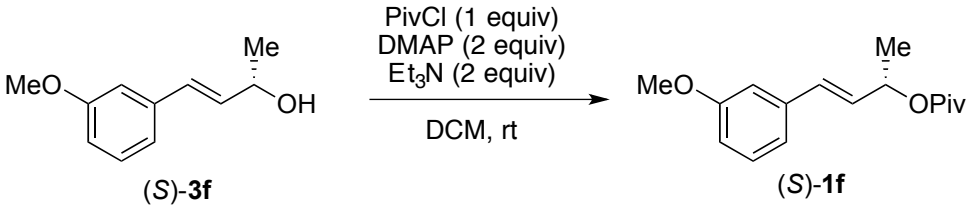


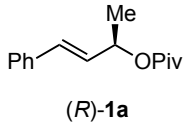
Figure S4. Hammett correlation between benzonitrile and enantiomeric ratio.

Preparation of Allylic Pivalates

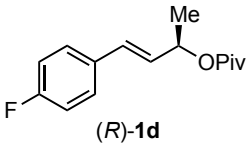
General Procedure D: Preparation of (*S,E*)-4-(3-methoxyphenyl)but-3-en-2-yl pivalate ((*S*)-1f)



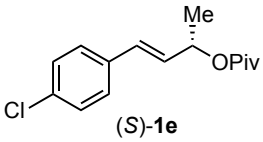
(*S*,*E*)-4-(3-Methoxyphenyl)but-3-en-2-ol ((*S*)-**3f**, 1.26 g, 7.08 mmol, 1.0 equiv, 99% ee), DMAP (173 mg, 1.42 mmol, 0.20 equiv), and CH_2Cl_2 (21 mL, 0.3 M) were combined. Et_3N (1.97 mL, 14.2 mmol, 2.0 equiv) and pivaloyl chloride (0.85 mL, 7.08 mmol, 1.0 equiv) were then added. The reaction mixture was stirred for 14 h at room temperature. H_2O (30 mL) was added. The mixture was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were washed with aq. KOH (2.0 M, 30 mL), dried ($MgSO_4$), filtered and concentrated. The resulting residue was purified by silica gel chromatography (5–40% EtOAc/hexanes) to give compound (*S*)-**1f** (1.36 g, 75%) as a colorless oil. The enantiomeric excess was determined to be 98% by chiral HPLC analysis (CHIRALPAK IA, 1 mL/min, 1% i-PrOH/hexane, λ=254 nm); t_R(major) = 5.555 min, t_R(minor) = 7.792 min. $[\alpha]_D^{24}$ = +94.4 (c 1.14, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.9 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.93 – 6.29 (m, 1H), 6.83 – 6.77 (m, 1H), 6.60 – 6.52 (m, 1H), 6.18 (dd, *J* = 15.9, 6.4 Hz, 1H), 5.54 – 5.45 (m, 1H), 3.82 (s, 3H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 159.9, 138.0, 131.0, 129.7, 129.6, 119.3, 113.6, 111.9, 70.6, 55.4, 38.9, 27.3, 20.4; FTIR (NaCl/thin film) 2976, 2934, 2872, 2835, 1724, 1599, 1480, 1280, 1157, 1041, 968, 773 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{16}H_{22}O_3$: 262.1569, found: 262.1570.



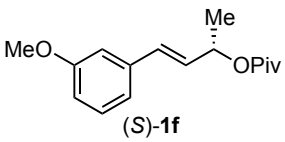
(*R*)-**1a**



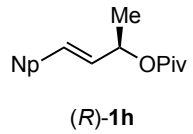
(*R*)-**1d**



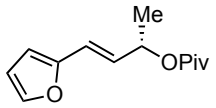
(*S*)-**1e**



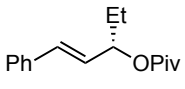
(*S*)-**1f**



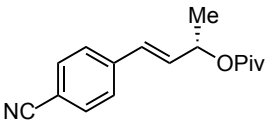
(*R*)-**1h**



(*S*)-**1j**

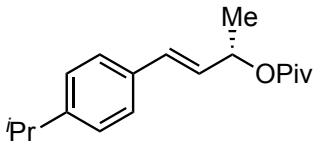


(*S*)-**1k**

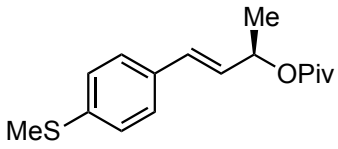


(*S*)-**1q**

Allylic Pivalates (*R*)-**1a**, (*R*)-**1d**, (*S*)-**1e**, (*S*)-**1f**, (*R*)-**1h**, (*S*)-**1j**, (*S*)-**1k** and (*S*)-**1q** were prepared via General Procedure D and the spectral of these compounds match that reported by our group.[10]



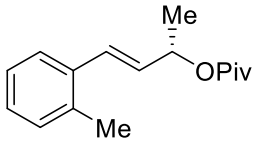
(*S*,*E*)-4-(4-isopropylphenyl)but-3-en-2-yl pivalate (**1b**). Prepared as a colorless oil via General Procedure D using (*S*)-**3b** (92% ee). The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IA, 1 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 4.722 min, t_R(minor) = 5.304 min. $[\alpha]_D^{24}$ = +101.5 (c 1.13, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.20 – 7.15 (m, 2H), 6.60 – 6.53 (m, 1H), 6.14 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.53 – 5.49 (m, 1H), 2.96 – 2.82 (m, 1H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 148.9, 134.2, 131.2, 128.3, 126.8, 126.7, 70.8, 38.9, 34.0, 27.3, 24.1, 20.5; FTIR (NaCl/thin film) 2961, 2932, 2871, 1726, 1479, 1457, 1280, 1162, 1040, 967 cm^{-1}; HRMS (EI+) [M]+ calculated for: $C_{18}H_{26}O_2$: 274.1933, found: 274.1952.



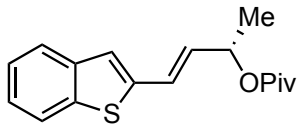
(*R*,*E*)-4-(4-(methylthio)phenyl)but-3-en-2-yl pivalate (1c). Prepared as a colorless oil via General Procedure D using (*R*)-**3c** (93% ee). The enantiomeric excess was determined

[10] Srinivas, H. D.; Zhou, Q.; Watson, M.P. *Org. Lett.* **2014**, *16*, 3596.

to be 93% by chiral HPLC analysis (CHIRALPAK IA, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.922 min, t_R(minor) = 8.812 min. $[\alpha]_D^{24}$ = +100.9 (c 2.84, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 2H), 6.57 – 6.48 (m, 1H), 6.14 (dd, *J* = 16.0, 6.5 Hz, 1H), 5.54 – 5.42 (m, 1H), 2.48 (s, 3H), 1.38 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 138.2, 133.5, 130.6, 128.6, 127.1, 126.6, 70.7, 38.9, 27.3, 20.5, 15.9; FTIR (NaCl/thin film) 2976, 2923, 1723, 1700, 1652, 1558, 1162, 976 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{16}H_{23}O_2S$: 279.1419, found: 279.1430.

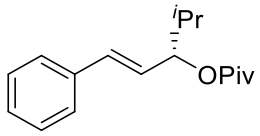


(*S*,*E*)-4-(o-Tolyl)but-3-en-2-yl pivalate (1g). Prepared as a colorless oil via General Procedure D using (*S*)-**3g** (94% ee). The enantiomeric excess was determined to be 94% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 4.614 min, t_R(minor) = 4.300 min. $[\alpha]_D^{24}$ = +41.9 (c 0.6, MeOH): ^{1}H NMR (400 MHz, $C(O)(CD_3)_2$) δ 7.52 – 7.42 (m, 1H), 7.21 – 7.13 (m, 3H), 6.86 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.18 (dd, *J* = 15.9, 6.0 Hz, 1H), 5.55 – 5.45 (m, 1H), 2.33 (s, 3H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $C(O)(CD_3)_2$) δ 177.5, 136.5, 136.4, 131.6, 131.2, 129.1, 128.6, 127.1, 126.4, 71.2, 39.3, 27.5, 20.8, 19.9; FTIR (NaCl/thin film) 2976, 1727, 1281, 1161, 1040, 966, 749; HRMS (LIFDI) [M]+ calculated for $C_{16}H_{22}O_2$: 246.1620, found: 246.1639.

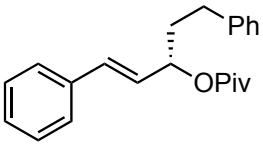


(*S*,*E*)-4-(benzothiophen-2-yl)but-3-en-2-yl pivalate (1i). Prepared as an off-white solid (mp 98−100 °C) via General Procedure D using (*S*)-**3i** (70% ee). The enantiomeric excess was determined to be 70% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 7.816 min, t_R(minor) = 9.201 min. $[\alpha]_D^{24}$ = +82.1 (c 1.16, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.71 – 7.66 (m, 1H),

7.42 – 7.30 (m, 2H), 7.16 (s, 1H), 6.83 – 6.78 (d, *J* = 15.6, 1H), 6.10 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.56 – 5.45 (m, 1H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.23 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 141.8, 140.1, 139.1, 131.5, 125.0, 124.9, 124.6, 123.64, 123.60, 122.3, 70.1, 39.0, 27.3, 20.3; FTIR (NaCl/thin film) 2973, 2933, 2870, 1723, 1478, 1279, 1152, 1036, 956, 743 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{17}H_{20}O_2S$: 288.1184, found: 288.1185.

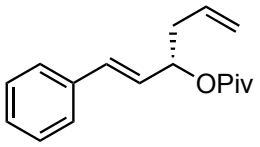


(*S*,*E*)-4-Methyl-1-phenylpent-1-en-3-yl pivalate (1l). Prepared as a colorless oil via General Procedure D using (*S*)-**3l**. (99% ee). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 1.0% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 4.747 min, t_R(minor) = 4.149 min. $[a]_D^{24}$ = +69.2 (c 0.24, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 7.2 Hz, 1H), 5.21 (ddd, *J* = 7.3, 6.1, 1.2 Hz, 1H), 1.97 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.24 (s, 9H), 0.97 (dd, *J* = 8.7, 6.8 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6, 136.6, 132.7, 127.7, 126.5, 126.5, 78.7, 39.0, 32.5, 27.2, 27.2, 18.3, 18.0; FTIR (NaCl/thin film) 3027, 2967, 2933, 2873, 1728, 1480, 1280, 1161, 967,747, 693 cm^{-1}; HRMS (CI) [M]+ calculated for $C_{17}H_{24}O_2$: 260.1776, found: 260.1758.

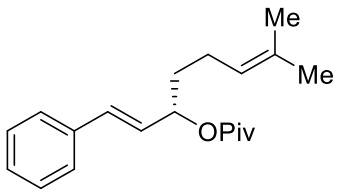


(*S*,*E*)-1,5-diphenylpent-1-en-3-yl pivalate (1m). Prepared as a pale yellow oil via General Procedure D using (*S*)-**3m** (99% ee). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IA, 1 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 6.342 min, t_R(minor) = 10.752 min. $[\alpha]_D^{24}$ = +20.6 (c 0.87, $CHCl_3$): ^{1}H NMR (600 MHz, CDCl3) δ 7.39 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.26 – 7.23 (m, 2H) 7.22 – 7.16 (m, 3H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.48 – 5.38 (m, 1H), 2.77 – 2.60 (m, 2H), 2.13 – 2.03 (m, 1H), 2.03 – 1.93 (m, 1H),

1.25 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 141.5, 136.6, 132.4, 128.7, 128.6, 128.5, 128.0, 127.8, 126.7, 126.1, 73.8, 39.1, 36.5, 31.7, 27.4; FTIR (NaCl/thin film) 3026, 2971, 2870, 1732, 1653, 1558, 1280, 1153, 965, 747, 694 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{22}H_{26}O_2$: 322.1933, found: 322.1935.

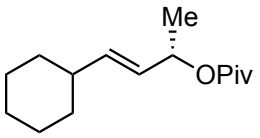


(*S*,*E*)-1-phenylhexa-1,5-dien-3-yl pivalate (1n). Prepared as a colorless oil via General Procedure D using (*S*)-**3n** (99% ee). The enantiomeric excess was determined to be 99% by chiral HPLC analysis (CHIRALPAK IC, 0.8 mL/min, 1% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 6.560 min, t_R(minor) = 7.178 min. $[\alpha]_D^{24}$ = +59.1 (c 1.13, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.83 – 5.77 (m, 1H), 5.52 – 5.45 (m, 1H), 5.14 – 5.06 (m, 2H), 2.53 – 2.47 (m, 2H), 1.22 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.8, 136.6, 133.4, 132.2, 128.7, 128.0, 127.5, 126.7, 118.2, 73.3, 39.4, 39.0, 27.3; FTIR (NaCl/thin film) 2973, 2932, 2871, 1723, 1478, 1278, 1153, 1035, 956, 743 cm^{-1}; HRMS (EI+) [M]+ calculated for 258.1620, found: 258.1615.

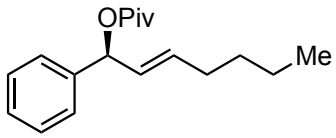


(*S*,*E*)-7-Methyl-1-phenylocta-1,6-dien-3-yl pivalate (1o). Prepared as a colorless oil via General Procedure D using (*S*)-**3o** (80% ee). The enantiomeric excess was determined to be 78% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 0.5% *i*-PrOH/hexane, λ=254 nm); t_R(major) = 6.508 min, t_R(minor) = 4.705 min. $[\alpha]_D^{24}$ = +47.6 (c 0.59, MeOH): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.29 (m, 2H), 7.25 – 7.23 (m, 2H), 7.19 – 7.15 (m, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.06 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.36 – 5.28 (m, 1H), 5.07 – 5.04 (m, 1H), 2.05 – 1.91 (m, *J* = 7.0 Hz, 2H), 1.77 – 1.66 (m, 1H), 1.66 – 1.58 (m, 4H), 1.52 (s, 3H), 1.15 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.7, 136.6, 132.3, 131.9, 128.5, 128.0, 127.8, 126.5, 123.4, 73.8, 38.9, 34.7, 27.2, 25.7, 23.8, 17.7;

FTIR (NaCl/thin film) 2970, 1728, 1280, 1153, 965, 748, 693; HRMS (LIFDI) [M]+ calculated for $C_{20}H_{28}O_2$: 300.2089, found: 300.2089.



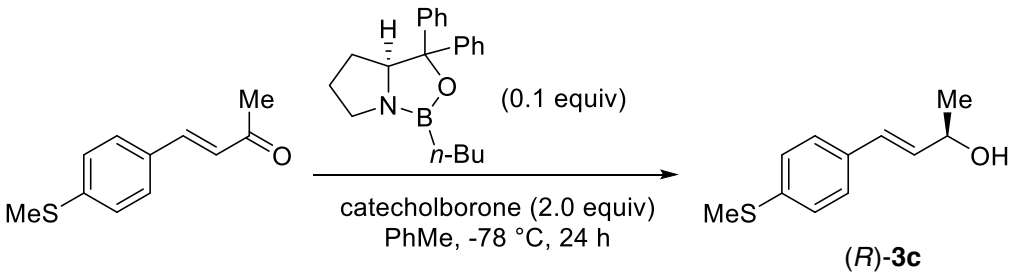
(*S*,*E*)-4-cyclohexylbut-3-en-2-yl pivalate (1p). Prepared as a colorless oil via General Procedure D using (*S*)-**3p** (99% ee). The enantiomeric excess was considered to be 99% based on the ee of precursor alcohol (*S*)-**3p**. $[\alpha]_D^{24}$ = +59.1 (c 1.35, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.61 (dd, J = 15.6, 6.5 Hz, 1H), 5.39 (dd, J = 15.6, 6.6 Hz, 1H), 5.34 – 5.23 (m, 1H), 1.97 – 1.88 (m, 1H), 1.75 – 1.60 (m, 5H), 1.30 – 1.24 (m, 5H), 1.18 (s, 9H), 1.17 – 1.10 (m, 1H), 1.10 – 1.00 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 138.5, 127.3, 70.8, 40.3, 32.9, 32.8, 27.3, 26.3, 26.1, 20.5; FTIR (NaCl/thin film) 2976, 2926, 2852, 1728, 1449, 1281, 1162, 1043, 967 cm^{-1}; HRMS (CI+) [M]+H calculated for $C_{15}H_{27}O_2$: 239.2011, found: 239.2022.



(*S*,*E*)-1-phenylhept-2-en-1-yl pivalate (1r). Prepared as a colorless oil via General Procedure D using (*S*)-**3r** (94% ee). The enantiomeric excess was considered to be 94% based on the ee of precursor alcohol (*S*)-**3r**. $[\alpha]_D^{24}$ = +8.0 (c 1.12, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 4H), 7.29 – 7.29 (m, 1H), 6.20 (d, *J* = 6.8 Hz, 1H), 5.73 (dd, *J* = 14.9, 6.8 Hz, 1H), 5.60 (dd, *J* = 15.4, 6.9 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.39 – 1.26 (m, 4H), 1.22 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 140.4, 134.6, 128.6, 128.5, 127.8, 126.7, 76.0, 39.0, 32.0, 31.2, 27.3, 22.3, 14.0; FTIR (NaCl/thin film) 2958, 2930, 2872, 1732, 1479, 1278, 1150, 967, 698 cm^{-1}; HRMS (EI+) [M]+ calculated for $C_{18}H_{26}O_2$: 274.1933, found: 274.1938.

Preparation of Allylic Alcohols

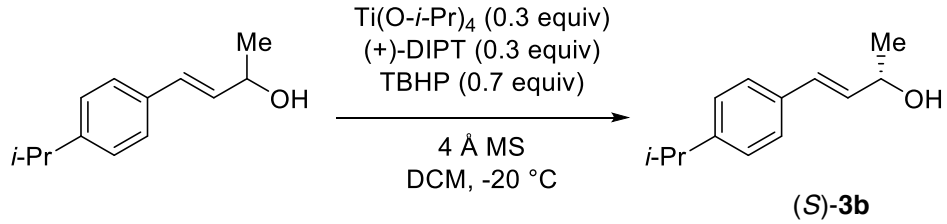
General Procedure E: Preparation of (*R,E*)-4-(4-(methylthio)phenyl)but-3-en-2-ol ((*R*)-3c) via CBS Reduction



(*R*)-**3c**

This procedure was adapted from that in the literature.[2] In an oven-dried round-bottomed flask, (*E*)-4-(4-isopropylphenyl)but-3-en-2-ol (1.08 g, 5.84 mmol, 1.0 equiv) was dissolved in 12 mL PhMe. Under a N_2 atmosphere, (*S*)-(−)-2-butyl-CBS-oxazaborolidine (0.58 mL, 0.58 mmol, 1.0 M in PhMe, 0.1 equiv) was added. After stirring at room temperature for 15 min, the mixture was cooled to −78 °C, and catecholborane (1.24 mL, 11.68 mmol, 2.0 equiv) was added slowly. The mixture was stirred at −78 °C for additional 24 h. The reaction was quenched with sat. $NaHCO_3$ (10 mL). The crude product was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with aq. NaOH (1.5 M) until the color of the solution was light yellow, indicating the full removal of residual catecholborane. The organic layers were then treated with sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (50% Et_2O/hexanes) to give compound (*R*)-**3c** (920mg, 92%) as pale yellow solid (mp 97−99 °C). The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 6% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 13.164 min, t_R(minor) = 15.211 min. $[\alpha]^D_{24}$= +39.7 (c 2.46, $CHCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.52 − 4.43 (pd, *J* = 6.4, 1.2 Hz, 1H), 2.48 (s, 3H), 1.59 (s, 1H), 1.37 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 133.8, 133.1, 129.0, 127.0, 126.8, 69.1, 23.6, 16.0; FTIR (NaCl/thin film) 3317(brs), 2977, 2884, 1653, 1418, 1124, 970, 803 cm^{-1}; HRMS (CI+) [M]+H calculated for: $C_{11}H_{15}OS$: 195.0844, found: 195.0837.

General Procedure F: Preparation of (*S,E*)-4-(4-isopropylphenyl)but-3-en-2-ol ((*S*)-3b) via Kinetic Resolution

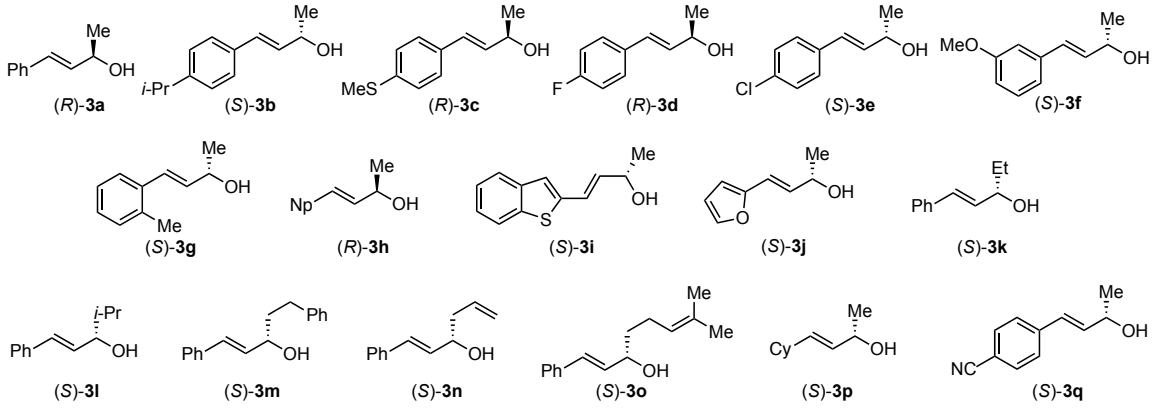


(*S*)-**3b**

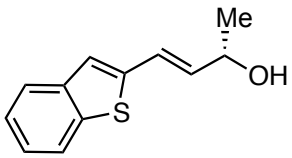
This procedure was adapated from that reported in the literature.[2] In an oven-dried, 100-mL round-bottomed flask, L-(+)-DIPT (0.74 mL, 3.54 mmol, 0.3 equiv) was added to a suspension of (*E*)-4-(4-isopropylphenyl)but-3-en-2-ol (1.76g, 11.8 mmol, 1.0 equiv), 4 Å MS (0.85 g, finely ground before use), and CH_2Cl_2 (47 mL). The suspension was then cooled to –20 °C, and Ti(O-*i*Pr)$_4$ (1.06 mL, 3.54 mmol, 0.3 equiv) and TBHP (1.5 mL, 8.25 mmol, 5.5 M in decane, 0.7 equiv) were added. The mixture was stirred for 3 h at –20 °C. $FeSO_4$•$7H_2O$ (6.5 g) and H_2O (40 mL) were then added, followed by tartaric acid (2.2 g), H_2O (20 mL), and aq. HCl (1.0 M, 30 mL) to dissolve the precipitate. The layers were separated. The organic layer was then washed with sat. NaCl, dried (Na_2SO_4), filtered, and concentrated. The resulting residue was purified by silica gel chromatography (15% Et_2O/hexanes) to give compound (*S*)-**3b** (240 mg, 27%) as colorless oil. The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK IB, 1 mL/min, 4% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 8.776 min, t_R(minor) = 9.385 min. $[\alpha]^D_{24}$ = +16.2 (c 0.33, $CHCl_3$). The spectra data for this compound matches that reported in the literature.[11]

[11] Gładkowski, W.; Skrobiszewski, A.; Mazur, M.; Siepka, M.; Pawlak, A.; Obmińska-Mrukowicz, B.; Białońska, A.; Poradowski, D.; Drynda, A.; Urbaniak, M.; *Tetrahedron*, **2013**, 69, 10414.

Preparation of Allylic Alcohols



(*R*)-**3a**[12], (*R*)-**3d**[13], (*S*)-**3e**[13], (*R*)-**3h**[13] were prepared via General Procedure E. (*S*)-**3b**[14], (*R*)-**3c**[15], (*S*)-**3f**[13], (*S*)-**3g**[15], (*S*)-**3i**, (*S*)-**3j**[13], (*S*)-**3k**[15], (*S*)-**3l**[12], (*S*)-**3m**[16], (*S*)-**3n**[17], (*S*)-**3o**, (*S*)-**3p**[18], and (*S*)-**3q**[10] were prepared via General Procedure F.



((*S*)-3i). Prepared following General Procedure F. The enantiomeric excess was determined to be 70% by chiral HPLC analysis (CHIRALPAK IC, 1 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 21.095 min, t_R(minor) = 23.755 min. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 – 7.67 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 (s, 1H), 6.92 – 6.78 (m, 1H), 6.22 (dd, *J* = 15.6, 6.0 Hz, 1H), 4.58 – 4.50 (m, 1H), 1.62 (s, 1H), 1.42 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.0, 140.1, 138.9, 135.8, 124.7, 124.4, 123.4, 123.2, 123.0, 122.2, 68.5, 23.4.

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[12] Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 13529.

[13] He, P.; Liu, X.; Zheng, H.; Li, W.; Lin, L.; Feng, X. *Org. Lett.* **2012**, *14*, 5134.

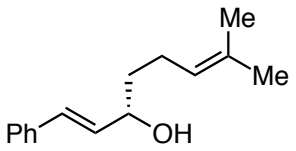
[14] Gładkowski, W.; Skrobiszewski, A.; Mazur, M.; Siepka, M.; Pawlak, A.; Obmińska-Mrukowicz, B.; Białońska, A.; Poradowski, D.; Drynda, A.; Urbaniak, M. *Tetrahedron* **2013**, *69*, 10414.

[15] Li, X.; Li, L.; Tang, Y.; Zhong, L.; Cun, L.; Zhu, J.; Liao, J.; Deng, J. *J. Org. Chem.* **2010**, *75*, 2981.

[16] Hodgson, D. M.; Persaud, R. S. D. *Org. Biomol. Chem.* **2012**, *10*, 7949.

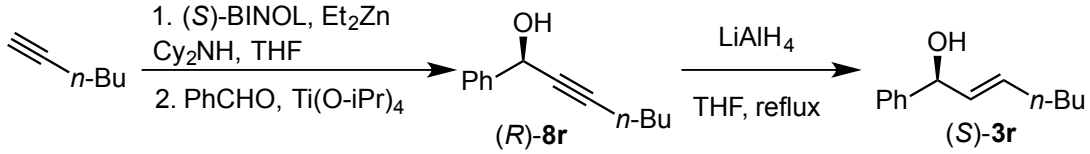
[17] Couto, T. R.; Freitas, J. C. R.; Cavalcanti, I. H.; Oliveira, R. A.; Menezes, P. H. *Tetrahedron* **2013**, *69*, 7006.

[18] Barker, G.; Johnson, D. G.; Young, P. C.; Macgregor, S. A.; Lee, A.-L. *Chem. Eur. J.* **2015**, *21*, 13748.



((*S*)-3o). Prepared as a colorless oil following General Procedure F in 41% yield. The enantiomeric excess was determined to be 80% by chiral HPLC analysis (CHIRALPAK IC, 1.0 mL/min, 3% *i*-PrOH/hexanes, λ=254 nm); t_R(major) = 10.883 min, t_R(minor) = 13.071 min. $[a]^D_{24}$ = +17.1 (c 0.26, MeOH): ^{1}H NMR (600 MHz, CDCl3) δ 7.42 - 7.20 (m, 5H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 6.6 Hz, 1H), 5.16 (t, *J* = 7.2 Hz, 1H), 4.30 (q, *J* = 6.5 Hz, 1H), 2.12 (q, *J* = 7.5 Hz, 2H), 1.85 – 1.49 (m, 8H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.8, 132.5, 132.3, 130.2, 128.6, 127.6, 126.5, 123.9, 72.7, 37.3, 25.7, 24.1, 17.7; FTIR (NaCl/thin film) 3321, 2973, 2949, 2042, 1154, 776 cm^{-1}; HRMS (LIFDI) [M]+H calculated for: $C_{15}H_{20}O$: 216.1514, found: 216.1521.

Preparation of (*S*,*E*)-1-phenylhept-2-en-1-ol ((*S*)-3r).



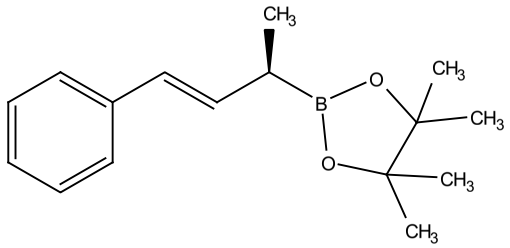
The following procedure was adapted from that reported in the literature.[19] In an oven-dried round-bottomed flask was placed (*S*)-BINOL (573 mg, 2 mmol, 0.4 equiv), Cy_2NH (50 μL, 0.25 mmol, 0.05 equiv), and THF (20 mL). The mixture was cooled to 0 °C, before Et_2Zn (1.53 mL, 15 mmol, 3.0 equiv) was added. The mixture was then stirred at room temperature for 16 h. 1-Hexyne (1.73 mL, 15 mmol, 3.0 equiv) was added, and the mixture was stirred at room temperature for additional 8 h. The mixture was cooled to 0 °C, before Ti(O*i*-Pr)$_4$ (1.49 mL, 5 mmol, 1.0 equiv) and then benzaldehyde (0.5 mL, 5 mmol, 1.0 equiv) were added. The mixture was stirred at room temperature for another 16 h. The reaction was quenched with sat. NH_4Cl and extracted with EtOAc. The organic layer was washed with sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The crude mixture was purified on silica gel chromatography (0−40% EtOAc/hexanes) to give (*R*)-

[19] Chen, W.; Tay, J.H.; Ying, J.; Yu, X.Q.; Pu, L. *J. Org. Chem.* **2013**, *78*, 2256.

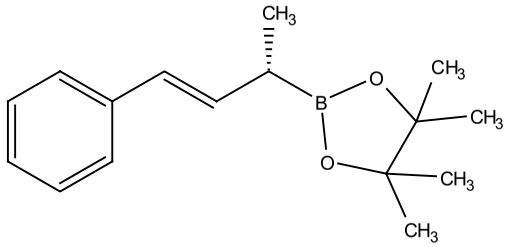
8r (787mg, 84%) as a yellow oil. The enantiomeric excess was determined to be 94% by chiral HPLC analysis (CHIRALPAK IB, 1.0 mL/min, 3.0% *i*-PrOH/hexane, λ = 210 nm); t_R(major) = 12.39 min, t_R(minor) = 9.24 min. The spectral data of this compound matches of that reported in the literature.[5]

In a round-bottomed flask equipped with a condenser was placed $LiAlH_4$ (174 mg, 4.6 mmol, 1.5 equiv) and THF (5 mL). A solution of (*R*)-**8r** (577 mg, 3.06 mmol, 1.0 equiv, 94% ee) and THF (10.3 mL) was added at room temperature. Then the mixture was refluxed for 1.5 h. The mixture was cooled in an ice-water bath, before the reaction was carefully quenched with sat. NH_4Cl. The product was extracted with Et_2O. The organic layer was washed with sat. NaCl, dried ($MgSO_4$), filtered, and concentrated. The crude mixture was purified on silica gel chromatography (5−10% Et_2O/hexanes) to give (*S*)-**3r** (400 mg, 69%) as a colorless oil. The spectra data of (*S*)-**3r** matches that reported in the literature.[20] The enantiomeric excess was considered to be 94% based on the precursor (*R*)-**8r**.

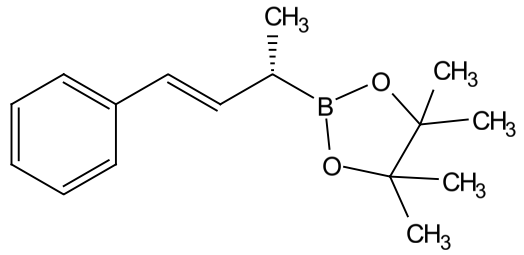
[20] Lurain, A. E.; Carroll, P. J.; Walsh, P. J. *J. Org. Chem*. **2005**, *70*, 1262.



(*R*)-**2a**
via General Procedure A



(*S*)-**2a**
via General Procedure B



(*S*)-**2a**
via General Procedure B

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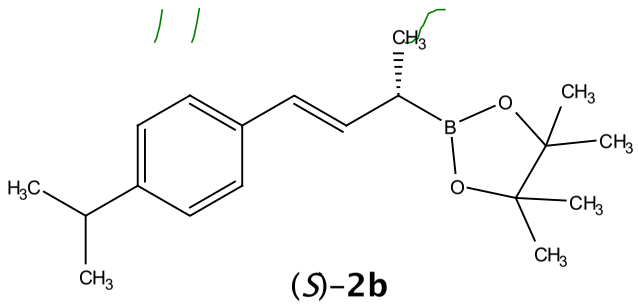

(*S*)-**2b**
via General Procedure A

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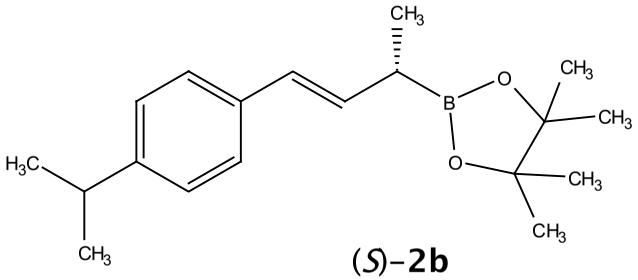
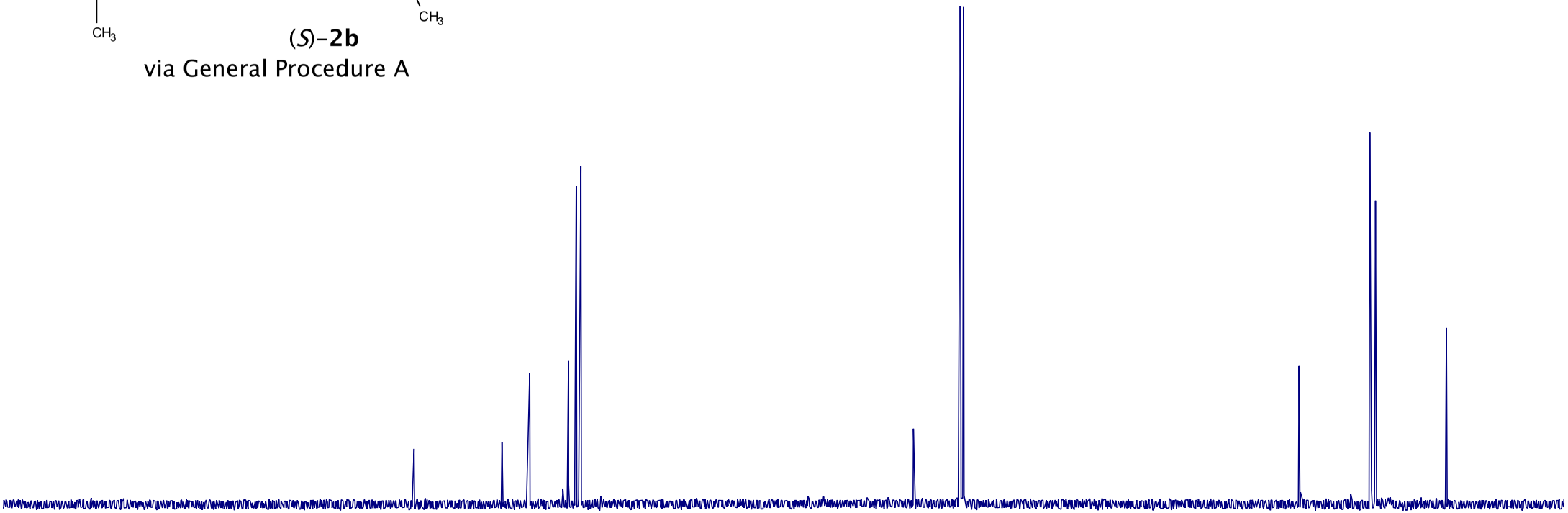
QZ-6-234-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 50

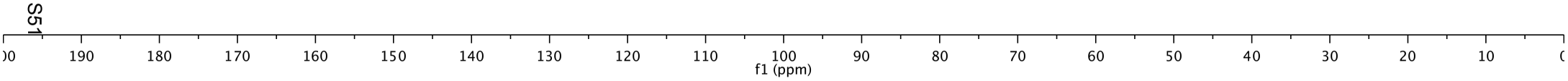
147.3638
136.0940
132.5355
127.5691
126.5756
125.9798
83.3679
77.1600 CDCl3
33.9421
24.8765
24.8105
24.1448
15.0603

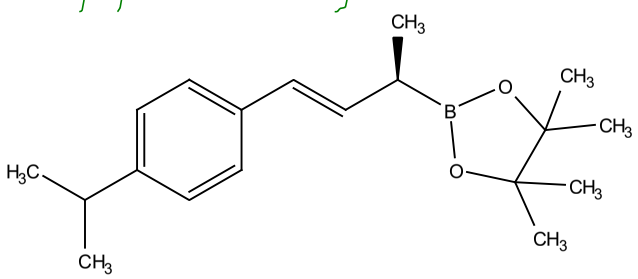


(*S*)-**2b**

via General Procedure A







(*R*)-**2b**

via General Procedure B

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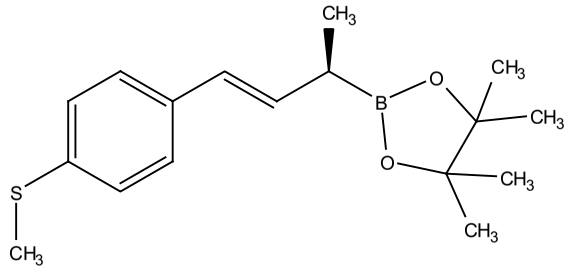

(*R*)-**2c**
via General Procedure A

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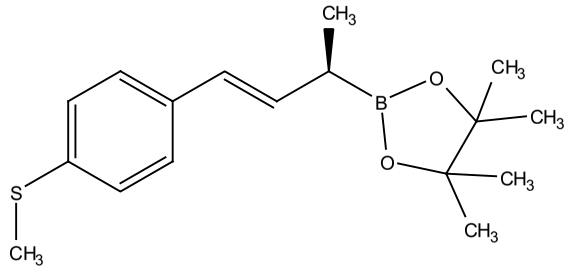
QZ-6-255-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 40

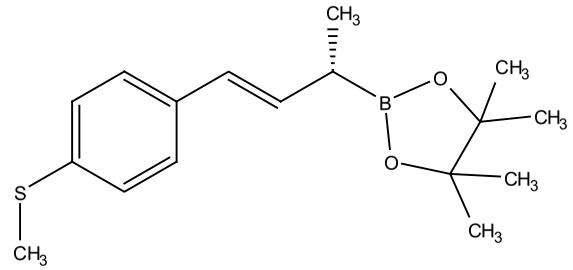


(*R*)-**2c**
via General Procedure A

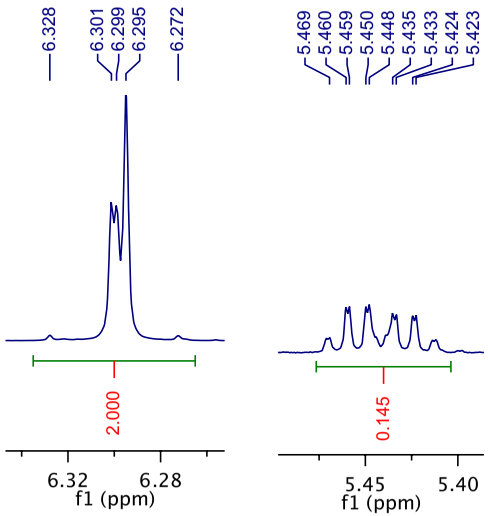
136.242
135.688
133.116
127.156
127.116
126.472
83.434
77.160 Chloroform-d
24.869
24.800
16.388
14.968

f1 (ppm)

QZ-6-255-2
QZ-6-255-2
qPROTON CDCl3 /opt/nmrdata qzhou 41



(*S*)-**2c**
via General Procedure B



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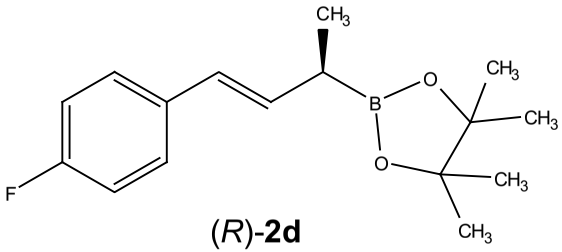
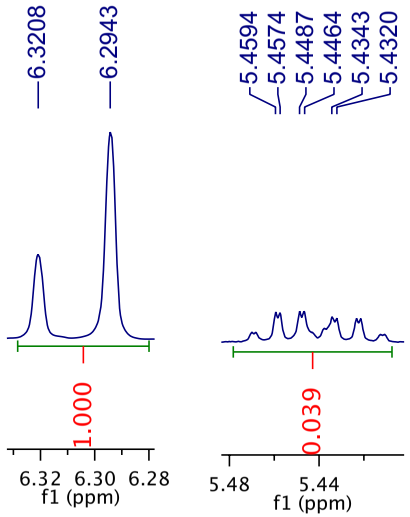
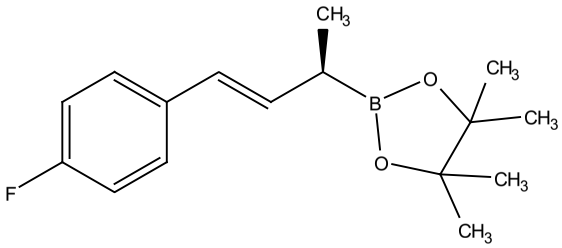


(*R*)-**2d**
via General Procedure A



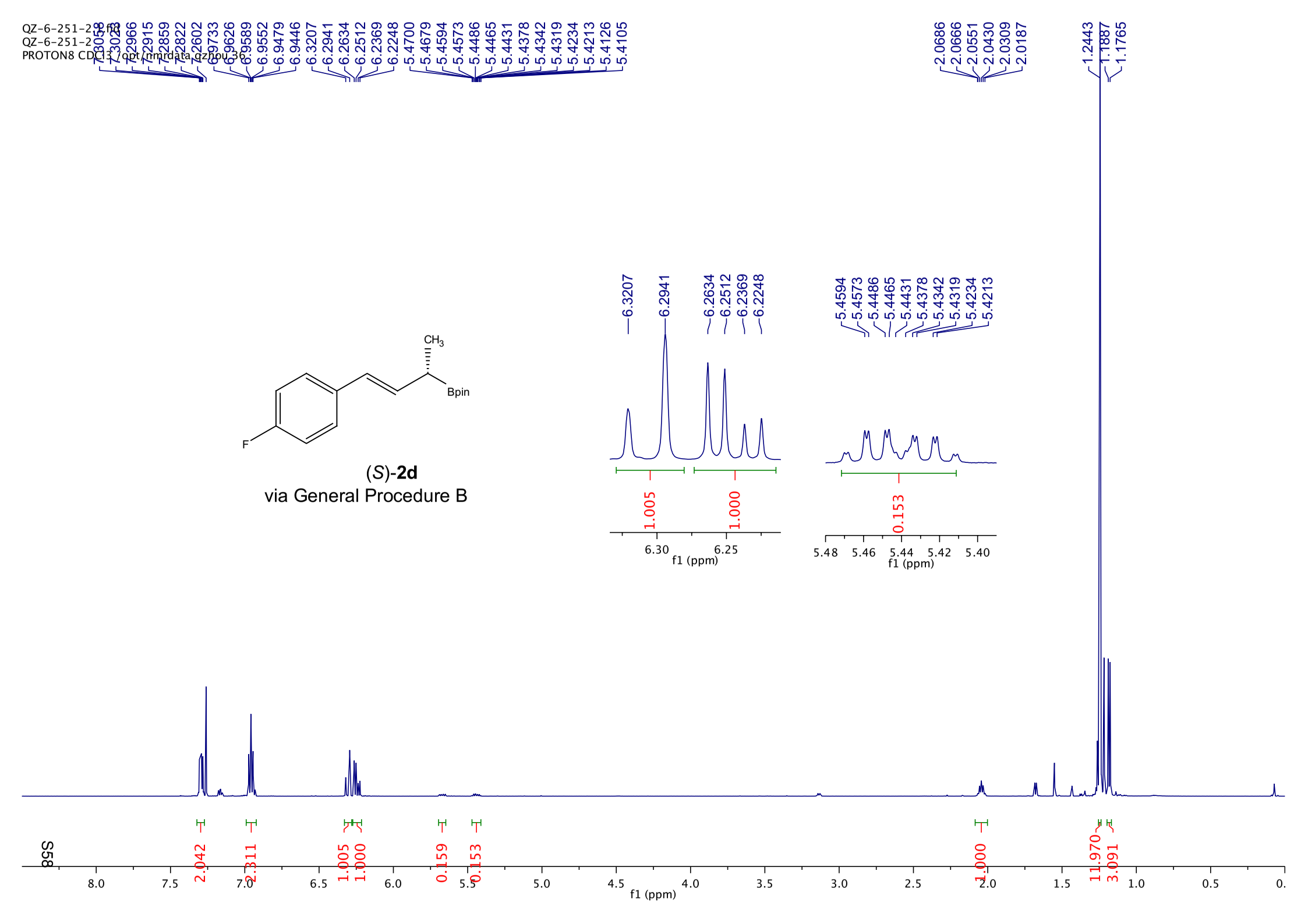
QZ-6-253.2.fid
QZ-6-253
C13CPD256 CDCl3 /opt/nmrdata qzhou 1

162.6613
161.0380
134.5883
134.5668
133.1996
133.1852
127.4062
127.3543
126.5990
115.3868
115.2456
83.4541
77.1600 CDCl3
24.8756
24.8120
14.9889



(*R*)-**2d**
via General Procedure A

f1 (ppm)


QZ-6-251-2.fid
QZ-6-251-2
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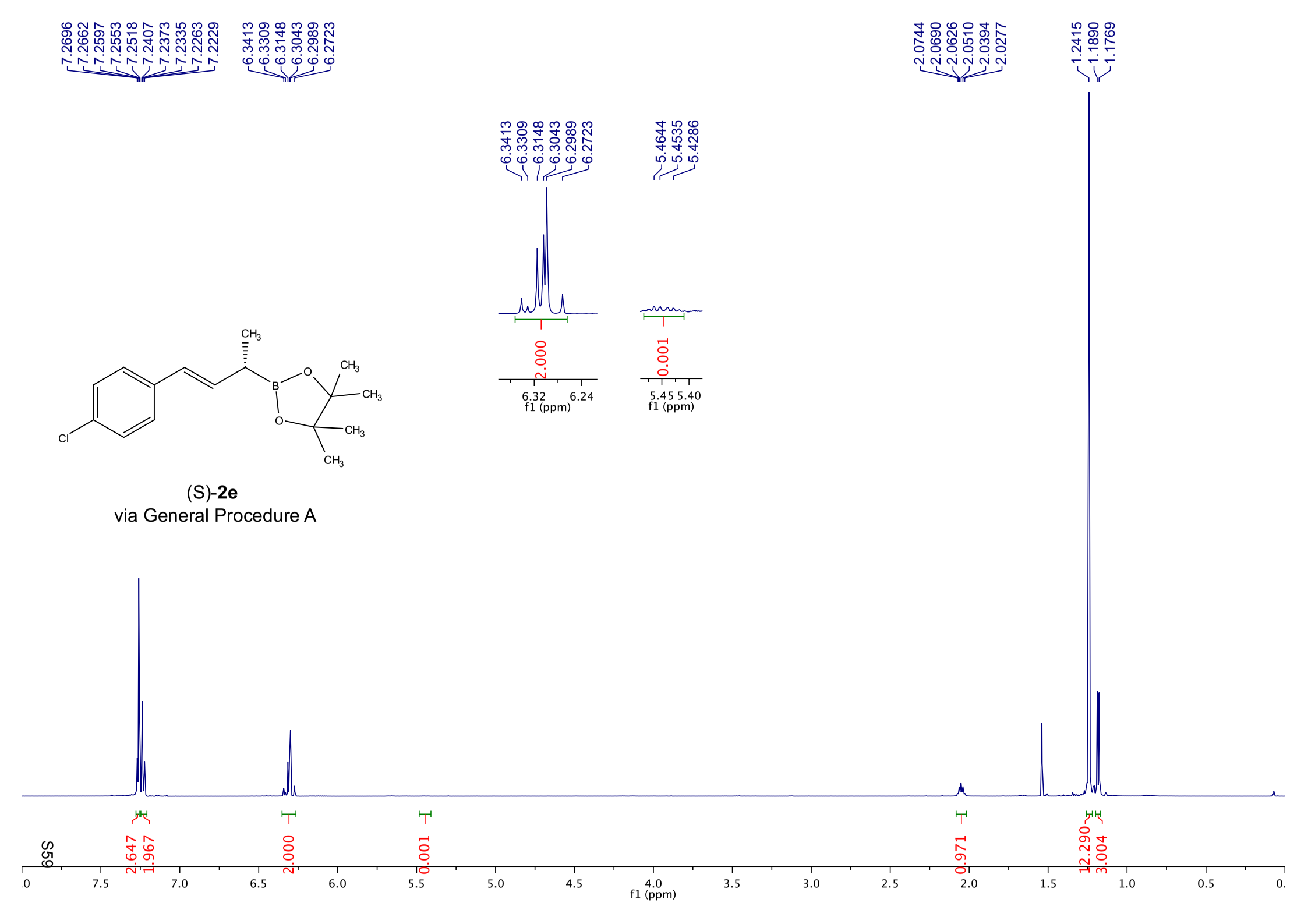
7.3054
7.3023
7.2966
7.2915
7.2859
7.2822
7.2602
6.9733
6.9626
6.9589
6.9552
6.9479
6.9446
6.3207
6.2941
6.2634
6.2512
6.2369
6.2248
5.4700
5.4679
5.4594
5.4573
5.4486
5.4465
5.4431
5.4378
5.4342
5.4319
5.4234
5.4213
5.4126
5.4105
2.0686
2.0666
2.0551
2.0430
2.0309
2.0187
1.2443
1.1887
1.1765
CH3
Bpin
F
(S)-2d
via General Procedure B
1.005
1.000
0.153
f1 (ppm)
2.042
2.311
1.005
1.000
0.159
0.153
1.000
11.970
3.091
S58


7.2696
7.2662
7.2597
7.2553
7.2518
7.2407
7.2373
7.2335
7.2263
7.2229
6.3413
6.3309
6.3148
6.3043
6.2989
6.2723
2.0744
2.0690
2.0626
2.0510
2.0394
2.0277
1.2415
1.1890
1.1769
5.4644
5.4535
5.4286
2.000
0.001
6.32
6.24
f1 (ppm)
5.45 5.40
f1 (ppm)
CH3
B
O
O
CH3
CH3
CH3
CH3
Cl
(S)-2e
via General Procedure A
2.647
1.967
2.000
0.001
0.971
12.290
3.004
S59
f1 (ppm)

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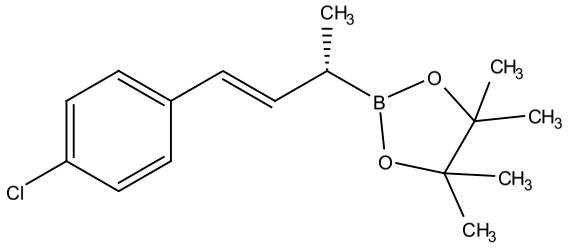
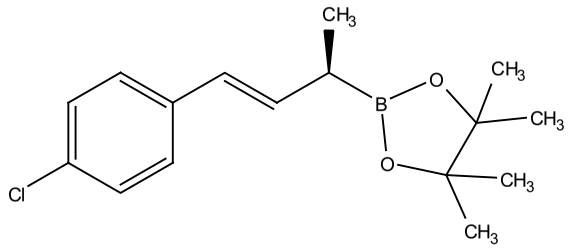
QZ-6-248
C13CPD256 CDCl3 /opt/nmrdata qzhou 55



(S)-**2e**
via General Procedure A



(*R*)-**2e**
via General Procedure B

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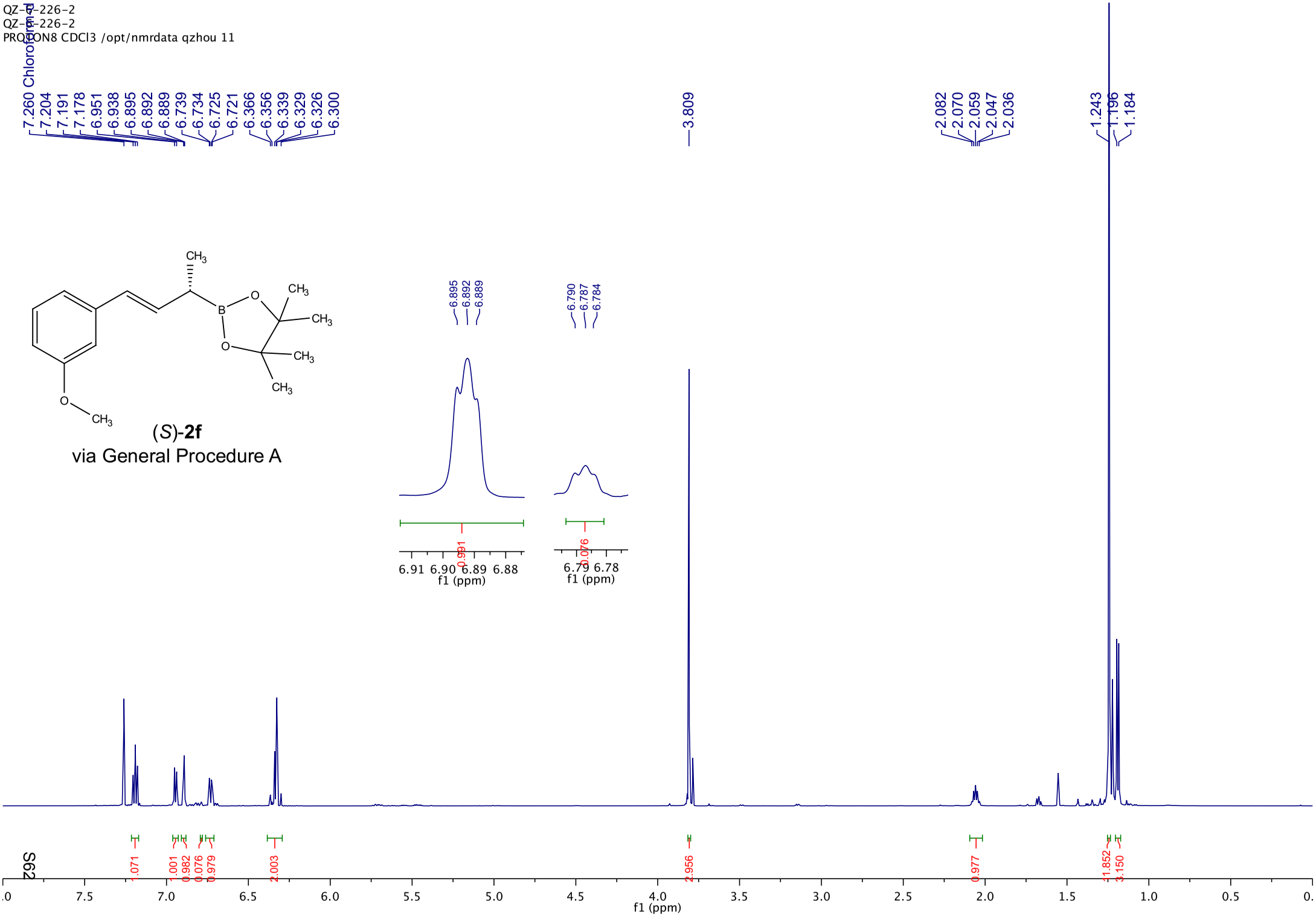
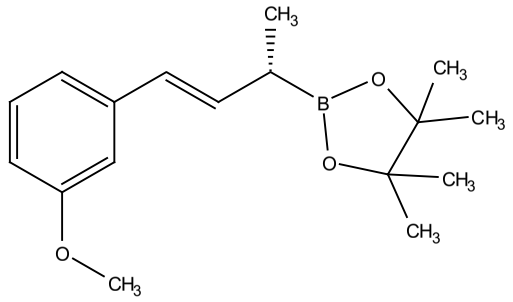
QZ-6-226-2
PROTON8 CDCl3 /opt/nmrdata qzhou 11



QZ-6-226-2
QZ-6-226-2
C13CPD256 CDCl3 /opt/nmrdata qzhou 11

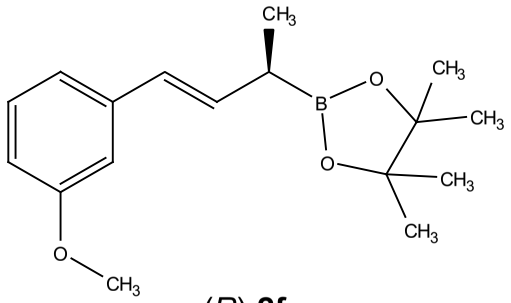
159.884
139.941
133.840
129.466
127.651
118.794
112.325
111.324
83.435
77.160 Chloroform-d
55.336
24.872
24.803
14.952



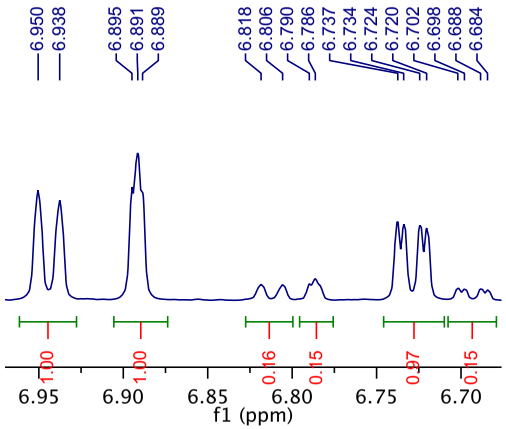
(*S*)-**2f**
via General Procedure A

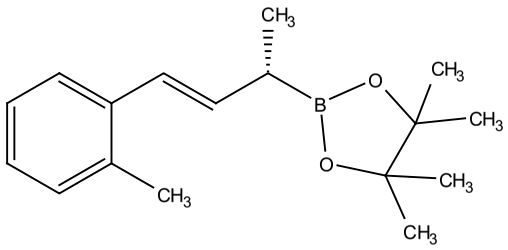
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

QZ-6-226-1
QZ-6-226-1
qPROTON CDCl3 /opt/nmrdata qzhou 10

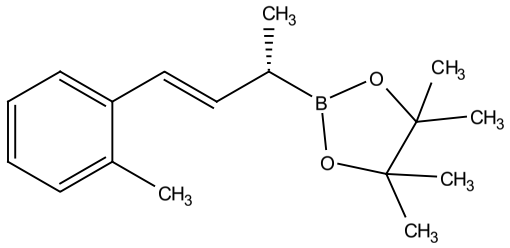


(*R*)-**2f**
via General Procedure B

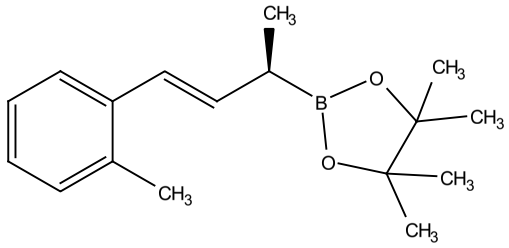




(*S*)-**2g**
via General Procedure A

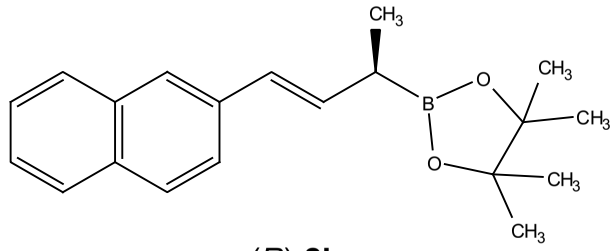


(*S*)-**2g**
via General Procedure A

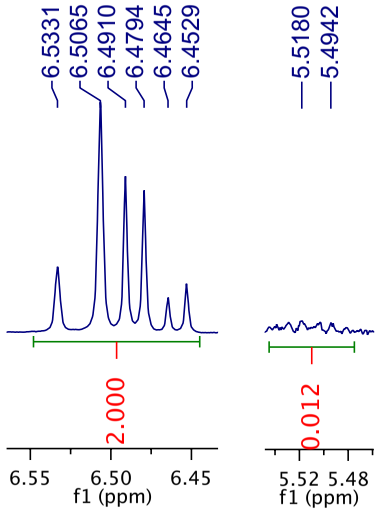


(*R*)-**2g**
via General Procedure B

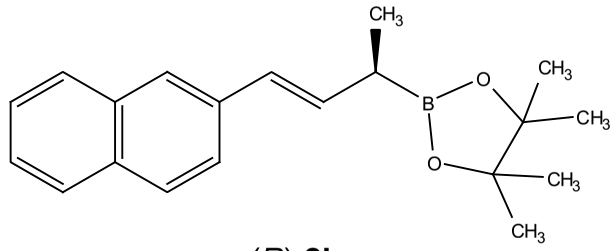
HH-5-252B
HH-5-252B
PROTON8 CDCl3 /opt/nmrdata hari 50



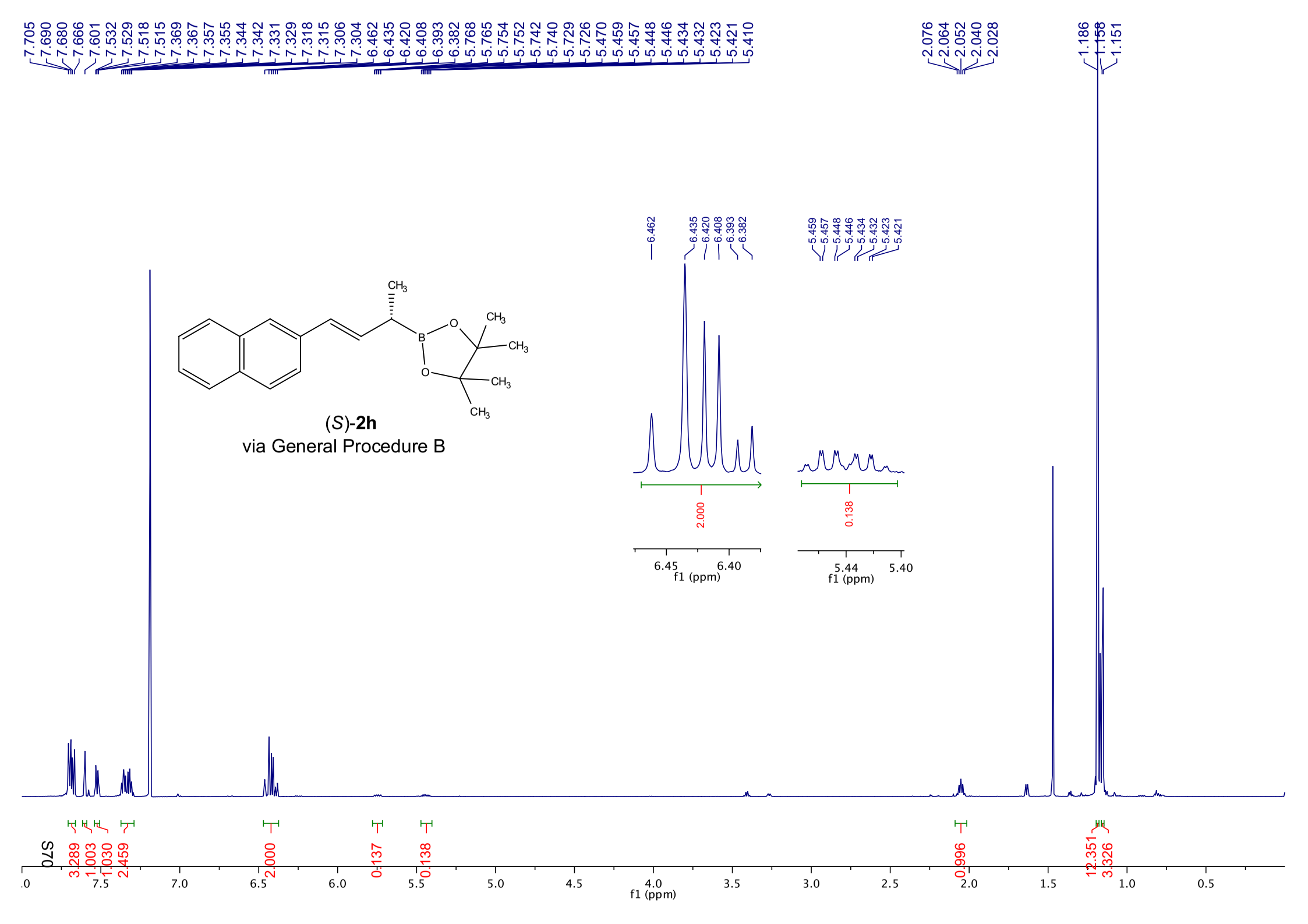
(*R*)-**2h**
via General Procedure A



HH-5-252B
HH-5-252B
C13CPD2048 CDCl3 /opt/nmrdata hari 50



(*R*)-**2h**
via General Procedure A

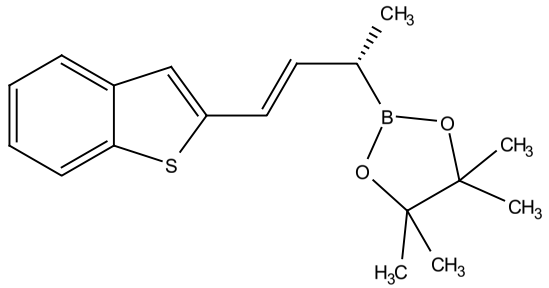

7.705
7.690
7.680
7.666
7.601
7.532
7.529
7.518
7.515
7.369
7.367
7.357
7.355
7.344
7.342
7.331
7.329
7.318
7.315
7.306
7.304
6.462
6.435
6.420
6.408
6.393
6.382
5.768
5.765
5.754
5.752
5.742
5.740
5.729
5.726
5.470
5.459
5.457
5.448
5.446
5.434
5.432
5.423
5.421
5.410
2.076
2.064
2.052
2.040
2.028
1.186
1.158
1.151
CH3
O
B
O
CH3
CH3
CH3
CH3
(S)-2h
via General Procedure B
6.462
6.435
6.420
6.408
6.393
6.382
2.000
6.45
6.40
f1 (ppm)
5.459
5.457
5.448
5.446
5.434
5.432
5.423
5.421
0.138
5.44
5.40
f1 (ppm)
3.289
1.003
1.030
2.459
2.000
0.137
0.138
0.996
12.351
3.326
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

QZ-7-012-1
QZ-7-012-1
qPROTON CDCl3 /opt/nmrdata qzhou 20

7.637 7.625 7.284 7.282 7.272 7.270 7.260 7.260 7.248 7.246 7.235 7.223 7.221 7.028 6.591 6.590 6.565 6.564 6.309 6.296 6.283 6.270

2.112 2.100 2.088 2.076 2.064

1.251 1.214 1.202



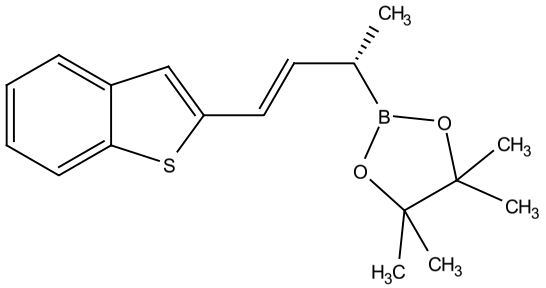
(*S*)-**2i**
via General Procedure A

0.98 1.01 1.03 1.04 1.00 1.02 0.99 1.01 12.42 3.06

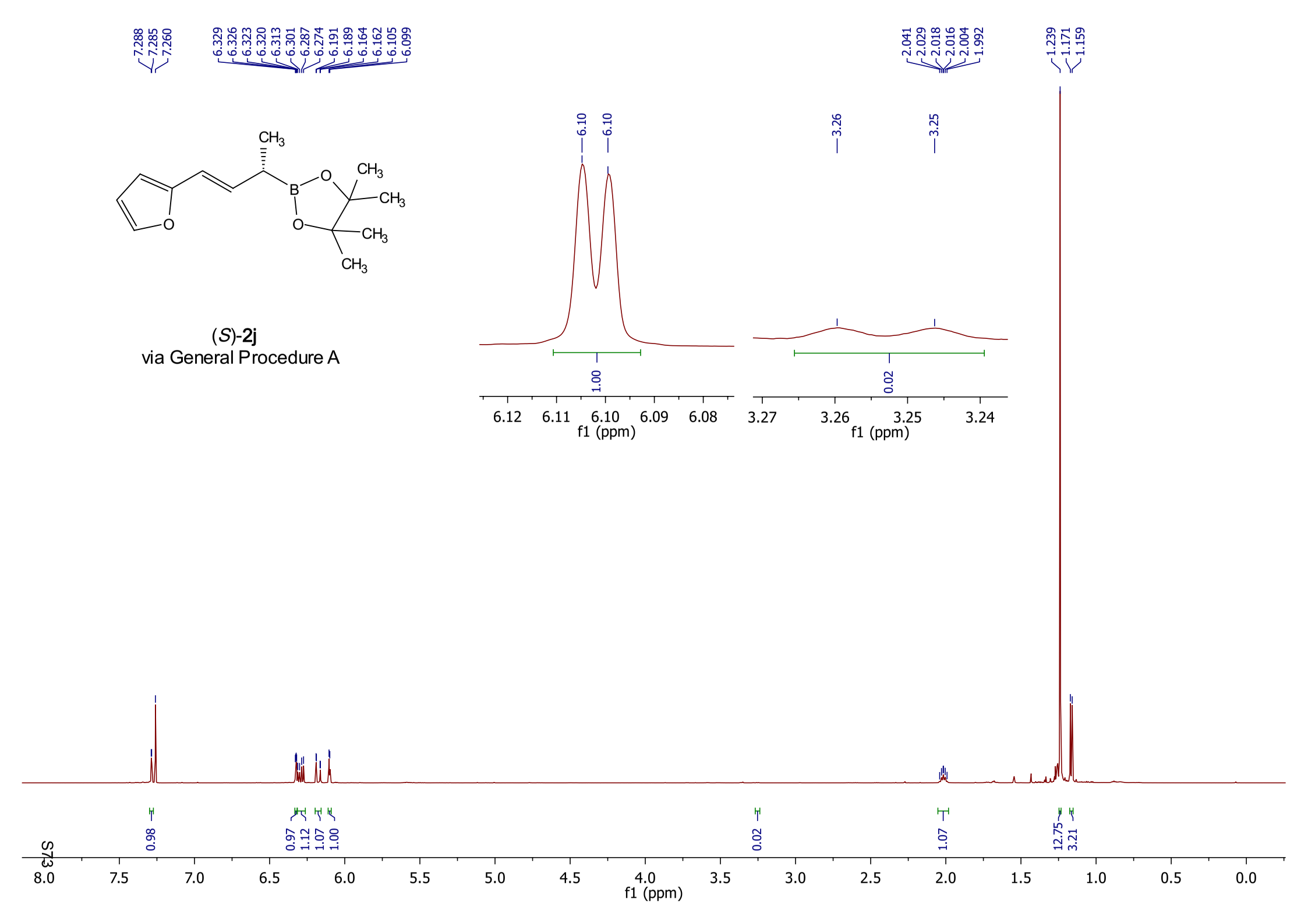
S71

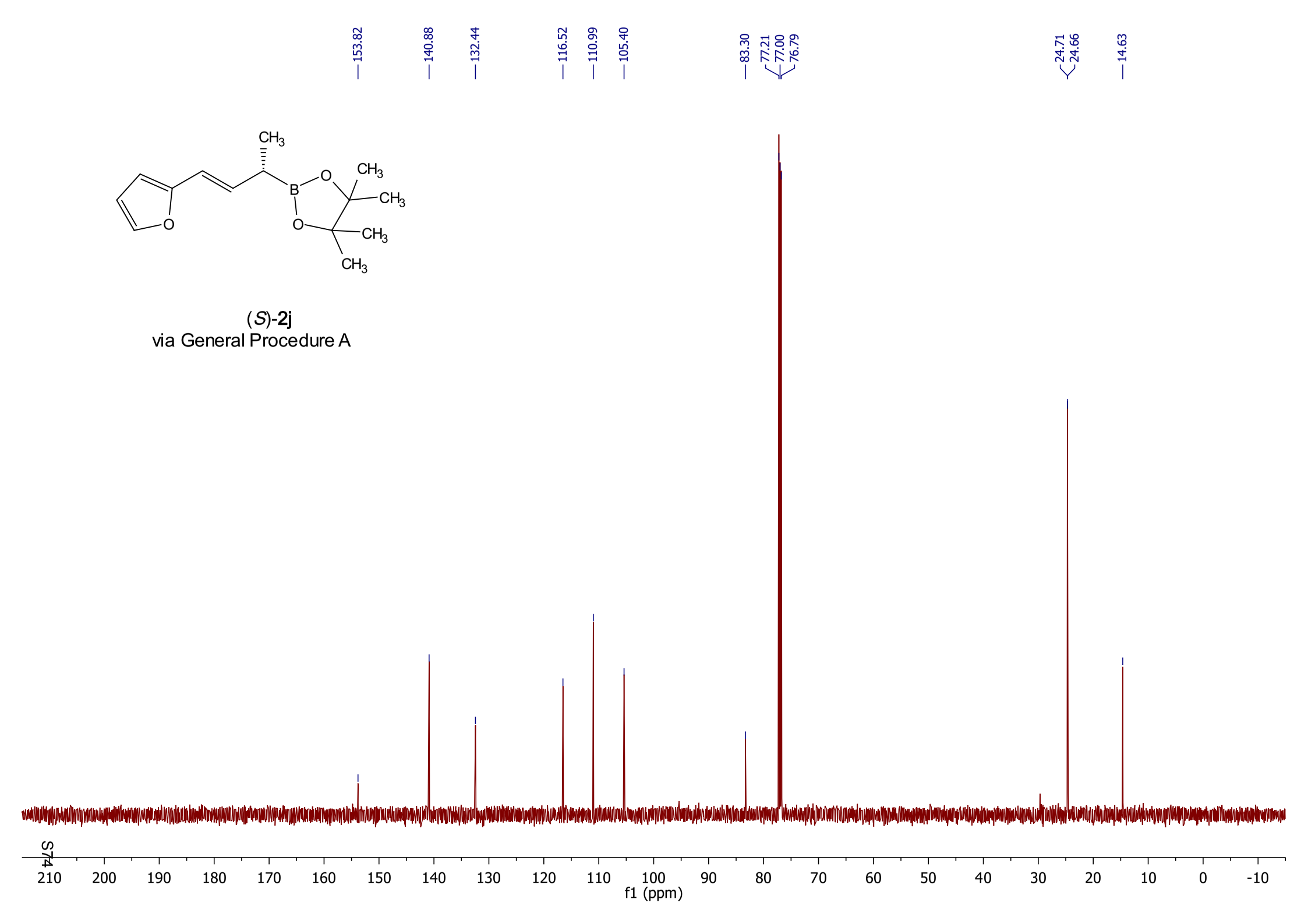
f1 (ppm)

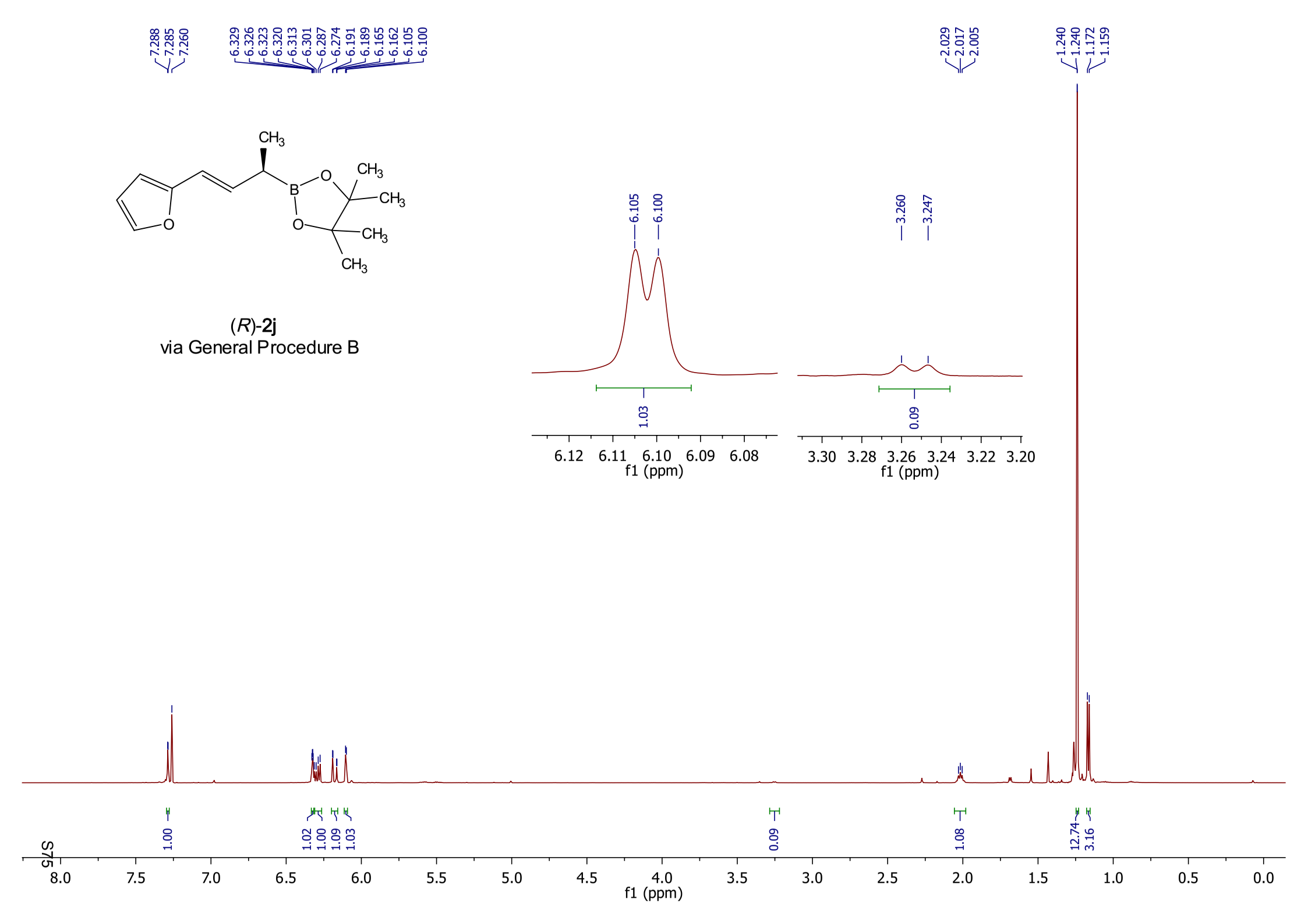
QZ-7-012-1
QZ-7-012-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 20

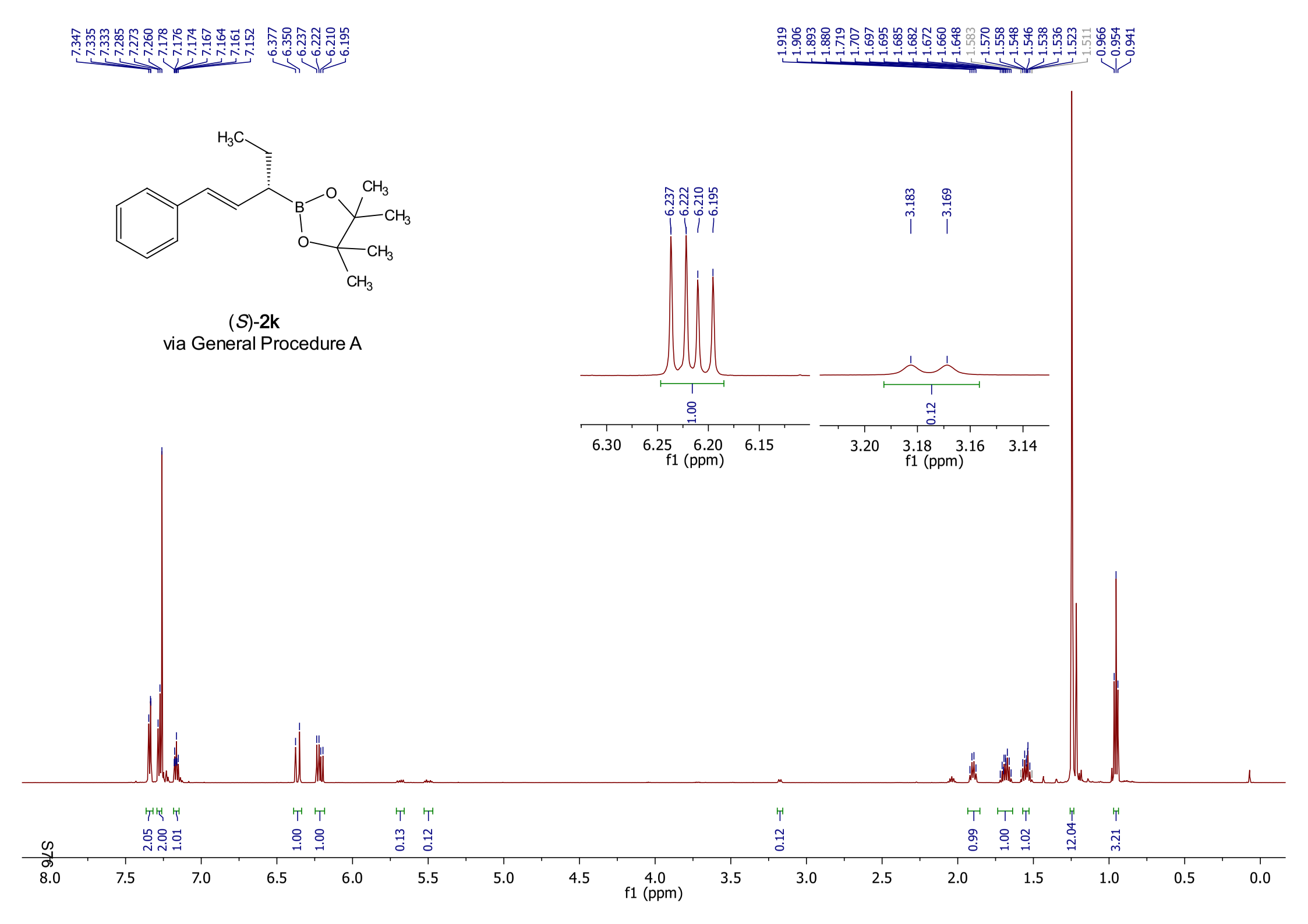


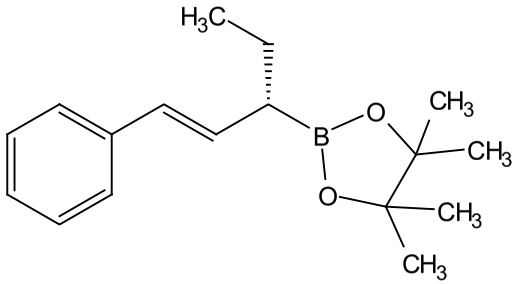
(*S*)-**2i**
via General Procedure A


7.288
7.285
7.260
6.329
6.326
6.323
6.320
6.313
6.301
6.287
6.274
6.191
6.189
6.164
6.162
6.105
6.099
2.041
2.029
2.018
2.016
2.004
1.992
1.239
1.171
1.159
CH3
O
B
O
O
CH3
CH3
CH3
CH3
(S)-2j
via General Procedure A
6.10
6.10
1.00
6.12
6.11
6.10
6.09
6.08
f1 (ppm)
3.26
3.25
0.02
3.27
3.26
3.25
3.24
f1 (ppm)
0.98
0.97
1.12
1.07
1.00
0.02
1.07
12.75
3.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

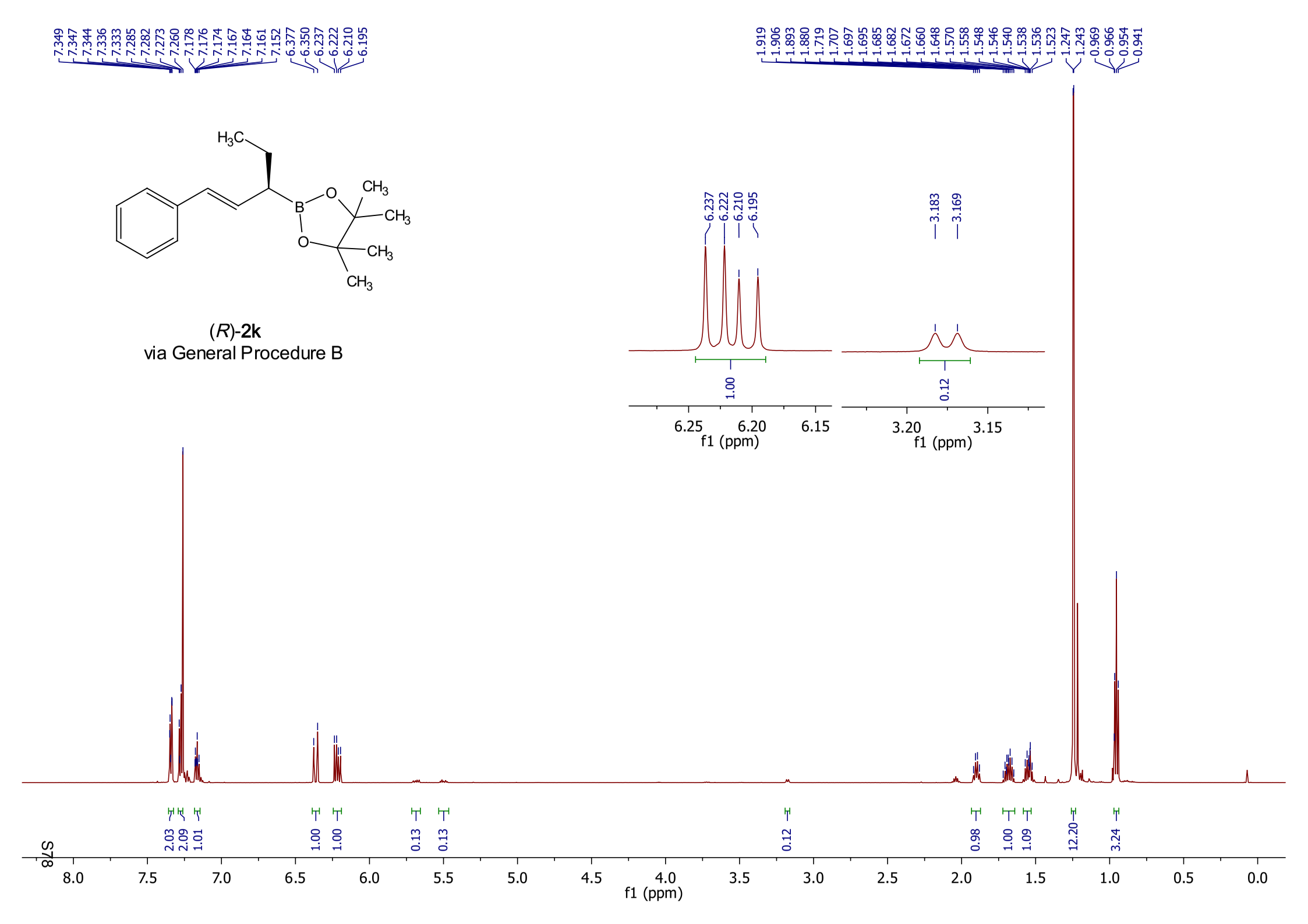

153.82
140.88
132.44
116.52
110.99
105.40
83.30
77.21
77.00
76.79
24.71
24.66
14.63
CH3
CH3
CH3
CH3
CH3
B
O
O
O
(S)-2j
via General Procedure A
S74
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

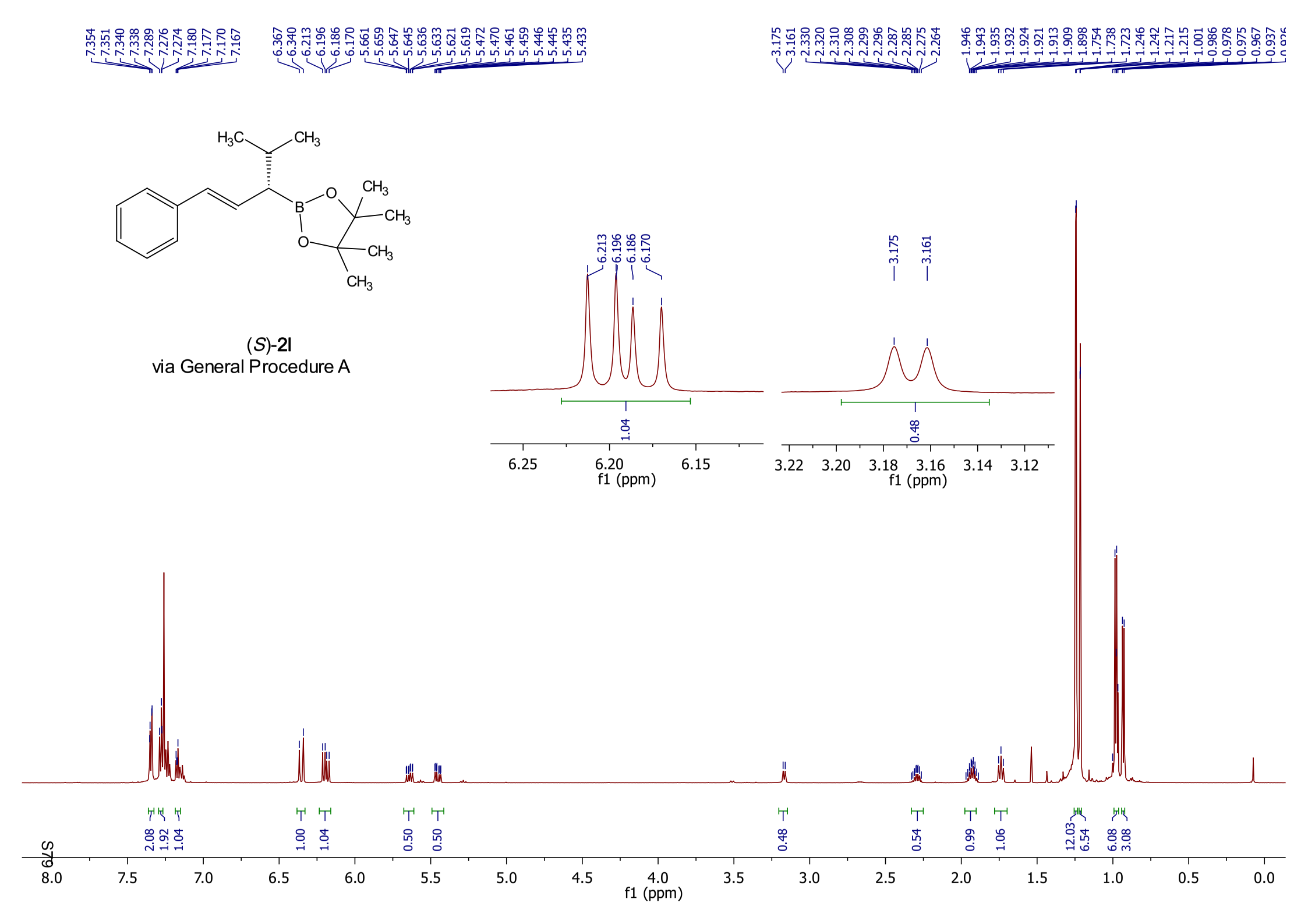

7.288
7.285
7.260
6.329
6.326
6.323
6.320
6.313
6.301
6.287
6.274
6.191
6.189
6.165
6.162
6.105
6.100
2.029
2.017
2.005
1.240
1.240
1.172
1.159
CH3
O
B
O
O
CH3
CH3
CH3
CH3
(R)-2j
via General Procedure B
6.105
6.100
1.03
6.12 6.11 6.10 6.09 6.08
f1 (ppm)
3.260
3.247
0.09
3.30 3.28 3.26 3.24 3.22 3.20
f1 (ppm)
1.00
1.02
1.00
1.09
1.03
0.09
1.08
12.74
3.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

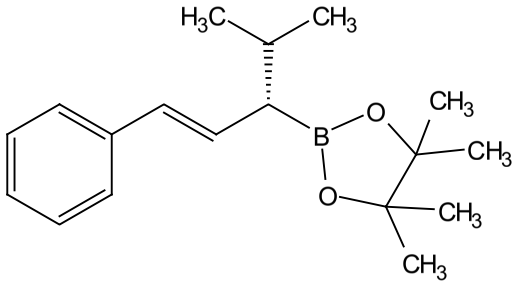

7.347
7.335
7.333
7.285
7.273
7.260
7.178
7.176
7.174
7.167
7.164
7.161
7.152
6.377
6.350
6.237
6.222
6.210
6.195
1.919
1.906
1.893
1.880
1.719
1.707
1.697
1.695
1.685
1.682
1.672
1.660
1.648
1.583
1.570
1.558
1.548
1.546
1.538
1.536
1.523
1.511
0.966
0.954
0.941
H3C
CH3
CH3
CH3
CH3
B
O
O
(S)-2k
via General Procedure A
6.237
6.222
6.210
6.195
1.00
6.30
6.25
6.20
6.15
f1 (ppm)
3.183
3.169
0.12
3.20
3.18
3.16
3.14
f1 (ppm)
2.05
2.00
1.01
1.00
1.00
0.13
0.12
0.12
0.99
1.00
1.02
12.04
3.21
S76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



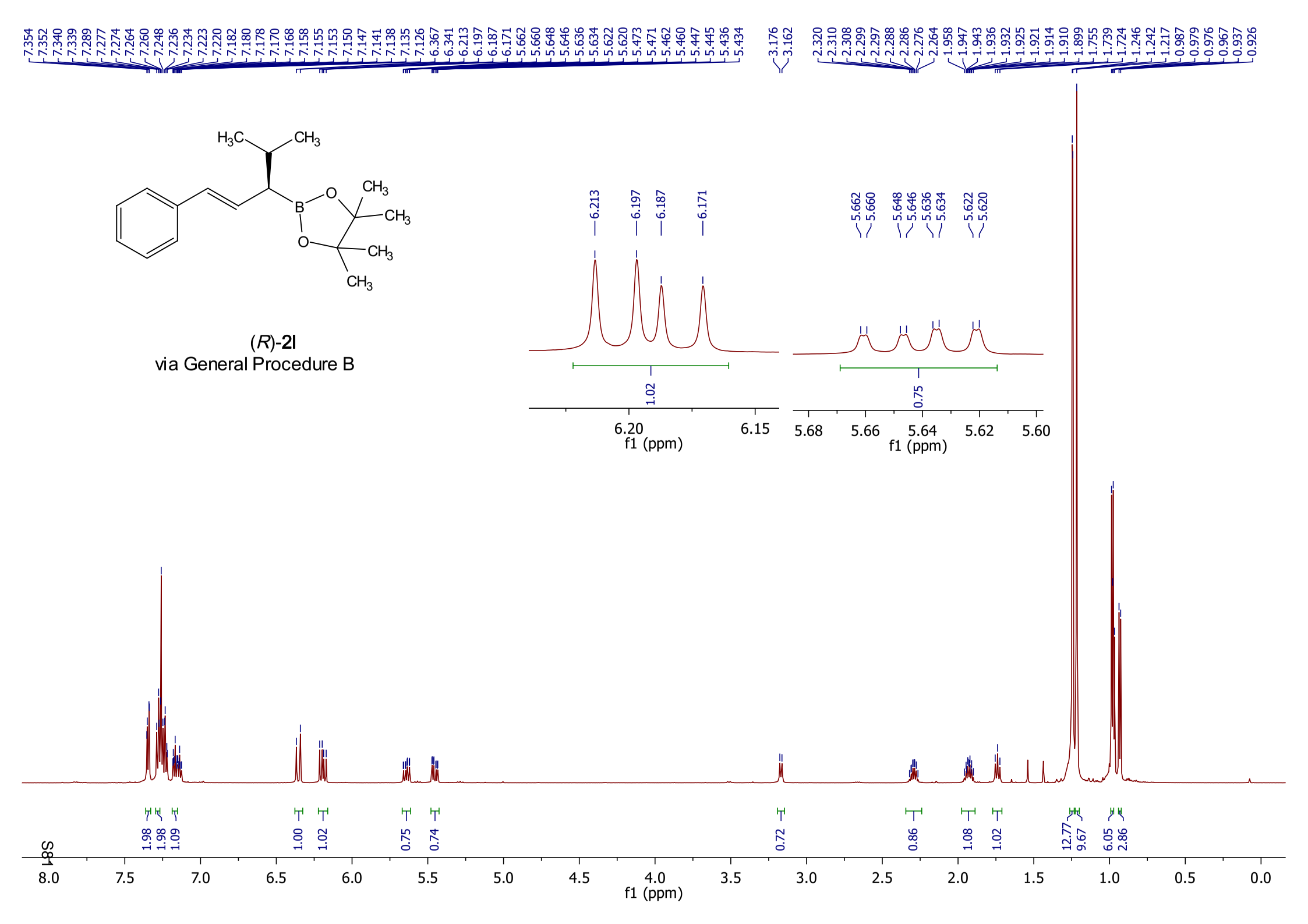
(*S*)-**2k**
via General Procedure A


7.349
7.347
7.344
7.336
7.333
7.285
7.282
7.273
7.260
7.178
7.176
7.174
7.167
7.164
7.161
7.152
6.377
6.350
6.237
6.222
6.210
6.195
1.919
1.906
1.893
1.880
1.719
1.707
1.697
1.695
1.685
1.682
1.672
1.660
1.648
1.570
1.558
1.548
1.546
1.540
1.538
1.536
1.523
1.247
1.243
0.969
0.966
0.954
0.941
H3C
CH3
CH3
CH3
CH3
B
O
O
(R)-2k
via General Procedure B
6.237
6.222
6.210
6.195
1.00
6.25
6.20
6.15
f1 (ppm)
3.183
3.169
0.12
3.20
3.15
f1 (ppm)
2.03
2.09
1.01
1.00
1.00
0.13
0.13
0.12
0.98
1.00
1.09
12.20
3.24
S78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

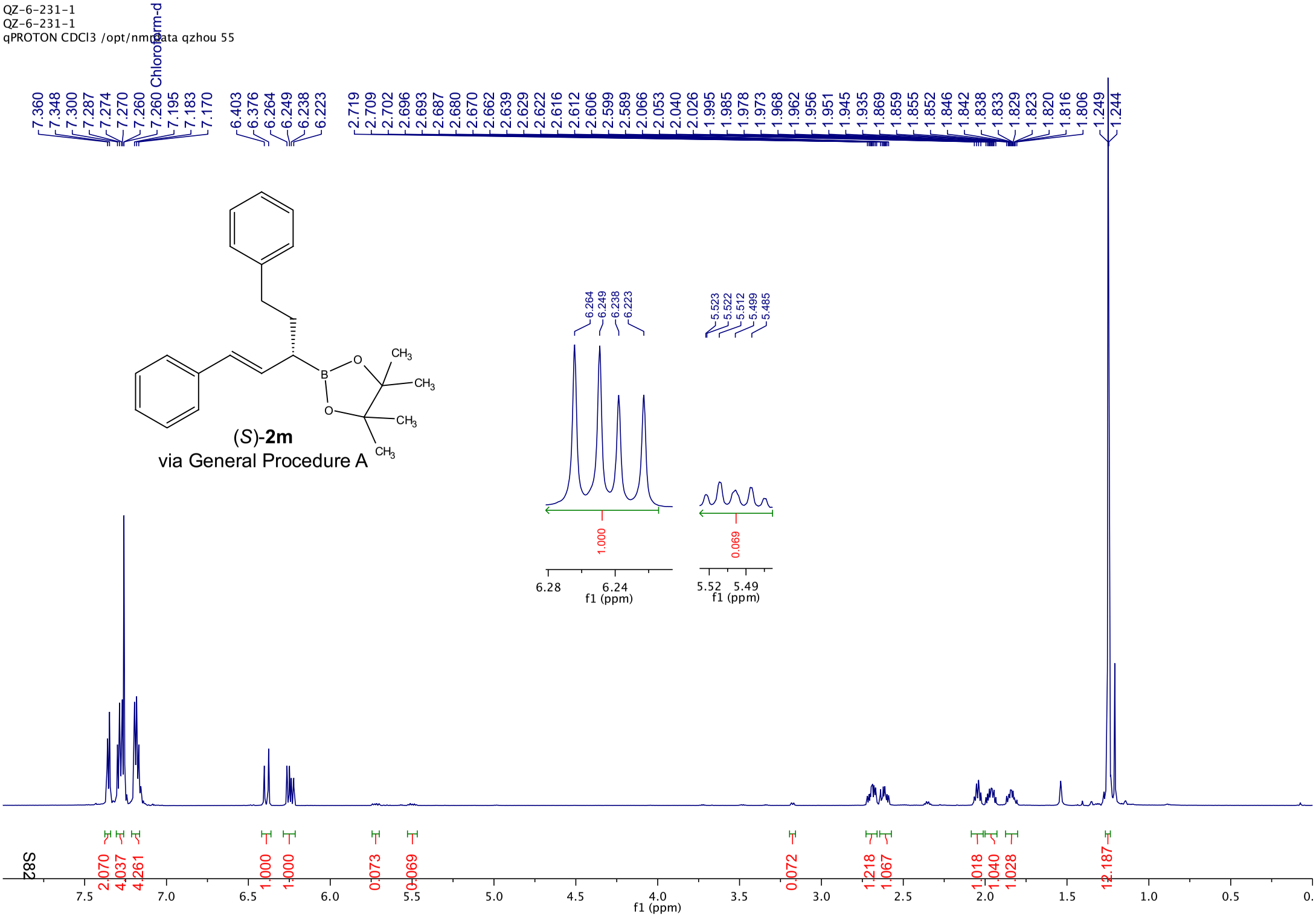

7.354
7.351
7.340
7.338
7.289
7.276
7.274
7.180
7.177
7.170
7.167
6.367
6.340
6.213
6.196
6.186
6.170
5.661
5.659
5.647
5.645
5.636
5.633
5.621
5.619
5.472
5.470
5.461
5.459
5.446
5.445
5.435
5.433
3.175
3.161
2.330
2.320
2.310
2.308
2.299
2.296
2.287
2.285
2.275
2.264
1.946
1.943
1.935
1.932
1.924
1.921
1.913
1.909
1.898
1.754
1.738
1.723
1.246
1.242
1.217
1.215
1.001
0.986
0.978
0.975
0.967
0.937
H3C
CH3
B
O
O
CH3
CH3
CH3
CH3
(S)-2l
via General Procedure A
6.213
6.196
6.186
6.170
1.04
6.25
6.20
6.15
f1 (ppm)
3.175
3.161
0.48
3.22
3.20
3.18
3.16
3.14
3.12
f1 (ppm)
2.08
1.92
1.04
1.00
1.04
0.50
0.50
0.48
0.54
0.99
1.06
12.03
6.54
6.08
3.08
S79
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(*S*)-**2l**
via General Procedure A

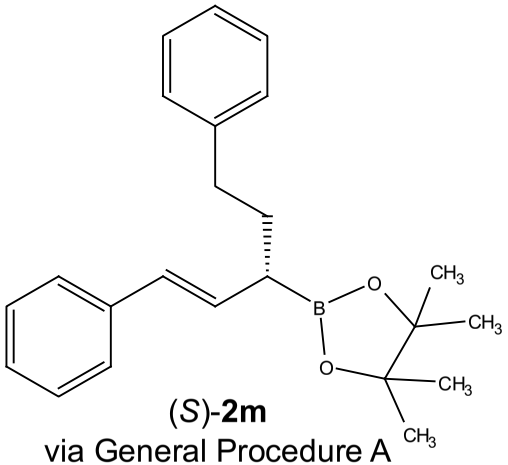

7.354 7.352 7.340 7.339 7.289 7.277 7.274 7.264 7.260 7.248 7.236 7.234 7.223 7.220 7.182 7.180 7.178 7.170 7.168 7.158 7.155 7.153 7.150 7.147 7.141 7.138 7.135 7.126 6.367 6.341 6.213 6.197 6.187 6.171 5.662 5.660 5.648 5.646 5.636 5.634 5.622 5.620 5.473 5.471 5.462 5.460 5.447 5.445 5.436 5.434
3.176 3.162
2.320 2.310 2.308 2.299 2.297 2.288 2.286 2.276 2.264
1.958 1.947 1.943 1.936 1.932 1.925 1.921 1.914 1.910 1.899 1.755 1.739 1.724 1.246 1.242 1.217 0.987 0.979 0.976 0.967 0.937 0.926
H3C CH3
B O O CH3 CH3 CH3 CH3
(R)-2l
via General Procedure B
6.213 6.197 6.187 6.171
1.02
6.20 6.15
f1 (ppm)
5.662 5.660 5.648 5.646 5.636 5.634 5.622 5.620
0.75
5.68 5.66 5.64 5.62 5.60
f1 (ppm)
1.98 1.98 1.09 1.00 1.02 0.75 0.74 0.72 0.86 1.08 1.02 12.77 9.67 6.05 2.86
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
S84

QZ-6-231-1
QZ-6-231-1
qPROTON CDCl3 /opt/nmrdata qzhou 55



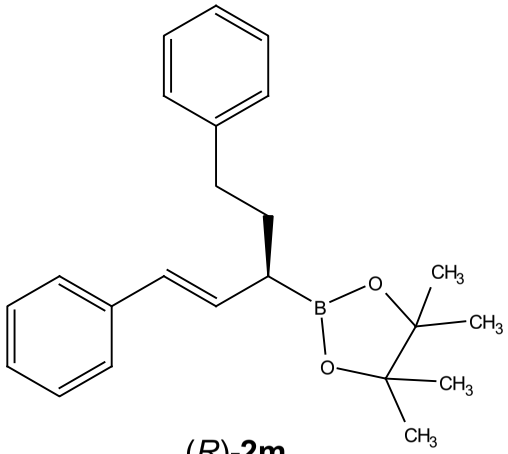
QZ-6-231-1
QZ-6-231-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 55

142.731
138.310
131.599
129.654
128.673
128.560
128.412
126.751
126.070
125.800
83.486
77.160 Chloroform-d
35.555
32.828
24.947
24.789

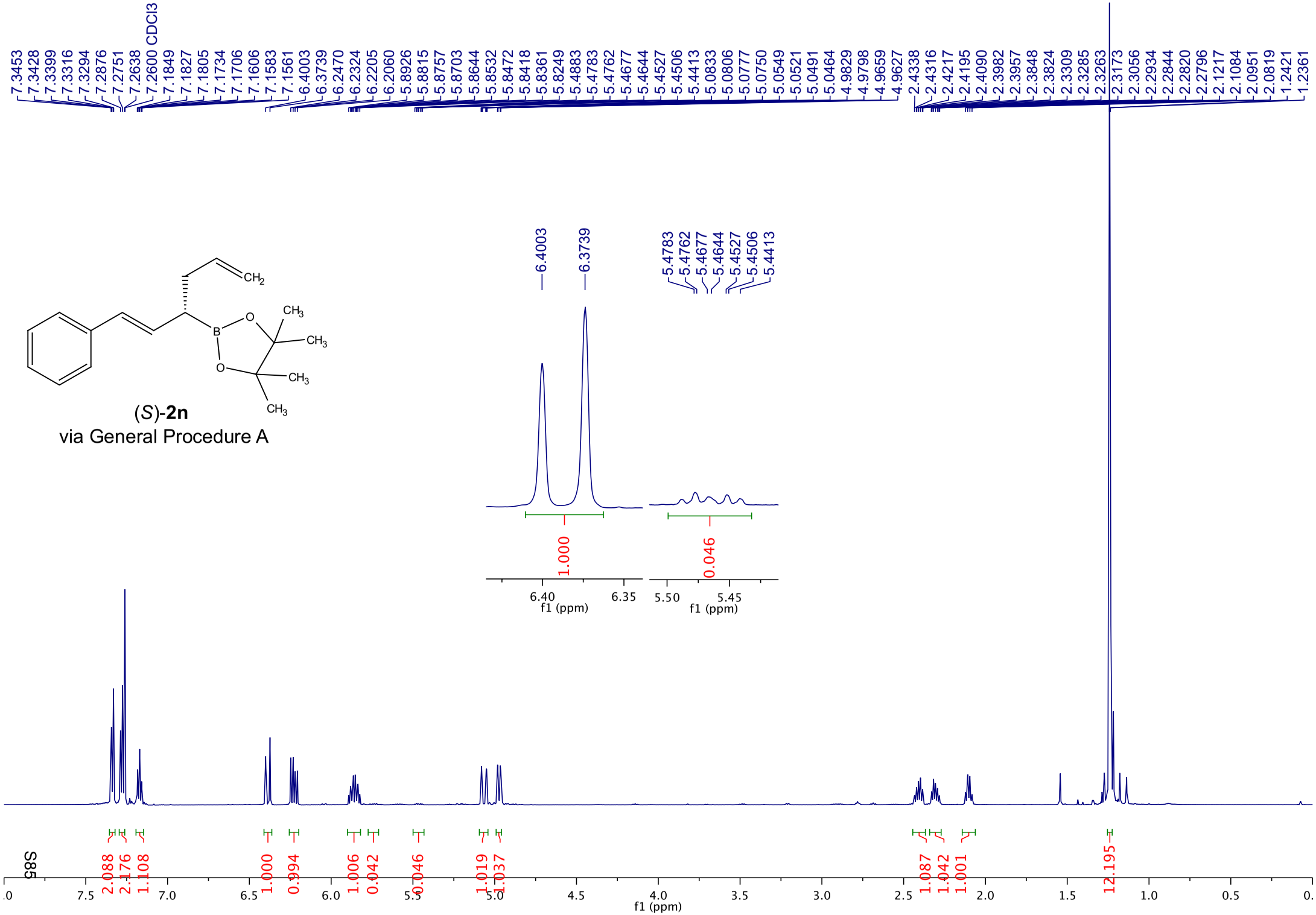


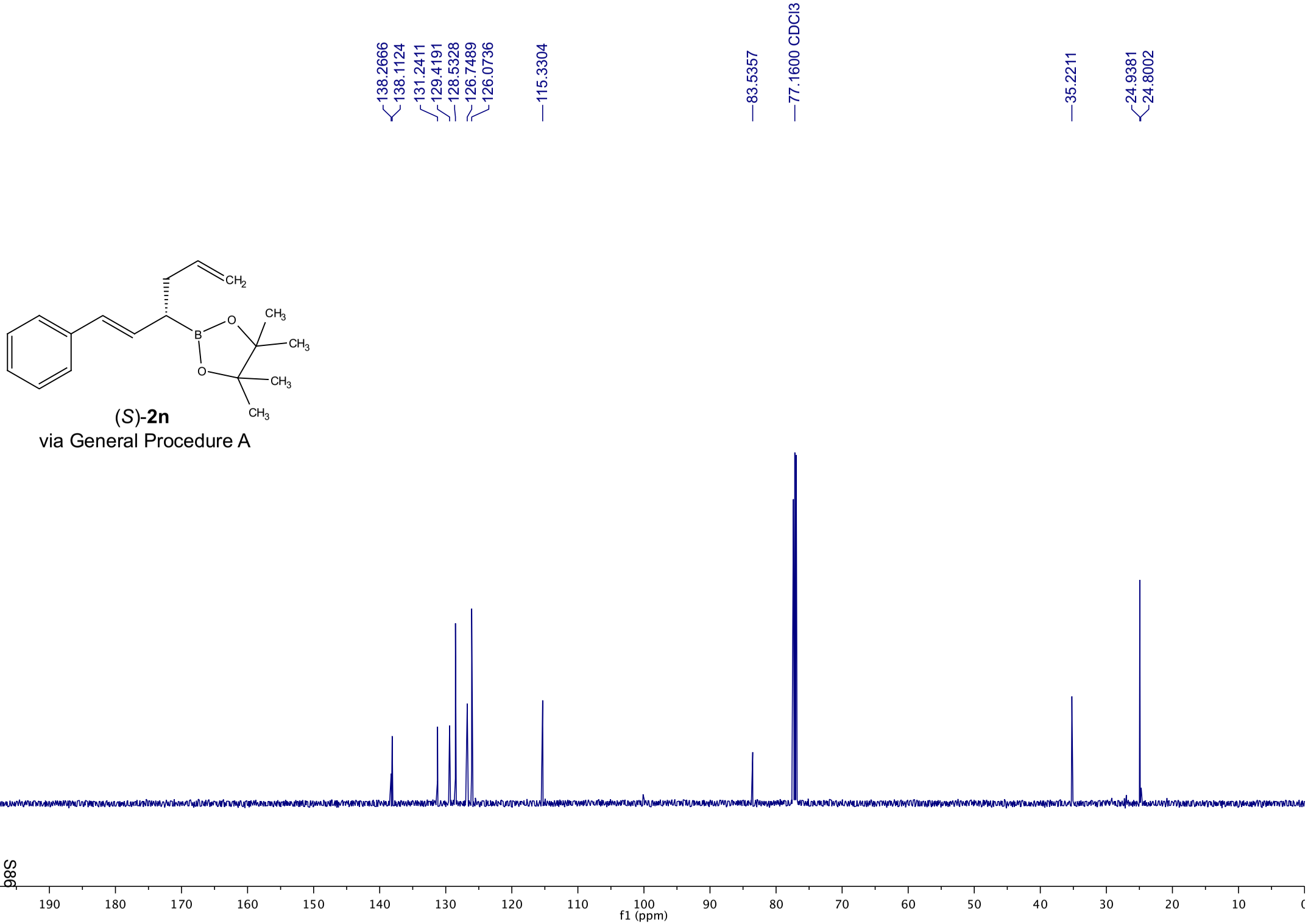
(*S*)-**2m**
via General Procedure A

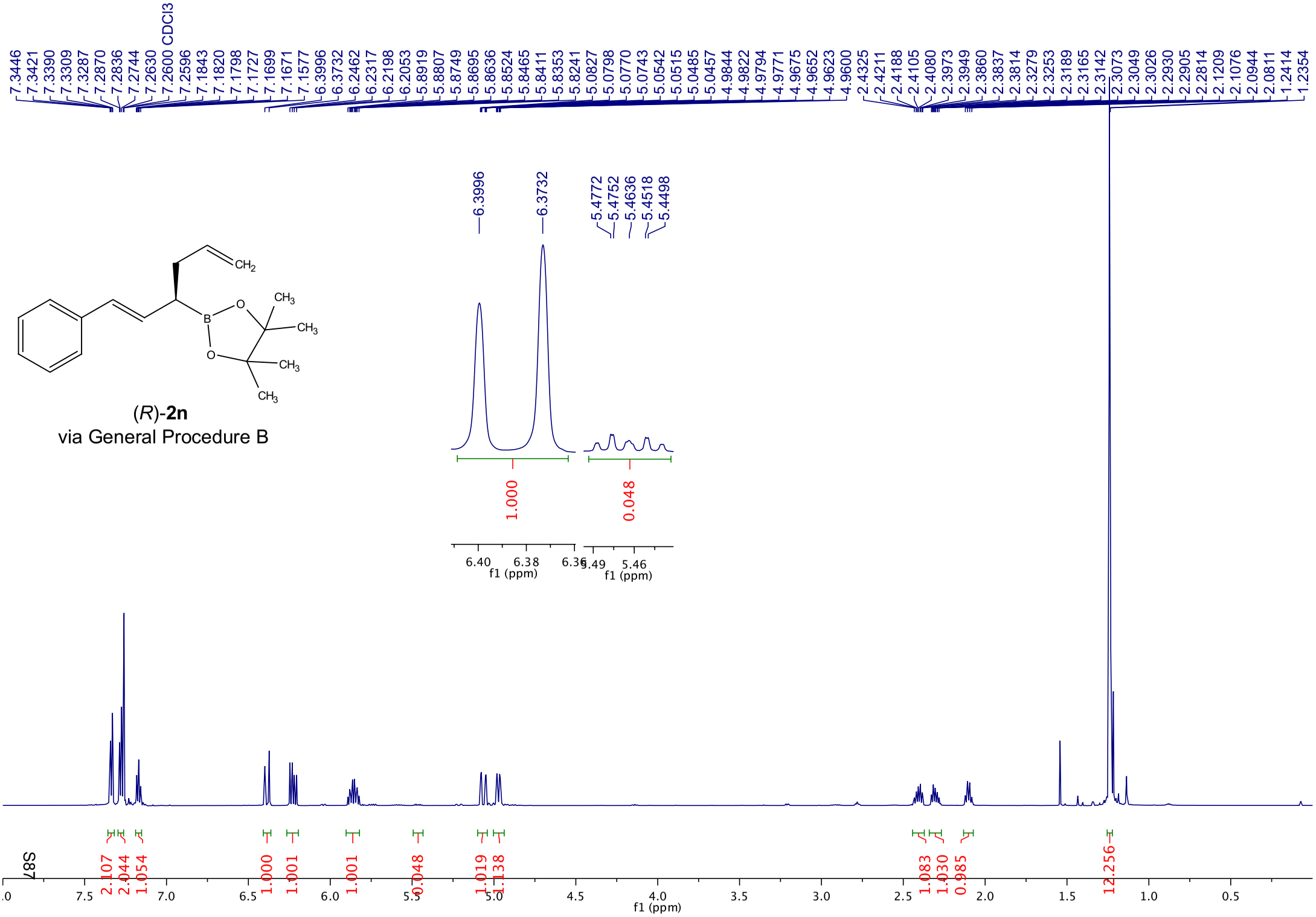
QZ-6-231-1
QZ-6-231-1
qPROTON CDCl3 /opt/nmrdata qzhou 55

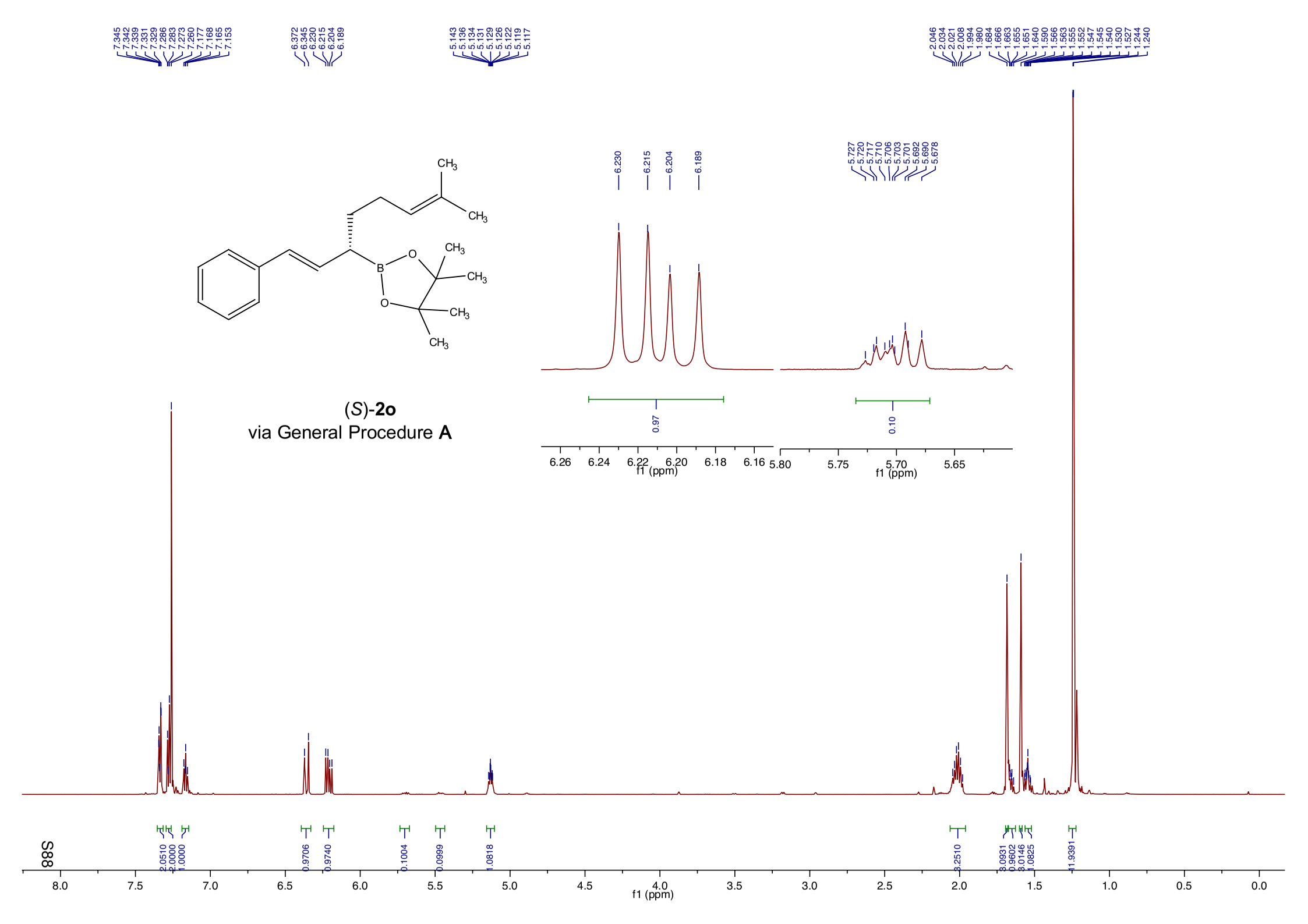


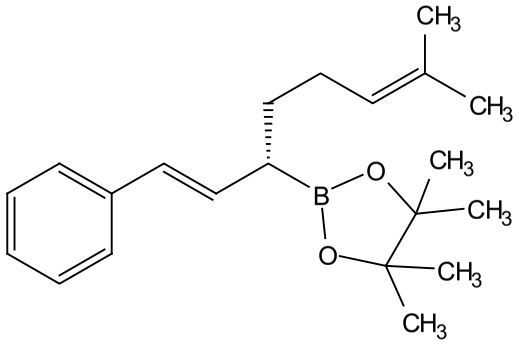
(*R*)-**2m**
via General Procedure B


7.3453
7.3428
7.3399
7.3316
7.3294
7.2876
7.2751
7.2638
CDCl3
7.2600
7.1849
7.1827
7.1805
7.1734
7.1706
7.1606
7.1583
7.1561
6.4003
6.3739
6.2470
6.2324
6.2205
6.2060
5.8926
5.8815
5.8757
5.8703
5.8644
5.8532
5.8472
5.8418
5.8361
5.8249
5.4883
5.4783
5.4762
5.4677
5.4644
5.4527
5.4506
5.4413
5.0833
5.0806
5.0777
5.0750
5.0549
5.0521
5.0491
5.0464
4.9829
4.9798
4.9659
4.9627
2.4338
2.4316
2.4217
2.4195
2.4090
2.3982
2.3957
2.3848
2.3824
2.3309
2.3285
2.3263
2.3173
2.3056
2.2934
2.2844
2.2820
2.2796
2.1217
2.1084
2.0951
2.0819
1.2421
1.2361
CH2
CH3
CH3
CH3
CH3
B
O
O
(S)-2n
via General Procedure A
6.4003
6.3739
5.4783
5.4762
5.4677
5.4644
5.4527
5.4506
5.4413
1.000
0.046
6.40
6.35
f1 (ppm)
5.50
5.45
f1 (ppm)
2.088
2.176
1.108
1.000
0.994
1.006
0.042
0.046
1.019
1.037
1.087
1.042
1.001
12.195
f1 (ppm)

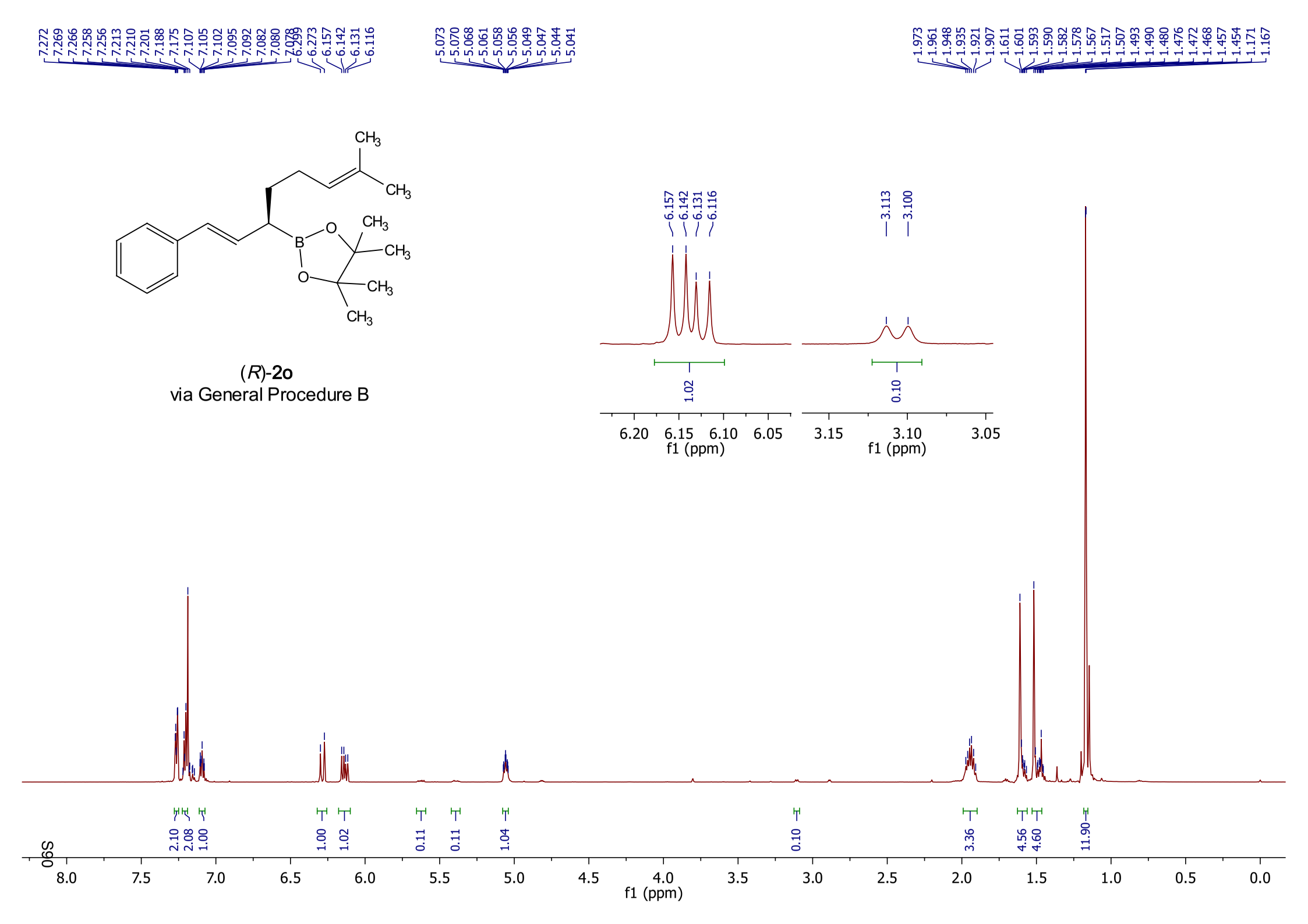

138.2666
138.1124
131.2411
129.4191
128.5328
126.7489
126.0736
115.3304
83.5357
77.1600 CDCl3
35.2211
24.9381
24.8002
CH2
CH3
CH3
CH3
CH3
B
O
O
(S)-2n
via General Procedure A
S86
f1 (ppm)


7.3446
7.3421
7.3390
7.3309
7.3287
7.2870
7.2836
7.2744
7.2630
7.2600 CDCl3
7.2596
7.1843
7.1820
7.1798
7.1727
7.1699
7.1671
7.1577
6.3996
6.3732
6.2462
6.2317
6.2198
6.2053
5.8919
5.8807
5.8749
5.8695
5.8636
5.8524
5.8465
5.8411
5.8353
5.8241
5.0827
5.0798
5.0770
5.0743
5.0542
5.0515
5.0485
5.0457
4.9844
4.9822
4.9794
4.9771
4.9675
4.9652
4.9623
4.9600
2.4325
2.4211
2.4188
2.4105
2.4080
2.3973
2.3949
2.3860
2.3837
2.3814
2.3279
2.3253
2.3189
2.3165
2.3142
2.3073
2.3049
2.3026
2.2930
2.2905
2.2814
2.1209
2.1076
2.0944
2.0811
1.2414
1.2354
CH2
CH3
CH3
CH3
CH3
B
O
O
(R)-2n
via General Procedure B
6.3996
6.3732
5.4772
5.4752
5.4636
5.4518
5.4498
1.000
0.048
6.40
6.38
6.36
f1 (ppm)
5.49
5.46
f1 (ppm)
2.107
2.044
1.054
1.000
1.001
1.001
0.048
1.019
1.138
1.083
1.030
0.985
12.256
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

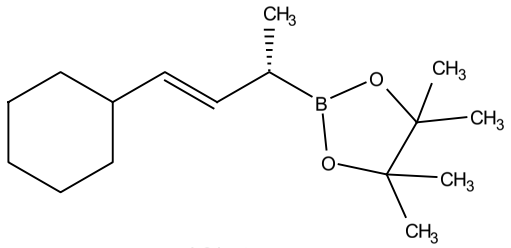

7.345
7.342
7.339
7.331
7.329
7.286
7.283
7.273
7.260
7.177
7.168
7.165
7.153
6.372
6.345
6.230
6.215
6.204
6.189
5.143
5.136
5.134
5.131
5.129
5.126
5.122
5.119
5.117
2.046
2.034
2.021
2.008
1.994
1.980
1.684
1.666
1.663
1.655
1.651
1.640
1.590
1.566
1.563
1.555
1.552
1.547
1.545
1.540
1.530
1.527
1.244
1.240
CH3
CH3
CH3
CH3
CH3
CH3
B
O
O
(S)-2o
via General Procedure A
6.230
6.215
6.204
6.189
0.97
6.26
6.24
6.22
6.20
6.18
6.16
f1 (ppm)
5.727
5.720
5.717
5.710
5.706
5.703
5.701
5.692
5.690
5.678
0.10
5.80
5.75
5.70
5.65
f1 (ppm)
S88
2.0510
2.0000
1.0000
0.9706
0.9740
0.1004
0.0999
1.0818
3.2510
3.0931
0.9602
3.0146
1.0825
11.9391
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(*S*)-**2o**
via General Procedure A


7.272
7.269
7.266
7.258
7.256
7.213
7.210
7.201
7.188
7.175
7.107
7.105
7.102
7.095
7.092
7.082
7.080
6.273
6.157
6.142
6.131
6.116
5.073
5.070
5.068
5.061
5.058
5.056
5.049
5.047
5.044
5.041
1.973
1.961
1.948
1.935
1.921
1.907
1.611
1.601
1.593
1.590
1.582
1.578
1.567
1.517
1.507
1.493
1.490
1.480
1.476
1.472
1.468
1.457
1.454
1.171
1.167
CH3
CH3
CH3
CH3
CH3
CH3
B
O
O
(R)-2o
via General Procedure B
6.157
6.142
6.131
6.116
1.02
6.20
6.15
6.10
6.05
f1 (ppm)
3.113
3.100
0.10
3.15
3.10
3.05
f1 (ppm)
2.10
2.08
1.00
1.00
1.02
0.11
0.11
1.04
0.10
3.36
4.56
4.60
11.90
S90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

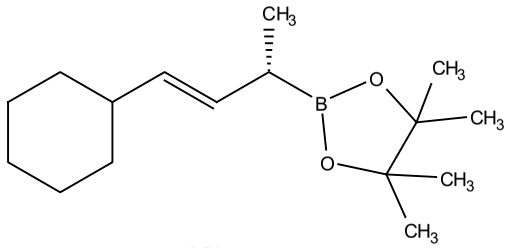
QZ-8-156-1-d6acetone
qPROTON Acetone /opt/nmrdata qzhou 36



(*S*)-**2p**
via General Procedure A

QZ-8-156-1-d6acetone
C13CPD256 Acetone /opt/nmrdata qzhou 36

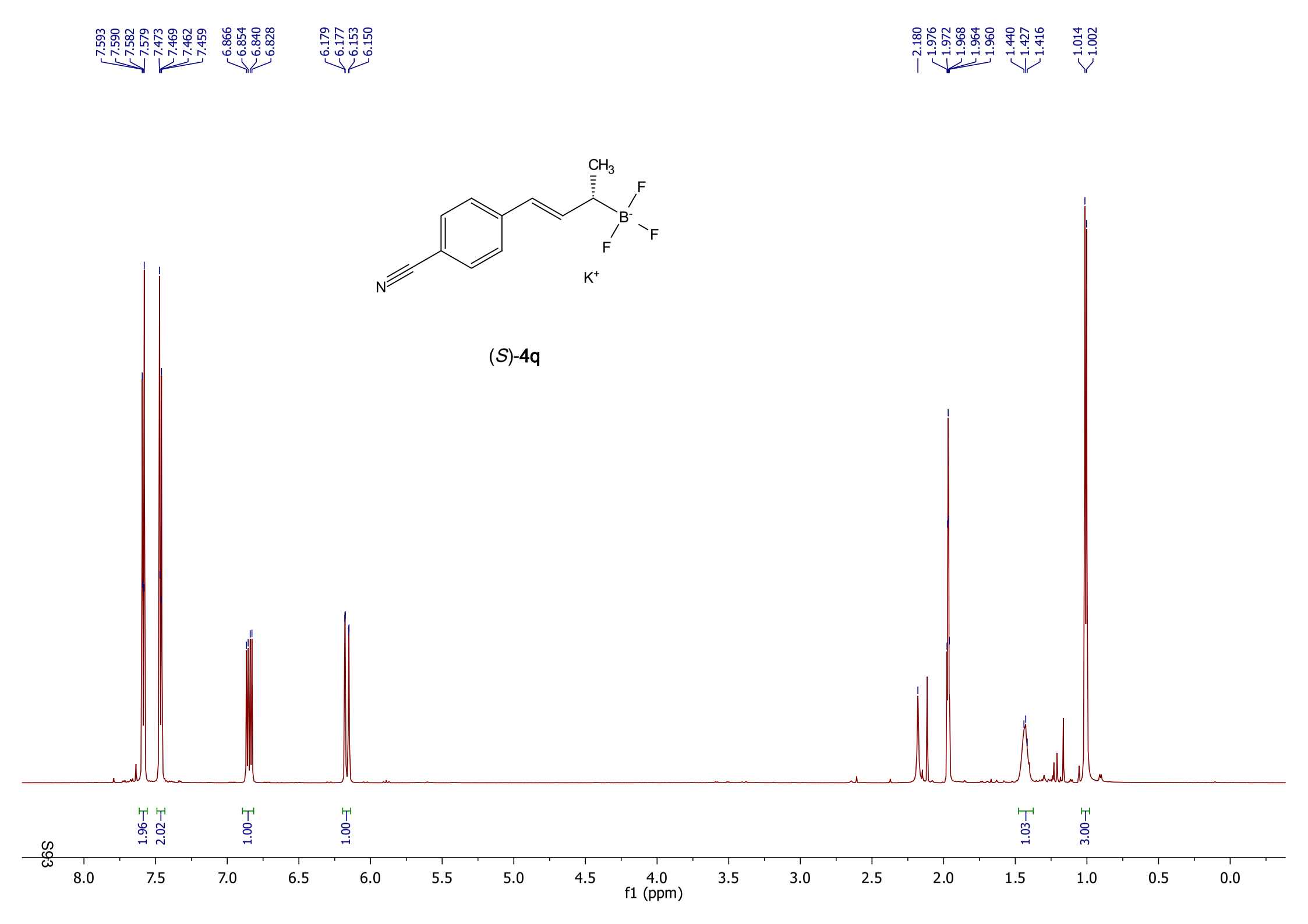
134.8190
131.1200
83.7673
41.9171
34.3904
30.3866 Acetone
30.2588 Acetone
30.1204 Acetone
30.0030
30.0023 Acetone
29.8740 Acetone
29.7460 Acetone
29.6176 Acetone
27.0598
26.9355
25.1928
25.1177
15.7510

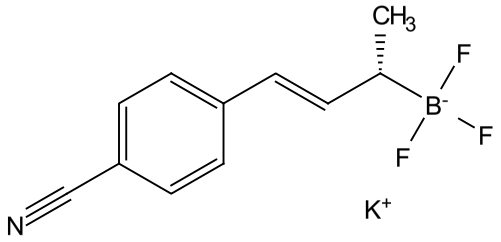


(*S*)-**2p**
via General Procedure A

S92

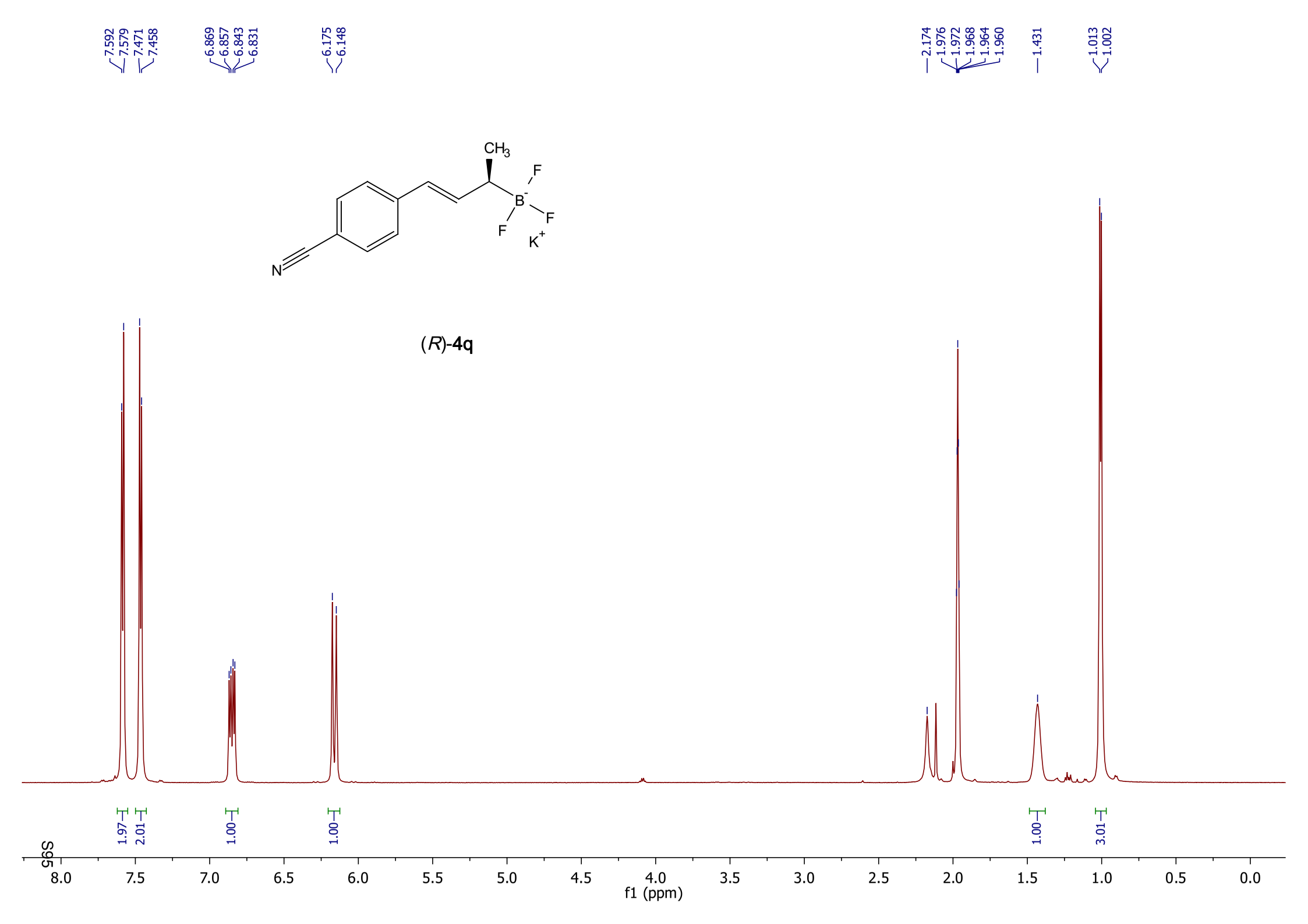
f1 (ppm)


7.593
7.590
7.582
7.579
7.473
7.469
7.462
7.459
6.866
6.854
6.840
6.828
6.179
6.177
6.153
6.150
2.180
1.976
1.972
1.968
1.964
1.960
1.440
1.427
1.416
1.014
1.002
CH3
F
B-
F
F
K+
N
(S)-4q
1.96
2.02
1.00
1.00
1.03
3.00
SG3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

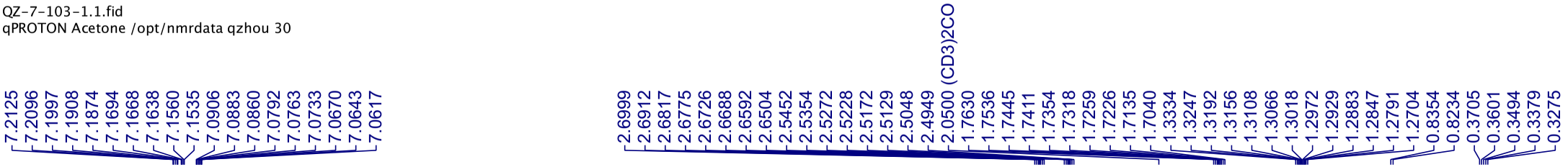

CH3
F
B-
F
F
K+
N

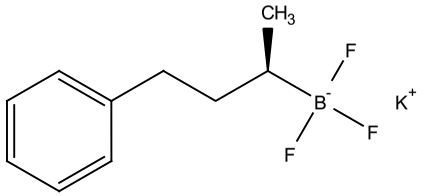
(*S*)-**4q**

148.81
145.78
133.24
126.43
121.71
120.34
118.26
108.51
14.72
1.68
1.55
1.53
1.41
1.27
1.13
0.99
0.86
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

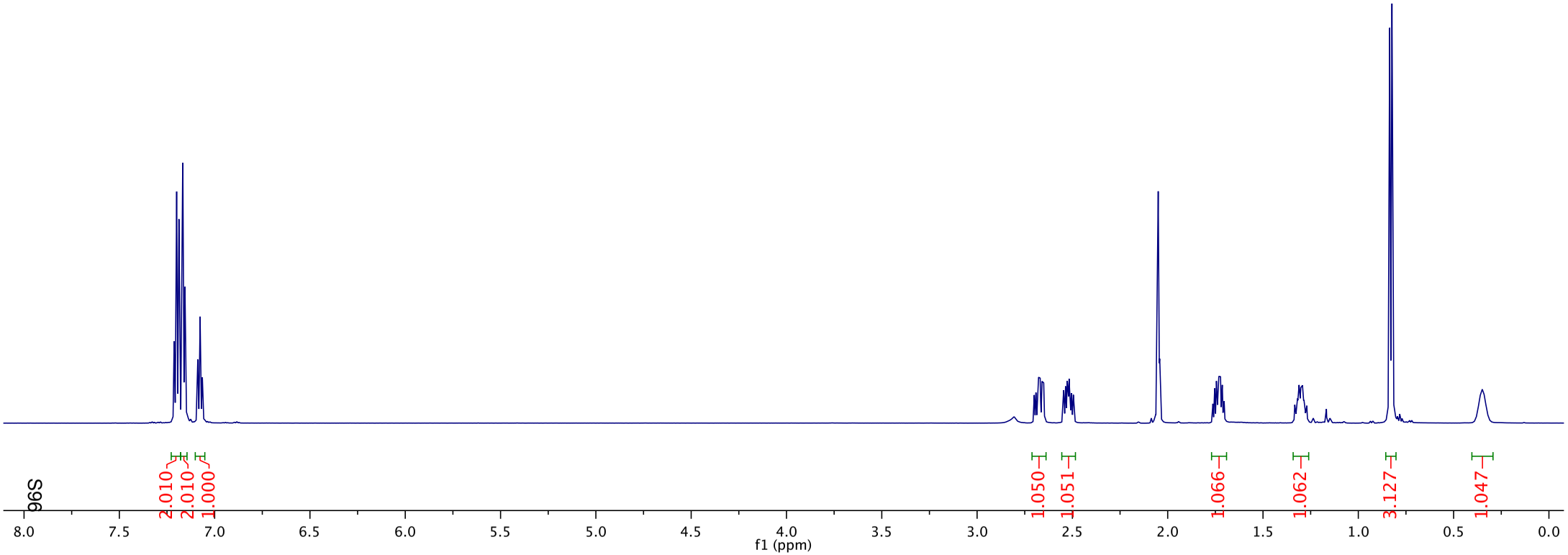

7.592
7.579
7.471
7.458
6.869
6.857
6.843
6.831
6.175
6.148
2.174
1.976
1.972
1.968
1.964
1.960
1.431
1.013
1.002
CH3
F
B-
F
F
K+
N
(R)-4q
1.97
2.01
1.00
1.00
1.00
3.01
S95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

QZ-7-103-1.1.fid
qPROTON Acetone /opt/nmrdata qzhou 30

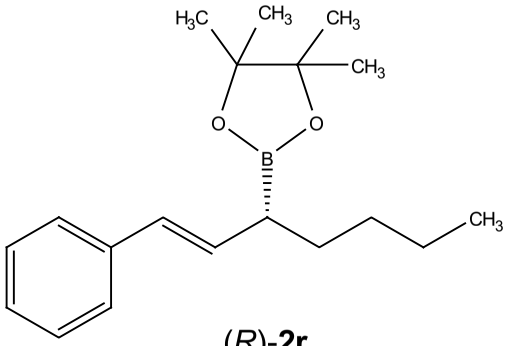




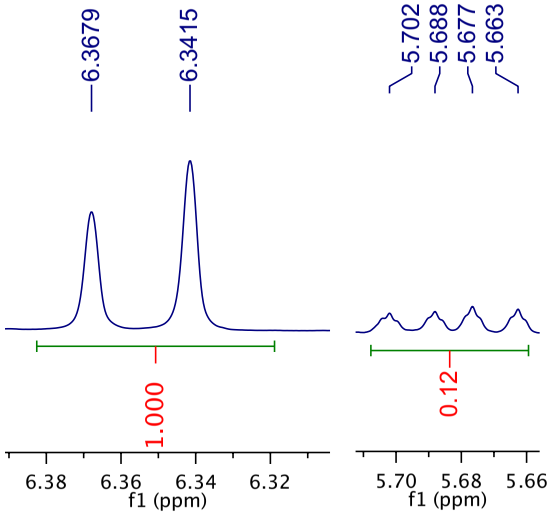
(*R*)-**7**



QZ-7-048-1
QZ-7-048-1
qPROTON CDCl3 /opt/nmrdata qzhou 17

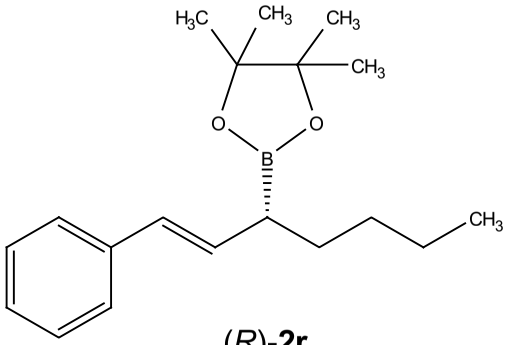


(*R*)-**2r**
via General Procedure B



QZ-7-048-1
QZ-7-048-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 17

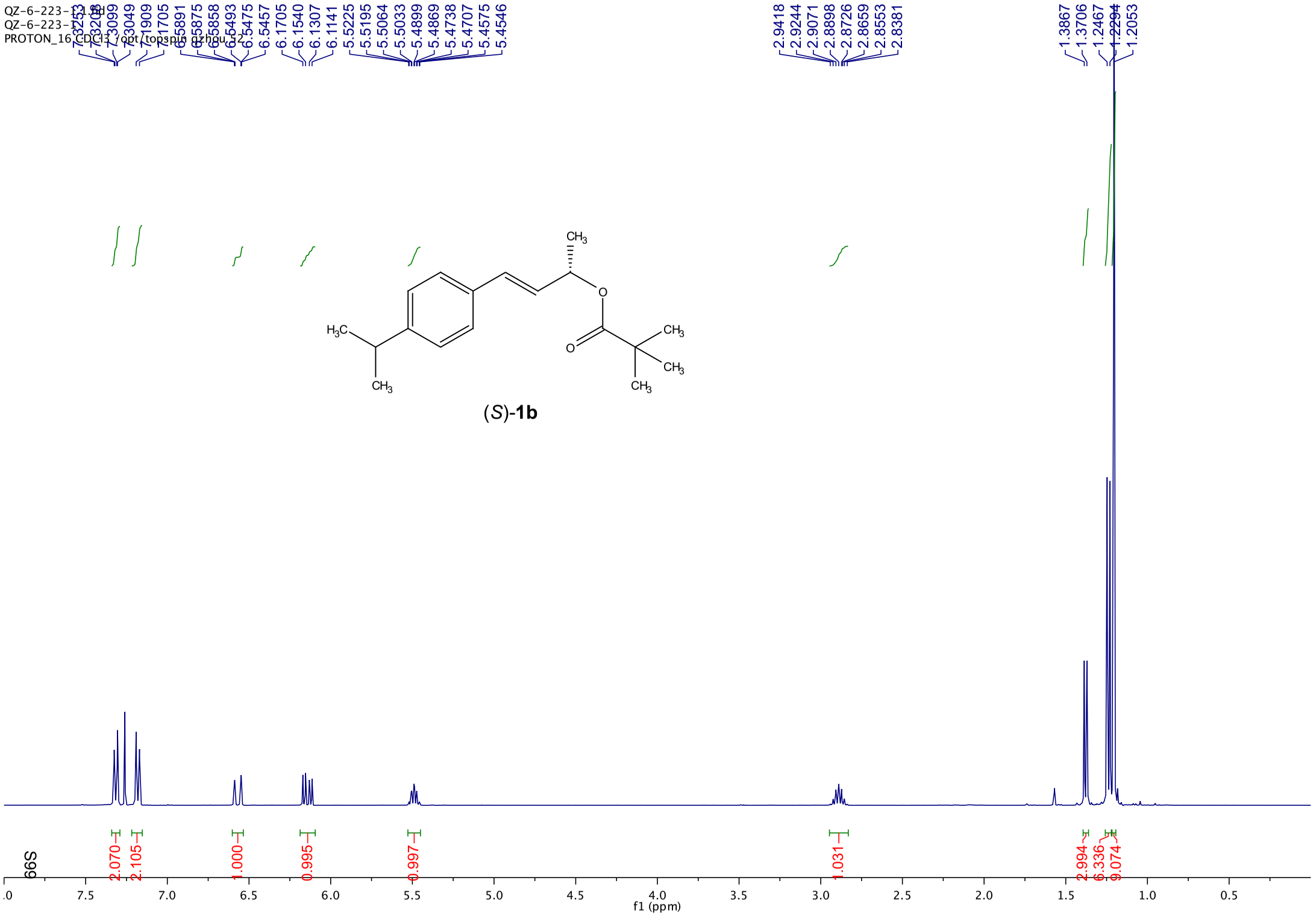
138.439
132.257
129.060
128.525
126.616
126.024
83.357
77.160 Chloroform-d
31.587
30.676
24.894
24.780
22.864
14.215



(*R*)-**2r**
via General Procedure B

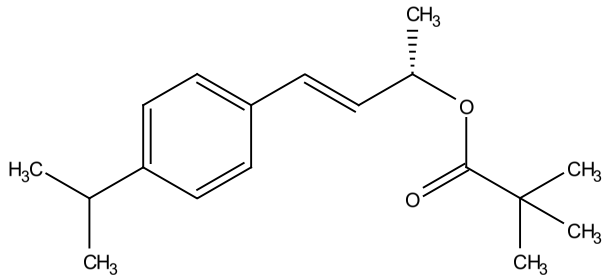
S98

f1 (ppm)


QZ-6-223-1.1fid
QZ-6-223-1
PROTON_16 CDCl3 /opt/topspin gzhou 32
7.3253
7.3206
7.3099
7.3049
7.1909
7.1705
6.5891
6.5875
6.5858
6.5493
6.5475
6.5457
6.1705
6.1540
6.1307
6.1141
5.5225
5.5195
5.5064
5.5033
5.4899
5.4869
5.4738
5.4707
5.4575
5.4546
2.9418
2.9244
2.9071
2.8898
2.8726
2.8659
2.8553
2.8381
1.3867
1.3706
1.2467
1.2294
1.2053
CH3
O
H3C
O
CH3
CH3
CH3
CH3
(S)-1b
2.070
2.105
1.000
0.995
0.997
1.031
2.994
6.336
9.074
S99
f1 (ppm)

QZ-6-223-1.2.fid
QZ-6-223-1
C13CPD1024 CDCl3 /opt/topspin qzhou 52

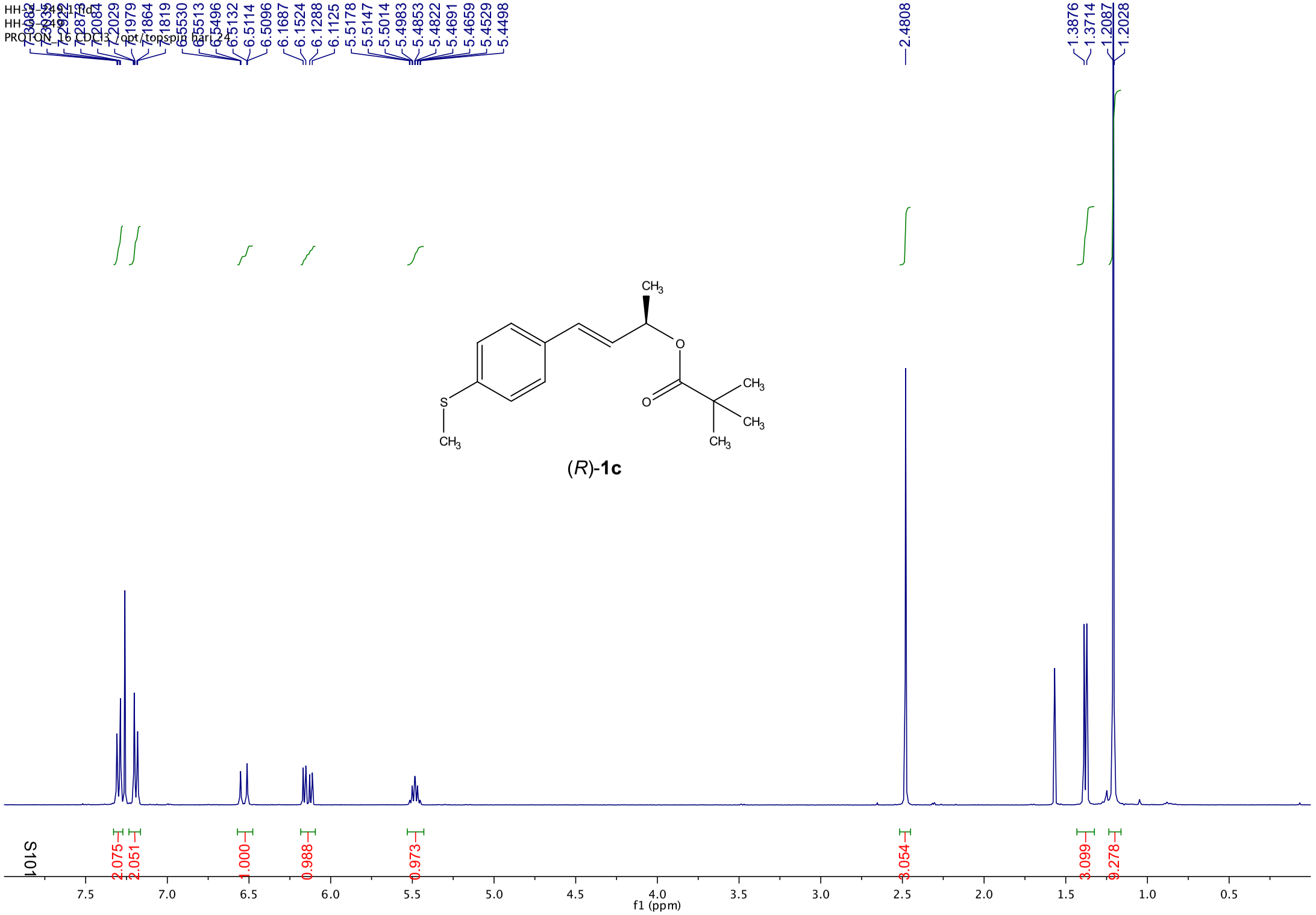
177.9066
148.8715
134.2168
131.1507
128.3327
126.7689
126.6558
70.7884
38.8947
34.0111
27.2852
24.0840
20.4866



(*S*)-**1b**

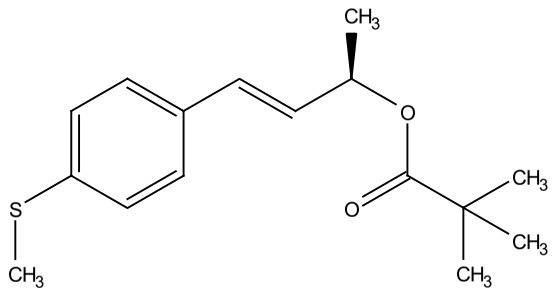
S100

f1 (ppm)


HH-3-349-1H
HH-3-349
PROTON_16 CDCl3 /opt/topspin3 par 24
7.3082
7.3035
7.2942
7.2873
7.2084
7.2029
7.1979
7.1864
7.1819
6.5530
6.5513
6.5496
6.5132
6.5114
6.5096
6.1687
6.1524
6.1288
6.1125
5.5178
5.5147
5.5014
5.4983
5.4853
5.4822
5.4691
5.4659
5.4529
5.4498
2.4808
1.3876
1.3714
1.2087
1.2028
CH3
O
O
CH3
CH3
CH3
S
CH3
(R)-1c
2.075
2.051
1.000
0.988
0.973
3.054
3.099
9.278
S101
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

HH-5-249.2.fid
HH-5-249
C13CPD1024 CDCl3 /opt/topspin hari 24

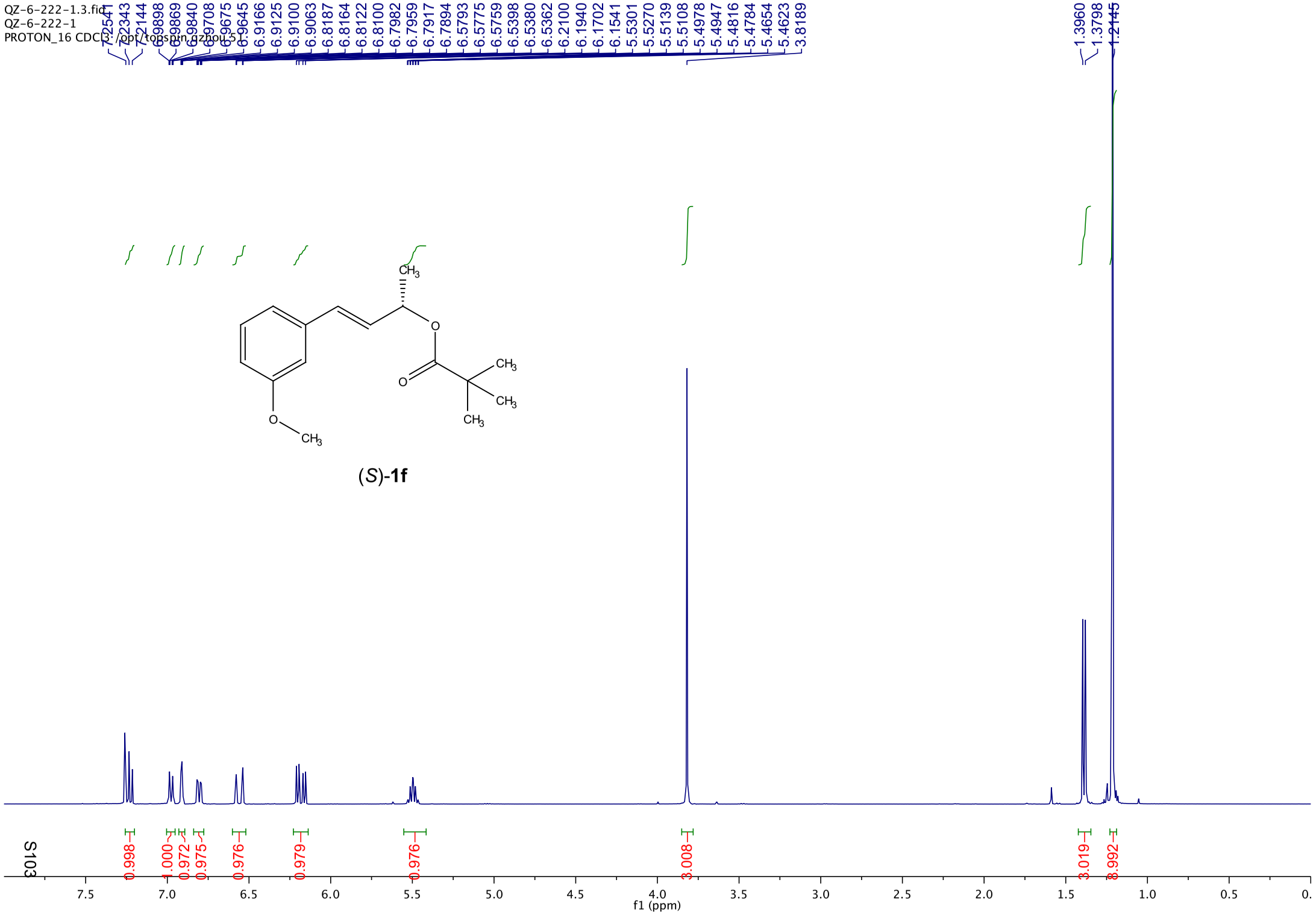
177.9226
138.1841
133.5038
130.5760
128.6320
127.0736
126.6418
70.6815
38.9110
27.2859
20.4525
15.9226



(*R*)-**1c**

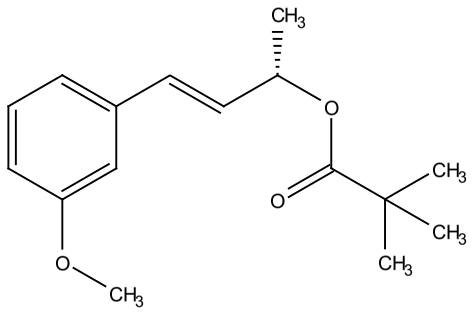
S102

f1 (ppm)


QZ-6-222-1.3.fid
QZ-6-222-1
PROTON_16 CDCl3 /opt/topspin_qzhou_5
7.2541
7.2343
7.2144
6.9898
6.9869
6.9840
6.9708
6.9675
6.9645
6.9166
6.9125
6.9100
6.9063
6.8187
6.8164
6.8122
6.8100
6.7982
6.7959
6.7917
6.7894
6.5793
6.5775
6.5759
6.5398
6.5380
6.5362
6.2100
6.1940
6.1702
6.1541
5.5301
5.5270
5.5139
5.5108
5.4978
5.4947
5.4816
5.4784
5.4654
5.4623
3.8189
1.3960
1.3798
1.2145
CH3
O
O
CH3
CH3
CH3
O
CH3
(S)-1f
0.998
1.000
0.972
0.975
0.976
0.979
0.976
3.008
3.019
8.992
S103
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

QZ-6-222-1.2.fid
QZ-6-222-1
C13CPD1024 CDCl3 /opt/topspin qzhou 51

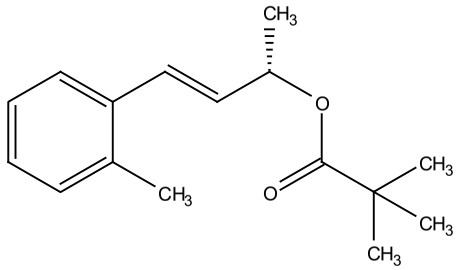
177.8941
159.8788
138.0492
131.0372
129.6756
129.5688
119.3215
113.5999
111.9016
70.5687
55.3714
38.9069
27.2846
20.4305



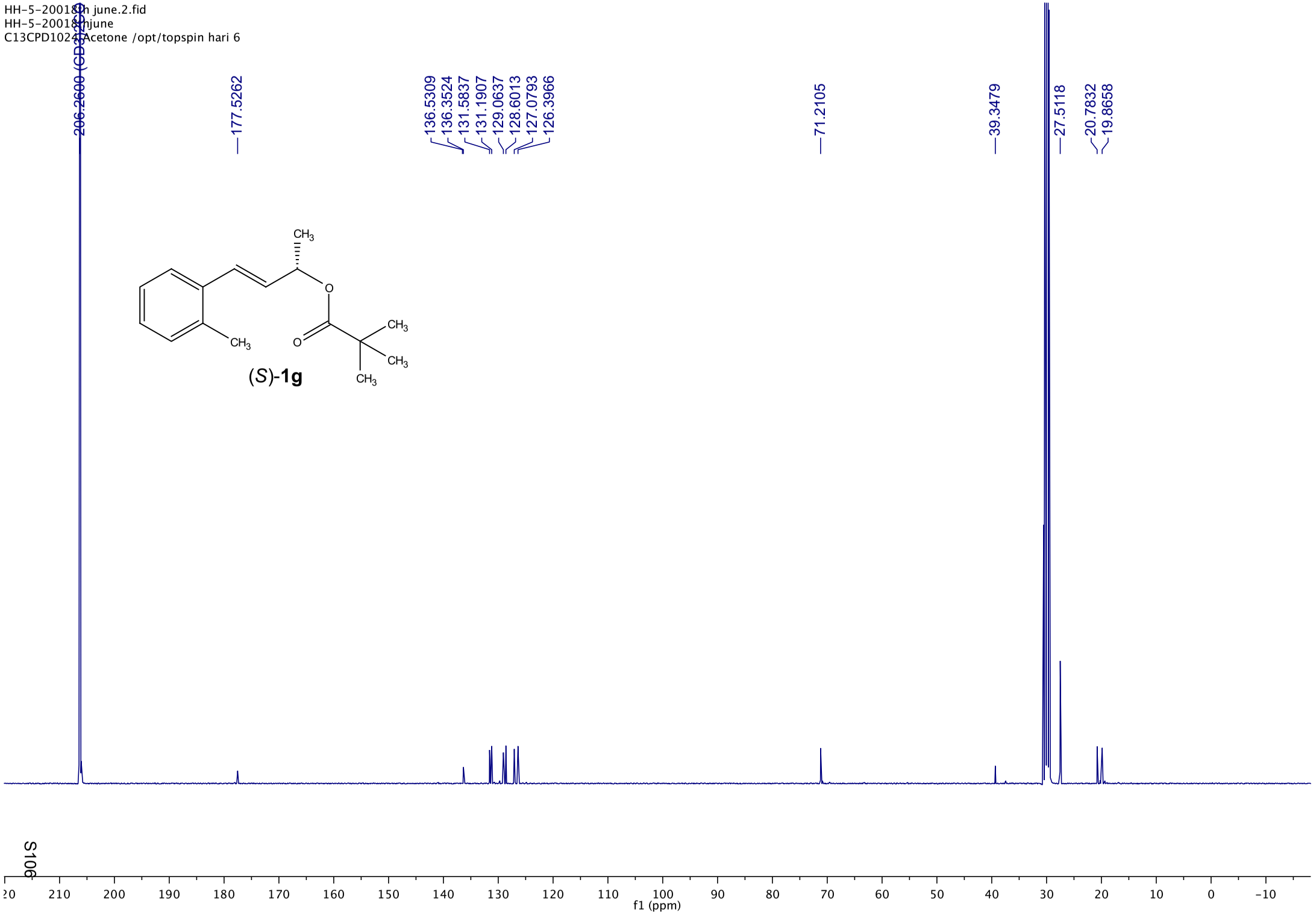
(*S*)-**1f**

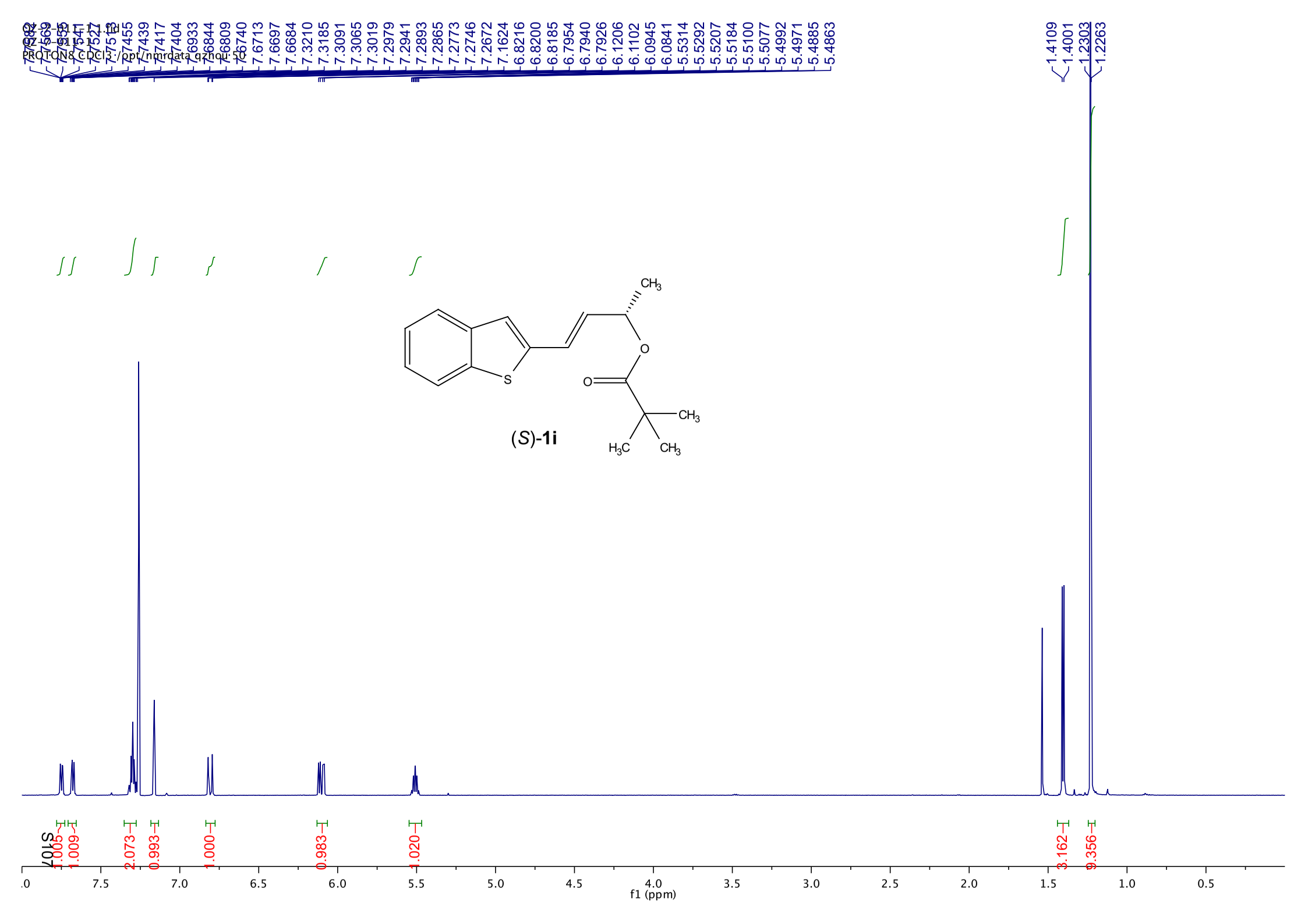
f1 (ppm)

HH-5-20018th june.1.fid
HH-5-20018thjune
PROTON_16 Acetone /opt/topspin hari 6

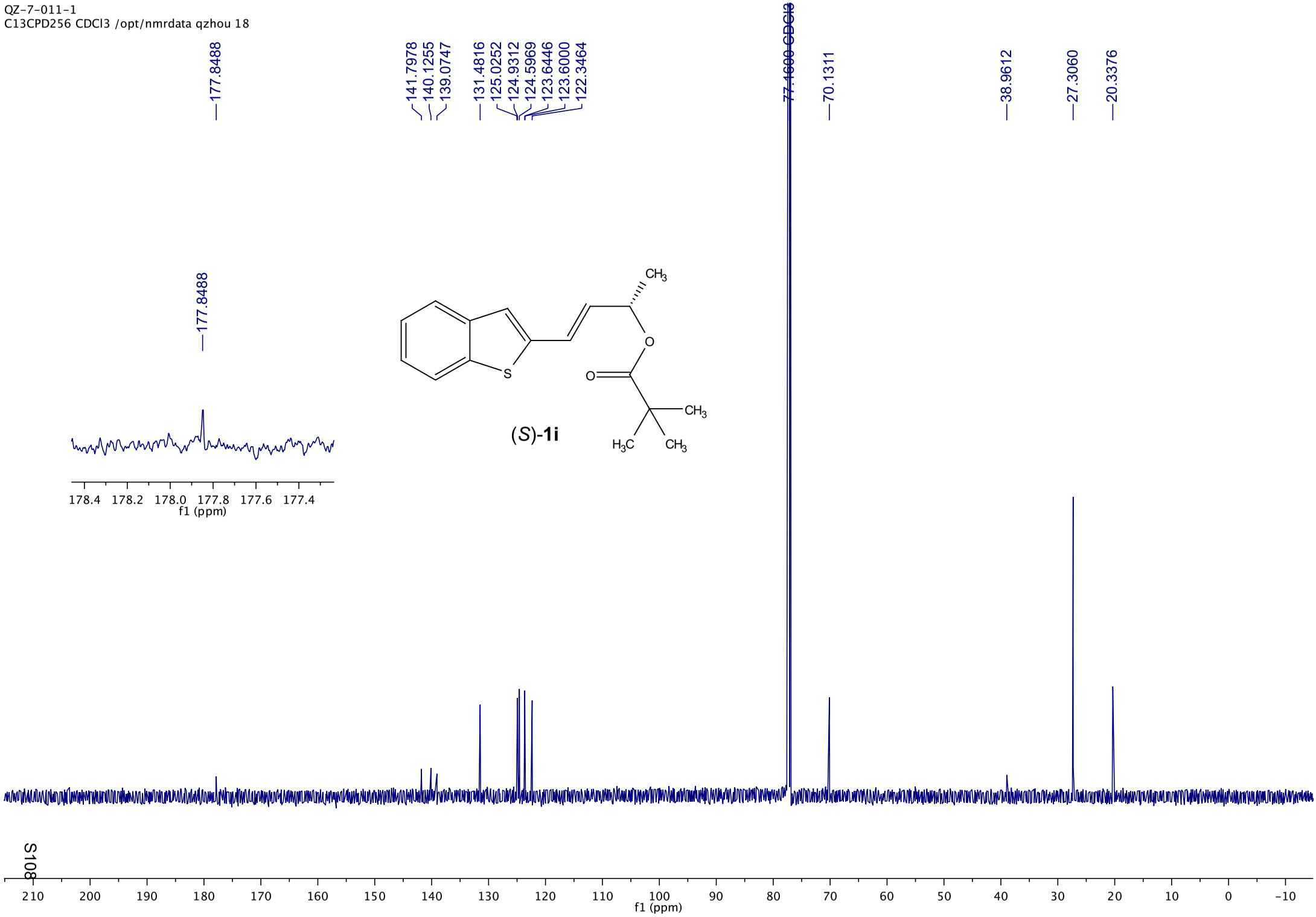


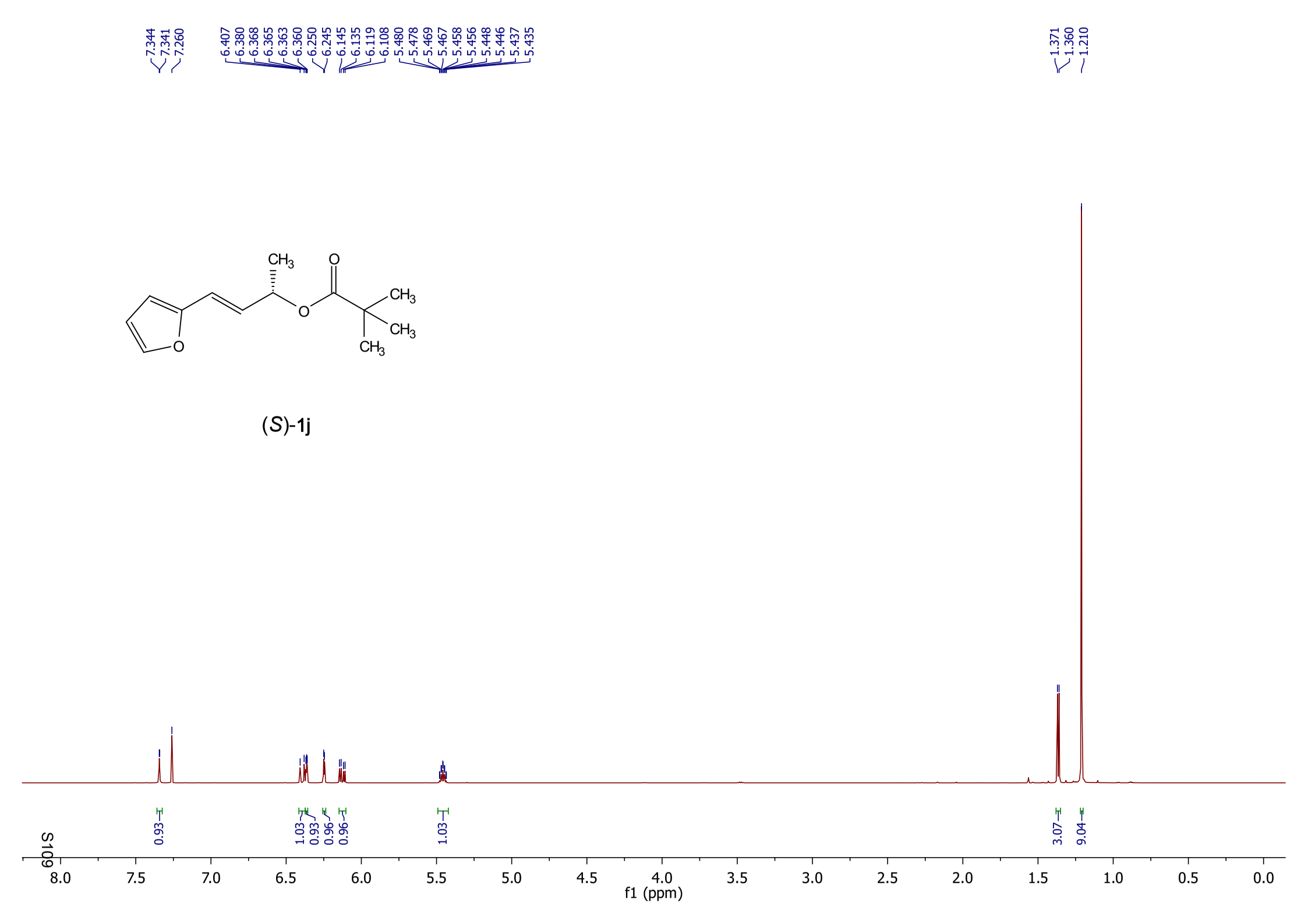
(*S*)-**1g**

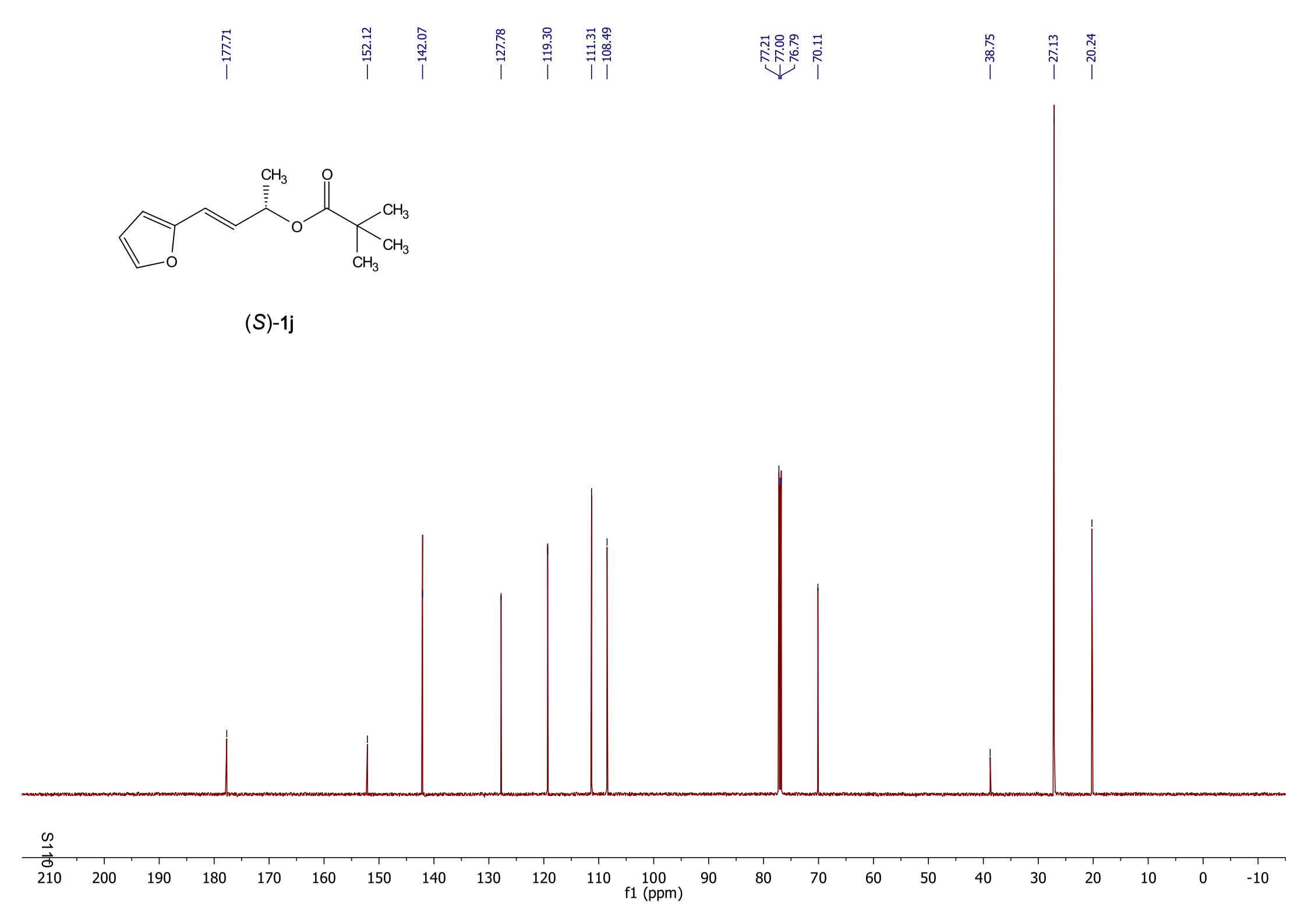

HH-5-20018th june.2.fid
HH-5-20018thjune
C13CPD1024 Acetone /opt/topspin hari 6
206.2600 (CD3)2CO
177.5262
136.5309
136.3524
131.5837
131.1907
129.0637
128.6013
127.0793
126.3966
71.2105
39.3479
27.5118
20.7832
19.8658
(S)-1g
S106
f1 (ppm)

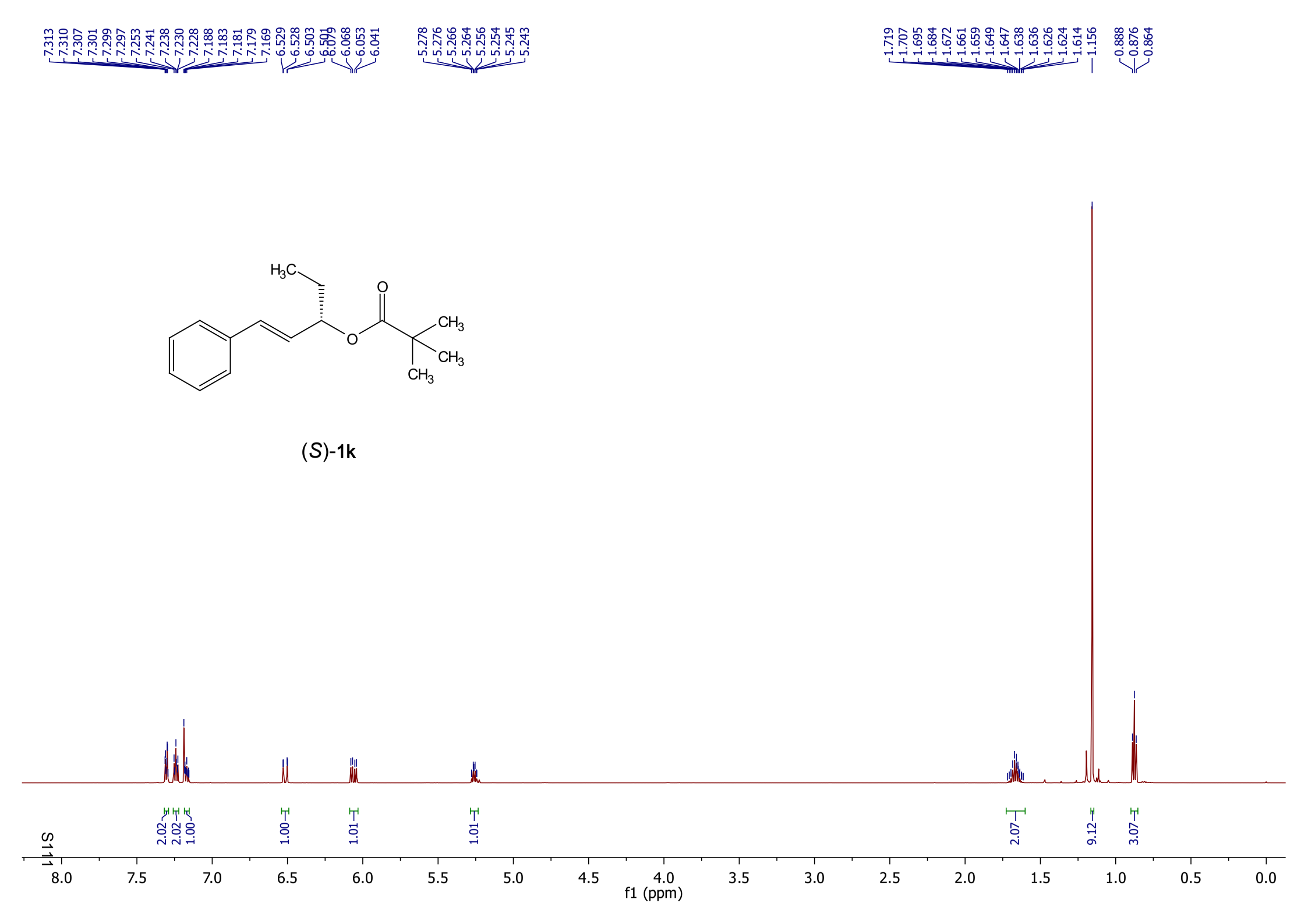

QZ-5-01-1.1fid
QZ-5-01-1
PROTON8 CDCl3 /opt/mnrdata qznoe 5
7.7682
7.7669
7.7541
7.7527
7.7513
7.7455
7.7439
7.7417
7.7404
7.6933
7.6844
7.6809
7.6740
7.6713
7.6697
7.6684
7.3210
7.3185
7.3091
7.3065
7.3019
7.2979
7.2941
7.2893
7.2865
7.2773
7.2746
7.2672
7.1624
6.8216
6.8200
6.8185
6.7954
6.7940
6.7926
6.1206
6.1102
6.0945
6.0841
5.5314
5.5292
5.5207
5.5184
5.5100
5.5077
5.4992
5.4971
5.4885
5.4863
1.4109
1.4001
1.2303
1.2263
(S)-1i
1.005
1.009
2.073
0.993
1.000
0.983
1.020
3.162
9.356
S107
f1 (ppm)

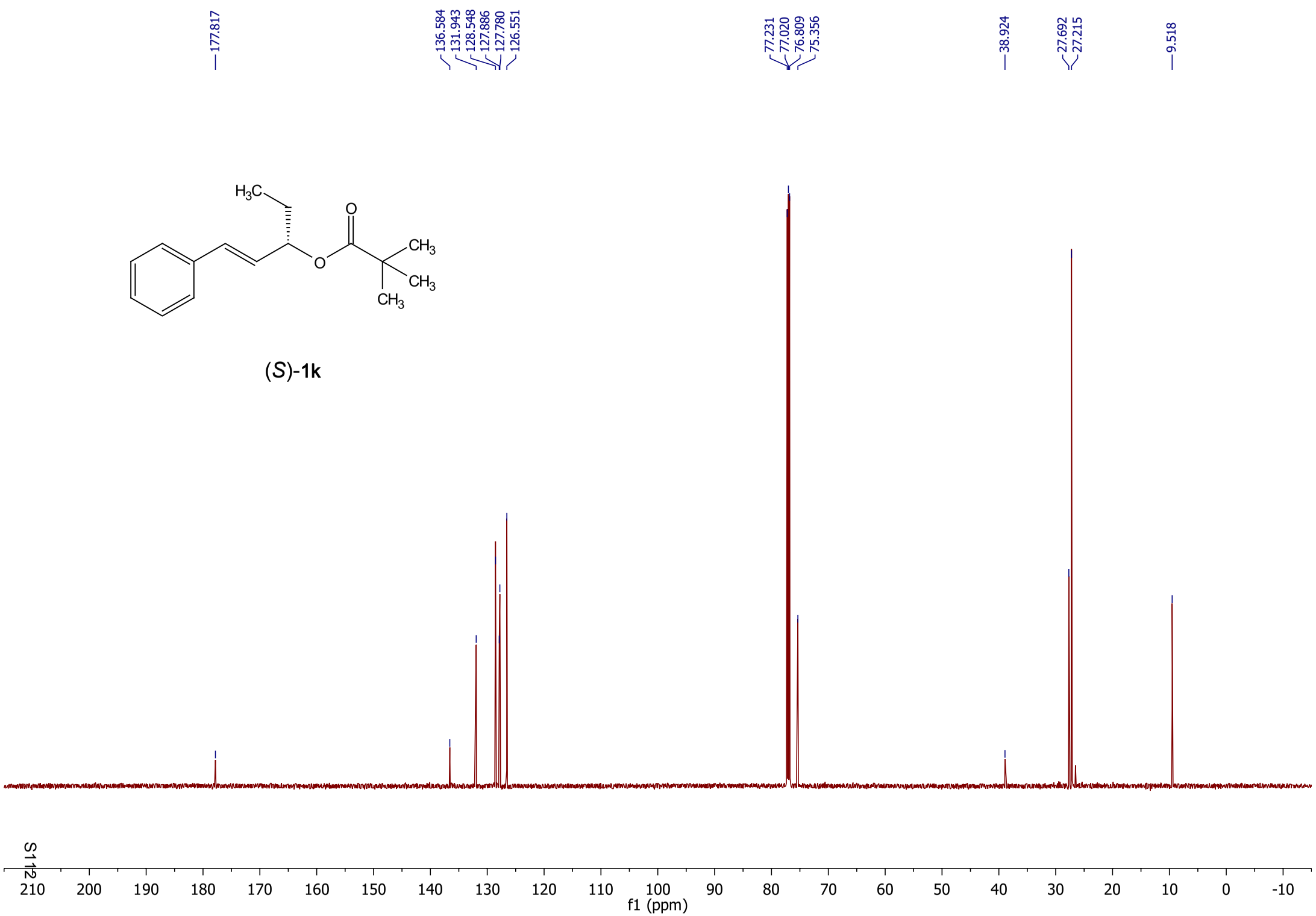
QZ-7-011-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 18

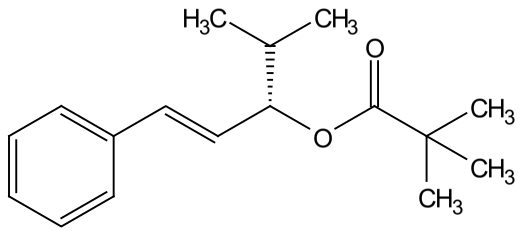



7.344
7.341
7.260
6.407
6.380
6.368
6.365
6.363
6.360
6.250
6.245
6.145
6.135
6.119
6.108
5.480
5.478
5.469
5.467
5.458
5.456
5.448
5.446
5.437
5.435
1.371
1.360
1.210
CH3
O
O
CH3
CH3
CH3
O
(S)-1j
0.93
1.03
0.93
0.96
0.96
1.03
3.07
9.04
S109
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

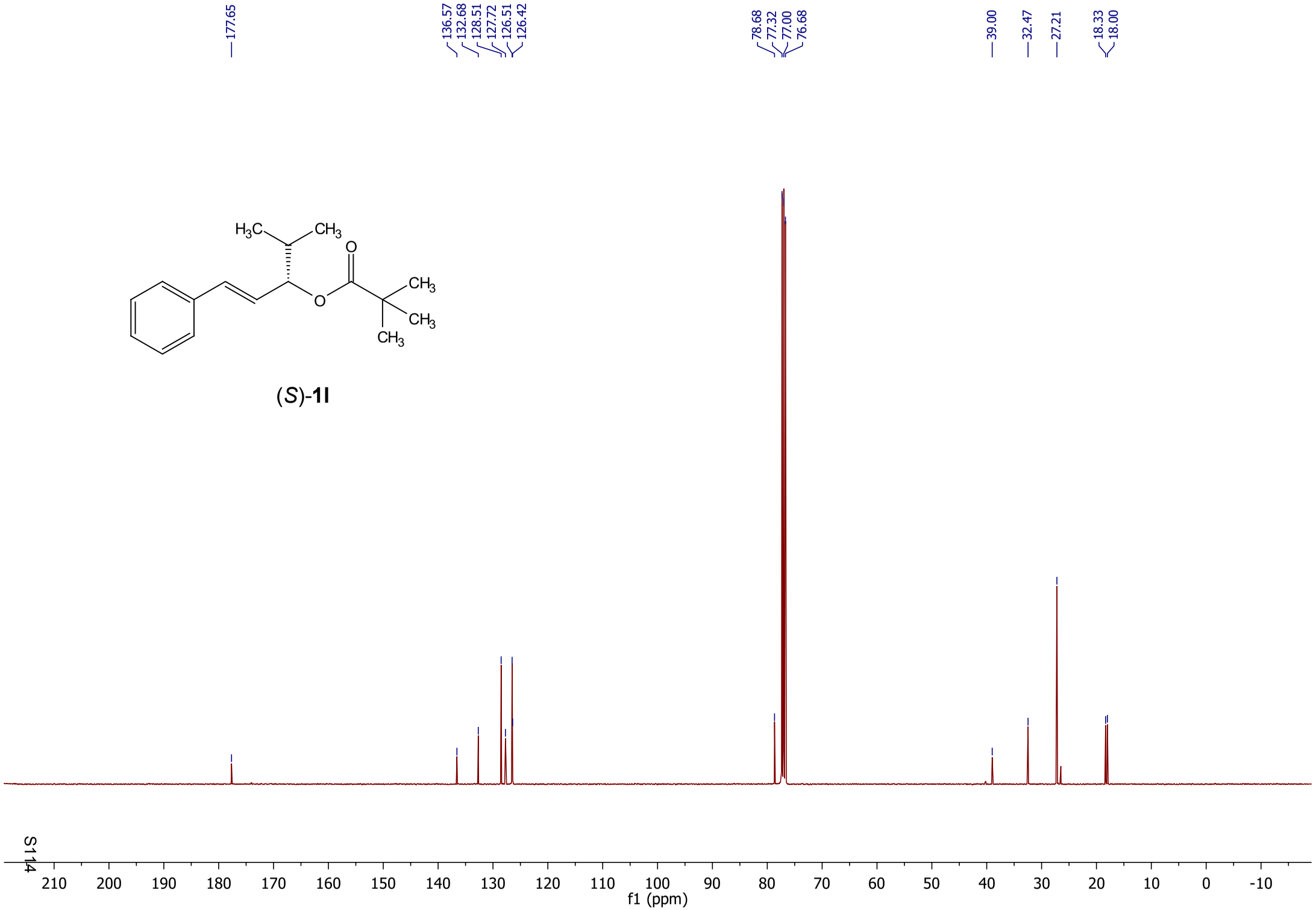

177.71
152.12
142.07
127.78
119.30
111.31
108.49
77.21
77.00
76.79
70.11
38.75
27.13
20.24
CH3
O
CH3
CH3
CH3
O
(S)-1j
S110
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

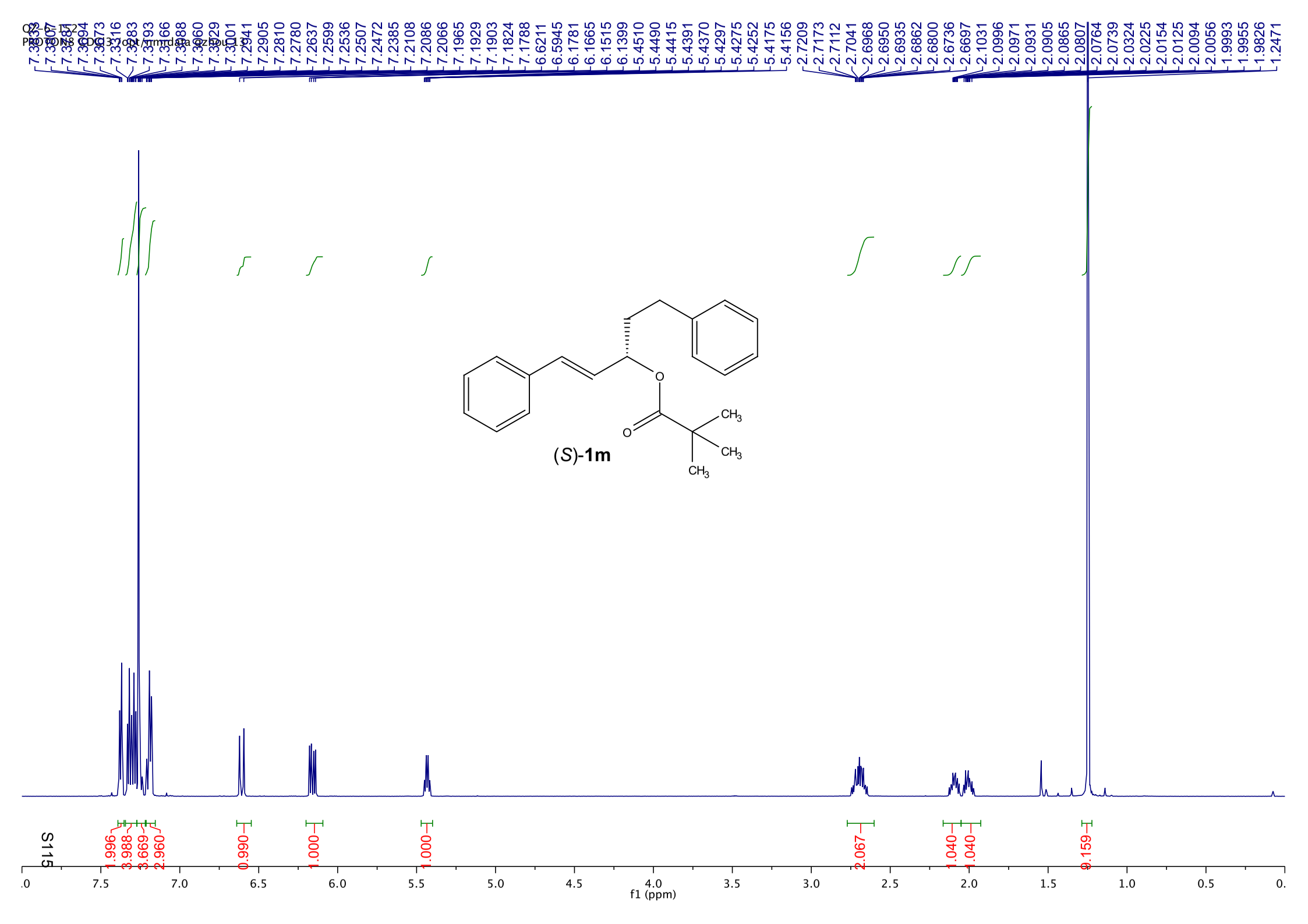

7.313
7.310
7.307
7.301
7.299
7.297
7.253
7.241
7.238
7.230
7.228
7.188
7.183
7.181
7.179
7.169
6.529
6.528
6.503
6.501
6.079
6.068
6.053
6.041
5.278
5.276
5.266
5.264
5.256
5.254
5.245
5.243
1.719
1.707
1.695
1.684
1.672
1.661
1.659
1.649
1.647
1.638
1.636
1.626
1.624
1.614
1.156
0.888
0.876
0.864
H3C
O
O
CH3
CH3
CH3
(S)-1k
2.02
2.02
1.00
1.00
1.01
1.01
2.07
9.12
3.07
S11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.817
136.584
131.943
128.548
127.886
127.780
126.551
77.231
77.020
76.809
75.356
38.924
27.692
27.215
9.518
H3C
O
O
CH3
CH3
CH3
(S)-1k
S112
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



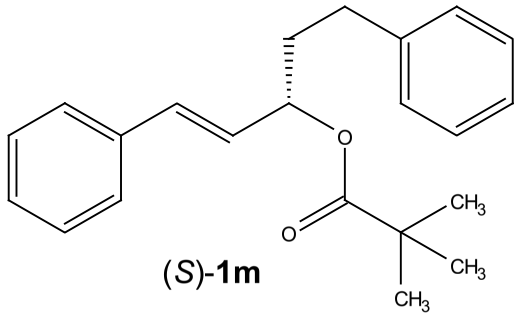
(*S*)-1l


177.65
136.57
132.68
128.51
127.72
126.51
126.42
78.68
77.32
77.00
76.68
39.00
32.47
27.21
18.33
18.00
H3C
CH3
O
O
CH3
CH3
CH3
(S)-1l
S114
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


(S)-1m
f1 (ppm)

QZ-6-157
C13CPD256 CDCl3 /opt/nmrdata qzhou 13

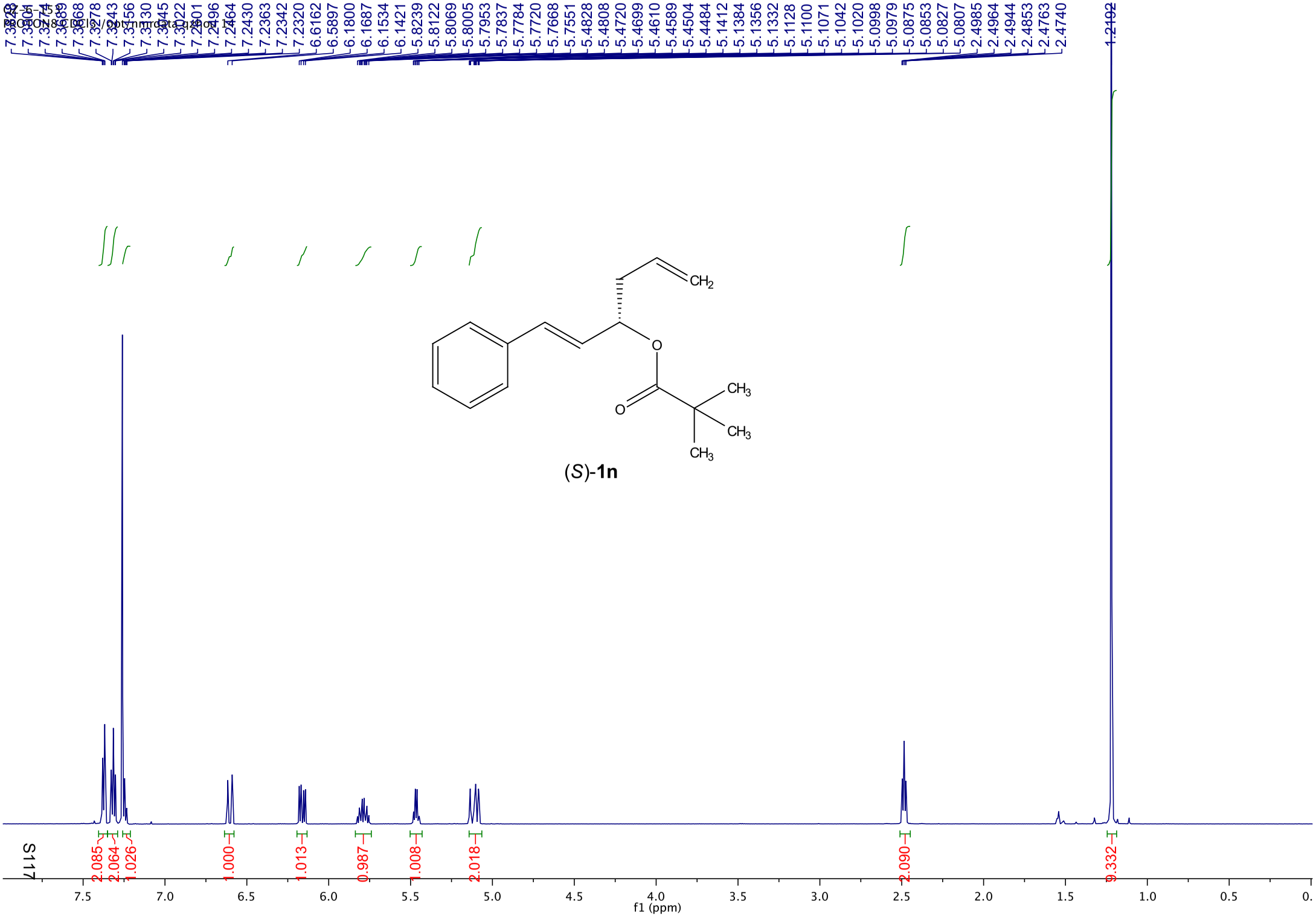
177.8587
141.5320
136.5819
132.4358
128.7064
128.6171
128.5074
128.0248
127.8020
126.7230
126.1478
73.8324
39.0815
36.5183
31.6806
27.3701



(*S*)-**1m**

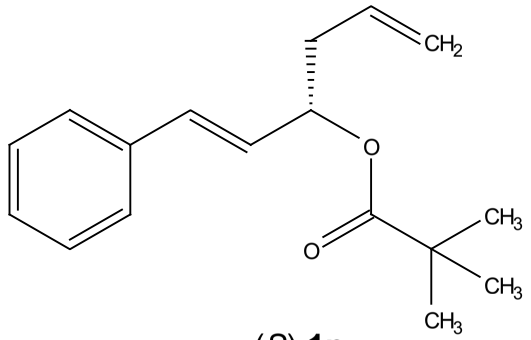
S116

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

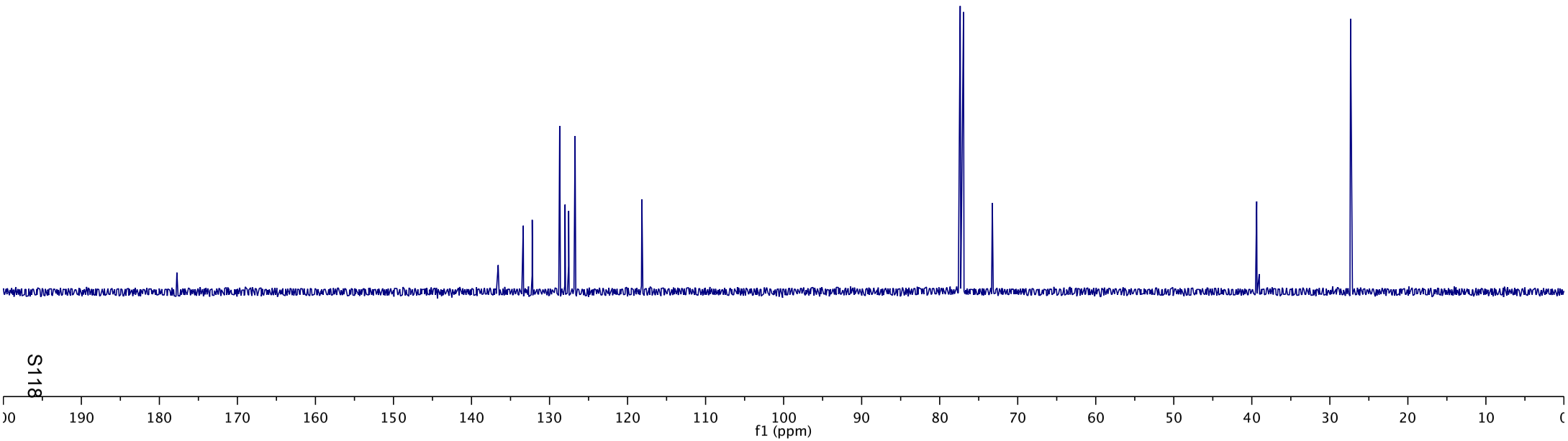

CH2
O
O
CH3
CH3
CH3
(S)-1n
f1 (ppm)

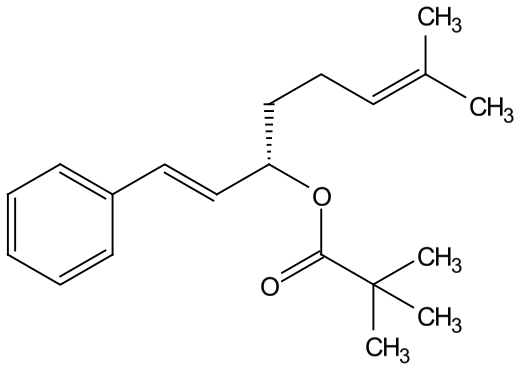
QZ-6-153
C13CPD256 CDCl3 /opt/nmrdata qzhou 14

177.7567
136.5824
133.3678
132.2199
128.7008
128.0101
127.5487
126.7274
118.1658
73.2527
39.3736
39.0437
27.3454

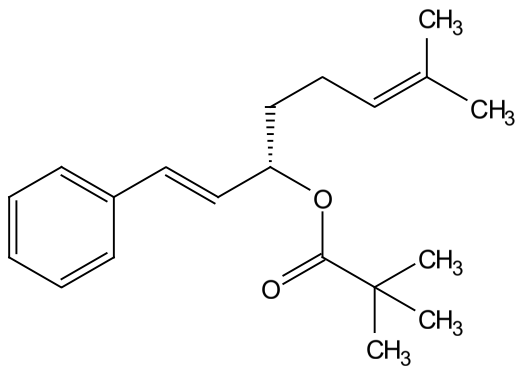


(*S*)-**1n**



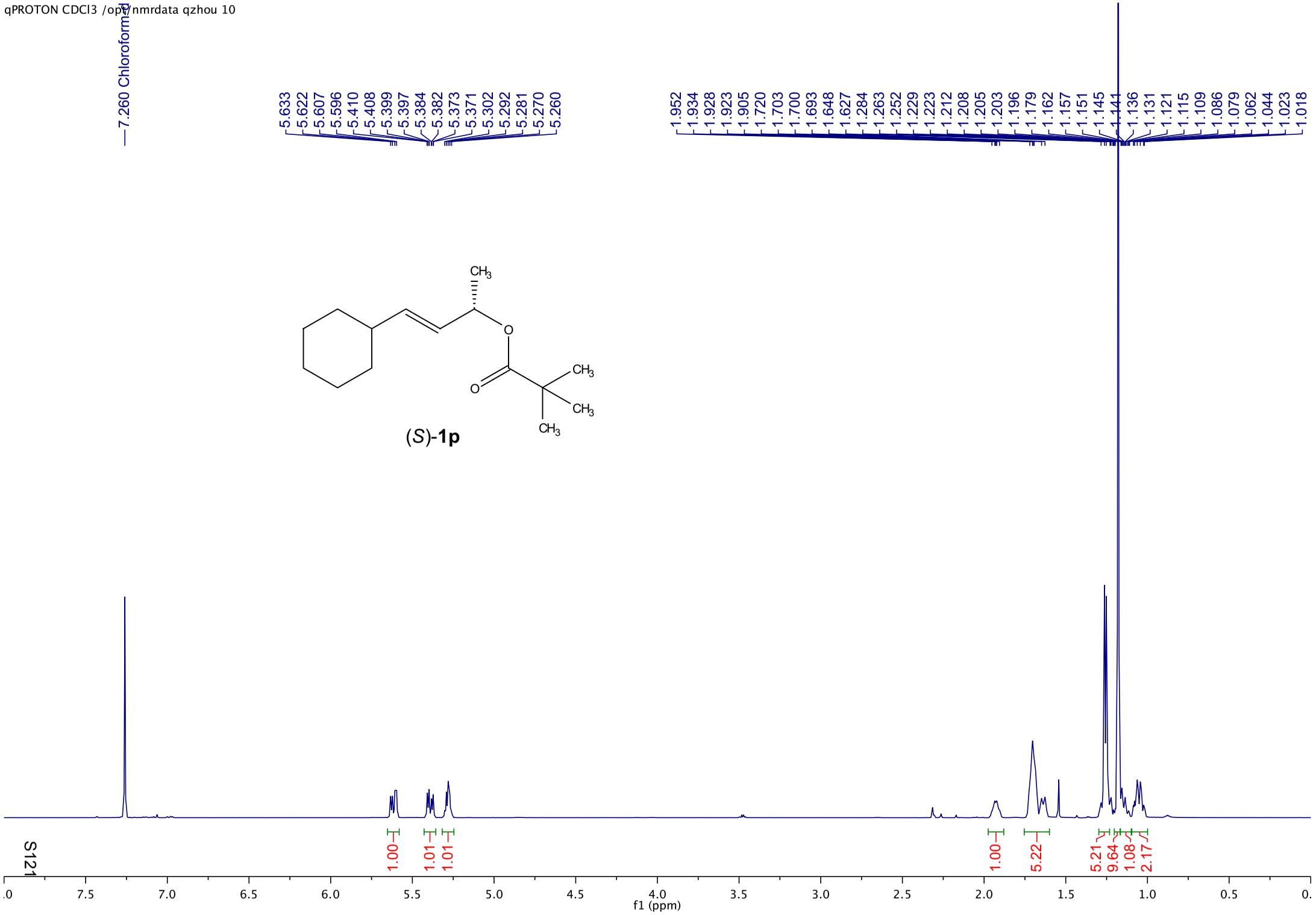


(*S*)-**1o**


CH3
CH3
O
O
CH3
CH3
CH3

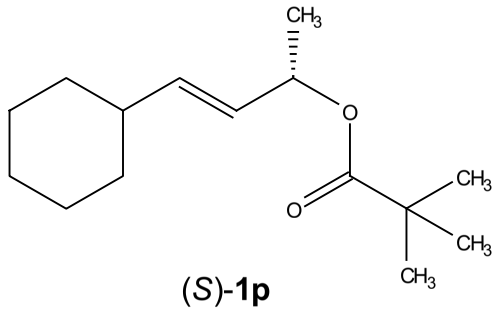
(*S*)-**1o**

177.71
136.57
132.31
131.90
128.52
128.00
127.75
126.53
123.36
77.21
77.00
76.79
73.84
38.88
34.71
27.19
25.70
23.78
17.66
S120
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

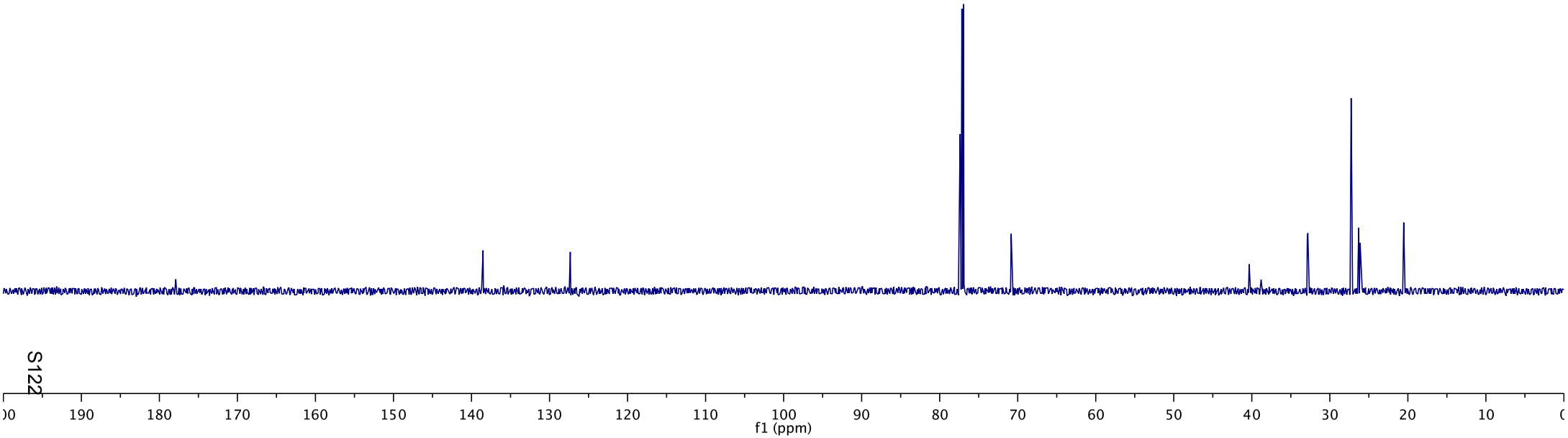

qPROTON CDCl3 /opt/nmrdata qzhou 10
7.260 Chloroform-d
5.633
5.622
5.607
5.596
5.410
5.408
5.399
5.397
5.384
5.382
5.373
5.371
5.302
5.292
5.281
5.270
5.260
1.952
1.934
1.928
1.923
1.905
1.720
1.703
1.700
1.693
1.648
1.627
1.284
1.263
1.252
1.229
1.223
1.212
1.208
1.205
1.203
1.196
1.179
1.162
1.157
1.151
1.145
1.141
1.136
1.131
1.121
1.115
1.109
1.086
1.079
1.062
1.044
1.023
1.018
CH3
O
O
CH3
CH3
CH3
(S)-1p
1.00
1.01
1.01
1.00
5.22
5.21
9.64
1.08
2.17
S121
f1 (ppm)

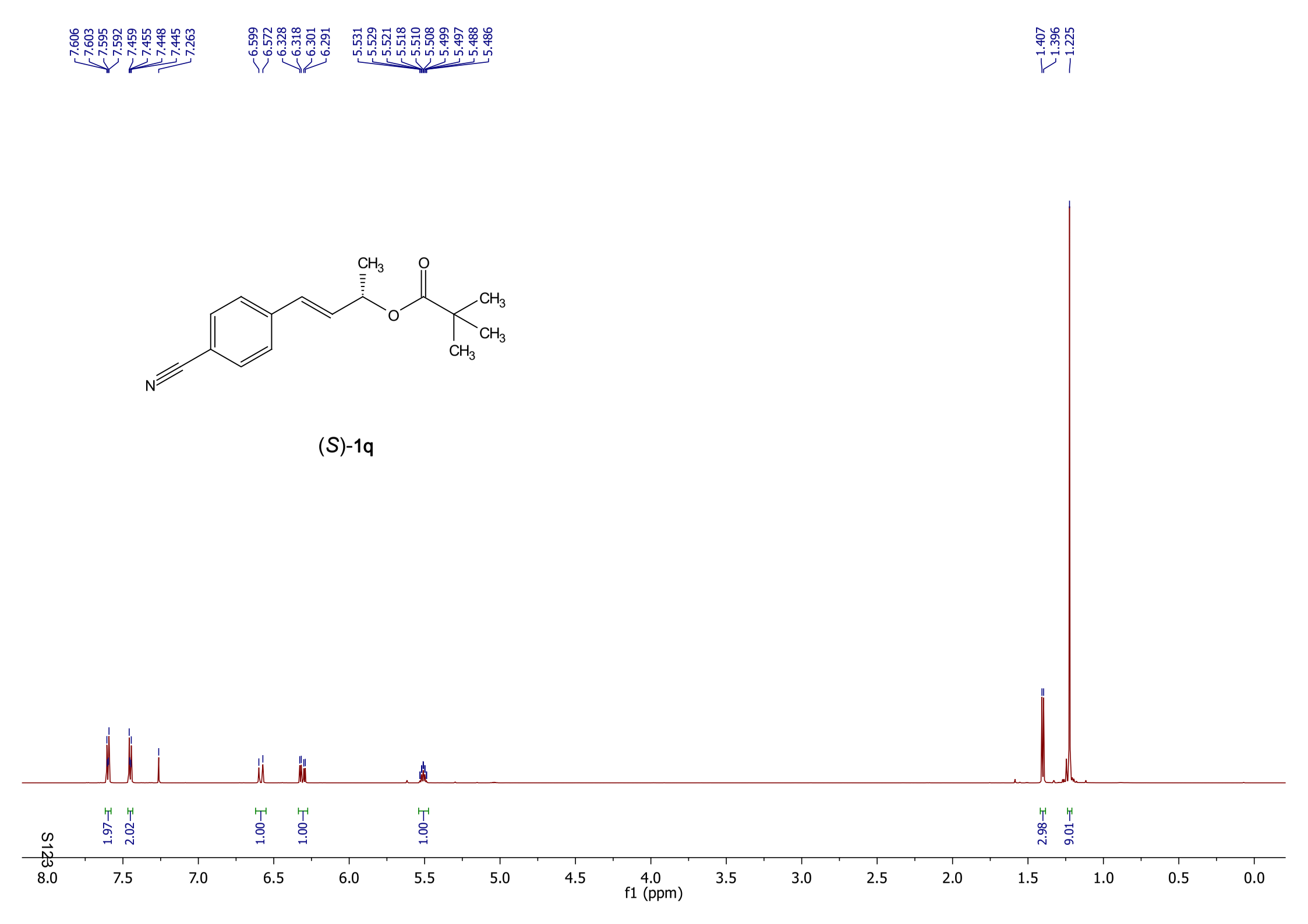
C13CPD256 CDCl3 /opt/nmrdata qzhou 10

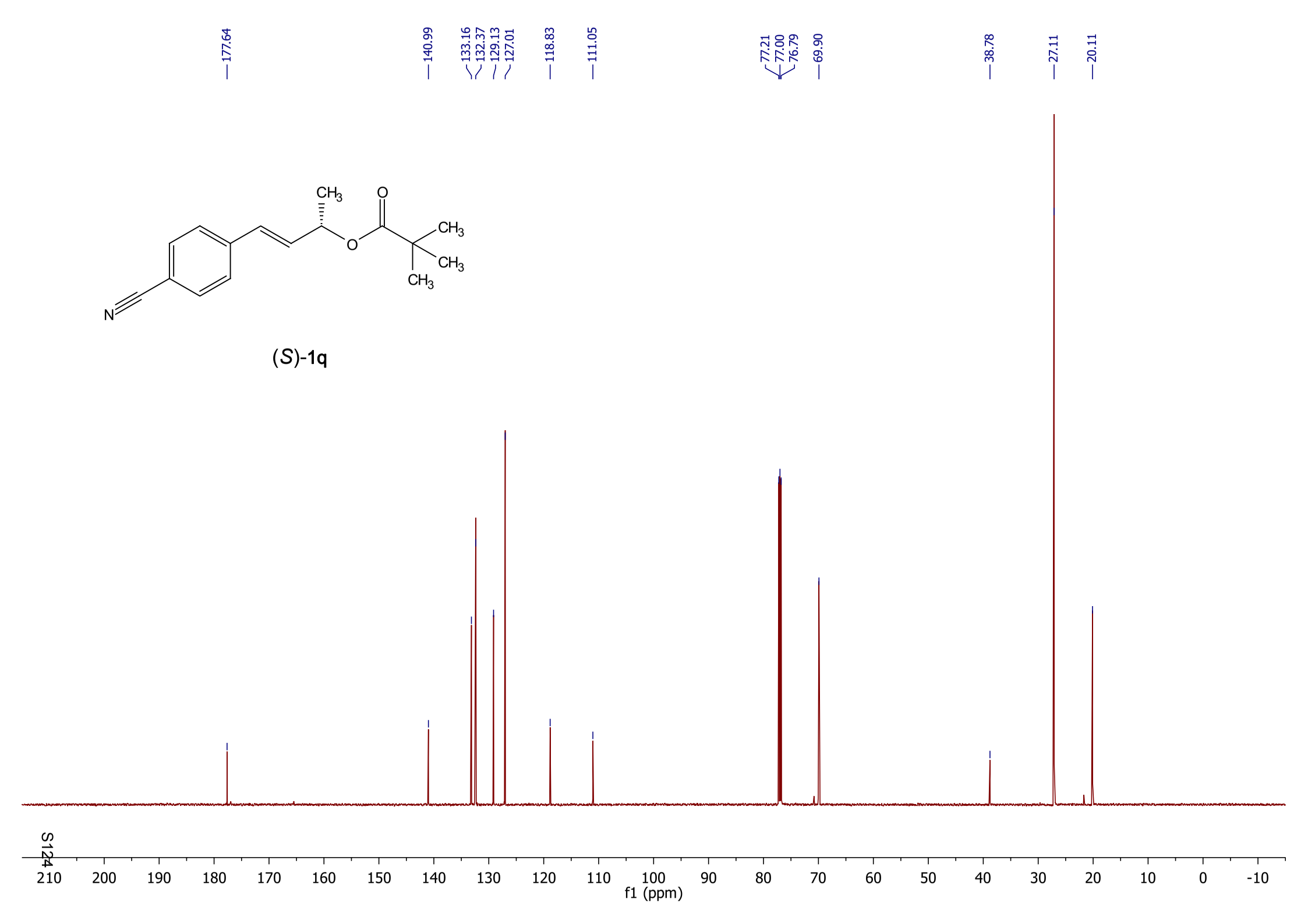
177.8957
138.5203
127.3409
77.1600 Chloroform-d
70.8384
40.3417
32.8952
32.8229
27.2712
26.3009
26.1195
20.5329

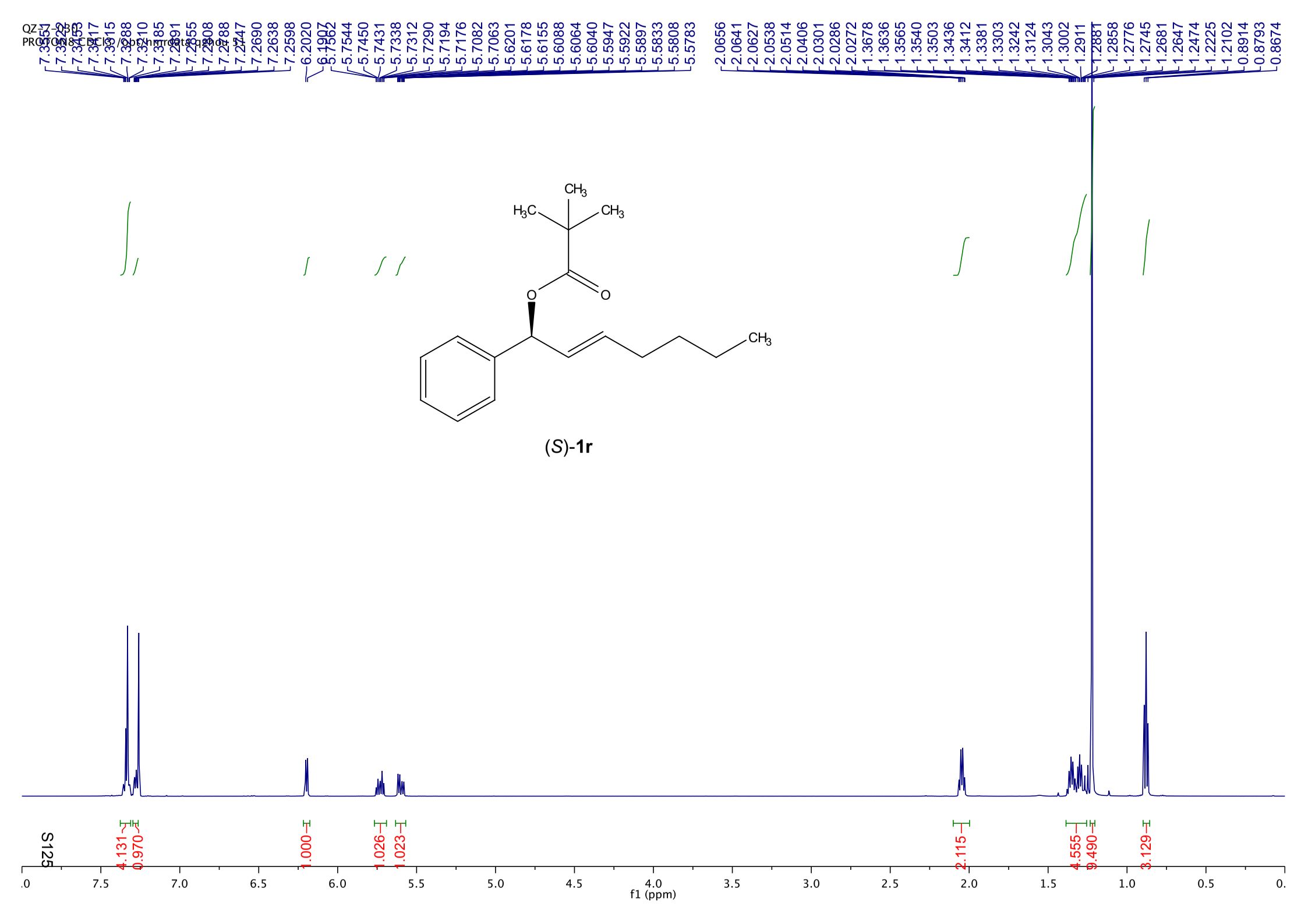


(*S*)-**1p**



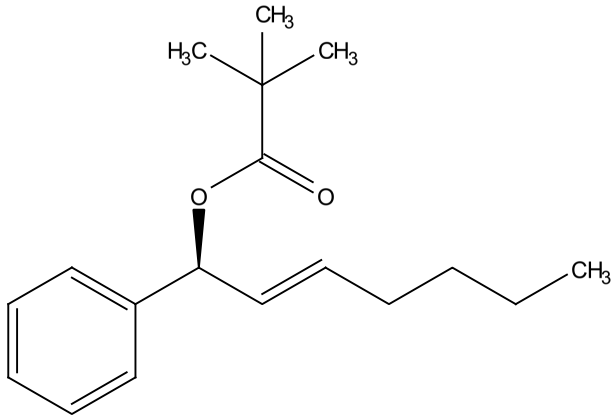

7.606
7.603
7.595
7.592
7.459
7.455
7.448
7.445
7.263
6.599
6.572
6.328
6.318
6.301
6.291
5.531
5.529
5.521
5.518
5.510
5.508
5.499
5.497
5.488
5.486
1.407
1.396
1.225
CH3
O
O
CH3
CH3
CH3
N
(S)-1q
1.97
2.02
1.00
1.00
1.00
2.98
9.01
S123
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.64
140.99
133.16
132.37
129.13
127.01
118.83
111.05
77.21
77.00
76.79
69.90
38.78
27.11
20.11
CH3
O
CH3
CH3
CH3
O
N
(S)-1q
S124
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

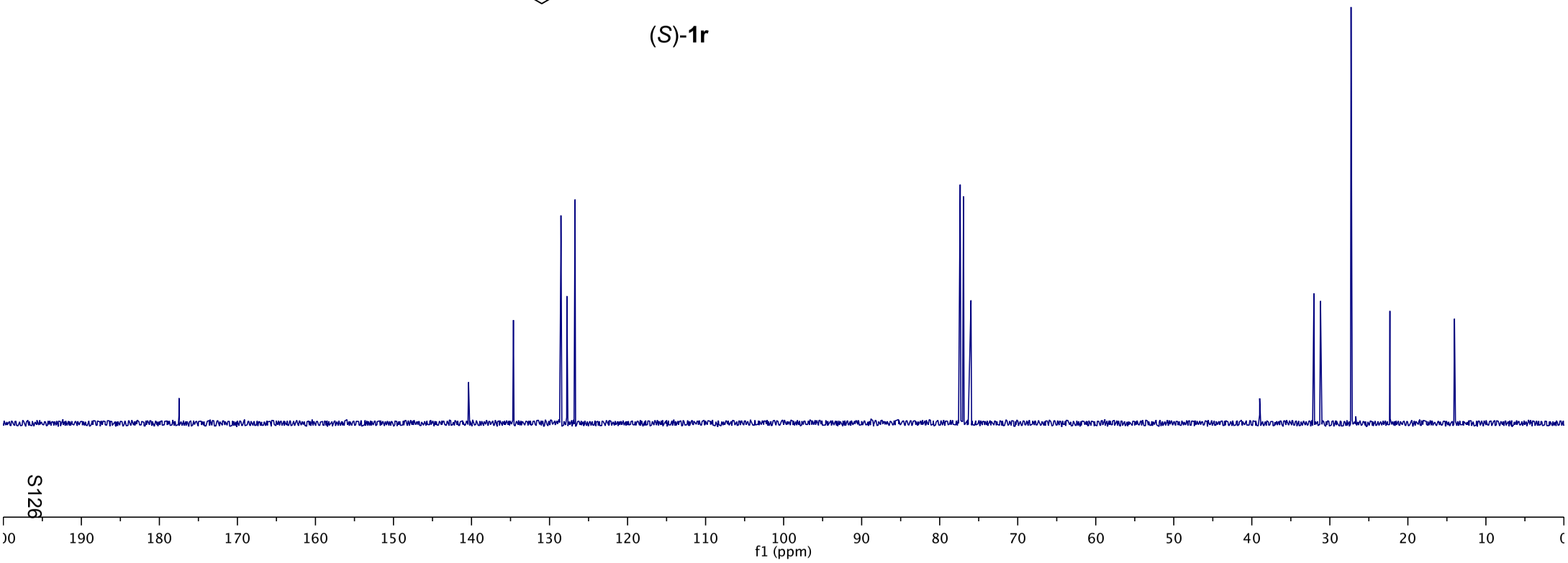

QZ-7-030
PROTON8 CDCl3 /Opt/nmrdata/qzhou 51
CH3
H3C
CH3
O
O
CH3
(S)-1r
4.131
0.970
1.000
1.026
1.023
2.115
4.555
0.490
3.129
f1 (ppm)

QZ-7-030
C13CPD256 CDCl3 /opt/nmrdata qzhou 51

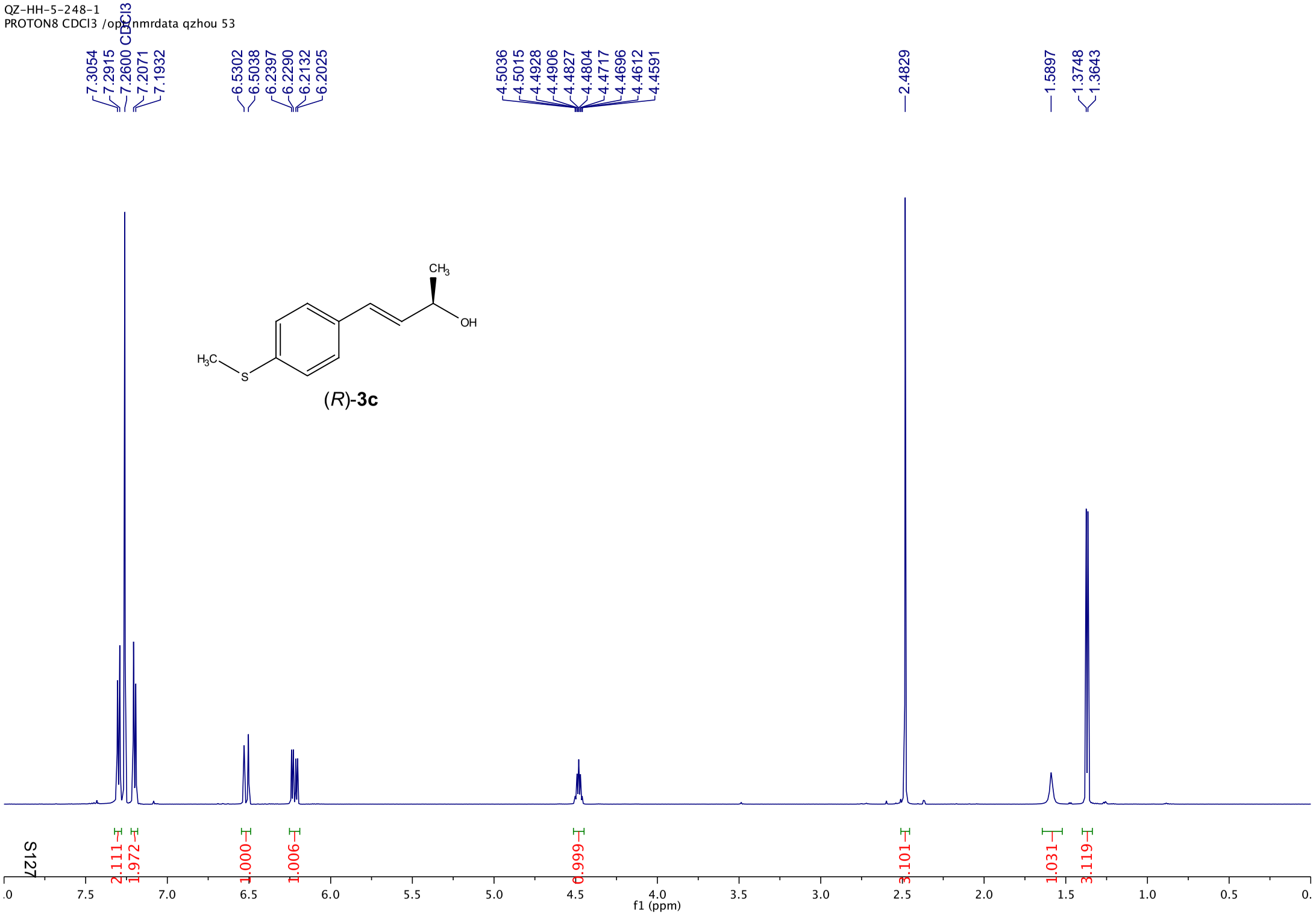
177.4832
140.3834
134.6255
128.5749
128.5387
127.7758
126.7337
77.1600 CDCl3
75.9878
38.9920
32.0386
31.1981
27.2799
22.2988
14.0292



(*S*)-**1r**

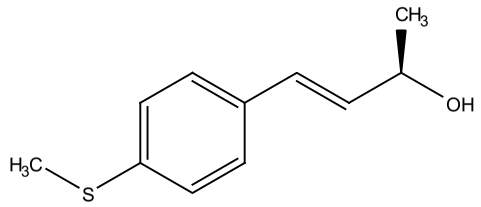


QZ-HH-5-248-1
PROTON8 CDCl3 /opt/nmrdata qzhou 53

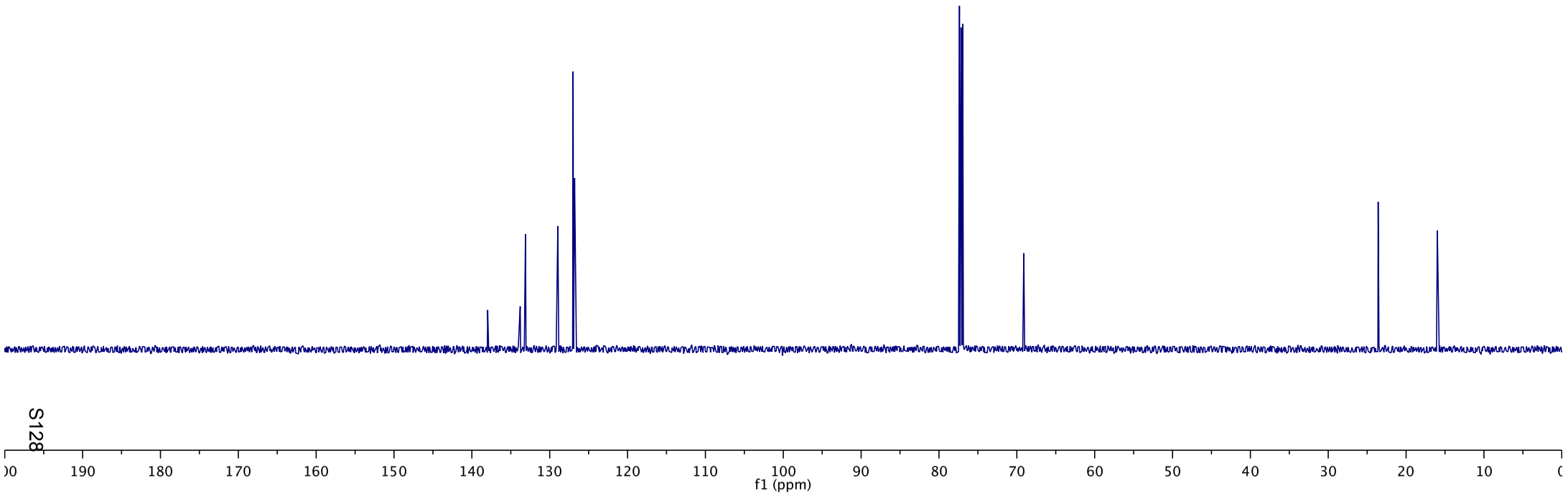


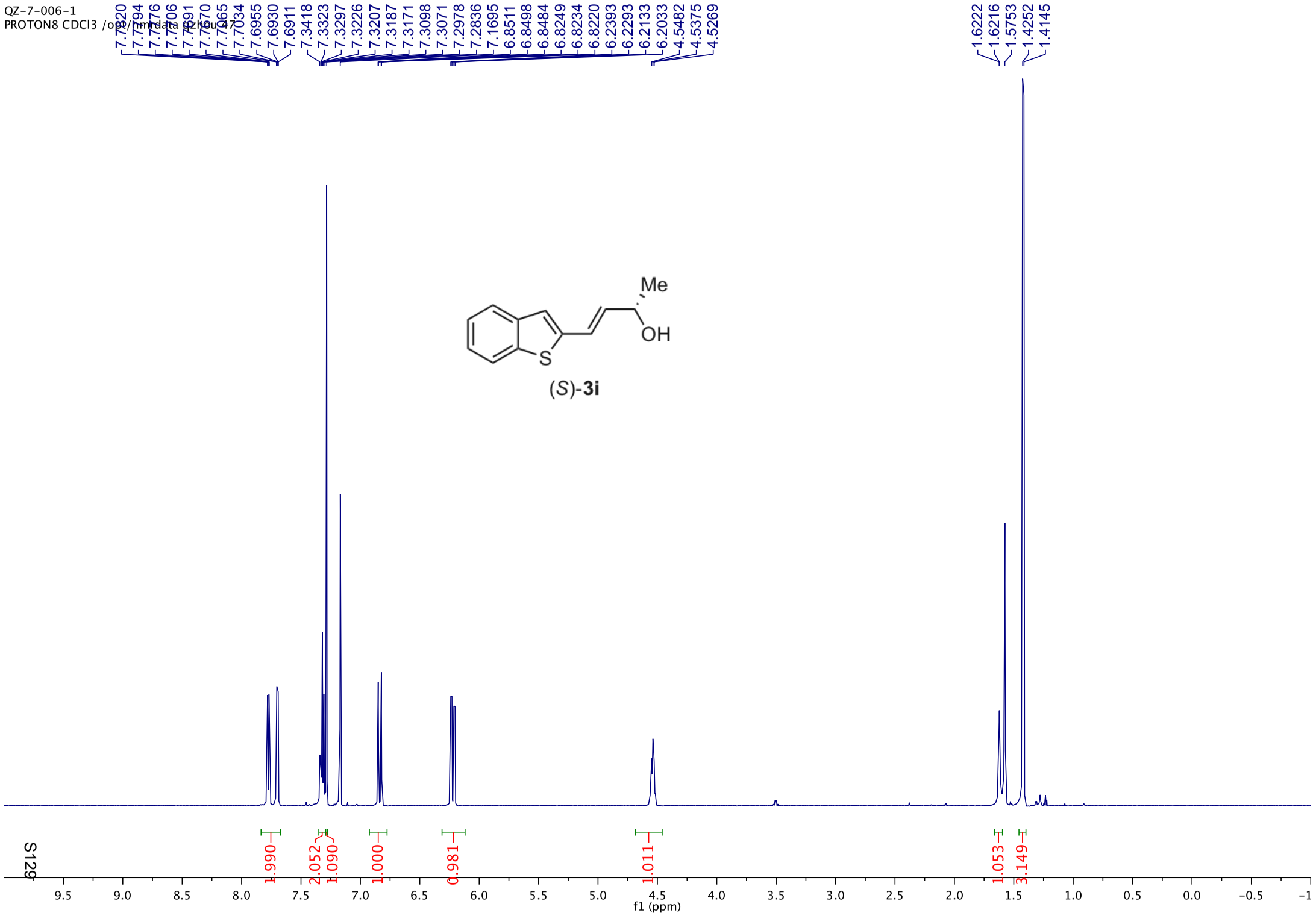
QZ-HH-5-248-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 53

137.9676
133.7906
133.1162
128.9581
126.9984
126.8082
77.1600 CDCl3
69.1025
23.5884
15.9872

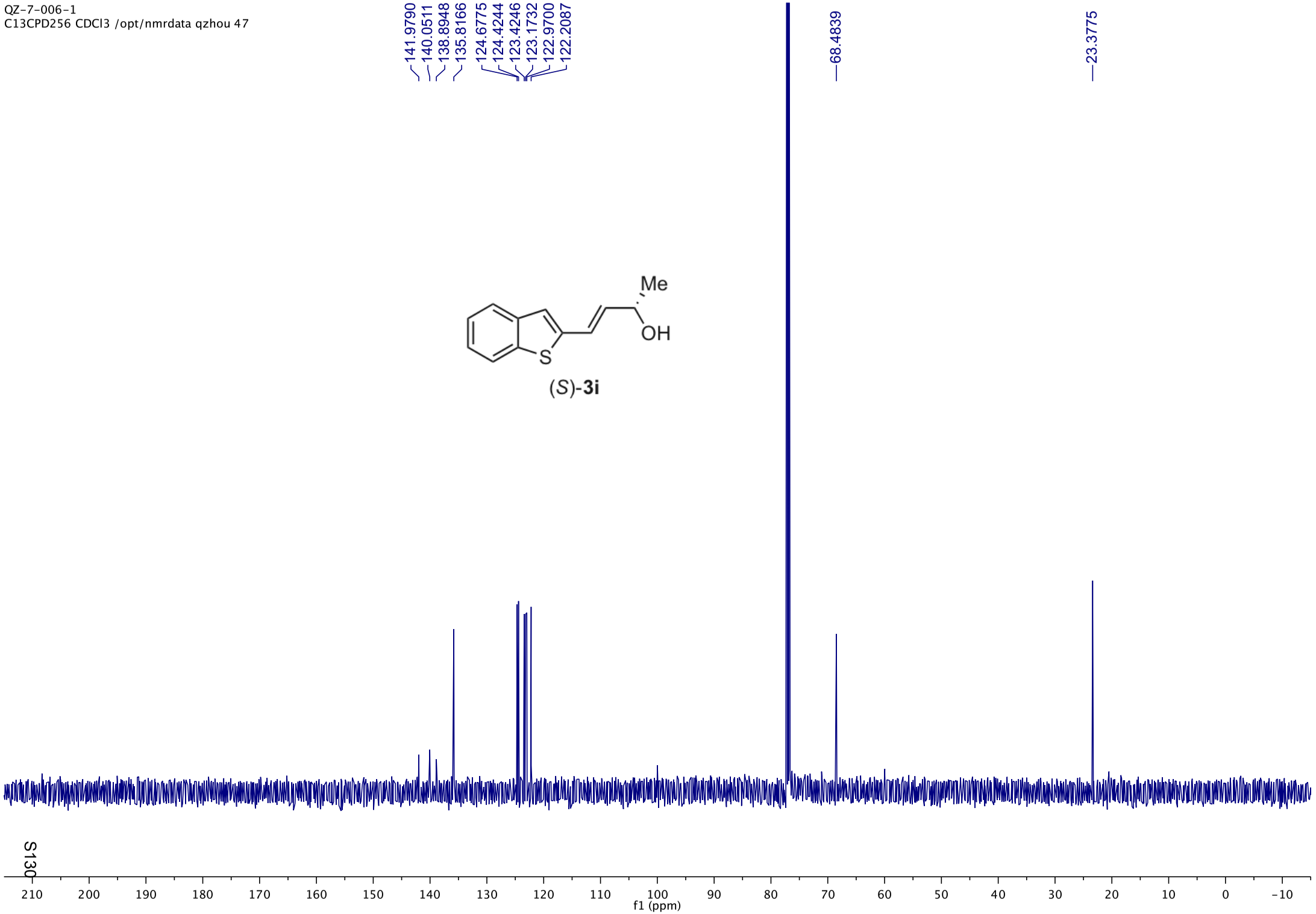


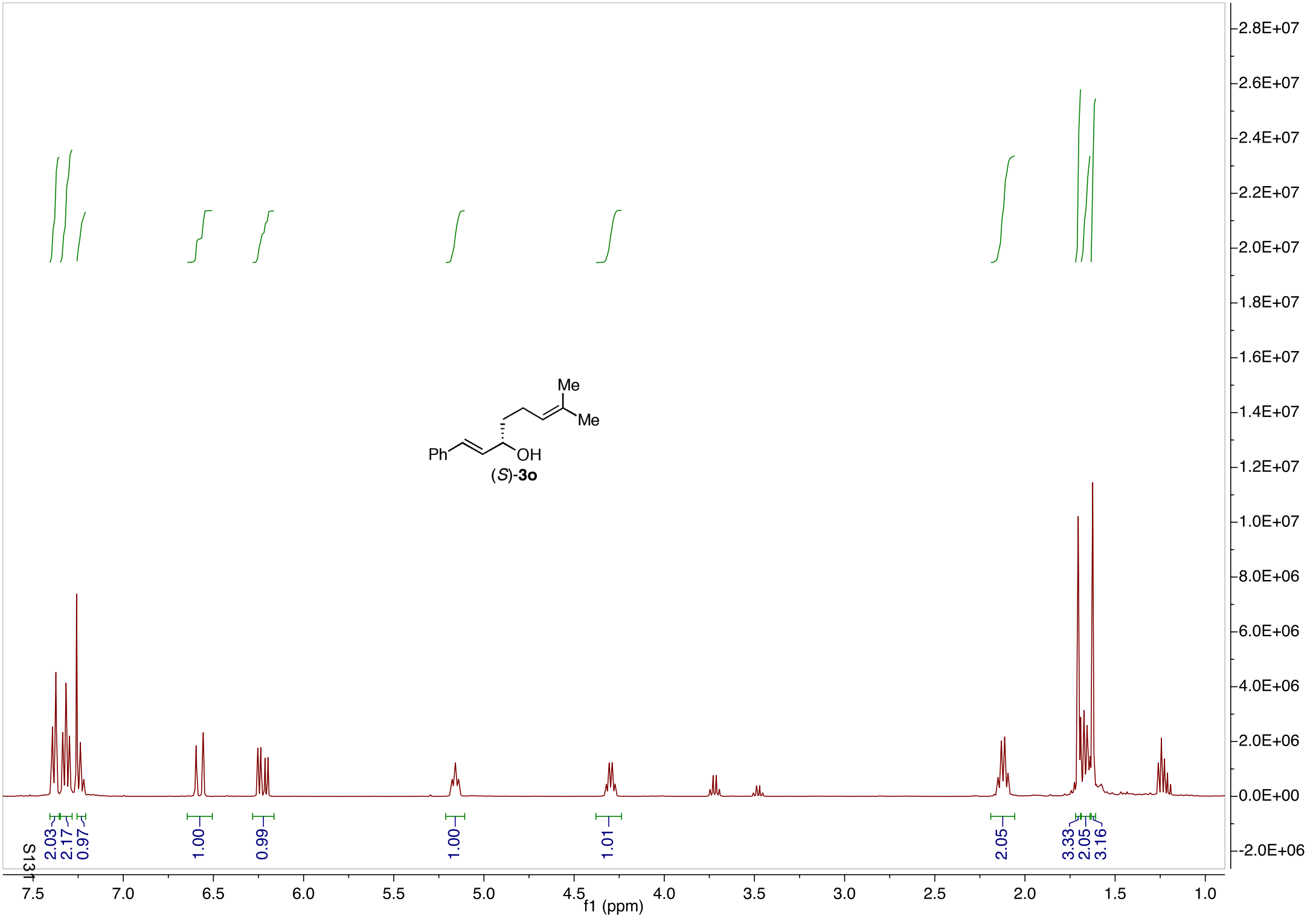
(*R*)-**3c**




QZ-7-006-1
PROTON8 CDCl3 /opt/nmrdata qzlou47
7.7820
7.7794
7.7776
7.7706
7.7691
7.7670
7.7465
7.7034
7.6955
7.6930
7.6911
7.3418
7.3323
7.3297
7.3226
7.3207
7.3187
7.3171
7.3098
7.3071
7.2978
7.2836
7.1695
6.8511
6.8498
6.8484
6.8249
6.8234
6.8220
6.2393
6.2293
6.2133
6.2033
4.5482
4.5375
4.5269
1.6222
1.6216
1.5753
1.4252
1.4145
Me
OH
S
(S)-3i
1.990
2.052
1.090
1.000
0.981
1.011
1.053
3.149
S129
f1 (ppm)

QZ-7-006-1
C13CPD256 CDCl3 /opt/nmrdata qzhou 47




Me
Me
Ph
OH
(S)-3o
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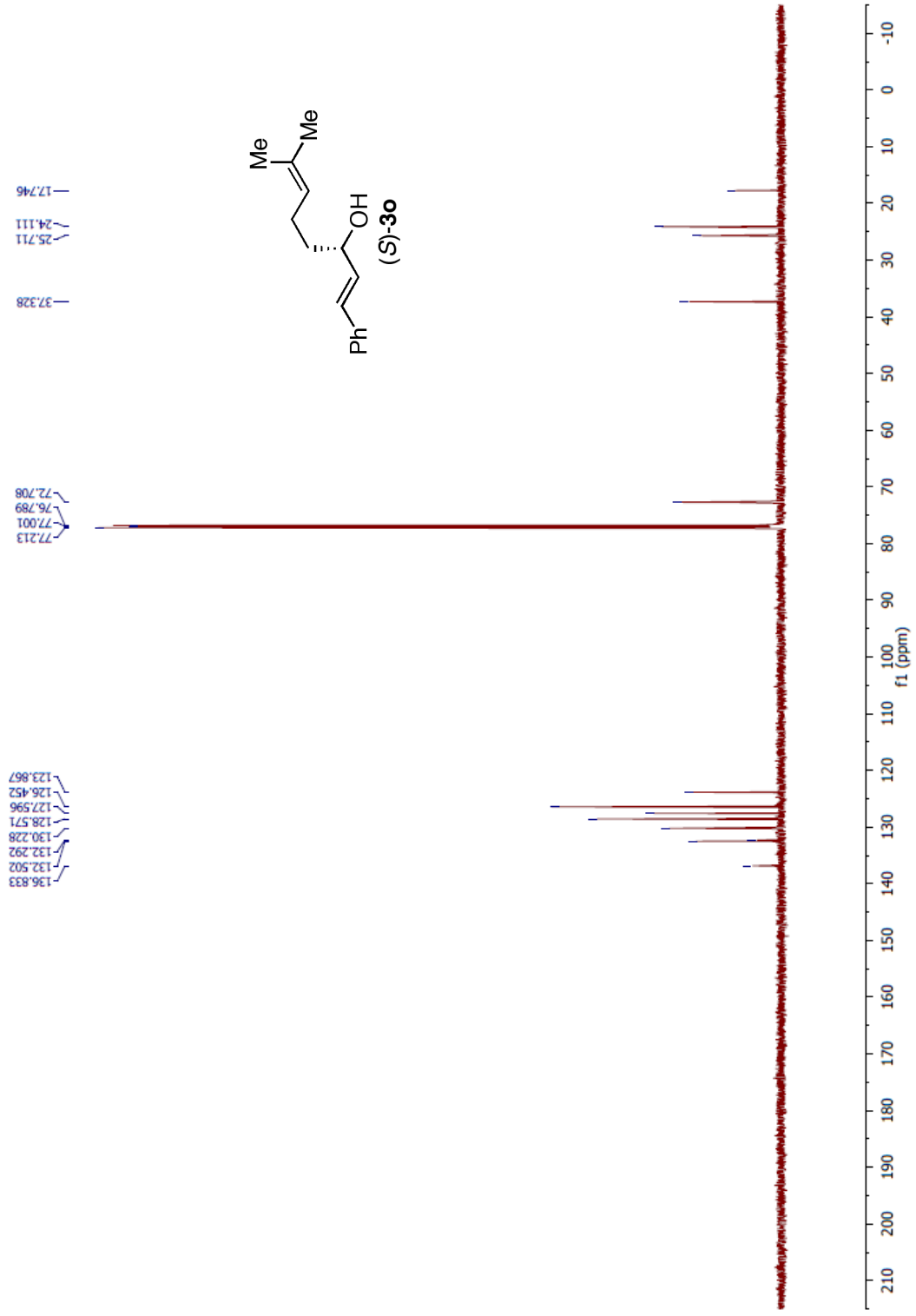
2.17
0.97
1.00
0.99
1.00
1.01
2.05
3.33
2.05
3.16
S131
f1 (ppm)


Me
Me
OH
Ph
(S)-3o
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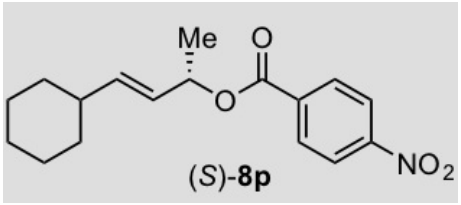
132.502
132.292
130.228
128.571
127.596
126.452
123.867
77.213
77.001
76.789
72.708
37.328
25.711
24.111
17.746
f1 (ppm)

PROTON8 CDCl3 7.dat/amidata tianqi 19

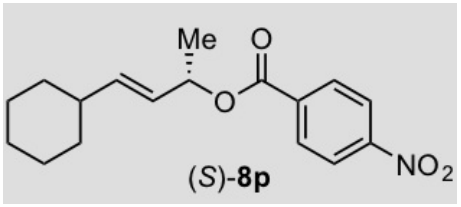


(*S*)-**8p**

f1 (ppm)

C13CPD1024 CDCl3 /opt/nmrdata tianqiu 19

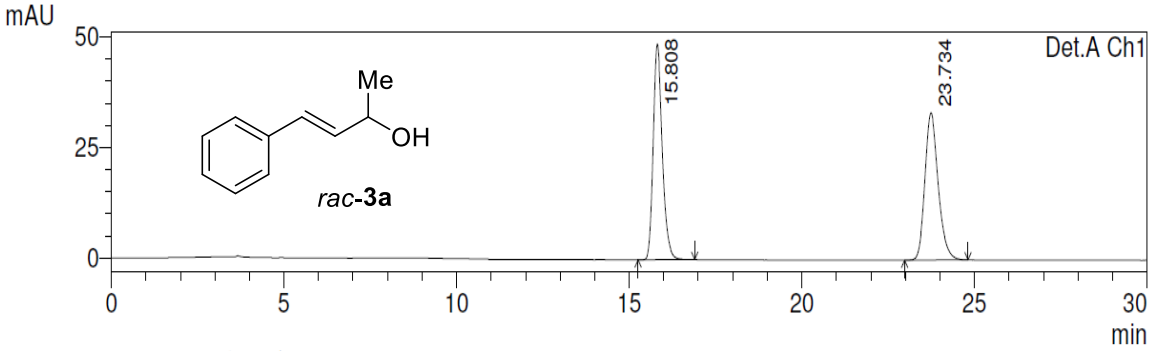
163.9327
150.4269
139.9929
136.3442
130.6605
126.3349
123.4276
77.2302 CDCl3
77.0192 CDCl3
76.8077 CDCl3
73.3608
40.2291
32.6077
32.5677
26.1000
25.9508
25.9378
20.5268



(*S*)-**8p**

f1 (ppm)

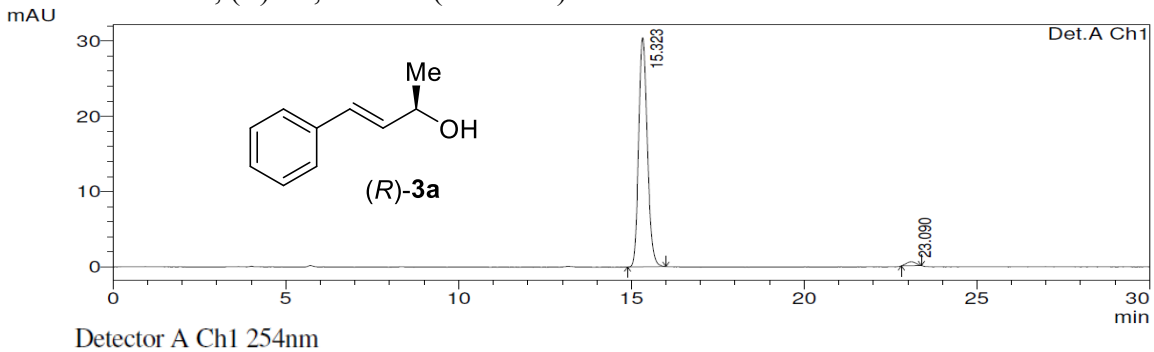
Racemic **3a**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.808	889522	48719	50.041	59.440
2	23.734	888065	33244	49.959	40.560
Total		1777588	81962	100.000	100.000

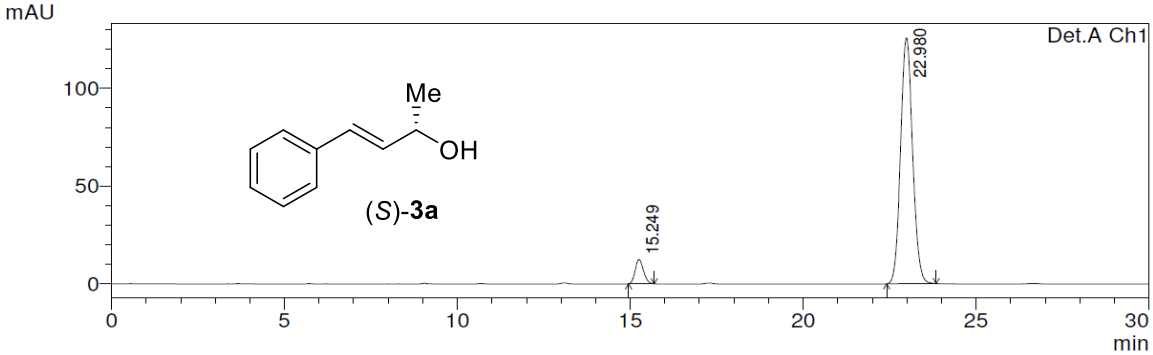
Enantioenriched, (*R*)-**3a**, 96% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.323	528124	30438	98.074	98.283
2	23.090	10373	532	1.926	1.717
Total		538497	30970	100.000	100.000

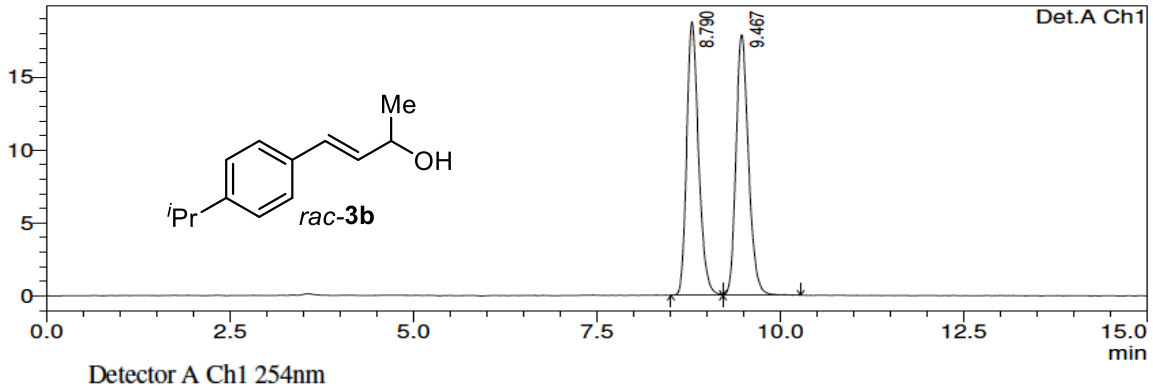
Enantioenriched, (*S*)-**3a**, 87% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.249	207636	12445	6.383	8.990
2	22.980	3045555	125979	93.617	91.010
Total		3253191	138424	100.000	100.000

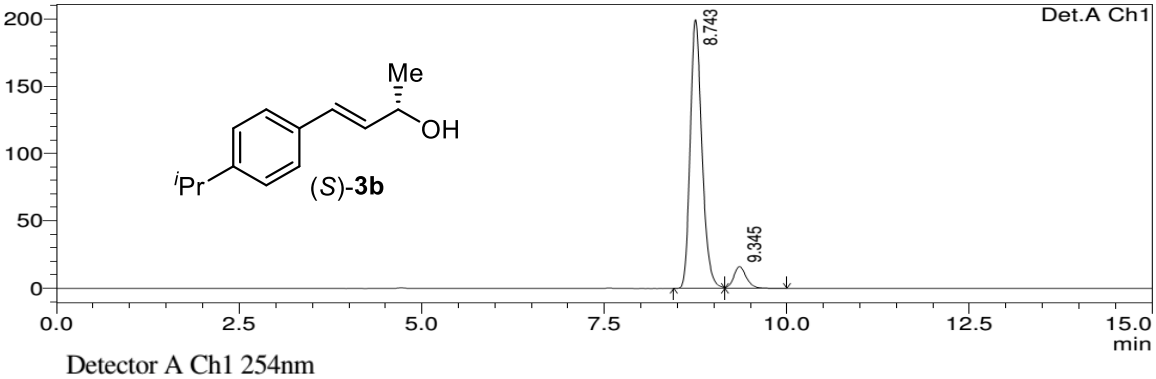
Racemic **3b**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.790	211145	18772	49.867	51.230
2	9.467	212268	17871	50.133	48.770
Total		423413	36644	100.000	100.000

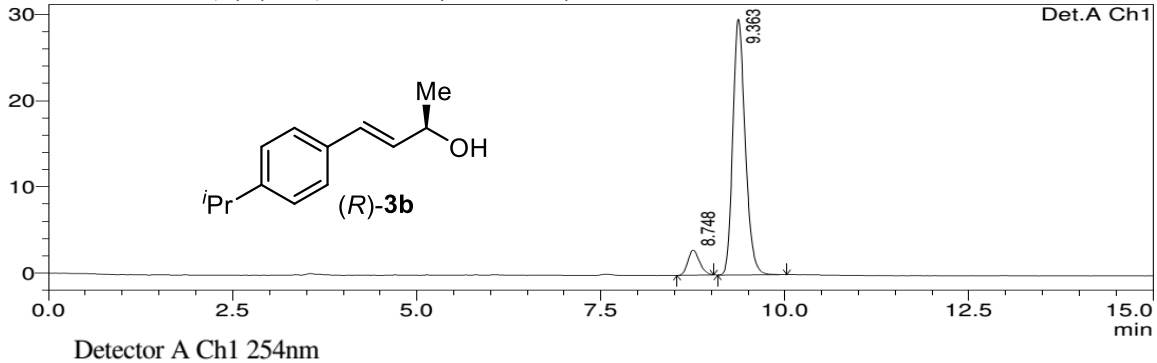
Enantioenriched, (*S*)-**3b**, 84% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.743	2240792	199732	91.989	92.449
2	9.345	195138	16313	8.011	7.551
Total		2435930	216045	100.000	100.000

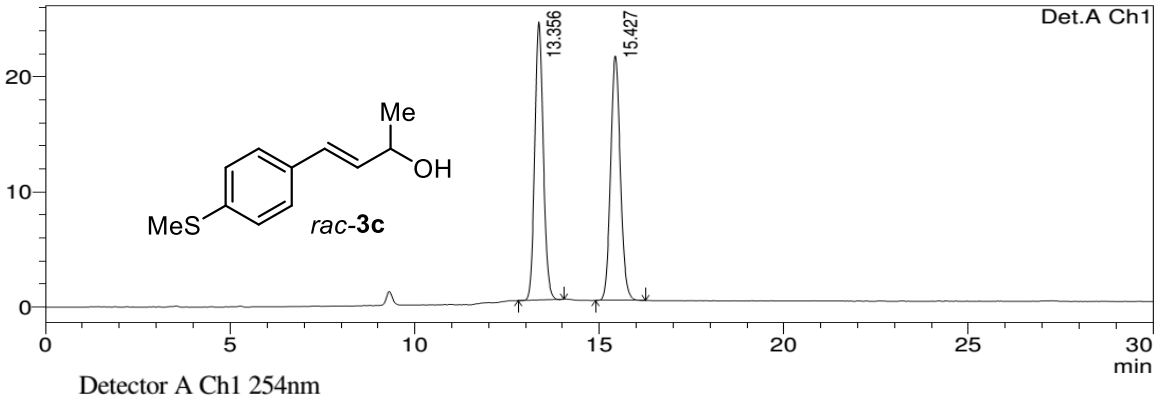
Enantioenriched, (*R*)-**3b**, 83% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.748	31741	2896	8.340	8.888
2	9.363	348823	29690	91.660	91.112
Total		380564	32586	100.000	100.000

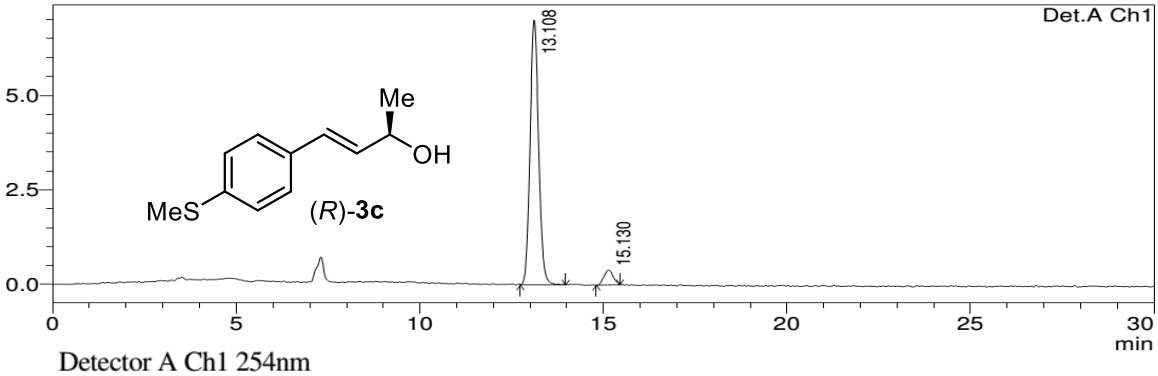
Racemic **3c**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.356	389340	24178	49.812	53.186
2	15.427	392281	21282	50.188	46.814
Total		781621	45460	100.000	100.000

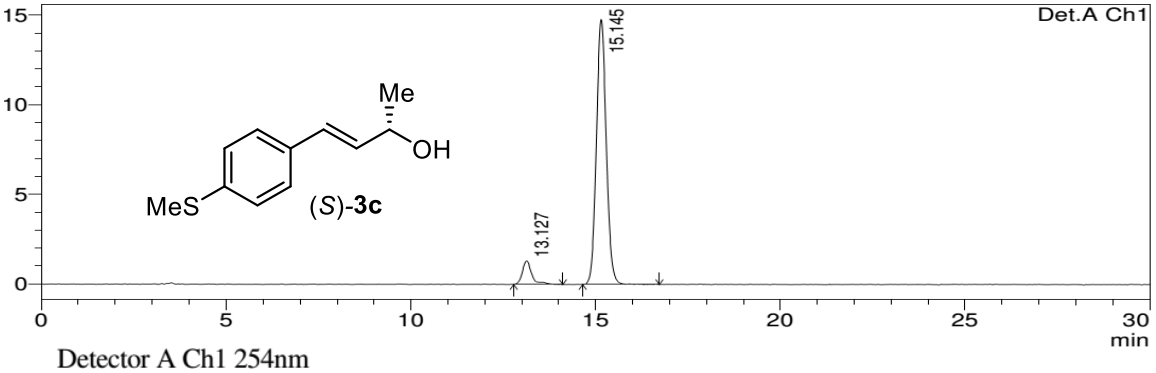
Enantioenriched, (*R*)-**3c**, 88% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.108	113915	7009	94.209	94.665
2	15.130	7002	395	5.791	5.335
Total		120917	7404	100.000	100.000

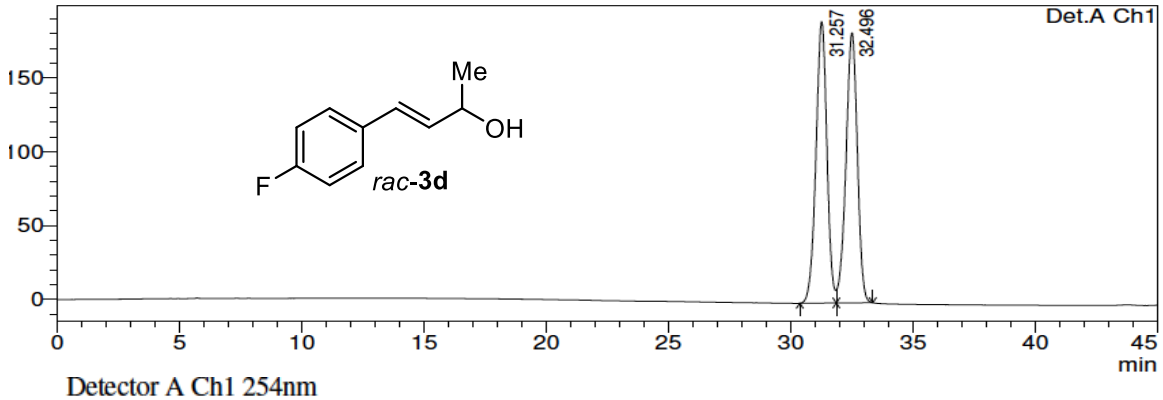
Enantioenriched, (*S*)-**3c**, 84% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.127	24170	1326	8.070	8.226
2	15.145	275327	14796	91.930	91.774
Total		299497	16122	100.000	100.000

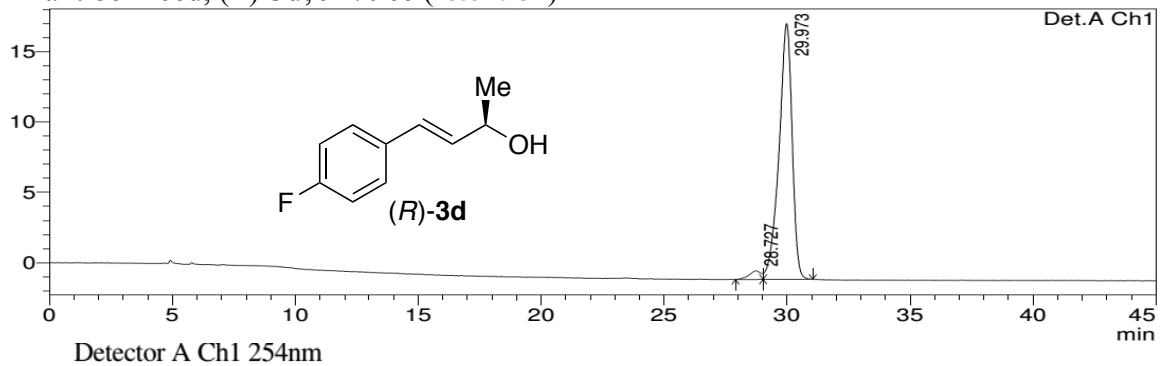
Racemic **3d**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.257	5951764	190544	50.088	51.022
2	32.496	5930932	182911	49.912	48.978
Total		11882696	373455	100.000	100.000

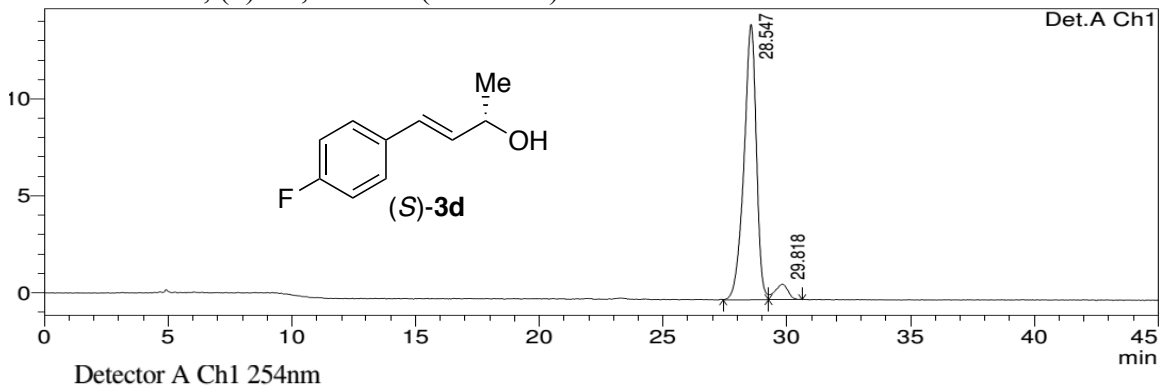
Enantioenriced, (*R*)-**3d**, 94% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.727	20598	612	2.953	3.257
2	29.973	676929	18171	97.047	96.743
Total		697527	18783	100.000	100.000

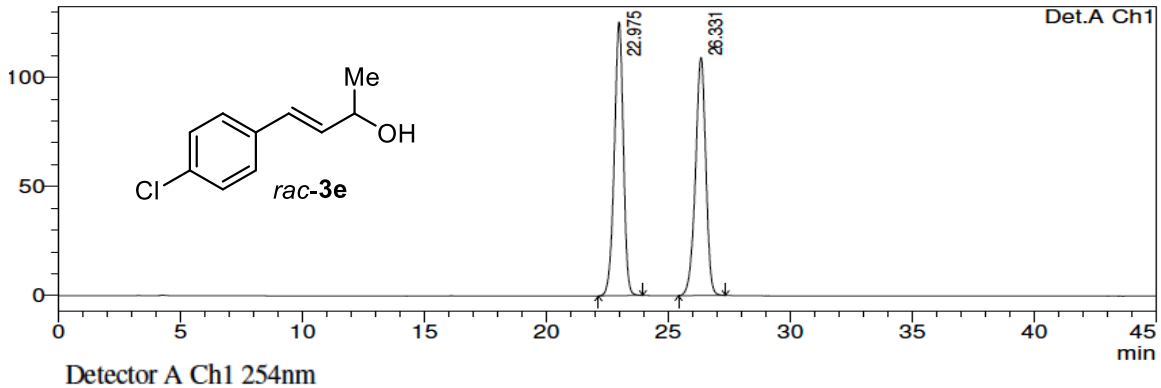
Enantioenriced, (*S*)-**3d**, 89% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.547	495380	14213	94.393	94.670
2	29.818	29425	800	5.607	5.330
Total		524805	15013	100.000	100.000

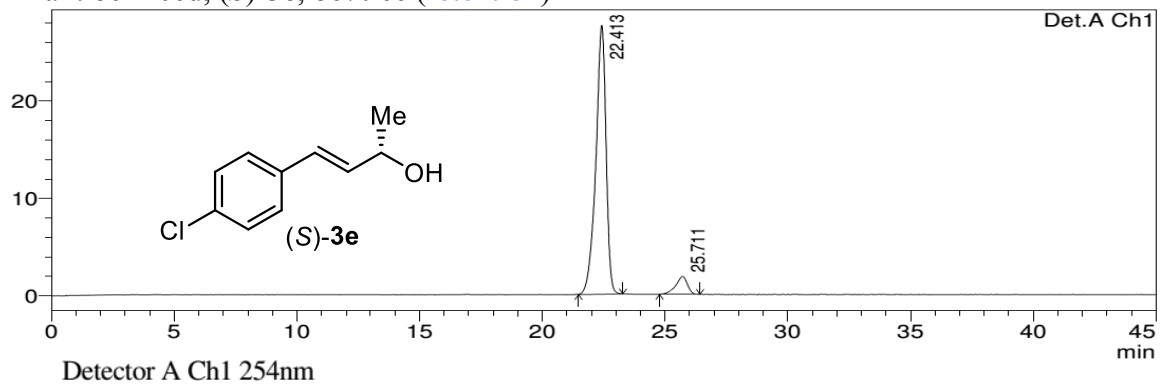
Racemic **3e**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.975	3227217	125247	50.021	53.460
2	26.331	3224470	109036	49.979	46.540
Total		6451687	234283	100.000	100.000

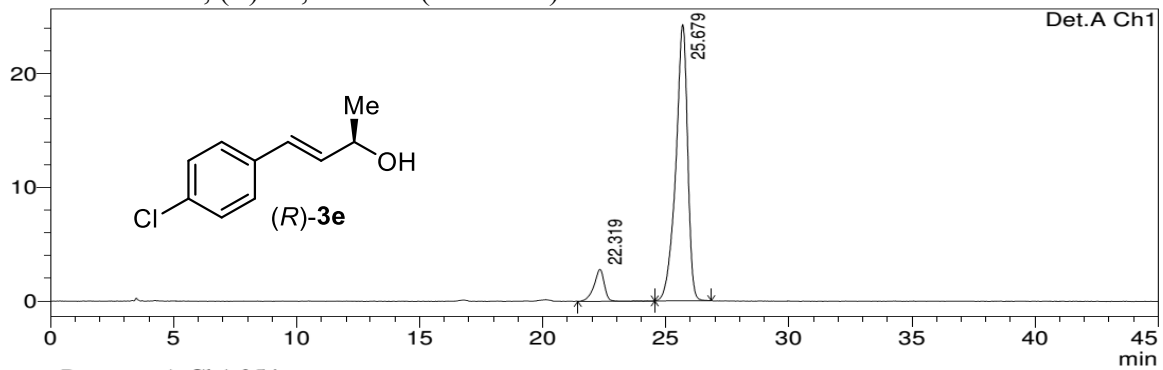
Enantioenriced, (*S*)-**3e**, 86% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.413	800719	27623	92.818	93.722
2	25.711	61960	1850	7.182	6.278
Total		862678	29474	100.000	100.000

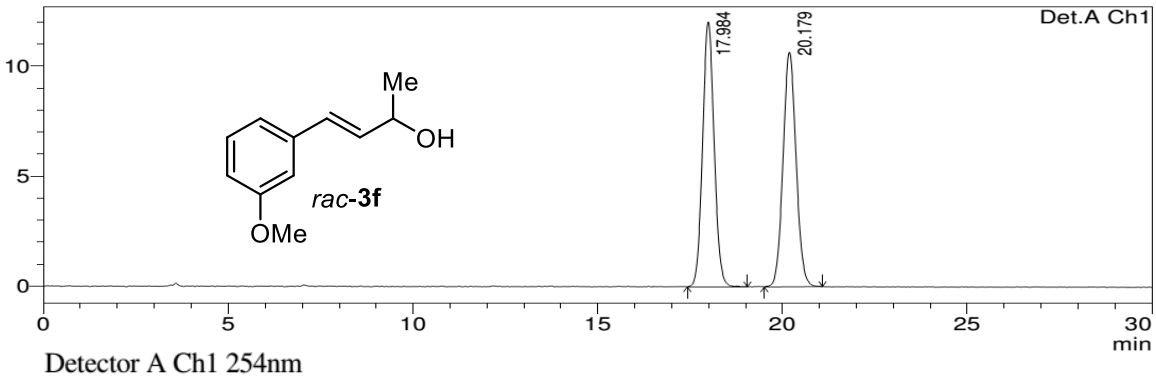
Enantioenriced, (*R*)-**3e**, 82% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.319	78955	2804	8.860	10.344
2	25.679	812148	24305	91.140	89.656
Total		891102	27109	100.000	100.000

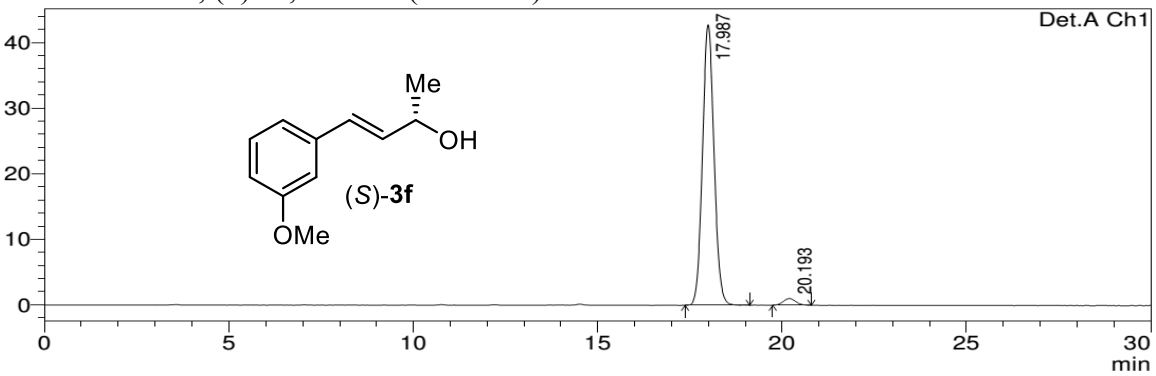
Racemic **3f**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.984	262479	12039	50.014	53.031
2	20.179	262328	10663	49.986	46.969
Total		524807	22702	100.000	100.000

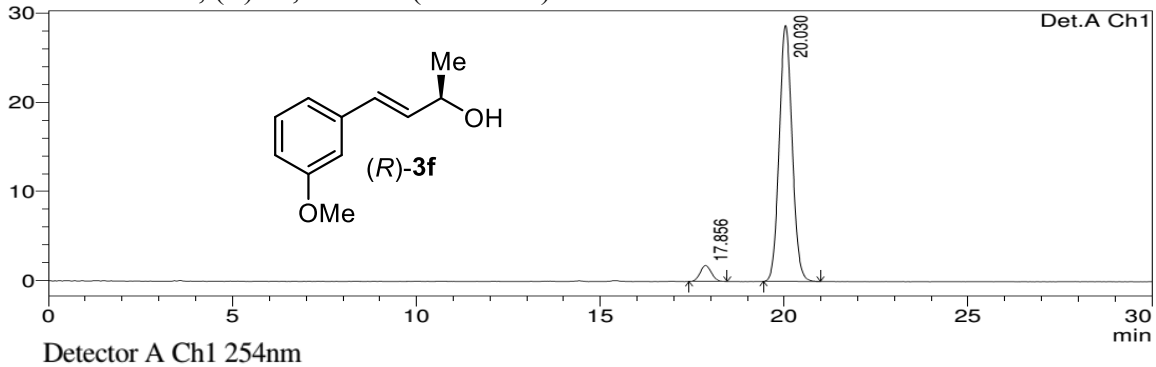
Enantioenriced, (*S*)-**3f**, 95% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.987	932391	42781	97.403	97.645
2	20.193	24861	1032	2.597	2.355
Total		957252	43813	100.000	100.000

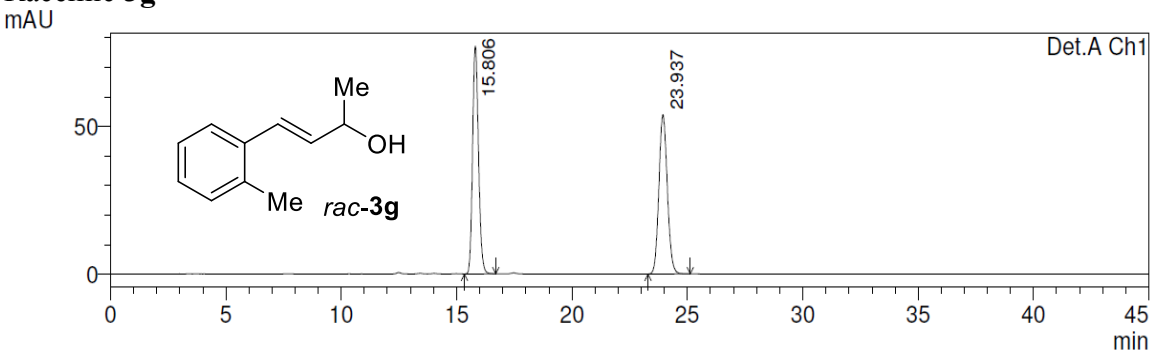
Enantioenriced, (*R*)-**3f**, 90% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.856	38100	1793	5.166	5.879
2	20.030	699408	28701	94.834	94.121
Total		737508	30494	100.000	100.000

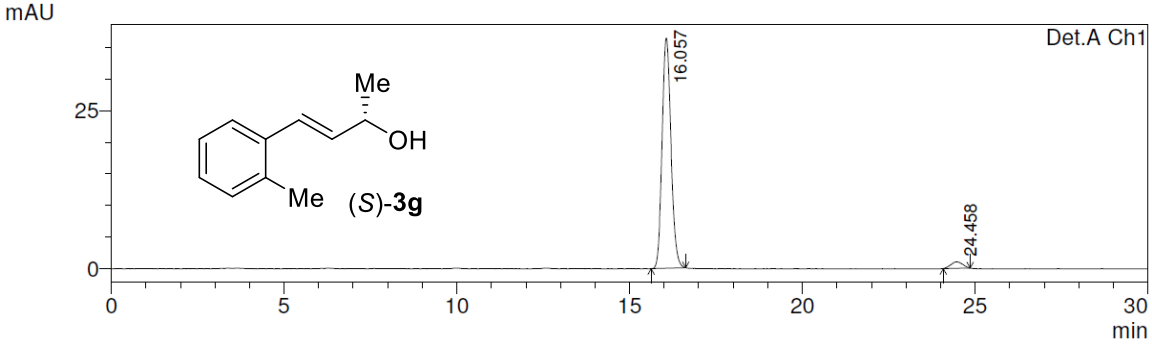
Racemic **3g**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.806	1374079	77208	49.958	58.847
2	23.937	1376411	53992	50.042	41.153
Total		2750490	131200	100.000	100.000

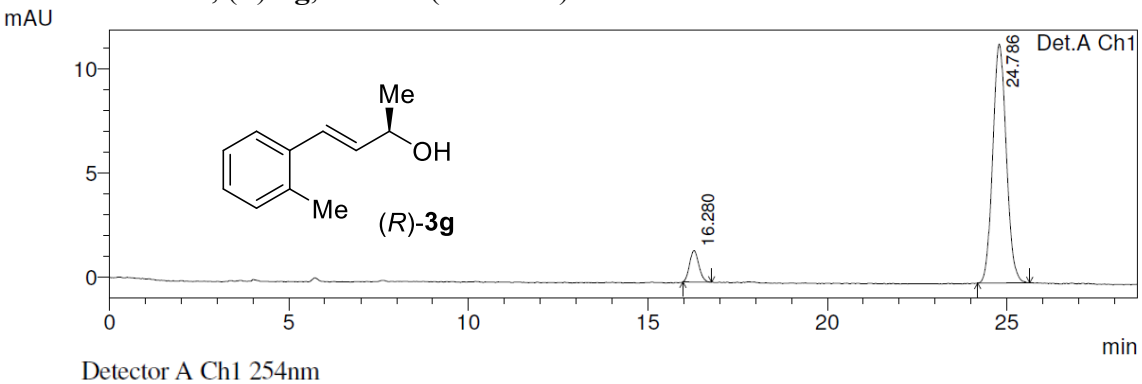
Enantioenriched, (*S*)-**3g**, 93% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.057	649583	36423	96.403	97.228
2	24.458	24239	1038	3.597	2.772
Total		673822	37461	100.000	100.000

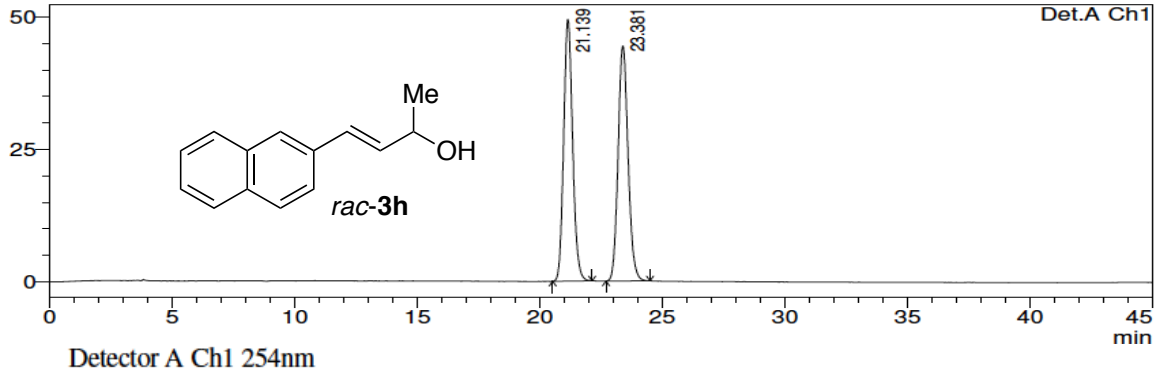
Enantioenriched, (*R*)-**3g**, 84% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.280	26876	1504	8.203	11.614
2	24.786	300781	11443	91.797	88.386
Total		327658	12947	100.000	100.000

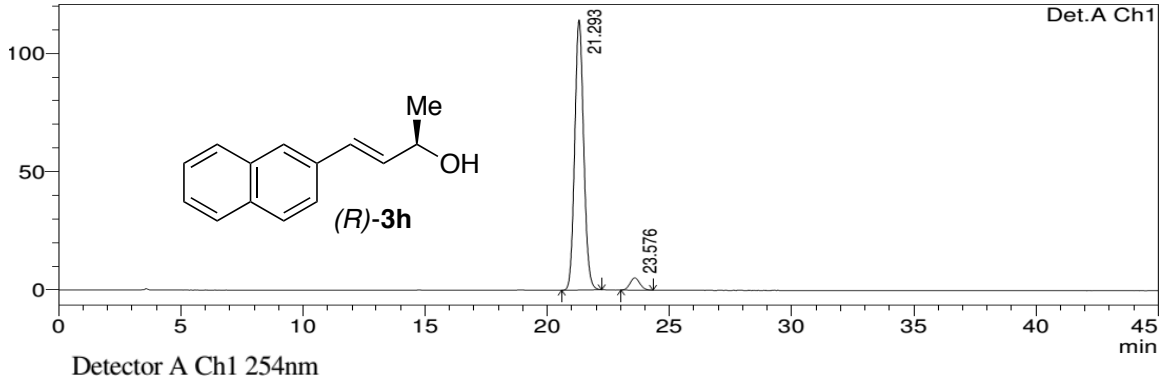
Racemic **3h**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.139	1257272	49382	49.980	52.669
2	23.381	1258302	44376	50.020	47.331
Total		2515575	93758	100.000	100.000

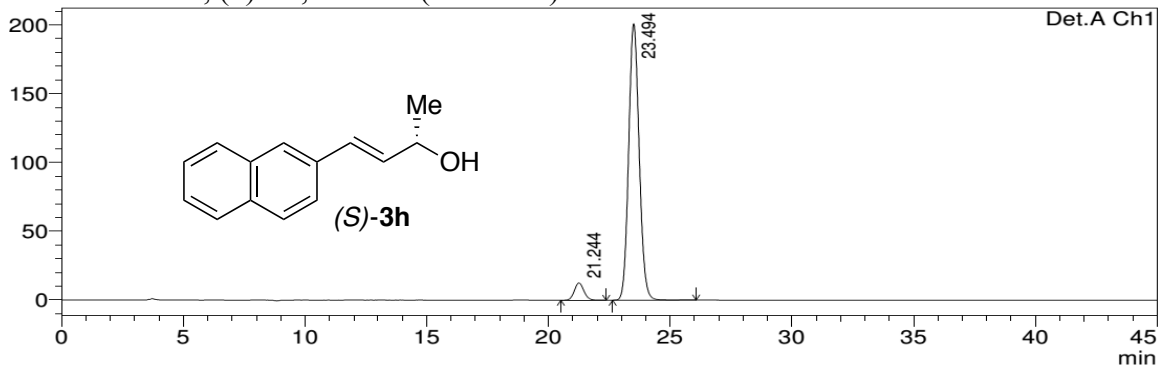
Enantioenriched, (*R*)-**3h**, 90% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.293	2921971	114195	95.273	95.665
2	23.576	144987	5174	4.727	4.335
Total		3066958	119369	100.000	100.000

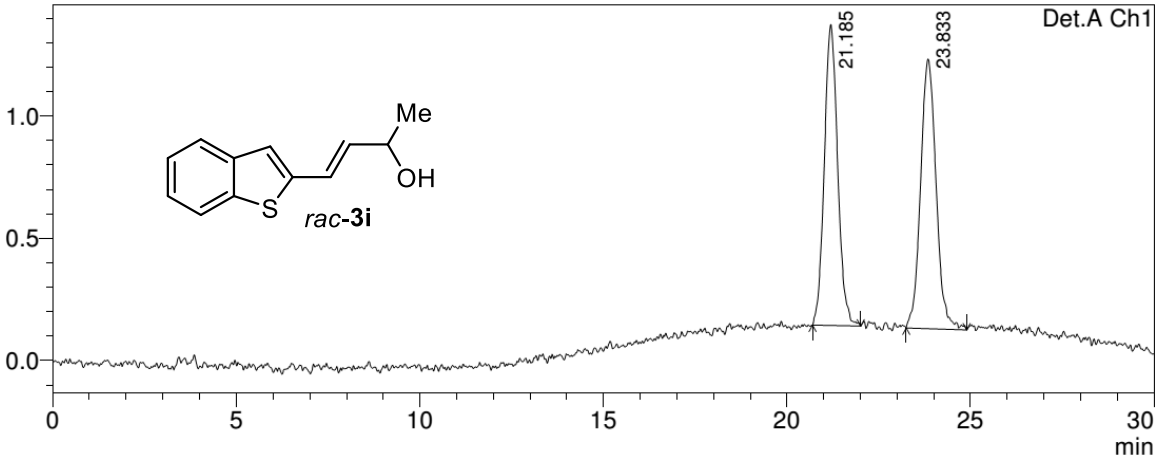
Enantioenriched, (*S*)-**3h**, 89% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.244	345469	12569	5.408	5.885
2	23.494	6042259	201018	94.592	94.115
Total		6387727	213587	100.000	100.000

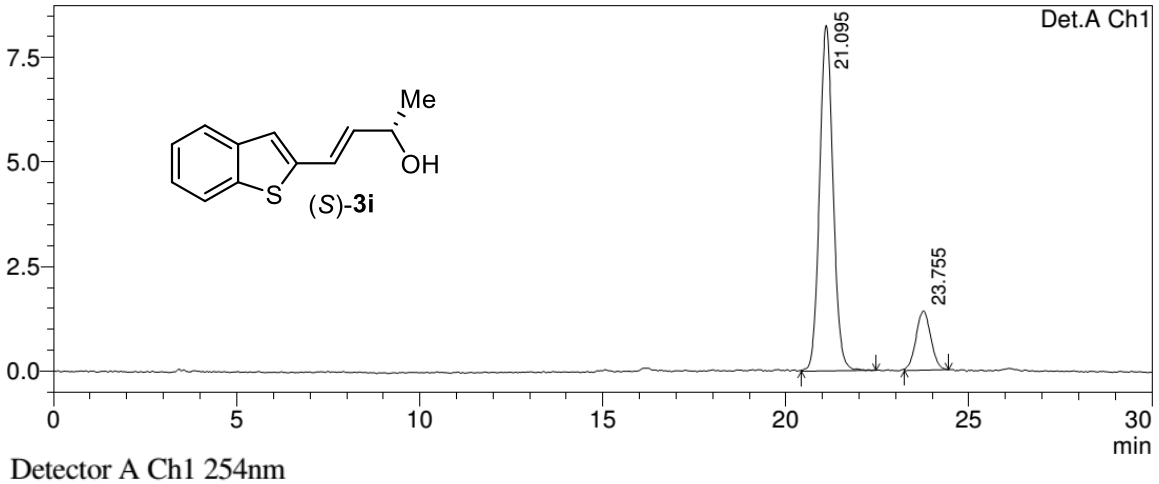
Racemic **3i**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.185	31140	1230	49.102	52.754
2	23.833	32280	1101	50.898	47.246
Total		63420	2331	100.000	100.000

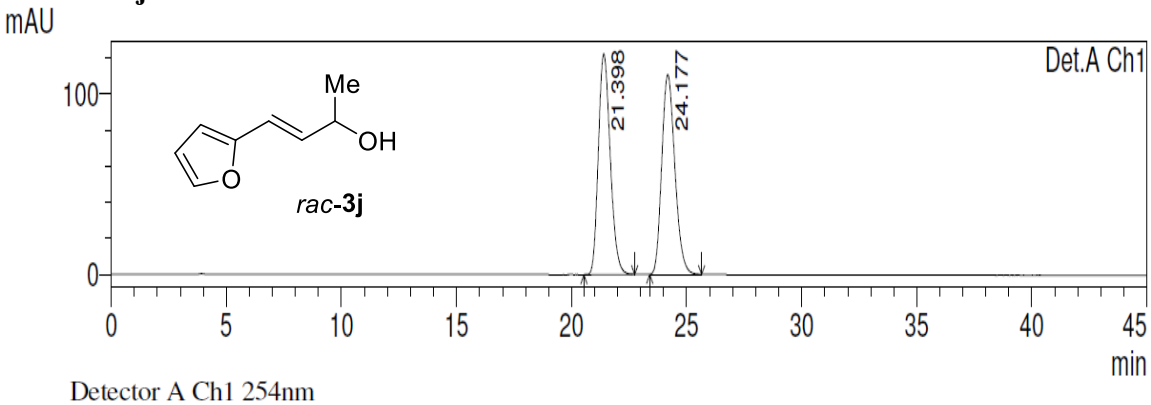
Enantioenriched, (*S*)-**3i**, 68% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.095	211809	8267	84.127	85.353
2	23.755	39964	1419	15.873	14.647
Total		251774	9686	100.000	100.000

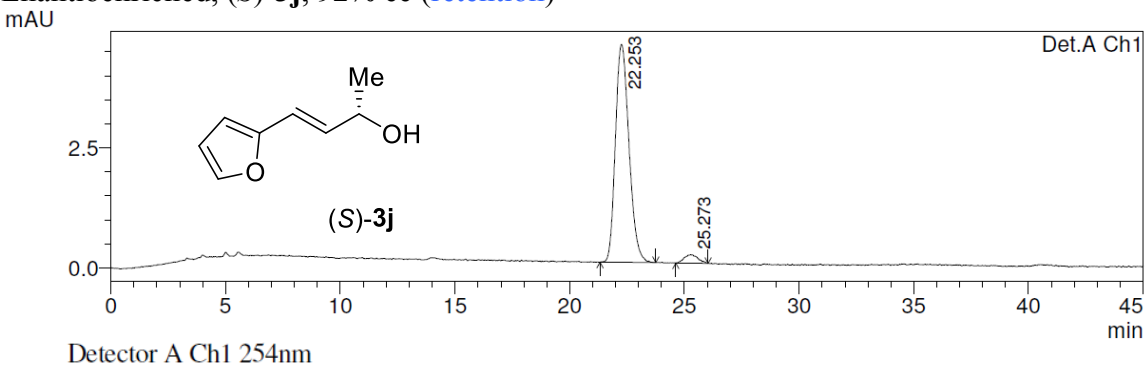
Racemic **3j**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.398	4396742	122528	50.015	52.487
2	24.177	4394091	110918	49.985	47.513
Total		8790833	233446	100.000	100.000

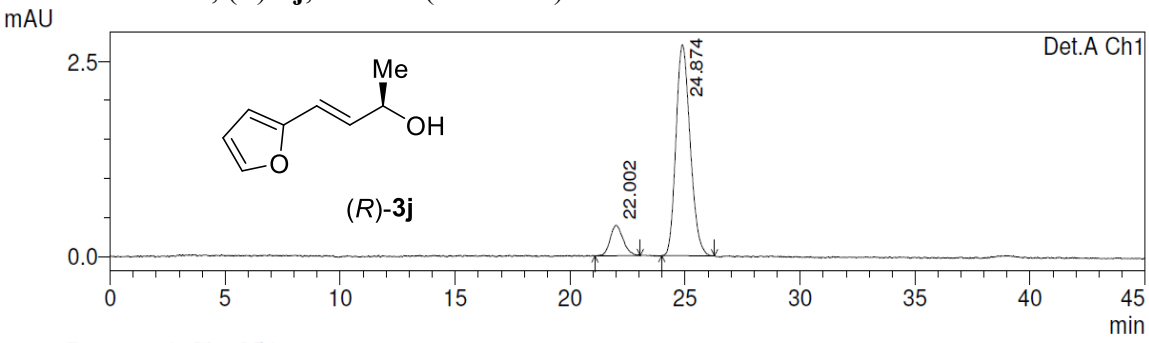
Enantioenriched, (*S*)-**3j**, 92% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.253	186677	4534	96.144	96.172
2	25.273	7487	180	3.856	3.828
Total		194163	4715	100.000	100.000

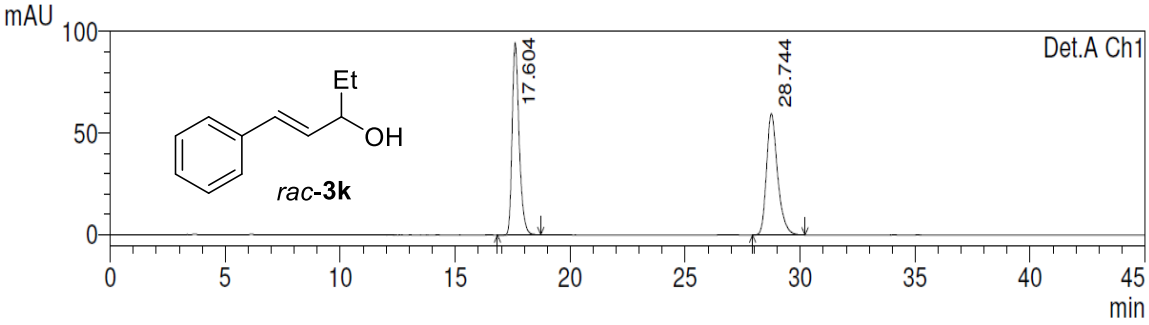
Enantioenriched, (*R*)-**3j**, 77% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.002	15326	391	11.646	12.614
2	24.874	116271	2708	88.354	87.386
Total		131598	3098	100.000	100.000

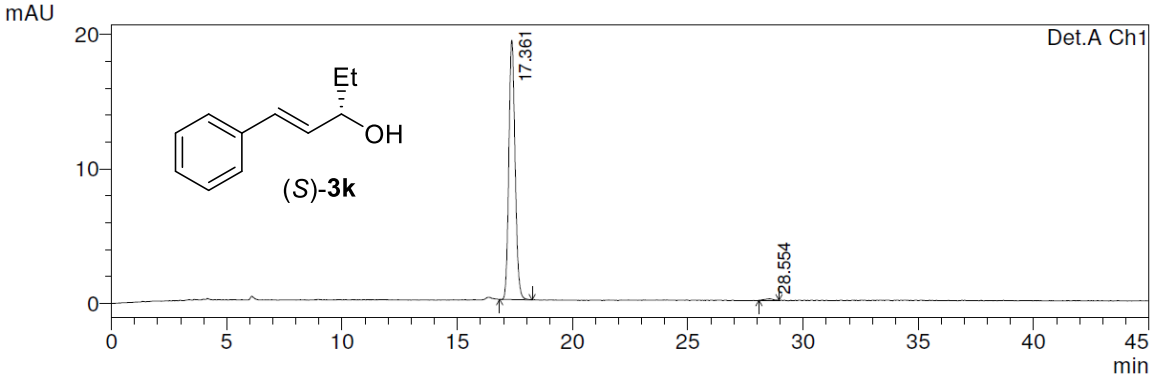
Racemic **3k**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.604	1996140	94709	50.003	61.323
2	28.744	1995903	59734	49.997	38.677
Total		3992043	154443	100.000	100.000

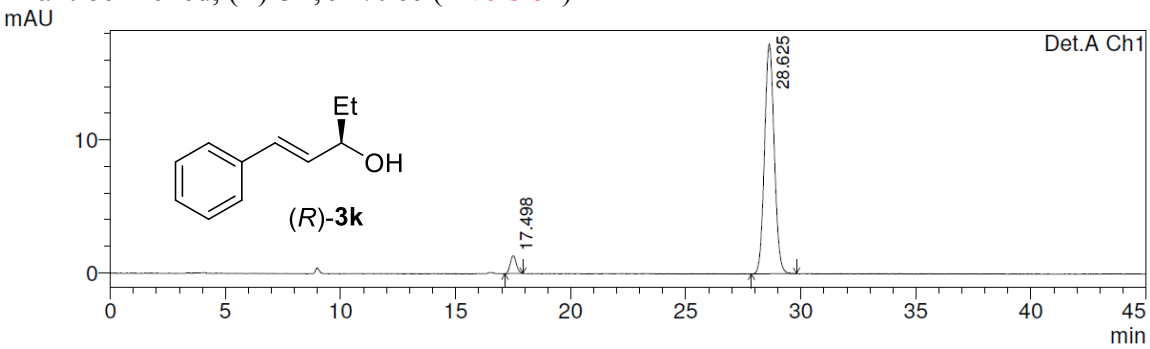
Enantioenriched, (*S*)-**3k**, 98% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.361	364256	19286	99.213	99.411
2	28.554	2890	114	0.787	0.589
Total		367147	19400	100.000	100.000

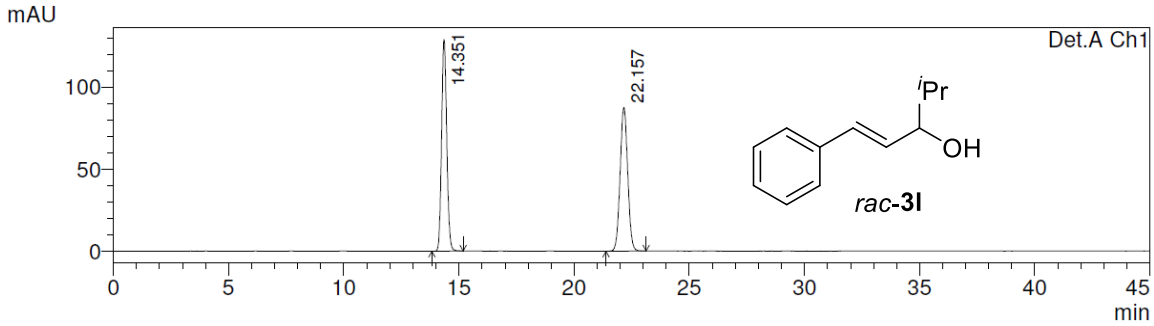
Enantioenriched, (*R*)-**3k**, 91% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.498	24845	1336	4.684	7.185
2	28.625	505608	17258	95.316	92.815
Total		530453	18594	100.000	100.000

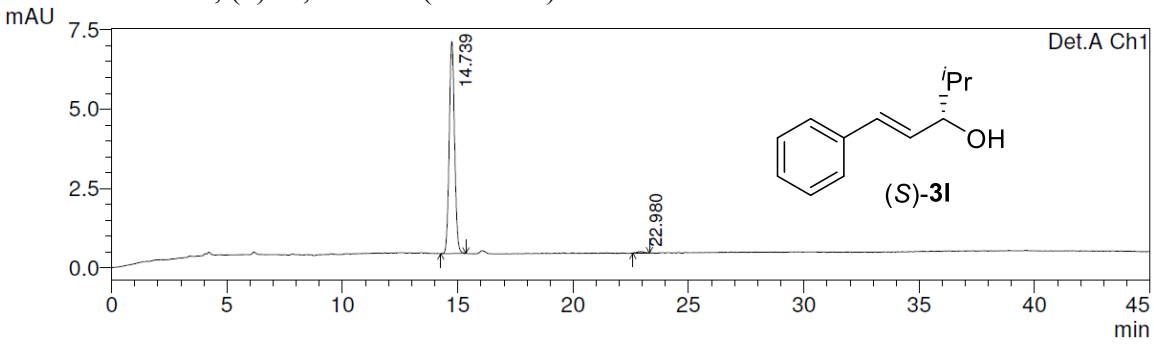
Racemic **3l**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.351	2006467	129008	49.967	59.598
2	22.157	2009095	87455	50.033	40.402
Total		4015562	216463	100.000	100.000

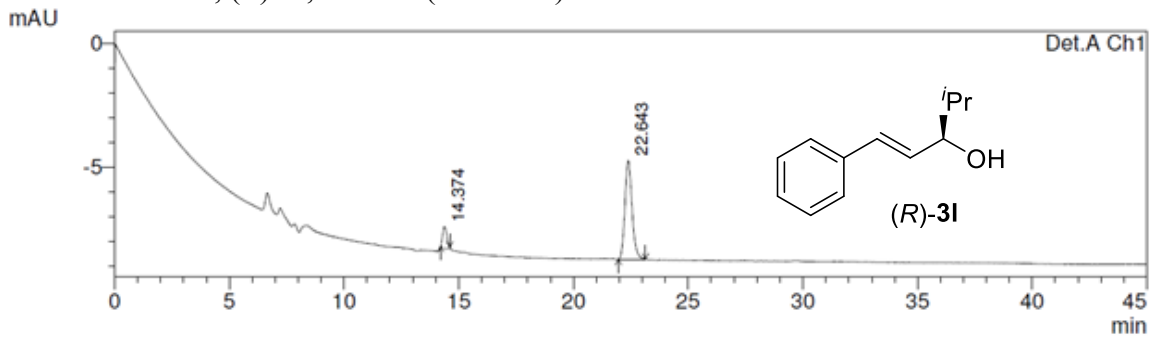
Enantioenriched, (*S*)-**3l**, 98% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.739	107690	6684	99.149	99.337
2	22.980	925	45	0.851	0.663
Total		108615	6728	100.000	100.000

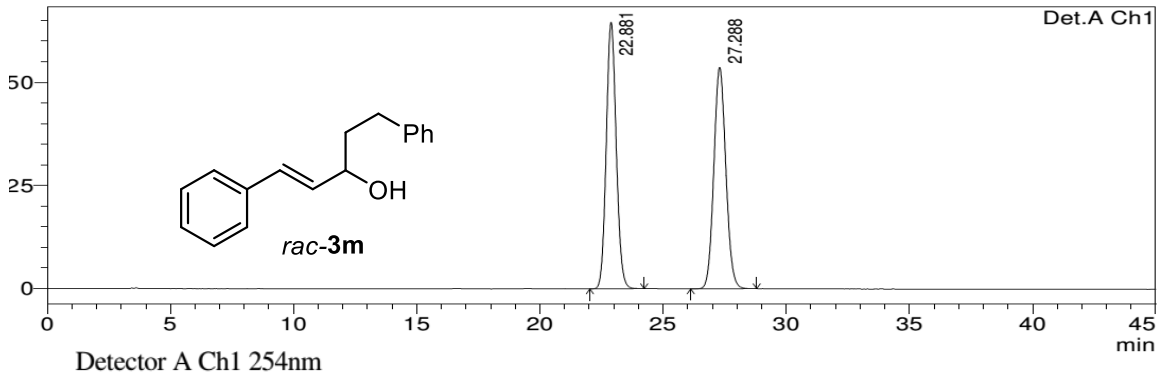
Enantioenriched, (*R*)-**3l**, 80% ee (inversion)



Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.374	10081	817	10.473	17.007
2	22.643	86180	3985	89.527	82.993
Total		96262	4801	100.000	100.000

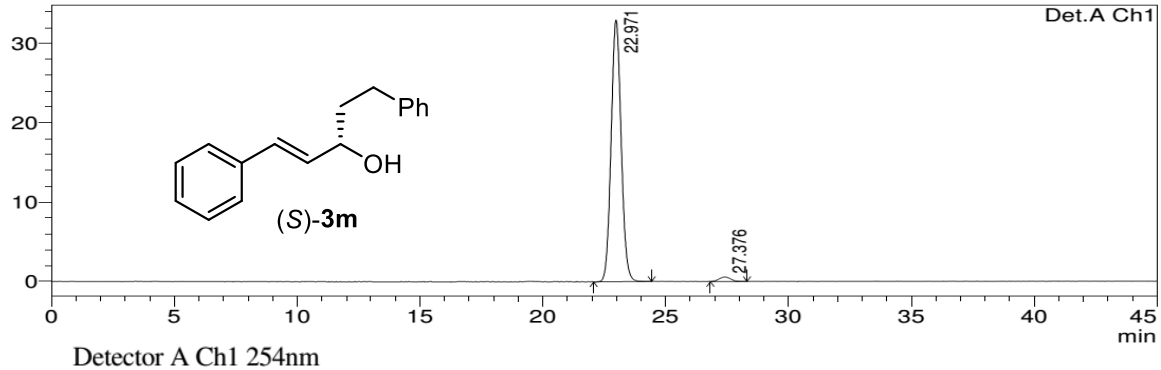
Racemic **3m**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.881	1824790	64649	49.988	54.622
2	27.288	1825632	53708	50.012	45.378
Total		3650422	118357	100.000	100.000

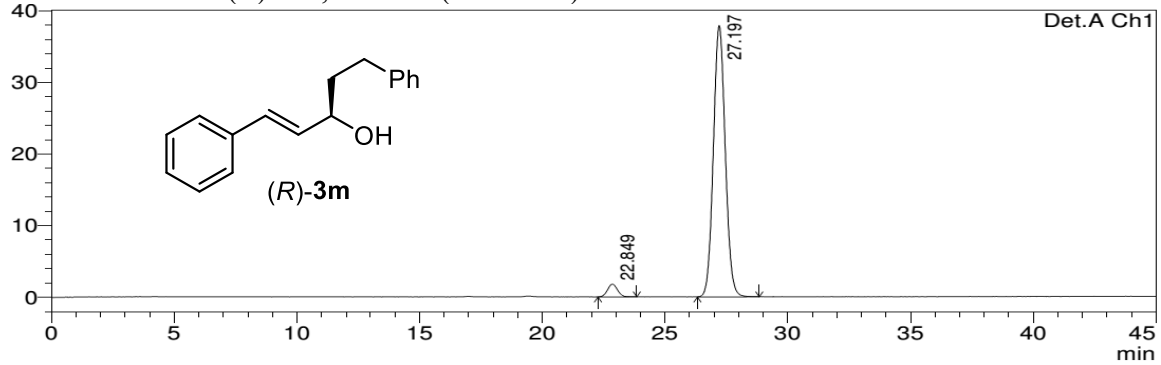
Enantioenriched (*S*)-**3m**, 96% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.971	940092	33007	97.931	98.281
2	27.376	19865	577	2.069	1.719
Total		959957	33584	100.000	100.000

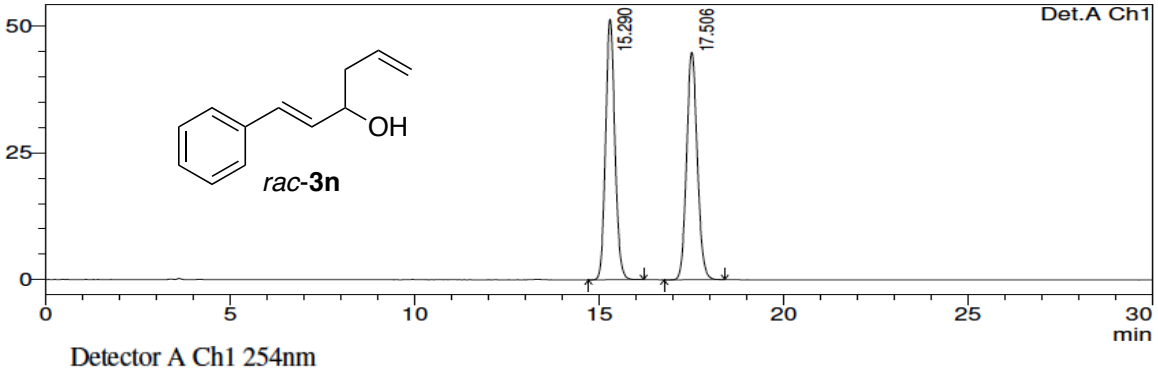
Enantioenriched (*R*)-**3m**, 92% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.849	51578	1799	3.882	4.532
2	27.197	1277040	37886	96.118	95.468
Total		1328618	39684	100.000	100.000

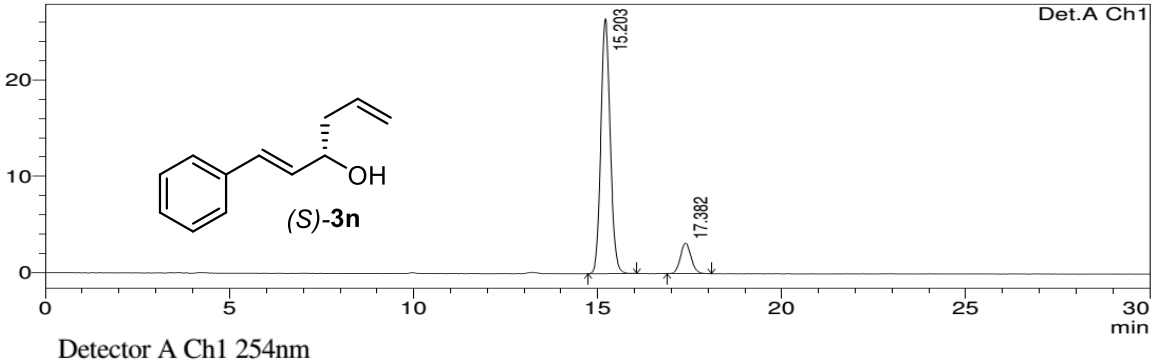
Racemic **3n**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.290	903612	51435	49.957	53.361
2	17.506	905164	44955	50.043	46.639
Total		1808777	96391	100.000	100.000

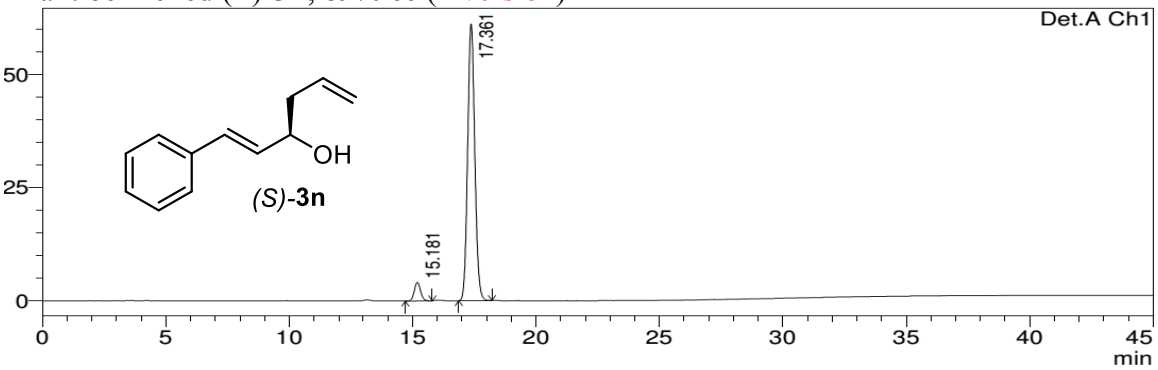
Enantioenriched (*S*)-**3n**, 79% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.203	469152	26467	87.868	89.267
2	17.382	64776	3182	12.132	10.733
Total		533929	29649	100.000	100.000

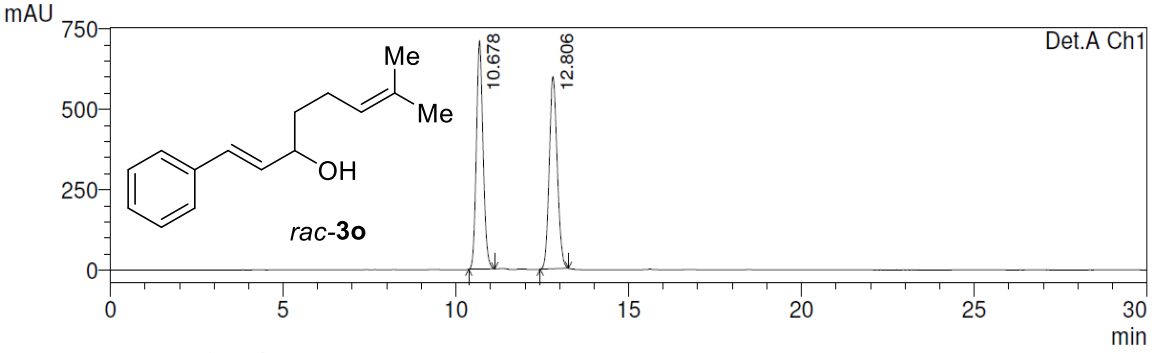
Enantioenriched (*R*)-**3n**, 89% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.181	72151	4092	5.534	6.271
2	17.361	1231557	61158	94.466	93.729
Total		1303709	65251	100.000	100.000

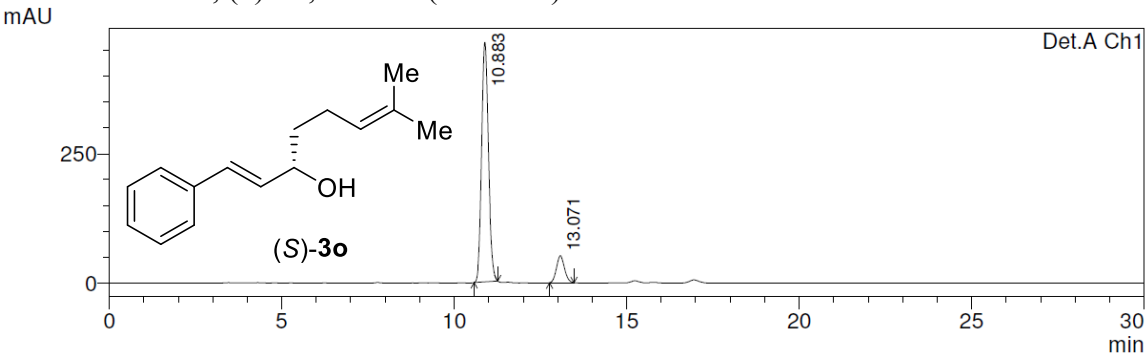
Racemic **3o**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.678	9706710	711675	50.112	54.327
2	12.806	9663496	598320	49.888	45.673
Total		19370206	1309995	100.000	100.000

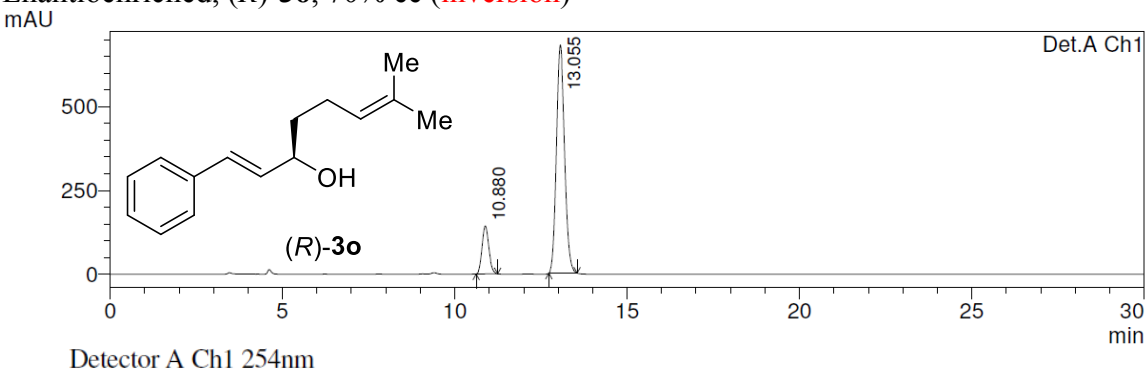
Enantioenriched, (*S*)-**3o**, 76% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.883	6364084	463297	88.310	89.871
2	13.071	842476	52218	11.690	10.129
Total		7206560	515515	100.000	100.000

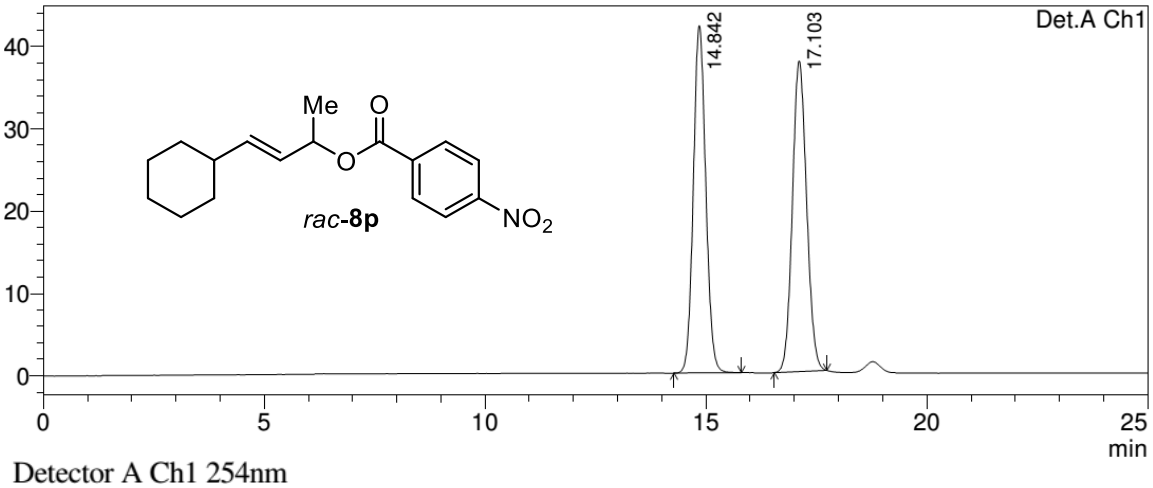
Enantioenriched, (*R*)-**3o**, 70% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.880	1939073	142960	14.760	17.358
2	13.055	11198627	680624	85.240	82.642
Total		13137700	823584	100.000	100.000

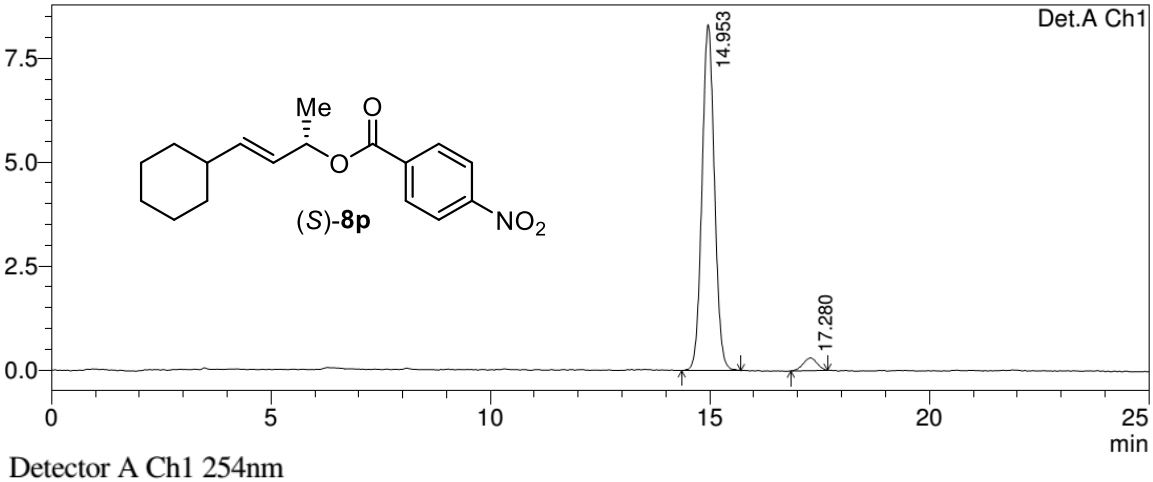
Racemic **8p**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.842	826154	42198	49.438	52.792
2	17.103	844935	37734	50.562	47.208
Total		1671089	79932	100.000	100.000

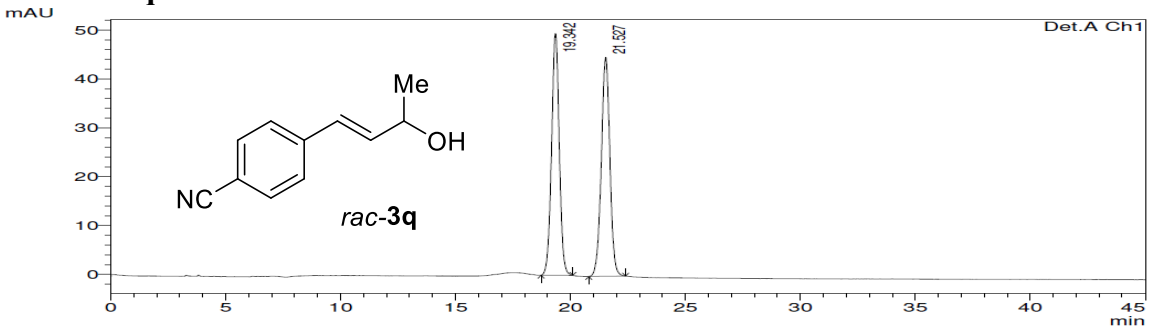
Enantioenriched, (*S*)-**8p**, 92% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.953	164549	8329	96.014	96.389
2	17.280	6831	312	3.986	3.611
Total		171381	8642	100.000	100.000

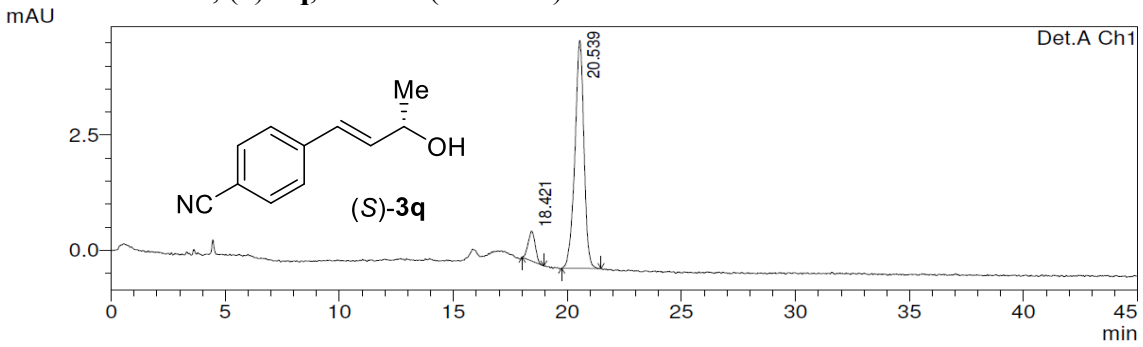
Racemic **3q**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.342	1155111	49477	49.791	52.459
2	21.527	1164813	44838	50.209	47.541
Total		2319925	94314	100.000	100.000

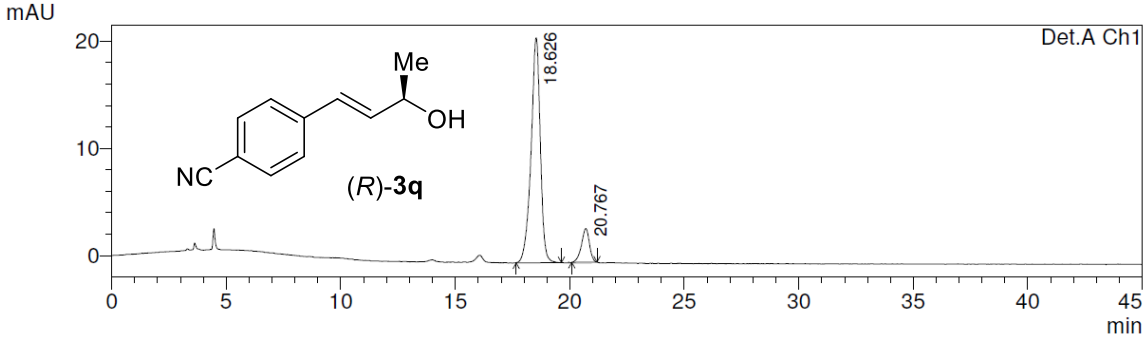
Enantioenriched, (*S*)-**3q**, 81% ee (retention)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.421	14121	651	9.377	11.620
2	20.539	136481	4953	90.623	88.380
Total		150602	5604	100.000	100.000

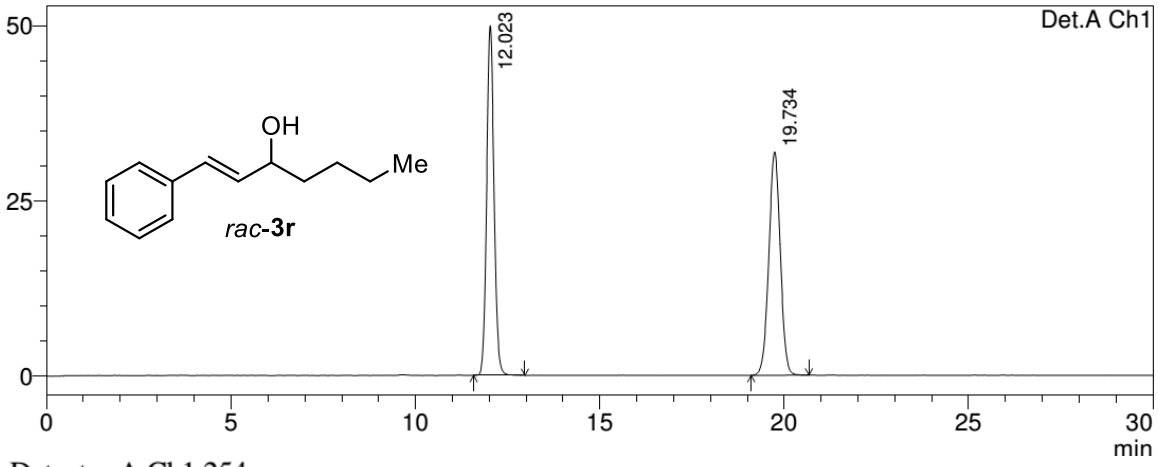
Enantioenriched, (*R*)-**3q**, 77% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.626	590432	20989	88.552	86.952
2	20.767	76334	3150	11.448	13.048
Total		666766	24139	100.000	100.000

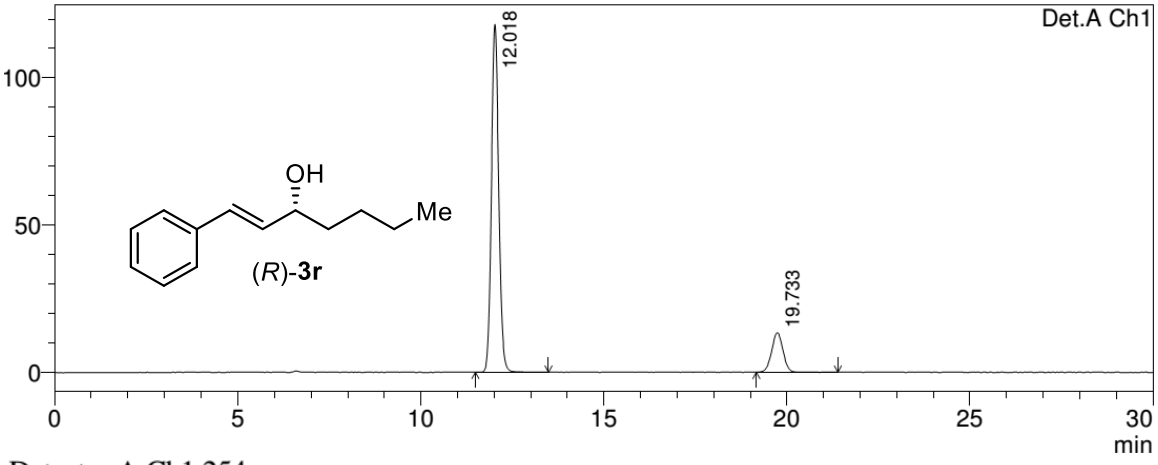
Racemic **3r**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.023	691681	49991	49.958	61.014
2	19.734	692858	31943	50.042	38.986
Total		1384539	81934	100.000	100.000

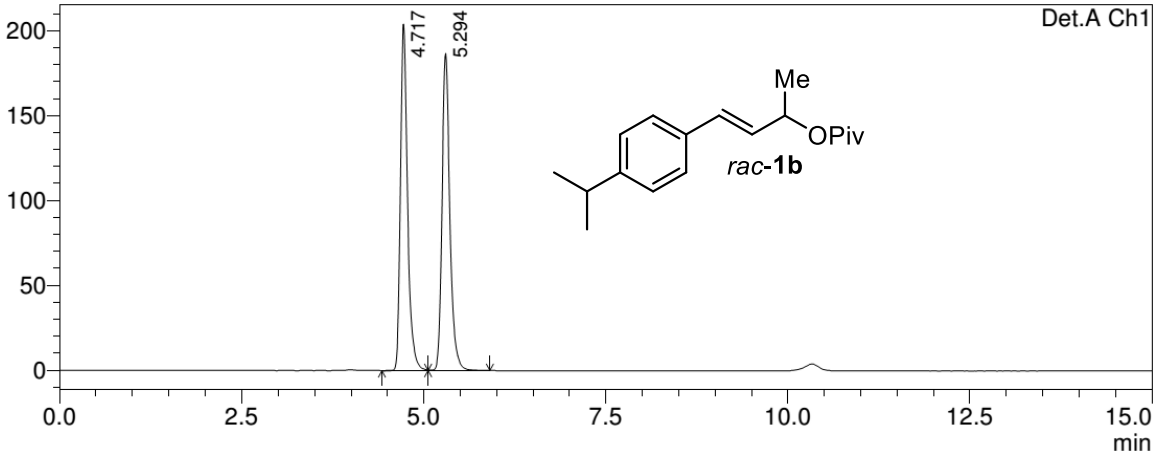
Enantioenriched, (*R*)-**3r**, 70% ee (inversion)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.018	1639195	118061	84.974	89.781
2	19.733	289866	13438	15.026	10.219
Total		1929061	131499	100.000	100.000

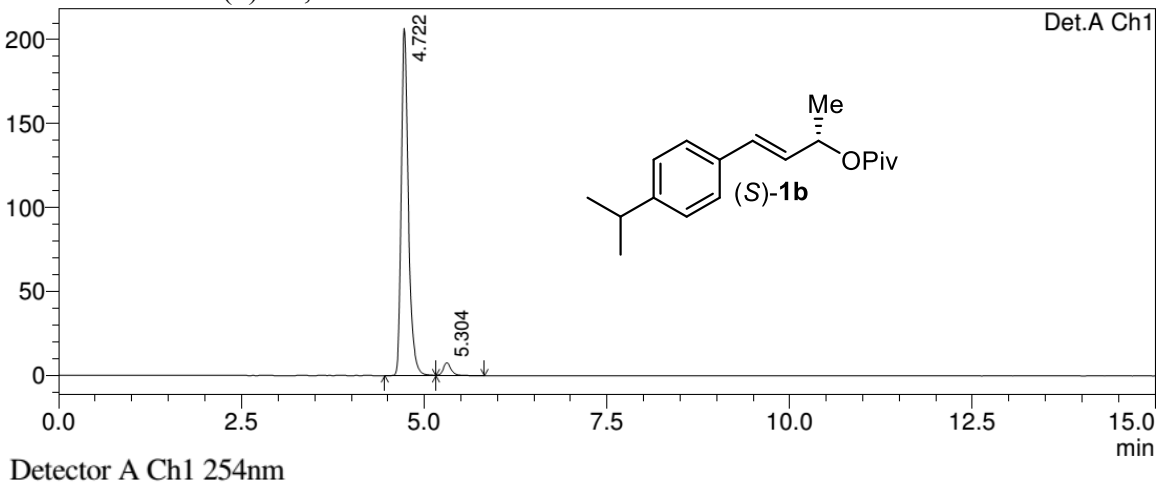
Racemic **1b**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.717	1392193	203778	49.938	52.175
2	5.294	1395650	186791	50.062	47.825
Total		2787843	390568	100.000	100.000

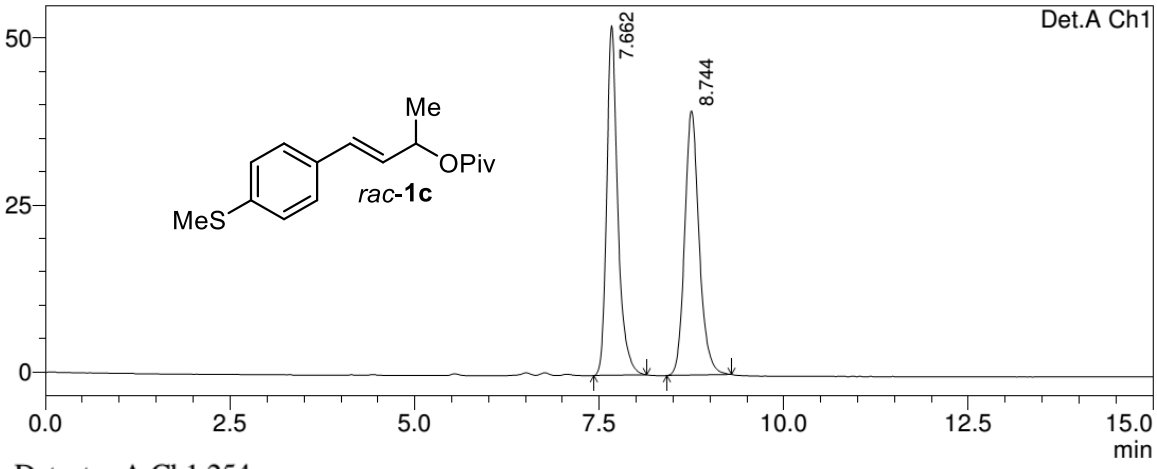
Enantioenriched (*S*)-**1b**, 92% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.722	1414357	206984	96.025	96.420
2	5.304	58546	7686	3.975	3.580
Total		1472902	214669	100.000	100.000

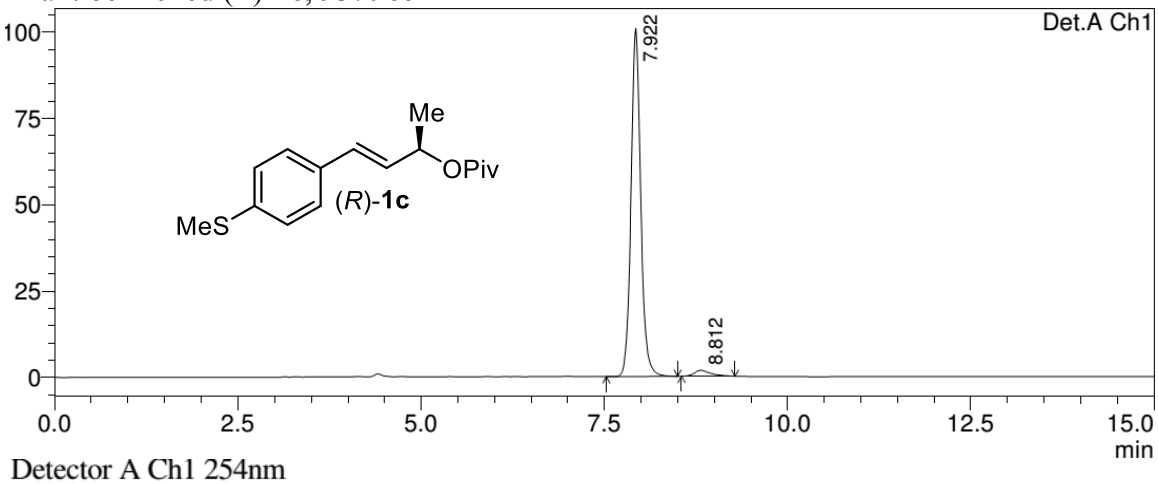
Racemic **1c**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.662	545452	52377	50.258	56.929
2	8.744	539849	39627	49.742	43.071
Total		1085301	92004	100.000	100.000

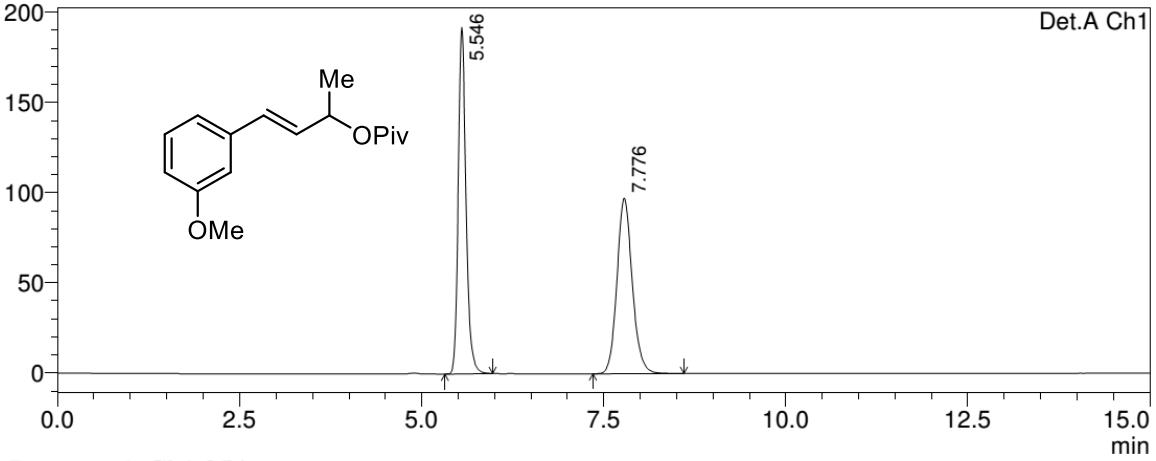
Enantioenriched (*R*)-**1c**, 93% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.922	929334	100908	97.154	98.318
2	8.812	27225	1726	2.846	1.682
Total		956559	102634	100.000	100.000

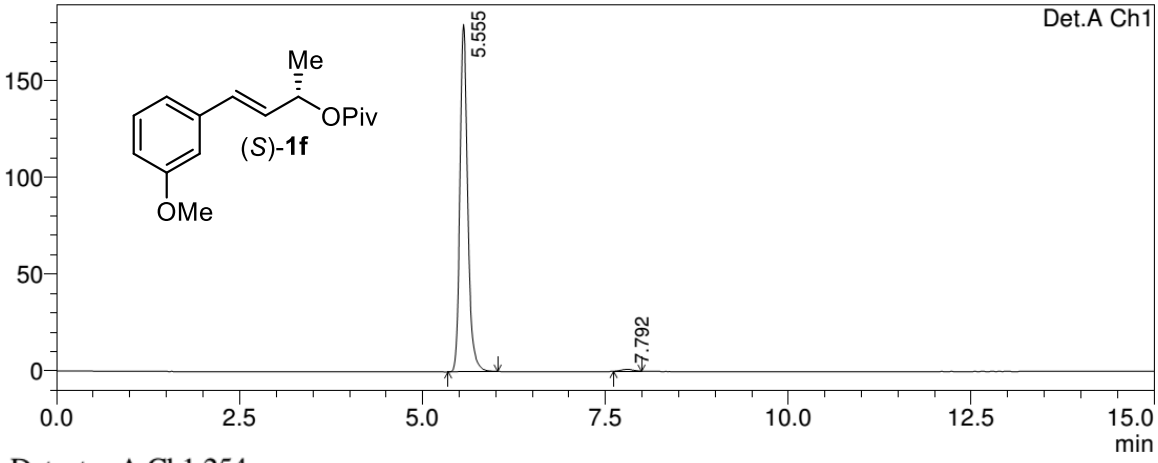
Racemic **1f**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.546	1421132	192117	49.933	66.385
2	7.776	1424963	97280	50.067	33.615
Total		2846095	289397	100.000	100.000

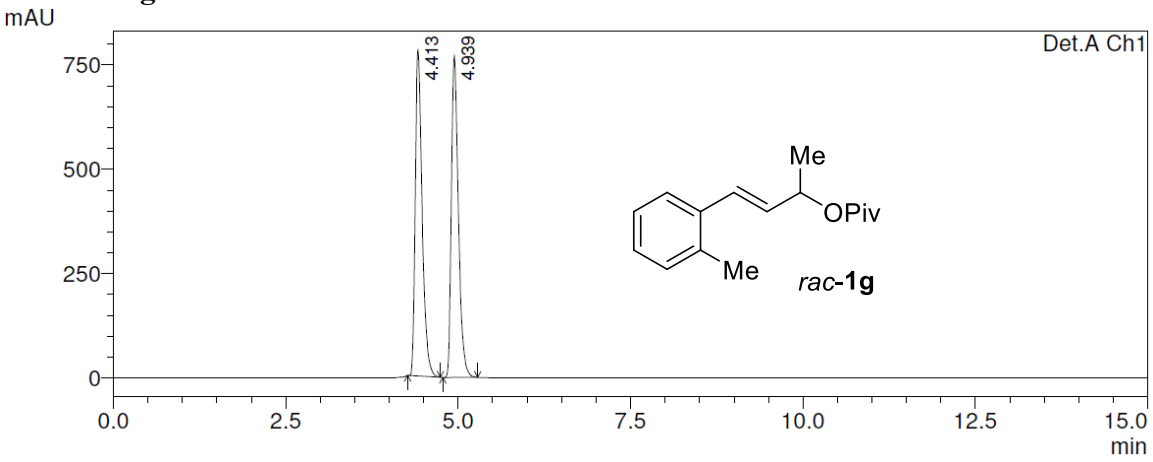
Enantioenriched (*S*)-**1f**, 98% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.555	1321114	179619	99.127	99.463
2	7.792	11641	971	0.873	0.537
Total		1332754	180589	100.000	100.000

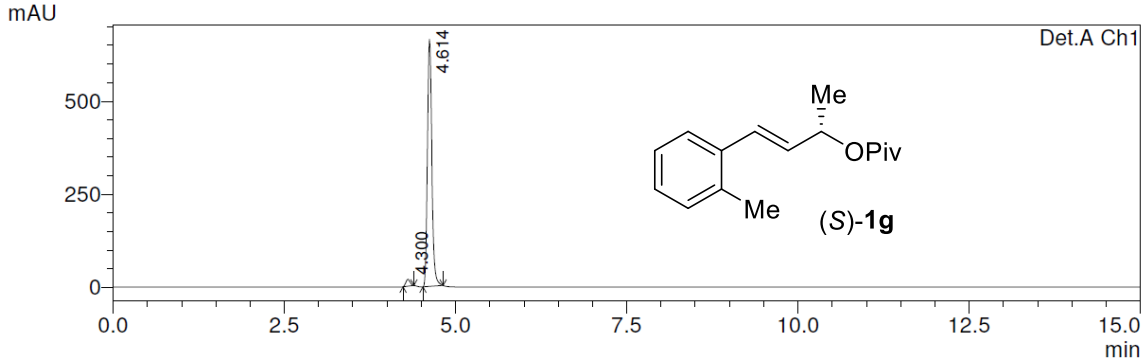
Racemic **1g**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.413	5415837	782608	49.859	50.324
2	4.939	5446528	772532	50.141	49.676
Total		10862365	1555140	100.000	100.000

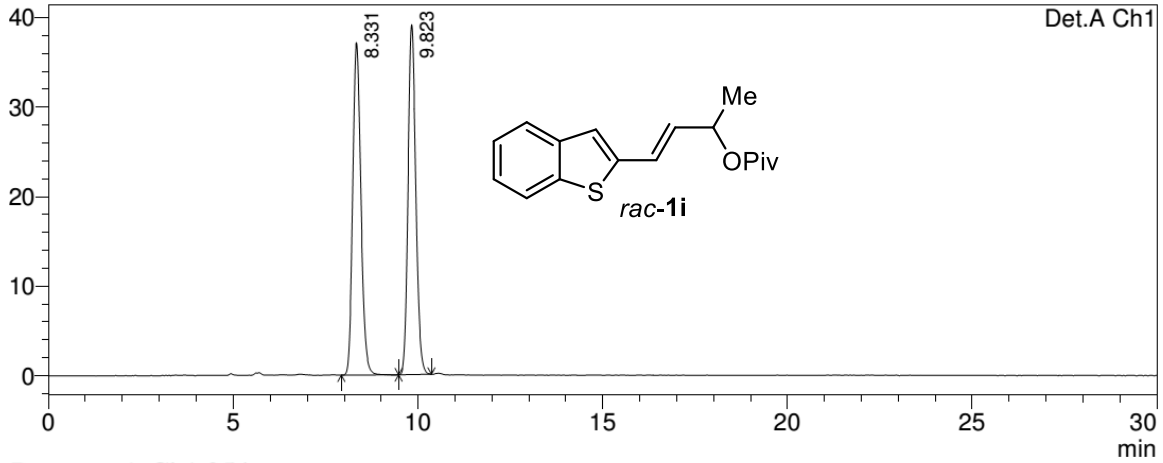
Enantioenriched (*S*)-**1g**, 94% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.300	83718	18747	2.715	2.745
2	4.614	2999625	664222	97.285	97.255
Total		3083343	682969	100.000	100.000

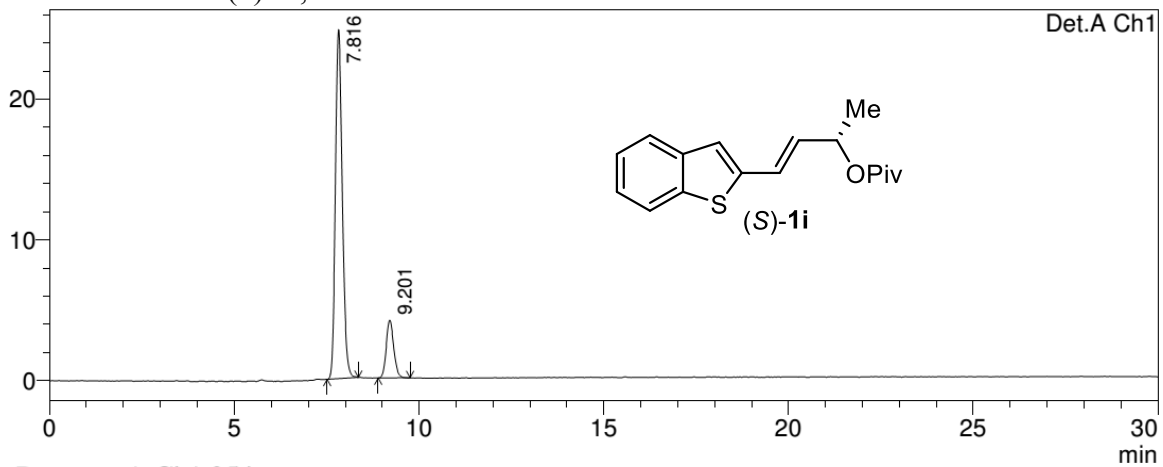
Racemic **1i**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.331	575382	37189	50.170	48.743
2	9.823	571493	39106	49.830	51.257
Total		1146875	76295	100.000	100.000

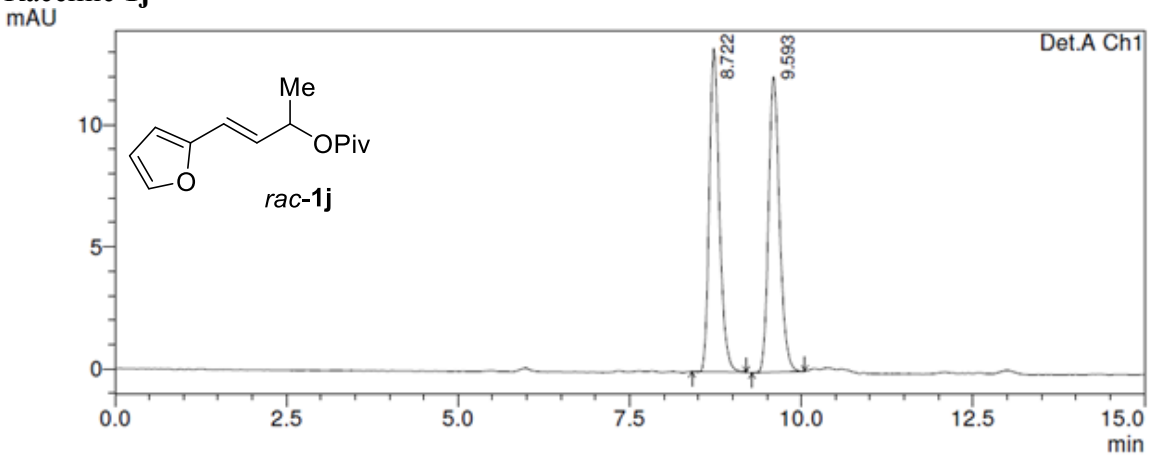
Enantioenriched (*S*)-**1i**, 70% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.816	321095	24793	84.870	85.840
2	9.201	57242	4090	15.130	14.160
Total		378336	28883	100.000	100.000

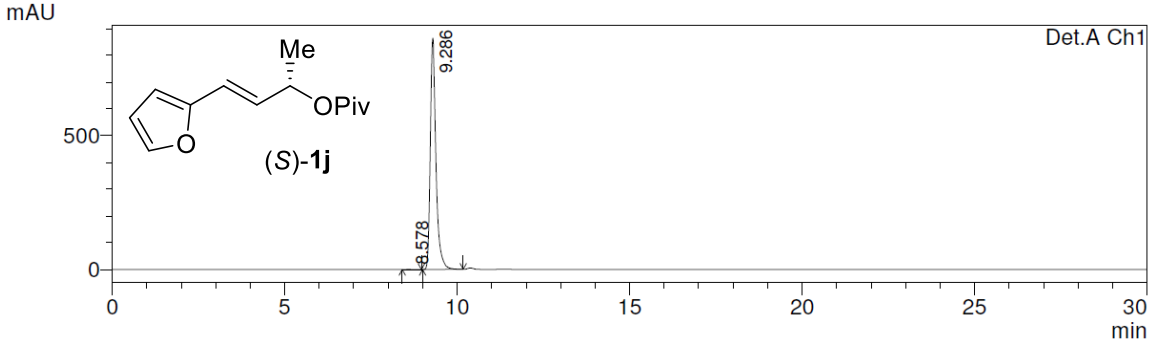
Racemic **1j**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.722	136201	13271	50.103	52.242
2	9.593	135642	12132	49.897	47.758
Total		271843	25403	100.000	100.000

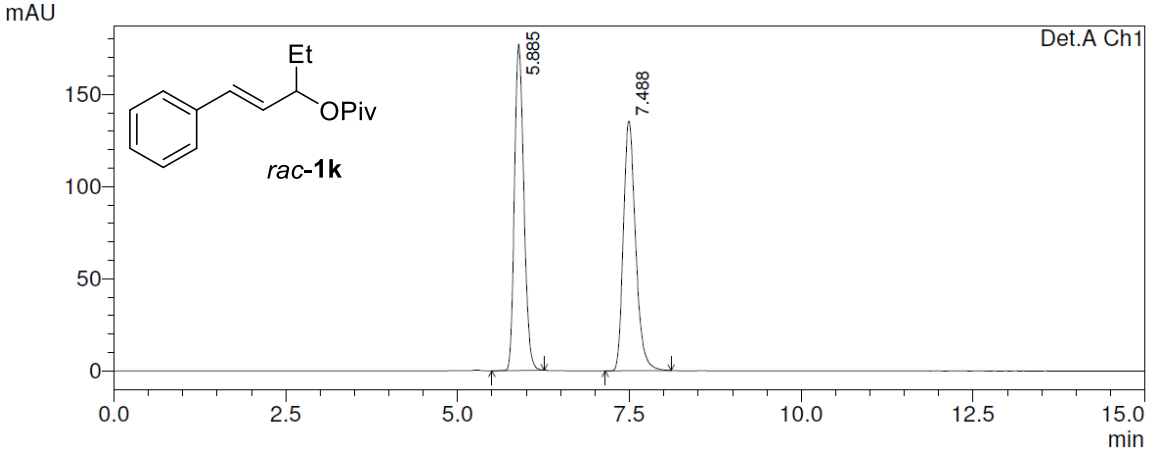
Enantioenriched (*S*)-**1j**, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.578	7142	571	0.072	0.066
2	9.286	9953521	863992	99.928	99.934
Total		9960662	864563	100.000	100.000

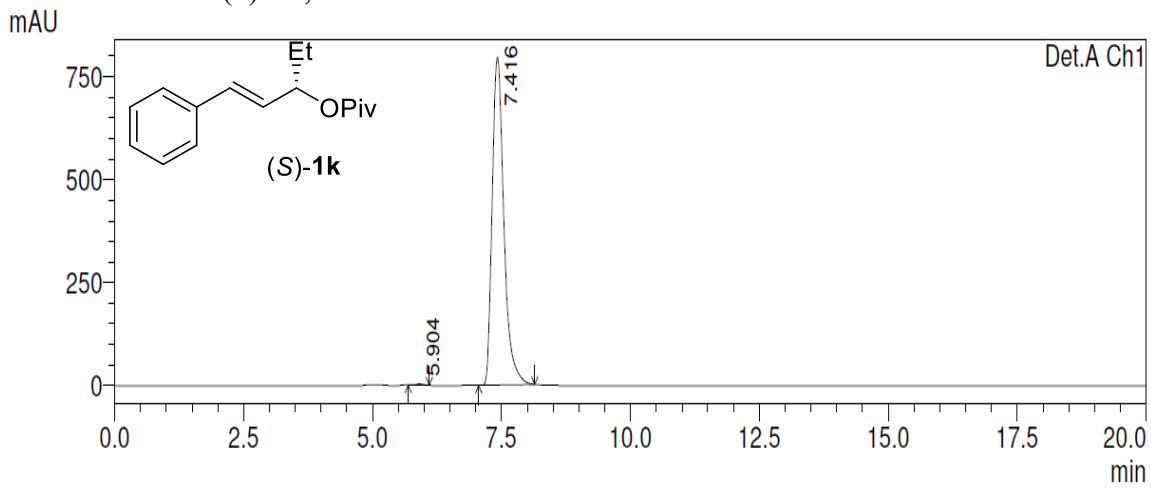
Racemic **1k**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.885	1677000	176994	50.017	56.641
2	7.488	1675869	135488	49.983	43.359
Total		3352870	312481	100.000	100.000

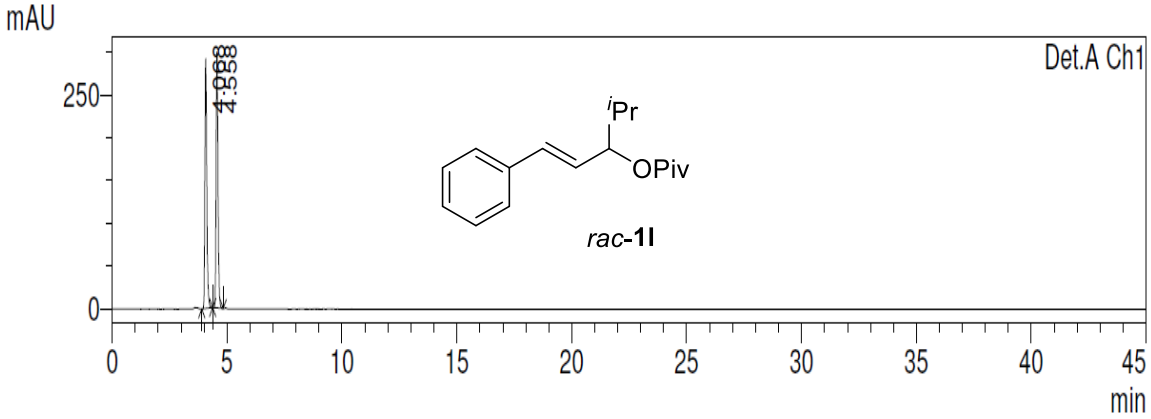
Enantioenriched (*S*)-**1k**, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.904	29135	3229	0.232	0.405
2	7.416	12554498	794821	99.768	99.595
Total		12583633	798050	100.000	100.000

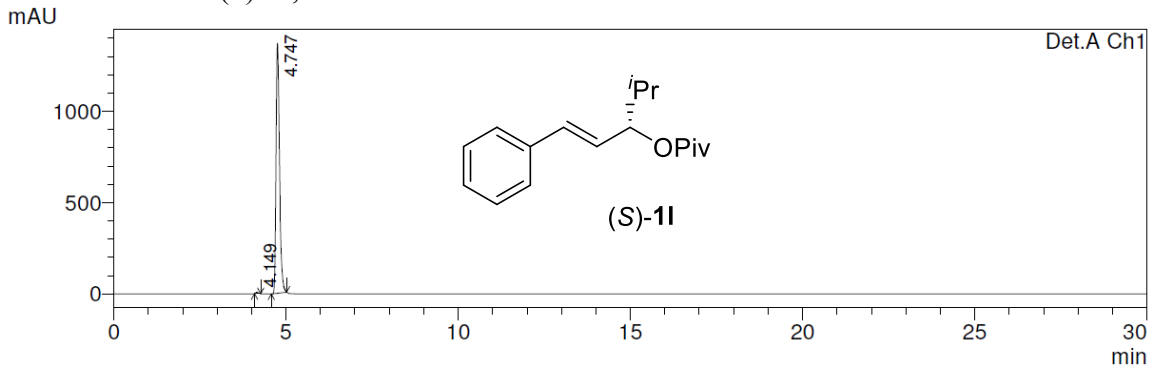
Racemic **1l**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.068	1669161	291954	49.996	49.430
2	4.558	1669422	298692	50.004	50.570
Total		3338582	590646	100.000	100.000

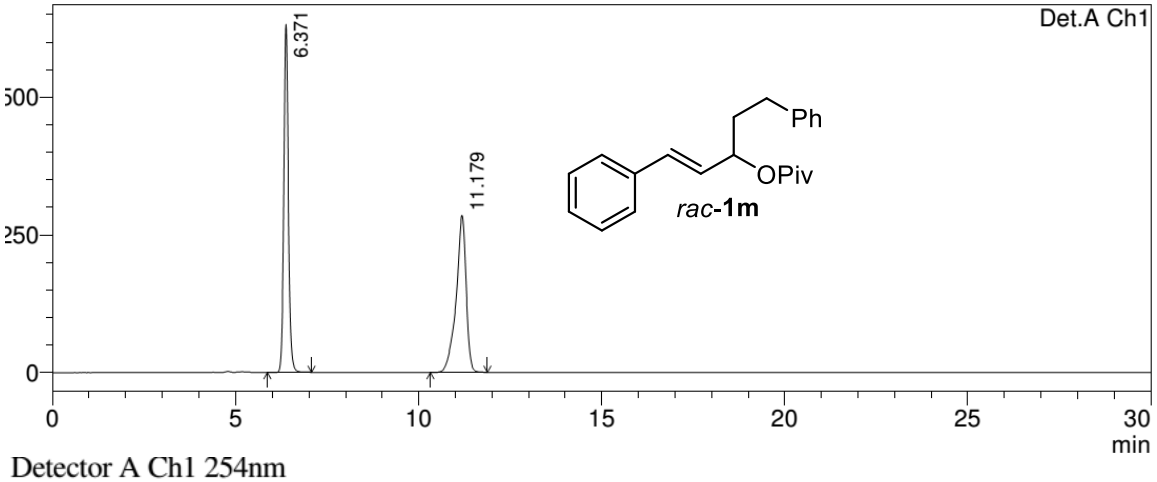
Enantioenriched (*S*)-**1l**, 99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.149	46047	8338	0.476	0.605
2	4.747	9626484	1369240	99.524	99.395
Total		9672531	1377578	100.000	100.000

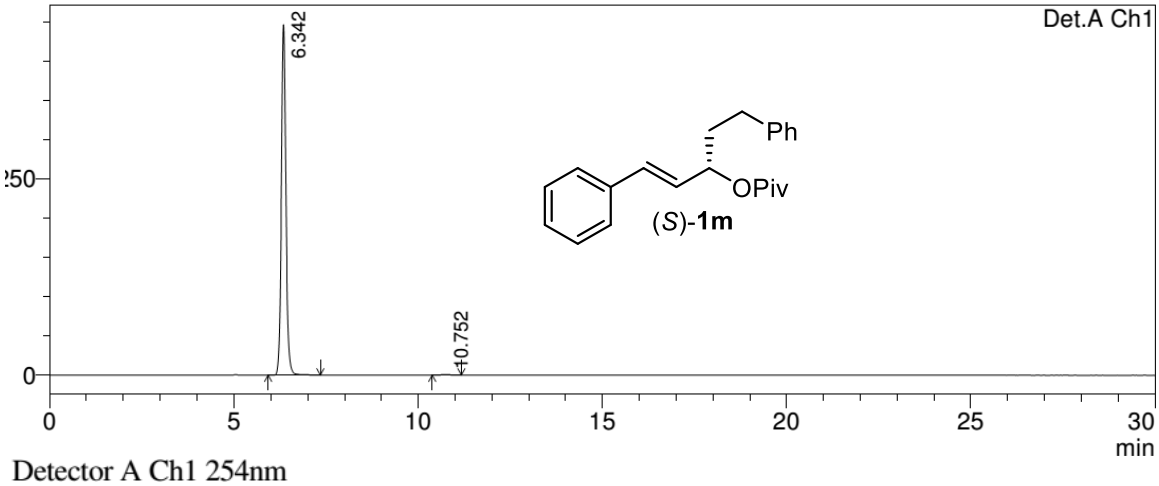
Racemic **1m**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.371	5421382	631961	49.966	68.882
2	11.179	5428694	285488	50.034	31.118
Total		10850076	917449	100.000	100.000

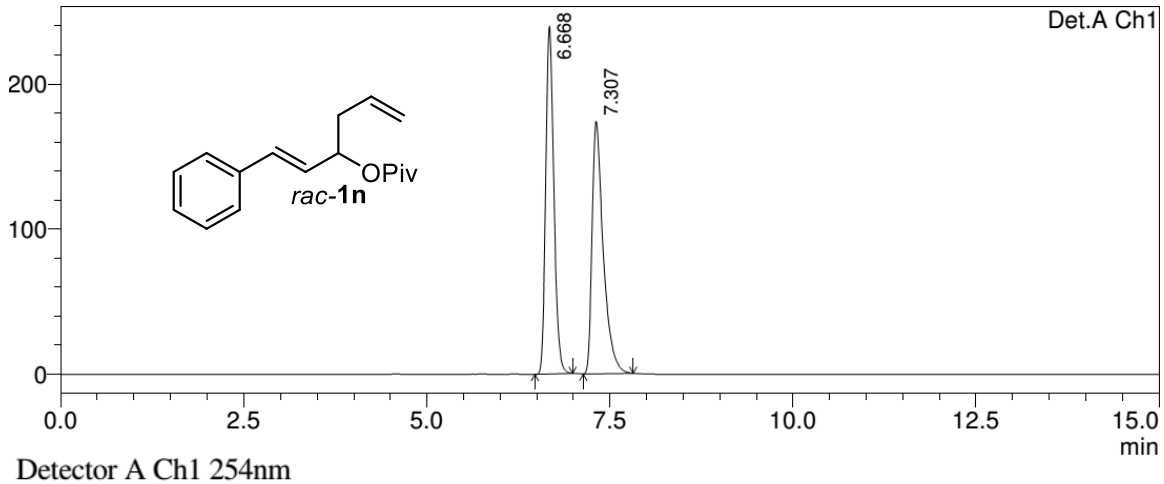
Enantioenriched (*S*)-**1m**, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.342	3836651	446020	99.772	99.885
2	10.752	8785	514	0.228	0.115
Total		3845436	446534	100.000	100.000

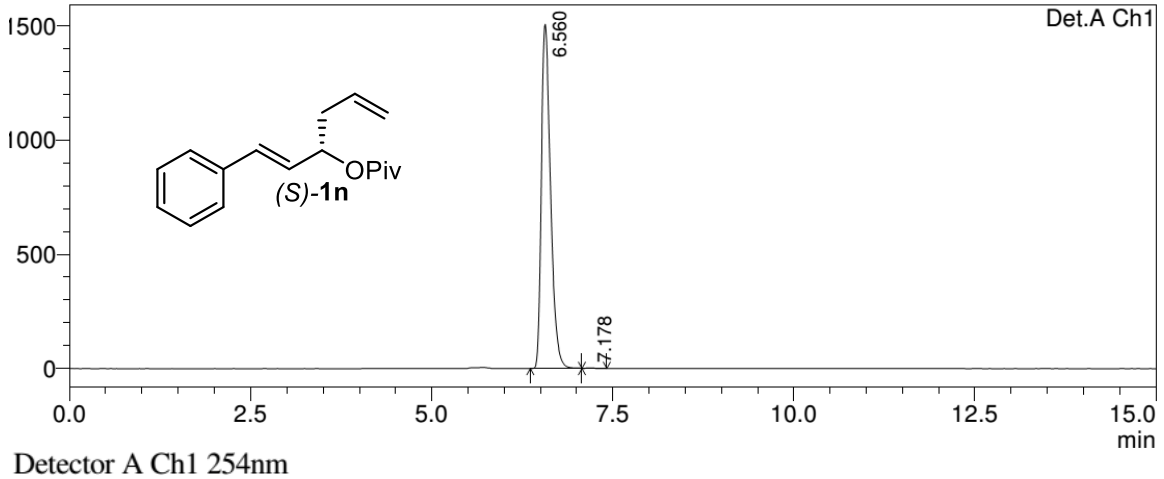
Racemic **1n**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.668	1856825	239598	50.111	57.948
2	7.307	1848604	173875	49.889	42.052
Total		3705428	413473	100.000	100.000

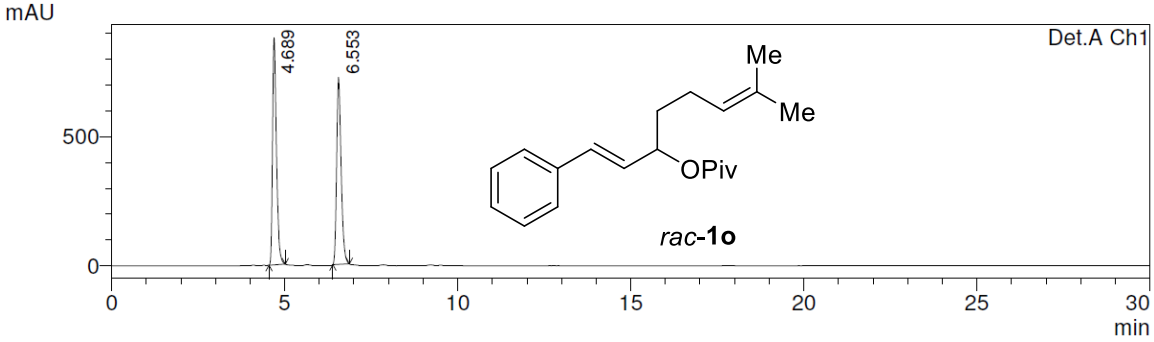
Enantioenriched (*S*)-**1n**, >99% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.560	13252275	1506598	99.935	99.911
2	7.178	8583	1338	0.065	0.089
Total		13260858	1507935	100.000	100.000

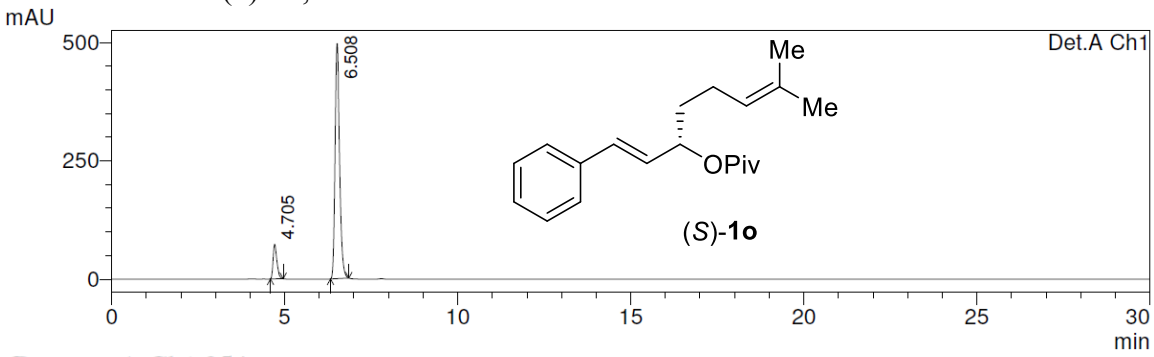
Racemic **1o**



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.689	6758149	879153	50.260	54.796
2	6.553	6688188	725245	49.740	45.204
Total		13446337	1604397	100.000	100.000

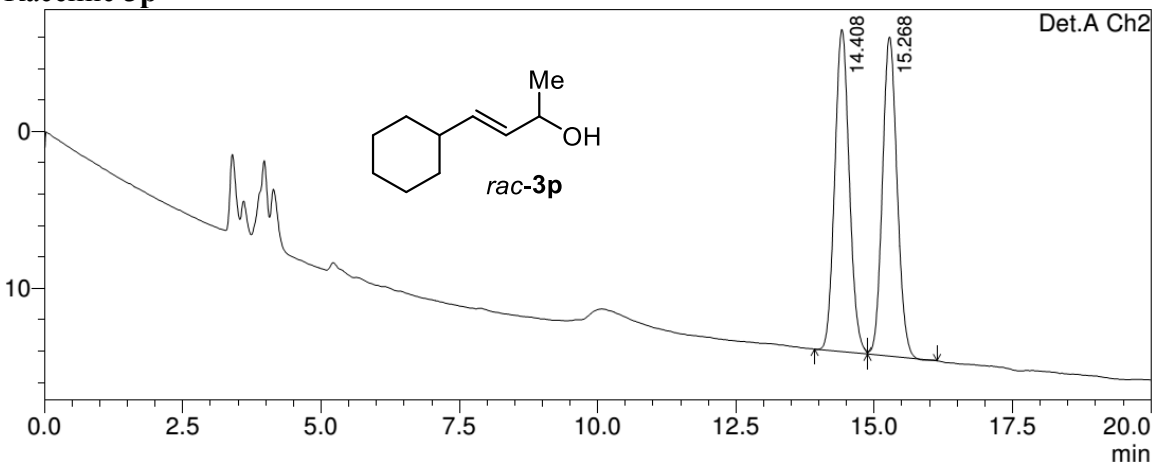
Enantioenriched (*S*)-**1o**, 78% ee



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.705	549103	73043	10.717	12.824
2	6.508	4574751	496540	89.283	87.176
Total		5123854	569583	100.000	100.000

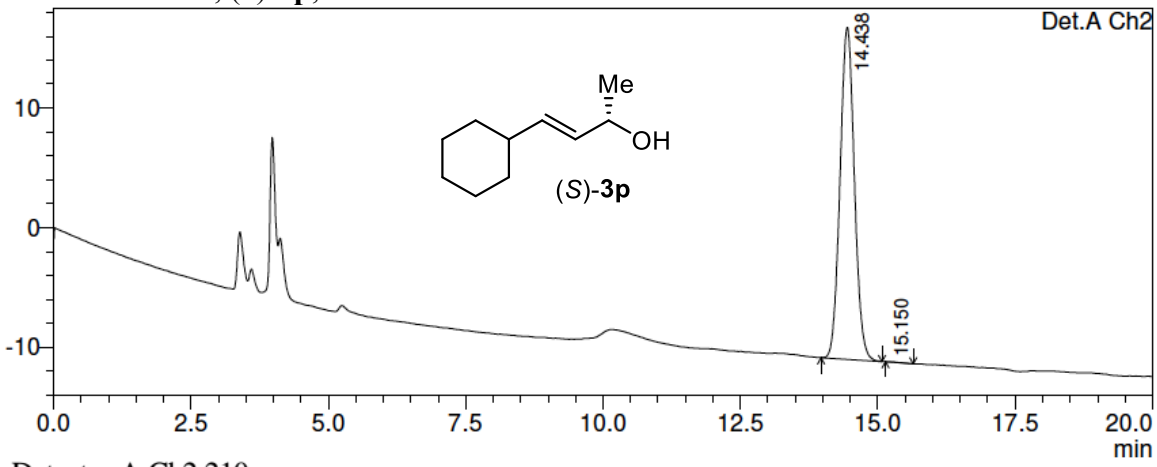
Racemic **3p**



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.408	376692	20530	50.110	50.215
2	15.268	375033	20354	49.890	49.785
Total		751724	40884	100.000	100.000

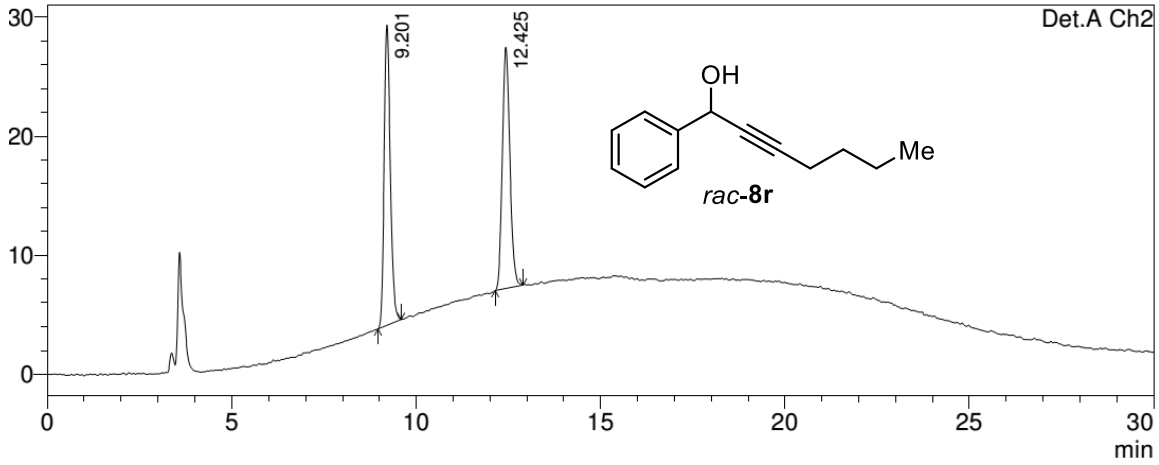
Enantioenriched, (*S*)-**3p**, >99% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.438	505358	27750	99.944	99.996
2	15.150	281	1	0.056	0.004
Total		505640	27751	100.000	100.000

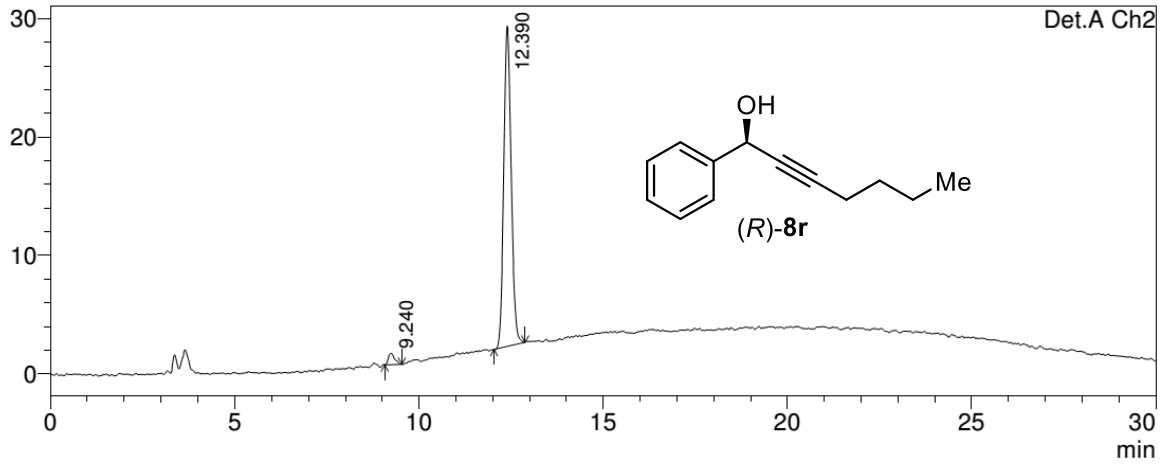
Racemic **8r**



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.201	292810	25239	50.298	55.461
2	12.425	289346	20268	49.702	44.539
Total		582156	45507	100.000	100.000

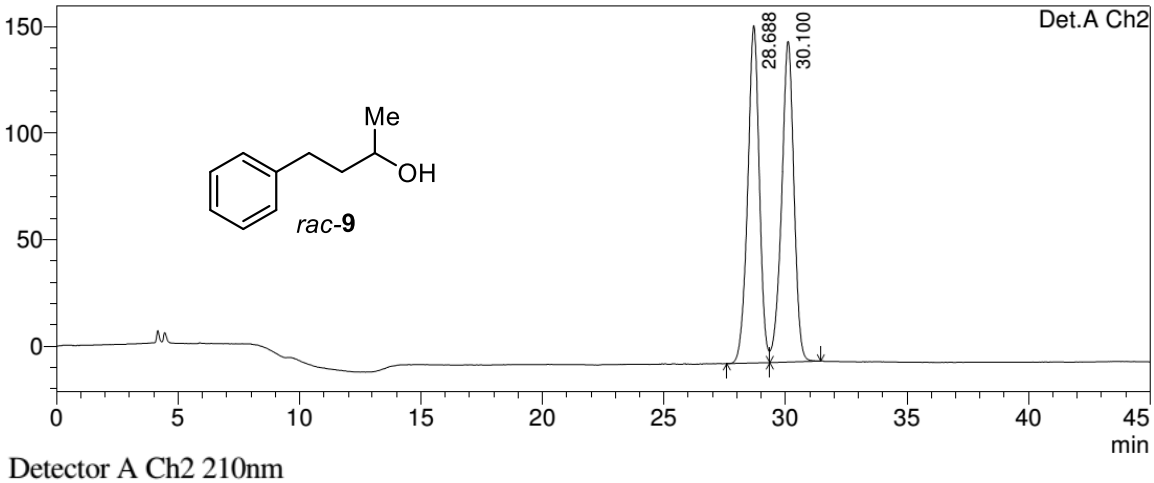
Enantioenriched, (*R*)-**8r**, 94% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.240	11371	942	2.909	3.367
2	12.390	379442	27046	97.091	96.633
Total		390813	27989	100.000	100.000

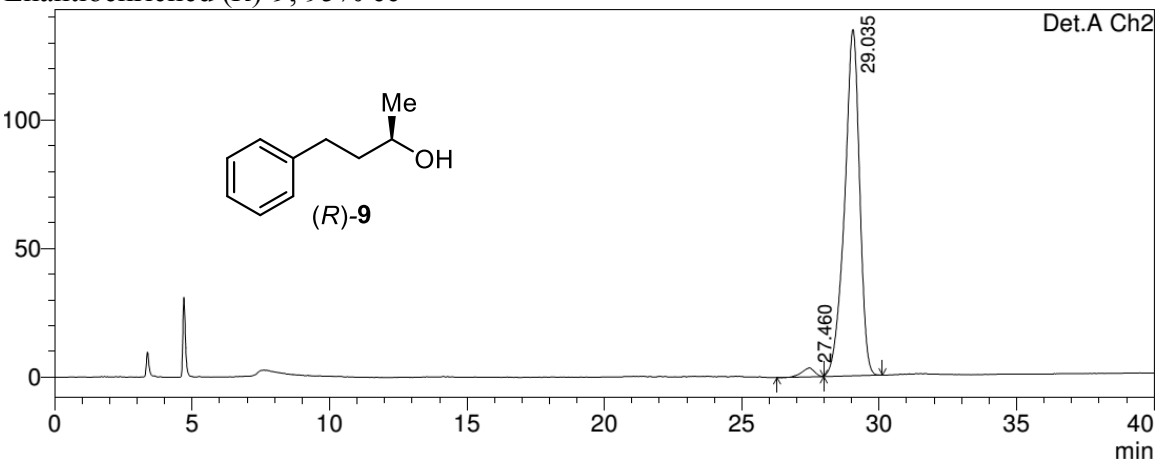
Racemic **9**



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.688	5275484	158371	49.824	51.253
2	30.100	5312766	150628	50.176	48.747
Total		10588250	309000	100.000	100.000

Enantioenriched (*R*)-**9**, 95% ee



Detector A Ch2 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.460	111513	3478	2.132	2.516
2	29.035	5118028	134752	97.868	97.484
Total		5229541	138229	100.000	100.000