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General Information.

All reactions were carried out in dry glassware under an Argon atmosphere using standard Schlenk line techniques or in a Vacuum Atmospheres glovebox under nitrogen atmosphere. All solvents were purified by passage through solvent purification columns and further degassed with Argon.[1] NMR solvents for air-sensitive compounds were degassed by sparging with nitrogen and passed through a solvent purification column prior to use. Commercially available reagents were used as received unless otherwise noted. Substrates in the liquid state were degassed with Argon and passed through a plug of neutral alumina prior to use. Solid substrates were used after purification by silica gel column chromatography.

Standard NMR spectroscopy experiments were conducted on a Varian INOVA 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer. Chemical shifts are referenced to the residual solvent peak ($CDCl_3$) multiplicity is reported as follows: (s: singlet, d: doublet, t: triplet: q: quartet, br: broad, m: multiplet). Spectra were analyzed and processed using MestReNova.

Gas chromatography data was obtained using an Agilent 6850 FID gas chromatograph equipped with an Agilent HP-5 5% phenyl methyl siloxane capillary column (J&W Scientific). GC instrument conditions: Inlet temperature- 250 °C; Detector temperature- 300 °C; Hydrogen flow- 30 mL/min; Air flow- 400

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996,** *15,* 1518-1520.

mL/min; Makeup flow- 25 mL/min. GC method: 50 °C for 1 min, then temperature ramp (35 °C/min) for 7 min to 300 °C followed by an isothermal period at 300 °C for 3 min. Chiral gas chromatography was carried out on an Agilent 6850 FID gas chromatograph equipped with an Agilent GTA column. GC instrument conditions: Inlet temperature- 180 °C; Detector temperature- 250 °C; Hydrogen flow- 32 mL/min; Air flow- 400 mL/min; Makeup flow- 30 mL/min. GC method: 80 °C for 12 min, isocratic.

High-resolution mass spectra (HRMS) data were obtained on a JEOL MSRoute mass spectrometer using FAB+ or EI+ methods. Analytical SFC data was obtained on a Mettler SFC supercritical CO_2 analytical chromatography system equipped with Chiracel OD-H, OJ–H or Chirapak AD-H columns (4.6 mm x 25 cm). Column temperature was maintained at 40°C. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm.

Substrates for AROCM

Substrates for AROCM were synthesized as previously reported in the literature: **2**,[2] **5a**,[3] **b**,[3] **c**,[4] **d**[5] were synthesized according to the provided references. Catalyst **1** was synthesized as previously reported.[6]

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[2] W. Kirmse, F. Scheidt, H-J. Vater, *J. Am. Chem. Soc.*, **1978**, *100*, 3945.
[3] A. H. Hoveyda, P. J. Lombardi, R. V. O'Brien, A. R. Zhugralin, *J. Am. Chem. Soc.* **2009**, *131*, 8378.
[4] R. Gandolfi, M. Ratti, L. Toma, C. De Micheli, *Heterocycles* **1979**, *12*, 897.

Representative Procedure for AROCM

In a glovebox, cyclobutene **2** (26.6 mg, 0.1 mmol, 1 equiv) and allyl benzoate (**6b**, 113 mg, 0.7 mmol, 7 equiv) were dissolved in 0.15 mL THF. To this solution was added 50 μL of a stock solution (0.02 M in THF) of catalyst **1**. The reaction vial was capped and stirred for 1.5 h and then quenched with an excess of ethyl vinyl ether. The reaction mixture was concentrated and *Z*/*E* ratios were determined by 500 MHz ^{1}H NMR (products **7a**-**c**, **e**-**k**) or GC (product **4**). The crude was subjected to flash chromatography or preparative TLC to afford the desired AROCM product (**7f**, 25.9 mg, 61% isolated yield, 88:12 Z/E, 97% ee (*Z*), 88% ee (*E*)). Pure products (or *E*/*Z* mixtures in the case of **7i**, and *E*-**7j**) were submitted to analytical SFC to determine enantiomer excess.

Characterization data for AROCM products

Acetate **4**.

79% yield (GC), 85% *Z*.

Z-**4**:

$[\alpha]_D^{25}$ – 9.34° (c = 0.52, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 10H), 5.88 – 5.77 (2x m, 1H), 5.71 – 5.64 (m, 1H), 5.34 (m, 1H), 5.29 (m, 1H), 4.64 (AB d, *J* = 10.5 Hz, 1H), 4.63 (AB d, *J* = 10.5 Hz, 1H), 4.61 (m, 1H), 4.51 – 4.46 (m, 1H), 4.45 (AB d, *J* = 10.5 Hz, 1H), 4.43 (AB d, *J* = 10.5 Hz, 1H), 4.21

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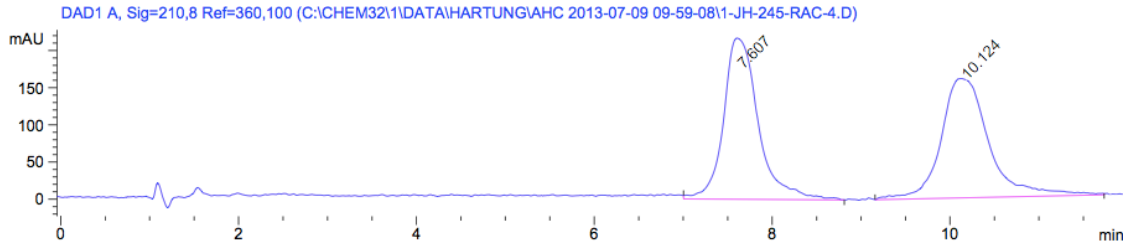
[5] A. H. Hoveyda, R. Khan, M. Kashif, P. J. Lombardi, R. V. O'Brien, S. Torker, A. R. Zhugralin, *J. Am. Chem. Soc.* **2012**, *134*, 12438.
[6] J. Hartung, R. H. Grubbs, *J. Am. Chem. Soc.* **2013**, *135*, 10183.

(ddd, J = 9.1, 5.0, 1.0 Hz, 1H), 3.87 (dd, J = 7.5, 5.0 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 138.6, 138.4, 135.5, 131.9, 128.5, 128.4, 128.4, 127.8, 127.7, 127.7, 127.5, 119.2, 82.2, 76.6, 70.7, 70.6, 60.8, 21.1. HRMS (FAB+) calculated for $C_{23}H_{27}O_4$ [M+H]: 367.1909; found 367.1904.

Separation conditions for *Z*-**4**: OJ-H, 5% IPA, 2.5 mL/min. 95% ee

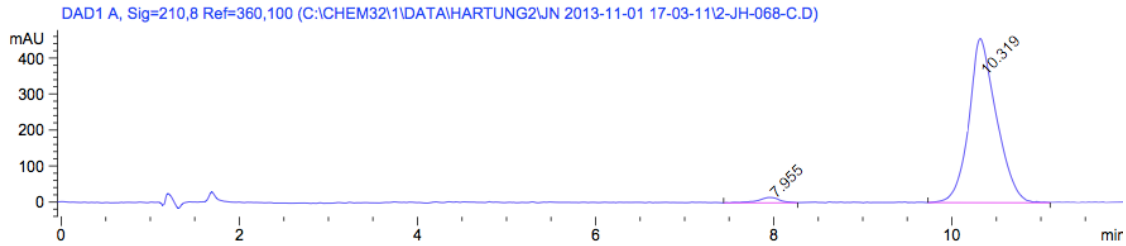
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.607	VV	0.4141	5907.10059	216.66869	49.4689
2	10.124	VB	0.5585	6033.94629	160.53769	50.5311
Totals :				1.19410e4	377.20638	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

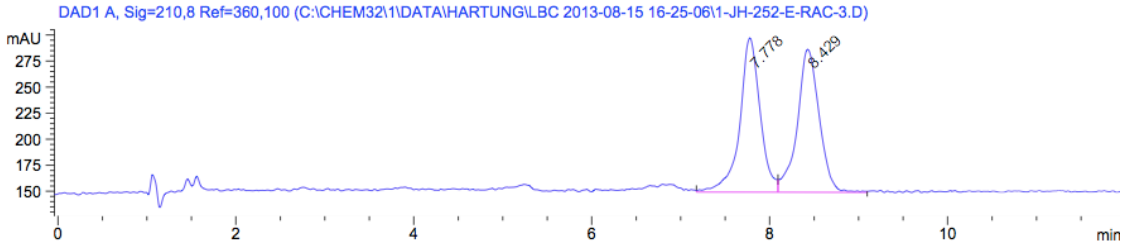
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.955	BV	0.2626	264.61841	14.94419	2.6277
2	10.319	BV	0.3029	9805.57031	456.01086	97.3723
Totals :				1.00702e4	470.95505	

E-**4**:

$[\alpha]_D^{25}$ – 11.8° (c = 0.24, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 10H), 5.88 – 5.74 (3x m, 1H), 5.33 (m, 1H), 5.29 (m, 1H), 4.65 (AB d, *J* = 9.3 Hz, 1H), 4.63 (AB d, 9.3 Hz, 1H), 4.61 (d, *J* = 6.0 Hz, 2H), 4.45 (AB d, *J* = 10.6 Hz, 1H), 4.43 (AB d, *J* = 10.7 Hz, 1H), 3.89 (dd, *J* = 6.4, 5.1 Hz, 1H), 3.85 (dd, *J* = 7.2, 5.1 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9, 138.41, 138.33, 135.5, 131.7, 128.46, 128.45, 128.40, 127.8, 127.75, 127.6, 127.55, 119.1, 82.4, 81.3, 70.9, 70.6, 64.4, 21.1. HRMS (FAB+) calculated for $C_{23}H_{27}O_4$ [M+H]: 367.1909; found 367.1922.

Separation conditions for *E*-**4**: OJ-H, 7% IPA, 2.5 mL/min. 85% ee

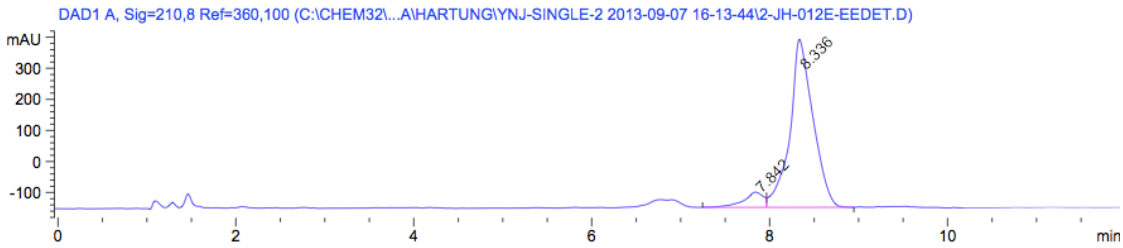
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.778	VV	0.2344	2366.55688	148.09634	50.1123
2	8.429	VB	0.2563	2355.94971	137.19626	49.8877
Totals :				4722.50659	285.29260	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.842	BV	0.2188	764.89539	48.82001	7.2443
2	8.336	VB	0.2556	9793.63672	540.08466	92.7557
Totals :				1.05585e4	588.90466	

Silyl ether **7a**.[7]

66% isolated yield, 88% *Z*.

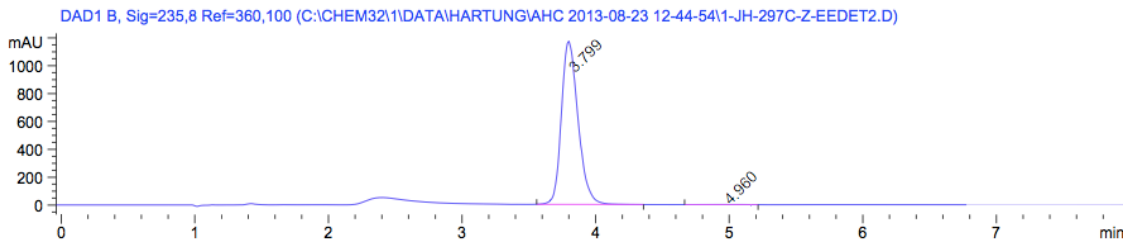
Z-**7a**:

$[\alpha]_D^{25}$ + 4.72° (c = 1.06, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.3, 10.4, 6.4 Hz, 1H), 5.80 – 5.75 (m, 1H), 5.49 (dddd, *J* = 11.2, 8.9, 1.7, 1.1 Hz, 1H), 5.23 (ddd, *J* = 17.3, 1.8, 1.2 Hz, 1H), 5.16 (ddd, *J* = 10.4, 1.8, 1.0 Hz, 1H), 4.34 (ddd, *J* = 8.9, 7.0, 1.1 Hz, 1H), 4.15 (m, 2H), 3.90 (ddt, *J* = 7.3, 6.4, 1.1 Hz, 1H), 2.31 (br, 1H), 0.88 (s, 9H), 0.86 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 134.4, 130.3, 116.5, 77.5, 72.8, 59.3, 26.1, 25.9, 18.5, 18.3, -4.2, -4.2, -4.3, -4.5. HRMS (EI+) calculated for $C_{19}H_{41}O_3Si_2$ [M+H]: 375.2594; found 375.2583.

Z-**7a** was derivatized by benzoylation and subsequent desilylation to afford a product spectroscopically identical to *Z*-**7b** prior to chiral SFC analysis, which indicated 99% ee (see directly below (p. S10) for racemic trace).

Enantioenriched:

[7] S. Saito, H. Itoh, Y. Ono, K. Nishioka, T. Moriwake, *Tetrahedron: Asymmetry* **1993**, *4*, 5.



Signal 2: DAD1 B, Sig=235,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.799	BB	0.1373	1.01426e4	1167.74316	99.7523
2	4.960	BV	0.1919	25.18901	1.83767	0.2477
Totals :				1.01678e4	1169.58084	

Diol **7b**.

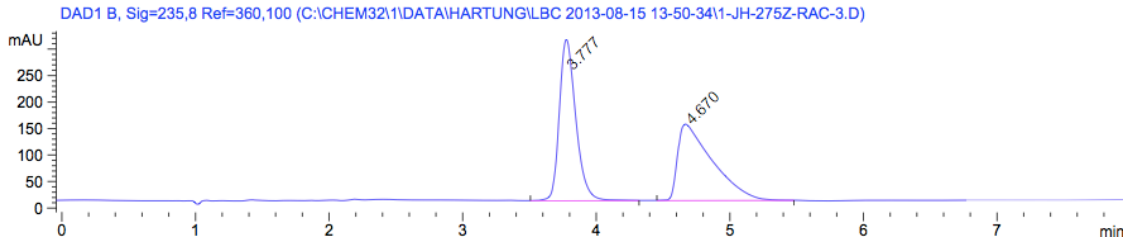
67% isolated yield, 75% *Z*.

Z-**7b**:

$[\alpha]_D^{25}$ – 30.7° (c = 0.60, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 5.89 (ddd, 17.3, 10.5, 6.2 Hz, 1H), 5.93 – 5.76 (2x m, 1H), 5.38 (ddd, *J* = 17.3, 1.5, 1.4 Hz, 1H), 5.28 (ddd, *J* = 10.6, 1.5, 1.4 Hz, 1H), 5.08 (ddd, *J* = 12.9, 7.7, 0.8 Hz, 1H), 4.83 (ddd, *J* = 12.6, 5.5, 1.0 Hz, 1H), 4.63 (dd, *J* = 8.0, 4.3 Hz, 1H), 4.25 (ddt, *J* = 6.8, 4.3, 1.3 Hz, 1H), 2.85 (br, 1H), 2.34 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 136.0, 133.3, 132.5, 130.0, 129.8, 128.6, 127.7, 118.0, 75.5, 70.4, 61.3. HRMS (EI+) calculated for $C_{14}H_{17}O_4$ [M+H]: 249.1127; found 249.1117.

Separation conditions for *Z*-**7b**: OD-H, 20% IPA, 2.5 mL/min. 91% ee

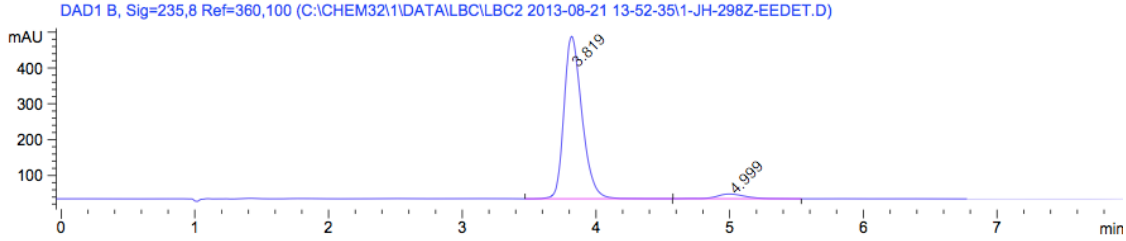
Racemate:



Signal 2: DAD1 B, Sig=235,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.777	BB	0.1325	2620.65259	304.35648	50.0092
2	4.670	BB	0.2558	2619.68433	144.28246	49.9908
Totals :				5240.33691	448.63893	

Enantioenriched:



Signal 2: DAD1 B, Sig=235,8 Ref=360,100

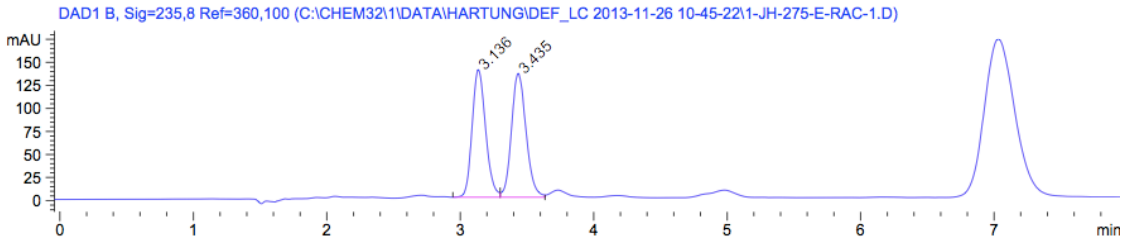
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.819	BB	0.1414	4247.60645	453.13589	95.4697
2	4.999	BB	0.2382	201.56192	13.19609	4.5303
Totals :				4449.16837	466.33198	

E-**7b**:

$[\alpha]_D^{25}$ – 1.57° (c = 0.06, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.41 (m, 2H), 6.02 (dtd, *J* = 15.7, 5.7, 1.3 Hz, 1H), 5.96 – 5.77 (m, 2H), 5.37 (ddd, *J* = 17.3, 1.5, 1.4 Hz, 1H), 5.29 (ddd, *J* = 10.6, 1.5, 1.4 Hz, 1H), 5.07 (m, 1H), 4.87 (m, 1H), 4.68 (m, 1H), 4.25 (m, 1H), 2.89 (br, 1H), 2.00 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 135.9, 133.3, 132.5, 130.1, 129.8, 128.6, 127.9, 118.0, 75.6, 70.3, 61.2.

Separation conditions for *E*-**7b**: OJ-H, 20% IPA, 2.5 mL/min. 67% ee

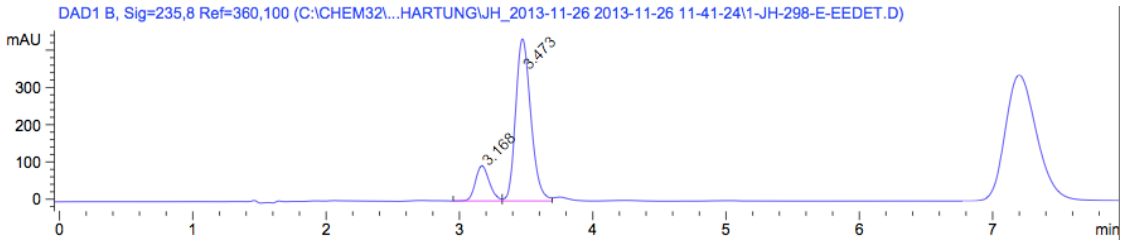
Racemate:



Signal 2: DAD1 B, Sig=235,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.136	BV	0.1100	971.22040	138.18152	48.7580
2	3.435	VV	0.1207	1020.70038	134.19174	51.2420
Totals :				1991.92078	272.37326	

Enantioenriched:



Signal 2: DAD1 B, Sig=235,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.168	BV	0.1130	686.64221	94.23962	16.5860
2	3.473	VV	0.1246	3453.24072	434.97318	83.4140
Totals :				4139.88293	529.21280	

Benzoate **7c**.

69% isolated yield, 75% *Z*.

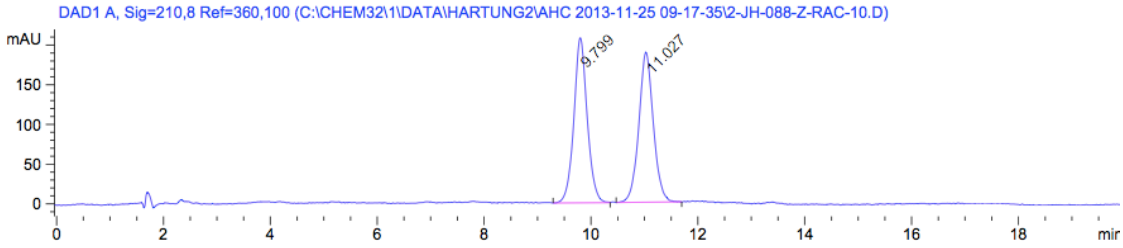
Z-**7c**:

$[\alpha]_D^{25}$ + 4.06° (c = 0.95, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 2H), 8.02 – 7.97 (m, 2H), 7.61 – 7.54 (2x m, 1H), 7.49 – 7.39 (2x m, 2H), 6.09 –

5.96 (3x m, 1H), 5.83 – 5.78 (m, 1H), 5.67 (dd, *J* = 11.0, 9.7 Hz, 1H), 5.52 (d, *J* = 17.3 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 4.56 (ddd, *J* = 13.4, 7.8, 1.4 Hz, 1H), 4.20 (ddd, *J* = 13.4, 5.7, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.6, 135.4, 133.5, 133.4, 131.8, 130.0, 129.9, 129.85, 129.80, 128.6, 128.6, 125.3, 120.4, 75.6, 71.4, 58.8. HRMS (FAB+) calculated for $C_{21}H_{21}O_5$ [M+H]: 353.1389; found 353.1381.

Separation conditions for *Z*-**7c**: OJ-H, 5% IPA, 2.5 mL/min. 96% ee

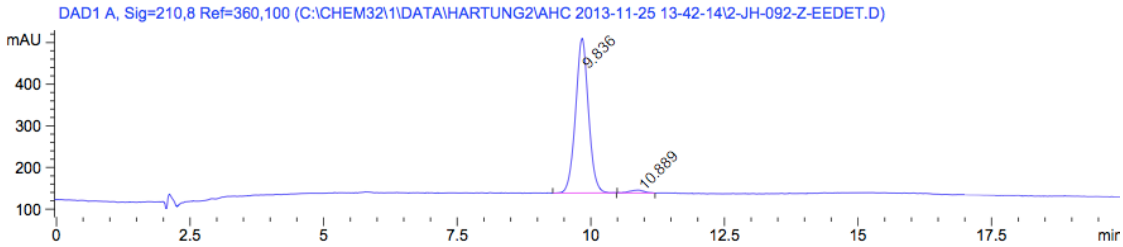
Racemate



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.799	BV	0.2620	3595.55029	207.71271	50.2636
2	11.027	BB	0.2878	3557.83179	188.87053	49.7364
Totals :				7153.38208	396.58324	

Enantioenriched



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

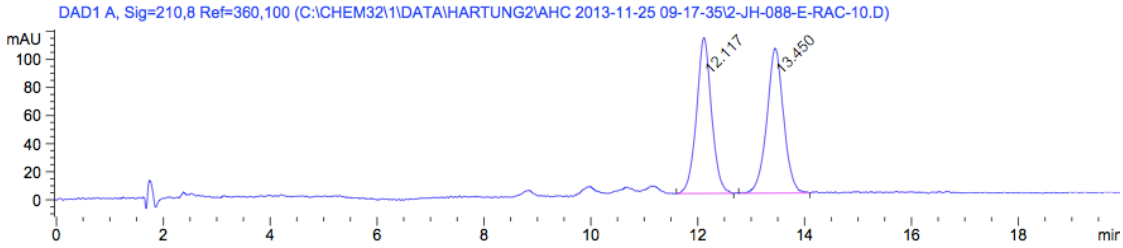
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.836	BB	0.2567	6250.97852	370.80807	97.9546
2	10.889	BB	0.2427	130.52478	6.96354	2.0454
Totals :				6381.50330	377.77162	

E-**7c**:

$[\alpha]_D^{25}$ – 1.14° (c = 0.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.97 (2x m, 2H), 7.60 – 7.52 (2x m, 1H), 7.48 – 7.39 (2x m, 2H), 6.10 (ddd, 15.5, 4.9, 4.8 Hz, 1H), 6.02 (ddd, 17.3, 10.6, 6.4 Hz, 1H), 5.92 (dddd, 15.4, 6.9, 1.7, 1.6 Hz, 1H), 5.84 (m, 1H), 5.80 (m, 1H), 5.49 (d, *J* = 17.2 Hz, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.24 – 4.18 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 165.5, 135.2, 133.3, 131.8, 130.1, 129.9, 128.6, 128.6, 124.4, 120.1, 75.7, 74.9, 62.8. HRMS (FAB+) calculated for $C_{21}H_{19}O_4$ [M–OH]: 335.1283; found 335.1271.

Separation conditions for *E*-**7c**: OJ-H, 5% IPA, 2.5 mL/min. 82% ee.

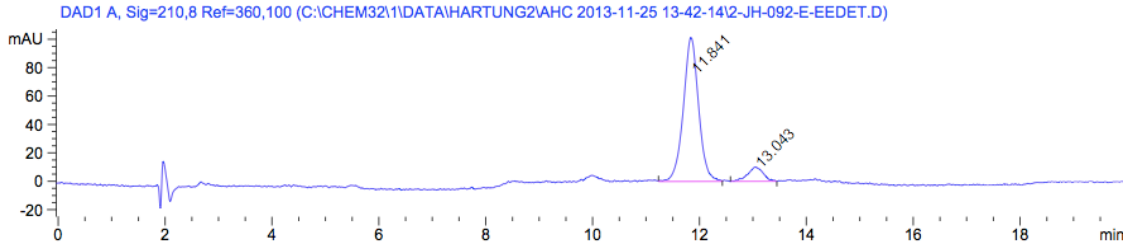
Racemate



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.117	BB	0.2964	2167.36914	110.68974	49.1751
2	13.450	BB	0.3262	2240.08228	102.82623	50.8249
Totals :				4407.45142	213.51597	

Enantioenriched



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.841	VV	0.3037	2009.88196	101.20198	90.8688
2	13.043	BB	0.3044	201.96896	9.96831	9.1312
Totals :				2211.85092	111.17029	

Alcohol **7e**.

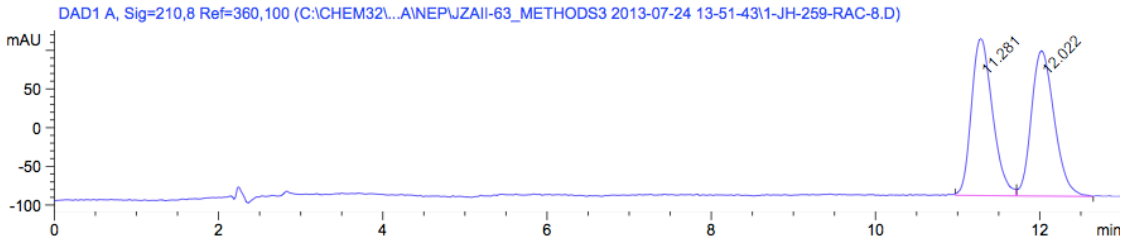
62% isolated yield, 89% *Z*.

Z-**7e**:

$[\alpha]_D^{25}$ – 2.95° (c = 0.76, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 10H), 6.02 (ddd, *J* = 11.1, 6.9, 6.8 Hz, 1H), 5.83 (ddd, *J* = 17.6, 10.4, 7.5 Hz, 1H), 5.56 (dd, *J* = 11.5, 8.9 Hz, 1H), 5.39 (m, 1H), 5.37 – 5.32 (m, 1H), 4.64 (AB d, *J* = 10.5 Hz, 1H), 4.62 (AB d, *J* = 11.0 Hz, 1H), 4.42 (AB d, *J* = 12.1 Hz, 1H), 4.38 (AB d, *J* = 11.7 Hz, 1H), 4.21 (dd, *J* = 8.6, 7.4, 1.0 Hz, 1H), 4.07 – 3.93 (2x m, 1H), 3.78 (dd, *J* = 7.2, 7.0 Hz, 1H), 2.13 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2, 137.7, 135.8, 133.7, 131.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 119.5, 81.5, 76.3, 70.8, 70.7, 58.5. HRMS (FAB+) calculated for $C_{21}H_{25}O_3$ [M+H]: 325.1804; found 325.1803.

Separation conditions for *Z*-**7e**: OJ-H, 10% IPA, 2.5 mL/min. 93% ee

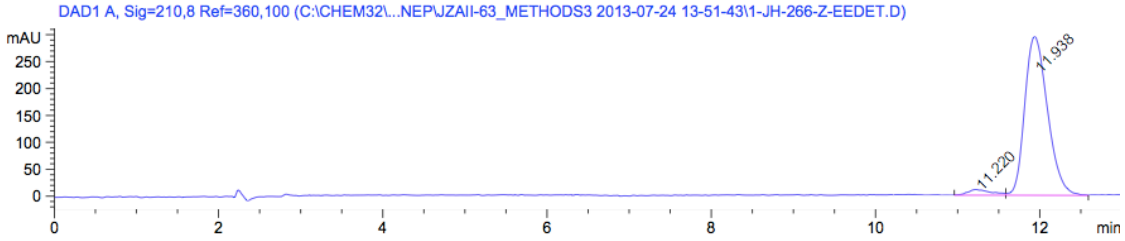
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.281	BV	0.2773	3639.78735	202.93092	49.9668
2	12.022	VB	0.3028	3644.62769	187.47997	50.0332
Totals :				7284.41504	390.41089	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.220	BV	0.2596	210.15450	10.58754	3.5605
2	11.938	VV	0.3010	5692.16504	295.11295	96.4395
Totals :				5902.31953	305.70049	

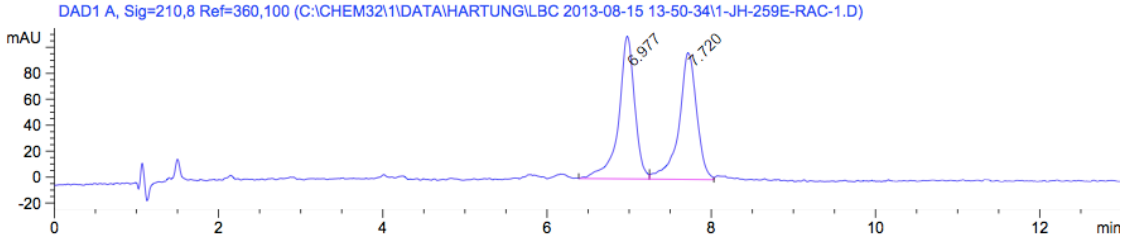
E-**7e**:

$[\alpha]_D^{25}$ – 2.93° (c = 0.30, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 10H), 5.93 – 5.79 (2x m, 1H), 5.71 (ddd, *J* = 15.7, 7.5, 7.3 Hz, 1H), 5.33 (m, 1H), 5.29 (m, 1H), 4.65 (AB d, *J* = 12.2 Hz, 1H), 4.62 (AB d, *J* = 12.2 Hz, 1H), 4.47 (AB d, *J* = 12.2 Hz, 1H), 4.43 (AB d, *J* = 12.1 Hz, 1H), 4.18 (m, 2H), 3.90 (dd, *J* = 7.9, 5.6 Hz, 1H), 3.86 (ddd, *J* = 7.4, 4.8, 0.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.6, 135.6, 133.7, 128.8, 128.4, 127.9, 127.8, 127.6, 127.5, 119.0,

82.5, 81.6, 70.8, 70.7, 63.2. HRMS (FAB+) calculated for $C_{21}H_{25}O_3$ [M+H]: 325.1804; found 325.1812.

Separation conditions for *E*-**7e**: OJ-H, 10% IPA, 2.5 mL/min. 86% ee

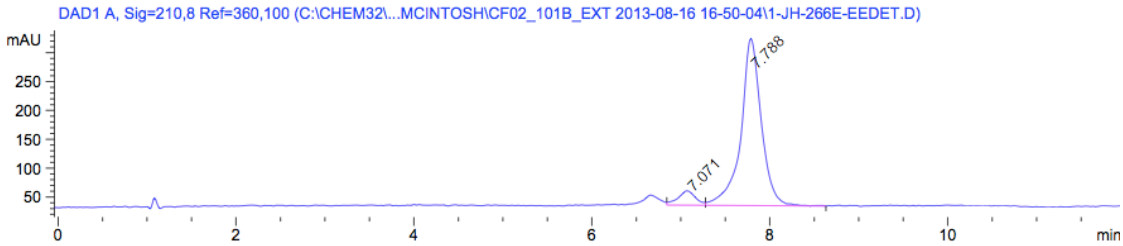
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.977	BV	0.1991	1499.56213	109.99121	50.4390
2	7.720	VV	0.2202	1473.45618	97.57201	49.5610
Totals :				2973.01831	207.56322	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.071	VV	0.2045	342.74240	24.91814	6.9119
2	7.788	VB	0.2345	4615.99463	288.76001	93.0881
Totals :				4958.73703	313.67815	

Benzoate **7f**.

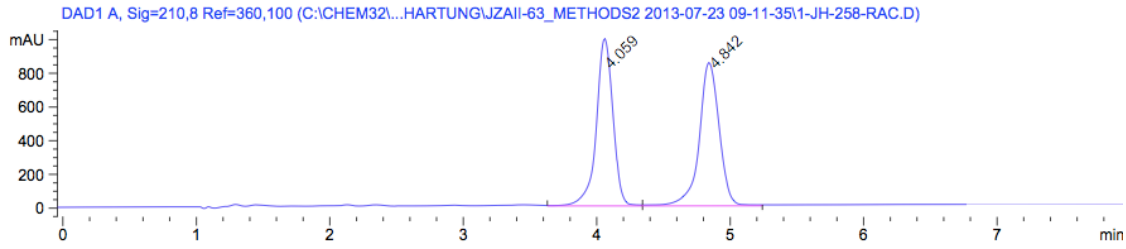
61% isolated yield, 88% *Z*.

Z-**7f**:

$[\alpha]_D^{25}$ – 50.9° (c = 0.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 7.37 – 7.22 (m, 10H), 5.97 (dddd, *J* = 11.3, 7.8, 5.8, 1.1 Hz, 2H), 5.85 (ddd, *J* = 17.1, 10.5, 7.5 Hz, 1H), 5.73 (ddd, *J* = 10.7, 9.2, 1.5 Hz, 1H), 5.35 – 5.33 (m, 1H), 5.31 (m, 1H), 4.87 (ddd, *J* = 13.2, 7.8, 1.4 Hz, 1H), 4.73 (ddd, *J* = 13.2, 5.8, 1.6 Hz, 2H), 4.68 (AB d, *J* = 12.2 Hz 1H), 4.64 (AB d, *J* = 12.1 Hz, 1H), 4.49 (AB d, *J* = 12.1 Hz, 1H), 4.44 (AB d, *J* = 12.2 Hz, 1H), 4.30 (ddd, *J* = 9.1, 5.0, 1.1 Hz, 2H), 3.90 (dd, *J* = 7.5, 5.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 138.6, 138.4, 135.5, 133.1, 132.1, 130.2, 129.7, 128.55, 128.50, 128.45, 128.40, 127.8, 127.75, 127.70, 127.5, 119.2, 82.3, 76.7, 70.7, 70.7, 61.2. HRMS (FAB+) calculated for $C_{28}H_{29}O_4$ [M+H]: 429.2066; found 429.2056.

Separation conditions for *Z*-**7f**: OJ-H, 20% IPA, 2.5 mL/min. 97% ee

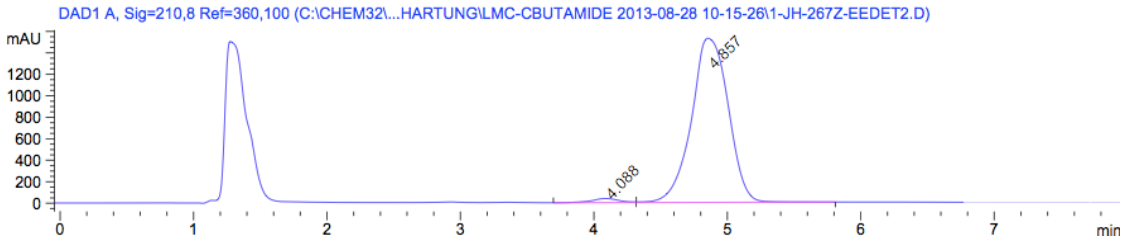
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.059	VV	0.1335	8624.85742	991.43774	49.2384
2	4.842	VB	0.1622	8891.65625	849.16925	50.7616
Totals :				1.75165e4	1840.60699	

Enantioenriched:

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Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.088 BV    0.2156  537.15137   38.29383   1.7991
   2   4.857 VB    0.2960 2.93192e4  1527.33167  98.2009

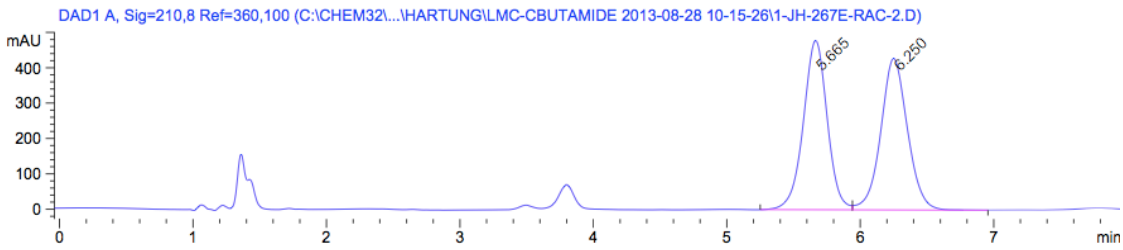
Totals :                  2.98564e4  1565.62550
```

E-**7f**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.61 – 7.54 (m, 1H), 7.45 (m, 2H), 7.36 – 7.21 (m, 10H), 5.98 – 5.79 (3x m, 1H), 5.34 (m, 1H), 5.29 (m, 1H), 4.87 (2x m, 1H), 4.64 (AB d, *J* = 12.0 Hz, 2H), 4.47 (AB d, *J* = 12.1 Hz, 1H), 4.43 (AB d, *J* = 12.1 Hz, 1H), 3.92 (dd, *J* = 6.8, 5.3 Hz, 1H), 3.87 (dd, *J* = 6.8, 5.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 138.50, 138.42, 135.6, 133.1, 131.8, 130.1, 129.82, 129.80, 128.55, 128.52, 128.44, 128.36, 127.8, 127.60, 127.56, 119.1, 82.4, 81.3, 70.9, 70.6, 64.8.

Separation conditions for *E*-**7f**: OD-H, 20% IPA, 2.5 mL/min. 88% ee

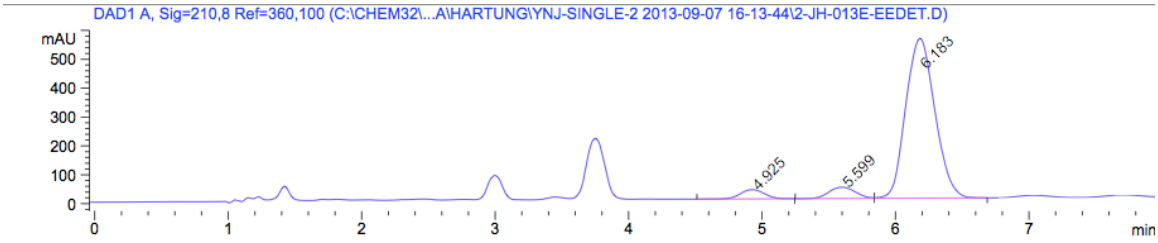
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.665	BV	0.1888	5934.12598	478.10345	49.9106
2	6.250	VB	0.2143	5955.37939	428.19113	50.0894
Totals :				1.18895e4	906.29459	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.925	BB	0.2038	401.86090	31.71189	4.3113
2	5.599	BV	0.2213	536.10181	38.78576	5.7514
3	6.183	VB	0.2409	8383.21680	552.90784	89.9373
Totals :				9321.17950	623.40548	

Silyl ether **7g**.

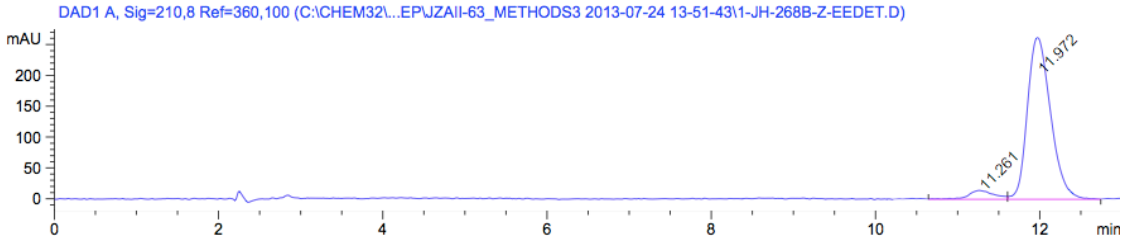
68% yield, 87% *Z*. Initial product mixture derivatized by treatment with TBAF (3 equiv) to aid in purification; isolated product is spectroscopically identical to alcohol **7e** (see above, p. S14).

Optical rotations and enantiopurity of derivatized products:

Derivative of *Z*-**7g**: $[\alpha]_D^{25}$ – 2.2° (c = 0.61, $CHCl_3$)

89% ee

Enantioenriched:

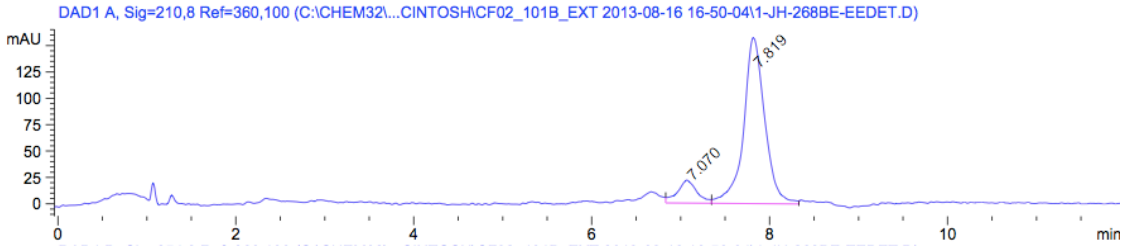


Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.261	VV	0.3050	316.99796	14.38933	5.7900
2	11.972	VV	0.3092	5157.96875	262.54877	94.2100
Totals :				5474.96671	276.93809	

Derivative of *E*-**7g**: $[\alpha]_D^{25}$ – 3.4° (c = 0.31, $CHCl_3$)

77% ee



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.070	VV	0.2254	329.41394	21.65948	11.2280
2	7.819	VB	0.2454	2604.45679	157.07635	88.7720
Totals :				2933.87073	178.73583	

Benzyl ether **7h**.

64% isolated yield, 86% *Z*.

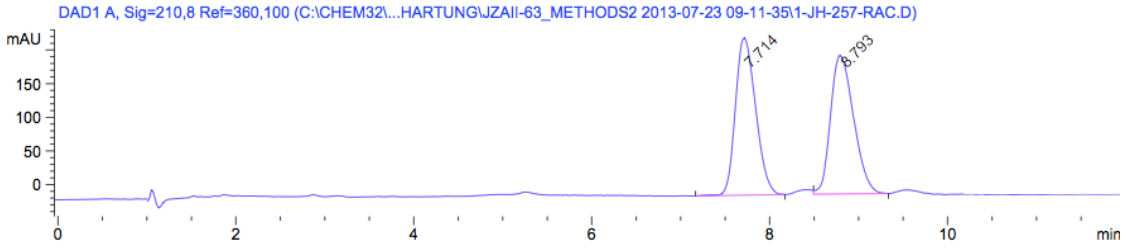
Z-**7h**:

$[\alpha]_D^{25}$ – 29.7° (c = 0.66, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 10H), 5.91 (dddd, *J* = 11.4, 7.3, 5.4, 1.1 Hz, 1H), 5.83 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.61 (dddd, *J* = 11.0, 9.2, 1.7, 1.6 Hz, 1H), 5.34 – 5.30 (m, 1H), 5.28 (m, 1H), 4.64 (AB d, *J* = 12.2 Hz, 1H), 4.61 (AB d, *J* = 12.1 Hz, 1H), 4.43 (AB d, *J* =

12.2 Hz, 1H), 4.43 – 4.41 (2x AB d, 1H), 4.40 (AB d, J = 12.1 Hz, 1H), 4.16 (ddd, J = 9.2, 4.9, 1.1 Hz, 1H), 4.04 (ddd, J = 12.6, 7.3, 1.6 Hz, 1H), 3.93 (ddd, J = 12.6, 5.4, 1.8 Hz, 1H), 3.82 (dddd, J = 7.6, 5.0, 1.2, 0.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 138.5, 138.3, 135.5, 131.6, 130.3, 128.52, 128.39, 128.36, 127.84, 127.81, 127.77, 127.76, 127.56, 127.53, 119.1, 82.5, 76.4, 72.5, 70.6, 70.4, 66.4. HRMS (FAB+) calculated for $C_{28}H_{31}O_3$ [M+H]: 415.2273; found 415.2260.

Separation conditions for *Z*-**7h**: OD-H, 15% IPA, 2.5 mL/min. 91% ee

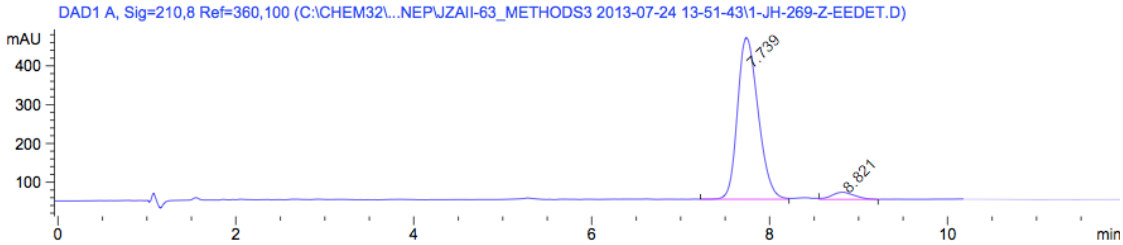
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.714	BB	0.2523	3691.89014	233.73363	49.8466
2	8.793	VB	0.2827	3714.60791	205.71669	50.1534
Totals :				7406.49805	439.45032	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.739	BV	0.2524	6725.33252	416.38754	95.2967
2	8.821	VB	0.2569	331.92462	18.54005	4.7033
Totals :				7057.25714	434.92760	

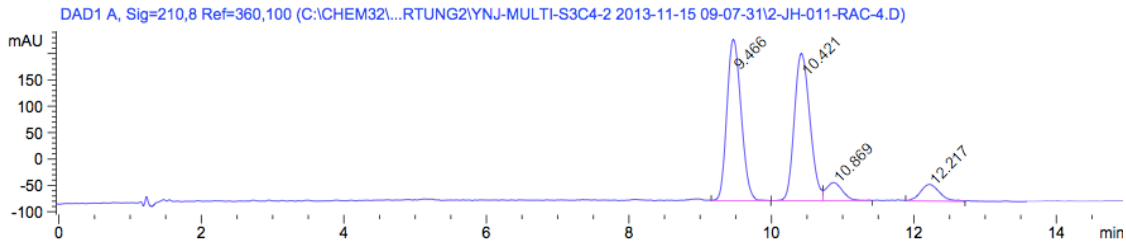
7i.

Isolated as an inseparable 9:1 *Z*/*E* mixture, 76% yield.

Z-**7i**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 10H), 7.06 – 7.00 (m, 2H), 6.79 – 6.75 (m, 2H), 5.95 – 5.82 (2x m, 1H), 5.54 (ddd, *J* = 11.0, 9.4, 1.7, 1.5 Hz, 1H), 5.37 (m, 1H), 5.29 (m, 1H), 4.67 (2x AB d, *J* = 12.2 Hz, 2H), 4.49 (AB d, *J* = 12.2 Hz, 1H), 4.47 (AB d, *J* = 12.1 Hz, 1H), 4.36 (ddd, *J* = 9.3, 4.8, 1.1 Hz, 1H), 3.89 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.78 (s, 3H), 3.34 – 3.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 138.77, 138.76, 135.7, 133.9, 132.4, 129.63, 129.45, 128.4, 128.0, 127.84, 127.78, 127.53, 127.49, 119.0, 114.0, 82.7, 76.3, 70.6, 70.3, 55.4, 33.4. HRMS (FAB+) calculated for $C_{28}H_{31}O_3$ [M+H]: 415.2273; found 415.2287.

Separation conditions for *Z*/*E* product mixture: AD-H, 10% IPA, 2.5 mL/min. *Z*: 93% ee; *E*: 79% ee.

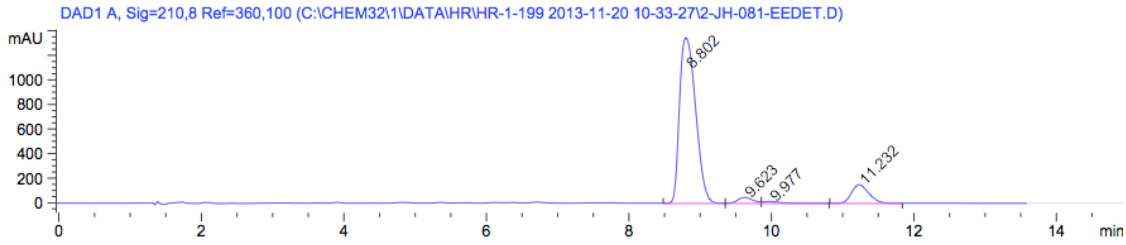
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.466	VB	0.2176	4234.35059	305.74072	44.0459
2	10.421	BV	0.2378	4251.52734	279.00278	44.2245
3	10.869	VV	0.2464	545.18933	34.12083	5.6711
4	12.217	VV	0.2952	582.43701	31.58193	6.0585
Totals :				9613.50427	650.44626	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.802	BV	0.2556	2.11839e4	1345.92456	85.3335
2	9.623	VV	0.2273	735.39227	48.94960	2.9623
3	9.977	VB	0.2593	298.80161	16.18907	1.2036
4	11.232	BV	0.2637	2606.73169	152.29791	10.5005
Totals :				2.48248e4	1563.36114	

Ketone **7j**.

65% isolated yield, 90% *Z*.

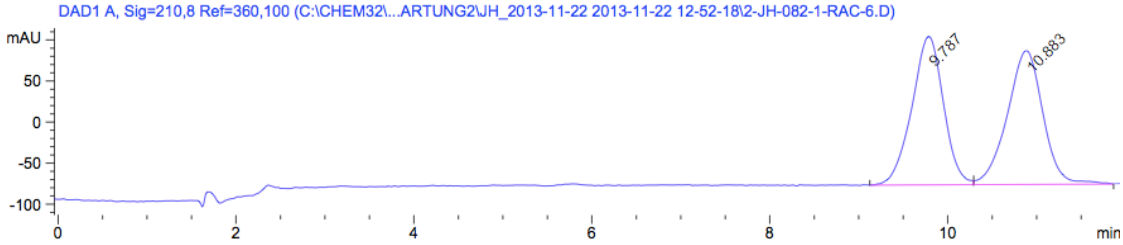
Z-**7j**:

$[\alpha]_D^{25}$ – 7.98° (c = 1.35, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 10H), 5.86 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.65 (dtd, *J* = 11.1, 7.5, 1.0 Hz, 1H), 5.46 (ddt, *J* = 10.9, 9.3, 1.6 Hz, 1H), 5.35 (m, 1H), 5.27 (m, 1H), 4.66 (AB d, *J* = 12.1 Hz, 1H), 4.61 (AB d, *J* = 12.2 Hz, 1H), 4.45 (AB d, *J* = 12.1 Hz, 1H), 4.43 (AB d, *J* = 12.2 Hz, 1H), 4.23 (ddd, *J* = 9.3, 5.0, 1.0 Hz, 1H), 3.84 (dd, *J* = 7.6, 5.0, 1H), 2.38 (m, 2H), 2.24 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.0, 138.753, 138.746, 135.7, 133.2, 128.6, 128.36, 128.34, 127.81, 127.75,

127.51, 127.49, 118.9, 82.6, 76.3, 70.6, 70.3, 43.3, 30.0, 22.3. HRMS (FAB+) calculated for $C_{24}H_{29}O_3$ [M+H]: 365.2117; found 365.2113.

Separation conditions for *Z*-**7j**: OJ-H, 5% IPA, 2.5 mL/min. 92% ee

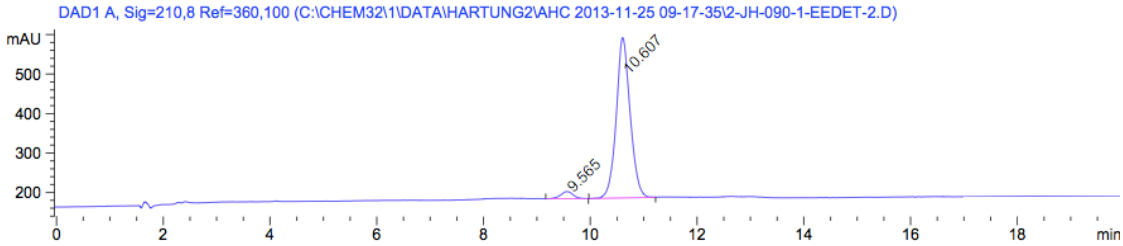
Racemate



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.787	BV	0.3728	4472.42529	180.68672	49.6322
2	10.883	VBA	0.4203	4538.71436	163.26811	50.3678
Totals :				9011.13965	343.95483	

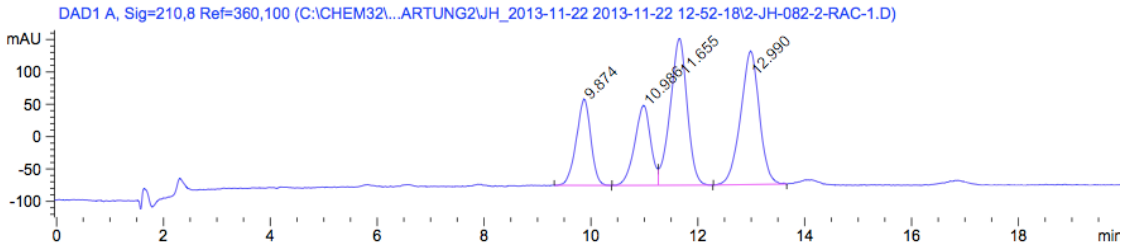
Enantioenriched



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.565	BB	0.2466	294.21240	18.00591	3.8669
2	10.607	BB	0.2664	7314.22949	405.54443	96.1331
Totals :				7608.44189	423.55034	

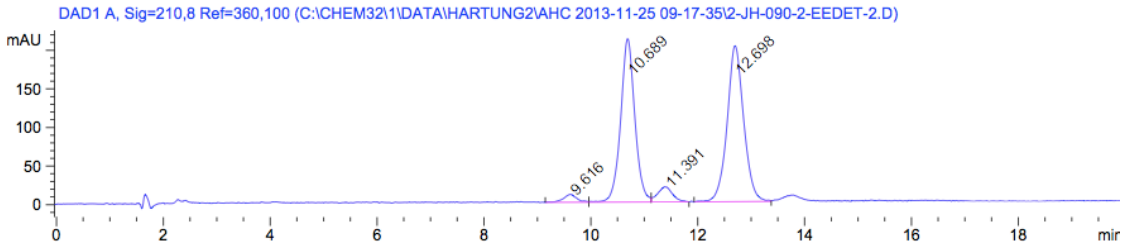
E/Z-***7j*** mixture:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.874	BB	0.2847	2521.13306	133.25986	16.6689
2	10.986	BV	0.3148	2570.48706	123.50429	16.9952
3	11.655	VB	0.3314	5003.31738	226.75299	33.0803
4	12.990	BB	0.3684	5029.84863	206.30301	33.2557
Totals :				1.51248e4	689.82014	

Enantioenriched: *E* 84% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.616	BV	0.2410	174.28995	10.11655	1.9790
2	10.689	VV	0.2750	3897.29248	211.45294	44.2520
3	11.391	VB	0.2866	379.96729	19.56160	4.3144
4	12.698	BV	0.3234	4355.48779	202.13602	49.4546
Totals :				8807.03751	443.26711	

Boronic ester **7k**.

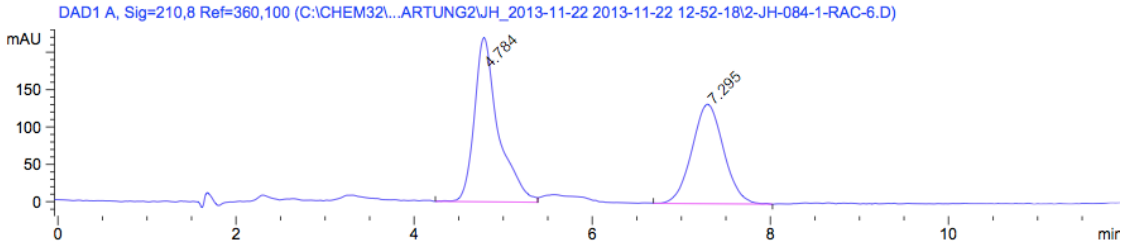
50% isolated yield of *Z* product.

$[\alpha]_D^{25}$ – 7.98° (c = 0.64, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 10H), 5.94 – 5.78 (2x m, 1H), 5.43 (dddd, *J* = 11.0, 9.3, 1.7, 1.5 Hz, 1H), 5.28 (m, 1H), 5.25 (m, 1H), 4.67 (AB d, *J* = 12.2 Hz, 1H), 4.64 (AB d, *J* = 12.3 Hz, 1H), 4.47 (AB d, *J* = 12.4 Hz, 1H), 4.44 (AB d, *J* = 12.2 Hz, 1H), 4.30 (ddd, *J* = 9.4, 4.0, 1.1 Hz, 1H), 3.88 (dd, *J* = 7.7, 4.0 Hz, 1H), 1.69 (m, 2H), 1.23 (s, 6H), 1.22

(s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 139.0, 135.7, 130.0, 128.31, 128.30, 127.7, 127.6, 127.34, 127.33, 126.9, 118.8, 83.5, 82.8, 76.2, 70.5, 70.1, 24.94, 24.93. HRMS (FAB+) calculated for $C_{20}H_{28}O_3B$ [M-OBn]: 327.2132; found 327.2138.

Separation conditions for *Z*-**7k**: OJ-H, 5% IPA, 2.5 mL/min. 91% ee

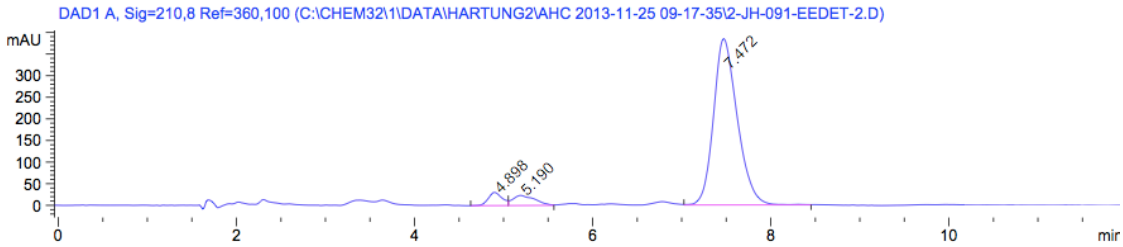
Racemate



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.784	BV	0.2705	4108.72510	219.40474	55.4931
2	7.295	VB	0.3813	3295.29712	132.87819	44.5069
Totals :				7404.02222	352.28293	

Enantioenriched



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.898	BV	0.1625	331.67175	30.59655	4.2149
2	5.190	VV	0.2376	402.79446	23.30932	5.1187
3	7.472	VV	0.2806	7134.57031	384.21341	90.6664
Totals :				7869.03653	438.11928	

Synthesis of (+)-*endo*-brevicomin, **11**

Alcohol **9**.

Alcohol **9** was synthesized following the general AROCM procedure in 85% isolated yield, 91% *Z*, and 1:1 dr.

Z-**9**:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 10H), 5.89 – 5.78 (2x m, 1H), 5.54 – 5.43 (dddd, *J* = 11.1, 9.8, 1.3, 1.0 Hz, 1H), 5.38 (m, 1H), 5.32 (m, 1H), 4.66 (AB d, *J* = 12.3 Hz, 2H), 4.59 (AB d, *J* = 12.2 Hz, 2H), 4.41 (AB d, *J* = 12.4 Hz, 2H), 4.38 (AB d, *J* = 12.1 Hz, 2H), 4.20 (ddd, *J* = 9.8, 6.9, 0.9 Hz, 2H), 3.78 (dd, *J* = 7.7, 6.9 Hz, 1H), 3.74 (m, 1H), 2.81 (br, 1H), 2.18 – 2.10 (m, 2H), 1.16 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 137.9, 135.9, 131.8, 131.1, 128.40, 128.37, 128.2, 127.82, 127.75, 127.6, 119.7, 81.2, 75.6, 70.23, 70.18, 66.9, 38.1, 23.2. HRMS (FAB+) calculated for $C_{23}H_{29}O_3$ [M+H]: 353.2117; found 353.2108.

Ketone **10**:

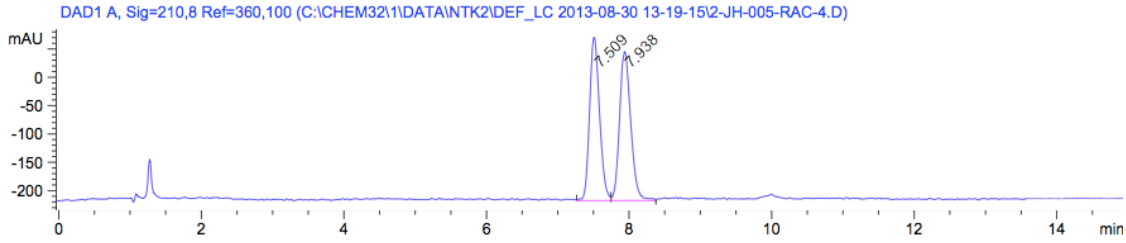
Dess-Martin periodinane (302 mg, 0.713 mmol, 2 equiv) was added in one portion to a cold (0°C) solution of alcohols *Z*-**9** (126 mg, 0.356 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Aqueous 1:1 $NaHCO_3$/ $Na_2S_2O_3$ solution was added and the biphasic mixture stirred vigorously for 1 h. The layers were separated, and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried over

$MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography to afford 110.4 mg, 88% yield of ketone **10**.

$[\alpha]_D^{25}$ – 14.4° (c = 0.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 10H), 5.93 (dddd, *J* = 11.1, 10.8, 7.2, 1.1 Hz, 1H), 5.85 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1H), 5.63 (dddd, *J* = 11.0, 9.1, 1.7, 1.4 Hz, 1H), 5.36 – 5.33 (m, 1H), 5.33 – 5.27 (m, 1H), 4.63 (2x ABd, *J* = 12.0 Hz, 2H), 4.43 (AB d, *J* = 10.8 Hz, 1H), 4.39 (AB d, *J* = Hz, 1H), 4.09 (ddd, *J* = 9.1, 5.2, 1.1 Hz, 1H), 3.84 (dd, *J* = 7.6, 5.3 Hz, 1H), 3.08 (dd, *J* = 7.2, 1.7 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 138.6, 138.4, 135.6, 130.7, 128.40, 128.37, 127.87, 127.86, 127.62, 127.58, 126.4, 119.1, 82.4, 76.3, 70.7, 70.3, 42.7, 29.8. HRMS (FAB+) calculated for $C_{23}H_{27}O_3$ [M+H]: 351.1960; found 351.1954.

Separation conditions for **10**: AD-H, 5% IPA, 2.5 mL/min. 95% ee

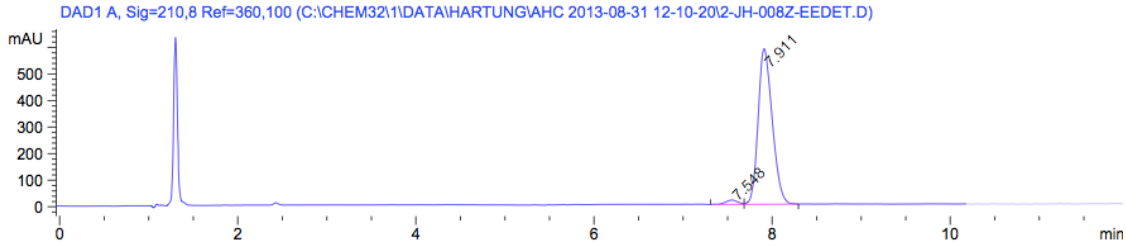
Racemate:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.509	VV	0.1535	2803.53540	288.06458	49.4751
2	7.938	VV	0.1670	2863.01855	262.90552	50.5249
Totals :				5666.55396	550.97009	

Enantioenriched:



Signal 1: DAD1 A, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.548	BV	0.1477	159.29933	16.64186	2.4029
2	7.911	VV	0.1731	6470.11279	584.80743	97.5971
Totals :				6629.41212	601.44930	

(+)-*endo*-brevicomin (**11**).

Ketone **10** (35 mg, 0.10 mmol) was dissolved in 5:1 MeOH/1 N HCl (aq.) and the reaction flask purged with Argon. Palladium on carbon (10%, 35 mg) was added, and the flask was purged by a balloon filled with H_2. The reaction mixture was stirred under 1 atm of H_2 for 2 h. The reaction flask was then purged with Argon and Celite was added. The suspension was filtered through Celite and the organic layer was extracted with pentane. The combined pentane layers were washed with water, brine, and dried over $MgSO_4$. The pentane layers were filtered and carefully concentrated to afford the crude reaction mixture (9.9 mg, 67% yield), containing 90% purity (+)-*endo*-brevicomin. Analytical samples were afforded by flash chromatography.

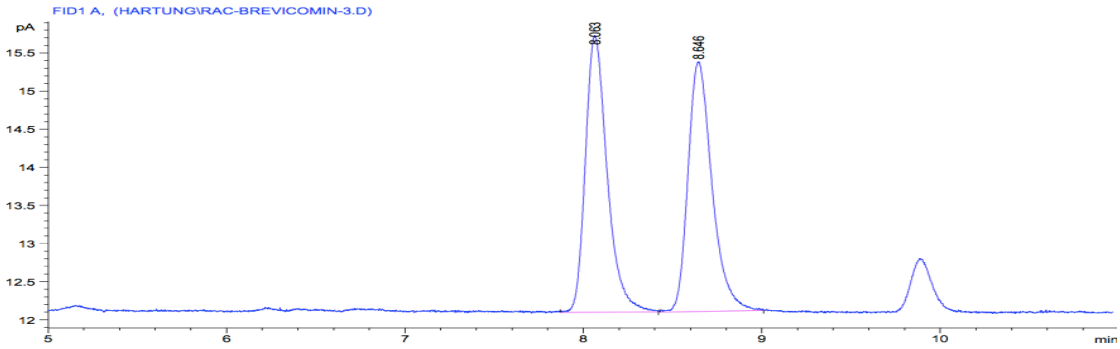
$[\alpha]_D^{25}$ + 49.6° (c = 0.11, $CHCl_3$), lit.[8] $[\alpha]_D^{20}$ + 49° (c = 1.0, ether, 96.5% ee, 90% purity), lit.[9] $[\alpha]_D^{20}$ + 77.9° (c = 1.2, ether, 99.3% ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (dt, *J* = 4.6, 2.3 Hz, 1H), 3.99 (tdd, *J* = 7.2, 4.1, 1.0 Hz, 1H), 1.99 – 1.72 (m,

[8] G. Pedrocchi-Fantoni, S. Servi, *J. Chem. Soc., Perkin. Trans. 1* **1991**, 1764.
[9] S. Singh, P. J. Guiry, *J. Org. Chem.* **2009**, *74*, 5758.

4H), 1.68 – 1.51 (m, 4H), 1.43 (s, 3H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 107.0, 81.6, 76.6, 34.4, 25.0, 23.6, 21.9, 17.6, 10.9. HRMS (FAB+) calculated for $C_9H_{17}O_2$ [M+H]: 157.1229; found 157.1206.

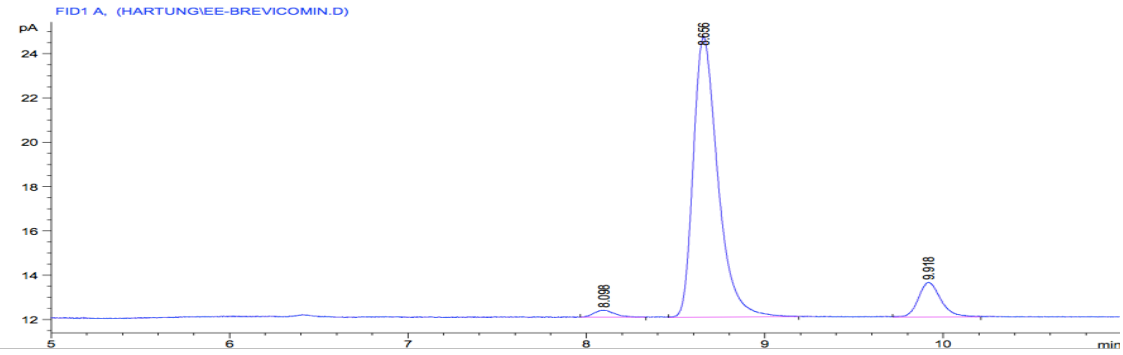
Separation conditions (GC, GTA column): 80ºC, isocratic. 96% ee

Racemate:



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.063	BB	0.1233	30.86736	3.62755	50.14859
2	8.646	BB	0.1302	30.68445	3.27842	49.85141

Enantioenriched:



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.098	BB	0.1045	2.60984	3.18731e-1	1.90416
2	8.656	BB	0.1424	120.87816	12.66055	88.19333
3	9.918	BB	0.1116	13.57243	1.55830	9.90251

Synthesis of ribose derivative **13**

Diol **12**.

To a biphasic mixture of 1:1 tBuOH/water containing diene *Z*-**7g** (38.5 mg, 0.089 mmol) was sequentially added potassium carbonate (37 mg, 0.27 mmol), potassium ferricyanide (89 mg, 0.27 mmol, 3 equiv), and potassium osmate dihydrate (1.7 mg, 4.6 μmol, 5 mol%) at 0ºC. The reaction was stirred vigorously at 23ºC for 24 h. Upon completion, solid Na_2SO_3 was added stirred continued at 23ºC for 2 h. EtOAc was added and the layers separated. The aqueous layer was extracted with EtOAc and the combined organic layers washed with water, brine, and dried over $MgSO_4$. After filtration and concentration, the crude residue was subject to flash chromatography to afford 27.5 mg, 66% yield of diol **12**.

Major diastereomer:

$[\alpha]_D^{25}$ – 62.1° (c = 1.35, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H), 7.60 – 7.55 (m, 1H), 7.44 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.37 – 7.22 (m, 26H), 6.05 – 5.97 (m, 1H), 5.86 – 5.78 (m, 1H), 4.89 – 4.83 (m, 2H), 4.77 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.65 – 4.62 (m, 1H), 4.60 (dd, *J* = 9.6, 4.6 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 3.72 (dt, *J* = 13.1, 5.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 138.1, 137.8, 133.3, 131.3, 129.87, 128.78, 128.65, 128.62, 128.58, 128.3, 128.02, 128.01, 128.0, 80.9, 76.1, 74.6, 72.1, 70.8, 66.3, 63.7, 61.2. HRMS (FAB+) calculated for $C_{28}H_{31}O_6$ [M+H]: 463.2121; found 463.2125.

Methyl glycoside **13**.

Diol **12** (34.6 mg, 0.075 mmol) was dissolved in 1:1 CH_2Cl_2/MeOH and cooled to -78ºC. Ozone was bubbled through the solution until a blue color persisted for 10 min. At this point, oxygen was bubbled through the solution until the reaction appeared colorless. Excess dimethyl sulfide (0.1 mL) was added and the reaction was allowed to come to room temperature and stir for 16 h. The reaction mixture was concentrated and the crude residue used in the following step.

The crude aldehyde was then dissolved in MeOH (5 mL) and cooled to 0ºC. HCl in MeOH (0.4 M, 0.5 mL) was added and the reaction was warmed to room temperature. The reaction was stirred for 14 h, at which time Amberlyst IRA-400 (OH^-) was added. The mixture was filtered and concentrated; preparative TLC afforded 10.6 mg (0.031 mmol, 47% yield over two steps) of methyl glycoside **13**. $[\alpha]_D^{25} = -36.4°$ (c = 0.27, $CHCl_3$), lit.[10] *ent*-**13** $[\alpha]_D^{25} = +31.7$ (c = 1.94, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 10H), 4.89 (s, 1H), 4.66 (AB d, *J* = 12.0 Hz, 1H), 4.63 (AB d, *J* = 12.0 Hz, 1H), 4.58 (AB d, *J* = 11.7 Hz, 1H), 4.49 (AB d, *J* = 11.7 Hz, 1H), 4.28 (m, 1H), 4.13 (dd, *J* = 7.1, 4.7 Hz, 1H), 3.87 (d, *J* = 4.7 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.58 (m, 1H), 3.37 (s, 3H), 1.95 (br, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.81, 137.79, 128.6, 128.1 (4C), 128.04 (3C), 128.00 (3C), 107.0, 82.4, 80.3, 77.4, 72.8, 72.6, 62.8, 55.7. HRMS (FAB+) calculated for $C_{20}H_{23}O_5$ [M+H-H_2]: 343.1545; found 343.1553.

[10] P. A. Wender, F. C. Bi, N. Buschmann, F. Gosselin, C. Kan, J-M. Kee, H. Ohmura, *Org. Lett.* **2006**, *8*, 5373.

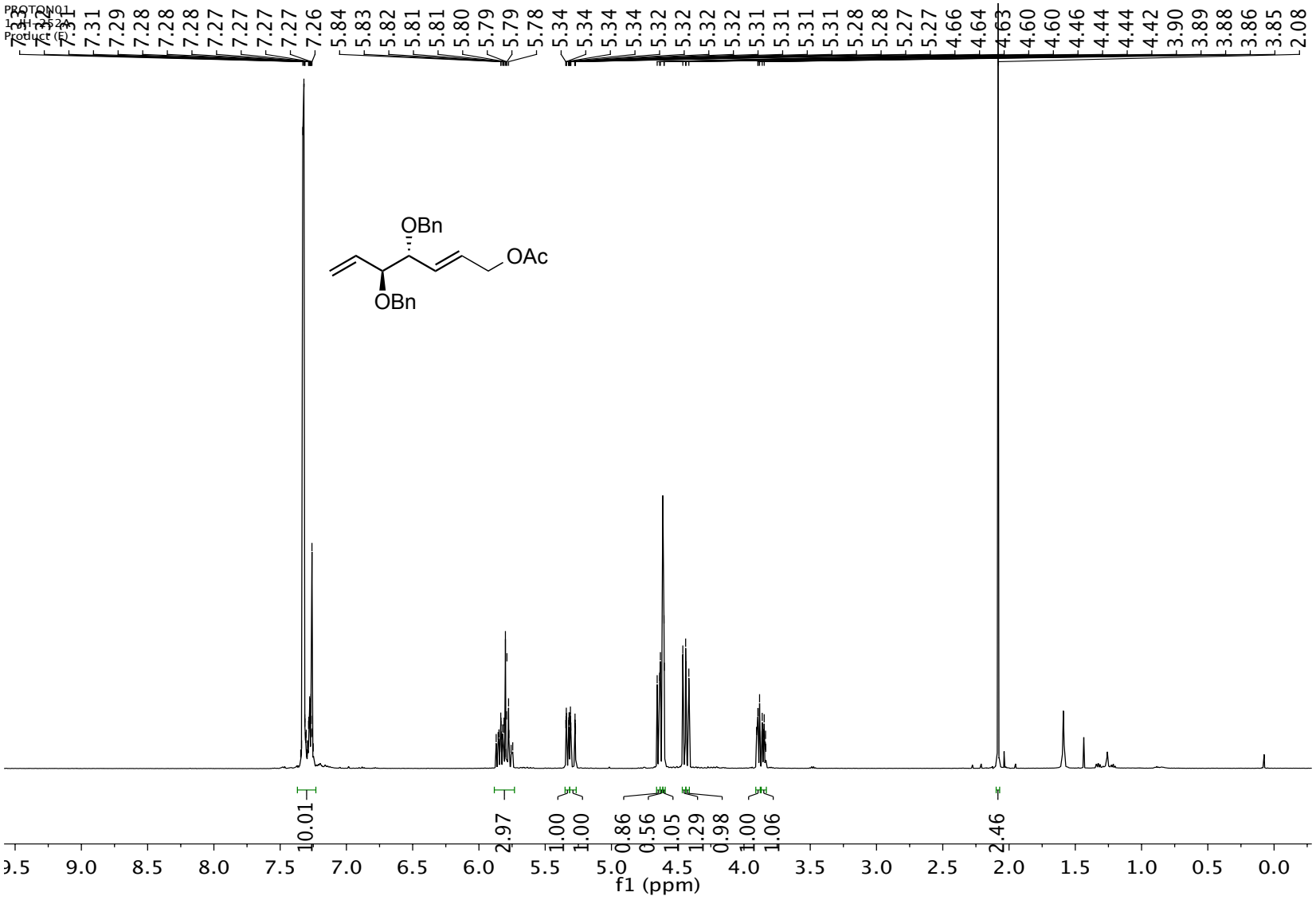


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$) of *E*-**4**.

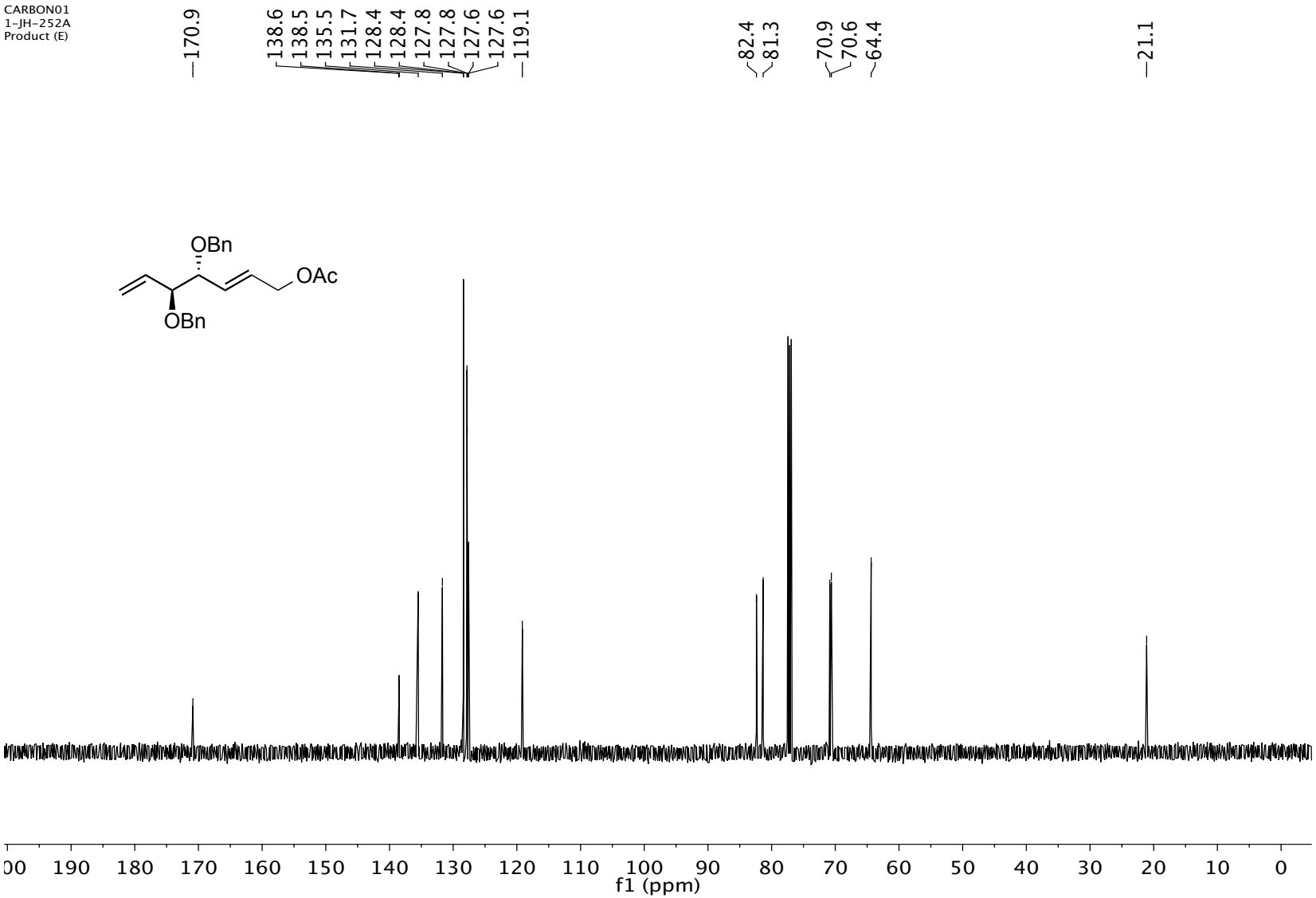


Figure S4. ^{13}C NMR (125 MHz, $CDCl_3$) of *E*-**4**.

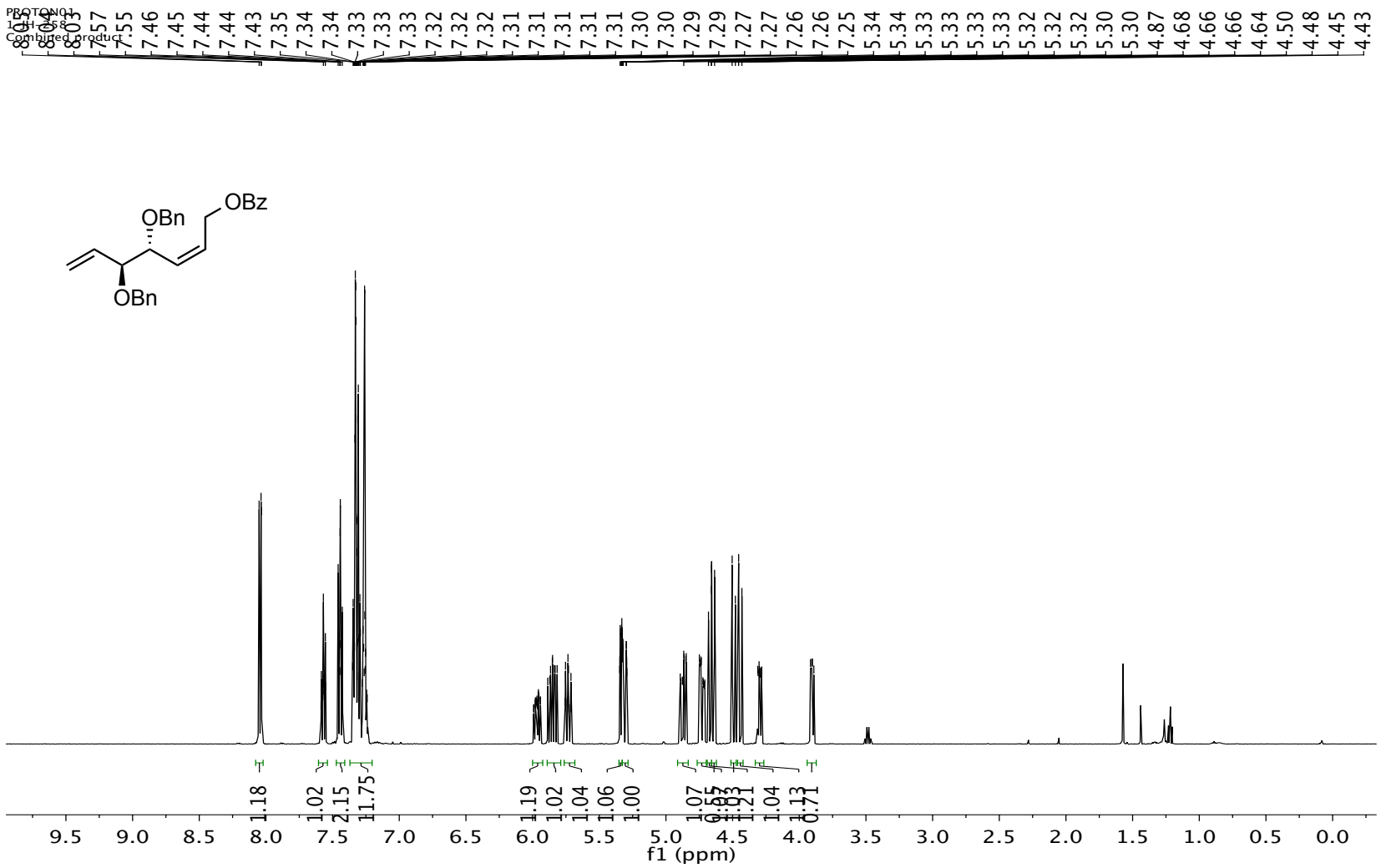


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7f**.

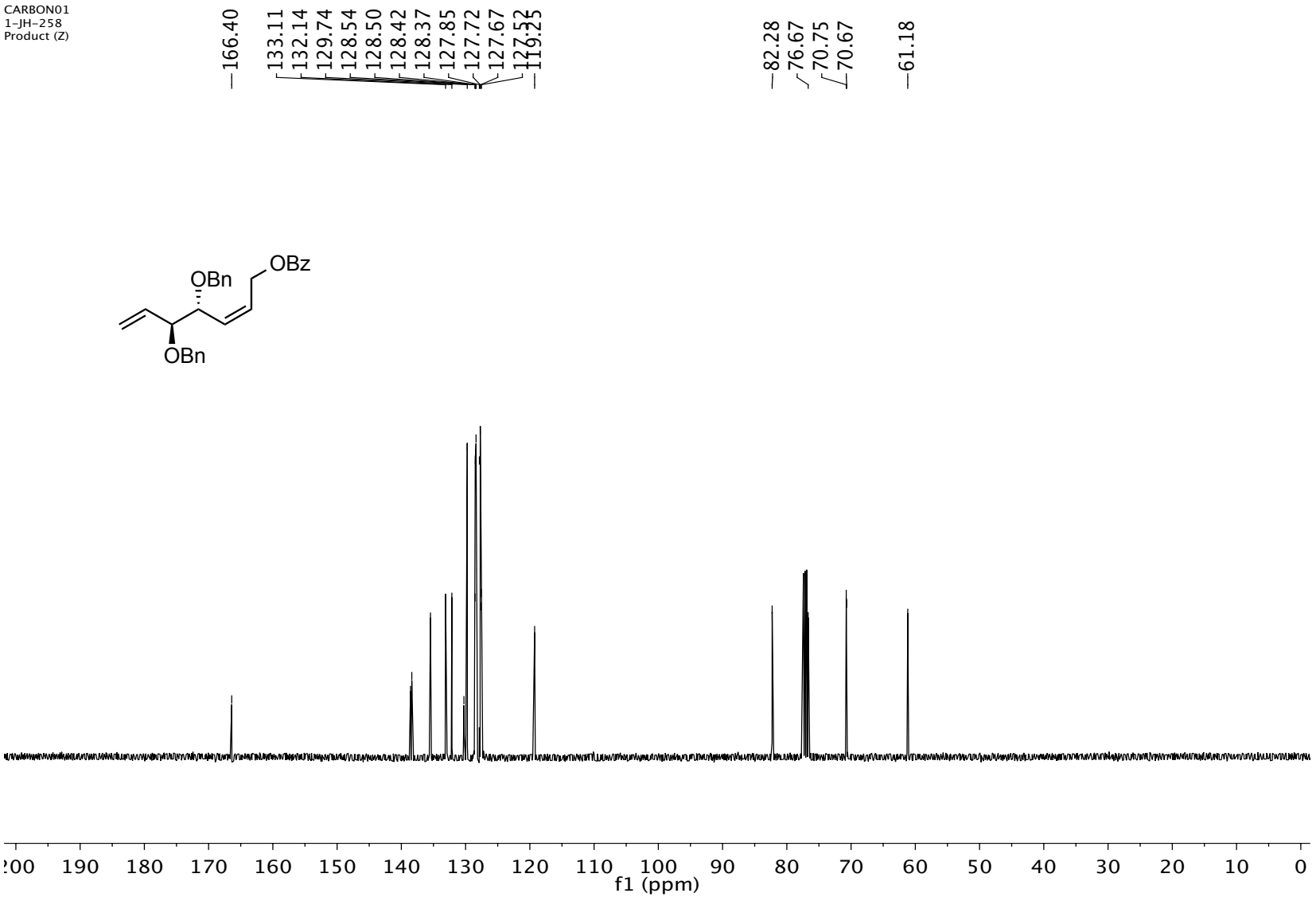


Figure S20. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7f**.

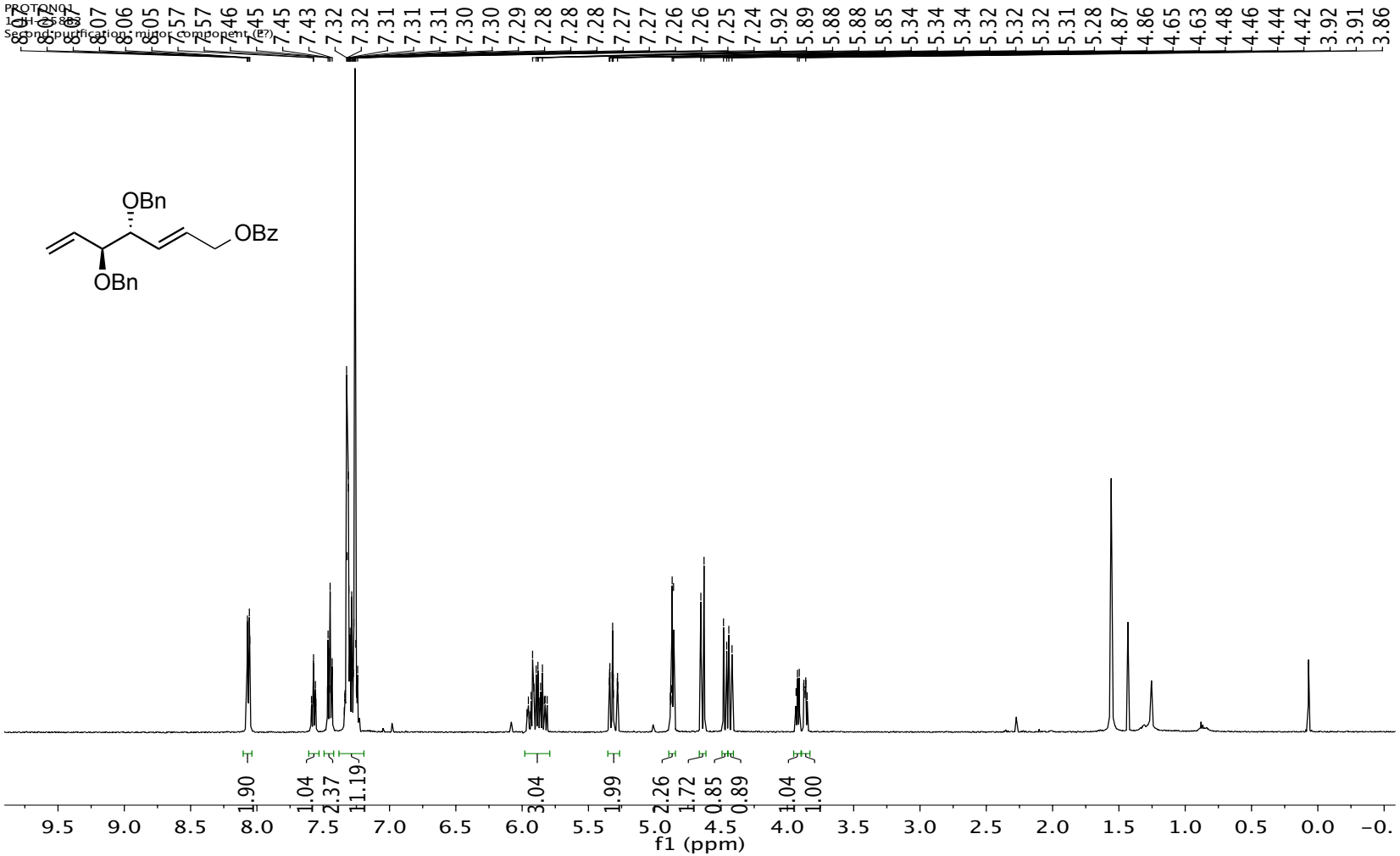


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) of *E*-**7f**.

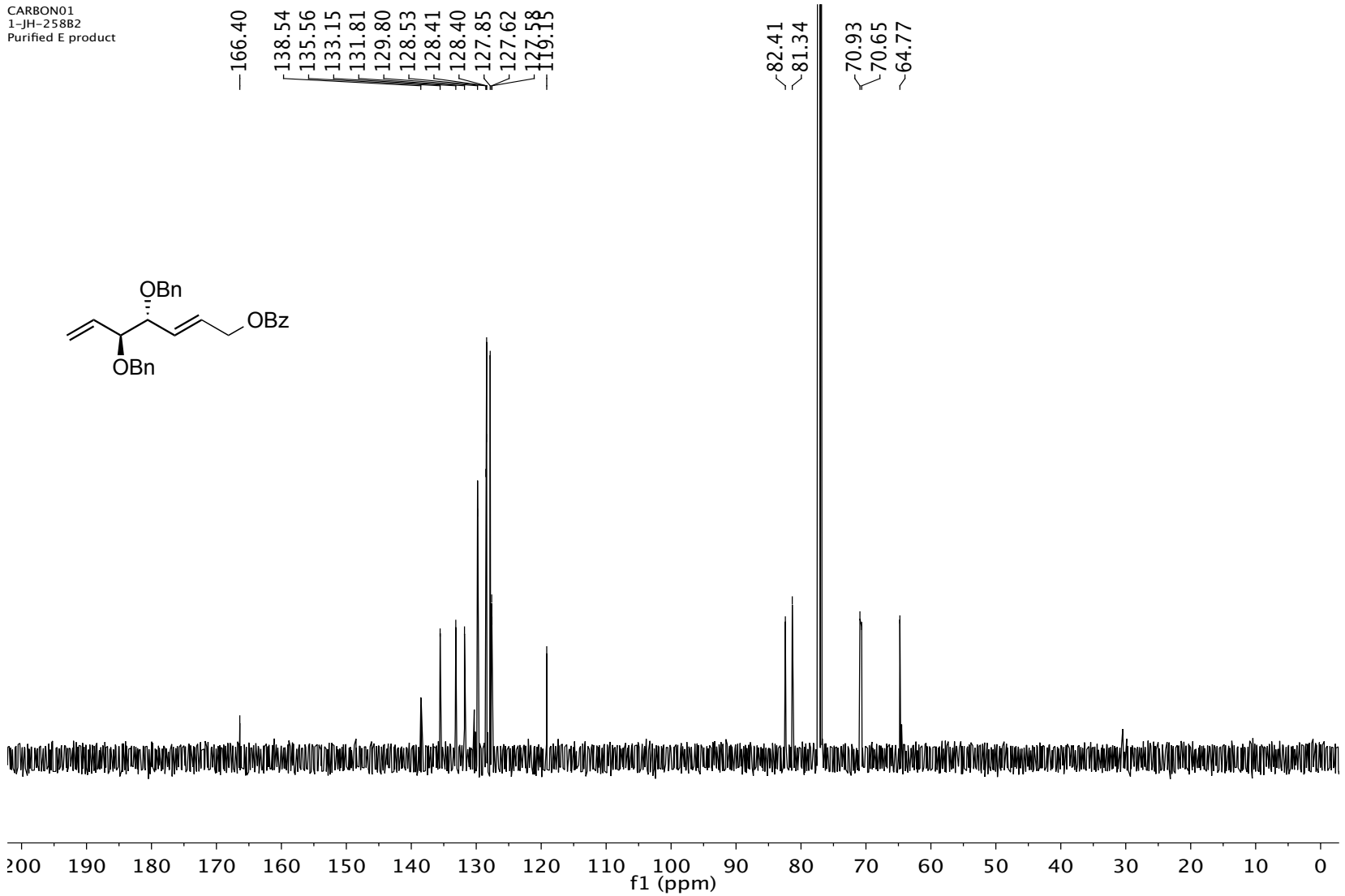


Figure S22. ^{13}C NMR (125 MHz, $CDCl_3$) of *E*-**7f**.

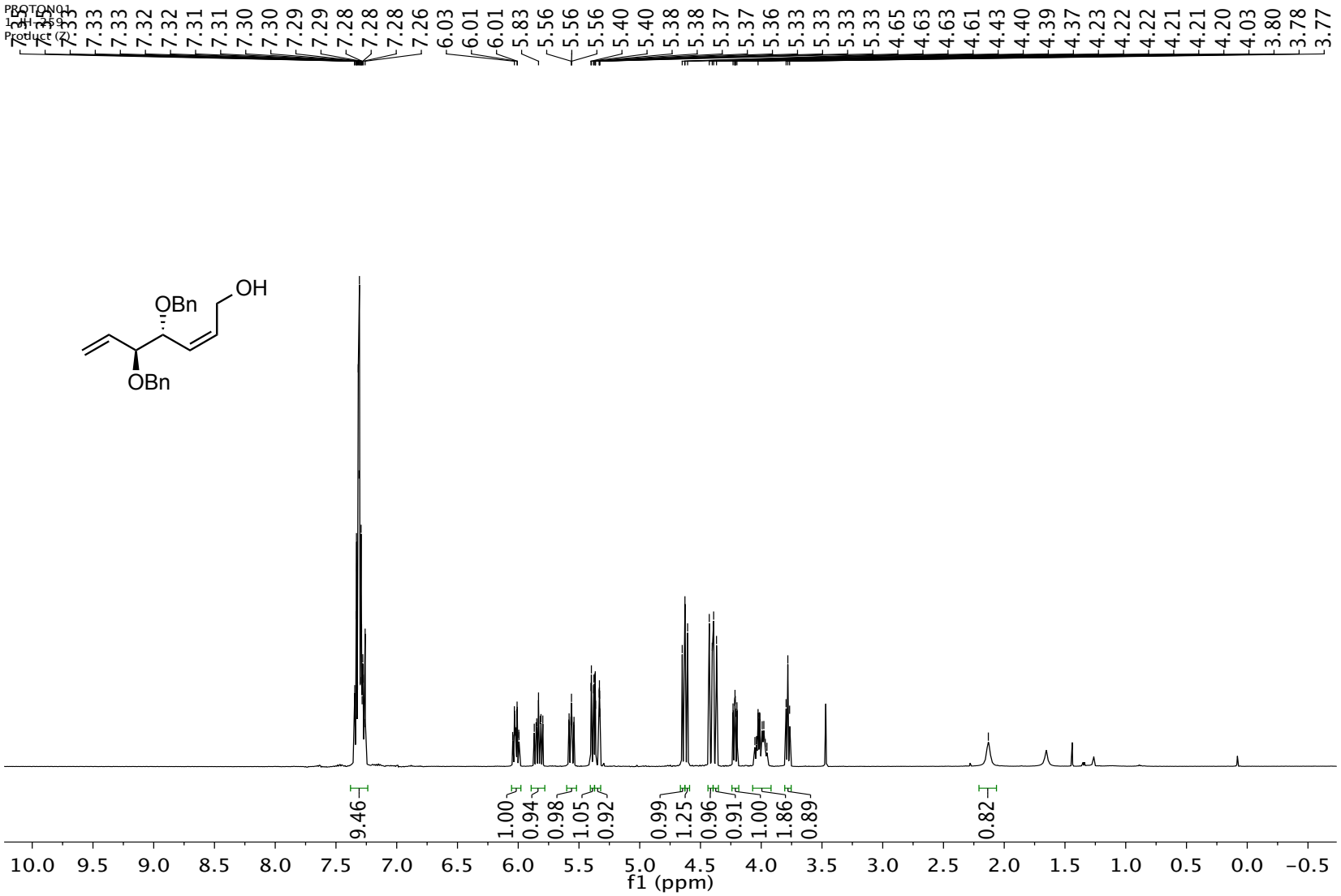


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7e**.

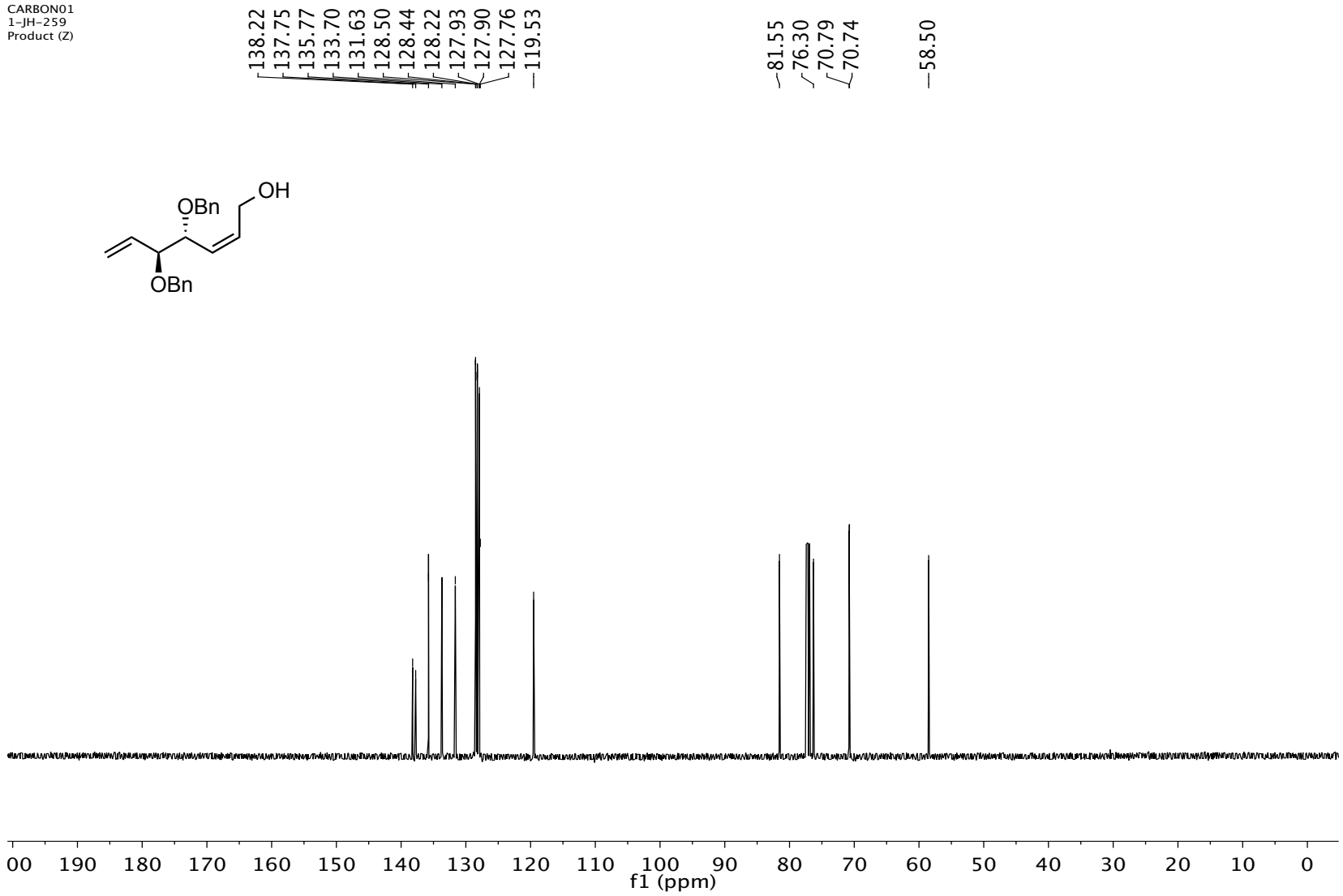


Figure S16. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7e**.

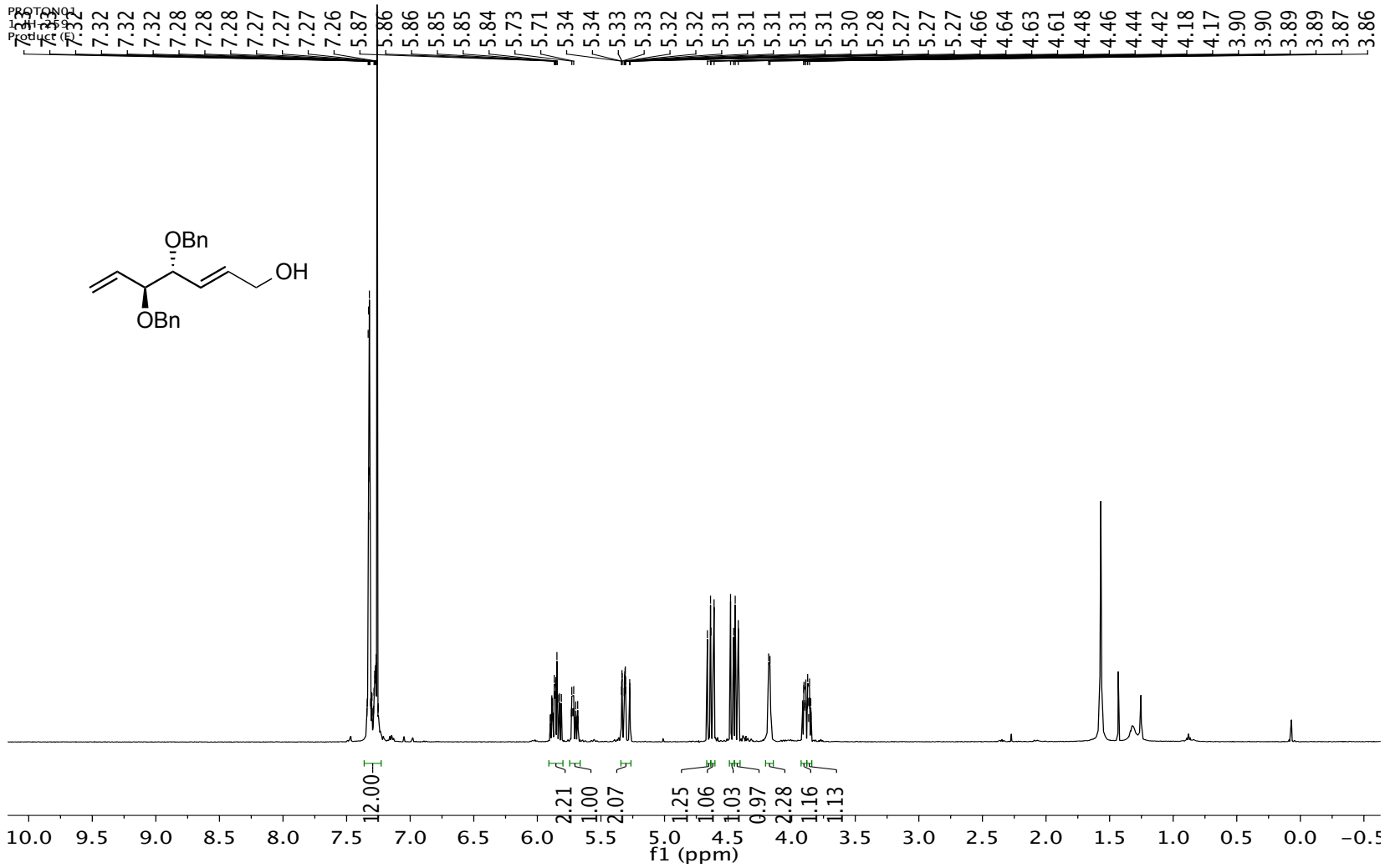


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) of *E*-**7e**.

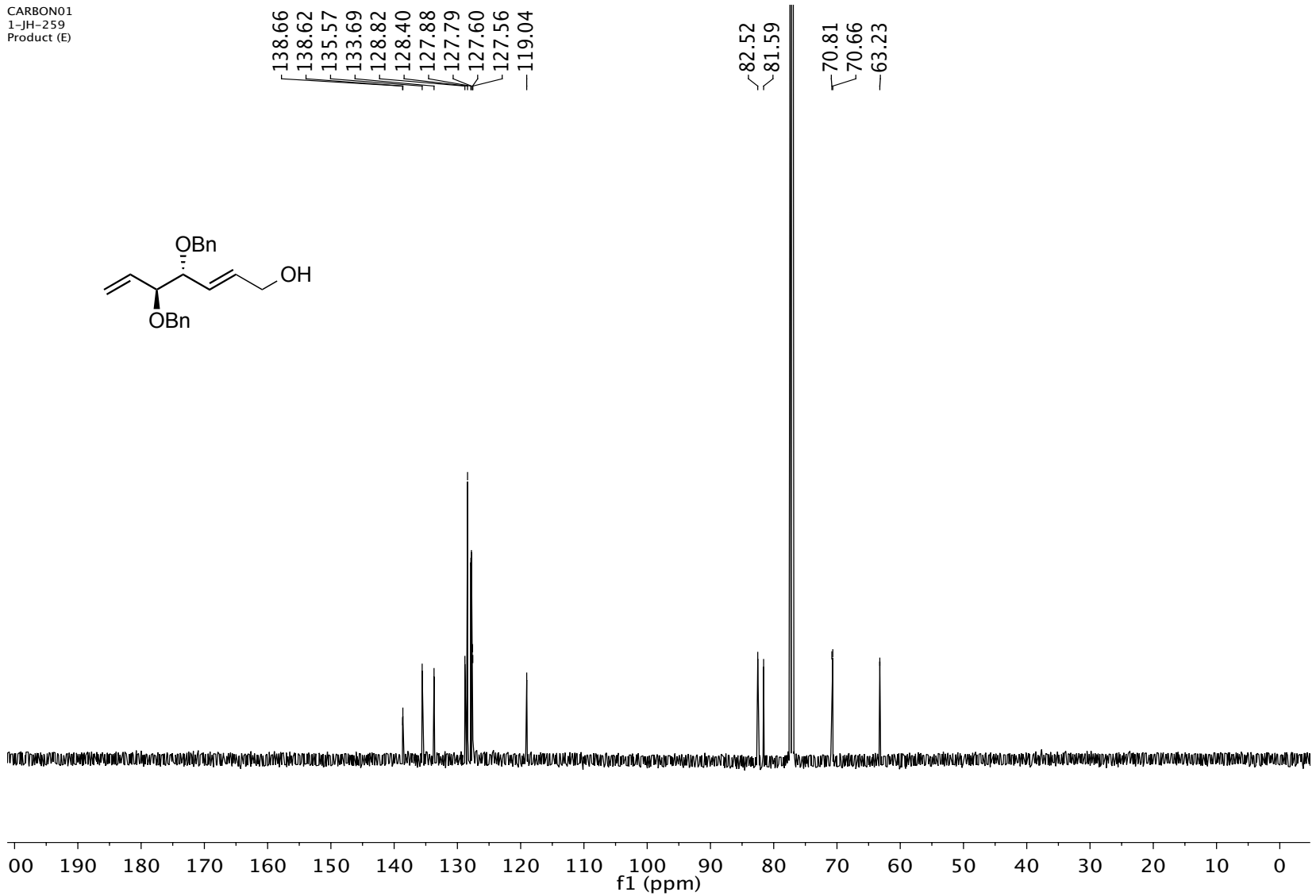


Figure S18. ^{13}C NMR (125 MHz, $CDCl_3$) of *E*-**7e**.

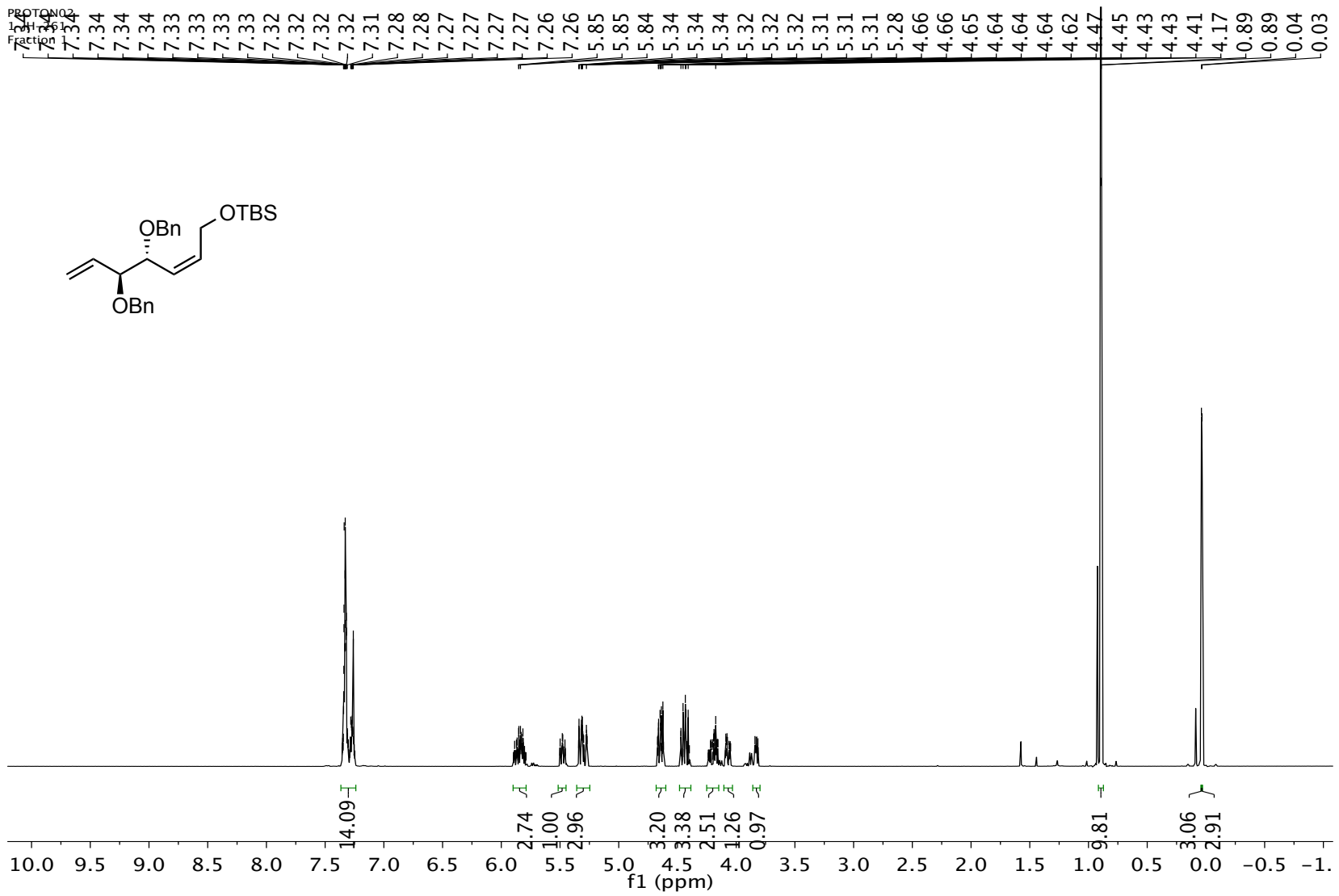


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7g**.

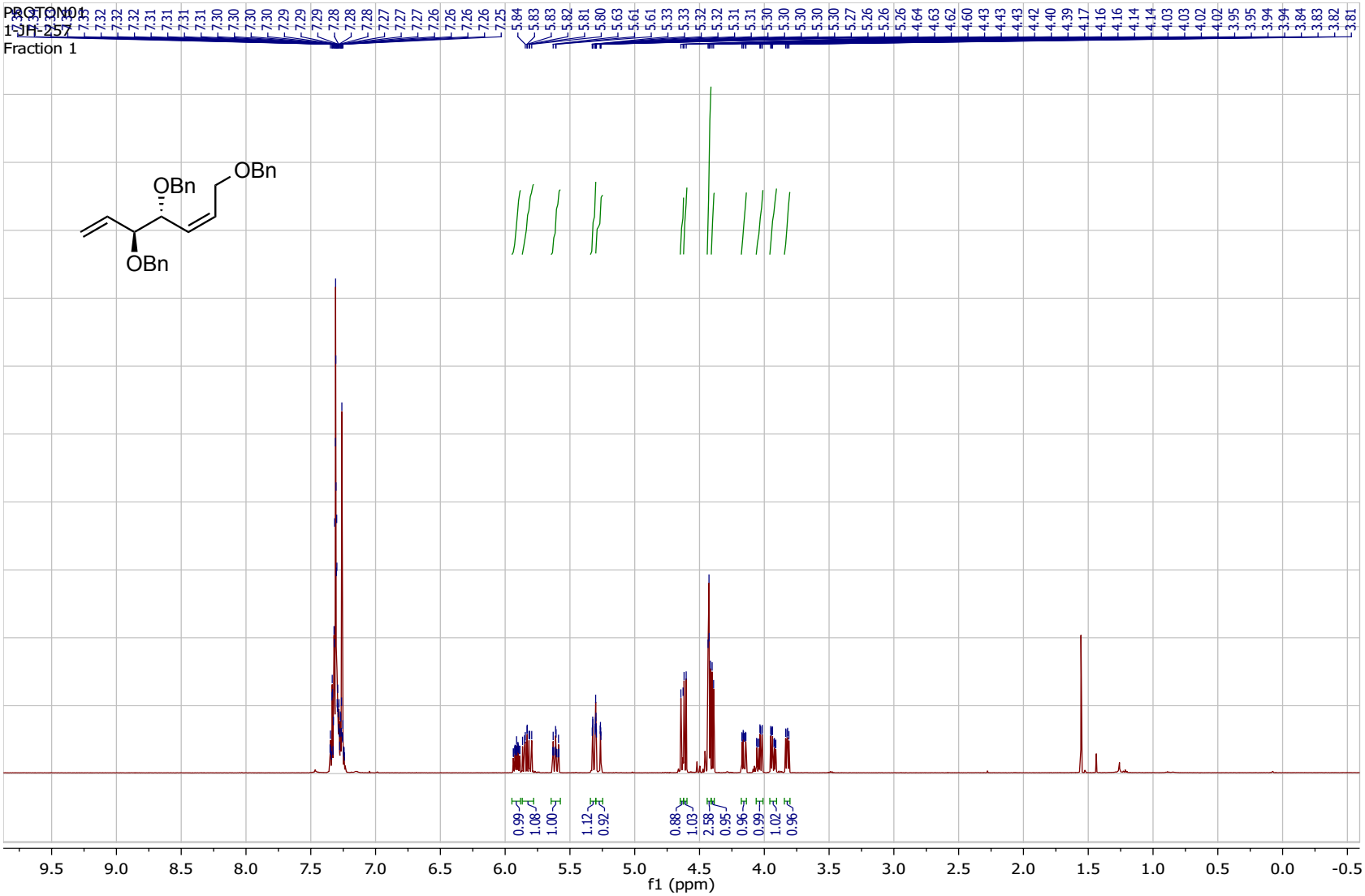


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7h**.

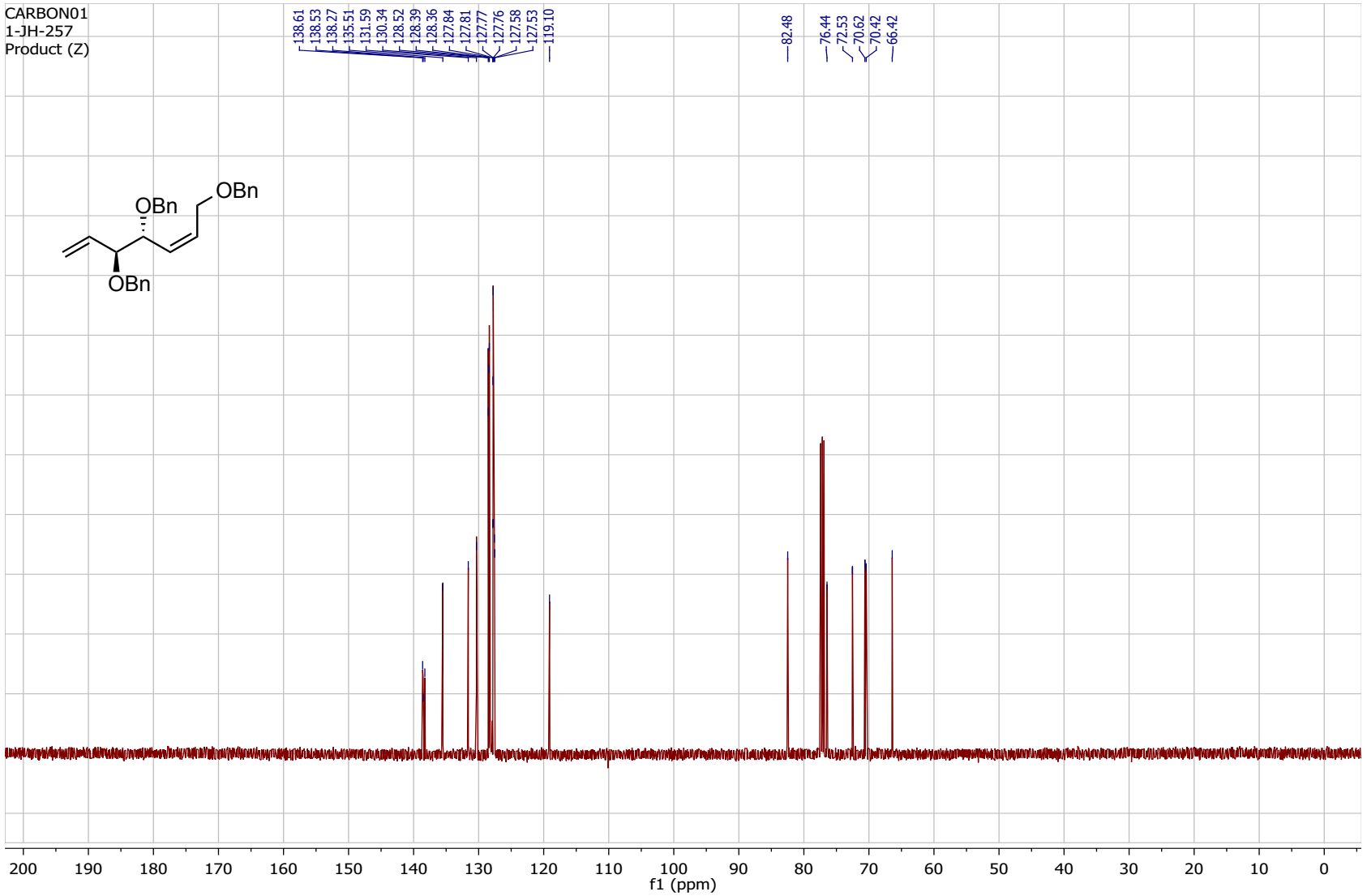


Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7h**.

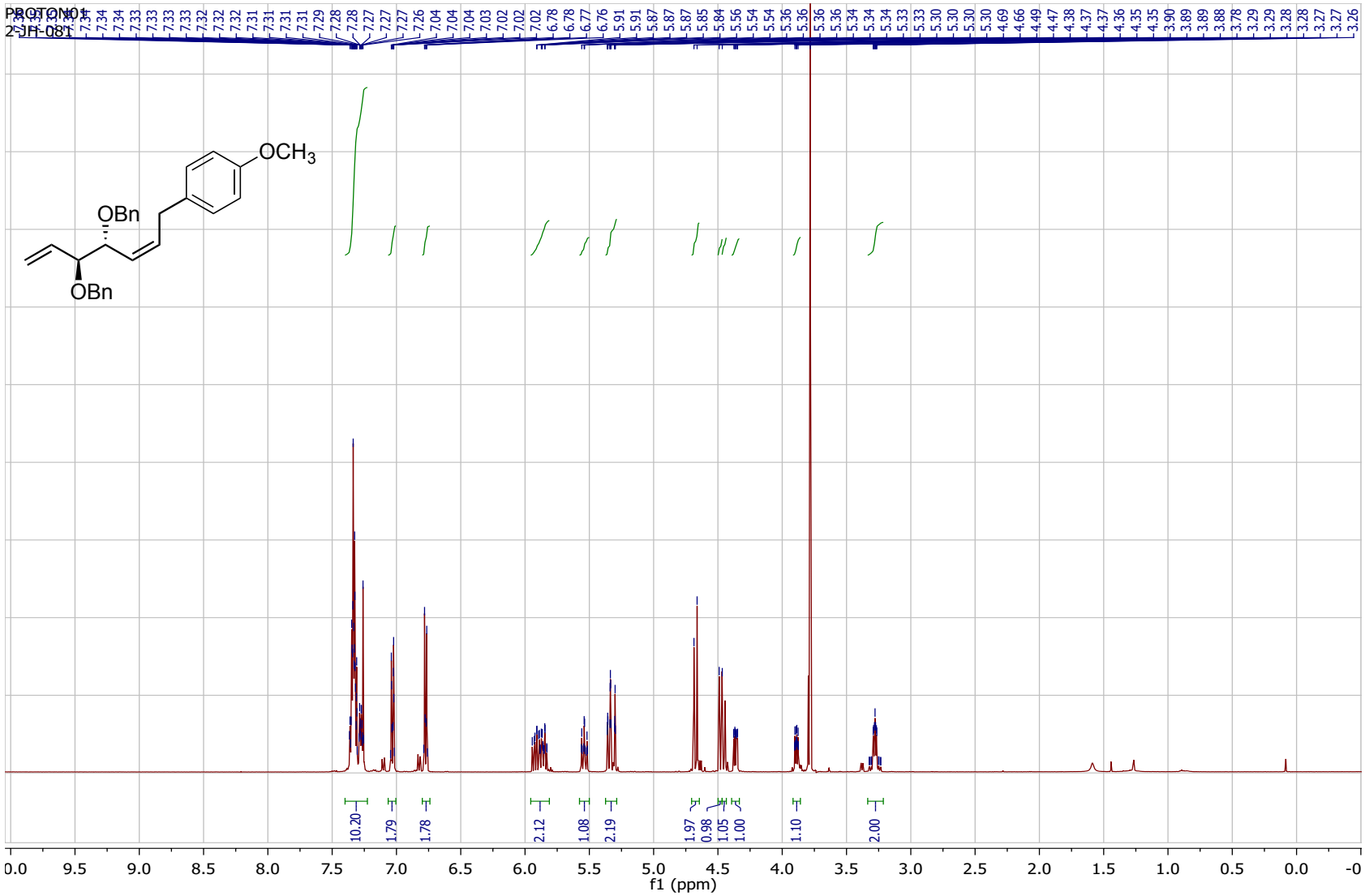


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) of **7i**.

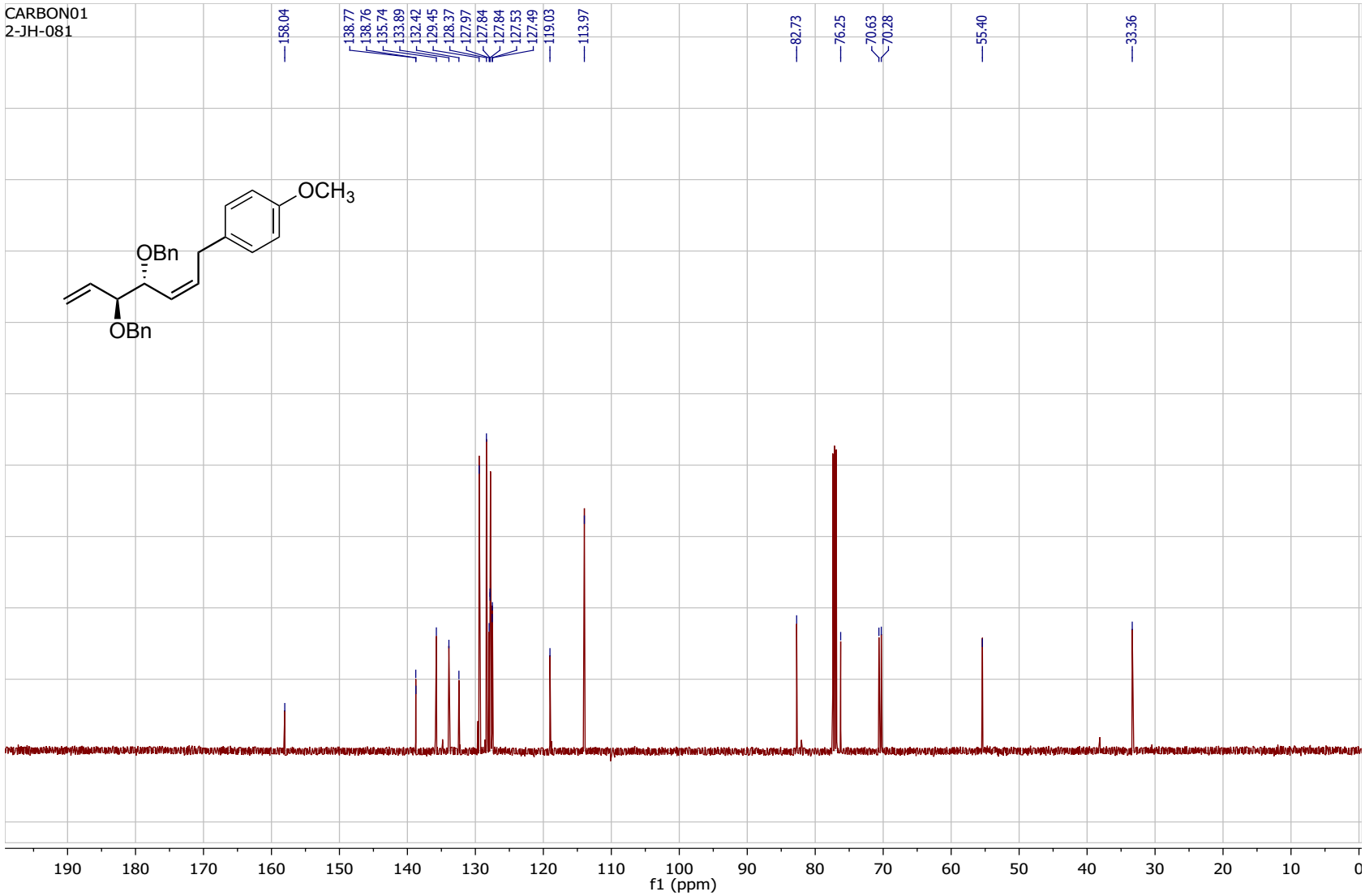


Figure S27. ^{13}C NMR (125 MHz, $CDCl_3$) of **7i**.

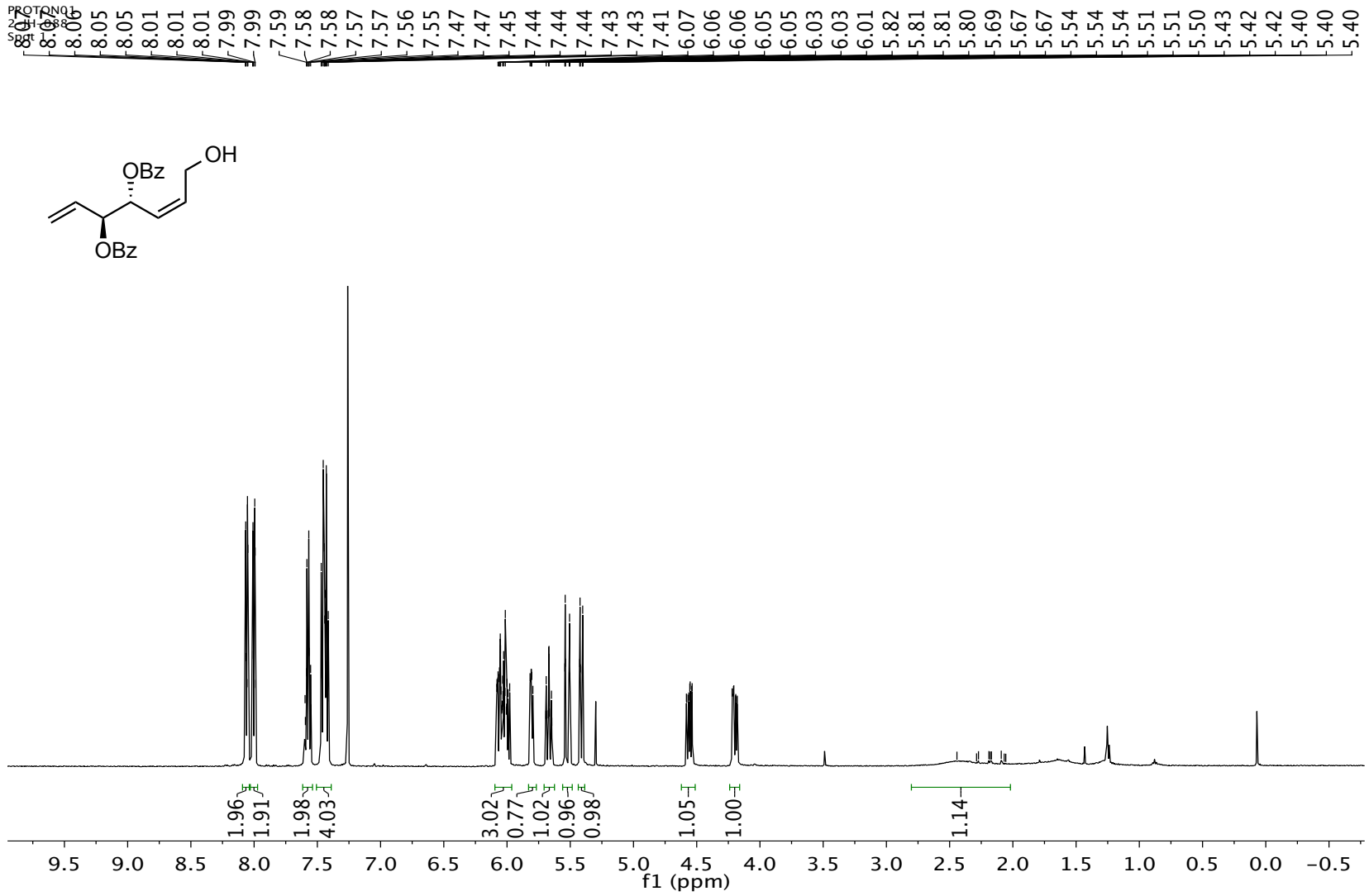


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7c**.

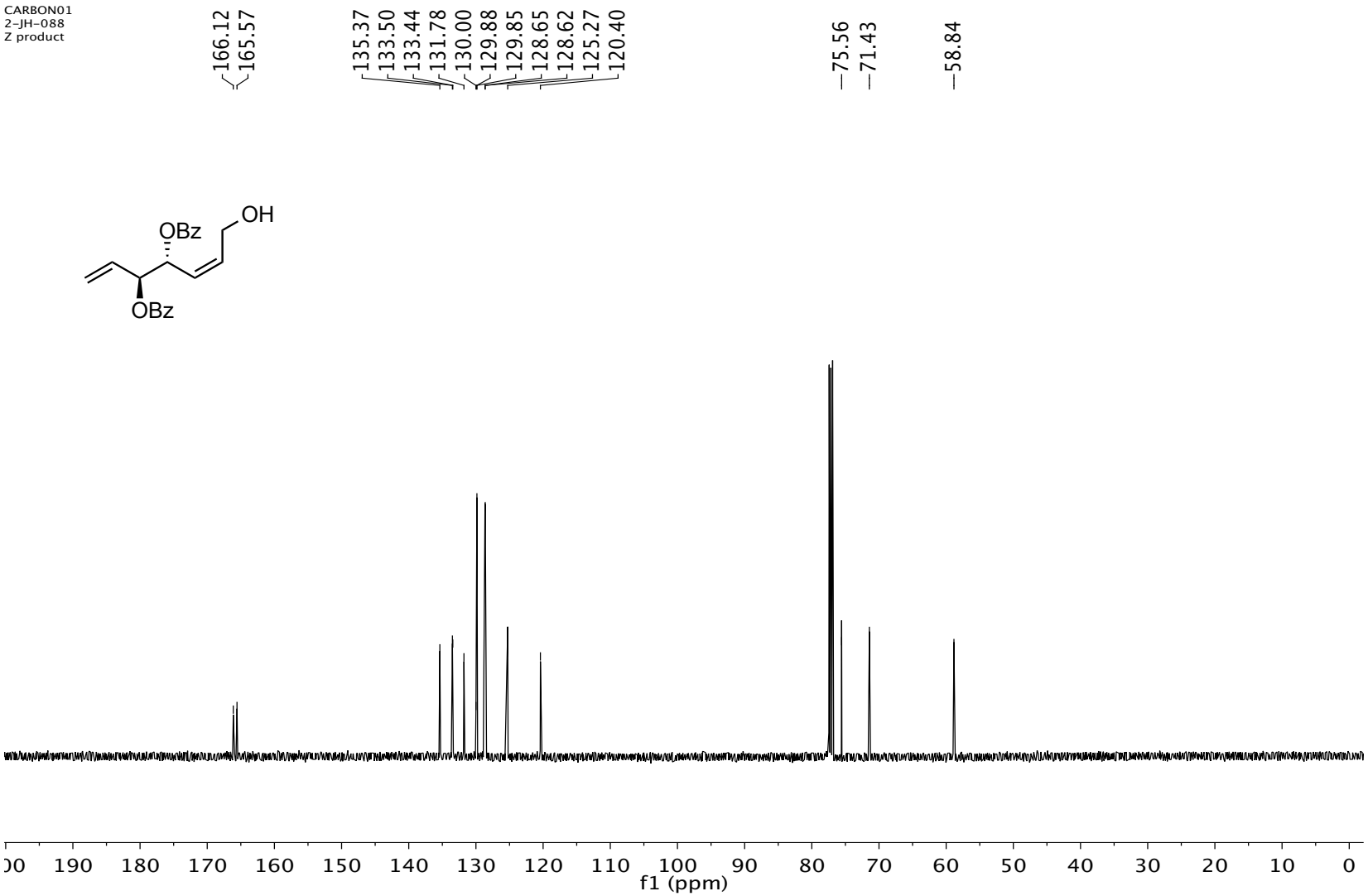


Figure S12. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7c**.

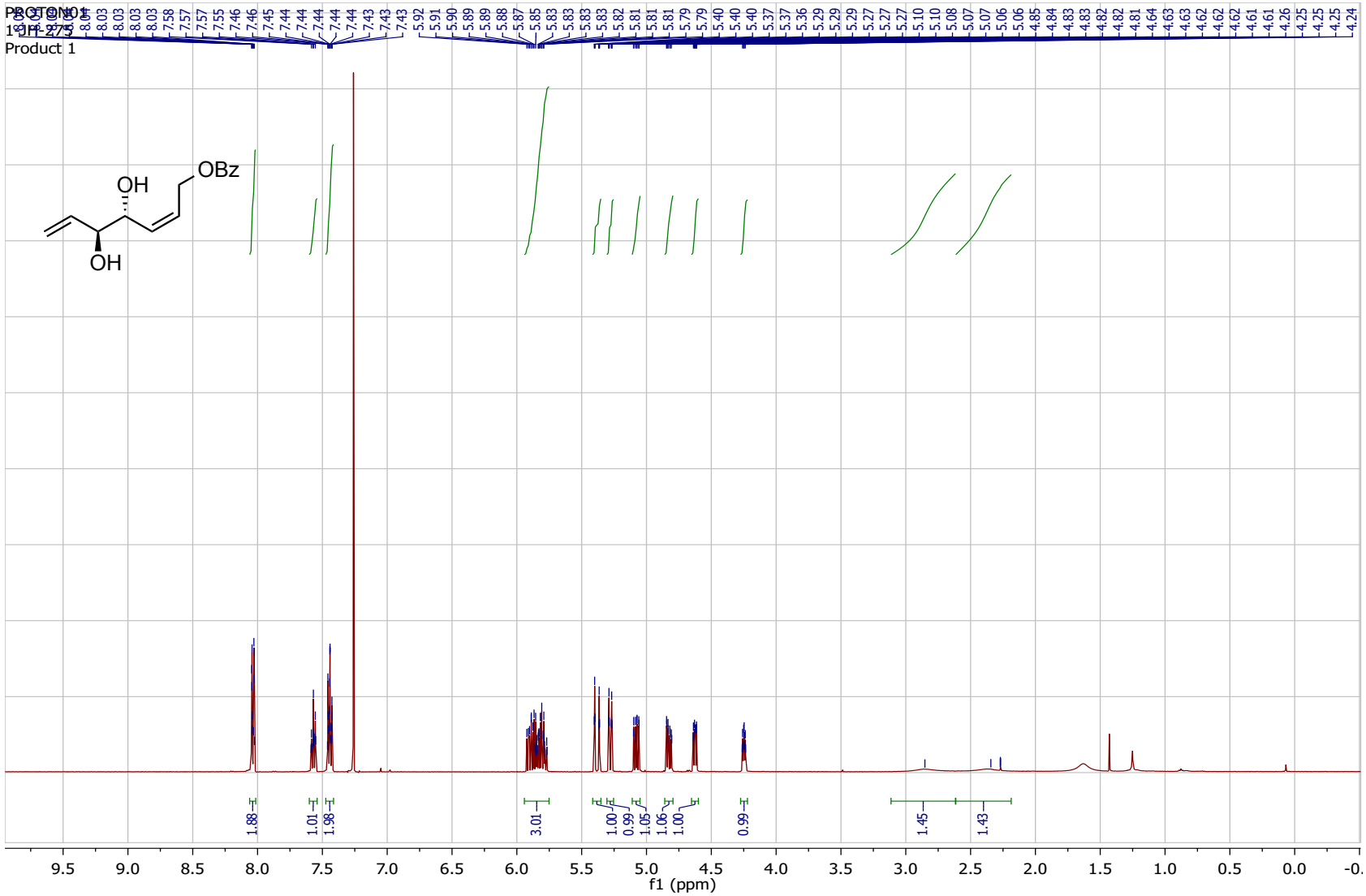


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7b**.

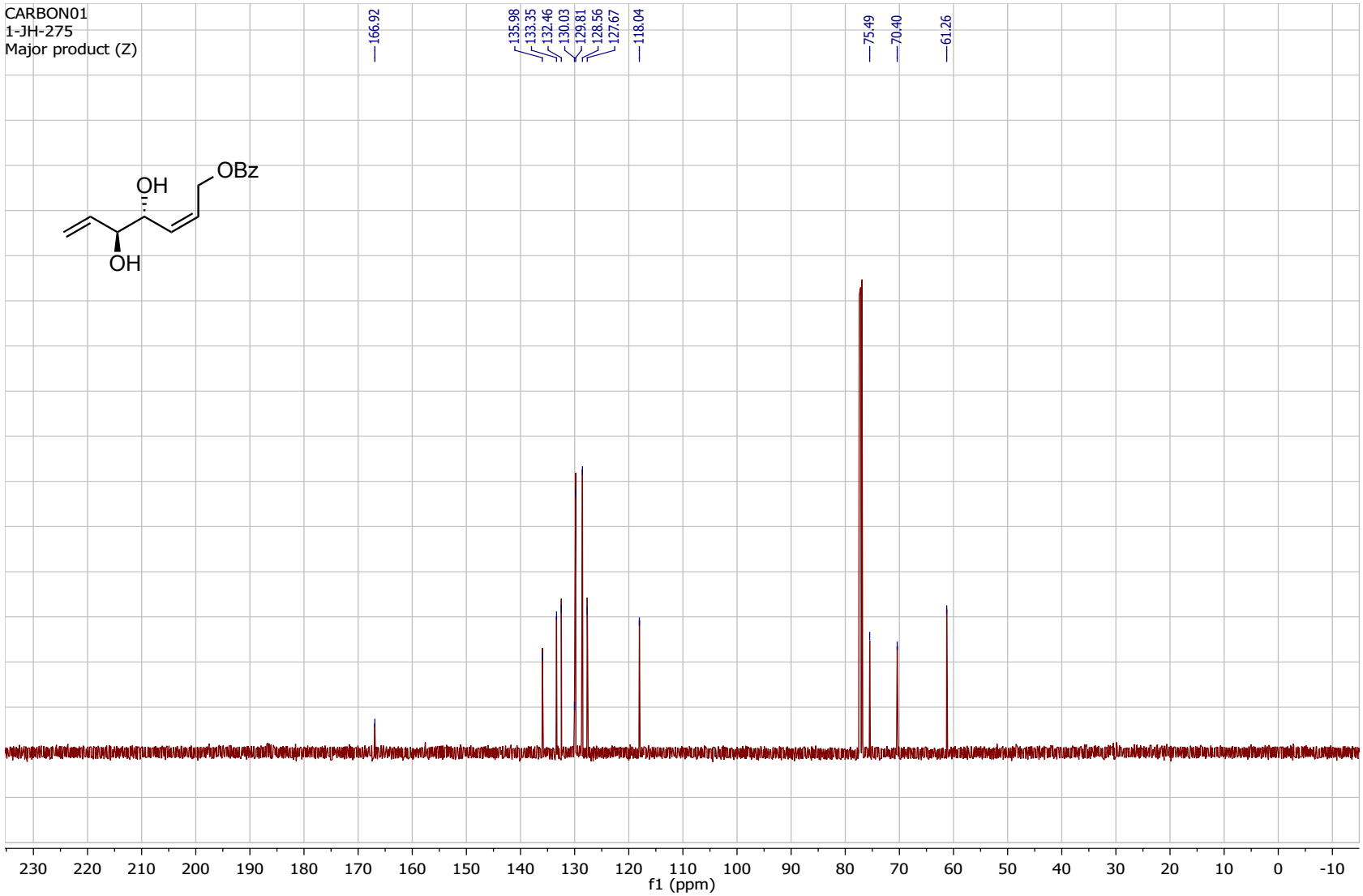


Figure S8. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7b**.

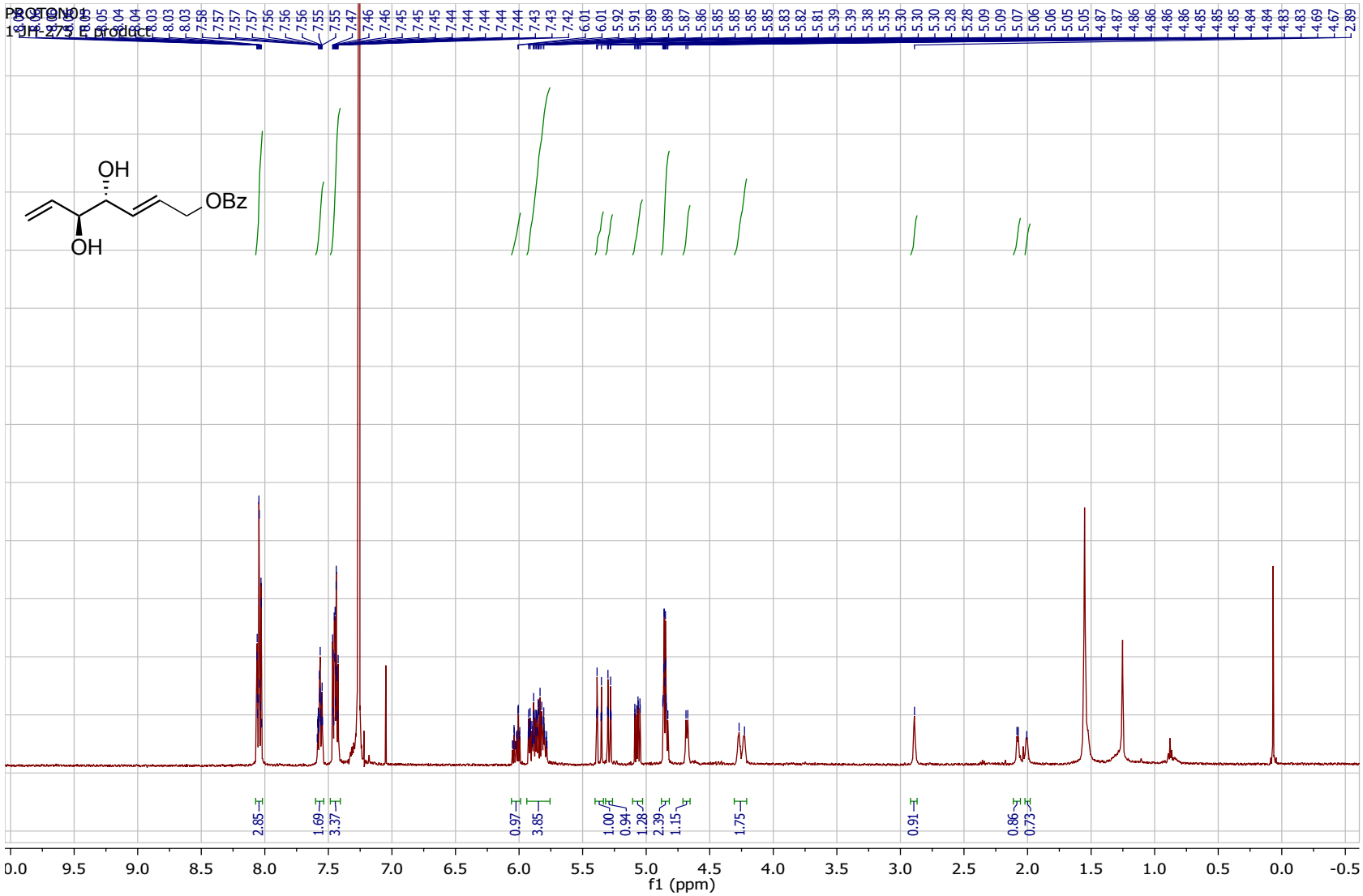


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) of *E*-**7b**.

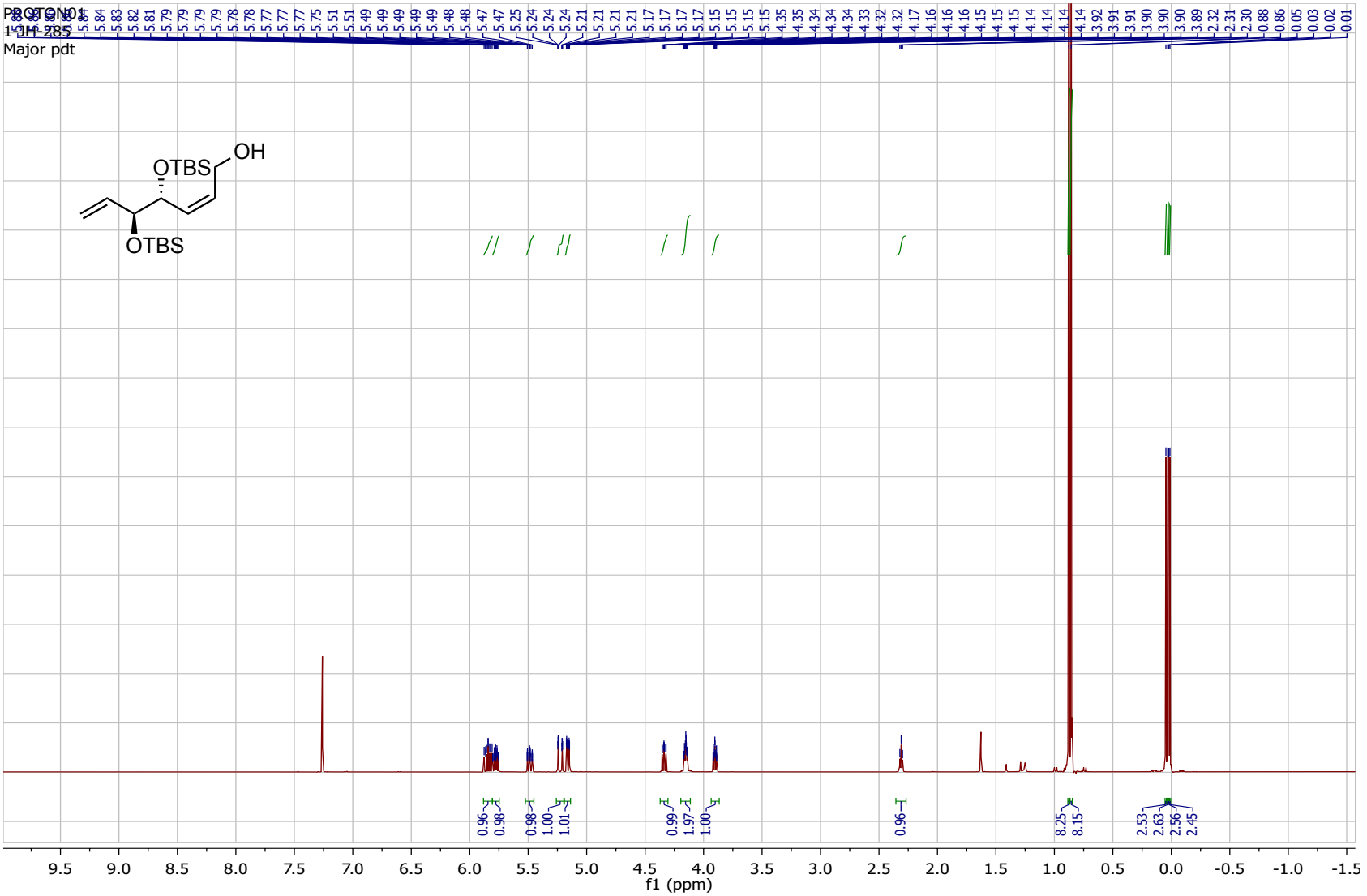


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7a**.

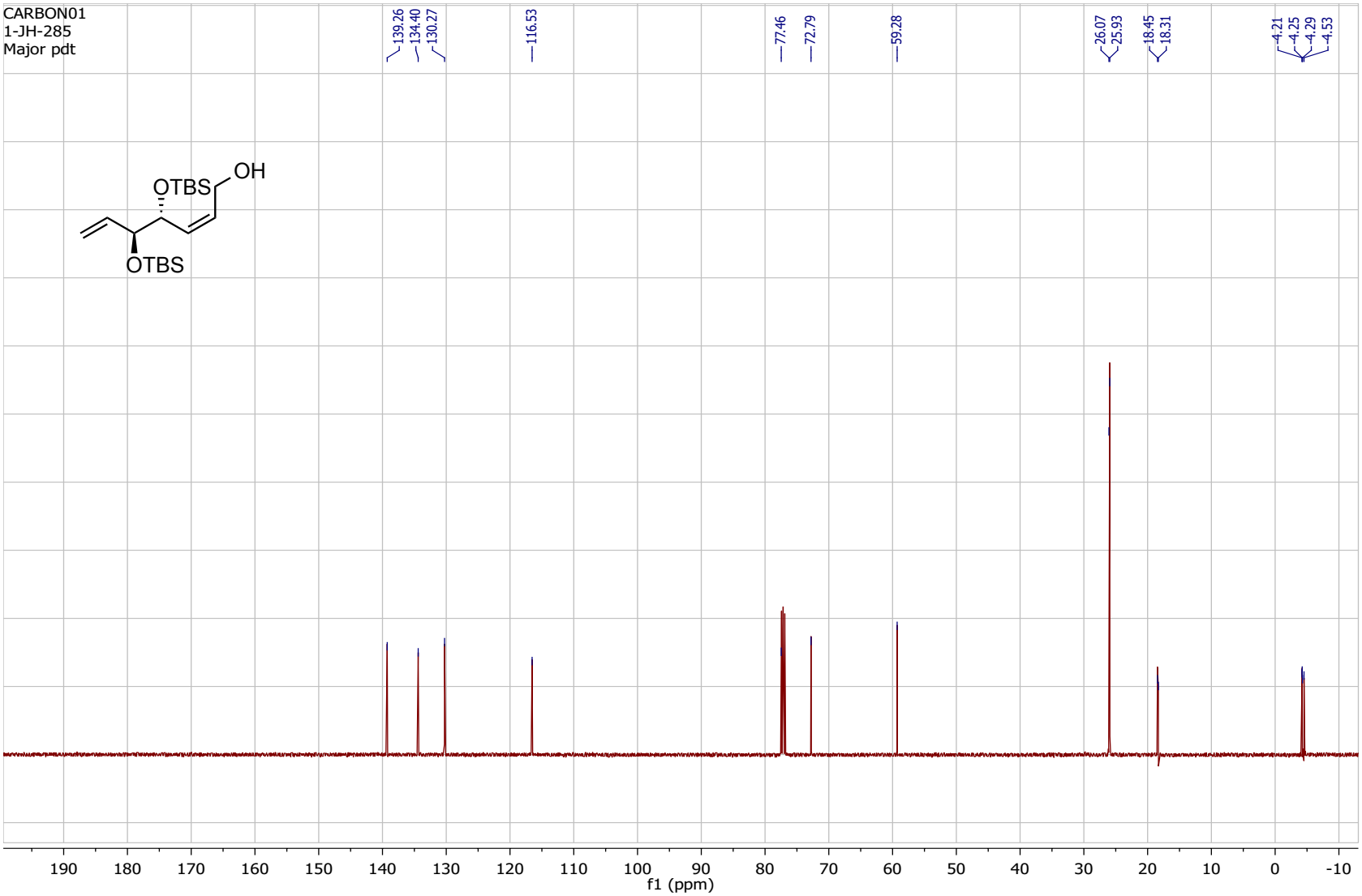


Figure S6. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7a**.

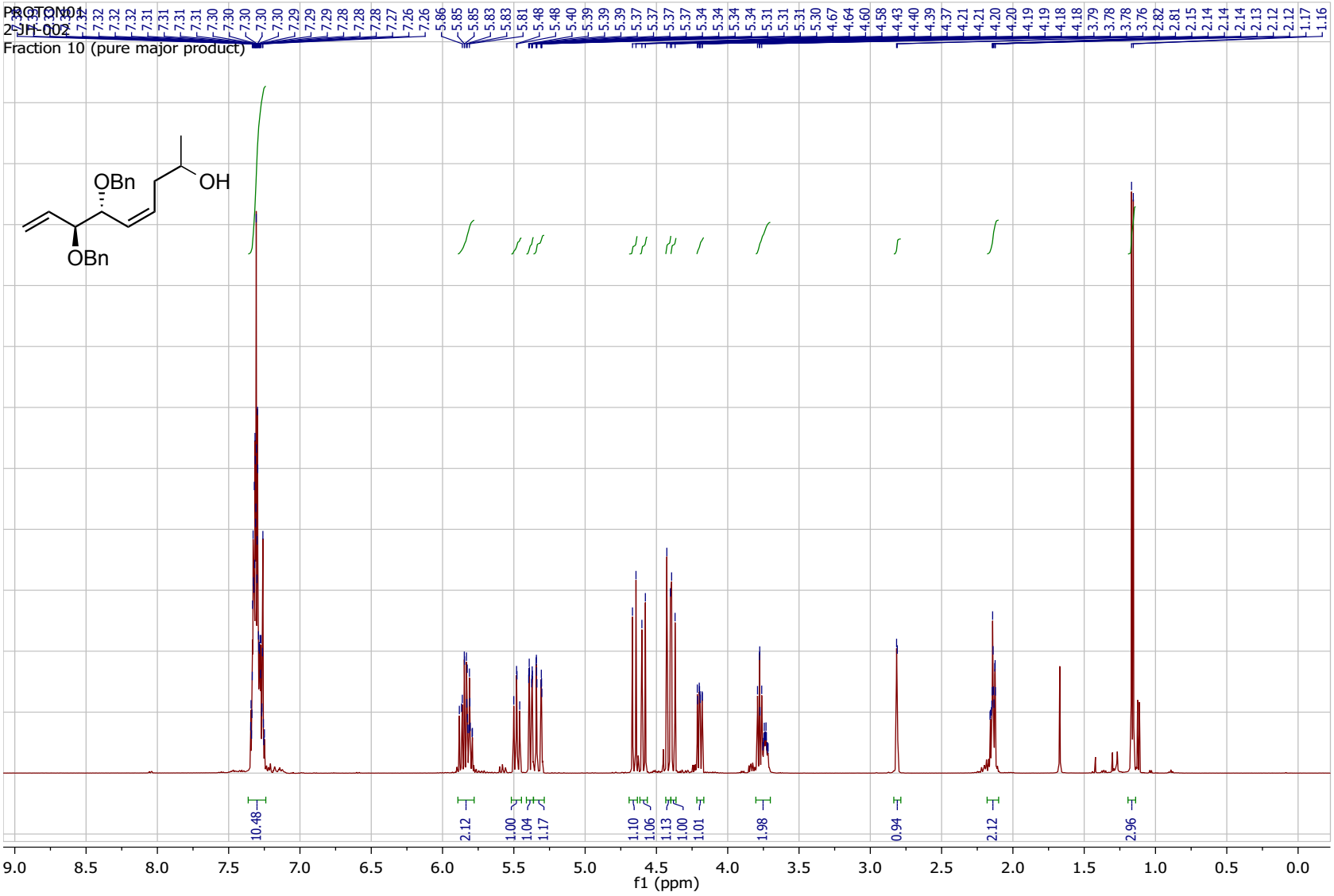


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**9**.

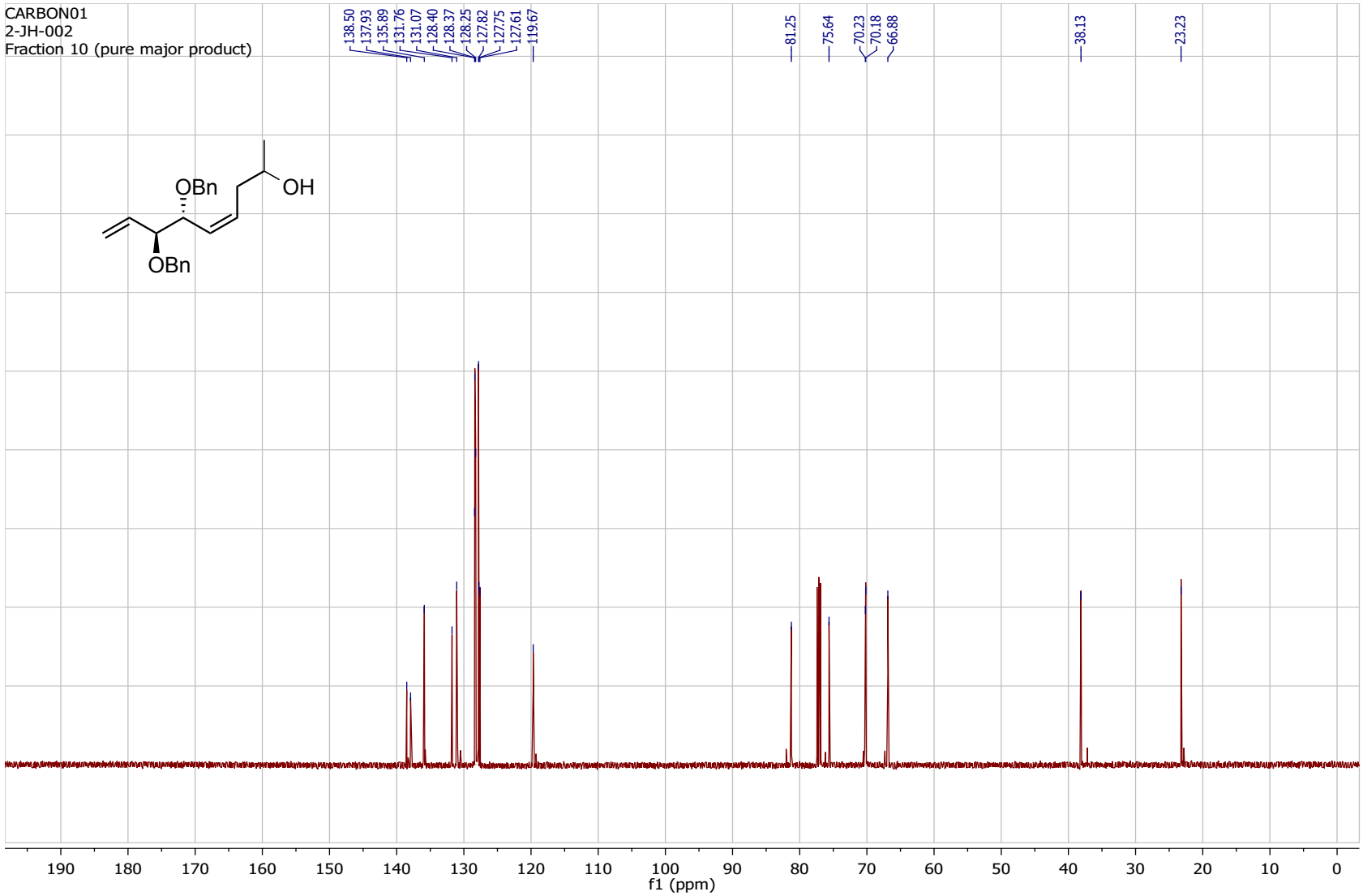


Figure S33. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**9**.

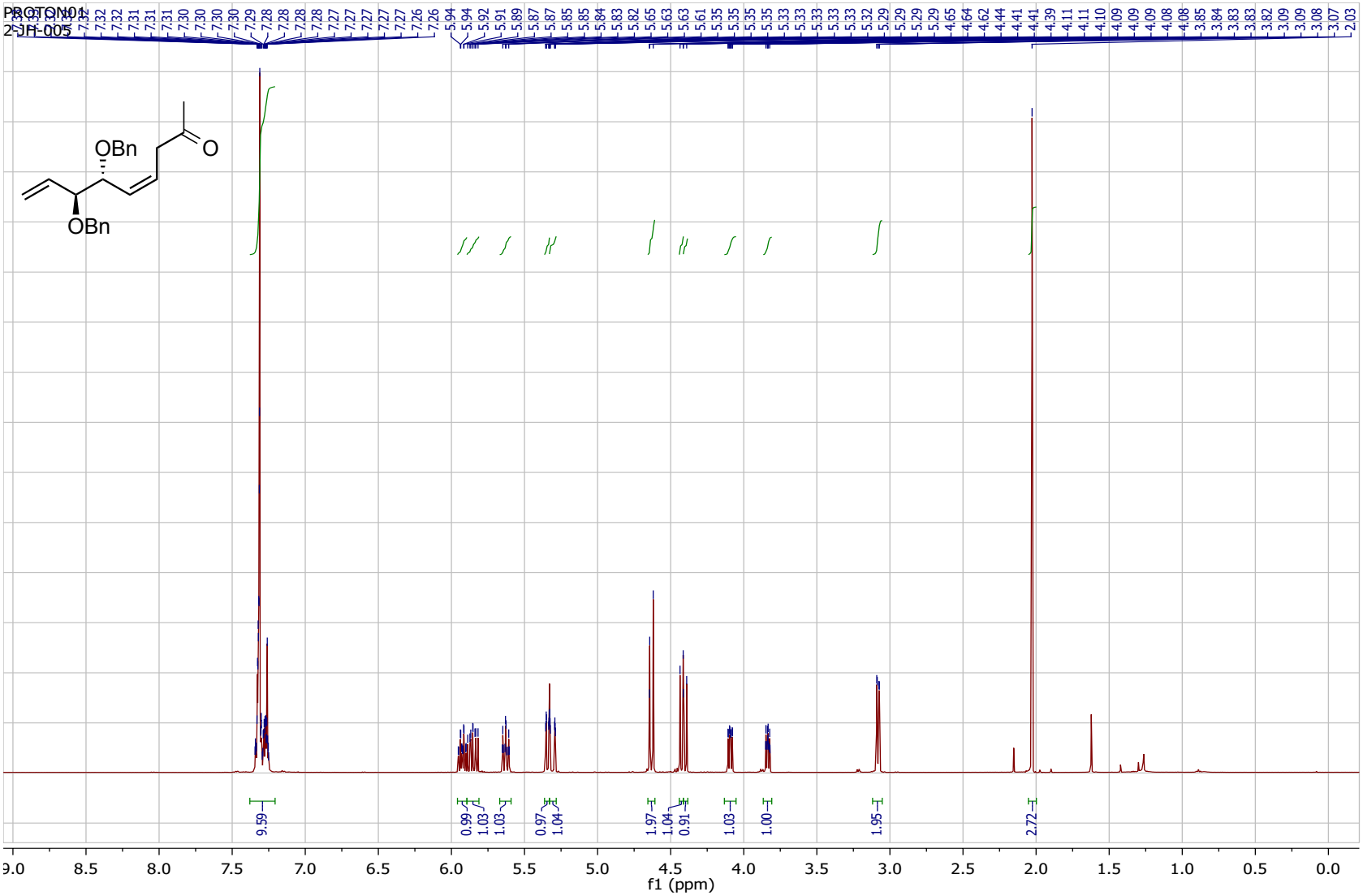


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) of **10**.

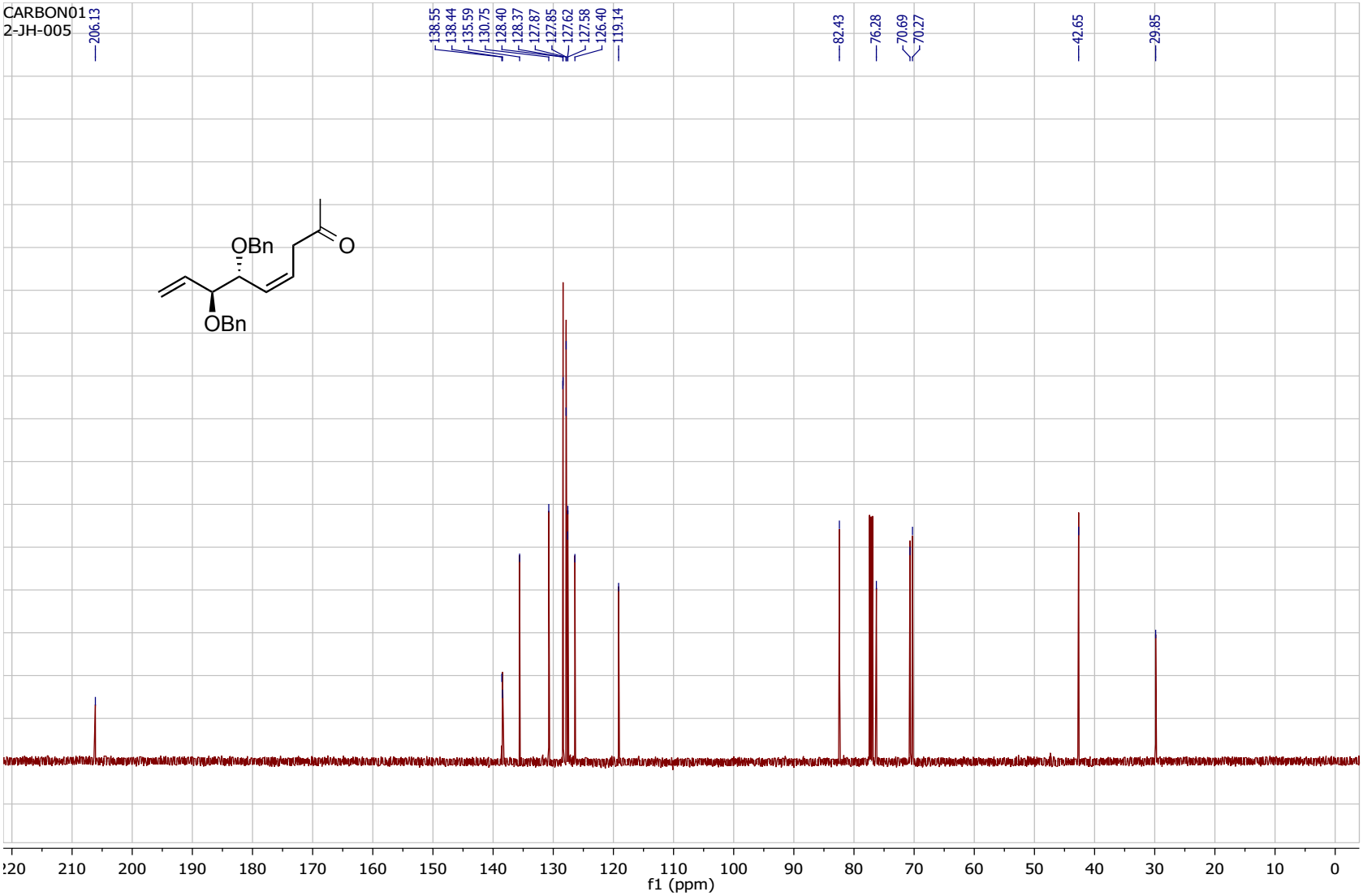


Figure S35. ^{13}C NMR (125 MHz, $CDCl_3$) of **10**.

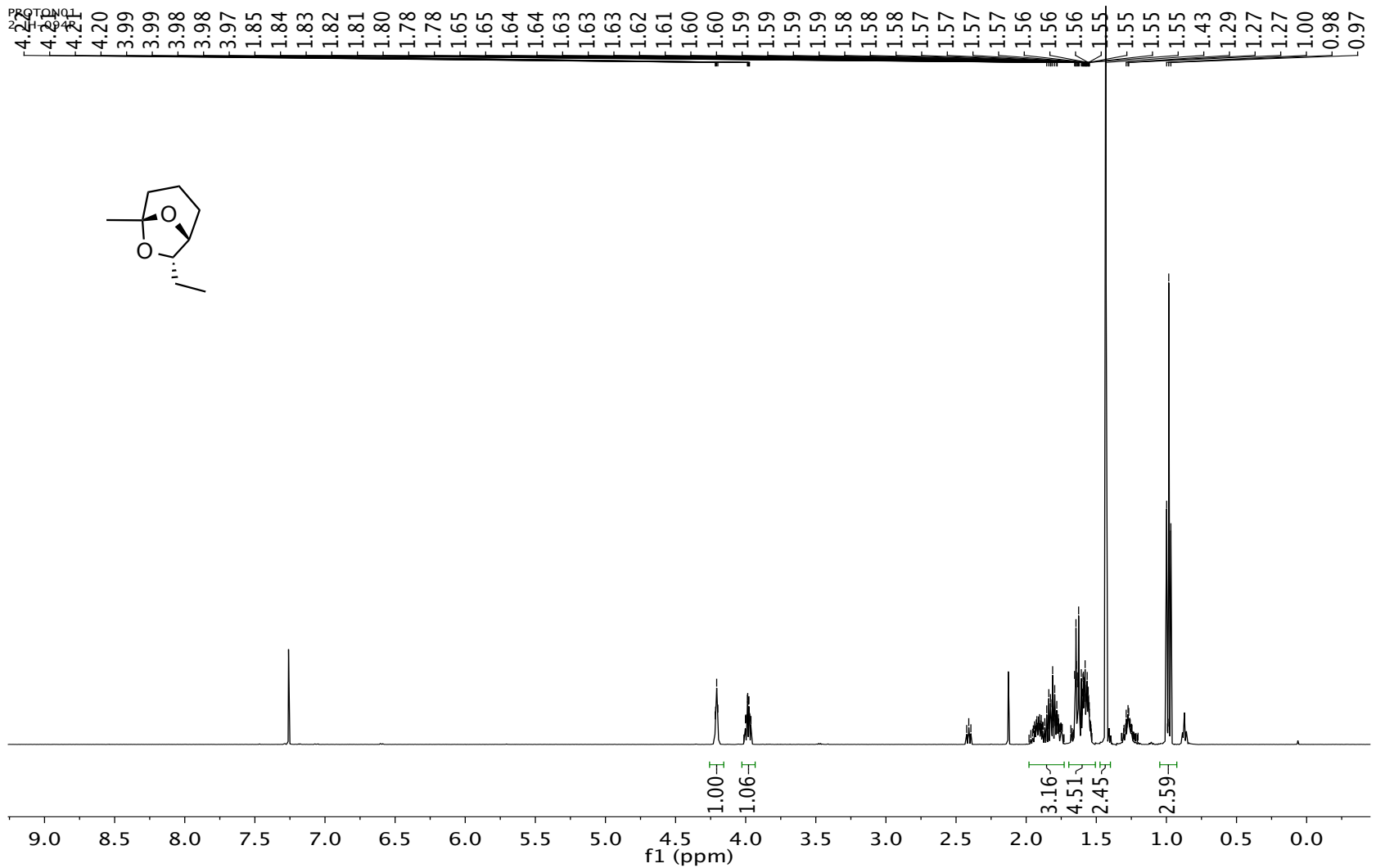


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) of **11**.

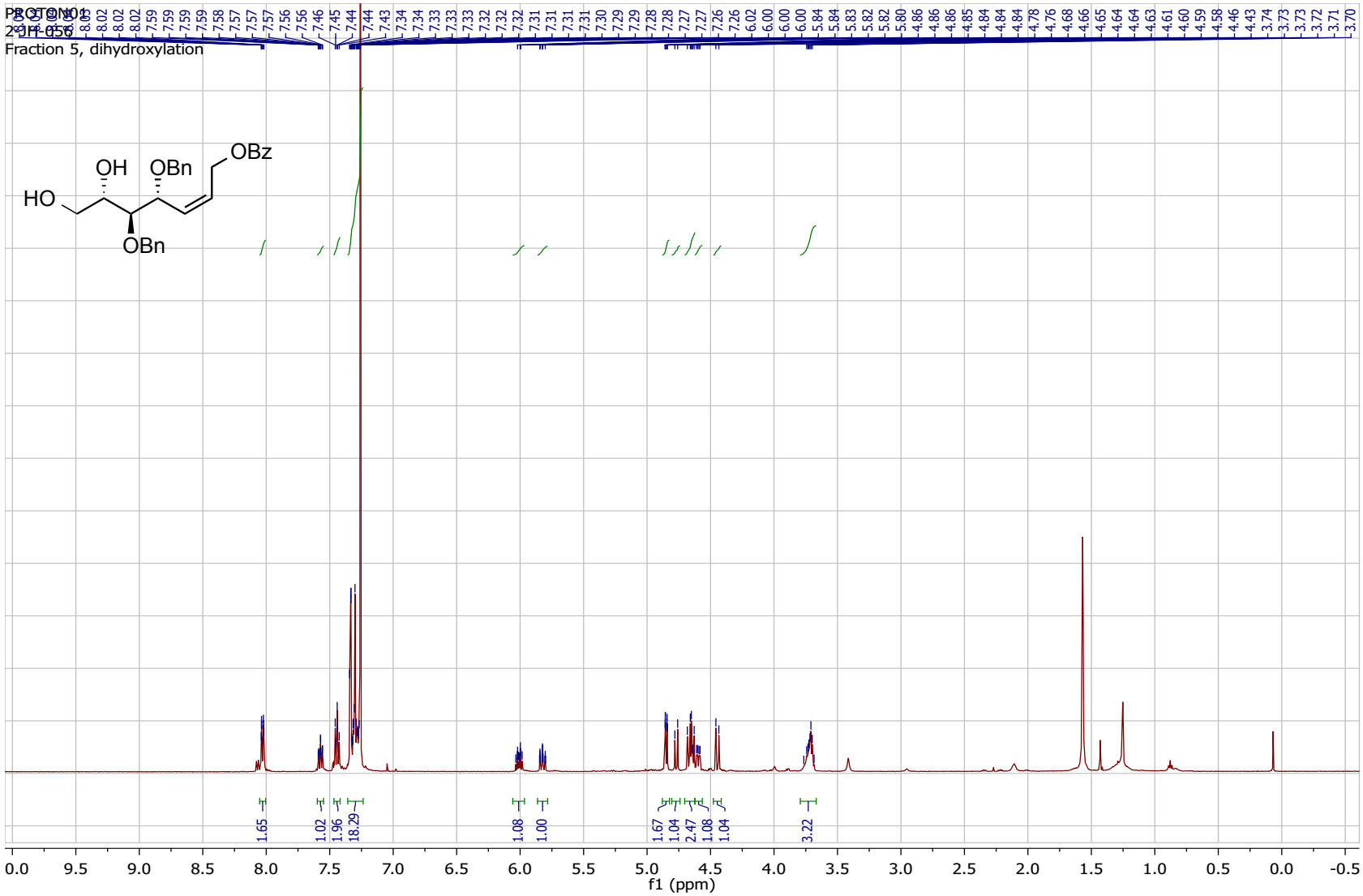


Figure S38. ^{1}H NMR (500 MHz, $CDCl_3$) of **12**.

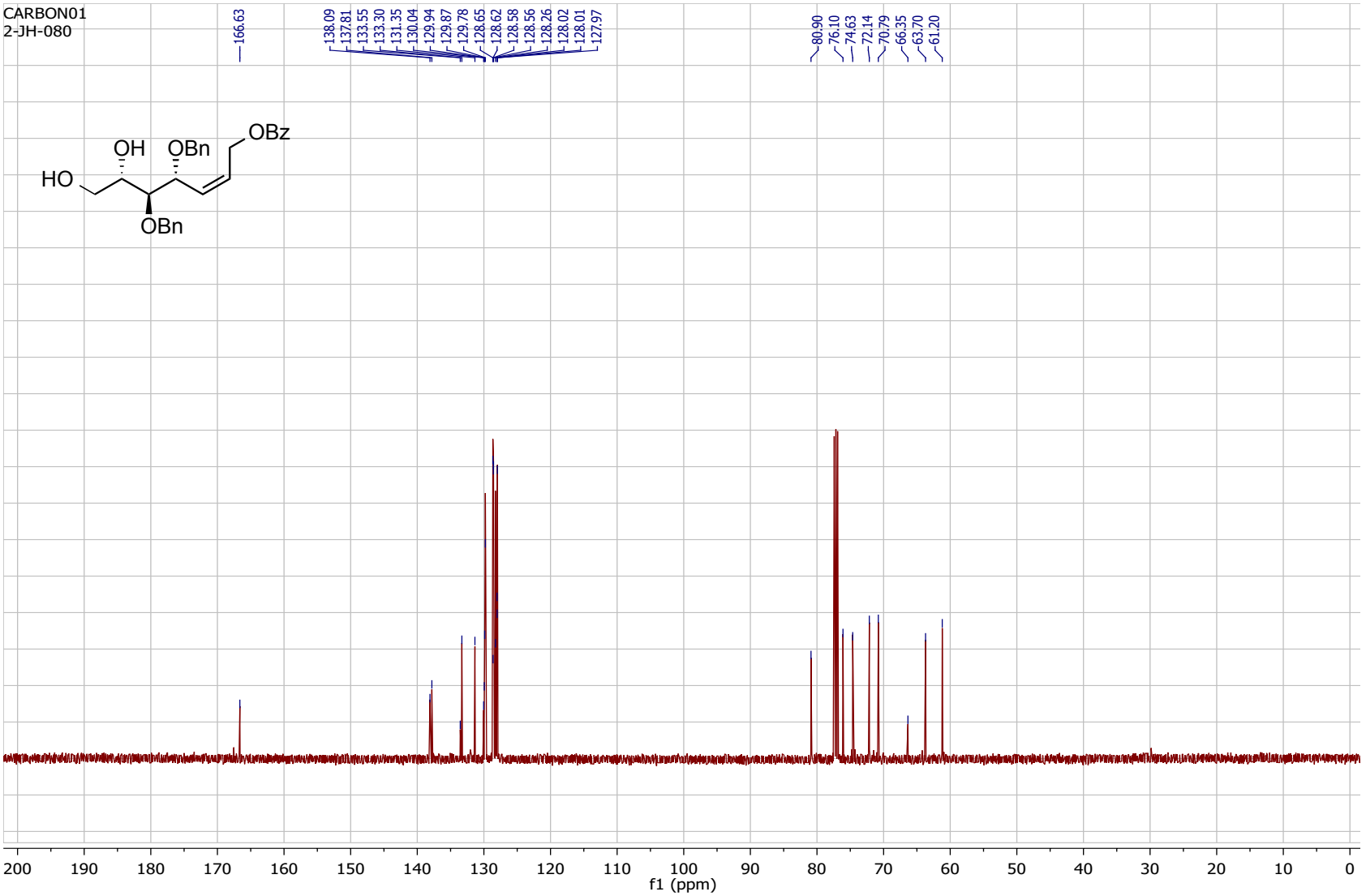


Figure S39. ^{13}C NMR (125 MHz, $CDCl_3$) of **12**.

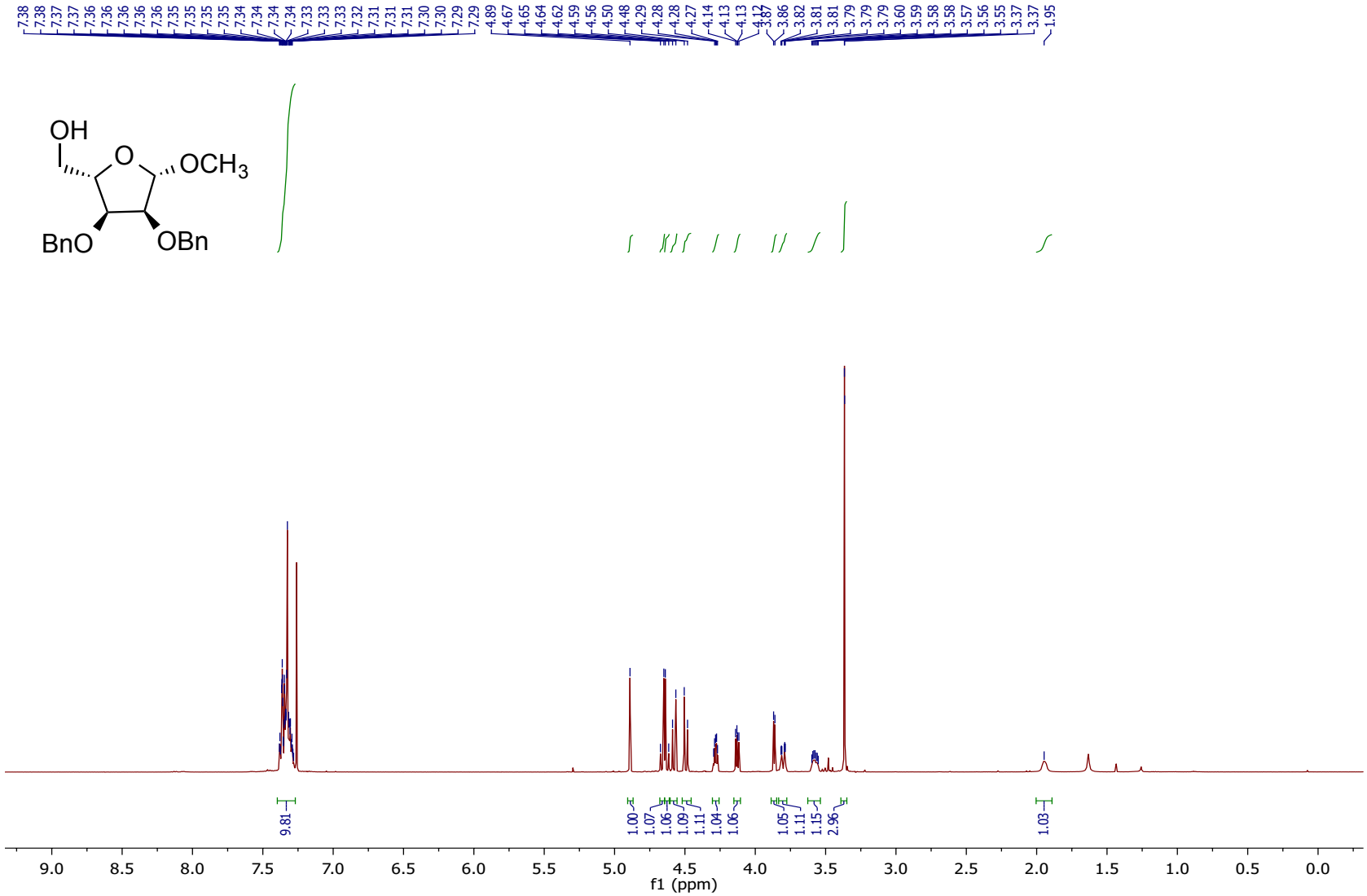


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) of **13**.

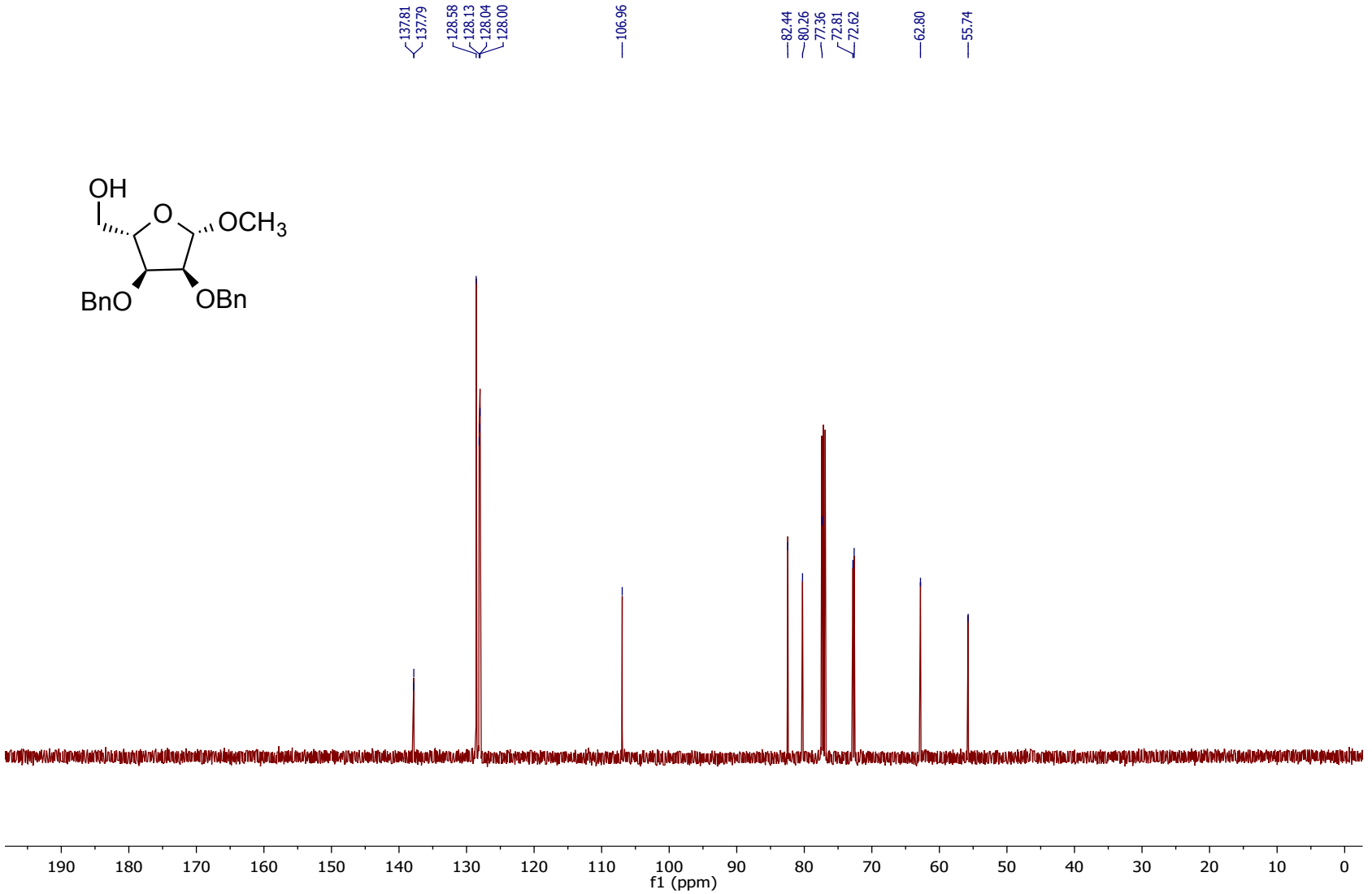


Figure S41. ^{13}C NMR (125 MHz, $CDCl_3$) of **13**.

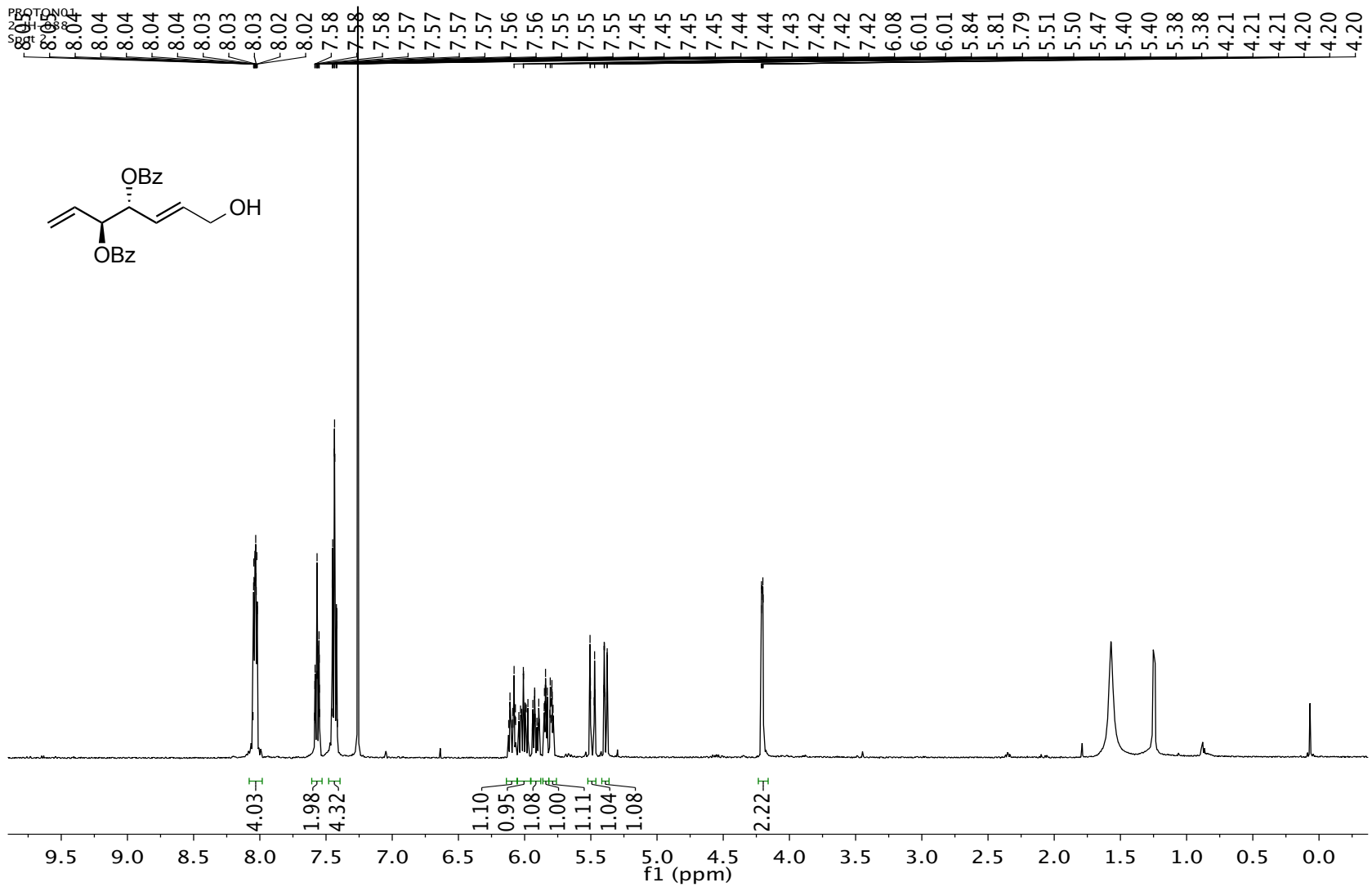


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) of *E*-**7c**.

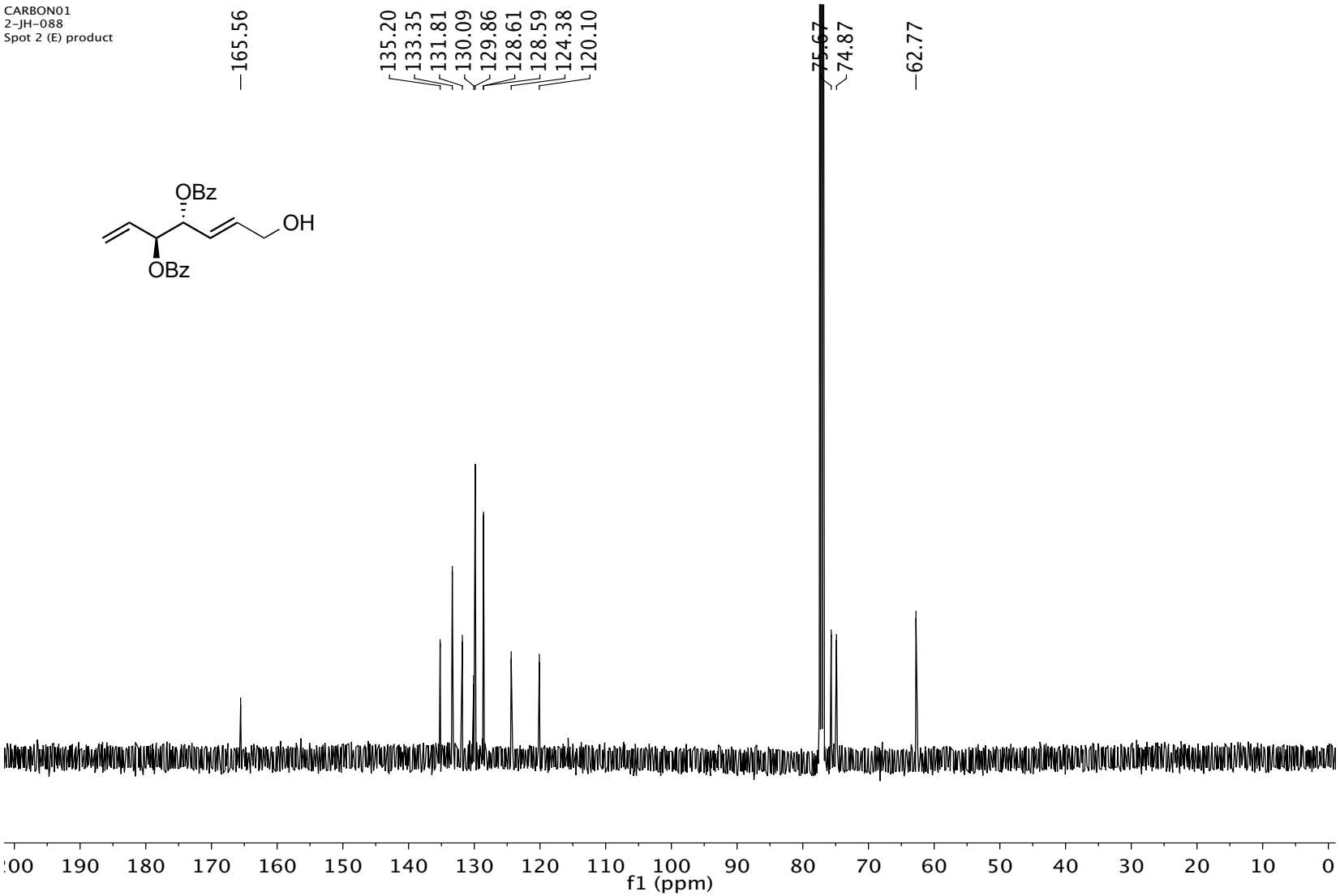


Figure S14. ^{13}C NMR (125 MHz, $CDCl_3$) of *E*-**7c**.

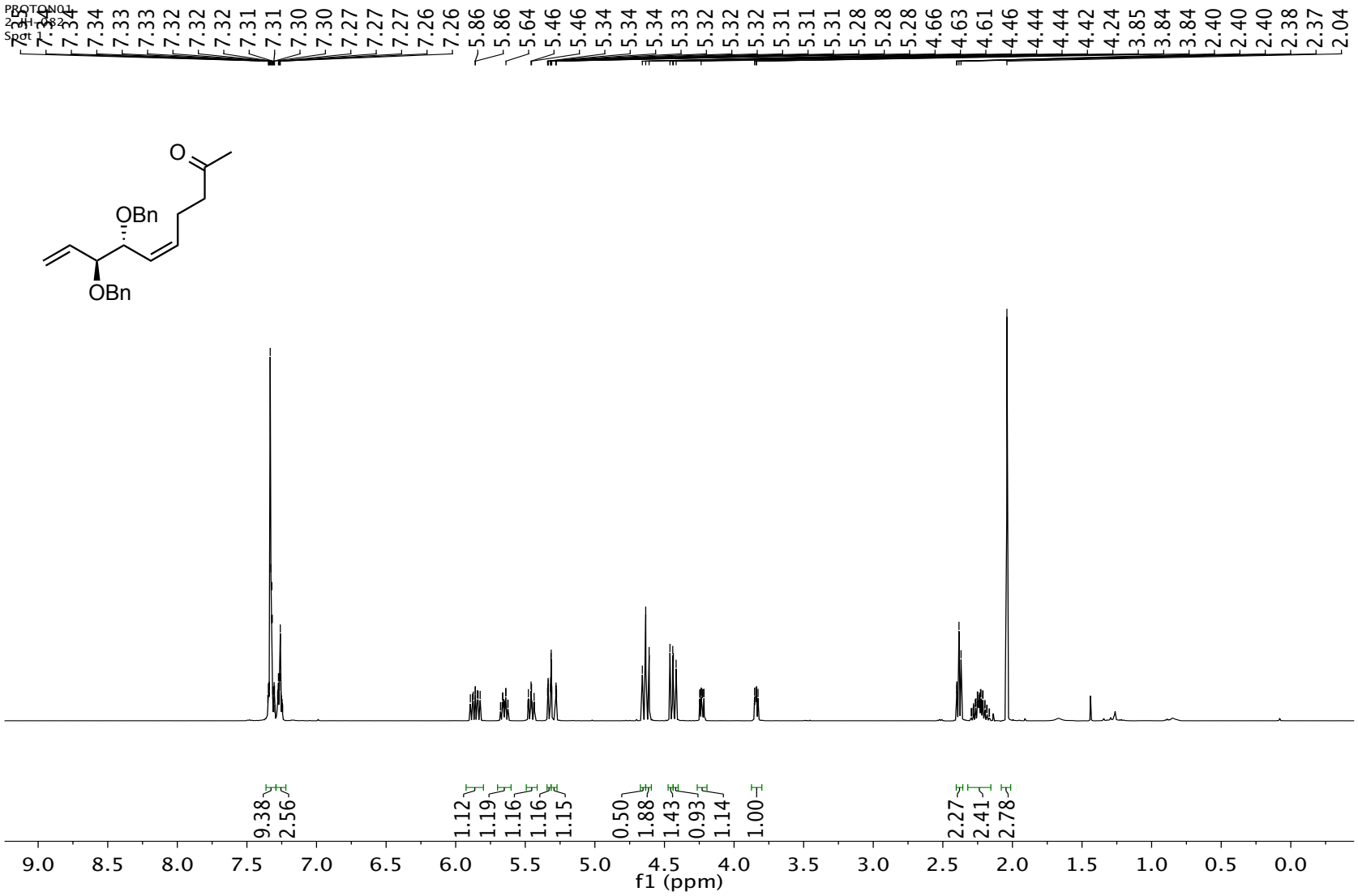


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7j**.

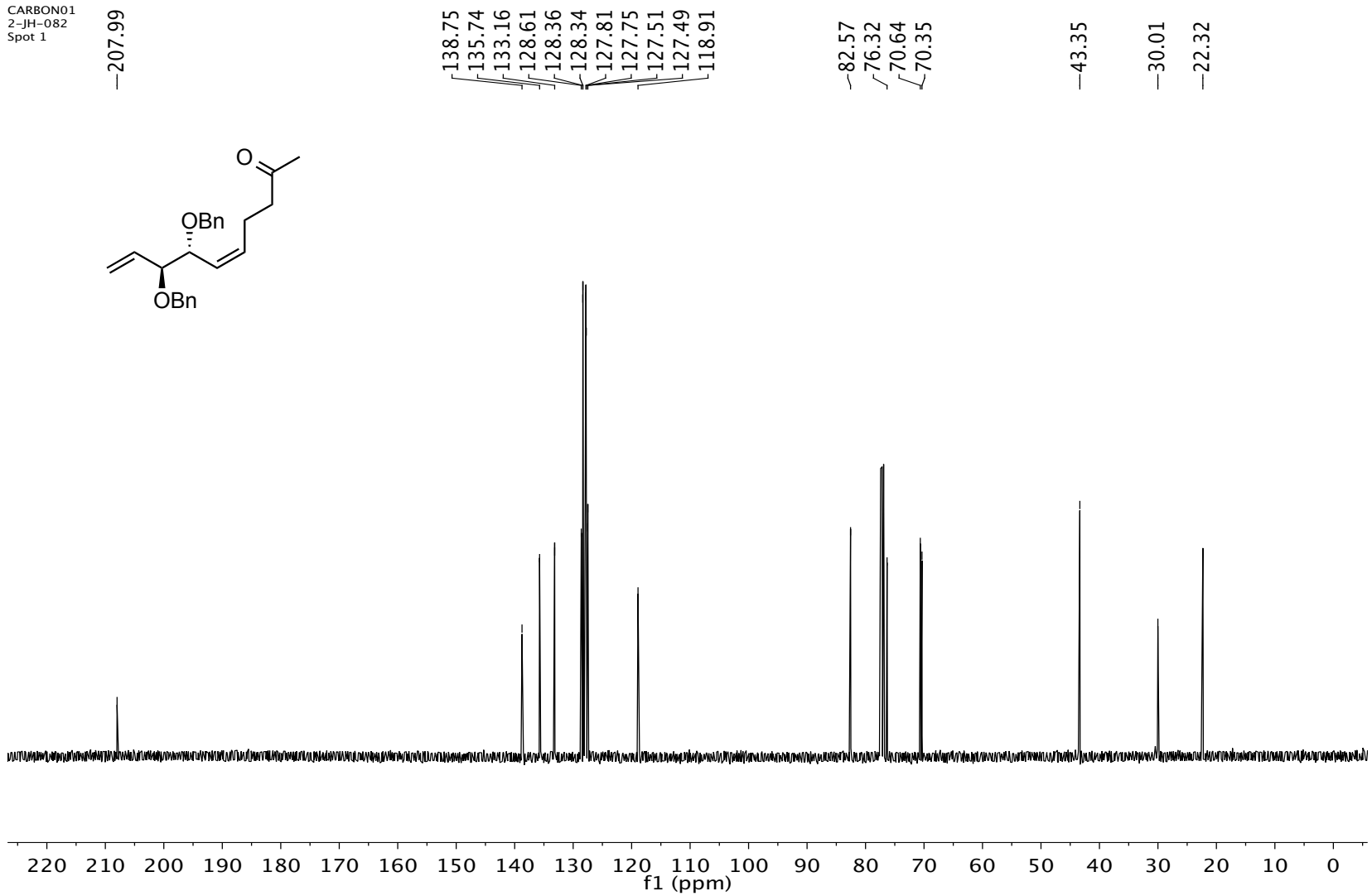


Figure S29. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7j**.

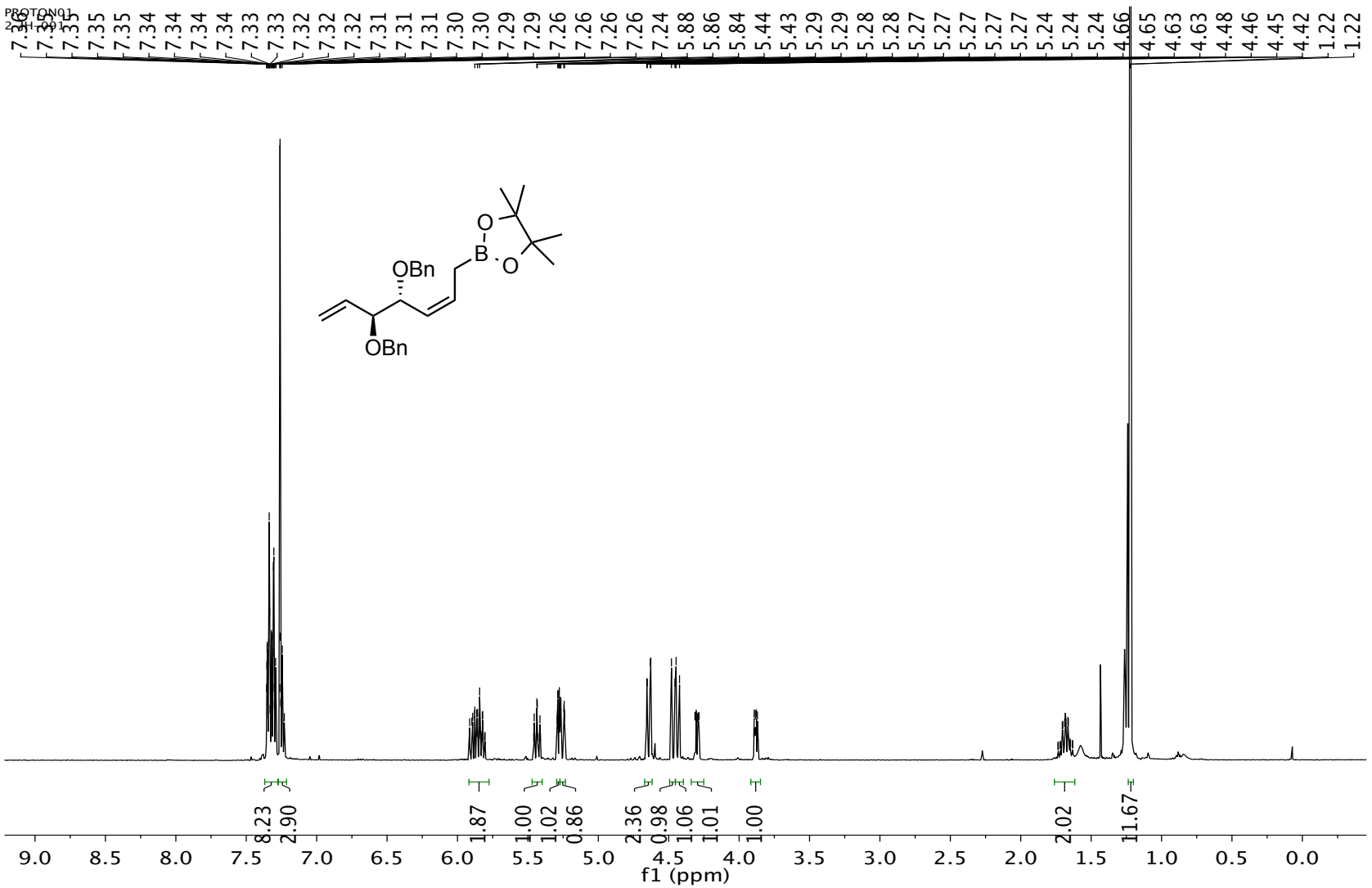


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**7k**.

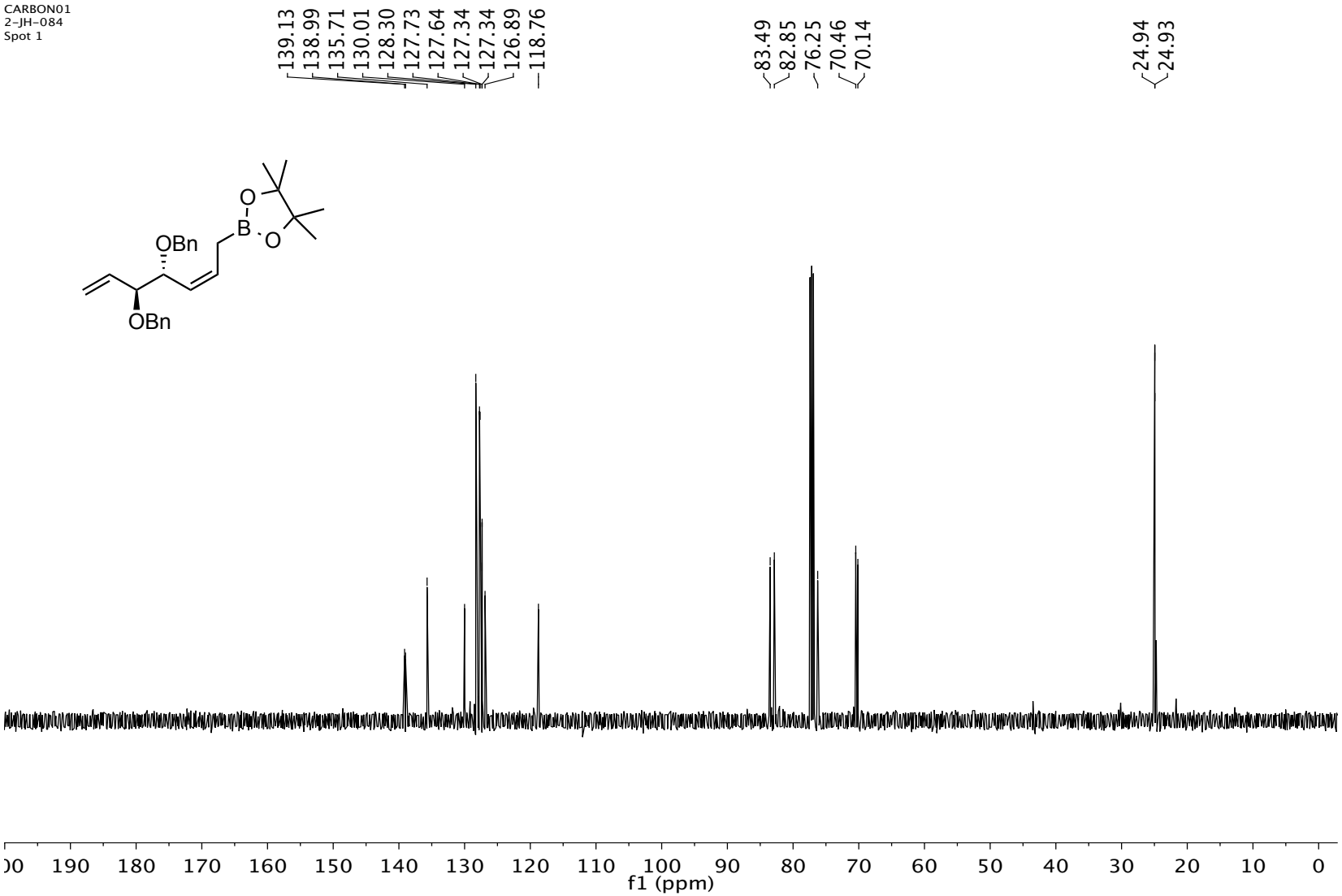


Figure S31. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**7k**.

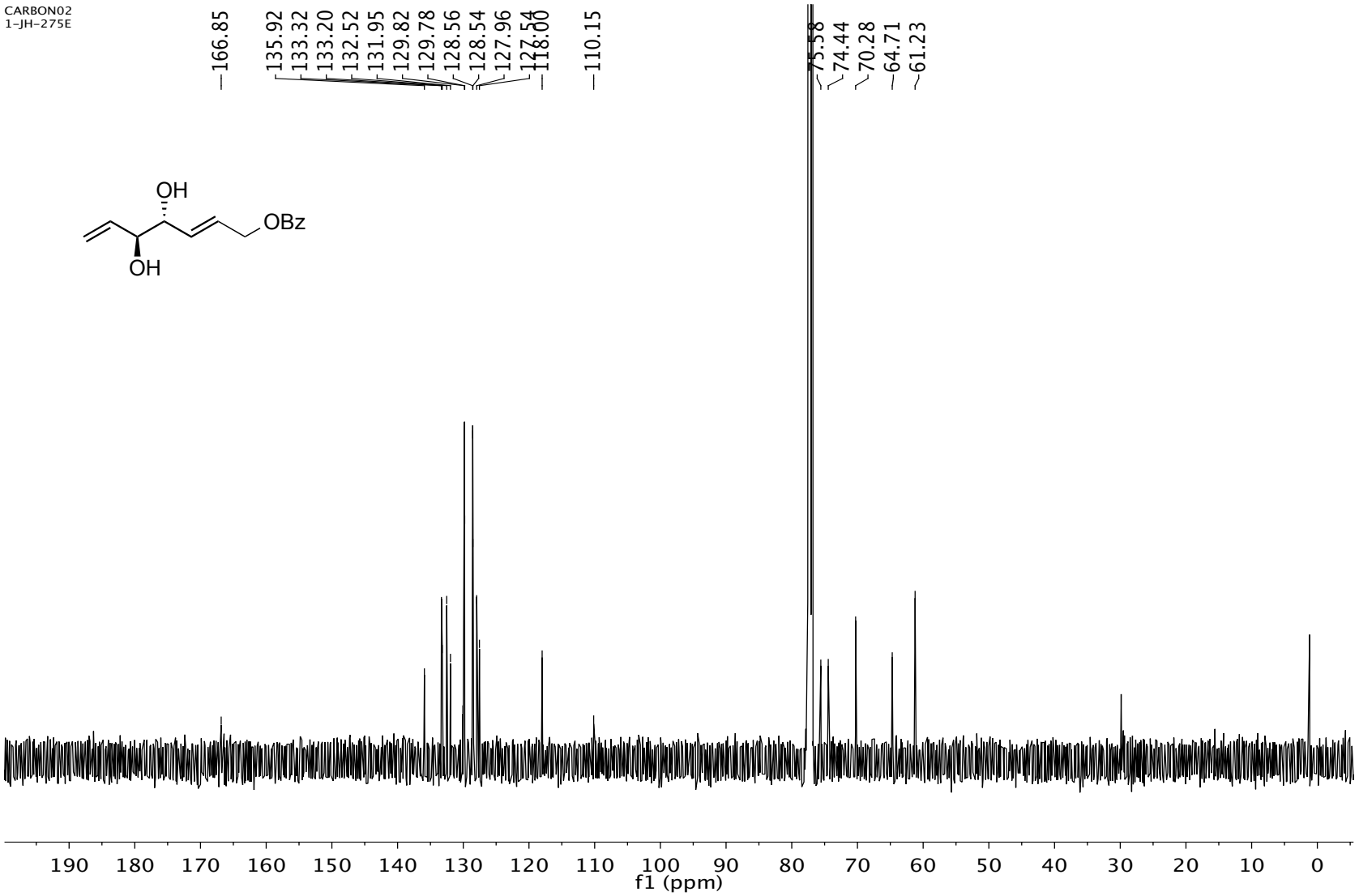


Figure S10. ^{13}C NMR (125 MHz, $CDCl_3$) of *E*-**7b**.

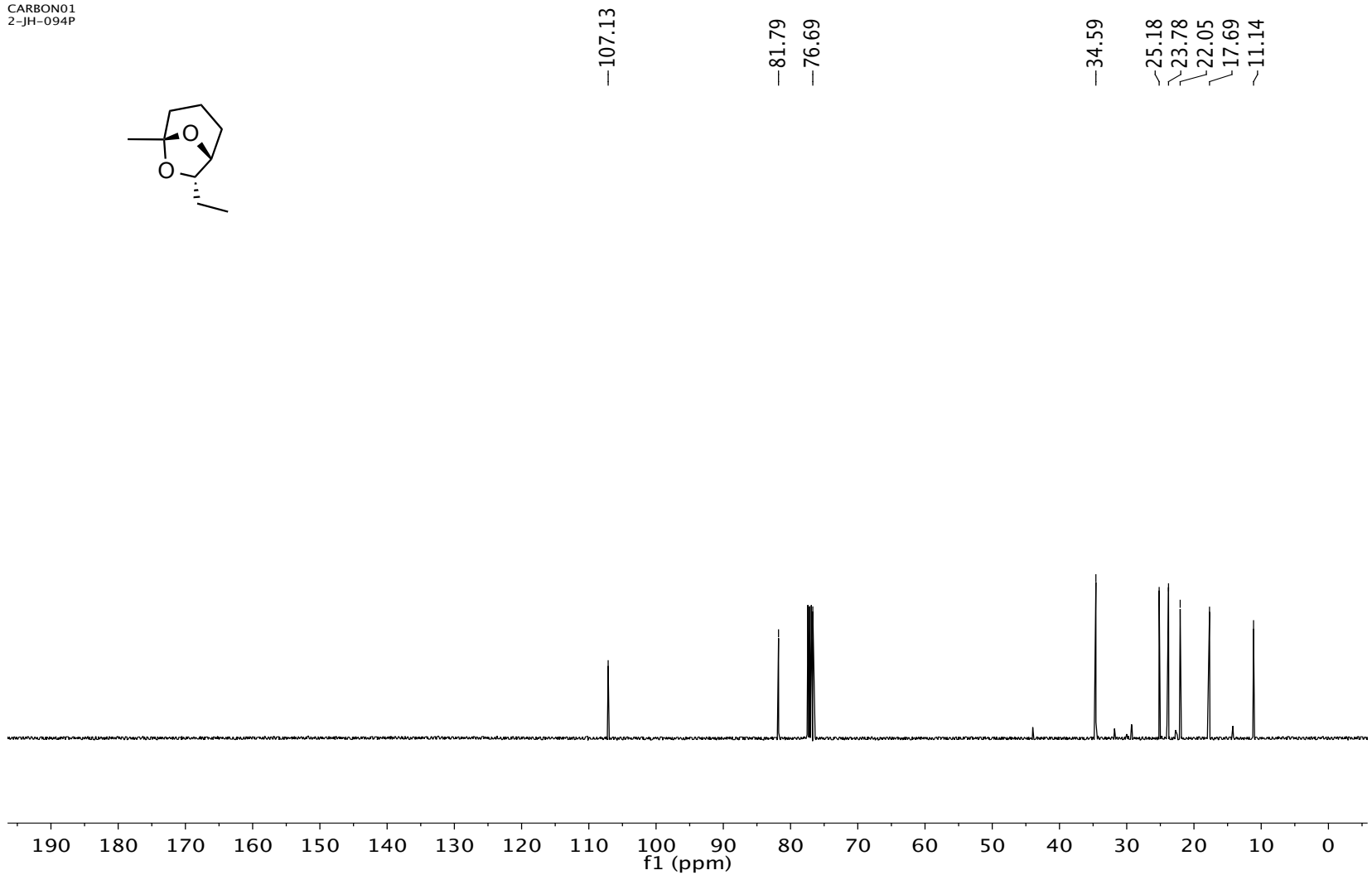


Figure S37. ^{13}C NMR (125 MHz, $CDCl_3$) of **11**.

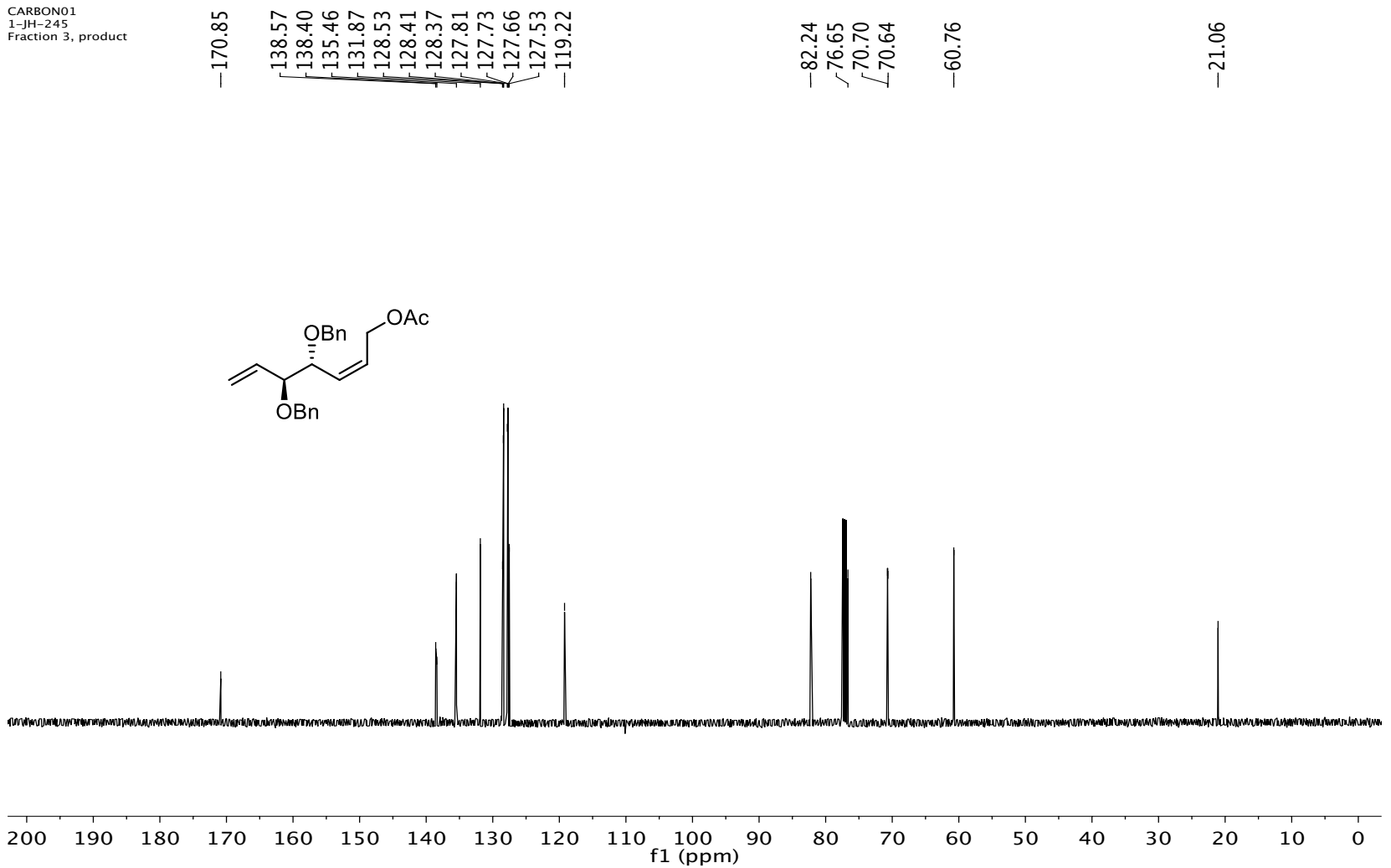


Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$) of *Z*-**4**.

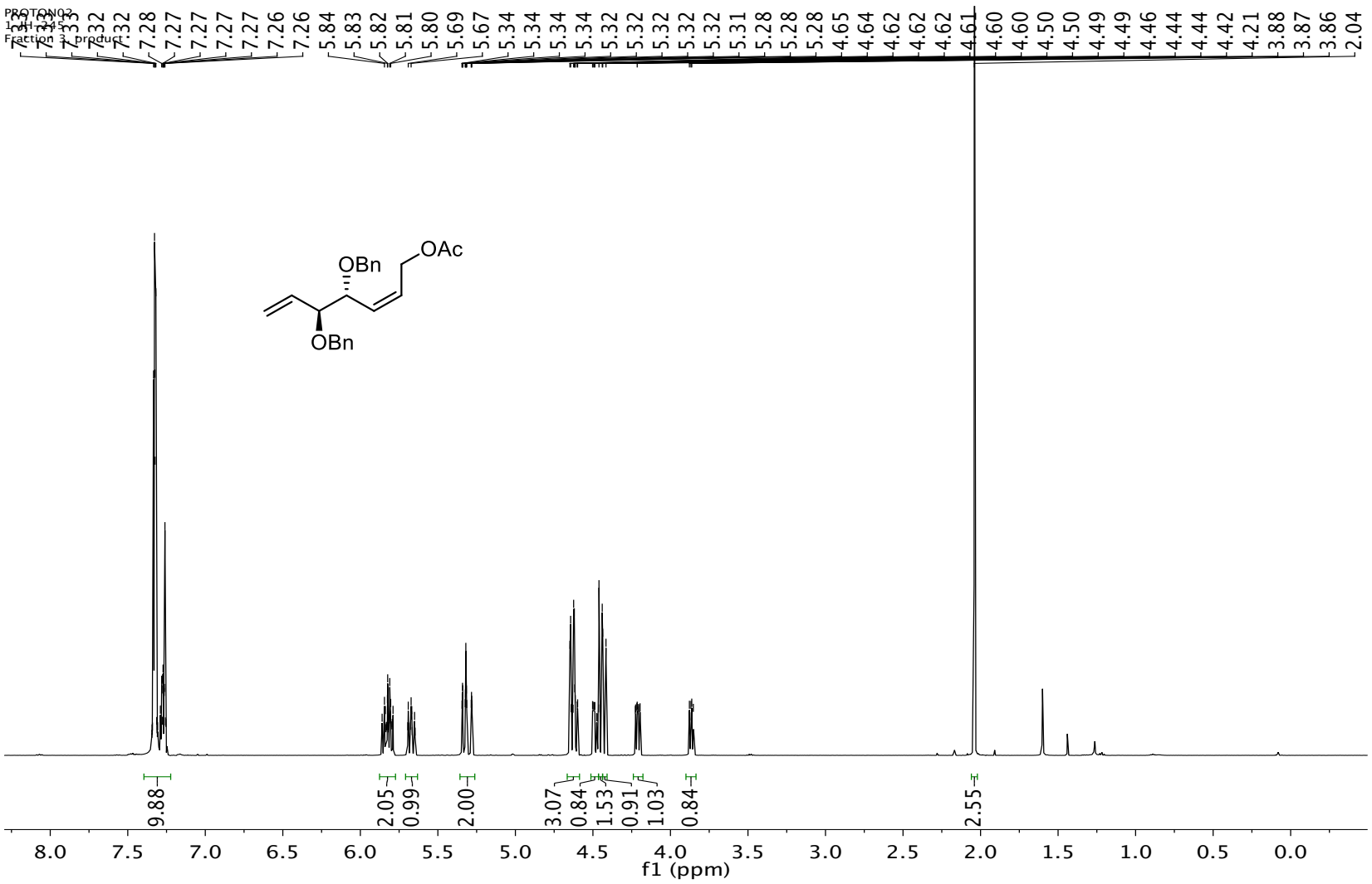


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) of *Z*-**4**.