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Supporting Information

γ-Silylboronates in the Chiral Brønsted Acid-Catalyzed Allylboration of Aldehydes

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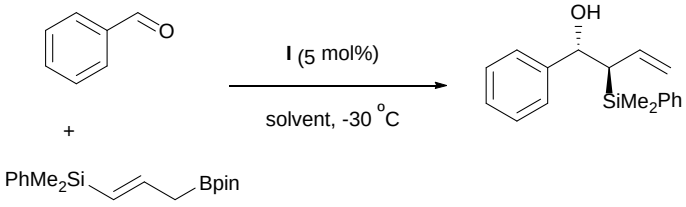
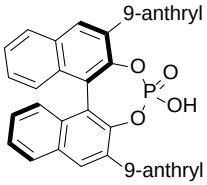
General information:

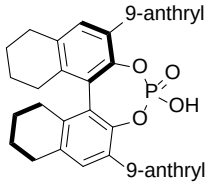
All the reactions were carried out under a nitrogen atmosphere unless otherwise indicated. The solvents were purified prior to use: THF and toluene were distilled from sodium / benzophenone and CH_2Cl_2 was distilled from calcium hydride. All reagents were used as received from the commercial supplier. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm E. Merck precoated silica gel plates. Visualization was carried out with UV light and aqueous ceric ammonium molybdate solution or potassium permanganate stain. Flash column chromatography was performed with the indicated solvents on silica gel 60 (particle size 0.040-0.063 mm). Melting points were measured on a Büchi B-540 apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 300 MHz Bruker AC300 spectrometer and 400 MHz Bruker Avance. Chemical shifts are given in ppm (δ), with reference to the residual proton resonances of the solvents. Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, q and sept stand for multiplet, singlet, doublet, triplet, quartet and septuplet respectively. The letters br indicate that the signal is broad. High-resolution mass spectra were carried out on VGmAutospec (VG Analytical, Micromass Instruments) by the Universidad de Valencia Mass Spectrometry Service.

Optimization study for Me_2PhSi derivatives:

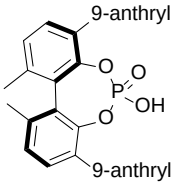




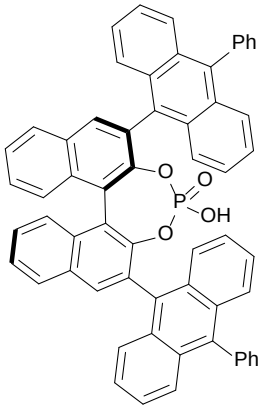
(*R*)-**Id**



(*R*)-**Ie**



(*R*)-**If**



(*R*)-**Ig**

Entry	**I**	Solv.	(%)	e.e. (%)
1	**Id**	TolH	72	59
2	**Id**	DCM	76	20
3	**Ie**	TolH	65	87
4	**If**	TolH	51	52
5	**Ig**	TolH	71	51

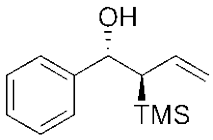
Experimental Procedures and Characterizations:

a) General procedure for the γ-functionalised allylboration:

To a solution of the corresponding benzaldehyde **2a-q** in toluene (0.1M), (*R*)-PA **Id** (5 mol%) was added. The reaction mixture was then cooled to -30ºC followed by the addition of the γ-trimethylsilyl allylboronic acid pinacol ester **1** (1.2 equiv). After the allylboration was completed (approximately 4-6 hours), the reaction mixture was allowed to reach room temperature and solvents were removed under reduced pressure to give crude product **3**, which was purified employing mixtures of *n*-hexane:ethyl acetate as eluents. The enantiomeric excess of the corresponding homoallylic alcohol was determined with the aid of HPLC analysis: Chiralcel OD-H (25 cm x 0.46 cm column), hexane:isopropanol 98:2 as eluent and flow = 1 mL/min unless otherwise indicated.

The compound **3f** has not been completely characterized due to decomposition in the NMR tube.

(1*S*,2*R*)-1-Phenyl-2-(trimethylsilyl)but-3-en-1-ol (3a):

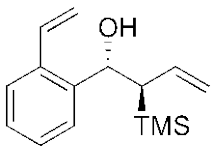


3a

Following the general procedure for the allylboration of benzaldehyde **2a**, the title compound was obtained in 66% yield and 95% ee with spectral properties identical to the reported in the literature.[1] The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 15.3 min, $t_{R\ major}$ = 33.5 min. $[\alpha]_D^{25}$ = + 47.0 (c 1.0; $CHCl_3$). The reported value[1] for the (1*S*,2*R*)-enantiomer (96% ee) is $[\alpha]_D^{25}$ = + 47.0 (c 2.8; $CHCl_3$).

[1] S. B. Han, X. Gao, M. J. Krische, *J. Am. Chem. Soc*. 2010, **132**, 9153.

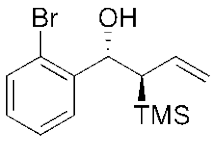
(1*S*,2*R*)-2-(Trimethylsilyl)-1-(2-vinylphenyl)but-3-en-1-ol (3b):



3b

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (10:1)] gave a colorless oil (68%, 92% ee). $[\alpha]_D^{25}$ = + 47.6 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.00 (s, 9H), 2.25 (d, *J*=2.3, 1H), 2.33 (dd, J_1=10.2 J_2=7.9, 1H), 5.12 (ddd, J_1=17.0 J_2=1.9 J_3=0.8, 1H), 5.23 (dd, J_1=10.3 J_2=2.0, 1H), 5.31 (dd, J_1=7.8 J_2=2.3, 1H), 5.49 (dd, J_1=10.9 J_2=1.5, 1H), 5.77 (dd, J_1=17.3 J_2=1.5, 1H), 6.03 (dt, J_1=17.1 J_2=10.3, 1H), 7.33 (dd, J_1=17.3 J_2=10.9, 1H), 7.40-7.46 (m, 2H), 7.55-7.62 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -2.4 (3xCH_3), 44.2 (CH), 71.2 (CH), 116.0 (CH_2), 116.4 (CH_2), 126.6 (CH), 127.2 (CH), 127.7 (CH), 127.7 (CH), 134.8 (CH), 136.2 (C), 136.3 (CH), 140.5 (C). HRMS (EI) calcd for $C_{15}H_{22}OSi$ $[M\text{-}OH]^+$: 229.1407, found: 229.1402. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 17.0 min, $t_{R\ major}$ = 19.1 min.

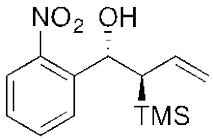
(1*S*,2*R*)-1-(2-Bromophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3c):



3c

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (50:1)] gave a colorless oil (65%, 52% ee). $[\alpha]_D^{25}$ = + 21.6 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.05 (s, 9H), 2.06 (d, *J*=3.1, OH), 2.13 (dd, J_1=10.5 J_2=4.4, 1H), 4.74 (ddd, J_1=17.1 J_2=2.2 J_3=0.8, 1H), 4.88-4.93 (m, 1H), 5.32-5.34 (m, 1H), 5.92 (dt, J_1=17.1 J_2=10.4, 1H), 7.08-7.14 (m, 1H), 7.28-7.34 (m, 1H), 7.46-7.52 (m, 2H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.0 (3xCH_3), 42.7 (CH), 73.2 (CH), 115.6 (CH_2), 122.1 (C), 127.6 (CH), 128.9 (CH), 129.1 (CH), 133.0 (CH), 135.6 (CH), 144.1 (C). HRMS (EI) calcd for $C_{13}H_{19}BrOSi$ $[M\text{-}OH\text{-}TMS]^+$: 208.9960, found: 208.9956. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 16.9 min, $t_{R\ major}$ = 15.5 min.

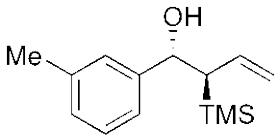
(1*S*,2*R*)-1-(2-Nitrophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3d):



3d

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (20:1)] gave a colorless oil (81%, 52% ee). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.06 (s, 9H), 2.07 (dd, J_1=10.7 J_2=3.8, 1H), 2.18 (br s, OH), 4.68 (ddd, J_1=17.0 J_2=2.2 J_3=0.8, 1H), 4.88 (dd, J_1=10.2 J_2=2.2, 1H), 5.62 (d, J=3.6, 1H), 5.93 (dt, J_1=17.1 J_2=10.5, 1H), 7.39 (ddd, J_1=8.6 J_2=7.3 J_3=1.5, 1H), 7.61 (td, J_1=7.6 J_2=1.4, 1H), 7.76 (dd, J_1=7.9 J_2=1.5, 1H), 7.88 (dd, J_1=8.1 J_2=1.4, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.1 (3xCH_3), 43.6 (CH), 69.6 (CH), 115.8 (CH_2), 124.8 (CH), 128.2 (CH), 129.4 (CH), 133.3 (CH), 135.2 (CH), 140.8 (C), 147.9 (C). HRMS (EI) calcd for $C_{13}H_{19}NO_3Si$ $[M-H_2O]^+$: 248.1101, found: 248.1090. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 19.0 min, $t_{R\ major}$ = 12.2 min.

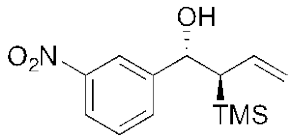
(1*S*,2*R*)-1-(*m*-Tolyl)-2-(trimethylsilyl)but-3-en-1-ol (3e):



3e

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (30:1)] gave a yellow oil (84%, 58% ee). $[\alpha]_D^{25}$ = + 16.7 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.16 (s, 9H), 2.05 (dd, J_1=10.3 J_2=7.7, 1H), 2.16 (br s, OH), 2.34 (s, 3H), 4.78 (d, J=7.6, 1H), 4.95 (ddd, J_1=17.1 J_2=2.1 J_3=0.8, 1H), 5.04 (ddd, J_1=10.3 J_2=2.1 J_3=0.4, 1H), 5.87 (dt, J_1=17.1 J_2=10.3, 1H), 7.06-7.23 (m, 4H). The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 10.1 min, $t_{R\ major}$ = 13.5 min.

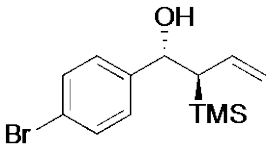
(1*S*,2*R*)-1-(3-Nitrophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3f):



3f

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (30:1)] gave a colorless oil (99%, 96% ee). $[\alpha]_D^{25}$ = + 7.4 (c 1.0; $CHCl_3$). ^1H NMR (300 MHz, CD_2Cl_2) δ -0.05 (s, 9H), 2.01 (ddd, J_1=10.4 J_2=6.3 J_3=0.6, 1H), 2.37 (br s, OH), 4.87 (ddd, J_1=17.1 J_2=2.0 J_3=0.8, 1H), 4.99-5.03 (m, 2H), 5.85 (dt, J_1=17.1 J_2=10.4, 1H), 7.51 (t, J=7.9, 1H), 7.65-7.68 (m, 1H), 8.09 (ddd, J_1=8.1 J_2=2.3 J_3=1.1, 1H), 8.17 (dd, J_1=2.3 J_2=1.1, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.1 (3xCH_3), 45.8 (CH), 74.0 (CH), 116.7 (CH_2), 121.9 (CH), 122.8 (CH), 129.7 (CH), 133.2 (CH), 135.6 (CH), 147.4 (C), 148.8 (C). HRMS (EI) calcd for $C_{13}H_{19}NO_3Si$ $[M\text{-}H_2O]^+$: 248.1101, found: 248.1089. The enantiomeric excess was determined with the aid of HPLC analysis: Chiralpak IC (25 cm x 0.46 cm column), hexane:isopropanol 97:3 as eluent and flow = 1 mL/min: $t_{R\ minor}$ = 9.2 min, $t_{R\ major}$ = 10.0 min.

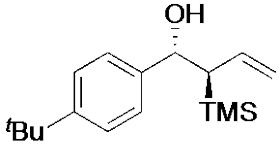
(1*S*,2*R*)-1-(4-Bromophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3g):



3g

Following the general procedure for the allylboration of benzaldehyde **2h**, the title compound was obtained in 92% yield and 94% ee with spectral properties identical to the reported in the literature.[1] The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 15.9 min, $t_{R\ major}$ = 13.2 min. $[\alpha]_D^{25}$ = + 10.3 (c 1.0; $CHCl_3$). The reported value[2] for the (1*S*,2*R*)-enantiomer (98% ee) is $[\alpha]_D^{25}$ = + 37.4 (c 0.62; CH_2Cl_2).

(1*S*,2*R*)-1-(4-(*tert*-Butyl)phenyl)-2-(trimethylsilyl)but-3-en-1-ol (3h):

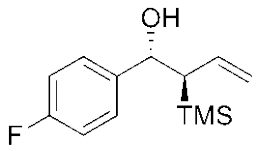


3h

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (50:1)] gave a

colorless oil (68%, 78% ee). $[\alpha]_D^{25}$ = + 25.7 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.17 (s, 9H), 1.31 (s, 9H), 2.06 (dd, J_1=10.3 J_2=7.8, 1H), 2.16 (br s, OH), 4.79 (d, J=7.8, 1H), 4.97 (ddd, J_1=17.1 J_2=2.1 J_3=0.9, 1H), 5.05 (dd, J_1=10.3 J_2=2.1, 1H), 5.89 (dt, J_1=17.1 J_2=10.3, 1H), 7.23-7.27 (m, 2H), 7.33-7.37 (m, 2H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.19 (3xCH_3), 31.7 (3xCH_3), 34.9 (C), 45.9 (CH), 74.6 (CH), 115.6 (CH_2), 125.6 (2xCH), 126.9 (2xCH), 137.5 (CH), 141.8 (C), 151.2 (C). HRMS (EI) calcd for $C_{17}H_{28}OSi$ $[M\text{-}OH]^+$: 259.1877, found: 259.1876. The enantiomeric excess was determined as described in the procedure using Chiralpak AD (25 cm x 0.46 cm column): $t_{R\ minor}$ = 8.7 min, $t_{R\ major}$ = 7.2 min.

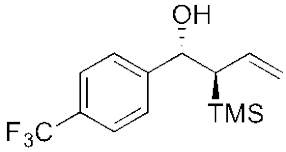
(1*S*,2*R*)-1-(4-Fluorophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3i):



3i

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (50:1)] gave a colorless oil (50%, 94% ee). $[\alpha]_D^{25}$ = + 29.2 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.15 (s, 9H), 2.01 (dd, J_1=10.3 J_2=7.8, 1H), 2.21 (d, J=1.8, OH), 4.82 (d, J=7.8, 1H), 4.96 (ddd, J_1=17.1 J_2=2.1 J_3=0.8, 1H), 5.06 (dd, J_1=10.3 J_2=2.0, 1H), 5.85 (dt, J_1=17.1 J_2=10.3, 1H), 6.98-7.06 (m, 2H), 7.28-7.35 (m, 2H). ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ -116.4 (tt, J_1=8.9 J_2=5.5). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.13 (3xCH_3), 46.3 (CH), 74.2 (CH), 115.5 (d, $^2J_{CF}$=21.3, 2xCH), 116.2 (CH_2), 128.9 (d, $^3J_{CF}$=8.2, 2xCH), 137.0 (CH), 140.8 (d, $^4J_{CF}$=2.9, C), 162.76 (d, $^1J_{CF}$=244.7, C). HRMS (EI) calcd for $C_{13}H_{19}FOSi$ $[M\text{-}H]^+$: 237.1105, found: 237.1094. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 10.2 min, $t_{R\ major}$ = 11.9 min.

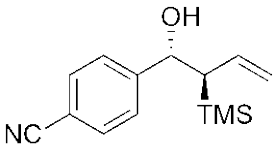
(1*S*,2*R*)-1-(4-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)but-3-en-1-ol (3j):



3j

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (50:1)] gave a colorless oil (80%, 94% ee). $[\alpha]_D^{25}$ = + 25.6 (c 1.0; $CHCl_3$). ^1H NMR (300 MHz, CD_2Cl_2) δ -0.09 (s, 9H), 2.00 (dd, J_1=10.4 J_2=6.6, 1H), 2.27 (d, J=2.7, 1H), 4.86-4.95 (m, 2H), 5.02 (dd, J_1=10.3 J_2=2.0, 1H), 5.85 (dt, J_1=17.0 J_2=10.3, 1H), 7.44-7.47 (m, 2H), 7.58-7.61 (m, 2H). ^{19}F NMR (282.4 MHz, CD_2Cl_2) δ -63.1 (s). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.13 (3xCH_3), 45.8 (CH), 74.3 (CH), 116.3 (CH_2), 124.9 (c, $^1J_{CF}$ = 271.8, C), 125.6 (c, $^3J_{CF}$=3.8, 2xCH), 127.5 (2xCH), 129.8 (c, $^2J_{CF}$=32.3, C), 136.1 (CH), 149.2 (C). HRMS (EI) calcd for $C_{14}H_{19}F_3OSi$ $[M\text{-}OH\text{-}TMS]^+$: 199.0729, found: 199.0728. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 10.1 min, $t_{R\ major}$ = 8.4 min.

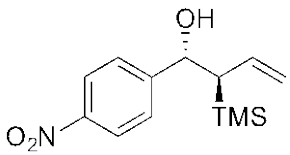
(1*S*,2*R*)-1-(4-Cyanophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3k):



3k

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (20:1)] gave a colorless oil (86%, 93% ee). $[\alpha]_D^{25}$ = + 15.8 (c 1.0; $CHCl_3$). ^1H NMR (300 MHz, CD_2Cl_2) δ -0.07 (s, 9H), 1.96 (ddt, J_1=10.5 J_2=6.3 J_3=0.5, 1H), 2.28 (br s, OH), 4.86 (ddd, J_1=17.0 J_2=1.9 J_3=0.8, 1H), 4.93 (d, J=6.3, 1H), 5.00 (dd, J_1=10.3 J_2=2.1, 1H), 5.82 (dt, J_1=17.0 J_2=10.3, 1H), 7.42-7.45 (m, 2H), 7.61-7.64 (m, 2H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.13 (3xCH_3), 45.7 (CH), 74.2 (CH), 111.5 (C), 116.4 (CH_2), 119.4 (C), 127.7 (2xCH), 132.6 (2xCH), 135.7 (CH), 150.4 (C). HRMS (EI) calcd for $C_{14}H_{19}NOSi$ $[M\text{-}H_2O]^+$: 228.1203, found: 228.1201. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 35.4 min, $t_{R\ major}$ = 29.9 min.

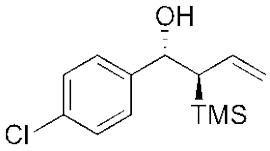
(1*S*,2*R*)-1-(4-Nitrophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3l):



3l

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (20:1)] gave a white solid (86%, 95% ee). $[\alpha]_D^{25}$ = + 15.5 (c 1.0; $CHCl_3$). mp 94-97 ºC. ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.5 (s, 9H), 1.98 (dd, J_1=10.8 J_2=6.1, 1H), 2.27 (br s, OH), 4.85 (ddd, J_1=17.0 J_2=1.9 J_3=0.8, 1H), 4.97-5.02 (m, 2H), 5.84 (dt, J_1=17.1 J_2=10.4, 1H), 7.47-7.52 (m, 2H), 8.15-8.19 (m, 2H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.1 (3xCH_3), 45.8 (CH), 74.0 (CH), 116.5 (CH_2), 123.9 (2xCH), 127.8 (2xCH), 135.5 (CH), 147.7 (C), 152.6 (C). HRMS (EI) calcd for $C_{13}H_{19}NO_3Si$ $[M\text{-}H_2O]^+$: 248.1101, found: 248.1100. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 31.4 min, $t_{R\ major}$ = 25.7 min.

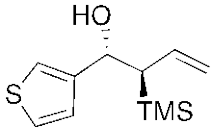
(1*S*,2*R*)-1-(4-Chlorophenyl)-2-(trimethylsilyl)but-3-en-1-ol (3m):



3m

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (50:1)] gave a colorless oil (70%, 59% ee). $[\alpha]_D^{25}$ = + 4.8 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.12 (s, 9H), 1.99 (dd, J_1=10.3 J_2=7.3, 1H), 2.20 (d, J=2.5, OH), 4.82 (dd, J_1=7.2 J_2=1.7, 1H), 4.93 (ddd, J_1=17.1 J_2=2.1 J_3=0.8, 1H), 5.04 (dd, J_1=10.3 J_2=2.0, 1H), 5.84 (dt, J_1=17.1 J_2=10.3, 1H), 7.26-7.33 (m, 4H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.1 (3xCH_3), 46.0 (CH), 74.1 (CH), 116.2 (CH_2), 128.7 (2xCH), 128.8 (2xCH), 133.4 (C), 136.6 (CH), 143.6 (C). HRMS (EI) calcd for $C_{13}H_{19}ClOSi$ $[M\text{-}OH\text{-}TMS]^+$: 165.0466, found: 165.0464. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 13.2 min, $t_{R\ major}$ = 12.2 min.

(1*S*,2*R*)-1-(Thiophen-3-yl)-2-(trimethylsilyl)but-3-en-1-ol (3n):

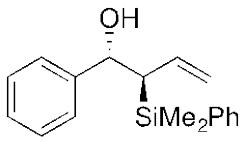


3n

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (30:1)] gave a colorless oil (73%, 91% ee). $[\alpha]_D^{25}$ = + 28.6 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, CD_2Cl_2) δ -0.12 (s, 9H), 2.07 (ddd, J_1=10.3 J_2=7.7 J_3=0.7, 1H), 2.17 (d, J=3.0, 1H),

4.92-5.01 (m, 2H), 5.06 (ddd, J_1=10.4 J_2=2.1 J_3=0.5, 1H), 5.86 (dt, J_1=17.1 J_2=10.3, 1H), 7.07 (dd, J_1=5.0 J_2=1.2, 1H), 7.18 (ddd, J_1=3.0 J_2=1.3 J_3=0.6, 1H), 7.29 (ddd, J_1=5.1 J_2=3.0 J_3=0.5, 1H). ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ -2.3 (3xCH_3), 45.4 (CH), 70.7 (CH), 115.8 (CH_2), 121.8 (CH), 126.4 (CH), 126.9 (CH), 137.2 (CH), 146.5 (C). HRMS (EI) calcd for $C_{11}H_{18}OSSi$ $[M\text{-}OH\text{-}TMS]^+$: 137.0419, found: 137.0408. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 13.3 min, $t_{R\ major}$ = 35.0 min.

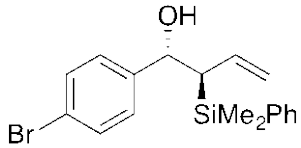
(1*S*,2*R*)-1-Phenyl-2-(dimethyl(phenyl)silyl)but-3-en-1-ol (3o):



3o

Following the general procedure for the allylboration of benzaldehyde **2a**, the title compound was obtained in 65% yield and 87% ee with spectral properties identical to the reported in the literature.[2] The enantiomeric excess was determined as described in the procedure using Chiralpak AD (95:5 hexane:^{i}PrOH): $t_{R\ major}$ = 6.3 min, $t_{R\ minor}$ = 8.1 min. $[\alpha]_D^{25}$ = + 6.6 (c 1.0; $CHCl_3$). The reported value[2] for the (1*R*,2*S*)-enantiomer (84% ee) is $[\alpha]_D^{25.8}$ = - 12.2 (c 1.13; $CHCl_3$).

(1*S*,2*R*)-1-(4-Bromophenyl)-2-(dimethyl(phenyl)silyl)but-3-en-1-ol (3p):



3p

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (20:1)] gave a colorless oil (87%, 87% ee). $[\alpha]_D^{25}$ = -7.7 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.19 (s, 3H), 2.00 (d, J=2.7, 1H), 2.11 (dd, J_1=10.3 J_2=6.7, 1H), 4.63 (dd, J_1=6.7 J_2=2.6, 1H), 4.83 (ddd, J_1=17.1 J_2=1.8 J_3=0.8, 1H), 4.99 (dd, J_1=10.3 J_2=1.8, 1H), 5.79 (dt, J_1=17.1 J_2=10.3, 1H), 6.97-6.99 (m, 2H), 7.18-7.35 (m, 7H). ^{13}C NMR

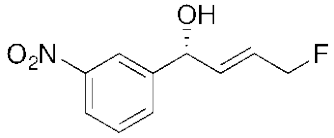
[2] M. Chen, W. R. Roush, *Org. Lett*. **2011**, *13*, 1992.

(75.5 MHz, $CDCl_3$) δ -3.9 (CH_3), -3.7 (CH_3), 45.0 (CH), 73.5 (CH), 116.6 (CH_2), 121.2 (C), 127.7 (2xCH), 128.3 (2xCH), 129.1 (CH), 131.1 (2xCH), 134.0 (2xCH), 135.1 (CH), 137.1 (C), 142.6 (C). HRMS (EI) calcd for $C_{18}H_{21}BrOSi$ $[M-H+Na]^+$: 383.0437, found: 383.0427. The enantiomeric excess was determined as described in the procedure using Chiralpak AD (hexane:isopropanol 95:5 as eluent): $t_{R\ major}$ = 12.3 min, $t_{R\ minor}$ = 34.4 min.

b) General procedure for the allylic fluorination:

To a solution of the corresponding homoallylic alcohol in acetonitrile (0.1 M), $NaHCO_3$ (1 equiv) and Selectfluor™ (1.5 equiv) were added. The reaction mixture was allowed to stir at room temperature for 6 hours. After this time, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, followed by extraction with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography employing mixtures of *n*-hexane:ethyl acetate as eluents. The enantiomeric excess of the corresponding allyl fluorinated compounds was determined with the aid of HPLC analysis: Chiralpak IC (25 cm x 0.46 cm column), hexane:isopropanol 96:4 as eluent and flow = 1 mL/min unless otherwise indicated.

(*R*,*E*)-4-Fluoro-1-(3-nitrophenyl)but-2-en-1-ol (4f):

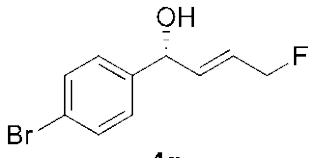


4f

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (10:1)] gave a colorless oil (55%, 94% ee). $[\alpha]_D^{25}$ = - 8.8 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (br s, OH), 4.83-4.84 (m, 1H), 4.98-5.00 (m, 1H), 5.38 (br s, 1H), 5.94-6.10 (m, 2H), 7.54 (t, *J*=7.9, 1H), 7.70-7.73 (m, 1H), 8.15 (ddd, J_1=8.2 J_2=2.3 J_3=1.1, 1H), 8.25 (t, *J*=2.0, 1H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ -216.2 to -215.8 (m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.2 (CH), 82.1 (d, $^1J_{CF}$=165.3, CH_2), 121.2 (CH), 122.8 (CH), 126.9 (d, $^2J_{CF}$=17.1, CH), 129.6 (CH), 132.3 (CH), 134.7 (d, $^3J_{CF}$=11.3, CH), 144.2 (d, $^5J_{CF}$=2.0, C), 148.4 (C). HRMS (EI) calcd for $C_{10}H_{10}FNO_3$ $[M+H]^+$: 212.0717, found:

212.0734. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 33.0 min, $t_{R\ major}$ = 49.9 min.

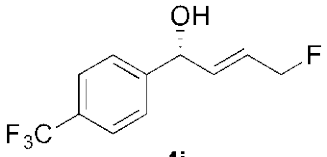
(*R*,*E*)-1-(4-Bromophenyl)-4-fluorobut-2-en-1-ol (4g):



4g

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (5:1)] gave a colorless oil (72%, 91% ee). $[\alpha]_D^{25}$ = + 8.0 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (br s, OH), 4.80-4.82 (m, 1H), 4.96-4.97 (m, 1H), 5.22-5.23 (m, 1H), 5.90-6.02 (m, 2H), 7.22-7.27 (m, 2H), 7.47-7.51 (m, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ -214.6 to -214.19 (m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.5 (CH), 82.4 (d, $^1J_{CF}$=164.3, CH_2), 121.8 (C), 125.8 (d, $^2J_{CF}$=17.1, CH), 128.0 (2xCH), 131.7 (2xCH), 135.7 (d, $^3J_{CF}$=11.3, CH), 141.1 (C). HRMS (EI) calcd for $C_{10}H_{10}BrFO$ $[M\text{-}H_2O]^+$: 226.9866, found: 226.9859. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 11.0 min, $t_{R\ major}$ = 12.1 min.

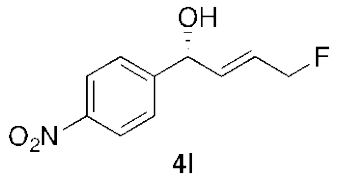
(*R*,*E*)-4-Fluoro-1-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (4j):



4j

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (10:1)] gave a colorless oil (79%, 91% ee). $[\alpha]_D^{25}$ = - 3.1 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (d, *J*=3.5, OH), 4.81-4.83 (m, 1H), 4.97-4.98 (m, 1H), 5.34 (d, *J*=2.9, 1H), 5.93-6.05 (m, 2H), 7.50 (d, *J*=8.3, 2H), 7.63 (d, *J*=8.2, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ -215.5 to -215.1 (m, 1F), -63.0 (m, 3F). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.6 (CH), 82.3 (d, *J*=164.7, CH_2), 124.0 (q, *J*=272.0, CF_3), 125.6 (q, *J*=3.7, 2xCH), 126.3 (d, *J*=17.1, CH), 126.5 (2xCH), 130.1 (q, *J*=32.6, C), 135.4 (d, *J*=11.3, CH), 145.9 (C). HRMS (EI) calcd for $C_{11}H_{10}F_4O$ $[M\text{-}OH]^+$: 217.0635, found: 217.0631. The enantiomeric excess was determined as described in the procedure using hexane:isopropanol 98:2 as eluent: $t_{R\ minor}$ = 11.9 min, $t_{R\ major}$ = 12.7 min.

(*R*,*E*)-4-Fluoro-1-(4-nitrophenyl)but-2-en-1-ol (4l):



4l

Flash chromatography of the crude reaction mixture [*n*-hexane:EtOAc (5:1)] gave a colorless oil (97%, 91% ee). $[\alpha]_D^{25}$ = - 11.4 (c 1.0; $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.17 (br s, OH), 4.82-4.83 (m, 1H), 4.97-4.99 (m, 1H), 5.38 (br s, 1H), 5.93-6.08 (m, 2H), 7.53-7.58 (m, 2H), 8.20-8.25 (m, 2H). ^{19}F NMR (282.4 MHz, $CDCl_3$) δ -216.3 to -215.9 (m). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.3 (CH), 82.1 (d, $^1J_{CF}$=165.4, CH_2), 123.8 (2xCH), 126.9 (d, $^2J_{CF}$=17.0, CH), 127.0 (2xCH), 134.6 (d, $^3J_{CF}$=11.4, CH), 147.5 (C), 149.1 (C). HRMS (EI) calcd for $C_{10}H_{10}FNO_3$ $[M+H]^+$: 212.0717, found: 212.0725. The enantiomeric excess was determined as described in the procedure: $t_{R\ minor}$ = 26.0 min, $t_{R\ major}$ = 28.8 min.

X-Ray Analysis

Table S1 - Crystal Data and Details of the Structure Determination for **3m** R = 0.04

Crystal Data

Formula	C13 H19 N O3 S
Formula Weight	269.36
Crystal System	Orthorhombic
Space group	P212121 (No. 19)
a, b, c [Angstrom]	11.3743(2) 14.0235(2) 18.6496(3)
V [Ang**3]	2974.75(8)
Z	8
D(calc) [g/cm**3]	1.203
Mu(CuKa) [/mm]	1.946
F(000)	1152
Crystal Size [mm]	0.10 x 0.13 x 0.48

Data Collection

Temperature (K)	100
Radiation [Angstrom] CuKa	1.54184
Theta Min-Max [Deg]	3.9, 71.0
Dataset	-13: 12 ; -17: 17 ; -22: 22
Tot., Uniq. Data, R(int)	26822, 5729, 0.057
Observed data [I > 2.0 sigma(I)]	5603

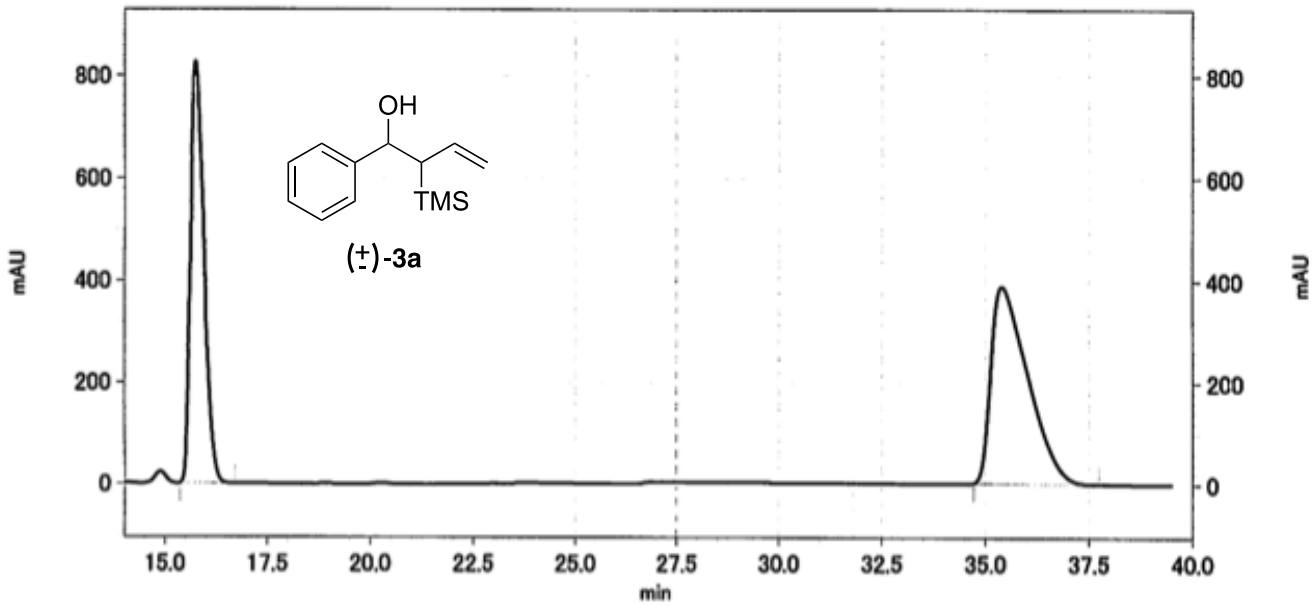
Refinement

Nref, Npar	5729, 349
R, wR2, S	0.0386, 0.1139, 1.06
w = 1/[\s^2^(Fo^2^)+(0.0804P)^2^+0.3357P]	where P=(Fo^2^+2Fc^2^)/3
Max. and Av. Shift/Error	0.00, 0.00
Flack x	0.154(14)
Hooft y	0.160(7)
Min. and Max. Resd. Dens. [e/Ang^3]	-0.44, 0.35

Analysis of the absolute structure using likelihood methods[3] was performed using Olex2.[4] The results indicated that the absolute structure had been correctly assigned. The method calculated that the probability that the structure is inverted is smaller than 10–99. The absolute structure parameter *y* was calculated using Olex2. The resulting

[3] R. W. W. Hooft, L. H. Straver & A. L. Spek, *J. Appl. Cryst.* 2008, **41**, 96.
[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

value was y=0.160(7), which together with Flack parameter value x=0.154(14), indicate that *the absolute structure has been determined correctly with essentially 100% probability* (the probability of misassignment is lesser than 10^{-99}).



Peak #	Retention time	Type	Area	Area %
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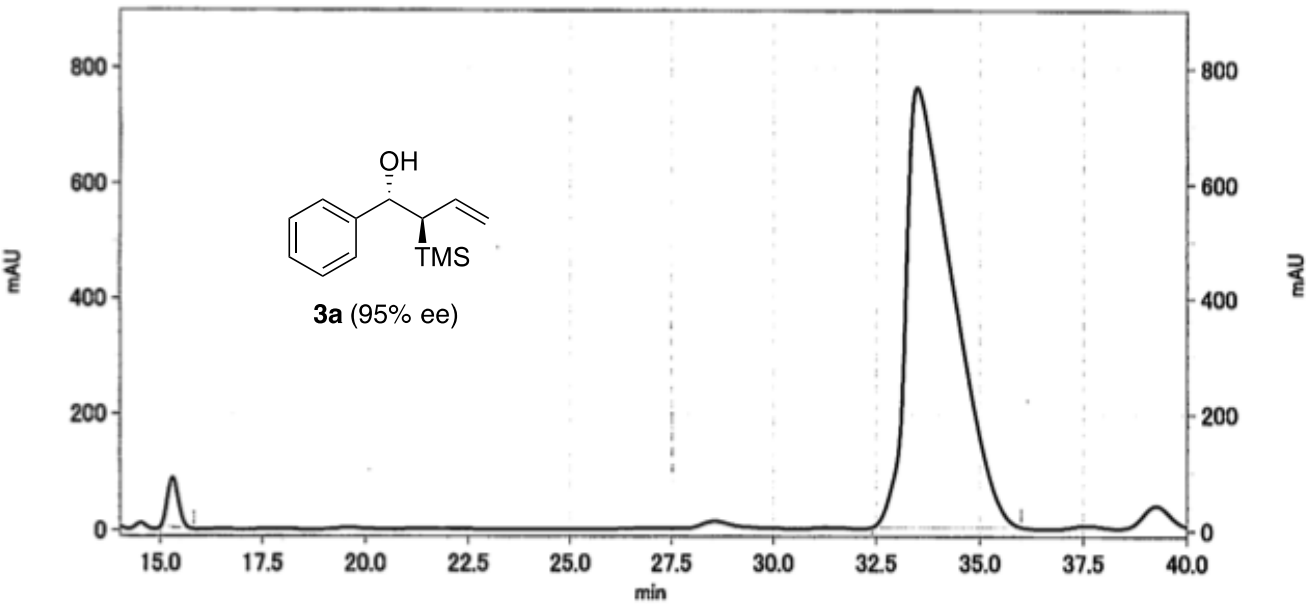
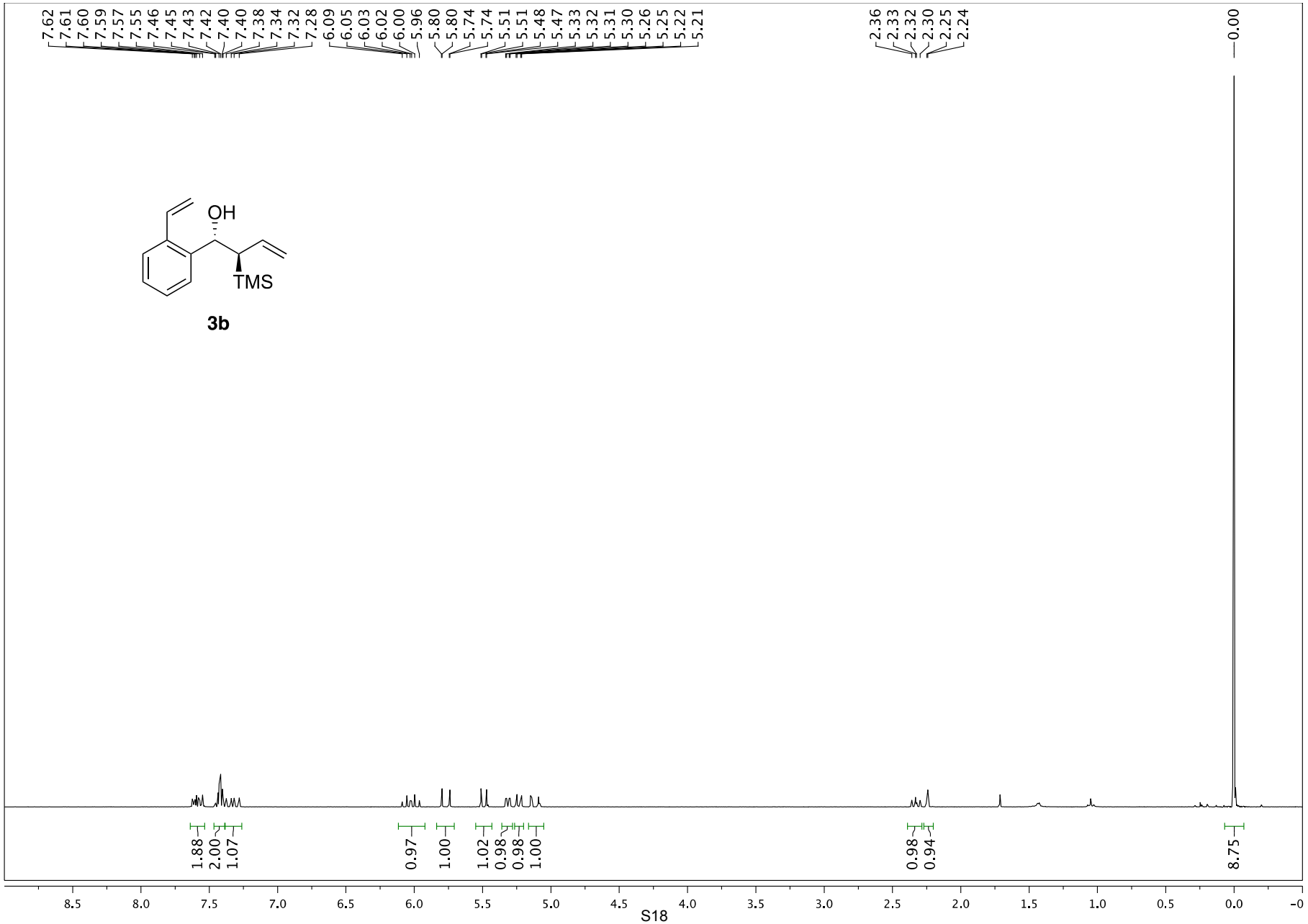
2	35.39	BB	95840072	55.840



Peak #	Retention time	Type	Area	Area %
1	15.30	IB	6366654	2.582
2	33.47	BI	240243705	97.418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7.34
7.32
7.28
6.09
6.05
6.03
6.02
6.00
5.96
5.80
5.80
5.74
5.74
5.51
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5.48
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2.30
2.25
2.24
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2.00
1.07
0.97
1.00
1.02
0.98
0.98
1.00
0.98
0.94
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8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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3.0
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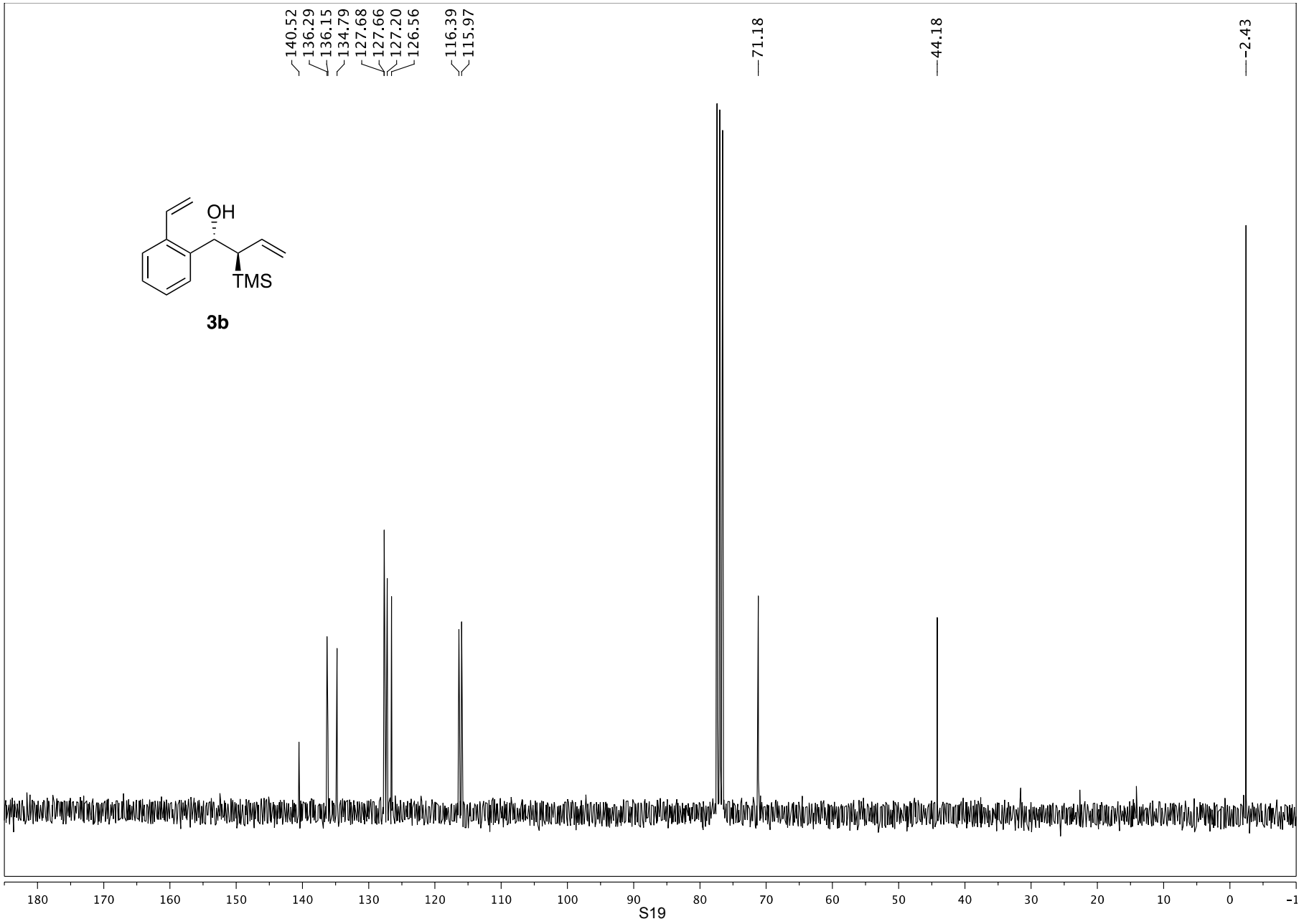
1.5
1.0
0.5
0.0
-0

3b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71.18
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OH
TMS
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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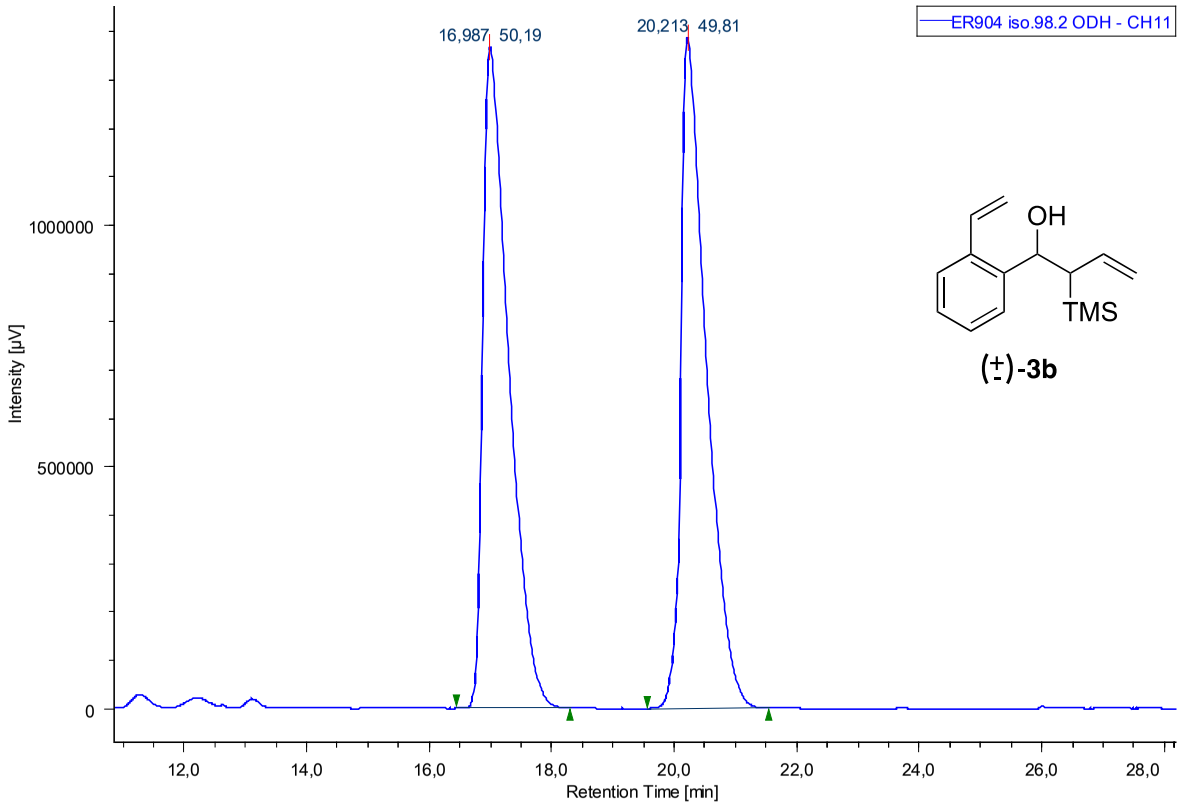
-1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16,987 50,19
20,213 49,81
OH
TMS
(±)-3b
Intensity [µV]
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0
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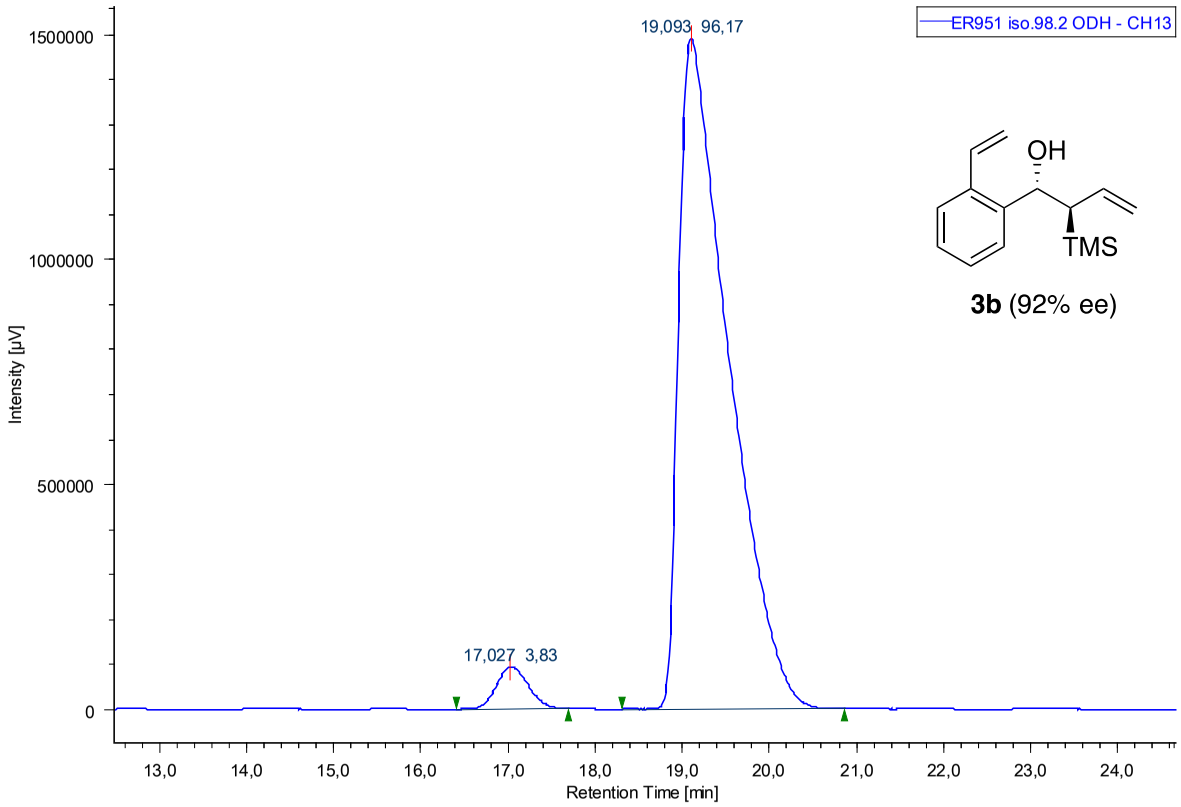
14,0
16,0
18,0
20,0
22,0
24,0
26,0
28,0
Retention Time [min]


ER951 iso.98.2 ODH - CH13
19,093 96,17
17,027 3,83
OH
TMS
3b (92% ee)
Intensity [µV]
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500000
0
13,0
14,0
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20,0
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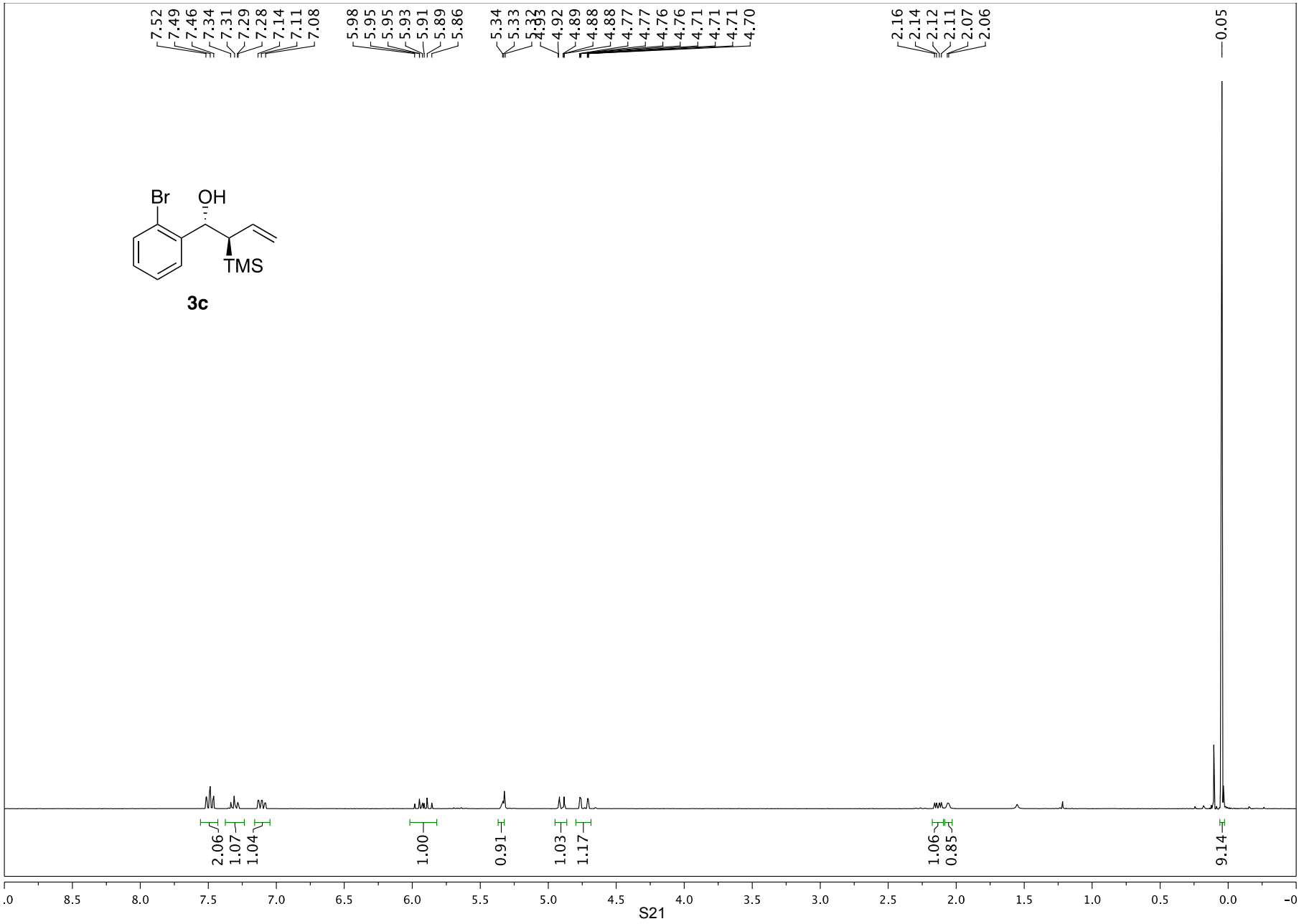
22,0
23,0
24,0
Retention Time [min]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4.71
4.70
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2.14
2.12
2.11
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2.06
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1.04
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0.91
1.03
1.17
1.06
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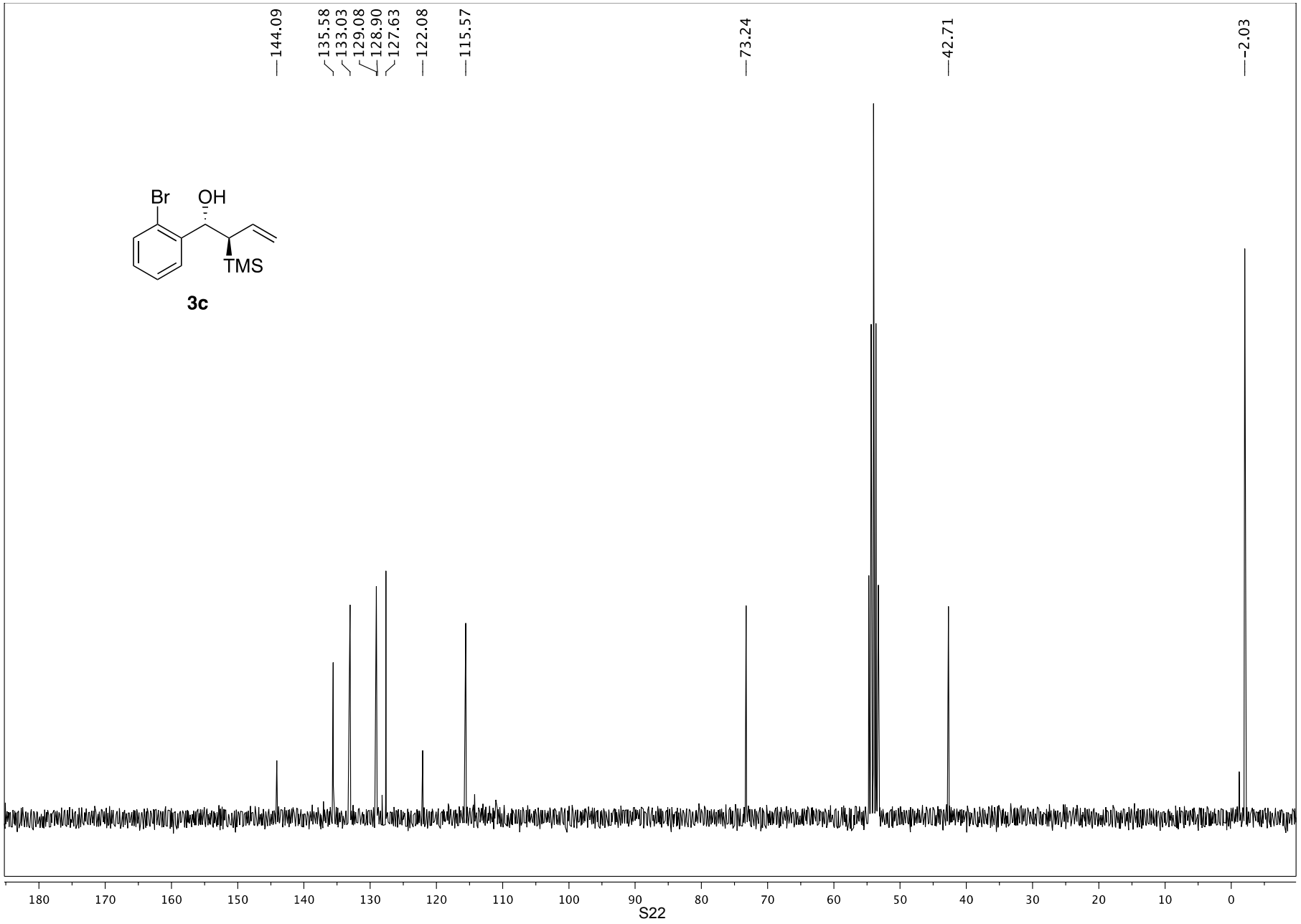
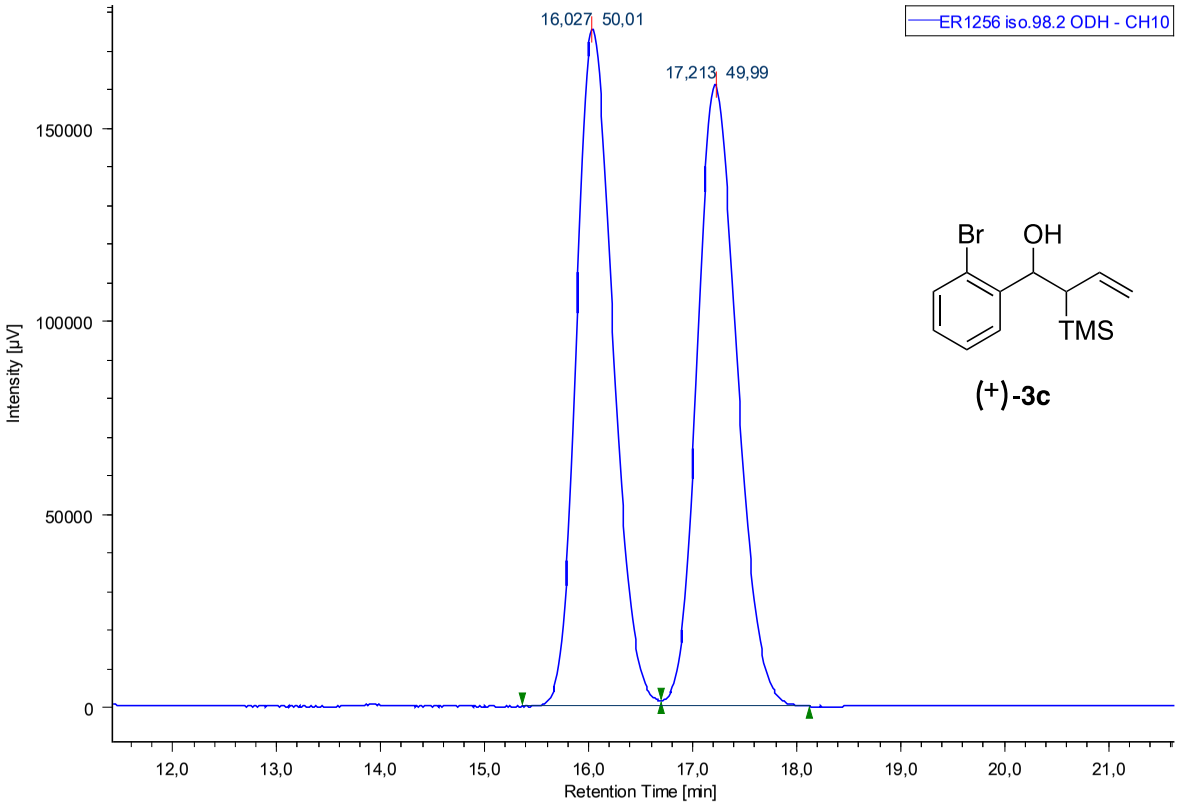
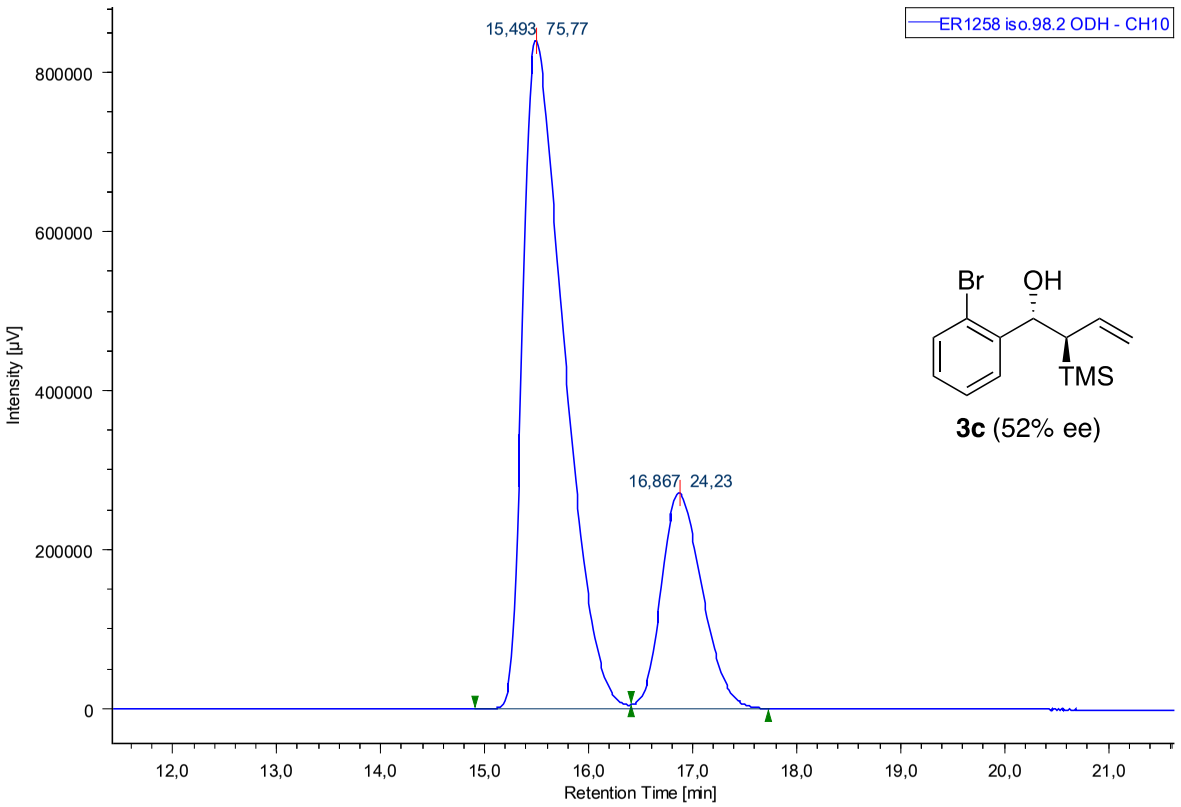
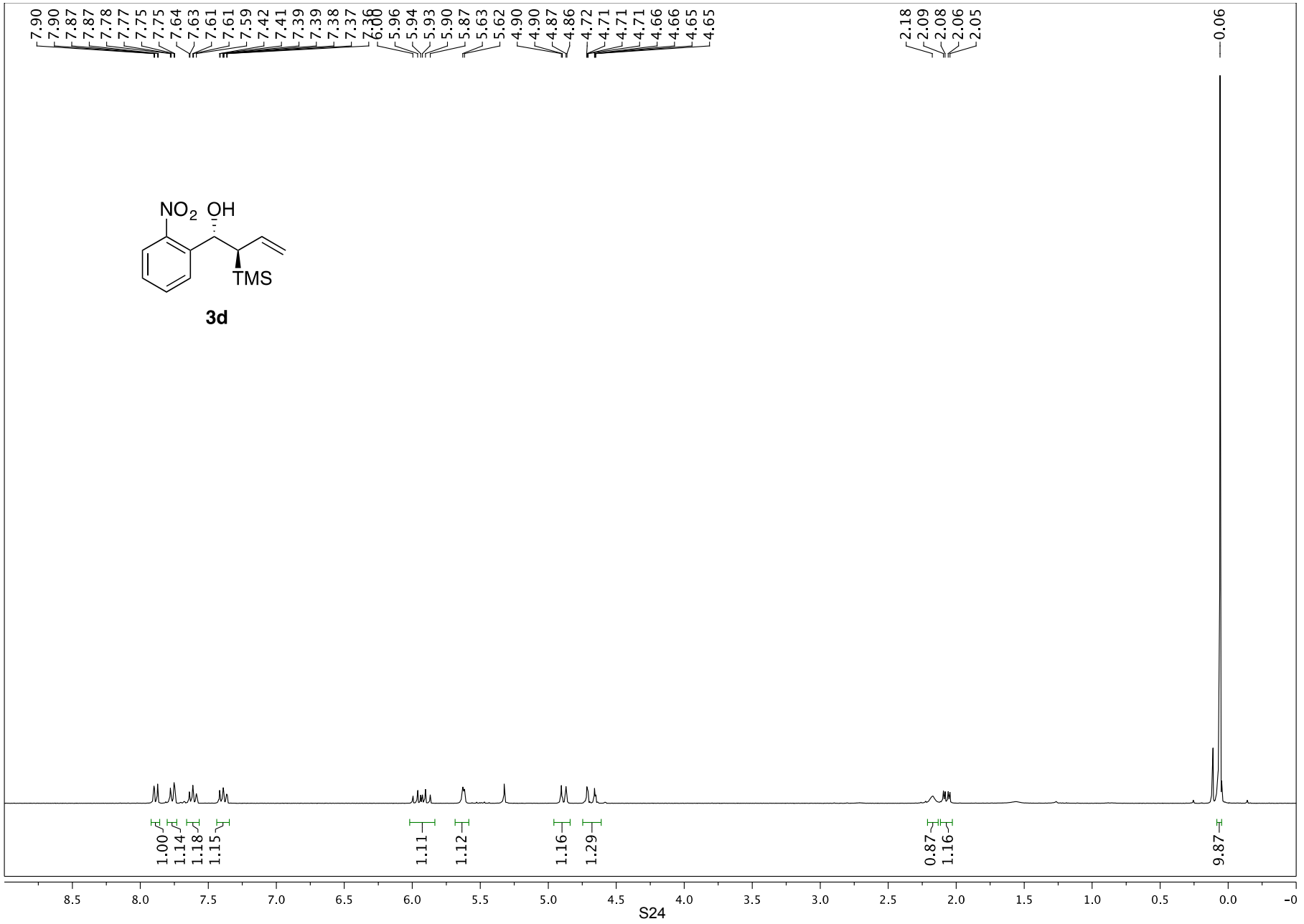
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

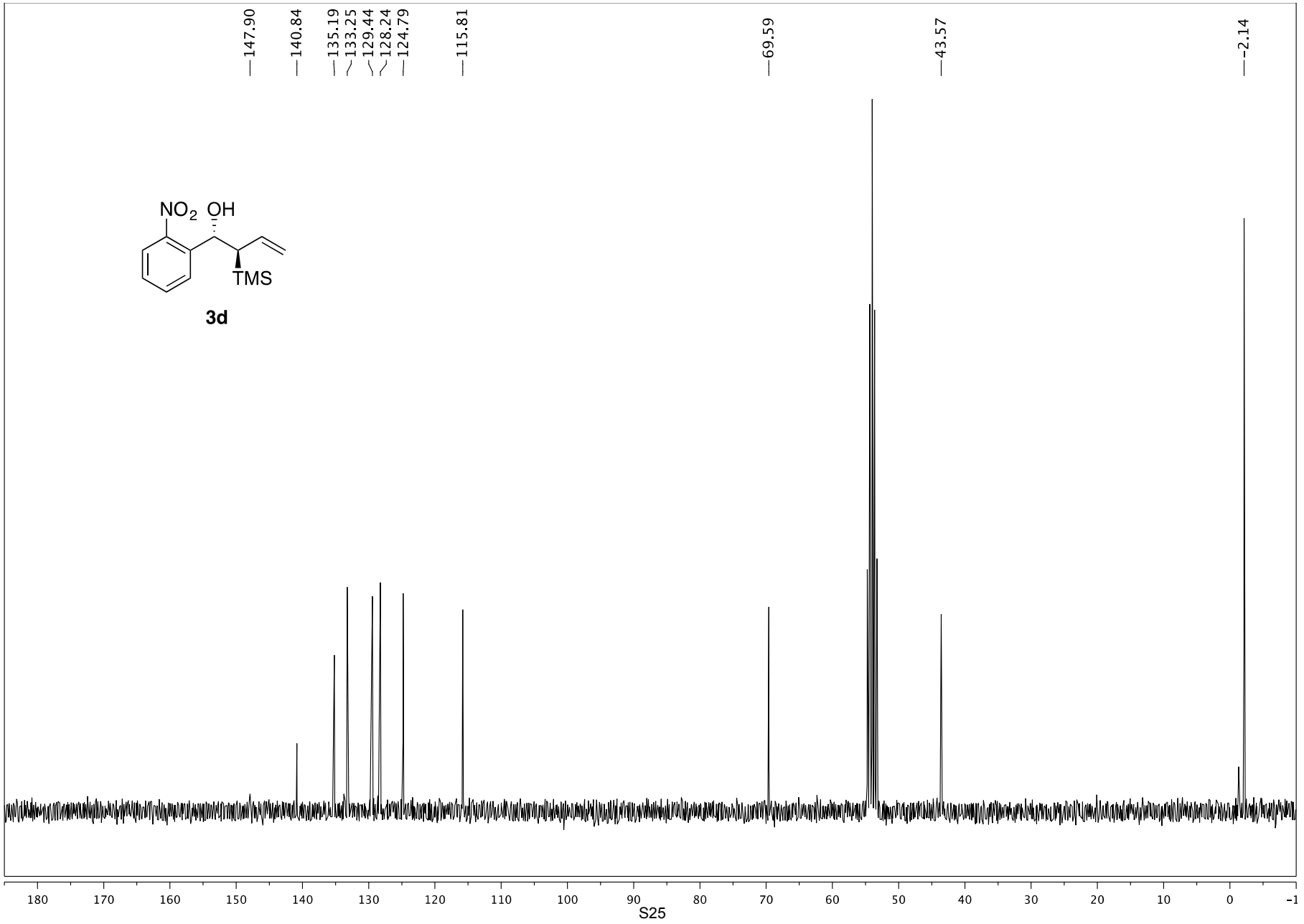

144.09
135.58
133.03
129.08
128.90
127.63
122.08
115.57
73.24
42.71
-2.03
Br
OH
TMS
3c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

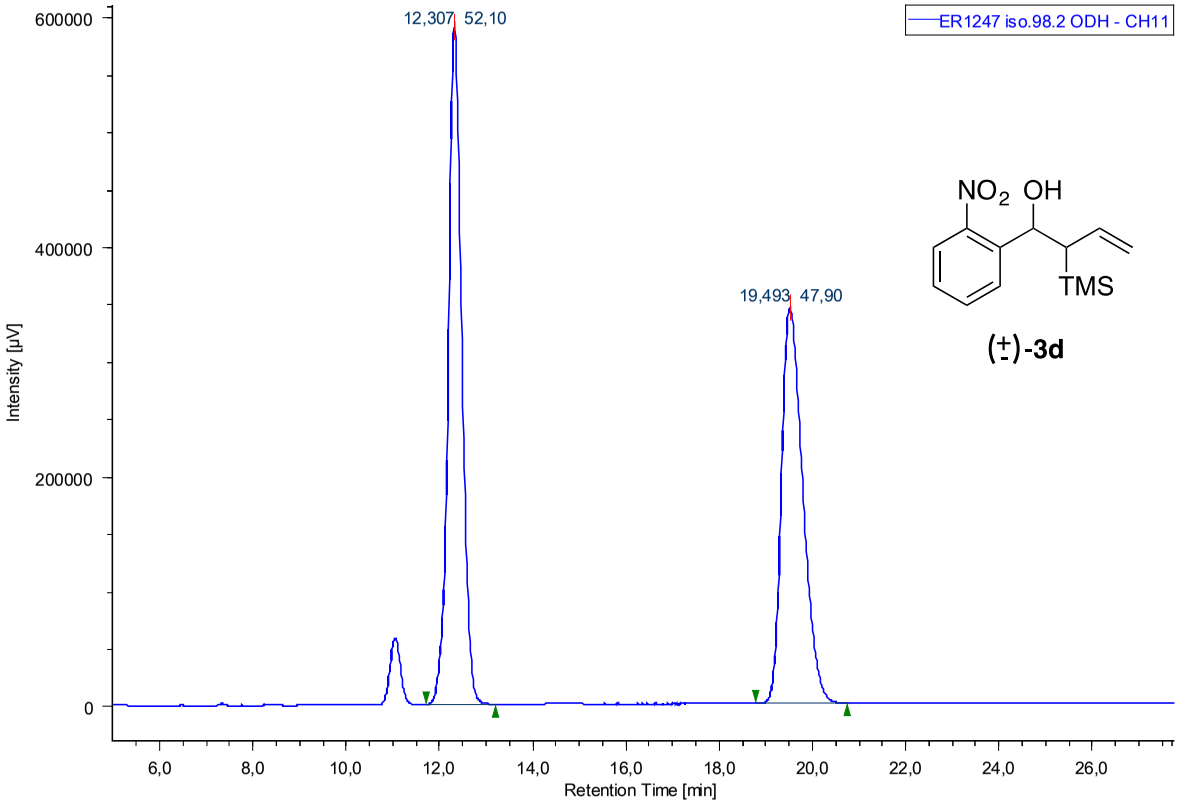

ER1256 iso.98.2 ODH - CH10
16,027 50,01
17,213 49,99
Br
OH
TMS
(+)-3c
Intensity [µV]
150000
100000
50000
0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
19,0
20,0
21,0
Retention Time [min]

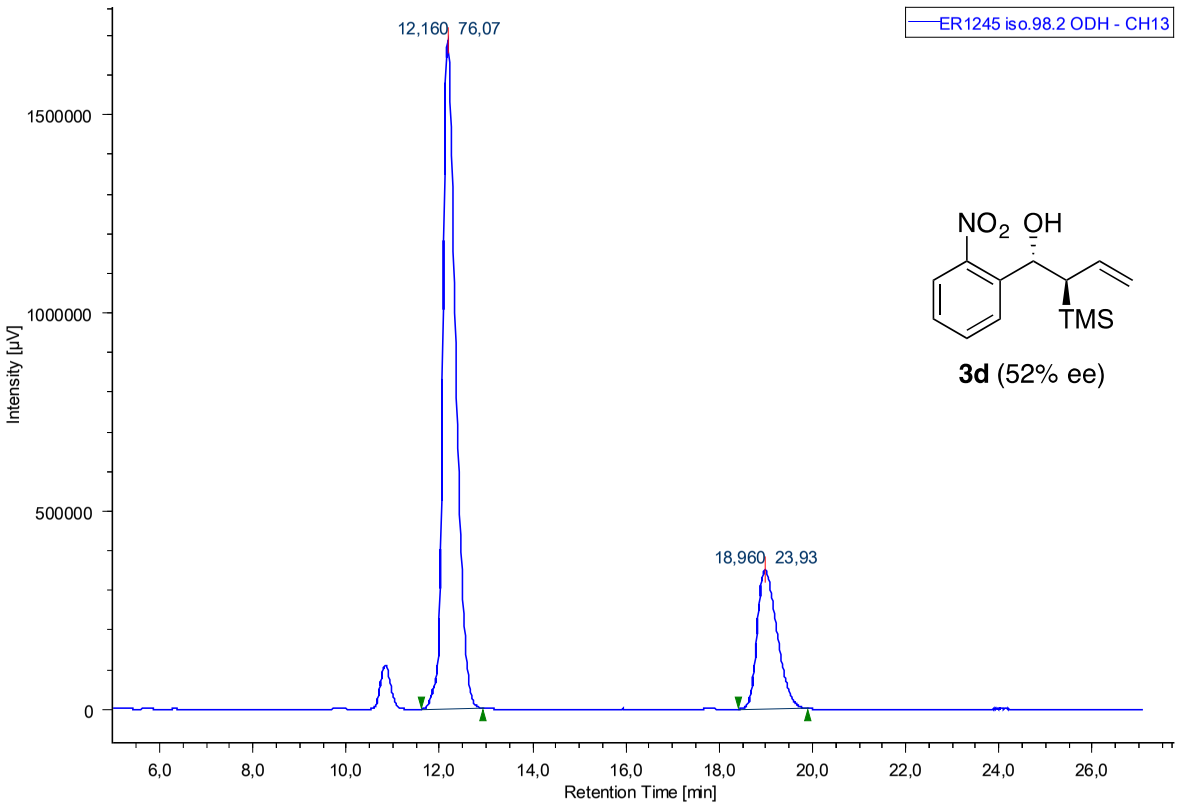

ER1258 iso.98.2 ODH - CH10
15,493 75,77
16,867 24,23
Br
OH
TMS
3c (52% ee)
Intensity [µV]
800000
600000
400000
200000
0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
19,0
20,0
21,0
Retention Time [min]

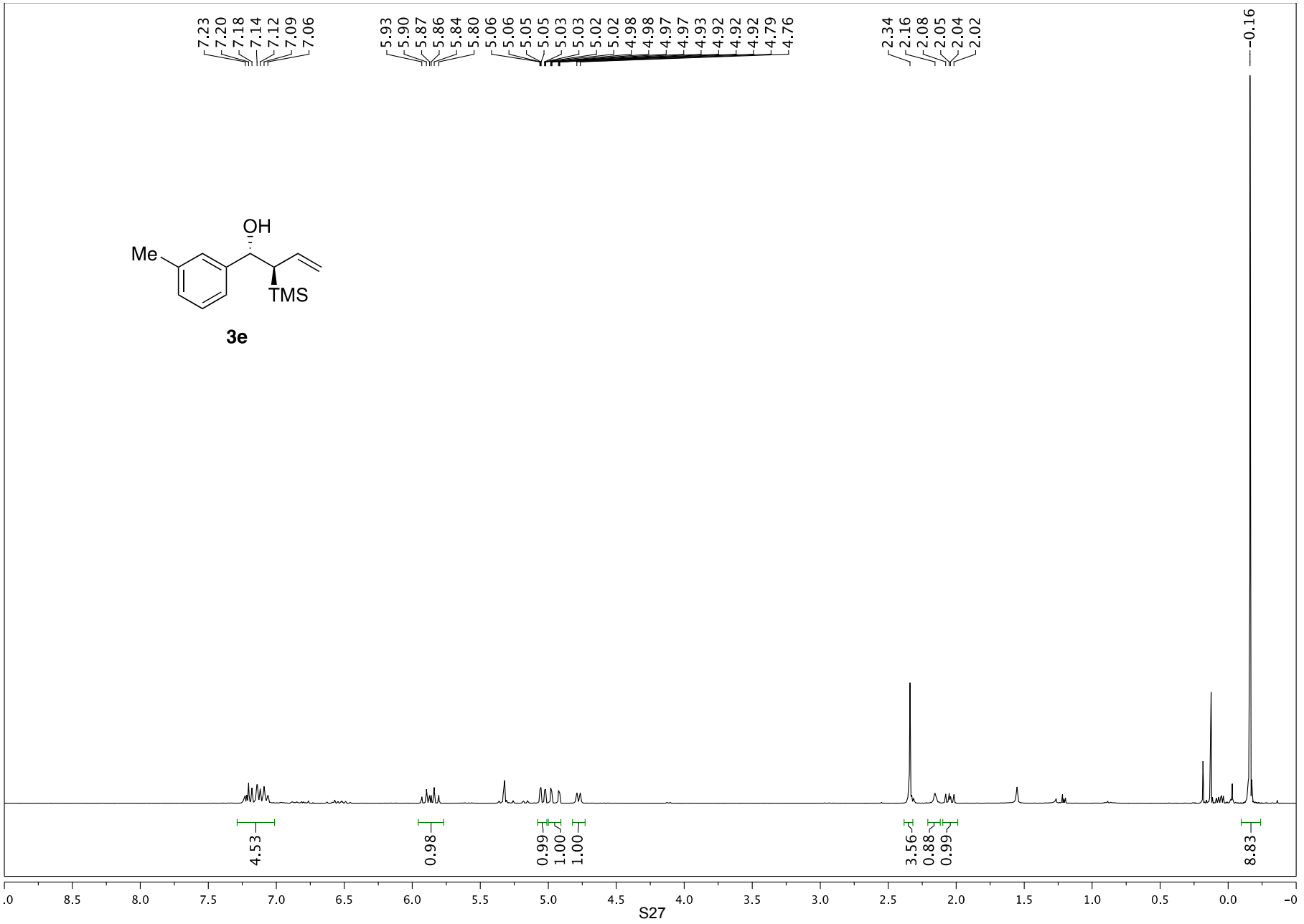

7.90
7.90
7.87
7.87
7.78
7.77
7.75
7.75
7.64
7.63
7.61
7.61
7.59
7.42
7.41
7.39
7.39
7.38
7.37
7.36
6.00
5.96
5.94
5.93
5.90
5.87
5.63
5.62
4.90
4.90
4.87
4.86
4.72
4.71
4.71
4.71
4.66
4.66
4.65
4.65
2.18
2.09
2.08
2.06
2.05
0.06
NO2
OH
TMS
1.00
1.14
1.18
1.15
1.11
1.12
1.16
1.29
0.87
1.16
9.87
8.5
8.0
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
-0

3d

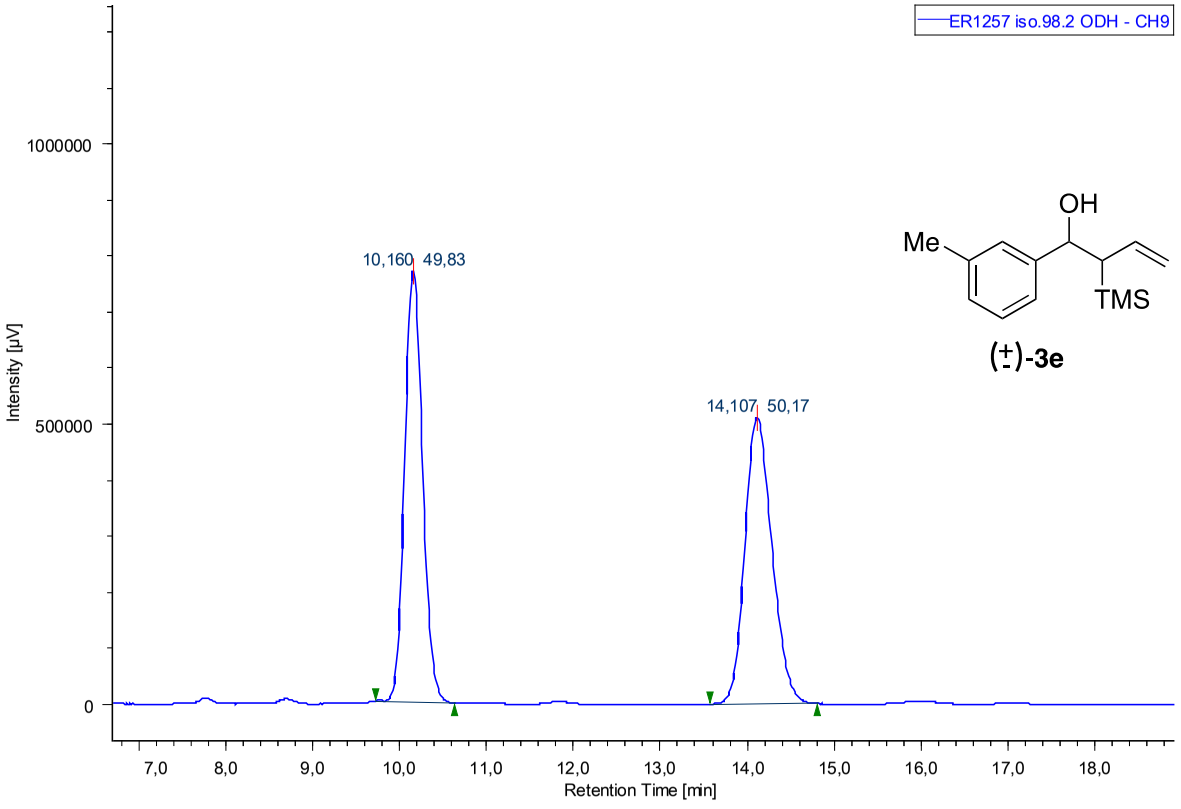

147.90
140.84
135.19
133.25
129.44
128.24
124.79
115.81
69.59
43.57
-2.14
NO2
OH
TMS
3d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


ER1247 iso.98.2 ODH - CH11
12,307 52,10
19,493 47,90
NO2 OH
TMS
(±)-3d
Intensity [µV]
Retention Time [min]

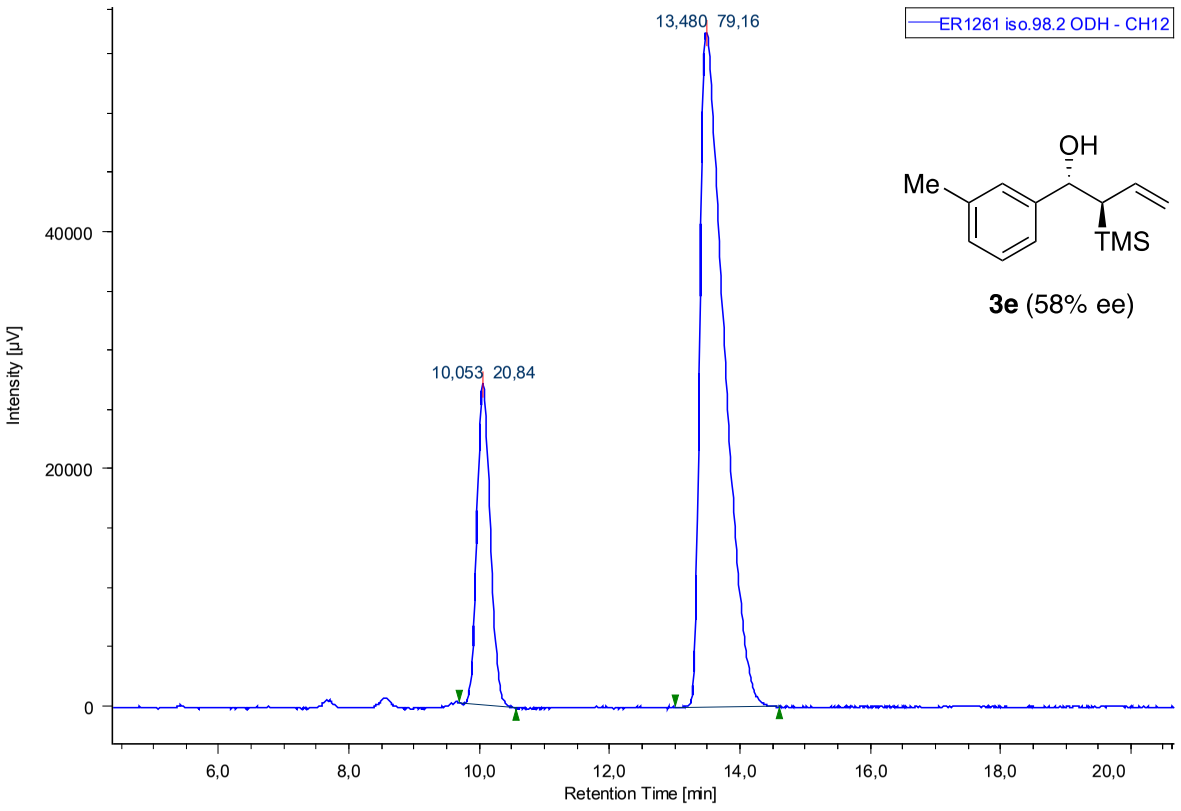

ER1245 iso.98.2 ODH - CH13
12,160 76,07
18,960 23,93
NO2 OH
TMS
3d (52% ee)
Intensity [µV]
Retention Time [min]


7.23
7.20
7.18
7.14
7.12
7.09
7.06
5.93
5.90
5.87
5.86
5.84
5.80
5.06
5.06
5.05
5.05
5.03
5.03
5.02
5.02
4.98
4.98
4.97
4.97
4.93
4.92
4.92
4.92
4.79
4.76
2.34
2.16
2.08
2.05
2.04
2.02
-0.16
OH
Me
TMS
4.53
0.98
0.99
1.00
1.00
3.56
0.88
0.99
8.83
.0
8.5
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
-0

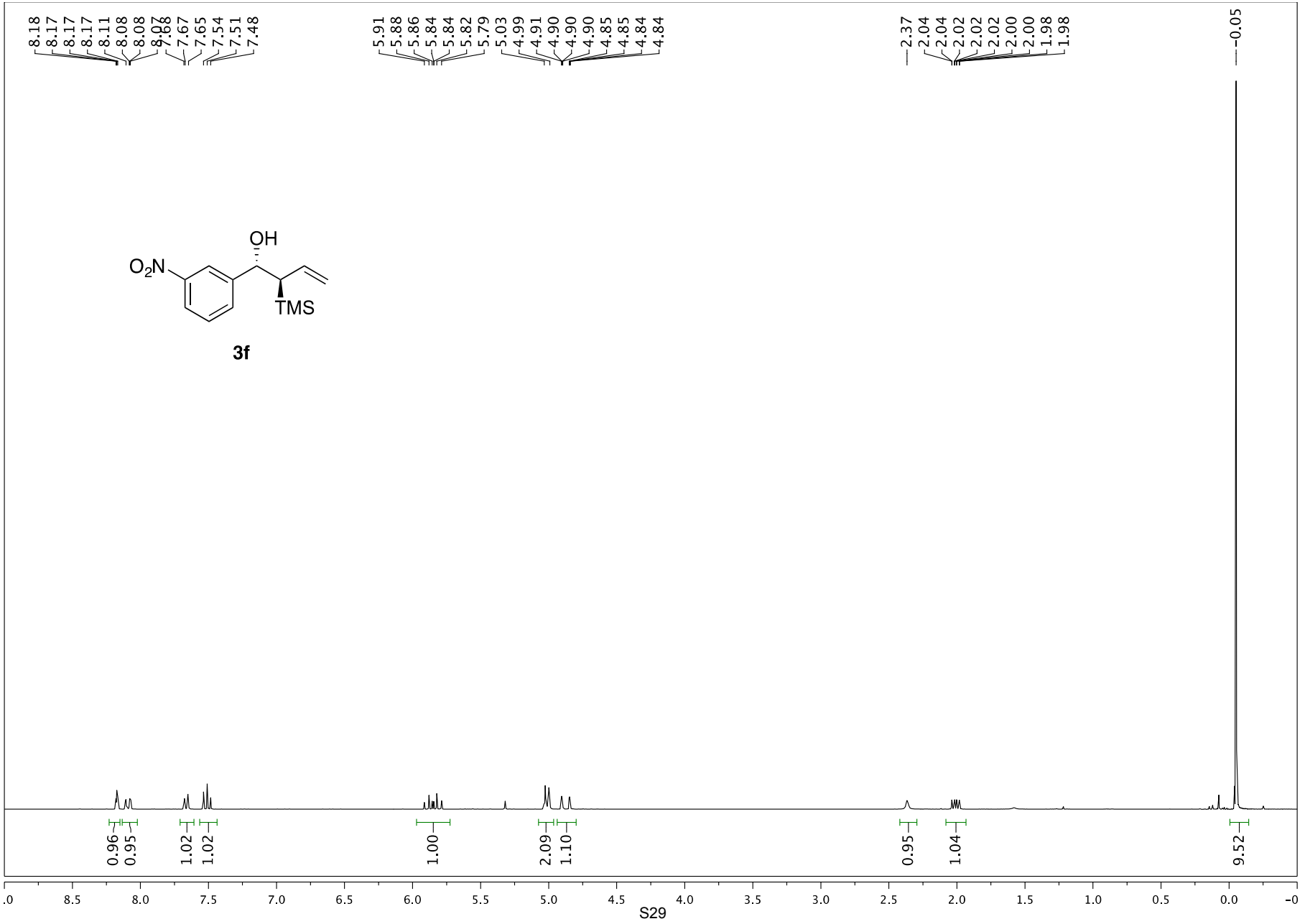
3e


ER1257 iso.98.2 ODH - CH9
1000000
500000
0
Intensity [µV]
10,160 49,83
14,107 50,17
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
Retention Time [min]
OH
Me
TMS

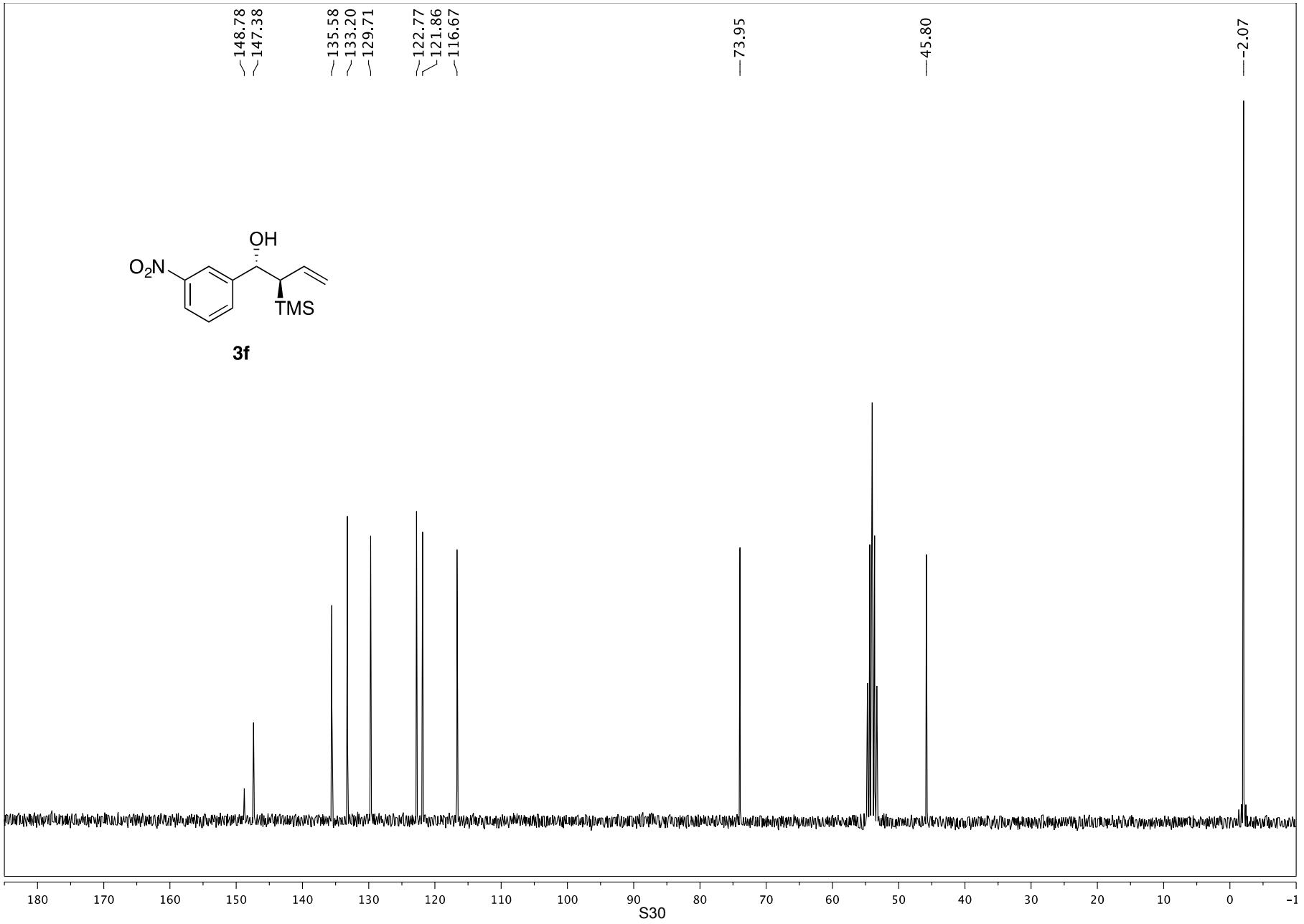
(±)-3e

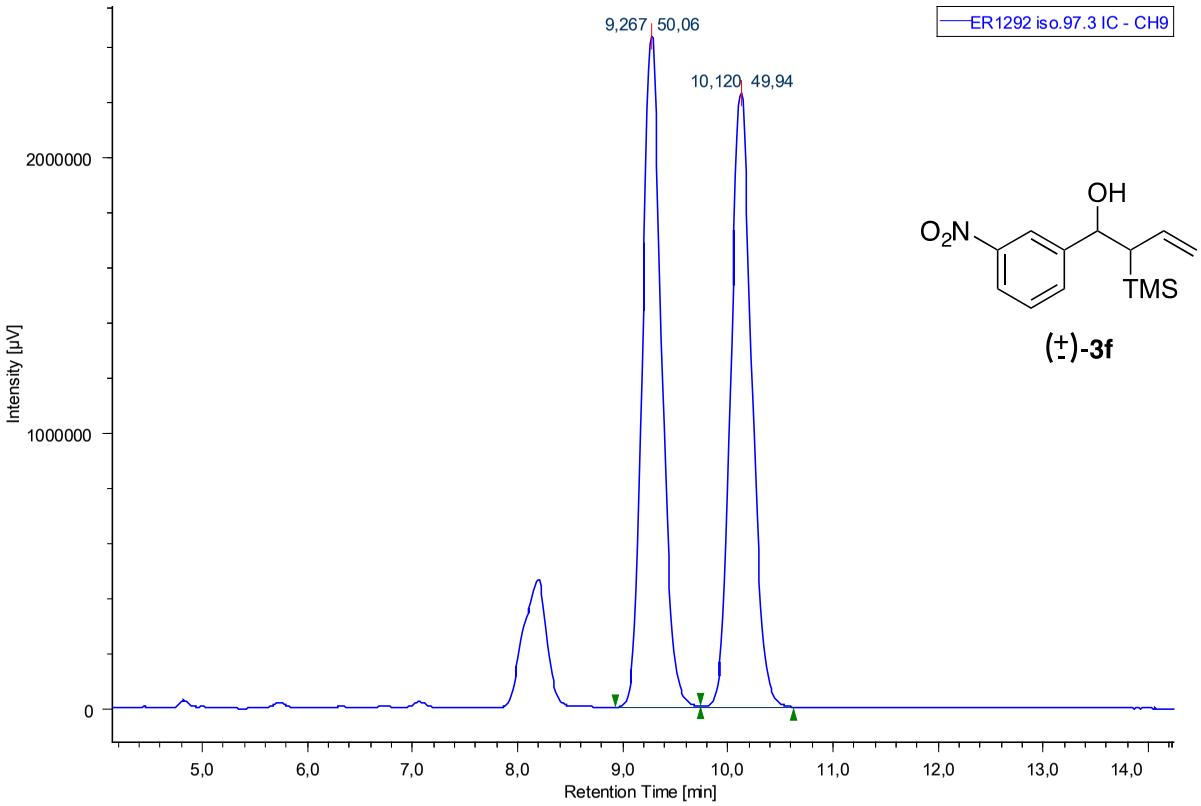

ER1261 iso.98.2 ODH - CH12
40000
20000
0
Intensity [µV]
13,480 79,16
10,053 20,84
6,0
8,0
10,0
12,0
14,0
16,0
18,0
20,0
Retention Time [min]
OH
Me
TMS

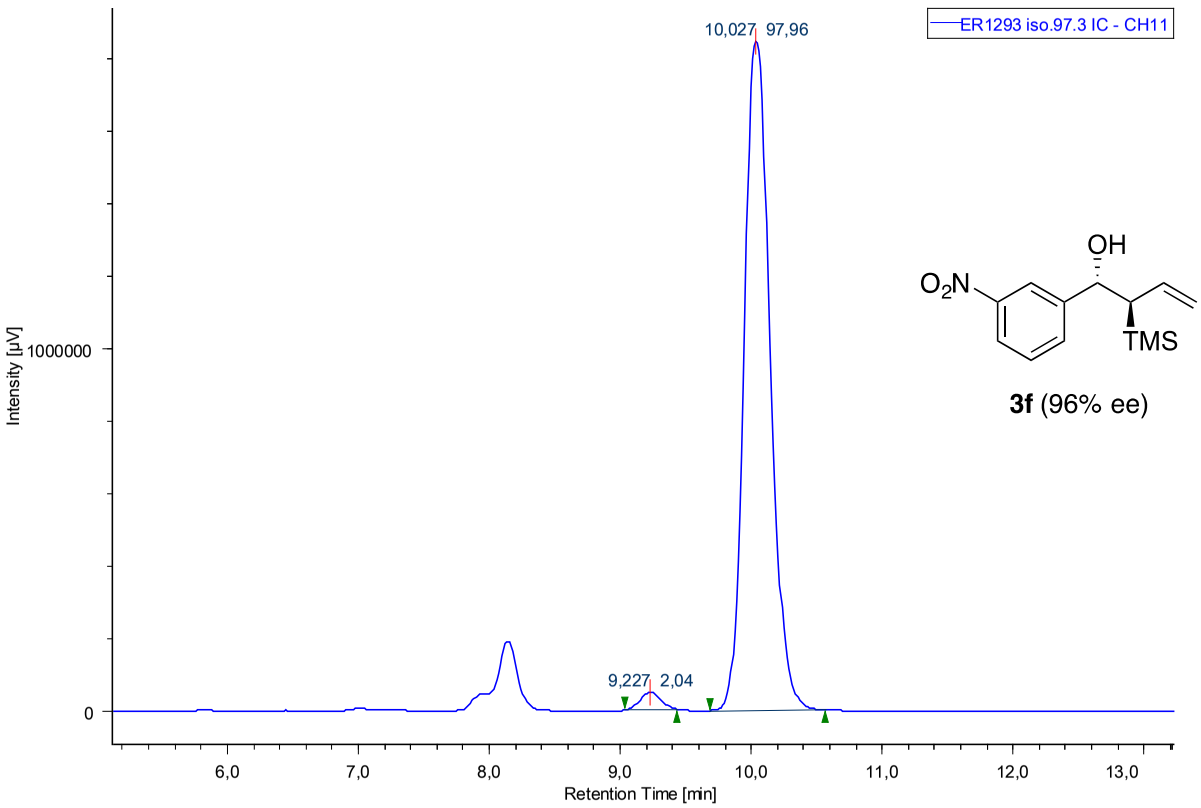
3e (58% ee)

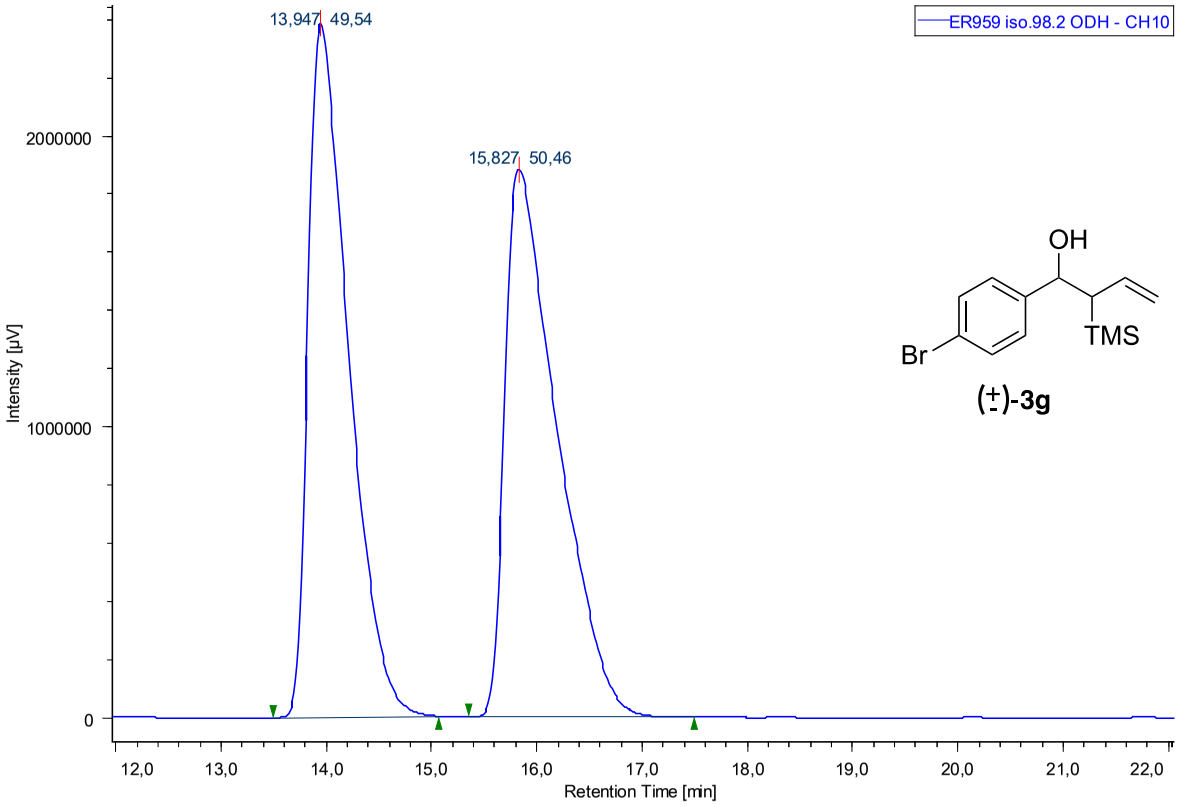

8.18
8.17
8.17
8.17
8.11
8.08
8.08
8.07
7.68
7.67
7.65
7.54
7.51
7.48
5.91
5.88
5.86
5.84
5.84
5.82
5.79
5.03
4.99
4.91
4.90
4.90
4.90
4.85
4.85
4.84
4.84
2.37
2.04
2.04
2.02
2.02
2.02
2.00
2.00
1.98
1.98
-0.05
OH
O2N
TMS
0.96
0.95
1.02
1.02
1.00
2.09
1.10
0.95
1.04
9.52
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

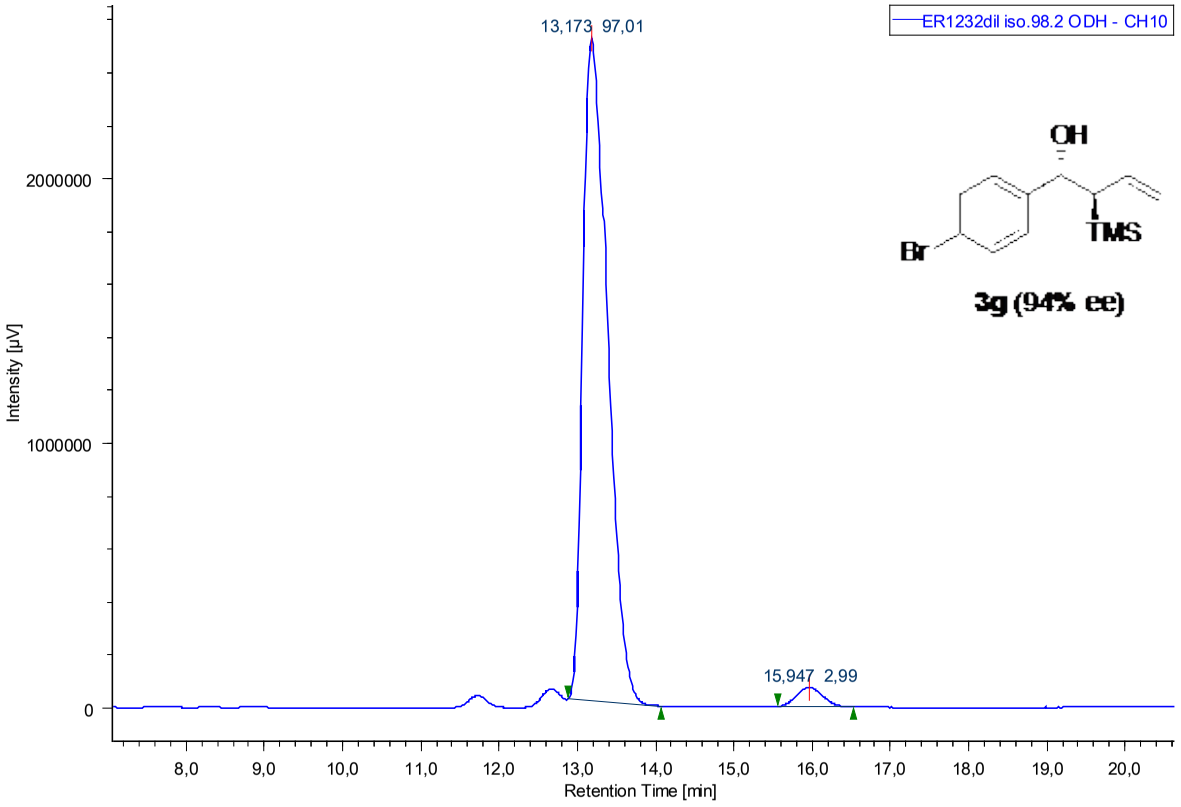
3f

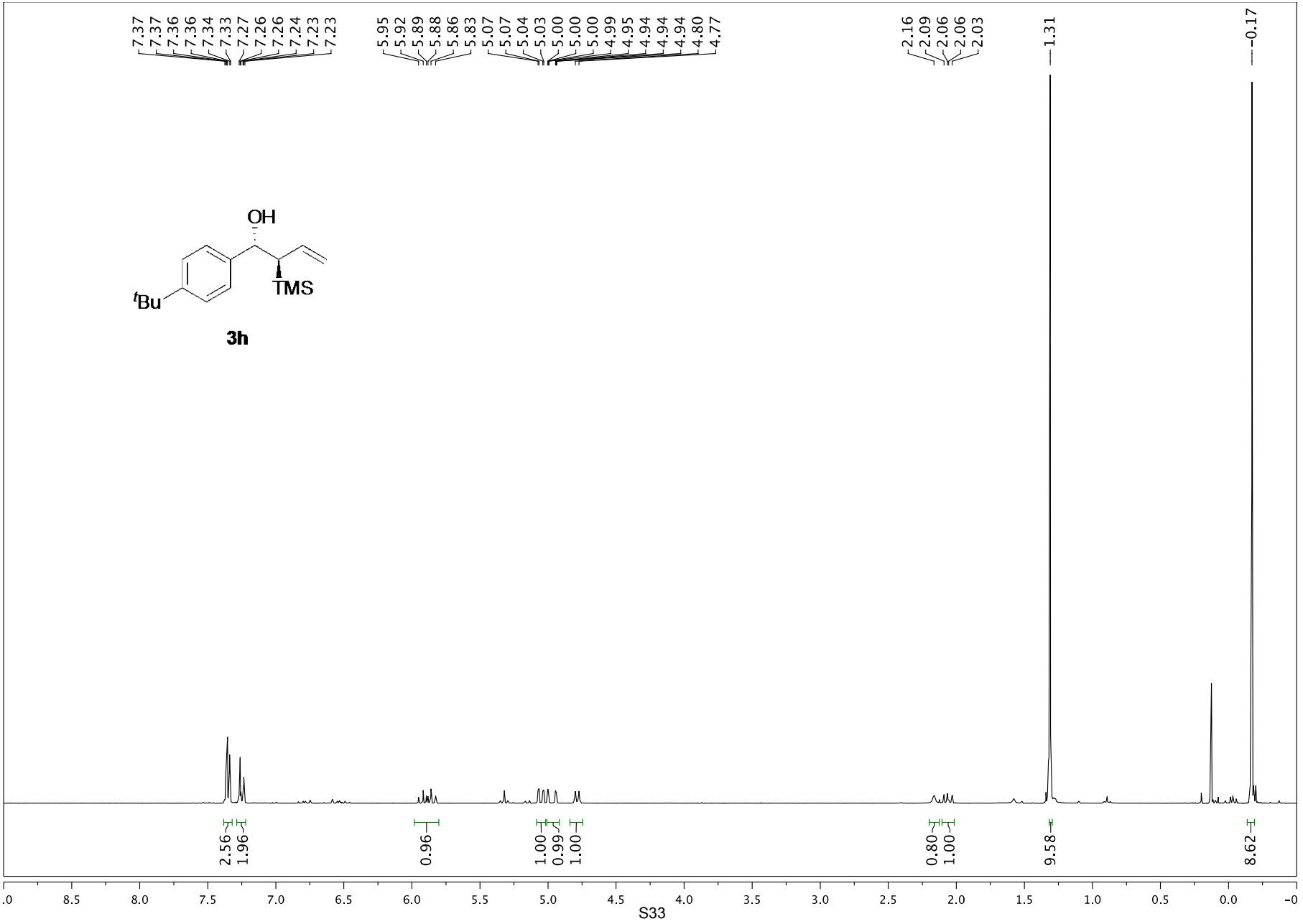

148.78
147.38
135.58
133.20
129.71
122.77
121.86
116.67
73.95
45.80
2.07
OH
O2N
TMS
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

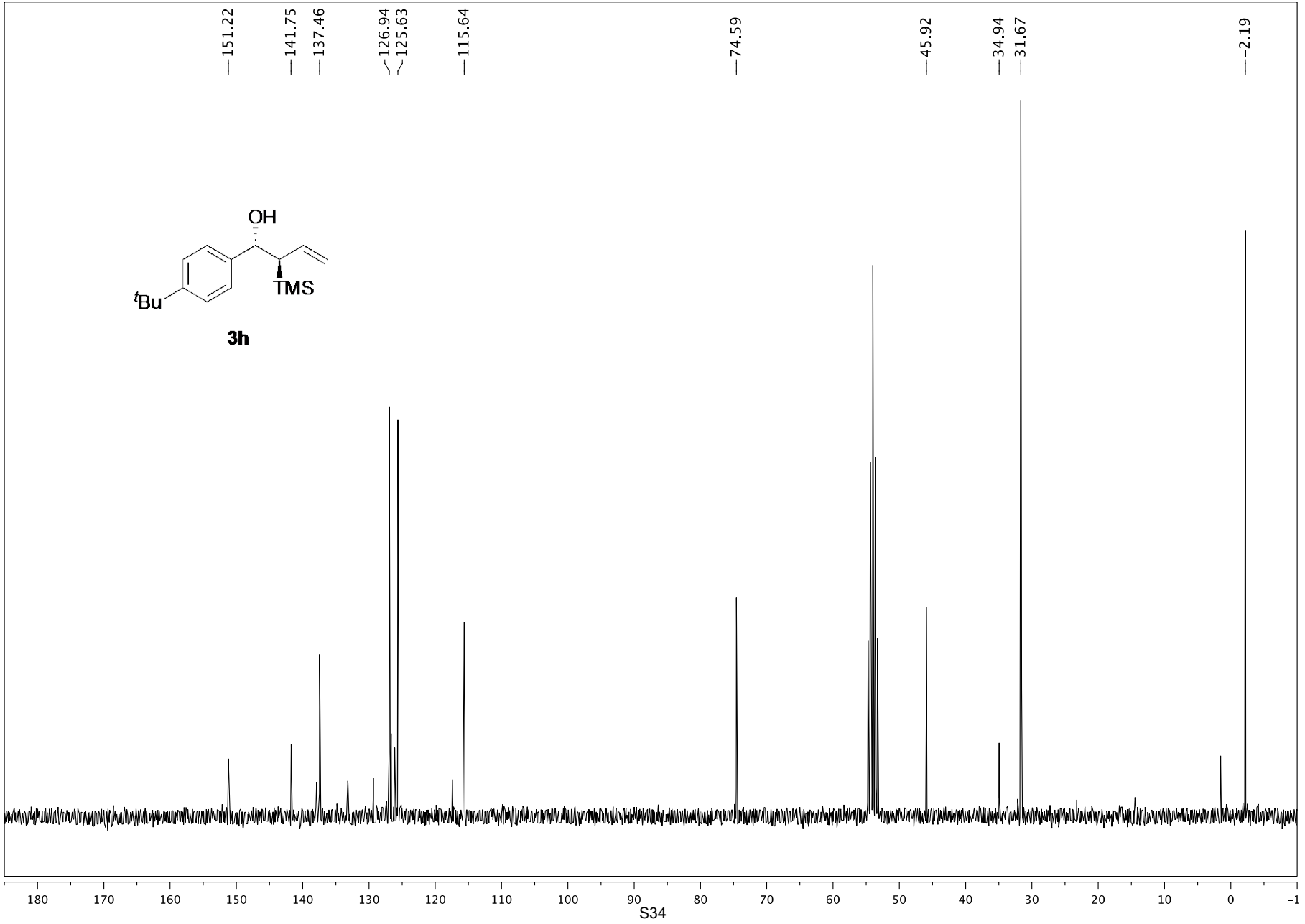

ER1292 iso.97.3 IC - CH9
9,267 50,06
10,120 49,94
2000000
1000000
0
Intensity [µV]
5,0
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
Retention Time [min]
OH
O2N
TMS
(±)-3f

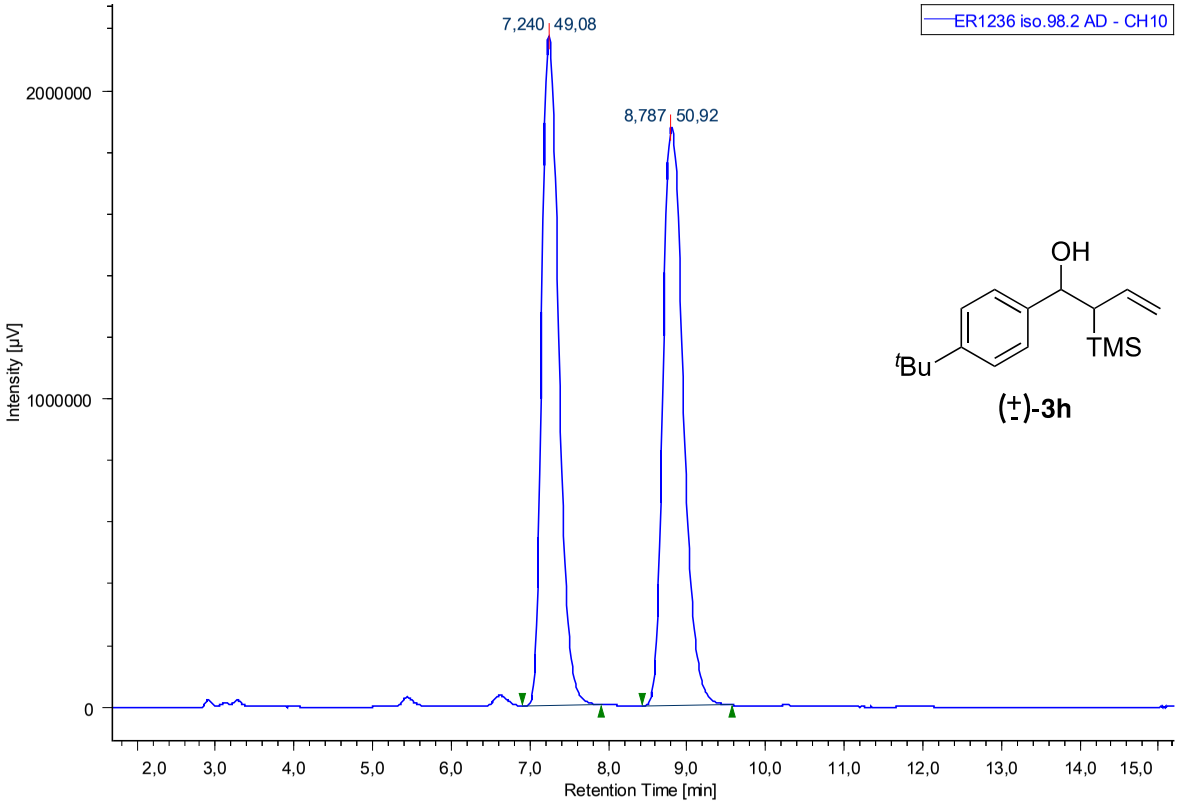

ER1293 iso.97.3 IC - CH11
10,027 97,96
9,227 2,04
1000000
0
Intensity [µV]
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
Retention Time [min]
OH
O2N
TMS
3f (96% ee)

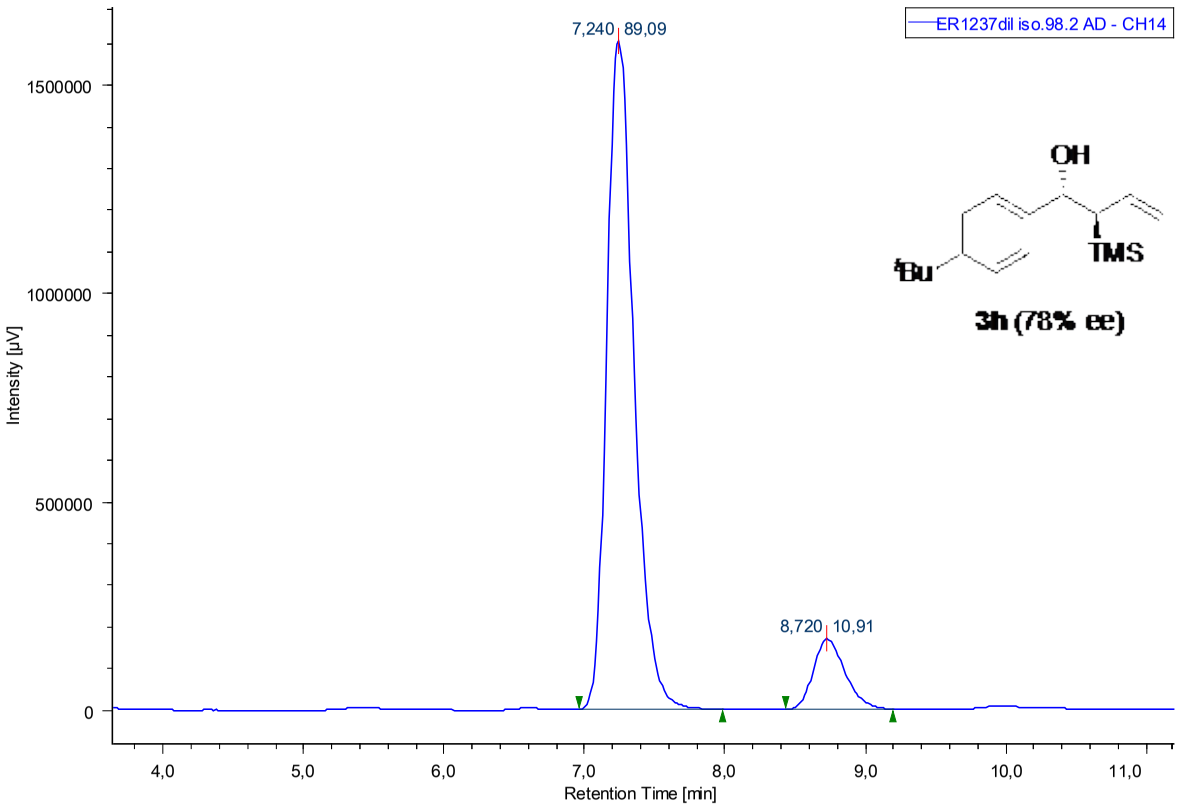

ER959 iso.98.2 ODH - CH10
13,947 49,54
15,827 50,46
OH
TMS
Br
(±)-3g
Intensity [µV]
2000000
1000000
0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
19,0
20,0
21,0
22,0
Retention Time [min]

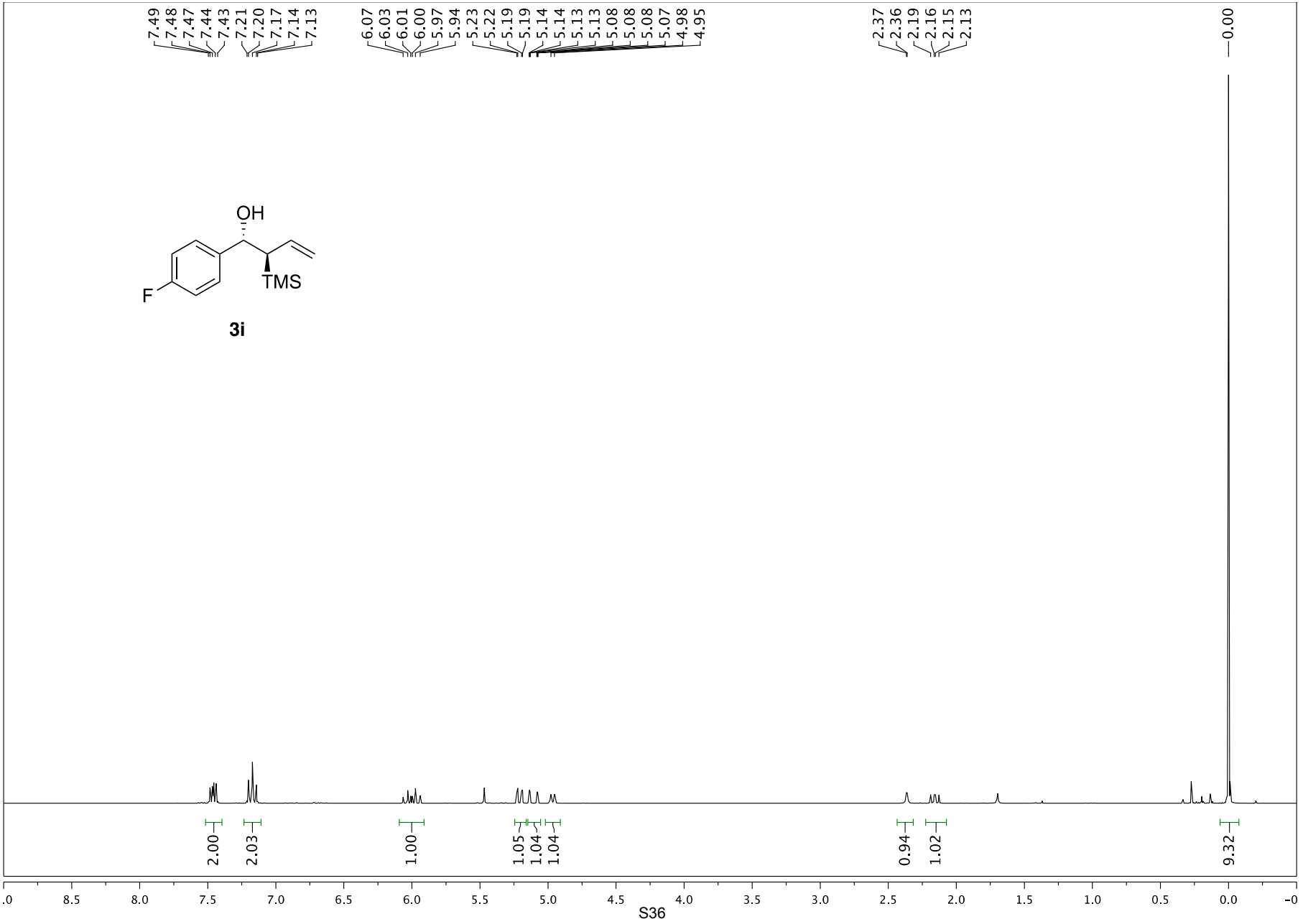

ER1232dil iso.98.2 ODH - CH10
13,173 97,01
15,947 2,99
OH
TMS
Br
3g (94% ee)
Intensity [µV]
2000000
1000000
0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
19,0
20,0
Retention Time [min]

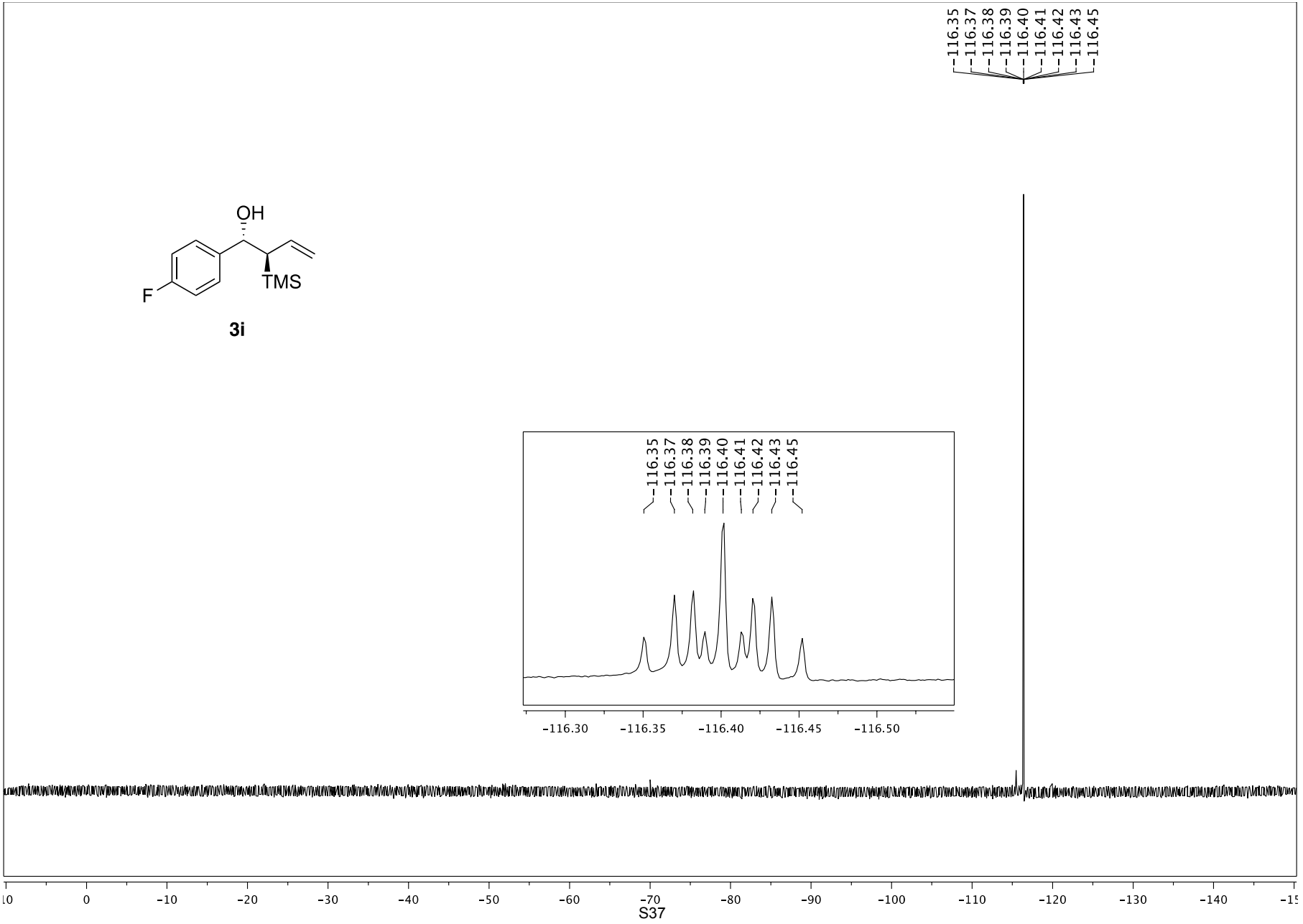

7.37
7.37
7.36
7.36
7.34
7.33
7.27
7.26
7.26
7.24
7.23
7.23
5.95
5.92
5.89
5.88
5.86
5.83
5.07
5.07
5.04
5.03
5.00
5.00
5.00
4.99
4.95
4.94
4.94
4.94
4.80
4.77
2.16
2.09
2.06
2.06
2.03
1.31
-0.17
OH
TMS
tBu
3h
2.56
1.96
0.96
1.00
0.99
1.00
0.80
1.00
9.58
8.62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

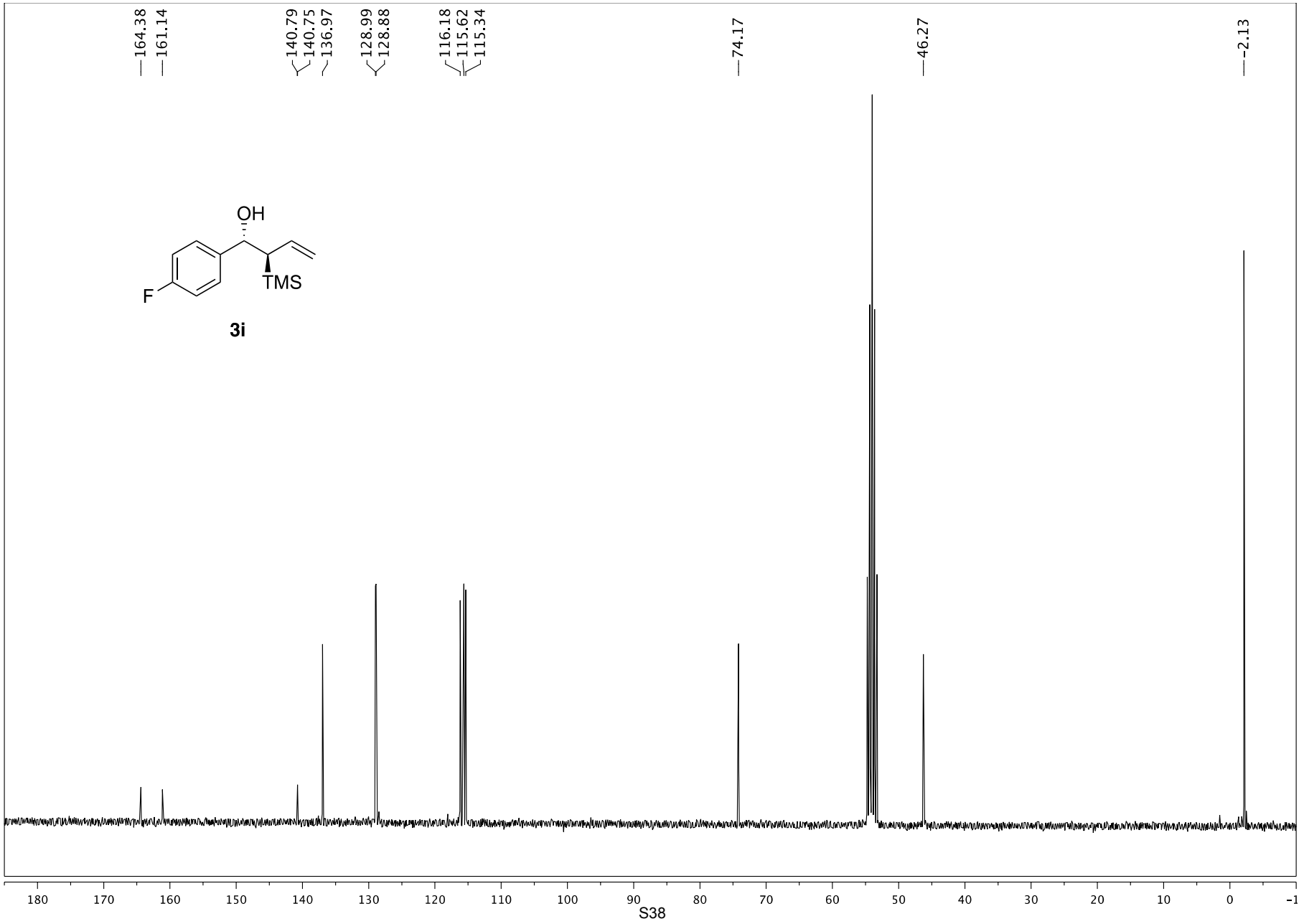

151.22
141.75
137.46
126.94
125.63
115.64
74.59
45.92
34.94
31.67
2.19
OH
TMS
tBu
3h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

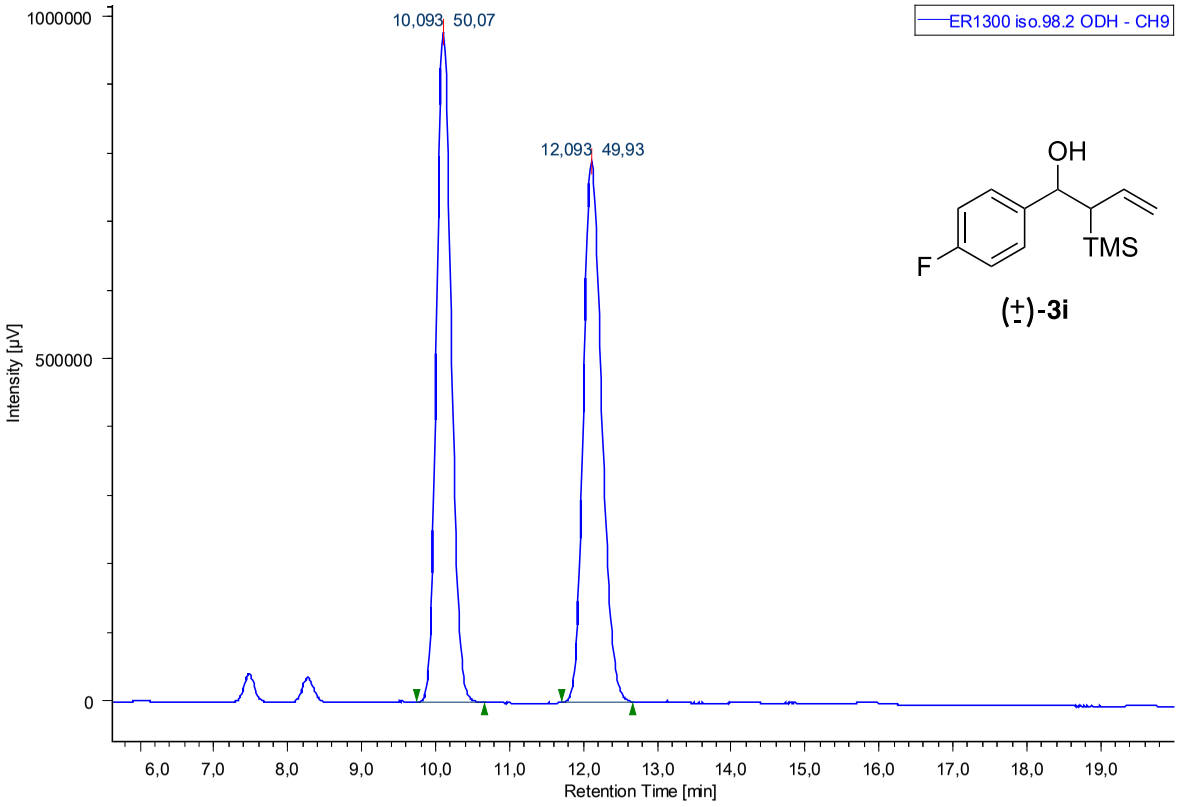

ER1236 iso.98.2 AD - CH10
7,240 49,08
8,787 50,92
2000000
1000000
0
Intensity [µV]
2,0 3,0 4,0 5,0 6,0 7,0 8,0 9,0 10,0 11,0 12,0 13,0 14,0 15,0
Retention Time [min]
OH
TMS
tBu
(±)-3h


ER1237dil iso.98.2 AD - CH14
7,240 89,09
8,720 10,91
1500000
1000000
500000
0
Intensity [µV]
4,0 5,0 6,0 7,0 8,0 9,0 10,0 11,0
Retention Time [min]
OH
TMS
tBu
3h (78% ee)

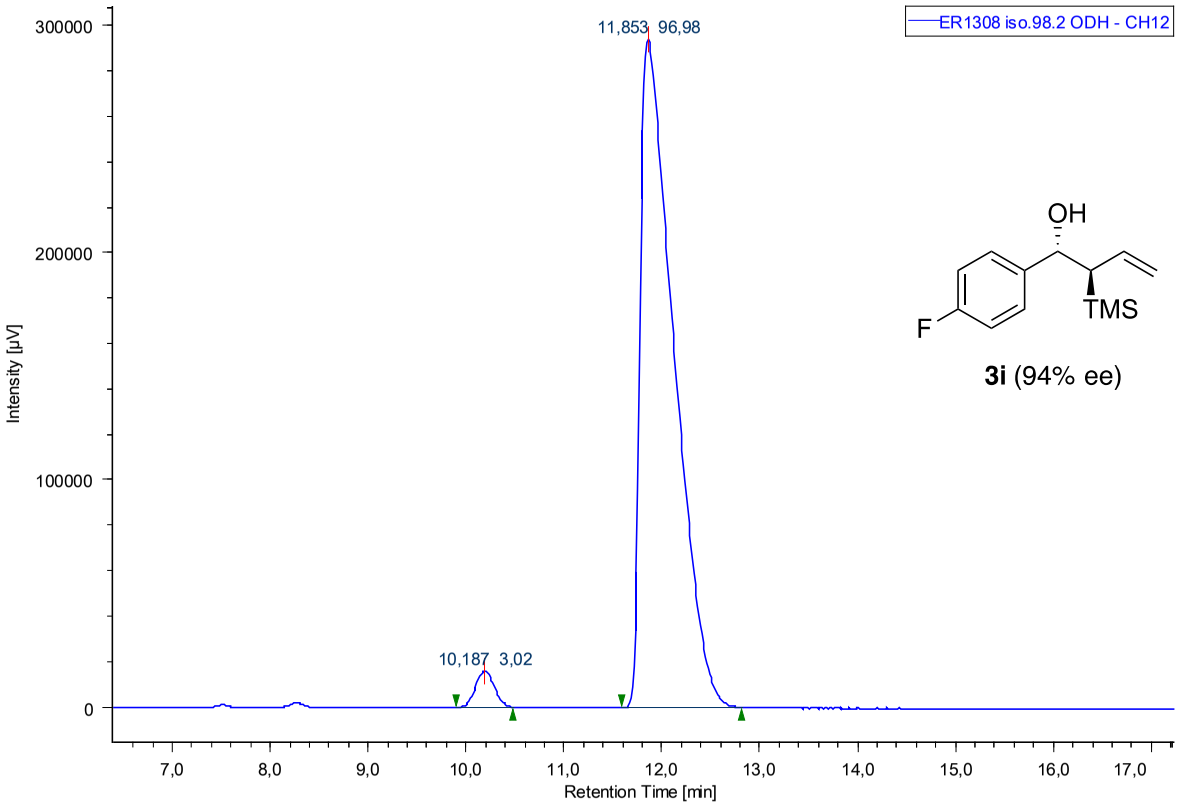

7.49
7.48
7.47
7.44
7.43
7.21
7.20
7.17
7.14
7.13
6.07
6.03
6.01
6.00
5.97
5.94
5.23
5.22
5.19
5.19
5.14
5.14
5.13
5.13
5.08
5.08
5.08
5.07
4.98
4.95
2.37
2.36
2.19
2.16
2.15
2.13
0.00
OH
TMS
F
3i
2.00
2.03
1.00
1.05
1.04
1.04
0.94
1.02
9.32
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0


116.35
116.37
116.38
116.39
116.40
116.41
116.42
116.43
116.45
OH
TMS
F
3i
-116.30
-116.35
-116.40
-116.45
-116.50
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140

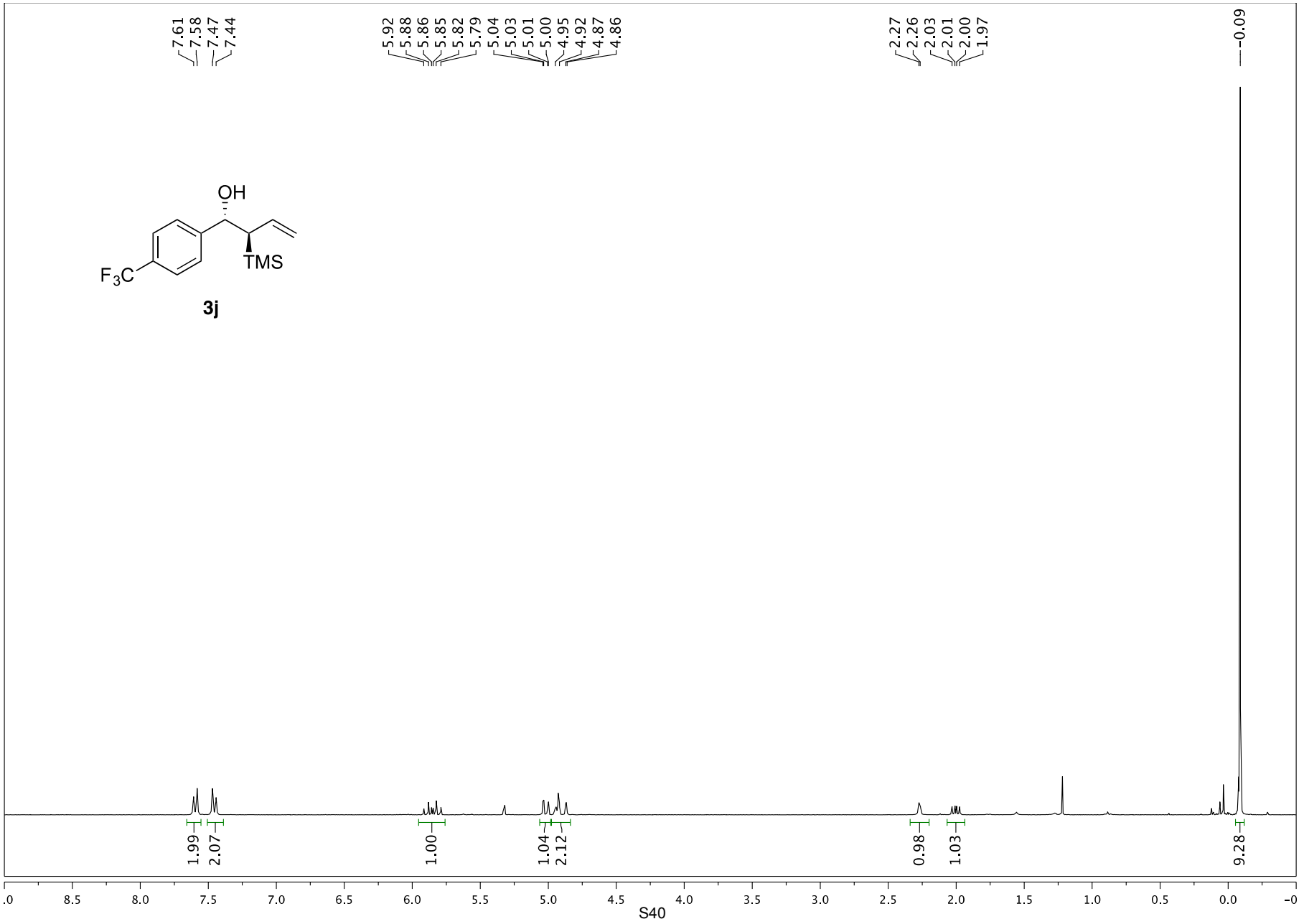

164.38
161.14
140.79
140.75
136.97
128.99
128.88
116.18
115.62
115.34
74.17
46.27
2.13
OH
TMS
F
3i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

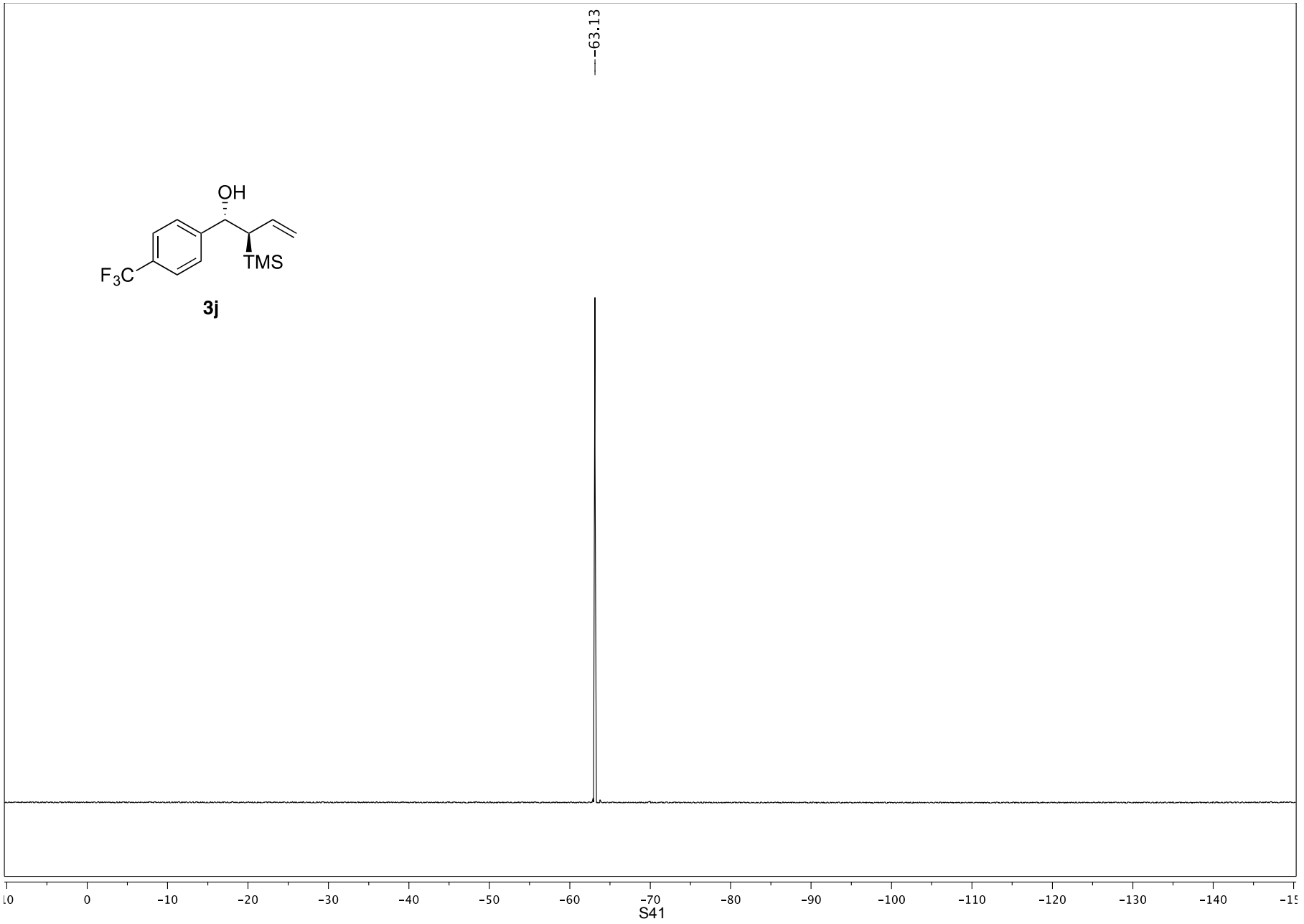

ER1300 iso.98.2 ODH - CH9
10,093 50,07
12,093 49,93
1000000
500000
0
Intensity [µV]
6,0 7,0 8,0 9,0 10,0 11,0 12,0 13,0 14,0 15,0 16,0 17,0 18,0 19,0
Retention Time [min]
OH
TMS
F

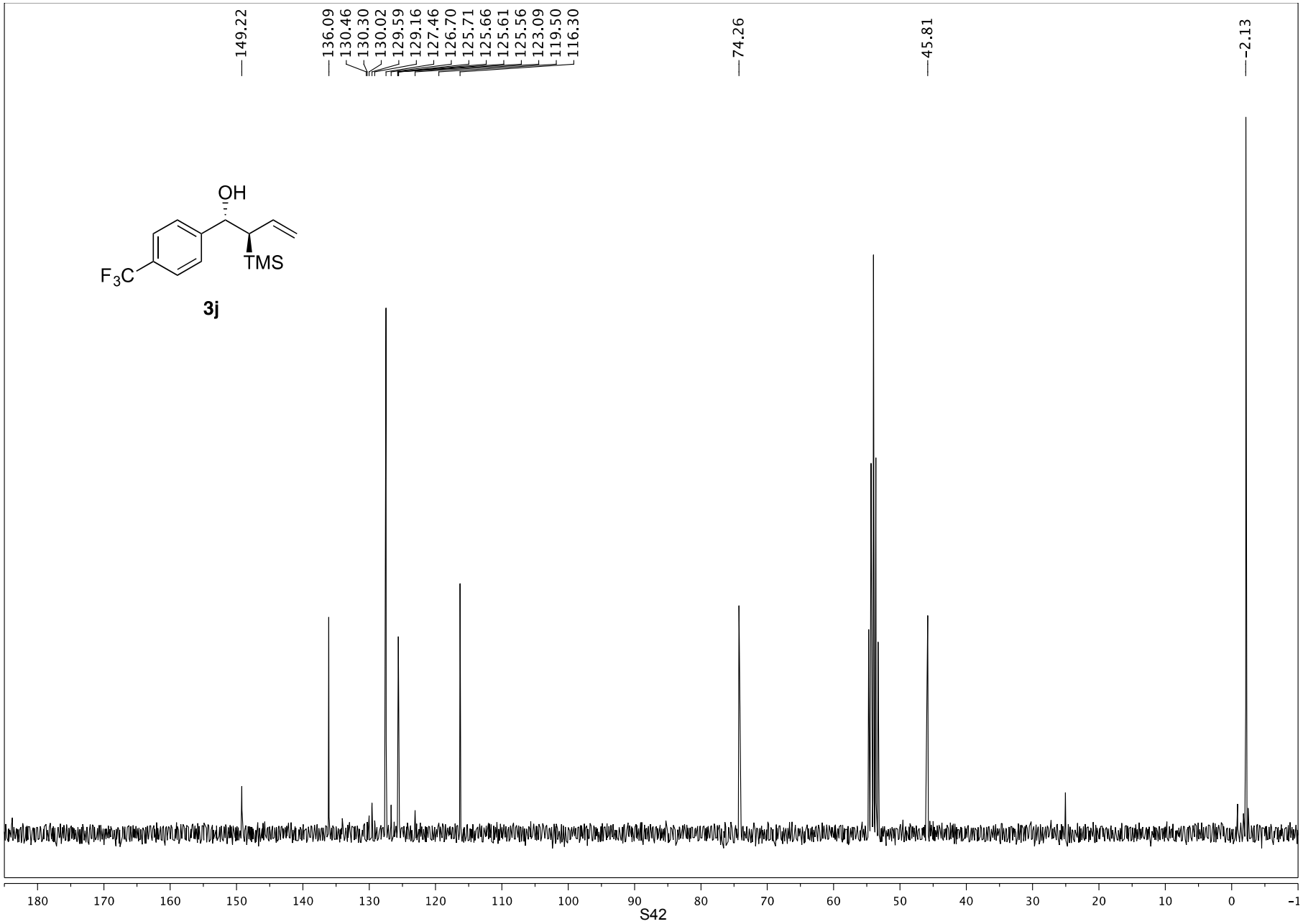
(±)-3i

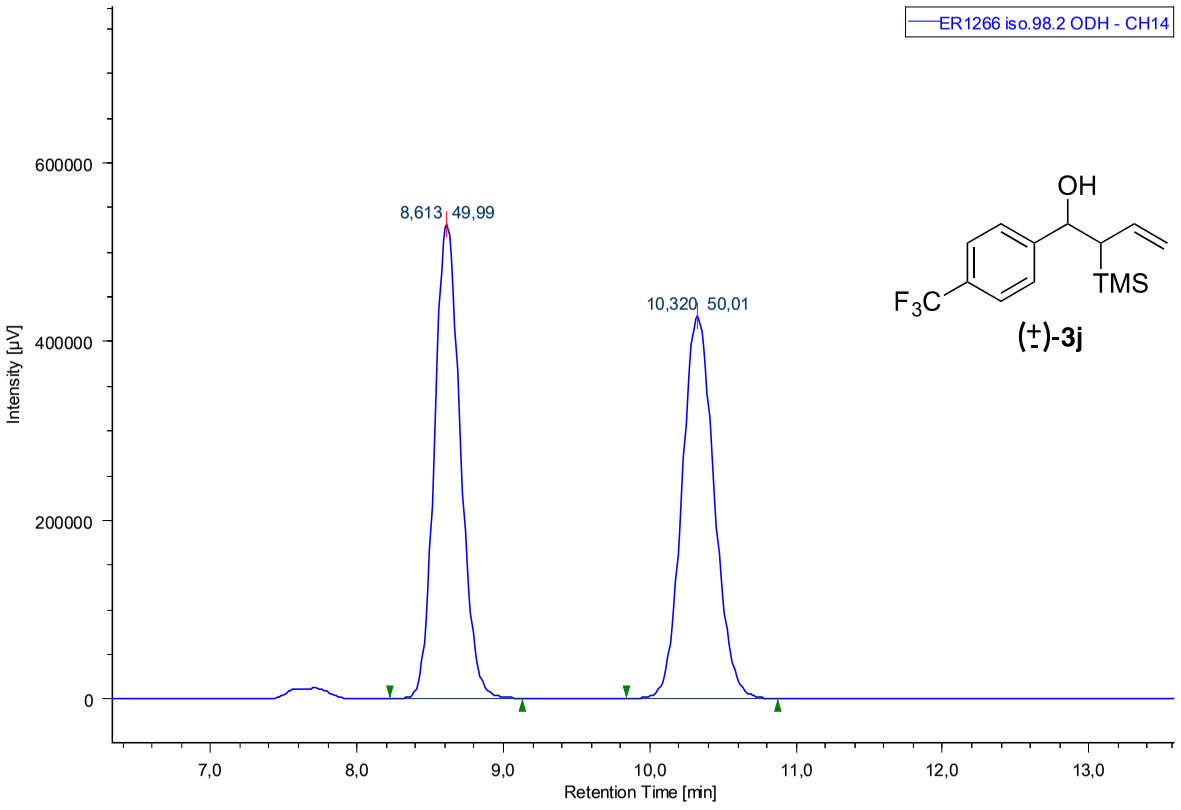

ER1308 iso.98.2 ODH - CH12
11,853 96,98
10,187 3,02
300000
200000
100000
0
Intensity [µV]
7,0 8,0 9,0 10,0 11,0 12,0 13,0 14,0 15,0 16,0 17,0
Retention Time [min]
OH
TMS
F

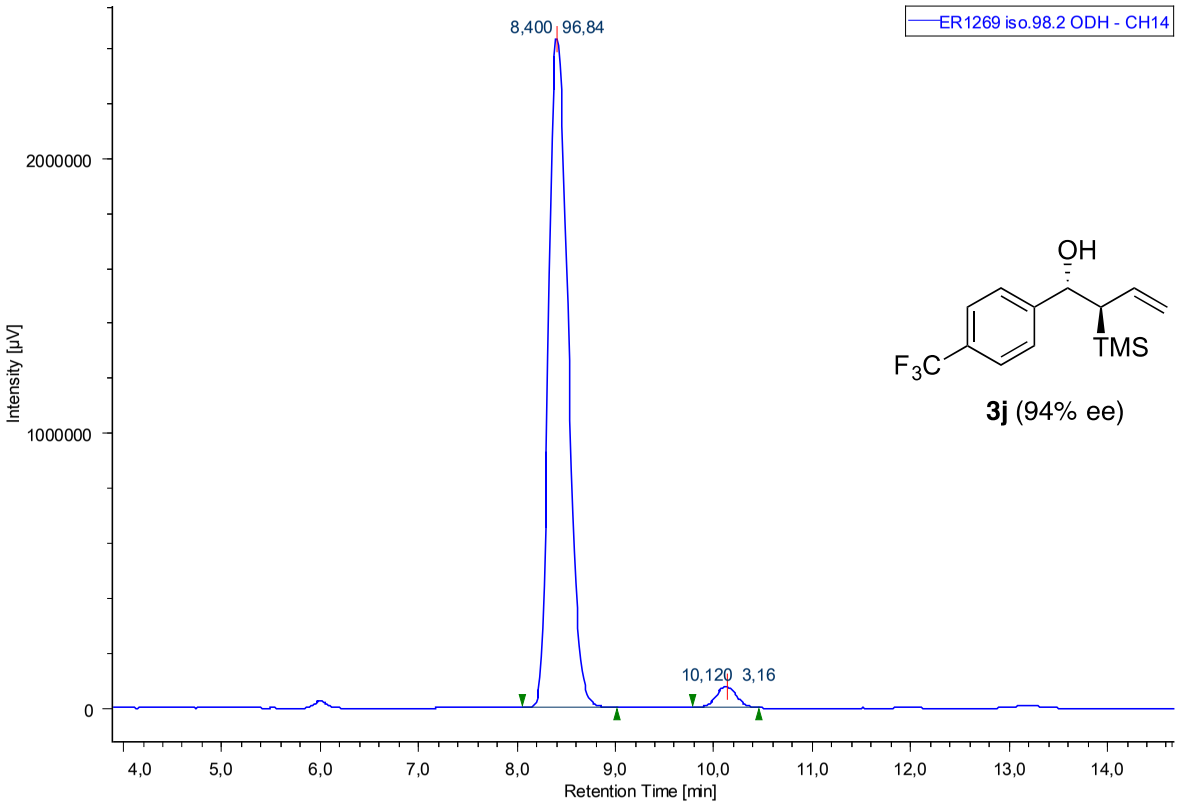
3i (94% ee)

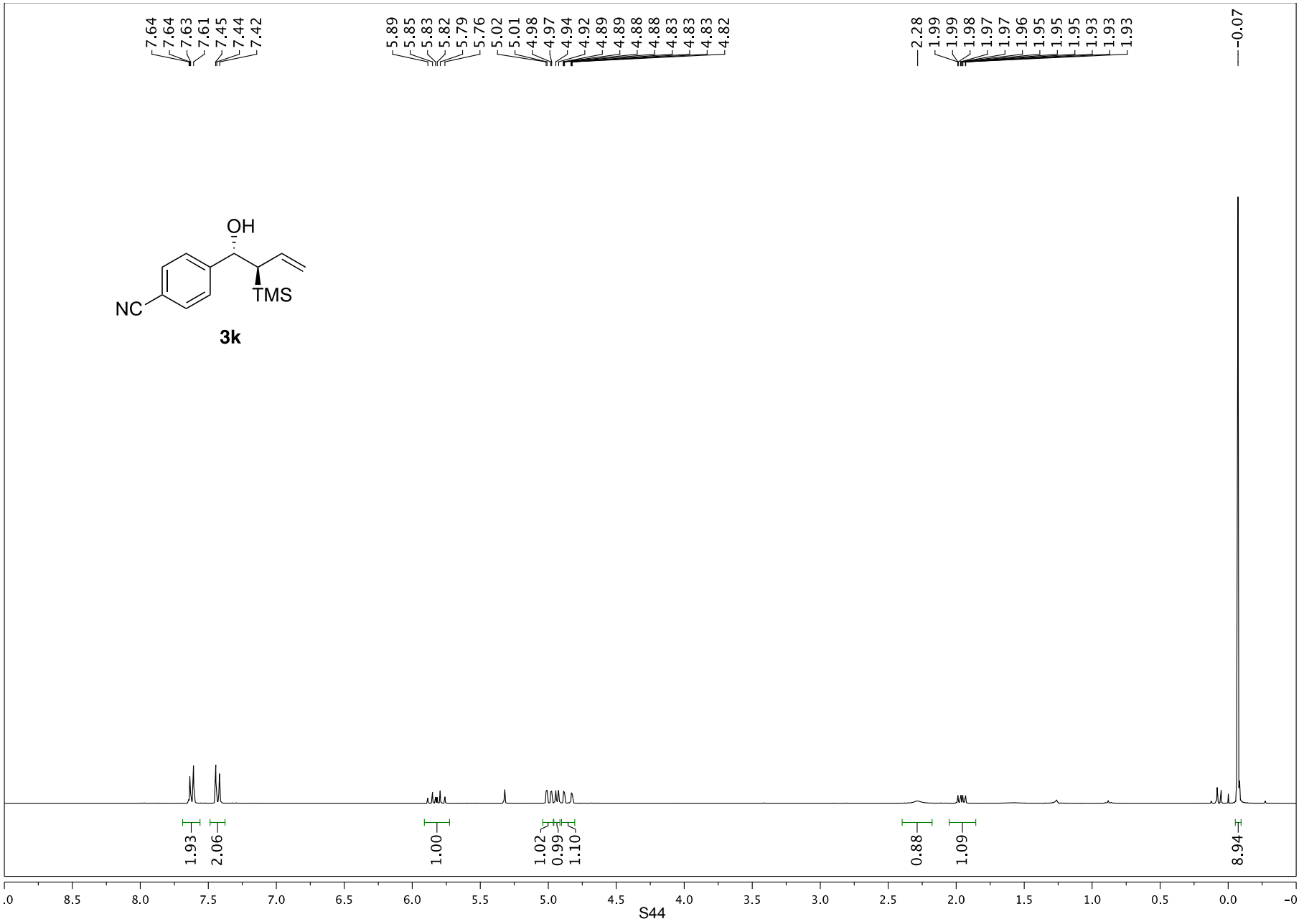

7.61
7.58
7.47
7.44
5.92
5.88
5.86
5.85
5.82
5.79
5.04
5.03
5.01
5.00
4.95
4.92
4.87
4.86
2.27
2.26
2.03
2.01
2.00
1.97
-0.09
OH
TMS
F3C
3j
1.99
2.07
1.00
1.04
2.12
0.98
1.03
9.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

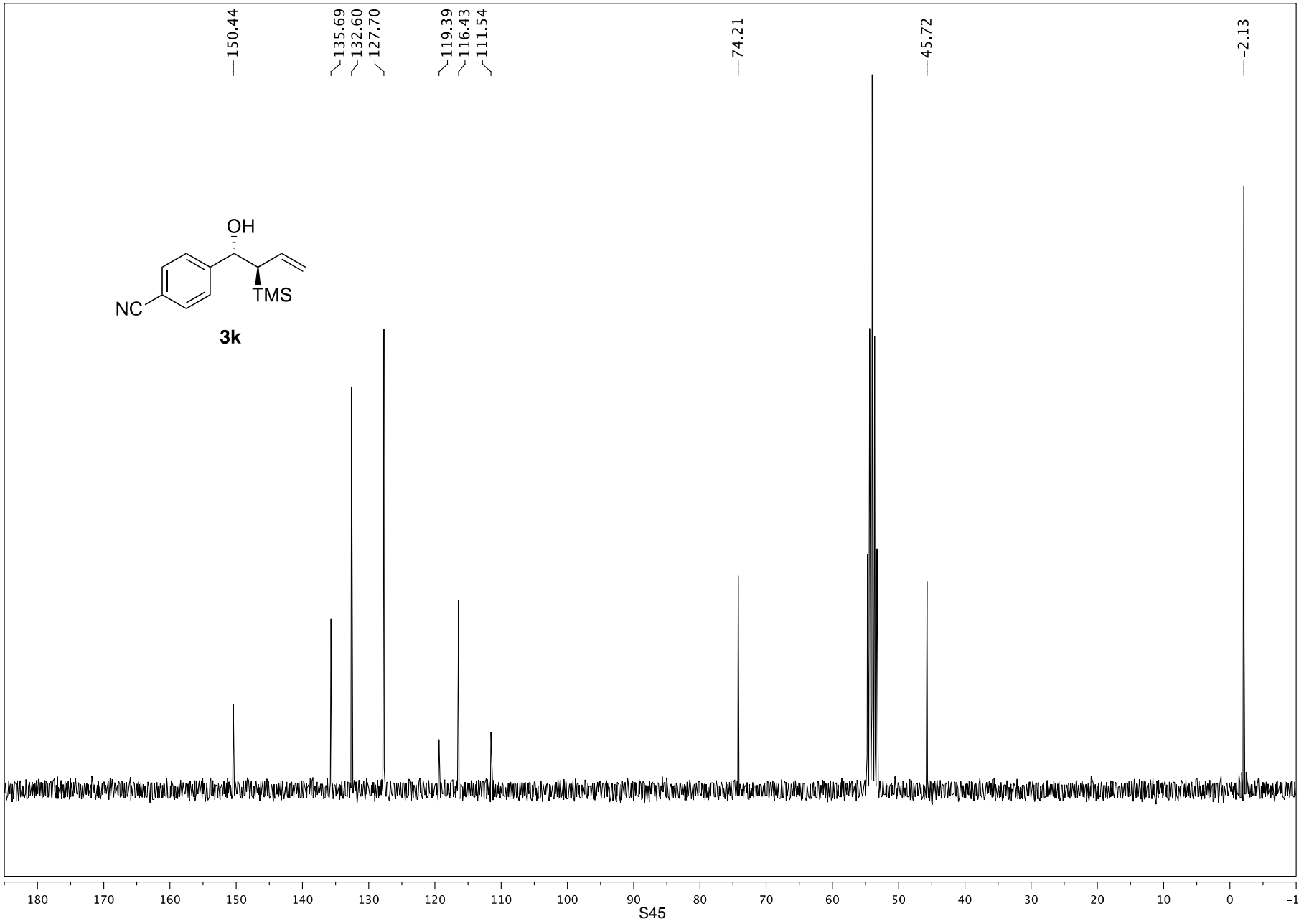

-63.13
OH
TMS
F3C
3j
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-15

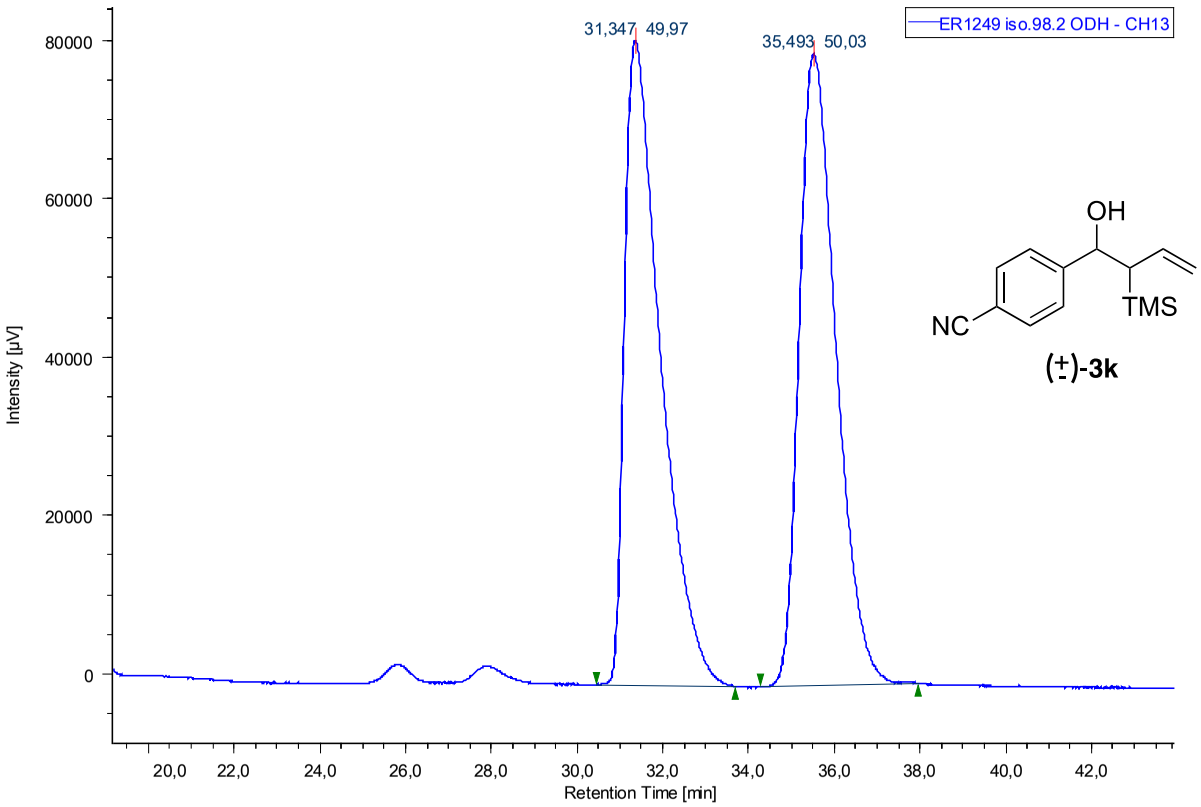

149.22
136.09
130.46
130.30
130.02
129.59
129.16
127.46
126.70
125.71
125.66
125.61
125.56
123.09
119.50
116.30
74.26
45.81
-2.13
OH
TMS
F3C
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

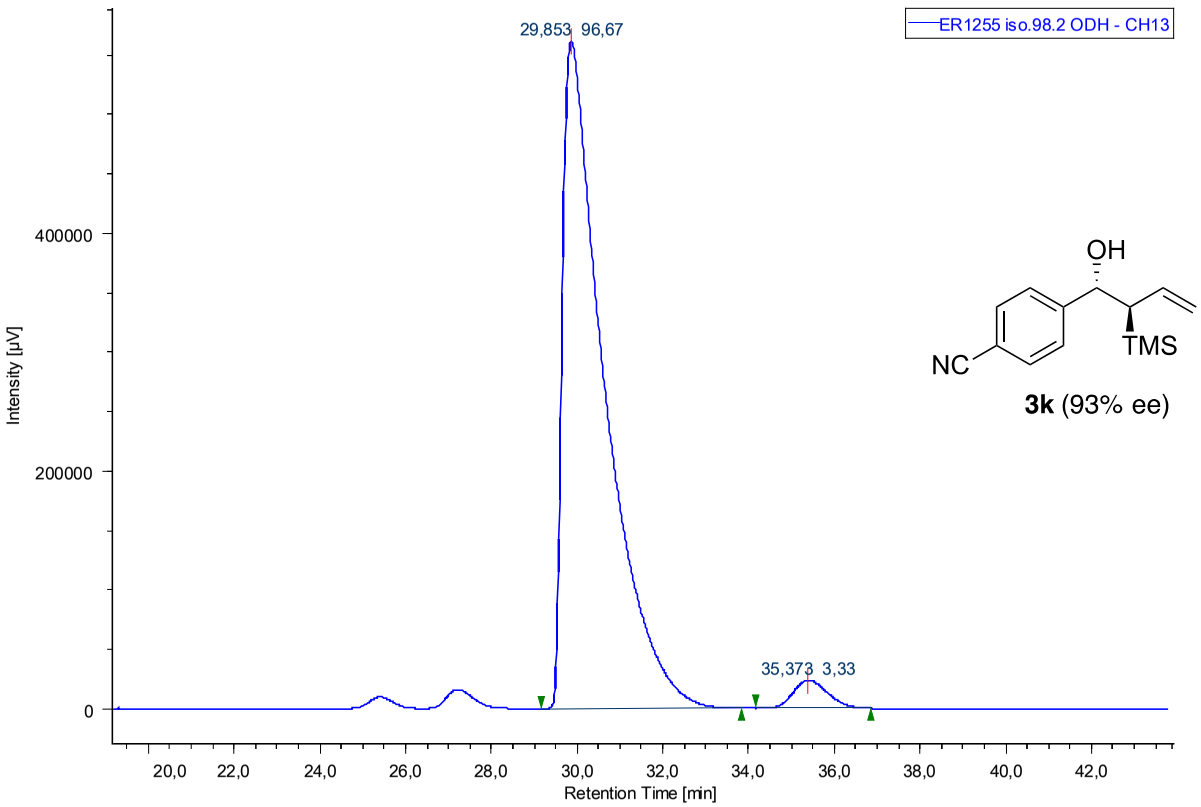

ER1266 iso.98.2 ODH - CH14
8,613 49,99
10,320 50,01
OH
TMS
F3C
(±)-3j
Intensity [µV]
600000
400000
200000
0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
Retention Time [min]

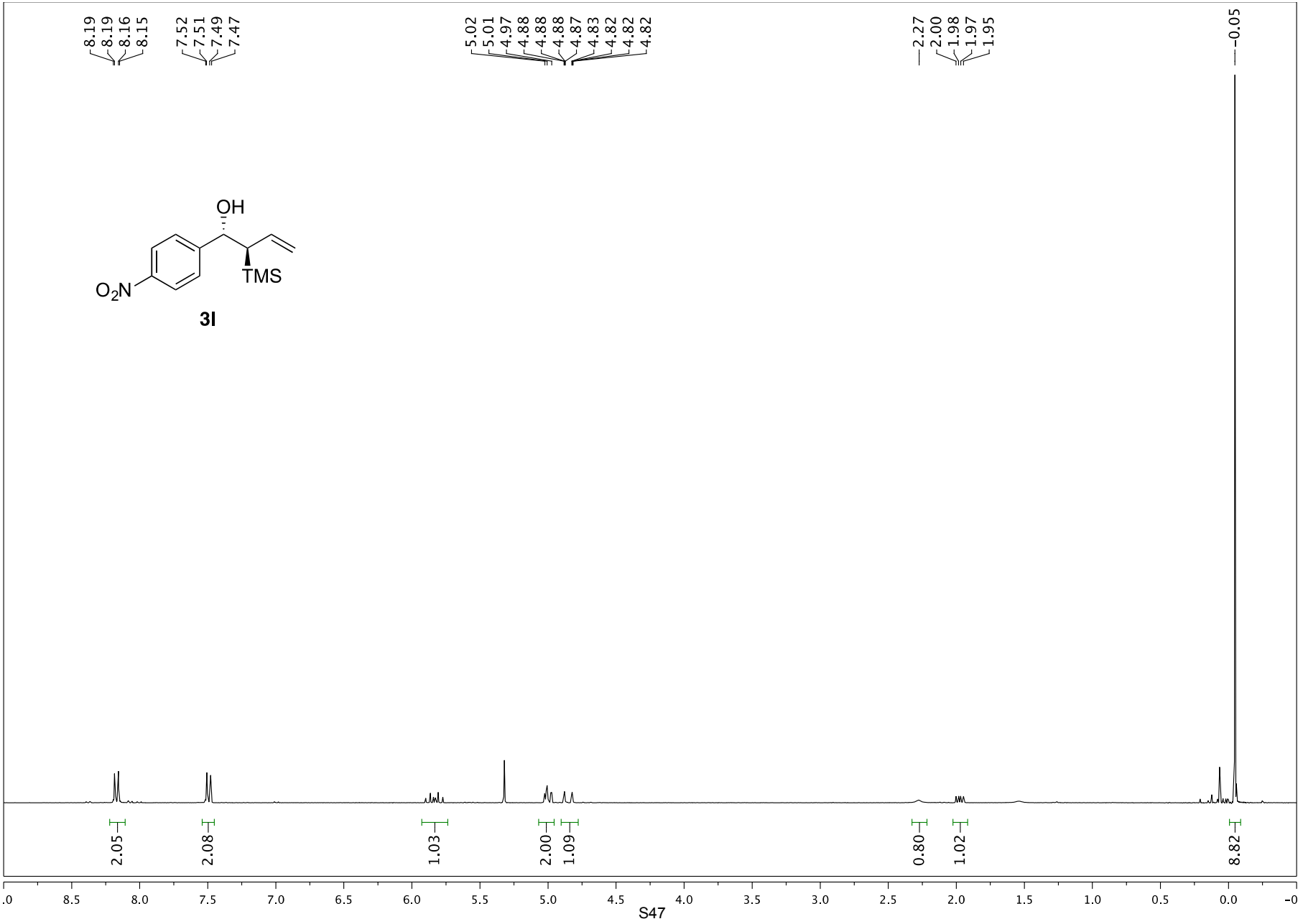

ER1269 iso.98.2 ODH - CH14
8,400 96,84
10,120 3,16
OH
TMS
F3C
3j (94% ee)
Intensity [µV]
2000000
1000000
0
4,0
5,0
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
Retention Time [min]

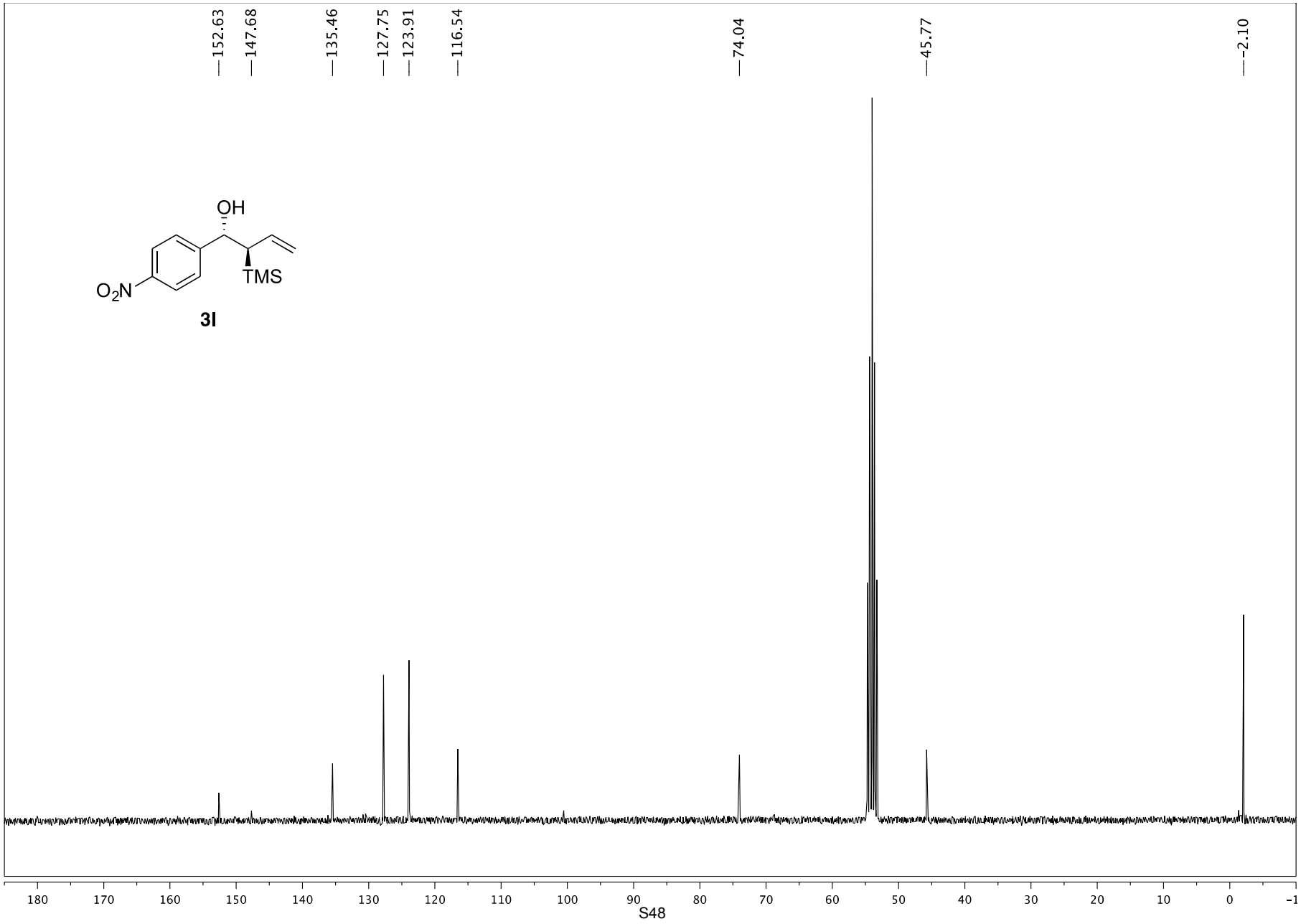

7.64
7.64
7.63
7.61
7.45
7.44
7.42
5.89
5.85
5.83
5.82
5.79
5.76
5.02
5.01
4.98
4.97
4.94
4.92
4.89
4.89
4.88
4.88
4.83
4.83
4.82
2.28
1.99
1.99
1.98
1.97
1.97
1.96
1.95
1.95
1.95
1.93
1.93
-0.07
OH
TMS
NC
3k
1.93
2.06
1.00
1.02
0.99
1.10
0.88
1.09
8.94
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

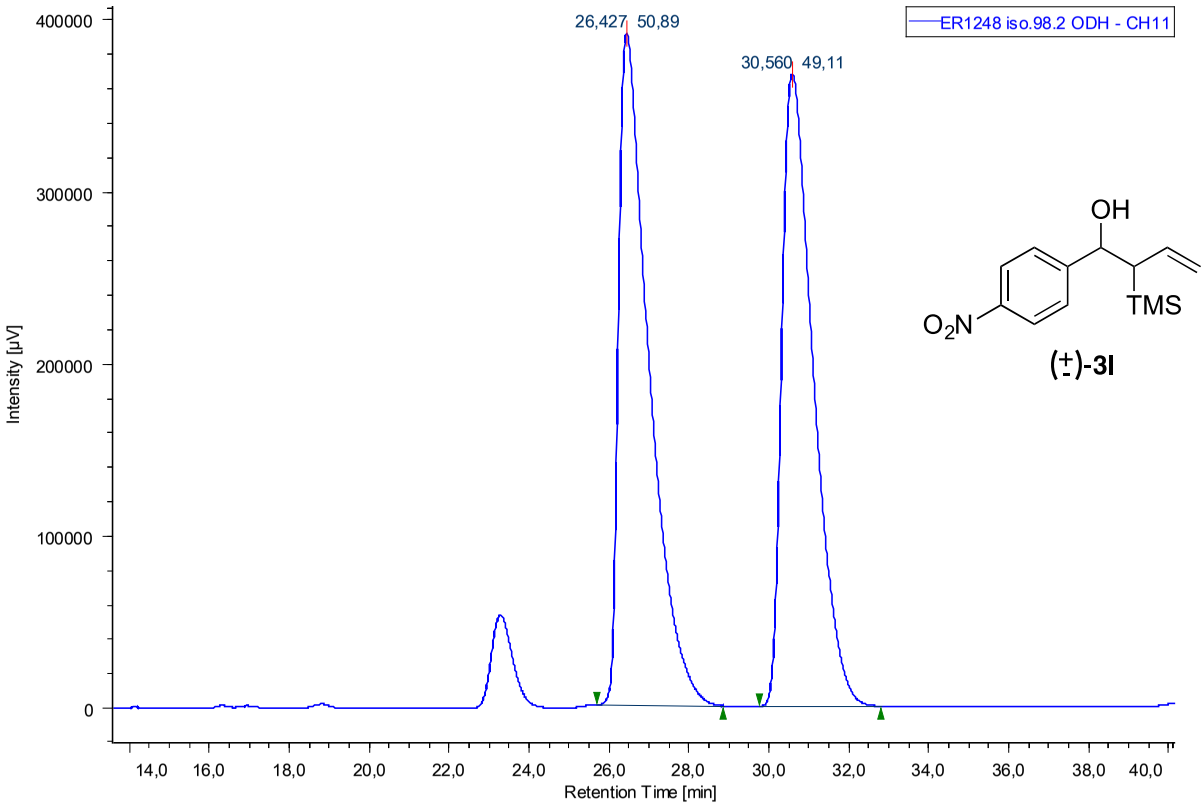

150.44
135.69
132.60
127.70
119.39
116.43
111.54
74.21
45.72
-2.13
OH
TMS
NC
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

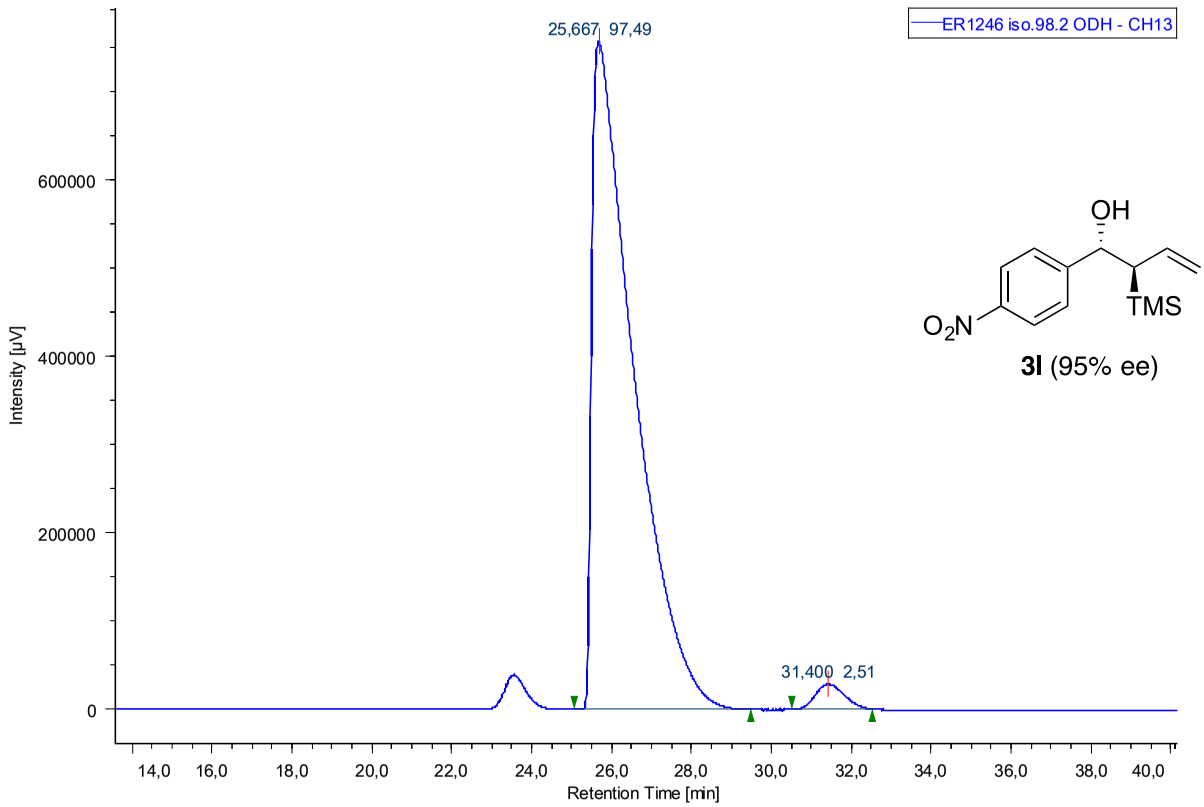

ER1249 iso.98.2 ODH - CH13
31,347 49,97
35,493 50,03
Intensity [µV]
80000
60000
40000
20000
0
20,0
22,0
24,0
26,0
28,0
30,0
32,0
34,0
36,0
38,0
40,0
42,0
Retention Time [min]
OH
TMS
NC
(±)-3k

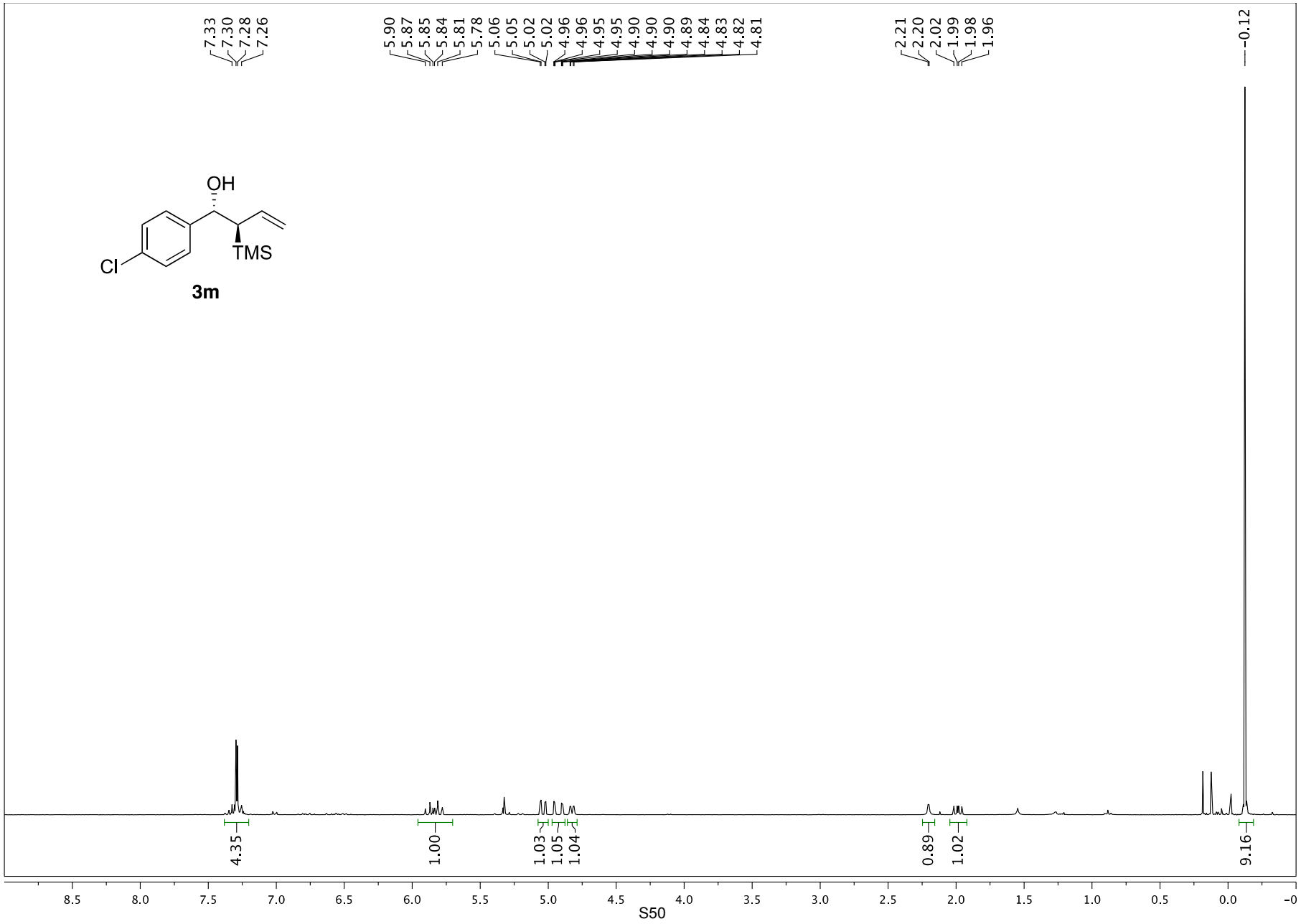

ER1255 iso.98.2 ODH - CH13
29,853 96,67
35,373 3,33
Intensity [µV]
400000
200000
0
20,0
22,0
24,0
26,0
28,0
30,0
32,0
34,0
36,0
38,0
40,0
42,0
Retention Time [min]
OH
TMS
NC
3k (93% ee)

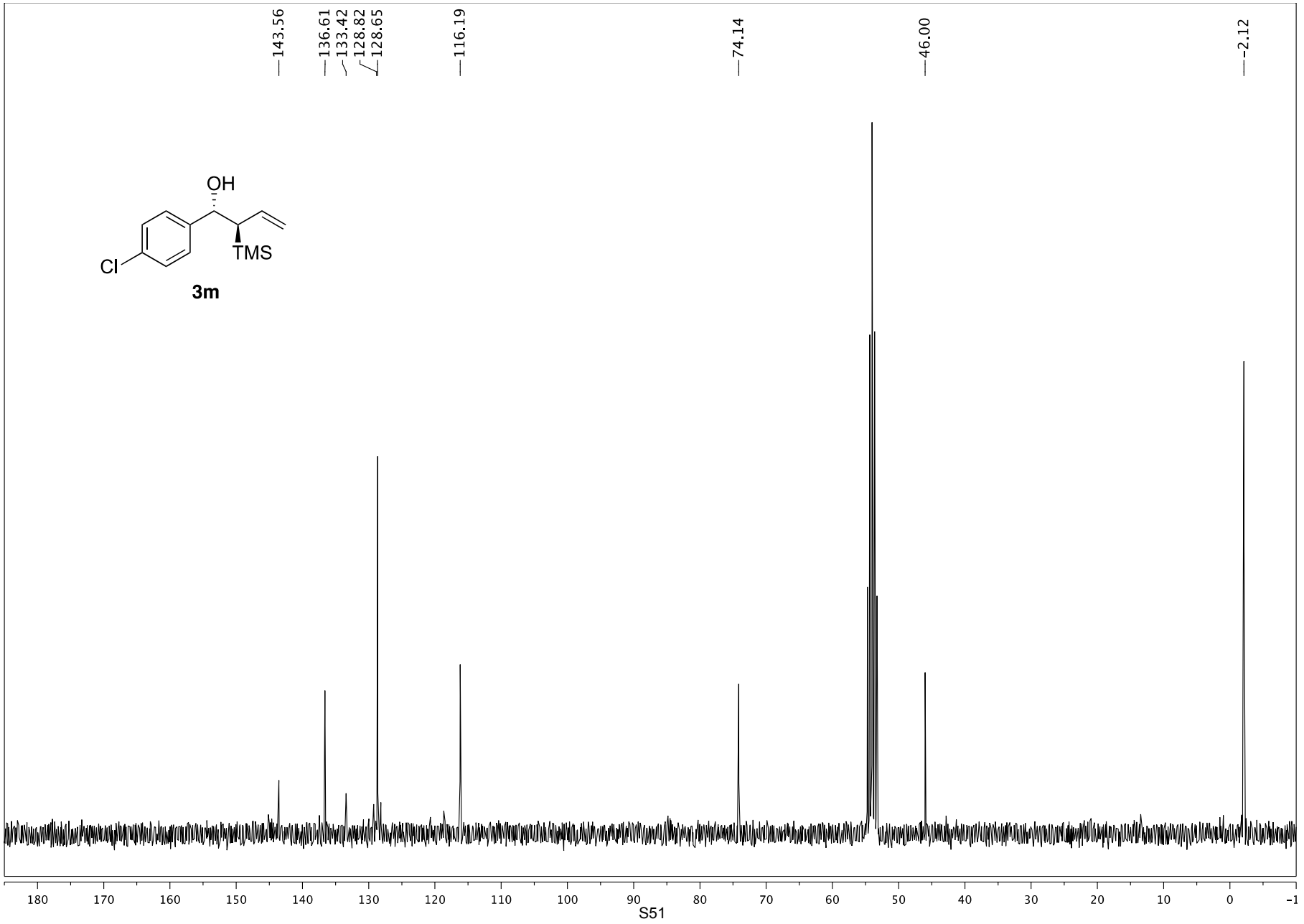

8.19
8.19
8.16
8.15
7.52
7.51
7.49
7.47
5.02
5.01
4.97
4.88
4.88
4.88
4.87
4.83
4.82
4.82
4.82
2.27
2.00
1.98
1.97
1.95
-0.05
OH
TMS
O2N
3l
2.05
2.08
1.03
2.00
1.09
0.80
1.02
8.82
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

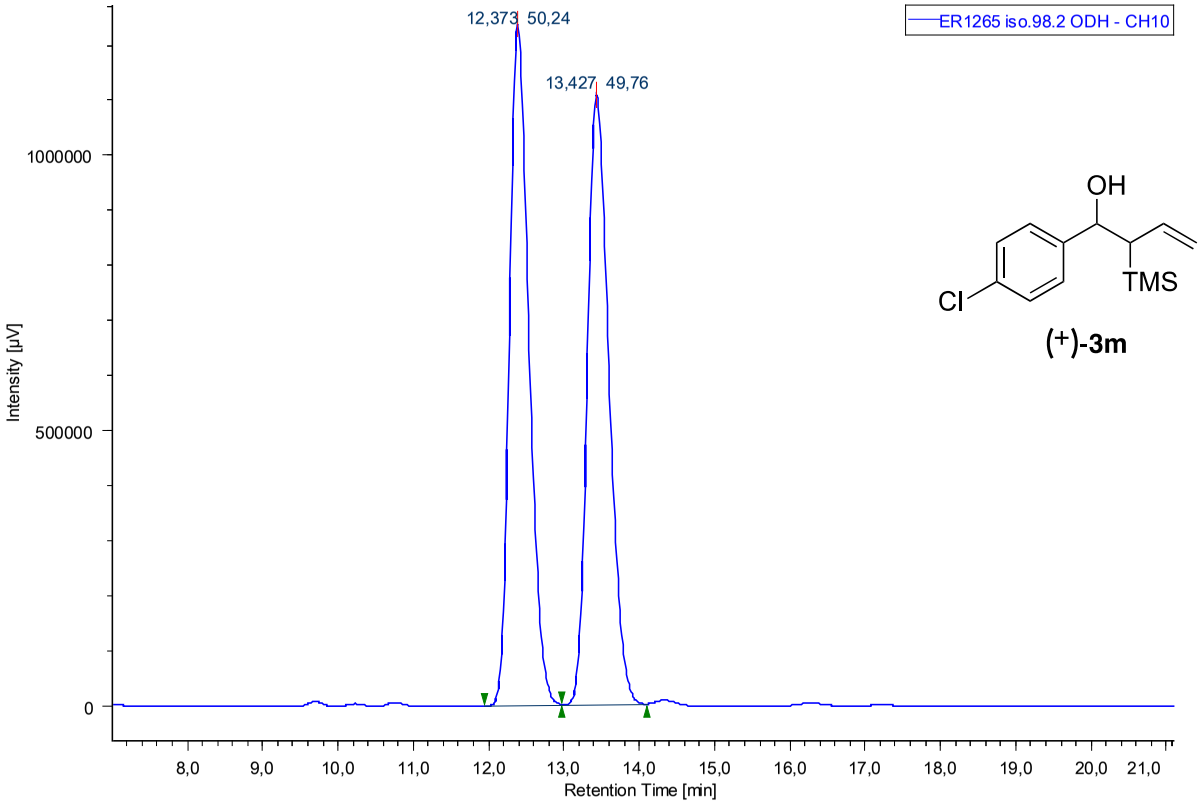

152.63
147.68
135.46
127.75
123.91
116.54
74.04
45.77
-2.10
OH
TMS
O2N
3l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

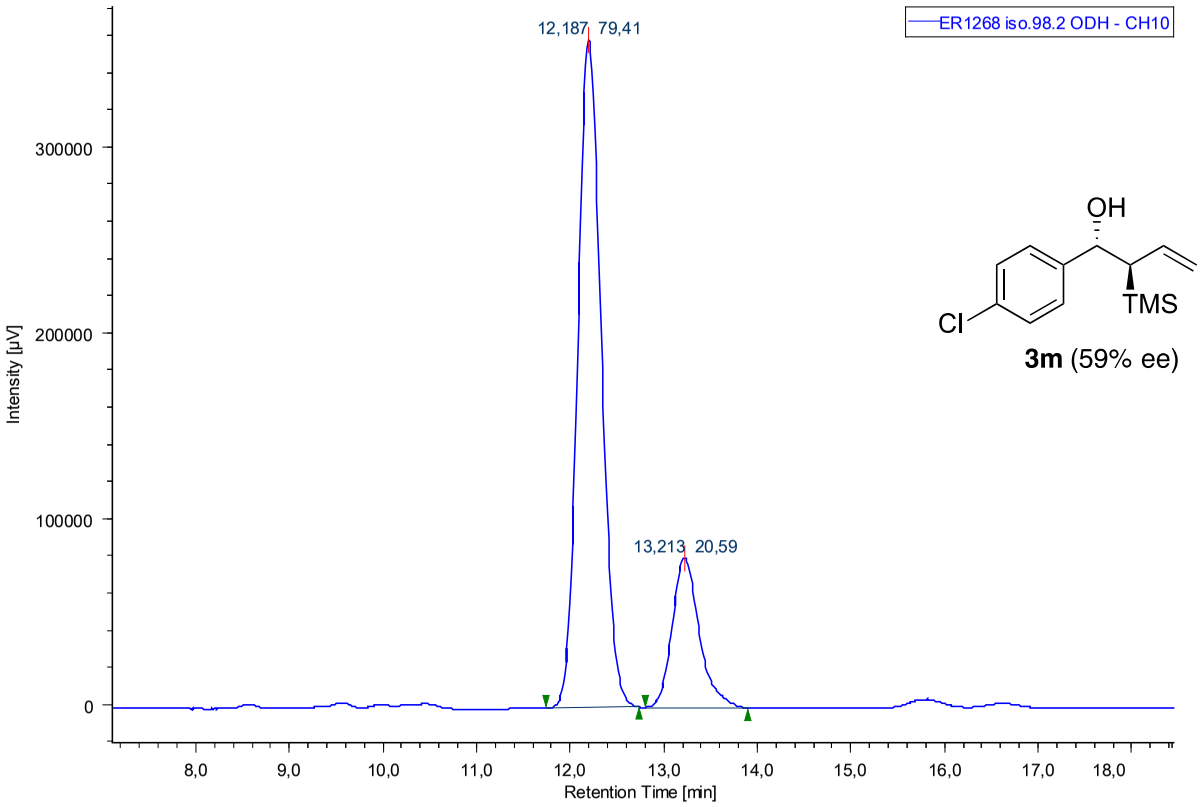

ER1248 iso.98.2 ODH - CH11
26,427 50,89
30,560 49,11
Intensity [µV]
Retention Time [min]
OH
TMS
O2N
(±)-3l

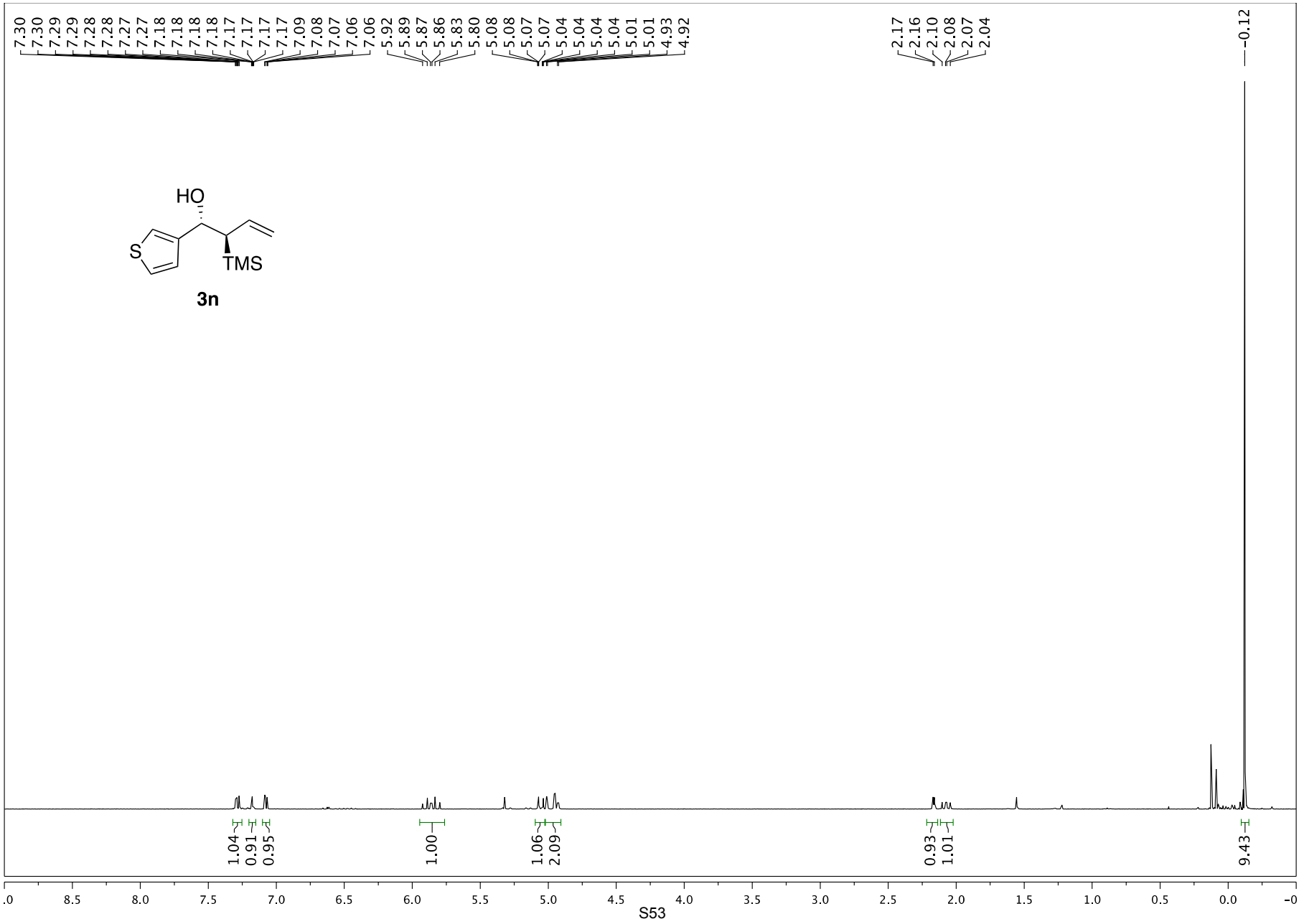

ER1246 iso.98.2 ODH - CH13
25,667 97,49
31,400 2,51
Intensity [µV]
Retention Time [min]
OH
TMS
O2N
3l (95% ee)


7.33
7.30
7.28
7.26
5.90
5.87
5.85
5.84
5.81
5.78
5.06
5.05
5.02
5.02
4.96
4.96
4.95
4.95
4.90
4.90
4.90
4.89
4.84
4.83
4.82
4.81
2.21
2.20
2.02
1.99
1.98
1.96
-0.12
OH
TMS
Cl
3m
4.35
1.00
1.03
1.05
1.04
0.89
1.02
9.16
8.5
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
-0

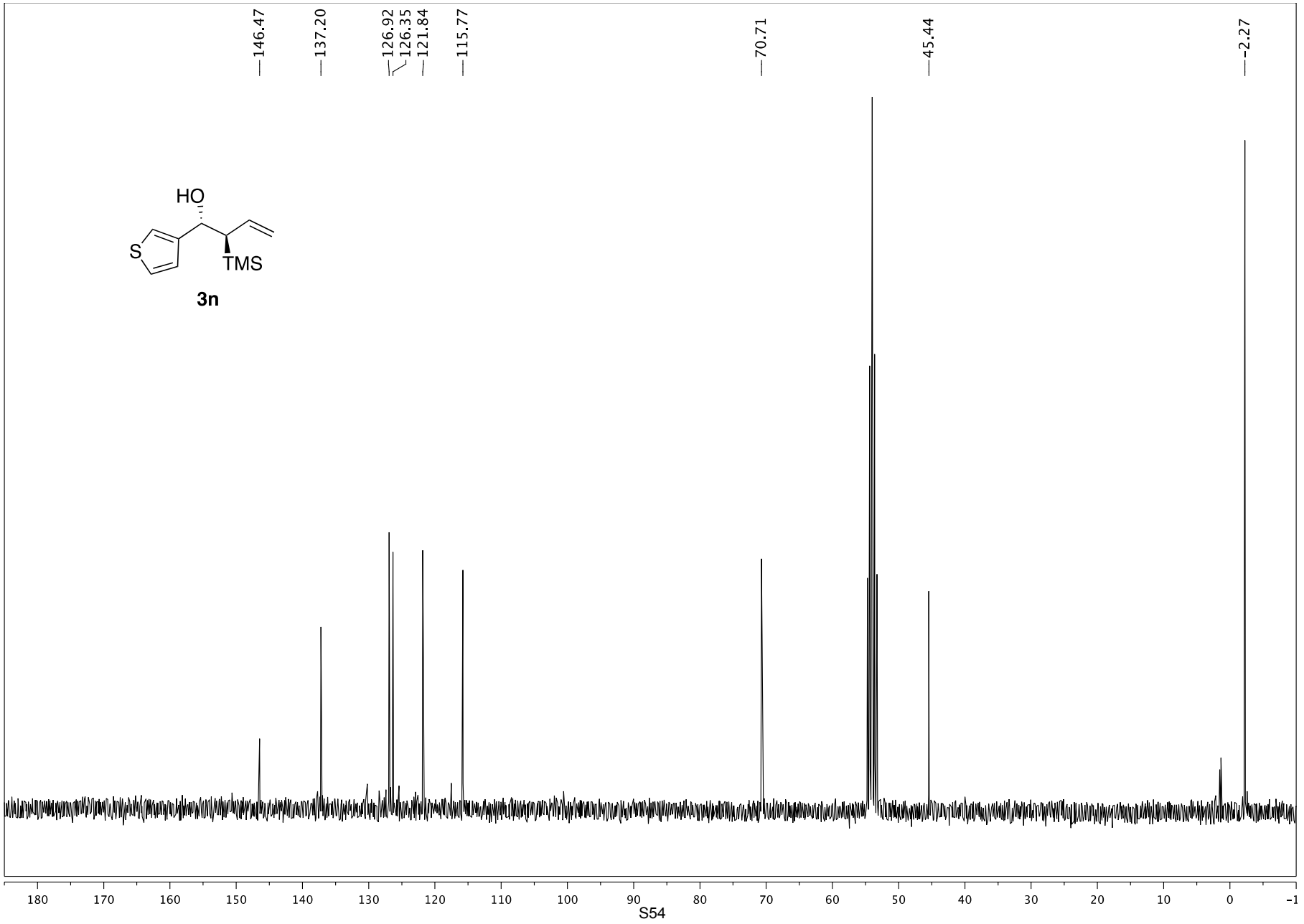

143.56
136.61
133.42
128.82
128.65
116.19
74.14
46.00
2.12
OH
TMS
Cl
3m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

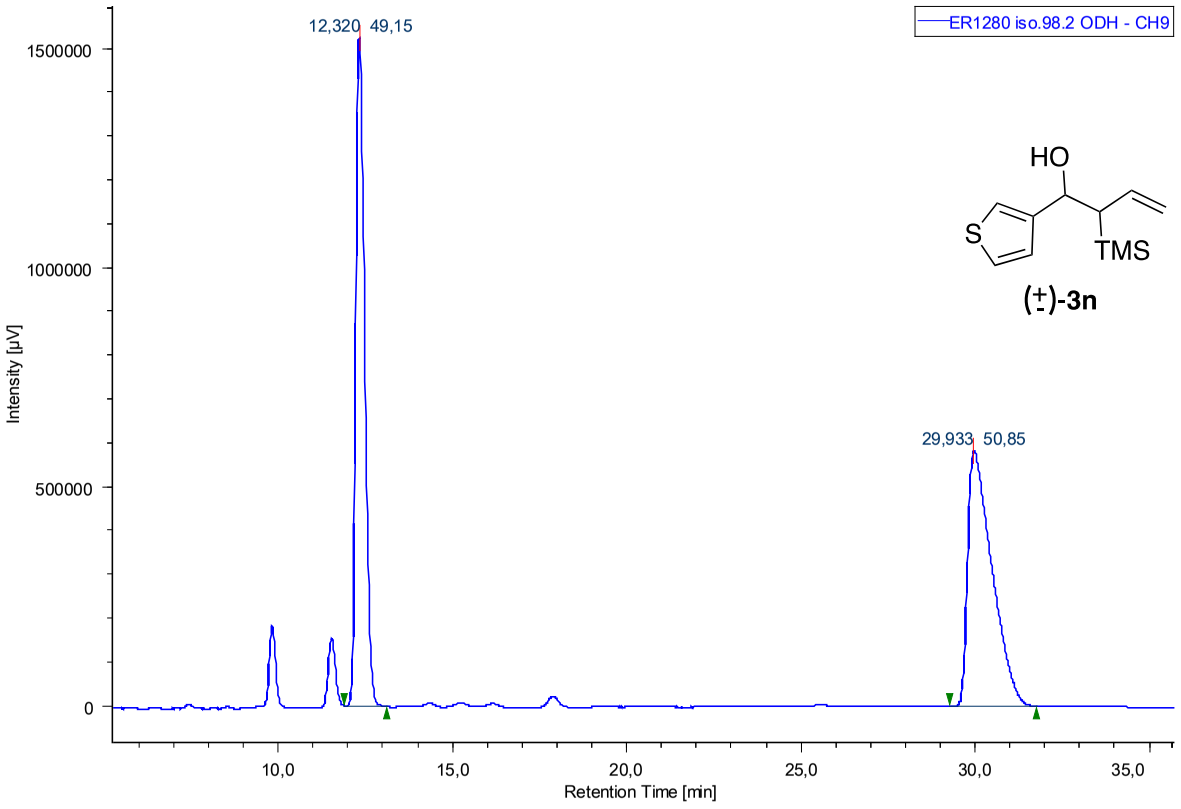

ER1265 iso.98.2 ODH - CH10
12,373 50,24
13,427 49,76
1000000
500000
0
Intensity [µV]
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
19,0
20,0
21,0
Retention Time [min]
OH
TMS
Cl
(+)-3m

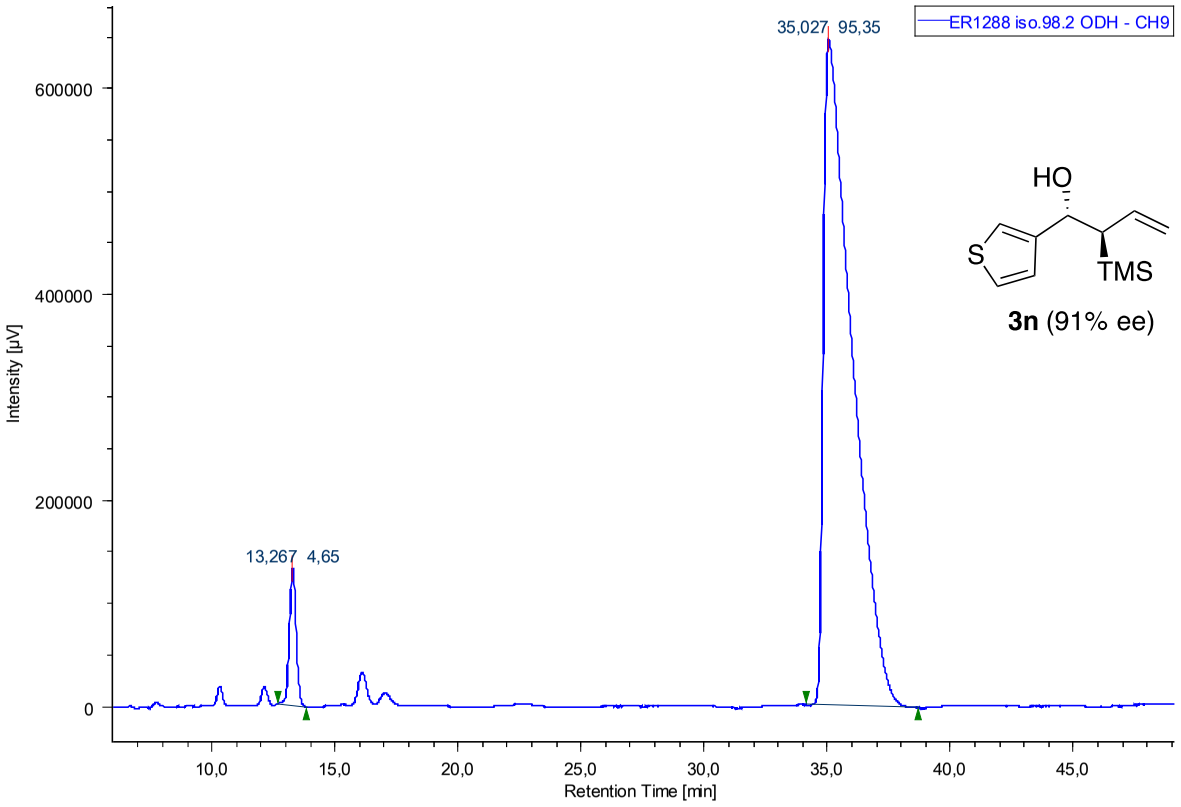

ER1268 iso.98.2 ODH - CH10
12,187 79,41
13,213 20,59
300000
200000
100000
0
Intensity [µV]
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
Retention Time [min]
OH
TMS
Cl
3m (59% ee)

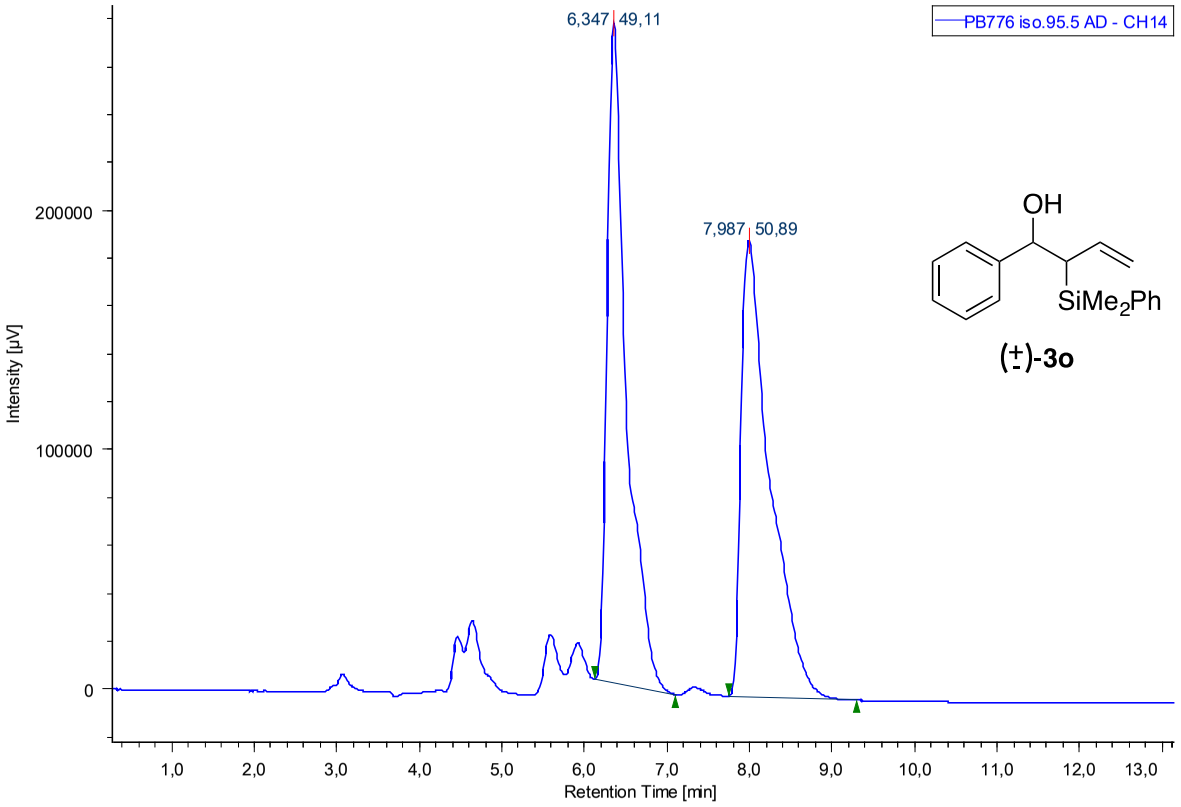

7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.18
7.18
7.18
7.18
7.17
7.17
7.17
7.17
7.09
7.08
7.07
7.06
7.06
5.92
5.89
5.87
5.86
5.83
5.80
5.08
5.08
5.07
5.07
5.04
5.04
5.04
5.04
5.01
5.01
4.93
4.92
2.17
2.16
2.10
2.08
2.07
2.04
-0.12
HO
S
TMS
1.04
0.91
0.95
1.00
1.06
2.09
0.93
1.01
9.43
.0
8.5
8.0
7.5
7.0
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
-0

3n

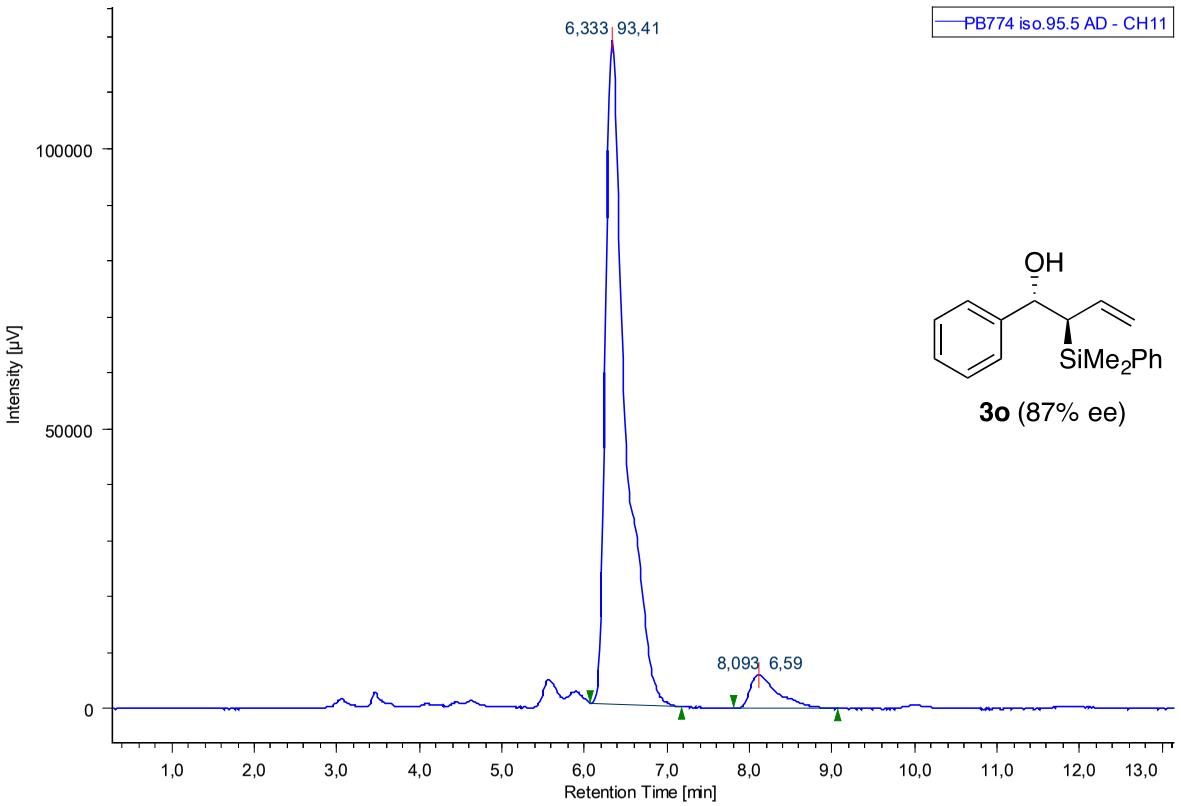

146.47
137.20
126.92
126.35
121.84
115.77
70.71
45.44
-2.27
HO
S
TMS
3n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


ER1280 iso.98.2 ODH - CH9
12,320 49,15
29,933 50,85
HO
S
TMS
(±)-3n
Intensity [µV]
Retention Time [min]

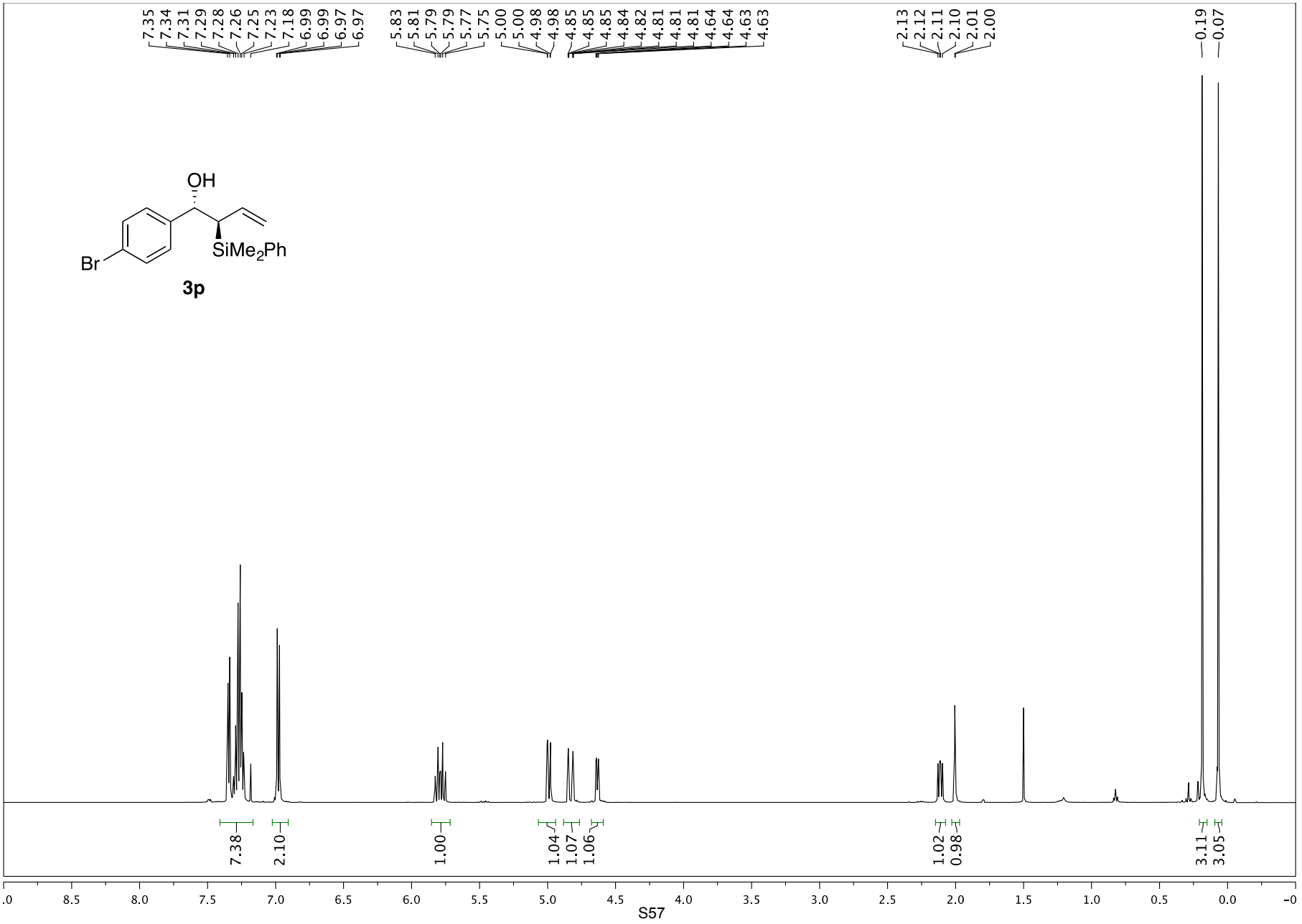

ER1288 iso.98.2 ODH - CH9
35,027 95,35
13,267 4,65
HO
S
TMS
3n (91% ee)
Intensity [µV]
Retention Time [min]

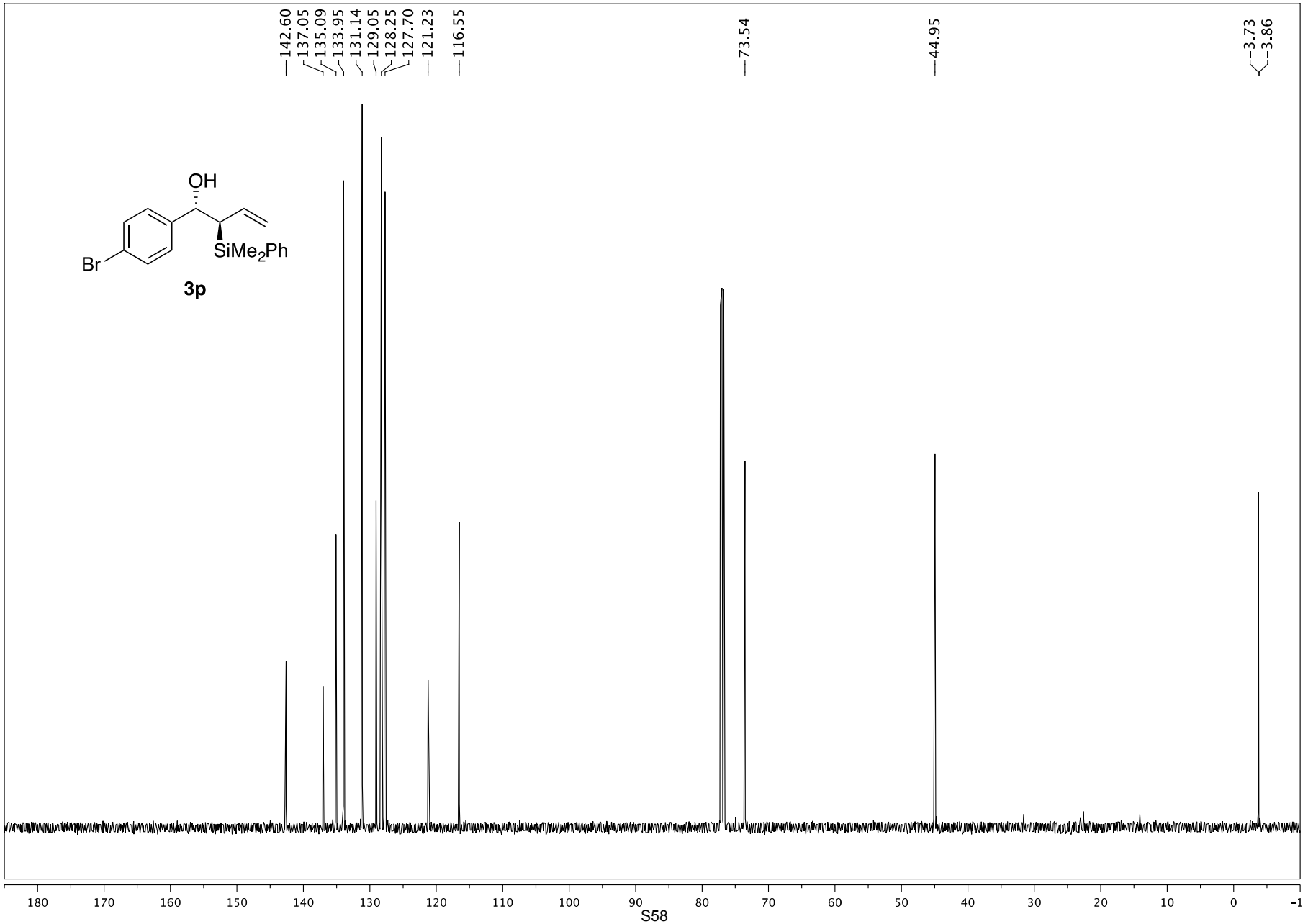

PB776 iso.95.5 AD - CH14
6,347 49,11
7,987 50,89
Intensity [µV]
200000
100000
0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
Retention Time [min]
OH
SiMe2Ph

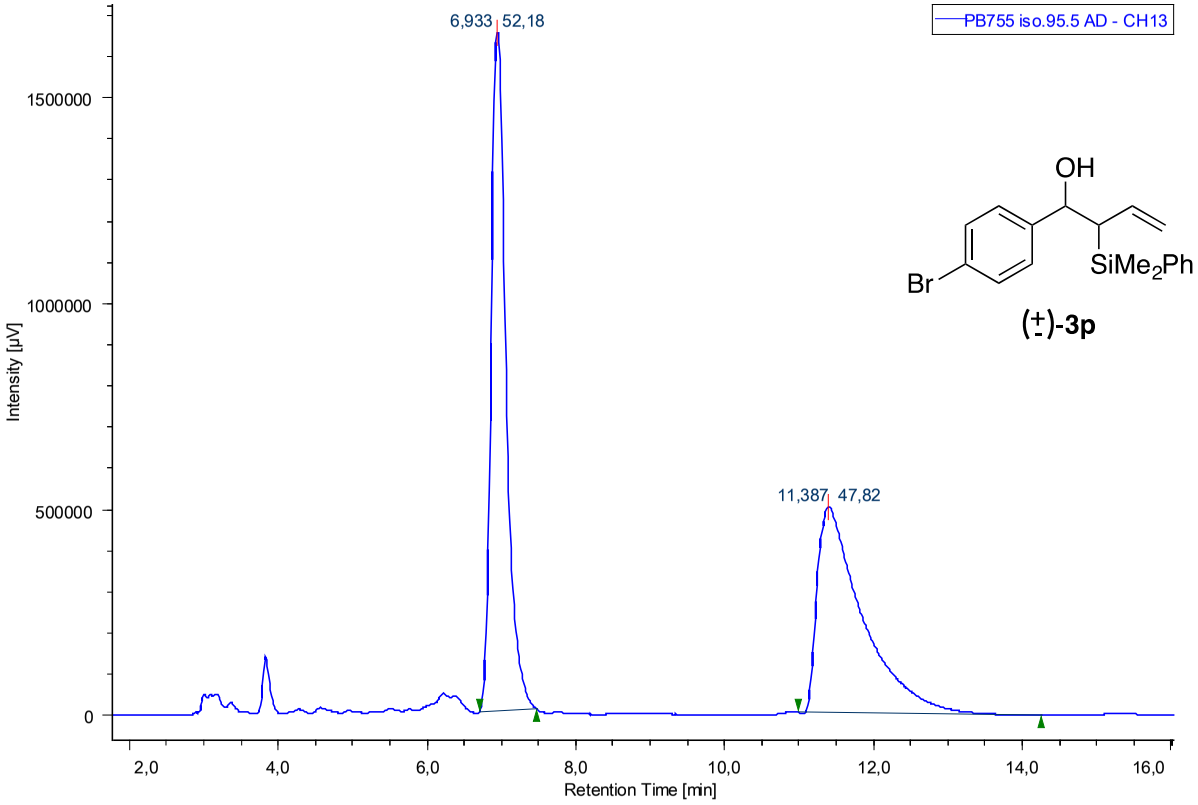
(±)-**3o**

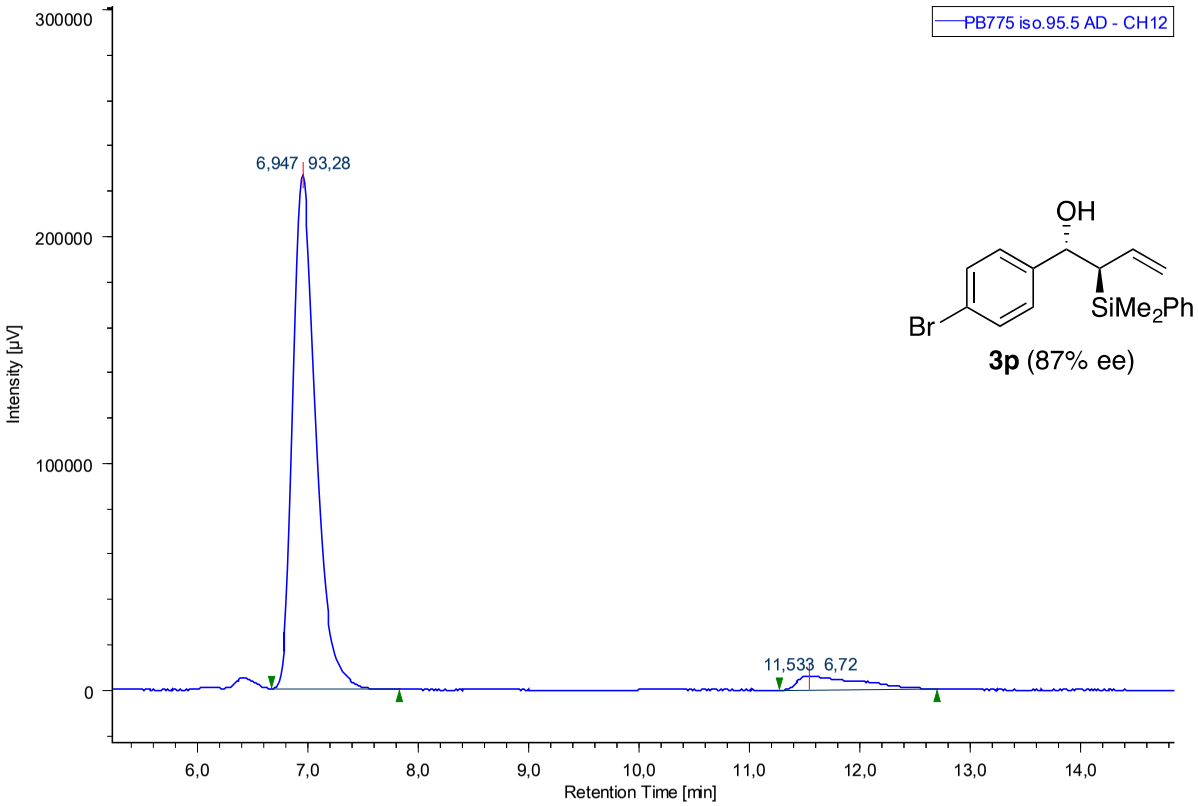

PB774 iso.95.5 AD - CH11
6,333 93,41
8,093 6,59
Intensity [µV]
100000
50000
0
1,0
2,0
3,0
4,0
5,0
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
Retention Time [min]
OH
SiMe2Ph

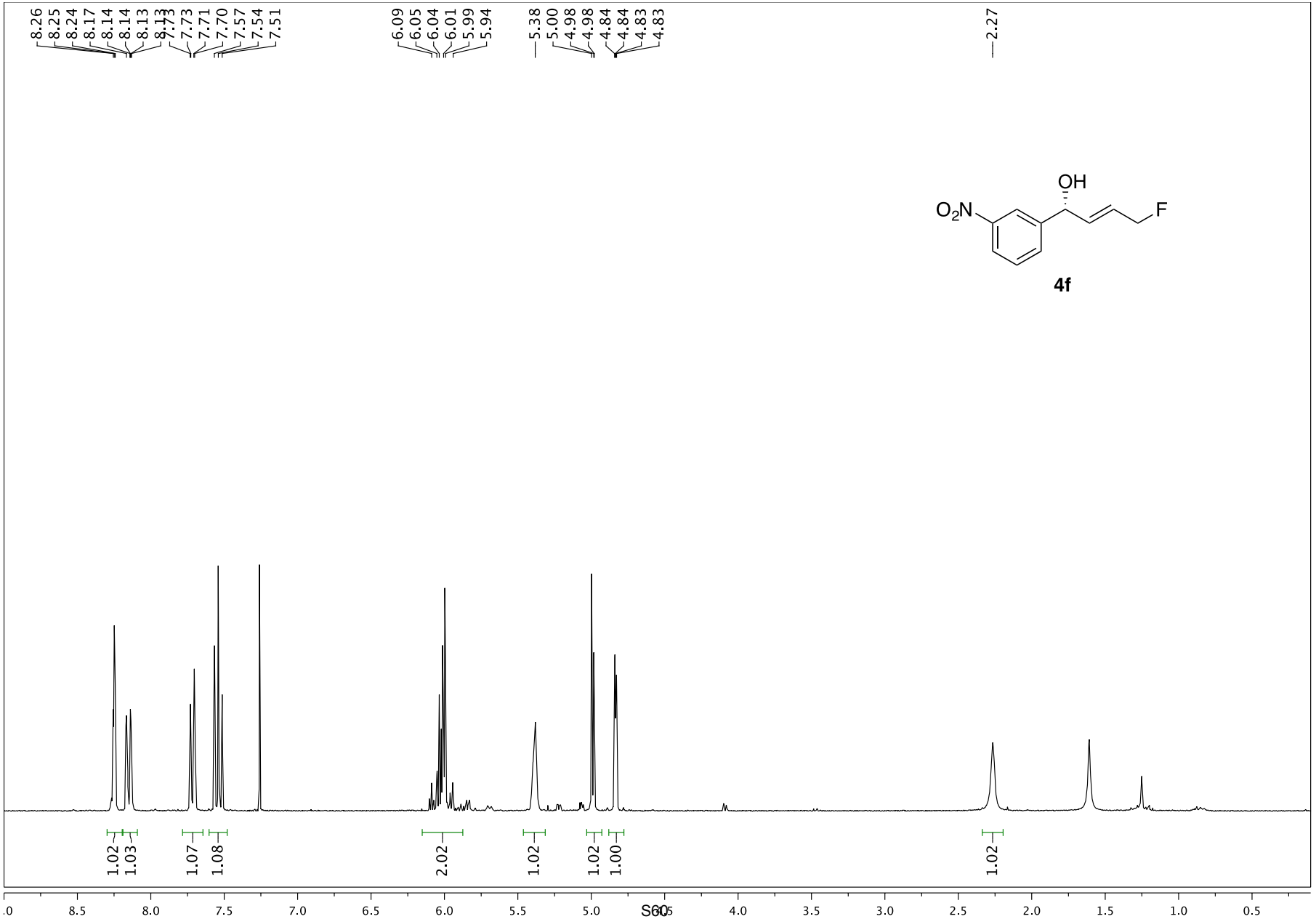
3o (87% ee)

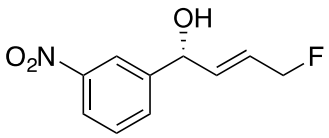

7.35
7.34
7.31
7.29
7.28
7.26
7.25
7.23
7.18
6.99
6.99
6.97
6.97
5.83
5.81
5.79
5.79
5.77
5.75
5.00
5.00
4.98
4.98
4.85
4.85
4.85
4.84
4.82
4.81
4.81
4.81
4.64
4.64
4.63
4.63
2.13
2.12
2.11
2.10
2.01
2.00
0.19
0.07
OH
SiMe2Ph
Br
3p
7.38
2.10
1.00
1.04
1.07
1.06
1.02
0.98
3.11
3.05
8.5
8.0
7.5
7.0
6.5
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


142.60
137.05
135.09
133.95
131.14
129.05
128.25
127.70
121.23
116.55
73.54
44.95
3.73
3.86
OH
Br
SiMe2Ph
3p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

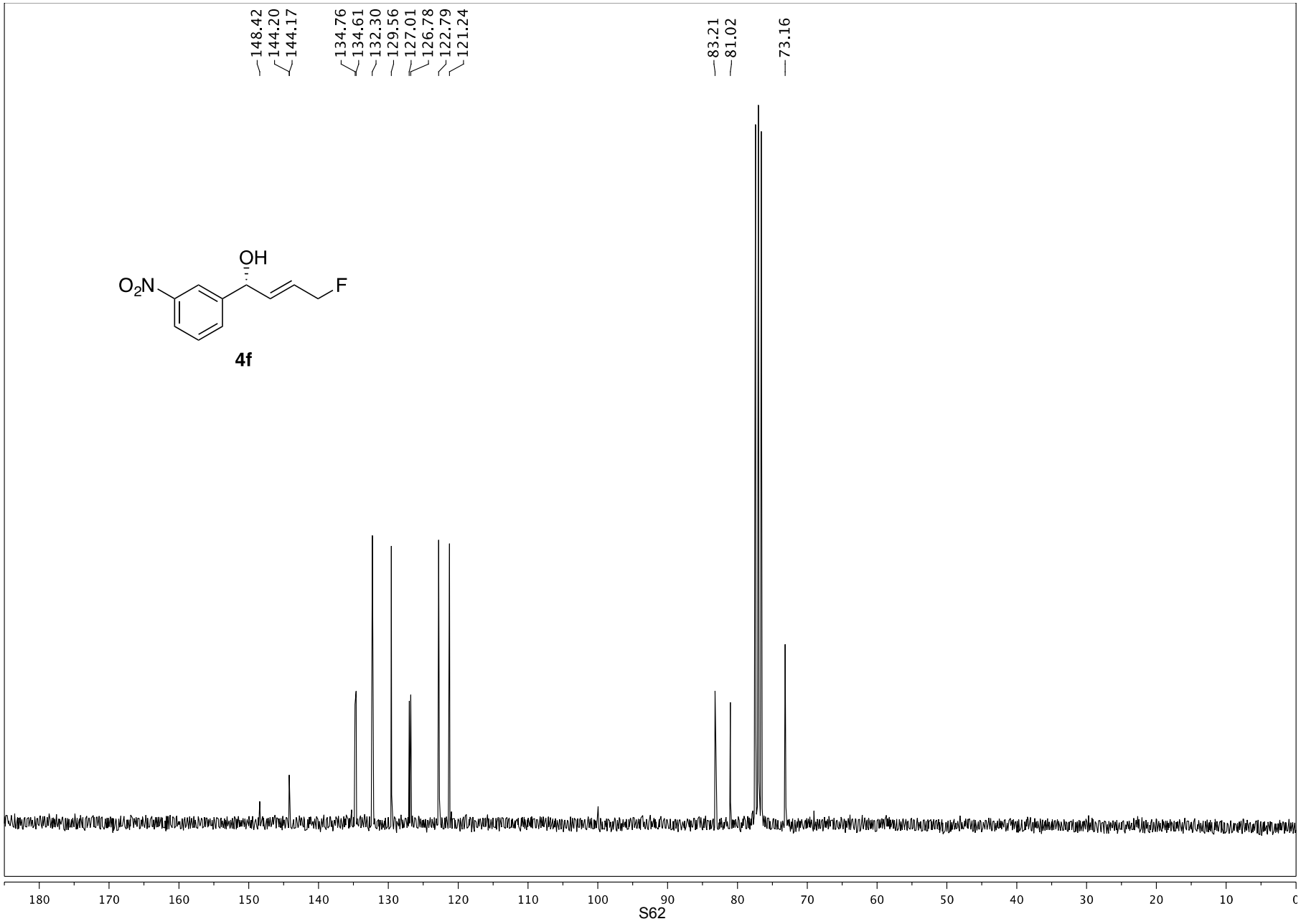

PB755 iso.95.5 AD - CH13
6,933 52,18
11,387 47,82
1500000
1000000
500000
0
Intensity [µV]
2,0
4,0
6,0
8,0
10,0
12,0
14,0
16,0
Retention Time [min]
OH
Br
SiMe2Ph
(±)-3p

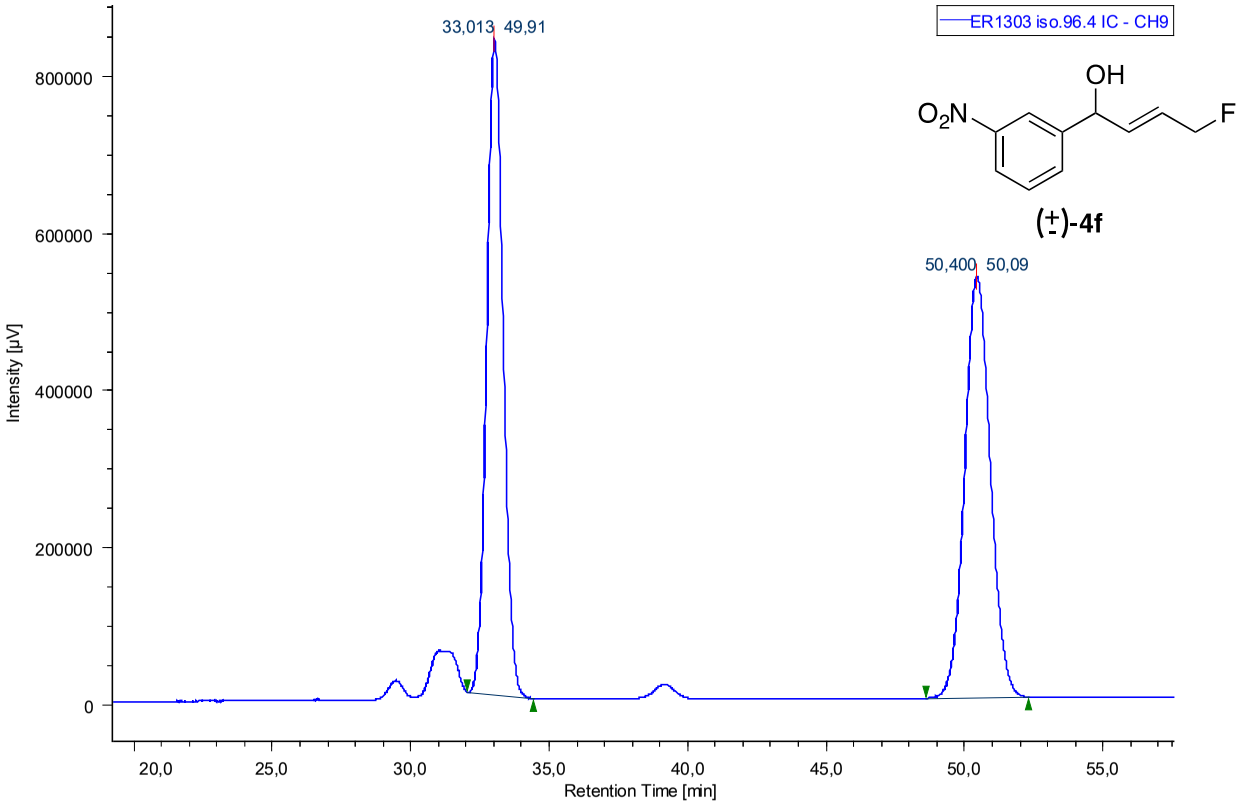

PB775 iso.95.5 AD - CH12
6,947 93,28
11,533 6,72
300000
200000
100000
0
Intensity [µV]
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
Retention Time [min]
OH
Br
SiMe2Ph
3p (87% ee)

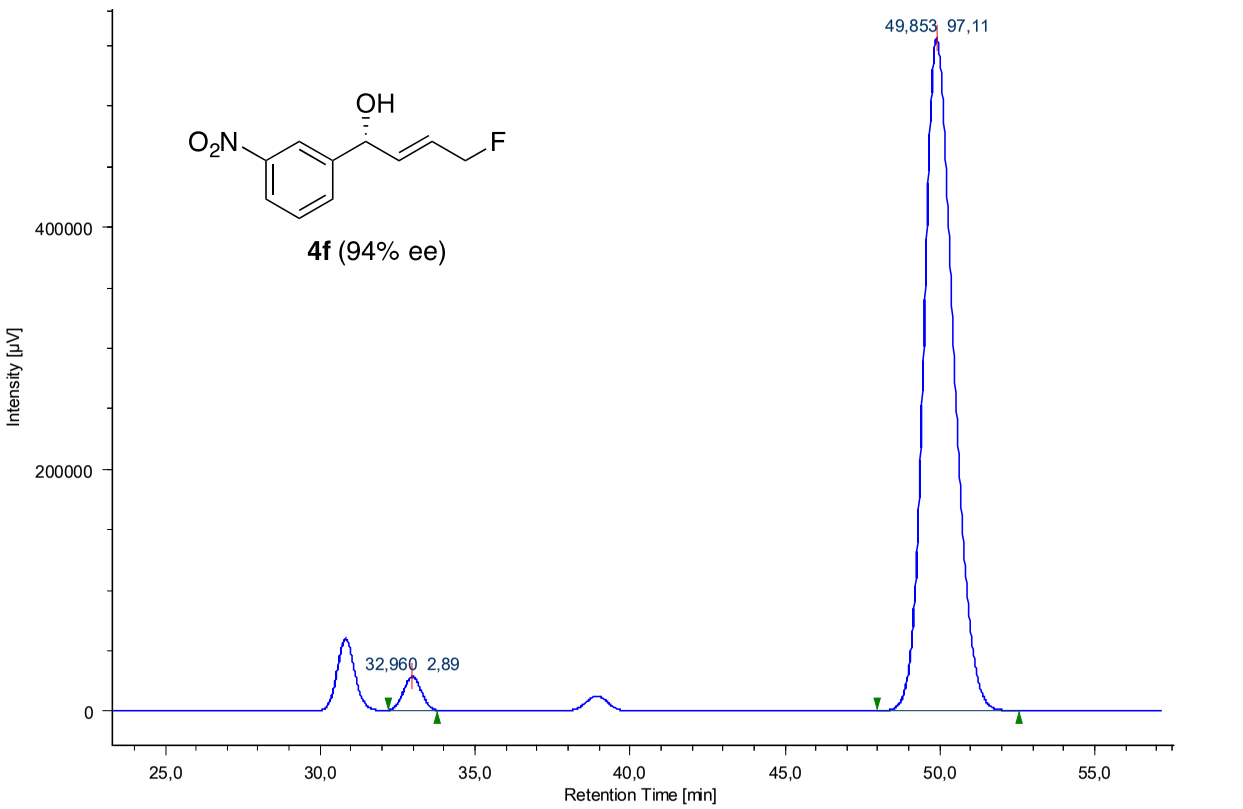

8.26
8.25
8.24
8.17
8.14
8.14
8.13
7.73
7.73
7.71
7.70
7.57
7.54
7.51
6.09
6.05
6.04
6.01
5.99
5.94
5.38
5.00
4.98
4.98
4.84
4.84
4.83
4.83
2.27
OH
O2N
F
4f
1.02
1.03
1.07
1.08
2.02
1.02
1.02
1.00
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

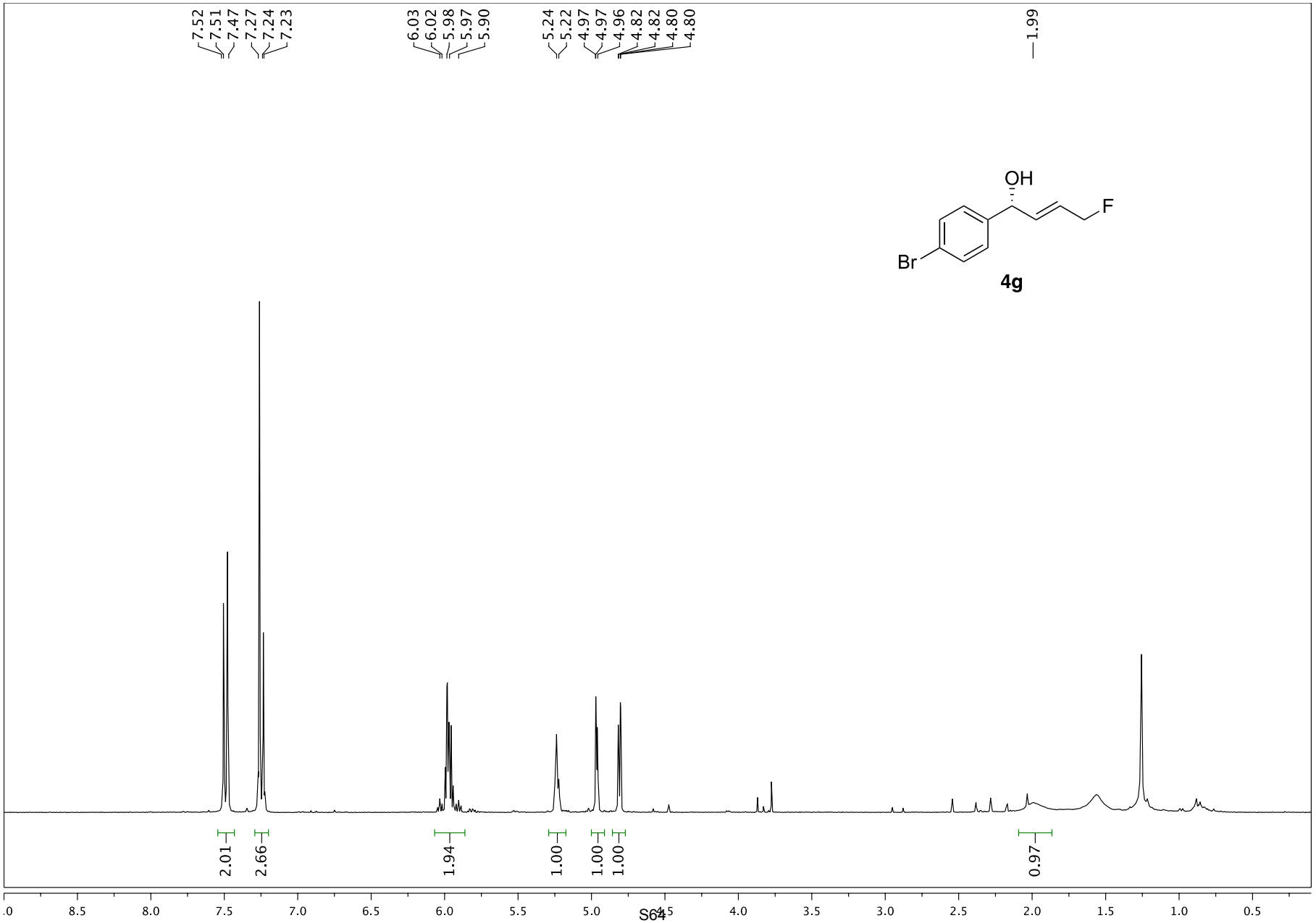


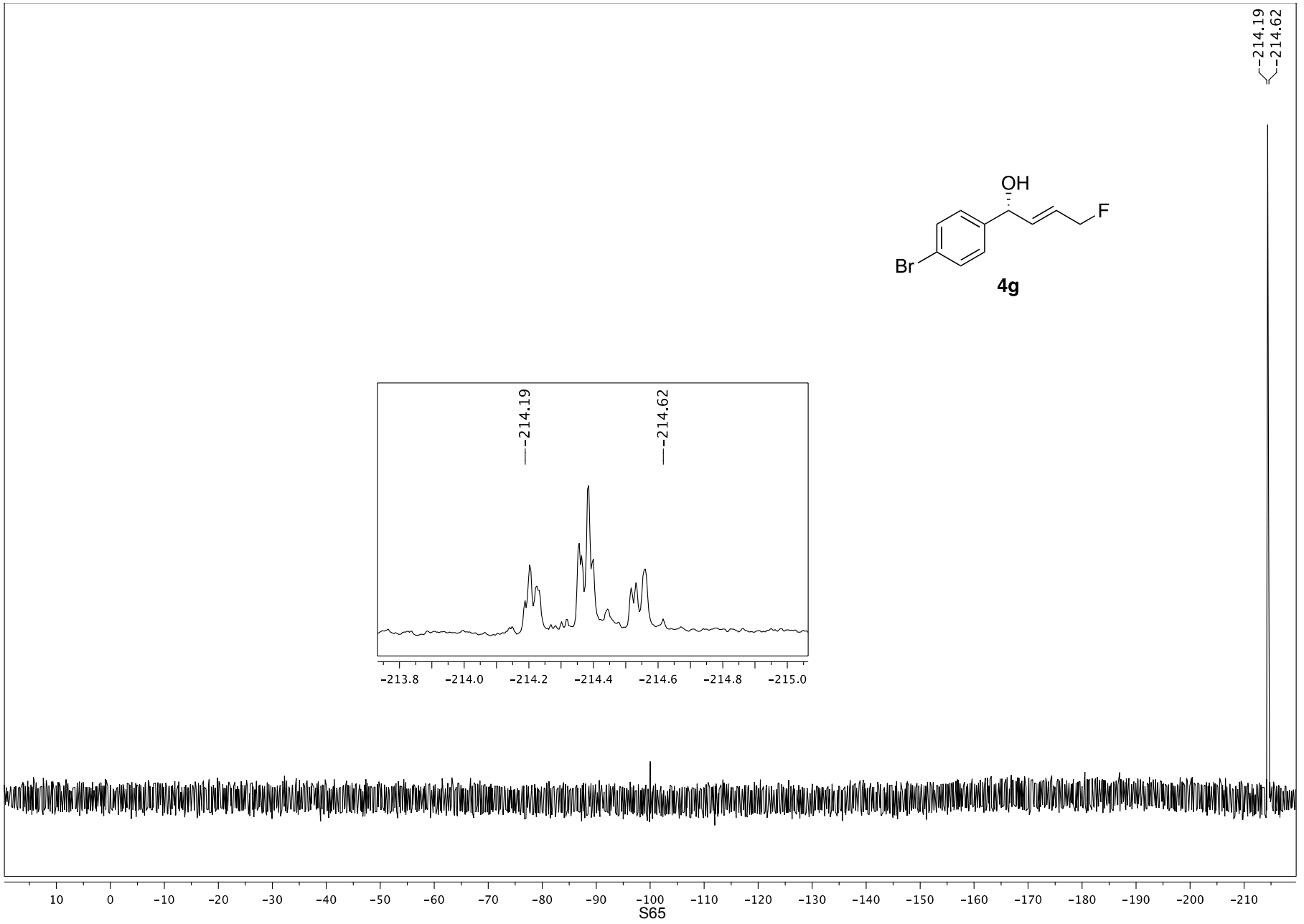
4f

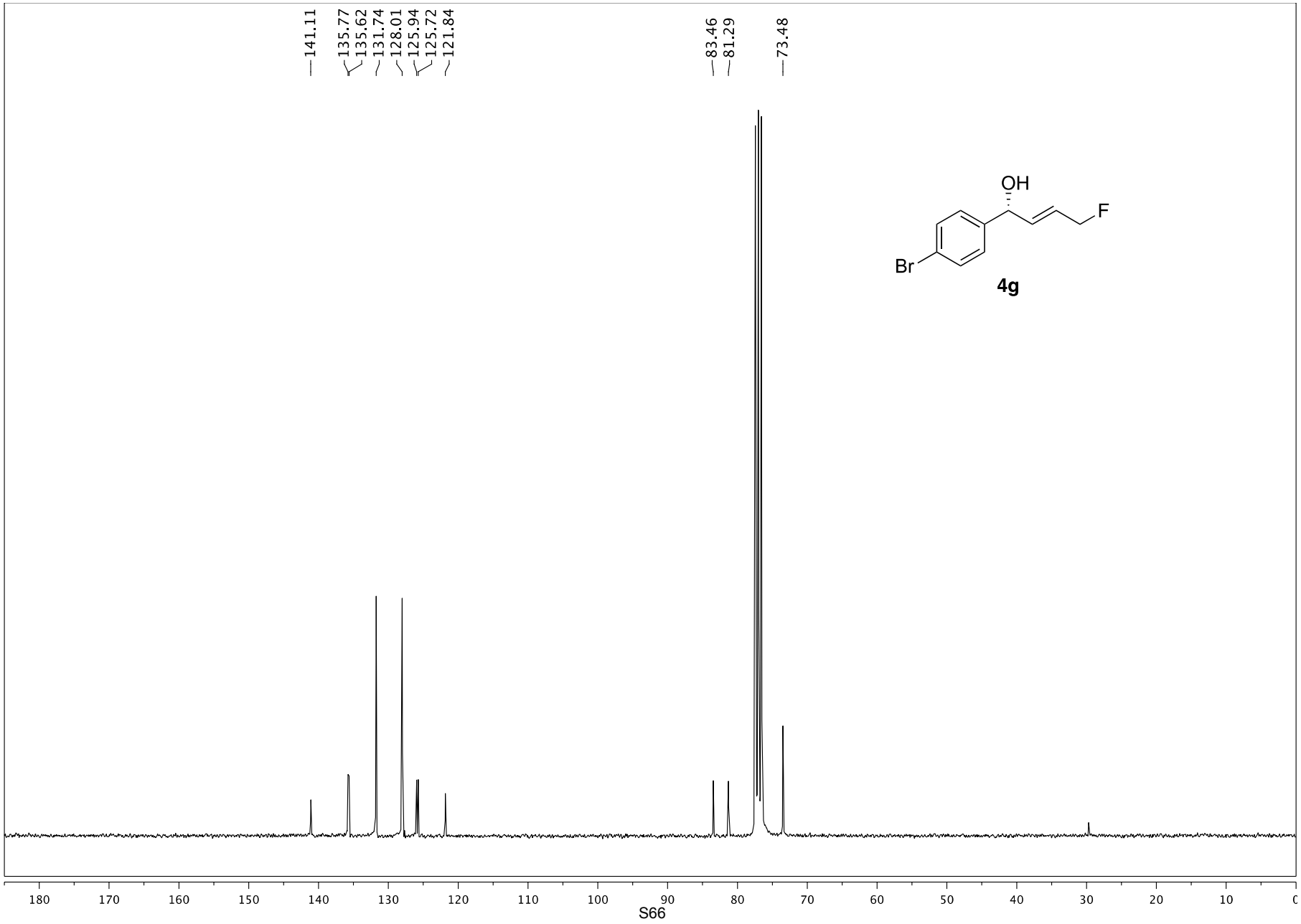

148.42
144.20
144.17
134.76
134.61
132.30
129.56
127.01
126.78
122.79
121.24
83.21
81.02
73.16
OH
O2N
F
4f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

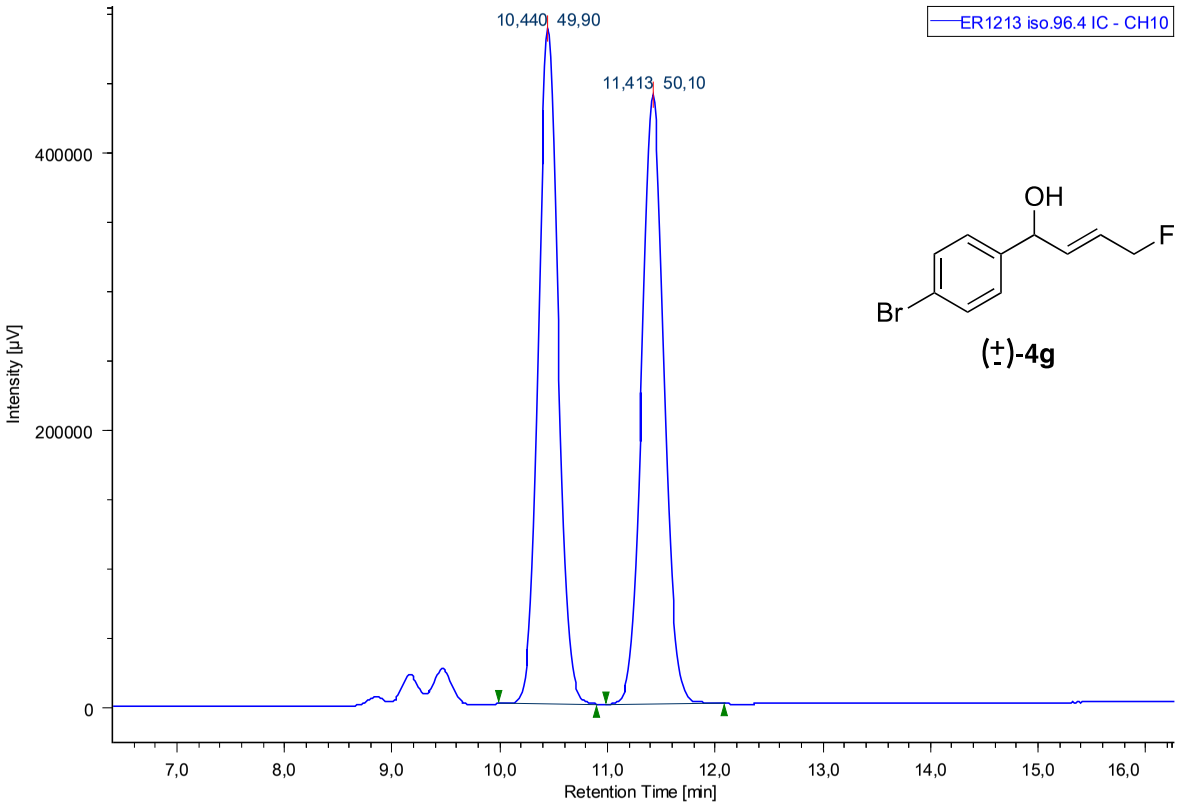

ER1303 iso.96.4 IC - CH9
33,013 49,91
50,400 50,09
OH
O2N
F
(±)-4f
Intensity [µV]
800000
600000
400000
200000
0
20,0
25,0
30,0
35,0
40,0
45,0
50,0
55,0
Retention Time [min]

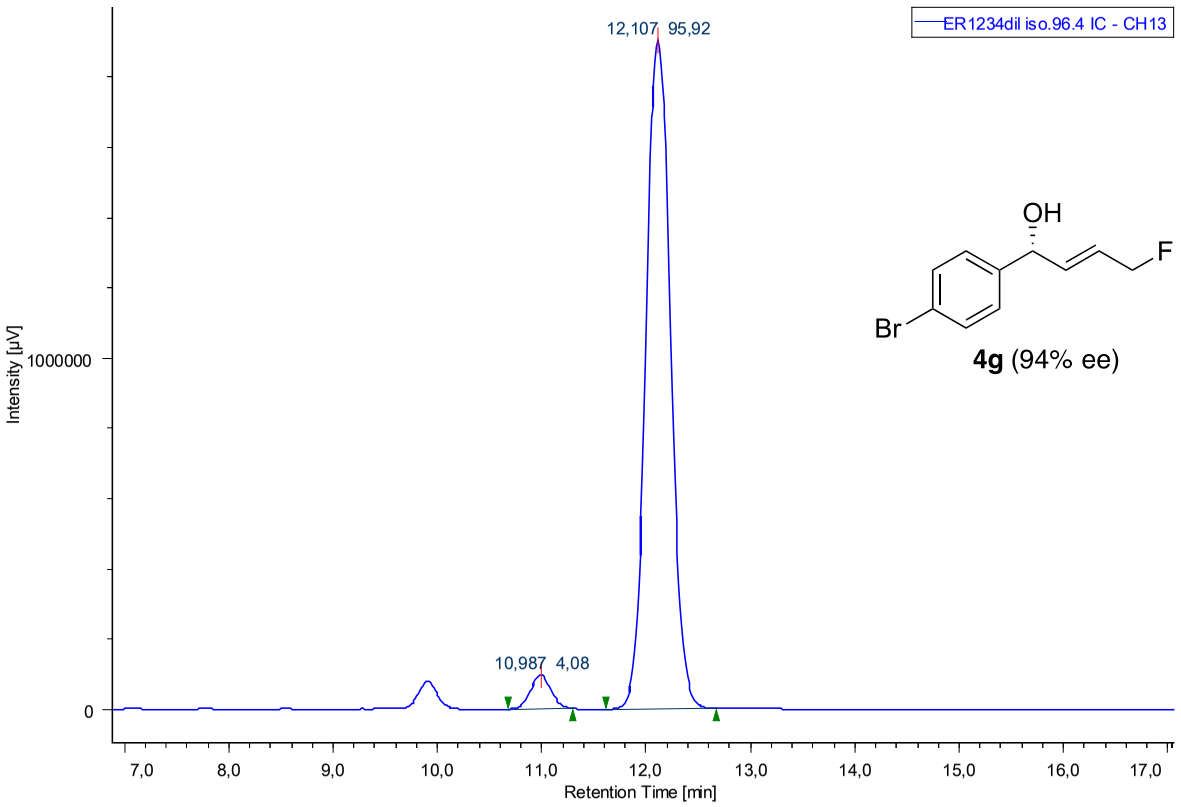

49,853 97,11
OH
O2N
F
4f (94% ee)
32,960 2,89
Intensity [µV]
400000
200000
0
25,0
30,0
35,0
40,0
45,0
50,0
55,0
Retention Time [min]

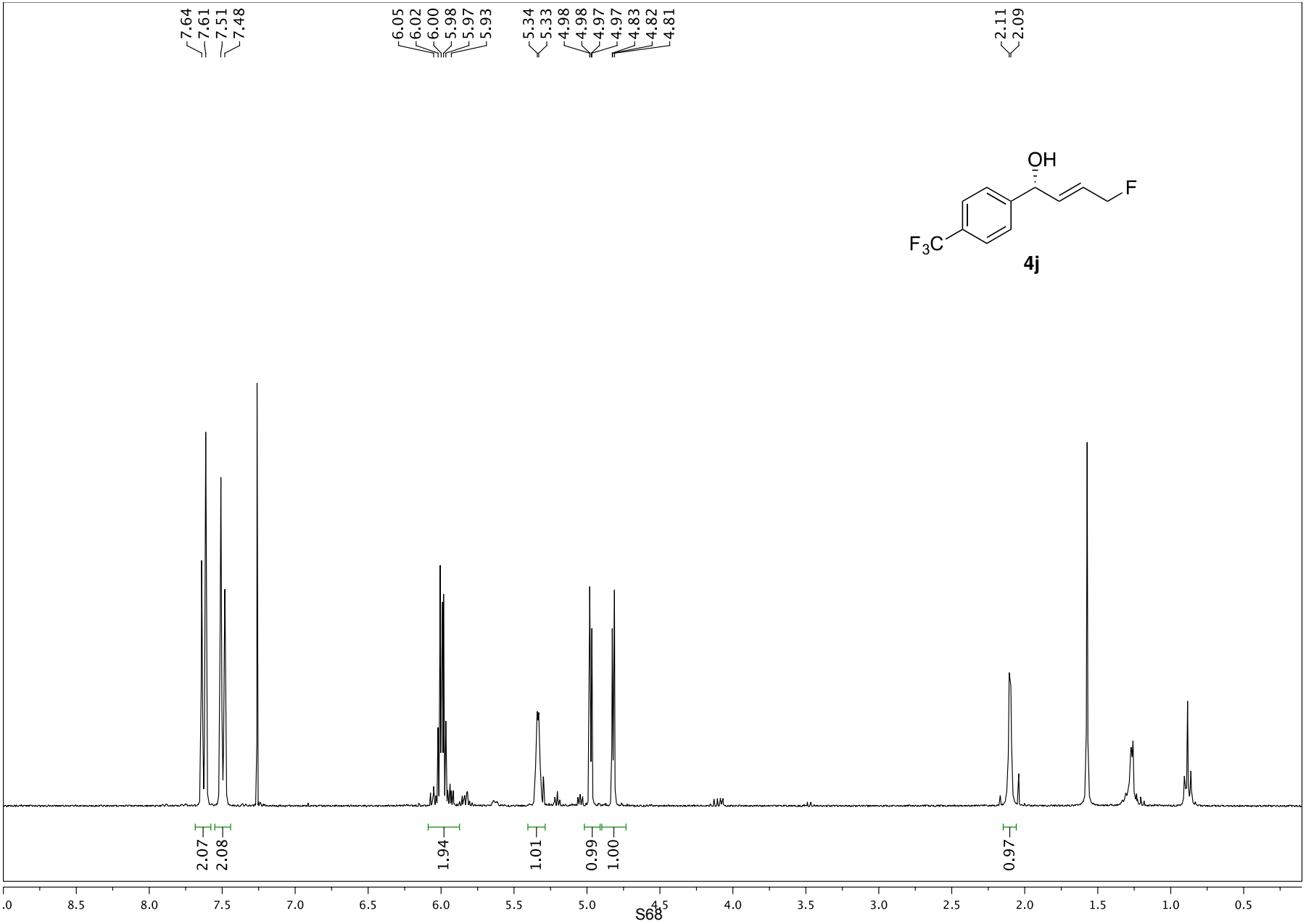

7.52
7.51
7.47
7.27
7.24
7.23
6.03
6.02
5.98
5.97
5.90
5.24
5.22
4.97
4.97
4.96
4.82
4.82
4.80
4.80
1.99
OH
F
Br
4g
2.01
2.66
1.94
1.00
1.00
1.00
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

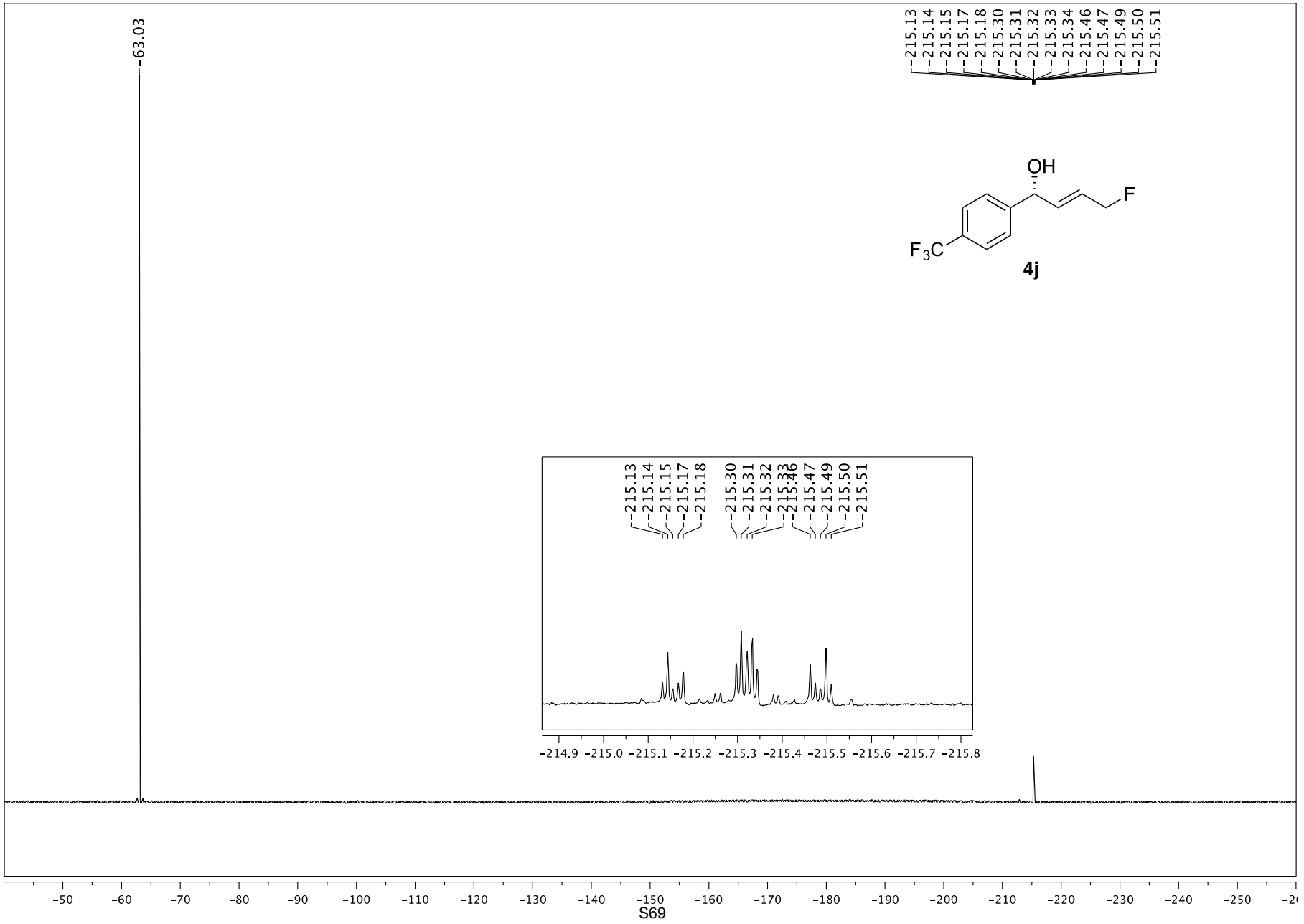

-214.19
-214.62
OH
F
Br
4g
-214.19
-214.62
-213.8
-214.0
-214.2
-214.4
-214.6
-214.8
-215.0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

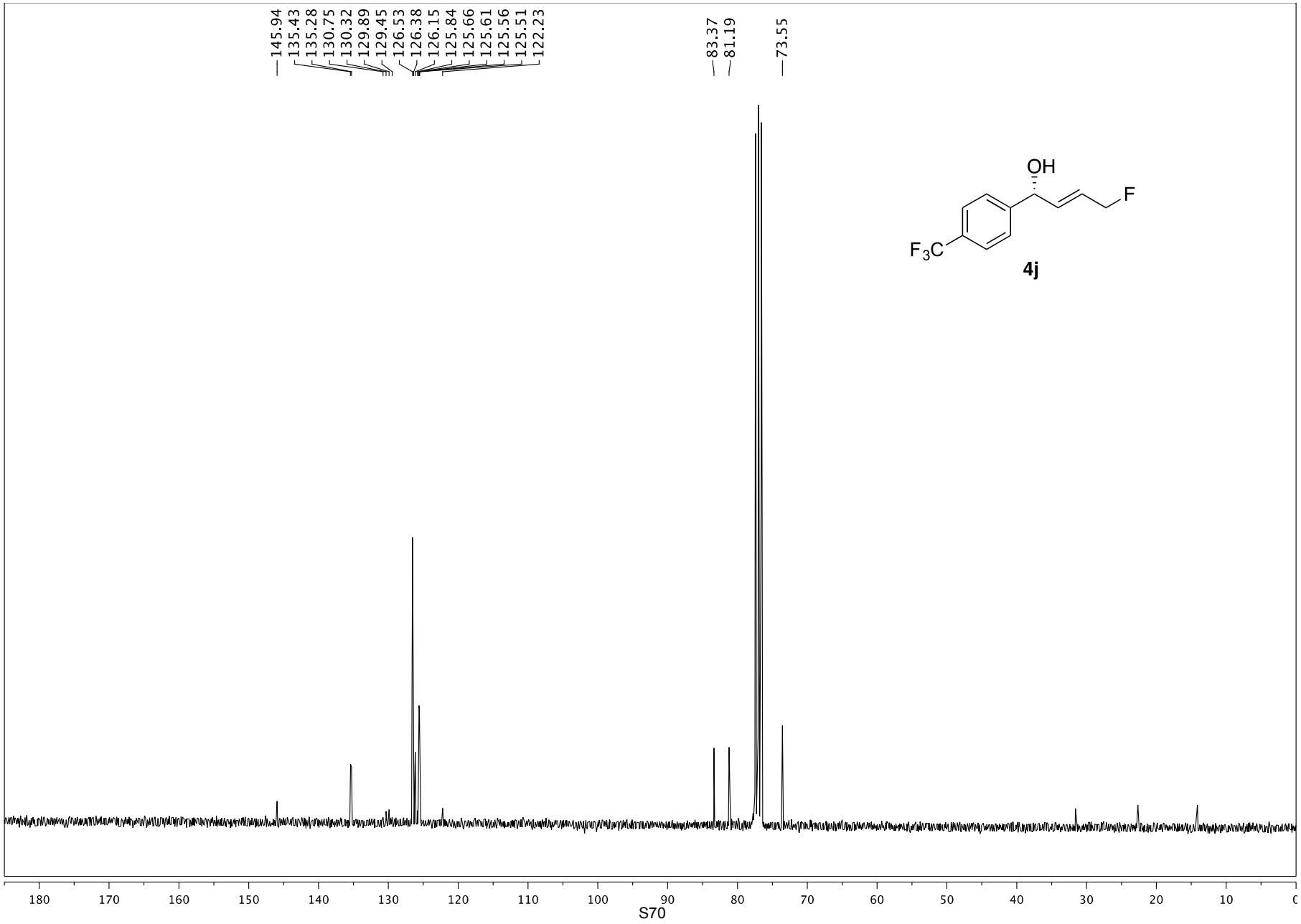

141.11
135.77
135.62
131.74
128.01
125.94
125.72
121.84
83.46
81.29
73.48
OH
F
Br
4g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

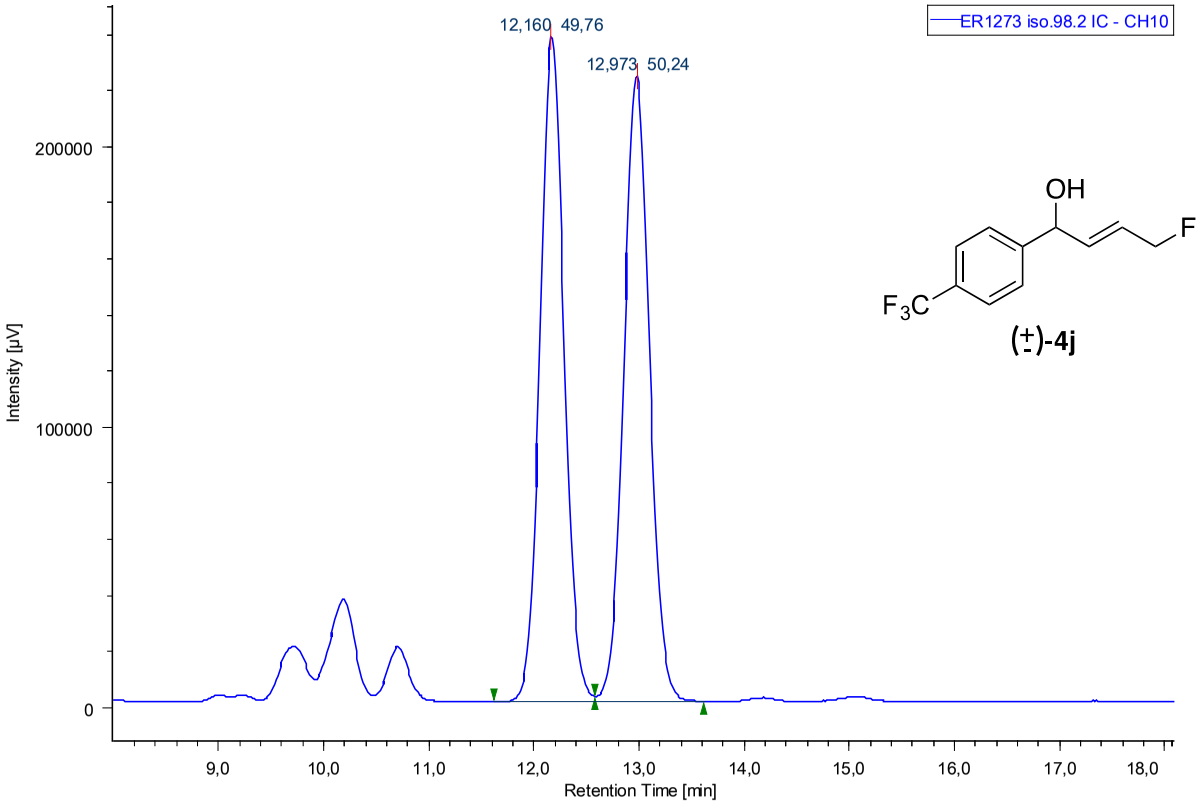

ER1213 iso.96.4 IC - CH10
10,440 49,90
11,413 50,10
400000
200000
0
Intensity [µV]
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
Retention Time [min]
OH
F
Br
(±)-4g

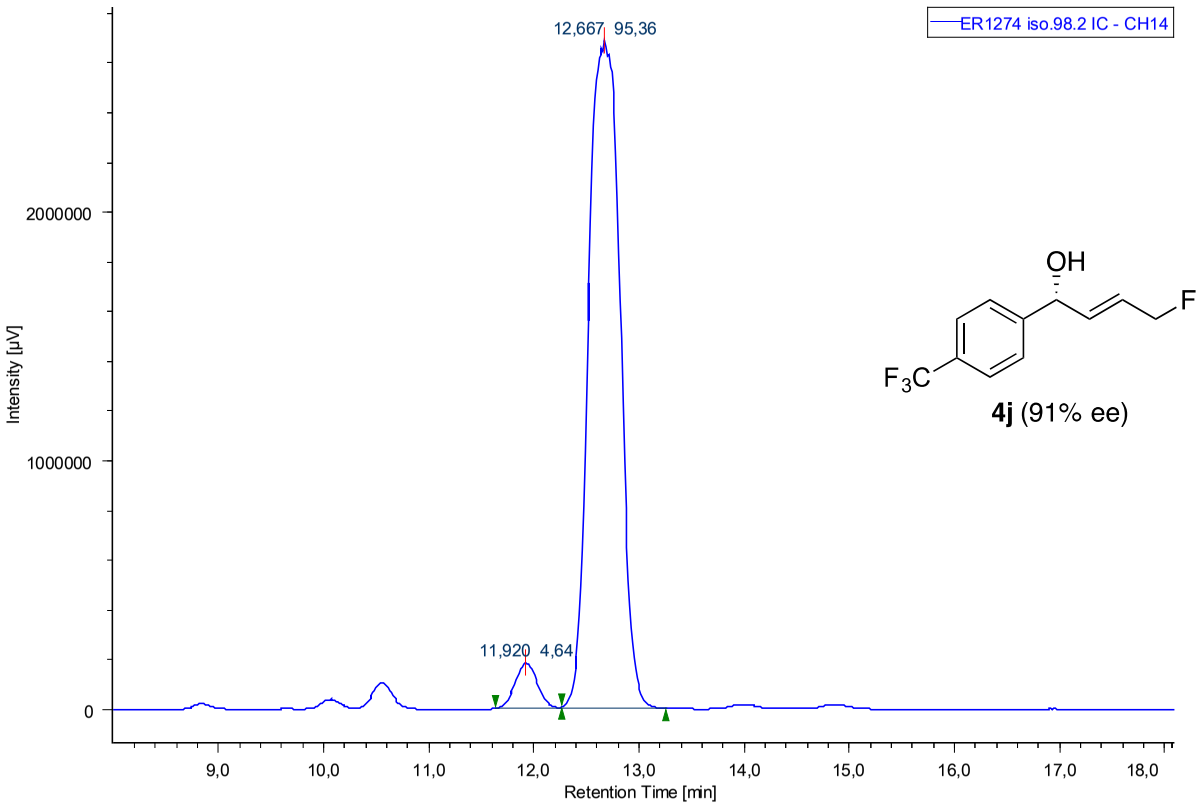

ER1234dil iso.96.4 IC - CH13
12,107 95,92
10,987 4,08
1000000
0
Intensity [µV]
7,0
8,0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
Retention Time [min]
OH
F
Br
4g (94% ee)

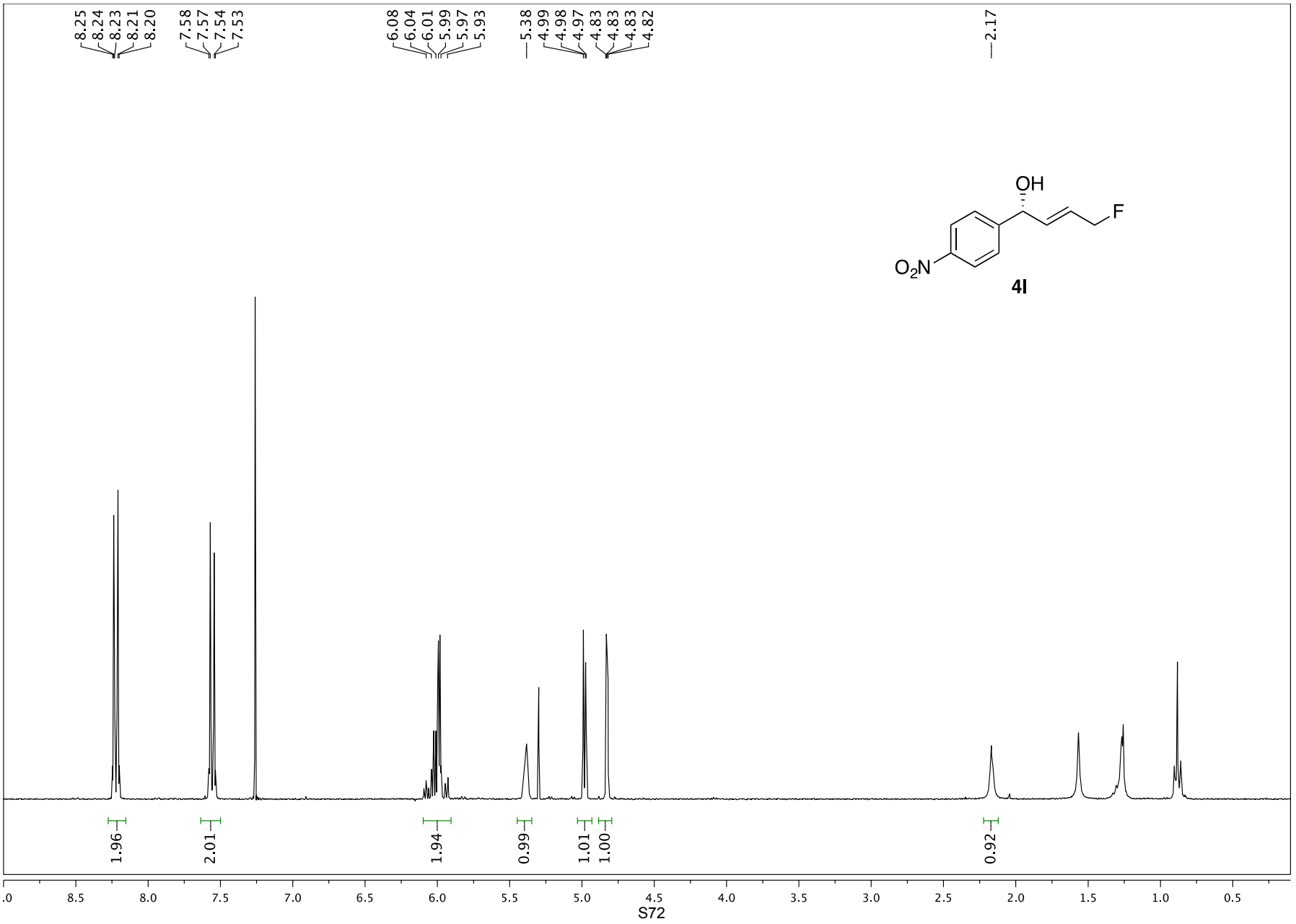

7.64
7.61
7.51
7.48
6.05
6.02
6.00
5.98
5.97
5.93
5.34
5.33
4.98
4.98
4.97
4.97
4.83
4.82
4.81
2.11
2.09
OH
F
F3C
4j
2.07
2.08
1.94
1.01
0.99
1.00
0.97
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

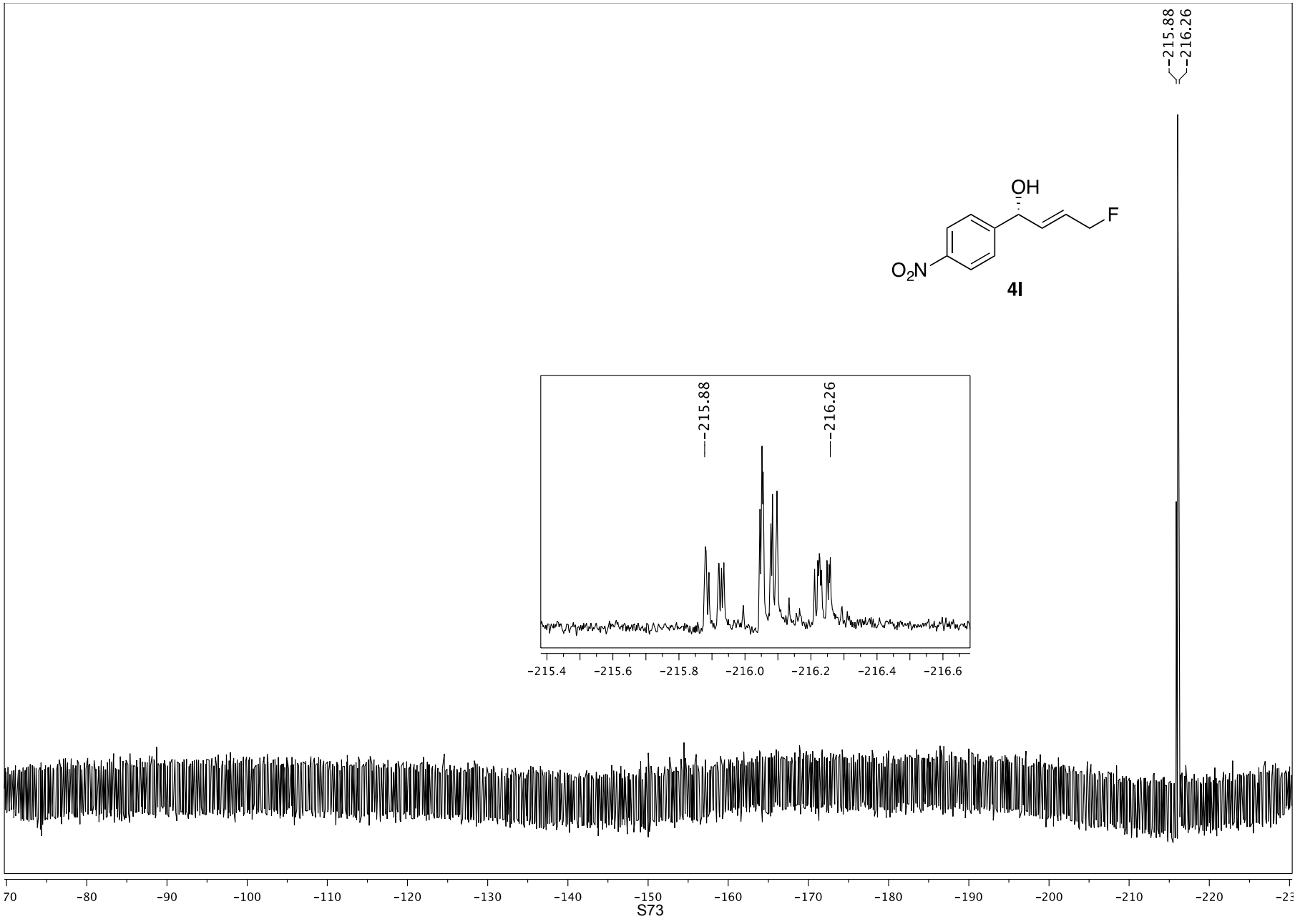

-63.03
-215.13
-215.14
-215.15
-215.17
-215.18
-215.30
-215.31
-215.32
-215.33
-215.46
-215.47
-215.49
-215.50
-215.51
OH
F
F3C
4j
-214.9 -215.0 -215.1 -215.2 -215.3 -215.4 -215.5 -215.6 -215.7 -215.8
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250

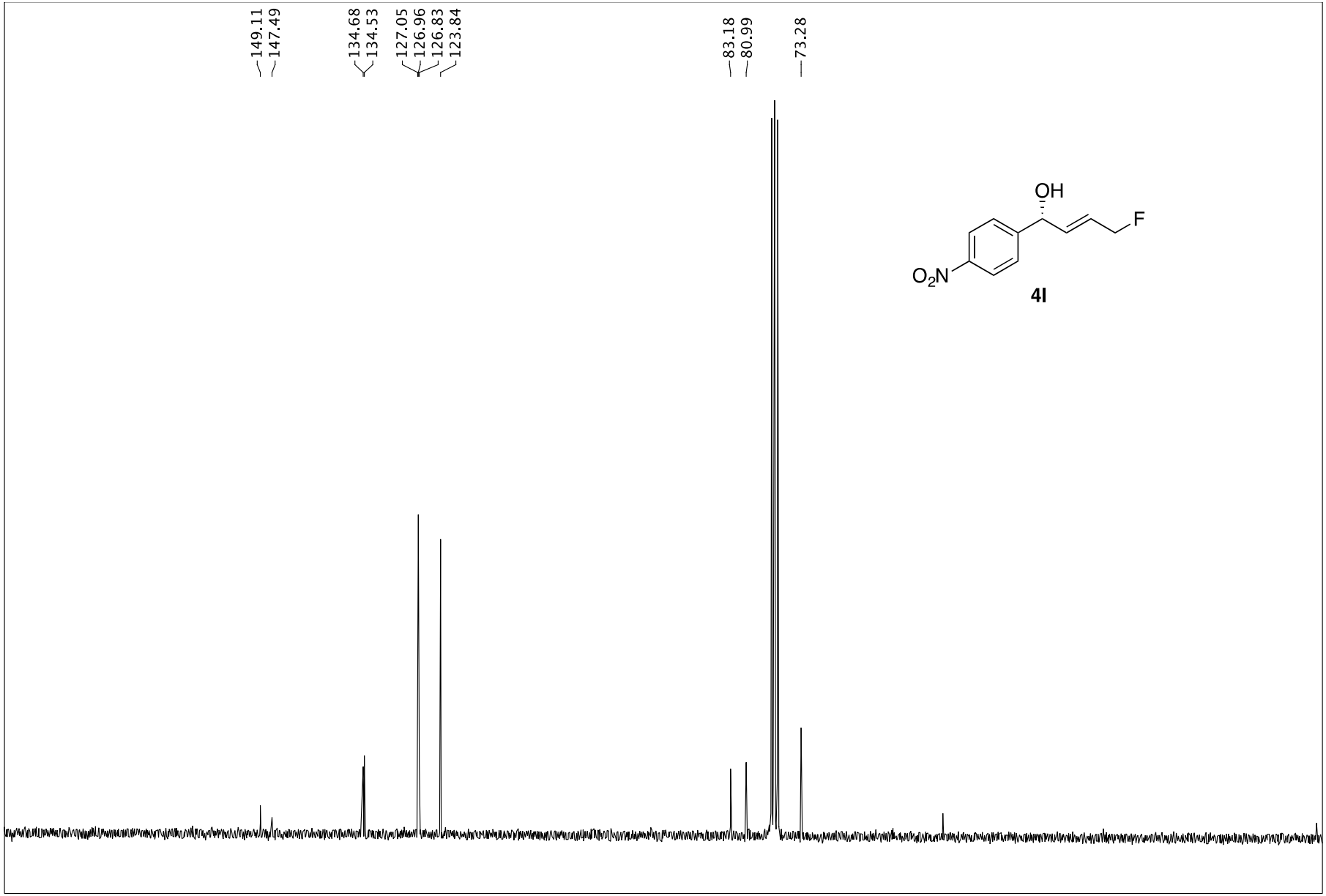

145.94
135.43
135.28
130.75
130.32
129.89
129.45
126.53
126.38
126.15
125.84
125.66
125.61
125.56
125.51
122.23
83.37
81.19
73.55
OH
F
F3C
4j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

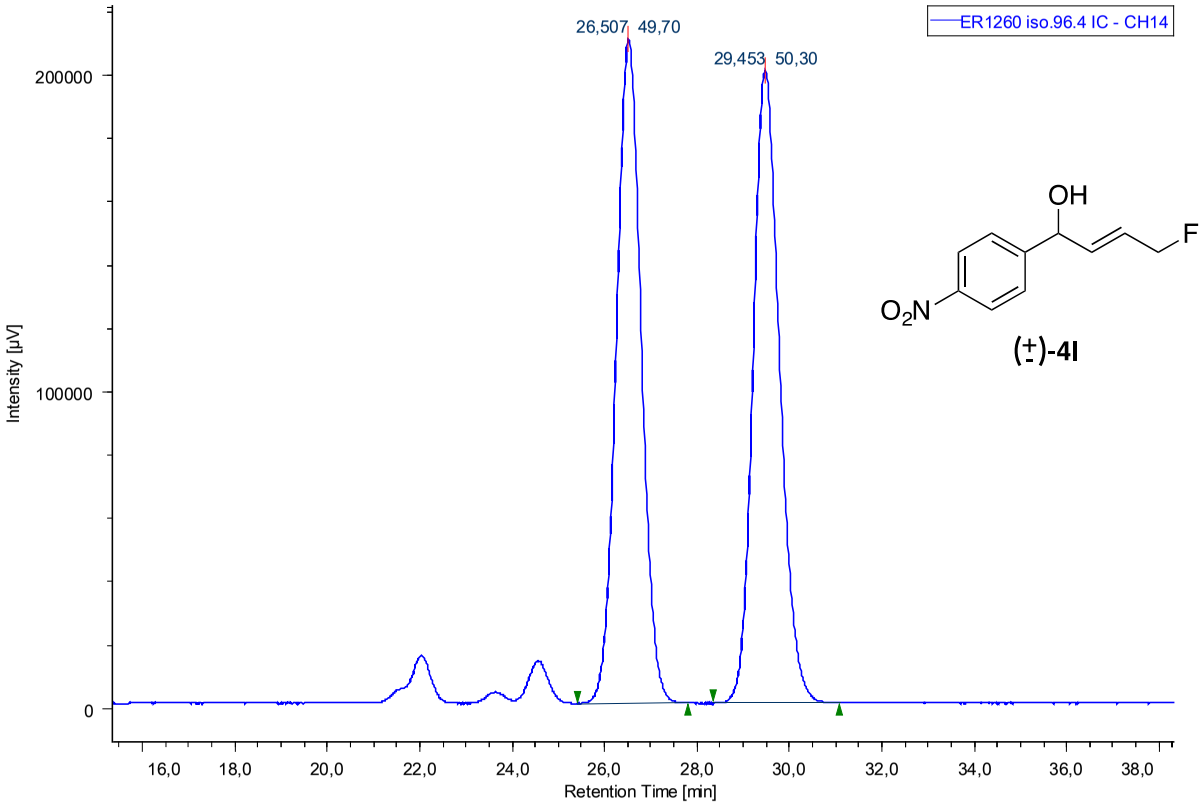

ER1273 iso.98.2 IC - CH10
12,160 49,76
12,973 50,24
Intensity [µV]
200000
100000
0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
Retention Time [min]
OH
F
F3C
(±)-4j

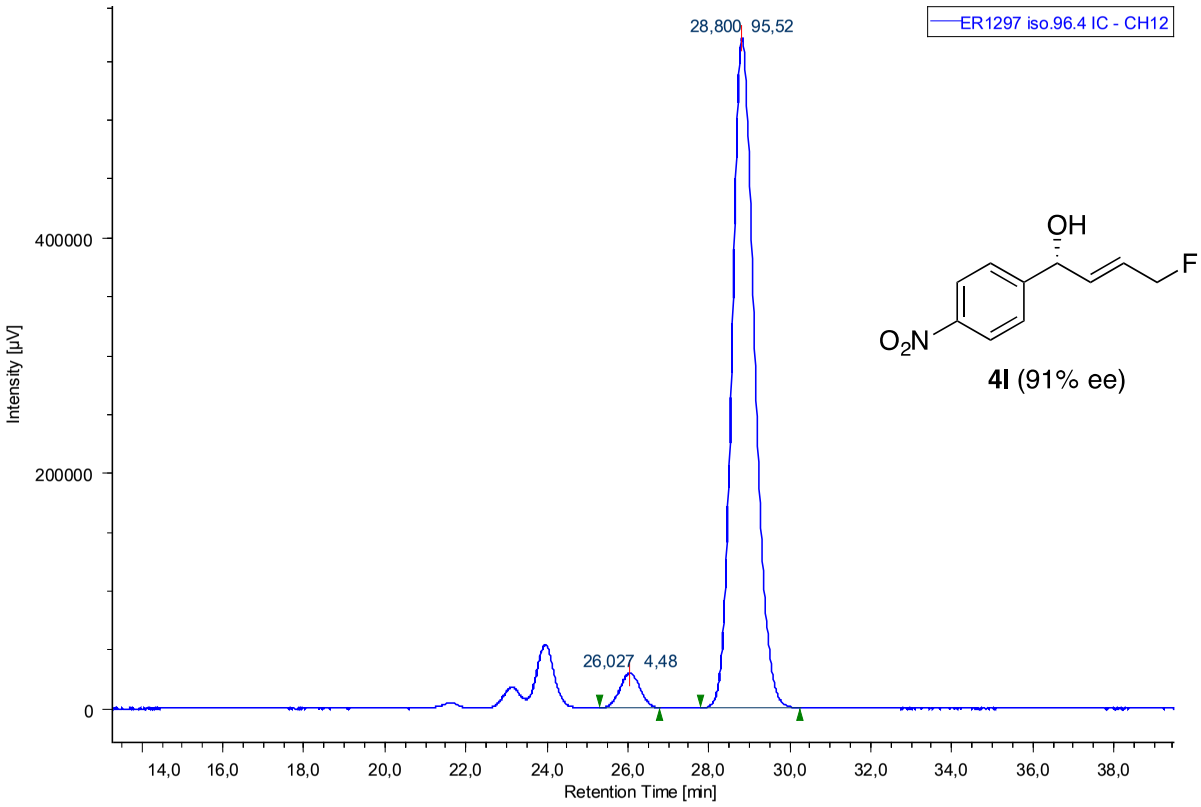

ER1274 iso.98.2 IC - CH14
12,667 95,36
11,920 4,64
Intensity [µV]
2000000
1000000
0
9,0
10,0
11,0
12,0
13,0
14,0
15,0
16,0
17,0
18,0
Retention Time [min]
OH
F
F3C
4j (91% ee)


8.25
8.24
8.23
8.21
8.20
7.58
7.57
7.54
7.53
6.08
6.04
6.01
5.99
5.97
5.93
5.38
4.99
4.98
4.97
4.83
4.83
4.82
2.17
OH
F
O2N
4l
1.96
2.01
1.94
0.99
1.01
1.00
0.92
.0
8.5
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


-215.88
-216.26
OH
F
O2N
4l
-215.88
-216.26
-215.4
-215.6
-215.8
-216.0
-216.2
-216.4
-216.6
70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220


149.11
147.49
134.68
134.53
127.05
126.96
126.83
123.84
83.18
80.99
73.28
OH
F
O2N
4l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


ER1260 iso.96.4 IC - CH14
26,507 49,70
29,453 50,30
Intensity [µV]
200000
100000
0
16,0 18,0 20,0 22,0 24,0 26,0 28,0 30,0 32,0 34,0 36,0 38,0
Retention Time [min]
OH
F
O2N
(±)-4l


ER1297 iso.96.4 IC - CH12
28,800 95,52
26,027 4,48
Intensity [µV]
400000
200000
0
14,0 16,0 18,0 20,0 22,0 24,0 26,0 28,0 30,0 32,0 34,0 36,0 38,0
Retention Time [min]
OH
F
O2N
4l (91% ee)